Synthesis of Diorcinols and *C*-acyl glycosidic compounds

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List of Publications

Articles

M. Schacht, G. J. Boehlich, J. de Vries, S. Bertram, G. Gabriel, P. Zimmermann, P. Heisig, N. Schützenmeister, Protecting-Group-Free Total Syntheses of Rubrolide R and S, *Eur. J. Org. Chem.* **2017**, 1745–1748.

G. J. Boehlich, N. Schützenmeister, Blickpunkt Synthese: Neues vom alten Eisen - eisenkatalysierte Kreuzkupplungen, *Nachrichten aus der Chemie* **2019**, *67* (3), 85–88.

G. J. Boehlich, N. Schützenmeister, β-Selective *C*-Glycosylation and its Application in the Synthesis of Scleropentaside A, *Angew. Chem.* **2019**, *58* (15), 5110–5113.

G. J. Boehlich, N. Schützenmeister, β-Selektive *C*-Glycosylierung und ihre Anwendung in der Synthese von Scleropentasid A, *Angew. Chem.*, **2019**, *131* (15), 5164–5167.

G. J. Boehlich, N. Schützenmeister, β-Selective One-Pot Synthesis of Acyl-*C*-Glycosides via Corey–Seebach Umpolung Reaction, *Synlett* **2019**, *30* (17), 1935–1939.

G. J. Boehlich, J. de Vries, O. Geismar, M. Gudzuhn, W. R. Streit, S. G. Wicha, N. Schützenmeister, Total Synthesis of Anti-MRSA Active Diorcinols and Analogues, *Chem. Eur. J.* **2020**, *26* (44), 9846–9850.

F. Demeter, G. J. Boehlich, A. Borbás, M. Herczeg, Synthesis of an Orthogonally Protected L-Idose Derivative Using Hydroboration/Oxidation, *Carbohydrate Chemistry: Proven Synthetic Methods*, CRC Press, **2021**, *5*, 233–240.

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G. J. Boehlich, H. Sterzel, J. Rehbein, N. Schützenmeister, Concise and Highly Stereoselective Synthesis of α and β *C*-Acyl Manno-, Rhamno- and Lyxopyranosides, *submitted manuscript*

Posters

G. J. Boehlich, N. Schützenmeister, Total Synthesis of Scleropentaside A, *ORCHEM* **2018**, Berlin.

G. J. Boehlich, N. Schützenmeister, Total Synthesis of Scleropentaside A, *DPhG Jahrestagung* **2018**, Hamburg.

G. J. Boehlich, N. Schützenmeister, Synthesis of Acyl-β-*C*-glycosides, *DPhG Jahrestagung* **2019**, Heidelberg.

List of Abbreviations

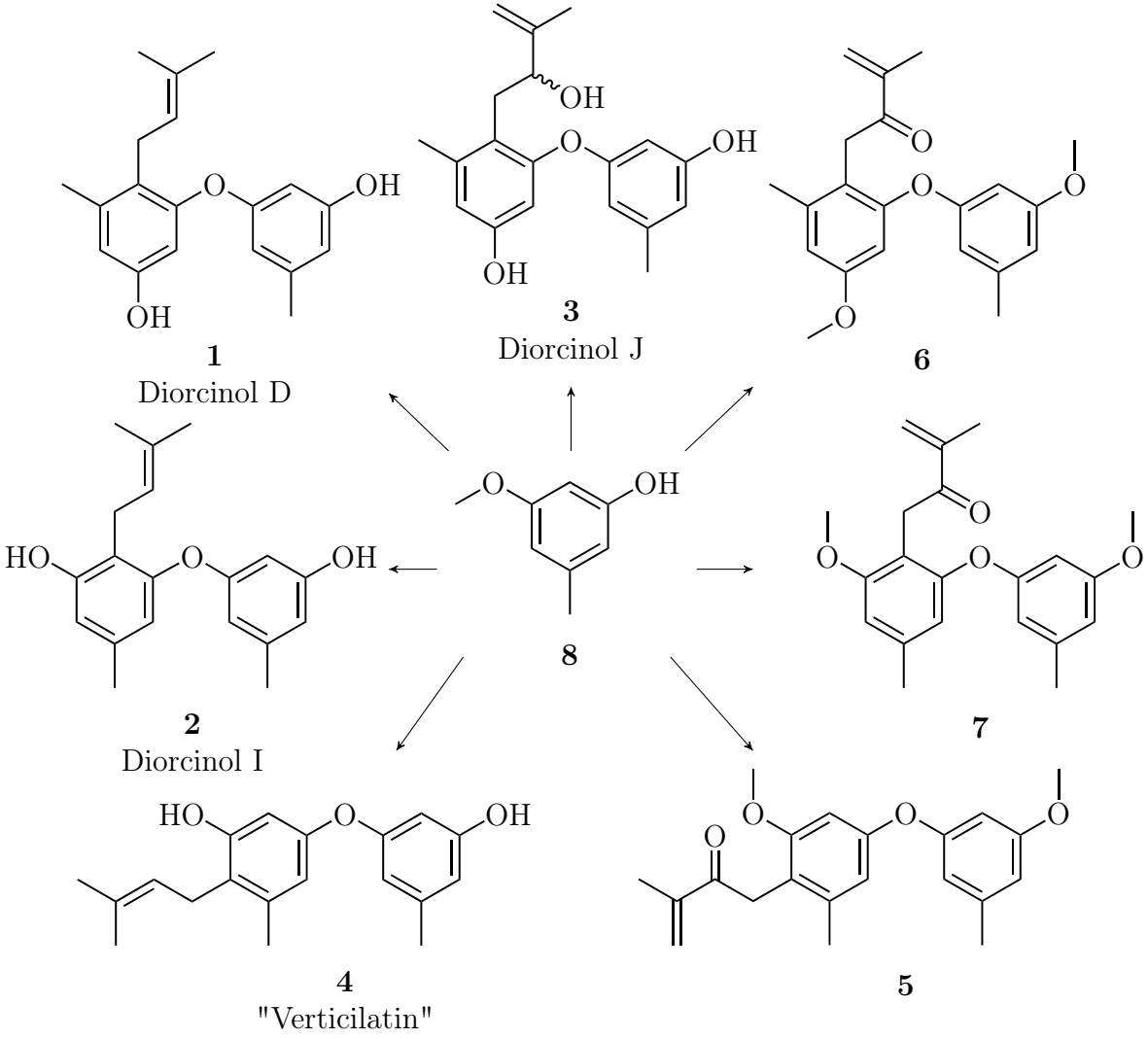
Ac	Acetyl
Ar	Aryl
ATR	Attenuated Total reflection
Ax.	Axial
bipy	2,2'-Bipyridine
Bn	Benzyl
Bu	Butyl
Bz	Benzoyl
calcd.	Calculated
CSA	Camphorsulfonic acid
COSY	Correlated Spectroscopy
dba	Dibenzylidenacetone
DCM	Dichloromethane
DEPTQ	Distorsionless Enhancement by Polarization Transfer Including Quaternary Nuclei
DIAD	Diisopropyl Azodicarboxylate
DMF	*N*,*N*-Dimethylformamide
DMI	1-3-Dimethyl-2-imidazolidinone
DMP	Dess–Martin periodinane
DMSO	Dimethylsulfoxide
DNA	Deoxyribonucleic acid
E. coli	*Escherichia coli*
equiv.	Equivalents
ESI	Electrospray Ionisation
Et	Ethyl
Eq.	Equatorial
glyme	1,2-Dimethoxyethane
HMBC	Heteronuclear Multiple Bond Correlation
HMDS	Hexamethyldisilazide
HRMS	High Resolution Mass Spectrometry
HSQC	Heteronuclear Single Quantum Coherence
IR	Infrared
Man	Mannose
*m*CPBA	*meta*-Chloroperoxybenzoic acid
Me	Methyl

M.p.	Melting Point
MRSA	Methicillin-Resistant *Staphylococcus aureus*
MS	Mass Spectrometry
MSSA	Methicillin-Sensitive *Staphylococcus aureus*
MW	Microwave
NMP	*N*-Methyl-2-pyrrolidone
NMR	Nuclear Magnetic Resonance
NOESY	Nuclear Overhauser Enhancement Spectroscopy
OTf	Triflate
PG	Protective group
Ph	Phenyl
phen	Phenanthroline
PIFA	Phenyliodine bis(trifluoroacetate)
r.t.	Room Temperature
RP	Reversed Phase
SCXRD	Single Crystal X-Ray Diffraction
SDS	Sodium Dodecyl Sulfate
SGLT	Sodium Dependent Glucose Transporter
TBA	Tetrabutylammonium
TC	Thiophene-2-carboxylate
TFA	Trifluoroacetic acid
THF	Tetrahydrofuran
TLC	Thin Layer Chromatography
TMS	Trimethylsiyl
Trp	Tryptophan
UV	Ultraviolet
Xphos	Dicyclohexyl[2',4',6'-tris(propan-2-yl)[1,1'-biphenyl]-2-yl]phosphane

Contents

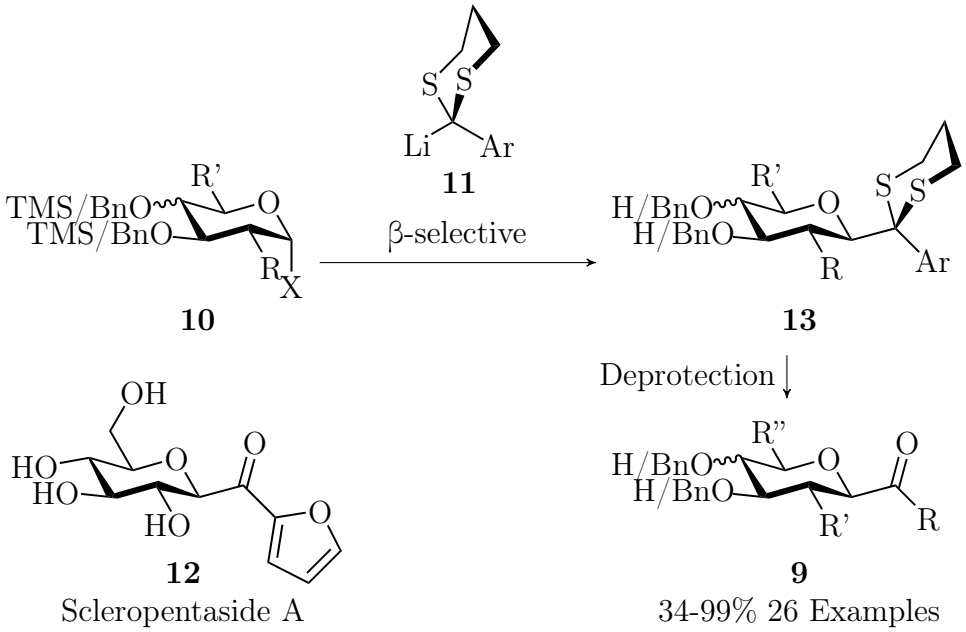
1 Abstract

Diorcinols and related prenylated diaryl ethers were reported to exhibit activity against *Staphylococcus aureus*. As part of this doctoral thesis the first syntheses of natural products diorcinols D **1**, I **2**, J **3** and the proposed structure of verticilatin **4** were developed. Syntheses for a supposedly naturally occurring antibacterial diaryl ether **5** and its isomers **6** and **7** were developed alongside. These syntheses gave access to the diaryl ethers in four to six steps starting from methylorcinol **8**. These syntheses also led to the structural revision of the natural product "verticilatin".[1]

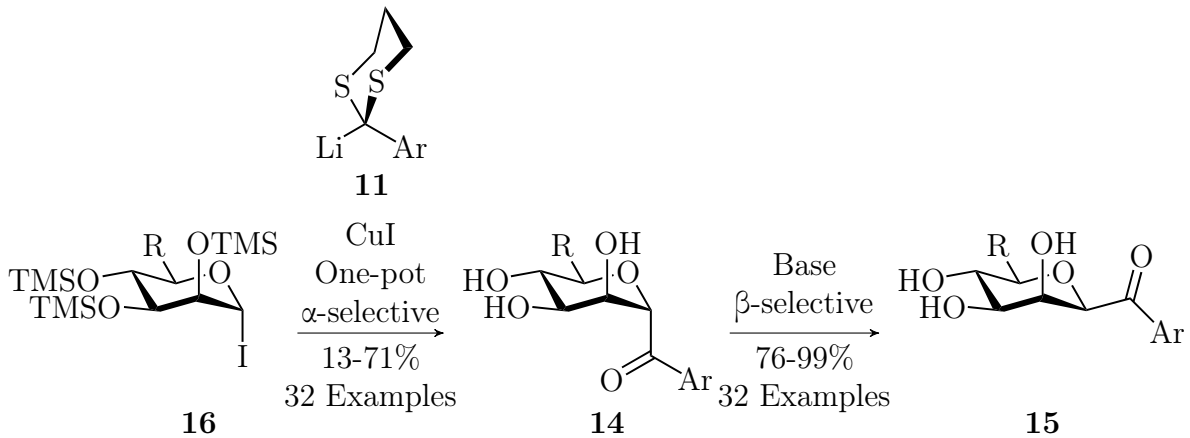


These syntheses gave diorcinols D **1**, I **2** and J **3** as well as the proposed structure of "verticilatin" **4** in gram-scale which facilitated further biological evaluation, revealing biological activity against both methicillin sensitive and resistant strains of *Staphylococcus aureus*.[1]

Furthermore, a new method for the synthesis of *C*-acyl glycosidic compounds **9** was developed. The method is a sequence of donor generation, Corey-Seebach reaction between glycosyl halide **10** and lithiated dithiane **11** and deprotection, which could usually be carried out in a one-pot procedure, giving *C*-acyl D-gluco-, D-galacto-, D-xylo-, D-arabino-, D-2-deoxy-D-gluco-, D-2-deoxy-D-galacto- and L-fucopyranosides **9** in good to excellent yields with excellent β-selectivity. This method allowed the first and shortest synthesis of scleropentaside A **12**.[2–4]

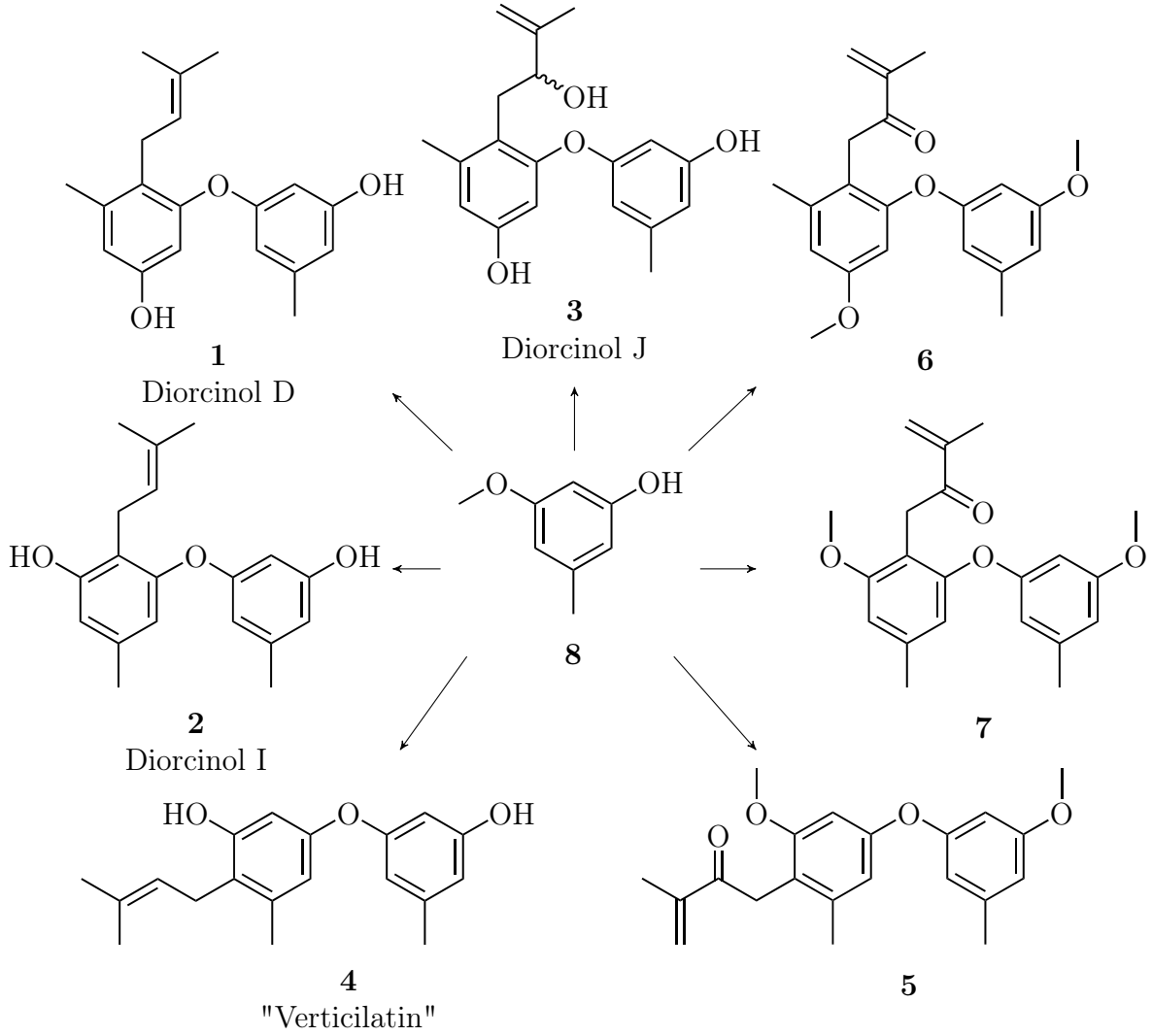


Modifiying this procedure by adding trace amounts of CuI allowed the α-selective synthesis of D-manno-, D-lyxo- and L-rhamnopyranosides **14**. These α-configured *C*-acyl pyranosides could easily be isomerized into their β-isomers under basic conditions **15**.[5]



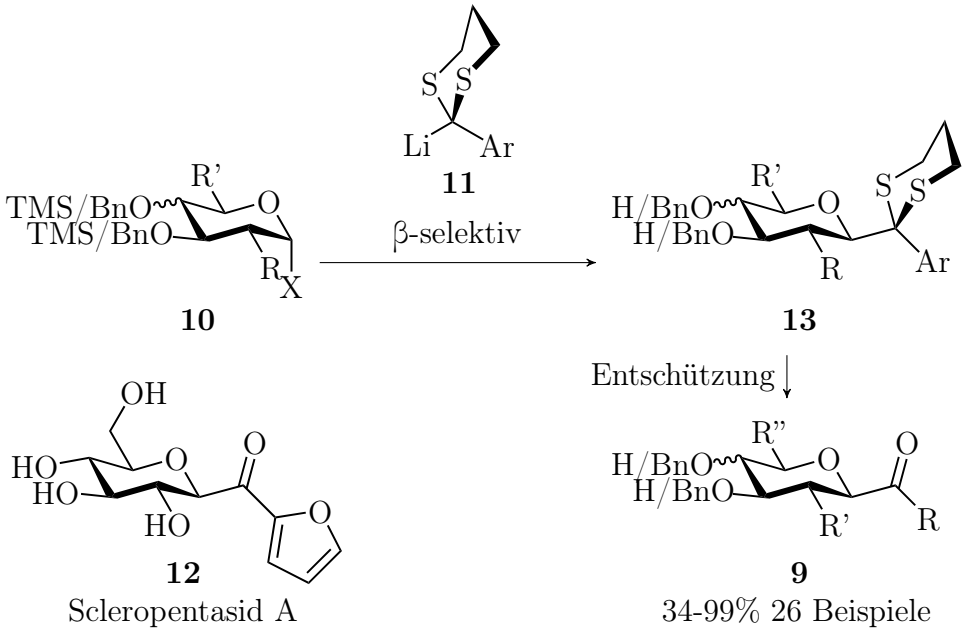
2 Zusammenfassung

Diorcinole und verwandte Diarylether zeigten Aktivität gegenüber *Staphylococcus aureus*. Als Teil dieser Doktorarbeit wurden die bisher einzigen Synthesen der Naturstoffe Diorcinole D **1**, I **2**, J **3** sowie die vermeintlichen Strukturen von "Verticilatin" **4** und eines antibakteriellen Diarylethers entwickelt. Die gewünschten Diarylether konnten ausgehend von Methylorcinol **8** in vier bis sechs Schritten synthetisiert werden. Diese Synthesen führten außerdem auch zu einer strukturellen Revision des Naturstoffes "Verticilatin".

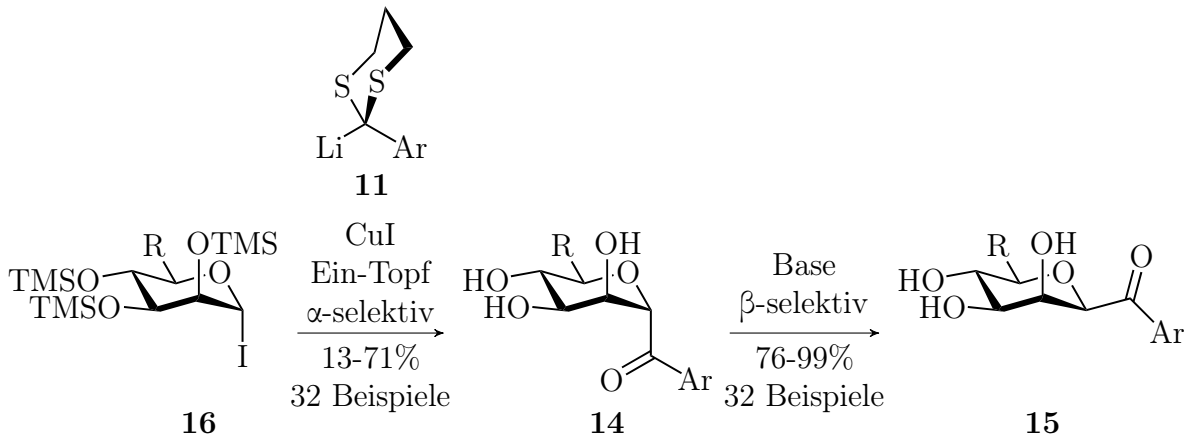


Da diese Synthesen im Gramm-Maßstab durchgeführt werden konnten, wurde außerdem auch genügend Material für weitere biologische Testungen erhalten. Diorcinole D **1**, I **2** J **3** und die angenommene Struktur von "Verticilatin" **4** wiesen ähnliche Aktiviäten gegen Methicillin-empfindliche und -resistente Stämme von *Staphylococcus aureus* auf.[1]

Des Weiteren wurde eine neue Methode zu Synthese von *C*-acyl glycosidischen Verbindungen entwickelt. Durch eine Ein-Topf Reaktion bestehend aus einer Corey-Seebach-Reaktion zwischen einem Glycosylhalogenid **10** und einem lithiierten Dithian **11** gefolgt von der Entschützung des Dithians konnten *C*-acyl D-Gluco-, D-Galacto-, D-Xylo-, D-Arabino- D-2-Deoxy D-gluco-, D-2-Deoxygalacto- and L-Fucopyranoside **9** β-selektiv in guten bis exzellent Ausbeuten erhalten werden. Durch diese Methode wurde die erste und bis heute effizienteste Synthese von Scleropentasid A **12** ermöglicht.[2–4]



Durch Spuren von CuI wurde außerdem die α-selektive Synthese von D-Manno-, D-Lyxo- and L-Rhamnopyranosiden **14** ermöglicht. Diese α-konfigurierten *C*-Acylpyranoside konnten durch den Einsatz einer Base in ihre β-Isomere **15** überführt werden.[5]

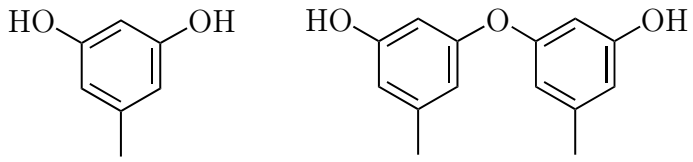


3 Introduction

The three main leading causes of death worldwide in descending order are cardiovascular diseases, cancer and infectious diseases.[6] While development of treatments for cardiovascular diseases and cancer is still widely pursued, development of novel antiinfectives, especially antibiotics has slowed down significantly due to lacking financial incentive.[7] This lack of financial interest compared to other therapeutics has three major causes: competetion against the cheap existing antibiotics; short treatment courses as microbial infections are usually not chronic; and conservation of novel antibiotics as last resort against multiresistant bacteria.[7] Although ∼200 antibiotics are known, most of them usually disrupt one of four mechanisms: cell wall biosynthesis (β-lactam and vancomycin-type antibiotics); protein biosynthesis (macrolides, tetracyclines, aminoglycosides, 2-oxazolidinones); DNA replication and repair (quinolones); and folate metabolism (sulfamides and trimethoprim).[8] The lack of new antibiotics will pose a problem in the future as antibiotic resistance is increasing over time and infections with multidrug resistant bacteria become more common. Thus the development of novel antibiotics with new structural motives is of importance. Especially since evolution of antibiotic resistance is accelerated by overuse of these compounds.[7]

3.1 Diorcinols

Diorcinols are naturally occuring diaryl ethers or dibenzofuranes derived from the condensation product of two orcinol molecules **17** which has been named diorcinol (A) **18** (Figure 1).[9]



17 Orcinol

18 Diorcinol (A)

Figure 1: Structures of orcinol and diorcinol[1]

Since 2004, a variety of these compounds, which exhibit antibacterial and anti-fungal properties, have been reported but not all of these compounds have been named diorcinols (Figure 2).[9–20] Most diorcinols bear one or more prenyl substituents at a the aromatic core or have side chains which seem to originate from these prenyl chains. The prenyl substituent might occur on any of the three possible positions of the aromatic cores as all three possible isomers of the monoprenylated diorcinol A have been reported.[9–11]

The modified side chains exhibit diol, ketone, allyl alcohol or cyclisation motifs. Diaryl ethers which seem to have been oxidized to a dibenzofuran have also been reported. The methylated diaryl ether **5**, which has a α,β-unsaturated ketone side chain modification was especially interesting as it was reported to exhibit anti-MRSA activity.[1]

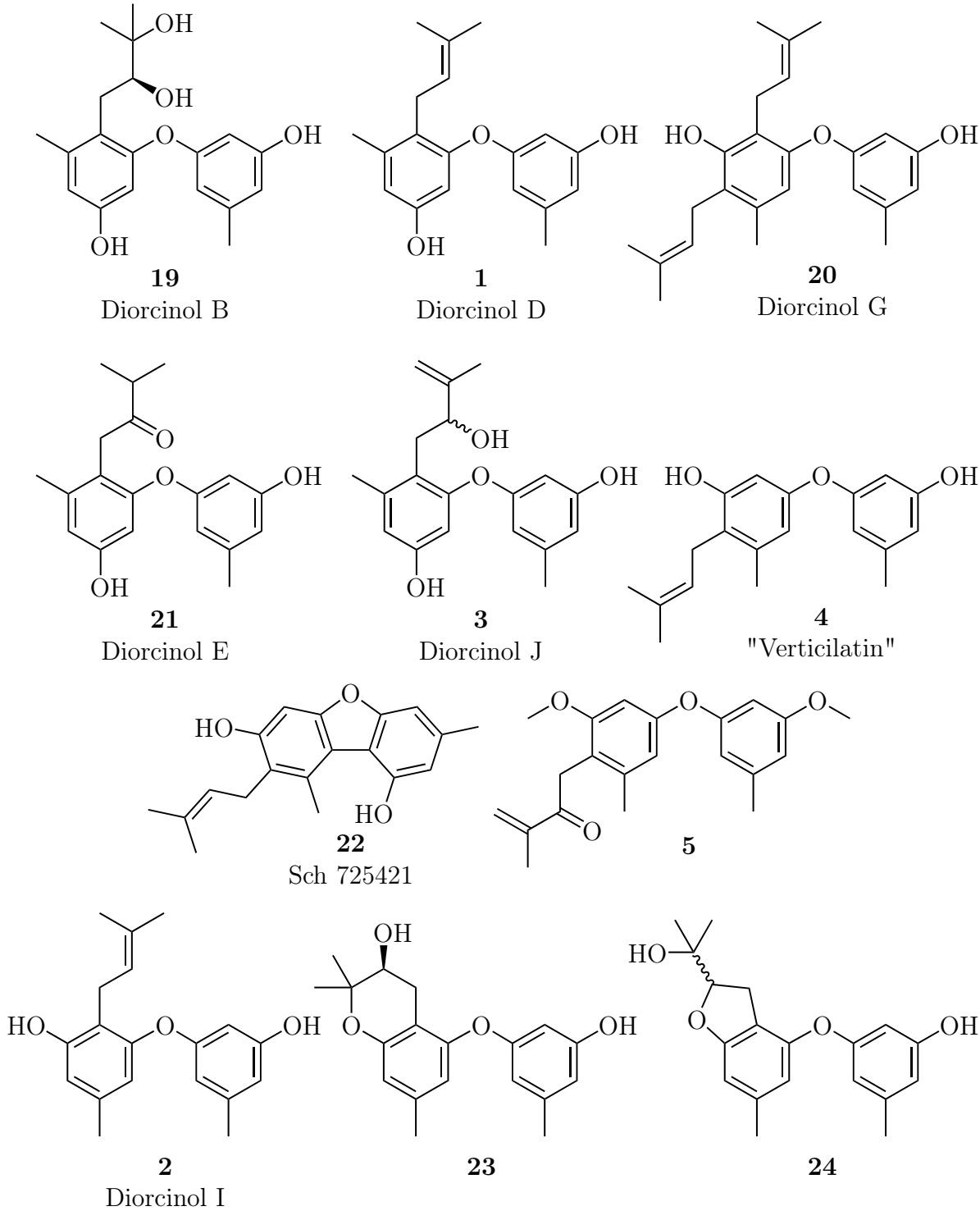
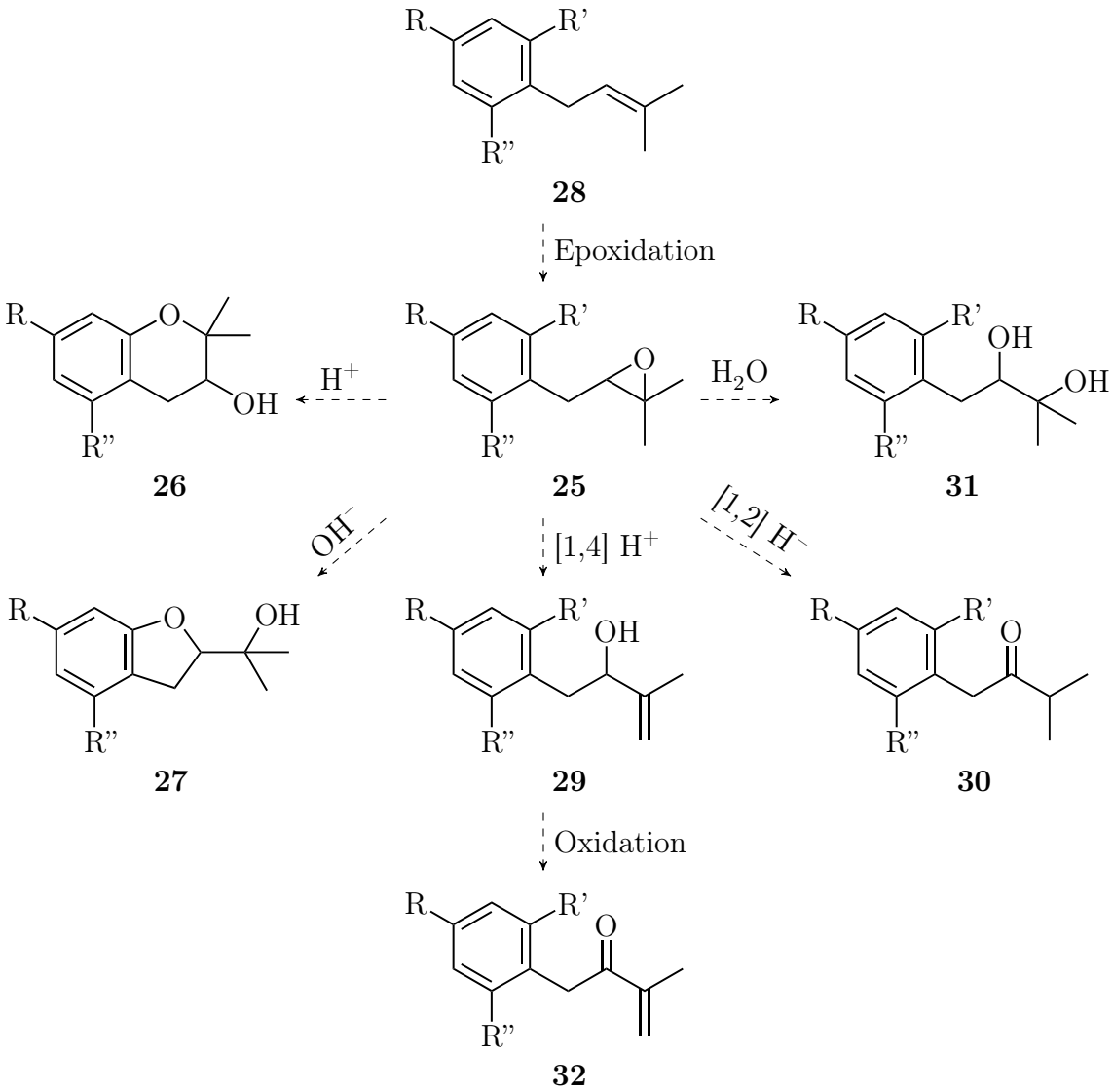


Figure 2: Examples of diorcinols[9–20]

3.1.1 Biosynthesis of diorcinols

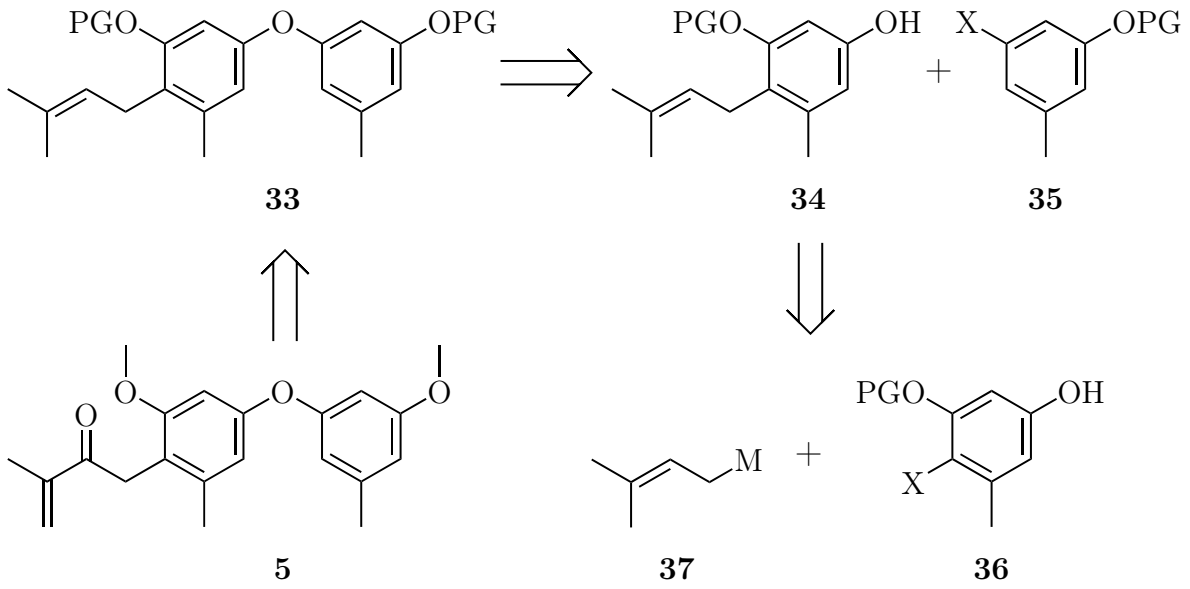
The biosynthesis of the modified side chains may be explained by an epoxide intermediate **25**. Epoxidation of the prenyl side chain may lead to an epoxide **25** from which all other side chain modifications may be formed. If a phenolic OH group is in proximity of the epoxide, acidic or enzymatic conditions may lead to formation of a chromane **26** while basic or enzymatic conditions may lead to to formation of a coumaran **27**. If, no OH group is in proximity, hydrolysis under basic or acidic conditions may cause formation of diol, a 1,2-hydride shift may cause formation of a ketone while a 1,4-proton shift may have caused formation of the allyl alcohol motif. Further oxidation of the allyl alcohol to an α,β-unsaturated ketone may have lead to formation of compound **5**, which was reported to have anti-MRSA activity (Scheme 1).[1,21,22]



Scheme 1: Possible biosynthesis of diorcinols via epoxide **25**.[1,21,22]

3.1.2 Retrosynthesis of diorcinols

Despite their interesting biological activities, no syntheses of these compounds had been reported so far. Synthetic access to prenylated diorcinols D **1**, I **2** and "verticilatin" **4** may also enable the synthesis of other diorcinols in a biomimetic approach. Protected "verticilatin" **33** may be synthesized by a diaryl ether coupling of a monoprotected prenylated orcinol **34** with a protected aryl halogenide **35** (Scheme 2).[1]



Scheme 2: Retrosynthesis of protected "verticilatin".[1]

The monoprotected prenylated orcinol **34** may be synthesized by a cross coupling approach between a halogenated orcinol **36** and a prenyl nucleophile **37**. Negishi[23–25], Stille[26,27] and Suzuki[28–30] protocols have been reported for this purpose.[1]

3.1.3 Syntheses of diarylethers

Since the diaryl ether motif occurs in many natural products like the COX-2 inhibitor rodgersinol **38**, the widely known antibiotic vancomycin **39** and the human geranylgeranyl diphosphate (GGPP) synthase inhibitor gerfelin **40**, multiple methods for the construction of such motifs have been developed (Figure 3).[31]

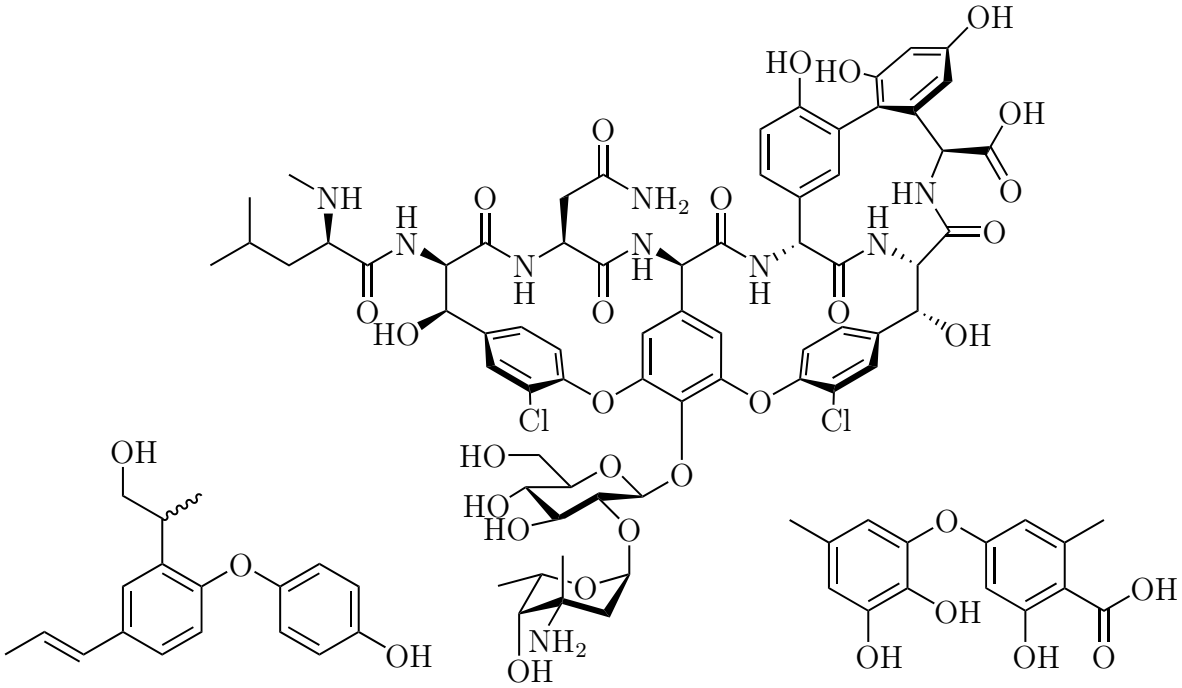
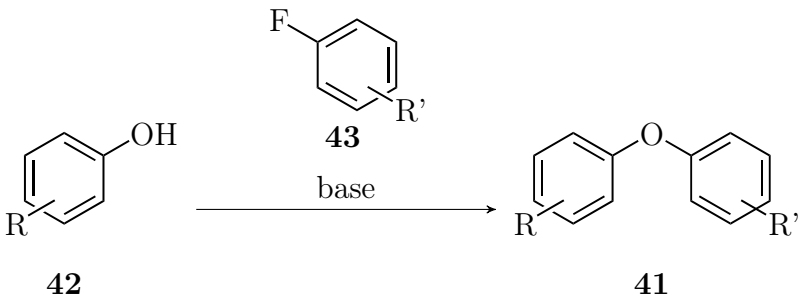


Figure 3: Naturally occuring diaryl ethers.[31]

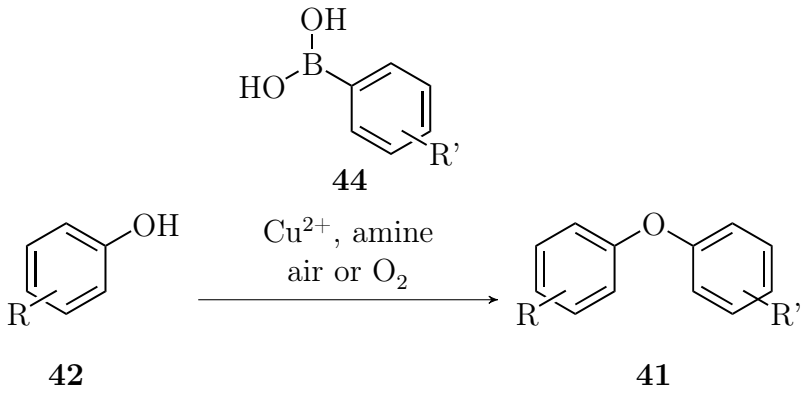
One commonly employed method for the synthesis of diarylethers **41** is the S_NAr reaction between a phenol **42** and an aryl fluoride **43** in presence of a base. Few reactions employing aryl chlorides or bromides have also been reported, but fluorides usually give the highest yields in these reactions (Scheme 3).[31]



Scheme 3: Synthesis diaryl ethers via S_NAr reaction.[31]

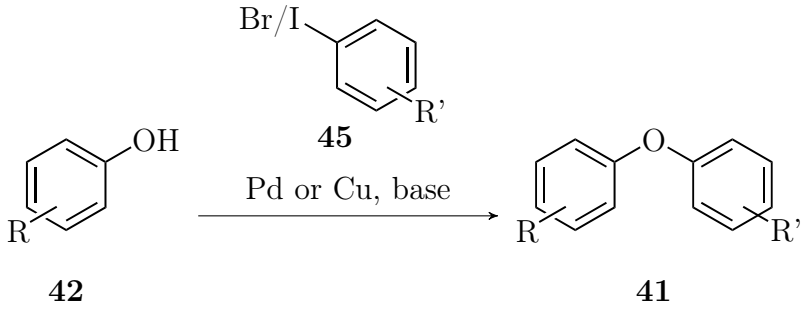
However, this reaction is limited to electron deficient aryl fluorides **43**. For this reaction to occur, the aryl fluoride needs to have an electron withdrawing substituent R' such as a carbonyl, carboxyl or nitro group in ortho or para position relative to the fluoride. The electron withdrawing substituents R' of the resulting diaryl ethers **41** usually have to be further modified or removed subsequently, resulting in additional synthetic steps.[31] This can be seen in the total syntheses of vancomycin **39**.[32–34] Since diorcinols are electron rich diaryl ethers, this method cannot be used for the synthesis of this compound class.

Another approach is the Chan-Lam coupling[35,36] of phenols **42** with aryl boronic acids **44** in presence of stoichiometric or catalytic amounts of Cu^{2+} and an amine, which serves as ligand and base. A major advantage of this method is that it can be carried out at room temperature under air. Since oxygen accelerates the reaction, protocols which run the reaction under oxygen atmosphere have been developed. However, the reaction becomes unreliable if halides or oxygen bearing groups are in vicinity of the boronic acid and such has only been applied to simple diaryl ethers such as rodgersinol **38**.[37,38] Another disadvantage of this method is that the boronic acid has to be synthesized from the respective aryl halide (Scheme 4).[31]



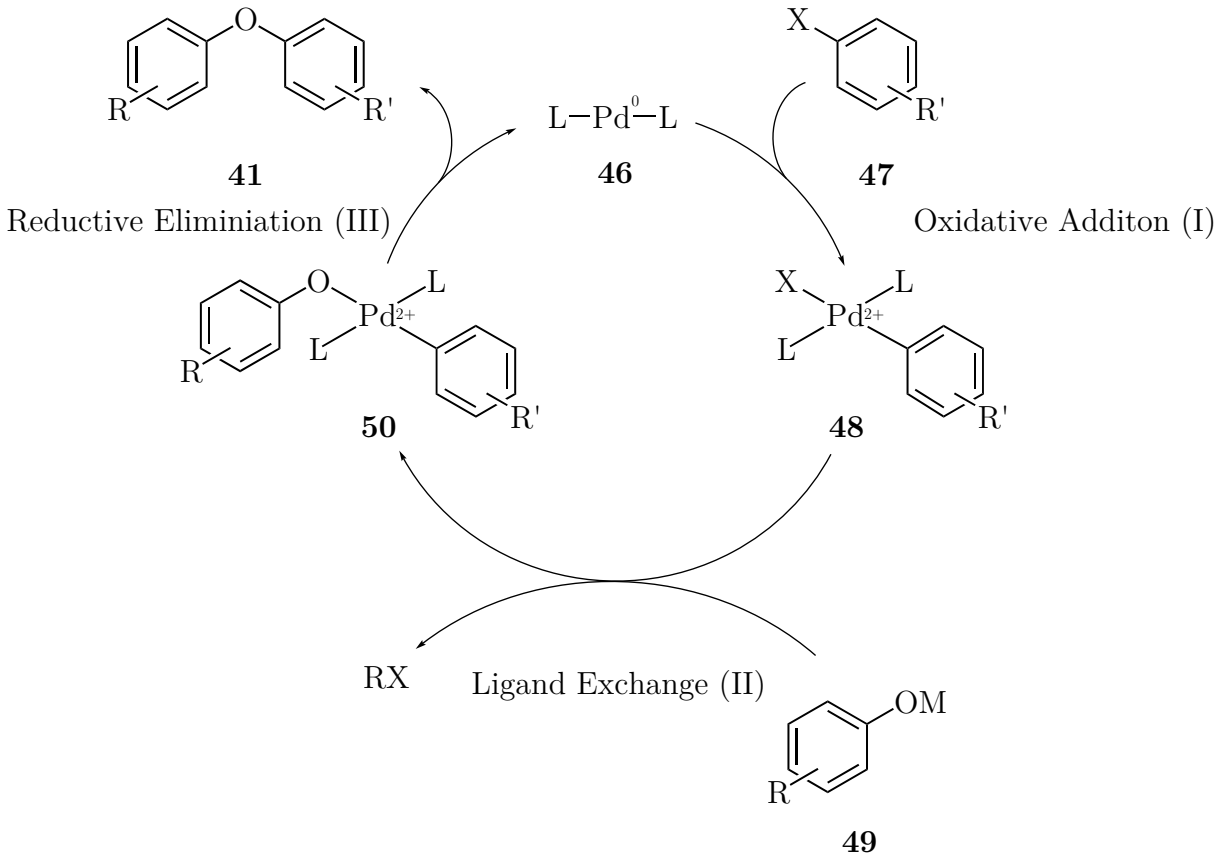
Scheme 4: Synthesis of diaryl ethers via Chan-Lam coupling.[35,36]

The most commonly used syntheses of diaryl ethers **41** are Cu-catalyzed Ullmann[39] couplings of phenols **42** with aryl bromides or iodides **45** in presence of a base. These protocols allow a wide range of substituents and thus have been employed in multiple syntheses of vancomycin[40–42] and other natural products. Similar Pd-catalyzed Buchwald-Hartwig[43,44] protocols, which are usually even milder, have also been developed (Scheme 5). This method was used for the synthesis of gerfelin **40**.[31,45]



Scheme 5: Synthesis of diaryl ethers via Ullmann or Buchwald-Hartwig coupling.[39,43,44]

The catalytic cycle of the Buchwald-Hartwig diaryl ether formation starts from the coordinationally unsaturated Pd^0-species **46**. The ligands L are usually phosphine based. In the first step, the Pd^0-complex **46** is reduced by oxidative addition (I) of the aryl halide **47**. This leads to the formation of the tetracoordinate Pd^{2+} complex **48**. In the next step, this Pd^{2+} complex **48** then undergoes ligand exchange (II) with the phenolate **49**, which has been previously generated from the respective phenol the base, to form **50** and a salt MX. After reductive elimination (III) of the product **41**, the catalyst **46** is Pd^0-species **46** reformed and can enter the catalytic cycle again (Scheme 6).[46]



Scheme 6: Mechanism of the Buchwald-Hartwig diaryl ether synthesis.[46]

3.2 *C*-glycosidic compounds

C-glycosidic compounds are carbohydrate derivatives bearing an anomeric C-C bond. Due to the stabilty of the anomeric C-C bond against acidic or enzymatic hydrolysis when compared to *O*- and *N*-glycosides, these types of compounds are investigated as mimics in drug discovery (Figure 4). Depending on the carbohydrate, these compounds may adress different targets. The *C*-D-glucoside dapaglifozin **51** is a SGLT-2 inhibitor used to treat type 2 diabetes.[47] *C*-D-mannoside **52** is a orally available FimH antagonist, which has shown to prevent biofilm formation of uropathogenic *Escherichia coli* in mouse models.[48] The *C*-L-fucoside **53** is a LecB antagonist, which has shown to prevent biofilm formation of *P. aeruginosa*.[49]

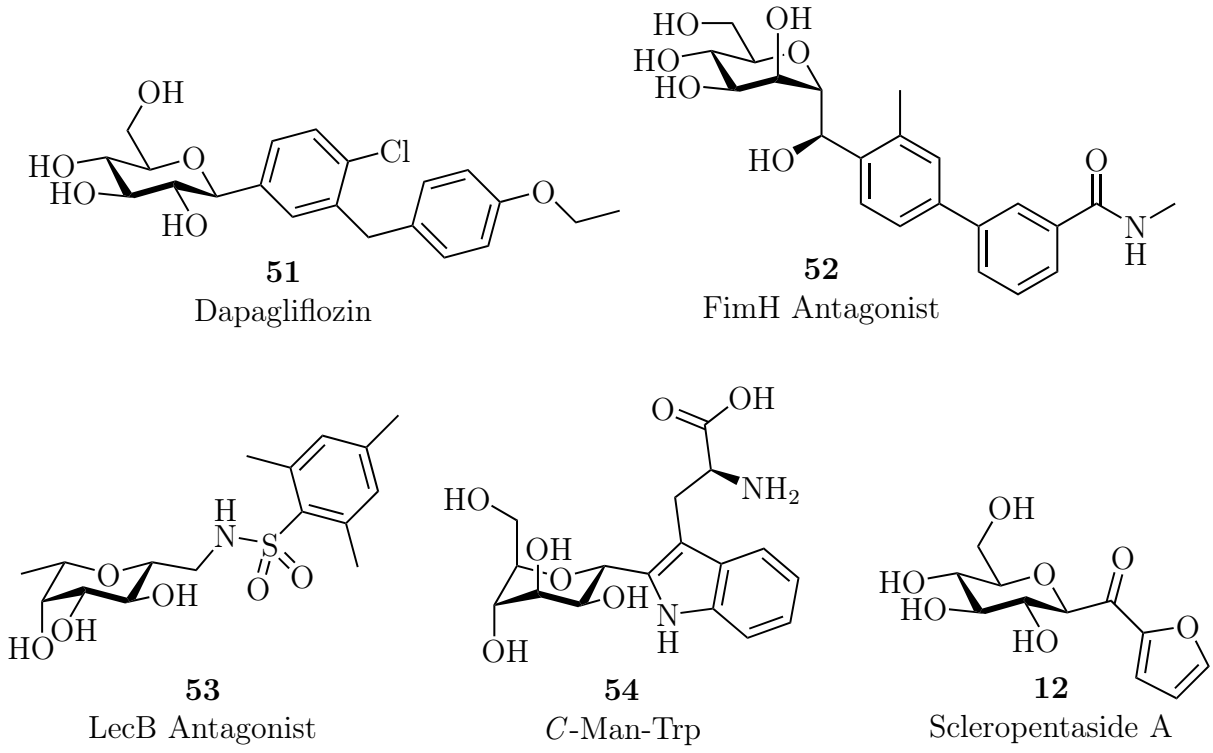
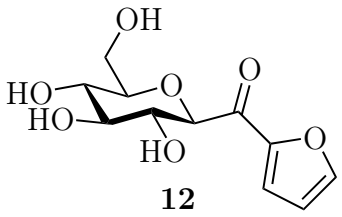


Figure 4: Examples of *C*-glycosidic compounds.[47–52]

There are also examples of naturally occuring *C*-glycosides such as *C*-Man-Trp **54**[50–52] and the *C*-acyl D-glucoside scleropentaside A **12**.[53]

3.2.1 Scleropentasides

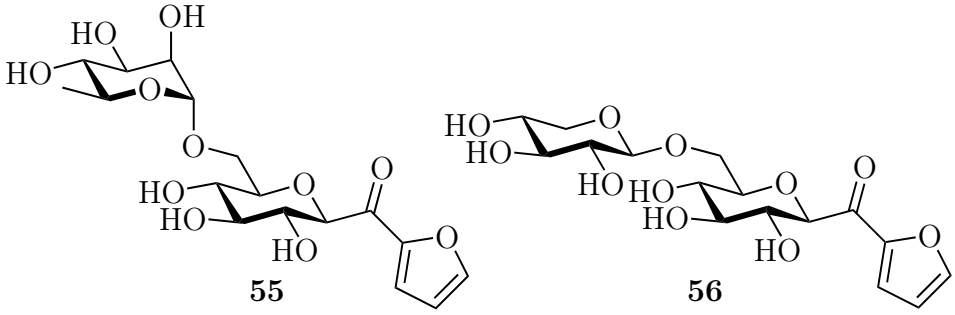
Scleropentasides are naturally occuring *C*-acyl D-glucosides that have been isolated in 2012 from the leaves and twigs of *Scleropyrum pentandrum*. All scleropentasides are furan-2-carbonyl β-*C*-glycosidic compounds of D-glucose. To this day, these are the only acyl-*C* glycosidic compounds isolated from natural sources. Scleropentaside A **12** is the simplest scleropentaside from which all other scleropentasides are derived (Figure 5).[53]



12
Scleropentaside A

Figure 5: Structure of scleropentaside A **12**.[53]

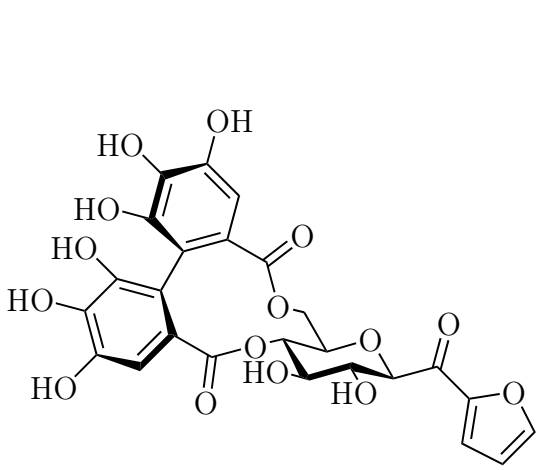
Four other scleropentasides have been isolated alongside scleropentaside A **12**. Scleropentaside B **55** and C **56** have an additional glycoside bound to 6-O via an *O*-glycosidic bond. In case of scleropentaside B **55**, this additional glycoside is α-L-rhamnopyranose and in case of scleropentaside C **56** it is β-D-xylopyranose (Figure 6).[53,54]



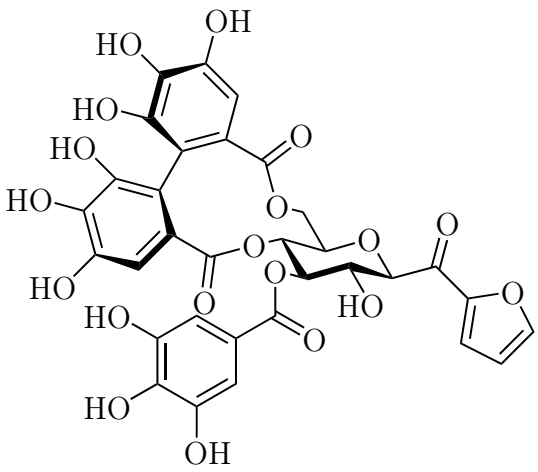
55 Scleropentaside B **56** Scleropentaside C

Figure 6: Structures of scleropentaside B **55** and scleropentaside C **56**.[53]

The three other scleropentasides D **57**, E **58** and F **59** bear typical tannine substituents. In case of scleropentaside D **57**, the D-glucopyranosyl ring is linked to a hexahydroxydiphenoyl-unit in 4 and 6-position. In addition to this motif, scleropentaside E **58** bears a galloyl unit in 3-position (Figure 7).[53]



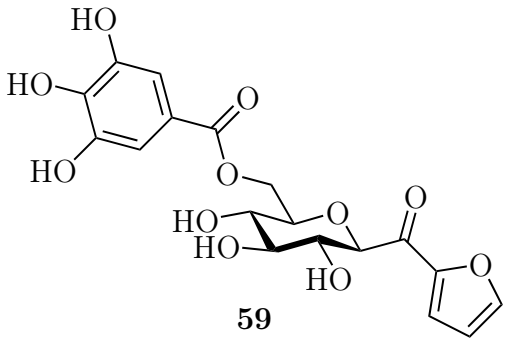
57
Scleropentaside D



58
Scleropentaside E

Figure 7: Structures of scleropentaside D **57** and scleropentaside E **58**.[53]

Scleropentaside F **59** was isolated in 2017 from *Dendrophthoe pentandra* which grew on *Tectona grandis* (teak). Scleropentaside F **59** has a galloyl unit in 6 position of the D-glucopyranosyl moiety. (Figure 8).[54]



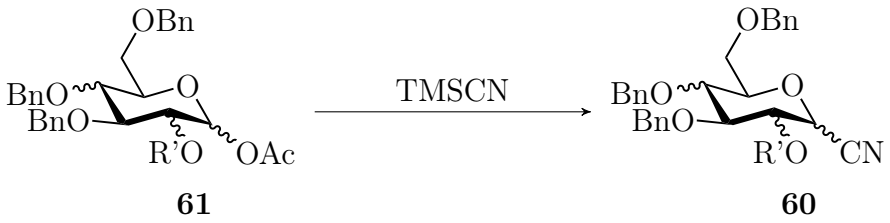
59
Scleropentaside F

Figure 8: Structure of scleropentaside F **59**.[54]

So far, only antioxidative properties of scleropentasides A-F have been reported. A synthetic approach to the scleropentaside natural product family would help to obtain more material for further biological evaluation, which is necessary to evaluate this interesting natural product class in detail. Since other *C*-glycosidic compounds have interesting biological activities this natural product class might also exhibit some undiscovered activities.

3.2.2 Syntheses of *C*-acyl glycosides

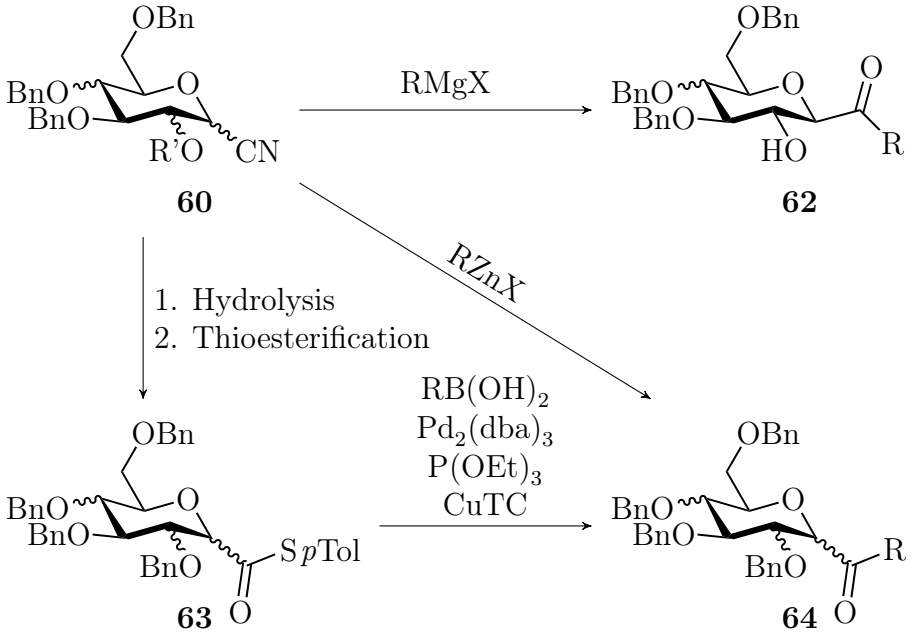
C-acyl glycopyranosides have mainly been synthesized by three approaches. Addition of organometallics to glycosyl cyanides (I), addition of organometallics to *C*-formyl glycosides in conjuction with an oxidation (II) and cross coupling approaches (III). Glycosyl cyanides **60** are usually obtained as ∼1:1 mixtures by cyanation of the respective glycosyl acetate **61** (Scheme 7).[48,55,56]



61 **60**

Scheme 7: Synthesis of glycosyl cyanides.

Addition of organozinc[55] or Grignard[57] reagents[56] to these benzyl protected glycosyl cyanides **60** then lead to *C*-acyl glycosides while retaining the anomeric configuration of the starting material (Scheme 8).



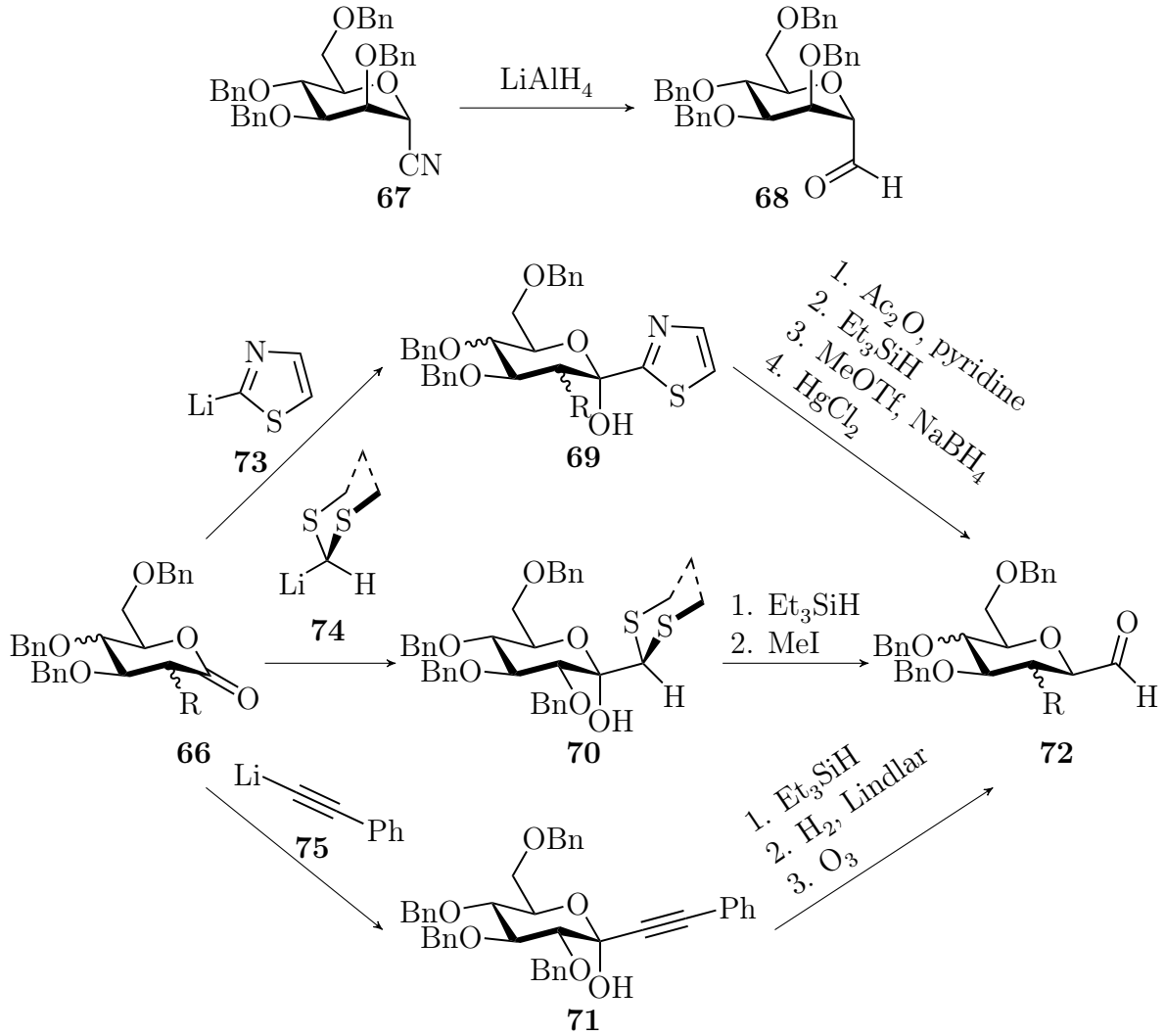
60 **62** **63** **64**

Scheme 8: Synthesis of *C*-acyl glycosides from glycosyl cyanides (I).

The reaction with organozinc nucleophiles may be used to yield D-gluco-, D-galacto- and manno-type *C*-acyl glycosides. If Grignard reagents are used, the 2-OH position of the carbohydrate has to be unprotected to prevent elimination of the 2-benzyloxy

group. Because 2-unprotected mannosyl cyanides are not easily obtainable, this method is limited to gluco- and galacto-type carbohydrates. Glycosyl cyanides have also been hydrolyzed and then converted into thioesters **63**, which were then used in a Liebeskind-Srogl coupling[58] to yield D-gluco-, D-galacto- and manno-type *C*-acyl glycosides while retaining the configuration of the starting cyanide.[59] A Liebeskind-Srogl approach using a pivaloyl protected equivalent of **63** has also been reported (Scheme 8).[60,61]

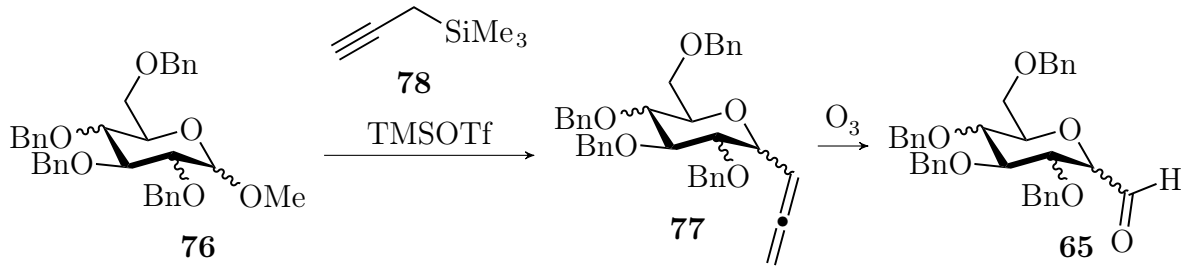
Benzyl protected *C*-formyl glycosides **65** were also used as intermediates for the synthesis of *C*-acyl glycosides. One of multiple methods for the synthesis of *C*-formyl glycosides is reduction of the respective glycosyl cyanide. Multiple methods which revolve around the addition of a carbon nucleophile as formyl surrogate to a glycolactone **66** were also reported (Scheme 9).[48]



Scheme 9: Syntheses of *C*-formyl glycosides.

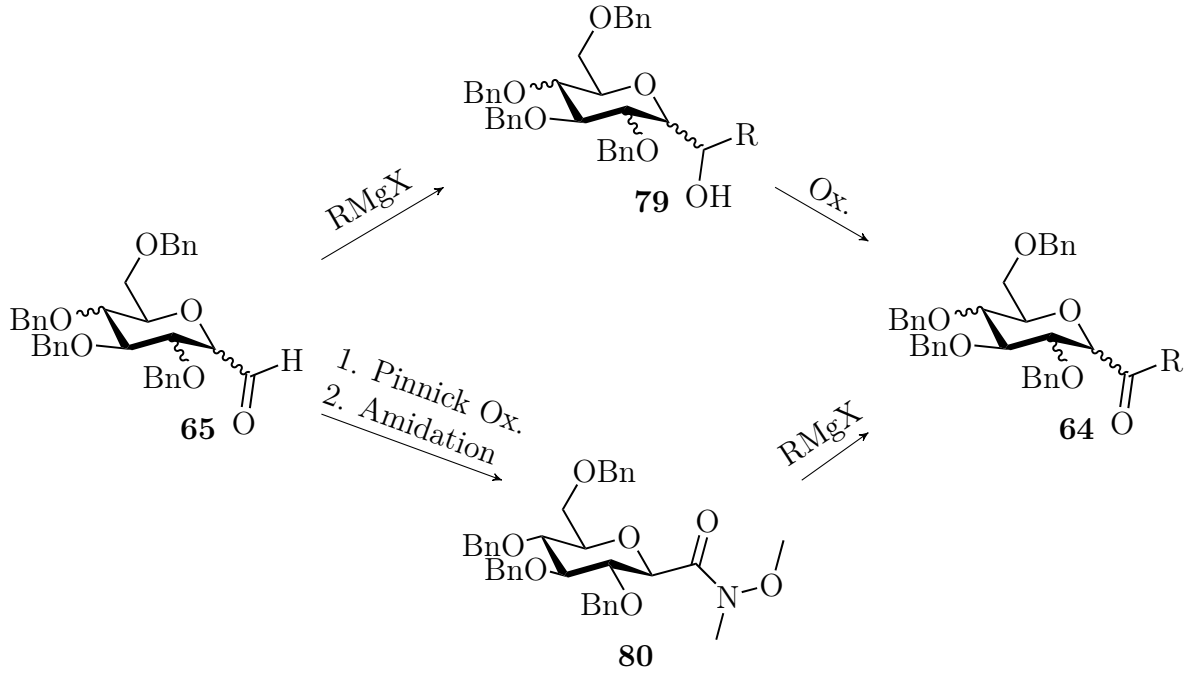
The nucleophiles may be lithiated thiazoles **73**[62], lithiated dithioacetals **74**[63,64] or lithiated phenylacetylene **75**[64]. The resulting lactols **69**, **70** and **71** were reduced β-selectively by Et_3SiH in presence of a lewis acid. In order to obtain the *C*-formyl glycosides from the glycosyl thiazoles they were converted into thiazolium salts by MeOTf, reduced by $NaBH_4$ and the resulting thioaminal cleaved by $HgCl_2$. The glycosyl dithianes were cleaved by MeI. Reduction of the triple bond by Lindlar[65] catalyst followed by ozonolysis were the final steps in the synthesis of benzylated *C*-formyl D-glucoside **72** from **71**.

Lastly a procedure employing allenylation followed by ozonolysis has also been reported (Scheme 10).[66]



Scheme 10: Synthesis of *C*-formyl glycosides by allenylation and ozonolysis.

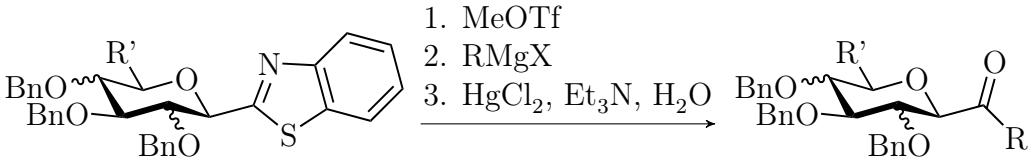
Addition of a Grignard reagent to these *C*-formyl glycosides **65** then leads to alcohols **79** which then have to be oxidized again to yield the desired *C*-acyl glycoside **64**.[48]



Scheme 11: Synthesis of *C*-acyl glycosides from *C*-formyl glycosides (II).

Another approach for *C*-acyl D-glucosides in which the aldehyde is first oxidized into a carboxylic acid[67,68] and then converted into the Weinreb amide **80**[69] has also been reported. Additon of Grignard reagents to this Weinreb amide then yielded *C*-acyl D-glucosides **64** (Scheme 11).[70]

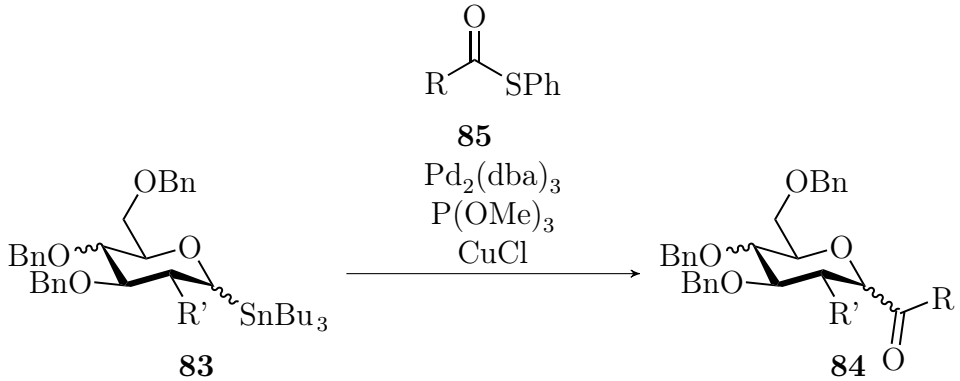
Addition of Grignard reagents to β configured glycosyl benzothiazolium salts which are synthesized in the same way as the glycosyl thiazoles in Scheme 9, followed by $HgCl_2$ mediated hydrolysis of the resulting thioaminal has also been reported to yield *C*-acyl β-glycosides (Scheme 12).[71]



81 **82**

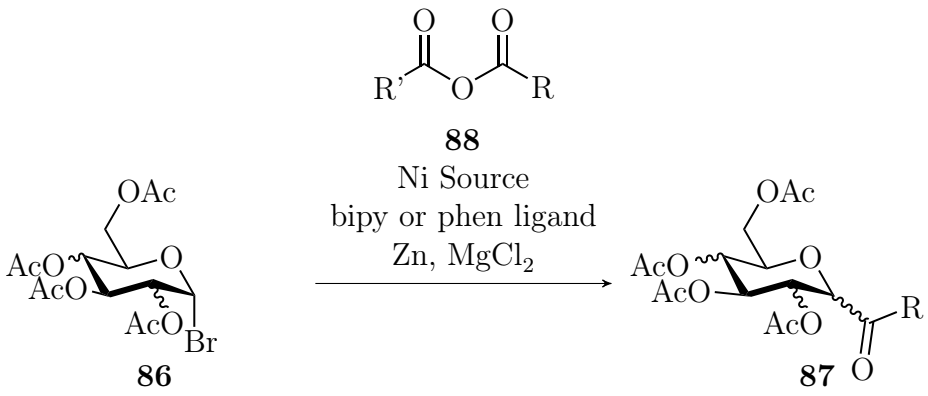
Scheme 12: Synthesis of *C*-formyl glycosides from glycosyl benzothiazoles.[71]

Zhu et al. reported a Stille type cross coupling approach which employs anomeric D-gluco- and D-galacto-type stannanes in three fold excess. The *C*-acyl glycosides retain the original configuration of the starting stannane (Scheme 13).[72]



Scheme 13: Synthesis of *C*-acyl glycosides via Stille cross coupling (III).[72]

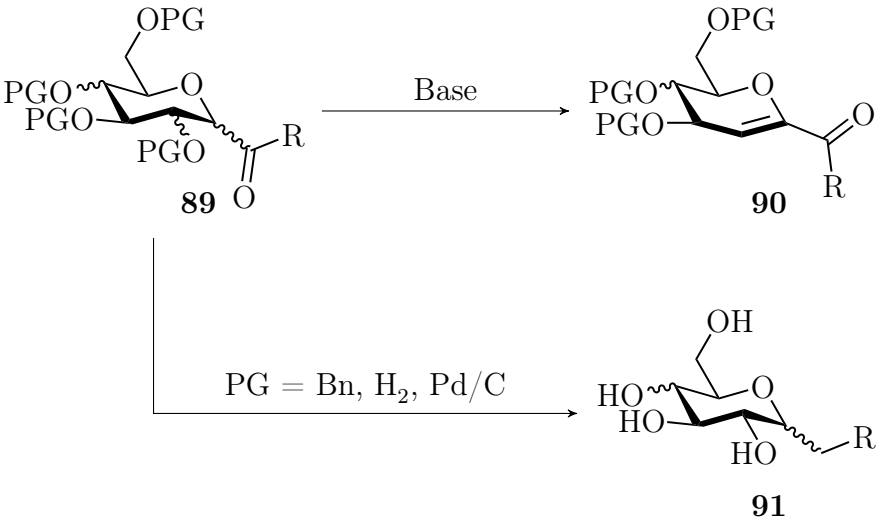
The most direct approach so far employs peracetylated glycosyl bromides in a reductive coupling with carboxylic acid anhydrides. This approach yields α/β-mixtures when D-gluco-type (α:β∼2:1) and D-galacto-type (α:β∼8:1) sugars are employed (Scheme 14).[73,74]



Scheme 14: Synthesis of *C*-acyl glycosides via reductive cross coupling (III).[73,74]

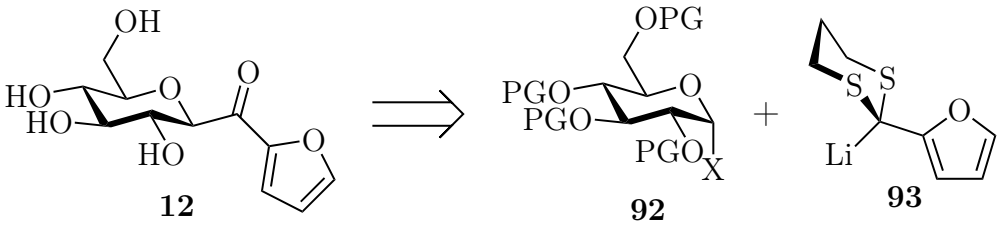
While reactions with 2,3,4,6-tetra-*O*-acetyl-α-D-mannopyranosyl bromide are α-selective, all synthesized peracetylated *C*-acyl α-mannosides were reported to be unstable.[73,74]

The instability of protected *C*-acyl glycosides is actually a major problem of these compounds. All *C*-acyl glycosides have been reported to eliminate the OPG group in 2-position under basic conditions. This is especially a problem if esters are used as protective groups as these are deprotected under basic conditions. Zou et al. have recently reported a workaround in which they protect the carbonyl as an acetal.[60,61] This acetal is cleaved under acidic conditions after basic hydrolysis of the ester to avoid this elimination. The deprotection of benzyl protected *C*-acyl glycosides is also problematic. The usually employed hydrogenative conditions also result in deoxygenation of the ketone if the substituent R is aromatic (Scheme 15).[70,72,75]



Scheme 15: Problems involving commonly used protective groups of *C*-acyl glycosides.

Because of these problems, syntheses of unprotected *C*-acyl glycosides have barely been reported. A more direct approach towards scleropentaside A **12** and *C*-acyl glycosides in general would be a Corey-Seebach reaction between a lithiated dithiane and a readily available protected D-glucosyl halide[76] (Scheme 16).

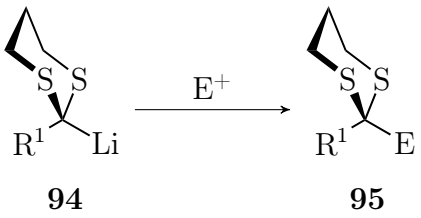


Scheme 16: Retrosynthesis of scleropentaside A **12**.

While preliminary results have already shown that this reaction is possible and scleropentaside A **12** can be synthesized by this method, the sequence had not been optimized.[77] A major advantage of this approach would be the low step count. Glucosyl halides are readily available and after the Corey-Seebach reaction only deprotection steps are required. Additionally the dithiane might act as protective group after the Corey-Seebach reaction to prevent the side reactions mentioned in Scheme 15. Ideally, this reaction proceeds through a S_N2-mechanism, resulting in a β-selective reaction.

3.2.3 Corey-Seebach reaction

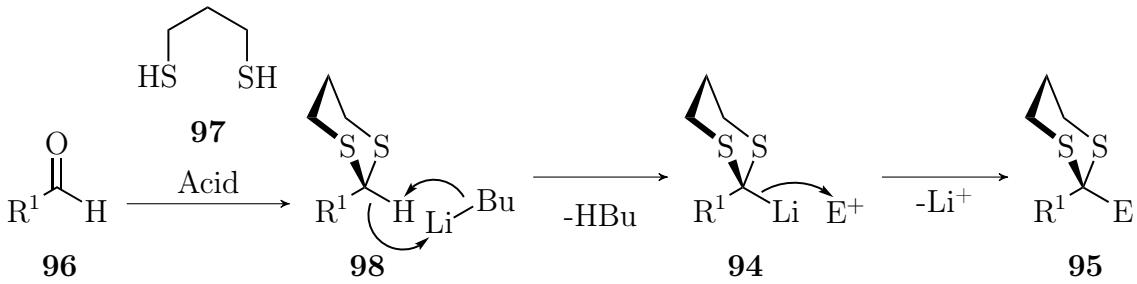
The Corey-Seebach reaction is a classic umpolung reaction between a lithiated dithiane **94** and an electrophile to form a C-C bond (Scheme 17).[78] The dithianes for this reaction are easily prepared and their lithiated species exhibit high nucleophilicity, which usually results in high yields. Thus this reaction has been widely used in organic synthesis.[79,80]



94 **95**

Scheme 17: Corey-Seebach reaction.[78]

The dithianes for this reaction are usually prepared by Brønsted or Lewis acid catalyzed condensation of the respective aldehyde **96** with 1,3-propanedithiol **97**. A major advantage of dithianes compared to other dithioacetals is the enhanced stability of the lithiated species compared to other lithiated dithioacetals. (Scheme 18).[78–80]

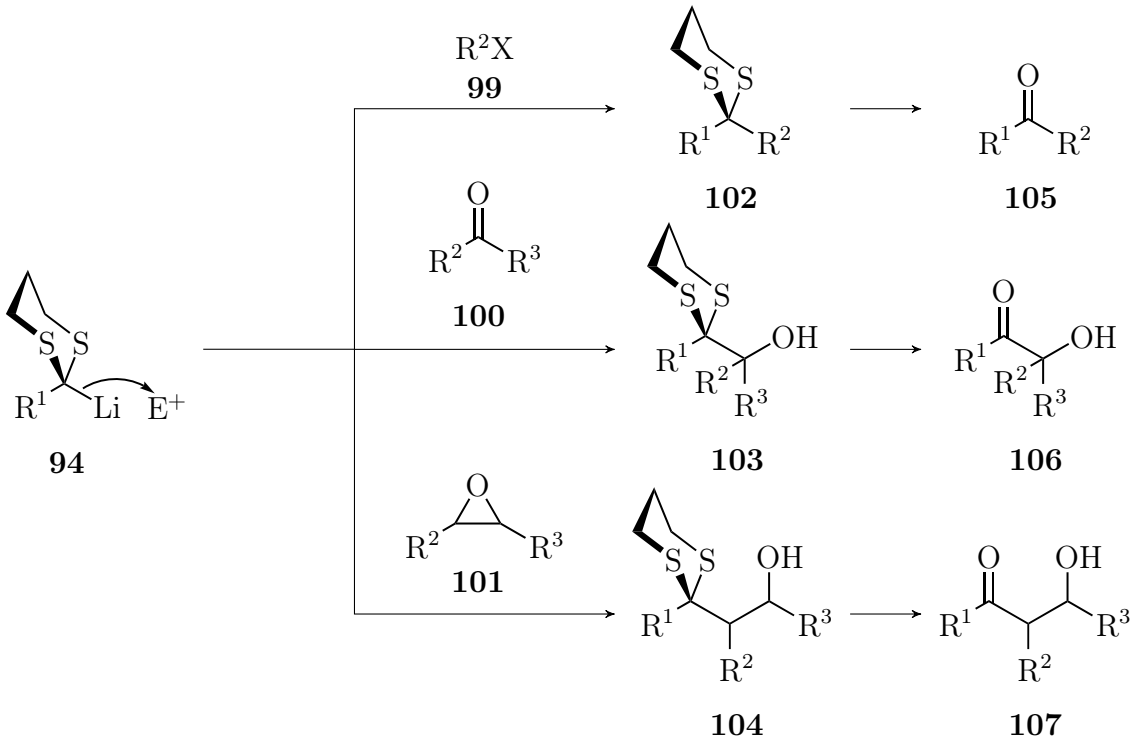


96 **98** **94** **95**

Scheme 18: Dithiane synthesis and Corey-Seebach reaction.[79]

Unlike the hydrogen atom of the starting aldehyde, the hydrogen atom of the dithioacetal is now acidic and can be abstracted. Usually *n*-BuLi is used for this deprotonation, but *t*-BuLi is recommended for substituted dithianes.[79] This turns the formerly electrophilic carbon atom of the carbonyl into a nucleophilic carbon atom enabling a C-C-bond forming reaction with an electrophile. This process, which inverts the reactivity of a carbon atom, is referred to as umpolung.[79]

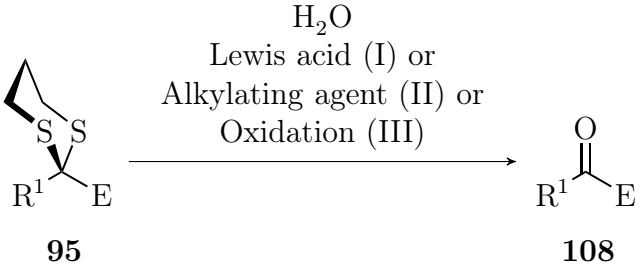
Suitable commonly used electrophiles for this reaction are alkylhalides **99**, carbonyl compounds **100** and epoxides **101** (Scheme 19).[79]



Scheme 19: Selection of suitable electrophiles for the Corey-Seenach reaction.[79]

The reaction with alkyl halides **99** gives simple dithianes **102**. Regeneration of the carbonyl unit then results in a ketone **105**. The reaction of a carbonyl compound **100** with the lithiated dithiane **94** generates a α-hydroxy-ketone after regeneration of the carbonyl unit, while the reaction with epoxides **101** leads to a β-hydroxy-ketone **107**.[79]

The carbonyl unit is then usually regenerated by hydrolysis (Scheme 20).[80]



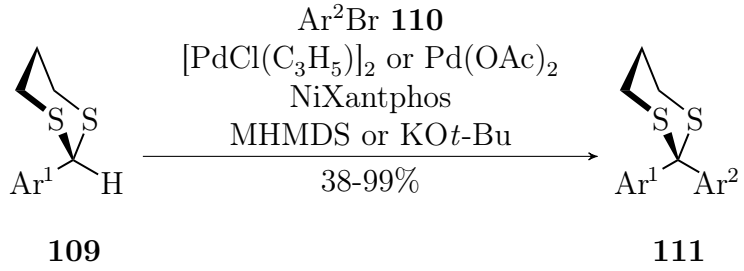
Scheme 20: Deprotection of dithianes.[79]

Due to the high stability of the dithianes this process has to be mediated by either a soft lewis acid which forms a complex with the propanedithiol (I), an alkylating agent which alkylates the thiols of propanedithiol (II) or an oxidizer which oxidizes the propanedithiol (III), giving the ketone. Employed Lewis acids are usually heavy metals such as Hg^{2+}, Ag^{+} or Cu^{2+} which should be avoided due to their toxicity. Although deprotection reaction

using alkylating agents such as methyl iodide propceed well, they require that no other alkylatable functional groups are present in the molecule. Alkylating agents are also usually potent carcinogens.[81] Methods employing oxidation by iodine or hypervalent iodine usually tolerate a wide range functional groups and are not toxic.[79,80]

In recent years, methods which do not use lithiated dithianes as nucleophiles to couple dithioacetals with more unusual electrophiles have been developed.

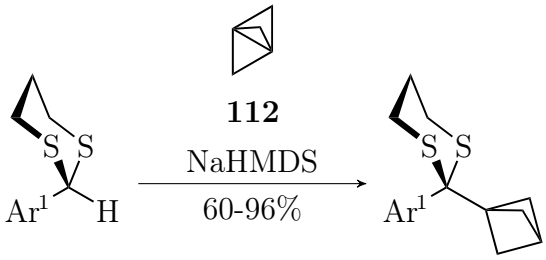
Two Pd-catalyzed cross coupling methods of aryl dithianes **109** with aryl bromides **110** have been reported. Both methods use NiXantphos as ligand, a Pd^{2+} source and employ LiHMDS, NaHMDS or KO*t*-Bu as base (Scheme 21).[82,83]



109 **111**

Scheme 21: Pd-catalyzed cross coupling of aryl dithianes.[82,83]

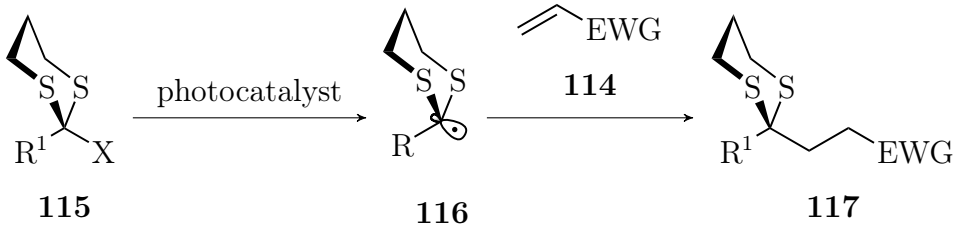
NaHMDS was also used in reactions of aryl dithianes **109** with the unusal electrophile [1.1.1]propellane **112** to give bicyclo[1.1.1]pentyl-substituted dithianes. Bicyclo[1.1.1]pentanes have recently gained interest in medicinal chemistry due to being possible bioisosterer of phenyl groups (Scheme 22).[84,85]



109 **113**

Scheme 22: Reaction of aryl dithianes **109** with [1.1.1]propellane **112**.[84,85]

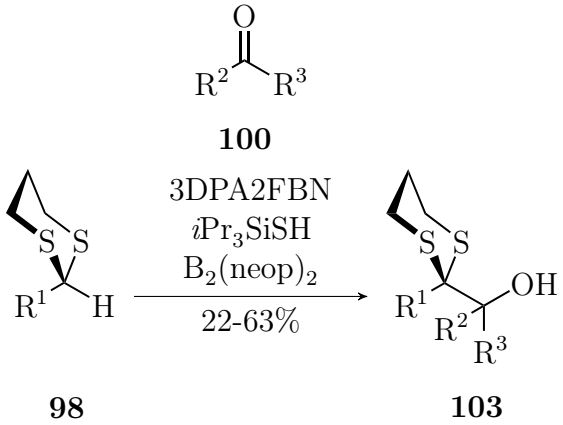
Not all approaches require a base. Recently, multiple methods involving photocatalytic generation of a dithianyl radical have been reported. These dithianyl radicals readily undergo conjugate addition to electron deficient alkenes **114** such as acrylnitriles, vinylsulfonates or acrylates.[86–89] This is useful since lithiated dithianes usually do not undergo 1,3-addition because they preferentially attack carbonyl groups.[78]



Scheme 23: Photocatalytic reaction of dithianes **115** with electron deficient alkenes.[86]

While these reactions were reported to occur with simple dithianes (X = H) in intramolecular reactions,[86] intermolecular reactions usually require a substituted dithioacetal (X = BF_3K[88] or COOH[89]) from which the radical is generated. Another approach used benzo[d][1,3]dithioles instead of dithianes as these did not react with the photocatalyst.[87]

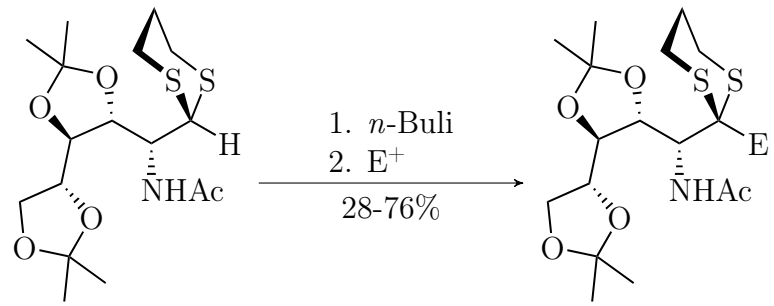
The dithianyl radical is not always the species undergoing C-C bond formation in photocatalytic reactions. In a recently reported method involving 2,4,6-Tris(diphenylamino)-3,5-difluorobenzonitrile (3DPA2FBN) as photocatalyst, *i*Pr_3SiSH as hydrogen atom transfer agent and bis(neopentyl glycolato)diboron as lewis acid, dithianyl anions are added to carbonyls. Although the dithianyl radical is formed, it is further converted to the dithianyl anion by the photocatalyst. The generated dithianyl anion then attacks the aldehyde or ketone.



Scheme 24: Photocatalytic addition of dithianes **98** to carbonyls **100**.[90]

This is particularly interesting since the reaction generates the dithianyl anion under base free conditions instead of using a strong base. The lack of heavy metals makes this synthetic method especially useful for medicinal chemistry.

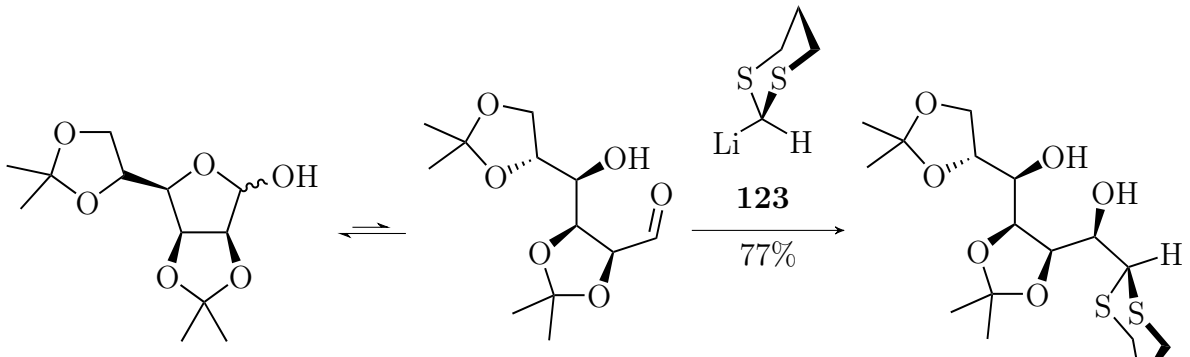
Carbohydrate derivatives have been used both as nucleophiles and electrophiles in Corey-Seebach reactions, as the lactols can be either converted into a dithiane or used as electrophile. In an example reported by Redlich et al. an open chained glucosamine derived dithiane **118** was deprotonated and then reacted with various electrophiles in moderate to good yields (Scheme 25).[91]



118 **119**

Scheme 25: D-Glucosamine derived dithiane **118** as nucleophile.[91]

Paulsen et al. reported the use of D-mannose-derivative **120** as electrophile stereoselectively yielding the 1,4-diol **121** in 77% yield in the synthesis of L-glycero-D-manno-heptose (Scheme 26).[92]



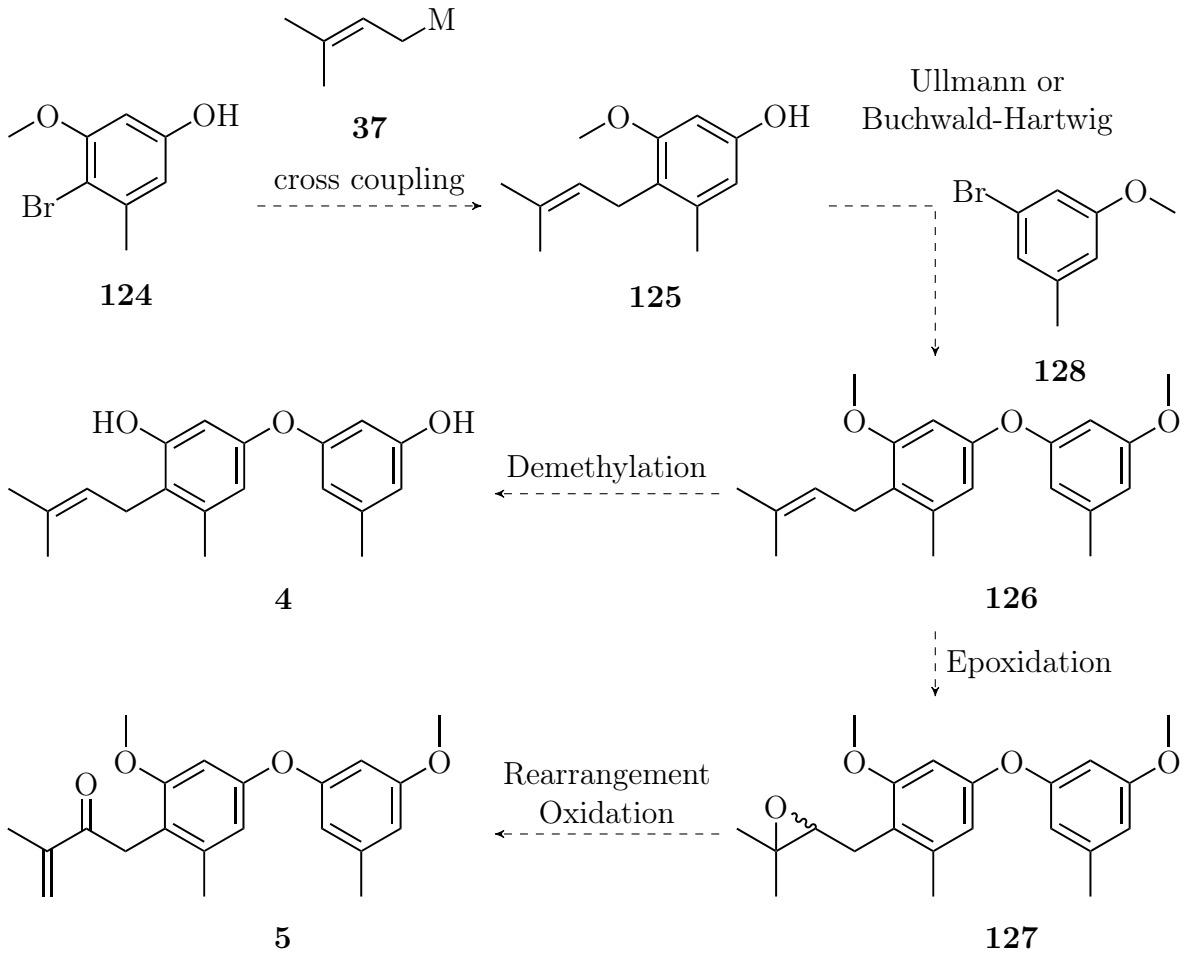
120 **122** **121**

Scheme 26: Corey-Seebach reaction with D-mannose-derivative as electrophile **120**.[92]

The reaction actually occured between the open chained carbohydrate **122**, which is in equillibrium with the lactol **120** and the lithiated dithiane **123**. Thus the Corey-Seebach reaction provided an open chained protected carbohydrate **121**. Removal of the dithiane yielded the corresponding aldehyde, which then cyclized again, yielding a pyranose. Thus, the reaction is an elegant method to elongate carbohydrates.

4 Aim of the project

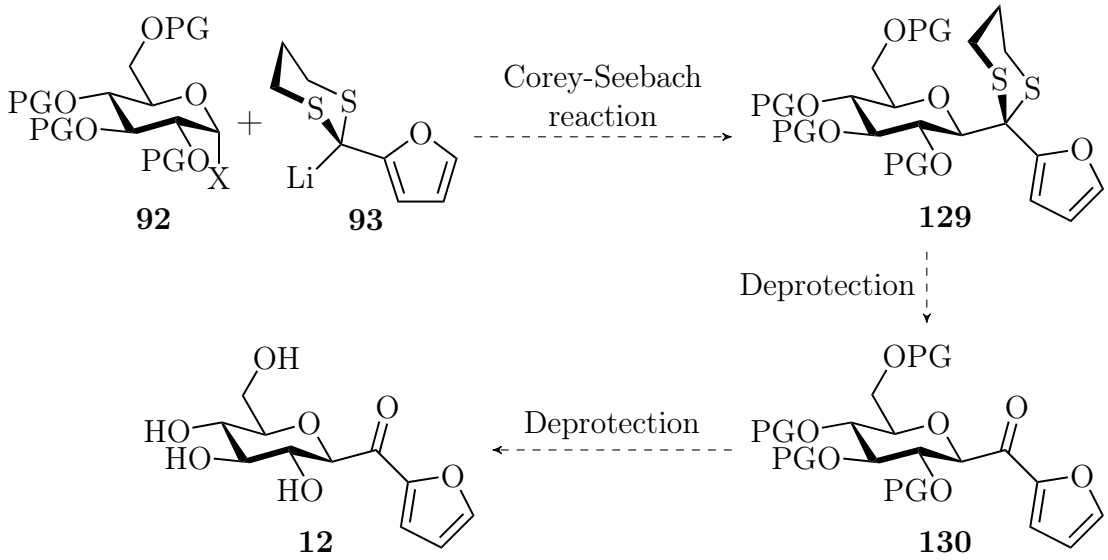
The aim of this project is the development of robust synthetic approaches towards the diorcinol compound **5**, which has been reported to have anti-MRSA activity (Scheme 27), as well as scleropentaside A **12** (Scheme 28).



Scheme 27: Planned syntheses of **5** and **4**.[1, 24, 25]

The prenylated orcinol is supposed to be synthesized by a cross coupling approach between literature known bromide **124** and a suitable prenyl-nucleophile **37**. Conversion to protected verticilatin **126** is then supposed to be achieved by an aryl ether coupling of prenylated orcinol between commercially available bromide **128** and prenylated orcinol **124**. A biomimetic sequence consisting of epoxidation, rearrangement and oxidation should then lead to the desired compound **5**. Removal of the methyl groups may also lead to verticilatin **4**. Employing other prenylated orcinols may also enable the synthesis of diorcinols D **1** and I **2**.[1]

Another goal was optimization of the synthesis of scleropentaside A **12**. The synthesis of scleropentaside A **12** revolves around the *C*-glycosylation step between a suitably protected D-glucosyl halide with a lithiated dithiane. In the optimal case this reaction proceeds through a S_N2 mechanism. The reaction requires protective groups for the glycosyl OH which can withstand the highly basic conditions of the Corey-Seebach reaction.[2–4]



Scheme 28: Planned synthesis of scleropentaside A **131**.[2–4]

Furthermore, conditions for the efficient removal of the dithiane and the protective groups have to be found. Although benzyl groups seem to be the natural choice for the Corey-Seebach reaction, they are difficult to remove. Since the protective groups are only required for the *C*-glycosylation step, more labile protective groups might be more suitable. TMS groups may be a good choice for this reaction as they are notably labile, but withstand highly basic anhydrous conditions. In addition, galacto- and manno-type donors as well as 2-deoxysugars should also be investigated as substrates. The scope of dithianes should also be investigated. Furthermore, the possibility to generate the α-isomers should also be evaluated.

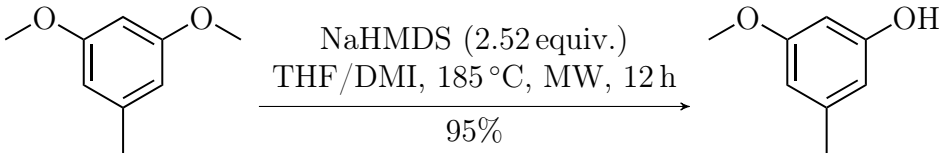
5 Results and discussion

5.1 Diorcinols

The first part of the thesis dealt with the development of a synthetic approach towards diorcinols, which have been reported to exhibit antibacterial activities.

5.1.1 Synthesis of prenylated orcinols

A procedure for the monodemethylation of dimethylorcinol **132** has already been reported.[93,94] However, the reported procedure uses NaSEt as demethylation agent which is unpleasant to handle. Thus, a different protocol that uses NaHMDS as demethylation agent was investigated (Scheme 29).[1,95]



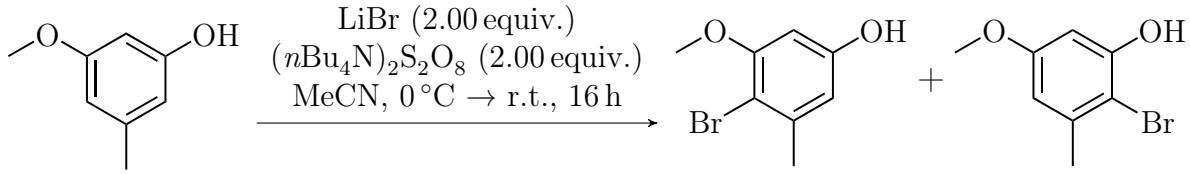
132 **8**

Scheme 29: Monodemethylation of **132**.[1,95]

In contrast, to the original procedure the reaction was carried out under microwave irradiation. The modified procedure was indeed applicable to dimethylorcinol **132** giving monomethylorcinol **8** in an excellent yield of 95% on a 700 mg scale. Due to the high temperatures the pressure in the reaction vessel reached ≈ 10 bar. Because of safety precautions, the reaction could not be scaled up further due to the limited volume of the reaction vessel. However, it was possible to run multiple reactions which were combined prior to workup, without any decrease in yield.[1,95]

To introduce a prenyl group via cross coupling, a bromine had to be installed in *p*-position to the phenolic hydroxyl group of **8** to act as leaving group. To achieve direct bromination a procedure that uses LiBr as bromine source and $(n\mathrm{Bu_4N})_2\mathrm{S_2O_8}$ as oxidant was used, giving the desired brominated compound **124** in 45% yield . The reaction was not regioselective as the isomer **133**[96] was also generated in 23% yield, resulting in a 2:1 ratio of isomers (Table 2, Entry 3). Interestingly, this ratio was inverted when the reaction was started at room temperature instead of 0 °C while the overall yield was not affected (Table 2, Entry 1).[1,97] Keeping the reaction at 0 °C did not lead to any conversion (Table 2, Entry 2). Attempts to achieve higher conversion of the starting material by using more than two equivalents of LiBr and $(n\mathrm{Bu_4N})_2\mathrm{S_2O_8}$ did not result

in a higher yield of **124** but instead led to the formation of undesired polybrominated products (Table 2, Entries 4-5). Overall this procedure is still an improvement over the literature-known four-step synthesis of **124**.[1,98]

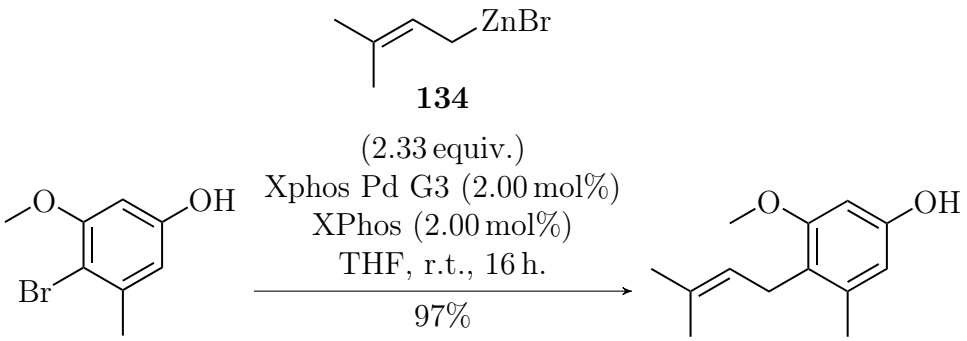


8 **124** 45% 58% b.r.s.m. **133** 23% 30% b.r.s.m.

Table 2: Screening results on the formation of **124** (t = 16 h in MeCN).[1]

	equiv. LiBr	equiv. $(n\mathrm{Bu_4N})_2\mathrm{S_2O_8}$	T	yield **124**	yield **133**	reisolated **8**
1	2.0	2.0	r.t.	25%	47%	5%
2	2.0	2.0	0 °C	-	-	98%
3	2.0	2.0	0 °C → r.t.	45%	23%	22%
4	2.5	2.5	0 °C → r.t.	41%	19%	-
5	2.0	2.5	0 °C → r.t.	43%	22%	-

Applying a procedure using prenylzinc bromide **134** as prenyl source in a Negishi cross-coupling reaction, which was catalyzed by a Pd complex generated from Xphos Pd G3 and additional Xphos, resulted in a clean conversion of bromide **124**, giving the desired prenylated orcinol **125** in an excellent yield of 97% (Scheme 30).[24,25]



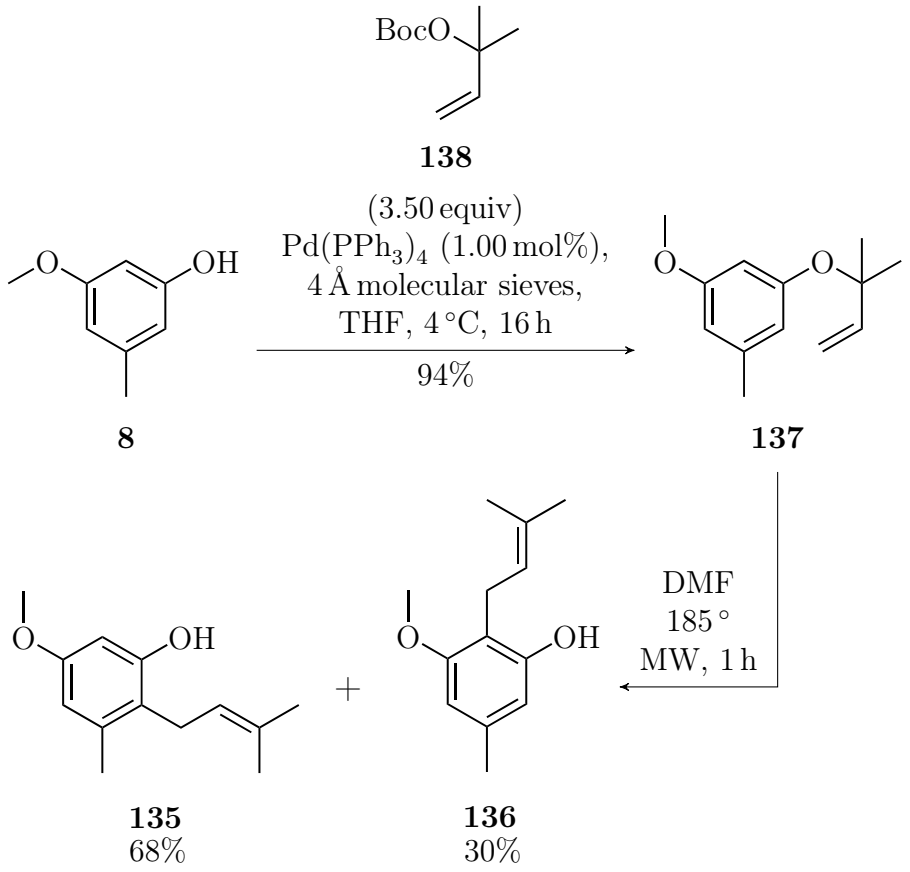
134

124 **125**

Scheme 30: Prenylation of **124** by Negishi cross-coupling.[1,24,25]

Application of a Suzuki protocol[30] was also attempted, but yielded no product.[1] Since the bromide **124** has an acidic proton, which destroys the C-Zn bond of prenylzinc bromide **134** by protodemetallation, an additional equivalent of prenylzinc bromide **134** had to be added.[1,24,25]

In order to generate the prenylated orcinols **135** and **136** in a divergent approach by Claisen rearrangement[99], allyl ether **137** had to be synthesized. This allyl ether **137** was successfully generated by Tsuji-Trost-allylation[100,101] of monomethylorcinol **8** with *tert*-butyl-(2-methylbut-3-en-2-yl) carbonate[102] **138** using $Pd(PPh_3)_4$ as precatalyst. In order for this reaction to succeed, it was extremely critical to tightly seal the reaction vessel, which caused a slight overpressure due to gas evolution.[1]

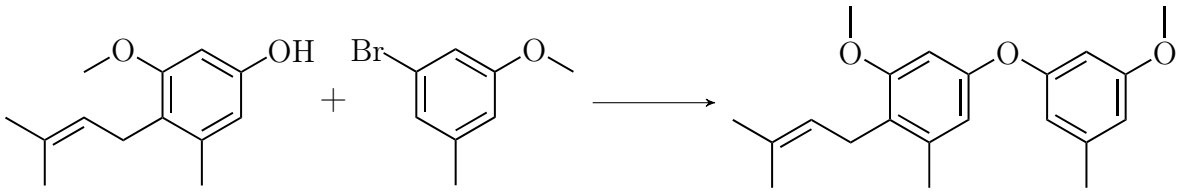


Scheme 31: Tjusi-Trost allylation of **8** and Claisen rearrangement of **137**.[1]

Claisen-rearrangement of the resulting allyl ether **137** proceeded smoothly, giving the desired prenylated orcinols **135** and **136** in a 2:1 ratio with a combined yield of 98% (Scheme 31).[1]

5.1.2 Diaryl ether coupling and endgame

The coupling of prenylated orcinol **125** with bromide **128** to generate diaryl ether **126** proved to be more difficult than expected. CuI based Ullmann procedures at high temperatures in high boling solvents such as NMP or DMF failed due to decomposition of the starting material (Table 3 Entries 1-2). A milder Ullmann procedure using a preformed Cu^+ catalyst in NMP lead to no conversion of the starting materials (Table 3 Entry 3). A Buchwald-Hartwig procedure using $Pd(OAc)_2$ as Pd source, *t*BuXPhos **139** as ligand and K_3PO_4 as base in toluene also lead to no conversion at all (Table 3 Entry 4).[1]



125 **128** **126**

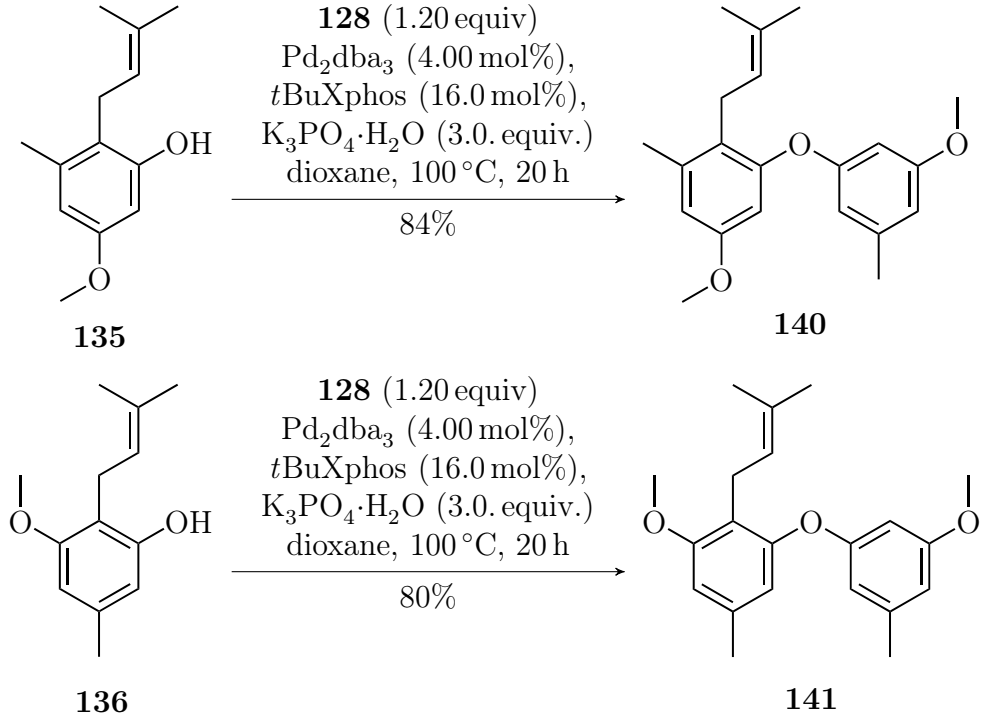
Table 3: Screening results on the formation of **126**. (1.20 equiv. of **128**)[1]

	Precatalyst (mol%)	**139** (mol%)	Base (equiv.)	Solvent	*T* (°C)	*t* (h)	yield
1[103]	CuI (10)	-	Cs_2CO_3 (2.0)	NMP	195	2	-
2[104]	CuI (1.0) + $Fe(acac)_3$ (2.0)	-	K_2CO_3 (2.0)	DMF	135	16	-
3[105]	$Cu(PPh_3)_3Br$ (20)	-	Cs_2CO_3 (3.0)	NMP	100	24	-
4[106]	$Pd(OAc)_2$ (2.0)	3.0	K_3PO_4 (2.0)	toluene	100	16	-
5[107]	$Pd_2(dba)_3$ (4.0)	16	K_3PO_4 (3.0)	dioxane water (1:1)	100	20	16%
6	$Pd_2(dba)_3$ (4.0)	16	K_3PO_4 (3.0)	dioxane	100	20	trace
7	$Pd_2(dba)_3$ (4.0)	16	$K_3PO_4 \cdot H_2O$ (3.0)	dioxane	100	20	88%
8	$Pd_2(dba)_3$ (2.0)	8.0	$K_3PO_4 \cdot H_2O$ (3.0)	dioxane	100	20	67%

Thus, reaction conditions that were originally reported to dimerize aryl bromides into diaryl ethers[107] were investigated. These conditions gave the desired diaryl ether **126** in low yield (Table 3 entry 5). A reason for the low yield was the generation of monomethyl orcinol **8** from bromide **128** by Pd-catalyzed substitution of bromide with hydroxide. Since only water can serve as hydroxide source in this reaction, the reaction was attempted

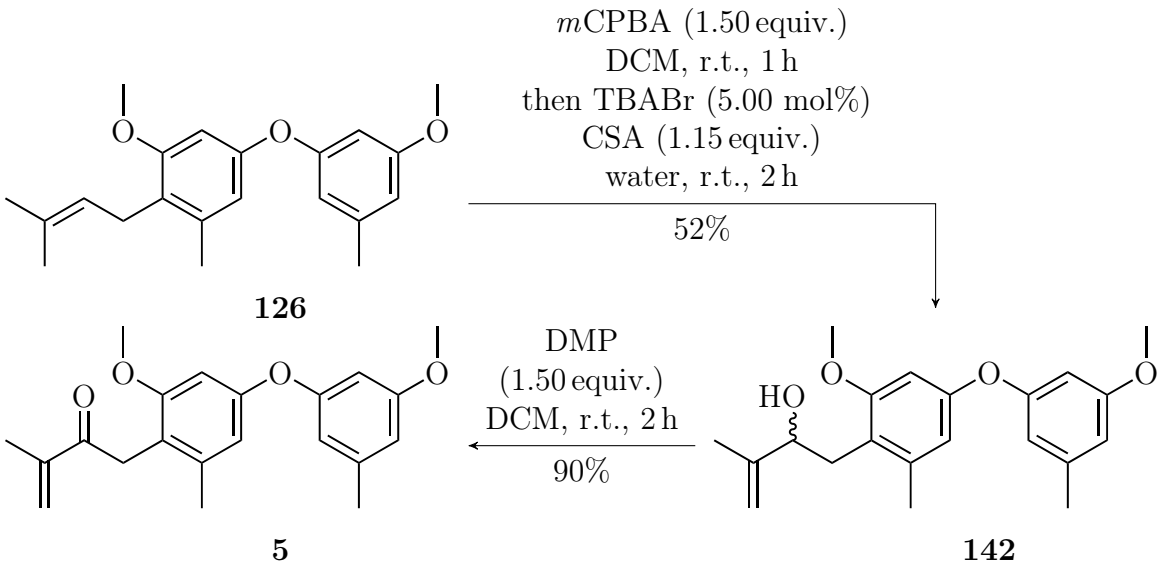
under anhydrous conditions (Table 3 Entry 6). This resulted in barely any conversion of the starting bromide, revealing that water was required for the diaryl ether coupling reaction to occur. Conveniently, employing $K_3PO_4 \cdot H_2O$ as base instead of anhydrous K_3PO_4 gave the product **126** in a yield of 88% (Table 3 Entry 7). Attempts to lower the catalyst loading lead to lower yields (Table 3 Entry 8). [1]

Applying the same conditions to prenylated monomethylorcinols **135** and **136** gave the regioisomers **140** and **141** with equally satisfying yields, showing that these conditions are generally useful for the diaryl ether coupling of electron rich substrates (Scheme 32).[1]



Scheme 32: Diaryl ether coupling of prenylated orcinols **135** and **136**.[1]

The final steps in the synthesis of **5** consisted of the supposed biomimetic approach, in which the double bond of the prenyl unit is epoxidized, rearranged and the resulting alcohol oxidized to the respective α,β-unsaturated ketone.[1] The double bond of **126** was epoxidized by *m*CPBA.[108] The resulting epoxide was directly converted in a one-pot reaction by camphorsulfonic acid and tetrabutylammonium bromide[109] to yield allylic alcohol **142** in 52% yield. Oxidation of the allylic alcohol by Dess-Martin periodinane[110] finally gave the target compound **5** in 90% yield (Scheme 33).[1]



Scheme 33: Endgame in the synthesis of **5**.[1]

The ^{1}H-NMR spectrum of compound **5** shows a upfield shifted singlet with an integral of three at 1.92 ppm, which can be assigned to the C-5" methyl protons of the side chain.

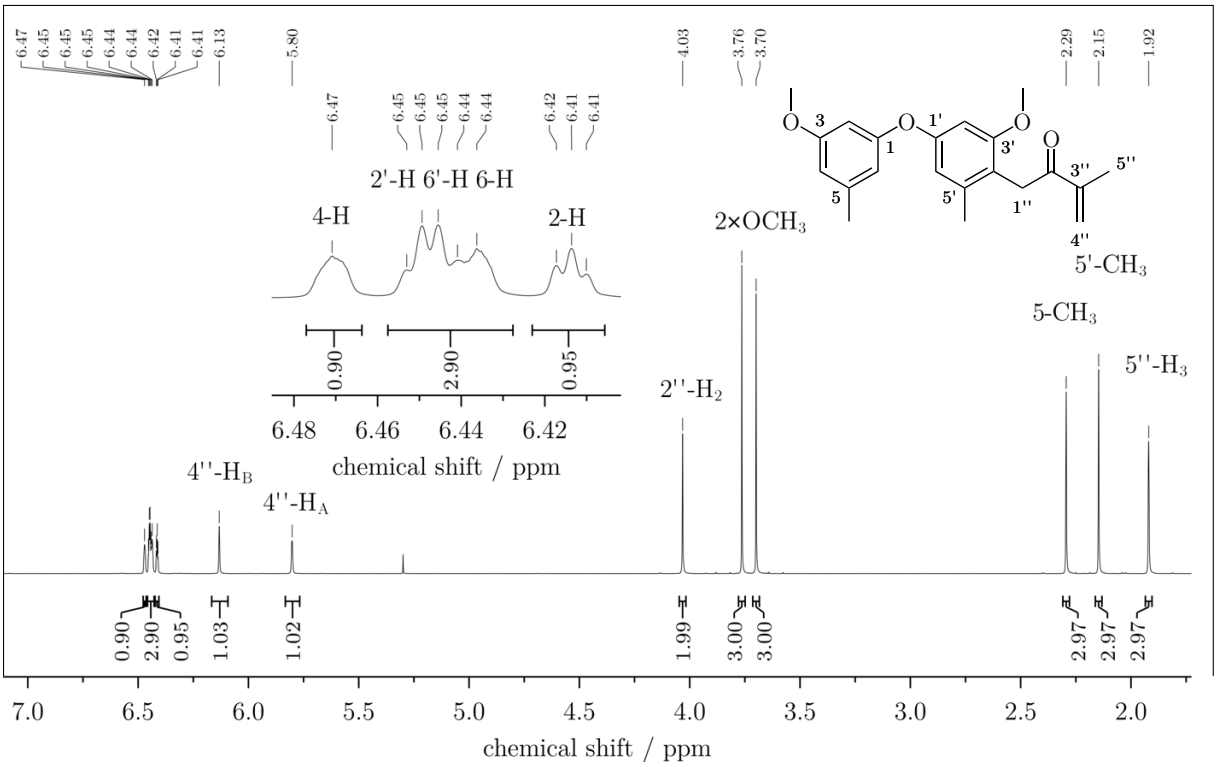


Figure 9: ^{1}H-NMR spectrum of **5** at 600 MHz in $CDCl_3$.[1]

The two singlets with an integral of three H at 2.15 and 2.29 ppm confirm the presence of the methyl groups bound to C-5' and C-5 of the aromatic rings. The two methoxy groups

bound to C-3' and C-3 resonate as two independent singlets with an integral of three at a higher chemical shift of 3.70 and 3.76 ppm due to the inductive effect of the oxygen atoms. The two benzylic protons bound to C-1" resonate as a singlet at 4.03 ppm. The terminal protons of the alkene resonate as broad singlets at 5.80 and 6.13 ppm because the coupling is not resolved. Further downfield 2-H resonates as a triplet at 6.41 ppm with a coupling constant of 2.1 Hz, indicating two ^4J couplings with two protons. This coupling is not not resolved in signals of 4-H and 6-H at 6.44 and 6.47 ppm as these resonate as broad singlets. The two protons H-2' and H-6' resonate as barely resolved doublets at 6.44 and 6.45 ppm with a coupling constant of 2.3 Hz, showing a strong roof effect due to their similar chemical shifts (Figure 9).

The DEPTQ-NMR spectrum showed a upfield shifted signal at 18.0 ppm corresponding to C-5" of the side chain. The carbon atoms of the two methyl groups bound to C-5' and C-5 resonate at 20.1 and 21.8 ppm, respectively.

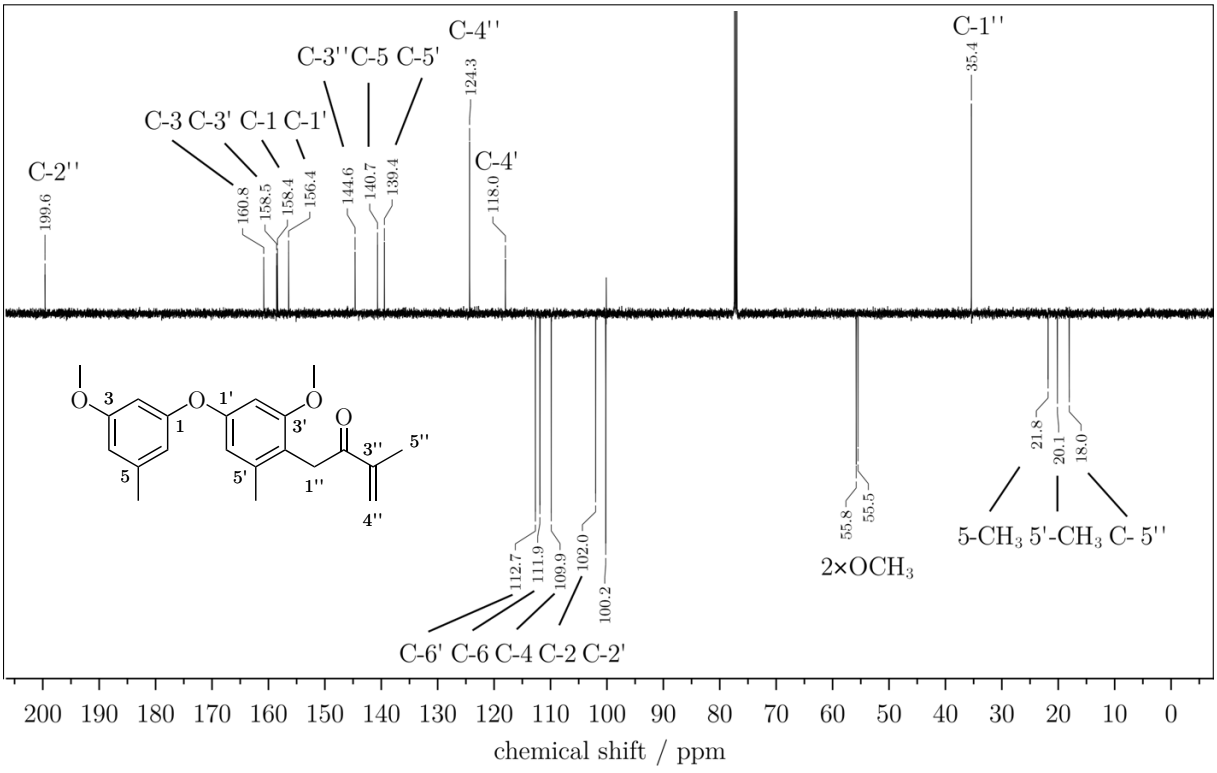
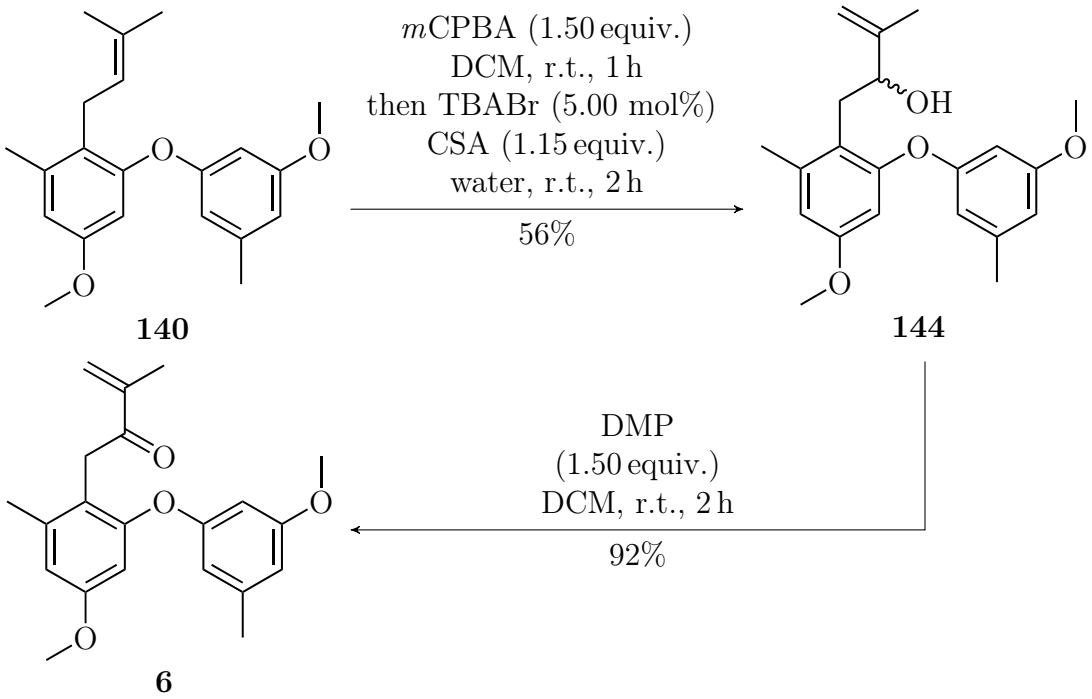


Figure 10: DEPTQ-NMR spectrum of **5** at 151 MHz in $CDCl_3$.[1]

The benzylic carbon C-2" resonates at 35.4 ppm. The two signals assigned to the methoxy groups bound to C-3 and C-3' resonate further downfield at at 55.5 and 55.8 ppm, due to the inductive effect of the oxygen atoms. The signals at $\delta = 100.2$ (C-2'), 102.0 (C-2), 109.9 (C-4), 111.9 (C-6), 112.7 (C-6'), were all assigned to aromatic carbon atoms bound to a proton. The carbon atom C-4', to which the side chain is bound, resonates at 118.0 ppm,

while the terminal carbon atom C-4" of the double bond resonates at 124.3 ppm. At 139.4 and 140.7 ppm the signals of the aromatic carbon atoms C-5' and C-5, to which methyl groups are bound, are present. The non-terminal carbon atom C-3" of the double bond shows a signal at 144.6 ppm. The aromatic carbon atoms bound to an oxygen are shifted even further downfield by the inductive effect. The aromatic carbon atoms C-1' and C-1, which are connected through an oxygen atom to form the diaryl ether, resonate at 156.4 and 158.4 ppm, while the two aromatic carbon atoms C-3' and C-3, to which the methoxy groups are bound, resonate at 158.5 and 160.8 ppm. Finally the signal at 199.6 ppm and the band at 1681 cm^{-1} in the IR spectrum confirm the presence of a carbonyl motif as the chemical shift of the ^{13}C-NMR signal and the wavenumber of the IR signal are both in typical ranges which are usually only occupied by carbonyl signals (Figure 10). HRMS showed a peak at m/z = 341.1747 which exactly matches the calculated mass of the molecular formula $C_{21}H_{24}O_4$ in association with a proton.[1]

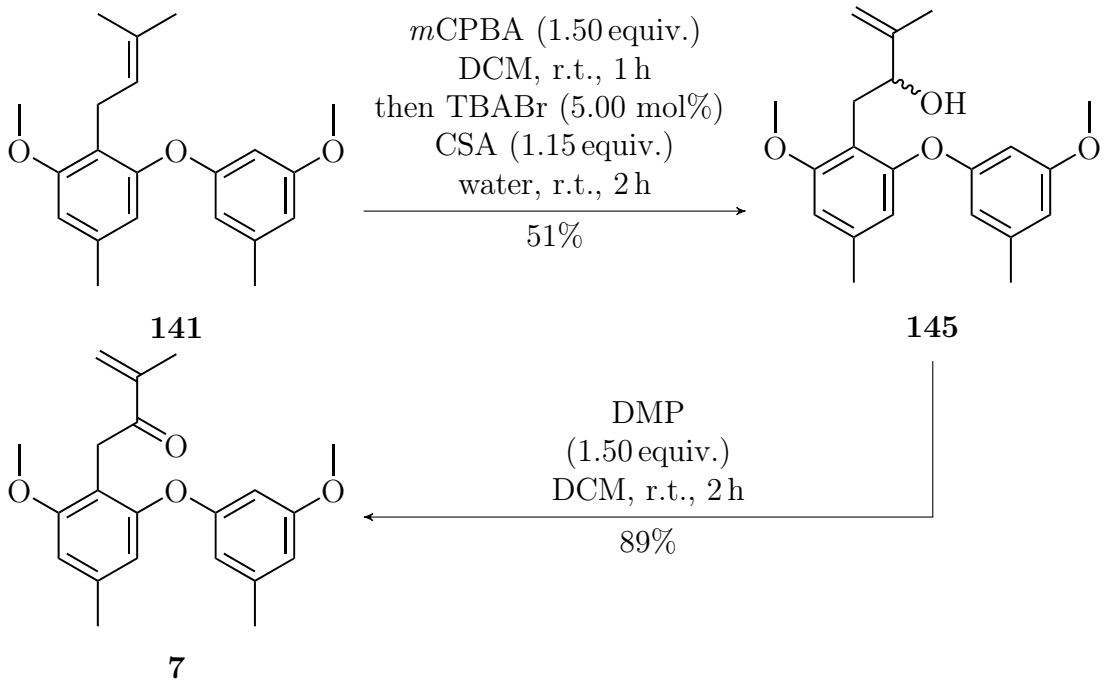
However, neither the IR nor the NMR data did match the reported data for compound **5**.[12] To rule out the possibility that the actual compound is a regioisomer of **5**, the regioisomers **6** and **7** were synthesized. The double bond of **140** was epoxidized by *m*CPBA[108] and the resulting epoxide directly converted in a one-pot reaction by camphorsulfonic acid (CSA) and tetrabutylammonium bromide (TBABr)[109] to yield allylic alcohol **143** in 56% yield (Scheme 34).[1]



Scheme 34: One-pot synthesis of isomer **6**.[1]

Oxidation of the allylic alcohol by Dess-Martin periodinane[110] gave the target compound **5** in 92% yield (Scheme 34).

For the final isomer, the one-pot epoxidation rearrangement reaction gave the desired allylic alcohol **145** in similar yield of 51% . The Dess-Martin oxidation[110] also proceeded smoothly giving the α,β-unsaturated ketone **7** in 89% yield (Scheme 35). Overall the yields for these reactions were very similar for all isomers (51-56% for the one-pot epoxidation-rearrangement reaction and 89-92% for the DMP oxidation).[1]

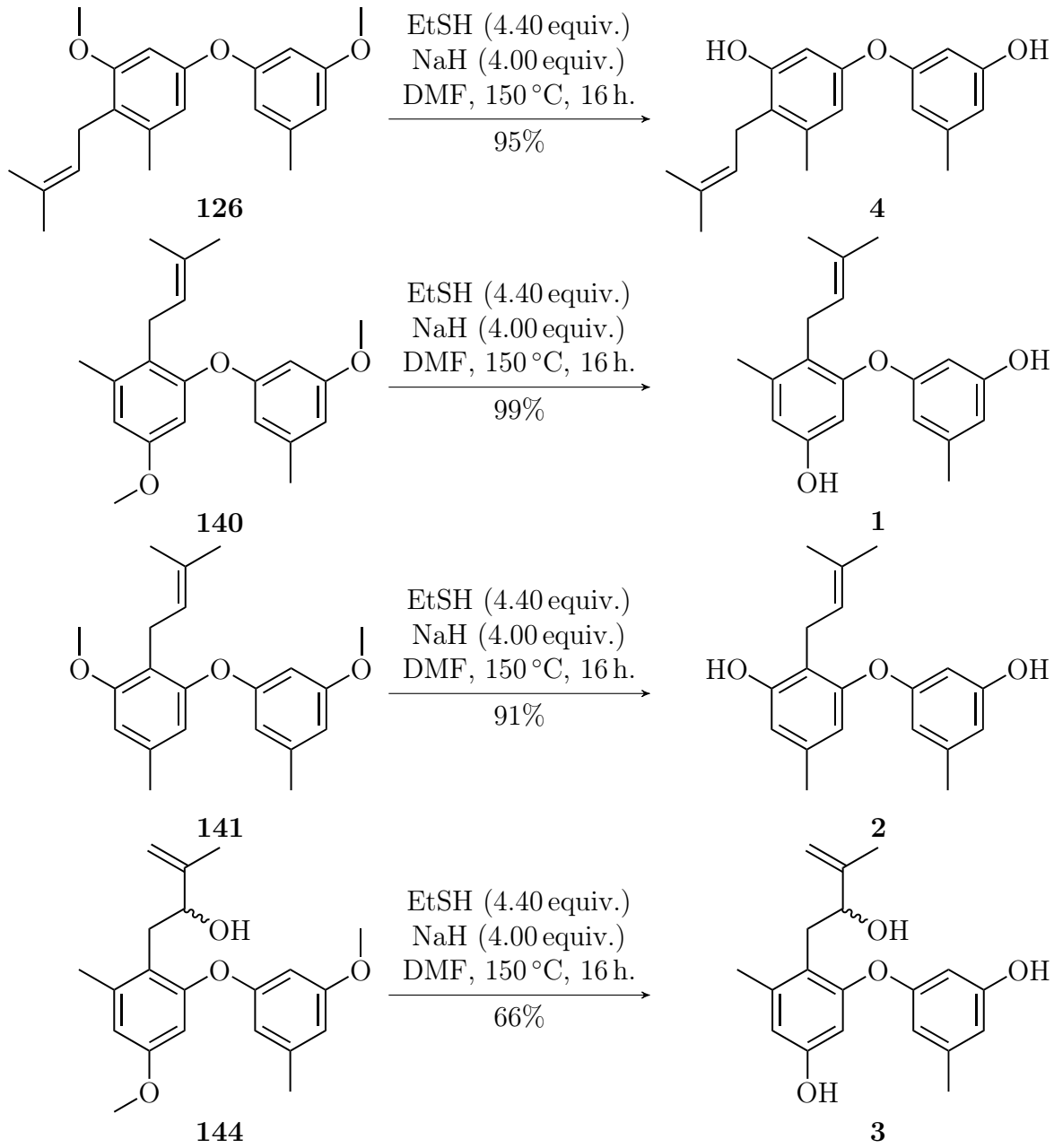


Scheme 35: One-pot synthesis of isomer **7**.[1]

Unfortunately, the NMR and IR data of these compounds also did not match the reported data. Thus the actual structure of the anti-MRSA active compound isolated by Li et al.[12] remains a mystery.

5.1.3 Deprotection of methylated orcinols

Since the deprotected forms of **126**[10], **140**[9], **141**[11] and **144**[14] were all reported to be natural products, deprotection of the methyl ethers was attempted (Scheme 36).[1]

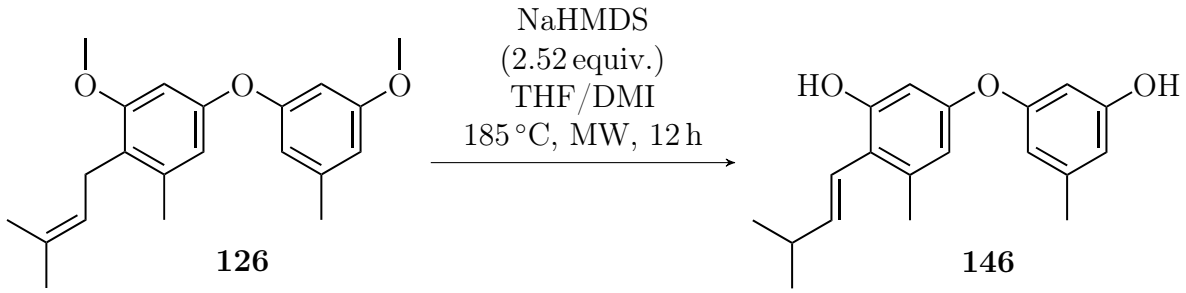


Scheme 36: Deprotection of methylated diorcinols.[1]

Deprotection of the methyl ethers with in situ generated NaSEt provided the proposed structure of verticilatin **4**, diorcinol D **1** and diorcinol I **2** in excellent yields of 91-99%. The reaction proceeded less cleanly with allyl ether **144** giving racemic diorcinol J **3** in a moderate yield of 66% (Scheme 36).[1]

Deprotection conditions using TMSI,[111] or BBr_3,[112] at -78 °C in DCM and led to complete decomposition of the starting materials, resulting in unidentifiable product mixtures.

While the demethylation procedure using NaHMDS[95] at a high temperature of 185 °C under microwave irradiation, which was used for the preparation of monomethylorcinol **8**, did achieve deprotection of the methyl groups, it also caused an unwanted isomerisation of the double bond (Scheme 37).



126 **146**

Scheme 37: Unwanted isomerization of the double bond by NaHMDS.

Apparently, NaHMDS was basic enough to abstract a proton in the benzylic position. Reprotonation then occured at the isopropyl position leading to the more stable conjugated double bond (Scheme 37).

The ^{1}H-NMR spectrum of compound **4** shows two upfield shifted singlets with an integral of three at 1.64 and 1.72 ppm which are typical for the methyl groups of the prenyl chain. The two singlets of the methyl groups with an integral of three at 2.16 and 2.27 ppm are shifted downfield slightly. The two benzylic protons at C-1" resonate as a doublet with a coupling constant of 7.0 Hz, which is typical for freely rotating bonds, at 3.20 ppm. The alkenyl proton 2-H" resonates at 5.02 ppm as multiplett due to ^3J coupling to the benzylic protons and ^{4}J coupling to the six methyl protons of the prenyl chain. Further shifted downfield resonates 2-H at 6.13 ppm as a triplet with a coupling constant of 2.0 Hz, indicating two ^4J couplings with two protons. This coupling is not resolved in signals of 4-H and 6-H at 6.22 and 6.31 ppm as these resonate as broad singlets. The two protons 2'-H and 6'-H resonate as doublets at 6.28 and 6.31 ppm with a coupling constant of 2.3 Hz, showing a strong roof effect due to their similar chemical shifts. The exchangeable phenolic protons resonate as slightly overlapping downfield shifted singlets at 9.35 and 9.39 ppm (Figure 11).

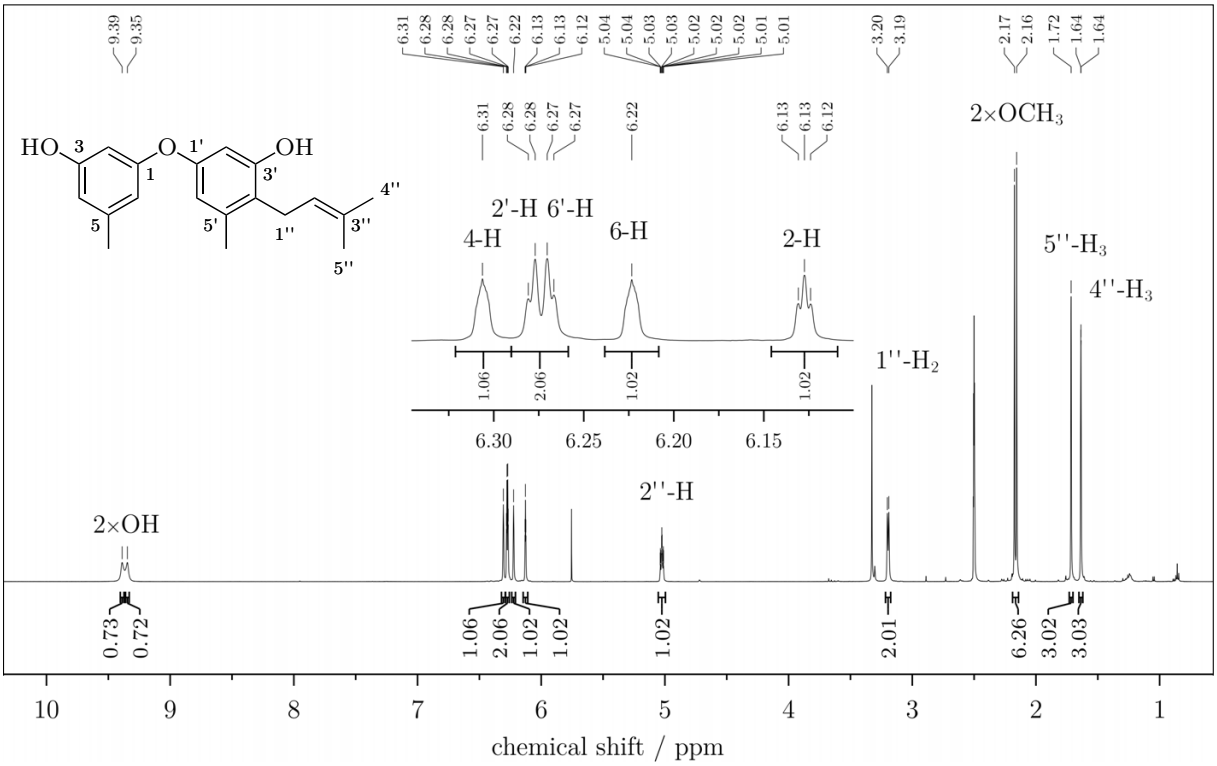


Figure 11: ^{1}H-NMR spectrum of **4** at 600 MHz in DMSO-d_6.[1]

The DEPTQ-spectrum shows two signals at 17.7 and 25.5 ppm corresponding to C-5" and C-4" of the prenyl chain. The carbon atoms of the two methyl groups bound to C-5' and C-5 of the aromatic rings resonate in a similar range at 19.4 and 21.1 ppm respectively, since the nearby aromatic ring has no strong effect on the chemical shift in ^{13}C-NMR. The benzylic carbon C-1" resonates at 24.5 ppm. Further downfield the signals at δ = 102.5 (C-2), 103.4 (C-2'), 109.7 (C-6), 110.8 (C-4), 111.3 (C-6'), were all assigned to aromatic carbon atoms bound to a proton. The carbon atom C-4', to which the prenyl chain is bound, resonates at 121.3 ppm while the carbon atoms C-2" and C-3" of the prenyl double bond resonate at 122.9 and 129.9 ppm. At 138.2 and 140.0 ppm the signals of the aromatic carbon atoms C-5' and C-5, to which methyl groups are bound, are present. The aromatic carbon atoms bound to an oxygen are shifted even further downfield by the inductive effect. The aromatic carbon atoms C-1' and C-1, which are connected through an oxygen atom to form the diaryl ether, resonate at 154.5 and 155.8 ppm, while the two aromatic carbon atoms C-3' and C-3, to which the hydroxyl groups are bound (assigned by HMBC), resonate at 158.0 and 158.4 ppm (Figure 12).

HRMS showed a peak at m/z = 299.1637 which corresponds to the calculated mass of 299.1642 of the molecular formula $C_{19}H_{22}O_3$ in association with a proton.[1]

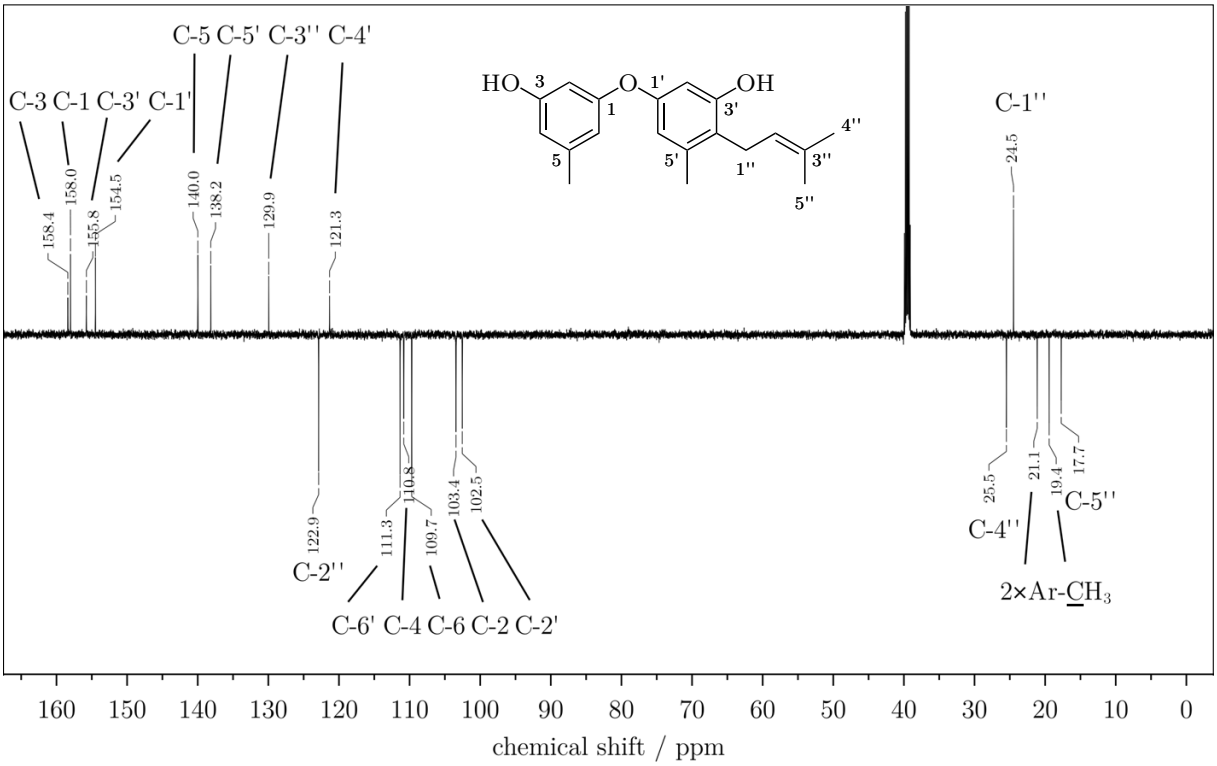


Figure 12: DEPTQ-NMR spectrum of **4** at 151 MHz in DMSO-d_6.[1]

The structures of diorcinol D **1** and diorcinol I **2** were further confirmed by SCXRD.

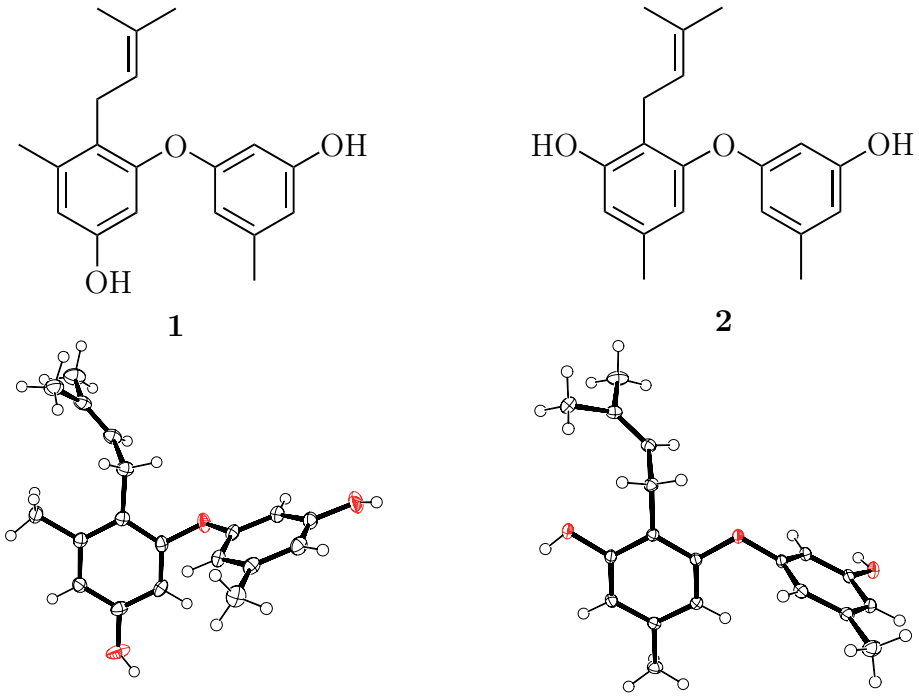


Figure 13: SCXRD structures of diorcinol D **1** (left) and diorcinol I **2** (right).[1]

The SCXRD-structures were much more three-dimensional than the drawn structures suggest. In both structures, the molecules assumed a structure in which the aryl rings stood perpendicular to each other. Additionally, the prenyl substituents were also twisted out of plane relative to the aryl-rings they were attached to. Both structures also showed intermolecular hydrogen bonds. (Figure 13).[1]

The collected IR, UV-Vis, MS and NMR data of the three isomers **4**, **1** and **2** were very similar. Significant differences were only visible in the aromatic region of their ^{1}H-NMR data (Figure 14).

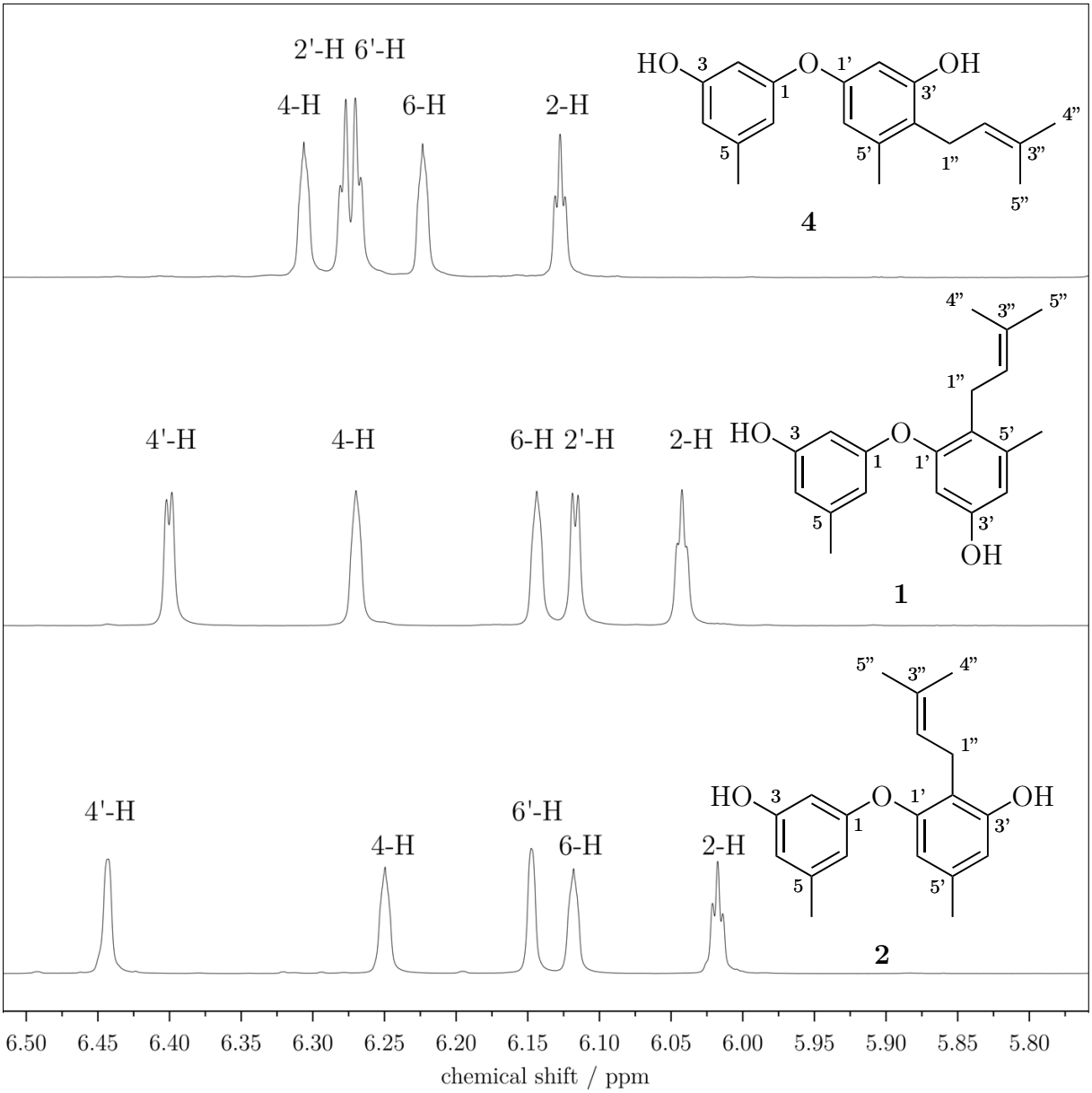


Figure 14: Aromatic ^{1}H-NMR signals of **4**, **1** and **2** at 600 MHz in DMSO-d_6.

In all cases, 2-H of the non-prenylated aromatic ring resonates as a triplet with a coupling constant of ≈ 2.0 Hz, indicating two ^4J couplings with two protons. This coupling is not resolved in signals of 4-H and 6-H as these resonate as broad singlets. In case of "verticilatin" **4** these signals are distributed over ≈ 0.3 ppm, while for diorcinol D **1** and diorcinol I **2** are spread over a range of ≈ 0.4 ppm. For "verticilatin", the two protons 2'-H and 6'-H bound to the prenylated aryl ring resonate as doublets at 6.28 and 6.31 ppm with a coupling constant of 2.3 Hz, showing a strong roof effect due to their similar chemical shifts. This roof effect is much less pronounced for 2'-H and 4'-H bound to the prenylated aryl ring of diorcinol D **1** as these couple with a similar coupling constant of 2.4 Hz but are much further apart at 6.18 and 6.43 ppm. 4-H and 6-H, which are attached to the prenylated aryl ring of diorcinol I **2**, resonate at similar shifts of 6.25 and 6.44 ppm. Unfortunately, their coupling is not resolved, resulting in slightly widened singlets.

The obtained NMR data of diorcinol D **1**[9], diorcinol I **2**[11] and diorcinol J **3**[14], which were measured in DMSO-d_6, matched the reported data. The data of **4**, which was acquired in methanol-d_4, did not match with the reported data[10] for "verticilatin". Instead, the NMR data obtained from diorcinol D **1** in methanol-d_4 matched the reported data for "verticilatin". This meant that the isolated compound called "verticilatin" was diorcinol D **1** all along and diaryl ether **4** has not been reported to be isolated from natural sources so far.

5.1.4 Antibacterial evaluation of diorcinols

The antibacterial properties of diorcinols **4**, **1**, **2**, **3** and α,β-unsaturated ketones **5**, **6**, **7** against Gram-positive bacteria (*Staphylococcus aureus* ATCC25923, MRSA GK2235, MRSA USA300 and *Enteroccocus faecalis* ATCC29212) as well as Gram-negative bacteria (*Pseudomonas aeruginosa* ATCC27853 and *Escherichia coli* ATCC25922), were evaluated by disc diffusion and minimal inhibitory concentration (MIC) broth dilution assays (Table 4). While the diorcinols **4**, **1** and **2** did not show growth inhibition of Gram-negative bacteria in disc diffusion and broth dilution assays, they were able to reduce biofilm formation of the Gram-negative *Stenotrophomonas maltophilia* strain K279a by up to 54% and the Gram-negative *Stenotrophomonas maltophilia* strain SKK55 by up to 63%. Further investigations revealed, that these compounds indeed showed excellent antibacterial activity against both strains.[1,113]

Table 4: MIC in mg/L of diorcinols and derivatives against Gram-positive bacteria. Tetracycline and vancomycin were used as references.[1]

Compound	MSSA ATCC25923	MRSA GK2235	MRSA USA300	*E. faecalis* ATCC29212
Tetracycline	1	64	1	16
Vancomycin **39**	2	2	1	4
Diaryl ether **4**	4	4	4	4
Diorcinol D **1**	8	8	4	8
Diorcinol I **2**	8	8	8	8
Diorcinol J **3**	>64	>64	>64	>64
Diaryl ether **5**	-	-	-	-
Diaryl ether **6**	-	-	-	-
Diaryl ether **7**	-	-	-	-

Diorcinols **4**, **1** and **2** exhibited antibacterial properties against the Gram-positive bacterial strains *E. faecalis* and *S. aureus* at concentrations of 4–8 mg/L, regardless of methicillin resistance (Table 4). Diorcinol J **3** only showed minuscule inhibition of *E. faecalis* and *S. aureus* in the disc diffusion assays. The so far non-natural diaryl ether **4** performed the best in terms of antibiotic activity.[1]

The α,β-unsaturated ketones **5**, **6** and **7** showed no antibacterial effects in the assays employing both methicillin sensitive and resistant isolates.[1]

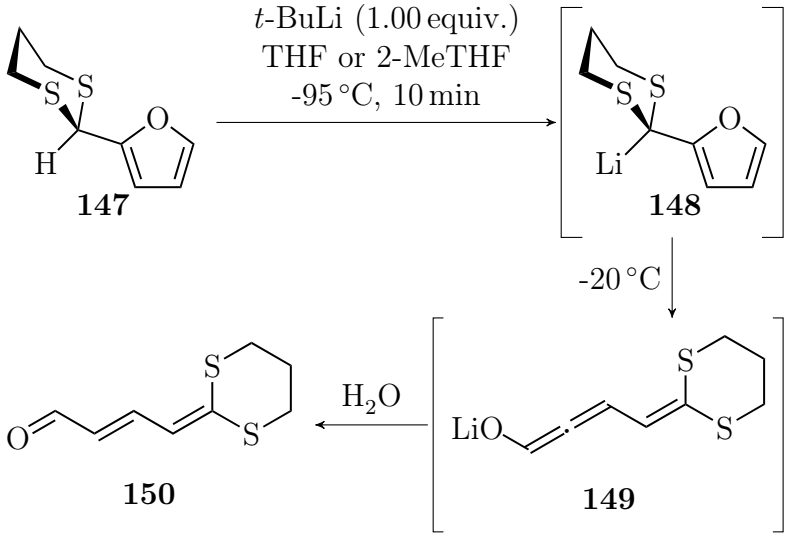
In summary, the first syntheses of the natural products diorcinol D **1**, I **2** and J **3** were achieved in only five linear steps with good overall yields (51% (**1**), 20% (**2**), 16% (**3**)). Additionally, compound **4**, which originally was assigned to verticilatin, and compound **5**, which was assigned to an antibiotic compound by Li et al., were synthesized in overall yields of 35% (**4**) and 17% (**5**). The synthesis revealed that verticilatin, which was originally assigned in literature[10] to have the structure of **4**, was actually diorcinol D **1**. The actual structure of the antibiotic compound **5** reported by Li et al. could not be determined. The analogues **6** and **7**, which also have been synthesized in six linear steps and overall yields of 26% (**6**) and 10% (**7**), did not match the reported data for the natural product either. Of all the synthesized compounds, diorcinol D **1**, I **2** and their synthetic isomer **4** showed significant inhibition of both methicillin sensitive (MSSA) and resistant (MRSA) strains of *S. aureus* as well as *E. faecalis*.[1]

5.2 Syntheses of *C*-acyl glycosides

The second part of the thesis dealt with the development of a synthetic approach towards *C*-acyl glycosides by reacting lithiated dithianes with glycosyl halides.

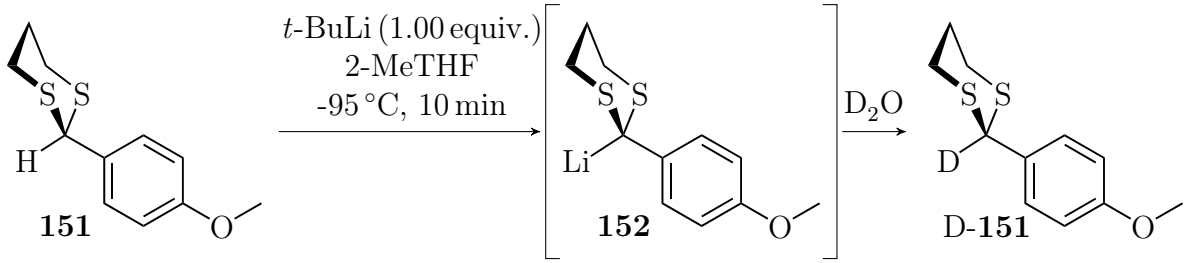
5.2.1 Lithiation of dithianes

In order to carry out the Corey-Seebach reaction 2-(1,3-dithian-2-yl)furan[114] **147** had to be lithiated. Unlike other lithiated dithianes, the lithiated dithiane **148** decomposes, especially when the temperature rises. The lithiated species **148** rearranges to form enolate **149**. In contact with water this enolate forms aldehyde **150** (Scheme 38).[2–4, 115]



Scheme 38: Lithiation and decomposition of 2-(1,3-dithian-2-yl)furan **147**.[2–4, 115]

In order to achieve fast and clean lithiation, dithiane **147** was deprotonated by *t*-BuLi instead of *n*-BuLi at -95 °C.[2–4] The success of the lithiation step with stable lithiated dithianes was checked by quenching the reaction with D_2O after lithiation (Scheme 39).



Scheme 39: H-Li-D exchange of **151**

If the lithiation was successful, the ^{1}H-NMR-spectrum shows a significant decrease of the integral for the acidic proton since most of it is replaced by deuterium. This is exemplified

in Figure 15, where the singulett resonating at 5.13 ppm, which was assigned to the acidic dithianyl proton of **151**, was reduced to 0.09 from 1.00.

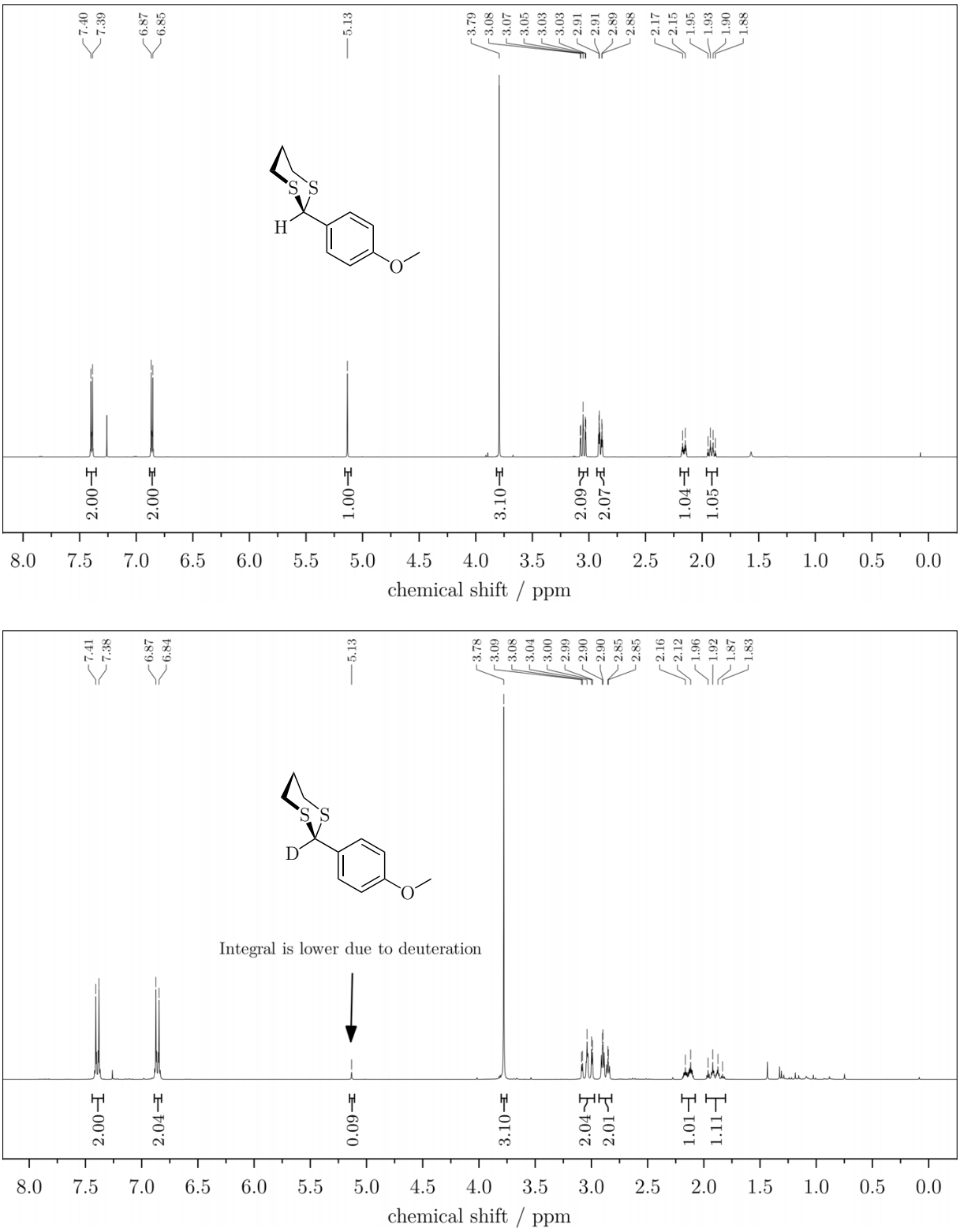
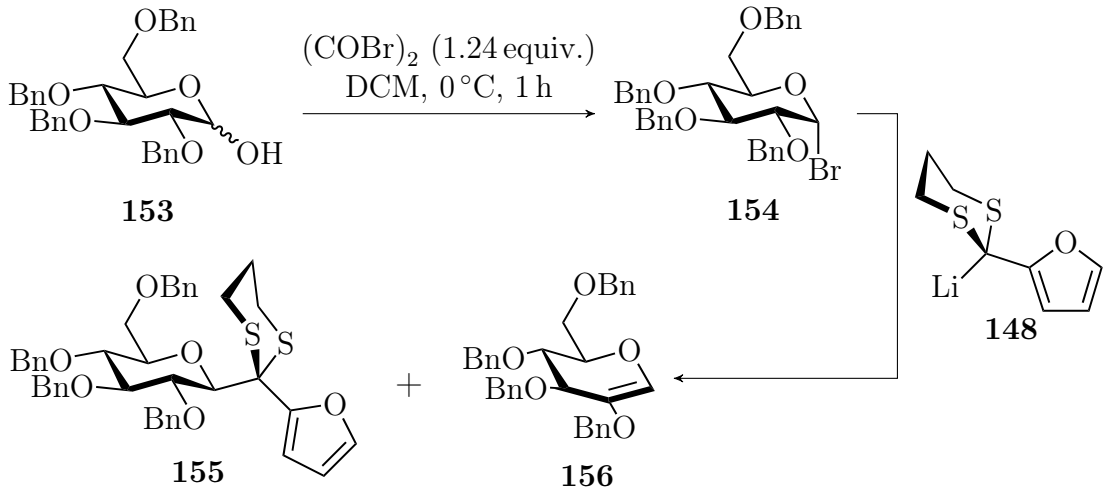


Figure 15: ^{1}H-NMR spectra of **151** in $CDCl_3$ before and after H-Li-D exchange.

5.2.2 Synthesis of benzyl protected *C*-acyl β-glucosides

The first attempt of a reaction between lithiated dithiane **148** and D-glucosyl bromide **154**, which was obtained from **153** and oxalyl bromide, yielded two major products: the desired substitution product **155** and the elimination product **156** (Scheme 40). The *β*-*C*-glycosidic compound **155** was the only isolated substitution product. The absence of the *α*-anomer indicates that the reaction proceeds through a S_N2 type mechanism.[2–4]



Scheme 40: Corey-Seebach reaction with D-glucosyl bromide **154**.[2–4]

The Corey-Seebach step was then optimized to maximize the yield of **155** (Table 5).

Table 5: Screening results on the formation of **155**.[2–4]

	T	t	solvent	equiv. **148**	yield of **155**	yield of **156**
1	-95 °C then r.t.	1 h	THF	2.00	32%	28%
2	-95 °C then r.t.	1 h	THF	1.20	17%	-
3	-95 °C	1 h	THF	1.20	no reaction	-
4	-95 °C → -35 °C	16 h	THF	1.20	56%	not isolated
5	-95 °C → -20 °C	16 h	THF	1.20	54%	11%
6	-95 °C → -35 °C	2 h	THF	1.20	57%	not isolated
7	-35 °C	16 h	THF	1.20	decomposition	-
8	-95 °C → -35 °C	3 h	THF	2.00	47%	not isolated
9	-95 °C → 0 °C	2 h	2-MeTHF	1.20	22%*	-
10	-95 °C → 0 °C	2 h	2-MeTHF	1.50	69%*	-
11	-95 °C → 0 °C	2 h	2-MeTHF	2.00	73%	-

*incomplete conversion of D-glucosyl bromide **154**.

Optimization of the reaction conditions revealed that only 1.20 equivalents of lithiated dithiane **148** were necessary to achieve full conversion in THF. Additionally, lowering the equivalents of lithiated dithiane **148** resulted in less formation of the elimination product **156**. The most drastic improvement was achieved by letting the reaction thaw slowly instead of removing the cooling bath after combining the reactants. In addition, the reaction appeared to be finished once the temperature had reached -35 °C. The yield was further improved by switching to 2-MeTHF as solvent. In 2-MeTHF the reaction required 2.00 equivalents of **148** to reach full conversion of bromide **154** (Table 5).[2–4]

In the ^{1}H-NMR-spectrum of **155** the six protons of the dithianyl unit all resonate as multiplets from 1.44 to 2.67 ppm. The protons of the CH_2 groups next to the sulfur atoms have a higher chemical shift due to the inductive effect caused by sulfur (Figure 16).

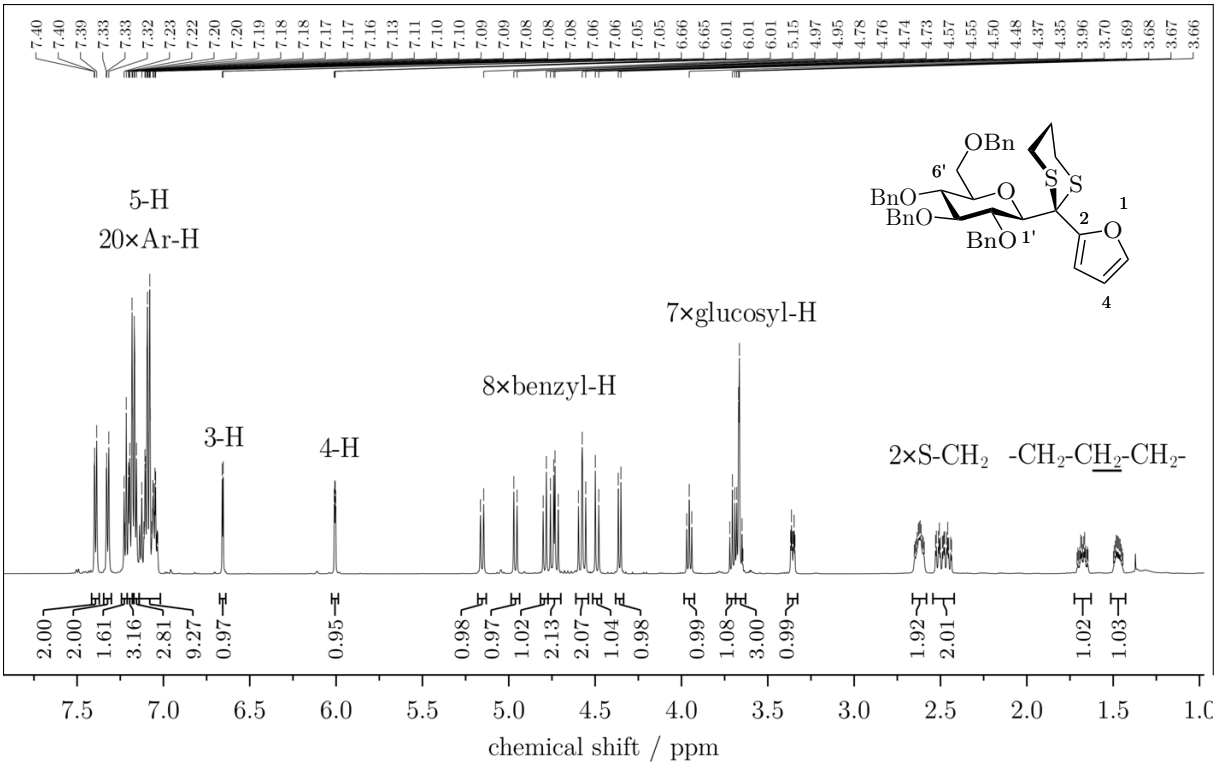


Figure 16: ^{1}H-NMR spectrum of **155** at 600 MHz in C_6D_6.[2,3]

At 3.35 ppm 5'-H resonates as doublet of triplet coupling with 4'-H with a coupling constant of 9.1 Hz and with the two protons 6'-H_2 with a coupling constant of 2.9 Hz. The two protons bound to C-6' of the resonate together at 3.66$,ppm as doublet with a coupling constant of 2.9 Hz, showing no geminal coupling. 4'-H, 3'-H and 2'-H of resonate as pseudo triplets with a average coupling constant of 9.1 Hz. The anomeric proton 1'-H resonates at 4.36 ppm as doublet with a coupling constant of 9.1 Hz. According to the Karplus-equation[116] a coupling constant of this magnitude can only occur if the bond

angle of the coupling protons is either 0 ° or 180 °. Thus the β-configuration and the D-glucosyl configuration are unambiguously confirmed by the coupling constants. From 4.35 to 5.16 ppm the benzylic protons all resonate as doublets with typical geminal coupling constants ranging from 11.1 to 12.6 Hz (Figure 17). The furyl proton 4-H resonates at 6.01 ppm as doublet of doublets with coupling constants of 3.3 and 1.8 Hz. The coupling constant of 3.3 Hz is also observable in the doublet of the vicinal furyl proton 3-H at 6.66 ppm. The signal of 5-H is overlapped by the signals of 16 aromatic protons of the benzyl protecting groups, forming a multiplett from 7.03 to 7.24 ppm. Four more aromatic protons of the benzyl protecting groups resonate as pseudodoublets at 7.33 and 7.40 ppm.

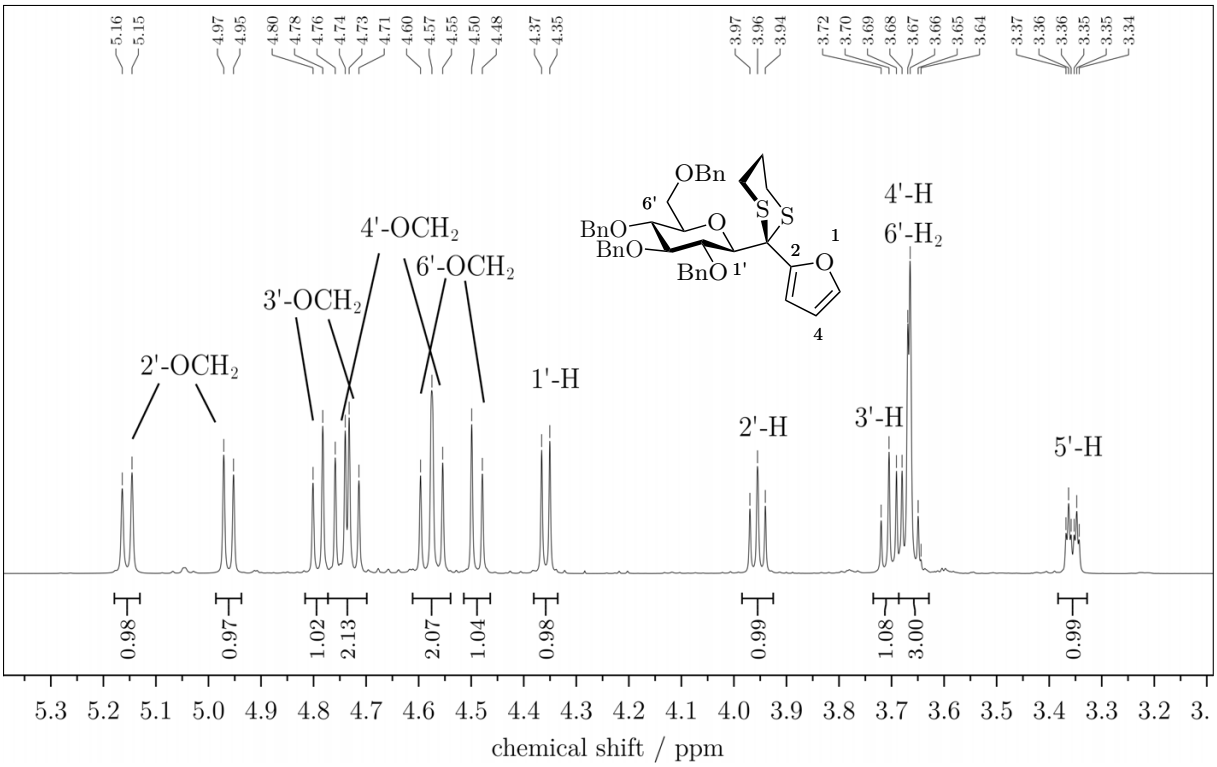


Figure 17: Expansion of the ^{1}H-NMR spectrum of **155** at 600 MHz in C_6D_6.[2, 3]

In the DEPTQ-spectrum the CH_2 carbon atoms of the dithianyl unit resonate at 25.3, 28.0 and 28.4 ppm. The carbon atom between the two sulfur atoms shows a signal at 55.5 ppm, which is small due to slow relaxation. The D-glucosyl carbon C-6' resonates at 69.0 ppm. The four benzylic carbon atoms show peaks at 7.36, 74.1, 74.7 and 75.7 ppm. The signals at $\delta = 78.4$ (C-4'), 80.0 (C-5'), 80.3 (C-2'), 86.0 (C-1'), 88.2 ppm (C-3'), were all assingned to the D-glucosyl ring. The signals at $\delta = 110.8$ (C-4) and 111.1 ppm (C-3) were assigned to the carbon atoms of the furan ring. The signals at $\delta = 142.4$ (C-5) and 153.5 (C-2) have a much higher chemical shift due to their proximity to the oxygen atom of the furan ring. The 20 aromatic carbon atoms of the benzyl protecting groups bound

to a proton resonate between 127.1 and 128.6 ppm, while their quarternary carbon atoms resonate between 139.2 and 139.8 ppm (Figure 18).

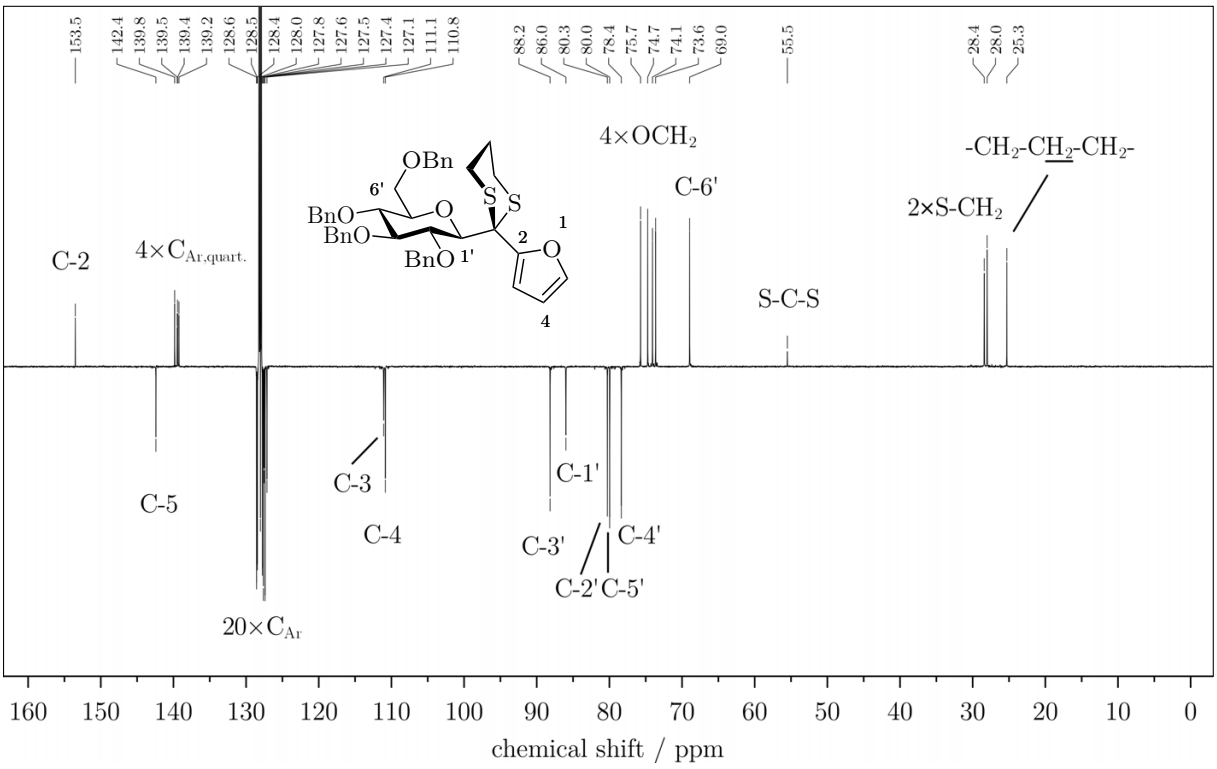
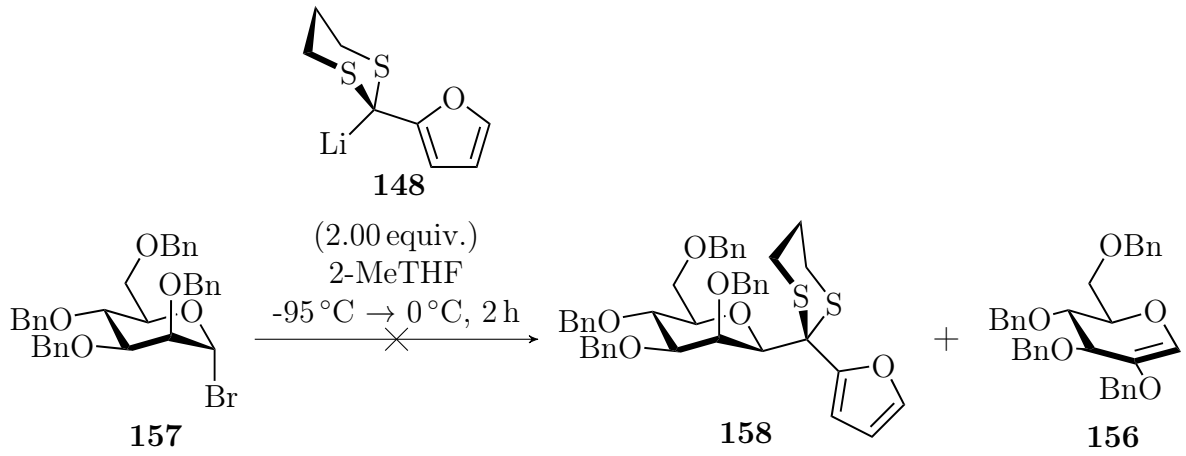


Figure 18: DEPTQ-spectrum of **155** at 151 MHz in C_6D_6.[2,3]

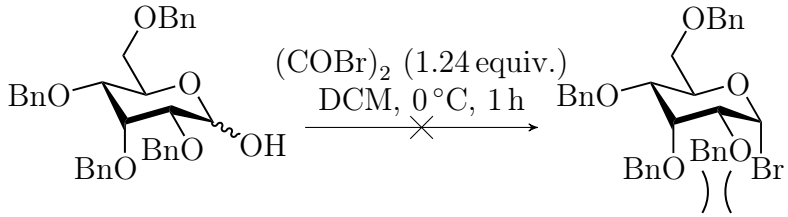
When the optimized conditions were applied to the D-mannosyl bromide **157**, no *C*-glycosidic product was formed (Scheme 41).[2–4]



Scheme 41: Attempted Corey-Seebach reaction with D-mannosyl bromide **157**.[2–4]

Instead, the starting bromide **157** was the only glycosyl compound that was detected in the ^{1}H-NMR spectrum of the crude mixture, indicating that the bromide **157** has

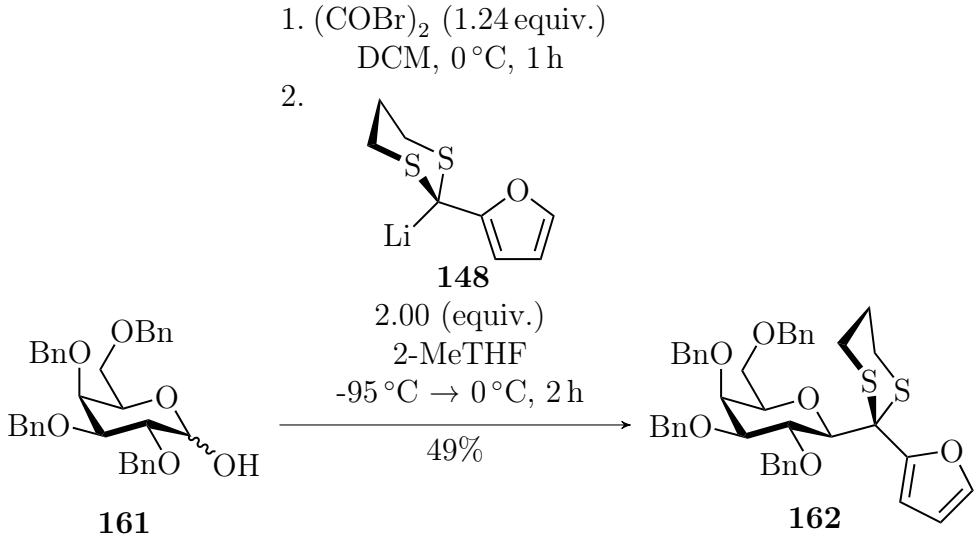
not reacted at all. The reaction is presumably hindered by the axial OBn group, which prevents the S_N2 attack of the lithiated dithiane. Absence of elimination product **156** also indicates that the elimination, which was observed with D-glucosyl bromide **154**, proceeds through an E2 mechanism as D-mannosyl bromide **157** cannot undergo an E2 elimination. The reaction was also not possible with D-allosyl bromide[117–119] **160**, as it was too unstable due to 1,3 diaxial interactions (Scheme 42).[2–4]



159 **160**

Scheme 42: Attempted generation of D-allosyl bromide **160**.[2–4]

Applying the optimized procedure to benzylated D-galactose **161** gave the desired product **162** in a slightly lower yield of 49% with excellent β-selectivity (Scheme 43).[2–4]

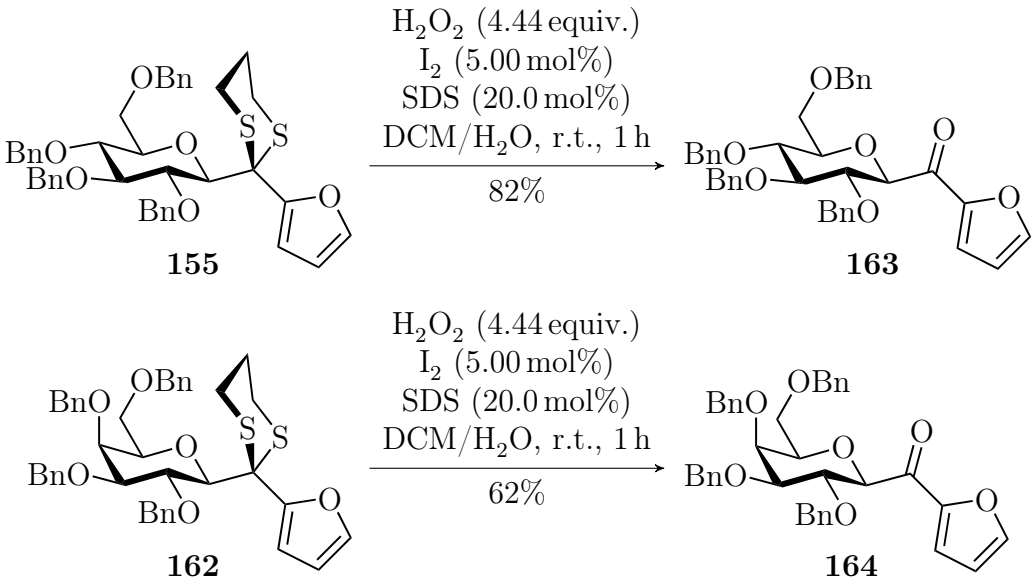


161 **162**

Scheme 43: Corey-Seebach reaction with D-galactose.[2–4]

The conversion of the dithiane moiety back into the carbonyl proved to be difficult due to the resulting furylketone being susceptible to further oxidation. The usually convenient procedure using PIFA[120] as deprotection agent only gave the desired product **163** in 34% yield. A milder procedure using iodine as catalyst and hydrogen peroxide as reoxidiant in a micellar system using SDS as surfactant proved to be more suitable for this substrate,

giving perbenzylated scleropentaside A **163** in 82% yield (Scheme 44). In contrast to the literature procedure[121], a small amount of DCM (1 µL/mg) had to be added to dissolve the dithiane starting material (Scheme 44).[2–4]



Scheme 44: Iodine mediated deprotection of dithianes.[2–4]

The same deprotection conditions were also applicable to the D-galactosyl-dithiane **162** giving the desired ketone **164** in a yield of 62%. A SCXRD structure of perbenzylated scleropentaside A **163** was also obtained, unambiguously confirming the β-configured *C*-furanoyl- D-glucosidic motif (Figure 19). The structure shows the β-configuration of the product with a dihedral angle of 171 ° between the anomeric and its vicinal proton, which is in agreement with the observed coupling constant of 9.6 Hz for the coupling between 1-H and 2-H of the pyranose ring [2–4]

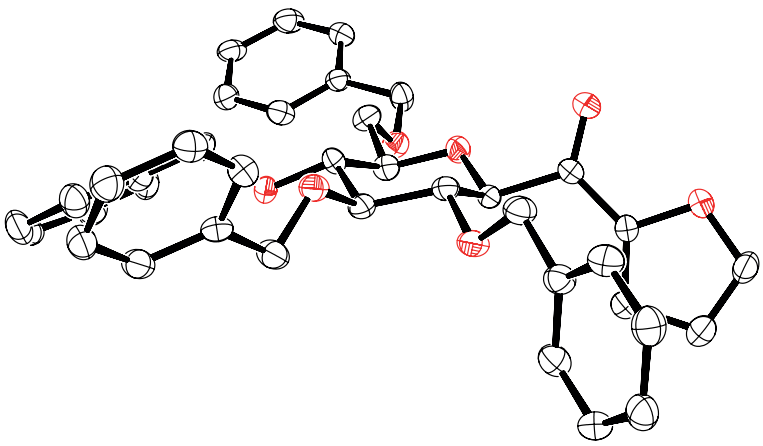
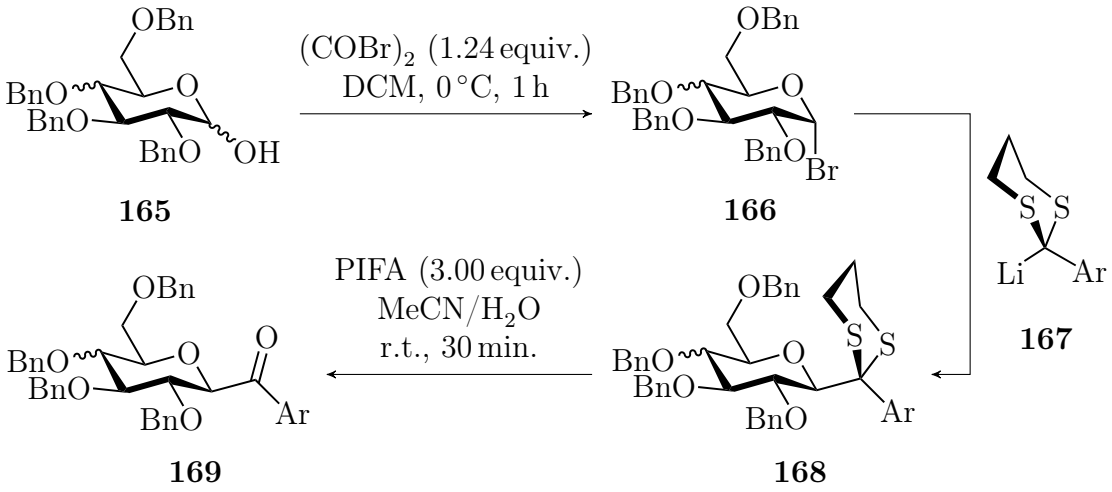


Figure 19: SCXRD structure of perbenzylated scleropentaside A **163**.[2–4]

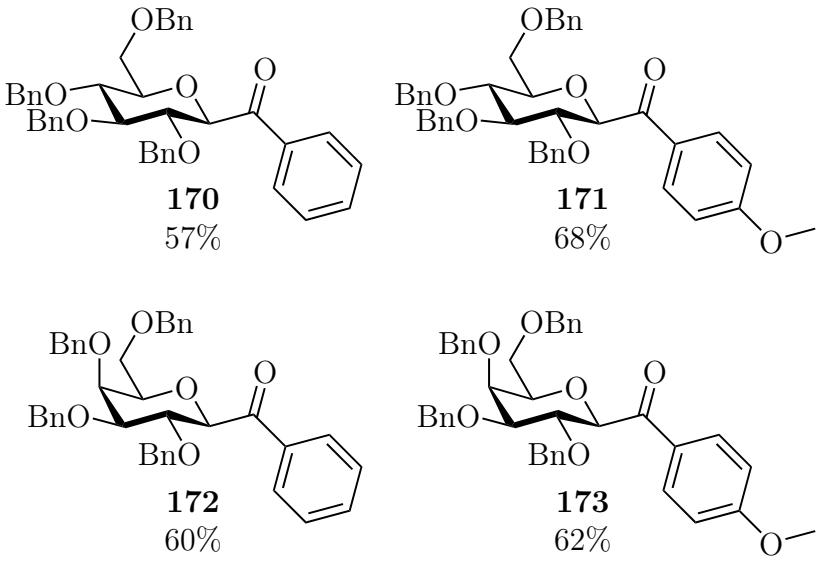
When dithianes bearing an aryl moiety stable towards oxidative conditions were used, the deprotection with PIFA proceeded smoothly. This allowed the development of a one-pot procedure where the starting material **165** is converted into its respective glycosyl bromide **166** which then undergoes a Corey-Seebach reaction with the aryl dithiane **167** to give the *C*-glycosidic compound **168**. The dithiane can then be directly cleaved in one-pot fashion by PIFA to give the desired *C*-acyl glycosidic compound **169** (Scheme 45).[2–4]



165 **166** **167** **168** **169**

Scheme 45: One-Pot synthesis of benzylated *C*-acyl β-glycosides **169**.[2–4]

Using this procedure, the D-gluco- and D-galactosides shown in Figure 20 were synthesized in good yields of 57-68% with complete β-selectivity.[2–4]



170 57% **171** 68% **172** 60% **173** 62%

Figure 20: Corey-Seebach reaction with D-glucosyl bromide **154**.

C-acyl D-glucoside **170** also gave crystals suitable for SCXRD. The structure shows the

β-configuration of the product with a dihedral angle of 174 ° between the anomeric proton and anomeric proton and its vicinal proton, which is in agreement with the observed coupling constant of 9.5 Hz for the coupling between 1-H and 2-H of the pyranose ring (Figure 21).

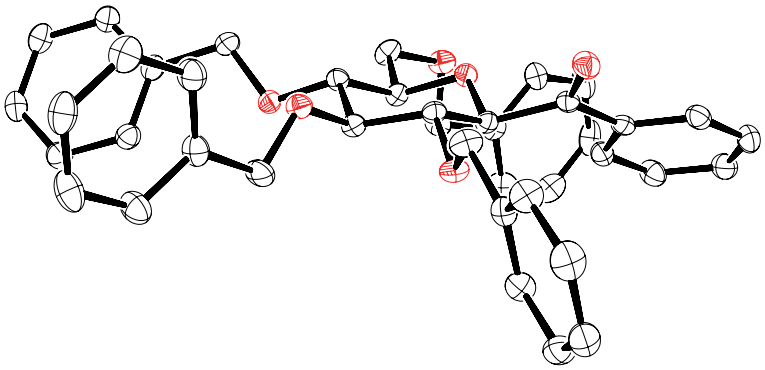
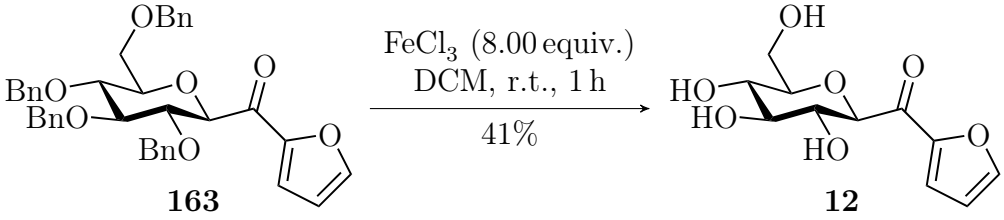


Figure 21: SCXRD structure of perbenzylated *C*-acyl D-glucoside **170**.

Deprotection of perbenzylated scleropentaside A **163** proved to be difficult, as catalytic hydrogenation, which is the established method for removing benzyl groups, is not compatible with aryl-ketone motif. Instead debenzylation was achieved by using anhydrous $FeCl_3$ as a Lewis acid to give scleropentaside A **12** in a moderate yield of 41% (Scheme 46).[122] The low yield may be caused by partial decomposition under the strongly lewis acidic conditions and the tedious workup required to remove the iron salts.[2–4]



Scheme 46: Synthesis of scleropentaside A **12**.[2–4]

The ^{1}H-NMR spectrum of scleropentaside A **12** shows a triplet of a doublet of 4'-H at 3.12 ppm exhibiting coupling constants of $J = 9.2$ Hz (coupling with 3'-H and 5'-H) 5.3 Hz (coupling 4'-OH). 3'-H and 5'-H overlap as multiplett from 3.25 to 3.31 ppm. 2'-H and 6'-H_A also overlap as multiplett from 3.40 to 3.49 ppm. 6'-H_B resonates at 3.67 ppm as doublet of doublet of doublet with geminal coupling constant of 11.8 Hz and two vicinal coupling constants of 5.7 Hz (coupling with 6'-OH) and 1.8 Hz (coupling with 5'-H). 1'-H resonates at 4.28 ppm as doublet coupling to 2'-H with a coupling constant of $J = 9.6$ Hz. According to the Karplus equation[116] a coupling constant of this magnitude can only

occur if the coupling protons are in anti configuration, unambiguously confirming the β-configuration of the product (Figure 22).

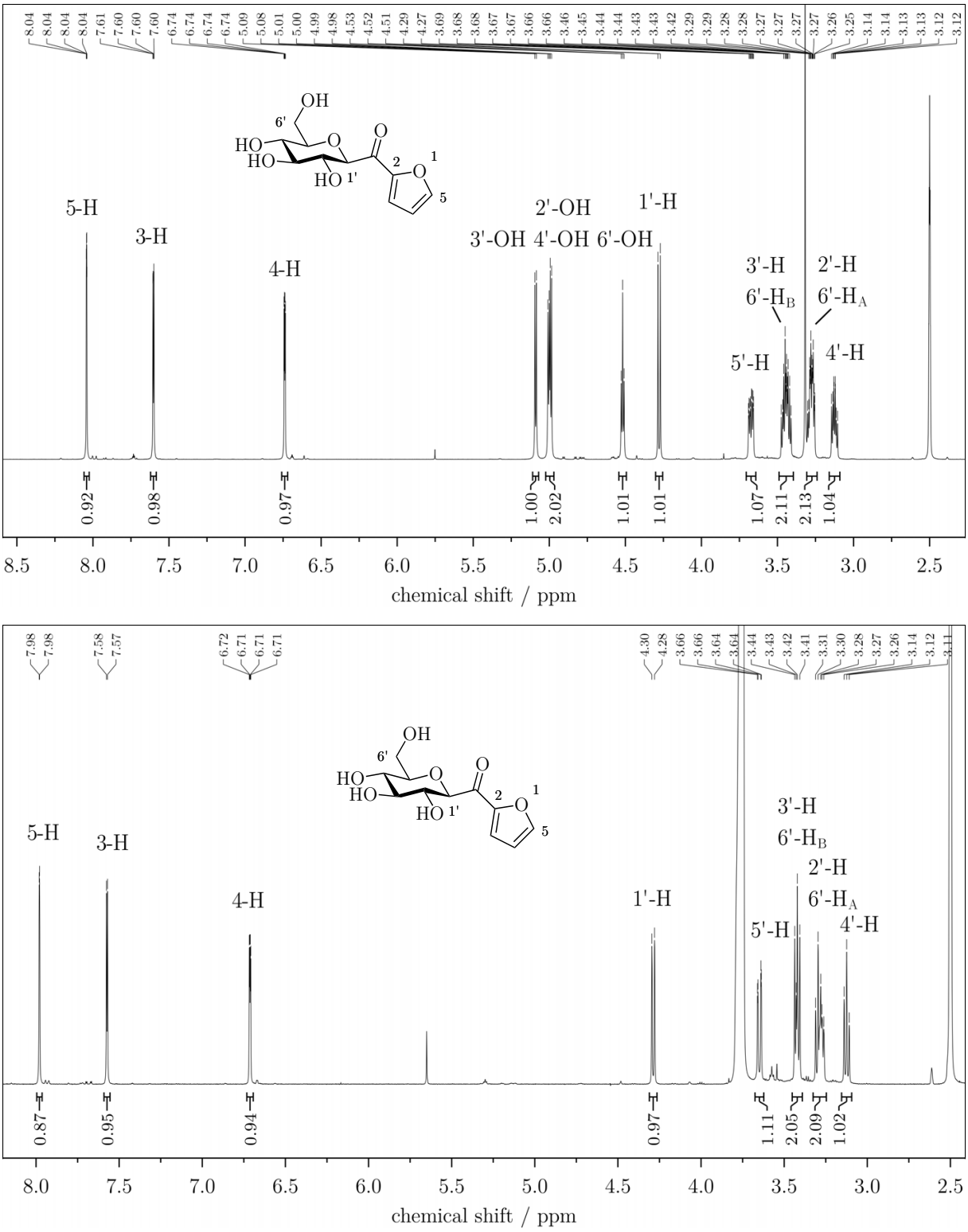


Figure 22: ^{1}H-NMR spectra of **12** at 600 MHz in DMSO-d_6 (top) and at 600 MHz in 9:1 DMSO-d_6/D_2O (bottom).[2,3]

The four signals between 4.50 ppm and 5.10 ppm were assigned to the four hydroxyl protons since these signals were suppressed by proton-deuterium exchange with D_2O (Figure 22). 6'-OH resonates as a triplet at 4.52 ppm with an integral of 1 H and a coupling constant of 5.8 Hz. The doublet at 4.99 ppm showed a vicinal coupling with 4'-H with a coupling constant of 5.3 Hz and thus was assigned to 4'-OH. The doublet at 5.00 ppm with an integral of 1 H and a coupling constant of 5.0 Hz showed a vicinal coupling with 2'-H and thus must be 2'-OH. 3'-OH resonates as doublet at 5.09 ppm with a coupling constant of 5.8 Hz.

In the range of protons bound to aromatic motifs, 3-H resonates as doublet of a doublet at 6.74 ppm with two ^3J coupling constants of 3.6 Hz and 1.7 Hz. The doublet of a doublet at 7.60 ppm with a ^3J coupling constant of 3.7 Hz and a ^4J coupling constant of 0.8 Hz was assigned to 2-H. 4-H resonates as doublet of a doublet at 8.04 ppm with a ^3J coupling constant of 1.7 Hz and a ^4J coupling constant of 0.8 Hz. The lower integral of 0.94 H might be caused by a long relaxation time of the proton.

The ^{13}C-NMR spectrum shows a signal at 61.1 ppm which was assigned to C'-6. The signals at 70.0 (C-4'), 71.5 (C-2'), 78.0 (C-3'), 79.6 (C-1'), 81.6 (C-5'), were all assigned to the D-glucosyl ring by HSQC (Figure 23).

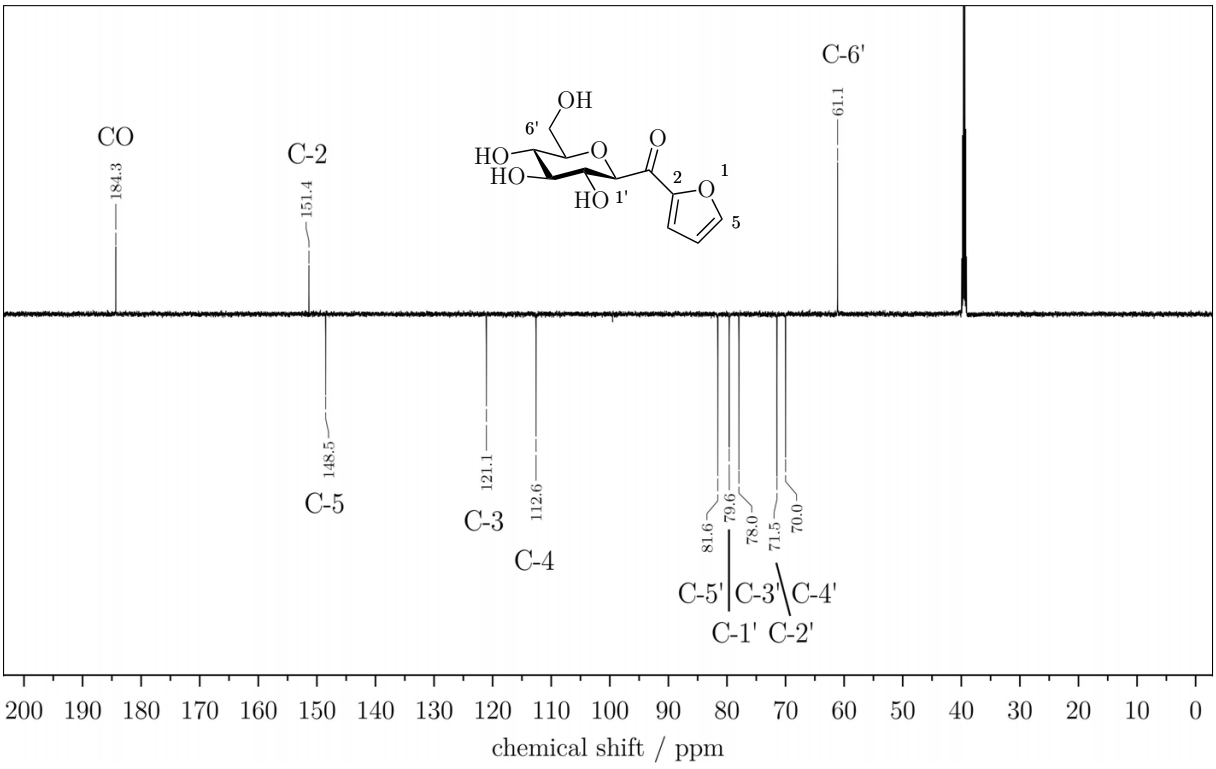


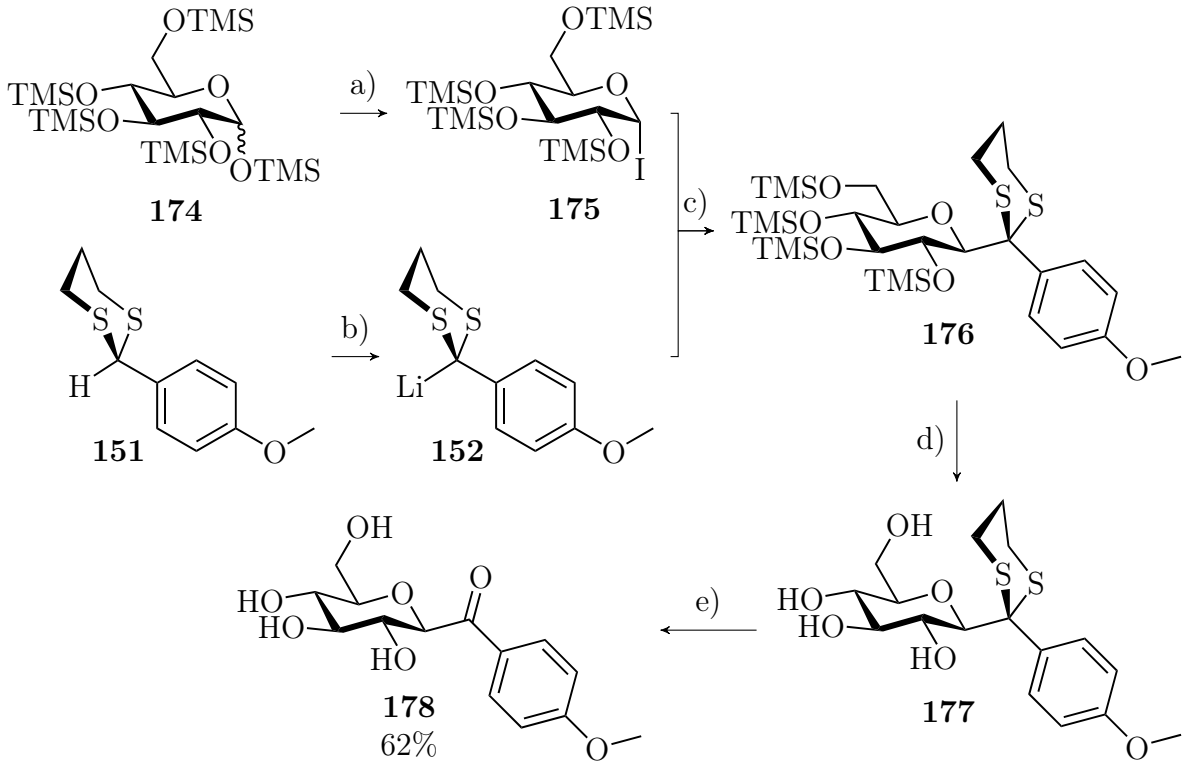
Figure 23: ^{13}C-NMR spectrum of **12** at 151 MHz in DMSO-d_6.[2,3]

The signals at 112.6 (C-3) and 121.1 (C-2) were in the range of aromatic signals and thus assigned to the carbon atoms of the furan ring. The signals at 148.5 (C-4) and 151.4 (C-1) have a much higher chemical shift due to their proximity to the oxygen atom of the furan ring. The signal at 184.3 ppm was confirms the presence of the carbonyl motif which was also confirmed by the IR-band at $\tilde{\nu} = 1656\,\mathrm{cm^{-1}}$ (Figure 23). The molecular formula $C_{11}H_{14}O_7$ was confirmed by a peak at m/z = 281.0633 which corresponds to the calculated mass of 281.0632 for the molecular formula in association with a sodium cation.[2–4]

Overall, scleropentaside A **12** was synthesized in 25% yield starting from 2,3,4,6-tetra-*O*-benzyl-D-glucopyranose **153**. The β-selective *C*-glycosylation was also applicable to D-galactosides. If dithianes other than 2-(1,3-dithian-2-yl)furan **147** were used the deprotection of the dithiane could even be carried out in one pot. Deprotection of the benzyl groups proved to be tedious.[2–4]

5.2.3 Direct synthesis of unprotected *C*-acyl β-glucosides

Because the removal of benzyl groups proved to be difficult, the application of more labile TMS protecting groups was investigated. TMS groups are notoriously labile under most conditions, but stable towards strong bases under aprotic conditions.[123] Persilylated pyranoses are also more easily prepared from their unprotected monosaccharides, resulting in a more atom economic procedure.[124,125] Only minor changes of the one-pot procedure developed for benzylated pyranoses were required. Persilylated D-glucose **174** was smoothly converted into the D-glucosyl iodide **175** by TMSI.[126] The Corey-Seebach reaction of the D-glucosyl iodide **175** with lithiated dithiane[127] **152** then gave *C*-D-glucoside **176**. Upon addition of MeOH, the TMS groups were sometimes deprotected. To ensure complete removal of the TMS groups NaOMe was added. Finally, cleavage of the dithiane by PIFA gave *C*-acyl glycoside **178** in 62% yield with complete β-selectivity (Scheme 47).[2–4]



Scheme 47: One-pot *C*-acylation reaction with persilylated D-glucose **174**. Reagents and conditions: a) Persilylated D-glucose **174** (1.00 equiv.), TMSI (1.14 equiv.), DCM, 0 °C, 15 min; b) Dithiane **151** (2.00 equiv.), *t*-BuLi (2.02 equiv.), 2-MeTHF, –95 °C, 10 min. c) 2-MeTHF, –95 °C → 0 °C; d) NaOMe (1.00 equiv.), r.t., MeOH, 10 min; e) PIFA (3.00 equiv.), r.t., MeOH/H_2O.[2–4]

Screening the conditions for the *C*-glycosylation step c) revealed that two equivalents of

lithiated dithiane **152** in 2-MeTHF were also optimal for persilylated iodides (Table 6).[2–4]

Table 6: Optimization of step c) in Scheme 47.[2–4]

	solvent	equiv. **152**	yield of **178**
1	2-MeTHF	2.00	62%
2	2-MeTHF	1.20	48%
3	THF	2.00	48%
4	THF	1.20	40%

Lowering the equivalents of lithiated dithiane **152** or running the reaction in THF resulted in less yield of the desired product **178**.

Investigating the scope of the reaction also revealed that the reaction also proceeds well with electron rich, electron neutral, electron deficient and polycylic aromatic dithianes. D-Galactosyl could also be employed giving the *C*-acyl glycosides with complete β-selectivity (Figure 24).[2–4]

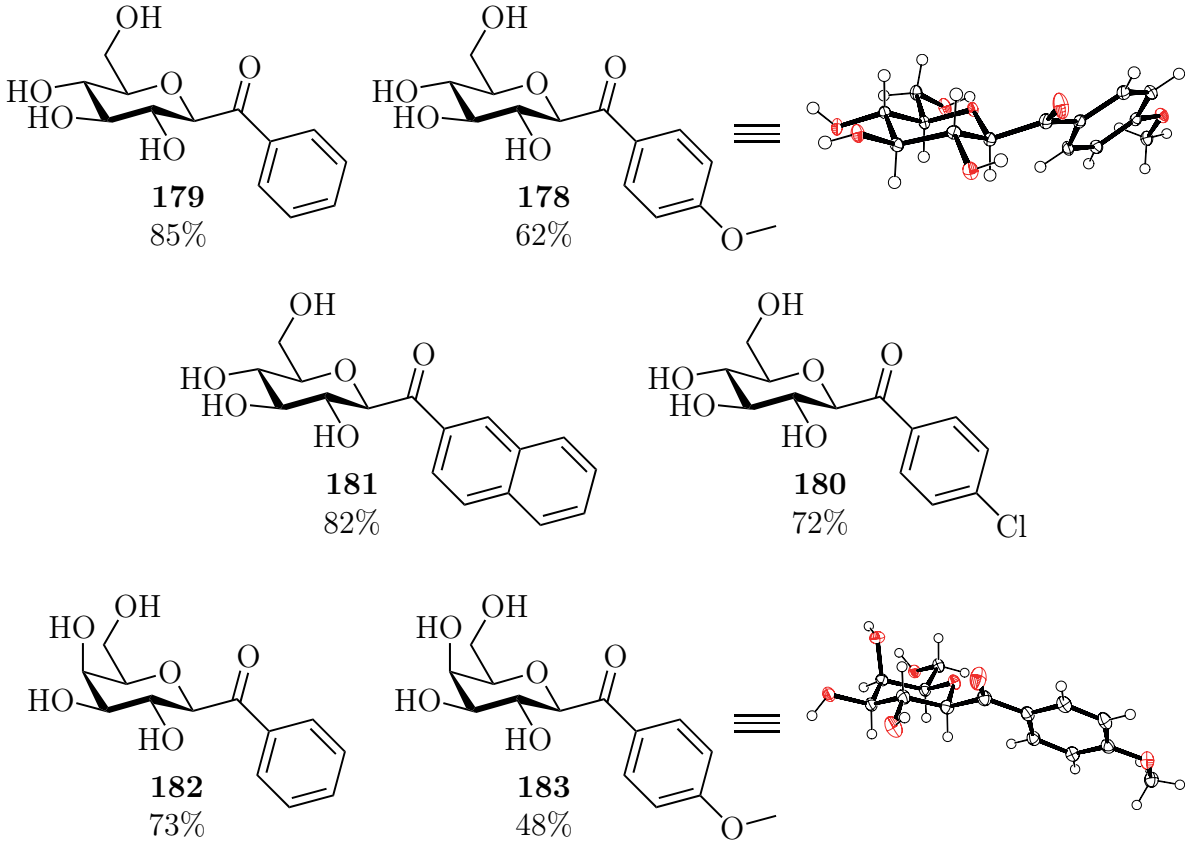


Figure 24: Scope of the one-pot *C*-acylation with persilylated glycopyranoses.[2–4]

SCXRD-structures were also aquired for *C*-acyl D-glucoside **178** and *C*-acyl D-galactoside **183**. The structures show the β-configuration of the products with a dihedral angle of 174 ° for the *C*-acyl D-glucoside **178** and 177 ° for the *C*-acyl D-galactoside **183** between the anomeric proton and its vicinal proton, which is in agreement with the observed coupling constant of 9.3 Hz for the coupling between 1-H and 2-H of both pyranoses (Figure 24).

D-Xylosyl, D-arabinosyl and L-fucosyl donors could also be employed giving the desired *C*-acyl D-glycosidic products in good to excellent yields with complete *trans* selectivity (Figure 25).

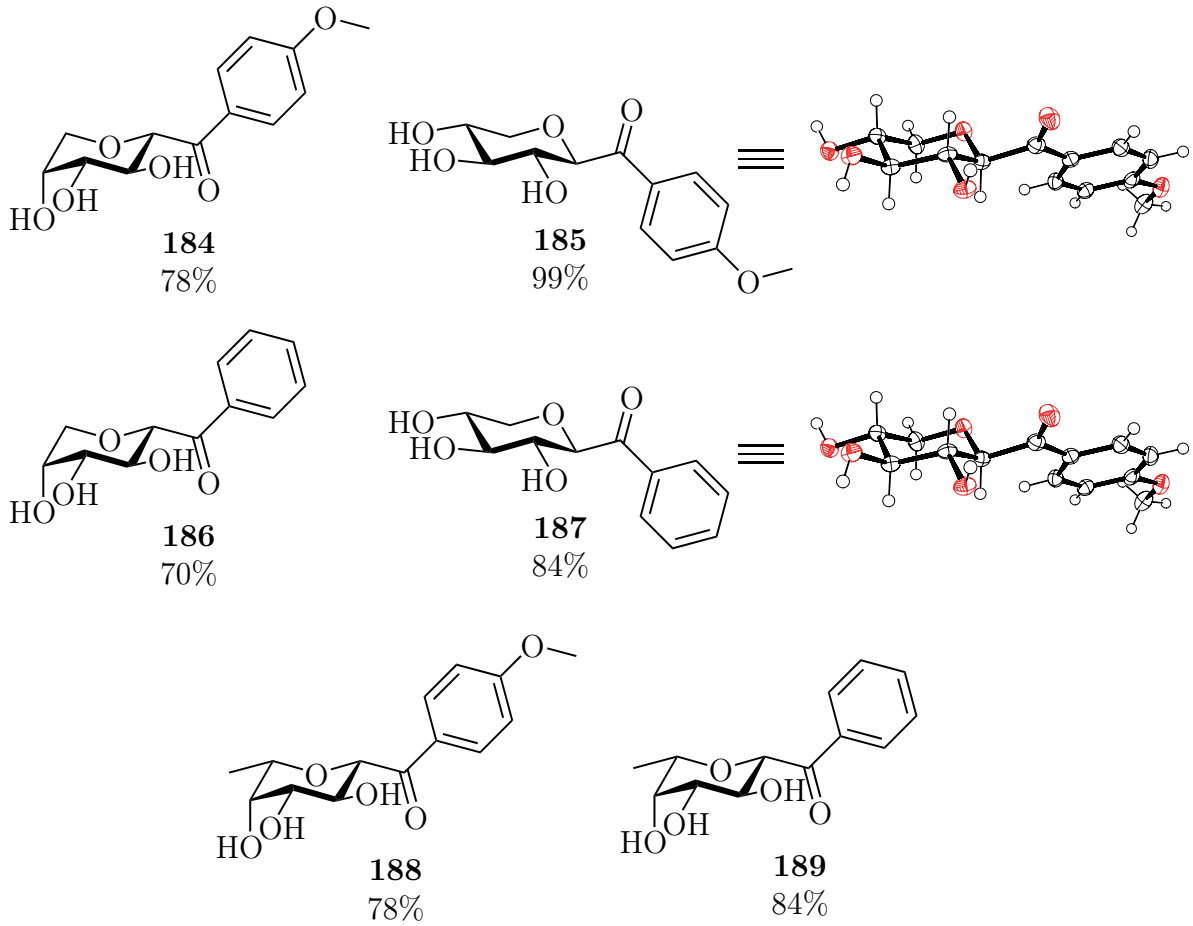
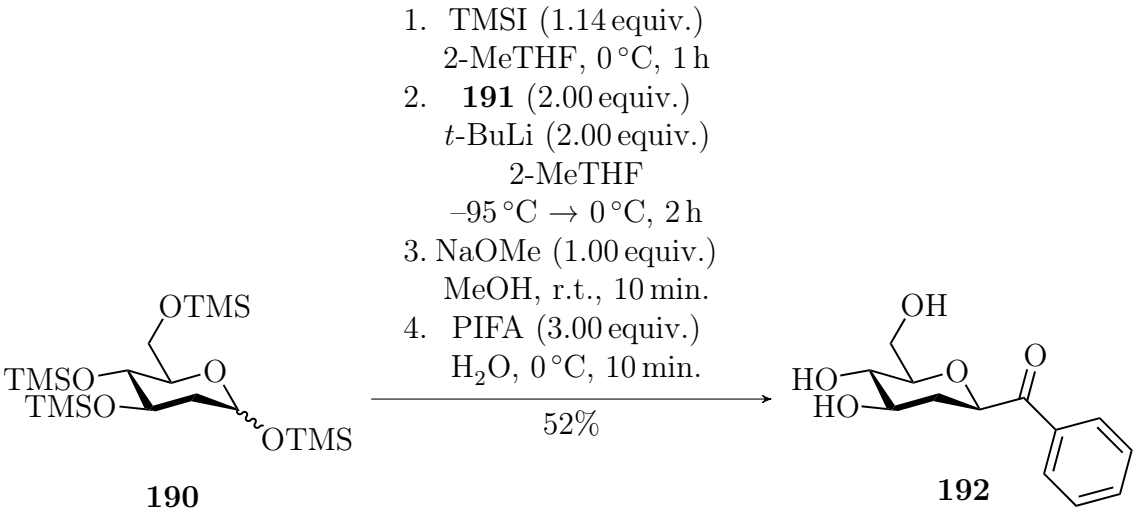


Figure 25: Scope of the one-pot *C*-acylation with persilylated glycopyranoses.[2–4]

SCXRD-structures were also aquired for *C*-acyl D-xylosides **185** and **185**. The SCXRD-structure of *C*-acyl D-xyloside **185** showed a dihedral angle of 178 ° between the anomeric proton and its vicinal proton, which is in agreement with the observed coupling constant of 9.2 Hz for the coupling between 1-H and 2-H. The dihedral angle between the anomeric proton and and its vicinal proton in the SCXRD structure of *C*-acyl D-xyloside **187** was slightly smaller with a value of 172 °. This small change may also be reflected in the slightly smaller coupling constant of 9.1 Hz. (Figure 25).

Additional experiments also revealed that glycosyl iodides can be prepared by adding TMSI to neat persilylated glycopyranoses at room temperature, simplifying the procedure even further.

When TMSI was added to perisilylated 2-deoxy-D-glucose **190** in DCM it instantly decomposed. Adding TMSI to neat persilylated 2-deoxy-D-glucose **190** also lead to decomposition. Luckily, the iodide was stable when generated in 2-MeTHF and the resulting solution could be used for the one-pot reaction with 2-phenyl-1,3-dithiane **191**, selectively giving the β-configured *C*-acyl glycoside **192** in 77% yield (Scheme 48).[2–4]



190 **192**

Scheme 48: One-pot *C*-acylation reaction with persilylated 2-deoxy-D-glucose **190**.[2–4]

These conditions were also applicable to 2-deoxy-D-galactose, which suffered from the same instability problem. The yields were lower with 2-deoxy-D-galactose though, presumably because the 2-deoxy-D-galactosyl iodide is less stable compared to the 2-deoxy-D-glucosyl iodide. The reaction still only gave β-configured products, whose configuration was also confirmed by SCXRD in addition to ^{1}H-NMR. For *C*-acyl 2-deoxy-D-glucoside **192** the coupling constants of the anomeric proton were 11.7 and 2.0 Hz, corresponding to one ax./ax. coupling and one ax./eq. coupling. This was also reflected in the SCXRD-structure which showed dihedral bond angles of 177 ° and 57 °. Similar observations were made for *C*-acyl 2-deoxy-D-glucoside **193** with coupling constants of 11.6 and 1.9 Hz and dihedral bond angles of 176 ° and 57 °. This is another strong indicator that the reaction does indeed proceed through a S_N2 mechanism, as there is no steric repulsion of an equatorial OTMS group in 2 position of the pyranose which could prevent formation of the α-configured product (Figure 26).[2–4]

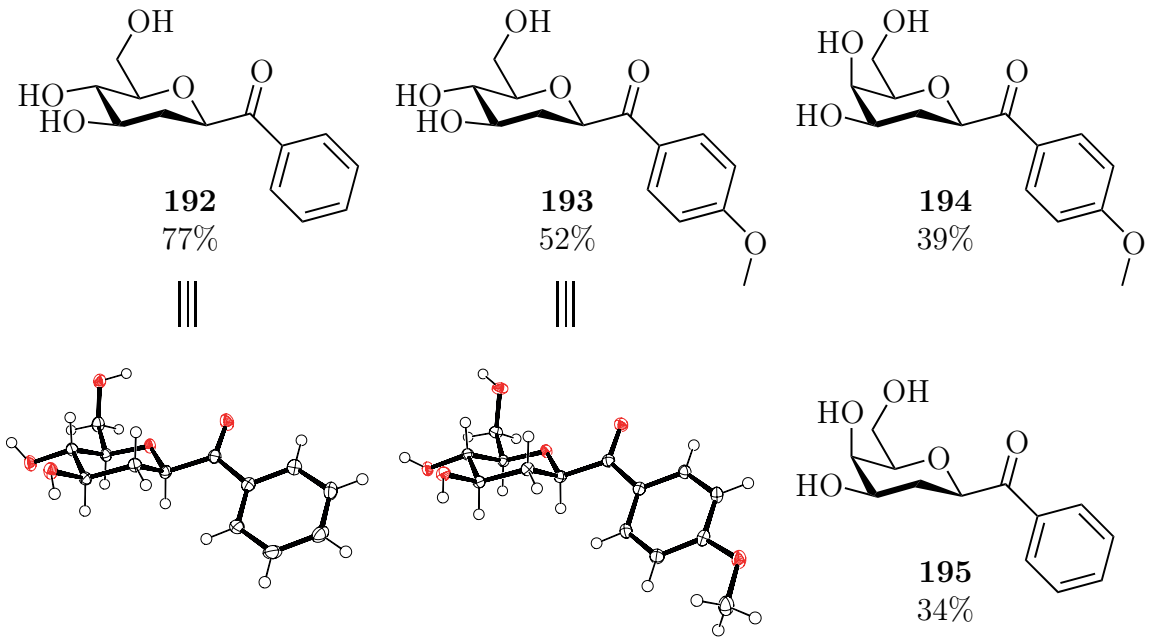
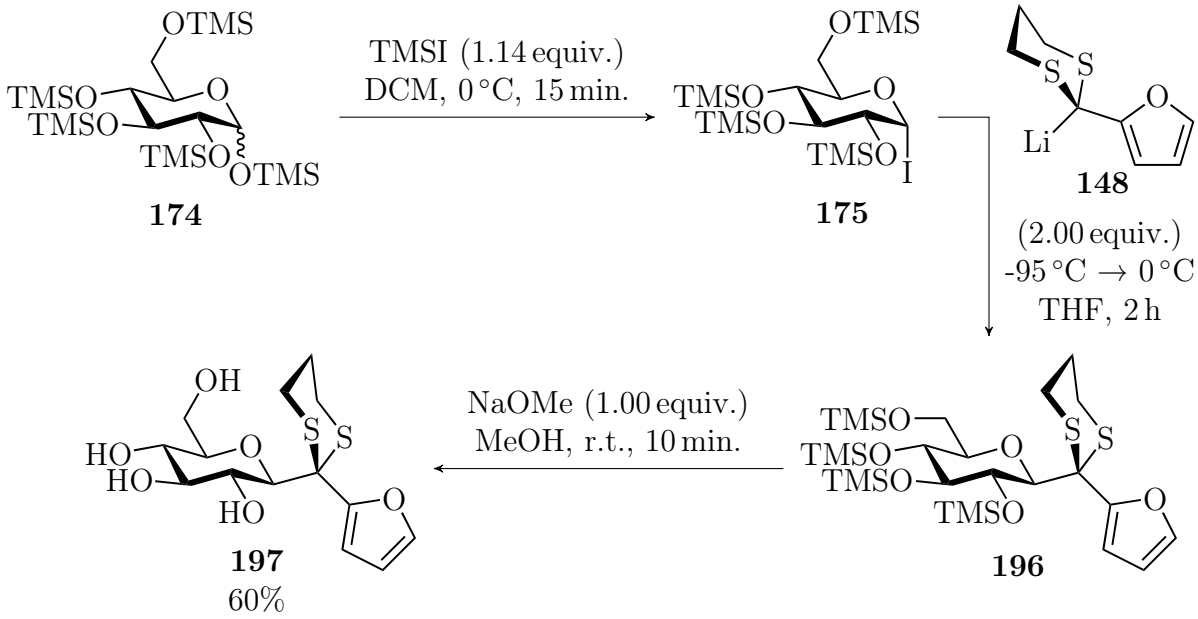


Figure 26: Synthesized *C*-acyl 2-deoxy D-gluco- and D-galactopyranosides.[2–4]

In analogy to the benzyl protected donors, reactions with lithiated furyl-dithiane **148** could not be carried in one-pot fashion due to instability of the *C*-furoyl motif towards PIFA. Skipping the deprotection step of the one-pot procedure, the β-configured dithianyl D-glucoside **196** was isolated in 60% yield. Additionally, the reaction had to be carried out in THF as the reaction only gave the product in 9% yield when it was carried out in 2-MeTHF (Scheme 49).[2–4]



Scheme 49: Corey-Seebach reaction of persilylated D-glucopyranose **175** with **148**.[2–4]

The conditions were also suitable to generate the D-galactosyl **198** and D-xylosyl **199** derivative β-selectively. These reactions conditions were however not applicable to 2-deoxy-D-glucose. Luckily, the 2-deoxy-D-glucosyl iodide was reactive enough in 2-MeTHF to give the dithianyl-2-deoxy-D-glucoside **200** β-selectively in 67% yield. In addition to ^{1}H-NMR, the β-configurations of D-xyloside **199** and 2-deoxy-D-glucoside **200** were also confirmed by SCRXD (Figure 27).[2–4]

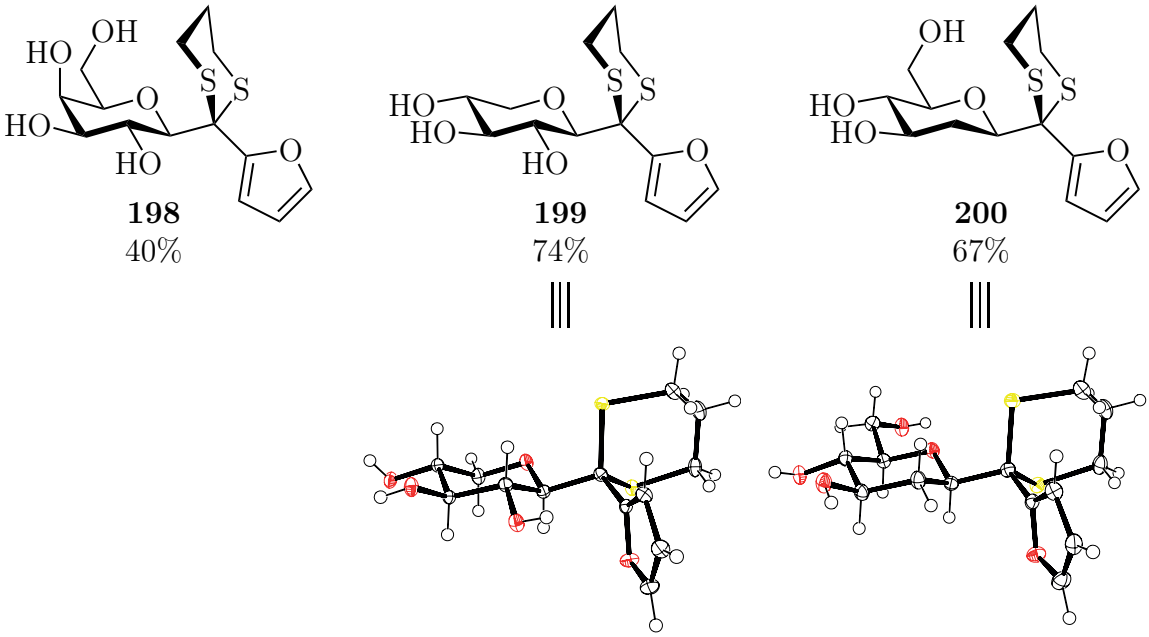
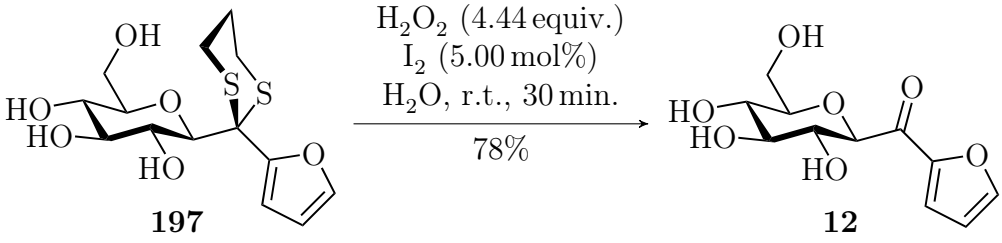


Figure 27: Furanyl-dithianyl-glycosides obtained by Corey-Seebach reaction.[2–4]

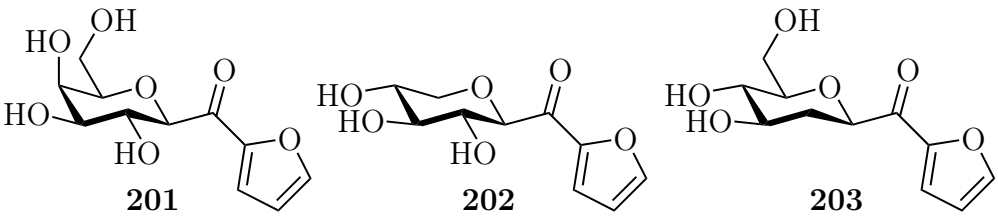
Deprotection of the dithiane was accomplished once more by iodine and hydrogen peroxide, giving scleropentaside A **12** in 78% yield. In contrast to the benzylated dithianyl glycosides, SDS as surfactant was not required for the reaction since unprotected dithianyl-glycosides are water soluble (Scheme 50).[2–4]



Scheme 50: Deprotection of the dithiane to yield scleropentaside A **12**.[2–4]

The deprotection was also carried out with the D-galactosyl, D-xylosyl and 2-deoxy-D-glucosyl derivatives giving the *C*-furoyl D-galactoside **201**, D-xyloside **202** in good yields.

2-Deoxy-D-glucoside **203** was aquired in an even better yield of 92%. The better yield in absence of 2-OH may suggest that a side reaction occurs with the other substrates at 2-OH which negatively impacts the yield. This may be elimination of 2-OH and the anomeric proton as it is a common unwanted reaction of *C*-acyl glycosides (Figure 28).[2–4]



201 77% **202** 70% **203** 92%

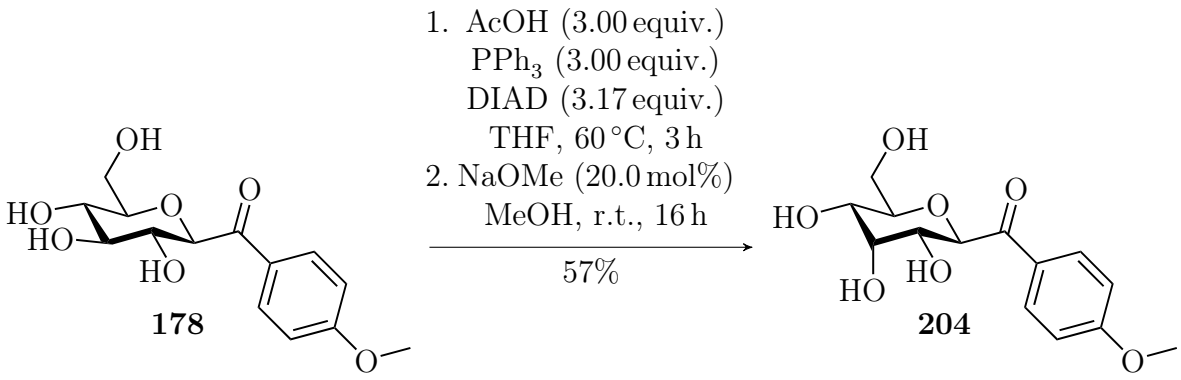
Figure 28: Synthesized *C*-furoyl glycosides.[2–4]

In conclusion, using persilylated D-glucose gave access to scleropentaside A **12** in an excellent overall yield of 47% over only 3 linear steps starting from D-glucose. This is a great improvement over the route using benzyl protecting groups, which gave scleropentaside A in 25% from 2,3,4,6-tetra-*O*-benzyl-D-glucopyranose **153**. This is the shortest and highest yielding synthetic approach to scleropentaside A **12**. When other aryl-dithianes were employed, the deprotection of the dithiane could be carried out in one pot, giving fast access to *C*-aroyl D-glucosides, D-galactosides, D-xylosides, D-arabinosides, 2-deoxy-D-glucosides, 2-deoxy-D-galactosides and L-fucosides with excellent *trans*-selectively in yields of 34-99%. The procedures were not applicable to D-mannosyl and D-allosyl donors. Just like the benzylated bromide, the persilylated D-allosyl iodide was too unstable and decomposed too fast. The D-mannosyl iodide simply did not react with the lithiated dithiane, which was indicated by detection of a α/β-mixture of methyl-D-mannospyranoside in the crude reaction mixture after quenching the reaction with methanol.[2,3,128].

5.2.4 Conversion of a *C*-acyl glucoside into a *C*-acyl alloside

The one-pot *C*-acylation procedure was not applicable to D-allosyl donors, due to instability of the allosyl donors caused by 1,3-diaxial inetractions. Interestingly, unprotected D-glucosides can be converted to D-allosides under Mitsunobu[129] conditions as inversion only occurs at C-3 of the pyranose ring.[130] Applying Mitsunobu conditions, to *C*-acyl D-glucoside **178** followed by deprotection of the resulting acetate under Zemplén[131] conditions did indeed lead to *C*-acyl D-alloside **204**. Aside from the desired product **204**, the crude reaction mixture after deprotection also contained the starting material **178** as well as products formed by elimination of the OH-group at C-2 of the pyranose which probably formed because of the basic Zemplén conditions. This explains

the moderate yield of 57% (Scheme 51). No α-configured carbohydrates were detected in the reaction mixture.



Scheme 51: Synthesis of *C*-acyl D-alloside **204**.

The correct assignment of the structure was also confirmed by SCXRD (Figure 29). In addition to the allo-configuration, the structure shows the β-configuration of the product with a dihedral angle of 169 ° between the anomeric proton and anomeric proton and its vicinal proton, which is in agreement with the observed coupling constant of 9.6 Hz for the coupling between 1-H and 2-H of the pyranose ring.

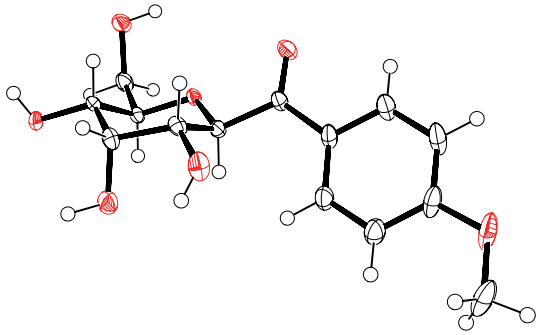
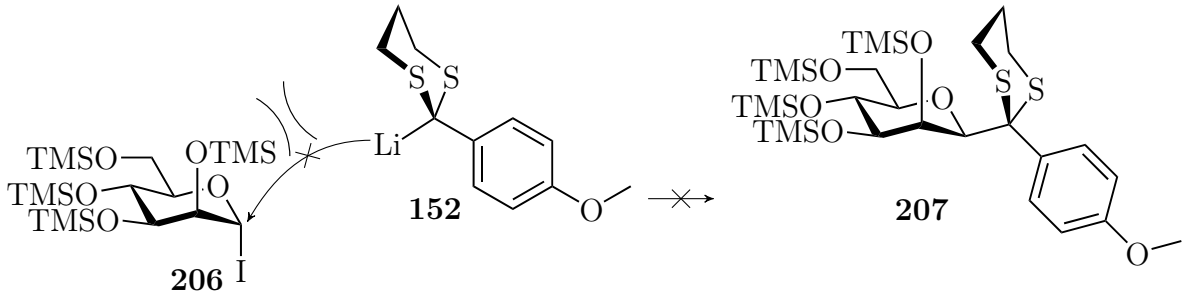


Figure 29: SCXRD structure of *C*-acyl D-alloside **204**.

While this reaction was not explored further, the results show that *C*-acyl D-allosides can be synthesized in simple fashion from *C*-acyl D-glucosides, which are easily accessible from the one-pot *C*-acylation procedure.

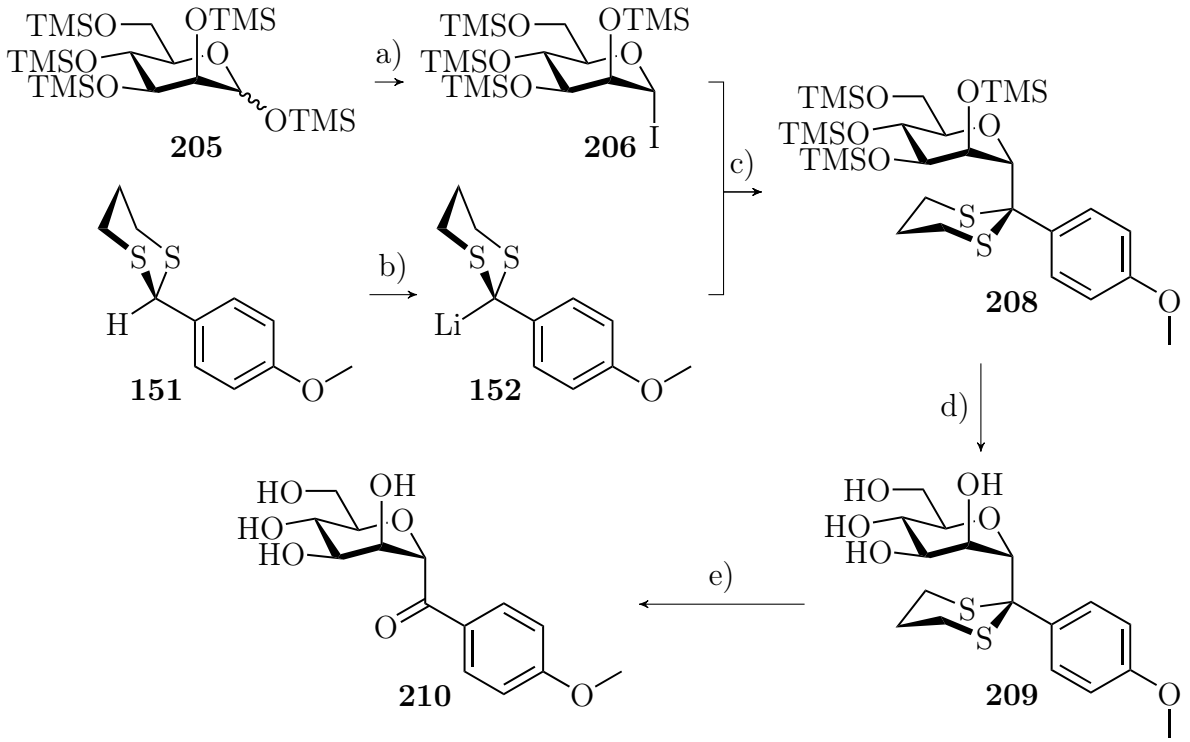
5.2.5 Synthesis of α-*C*-acyl mannosides

The one-pot acylation procedure had always failed when applied to persilylated D-mannose **205**, as the reaction failed due to steric hindrance by the axial 2-OTMS group (Scheme 52).



Scheme 52: Hinderance of the S_N2 attack by the 2-OTMS group.

In hope to achieve conversion of the starting material, the reaction was attempted a higher temperature of 0 °C (Scheme 53).[5]



Scheme 53: One-pot *C*-acylation reaction with persilylated D-mannose **205**. Reagents and conditions: a) Persilylated D-mannose **205** (1.00 equiv.), TMSI (1.14 equiv.), neat, r.t., 15 min; b) Dithiane **151** (2.00 equiv.), *t*-BuLi (2.02 equiv.), glyme, 0 °C, 10 min. c) glyme, 0 °, 3 h; d) NaOMe (2.00 equiv.), r.t., MeOH, 10 min; e) PIFA (2.50 equiv.), r.t., $MeOH/H_2O$ then L-ascorbic acid (2.00 equiv.).[5]

Interestingly, in one attempt *C*-mannosylated product **210** was obtained in this reaction in 11% yield. This result was not in agreement with previously carried out experiments, where no *C*-mannosylated product was obtained. Solvent screening revealed, that the reaction performed best in glyme. However, the reaction still suffered from low reproducibility at this point (Table 7: Entry 4). Further experiments revealed that traces of Cu, which was used as stabilizing agent for the TMSI, was responsible for the change in reactivity. Over time the Cu reacts to CuI, which might play a role in this reaction. Investigating the effect of CuI did in fact reveal that traces of CuI had a beneficial effect on the reaction (Table 7: Entries 8-10), resulting in a cleaner reaction and higher yields but only at low catalyst loadings. High loadings of copper iodide had an inhibiting effect on the reaction (Table 7: Entries 5-7). Although the beneficial effect could already be observed when only a tiny speck of copper iodide (0.0025 mol%) was added (Table 7: Entry 10), 0.26 mol% where used for further reactions as this amount was more easy to handle and the results more comparable. This also explains why the earlier experiments in MeTHF yielded no product, as TMSI which was stored over aluminium was used in these attempts.

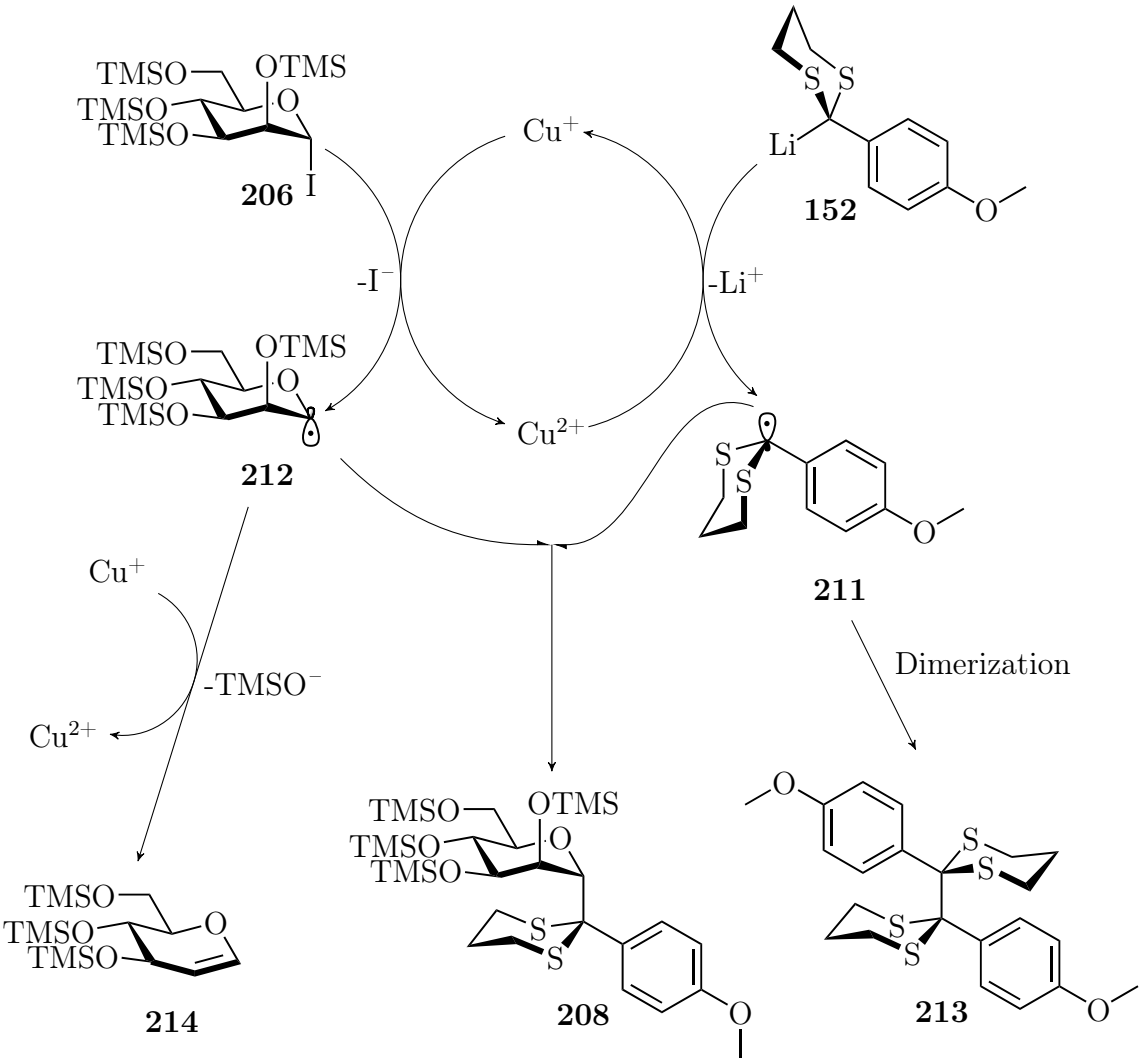
Table 7: Optimization of step c) in Scheme 53.[5]

	T	t	solvent	equiv. CuI	yield of **210**
1	-95 °C → r.t.	16 h	2-MeTHF	-	0%
2	0 °C	3 h	2-MeTHF	-	0-11%
3	0 °C	3 h	THF	-	16-22%
4	0 °C	3 h	glyme	-	30-40%
5[a)]	0 °C	3 h	glyme	1 equiv.	0%
6[a)]	0 °C	3 h	glyme	10.0 mol%	not isolated
7[a)]	0 °C	3 h	glyme	1.00 mol%	not isolated
8	0 °C	3 h	glyme	0.50 mol%	39%
9	0 °C	3 h	glyme	0.26 mol%	40%
10	0 °C	3 h	glyme	0.0025 mol%	37%
11[b)]	0 °C	3 h	glyme	-	9%
12[c)]	0 °C	3 h	glyme	0.26 mol%	8%
13[d)]	0 °C	3 h	glyme	0.26 mol%	44%

a) incomplete conversion of D-mannosyl iodide **206**. b) TMSI stabilized over Al was used. c) 10 mol-% BHT was added. d) L-Ascorbic acid added after deprotection with PIFA.

The control experiment using TMSI stabilized by aluminium also confirmed this hypothesis (Table 7: Entry 11). As reactions of CuI with alkyl halides may proceed through a radical mechanism, BHT was added as radical inhibitor to confirm this assumption. Addition of BHT did indeed suffocate the reaction (Table 7: Entry 12) indicating that this reaction proceeds through a radical mechanism.[5] The reaction was further optimized by adding L-ascorbic acid after deprotection of the dithiane with PIFA to suppress decomposition of the product, which otherwise occurred during work-up. This improved the yield to 44% while still keeping the α-selectivity according to the ^{1}H-NMR spectrum of the crude mixture.[5]

Since the reaction was dependent on the presence of Cu^+ and the radical inhibitor BHT had a negative effect on the outcome of the reaction, the reaction may proceed through a radical mechanism catalyzed by Cu^+ (Scheme 54).



Scheme 54: Proposed reaction mechanism of the *C*-mannosylation step.[5]

In a possible radical mechanism, Cu^{+} first donates an electron to the donor **206**, generating D-mannosyl radical **212** and I^{-}. The Cu^{+} species is then regenerated by reduction of the newly formed Cu^{2+} by the lithiated dithiane **152**, forming dithiany lradical **211**. Combination of the radicals **212** and **211** then forms the *C*-mannoside **208**. Further evidence of a radical mechanism is the formation of side products **214** and **213**. D-glucal **214** may be formed by reduction of D-mannosyl radical **212** by Cu^{+}, resulting in overall reductive elimination of a $TMSO^{-}$ group and I^{-}. The oxidative dimerization yields product **213**, which is known to form under radical conditions[90] and is presumably formed by dimerization of two dithianyl radicals **211** (Scheme 54).[5]

In the ^{1}H-NMR of **210** all signals resonate downfield of 3 ppm due to all protons being either bound to carbon atoms bearing an electron withdrawing oxygen substituent or aromatic carbon atoms. The exchangeable protons bound to oxygen atoms are not visible in MeOD due to H/D exchange. 5'-H resonates at 3.36 ppm as doublet of doublet of doublet coupling to 4'-H with a coupling constant of 9.4 Hz and coupling to the two protons at C-6' with coupling constants of 6.2 and 2.5 Hz.

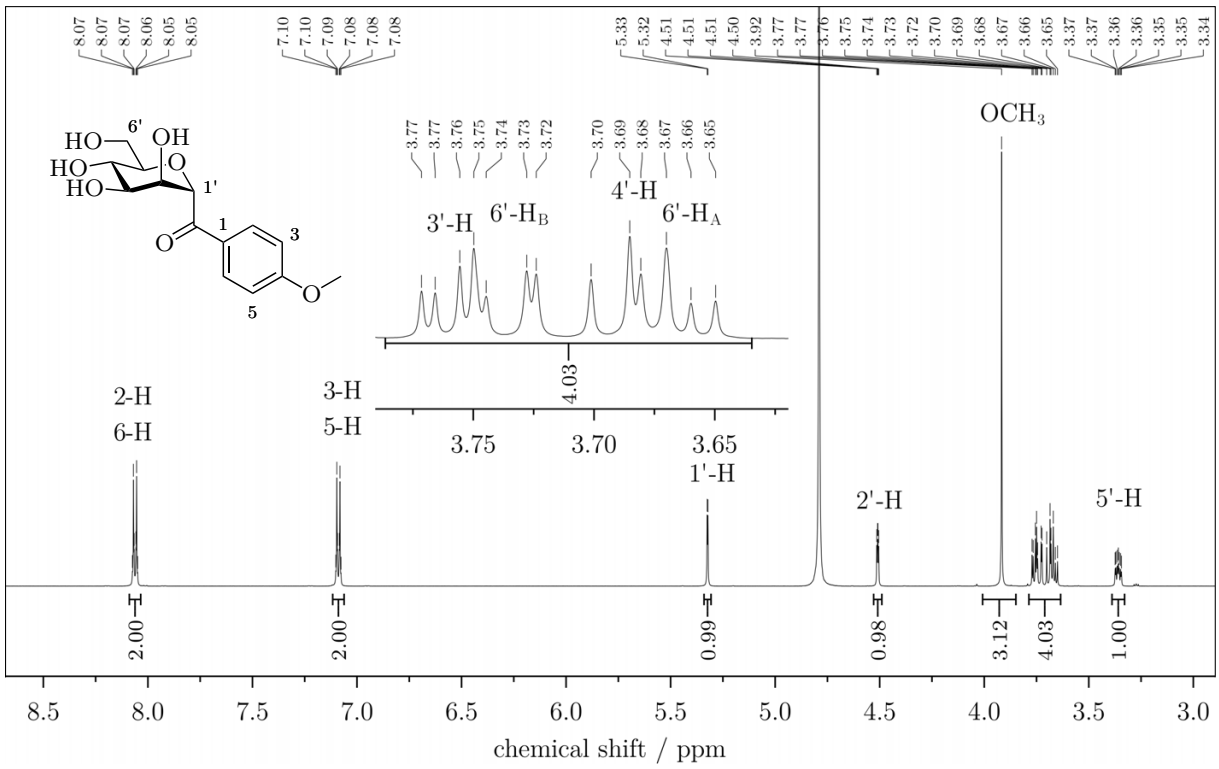


Figure 30: ^{1}H-NMR spectrum of *C*-acyl D-mannoside **210** at 600 MHz in D_2O.[5]

At 3.66 ppm 6-H_A resonates as doublet of doublet with a geminal coupling constant of 12.6 Hz and a vicinal coupling constant of 6.2 Hz. 4'-H resonates as pseudotriplet with a due to two ax./ax. couplings with 3-H and 5-H which is indicated by the coupling constant

of 9.4 Hz. At 3.74 ppm 6-H_B resonates as doublet of doublet with a geminal coupling constant of 12.6 Hz and a vicinal coupling constant of 2.5 Hz. The doublet of doublet at 3.77 ppm with coupling constants of 9.4 Hz (ax./ax. coupling with 4'-H) and 3.4 Hz (ax./eq. coupling with 2'-H) was assigned to 3'-H. The three protons of the methoxy group resonate as a singlet at 3.92 ppm. 2'-H resonates as a doublet of doublet at 4.51 ppm with coupling constants of 3.4 Hz (ax./eq. coupling with 3'-H) and 2.2 Hz (eq./eq. coupling with 1'-H). The anomeric proton 1'-H resonates at 5.32 ppm with a coupling constant of 2.2 Hz. Although the coupling constants confirm the D-manno-configuration of the product according to the Karplus-equation, assignment of the anomeric configuration is not possible. While ax./ax. coupling constants are within a range of ≈ 9-12 Hz, ax./eq. coupling constants usually lie within a range ≈ 2-3 Hz and eq./eq. coupling constants lie within ≈ 2-6 Hz.[132] The anomeric coupling constant of 2.2 Hz is therefore not suitable for unambiguous determination of the α-anomeric configuration. Further downfield, the four aromatic protons resonate as two multipletts at typical shifts of 7.08 ppm and 8.06 ppm, each with an integral of 2 H (Figure 30).

Since the anomeric configuration cannot be assigned by the coupling constant, a NOESY spectrum of **210** was acquired. The absence of cross-relaxations in the NOESY between 1'-H and the axial protons 3'-H and 5-H' suggested that the product is α-configured (Figure 31).

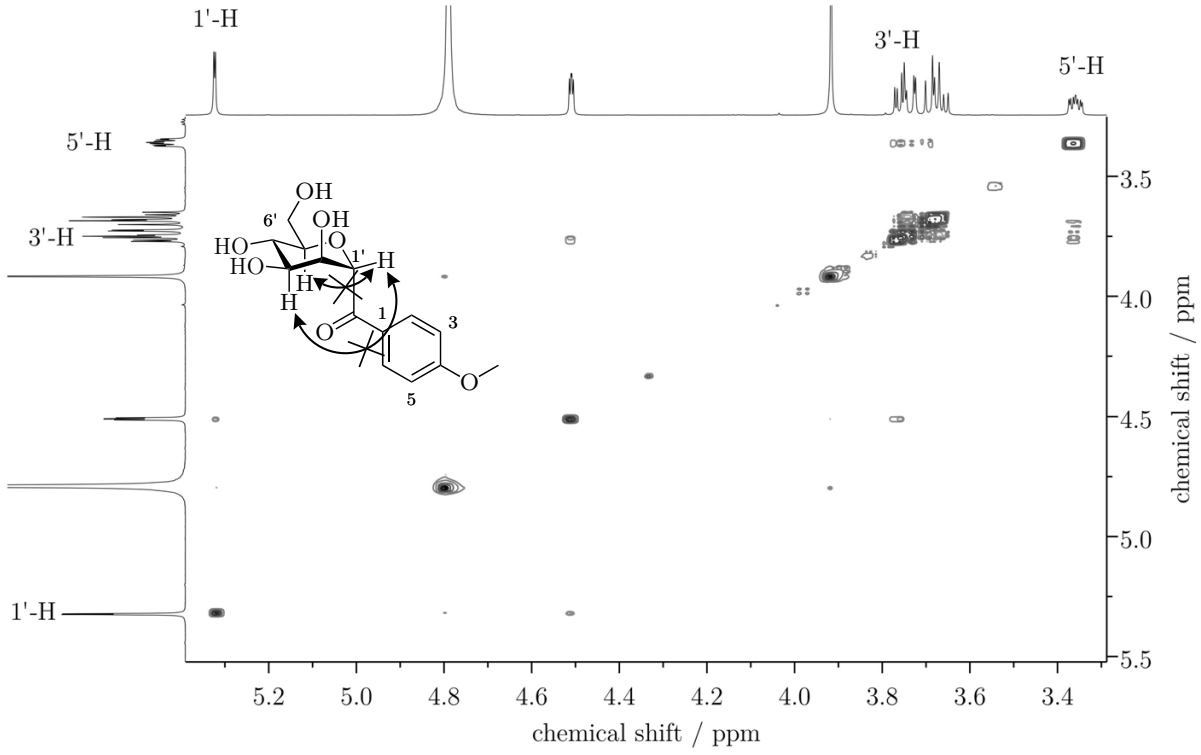


Figure 31: NOESY spectrum of *C*-acyl D-mannoside **210** in D_2O.[5]

The ^{13}C-NMR of **210** shows a peak at 55.6 ppm, corresponding to the methoxy group. C-6' resonates at 61.0 ppm. The signals at 66.9 (C-4'), 68.9 (C-2'), 71.1 (C-3'), 77.3 (C-5') and 80.1 ppm (C-1') were all assigned to the D-mannosyl-ring by HSQC. The four aromatic carbon atoms C-2, C-3, C-5 and C-6 bound to a proton resonate further downfield as two peaks at typical shifts of 114.0 and 131.8 ppm. The quarternary aromatic carbon atom C-1 which is next to the carbonyl resonates at 127.3 ppm, while the quarternary aromatic carbon atom C-4 to which the methoxy group is bound resonates further downfield due to the inductive effect of the oxygen atom at 164.0 ppm. The downfield peak at 199.7 ppm and the band at 1651 cm^{-1} in the infrared spectrum confirm the presence of the carbonyl motif as the chemical shift of the ^{13}C-NMR signal and the wavenumber of the IR signal are both in typical ranges which are usually only occupied by carbonyl signals (Figure 32).

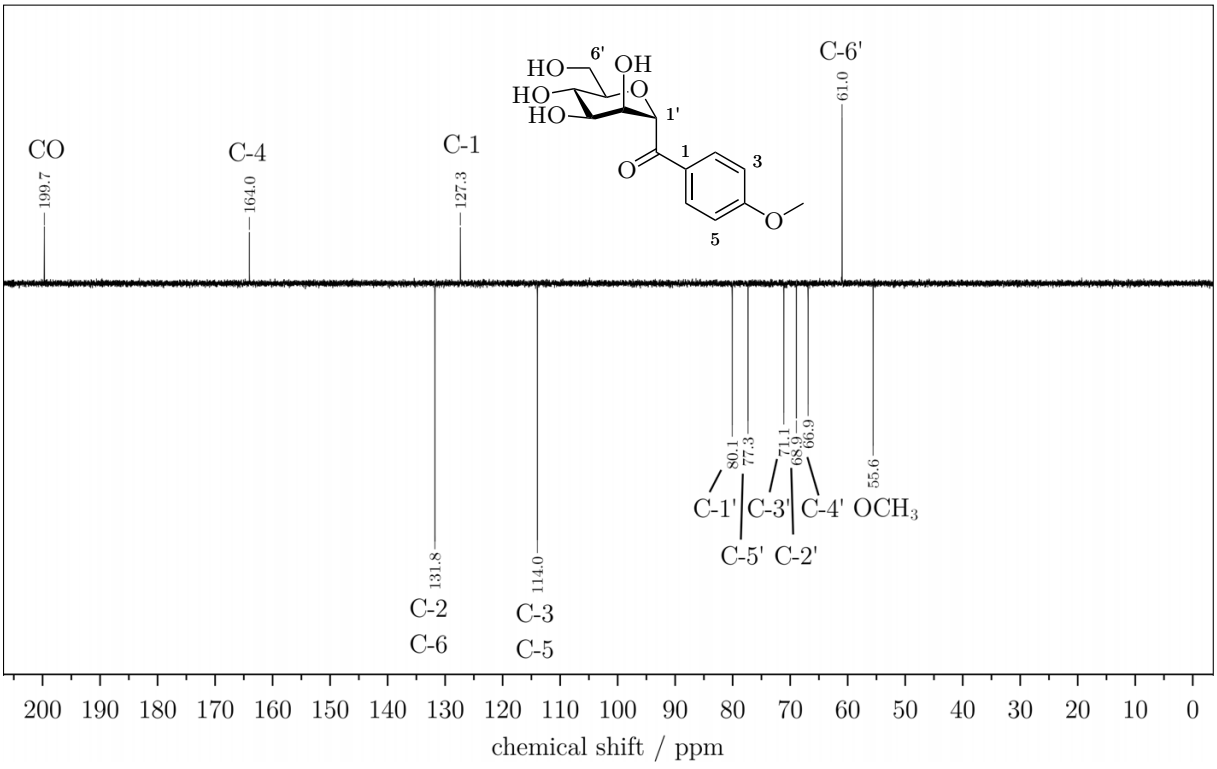


Figure 32: DEPTQ-NMR spectrum of *C*-acyl D-mannoside **210** at 151 MHz in D_2O.[5]

The molecular formula $C_{14}H_{18}O_7$ was confirmed by a peak at m/z = 321.0938 which corresponds to the calculated mass of 321.0945 for the molecular formula in association with a sodium cation. The structure of the product was also confirmed by SCXRD (Figure 33). In the obtained SCXRD-structure the *C*-acyl D-mannoside **210** crystallized in the unit cell as tetramer with six units of water. The structure shows the α-configuration of the product with a dihedral angle of 66-68 ° between the anomeric proton and 2'-H, which is in agreement with the observed coupling constant of 2.2 Hz.[5]

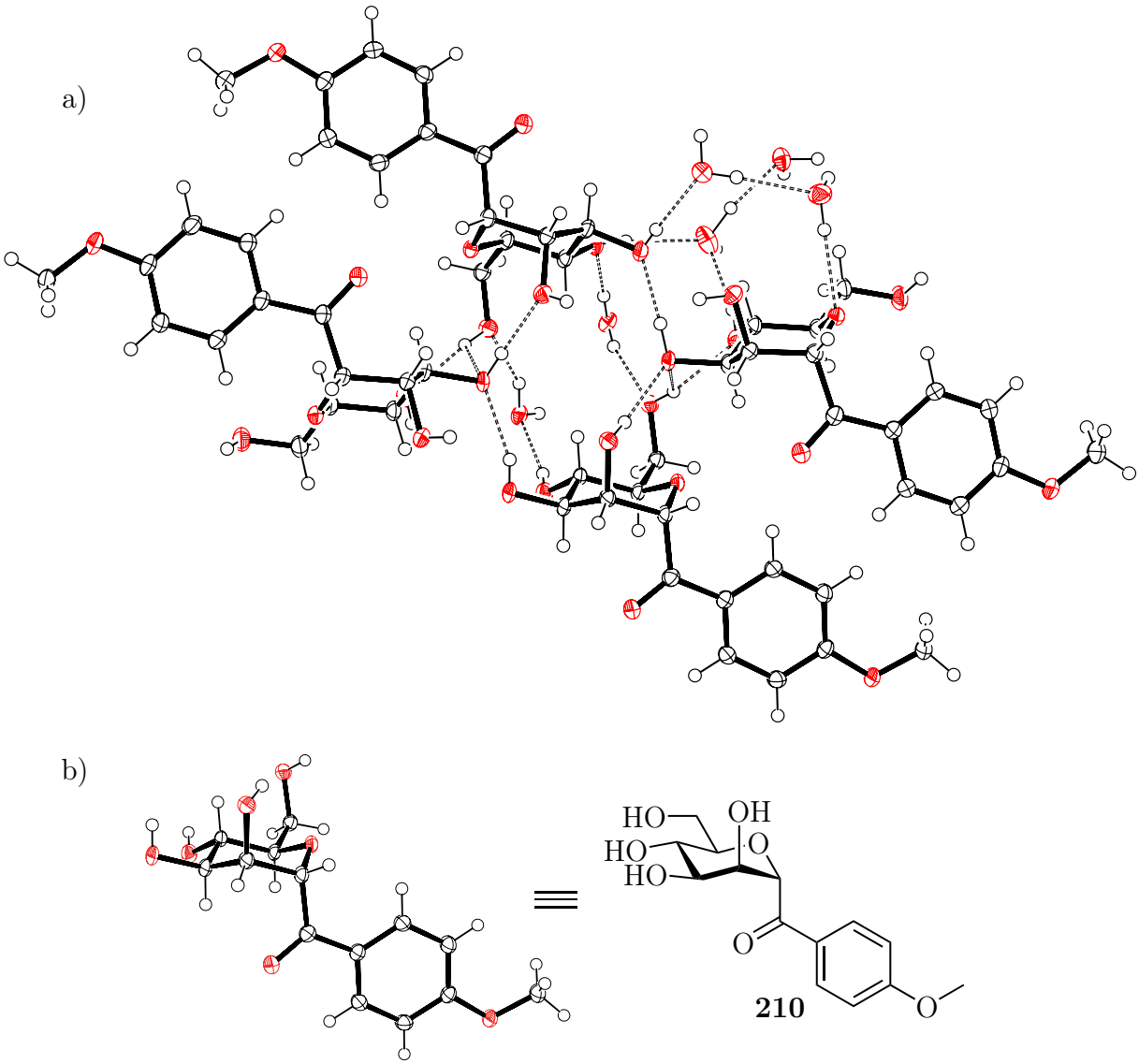


Figure 33: a) Full SCXRD structure of *C*-acyl D-mannoside **210**; b) Excerpt from the same structure showing a single molecule of *C*-acyl D-mannoside **210**.[5]

Investigating the scope of the reaction revealed that the procedure was exclusively α-selective when applied to persilylated D-mannose **205**. The reaction was only applicable to *p* and *m* substituted aryl dithianes, as alkyl and alkenyl dithianes did not yield *C*-acyl D-mannosides. Overall, electron-rich aryl dithianes gave higher yields than electron deficient aryl dithianes. Dithianes bearing an unprotected phenolic hydroxyl group could also be used as substrates by doubling the equivalents of *t*-BuLi to achieve deprotonation of the hydroxyl group. *O*-glycosylated products were not observed in these cases. Employing TMS-protected alkynyl-dithiane **215** as starting material gave the alkyne derivative **216** as the alkynyl TMS group was also cleaved alongside with the O-TMS groups (Figure 34).[5]

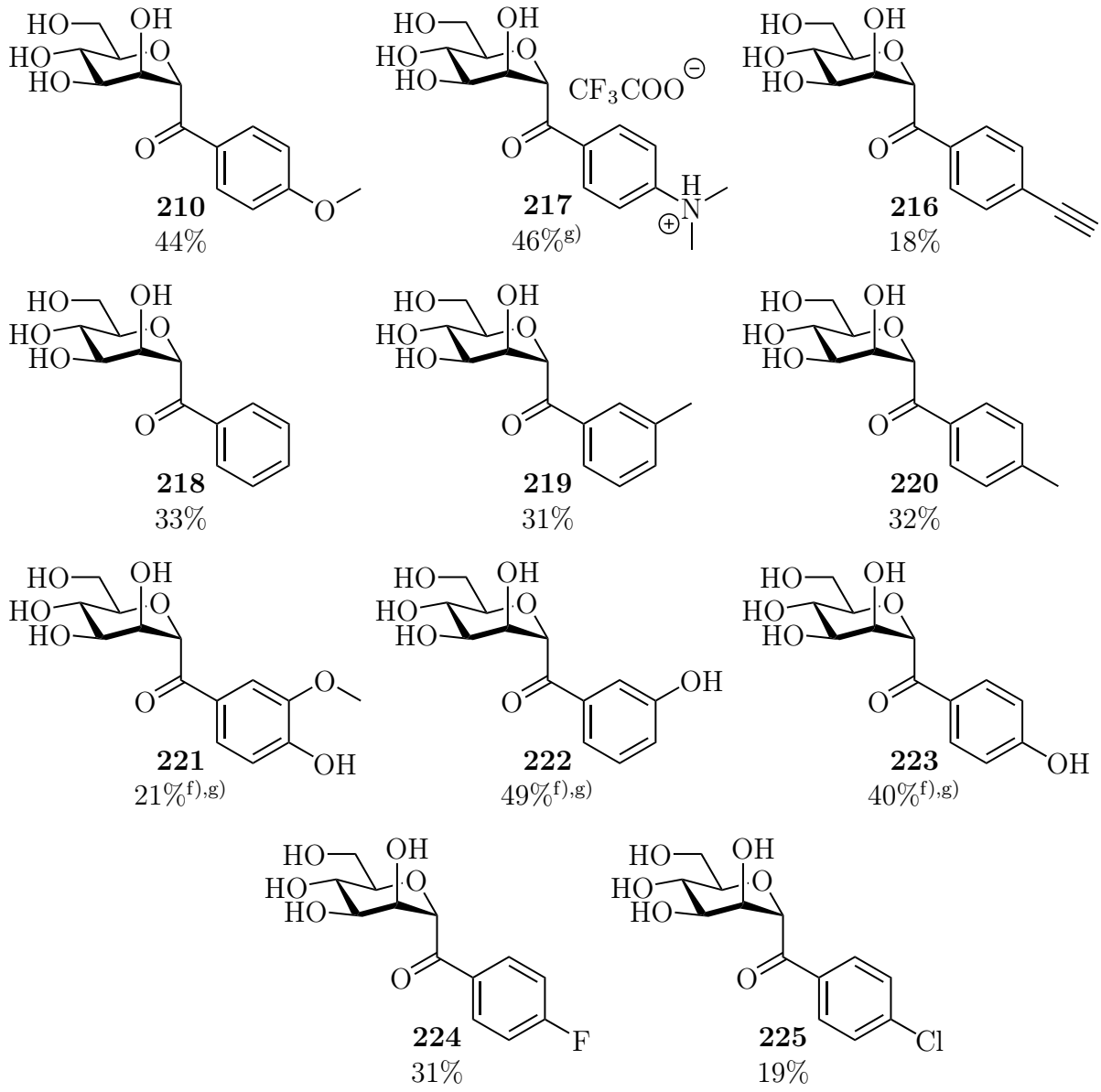


Figure 34: Reaction scope for the *C*-glycosylation of D-mannopyranose. Reagents and conditions: a) Persilylated D-mannose **205** (1.00 equiv.), TMSI (1.14 equiv.), neat, r.t., 15 min; b) Dithiane (2.00 equiv.), *t*-BuLi (≈ 2.00 equiv.), glyme, 0 °C, 10 min. c) glyme, 0 °, 3 h; d) NaOMe (2.00 equiv.), r.t., MeOH, 10 min; e) TFA (3.04 equiv.), PIFA (2.50 equiv.), r.t., MeOH/H_2O then L-ascorbic acid (2.00 equiv.).[5]; f) ≈ 4.00 equiv. of *t*-BuLi used in step b); g) 4.95 equiv. of TFA used in step e).[5]

Applying the reaction conditions to persilylated L-rhamnose **226** yielded *C*-acyl L-rhamnopyranosides in slightly lower yields when compared to D-mannose derivatives. In general, the reaction was still α-selective, but for *p*-phenolic products **235** and **233** trace amounts (<3%) of the β-isomers were detectable in the ^{1}H-NMR spectrum after purification. The α- and β-isomers were always separated during column chromatography but still present after evaporation of the solvent. (Figure 35).

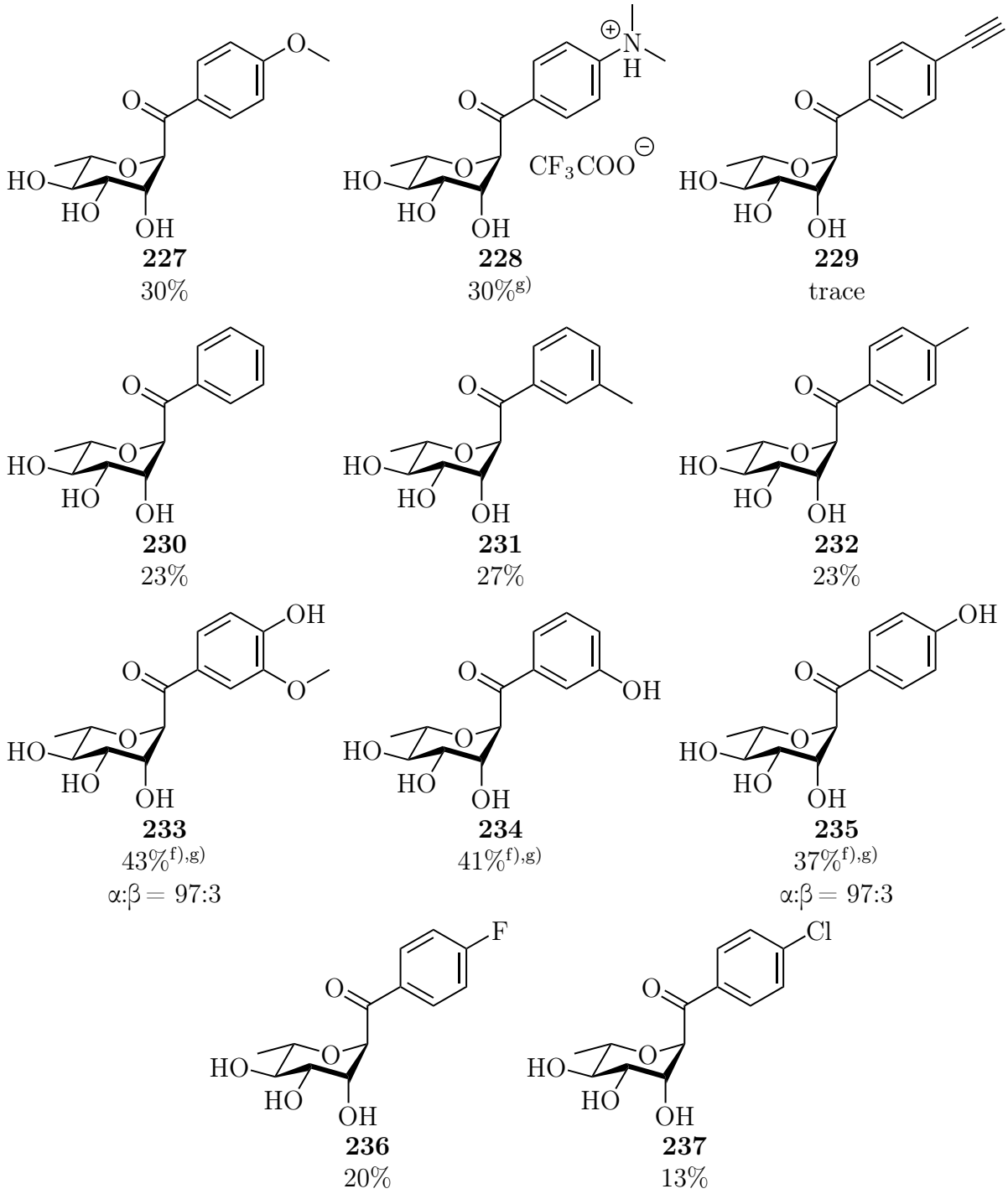


Figure 35: Reaction scope for the *C*-glycosylation of L-rhamnopyranose. Reagents and conditions: a) Persilylated L-rhamnose **238** (1.00 equiv.), TMSI (1.14 equiv.), neat, r.t., 15 min; b) Dithiane (2.00 equiv.), *t*-BuLi (≈ 2.00 equiv.), glyme, 0 °C, 10 min. c) glyme, 0 °, 3 h; d) NaOMe (2.00 equiv.), r.t., MeOH, 10 min; e) TFA (3.04 equiv.), PIFA (2.50 equiv.), r.t., $MeOH/H_2O$ then L-ascorbic acid (2.00 equiv.); f) ≈ 4.00 equiv. of *t*-BuLi used in step b); g) 4.95 equiv. of TFA used in step e).[5]

As these trace amounts of β-isomers were only observed for the *p*-phenolic products, they may be formed by isomerization triggered by the molecule itself as the *p*-phenolic hydroxy group is more acidic (Figure 35).

Running the reaction with D-lyxopyranose gave the *C*-acyl D-lyxosides in yields similar or better when compared to the D-mannose derivatives (Figure 36).

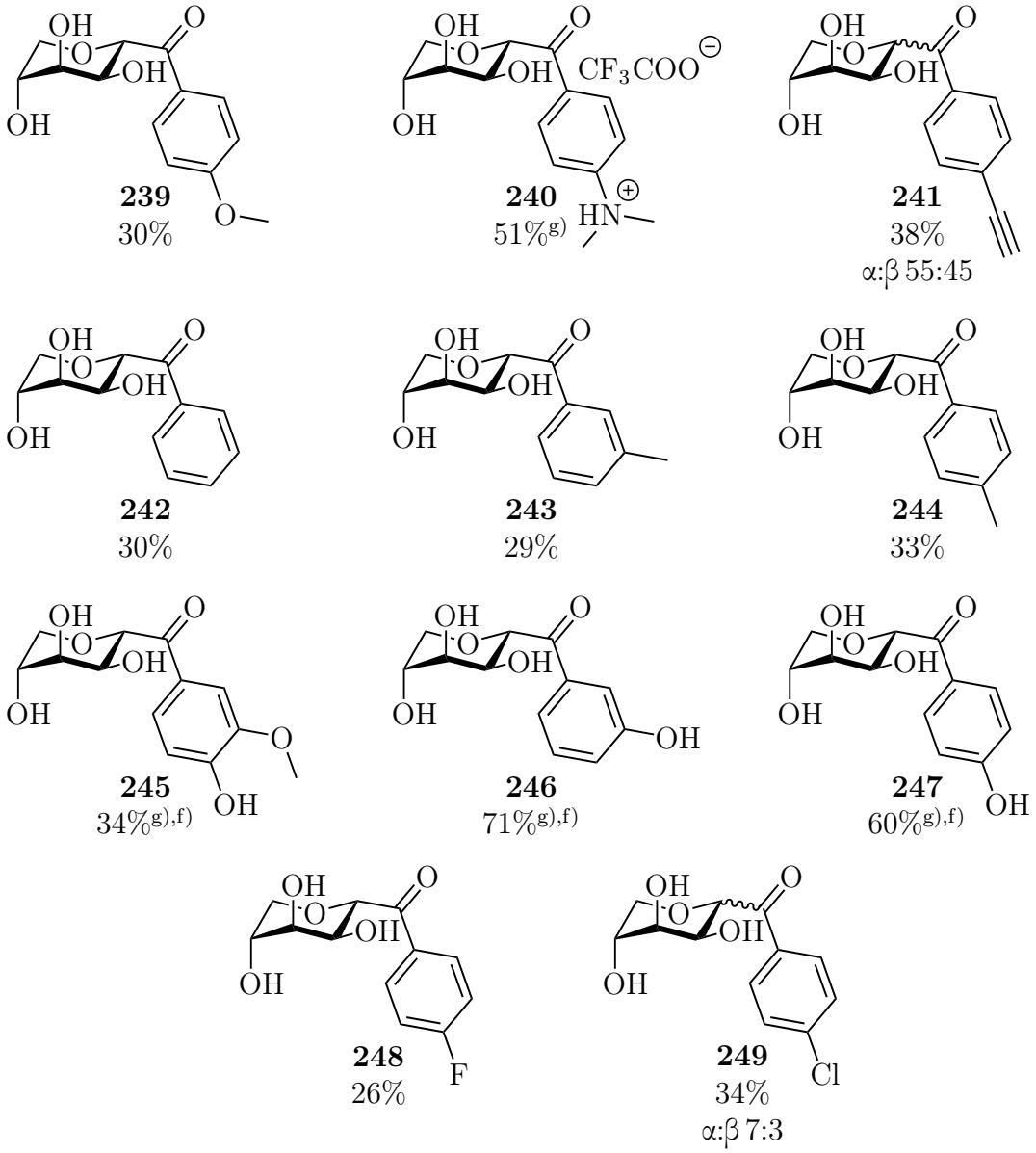


Figure 36: Reaction scope for the *C*-glycosylation of D-lyxopyranose. Reagents and conditions: a) Persilylated D-lyxose **250** (1.00 equiv.), TMSI (1.14 equiv.), neat, 0 °C., 15 min; b) Dithiane (2.00 equiv.), *t*-BuLi (≈ 2.00 equiv.), glyme, 0 °C, 10 min. c) glyme, 0 °, 3 h; d) NaOMe (2.00 equiv.), r.t., MeOH, 10 min; e) TFA (3.04 equiv.), PIFA (2.50 equiv.), r.t., MeOH/H_2O then L-ascorbic acid (2.00 equiv.).[5]; f) ≈ 4.00 equiv. of *t*-BuLi used in step b); g) 4.95 equiv. of TFA used in step e).[5]

When dithianes with electron-withdrawing substituents at the aromatic core were employed, the reaction yielded separable anomeric mixtures (compounds **241** and **241**). In these cases the α/β-mixture definitely formed during the C-C bond formation, as the α/β-mixtures were detected in crude NMR prior to deprotection of the unisomerizable dithianes. The yields of these unselective reactions were significantly higher when compared to D-mannose (Figure 36).

Unlike the *C*-acyl D-manno- and L-rhamnopyranosides, these D-lyxopyranosides adopted the uncommon $^1C_4$-conformation according to ^{1}H-NMR and SCXRD data.
In the ^{1}H-NMR-spectrum of **245** the equatorial proton bound to C-5' resonates at 3.75 ppm as doublet of doublet with a geminal coupling constant of 12.6 Hz and a vicinal coupling constant of 2.9 Hz. 4'-H in equatorial position and the three protons of the methoxy group overlapped as a multiplett from 3.92 to 3.95 ppm. The axial proton bound to C-5' resonates at 4.01 ppm as doublet of doublet with a geminal coupling constant of 12.6 Hz and a vicinal coupling constant of 2.0 Hz. 3'-H resonates as pseudotriplet coupling with the vicinal protons with a coupling constant of 3.9 Hz due to eq./eq. coupling to 4'-H and eq./ax. coupling to 2'-H The doublet of doublet at 4.20 ppm with coupling constants of 8.8 Hz (coupling with 1'-H) and 3.9 Hz (coupling with 3'-H) was assigned to 2'-H (Figure 37).

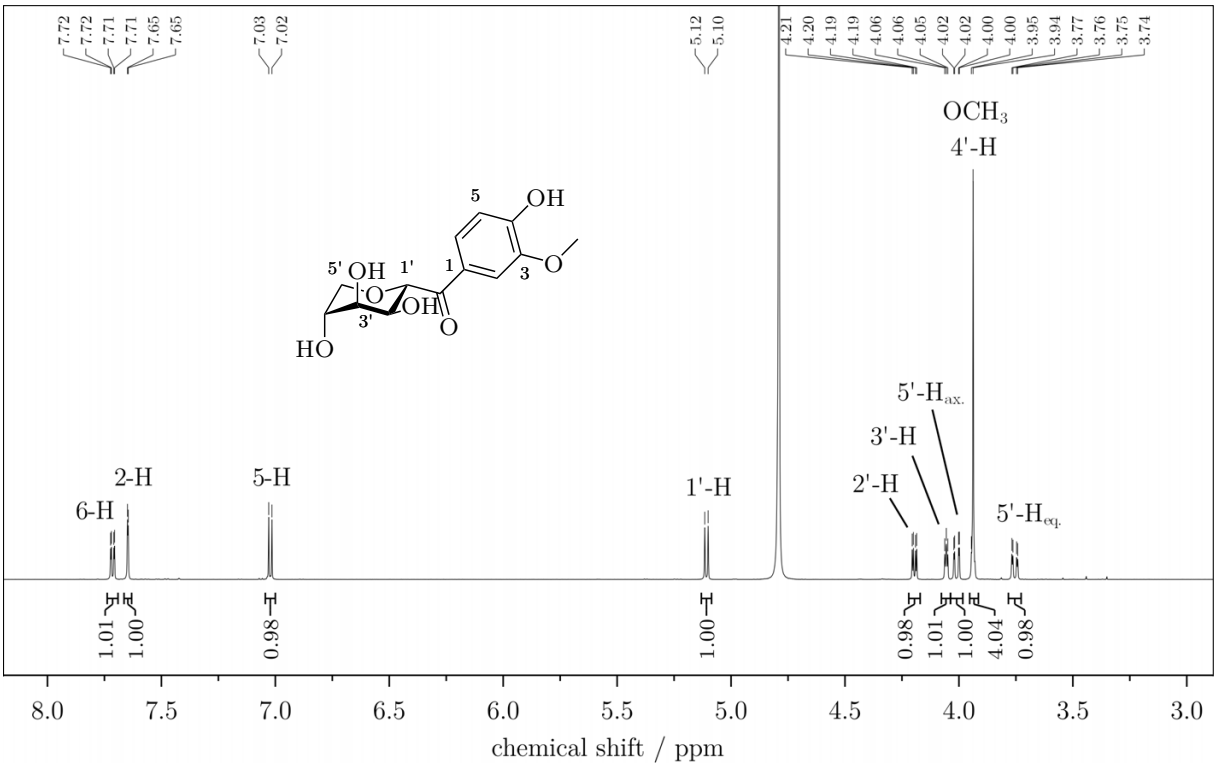


Figure 37: ^{1}H-NMR spectrum of *C*-acyl D-lyxoside **245** at 600 MHz in D_2O.[5]

The anomeric proton 1'-H resonates at 5.11 ppm with a coupling constant of 8.8 Hz. According to the Karplus-equation, a coupling constant of this magnitude indicates anti-configured protons in ax./ax. configuration. For D-lyxopyranosides this is only possible if the product is α-configured and in $^1C_4$ configuration as in all other cases the protons would be ax./ax or ax/eq. configuration resulting in a coupling constant of ≈ 2-6 Hz. The absence of a cross-relaxation between 1'-H and 3'-H as well as the observed cross-relaxation between 1'-H and the equatorial proton bound to C-5' in the NOESY also confirm this hypothesis (Figure 38). Further downfield at 7.02 ppm the aromatic proton 5-H resonates as doublet with a ^3J coupling constant of 8.8 Hz. 2-H resonates at 7.65 ppm as doublet with a ^4J coupling constant of 2.1 Hz. 6-H resonates as doublet of doublet with a ^3J coupling constant of 8.8 Hz and a ^4J coupling constant of 2.1 Hz.

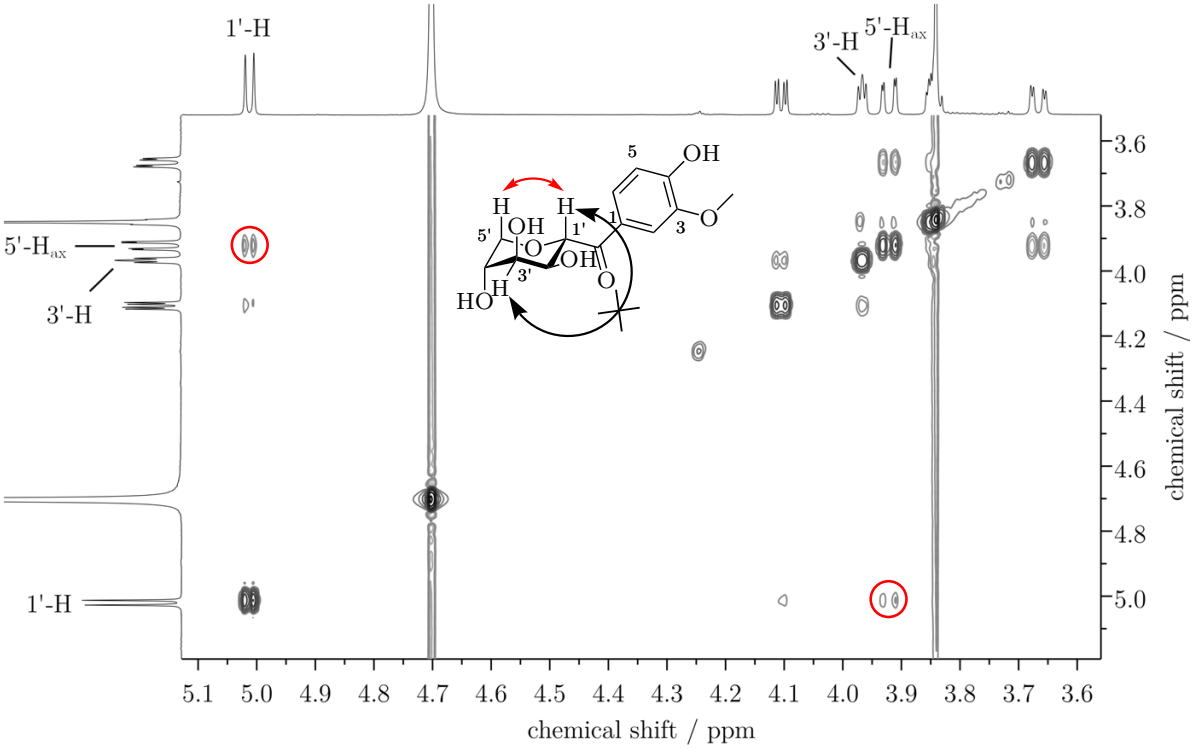


Figure 38: NOESY spectrum of of *C*-acyl D-lyxoside **245** in D_2O.[5]

The ^{13}C-NMR of **245** shows a peak at 55.9 ppm, corresponding to the methoxy group. The signals at 66.6 (C-5'), 66.7 (C-5'), 68.8 (C-4'), 69.8 (C-3') and 75.7 ppm (C-1') were all assigned to the D-lyxosyl-ring by HSQC. The three aromatic carbon atoms C-2, C-5, C-6 bound to a proton resonate at 112.2, 115,0 and 125.3 ppm. C-1 which is next to the carbonyl resonates at 128.1 ppm. Due to the inductive effect of the oxygen atoms the aromatic carbon atom C-3, to which the methoxy group is bound, resonates at 147.4 ppm and the aromatic carbon atom C-4 to which the hydroxy group is bound resonates at 151.6 ppm. The peak at 198.4 ppm and the band at 1651 cm^{-1} in the infrared spectrum

confirm the presence of the carbonyl motif as the chemical shift of the ^{13}C-NMR signal and the wavenumber of the IR signal are both in typical ranges which are usually only occupied by carbonyl signals (Figure 39).

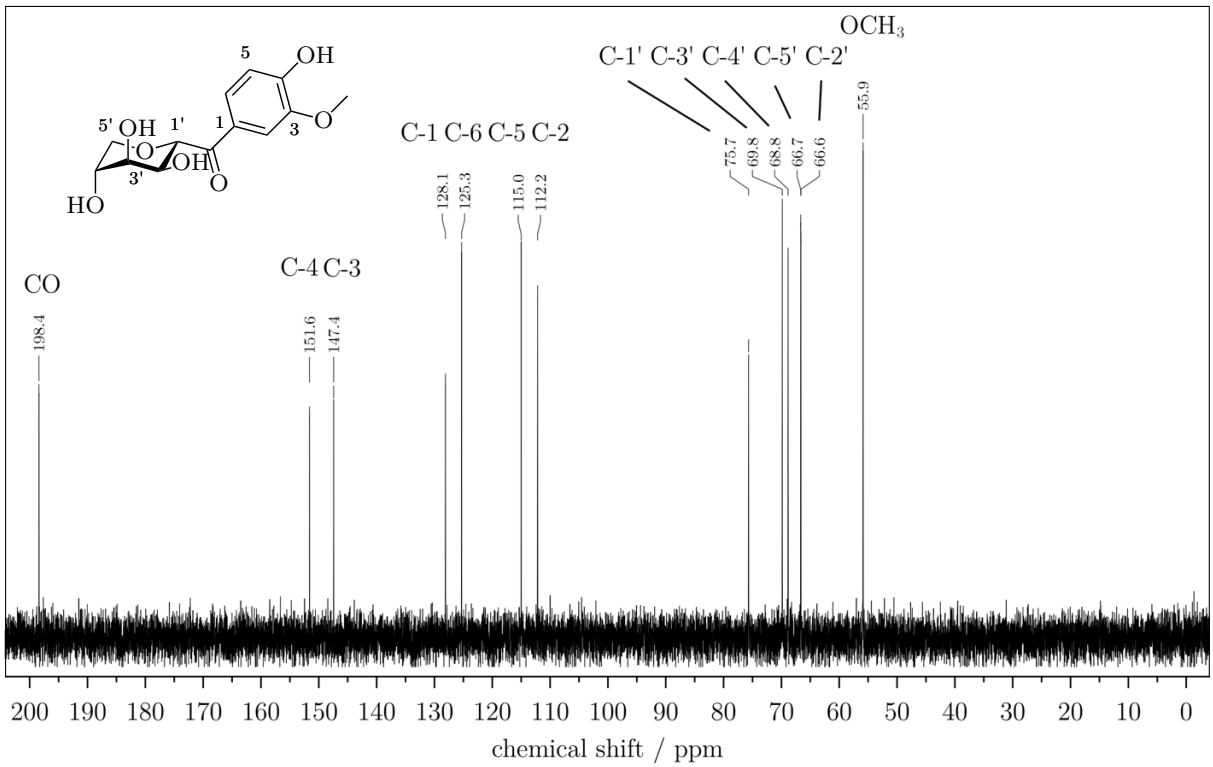


Figure 39: ^{13}C-NMR spectrum of *C*-acyl D-lyxoside **245** at 151 MHz in D_2O.[5]

The molecular formula $C_{13}H_{16}O_7$ was confirmed by a HRMS peak at m/z = 307.0788 which exactly matches the molecular formula in association with a sodium cation. The structural assignments were also confirmed by SCXRD (Figure 40). The structure shows the $^1C_4$-conformation in conjunction with the α-configuration of the product. The dihedral angle of 180 ° between the anomeric proton and 2'-H is in agreement with the observed coupling constant of 8.8 Hz for the coupling between 1'-H and 2'-H of the pyranose ring.[5]

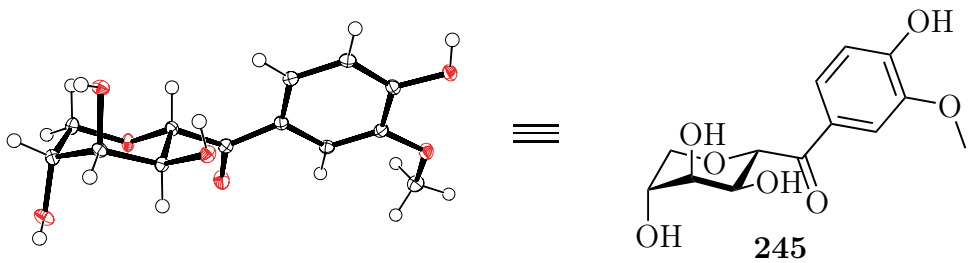
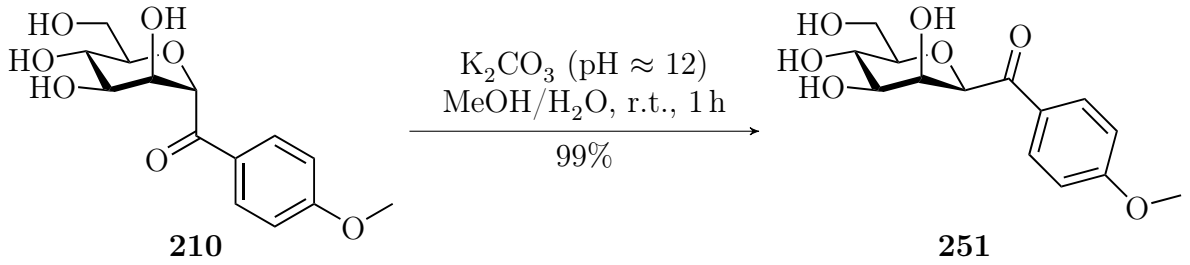


Figure 40: SCXRD structure of *C*-acyl D-lyxoside **245**.[5]

5.2.6 Synthesis of β-*C*-acyl mannosides

Due to the anomeric effect[133] and steric repulsion, the selective synthesis of β-D-mannosides is difficult to achieve. However, the anomeric effect does not apply to *C*-glycosides.[134] *C*-acyl α-D-mannopyranosides could be isomerized into their thermodynamically favored *C*-acyl β-D-mannopyranosides under basic conditions, due to the acidity of the anomeric proton caused by the carbonyl. Isomerization of **210** was achieved in quantitative yield after 1 h by using K_2CO_3 as base. (Scheme 55).[5]



Scheme 55: Isomerization of **210** under basic conditions.[5]

In the ^{1}H-NMR spectrum of **251** all signals resonate downfield of 3 ppm due to all protons being either bound to carbon atoms bearing an electron withdrawing oxygen substituent or aromatic carbon atoms (Figure 41).

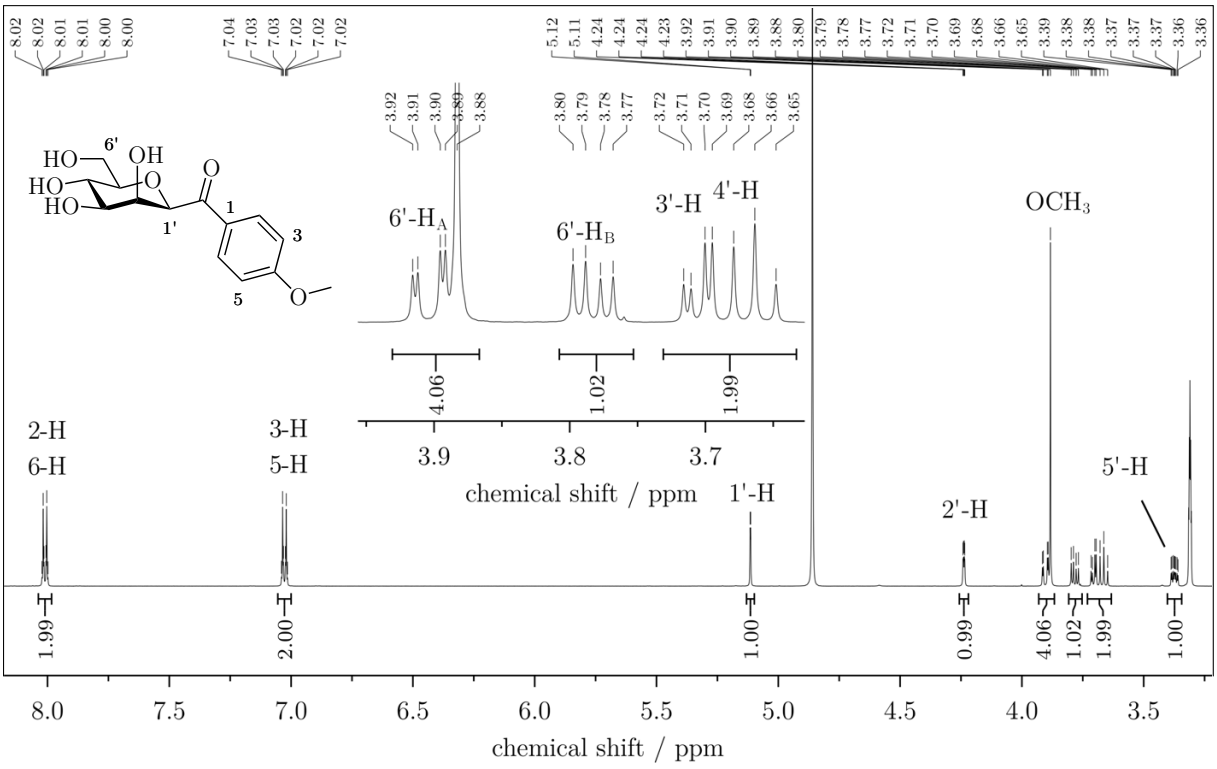


Figure 41: ^{1}H-NMR spectrum of *C*-acyl D-mannoside **251** at 600 MHz in methanol-d_4.[5]

5'-H resonates at 3.37 ppm as doublet of doublet of doublet coupling to 4'-H with a coupling constant of 9.4 Hz and coupling to the two protons at C-6' with coupling constants of 5.6 and 2.3 Hz. 4'-H resonates as pseudotriplet at 3.66 ppm coupling with the vicinal protons with a coupling constant of 9.4 Hz due to ax./ax. coupling. The doublet of doublet at 3.71 ppm with coupling constants of 9.4 Hz (ax./ax. coupling with 4'-H) and 3.2 Hz (ax./eq. coupling with 2'-H) was assigned to 3'-H. At 3.78 ppm 6-H_A resonates as doublet of doublet with a geminal coupling constant of 12.6 Hz and a vicinal coupling constant of 5.6 Hz. The three protons of the methoxy group resonate as a singlet at 3.88 ppm. At 3.90 ppm 6-H_B resonates as doublet of doublet with a geminal coupling constant of 12.2 Hz and a vicinal coupling constant of 2.3 Hz. 2'-H resonates as a doublet of doublet at 4.24 ppm with coupling constants of 3.2 Hz (eq./ax. coupling with 3'-H) and 1.3 Hz (eq./ax. coupling with 1'-H). The anomeric proton 1'-H resonates at 5.11 ppm with a coupling constant of 1.3 Hz (Figure 41). The observed coupling constants once more confirm the manno-type configuration of the product, but not the anomeric configuration. At 7.03 ppm and 8.02 ppm the four aromatic protons resonate as two multipletts with an integral of 2 H. Since the anomeric configuration cannot be assigned by the coupling constant, a NOESY spectrum of **251** was acquired. The obseverd cross-relaxations in the NOESY between 1'-H and the axial protons 3'-H and 5-H', which were not present in the α-configured isomer **210**, confirmed that the product is β-configured (Figure 42).

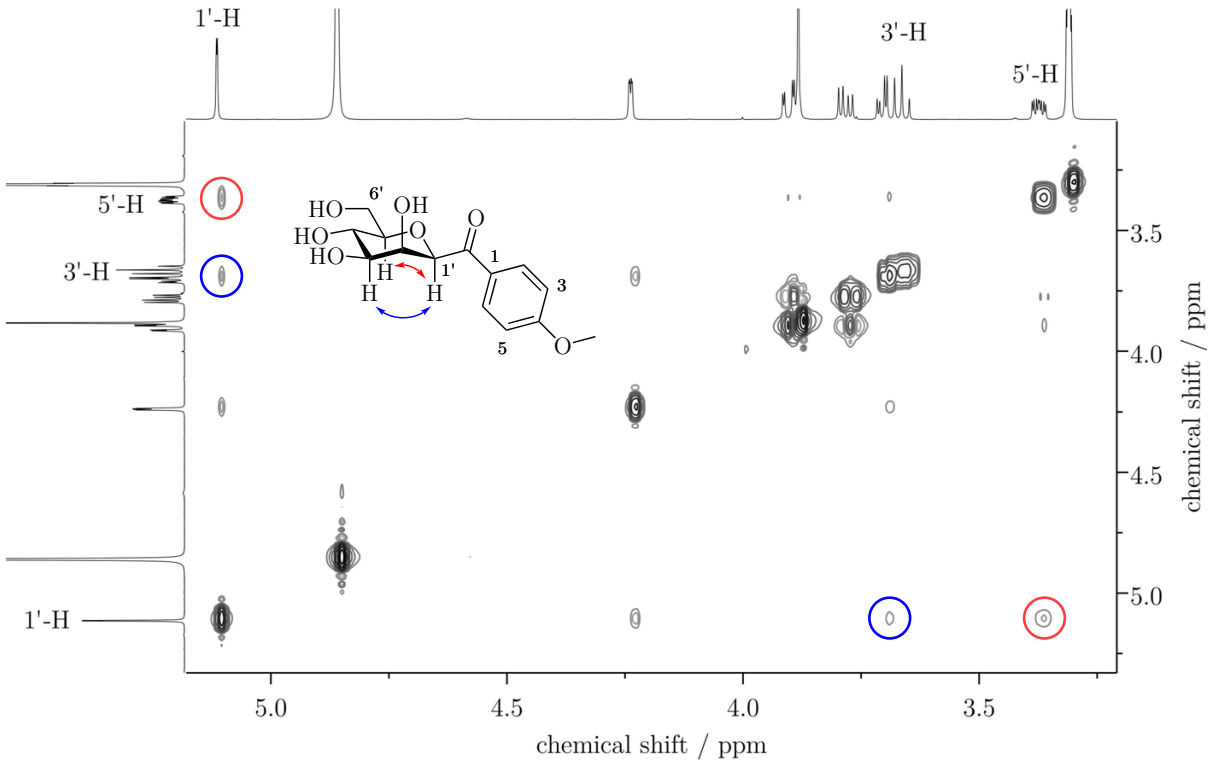


Figure 42: NOESY spectrum of **251** in methanol-d_4.[5]

The ^{13}C-NMR of **251** shows a peak at 56.1 ppm, corresponding to the methoxy group. C-6' resonates at 62.9 ppm. The signals at 68.2 (C-4'), 72.6 (C-3'), 76.0 (C-2'), 81.8 (C-1') and 81.9 ppm (C-5') were all assigned to the D-mannosyl-ring. The four aromatic carbon atoms C-2, C-3, C-5 and C-6 resonate as 2 peaks at 114.9 and 132.2 ppm. C-1 which is next to the carbonyl resonates at 129.1 ppm, while the aromatic carbon atom C-4 to which the methoxy group is bound resonates further downfield due to the inductive effect of the oxygen atom at 165.6 ppm . The peak at 197.0 ppm and the band at 1664 cm^{-1} in the infrared spectrum confirm presence of the carbonyl motif as the chemical shift of the ^{13}C-NMR signal and the wavenumber of the IR signal are both in typical ranges which are usually only occupied by carbonyl signals (Figure 43).

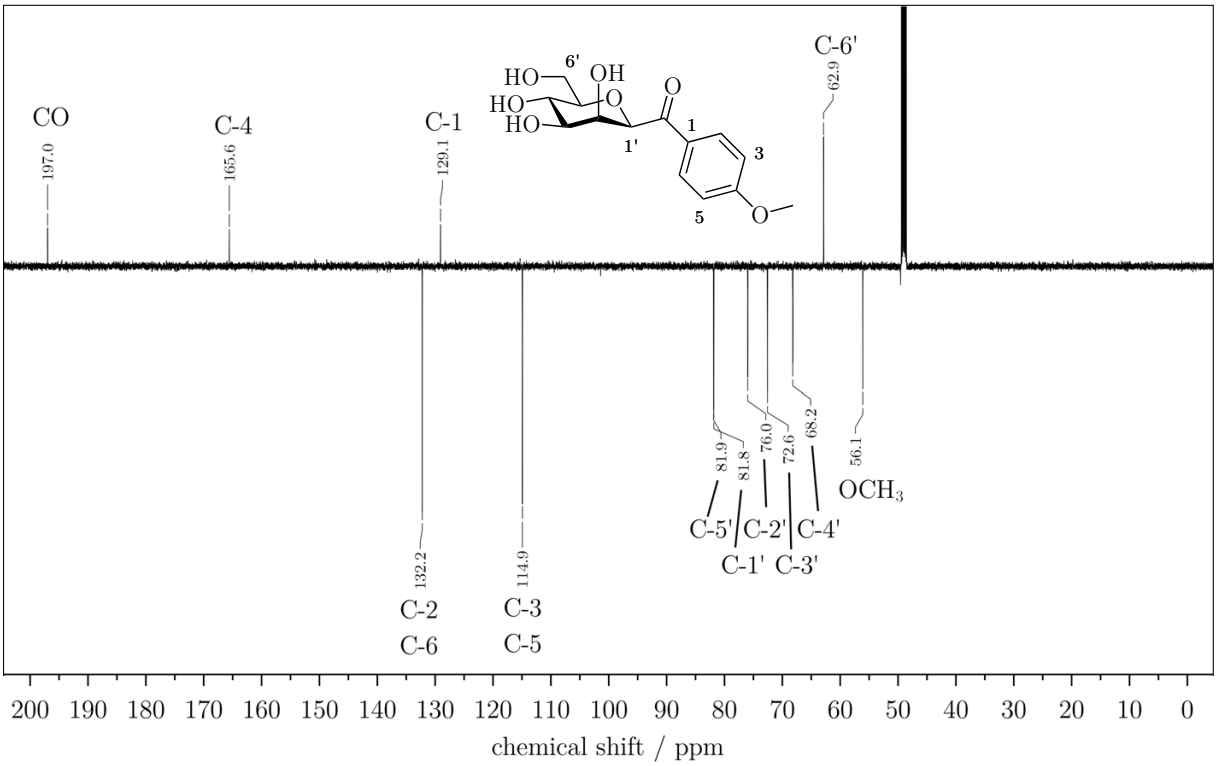


Figure 43: DEPTQ-NMR spectrum of **251** at 151 MHz in methanol-d_4.[5]

The molecular formula $C_{14}H_{18}O_7$ was confirmed by a HRMS peak at m/z = 321.0943 which corresponds to the calculated mass of 321.0945 for the molecular formula in association with a sodium cation. The structure of the β-configured *C*-acyl D-mannoside **251** was also confirmed by SCXRD (Figure 44). The structure shows the usual $^4C_1$-conformation in conjunction with the β-configuration of the product. The dihedral angle of 45 ° between the anomeric proton and 2'-H is in agreement with the small coupling constant of 1.3 Hz for the coupling between 1-H and 2-H, as coupling constants reach their minimum at exactly this angle according to the Karplus-equation.[5]

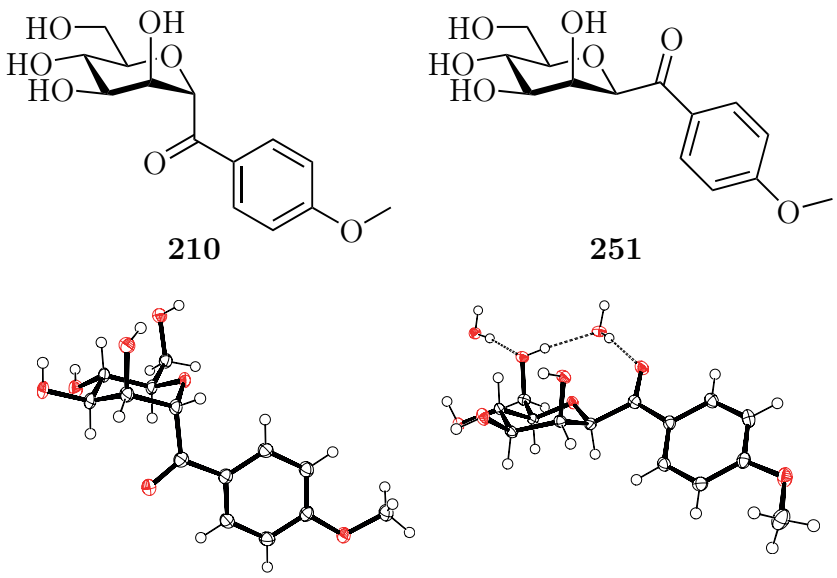


Figure 44: SCXRD-structures of *C*-acyl mannosides **210** and **251**.[5]

These obervations are also congruent in comparison with its α-isomer which showed a larger dihedral angle of 66-68 ° in conjuction with a larger coupling constant of 2.2 Hz.[5]

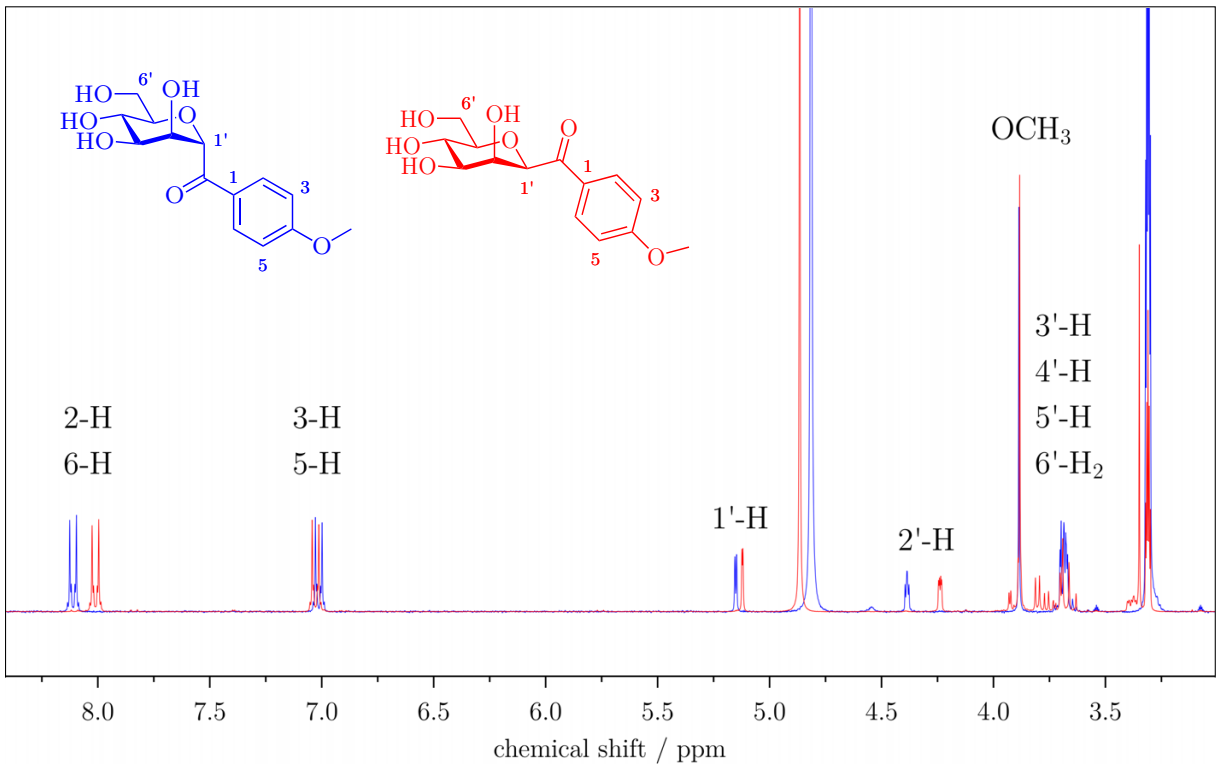


Figure 45: ^{1}H-NMR spectra of *C*-acyl D-mannosides at 300 MHz in methanol-d_4.[5]

The ^{1}H-NMR spectra of the α-*C*-acyl mannoside **210** and its β-isomer are **251** similar, but not indistinguishable (Figure 45). The aromatic signals resonate at very similar shifts.

The signals of 1'-H also resonates at almost identical shifts of 5.12 and 5.15 ppm and differ in their coupling constants by only 0.9 Hz. The differences for the signal of 2'-H were more pronounced as they resonate 0.15 ppm apart. Additionally 2'-H of the α-isomer resonates as pseudotriplett whereas the β-isomer resonates as doublett of doublett. While the signals of 3'-H, 4'-H and 6'-H_2 of the α-isomer resonate as multiplett from 3.62-3.73 ppm when measured in methanol-d_4, these signals were distributed from 3.65 to 3.90 ppm and also resolved in case of the β-isomer. The signals of 5'-H barely differ in these spectra and the signal of the methoxy group was not affected at all by the change in configuration. For these reasons, NOESY data is always acquired for identification and differentiation of isomers. A noticeable difference is also visible in ESI-MS. The anomeric bonds of α-isomers show a higher tendency to fragment during mass spectrometry, which is indicated by detection of benzylidyneoxonium-ions.

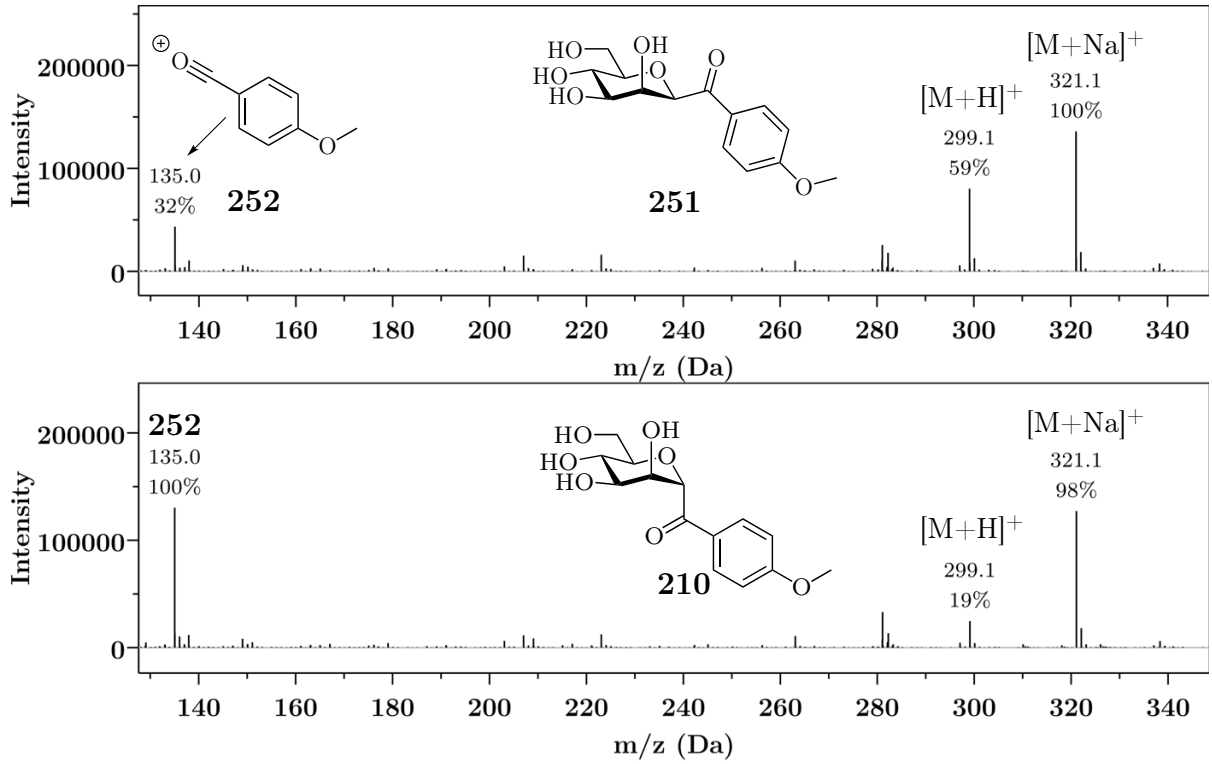


Figure 46: ESI mass spectra of α-*C*-acyl mannoside **210** and β-*C*-acyl mannoside **251**.[5]

As seen in Figure 46, the mass spectrum of α-*C*-acyl mannoside **210** shows a much higher relative abundance of the (4-methoxybenzylidyne)oxonium-ion **252** than the mass spectrum of β-*C*-acyl mannoside **251**. The higher tendency of α-anomeric bonds to break, was also observed in the in the synthesis of these compounds. Synthesized α-*C*-acyl glycosides decomposed if the reaction mixture after deprotection with PIFA was not quenched by L-ascorbic acid, while no such effect was observed for β-*C*-acyl glycosides.

Isomerization of all other synthesized α-configured *C*-acyl D-mannopyranosides was also possible in excellent yields. Derivatives bearing a phenolic hydroxyl group in *p*-position to the carbonyl reacted much slower. These derivatives had to be isomerized with the stronger base KOH under extended reaction times to yield β-configured *C*-acyl-mannopyranosides **258** and **260** (Figure 47).[5]

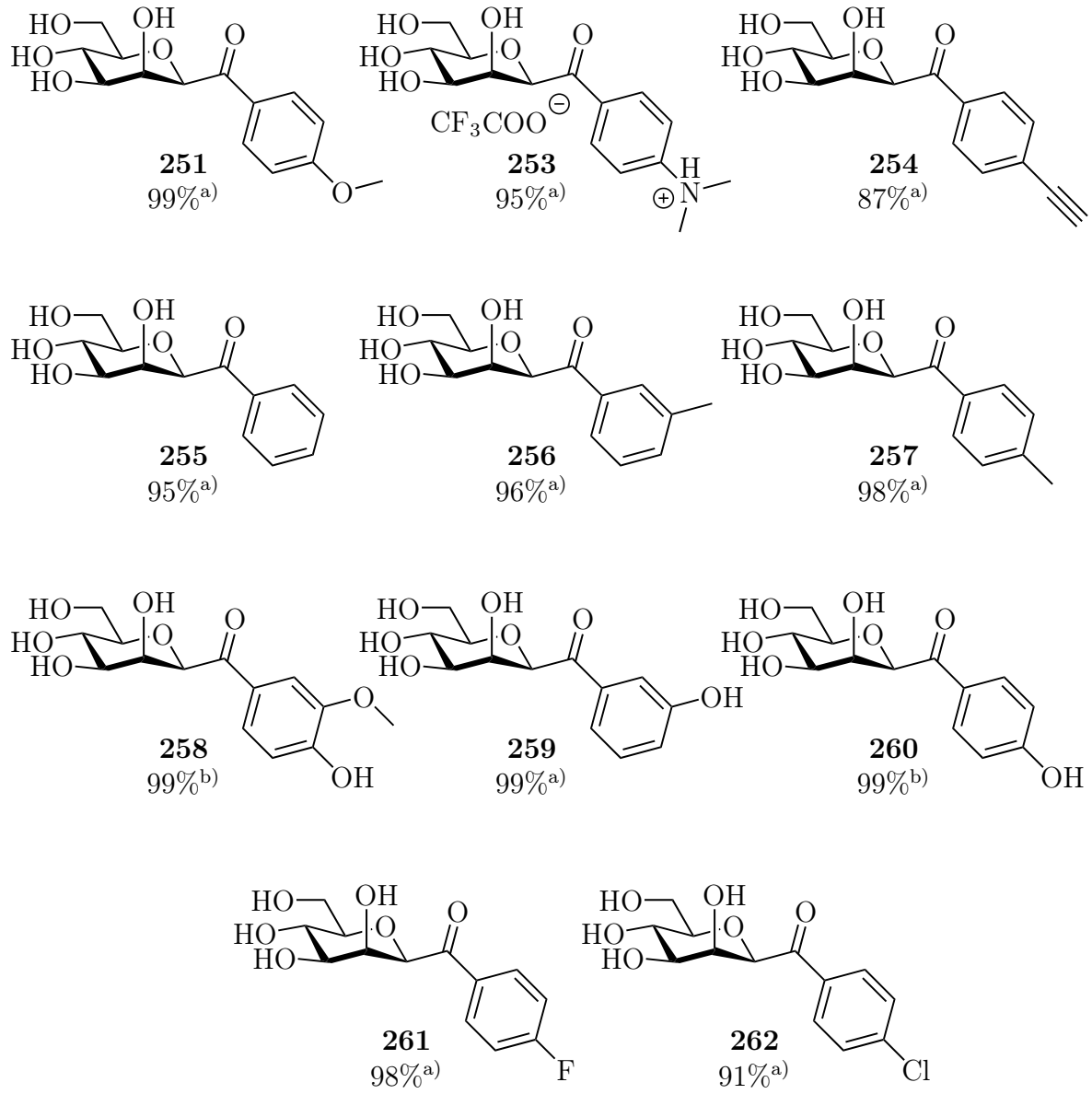


Figure 47: Reaction scope for the isomerization of α-configured *C*-acyl D-mannopyranosides into their β-configured isomers. Reagents and conditions: a) *C*-acyl α-mannopyranoside, K_2CO_3 (pH = 12) in H_2O/MeOH (1:1), r.t., 1 h; b) *C*-acyl α-mannopyranoside, KOH (pH = 13) in H_2O, r.t., 24 h.[5]

The isomerization of α-L-rhamnosyl derivatives appeared to be slower in comparision to D-mannosyl derivatives. Additionally, these reactions did not reach full conversion as the reaction seemed to reach an equilibrium between α- and β-isomer in most cases (Figure 48).[5]

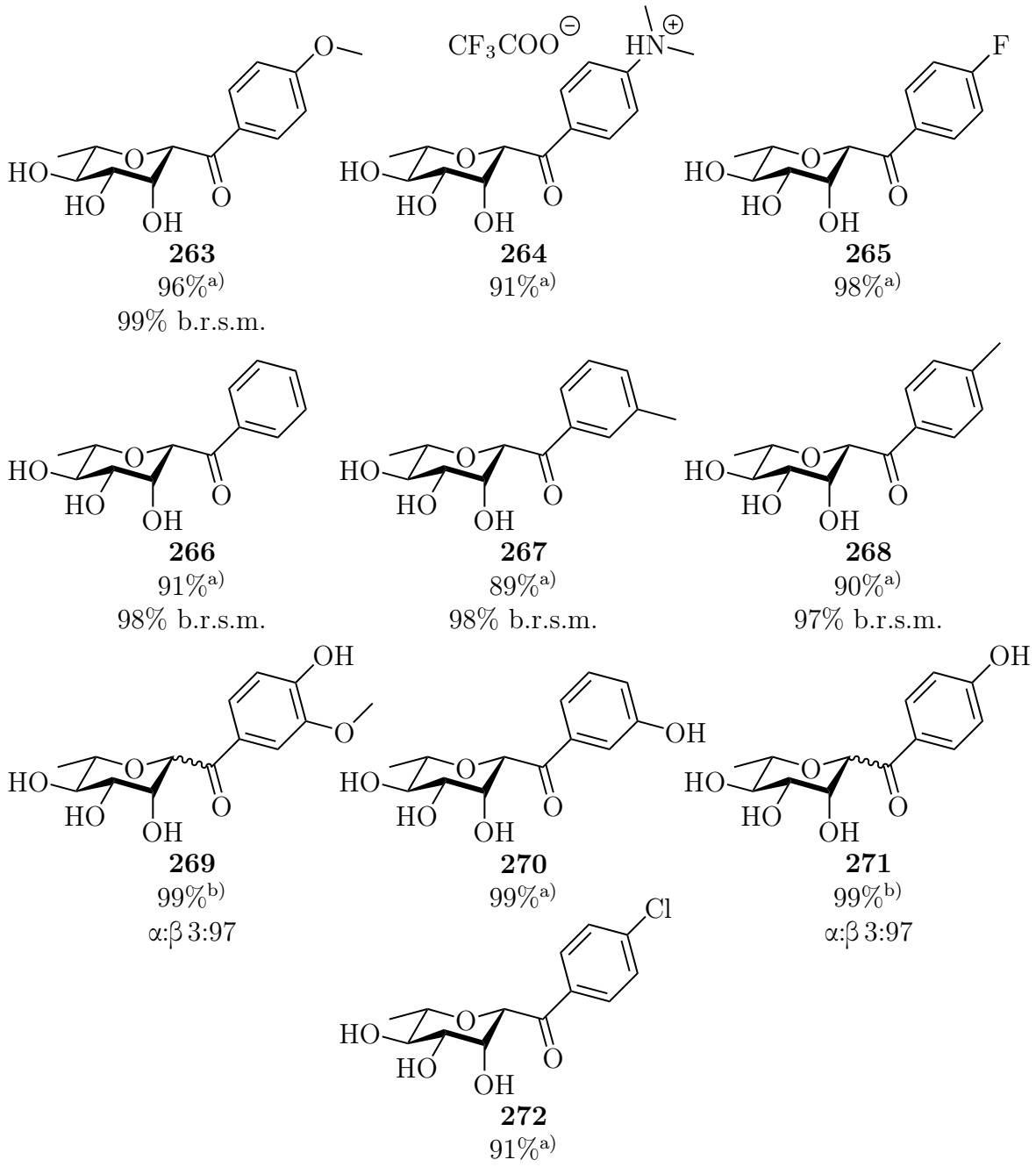


Figure 48: Reaction scope for the isomerization of α-configured *C*-acyl L-rhamnopyranosides into their β-configured isomers. Reagents and conditions: a) *C*-acyl α-rhamnopyranoside, K_2CO_3 (pH = 12) in H_2O/MeOH (1:1), r.t., 1 h; b) *C*-acyl α-rhamnopyranoside, KOH (pH = 13) in H_2O, r.t., 24 h.[5]

The isomerization of α-lyxosyl derivatives was much slower when compared to *C*-acyl α-D-manno- and L-rhamnosides. The yields of the isomerization also slightly decreased as more starting material remained at the equilibrium point. The *C*-acyl β-D-lyxosides preferred the more common $^4C_1$-conformation, unlike their α-configured counterparts (Figure 49).[5]

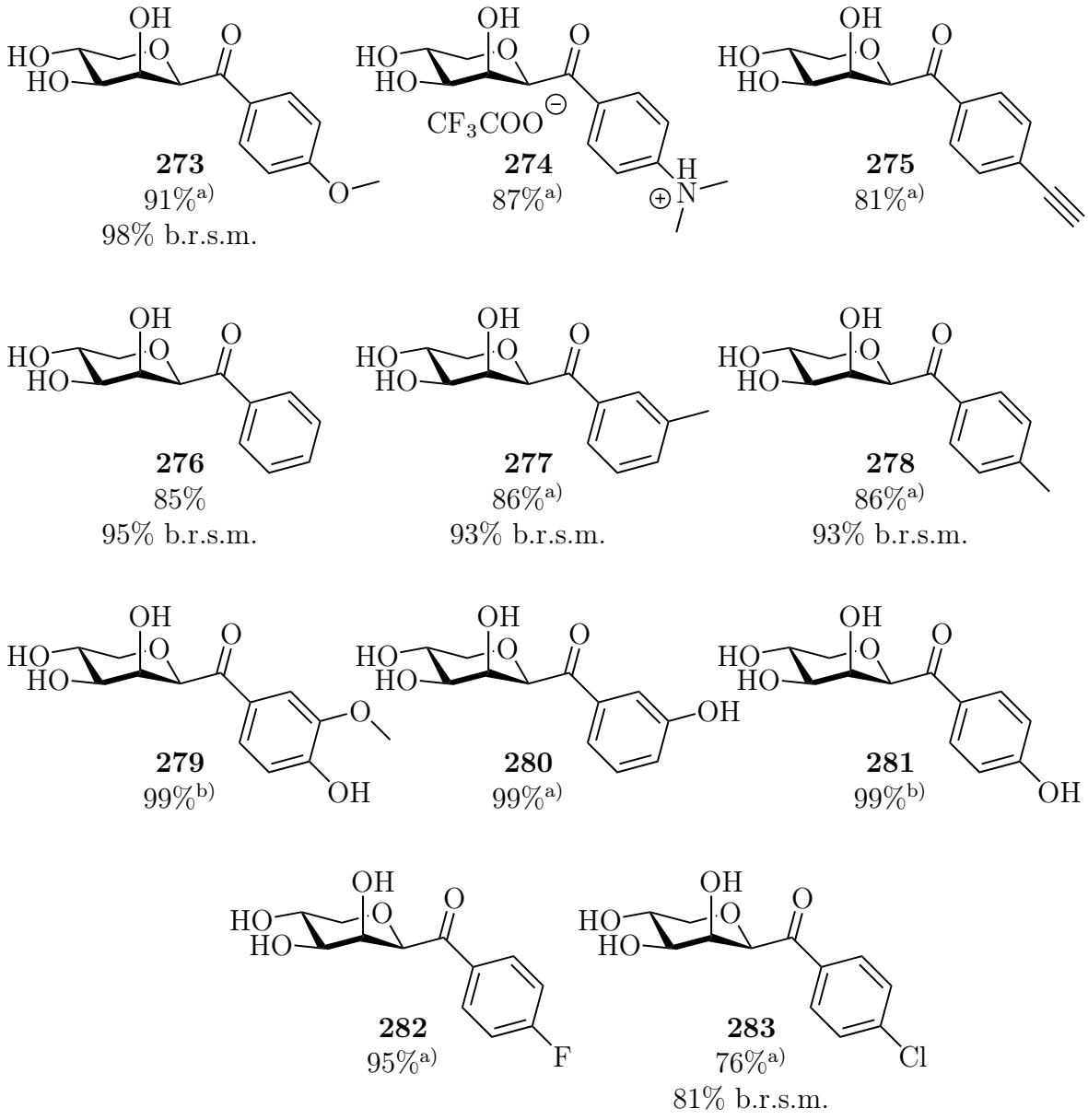
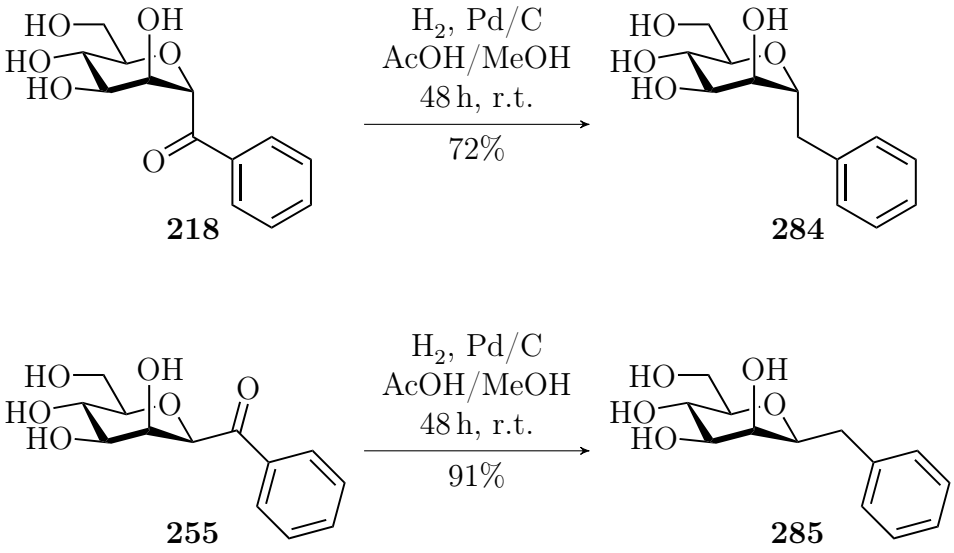


Figure 49: Reaction scope for the isomerization of α-configured *C*-acyl D-lyxopyranosides into their β-configured isomers. Reagents and conditions: a) *C*-acyl α-lyxopyranoside, K_2CO_3 (pH = 12) in H_2O/MeOH (1:1), r.t., 2 h; b) *C*-acyl α-lyxopyranoside, KOH (pH = 13) in H_2O, r.t., 24 h.[5]

5.2.7 Benzylic deoxygenation of *C*-acyl D-mannosides

C-benzyl glycosidic compounds are also of interest in medicinal chemistry.[135] Thus deoxygenation of both anomers of the *C*-acyl D-mannopyranosides **218** and **255** was attempted (Scheme 56).[5]



Scheme 56: Benzylic deoxygenation of *C*-acyl Mannosides.[5]

Under slightly acidic hydrogenation conditions, these *C*-acyl glycosides yielded the respective *C*-benzyl D-mannopyranosides **284** and **284** in high yields while retaining the anomeric configuration of their starting materials. The addition of acid was mandatory for any reaction to occur. The long reaction times were necessary, as incomplete reduction of the carbonyl to the corresponding alcohol was observed otherwise.[5]

In conclusion, using trace amounts of CuI in the Corey-Seebach step allowed the synthesis of α-configured D-manno, L-rhamno and D-lyxopyranosides. The reaction was usually α-selective and except for reactions involving electron deficient dithianes and D-lyxose. This method allowed the first synthesis of unprotected *C*-acyl manno-type pyranosides with yields of 13-71%. These α-configured *C*-acyl pyranosides were all isomerized under basic conditions giving their β-isomers in yields of 76-99%. In general the reaction was limited to aryl-dithianes.[5]

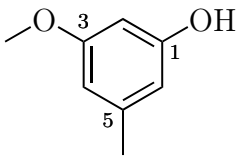
6 Experimental

6.1 General information

All reactions were run at anhydrous conditions under nitrogen atmosphere unless otherwise stated. Reactions carried out at 0 °C employed an ice bath and at -95 °C a liquid nitrogen/acetone bath. Other sub-zero temperatures were produced using a Julabo FT402 cryostat. Reactions at 4 °C were carried out by placing the reaction flask and stirrer in a refrigerator. All commercially purchased chemicals were used without further purification, unless otherwise noted. THF and 2-MeTHF were dried by storing them under nitrogen atmosphere over 4 Å molecular sieves. The concentrations of *tert*-butyllithium solutions were determined by titration of menthol in THF with 1,10-phenantroline as indicator.[136] Infrared spectra were obtained from neat solids or liquids on a Shimadzu IRAffinity-1S using a Specac Quest ATR unit. Optical rotations were measured with a Krüss P8000 polarimeter using a quartz cell with 1 mL capacity and a 1 dm path length. Concentrations (c) of specific rotations are given in g/100 mL. Melting points were determined in open capillary tubes and are uncorrected. High resolution mass spectra were measured with an Agilent 6224 ESI-TOF. ^{1}H-NMR and ^{13}C-NMR spectra were recorded on a Bruker Fourier 300 MHz, Bruker AVANCE I 400 MHz, Bruker AVANCE I 500 MHz or a Bruker AVANCE III HD 600 MHz instrument at 298 K. As internal standards, the residual proton signals of deuterated solvents $\delta^{1}H/^{13}C$ (solvent) = 7.26/77.16 ppm ($CDCl_3$); 7.16/128.06 ppm (benzene-d_6); 2.50/39.52 ppm (DMSO-d_6); 3.31/49.00 ppm (methanol-d_4); (D_2O) 4.79 ppm were used and are tabulated as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet) and coupling constant(s), number of protons. Reactions were monitored by thin layer chromatography on silica-coated aluminium plates (Macherey-Nagel, DC silica gel Alugram® Xtra SIL G/UV254, layer thickness 0.2 mm). Low and non-fluorescent compounds were visualised with a Seebach staining (10.0 g $Ce(SO_4)_2 \cdot H_2O$, 25.0 g phosphomolybdic acid, 60.0 mL sulfuric acid and 940 mL water).[137] Flash chromatography was performed using silica 60 M (particle size 0.040-0.063 nm, 230-400 mesh, Macherey-Nagel) or Polygoprep 100-50 C18 (particle size 0.040-0.063 nm, Macherey-Nagel) at r.t. using a MPLC-System (Biotage Isolera Prime 3.0).

6.2 Syntheses of prenylated orcinols

6.2.1 3-Methoxy-5-methylphenol 8



8

A microwave vial equipped with a magnetic stir bar was charged with 1,3-dimethoxy-5-methylbenzene **132** (700 mg, 4.60 µmol, 1.00 equiv.) and flushed with argon. Then, 1,3-dimethyl-2-imidazolidinone (4.60 mL) and NaHMDS (c = 2.00 M in THF, 5.80 mL, 11.6 mmol, 2.52 equiv.) were added. The vial was capped, heated to 185 °C by microwave irradiation and stirred at this temperature for 12 h. After cooling to r.t. aqueous HCl (3 M, 10.0 mL) was added and the mixture extracted with diethyl ether (3 × 20.0 mL). The combined organic extracts were washed with aqueous HCl (1 M, 2 × 20.0 mL), dried over $MgSO_4$, filtered and the solvent was removed in vacuum. The residue was purified by column chromatography (SiO_2, PE/EtOAc 9:1 → PE/EtOAc 7:3) to yield 3-methoxy-5-methylphenol **8** (606 mg, 4.38 mmol, 95%) as colorless crystalline solid.

TLC: R_f= 0.21 (PE/EtOAc 9:1).

M.p.: 58 °C.

UV (MeCN) λ_{max} = 202, 274 nm.

IR (ATR): $\tilde{\nu}$= 3352, 3007, 2945, 2845, 1595, 1506, 1471, 1338, 1301, 1211, 1151, 1060, 869, 829, 684 cm^{-1}.

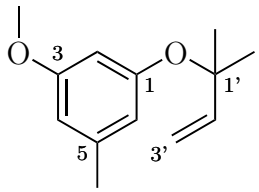
^{1}H-NMR (600 MHz, $CDCl_3$): δ (ppm) = 2.20 (s, 3 H, 5-CH_3), 3.69 (s, 3 H, 3-OCH_3), 4.70 (s, 1 H, 1-OH), 6.15 (t, J = 2.2 Hz, 1 H, 2-H), 6.18 (s, 1 H, 6-H), 6.25 (s, 1 H, 4-H).

^{13}C-NMR (151 MHz, $CDCl_3$): δ (ppm) = 21.7 (5-$\underline{C}H_3$), 55.4 (3-OCH_3), 98.7 (C-2), 107.5 (C-4), 108.7 (C-6), 140.7 (C-5), 156.6 (C-1), 160.9 (C-3).

MS (EI): m/z(%) = 107.1 (61) [M - OMe]$^+$, 138.1 (100) [M]$^+$.

$C_8H_{10}O_2$ (138.17).

6.2.2 1-Methoxy-3-methyl-5-((2-methylbut-3-en-2-yl)oxy)benzene 137



137

A solution of 3-methoxy-5-methylphenol **8** (1.00 g, 7.24 mmol, 1.00 equiv.) and *tert*-butyl-(2-methylbut-3-en-2-yl) carbonate (4.72 g, 25.3 mmol, 3.50 equiv.) in THF (50.0 mL) was cooled to 0 °C. Molecular sieves (4 Å, 5.00 g) and $Pd(PPh_3)_4$ (83.6 mg, 724 µmol, 1.00 mol%) were added and the mixture was stirred under nitrogen atmosphere at 4 °C for 16 h. The reaction mixture was filtered through a pad of celite and the solvent was removed in vacuum. The residue was purified by column chromatography (SiO2, PE → PE/EtOAc 4:1) to yield 1-methoxy-3-methyl-5-((2-methylbut-3-en-2-yl)oxy)benzene **137** (1.41 g, 6.84 mmol, 94%) as colorless liquid.

TLC: R_f = 0.73 (PE/EtOAc 9:1).

UV (MeCN) λ_{max} = 204, 276 nm.

IR (ATR): $\tilde{\nu}$ = 2980, 2933, 2837, 1591, 1465, 1413, 1323, 1253, 1195, 1124, 1064, 983, 831, 686 cm^{-1}.

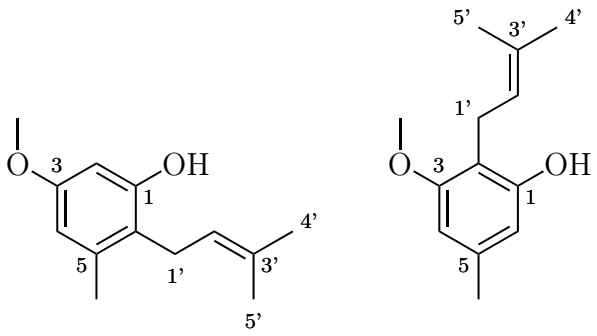
^{1}H-NMR (600 MHz, $CDCl_3$): δ (ppm) = 1.45 (s, 6 H, 2 × 1'-CH_3), 2.26 (s, 3 H, 5-CH_3), 3.74 (s, 3 H, 3-OCH_3), 5.13 (dd, J = 10.9, 0.8 Hz, 1 H, 3'-H_A), 5.18 (dd, J = 17.6, 0.8 Hz, 1 H, 3'-H_B), 6.14 (dd, J = 17.6, 10.9 Hz, 1 H, 2'-H), 6.37 (s, 1 H, 6-H), 6.39 (t, J = 2.1 Hz, 1 H, 2-H), 6.42 (s, 1 H, 4-H).

^{13}C-NMR (151 MHz, $CDCl_3$): δ (ppm) = 21.9 (5-CH_3), 27.2 (2 × 1'-$\underline{C}H_3$), 55.3 (3-O$\underline{C}H_3$), 79.5 (C-1'), 104.6 (C-2), 108.6 (C-6), 113.3 (C-3'), 114.8 (C-4), 139.5 (C-5), 144.8 (C-2'), 157.2 (C-1), 160.1 (C-3).

MS (EI): m/z(%) = 138.1 (100) [M - isoprene]$^+$, 151.1 (12) [M - isobutenyl]$^+$, 191.1 (5) [M - CH_3], 206.1 (8) [M]$^+$.

$C_{13}H_{18}O_2$ (206.29).

6.2.3 Claisen rearrangement of 137. Synthesis of 5-methoxy-3-methyl-2-(3-methylbut-2-en-1-yl)phenol 135 and 3-methoxy-5-methyl-2-(3-methylbut-2-en-1-yl)phenol 136.



135 **136**

A microwave vial was charged with 1-methoxy-3-methyl-5-((2-methylbut-3-en-2-yl)oxy)benzene **137** (3.60 g, 17.5 mmol, 1.00 equiv.), DMF (17.5 mL), and was then flushed with argon. The vial was sealed, heated to 185 °C by microwave irradiation and stirred at this temperature for 1 h. After cooling to r.t. aqueous HCl (1 m, 40.0 mL) was added and the mixture extracted with diethyl ether (3×20.0 mL). The combined organic extracts were dried over MgSO4, filtered and the solvent was removed in vacuum. The residue was purified by column chromatography (SiO_2, PE $\rightarrow$ PE/ Et_2O 7:3). 3-methoxy-5-methyl-2-(3-methylbut-2-en-1-yl)phenol **136** (1.08 g, 5.24 mmol, 30%) eluted first as slightly yellow liquid, followed by 5-methoxy-3-methyl-2-(3-methylbut-2-en-1-yl)phenol **135** (2.46 g, 11.9 mmol 68%) as colorless crystalline solid.

Analytical data for 5-methoxy-3-methyl-2-(3-methylbut-2-en-1-yl)phenol **135** :

TLC: R_f= 0.48 (PE/EtOAc 4:1).

M.p.: 44 °C

UV (MeCN) λ_{max} = 205, 271 nm.

IR (ATR): $\tilde{\nu}$= 3280, 2968, 2929, 2837, 1617, 1583, 1497, 1436, 1311, 1196, 1142, 1059, 1042, 839, 812 cm^{-1}.

^{1}H-NMR (600 MHz, $CDCl_3$): δ (ppm) = 1.73 (s, 3 H, 5'-H_3), 1.81 (s, 3 H, 4'-H_3), 2.27 (s, 3 H, 5-CH_3), 3.30 (d, J = 6.9 Hz, 2 H, 1'-H_2), 3.74 (s, 3 H 3-OCH_3), 5.11 (s, 1 H, 1-OH), 5.13–5.18 (m, 1 H, 2'-H), 6.28 (d, J = 2.5 Hz, 1 H, 2-H), 6.34 (d, J = 2.5 Hz, 1 H, 4-H).

^{13}C-NMR (151 MHz, $CDCl_3$): δ (ppm) = 18.0 (C-4'), 20.4 (5-$\underline{C}H_3$), 25.4 (C-1'), 25.9 (C-5'), 55.3 (3-O$\underline{C}H_3$), 99.7 (C-2), 108.6, (C-4) 117.9 (C-6), 122.3 (C-2'), 133.9 (C-3'), 138.3 (C-5), 155.4 (C-1), 158.5 (C-3).

MS (EI): m/z(%) = 151.1 (100) [M - isobutenyl]$^+$, 191.1 (32) [M - CH_3], 206.1 (35) [M]$^+$.

Analytical data for 3-methoxy-5-methyl-2-(3-methylbut-2-en-1-yl)phenol **136**:

TLC: R_f= 0.59 (PE/EtOAc 4:1).

UV (MeCN) λ_{max} = 203, 280 nm.

IR (ATR): $\tilde{\nu}$= 3448, 2914, 2856, 1616, 1591, 1462, 1415, 1334, 1213, 1163, 1084, 814 cm^{-1}.

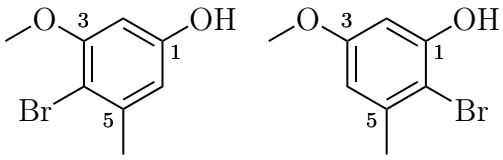
^{1}H-NMR (600 MHz, $CDCl_3$): δ (ppm) = 1.73 (s, 3 H, 5'-H_3), 1.81 (s, 3 H, 4'-H_3), 2.28 (s, 3 H, 5-CH_3), 3.37 (d, J = 7.1 Hz, 2 H, 1'-H_2), 3.80 (s, 3 H, 3-OCH_3), 5.17 (s, 1 H, 1-OH), 5.20–5.25 (m, 1 H, 2'-H), 6.31 (s, 1 H, 4-H), 6.31 (s, 1 H, 6-H).

^{13}C-NMR (151 MHz, $CDCl_3$): δ (ppm) = 17.9 (C-4'), 21.7 (5-$\underline{C}H_3$), 22.2 (C-1'), 25.9 (C-5'), 55.9 (3-O$\underline{C}H_3$), 104.4 (C-4), 109.6 (C-6), 112.3 (C-2), 122.5 (C-2'), 134.1 (C-3'), 137.4 (C-5), 155.3 (C-1), 157.9 (C-3).

MS (EI): m/z(%) = 151.1 (100) [M - isobutenyl]$^+$, 191.1 (22) [M - CH_3], 206.1 (42) [M]$^+$.

$C_{13}H_{18}O_2$ (206.29).

6.2.4 Synthesis of 4-bromo-3-methoxy-5-methylphenol 124 and 2-bromo-5-methoxy-3-methylphenol 133



124 **133**

A mixture of 3-methoxy-5-methylphenol **8** (500 mg, 3.62 mmol, 1.00 equiv.) and LiBr (629 mg, 7.24 mmol, 2.00 equiv.) in acetonitrile (15.0 mL) was cooled to 0 °C, tetrabutylammonium peroxodisulfate (4.90 g, 7.24 mmol, 2.00 equiv.) was added, the mixture was warmed to r.t. and stirred for 16 h. Then, aqueous HCl (3 M, 20.0 mL) was added and the mixture extracted with diethyl ether (3 × 20.0 mL). The combined organic extracts were washed with aqueous HCl (3 M, 2 × 20.0 mL), dried over $MgSO_4$,

filtered and the solvent was removed in vacuum. The residue was purified by column chromatography (SiO_2, PE → PE/EtOAc 2:1). 2-bromo-5-methoxy-3-methylphenol **133** (181 mg, 838 µmol, 23%) eluted first as colorless crystalline solid, followed by the starting material **8** (110 mg, 796 µmol, 22%). 4-bromo-3-methoxy-5-methylphenol **124** (355 mg, 1.64 mmol 45%) eluted last as colorless crystalline solid.

Analytical data for 2-bromo-5-methoxy-3-methylphenol **133**:

TLC: R_f = 0.33 (PE/EtOAc 9:1).

M.p.: 73 °C.

UV (MeCN) λ_{max} = 202, 281 nm.

IR (ATR): $\tilde{\nu}$= 3329, 2933, 2843, 1579, 1481, 1417, 1344, 1303, 1253, 1193, 1159, 1020, 977, 943, 837 cm^{-1}.

^{1}H-NMR (600 MHz, $CDCl_3$): δ (ppm) = 2.36 (s, 3 H, 5-CH_3), 3.76 (s, 3 H, 3-OCH_3), 5.59 (s, 1 H, 1-OH), 6.42 (d, J = 2.9 Hz, 1 H, 4-H), 6.46 (d, J = 2.9 Hz, 1 H, 2-H).

^{13}C-NMR (151 MHz, $CDCl_3$): δ (ppm) = 23.4 (5-$\underline{C}H_3$), 55.6 (3-O$\underline{C}H_3$), 98.9 (C-2), 104.1 (C-6), 109.3 (C-4), 139.0 (C-5), 153.1 (C-1), 159.7 (C-3).

MS (EI): m/z(%) = 216.0 (100) $[M]^+$.

Analytical data for 4-bromo-3-methoxy-5-methylphenol **124**:

TLC: R_f = 0.12 (PE/EtOAc 9:1).

M.p.: 118 °C.

UV (MeCN) λ_{max} = 202, 281 nm.

IR (ATR): $\tilde{\nu}$= 3329, 2978, 2839, 1604, 1585, 1473, 1413, 1330, 1184, 1155, 1087, 1014, 989, 929, 831 cm^{-1}.

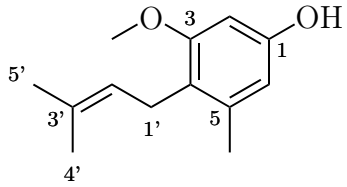
^{1}H-NMR (600 MHz, $CDCl_3$): δ (ppm) = 2.35 (s, 3 H, 5-CH_3), 3.85 (s, 3 H, 3-OCH_3), 4.74 (s, 1 H, 1-OH), 6.31 (d, J = 2.7 Hz, 1 H, 2-H), 6.36 (d, J = 2.7 Hz, 1 H, 6-H).

^{13}C-NMR (151 MHz, $CDCl_3$): δ (ppm) = 23.3 (5-$\underline{C}H_3$), 56.3 (3-O$\underline{C}H_3$), 97.7 (C-2), 105.0 (C-4), 109.6 (C-6), 140.1 (C-5), 155.2 (C-1), 156.8 (C-3).

MS (EI): m/z(%) = 216.0 (100) $[M]^+$.

$C_8H_9BrO_2$ (217.06).

6.2.5 3-Methoxy-5-methyl-4-(3-methylbut-2-en-1-yl)phenol 125



125

Under nitrogen atmosphere 4-bromo-3-methoxy-5-methylphenol **124** (420 mg, 1.94 mmol, 1.00 equiv.), PdXPhos G3 (32.8 mg, 38.7 mmol, 2.00 mol%) and XPhos (18.4 mg, 38.7 mmol, 2.00 mol%) were dissolved in anhydrous THF (770 µL) at r.t.. Then, a solution of prenylzinc bromide (c = 0.9 M in THF,[138] 5.00 mL, 4.50 mmol, 2.33 equiv.) was added and the mixture stirred for 16 h at r.t.. Afterwards, aqueous HCl (1 M, 20.0 mL) was added. The mixture was extracted with diethyl ether (3 × 20.0 mL), dried over $MgSO_4$, filtered and the solvent was removed in vacuum. The residue was purified by column chromatography (SiO_2, PE → PE/EtOAc 3:1) to yield 3-methoxy-5-methyl-4-(3-methylbut-2-en-1-yl)phenol **125** (386 mg, 1.87 mmol, 97%) as colorless oil, which slowly crystallized.

TLC: R_f = 0.42 (PE/EtOAc 4:1).

M.p.: 46 °C.

UV (MeCN) λ_{max} = 203, 279 nm.

IR (ATR): $\tilde{\nu}$ = 3350, 2964, 2926, 2854, 1600, 1437, 1305, 1190, 1163, 1139, 1085, 1014, 989, 949, 837 cm^{-1}.

^{1}H-NMR (600 MHz, $CDCl_3$): δ (ppm) = 1.67 (s, 3 H, 5'-H_3), 1.76 (s, 3 H, 4'-H_3), 2.22 (s, 3 H, 5-CH_3), 3.26 (d, J = 6.8 Hz, 2 H, 1'-H_2), 3.77 (s, 3 H, 3-OCH_3), 4.72 (s, 1 H, 1-OH), 5.00–5.09 (m, 1 H, 2'-H), 6.25 (d, J = 2.4 Hz, 1 H, 6-H), 6.28 (d, J = 2.4 Hz, 1 H, 2-H).

^{13}C-NMR (151 MHz, $CDCl_3$): δ (ppm) = 17.9 (C-4'), 19.8 (5-CH_3), 24.9 (C-1'), 25.9 (C-5'), 55.7 (3-OCH_3), 96.8 (C-2), 109.0 (C-6), 121.1 (C-4), 123.1 (C-2'), 131.0 (C-3'), 138.5 (C-5), 154.1 (C-1), 158.5 (C-3).

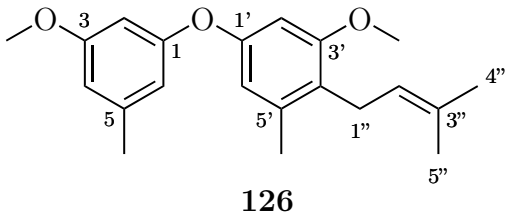
MS (ESI): m/z(%) = 151.1 (100) [M - isobutenyl]$^+$, 207.1 (24) [M + H]$^+$.

calcd.: 207.1380 [M + H]$^+$,
found: 207.1376 (ESI-HRMS).

$C_{13}H_{18}O_2$ (206.29).

6.3 Diaryl ether coupling

6.3.1 Synthesis of the methylated proposed structure of verticilatin 126



126

Under nitrogen atmosphere 3-methoxy-5-methyl-4-(3-methylbut-2-en-1-yl)phenol **125** (500 mg, 2.42 mmol, 1.00 equiv.), $Pd_2(dba)_3$ (88.8 mg, 97.0 µmol, 4.00 mol%) and *t*BuXPhos (165 mg, 388 µmol, 16.0 mol%) were dissolved in anhydrous dioxane (12.0 mL) at r.t.. Then, finely ground $K_3PO_4 \cdot H_2O$ (1.67 g, 7.27 mmol, 3.00 equiv.) and 1-bromo-3-methoxy-5-methylbenzene **128** (585 mg, 2.91 mmol, 1.20 equiv.) were added, the vessel was sealed and the mixture stirred at 100 °C for 20 h. Then, water (20.0 mL) was added and the mixture extracted with diethyl ether (3×20.0 mL), dried over $MgSO_4$, filtered and the solvent was removed in vacuum. The residue was purified by column chromatography (SiO_2, PE $\rightarrow$ PE/MTBE 4:1) to yield diaryl ether **126** (698 mg, 2.14 mmol, 88%) as colorless oil which slowly crystallized.

TLC: R_f= 0.47 (PE/EtOAc 9:1).

M.p.: 40 °C.

UV (MeCN) λ_{max} = 203, 279 nm.

IR (ATR): $\tilde{\nu}$= 3003, 2968, 2916, 1581, 1454, 1327, 1290, 1197, 1151, 1085, 829, 684 cm^{-1}.

^{1}H-NMR (600 MHz, $CDCl_3$): δ (ppm) = 1.69 (s, 3 H, 4"-H_3), 1.77 (s, 3 H, 5"-H_3), 2.24 (s, 3 H, 5'-CH_3), 2.29 (s, 3 H, 5-CH_3), 3.31 (d, J = 6.8 Hz, 2 H, 1"-H_2), 3.75 (s, 3 H, 3'-OCH_3), 3.76 (s, 3 H, 3-OCH_3), 5.05–5.10 (m, 1 H, 2"-H), 6.37–6.39 (m, 1 H, 2-H), 6.41–6.42 (m, 2 H, 6-H, 6'-H), 6.45–6.46 (m, 2 H, 4-H, 2'-H).

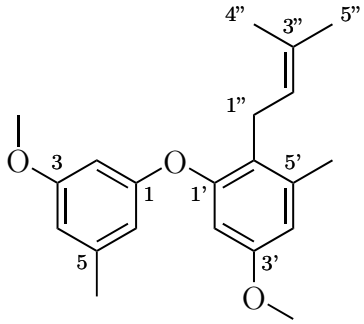
^{13}C-NMR (151 MHz, $CDCl_3$): δ (ppm) = 18.0 (C-5"), 19.9 (5'-CH_3), 21.8 (5-CH_3), 25.1 (C-1"), 25.9 (C-4"), 55.5 (3'-$\underline{O}CH_3$), 55.8 (3-$O\underline{C}H_3$), 100.6 (C-2'), 101.7 (C-2), 109.5 (C-4), 111.6 (C-6), 113.0 (C-6'), 122.8 (C-2"), 123.9 (C-4'), 131.3 (C-3"), 138.6 (C-5'), 140.6 (C-5), 155.3 (C-1'), 158.4 (C-3'), 158.8 (C-1), 160.8 (C-3).

MS (ESI): m/z(%) = 271.1 (16) [M - isobutenyl]$^+$, 327.2 (100) [M + H]$^+$.

calcd.: 327.1955 $[M + H]^+$,
found: 327.1959 (ESI-HRMS).

$C_{21}H_{26}O_3$ (326.44).

6.3.2 Synthesis of dimethylated diorcinol D 140



140

Under nitrogen atmosphere 5-methoxy-3-methyl-2-(3-methylbut-2-en-1-yl)phenol **135** (500 mg, 2.42 mmol, 1.00 equiv.), $Pd_2(dba)_3$ (88.8 mg, 97.0 µmol, 4.00 mol%) and *t*BuXPhos (165 mg, 388 µmol, 16.0 mol%) were dissolved in anhydrous dioxane (12.0 mL) at r.t.. Then, finely ground $K_3PO_4 \cdot H_2O$ (1.67 g, 7.27 mmol, 3.00 equiv.) and 1-bromo-3-methoxy-5-methylbenzene **128** (585 mg, 2.91 mmol, 1.20 equiv.) were added, the vessel was sealed and the mixture stirred at 100 °C for 20 h. Afterwards, water (20.0 mL) was added and the mixture extracted with diethyl ether (3×20.0 mL), dried over $MgSO_4$, filtered and the solvent was removed in vacuum. The residue was purified by column chromatography (SiO_2, PE $\rightarrow$ PE/MTBE 4:1) to yield diaryl ether **140** (662 mg, 2.02 mmol, 84%) as colorless oil.

TLC: $R_f = 0.47$ (PE/EtOAc 9:1).

UV (MeCN) $\lambda_{max} = 203, 278$ nm.

IR (ATR): $\tilde{\nu} =$ 2916, 2835, 1606, 1575, 1465, 1421, 1321, 1294, 1234, 1193, 1141, 1060, 831 cm^{-1}.

^{1}H-NMR (600 MHz, $CDCl_3$): δ (ppm) = 1.64 (s, 3 H, 4”-H_3), 1.66 (s, 3 H, 5”-H_3), 2.27 (s, 3 H, 5-CH_3), 2.32 (s, 3 H, 5’-CH_3), 3.26 (d, $J = 6.9$ Hz, 2 H, 1”-H_2), 3.71 (s, 3 H, 3’-OCH_3), 3.75 (s, 3 H, 3-OCH_3), 5.04–5.09 (m, 1 H, 2”-H), 6.30 (t, $J = 2.2$ Hz, 1 H, 2-H), 6.32 (s, 1 H, 6-H), 6.36 (d, $J = 2.6$ Hz, 1 H, 2’-H), 6.42 (s, 1 H, 4-H), 6.55 (d, $J = 2.6$ Hz, 1 H, 4’-H).

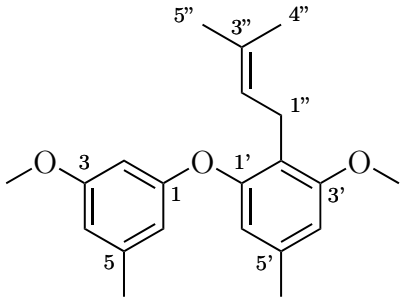
^{13}C-NMR (151 MHz, $CDCl_3$): δ (ppm) = 17.9 (C-5"), 20.1 (5'-$\underline{C}H_3$), 21.8 (5-$\underline{C}H_3$), 25.4 (C-1"), 25.8 (C-4"), 55.4 (3-O$\underline{C}H_3$), 55.4 (3'-O$\underline{C}H_3$), 100.9 (C-2), 103.7 (C-2'), 109.0 (C-4), 110.7 (C-6), 112.1 (C-4'), 122.7 (C-2"), 124.5 (C-6'), 131.3 (C-3"), 139.3 (C-5'), 140.5 (C-5), 154.8 (C-1'), 158.3 (C-3'), 159.3 (C-1), 160.8 (C-3).

MS (ESI): m/z(%) = 271.1 (100) [M - isobutenyl]$^+$, 327.2 (32) [M + H]$^+$.

calcd.: 327.1955 [M + H]$^+$,
found: 327.1955 (ESI-HRMS).

$C_{21}H_{26}O_3$ (326.44).

6.3.3 Synthesis of dimethylated diorcinol I 141



141

Under nitrogen atmosphere 3-methoxy-5-methyl-2-(3-methylbut-2-en-1-yl)phenol **136** (500 mg, 2.42 mmol, 1.00 equiv.), $Pd_2(dba)_3$ (88.8 mg, 97.0 µmol, 4.00 mol%) and *t*BuXPhos (165 mg, 388 µmol, 16.0 mol%) were dissolved in anhydrous dioxane (12.0 mL) at r.t.. Then, finely ground $K_3PO_4 \cdot H_2O$ (1.67 g, 7.27 mmol, 3.00 equiv.) and 1-bromo-3-methoxy-5-methylbenzene **128** (585 mg, 2.91 mmol, 1.20 equiv.) were added, the vessel was sealed and the mixture stirred at 100 °C for 20 h. Afterwards, water (20.0 mL) was added and the mixture extracted with diethyl ether (3×20.0 mL), dried over $MgSO_4$, filtered and the solvent was removed in vacuum. The residue was purified by column chromatography (SiO_2, PE $\rightarrow$ PE/MTBE 4:1) to yield diaryl ether **141** (635 mg, 1.95 mmol, 80%) as colorless oil.

TLC: R_f= 0.48 (PE/EtOAc 9:1).

UV (MeCN) λ_{max} = 204, 278 nm.

IR (ATR): $\tilde{\nu}$= 2960, 2918, 2854, 1577, 1454, 1411, 1259, 1222, 1193, 1141, 1085, 1024, 827 cm^{-1}.

^{1}H-NMR (600 MHz, $CDCl_3$): δ (ppm) =1.62 (s, 3 H, 4”-H_3), 1.64 (s, 3 H, 5”-H_3), 2.27 (s, 3 H, 5’-CH_3), 2.27 (s, 3 H, 5-CH_3), 3.29 (d, J = 7.2 Hz, 2 H, 1”-H_2), 3.75 (s, 3 H, 3-OCH_3), 3.84 (s, 3 H, 3’-OCH_3), 5.16–5.24 (m, 1 H, 2”-H), 6.31 (t, J = 2.1 Hz, 1 H, 2-H), 6.31 (s, 1 H, 6-H), 6.38 (s, 1 H, 6’-H), 6.42 (s, 1 H, 4-H), 6.50 (s, 1 H, 4’-H).

^{13}C-NMR (151 MHz, $CDCl_3$): δ (ppm) = 17.8 (C-5”), 21.7 (5’-$\underline{C}H_3$), 21.8 (5-$\underline{C}H_3$), 22.8 (C-1”), 25.9 (C-4”), 55.4 (3-O$\underline{C}H_3$), 55.8 (3’-O$\underline{C}H_3$), 101.1 (C-2), 107.5 (C-4’), 108.9 (C-4), 110.9 (C-6), 113.3 (C-6’), 119.5 (C-2’), 122.8 (C-2”), 131.3 (C-3”), 137.1 (C-5’), 140.4 (C-5), 154.6 (C-1’), 158.5 (C-3’), 159.4 (C-1), 160.7 (C-3).

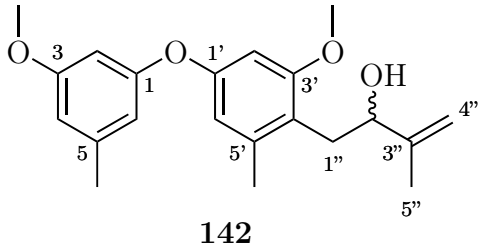
MS (ESI): m/z(%) = 271.1 (100) [M - isobutenyl]$^+$, 327.2 (17) [M + H]$^+$.

calcd.: 327.1955 [M + H]$^+$,
found: 327.1951 (ESI-HRMS).

$C_{21}H_{26}O_3$ (326.44).

6.4 Epoxidation and rearrangement of diaryl ethers

6.4.1 Synthesis of allylic alcohol 142



142

A solution of diaryl ether **126** (600 mg, 1.84 mmol, 1.00 equiv.) in DCM (28.0 mL) was cooled to 0 °C. Then, mCPBA (618 mg, 2.76 mmol, 1.50 equiv.) was added and the reaction mixture was warmed to r.t. and stirred for 1 h. Afterwards, the reaction mixture was cooled to 0 °C and a solution of camphorsulfonic acid (491 mg, 2.11 mmol, 1.15 equiv.) in water (2.10 mL) as well as $n$$Bu_4NBr$ (29.6 mg, 91.9 µmol, 5.00 mol%) were added to the mixture, which was then further stirred for 2 h. Then, saturated aqueous $NaHCO_3$ solution (30.0 mL) was added and the aqueous layer extracted with DCM (3 × 30.0 mL). The combined extracts were dried over $MgSO_4$, filtered and the solvent was removed in

vacuum. The residue was purified by column chromatography (SiO_2, PE → PE/EA 4:1) to yield allylic alcohol **142** (329 mg, 961 µmol, 52%) as colorless oil.

TLC: R_f = 0.20 (PE/EtOAc 9:1).

UV (MeCN) λ_{max} = 201, 279 nm.

IR (ATR): $\tilde{\nu}$ = 3539, 2939, 2837, 2583, 1454, 1321, 1294, 1190, 1147, 1093, 1062, 1026, 993, 896, 833 cm^{-1}.
^{1}H-NMR (600 MHz, $CDCl_3$): δ (ppm) = 1.85 (s, 3 H, 5"-H_3), 2.29 (s, 3 H, 5'-CH_3), 2.30 (s, 3 H, 5-CH_3), 2.87 (dd, J = 13.9, 4.8 Hz, 1 H, 1"-H_A), 2.89 (dd, J = 13.9, 8.1 Hz, 1 H, 1"-H_B), 3.77 (s, 3 H, 3-OCH_3), 3.78 (s, 3 H, 3'-OCH_3), 4.24 (dd, J = 8.1, 4.8 Hz, 1 H, 2"-H), 4.85 (s, 1 H, 4"-H_A), 5.01 (s, 1 H, 4"-H_B), 6.39 (t, J = 2.1 Hz, 1 H, 2-H), 6.42 (s, 1 H, 6-H), 6.46 (d, J = 2.1 Hz, 1 H, 6'-H), 6.47–6.49 (m, 2 H, 4-H, 2'-H).

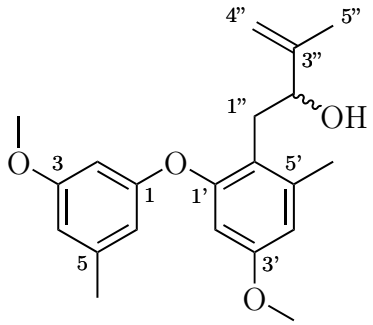
^{13}C-NMR (151 MHz, $CDCl_3$): δ (ppm) = 18.2 (C-5"), 20.3 (5'-$\underline{C}H_3$), 21.8 (5-$\underline{C}H_3$), 33.1 (C-1"), 55.5 (3-O$\underline{C}H_3$), 55.8 (3'-O$\underline{C}H_3$), 76.1 (C-2"), 100.4 (C-2'), 102.0 (C-2), 109.8 (C-4), 110.3 (C-4"), 111.8 (C-6), 113.3 (C-6'), 120.8 (C-4'), 139.5 (C-5'), 140.7 (C-5), 148.1 (C-3"), 156.0 (C-1'), 158.4 (C-1), 158.8 (C-3'), 160.8 (C-3).

MS (ESI): m/z(%) = 325.2 (100) [M - OH]$^+$, 343.2 (21) [M + H]$^+$.

calcd.: 343.1904 [M + H]$^+$,
found: 343.1905 (ESI-HRMS).

$C_{21}H_{26}O_4$ (342.44).

6.4.2 Synthesis of allylic alcohol 144



144

A solution of diaryl ether **140** (600 mg, 1.84 mmol, 1.00 equiv.) in DCM (28.0 mL) was cooled to 0 °C. Then, *m*CPBA (618 mg, 2.76 mmol, 1.50 equiv.) was added and the

reaction mixture was warmed to r.t. and stirred for 1 h. Afterwards, the reaction mixture was cooled to 0 °C and a solution of camphorsulfonic acid (491 mg, 2.11 mmol, 1.15 equiv.) in water (2.10 mL) as well as nBu$_4$NBr (29.6 mg, 91.9 µmol, 5.00 mol%) were added to the mixture, which was then further stirred for 2 h. Then, saturated aqueous $NaHCO_3$ solution (30.0 mL) was added and the aqueous layer extracted with DCM (3×30.0 mL). The combined extracts were dried over $MgSO_4$, filtered and the solvent was removed in vacuum. The residue was purified by column chromatography (SiO_2, PE $\rightarrow$ PE/EA 4:1) to yield allylic alcohol **144** (352 mg, 1.03 mmol, 56%) as colorless oil.

TLC: R_f= 0.16 (PE/EtOAc 9:1).

UV (MeCN) λ_{max} = 202, 279 nm.

IR (ATR): $\tilde{\nu}$= 3545, 2941, 2837, 1606, 1575, 1465, 1454, 1421, 1321, 1294, 1192, 1141, 1060, 898, 833 cm^{-1}.

^{1}H-NMR (600 MHz, $CDCl_3$): δ (ppm) = 1.79 (s, 3 H, 5"-H_3), 2.28 (s, 3 H 5-CH_3), 2.38 (s, 3 H, 5'-CH_3), 2.78 (dd, J = 14.1, 9.3 Hz, 1 H, 1"-H_A), 2.86 (dd, J = 14.1, 3.8 Hz, 1 H, 1"-H_B), 3.71 (s, 3 H, 3'-OCH_3), 3.75 (s, 3 H, 3-OCH_3), 4.28 (dd, J = 9.3, 3.8 Hz, 1 H, 2"-H), 4.70–4.87 (m, 1 H, 4"-H_A), 4.94 – 5.01 (m, 1 H, 4"-H_B), 6.29–6.35 (m, 2 H, 2-H, 2'-H), 6.36 (s, 1 H, 6-H), 6.45 (s, 1 H, 4-H), 6.56 (d, J = 2.5 Hz, 1 H, 4'-H).

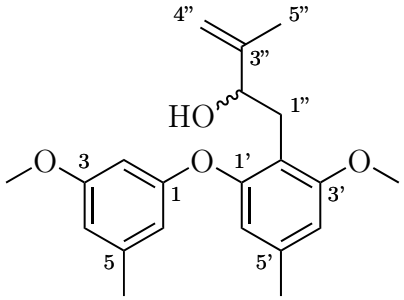
^{13}C-NMR (151 MHz, $CDCl_3$): δ (ppm) = 8.2 (C-5"), 20.6 (5'-$\underline{C}H_3$), 21.8 (5-$\underline{C}H_3$), 33.2 (C-1"), 55.5 (3'-O$\underline{C}H_3$), 55.5 (3-O$\underline{C}H_3$), 76.1 (C-2"), 101.4 (C-2), 103.2 (C-2'), 109.6 (C-4), 110.4 (C-4"), 111.1 (C-6), 111.8 (C-4'), 121.0 (C-6'), 140.1 (C-5'), 140.8 (C-5), 147.9 (C-3"), 155.9 (C-1'), 158.3 (C-1), 158.7 (C-3'), 160.9 (C-3).

MS (ESI): m/z(%) = 325.2 (100) [M - OH]$^+$, 343.2 (41) [M + H]$^+$.

calcd.: 343.1904 [M + H]$^+$,
found: 343.1903 (ESI-HRMS).

$C_{21}H_{26}O_4$ (342.44).

6.4.3 Synthesis of allylic alcohol 145



145

A solution of diaryl ether **141** (600 mg, 1.84 mmol, 1.00 equiv.) in DCM (28.0 mL) was cooled to 0 °C. Then, *m*CPBA (618 mg, 2.76 mmol, 1.50 equiv.) was added and the reaction mixture was warmed to r.t. and stirred for 1 h. Afterwards, the reaction mixture was cooled to 0 °C and a solution of camphorsulfonic acid (491 mg, 2.11 mmol, 1.15 equiv.) in water (2.10 mL) as well as nBu$_4$NBr (29.6 mg, 91.9 µmol, 5.00 mol%) were added to the mixture, which was then further stirred for 2 h. Then, saturated aqueous NaHCO$_3$ solution (30.0 mL) was added and the aqueous layer extracted with DCM (3 × 30.0 mL). The combined extracts were dried over MgSO$_4$, filtered and the solvent was removed in vacuum. The residue was purified by column chromatography (SiO$_2$, PE → PE/EA 4:1) to yield allylic alcohol **145** (322 mg, 940 µmol, 51%) as colorless oil.

TLC: R_f = 0.18 (PE/EtOAc 9:1).

UV (MeCN) λ_{max} = 204, 274 nm.

IR (ATR): $\tilde{\nu}$ = 3543, 2935, 2837, 1577, 1411, 1327, 1296, 1230, 1192, 1134, 1089, 1062, 896, 827 cm^{-1}.

^{1}H-NMR (600 MHz, $CDCl_3$): δ (ppm) = 1.77 (s, 3 H, 5”-H$_3$), 2.28 (s, 6 H, 5-CH$_3$, 5’-CH$_3$), 2.83 (dd, J = 13.8, 8.9 Hz, 1 H, 1”-H$_A$), 2.98 (dd, J = 13.8, 3.7 Hz, 1 H, 1”-H$_B$), 3.75 (s, 3 H, 3-OCH$_3$), 3.86 (s, 3 H, 3’-OCH$_3$), 4.23 (dd, J = 8.9, 3.7 Hz, 1 H, 2”-H), 4.77 (s, 1 H, 4”-H$_A$), 4.92 (s, 1 H, 4”-H$_B$), 6.33 (t, J = 2.2 Hz, 1 H, 2-H), 6.35 (s, 1 H, 6-H), 6.39 (s, 1 H, 6’-H), 6.44 (s, 1 H, 4-H), 6.51 (s, 1 H, 4’-H).

^{13}C-NMR (151 MHz, $CDCl_3$): δ (ppm) = 18.2 (C-5”), 21.8, 21.8 (5-C$\underline{\text{C}}$H$_3$, 5’-C$\underline{\text{C}}$H$_3$), 30.4 (C-1”), 55.5 (3-OC$\underline{\text{C}}$H$_3$), 55.9 (3-OC$\underline{\text{C}}$H$_3$), 76.2 (C-2”), 101.4 (C-2), 107.3 (C-4’), 109.4 (C4), 110.1 (C-4”), 111.2 (C-6), 113.0 (C-6’), 116.0 (C-2’), 138.1 (C-5’), 140.7 (C-5), 147.8 (C-3”), 155.5 (C-1’), 158.7 (C-1), 158.8 (C-3’), 160.8 (C-3).

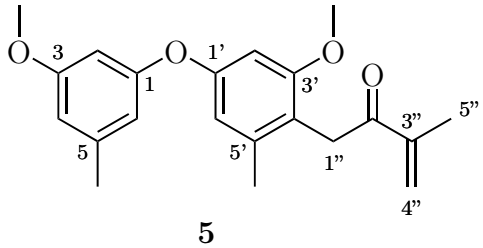
MS (ESI): m/z(%) = 325.2 (46) [M - OH]$^+$, 343.2 (1) [M + H]$^+$.

calcd.: 325.1798 $[M - OH]^+$,
found: 325.1796 (ESI-HRMS).

$C_{21}H_{26}O_4$ (342.44).

6.5 Oxidation of allyalcohols to α,β-unsaturated Ketones

6.5.1 Synthesis of ketone 5



5

To a solution of allylic alcohol **142** (190 mg, 555 µmol, 1.00 equiv.) in DCM (4.00 mL) was added Dess-Martin periodinane (353 mg, 832 µmol, 1.50 equiv.) and the reaction mixture was stirred at r.t. for 2 h. Then, saturated aqueous $NaHCO_3$ solution (10.0 mL) was added and the mixture extracted with DCM (3×15.0 mL). The combined organic extracts were dried over $MgSO_4$, filtered and the solvent was removed in vacuum. The residue was purified by column chromatography (SiO_2, PE → PE/EA 4:1) to yield ketone **5** (170 mg, 499 µmol, 90%) as colorless oil, which slowly crystallized.

TLC: $R_f = 0.30$ (PE/EtOAc 9:1).

M.p.: 65 °C.

UV (MeCN) $\lambda_{max} = 203, 279$ nm.

IR (ATR): $\tilde{\nu} =$ 2924, 2837, 1681, 1583, 1454, 1419, 1323, 1294, 1192, 1149, 1089, 1064, 1026, 931, 833 cm^{-1}.

^{1}H-NMR (600 MHz, $CDCl_3$): δ (ppm) = 1.92 (s, 3 H, 5"-H_3), 2.15 (s, 3 H, 5'-CH_3), 2.29 (s, 3 H, 5-CH_3), 3.70 (s, 3 H, 3'-OCH_3), 3.76 (s, 3 H, 3-OCH_3), 4.03 (s, 2 H, 1"-H_2), 5.80 (s, 1 H, 4"-H_A), 6.13 (s, 1 H, 4"-H_B), 6.41 (t, $J = 2.1$ Hz, 1 H, 2-H), 6.44 (s, 1 H, 6-H), 6.44 (d, $J = 2.3$ Hz, 1 H, 6'-H), 6.45 (d, $J = 2.3$ Hz, 1 H, 2'-H), 6.47 (s, 1 H, 4-H).

^{13}C-NMR (151 MHz, $CDCl_3$): δ (ppm) = 18.0 (C-5"), 20.1 (5'-$\underline{C}H_3$), 21.8 (5-$\underline{C}H_3$), 35.4 (C-1"), 55.5 (3-O$\underline{C}H_3$), 55.8 (3'-O$\underline{C}H_3$), 100.2 (C-2'), 102.0 (C-2), 109.9 (C-4), 111.9 (C-6),

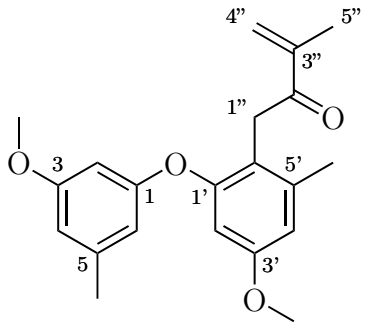
112.7 (C-6'), 118.0 (C-4'), 124.3 (C-4"), 139.4 (C-5'), 140.7 (C-5), 144.6 (C-3"), 156.4 (C-1'), 158.4 (C-1), 158.5 (C-3'), 160.8 (C-3), 199.6 (C-2").

MS (ESI): $m/z(\%)$ = 271.1 (10) [M - methacryl]$^+$, 341.2 (100) [M + H]$^+$.

calcd.: 341.1747 [M + H]$^+$,
found: 341.1747 (ESI-HRMS).

$C_{21}H_{24}O_4$ (340.42).

6.5.2 Synthesis of ketone 6



6

To a solution of diaryl ether **144** (195 mg, 569 µmol, 1.00 equiv.) in DCM (4.00 mL) was added Dess-Martin periodinane (362 mg, 854 µmol, 1.50 equiv.) and the reaction mixture was stirred at r.t. for 2 h. Then, saturated aqueous $NaHCO_3$ solution (10.0 mL) was added and the mixture extracted with DCM (3 × 15.0 mL). The combined organic extracts were dried over $MgSO_4$, filtered and the solvent was removed in vacuum. The residue was purified by column chromatography (SiO_2, PE → PE/EA 4:1) to yield ketone **6** (179 mg, 526 µmol, 92%) as colorless oil which slowly crystallized.

TLC: R_f= 0.30 (PE/EtOAc 9:1).

M.p.: 76 °C.

UV (MeCN) λ_{max} = 205, 276 nm.

IR (ATR): $\tilde{\nu}$= 2955, 2922, 2937, 1680, 1606, 1575, 1490, 1452, 1423, 1323, 1294, 1192, 1142, 1064, 931, 833 cm^{-1}.
^{1}H-NMR (600 MHz, $CDCl_3$): δ (ppm) = 1.85 (s, 3 H, 5"-H_3), 2.22 (s, 3 H, 5'-CH_3), 2.25 (s, 3 H, 5-CH_3), 3.71 (s, 3 H, 3'-OCH_3), 3.73 (s, 3 H, 3-OCH_3), 4.01 (s, 2 H, 1"-H_2),

5.71–5.75 (m, 1 H, 4”-H_A), 6.03 (s, 1 H, 4”-H_B), 6.29 (t, $J = 2.1$ Hz, 1 H, 2-H), 6.31 (s, 1 H, 6-H), 6.33 (d, $J = 2.5$ Hz, 1 H, 2’-H), 6.42 (s, 1 H, 4-H), 6.57 (d, $J = 2.5$ Hz, 1 H, 4’-H).

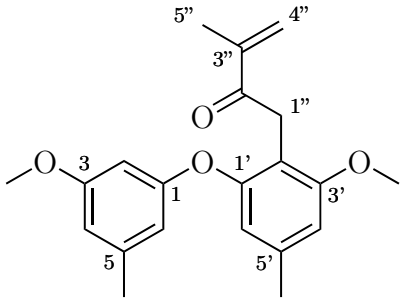
^{13}C-NMR (151 MHz, $CDCl_3$): δ (ppm) = 18.0 (C-5”), 20.4 (5–CH_3), 21.8 (5-CH_3), 35.4 (C-1”), 55.4 (3’-O$\underline{C}H_3$), 55.4 (3-O$\underline{C}H_3$), 101.3 (C-2), 103.1 (C-2’), 109.7 (C-4), 111.3 (C-6), 111.6 (C-4’), 118.4 (C-6’), 124.4 (C-4”), 140.0 (C-5’), 140.6 (C-5), 144.5 (C-3”), 155.7 (C-1’), 158.6 (C-1), 159.1 (C-3’), 160.8 (C-3), 199.1 (C-2”).

MS (ESI): m/z(%) = 271.1 (8) [M - methacryl]$^+$, 341.2 (100) [M + H]$^+$.

calcd.: 341.1747 [M + H]$^+$,
found: 341.1733 (ESI-HRMS).

$C_{21}H_{24}O_4$ (340.42).

6.5.3 Synthesis of ketone 7



7

To a solution of diaryl ether **145** (182 mg, 531 µmol, 1.00 equiv.) in DCM (4.00 mL) was added Dess-Martin periodinane (338 mg, 797 µmol, 1.50 equiv.) and the reaction mixture was stirred at r.t. for 2 h. Then, saturated aqueous $NaHCO_3$ solution (10.0 mL) was added and the mixture extracted with DCM (3×15.0 mL). The combined organic extracts were dried over $MgSO_4$, filtered and the solvent was removed in vacuum. The residue was purified by column chromatography (SiO_2, PE $\rightarrow$ PE/EA 4:1) to yield ketone **7** (161 mg, 473 µmol, 89%) as colorless crystalline solid.

TLC: R_f= 0.31 (PE/EtOAc 9:1).

M.p.: 102 °C.

UV (MeCN) λ_{max} = 260, 273 nm.

IR (ATR): $\tilde{\nu}$ = 3008, 2939, 2841, 1674, 1614, 1577, 1454, 1413, 1309, 1234, 1195, 1155, 1138, 1070, 823 cm^{-1}.

^{1}H-NMR (600 MHz, $CDCl_3$): δ (ppm) = 1.85 (s, 3 H, 5”-H_3), 2.26 (s, 3 H, 5-CH_3), 2.28 (s, 3 H, 5’-CH_3), 3.74 (s, 3 H, 3-OCH_3), 3.78 (s, 3 H, 3’-OCH_3), 4.01 (s, 2 H, 1”-H_2), 5.70 (s, 1 H, 4”-H_A), 6.00 (s, 1 H, 4’-H_B), 6.32 (t, J = 2.1 Hz, 1 H, 2-H), 6.34 (s, 1 H, 6-H), 6.36 (s, 1 H, 6’-H), 6.42 (s, 1 H, 4-H), 6.50 (s, 1 H, 4’-H).

^{13}C-NMR (151 MHz, $CDCl_3$): δ (ppm) = 18.0 (C-5”), 21.8 (5-CH_3), 21.9 (5’-CH_3), 33.3 (C-1”), 55.5 (3-OCH_3), 55.9 (3’-OCH_3), 101.5 (C-2), 107.2 (C-4’), 109.6 (C-4), 111.5 (C-6), 112.5 (C-6’), 113.5 (C-2’), 124.0 (C-4”), 138.5 (C-5’), 140.5 (C-5), 144.5 (C-3”), 155.5 (C-1’), 158.6 (C-3’), 158.7 (C-1), 160.7 (C-3), 199.3 (C-2”).

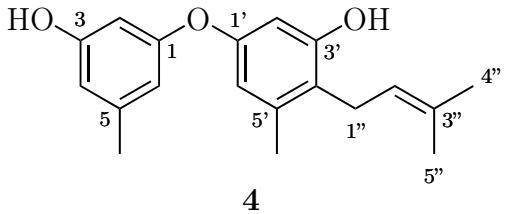
MS (ESI): m/z(%) = 271.1 (9) [M - methacryl]$^+$, 341.2 (100) [M + H]$^+$.

calcd.: 341.1747 [M + H]$^+$,
found: 341.1742 (ESI-HRMS).

$C_{21}H_{24}O_4$ (340.42).

6.6 Demethylation of diaryl ethers

6.6.1 Synthesis of the proposed structure of verticilatin 4



4

Under nitrogen atmosphere a solution of diaryl ether **126** (150 mg, 460 µmol, 1.00 equiv.) in anhydrous DMF (4.00 mL) was cooled to 0 °C. Then, NaH (dispersed in mineral oil c = 60.0%, 73.5 mg, 1.84 mmol, 4.00 equiv.) was added followed by dropwise addition of ethanethiol (150 µL, 126 mg, 2.03 mmol, 4.41 equiv.). After that the reaction mixture was stirred at 150 °C for 16 h. After cooling to r.t., aqueous HCl (1 M, 10.0 mL) was added and the mixture extracted with diethyl ether (3 × 10.0 mL), dried over $MgSO_4$, filtered and the solvent was removed in vacuum. The residue was purified by column chromatography (SiO_2, PE → PE/EtOAc 3:1) to yield diaryl ether **4** (130 mg, 436 µmol, 95%) as slightly yellowish oil.

TLC: R_f= 0.42 (PE/EtOAc 4:1).

UV (MeCN) λ_{max} = 208, 280 nm.

IR (ATR): $\tilde{\nu}$= 3410, 2964, 2918, 2856, 1585, 1489, 1454, 1317, 1203, 1143, 1049, 1029, 974, 833 cm^{-1}.

^{1}H-NMR (600 MHz, DMSO-d_6): δ (ppm) = 1.64 (s, 3 H, 4"-H_3), 1.72 (s, 3 H, 5"-H_3), 2.16 (s, 3 H, 5'-CH_3), 2.17 (s, 3 H, 5-CH_3), 3.20 (d, J = 7.0 Hz, 2 H, 1"-H_2), 4.99–5.05 (m, 1 H, 2"-H), 6.13 (t, J = 2.0 Hz, 1 H, 2-H), 6.22 (s, 1 H, 6-H), 6.27 (d, J = 2.3 Hz, 1 H, 6'-H), 6.28 (d, J = 2.3 Hz, 1 H, 2'-H), 6.31 (s, 1 H, 4-H), 9.35 (s, 1 H, 3'-OH), 9.39 (s, 1 H, 3-OH).

^{13}C-NMR (151 MHz, DMSO-d_6): δ (ppm) = 17.7 (C-5"), 19.4 (5'-$\underline{C}H_3$), 21.1 (5-$\underline{C}H_3$), 24.5 (C-1"), 25.5 (C-4"), 102.5 (C-2), 103.4 (C-2'), 109.7 (C-6), 110.8 (C-4), 111.3 (C-6'), 121.3 (C-4'), 122.9 (C-2"), 129.9 (C-3"), 138.2 (C-5'), 140.0 (C-5), 154.5 (C-1'), 155.8 (C-3'), 158.0 (C-1), 158.4 (C-3).

^{1}H-NMR (600 MHz, methanol-d_4): δ (ppm) = 1.68 (s, 3 H, 4"-H_3), 1.76 (s, 3 H, 5"-H_3), 2.18 (s, 3 H, 5'-CH_3), 2.20 (s, 3 H, 5-CH_3), 3.28 (d, J = 6.9 Hz, 2 H, 1"-H_2), 5.04–5.08 (m, 1 H, 2"-H), 6.16 (t, J = 2.0 Hz, 1 H, 2-H), 6.26 (s, 1 H, 6-H), 6.28 (s, 2 H, 2'-H, 6'-H), 6.32 (s, 1 H, 4-H).

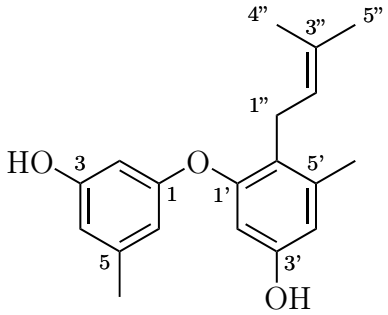
^{13}C-NMR (151 MHz, methanol-d_4): δ (ppm) = 17.9 (C-5"), 20.0 (5'-$\underline{C}H_3$), 21.6 (5-$\underline{C}H_3$), 25.8 (C-1"), 25.9 (C-4"), 103.7 (C-2), 104.9 (C-2'), 111.4 (C-6), 111.6 (C-4), 113.1 (C6'), 123.1 (C-4'), 124.4 (C-2"), 131.4 (C-3"), 139.7 (C-5'), 141.5 (C-5), 156.5 (C-1'), 157.0 (C-3'), 159.5 (C-3), 160.2 (C-1).

MS (ESI): m/z(%) = 243.1 (16) [M - isobutenyl]$^+$, 299.2 (100) [M + H]$^+$.

calcd.: 299.1642 [M + H]$^+$,
found: 299.1637 (ESI-HRMS).

$C_{19}H_{22}O_3$ (298.38).

6.6.2 Synthesis of Diorcinol D 1



1

Under nitrogen atmosphere a solution of diaryl ether **140** (198 mg, 607 µmol, 1.00 equiv.) in anhydrous DMF (5.50 mL) was cooled to 0 °C. Then, NaH (dispersed in mineral oil c = 60.0%, 97.0 mg, 2.43 mmol, 4.00 equiv.) was added followed by dropwise addition ethanethiol (200 µL, 168 mg, 2.70 mmol, 4.46 equiv.). After that the reaction mixture was stirred at 150 °C for 16 h. After cooling to r.t., aqueous HCl (1 M, 10.0 mL) was added and the mixture extracted with diethyl ether (3×10.0 mL), dried over $MgSO_4$, filtered and the solvent was removed in vacuum. The residue was purified by column chromatography (SiO_2, PE $\rightarrow$ PE/EtOAc 3:1) to yield diorcinol D **1** (179 mg, 600 µmol, quant.) as colorless oil which slowly crystallized.

TLC: R_f = 0.36 (PE/EtOAc 4:1).

M.p.: 123 °C.

UV (MeCN) λ_{max} = 202, 280 nm.

IR (ATR): $\tilde{\nu}$ = 3263, 2962, 2924, 2852, 1604, 1583, 1456, 1363, 1313, 1219, 1138, 1053, 979, 829, 682 cm^{-1}.

^{1}H-NMR (600 MHz, DMSO-d_6): δ (ppm) = 1.59 (s, 3 H, 4”-H_3), 1.61 (s, 3 H, 5”-H_3), 2.16 (s, 3 H, 5-CH_3), 2.19 (s, 3 H, 5’-CH_3), 3.12 (d, J = 6.9 Hz, 2 H, 1”-H_2), 4.92–5.03 (m, 1 H, 2”-H), 6.04 (t, J = 1.9 Hz, 1 H, 2-H), 6.12 (d, J = 2.3 Hz, 1 H, 2’-H), 6.14 (s, 1 H, 6-H), 6.27 (s, 1 H, 4-H), 6.40 (d, J = 2.3 Hz, 1 H, 4’-H), 9.22 (s, 1 H, 3’-OH), 9.34 (s, 1 H, 3-OH).

^{13}C-NMR (151 MHz, DMSO-d_6): δ (ppm) = 17.6 (C-5”), 19.4 (5’-CH_3), 21.1 (5-CH_3), 24.6 (C-1”), 25.5 (C-4”), 101.5 (C-2), 104.6 (C-2’), 108.7 (C-6), 110.3 (C-4), 113.1 (C4’), 121.5 (C-6’), 122.7 (C-2”), 130.2 (C-3”), 138.6 (C-5’), 139.9 (C-5), 154.2 (C-1’), 155.8 (C-3’), 158.4 (C-3), 158.7 (C-1).

^{1}H-NMR (600 MHz, methanol-d_4): δ (ppm) = 1.61 (s, 3 H, 4”-H_3), 1.64 (s, 3 H, 5”-H_2), 2.20 (s, 3 H, 5-CH_3), 2.24 (s, 3 H, 5’-CH_3), 3.21 (d, J = 6.8 Hz, 2 H, 1”-H_2), 4.98–5.01 (m, 1 H, 2”-H), 6.09 (t, J = 2.1 Hz, 1 H, 2-H), 6.17 (s, 1 H, 6-H), 6.18 (d, J = 2.4 Hz, 1 H, 2’-H), 6.29 (s, 1 H, 4-H), 6.43 (d, J = 2.4 Hz, 1 H, 4’-H).

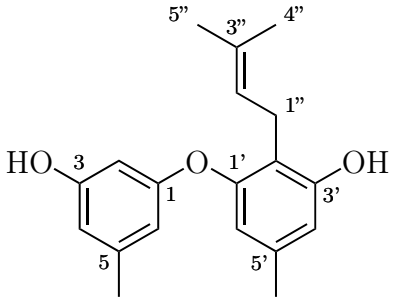
^{13}C-NMR (151 MHz, methanol-d_4): δ (ppm) = 17.9 (C-5”), 19.9 (5’-CH_3), 21.6 (5-CH_3), 25.9 (C-4”), 26.0 (C-1”), 102.8 (C-2), 106.1 (C-2’), 110.4 (C-6), 111.0 (C-4), 114.1 (C4’), 124.1 (2 C, C-6’, C-2”), 131.7 (C-3”), 140.1 (C-5’), 141.4 (C-5), 156.1 (C-1’), 156.9 (C-3’), 159.4 (C-3), 160.8 (C-1).

MS (ESI): m/z(%) = 243.1 (100) [M - isobutenyl]$^+$, 299.2 (25) [M + H]$^+$.

calcd.: 299.1642 [M + H]$^+$,
found: 299.1643 (ESI-HRMS).

$C_{19}H_{22}O_3$ (298.38).

6.6.3 Synthesis of Diorcinol I 2



2

Under nitrogen atmosphere a solution of diaryl ether **141** (150 mg, 460 µmol, 1.00 equiv.) in anhydrous DMF (4.00 mL) was cooled to 0 °C. Then, NaH (dispersed in mineral oil c = 60.0%, 73.5 mg, 1.84 mmol, 4.00 equiv.) was added followed by dropwise addition ethanethiol (150 µL, 126 mg, 2.03 mmol, 4.41 equiv.). After that the reaction mixture was stirred at 150 °C for 16 h. After cooling to r.t., aqueous HCl (1 M, 10.0 mL) was added and the mixture extracted with diethyl ether (3 × 10.0 mL), dried over $MgSO_4$, filtered and the solvent was removed in vacuum. The residue was purified by column chromatography (SiO_2, PE → PE/EtOAc 3:1) to yield diorcinol I **2** (125 mg, 419 µmol, 91%) as colorless oil which slowly crystallized.
TLC: R_f = 0.47 (PE/EtOAc 4:1).

M.p.: 123 °C.

UV (MeCN) λ_{max} = 204, 274 nm.

IR (ATR): $\tilde{\nu}$ = 3288, 2974, 2922, 2854, 1618, 1587, 1514, 1413, 1311, 1163, 1143, 968, 852, 819 cm^{-1}.

^{1}H-NMR (600 MHz, DMSO-d_6): δ (ppm) = 1.56 (s, 6 H, 4"-H_3, 5"-H_3), 2.13 (s, 3 H, 5'-CH_3), 2.15 (s, 3 H, 5-CH_3), 3.10 (d, J = 7.1 Hz, 2 H, 1"-H_2), 5.08–5.15 (m, 1 H, 2"-H), 6.02 (t, J = 2.1 Hz, 1 H, 2-H), 6.12 (s, 1 H, 6-H), 6.15 (s, 1 H, 6'-H), 6.25 (s, 1 H, 4 H), 6.44 (s, 1 H, 4'-H), 9.31 (s, 1 H, 3-OH), 9.41 (s, 1 H, 3'-OH).

^{13}C-NMR (151 MHz, DMSO-d_6): δ (ppm) = 17.5 (C-5"), 20.8 (5'-$\underline{C}H_3$), 21.2 (5'-$\underline{C}H_3$), 22.2 (C-1"), 25.5 (C-4"), 101.3 (C-2), 108.4 (C-6), 110.1 (C-4), 111.5 (C-6'), 111.7 (C-4'), 116.9 (C-2'), 122.8 (C-2"), 130.0 (C-3"), 136.3 (C-5'), 139.7 (C-5), 154.2 (C-1'), 156.2 (C-3'), 158.3 (C-3), 158.9 (C-1).

^{1}H-NMR (600 MHz, methanol-d_4): δ (ppm) = 1.58 (s, 6 H, 4"-H_3, 5"-H_3), 2.17 (s, 3 H, 5'-CH_3), 2.19 (s, 3 H, 5-CH_3), 3.20 (d, J = 7.2 Hz, 2 H, 1"-H_2), 5.14–5.19 (m, 1 H. 2"-H), 6.07 (t, J = 2.1 Hz, 1 H, 2-H), 6.15 (s, 1 H, 6-H), 6.20 (s, 1 H, 6'-H), 6.28 (s, 1 H, 4-H), 6.43 (s, 1 H, 4'-H).

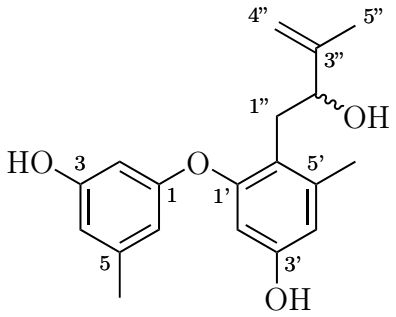
^{13}C-NMR (151 MHz, methanol-d_4): δ (ppm) = 17.8 (C-5"), 21.2 (5'-$\underline{C}H_3$), 21.6 (5-$\underline{C}H_3$), 23.5 (C-1"), 25.9 (C-4"), 102.6 (C-2), 110.2 (C-6), 110.8 (C-4), 112.6 (C-4'), 113.3 (C-6'), 119.0 (C-2'), 124.1 (C-2"), 131.4 (C-3"), 137.9 (C-5'), 141.3 (C-5), 156.1 (C1'), 157.5 (C-3'), 159.3 (C-3), 160.9 (C-1).

MS (ESI): m/z(%) = 243.1 (100) [M - isobutenyl]$^+$, 299.2 (68) [M + H]$^+$.

calcd.: 299.1642 [M + H]$^+$,
found: 299.1647 (ESI-HRMS).

$C_{19}H_{22}O_3$ (298.38).

6.6.4 Synthesis of *rac*-Diorcinol J 3



3

Under nitrogen atmosphere a solution of diaryl ether **144** (298 mg, 870 µmol, 1.00 equiv.) in anhydrous DMF (10.0 mL) was cooled to 0 °C. Then, NaH (dispersed in mineral oil, c = 60.0%, 174 mg, 4.35 mmol, 5.00 equiv.) was added followed by dropwise addition ethanethiol (350 µL, 168 mg, 4.73 mmol, 5.44 equiv.). After that the reaction mixture was stirred at 150 °C for 16 h. After cooling to r.t., aqueous HCl (1 M, 10.0 mL) was added and the mixture extracted with diethyl ether (3×10.0 mL), dried over $MgSO_4$, filtered and the solvent was removed in vacuum. The residue was purified by column chromatography (SiO_2, PE → PE/EtOAc 1:1) followed by reversed phase chromatography (RP-C18, H_2O → H_2O/MeCN 3:1) to yield racemic diorcinol J **3** (180 mg, 573 µmol, 66%) as colorless amorphous solid.

TLC: $R_f = 0.07$ (PE/EtOAc 4:1).

UV (MeCN) $\lambda_{max} = 201, 279$ nm.

IR (ATR): $\tilde{\nu} =$ 3358, 2968, 2920, 1587, 1462, 1315, 1211, 1139, 1060, 1016, 985, 902, 835 cm^{-1}.

^{1}H-NMR (600 MHz, DMSO-d_6): δ (ppm) = 1.66 (s, 3 H, 5"-H_3), 2.17 (s, 3 H, 5-CH_3), 2.25 (s, 3 H. 5'-CH_3), 2.53 (dd, J = 13.5, 7.8 Hz, 1 H, 1"-H_A), 2.64 (dd, J = 13.5, 5.6 Hz, 1 H, 1"-H_B), 4.03–4.08 (m, 1 H, 2"-H), 4.63 (s, 1 H, 4"-H_A), 4.67 (s, 1 H, 4"-H_B), 4.69 (d, J = 4.3 Hz, 1 H, 2"-OH), 6.08 (d, J = 2.4 Hz, 1 H, 2'-H), 6.09 (t, J = 2.0 Hz, 1 H, 2-H), 6.18 (s, 1 H, 6-H), 6.29 (s, 1 H, 4-H), 6.36 (d, J = 2.4 Hz, 1 H, 4'-H), 9.17 (s, 1 H, 3'-OH), 9.37 (s, 1 H, 3-OH).

^{13}C-NMR (151 MHz, DMSO-d_6): δ (ppm) = 17.7 (C-5"), 20.1 (5'-CH_3), 21.2 (5-CH_3), 32.6 (C-1"), 74.7 (C-2"), 101.9 (C-2), 103.8 (C-2'), 109.0 (C-6), 109.5 (C-4"), 110.5 (C4), 112.6 (C-4'), 119.7 (C-6'), 139.6 (C-5), 139.9 (C-5'), 148.6 (C-3"), 155.2 (C-1'), 155.7 (C-3'), 158.3 (C-1), 158.4 (C-3).

MS (ESI): $m/z(\%)$ = 241.1 (100) [M - butoxide]$^+$, 297.1 (100) [M - OH]$^+$, 337.1 (14) [M + Na]$^+$.

calcd.: 337.1410 [M + Na]$^+$,
found: 337.1392 (ESI-HRMS).

$C_{19}H_{22}O_4$ (314.38).

6.7 Syntheses of 1,3-Dithianes

2-methyl-1,3-dithiane **286** was purchased from ABCR. All other 1,3-dithianes except ((4-(1,3-dithian-2-yl)phenyl)ethynyl)trimethylsilane **215** were synthesized according to reported procedures.

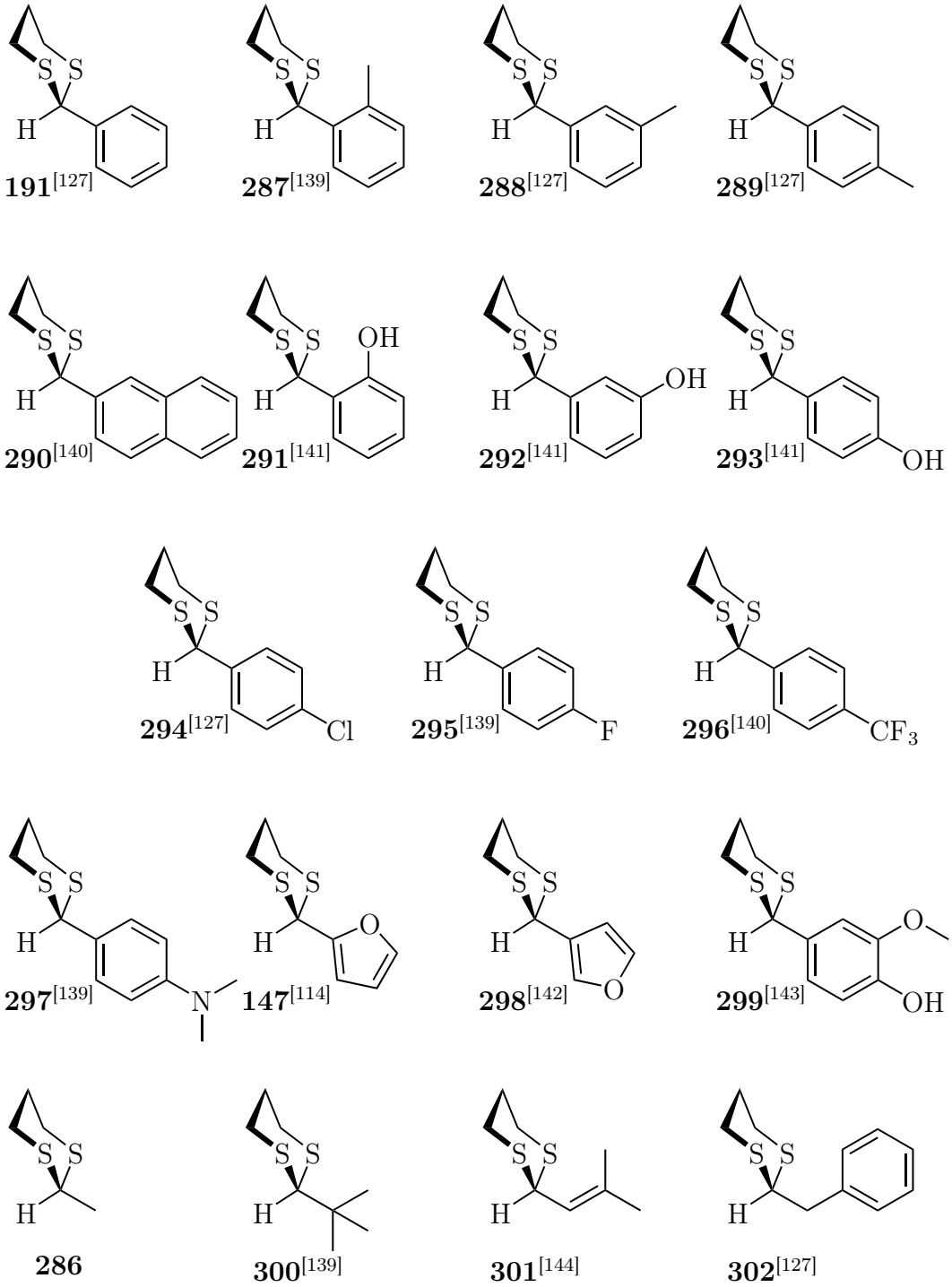
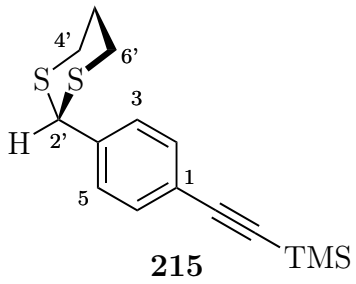


Figure 50: Dithianes investigated in *C*-glycosylation reactions.

6.7.1 ((4-(1,3-Dithian-2-yl)phenyl)ethynyl)trimethylsilane 215



215

To a solution of 4-((trimethylsilyl)ethynyl)benzaldehyde[145] (5.30 g, 26.2 mmol, 1.00 equiv.) in abs. DCM (30.0 mL) were added 1,3-propanedithiol (2.90 mL, 3.12 g, 28.8 mmol, 1.10 equiv.) and molecular sieves (3 Å, 3.00 g). The mixture was cooled to 0 °C and $BF_3{\cdot}OEt_2$ (1.00 mL, 1.12 g, 7.86 mmol, 33.3 mol%) was added. The solution was warmed to r.t. and stirred for 16 h. Then, the reaction mixture was filtered and the filtrate neutralized with saturated aqueous $NaHCO_3$-solution (30.0 mL). The layers were separated and the aqueous layer was extracted with DCM (2×50.0 mL). The combined organic layers were washed with brine (100 mL), dried over $MgSO_4$ and filtered. After removal of the solvent in vacuum, the product was purified by recrystallization from MeOH to yield ((4-(1,3-dithian-2-yl)phenyl)ethynyl)trimethylsilane **215** (5.31 g, 18.2 mmol, 69%) as colorless crystalline solid.

TLC: $R_f = 0.51$ (PE/EtOAc 19:1).

M.p.: 75 °C.

UV (MeCN): $\lambda_{max} = 253$, 264 nm.

IR (ATR): $\tilde{\nu} = 3030$, 2957, 2895, 2831, 2158, 1494, 1404, 1279, 1248, 854, 835, 758, 677, 638, 543 cm^{-1}.

^{1}H-NMR (400 MHz, benzene-d_6): δ (ppm) = 0.23 (s, 9 H, $SiMe_3$), 1.39 (dtt, J = 14.0, 4.6, 2.5 Hz, 1 H, 5'-$H_{eq.}$), 1.57 (dtt, J = 14.0, 12.1, 3.1 Hz, 1 H, 5'-$H_{ax.}$), 2.30 (ddd, J = 14.3, 4.6, 3.1 Hz, 2 H, 4'-$H_{eq.}$, 6'-$H_{eq.}$), 2.43 (ddd, J = 14.6, 12.1, 2.5 Hz, 2 H, 4'-$H_{ax.}$, 6'-$H_{ax.}$), 4.85 (s, 1 H, 2'-H), 7.34–7.37 (m, 2 H, 3-H, 5-H), 7.37–7.41 (m, 2 H, 2-H, 6-H).

^{13}C-NMR (100 MHz, benzene-d_6): δ (ppm) = 0.1 (3 C, $SiMe_3$), 25.2 (C-5'), 31.7 (2 C, C-4', C-6'), 51.4 (C-2'), 94.9 (1-C≡<u>C</u>-TMS), 105.6 (1-<u>C</u>≡C-TMS), 123.8 (C-4), 128.4 (2 C, C-3, C-5), 132.6 (2 C, C-2, C-6), 140.3 (C-1).

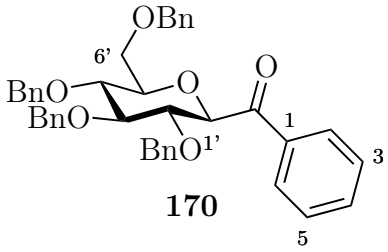
MS (ESI): m/z (%) = 293.1 (31) $[M + H]^+$, 585.2 (31) $[2\ M + H]^+$.

calcd.: 293.0848 $[M+H]^+$,
found: 293.0849 (ESI-HRMS).

$C_{15}H_{20}S_2Si$ (292.53).

6.8 Syntheses of β-carbonyl-*C*-D-glucopyranosides

6.8.1 Phenyl (2,3,4,6-tetra-*O*-benzyl-β-D-glucopyranosyl) ketone 170



170

A solution of 2,3,4,6-tetra-*O*-benzyl-D-glucopyranose **153** (500 mg, 925 µmol, 1.00 equiv.) in DCM (5.00 mL) was cooled to 0 °C, oxalyl bromide (108 µL, 248 µg, 1.15 µmol, 1.24 equiv.) was added and the solution was stirred at r.t. for 1 h. The solvent was removed in vacuum and 2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranosyl bromide **154** was obtained as orange oil, which was dissolved in 2-MeTHF (5.00 mL) and cooled to -95 °C. In a seperate vessel, a solution of 2-phenyl-1,3-dithiane **191** (363 mg, 1.85 mmol, 2.00 equiv.) in 2-MeTHF (5.00 mL) was cooled to -95 °C and a solution of *t*-BuLi (c = 1.70 M in *n*-pentane, 1.10 mL, 1.87 mmol, 2.02 equiv.) was added. The solution was stirred at -95 °C for 10 min and then transferred to the precooled solution of 2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranosyl bromide **154** in 2-MeTHF. The reaction mixture was warmed to 0 °C over 2 h. Then, MeOH (10.0 mL) was added and the solvent was removed in vacuum. The residue was dissolved in MeCN/H_2O (9:1, 10.0 mL) and PIFA (1.19 g, 2.77 mmol, 3.00 equiv.) was added. The reaction mixture was stirred for 30 min, then poured into saturated aqueous $NaHCO_3$-solution (20.0 mL) and extracted with Et_2O (3 × 20.0 mL). The combined organic layers were dried over $MgSO_4$, filtered and the solvent was removed in vacuum. The residue was purified by column chromatography (SiO_2, PE/EtOAc 9:1 → PE/EtOAc 2:1) to yield the *C*-glycosidic compound **170** (332 mg, 527 µmol, 57%) as colorless crystalline solid.

TLC: R_f = 0.67 (PE/EtOAc 4:1).

M.p.: 111 °C.

$[\alpha]_D^{25} = 13.8$ (c = 1.00, $CHCl_3$).

UV (H_2O): $\lambda_{max} = 203, 231$ nm.

IR (ATR): $\tilde{\nu} =$ 2916, 1685, 1597, 1496, 1451, 1405, 1352, 1308, 1227, 1100, 890, 776, 732, 695 cm^{-1}.

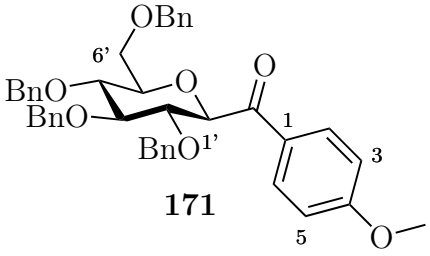
^{1}H-NMR (600 MHz, $CDCl_3$): δ (ppm) = 3.65–3.72 (m, 3 H, 4'-H, 5'-H, 6'-H_A), 3.77 (d, $J = 10.0$ Hz, 1 H, 6'-H_B), 3.86 (t, $J = 9.5$ Hz, 1 H, 3'-H), 4.05 (t, $J = 9.5$ Hz, 1 H, 2'-H), 4.51 (d, $J = 12.1$ Hz, 1 H, 6'-O-CH_A), 4.56 (d, $J = 12.1$ Hz, 1 H, 6'-O-CH_B), 4.60 (d, $J = 10.5$ Hz, 1 H, 2'-O-CH_A), 4.62 (d, $J = 10.8$ Hz, 1 H, 4'-O-CH_A), 4.65 (d, $J = 9.5$ Hz, 1 H, 1'-H), 4.72 (d, $J = 10.5$ Hz, 1 H, 2'-O-CH_B), 4.86 (d, $J = 10.8$ Hz, 1 H, 4'-O-CH_B), 4.92 (d, $J = 11.1$ Hz, 1 H, 3'-O-CH_A), 4.95 (d, $J = 11.1$ Hz, 1 H, 3'-O-CH_B), 6.99–7.03 (m, 2 H, 2 × Ar-H), 7.15–7.22 (m, 5 H, 5 × Ar-H), 7.26–7.36 (m, 13 H, 13 × Ar-H), 7.44 (t, $J = 8.0$ Hz, 2 H, 3-H, 5-H), 7.58 (t, $J = 8.0$ Hz, 1 H, 4-H), 8.08 (d, $J = 8.0$ Hz, 2 H, 2-H, 6-H).
^{13}C-NMR (151 MHz, $CDCl_3$): δ (ppm) = 69.2 (C-6'), 73.6 (C-6'-O$\underline{C}H_2$), 75.2 (C-2'-O$\underline{C}H_2$), 75.3 (C-4'-O$\underline{C}H_2$), 75.9 (C-3'-O$\underline{C}H_2$), 78.2 (C-4'), 79.1 (C-1'), 79.7 (C-5'), 80.2 (C-2'), 87.2 (C-3'), 127.7, 127.8 (4 C), 128.0, 128.2 (2 C), 128.2 (2 C), 128.4 (2 C), 128.5 (2 C), 128.6 (2 C), 128.6 (2 C) (20 × C-Ar), 128.7 (2 C, C-3, C-5), 129.5 (2 C, C-2, C-6), 133.7 (C-4), 136.0 (C-1), 137.9, 138.1, 138.3, 138.6 (4 × C-Ar, quart.), 195.0 (CO).

MS (ESI): m/z (%) = 629.3 (16) $[M + H]^+$, 646.3 (65) $[M + NH_4]^+$, 651.3 (100) $[M + Na]^+$.

calcd.: 651.2717 $[M + Na]^+$,
found: 651.2717 (ESI-HRMS).

$C_{41}H_{40}O_6$ (628.77).

6.8.2 (4-Methoxyphenyl)(2,3,4,6-tetra-*O*-benzyl-β-D-glucopyranosyl) ketone 171



171

A solution of 2,3,4,6-tetra-*O*-benzyl-D-glucopyranose **153** (500 mg, 925 µmol, 1.00 equiv.) in DCM (5.00 mL) was cooled to 0 °C, oxalyl bromide (108 µL, 248 µg, 1.15 µmol, 1.24 equiv.) was added and the solution was stirred at r.t. for 1 h. The solvent was removed in vacuum and 2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranosyl bromide **154** was obtained as orange oil, which was dissolved in 2-MeTHF (5.00 mL) and cooled to -95 °C. In a seperate vessel, a solution of 2-(4-methoxyphenyl)-1,3-dithiane **151** (419 mg, 1.85 mmol, 2.00 equiv.) in 2-MeTHF (5.00 mL) was cooled to -95 °C and a solution of *t*-BuLi (c = 1.70 M in *n*-pentane, 1.10 mL, 1.87 mmol, 2.02 equiv.) was added. The solution was stirred at -95 °C for 10 min and then transferred to the precooled solution of 2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranosyl bromide **154** in 2-MeTHF. The reaction mixture was warmed to 0 °C over 2 h. Then, MeOH (10.0 mL) was added and the solvent was removed in vacuum. The residue was dissolved in MeCN/H_2O (9:1, 10.0 mL) and PIFA (1.19 g, 2.77 mmol, 3.00 equiv.) was added. The reaction mixture was stirred for 30 min, then poured into saturated aqueous $NaHCO_3$-solution (20.0 mL) and extracted with Et_2O (3 × 20.0 mL). The combined organic layers were dried over $MgSO_4$, filtered and the solvent was removed in vacuum. The residue was purified by column chromatography (SiO_2, PE/EtOAc 9:1 → PE/EtOAc 2:1) to yield the *C*-glycosidic compound **171** (413 mg, 627 µmol, 68%) as colorless crystalline solid.

TLC: R_f = 0.49 (PE/EtOAc 4:1).

M.p.: 97 °C.

$[a]_D^{25}$ = 16.0 (c = 1.00, $CHCl_3$).

UV (MeCN): λ_{max} = 204, 284 nm.

IR (ATR): $\tilde{\nu}$ = 2867, 1679, 1602, 1496, 1454, 1351, 1303, 1254, 1179, 1084, 890, 839, 732, 694, 586 cm^{-1}.

^{1}H-NMR (600 MHz, $CDCl_3$): δ (ppm) = 3.63–3.72 (m, 3 H, 4'-H, 5'-H, 6'-H_A), 3.77 (d, J = 10.4 Hz, 1 H, 6'-H_B), 3.85 (t, J = 9.0 Hz, 1 H, 3'-H), 3.86 (s, 3 H, OCH_3), 4.03 (t, J = 9.0 Hz, 1 H, 2'-H), 4.51 (d, J = 12.1 Hz, 1 H, 6'-O-CH_A), 4.55 (d, J = 12.1 Hz, 1 H, 6'-O-CH_B), 4.58 (d, J = 10.5 Hz, 1 H, 2'-O-CH_A), 4.60 (d, J = 9.0 Hz, 1 H, 1'-H), 4.60 (d, J = 10.8 Hz, 1 H, 4'-O-CH_A), 4.69 (d, J = 10.5 Hz, 1 H, 2'-O-CH_B), 4.86 (d, J = 10.8 Hz, 1 H, 4'-O-CH_B), 4.91 (d, J = 11.0 Hz, 1 H, 3'-O-CH_A), 4.94 (d, J = 11.0 Hz, 1 H, 3'-OCH_B), 6.89 (d, J = 8.9 Hz, 1 H, 3-H, 5-H), 6.99–7.03 (m, 2 H, 2 × Ar-H), 7.16–7.22 (m, 5 H, 5 × Ar-H), 7.25–7.36 (m, 13 H, 13 × Ar-H), 8.06 (d, J = 8.9 Hz, 2 H, 2-H, 6-H).

^{13}C-NMR (151 MHz, $CDCl_3$): δ (ppm) = 55.6 (CH_3), 69.3 (C-6'), 73.6 (C-6'-O$\underline{C}H_2$), 75.1 (C-2'-O$\underline{C}H_2$), 75.3 (C-4'-O$\underline{C}H_2$), 75.9 (C-3'-O$\underline{C}H_2$), 78.2 (C-4'), 79.2 (C-1'), 79.9 (C-2'),

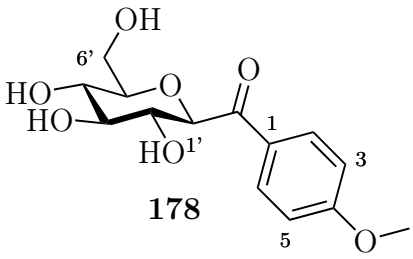
80.2 (C-5'), 87.2 (C-3'), 113.9 (2 C, C-3, C-5), 127.7, 127.8, 127.8, 127.8 (4 C), 128.0, 128.2 (2 C), 128.3 (2 C), 128.3 (2 C), 128.4 (2 C), 128.6 (4 C) (20 × C-Ar), 129.1 (C-1), 131.9 (2 C, C-2, C-6), 138.0, 138.1, 138.3, 138.7 (4 × C-Ar, quart.), 164.0 (C-4), 193.4 (CO).

MS (ESI): *m/z* (%) = 659.3 (100) $[M + H]^+$, 676.3 (60) $[M + NH_4]^+$, 681.3 (70) $[M + Na]^+$.

calcd.: 659.3003 $[M + H]^+$,
found: 659.3003 (ESI-HRMS).

$C_{42}H_{42}O_7$ (658.79).

6.8.3 (4-Methoxyphenyl)(β-D-glucopyranosyl) ketone 178



178

A solution of 1,2,3,4,6-pentakis-*O*-trimethylsilyl-D-glucopyranose **174** (500 mg, 924 µmol, 1.00 equiv.) in DCM (5.00 mL) was cooled to 0 °C, TMSI (150 µL, 211 µg, 1.05 mmol, 1.14 equiv.) was added and the solution was stirred at r.t. for 15 min. The solvent was removed in vacuum and 2,3,4,6-tetrakis-*O*-trimethylsilyl-α-D-glucopyranosyl iodide **175** was obtained as orange oil, which was dissolved in 2-MeTHF (5.00 mL) and cooled to -95 °C. In a seperate vessel, a solution of 2-(4-methoxyphenyl)-1,3-dithiane **151** (419 mg, 1.85 mmol, 2.00 equiv.) in 2-MeTHF (5.00 mL) was cooled to -95 °C and a solution of *t*-BuLi (c = 1.70 M in *n*-pentane, 1.10 mL, 1.87 mmol, 2.02 equiv.) was added. The solution was stirred at -95 °C for 10 min and then transferred to the precooled solution of 2,3,4,6-tetrakis-*O*-trimethylsilyl-α-D-glucopyranosyl iodide **175** in 2-MeTHF. The reaction mixture was warmed to 0 °C over 2 h. Then, MeOH (10.0 mL) and NaOMe (49.9 mg, 924 µmol, 1.00 equiv.) were added and the reaction mixture was stirred at r.t. for 10 min. Afterwards, the solvent was removed in vacuum. The residue was dissolved in MeOH/H_2O (9:1, 10.0 mL) and PIFA (1.19 g, 2.77 mmol, 3.00 equiv.) was added. The reaction mixture was stirred for 30 min, then diluted with water (20.0 mL) and washed with *n*-pentane (3 × 20.0 mL). The solvent was removed in vacuum and the

residue purified by reversed phase chromatography (RP-C18, $H_2O \rightarrow H_2O$/MeCN 3:1) to yield *C*-glycosidic compound **178** (170 mg, 570 µmol, 62%) as colorless crystalline solid.

TLC: R_f = 0.59 (EtOAc/MeCN/*n*-PrOH/H_2O 12:8:5:5).

M.p.: 92 °C.

$[\alpha]_D^{25}$ = -32.4 (c = 1.00, H_2O).

UV (H_2O): λ_{max} = 222, 290 nm.

IR (ATR): $\tilde{\nu}$ = 3384, 3302, 2919, 1664, 1597, 1511, 1422, 1252, 1173, 1014, 898, 837, 759, 615 cm^{-1}.

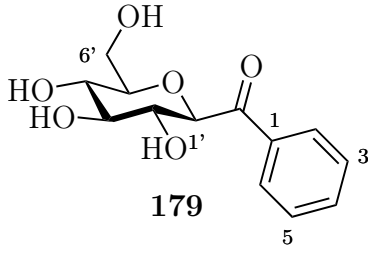
^{1}H-NMR (600 MHz, DMSO-d_6): δ (ppm) = 3.13 (td, J = 9.3, 4.9 Hz, 1 H, 4'-H), 3.29–3.36 (m, 2 H, 3'-H, 5'-H), 3.43 (dt, J = 11.8, 5.6 Hz, 1 H, 6'-H_A), 3.53 (td, J = 9.3, 5.6 Hz, 1 H, 2'-H), 3.68 (ddd, J = 11.8, 5.6, 1.8 Hz, 1 H, 6'-H_B), 3.85 (s, 3 H, CH_3), 4.49 (d, J = 9.3 Hz, 1 H, 1'-H), 4.50 (t, J = 5.6 Hz, 1 H, 6'-OH) 4.96–5.02 (m, 3 H, 2'-OH, 3'-OH, 4'-OH), 7.03–7.06 (m, 2 H, 3-H, 5-H), 8.00–8.03 (m, 2 H, 2-H, 6-H).

^{13}C-NMR (151 MHz, DMSO-d_6): δ (ppm) = 55.6 (CH_3), 61.1 (C-6'), 70.1 (C-4'), 71.3 (C2'), 78.1 (C-3'), 78.6 (C-1'), 81.6 (C-5'), 113.8 (2 C, C-3, C-5), 129.1 (C-1), 131.3 (C-2, C6), 163.3 (C-4), 194.1 (CO).
MS (ESI): m/z (%) = 321.1 (100) $[M + Na]^+$.

calcd.: 321.0945 $[M + Na]^+$,
found: 321.0940 (ESI-HRMS).

$C_{14}H_{18}O_7$ (298.29).

6.8.4 Phenyl (β-D-glucopyranosyl) ketone 179



179

A solution of 1,2,3,4,6-pentakis-*O*-trimethylsilyl-D-glucopyranose **174** (500 mg, 924 µmol, 1.00 equiv.) in DCM (5.00 mL) was cooled to 0 °C, TMSI (150 µL, 211 µg, 1.05 mmol, 1.14 equiv.) was added and the solution was stirred at r.t. for 15 min. The solvent was removed in vacuum and 2,3,4,6-tetrakis-*O*-trimethylsilyl-α-D-glucopyranosyl iodide **175** was obtained as orange oil, which was dissolved in 2-MeTHF (5.00 mL) and cooled to -95 °C. In a seperate vessel, a solution of 2-phenyl-1,3-dithiane **191** (363 mg, 1.85 mmol, 2.00 equiv.) in 2-MeTHF (5.00 mL) was cooled to -95 °C and a solution of *t*-BuLi (c = 1.70 M in *n*-pentane, 1.10 mL, 1.87 mmol, 2.02 equiv.) was added. The solution was stirred at -95 °C for 10 min and then transferred to the precooled solution of 2,3,4,6-tetrakis-*O*-trimethylsilyl-α-D-glucopyranosyl iodide **175** in 2-MeTHF. The reaction mixture was warmed to 0 °C over 2 h. Then, MeOH (10.0 mL) and NaOMe (49.9 mg, 924 µmol, 1.00 equiv.) were added and the reaction mixture was stirred at r.t. for 10 min. Afterwards, the solvent was removed in vacuum. The residue was dissolved in MeOH/H_2O (9:1, 10.0 mL) and PIFA (1.19 g, 2.77 mmol, 3.00 equiv.) was added. The reaction mixture was stirred for 30 min, then diluted with water (20.0 mL) and washed with *n*-pentane (3 × 20.0 mL). The solvent was removed in vacuum and the residue purified by reversed phase chromatography (RP-C18, H_2O → H_2O/MeCN 3:1) to yield *C*-glycosidic compound **179** (210 mg, 782 µmol, 85%) as colorless crystalline solid.

TLC: R_f = 0.73 (EtOAc/MeCN/*n*-PrOH/H_2O 12:8:5:5).

M.p.: 159 °C.

$[\alpha]_D^{25}$ = -18.2 (c = 1.00, H_2O).

UV (H_2O): λ_{max} = 254 nm.

IR (ATR): $\tilde{\nu}$ = 3335, 2926, 2865, 1686, 1597, 1451, 1357, 1211, 1083, 1010, 892, 828, 778, 711, 606 cm^{-1}.

^{1}H-NMR (600 MHz, DMSO-d_6): δ (ppm) = 3.14 (td, J = 9.3, 4.6 Hz, 1 H, 4'-H), 3.33–3.37 (m, 2 H, 3'-H, 5'-H), 3.44 (dt, J = 11.9, 5.6 Hz, 1 H, 6'-H_A), 3.54 (td, J = 9.2, 5.6 Hz, 1 H, 2'-H), 3.66–3.71 (ddd, J = 11.9, 5.6, 1.6 Hz, 1 H, 6'-H_B), 4.51 (t, J = 5.6 Hz, 1 H, 6'-OH), 4.54 (d, J = 9.5 Hz, 1 H, 1'-H), 5.00–5.06 (m, 2 H, 3'-OH, 4'-OH), 5.07 (d, J = 5.5 Hz, 1 H, 2'-OH), 7.54 (t, J = 7.5 Hz, 2 H, 3-H, 5-H), 7.65 (t, J = 7.5 Hz, 1 H, 4-H), 8.03 (d, J = 7.5 Hz, 2 H, 2-H, 6-H).

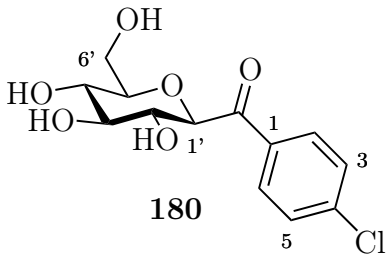
^{13}C-NMR (151 MHz, DMSO-d_6): δ (ppm) = 61.1 (C-6'), 70.1 (C-4'), 71.3 (C-2'), 78.1 (C-3'), 78.7 (C-1'), 81.7 (C-5'), 128.6 (2 C, C-3, C-5), 128.9 (2 C, C-2, C-6), 133.4 (C-4), 136.1 (C-1), 195.9 (CO).

MS (ESI): m/z (%) = 291.1 (100) $[M + Na]^+$.

calcd.: 291.0839 $[M + Na]^+$,
found: 291.0840 (ESI-HRMS).

$C_{13}H_{16}O_6$ (268.27).

6.8.5 (4-Chlorophenyl)(β-D-glucopyranosyl) ketone 180



180

To neat 1,2,3,4,6-pentakis-*O*-trimethylsilyl-D-glucopyranose **174** (500 mg, 924 µmol, 1.00 equiv.) was added TMSI (150 µL, 211 µg, 1.05 mmol, 1.14 equiv.) and the mixture was stirred at r.t. for 15 min to give 2,3,4,6-tetrakis-*O*-trimethylsilyl-α-D-glucopyranosyl iodide **175** as orange oil, which was dissolved in 2-MeTHF (5.00 mL) and cooled to -95 °C. In a seperate vessel, a solution of 2-(4-chlorophenyl)-1,3-dithiane **294** (427 mg, 1.85 mmol, 2.00 equiv.) in 2-MeTHF (5.00 mL) was cooled to -95 °C and a solution of *t*-BuLi (c = 1.74 M in *n*-pentane, 1.05 mL, 1.82 mmol, 1.98 equiv.) was added. The solution was stirred at -95 °C for 10 min and then transferred to the precooled solution of 2,3,4,6-tetrakis-*O*-trimethylsilyl-α-D-glucopyranosyl iodide **175** in 2-MeTHF. The reaction mixture was warmed to 0 °C over 2 h. Then, MeOH (35.0 mL) and NaOMe (49.9 mg, 924 µmol, 1.00 equiv.) were added and the reaction mixture was stirred at r.t. for 10 min. Afterwards, the mixture was diluted with water (5.00 mL), cooled to 0 °C and PIFA (994 mg, 2.31 mmol, 2.50 equiv.) was added. The reaction mixture was stirred at 0 °C for 10 min. Then, water (5.00 mL) and L-ascorbic acid (326 mg, 1.55 mmol, 2.00 equiv.) were added and the reaction mixture was stirred at r.t. for another 10 min, then diluted with water (10.0 mL) and washed with *n*-pentane (3 × 30.0 mL). MeOH was removed from the aqueous phase in vacuum. The remaining concentrated aqueous phase was filtered to remove solid impurities. Without further removal of the solvent, the aqueous phase was directly purified by reversed phase column chromatography (RP-C18, $H_2O \rightarrow H_2O$/MeCN 3:1) to yield *C*-glycosidic compound **180** (200 mg, 661 µmol, 72%) as colorless crystalline solid.

TLC: R_f = 0.21 (DCM/MeOH 9:1).

M.p.: 164 °C.

$[\alpha]_D^{25}$ = -13.0 (c = 1.00, MeCN).

UV (MeCN): λ_{max} = 256 nm.

IR (ATR): $\tilde{\nu}$ = 3323, 2947, 2912, 1686, 1676, 1651, 1595, 1421, 1400, 1251, 1076, 1018, 970, 744, 601 cm^{-1}.

^{1}H-NMR (600 MHz, methanol-d_4): δ (ppm) = 3.39 (t, J = 9.3 Hz, 1 H, 4'-H), 3.48 (ddd, J = 9.3, 5.6, 2.2 Hz, 1 H, 5'-H), 3.52 (t, J = 9.3 Hz, 1 H, 3'-H), 3.68 (dd, J = 12.2, 5.6 Hz, 1 H, 6'-H_A), 3.69 (t, J = 9.3 Hz, 1 H, 2'-H), 3.87 (dd, J = 12.2, 2.2 Hz, 1 H, 6'-H_B), 4.64 (d, J = 9.3 Hz, 1 H, 1'-H), 7.50–7.54 (m, 2 H, 3-H, 5-H), 8.05–8.11 (m, 2 H, 2-H, 6-H).

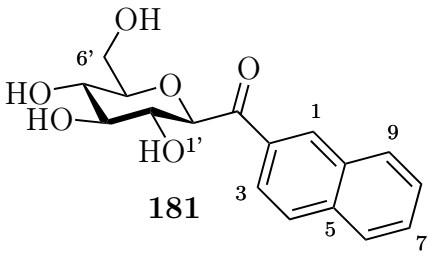
^{13}C-NMR (151 MHz, methanol-d_4): δ (ppm) = 62.7 (C-6'), 71.3 (C-4'), 72.9 (C-2'), 79.5 (C-3'), 80.6 (C-1'), 82.7 (C-5'), 129.8 (2 C, C-3, C-5), 132.1 (2 C, C-2, C-6), 136.0 (C-4), 141.0 (C-1), 196.9 (CO).

MS (ESI): m/z (%) = 325.1 (29) $[M + Na]^+$.

calcd.: 325.0449 $[M + Na]^+$,
found: 325.0453 (ESI-HRMS).

$C_{13}H_{15}ClO_6$ (302.71).

6.8.6 (Naphthalen-2-yl)(β-D-glucopyranosyl) ketone 181



181

To neat 1,2,3,4,6-pentakis-*O*-trimethylsilyl-D-glucopyranose **174** (500 mg, 924 µmol, 1.00 equiv.) was added TMSI (150 µL, 211 µg, 1.05 mmol, 1.14 equiv.) and the mixture was stirred at r.t. for 15 min to give 2,3,4,6-tetrakis-*O*-trimethylsilyl-α-D-glucopyranosyl

iodide **175** as orange oil, which was dissolved in 2-MeTHF (5.00 mL) and cooled to -95 °C. In a seperate vessel, a solution of 2-(naphthalen-2-yl)-1,3-dithiane **290** (455 mg, 1.85 mmol, 2.00 equiv.) in 2-MeTHF (5.00 mL) was cooled to -95 °C and a solution of *t*-BuLi (c = 1.73 M in *n*-pentane, 1.05 mL, 1.82 mmol, 1.97 equiv.) was added. The solution was stirred at -95 °C for 10 min and then transferred to the precooled solution of 2,3,4,6-tetrakis-*O*-trimethylsilyl-α-D-glucopyranosyl iodide **175** in 2-MeTHF. The reaction mixture was warmed to 0 °C over 2 h. Then, MeOH (35.0 mL) and NaOMe (49.9 mg, 924 µmol, 1.00 equiv.) were added and the reaction mixture was stirred at r.t. for 10 min. Afterwards, the mixture was diluted with water (5.00 mL), cooled to 0 °C and PIFA (994 mg, 2.31 mmol, 2.50 equiv.) was added. The reaction mixture was stirred at 0 °C for 10 min. Then, water (5.00 mL) and L-ascorbic acid (326 mg, 1.55 mmol, 2.00 equiv.) were added and the reaction mixture was stirred at r.t. for another 10 min, then diluted with water (10.0 mL) and washed with *n*-pentane (3 × 30.0 mL). MeOH was removed from the aqueous phase in vacuum. The remaining concentrated aqueous phase was filtered to remove solid impurities. Without further removal of the solvent, the aqueous phase was directly purified by reversed phase column chromatography (RP-C18, $H_2O \rightarrow H_2O$/MeCN 3:1) to yield *C*-glycosidic compound **181** (240 mg, 754 µmol, 82%) as colorless crystalline solid.

TLC: R_f = 0.22 (DCM/MeOH 9:1).

M.p.: 171 °C.

$[a]_D^{25}$ = -38.4 (c = 1.00, MeCN).

UV (MeCN): λ_{max} = 208, 250, 284, 335 nm.

IR (ATR): $\tilde{\nu}$ = 3315, 2949, 2900, 1667, 1595, 1458, 1421, 1394, 1255, 1078, 1018, 835, 761, 603, 476 cm^{-1}.

^{1}H-NMR (600 MHz, methanol-d_4): δ (ppm) = 3.45 (t, J = 9.3 Hz, 1 H, 4'-H), 3.57 (ddd, J = 9.3, 5.6, 2.2 Hz, 1 H, 5'-H), 3.60 (t, J = 9.3 Hz, 1 H, 3'-H), 3.71 (dd, J = 12.3, 5.6 Hz, 1 H, 6'-H_A), 3.77 (t, J = 9.3 Hz, 1 H, 2'-H), 3.90 (dd, J = 12.3, 2.2 Hz, 1 H, 6'-H_B), 4.88 (d, J = 9.3 Hz, 1 H, 1'-H), 7.56–7.61 (m, 1 H, 7-H), 7.62–7.66 (m, 1 H, 8-H), 7.90–7.96 (m, 2 H, 4-H, 9-H), 8.06–8.11 (m, 2 H, 3-H, 6-H), 8.73 (s, 1 H, 1-H).

^{13}C-NMR (151 MHz, methanol-d_4): δ (ppm) = 62.8 (C-6'), 71.4 (C-4'), 73.1 (C-2'), 79.6 (C-3'), 80.4 (C-1'), 82.7 (C-5'), 125.3 (C-3), 127.9 (C-7), 128.8 (C-9), 129.3 (C-4), 130.0 (C-8), 131.0 (C-6), 133.1 (C-1), 134.0 (C-10), 134.8 (C-2), 137.3 (C-5), 198.1 (CO).

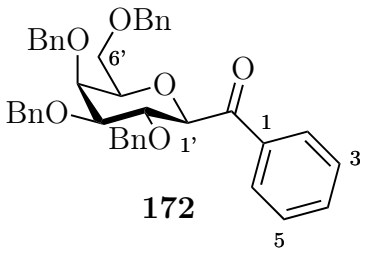
MS (ESI): m/z (%) = 341.1 (100) $[M + Na]^+$.

calcd.: 341.0996 $[M + Na]^+$,
found: 341.0992 (ESI-HRMS).

$C_{13}H_{15}ClO_6$ (302.71).

6.9 Syntheses of β-carbonyl-*C*-galactopyranosides

6.9.1 Phenyl (2,3,4,6-tetra-*O*-benzyl-β-D-galactopyranosyl) ketone 172



172

A solution of 2,3,4,6-tetra-*O*-benzyl-D-galactopyranose **161** (500 mg, 925 µmol, 1.00 equiv.) in DCM (5.00 mL) was cooled to 0 °C, oxalyl bromide (108 µL, 248 µg, 1.15 µmol, 1.24 equiv.) was added and the solution was stirred at r.t. for 1 h. The solvent was removed in vacuum and 2,3,4,6-tetra-*O*-benzyl-α-D-galactopyranosyl bromide **303** was obtained as orange oil, which was dissolved in 2-MeTHF (5.00 mL) and cooled to -95 °C. In a seperate vessel, a solution of 2-phenyl-1,3-dithiane **191** (363 mg, 1.85 mmol, 2.00 equiv.) in 2-MeTHF (5.00 mL) was cooled to -95 °C and a solution of *t*-BuLi (c = 1.70 M in *n*-pentane, 1.10 mL, 1.87 mmol, 2.02 equiv.) was added. The solution was stirred at -95 °C for 10 min and then transferred to the precooled solution of 2,3,4,6-tetra-*O*-benzyl-α-D-galactopyranosyl bromide **303** in 2-MeTHF. The reaction mixture was warmed to 0 °C over 2 h. Then, MeOH (10.0 mL) was added and the solvent was removed in vacuum. The residue was dissolved in MeCN/H_2O (9:1, 10.0 mL) and PIFA (1.19 g, 2.77 mmol, 3.00 equiv.) was added. The reaction mixture was stirred for 30 min, then poured into saturated aqueous $NaHCO_3$-solution (20.0 mL) and extracted with Et_2O (3 × 20.0 mL). The combined organic layers were dried over $MgSO_4$, filtered and the solvent was removed in vacuum. The residue was purified by column chromatography (SiO_2, PE/EtOAc 9:1 → PE/EtOAc 2:1) to yield the *C*-glycosidic compound **172** (352 mg, 559 µmol, 60%) as colorless crystalline solid.

TLC: R_f = 0.57 (PE/EtOAc 4:1).

M.p.: 107 °C.

$[\alpha]_D^{25} = 5.6$ (c = 1.00, $CHCl_3$).

UV (H_2O): $\lambda_{max} = 203, 247$ nm.

IR (ATR): $\tilde{\nu} =$ 2882, 1684, 1596, 1496, 1452, 1361, 1308, 1248, 1091, 907, 838, 733, 694 cm^{-1}.

^{1}H-NMR (600 MHz, $CDCl_3$): δ (ppm) = 3.61 (d, $J = 6.3$ Hz, 2 H, 6'-H_2), 3.73–3.77 (m, 2 H, 3'-H, 5'-H), 4.06 (d, $J = 2.4$ Hz, 1 H, 4'-H), 4.40 (d, $J = 11.8$ Hz, 1 H, 6'-O-CH_A), 4.45 (d, $J = 11.8$ Hz, 1 H, 6'-O-CH_B), 4.46 (t, $J = 9.0$ Hz, 1 H, 2'-H), 4.48 (d, $J = 9.0$ Hz, 1 H, 1'-H), 4.59 (d, $J = 10.4$ Hz, 1 H, 2'-O-CH_A), 4.65 (d, $J = 11.5$ Hz, 1 H, 4'-O-CH_A), 4.75 (d, $J = 11.7$ Hz, 1 H, 3'-O-CH_A), 4.77 (d, $J = 10.4$ Hz, 1 H, 2'-O-CH_B), 4.80 (d, $J = 11.7$ Hz, 1 H, 3'-O-CH_B), 5.03 (d, $J = 11.5$ Hz, 1 H, 4'-O-CH_B), 7.05–7.11 (m, 2 H, 2 × Ar-H), 7.17–7.20 (m, 3 H, 3 × Ar-H), 7.23–7.26 (m, 2 H, 2 × Ar-H), 7.27–7.40 (m, 15 H, 3-H, 5-H, 13 × Ar-H), 7.53 (t, $J = 7.4$ Hz, 1 H, 4-H), 8.09–8.15 (m, 2 H, 2-H, 6-H).

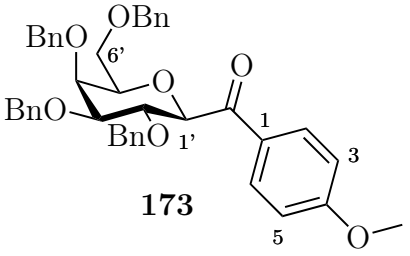
^{13}C-NMR (151 MHz, $CDCl_3$): δ (ppm) = 69.1 (C-6'), 72.6 (C-3'-O$\underline{C}H_2$), 73.7 (C-6'O$\underline{C}H_2$), 73.7 (C-4'), 74.6 (C-4'-O$\underline{C}H_2$), 75.3 (C-2'-O$\underline{C}H_2$), 76.1 (C-2'), 78.3 (C-5'), 81.1 (C-1'), 84.6 (C-3'), 127.7 (3 C), 127.7, 127.9, 127.9, 128.0 (2 C), 128.0 (2 C), 128.3 (2 C), 128.4 (2 C), 128.4 (2 C), 128.5 (2 C), 128.6 (2 C), 128.6 (2 C) (C-3, C-5, 20 × C-Ar), 129.7 (2 C, C-2, C-6), 133.4 (C-4), 135.6 (C-1), 138.0, 138.2, 138.4, 138.8 (4 × C-Ar, quart.), 194.7 (CO).

MS (ESI): m/z (%) = 521.2 (44) [M - OBn]$^+$, 629.3 (5) [M + H]$^+$, 646.3 (100) [M + NH_4]$^+$, 651.3 (61) [M + Na]$^+$.

calcd.: 646.3163 [M + NH_4]$^+$],
found: 646.3161 (ESI-HRMS).

$C_{41}H_{40}O_6$ (628.77).

6.9.2 (4-Methoxyphenyl)(2,3,4,6-tetra-*O*-benzyl-β-D-galactopyranosyl) ketone 173



173

A solution of 2,3,4,6-tetra-*O*-benzyl-D-galactopyranose **161** (500 mg, 925 µmol, 1.00 equiv.) in DCM (5.00 mL) was cooled to 0 °C, oxalyl bromide (108 µL, 248 µg, 1.15 µmol, 1.24 equiv.) was added and the solution was stirred at r.t. for 1 h. The solvent was removed in vacuum and 2,3,4,6-tetra-*O*-benzyl-α-D-galactopyranosyl bromide **303** was obtained as orange oil, which was dissolved in 2-MeTHF (5.00 mL) and cooled to -95 °C. In a seperate vessel, a solution of 2-(4-methoxyphenyl)-1,3-dithiane **151** (419 mg, 1.85 mmol, 2.00 equiv.) in 2-MeTHF (5.00 mL) was cooled to -95 °C and a solution of *t*-BuLi (c = 1.70 M in *n*-pentane, 1.10 mL, 1.87 mmol, 2.02 equiv.) was added. The solution was stirred at -95 °C for 10 min and then transferred to the precooled solution of 2,3,4,6-tetra-*O*-benzyl-α-D-galactopyranosyl bromide **303** in 2-MeTHF. The reaction mixture was warmed to 0 °C over 2 h. Then, MeOH (10.0 mL) was added and the solvent was removed in vacuum. The residue was dissolved in MeCN/H_2O (9:1, 10.0 mL) and PIFA (1.19 g, 2.77 mmol, 3.00 equiv.) was added. The reaction mixture was stirred for 30 min, then poured into saturated aqueous $NaHCO_3$-solution (20.0 mL) and extracted with Et_2O (3 × 20.0 mL). The combined organic layers were dried over $MgSO_4$, filtered and the solvent was removed in vacuum. The residue was purified by column chromatography (SiO_2, PE/EtOAc 9:1 → PE/EtOAc 2:1) to yield the *C*-glycosidic compound **173** (376 mg, 571 µmol, 62%) as colorless crystalline solid.

TLC: R_f = 0.43 (PE/EtOAc 4:1).

M.p.: 124 °C.

$[\alpha]_D^{25}$ = -0.6 (c = 1.00, $CHCl_3$).

UV (MeCN): λ_{max} = 208, 281 nm.

IR (ATR): $\tilde{\nu}$ = 2877, 1674, 1599, 1510, 1454, 1361, 1252, 1173, 1097, 1026, 897, 833, 732, 695, 602 cm^{-1}.

^{1}H-NMR (600 MHz, $CDCl_3$): δ (ppm) = 3.60 (dd, J = 9.6, 6.3, Hz, 1 H, 6'-H_A), 3.62 (dd, J = 9.6, 6.3, Hz, 1 H, 6'-H_B), 3.72 (t, J = 6.3 Hz, 1 H, 5'-H), 3.74 (dd, J = 9.2, 2.6 Hz, 2 H, 3'-H), 3.84 (s, 3 H, CH_3), 4.06 (d, J = 2.6 Hz, 1 H, 4'-H), 4.41 (d, J = 11.8 Hz, 1 H, 6'-O-CH_A), 4.42 (d, J = 9.2 Hz, 1 H, 1'-H), 4.45 (t, J = 9.2 Hz, 1 H, 2'-H), 4.47 (d, J = 11.8 Hz, 1 H, 6'-O-CH_B), 4.57 (d, J = 10.4 Hz, 1 H, 2'-O-CH_A), 4.64 (d, J = 11.4 Hz, 1 H, 4'-O-CH_A), 4.74 (d, J = 10.4 Hz, 1 H, 2'-O-CH_B), 4.76 (d, J = 11.8 Hz, 1 H, 3'-O-CH_A), 4.80 (d, J = 11.8 Hz, 1 H, 3'-O-CH_B), 5.03 (d, J = 11.4 Hz, 1 H, 4'-O-CH_B), 6.79–6.83 (m, 2 H, 3-H, 5-H), 7.08–7.12 (m, 2 H, 2 × Ar-H), 7.16–7.21 (m, 3 H, 3 × Ar-H), 7.24–7.40 (m, 15 H, 15 × Ar-H), 8.09–8.15 (m, 2 H, 2-H, 6-H).

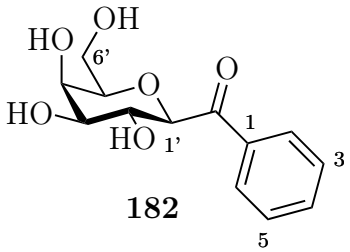
^{13}C-NMR (151 MHz, $CDCl_3$): δ (ppm) = 55.6 (CH_3), 69.1 (C-6'), 72.6 (C-3'-O$\underline{C}H_2$), 73.7 (C-6'-O$\underline{C}H_2$), 73.7 (C-4'), 74.6 (C-4'-O$\underline{C}H_2$), 75.2 (C-2'-O$\underline{C}H_2$), 76.3 (C-2'), 78.1 (C-5'), 81.5 (C-1'), 84.6 (C-3'), 113.7 (2 C, C-3, C-5), 127.7 (4 C), 127.8, 127.9, 128.0 (2 C), 128.1 (2 C), 128.3 (2 C), 128.4 (2 C), 128.4 (2 C), 128.5 (2 C), 128.6 (2 C) (20 × C-Ar), 128.6 (C-1), 132.2 (2 C, C-2, C-6), 138.0, 138.2, 138.5, 138.9 (4 × C-Ar, quart.), 163.7 (C-4), 193.3 (CO).

MS (ESI): *m/z* (%) = 551.2 (44) $[M - OBn]^+$, 659.3 (61) $[M + H]^+$, 676.3 (100) $[M + NH_4]^+$, 681.3 (61) $[M + Na]^+$.

calcd.: 676.3269 $[M + Na]^+$,
found: 676.3268 (ESI-HRMS).

$C_{42}H_{42}O_7$ (658.79).

6.9.3 Phenyl (β-D-galactopyranosyl) ketone 182



182

A solution of 1,2,3,4,6-pentakis-*O*-trimethylsilyl-D-galactopyranose **304** (500 mg, 924 µmol, 1.00 equiv.) in DCM (5.00 mL) was cooled to 0 °C, TMSI (150 µL, 211 µg, 1.05 mmol, 1.14 equiv.) was added and the solution was stirred at r.t. for 15 min. The solvent was removed in vacuum and 2,3,4,6-tetrakis-*O*-trimethylsilyl-α-D-galactopyranosyl iodide **305** was obtained as orange oil, which was dissolved in 2-MeTHF (5.00 mL) and cooled to -95 °C. In a seperate vessel, a solution of 2-phenyl-1,3-dithiane **191** (363 mg, 1.85 mmol, 2.00 equiv.) in 2-MeTHF (5.00 mL) was cooled to -95 °C and a solution of *t*-BuLi (c = 1.70 M in *n*-pentane, 1.10 mL, 1.87 mmol, 2.02 equiv.) was added. The solution was stirred at -95 °C for 10 min and then transferred to the precooled solution of 2,3,4,6-tetrakis-*O*-trimethylsilyl-α-D-galactopyranosyl iodide **305** in 2-MeTHF. The reaction mixture was warmed to 0 °C over 2 h. Then, MeOH (10.0 mL) and NaOMe (49.9 mg, 924 µmol, 1.00 equiv.) were added and the reaction mixture was stirred at r.t. for 10 min. Afterwards, the solvent was removed in vacuum. The residue was dissolved

in MeOH/H_2O (9:1, 10.0 mL) and PIFA (1.19 g, 2.77 mmol, 3.00 equiv.) was added. The reaction mixture was stirred for 30 min, then diluted with water (20.0 mL) and washed with *n*-pentane (3×20.0 mL). The solvent was removed in vacuum and the residue purified by reversed phase chromatography (RP-C18, $H_2O \rightarrow H_2O$/MeCN 3:1) to yield *C*-glycosidic compound **182** (181 mg, 675 µmol, 73%) as colorless crystalline solid.

TLC: R_f = 0.57 (EtOAc/MeCN/*n*-PrOH/H_2O 12:8:5:5).

M.p.: 158 °C.

$[a]_D^{25}$ = -6.6 (c = 1.00, H_2O).

UV (H_2O): λ_{max} = 252 nm.

IR (ATR): $\tilde{\nu}$ = 3464, 3329, 2919, 1675, 1597, 1450, 1361, 1213, 1041, 984, 930, 878, 714, 613 cm^{-1}.

^{1}H-NMR (600 MHz, DMSO-d_6): δ (ppm) = 3.41–3.46 (m, 1 H, 3'-H), 3.46–3.59 (m, 3 H, 5'-H, $2 \times$ 6'-H), 3.77 (t, J = 3.3 Hz, 1 H, 4'-H), 3.92 (td, J = 9.4, 5.7 Hz, 1 H, 2'-H), 4.32 (d, J = 9.4 Hz, 1 H, 1'-H), 4.57–4.63 (m, 2 H, 4'-OH, 6'-OH), 4.81–4.86 (m, 1 H, 3'-OH), 4.91 (d, J = 5.7 Hz, 1 H, 2'-OH), 7.52 (t, J = 7.6 Hz, 2 H, 3-H, 5-H), 7.64 (t, J = 7.6 Hz, 1 H, 4-H), 8.10 (d, J = 7.6 Hz, 2 H, 2-H, 6-H).

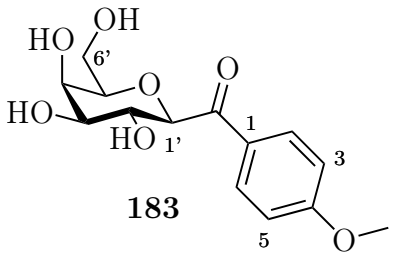
^{13}C-NMR (151 MHz, DMSO-d_6): δ (ppm) = 61.3 (C-6'), 68.6 (C-2'), 69.1 (C-4'), 75.1 (C-3'), 80.4 (C-5'), 81.6 (C-1'), 129.0 (2 C, C-3, C-5), 129.6 (2 C, C-2, C-6), 133.8 (C-4), 136.1 (C-1), 196.3 (CO).

MS (ESI): *m/z* (%) = 291.1 (100) $[M + Na]^+$.

calcd.: 291.0830 $[M + Na]^+$,
found: 291.0840 (ESI-HRMS).

$C_{13}H_{16}O_6$ (268.27).

6.9.4 (4-Methoxyphenyl)(β-D-galactopyranosyl) ketone 183



183

A solution of 1,2,3,4,6-pentakis-*O*-trimethylsilyl-D-galactopyranose **304** (500 mg, 924 µmol, 1.00 equiv.) in DCM (5.00 mL) was cooled to 0 °C, TMSI (150 µL, 211 µg, 1.05 mmol, 1.14 equiv.) was added and the solution was stirred at r.t. for 15 min. The solvent was removed in vacuum and 2,3,4,6-tetrakis-*O*-trimethylsilyl-α-D-galactopyranosyl iodide **305** was obtained as orange oil, which was dissolved in 2-MeTHF (5.00 mL) and cooled to -95 °C. In a seperate vessel, a solution of 2-(4-methoxyphenyl)-1,3-dithiane **151** (419 mg, 1.85 mmol, 2.00 equiv.) in 2-MeTHF (5.00 mL) was cooled to -95 °C and a solution of *t*-BuLi (c = 1.70 M in *n*-pentane, 1.10 mL, 1.87 mmol, 2.02 equiv.) was added. The solution was stirred at -95 °C for 10 min and then transferred to the precooled solution of 2,3,4,6-tetrakis-*O*-trimethylsilyl-α-D-galactopyranosyl iodide **305** in 2-MeTHF. The reaction mixture was warmed to 0 °C over 2 h. Then, MeOH (10.0 mL) and NaOMe (49.9 mg, 924 µmol, 1.00 equiv.) were added and the reaction mixture was stirred at r.t. for 10 min. Afterwards, the solvent was removed in vacuum. The residue was dissolved in MeOH/H_2O (9:1, 10.0 mL) and PIFA (1.19 g, 2.77 mmol, 3.00 equiv.) was added. The reaction mixture was stirred for 30 min, then diluted with water (20.0 mL) and washed with *n*-pentane (3 × 20.0 mL). The solvent was removed in vacuum and the residue purified by reversed phase chromatography (RP-C18, H_2O → H_2O/MeCN 3:1) to yield *C*-glycosidic compound **183** (140 mg, 446 µmol, 48%) as colorless crystalline solid.

TLC: R_f = 0.54 (EtOAc/MeCN/*n*-PrOH/H_2O 12:8:5:5).

M.p.: 183 °C.

$[\alpha]_D^{25}$ = -1.6 (c = 1.00, H_2O).

UV (H_2O): λ_{max} = 222, 289 nm.

IR (ATR): $\tilde{\nu}$ = 3458, 3337, 2962, 1673, 1600, 1510, 1420, 1261, 1216, 1174, 1043, 876, 786, 740, 610 cm^{-1}.

^{1}H-NMR (600 MHz, DMSO-d_6): δ (ppm) = 3.42 (ddd, J = 9.3, 5.8, 3.5 Hz, 1 H, 3'-H), 3.46–3.55 (m, 3 H, 5'-H, 6'-H_2), 3.77 (t, J = 3.5 Hz, 1 H, 4'-H), 3.84 (s, 3 H, CH_3), 3.91 (td, J = 9.3, 5.9 Hz, 1 H, 2'-H), 4.24 (d, J = 9.3 Hz, 1 H, 1'-H), 4.57 (d, J = 3.9 Hz, 1 H, 4'-OH), 4.59 (t, J = 5.2 Hz, 1 H, 6'-OH), 4.79 (d, J = 5.8 Hz, 1 H, 3'-OH), 4.84 (d, J = 5.9 Hz, 1 H, 2'-OH), 7.01–7.05 (m, 2 H, 3-H, 5-H), 8.06–8.08 (m, 2 H, 2-H, 6-H).

^{13}C-NMR (151 MHz, DMSO-d_6): δ (ppm) = 55.5 (CH_3), 60.8 (C-6'), 68.2 (C-2'), 68.6 (C-4'), 74.6 (C-3'), 79.8 (C-5'), 81.3 (C-1'), 113.7 (2 C, C-3, C-5), 128.5 (C-1), 131.5 (2 C, C-2, C-6), 163.2 (C-4), 194.2 (CO).

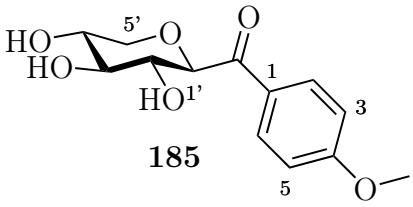
MS (ESI): m/z (%) = 321.1 (100) $[M + Na]^+$.

calcd.: 321.0945 $[M + Na]^+$,
found: 321.0947 (ESI-HRMS).

$C_{14}H_{18}O_7$ (298.29).

6.10 Syntheses of β-carbonyl-*C*-xylopyranosides

6.10.1 (4-Methoxyphenyl)(β-D-xylopyranosyl) ketone 185



185

A solution of 1,2,3,4,-tetrakis-*O*-trimethylsilyl-D-xylopyranose **306** (405 mg, 925 µmol, 1.00 equiv.) in DCM (5.00 mL) was cooled to 0 °C, TMSI (150 µL, 211 µg, 1.05 mmol, 1.14 equiv.) was added and the solution was stirred at r.t. for 15 min. The solvent was removed in vacuum and 2,3,4-tris-*O*-trimethylsilyl-α-D-xylopyranosyl iodide **307** was obtained as yellow oil, which was dissolved in 2-MeTHF (5.00 mL) and cooled to -95 °C. In a seperate vessel, a solution of 2-(4-methoxyphenyl)-1,3-dithiane **151** (419 mg, 1.85 mmol, 2.00 equiv.) in 2-MeTHF (5.00 mL) was cooled to -95 °C and a solution of *t*-BuLi (c = 1.70 M in *n*-pentane, 1.10 mL, 1.87 mmol, 2.02 equiv.) was added. The solution was stirred at -95 °C for 10 min and then transferred to the precooled solution of 2,3,4-tris-*O*-trimethylsilyl-α-D-xylopyranosyl iodide **307** in 2-MeTHF. The reaction mixture was warmed to 0 °C over 2 h. Then, MeOH (10.0 mL) and NaOMe (49.9 mg, 924 µmol, 1.00 equiv.) were added and the reaction mixture was stirred at r.t. for 10 min. Afterwards, the solvent was removed in vacuum. The residue was dissolved in MeOH/H_2O (9:1, 10.0 mL) and PIFA (1.19 g, 2.77 mmol, 3.00 equiv.) was added. The reaction mixture was stirred for 30 min, then diluted with water (20.0 mL) and washed with *n*-pentane (3 × 20.0 mL). The solvent was removed in vacuum and the residue purified by reversed phase chromatography (RP-C18, $H_2O \rightarrow H_2O$/MeCN 3:1) to yield *C*-glycosidic compound **185** (246 mg, 917 µmol, 99%) as colorless crystalline solid.

TLC: R_f = 0.80 (EtOAc/MeCN/*n*-PrOH/H_2O 12:8:5:5).

M.p.: 158 °C.

$[\alpha]_D^{25}$ = -23.0 (c = 1.00, MeOH).

UV (MeOH): λ_{max} = 201, 220, 283 nm.

IR (ATR): $\tilde{\nu}$ = 3328, 2913, 2843, 1679, 1602, 1574, 1247, 1174, 1091, 1059, 1017, 986, 638, 617, 566 cm^{-1}.

^{1}H-NMR (600 MHz, methanol-d_4): δ (ppm) = 3.39 (t, J = 10.8 Hz, 1 H, 5'-H_A), 3.46 (t, J = 9.2 Hz, 1 H, 3'-H), 3.57 (ddd, J = 10.8, 9.2, 5.4 Hz, 1 H, 4'-H), 3.71 (t, J = 9.2 Hz, 1 H, 2'-H), 3.88 (s, 3 H, CH_3), 3.97 (dd, J = 10.8, 5.4 Hz, 1 H, 5'-H_B), 4.55 (d, J = 9.2 Hz, 1 H, 1'-H), 6.99–7.04 (m, 2 H, 3-H, 5-H), 8.02–8.07 (m, 2 H, 2-H, 6-H).

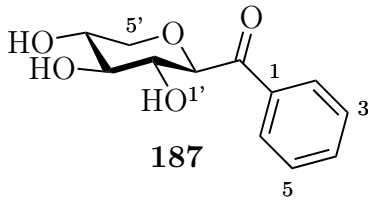
^{13}C-NMR (151 MHz, methanol-d_4): δ (ppm) = 56.1 (CH_3), 71.1 (C-4'), 71.4 (C-5'), 72.8 (C-2'), 79.6 (C-3'), 81.0 (C-1'), 114.8 (2 C, C-3, C-5), 130.3 (C-1), 132.8 (2 C, C-2, C-6), 165.7 (C-4), 196.2 (CO).

MS (ESI): m/z (%) = 269.1 (33) $[M + H]^+$, 291.1 (100) $[M + Na]^+$, 559.2 (100) $[2\ M + Na]^+$.

calcd.: 291.0839 $[M + Na]^+$,
found: 291.0838 (ESI-HRMS).

$C_{13}H_{16}O_6$ (268.27).

6.10.2 Phenyl (β-D-xylopyranosyl) ketone 187



187

A solution of 1,2,3,4,-tetrakis-*O*-trimethylsilyl-D-xylopyranose **306** (405 mg, 925 µmol, 1.00 equiv.) in DCM (5.00 mL) was cooled to 0 °C, TMSI (150 µL, 211 µg, 1.05 mmol, 1.14 equiv.) was added and the solution was stirred at r.t. for 15 min. The solvent was removed in vacuum and 2,3,4-tris-*O*-trimethylsilyl-α-D-xylopyranosyl iodide **307** was obtained as yellow oil, which was dissolved in 2-MeTHF (5.00 mL) and cooled to -95 °C. In a seperate vessel, a solution of 2-phenyl-1,3-dithiane **191** (363 mg, 1.85 mmol, 2.00 equiv.)

in 2-MeTHF (5.00 mL) was cooled to -95 °C and a solution of *t*-BuLi (c = 1.70 M in *n*-pentane, 1.10 mL, 1.87 mmol, 2.02 equiv.) was added. The solution was stirred at -95 °C for 10 min and then transferred to the precooled solution of 2,3,4-tris-*O*-trimethylsilyl-α-D-xylopyranosyl iodide **307** in 2-MeTHF. The reaction mixture was warmed to 0 °C over 2 h. Then, MeOH (10.0 mL) and NaOMe (49.9 mg, 924 µmol, 1.00 equiv.) were added and the reaction mixture was stirred at r.t. for 10 min. Afterwards, the solvent was removed in vacuum. The residue was dissolved in MeOH/H_2O (9:1, 10.0 mL) and PIFA (1.19 g, 2.77 mmol, 3.00 equiv.) was added. The reaction mixture was stirred for 30 min, then diluted with water (20.0 mL) and washed with *n*-pentane (3 × 20.0 mL). The solvent was removed in vacuum and the residue purified by reversed phase chromatography (RP-C18, H_2O → H_2O/MeCN 3:1) to yield *C*-glycosidic compound **187** (185 mg, 777 µmol, 84%) as colorless crystalline solid.

TLC: R_f = 0.82 (EtOAc/MeCN/*n*-PrOH/H_2O 12:8:5:5).

M.p.: 179 °C.

$[a]_D^{25}$ = -29.6 (c = 1.00, MeOH).

UV (MeOH): λ_{max} = 203, 247 nm.

IR (ATR): $\tilde{\nu}$ = 3365, 2921, 2870, 1678, 1371, 1222, 1129, 1091, 1063, 1011, 973, 713, 687, 616, 556 cm^{-1}.

^{1}H-NMR (600 MHz, methanol-d_4): δ (ppm) = 3.41 (t, J = 10.7 Hz, 1 H, 5'-H_A), 3.47 (t, J = 9.1 Hz, 1 H, 3'-H), 3.57 (ddd, J = 10.7, 9.1, 5.3 Hz, 1 H, 4'-H), 3.73 (t, J = 9.1 Hz, 1 H, 2'-H), 3.98 (dd, J = 10.7, 5.3 Hz, 1 H, 5'-H_B), 4.59 (d, J = 9.1 Hz, 1 H, 1'-H), 7.53–7.48 (m, 2 H, 3-H, 5-H), 7.64–7.60 (m, 1 H, 4-H), 8.07–8.03 (m, 2 H, 2-H, 6-H).

^{13}C-NMR (151 MHz, methanol-d_4): δ (ppm) = 71.1 (C-4'), 71.4 (C-5'), 72.8 (C-2'), 79.5 (C-3'), 81.1 (C-1'), 129.6 (2 C, C-3, C-5), 130.3 (2 C, C-2, C-6), 134.7 (C-4), 137.4 (C-1), 197.6 (CO).

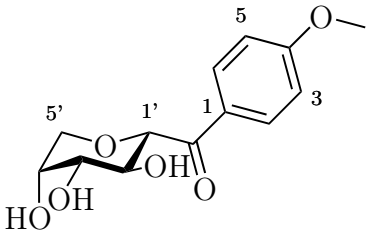
MS (ESI): m/z (%) = 261.1 (100) $[M + Na]^+$.

calcd.: 261.0733 $[M + Na]^+$,
found: 261.0731 (ESI-HRMS).

$C_{12}H_{14}O_5$ (238.24).

6.11 Syntheses of α carbonyl-*C*-D-arabinopyranosides

6.11.1 (4-Methoxyphenyl)(α-D-arabinopyranosyl) ketone 184



184

To neat 1,2,3,4-tetrakis-*O*-trimethylsilyl-D-arabinopyranose **308** (405 mg, 925 µmol, 1.00 equiv.) was added TMSI (150 µL, 211 µg, 1.05 mmol, 1.14 equiv.) and the mixture was stirred at r.t. for 15 min to give 2,3,4-tris-*O*-trimethylsilyl-α-D-arabinopyranosyl iodide **309** as orange oil, which was dissolved in 2-MeTHF (5.00 mL) and cooled to -95 °C. In a seperate vessel, a solution of 2-(4-methoxyphenyl)-1,3-dithiane **151** (419 mg, 1.85 mmol, 2.00 equiv.) in 2-MeTHF (5.00 mL) was cooled to -95 °C and a solution of *t*-BuLi (c = 1.70 M in *n*-pentane, 1.10 mL, 1.87 mmol, 2.02 equiv.) was added. The solution was stirred at -95 °C for 10 min and then transferred to the precooled solution of 2,3,4-tris-*O*-trimethylsilyl-α-D-arabinopyranosyl iodide **309** in 2-MeTHF. The reaction mixture was warmed to 0 °C over 2 h. Then, MeOH (35.0 mL) and NaOMe (49.9 mg, 924 µmol, 1.00 equiv.) were added and the reaction mixture was stirred at r.t. for 10 min. Afterwards, the mixture was diluted with water (5.00 mL), cooled to 0 °C and PIFA (994 mg, 2.31 mmol, 2.50 equiv.) was added. The reaction mixture was stirred at 0 °C for 10 min. Then, water (5.00 mL) and L-ascorbic acid (326 mg, 1.55 mmol, 2.00 equiv.) were added and the reaction mixture was stirred at r.t. for another 10 min, then diluted with water (10.0 mL) and washed with *n*-pentane (3 × 30.0 mL). MeOH was removed from the aqueous phase in vacuum. The remaining concentrated aqueous phase was filtered to remove solid impurities. Without further removal of the solvent, the aqueous phase was directly purified by reversed phase column chromatography (RP-C18, $H_2O \rightarrow H_2O$/MeCN 3:1) to yield *C*-glycosidic compound **184** (193 mg, 719 µmol, 78%) as colorless crystalline solid.

TLC: R_f = 0.43 (DCM/MeOH 9:1).

M.p.: 132 °C.

$[a]_D^{25}$ = -17.0 (c = 1.00, MeCN).

UV (MeCN): λ_{max} = 219, 277 nm.

IR (ATR): $\tilde{\nu}$ = 3393, 2964, 2937, 2906, 2856, 1681, 1267, 1238, 1176, 1091, 1064, 1008, 887, 833, 648 cm^{-1}.

^{1}H-NMR (600 MHz, methanol-d_4): δ (ppm) = 3.63 (dd, J = 9.3, 3.5 Hz, 1 H, 3'-H), 3.76 (dd, J = 12.3, 1.3 Hz, 1 H, 5'-H_A), 3.88 (s, 3 H, 4-OC$\underline{H_3}$), 3.92 (ddd, J = 3.5, 2.2, 1.3 Hz, 1 H, 4'-H), 4.00 (dd, J = 12.3, 2.2 Hz, 1 H, 5'-H_B), 4.09 (t, J = 9.3 Hz, 1 H, 2'-H), 4.39 (d, J = 9.3 Hz, 1 H, 1'-H), 6.99–7.03 (m, 2 H, 3-H, 5-H), 8.07–8.13 (m, 2 H, 2-H, 6-H).

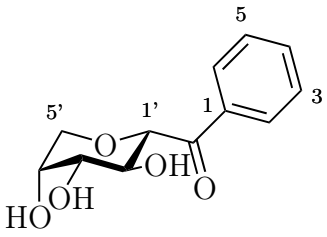
^{13}C-NMR (151 MHz, methanol-d_4): δ (ppm) = 56.1 (C-4-O$\underline{C}H_3$), 69.9 (C-2'), 70.6 (C-4'), 71.9 (C-5'), 75.5 (C-3'), 82.2 (C-1'), 114.7 (2 C, C-3, C-5), 130.1 (C-1), 133.0 (2 C, C-2, C-6), 165.6 (C-4), 196.3 (CO).

MS (ESI): m/z (%) = 135.0 (43) [(4-methoxybenzylidyne)oxonium], 291.1 (100) $[M + Na]^+$, 559.2 (19) $[2M + Na]^+$.

calcd.: 291.0839 $[M + Na]^+$,
found: 291.0834 (ESI-HRMS).

$C_{13}H_{16}O_6$ (268.27).

6.11.2 Phenyl (α-D-arabinopyranosyl) ketone 186



186

To neat 1,2,3,4-tetrakis-*O*-trimethylsilyl-D-arabinopyranose **308** (405 mg, 925 µmol, 1.00 equiv.) was added TMSI (150 µL, 211 µg, 1.05 mmol, 1.14 equiv.) and the mixture was stirred at r.t. for 15 min to give 2,3,4-tris-*O*-trimethylsilyl-α-D-arabinopyranosyl iodide **309** as orange oil, which was dissolved in 2-MeTHF (5.00 mL) and cooled to -95 °C. In a seperate vessel, a solution of 2-phenyl-1,3-dithiane **191** (363 mg, 1.85 mmol, 2.00 equiv.) in 2-MeTHF (5.00 mL) was cooled to -95 °C and a solution of *t*-BuLi (c = 1.73 M in *n*-pentane, 1.05 mL, 1.82 mmol, 1.97 equiv.) was added. The solution was stirred at -95 °C for 10 min and then transferred to the precooled solution of 2,3,4-tris-*O*-trimethylsilyl-α-D-arabinopyranosyl iodide **309** in 2-MeTHF. The reaction mixture was warmed to 0 °C over

2 h. Then, MeOH (35.0 mL) and NaOMe (49.9 mg, 924 µmol, 1.00 equiv.) were added and the reaction mixture was stirred at r.t. for 10 min. Afterwards, the mixture was diluted with water (5.00 mL), cooled to 0 °C and PIFA (994 mg, 2.31 mmol, 2.50 equiv.) was added. The reaction mixture was stirred at 0 °C for 10 min. Then, water (5.00 mL) and L-ascorbic acid (326 mg, 1.55 mmol, 2.00 equiv.) were added and the reaction mixture was stirred at r.t. for another 10 min, then diluted with water (10.0 mL) and washed with *n*-pentane (3 × 30.0 mL). MeOH was removed from the aqueous phase in vacuum. The remaining concentrated aqueous phase was filtered to remove solid impurities. Without further removal of the solvent, the aqueous phase was directly purified by reversed phase column chromatography (RP-C18, $H_2O \rightarrow H_2O$/MeCN 3:1) to yield *C*-glycosidic compound **186** (155 mg, 651 µmol, 70%) as colorless crystalline solid.

TLC: R_f = 0.43 (DCM/MeOH 9:1).

M.p.: 126 °C.

$[\alpha]_D^{25}$ = -22.4 (c = 1.00, MeCN).

UV (MeCN): λ_{max} = 247 nm.

IR (ATR): $\tilde{\nu}$ = 3364, 2970, 2939, 2908, 2858, 1685, 1319, 1093, 1066, 1010, 885, 833, 773, 694, 646 cm^{-1}.

^{1}H-NMR (600 MHz, methanol-d_4): δ (ppm) = 3.64 (dd, J = 9.2, 3.5 Hz, 1 H, 3'-H), 3.77 (dd, J = 12.3, 1.4 Hz, 1 H, 5'-H_A), 3.93 (ddd, J = 3.5, 2.3, 1.4 Hz, 1 H, 4'-H), 4.00 (dd, J = 12.3, 2.3 Hz, 1 H, 5'-H_B), 4.12 (t, J = 9.2 Hz, 1 H, 2'-H), 4.44 (d, J = 9.2 Hz, 1 H, 1'-H), 7.47–7.51 (m, 2 H, 3-H, 5-H), 7.58–7.63 (m, 1 H, 4-H), 8.08–8.13 (m, 2 H, 2-H, 6-H).

^{13}C-NMR (151 MHz, methanol-d_4): δ (ppm) = 69.8 (C-2'), 70.5 (C-4'), 71.9 (C-5'), 75.4 (C-3'), 82.2 (C-1'), 129.5 (2 C, C-3, C-5), 130.4 (2 C, C-2, C-6), 134.6 (C-4), 137.3 (C-1), 197.7 (CO).

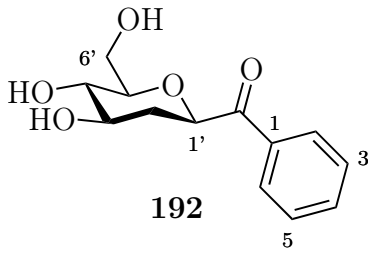
MS (ESI): m/z (%) = 261.1 (100) $[M + Na]^+$.

calcd.: 261.0733 $[M + Na]^+$,
found: 261.0725 (ESI-HRMS).

$C_{12}H_{14}O_5$ (238.24).

6.12 Syntheses of β-carbonyl-*C*-2-deoxy-D-glucopyranosides

6.12.1 Phenyl (β-2-deoxy-D-glucopyranosyl) ketone 192



192

A solution of 1,3,4,6-tetrakis-*O*-trimethylsilyl-2-deoxy-D-glucopyranose **190** (418 mg, 923 µmol, 1.00 equiv.) in 2-MeTHF (5.00 mL) was cooled to 0 °C, TMSI (150 µL, 211 µg, 1.05 mmol, 1.14 equiv.) was added and the solution was stirred at 0 °C for 1 h. Then, the solution was cooled to -95 °C. In a seperate vessel, a solution of 2-phenyl-1,3-dithiane **191** (363 mg, 1.85 mmol, 2.00 equiv.) in 2-MeTHF (5.00 mL) was cooled to -95 °C and a solution of *t*-BuLi (c = 1.70 M in *n*-pentane, 1.10 mL, 1.87 mmol, 2.02 equiv.) was added. The solution was stirred at -95 °C for 10 min and then transferred to the precooled solution of 3,4,6-tris-*O*-trimethylsilyl-α-2-deoxy-D-glucopyranosyl iodide **310** in 2-MeTHF. The reaction mixture was warmed to 0 °C over 2 h. Then, MeOH (10.0 mL) and NaOMe (49.9 mg, 924 µmol, 1.00 equiv.) were added and the reaction mixture was stirred at r.t. for 10 min. Afterwards, the solvent was removed in vacuum. The residue was dissolved in MeOH/H_2O (9:1, 10.0 mL) and PIFA (1.19 g, 2.77 mmol, 3.00 equiv.) was added. The reaction mixture was stirred for 30 min, then diluted with water (20.0 mL) and washed with *n*-pentane (3 × 20.0 mL). The solvent was removed in vacuum and the residue purified by reversed phase chromatography (RP-C18, H_2O → H_2O/MeCN 3:1) to yield *C*-glycosidic compound **192** (179 mg, 709 µmol, 77%) as colorless crystalline solid.

TLC: R_f = 0.65 (EtOAc/MeCN/*n*-PrOH/H_2O 12:8:5:5).

M.p.: 181 °C.

$[\alpha]_D^{25}$ = 44.2 (c = 1.00, H_2O).

UV (H_2O): λ_{max} = 249 nm.

IR (ATR): $\tilde{\nu}$ = 3393, 1682, 1354, 1254, 1099, 1044, 1009, 974, 774, 698, 598 cm^{-1}.

^{1}H-NMR (600 MHz, DMSO-d_6): δ (ppm) = 1.48 (dt, 1 H, J = 12.9, 11.7 Hz, 2'-H_{ax}), 2.00 (ddd, J = 12.9, 5.0, 2.0 Hz, 1 H, 2'-H_{eq}), 3.04 (td, J = 9.2, 5.1 Hz, 1 H, 4'-H), 3.33

(ddd, $J = 9.2$, 5.9, 2.0 Hz, 1 H, 5'-H), 3.47 (dt, $J = 11.9$, 5.9 Hz, 1 H, 6'-H_A), 3.56–3.63 (m, 3'-H), 3.72 (ddd, $J = 11.9$, 5.9, 2.0 Hz, 1 H, 6'-H_B), 4.49 (t, $J = 5.9$ Hz, 1 H, 6'-OH) 4.88 (dd, $J = 11.7$, 2.0 Hz, 1 H, 1'-H), 4.92 (d, $J = 4.9$ Hz, 1 H, 3'-OH), 4.98 (d, $J = 5.1$ Hz, 1 H, 4'-OH), 7.61–7.66 (m, 2 H, 3-H, 5-H), 7.61–7.66 (m, 1 H, 4-H), 7.98–8.02 (m, 2 H, 2-H, 6-H).

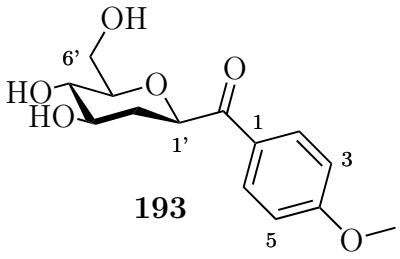
^{13}C-NMR (151 MHz, DMSO-d_6): δ (ppm) = 35.9 (C-2'), 61.2 (C-6'), 71.6 (C-4'), 71.7 (C-3'), 76.3 (C-1'), 81.7 (C-5'), 128.7 (C-3, C-5') 128.9 (2 C, C-2, C-6), 133.4 (C-4), 134.9 (C-1), 196.5 (CO).

MS (ESI): m/z (%) = 275.1 (100) $[M + Na]^+$.

calcd.: 275.0890 $[M + Na]^+$,
found: 275.0889 (ESI-HRMS).

$C_{13}H_{16}O_5$ (252.27).

6.12.2 (4-Methoxyphenyl)(β-2-deoxy-D-glucopyranosyl) ketone 193



193

A solution of 1,3,4,6-tetrakis-*O*-trimethylsilyl-2-deoxy-D-glucopyranose **190** (418 mg, 923 µmol, 1.00 equiv.) in 2-MeTHF (5.00 mL) was cooled to 0 °C, TMSI (150 µL, 211 µg, 1.05 mmol, 1.14 equiv.) was added and the solution was stirred 0 °C for 1 h. Then, the solution was cooled to -95 °C. In a seperate vessel, a solution of 2-(4-methoxyphenyl)-1,3-dithiane **151** (419 mg, 1.85 mmol, 2.00 equiv.) in 2-MeTHF (5.00 mL) was cooled to -95 °C and a solution of *t*-BuLi (c = 1.70 M in *n*-pentane, 1.10 mL, 1.87 mmol, 2.02 equiv.) was added. The solution was stirred at -95 °C for 10 min and then transferred to the precooled solution of 3,4,6-tris-*O*-trimethylsilyl-α-2-deoxy-D-glucopyranosyl iodide **310** in 2-MeTHF. The reaction mixture was warmed to 0 °C over 2 h. Then, MeOH (10.0 mL) and NaOMe (49.9 mg, 924 µmol, 1.00 equiv.) were added and the reaction mixture was stirred at r.t. for 10 min. Afterwards, the solvent was removed in vacuum. The residue

was dissolved in MeOH/H_2O (9:1, 10.0 mL) and PIFA (1.19 g, 2.77 mmol, 3.00 equiv.) was added. The reaction mixture was stirred for 30 min, then diluted with water (20.0 mL) and washed with *n*-pentane (3×20.0 mL). The solvent was removed in vacuum and the residue purified by reversed phase chromatography (RP-C18, $H_2O \rightarrow H_2O$/MeCN 3:1) to yield *C*-glycosidic compound **193** (138 mg,479 µmol, 52%) as colorless crystalline solid.

TLC: R_f = 0.68 (EtOAc/MeCN/*n*-PrOH/H_2O 12:8:5:5).

M.p.: 192 °C.

$[\alpha]_D^{25}$ = 33.2 (c = 1.00, H_2O).

UV (H_2O): λ_{max} = 220, 285 nm.

IR (ATR): $\tilde{\nu}$ = 3391, 1676, 1593, 1258, 1168, 1096, 1060, 1038, 1015, 974, 835, 593 cm^{-1}.

^{1}H-NMR (600 MHz, DMSO-d_6): δ (ppm) = 1.47 (dt, 1 H, J = 12.8, 11.6 Hz, 2'-H_{ax}), 1.97 (ddd, J = 12.8, 5.0, 1.9 Hz, 1 H, 2'-H_{eq}), 3.03 (td, J = 9.2, 5.1 Hz, 1 H, 4'-H), 3.31 (ddd, J = 9.2, 5.8, 2.0 Hz, 1 H, 5'-H), 3.47 (dt, J = 11.8, 5.8 Hz, 1 H, 6'-H_A), 3.55–3.63 (m, 1 H, 3'-H), 3.72 (ddd, J = 11.8, 5.8, 2.0 Hz, 1 H, 6'-H_B), 3.84 (s, 3 H, 4-OC$\underline{H_3}$), 4.49 (t, J = 5.8 Hz, 1 H, 6'-OH) 4.80 (dd, J = 11.6, 1.9 Hz, 1 H, 1'-H), 4.90 (d, J = 4.9 Hz, 1 H, 3'-OH), 4.96 (d, J = 5.1 Hz, 1 H, 4'-OH), 7.00–7.06 (m, 2 H, 3-H, 5-H), 7.97–8.02 (m, 2 H, 2-H, 6-H).

^{13}C-NMR (151 MHz, DMSO-d_6): δ (ppm) = 36.0 (C-2'), 55.6 (C-4-O$\underline{C}H_3$), 61.3 (C-6'), 71.7 (C-4'), 71.7 (C-3'), 76.3 (C-1'), 81.7 (C-5'), 113.9 (2 C, C-3, C-5), 127.7 (C-1), 131.4 (2 C, C-2, C-6), 163.3 (C-4), 194.8 (CO).

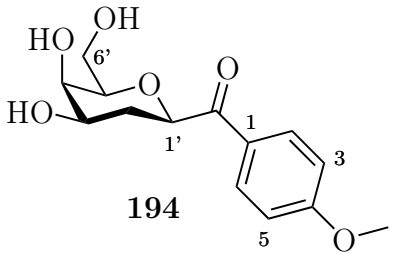
MS (ESI): *m/z* (%) = 305.1(100) $[M + Na]^+$.

calcd.: 305.0995 $[M + Na]^+$,
found: 305.0995 (ESI-HRMS).

$C_{14}H_{18}O_6$ (282.29).

6.13 Syntheses of β-carbonyl-*C*-2-deoxy-D-galactopyranosides

6.13.1 (4-Methoxyphenyl)(β-2-deoxy-D-galactopyranosyl) ketone 194



194

A solution of 1,3,4,6-tetrakis-*O*-trimethylsilyl-2-deoxy-D-galactopyranose **311** (418 mg, 923 µmol, 1.00 equiv.) in 2-MeTHF (5.00 mL) was cooled to 0 °C, TMSI (150 µL, 211 µg, 1.05 mmol, 1.14 equiv.) was added. The solution was warmed to r.t. an stirred for 30 min to give a solution of 3,4,6-tris-*O*-trimethylsilyl-α-2-deoxy-D-galactopyranosyl iodide **312** in 2-MeTHF. In a seperate vessel, a solution of 2-(4-methoxyphenyl)-1,3-dithiane **151** (419 mg, 1.85 mmol, 2.00 equiv.) in 2-MeTHF (5.00 mL) was cooled to -95 °C and a solution of *t*-BuLi (c = 1.73 M in *n*-pentane, 1.05 mL, 1.82 mmol, 1.97 equiv.) was added. The solution was stirred at -95 °C for 10 min and then transferred to the precooled solution of 3,4,6-tris-*O*-trimethylsilyl-α-2-deoxy-D-galactopyranosyl iodide **312** in 2-MeTHF. The reaction mixture was warmed to 0 °C over 2 h. Then, MeOH (35.0 mL) and NaOMe (49.9 mg, 924 µmol, 1.00 equiv.) were added and the reaction mixture was stirred at r.t. for 10 min. Afterwards, the mixture was diluted with water (5.00 mL), cooled to 0 °C and PIFA (994 mg, 2.31 mmol, 2.50 equiv.) was added. The reaction mixture was stirred at 0 °C for 10 min. Then, water (5.00 mL) and L-ascorbic acid (326 mg, 1.55 mmol, 2.00 equiv.) were added and the reaction mixture was stirred at r.t. for another 10 min, then diluted with water (10.0 mL) and washed with *n*-pentane (3 × 30.0 mL). MeOH was removed from the aqueous phase in vacuum. The remaining concentrated aqueous phase was filtered to remove solid impurities. Without further removal of the solvent, the aqueous phase was directly purified by reversed phase column chromatography (RP-C18, $H_2O \rightarrow H_2O$/MeCN 3:1) to yield *C*-glycosidic compound **194** (101 mg, 358 µmol, 39%) as colorless crystalline solid.

TLC: R_f = 0.32 (DCM/MeOH 9:1).

M.p.: 127 °C.

$[\alpha]_D^{25}$ = 17.8 (c = 1.00, MeCN).

UV (MeCN): λ_{max} = 217, 275 nm.

IR (ATR): $\tilde{\nu}$ = 3332, 2916, 2843, 1678, 1598, 1510, 1263, 1242, 1170, 1149, 1087, 1018, 964, 835, 607 cm^{-1}.

^{1}H-NMR (600 MHz, DMSO-d_6): δ (ppm) = 1.65 (ddd, J = 12.0, 4.1, 2.0 Hz, 1 H, 2'-$H_{eq.}$), 1.82 (q, J = 12.0 Hz, 1 H, 2'-$H_{ax.}$), 3.46–3.58 (m, 3 H, 5'-H, 6'-H_2), 3.63–3.67 (m, 1 H, 4'-H), 3.71–3.77 (m, 1 H, 3'-H), 3.84 (s, 3 H, 4-OC$\underline{H}_3$), 4.35 (d, J = 4.3 Hz, 1 H, 4'-OH), 4.58–4.61 (m, 1 H, 6'-OH), 4.65 (dd, J = 12.0, 2.3 Hz, 1 H, 1'-H), 4.74 (d, J = 5.9 Hz, 1 H 3'-OH), 7.00–7.05 (m, 2 H, 3-H, 5-H), 8.01–8.06 (m, 2 H, 2-H, 6-H).

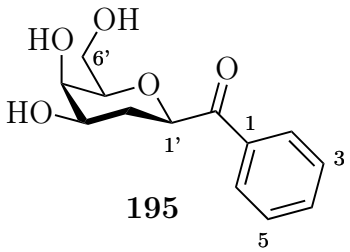
^{13}C-NMR (151 MHz, DMSO-d_6): δ (ppm) = 31.2 (C-2'), 55.5 (C-4-O$\underline{C}H_3$), 61.1 (C-6'), 67.1 (C-4'), 68.7 (C-3'), 77.9 (C-1'), 79.8 (C-5'), 113.8 (2 C, C-3, C-5), 127.6 (C-1), 131.5 (2 C, C-2, C-6), 163.2 (C-4), 195.4 (CO).

MS (ESI): m/z (%) = 305.1 (100) $[M + Na]^+$, 587.2 (14) $[2\,M + Na]^+$.

calcd.: 305.0996 $[M + Na]^+$,
found: 305.0998 (ESI-HRMS).

$C_{14}H_{18}O_6$ (282.29).

6.13.2 Phenyl (β-2-deoxy-D-galactopyranosyl) ketone 195



195

A solution of 1,3,4,6-tetrakis-*O*-trimethylsilyl-2-deoxy-D-galactopyranose **311** (418 mg, 923 µmol, 1.00 equiv.) in 2-MeTHF (5.00 mL) was cooled to 0 °C, TMSI (150 µL, 211 µg, 1.05 mmol, 1.14 equiv.) was added. The solution was warmed to r.t. an stirred for 30 min to give a solution of 3,4,6-tris-*O*-trimethylsilyl-α-2-deoxy-D-galactopyranosyl iodide **312** in 2-MeTHF. In a seperate vessel, a solution of 2-phenyl-1,3-dithiane **191** (363 mg, 1.85 mmol, 2.00 equiv.) in 2-MeTHF (5.00 mL) was cooled to -95 °C and a solution of *t*-BuLi (c = 1.73 M in *n*-pentane, 1.05 mL, 1.82 mmol, 1.97 equiv.) was added. The solution was stirred at -95 °C for 10 min and then transferred to the precooled solution of 3,4,6-tris-*O*-trimethylsilyl-α-2-deoxy-D-galactopyranosyl iodide **312** in 2-MeTHF. The

reaction mixture was warmed to 0 °C over 2 h. Then, MeOH (35.0 mL) and NaOMe (49.9 mg, 924 µmol, 1.00 equiv.) were added and the reaction mixture was stirred at r.t. for 10 min. Afterwards, the mixture was diluted with water (5.00 mL), cooled to 0 °C and PIFA (994 mg, 2.31 mmol, 2.50 equiv.) was added. The reaction mixture was stirred at 0 °C for 10 min. Then, water (5.00 mL) and L-ascorbic acid (326 mg, 1.55 mmol, 2.00 equiv.) were added and the reaction mixture was stirred at r.t. for another 10 min, then diluted with water (10.0 mL) and washed with *n*-pentane (3 × 30.0 mL). MeOH was removed from the aqueous phase in vacuum. The remaining concentrated aqueous phase was filtered to remove solid impurities. Without further removal of the solvent, the aqueous phase was directly purified by reversed phase column chromatography (RP-C18, $H_2O \rightarrow H_2O$/MeCN 3:1) to yield *C*-glycosidic compound **195** (80.2 mg, 318 µmol, 34%) as colorless crystalline solid.

TLC: R_f = 0.35 (DCM/MeOH 9:1).

M.p.: 132 °C.

$[\alpha]_D^{25}$ = 23.6 (c = 1.00, MeCN).

UV (MeCN): λ_{max} = 243 nm.

IR (ATR): $\tilde{\nu}$ = 3315, 2968, 2910, 2854, 1674, 1595, 1448, 1267, 1221, 1056, 1024, 966, 866, 688, 640 cm^{-1}.

^{1}H-NMR (600 MHz, DMSO-d_6): δ (ppm) = 1.68 (ddd, J = 12.2, 4.4, 2.2 Hz, 1 H, 2'-$H_{eq.}$), 1.81 (q, J = 12.2 Hz, 1 H, 2'-$H_{ax.}$), 3.46–3.58 (m, 3 H, 5'-H, 6'-H_2), 3.65 (t, J = 4.0 Hz, 1 H, 4'-H), 3.72–3.78 (m, 1 H, 3'-H), 4.35 (d, J = 4.0 Hz, 1 H, 4'-OH), 4.57–4.61 (m, 1 H, 6'-OH), 4.74 (d, J = 5.7 Hz, 1 H, 3'-OH), 4.75 (dd, J = 12.2, 2.2 Hz, 1 H, 1'-H) 7.49–7.54 (m, 2 H, 3-H, 5-H), 7.61–7.65 (m, 1 H, 4-H), 8.01–8.05 (m, 2 H, 2-H, 6-H).

^{13}C-NMR (151 MHz, DMSO-d_6): δ (ppm) = 31.0 (C-2'), 61.1 (C-6'), 67.0 (C-4'), 68.7 (C-3'), 77.7 (C-1'), 79.8 (C-5'), 128.5 (2 C, C-3, C-5), 129.0 (2 C, C-2, C-6), 133.3 (C-4), 134.8 (C-1), 197.0 (CO).

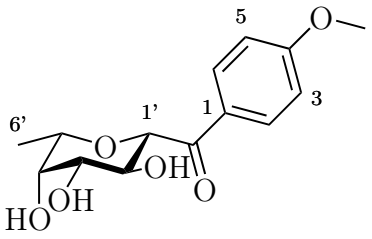
MS (ESI): m/z (%) = 275.1 (100) $[M + Na]^+$, 527.2 (5) $[2\,M + Na]^+$.

calcd.: 275.0890 $[M + Na]^+$,
found: 275.0886 (ESI-HRMS).

$C_{13}H_{16}O_5$ (252.27).

6.14 Syntheses of β-carbonyl-*C*-fucopyranosides

6.14.1 (4-Methoxyphenyl)(β-L-fucopyranosyl) ketone 188



188

To neat 1,2,3,4-tetrakis-*O*-trimethylsilyl-L-fucopyranose **313** (418 mg, 923 µmol, 1.00 equiv.) was added TMSI (150 µL, 211 µg, 1.05 mmol, 1.14 equiv.) and the mixture was stirred at r.t. for 15 min to give 2,3,4-tris-*O*-trimethylsilyl-α-L-fucopyranosyl iodide **314** as orange oil, which was dissolved in 2-MeTHF (5.00 mL) and cooled to -95 °C. In a seperate vessel, a solution of 2-(4-methoxyphenyl)-1,3-dithiane **151** (419 mg, 1.85 mmol, 2.00 equiv.) in 2-MeTHF (5.00 mL) was cooled to -95 °C and a solution of *t*-BuLi (c = 1.73 M in *n*-pentane, 1.05 mL, 1.82 mmol, 1.97 equiv.) was added. The solution was stirred at -95 °C for 10 min and then transferred to the precooled solution of 2,3,4-tris-*O*-trimethylsilyl-α-L-fucopyranosyl iodide **314** in 2-MeTHF. The reaction mixture was warmed to 0 °C over 2 h. Then, MeOH (35.0 mL) and NaOMe (49.9 mg, 924 µmol, 1.00 equiv.) were added and the reaction mixture was stirred at r.t. for 10 min. Afterwards, the mixture was diluted with water (5.00 mL), cooled to 0 °C and PIFA (994 mg, 2.31 mmol, 2.50 equiv.) was added. The reaction mixture was stirred at 0 °C for 10 min. Then, water (5.00 mL) and L-ascorbic acid (326 mg, 1.55 mmol, 2.00 equiv.) were added and the reaction mixture was stirred at r.t. for another 10 min, then diluted with water (10.0 mL) and washed with *n*-pentane (3 × 30.0 mL). MeOH was removed from the aqueous phase in vacuum. The remaining concentrated aqueous phase was filtered to remove solid impurities. Without further removal of the solvent, the aqueous phase was directly purified by reversed phase column chromatography (RP-C18, H_2O → H_2O/MeCN 3:1) to yield *C*-glycosidic compound **188** (204 mg, 723 µmol, 78%) as colorless crystalline solid.

TLC: R_f = 0.51 (DCM/MeOH 9:1).

M.p.: 230 °C.

$[a]_D^{25}$ = 13.4 (c = 1.00, MeCN/H_2O 1:1).

UV (MeCN): λ_{max} = 219, 279 nm.

IR (ATR): $\tilde{\nu}$ = 3429, 2976, 2935, 2916, 2875, 1678, 1608, 1575, 1176, 1093, 1058, 1022, 844, 783, 588 cm^{-1}.

^{1}H-NMR (600 MHz, DMSO-d_6): δ (ppm) = 1.13 (d, J = 6.5 Hz, 3 H, 6'-H_3), 3.43 (ddd, J = 9.4, 6.0, 3.6 Hz, 1 H, 3'-H), 3.54 (t, J = 3.6 Hz, 1 H, 4'-H), 3.71 (q, J = 6.5 Hz, 1 H, 5'-H), 3.84 (s, 3 H, 4-OC$\underline{H}_3$), 3.87 (td, J = 9.4, 5.9 Hz, 1 H, 2'-H), 4.24 (d, J = 9.4 Hz, 1 H, 1'-H), 4.62 (d, J = 3.6 Hz, 1 H, 4'-OH), 4.75 (d, J = 5.9 Hz, 1 H, 2'-OH), 4.81 (d, J = 6.0 Hz, 1 H, 3'-OH), 7.01–7.06 (m, 2 H, 3-H, 5-H), 8.05–8.10 (m, 2 H, 2-H, 6-H).

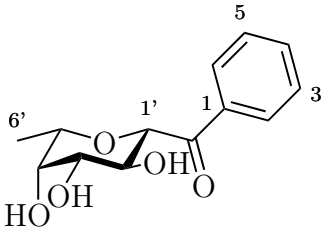
^{13}C-NMR (151 MHz, DMSO-d_6): δ (ppm) = 17.1 (C-6'), 55.5 (C-4-O$\underline{C}$H$_3$), 67.8 (C-2'), 71.4 (C-4'), 74.6 (C-5'), 74.8 (C-3'), 81.2 (C-1'), 113.7 (2 C, C-3, 5-C), 128.5 (C-1), 131.5 (2 C, C-2, C-6), 163.2 (C-4), 194.2 (CO).

MS (ESI): m/z (%) = 135.0 (67) [(4-methoxybenzylidyne)oxonium], 305.1 (100) $[M + Na]^+$.

calcd.: 305.0996 $[M + Na]^+$,
found: 305.0994 (ESI-HRMS).

$C_{14}H_{18}O_6$ (282.29).

6.14.2 Phenyl (β-L-fucopyranosyl) ketone 189



189

To neat 1,2,3,4-tetrakis-*O*-trimethylsilyl-L-fucopyranose **313** (418 mg, 923 µmol, 1.00 equiv.) was added TMSI (150 µL, 211 µg, 1.05 mmol, 1.14 equiv.) and the mixture was stirred at r.t. for 15 min to give 2,3,4-tris-*O*-trimethylsilyl-α-L-fucopyranosyl iodide **314** as orange oil, which was dissolved in 2-MeTHF (5.00 mL) and cooled to -95 °C. In a seperate vessel, a solution of 2-phenyl-1,3-dithiane **191** (363 mg, 1.85 mmol, 2.00 equiv.) in 2-MeTHF (5.00 mL) was cooled to -95 °C and a solution of *t*-BuLi (c = 1.73 M in *n*-pentane, 1.05 mL, 1.82 mmol, 1.97 equiv.) was added. The solution was stirred at -95 °C for 10 min and then transferred to the precooled solution of

2,3,4-tris-*O*-trimethylsilyl-α-L-fucopyranosyl iodide **314** in 2-MeTHF. The reaction mixture was warmed to 0 °C over 2 h. Then, MeOH (35.0 mL) and NaOMe (49.9 mg, 924 µmol, 1.00 equiv.) were added and the reaction mixture was stirred at r.t. for 10 min. Afterwards, the mixture was diluted with water (5.00 mL), cooled to 0 °C and PIFA (994 mg, 2.31 mmol, 2.50 equiv.) was added. The reaction mixture was stirred at 0 °C for 10 min. Then, water (5.00 mL) and L-ascorbic acid (326 mg, 1.55 mmol, 2.00 equiv.) were added and the reaction mixture was stirred at r.t. for another 10 min, then diluted with water (10.0 mL) and washed with *n*-pentane (3 × 30.0 mL). MeOH was removed from the aqueous phase in vacuum. The remaining concentrated aqueous phase was filtered to remove solid impurities. Without further removal of the solvent, the aqueous phase was directly purified by reversed phase column chromatography (RP-C18, H_2O → H_2O/MeCN 3:1) to yield *C*-glycosidic compound **315** (195 mg, 773 µmol, 84%) as colorless crystalline solid.
TLC: R_f = 0.51 (DCM/MeOH 9:1).

M.p.: 245 °C.

$[a]_D^{25}$ = 15.2 (c = 1.00, MeCN).

UV (MeCN): λ_{max} = 245 nm.

IR (ATR): $\tilde{\nu}$ = 3412, 2997, 2978, 2935, 1685, 1598, 1581, 1450, 1097, 1056, 1001, 879, 775, 700, 592 cm^{-1}.

^{1}H-NMR (600 MHz, methanol-d_4): δ (ppm) = 1.28 (d, J = 6.5 Hz, 3 H, 6'-H_3), 3.62 (dd, J = 9.5, 3.4 Hz, 1 H, 3'-H), 3.72 (dd, J = 3.4, 1.1 Hz, 1 H, 4'-H), 3.86 (qd, J = 6.5, 1.1 Hz, 1 H, 5'-H), 4.07 (t, J = 9.5 Hz, 1 H, 2'-H), 4.48 (d, J = 9.5 Hz, 1 H, 1'-H), 7.47–7.51 (m, 2 H, 3-H, 5-H), 7.59–7.63 (m, 1 H, 4-H), 8.10–8.13 (m, 2 H, 2-H, 6-H).

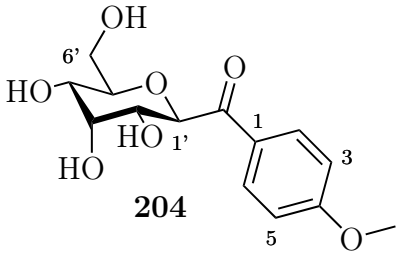
^{13}C-NMR (151 MHz, methanol-d_4): δ (ppm) = 17.2 (C-6'), 69.4 (C-2'), 73.4 (C-4'), 76.4 (C-3'), 76.8 (C-5'), 81.7 (C-1'), 129.5 (2 C, C-3, C-5), 130.5 (2 C, C-2, C-6), 134.6 (C-4), 137.3 (C-1), 197.6 (CO).

MS (ESI): m/z (%) = 275.1 (100) $[M + Na]^+$. 527.2 (7) $[2M + Na]^+$.

calcd.: 275.0890 $[M + Na]^+$,
found: 275.0889 (ESI-HRMS).

$C_{13}H_{16}O_5$ (252.27).

6.15 (4-Methoxyphenyl)(β-D-allopyranosyl) ketone 204



204

To a solution of (4-methoxyphenyl)(β-D-glucopyranosyl) ketone **178** (359 mg, 1.20 mmol, 1.00 equiv.) in THF (6.00 mL) were added triphenylphosphine (1.58 g, 3.61 mmol, 3.00 equiv.) and AcOH (207 µL, 217 mg, 3.61 mmol, 3.00 equiv.). Then the reaction mixture was heated to 60 °C and DIAD (750 µL, 813 mg, 3.17 mmol, 3.17 equiv.) was added over 30 min. Afterwards, the reaction mixture was stirred at 80 °C for 3 h. The reaction mixture was cooled to r.t. and diluted with diethyl ether (50.0 mL). The mixture was washed with saturated aqueous $NaHCO_3$-solution (50.0 mL) and brine (50.0 mL). The organic layer was dried over $MgSO_4$, filtered and the solvent was removed in vacuum. The residue was dissolved in MeOH (20.0 mL), NaOMe was added (13.0 mg, 241 mmol, 20.0 mol%.) and the mixture stirred at r.t. for 16 h. The mixture was diluted with AcOH (1.00 mL) and water (50.0 mL) and then washed with DCM (2 × 50.0 mL). After removal of the solvent in vacuum, the residue was purified by reversed phase column chromatography (RP-C18, $H_2O \rightarrow H_2O$/MeCN 3:1) to yield *C*-glycosidic compound **204** (206 mg, 691 µmol, 57%) as colorless crystalline solid.

TLC: R_f = 0.32 (DCM/MeOH 9:1).

M.p.: 89 °C.

$[\alpha]_D^{25}$ = -13.8 (c = 1.00, MeCN).

UV (MeCN: λ_{max} = 219, 278 nm.

IR (ATR): $\tilde{\nu}$ = 3321, 2939, 2908, 2843, 1651, 1598, 1573, 1421, 1251, 1176, 1076, 1031, 1020, 846, 609 cm^{-1}.

^{1}H-NMR (600 MHz, methanol-d_4): δ (ppm) = 3.58 (dd, J = 9.9, 2.8 Hz, 1 H, 4'-H), 3.68 (dd, J = 12.1, 5.3 Hz, 1 H, 6'-H_A), 3.76 (ddd, J = 9.9, 5.3, 2.2 Hz, 1 H, 5'-H), 3.79 (dd, J = 9.6, 2.8 Hz, 1 H, 2'-H), 3.85 (dd, J = 12.1, 2.2 Hz, 1 H, 6'-H_B), 3.88 (s, 3 H, 4-OC$\underline{H_3}$), 4.12 (t, J = 2.8 Hz, 1 H, 3'-H), 5.03 (d, J = 9.6 Hz, 1 H, 1'-H), 6.99–7.04 (m, 2 H, 3-H, 5-H), 8.05–8.10 (m, 2 H, 2-H, 6-H).

^{13}C-NMR (151 MHz, methanol-d_4): δ (ppm) = 56.1 (C-4-O<u>C</u>H$_3$), 62.9 (C-6'), 68.4 (C-4'), 70.9 (C-2'), 73.0 (C-3'), 75.8 (C-1'), 77.5 (C-5'), 114.8 (2 C, C-3, C-5), 130.7 (C-1), 132.9 (2 C, C-2, C-6), 165.7 (C-4), 198.3 (CO).

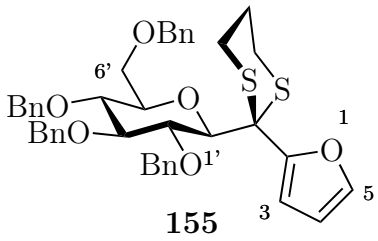
MS (ESI): *m/z* (%) = 135.0 (54) [(4-methoxybenzylidyne)oxonium], 321.1 (100) $[M + Na]^+$ 619.2 (16) $[2\,M + Na]^+$.

calcd.: 321.0945 $[M + Na]^+$,
found: 321.0948 (ESI-HRMS).

$C_{14}H_{18}O_7$ (298.29).

6.16 Synthesis of 1-(2-(furan-2-yl)-1,3-dithian-2-yl)-pyranosides

6.16.1 1-(2-(Furan-2-yl)-1,3-dithian-2-yl)-2,3,4,6-tetra-*O*-benzyl-β-D-glucopyranoside 155



155

A solution of 2,3,4,6-tetra-*O*-benzyl-D-glucopyranose **153** (500 mg, 925 µmol, 1.00 equiv.) in DCM (5.00 mL) was cooled to 0 °C, oxalyl bromide (108 µL, 248 µg, 1.15 µmol, 1.24 equiv.) was added and the solution was stirred at r.t. for 1 h. The solvent was removed in vacuum and 2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranosyl bromide **154** was obtained as orange oil, which was dissolved in 2-MeTHF (5.00 mL) and cooled to -95 °C. In a seperate vessel, a solution of 2-(1,3-dithian-2-yl)furan **147** (345 mg, 1.85 mmol, 2.00 equiv.) in 2-MeTHF (5.00 mL) was cooled to -95 °C and a solution of *t*-BuLi (c = 1.70 M in *n*-pentane, 1.10 mL, 1.87 mmol, 2.02 equiv.) was added. The solution was stirred at -95 °C for 10 min and then transferred to the precooled solution of 2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranosyl bromide **154** in 2-MeTHF. The reaction mixture was warmed to 0 °C over 2 h. Then, aqueous HCl (1 M, 10.0 mL) was added and the mixture extracted with Et_2O (3 × 20.0 mL). The combined organic layers were dried over $MgSO_4$, filtered and the solvent was removed in vacuum. The residue was purified by

column chromatography (SiO_2, PE/EtOAc 9:1 → PE/EtOAc 3:1) to yield *C*-glycosidic compound **155** (480 mg, 677 µmol, 73%) as pale yellow oil.

TLC: R_f = 0.59 (PE/EtOAc 4:1).

$[\alpha]_D^{25}$ = -1.8 (c = 1.03, $CHCl_3$).

UV (H_2O): λ_{max} = 204, 249 nm.

IR (ATR): $\tilde{\nu}$ = 1454, 1360, 1151, 1090, 1072, 1027, 1011, 732, 695, 599 cm^{-1}.

^{1}H-NMR (600 MHz, C_6D_6): δ (ppm) = 1.44–1.51 (m, 1 H, 1'-C-S-CH_2-C$\underline{H_A}$), 1.63–1.73 (m, 1 H, 1'-C-S-CH_2-C$\underline{H_B}$), 2.46 (ddd, *J* = 13.5, 9.8, 3.0 Hz, 1 H, 1'-C-S-CH), 2.51 (ddd, *J* = 13.6, 10.0, 3.0 Hz, 1 H, 1'-C-S-CH), 2.58–2.67 (m, 2 H, 2 × 1'-C-S-CH), 3.36 (dt, *J* = 9.3, 2.9 Hz, 1 H, 5'-H), 3.65–3.69 (m, 3 H, 4'-H, 6'-H_2), 3.71 (t, *J* = 9.0 Hz, 1 H, 3'-H), 3.95 (t, *J* = 9.0 Hz, 1 H, 2'-H), 4.36 (d, *J* = 9.0 Hz, 1 H, 1'-H), 4.49 (d, *J* = 12.3 Hz, 1 H, 6'-O-CH_A), 4.56 (d, *J* = 11.6 Hz, 1 H, 4'-O-CH_A), 4.60 (d, *J* = 12.3 Hz, 1 H, 6'-OCH_B), 4.72 (d, *J* = 11.2 Hz, 1 H, 3'-O-CH_A), 4.75 (d, *J* = 11.6 Hz, 1 H, 4'-O-CH_B), 4.79 (d, *J* = 11.2 Hz, 1 H, 3'-O-CH_B), 4.96 (d, *J* = 11.1 Hz, 1 H, 2'-O-CH_A), 5.15 (d, *J* = 11.1 Hz, 1 H, 2'-O-CH_B), 6.01 (dd, *J* = 3.3, 1.8 Hz, 1 H, 4-H), 6.66 (d, *J* = 3.3 Hz, 1 H, 3-H), 7.03–7.14 (m, 9 H, 5-H, 8 × Ar-H), 7.15–7.24 (m, 8 H, 8 × Ar-H), 7.30–7.34 (m, 2 H, 2 × Ar-H), 7.37–7.42 (m, 2 H, 2 × Ar-H).

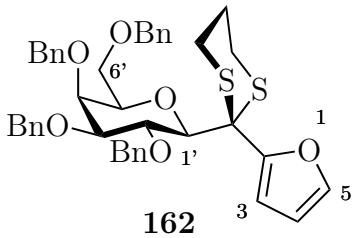
^{13}C-NMR (151 MHz, C_6D_6): δ (ppm) = 25.3 (1'-C-S-CH_2-$\underline{C}H_2$), 28.0, 28.4 (2 × 1'-C-S$\underline{C}H_2$), 55.5 (1'-CS_2), 69.0 (C-6'), 73.6 (C-6'-O$\underline{C}H_2$), 74.1 (C-2'-O$\underline{C}H_2$), 74.7 (C-4'-O$\underline{C}H_2$), 75.7 (C-3'-O$\underline{C}H_2$), 78.4 (C-4'), 80.0 (C-5'), 80.3 (C-2'), 86.0 (C-1'), 88.2 (C-3'), 110.8 (C-4), 111.1 (C-3), 127.1, 127.4, 127.5, 127.6, 127.8, 128.0, 128.4, 128.5, 128.6 (20 × C-Ar), 139.2, 139.4, 139.5, 139.8 (4 × C-Ar, quart.), 142.4 (C-5), 153.5 (C-2).

MS (ESI): *m/z* (%) = 709.3 (35) $[M + H]^+$, 726.3 (100) $[M + NH_4]^+$, 731.2 (84) $[M + Na]^+$.

calcd.: 726.2918 $[M + NH_4]^+$,
found: 726.2929 (ESI-HRMS).

$C_{42}H_{44}O_6S_2$ (708.93).

6.16.2 1-(2-(Furan-2-yl)-1,3-dithian-2-yl)-2,3,4,6-tetra-*O*-benzyl-β-D-galactopyranoside 162



162

A solution of 2,3,4,6-tetra-*O*-benzyl-D-galactopyranose **161** (500 mg, 925 µmol, 1.00 equiv.) in DCM (5.00 mL) was cooled to 0 °C, oxalyl bromide (108 µL, 248 µg, 1.15 µmol, 1.24 equiv.) was added and the solution was stirred at r.t. for 1 h. The solvent was removed in vacuum and 2,3,4,6-tetra-*O*-benzyl-α-D-galactopyranosyl bromide **303** was obtained as orange oil, which was dissolved in 2-MeTHF (5.00 mL) and cooled to -95 °C. In a seperate vessel, a solution of 2-(1,3-dithian-2-yl)furan **147** (345 mg, 1.85 mmol, 2.00 equiv.) in 2-MeTHF (5.00 mL) was cooled to -95 °C and a solution of *t*-BuLi (c = 1.70 M in *n*-pentane, 1.10 mL, 1.87 mmol, 2.02 equiv.) was added. The solution was stirred at -95 °C for 10 min and then transferred to the precooled solution of 2,3,4,6-tetra-*O*-benzyl-α-D-galactopyranosyl bromide **303** in 2-MeTHF. The reaction mixture was warmed to 0 °C over 2 h. Then, aqueous HCl (1 M, 10.0 mL) was added and the mixture extracted with Et_2O (3 × 20.0 mL). The combined organic layers were dried over $MgSO_4$, filtered and the solvent was removed in vacuum. The residue was purified by column chromatography (SiO_2, PE/EtOAc 9:1 → PE/EtOAc 3:1) to yield *C*-glycosidic compound **162** (321 mg, 453 µmol, 49%) as pale yellow oil.

TLC: R_f = 0.52 (PE/EtOAc 4:1).

$[\alpha]_D^{25}$ = -0.8 (c = 1.00, $CHCl_3$).

UV (MeCN): λ_{max} = 204, 276 nm.

IR (ATR): $\tilde{\nu}$ = 2859, 1496, 1454, 1361, 1207, 1092, 1027, 908, 802, 731, 695, 597 cm^{-1}.

^{1}H-NMR (600 MHz, C_6D_6): δ (ppm) = 1.42–1.51 (m, 1 H, 1'-C-S-CH_2-C$\underline{H_A}$), 1.60–1.73 (m, 1 H, 1'-C-S-CH_2-C$\underline{H_B}$), 2.45–2.58 (m, 2 H, 2 × 1'-C-S-CH), 2.59–2.67 (m, 2 H, 2 × 1'-C-S-CH), 3.44 (dd, *J* = 9.0, 2.4 Hz, 1 H, 3'-H), 3.52 (t, *J* = 6.3 Hz, 1 H, 5'-H), 3.68 (dd, *J* = 9.3, 6.3 Hz, 1 H, 6'-H_A), 3.70 (dd, *J* = 9.3, 6.3 Hz, 1 H, 6'-H_B), 3.75 (d, *J* = 2.4 Hz, 1 H, 4'-H), 4.25 (d, *J* = 11.8 Hz, 1 H, 6'-O-CH_A), 4.27 (d, *J* = 11.6 Hz, 1 H, 3'-O-CH_A), 4.30 (d, *J* = 11.6 Hz, 1 H, 3'-O-CH_B), 4.35 (d, *J* = 11.8 Hz, 1 H, 6'-O-CH_B), 4.38 (d, *J* = 9.0 Hz,

1 H, 1'-H), 4.41 (t, $J = 9.0$ Hz, 1 H, 2'-H), 4.52 (d, $J = 11.8$ Hz, 1 H, 4'-O-CH_A), 4.95 (d, $J = 11.8$ Hz, 1 H, 4'-O-CH_B), 4.97 (d, $J = 11.2$ Hz, 1 H, 2'-O-CH_A), 5.09 (d, $J = 11.2$ Hz, 1 H, 2'-O-CH_B), 6.02 (dd, $J = 3.2$, 1.8 Hz, 1 H, 4-H), 6.67 (dd, $J = 3.2$, 0.8 Hz, 1 H, 3-H), 7.03–7.12 (m, 7 H, 5-H, 6 × Ar-H), 7.13–7.20 (m, 8 H, 8 × Ar-H), 7.24–7.28 (m, 2 H, 2 × Ar-H), 7.29–7.35 (m, 4 H, 4 × Ar-H).

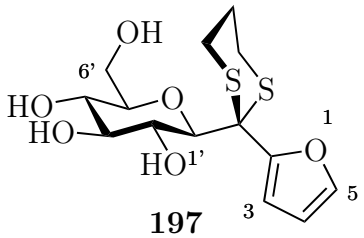
^{13}C-NMR (151 MHz, C_6D_6): δ (ppm) = 25.3 (1'-C-S-CH_2-$\underline{C}H_2$), 28.0, 28.6 (2 × 1'-C-S$\underline{C}H_2$), 55.8 (1'-CS_2), 69.4 (C-6'), 72.5 (C-3'-O$\underline{C}H_2$), 73.6 (C-6'-O$\underline{C}H_2$), 74.0 (C-4'), 74.2 (C-2'-O$\underline{C}H_2$), 74.4 (C-4'-O$\underline{C}H_2$), 77.0 (C-2'), 77.5 (C-5'), 86.0 (C-3'), 86.1 (C-1'), 110.8 (C-3), 110.8 (C-4), 127.0, 127.4, 127.5, 127.6, 127.7, 127.8, 128.0, 128.1, 128.1, 128.4, 128.5, 128.6 (20 × C-Ar), 139.0, 139.8, 140.2 (4 × C-Ar, quart.), 142.2 (C-5), 153.8 (C-2).

MS (ESI): m/z (%) = 709.3 (100) $[M + H]^+$, 726.3 (85) $[M + NH_4]^+$, 731.3 (74) $[M + Na]^+$.

calcd.: 709.2652 $[M + H]^+$,
found: 709.2652 (ESI-HRMS).

$C_{42}H_{44}O_6S_2$ (708.93).

6.16.3 1-(2-(Furan-2-yl)-1,3-dithian-2-yl)-β-D-glucopyranoside 197



197

A solution of 1,2,3,4,6-pentakis-*O*-trimethylsilyl-D-glucopyranose **174** (500 mg, 924 µmol, 1.00 equiv.) in DCM (5.00 mL) was cooled to 0 °C, TMSI (150 µL, 211 µg, 1.05 mmol, 1.14 equiv.) was added and the solution was stirred at r.t. for 15 min. The solvent was removed in vacuum and 2,3,4,6-tetrakis-*O*-trimethylsilyl-α-D-glucopyranosyl iodide **175** was obtained as orange oil, which was dissolved in THF (5.00 mL) and cooled to -95 °C. In a seperate vessel, a solution of 2-(1,3-dithian-2-yl)furan **147** (345 mg, 1.85 mmol, 2.00 equiv.) in THF (5.00 mL) was cooled to -95 °C and a solution of *t*-BuLi (c = 1.70 M in *n*-pentane, 1.10 mL, 1.87 mmol, 2.02 equiv.) was added. The solution was stirred at -95 °C for 10 min

and then transferred to the precooled solution of 2,3,4,6-tetrakis-*O*-trimethylsilyl-α-D-glucopyranosyl iodide **175** in THF. The reaction mixture was warmed to 0 °C over 2 h. Then, MeOH (10.0 mL) and NaOMe (49.9 mg, 924 µmol, 1.00 equiv.) were added and the reaction mixture was stirred at r.t. for 10 min. Afterwards, the solvent was removed in vacuum and the residue purified by reversed phase chromatography (RP-C18, $H_2O \rightarrow H_2O$/MeCN 3:1) to yield *C*-glycosidic compound **197** (194 mg, 556 µmol, 60%) as pale yellow solid.

TLC: R_f = 0.73 (EtOAc/MeCN/*n*-PrOH/H_2O 12:8:5:5).

M.p.: 92 °C.

$[\alpha]_D^{25}$ = -20.8 (c = 1.00, H_2O).

UV (H_2O): λ_{max} = 223 nm.

IR (ATR): $\tilde{\nu}$ = 3378, 2910, 1420, 1360, 1278, 1222, 1081, 1011, 904, 739 cm^{-1}.

^{1}H-NMR (600 MHz, D_2O: δ (ppm) = 1.86 (dddd, J = 14.7, 12.0, 6.9, 3.6 Hz, 1 H, 1'-C-SCH_2-C$\underline{H}_A$), 2.06 (dp, J = 14.7, 3.6 Hz, 1 H, 1'-C-S-CH_2-C$\underline{H}_B$), 2.82 (dd, J = 6.9, 3.6 Hz, 2 H, 1'-C-S-CH2), 2.88 (dt, J = 14.5, 3.6 Hz, 1 H, 1'-C-S-CH), 3.02 (ddd, J = 14.5, 12.0, 3.6 Hz, 1 H, 1'-C-S-CH), 3.34 (dd, J = 9.7, 9.1 Hz, 1 H, 4'-H), 3.42 (ddd, J = 9.7, 5.7, 2.3 Hz, 1 H, 5'-H), 3.44 (t, J = 9.1 Hz, 1 H, 3'-H), 3.48 (t, J = 9.1 Hz, 1 H, 2'-H), 3.74 (dd, J = 12.6, 5.7 Hz, 1 H, 6'-H_A), 3.82 (d, J = 9.1 Hz, 1 H, 1'-H), 3.92 (dd, J = 12.6, 2.3 Hz, 1 H, 6'-H_B), 6.54 (dd, J = 3.3, 1.9 Hz, 1 H, 4-H), 6.75 (dd, J = 3.3, 0.8 Hz, 1 H, 3-H), 7.57 (dd, J = 1.8, 0.8 Hz, 1 H, 5-H).

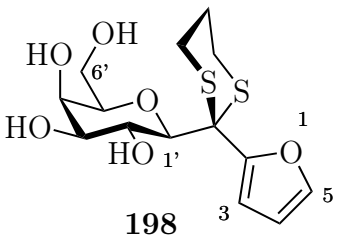
^{13}C-NMR (151 MHz, D_2O: δ (ppm) = 24.5 (1'-C-S-CH_2-$\underline{C}H_2$, 27.0, 27.3 (2 × 1'-C-S$\underline{C}H_2$), 55.3 (1'-CS_2), 60.8 (C-6'), 69.2 (C-4'), 70.9 (C-2'), 77.7 (C-3'), 80.0 (C-5'), 83.6 (C-1'), 110.9 (C-4), 112.7 (C-3), 142.9 (C-5), 150.7 (C-2).

MS (ESI): m/z (%) = 349.1 (94) $[M + H]^+$, 371.1 (100) $[M + Na]^+$.

calcd.: 371.0594 $[M + Na]^+$,
found: 371.0594 (ESI-HRMS).

$C_{14}H_{20}O_6S_2$ (348.43).

6.16.4 1-(2-(Furan-2-yl)-1,3-dithian-2-yl)-β-D-galactopyranoside 198



198

A solution of 1,2,3,4,6-pentakis-*O*-trimethylsilyl-D-galactopyranose **304** (500 mg, 924 µmol, 1.00 equiv.) in DCM (5.00 mL) was cooled to 0 °C, TMSI (150 µL, 211 µg, 1.05 mmol, 1.14 equiv.) was added and the solution was stirred at r.t. for 15 min. The solvent was removed in vacuum and 2,3,4,6-tetrakis-*O*-trimethylsilyl-α-D-galactopyranosyl iodide **305** was obtained as orange oil, which was dissolved in THF (5.00 mL) and cooled to -95 °C. In a seperate vessel, a solution of 2-(1,3-dithian-2-yl)furan **147** (345 mg, 1.85 mmol, 2.00 equiv.) in THF (5.00 mL) was cooled to -95 °C and a solution of *t*-BuLi (c = 1.70 M in *n*-pentane, 1.10 mL, 1.87 mmol, 2.02 equiv.) was added. The solution was stirred at -95 °C for 10 min and then transferred to the precooled solution of 2,3,4,6-tetrakis-*O*-trimethylsilyl-α-D-galactopyranosyl iodide **305** in THF. The reaction mixture was warmed to 0 °C over 2 h. Then, MeOH (10.0 mL) and NaOMe (49.9 mg, 924 µmol, 1.00 equiv.) were added and the reaction mixture was stirred at r.t. for 10 min. Afterwards, the solvent was removed in vacuum and the residue purified by reversed phase chromatography (RP-C18, $H_2O \rightarrow H_2O$/MeCN 3:1) to yield *C*-glycosidic compound **198** (128 mg, 367 µmol, 40%) as pale yellow solid.

TLC: R_f = 0.61 (EtOAc/MeCN/*n*-PrOH/H_2O 12:8:5:5).

M.p.: 83 °C.

$[\alpha]_D^{25}$ = -4.2 (c = 1.00, H_2O).

UV (H_2O): λ_{max} = 226 nm.

IR (ATR): $\tilde{\nu}$ = 3401, 3336, 2903, 1420, 1278, 1220, 1071, 884, 743, 596 cm^{-1}.

^{1}H-NMR (600 MHz, D_2O: δ (ppm) = 1.79–1.91 (m, 1 H, 1'-C-S-CH_2-C$\underline{H_A}$), 2.02–2.09 (m, 1 H, 1'-C-S-CH_2-C$\underline{H_B}$), 2.76–2.85 (m, 2 H, 1'-C-S-CH2), 2.88 (dt, *J* = 14.5, 3.9 Hz, 1 H, 1'-C-S-CH), 3.03 (ddd, *J* = 14.5, 12.0, 2.8 Hz, 1 H, 1'-C-S-CH), 3.59 (dd, *J* = 9.0, 3.5 Hz, 1 H, 3'-H), 3.68 (dd, *J* = 7.7, 4.5 Hz, 1 H, 5'-H), 3.72 (dd, *J* = 11.7, 4.5 Hz, 1 H, 6'-H_A), 3.73 (t, *J* = 9.0 Hz, 1 H, 2'-H), 3.76 (d, *J* = 9.0 Hz, 1 H, 1'-H), 3.83 (dd, *J* = 11.7, 7.7 Hz,

1 H, 6'-H_B), 3.94 (d, $J = 3.5$ Hz, 1 H, 4'-H), 6.53 (dd, $J = 3.3$, 1.8 Hz, 1 H, 4-H), 6.75 (d, $J = 3.3$ Hz, 1 H, 3-H), 7.57 (d, $J = 1.8$ Hz, 1 H, 5-H).

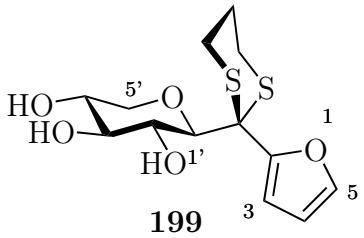
^{13}C-NMR (151 MHz, D_2O: δ (ppm) = 24.4 (1'-C-S-CH_2-$\underline{C}H_2$), 27.0, 27.3 ($2 \times$ 1'-C-S$\underline{C}H_2$), 55.5 (1'-CS_2), 61.1 (C-6'), 68.1 (C-2'), 68.6 (C-4'), 74.4 (C-3'), 79.2 (C-5'), 84.3 (C-1'), 110.9 (C-4), 112.6 (C-3), 142.9 (C-5), 150.9 (C-2).

MS (ESI): m/z (%) = 349.1 (47) $[M + H]^+$, 371.1 (100) $[M + Na]^+$.

calcd.: 371.0594 $[M + Na]^+$,
found: 371.0593 (ESI-HRMS).

$C_{14}H_{20}O_6S_2$ (348.43).

6.16.5 1-(2-(Furan-2-yl)-1,3-dithian-2-yl)-β-D-xylopyranoside 199



199

A solution of 1,2,3,4,-tetrakis-*O*-trimethylsilyl-D-xylopyranose **306** (405 mg, 925 µmol, 1.00 equiv.) in DCM (5.00 mL) was cooled to 0 °C, TMSI (150 µL, 211 µg, 1.05 mmol, 1.14 equiv.) was added and the solution was stirred at r.t. for 15 min. The solvent was removed in vacuum and 2,3,4-tris-*O*-trimethylsilyl-α-D-xylopyranosyl iodide **307** was obtained as yellow oil, which was dissolved in THF (5.00 mL) and cooled to -95 °C. In a seperate vessel, a solution of 2-(1,3-dithian-2-yl)furan **147** (345 mg, 1.85 mmol, 2.00 equiv.) in THF (5.00 mL) was cooled to -95 °C and a solution of *t*-BuLi (c = 1.70 M in *n*-pentane, 1.10 mL, 1.87 mmol, 2.02 equiv.) was added. The solution was stirred at -95 °C for 10 min and then transferred to the precooled solution of 2,3,4-tris-*O*-trimethylsilyl-α-D-xylopyranosyl iodide **307** in THF. The reaction mixture was warmed to 0 °C over 2 h. Then, MeOH (10.0 mL) and NaOMe (49.9 mg, 924 µmol, 1.00 equiv.) were added and the reaction mixture was stirred at r.t. for 10 min. Afterwards, the solvent was removed in vacuum and the residue purified by reversed phase chromatography (RP-C18, $H_2O \rightarrow H_2O$/MeCN 3:1) to yield *C*-glycosidic compound **199** (218 mg, 685 µmol, 74%) as pale yellow solid.

TLC: R_f = 0.84 (EtOAc/MeCN/*n*-PrOH/H_2O 12:8:5:5).

M.p.: 122 °C.

$[\alpha]_D^{25}$ = -19.8 (c = 1.00, MeOH).

UV (MeOH): λ_{max} = 224 nm.

IR (ATR): $\tilde{\nu}$ = 3511, 3358, 2911, 2860, 1300, 1112, 1092, 1060, 1012, 989, 936, 796, 763, 588, 532 cm^{-1}.

^{1}H-NMR (600 MHz, D_2O: δ (ppm) = 1.78–1.89 (m, 1 H, 1'-C-S-CH_2-C$\underline{H_A}$), 2.02–2.10 (m, 1 H, 1'-C-S-CH_2-C$\underline{H_B}$), 2.76 (dt, J = 14.6, 4.1 Hz, 1 H, 1'-C-S-CH), 2.83 (ddd, J = 14.6, 9.1, 2.9 Hz, 2 H, 2 × 1'-C-S-CH), 2.99 (ddd, J = 14.6, 12.2, 2.8 Hz, 1 H, 1'C-S-CH), 3.28 (t, J = 11.0 Hz, 1 H, 5'-H_A), 3.38 (t, J = 9.1 Hz, 1 H, 3'-H), 3.44 (t, J = 9.1 Hz, 1 H, 2'-H), 3.51 (ddd, J = 11.0, 9.1, 5.5 Hz, 1 H, 4'-H), 3.74 (d, J = 9.1 Hz, 1 H, 1'-H), 3.98 (dd, J = 11.0, 5.5 Hz, 1 H, 5'-H_B), 6.54 (dd, J = 3.3, 1.9 Hz, 1 H, 4-H), 6.75 (dd, J = 3.3, 0.9 Hz, 1 H, 3-H), 7.57 (dd, J = 1.9, 0.9 Hz, 1 H, 5-H).

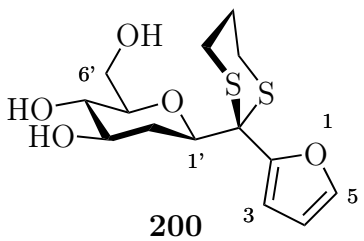
^{13}C-NMR (151 MHz, D_2O: δ (ppm) = 24.5 (1'-C-S-CH_2-$\underline{C}H_2$), 26.8, 27.2 (2 × 1'CS$\underline{C}H_2$), 55.2 (1'-CS_2), 68.8 (C-4'), 68.9 (C-5'), 70.9 (C-2'), 77.7 (C-3'), 83.9 (C-1'), 110.9 (C-4), 113.0 (C-3), 143.1 (C-2), 150.6 (C-5).

MS (ESI): m/z (%) = 319.1 (68) $[M + H]^+$, 341.0 (100) $[M + Na]^+$, 659.1 (89) $[2 M + Na]^+$.

calcd.: 341.0488 $[M + Na]^+$,
found: 341.0489 (ESI-HRMS).

$C_{13}H_{18}O_5S_2$ (318.40).

6.16.6 1-(2-(Furan-2-yl)-1,3-dithian-2-yl)-β-2-deoxy-D-glucopyranoside 200



200

A solution of 1,3,4,6-tetrakis-*O*-trimethylsilyl-2-deoxy-D-glucopyranose **190** (418 mg, 923 µmol, 1.00 equiv.) in 2-MeTHF (5.00 mL) was cooled to 0 °C, TMSI (150 µL, 211 µg, 1.05 mmol, 1.14 equiv.) was added and the solution was stirred 0 °C for 1 h. Then, the solution was cooled to -95 °C. In a seperate vessel, a solution of 2-(1,3-dithian-2-yl)furan **147** (345 mg, 1.85 mmol, 2.00 equiv.) in 2-MeTHF (5.00 mL) was cooled to -95 °C and a solution of *t*-BuLi (c = 1.70 M in *n*-pentane, 1.10 mL, 1.87 mmol, 2.02 equiv.) was added. The solution was stirred at -95 °C for 10 min and then transferred to the precooled solution of 3,4,6-tris-*O*-trimethylsilyl-α-2-deoxy-D-glucopyranosyl iodide **310** in 2-MeTHF. The reaction mixture was warmed to 0 °C over 2 h. Then, MeOH (10.0 mL) and NaOMe (49.9 mg, 924 µmol, 1.00 equiv.) were added and the reaction mixture was stirred at r.t. for 10 min. Afterwards, the solvent was removed in vacuum and the residue purified by reversed phase chromatography (RP-C18, $H_2O \rightarrow H_2O$/MeCN 3:1) to yield *C*-glycosidic compound **200** (206 mg, 620 µmol, 67%) as pale yellow solid.

TLC: R_f = 0.75 (EtOAc/MeCN/*n*-PrOH/H_2O 12:8:5:5).

M.p.: 179 °C.

$[\alpha]_D^{25}$ = -9.4 (c = 1.00, MeOH).

UV (MeOH): λ_{max} = 222 nm.

IR (ATR): $\tilde{\nu}$ = 3562, 3339, 1419, 1359, 1089, 1065, 1033, 1013, 948, 895, 786, 712, 601, 549 cm^{-1}.

^{1}H-NMR (600 MHz, methanol-d_4): δ (ppm) = 1.48 (dt, 1 H, J = 13.0, 11.4 Hz, 2'-H_{ax}), 1.83 (ddd, J = 13.0, 5.0, 1.7 Hz, 1 H, 2'-H_{eq}), 1.86–1.92 (m, 1 H, 1'-C-S-CH_2-C$\underline{H}_A$), 1.98–2.04 (m, 1 H, 1'-C-S-CH_2-C$\underline{H}_B$), 2.76–2.90 (m, 4 H, 2 × 1'-C-S-CH_2), 3.08 (t, J = 9.1 Hz, 1 H, 4'-H), 3.18 (ddd, J = 9.1, 5.7, 2.5 Hz, 1 H, 5'-H), 3.47 (ddd, J = 11.4, 9.1, 5.0 Hz, 1 H, 3'-H), 3.66 (dd, J = 12.1, 5.7 Hz, 1 H, 6'-H_A), 3.83 (dd, J = 12.1, 2.5 Hz, 1 H, 6'-H_B), 3.85 (dd, J = 11.4, 1.7 Hz, 1 H, 1'-H), 6.45 (dd, J = 3.2, 1.8 Hz, 1 H, 4-H), 6.63 (dd, J = 3.2, 0.6 Hz, 1 H, 3-H), 7.53 (dd, J = 1.8, 0.6 Hz, 1 H, 5-H).

^{13}C-NMR (151 MHz, methanol-d_4): δ (ppm) = 25.0 (1'-C-S-CH_2-$\underline{C}H_2$, 27.2, 27.4 (2 × 1'-C-S$\underline{C}H_2$), 34.3 (C-2'), 56.2 (1'-CS_2), 62.7 (C-6'), 71.7 (C-4'), 72.4 (C-3'), 81.0 (C-5'), 81.8 (C-1'), 110.4 (C-4), 111.8 (C-3), 142.6 (C-5), 152.0 (C-2).

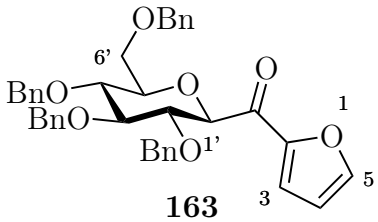
MS (ESI): m/z (%) = 333.1 (23) $[M + H]^+$, 355.1 (100) $[M + Na]^+$.

calcd.: 355.0644 $[M + Na]^+$,
found: 355.0647 (ESI-HRMS).

$C_{14}H_{20}O_5S_2$ (332.43).

6.17 Synthesis of *C*-furoyl glycopyranosides

6.17.1 (Furan-2-yl)(2,3,4,6-tetra-*O*-benzyl-β-D-glucopyranosyl) ketone 163



163

To a suspension of *C*-(1,3-dithian-2-yl)-D-glucopyranoside **155** (703 mg, 992 µmol, 1.00 equiv.) in water (5.00 mL) were added DCM (703 µL), sodium dodecyl sulfate (57.2 mg, 198 µmol, 20.0 mol%), aqueous H_2O_2-solution (c = 30.0%, 450 µL, 4.40 mmol, 4.44 equiv.) and iodine (12.6 mg, 50.0 µmol, 5.00 mol%). The reaction mixture was stirred at r.t. for 1 h. Saturated aqueous $Na_2S_2O_3$-solution (5.00 mL) was added and the mixture extracted with EtOAc (3 × 10.0 mL). The combined organic layers were washed with water (2 × 10.0 mL) and brine (10.0 mL), dried over $MgSO_4$ and filtered. After removal of the solvent in vacuum the residue was purified by recrystallisation from MeOH to yield perbenzylated scleropentaside A **163** (501 mg, 810 µmol, 82%) as colorless solid.

TLC: R_f = 0.45 (PE/EtOAc 4:1).

M.p.: 92 °C.

$[\alpha]_D^{25}$ = 15.6 (c = 1.01, $CHCl_3$).

UV (MeCN): λ_{max} = 204, 228, 277 nm.

IR (ATR): $\tilde{\nu}$ = 1667, 1466, 1089, 1067, 1038, 1028, 1006, 734, 695, 589 cm^{-1}.

^{1}H-NMR (600 MHz, $CDCl_3$): δ (ppm) = 3.61 (ddd, J = 9.8, 4.8, 1.9 Hz, 1 H, 5'-H), 3.72–3.66 (m, 2 H, 4'-H, 6'-H_A), 3.75 (dd, J = 11.0, 1.9 Hz, 1 H, 6'-H_B), 3.82 (t, J = 9.0 Hz, 1 H, 3'-H), 3.94 (dd, J = 9.0, 9.6 Hz, 1 H, 2'-H), 4.46 (d, J = 9.6 Hz, 1 H, 1'-H), 4.52 (d, J = 10.5 Hz, 1 H, 2'-O-CH_A), 4.53 (d, J = 12.1 Hz, 1 H, 6'-O-CH_A), 4.57 (d, J = 12.1 Hz,

1 H, 6'-O-CH_B), 4.59 (d, $J = 10.8$ Hz, 1 H, 4'-O-CH_A), 4.69 (d, $J = 10.5$ Hz, 1 H, 2'-O-CH_B), 4.84 (d, $J = 10.8$ Hz, 1 H, 4'-O-CH_B), 4.90 (d, $J = 11.1$ Hz, 1 H, 3'-O-CH_A), 4.94 (d, $J = 11.1$ Hz, 1 H, 3'-O-CH_B), 6.51 (dd, $J = 3.6$, 1.7 Hz, 1 H, 4-H), 7.03–7.06 (m, 2 H, 2 × Ar-H), 7.17–7.22 (m, 5 H, 5 × Ar-H), 7.27–7.35 (m, 13 H, 13 × Ar-H), 7.39 (dd, $J = 3.6$, 0.7 Hz, 1 H, 3-H), 7.63 (dd, $J = 1.7$, 0.7 Hz, 1 H, 5-H)

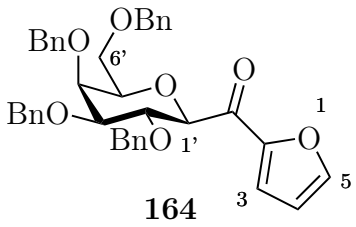
^{13}C-NMR (151 MHz, $CDCl_3$): δ (ppm) = 69.1 (C-6'), 73.6 (C-6'-O<u>C</u>H_2), 75.2 (C2'O<u>C</u>H_2), 75.3 (C-4'-O<u>C</u>H_2), 75.8 (C-3'-O<u>C</u>H_2), 78.0 (C-4'), 79.8 (C-1'), 79.9 (C-5'), 80.0 (C-2'), 86.9 (C-3'), 112.6 (C-4), 120.5 (C-3), 127.7, 127.8 (2 C), 127.8, 127.9 (3 C), 128.0, 128.2 (2 C), 128.3 (2 C), 128.4 (2 C), 128.5 (2 C), 128.6 (2 C), 128.6 (2 C) (20 × C-Ar), 137.5, 137.9, 138.1, 138.5 (4 × C-Ar, quart.), 147.4 (C-5), 151.6 (C-2), 183.9 (CO).

MS (ESI): *m/z* (%) = 619.3 (37) $[M + H]^+$, 636.3 (54) $[M + NH_4]^+$, 641.3 (100) $[M + Na]^+$.

calcd.: 641.2519 $[M + Na]^+$,
found: 641.2510 (ESI-HRMS).

$C_{39}H_{38}O_7$ (618.73).

6.17.2 (Furan-2-yl)(2,3,4,6-tetra-*O*-benzyl-β-D-galactopyranosyl) ketone 164



164

To a suspension of benzylated *C*-(1,3dithian-2-yl)galactopyranoside **162** (100 mg, 141 µmol, 1.00 equiv.) in water (5.00 mL) were added DCM (100 µL), sodium dodecyl sulfate (8.10 mg, 28.1 µmol, 19.9 mol%), aqueous H_2O_2-solution (c = 30.0%, 64.0 µL, 626 µmol, 4.44 equiv.) and iodine (1.80 mg, 7.09 µmol, 5.03 mol%). The reaction mixture was stirred at r.t. for 1 h. Saturated aqueous $Na_2S_2O_3$-solution (5.00 mL) was added and the mixture extracted with EtOAc (3 × 10.0 mL). The combined organic layers were washed with water (2 × 10.0 mL) and brine (10.0 mL), dried over $MgSO_4$ and filtered. After removal of the solvent in vacuum the residue was purified by column chromatography

(SiO_2, PE/EtOAc 9:1 → PE/EtOAc 2:1) *C*-furoyl glycosidic compound **164** (54.0 mg, 87.3 µmol, 62%) as colorless solid.

TLC: R_f = 0.25 (PE/EtOAc 4:1).

M.p.: 67 °C.

$[\alpha]_D^{25}$ = 2.0 (c = 1.00, $CHCl_3$).

UV (MeCN): λ_{max} = 204, 276 nm.

IR (ATR): $\tilde{\nu}$ = 2922, 2869, 1670, 1565, 1465, 1363, 1271, 1210, 1092, 1027, 982, 883, 733, 695, 591 cm^{-1}.

^{1}H-NMR (600 MHz, $CDCl_3$): δ (ppm) = 3.60 (d, J = 6.3 Hz, 2 H, 2 × 6'-H), 3.69 (t, J = 6.3 Hz, 1 H, 5'-H), 3.72 (dd, J = 9.4, 2.7 Hz, 1 H, 3'-H), 4.04 (d, J = 2.7 Hz, 1 H, 4'-H), 4.29 (d, J = 9.4 Hz, 1 H, 1'-H), 4.33 (t, J = 9.4 Hz, 1 H, 2'-H), 4.42 (d, J = 11.8 Hz, 1 H, 6'-O-CH_A), 4.47 (d, J = 11.8 Hz, 1 H, 6'-O-CH_B), 4.56 (d, J = 10.5 Hz, 1 H, 2'-O-CH_A), 4.63 (d, J = 11.4 Hz, 1 H, 4'-O-CH_A), 4.74 (d, J = 10.5 Hz, 1 H, 2'-O-CH_B) 4.75 (d, J = 11.7 Hz, 1 H, 3'-O-CH_A) 4.79 (d, J = 11.7 Hz, 1 H, 3'-O-CH_B), 5.01 (d, J = 11.4 Hz, 1 H, 4'-O-CH_B), 6.41 (dd, J = 3.6, 1.6 Hz, 1 H, 4-H), 7.09–7.13 (m, 2 H, 2 × Ar-H), 7.16–7.23 (m, 3 H, 3 × Ar-H), 7.25–7.40 (m, 15 H, 15 × Ar-H), 7.42 (d, J = 3.6 Hz, 1 H, 3-H), 7.58 (d, J = 1.6 Hz, 1 H, 5-H).

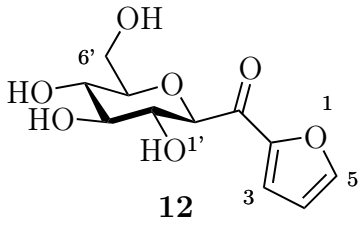
^{13}C-NMR (151 MHz, $CDCl_3$): δ (ppm) = 69.0 (C-6'), 72.7 (C-3'-O$\underline{C}H_2$), 73.7 (C-6'O$\underline{C}H_2$), 73.8 (C-4'), 74.7 (C-4'-O$\underline{C}H_2$), 75.2 (C-2'-O$\underline{C}H_2$), 76.3 (C-2'), 78.0 (C-5'), 81.6 (C-1'), 84.5 (C-3'), 112.3 (C-4), 120.8 (C-3), 127.6 (2 C), 127.7, 127.8, 127.8, 128.0, 128.1 (2 C), 128.1 (2 C), 128.3 (2 C), 128.4 (2 C), 128.5 (2 C), 128.6 (2 C), 128.6 (2 C) (20 × C-Ar), 137.9, 137.9, 138.4, 138.8 (4 × C-Ar, quart.), 147.2 (C-5), 151.0 (C-2), 183.9 (CO).

MS (ESI): m/z (%) = 511.2 (87) [M - OBn]$^+$, 619.3 (13) [M + H]$^+$, 636.3 (100) [M + NH_4]$^+$, 641.3 (58) [M + Na]$^+$.

calcd.: 636.2956 [M + NH_4]$^+$,
found: 636.2956 (ESI-HRMS).

$C_{39}H_{38}O_7$ (618.73).

6.17.3 Scleropentaside A 12



12

Method A: To a solution of *C*-1,3-dithian-2-yl-glycosidic compound **197** (171 mg, 491 µmol, 1.00 equiv.) in water (5.00 mL) were added aqueous H_2O_2-solution (c = 30.0%, 223 µL, 2.18 mmol, 4.44 equiv.) and iodine (6.20 mg, 24.4 µmol, 4.98 mol%). The reaction mixture was stirred at r.t. for 30 min. The reaction was cooled to 0 °C. Then, KI (8.20 mg, 4.94 mmol, 10.1 mol%) was added, the mixture diluted with water (20.0 mL) and washed with *n*-pentane (3 × 20.0 mL). The solvent was removed in vacuum and the residue was purified by reversed phase chromatography (RP-C18, H_2O → H_2O/MeCN 9:1) to yield scleropentaside A **12** (99.1 mg, 383 µmol, 78%) as colorless solid.

Method B: To a solution of perbenzylated scleropentaside A **163** (501 g, 810 µmol, 1.00 equiv.) in DCM (20.0 mL) was added $FeCl_3$(1.05 g, 6.48 mmol, 8.00 equiv.) and the reaction mixture was stirred at r.t. for 1 h. Afterwards, water (20.0 mL) was added. The layers were seperated and the organic layer extracted with water (3 × 20.0 mL). Aqueous NaOH-solution (3 M) was added to the combined aqueous layers until pH = 14. The precipitate was filtered off and the filtrate neutralized with aqueous HCl (3 M). The solvent was removed in vacuum and the residue taken up in MeOH (50.0 mL). The insoluable salts were removed by filtration and the solvent was removed in vacuum. The residue was purified by column chromatography (SiO_2, DCM/MeOH 9:1) to give crude scleropentaside A **12**, which was further purified by reversed phase chromatography (RP-C18, H_2O → H_2O/MeCN 9:1) to yield scleropentaside A **12** (85.0 mg, 329 µmol, 41%) as colorless crystalline solid.

TLC: R_f = 0.21 (DCM/MeOH 4:1).

M.p.: 162 °C.

$[\alpha]_D^{25}$ = -35.7 (c = 1.03, H_2O).

UV (H_2O): λ_{max} = 230, 284 nm.

IR (ATR): $\tilde{\nu}$ = 1656, 1083, 1054, 1039, 1024, 1007, 991, 785, 751, 586 cm^{-1}.

^{1}H-NMR (600 MHz, DMSO-d_6): δ (ppm) = 3.12 (td, J = 9.2, 5.3 Hz, 1 H, 4'-H), 3.25–3.31 (m, 2 H, 3'-H, 5'-H), 3.40–3.49 (m, 2 H, 2'-H, 6'-H_A), 3.67 (ddd, J = 11.8, 5.7, 1.8 Hz, 1 H, 6'-H_B), 4.28 (d, J = 9.6 Hz, 1 H, 1'-H), 4.52 (t, J = 5.8 Hz, 1 H, 6'-OH), 4.99 (d, J = 5.3 Hz, 1 H, 4'-OH), 5.00 (d, J = 5.0 Hz, 1 H, 2'-OH), 5.09 (d, J = 5.8 Hz, 1 H, 3'-OH), 6.74 (dd, J = 3.6, 1.7 Hz, 1 H, 4-H), 7.60 (d, J = 3.6 Hz, 1 H, 3-H), 8.04 (d, J = 1.7 Hz, 1 H, 5-H).

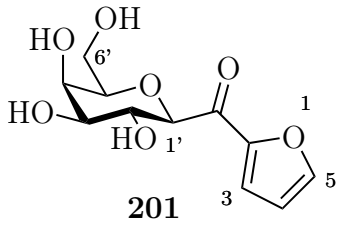
^{13}C-NMR (151 MHz, DMSO-d_6): δ (ppm) = 61.1 (C-6'), 70.0 (C-4'), 71.5 (C-2'), 78.0 (C-3'), 79.6 (C-1'), 81.6 (C-5'), 112.6 (C-4), 121.1 (C-3), 148.5 (C-5), 151.4 (C-2), 184.3 (CO).

MS (ESI): m/z (%) = 281.1 (100) $[M + Na]^+$.

calcd.: 281.0633 $[M + Na]^+$,
found: 281.0632 (ESI-HRMS).

$C_{11}H_{14}O_7$ (258.23).

6.17.4 (Furan-2-yl)(β-D-galactopyranosyl) ketone 201



201

To a solution of *C*-1,3-dithian-2-yl-glycosidic compound **198** (58.0 mg, 166 µmol, 1.00 equiv.) in water (1.70 mL) were added aqueous H_2O_2-solution (c = 30.0%, 76.0 µL, 744 µmol, 4.47 equiv.) and iodine (2.10 mg, 8.27 µmol, 4.98 mol%). The reaction mixture was stirred at r.t. for 30 min. The reaction was cooled to 0 °C. Then, KI (2.80 mg, 16.9 mmol, 10.2 mol%) was added, the mixture diluted with water (20.0 mL) and washed with *n*-pentane (3 × 20.0 mL). The solvent was removed in vacuum and the residue was purified by reversed phase chromatography (RP-C18, H_2O → H_2O/MeCN 9:1) to yield *C*-glycosidic compound **201** (33.1 mg, 128 µmol, 77%) as colorless solid.

TLC: R_f = 0.45 (EtOAc/MeCN/*n*-PrOH/H_2O 12:8:5:5).

M.p.: 135 °C.

$[a]_D^{25}$ = 1.8 (c = 1.00, H_2O).

UV (H_2O): λ_{max} = 231, 284 nm.

IR (ATR): $\tilde{\nu}$ = 3378, 2900, 1659, 1566, 1463, 1395, 1282, 1054, 883, 778, 695, 587 cm^{-1}.

^{1}H-NMR (600 MHz, DMSO-d_6): δ (ppm) = 3.40 (dd, J = 9.4, 3.2 Hz, 1 H, 3'-H), 3.45–3.57 (m, 3 H, 5'-H, 2 × 6'-H), 3.76 (d, J = 3.2 Hz, 1 H, 4'-H), 3.82 (t, J = 9.4 Hz, 1 H, 2'-H), 4.07 (d, J = 9.4 Hz, 1 H, 1'-H), 4.38–5.31 (m, 4 H, 4 × OH), 6.73 (dd, J = 3.6, 1.6 Hz, 1 H, 4-H), 7.63 (d, J = 3.6 Hz, 1 H, 3-H), 8.02 (d, J = 1.6 Hz, 1 H, 5-H).

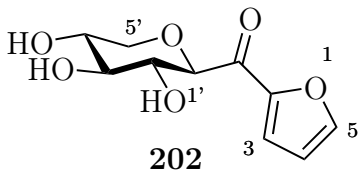
^{13}C-NMR (151 MHz, DMSO-d_6): δ (ppm) = 60.8 (C-6'), 68.6 (C-4'), 68.6 (C-2'), 74.5 (C-3'), 79.7 (C-5'), 81.7 (C-1'), 112.5 (C-4), 121.1 (C-3), 148.2 (C-5), 150.8 (C-2), 184.6 (CO).

MS (ESI): m/z (%) = 281.1 (100) $[M + Na]^+$.

calcd.: 281.0632 $[M + Na]^+$,
found: 281.0630 (ESI-HRMS).

$C_{11}H_{14}O_7$ (258.23).

6.17.5 (Furan-2-yl)(β-D-xylopyranosyl) ketone 202



202

To a solution of *C*-1,3-dithian-2-yl-glycosidic compound **199** (189 mg, 593 µmol, 1.00 equiv.) in water (3.00 mL) were added aqueous H_2O_2-solution (c = 30.0%, 269 µL, 2.60 mmol, 4.38 equiv.) and iodine (7.50 mg, 29.5 µmol, 4.97 mol%). The reaction mixture was stirred at r.t. for 30 min and cooled to 0 °C. Then, KI (9.80 mg, 59.0 µmol, 9.95 mol%) was added, the mixture diluted with water (20.0 mL) and washed with *n*-pentane (3 × 20.0 mL). The solvent was removed in vacuum and the residue was purified by reversed phase chromatography (RP-C18, H_2O → H_2O/MeCN 3:1) to yield *C*-glycosidic compound **202** (94.2 mg, 413 µmol, 70%) as colorless solid.

TLC: R_f = 0.76 (EtOAc/MeCN/*n*-PrOH/H_2O 12:8:5:5).

M.p.: 132 °C.

$[\alpha]_D^{25}$ = -30.2 (c = 1.00, MeOH).

UV (MeOH): λ_{max} = 222, 274 nm.

IR (ATR): $\tilde{\nu}$ = 3380, 2927, 1670, 1566, 1464, 1396, 1241, 1038, 770, 591, 528 cm^{-1}.

^{1}H-NMR (600 MHz, methanol-d_4): δ (ppm) = 3.33 (t, J = 10.7 Hz, 1 H, 5'-H_A), 3.43 (t, J = 9.2 Hz, 1 H, 3'-H), 3.57 (ddd, J = 10.7, 9.2, 5.4 Hz, 1 H, 4'-H), 3.64 (t, J = 9.2 Hz, 1 H, 2'-H), 3.97 (dd, J = 10.7, 5.4 Hz, 1 H, 5'-H_B), 4.35 (d, J = 9.2 Hz, 1 H, 1'-H), 6.67 (dd, J = 3.7, 1.7 Hz, 1 H, 4-H), 7.52 (dd, J = 3.7, 0.7 Hz, 1 H, 3-H), 7.85 (dd, J = 1.7, 0.7 Hz, 1 H, 5-H).

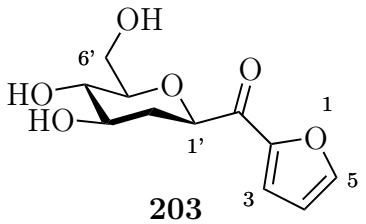
^{13}C-NMR (151 MHz, methanol-d_4): δ (ppm) = 71.0 (C-4'), 71.4 (C-5'), 73.0 (C-2'), 79.5 (C-3'), 82.1 (C-1'), 113.6 (C-4), 122.2 (C-3), 149.7 (C-5), 153.1 (C-2), 186.3 (CO).

MS (ESI): m/z (%) = 251.1 (100) $[M + Na]^+$, 479.1 (100) $[2 M + Na]^+$.

calcd.: 251.0526 $[M + Na]^+$,
found: 251.0526 (ESI-HRMS).

$C_{10}H_{12}O_6$ (228.20).

6.17.6 (Furan-2-yl)(β-2-deoxy-D-glucopyranosyl) ketone 203



203

To a solution of *C*-1,3-dithian-2-yl-glycosidic compound **200** (179 mg, 538 µmol, 1.00 equiv.) in water (2.70 mL) were added aqueous H_2O_2-solution (c = 30.0%, 269 µL, 2.37 mmol, 4.41 equiv.) and iodine (6.80 mg, 26.8 µmol, 4.98 mol%). The reaction mixture was stirred at r.t. for 30 min and cooled to 0 °C. Then, KI (8.90 mg, 53.5 µmol,

10.0 mol%) was added, the mixture diluted with water (20.0 mL) and washed with *n*-pentane (3 × 20.0 mL). The solvent was removed in vacuum and the residue was purified by reversed phase chromatography (RP-C18, $H_2O \rightarrow H_2O$/MeCN 3:1) to yield *C*-glycosidic compound **203** (120 mg, 495 µmol, 92%) as colorless solid.

TLC: R_f = 0.63 (EtOAc/MeCN/*n*-PrOH/H_2O 12:8:5:5).

M.p.: 139 °C.

$[a]_D^{25}$ = 29.6 (c = 1.00, H_2O).

UV (H_2O): λ_{max} = 235, 280 nm.

IR (ATR): $\tilde{\nu}$ = 3330, 1664, 1458, 1401, 1078, 1022, 957, 889, 779, 707, 594, 558, 549 cm^{-1}.

^{1}H-NMR (600 MHz, DMSO-d_6): δ (ppm) = 1.41 (dt, 1 H, J = 12.7, 11.6 Hz, 2'-H_{ax}), 2.04 (ddd, J = 12.7, 5.0, 2.1 Hz, 1 H, 2'-H_{eq}), 3.03 (t, J = 8.7 Hz, 1 H, 4'-H), 3.25 (ddd, J = 8.7, 6.2, 1.9 Hz, 1 H, 5'-H), 3.49 (dd, J = 11.8, 6.2 Hz, 1 H, 6'-H_A), 3.54 (ddd, J = 11.6, 8.7, 5.0 Hz, 1 H, 3'-H), 3.75 (dd, J = 11.8, 1.9 Hz, 1 H, 6'-H_B), 4.52 (dd, J = 11.6, 2.1 Hz, 1 H, 1'-H), 4.59 (s, 1 H, 6'-OH) 4.99 (s, 2 H, 3'-OH, 4'-OH), 6.73 (dd, J = 3.6, 1.7 Hz, 1 H, 4-H), 7.70 (d, J = 3.6 Hz, 1 H, 3-H), 8.03 (d, J = 1.7 Hz, 1 H, 5-H).

^{13}C-NMR (151 MHz, DMSO-d_6): δ (ppm) = 36.8 (C-2'), 61.7 (C-6'), 72.0 (C-4'), 72.1 (C3'), 77.7 (C-1'), 82.0 (C-5'), 113.0 (C-4), 122.0 (C-3), 148.8 (C-5), 150.3 (C-2), 196.5 (CO).

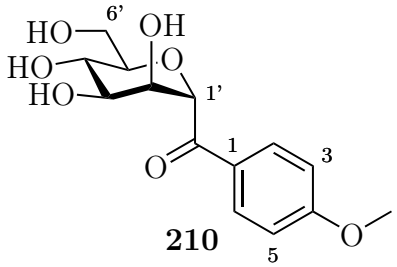
MS (ESI): m/z (%) = 265.1 (100) $[M + Na]^+$.

calcd.: 265.0683 $[M + Na]^+$,
found: 265.0682 (ESI-HRMS).

$C_{11}H_{14}O_6$ (242.23).

6.18 Syntheses of *C*-acyl α-D-mannopyranosides

6.18.1 (4-Methoxyphenyl)(α-D-mannopyranosyl) ketone 210



210

To neat 1,2,3,4,6-pentakis-*O*-trimethylsilyl-D-mannopyranose **205** (1.00 g, 1.85 mmol, 1.00 equiv.) was added TMSI (300 µL, 422 mg, 2.11 mmol, 1.14 equiv.) and the mixture was stirred at r.t. for 15 min to give 2,3,4,6-tetrakis-*O*-trimethylsilyl-α-D-mannopyranosyl iodide **206** as orange oil, which was dissolved in glyme (10.0 mL) and cooled to 0 °C.

In a separate vessel, a solution of 2-(4-methoxyphenyl)-1,3-dithiane **151** (837 mg, 3.70 mmol, 2.00 equiv.) in glyme (10.0 mL) was cooled to 0 °C and a solution of *t*-BuLi (c = 1.74 M in *n*-pentane, 2.10 mL, 3.65 mmol, 1.98 equiv.) was added. The mixture was stirred at 0 °C for 5 min and then CuI (900 µg, 4.72 µmol, 2.55 mol‰) and the precooled solution of 2,3,4,6-tetrakis-*O*-trimethylsilyl-α-D-mannopyranosyl iodide **206** in glyme were added. The reaction mixture was stirred at 0 °C for 3 h.

Then, the mixture was added to MeOH (70.0 mL) in a separate flask, NaOMe (200 mg, 924 µmol, 2.00 equiv.) was added and the mixture was stirred at r.t. for 10 min.

Afterwards, the mixture was diluted with water (10.0 mL), cooled to 0 °C and TFA (430 µL, 636 mg, 5.58 mmol, 3.04 equiv.) and PIFA (1.99 g, 4.62 mmol, 2.50 equiv.) were added. The reaction mixture was stirred at 0 °C for 10 min. Then, water (10.0 mL) and L-ascorbic acid (651 mg, 3.70 mmol, 2.00 equiv.) were added and the reaction mixture was stirred at r.t. for another 10 min.

The mixture was again diluted with water (30.0 mL) and impurities were removed by washing with *n*-pentane (3 × 50.0 mL). MeOH and glyme were removed from the aqueous phase in vacuum. The remaining concentrated aqueous phase was filtered to remove solid impurities. Without further removal of the solvent, the aqueous phase was directly purified by reversed phase column chromatography (RP-C18, $H_2O \rightarrow H_2O$/MeCN 3:1) to yield *C*-glycosidic compound **210** (240 mg, 805 µmol, 44%) as pale yellow solid.

TLC: $R_f = 0.58$ (DCM/MeOH 17:3).

M.p.: 144 °C (from water).

$[a]_D^{25} = 44.4$ (c = 1.00, MeOH).

UV (MeOH): $\lambda_{max} = 219$, 281 nm.

IR (ATR): $\tilde{\nu} = 3286$, 2927, 2897, 2843, 1651, 1602, 1575, 1425, 1325, 1257, 1101, 1066, 1028, 806, 605 cm^{-1}.

^{1}H-NMR (600 MHz, D_2O): δ (ppm) = 3.36 (ddd, J = 9.4, 6.2, 2.5 Hz, 1 H, 5'-H), 3.67 (dd, J = 12.6, 6.2 Hz, 1 H, 6'-H_A), 3.69 (t, J = 9.4 Hz, 1 H, 4'-H), 3.74 (dd, J = 12.6, 2.5 Hz, 1 H, 6'-H_B), 3.76 (dd, J = 9.4, 3.4 Hz, 1 H, 3'-H), 3.92 (s, 3 H, OCH_3), 4.51 (dd, J = 3.4, 2.2 Hz, 1 H, 2'-H), 5.32 (d, J = 2.2 Hz, 1 H, 1'-H), 7.07–7.11 (m, 2 H, 3-H, 5-H), 8.04–8.08 (m, 2 H, 2-H, 6-H).

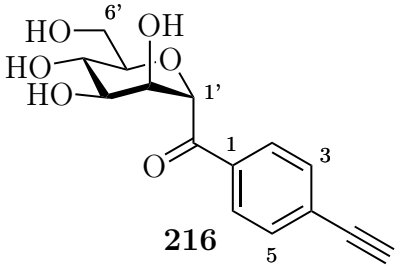
^{13}C-NMR (151 MHz, D_2O): δ (ppm) = 55.6 (OCH_3), 61.0 (C-6'), 66.9 (C-4'), 68.9 (C-2'), 71.1 (C-3'), 77.3 (C-5'), 80.1 (C-1'), 114.0 (2 C, C-3, C-5), 127.3 (C-1), 131.8 (2 C, C-2, C-6), 164.0 (C-4), 199.7 (CO).

MS (ESI): m/z (%) = 135.0 (100) [(4-methoxybenzylidyne)oxonium], 299.1 (19) $[M + H]^+$, 321.1 (98) $[M + Na]^+$.

calcd.: 321.0945 $[M + Na]^+$,
found: 321.0938 (ESI-HRMS).

$C_{14}H_{18}O_7$ (298.29).

6.18.2 (4-Ethynylphenyl)(α-D-mannopyranosyl) ketone 216



216

To neat 1,2,3,4,6-pentakis-*O*-trimethylsilyl-D-mannopyranose **205** (1.00 g, 1.85 mmol, 1.00 equiv.) was added TMSI (300 µL, 422 mg, 2.11 mmol, 1.14 equiv.) and the mixture

was stirred at r.t. for 15 min to give 2,3,4,6-tetrakis-*O*-trimethylsilyl-α-D-mannopyranosyl iodide **206** as orange oil, which was dissolved in glyme (10.0 mL) and cooled to 0 °C.

In a separate vessel, a solution of ((4-(1,3-dithian-2-yl)phenyl)ethynyl)trimethylsilane **215** (1.08 g, 3.70 mmol, 2.00 equiv.) in glyme (10.0 mL) was cooled to 0 °C and a solution of *t*-BuLi (c = 1.74 M in *n*-pentane, 2.10 mL, 3.65 mmol, 1.98 equiv.) was added. The solution was stirred at 0 °C for 5 min and then CuI (900 µg, 4.72 µmol, 2.55 mol‰) and the precooled solution of 2,3,4,6-tetrakis-*O*-trimethylsilyl-α-D-mannopyranosyl iodide **206** in glyme were added. The reaction mixture was stirred at 0 °C for 3 h.

Then, the mixture was added to MeOH (70.0 mL) in a separate flask, NaOMe (200 mg, 924 µmol, 2.00 equiv.) was added and the mixture was stirred at r.t. for 10 min.

Afterwards, the mixture was diluted with water (10.0 mL), cooled to 0 °C and TFA (430 µL, 636 mg, 5.58 mmol, 3.04 equiv.) and PIFA (1.99 g, 4.62 mmol, 2.50 equiv.) were added. The reaction mixture was stirred at 0 °C for 10 min. Then, water (10.0 mL) and L-ascorbic acid (651 mg, 3.70 mmol, 2.00 equiv.) were added and the reaction mixture was stirred at r.t. for another 10 min.

The mixture was again diluted with water (30.0 mL) and impurities were removed by washing with *n*-pentane (3 × 50.0 mL). MeOH and glyme were removed from the aqueous phase in vacuum. The remaining concentrated aqueous phase was filtered to remove solid impurities. Without further removal of the solvent, the aqueous phase was directly purified by reversed phase column chromatography (RP-C18, $H_2O \rightarrow H_2O$/MeCN 3:1) to yield *C*-glycosidic compound **216** (105 mg, 359 µmol, 19%) as colorless crystalline solid.

TLC: $R_f = 0.61$ (DCM/MeOH 17:3).

M.p.: 147 °C (from water).

$[\alpha]_D^{25} = 47.6$ (c = 1.00, MeOH).

UV (MeOH): $\lambda_{max} = 212, 273$ nm.

IR (ATR): $\tilde{\nu} = 3350, 3278, 2924, 2885, 2100, 1674, 1602, 1406, 1219, 1060, 1029, 804, 663, 621, 524$ cm^{-1}.

^{1}H-NMR (600 MHz, methanol-d_4): δ (ppm) = δ3.17–3.25 (m, 1 H, 5'-H), 3.63–3.71 (m, 4 H, 3'-H, 4'-H, 6'-H_2), 3.77 (s, 1 H, 4-C≡CH), 4.40 (t, $J = 2.4$ Hz, 1 H, 2'-H), 5.19 (d, $J = 2.4$ Hz, 1 H, 1'-H), 7.55–7.60 (m, 2 H, 3-H, 5-H), 8.06–8.11 (m, 2 H, 2-H, 6-H).

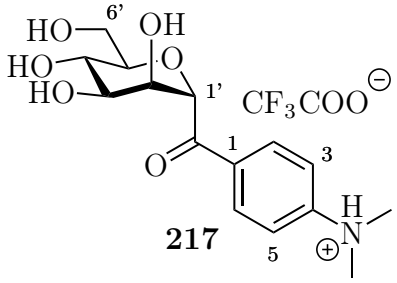
^{13}C-NMR (151 MHz, methanol-d_4): δ (ppm) = 62.8 (C-6'), 68.7 (C-4'), 70.3 (C-2'), 73.1 (C-3'), 79.5 (C-5'), 81.6 (C-1'), 82.2 (4-C≡CH), 83.6 (4-C≡CH), 128.9 (C-1), 130.3 (2 C, C-2, C-6), 133.1 (2 C, C-3, C-5), 136.2 (C-4), 199.9 (CO).

MS (ESI): *m/z* (%) = 129.0 (36) [(4-ethynylbenzylidyne)oxonium], 315.1 (48) $[M + Na]^+$.

calcd.: 315.0839 $[M + Na]^+$,
found: 315.0845 (ESI-HRMS).

$C_{15}H_{16}O_6$ (292.29).

6.18.3 (4-Dimethylaminophenyl)(α-D-mannopyranosyl) ketone TFA salt 217



217

To neat 1,2,3,4,6-pentakis-*O*-trimethylsilyl-D-mannopyranose **205** (1.00 g, 1.85 mmol, 1.00 equiv.) was added TMSI (300 µL, 422 mg, 2.11 mmol, 1.14 equiv.) and the mixture was stirred at r.t. for 15 min to give 2,3,4,6-tetrakis-*O*-trimethylsilyl-α-D-mannopyranosyl iodide **206** as orange oil, which was dissolved in glyme (10.0 mL) and cooled to 0 °C.

In a separate vessel, a solution of 2-(4-dimethylaminophenyl)-1,3-dithiane **297** (885 mg, 3.70 mmol, 2.00 equiv.) in glyme (10.0 mL) was cooled to 0 °C and a solution of *t*-BuLi (c = 1.80 M in *n*-pentane, 2.00 mL, 3.65 mmol, 1.95 equiv.) was added. The solution was stirred at 0 °C for 5 min and then CuI (900 µg, 4.72 µmol, 2.55 mol‰) and the precooled solution of 2,3,4,6-tetrakis-*O*-trimethylsilyl-α-D-mannopyranosyl iodide **206** in glyme were added. The reaction mixture was stirred at 0 °C for 3 h.

Then, the mixture was added to MeOH (70.0 mL) in a separate flask, NaOMe (200 mg, 924 µmol, 2.00 equiv.) was added and the mixture was stirred at r.t. for 10 min.

Afterwards, the mixture was diluted with water (10.0 mL), cooled to 0 °C and TFA (700 µL, 1.05 g, 9.24 mmol, 4.95 equiv.) and PIFA (1.99 g, 4.62 mmol, 2.50 equiv.) were added. The reaction mixture was stirred at 0 °C for 10 min. Then, water (10.0 mL) and L-ascorbic

acid (651 mg, 3.70 mmol, 2.00 equiv.) were added and the reaction mixture was stirred at r.t. for another 10 min.

The mixture was again diluted with water (30.0 mL) and impurities were removed by washing with *n*-pentane (3 × 50.0 mL). MeOH and glyme were removed from the aqueous phase in vacuum. The remaining concentrated aqueous phase was filtered to remove solid impurities. Without further removal of the solvent, the aqueous phase was directly purified by reversed phase column chromatography (RP-C18, H_2O + 0.1% TFA → H_2O/MeCN 3:1 + 0.1% TFA) to yield *C*-glycosidic compound **217** (358 mg, 841 µmol, 46%) as beige solid.

TLC: $R_f = 0.23$ (DCM/MeOH 9:1).

$[a]_D^{20} = 30.4$ (c = 0.97, H_2O/TFA 9:1).

UV (MeOH): $\lambda_{max} = 242$, 359 nm.

IR (ATR): $\tilde{\nu} = 3309$, 2920, 2870, 1649, 1633, 1602, 1543, 1433, 1382, 1184, 1068, 1029, 813, 719, 646 cm^{-1}.

^{1}H-NMR (600 MHz, DMSO-d_6): δ (ppm) = 3.02 (s, 6 H, $N(CH_3)_2$), 3.28 (ddd, J = 8.7, 5.7, 2.7 Hz, 1 H, 5'-H), 3.47 (t, J = 8.7 Hz, 1 H, 4'-H), 3.48 (dd, J = 11.8, 5.7 Hz, 6'-H_A), 3.48 (dd, J = 8.7, 2.8 Hz, 3'-H), 3.53 (dd, J = 11.8, 2.7 Hz, 1 H, 6'-H_B), 4.14 (t, J = 2.8 Hz, 1 H, 2'-H), 4.96 (d, J = 2.8 Hz, 1 H, 1'-H), 6.67–6.73 (m, 2 H, 3-H, 5-H), 7.88–7.93 (m, 2 H, 2-H, 6-H).

^{13}C-NMR (151 MHz, DMSO-d_6): δ (ppm) = 39.6 (2 C, $N(CH_3)_2$), 61.3 (C-6'), 67.3 (C-4'), 68.6 (C-2'), 71.3 (C-3'), 78.2 (C-5'), 78.7 (C-1'), 110.5 (2 C, C-3, C-5), 122.7 (C-1), 130.9 (2 C, C-2, C-6), 153.4 (C-4), 196.1 (CO).

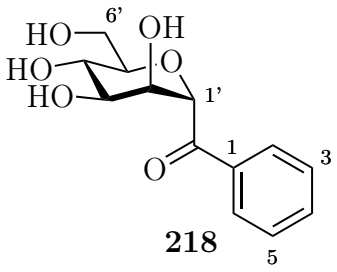
^{19}F-NMR (565 MHz, DMSO-d_6): δ (ppm) = 74.8 (m, CF_3COO^-).

MS (ESI): *m/z* (%) = 148.1 (15) [(4-dimethylaminobenzylidyne)oxonium], 312.1 (100) $[M - CF_3COO]^+$, 334.1 (20) $[M - CF_3COOH + Na]^+$.

calcd.: 312.1442 $[M - CF_3COO^-]^+$,
found: 312.1444 (ESI-HRMS).

$C_{17}H_{22}F_3NO_8$ (425.36).

6.18.4 Phenyl (α-D-mannopyranosyl) ketone 218



218

To neat 1,2,3,4,6-pentakis-*O*-trimethylsilyl-D-mannopyranose **205** (1.00 g, 1.85 mmol, 1.00 equiv.) was added TMSI (300 µL, 422 mg, 2.11 mmol, 1.14 equiv.) and the mixture was stirred at r.t. for 15 min to give 2,3,4,6-tetrakis-*O*-trimethylsilyl-α-D-mannopyranosyl iodide **206** as orange oil, which was dissolved in glyme (10.0 mL) and cooled to 0 °C.

In a separate vessel, a solution of 2-phenyl-1,3-dithiane **191** (726 mg, 3.70 mmol, 2.00 equiv.) in glyme (10.0 mL) was cooled to 0 °C and a solution of *t*-BuLi (c = 1.74 M in *n*-pentane, 2.10 mL, 3.65 mmol, 1.98 equiv.) was added. The solution was stirred at 0 °C for 5 min and then CuI (900 µg, 4.72 µmol, 2.55 mol‰) and the precooled solution of 2,3,4,6-tetrakis-*O*-trimethylsilyl-α-D-mannopyranosyl iodide **206** in glyme were added. The reaction mixture was stirred at 0 °C for 3 h.

Then, the mixture was added to MeOH (70.0 mL) in a separate flask, NaOMe (200 mg, 924 µmol, 2.00 equiv.) was added and the mixture was stirred at r.t. for 10 min.

Afterwards, the mixture was diluted with water (10.0 mL), cooled to 0 °C and TFA (430 µL, 636 mg, 5.58 mmol, 3.04 equiv.) and PIFA (1.99 g, 4.62 mmol, 2.50 equiv.) were added. The reaction mixture was stirred at 0 °C for 10 min. Then, water (10.0 mL) and L-ascorbic acid (651 mg, 3.70 mmol, 2.00 equiv.) were added and the reaction mixture was stirred at r.t. for another 10 min.

The mixture was again diluted with water (30.0 mL) and impurities were removed by washing with *n*-pentane (3 × 50.0 mL). MeOH and glyme were removed from the aqueous phase in vacuum. The remaining concentrated aqueous phase was filtered to remove solid impurities. Without further removal of the solvent, the aqueous phase was directly purified by reversed phase column chromatography (RP-C18, $H_2O \rightarrow H_2O$/MeCN 4:1) to yield *C*-glycosidic compound **218** (163 mg, 608 µmol, 33%) as pale yellow glassy solid.

TLC: $R_f = 0.55$ (DCM/MeOH 17:3).

$[a]_D^{25} = 33.9$ (c = 1.03, MeOH).

UV (MeOH): $\lambda_{max} = 247$ nm.

IR (ATR): $\tilde{\nu} = 3342$, 2929, 1678, 1598, 1448, 1421, 1336, 1259, 1220, 1066, 1022, 794, 759, 686, 636 cm^{-1}.

^{1}H-NMR (600 MHz, methanol-d_4): δ (ppm) = 3.27–3.30 (m, 1 H, 5'-H), 3.65–3.73 (m, 4 H, 3'-H, 4'-H, 6'-H_2), 4.40 (dd, $J = 3.3$, 2.2 Hz, 1 H, 2'-H), 5.22 (d, $J = 2.2$ Hz, 1 H, 1'-H), 7.48–7.52 (m, 2 H, 3-H, 5-H), 7.60–7.64 (m, 1 H, 4-H), 8.07–8.11 (m, 2 H, 2-H, 6-H).

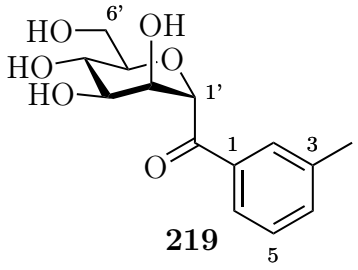
^{13}C-NMR (151 MHz, methanol-d_4): δ (ppm) = 62.8 (C-6'), 68.6 (C-4'), 70.5 (C-2'), 73.1 (C-3'), 79.3 (C-5'), 81.6 (C-1'), 129.6 (2 C, C-3, C-5), 130.2 (2 C, C-2, C-6), 134.7 (C-4), 136.6 (C-1), 200.6 (CO).

MS (ESI): m/z (%) = 291.1 (31) $[M + Na]^+$.

calcd.: 291.0839 $[M + Na]^+$,
found: 291.0839 (ESI-HRMS).

$C_{13}H_{16}O_6$ (268.27).

6.18.5 (3-Methylphenyl)(α-D-mannopyranosyl) ketone 219



219

To neat 1,2,3,4,6-pentakis-*O*-trimethylsilyl-D-mannopyranose **205** (1.00 g, 1.85 mmol, 1.00 equiv.) was added TMSI (300 µL, 422 mg, 2.11 mmol, 1.14 equiv.) and the mixture was stirred at r.t. for 15 min to give 2,3,4,6-tetrakis-*O*-trimethylsilyl-α-D-mannopyranosyl iodide **206** as orange oil, which was dissolved in glyme (10.0 mL) and cooled to 0 °C.

In a separate vessel, a solution of 2-(3-methylphenyl)-1,3-dithiane **288** (778 mg, 3.70 mmol, 2.00 equiv.) in glyme (10.0 mL) was cooled to 0 °C and a solution of *t*-BuLi (c = 1.72 M in *n*-pentane, 2.10 mL, 3.61 mmol, 1.95 equiv.) was added. The solution was stirred at 0 °C for 5 min and then CuI (900 µg, 4.72 µmol, 2.55 mol‰) and the precooled solution

of 2,3,4,6-tetrakis-*O*-trimethylsilyl-α-D-mannopyranosyl iodide **206** in glyme were added. The reaction mixture was stirred at 0 °C for 3 h.

Then, the mixture was added to MeOH (70.0 mL) in a separate flask, NaOMe (200 mg, 924 µmol, 2.00 equiv.) was added and the mixture was stirred at r.t. for 10 min.

Afterwards, the mixture was diluted with water (10.0 mL), cooled to 0 °C and TFA (430 µL, 636 mg, 5.58 mmol, 3.04 equiv.) and PIFA (1.99 g, 4.62 mmol, 2.50 equiv.) were added. The reaction mixture was stirred at 0 °C for 10 min. Then, water (10.0 mL) and L-ascorbic acid (651 mg, 3.70 mmol, 2.00 equiv.) were added and the reaction mixture was stirred at r.t. for another 10 min.

The mixture was again diluted with water (30.0 mL) and impurities were removed by washing with *n*-pentane (3 × 50.0 mL). MeOH and glyme were removed from the aqueous phase in vacuum. The remaining concentrated aqueous phase was filtered to remove solid impurities. Without further removal of the solvent, the aqueous phase was directly purified by reversed phase column chromatography (RP-C18, H_2O → H_2O/MeCN 3:1) followed by normal phase column chromatography (SiO_2, DCM → DCM/MeOH 9:1). To remove remaining silica gel, the residue was dissolved in water (10.0 mL) and filtered through a syringe filter. Removal of the solvent in vacuum yielded *C*-glycosidic compound **219** (150 mg, 531 µmol, 29%) as colorless glassy solid.

TLC: $R_f = 0.61$ (DCM/MeOH 17:3).

$[a]_D^{25} = 43.2$ (c = 1.00, MeOH).

UV (MeOH): $\lambda_{max} = 203$, 252 nm.

IR (ATR): $\tilde{\nu} = 3336$, 2924, 2877, 1678, 1602, 1585, 1419, 1336, 1247, 1055, 1031, 786, 765, 680, 638 cm^{-1}.

^{1}H-NMR (600 MHz, methanol-d_4): δ (ppm) = 2.41 (s, 3 H, 3-CH_3), 3.32 (dt, J = 9.1, 4.0 Hz 1 H, 5'-H), 3.67 (dd, J = 9.1, 3.2 Hz, 1 H, 3'-H), 3.67 (d, J = 4.0 Hz, 2 H, 6'-H_2), 3.70 (t, J = 9.1 Hz, 1 H, 4'-H), 4.39 (dd, J = 3.2, 2.3 Hz, 1 H, 2'-H), 5.20 (d, J = 2.3 Hz, 1 H, 1'-H), 7.38 (t, J = 7.6 Hz, 1 H, 5-H), 7.44 (d, J = 7.6 Hz, 1 H, 4-H), 7.87 (d, J = 7.6 Hz, 1 H, 6-H), 7.90 (s, 1 H, 2-H).

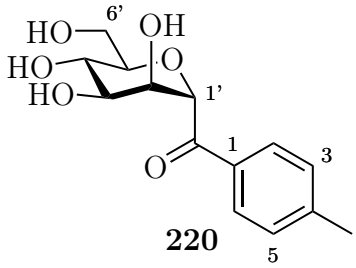
^{13}C-NMR (151 MHz, methanol-d_4): δ (ppm) = 21.3 (3-$\underline{C}H_3$), 62.8 (C-6'), 68.6 (C-4'), 70.6 (C-2'), 73.1 (C-3'), 79.2 (C-5'), 81.7 (C-1'), 127.4 (C-6), 129.5 (C-5), 130.5 (C-2), 135.4 (C-4), 136.7 (C-1), 139.7 (C-3), 200.8 (CO).

MS (ESI): m/z (%) = 119.1 (26) [(3-methylbenzylidyne)oxonium], 305.1 (41) $[M + Na]^+$.

calcd.: 305.0996 $[M + Na]^+$,
found: 305.0996 (ESI-HRMS).

$C_{14}H_{18}O_6$ (282.29).

6.18.6 (4-Methylphenyl)(α-D-mannopyranosyl) ketone 220



220

To neat 1,2,3,4,6-pentakis-*O*-trimethylsilyl-D-mannopyranose **205** (1.00 g, 1.85 mmol, 1.00 equiv.) was added TMSI (300 µL, 422 mg, 2.11 mmol, 1.14 equiv.) and the mixture was stirred at r.t. for 15 min to give 2,3,4,6-tetrakis-*O*-trimethylsilyl-α-D-mannopyranosyl iodide **206** as orange oil, which was dissolved in glyme (10.0 mL) and cooled to 0 °C.

In a separate vessel, a solution of 2-(4-methylphenyl)-1,3-dithiane **289** (778 mg, 3.70 mmol, 2.00 equiv.) in glyme (10.0 mL) was cooled to 0 °C and a solution of *t*-BuLi (c = 1.85 M in *n*-pentane, 2.00 mL, 3.69 mmol, 2.00 equiv.) was added. The solution was stirred at 0 °C for 5 min and then CuI (900 µg, 4.72 µmol, 2.55 mol‰) and the precooled solution of 2,3,4,6-tetrakis-*O*-trimethylsilyl-α-D-mannopyranosyl iodide **206** in glyme were added. The reaction mixture was stirred at 0 °C for 3 h.

Then, the mixture was added to MeOH (70.0 mL) in a separate flask, NaOMe (200 mg, 924 µmol, 2.00 equiv.) was added and the mixture was stirred at r.t. for 10 min.

Afterwards, the mixture was diluted with water (10.0 mL), cooled to 0 °C and TFA (430 µL, 636 mg, 5.58 mmol, 3.04 equiv.) and PIFA (1.99 g, 4.62 mmol, 2.50 equiv.) were added. The reaction mixture was stirred at 0 °C for 10 min. Then, water (10.0 mL) and L-ascorbic acid (651 mg, 3.70 mmol, 2.00 equiv.) were added and the reaction mixture was stirred at r.t. for another 10 min.

The mixture was again diluted with water (30.0 mL) and impurities were removed by washing with *n*-pentane (3 × 50.0 mL). MeOH and glyme were removed from the aqueous phase in vacuum. The remaining concentrated aqueous phase was filtered to remove

solid impurities. Without further removal of the solvent, the aqueous phase was directly purified by reversed phase column chromatography (RP-C18, $H_2O \rightarrow H_2O$/MeCN 3:1) to yield *C*-glycosidic compound **220** (169 mg, 599 µmol, 32%) as colorless glassy solid.

TLC: $R_f = 0.59$ (DCM/MeOH 17:3).

$[a]_D^{25} = 55.4$ (c = 1.04, MeOH).

UV (MeOH): $\lambda_{max} = 202, 259$ nm.

IR (ATR): $\tilde{\nu} = 3358, 2922, 2883, 1674, 1604, 1408, 1226, 1066, 1031, 869, 802, 771, 669, 599, 482$ cm^{-1}.

^{1}H-NMR (600 MHz, methanol-d_4): δ (ppm) = 2.41 (s, 3 H, 4-CH_3), 3.26–3.32 (m, 1 H, 5'-H), 3.64–3.69 (m, 2 H, 6'-H_2), 3.68 (dd, J = 8.9, 3.0 Hz, 1 H, 3'-H), 3.70 (t, J = 8.9 Hz, 1 H, 4'-H), 4.39 (dd, J = 3.0, 2.2 Hz, 1 H, 2'-H), 5.18 (d, J = 2.2 Hz, 1 H, 1'-H), 7.29–7.33 (m, 2 H, 2 H, 3-H, 5-H), 7.96–8.02 (m, 2 H, 2-H, 6-H).

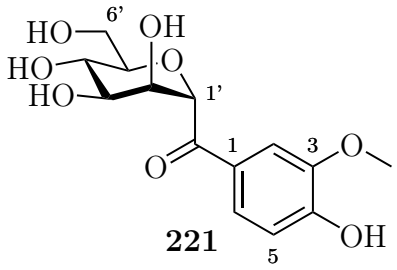
^{13}C-NMR (151 MHz, methanol-d_4): δ (ppm) = 21.7 (4-$\underline{C}H_3$), 62.8 (C-6'), 68.7 (C-4'), 70.5 (C-2'), 73.1 (C-3'), 79.2 (C-5'), 81.6 (C-1'), 130.2 (2 C, C-3, C-5) 130.4 (2 C, C-2, C-6), 134.1 (C-1), 145.9 (C-4), 200.1 (CO).

MS (ESI): *m/z* (%) = 119.1 (50) [(4-methylbenzylidyne)oxonium], 305.1 (68) $[M + Na]^+$.

calcd.: 305.0996 $[M + Na]^+$,
found: 305.0996 (ESI-HRMS).

$C_{14}H_{18}O_6$ (282.29).

6.18.7 (3-Methoxy-4-hydroxylphenyl)(α-D-mannopyranosyl) ketone 221



221

To neat 1,2,3,4,6-pentakis-*O*-trimethylsilyl-D-mannopyranose **205** (1.00 g, 1.85 mmol, 1.00 equiv.) was added TMSI (300 µL, 422 mg, 2.11 mmol, 1.14 equiv.) and the mixture

was stirred at r.t. for 15 min to give 2,3,4,6-tetrakis-*O*-trimethylsilyl-α-D-mannopyranosyl iodide **206** as orange oil, which was dissolved in glyme (10.0 mL) and cooled to 0 °C.

In a separate vessel, a solution of 2-(3-methoxy-4-hydroxyphenyl)-1,3-dithiane **299** (896 mg, 3.70 mmol, 2.00 equiv.) in glyme (10.0 mL) was cooled to 0 °C and a solution of *t*-BuLi (c = 1.72 M in *n*-pentane, 4.30 mL, 7.40 mmol, 4.00 equiv.) was added dropwise. The solution was stirred at 0 °C for 5 min and then CuI (900 µg, 4.72 µmol, 2.55 mol‰) and the precooled solution of 2,3,4,6-tetrakis-*O*-trimethylsilyl-α-D-mannopyranosyl iodide **206** in glyme were added. The reaction mixture was stirred at 0 °C for 3 h.

Then, the mixture was added to MeOH (70.0 mL) in a separate flask, NaOMe (200 mg, 924 µmol, 2.00 equiv.) was added and the mixture was stirred at r.t. for 10 min.

Afterwards, the mixture was diluted with water (10.0 mL), cooled to 0 °C and TFA (700 µL, 1.05 g, 9.24 mmol, 4.95 equiv.) and PIFA (1.99 g, 4.62 mmol, 2.50 equiv.) were added. The reaction mixture was stirred at 0 °C for 10 min. Then, water (10.0 mL) and L-ascorbic acid (651 mg, 3.70 mmol, 2.00 equiv.) were added and themixture was stirred at r.t. for another 10 min.
The mixture was again diluted with water (30.0 mL) and impurities were removed by washing with diethyl ether (3 × 50.0 mL). MeOH and glyme were removed from the aqueous phase in vacuum. The remaining concentrated aqueous phase was filtered to remove solid impurities. Without further removal of the solvent, the aqueous phase was directly purified by reversed phase column chromatography (RP-C18, H_2O + 0.1% TFA → H_2O/MeCN 4:1+ 0.1% TFA) to yield *C*-glycosidic compound **221** (124 mg, 395 µmol, 21%) as pale yellow solid.

TLC: $R_f = 0.37$ (DCM/MeOH 17:3).

$[\alpha]_D^{25} = 41.3$ (c = 0.97, MeOH).

UV (MeOH): $\lambda_{max} = 203, 232, 281, 310$ nm.

IR (ATR): $\tilde{\nu} = 3361, 2937, 1664, 1589, 1514, 1427, 1273, 1197, 1114, 1064, 1026, 918, 815, 759, 621$ cm^{-1}.

^{1}H-NMR (600 MHz, D_2O): δ (ppm) = 3.42 (ddd, J = 9.5, 6.0, 2.4 Hz, 1 H, 5'-H), 3.69 (dd, J = 12.5, 6.0 Hz, 1 H, 6'-H_A), 3.71 (t, J = 9.5 Hz, 1 H, 4'-H), 3.76 (dd, J = 12.5, 2.4 Hz, 1 H, 6'-H_A), 3.78 (dd, J = 9.5, 3.4 Hz, 1 H, 3'-H), 3.92 (s, 3 H, OCH_3), 4.51 (dd, J = 3.4, 2.2 Hz, 1 H, 2'-H), 5.31 (d, J = 2.2 Hz, 1 H, 1'-H), 6.99 (d, J = 8.3 Hz, 1 H, 5-H), 7.60 (d, J = 2.0 Hz, 1 H, 2-H), 7.71 (dd, J = 8.4, 2.0 Hz, 1 H, 6-H).

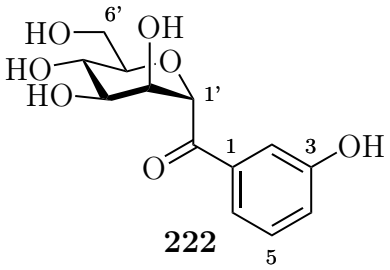
^{13}C-NMR (151 MHz, D_2O): δ (ppm) = 55.9 (OCH_3), 61.0 (C-6'), 66.9 (C-4'), 69.0 (C-2'), 71.1 (C-3'), 77.3 (C-5'), 80.0 (C-1'), 112.3 (C-2), 114.9 (C-5), 125.0 (C-6), 127.2 (C-1), 147.3 (C-3), 151.3 (C-4), 199.3 (CO).

MS (ESI): m/z (%) = 151.0 (80) [(4-hydroxy-3-methoxybenzylidyne)oxonium], 337.1 (71) $[M + Na]^+$.

calcd.: 337.0894 $[M + Na]^+$,
found: 337.0894 (ESI-HRMS).

$C_{14}H_{18}O_8$ (314.29).

6.18.8 (3-Hydroxylphenyl)(α-D-mannopyranosyl) ketone 222



222

To neat 1,2,3,4,6-pentakis-*O*-trimethylsilyl-D-mannopyranose **205** (1.00 g, 1.85 mmol, 1.00 equiv.) was added TMSI (300 µL, 422 mg, 2.11 mmol, 1.14 equiv.) and the mixture was stirred at r.t. for 15 min to give 2,3,4,6-tetrakis-*O*-trimethylsilyl-α-D-mannopyranosyl iodide **206** as orange oil, which was dissolved in glyme (10.0 mL) and cooled to 0 °C.

In a separate vessel, a solution of 2-(3-hydroxyphenyl)-1,3-dithiane **292** (785 mg, 3.70 mmol, 2.00 equiv.) in glyme (10.0 mL) was cooled to 0 °C and a solution of *t*-BuLi (c = 1.72 M in *n*-pentane, 4.30 mL, 7.40 mmol, 4.00 equiv.) was added dropwise. The solution was stirred at 0 °C for 5 min and then CuI (900 µg, 4.72 µmol, 2.55 mol‰) and the precooled solution of 2,3,4,6-tetrakis-*O*-trimethylsilyl-α-D-mannopyranosyl iodide **206** in glyme were added. The reaction mixture was stirred at 0 °C for 3 h.

Then, the mixture was added to MeOH (70.0 mL) in a separate flask, NaOMe (200 mg, 924 µmol, 2.00 equiv.) was added and the mixture was stirred at r.t. for 10 min.

Afterwards, the mixture was diluted with water (10.0 mL), cooled to 0 °C and TFA (700 µL, 1.05 g, 9.24 mmol, 4.95 equiv.) and PIFA (1.99 g, 4.62 mmol, 2.50 equiv.) were added. The reaction mixture was stirred at 0 °C for 10 min. Then, water (10.0 mL) and L-ascorbic

acid (651 mg, 3.70 mmol, 2.00 equiv.) were added and the reaction mixture was stirred at r.t. for another 10 min.

The mixture was again diluted with water (30.0 mL) and impurities were removed by washing with *n*-pentane (3 × 50.0 mL). MeOH and glyme were removed from the aqueous phase in vacuum. The remaining concentrated aqueous phase was filtered to remove solid impurities. Without further removal of the solvent, the aqueous phase was directly purified by reversed phase column chromatography (RP-C18, H_2O + 0.1% TFA → H_2O/MeCN 4:1+ 0.1% TFA) to yield *C*-glycosidic compound **222** (258 mg, 908 µmol, 49%) as pale yellow solid.

TLC: R_f = 0.37 (DCM/MeOH 17:3).

$[a]_D^{25} = 48.6$ (c = 0.99, MeOH).

UV (MeOH): $\lambda_{max} = 218, 255, 315$ nm.

IR (ATR): $\tilde{\nu} = 3313, 2933, 1674, 1585, 1450, 1284, 1240, 1112, 1065, 1033, 927, 839, 773, 678, 636$ cm^{-1}.

^{1}H-NMR (600 MHz, D_2O): δ (ppm) = 3.39 (ddd, J = 9.0, 6.1, 2.4 Hz, 1 H, 5'-H), 3.67 (dd, J = 12.4, 6.1 Hz, 1 H, 6'-H_A), 3.69 (t, J = 9.0 Hz, 1 H, 4'-H), 3.72 (dd, J = 9.0, 3.0 Hz, 1 H, 3'-H), 3.75 (dd, J = 12.4, 2.4 Hz, 1 H, 6'-H_B), 4.51 (dd, J = 3.0, 2.1 Hz, 1 H, 2'-H), 5.34 (d, J = 2.1 Hz, 1 H, 1'-H), 7.20 (ddd, J = 8.0, 2.5, 0.9 Hz, 1 H, 4-H), 7.45 (t, J = 8.0 Hz, 1 H, 5-H), 7.46 (dd, J = 2.5 Hz, 1.6 Hz, 1 H, 2-H), 7.59 (ddd, J = 8.0, 1.6, 0.9 Hz, 1 H, 6-H).

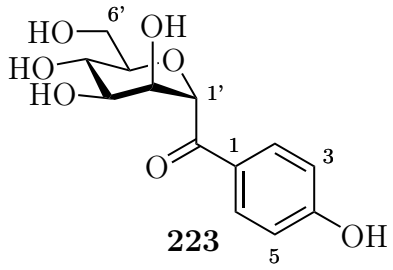
^{13}C-NMR (151 MHz, D_2O): δ (ppm) = 61.0 (C-6'), 66.8 (C-4'), 68.9 (C-2'), 71.0 (C-3'), 77.4 (C-5'), 80.4 (C-1'), 115.1 (C-2), 121.3 (C-4), 121.5 (C-6), 130.2 (C-5), 136.0 (C-1), 155.7 (C-3), 201.3 (CO).

MS (ESI): m/z (%) = 121.0 (26) [(3-hydroxybenzylidyne)oxonium], 307.1 (23) $[M + Na]^+$.

calcd.: 307.0788 $[M + Na]^+$,
found: 307.0786 (ESI-HRMS).

$C_{13}H_{16}O_7$ (284.26).

6.18.9 (4-Hydroxylphenyl)(α-D-mannopyranosyl) ketone 223



223

To neat 1,2,3,4,6-pentakis-*O*-trimethylsilyl-D-mannopyranose **205** (1.00 g, 1.85 mmol, 1.00 equiv.) was added TMSI (300 µL, 422 mg, 2.11 mmol, 1.14 equiv.) and the mixture was stirred at r.t. for 15 min to give 2,3,4,6-tetrakis-*O*-trimethylsilyl-α-D-mannopyranosyl iodide **206** as orange oil, which was dissolved in glyme (10.0 mL) and cooled to 0 °C.

In a separate vessel, a solution of 2-(4-hydroxyphenyl)-1,3-dithiane **293** (785 mg, 3.70 mmol, 2.00 equiv.) in glyme (10.0 mL) was cooled to 0 °C and a solution of *t*-BuLi (c = 2.20 M in *n*-pentane, 3.30 mL, 7.26 mmol, 3.93 equiv.) was added dropwise. The solution was stirred at 0 °C for 5 min and then CuI (900 µg, 4.72 µmol, 2.55 mol‰) and the precooled solution of 2,3,4,6-tetrakis-*O*-trimethylsilyl-α-D-mannopyranosyl iodide **206** in glyme were added. The reaction mixture was stirred at 0 °C for 3 h.

Then, the mixture was added to MeOH (70.0 mL) in a separate flask, NaOMe (200 mg, 924 µmol, 2.00 equiv.) was added and the mixture was stirred at r.t. for 10 min.

Afterwards, the mixture was diluted with water (10.0 mL), cooled to 0 °C and TFA (700 µL, 1.05 g, 9.24 mmol, 4.95 equiv.) and PIFA (1.99 g, 4.62 mmol, 2.50 equiv.) were added. The reaction mixture was stirred at 0 °C for 10 min. Then, water (10.0 mL) and L-ascorbic acid (651 mg, 3.70 mmol, 2.00 equiv.) were added and the reaction mixture was stirred at r.t. for another 10 min.

The mixture was again diluted with water (30.0 mL) and impurities were removed by washing with *n*-pentane (3 × 50.0 mL). MeOH and glyme were removed from the aqueous phase in vacuum. The remaining concentrated aqueous phase was filtered to remove solid impurities. Without further removal of the solvent, the aqueous phase was directly purified by reversed phase column chromatography (RP-C18, H_2O + 0.1% TFA → H_2O/MeCN 4:1+ 0.1% TFA) to yield *C*-glycosidic compound **223** (208 mg, 908 µmol, 40%) as colorless solid.

TLC: $R_f = 0.28$ (DCM/MeOH 17:3).

$[a]_D^{25} = 50.0$ (c = 1.00, MeOH).

UV (MeOH): $\lambda_{max} = 221, 284$ nm.

IR (ATR): $\tilde{\nu} = 3342, 1660, 1598, 1581, 1514, 1442, 1382, 1334, 1220, 1170, 1111, 1060, 819, 781, 603$ cm^{-1}.

^{1}H-NMR (600 MHz, D_2O): δ (ppm) = 3.38 (ddd, J = 9.4, 6.1, 2.3 Hz, 1 H, 5'-H), 3.67 (dd, J = 12.4, 6.1 Hz, 1 H, 6'-H_A), 3.68 (t, J = 9.4 Hz, 1 H, 4'-H), 3.75 (dd, J = 12.4, 2.3 Hz, 1 H, 6'-H_B), 3.76 (dd, J = 9.4, 3.4 Hz, 1 H, 3'-H), 4.51 (dd, J = 3.4, 2.1 Hz, 1 H, 2'-H), 5.32 (d, J = 2.1 Hz, 1 H, 1'-H), 6.96–7.02 (m, 2 H, 3-H, 5-H), 7.98–8.05 (m, 2 H, 2-H, 6-H).

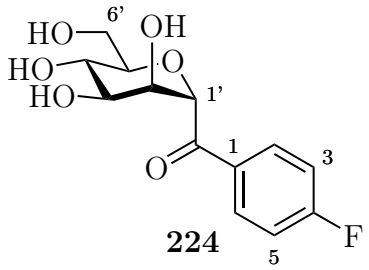
^{13}C-NMR (151 MHz, D_2O): δ (ppm) = 61.0 (C-6'), 66.9 (C-4'), 69.0 (C-2'), 71.1 (C-3'), 77.3 (C-5'), 80.0 (C-1'), 115.4 (2 C, C-3, C-5), 126.9 (C-1), 132.1 (2 C, C-2, C-6), 161.6 (C-4), 199.6 (CO).

MS (ESI): m/z (%) = 121.0 (34) [(4-hydroxybenzylidyne)oxonium], 307.1 (20) $[M + Na]^+$.

calcd.: 307.0788 $[M + Na]^+$,
found: 307.0784 (ESI-HRMS).

$C_{13}H_{16}O_7$ (284.26).

6.18.10 (4-Fluorophenyl)(α-D-mannopyranosyl) ketone 224



224

To neat 1,2,3,4,6-pentakis-*O*-trimethylsilyl-D-mannopyranose **205** (1.00 g, 1.85 mmol, 1.00 equiv.) was added TMSI (300 µL, 422 mg, 2.11 mmol, 1.14 equiv.) and the mixture was stirred at r.t. for 15 min to give 2,3,4,6-tetrakis-*O*-trimethylsilyl-α-D-mannopyranosyl iodide **206** as orange oil, which was dissolved in glyme (10.0 mL) and cooled to 0 °C.

In a separate vessel, a solution of 2-(4-fluorophenyl)-1,3-dithiane **295** (792 mg, 3.70 mmol, 2.00 equiv.) in glyme (10.0 mL) was cooled to 0 °C and a solution of *t*-BuLi (c = 1.70 M

in *n*-pentane, 2.20 mL, 3.74 mmol, 2.02 equiv.) was added. The solution was stirred at 0 °C for 5 min and then CuI (900 µg, 4.72 µmol, 2.55 mol‰) and the precooled solution of 2,3,4-tris-*O*-trimethylsilyl-D-lyxopyranosyl iodide **206** in glyme were added. The reaction mixture was stirred at 0 °C for 3 h.

Then, the mixture was added to MeOH (70.0 mL) in a separate flask, NaOMe (200 mg, 924 µmol, 2.00 equiv.) was added and the mixture was stirred at r.t. for 10 min.

Afterwards, the mixture was diluted with water (10.0 mL), cooled to 0 °C and TFA (430 µL, 636 mg, 5.58 mmol, 3.04 equiv.) and PIFA (1.99 g, 4.62 mmol, 2.50 equiv.) were added. The reaction mixture was stirred at 0 °C for 10 min. Then, water (10.0 mL) and L-ascorbic acid (651 mg, 3.70 mmol, 2.00 equiv.) were added and the reaction mixture was stirred at r.t. for another 10 min.

The mixture was again diluted with water (30.0 mL) and impurities were removed by washing with *n*-pentane (3 × 50.0 mL). MeOH and glyme were removed from the aqueous phase in vacuum. The remaining concentrated aqueous phase was filtered to remove solid impurities. Without further removal of the solvent, the aqueous phase was directly purified by reversed phase column chromatography (RP-C18, $H_2O \rightarrow H_2O$/MeCN 3:1) to yield *C*-glycosidic compound **224** (162 mg, 566 µmol, 31%) as pale yellow solid.

TLC: $R_f = 0.60$ (DCM/MeOH 9:1).

M.p.: 165 °C (from water).

$[a]_D^{25} = 41.0$ (c = 1.00, MeOH).

UV (MeOH): $\lambda_{max} = 251$ nm.

IR (ATR): $\tilde{\nu} =$ cm^{-1}.

^{1}H-NMR (600 MHz, methanol-d_4): δ (ppm) = 3.20 (ddd, $J = 8.3, 5.3, 3.0$ Hz, 1 H, 5'-H), 3.64–3.71 (m, 4 H, 3'-H, 4'-H, 6'-H_2), 4.41 (t, $J = 2.3$ Hz, 1 H, 2'-H), 5.17 (d, $J = 2.3$ Hz, 1 H, 1'-H), 7.18–7.25 (m, 2 H, 3-H, 5-H), 8.17–8.22 (m, 2 H, 2-H, 6-H).

^{13}C-NMR (151 MHz, methanol-d_4): δ (ppm) = 62.8 (C-6'), 68.8 (C-4'), 70.3 (C-2'), 73.1 (C-3'), 79.5 (C-5'), 81.6 (C-1'), 116.5 (d, $J = 22.2$ Hz, 2 C, C-3, C-5), 133.1 (d, $J = 2.9$ Hz, C1), 133.4 (d, $J = 9.4$ Hz, 2 C, C-2, C-6), 167.4 (d, $J = 253.8$ Hz, C-4), 199.0 (CO).

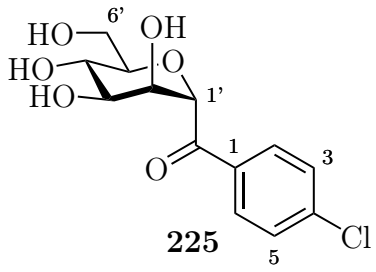
^{19}F-NMR (565 MHz, Methanol-d_4): δ (ppm) = 106.8 (m, 4-F).

MS (ESI): *m/z* (%) = 123.0 (15) [(4-fluorobenzylidyne)oxonium], 309.1 (72) $[M + Na]^+$.

calcd.: 309.0745 $[M + Na]^+$,
found: 309.0744 (ESI-HRMS).

$C_{13}H_{15}FO_6$ (286.26).

6.18.11 (4-Chlorophenyl)(α-D-mannopyranosyl) ketone 225



225

To neat 1,2,3,4,6-pentakis-*O*-trimethylsilyl-D-mannopyranose **205** (1.00 g, 1.85 mmol, 1.00 equiv.) was added TMSI (300 µL, 422 mg, 2.11 mmol, 1.14 equiv.) and the mixture was stirred at r.t. for 15 min to give 2,3,4,6-tetrakis-*O*-trimethylsilyl-α-D-mannopyranosyl iodide **206** as orange oil, which was dissolved in glyme (10.0 mL) and cooled to 0 °C.

In a separate vessel, a solution of 2-(4-chlorophenyl)-1,3-dithiane **294** (853 mg, 3.70 mmol, 2.00 equiv.) in glyme (10.0 mL) was cooled to 0 °C and a solution of *t*-BuLi (c = 1.80 M in *n*-pentane, 2.00 mL, 3.65 mmol, 1.95 equiv.) was added. The solution was stirred at 0 °C for 5 min and then CuI (900 µg, 4.72 µmol, 2.55 mol‰) and the precooled solution of 2,3,4,6-tetrakis-*O*-trimethylsilyl-α-D-mannopyranosyl iodide **206** in glyme were added. The reaction mixture was stirred at 0 °C for 3 h.

Then, the mixture was added to MeOH (70.0 mL) in a separate flask, NaOMe (200 mg, 924 µmol, 2.00 equiv.) was added and the mixture was stirred at r.t. for 10 min.

Afterwards, the mixture was diluted with water (10.0 mL), cooled to 0 °C and TFA (430 µL, 636 mg, 5.58 mmol, 3.04 equiv.) and PIFA (1.99 g, 4.62 mmol, 2.50 equiv.) were added. The reaction mixture was stirred at 0 °C for 10 min. Then, water (10.0 mL) and L-ascorbic acid (651 mg, 3.70 mmol, 2.00 equiv.) were added and the reaction mixture was stirred at r.t. for another 10 min.

The mixture was again diluted with water (30.0 mL) and impurities were removed by washing with *n*-pentane (3 × 50.0 mL). MeOH and glyme were removed from the aqueous phase in vacuum. The remaining concentrated aqueous phase was filtered to remove

solid impurities. Without further removal of the solvent, the aqueous phase was directly purified by reversed phase column chromatography (RP-C18, $H_2O \rightarrow H_2O$/MeCN 3:1) to yield *C*-glycosidic compound **225** (105 mg, 347 µmol, 19%) as pale yellow solid.

TLC: $R_f = 0.61$ (DCM/MeOH 17:3).

$[\alpha]_D^{25} = 55.4$ (c = 1.03, MeOH).

UV (MeOH): $\lambda_{max} = 201$, 257 nm.

IR (ATR): $\tilde{\nu} = 3336$, 2927, 1678, 1587, 1400, 1338, 1286, 1217, 1068, 1010, 918, 869, 794, 665, 478 cm^{-1}.

^{1}H-NMR (600 MHz, methanol-d_4): δ (ppm) = 3.19 (ddd, J = 8.5, 4.9, 2.6 Hz, 1 H, 5'-H), 3.63–3.70 (m, 4 H, 3'-H, 4'-H, 6'-H_2), 4.40 (t, J = 2.5 Hz, 1 H, 2'-H), 5.17 (d, J = 2.5 Hz, 1 H, 1'-H), 7.48–7.53 (m, 2 H, 3-H, 5-H), 8.08–8.13 (m, 2 H, 2-H, 6-H).

^{13}C-NMR (151 MHz, methanol-d_4): δ (ppm) = 62.8 (C-6'), 68.7 (C-4'), 70.2 (C-2'), 73.0 (C-3'), 79.5 (C-5'), 81.6 (C-1'), 129.8 (2 C, C-3, C-5), 132.0 (2 C, C-2, C-6), 135.0 (C-4), 140.9 (C-1), 199.5 (CO).

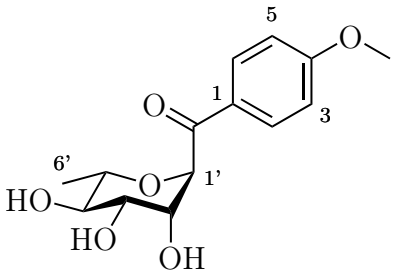
MS (ESI): m/z (%) = 139.0 (15) [(4-chlorobenzylidyne)oxonium], 325.0 (43) $[M + Na]^+$.

calcd.: 325.0449 $[M + Na]^+$,
found: 325.0450 (ESI-HRMS).

$C_{13}H_{15}ClO_6$ (302.71).

6.19 Syntheses of *C*-acyl α-L-rhamnopyranosides

6.19.1 (4-Methoxyphenyl)(α-L-rhamnopyranosyl) ketone 227



227

To neat 1,2,3,4-tetrakis-*O*-trimethylsilyl-L-rhamnopyranose **238** (837 mg, 1.85 mmol, 1.00 equiv.) was added TMSI (300 µL, 422 mg, 2.11 mmol, 1.14 equiv.) and the mixture was stirred at r.t. for 15 min to give 2,3,4,-tris-*O*-trimethylsilyl-L-rhamnopyranosyl iodide **316** as orange oil, which was dissolved in glyme (10.0 mL) and cooled to 0 °C.

In a separate vessel, a solution of 2-(4-methoxyphenyl)-1,3-dithiane **151** (837 mg, 3.70 mmol, 2.00 equiv.) in glyme (10.0 mL) was cooled to 0 °C and a solution of *t*-BuLi (c = 1.85 M in *n*-pentane, 2.00 mL, 3.70 mmol, 2.00 equiv.) was added. The solution was stirred at 0 °C for 5 min and then CuI (900 µg, 4.72 µmol, 2.55 mol‰) and the precooled solution of 2,3,4,-tris-*O*-trimethylsilyl-L-rhamnopyranosyl iodide **316** in glyme were added. The reaction mixture was stirred at 0 °C for 3 h.

Then, the mixture was added to MeOH (70.0 mL) in a separate flask, NaOMe (200 mg, 924 µmol, 2.00 equiv.) was added and the mixture was stirred at r.t. for 10 min.

Afterwards, the mixture was diluted with water (10.0 mL), cooled to 0 °C and TFA (430 µL, 636 mg, 5.58 mmol, 3.04 equiv.) and PIFA (1.99 g, 4.62 mmol, 2.50 equiv.) were added. The reaction mixture was stirred at 0 °C for 10 min. Then, water (10.0 mL) and L-ascorbic acid (651 mg, 3.70 mmol, 2.00 equiv.) were added and the reaction mixture was stirred at r.t. for another 10 min.

The mixture was again diluted with water (30.0 mL) and impurities were removed by washing with *n*-pentane (3 × 50.0 mL). MeOH and glyme were removed from the aqueous phase in vacuum. The remaining concentrated aqueous phase was filtered to remove solid impurities. Without further removal of the solvent, the aqueous phase was directly purified by reversed phase column chromatography (RP-C18, $H_2O \rightarrow H_2O$/MeCN 3:1) to yield *C*-glycosidic compound **227** (155 mg, 549 µmol, 30%) as pale yellow crystalline solid.

TLC: $R_f = 0.52$ (DCM/MeOH 9:1).

M.p.: 201 °C (from water).

$[a]_D^{20} = -38.0$ (c = 1.00, MeOH).

UV (MeOH): $\lambda_{max} = 218, 280$ nm.

IR (ATR): $\tilde{\nu} = 3460, 3406, 3365, 2980, 2964, 2933, 2910, 2891, 2864, 2839, 1666, 1595, 1060, 821, 530$ cm^{-1}.

^{1}H-NMR (600 MHz, methanol-d_4): δ (ppm) = 1.16 (d, J = 6.1 Hz, 3 H, 6'-H_3), 3.19 (dq, J = 9.3, 6.1 Hz, 1 H, 5'-H), 3.40 (t, J = 9.3 Hz, 1 H, 4'-H), 3.65 (dd, J = 9.3, 3.5 Hz, 1 H,

3'-H), 3.88 (s, 3 H, OCH_3), 4.41 (dd, $J = 3.5$, 2.1 Hz, 1 H. 2'-H), 5.06 (d, $J = 2.1$ Hz, 1 H, 1'-H), 6.99–7.03 (m, 2 H, 3-H, 5-H), 8.05–8.10 (m, 2 H, 2-H, 6-H).

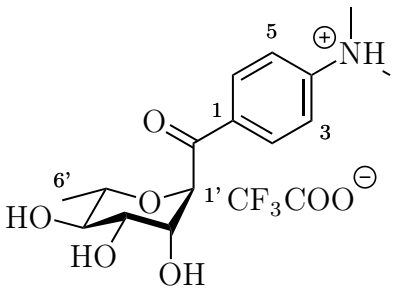
^{13}C-NMR (151 MHz, methanol-d_4): δ (ppm) = 18.3 (C-6'), 56.1 (OCH_3), 70.6 (C-2'), 73.1 (C-3'), 74.0 (C-4'), 74.7 (C-5'), 81.8 (C-1'), 114.7 (2 C, C-3, C-5), 129.5 (C-1), 132.6 (2 C, C-2, C-6), 165.6 (C-4), 199.2 (CO).

MS (ESI): m/z (%) = 135.0 (100) [(4-methoxybenzylidyne)oxonium], 283.1 (23) $[M + H]^+$ 305.1 (94) $[M + Na]^+$.

calcd.: 305.0996 $[M + Na]^+$,
found: 305.0996 (ESI-HRMS).

$C_{14}H_{18}O_6$ (282.29).

6.19.2 (4-Dimethylaminophenyl)(α-L-rhamnopyranosyl) ketone TFA salt 228



228

To neat 1,2,3,4-tetrakis-*O*-trimethylsilyl-L-rhamnopyranose **238** (837 mg, 1.85 mmol, 1.00 equiv.) was added TMSI (300 µL, 422 mg, 2.11 mmol, 1.14 equiv.) and the mixture was stirred at r.t. for 15 min to give 2,3,4,-tris-*O*-trimethylsilyl-L-rhamnopyranosyl iodide **316** as orange oil, which was dissolved in glyme (10.0 mL) and cooled to 0 °C.

In a separate vessel, a solution of 2-(4-dimethylaminophenyl)-1,3-dithiane **297** (885 mg, 3.70 mmol, 2.00 equiv.) in glyme (10.0 mL) was cooled to 0 °C and a solution of *t*-BuLi (c = 1.75 M in *n*-pentane, 2.10 mL, 3.68 mmol, 1.99 equiv.) was added. The solution was stirred at 0 °C for 5 min and then CuI (900 µg, 4.72 µmol, 2.55 mol‰) and the precooled solution of 2,3,4,-tris-*O*-trimethylsilyl-L-rhamnopyranosyl iodide **316** in glyme were added. The reaction mixture was stirred at 0 °C for 3 h.

Then, the mixture was added to MeOH (70.0 mL) in a separate flask, NaOMe (200 mg, 924 µmol, 2.00 equiv.) was added and the mixture was stirred at r.t. for 10 min.

Afterwards, the mixture was diluted with water (10.0 mL), cooled to 0 °C and TFA (700 µL, 1.05 g, 9.24 mmol, 4.95 equiv.) and PIFA (1.99 g, 4.62 mmol, 2.50 equiv.) were added. The reaction mixture was stirred at 0 °C for 10 min. Then, water (10.0 mL) and L-ascorbic acid (651 mg, 3.70 mmol, 2.00 equiv.) were added and the mixture was stirred at r.t. for another 10 min.
The mixture was again diluted with water (30.0 mL) and impurities were removed by washing with *n*-pentane (3 × 50.0 mL). MeOH and glyme were removed from the aqueous phase in vacuum. The remaining concentrated aqueous phase was filtered to remove solid impurities. Without further removal of the solvent, the aqueous phase was directly purified by reversed phase column chromatography (RP-C18, H_2O + 0.1% TFA → H_2O/MeCN 3:1 + 0.1% TFA) to yield *C*-glycosidic compound **228** (225 mg, 550 µmol, 30%) as beige solid.

TLC: $R_f = 0.49$ (DCM/MeOH 9:1).

$[\alpha]_D^{20} = -32.7$ (c = 0.99, H_2O/TFA 9:1).

UV (MeOH): $\lambda_{max} = 241$, 358 nm.

IR (ATR): $\tilde{\nu} = 3525$, 3275, 2981, 2914, 2845, 1651, 1606, 1544, 1435, 1379, 1348, 1190, 1111, 1056, 798 cm^{-1}.

^{1}H-NMR (600 MHz, DMSO-d_6): δ (ppm) = 1.06 (d, J = 5.6 Hz, 3 H, 6'-H_3), 3.02 (s, 6 H, $N(CH_3)_2$), 3.18–3.23 (m, 2 H, 4'-H, 5'-H), 3.37–3.43 (m, 1 H, 3'-H), 4.16 (dd, J = 3.4, 2.2 Hz, 1 H, 2'-H), 4.93 (d, J = 2.2 Hz, 1 H, 1'-H), 6.69–6.75 (m, 2 H, 3-H, 5-H), 7.83–7.89 (m, 2 H, 2-H, 6-H).

^{13}C-NMR (151 MHz, DMSO-d_6): δ (ppm) = 27.8 (C-6'), 49.0 (2 C, $N(CH_3)_2$), 78.5 (C-2'), 80.8 (C-3'), 81.6 (C-4'), 82.4 (C-5'), 89.1 (C-1'), 119.9 (2 C, C-3, C-5), 132.1 (C-1), 140.2 (2 C, C-2, C-6), 162.8 (C-4), 206.0 (CO).

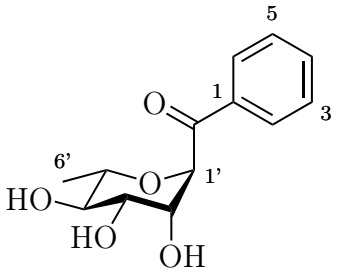
^{19}F-NMR (565 MHz, DMSO-d_6): δ (ppm) = 74.6 (m, CF_3COO^-).

MS (ESI): m/z (%) = 148.1 (4) [(4-dimethylaminobenzylidyne)oxonium], 296.2 (100) [M - CF_3COO]$^+$, 318.1 (20) [M - CF_3COOH + Na]$^+$.

calcd.: 296.1492 [M - CF_3COO^-]$^+$,
found: 296.1496 (ESI-HRMS).

$C_{17}H_{22}F_3NO_7$ (409.36).

6.19.3 Phenyl (α-L-rhamnopyranosyl) ketone 230



230

To neat 1,2,3,4-tetrakis-*O*-trimethylsilyl-L-rhamnopyranose **238** (837 mg, 1.85 mmol, 1.00 equiv.) was added TMSI (300 µL, 422 mg, 2.11 mmol, 1.14 equiv.) and the mixture was stirred at r.t. for 15 min to give 2,3,4,-tris-*O*-trimethylsilyl-L-rhamnopyranosyl iodide **316** as orange oil, which was dissolved in glyme (10.0 mL) and cooled to 0 °C.

In a separate vessel, a solution of 2-phenyl-1,3-dithiane **191** (726 mg, 3.70 mmol, 2.00 equiv.) in glyme (10.0 mL) was cooled to 0 °C and a solution of *t*-BuLi (c = 1.69 M in *n*-pentane, 2.20 mL, 3.72 mmol, 2.01 equiv.) was added. The solution was stirred at 0 °C for 5 min and then CuI (900 µg, 4.72 µmol, 2.55 mol‰) and the precooled solution of 2,3,4,-tris-*O*-trimethylsilyl-L-rhamnopyranosyl iodide **316** in glyme were added. The reaction mixture was stirred at 0 °C for 3 h.

Then, the mixture was added to MeOH (70.0 mL) in a separate flask, NaOMe (200 mg, 924 µmol, 2.00 equiv.) was added and the mixture was stirred at r.t. for 10 min.

Afterwards, the mixture was diluted with water (10.0 mL), cooled to 0 °C and TFA (430 µL, 636 mg, 5.58 mmol, 3.04 equiv.) and PIFA (1.99 g, 4.62 mmol, 2.50 equiv.) were added. The reaction mixture was stirred at 0 °C for 10 min. Then, water (10.0 mL) and L-ascorbic acid (651 mg, 3.70 mmol, 2.00 equiv.) were added and the reaction mixture was stirred at r.t. for another 10 min.

The mixture was again diluted with water (30.0 mL) and impurities were removed by washing with *n*-pentane (3 × 50.0 mL). MeOH and glyme were removed from the aqueous phase in vacuum. The remaining concentrated aqueous phase was filtered to remove solid impurities. Without further removal of the solvent, the aqueous phase was directly purified by reversed phase column chromatography (RP-C18, $H_2O \rightarrow H_2O$/MeCN 3:1) to yield *C*-glycosidic compound **230** (106 mg, 420 µmol, 23%) as colorless solid.

TLC: $R_f = 0.47$ (DCM/MeOH 9:1).

$[\alpha]_D^{20}$ = -36.8 (c = 1.03, MeOH).

UV (MeOH): λ_{max} = 247 nm.

IR (ATR): $\tilde{\nu}$ = 3365, 2976, 2933, 1678, 1597, 1448, 1219, 1114, 1055, 970, 840, 786, 759, 694, 636 cm^{-1}.

^{1}H-NMR (600 MHz, methanol-d_4): δ (ppm) = 1.14 (d, J = 6.1 Hz, 3 H, 6'-H_3), 3.18 (dq, J = 9.3, 6.1 Hz, 1 H, 5'-H), 3.41 (t, J = 9.3 Hz, 1 H, 4'-H), 3.62 (dd, J = 9.3, 3.5 Hz, 1 H, 3'-H), 4.43 (dd, J = 3.5, 2.1 Hz, 1 H, 2'-H), 5.12 (d, J = 2.1 Hz, 1 H, 1'-H), 7.47–7.53 (m, 2 H, 3-H, 5-H), 7.59–7.66 (m, 1 H, 4-H), 8.03–8.09 (m, 2 H, 2-H, 6-H).

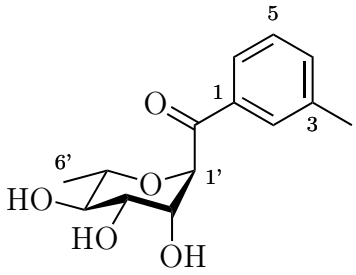
^{13}C-NMR (151 MHz, methanol-d_4): δ (ppm) = 18.2 (C-6'), 70.5 (C-2'), 73.0 (C-3'), 73.9 (C-4'), 74.8 (C-5'), 82.0 (C-1'), 129.6 (2 C, C-3, C-5), 130.1 (2 C, C-2, C-6), 134.7 (C-4), 136.7 (C-1), 201.0 (CO).

MS (ESI): m/z (%) = 275.1 (15) $[M + Na]^+$.

calcd.: 275.0890 $[M + Na]^+$,
found: 275.0878 (ESI-HRMS).

$C_{13}H_{16}O_5$ (252.27).

6.19.4 (3-Methylphenyl)(α-L-rhamnopyranosyl) ketone 231



231

To neat 1,2,3,4-tetrakis-*O*-trimethylsilyl-L-rhamnopyranose **238** (837 mg, 1.85 mmol, 1.00 equiv.) was added TMSI (300 µL, 422 mg, 2.11 mmol, 1.14 equiv.) and the mixture was stirred at r.t. for 15 min to give 2,3,4,-tris-*O*-trimethylsilyl-L-rhamnopyranosyl iodide **316** as orange oil, which was dissolved in glyme (10.0 mL) and cooled to 0 °C.

In a separate vessel, a solution of 2-(3-methylphenyl)-1,3-dithiane **288** (778 mg, 3.70 mmol, 2.00 equiv.) in glyme (10.0 mL) was cooled to 0 °C and a solution of *t*-BuLi (c = 1.69 M

in *n*-pentane, 2.20 mL, 3.72 mmol, 2.01 equiv.) was added. The solution was stirred at 0 °C for 5 min and then CuI (900 µg, 4.72 µmol, 2.55 mol‰) and the precooled solution of 2,3,4,-tris-*O*-trimethylsilyl-L-rhamnopyranosyl iodide **316** in glyme were added. The reaction mixture was stirred at 0 °C for 3 h.

Then, the mixture was added to MeOH (70.0 mL) in a separate flask, NaOMe (200 mg, 924 µmol, 2.00 equiv.) was added and the mixture was stirred at r.t. for 10 min.

Afterwards, the mixture was diluted with water (10.0 mL), cooled to 0 °C and TFA (430 µL, 636 mg, 5.58 mmol, 3.04 equiv.) and PIFA (1.99 g, 4.62 mmol, 2.50 equiv.) were added. The reaction mixture was stirred at 0 °C for 10 min. Then, water (10.0 mL) and L-ascorbic acid (651 mg, 3.70 mmol, 2.00 equiv.) were added and the reaction mixture was stirred at r.t. for another 10 min.

The mixture was again diluted with water (30.0 mL) and impurities were removed by washing with *n*-pentane (3 × 50.0 mL). MeOH and glyme were removed from the aqueous phase in vacuum. The remaining concentrated aqueous phase was filtered to remove solid impurities. Without further removal of the solvent, the aqueous phase was directly purified by reversed phase column chromatography (RP-C18, $H_2O \rightarrow H_2O$/MeCN 7:3) to yield *C*-glycosidic compound **231** (131 mg, 491 µmol, 27%) as colorless, glassy solid.

TLC: $R_f = 0.45$ (DCM/MeOH 9:1).

$[a]_D^{20} =$ -45,6 (c = 1.00, MeOH).

UV (MeOH): $\lambda_{max} = 203, 251, 290$ nm.

IR (ATR): $\tilde{\nu} = 3381, 2976, 2929, 1678, 1602, 1585, 1448, 1381, 1336, 1247, 1116, 1055, 785, 761, 640$ cm^{-1}.

^{1}H-NMR (600 MHz, methanol-d_4): δ (ppm) = 1.15 (d, $J = 6.1$ Hz, 3 H, 6'-H_3), 2.41 (s, 3 H, 3-CH_3), 3.20 (dq, $J = 9.3, 6.1$ Hz, 1 H, 5'-H), 3.41 (t, $J = 9.3$ Hz, 1 H, 4'-H), 3.61 (dd, $J = 9.3, 3.5$ Hz, 1 H, 3'-H), 4.42 (dd, $J = 3.5, 2.1$ Hz, 1 H, 2'-H), 5.10 (d, $J = 2.1$ Hz, 1 H, 1'-H), 7.38 (t, $J = 7.6$ Hz, 1 H, 5-H), 7.45 (d, $J = 7.6$ Hz, 1 H, 4-H), 7.85 (d, $J = 7.6$ Hz, 1 H, 6-H), 7.86 (s, 1 H, 2-H).

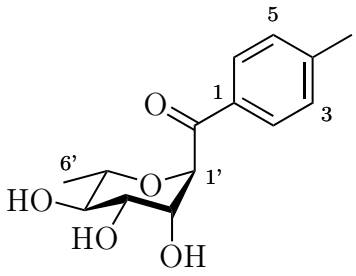
^{13}C-NMR (151 MHz, methanol-d_4): δ (ppm) = 18.3 (C-6'), 21.3 (3-$\underline{C}H_3$), 70.6 (C-2'), 73.0 (C-3'), 73.9 (C-4'), 74.8 (C-5'), 82.0 (C-1'), 127.3 (C-6), 129.5 (C-5), 130.4 (C-2), 135.3 (C-4), 136.8 (C-1), 139.6 (C-3), 201.1 (CO).

MS (ESI): *m/z* (%) = 119.1 (55) [(3-methylbenzylidyne)oxonium], 289.0 (53) $[M + Na]^+$.

calcd.: 289.1046 $[M + Na]^+$,
found: 289.1039 (ESI-HRMS).

$C_{14}H_{18}O_5$ (266.29).

6.19.5 (4-Methylphenyl)(α-L-rhamnopyranosyl) ketone 232



232

To neat 1,2,3,4-tetrakis-*O*-trimethylsilyl-L-rhamnopyranose **238** (837 mg, 1.85 mmol, 1.00 equiv.) was added TMSI (300 µL, 422 mg, 2.11 mmol, 1.14 equiv.) and the mixture was stirred at r.t. for 15 min to give 2,3,4,-tris-*O*-trimethylsilyl-L-rhamnopyranosyl iodide **316** as orange oil, which was dissolved in glyme (10.0 mL) and cooled to 0 °C.

In a separate vessel, a solution of 2-(4-methylphenyl)-1,3-dithiane **289** (778 mg, 3.70 mmol, 2.00 equiv.) in glyme (10.0 mL) was cooled to 0 °C and a solution of *t*-BuLi (c = 1.69 M in *n*-pentane, 2.20 mL, 3.72 mmol, 2.01 equiv.) was added. The solution was stirred at 0 °C for 5 min and then CuI (900 µg, 4.72 µmol, 2.55 mol‰) and the precooled solution of 2,3,4,-tris-*O*-trimethylsilyl-L-rhamnopyranosyl iodide **316** in glyme were added. The reaction mixture was stirred at 0 °C for 3 h.

Then, the mixture was added to MeOH (70.0 mL) in a separate flask, NaOMe (200 mg, 924 µmol, 2.00 equiv.) was added and the mixture was stirred at r.t. for 10 min.

Afterwards, the mixture was diluted with water (10.0 mL), cooled to 0 °C and TFA (430 µL, 636 mg, 5.58 mmol, 3.04 equiv.) and PIFA (1.99 g, 4.62 mmol, 2.50 equiv.) were added. The reaction mixture was stirred at 0 °C for 10 min. Then, water (10.0 mL) and L-ascorbic acid (651 mg, 3.70 mmol, 2.00 equiv.) were added and the reaction mixture was stirred at r.t. for another 10 min.

The mixture was again diluted with water (30.0 mL) and impurities were removed by washing with *n*-pentane (3 × 50.0 mL). MeOH and glyme were removed from the aqueous

phase in vacuum. The remaining concentrated aqueous phase was filtered to remove solid impurities. Without further removal of the solvent, the aqueous phase was directly purified by reversed phase column chromatography (RP-C18, $H_2O \rightarrow H_2O$/MeCN 7:3) to yield *C*-glycosidic compound **232** (111 mg, 417 µmol, 23%) as colorless crystalline solid.

TLC: $R_f = 0.48$ (DCM/MeOH 9:1).

M.p.: 162 °C (from water).

$[a]_D^{20} = -41.9$ (c = 0.98, MeOH).

UV (MeOH): $\lambda_{max} = 258$ nm.

IR (ATR): $\tilde{\nu} = 3421, 3383, 2980, 2941, 2912, 2899, 2858, 1666, 1604, 1083, 1062, 812, 765, 628, 472$ cm^{-1}.

^{1}H-NMR (600 MHz, methanol-d_4): δ (ppm) = 1.15 (d, J = 6.1 Hz, 3 H, 6'-H_3), 2.42 (s, 3 H, 4-CH_3), 3.19 (dq, J = 9.3, 6.1 Hz, 1 H, 5'-H), 3.40 (t, J = 9.3 Hz, 1 H, 4'-H), 3.63 (dd, J = 9.3, 3.5 Hz, 1 H, 3'-H), 4.42 (dd, J = 3.5, 2.1 Hz, 1 H, 2'-H), 5.08 (d, J = 2.1 Hz, 1 H, 1'-H), 7.29–7.34 (m, 2 H, 3-H, 5-H), 7.94–7.99 (m, 2 H, 2-H, 6-H).

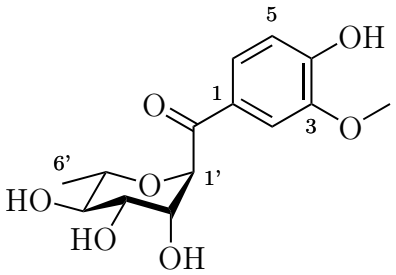
^{13}C-NMR (151 MHz, methanol-d_4): δ (ppm) = 18.3 (C-6'), 21.7 (4-$\underline{C}H_3$), 70.6 (C-2'), 73.0 (C-3'), 74.0 (C-4'), 74.8 (C-5'), 81.9 (C-1'), 130.2 (2 C, C-3, C-5), 130.3 (2 C, C-2, C-6), 134.1 (C-1), 145.9 (C-4), 200.5 (CO).

MS (ESI): m/z (%) = 119.1 (55) [(4-methylbenzylidyne)oxonium], 289.1 (30) $[M + Na]^+$.

calcd.: 289.1046 $[M + Na]^+$,
found: 289.1049 (ESI-HRMS).

$C_{14}H_{18}O_5$ (266.29).

6.19.6 (3-Methoxy-4-hydroxylphenyl)(α-L-rhamnopyranosyl) ketone 233



233

To neat 1,2,3,4-tetrakis-*O*-trimethylsilyl-L-rhamnopyranose **238** (837 mg, 1.85 mmol, 1.00 equiv.) was added TMSI (300 µL, 422 mg, 2.11 mmol, 1.14 equiv.) and the mixture was stirred at r.t. for 15 min to give 2,3,4,-tris-*O*-trimethylsilyl-L-rhamnopyranosyl iodide **316** as orange oil, which was dissolved in glyme (10.0 mL) and cooled to 0 °C.

In a separate vessel, a solution of 2-(3-methoxy-4-hydroxyphenyl)-1,3-dithiane **299** (896 mg, 3.70 mmol, 2.00 equiv.) in glyme (10.0 mL) was cooled to 0 °C and a solution of *t*-BuLi (c = 1.75 M in *n*-pentane, 2.10 mL, 7.35 mmol, 3.98 equiv.) was added. The solution was stirred at 0 °C for 5 min and then CuI (900 µg, 4.72 µmol, 2.55 mol‰) and the precooled solution of 2,3,4,-tris-*O*-trimethylsilyl-L-rhamnopyranosyl iodide **316** in glyme were added. The reaction mixture was stirred at 0 °C for 3 h.

Then, the mixture was added to MeOH (70.0 mL) in a separate flask, NaOMe (200 mg, 924 µmol, 2.00 equiv.) was added and the mixture was stirred at r.t. for 10 min.

Afterwards, the mixture was diluted with water (10.0 mL), cooled to 0 °C and TFA (700 µL, 1.05 g, 9.24 mmol, 4.95 equiv.) and PIFA (1.99 g, 4.62 mmol, 2.50 equiv.) were added. The reaction mixture was stirred at 0 °C for 10 min. Then, water (10.0 mL) and L-ascorbic acid (651 mg, 3.70 mmol, 2.00 equiv.) were added and the reaction mixture was stirred at r.t. for another 10 min.

The mixture was again diluted with water (30.0 mL) and impurities were removed by washing with *n*-pentane (3 × 50.0 mL). MeOH and glyme were removed from the aqueous phase in vacuum. The remaining concentrated aqueous phase was filtered to remove solid impurities. Without further removal of the solvent, the aqueous phase was directly purified by reversed phase column chromatography (RP-C18, H_2O + 0.1% TFA → H_2O/MeCN 3:1 + 0.1% TFA) to yield *C*-glycosidic compound **233** (182 mg, 678 µmol, 37%) as colorless solid.

TLC: R_f = 0.35 (DCM/MeOH 9:1).

$[\alpha]_D^{20}$ = -30.0 (c = 1.00, MeOH).

UV (MeOH): λ_{max} = 203, 232, 282, 307 nm.

IR (ATR): $\tilde{\nu}$ = 3390, 2976, 2937, 1666, 1589, 1514, 1427, 1273, 1199, 1170, 1056, 815, 758, 650, 619 cm^{-1}.

^{1}H-NMR (600 MHz, D_2O): δ (ppm) = 1.18 (d, J = 6.1 Hz, 3 H, 6'-H_3), 3.36 (dq, J = 9.5, 6.1 Hz, 1 H, 5'-H), 3.47 (t, J = 9.5 Hz, 1 H, 4'-H), 3.70 (dd, J = 9.5, 3.4 Hz, 1 H, 3'-H), 3.89

(s, 3 H, OCH_3), 4.49 (dd, $J = 3.4$, 2.1 Hz, 1 H, 2'-H), 5.21 (d, $J = 2.1$ Hz, 1 H, 1'-H), 6.96 (d, $J = 8.4$ Hz, 1 H, 5-H), 7.54 (d, $J = 2.0$ Hz, 1 H, 2-H), 7.62 (dd, $J = 8.4$, 2.0 Hz, 1 H, 6-H).

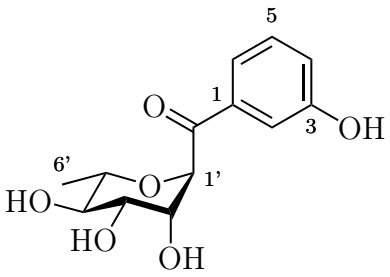
^{13}C-NMR (151 MHz, D_2O): δ (ppm) = 17.0 (C-6'), 55.9 (OCH_3), 69.1 (C-2'), 70.9 (C-3'), 72.1 (C-4'), 73.5 (C-5'), 80.2 (C-1'), 112.2 (C-2), 114.9 (C-5), 124.7 (C-6), 127.2 (C-1), 147.2 (C-3), 151.2 (C-4), 199.3 (CO).

MS (ESI): *m/z* (%) = 151.0 (22) [(4-hydroxy-3-methoxybenzylidyne)oxonium], 321.1 (37) $[M + Na]^+$.
calcd.: 321.0945 $[M + Na]^+$, found: 321.0949 (ESI-HRMS).

calcd.: 321.0945 $[M + Na]^+$,
found: 321.0949 (ESI-HRMS).

$C_{14}H_{18}O_7$ (298.29).

6.19.7 (3-Hydroxylphenyl)(α-L-rhamnopyranosyl) ketone 234



234

To neat 1,2,3,4-tetrakis-*O*-trimethylsilyl-L-rhamnopyranose **238** (837 mg, 1.85 mmol, 1.00 equiv.) was added TMSI (300 µL, 422 mg, 2.11 mmol, 1.14 equiv.) and the mixture was stirred at r.t. for 15 min to give 2,3,4,-tris-*O*-trimethylsilyl-L-rhamnopyranosyl iodide **316** as orange oil, which was dissolved in glyme (10.0 mL) and cooled to 0 °C.

In a separate vessel, a solution of 2-(3-hydroxyphenyl)-1,3-dithiane **292** (785 mg, 3.70 mmol, 2.00 equiv.) in glyme (10.0 mL) was cooled to 0 °C and a solution of *t*-BuLi (c = 1.75 M in *n*-pentane, 2.10 mL, 7.35 mmol, 3.98 equiv.) was added. The solution was stirred at 0 °C for 5 min and then CuI (900 µg, 4.72 µmol, 2.55 mol‰) and the precooled solution of 2,3,4,-tris-*O*-trimethylsilyl-L-rhamnopyranosyl iodide **316** in glyme were added. The reaction mixture was stirred at 0 °C for 3 h.

Then, the mixture was added to MeOH (70.0 mL) in a separate flask, NaOMe (200 mg, 924 µmol, 2.00 equiv.) was added and the mixture was stirred at r.t. for 10 min.

Afterwards, the mixture was diluted with water (10.0 mL), cooled to 0 °C and TFA (700 µL, 1.05 g, 9.24 mmol, 4.95 equiv.) and PIFA (1.99 g, 4.62 mmol, 2.50 equiv.) were added. The reaction mixture was stirred at 0 °C for 10 min. Then, water (10.0 mL) and L-ascorbic acid (651 mg, 3.70 mmol, 2.00 equiv.) were added and the reaction mixture was stirred at r.t. for another 10 min.

The mixture was again diluted with water (30.0 mL) and impurities were removed by washing with *n*-pentane (3 × 50.0 mL). MeOH and glyme were removed from the aqueous phase in vacuum. The remaining concentrated aqueous phase was filtered to remove solid impurities. Without further removal of the solvent, the aqueous phase was directly purified by reversed phase column chromatography (RP-C18, H_2O + 0.1% TFA → H_2O/MeCN 3:1 + 0.1% TFA) to yield *C*-glycosidic column compound **234** (204 mg, 760 µmol, 41%) as pale yellow solid.

TLC: $R_f = 0.25$ (DCM/MeOH 9:1).

$[\alpha]_D^{20} =$ -35,6 (c = 1.00, MeOH).

UV (MeOH): $\lambda_{max} = 218, 254, 316$ nm.

IR (ATR): $\tilde{\nu} = 3354, 2978, 2933, 1674, 1583, 1448, 1224, 1055, 840, 767, 678, 638$ cm^{-1}.

^{1}H-NMR (600 MHz, D_2O): δ (ppm) = 1.17 (d, J = 6.1 Hz, 3 H, 6'-H_3), 3.35 (dq, J = 9.5, 6.1 Hz, 1 H, 5'-H), 3.47 (t, J = 9.5 Hz, 1 H, 4'-H), 3.66 (dd, J = 9.5, 3.4 Hz, 1 H, 3'-H), 4.50 (dd, J = 3.4, 2.1 Hz, 1 H, 2'-H), 5.25 (d, J = 2.1 Hz, 1 H, 1'-H), 7.18 (ddd, J = 8.0, 2.6, 1.0 Hz, 1 H, 4-H), 7.40 (dd, J = 2.6, 1.7 Hz, 1 H, 2-H), 7.43 (t, J = 8.0 Hz, 1 H, 5-H), 7.53 (ddd, J = 8.0, 1.7, 1.0 Hz, 1 H, 6-H).

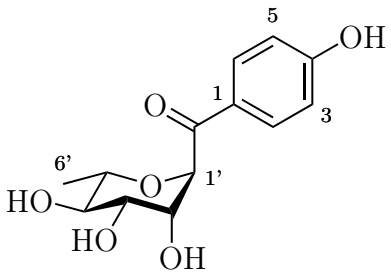
^{13}C-NMR (151 MHz, D_2O): δ (ppm) = 17.0 (C-6'), 69.0 (C-2'), 70.8 (C-3'), 71.9 (C-4'), 73.6 (C-5'), 80.6 (C-1'), 115.0 (C-2), 121.1 (C-6), 121.4 (C-4), 130.2 (C-5), 136.1 (C-1), 155.8 (C-3), 201.4 (CO).

MS (ESI): m/z (%) = 121.0 (13) [(3-hydroxybenzylidyne)oxonium], 291.1 (10) $[M + Na]^+$.

calcd.: 291.0839 $[M + Na]^+$,
found: 291.0845 (ESI-HRMS).

$C_{13}H_{16}O_6$ (268.27).

6.19.8 (4-Hydroxylphenyl)(α-L-rhamnopyranosyl) ketone 235



235

To neat 1,2,3,4-tetrakis-*O*-trimethylsilyl-L-rhamnopyranose **238** (837 mg, 1.85 mmol, 1.00 equiv.) was added TMSI (300 µL, 422 mg, 2.11 mmol, 1.14 equiv.) and the mixture was stirred at r.t. for 15 min to give 2,3,4,-tris-*O*-trimethylsilyl-L-rhamnopyranosyl iodide **316** as orange oil, which was dissolved in glyme (10.0 mL) and cooled to 0 °C.

In a separate vessel, a solution of 2-(4-hydroxyphenyl)-1,3-dithiane **293** (785 mg, 3.70 mmol, 2.00 equiv.) in glyme (10.0 mL) was cooled to 0 °C and a solution of *t*-BuLi (c = 1.75 M in *n*-pentane, 2.10 mL, 7.35 mmol, 3.98 equiv.) was added. The solution was stirred at 0 °C for 5 min and then CuI (900 µg, 4.72 µmol, 2.55 mol‰) and the precooled solution of 2,3,4,-tris-*O*-trimethylsilyl-L-rhamnopyranosyl iodide **316** in glyme were added. The reaction mixture was stirred at 0 °C for 3 h.

Then, the mixture was added to MeOH (70.0 mL) in a separate flask, NaOMe (200 mg, 924 µmol, 2.00 equiv.) was added and the mixture was stirred at r.t. for 10 min.

Afterwards, the mixture was diluted with water (10.0 mL), cooled to 0 °C and TFA (700 µL, 1.05 g, 9.24 mmol, 4.95 equiv.) and PIFA (1.99 g, 4.62 mmol, 2.50 equiv.) were added. The reaction mixture was stirred at 0 °C for 10 min. Then, water (10.0 mL) and L-ascorbic acid (651 mg, 3.70 mmol, 2.00 equiv.) were added and the reaction mixture was stirred at r.t. for another 10 min.

The mixture was again diluted with water (30.0 mL) and impurities were removed by washing with *n*-pentane (3 × 50.0 mL). MeOH and glyme were removed from the aqueous phase in vacuum. The remaining concentrated aqueous phase was filtered to remove solid impurities. Without further removal of the solvent, the aqueous phase was directly purified by reversed phase column chromatography (RP-C18, H_2O + 0.1% TFA → H_2O/MeCN 3:1 + 0.1% TFA) to yield *C*-glycosidic compound **235** (182 mg, 678 µmol, 37%) as colorless solid.

TLC: $R_f = 0.24$ (DCM/MeOH 9:1).

$[\alpha]_D^{20}$ = -32,9 (c = 1.01, MeOH).

UV (MeOH): λ_{max} = 220, 284 nm.

IR (ATR): $\tilde{\nu}$ = 3338, 2976, 2933, 1668, 1654, 1600, 1581, 1219, 1170, 1055, 823, 777, 601 cm^{-1}.

^{1}H-NMR (600 MHz, D_2O): δ (ppm) = 1.18 (d, J = 6.1 Hz, 3 H, 6'-H_3), 3.36 (dq, J = 9.5, 6.1 Hz, 1 H, 5'-H), 3.47 (t, J = 9.5 Hz, 1 H, 4'-H), 3.71 (dd, J = 9.5, 3.5 Hz, 1 H, 3'-H), 4.50 (dd, J = 3.5, 2.1 Hz, 1 H, 2'-H), 5.24 (d, J = 2.1 Hz, 1 H, 1'-H), 6.95–7.00 (m, 2 H, 3-H, 5-H), 7.95–7.98 (m, 2 H, 2-H, 6-H).

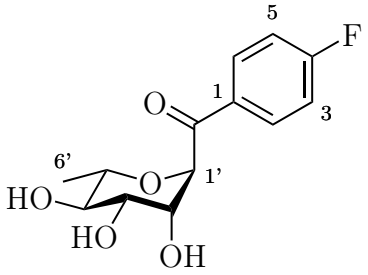
^{13}C-NMR (151 MHz, D_2O): δ (ppm) = 17.0 (C-6'), 69.1 (C-2'), 70.9 (C-3'), 72.1 (C-4'), 73.5 (C-5'), 80.2 (C-1'), 115.4 (2 C, C-3, C-5), 127.0 (C-1), 131.9 (2 C, C-2, C-6), 161.5 (C-4), 199.6 (CO).

MS (ESI): m/z (%) = 121.0 (100) [(4-hydroxybenzylidyne)oxonium], 291.1 (52) $[M + Na]^+$.

calcd.: 291.0839 $[M + Na]^+$,
found: 291.0837 (ESI-HRMS).

$C_{13}H_{16}O_6$ (268.27).

6.19.9 (4-Fluorophenyl)(α-L-rhamnopyranosyl) ketone 236



236

To neat 1,2,3,4-tetrakis-*O*-trimethylsilyl-L-rhamnopyranose **238** (837 mg, 1.85 mmol, 1.00 equiv.) was added TMSI (300 µL, 422 mg, 2.11 mmol, 1.14 equiv.) and the mixture was stirred at r.t. for 15 min to give 2,3,4,-tris-*O*-trimethylsilyl-L-rhamnopyranosyl iodide **316** as orange oil, which was dissolved in glyme (10.0 mL) and cooled to 0 °C.

In a separate vessel, a solution of 2-(4-fluorophenyl)-1,3-dithiane **295** (792 mg, 3.70 mmol, 2.00 equiv.) in glyme (10.0 mL) was cooled to 0 °C and a solution of *t*-BuLi (c = 1.70 M in *n*-pentane, 2.20 mL, 3.74 mmol, 2.02 equiv.) was added. The solution was stirred at 0 °C for 5 min and then CuI (900 µg, 4.72 µmol, 2.55 mol‰) and the precooled solution of 2,3,4-tris-*O*-trimethylsilyl-D-rhamnopyranosyl iodide **316** in glyme were added. The reaction mixture was stirred at 0 °C for 3 h.

Then, the mixture was added to MeOH (70.0 mL) in a separate flask, NaOMe (200 mg, 924 µmol, 2.00 equiv.) was added and the mixture was stirred at r.t. for 10 min.

Afterwards, the mixture was diluted with water (10.0 mL), cooled to 0 °C and TFA (430 µL, 636 mg, 5.58 mmol, 3.04 equiv.) and PIFA (1.99 g, 4.62 mmol, 2.50 equiv.) were added. The reaction mixture was stirred at 0 °C for 10 min. Then, water (10.0 mL) and L-ascorbic acid (651 mg, 3.70 mmol, 2.00 equiv.) were added and the reaction mixture was stirred at r.t. for another 10 min.

The mixture was again diluted with water (30.0 mL) and impurities were removed by washing with *n*-pentane (3 × 50.0 mL). MeOH and glyme were removed from the aqueous phase in vacuum. The remaining concentrated aqueous phase was filtered to remove solid impurities. Without further removal of the solvent, the aqueous phase was directly purified by reversed phase column chromatography (RP-C18, $H_2O \rightarrow H_2O$/MeCN 7:3) to yield *C*-glycosidic compound **236** (101 mg, 373 µmol, 20%) as colorless, glassy solid.

TLC: $R_f = 0.69$ (DCM/MeOH 9:1).

$[\alpha]_D^{25} = -39.2$ (c = 1.00, MeOH).

UV (MeOH): $\lambda_{max} = 203, 249$ nm.

IR (ATR): $\tilde{\nu} = 3363, 2935, 1680, 1597, 1506, 1411, 1226, 1080, 1055, 1014, 972, 871, 813, 642, 594$ cm^{-1}.

^{1}H-NMR (600 MHz, methanol-d_4): δ (ppm) = 1.14 (d, J = 6.1 Hz, 3 H, 6'-H_3), 3.11 (dq, J = 9.2, 6.1 Hz, 1 H, 5'-H), 3.40 (t, J = 9.3 Hz, 1 H, 4'-H), 3.62 (dd, J = 9.3, 3.5 Hz, 1 H, 3'-H), 4.42 (dd, J = 3.4, 2.2 Hz, 1 H, 2'-H), 5.08 (d, J = 2.1 Hz, 1 H, 1'-H), 7.19–7.25 (m, 2 H, 3-H, 5-H), 8.13–8.17 (m, 2 H, 2-H, 6-H).

^{13}C-NMR (151 MHz, Methanol-d_4): δ (ppm) = 16.8 (C-6'), 69.0 (C-2'), 71.6 (C-3'), 72.5 (C-4'), 73.5 (C-5'), 80.5 (C-1'), 115.1 (d, J = 22.1 Hz, 2 C, C-3, C-5), 131.8 (d, J = 9.4 Hz, 2 C, C-2, C-6), 131.8 (d, J = 2.9 Hz, C-1), 165.9 (d, J = 253.8 Hz, C-4), 197.9 (CO).

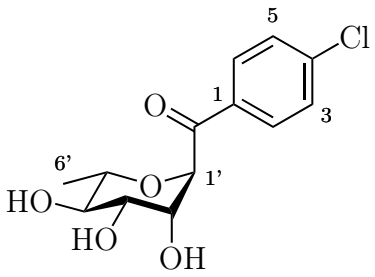
^{19}F-NMR (565 MHz, Methanol-d_4): δ (ppm) = 107.6 (m, 4-F).

MS (ESI): m/z (%) = 123.0 (100) [(4-fluorobenzylidyne)oxonium], 293.1 (39) $[M + Na]^+$.

calcd.: 293.0796 $[M + Na]^+$,
found: 293.0806 (ESI-HRMS).

$C_{13}H_{15}FO_5$ (270.26).

6.19.10 (4-Chlorophenyl)(α-L-rhamnopyranosyl) ketone 237



237

To neat 1,2,3,4-tetrakis-*O*-trimethylsilyl-L-rhamnopyranose **238** (837 mg, 1.85 mmol, 1.00 equiv.) was added TMSI (300 µL, 422 mg, 2.11 mmol, 1.14 equiv.) and the mixture was stirred at r.t. for 15 min to give 2,3,4,-tris-*O*-trimethylsilyl-L-rhamnopyranosyl iodide **316** as orange oil, which was dissolved in glyme (10.0 mL) and cooled to 0 °C.

In a separate vessel, a solution of 2-(4-chlorophenyl)-1,3-dithiane **294** (853 mg, 3.70 mmol, 2.00 equiv.) in glyme (10.0 mL) was cooled to 0 °C and a solution of *t*-BuLi (c = 1.69 M in *n*-pentane, 2.20 mL, 3.72 mmol, 2.01 equiv.) was added. The solution was stirred at 0 °C for 5 min and then CuI (900 µg, 4.72 µmol, 2.55 mol‰) and the precooled solution of 2,3,4,-tris-*O*-trimethylsilyl-L-rhamnopyranosyl iodide **316** in glyme were added. The reaction mixture was stirred at 0 °C for 3 h.

Then, the mixture was added to MeOH (70.0 mL) in a separate flask, NaOMe (200 mg, 924 µmol, 2.00 equiv.) was added and the mixture was stirred at r.t. for 10 min.

Afterwards, the mixture was diluted with water (10.0 mL), cooled to 0 °C and TFA (430 µL, 636 mg, 5.58 mmol, 3.04 equiv.) and PIFA (1.99 g, 4.62 mmol, 2.50 equiv.) were added. The reaction mixture was stirred at 0 °C for 10 min. Then, water (10.0 mL) and L-ascorbic acid (651 mg, 3.70 mmol, 2.00 equiv.) were added and the reaction mixture was stirred at r.t. for another 10 min.

The mixture was again diluted with water (30.0 mL) and impurities were removed by washing with *n*-pentane (3 × 50.0 mL). MeOH and glyme were removed from the aqueous phase in vacuum. The remaining concentrated aqueous phase was filtered to remove solid impurities. Without further removal of the solvent, the aqueous phase was directly purified by reversed phase column chromatography (RP-C18, $H_2O \rightarrow H_2O$/MeCN 3:1) to yield *C*-glycosidic compound **237** (68.1 mg, 238 µmol, 13%) as colorless solid.

TLC: $R_f = 0.48$ (DCM/MeOH 9:1).

$[\alpha]_D^{20} = -45.8$ (c = 0.98, MeOH).

UV (MeOH): $\lambda_{max} = 256$ nm.

IR (ATR): $\tilde{\nu} = 3383, 2976, 2933, 2680, 1587, 1400, 1217, 1114, 1083, 1056, 812, 788, 650, 474\ cm^{-1}$.

^{1}H-NMR (600 MHz, methanol-d_4): δ (ppm) = 1.15 (d, J = 6.1 Hz, 3 H, 6'-H_3), 3.11 (dq, J = 9.3, 6.1 Hz, 1 H, 5'-H), 3.41 (t, J = 9.3 Hz, 1 H, 4'-H), 3.61 (dd, J = 9.3, 3.5 Hz, 1 H, 3'-H), 4.42 (dd, J = 3.5, 2.2 Hz, 1 H, 2'-H), 5.09 (d, J = 2.2 Hz, 1 H, 1'-H), 7.51–7.54 (m, 2 H, 3-H, 5-H), 8.05–8.08 (m, 2 H, 2-H, 6-H).

^{13}C-NMR (151 MHz, methanol-d_4): δ (ppm) = 16.8 (C-6'), 68.9 (C-2'), 71.6 (C-3'), 72.5 (C-4'), 73.6 (C-5'), 80.5 (C-1'), 128.4 (2 C, C-3, C-5), 130.4 (2 C, C-2, C-6) 133.7 (C-4), 139.5 (C-1), 198.4 (CO).

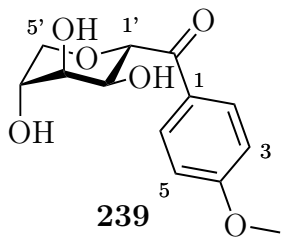
MS (ESI): *m/z* (%) = 139.0 (12) [(4-chlorobenzylidyne)oxonium], 309.1 (6) $[M + Na]^+$.

calcd.: 309.0500 $[M + Na]^+$,
found: 309.0511 (ESI-HRMS).

$C_{13}H_{15}ClO_5$ (286.71).

6.20 Syntheses of *C*-acyl α-D-lyxopyranosides

6.20.1 (4-Methoxyphenyl)(α-D-lyxopyranosyl) ketone 239



239

To neat 1,2,3,4-tetrakis-*O*-trimethylsilyl-D-lyxopyranose **250** (811 mg, 1.85 mmol, 1.00 equiv.) was added TMSI (300 µL, 422 mg, 2.11 mmol, 1.14 equiv.) and the mixture was stirred at 0 °C for 15 min to give 2,3,4-tris-*O*-trimethylsilyl-D-lyxopyranosyl iodide **317** as orange oil, which was dissolved in glyme (10.0 mL) and cooled to 0 °C.

In a separate vessel, a solution of 2-(4-methoxyphenyl)-1,3-dithiane **151** (837 mg, 3.70 mmol, 2.00 equiv.) in glyme (10.0 mL) was cooled to 0 °C and a solution of *t*-BuLi (c = 1.85 M in *n*-pentane, 2.00 mL, 3.70 mmol, 2.00 equiv.) was added. The solution was stirred at 0 °C for 5 min and then CuI (900 µg, 4.72 µmol, 2.55 mol‰) and the precooled solution of 2,3,4-tris-*O*-trimethylsilyl-D-lyxopyranosyl iodide **317** in glyme were added. The reaction mixture was stirred at 0 °C for 3 h.

Then, the mixture was added to MeOH (70.0 mL) in a separate flask, NaOMe (200 mg, 924 µmol, 2.00 equiv.) was added and the mixture was stirred at r.t. for 10 min.

Afterwards, the mixture was diluted with water (10.0 mL), cooled to 0 °C and TFA (430 µL, 636 mg, 5.58 mmol, 3.04 equiv.) and PIFA (1.99 g, 4.62 mmol, 2.50 equiv.) were added. The reaction mixture was stirred at 0 °C for 10 min. Then, water (10.0 mL) and L-ascorbic acid (651 mg, 3.70 mmol, 2.00 equiv.) were added and the reaction mixture was stirred at r.t. for another 10 min.

The mixture was again diluted with water (30.0 mL) and impurities were removed by washing with *n*-pentane (3 × 50.0 mL). MeOH and glyme were removed from the aqueous phase in vacuum. The remaining concentrated aqueous phase was filtered to remove solid impurities. Without further removal of the solvent, the aqueous phase was directly purified by reversed phase column chromatography (RP-C18, $H_2O \rightarrow H_2O$/MeCN 3:1) to yield *C*-glycosidic compound **239** (147 mg, 548 µmol, 30%) as pale yellow crystalline solid.

TLC: $R_f = 0.47$ (DCM/MeOH 9:1).

M.p.: 172 °C (from water).

$[a]_D^{20} = 23.6$ (c = 1.02, MeOH).

UV (MeOH): $\lambda_{max} = 220$, 281 nm.

IR (ATR): $\tilde{\nu} = 3446$, 3385, 3327, 2937, 2918, 2893, 2856, 1658, 1593, 1263, 1176, 1074, 1016, 827, 590 cm^{-1}.

^{1}H-NMR (600 MHz, methanol-d_4): δ (ppm) = 3.65 (dd, J = 12.1, 2.4 Hz, 1 H, 5'-$H_{eq.}$), 3.77 (dt, J = 3.9, 2.4 Hz, 1 H, 4'-H), 3.88 (s, 3 H, OCH_3) 3.94 (t, J = 3.9 Hz, 1 H, 3'-H),

3.96 (dd, $J = 12.1$, 2.4 Hz, 1 H, 5'-H_{ax}), 4.20 (dd, $J = 8.7$, 3.9 Hz, 1 H, 2'-H), 4.87 (d, $J = 8.7$ Hz, 1 H, 1'-H), 6.98–7.04 (m, 2 H, 3-H, 5-H), 8.05–8.12 (m, 2 H, 2-H, 6-H).

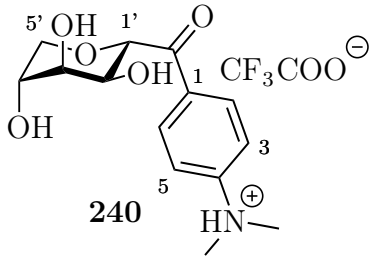
^{13}C-NMR (151 MHz, methanol-d_4): δ (ppm) = 56.1 (OCH_3), 67.8 (C-2'), 68.2 (C-5'), 70.9 (C-4'), 71.9 (C-3'), 78.0 (C-1'), 114.7 (2 C, C-3, C-5), 130.3 (C-1), 132.8 (2 C, C-2, C-6), 165.6 (C-4), 197.9 (CO).

MS (ESI): m/z (%) = 135.0 (93) [(4-methoxybenzylidyne)oxonium], 269.1 (40) $[M + H]^+$ 291.1 (98) $[M + Na]^+$.

calcd.: 291.0839 $[M + Na]^+$,
found: 291.0838 (ESI-HRMS).

$C_{13}H_{16}O_6$ (268.27).

6.20.2 (4-Dimethylaminophenyl)(α-D-lyxopyranosyl) ketone TFA salt 240



240

To neat 1,2,3,4-tetrakis-*O*-trimethylsilyl-D-lyxopyranose **250** (811 mg, 1.85 mmol, 1.00 equiv.) was added TMSI (300 µL, 422 mg, 2.11 mmol, 1.14 equiv.) and the mixture was stirred at 0 °C for 15 min to give 2,3,4-tris-*O*-trimethylsilyl-D-lyxopyranosyl iodide **317** as orange oil, which was dissolved in glyme (10.0 mL) and cooled to 0 °C.

In a separate vessel, a solution of 2-(4-dimethylaminophenyl)-1,3-dithiane **297** (885 mg, 3.70 mmol, 2.00 equiv.) in glyme (10.0 mL) was cooled to 0 °C and a solution of *t*-BuLi (c = 1.75 M in *n*-pentane, 2.10 mL, 3.68 mmol, 1.99 equiv.) was added. The solution was stirred at 0 °C for 5 min and then CuI (900 µg, 4.72 µmol, 2.55 mol‰) and the precooled solution of 2,3,4-tris-*O*-trimethylsilyl-D-lyxopyranosyl iodide **317** in glyme were added. The reaction mixture was stirred at 0 °C for 3 h.

Then, the mixture was added to MeOH (70.0 mL) in a separate flask, NaOMe (200 mg, 924 µmol, 2.00 equiv.) was added and the mixture was stirred at r.t. for 10 min.

Afterwards, the mixture was diluted with water (10.0 mL), cooled to 0 °C and TFA (700 µL, 1.05 g, 9.24 mmol, 4.95 equiv.) and PIFA (1.99 g, 4.62 mmol, 2.50 equiv.) were added. The reaction mixture was stirred at 0 °C for 10 min. Then, water (10.0 mL) and L-ascorbic acid (651 mg, 3.70 mmol, 2.00 equiv.) were added and the reaction mixture was stirred at r.t. for another 10 min.

The mixture was again diluted with water (30.0 mL) and impurities were removed by washing with *n*-pentane (3 × 50.0 mL). MeOH and glyme were removed from the aqueous phase in vacuum. The remaining concentrated aqueous phase was filtered to remove solid impurities. Without further removal of the solvent, the aqueous phase was directly purified by reversed phase column chromatography (RP-C18, H_2O + 0.1% TFA → H_2O/MeCN 3:1 + 0.1% TFA) to yield *C*-glycosidic compound **240** (369 mg, 933 µmol, 51%) as beige solid.

TLC: $R_f = 0.48$ (DCM/MeOH 9:1).

$[a]_D^{20} = 27.7$ (c = 0.98, H_2O/TFA 9:1).

UV (MeOH): $\lambda_{max} = 242$, 361 nm.

IR (ATR): $\tilde{\nu} = 3433$, 3323, 2922, 2872, 1672, 1656, 1598, 1452, 1433, 1413, 1083, 1058, 1026, 700, 501 cm^{-1}.

^{1}H-NMR (600 MHz, DMSO-d_6): δ (ppm) = 3.02 (s, 6 H, $N(CH_3)_2$), 3.50 (dd, J = 11.8, 2.2 Hz, 1 H, 5'-$H_{eq.}$), 3.60 (dt, J = 3.7, 2.2 Hz, 1 H, 4'-H), 3.71 (t, J = 3.7 Hz, 1 H, 3'-H), 3.74 (dd, J = 11.8, 2.2 Hz, 1 H, 5'-$H_{ax.}$), 4.06 (dd, J = 8.9, 3.7 Hz, 1 H, 2'-H), 4.59 (d, J = 8.9 Hz, 1 H, 1'-H), 6.69–6.73 (m, 2 H, 3-H, 5-H), 7.86–7.90 (m, 2 H, 2-H, 6-H).

^{13}C-NMR (151 MHz, DMSO-d_6): δ (ppm) = 39.6 (2 C, $N(CH_3)_2$), 66.0 (C-2'), 66.8 (C-5'), 69.1 (C-4'), 70.3 (C-3'), 76.5 (C-1'), 110.5 (2 C, C-3, C-5), 123.5 (C-1), 131.0 (2 C, C-2, C-6), 153.3 (C-4), 194.2 (CO).

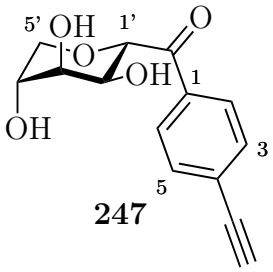
^{19}F-NMR (565 MHz, DMSO-d_6): δ (ppm) = 74.6 (m, CF_3COO^-).

MS (ESI): *m/z* (%) = 148.1 (5) [(4-dimethylaminobenzylidyne)oxonium], 282.1 (100) $[M - CF_3COO]^+$, 304.1 (35) $[M - CF_3COOH + Na]^+$.
calcd.: 282.1336 $[M - CF_3COO^-]^+$, found: 282.1335 (ESI-HRMS).

calcd.: 282.1336 $[M - CF_3COO^-]^+$,
found: 282.1335 (ESI-HRMS).

$C_{16}H_{20}F_3NO_7$ (395.33).

6.20.3 (4-Ethynylphenyl)(D-lyxopyranosyl) ketones 241 and 275



247

To neat 1,2,3,4-tetrakis-*O*-trimethylsilyl-D-lyxopyranose **250** (811 mg, 1.85 mmol, 1.00 equiv.) was added TMSI (300 µL, 422 mg, 2.11 mmol, 1.14 equiv.) and the mixture was stirred at 0 °C for 15 min to give 2,3,4-tris-*O*-trimethylsilyl-D-lyxopyranosyl iodide **317** as orange oil, which was dissolved in glyme (10.0 mL) and cooled to 0 °C.

In a separate vessel, a solution of ((4-(1,3-dithian-2-yl)phenyl)ethynyl)trimethylsilane **215** (1.08 g, 3.70 mmol, 2.00 equiv.) in glyme (10.0 mL) was cooled to 0 °C and a solution of *t*-BuLi (c = 1.71 M in *n*-pentane, 2.10 mL, 3.59 mmol, 1.94 equiv.) was added. The solution was stirred at 0 °C for 5 min and then CuI (900 µg, 4.72 µmol, 2.55 mol‰) and the precooled solution of 2,3,4-tris-*O*-trimethylsilyl-D-lyxopyranosyl iodide **317** in glyme were added. The reaction mixture was stirred at 0 °C for 3 h.

Then, the mixture was added to MeOH (70.0 mL) in a separate flask, NaOMe (200 mg, 924 µmol, 2.00 equiv.) was added and the mixture was stirred at r.t. for 10 min.

Afterwards, the mixture was diluted with water (10.0 mL), cooled to 0 °C and TFA (430 µL, 636 mg, 5.58 mmol, 3.04 equiv.) and PIFA (1.99 g, 4.62 mmol, 2.50 equiv.) were added. The reaction mixture was stirred at 0 °C for 10 min. Then, water (10.0 mL) and L-ascorbic acid (651 mg, 3.70 mmol, 2.00 equiv.) were added and the reaction mixture was stirred at r.t. for another 10 min.

The mixture was again diluted with water (30.0 mL) and impurities were removed by washing with *n*-pentane (3 × 50.0 mL). MeOH and glyme were removed from the aqueous phase in vacuum. The remaining concentrated aqueous phase was filtered to remove solid impurities. Without further removal of the solvent, the aqueous phase was directly purified by reversed phase column chromatography (RP-C18, $H_2O \rightarrow H_2O$/MeCN 3:1) to yield *C*-glycosidic compound **275** (80.6 mg, 307 µmol, 17%) followed by *C*-glycosidic compound **241** (101 mg, 385 µmol, 21%) as pale yellow solids.

For analytical data of **275** see section 8.10.

Analytical data for **241**:

TLC: $R_f = 0.48$ (DCM/MeOH 9:1).

$[\alpha]_D^{20} = 17.4$ (c = 0.94, MeOH).

UV (MeOH): $\lambda_{max} = 212$, 273 nm.

IR (ATR): $\tilde{\nu} = 3375$, 3257, 2924, 2877, 2120, 1695, 1602, 1404, 1280, 1213, 1085, 1037, 1008, 891, 827 cm^{-1}.

^{1}H-NMR (600 MHz, methanol-d_4): δ (ppm) = 3.66 (ddd, J = 12.1, 2.5 Hz, 1 H 5'-$H_{eq.}$), 3.76 (s, 1 H, 4-C≡CH), 3.78 (dt, J = 4.6, 2.5 Hz, 1 H, 4'-H), 3.94 (dd, J = 4.6, 3.2 Hz, 1 H, 3'-H), 3.98 (dd, J = 12.1, 2.5 Hz, 1 H, 5'-$H_{ax.}$), 4.21 (dd, J = 8.9, 3.2 Hz, 1 H, 2'-H), 4.88 (d, J = 8.9 Hz, 1 H, 1'-H), 7.57–7.60 (m, 2 H, 3-H, 5-H), 8.06–8.09 (m, 2 H, 2-H, 6-H).

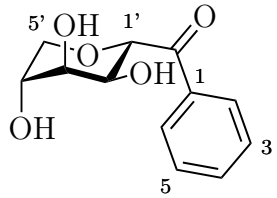
^{13}C-NMR (151 MHz, methanol-d_4): δ (ppm) = 67.6 (C-2'), 68.3 (C-5'), 70.9 (C-4'), 71.8 (C-3'), 78.3 (C-1'), 83.2 (4-C≡CH), 128.8 (C-1), 130.4 (2 C, C-2, C-6), 133.0 (2 C, C-3, C-5), 137.0 (C-4), 198.4 (CO).

MS (ESI): m/z (%) = 129.0 (13) [(4-ethynylbenzylidyne)oxonium], 285.1 (33) $[M + Na]^+$.

calcd.: 285.0733$[M + Na]^+$,
found: 285.0730(ESI-HRMS).

$C_{14}H_{14}O_5$ (262.26).

6.20.4 Phenyl (α-D-lyxopyranosyl) ketone 242



242

To neat 1,2,3,4-tetrakis-*O*-trimethylsilyl-D-lyxopyranose **250** (811 mg, 1.85 mmol, 1.00 equiv.) was added TMSI (300 µL, 422 mg, 2.11 mmol, 1.14 equiv.) and the mixture was stirred at 0 °C for 15 min to give 2,3,4-tris-*O*-trimethylsilyl-D-lyxopyranosyl iodide **317** as orange oil, which was dissolved in glyme (10.0 mL) and cooled to 0 °C.

In a separate vessel, a solution of 2-phenyl-1,3-dithiane **191** (726 mg, 3.70 mmol, 2.00 equiv.) in glyme (10.0 mL) was cooled to 0 °C and a solution of *t*-BuLi (c = 1.74 M in *n*-pentane, 2.10 mL, 3.65 mmol, 1.98 equiv.) was added. The solution was stirred at 0 °C for 5 min and then CuI (900 µg, 4.72 µmol, 2.55 mol‰) and the precooled solution of 2,3,4-tris-*O*-trimethylsilyl-D-lyxopyranosyl iodide **317** in glyme were added. The reaction mixture was stirred at 0 °C for 3 h.

Then, the mixture was added to MeOH (70.0 mL) in a separate flask, NaOMe (200 mg, 924 µmol, 2.00 equiv.) was added and the mixture was stirred at r.t. for 10 min.

Afterwards, the mixture was diluted with water (10.0 mL), cooled to 0 °C and TFA (430 µL, 636 mg, 5.58 mmol, 3.04 equiv.) and PIFA (1.99 g, 4.62 mmol, 2.50 equiv.) were added. The reaction mixture was stirred at 0 °C for 10 min. Then, water (10.0 mL) and L-ascorbic acid (651 mg, 3.70 mmol, 2.00 equiv.) were added and the reaction mixture was stirred at r.t. for another 10 min.

The mixture was again diluted with water (30.0 mL) and impurities were removed by washing with *n*-pentane (3 × 50.0 mL). MeOH and glyme were removed from the aqueous phase in vacuum. The remaining concentrated aqueous phase was filtered to remove solid impurities. Without further removal of the solvent, the aqueous phase was directly purified by reversed phase column chromatography (RP-C18, $H_2O \rightarrow H_2O$/MeCN 4:1) to yield *C*-glycosidic compound **242** (130 mg, 546 µmol, 30%) as pale yellow glassy solid.

TLC: $R_f = 0.47$ (DCM/MeOH 9:1).

$[\alpha]_D^{20} = 18.2$ (c = 1.02, MeOH).

UV (MeOH): $\lambda_{max} = 202$, 256 nm.

IR (ATR): $\tilde{\nu} = 3383$, 3064, 2916, 2862, 1676, 1597, 1579, 1448, 1263, 1213, 1109, 1043, 887, 831, 692 cm^{-1}.

^{1}H-NMR (600 MHz, methanol-d_4): δ (ppm) = 3.66 (dd, J = 12.1, 2.4 Hz, 1 H, 5'-$H_{eq.}$), 3.79 (dt, J = 4.0, 2.4 Hz, 1 H, 4'-H), 3.94 (t, J = 4.0 Hz, 1 H, 3'-H), 3.98 (dd, J = 12.1, 2.4 Hz, 1 H, 5'-$H_{ax.}$), 4.23 (dd, J = 8.7, 4.0 Hz, 1 H, 2'-H), 4.92 (d, J = 8.7 Hz, 1 H, 1'-H), 7.47–7.52 (m, 2 H, 3-H, 5-H), 7.59–7.63 (m, 1 H, 4-H), 8.07–8.11 (m, 2 H, 2-H, 6-H).

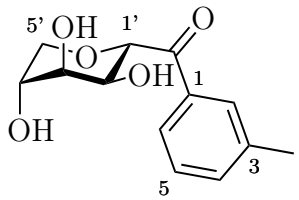
^{13}C-NMR (151 MHz, methanol-d_4): δ (ppm) = 67.7 (C-2'), 68.3 (C-5'), 70.9 (C-4'), 71.9 (C-3'), 78.1 (C-1'), 129.5 (2 C, C-3, C-5), 130.3 (2 C, C-2, C-6), 134.6 (C-4), 137.4 (C-1), 199.3 (CO).

MS (ESI): m/z (%) = (27) $[M + Na]^+$.

calcd.: 261.0733 $[M + Na]^+$,
found: 261.0733 (ESI-HRMS).

$C_{12}H_{14}O_5$ (238.24).

6.20.5 (3-Methylphenyl)(α-D-lyxopyranosyl) ketone 243



243

To neat 1,2,3,4-tetrakis-*O*-trimethylsilyl-D-lyxopyranose **250** (811 mg, 1.85 mmol, 1.00 equiv.) was added TMSI (300 µL, 422 mg, 2.11 mmol, 1.14 equiv.) and the mixture was stirred at 0 °C for 15 min to give 2,3,4-tris-*O*-trimethylsilyl-D-lyxopyranosyl iodide **317** as orange oil, which was dissolved in glyme (10.0 mL) and cooled to 0 °C.

In a separate vessel, a solution of 2-(3-methylphenyl)-1,3-dithiane **288** (778 mg, 3.70 mmol, 2.00 equiv.) in glyme (10.0 mL) was cooled to 0 °C and a solution of *t*-BuLi (c = 1.74 M in *n*-pentane, 2.10 mL, 3.65 mmol, 1.98 equiv.) was added. The solution was stirred at 0 °C for 5 min and then CuI (900 µg, 4.72 µmol, 2.55 mol‰) and the precooled solution of 2,3,4-tris-*O*-trimethylsilyl-D-lyxopyranosyl iodide **317** in glyme were added. The reaction mixture was stirred at 0 °C for 3 h.

Then, the mixture was added to MeOH (70.0 mL) in a separate flask, NaOMe (200 mg, 924 µmol, 2.00 equiv.) was added and the mixture was stirred at r.t. for 10 min.

Afterwards, the mixture was diluted with water (10.0 mL), cooled to 0 °C and TFA (430 µL, 636 mg, 5.58 mmol, 3.04 equiv.) and PIFA (1.99 g, 4.62 mmol, 2.50 equiv.) were added. The reaction mixture was stirred at 0 °C for 10 min. Then, water (10.0 mL) and L-ascorbic acid (651 mg, 3.70 mmol, 2.00 equiv.) were added and the reaction mixture was stirred at r.t. for another 10 min.

The mixture was again diluted with water (30.0 mL) and impurities were removed by washing with *n*-pentane (3 × 50.0 mL). MeOH and glyme were removed from the aqueous phase in vacuum. The remaining concentrated aqueous phase was filtered to remove solid impurities. Without further removal of the solvent, the aqueous phase was directly

purified by reversed phase column chromatography (RP-C18, $H_2O \rightarrow H_2O$/MeCN 3:1) to yield *C*-glycosidic compound **243** (137 mg, 543 µmol, 29%) as colorless, glassy solid.

TLC: $R_f = 0.50$ (DCM/MeOH 9:1).

$[a]_D^{20} = 18.7$ (c = 1.02, MeOH).

UV (MeOH): $\lambda_{max} = 205, 251, 290$ nm.

IR (ATR): $\tilde{\nu} = 3385, 2918, 2864, 1676, 1600, 1583, 1384, 1342, 1269, 1246, 1107, 1050, 812, 715, 644$ cm^{-1}.

^{1}H-NMR (600 MHz, methanol-d_4): δ (ppm) = 2.41 (s, 3 H, 3-CH_3), 3.65 (dd, J = 12.1, 2.5 Hz, 1 H, 5'-$H_{eq.}$), 3.78 (dt, J = 4.7, 2.5 Hz, 1 H, 4'-H), 3.93 (dd, J = 4.7, 3.2 Hz, 1 H, 3'-H), 3.97 (dd, J = 12.1, 2.5 Hz, 1 H, 5'-$H_{ax.}$), 4.22 (dd, J = 8.6, 3.2 Hz, 1 H, 2'-H), 4.91 (d, J = 8.6 Hz, 1 H, 1'-H), 7.38 (t, J = 7.6 Hz, 1 H, 5-H), 7.44 (d, J = 7.6 Hz, 1 H, 4-H), 7.88 (d, J = 7.6 Hz, 1 H, 6-H), 7.89 (d, J = 7.6 Hz, 1 H, 2-H).

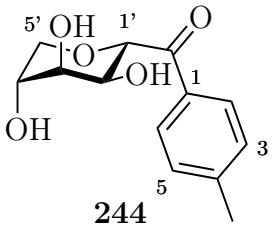
^{13}C-NMR (151 MHz, methanol-d_4): δ (ppm) = 21.3 (3-$\underline{C}H_3$), 67.8 (C-2'), 68.3 (C-5'), 70.9 (C-4'), 71.9 (C-3'), 78.0 (C-1'), 127.6 (C-6), 129.4 (C-2), 130.6 (C-5), 135.3 (C-4), 137.5 (C-1), 139.5 (C-3), 199.5 (CO).

MS (ESI): m/z (%) = 119.1 (77) [(3-methylbenzylidyne)oxonium], 275.1 (100) $[M + Na]^+$.

calcd.: 275.0890 $[M + Na]^+$,
found: 275.0891 (ESI-HRMS).

$C_{13}H_{16}O_5$ (252.27).

6.20.6 (4-Methylphenyl)(α-D-lyxopyranosyl) ketone 244



244

To neat 1,2,3,4-tetrakis-*O*-trimethylsilyl-D-lyxopyranose **250** (811 mg, 1.85 mmol, 1.00 equiv.) was added TMSI (300 µL, 422 mg, 2.11 mmol, 1.14 equiv.) and the mixture

was stirred at 0 °C for 15 min to give 2,3,4-tris-*O*-trimethylsilyl-D-lyxopyranosyl iodide **317** as orange oil, which was dissolved in glyme (10.0 mL) and cooled to 0 °C.

In a separate vessel, a solution of 2-(4-methylphenyl)-1,3-dithiane **289** (778 mg, 3.70 mmol, 2.00 equiv.) in glyme (10.0 mL) was cooled to 0 °C and a solution of *t*-BuLi (c = 1.74 M in *n*-pentane, 2.10 mL, 3.65 mmol, 1.98 equiv.) was added. The solution was stirred at 0 °C for 5 min and then CuI (900 µg, 4.72 µmol, 2.55 mol‰) and the precooled solution of 2,3,4-tris-*O*-trimethylsilyl-D-lyxopyranosyl iodide **317** in glyme were added. The reaction mixture was stirred at 0 °C for 3 h.

Then, the mixture was added to MeOH (70.0 mL) in a separate flask, NaOMe (200 mg, 924 µmol, 2.00 equiv.) was added and the mixture was stirred at r.t. for 10 min.

Afterwards, the mixture was diluted with water (10.0 mL), cooled to 0 °C and TFA (430 µL, 636 mg, 5.58 mmol, 3.04 equiv.) and PIFA (1.99 g, 4.62 mmol, 2.50 equiv.) were added. The reaction mixture was stirred at 0 °C for 10 min. Then, water (10.0 mL) and L-ascorbic acid (651 mg, 3.70 mmol, 2.00 equiv.) were added and the reaction mixture was stirred at r.t. for another 10 min.

The mixture was again diluted with water (30.0 mL) and impurities were removed by washing with *n*-pentane (3 × 50.0 mL). MeOH and glyme were removed from the aqueous phase in vacuum. The remaining concentrated aqueous phase was filtered to remove solid impurities. Without further removal of the solvent, the aqueous phase was directly purified by reversed phase column chromatography (RP-C18, $H_2O \rightarrow H_2O$/MeCN 3:1) to yield *C*-glycosidic compound **244** (154 mg, 611 µmol, 33%) as colorless, glassy solid.

TLC: $R_f = 0.48$ (DCM/MeOH 9:1).

$[a]_D^{20} = 19.8$ (c = 1.00, MeOH).

UV (MeOH): $\lambda_{max} = 202, 255$ nm.

IR (ATR): $\tilde{\nu} = 3412, 2916, 2873, 1676, 1664, 1604, 1409, 1261, 1230, 1184, 1111, 1045, 891, 819, 476$ cm^{-1}.

^{1}H-NMR (600 MHz, methanol-d_4): δ (ppm) = 2.41 (s, 3 H, 4-CH_3), 3.65 (dd, J = 12.1, 2.5 Hz, 1 H, 5'-$H_{eq.}$), 3.78 (dt, J = 4.0, 2.5 Hz, 1 H, 4'-H), 3.93 (t, J = 4.0 Hz, 1 H, 3'-H), 3.96 (dd, J = 12.1, 2.5 Hz, 1 H, 5'-$H_{ax.}$), 4.22 (dd, J = 8.7, 4.0 Hz, 1 H, 2'-H), 4.89 (d, J = 8.7 Hz, 1 H, 1'-H), 7.29–7.33 (m, 2 H, 3-H, 5-H), 7.97–8.00 (m, 2 H, 2-H, 6-H).

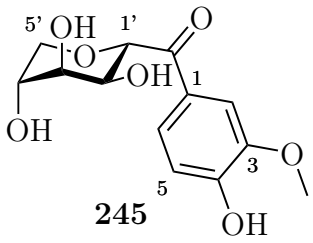
^{13}C-NMR (151 MHz, methanol-d_4): δ (ppm) = 21.7 (4-CH_3), 67.8 (C-2'), 68.3 (C-5'), 70.9 (C-4'), 71.9 (C-3'), 78.0 (C-1'), 130.2 (2 C, C-3, C-5), 130.5 (2 C, C-2, C-6), 134.9 (C-1), 145.8 (C-4), 198.9 (CO).

MS (ESI): *m/z* (%) = 119.1 (59) [(4-methylbenzylidyne)oxonium], 275.1 (65) $[M + Na]^+$.

calcd.: 275.0890 $[M + Na]^+$,
found: 275.0887 (ESI-HRMS).

$C_{13}H_{16}O_5$ (252.27).

6.20.7 (3-Methoxy-4-hydroxylphenyl)(α-D-lyxopyranosyl) ketone 245



245

To neat 1,2,3,4-tetrakis-*O*-trimethylsilyl-D-lyxopyranose **250** (811 mg, 1.85 mmol, 1.00 equiv.) was added TMSI (300 µL, 422 mg, 2.11 mmol, 1.14 equiv.) and the mixture was stirred at 0 °C for 15 min to give 2,3,4-tris-*O*-trimethylsilyl-D-lyxopyranosyl iodide **317** as orange oil, which was dissolved in glyme (10.0 mL) and cooled to 0 °C.

In a separate vessel, a solution of 2-(3-methoxy-4-hydroxyphenyl)-1,3-dithiane **299** (896 mg, 3.70 mmol, 2.00 equiv.) in glyme (10.0 mL) was cooled to 0 °C and a solution of *t*-BuLi (c = 1.75 M in *n*-pentane, 2.10 mL, 3.68 mmol, 3.98 equiv.) was added. The solution was stirred at 0 °C for 5 min and then CuI (900 µg, 4.72 µmol, 2.55 mol‰) and the precooled solution of 2,3,4-tris-*O*-trimethylsilyl-D-lyxopyranosyl iodide **317** in glyme were added. The reaction mixture was stirred at 0 °C for 3 h.

Then, the mixture was added to MeOH (70.0 mL) in a separate flask, NaOMe (200 mg, 924 µmol, 2.00 equiv.) was added and the mixture was stirred at r.t. for 10 min.

Afterwards, the mixture was diluted with water (10.0 mL), cooled to 0 °C and TFA (700 µL, 1.05 g, 9.24 mmol, 4.95 equiv.) and PIFA (1.99 g, 4.62 mmol, 2.50 equiv.) were added. The reaction mixture was stirred at 0 °C for 10 min. Then, water (10.0 mL) and L-ascorbic

acid (651 mg, 3.70 mmol, 2.00 equiv.) were added and the reaction mixture was stirred at r.t. for another 10 min.

The mixture was again diluted with water (30.0 mL) and impurities were removed by washing with *n*-pentane (3 × 50.0 mL). MeOH and glyme were removed from the aqueous phase in vacuum. The remaining concentrated aqueous phase was filtered to remove solid impurities. Without further removal of the solvent, the aqueous phase was directly purified by reversed phase column chromatography (RP-C18, H_2O + 0.1% TFA → H_2O/MeCN 4:1+ 0.1% TFA) to yield *C*-glycosidic compound **245** (176 mg, 619 µmol, 34%) as colorless, crystalline solid.

TLC: $R_f = 0.32$ (DCM/MeOH 9:1).

M.p.: 200 °C (from water).

$[\alpha]_D^{20} = 20.2$ (c = 1.00, MeOH).

UV (MeOH): $\lambda_{max} = 203, 231, 278, 307$ nm.

IR (ATR): $\tilde{\nu} = 3502, 3358, 3120, 3082, 1651, 1585, 1525, 1408, 1263, 1064, 1022, 825, 785, 515$ cm^{-1}.

^{1}H-NMR (600 MHz, D_2O): δ (ppm) = 3.75 (dd, J = 12.6, 2.9 Hz, 1 H, 5'-$H_{eq.}$), 3.92–3.95 (m, 4 H, 4'-H, OCH_3), 4.01 (dd, J = 12.6, 2.0 Hz, 1 H, 5'-$H_{ax.}$), 4.06 (t, J = 3.9 Hz, 1 H, 3'-H), 4.20 (dd, J = 8.8, 3.9 Hz, 1 H, 2'-H), 5.11 (d, J = 8.8 Hz, 1 H, 1'-H), 7.02 (d, J = 8.4 Hz, 1 H, 5-H), 7.65 (d, J = 2.1 Hz, 1 H, 2-H), 7.71 (dd, J = 8.4, 2.1 Hz, 1 H, 6-H).

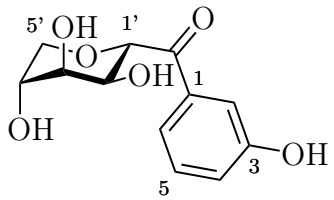
^{13}C-NMR (151 MHz, D_2O): δ (ppm) = 55.9 (OCH_3), 66.6 (C-2'), 66.7 (C-5'), 68.8 (C-4'), 69.8 (C-3'), 75.7 (C-1'), 112.2 (C-2), 115.0 (C-5), 125.3 (C-6), 128.1 (C-1), 147.4 (C-3), 151.6 (C-4), 198.4 (CO).

MS (ESI): *m/z* (%) = 151.0 (48) [(4-hydroxy-3-methoxybenzylidyne)oxonium], 285.1 (43) $[M + Na]^+$, 307.1 (100) $[M + Na]^+$.

calcd.: 307.0788$[M + Na]^+$,
found: 307.0788(ESI-HRMS).

$C_{13}H_{16}O_7$ (284.27).

6.20.8 (3-Hydroxylphenyl)(α-D-mannopyranosyl) ketone 246



246

To neat 1,2,3,4-tetrakis-*O*-trimethylsilyl-D-lyxopyranose **250** (811 mg, 1.85 mmol, 1.00 equiv.) was added TMSI (300 µL, 422 mg, 2.11 mmol, 1.14 equiv.) and the mixture was stirred at 0 °C for 15 min to give 2,3,4-tris-*O*-trimethylsilyl-D-lyxopyranosyl iodide **317** as orange oil, which was dissolved in glyme (10.0 mL) and cooled to 0 °C.

In a separate vessel, a solution of 2-(3-hydroxyphenyl)-1,3-dithiane **292** (785 mg, 3.70 mmol, 2.00 equiv.) in glyme (10.0 mL) was cooled to 0 °C and a solution of *t*-BuLi (c = 1.75 M in *n*-pentane, 2.10 mL, 3.68 mmol, 3.98 equiv.) was added. The solution was stirred at 0 °C for 5 min and then CuI (900 µg, 4.72 µmol, 2.55 mol‰) and the precooled solution of 2,3,4-tris-*O*-trimethylsilyl-D-lyxopyranosyl iodide **317** in glyme were added. The reaction mixture was stirred at 0 °C for 3 h.

Then, the mixture was added to MeOH (70.0 mL) in a separate flask, NaOMe (200 mg, 924 µmol, 2.00 equiv.) was added and the mixture was stirred at r.t. for 10 min.

Afterwards, the mixture was diluted with water (10.0 mL), cooled to 0 °C and TFA (700 µL, 1.05 g, 9.24 mmol, 4.95 equiv.) and PIFA (1.99 g, 4.62 mmol, 2.50 equiv.) were added. The reaction mixture was stirred at 0 °C for 10 min. Then, water (10.0 mL) and L-ascorbic acid (651 mg, 3.70 mmol, 2.00 equiv.) were added and the reaction mixture was stirred at r.t. for another 10 min.

The mixture was again diluted with water (30.0 mL) and impurities were removed by washing with *n*-pentane (3 × 50.0 mL). MeOH and glyme were removed from the aqueous phase in vacuum. The remaining concentrated aqueous phase was filtered to remove solid impurities. Without further removal of the solvent, the aqueous phase was directly purified by reversed phase column chromatography (RP-C18, H_2O + 0.1% TFA → H_2O/MeCN 4:1+ 0.1% TFA) to yield *C*-glycosidic compound **246** (334 mg, 1.31 mmol, 71%) as pale yellow solid.

TLC: $R_f = 0.23$ (DCM/MeOH 9:1).

$[a]_D^{20} = 17.1$ (c = 1.01, MeOH).

UV (MeOH): $\lambda_{max} = 218, 255, 316$ nm.

IR (ATR): $\tilde{\nu} = 3352, 2920, 1672, 1583, 1450, 1284, 1222, 1182, 1105, 1043, 821, 675$ cm^{-1}.

^{1}H-NMR (600 MHz, D_2O): δ (ppm) = 3.72 (dd, $J = 12.6, 2.7$ Hz, 1 H, 5'-$H_{eq.}$), 3.93 (dt, $J = 4.9, 2.7$ Hz, 1 H, 4'-H), 4.00 (dd, $J = 12.6, 2.7$ Hz, 1 H, 5'-$H_{ax.}$), 4.02 (dd, $J = 4.9, 3.3$ Hz, 1 H, 3'-H), 4.19 (dd, $J = 8.5, 3.3$ Hz, 1 H, 2'-H), 5.11 (d, $J = 8.5$ Hz, 1 H, 1'-H), 7.20 (ddd, $J = 8.0, 2.6, 1.0$ Hz, 1 H, 4-H), 7.20 (t, $J = 8.0$ Hz, 1 H, 5-H), 7.20 (dd, $J = 2.6, 1.8$ Hz, 1 H, 2-H), 7.60 (ddd, $J = 8.0, 1.8, 1.0$ Hz, 1 H, 6-H).

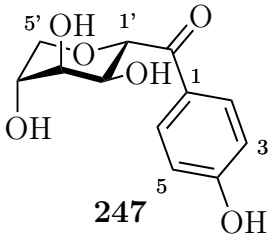
^{13}C-NMR (151 MHz, D_2O): δ (ppm) = 66.7 (2 C, C-2', C-5'), 68.7 (C-4'), 69.9 (C-3'), 76.2 (C-1'), 115.1 (C-2), 121.5 (C-6), 121.7 (C-4), 130.3 (C-5), 136.8 (C-1), 155.9 (C-3), 200.3 (CO).

MS (ESI): m/z (%) = 121.0 (60) [(3-hydroxybenzylidyne)oxonium], 277.1 (100) $[M + Na]^+$.

calcd.: 277.0683 $[M + Na]^+$,
found: 277.0686 (ESI-HRMS).

$C_{12}H_{14}O_6$ (254.24).

6.20.9 (4-Hydroxylphenyl)(α-D-mannopyranosyl) ketone 247



247

To neat 1,2,3,4-tetrakis-*O*-trimethylsilyl-D-lyxopyranose **250** (811 mg, 1.85 mmol, 1.00 equiv.) was added TMSI (300 µL, 422 mg, 2.11 mmol, 1.14 equiv.) and the mixture was stirred at 0 °C for 15 min to give 2,3,4-tris-*O*-trimethylsilyl-D-lyxopyranosyl iodide **317** as orange oil, which was dissolved in glyme (10.0 mL) and cooled to 0 °C.

In a separate vessel, a solution of 2-(4-hydroxyphenyl)-1,3-dithiane **293** (785 mg, 3.70 mmol, 2.00 equiv.) in glyme (10.0 mL) was cooled to 0 °C and a solution of *t*-BuLi (c = 1.75 M in *n*-pentane, 2.10 mL, 3.68 mmol, 3.98 equiv.) was added. The solution was

stirred at 0 °C for 5 min and then CuI (900 µg, 4.72 µmol, 2.55 mol‰) and the precooled solution of 2,3,4-tris-*O*-trimethylsilyl-D-lyxopyranosyl iodide **317** in glyme were added. The reaction mixture was stirred at 0 °C for 3 h.

Then, the mixture was added to MeOH (70.0 mL) in a separate flask, NaOMe (200 mg, 924 µmol, 2.00 equiv.) was added and the mixture was stirred at r.t. for 10 min.

Afterwards, the mixture was diluted with water (10.0 mL), cooled to 0 °C and TFA (700 µL, 1.05 g, 9.24 mmol, 4.95 equiv.) and PIFA (1.99 g, 4.62 mmol, 2.50 equiv.) were added. The reaction mixture was stirred at 0 °C for 10 min. Then, water (10.0 mL) and L-ascorbic acid (651 mg, 3.70 mmol, 2.00 equiv.) were added and the reaction mixture was stirred at r.t. for another 10 min.

The mixture was again diluted with water (30.0 mL) and impurities were removed by washing with *n*-pentane (3 × 50.0 mL). MeOH and glyme were removed from the aqueous phase in vacuum. The remaining concentrated aqueous phase was filtered to remove solid impurities. Without further removal of the solvent, the aqueous phase was directly purified by reversed phase column chromatography (RP-C18, H_2O + 0.1% TFA → H_2O/MeCN 4:1+ 0.1% TFA) to yield *C*-glycosidic compound **247** (284 mg, 1.12 mmol, 61%) as colorless solid.

TLC: $R_f = 0.21$ (DCM/MeOH 9:1).

$[a]_D^{20} = 23.6$ (c = 1.01, MeOH).

UV (MeOH): $\lambda_{max} = 221, 285$ nm.

IR (ATR): $\tilde{\nu} = 3358, 2916, 1660, 1600, 1583, 1440, 1274, 1220, 1170, 1111, 1045, 893, 839, 609, 507$ cm^{-1}.

^{1}H-NMR (600 MHz, D_2O): δ (ppm) = 3.75 (dd, J = 12.6, 2.3 Hz, 1 H, 5'-$H_{eq.}$), 3.93 (dt, J = 4.0, 2.3 Hz, 1 H, 4'-H), 4.01 (dd, J = 12.6, 2.3 Hz, 1 H, 5'-$H_{ax.}$), 4.05 (t, J = 4.0 Hz, 1 H, 3'-H), 4.18 (dd, J = 8.7, 4.0 Hz, 1 H, 2'-H), 5.11 (d, J = 8.7 Hz, 1 H, 1'-H), 6.97–7.02 (m, 2 H, 3-H, 5-H), 7.99–8.04 (m, 2 H, 2-H, 6-H).

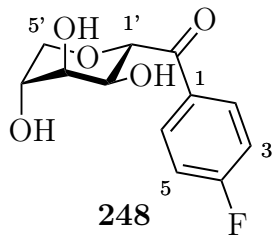
^{13}C-NMR (151 MHz, D_2O): δ (ppm) = 66.6 (C-2'), 66.6 (C-5'), 68.8 (C-4'), 69.9 (C-3'), 75.6 (C-1'), 115.5 (2 C, C-3, C-5), 127.8 (C-1), 132.2 (2 C, C-2, C-6), 161.9 (C-4), 198.6 (CO).

MS (ESI): *m/z* (%) = 121.0 (87) [(4-hydroxybenzylidyne)oxonium], 255.1 (25) $[M + H]^+$, 277.1 (100) $[M + Na]^+$.

calcd.: 277.0683 $[M + Na]^+$,
found: 277.0679 (ESI-HRMS).

$C_{12}H_{14}O_6$ (254.24).

6.20.10 (4-Fluorophenyl)(α-D-lyxopyranosyl) ketone 248



248

To neat 1,2,3,4-tetrakis-*O*-trimethylsilyl-D-lyxopyranose **250** (811 mg, 1.85 mmol, 1.00 equiv.) was added TMSI (300 µL, 422 mg, 2.11 mmol, 1.14 equiv.) and the mixture was stirred at 0 °C for 15 min to give 2,3,4-tris-*O*-trimethylsilyl-D-lyxopyranosyl iodide **317** as orange oil, which was dissolved in glyme (10.0 mL) and cooled to 0 °C.

In a separate vessel, a solution of 2-(4-fluorophenyl)-1,3-dithiane **295** (792 mg, 3.70 mmol, 2.00 equiv.) in glyme (10.0 mL) was cooled to 0 °C and a solution of *t*-BuLi (c = 1.70 M in *n*-pentane, 2.20 mL, 3.74 mmol, 2.02 equiv.) was added. The solution was stirred at 0 °C for 5 min and then CuI (900 µg, 4.72 µmol, 2.55 mol‰) and the precooled solution of 2,3,4-tris-*O*-trimethylsilyl-D-lyxopyranosyl iodide **317** in glyme were added. The reaction mixture was stirred at 0 °C for 3 h.

Then, the mixture was added to MeOH (70.0 mL) in a separate flask, NaOMe (200 mg, 924 µmol, 2.00 equiv.) was added and the mixture was stirred at r.t. for 10 min.

Afterwards, the mixture was diluted with water (10.0 mL), cooled to 0 °C and TFA (430 µL, 636 mg, 5.58 mmol, 3.04 equiv.) and PIFA (1.99 g, 4.62 mmol, 2.50 equiv.) were added. The reaction mixture was stirred at 0 °C for 10 min. Then, water (10.0 mL) and L-ascorbic acid (651 mg, 3.70 mmol, 2.00 equiv.) were added and the reaction mixture was stirred at r.t. for another 10 min.

The mixture was again diluted with water (30.0 mL) and impurities were removed by washing with *n*-pentane (3 × 50.0 mL). MeOH and glyme were removed from the aqueous phase in vacuum. The remaining concentrated aqueous phase was filtered to remove solid impurities. Without further removal of the solvent, the aqueous phase was directly

purified by reversed phase column chromatography (RP-C18, $H_2O \rightarrow H_2O$/MeCN 3:1) to yield *C*-glycosidic compound **248** (121 mg, 472 µmol, 26%) as colorless, glassy solid.

TLC: $R_f = 0.53$ (DCM/MeOH 9:1).

$[\alpha]_D^{25} = 16.1$ (c = 1.00, MeOH).

UV (MeOH): $\lambda_{max} = 202, 249$ nm.

IR (ATR): $\tilde{\nu} = 3383, 2920, 1678, 1595, 1508, 1411, 1228, 1043, 1020, 1012, 993, 891, 839, 752, 597$ cm^{-1}.

^{1}H-NMR (600 MHz, methanol-d_4): δ (ppm) = 3.66 (dd, $J = 12.1$, 2.3 Hz, 1 H, 1-$H_{ax.}$), 3.78 (dt, $J = 4.6$, 2.3 Hz, 1 H, 4'-H), 3.94 (dd, $J = 4.6$, 3.2 Hz, 1 H, 3'-H), 3.97 (dd, $J = 12.1$, 2.3 Hz, 1 H, 5'-$H_{eq.}$), 4.21 (dd, $J = 9.0$, 3.2 Hz, 1 H, 2'-H), 4.86 (d, $J = 9.0$ Hz, 1 H, 1'-H), 7.18–7.25 (m, 2 H, 3-H 5-H), 8.14–8.21 (m, 2 H, 2-H, 6-H).

^{13}C-NMR (151 MHz, Methanol-d_4): δ (ppm) = 67.6 (C-2'), 68.2 (C-5'), 70.9 (C-4'), 71.8 (C-3'), 78.3 (C-1'), 116.4 (d, $J = 22.1$ Hz, 2 C, C-3, C-5), 133.4 (d, $J = 9.5$ Hz, 2 C, C-2, C-6), 133.9 (d, $J = 2.9$ Hz, C-1), 167.4 (d, $J = 253.8$ Hz, C-4), 197.7 (CO).

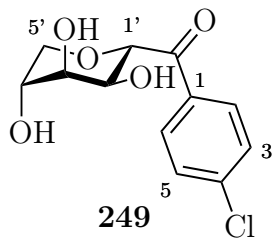
^{19}F-NMR (565 MHz, Methanol-d_4): δ (ppm) = 107.1 (m, 4-F).

MS (ESI): *m/z* (%) = 123.0 (100) [(4-fluorobenzylidyne)oxonium], 279.1 (78) $[M + Na]^+$.

calcd.: 279.0639$[M + Na]^+$,
found: 279.0636(ESI-HRMS).

$C_{12}H_{13}FO_5$ (256.23).

6.20.11 (4-Chlorophenyl)(D-lyxopyranosyl) ketones 249 and 283



249

TMSI (300 µL, 422 mg, 2.11 mmol, 1.14 equiv.) was added to neat 1,2,3,4-tetrakis-*O*-trimethylsilyl-D-lyxopyranose **250** (811 mg, 1.85 mmol, 1.00 equiv.) and the mixture was

stirred at 0 °C for 15 min to give 2,3,4-tris-*O*-trimethylsilyl-D-lyxopyranosyl iodide **317** as orange oil, which was dissolved in glyme (10.0 mL) and cooled to 0 °C.

In a separate vessel, a solution of 2-(4-chlorophenyl)-1,3-dithiane **294** (853 mg, 3.70 mmol, 2.00 equiv.) in glyme (10.0 mL) was cooled to 0 °C and a solution of *t*-BuLi (c = 1.74 M in *n*-pentane, 2.10 mL, 3.65 mmol, 1.98 equiv.) was added. The solution was stirred at 0 °C for 5 min and then CuI (900 µg, 4.72 µmol, 2.55 mol‰) and the precooled solution of 2,3,4-tris-*O*-trimethylsilyl-D-lyxopyranosyl iodide **317** in glyme were added. The reaction mixture was stirred at 0 °C for 3 h.

Then, the mixture was added to MeOH (70.0 mL) in a separate flask, NaOMe (200 mg, 924 µmol, 2.00 equiv.) was added and the mixture was stirred at r.t. for 10 min.

Afterwards, the mixture was diluted with water (10.0 mL), cooled to 0 °C and TFA (430 µL, 636 mg, 5.58 mmol, 3.04 equiv.) and PIFA (1.99 g, 4.62 mmol, 2.50 equiv.) were added. The reaction mixture was stirred at 0 °C for 10 min. Then, water (10.0 mL) and L-ascorbic acid (651 mg, 3.70 mmol, 2.00 equiv.) were added and the reaction mixture was stirred at r.t. for another 10 min.

The mixture was again diluted with water (30.0 mL) and impurities were removed by washing with *n*-pentane (3 × 50.0 mL). MeOH and glyme were removed from the aqueous phase in vacuum. The remaining concentrated aqueous phase was filtered to remove solid impurities. Without further removal of the solvent, the aqueous phase was directly purified by reversed phase column chromatography (RP-C18, $H_2O \rightarrow H_2O$/MeCN 3:1) to yield *C*-glycosidic compound **283** (48.2 mg, 177 µmol, 10%) followed by *C*-glycosidic compound **249** (119 mg, 436 µmol, 26%) as colorless solids.
For analytical data of **283** see section 8.9.

Analytical data for **249**:

TLC: $R_f = 0.47$ (DCM/MeOH 9:1).

$[\alpha]_D^{20} = 14.2$ (c = 1.00, MeOH).

UV (MeOH): $\lambda_{max} = 203, 256$ nm.

IR (ATR): $\tilde{\nu} = 3371, 2918, 1678, 1587, 1402, 1213, 1043, 1010, 889, 829, 763, 732, 478\ cm^{-1}$.

^{1}H-NMR (600 MHz, methanol-d_4): δ (ppm) = 3.66 (dd, J = 12.2, 2.2 Hz, 1 H, 5'-$H_{eq.}$), 3.78 (dt, J = 4.5, 2.2 Hz, 1 H, 4'-H), 3.94 (dd, J = 4.5, 3.1 Hz, 1 H, 3'-H), 3.97 (dd, J = 12.2, 2.2 Hz, 1 H, 5'-$H_{ax.}$), 4.21 (dd, J = 8.9, 3.1 Hz, 1 H, 2'-H), 4.85 (d, J = 8.9 Hz, 1 H, 1'-H), 7.49–7.53 (m, 2 H, 3-H, 5-H), 8.07–8.10 (m, 2 H, 2-H, 6-H).

^{13}C-NMR (151 MHz, methanol-d_4): δ (ppm) = 67.6 (C-2'), 68.3 (C-5'), 70.9 (C-4'), 71.8 (C-3'), 78.4 (C-1'), 129.8 (2 C, C-3, C-5), 132.0 (2 C, C-2, C-6), 135.8 (C-4), 140.8 (C-1), 198.1 (CO).

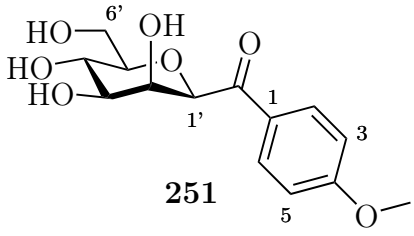
MS (ESI): m/z (%) = 139.0 (28) [(4-chlorobenzylidyne)oxonium], 295.0 (18) $[M + Na]^+$.

calcd.: 295.0344$[M + Na]^+$,
found: 295.0346(ESI-HRMS).

$C_{12}H_{13}ClO_5$ (272.68).

6.21 Syntheses of *C*-acyl β-D-mannopyranosides

6.21.1 (4-Methoxyphenyl)(β-D-mannopyranosyl) ketone 251



251

To a solution of *C*-glycosidic compound **210** (121 mg, 406 µmol, 1.00 equiv.) in MeOH (8.00 mL) was added a solution of aq. K_2CO_3 (c = 1.00 M, 8.00 mL, 8.00 mmol, 19.7 equiv.) at r.t. and the reaction mixture was stirred at the same temperature for 1 h. Then, aq. HCl (c = 3.00 M, 16.0 mL, 48.0 mmol, 118 equiv.) was added. MeOH was removed in vacuum and the aqueous residue was directly purified by reversed phase column chromatography (RP-C18, $H_2O \rightarrow H_2O$/MeCN 3:1) to yield *C*-glycosidic compound **251** (120 mg, 402 µmol, 99%) as colorless, crystalline solid.

TLC: R_f = 0.30 (DCM/MeOH 17:3).

M.p.: 165 °C (from water).

$[a]_D^{25}$ = 27.8 (c = 0.97, MeOH).

UV (MeOH): λ_{max} = 218, 275 nm.

IR (ATR): $\tilde{\nu}$ = 3475, 3361, 3253, 2968, 2939, 2908, 2887, 1664, 1602, 1573, 1259, 1101, 1064, 837, 520 cm^{-1}.

^{1}H-NMR (600 MHz, methanol-d_4): δ (ppm) = 3.37 (ddd, J = 9.4, 5.6, 2.3 Hz, 1 H, 5'-H), 3.66 (t, J = 9.4 Hz, 1 H, 4'-H), 3.71 (dd, J = 9.4, 3.2 Hz, 1 H, 3'-H), 3.78 (dd, J = 12.2, 5.6 Hz, 1 H, 6'-H_A), 3.88 (s, 3 H, OCH_3), 3.90 (dd, J = 12.2, 2.3 Hz, 1 H, 6'-H_B), 4.24 (dd, J = 3.2, 1.3 Hz, 1 H, 2'-H), 5.11 (d, J = 1.3 Hz, 1 H, 1'-H), 7.00–7.06 (m, 2 H, 3-H, 5-H), 7.98–8.04 (m, 2 H, 2-H, 6-H).

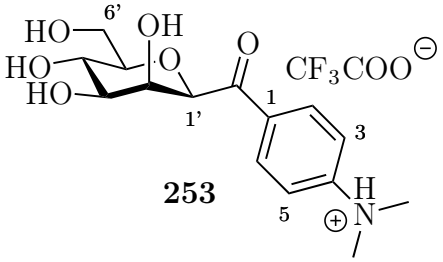
^{13}C-NMR (151 MHz, methanol-d_4): δ (ppm) = 56.1 (OCH_3), 62.9 (C-6'), 68.2 (C-4'), 72.6 (C-2'), 76.0 (C-3'), 81.8 (C-1'), 81.9 (C-5'), 114.9 (2 C, C-3, C-5), 129.1 (C-1), 132.2 (2 C, C-2, C-6), 165.6 (C-4), 197.0 (CO).

MS (ESI): m/z (%) = 135.0 (32) [(4-methoxybenzylidyne)oxonium], 299.1 (59) $[M+H]^+$ 321.1 (100) $[M+Na]^+$, 619.2 (5) $[2\,M+Na]^+$.

calcd.: 321.0945 $[M+Na]^+$,
found: 321.0943 (ESI-HRMS).

$C_{14}H_{18}O_7$ (298.29).

6.21.2 (4-Dimethylaminophenyl)(β-D-mannopyranosyl) ketone TFA salt 253



253

To a solution of *C*-glycosidic compound **217** (145 mg, 340 µmol, 1.00 equiv.) in MeOH (7.00 mL) was added a solution of aq. K_2CO_3 (c = 1.00 M, 7.00 mL, 7.00 mmol, 20.6 equiv.) at r.t. and the reaction mixture was stirred at r.t. for 1 h. Then, TFA (1.80 mL, 2.66 g, 23.4 mmol, 68.7 equiv.) was added. MeOH was removed in vacuum and the aqueous residue was directly purified by reversed phase column chromatography (RP-C18, H_2O + 0.1% TFA → H_2O/MeCN 3:1 + 0.1% TFA) to yield *C*-glycosidic compound **253** (137 mg, 322 µmol, 95%) as colorless, crystalline solid.

TLC: R_f = 0.14 (DCM/MeOH 9:1).

M.p.: 242 °C (from water).

$[a]_D^{20}$ = 40.6 (c = 0.99, H_2O/TFA 9:1).

UV (MeOH): $\lambda_{max} = 237, 352$ nm.

IR (ATR): $\tilde{\nu} = 3358, 2920, 2889, 2858, 1658, 1587, 1544, 1375, 1232, 1190, 1060, 1043, 817, 740, 617$ cm^{-1}.

^{1}H-NMR (600 MHz, DMSO-d_6): δ (ppm) = 3.01 (s, 6 H, $N(CH_3)_2$), 3.18 (ddd, $J = 9.4$, 6.6, 2.0 Hz, 1 H, 5'-H), 3.38 (t, $J = 9.4$ Hz, 1 H, 4'-H), 3.50 (dd, $J = 11.7$, 6.6 Hz, 1 H, 6'-H_A), 3.50 (dd, $J = 9.4$, 3.5 Hz, 1 H, 3'-H), 3.75 (dd, $J = 11.7$, 2.0 Hz, 1 H, 6'-H_B), 3.97 (dd, $J = 3.5$, 1.0 Hz, 1 H, 2'-H), 4.70 (d, $J = 1.0$ Hz, 1 H, 1'-H), 6.65–6.71 (m, 2 H, 3-H, 5-H), 7.86–7.92 (m, 2 H, 2-H, 6-H).

^{13}C-NMR (151 MHz, DMSO-d_6): δ (ppm) = 40.1 (2 C, $N(CH_3)_2$), 62.1 (C-6'), 67.6 (C-4'), 71.6 (C-2'), 74.9 (C-3'), 81.8 (C-5'), 82.0 (C-1'), 110.8 (2 C, C-3, C-5), 123.7 (C1), 131.5 (2 C, C-2, C-6), 153.5 (C-4), 194.3 (CO).

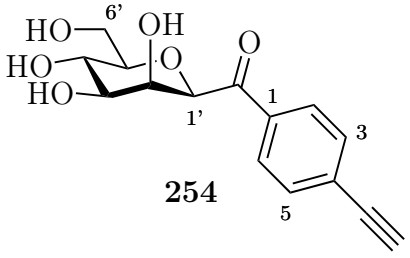
^{19}F-NMR (565 MHz, DMSO-d_6): δ (ppm) = 73.6 (m, CF_3COO^-).

MS (ESI): m/z (%) = 148.1 (5) [(4-dimethylaminobenzylidyne)oxonium], 312.1 (100) [M - CF_3COO]$^+$, 334.1 (66) [M - CF_3COOH + Na]$^+$.

calcd.: 312.1442 [M - CF_3COO^-]$^+$,
found: 312.1442 (ESI-HRMS).

$C_{17}H_{22}F_3NO_8$ (425.36).

6.21.3 (4-Ethynylphenyl)(β-D-mannopyranosyl) ketone 254



254

To a solution of *C*-glycosidic compound **216** (85.0 mg, 291 µmol, 1.00 equiv.) in MeOH (6.00 mL) was added a solution of aq. K_2CO_3 (c = 1.00 M, 6.00 mL, 6.00 mmol, 20.6 equiv.) at r.t. and the reaction mixture was stirred at r.t. for 1 h. Then, aq. HCl (c = 3.00 M, 12.0 mL, 36.0 mmol, 124 equiv.) was added. MeOH was removed in vacuum and the

aqueous residue was directly purified by reversed phase column chromatography (RP-C18, $H_2O \rightarrow H_2O$/MeCN 3:1) to yield *C*-glycosidic compound **254** (74.2 mg, 254 µmol, 87%) as pale yellow solid.

TLC: $R_f = 0.41$ (DCM/MeOH 17:3).

$[a]_D^{25} = 48.4$ (c = 1.00, MeOH).

UV (MeOH): $\lambda_{max} = 202$, 272 nm.

IR (ATR): $\tilde{\nu} = 3485$, 3387, 3277, 2939, 2854, 2110, 1683, 1600, 1448, 1224, 1107, 1070, 1001, 850, 611 cm^{-1}.

^{1}H-NMR (600 MHz, methanol-d_4): δ (ppm) = 3.38 (ddd, J = 9.4, 5.7, 2.3 Hz, 1 H, 5'-H), 3.65 (t, J = 9.4 Hz, 1 H, 4'-H), 3.69 (dd, J = 9.4, 3.2 Hz, 1 H, 3'-H), 3.77 (s, 1 H, 4-C≡CH) 3.78 (dd, J = 12.2, 5.7 Hz, 1 H, 6'-H_A), 3.91 (dd, J = 12.2, 2.3 Hz, 1 H, 6'-H_B), 4.22 (dd, J = 3.2, 1.4 Hz, 1 H, 2'-H), 5.10 (d, J = 1.4 Hz, 1 H, 1'-H), 7.53–7.66 (m, 2 H, 3-H, 5-H), 7.93–8.05 (m, 2 H, 2-H, 6-H).

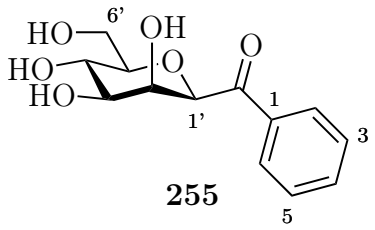
^{13}C-NMR (151 MHz, methanol-d_4): δ (ppm) = 62.9 (C-6'), 68.2 (C-4'), 72.2 (C-2'), 75.9 (C-3'), 82.1 (C-5'), 82.2 (4-C≡<u>C</u>H), 82.5 (C-1'), 83.5 (4-<u>C</u>≡CH), 128.8 (C-1), 129.9 (2 C, C-2, C-6), 133.1 (2 C, C-3, C-5), 136.3 (C-4), 198.0 (CO).

MS (ESI): m/z (%) = 129.0 (9) [(4-ethynylbenzylidyne)oxonium], 315.1 (33) $[M + Na]^+$.

calcd.: 315.0839 $[M + Na]^+$,
found: 315.0838 (ESI-HRMS).

$C_{15}H_{16}O_6$ (292.29).

6.21.4 Phenyl (β-D-mannopyranosyl) ketone 255



255

To a solution of *C*-glycosidic compound **218** (133 mg, 496 µmol, 1.00 equiv.) in MeOH (10.0 mL) was added a solution of aq. K_2CO_3 (c = 1.00 M, 10.0 mL, 10.0 mmol, 20.2 equiv.)

at r.t. and the reaction mixture was stirred at the same temperature for 1 h. Then, aq. HCl (c = 3.00 M, 20.0 mL, 60.0 mmol, 121 equiv.) was added. MeOH was removed in vacuum and the aqueous residue was directly purified by reversed phase column chromatography (RP-C18, $H_2O \rightarrow H_2O$/MeCN 4:1) to yield *C*-glycosidic compound **255** (126 mg, 470 µmol, 95%) as colorless, crystalline solid.

TLC: $R_f = 0.37$ (DCM/MeOH 17:3).

M.p.: 197 °C (from water).

$[a]_D^{25} = 41.3$ (c = 0.97, MeOH).

UV (MeOH): $\lambda_{max} = 201, 242$ nm.

IR (ATR): $\tilde{\nu} = 3352, 2954, 2924, 2864, 1689, 1595, 1338, 1219, 1070, 840, 806, 769, 725, 686, 613$ cm^{-1}.

^{1}H-NMR (600 MHz, methanol-d_4): δ (ppm) = 3.39 (ddd, $J = 9.4, 5.7, 2.3$ Hz, 1 H, 5'-H), 3.66 (t, $J = 9.4$ Hz, 1 H, 4'-H), 3.71 (dd, $J = 9.4, 3.3$ Hz, 1 H, 3'-H), 3.79 (dd, $J = 12.2, 5.7$ Hz, 1 H, 6'-H_A), 3.91 (dd, $J = 12.2, 2.3$ Hz, 1 H, 6'-H_B), 4.23 (dd, $J = 3.3, 1.3$ Hz, 1 H, 2'-H), 5.18 (d, $J = 1.3$ Hz, 1 H, 1'-H), 7.49–7.55 (m, 2 H, 3-H, 5-H), 7.61–7.65 (m, 1 H, 4-H), 7.98–8.01 (m, 2 H, 2-H, 6-H).

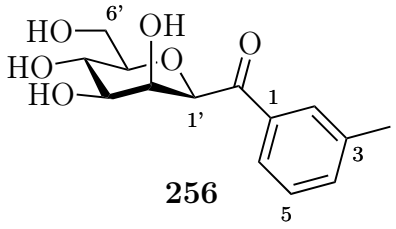
^{13}C-NMR (151 MHz, methanol-d_4): δ (ppm) = 62.9 (C-6'), 68.2 (C-4'), 72.3 (C-2'), 75.9 (C-3'), 81.9 (C-5'), 82.2 (C-1'), 129.7 (2 C, C-3, C-5), 129.8 (2 C, C-2, C-6), 134.6 (C-4), 136.5 (C-1), 198.7 (CO).

MS (ESI): *m/z* (%) = 291.1 (100) $[M + Na]^+$.

calcd.: 291.0839 $[M + Na]^+$,
found: 291.0840 (ESI-HRMS).

$C_{13}H_{16}O_6$ (268.27).

6.21.5 (3-Methylphenyl)(β-D-mannopyranosyl) ketone 256



256

To a solution of *C*-glycosidic compound **219** (77.3 mg, 274 µmol, 1.00 equiv.) in MeOH (5.50 mL) was added a solution of aq. K_2CO_3 (c = 1.00 M, 5.50 mL, 5.50 mmol, 20.1 equiv.) at r.t. and the reaction mixture was stirred at the same temperature for 1 h. Then, aq. HCl (c = 3.00 M, 11.0 mL, 33.0 mmol, 121 equiv.) was added. MeOH was removed in vacuum and the aqueous residue was directly purified by reversed phase column chromatography (RP-C18, $H_2O \rightarrow H_2O$/MeCN 3:1) to yield *C*-glycosidic compound **256** (74.0 mg, 262 µmol, 96%) as colorless, glassy solid.

TLC: $R_f = 0.45$ (DCM/MeOH 17:3).

$[\alpha]_D^{25} = 39.6$ (c = 1.00, MeOH).

UV (MeOH): $\lambda_{max} = 204, 248$ nm.

IR (ATR): $\tilde{\nu} = 3385, 2920, 2873, 1687, 1602, 1585, 1423, 1265, 1101, 1060, 1039, 866, 819, 777, 688$ cm^{-1}.

^{1}H-NMR (600 MHz, methanol-d_4): δ (ppm) = 2.42 (s, 3 H, 3-CH_3), 3.39 (ddd, J = 9.5, 5.6, 2.3 Hz, 1 H, 5'-H), 3.65 (t, J = 9.5 Hz, 1 H, 4'-H), 3.71 (dd, J = 9.5, 3.3 Hz, 1 H, 3'-H), 3.78 (dd, J = 12.2, 5.6 Hz, 1 H, 6'-H_A), 3.91 (dd, J = 12.2, 2.3 Hz, 1 H, 6'-H_B), 4.22 (dd, J = 3.3, 1.5 Hz, 1 H, 2'-H), 5.18 (d, J = 1.5 Hz, 1 H, 1'-H), 7.40 (t, J = 7.6 Hz, 1 H, 5-H), 7.46 (d, J = 7.6 Hz, 1 H, 4-H), 7.78 (d, J = 7.6 Hz, 1 H, 6-H), 7.81 (s, 1 H, 2-H).

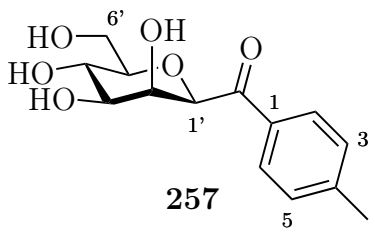
^{13}C-NMR (151 MHz, Methanol-d_4): δ (ppm) = 21.3 (3-$\underline{C}H_3$), 62.9 (C-6'), 68.2 (C-4'), 72.4 (C-2'), 75.9 (C-3'), 81.9 (C-5'), 82.1 (C-1'), 126.9 (C-6), 129.6 (C-5), 130.1 (C-2), 135.3 (C-4), 136.5 (C-1), 139.9 (C-3), 198.8 (CO).

MS (ESI): m/z (%) = 119.1 (16) [(3-methylbenzylidyne)oxonium], 283.1 (25) $[M + H]^+$, 305.1 (100) $[M + Na]^+$, 587.2 (5) $[2\ M + Na]^+$.

calcd.: 305.0996 $[M + Na]^+$,
found: 305.0994 (ESI-HRMS).

$C_{14}H_{18}O_6$ (282.29).

6.21.6 (4-Methylphenyl)(β-D-mannopyranosyl) ketone 257



257

To a solution of *C*-glycosidic compound **220** (45.1 mg, 160 µmol, 1.00 equiv.) in MeOH (3.20 mL) was added a solution of aq. K_2CO_3 (c = 1.00 M, 3.20 mL, 3.20 mmol, 20.0 equiv.) at r.t. and the reaction mixture was stirred at r.t. for 1 h. Then, aq. HCl (c = 3.00 M, 6.40 mL, 19.2 mmol, 120 equiv.) was added. MeOH was removed in vacuum and the aqueous residue was directly purified by reversed phase column chromatography (RP-C18, $H_2O \rightarrow H_2O$/MeCN 3:1) to yield *C*-glycosidic compound **257** (44.0 mg, 156 µmol, 98%) as colorless, crystalline solid.

TLC: $R_f = 0.37$ (DCM/MeOH 17:3).

M.p.: 196 °C (from water).

$[a]_D^{25} = 40.5$ (c = 1.03, MeOH).

UV (MeOH): $\lambda_{max} = 202$, 254 nm.

IR (ATR): $\tilde{\nu} = 3375$, 2947, 2862, 2845, 1683, 1602, 1460, 1292, 1207, 1093, 1060, 1006, 825, 738, 605 cm^{-1}.

^{1}H-NMR (600 MHz, methanol-d_4): δ (ppm) = 2.42 (s, 3 H, 4-CH_3), 3.38 (ddd, J = 9.4, 5.6, 2.3 Hz, 1 H, 5'-H), 3.66 (t, J = 9.4 Hz, 1 H, 4'-H), 3.71 (dd, J = 9.4, 3.3 Hz, 1 H, 3'-H), 3.79 (dd, J = 12.2, 5.6 Hz, 1 H, 6'-H_A), 3.90 (dd, J = 12.2, 2.3 Hz, 1 H, 6'-H_B), 4.23 (dd, J = 3.3, 1.4 Hz, 1 H, 2'-H), 5.15 (d, J = 1.4 Hz, 1 H, 1'-H), 7.25–7.38 (m, 2 H, 3-H, 5-H), 7.82–7.95 (m, 2 H, 2-H, 6-H).

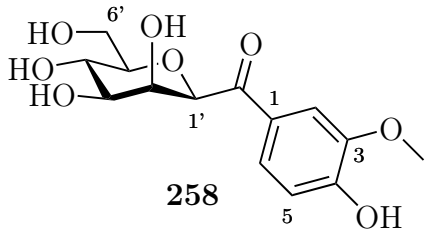
^{13}C-NMR (151 MHz, methanol-d_4): δ (ppm) = 21.7 (4-$\underline{C}H_3$), 62.8 (C-6'), 68.2 (C-4'), 72.4 (C-2'), 75.9 (C-3'), 81.9 (C-5'), 82.0 (C-1'), 129.9 (2 C, C-2, C-6), 130.4 (2 C, C-3, C-5), 133.8 (C-1), 145.9 (C-4), 198.2 (CO).

MS (ESI): m/z (%) = 119.1 (36) [(4-methylbenzylidyne)oxonium], 305.1 (95) $[M + Na]^+$.

calcd.: 305.0996 $[M + Na]^+$,
found: 305.0984 (ESI-HRMS).

$C_{14}H_{18}O_6$ (282.29).

6.21.7 (3-Methoxy-4-hydroxylphenyl)(β-D-mannopyranosyl) ketone 258



258

A solution of *C*-glycosidic compound **221** (121 mg, 385 µmol, 1.00 equiv.) in aq. KOH (c = 100 mM, 15.0 mL, 1.50 mmol, 3.90 equiv.) was stirred at r.t. for 24 h. Then, aq. HCl (c = 1.00 M, 4.00 mL, 4.00 mmol, 10.4 equiv.) was added. The aqueous mixture was purified by reversed phase column chromatography (RP-C18, H_2O + 0.1% TFA → H_2O/MeCN 4:1+ 0.1% TFA) to yield *C*-glycosidic compound **258** (120 mg, 381 µmol, 99%) as colorless, crystalline solid.

TLC: $R_f = 0.20$ (DCM/MeOH 17:3).

$[\alpha]_D^{25} = 19.7$ (c = 0.98, MeOH).

UV (MeOH): $\lambda_{max} = 202, 229, 279, 304$ nm.

IR (ATR): $\tilde{\nu} = 3365, 2931, 2883, 2668, 1589, 1517, 1427, 1377, 1278, 1199, 1101, 1029, 883, 765, 632\ cm^{-1}$.

^{1}H-NMR (600 MHz, D_2O): δ (ppm) = 3.53 (ddd, $J = 9.7, 6.2, 2.2$ Hz, 1 H, 5'-H), 3.66 (t, $J = 9.7$ Hz, 1 H, 4'-H), 3.82 (dd, $J = 12.5, 6.2$ Hz, 1 H, 6'-H_A), 3.88 (dd, $J = 9.7, 3.5$ Hz, 1 H, 3'-H), 3.92 (s, 3 H, OCH_3), 3.97 (dd, $J = 12.5, 2.2$ Hz, 1 H, 6'-H_B), 4.34 (dd, $J = 3.5, 1.3$ Hz, 1 H, 2'-H), 5.31 (d, $J = 1.3$ Hz, 1 H, 1'-H), 6.99 (d, $J = 8.4$ Hz, 1 H, 5-H), 7.52 (d, $J = 2.1$ Hz, 1 H, 2-H), 7.56 (dd, $J = 8.4, 2.1$ Hz, 1 H, 6-H).

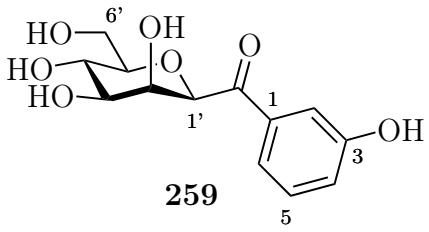
^{13}C-NMR (151 MHz, D_2O): δ (ppm) = 55.9 (OCH_3), 61.1 (C-6'), 66.6 (C-4'), 71.0 (C-2'), 73.7 (C-3'), 79.6 (C-5'), 79.9 (C-1'), 111.8 (C-2), 115.0 (C-5), 124.0 (C-6), 126.6 (C-1), 147.6 (C-3), 151.2 (C-4), 197.0 (CO).

MS (ESI): *m/z* (%) = 151.0 (18) [(4-hydroxy-3-methoxybenzylidyne)oxonium], 315.1 (52) $[M + H]^+$, 337.1 (100) $[M + Na]^+$, 651.2 (4) $[2\ M + Na]^+$.

calcd.: 337.0894 $[M + Na]^+$,
found: 337.0899 (ESI-HRMS).

$C_{14}H_{18}O_8$ (314.29).

6.21.8 (3-Hydroxylphenyl)(β-D-mannopyranosyl) ketone 259



259

To a solution of *C*-glycosidic compound **222** (100 mg, 353 µmol, 1.00 equiv.) in MeOH (7.00 mL) was added a solution of aq. K_2CO_3 (c = 1.00 M, 7.00 mL, 7.00 mmol, 19.9 equiv.) at r.t. and the reaction mixture was stirred at r.t. for 1 h. Then, aq. HCl (c = 3.00 M, 14.0 mL, 42.0 mmol, 119 equiv.) was added. MeOH was removed in vacuum and the aqueous residue was directly purified by reversed phase column chromatography (RP-C18, H_2O + 0.1% TFA → H_2O/MeCN 4:1+ 0.1% TFA) to yield *C*-glycosidic compound **259** (99.3 mg, 349 µmol, 99%) as colorless, glassy solid.

TLC: R_f = 0.20 (DCM/MeOH 17:3).

$[a]_D^{25}$ = 28.4 (c = 1.03, MeOH).

UV (MeOH): λ_{max} = 217, 251, 309 nm.

IR (ATR): $\tilde{\nu}$ = 3334, 2924, 2891, 2856, 1681, 1585, 1450, 1282, 1190, 1099, 1060, 885, 786, 684, 524 cm^{-1}.

^{1}H-NMR (600 MHz, D_2O): δ (ppm) = 3.54 (ddd, J = 9.7, 6.2, 2.2 Hz, 1 H, 5'-H), 3.65 (t, J = 9.7 Hz, 1 H, 4'-H), 3.82 (dd, J = 12.5, 6.2 Hz, 1 H, 6-H_A), 3.88 (dd, J = 9.7, 3.5 Hz, 1 H, 3'-H), 3.98 (dd, J = 12.5, 2.2 Hz, 1 H, 6'-H_B), 4.32 (dd, J = 3.5, 1.3 Hz, 1 H, 2'-H), 5.34 (d, J = 1.3 Hz, 1 H, 1'-H), 7.21 (ddd, J = 7.9, 2.6, 1.4 Hz, 1 H, 4-H), 7.36 (dd, J = 2.6, 1.4 Hz, 1 H, 2-H), 7.46 (t, J = 7.9 Hz, 1 H, 5-H), 7.49 (dt, J = 7.9, 1.4 Hz, 1 H, 6-H).

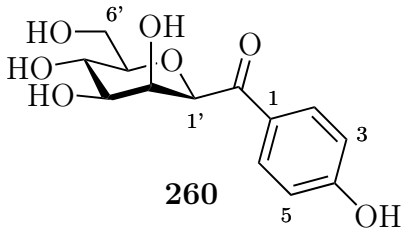
^{13}C-NMR (151 MHz, D_2O): δ (ppm) = 61.1 (C-6'), 66.6 (C-4'), 70.5 (C-2'), 73.6 (C-3'), 79.6 (C-5'), 80.4 (C-1'), 114.6 (C-2), 120.6 (C-6), 121.4 (C-4), 130.4 (C-5), 135.6 (C-1), 156.0 (C-3), 198.9 (CO).

MS (ESI): m/z (%) = 121.0 (10) [(3-hydroxybenzylidyne)oxonium], 307.1 (88) $[M + Na]^+$.

calcd.: 307.0788$[M + Na]^+$,
found: 307.0788(ESI-HRMS).

$C_{13}H_{16}O_7$ (284.26).

6.21.9 (4-Hydroxylphenyl)(β-D-mannopyranosyl) ketone 260



260

A solution of *C*-glycosidic compound **223** (70.2 mg, 247 µmol, 1.00 equiv.) in aq. KOH (c = 100 mM, 10.0 mL, 1.00 mmol, 4.05 equiv.) was stirred at r.t. for 24 h. Then, aq. HCl (c = 1.00 M, 2.50 mL, 2.50 mmol, 10.1 equiv.) was added. The aqueous mixture was purified by reversed phase column chromatography (RP-C18, H_2O + 0.1% TFA → H_2O/MeCN 4:1+ 0.1% TFA) to yield *C*-glycosidic compound **260** (70.0 mg, 246 µmol, quant.) as colorless, crystalline solid.

TLC: $R_f = 0.15$ (DCM/MeOH 17:3).

M.p.: 221 °C (from water).

$[\alpha]_D^{25} = 42.2$ (c = 0.96, MeOH).

UV (MeOH): $\lambda_{max} = 219, 281$ nm.

IR (ATR): $\tilde{\nu} = 3356, 2918, 2887, 2858, 1672, 1602, 1544, 1438, 1344, 1282, 1101, 1068, 815, 615, 524$ cm^{-1}.

^{1}H-NMR (600 MHz, D_2O): δ (ppm) = 3.53 (ddd, J = 9.7, 6.2, 2.2 Hz, 1 H, 5'-H), 3.66 (t, J = 9.7 Hz, 1 H, 4'-H), 3.82 (dd, J = 12.5, 6.2 Hz, 1 H, 6'-H_A), 3.88 (dd, J = 9.7, 3.6 Hz, 1 H, 3'-H), 3.97 (dd, J = 12.5, 2.2 Hz, 1 H, 6'-H_B), 4.33 (dd, J = 3.6, 1.3 Hz, 1 H, 2'-H), 5.33 (d, J = 1.3 Hz, 1 H, 1'-H), 6.94–7.07 (m, 2 H, 3-H, 5-H), 7.84–7.99 (m, 2 H, 2-H, 6-H).

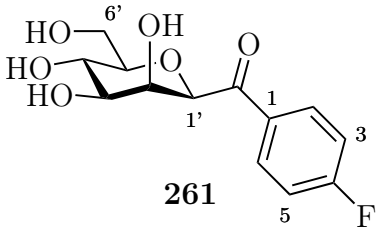
^{13}C-NMR (151 MHz, D_2O): δ (ppm) = 61.1 (C-6'), 66.6 (C-4'), 70.8 (C-2'), 73.7 (C-3'), 79.6 (C-5'), 79.9 (C-1'), 115.7 (2 C, C-3, C-5), 126.2 (C-1), 131.3 (2 C, C-2, C-6), 161.6 (C-4), 197.2 (CO).

MS (ESI): m/z (%) = 121.0 (18) [(4-hydroxybenzylidyne)oxonium], 307.1 (82) $[M + Na]^+$.

calcd.: 307.0788 $[M + Na]^+$,
found: 307.0790 (ESI-HRMS).

$C_{13}H_{16}O_7$ (284.26).

6.21.10 (4-Fluorophenyl)(β-D-mannopyranosyl) ketone 261



261

To a solution of *C*-glycosidic compound **224** (65.5 mg, 229 µmol, 1.00 equiv.) in MeOH (5.00 mL) was added a solution of aq. K_2CO_3 (c = 1.00 M, 5.00 mL, 5.00 mmol, 20.5 equiv.) at r.t. and the reaction mixture was stirred at r.t. for 1 h. Then, aq. HCl (c = 3.00 M, 10.0 mL, 30.0 mmol, 131 equiv.) was added. MeOH was removed in vacuum and the aqueous residue was directly purified by reversed phase column chromatography (RP-C18, H_2O → H_2O/MeCN 3:1) to yield *C*-glycosidic compound **261** (64.1 mg, 224 µmol, 98%) as colorless, crystalline solid.

TLC: R_f = 0.42 (DCM/MeOH 9:1).

M.p.: 132 °C (from water).

$[\alpha]_D^{25}$ = 32.0 (c = 1.00, MeOH).

UV (MeOH): λ_{max} = 204, 245 nm.

IR (ATR): $\tilde{\nu}$ = 3369, 2943, 1676, 1597, 1512, 1415, 1388, 1336, 1228, 1099, 1064, 1002, 844, 788, 607 cm^{-1}.

^{1}H-NMR (600 MHz, methanol-d_4): δ (ppm) = 3.38 (ddd, J = 9.3, 5.7, 2.3 Hz, 1 H, 5'-H), 3.65 (t, J = 9.3 Hz, 1 H, 4'-H), 3.69 (dd, J = 9.3, 3.2 Hz, 1 H, 3'-H), 3.77 (dd, J = 12.2, 5.7 Hz, 1 H, 6'-H_A), 3.90 (dd, J = 12.2, 2.3 Hz, 1 H, 6'-H_B), 4.22 (dd, J = 3.2, 1.4 Hz, 1 H, 2'-H), 5.08 (d, J = 1.4 Hz, 1 H, 1'-H), 7.15–7.30 (m, 2 H, 3-H, 5-H), 8.00–8.14 (m, 2 H, 2-H, 6-H).

^{13}C-NMR (151 MHz, methanol-d_4): δ (ppm) = 61.5 (C-6'), 66.8 (C-4'), 70.9 (C-2'), 74.5 (C-3'), 80.6 (C-5'), 81.0 (C-1'), 115.2 (d, J = 22.1 Hz, 2 C, C-3, C-5), 131.5 (d, J = 9.4 Hz, 2 C, C-2, C-6), 131.7 (d, J = 2.8 Hz, C-1), 165.9 (d, J = 253.7 Hz, C-4), 195.9 (CO).

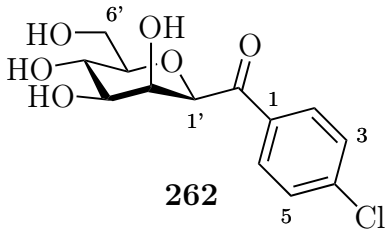
^{19}F-NMR (565 MHz, Methanol-d_4): δ (ppm) = 107.0 (m, 4-F).

MS (ESI): m/z (%) = 123.0 (24) [(4-fluorobenzylidyne)oxonium], 309.1 (100) $[M + Na]^+$.

calcd.: 309.0745 $[M + Na]^+$,
found: 309.0749 (ESI-HRMS).

$C_{13}H_{15}FO_6$ (286.26).

6.21.11 (4-Chlorophenyl)(β-D-mannopyranosyl) ketone 262



262

To a solution of *C*-glycosidic compound **225** (133 mg, 439 µmol, 1.00 equiv.) in MeOH (9.00 mL) was added a solution of aq. K_2CO_3 (c = 1.00 M, 9.00 mL, 9.00 mmol, 20.5 equiv.) at r.t. and the reaction mixture was stirred at r.t. for 1 h. Then, aq. HCl (c = 3.00 M, 18.0 mL, 54.0 mmol, 123 equiv.) was added. MeOH was removed in vacuum and the aqueous residue was directly purified by reversed phase column chromatography (RP-C18, H_2O → H_2O/MeCN 3:1) to yield *C*-glycosidic compound **262** (121 mg, 400 µmol, 91%) as pale yellow, crystalline solid.

TLC: R_f = 0.38 (DCM/MeOH 17:3).

M.p.: 197 °C (from water).

$[a]_D^{25}$ = 41.0 (c = 1.00, MeOH).

UV (MeOH): λ_{max} = 201, 254 nm.

IR (ATR): $\tilde{\nu}$ = 3520, 3425, 3379, 3209, 2941, 2912, 2879, 1678, 1589, 1406, 1259, 1091, 1002, 827, 601 cm^{-1}.

^{1}H-NMR (600 MHz, methanol-d_4): δ (ppm) = 3.38 (ddd, J = 9.3, 5.8, 2.3 Hz, 1 H, 5'-H), 3.65 (t, J = 9.3 Hz, 1 H, 4'-H), 3.69 (dd, J = 9.3, 3.2 Hz, 1 H, 3'-H), 3.77 (dd, J = 12.2, 5.8 Hz, 1 H, 6'-H_A), 3.91 (dd, J = 12.2, 2.3 Hz, 1 H, 6'-H_B), 4.22 (dd, J = 3.2, 1.4 Hz, 1 H, 2'-H), 5.06 (d, J = 1.4 Hz, 1 H, 1'-H), 7.48–7.57 (m, 2 H, 3-H, 5-H), 7.97–8.04 (m, 2 H, 2-H, 6-H).

^{13}C-NMR (151 MHz, methanol-d_4): δ (ppm) = 62.9 (C-6'), 68.2 (C-4'), 72.2 (C-2'), 75.9 (C-3'), 82.1 (C-5'), 82.6 (C-1'), 129.9 (2 C, C-3, C-5), 131.7 (2 C, C-2, C-6), 135.2 (C-4), 140.7 (C-1), 197.7 (CO).

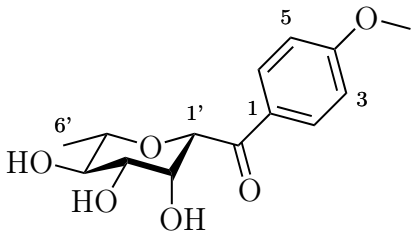
MS (ESI): *m/z* (%) = 139.0 (26) [(4-chlorobenzylidyne)oxonium], 303.1 (30) $[M + Na]^+$, 325.0 (100) $[M + Na]^+$.

calcd.: 325.0449 $[M + Na]^+$,
found: 325.0449 (ESI-HRMS).

$C_{13}H_{15}ClO_6$ (302.71).

6.22 Syntheses of *C*-acyl β-L-rhamnopyranosides

6.22.1 (4-Methoxyphenyl)(β-L-rhamnopyranosyl) ketone 263



263

To a solution of *C*-glycosidic compound **227** (104 mg, 368 µmol, 1.00 equiv.) in MeOH (7.50 mL) was added a solution of aq. K_2CO_3 (c = 1.00 M, 7.50 mL, 7.50 mmol, 20.4 equiv.) at r.t. and the reaction mixture was stirred at r.t. for 1 h. Then, aq. HCl (c = 3.00 M, 15.0 mL, 45.0 mmol, 122 equiv.) was added. MeOH was removed in vacuum and the aqueous residue was directly purified by reversed phase column chromatography (RP-C18, H_2O → H_2O/MeCN 3:1) to yield *C*-glycosidic compound **263** (100 mg, 354 µmol, 96%) as pale yellow, crystalline solid.

TLC: R_f = 0.35 (DCM/MeOH 9:1).

M.p.: 168 °C (from water).

$[a]_D^{20}$ = -26.0 (c = 1.01, MeOH).

UV (MeOH): λ_{max} = 217, 274 nm.

IR (ATR): $\tilde{\nu} = 3435$, 3061, 3007, 2974, 2935, 2854, 2841, 1670, 1598, 1510, 1255, 1087, 819, 621, 470 cm^{-1}.

^{1}H-NMR (600 MHz, D_2O): δ (ppm) = 1.38 (d, $J = 6.1$ Hz, 3 H, 6'-H_3), 3.45 (t, $J = 9.5$ Hz, 1 H, 4'-H), 3.56 (dq, $J = 9.5$, 6.1 Hz, 1 H, 5'-H), 3.83 (dd, $J = 9.5$, 3.5 Hz, 1 H, 3'-H), 3.92 (s, 3 H, OCH_3), 4.32 (dd, $J = 3.5$, 1.1 Hz, 1 H, 2'-H), 5.28 (d, $J = 1.1$ Hz, 1 H, 1'-H), 7.07–7.13 (m, 2 H, 3-H, 5-H), 7.92–7.98 (m, 2 H, 2-H, 6-H).

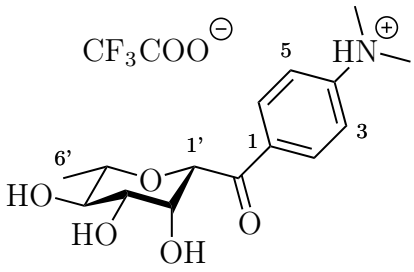
^{13}C-NMR (151 MHz, D_2O): δ (ppm) = 16.9 (C-6'), 55.6 (OCH_3), 70.8 (C-2'), 71.9 (C-4'), 73.4 (C-3'), 75.8 (C-5'), 80.0 (C-1'), 114.2 (2 C, C-3, C-5), 126.9 (C-1), 131.0 (2 C, C-2, C-6), 163.9 (C-4), 197.1 (CO).

MS (ESI): m/z (%) = 135.0 (30) [(4-methoxybenzylidyne)oxonium], 283.1 (17) $[M + H]^+$ 305.1 (100) $[M + Na]^+$.

calcd.: 305.0996 $[M + Na]^+$,
found: 305.0994 (ESI-HRMS).

$C_{14}H_{18}O_6$ (282.29).

6.22.2 (4-Dimethylaminophenyl)(β-L-rhamnopyranosyl) ketone TFA salt 264



264

To a solution of *C*-glycosidic compound **228** (71.2 mg, 174 µmol, 1.00 equiv.) in MeOH (3.50 mL) was added a solution of aq. K_2CO_3 (c = 1.00 M, 3.50 mL, 3.50 mmol, 20.0 equiv.) at r.t. and the reaction mixture was stirred at r.t. for 1 h. Then, TFA (1.70 mL, 1.33 g, 11.7 mmol, 67.2 equiv.) was added. MeOH was removed in vacuum and the aqueous residue directly purified by reversed phase column chromatography (RP-C18, H_2O + 0.1% TFA → H_2O/MeCN 3:1 + 0.1% TFA) to yield *C*-glycosidic compound **264** (65.0 mg, 159 µmol, 91%) as beige solid.

TLC: $R_f = 0.33$ (DCM/MeOH 9:1).

$[\alpha]_D^{20}$ = -28.9 (c = 0.98, H_2O/TFA 9:1).

UV (MeOH): λ_{max} = 237, 350 nm.

IR (ATR): $\tilde{\nu}$ = 3498, 3419, 2997, 2974, 2906, 2858, 1680, 1589, 1544, 1377, 1186, 1149, 1124, 1082 cm^{-1}.

^{1}H-NMR (600 MHz, DMSO-d_6): δ (ppm) = 1.22 (d, J = 5.5 Hz, 3 H, 6'-H_3), 3.00 (s, 6 H, $N(CH_3)_2$), 3.20–3.26 (m, 2 H, 4'-H, 5'-H), 3.46 (dd, J = 8.9, 3.3 Hz, 1 H, 3'-H), 3.98 (dd, J = 3.3, 1.3 Hz, 1 H, 2'-H), 4.70 (d, J = 1.3 Hz, 1 H, 1'-H), 6.66–6.71 (m, 2 H, 3-H, 5-H), 7.83–7.87 (m, 2 H, 2-H, 6-H).

^{13}C-NMR (151 MHz, DMSO-d_6): δ (ppm) = 18.2 (C-6'), 39.6 (2 C, $N(CH_3)_2$), 71.3 (C-2'), 71.9 (C-4'), 74.2 (C-3'), 75.7 (C-5'), 81.5 (C-1'), 110.4 (2 C, C-3, C-5), 123.2 (C-1), 130.9 (2 C, C-2, C-6), 153.0 (C-4), 193.9 (CO).

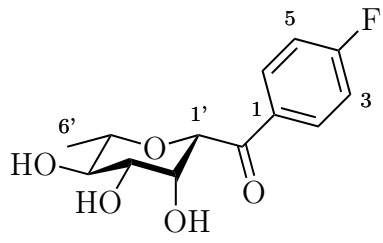
^{19}F-NMR (565 MHz, DMSO-d_6): δ (ppm) = 74.8 (m, CF_3COO^-).

MS (ESI): m/z (%) = 148.1 (4) [(4-dimethylaminobenzylidyne)oxonium], 296.2 (100) [M - CF_3COO]$^+$, 318.1 (30) [M - CF_3COOH + Na]$^+$, 613.3 (30) [2 M – 2 CF_3COOH + Na]$^+$.

calcd.: 296.1492 [M - CF_3COO^-]$^+$,
found: 296.1493 (ESI-HRMS).

$C_{17}H_{22}F_3NO_7$ (409.36).

6.22.3 (4-Fluorophenyl)(β-D-rhamnopyranosyl) ketone 265



265

To a solution of *C*-glycosidic compound **236** (40.0 mg, 148 µmol, 1.00 equiv.) in MeOH (3.00 mL) was added a solution of aq. K_2CO_3 (c = 1.00 M, 3.00 mL, 3.00 mmol, 20.3 equiv.) at r.t. and the reaction mixture was stirred at r.t. for 1 h. Then, aq. HCl (c = 3.00 M,

6.00 mL, 18.0 mmol, 122 equiv.) was added. MeOH was removed in vacuum and the aqueous residue directly purified by reversed phase column chromatography (RP-C18, $H_2O \rightarrow H_2O$/MeCN 7:3) to yield *C*-glycosidic compound **265** (38.6 mg, 143 µmol, 97%) as colorless solid.

TLC: $R_f = 0.60$ (DCM/MeOH 9:1).

M.p.: 183 °C (from water).

$[\alpha]_D^{25} = -30.8$ (c = 1.00, MeOH).

UV (MeOH): $\lambda_{max} = 202, 246$ nm.

IR (ATR): $\tilde{\nu} = 3377, 2943, 1674, 1597, 1504, 1411, 1228, 1089, 1068, 964, 837, 773, 609$ cm^{-1}.

^{1}H-NMR (600 MHz, methanol-d_4): δ (ppm) = 1.37 (d, J = 5.7 Hz, 3 H, 6'-H_3), 3.38–3.44 (m, 2 H, 4'-H, 5'-H), 3.59–3.64 (m, 1 H, 3'-H), 4.23 (dd, J = 3.5, 1.4 Hz, 1 H, 2'-H), 4.91 (d, J = 1.4 Hz, 1 H, 1'-H), 7.19–7.23 (m, 2 H, 3-H, 5-H), 8.07–8.11 (m, 2 H, 2-H, 6-H).

^{13}C-NMR (151 MHz, Methanol-d_4): δ (ppm) = 18.2 (C-6'), 72.3 (C-2'), 73.8 (C-4'), 75.8 (C-3'), 77.7 (C-5'), 83.0 (C-1'), 116.4 (d, J = 22.1 Hz, 2 C, C-3, C-5), 133.1 (d, J = 9.3 Hz, 2 C, C-2, C-6), 133.6 (d, J = 3.1 Hz, 1-H), 167.1 (d, J = 253.3 Hz, C-4), 197.3 (CO).

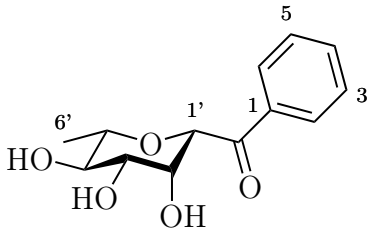
^{19}F-NMR (565 MHz, Methanol-d_4): δ (ppm) = 107.6 (m, 4-F).

MS (ESI): m/z (%) = 123.0 (100) [(4-fluorobenzylidyne)oxonium], 293.1 (84) $[M + Na]^+$.

calcd.: 293.0796 $[M + Na]^+$,
found: 293.0797 (ESI-HRMS).

$C_{13}H_{15}FO_5$ (270.26).

6.22.4 Phenyl (β-L-rhamnopyranosyl) ketone 266



266

To a solution of *C*-glycosidic compound **230** (76.5 mg, 303 µmol, 1.00 equiv.) in MeOH (6.00 mL) was added a solution of aq. K_2CO_3 (c = 1.00 M, 6.00 mL, 6.00 mmol, 19.8 equiv.) at r.t. and the reaction mixture was stirred at r.t. for 1 h. Then, aq. HCl (c = 3.00 M, 12.0 mL, 36.0 mmol, 119 equiv.) was added. MeOH was removed in vacuum and the aqueous residue was directly purified by reversed phase column chromatography (RP-C18, $H_2O \rightarrow H_2O$/MeCN 3:1) to yield *C*-glycosidic compound **266** (69.2 mg, 274 µmol, 91%) as colorless solid.

TLC: $R_f = 0.39$ (DCM/MeOH 9:1).

$[\alpha]_D^{20} = -24.2$ (c = 0.99, MeOH).

UV (MeOH): $\lambda_{max} = 241$ nm.

IR (ATR): $\tilde{\nu} = 3398, 3068, 2978, 2933, 1689, 1597, 1579, 1448, 1222, 1151, 1076, 972, 688, 609$ cm^{-1}.

^{1}H-NMR (600 MHz, methanol-d_4): δ (ppm) = 1.38 (d, J = 5.6 Hz, 3 H, 6'-H_3), 3.37–3.46 (m, 2 H, 4'-H, 5'-H), 3.60–3.67 (m, 1 H, 3'-H), 4.24 (dd, J = 3.5, 1.4 Hz, 1 H, 2'-H), 5.02 (d, J = 1.4 Hz, 1 H, 1'-H), 7.47–7.51 (m, 2 H, 3-H, 5-H), 7.58–7.62 (m, 1 H, 4-H), 7.96–8.01 (m, 2 H, 2-H, 6-H).

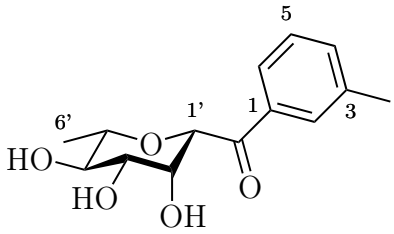
^{13}C-NMR (151 MHz, methanol-d_4): δ (ppm) = 18.1 (C-6'), 72.3 (C-2'), 73.8 (C-4'), 75.8 (C-3'), 77.7 (C-5'), 82.6 (C-1'), 129.5 (2 C, C-3, C-5), 129.9 (2 C, C-2, C-6), 134.3 (C-4), 136.9 (C-1), 198.5 (CO).

MS (ESI): m/z (%) = (100) $[M + Na]^+$.

calcd.: 275.0890 $[M + Na]^+$,
found: 275.0886 (ESI-HRMS).

$C_{13}H_{16}O_5$ (252.27).

6.22.5 (3-Methylphenyl)(β-L-rhamnopyranosyl) ketone 267



267

To a solution of *C*-glycosidic compound **231** (106 mg, 398 µmol, 1.00 equiv.) in MeOH (8.00 mL) was added a solution of aq. K_2CO_3 (c = 1.00 M, 8.00 mL, 8.00 mmol, 20.1 equiv.) at r.t. and the reaction mixture was stirred at r.t. for 1 h. Then, aq. HCl (c = 3.00 M, 16.0 mL, 48.0 mmol, 121 equiv.) was added. MeOH was removed in vacuum and the aqueous residue directly purified by reversed phase column chromatography (RP-C18, $H_2O \rightarrow H_2O$/MeCN 7:3) to yield *C*-glycosidic compound **267** (94.7 mg, 356 µmol, 89%) as colorless solid.

TLC: $R_f = 0.41$ (DCM/MeOH 9:1).

$[a]_D^{25} =$ -26,4 (c = 1.02, MeOH).

UV (MeOH): $\lambda_{max} = 204, 246, 286$ nm.

IR (ATR): $\tilde{\nu} = 3398, 2978, 2920, 1687, 1602, 1585, 1448, 1384, 1261, 1149, 1078, 974, 864, 775, 688$ cm^{-1}.

^{1}H-NMR (600 MHz, methanol-d_4): δ (ppm) = 1.38 (d, $J = 5.6$ Hz, 3 H, 6'-H_3), 2.41 (s, 3 H, 3-CH_3), 3.37–3.46 (m, 2 H, 4'-H, 5'-H), 3.64 (dd, $J = 8.9, 3.5$ Hz, 1 H, 3'-H), 4.22 (dd, $J = 3.5, 1.4$ Hz, 1 H, 2'-H), 5.03 (d, $J = 1.4$ Hz, 1 H, 1'-H), 7.37 (t, $J = 7.7$ Hz, 1 H, 5-H), 7.43 (d, $J = 7.7$ Hz, 1 H, 4-H), 7.77 (d, $J = 7.7$ Hz, 1 H, 6-H), 7.79 (s, 1 H, 2-H).

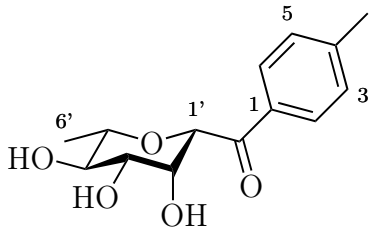
^{13}C-NMR (151 MHz, methanol-d_4): δ (ppm) = 18.1 (C-6'), 21.3 (3-$\underline{C}H_3$), 72.3 (C-2'), 73.7 (C-4'), 75.8 (C-3'), 77.6 (C-5'), 82.4 (C-1'), 127.0 (C-6), 129.5 (C-5), 130.2 (C-2), 135.0 (C-4), 136.9 (C-1), 139.6 (C-3), 198.6 (CO).

MS (ESI): *m/z* (%) = 119.1 (23) [(3-methylbenzylidyne)oxonium], 267.1 (4) $[M + H]^+$, 289.1 (100) $[M + Na]^+$.

calcd.: 289.1046 $[M + Na]^+$,
found: 289.1049 (ESI-HRMS).

$C_{14}H_{18}O_5$ (266.29).

6.22.6 (4-Methylphenyl)(β-L-rhamnopyranosyl) ketone 268



268

To a solution of *C*-glycosidic compound **232** (90.1 mg, 338 µmol, 1.00 equiv.) in MeOH (7.00 mL) was added a solution of aq. K_2CO_3 (c = 1.00 M, 7.00 mL, 7.00 mmol, 20.7 equiv.) at r.t. and the reaction mixture was stirred at r.t. for 1 h. Then, aq. HCl (c = 3.00 M, 14.0 mL, 42.0 mmol, 124 equiv.) was added. MeOH was removed in vacuum and the aqueous residue directly purified by reversed phase column chromatography (RP-C18, $H_2O \rightarrow H_2O$/MeCN 7:3) to yield *C*-glycosidic compound **268** (81.3 mg, 305 µmol, 90%) as colorless, crystalline solid.

TLC: $R_f = 0.37$ (DCM/MeOH 9:1).

M.p.: 194 °C (from water).

$[\alpha]_D^{20} = -25.8$ (c = 1.00, MeOH).

UV (MeOH): $\lambda_{max} = 203, 253$ nm.

IR (ATR): $\tilde{\nu} = 3500, 3423, 2997, 2972, 2926, 2906, 2856, 2816, 1681, 1606, 1083, 1055, 1014, 771, 615$ cm^{-1}.

^{1}H-NMR (600 MHz, Methanol-d_4): δ (ppm) = 1.37 (d, J = 5.8 Hz, 3 H, 6'-H_3), 2.41 (s, 3 H, 4-CH_3), 3.38–3.44 (m, 2 H, 4'-H, 5'-H), 3.59–3.67 (m, 1 H, 3'-H), 4.23 (dd, J = 3.5, 1.4 Hz, 1 H, 2'-H), 4.99 (d, J = 1.4 Hz, 1 H, 1'-H), 7.28–7.34 (m, 2 H, 3-H, 5-H), 7.87–7.91 (m, 2 H, 2-H, 6-H).

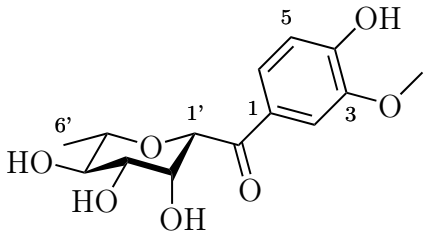
^{13}C-NMR (151 MHz, methanol-d_4): δ (ppm) = 18.1 (C-6'), 21.6 (3-$\underline{C}H_3$), 72.4 (C-2'), 73.8 (C-4'), 75.8 (C-3'), 77.7 (C-5'), 82.4 (C-1'), 130.0 (2 C, C-2, C-6), 130.2 (2 C, C-3, C-5), 134.3 (C-1), 145.5 (C-4), 198.0 (CO).

MS (ESI): m/z (%) = 119.1 (27) [(4-methylbenzylidyne)oxonium], 267.1 (4) $[M+H]^+$. 289.1 (100) $[M+Na]^+$.

calcd.: 289.1046 $[M + Na]^+$,
found: 289.1046 (ESI-HRMS).

$C_{14}H_{18}O_5$ (266.29).

6.22.7 (3-Methoxy-4-hydroxylphenyl)(β-L-rhamnopyranosyl) ketone 269



269

A solution of *C*-glycosidic compound **233** (100 mg, 335 µmol, 1.00 equiv.) in aq. KOH (c = 100 mM, 14.0 mL, 1.40 mmol, 4.18 equiv.) was stirred at r.t. for 24 h. Then, aq. HCl (c = 1.00 M, 3.50 mL, 3.50 mmol, 10.4 equiv.) was added. The aqueous mixture was purified by reversed phase column chromatography (RP-C18, H_2O + 0.1% TFA → H_2O/MeCN 3:1 + 0.1% TFA) to yield *C*-glycosidic compound **269** (98.7 mg, 331 µmol, 99%) as colorless, crystalline solid.

TLC: $R_f = 0.19$ (DCM/MeOH 9:1).

$[\alpha]_D^{20} = -8.7$ (c = 1.01, MeOH).

UV (MeOH): $\lambda_{max} = 203, 278, 304$ nm.

IR (ATR): $\tilde{\nu} = 3387, 2978, 2935, 1672, 1589, 1516, 1427, 1274, 1199, 1149, 1078, 1028, 881, 763, 628\ cm^{-1}$.

^{1}H-NMR (600 MHz, D_2O): δ (ppm) = 1.37 (d, J = 6.1 Hz, 3 H, 6'-H_3), 3.43 (t, J = 9.6 Hz, 1 H, 4'-H), 3.53 (dq, J = 9.6, 6.1 Hz, 1 H, 5'-H), 3.81 (dd, J = 9.6, 3.5 Hz, 1 H, 3'-H), 3.89 (s, 3 H, OCH_3), 4.31 (dd, J = 3.5, 1.0 Hz, 1 H, 2'-H), 5.21 (d, J = 1.0 Hz, 1 H, 1'-H), 6.96 (d, J = 8.4 Hz, 1 H, 5-H), 7.47 (d, J = 2.0 Hz, 1 H, 2-H), 7.51 (dd, J = 8.4, 2.0 Hz, 1 H, 6-H).

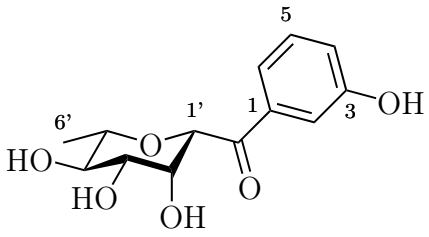
^{13}C-NMR (151 MHz, D_2O): δ (ppm) = 16.9 (C-6'), 55.9 (OCH_3), 71.0 (C-2'), 71.9 (C-4'), 73.4 (C-3'), 75.8 (C-5'), 79.9 (C-1'), 111.7 (C-2), 115.0 (C-5), 123.9 (C-6), 126.6 (C-1), 147.5 (C-3), 151.1 (C-4), 196.7 (CO).

MS (ESI): *m/z* (%) = 151.0 (20) [(4-hydroxy-3-methoxybenzylidyne)oxonium], 299.1 (25) $[M+H]^+$, 321.1 (81) $[M+Na]^+$, 619.2 (41) $[2\ M+Na]^+$.

calcd.: 321.0945 $[M+Na]^+$,
found: 321.0947 (ESI-HRMS).

$C_{14}H_{18}O_7$ (298.29).

6.22.8 (3-Hydroxylphenyl)(β-L-rhamnopyranosyl) ketone 270



270

To a solution of *C*-glycosidic compound **234** (99.7 mg, 371 µmol, 1.00 equiv.) in MeOH (7.50 mL) was added a solution of aq. K_2CO_3 (c = 1.00 M, 7.50 mL, 7.50 mmol, 20.2 equiv.) at r.t. and the reaction mixture was stirred at r.t. for 1 h. Then, aq. HCl (c = 3.00 M, 15.0 mL, 45.0 mmol, 121 equiv.) was added. MeOH was removed in vacuum and the aqueous residue directly purified by reversed phase column chromatography (RP-C18, H_2O + 0.1% TFA → H_2O/MeCN 3:1 + 0.1% TFA) to yield *C*-glycosidic compound **270** (98.5 mg, 367 µmol, 99%) as colorless, glassy solid.

TLC: R_f = 0.13 (DCM/MeOH 9:1).

$[\alpha]_D^{20}$ = -15.2 (c = 1.04, MeOH).

UV (MeOH): λ_{max} = 217, 251, 311 nm.

IR (ATR): $\tilde{\nu}$ = 3363, 2983, 2937, 2875, 1687, 1597, 1585, 1448, 1282, 1076, 883, 785, 684 cm^{-1}.

^{1}H-NMR (600 MHz, D_2O): δ (ppm) = 1.37 (d, *J* = 6.1 Hz, 3 H, 6'-H_3), 3.42 (t, *J* = 9.5 Hz, 1 H, 4'-H), 3.55 (dq, *J* = 9.5, 6.1 Hz, 1 H, 5'-H), 3.80 (dd, *J* = 9.5, 3.6 Hz, 1 H, 3'-H), 4.29 (dd, *J* = 3.6, 1.3 Hz, 1 H, 2'-H), 5.28 (d, *J* = 1.3 Hz, 1 H, 1'-H), 7.19 (ddd, *J* = 7.8, 2.5, 1.5 Hz, 1 H, 4-H), 7.33 (dd, *J* = 2.5, 1.5 Hz, 1 H, 2-H), 7.43 (t, *J* = 7.8 Hz, 1 H, 5-H), 7.46 (dt, *J* = 7.8, 1.5 Hz, 1 H, 6-H).

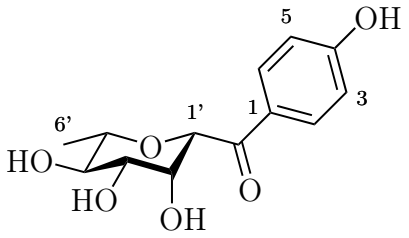
^{13}C-NMR (151 MHz, D_2O): δ (ppm) = 16.8 (C-6'), 70.5 (C-2'), 71.9 (C-4'), 73.3 (C-3'), 75.8 (C-5'), 80.4 (C-1'), 114.5 (C-2), 120.5 (C-6), 121.3 (C-4), 130.4 (C-5), 135.6 (C1), 156.0 (C-3), 198.7 (CO).

MS (ESI): *m/z* (%) = 121.0 (21) [(3-hydroxybenzylidyne)oxonium], 269.1 (4) $[M+H]^+$, 291.1 (100) $[M+Na]^+$, 559.2 (53) $[2\ M+Na]^+$.

calcd.: 291.0839 $[M+Na]^+$,
found: 291.0835 (ESI-HRMS).

$C_{13}H_{16}O_6$ (268.27).

6.22.9 (4-Hydroxylphenyl)(β-L-rhamnopyranosyl) ketone 271



271

A solution of *C*-glycosidic compound **235** (101 mg, 377 µmol, 1.00 equiv.) in aq. KOH (c = 100 mM, 15.0 mL, 1.50 mmol, 3.98 equiv.) was stirred at r.t. for 24 h. Then, aq. HCl (c = 1.00 M, 3.80 mL, 3.80 mmol, 10.1 equiv.) was added. The aqueous mixture was purified by reversed phase column chromatography (RP-C18, H_2O + 0.1% TFA → H_2O/MeCN 3:1 + 0.1% TFA) to yield *C*-glycosidic compound **271** (100 mg, 373 µmol, 99%) as colorless crystalline solid.

TLC: R_f = 0.13 (DCM/MeOH 9:1).

$[\alpha]_D^{20}$ = -20.6 (c = 0.99, MeOH).

UV (MeOH): λ_{max} = 218, 277 nm.

IR (ATR): $\tilde{\nu}$ = 3360, 2980, 2906, 2877, 2816, 1676, 1602, 1444, 1386, 1226, 1172, 1080, 842, 611 cm^{-1}.

^{1}H-NMR (600 MHz, D_2O): δ (ppm) = 1.38 (d, *J* = 6.1 Hz, 3 H, 6'-H_3), 3.44 (t, *J* = 9.6 Hz, 1 H, 4'-H), 3.55 (dq, *J* = 9.6, 6.1 Hz, 1 H, 5'-H), 3.82 (dd, *J* = 9.6, 3.6 Hz, 1 H, 3'-H), 4.32

(dd, $J = 3.6$, 1.0 Hz, 1 H, 2'-H), 5.27 (d, $J = 1.0$ Hz, 1 H, 1'-H), 6.97–7.01 (m, 2 H, 3-H, 5-H), 7.88–7.92 (m, 2 H, 2-H, 6-H).

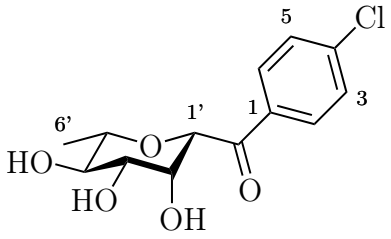
^{13}C-NMR (151 MHz, D_2O): δ (ppm) = 16.8 (C-6'), 70.8 (C-2'), 71.9 (C-4'), 73.4 (C-3'), 75.8 (C-5'), 79.9 (C-1'), 115.6 (2 C, 3-C, 5-C), 126.3 (C-1), 131.3 (2 C, 2-C, 6-C), 161.5 (C-4), 197.0 (CO).

MS (ESI): m/z (%) = 121.0 (34) [(4-hydroxybenzylidyne)oxonium], 291.1 (99) $[M + Na]^+$, 559.2 (100) $[2\ M + Na]^+$.

calcd.: 291.0839 $[M + Na]^+$,
found: 291.0845 (ESI-HRMS).

$C_{13}H_{16}O_6$ (268.27).

6.22.10 (4-Chlorophenyl)(β-L-rhamnopyranosyl) ketone 272



272

To a solution of *C*-glycosidic compound **237** (45.0 mg, 157 µmol, 1.00 equiv.) in MeOH (3.00 mL) was added a solution of aq. K_2CO_3 (c = 1.00 M, 3.00 mL, 3.00 mmol, 19.1 equiv.) at r.t. and the reaction mixture was stirred at r.t. for 1 h. Then, aq. HCl (c = 3.00 M, 6.00 mL, 18.0 mmol, 115 equiv.) was added. MeOH was removed in vacuum and the aqueous residue directly purified by reversed phase column chromatography (RP-C18, $H_2O \rightarrow H_2O$/MeCN 3:1) to yield *C*-glycosidic compound **272** (81.3 mg, 305 µmol, 86%) as colorless, crystalline solid.

TLC: $R_f = 0.41$ (DCM/MeOH 9:1).

M.p.: 220 °C (from water).

$[\alpha]_D^{20}$ = -24.8 (c = 1.00, MeOH).

UV (MeOH): $\lambda_{max} = 203$, 252 nm.

IR (ATR): $\tilde{\nu} = 3445$, 3070, 2997, 2980, 2933, 2862, 2816, 1678, 1589, 1413, 1338, 1290, 1228, 1083, 1012 cm^{-1}.

^{1}H-NMR (600 MHz, methanol-d_4): δ (ppm) = 1.37 (d, $J = 5.7$ Hz, 3 H, 6'-H_3), 3.36–3.44 (m, 2 H, 4'-H, 5'-H), 3.58–3.63 (m, 1 H, 3'-H), 4.22 (dd, $J = 3.4$, 1.4 Hz, 1 H, 2'-H), 4.90 (d, $J = 1.4$ Hz, 1 H, 1'-H), 7.48–7.51 (m, 2 H, 3-H, 5-H), 7.98–8.01 (m, 2 H, 2-H, 6-H).

^{13}C-NMR (151 MHz, methanol-d_4): δ (ppm) = 18.2 (C-6'), 72.2 (C-2'), 73.7 (C-4'), 75.8 (C-3'), 77.7 (C-5'), 83.1 (C-1'), 129.6 (2 C, C-3, C-5), 131.8 (2 C, C-2, C-6), 135.6 (C-4), 140.4 (C-1), 197.7 (CO).

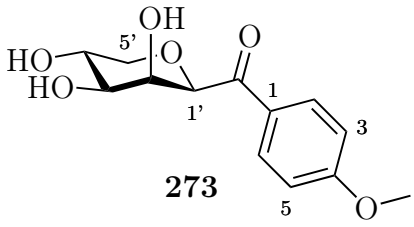
MS (ESI): m/z (%) = 139.0 (9) [(4-chlorobenzylidyne)oxonium], 309.1 (36) $[M + Na]^+$.

calcd.: 309.0500 $[M + Na]^+$,
found: 309.0504 (ESI-HRMS).

$C_{13}H_{15}ClO_5$ (286.71).

6.23 Syntheses of *C*-acyl β-D-lyxopyranosides

6.23.1 (4-Methoxyphenyl)(β-D-lyxopyranosyl) ketone 273



273

To a solution of *C*-glycosidic compound **239** (138 mg, 514 µmol, 1.00 equiv.) in MeOH (10.0 mL) was added a solution of aq. K_2CO_3 (c = 1.00 M, 10.0 mL, 10.0 mmol, 19.4 equiv.) at r.t. and the reaction mixture was stirred at r.t. for 2 h. Then, aq. HCl (c = 3.00 M, 20.0 mL, 60.0 mmol, 117 equiv.) was added. MeOH was removed in vacuum and the aqueous residue directly purified by reversed phase column chromatography (RP-C18, $H_2O \rightarrow H_2O$/MeCN 3:1) to yield *C*-glycosidic compound **273** (125 mg, 466 µmol, 91%) as colorless, crystalline solid.

TLC: $R_f = 0.23$ (DCM/MeOH 9:1).

M.p.: 184 °C (from water).

$[\alpha]_D^{20} = 22.6$ (c = 0.99, MeOH).

UV (MeOH): $\lambda_{max} = 217$, 272 nm.

IR (ATR): $\tilde{\nu} =$ 3531, 3446, 3257, 3155, 2980, 2927, 2897, 2873, 1681, 1600, 1261, 1215, 1078, 1033, 829 cm^{-1}.

^{1}H-NMR (600 MHz, methanol-d_4): δ (ppm) = 3.27 (t, J = 10.8 Hz, 1 H, 5'-$H_{ax.}$), 3.62 (dd, J = 9.5, 3.4 Hz, 1 H, 3'-H), 3.86 (ddd, J = 10.8, 9.5, 5.5 Hz, 1 H, 4'-H), 3.88 (s, 3 H, OCH_3), 4.04 (dd, J = 10.8, 5.5 Hz, 1 H, 5'-$H_{eq.}$), 4.24 (dd, J = 3.4, 1.3 Hz, 1 H, 2'-H), 4.93 (d, J = 1.3 Hz, 1 H, 1'-H), 6.98–7.04 (m, 2 H, 3-H, 5-H), 7.96–8.02 (m, 2 H, 2-H, 6-H).

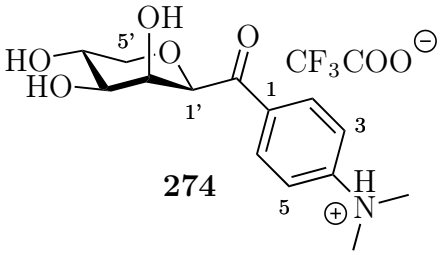
^{13}C-NMR (151 MHz, methanol-d_4): δ (ppm) = 56.1 (OCH_3), 67.9 (C-4'), 70.8 (C-5'), 72.3 (C-2'), 76.1 (C-3'), 83.1 (C-1'), 114.8 (2 C, C-3, C-5), 129.4 (C-1), 132.3 (2 C, C-2, C-6), 165.4 (C-4), 196.6 (CO).

MS (ESI): m/z (%) = 135.0 (28) [(4-methoxybenzylidyne)oxonium], 269.1 (13) $[M + H]^+$ 291.1 (100) $[M + Na]^+$, 559.2 (35) $[2\ M + Na]^+$.

calcd.: 291.0839 $[M + Na]^+$,
found: 291.0843 (ESI-HRMS).

$C_{13}H_{16}O_6$ (268.27).

6.23.2 (4-Dimethylaminophenyl)(β-D-lyxopyranosyl) ketone TFA salt 274



274

To a solution of *C*-glycosidic compound **240** (150 mg, 379 µmol, 1.00 equiv.) in MeOH (7.50 mL) was added a solution of aq. K_2CO_3 (c = 1.00 M, 7.50 mL, 7.50 mmol, 19.8 equiv.) at r.t. and the reaction mixture was stirred at r.t. for 2 h. Then, TFA (2.00 mL, 2.96 g, 26.0 mmol, 68.4 equiv.) was added. MeOH was removed in vacuum and the aqueous residue directly purified by reversed phase column chromatography (RP-C18, H_2O + 0.1% TFA → H_2O/MeCN 3:1 + 0.1% TFA) to yield *C*-glycosidic compound **274** (131 mg, 331 µmol, 87%) as colorless, crystalline solid.

TLC: $R_f = 0.21$ (DCM/MeOH 9:1).

M.p.: 238 °C (from water).

$[\alpha]_D^{20} = 31.6$ (c = 1.00, H_2O/TFA 9:1).

UV (MeOH): $\lambda_{max} = 237$, 352 nm.

IR (ATR): $\tilde{\nu} = 3533$, 3452, 3385, 3332, 3246, 2935, 2877, 1660, 1602, 1226, 1101, 1078, 1035, 821, 609 cm^{-1}.

^{1}H-NMR (600 MHz, DMSO-d_6): δ (ppm) = 3.00 (s, 6 H, $N(CH_3)_2$), 3.06 (t, J = 10.7 Hz, 1 H, 5'-$H_{ax.}$), 3.45 (dd, J = 9.3, 3.4 Hz, 1 H, 3'-H), 3.65 (ddd, J = 10.7, 9.3, 5.5 Hz, 1 H, 4'-H), 3.82 (dd, J = 10.7, 5.5 Hz, 1 H, 5'-$H_{eq.}$), 3.99 (dd, J = 3.4, 1.3 Hz, 1 H, 2'-H), 4.68 (d, J = 1.3 Hz, 1 H, 1'-H), 6.67–6.71 (m, 2 H, 3-H, 5-H), 7.80–7.85 (m, 2 H, 2-H, 6-H).

^{13}C-NMR (151 MHz, DMSO-d_6): δ (ppm) = 39.6 (2 C, $N(CH_3)_2$), 66.1 (C-4'), 69.5 (C-5'), 71.1 (C-2'), 74.5 (C-3'), 82.2 (C-1'), 110.4 (2 C, C-3, C-5), 123.0 (C-1), 130.8 (2 C, C-2, C-6), 153.1 (C-4), 193.7 (CO).

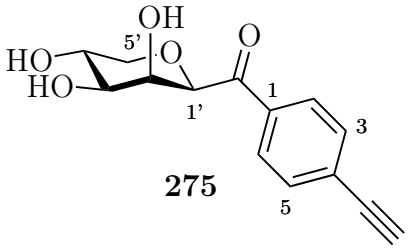
^{19}F-NMR (565 MHz, DMSO-d_6): δ (ppm) = 74.1 (m, CF_3COO^-).

MS (ESI): m/z (%) = 148.1 (4) [(4-dimethylaminobenzylidyne)oxonium], 282.1 (100) [M - CF_3COO]$^+$, 304.1 (42) [M - CF_3COOH + Na]$^+$, 585.2 (30) [2 M - 2 CF_3COOH + Na]$^+$.

calcd.: 282.1336 [M - CF_3COO^-]$^+$,
found: 282.1338 (ESI-HRMS).

$C_{16}H_{20}F_3NO_7$ (395.33).

6.23.3 (4-Ethynylphenyl)(β-D-lyxopyranosyl) ketone 275



275

To a solution of *C*-glycosidic compound **241** (20.0 mg, 76.3 µmol, 1.00 equiv.) in MeOH (1.50 mL) was added a solution of aq. K_2CO_3 (c = 1.00 M, 1.50 mL, 1.50 mmol, 19.7 equiv.)

at r.t. and the reaction mixture was stirred at r.t. for 2 h. Then, aq. HCl (c = 3.00 M, 3.00 mL, 9.00 mmol, 118 equiv.) was added. MeOH was removed in vacuum and the aqueous residue directly purified by reversed phase column chromatography (RP-C18, $H_2O \rightarrow H_2O$/MeCN 3:1) to yield *C*-glycosidic compound **275** (16.2 mg, 61.8 µmol, 81%) as colorless, crystalline solid.

TLC: $R_f = 0.30$ (DCM/MeOH 9:1).

$[\alpha]_D^{20} = 39.9$ (c = 0.98, MeOH).

UV (MeOH): $\lambda_{max} = 201, 211, 268$ nm.

IR (ATR): $\tilde{\nu} = 3452, 3332, 3236, 2960, 2873, 2100, 1685, 1600, 1215, 1141, 1080, 1033, 854, 835, 605$ cm^{-1}.

^{1}H-NMR (600 MHz, methanol-d_4): δ (ppm) = 3.27 (t, J = 10.7 Hz, 1 H, 5'-$H_{ax.}$), 3.61 (dd, J = 9.4, 3.4 Hz, 1 H, 3'-H), 3.75 (s, 1 H, 4-C≡CH), 3.86 (ddd, J = 10.7, 9.4, 5.5 Hz, 1 H, 4'-H), 4.04 (dd, J = 10.7, 5.5 Hz, 1 H, 5'-$H_{eq.}$), 4.23 (dd, J = 3.4, 1.3 Hz, 1 H, 2'-H), 4.92 (d, J = 1.3 Hz, 1 H, 1'-H), 7.55–7.59 (m, 2 H, 3-H, 5-H), 7.94–7.99 (m, 2 H, 2-H, 6-H).

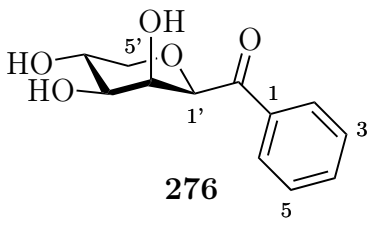
^{13}C-NMR (151 MHz, methanol-d_4): δ (ppm) = 67.8 (C-4'), 70.9 (C-5'), 72.0 (C-2'), 76.0 (C-3'), 83.1 (4-C≡CH), 83.7 (C-1'), 128.6 (C-1), 130.0 (2 C, C-2, C-6), 133.0 (2 C, C-3, C-5), 136.7 (C-4), 197.8 (CO).

MS (ESI): m/z (%) = 129.0 (25) [(4-ethynylbenzylidyne)oxonium], 285.1 (89) $[M + Na]^+$, 547.2 (18) $[2\ M + Na]^+$.

calcd.: 285.0733 $[M + Na]^+$,
found: 285.0730 (ESI-HRMS).

$C_{14}H_{14}O_5$ (262.26).

6.23.4 Phenyl (β-D-lyxopyranosyl) ketone 276



276

To a solution of *C*-glycosidic compound **242** (101 mg, 424 µmol, 1.00 equiv.) in MeOH (8.50 mL) was added a solution of aq. K_2CO_3 (c = 1.00 M, 8.50 mL, 8.50 mmol, 20.0 equiv.) at r.t. and the reaction mixture was stirred at r.t. for 2 h. Then, aq. HCl (c = 3.00 M, 17.0 mL, 51.0 mmol, 120 equiv.) was added. MeOH was removed in vacuum and the aqueous residue directly purified by reversed phase column chromatography (RP-C18, $H_2O \rightarrow H_2O$/MeCN 4:1) to yield *C*-glycosidic compound **276** (85.9 mg, 361 µmol, 85%) as colorless, crystalline solid.

TLC: $R_f = 0.21$ (DCM/MeOH 9:1).

M.p.: 122 °C (from water).

$[\alpha]_D^{20} = 19.8$ (c = 1.02, MeOH).

UV (MeOH): $\lambda_{max} = 201, 242$ nm.

IR (ATR): $\tilde{\nu} = 3525, 3450, 3369, 3257, 2974, 2927, 2893, 2872, 1685, 1597, 1215, 1101, 1068, 1035, 1012$ cm^{-1}.

^{1}H-NMR (600 MHz, methanol-d_4): δ (ppm) = 3.28 (t, J = 10.8 Hz, 1 H, 5'-$H_{ax.}$), 3.62 (dd, J = 9.4, 3.4 Hz, 1 H, 3'-H), 3.86 (ddd, J = 10.8, 9.4, 5.5 Hz, 1 H, 4'-H), 4.05 (dd, J = 10.8, 5.5 Hz, 1 H, 5'-$H_{eq.}$), 4.24 (dd, J = 3.4, 1.2 Hz, 1 H, 2'-H), 4.99 (d, J = 1.2 Hz, 1 H, 1'-H), 7.48–7.52 (m, 2 H, 3-H, 5-H), 7.59–7.63 (m, 1 H, 4-H), 7.96–7.99 (m, 2 H, 2 H, 6-H).

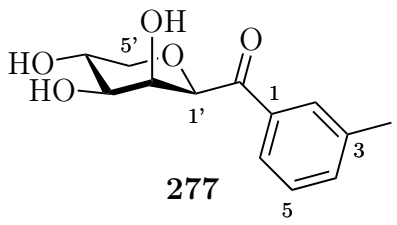
^{13}C-NMR (151 MHz, methanol-d_4): δ (ppm) = 67.8 (C-4'), 70.8 (C-5'), 72.1 (C-2'), 76.1 (C-3'), 83.4 (C-1'), 129.6 (2 C, C-3, C-5), 129.8 (2 C, C-2, C-6) 134.4 (C-4), 136.8 (C-1), 198.3 (CO).

MS (ESI): m/z (%) = 261.1 (41) $[M + Na]^+$.

calcd.: 261.0733 $[M + Na]^+$,
found: 261.0735 (ESI-HRMS).

$C_{12}H_{14}O_5$ (238.24).

6.23.5 (3-Methylphenyl)(β-D-lyxopyranosyl) ketone 277



277

To a solution of *C*-glycosidic compound **243** (121 mg, 508 µmol, 1.00 equiv.) in MeOH (10.0 mL) was added a solution of aq. K_2CO_3 (c = 1.00 M, 10.0 mL, 10.0 mmol, 19.7 equiv.) at r.t. and the reaction mixture was stirred at r.t. for 2 h. Then, aq. HCl (c = 3.00 M, 20.0 mL, 60.0 mmol, 118 equiv.) was added. MeOH was removed in vacuum and the aqueous residue directly purified by reversed phase column chromatography (RP-C18, $H_2O \rightarrow H_2O$/MeCN 3:1) to yield *C*-glycosidic compound **277** (104 mg, 437 µmol, 86%) as colorless, glassy solid.

TLC: $R_f = 0.23$ (DCM/MeOH 9:1).

$[\alpha]_D^{20} = 21.6$ (c = 0.99, MeOH).

UV (MeOH): $\lambda_{max} = 204, 247, 284$ nm.

IR (ATR): $\tilde{\nu} = 3429, 2970, 2924, 2902, 2862, 1683, 1602, 1456, 1423, 1263, 1101, 1074, 1037, 852, 686$ cm^{-1}.

^{1}H-NMR (600 MHz, methanol-d_4): δ (ppm) = 2.41 (s, 3 H, 3-CH_3), 3.28 (t, J = 10.8 Hz, 1 H, 5'-$H_{ax.}$), 3.62 (dd, J = 9.4, 3.4 Hz, 1 H, 3'-H), 3.85 (ddd, J = 10.8, 9.4, 5.5 Hz, 1 H, 4'-H), 4.04 (dd, J = 10.8, 5.5 Hz, 1 H, 5'-$H_{eq.}$), 4.23 (dd, J = 3.4, 1.4 Hz, 1 H, 2'-H), 5.00 (d, J = 1.4 Hz, 1 H, 1'-H), 7.38 (t, J = 7.7 Hz, 1 H, 5-H), 7.44 (d, J = 7.7 Hz, 1 H, 4-H), 7.76 (d, J = 7.7 Hz, 1 H, 6-H), 7.78 (s, 1 H, 2-H).

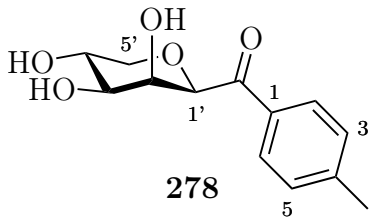
^{13}C-NMR (151 MHz, methanol-d_4): δ (ppm) = 21.3 (3-$\underline{C}H_3$), 67.8 (C-4'), 70.8 (C-5'), 72.1 (C-2'), 76.0 (C-3'), 83.2 (C-1'), 126.9 (C-6), 129.5 (C-5), 130.1 (C-2), 135.1 (C-4), 136.8 (C-1), 139.7 (C-3), 198.4 (CO).

MS (ESI): m/z (%) = 119.1 (35) [(3-methylbenzylidyne)oxonium], 275.1 (100) $[M + Na]^+$, 527.2 (23) $[2\ M + Na]^+$.

calcd.: 275.0890 $[M + Na]^+$,
found: 275.0889 (ESI-HRMS).

$C_{13}H_{16}O_5$ (252.27).

6.23.6 (4-Methylphenyl)(β-D-lyxopyranosyl) ketone 278



278

To a solution of *C*-glycosidic compound **244** (130 mg, 515 µmol, 1.00 equiv.) in MeOH (10.0 mL) was added a solution of aq. K_2CO_3 (c = 1.00 M, 10.0 mL, 10.0 mmol, 19.4 equiv.) at r.t. and the reaction mixture was stirred at r.t. for 2 h. Then, aq. HCl (c = 3.00 M, 20.0 mL, 60.0 mmol, 116 equiv.) was added. MeOH was removed in vacuum and the aqueous residue directly purified by reversed phase column chromatography (RP-C18, $H_2O \rightarrow H_2O$/MeCN 3:1) to yield *C*-glycosidic compound **278** (112 mg, 444 µmol, 86%) as colorless, crystalline solid.

TLC: $R_f = 0.23$ (DCM/MeOH 9:1).

M.p.: 175 °C (from water).

$[\alpha]_D^{20} = 26.8$ (c = 1.02, MeOH).

UV (MeOH): $\lambda_{max} = 202, 254$ nm.

IR (ATR): $\tilde{\nu} = 3560, 3456, 3400, 2970, 2933, 2889, 2856, 1681, 1602, 1251, 1207, 1109, 1095, 1029, 603$ cm^{-1}.

^{1}H-NMR (600 MHz, methanol-d_4): δ (ppm) = 2.41 (s, 3 H, 4-CH_3) 3.27 (t, J = 10.8 Hz, 1 H, 5'-$H_{ax.}$), 3.62 (dd, J = 9.4, 3.4 Hz, 1 H, 3'-H), 3.86 (ddd, J = 10.8, 9.4, 5.5 Hz, 1 H, 4'-H), 4.04 (dd, J = 10.8, 5.5 Hz, 1 H, 5'-$H_{eq.}$), 4.23 (dd, J = 3.4, 1.2 Hz, 1 H, 2'-H), 4.97 (d, J = 1.2 Hz, 1 H, 1'-H), 7.29–7.34 (m, 2 H, 3-H, 5-H), 7.86–7.90 (m, 2 H, 2-H, 6-H).

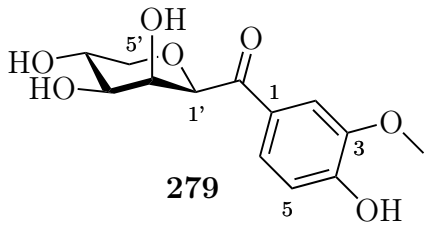
^{13}C-NMR (151 MHz, methanol-d_4): δ (ppm) = 21.6 (4-$\underline{C}H_3$), 67.8 (C-4'), 70.8 (C-5'), 72.2 (C-2'), 76.1 (C-3'), 83.2 (C-1'), 129.9 (2 C, C-2, C-6), 130.2 (2 C, C-3, C-5), 134.1 (C-1), 145.6 (C-4), 197.8 (CO).

MS (ESI): m/z (%) = 119.1 (33) [(4-methylbenzylidyne)oxonium], 275.1 (99) $[M + Na]^+$, 527.2 (22) $[2\ M + Na]^+$.

calcd.: 275.0890 $[M + Na]^+$,
found: 275.0889 (ESI-HRMS).

$C_{13}H_{16}O_5$ (252.27).

6.23.7 (3-Methoxy-4-hydroxylphenyl)(β-D-lyxopyranosyl) ketone 279



279

A solution of *C*-glycosidic compound **245** (100 mg, 352 µmol, 1.00 equiv.) in aq. KOH (c = 100 mM, 14.0 mL, 1.40 mmol, 3.98 equiv.) was stirred at r.t. for 24 h. Then, aq. HCl (c = 1.00 M, 3.50 mL, 3.50 mmol, 9.95 equiv.) was added. The aqueous mixture was purified by reversed phase column chromatography (RP-C18, H_2O + 0.1% TFA → H_2O/MeCN 4:1+ 0.1% TFA) to yield *C*-glycosidic compound **279** (99.1 mg, 349 µmol, 99%) as colorless, crystalline solid.

TLC: $R_f = 0.12$ (DCM/MeOH 9:1).

M.p.: 167 °C (from water).

$[a]_D^{20} = 5.9$ (c = 0.99, MeOH).

UV (MeOH): $\lambda_{max} = 203, 228, 277, 306$ nm.

IR (ATR): $\tilde{\nu} = 3468, 3316, 2962, 2879, 1683, 1587, 1514, 1429, 1429, 1373, 1282, 1215, 1174, 1068, 1031$ cm^{-1}.

^{1}H-NMR (600 MHz, D_2O): δ (ppm) = 3.36 (t, J = 10.9 Hz, 1 H, 5'-$H_{ax.}$), 3.80 (dd, J = 9.8, 3.4 Hz, 1 H, 3'-H), 3.88 (ddd, J = 10.9, 9.8, 5.5 Hz, 1 H, 4'-H), 3.91 (s, 3 H, OCH_3), 4.12 (dd, J = 10.9, 5.5 Hz, 1 H, 5'-$H_{eq.}$), 4.33 (dd, J = 3.4, 1.1 Hz, 1 H, 2'-H), 5.21 (d, J = 1.1 Hz, 1 H, 1'-H), 6.98 (d, J = 8.4 Hz, 1 H, 5-H), 7.49 (d, J = 2.0 Hz, 1 H, 2-H), 7.54 (dd, J = 8.4, 2.0 Hz, 1 H, 6-H).

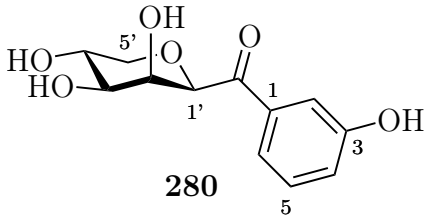
^{13}C-NMR (151 MHz, D_2O): δ (ppm) = 55.9 (OCH_3), 66.1 (C-4'), 68.5 (C-5'), 70.8 (C-2'), 73.7 (C-3'), 80.7 (C-1'), 111.7 (C-2), 115.0 (C-5), 124.0 (C-6), 126.6 (C-1), 147.6 (C-3), 151.2 (C-4), 196.6 (CO).

MS (ESI): *m/z* (%) = 151.0 (19) [(4-hydroxy-3-methoxybenzylidyne)oxonium], 285.1 (16) $[M + Na]^+$, 307.1 (100) $[M + Na]^+$, 591.2 (44) $[2\ M + Na]^+$.

calcd.: 307.0788 $[M + Na]^+$,
found: 307.0791 (ESI-HRMS).

$C_{13}H_{16}O_7$ (284.27).

6.23.8 (3-Hydroxylphenyl)(β-D-lyxopyranosyl) ketone 280



280

To a solution of *C*-glycosidic compound **246** (140 mg, 551 µmol, 1.00 equiv.) in MeOH (11.0 mL) was added a solution of aq. K_2CO_3 (c = 1.00 M, 11.0 mL, 11.0 mmol, 20.0 equiv.) at r.t. and the reaction mixture was stirred at r.t. for 2 h. Then, aq. HCl (c = 3.00 M, 22.0 mL, 22.0 mmol, 120 equiv.) was added. MeOH was removed in vacuum and the aqueous residue directly purified by reversed phase column chromatography (RP-C18, H_2O + 0.1% TFA → H_2O/MeCN 4:1+ 0.1% TFA) to yield *C*-glycosidic compound **280** (138 mg, 543 µmol, 99%) as colorless, glassy solid.

TLC: R_f = 0.08 (DCM/MeOH 9:1).

$[\alpha]_D^{20}$ = 13.0 (c = 0.98, MeOH).

UV (MeOH): λ_{max} = 217, 251, 309 nm.

IR (ATR): $\tilde{\nu}$ = 3400, 3251, 2985, 2941, 2893, 2856, 1691, 1585, 1284, 1099, 1074, 1028, 796, 682, 628 cm^{-1}.

^{1}H-NMR (600 MHz, D_2O): δ (ppm) = 3.36 (t, J = 10.8 Hz, 1 H, 5'-$H_{ax.}$), 3.79 (dd, J = 9.7, 3.4 Hz, 1 H, 3'-H), 3.87 (ddd, 10.8, 9.7, 5.5 Hz, 1 H, 4'-H), 4.12 (dd, J = 10.8, 5.5 Hz, 1 H, 5'-$H_{eq.}$), 4.31 (dd, J = 3.4, 1.3 Hz, 1 H, 2'-H), 5.24 (d, J = 1.3 Hz, 1 H, 1'-H), 7.19 (ddd, J = 7.7, 2.6, 1.6 Hz, 1 H, 4-H), 7.34 (dd, J = 2.6, 1.6 Hz, 1 H, 2-H), 7.44 (t, J = 7.7 Hz, 1 H, 5-H) 7.46 (dt, J = 7.7, 1.6 Hz, 1 H, 6-H).

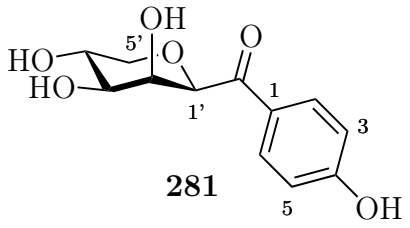
^{13}C-NMR (151 MHz, D_2O): δ (ppm) = 66.0 (C-4'), 68.5 (C-5'), 70.3 (C-2'), 73.6 (C-3'), 81.3 (C-1'), 114.5 (C-2), 120.5 (C-6), 121.4 (C-4), 130.4 (C-5), 135.6 (C-1), 156.0 (C-3), 198.6 (CO).

MS (ESI): *m/z* (%) = 121.0 (40) [(3-hydroxybenzylidyne)oxonium], 277.1 (100) $[M + Na]^+$, 531.2 (27) $[2\ M + Na]^+$.

calcd.: 277.0683 $[M + Na]^+$,
found: 277.0681 (ESI-HRMS).

$C_{12}H_{14}O_6$ (254.24).

6.23.9 (4-Hydroxylphenyl)(β-D-lyxopyranosyl) ketone 281



281

A solution of *C*-glycosidic compound **247** (100 mg, 393 µmol, 1.00 equiv.) in aq. KOH (c = 100 mM, 16.0 mL, 1.60 mmol, 4.07 equiv.) was stirred at r.t. for 24 h. Then, aq. HCl (c = 1.00 M, 4.00 mL, 4.00 mmol, 10.2 equiv.) was added. The aqueous mixture was purified by reversed phase column chromatography (RP-C18, H_2O + 0.1% TFA → H_2O/MeCN 4:1+ 0.1% TFA) to yield *C*-glycosidic compound **281** (98.9 mg, 389 µmol, 99%) as colorless, crystalline solid.

TLC: R_f = 0.06 (DCM/MeOH 9:1).

M.p.: 208 °C (from water).

$[\alpha]_D^{20}$ = 22.8 (c = 1.02, MeOH).

UV (MeOH): λ_{max} = 218, 279 nm.

IR (ATR): $\tilde{\nu}$ = 3473, 3321, 2960, 2879, 1683, 1602, 1583, 1435, 1371, 1219, 1066, 1035, 856, 837, 605 cm^{-1}.

^{1}H-NMR (600 MHz, D_2O): δ (ppm) = 3.36 (t, *J* = 10.8 Hz, 1 H, 5'-$H_{ax.}$), 3.80 (dd, *J* = 9.7, 3.4 Hz, 1 H, 3'-H), 3.89 (ddd, *J* = 10.8, 9.7, 5.5 Hz, 1 H, 4'-H), 4.12 (dd, *J* = 10.8, 5.5 Hz,

1 H, 5'-$H_{eq.}$), 4.33 (dd, $J = 3.4$, 1.2 Hz, 1 H, 2'-H), 5.22 (d, $J = 1.2$ Hz, 1 H, 1'-H), 6.97–7.01 (m, 2 H, 3-H, 5-H), 7.87–7.91 (m, 2 H, 2-H, 6-H).

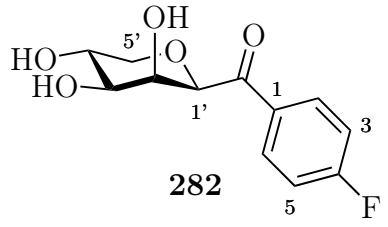
^{13}C-NMR (151 MHz, D_2O): δ (ppm) = 66.1 (C-4'), 68.5 (C-5'), 70.7 (C-2'), 73.7 (C-3'), 80.8 (C-1'), 115.6 (2 C, C-3, C-5), 126.3 (C-1), 131.3 (2 C, C-2, C-6), 161.5 (C-4), 196.9 (CO).

MS (ESI): *m/z* (%) = 121.0 (42) [(4-hydroxybenzylidyne)oxonium], 277.1 (100) $[M + Na]^+$, 531.2 (25) $[2\ M + Na]^+$.

calcd.: 277.0683 $[M + Na]^+$,
found: 277.0687 (ESI-HRMS).

$C_{12}H_{14}O_6$ (254.24).

6.23.10 (4-Fluorophenyl)(β-D-lyxopyranosyl) ketone 282



282

To a solution of *C*-glycosidic compound **248** (40.0 mg, 150 µmol, 1.00 equiv.) in MeOH (3.00 mL) was added a solution of aq. K_2CO_3 (c = 1.00 M, 3.00 mL, 3.00 mmol, 20.0 equiv.) at r.t. and the reaction mixture was stirred at r.t. for 2 h. Then, aq. HCl (c = 3.00 M, 6.00 mL, 18.0 mmol, 120 equiv.) was added. MeOH was removed in vacuum and the aqueous residue directly purified by reversed phase column chromatography (RP-C18, $H_2O \rightarrow H_2O$/MeCN 3:1) to yield *C*-glycosidic compound **282** (38.1 mg, 143 µmol, 95%) as colorless solid.

TLC: $R_f = 0.52$ (DCM/MeOH 9:1).

$[\alpha]_D^{25} = 8.6$ (c = 0.56, MeOH).

UV (MeOH): $\lambda_{max} = 202$, 244 nm.

IR (ATR): $\tilde{\nu} = 3381$, 2920, 1685, 1597, 1508, 1411, 1228, 1147, 1099, 1070, 1035, 1010, 854, 839, 611 cm^{-1}.

^{1}H-NMR (600 MHz, methanol-d_4): δ (ppm) = 3.27 (t, J = 10.8 Hz, 1 H, 5'-$H_{ax.}$), 3.60 (dd, J = 9.4, 3.4 Hz, 1 H, 3'-H), 3.87 (ddd, J = 10.8, 9.4, 5.5 Hz, 1 H, 4'-H), 4.05 (dd, J = 10.8, 5.5 Hz, 1 H, 5'-$H_{eq.}$), 4.23 (dd, J = 3.5, 1.4 Hz, 1 H, 2'-H), 4.89 (d, J = 1.4 Hz, 1 H, 1'-H), 7.18–7.25 (m, 2 H, 3-H, 5-H), 8.04–8.11 (m, 2 H, 2-H, 6-H).

^{13}C-NMR (151 MHz, Methanol-d_4): δ (ppm) = 67.83 (C-4'), 70.88 (C-5'), 72.07 (C-2'), 76.05 (C-3'), 83.76 (C-1'), 116.43 (d, J = 22.1 Hz, 2 C, C-3, C-5), 132.97 (d, J = 9.3 Hz, 2 C, C-2, C-6), 133.49 (d, J = 2.9 Hz, C-1), 167.17 (d, J = 253.2 Hz, C-4), 197.08 (CO).

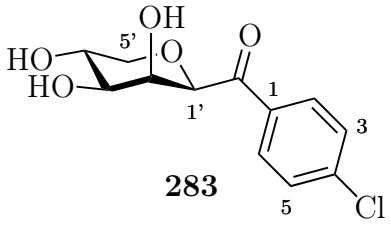
^{19}F-NMR (565 MHz, Methanol-d_4): δ (ppm) = 107.4 (m, 4-F).

MS (ESI): m/z (%) = 123.0 (100) [(4-fluorobenzylidyne)oxonium], 279.1 (79) $[M + Na]^+$. 535.1 (9) $[2\ M + Na]^+$.

calcd.: 279.0639 $[M + Na]^+$,
found: 279.0647 (ESI-HRMS).

$C_{12}H_{13}FO_5$ (256.23).

6.23.11 (4-Chlorophenyl)(β-D-lyxopyranosyl) ketone 283



283

To a solution of *C*-glycosidic compound **249** (82.4 mg, 302 µmol, 1.00 equiv.) in MeOH (6.00 mL) was added a solution of aq. K_2CO_3 (c = 1.00 M, 6.00 mL, 6.00 mmol, 19.9 equiv.) at r.t. and the reaction mixture was stirred at r.t. for 2 h. Then, aq. HCl (c = 3.00 M, 12.0 mL, 36.0 mmol, 119 equiv.) was added. MeOH was removed in vacuum and the aqueous residue directly purified by reversed phase column chromatography (RP-C18, H_2O → H_2O/MeCN 3:1) to yield *C*-glycosidic compound **283** (62.4 mg, 229 µmol, 76%) as colorless solid.

TLC: R_f = 0.29 (DCM/MeOH 9:1).

$[a]_D^{20}$ = 23.2 (c = 1.00, MeOH).

UV (MeOH): $\lambda_{max} = 203, 252\,nm$.

IR (ATR): $\tilde{\nu} = 3387, 2964, 2927, 2862, 1689, 1587, 1402, 1215, 1101, 1070, 1033, 1008, 867, 603, 472\ cm^{-1}$.

^{1}H-NMR (600 MHz, methanol-d_4): δ (ppm) = 3.26 (t, $J = 10.8$ Hz, 1 H, 5'-$H_{ax.}$), 3.60 (dd, $J = 9.4, 3.4$ Hz, 1 H, 3'-H), 3.86 (ddd, $J = 10.8, 9.4, 5.5$ Hz, 1 H, 4'-H), 4.04 (dd, $J = 10.8, 5.5$ Hz, 1 H, 5'-$H_{eq.}$), 4.23 (dd, $J = 3.4, 1.3$ Hz, 1 H, 2'-H), 4.88 (d, $J = 1.3$ Hz, 1 H, 1'-H), 7.47–7.53 (m, 2 H, 3-H, 5-H), 7.96–8.01 (m, 2 H, 2-H, 6-H).

^{13}C-NMR (151 MHz, Methanol-d_4): δ (ppm) = 67.8 (C-4'), 70.9 (C-5'), 72.0 (C-2'), 76.0 (C-3'), 83.9 (C-1'), 129.7 (2 C, C-3, C-5), 131.7 (2 C, C-2, C-6), 135.5 (C-4), 140.5 (C-1), 197.5 (CO).

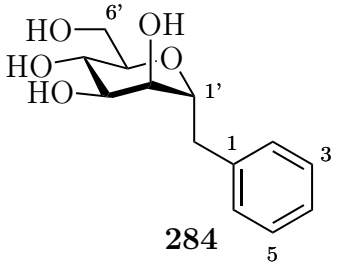
MS (ESI): m/z (%) = 139.0 (10) [(4-chlorobenzylidyne)oxonium], 295.0 (28) $[M + Na]^+$. 567.1 (4) $[2\ M + Na]^+$

calcd.: 295.0344 $[M + Na]^+$,
found: 295.0347 (ESI-HRMS).

$C_{12}H_{13}ClO_5$ (272.68).

6.24 Deoxygenation of *C*-acyl-mannopyranosides

6.24.1 Phenyl (α-D-mannopyranosyl) methane 284



284

To a solution of *C*-glycosidic compound **218** (72.0 mg, 268 µmol, 1.00 equiv.) in MeOH (10.0 mL) under argon atmosphere were added Pd/C (10% Pd, 200 mg) and AcOH (50.0 µL) at r.t.. The argon atmosphere was exchanged with hydrogen (1.00 bar) and stirred for 48 h. Then, the mixture was filtered through celite®, the solvent removed in vacuum and the residue purified by reversed phase column chromatography (RP-C18,

$H_2O \rightarrow H_2O$/MeCN 4:1) to yield *C*-glycosidic compound **284** (49.2 mg, 194 µmol, 72%) as colorless, crystalline solid.

TLC: $R_f = 0.21$ (DCM/MeOH 9:1).

M.p.: 152 °C (from water).

$[\alpha]_D^{20} = 34.0$ (c = 0.86, MeOH).

UV (MeOH): $\lambda_{max} = 206$ nm.

IR (ATR): $\tilde{\nu} = 3406$, 3358, 3309, 2937, 2926, 2904, 2879, 1602, 1139, 1116, 1089, 1066, 1049, 698, 493 cm^{-1}.

^{1}H-NMR (600 MHz, methanol-d_4): δ (ppm) = 2.90 (dd, J = 14.0, 7.0 Hz, 1 H, benzyl-H_A), 3.02 (dd, J = 14.0, 8.4 Hz, 1 H, benzyl-H_B), 3.63 (ddd, J = 8.7, 5.5, 2.7 Hz, 1 H, 5'-H), 3.67 (t, J = 8.7 Hz, 1 H, 4'-H), 3.71 (dd, J = 11.6, 5.5 Hz, 1 H, 6'-H_A), 3.77 (dd, J = 3.3, 2.5 Hz, 1 H, 2'-H), 3.78 (dd, J = 11.6, 2.7 Hz, 1 H, 6'-H_B), 3.82 (dd, J = 8.7, 3.3 Hz, 1 H, 3'-H), 4.08 (ddd, J = 8.4, 7.0, 2.5 Hz, 1 H, 1'-H), 7.18–7.21 (m, 1 H, 4-H), 7.25–7.27 (m, 2 H, 2-H, 6-H), 7.27–7.30 (m, 2 H, 3-H, 5-H).

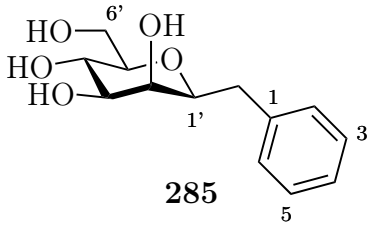
^{13}C-NMR (151 MHz, methanol-d_4): δ (ppm) = 36.4 (C_{benzyl}), 63.1 (C-6'), 69.3 (C-4'), 72.0 (C-2'), 72.6 (C-3'), 76.2 (C-5'), 80.6 (C-1'), 127.4 (C-4), 129.5 (2 C, C-3, C-5), 130.2 (2 C, C-2, C-6), 139.9 (C-1).

MS (ESI): m/z (%) = 277.1 (100) $[M + Na]^+$.

calcd.: 277.1046 $[M + Na]^+$,
found: 277.1040 (ESI-HRMS).

$C_{13}H_{18}O_5$ (254.28).

6.24.2 Phenyl (β-D-mannopyranosyl) methane 285



285

To a solution of *C*-glycosidic compound **255** (80.0 mg, 298 µmol, 1.00 equiv.) in MeOH (10.0 mL) under argon atmosphere were added Pd/C (10% Pd, 200 mg) and AcOH (50.0 µL) at r.t.. The argon atmosphere was exchanged with hydrogen (1.00 bar) and stirred for 48 h. Then, the mixture was filtered through celite®, the solvent removed in vacuum and the residue purified by reversed phase column chromatography (RP-C18, $H_2O \rightarrow H_2O$/MeCN 4:1) to yield *C*-glycosidic compound **285** (69.1 mg, 271 µmol, 91%) as colorless solid.

TLC: $R_f = 0.24$ (DCM/MeOH 9:1).

$[a]_D^{20} = -10.3$ (c = 1.03, MeOH).

UV (MeOH): $\lambda_{max} = 206$ nm.

IR (ATR): $\tilde{\nu} = 3431, 3315, 2924, 2906, 2858, 1452, 1423, 1402, 1244, 1053, 1026, 925, 769, 700, 499$ cm^{-1}.

^{1}H-NMR (600 MHz, methanol-d_4): δ (ppm) = 2.92 (dd, J = 13.5, 7.5 Hz, 1 H, benzyl-H_A), 2.97 (dd, J = 13.5, 6.6 Hz, 1 H, benzyl-H_B), 3.18 (ddd, J = 9.5, 5.6, 2.4 Hz, 1 H, 5'-H), 3.37 (dd, J = 9.5, 3.3 Hz, 1 H, 3'-H), 3.57–3.63 (m, 3 H, 1'-H, 2'-H, 4'-H), 3.70 (dd, J = 11.7, 5.6 Hz, 1 H, 6'-H_A), 3.82 (dd, J = 11.7, 2.4 Hz, 1 H, 6'-H_B), 7.16–7.20 (m, 1 H, 4-H), 7.24–7.30 (m, 4 H, 2-H, 3-H, 5-H, 6-H).

^{13}C-NMR (151 MHz, methanol-d_4): δ (ppm) = 38.2 (C_{benzyl}), 63.1 (C-6'), 68.8 (C-4'), 71.4 (C-2'), 76.8 (C-3'), 80.8 (C-1'), 82.0 (C-5'), 127.3 (C-4), 129.3, 130.5 (4 C, C-2, C-3, C-5, C-6), 139.7 (C-1).

MS (ESI): m/z (%) = 277.1 (31) $[M + Na]^+$.

calcd.: 277.1046 $[M + Na]^+$,
found: 277.1046 (ESI-HRMS).

$C_{13}H_{18}O_5$ (254.28).

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8 Appendix

8.1 Safety and Disposal[146]

Compound	GHS-Piktogram	H-Sätze	P-Sätze	Disposal
acetic acid		H226, H302, H314, H330	P210, P260, P280, P304+P340+P310, P305+P351+P338, P370+P378	dissolve in water, acidify, then (3)
acetone		H225, H319, H336	P210, P280, P304+P340+P312, P305+P351+P338, P337+P313, P403+P235	(1)
acetonitrile		H225, H302+H312+H332, H319	P210, P261, P280, P305+P351+P338, P370+P378, P403+P235	(1)
acetyl chloride		H225, H314	P210, P280, P301+P330+P331, P303+P361+P353, P305+P351+P338+P310	dissolve in methanol, then (1)
ascorbic acid	not a Hazardous substance or mixture according to Regulation (EC) No. 1272/2008.			dissolve in water, acidify, then (3)
benzaldehyde		H302+H332, H315, H319, H335, H412	P261, P273, P301+P312, P302+P352, P304+P340+P312, P305+P351+P338	(1)
benzene		H225, H304, H315, H319, H340, H350, H372, H412	P210, P273, P301+P310, P303+P361+P353, P305+P351+P338, P331	(1)

Compound	GHS-Piktogram	H-Sätze	P-Sätze	Disposal
$BF_3{\cdot}OEt_2$		H226, H302, H314, H330, H372, H412	P210, P273, P280, P303+P361+P353, P304+P340+P310, P305+P351+P338	dissolve in water, acidify, then (3)
celite®		H319, H335, H373	P261, P305+P351+P338	(6)
$Ce(SO_4)_2$		H314, H410	P260, P273, P280, P301+P330+P331, P303+P361+P353, P305+P351+P338	(6)
chloroform		H302, H315, H319, H331, H336, H351, H361d, H372	P260, P280, P301+P312+P330, P304+P340+P312, P305+P351+P338, P403+P233	(5)
cinnamaldehyde		H312, H315, H317, H319, H412	P261, P264, P273, P280, P302+P352+P312, P305+P351+P338	(1)
CSA		H314	P260, P260, P280, P301+P330+P331, P303+P361+P353, P304+P340+P310, P305+P351+P338	(5)
Cs_2CO_3		H318, H361f, H373	P201, P202, P260, P280, P305+P351+P338, P308+P313	dissolve in water, then (2)
CuBr	not a Hazardous substance or mixture according to Regulation (EC) No. 1272/2008.			dissolve in water, acidify, then (4)
CuI		H302, H315, H317, H318, H410	P273, P280, P301+P312+P330, P302+P352, P305+P351+P338+P310	dissolve in water, acidify, then (4)

Compound	GHS-Piktogram	H-Sätze	P-Sätze	Disposal
$CuSO_4$		H302, H315, H319, H410	P273, P305+P351+P338, P501	dissolve in water, acidify, then (4)
DCM		H315, H319, H335, H336, H351, H371	P260, P280, P305+P351+P338	(5)
DIAD		H315, H319, H335, H351, H411	P202, P261, P273, P302+P352, P305+P351+P338, P308+P313	(1)
diethyl ether		H224, H302, H336	P210, P261	(1)
3,5-Dimethoxytoluene		H315, H319, H335	P302+P352, P305+P351+P338	(1)
1,4-dioxane		H315, H319, H335	P302+P352, P305+P351+P338	(1)
Di-*tert*-Butyldicarbonat		H226, H315, H317, H318, H330, H335	P210, P233, P280, P303+P361+P353, P304+P340+P310, P305+P351+P338	dissolve in methanol, then (1)
DMF		H226, H312+H332, H319, H360D	P201, P210, P261, P280, P308+P313, P370+P378	(1)
DMI		H302, H318, H361fd	P201, P202, P280, P301+P312, P305+P351+P338, P308+P313	(1)
DMP		H272, H315, H319, H335	P210, P220, P221, P305+P351+P338, P370+P378	dissolve in water, reduce, acidify, then (3)
DMSO	not a Hazardous substance or mixture according to Regulation (EC) No. 1272/2008.			(1)

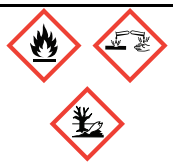
Compound	GHS-Piktogram	H-Sätze	P-Sätze	Disposal
ethyl acetate		H225, H319, H336	P210, P305+P351+P338, P370+P378, P403+P235	(1)
ethanol		H225, H319	P210, P305+P351+P338	(1)
ethanthiol		H224, H302+H332, H410	P210, P273, P301+P312+P330, P304+P340+P312, P403+P233	oxidize then dissolve in water, acidify, then (3)
$Fe(acac)_3$		H302+H312+H332, H318	P261, P280, P301+P312, P302+P352+P312, P304+P340+P312, P305+P351+P338	dissolve in water, acidify, then (4)
$FeCl_3$		H290, H302, H315, H318	P280, P305+P351+P338	dissolve in water, acidify, then (4)
3-Furan-carboxaldehyde		H226, H315, H319, H335	P210, P302+P352, P305+P351+P338	(1)
furfural		H301, H312, H315, H319, H330, H335, H351	P260, P280, P304+P340+P310, P305+P351+P338, P403+P233	(1)
glyme		H225, H315, H332, H360FD	P202, P210, P233, P303+P361+P353, P304+P340+P312, P308+P313	(1)
H_2		H220, H280	P210, P377, P381, P410+P403	
H_2O_2		H302, H318, H412	P280, P301+P312+P330, P305+P351+P338, P310	dissolve in water, reduce, acidify, then (3)

Compound	GHS-Piktogram	H-Sätze	P-Sätze	Disposal
hydrochloric acid		H290, H314, H335	P261, P280, P305+P351+P338, P310	dissolve in water, acidify, then (3)
iodine		H312+H332, H315, H319, H335, H372, H400	P261, P273, P280, P305+P351+P338, P314	dissolve in water, reduce, acidify, then (3)
K_2CO_3		H315, H319, H335	P261, P264, P271, P280, P302+P352, P305+P351+P338	dissolve in water, then (2)
K_3PO_4		H318, H335	P261, P271, P280, P304+P340+P312, P305+P351+P338, P403+P233	dissolve in water, then (2)
$K_3PO_4 \cdot H_2O$		H318, H335	P280, P305+P351+P338	dissolve in water, then (2)
KOH		H290, H302, H314	P234, P260, P280, P301+P312, P303+P361+P353, P305+P351+P338	dissolve in water, then (2)
LiBr		H302, H315, H317, H319	P261, P264, P280, P301+P312, P302+P352, P305+P351+P338	dissolve in water, acidify, then (3)
*m*CPBA		H242, H315, H317, H319, H335	P210, P235, P280, P302+P352, P370+P378, P410	dissolve in water, reduce, acidify, then (3)
methanol		H225, H301+H311+H331, H370	P210, P280, P302+P352+P312, P304+P340+P312, P370+P378, P403+P235	(1)

Compound	GHS-Piktogram	H-Sätze	P-Sätze	Disposal
2-MeTHF		H225, H302, H315, H318	P210, P233, P280, P301+P312, P303+P361+P353, P305+P351+P338	(1)
2-Methyl-3-buten-2-ol		H225, H302, H315, H319	P210, P301+P312+P330, P302+P352, P305+P351+P338	(1)
3-Methyl-crotonaldehyde		H226, H302, H314, H317, H331	P210, P280, P301+P330+P331, P303+P361+P353, P304+P340+P311, P305+P351+P338	(1)
Methyl iodide		H226, H301+H331, H312, H315, H319, H335, H351, H410	P210, P273, P280, P301+P310, P303+P361+P353, P304+P340+P311	(1)
$MgSO_4$	not a Hazardous substance or mixture according to Regulation (EC) No. 1272/2008.			dissolve in water, acidify, then (3)
molecular sieves 4 Å	not a Hazardous substance or mixture according to Regulation (EC) No. 1272/2008.			(6)
m-tolualdehyde	not a Hazardous substance or mixture according to Regulation (EC) No. 1272/2008.			(1)
m-hydroxy-benzaldehyde		H315, H319	P264, P280, P302+P352, P305+P351+P338, P332+P313, P337+P313	(1)
NaCl	not a Hazardous substance or mixture according to Regulation (EC) No. 1272/2008.			dissolve in water, acidify, then (3)
NaH in mineral oil		H260	P231+P232, P335+P334, P370+P378, P402+P404	dissolve in methanol, then (1)

Compound	GHS-Piktogram	H-Sätze	P-Sätze	Disposal
$NaHCO_3$	not a Hazardous substance or mixture according to Regulation (EC) No. 1272/2008.			dissolve in water, then (2)
NaHMDS in THF		H225, H314, H335, H336, H351	P201, P210, P280, P303+P361+P353, P304+P340+P310, P305+P351+P338	dissolve in toluene, then isopropanol, then ethanol, then methanol and (1)
2-Naphthaldehyde	not a Hazardous substance or mixture according to Regulation (EC) No. 1272/2008.			dissolve in methanol, then (1)
NaOH		H290, H314	P280, P303+P361+P353, P304+P340+P310, P305+P351+P338	dissolve in water, then (2)
NaOMe		H228, H251, H290, H302, H314	P210, P235, P260, P280, P303+P361+P353, P305+P351+P338	dissolve in water, then (2)
n-BuLi in hexanes		H225, H250, H261, H304, H314, H336, H361f, H373, H411	P210, P222, P231+P232, P261, P273, P422	dissolve in toluene, then isopropanol, then ethanol, then methanol and (1)
NMP		H315, H319, H335, H360FD	P201, P202, P261, P302+P352, P305+P351+P338, P308+P313	(1)
o-tolualdehyde		H302+H312+H332, H315, H319, H335, H412	P273, P280, P301+P312, P302+P352+P312, P304+P340+P312, P305+P351+P338	(1)
oxalyl bromide		H314, H332	P280, P305+P351+P338, P310	dissolve in water, acidify, then (3)

Compound	GHS-Piktogram	H-Sätze	P-Sätze	Disposal
Oxone®		H314	P260, P280, P303+P361+P353, P304+P340+P310, P305+P351+P338	dissolve in water, reduce, acidify, then (3)
p-anisaldehyde	not a Hazardous substance or mixture according to Regulation (EC) No. 1272/2008.			(1)
p-chloro-benzaldehyde		H302, H315, H317, H319, H411	P261, P273, P280, P301+P312, P302+P352, P305+P351+P338	(5)
Pd/C	not a Hazardous substance or mixture according to Regulation (EC) No. 1272/2008.			(6)
$Pd_2(dba)_3$		H317, H411	P261, P272, P273, P280, P302+P352, P333+P313	dissolve in water, acidify, then (4)
$Pd(OAc)_2$		H317, H318, H410	P261, P272, P273, P280, P302+P352, P305+P351+P338	dissolve in water, acidify, then (4)
$Pd(PPh_3)_4$		H302, H317, H413	P261, P264, P273, P280, P301+P312, P302+P352	dissolve in water, acidify, then (4)
$Pd(PPh_3)_2Cl_2$		H317, H413	P261, P272, P273, P280, P302+P352, P333+P313	dissolve in water, acidify, then (4)
pentane		H225, H304, H336, H411	P210, P261, P273, P301+P310, P331	(1)
petroleum ether		H225, H302, H304, H315, H336, H411	P210, P301+P310, P331, P370+P378, P403+P235	(1)
phenylacetaldehyde		H302, H314, H317	P261, P270, P280, P301+P312, P303+P361+P353, P305+P351+P338	(1)

Compound	GHS-Piktogram	H-Sätze	P-Sätze	Disposal
p-bromo-benzaldehyde		H302, H315, H317, H319, H335	P280, P301+P312+P330, P302+P352, P305+P351+P338	(5)
p-dimethylamino-benzaldehyde		H317	P261, P272, P280, P302+P352, P333+P313, P362+P364	(1)
p-fluoro-benzaldehyde		H226, H315, H319, H335	P210, P233, P240, P241, P303+P361+P353, P305+P351+P338	(5)
p-hydroxy-benzaldehyde		H318	P280, P305+P351+P338	(1)
PIFA		H315, H319, H335	P302+P352, P305+P351+P338	dissolve in water, reduce, acidify, then (3)
pivalaldehyde		H225	P210, P233, P240, P241, P242, P243	(1)
PPh_3		H302, H317, H318, H372	P280, P301+P312+P330, P302+P352, P305+P351+P338+P310, P314	(1)
Prenyl bromide		H226, H314, H410	P210, P273, P280, P301+P330+P331, P303+P361+P353, P305+P351+P338+P310	dissolve in methanol, then (1)
pyridine		H225, H302+312+332, H315, H319	P210, P280, P301+P312, P303+P361+P353, P304+P340+P312, P305+P351+P338	(1)

Compound	GHS-Piktogram	H-Sätze	P-Sätze	Disposal
1,3-propanedithiol		H315, H319, H335	P305+P351+P338	(1)
p-(trifluormethyl)-benzaldehyde		H302, H315, H319	P264, P270, P280, P301+P312, P302+P352, P305+P351+P338	(5)
p-tolualdehyde		H302, H315, H319	P301+P312+P330, P302+P352, P305+P351+P338	(1)
Raney®-Nickel		H250, H317, H351, H372, H412	P210, P273, P280, P302+P334, P314, P422	dissolve in water, acidify, then (4)
Salicylaldehyd		H302, H315, H319, H341, H411	P202, P273, P301+P312, P302+P352, P305+P351+P338, P308+P313	dissolve in water, acidify, then (3)
SDS		H228, H302+H332, H315, H318, H335, H412	P210, P261, P280, P301+P312+P330, P305+P351+P338, P310, P370+P378	dissolve in methanol, then (1)
silica gel	not a Hazardous substance or mixture according to Regulation (EC) No. 1272/2008.			(6)
$SrCl_2 \cdot 6\,H_2O$		H315, H318, H335	P261, P280, P305+P351+P338	dissolve in water, acidify, then (3)
sulfuric acid		H290, H314	P234, P280, P303+P361+P353, P304+P340+P310, P305+P351+P338, P363	dissolve in water, acidify, then (3)
TBABr		H302, H315, H319, H412	P264, P270, P273, P301+P312, P302+P352, P305+P351+P338	dissolve in water, acidify, then (3)

Compound	GHS-Piktogram	H-Sätze	P-Sätze	Disposal
t-BuLi in pentane		H225, H250, H260, H304, H314, H336, H411	P210, P222, P223, P231+P232, P370+P378, P422	dissolve in toluene, then isopropanol, then ethanol, then methanol and (1)
t-BuXPhos	not a Hazardous substance or mixture according to Regulation (EC) No. 1272/2008.			dissolve in methanol, then (1)
TFA		H314, H332, H412	P261, P273, P280, P303+P361+P353, P304+P340+P310, P305+P351+P338	dissolve in water, acidify, then (3)
THF		H225, H302, H319, H335, H336, H351	P201, P202, P210, P301+P312, P305+P351+P338, P308+P313	(1)
TMSCl		H225, H301+H331, H312, H314	P210, P261, P280, P301+P310, P305+P351+P338, P310	dissolve in methanol, then (1)
TMSI		H225, H314	P210, P233, P240, P280, P303+P361+P353, P305+P351+P338	dissolve in methanol, then (1)
toluene		H225, H304, H315, H336, H361d, H373, H412	P202, P210, P273, P301+P310, P303+P361+P353, P331	(1)
Vanillin		H319	P264, P280, P305+P351+P338, P337+P313	dissolve in methanol, then (1)
XPhos	not a Hazardous substance or mixture according to Regulation (EC) No. 1272/2008.			dissolve in methanol, then (1)
XPhos Pd G3	not a Hazardous substance or mixture according to Regulation (EC) No. 1272/2008.			dissolve in water, acidify, then (4)

Compound	GHS-Piktogram	H-Sätze	P-Sätze	Disposal
Zinc		H273	P410	dissolve in water, acidify, then (4)

(1) dispose in container for non halogenated organic solvents.
(2) dispose in container for other bases.
(3) dispose in container for other acids.
(4) dispose in container for heavy metal waste.
(5) dispose in container for halogenated organic solvents.
(6) dispose in container for filter materials.

8.2 NMR-spectra

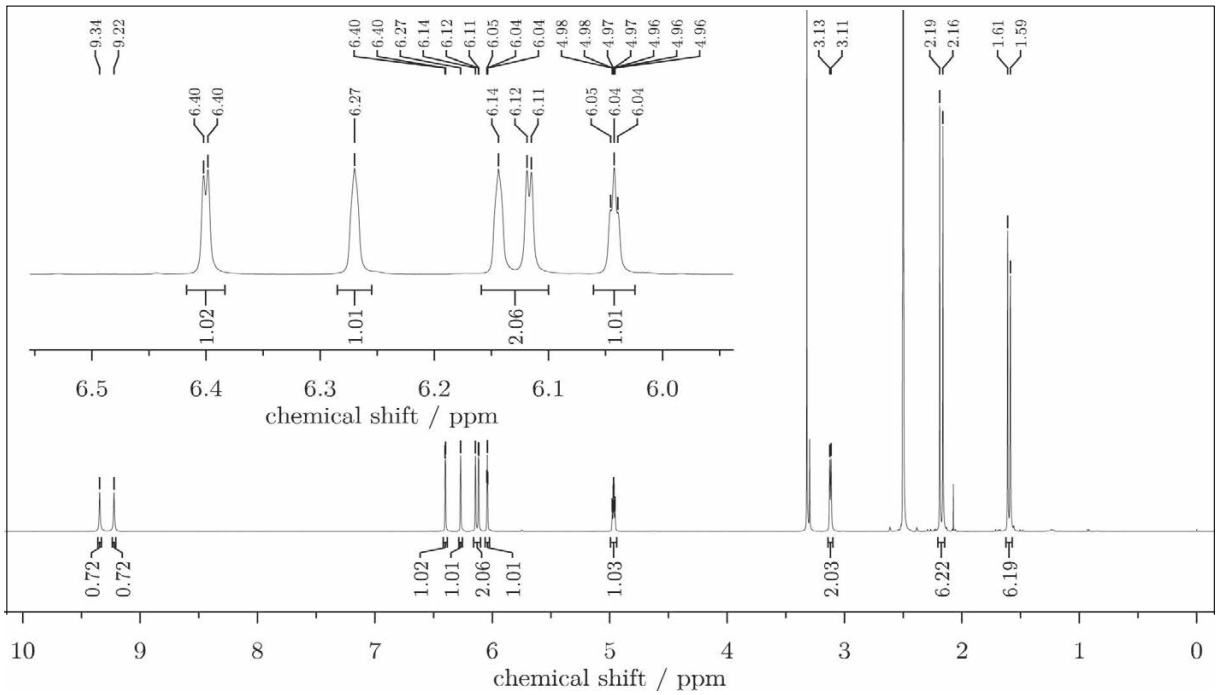


Figure 51: ^{1}H-NMR spectrum of **1** at 400 MHz in benzene-d_6.

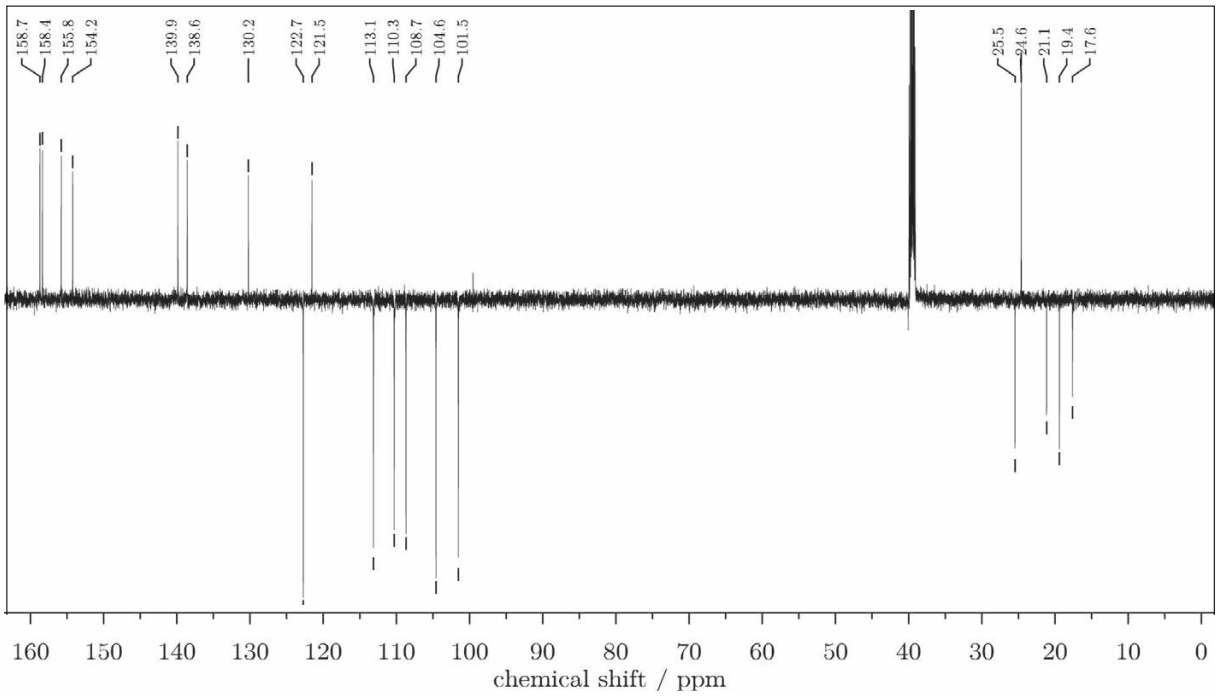


Figure 52: DEPTQ-NMR spectrum of **1** at 100 MHz in benzene-d_6.

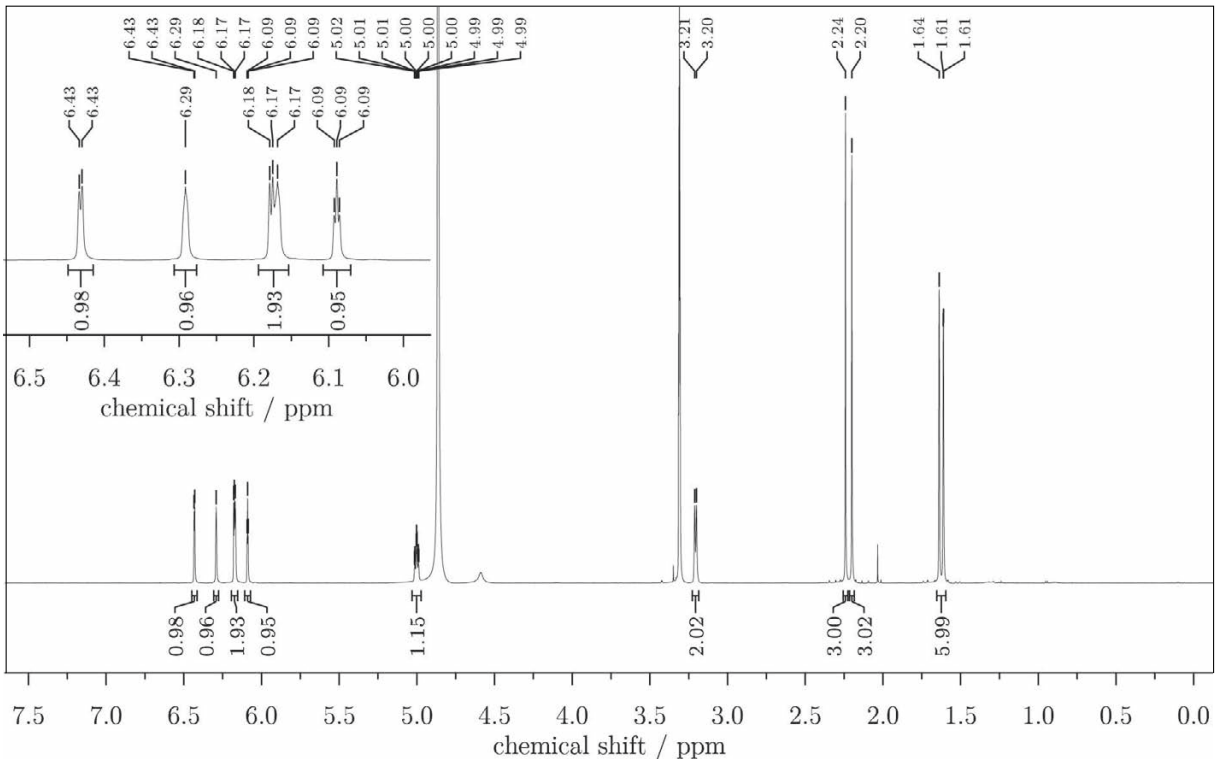


Figure 53: ^{1}H-NMR spectrum of **1** at 600 MHz in methanol-d_4.

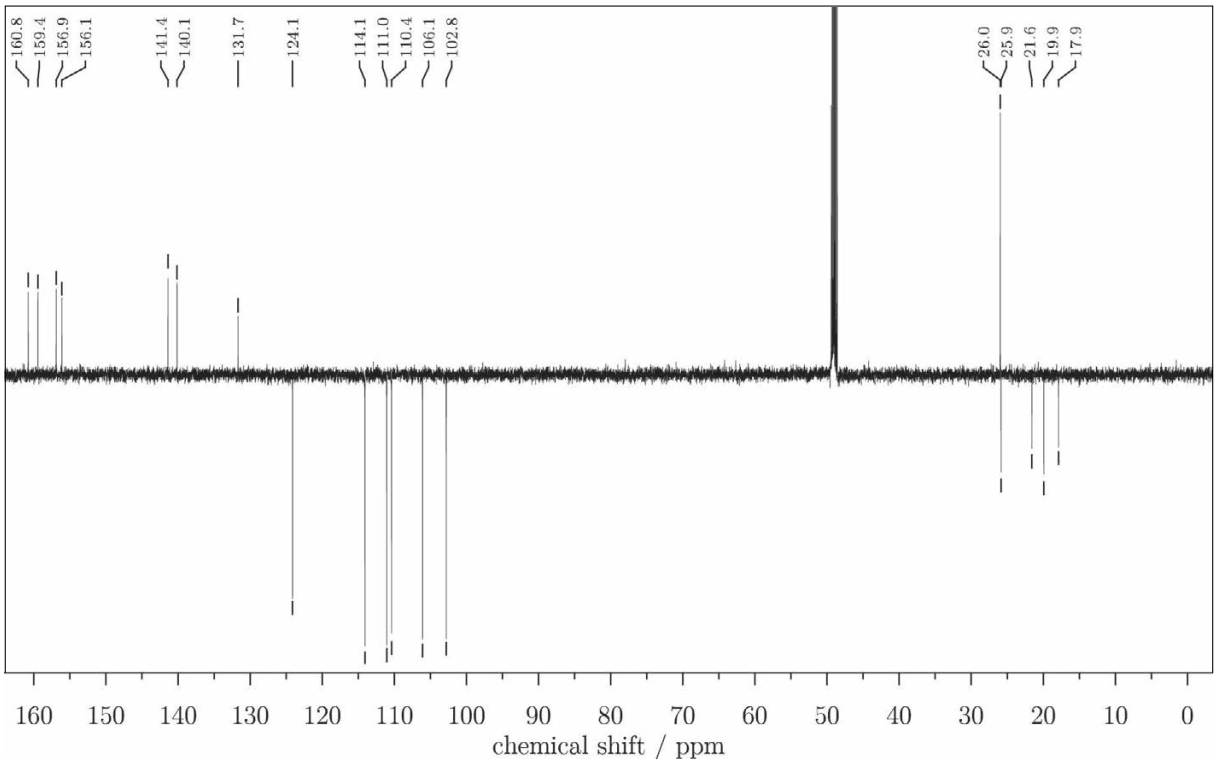


Figure 54: DEPTQ-NMR spectrum of **1** at 151 MHz in methanol-d_4.

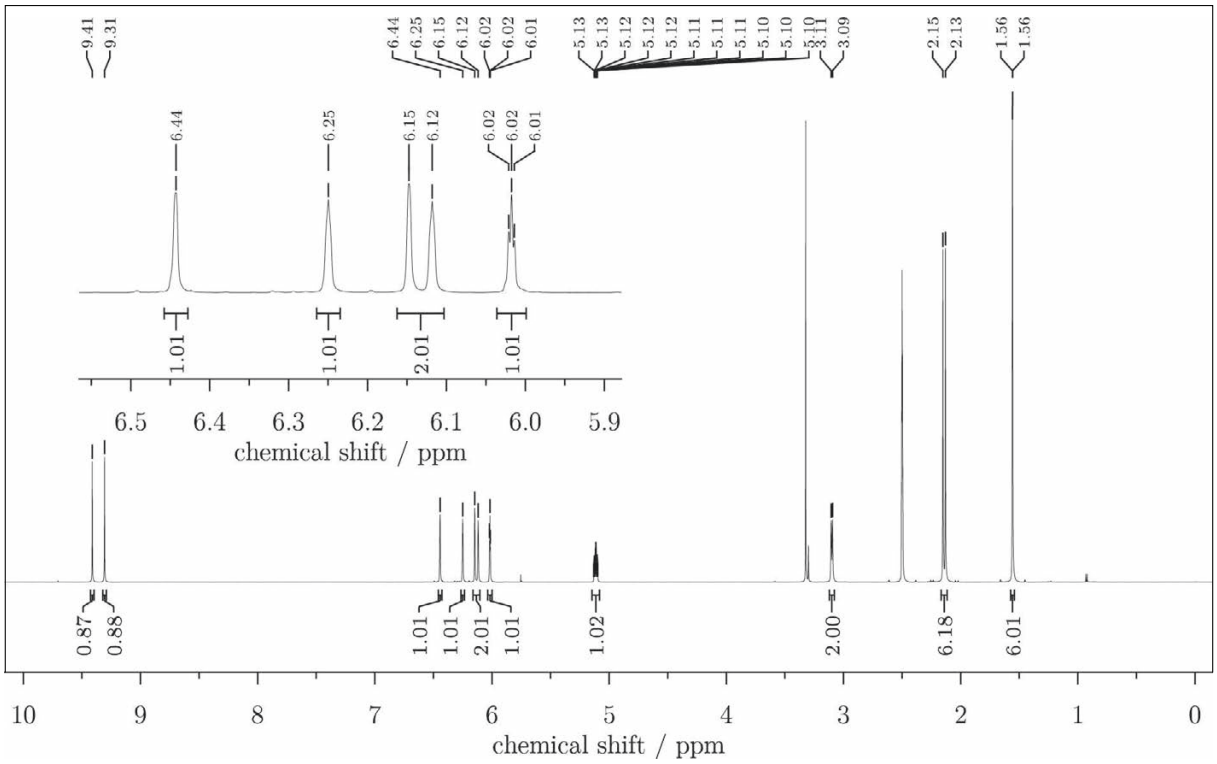


Figure 55: ^{1}H-NMR spectrum of **2** at 600 MHz in DMSO-d_6.

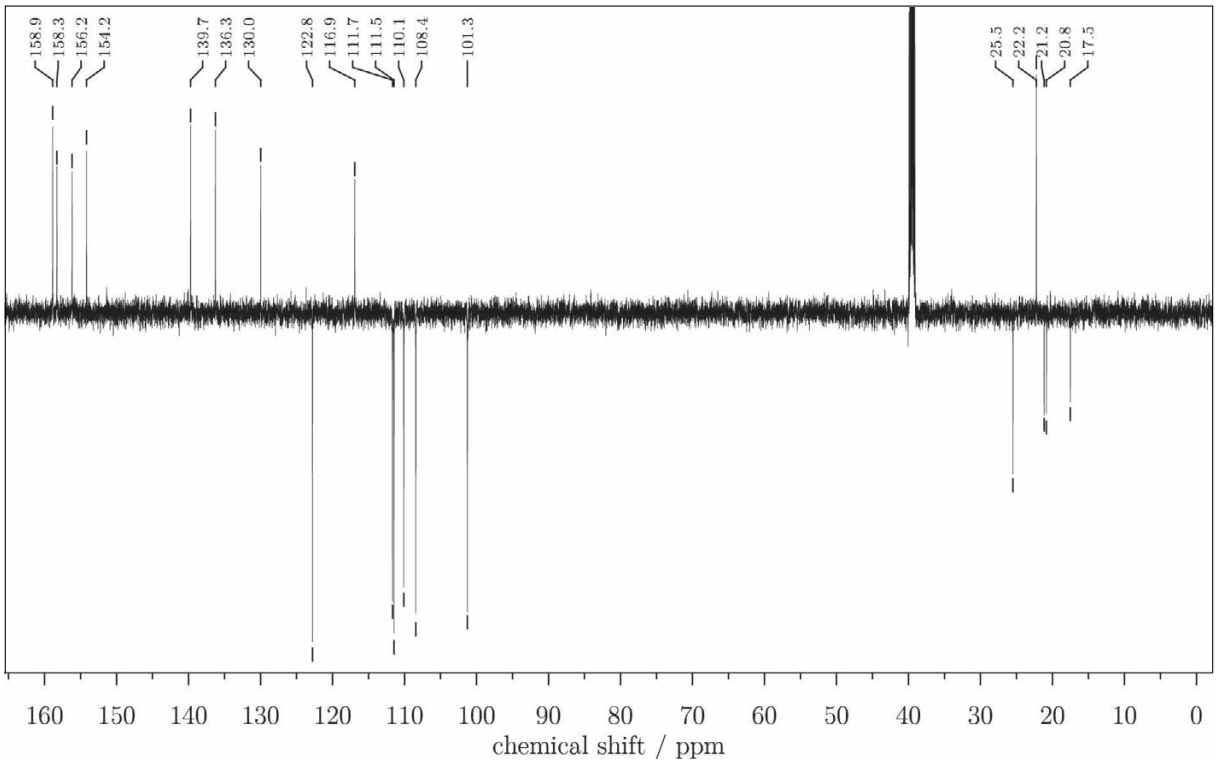


Figure 56: DEPTQ-NMR spectrum of **2** at 151 MHz in DMSO-d_6.

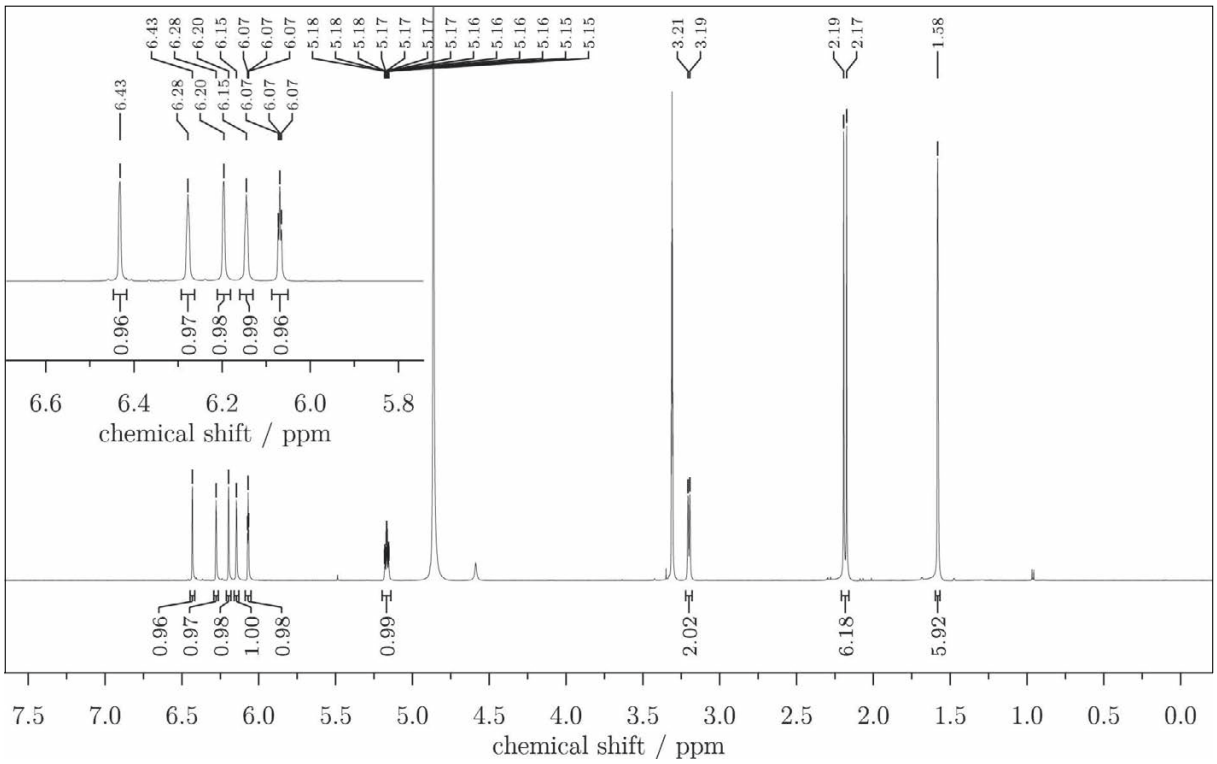


Figure 57: ^{1}H-NMR spectrum of **2** at 600 MHz in methanol-d_4.

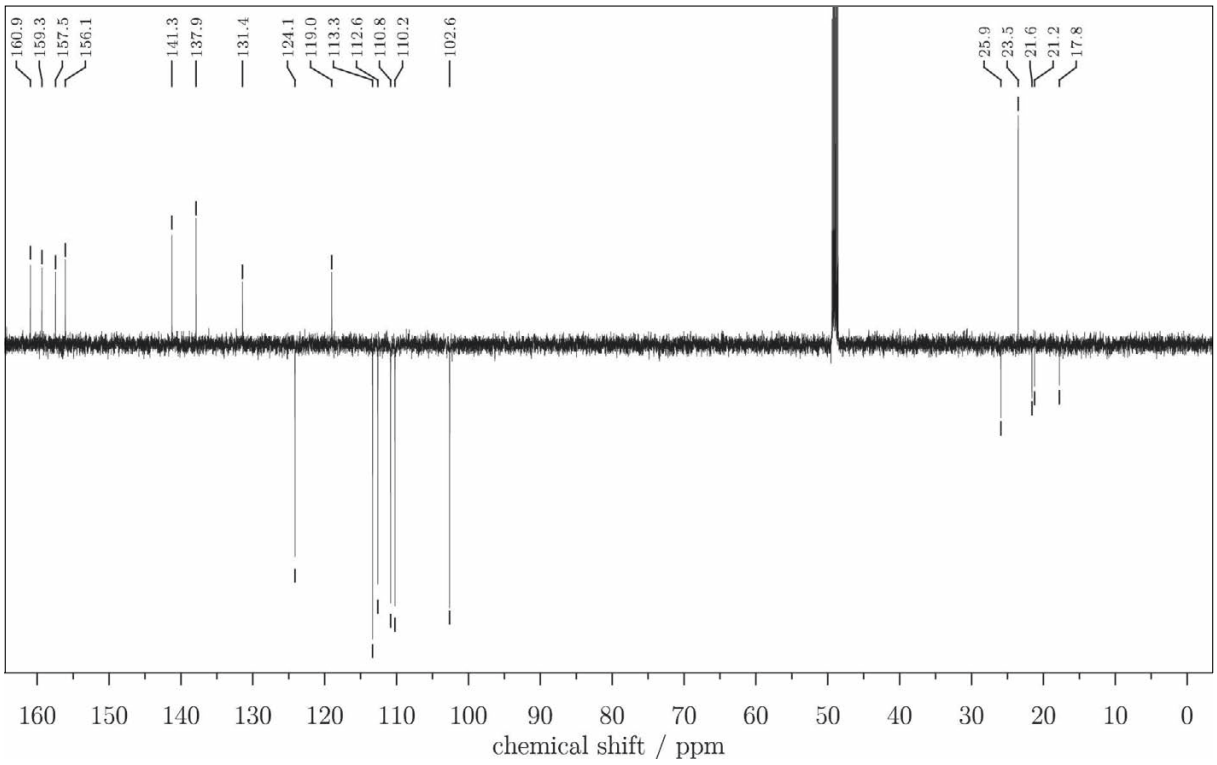


Figure 58: DEPTQ-NMR spectrum of **2** at 151 MHz in methanol-d_4.

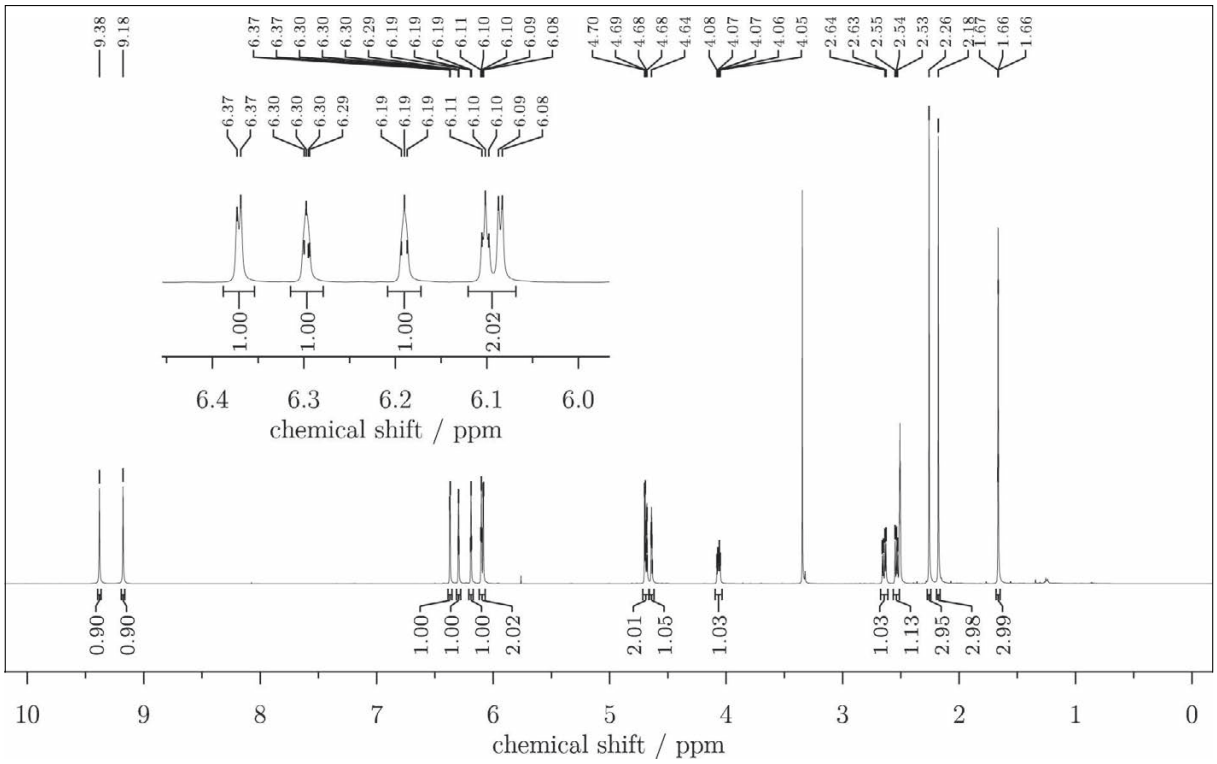


Figure 59: ^{1}H-NMR spectrum of **3** at 600 MHz in DMSO-d_6.

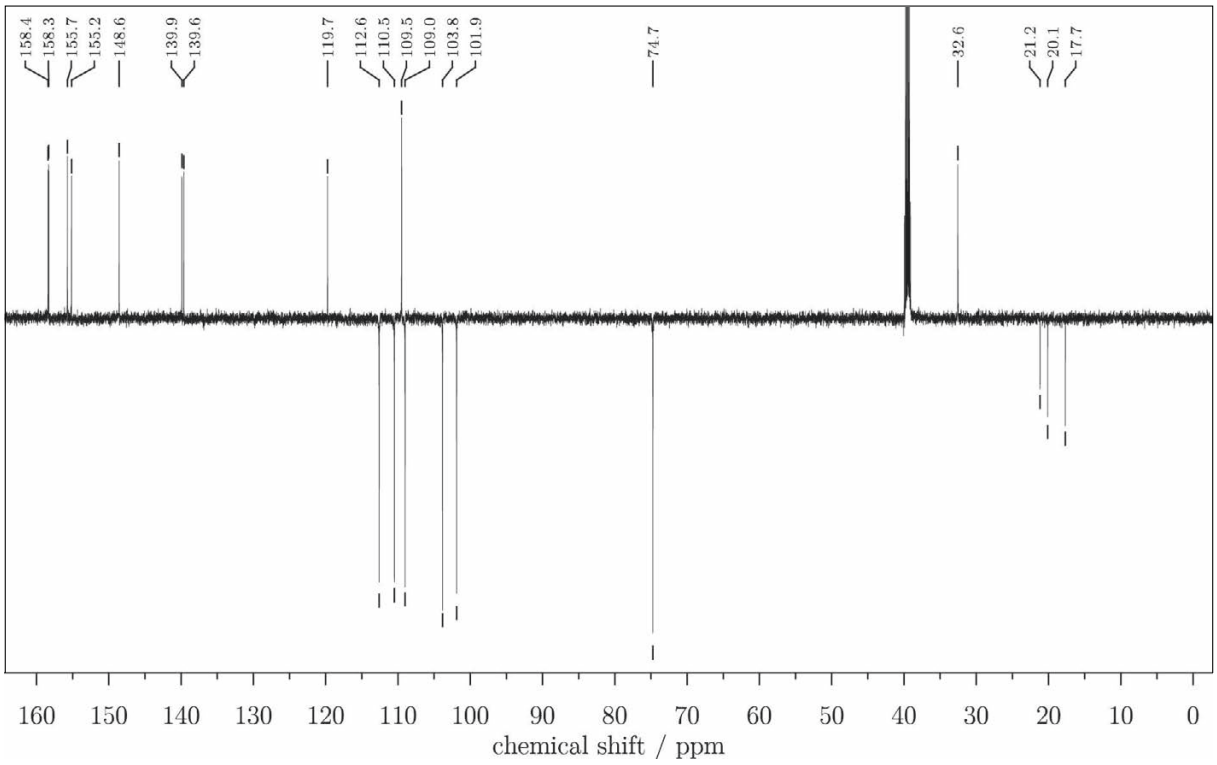


Figure 60: DEPTQ-NMR spectrum of **3** at 151 MHz in DMSO-d_6.

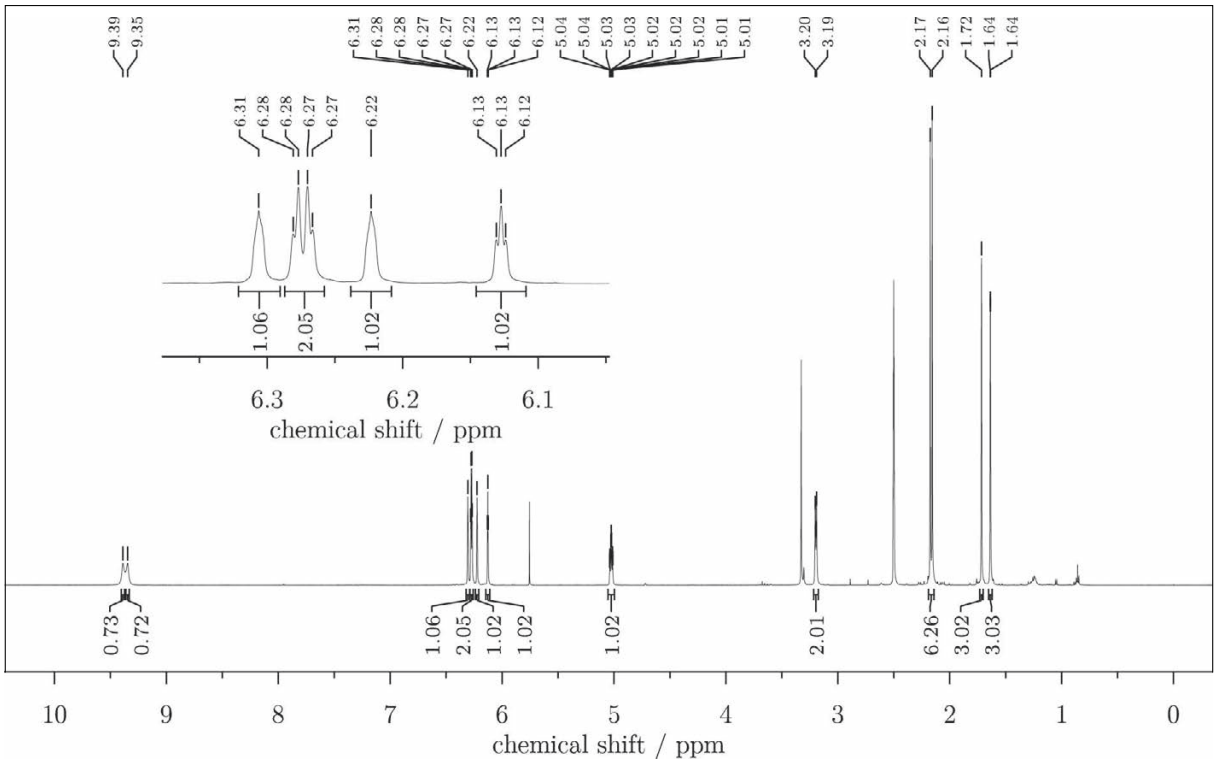


Figure 61: ^{1}H-NMR spectrum of **4** at 600 MHz in DMSO-d_6.

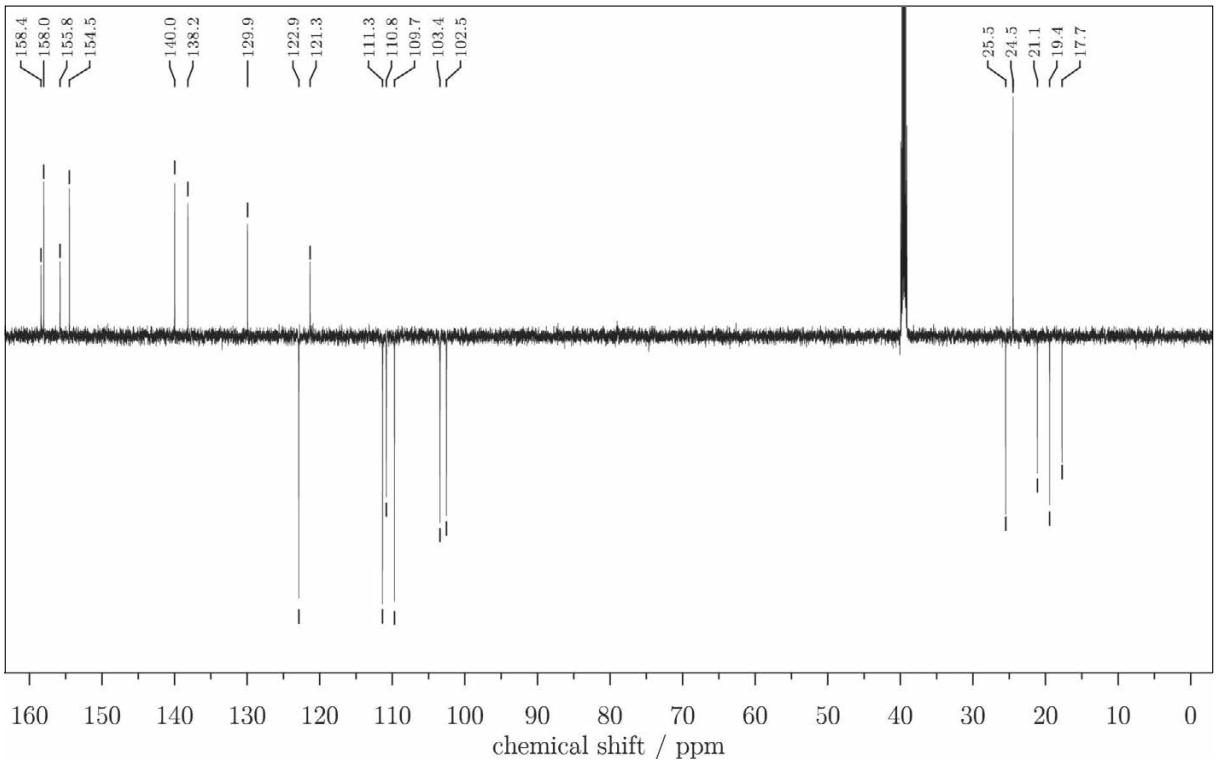


Figure 62: DEPTQ-NMR spectrum of **4** at 151 MHz in DMSO-d_6.

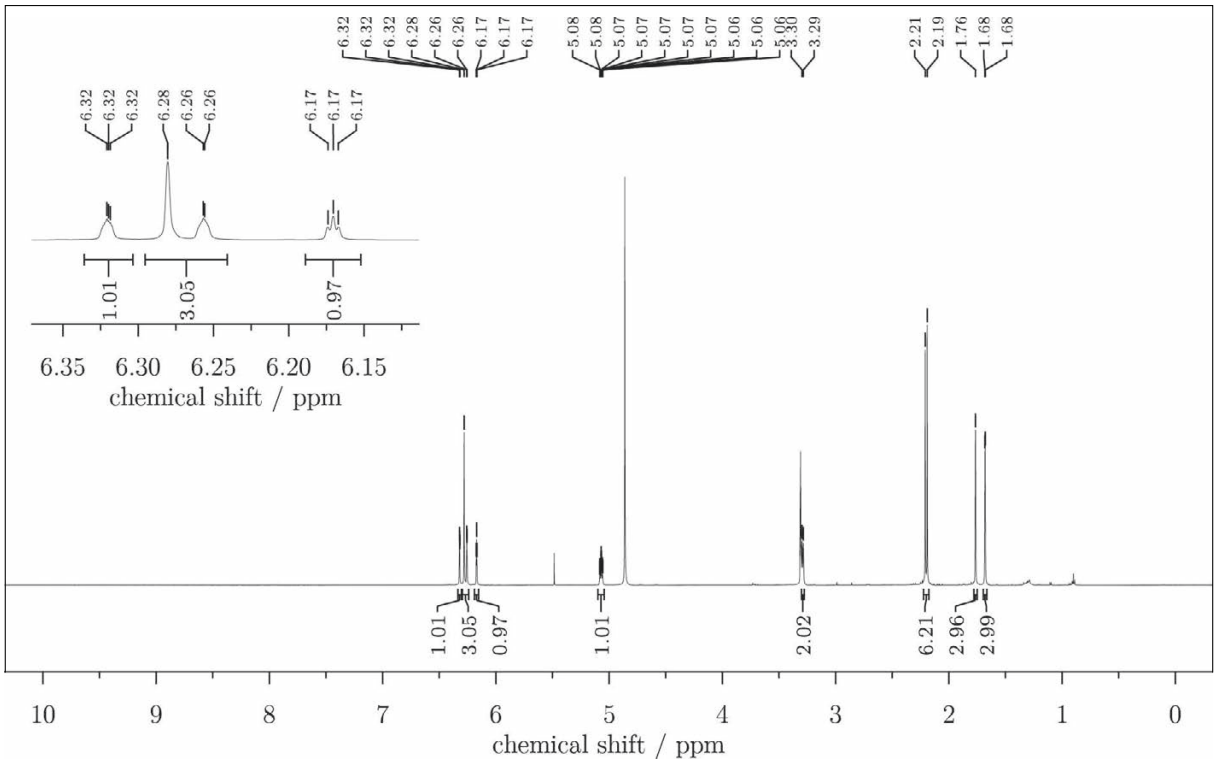


Figure 63: ^{1}H-NMR spectrum of **4** at 600 MHz in methanol-d_4.

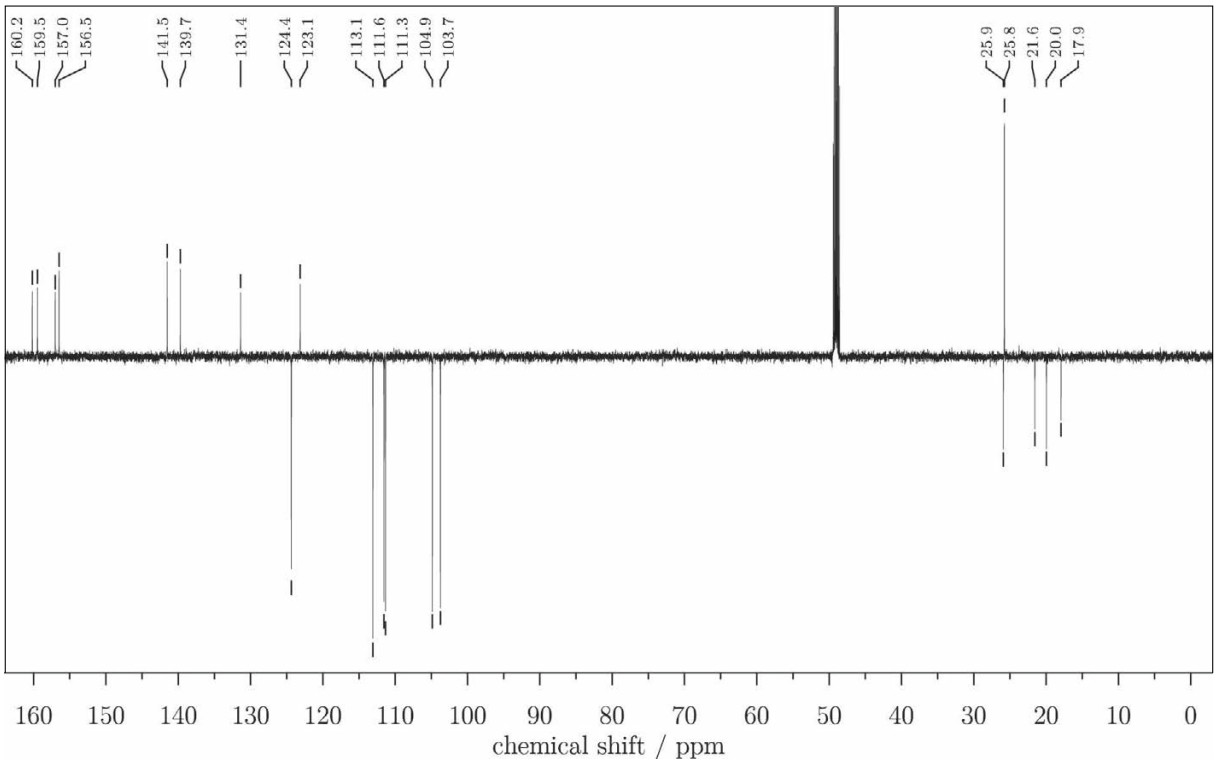


Figure 64: DEPTQ-NMR spectrum of **4** at 151 MHz in methanol-d_4.

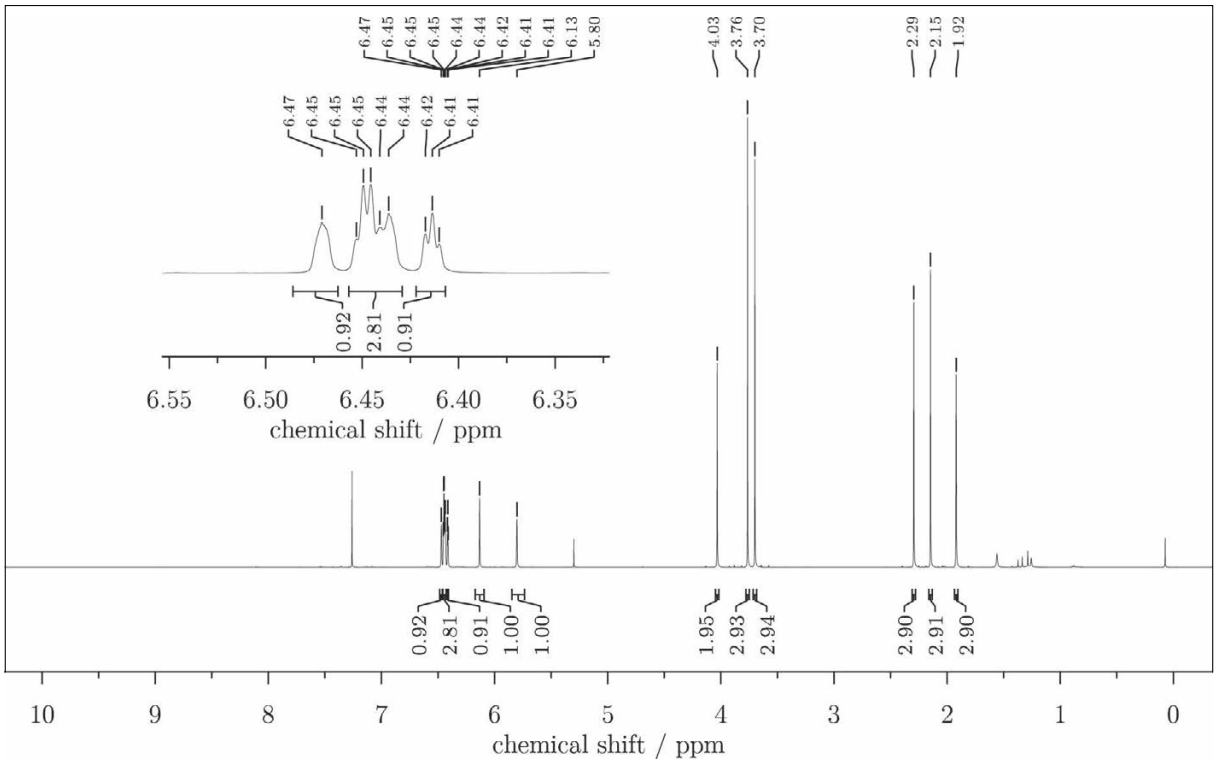


Figure 65: ^{1}H-NMR spectrum of **5** at 600 MHz in $CDCl_3$.

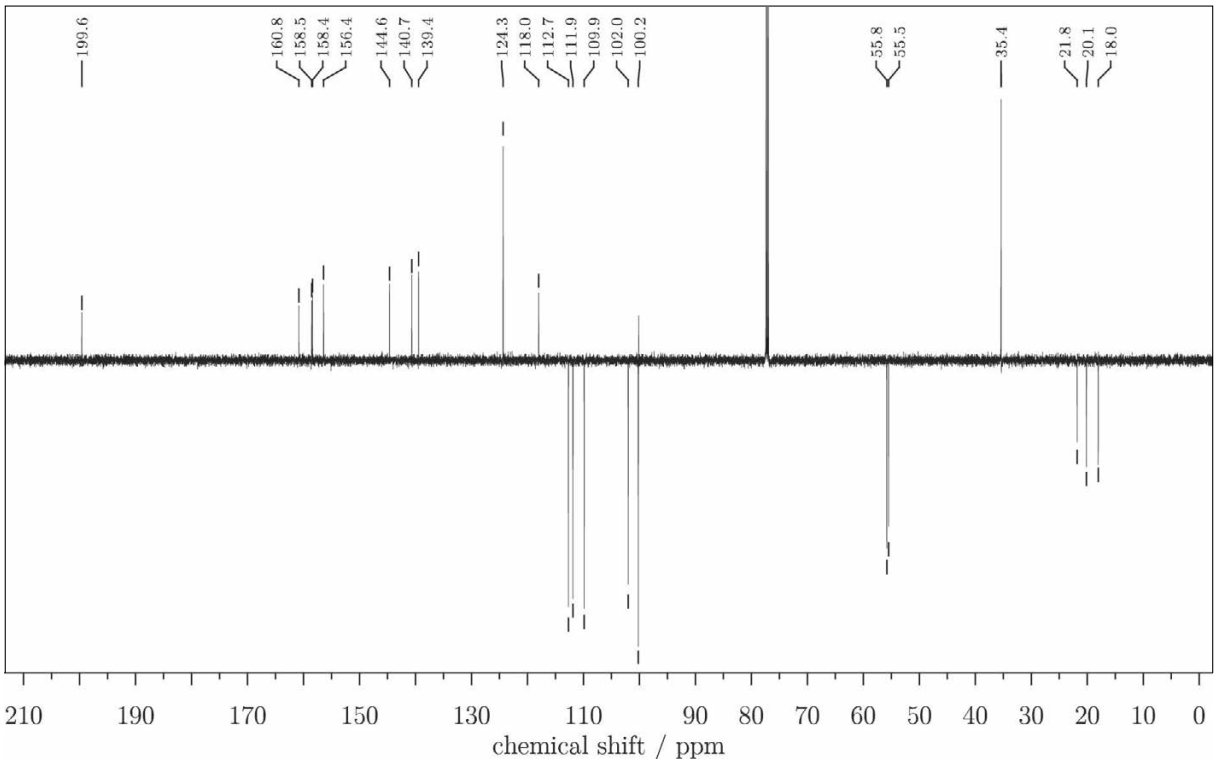


Figure 66: DEPTQ-NMR spectrum of **5** at 151 MHz in $CDCl_3$.

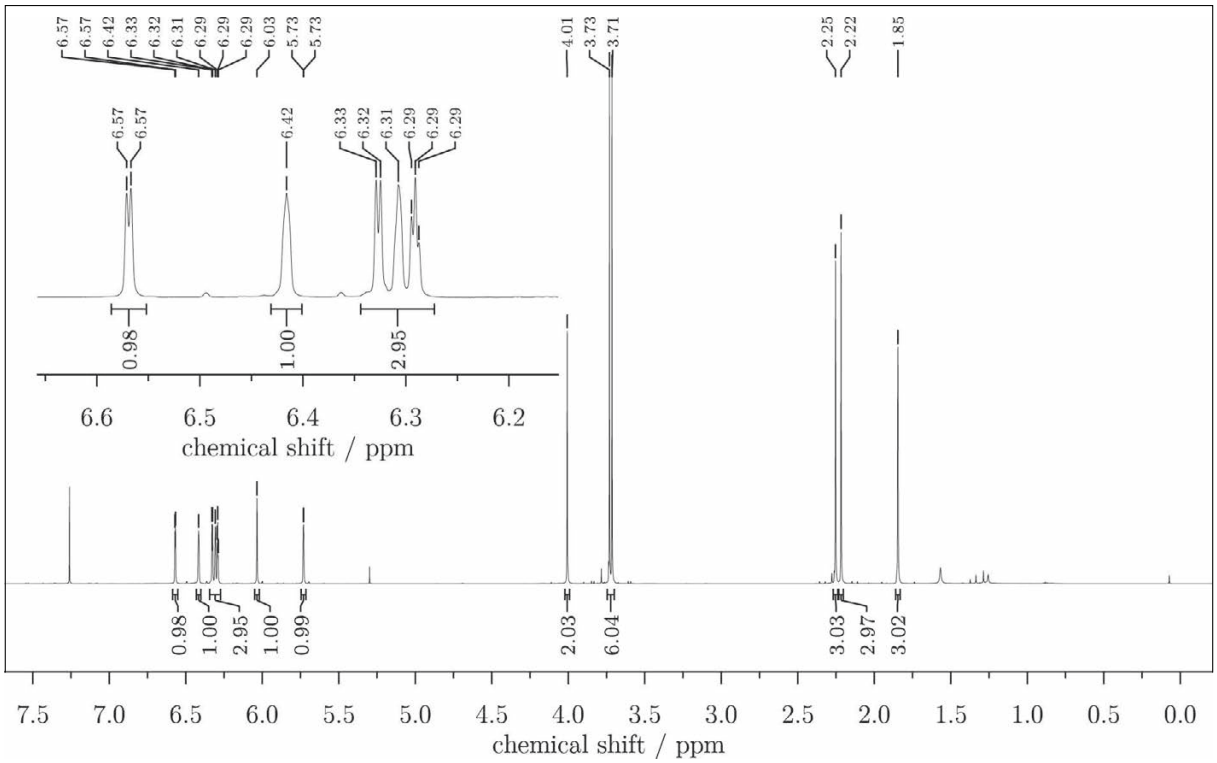


Figure 67: ^{1}H-NMR spectrum of **6** at 600 MHz in $CDCl_3$.

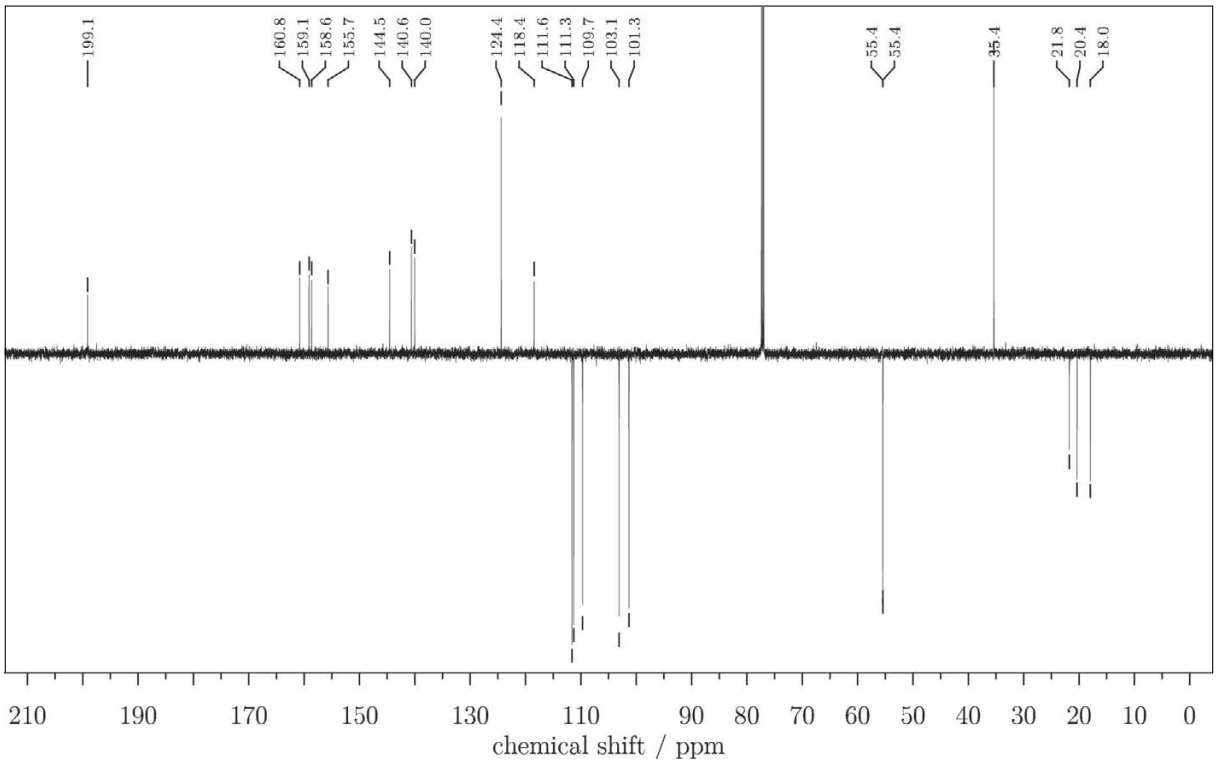


Figure 68: DEPTQ-NMR spectrum of **6** at 151 MHz in $CDCl_3$.

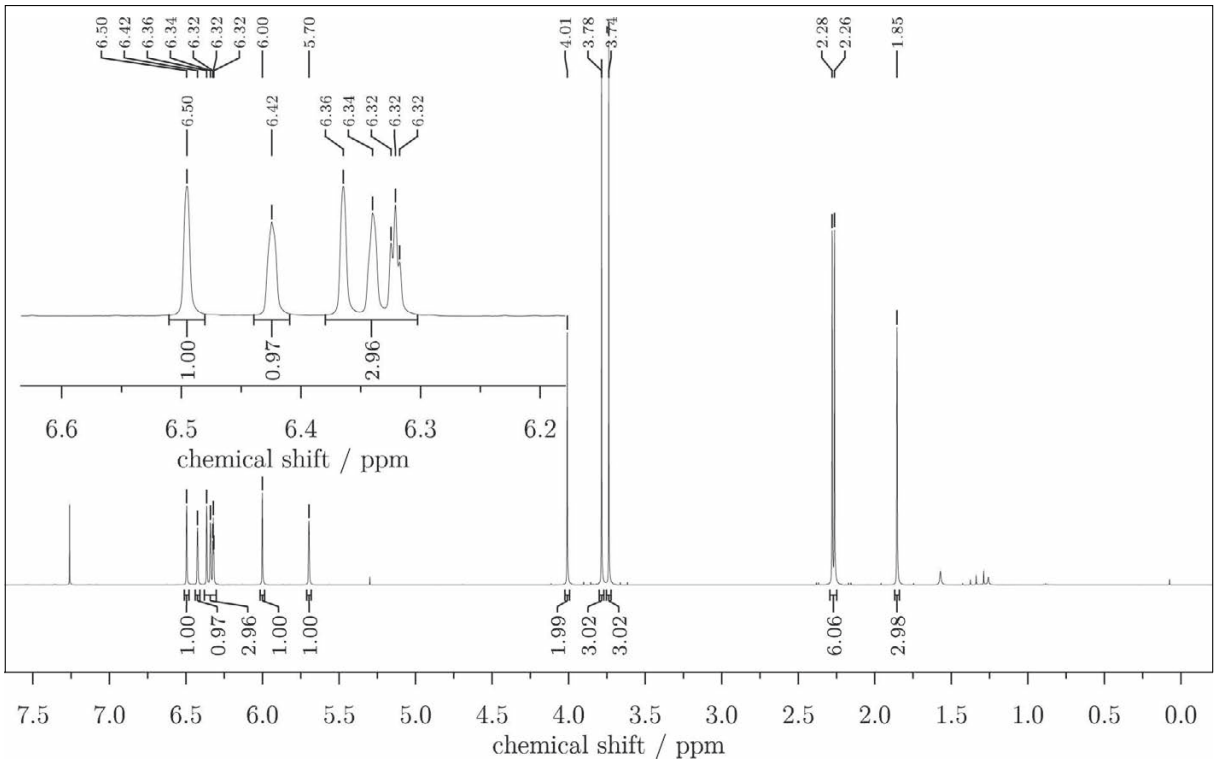


Figure 69: ^{1}H-NMR spectrum of **7** at 600 MHz in $CDCl_3$.

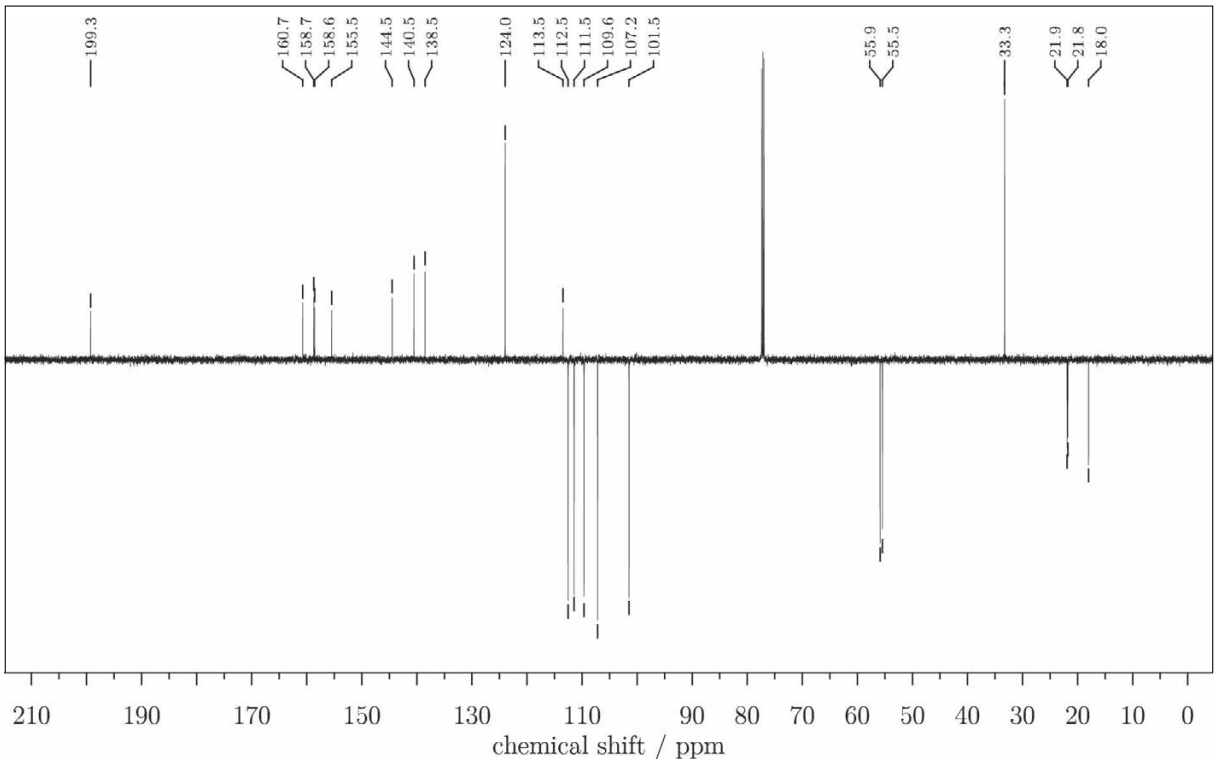


Figure 70: DEPTQ-NMR spectrum of **7** at 151 MHz in $CDCl_3$.

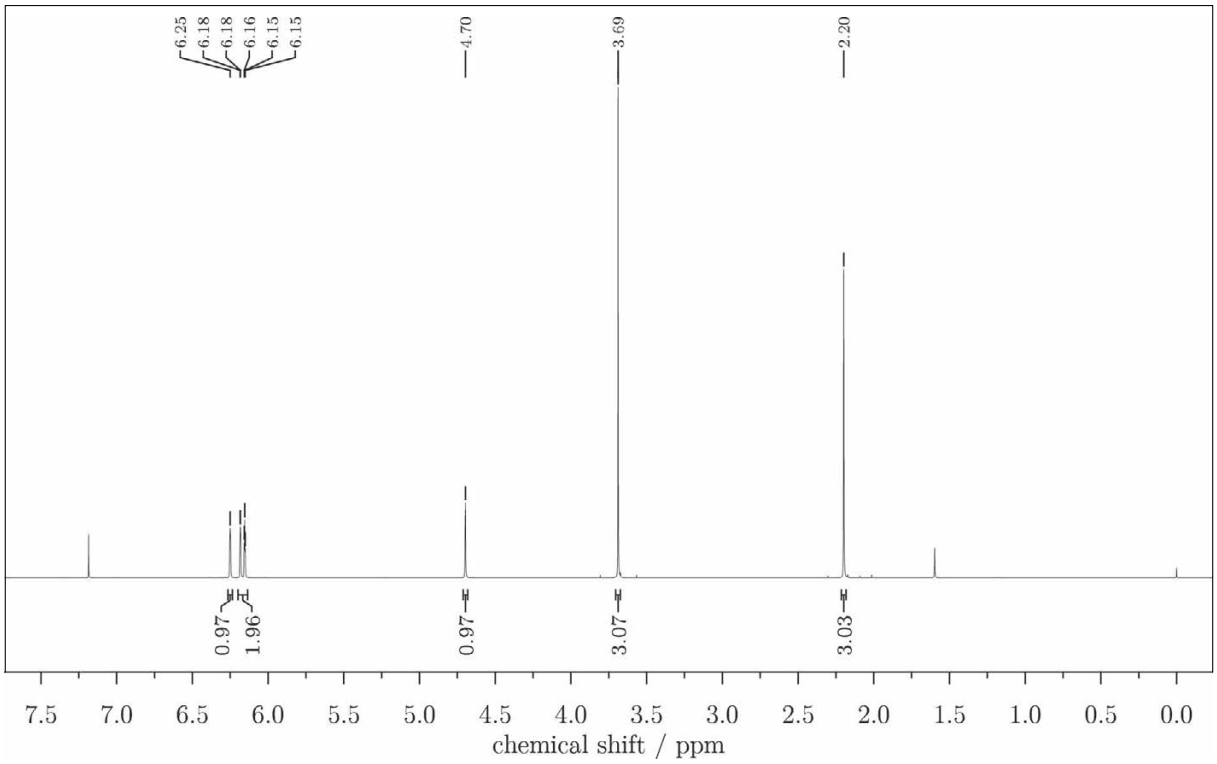


Figure 71: ^{1}H-NMR spectrum of **8** at 600 MHz in $CDCl_3$.

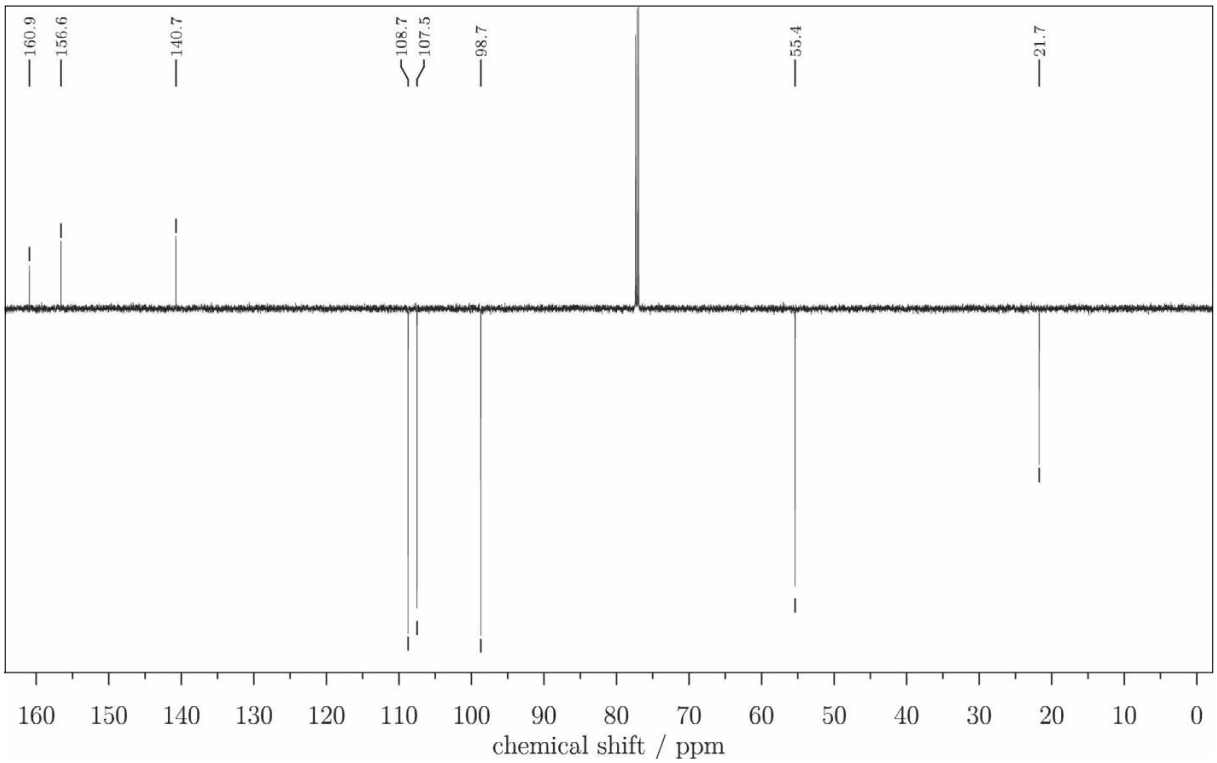


Figure 72: DEPTQ-NMR spectrum of **8** at 151 MHz in $CDCl_3$.

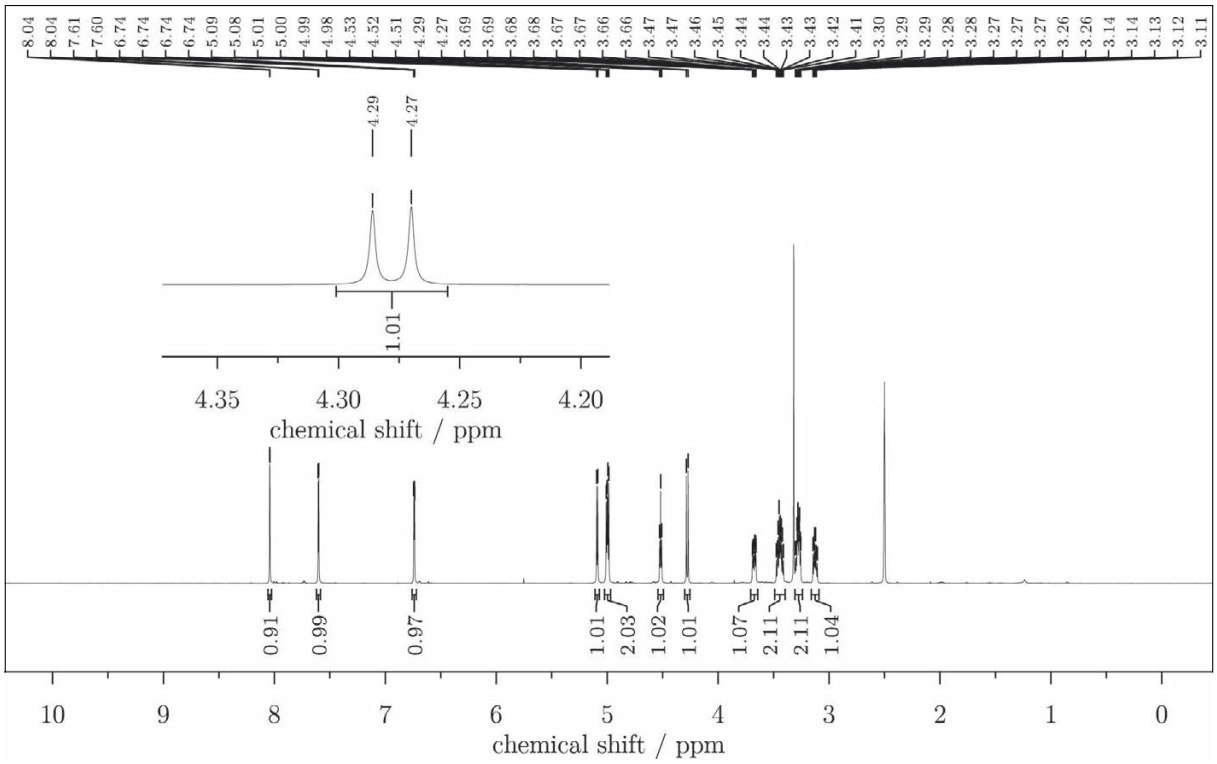


Figure 73: [1]H-NMR spectrum of **12** at 600 MHz in DMSO-d_6.

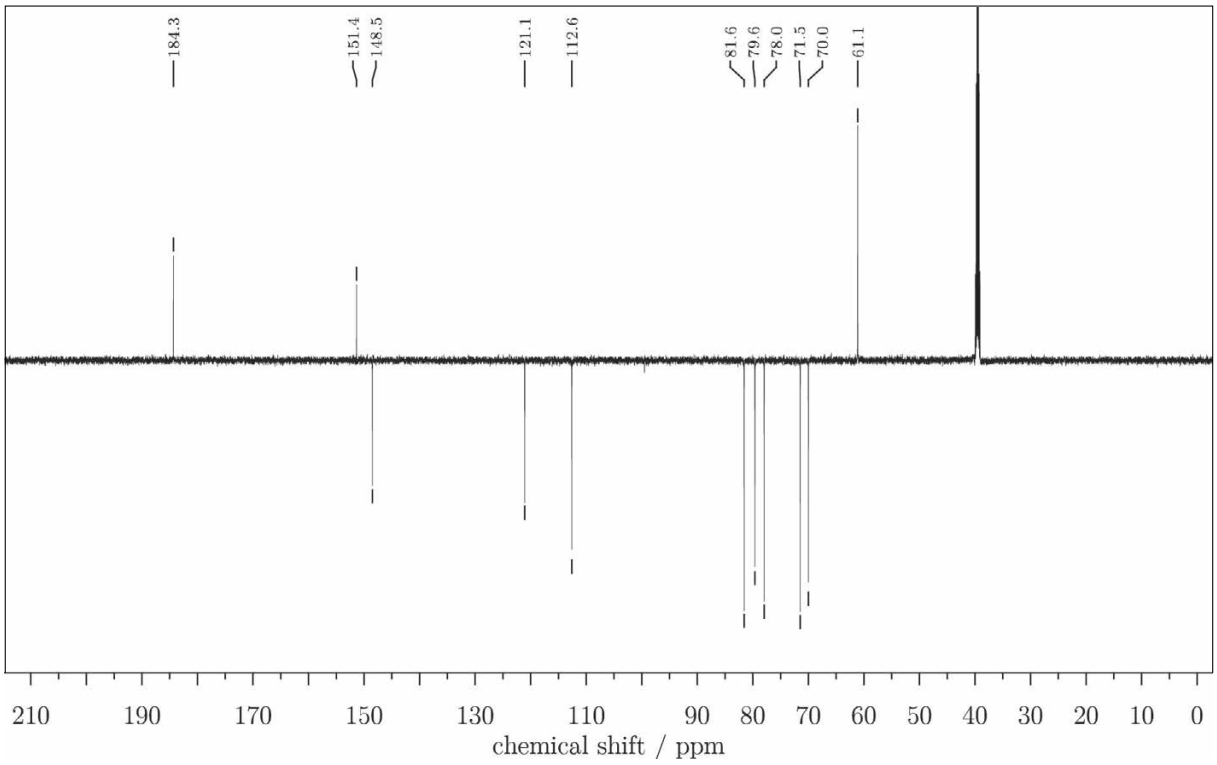


Figure 74: DEPTQ-NMR spectrum of **12** at 151 MHz in DMSO-d_6.

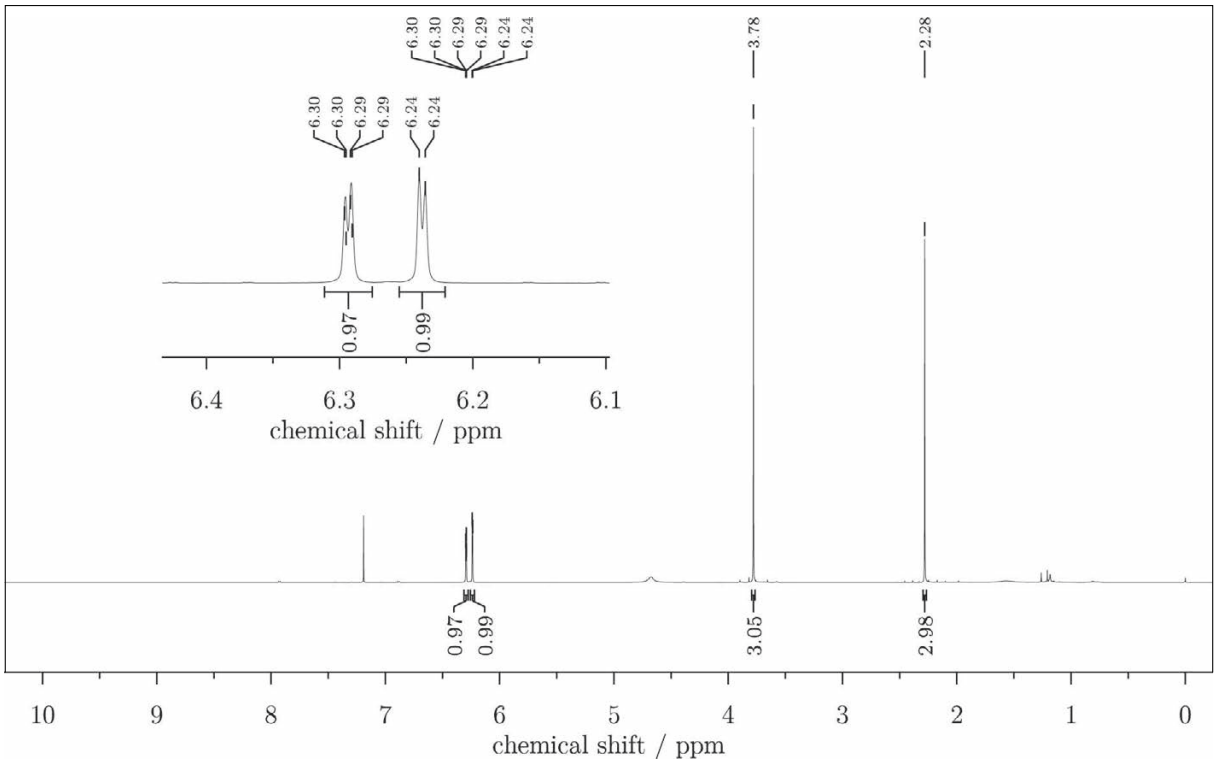


Figure 75: ^{1}H-NMR spectrum of **124** at 600 MHz in $CDCl_3$.

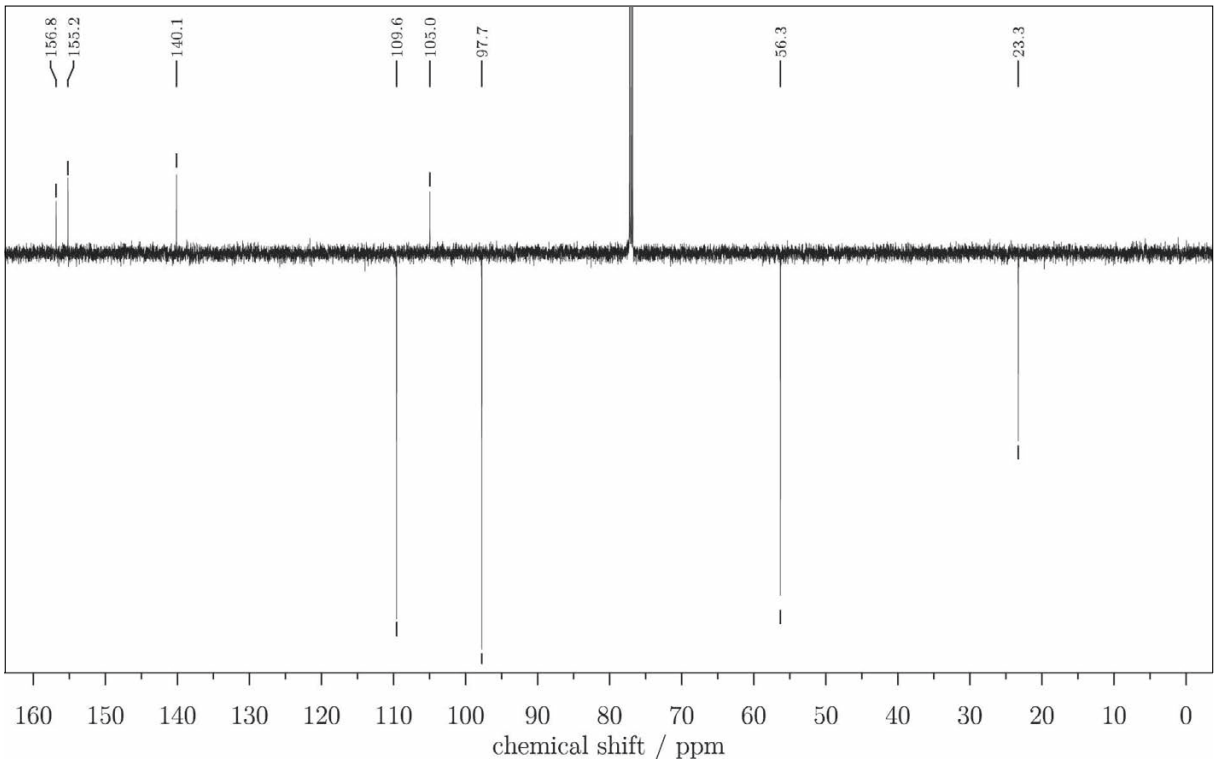


Figure 76: DEPTQ-NMR spectrum of **124** at 151 MHz in $CDCl_3$.

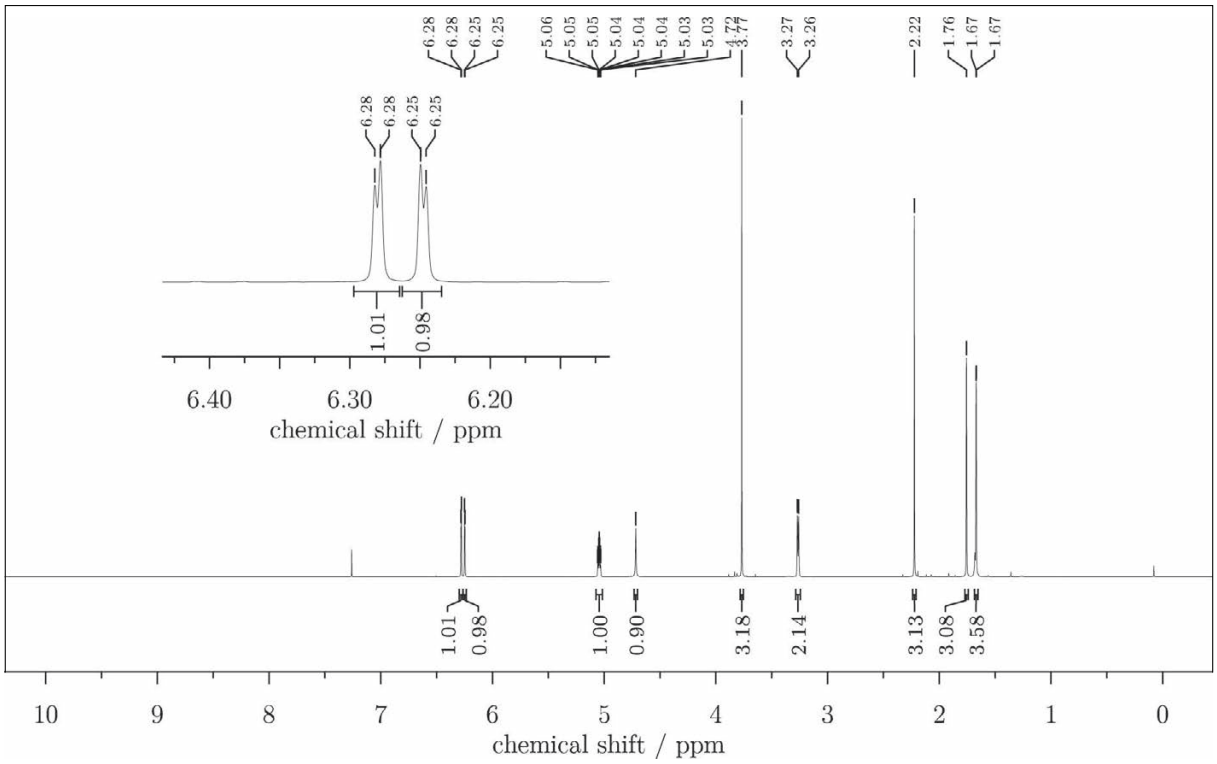


Figure 77: ^{1}H-NMR spectrum of **125** at 600 MHz in $CDCl_3$.

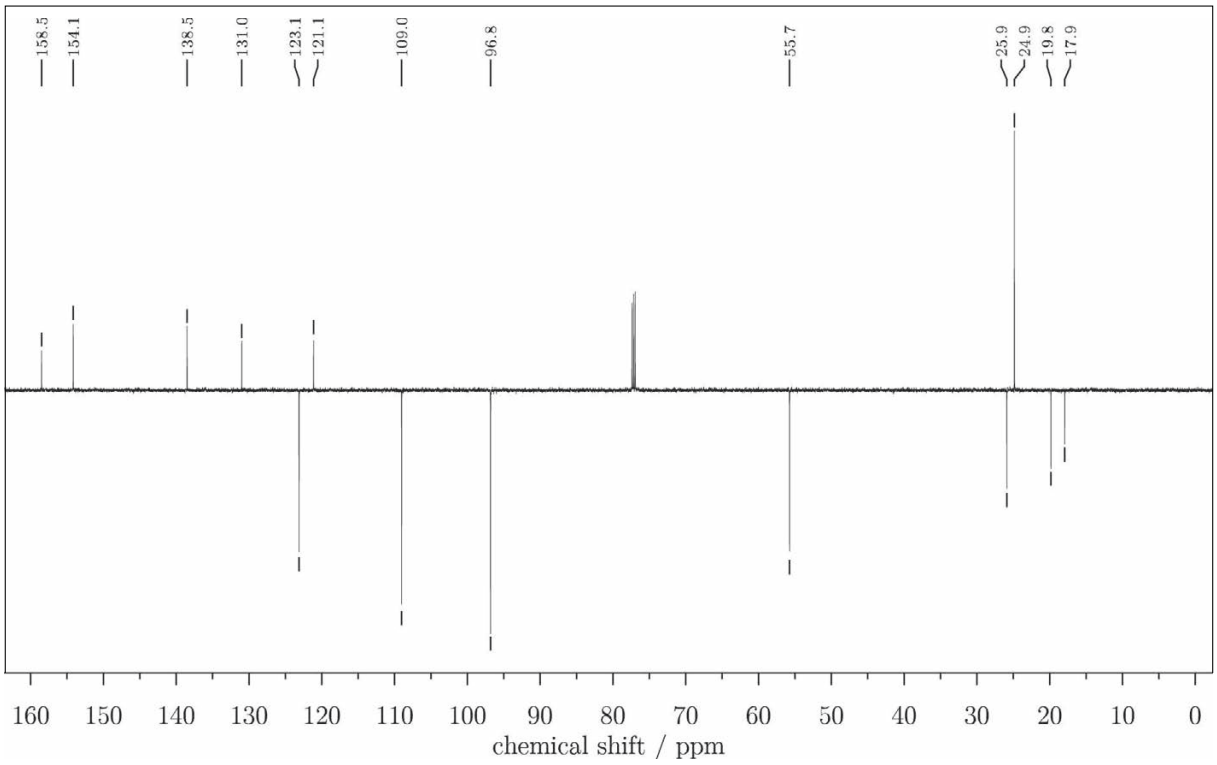


Figure 78: DEPTQ-NMR spectrum of **125** at 151 MHz in $CDCl_3$.

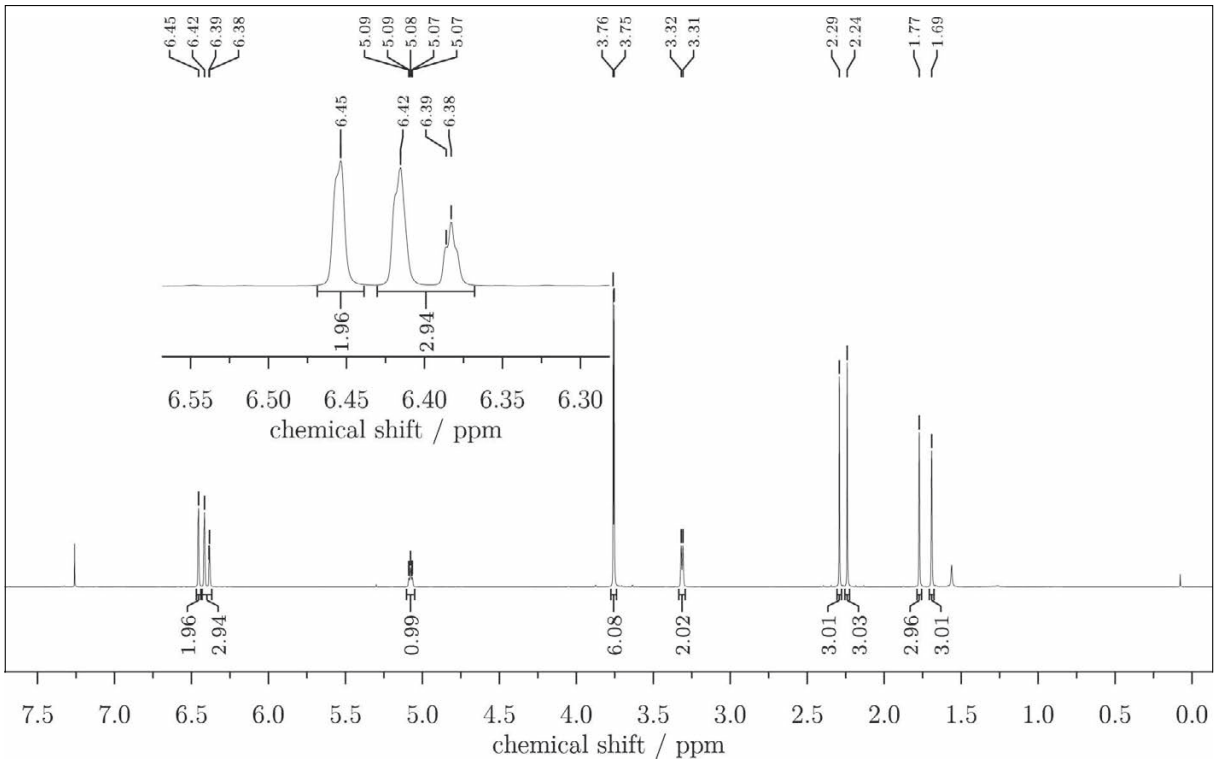


Figure 79: ^{1}H-NMR spectrum of **126** at 600 MHz in $CDCl_3$.

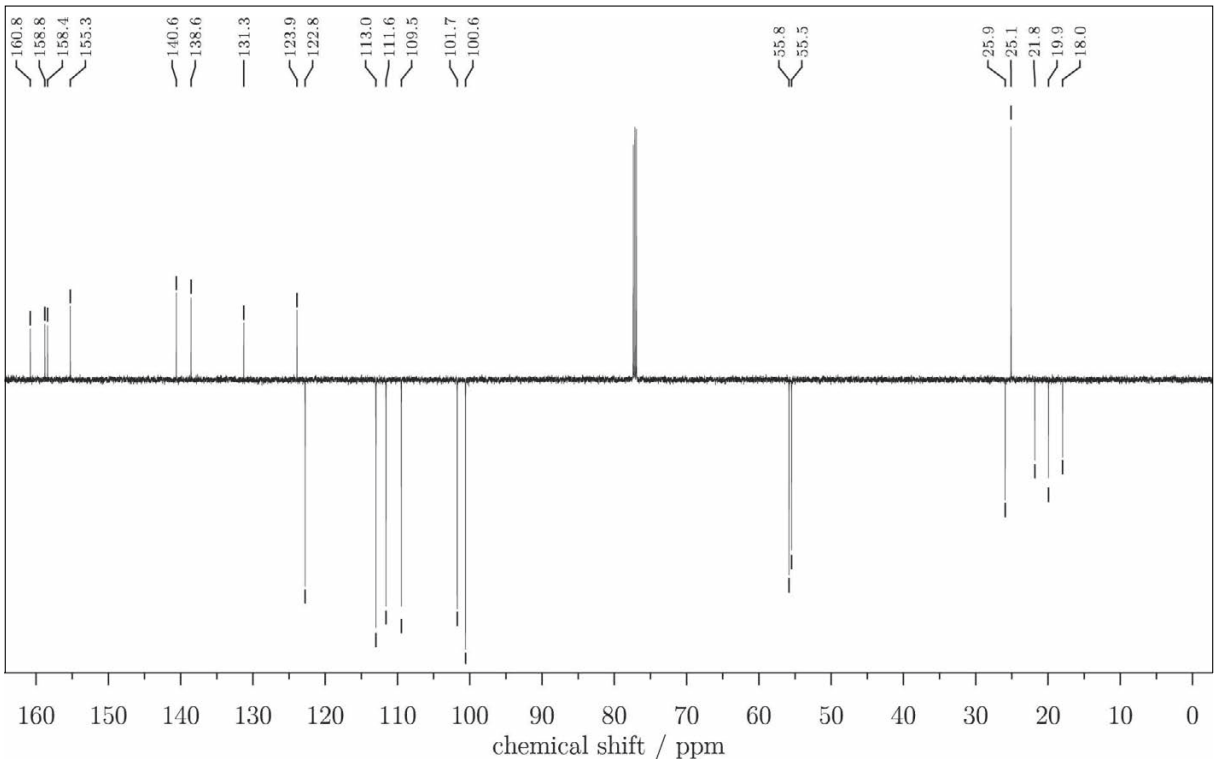


Figure 80: DEPTQ-NMR spectrum of **126** at 151 MHz in $CDCl_3$.

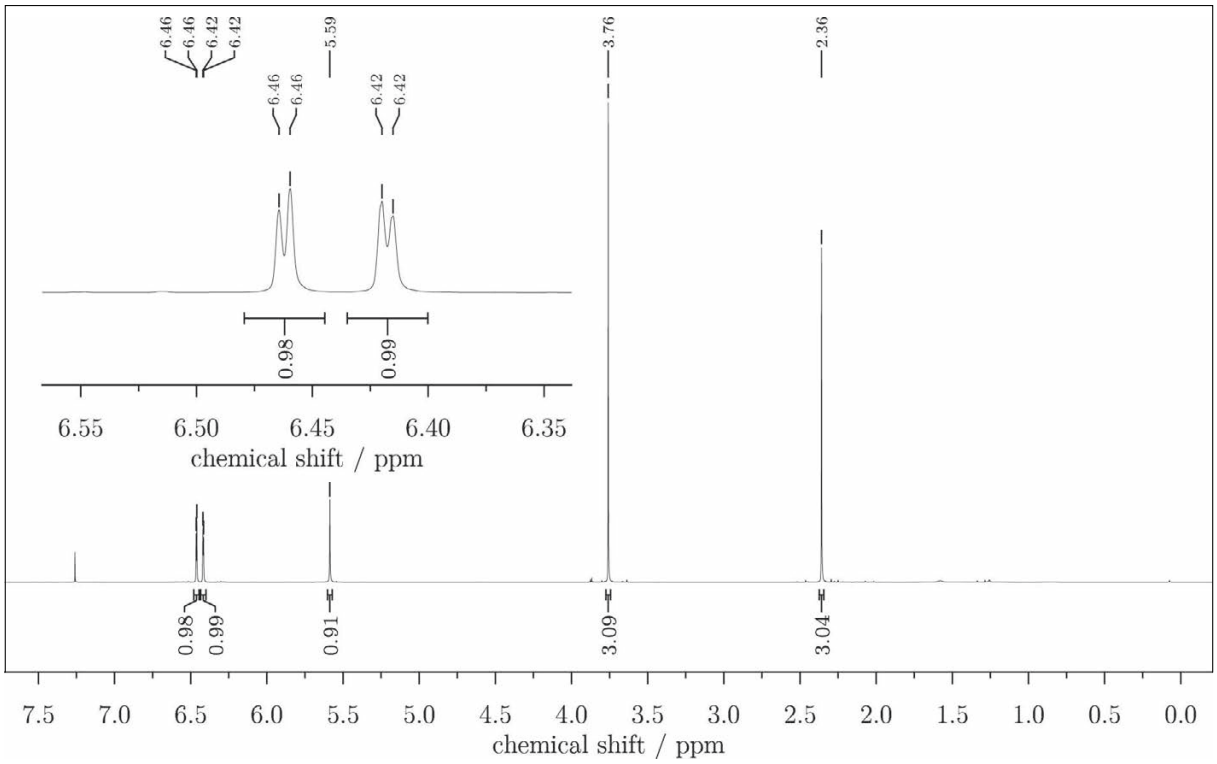


Figure 81: ^{1}H-NMR spectrum of **133** at 600 MHz in $CDCl_3$.

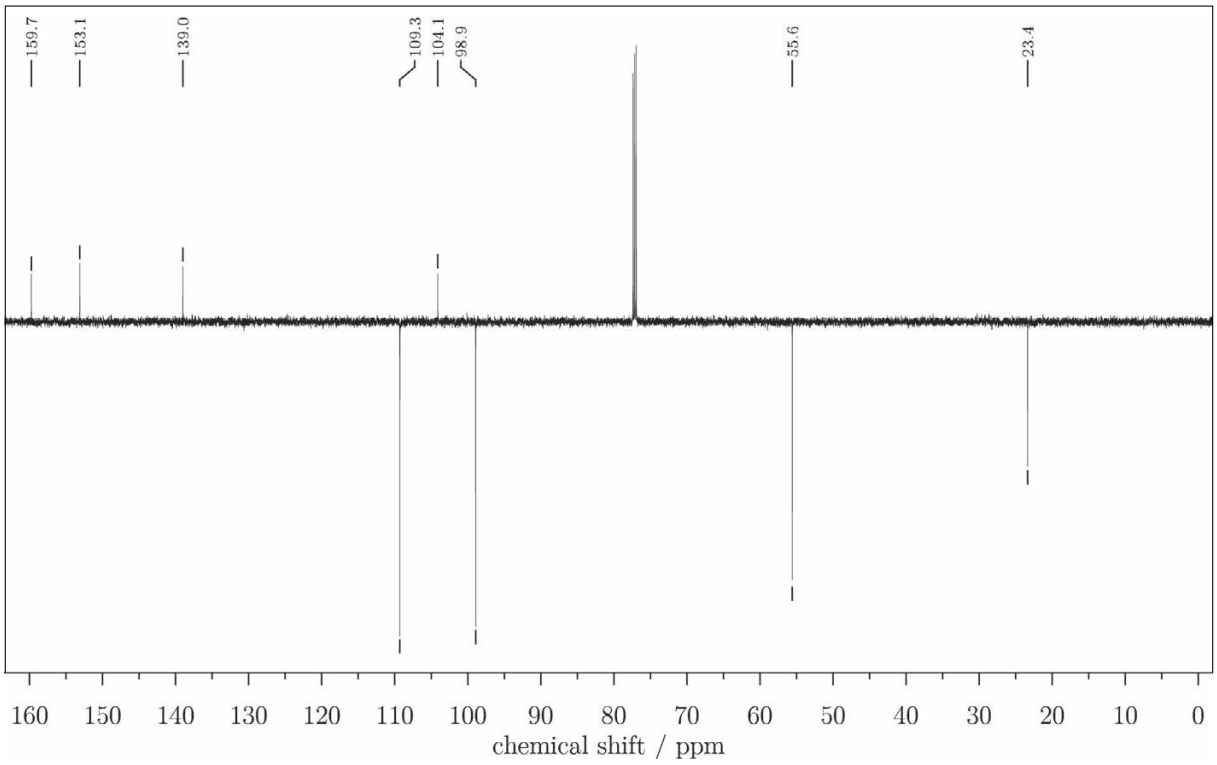


Figure 82: DEPTQ-NMR spectrum of **133** at 151 MHz in $CDCl_3$.

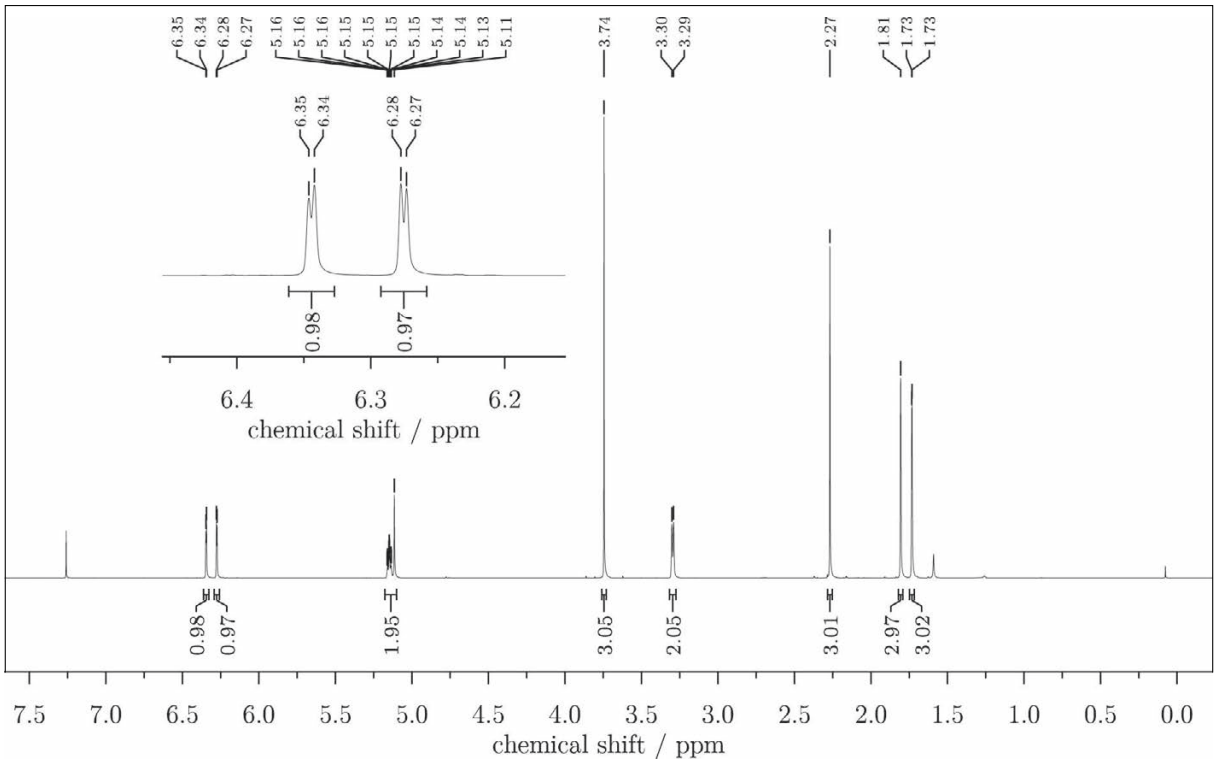


Figure 83: ^{1}H-NMR spectrum of **135** at 600 MHz in $CDCl_3$.

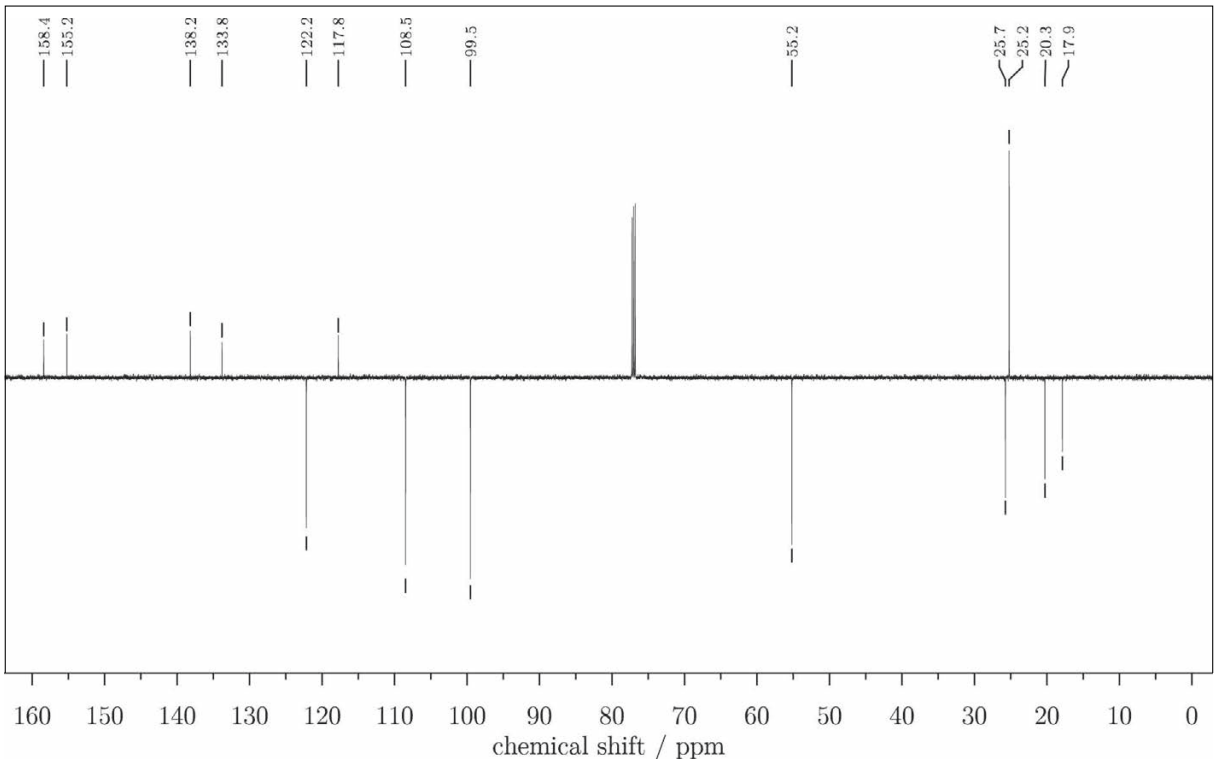


Figure 84: DEPTQ-NMR spectrum of **135** at 151 MHz in $CDCl_3$.

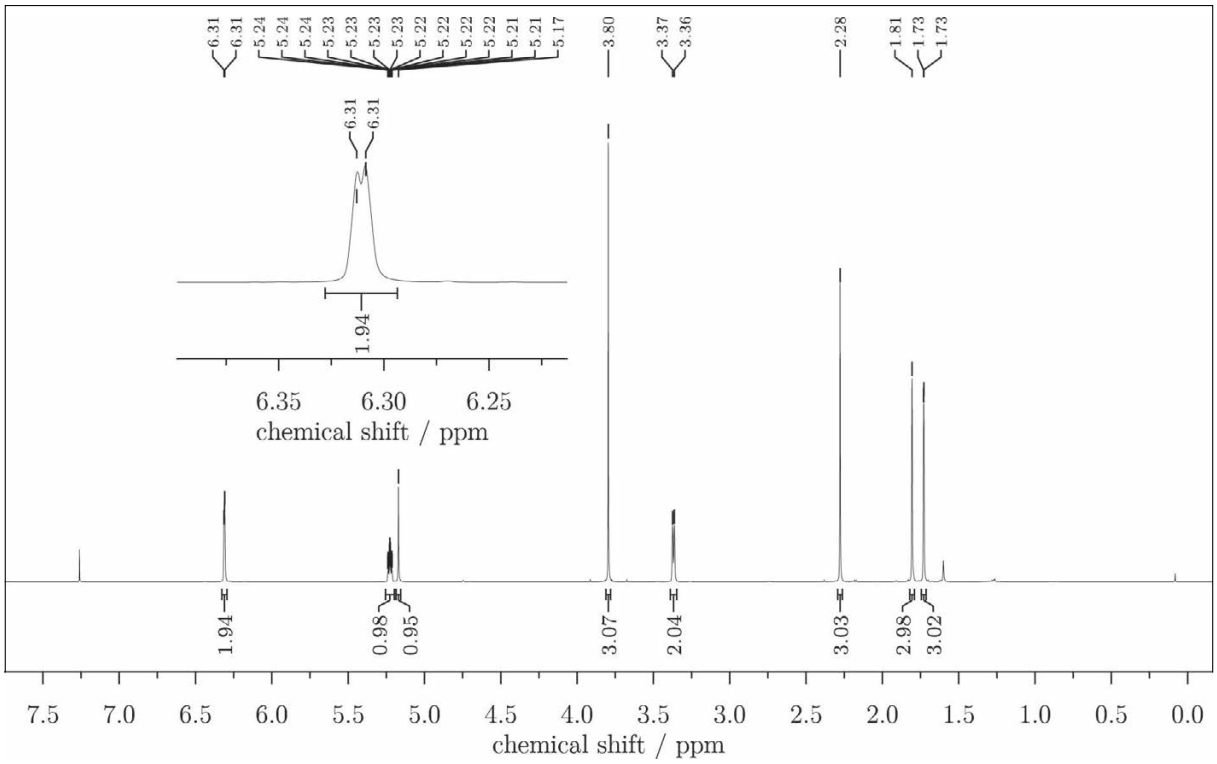


Figure 85: ^{1}H-NMR spectrum of **136** at 600 MHz in $CDCl_3$.

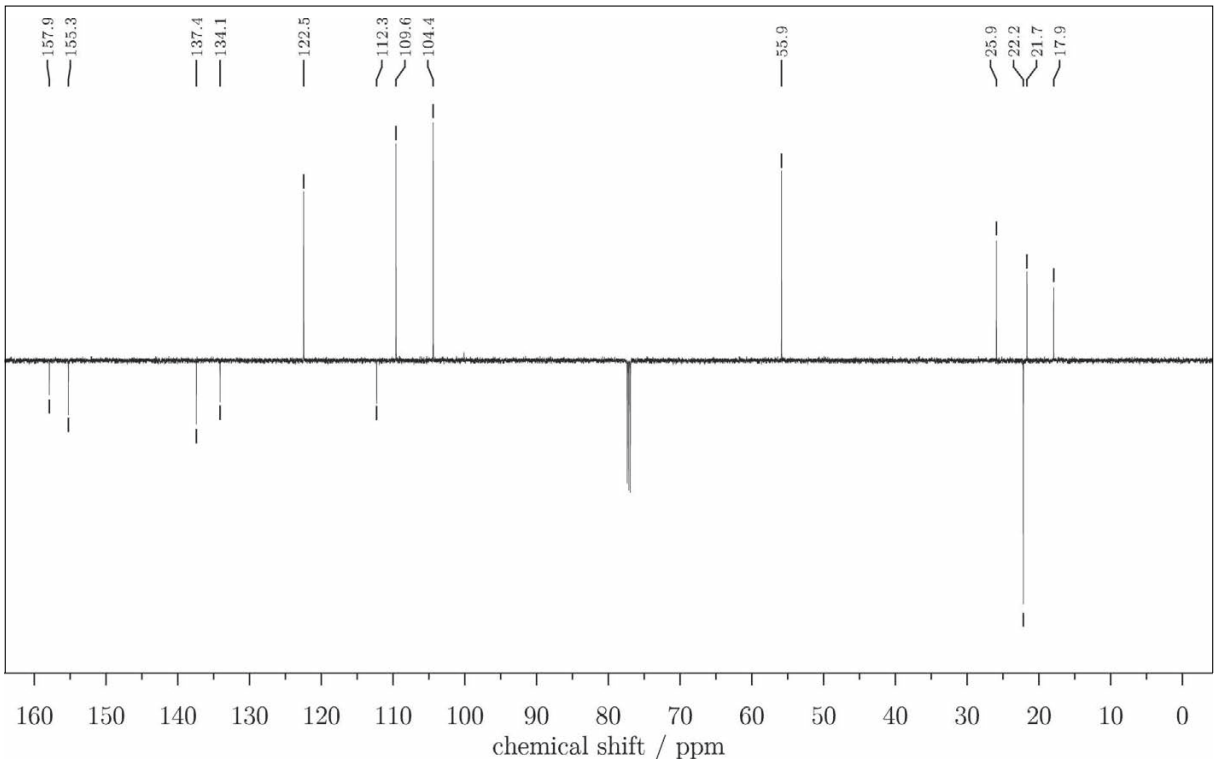


Figure 86: DEPTQ-NMR spectrum of **136** at 151 MHz in $CDCl_3$.

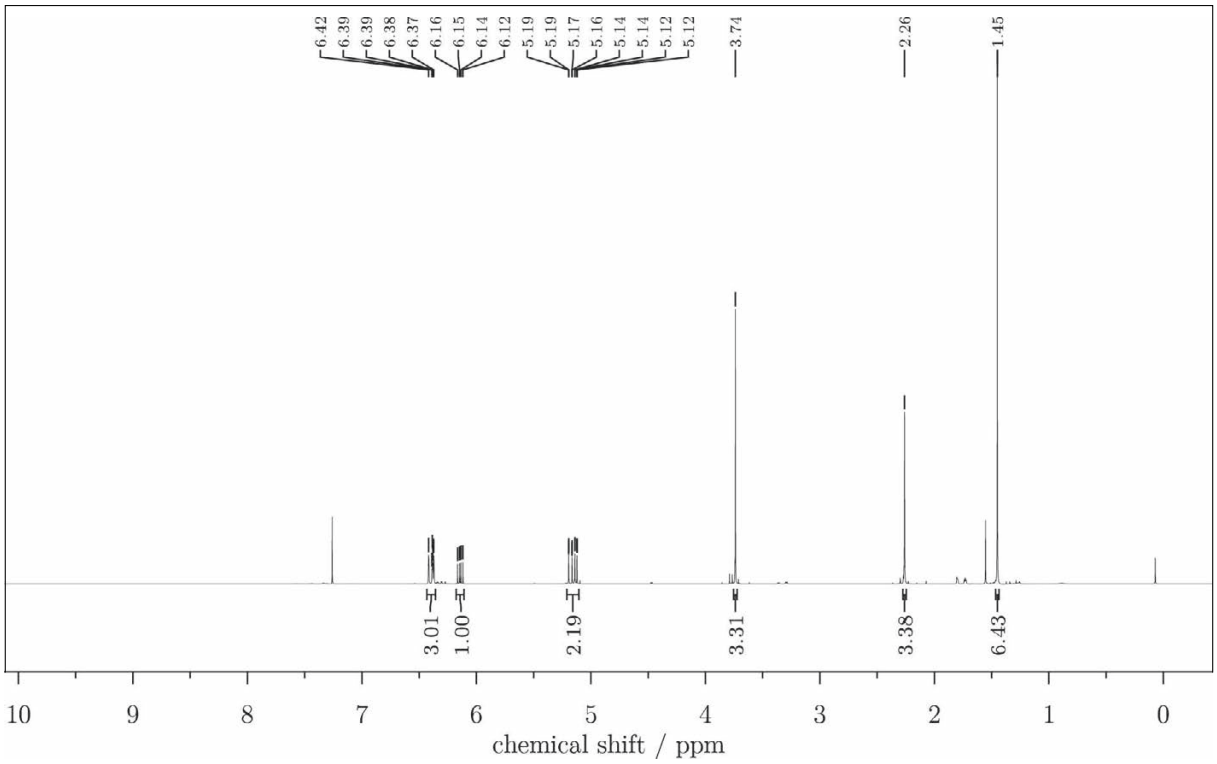


Figure 87: ^{1}H-NMR spectrum of **137** at 600 MHz in $CDCl_3$.

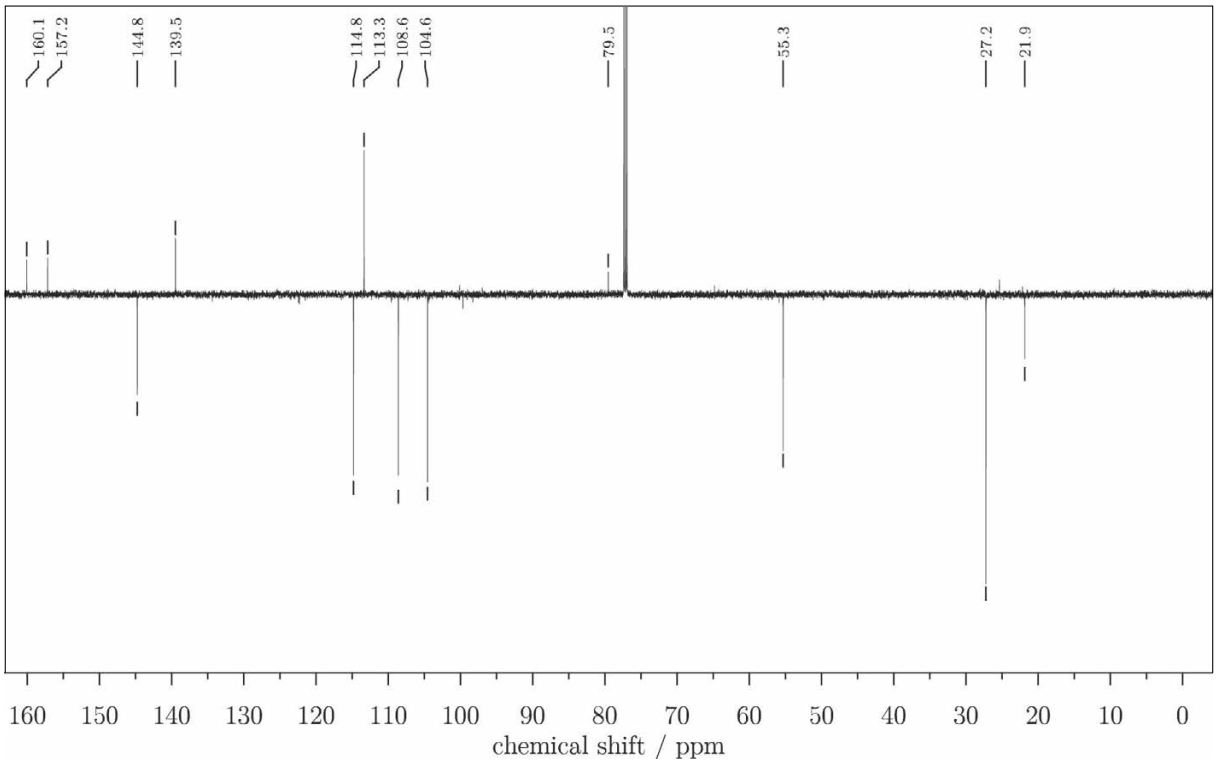


Figure 88: DEPTQ-NMR spectrum of **137** at 151 MHz in $CDCl_3$.

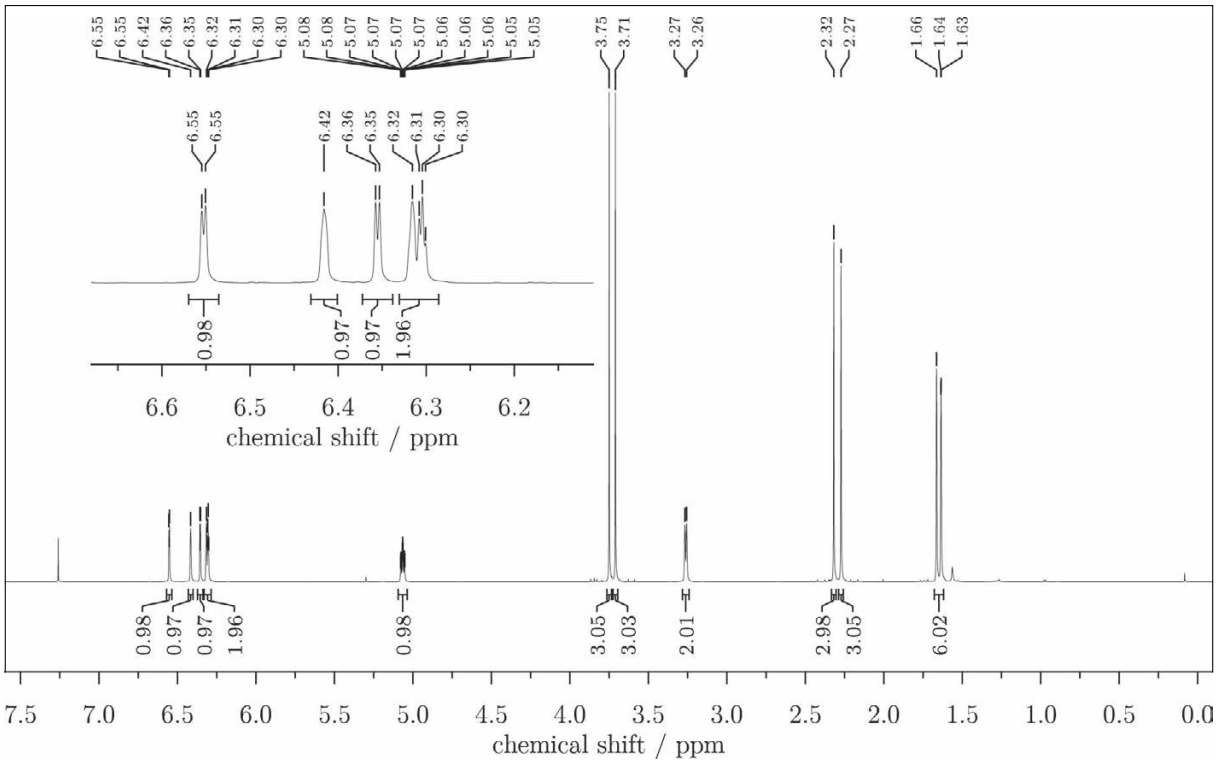


Figure 89: ^{1}H-NMR spectrum of **140** at 600 MHz in $CDCl_3$.

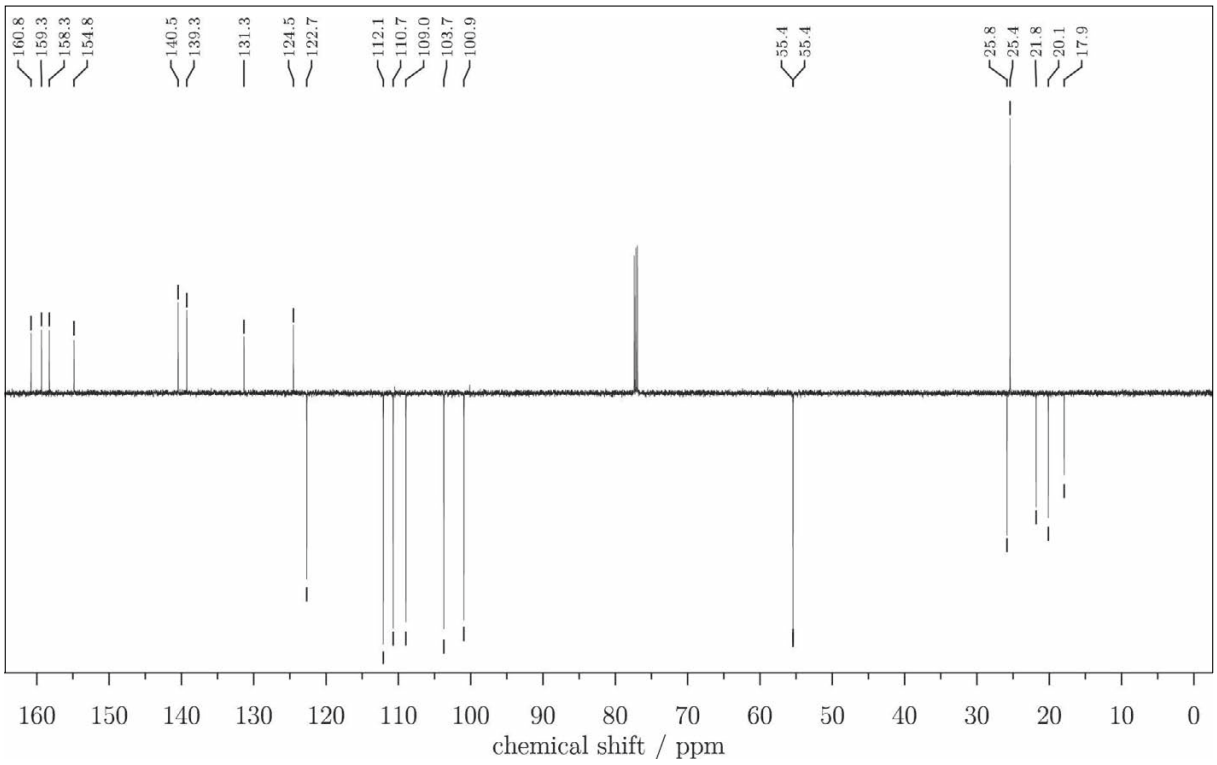


Figure 90: DEPTQ-NMR spectrum of **140** at 151 MHz in $CDCl_3$.

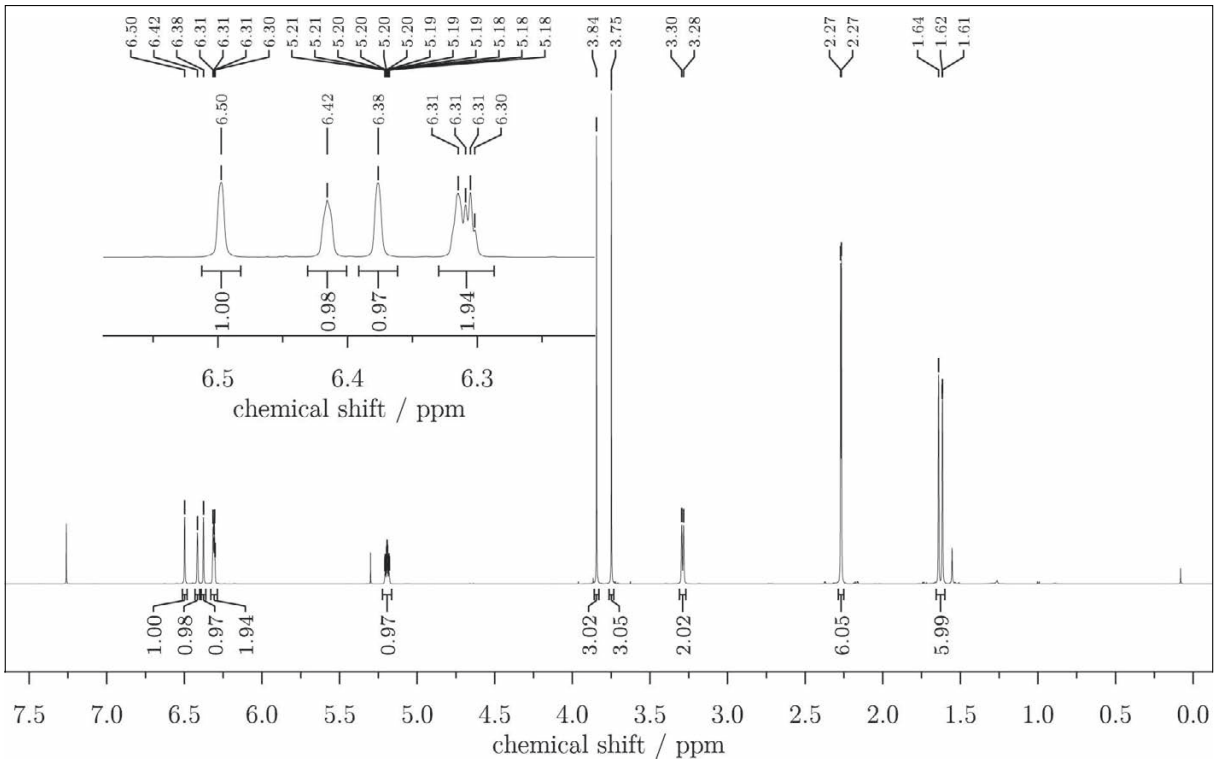


Figure 91: ^{1}H-NMR spectrum of **141** at 600 MHz in $CDCl_3$.

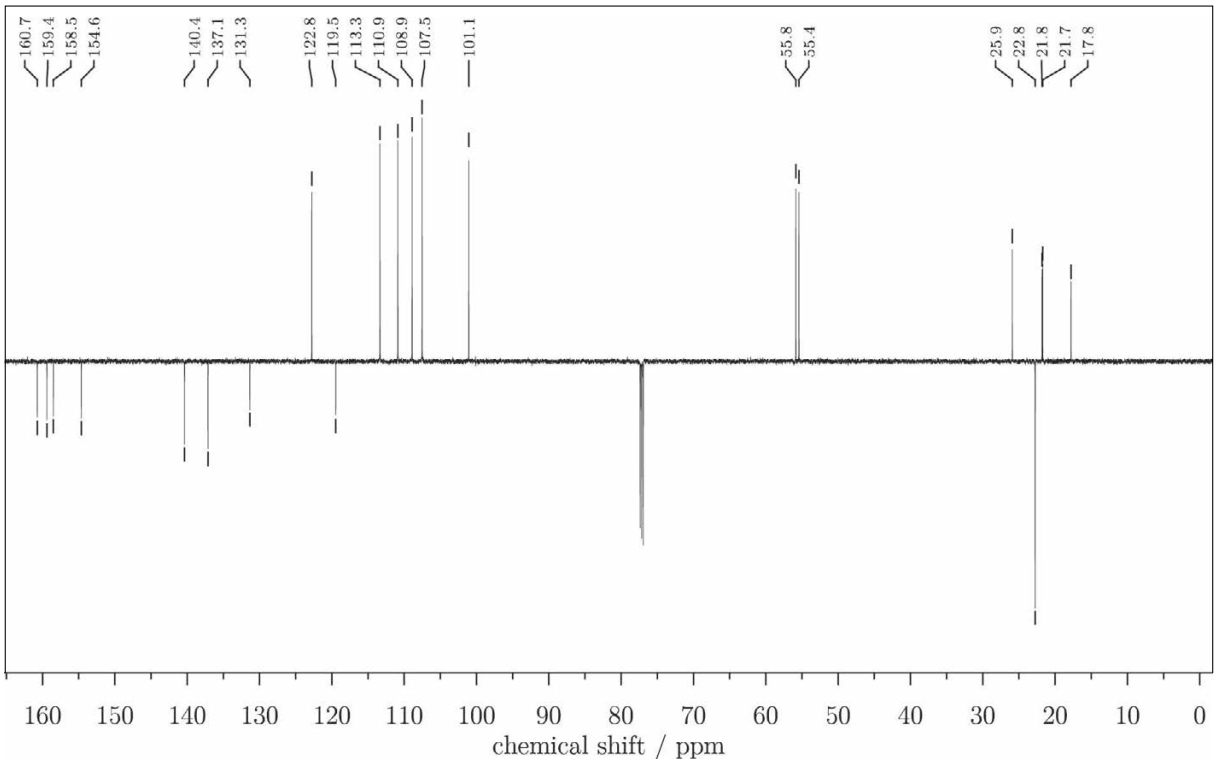


Figure 92: DEPTQ-NMR spectrum of **141** at 151 MHz in $CDCl_3$.

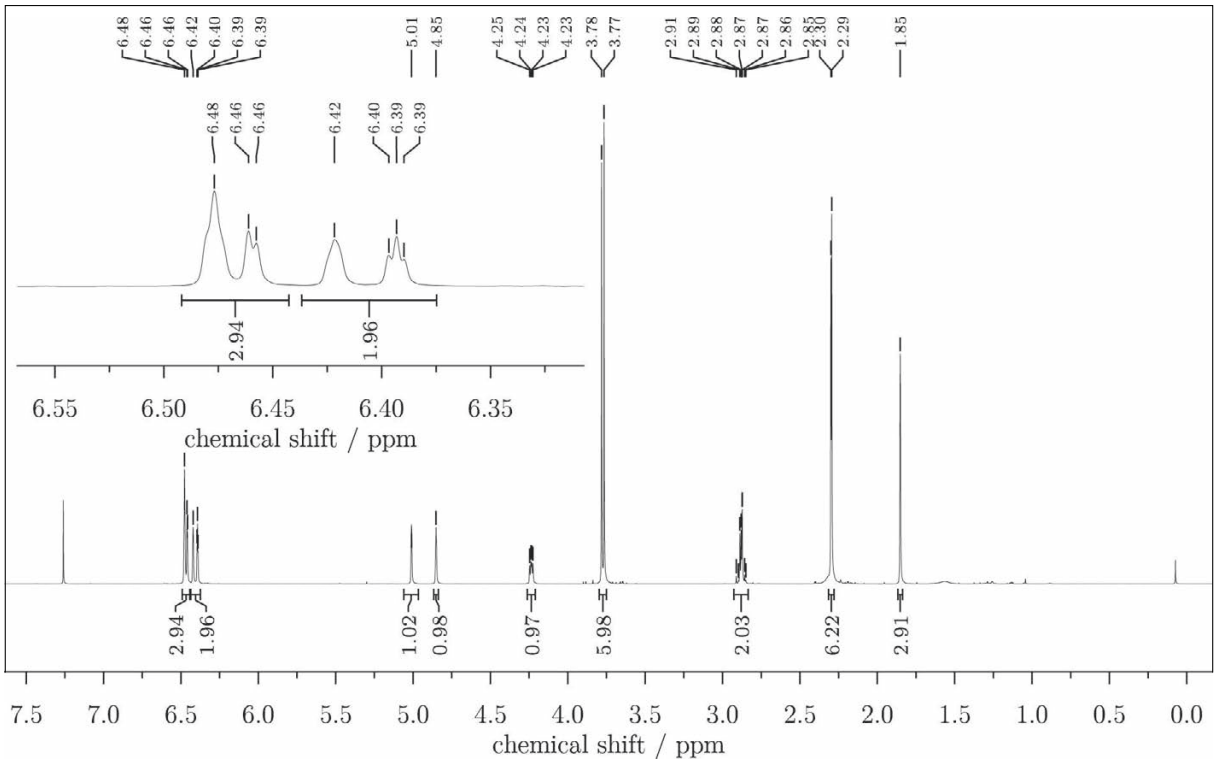


Figure 93: ^{1}H-NMR spectrum of **142** at 600 MHz in $CDCl_3$.

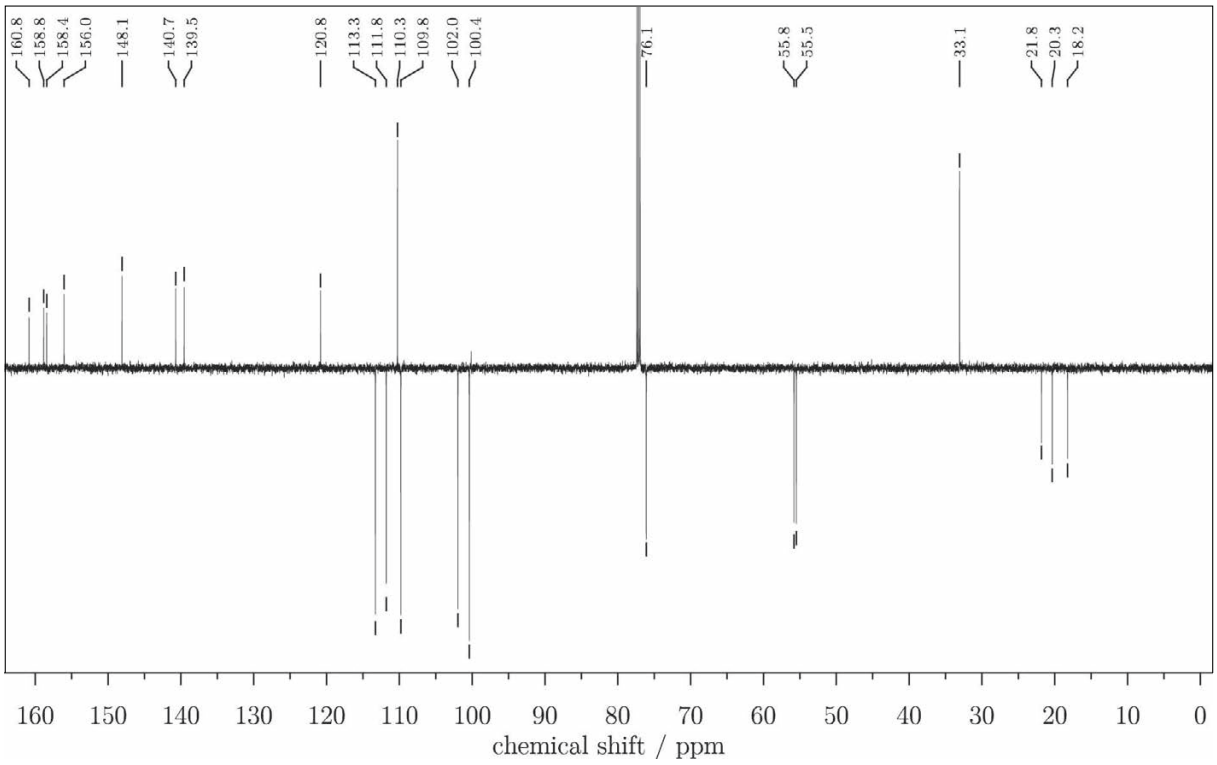


Figure 94: DEPTQ-NMR spectrum of **142** at 151 MHz in $CDCl_3$.

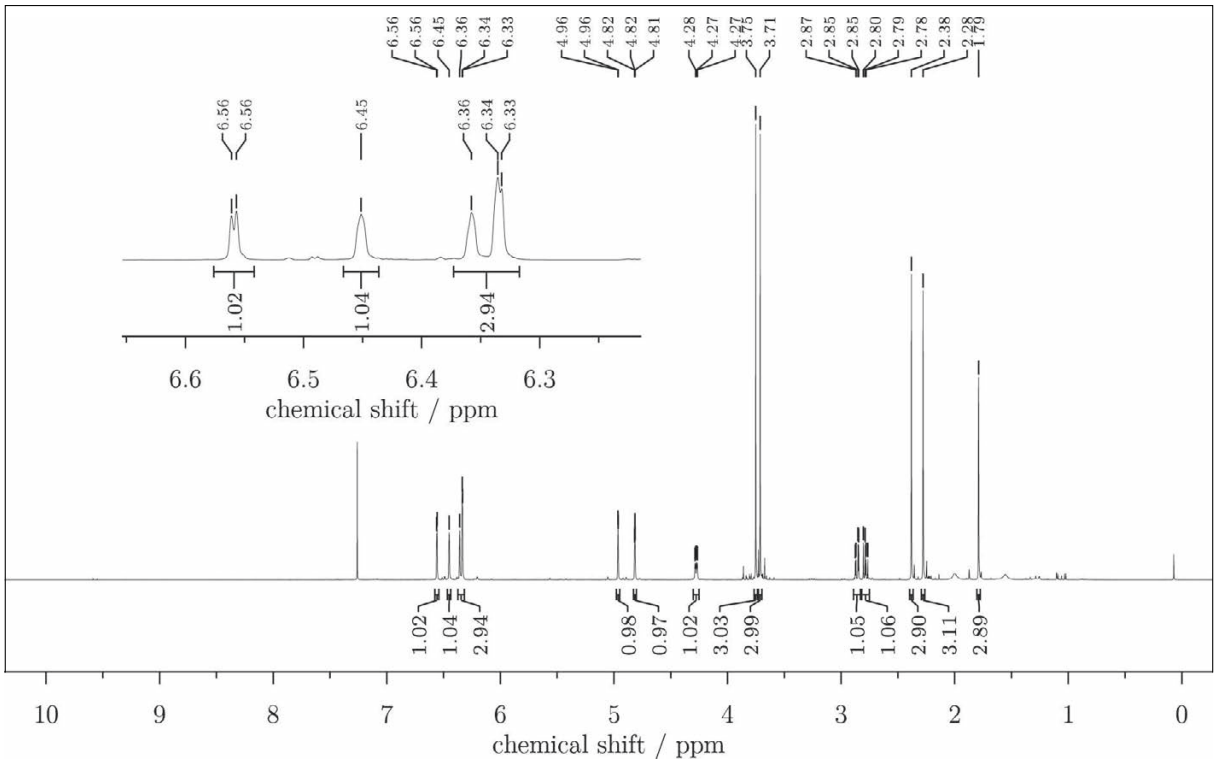


Figure 95: ^{1}H-NMR spectrum of **144** at 600 MHz in $CDCl_3$.

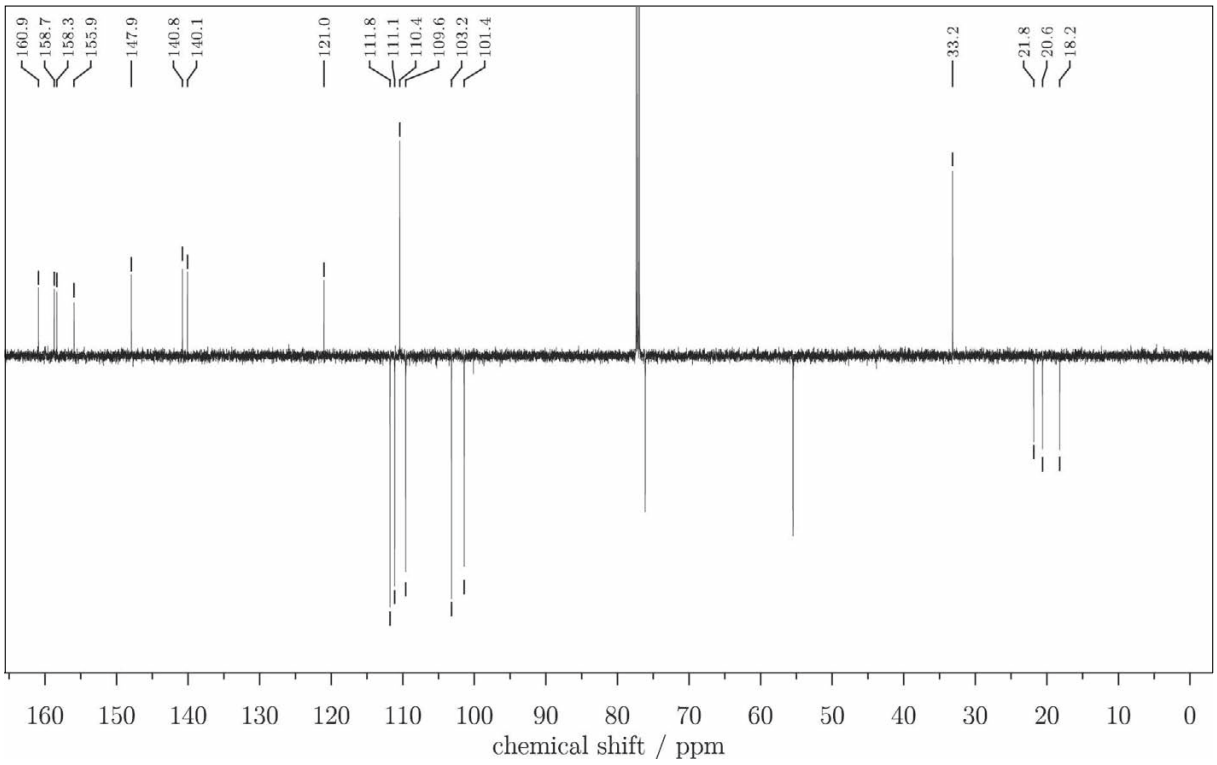


Figure 96: DEPTQ-NMR spectrum of **144** at 151 MHz in $CDCl_3$.

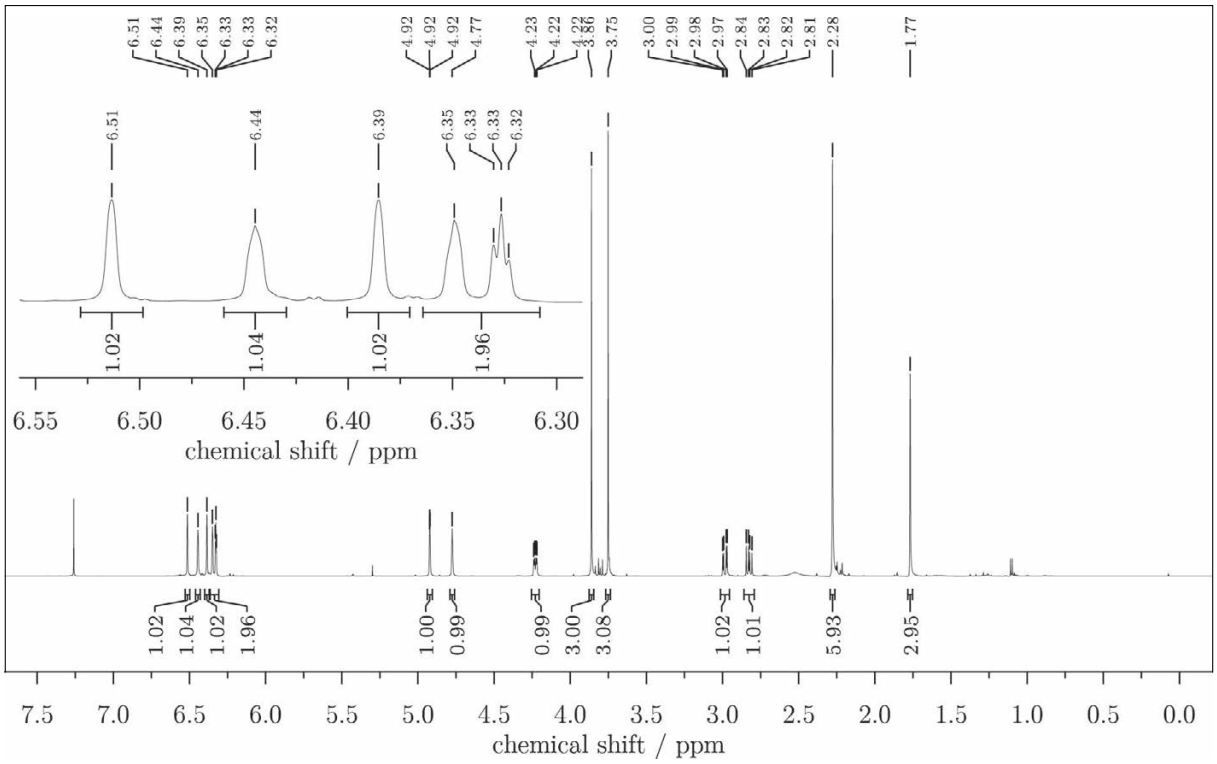


Figure 97: ^{1}H-NMR spectrum of **145** at 600 MHz in $CDCl_3$.

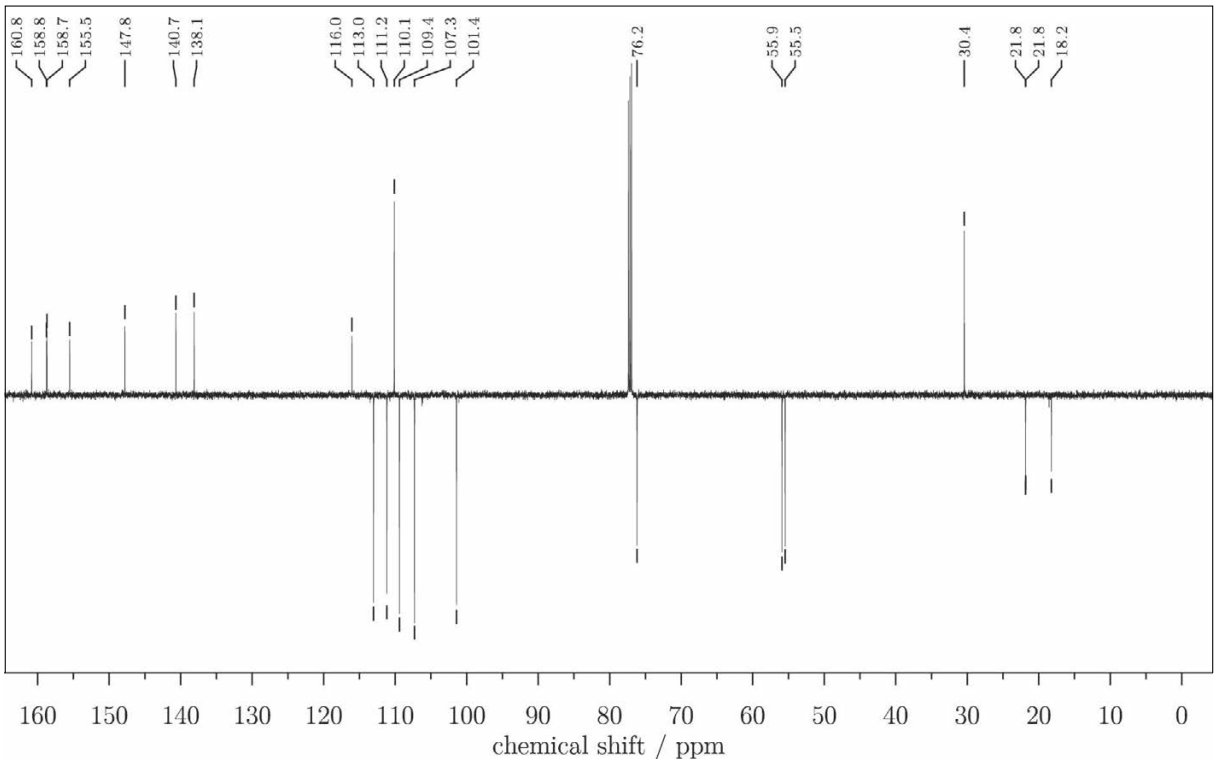


Figure 98: DEPTQ-NMR spectrum of **145** at 151 MHz in $CDCl_3$.

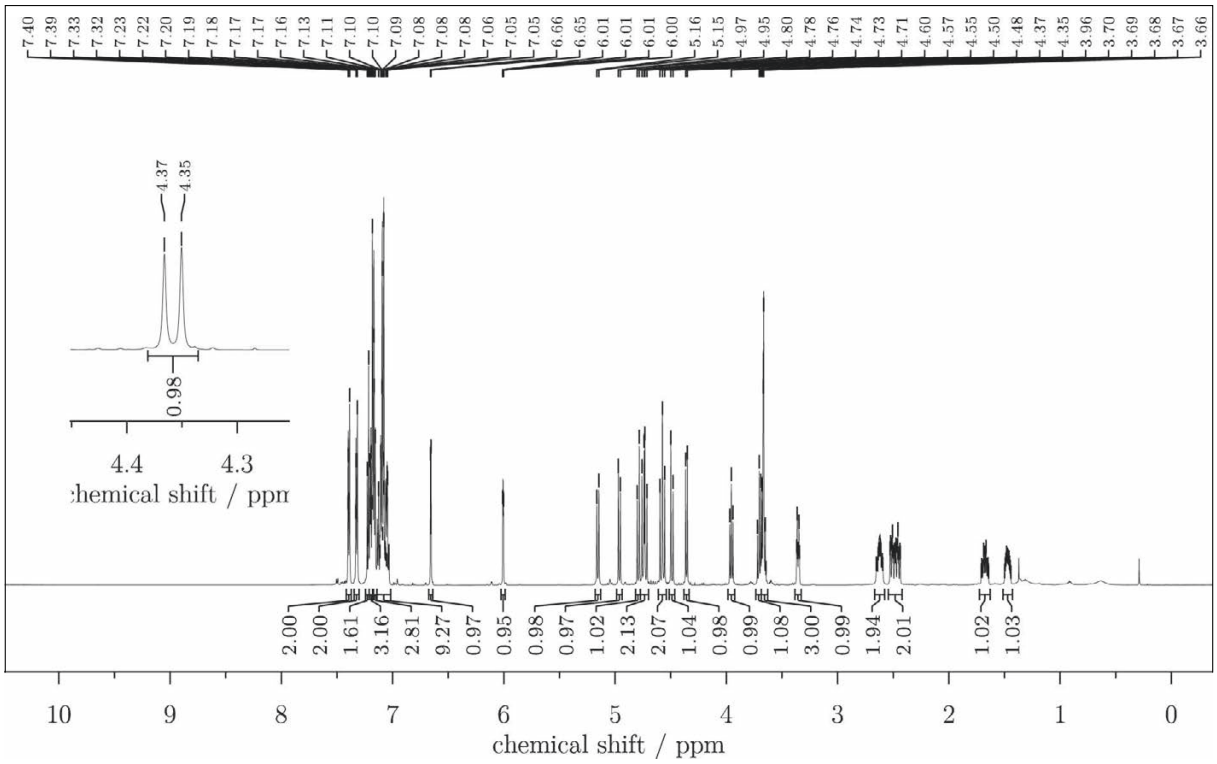


Figure 99: ^{1}H-NMR spectrum of **155** at 600 MHz in C_6D_6.

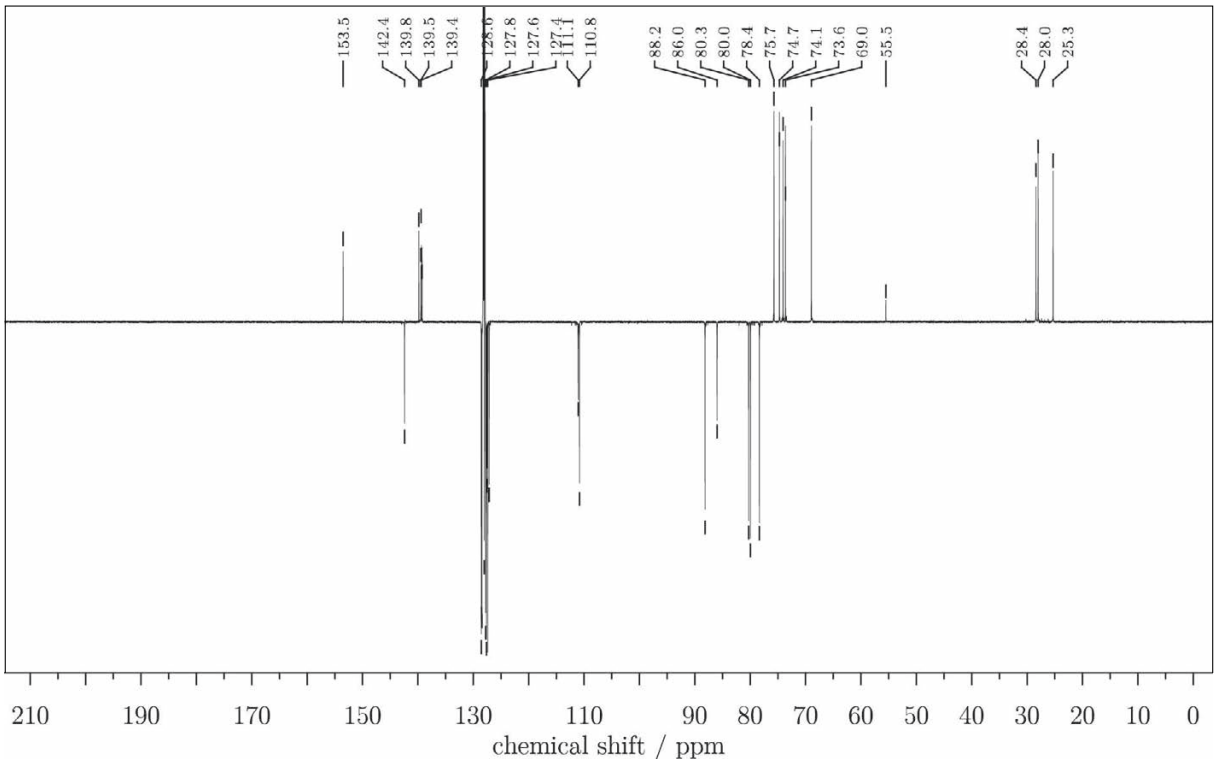


Figure 100: DEPTQ-NMR spectrum of **155** at 151 MHz in C_6D_6.

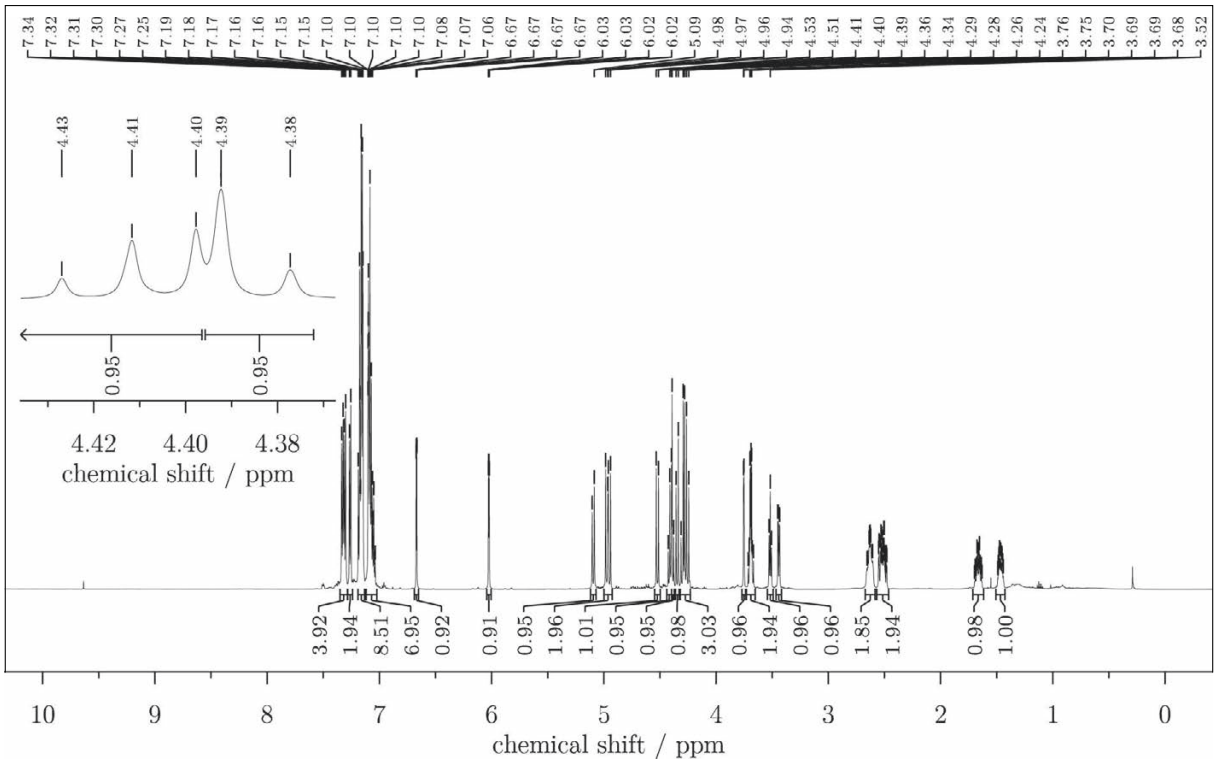


Figure 101: ^{1}H-NMR spectrum of **162** at 600 MHz in C_6D_6.

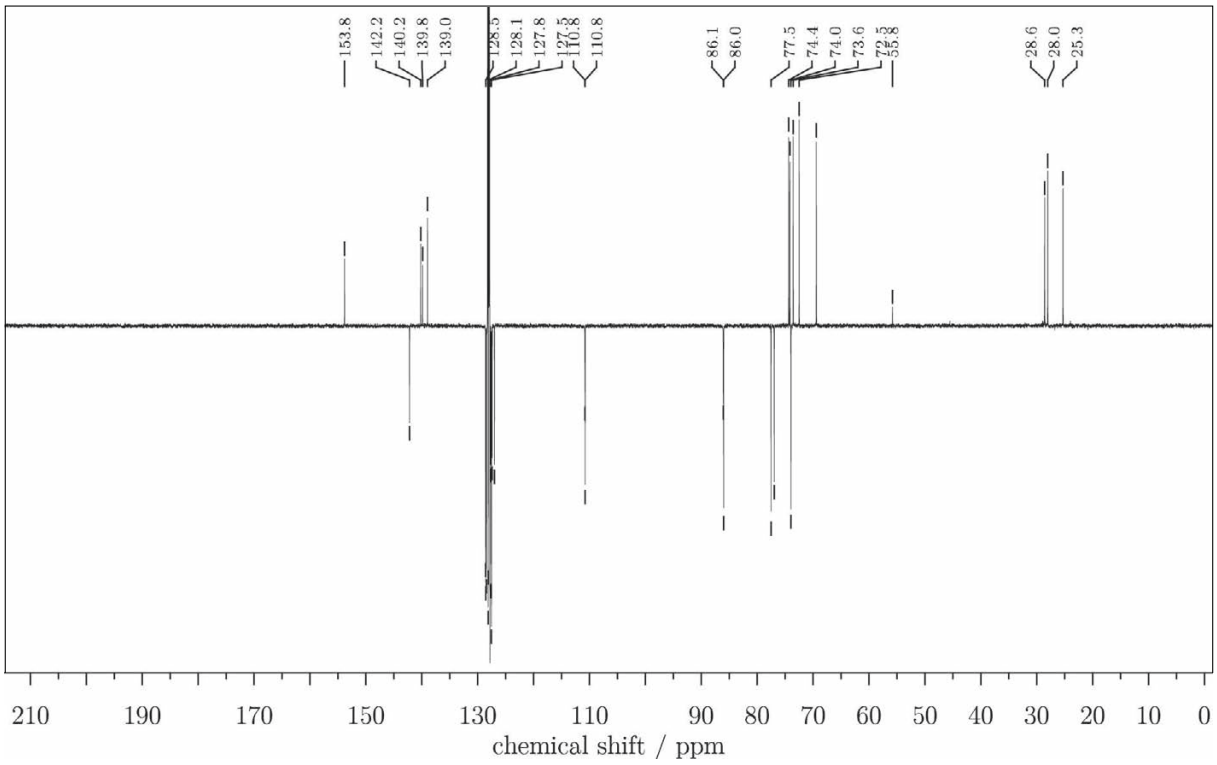


Figure 102: DEPTQ-NMR spectrum of **162** at 151 MHz in C_6D_6.

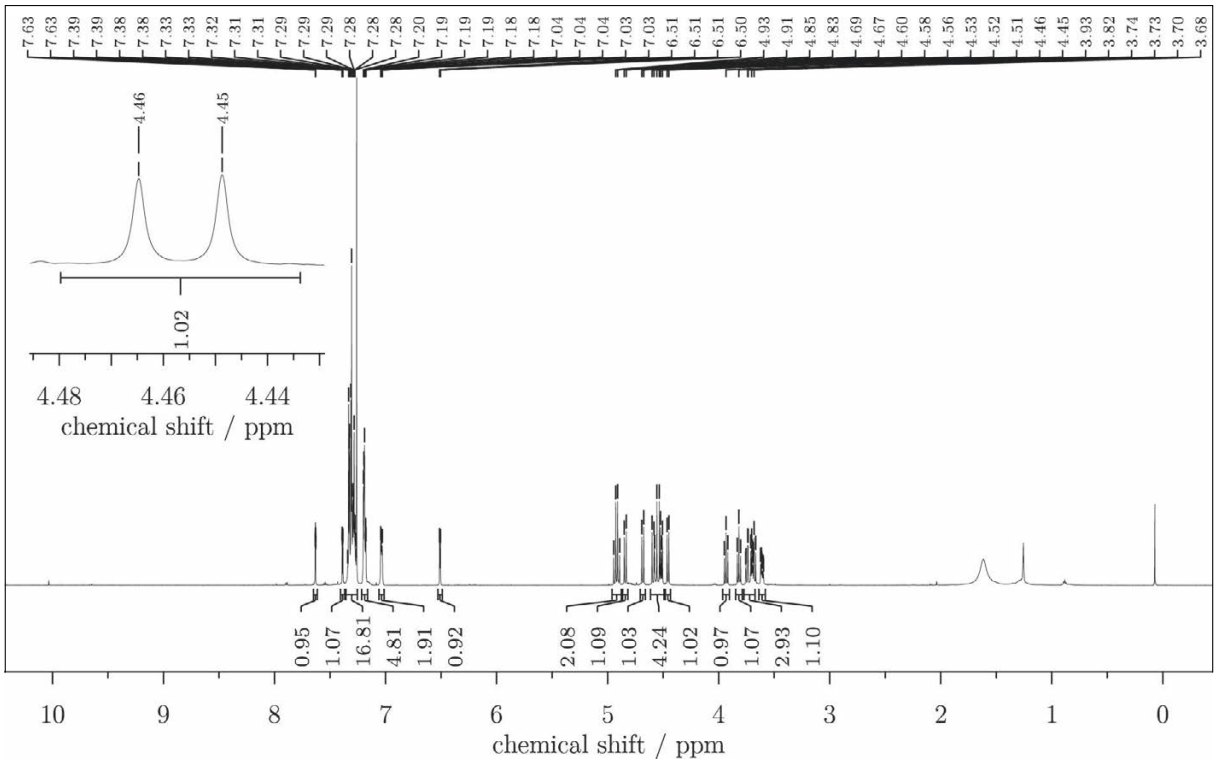


Figure 103: ^{1}H-NMR spectrum of **163** at 600 MHz in $CDCl_3$.

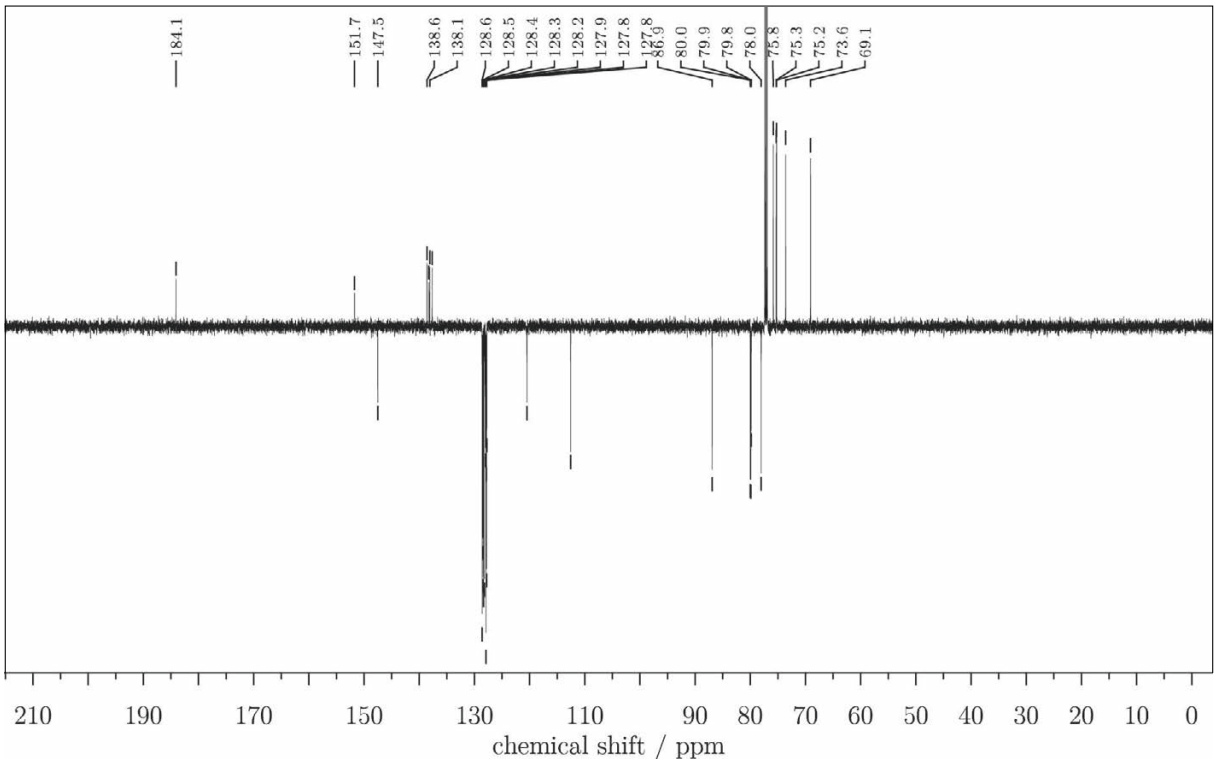


Figure 104: DEPTQ-NMR spectrum of **163** at 151 MHz in $CDCl_3$.

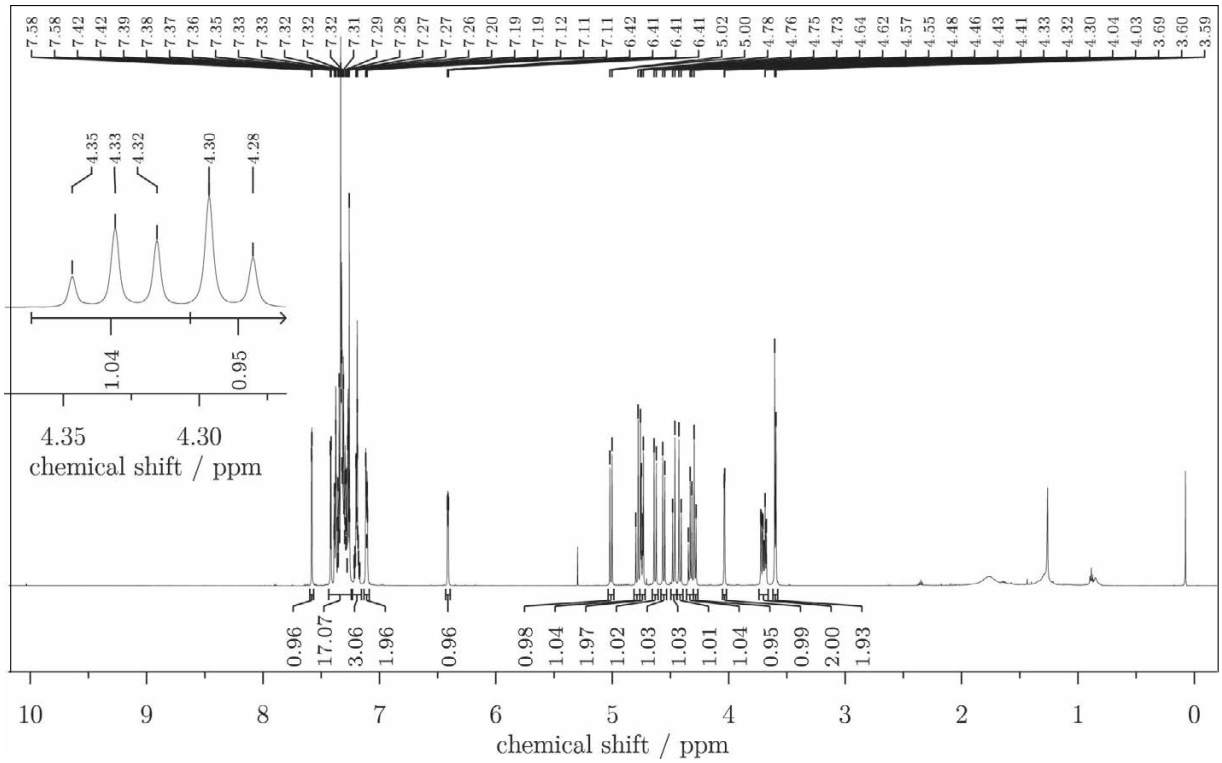


Figure 105: ^{1}H-NMR spectrum of **164** at 600 MHz in $CDCl_3$.

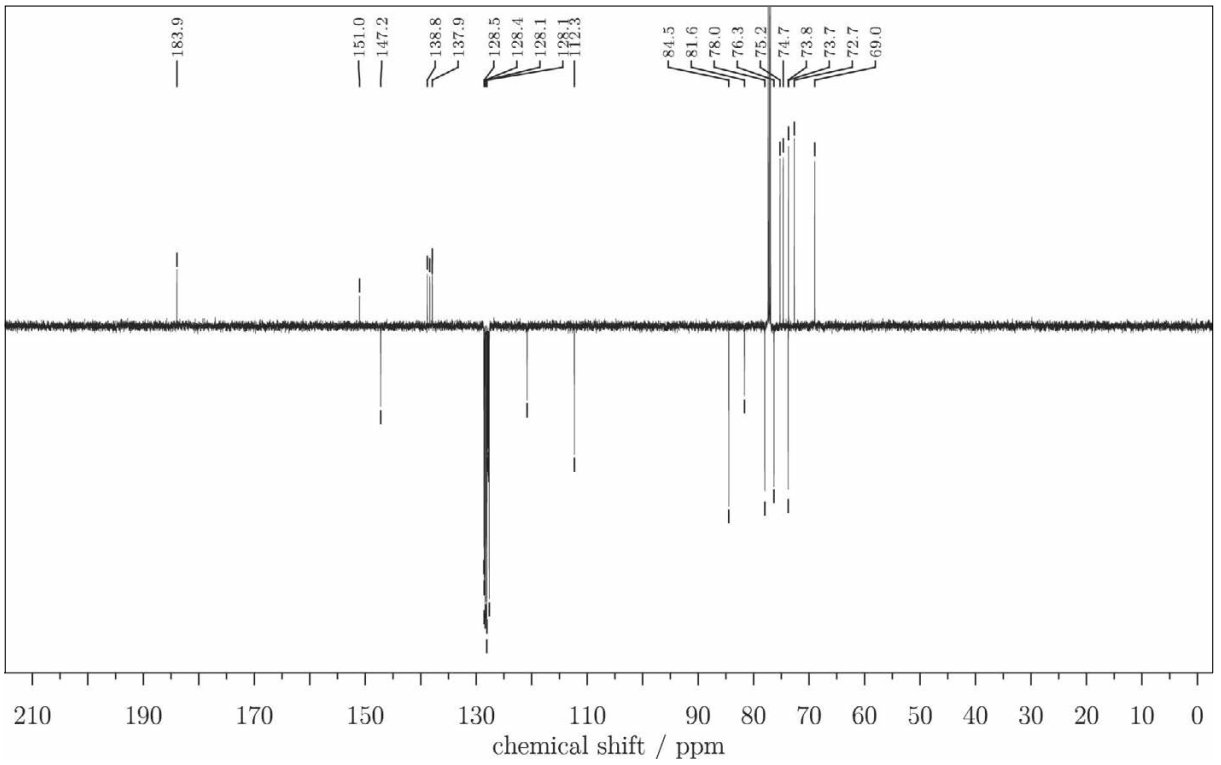


Figure 106: DEPTQ-NMR spectrum of **164** at 151 MHz in $CDCl_3$.

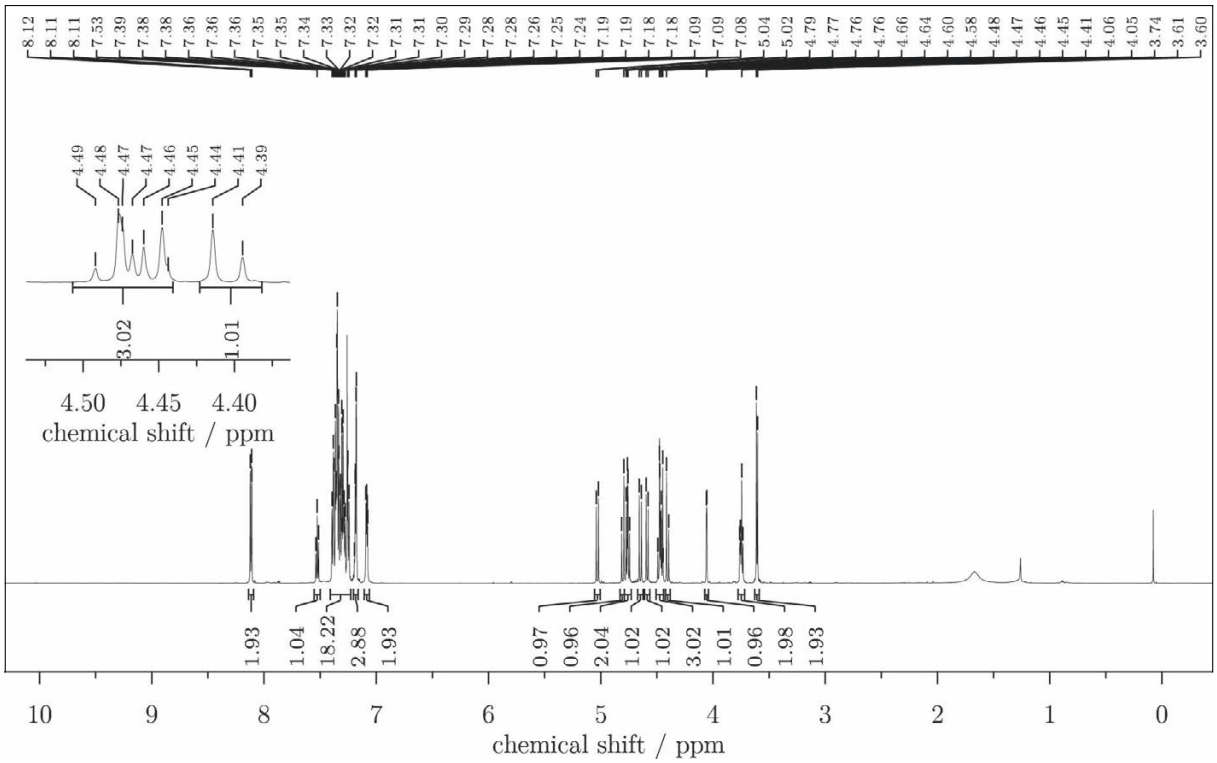


Figure 107: ^{1}H-NMR spectrum of **170** at 600 MHz in $CDCl_3$.

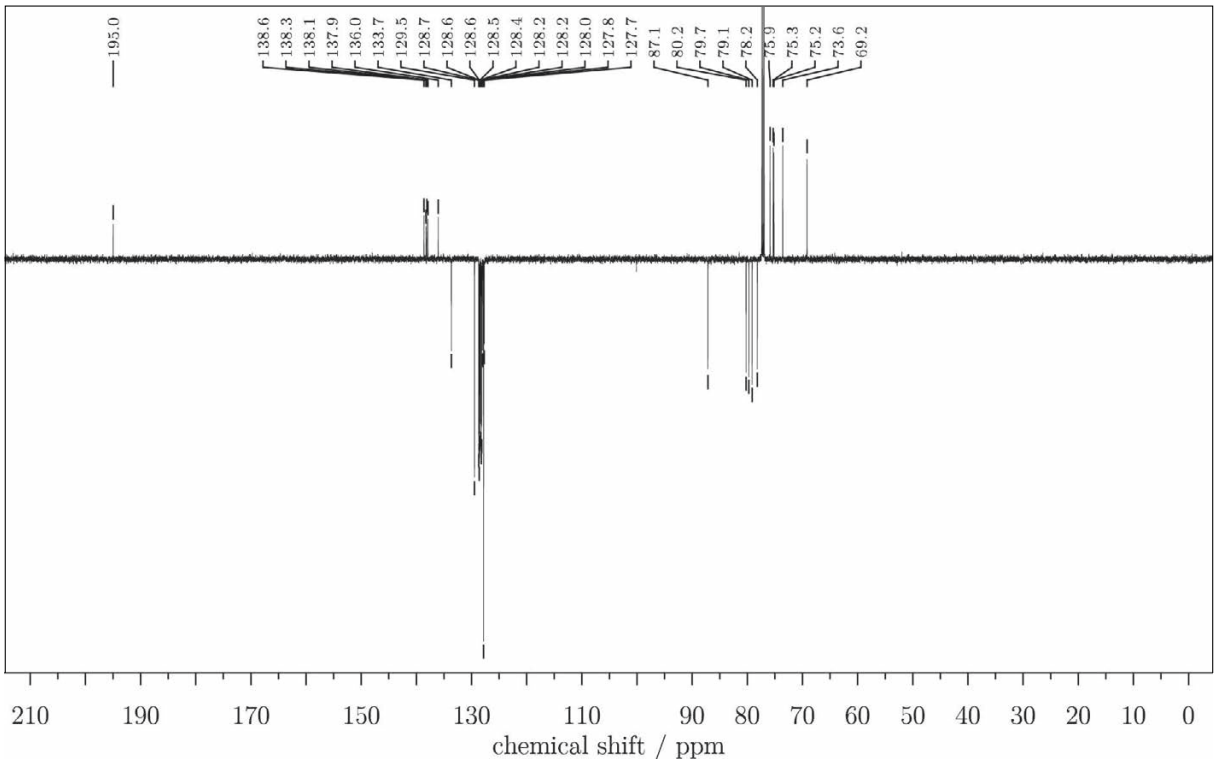


Figure 108: DEPTQ-NMR spectrum of **170** at 151 MHz in $CDCl_3$.

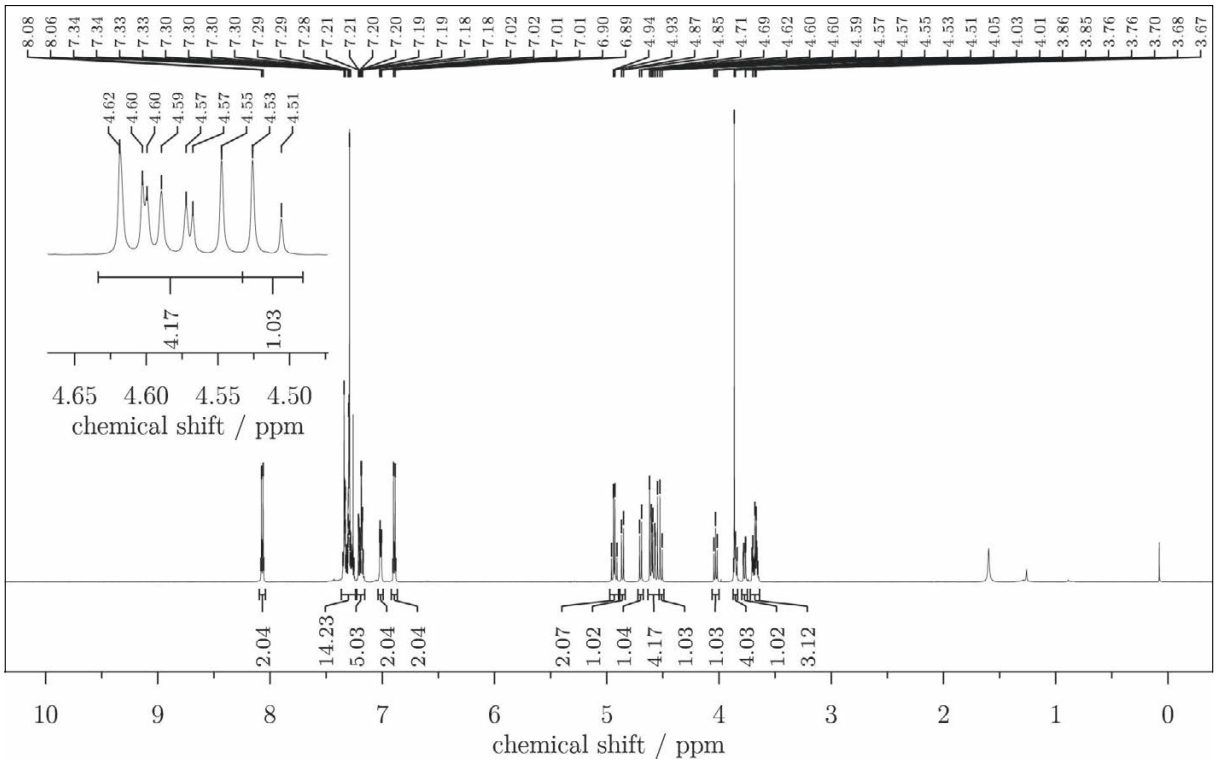


Figure 109: ^{1}H-NMR spectrum of **171** at 600 MHz in $CDCl_3$.

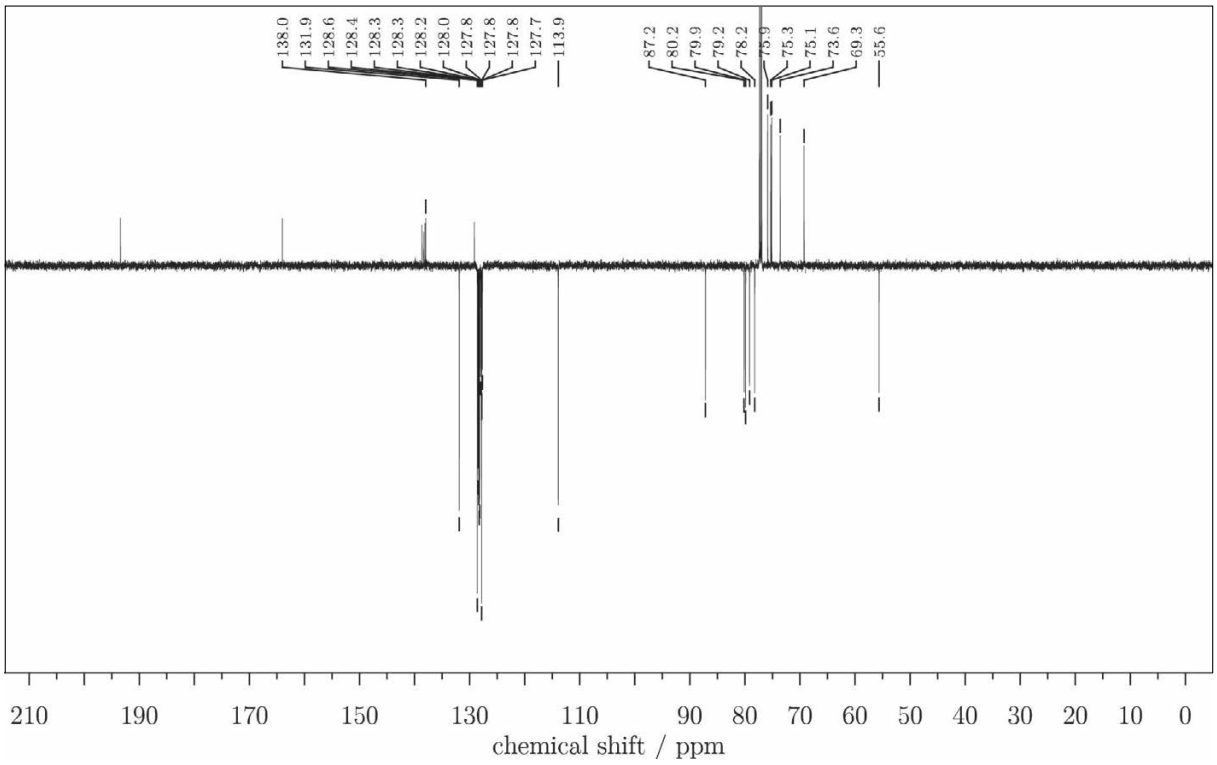


Figure 110: DEPTQ-NMR spectrum of **171** at 151 MHz in $CDCl_3$.

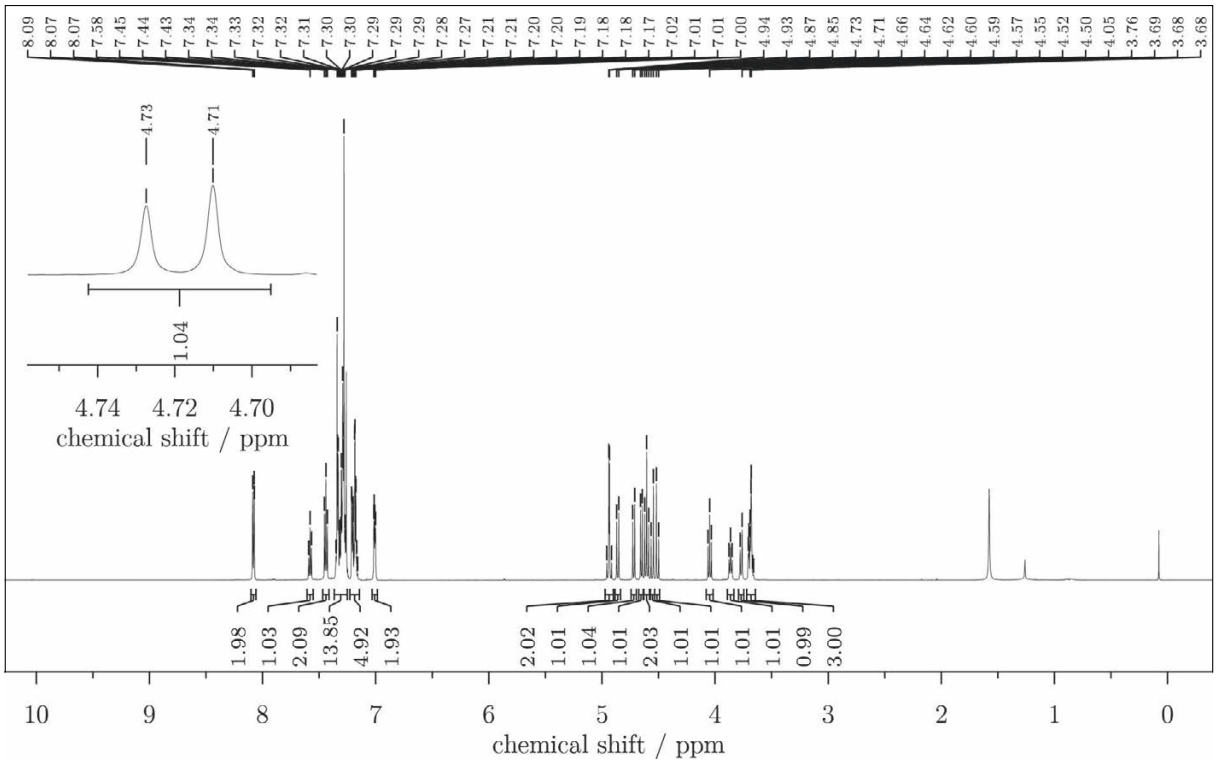


Figure 111: ^{1}H-NMR spectrum of **172** at 600 MHz in $CDCl_3$.

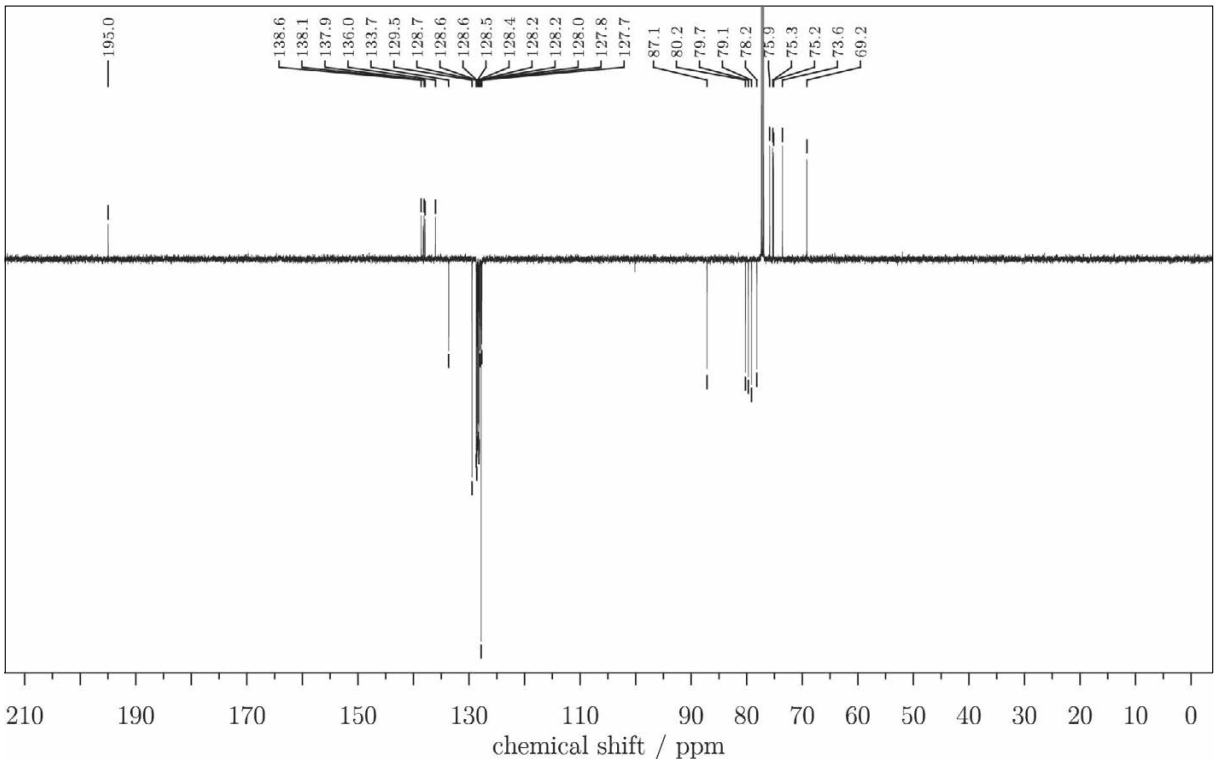


Figure 112: DEPTQ-NMR spectrum of **172** at 151 MHz in $CDCl_3$.

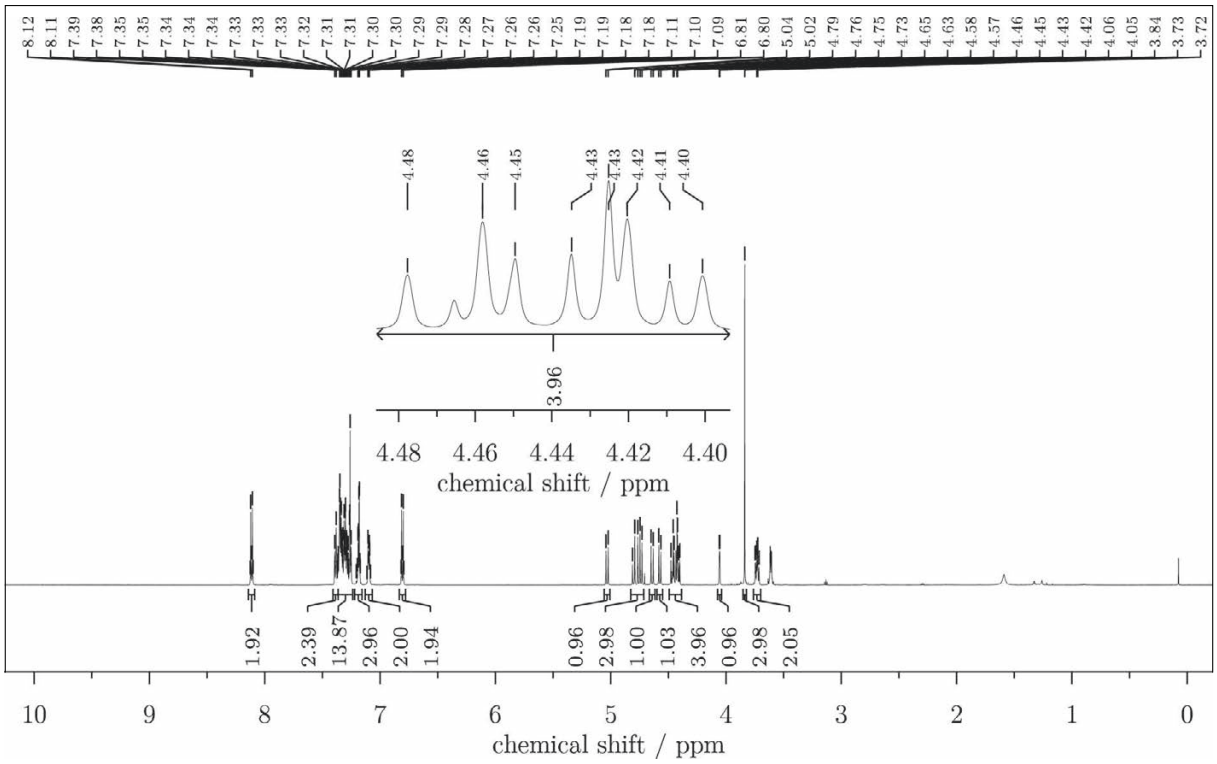


Figure 113: ^{1}H-NMR spectrum of **173** at 600 MHz in $CDCl_3$.

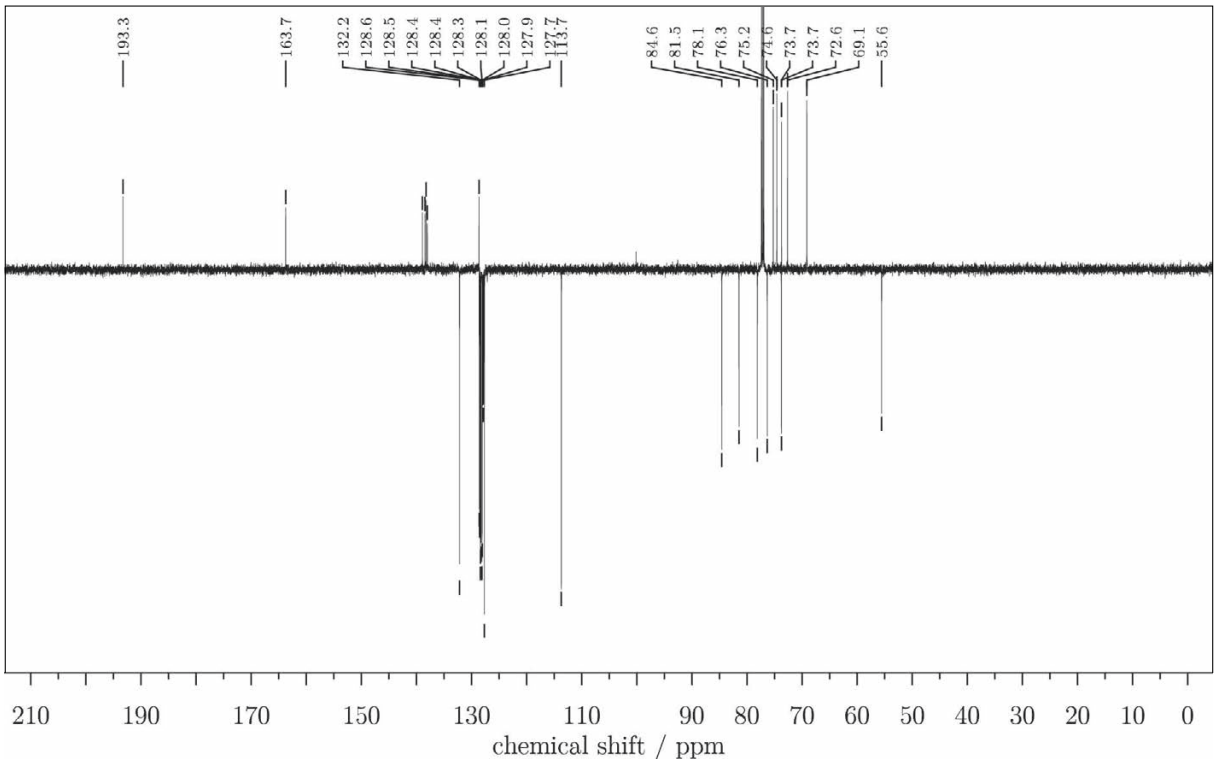


Figure 114: DEPTQ-NMR spectrum of **173** at 151 MHz in $CDCl_3$.

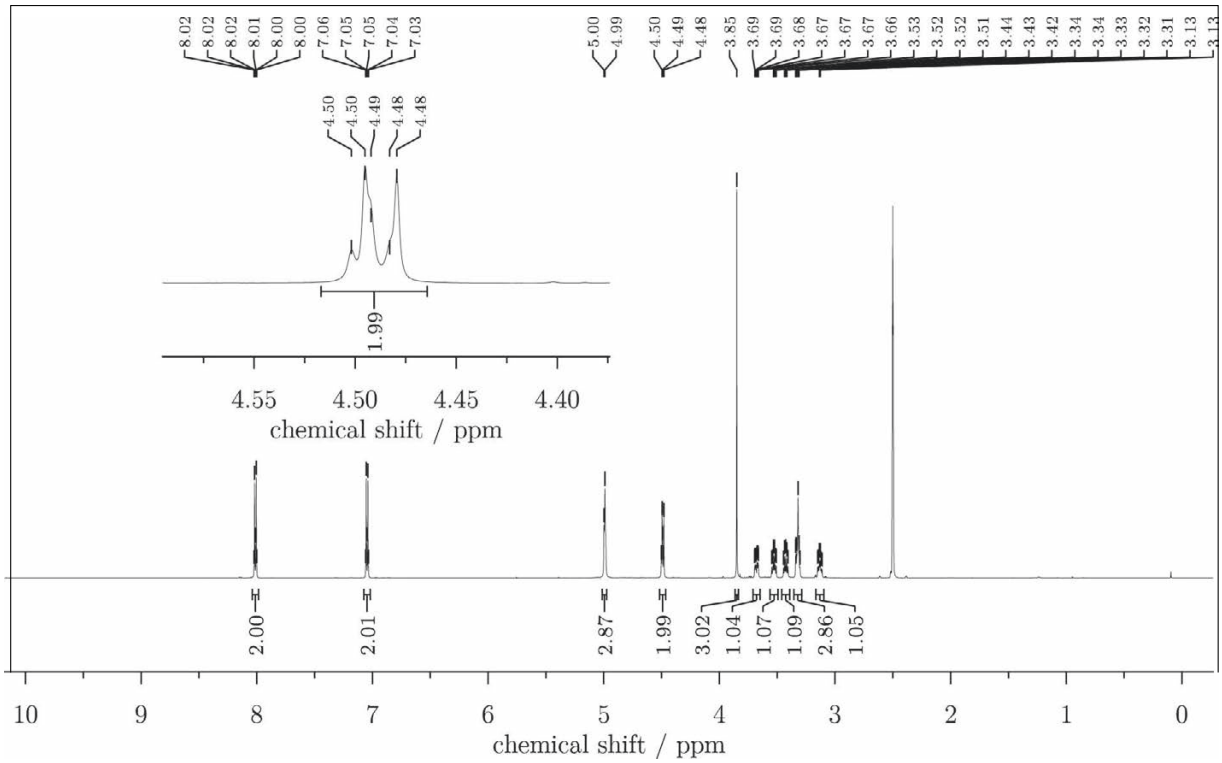


Figure 115: ^{1}H-NMR spectrum of **178** at 600 MHz in DMSO-d_6.

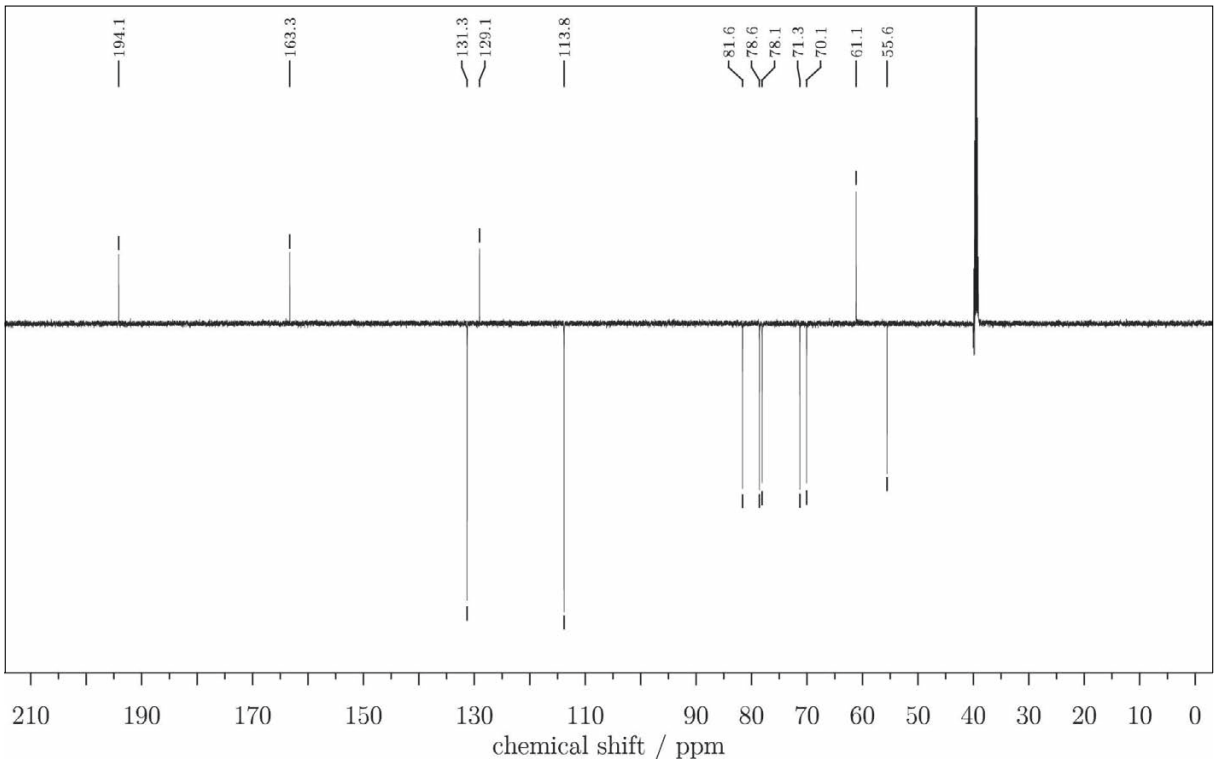


Figure 116: DEPTQ-NMR spectrum of **178** at 151 MHz in DMSO-d_6.

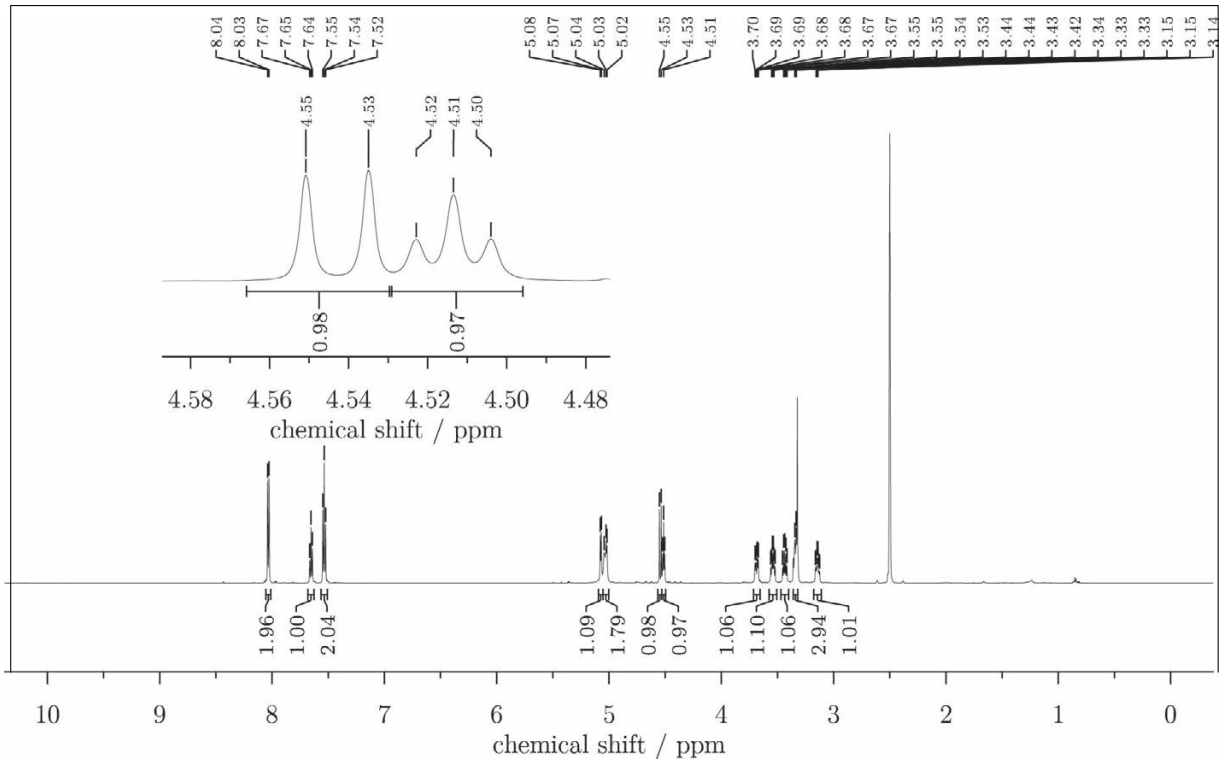


Figure 117: [1]H-NMR spectrum of **179** at 600 MHz in DMSO-d_6.

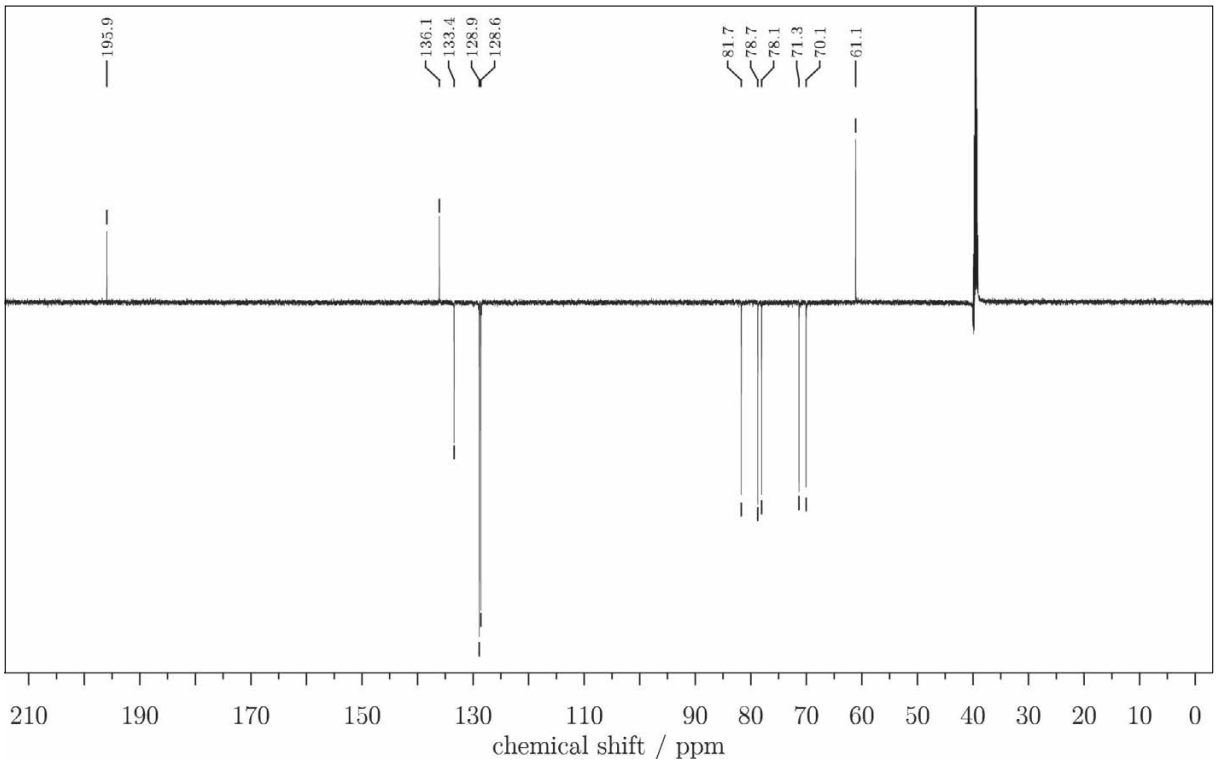


Figure 118: DEPTQ-NMR spectrum of **179** at 151 MHz in DMSO-d_6.

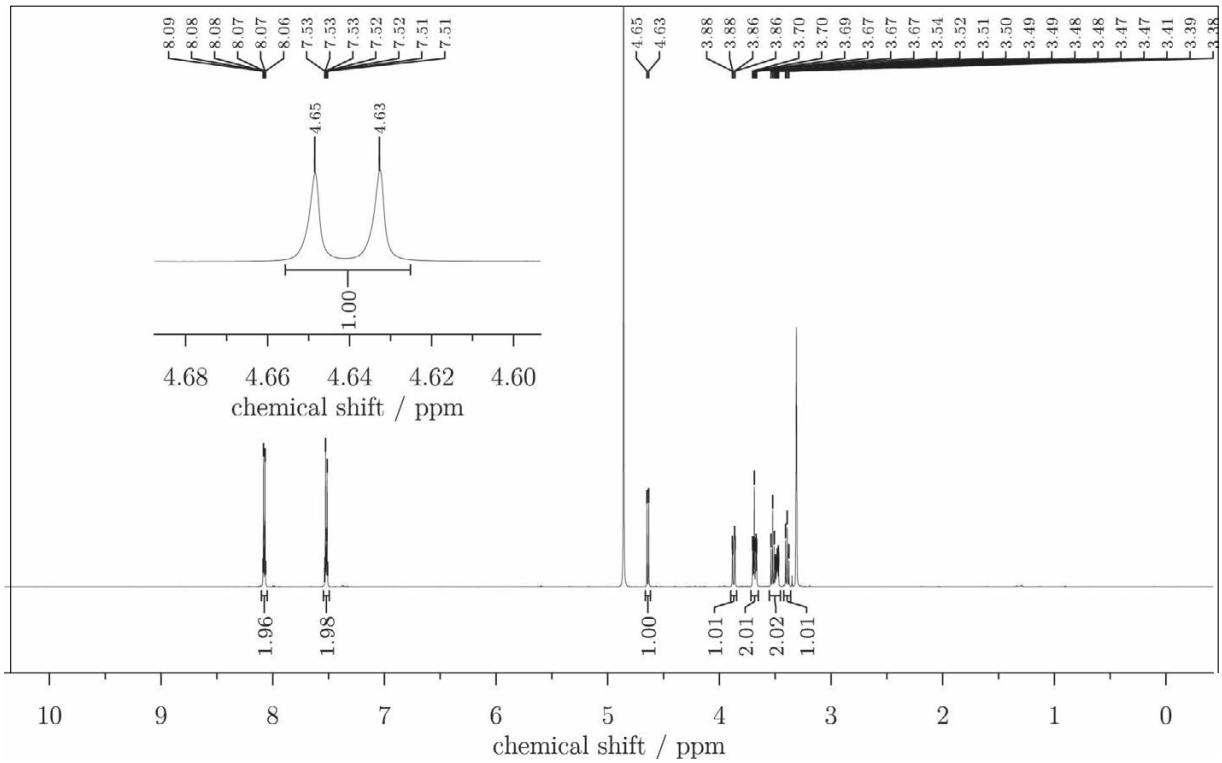


Figure 119: ^{1}H-NMR spectrum of **180** at 600 MHz in methanol-d_4.

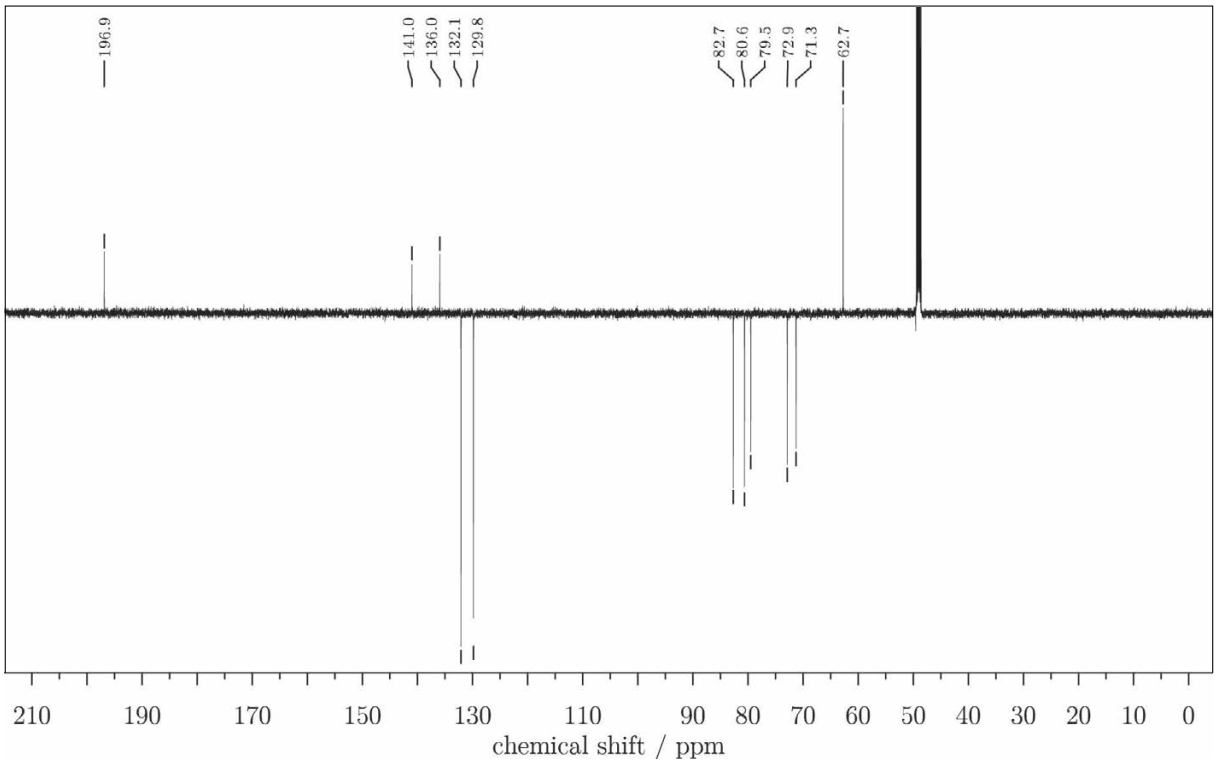


Figure 120: DEPTQ-NMR spectrum of **180** at 151 MHz in methanol-d_4.

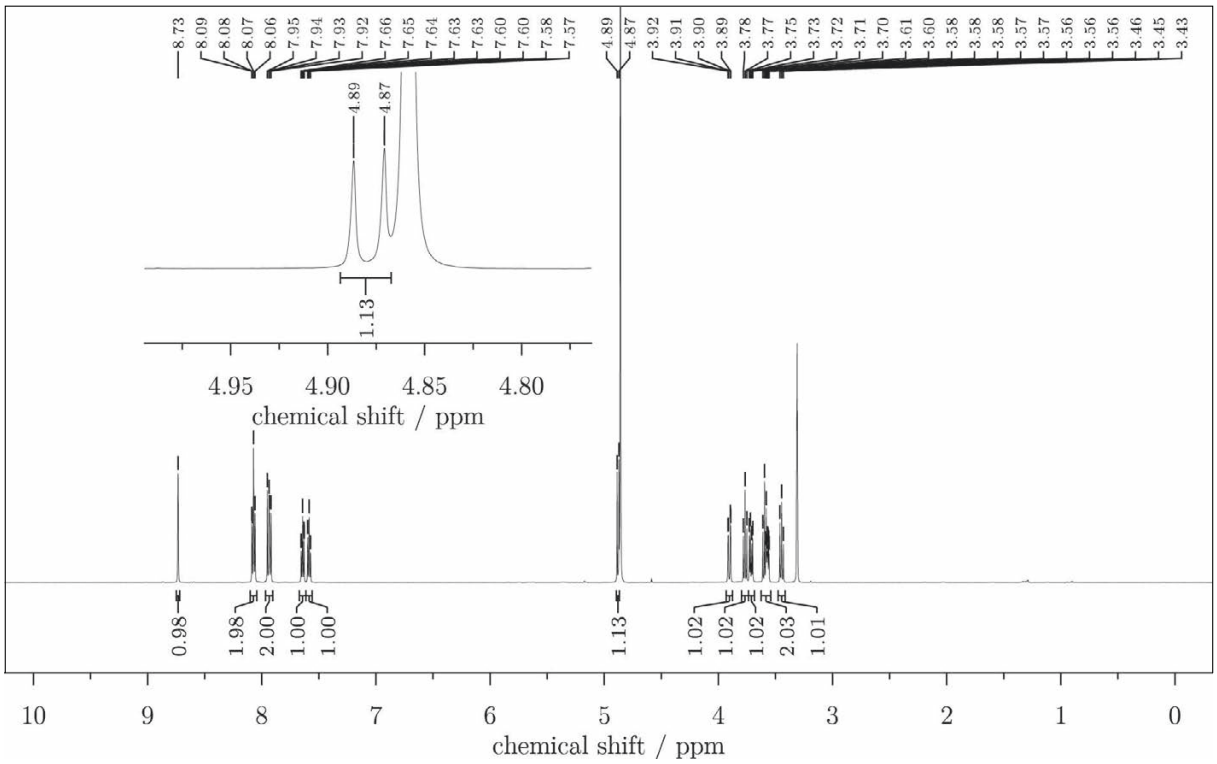


Figure 121: ^{1}H-NMR spectrum of **181** at 600 MHz in methanol-d_4.

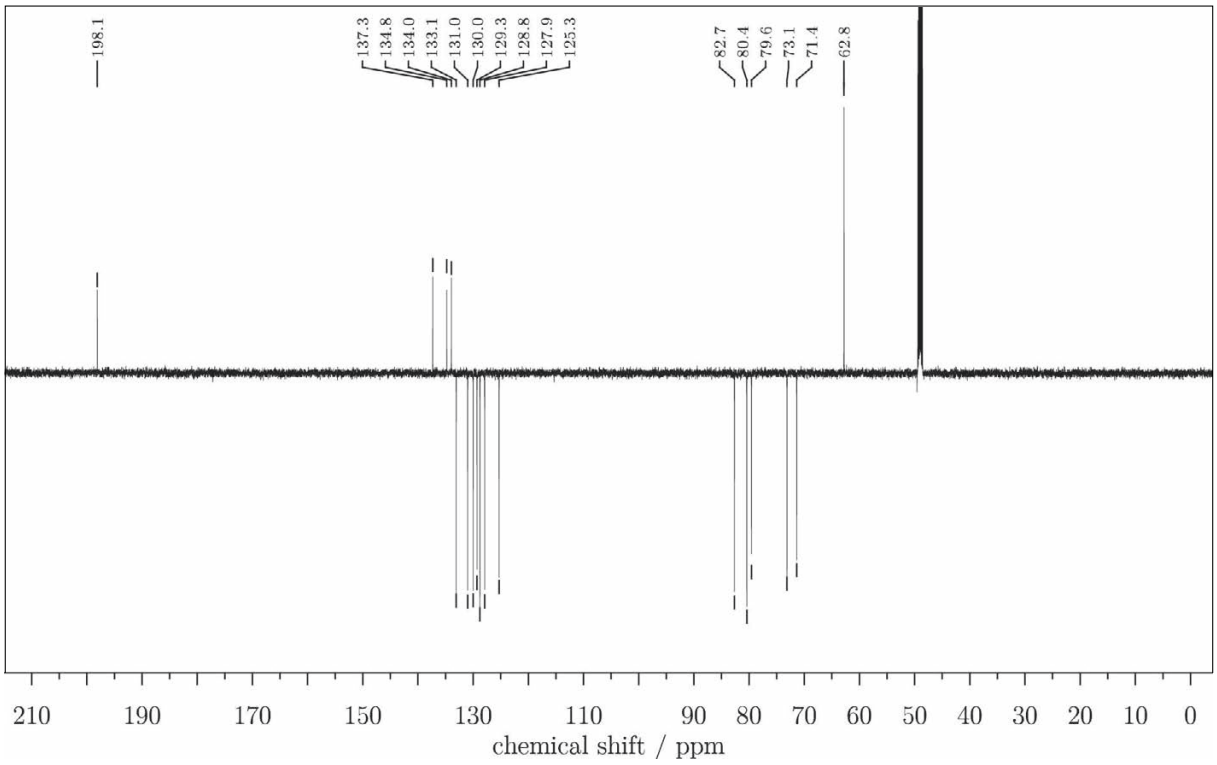


Figure 122: DEPTQ-NMR spectrum of **181** at 151 MHz in methanol-d_4.

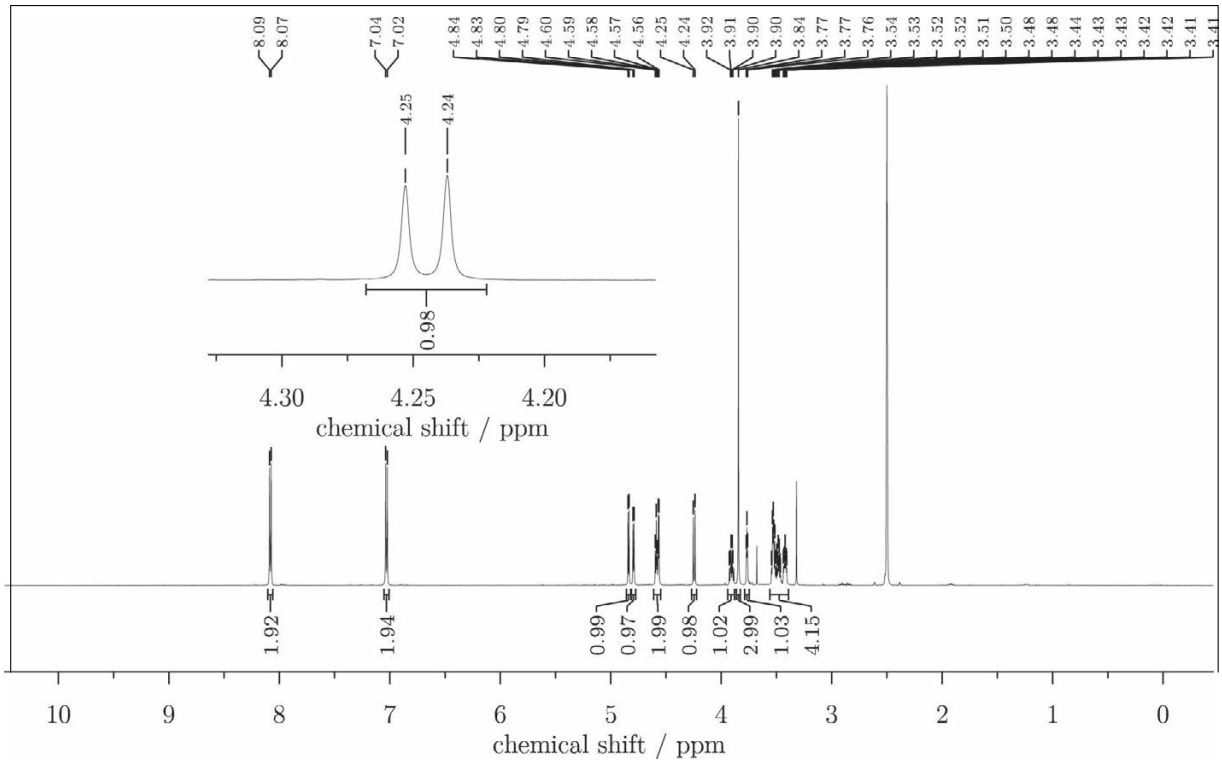


Figure 123: ^{1}H-NMR spectrum of **183** at 600 MHz in DMSO-d_6.

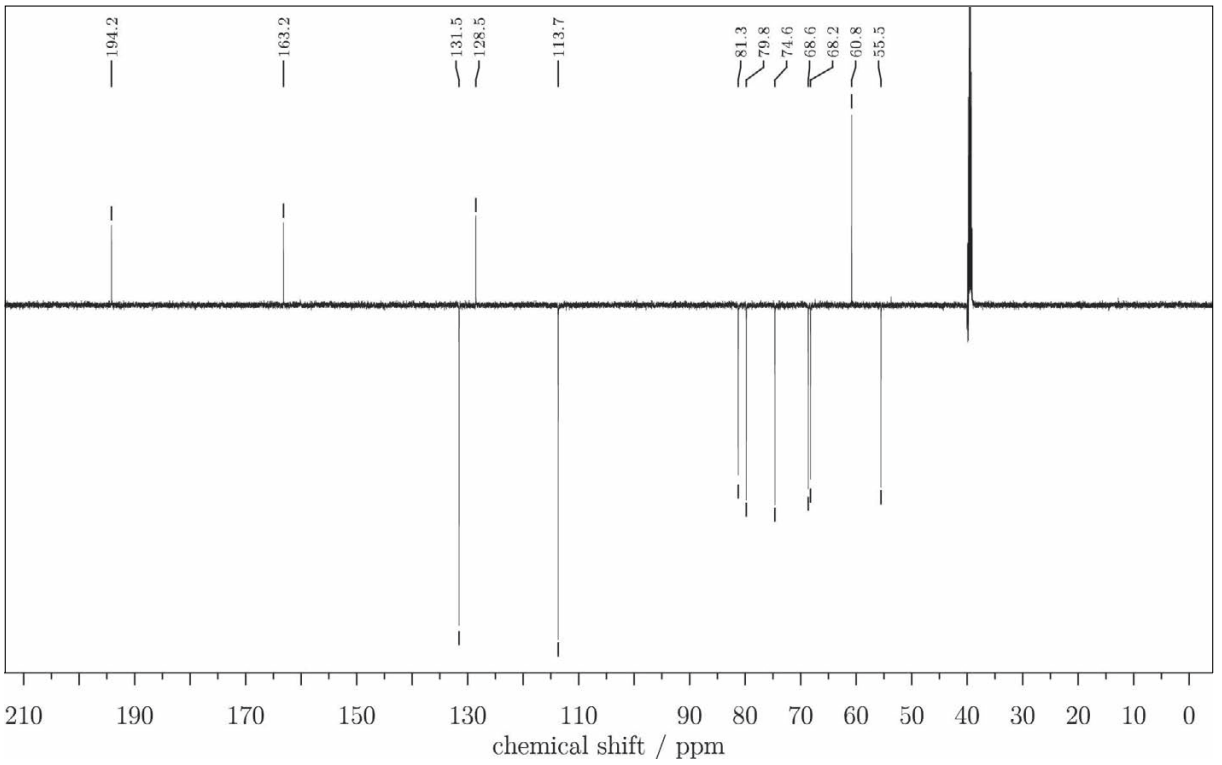


Figure 124: DEPTQ-NMR spectrum of **183** at 151 MHz in DMSO-d_6.

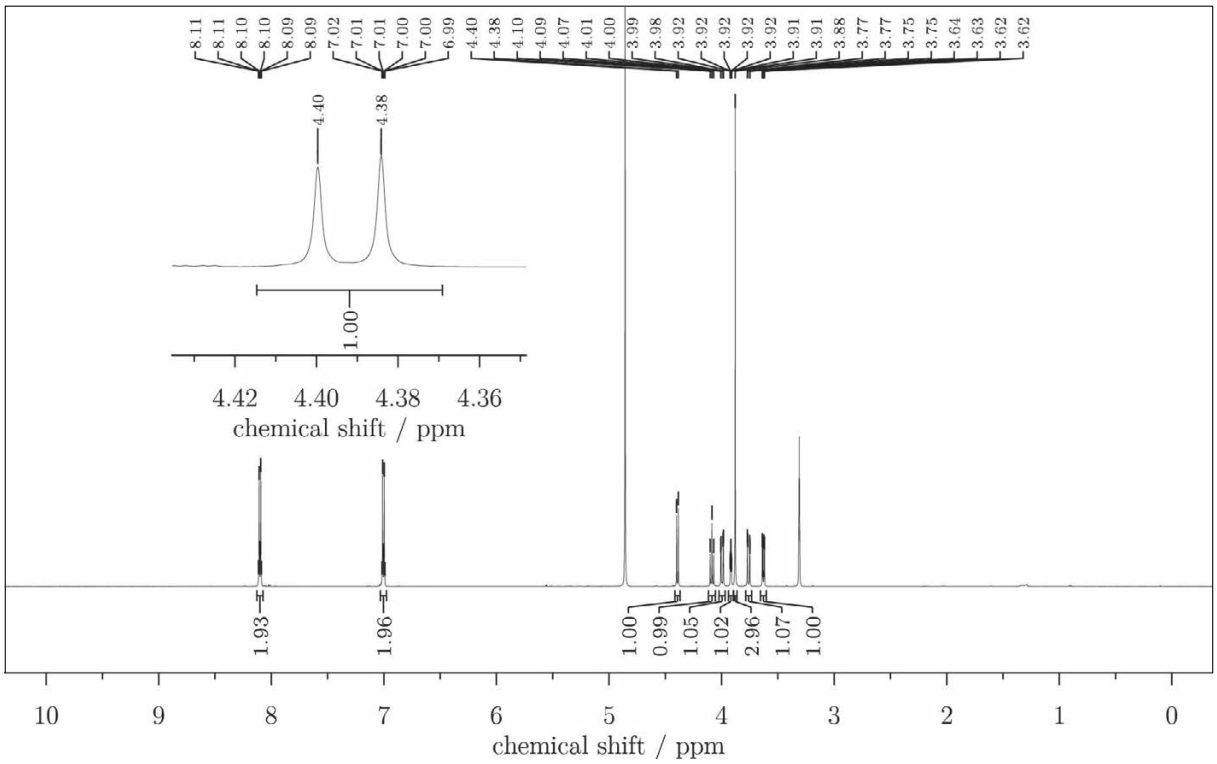


Figure 125: ^{1}H-NMR spectrum of **184** at 600 MHz in methanol-d_4.

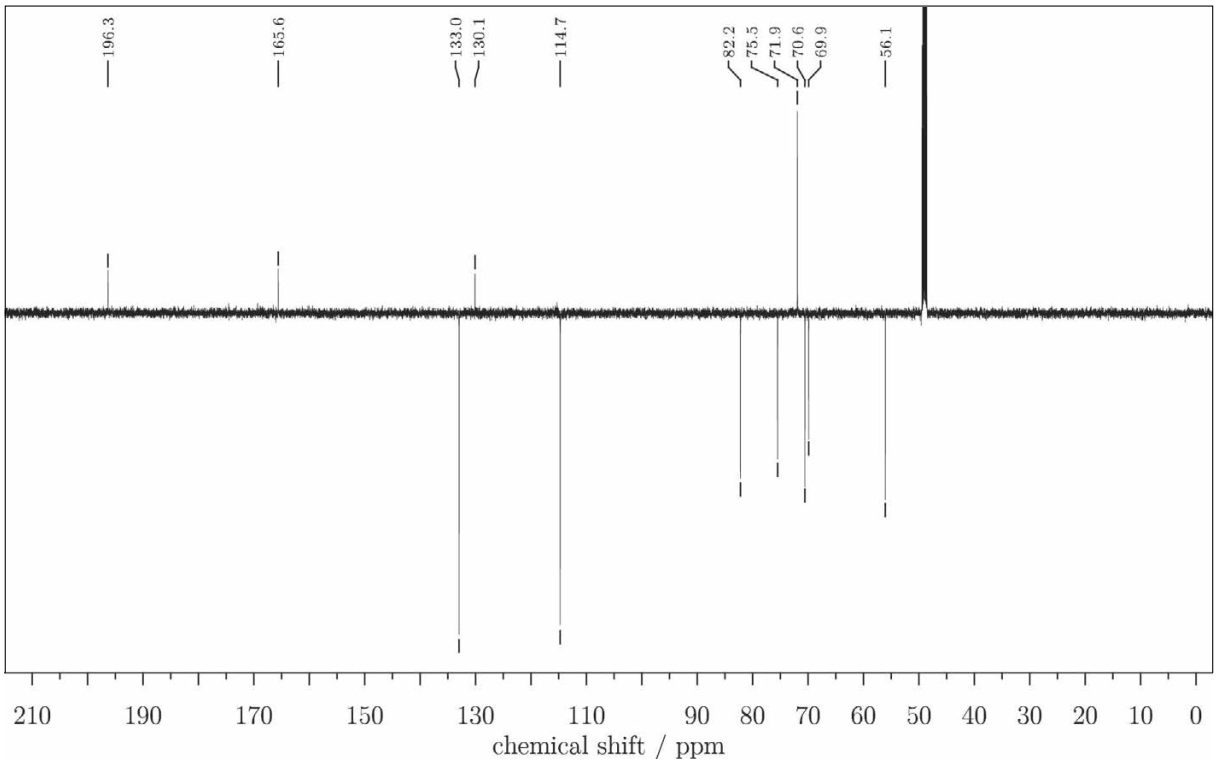


Figure 126: DEPTQ-NMR spectrum of **184** at 151 MHz in methanol-d_4.

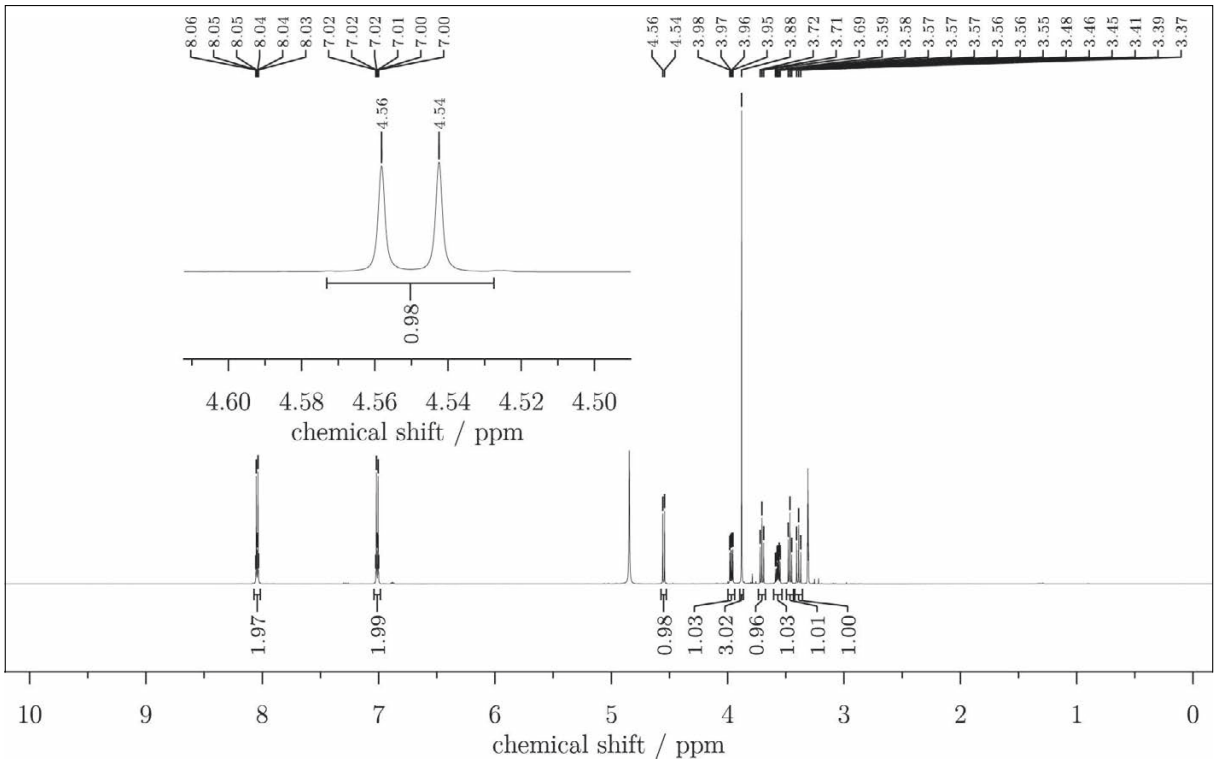


Figure 127: ^{1}H-NMR spectrum of **185** at 600 MHz in methanol-d_4.

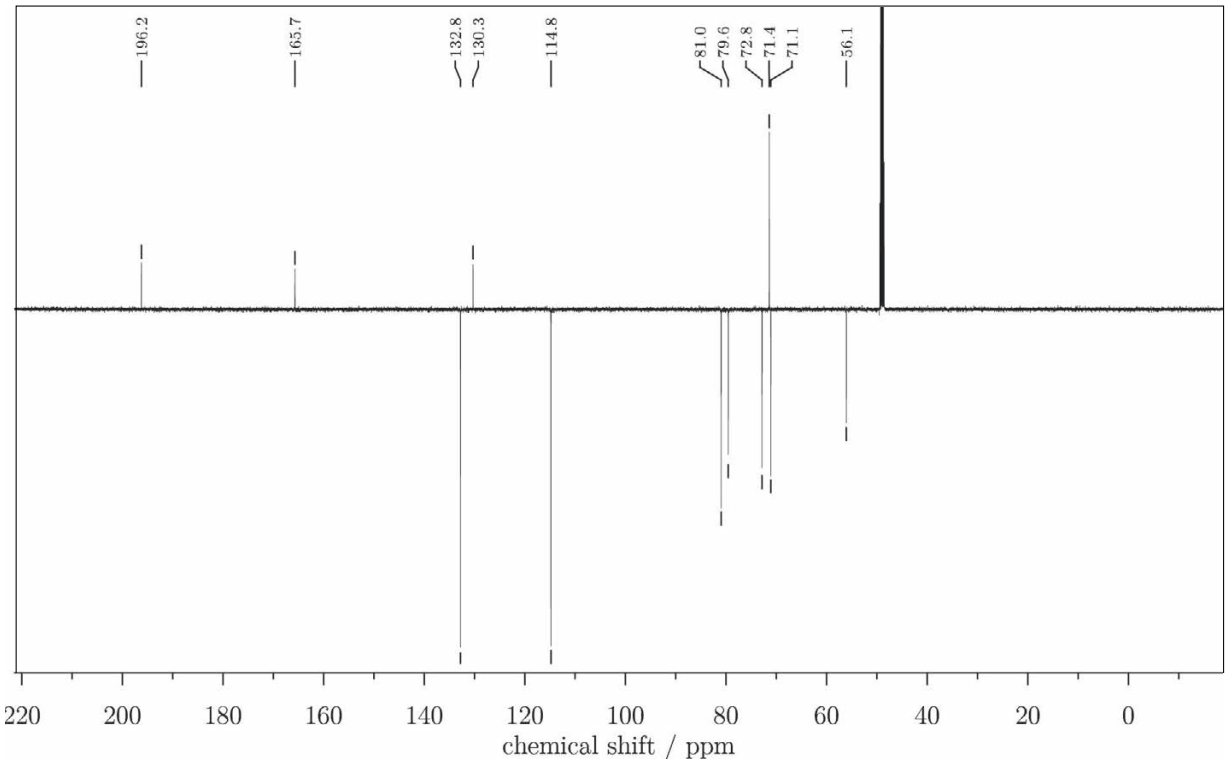


Figure 128: DEPTQ-NMR spectrum of **185** at 151 MHz in methanol-d_4.

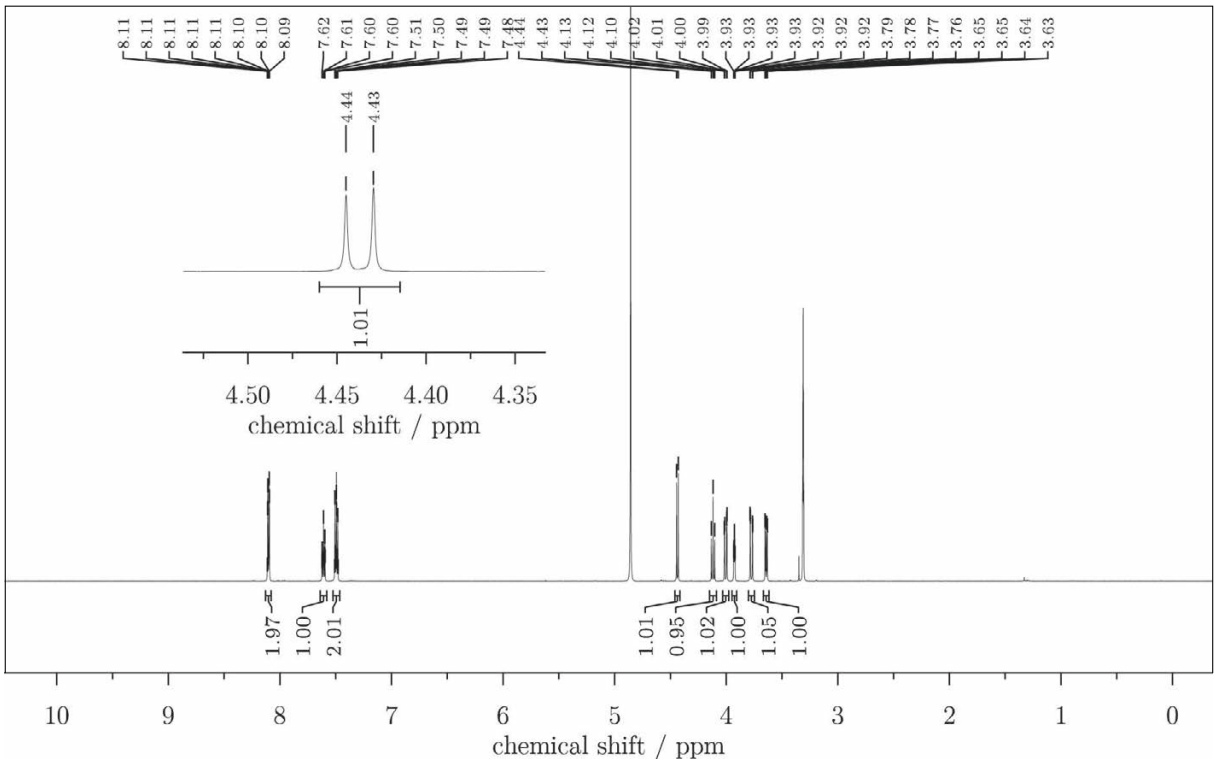


Figure 129: ^{1}H-NMR spectrum of **186** at 600 MHz in methanol-d_4.

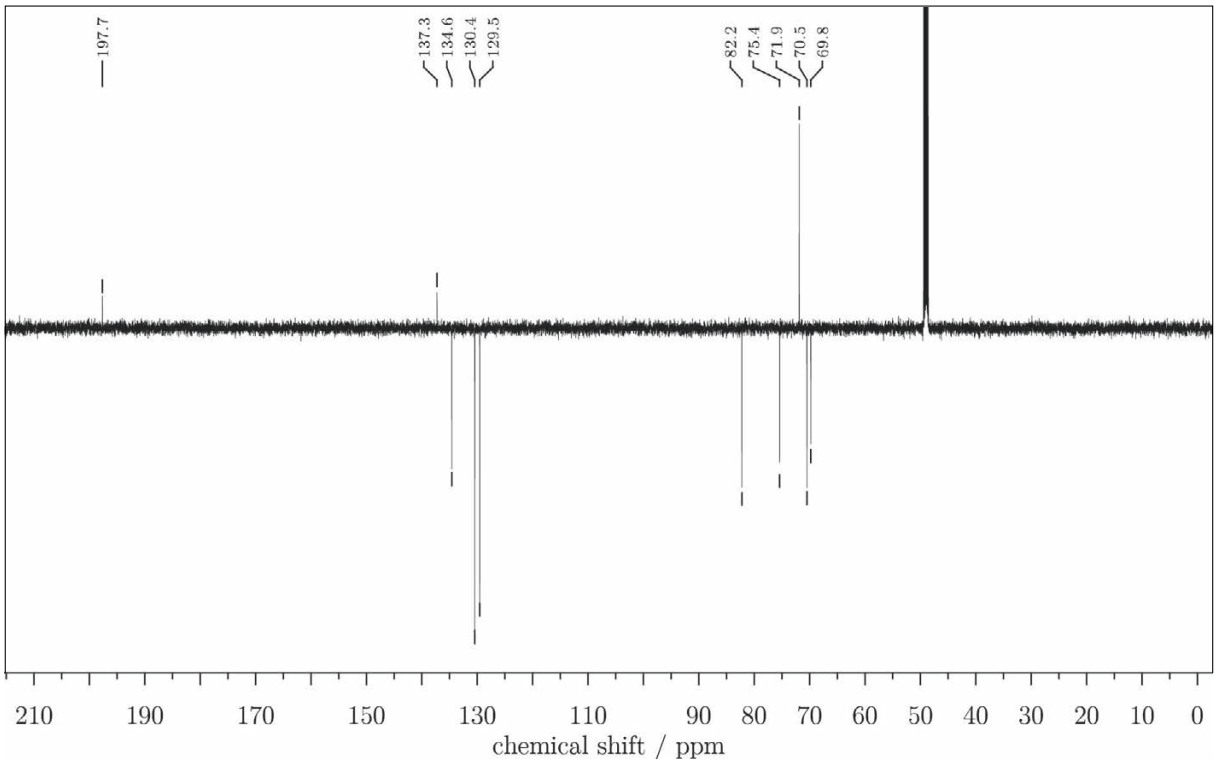


Figure 130: DEPTQ-NMR spectrum of **186** at 151 MHz in methanol-d_4.

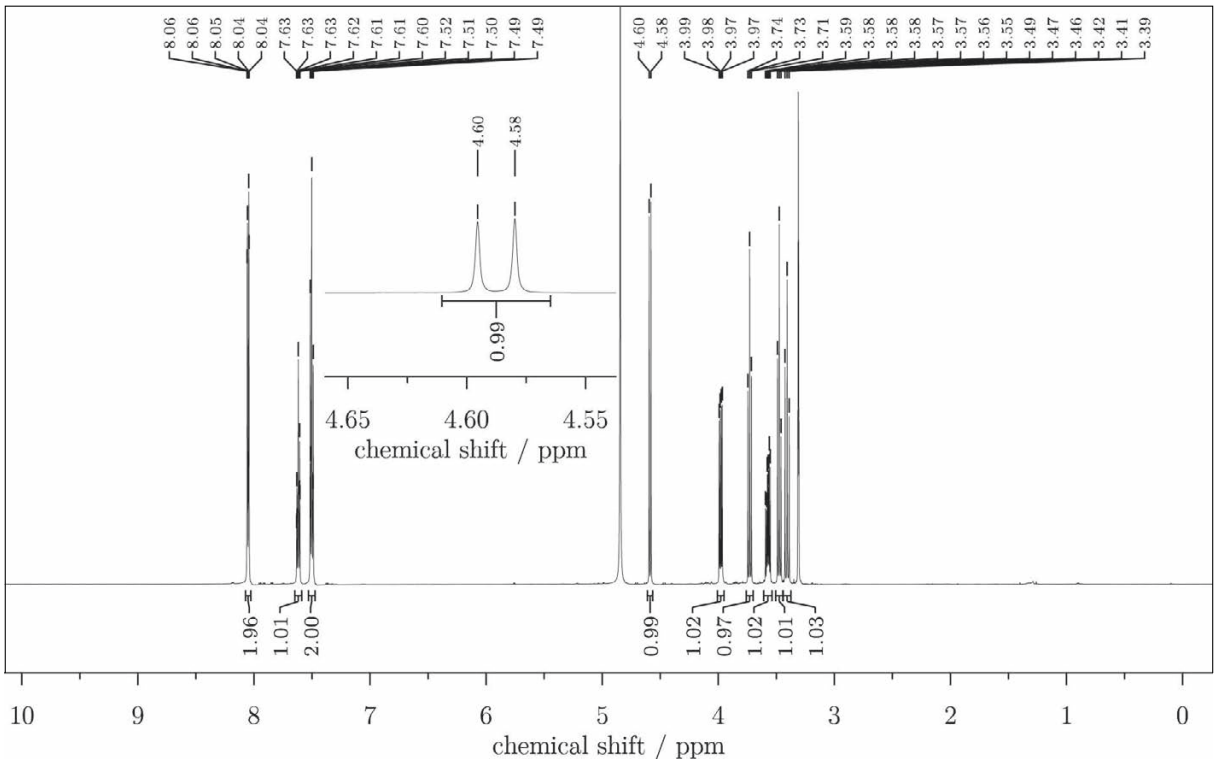


Figure 131: ^{1}H-NMR spectrum of **187** at 600 MHz in methanol-d_4.

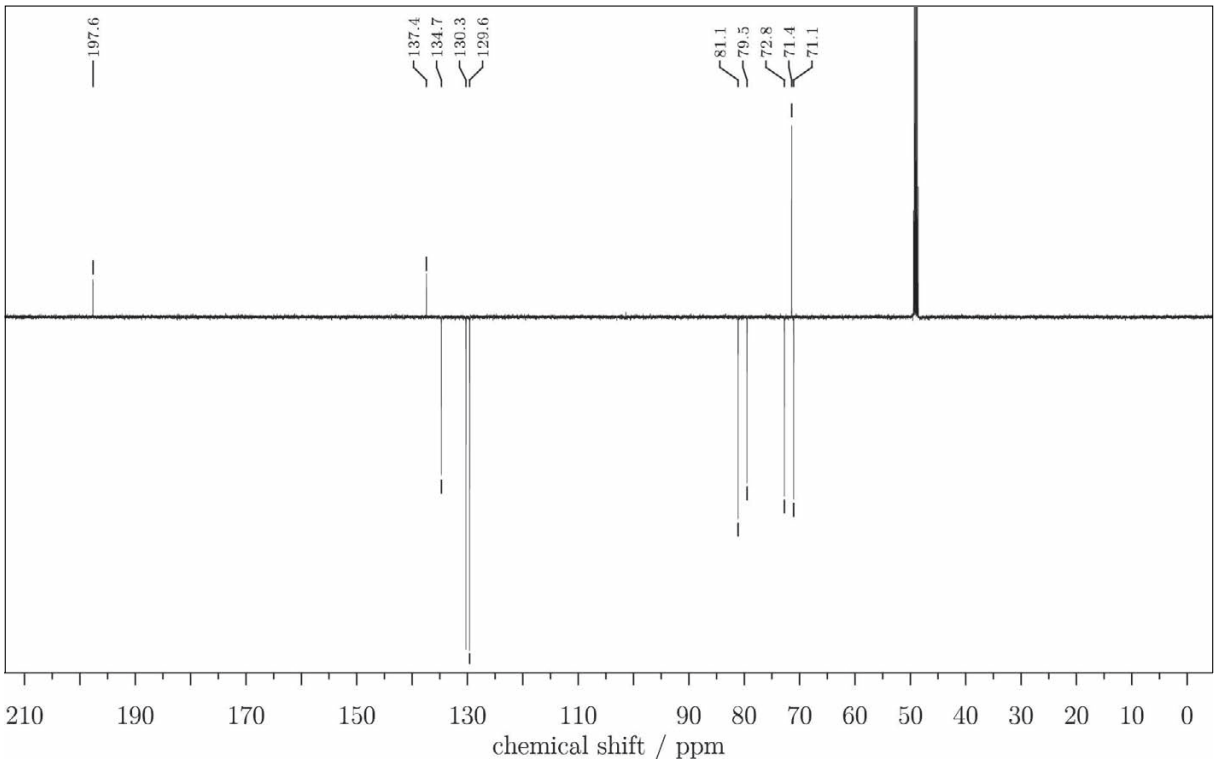


Figure 132: DEPTQ-NMR spectrum of **187** at 151 MHz in methanol-d_4.

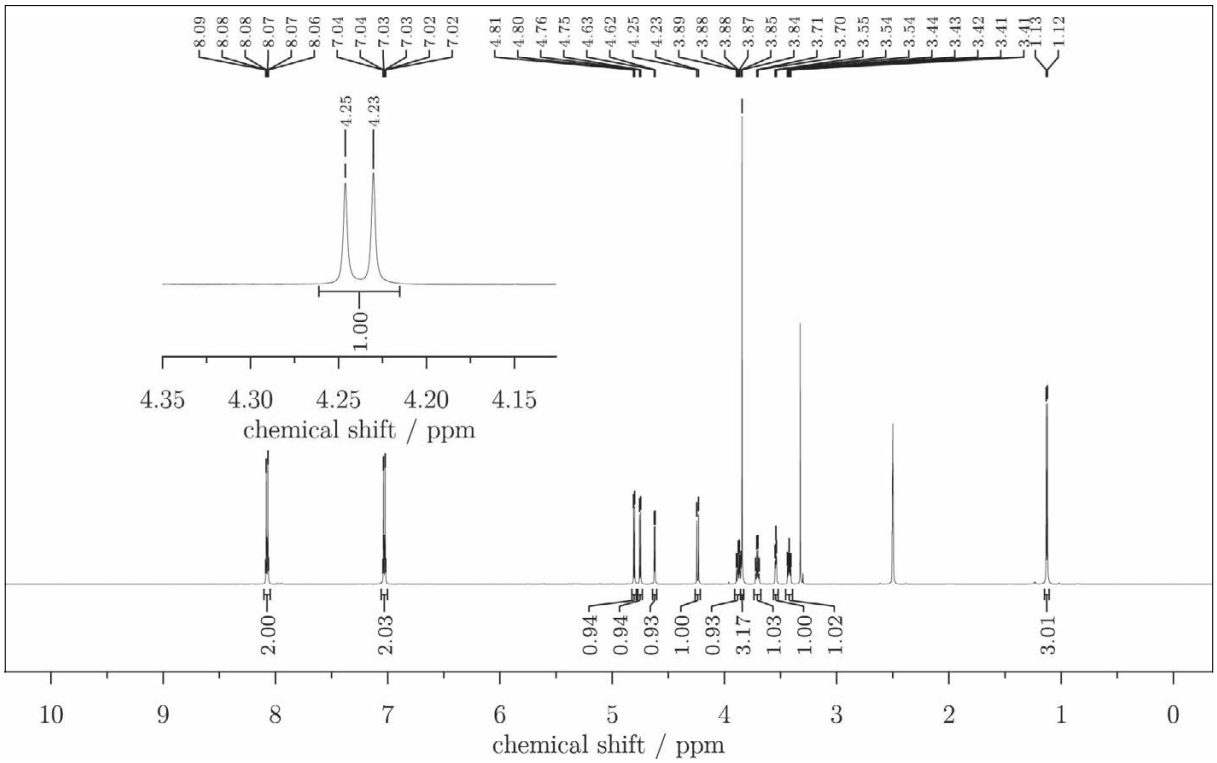


Figure 133: ^{1}H-NMR spectrum of **188** at 600 MHz in DMSO-d_6.

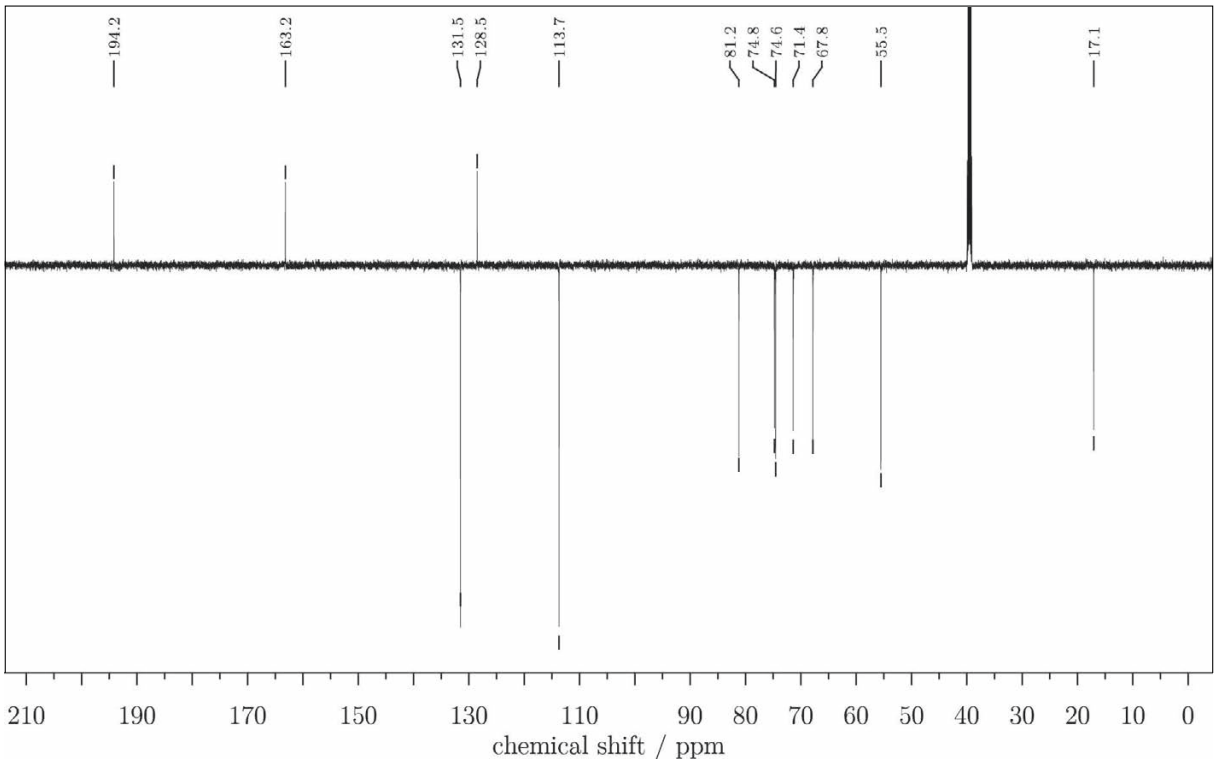


Figure 134: DEPTQ-NMR spectrum of **188** at 151 MHz in DMSO-d_6.

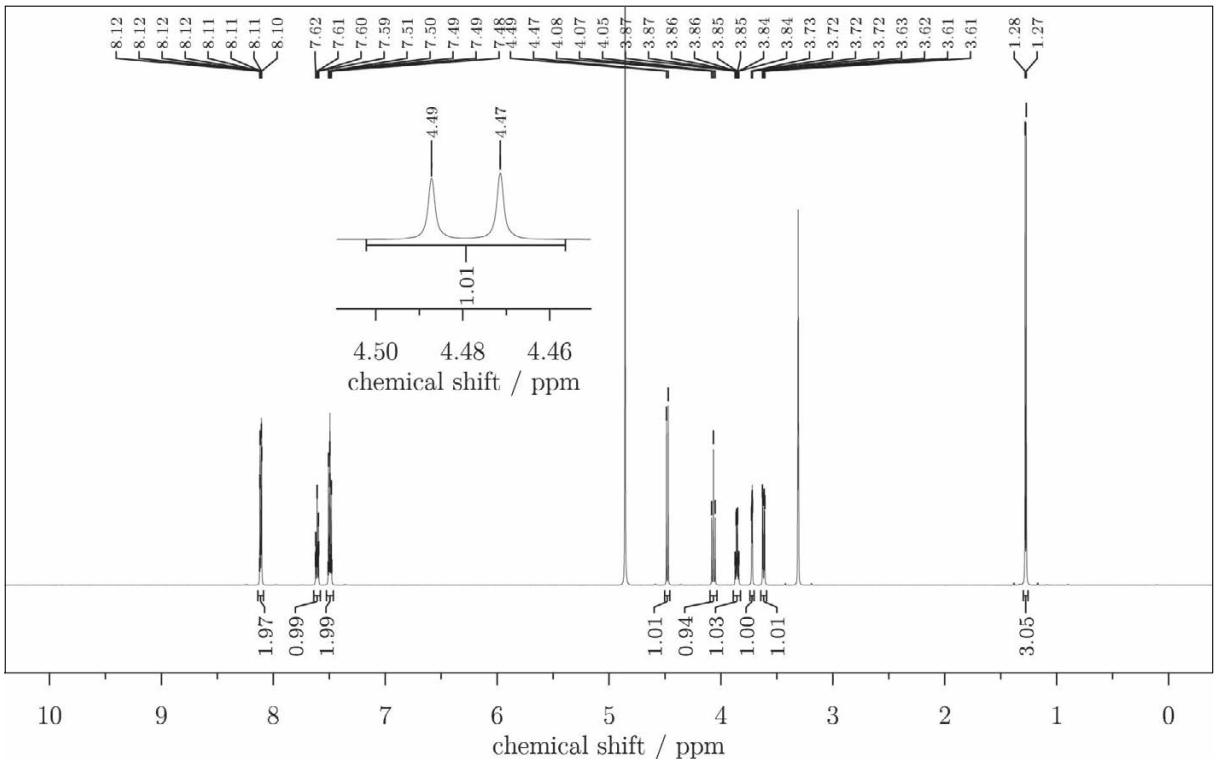


Figure 135: ^{1}H-NMR spectrum of **189** at 600 MHz in methanol-d_4.

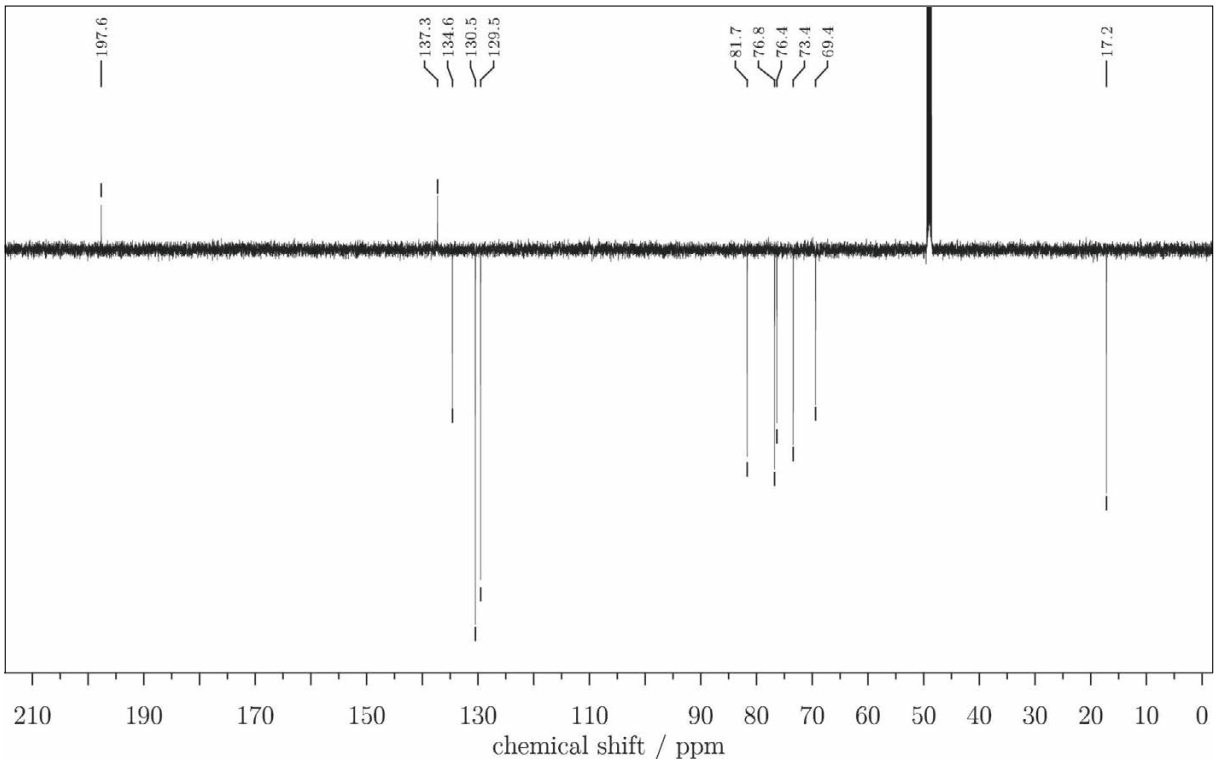


Figure 136: DEPTQ-NMR spectrum of **189** at 151 MHz in methanol-d_4.

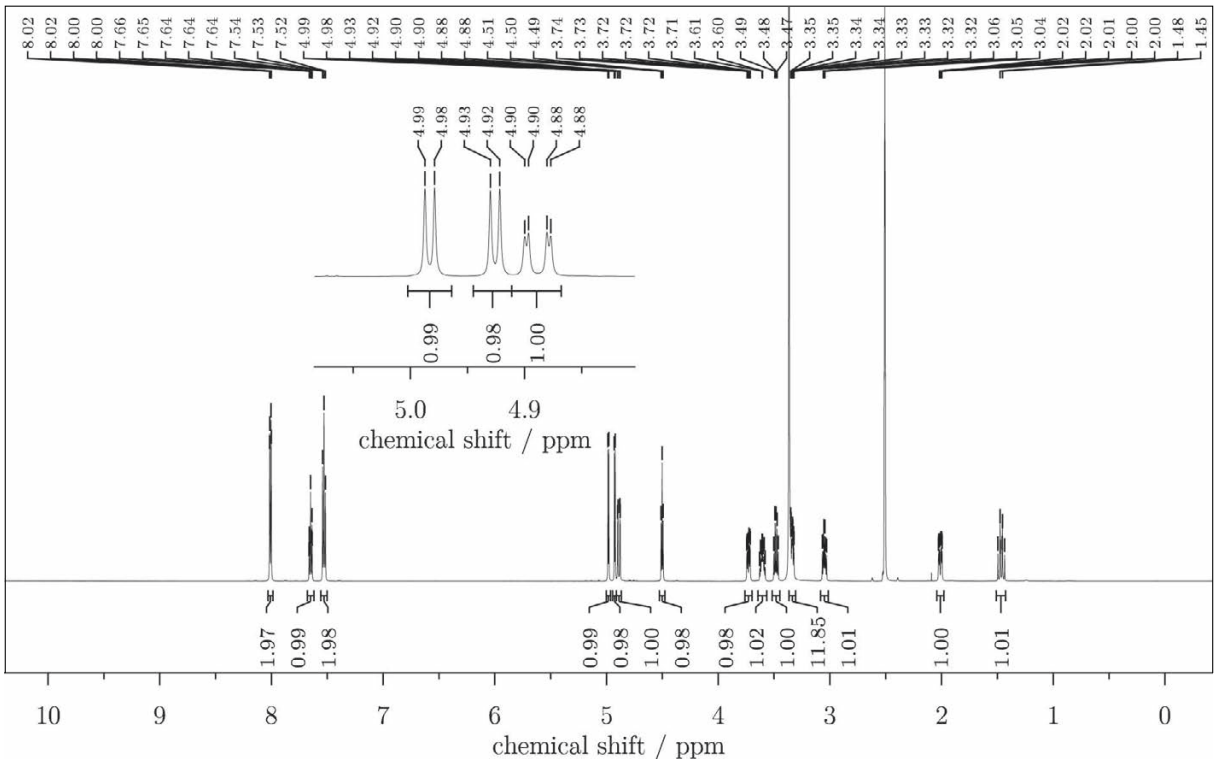


Figure 137: [1]H-NMR spectrum of **192** at 600 MHz in DMSO-d_6.

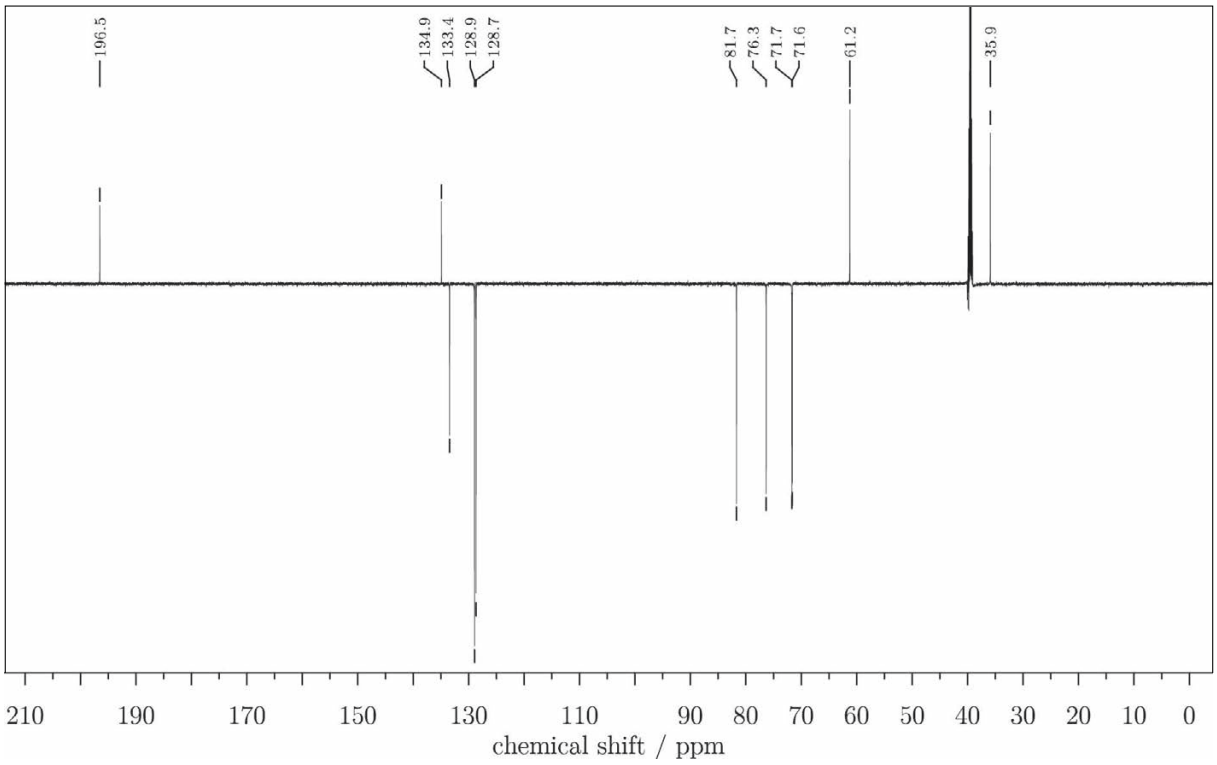


Figure 138: DEPTQ-NMR spectrum of **192** at 151 MHz in DMSO-d_6.

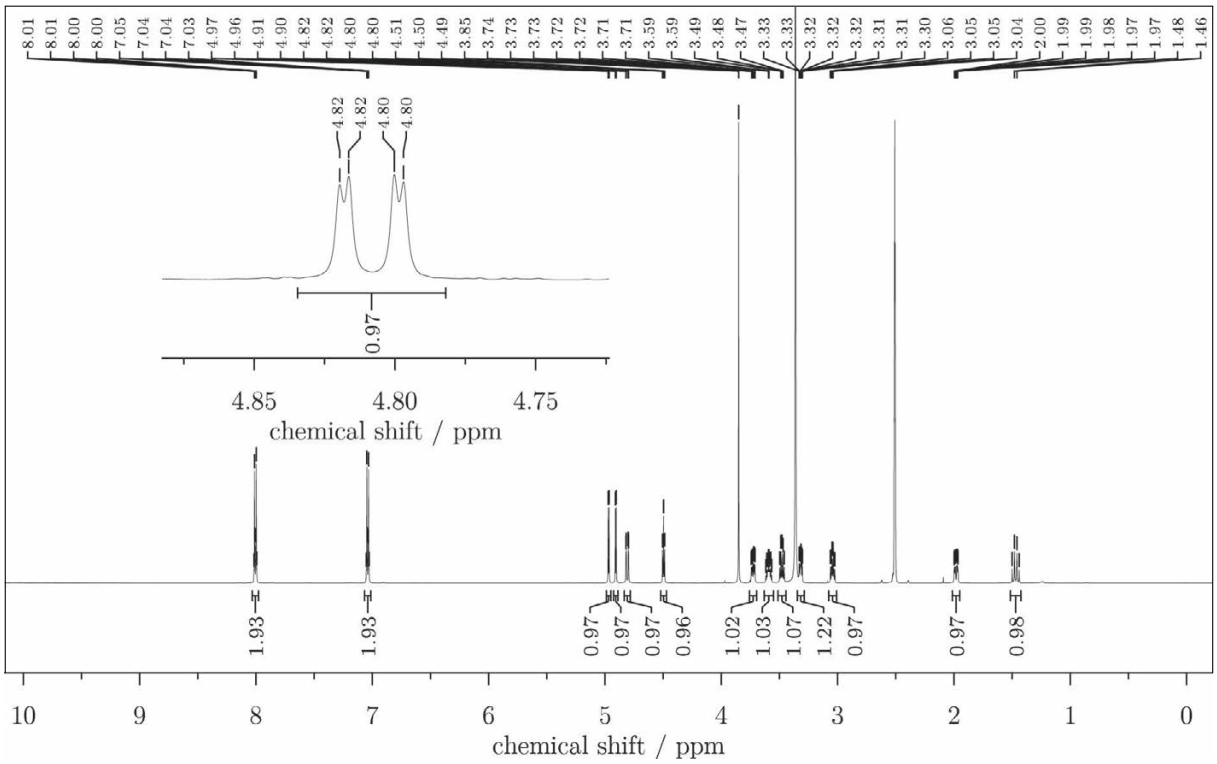


Figure 139: ^{1}H-NMR spectrum of **193** at 600 MHz in DMSO-d_6.

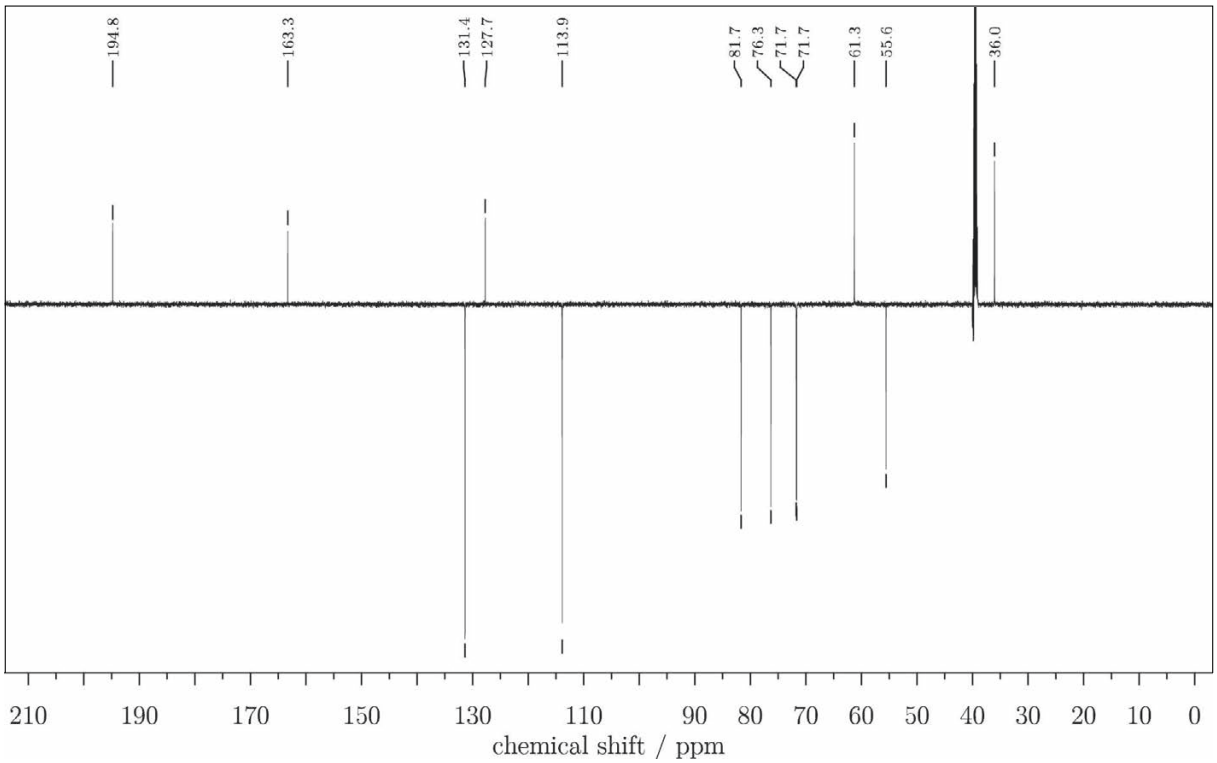


Figure 140: DEPTQ-NMR spectrum of **193** at 151 MHz in DMSO-d_6.

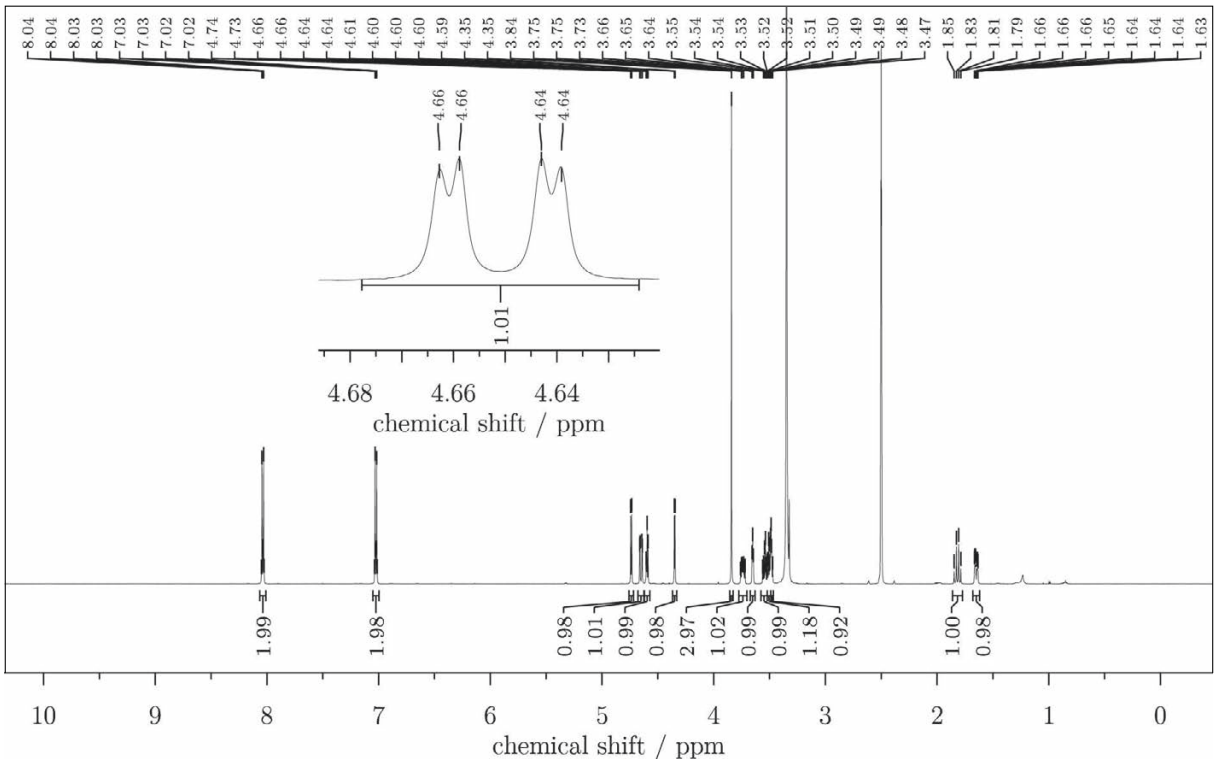


Figure 141: ^{1}H-NMR spectrum of **194** at 600 MHz in DMSO-d_6.

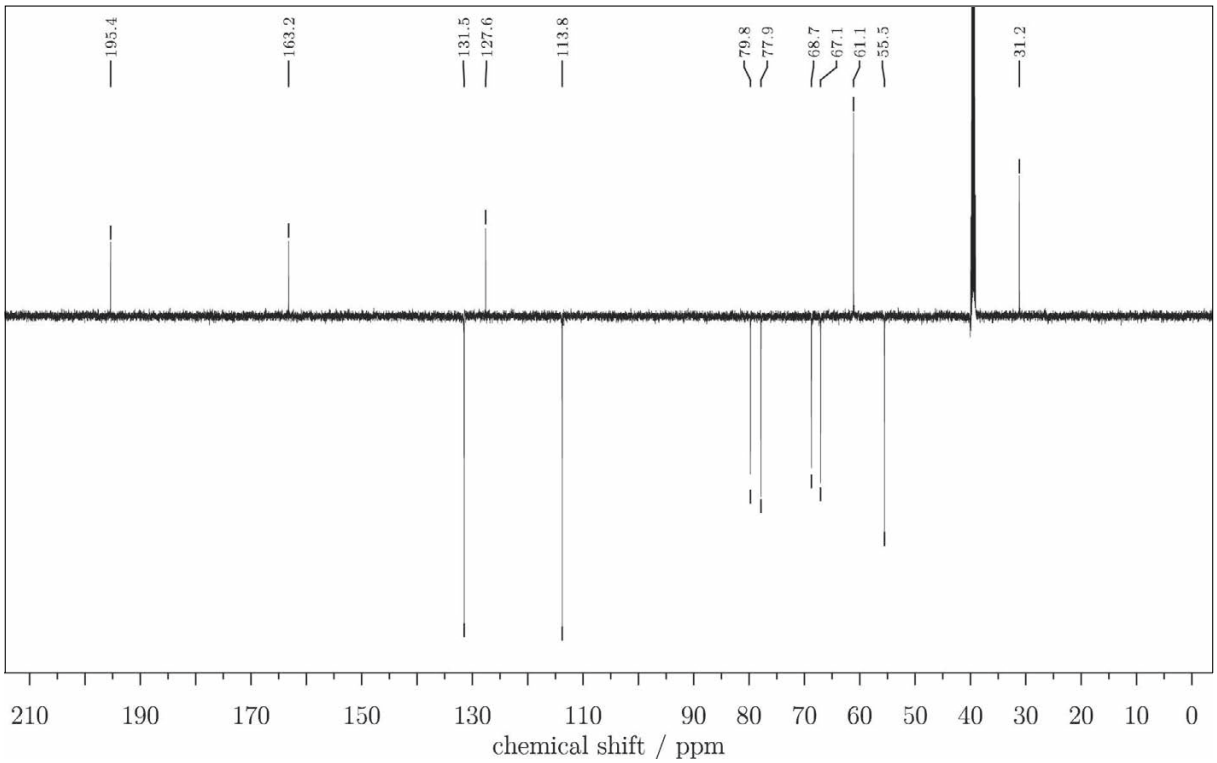


Figure 142: DEPTQ-NMR spectrum of **194** at 151 MHz in DMSO-d_6.

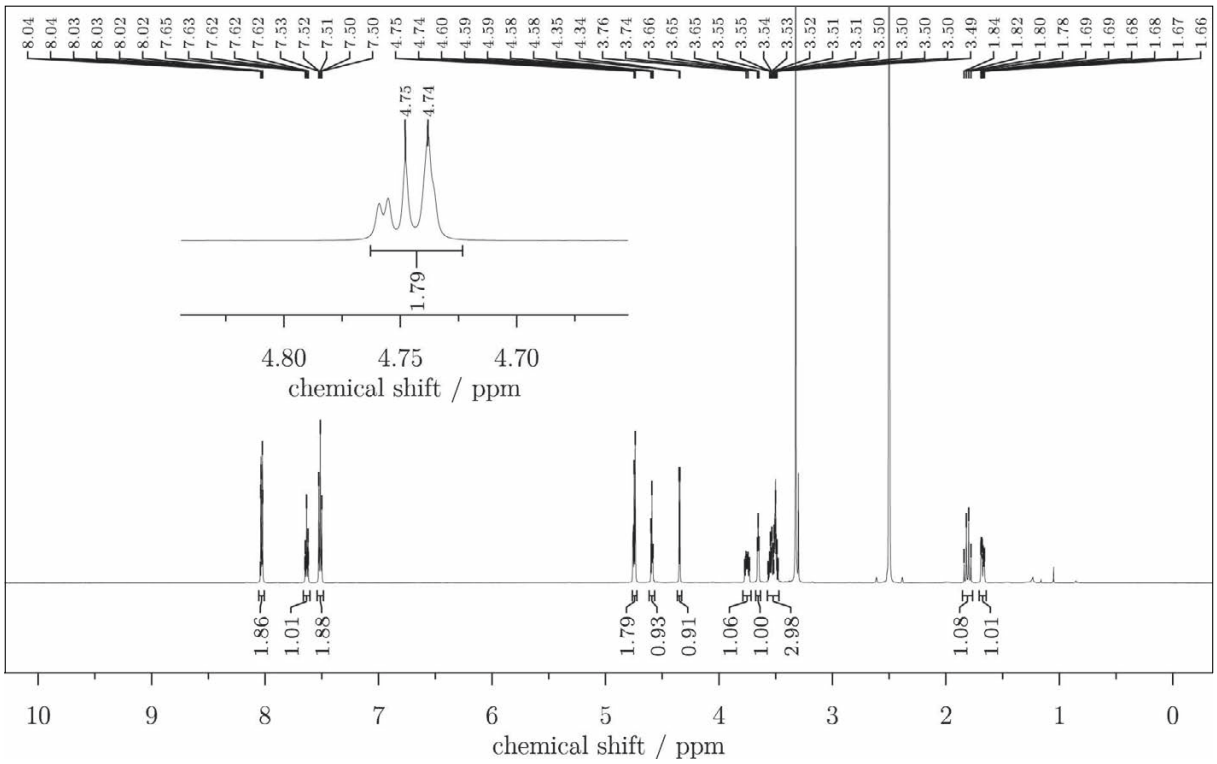


Figure 143: ^{1}H-NMR spectrum of **195** at 600 MHz in DMSO-d_6.

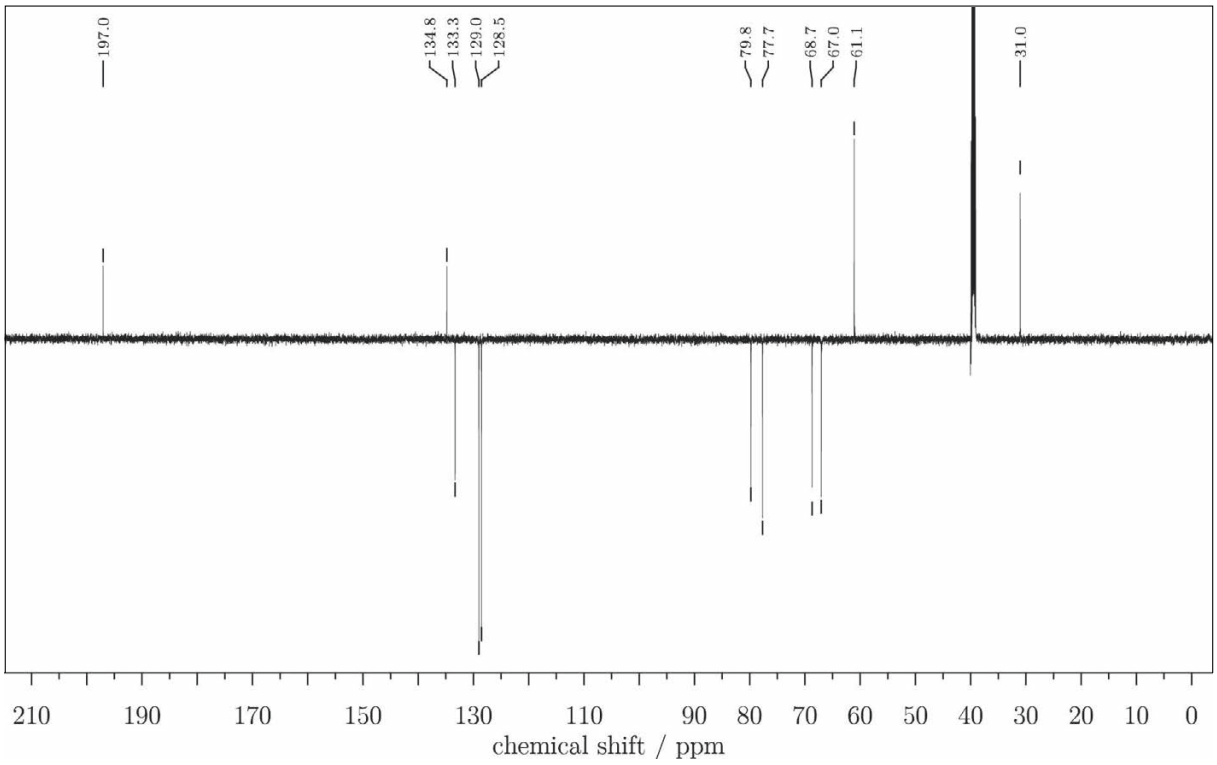


Figure 144: DEPTQ-NMR spectrum of **195** at 151 MHz in DMSO-d_6.

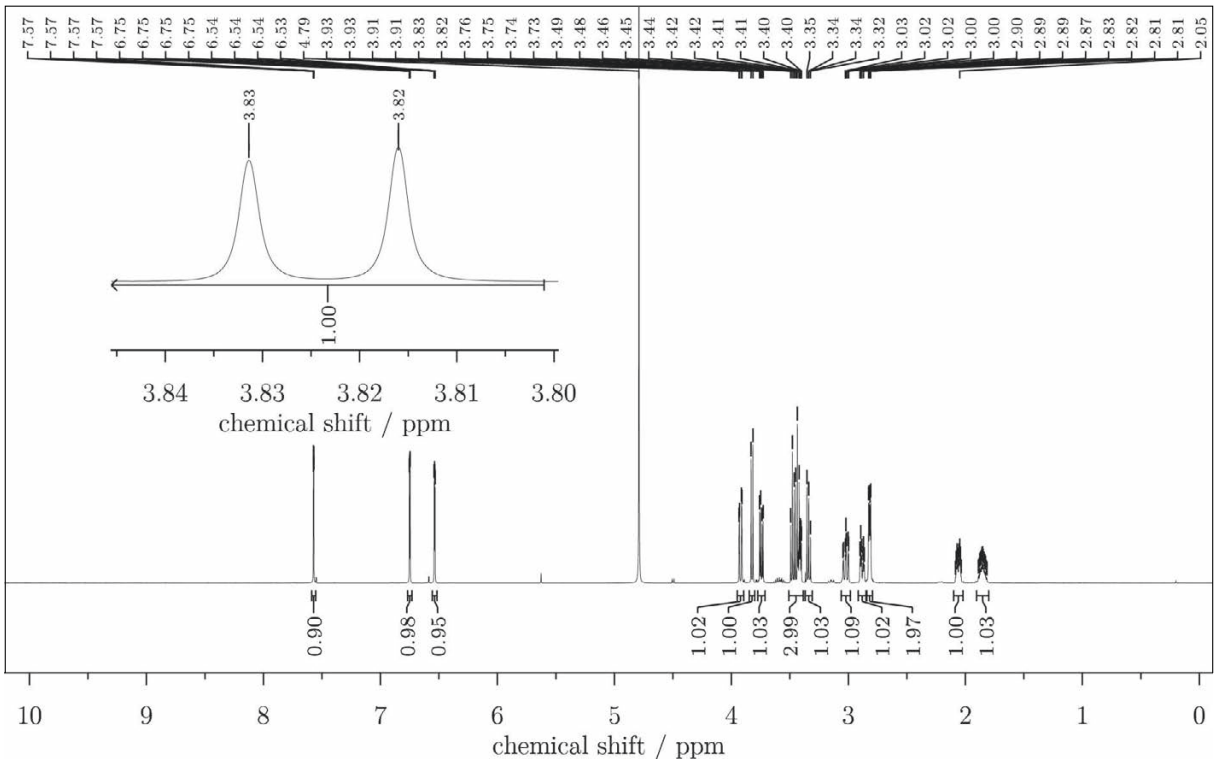


Figure 145: ^{1}H-NMR spectrum of **197** at 600 MHz in D_2O.

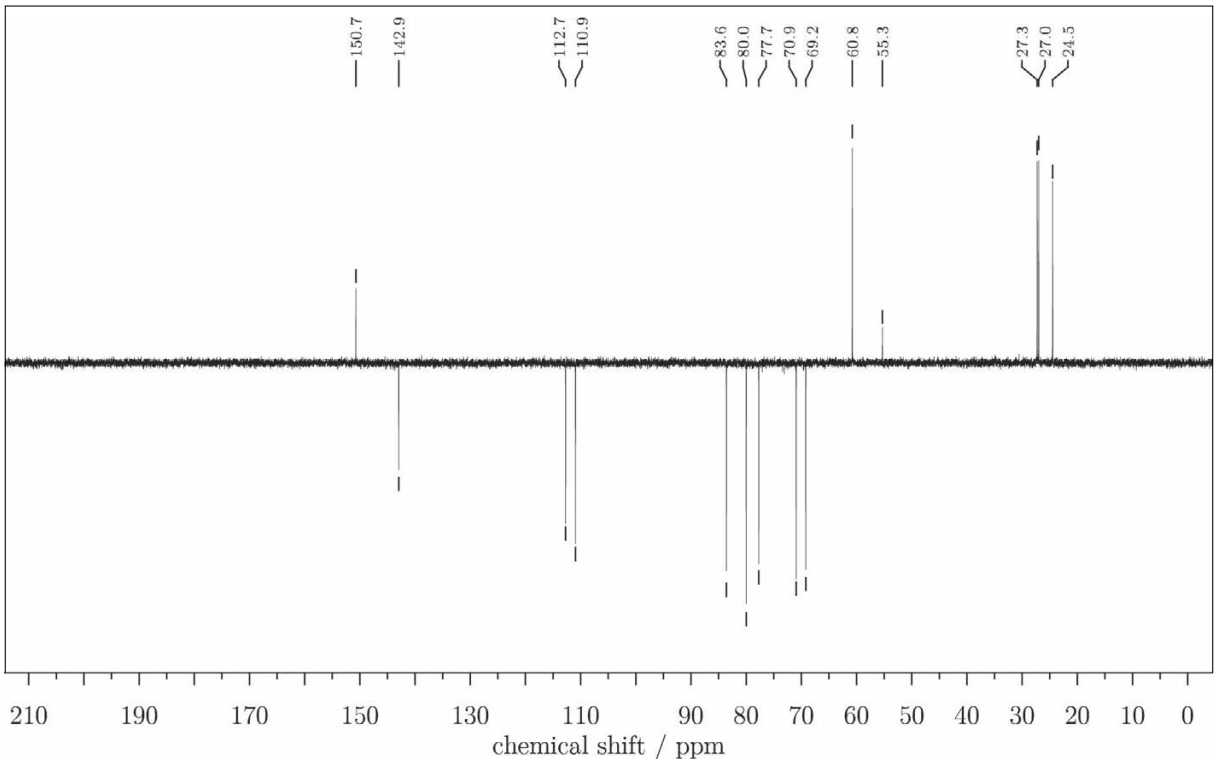


Figure 146: DEPTQ-NMR spectrum of **197** at 151 MHz in D_2O.

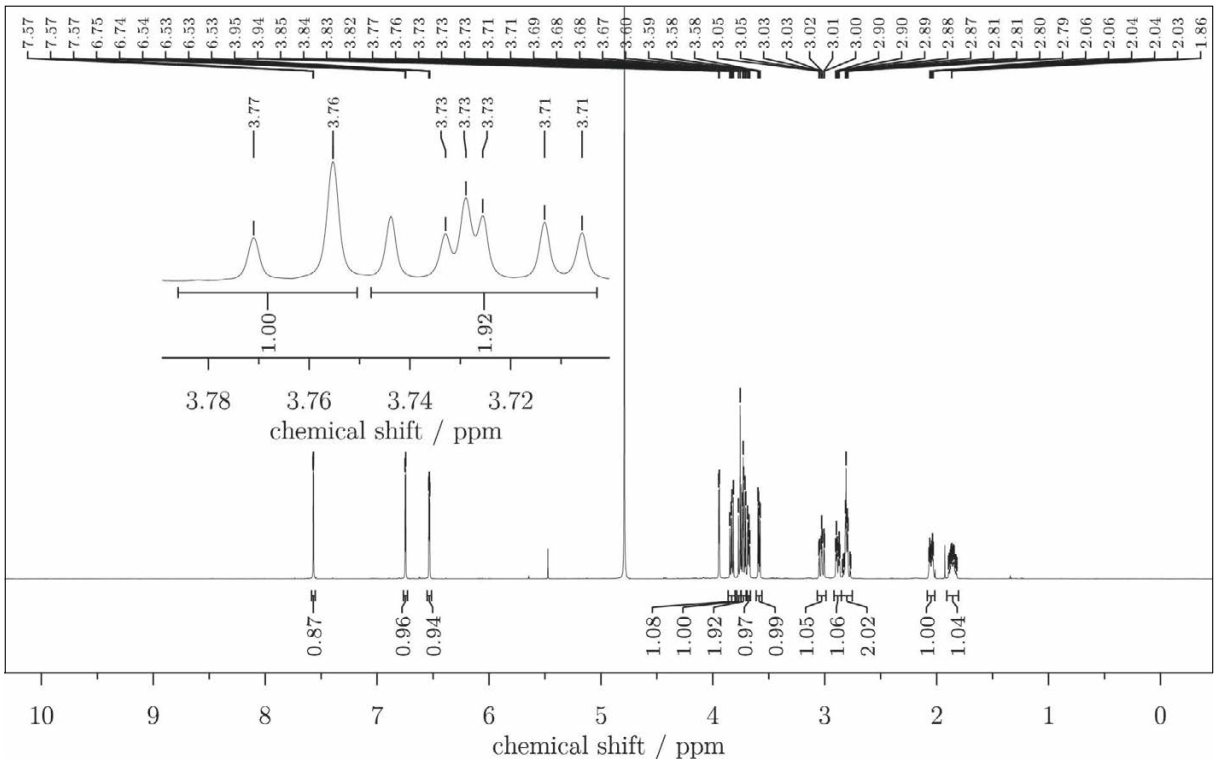


Figure 147: ^{1}H-NMR spectrum of **198** at 600 MHz in D_2O.

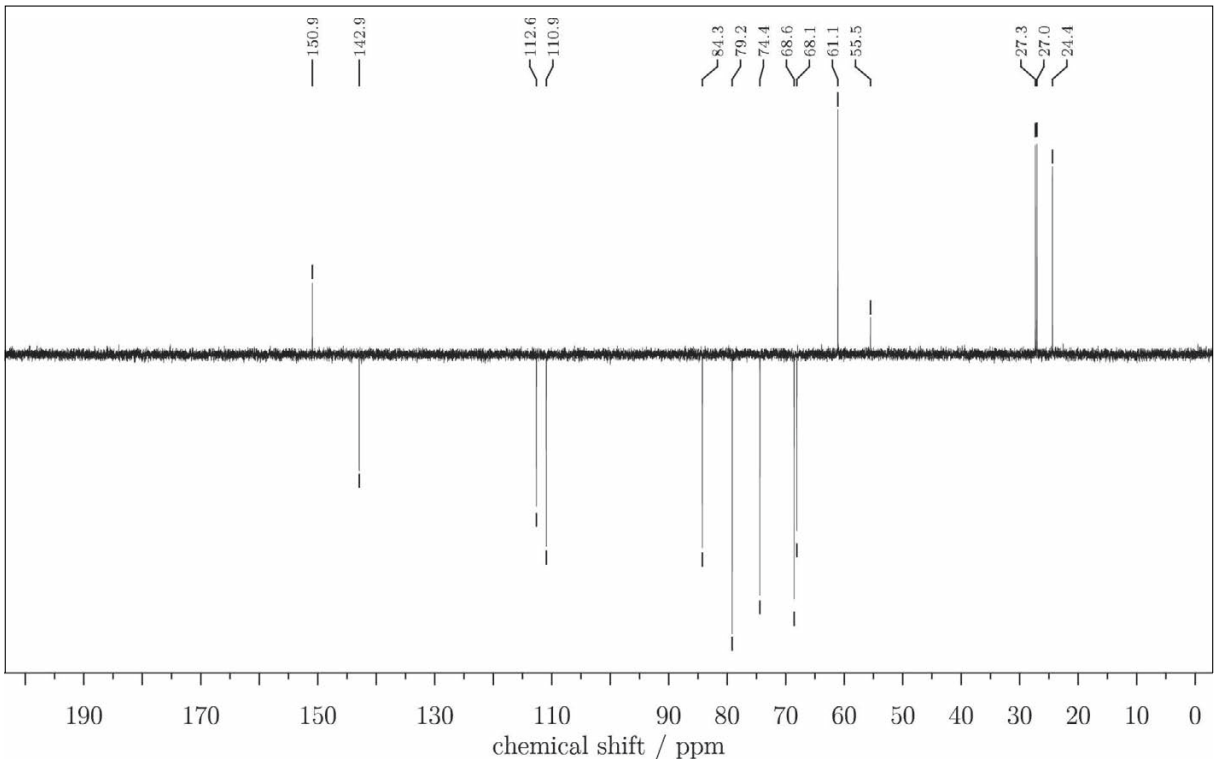


Figure 148: DEPTQ-NMR spectrum of **198** at 151 MHz in D_2O.

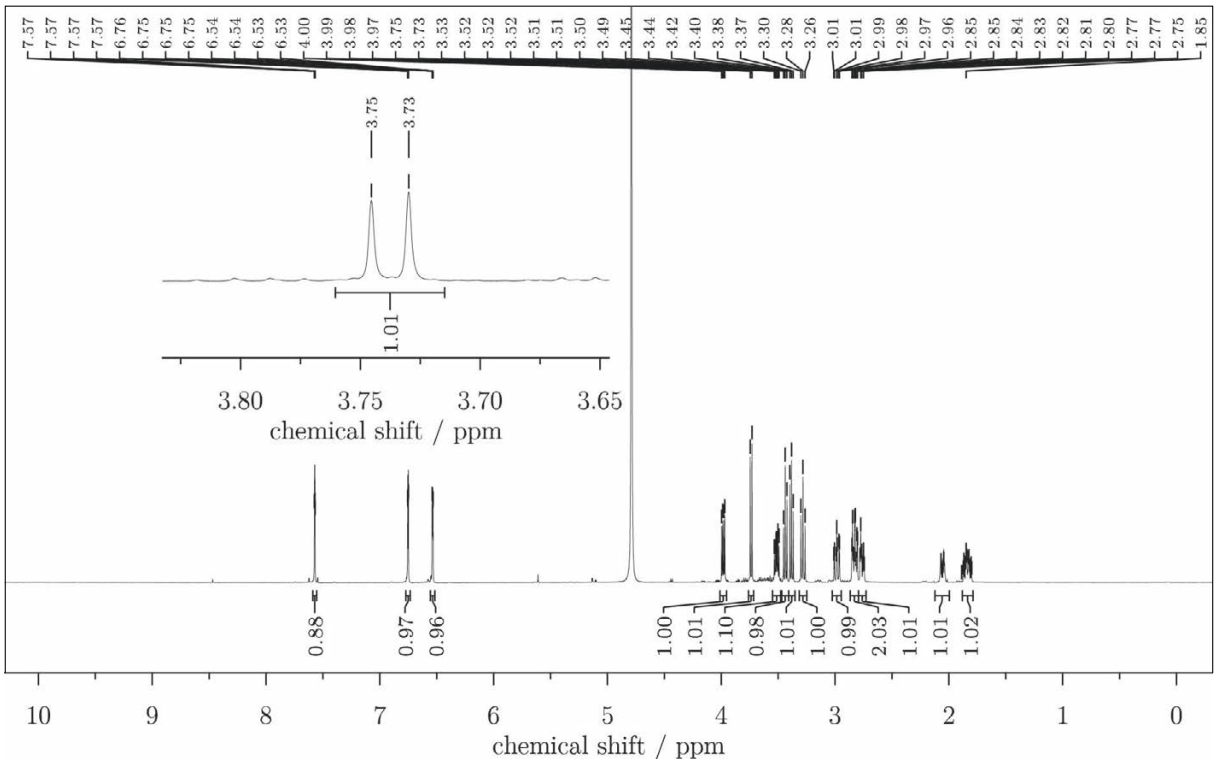


Figure 149: ^{1}H-NMR spectrum of **199** at 600 MHz in D_2O.

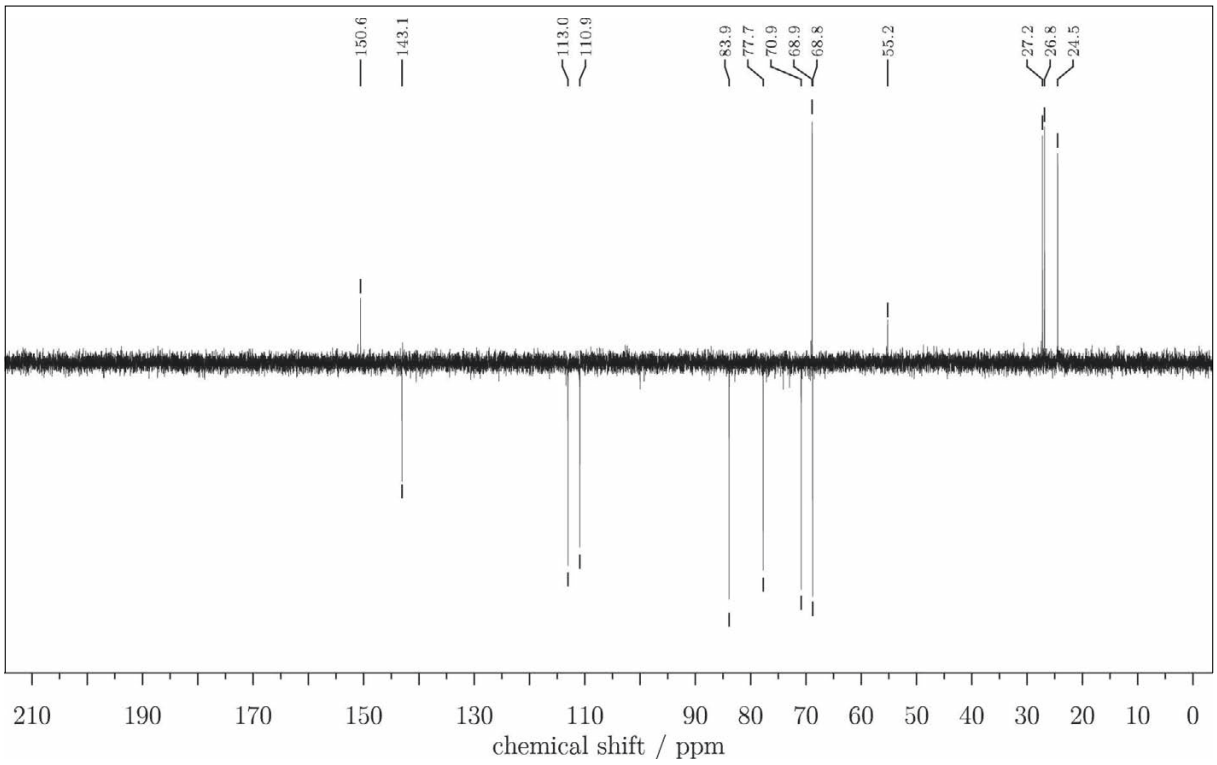


Figure 150: DEPTQ-NMR spectrum of **199** at 151 MHz in D_2O.

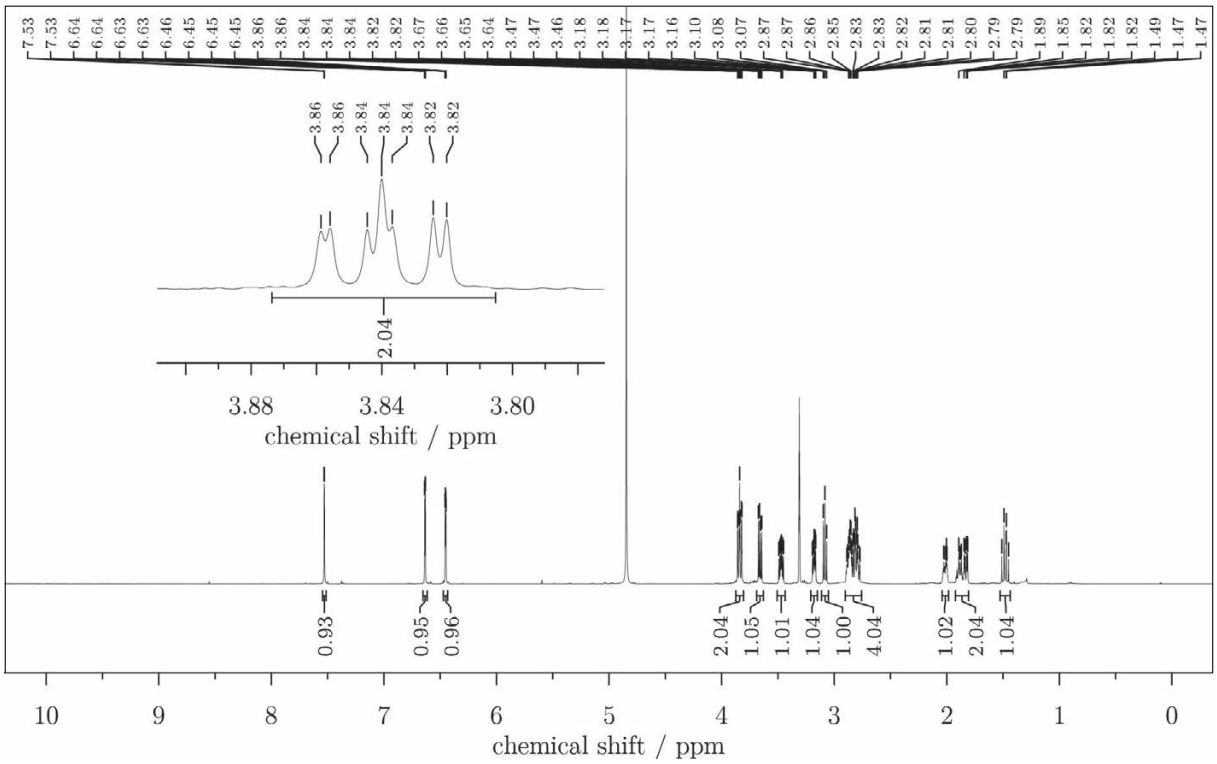


Figure 151: ^{1}H-NMR spectrum of **200** at 600 MHz in methanol-d_4.

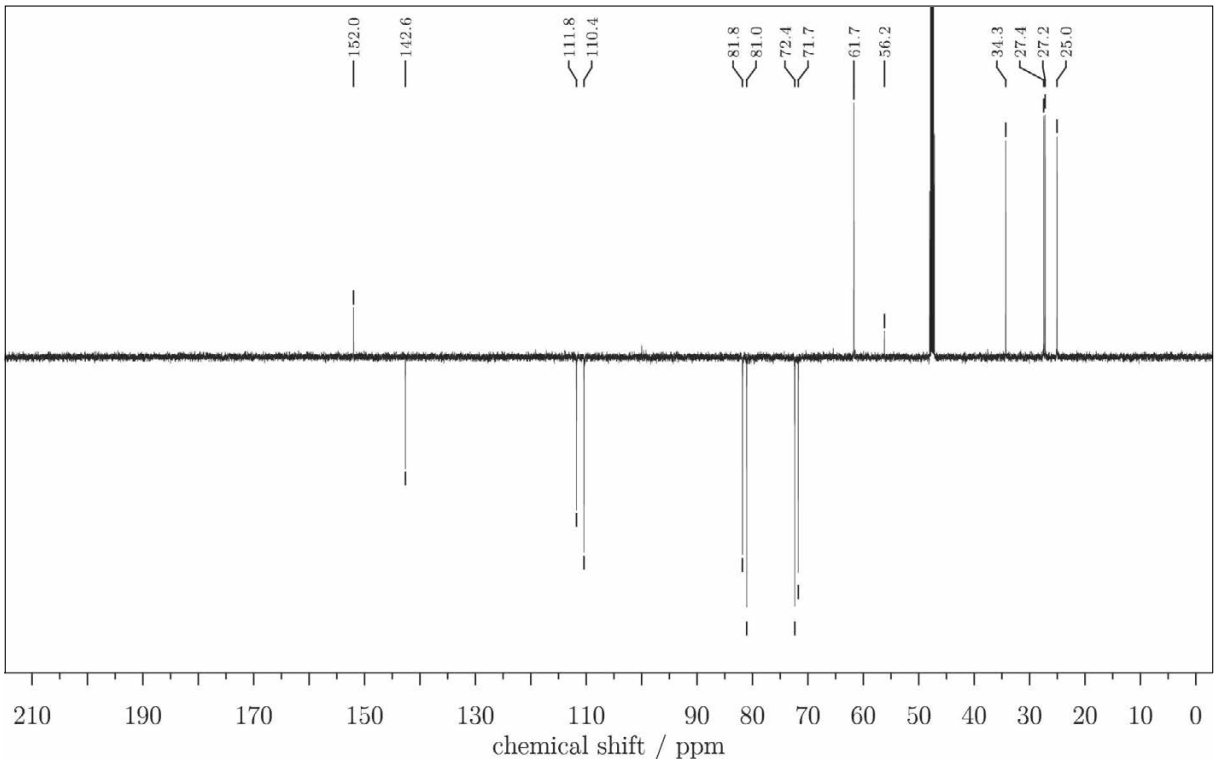


Figure 152: DEPTQ-NMR spectrum of **200** at 151 MHz in methanol-d_4.

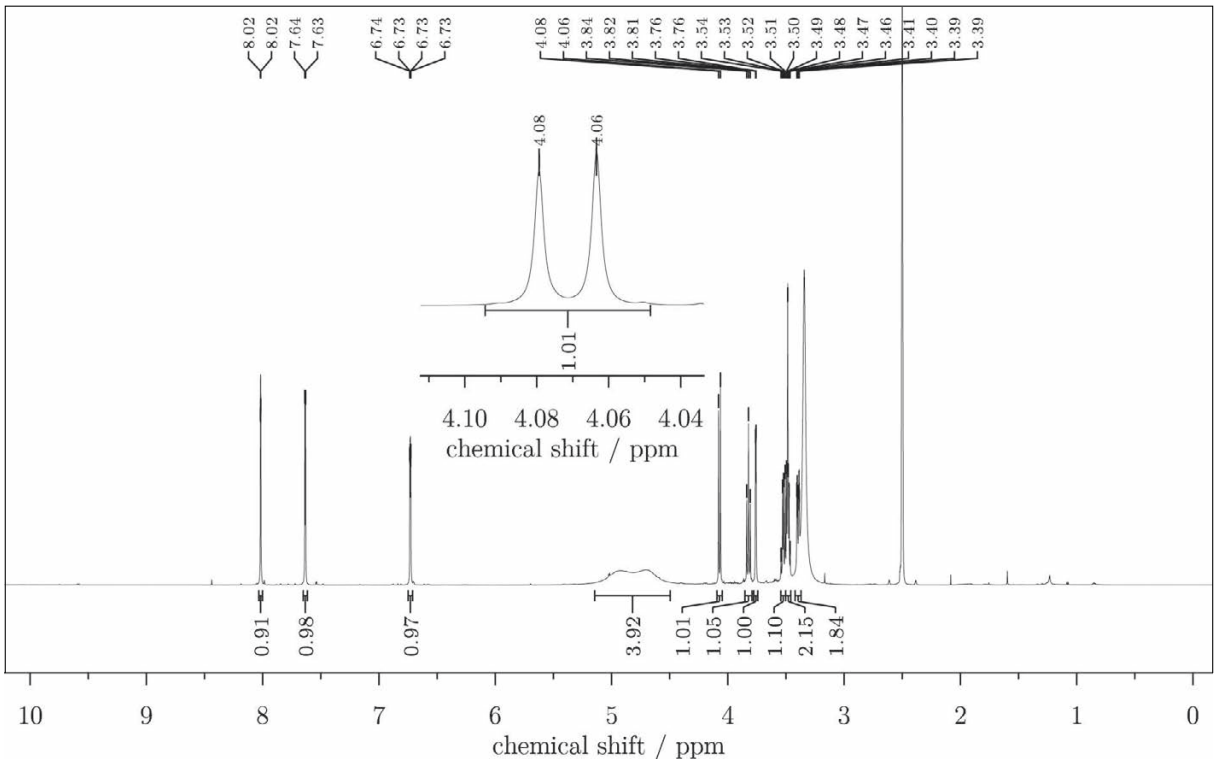


Figure 153: ^{1}H-NMR spectrum of **201** at 600 MHz in DMSO-d_6.

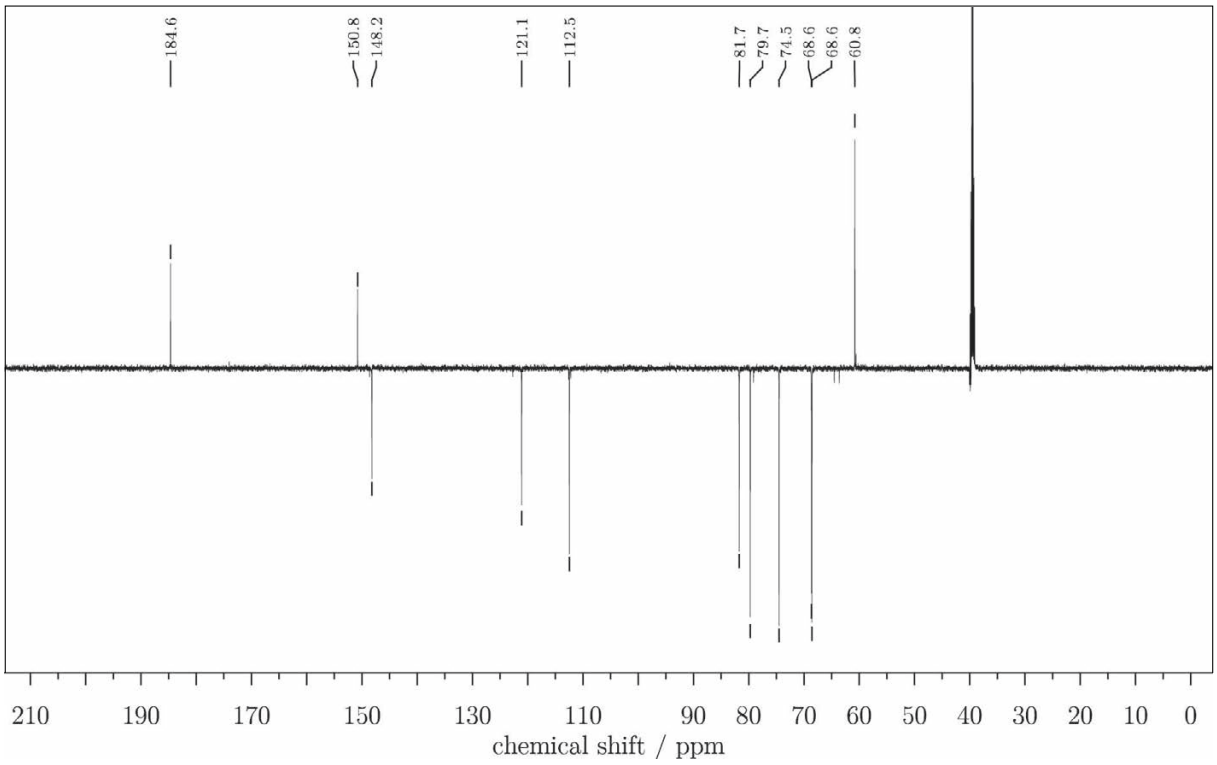


Figure 154: DEPTQ-NMR spectrum of **201** at 151 MHz in DMSO-d_6.

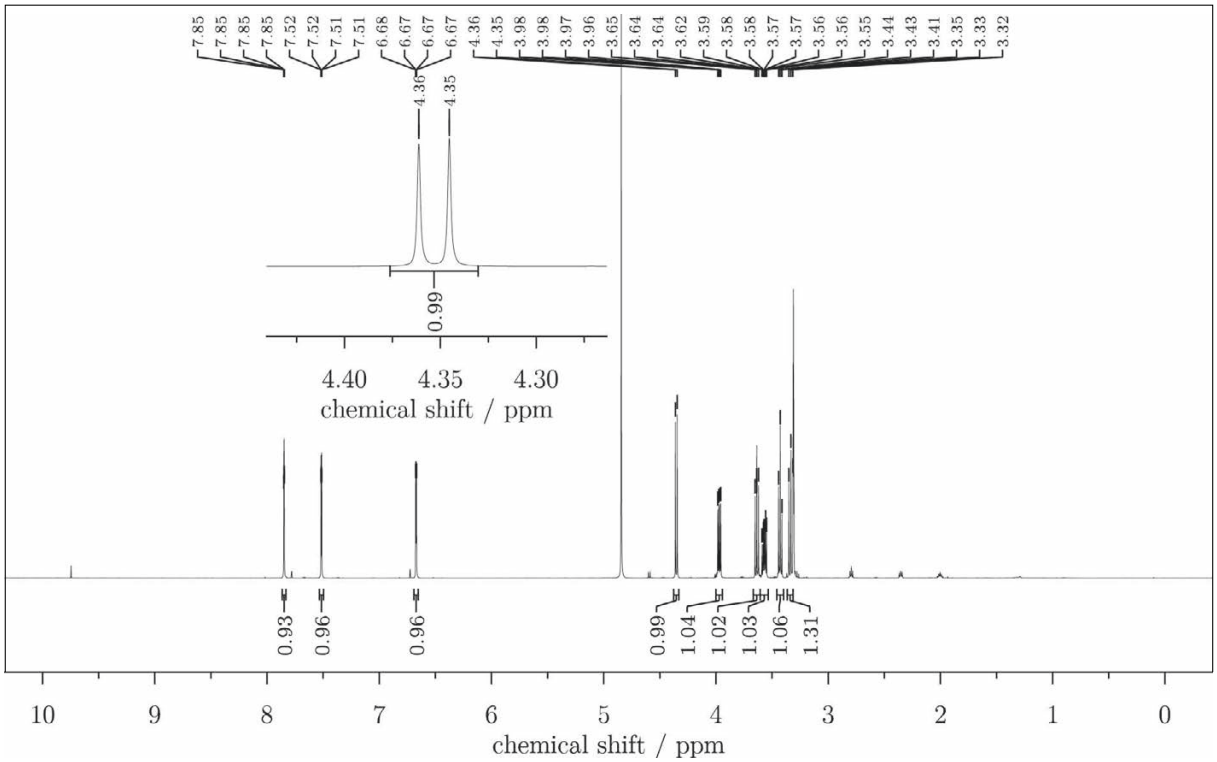


Figure 155: ^{1}H-NMR spectrum of **202** at 600 MHz in methanol-d_4.

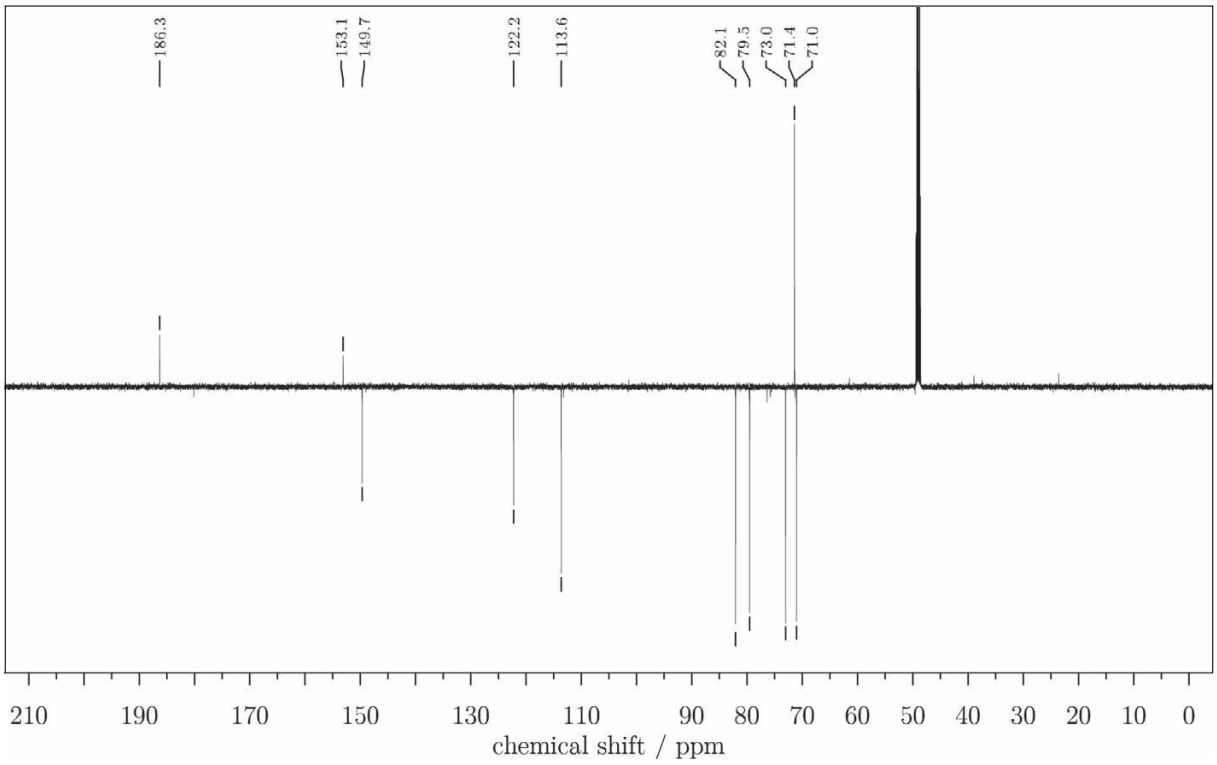


Figure 156: DEPTQ-NMR spectrum of **202** at 151 MHz in methanol-d_4.

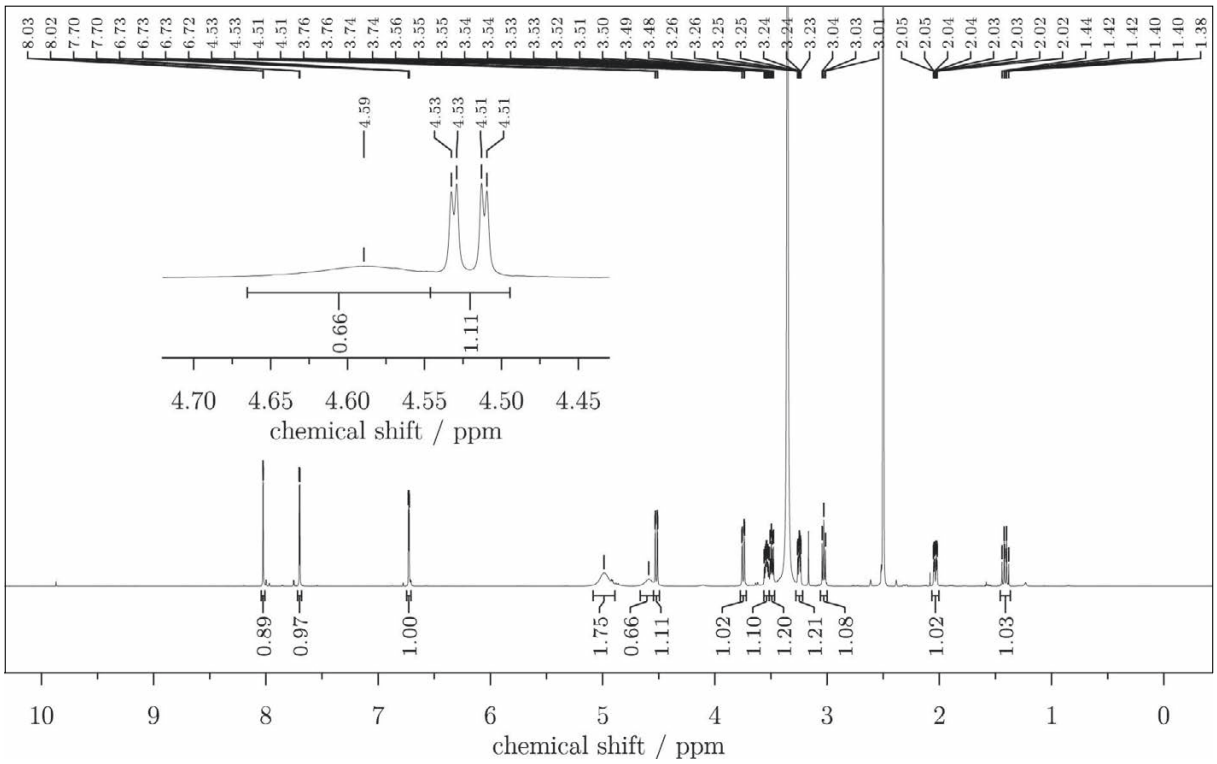


Figure 157: ^{1}H-NMR spectrum of **203** at 600 MHz in DMSO-d_6.

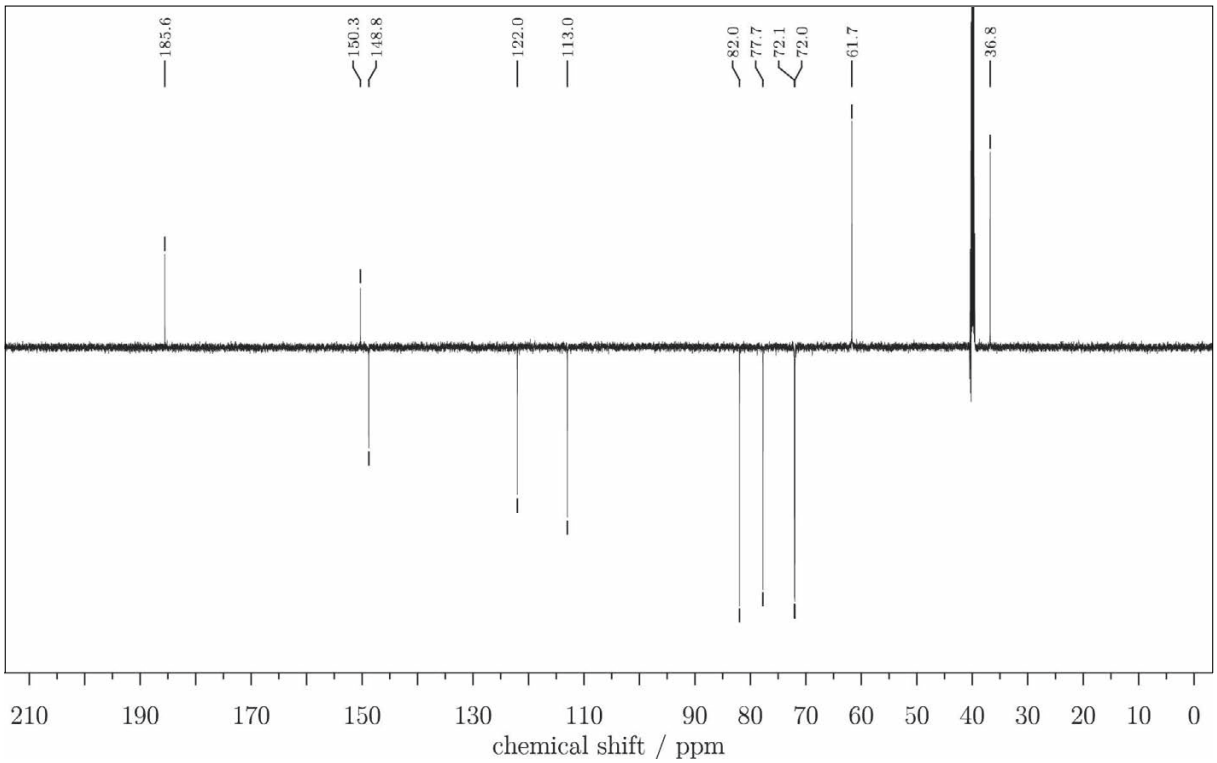


Figure 158: DEPTQ-NMR spectrum of **203** at 151 MHz in DMSO-d_6.

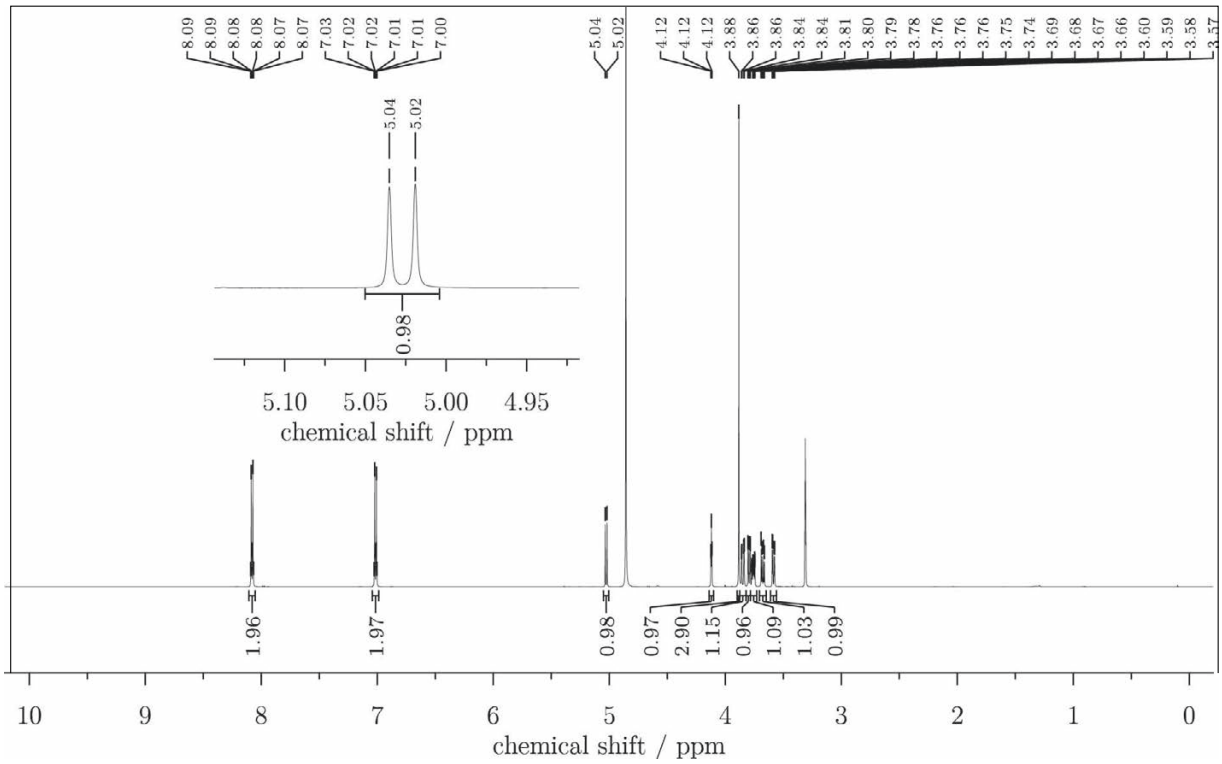


Figure 159: ^{1}H-NMR spectrum of **204** at 600 MHz in methanol-d_4.

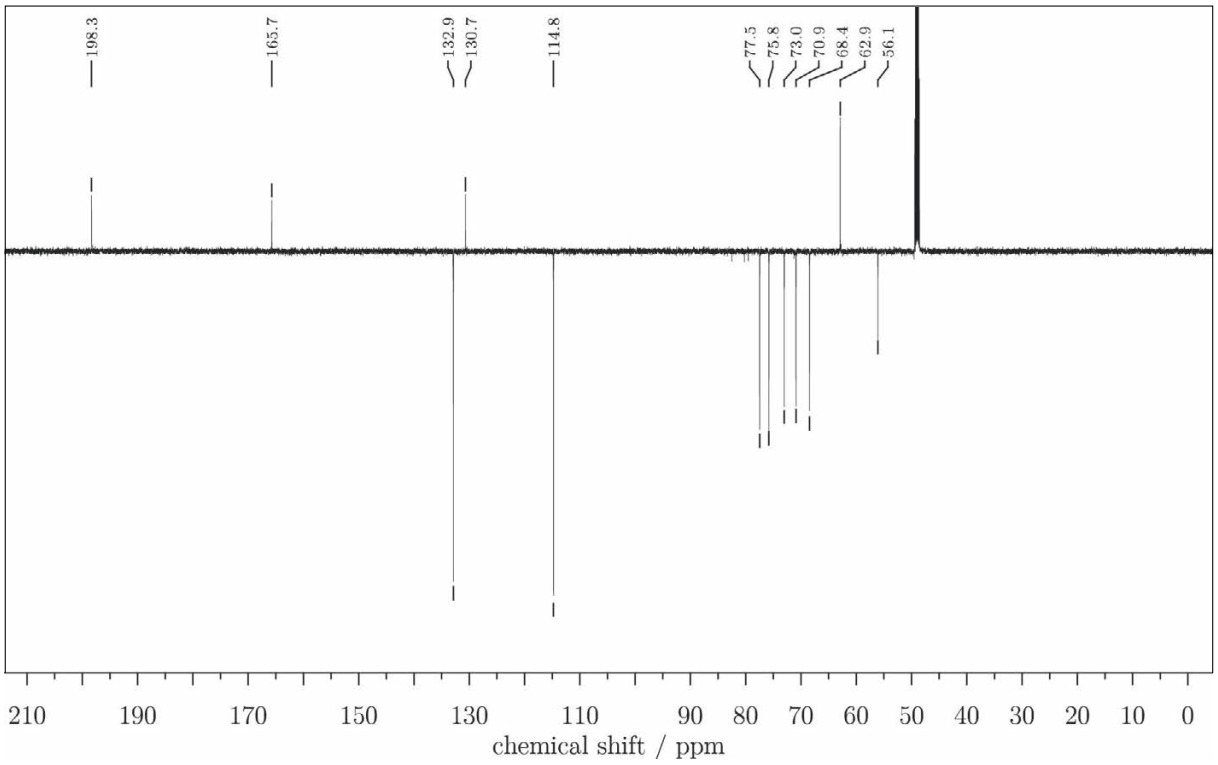


Figure 160: DEPTQ-NMR spectrum of **204** at 151 MHz in methanol-d_4.

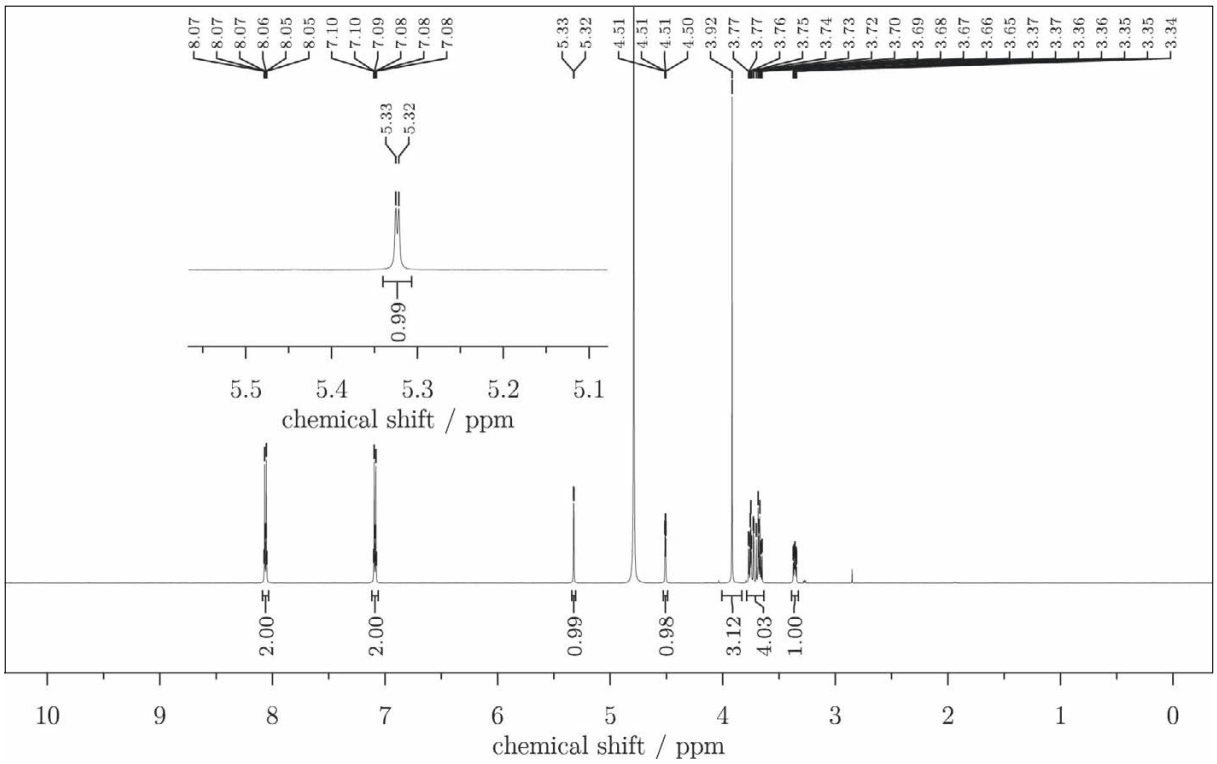


Figure 161: ^{1}H-NMR spectrum of **210** at 600 MHz in D_2O.

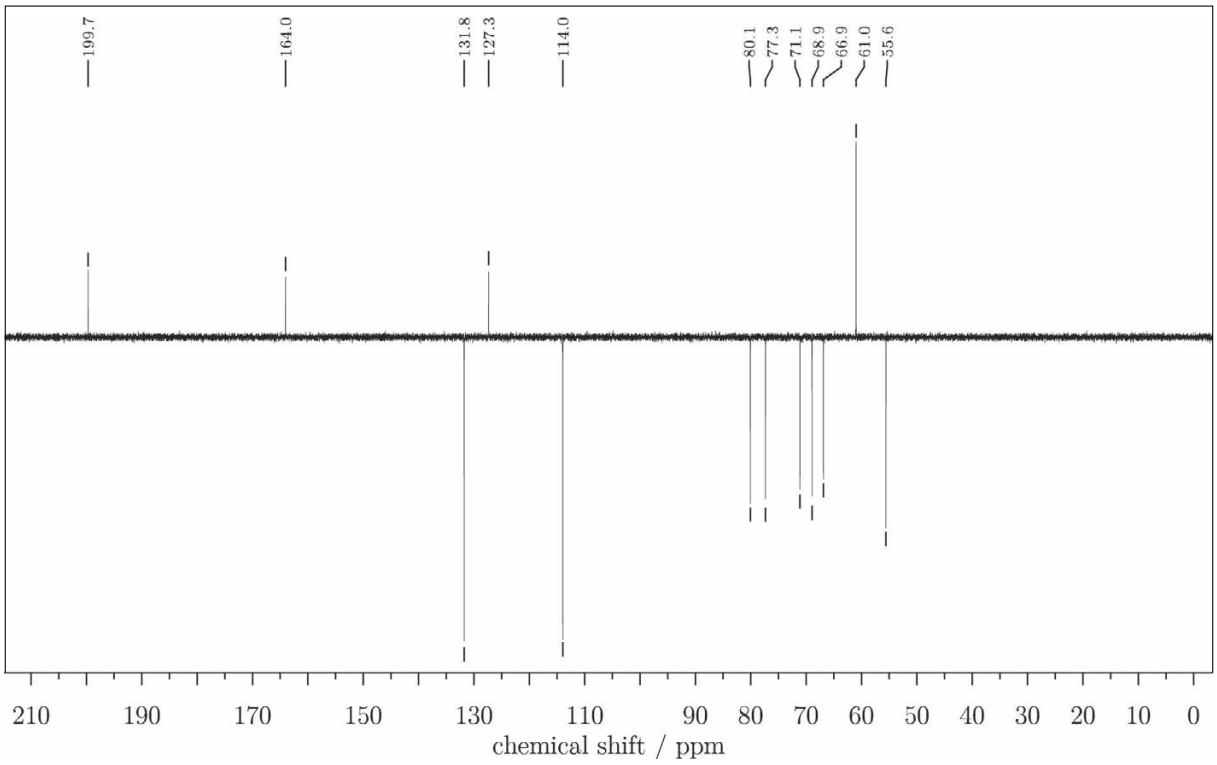


Figure 162: DEPTQ-NMR spectrum of **210** at 151 MHz in D_2O.

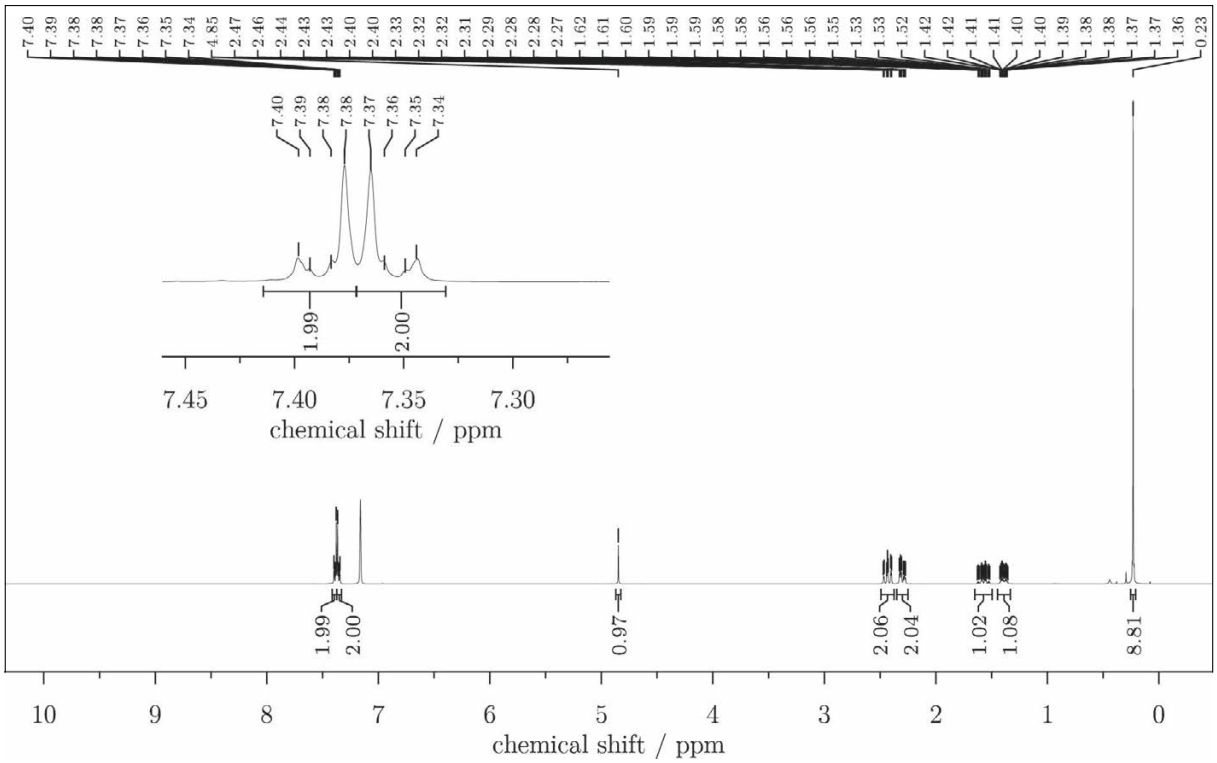


Figure 163: ^{1}H-NMR spectrum of **215** at 400 MHz in benzene-d_6.

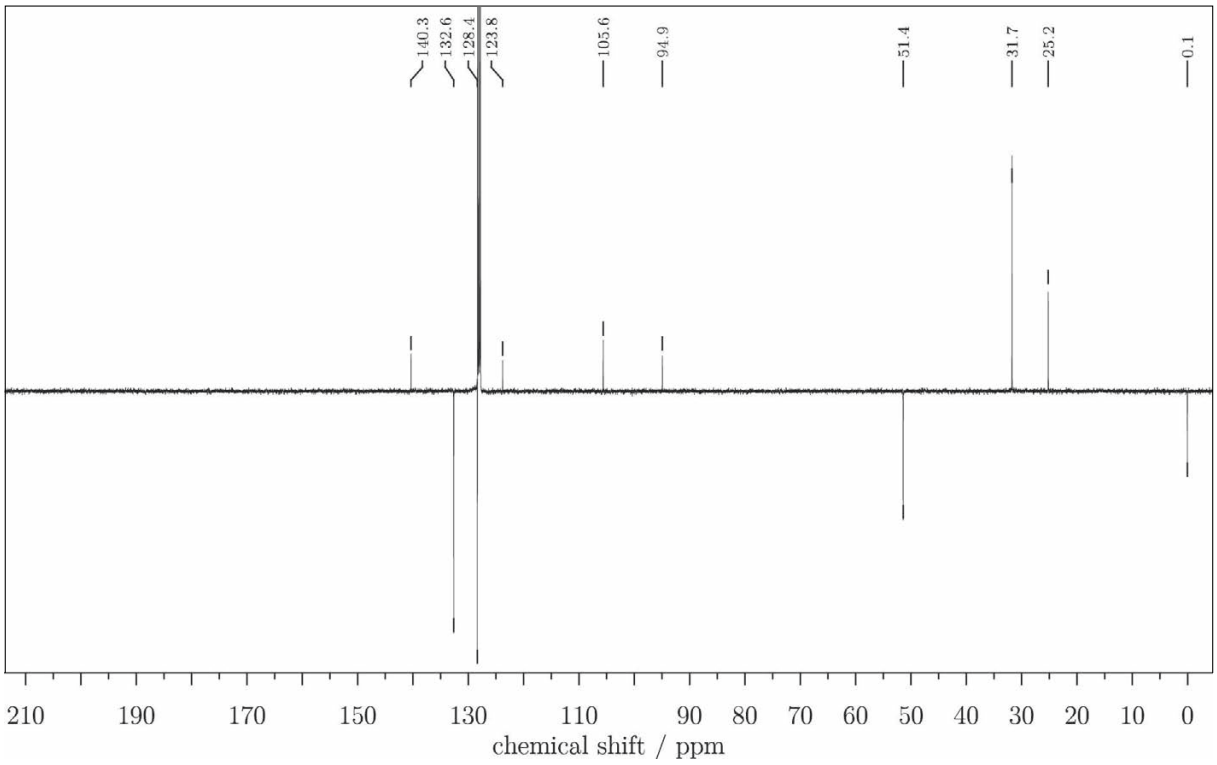


Figure 164: DEPTQ-NMR spectrum of **215** at 100 MHz in benzene-d_6.

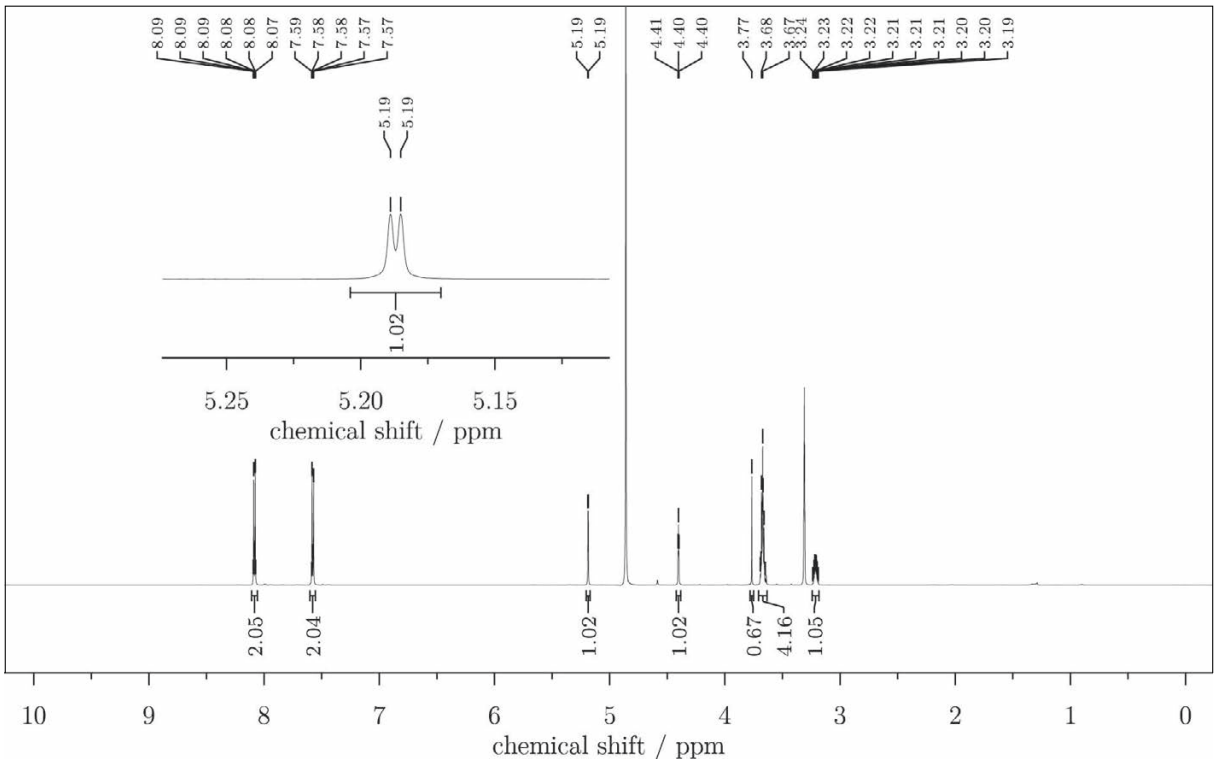


Figure 165: ^{1}H-NMR spectrum of **216** at 600 MHz in methanol-d_4.

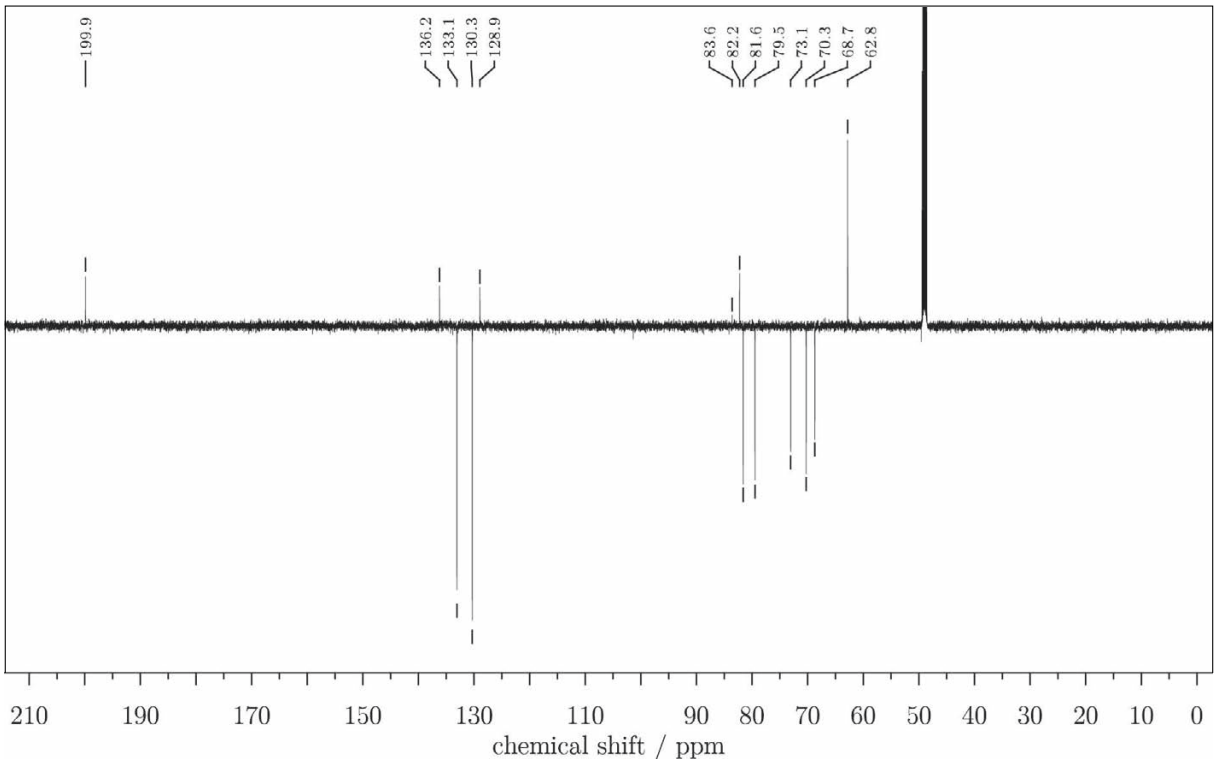


Figure 166: DEPTQ-NMR spectrum of **216** at 151 MHz in methanol-d_4.

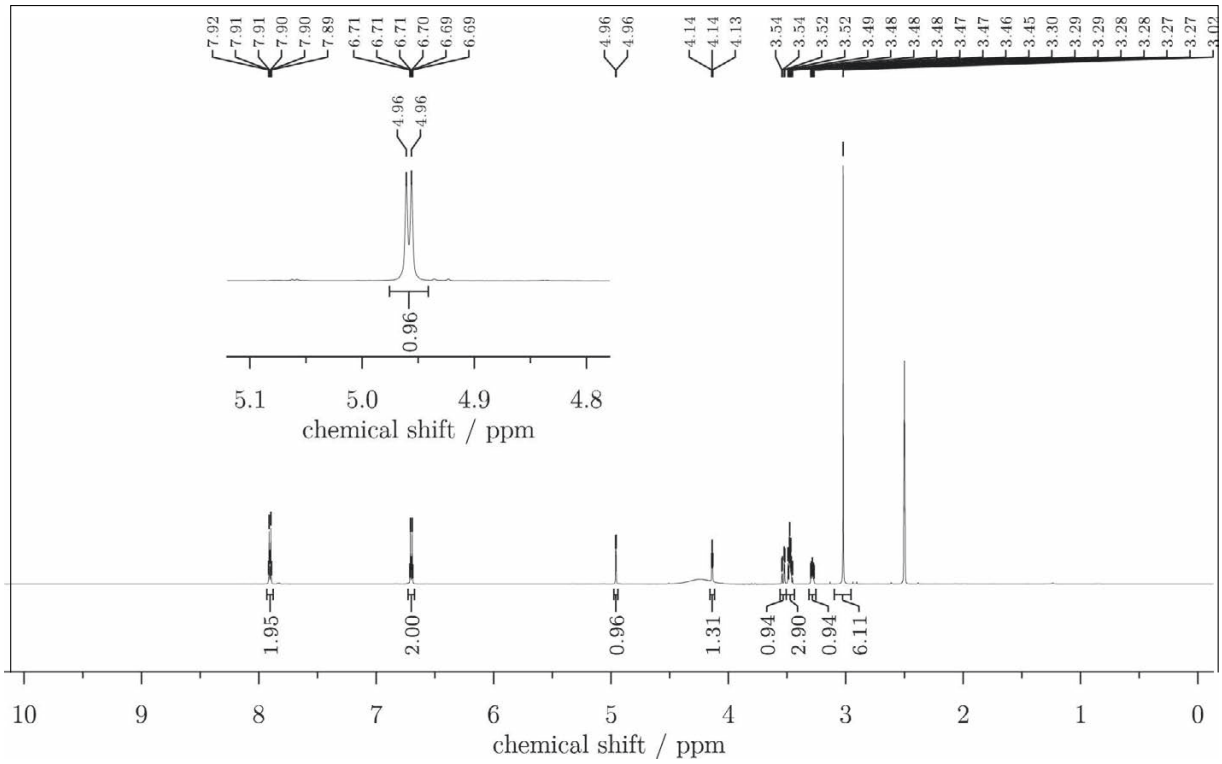


Figure 167: ^{1}H-NMR spectrum of **217** at 600 MHz in DMSO-d_6.

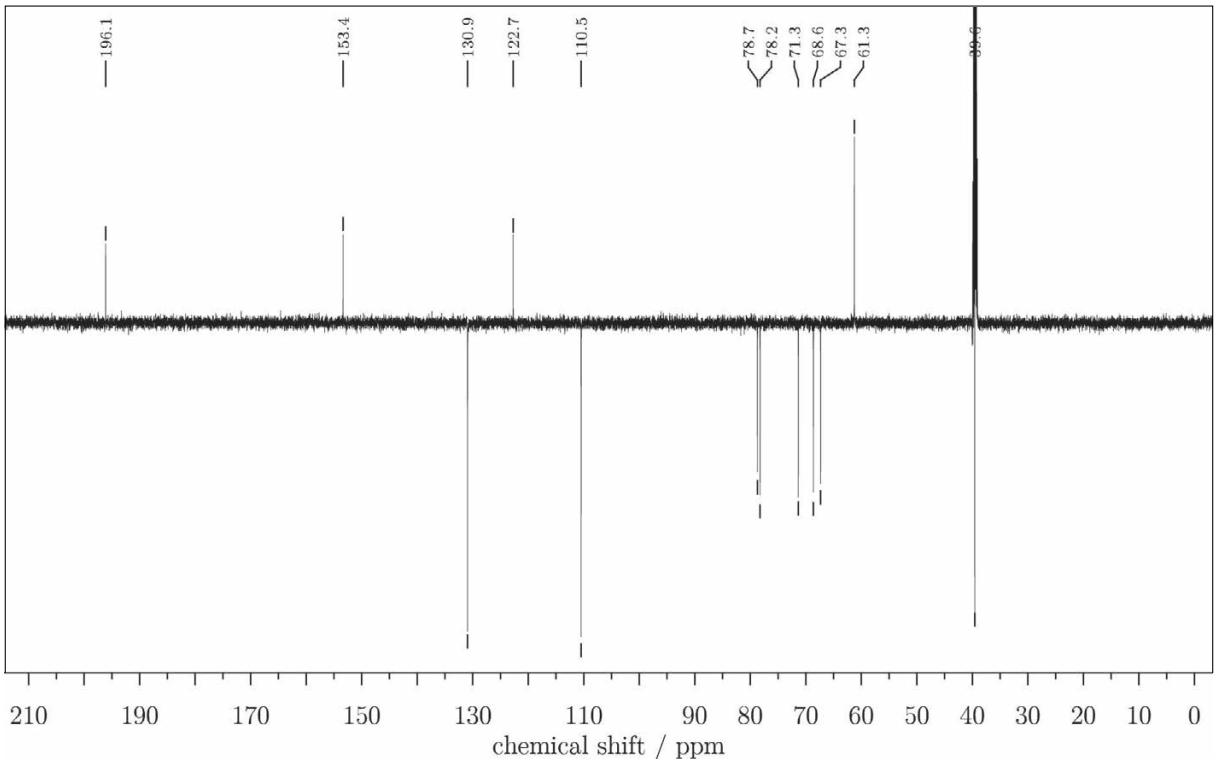


Figure 168: DEPTQ-NMR spectrum of **217** at 151 MHz in DMSO-d_6.

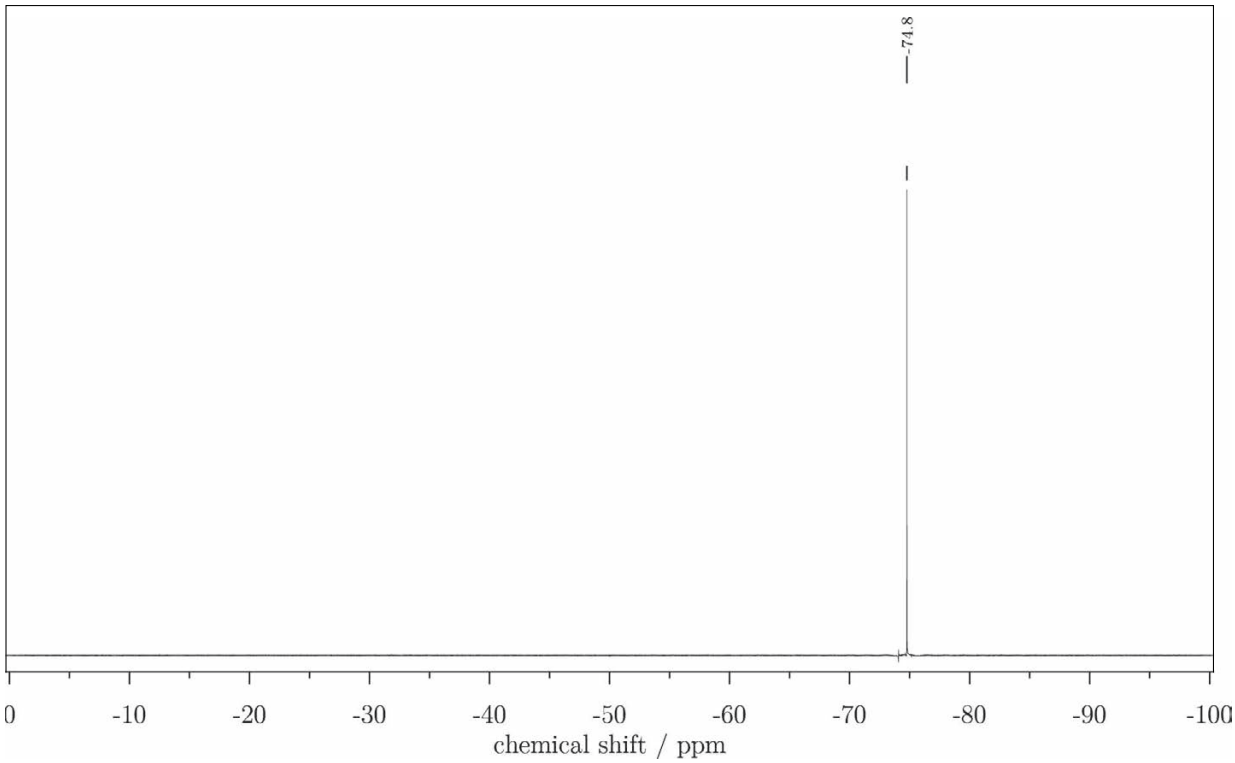


Figure 169: ^{19}F-NMR Spectrum of **217** at 565 MHz in DMSO-d_6.

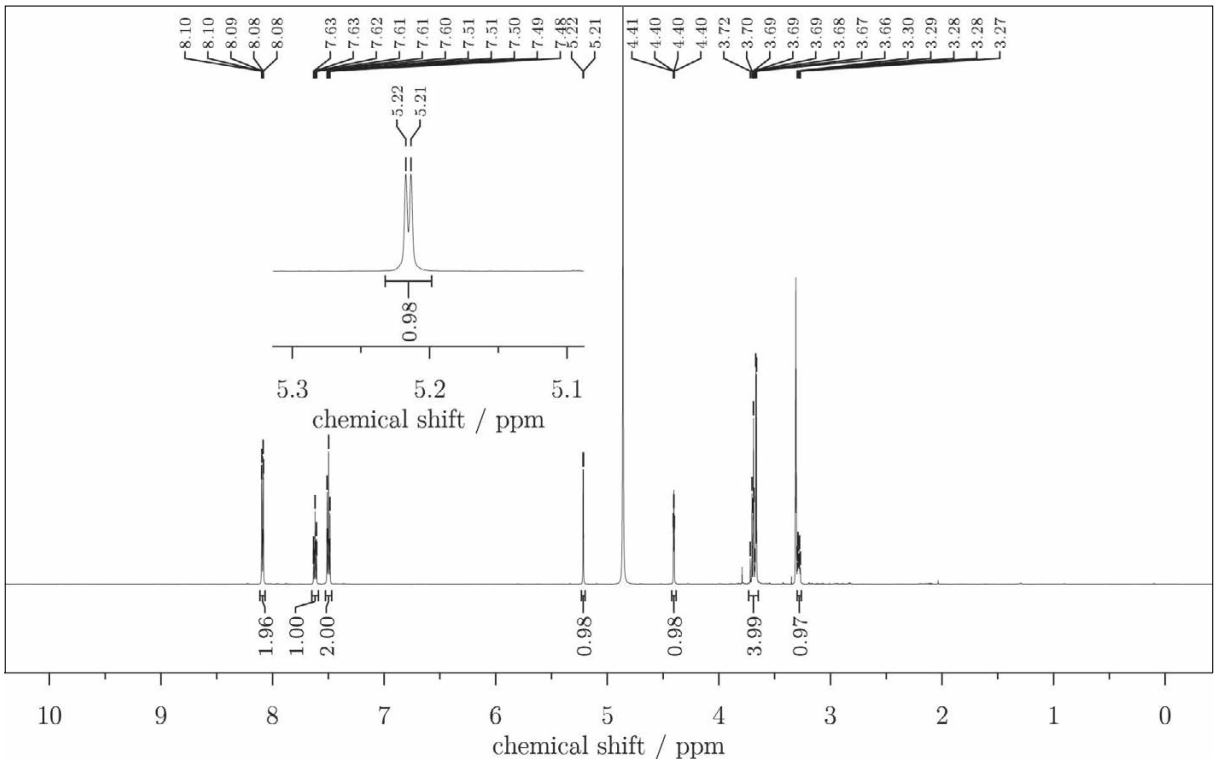


Figure 170: ^{1}H-NMR spectrum of **218** at 600 MHz in methanol-d_4.

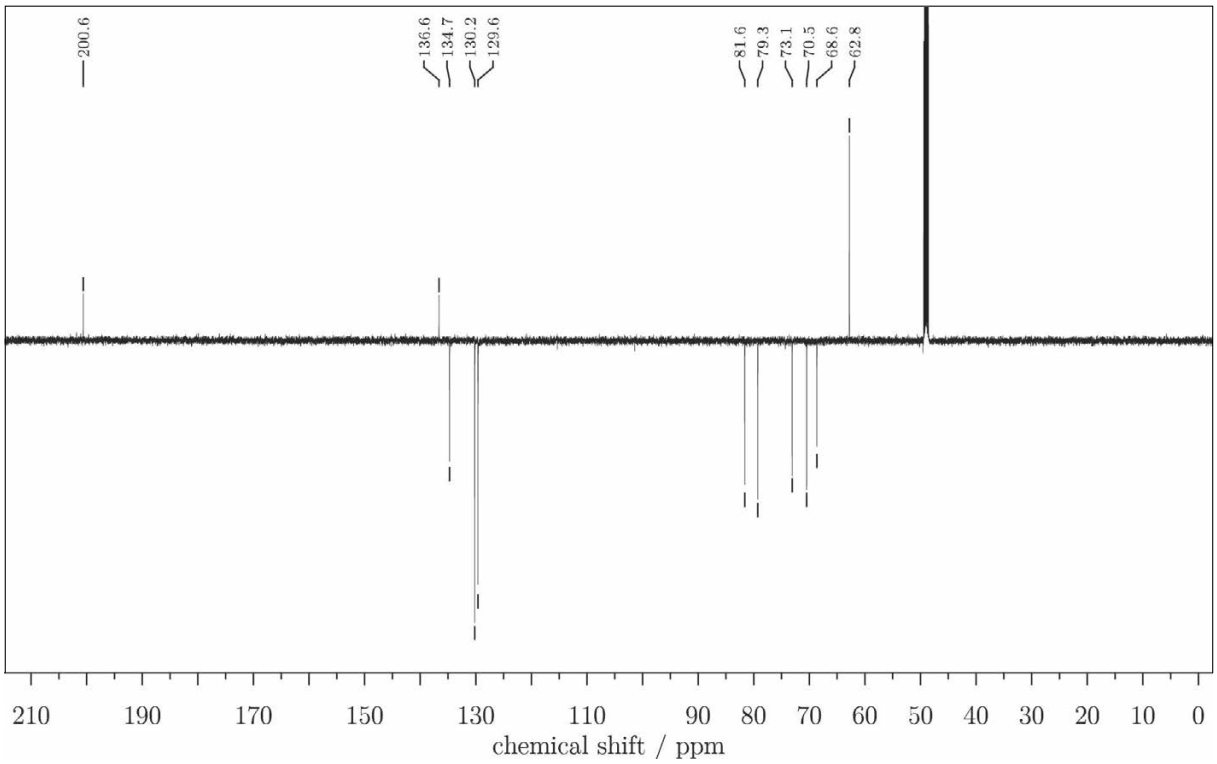


Figure 171: DEPTQ-NMR spectrum of **218** at 151 MHz in methanol-d_4.

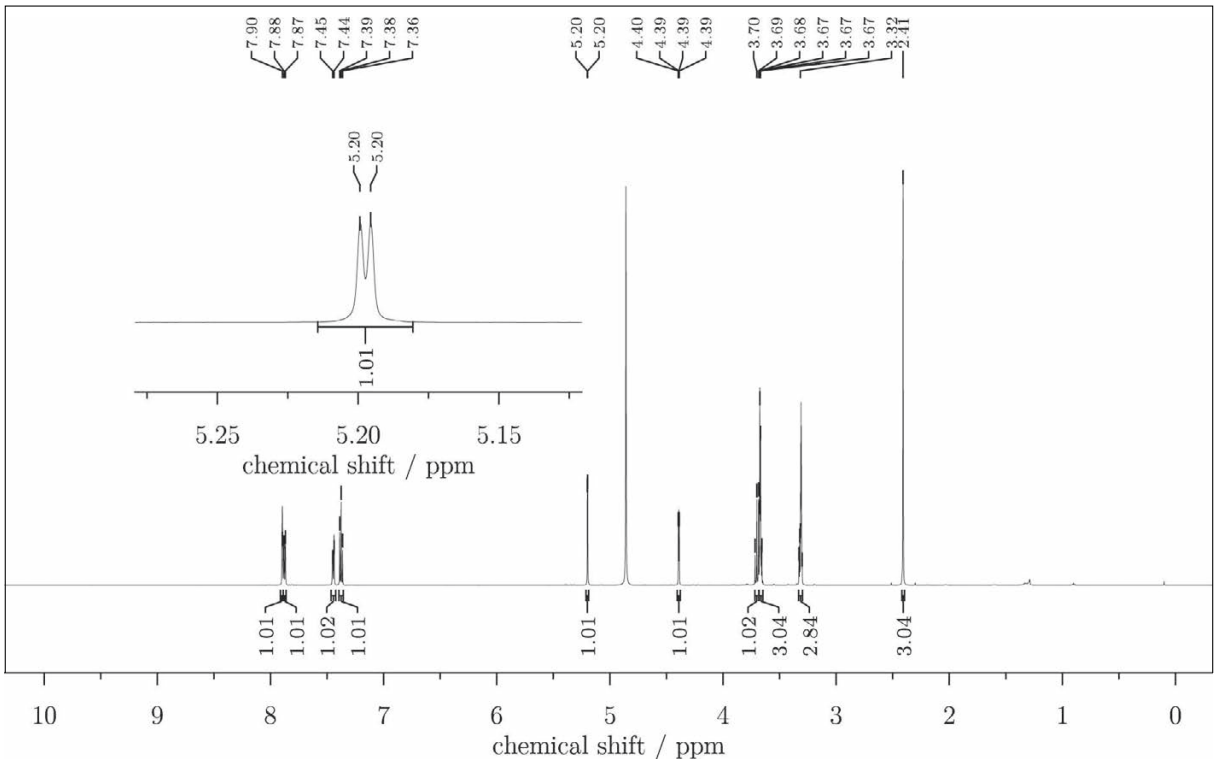


Figure 172: ^{1}H-NMR spectrum of **219** at 600 MHz in methanol-d_4.

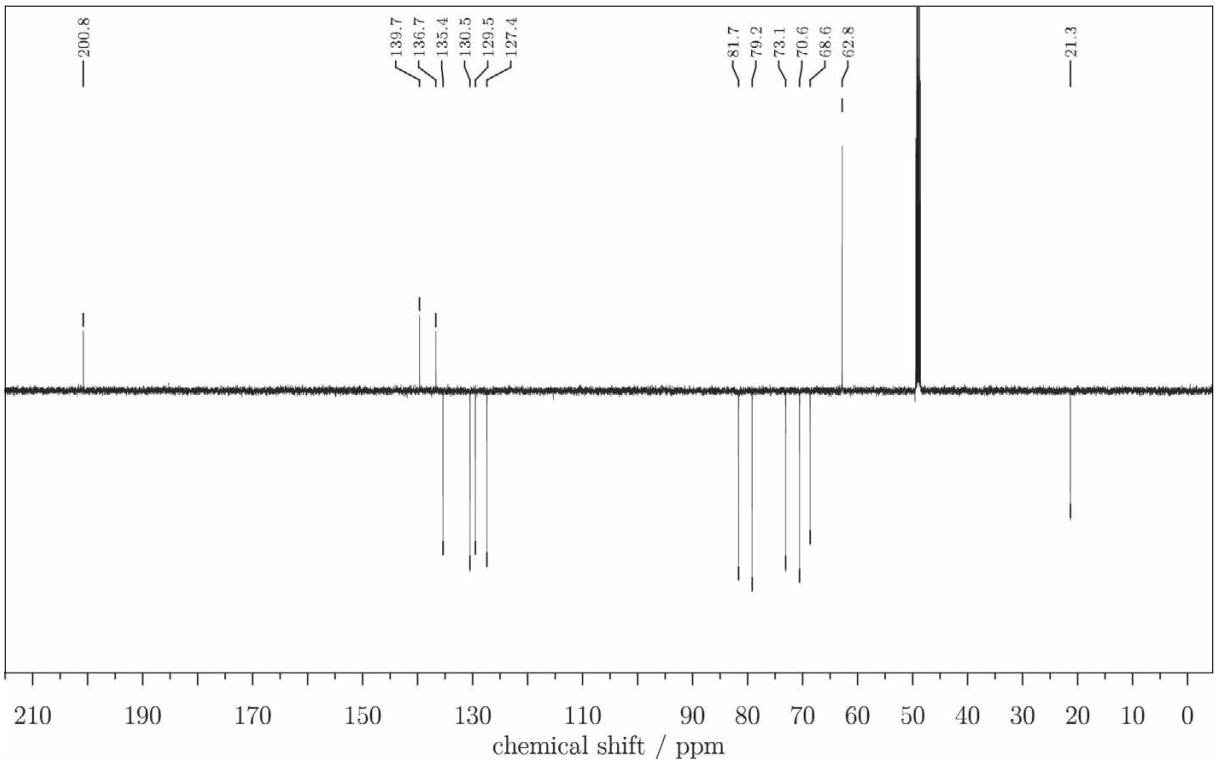


Figure 173: DEPTQ-NMR spectrum of **219** at 151 MHz in methanol-d_4.

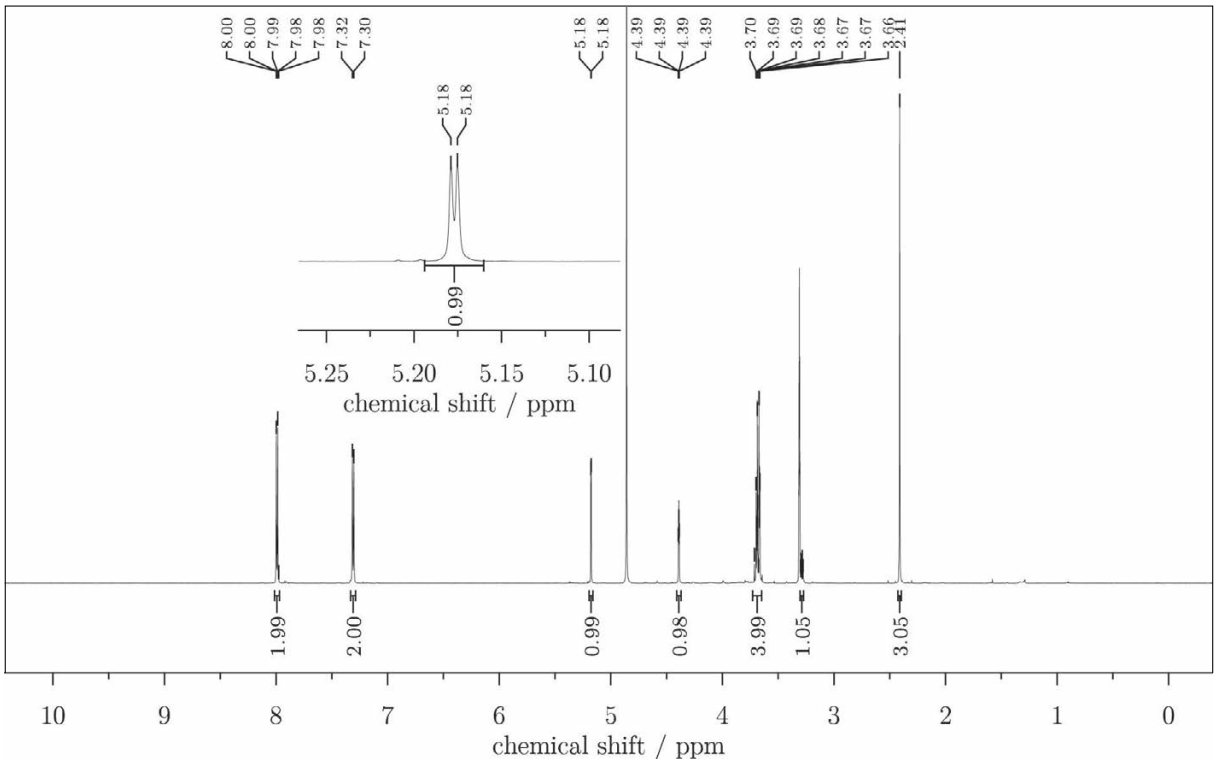


Figure 174: ^{1}H-NMR spectrum of **220** at 600 MHz in methanol-d_4.

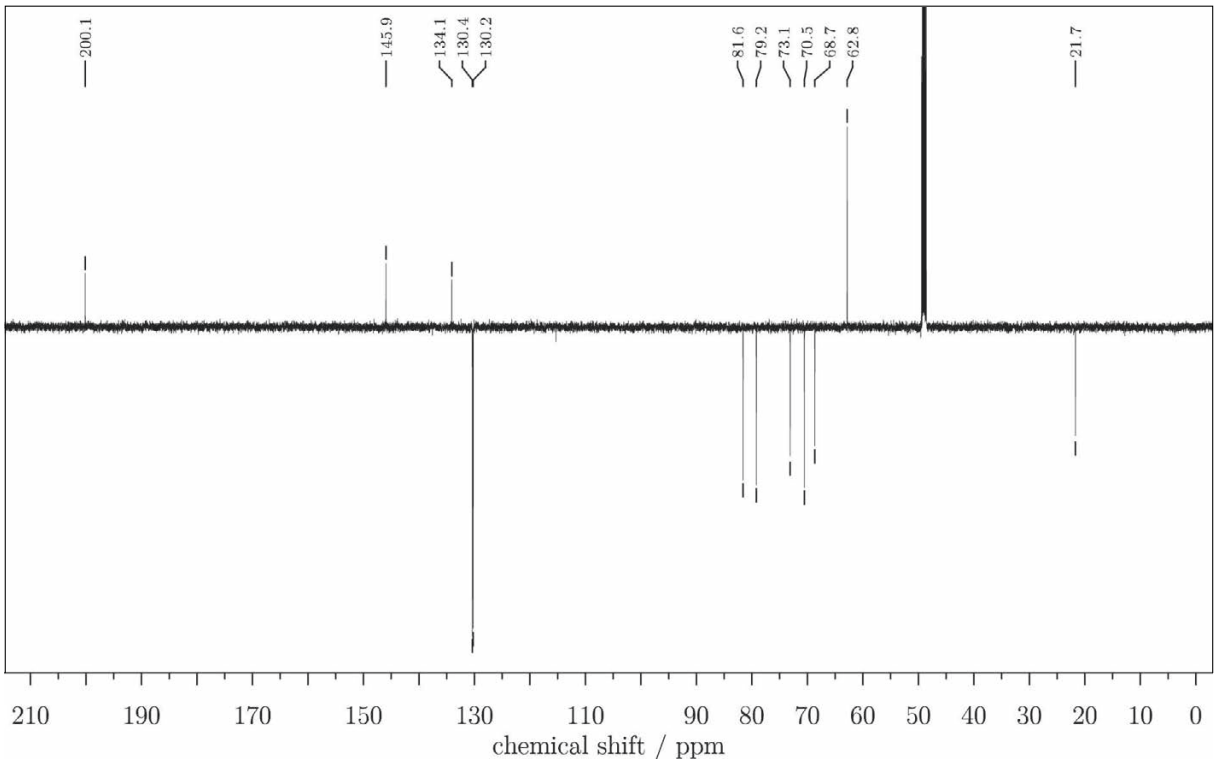


Figure 175: DEPTQ-NMR spectrum of **220** at 151 MHz in methanol-d_4.

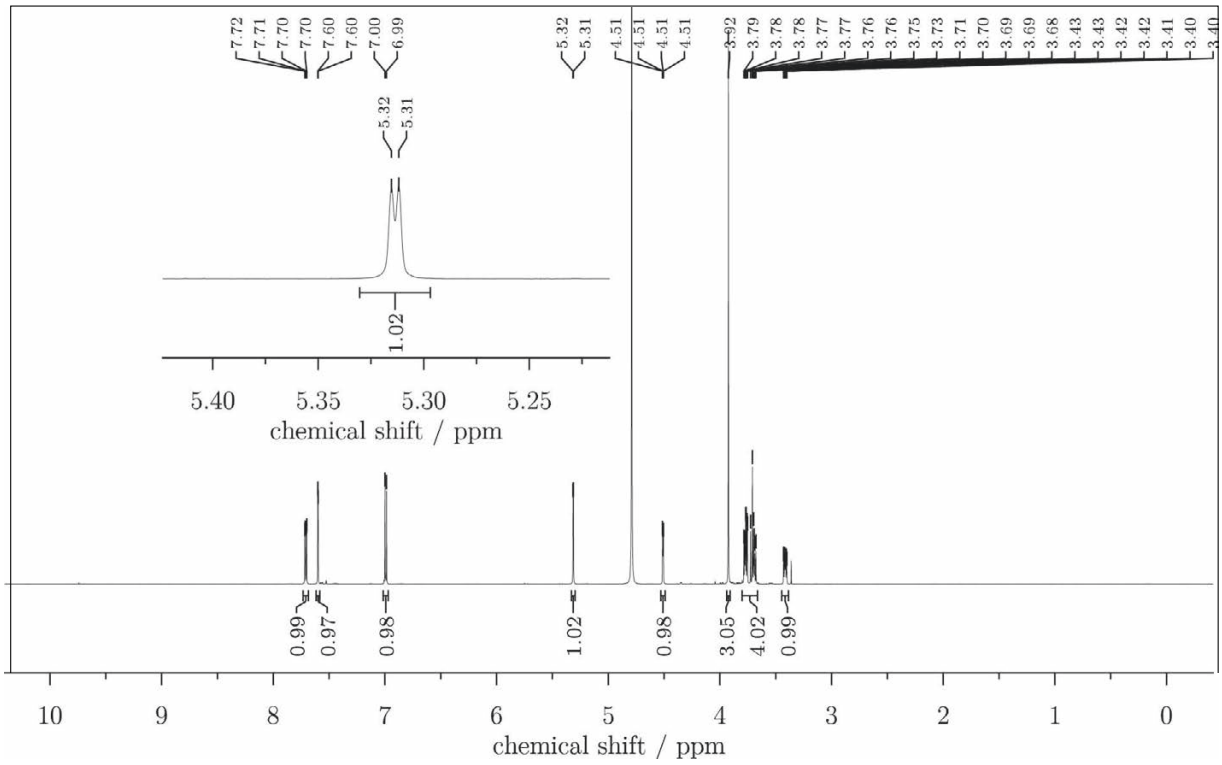


Figure 176: ^{1}H-NMR spectrum of **221** at 600 MHz in D_2O.

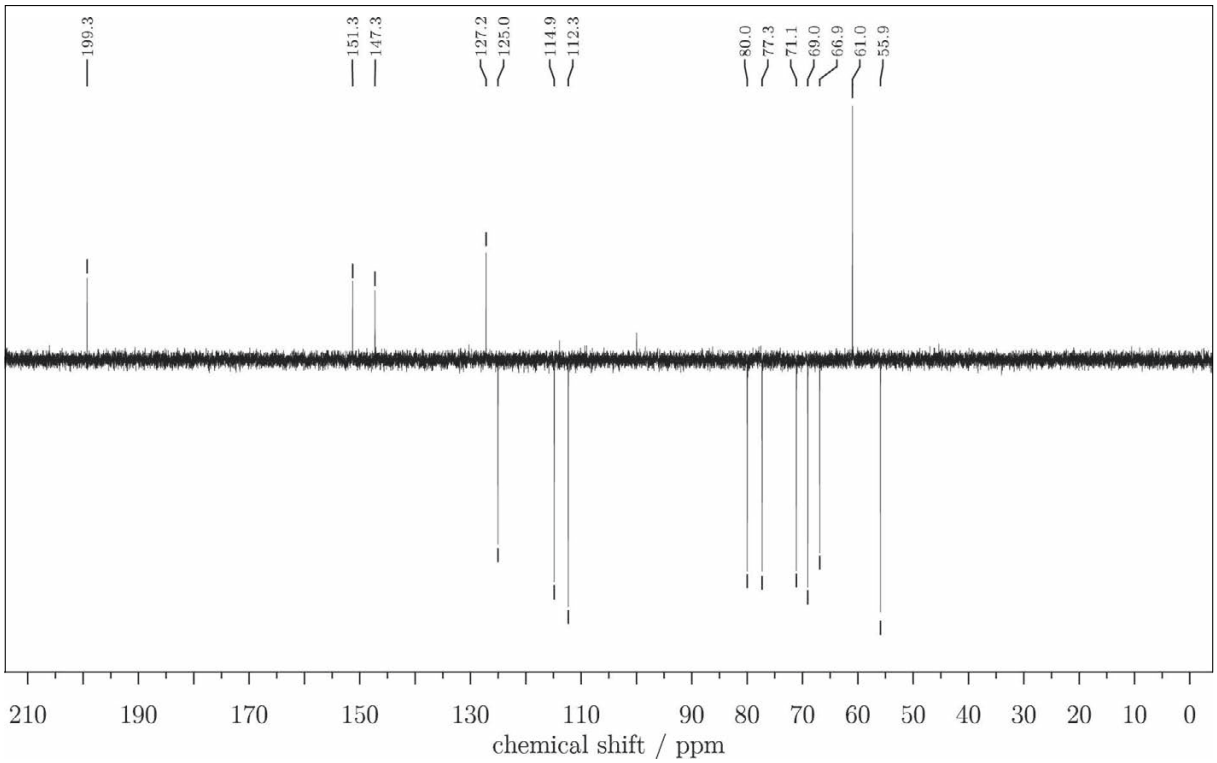


Figure 177: DEPTQ-NMR spectrum of **221** at 151 MHz in D_2O.

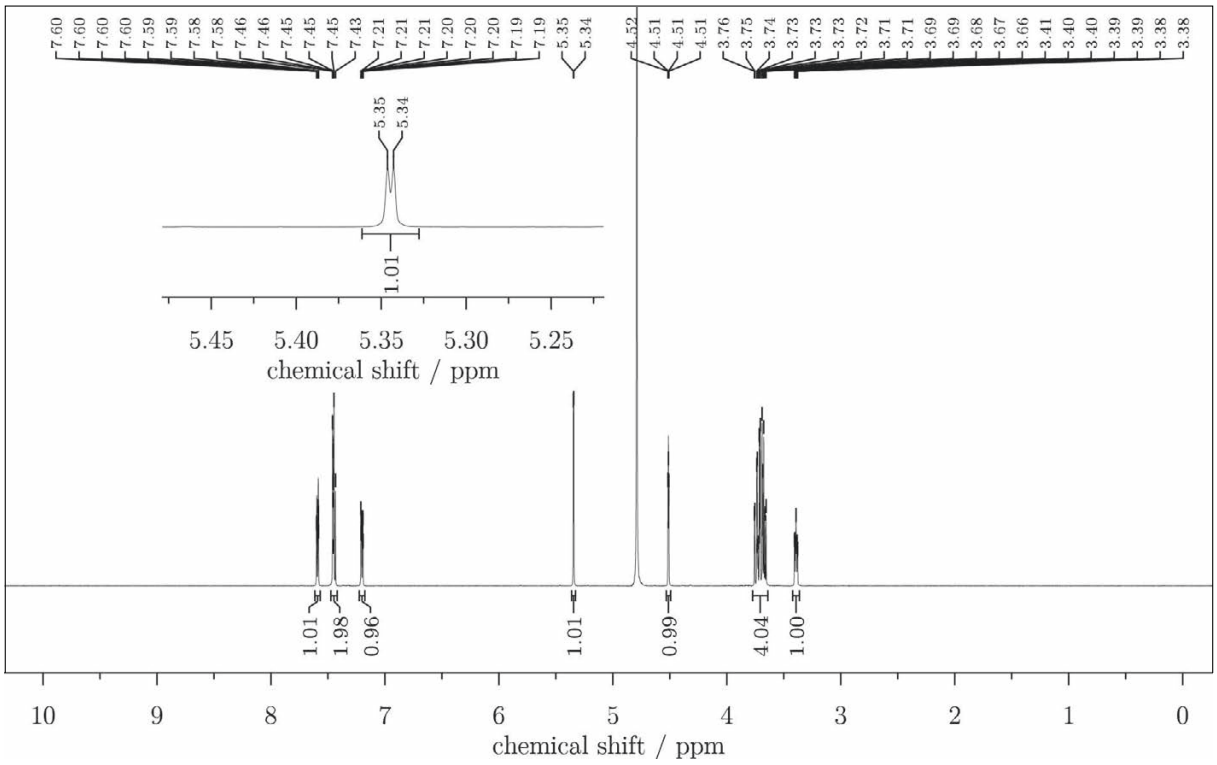


Figure 178: ^{1}H-NMR spectrum of **222** at 600 MHz in D_2O.

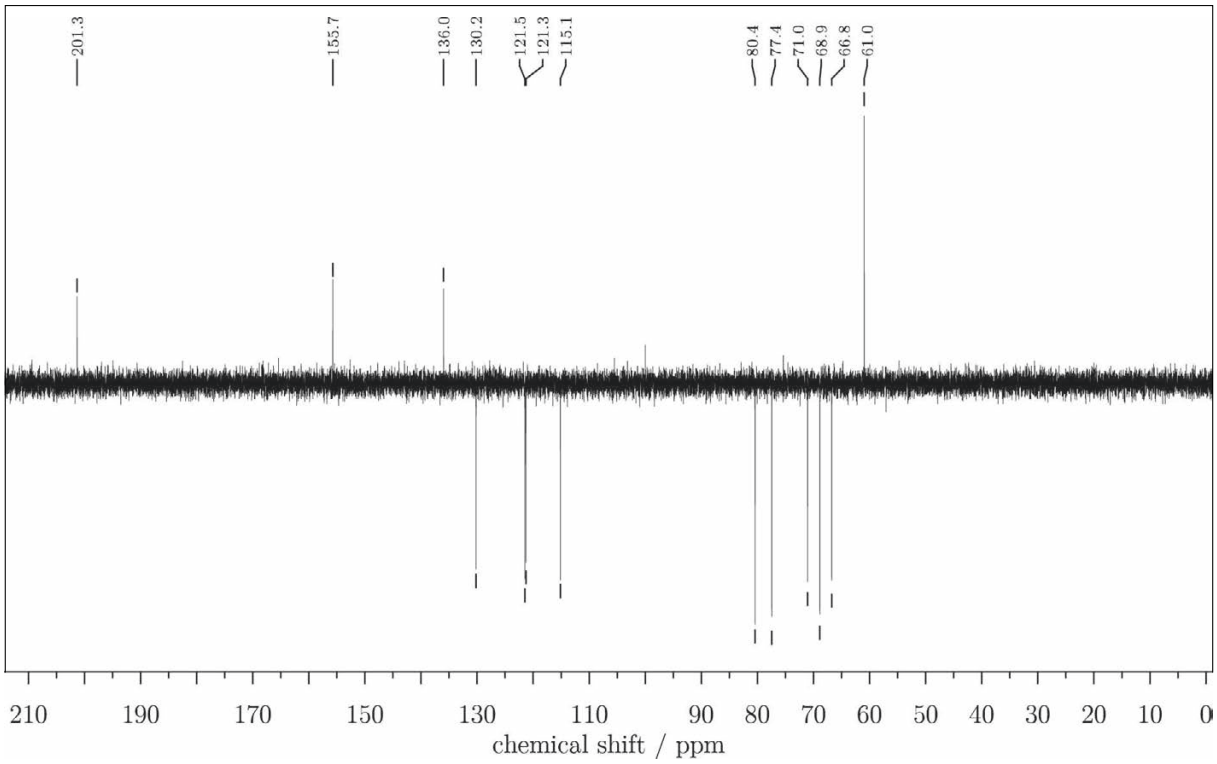


Figure 179: DEPTQ-NMR spectrum of **222** at 151 MHz in D_2O.

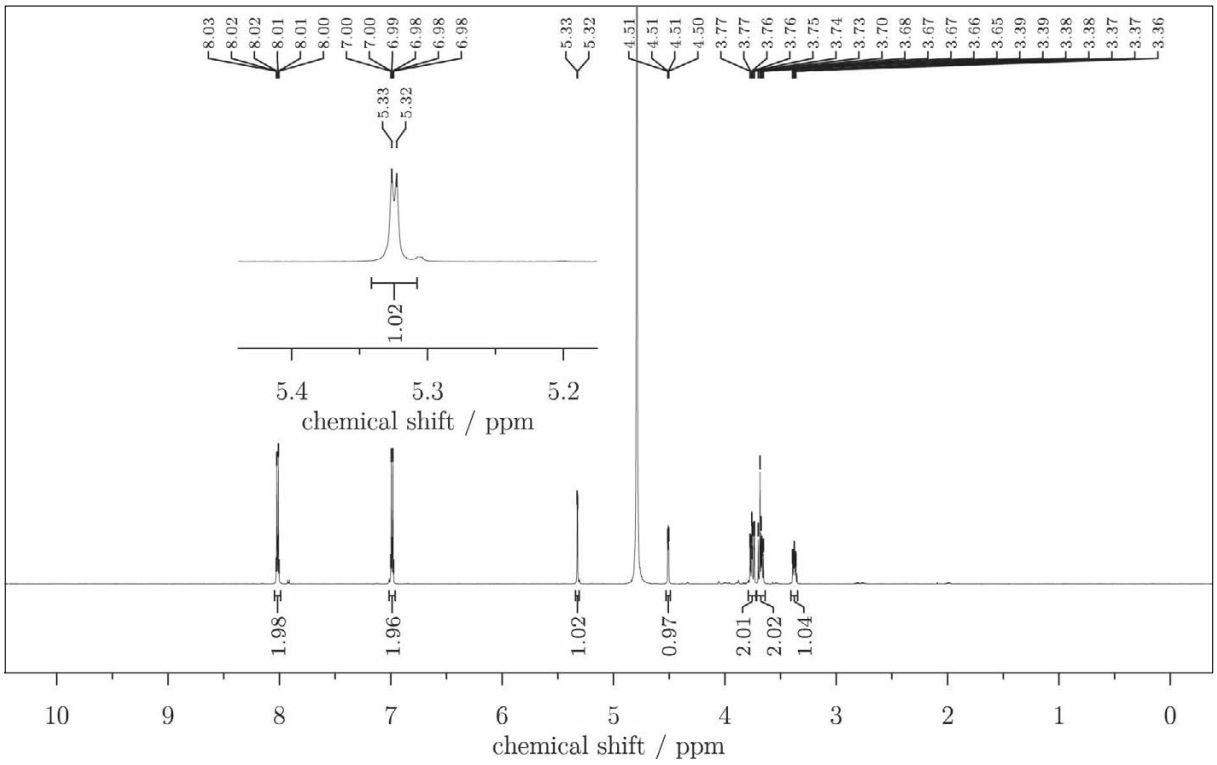


Figure 180: ^{1}H-NMR spectrum of **223** at 600 MHz in D_2O.

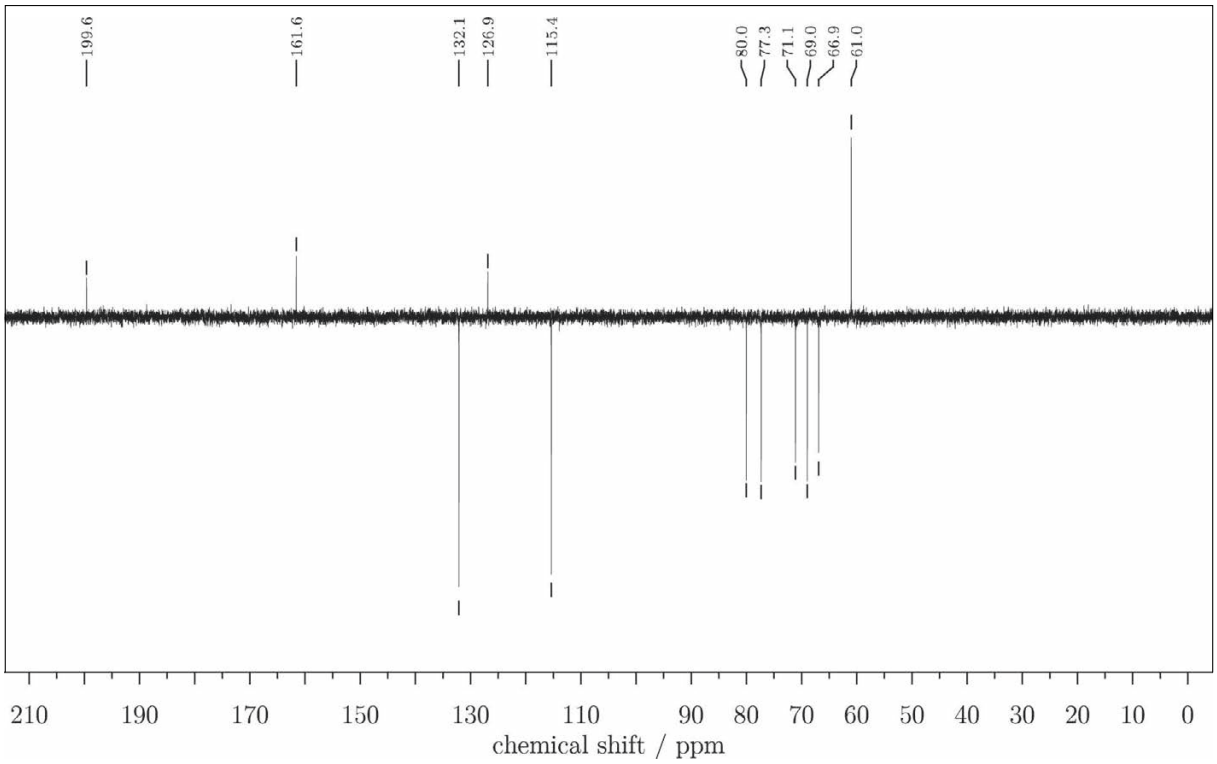


Figure 181: DEPTQ-NMR spectrum of **223** at 151 MHz in D_2O.

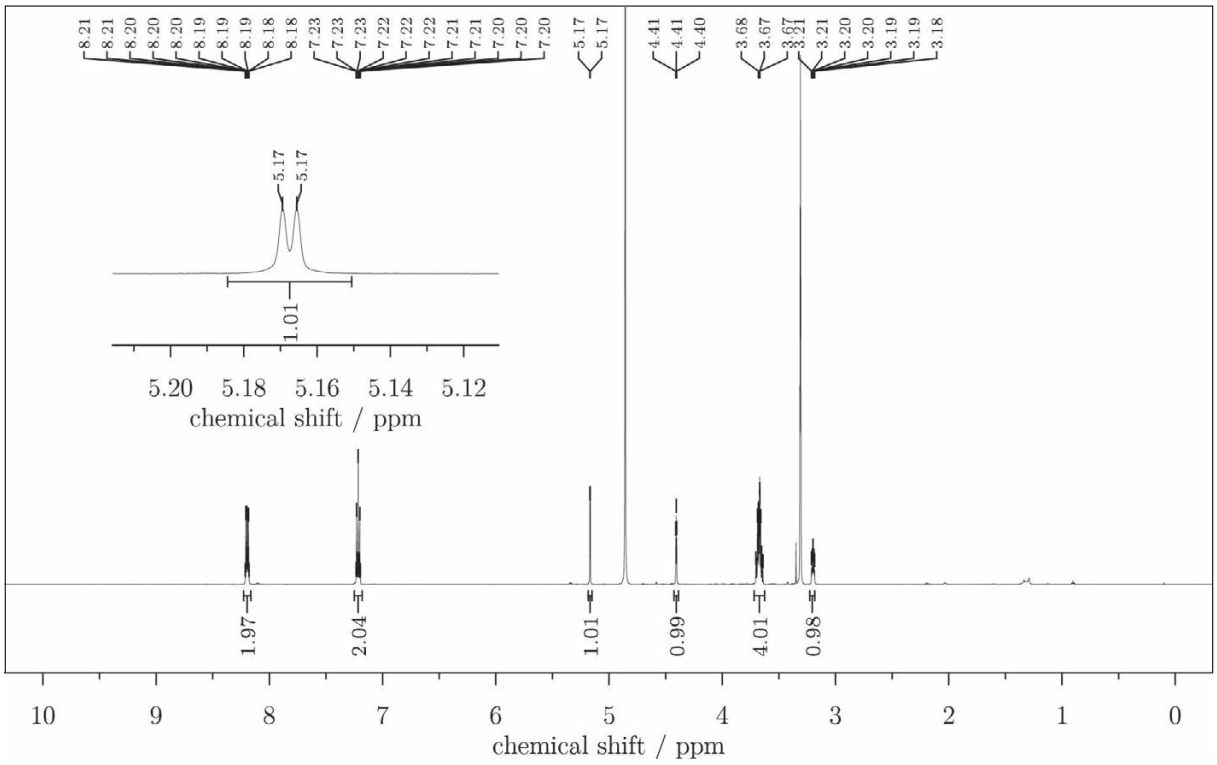


Figure 182: ^{1}H-NMR spectrum of **224** at 600 MHz in methanol-d_4.

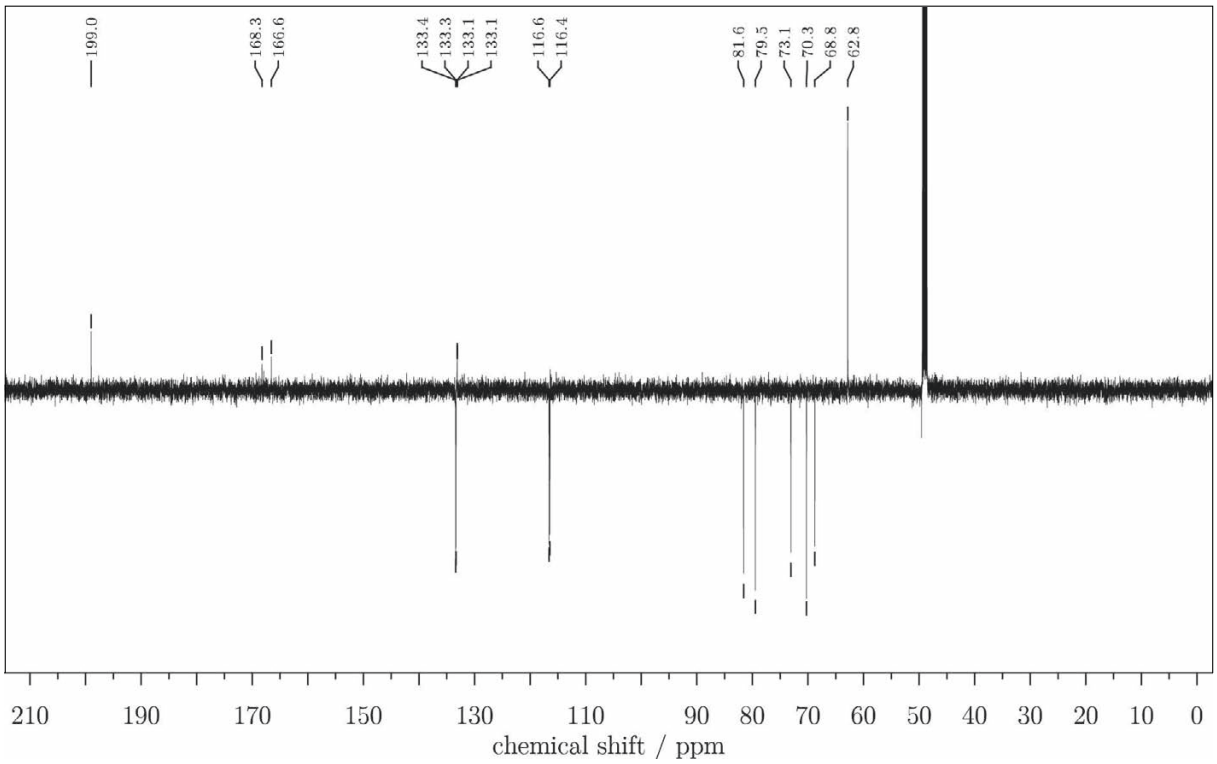


Figure 183: DEPTQ-NMR spectrum of **224** at 151 MHz in methanol-d_4.

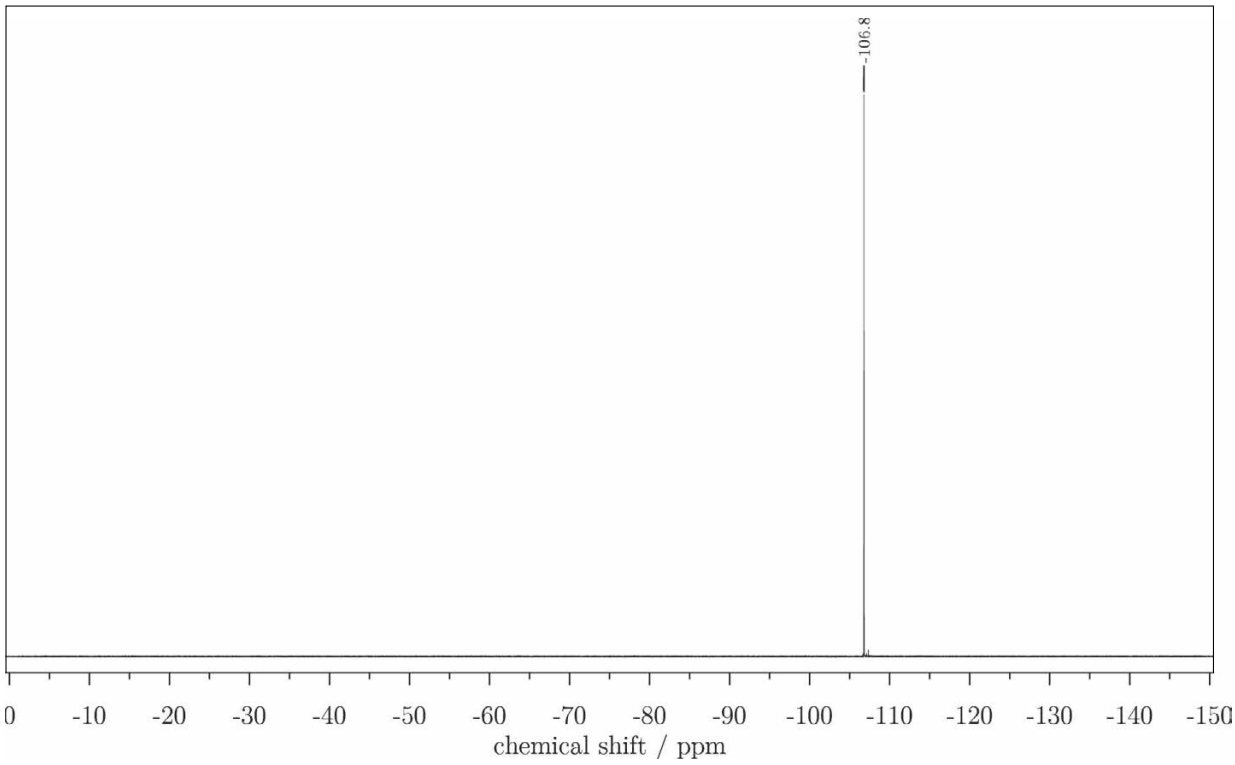


Figure 184: ^{19}F-NMR Spectrum of **224** at 565 MHz in methanol-d_4.

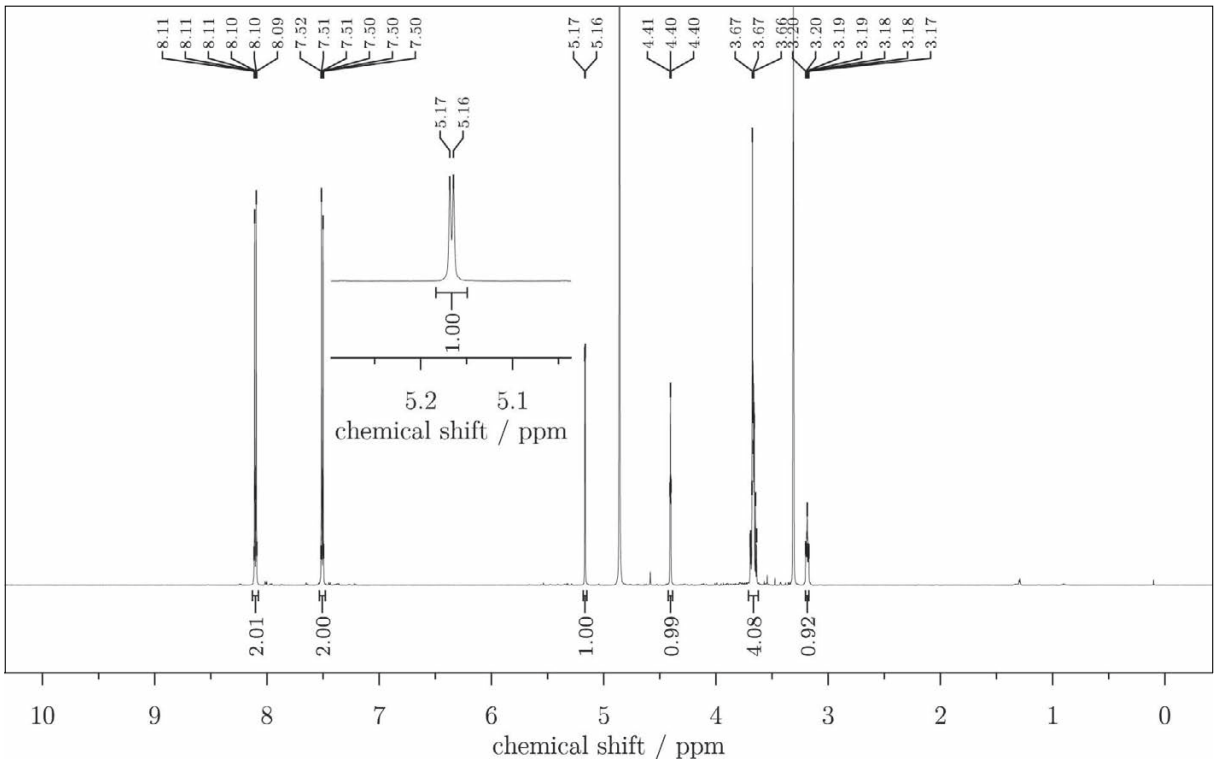


Figure 185: ^{1}H-NMR spectrum of **225** at 600 MHz in methanol-d_4.

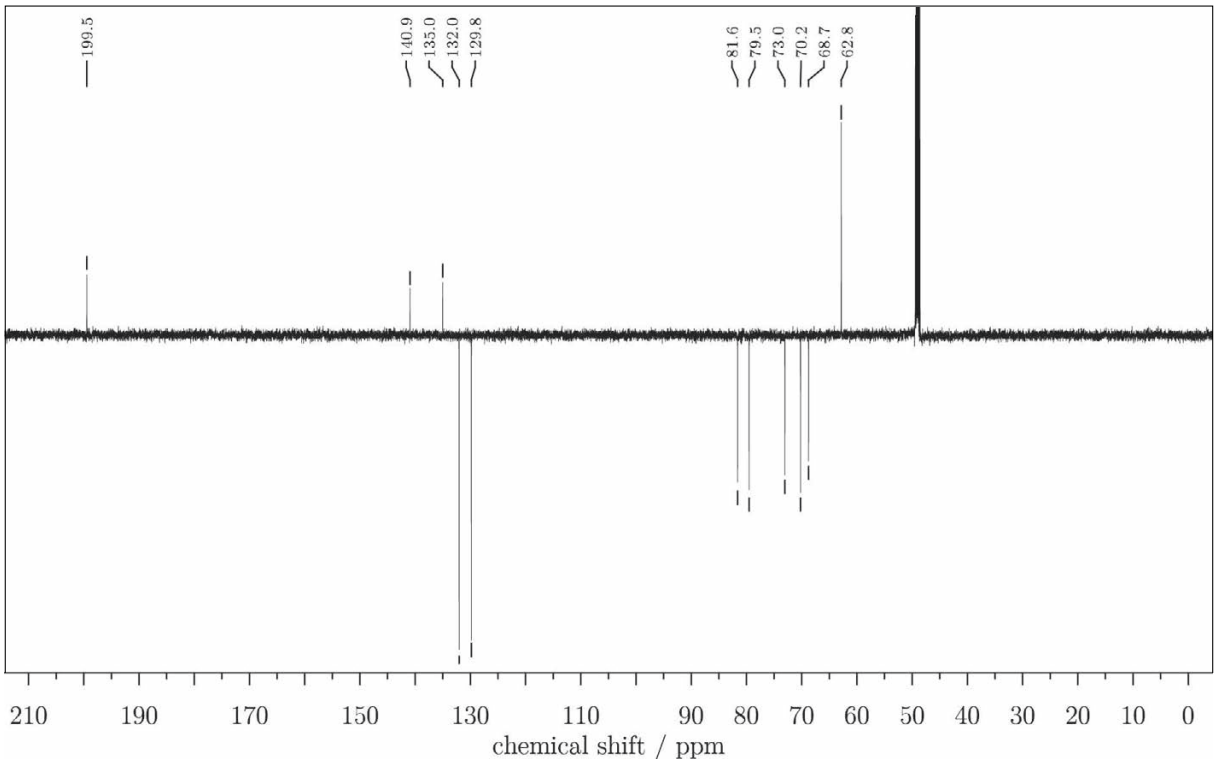


Figure 186: DEPTQ-NMR spectrum of **225** at 151 MHz in methanol-d_4.

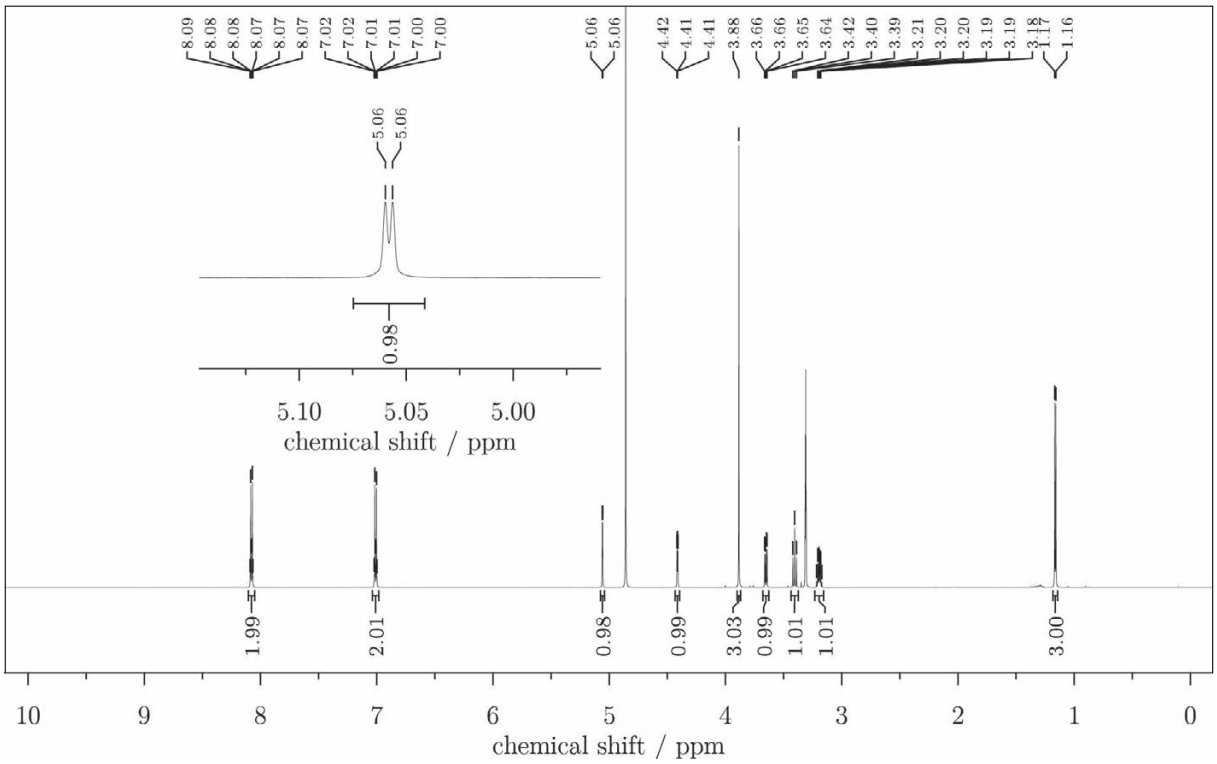


Figure 187: ^{1}H-NMR spectrum of **227** at 600 MHz in methanol-d_4.

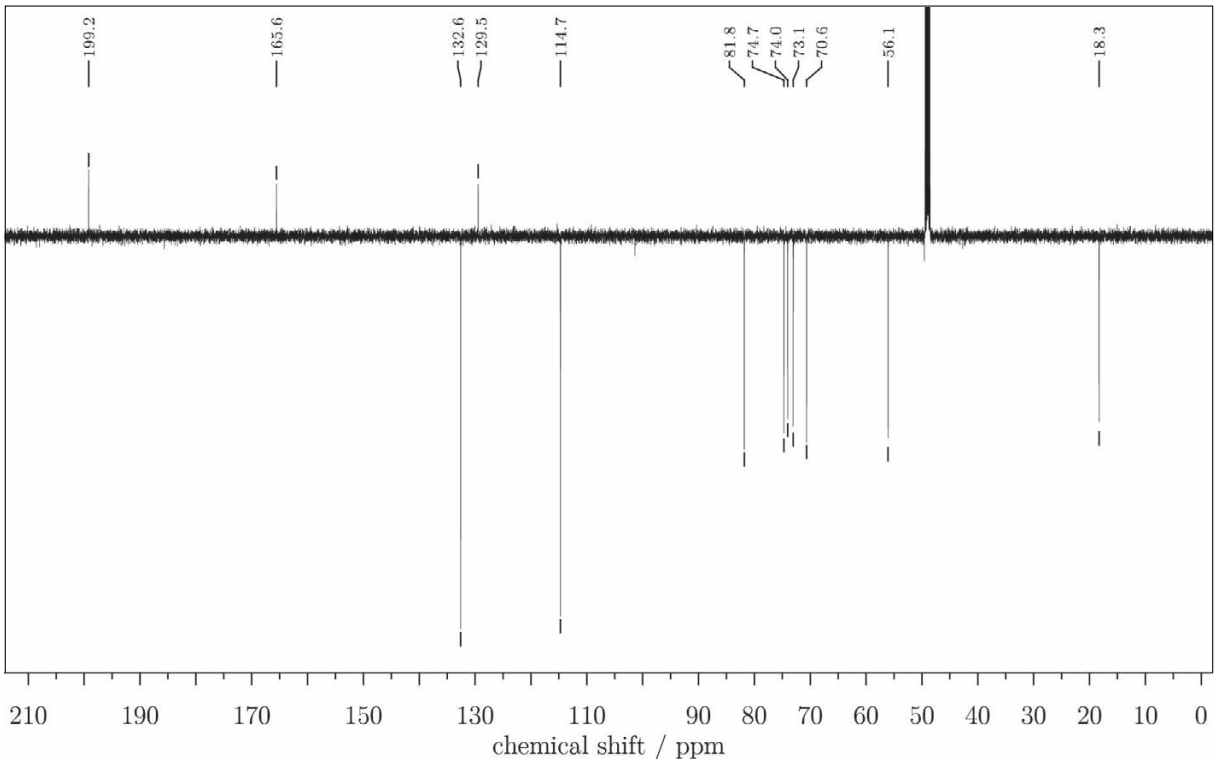


Figure 188: DEPTQ-NMR spectrum of **227** at 151 MHz in methanol-d_4.

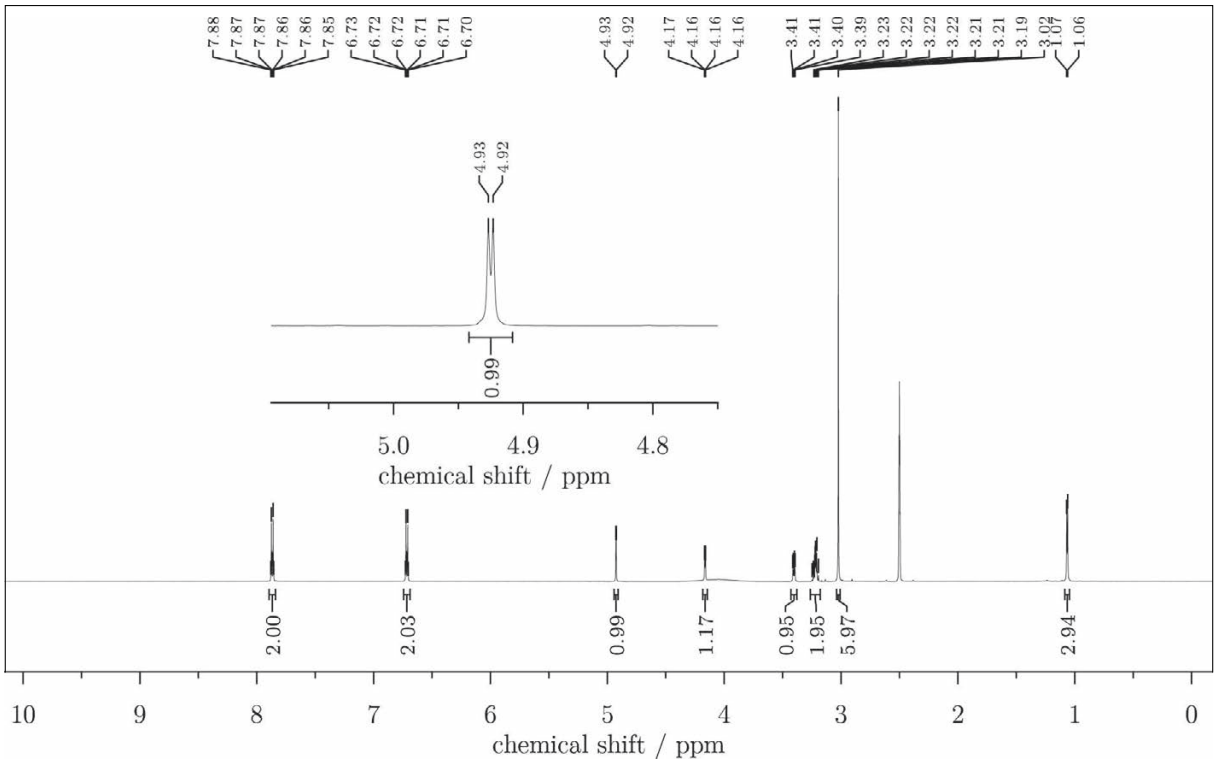


Figure 189: ^{1}H-NMR spectrum of **228** at 600 MHz in DMSO-d_6.

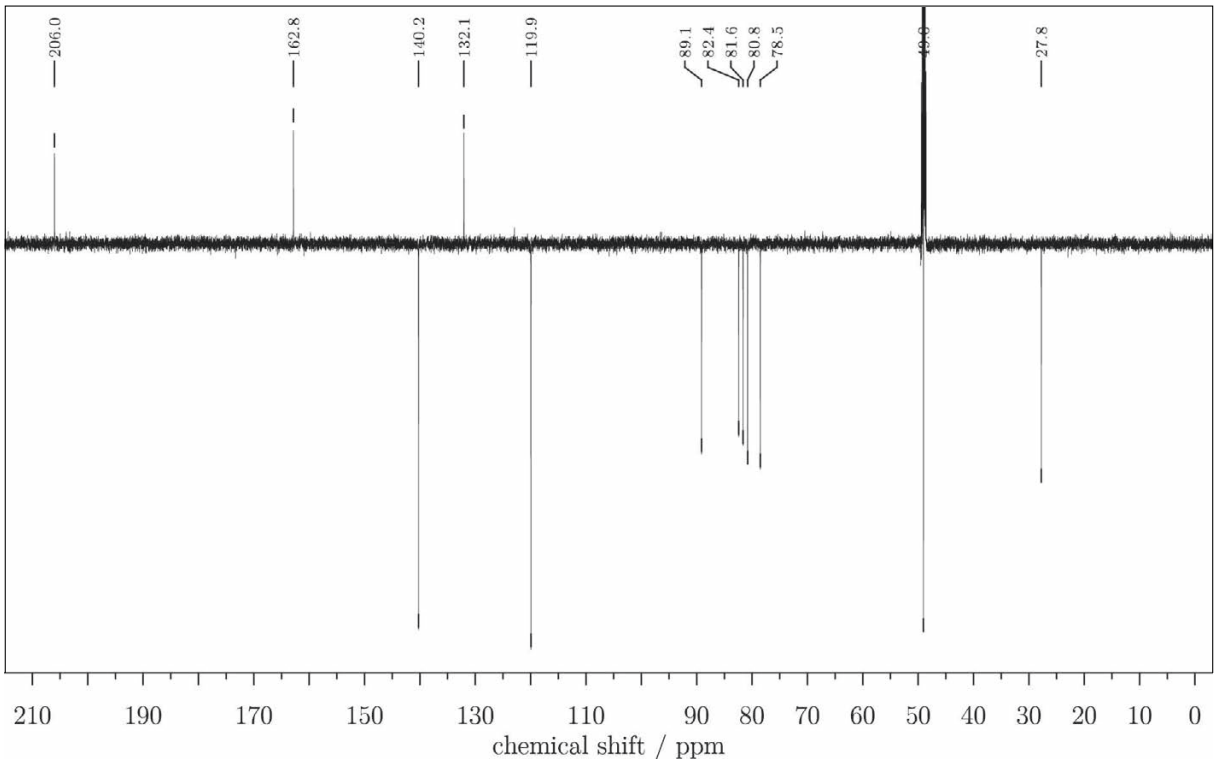


Figure 190: DEPTQ-NMR spectrum of **228** at 151 MHz in DMSO-d_6.

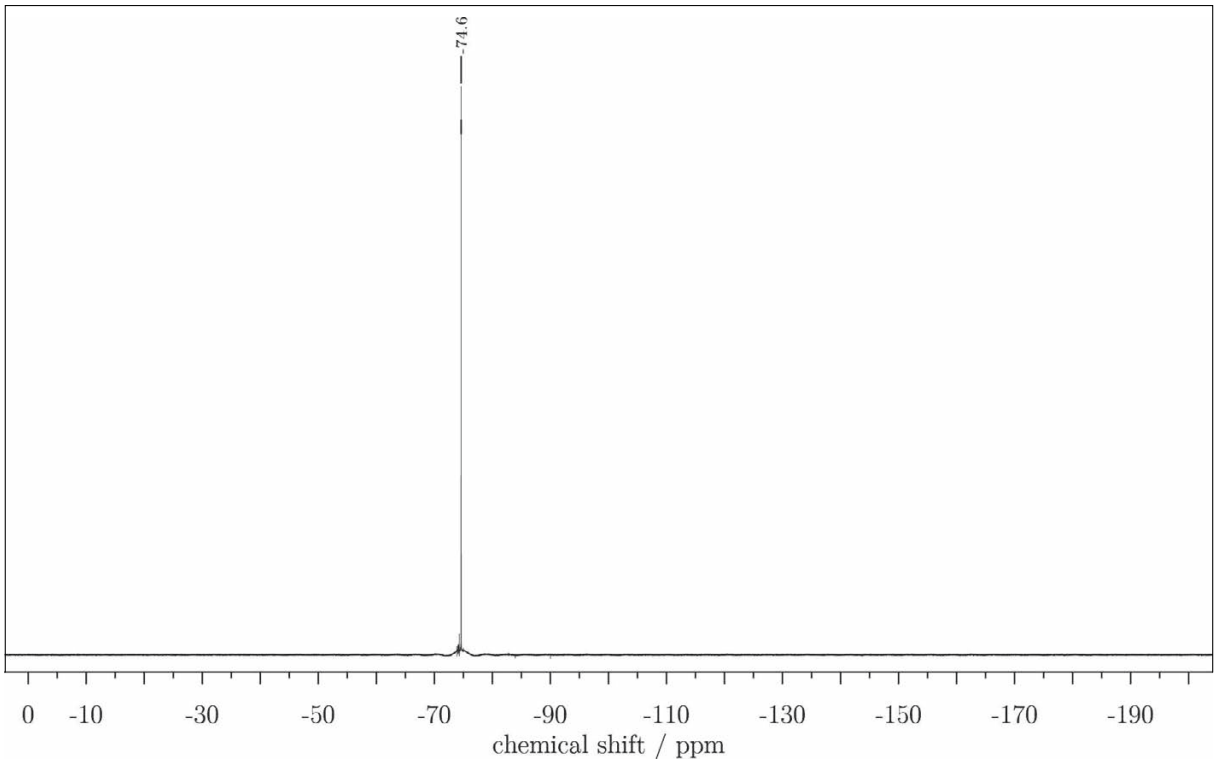


Figure 191: ^{19}F-NMR Spectrum of **228** at 565 MHz in DMSO-d_6.

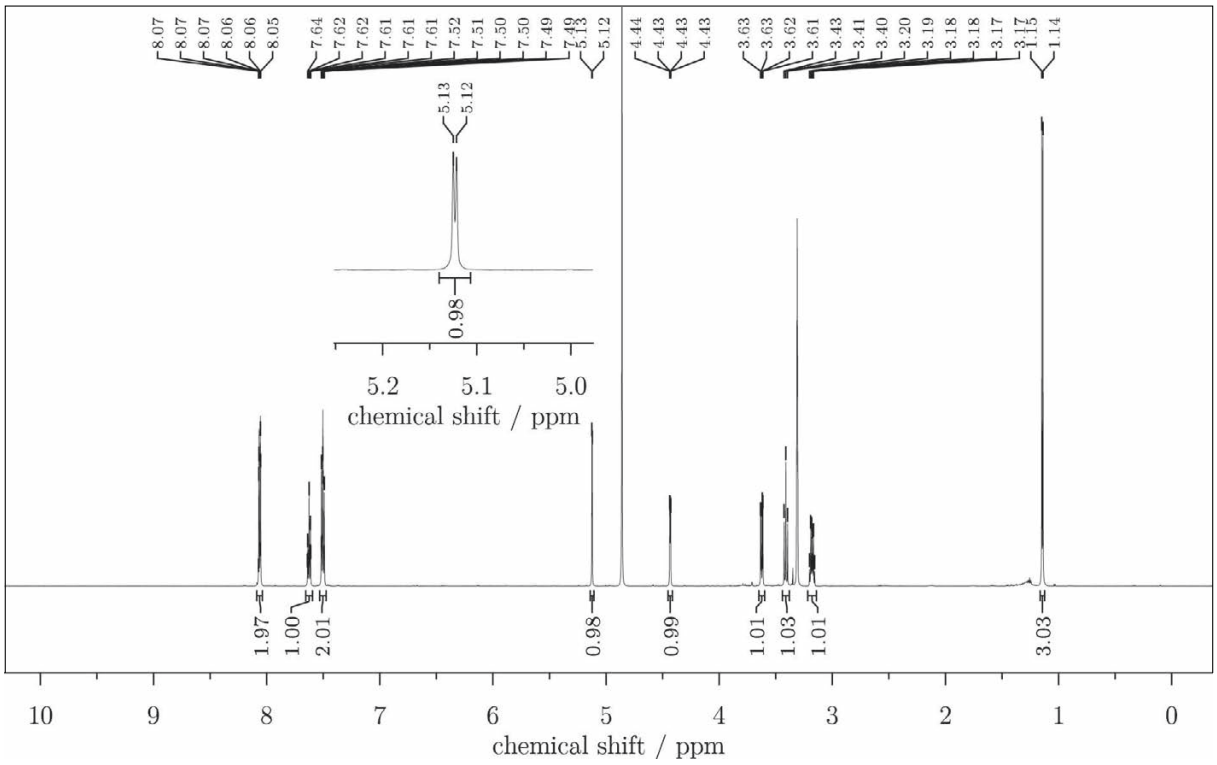


Figure 192: ^{1}H-NMR spectrum of **230** at 600 MHz in methanol-d_4.

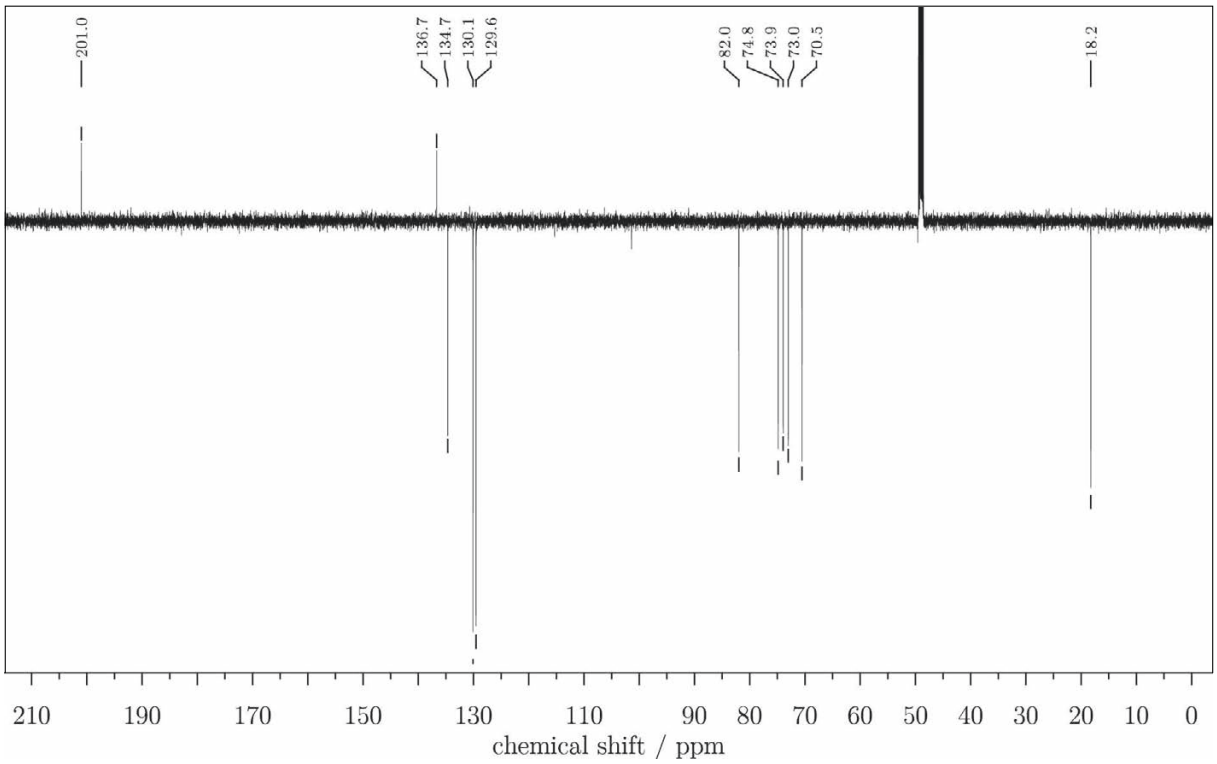


Figure 193: DEPTQ-NMR spectrum of **230** at 151 MHz in methanol-d_4.

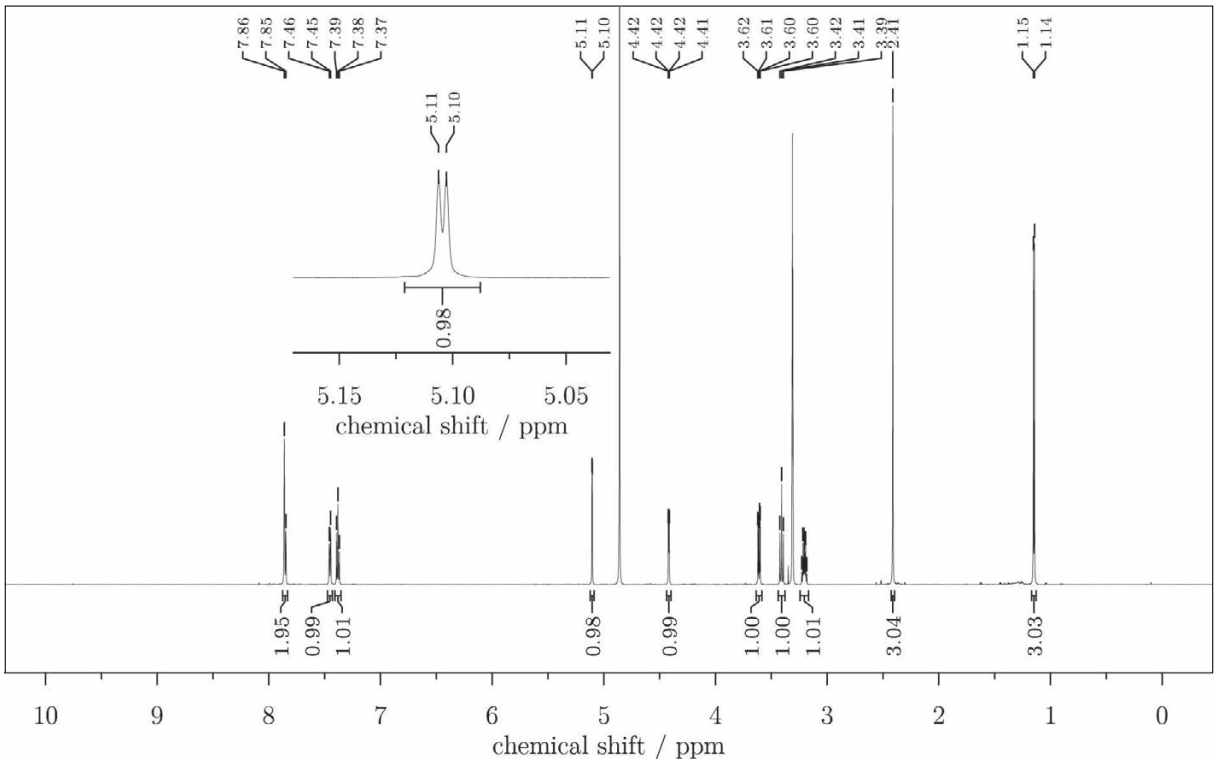


Figure 194: ^{1}H-NMR spectrum of **231** at 600 MHz in methanol-d_4.

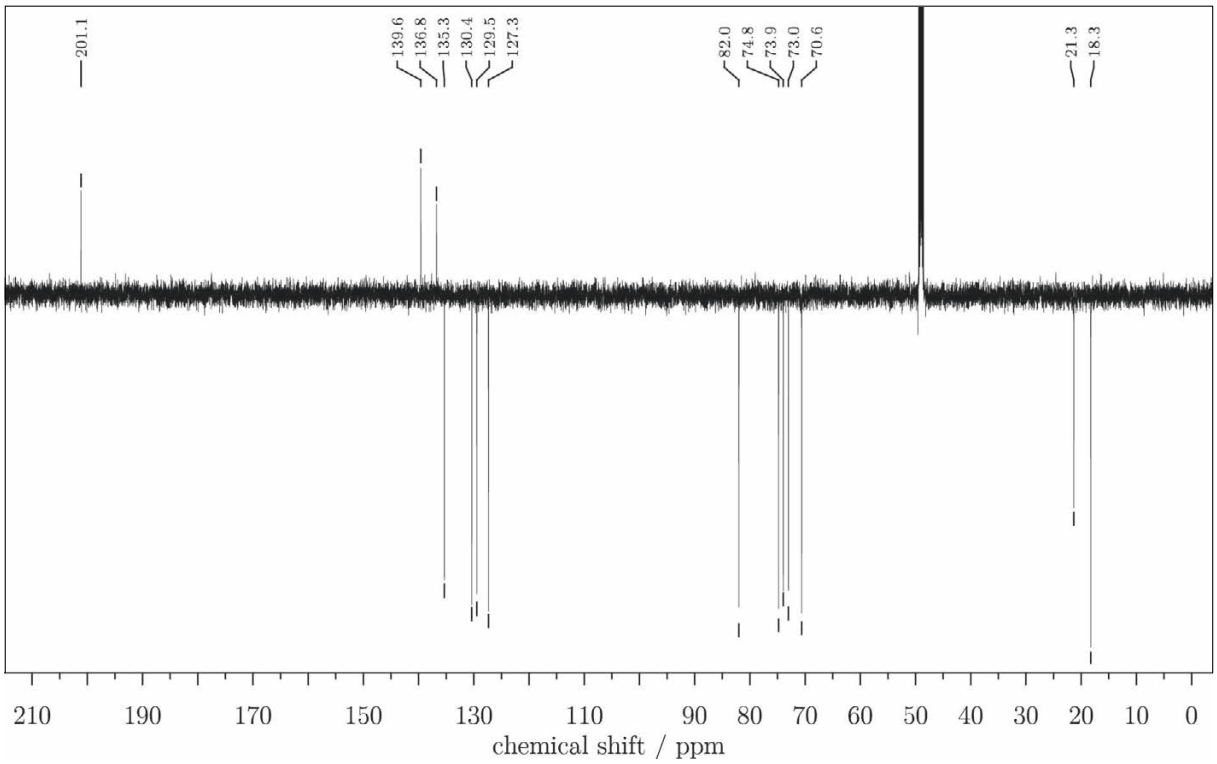


Figure 195: DEPTQ-NMR spectrum of **231** at 151 MHz in methanol-d_4.

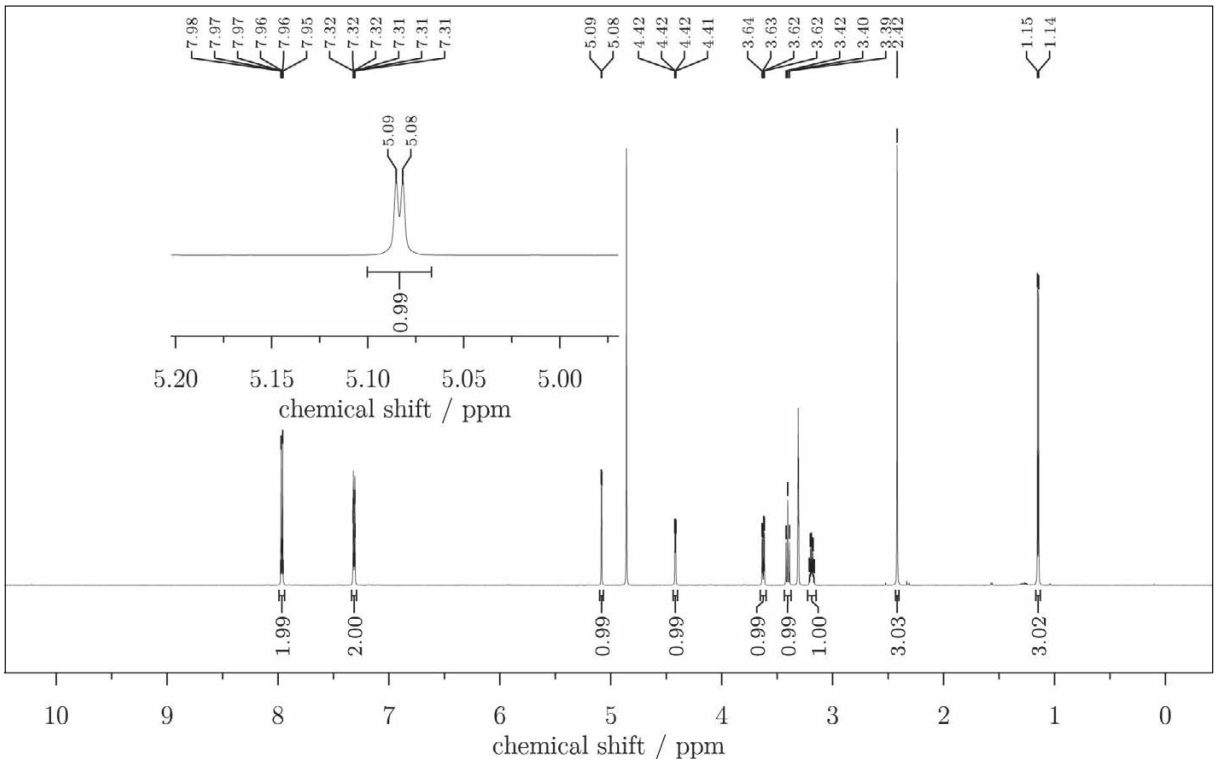


Figure 196: ^{1}H-NMR spectrum of **232** at 600 MHz in methanol-d_4.

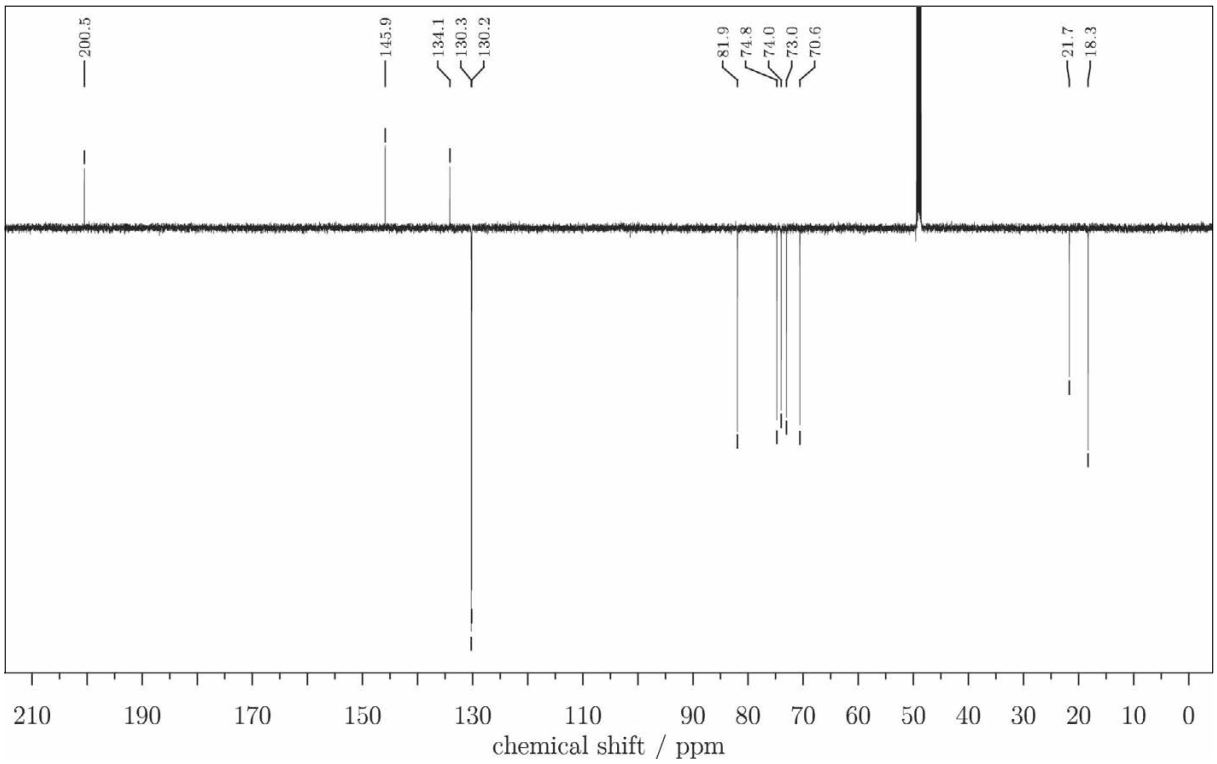


Figure 197: DEPTQ-NMR spectrum of **232** at 151 MHz in methanol-d_4.

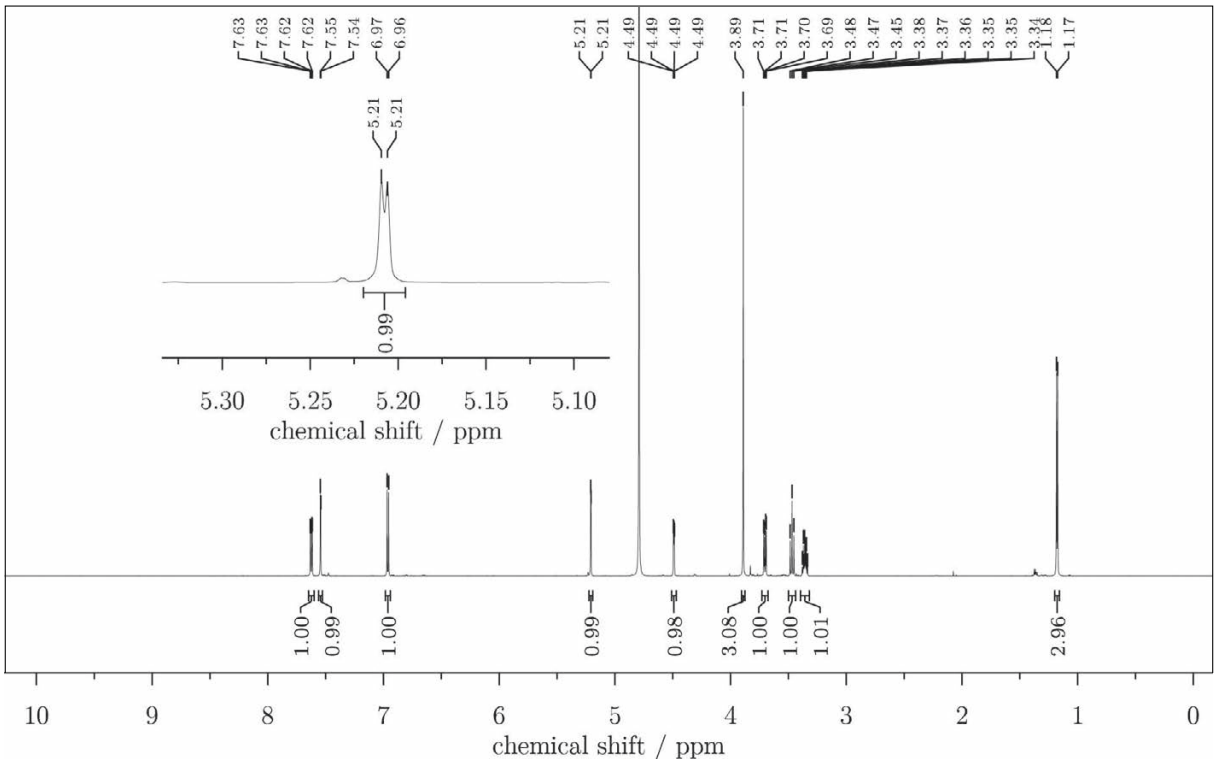


Figure 198: ^{1}H-NMR spectrum of **233** at 600 MHz in D_2O.

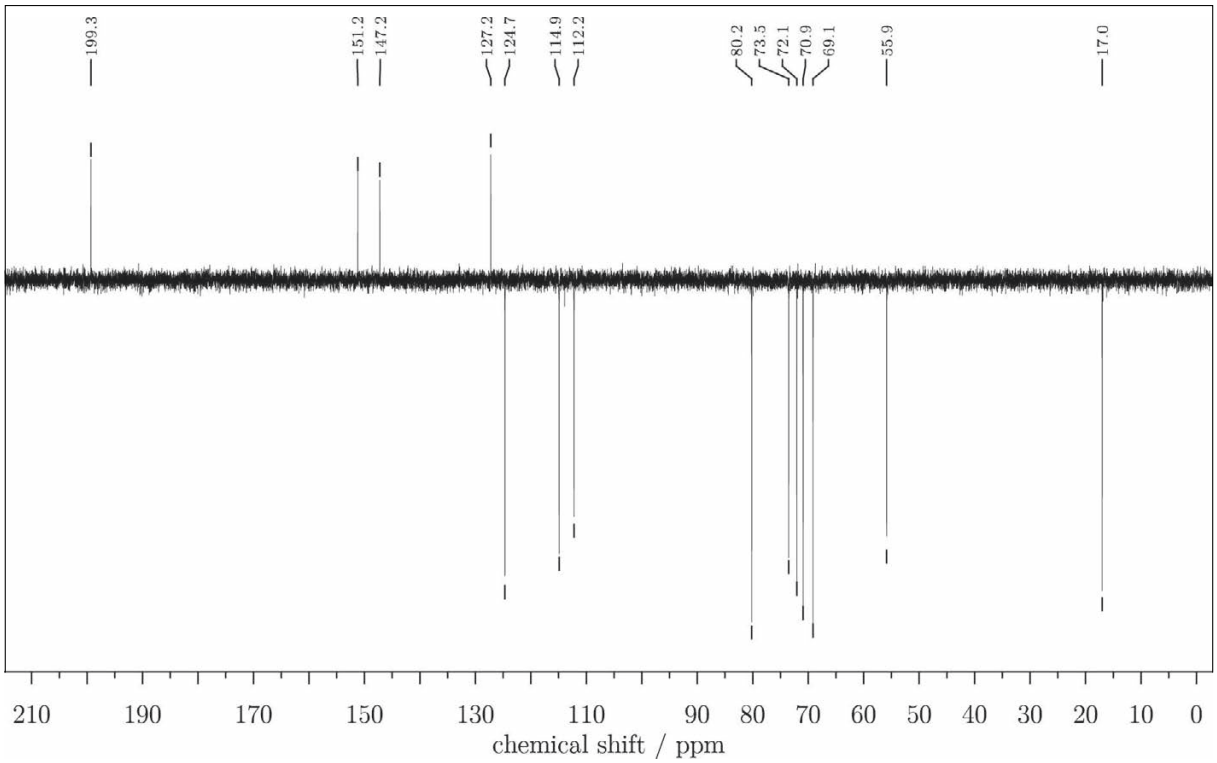


Figure 199: DEPTQ-NMR spectrum of **233** at 151 MHz in D_2O.

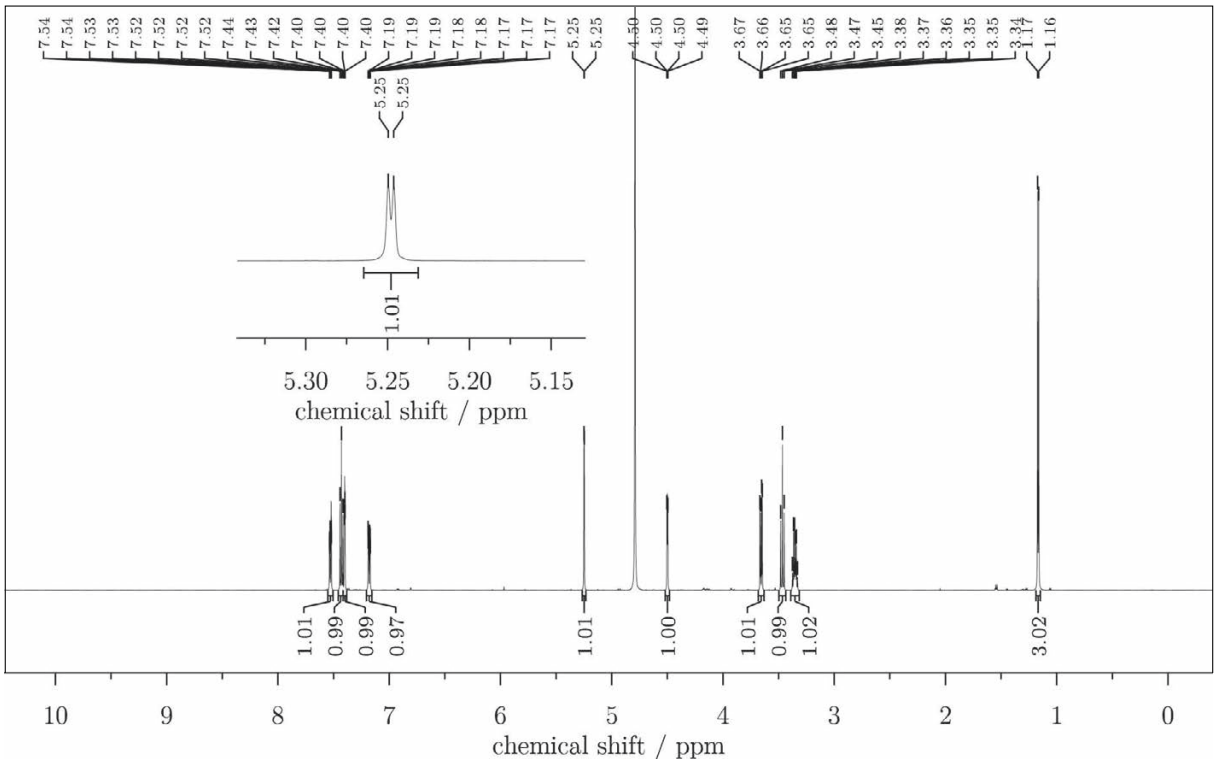


Figure 200: ^{1}H-NMR spectrum of **234** at 600 MHz in D_2O.

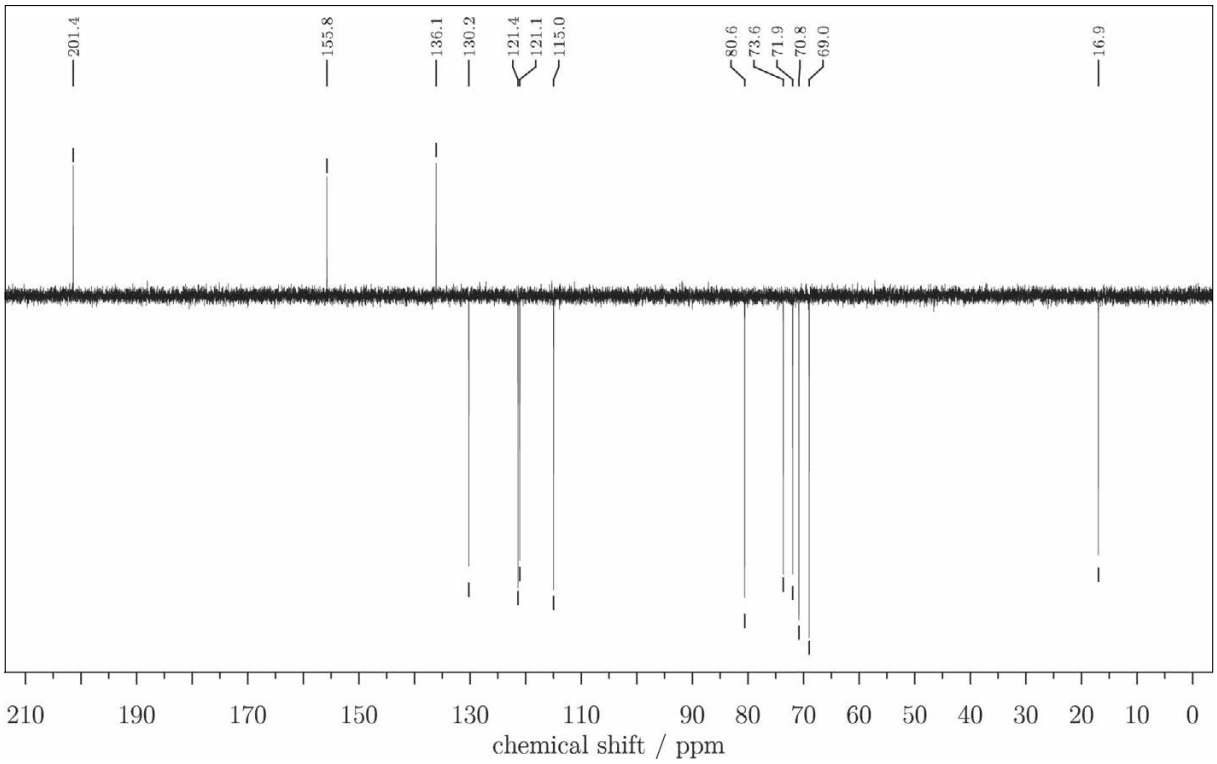


Figure 201: DEPTQ-NMR spectrum of **234** at 151 MHz in D_2O.

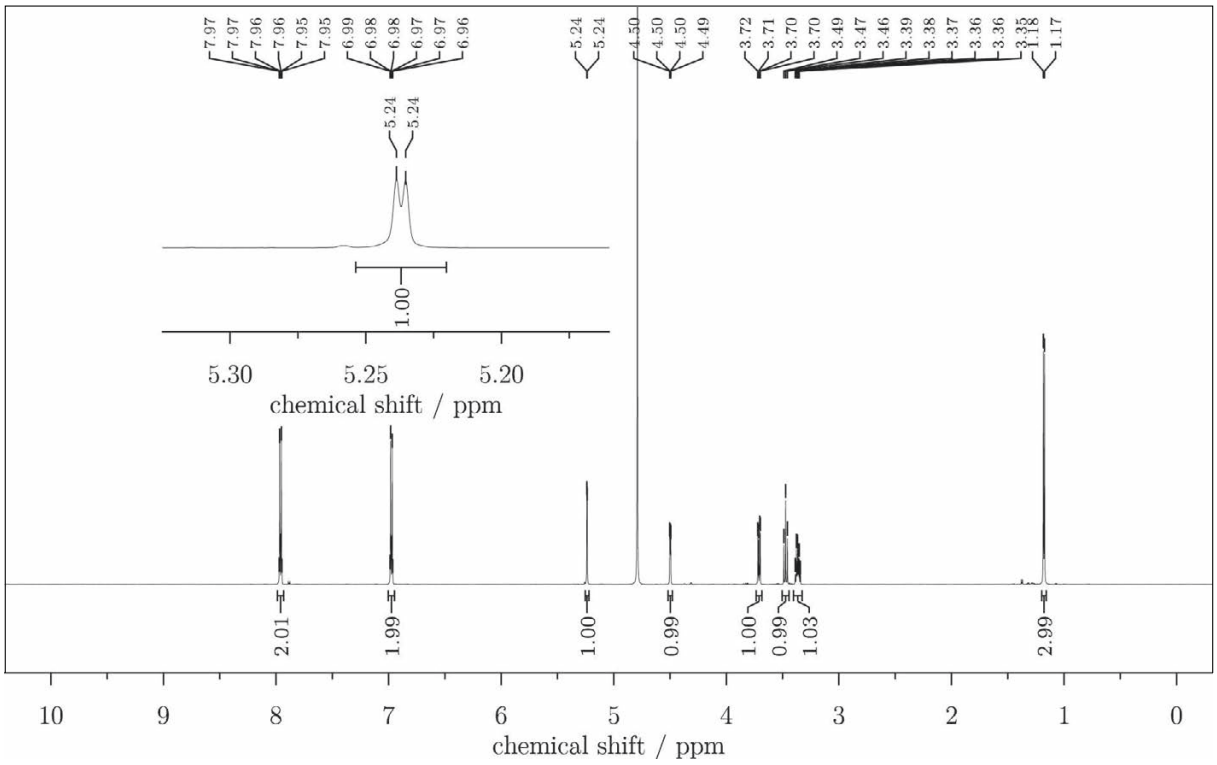


Figure 202: ^{1}H-NMR spectrum of **235** at 600 MHz in D_2O.

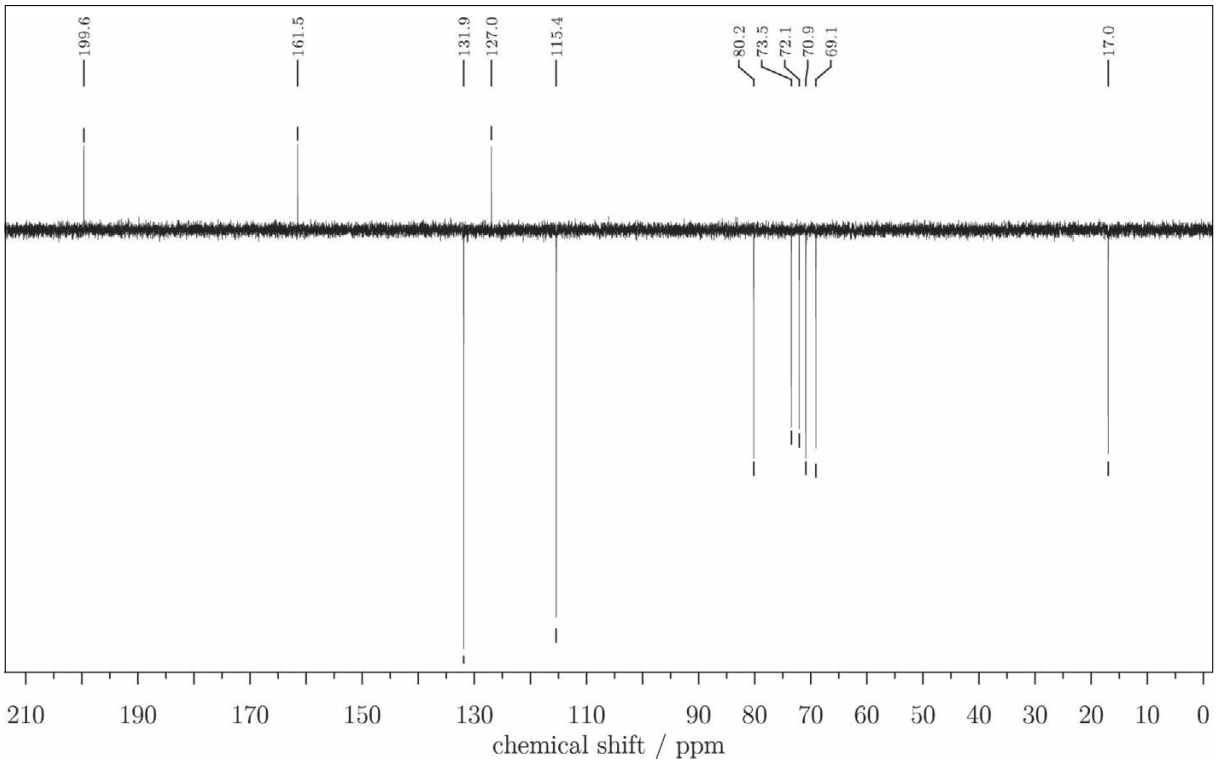


Figure 203: DEPTQ-NMR spectrum of **235** at 151 MHz in D_2O.

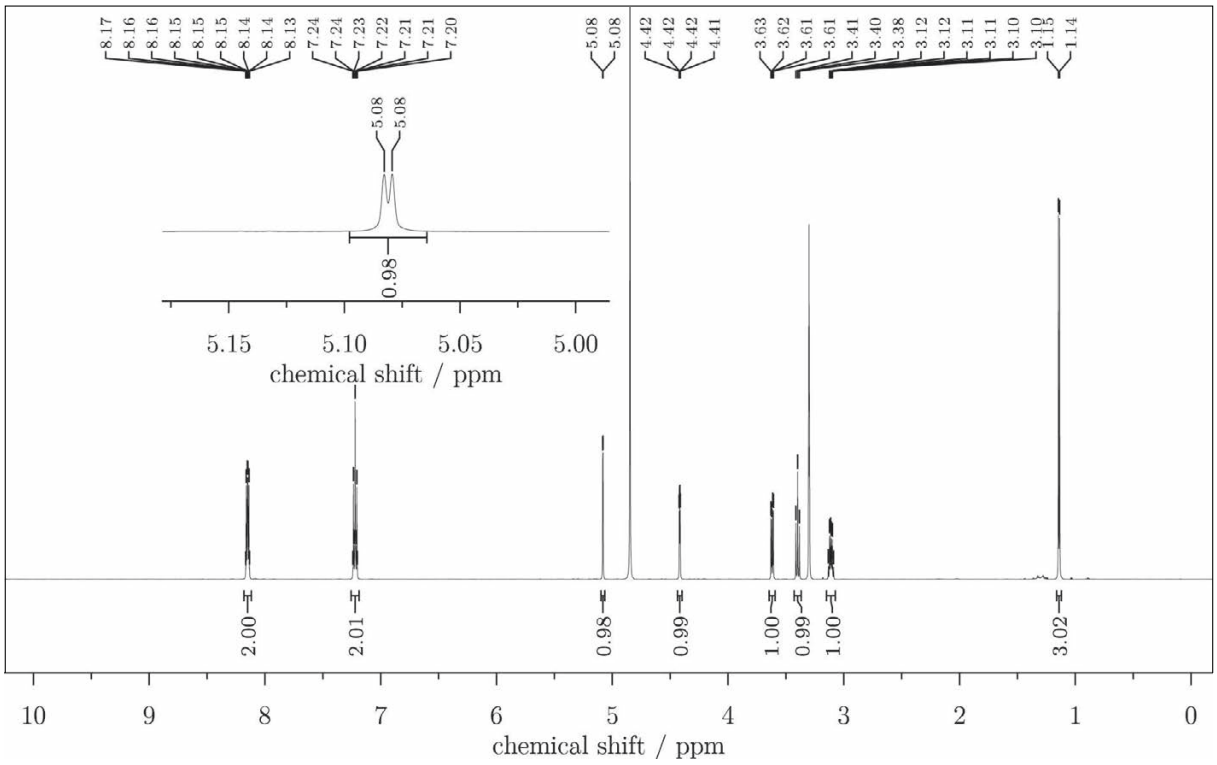


Figure 204: ^{1}H-NMR spectrum of **236** at 600 MHz in methanol-d_4.

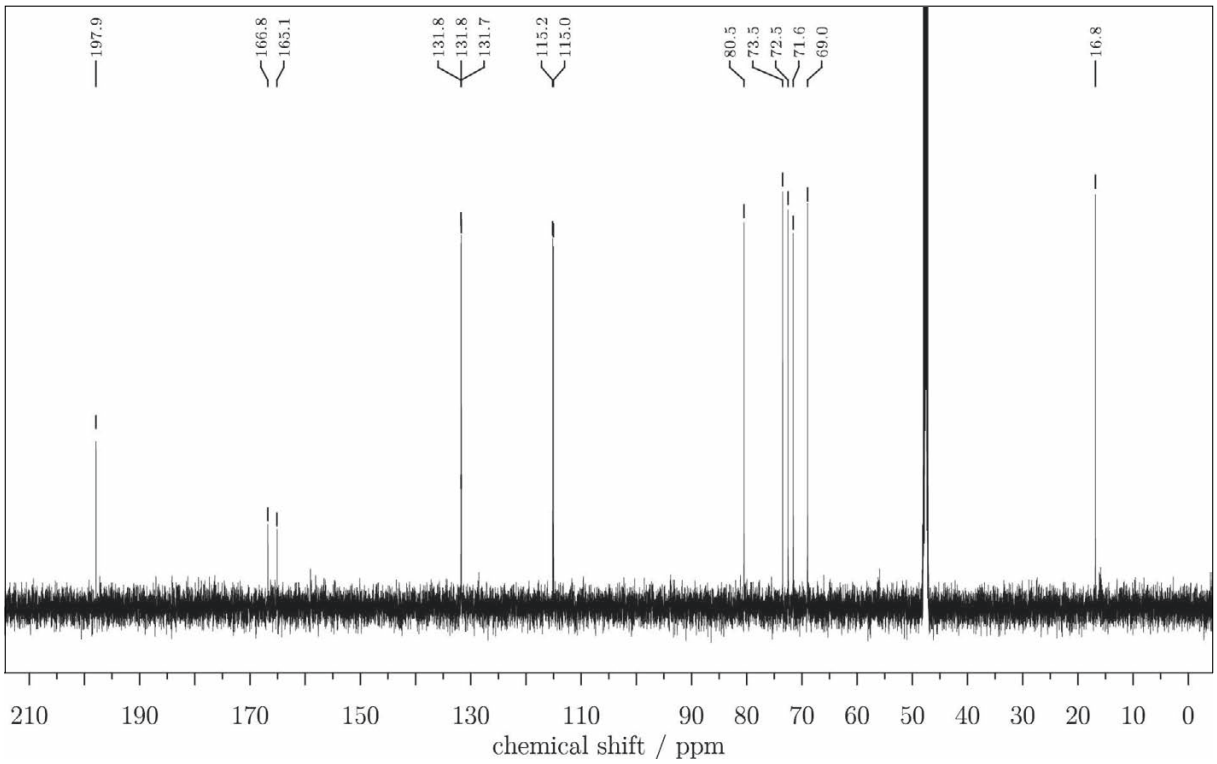


Figure 205: ^{13}C-NMR Spectrum of **236** at 151 MHz in methanol-d_4.

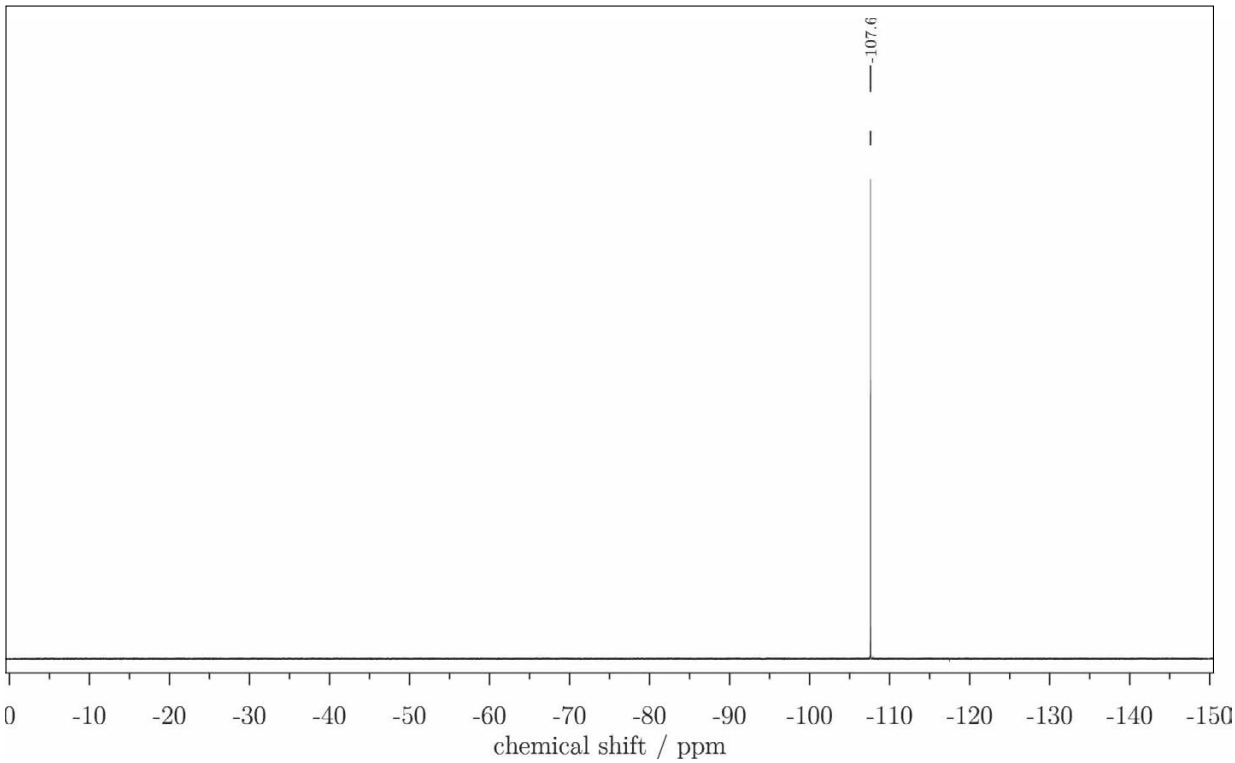


Figure 206: ^{19}F-NMR Spectrum of **236** at 565 MHz in methanol-d_4.

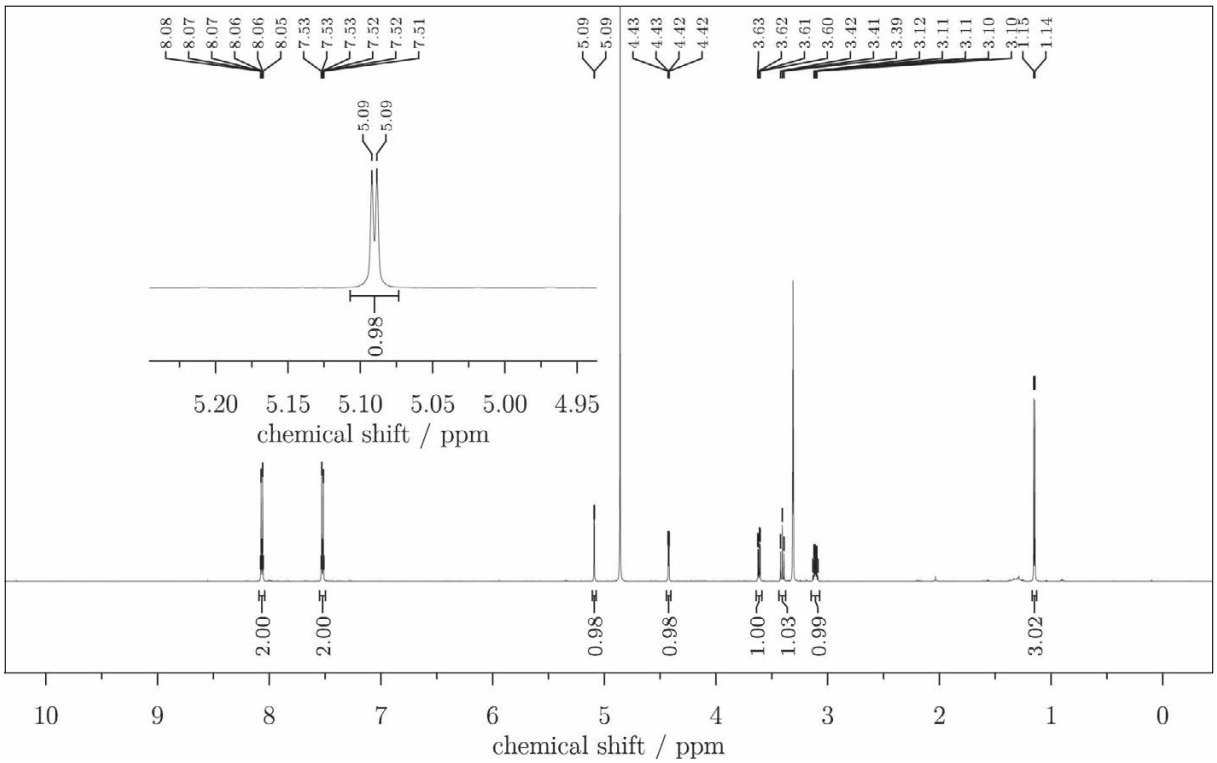


Figure 207: ^{1}H-NMR spectrum of **237** at 600 MHz in methanol-d_4.

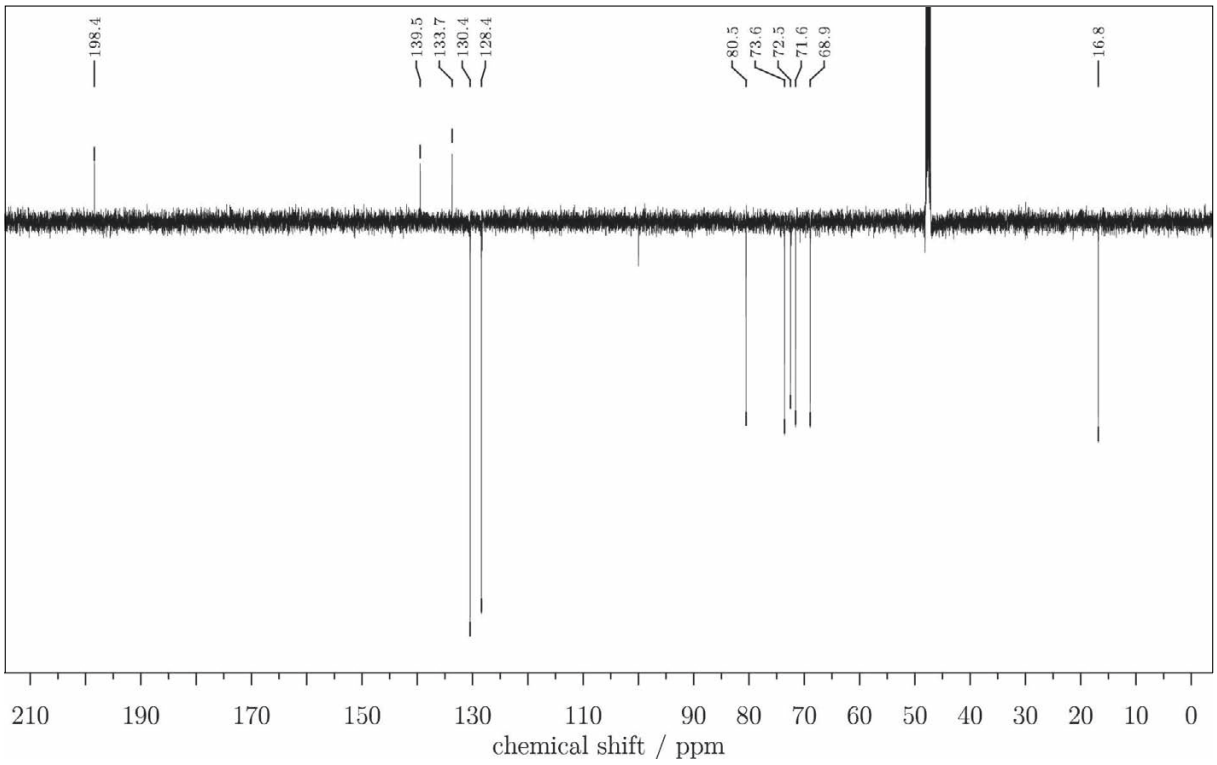


Figure 208: DEPTQ-NMR spectrum of **237** at 151 MHz in methanol-d_4.

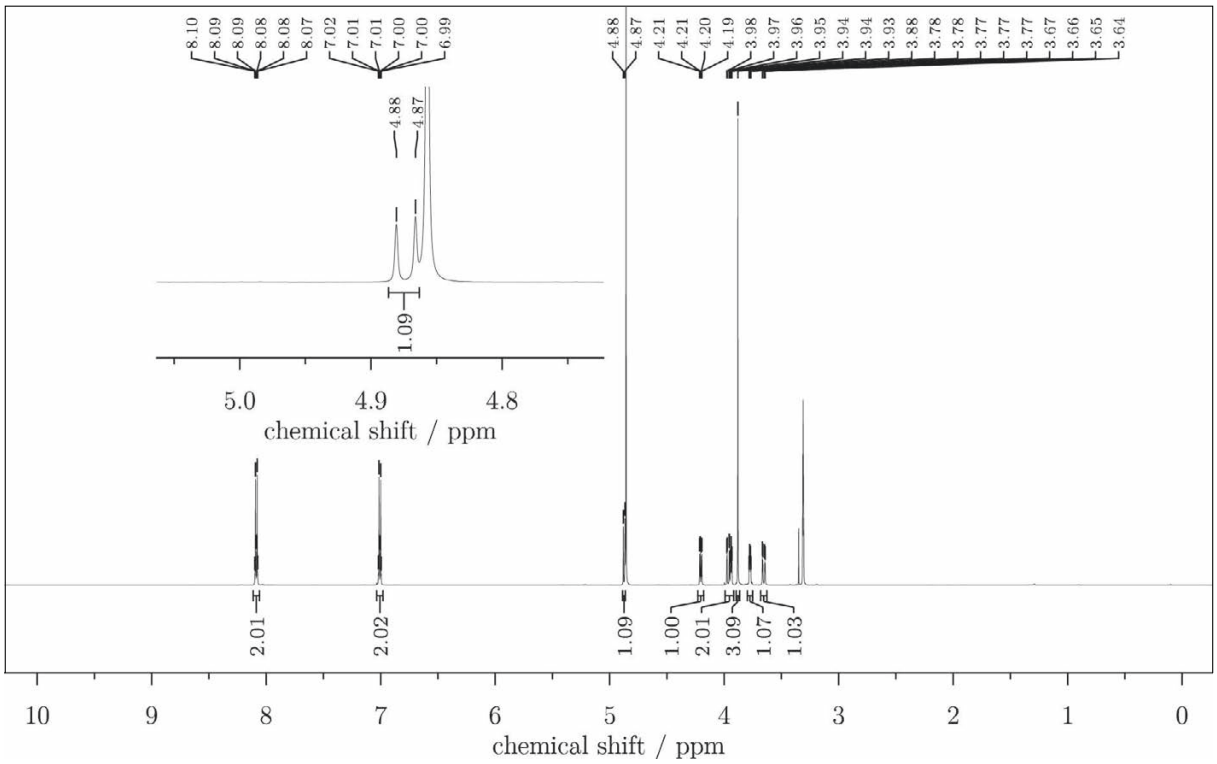


Figure 209: ^{1}H-NMR spectrum of **239** at 600 MHz in methanol-d_4.

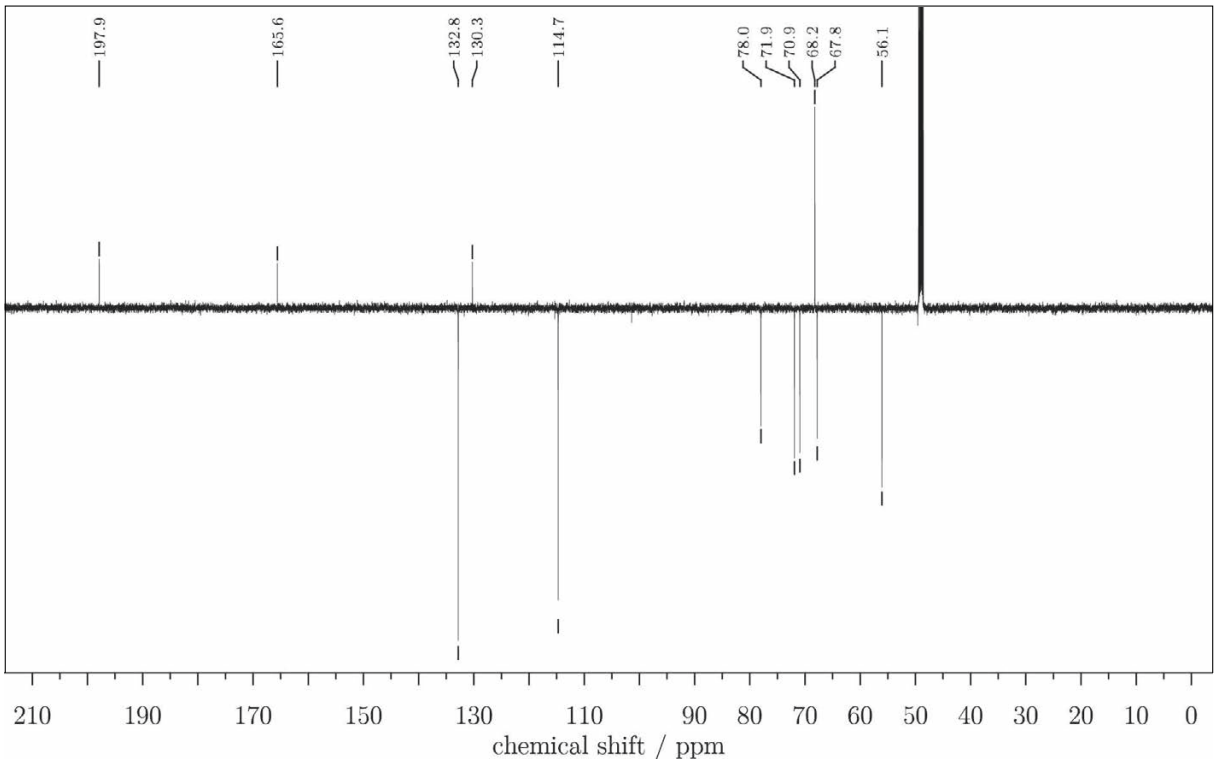


Figure 210: DEPTQ-NMR spectrum of **239** at 151 MHz in methanol-d_4.

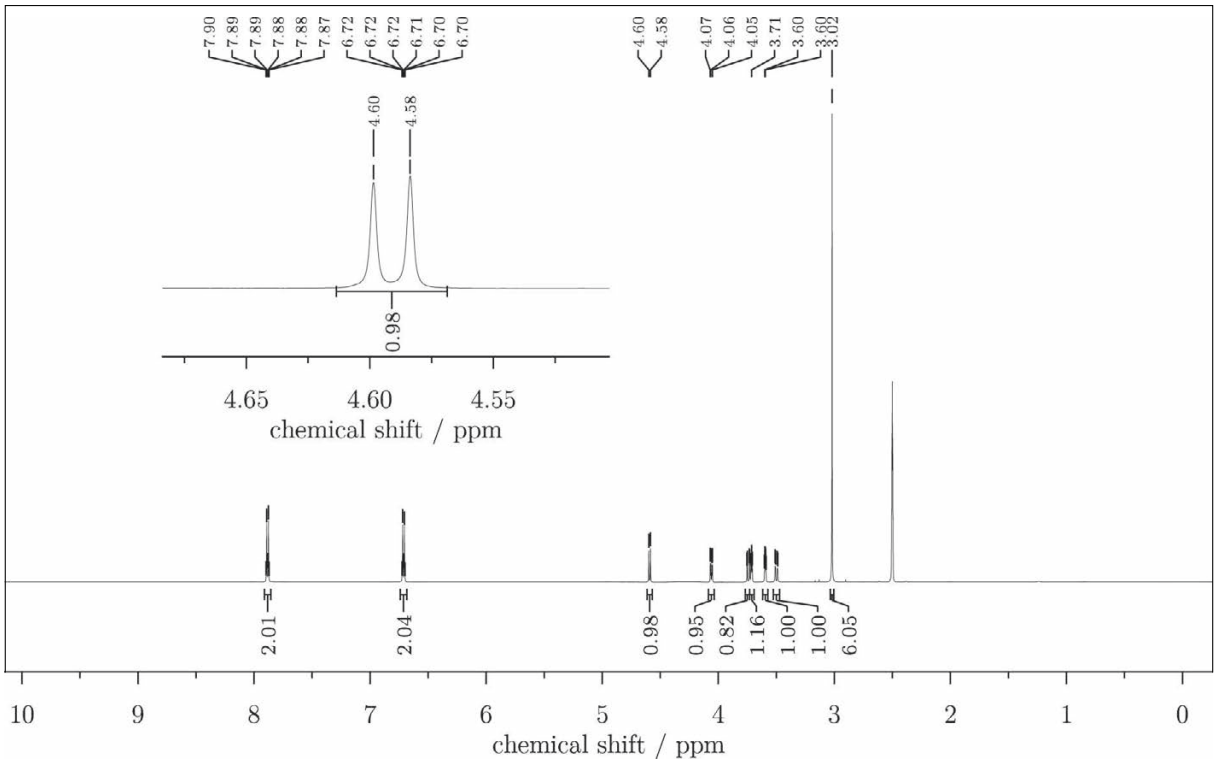


Figure 211: ^{1}H-NMR spectrum of **240** at 600 MHz in DMSO-d_6.

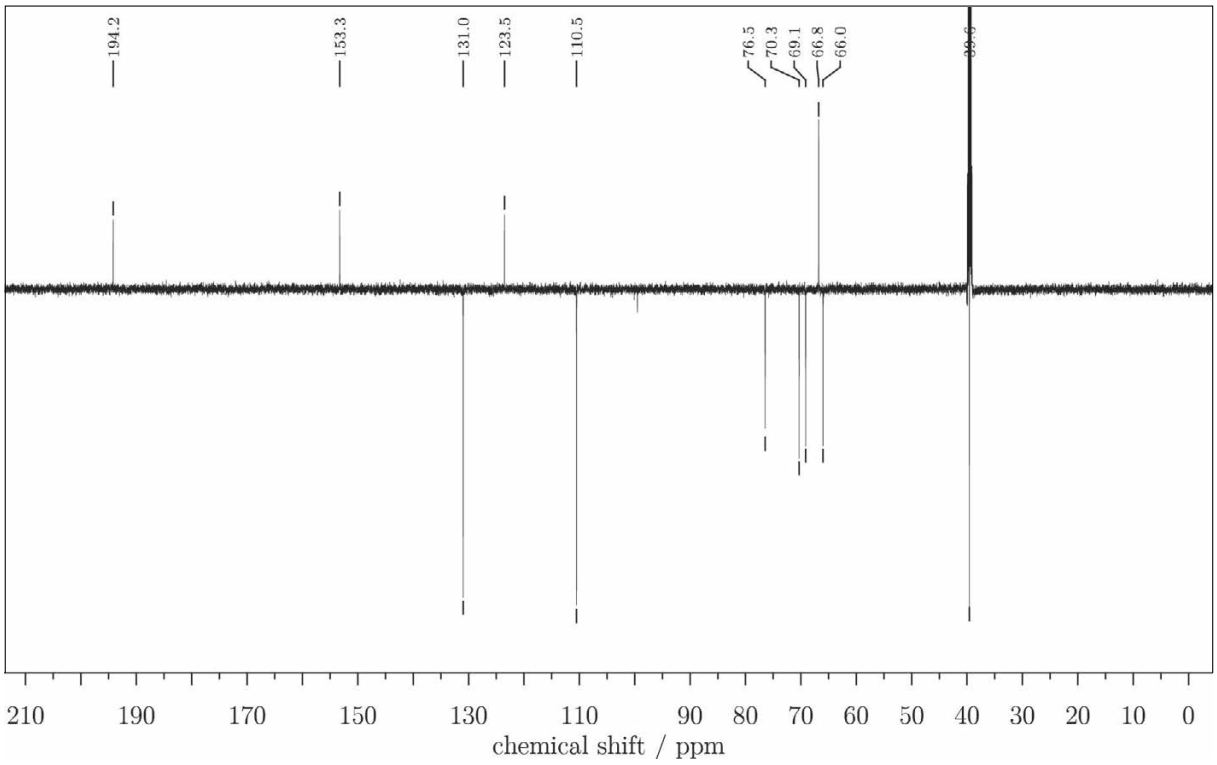


Figure 212: DEPTQ-NMR spectrum of **240** at 151 MHz in DMSO-d_6.

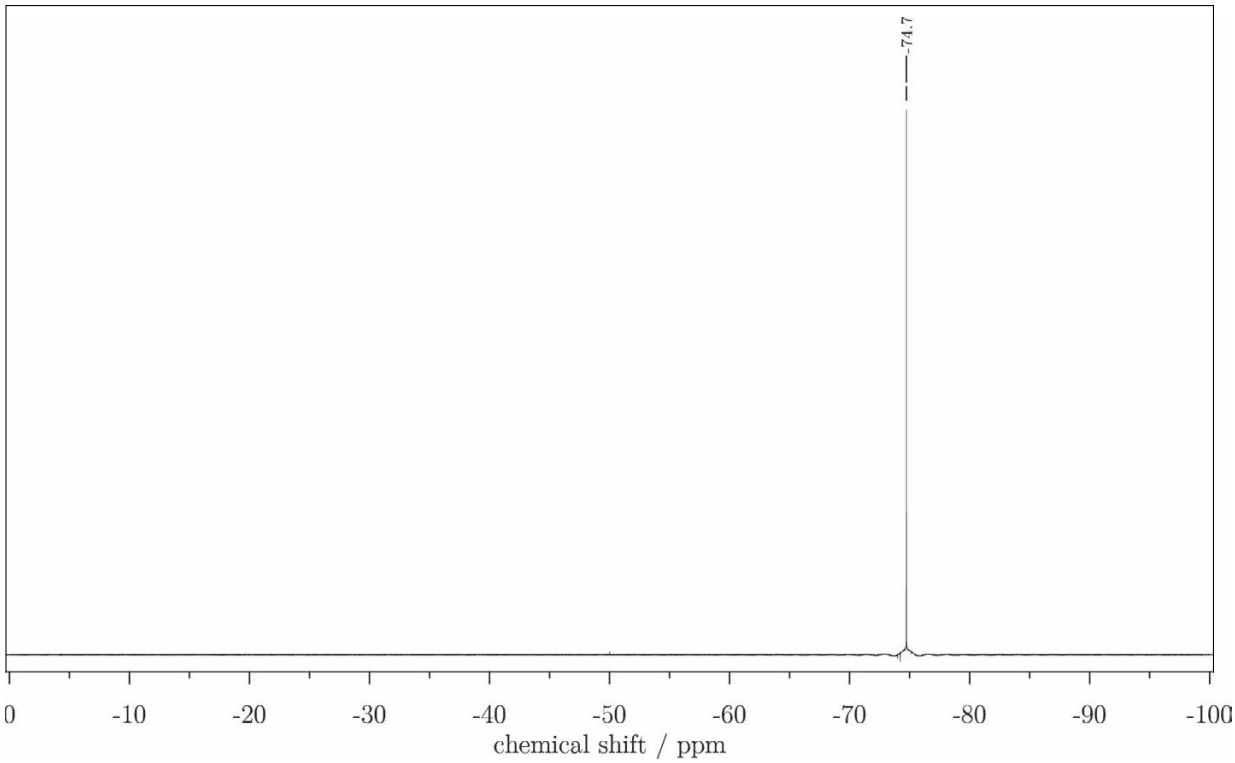


Figure 213: ^{19}F-NMR Spectrum of **240** at 565 MHz in DMSO-d_6.

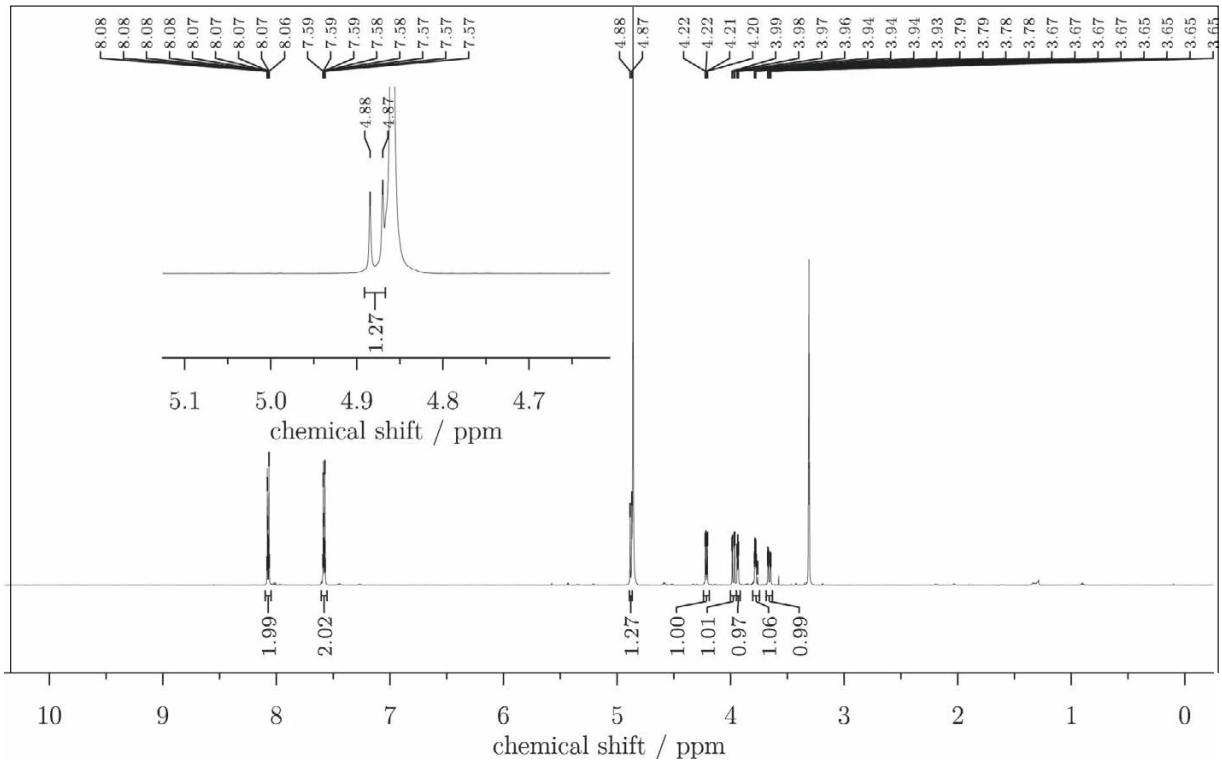


Figure 214: ^{1}H-NMR spectrum of **241** at 600 MHz in methanol-d_4.

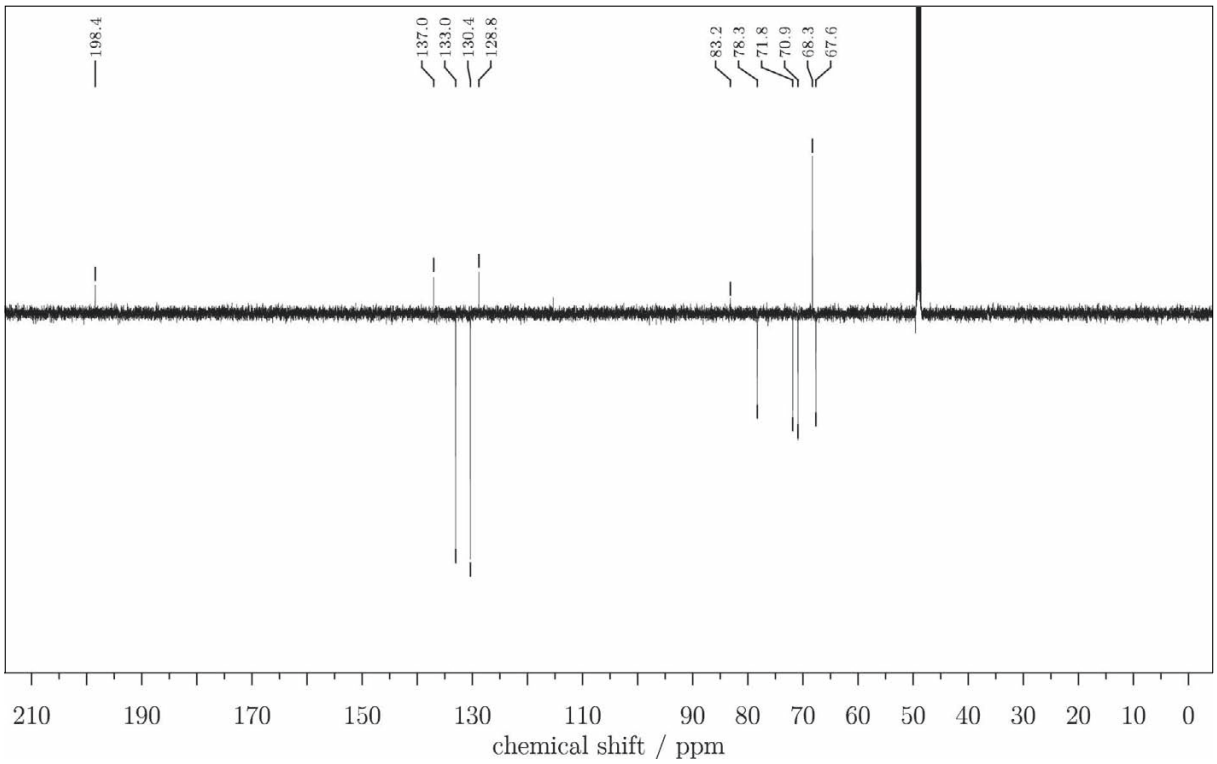


Figure 215: DEPTQ-NMR spectrum of **241** at 151 MHz in methanol-d_4.

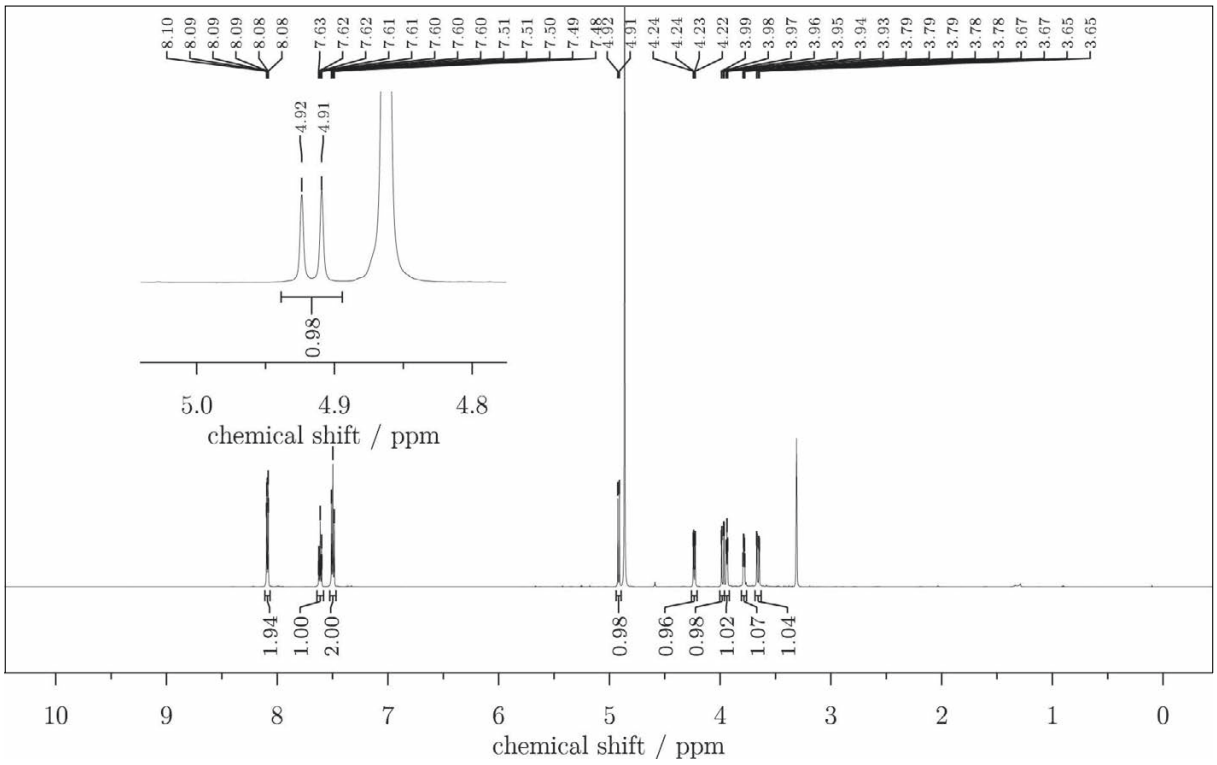


Figure 216: ^{1}H-NMR spectrum of **242** at 600 MHz in methanol-d_4.

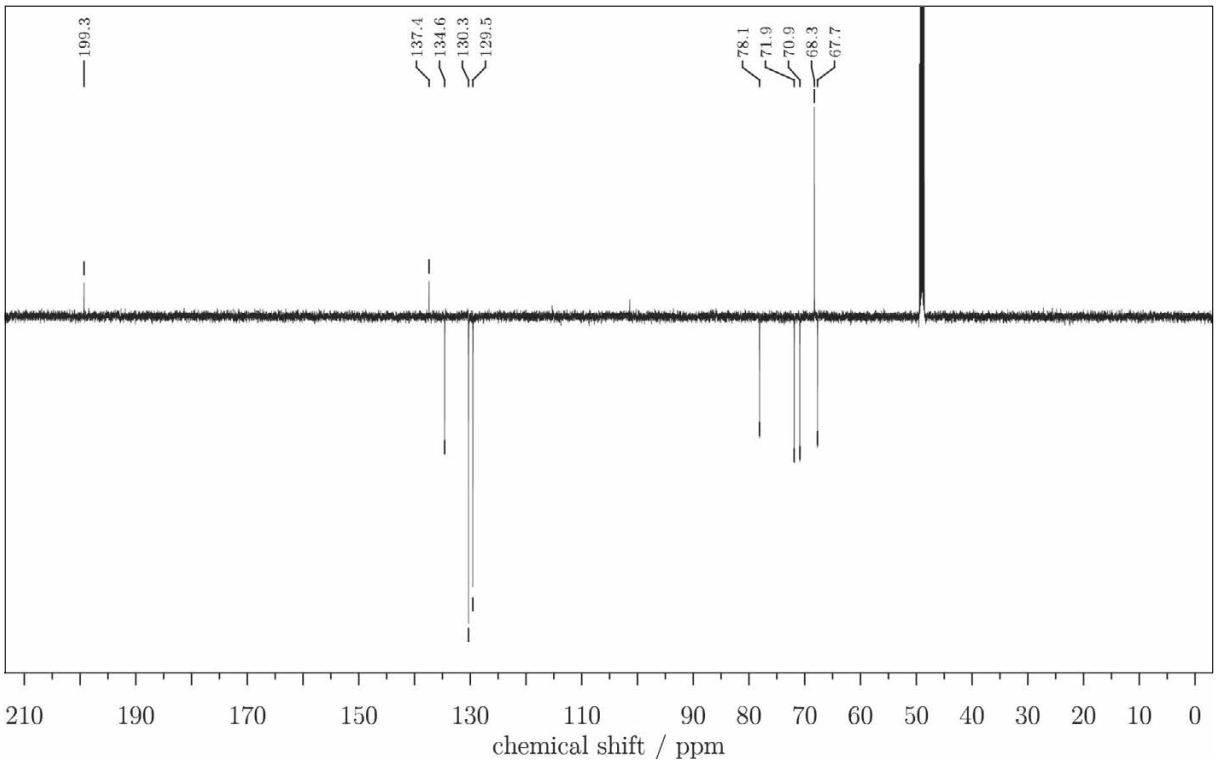


Figure 217: DEPTQ-NMR spectrum of **242** at 151 MHz in methanol-d_4.

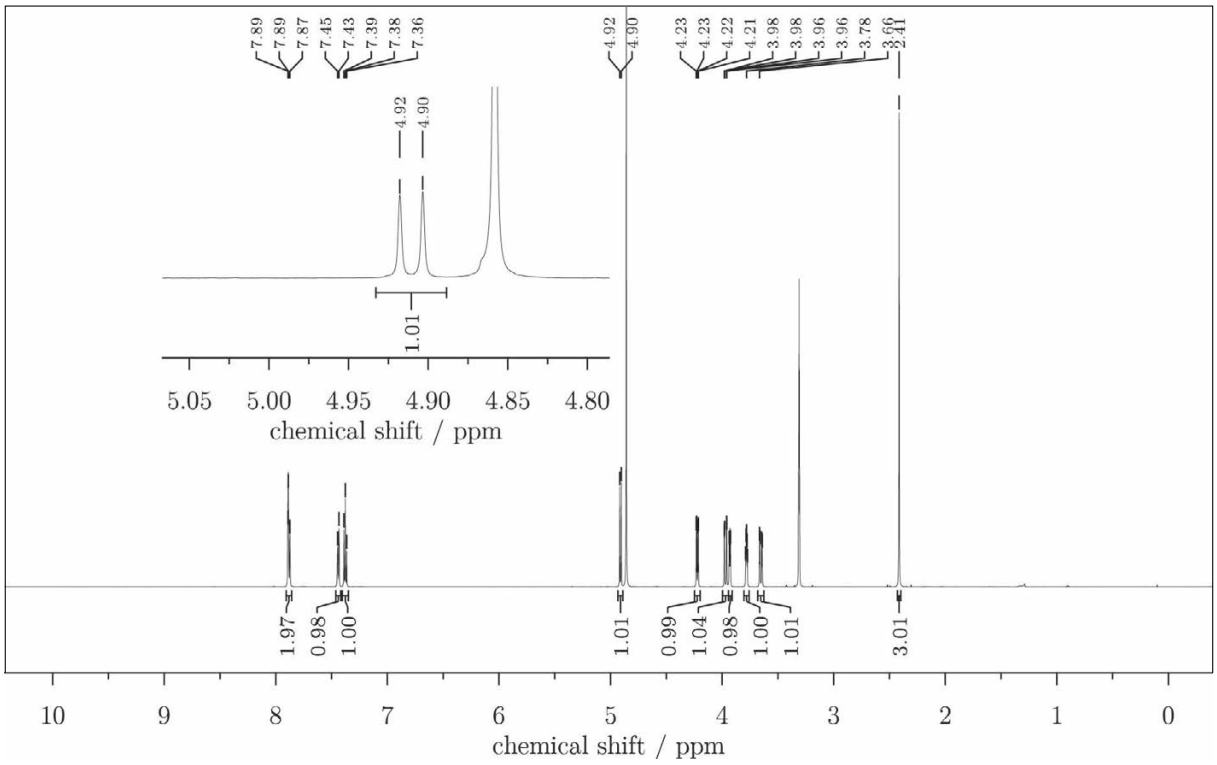


Figure 218: ^{1}H-NMR spectrum of **243** at 600 MHz in methanol-d_4.

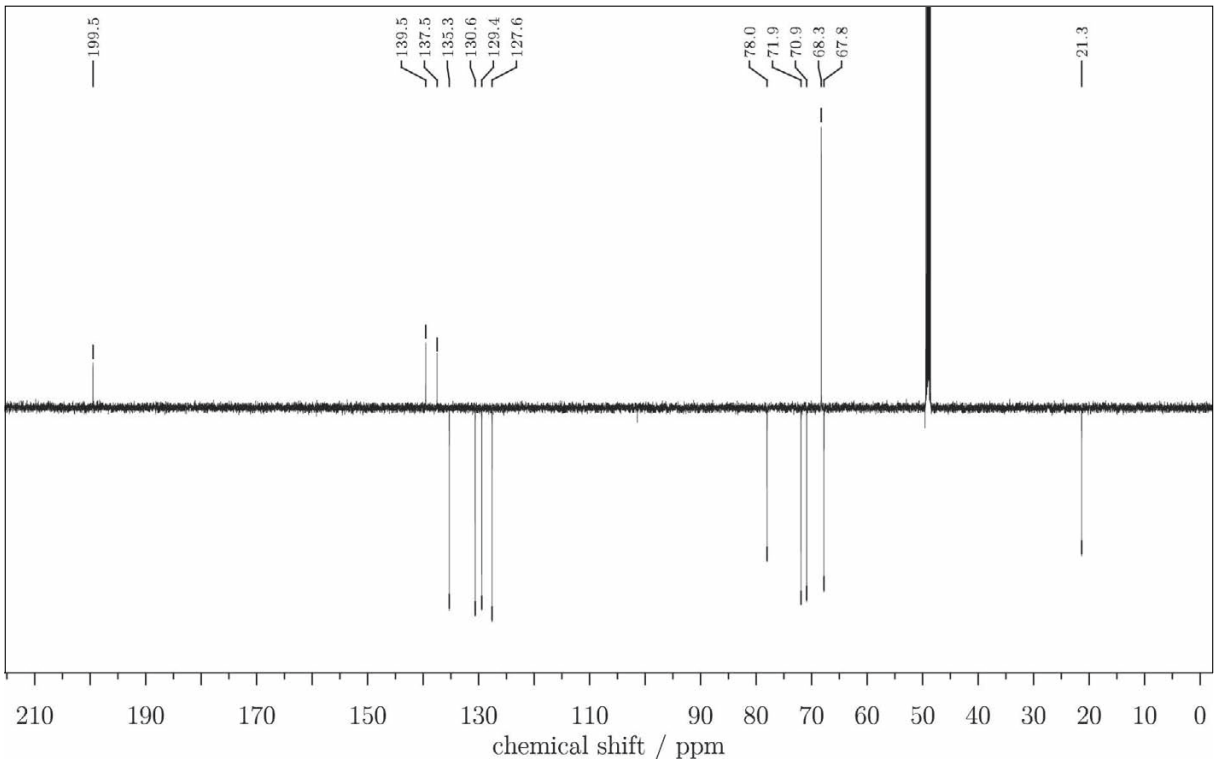


Figure 219: DEPTQ-NMR spectrum of **243** at 151 MHz in methanol-d_4.

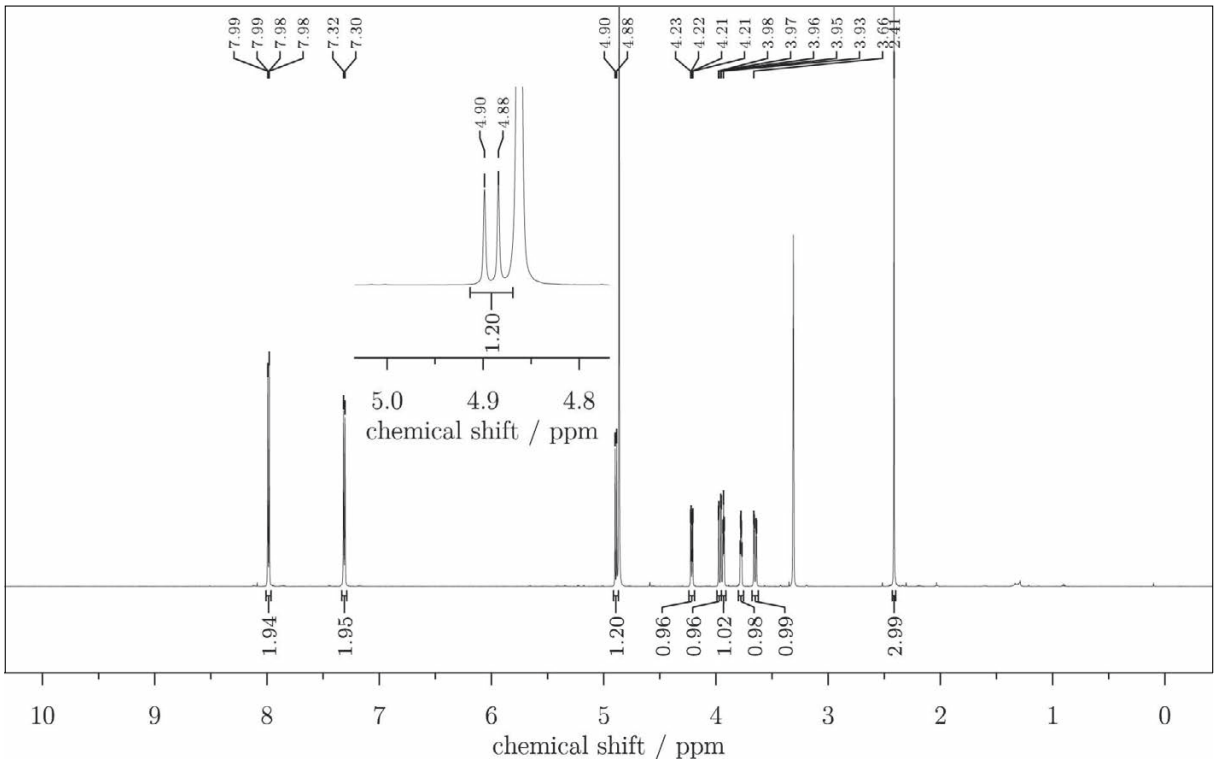


Figure 220: ^{1}H-NMR spectrum of **244** at 600 MHz in methanol-d_4.

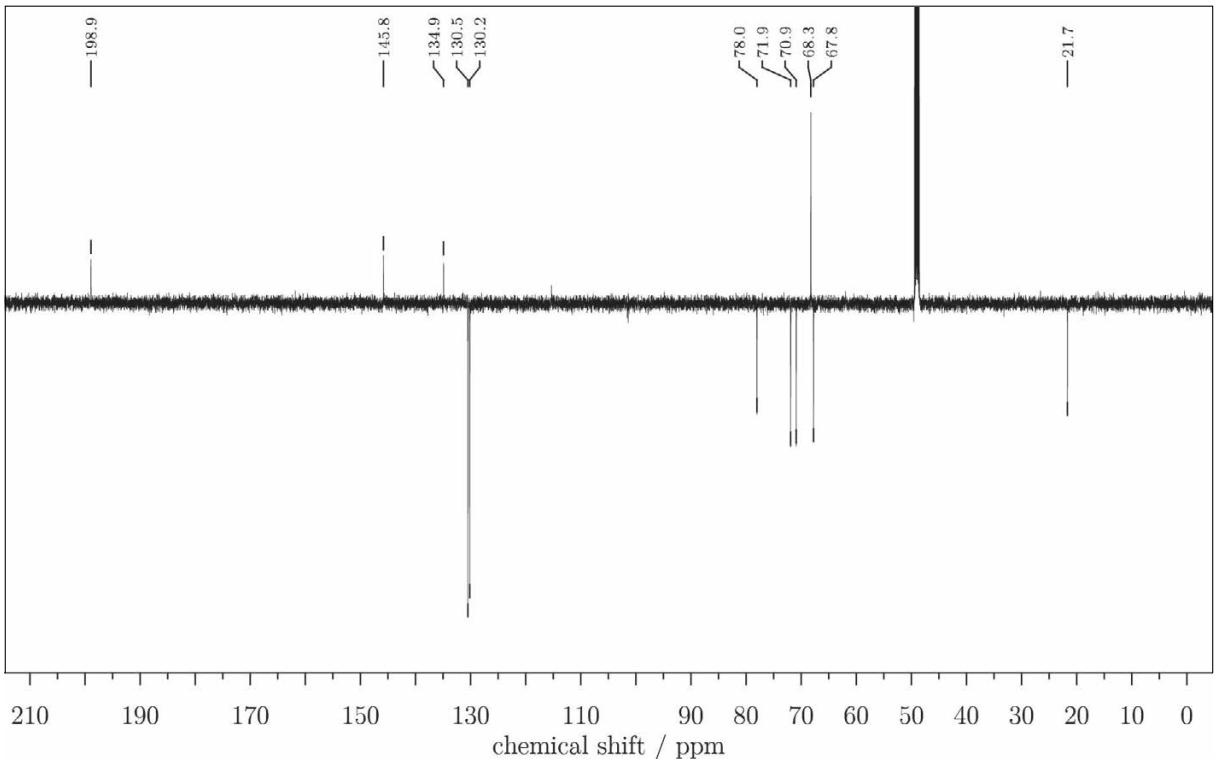


Figure 221: DEPTQ-NMR spectrum of **244** at 151 MHz in methanol-d_4.

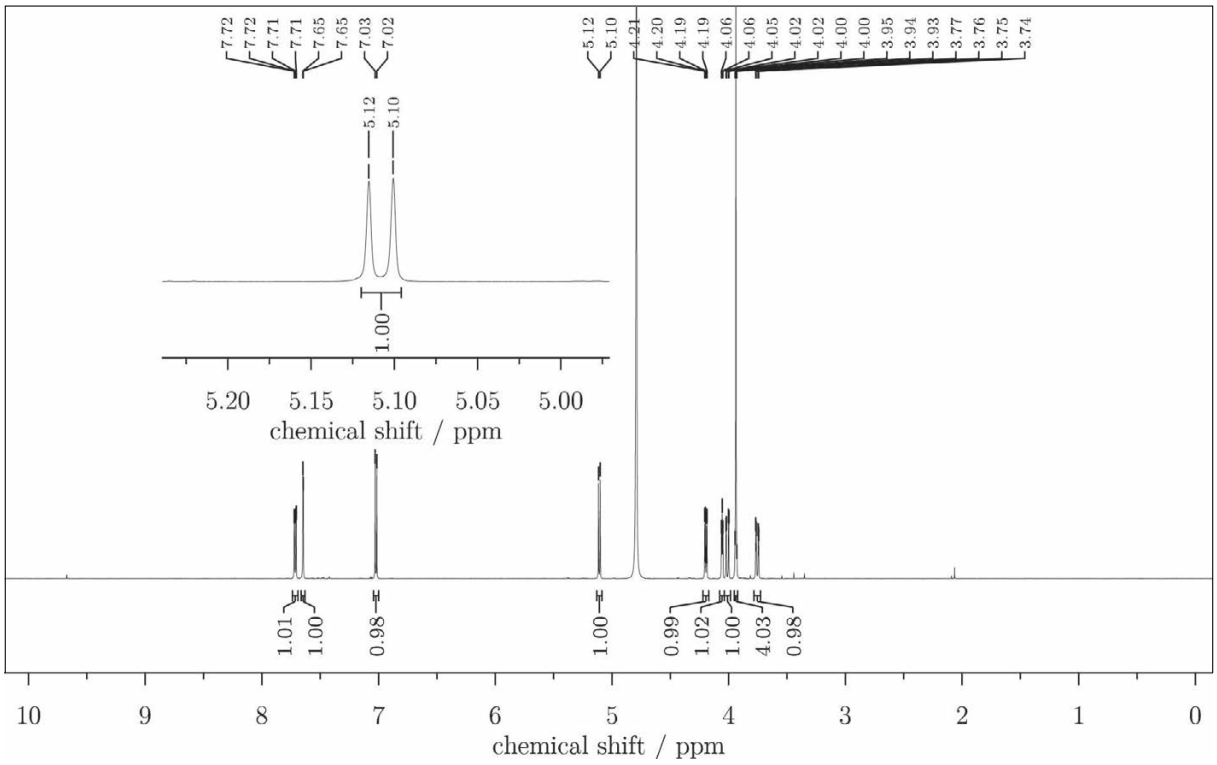


Figure 222: ^{1}H-NMR spectrum of **245** at 600 MHz in D_2O.

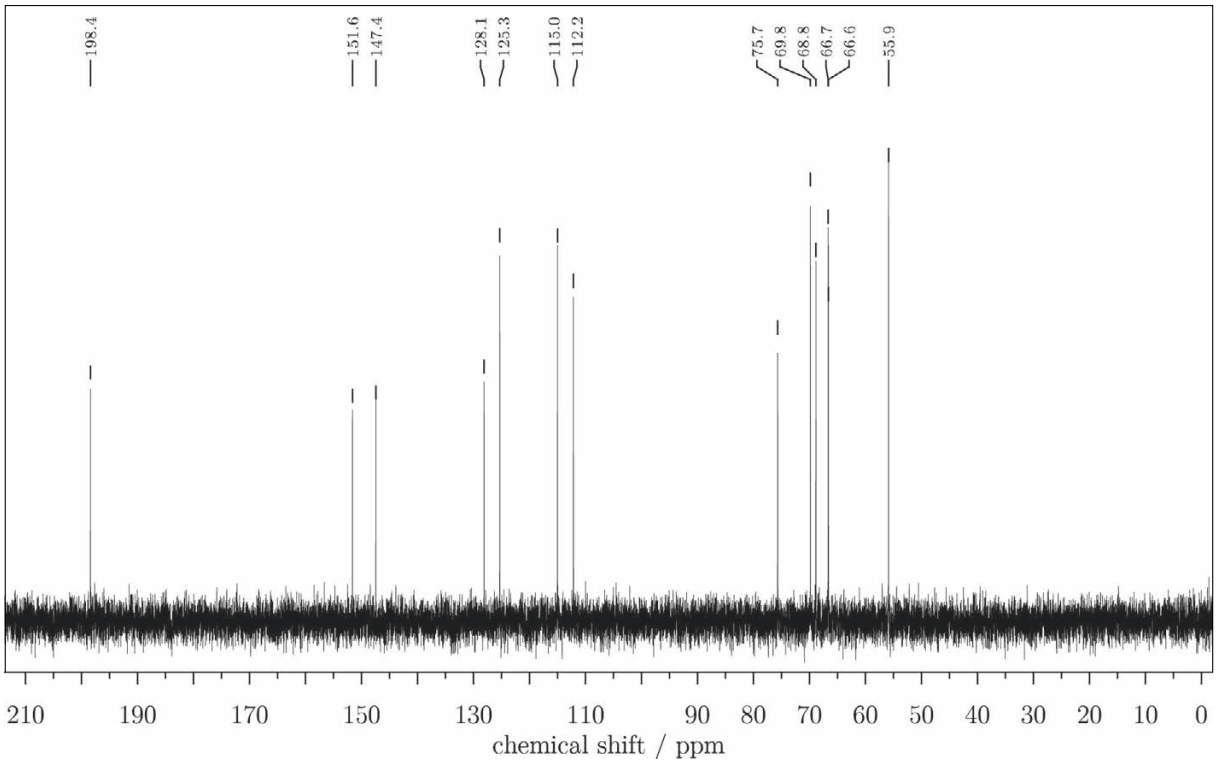


Figure 223: ^{13}C-NMR Spectrum of **245** at 151 MHz in D_2O.

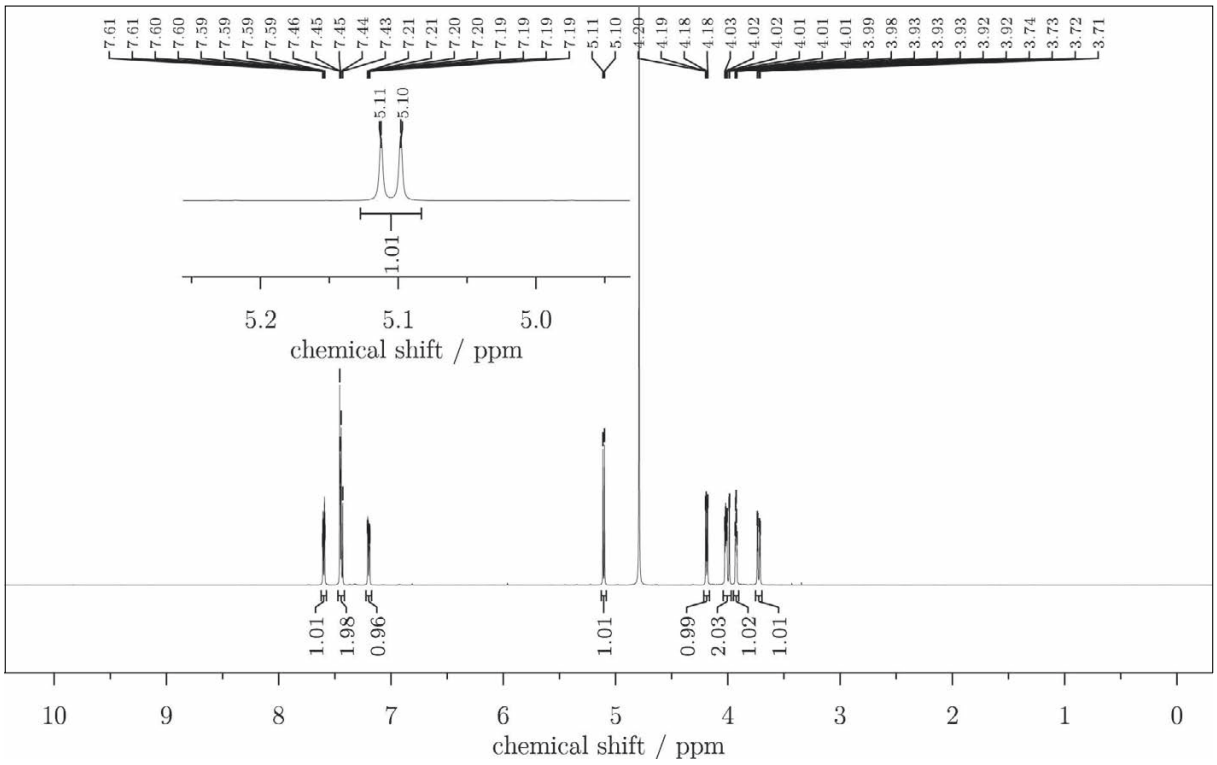


Figure 224: ^{1}H-NMR spectrum of **246** at 600 MHz in D_2O.

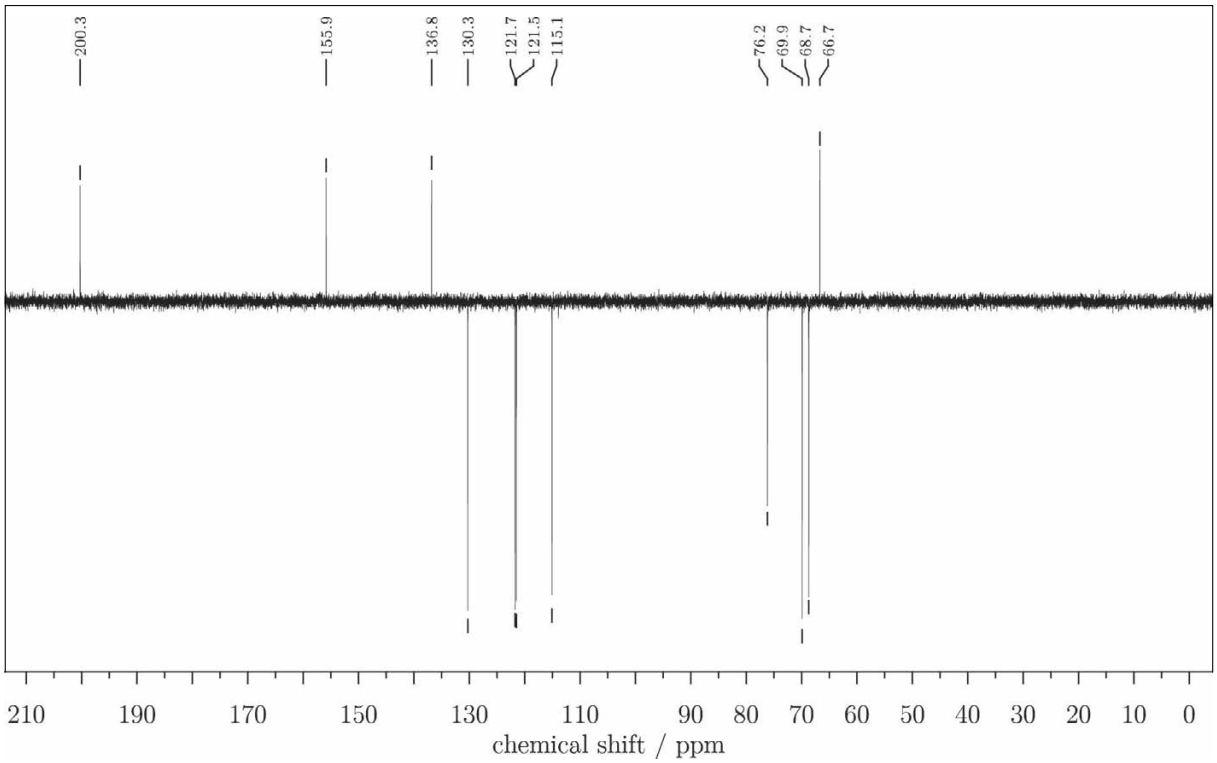


Figure 225: DEPTQ-NMR spectrum of **246** at 151 MHz in D_2O.

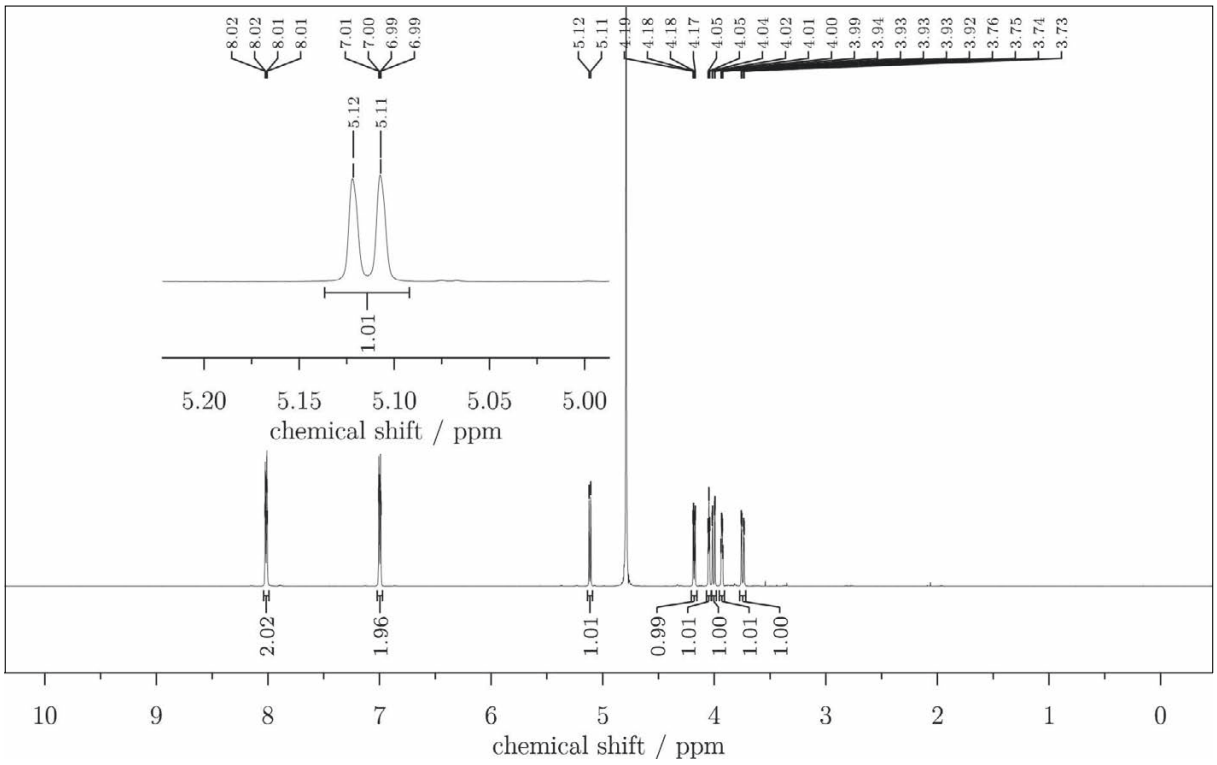


Figure 226: ^{1}H-NMR spectrum of **247** at 600 MHz in D_2O.

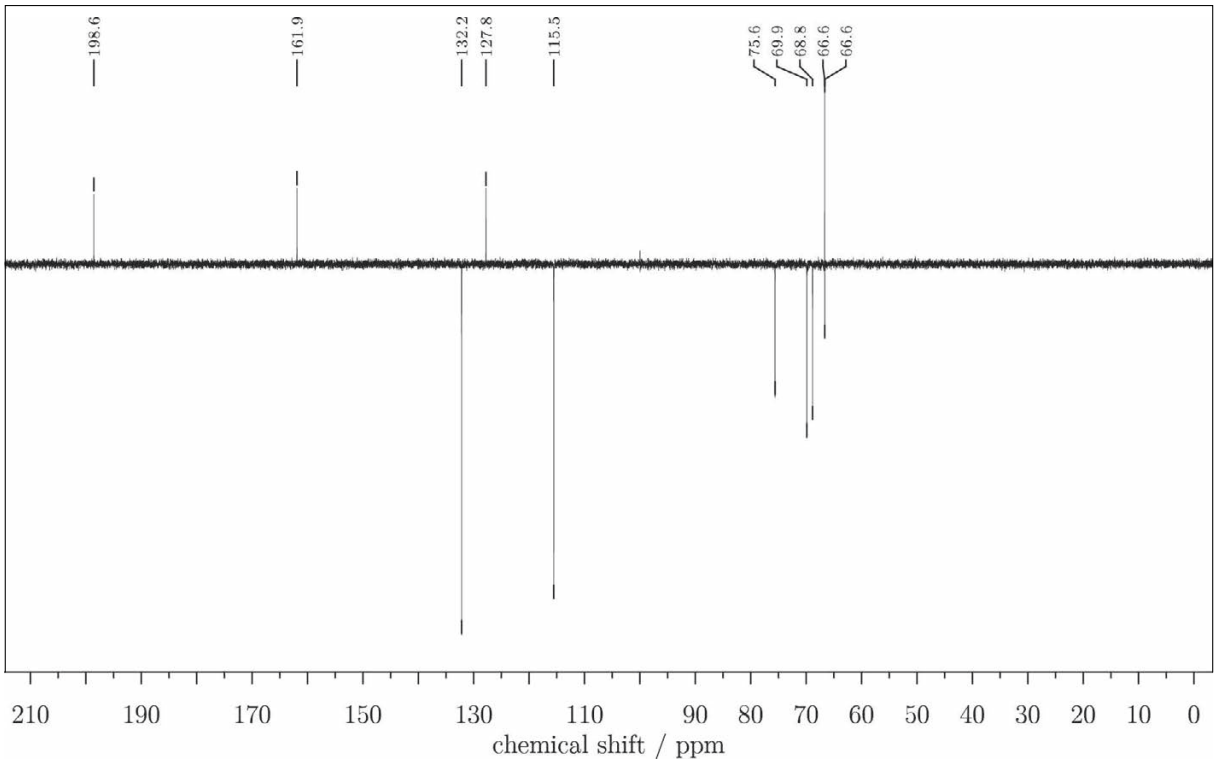


Figure 227: DEPTQ-NMR spectrum of **247** at 151 MHz in D_2O.

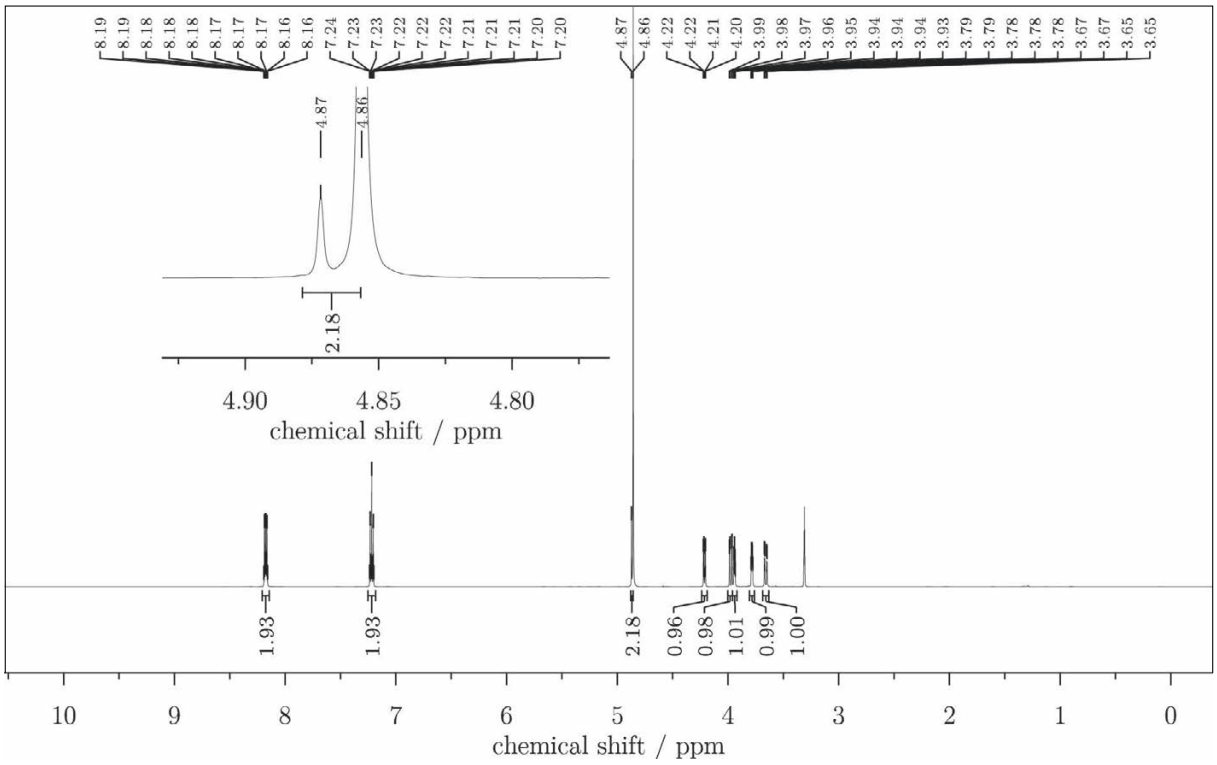


Figure 228: ^{1}H-NMR spectrum of **248** at 600 MHz in methanol-d_4.

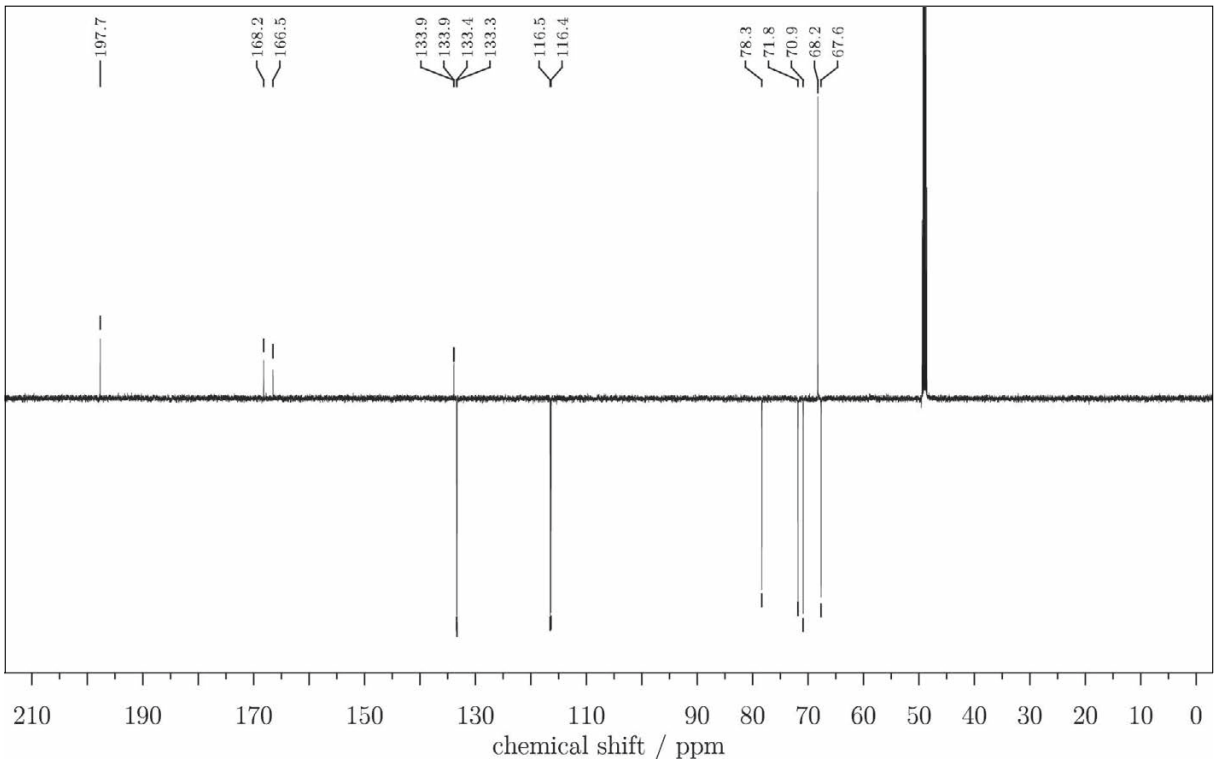


Figure 229: DEPTQ-NMR spectrum of **248** at 151 MHz in methanol-d_4.

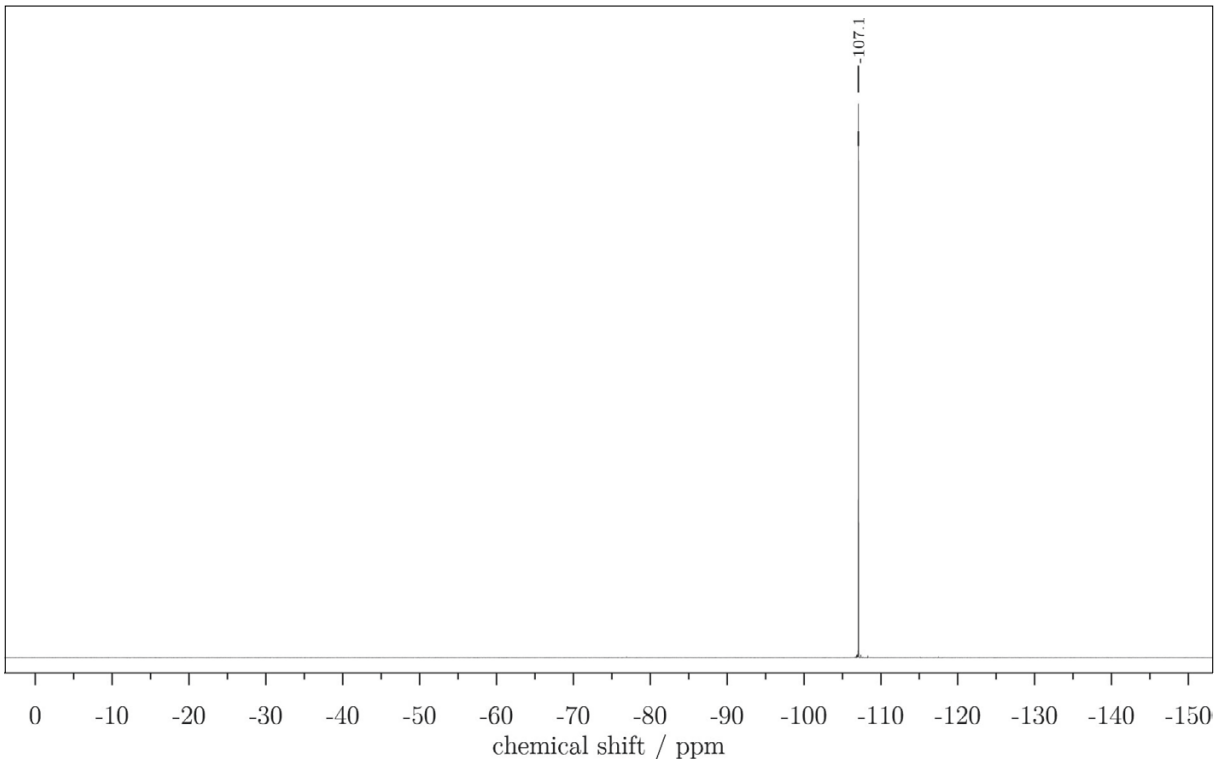


Figure 230: ^{19}F-NMR Spectrum of **248** at 565 MHz in methanol-d_4.

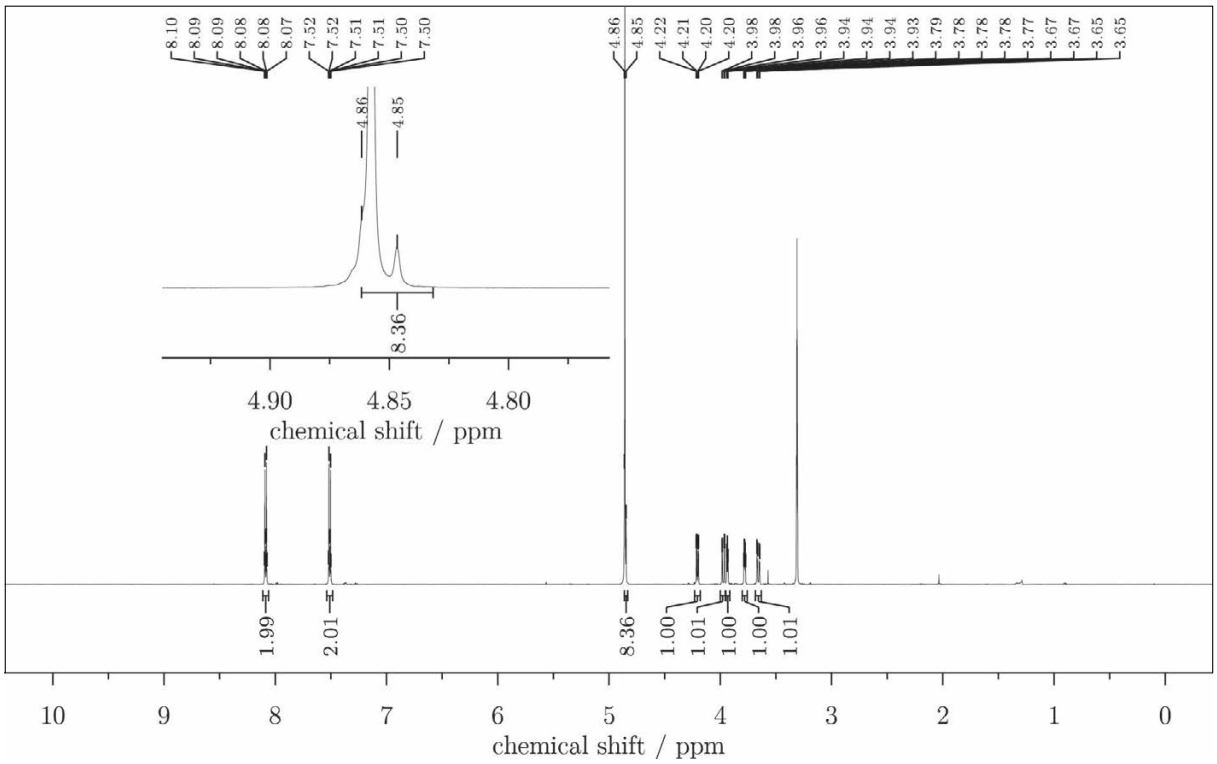


Figure 231: ^{1}H-NMR spectrum of **249** at 600 MHz in methanol-d_4.

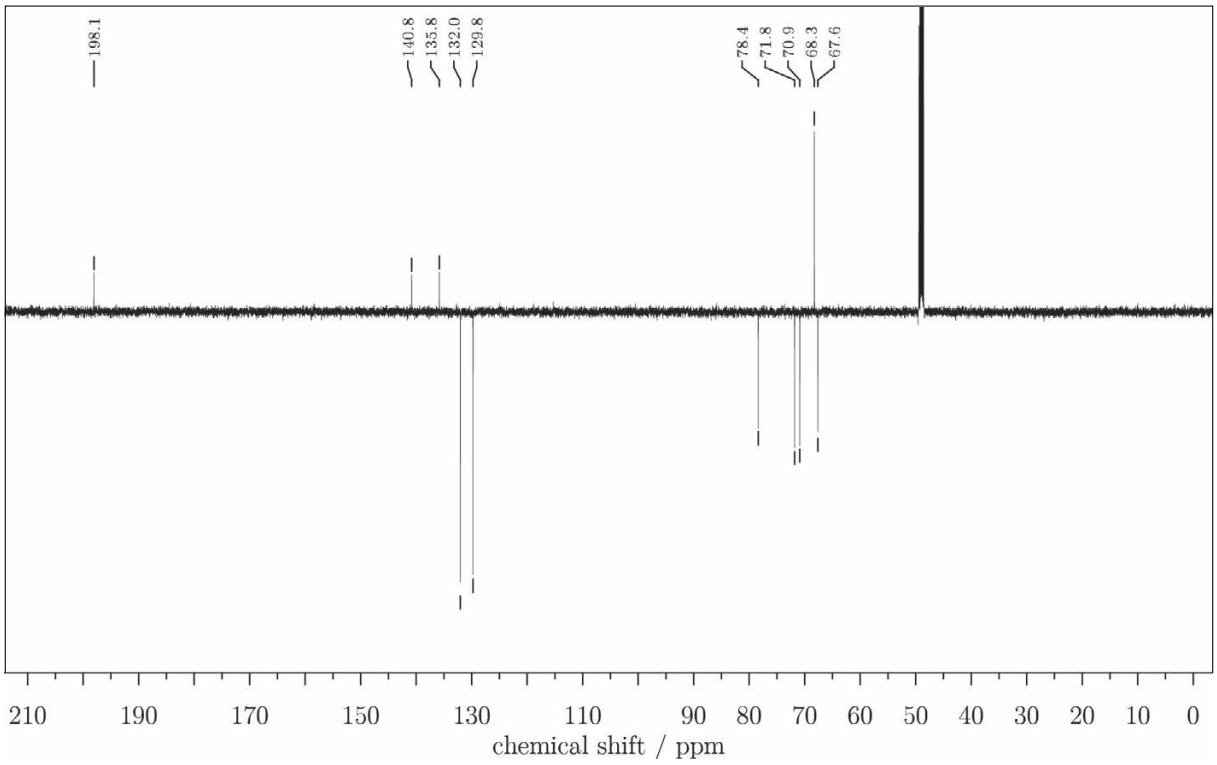


Figure 232: DEPTQ-NMR spectrum of **249** at 151 MHz in methanol-d_4.

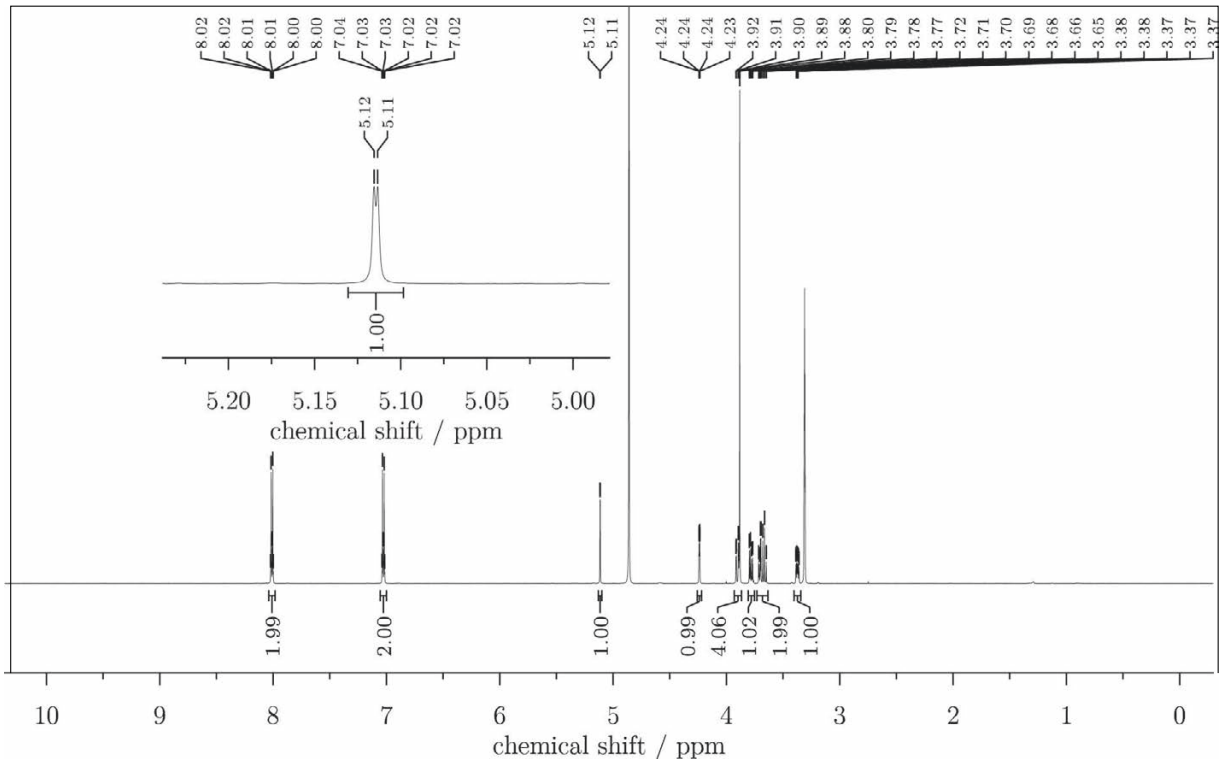


Figure 233: ^{1}H-NMR spectrum of **251** at 600 MHz in methanol-d_4.

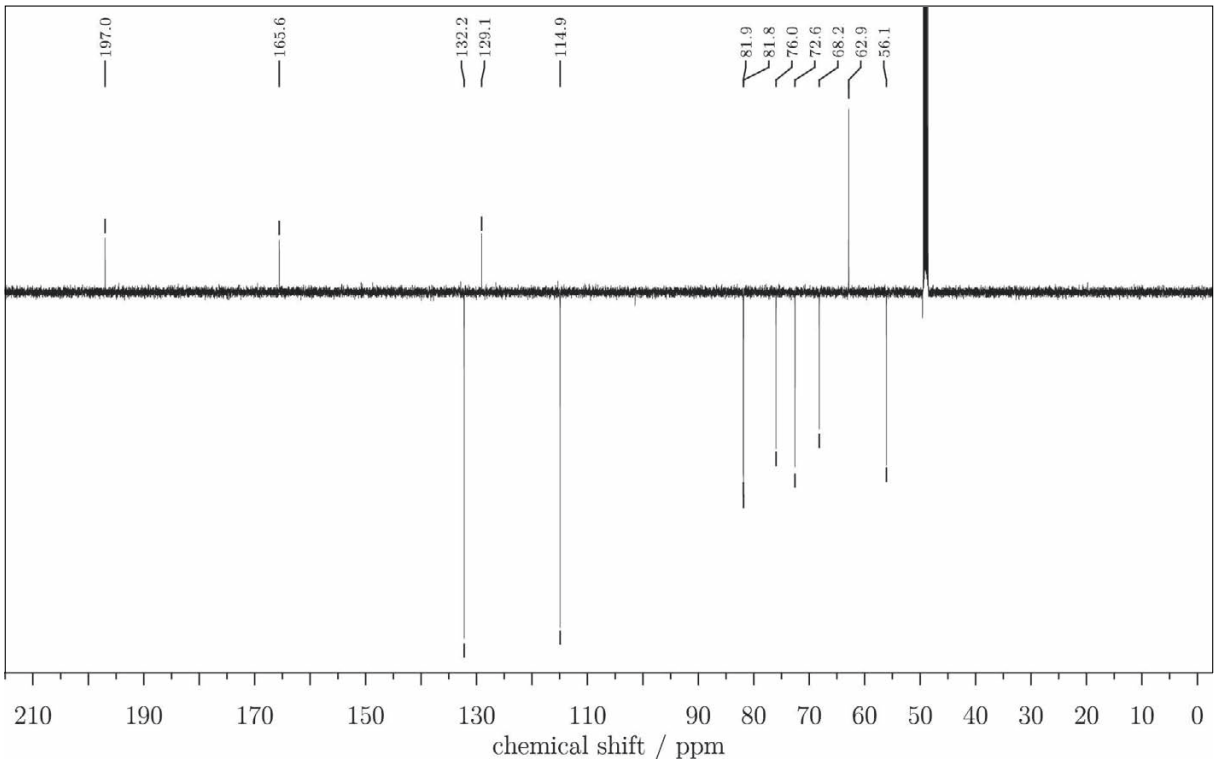


Figure 234: DEPTQ-NMR spectrum of **251** at 151 MHz in methanol-d_4.

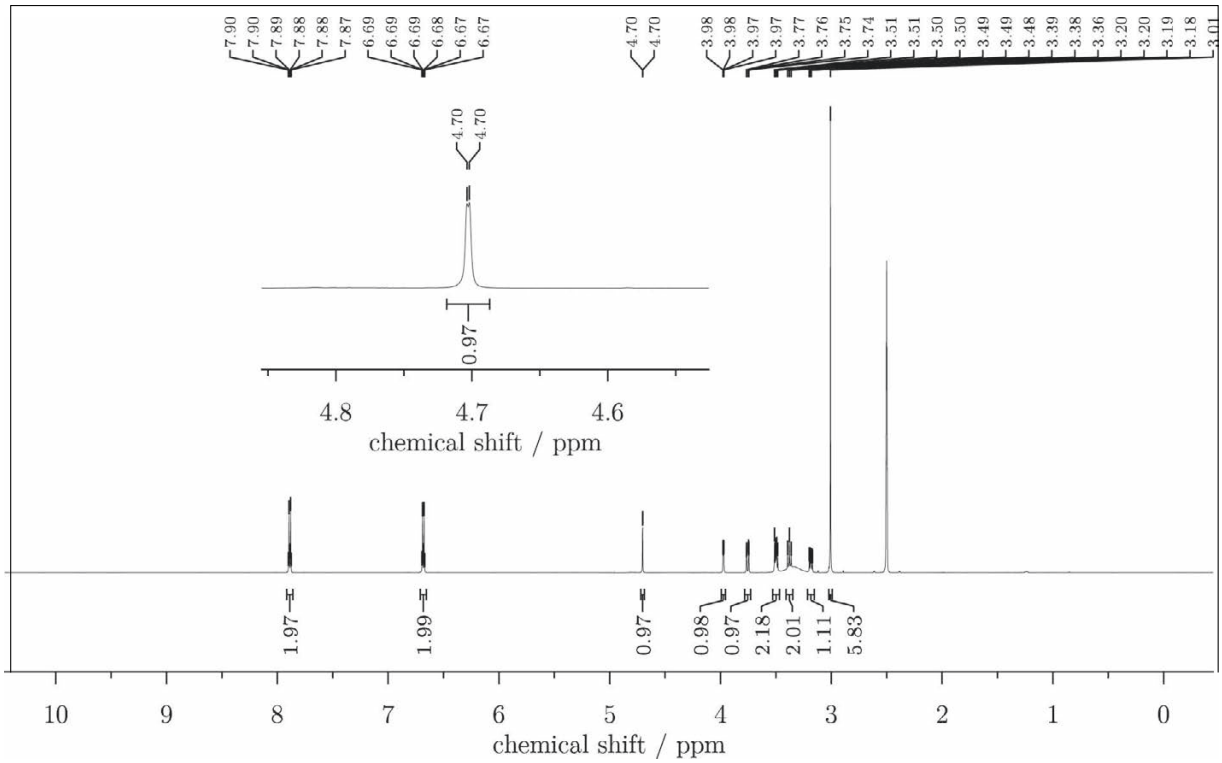


Figure 235: ^{1}H-NMR spectrum of **253** at 600 MHz in DMSO-d_6.

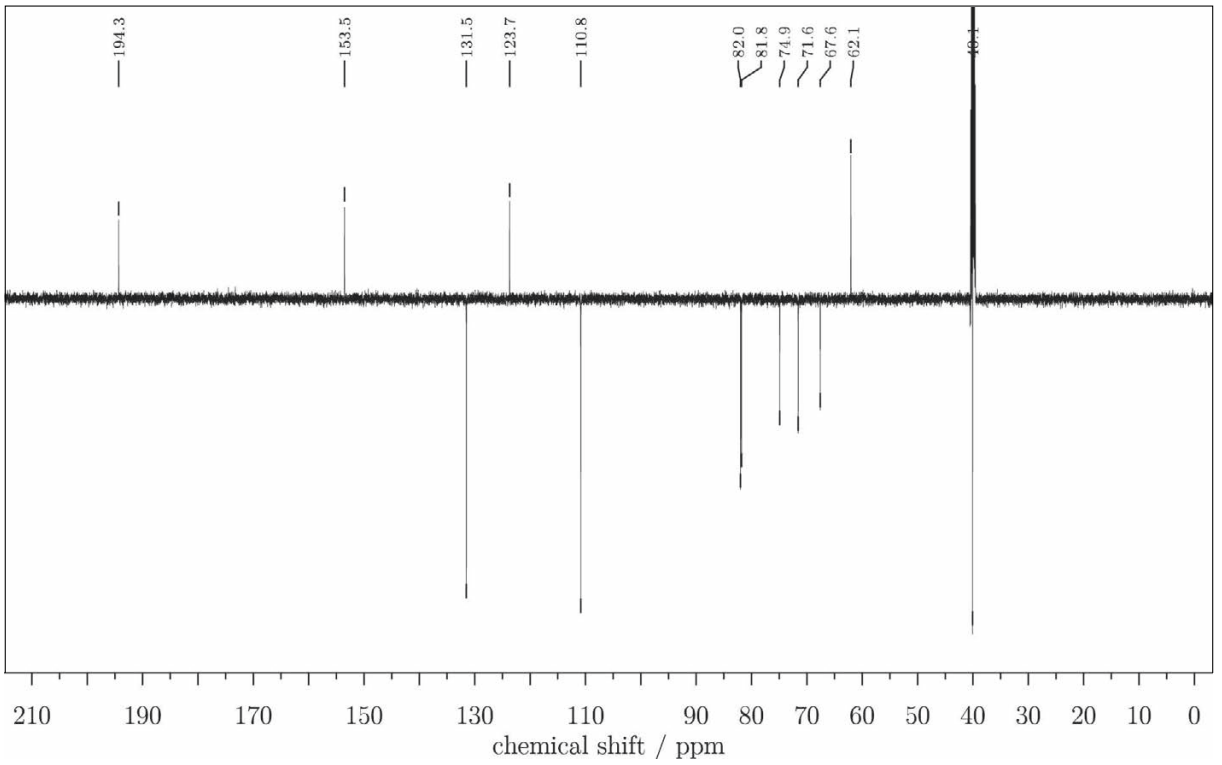


Figure 236: DEPTQ-NMR spectrum of **253** at 151 MHz in DMSO-d_6.

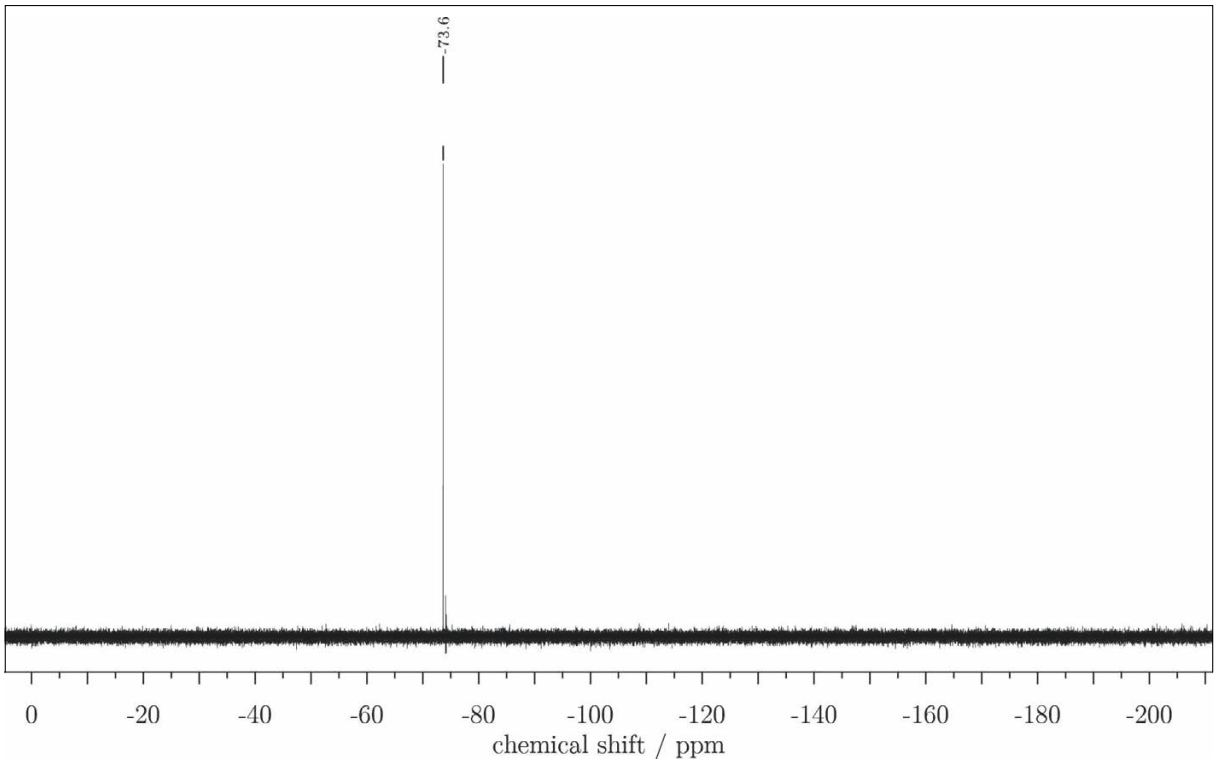


Figure 237: ^{19}F-NMR Spectrum of **253** at 565 MHz in DMSO-d_6.

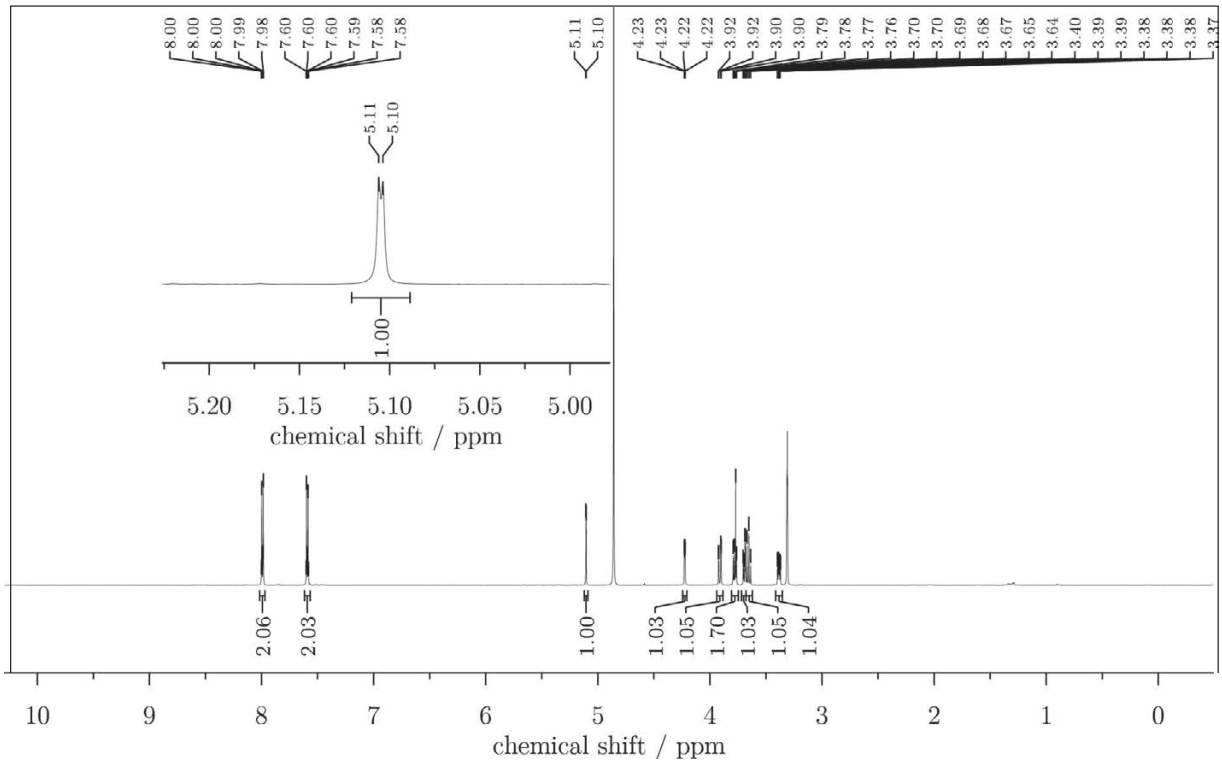


Figure 238: ^{1}H-NMR spectrum of **254** at 600 MHz in methanol-d_4.

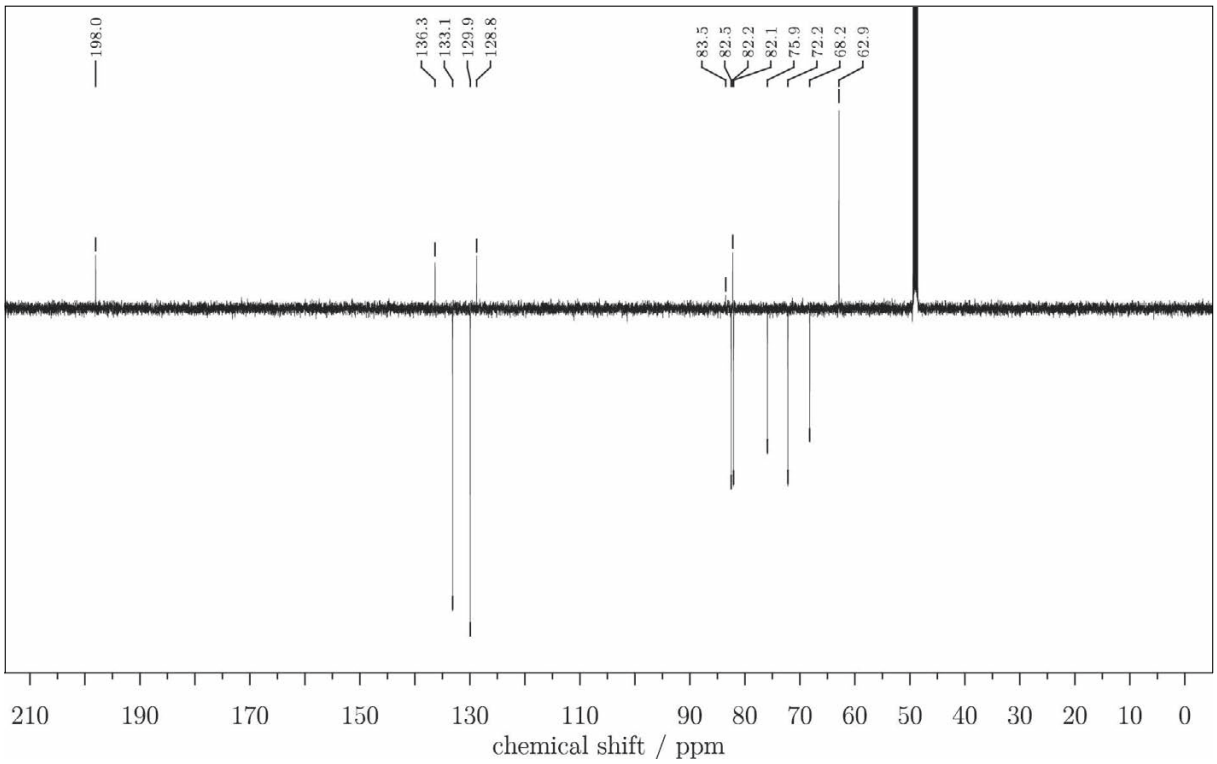


Figure 239: DEPTQ-NMR spectrum of **254** at 151 MHz in methanol-d_4.

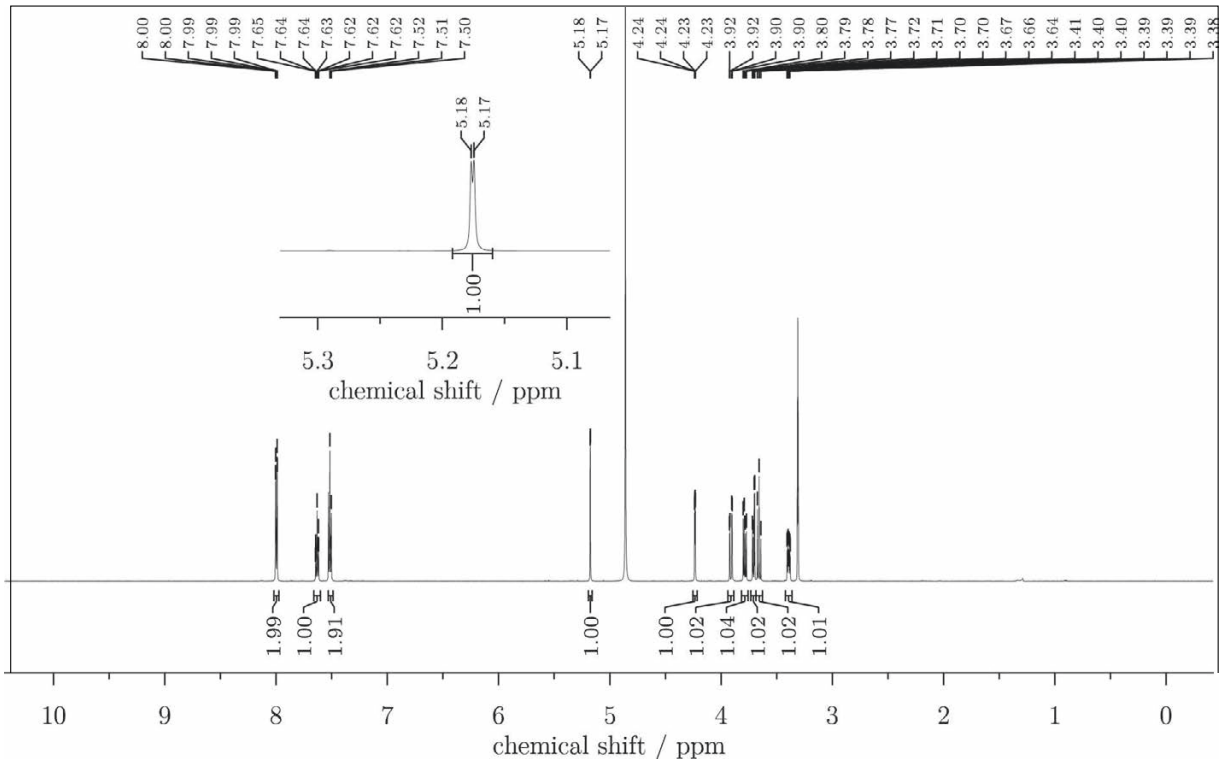


Figure 240: ^{1}H-NMR spectrum of **255** at 600 MHz in methanol-d_4.

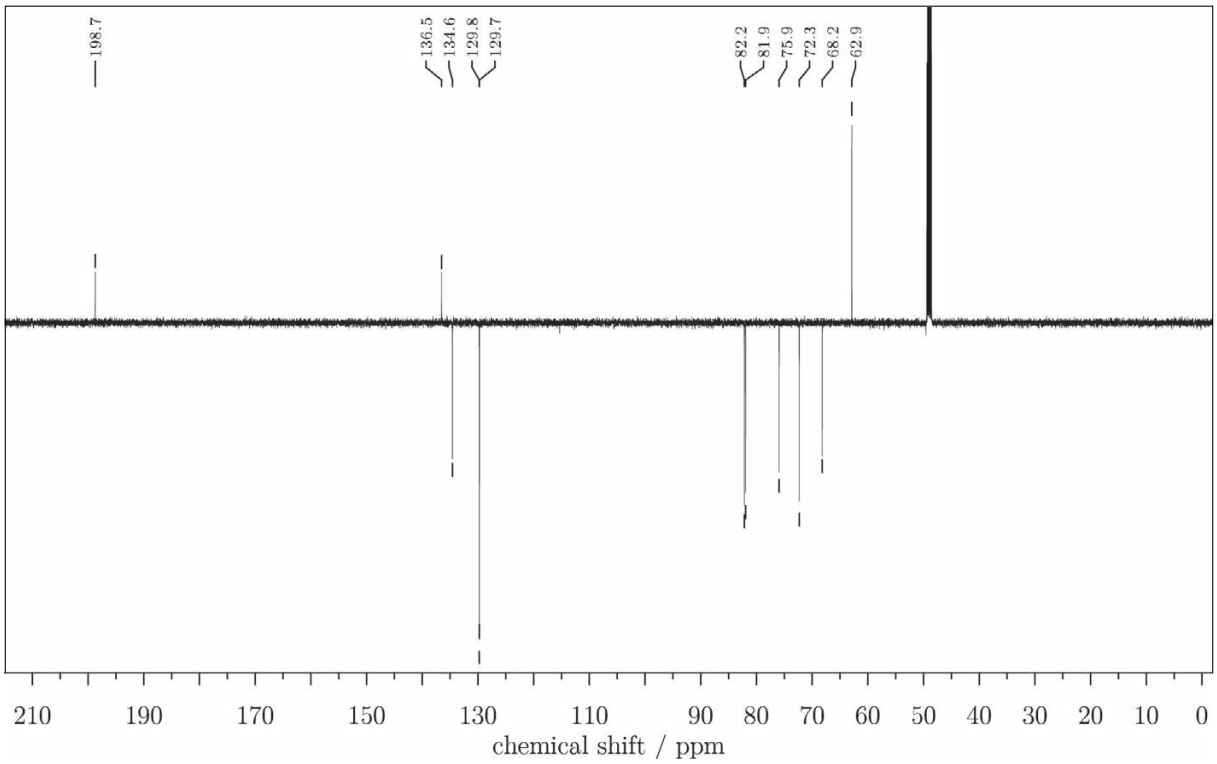


Figure 241: DEPTQ-NMR spectrum of **255** at 151 MHz in methanol-d_4.

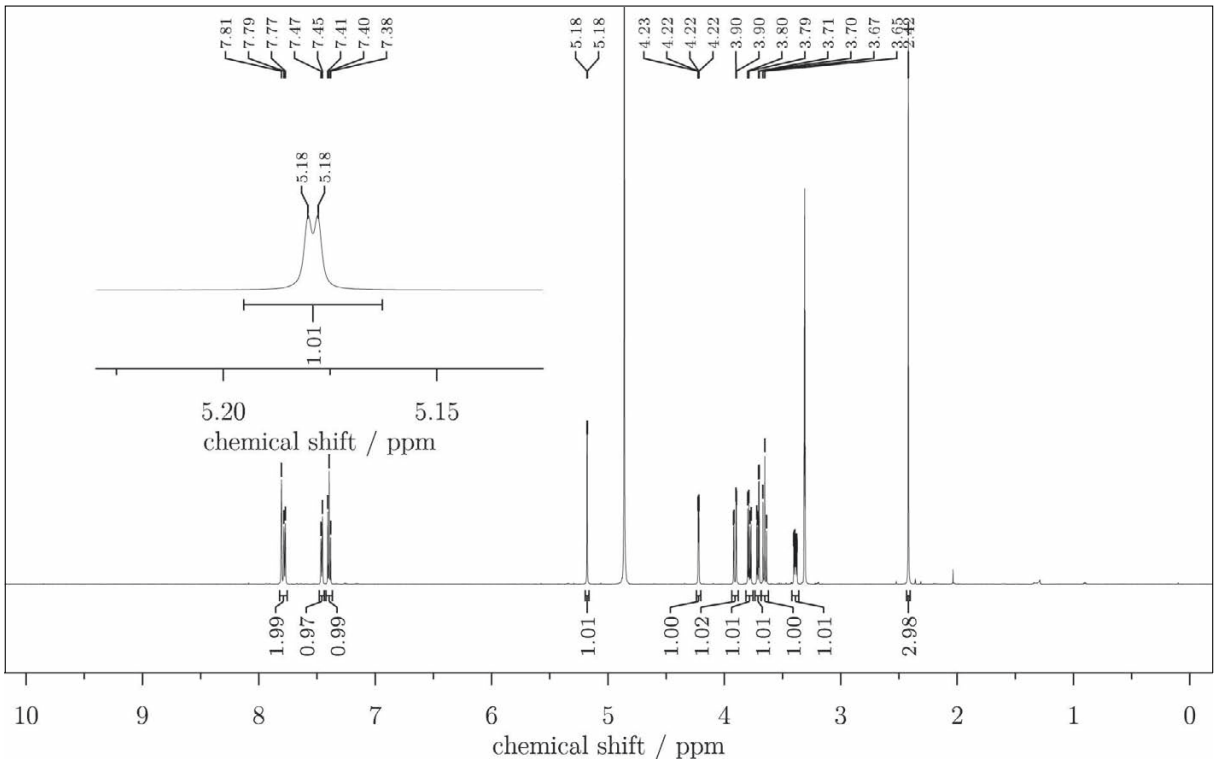


Figure 242: ^{1}H-NMR spectrum of **256** at 600 MHz in methanol-d_4.

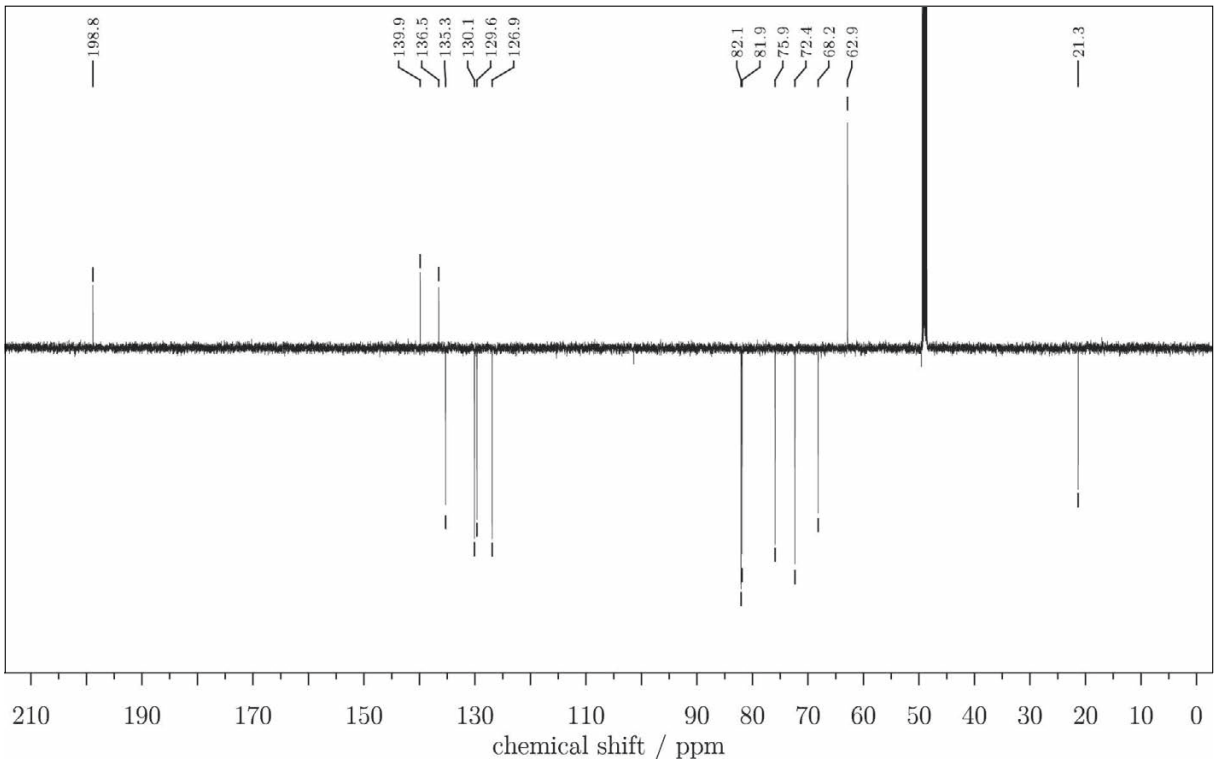


Figure 243: DEPTQ-NMR spectrum of **256** at 151 MHz in methanol-d_4.

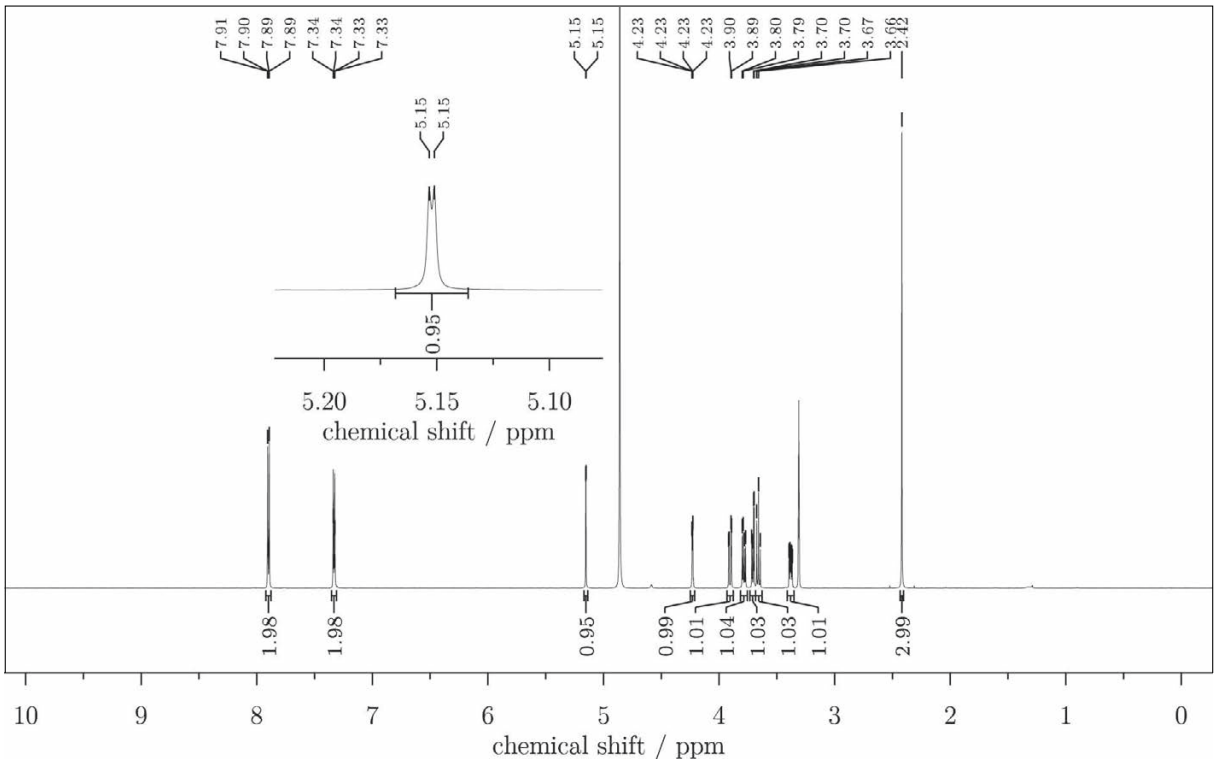


Figure 244: ^{1}H-NMR spectrum of **257** at 600 MHz in methanol-d_4.

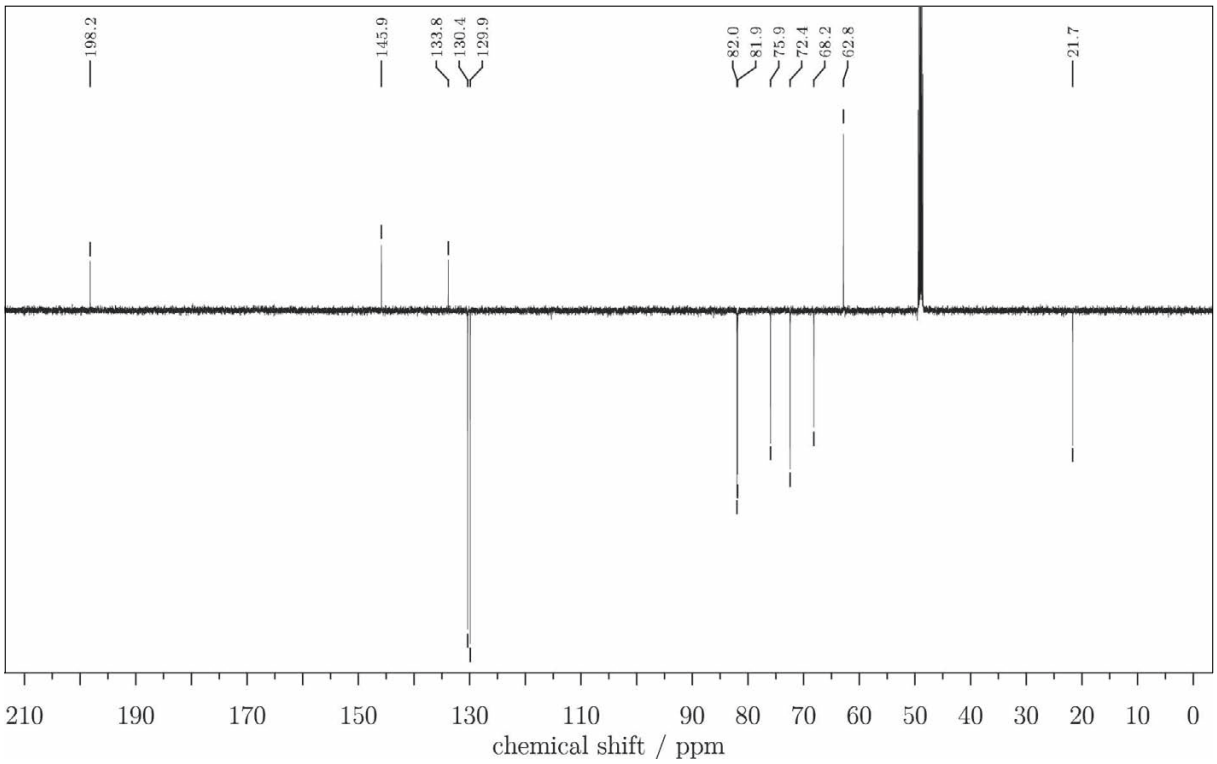


Figure 245: DEPTQ-NMR spectrum of **257** at 151 MHz in methanol-d_4.

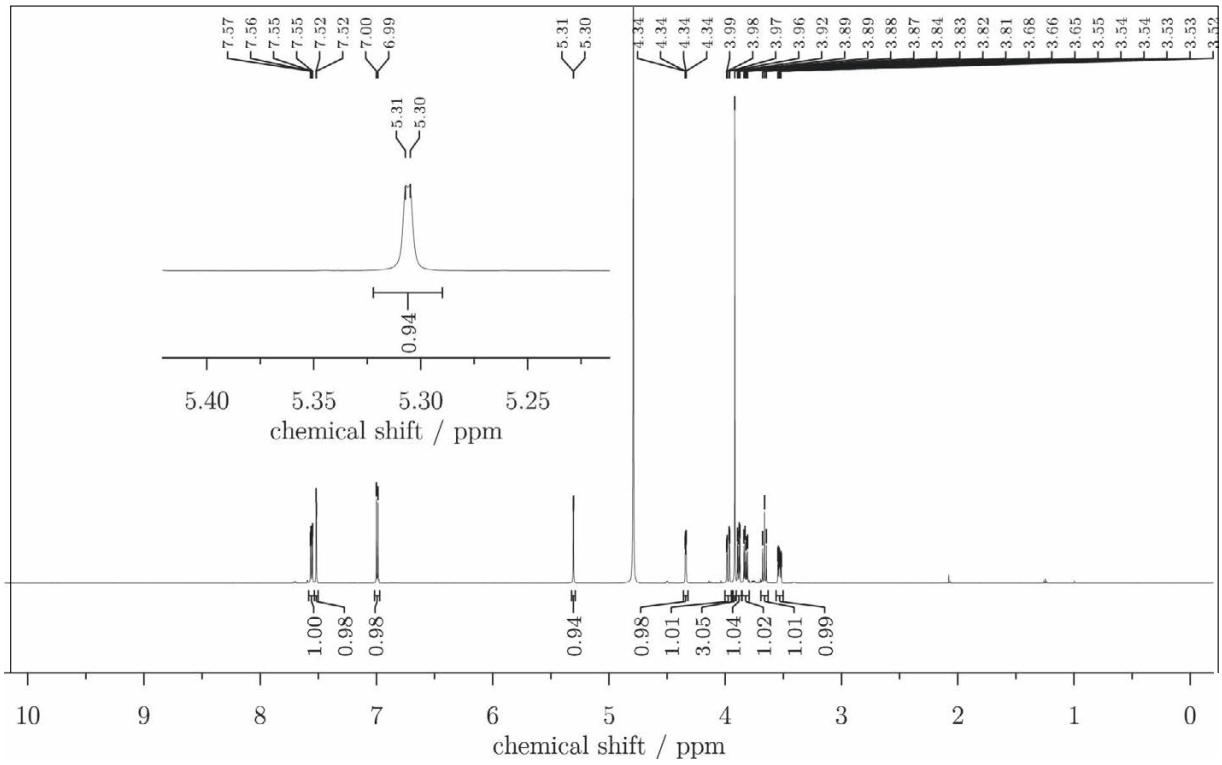


Figure 246: ^{1}H-NMR spectrum of **258** at 600 MHz in D_2O.

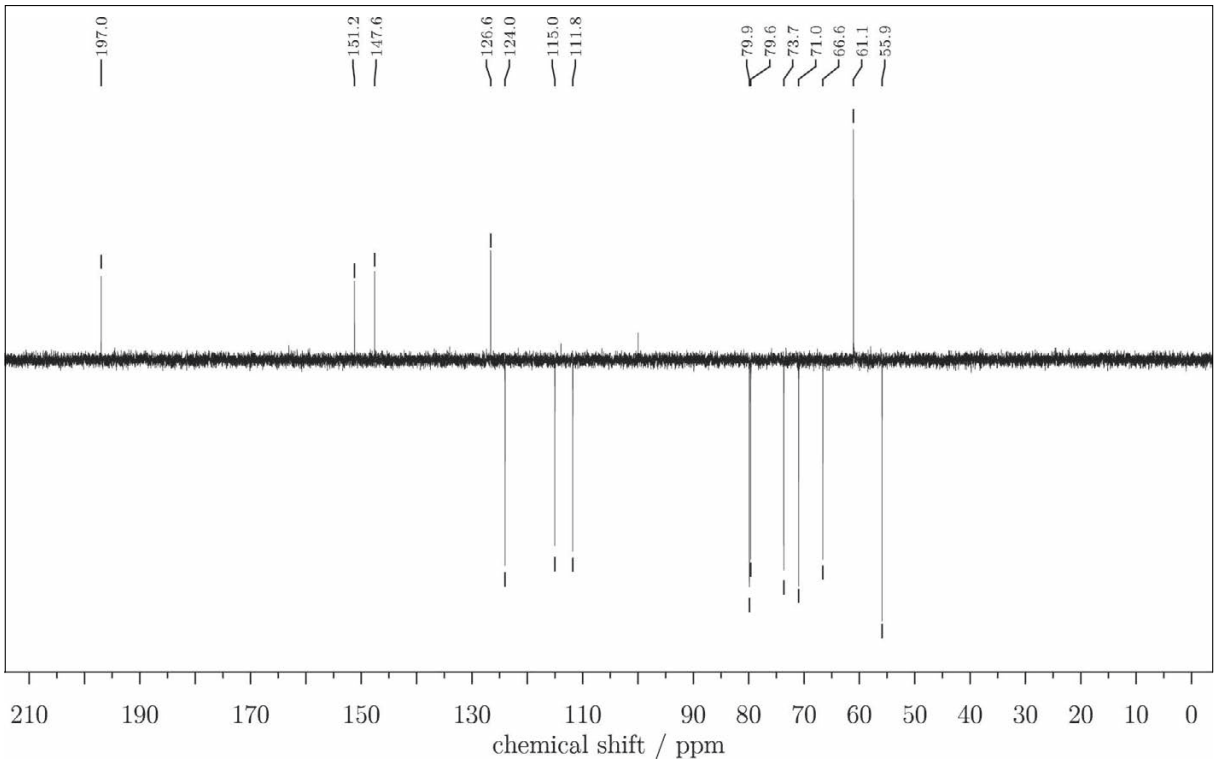


Figure 247: DEPTQ-NMR spectrum of **258** at 151 MHz in D_2O.

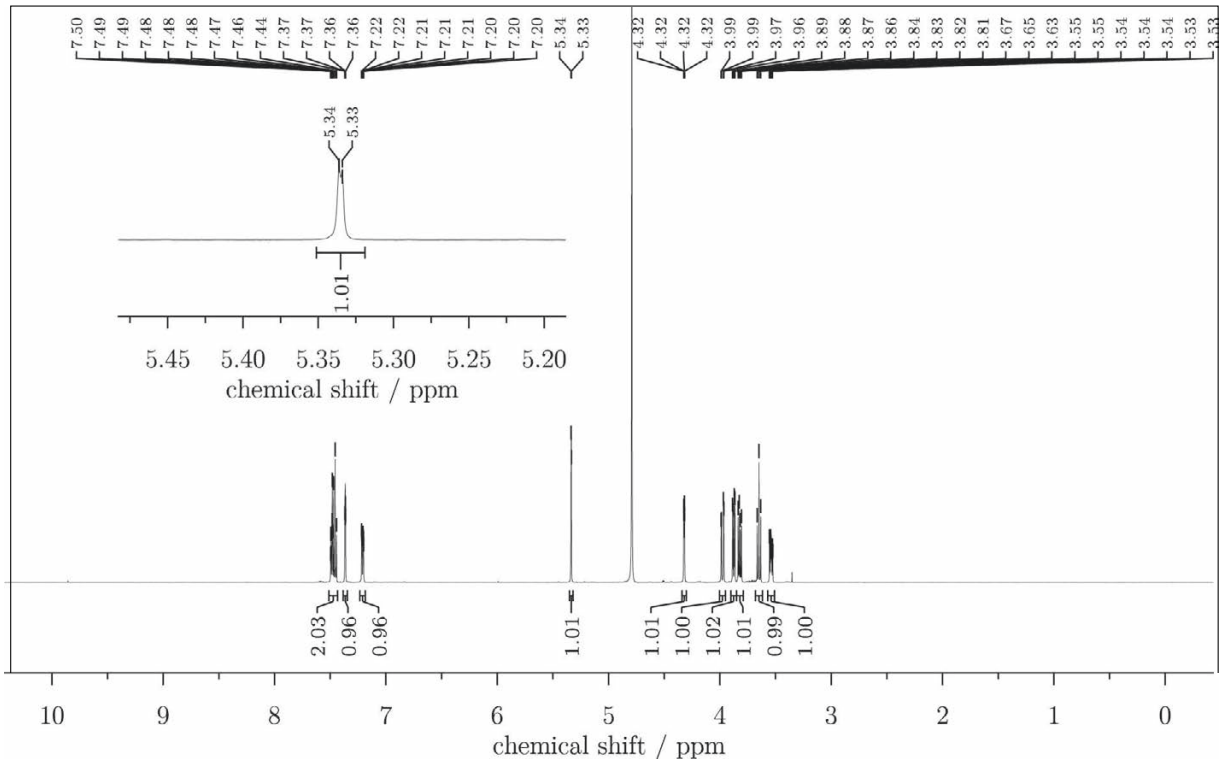


Figure 248: ^{1}H-NMR spectrum of **259** at 600 MHz in D_2O.

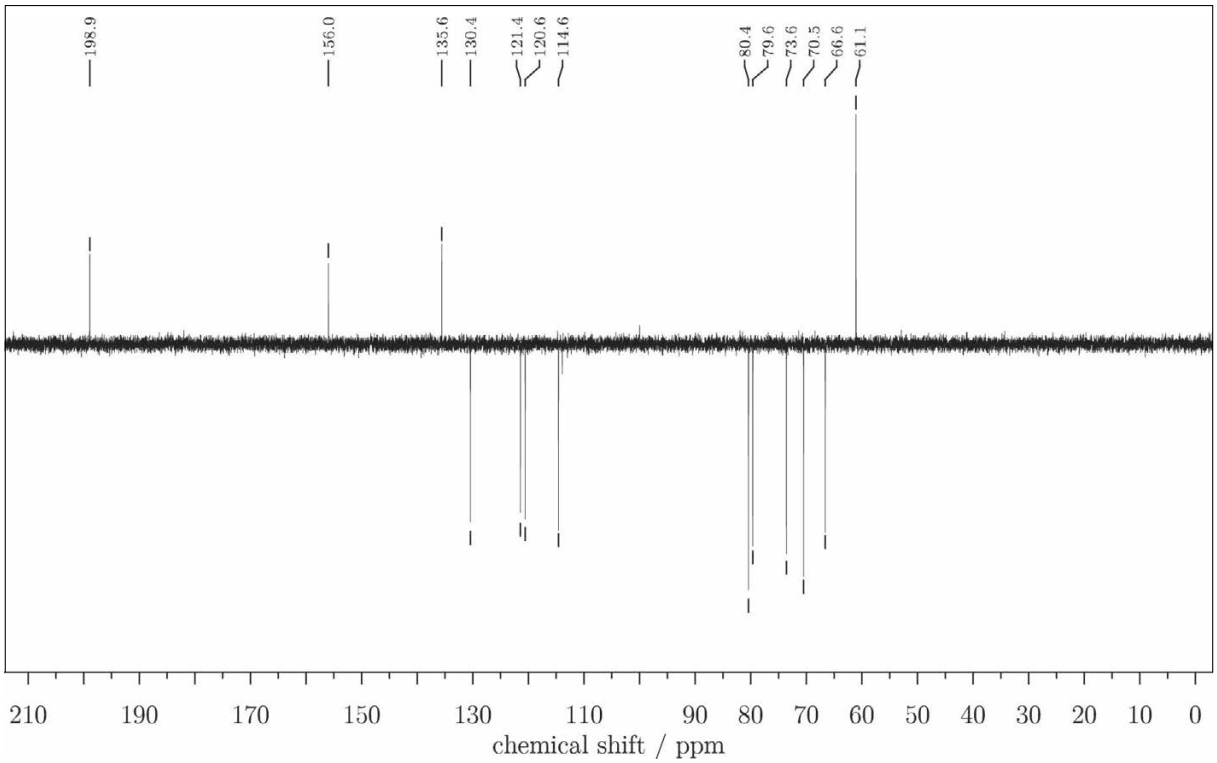


Figure 249: DEPTQ-NMR spectrum of **259** at 151 MHz in D_2O.

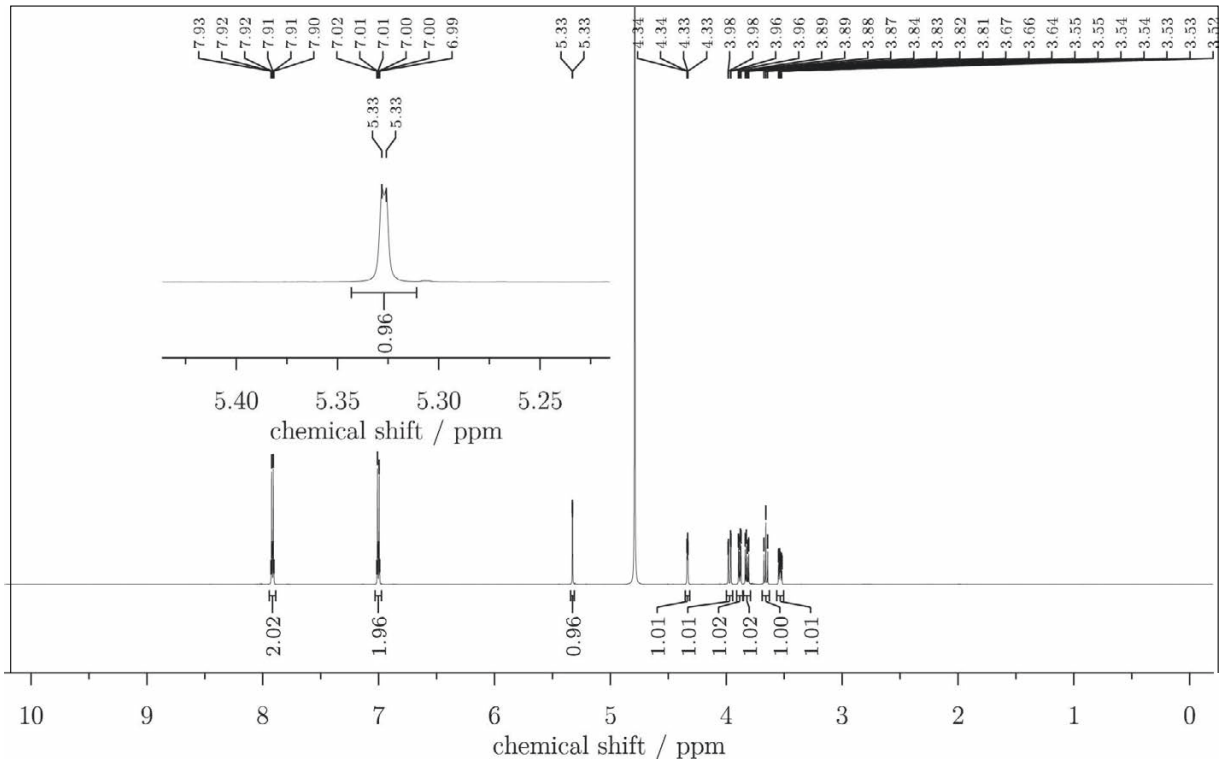


Figure 250: ^{1}H-NMR spectrum of **260** at 600 MHz in D_2O.

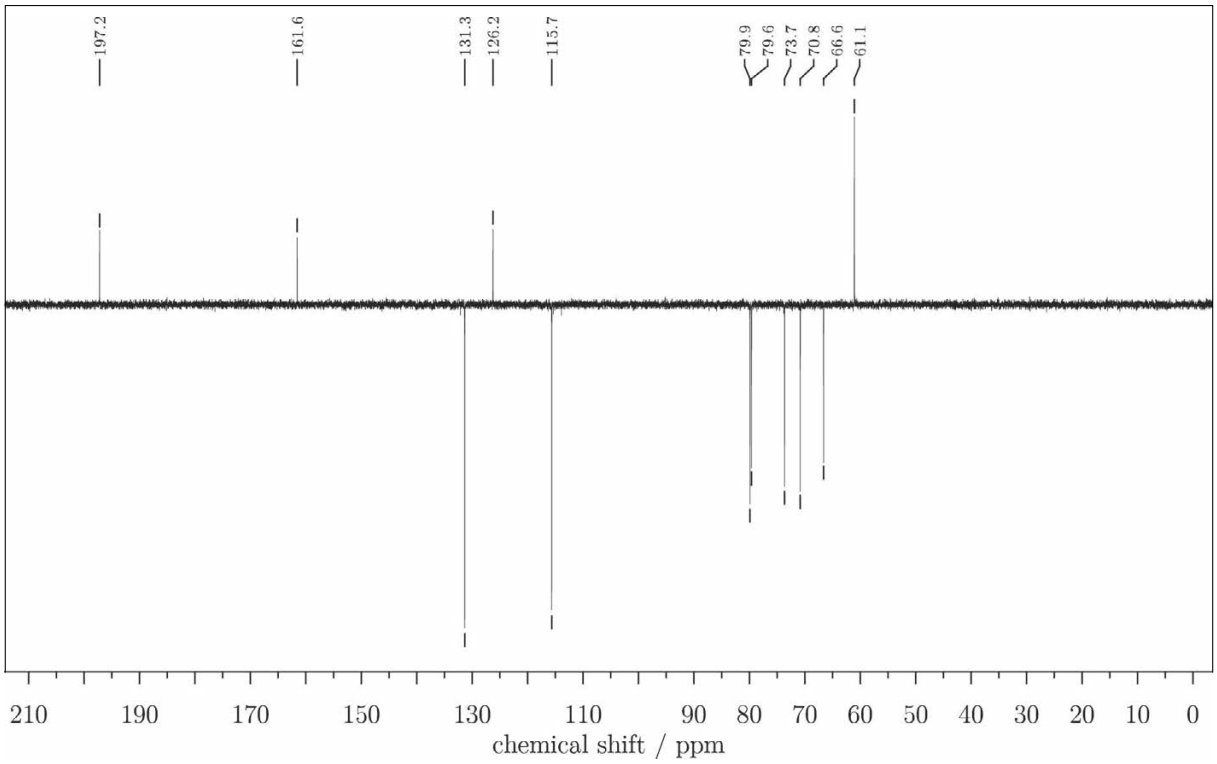


Figure 251: DEPTQ-NMR spectrum of **260** at 151 MHz in D_2O.

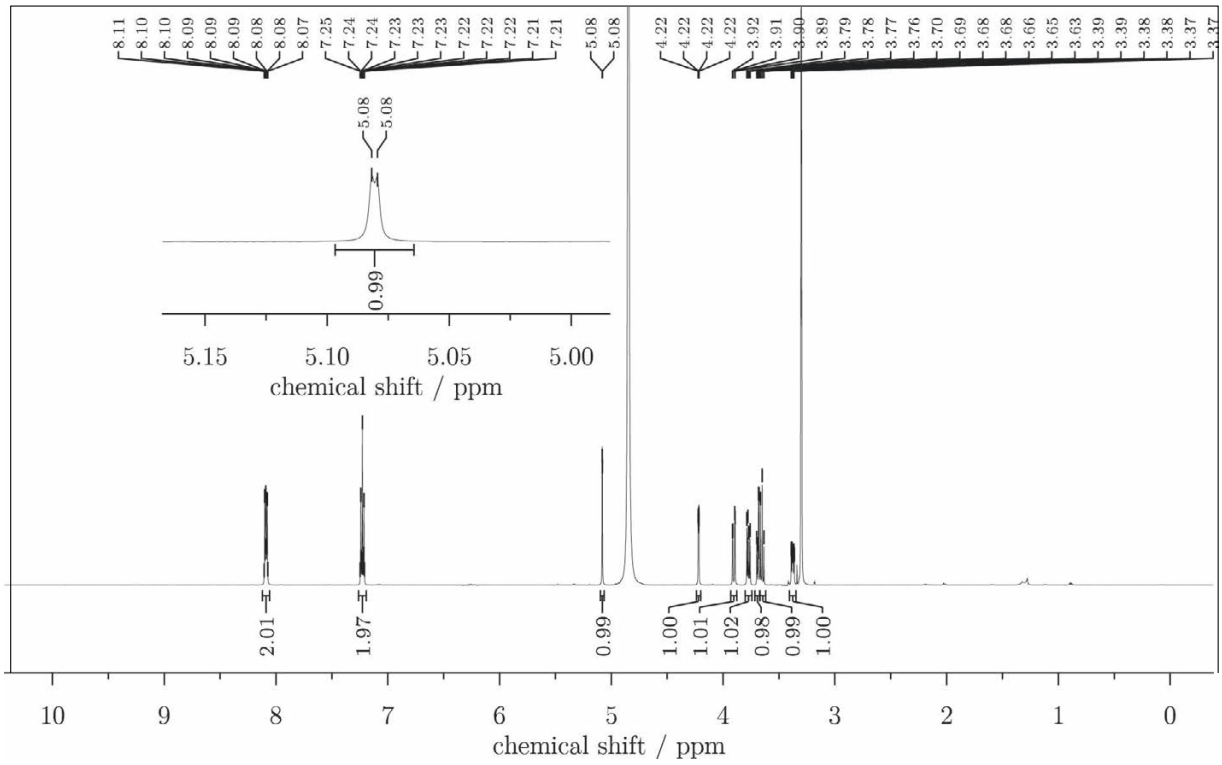


Figure 252: ^{1}H-NMR spectrum of **261** at 600 MHz in methanol-d_4.

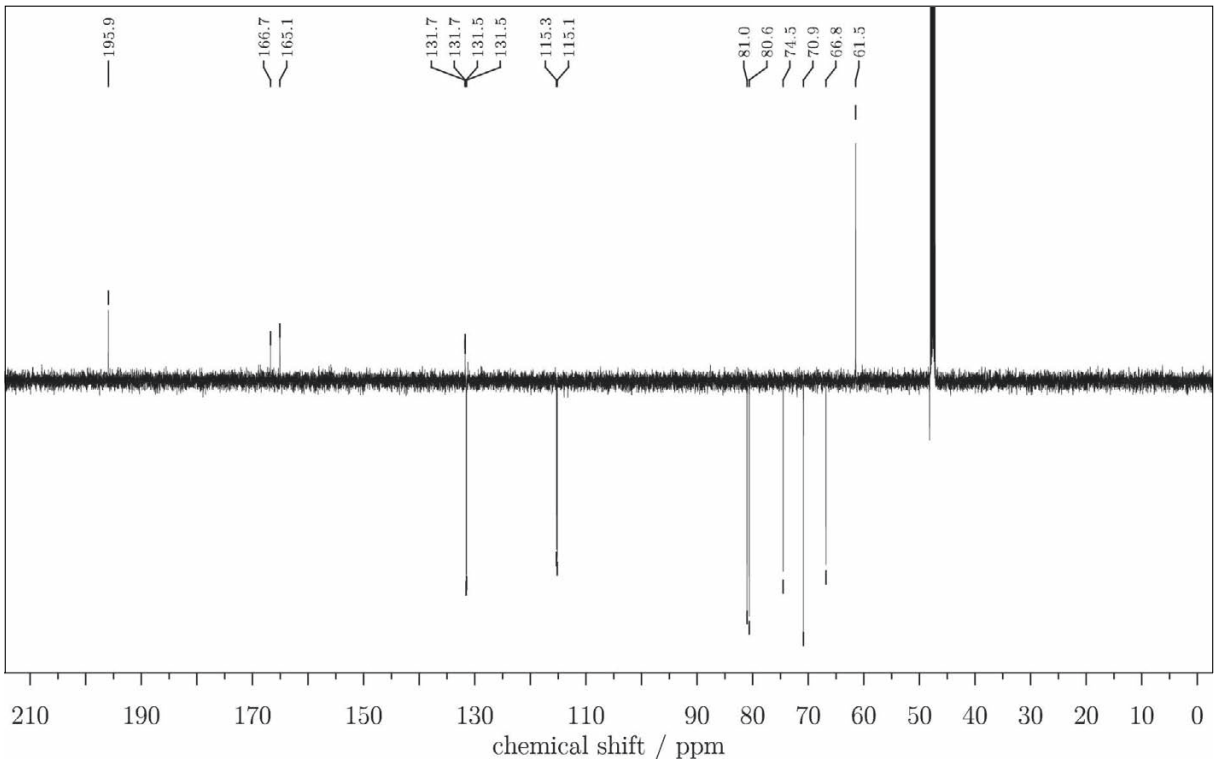


Figure 253: DEPTQ-NMR spectrum of **261** at 151 MHz in methanol-d_4.

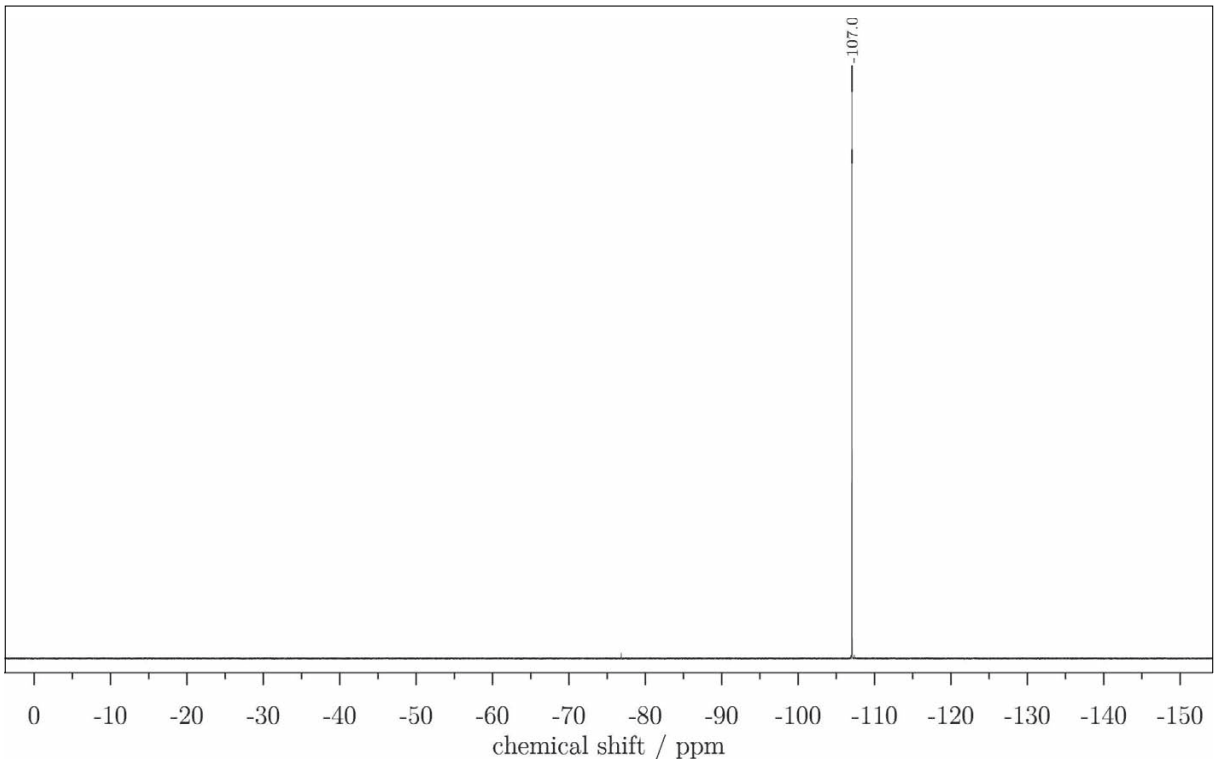


Figure 254: ^{19}F-NMR Spectrum of **261** at 565 MHz in methanol-d_4.

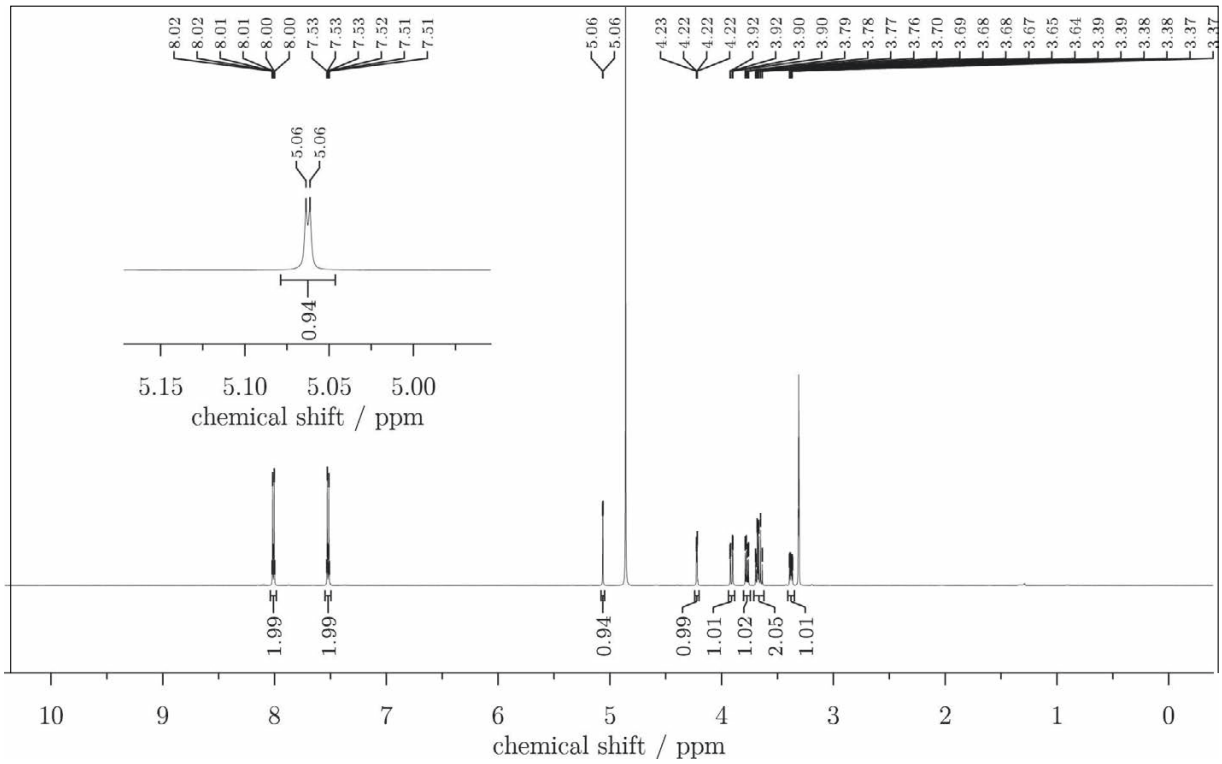


Figure 255: ^{1}H-NMR spectrum of **262** at 600 MHz in methanol-d_4.

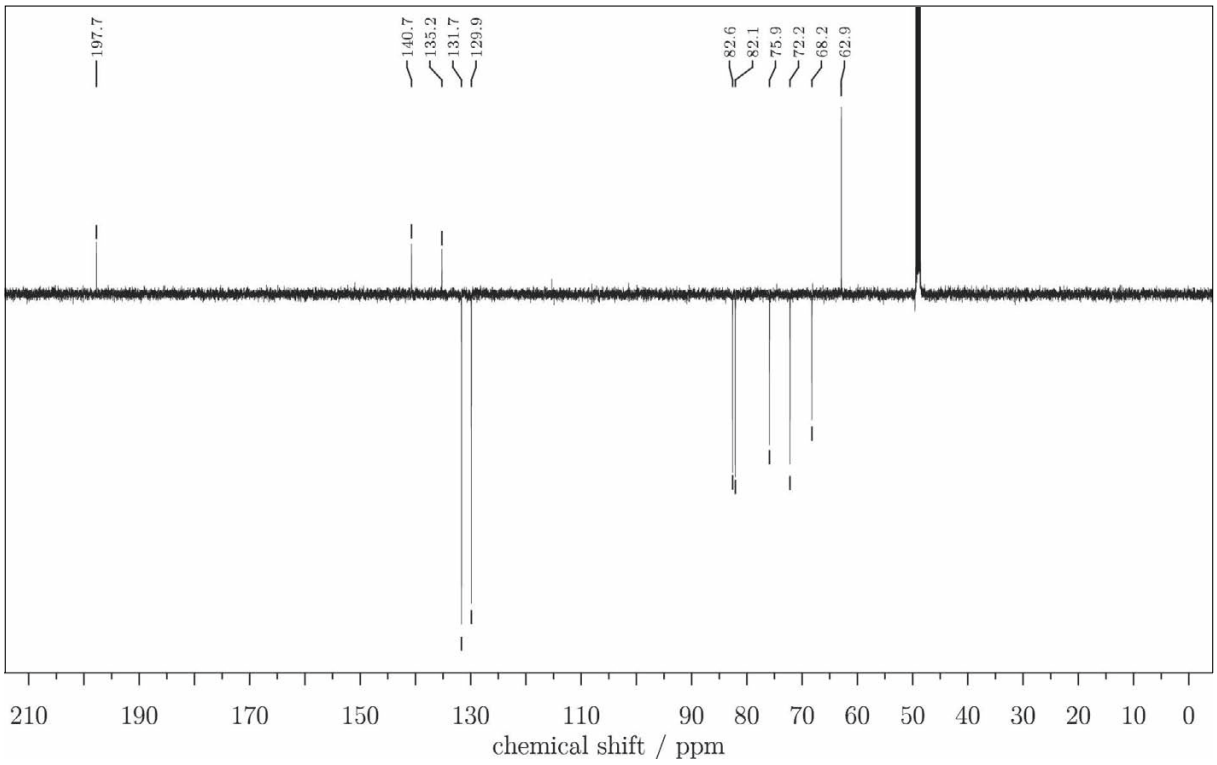


Figure 256: DEPTQ-NMR spectrum of **262** at 151 MHz in methanol-d_4.

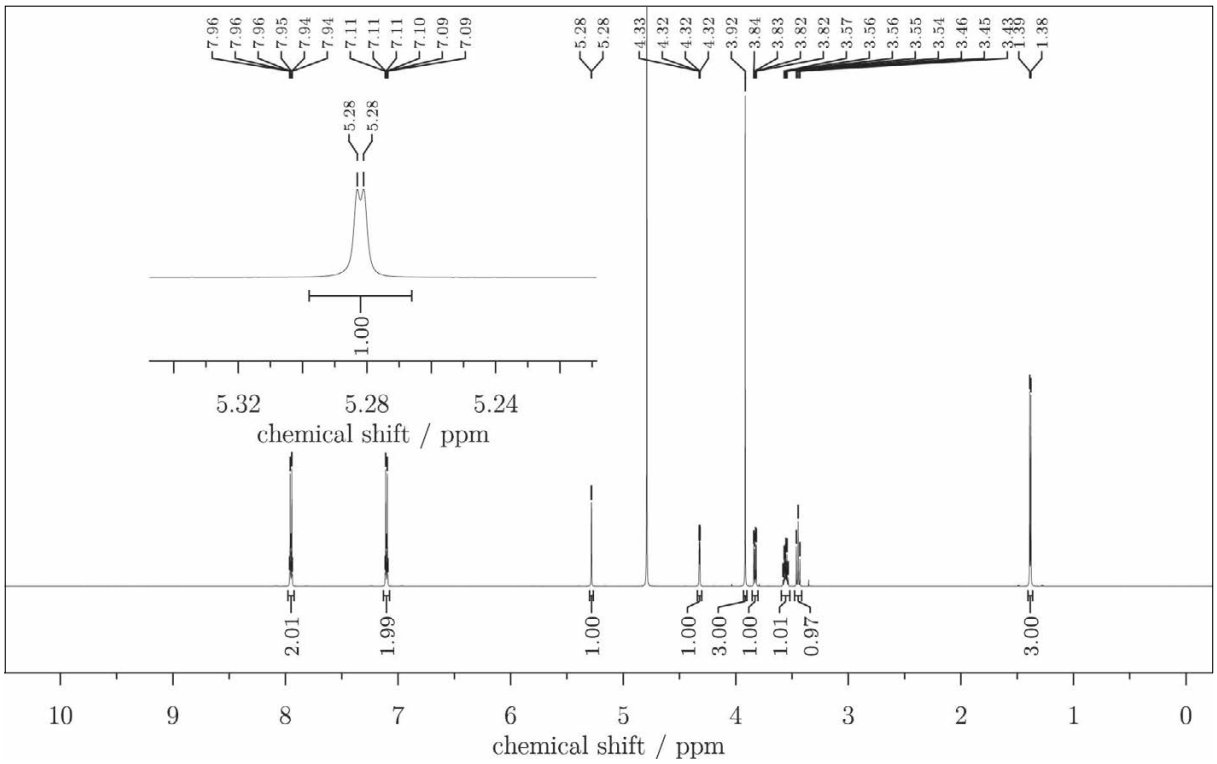


Figure 257: ^{1}H-NMR spectrum of **263** at 600 MHz in D_2O.

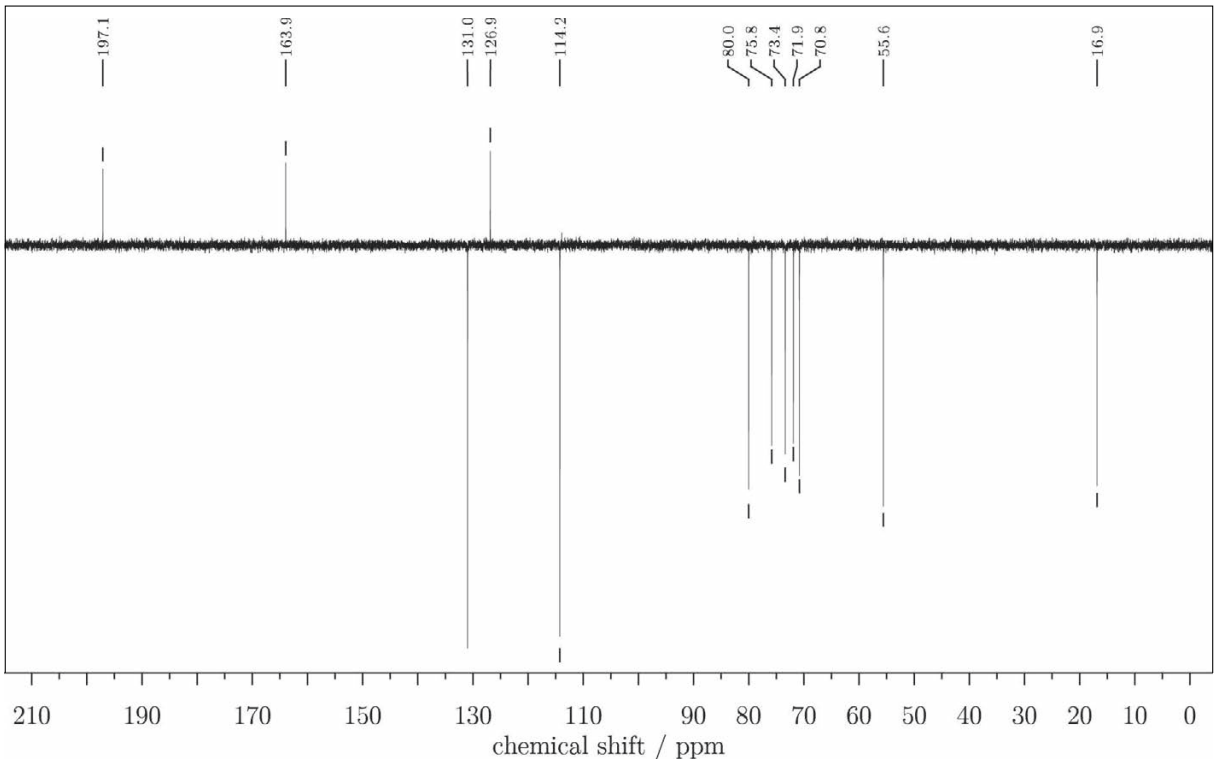


Figure 258: DEPTQ-NMR spectrum of **263** at 151 MHz in D_2O.

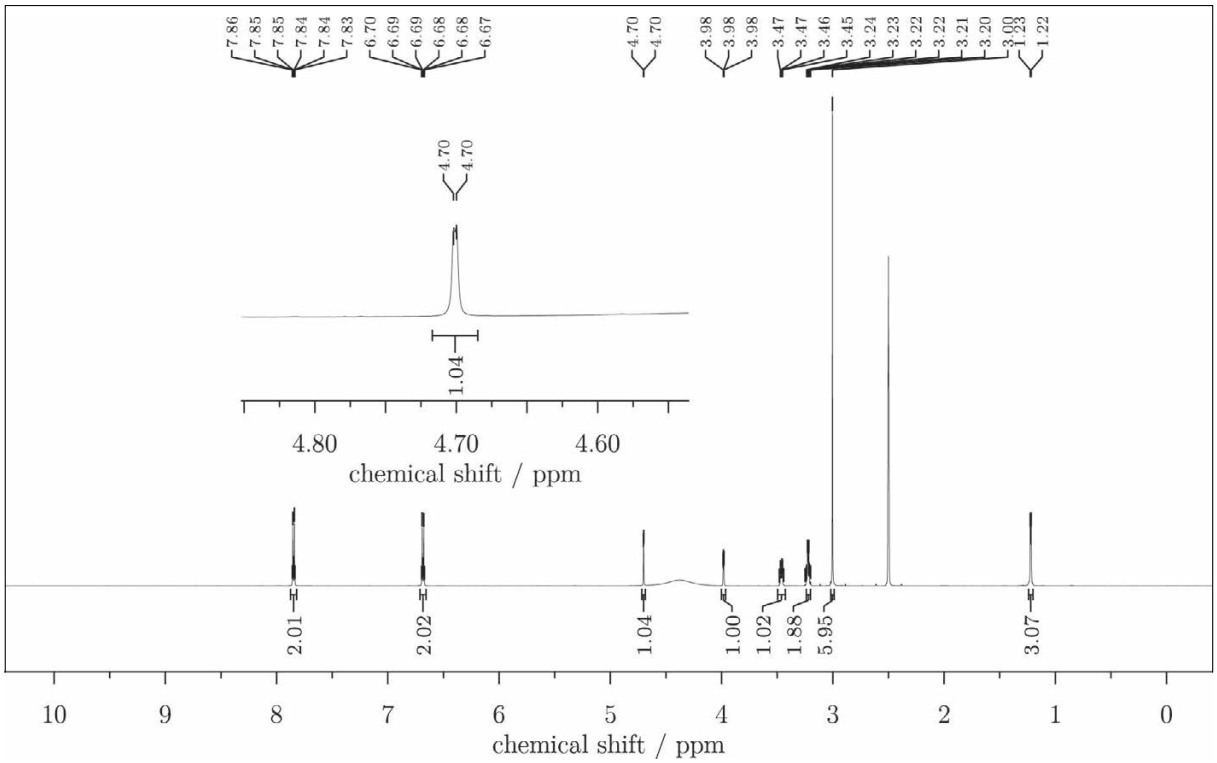


Figure 259: [1]H-NMR spectrum of **264** at 600 MHz in DMSO-d_6.

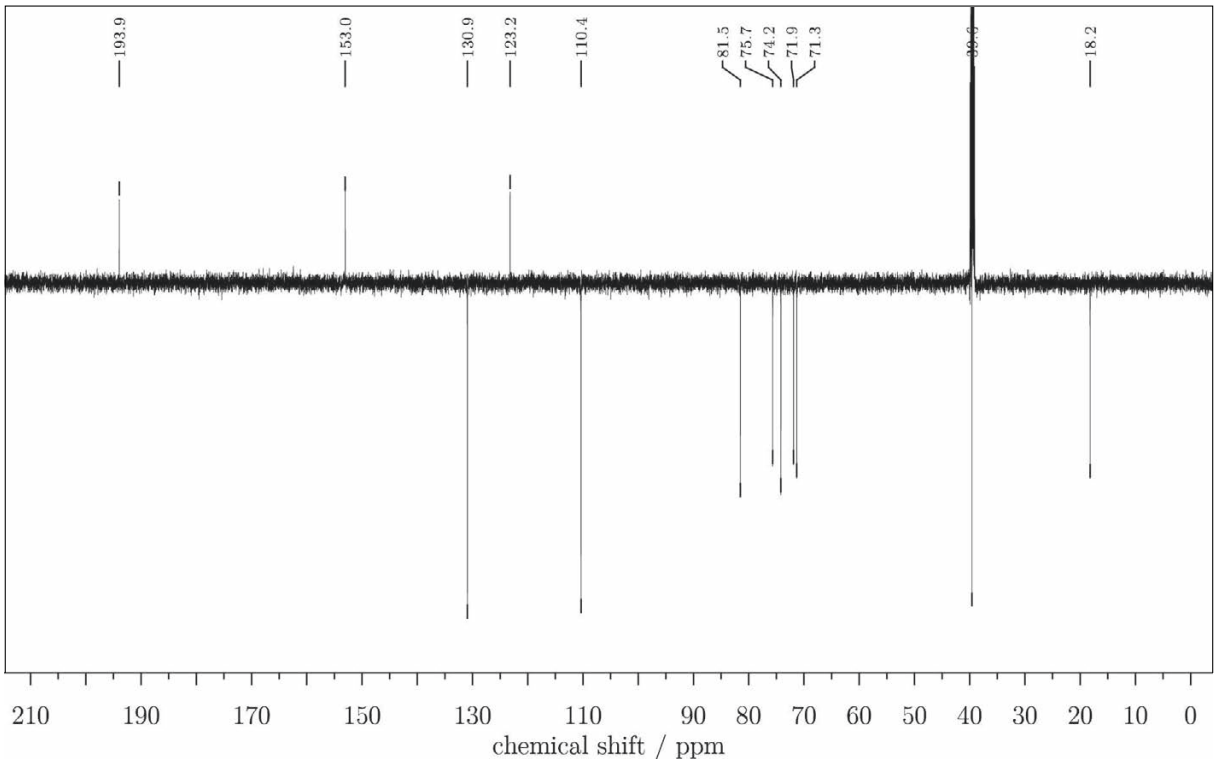


Figure 260: DEPTQ-NMR spectrum of **264** at 151 MHz in DMSO-d_6.

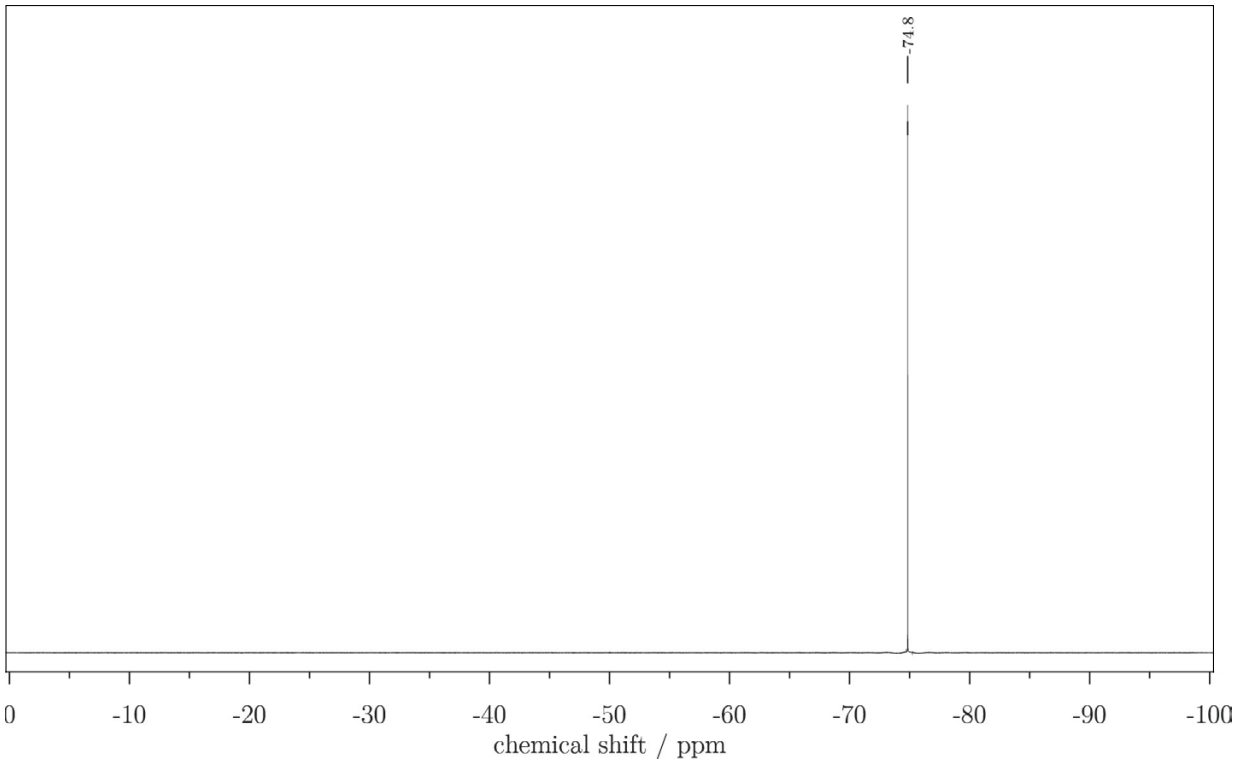


Figure 261: ^{19}F-NMR Spectrum of **264** at 565 MHz in DMSO-d_6.

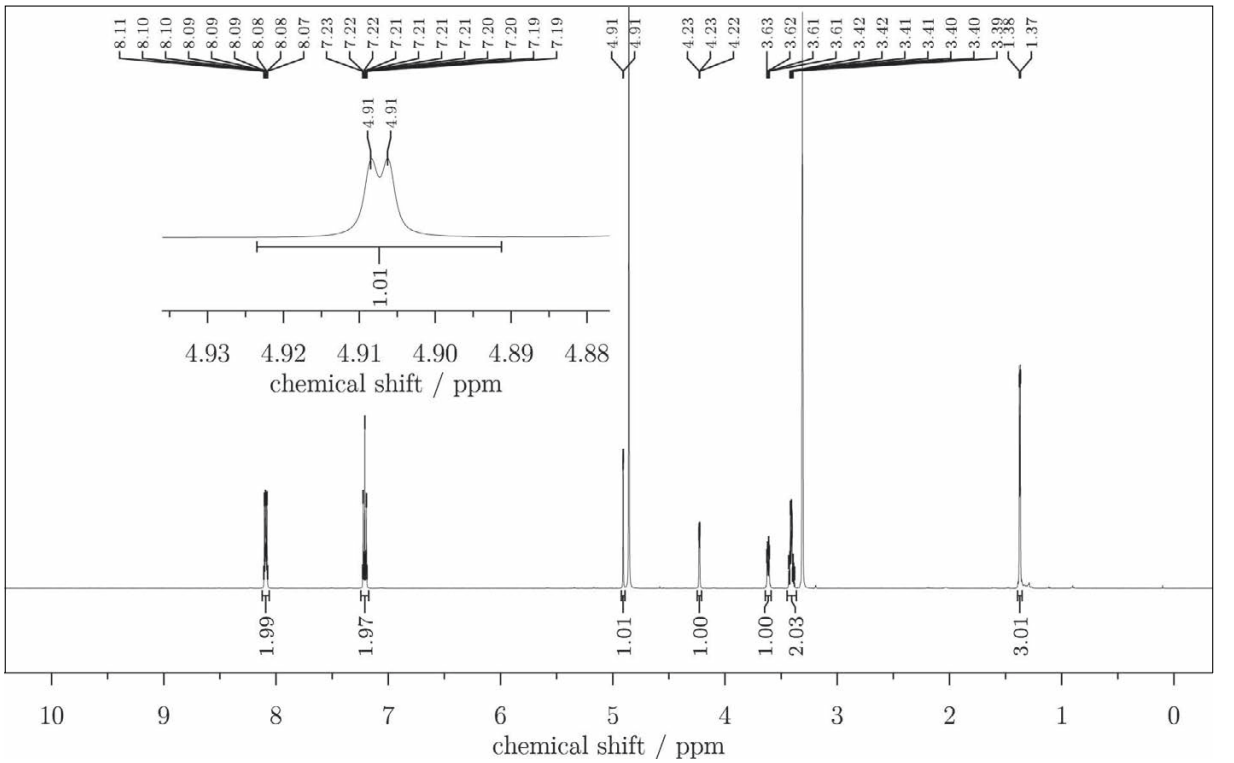


Figure 262: ^{1}H-NMR spectrum of **265** at 600 MHz in methanol-d_4.

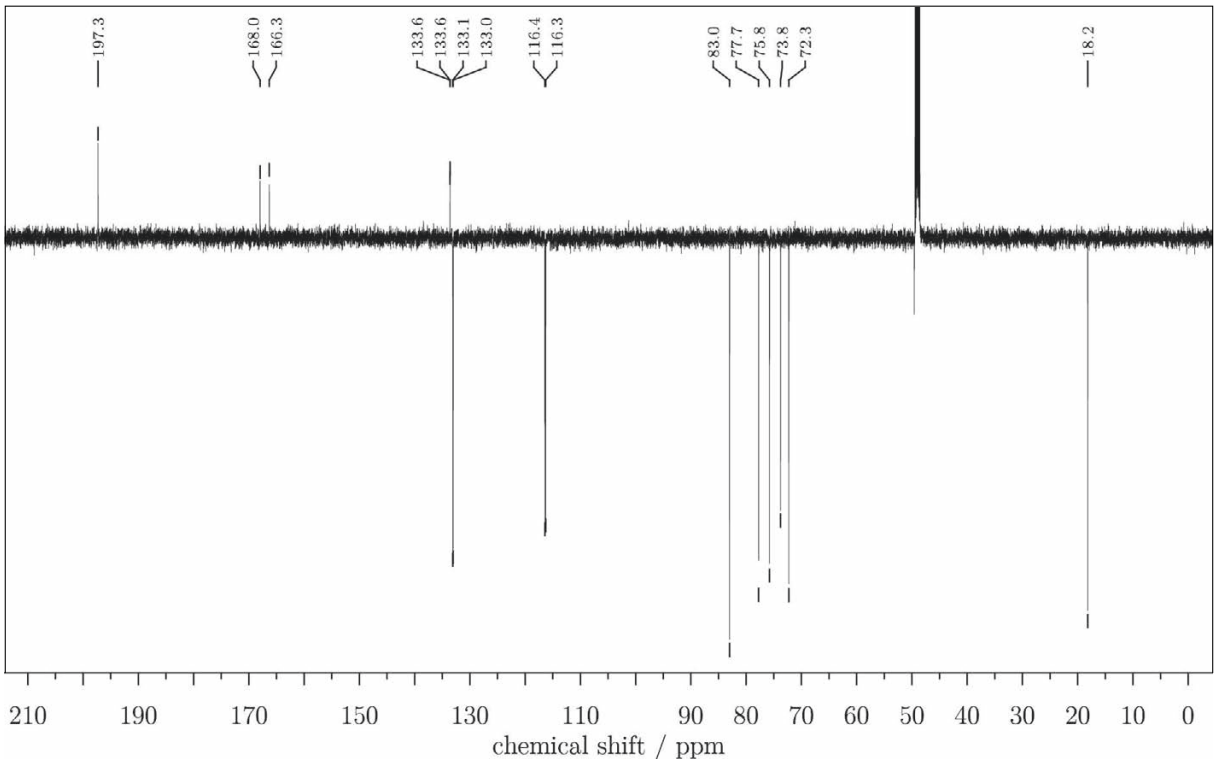


Figure 263: DEPTQ-NMR spectrum of **265** at 151 MHz in methanol-d_4.

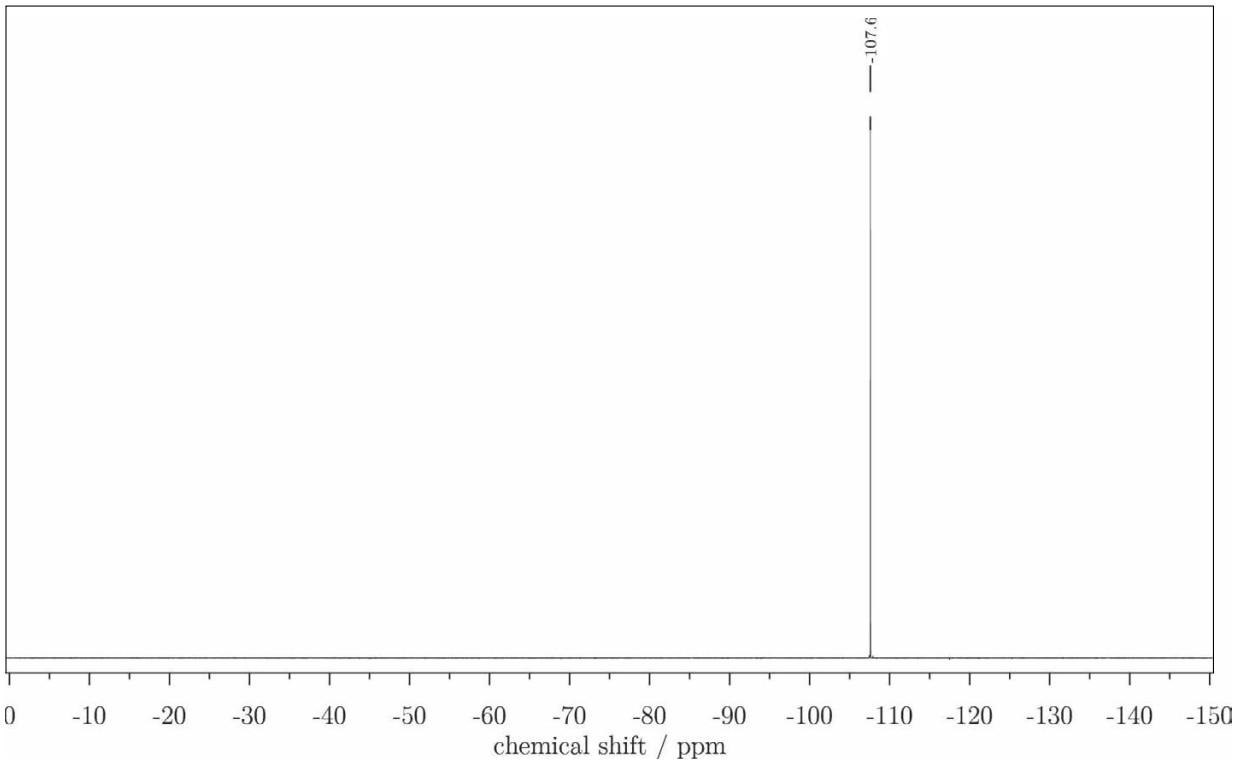


Figure 264: ^{19}F-NMR Spectrum of **265** at 565 MHz in methanol-d_4.

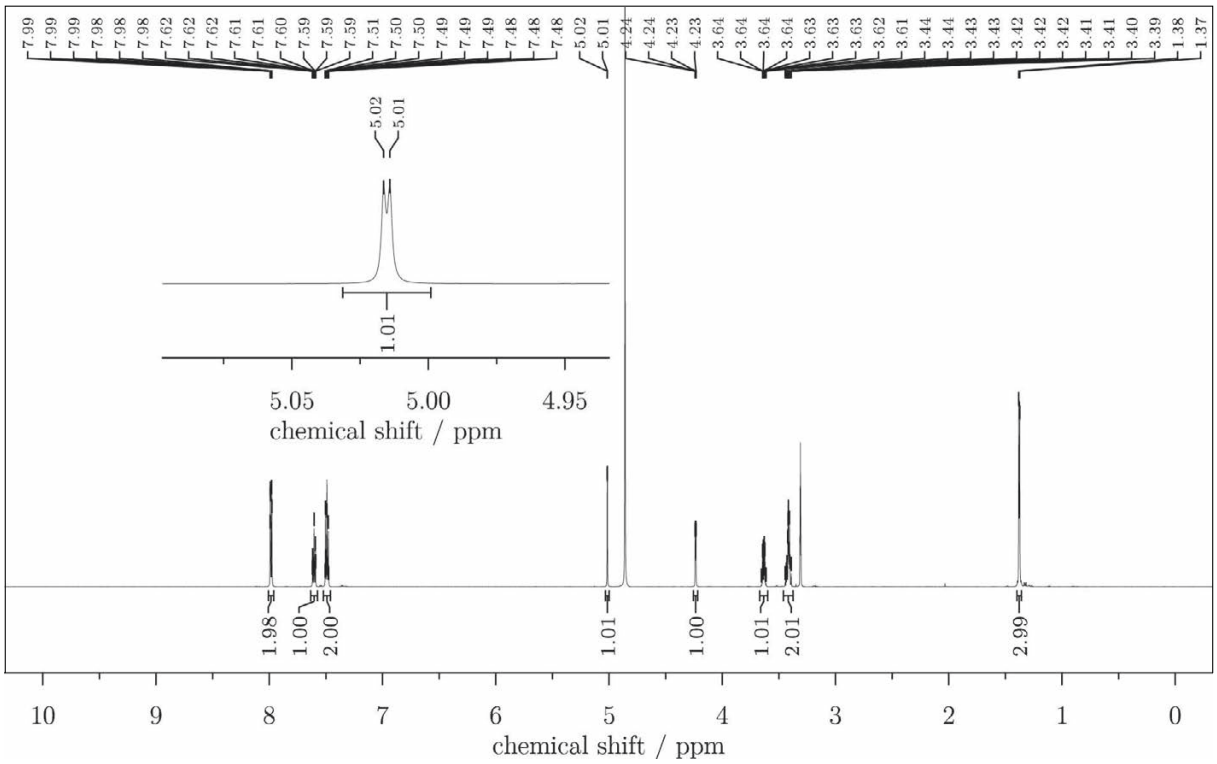


Figure 265: ^{1}H-NMR spectrum of **266** at 600 MHz in methanol-d_4.

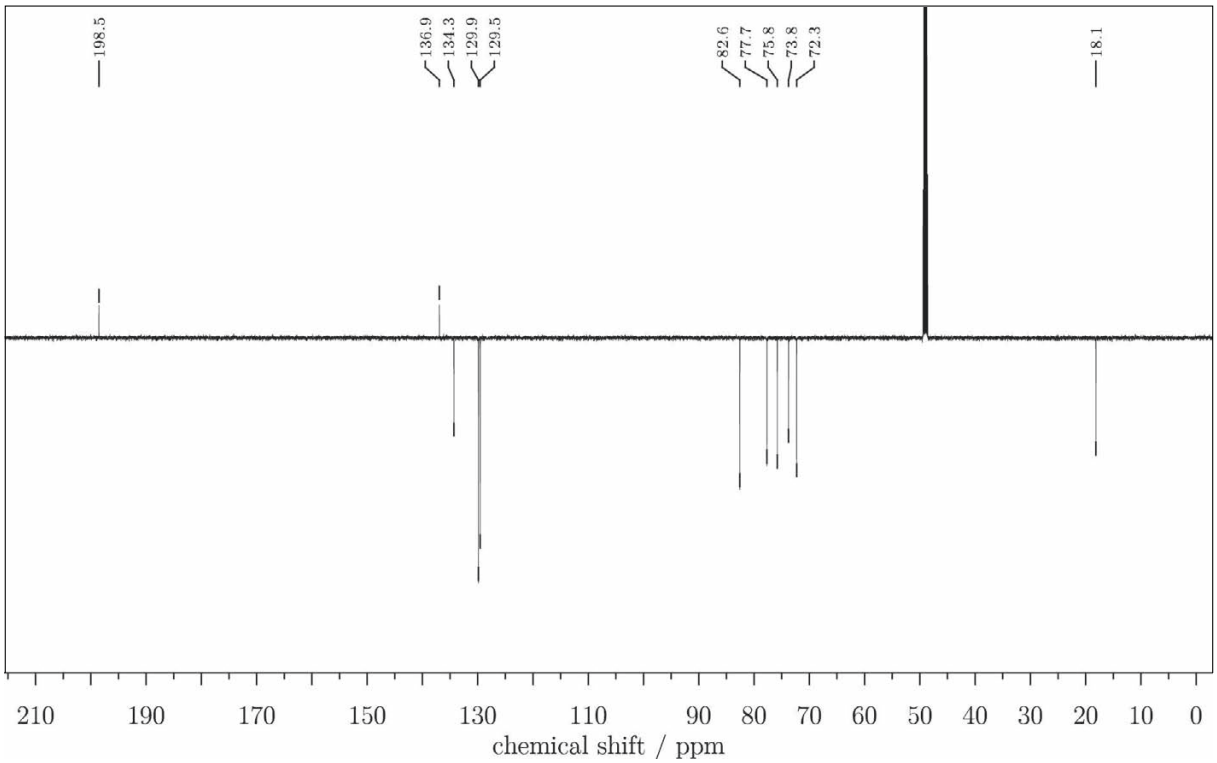


Figure 266: DEPTQ-NMR spectrum of **266** at 151 MHz in methanol-d_4.

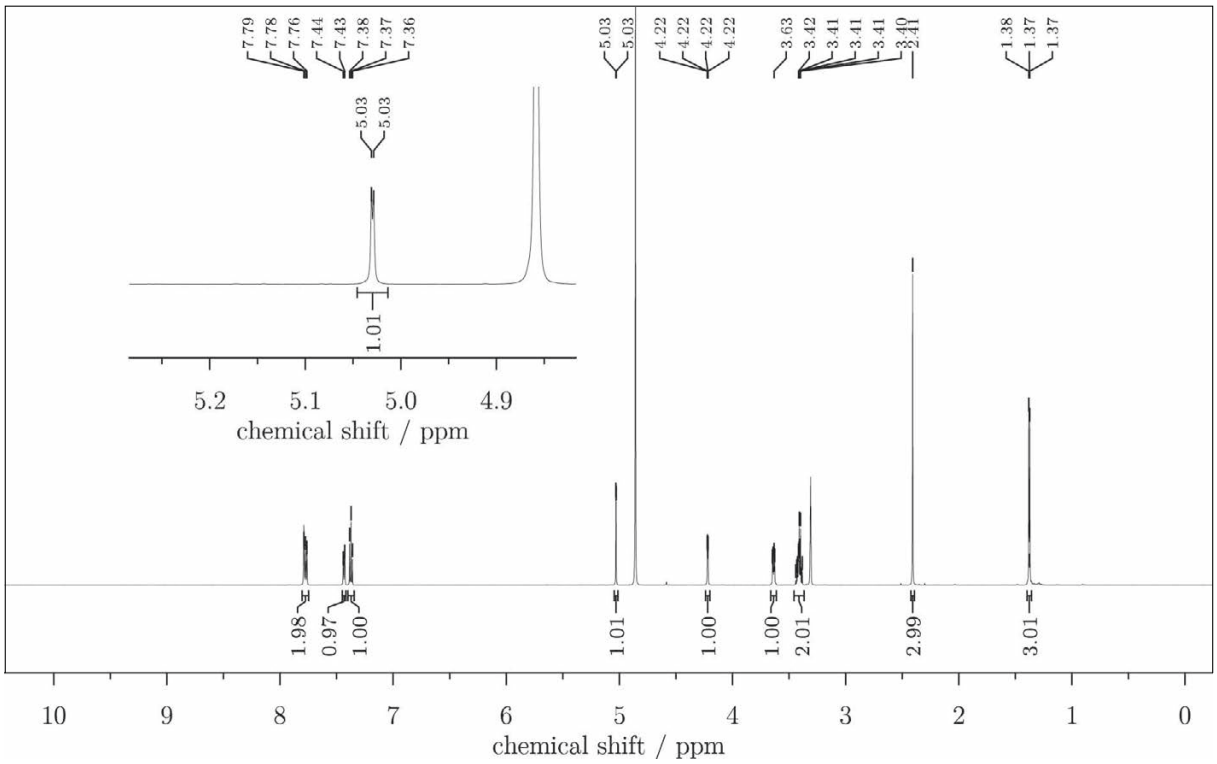


Figure 267: ^{1}H-NMR spectrum of **267** at 600 MHz in methanol-d_4.

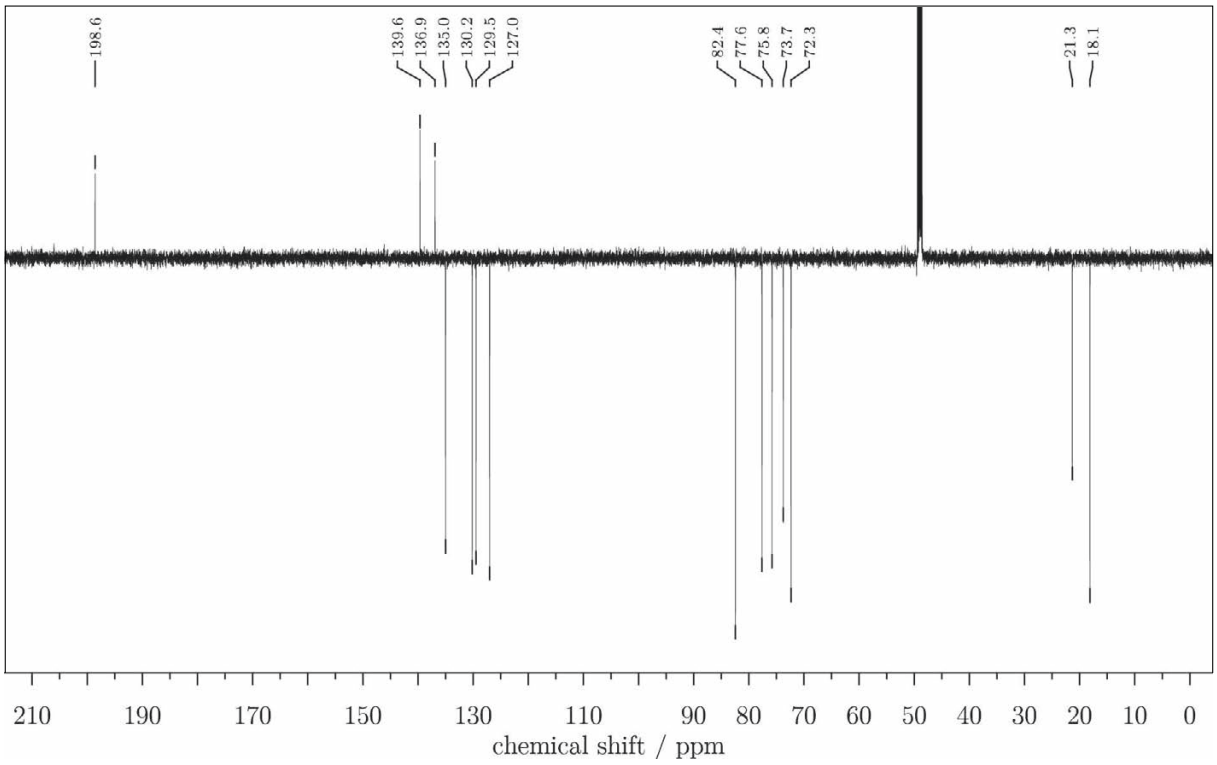


Figure 268: DEPTQ-NMR spectrum of **267** at 151 MHz in methanol-d_4.

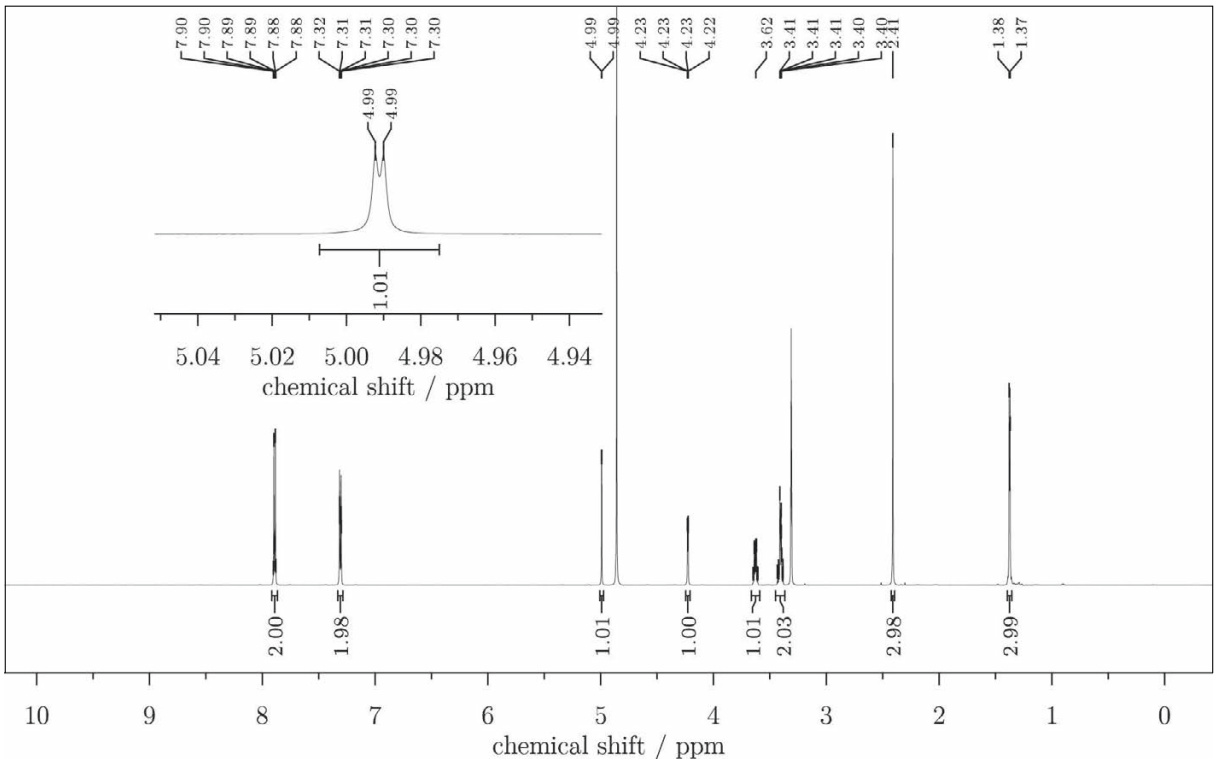


Figure 269: ^{1}H-NMR spectrum of **268** at 600 MHz in methanol-d_4.

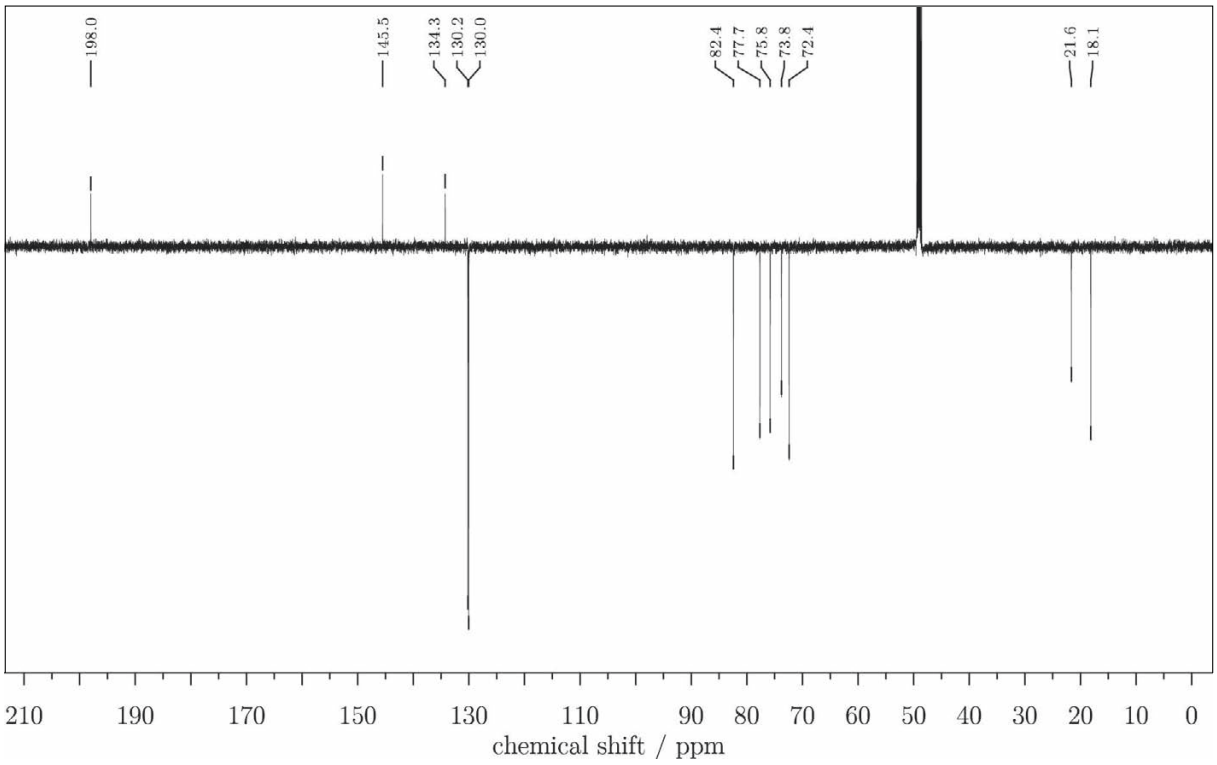


Figure 270: DEPTQ-NMR spectrum of **268** at 151 MHz in methanol-d_4.

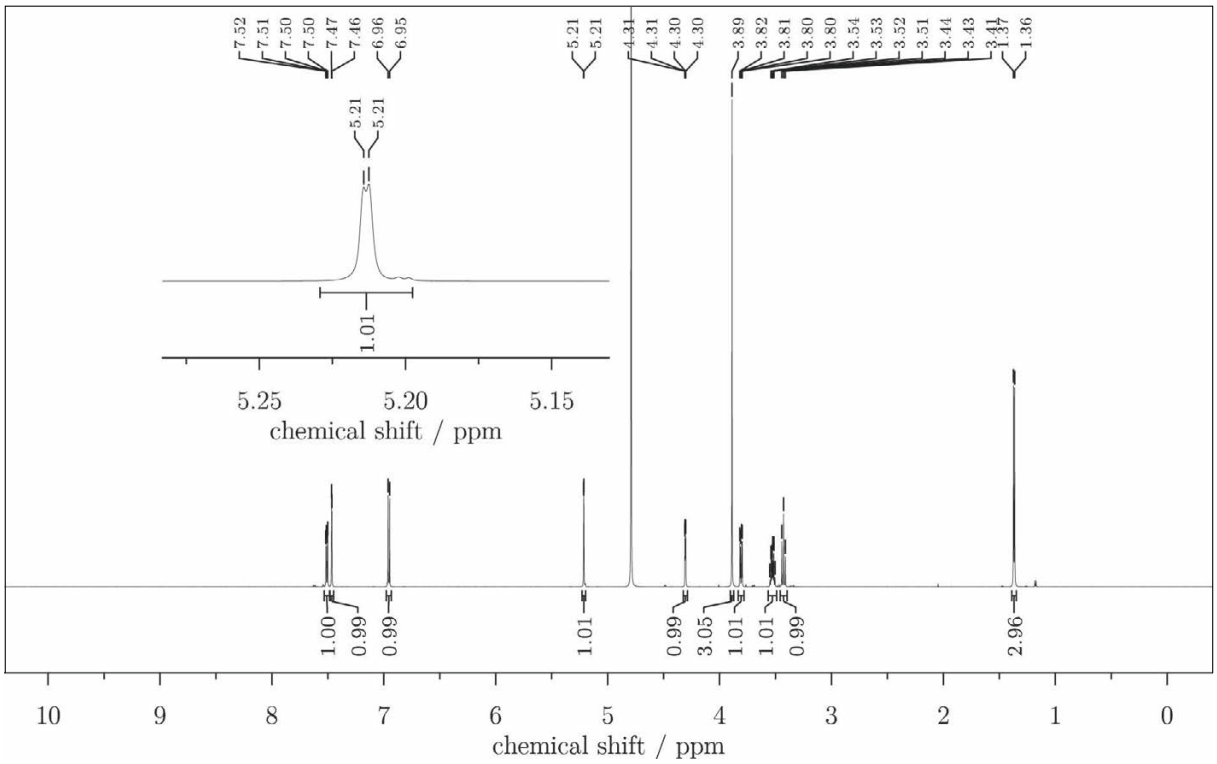


Figure 271: ^{1}H-NMR spectrum of **269** at 600 MHz in D_2O.

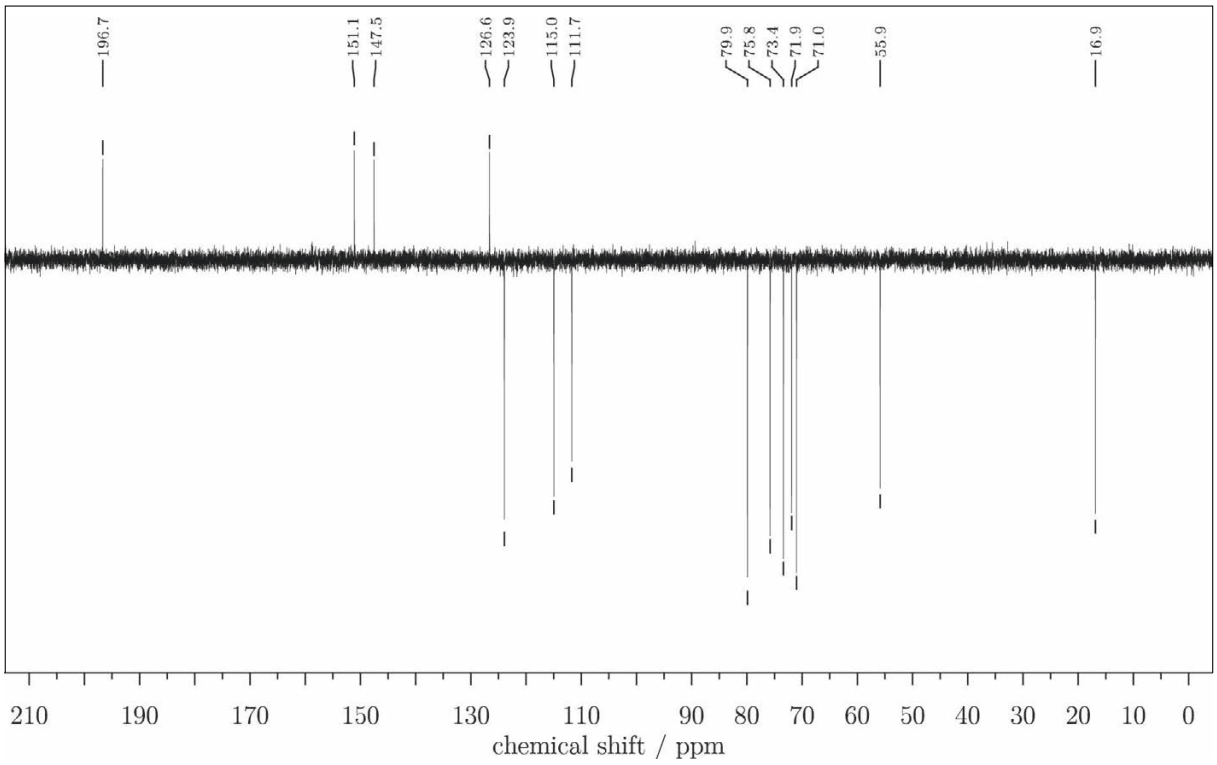


Figure 272: DEPTQ-NMR spectrum of **269** at 151 MHz in D_2O.

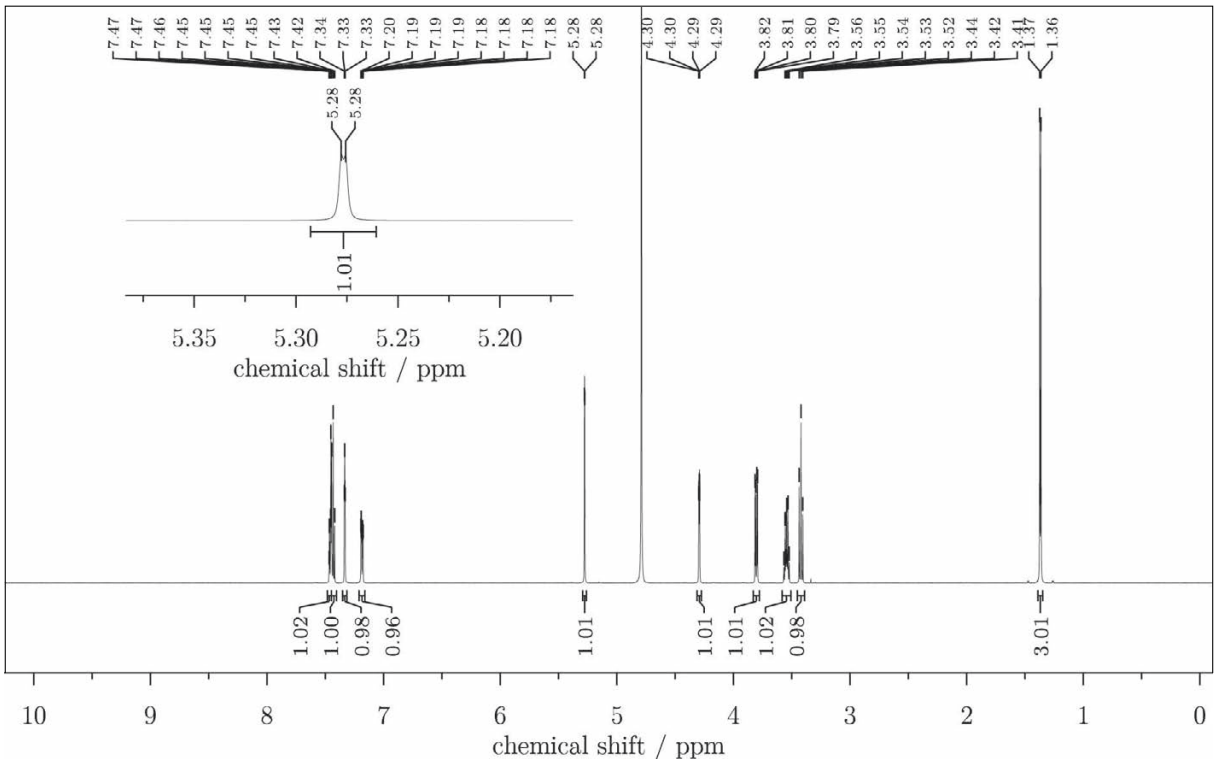


Figure 273: ^{1}H-NMR spectrum of **270** at 600 MHz in D_2O.

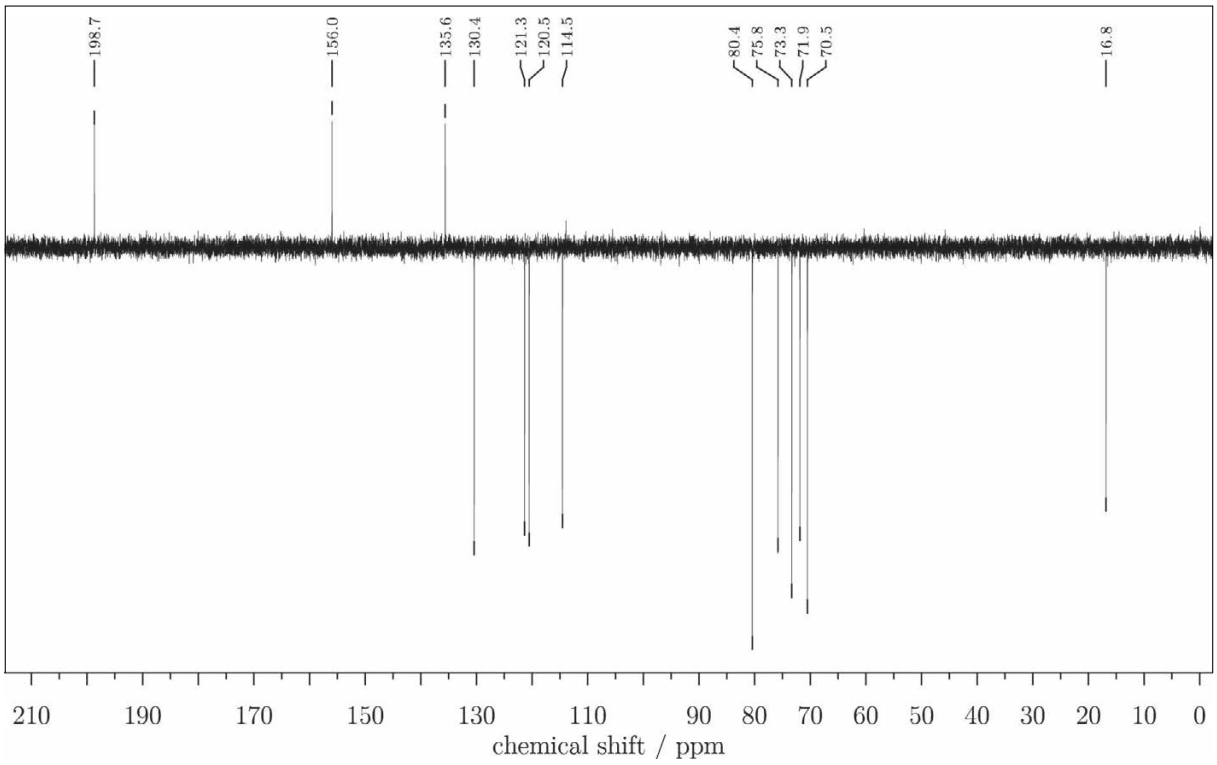


Figure 274: DEPTQ-NMR spectrum of **270** at 151 MHz in D_2O.

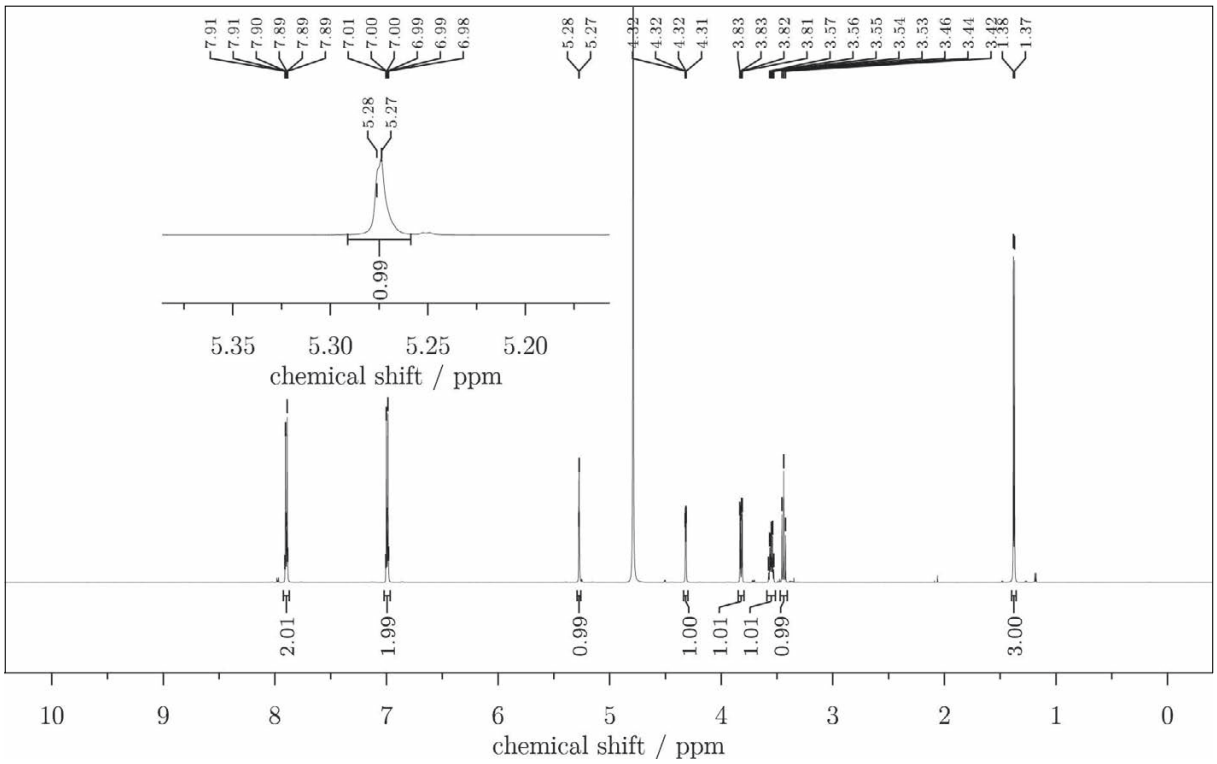


Figure 275: ^{1}H-NMR spectrum of **271** at 600 MHz in D_2O.

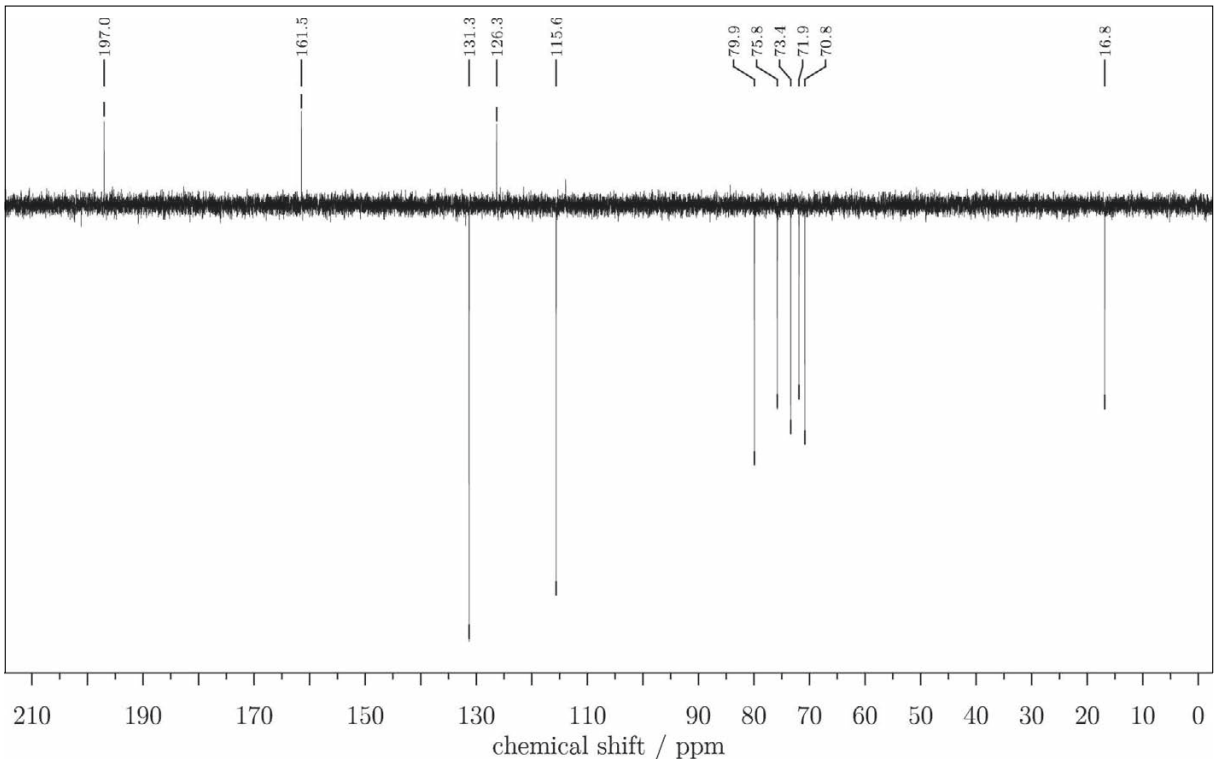


Figure 276: DEPTQ-NMR spectrum of **271** at 151 MHz in D_2O.

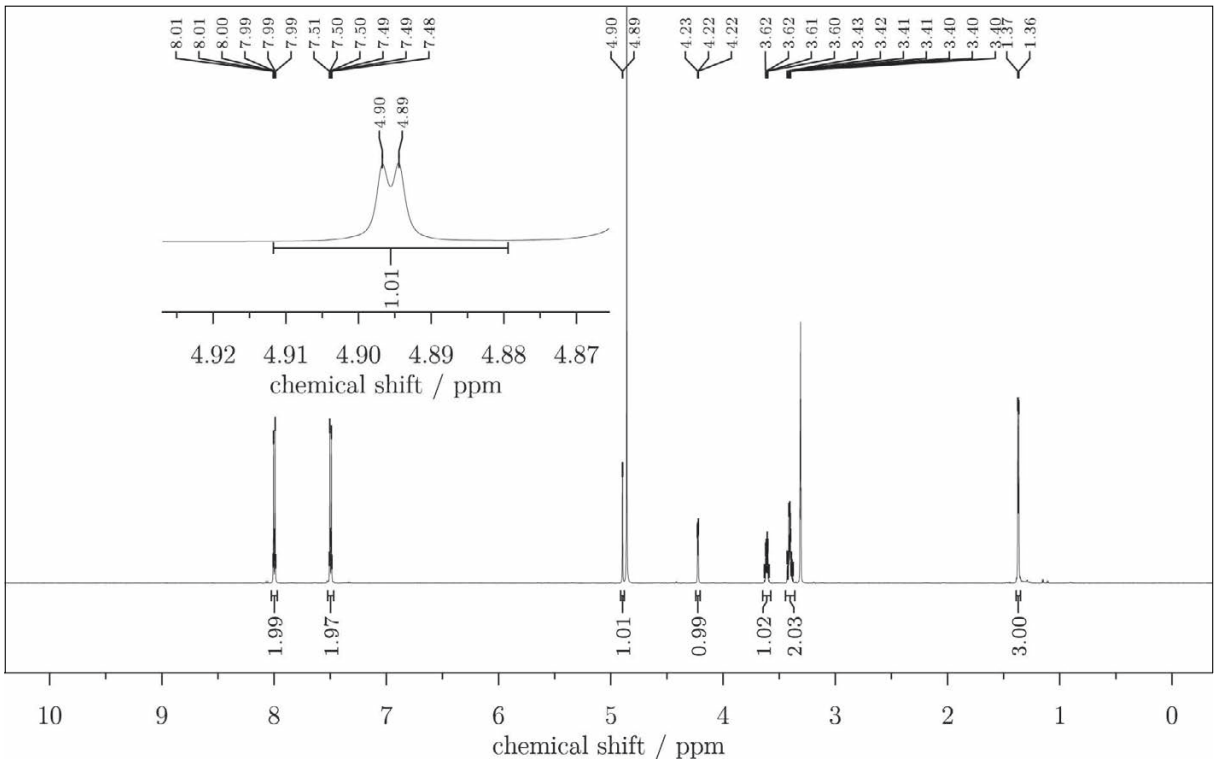


Figure 277: ^{1}H-NMR spectrum of **272** at 600 MHz in methanol-d_4.

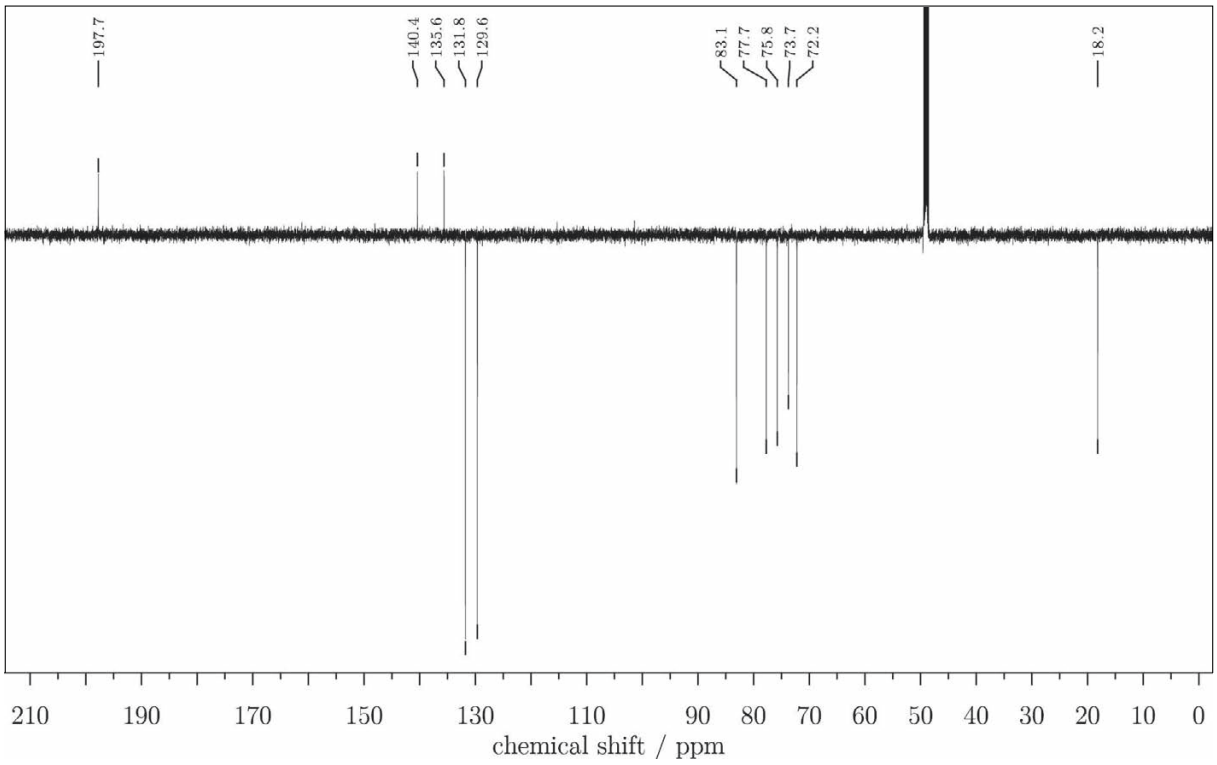


Figure 278: DEPTQ-NMR spectrum of **272** at 151 MHz in methanol-d_4.

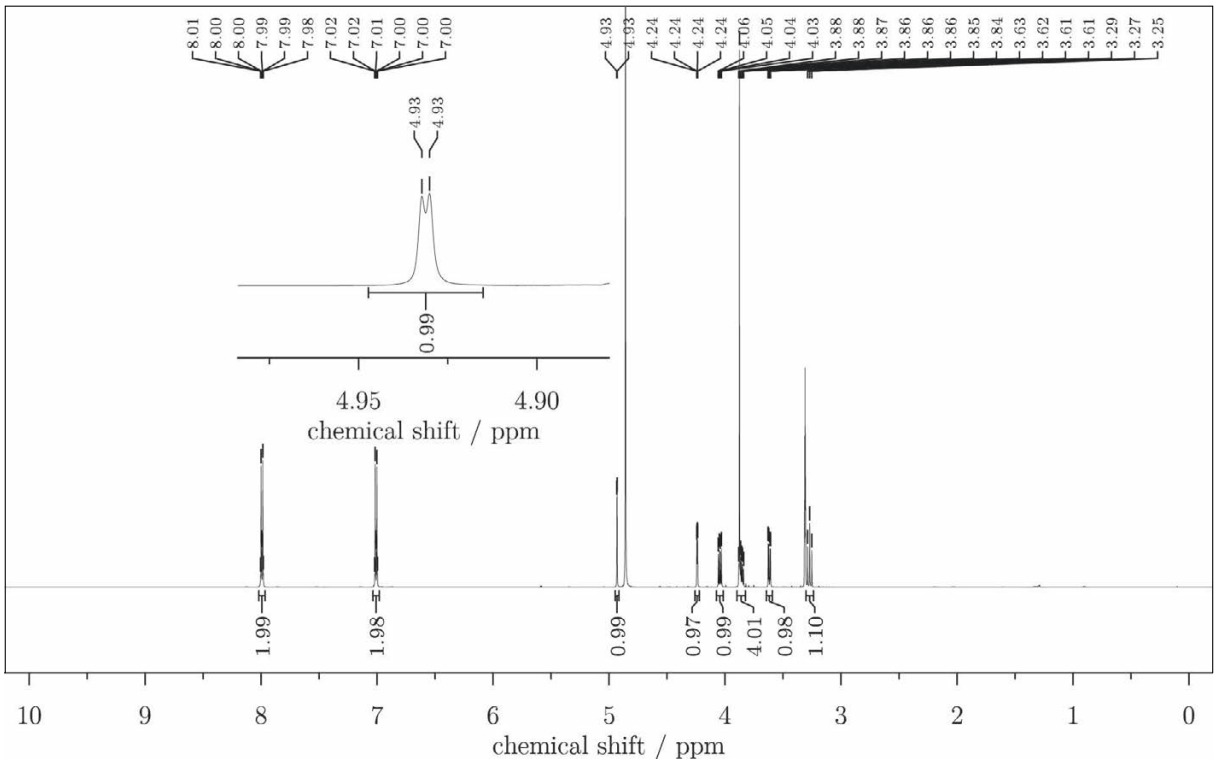


Figure 279: ^{1}H-NMR spectrum of **273** at 600 MHz in methanol-d_4.

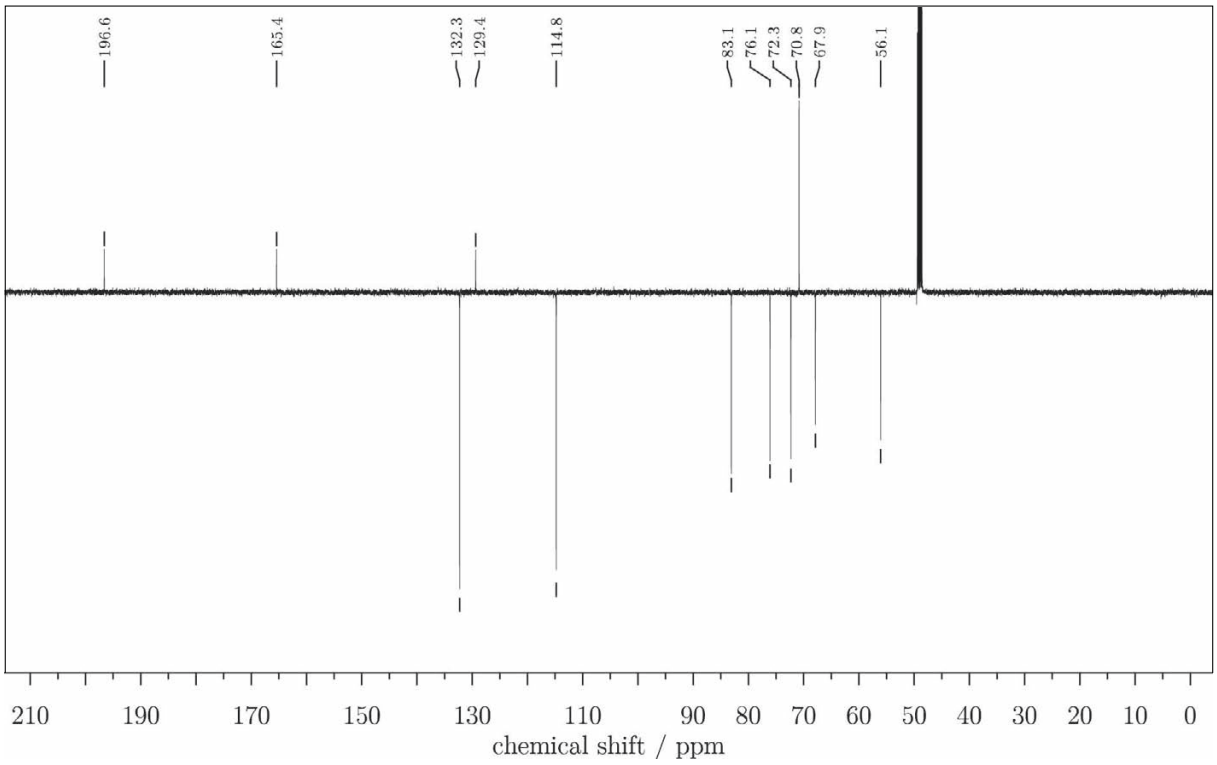


Figure 280: DEPTQ-NMR spectrum of **273** at 151 MHz in methanol-d_4.

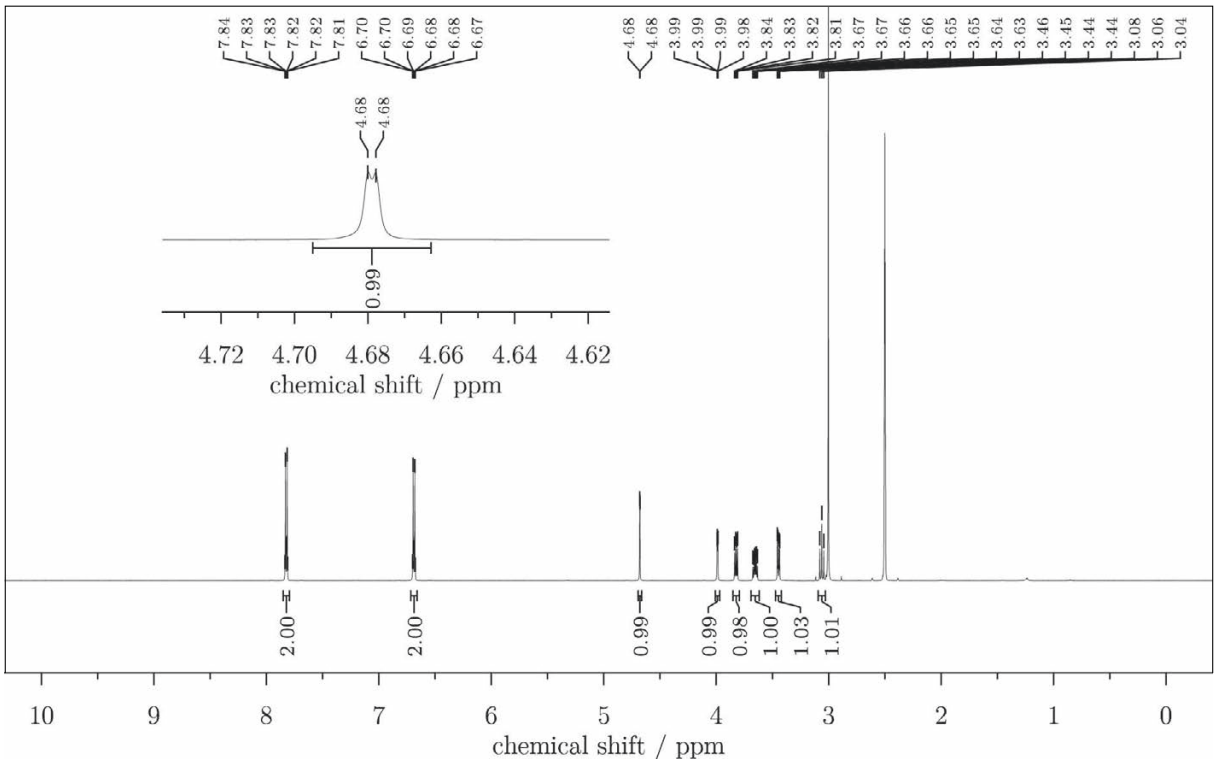


Figure 281: ^{1}H-NMR spectrum of **274** at 600 MHz in DMSO-d_6.

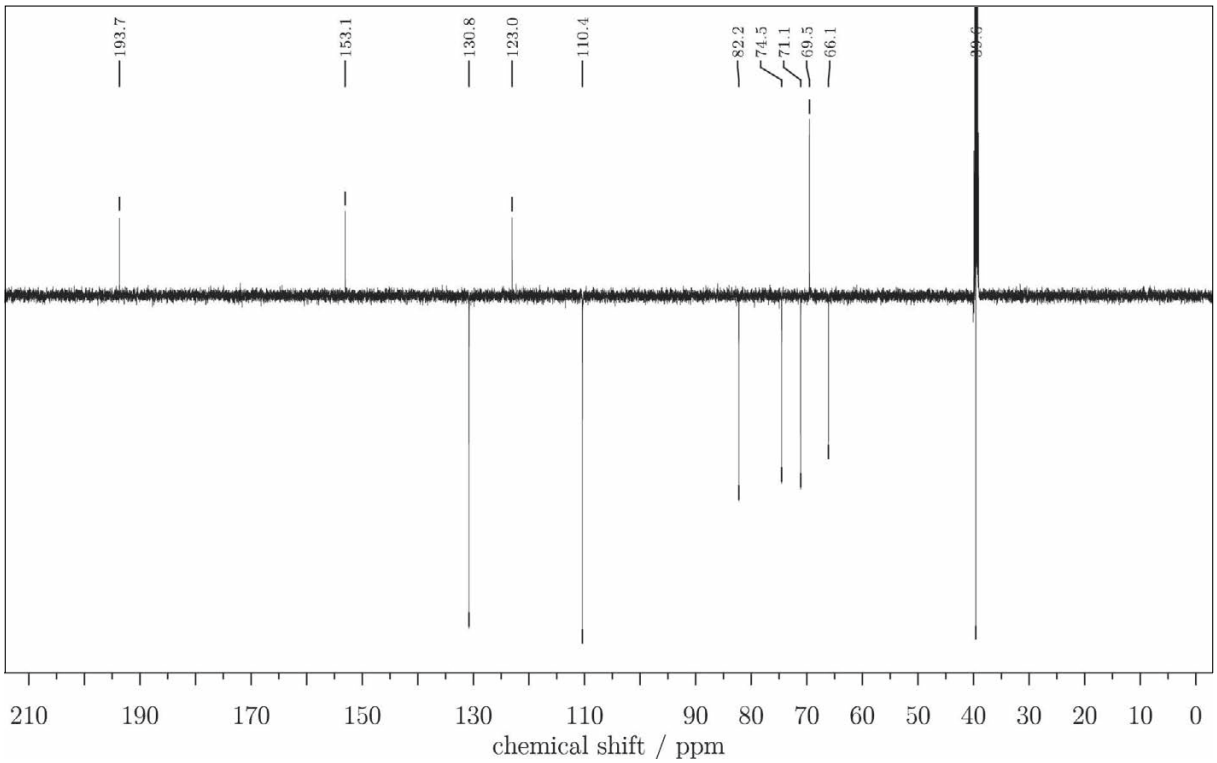


Figure 282: DEPTQ-NMR spectrum of **274** at 151 MHz in DMSO-d_6.

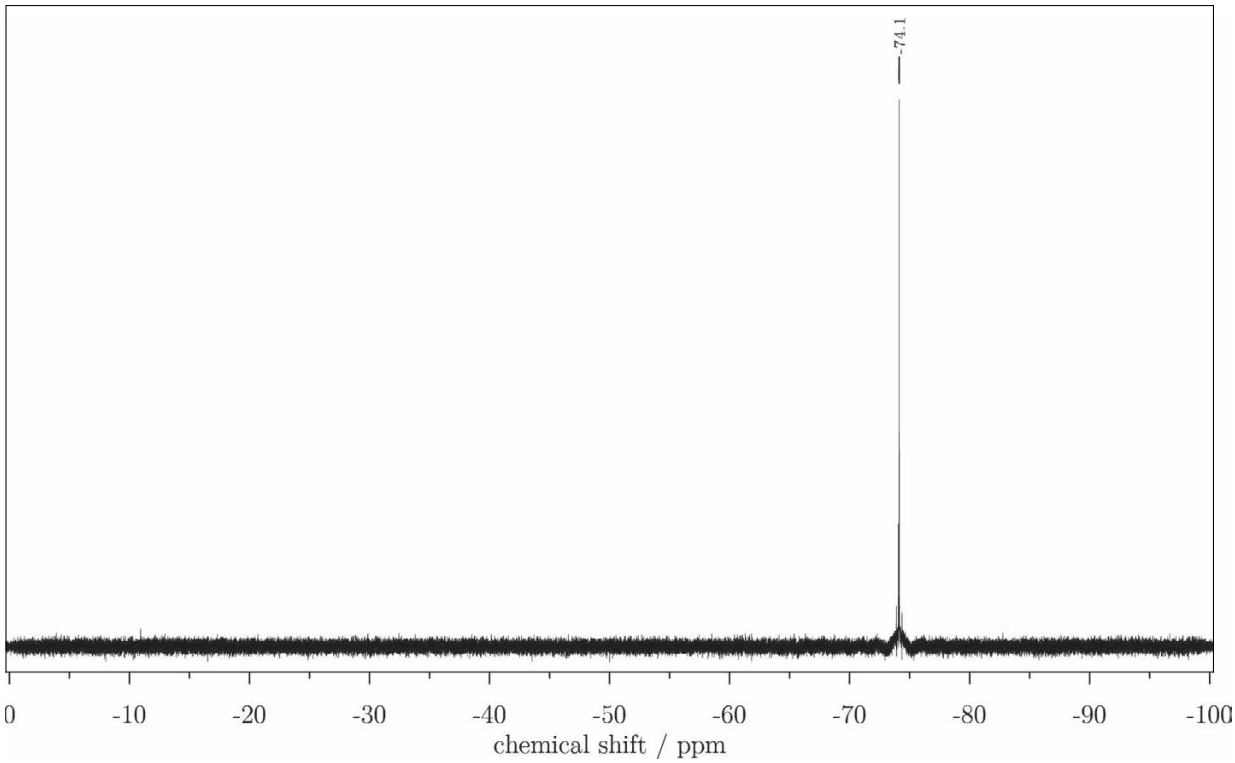


Figure 283: ^{19}F-NMR Spectrum of **274** at 565 MHz in DMSO-d_6.

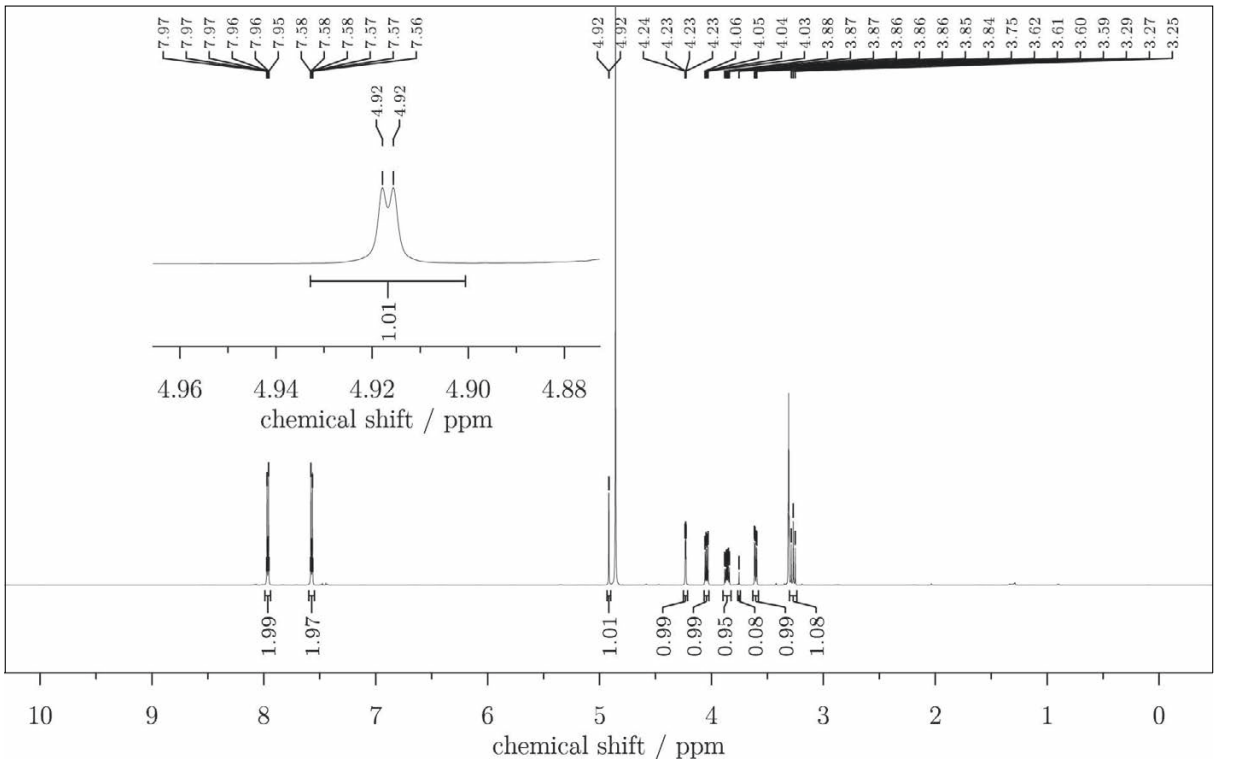


Figure 284: ^{1}H-NMR spectrum of **275** at 600 MHz in methanol-d_4.

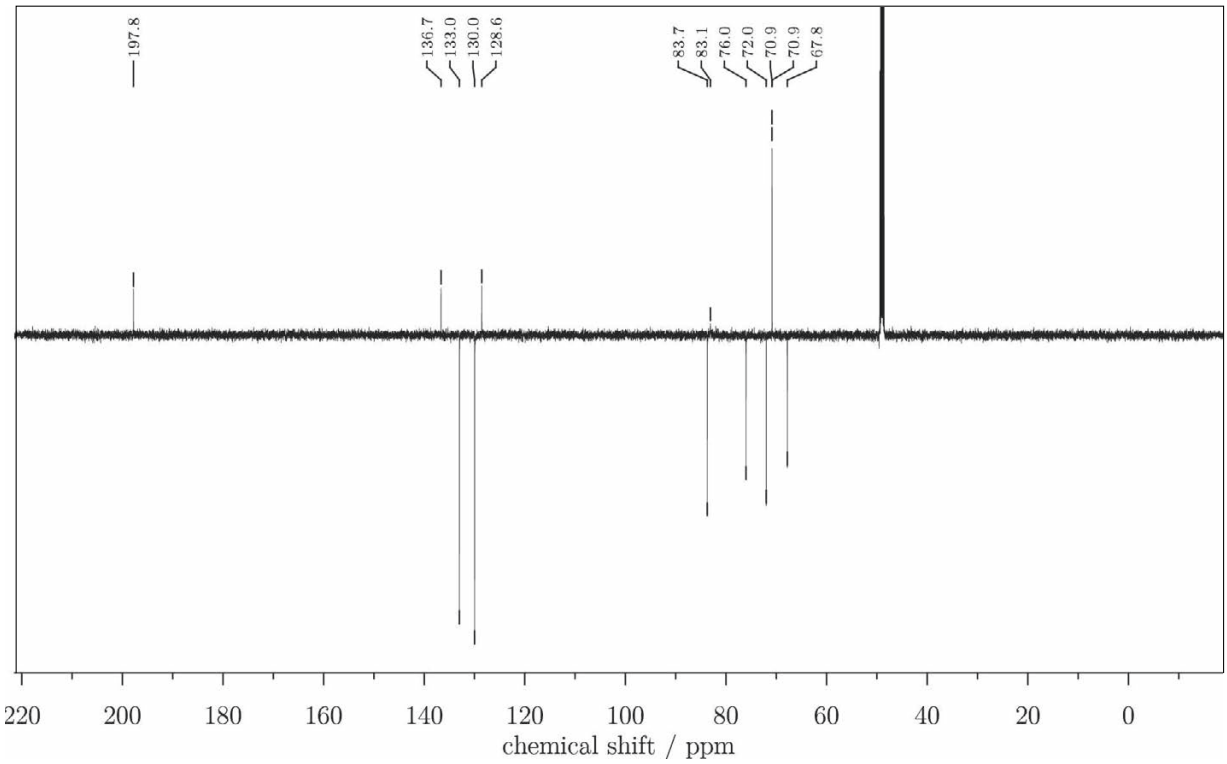


Figure 285: DEPTQ-NMR spectrum of **275** at 151 MHz in methanol-d_4.

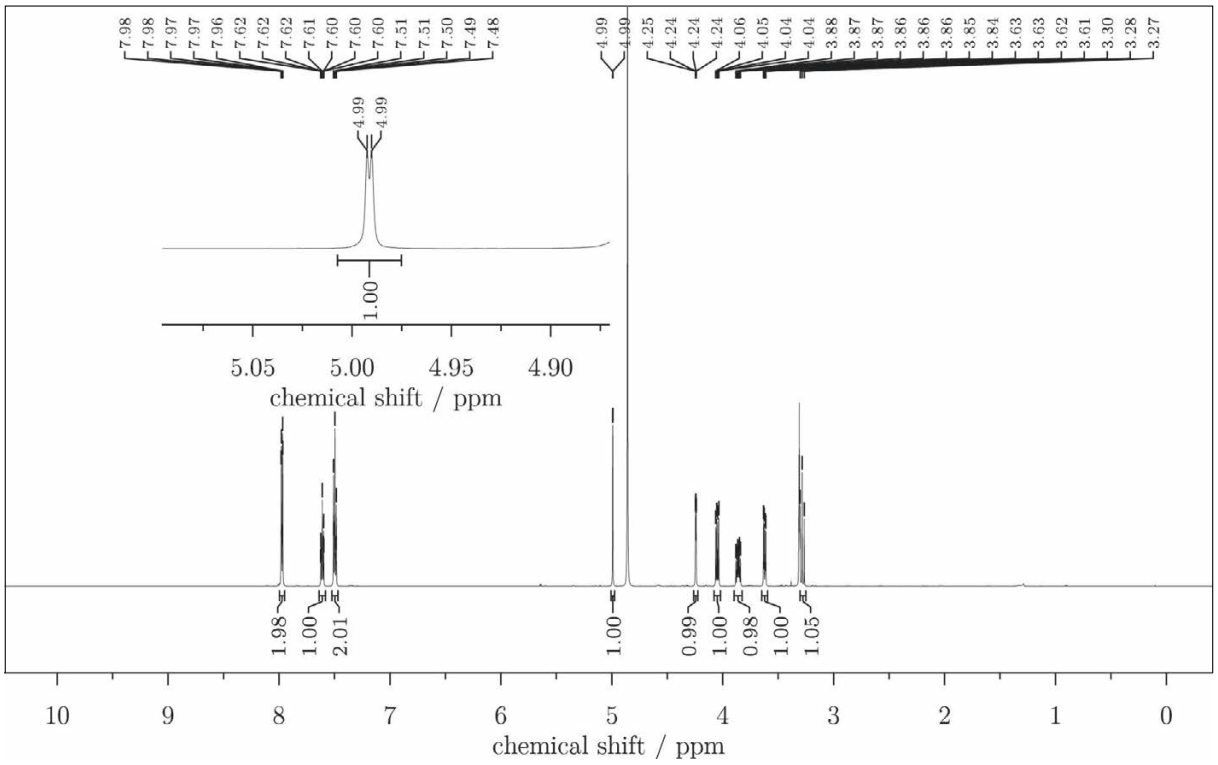


Figure 286: ^{1}H-NMR spectrum of **276** at 600 MHz in methanol-d_4.

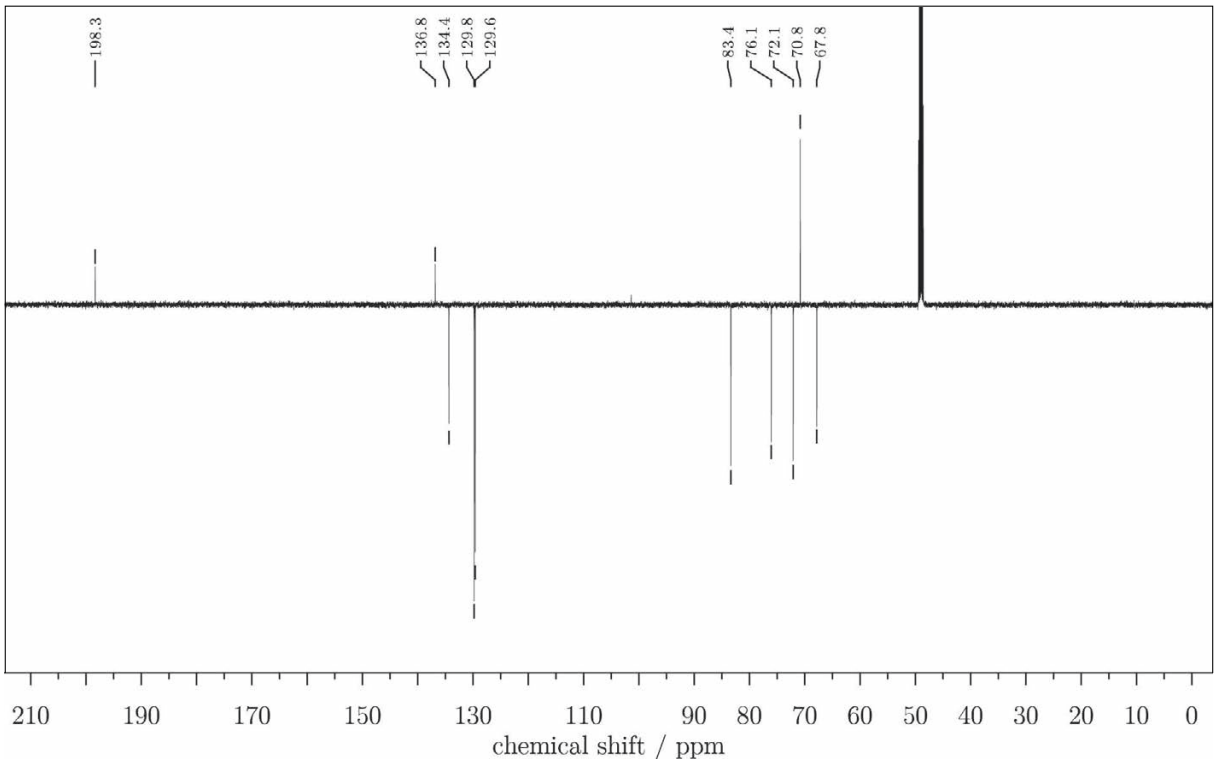


Figure 287: DEPTQ-NMR spectrum of **276** at 151 MHz in methanol-d_4.

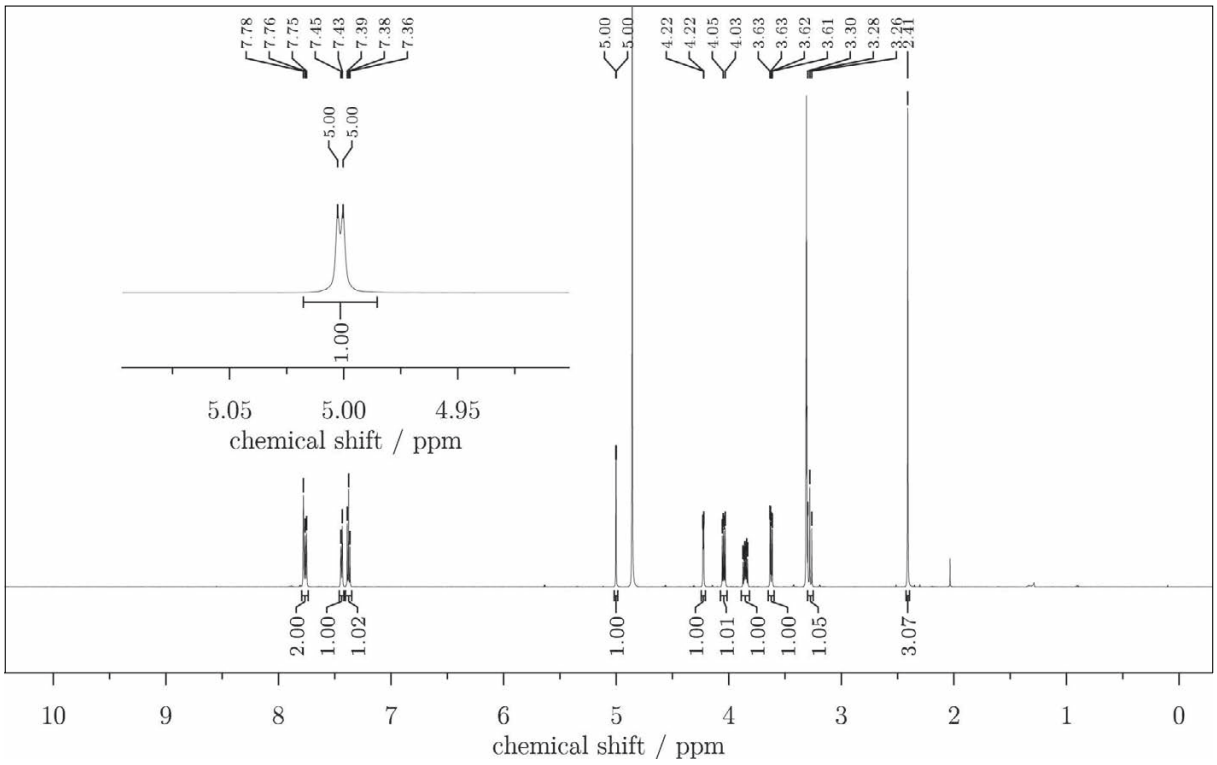


Figure 288: ^{1}H-NMR spectrum of **277** at 600 MHz in methanol-d_4.

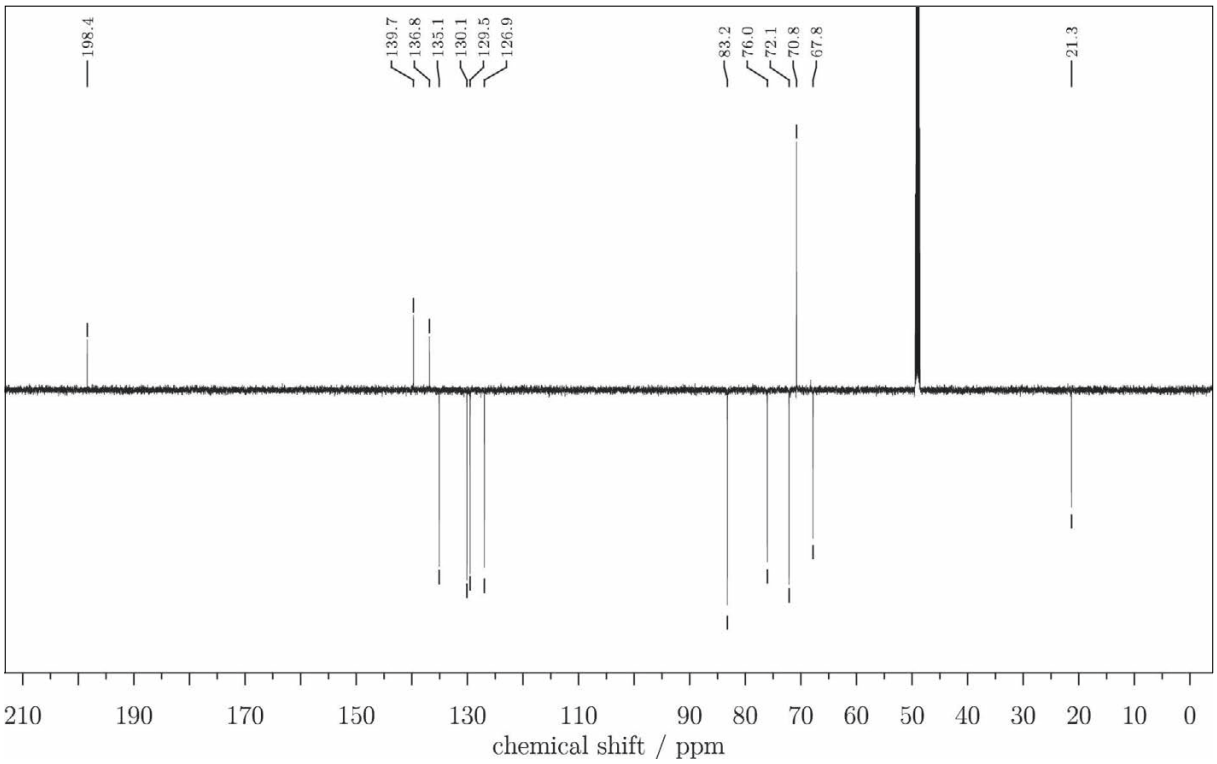


Figure 289: DEPTQ-NMR spectrum of **277** at 151 MHz in methanol-d_4.

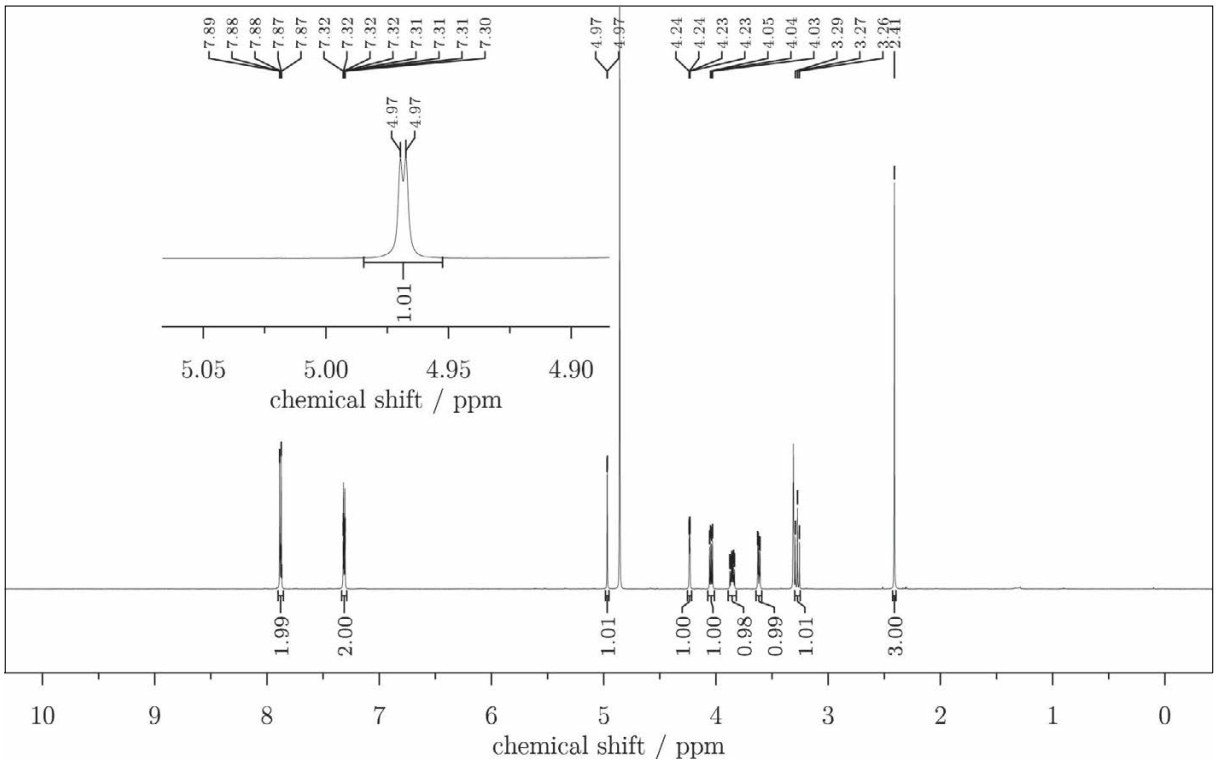


Figure 290: ^{1}H-NMR spectrum of **278** at 600 MHz in methanol-d_4.

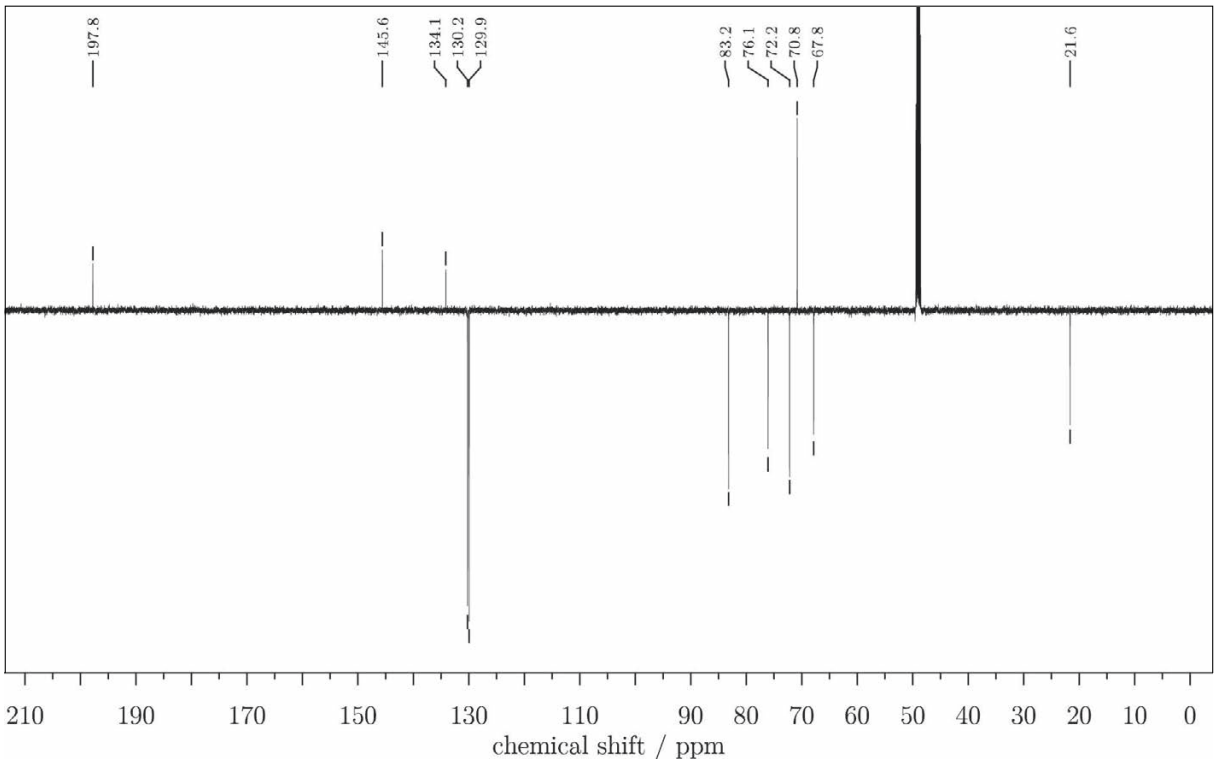


Figure 291: DEPTQ-NMR spectrum of **278** at 151 MHz in methanol-d_4.

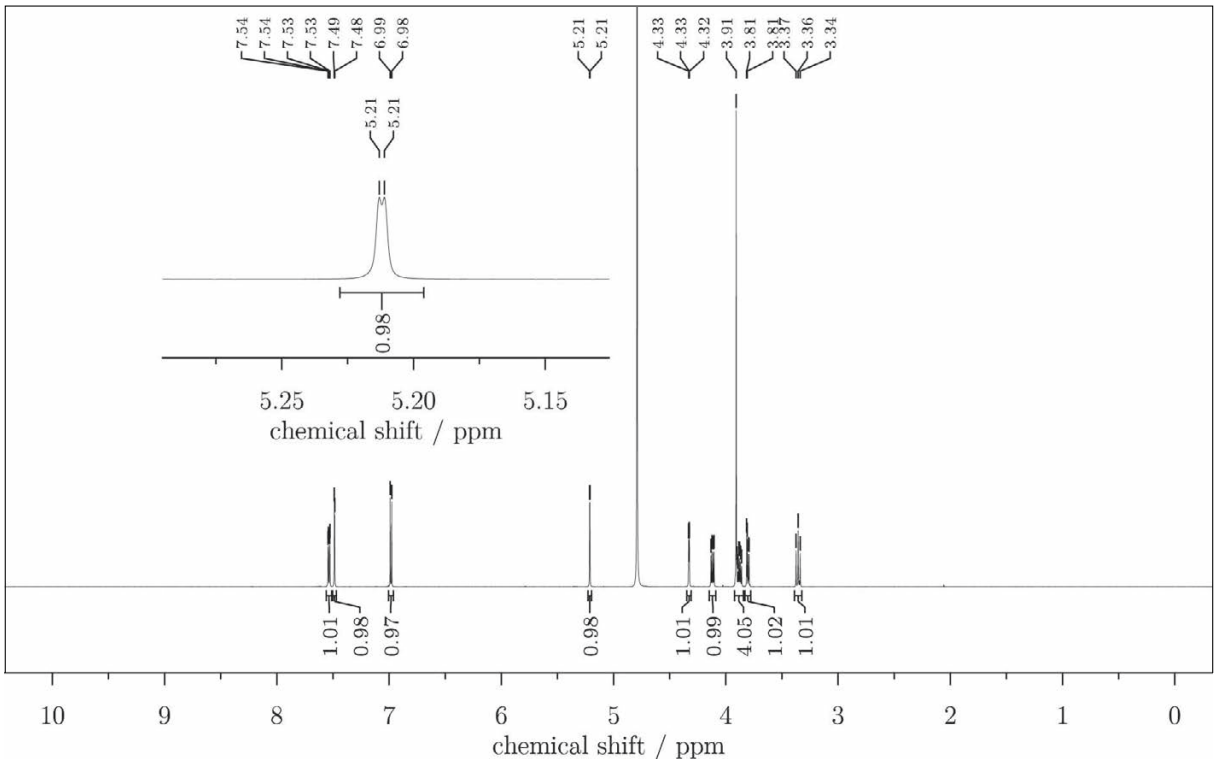


Figure 292: ^{1}H-NMR spectrum of **279** at 600 MHz in D_2O.

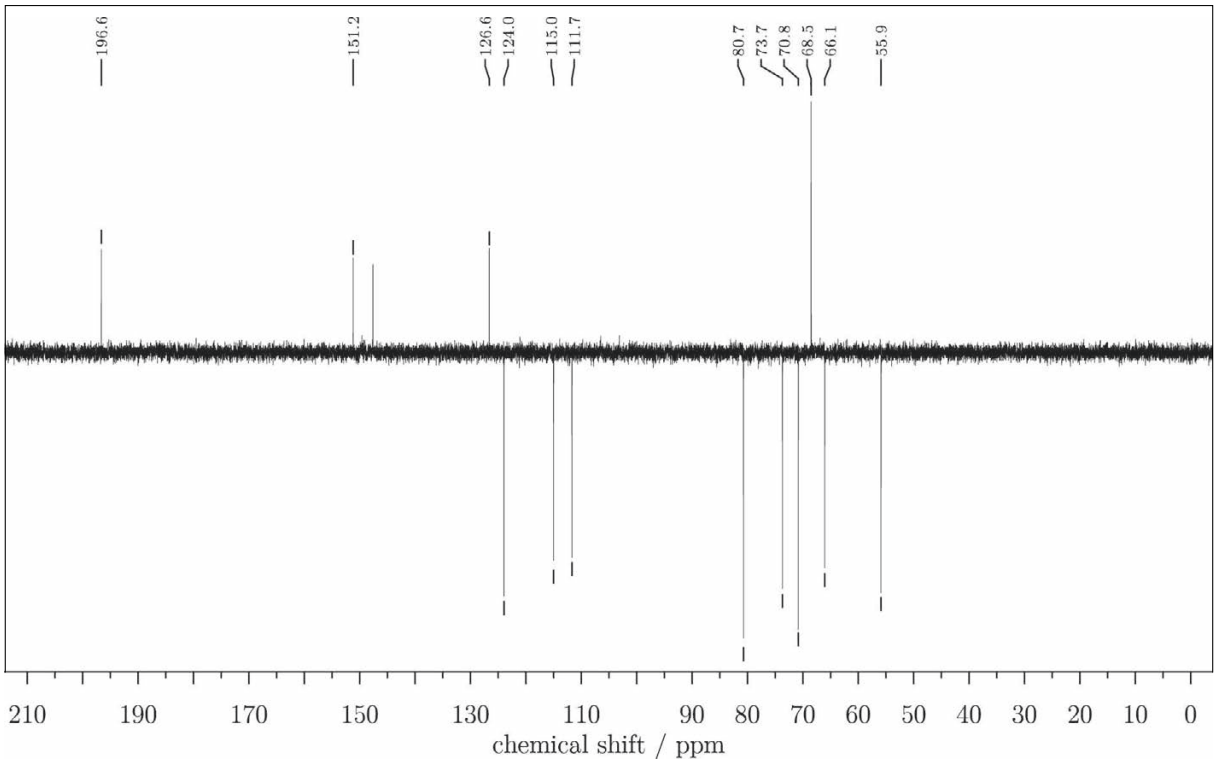


Figure 293: DEPTQ-NMR spectrum of **279** at 151 MHz in D_2O.

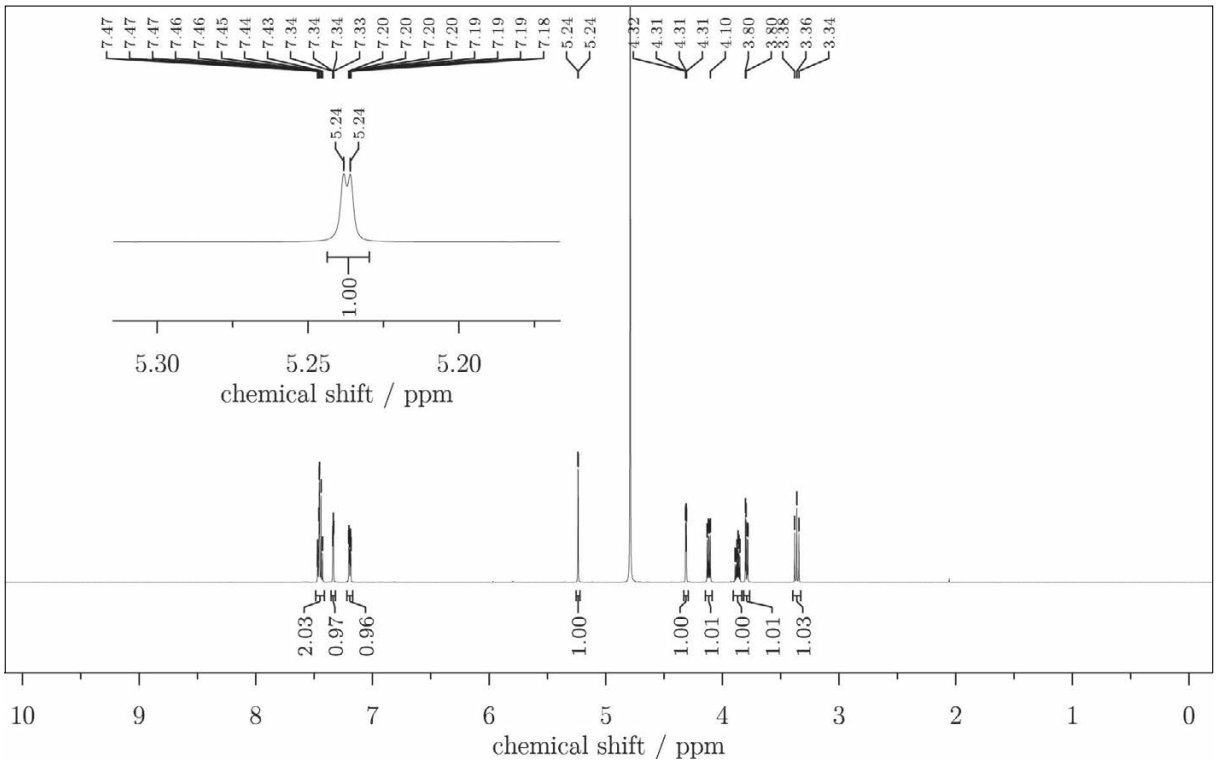


Figure 294: ^{1}H-NMR spectrum of **280** at 600 MHz in D_2O.

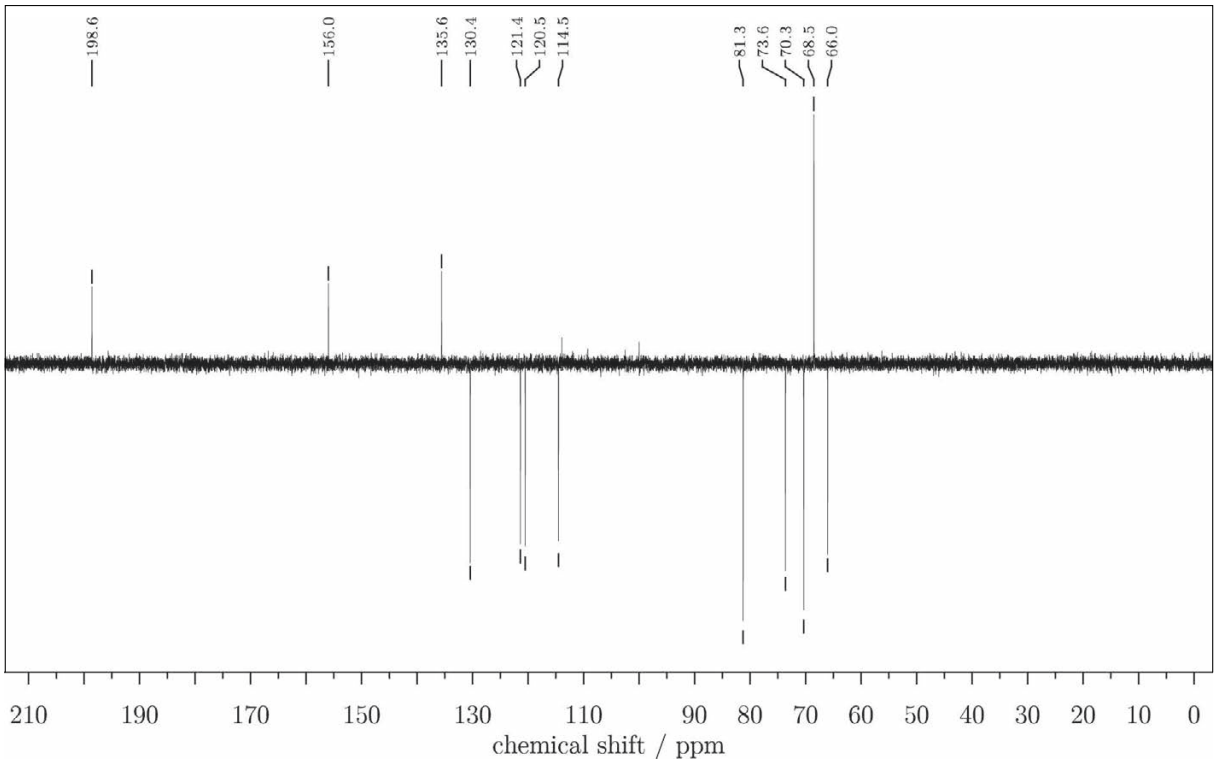


Figure 295: DEPTQ-NMR spectrum of **280** at 151 MHz in D_2O.

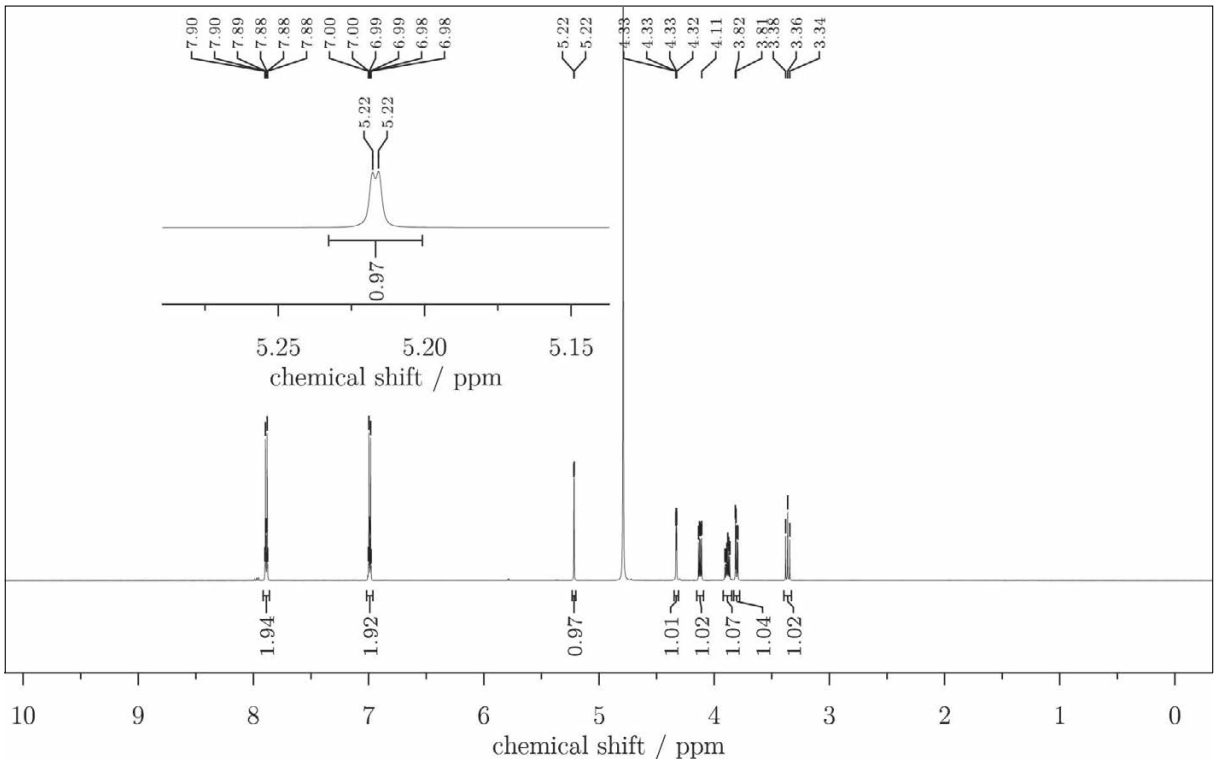


Figure 296: ^{1}H-NMR spectrum of **281** at 600 MHz in D_2O.

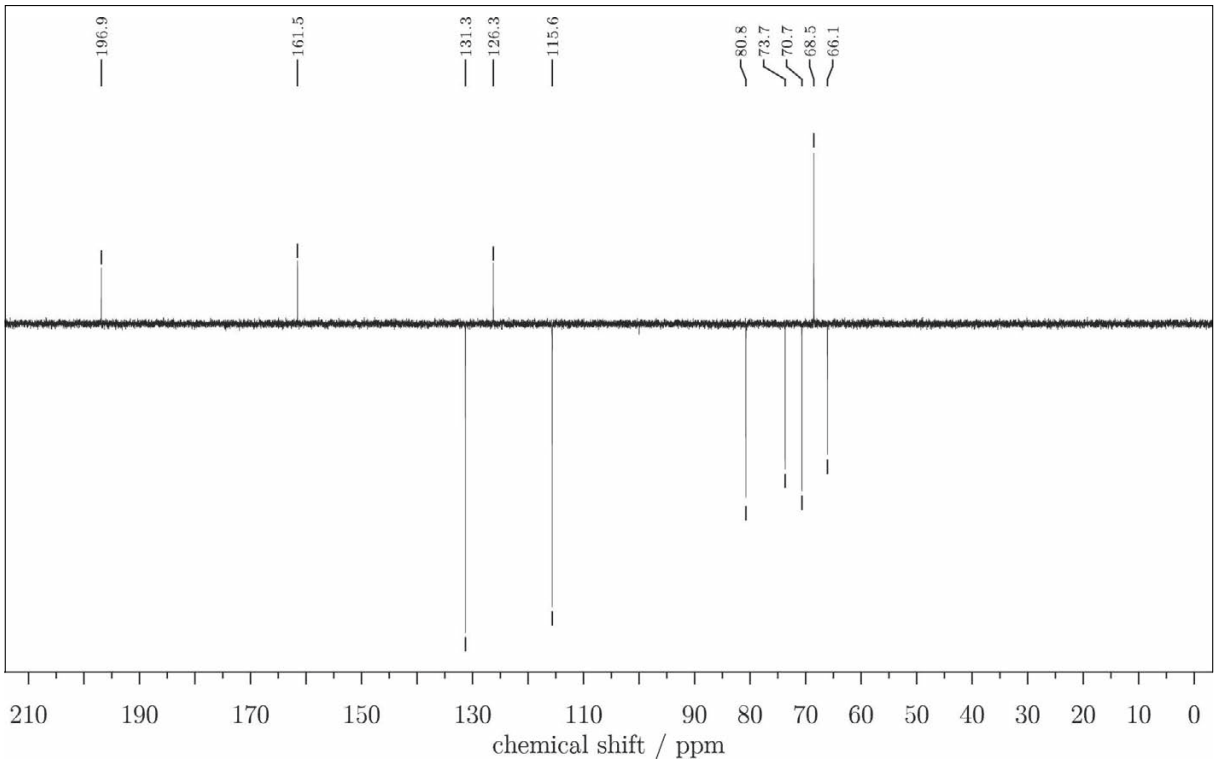


Figure 297: DEPTQ-NMR spectrum of **281** at 151 MHz in D_2O.

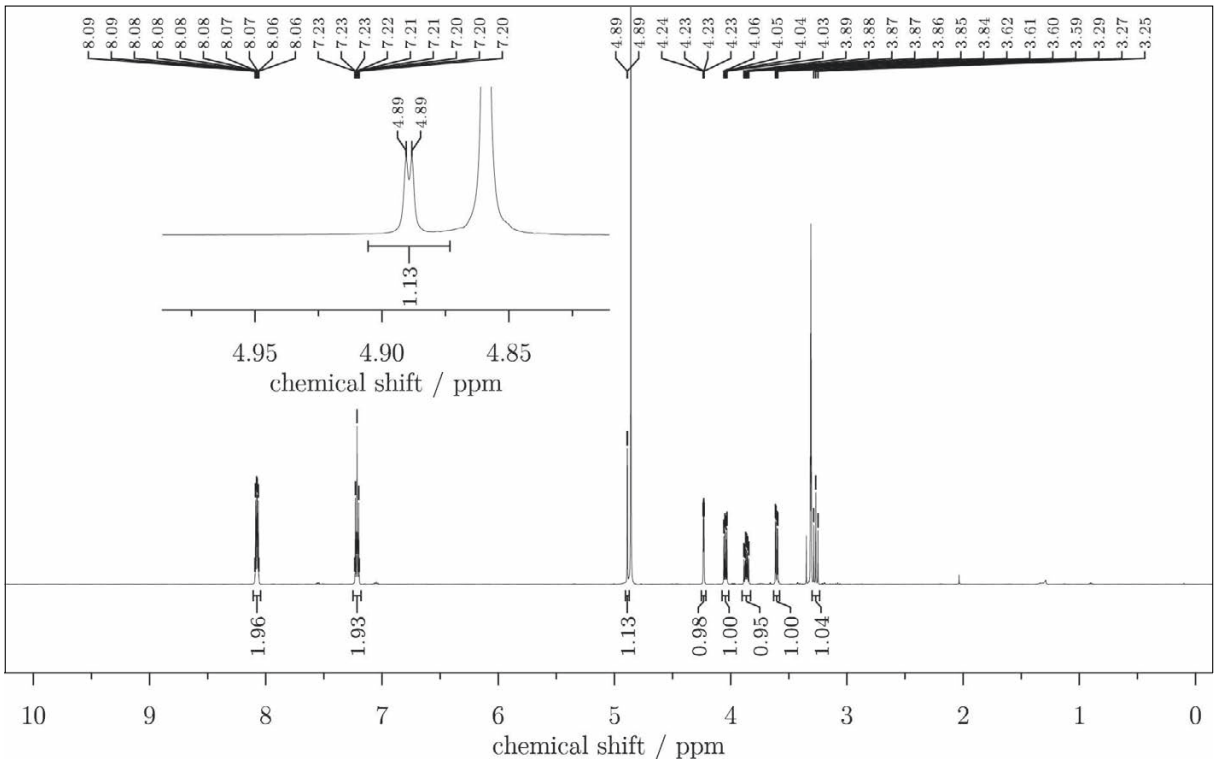


Figure 298: ^{1}H-NMR spectrum of **282** at 600 MHz in methanol-d_4.

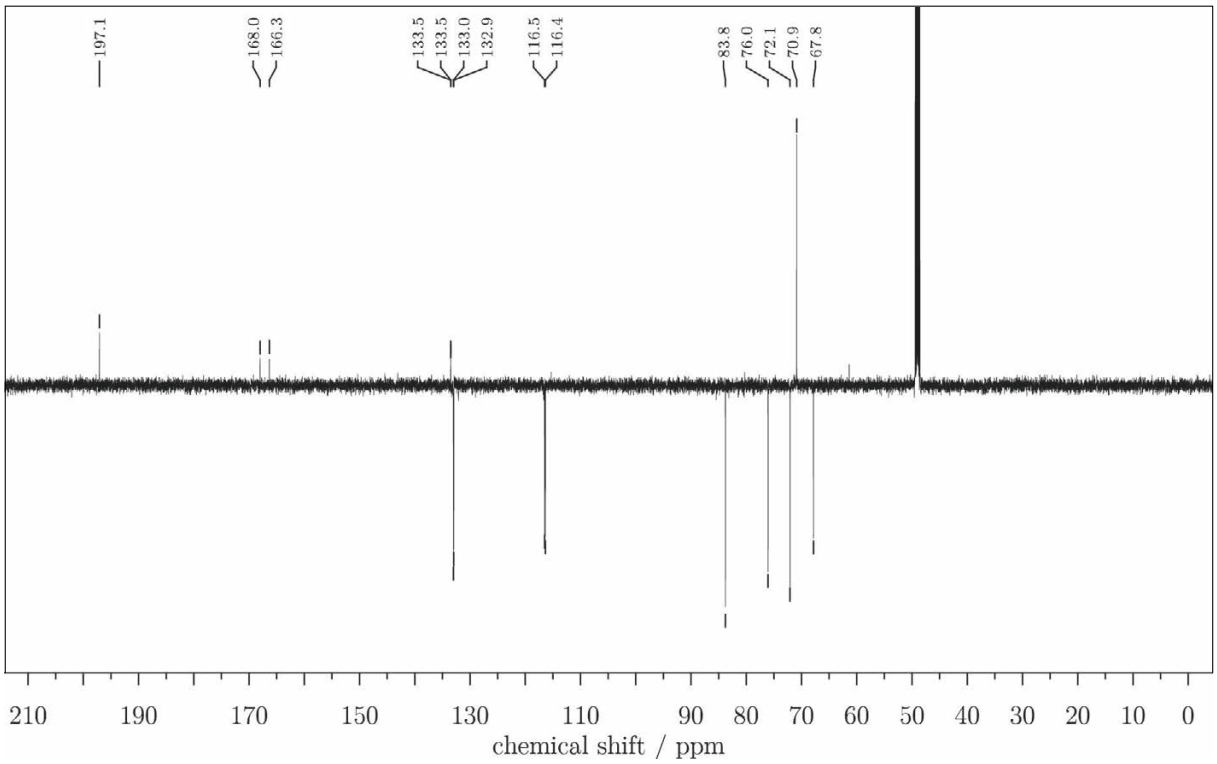


Figure 299: DEPTQ-NMR spectrum of **282** at 151 MHz in methanol-d_4.

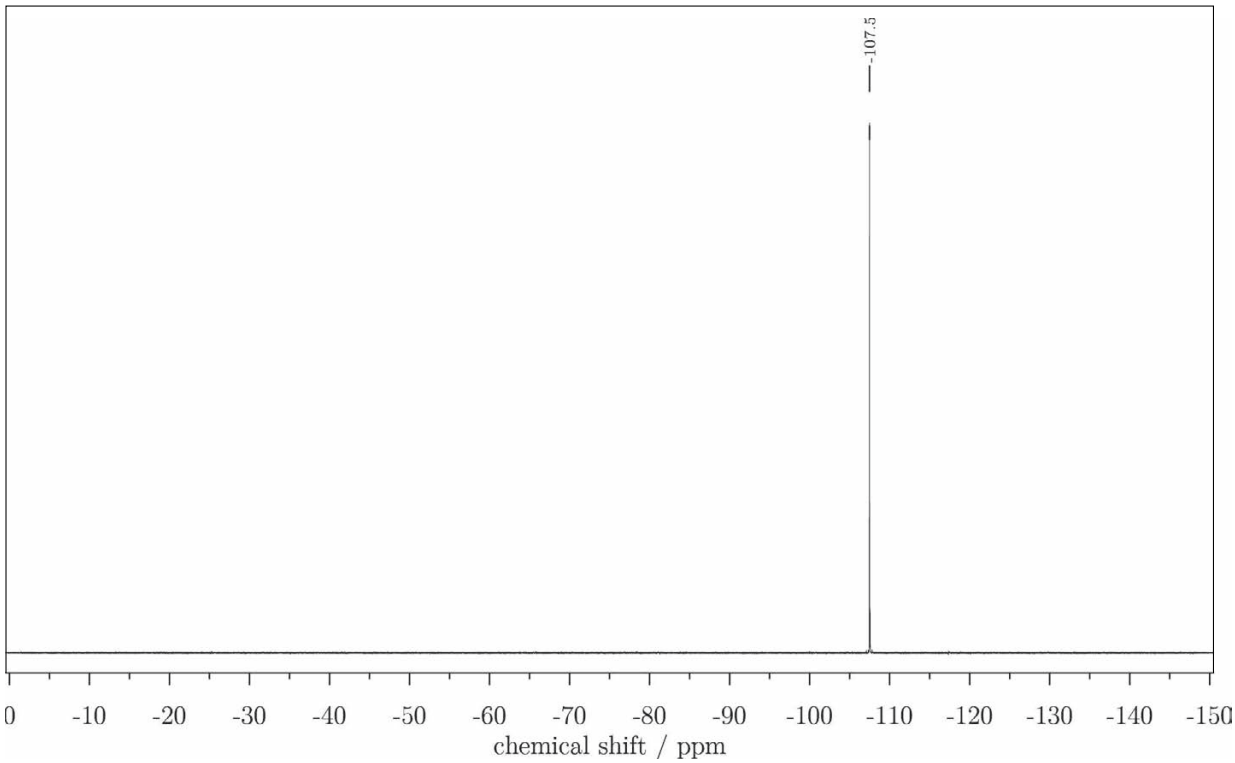


Figure 300: ^{19}F-NMR Spectrum of **282** at 565 MHz in methanol-d_4.

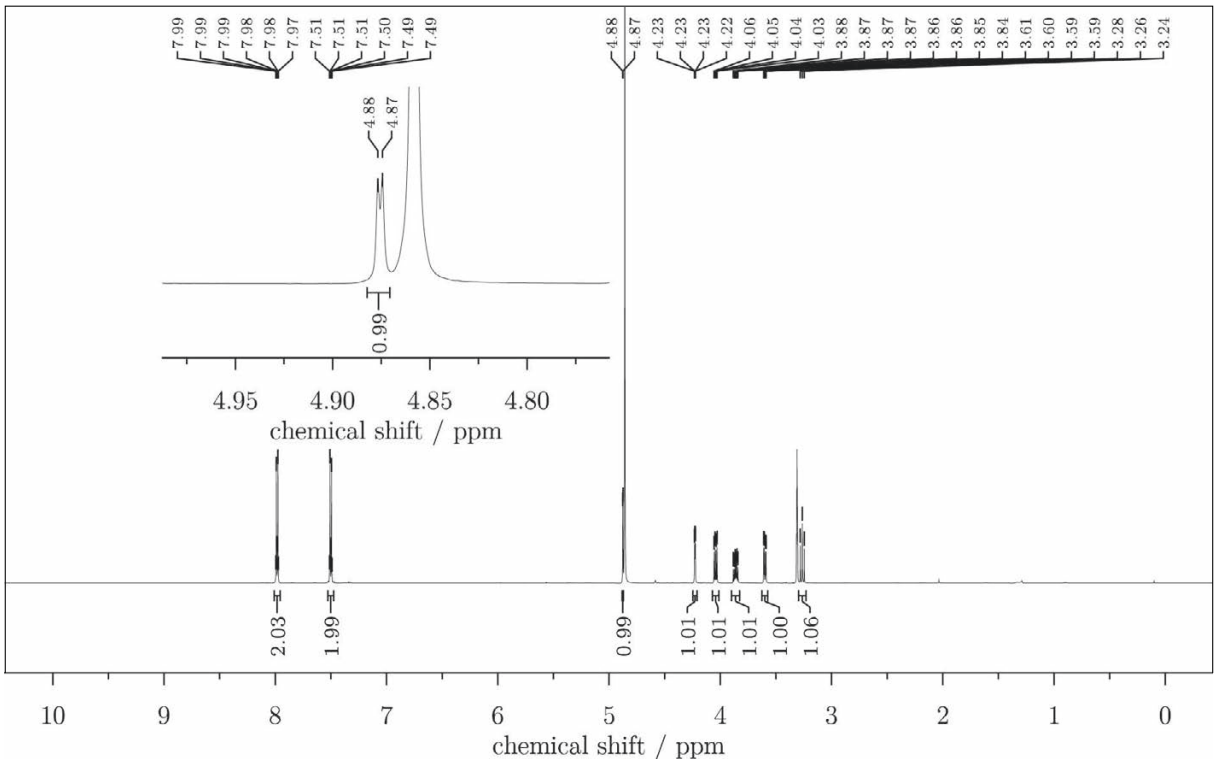


Figure 301: ^{1}H-NMR spectrum of **283** at 600 MHz in methanol-d_4.

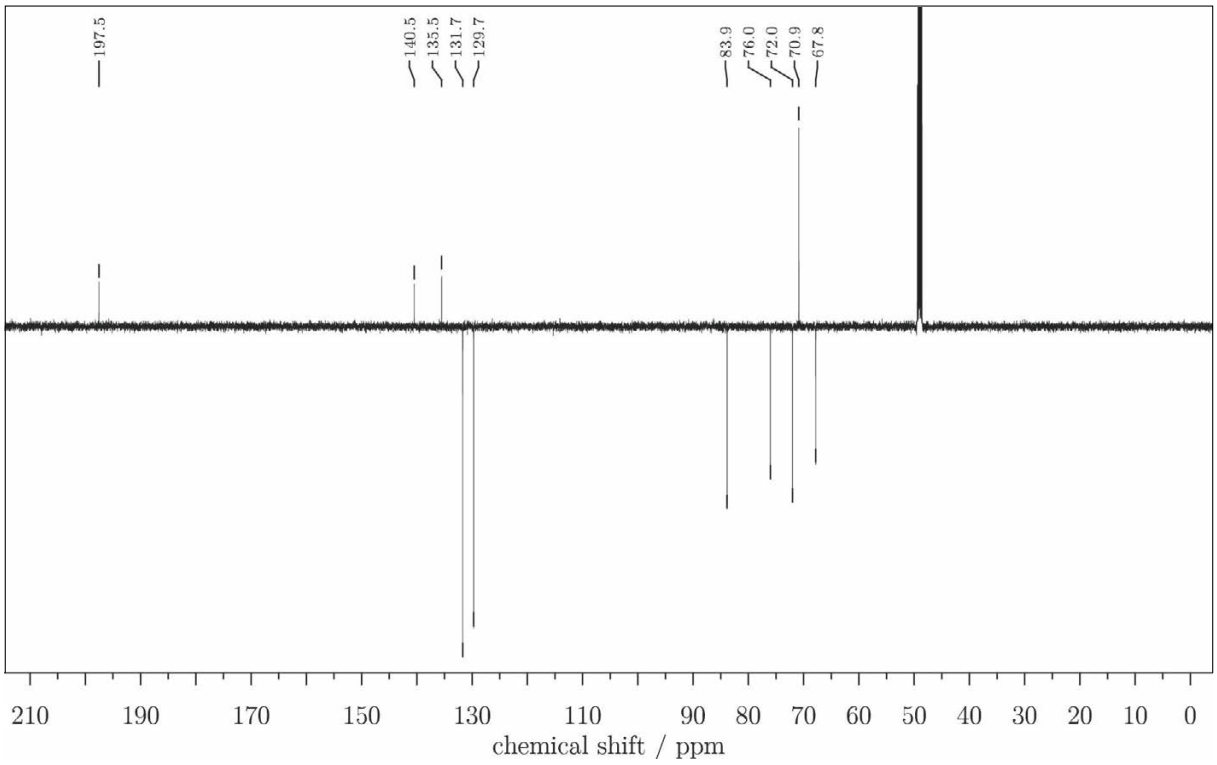


Figure 302: DEPTQ-NMR spectrum of **283** at 151 MHz in methanol-d_4.

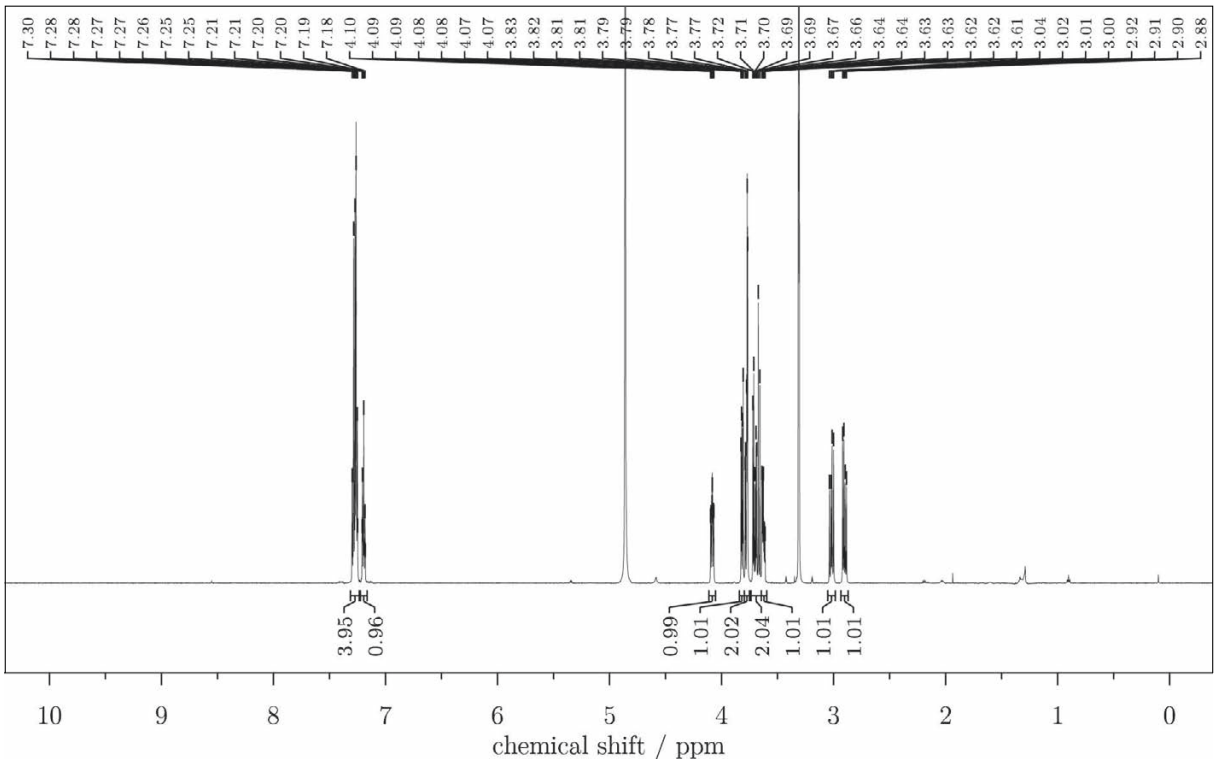


Figure 303: ^{1}H-NMR spectrum of **284** at 600 MHz in methanol-d_4.

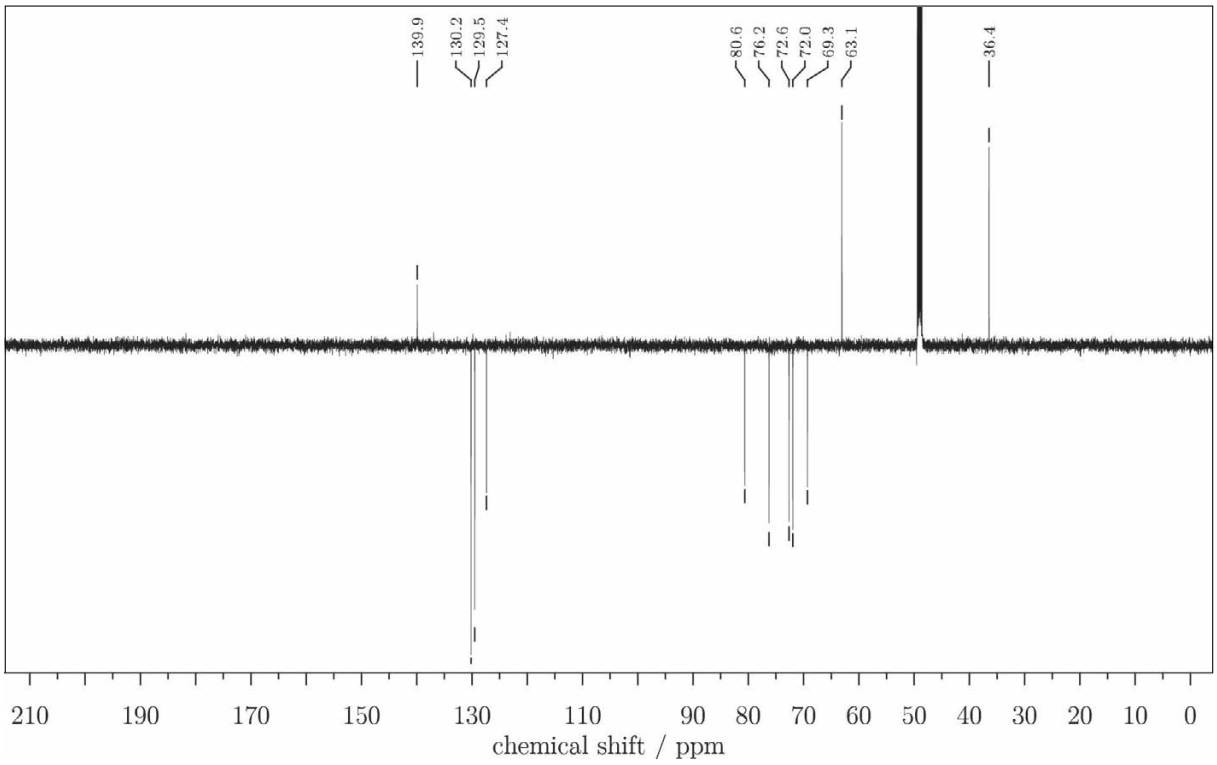


Figure 304: DEPTQ-NMR spectrum of **284** at 151 MHz in methanol-d_4.

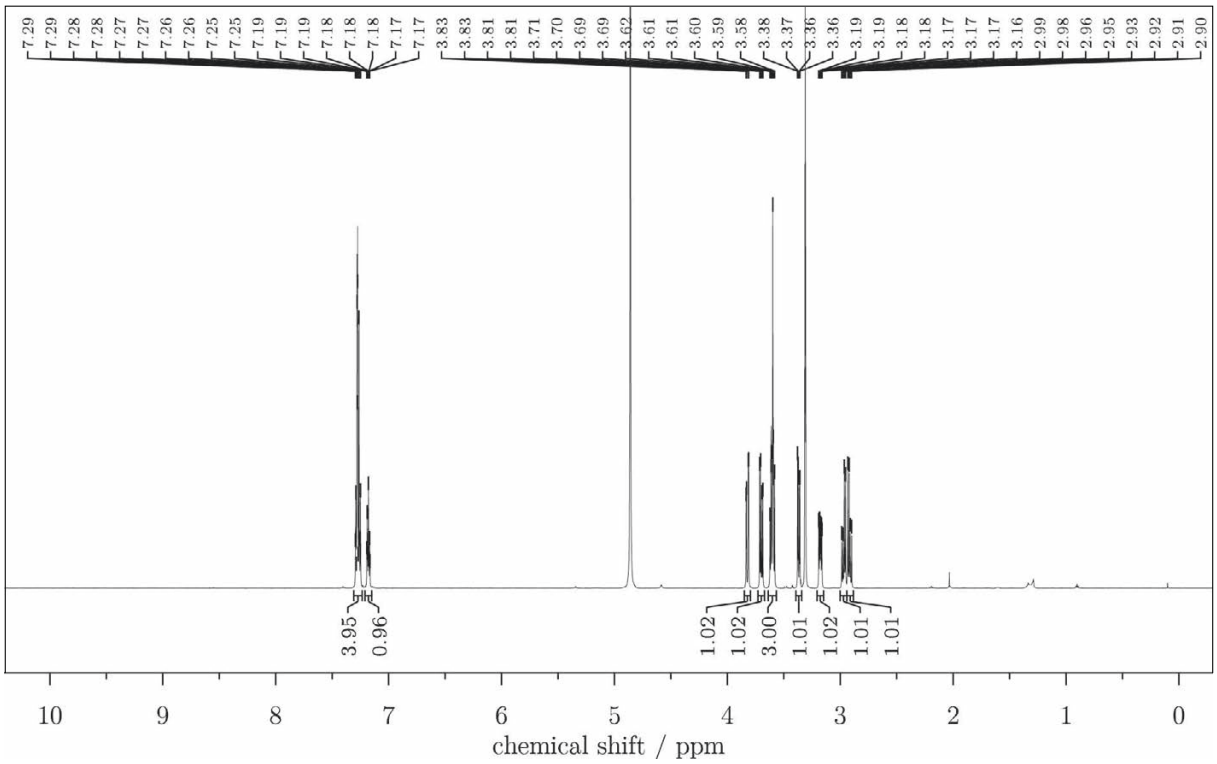


Figure 305: ^{1}H-NMR spectrum of **285** at 600 MHz in methanol-d_4.

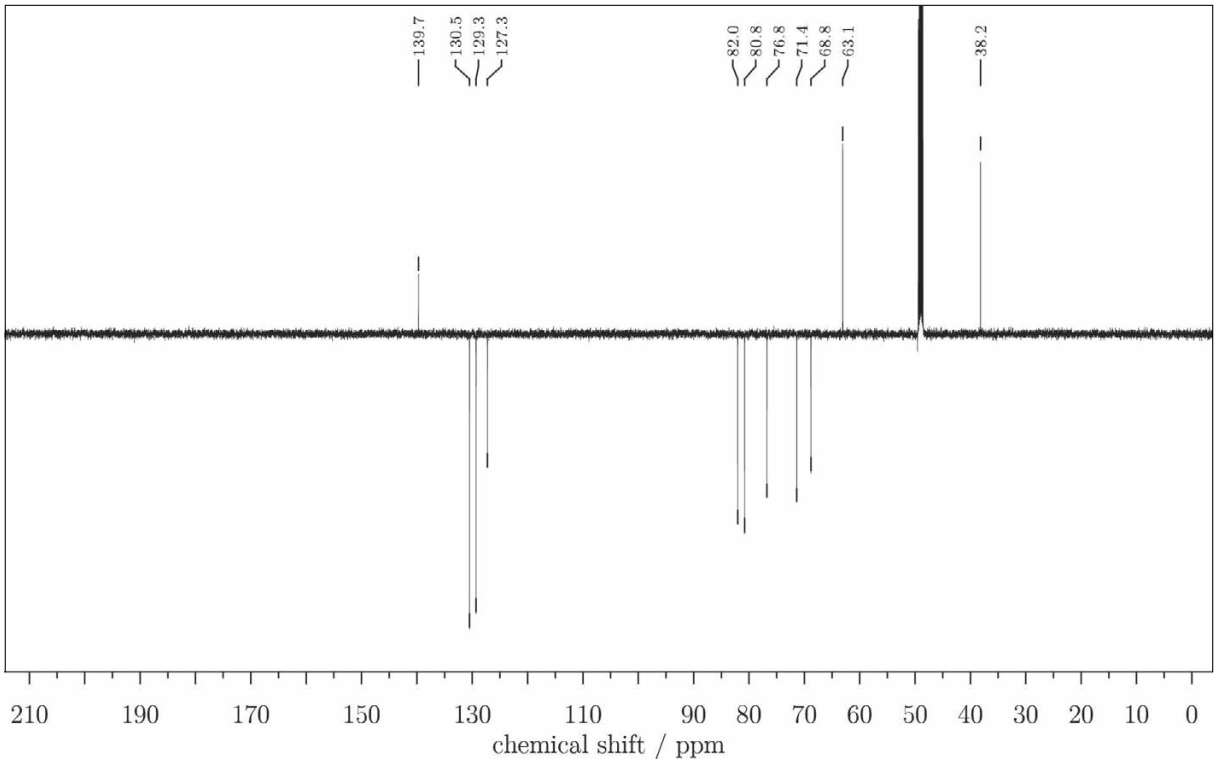


Figure 306: DEPTQ-NMR spectrum of **285** at 151 MHz in methanol-d_4.

8.3 SCXRD-structures

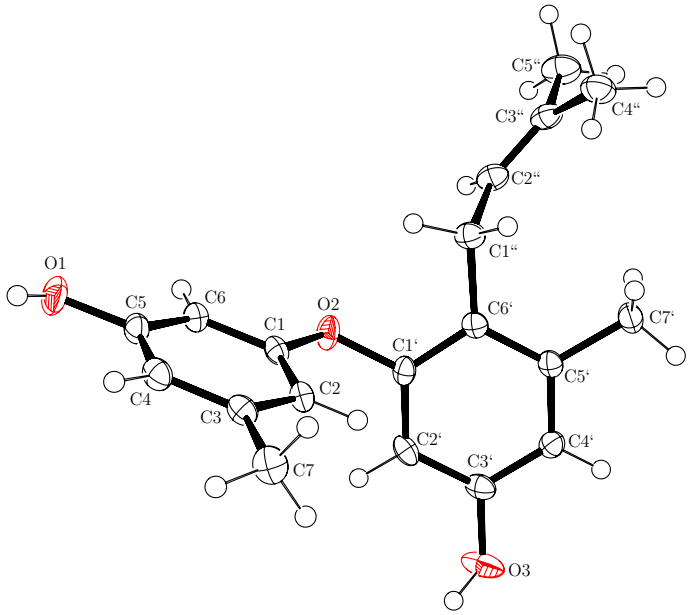


Figure 307: Single-crystal X-ray structure of **1** with labels. Thermal ellipsoids are shown at 50% probability level.

Compound	**1**	Z	2
Formula	$C_{19}H_{22}O_3$	Wavelength/Å	1.54184
$D_{calc.}$/	1.227	Radiation type	CuK_α
μ/mm^{-1}	0.652	Θ_{min}/°	4.1670
Formula Weight	298.36	Θ_{max}/°	76.310
Color	Colorless	Measured Refl.	16637
Shape	Plate	Independent Refl.	3359
Size/mm^3	0.208 × 0.101 × 0.058	Reflections used	9921
T/K	100	R_{int}	0.0352
Crystal System	triclinic	Parameters	213
Space Group	P-1	Restraints	0
a/Å	8.5202 (3)	Largest Peak	0.198
b/Å	9.2331 (3)	Deepest Hole	-0.195
c/Å	11.3314 (5)	GooF	1.036
α/°	80.014 (3)	wR_2 (all data)	0.0974
β/°	69.961 (4)	wR_2	0.0942
γ/°	75.725 (3)	R_1 (all data)	0.0436
V/Å$_3$	807.71 (6)	R_1	0.0394

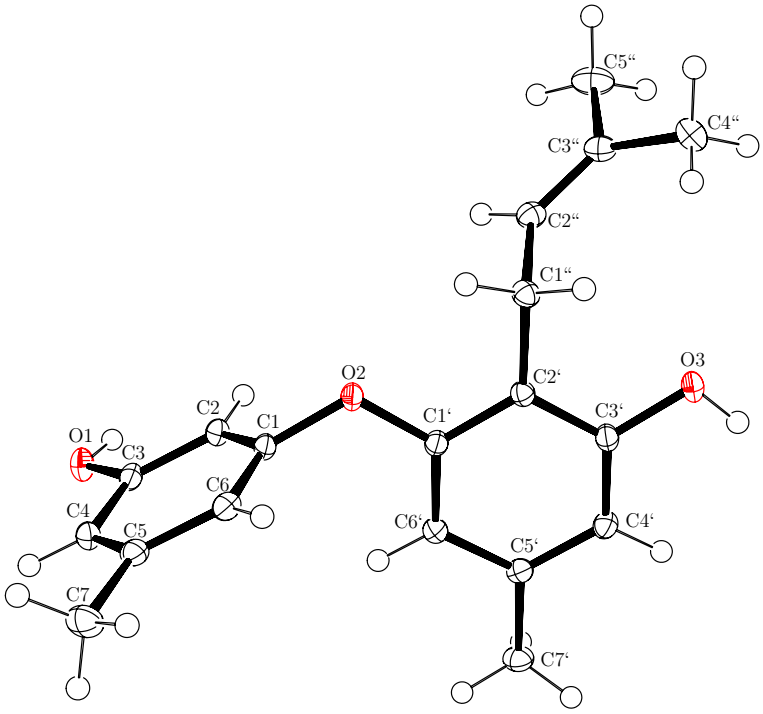


Figure 308: Single-crystal X-ray structure of **2** with labels. Thermal ellipsoids are shown at 50% probability level.

Compound	**2**	Z	2
Formula	$C_{19}H_{22}O_3$	Wavelength/Å	0.71073
$D_{calc.}$/	1.217	Radiation type	MoK_α
μ/mm^{-1}	0.081	Θ_{min}/°	2.198
Formula Weight	298.36	Θ_{max}/°	31.592
Color	Colorless	Measured Refl.	42515
Shape	Plate	Independent Refl.	5420
Size/mm^3	0.20 × 0.20 × 0.05	Reflections used	?
T/K	273.15	R_{int}	0.0242
Crystal System	triclinic	Parameters	211
Space Group	P-1	Restraints	0
a/Å	9.4282 (2)	Largest Peak	0.53
b/Å	9.9819 (3)	Deepest Hole	-0.27
c/Å	10.0754 (3)	GooF	1.004
α/°	74.3200 (10)	wR_2 (all data)	0.1280
β/°	68.7360 (10)	wR_2	0.1234
γ/°	69.0210 (10)	R_1 (all data)	0.0464
V/Å$_3$	814.26(4)	R_1	0.0417

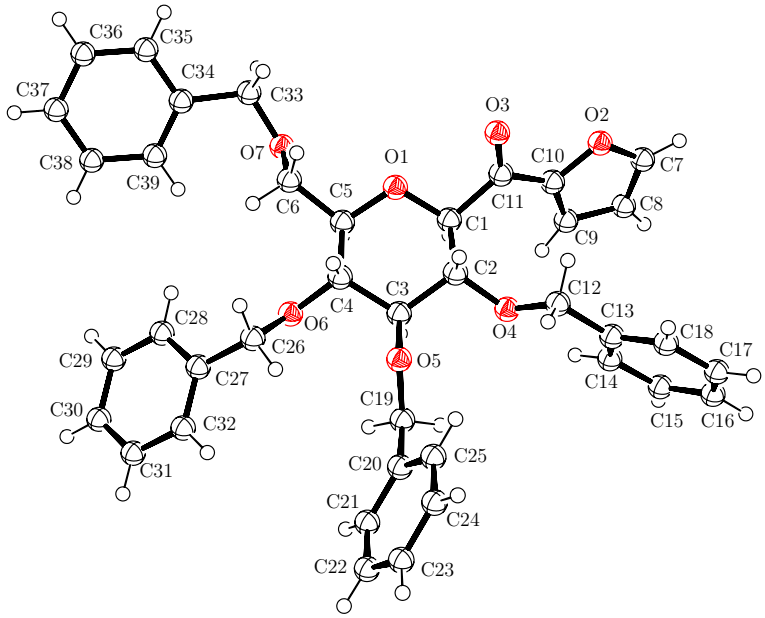


Figure 309: Single-crystal X-ray structure of **163** with labels. Thermal ellipsoids are shown at 50% probability level.

Compound	**163**	Z	2
Formula	$C_{39}H_{38}O_7$	Wavelength/Å	1.54184
$D_{calc.}$/	1.294	Radiation type	CuK_α
μ/mm^{-1}	0.713	Θ_{min}/°	6.544
Formula Weight	618.69	Θ_{max}/°	75.8960
Color	Colorless	Measured Refl.	9501
Shape	Needle	Independent Refl.	5755
Size/mm^3	0.32 x 0.04 x 0.03	Reflections used	4172
T/K	99.95(18)	R_{int}	0.0351
Crystal System	monoclinic	Parameters	415
Space Group	$P2_1$	Restraints	1
a/Å	13.8668(6)	Largest Peak	0.23
b/Å	5.54237(18)	Deepest Hole	-0.33
c/Å	21.2114(9)	GooF	1.099
α/°	90	wR_2 (all data)	0.1573
β/°	103.109(4)	wR_2	0.1312
γ/°	90	R_1 (all data)	0.0577
V/Å$_3$	1587.72(11)	R_1	0.0478

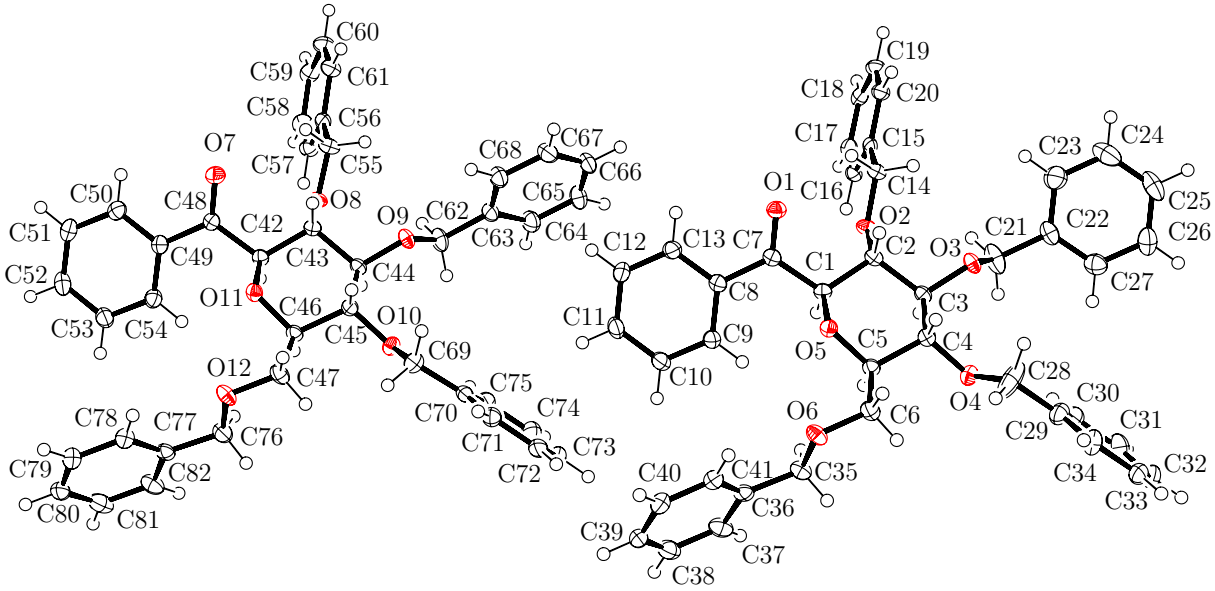


Figure 310: Single-crystal X-ray structure of **170** with labels. Thermal ellipsoids are shown at 50% probability level. Hydrogen atoms are omitted for clarity

Compound	**170**	Z	4
Formula	$C_{41}H_{40}O_6$	Wavelength/Å	1.54184
$D_{calc.}$/	1.273	Radiation type	CuK_α
μ/mm^{-1}	0.675	Θ_{min}/°	7.266
Formula Weight	628.73	Θ_{max}/°	76.301
Color	Colorless	Measured Refl.	60067
Shape	Needle	Independent Refl.	13501
Size/mm^3	0.25 × 0.04 × 0.03	Reflections used	22404
T/K	99.99(14)	R_{int}	0.0392
Crystal System	monoclinic	Parameters	847
Space Group	$P2_1$	Restraints	1
a/Å	20.3293(3)	Largest Peak	0.30
b/Å	5.64900(10)	Deepest Hole	-0.41
c/Å	28.6741(5)	GooF	1.015
α/°	90	wR_2 (all data)	0.0898
β/°	94.828(2)	wR_2	0.0865
γ/°	90	R_1 (all data)	0.0402
V/Å$_3$	3281.26(10)	R_1	0.0349

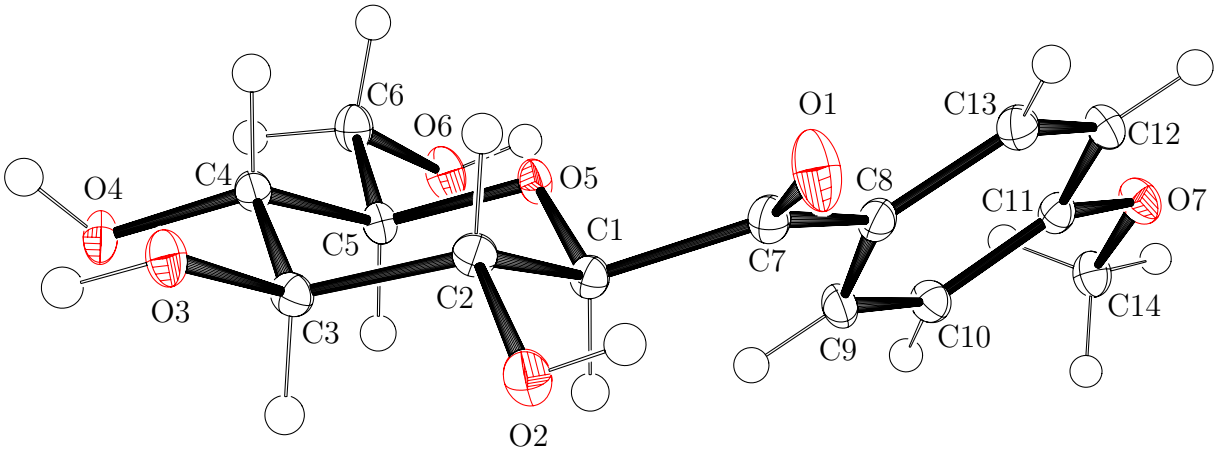


Figure 311: Single-crystal X-ray structure of **178** with labels. Thermal ellipsoids are shown at 50% probability level.

Compound	**178**	Z	2
Formula	$C_{14}H_{18}O_7$	Wavelength/Å	1.54184
$D_{calc.}$/	1.466	Radiation type	CuK_α
μ/mm^{-1}	1.006	Θ_{min}/°	9.374
Formula Weight	298.29	Θ_{max}/°	76.401
Color	Colorless	Measured Refl.	7541
Shape	Block	Independent Refl.	2671
Size/mm^3	0.42 × 0.26 × 0.22	Reflections used	6224
T/K	104(6)	R_{int}	0.0485
Crystal System	monoclinic	Parameters	193
Space Group	$P2_1$	Restraints	0
a/Å	9.3546(2)	Largest Peak	0.20
b/Å	6.98170(10)	Deepest Hole	-0.23
c/Å	11.2146(3)	GooF	1.023
α/°	90	wR_2 (all data)	0.0738
β/°	112.716(3)	wR_2	0.0738
γ/°	90	R_1 (all data)	0.0261
V/Å$_3$	675.62(3)	R_1	0.0261

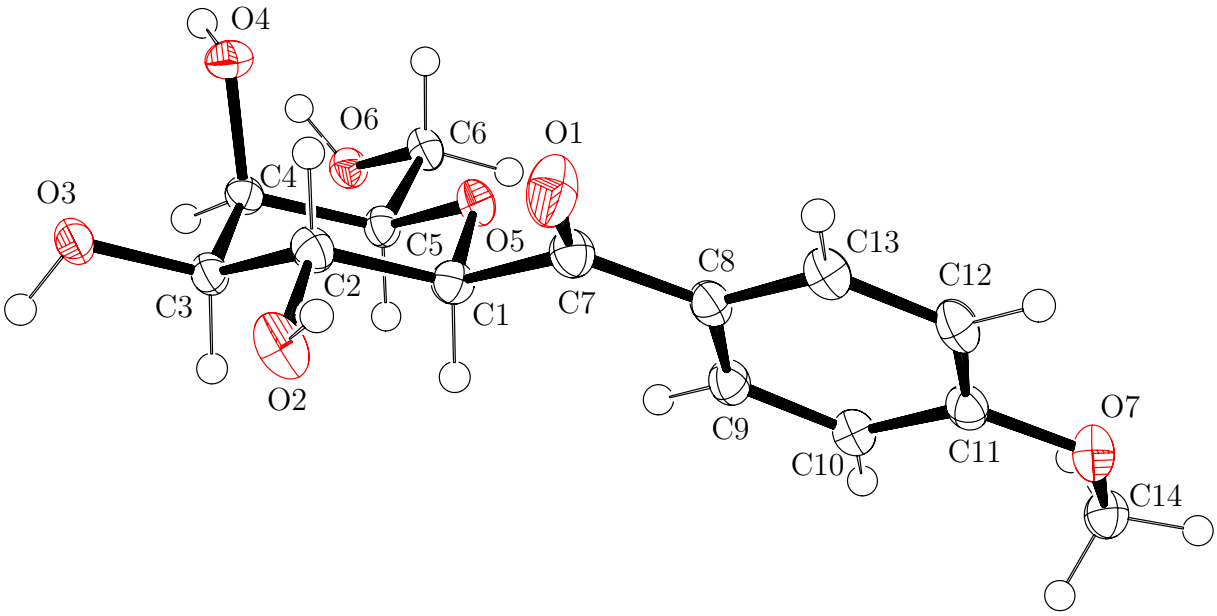


Figure 312: Single-crystal X-ray structure of **183** with labels. Thermal ellipsoids are shown at 50% probability level.

Compound	**183**	Z	2
Formula	$C_{14}H_{18}O_7$	Wavelength/Å	1.54184
$D_{calc.}$/	1.476	Radiation type	CuK_α
μ/mm^{-1}	1.013	Θ_{min}/°	11.234
Formula Weight	298.29	Θ_{max}/°	76.386
Color	Colorless	Measured Refl.	11200
Shape	Needle	Independent Refl.	2530
Size/mm^3	0.3 × 0.04 × 0.03	Reflections used	5451
T/K	99.97(13)	R_{int}	0.0371
Crystal System	monoclinic	Parameters	207
Space Group	$P2_1$	Restraints	1
a/Å	4.8668(2)	Largest Peak	0.22
b/Å	9.2940(5)	Deepest Hole	-0.18
c/Å	14.9475(7)	GooF	1.054
α/°	90	wR_2 (all data)	0.0752
β/°	97.038(4)	wR_2	0.0731
γ/°	90	R_1 (all data)	0.0317
V/Å$_3$	671.01(6)	R_1	0.0292

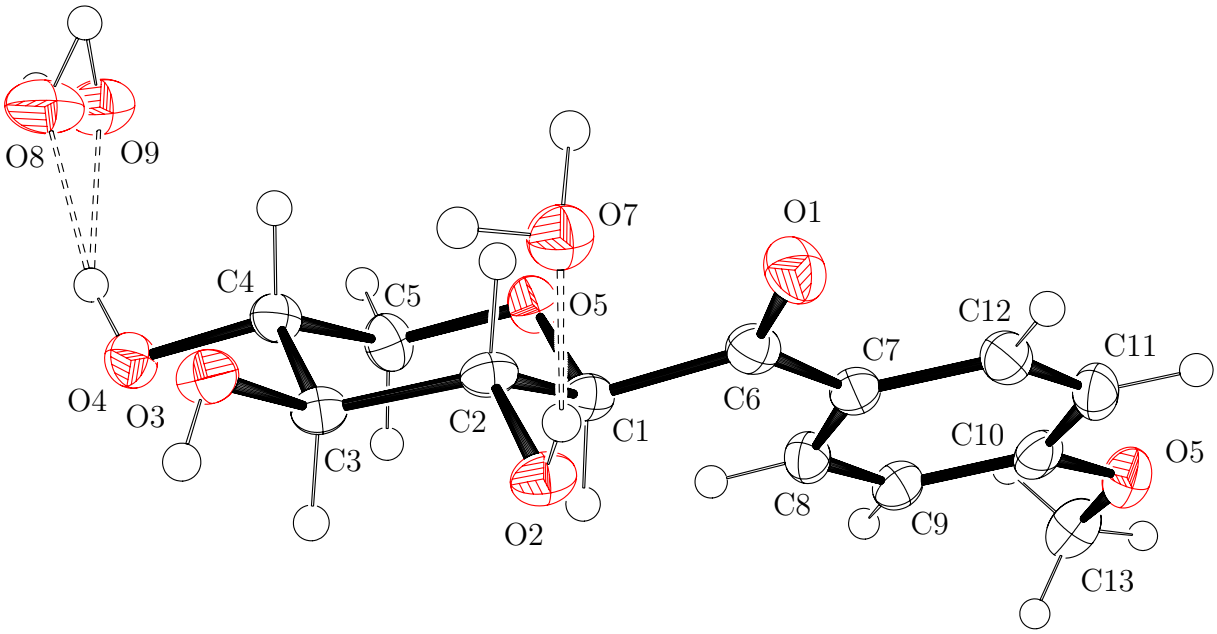


Figure 313: Single-crystal X-ray structure of **185** with labels. Thermal ellipsoids are shown at 50% probability level.

Compound	**185**	Z	4
Formula	$C_{13}H_{20}O_8$	Wavelength/Å	1.54184
$D_{calc.}$/	1.398	Radiation type	CuK_α
μ/mm^{-1}	1.000	Θ_{min}/°	9.128
Formula Weight	304.29	Θ_{max}/°	76.209
Color	Colorless	Measured Refl.	25040
Shape	Plate	Independent Refl.	3013
Size/mm^3	0.32 × 0.12 × 0.1	Reflections used	11804
T/K	99.97(15)	R_{int}	0.0379
Crystal System	orthorhombic	Parameters	229
Space Group	$P2_12_12_1$	Restraints	0
a/Å	4.46090(10)	Largest Peak	0.25
b/Å	10.1702(2)	Deepest Hole	-0.23
c/Å	31.8640(6)	GooF	1.067
α/°	90	wR_2 (all data)	0.0938
β/°	90	wR_2	0.0927
γ/°	90	R_1 (all data)	0.0350
V/Å$_3$	1445.61(5)	R_1	0.0336

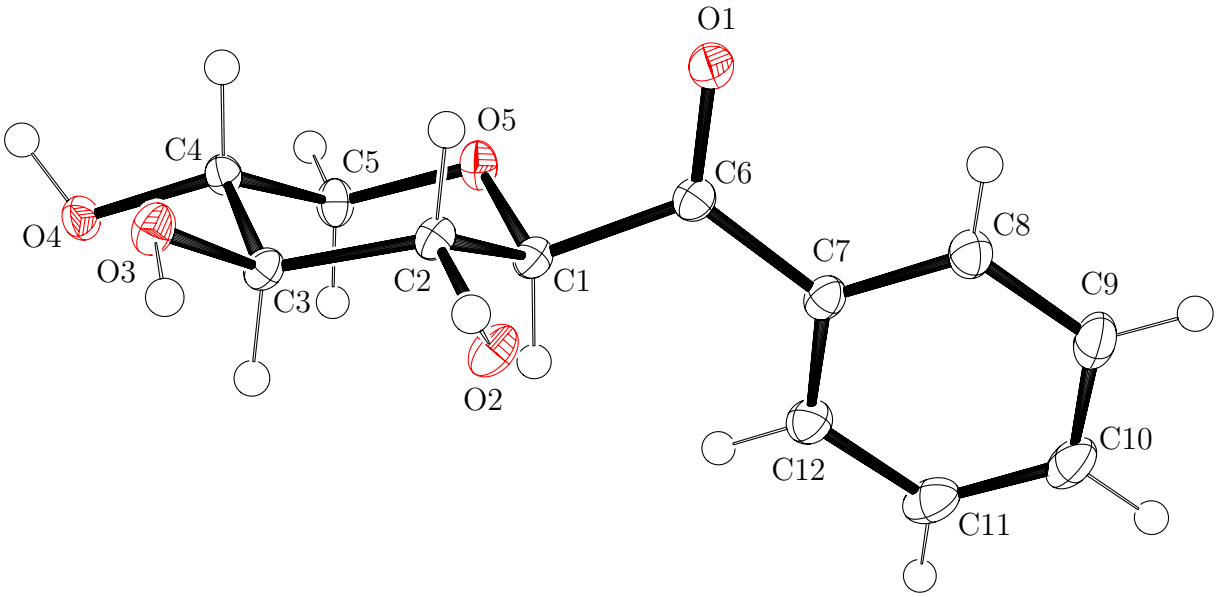


Figure 314: Single-crystal X-ray structure of **187** with labels. Thermal ellipsoids are shown at 50% probability level.

Compound	**187**	Z	4
Formula	$C_{12}H_{14}O_5$	Wavelength/Å	1.54184
$D_{calc.}$/	1.434	Radiation type	CuK_α
μ/mm^{-1}	0.945	Θ_{min}/°	13.182
Formula Weight	238.23	Θ_{max}/°	76.34
Color	Colorless	Measured Refl.	21134
Shape	Block	Independent Refl.	2305
Size/mm^3	0.32 × 0.12 × 0.1	Reflections used	17608
T/K	99.98(11)	R_{int}	0.0307
Crystal System	orthorhombic	Parameters	166
Space Group	$P2_12_12_1$	Restraints	0
a/Å	6.86322(6)	Largest Peak	0.22
b/Å	7.02544(5)	Deepest Hole	-0.18
c/Å	22.89155(15)	GooF	0.985
α/°	90	wR_2 (all data)	0.0689
β/°	90	wR_2	0.0685
γ/°	90	R_1 (all data)	0.0255
V/Å$_3$	1103.766(15)	R_1	0.0252

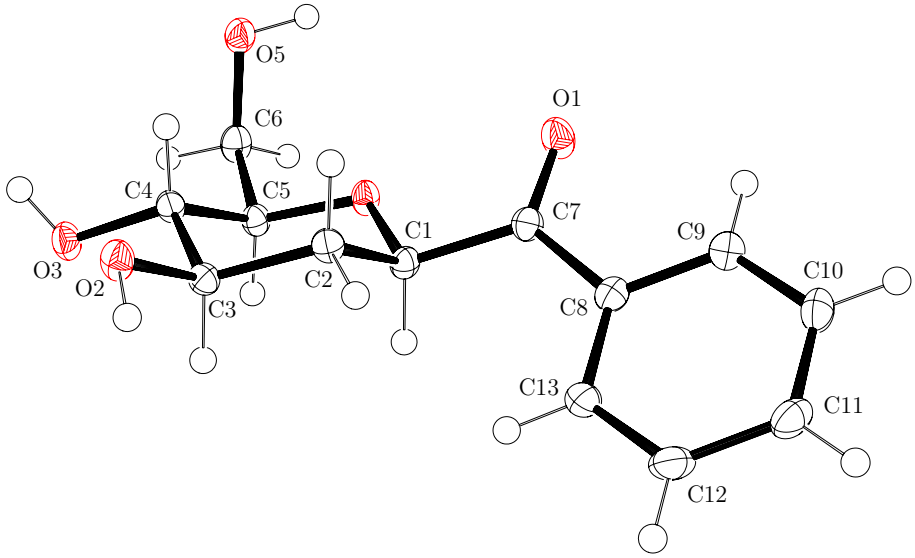


Figure 315: Single-crystal X-ray structure of **192** with labels. Thermal ellipsoids are shown at 50% probability level.

Compound	**192**	Z	4
Formula	$C_{13}H_{16}O_5$	Wavelength/Å	1.54184
$D_{calc.}$/	1.411	Radiation type	CuK_α
μ/mm^{-1}	0.909	Θ_{min}/°	7.408
Formula Weight	252.26	Θ_{max}/°	76.176
Color	Colorless	Measured Refl.	10154
Shape	Plate	Independent Refl.	2463
Size/mm^3	0.27 × 0.2 × 0.05	Reflections used	9147
T/K	99.98(10)	R_{int}	0.0181
Crystal System	monoclinic	Parameters	175
Space Group	C2	Restraints	1
a/Å	15.5771(4)	Largest Peak	0.22
b/Å	6.38930(10)	Deepest Hole	-0.16
c/Å	14.5777(3)	GooF	1.073
α/°	90	wR_2 (all data)	0.0645
β/°	125.044(3)	wR_2	0.0643
γ/°	90	R_1 (all data)	0.0237
V/Å$_3$	1187.84(6)	R_1	0.0235

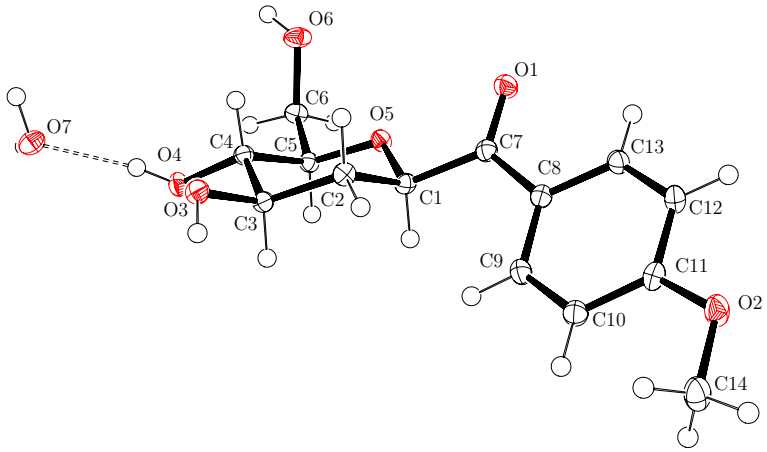


Figure 316: Single-crystal X-ray structure of **193** with labels. Thermal ellipsoids are shown at 50% probability level.

Compound	**193**	Z	4
Formula	$C_{14}H_{20}O_7$	Wavelength/Å	1.54184
$D_{calc.}$/	1.414	Radiation type	CuK_α
μ/mm^{-1}	0.964	Θ_{min}/°	6.564
Formula Weight	300.30	Θ_{max}/°	76.202
Color	Colorless	Measured Refl.	25702
Shape	Plate	Independent Refl.	2945
Size/mm^3	0.27 × 0.25 × 0.07	Reflections used	22038
T/K	100.00(10)	R_{int}	0.0235
Crystal System	orthorhombic	Parameters	211
Space Group	$P2_12_12_1$	Restraints	0
a/Å	7.06189(6)	Largest Peak	0.22
b/Å	7.41748(4)	Deepest Hole	-0.17
c/Å	26.93514(16)	GooF	1.050
α/°	90	wR_2 (all data)	0.0643
β/°	90	wR_2	0.0642
γ/°	90	R_1 (all data)	0.0230
V/Å$_3$	1410.901(16)	R_1	0.0229

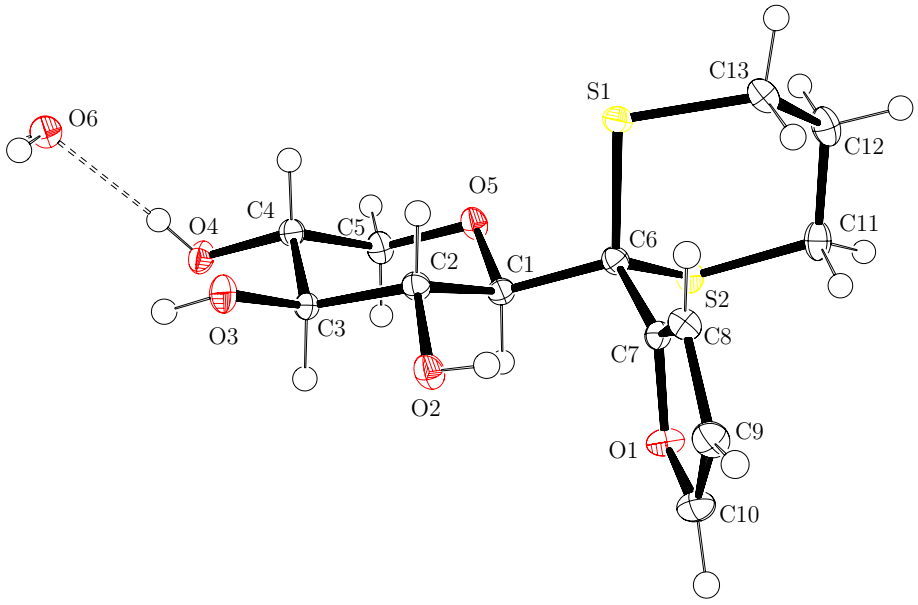


Figure 317: Single-crystal X-ray structure of **199** with labels. Thermal ellipsoids are shown at 50% probability level.

Compound	**199**	Z	2
Formula	$C_{13}H_{20}O_6S_2$	Wavelength/Å	1.54184
$D_{calc.}$/	1.512	Radiation type	CuK_α
μ/mm^{-1}	3.505	Θ_{min}/°	6.488
Formula Weight	336.41	Θ_{max}/°	76.1040
Color	Colorless	Measured Refl.	16391
Shape	Needle	Independent Refl.	2861
Size/mm^3	0.35 × 0.04 × 0.03	Reflections used	12869
T/K	99.94(16)	R_{int}	0.0307
Crystal System	monoclinic	Parameters	210
Space Group	$P2_1$	Restraints	1
a/Å	7.39110(10)	Largest Peak	0.18
b/Å	7.33740(10)	Deepest Hole	-0.15
c/Å	14.1095(2)	GooF	1.042
α/°	90	wR_2 (all data)	0.0504
β/°	105.0870(10)	wR_2	0.0502
γ/°	90	R_1 (all data)	0.0194
V/Å$_3$	738.804(18)	R_1	0.0192

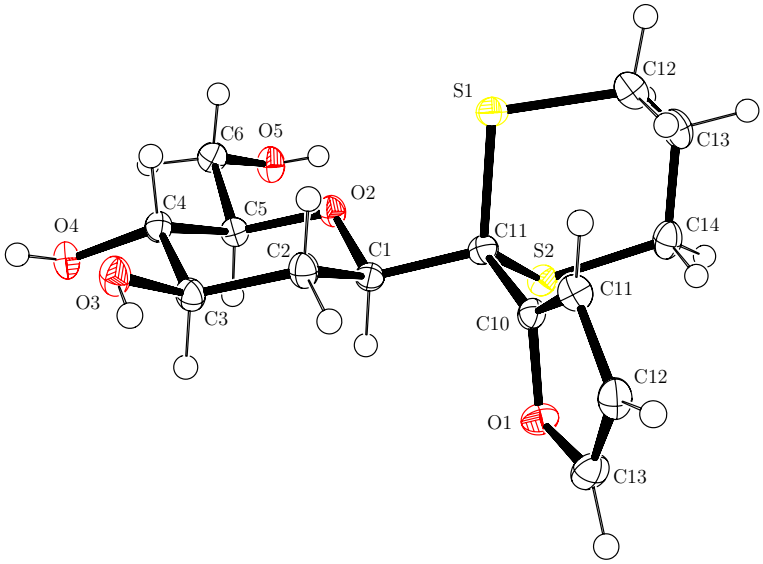


Figure 318: Single-crystal X-ray structure of **200** with labels. Thermal ellipsoids are shown at 50% probability level.

Compound	**200**	Z	4
Formula	$C_{14}H_{20}O_5S_2$	Wavelength/Å	1.54184
$D_{calc.}$/	1.483	Radiation type	CuK_α
μ/mm^{-1}	3.422	Θ_{min}/°	9.374
Formula Weight	332.42	Θ_{max}/°	76.4010
Color	Colorless	Measured Refl.	28775
Shape	Needle	Independent Refl.	3119
Size/mm^3	0.3 × 0.1 × 0.05	Reflections used	15409
T/K	99.98(13)	R_{int}	0.0485
Crystal System	orthorhombic	Parameters	193
Space Group	$P2_12_12_1$	Restraints	0
a/Å	7.34901(11)	Largest Peak	0.28
b/Å	10.73447(19)	Deepest Hole	-0.28
c/Å	18.8677(4)	GooF	1.068
α/°	90	wR_2 (all data)	0.0728
β/°	90	wR_2	0.0721
γ/°	90	R_1 (all data)	0.0276
V/Å$_3$	1488.43(5)	R_1	0.0270

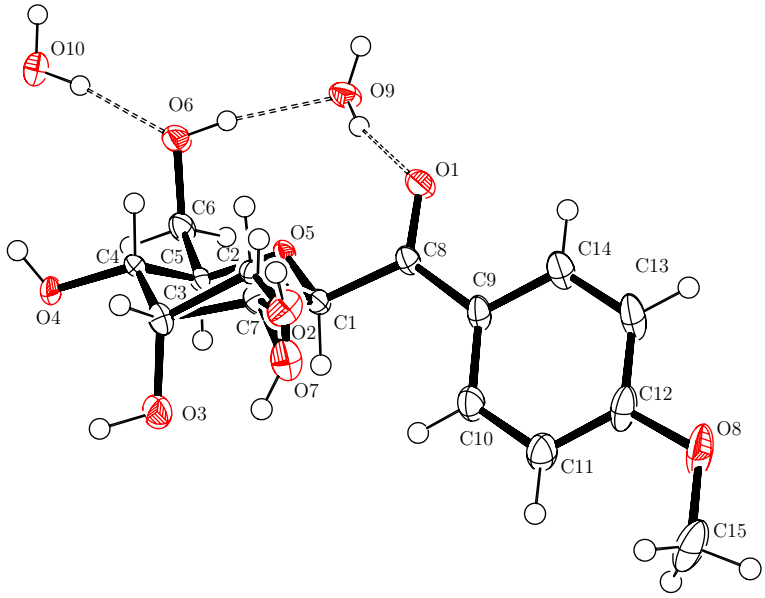


Figure 319: Single-crystal X-ray structure of **204** with labels. Thermal ellipsoids are shown at 50% probability level.

Compound	**204**	Z	4
Formula	$C_{14}H_{22}O_9$	Wavelength/Å	1.54184
$D_{calc.}$/	1.429	Radiation type	CuK_α
μ/mm^{-1}	1.032	Θ_{min}/°	9.598
Formula Weight	334.31	Θ_{max}/°	76.234
Color	Colorless	Measured Refl.	28336
Shape	Needle	Independent Refl.	3224
Size/mm^3	0.35 × 0.04 × 0.03	Reflections used	15495
T/K	99.97(13)	R_{int}	0.0422
Crystal System	orthorhombic	Parameters	255
Space Group	$P2_12_12_1$	Restraints	0
a/Å	4.73720(10)	Largest Peak	0.59
b/Å	9.56610(10)	Deepest Hole	-0.23
c/Å	34.2950(4)	GooF	1.070
α/°	90	wR_2 (all data)	0.1121
β/°	90	wR_2	0.1116
γ/°	90	R_1 (all data)	0.0427
V/Å$_3$	1554.13(4)	R_1	0.0418

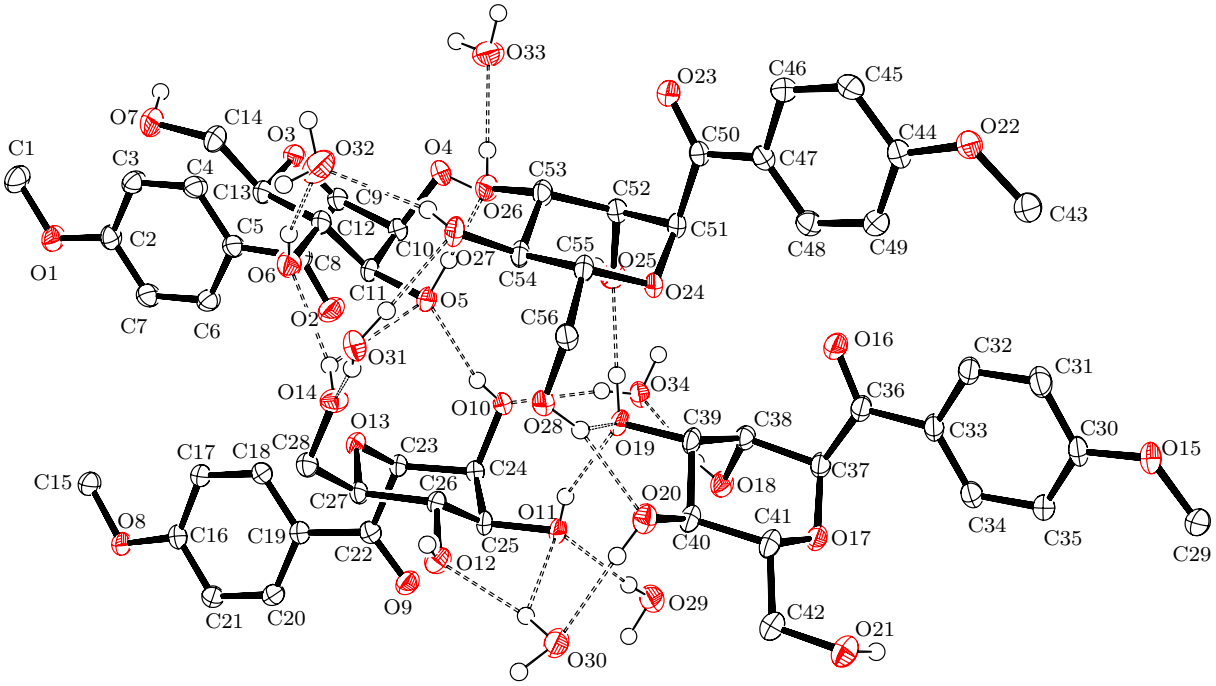


Figure 320: Single-crystal X-ray structure of **210** with labels. Thermal ellipsoids are shown at 50% probability level.

Compound	**210**	Z	1
Formula	$C_{28}H_{42}O_{17}$	Wavelength/Å	1.54184
$D_{calc.}$/	1.453	Radiation type	CuK_α
μ/mm^{-1}	1.038	Θ_{min}/°	4.2000
Formula Weight	650.61	Θ_{max}/°	75.8460
Color	Colorless	Measured Refl.	55990
Shape	Needle	Independent Refl.	11137
Size/mm^3	0.35 x 0.05 x 0.04	Reflections used	37828
T/K	99.9(3)	R_{int}	0.0440
Crystal System	triclinic	Parameters	906
Space Group	P1	Restraints	3
a/Å	7.51350(10)	Largest Peak	0.35
b/Å	12.2717(2)	Deepest Hole	-0.22
c/Å	16.6604(3)	GooF	1.039
α/°	97.140(2)	wR_2 (all data)	0.0983
β/°	102.519(2)	wR_2	0.0976
γ/°	90.8310(10)	R_1 (all data)	0.0364
V/Å$_3$	1486.63(4)	R_1	0.0358

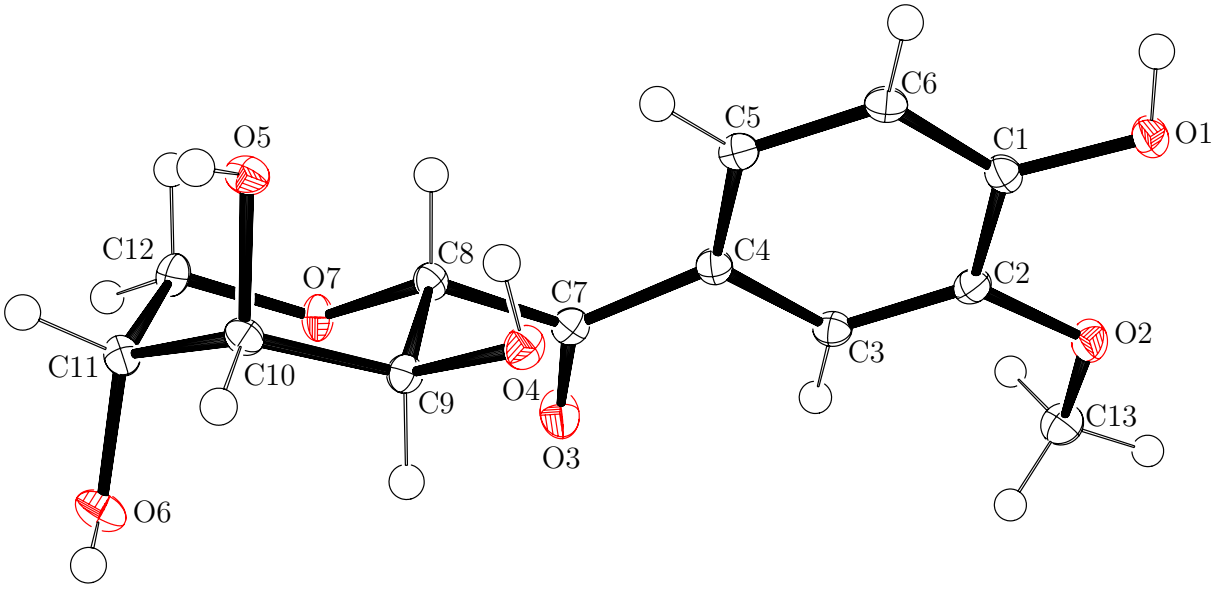


Figure 321: Single-crystal X-ray structure of **245** with labels. Thermal ellipsoids are shown at 50% probability level.

Compound			
Formula	$C_{13}H_{16}O_7$	Z	4
$D_{calc.}$/	1.516	Wavelength/Å	1.54184
μ/mm^{-1}	1.062	Radiation type	CuK_α
Formula Weight	284.26	Θ_{min}/°	4.3050
Color	Colorless	Θ_{max}/°	76.0640
Shape	Needle	Measured Refl.	48377
Size/mm^3	0.32 x 0.1 x 0.08	Independent Refl.	2597
T/K	99.95(15)	Reflections used	36346
Crystal System	orthorhombic	R_{int}	0.0395
Space Group	$P2_12_12_1$	Parameters	198
a/Å	4.93020(3)	Restraints	0
b/Å	11.53370(8)	Largest Peak	0.23
c/Å	21.90560(19)	Deepest Hole	-0.19
α/°	90	GooF	1.037
β/°	90	wR_2 (all data)	0.0645
γ/°	90	wR_2	0.0642
V/Å$_3$	1245.628(16)	R_1 (all data)	0.0236
		R_1	0.0233

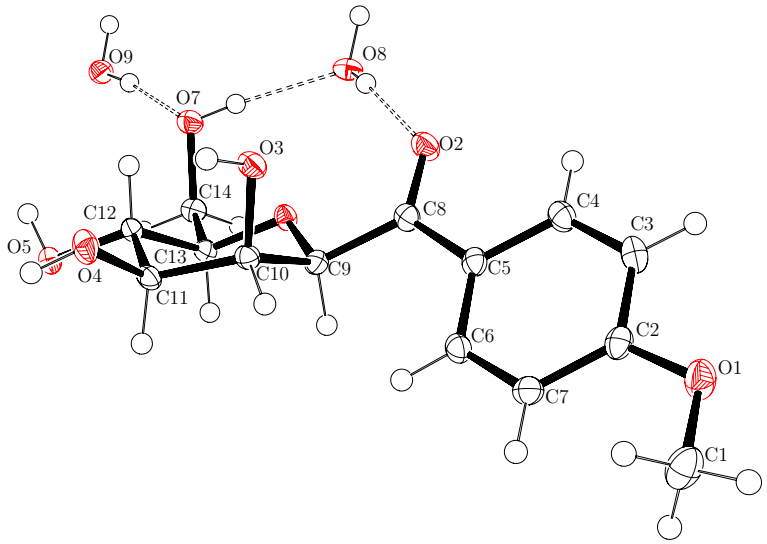


Figure 322: Single-crystal X-ray structure of **251** with labels. Thermal ellipsoids are shown at 50% probability level.

Compound	**251**	Z	1
Formula	$C_{14}H_{22}O_9$	Wavelength/Å	1.54184
$D_{calc.}$/	1.465	Radiation type	CuK_α
μ/mm^{-1}	1.058	Θ_{min}/°	4.6860
Formula Weight	334.31	Θ_{max}/°	75.9360
Color	Colorless	Measured Refl.	83810
Shape	Needle	Independent Refl.	3147
Size/mm^3	0.3 x 0.04 x 0.02	Reflections used	35489
T/K	99.9(2)	R_{int}	0.0784
Crystal System	orthorhombic	Parameters	241
Space Group	$P2_12_12_1$	Restraints	0
a/Å	4.67340(10)	Largest Peak	0.20
b/Å	9.7092(2)	Deepest Hole	-0.21
c/Å	33.4069(4)	GooF	1.058
α/°	90	wR_2 (all data)	0.0932
β/°	90	wR_2	0.0925
γ/°	90	R_1 (all data)	0.0371
V/Å$_3$	1515.84(5)	R_1	0.0359

9 Danksagung

An dieser Stelle möchte ich mich bei allen bedanken, die mich unterstützt haben.

Der Stadt Hamburg möchte ich für die finanzielle Unterstützung in Form des Promotionsstipendiums danken.

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10 Eidesstattliche Versicherung

Hiermit versichere ich an Eides statt, die vorliegende Dissertation selbst verfasst und keine anderen als die angegebenen Hilfsmittel benutzt zu haben. Die eingereichte schriftliche Fassung entspricht der auf dem elektronischen Speichermedium. Ich versichere, dass diese Dissertation nicht in einem früheren Promotionsverfahren eingereicht wurde.

Hamburg, _____