SUMMARY

Bicyclic thiosugars are important compounds according to their biological activities. They are potential *anti*-thrombotics and potential glucosidase inhibitors. They are also suitable precursors for the synthesis of Locked Nucleic Acids (LNA) and for the synthesis of 4-thiofuranoses or 3-thietanoses. We therefore developed new pathways for the synthesis of 2,5- and 3,5-chalcogenoanhydropentofuranosides. Depending on the nature of the chalcogene different strategies were necessary.

Oxygen

We applied the intramolecular Mitsunobu reaction for the preparation of the epoxysugar **4a** from **9a**. The bicyclic azidosugar **22a** was obtained in two further steps from **4a** including another intramolecular Mitsunobu reaction of **21a**.
Similarly the intramolecular Mitsunobu reaction can be also used to prepare **17a** from **15a**.

Sulfur

The thio-Mitsunobu reaction was applied for the introduction of sulfur into the sugar. Only primary hydroxy groups were attacked. Subsequently the thietano sugar **40a** was obtained from **38a** *via* **39a** by an intramolecular S_N2 reaction. This reaction sequence can also be performed with the corresponding β-anomer of **10a** as well as with xylofuranosides and ribofuranosides. Xylofuranosides are yielding 2,5-thioanhydrofuranosides and ribofuranosides are yielding 2,5- or 3,5-thioanhydrofuranosides depending on the reaction conditions.
Again using the intramolecular Mitsunobu reaction the epoxysugar **3b** was prepared from **9b**. Subsequent thio-Mitsunobu reaction and cyclization of **32b** yielded the 3,5-thioanhydrofuranoside **33b**. A 2,5-thioanhydrofuranoside could not be detected in this case. Similarly **47a** can be prepared from **45a** *via* **46a**. Several X-ray measurements could be performed and confirmed the correct structures of these thioanhydrofuranosides.

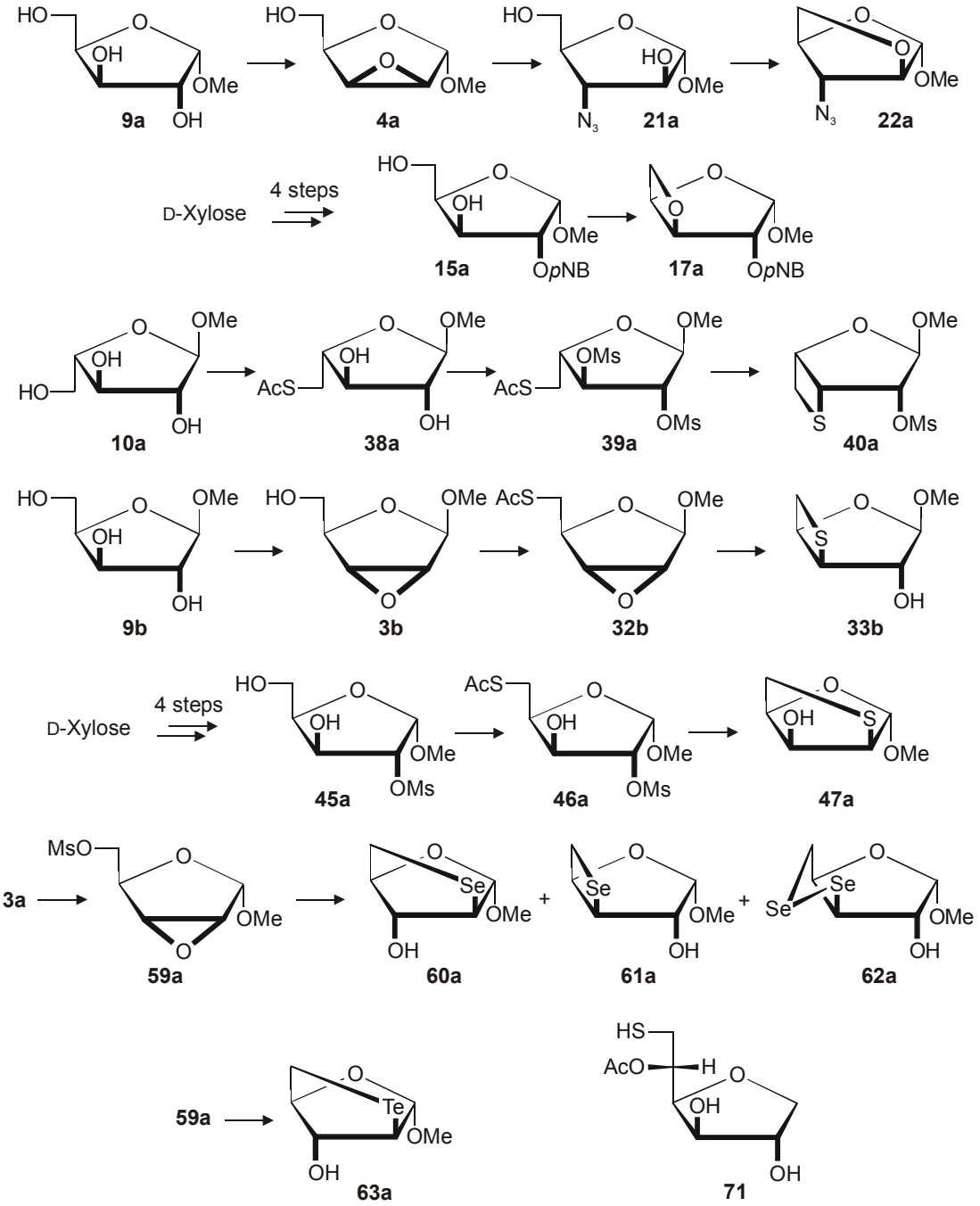
Selenium and Tellurium

The seleno- and telluroanhydrofuranosides were prepared from **3a** *via* **59a** by using *in situ* prepared NaHSe or NaHTe, respectively. Depending on the reaction conditions three different seleno derivates **60a**, **61a** and **62a** were formed in varying product ratios. The structure of the diselenide **62a** could be confirmed by an X-ray measurement. In the tellurium series only compound **63a** could be isolated, representing the first telluroanhydrosugar to the best of our knowledge.

Reactions in the alditol series

When we applied the thio-Mitsunobu reaction with pentofuranosides we observed total chemoselectivity, i.e. primary hydroxy groups can be selectively replaced by acetylthiogroups in the presence of secondary hydroxy groups. This prompted us to try analogous reactions in the alditol series. Alditols possess two primary hydroxy groups.

When we used D-glucitol we did not get the expected di-*S*-acetyl compound. Instead the anhydrohexitol **71** was formed in a good yield. When we used D-mannitol the expected di-*S*-acetyl compound was formed in poor yield beside some anhydrohexitol byproducts. Galactitol yielded a complex product mixture. Obviously glucitol reacts much better in a thio-Mitsunobu reaction than mannitol or galactitol. This might be caused by the unique hydrogen bonding feature of glucitol compared to other alditols. This could be verified by a density functional theory (DFT) type MO calculation of glucitol.



*p*NB = 4-nitrobenzoyl
Ms = methylsulfonyl