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Formation of C-Si bond in carbohydrates

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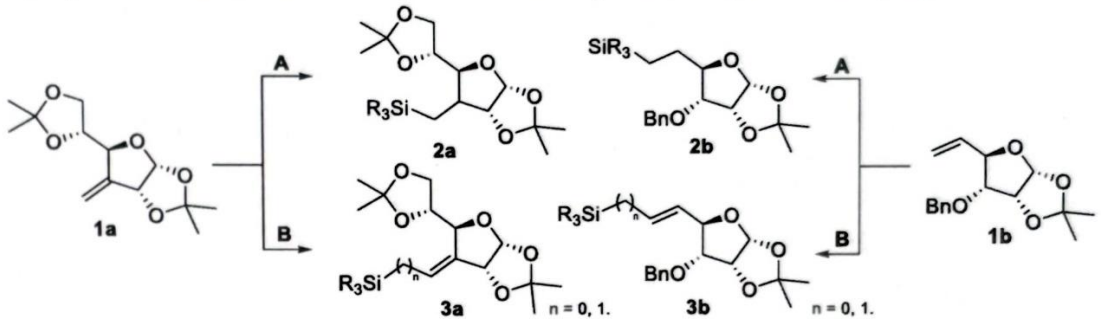
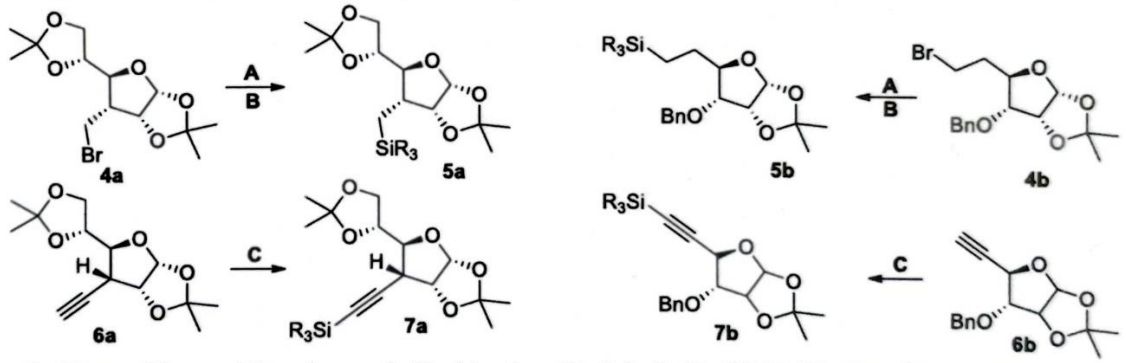
It is known that nucleosides can be linked by phosphate or peptide linkers. In this work we start the development of novel C-Si-C linkers, which could influence the properties of oligomers such as biological and chemical activity, stability and bond flexibility.[1,2] The work begins with C-Si bond formation in 3-deoxyallose and 5-deoxyribose. Several different methods for creating C-Si bonds were tried.

Terminal alkenes **1a** and **1b** were subjected to transition metal catalyzed hydrosilylation (Scheme 1, **A**) and metathesis reactions with alkenylsilanes (Scheme 2, **B**).



Scheme 1. Use of alkenes **1a** and **1b** (**A**: $HSiR_3$, cat., **B** alkenylsilane, Grubbs 2nd)

Bromides **4a** and **4b** and terminal alkynes **6a** un **6b** were lithiated and silylated with halosilanes (Scheme 2, **A** and C, respectively).



Scheme 2. Use of bromides **4a** and **4b** (**A**: 1. *t*-BuLi, 2. R_3SiCl, THF, -78° C, **B**: R_3SiLi, THF, -78° C, **C**: 1. *n*-BuLi, 2. R_3SiCl, THF).

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References

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2. Franz, A. K.; Wilson, S. O. *J. Med. Chem.* **2013**, *56*, 388-405.