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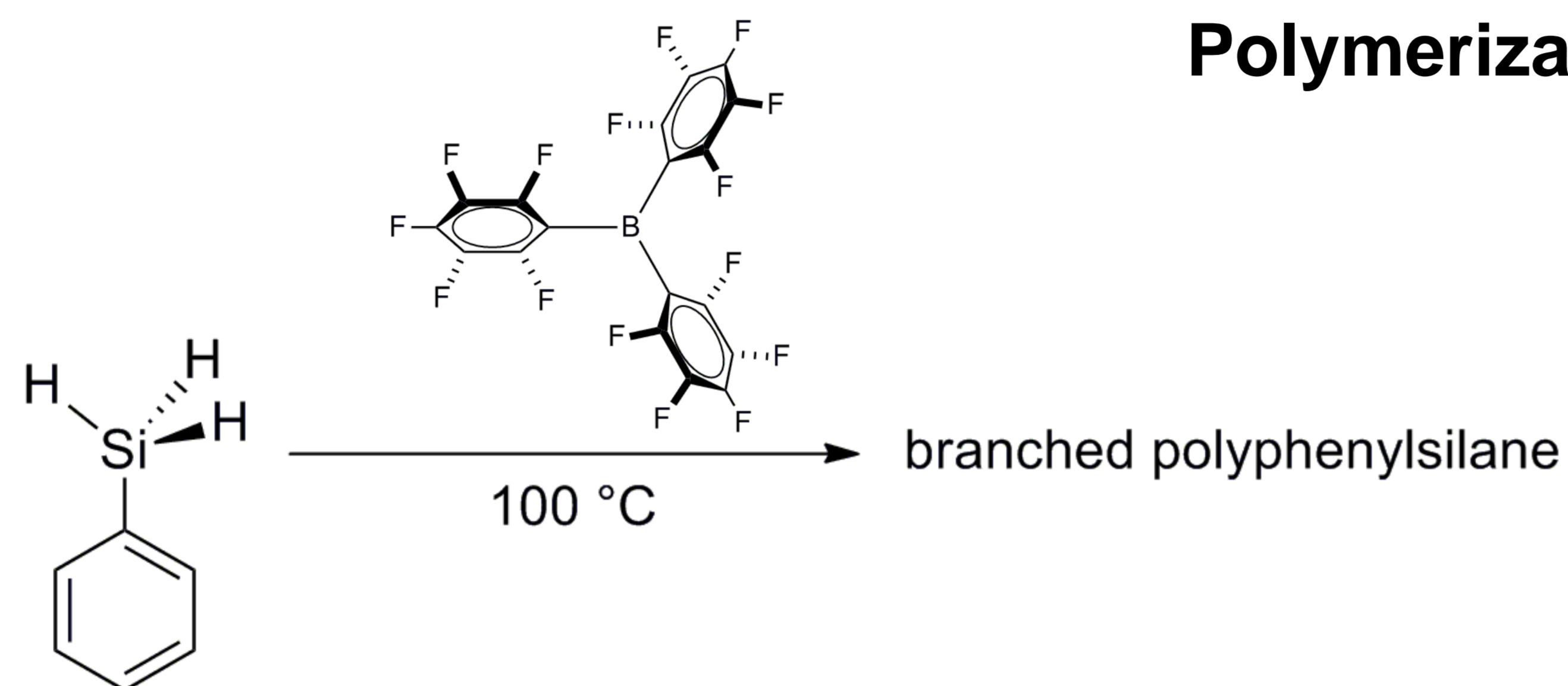
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### Introduction

Polysilanes, which consist exclusively of catenated silicon atoms in their backbone, have been known since the early 1920s.<sup>[1-3]</sup> Nonetheless reports on branched polysilanes are still rare.<sup>[4-7]</sup> In our studies we explored a novel metal-free synthesis of branched polyphenylsilanes of irregular substitution pattern using the strong organoborane Lewis acid tris(pentafluorophenyl)borane as catalyst. The polymerization mechanism was determined to be cationic by density functional theory calculations, which is presented in the second part of this study.

### Polymerization of Phenylsilane

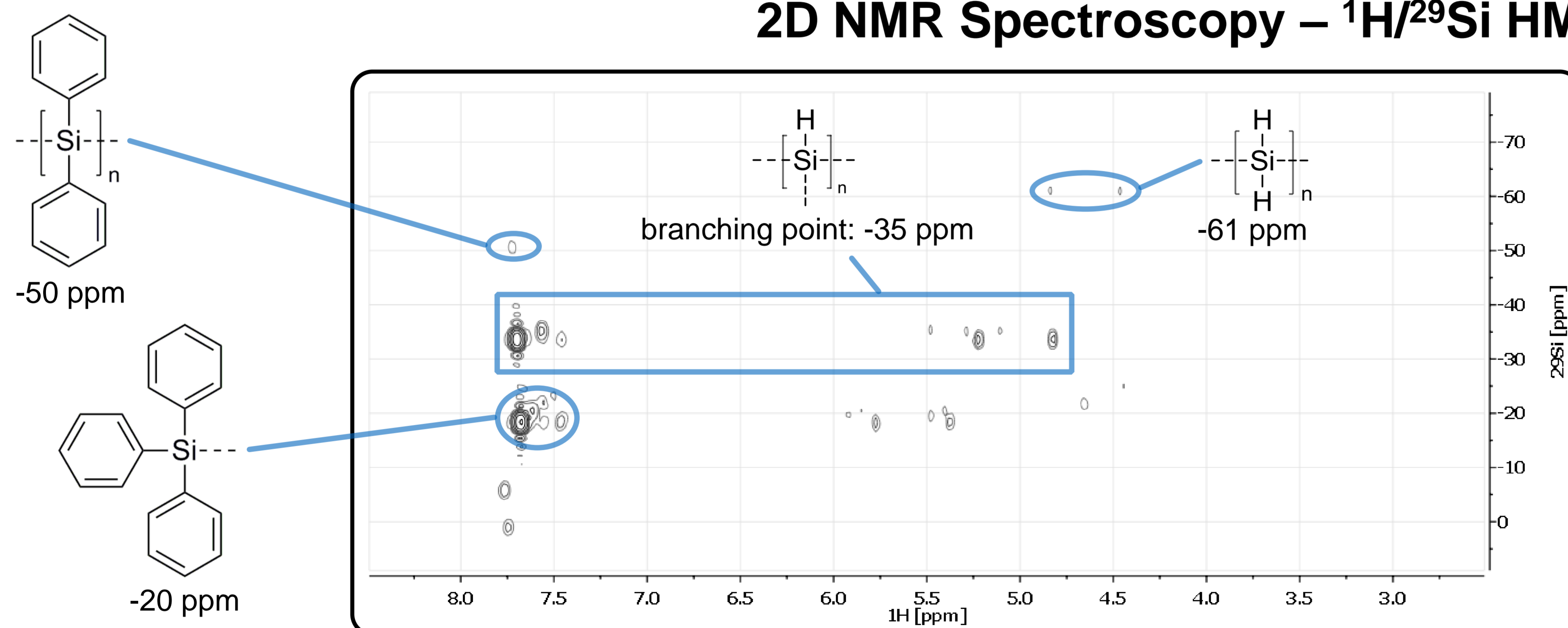


**Polymerization procedure:** 1 mL phenylsilane is added to B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> (substrate/catalyst ratio see table on the right) in a 50 mL Schlenk flask under cooling with liquid nitrogen. After degassing the reaction mixture is heated to the reaction temperature and is stirred for 24 hours under argon atmosphere. Unreacted monomer and the side product benzene were separated from the polymer under reduced pressure. The borane catalyst is removed via filtration from the polymer with neutral aluminum oxide and dry diethyl ether. Depending on the degree of polymerization, the polymer was obtained as a viscous, yellow liquid or a sticky brownish solid.

Entry	PhSiH <sub>3</sub> /B(C <sub>6</sub> F <sub>5</sub> ) <sub>3</sub>	Temperature /°C	M <sub>n</sub> /g·mol <sup>-1</sup>	M <sub>w</sub> /g·mol <sup>-1</sup>	Evolution of SiH <sub>4</sub>
1	230	60	–	–	–
2	230	100	800	900	–
3	230	120	1670	2700	–
4	16	60	1450	2000	+
5	16	100	1500	2170	+

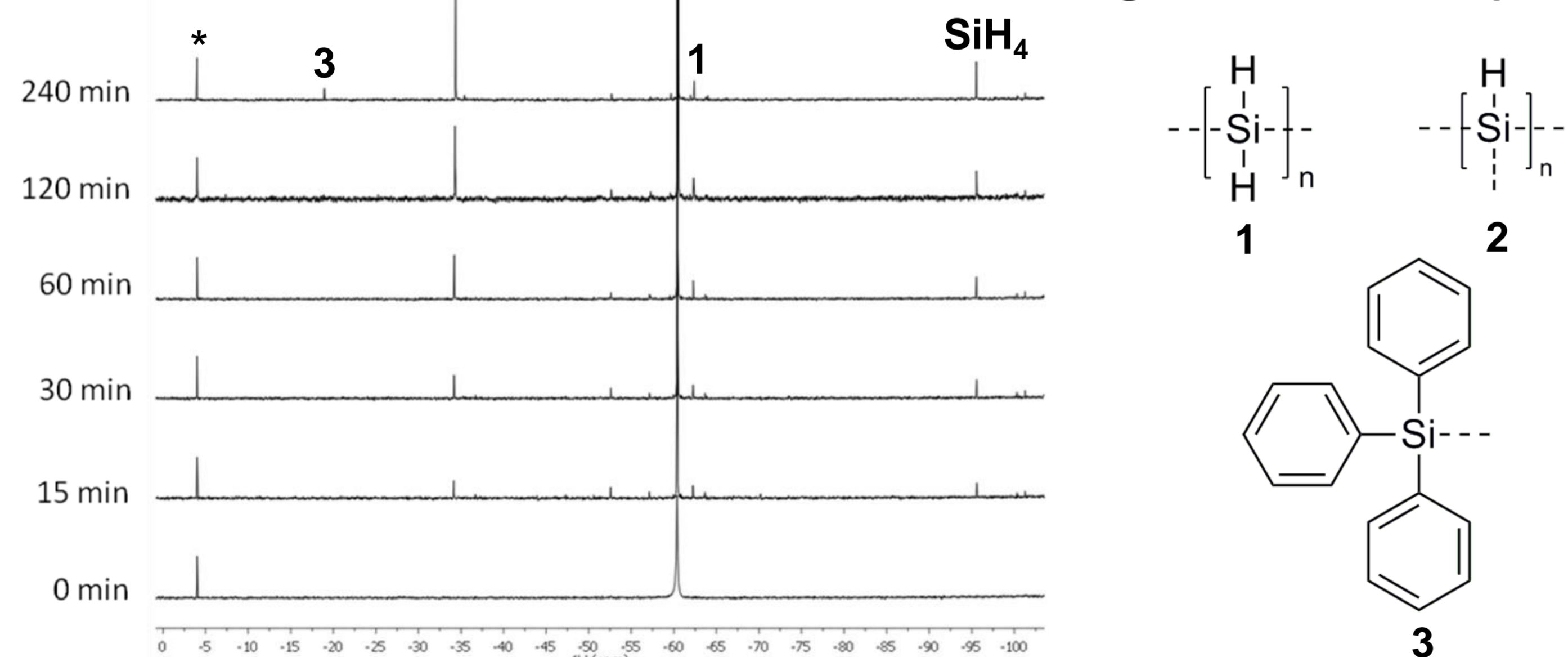
- a low substrate/catalyst ratio leads to low molecular weights and to the evolution of the side product SiH<sub>4</sub>
- a high substrate/catalyst ratio and an increased temperature result in a higher degree of polymerization and suppress the formation of SiH<sub>4</sub>

### 2D NMR Spectroscopy – <sup>1</sup>H/<sup>29</sup>Si HMBC



- multiple signals for different silicon species indicate substituent scrambling
- the most likely fragment HSiPh could not be found in the <sup>1</sup>H/<sup>29</sup>Si HMBC spectrum (-65 ppm)
- signals at -35 ppm hint at a branched structure

### <sup>29</sup>Si NMR Kinetics



- branching and scrambling occur within 15 minutes
- calculated degree of branching DB = 0.3
- low amount of terminal groups compared to the branching points suggests internal ring formation

\* divinyltetramethyldisiloxane (external standard)

### Other Borane Catalysts

Entry*	Catalyst	Substrate	M <sub>n</sub> /g·mol <sup>-1</sup>	M <sub>w</sub> /g·mol <sup>-1</sup>	Evolution of SiH <sub>4</sub>
1	BCl <sub>3</sub>	phenylsilane	750	850	–
2	B(C <sub>6</sub> F <sub>5</sub> ) <sub>3</sub>	phenylsilane	1500	2170	+
3	HB(C <sub>6</sub> F <sub>5</sub> ) <sub>2</sub>	phenylsilane	950	1150	–
4	B(C <sub>6</sub> F <sub>5</sub> ) <sub>3</sub>	diphenylsilane	–	–	–
5	HB(C <sub>6</sub> F <sub>5</sub> ) <sub>2</sub>	diphenylsilane	860	900	–

\* reaction at 100 °C; substrate/catalyst ratio = 16

- BCl<sub>3</sub> and HB(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub> catalyze the reaction as well, but the molecular weights of the resulting polymers are lower
- diphenylsilane can only be polymerized by the sterically less hindered Lewis acidic catalyst HB(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub> and not by BCl<sub>3</sub>

### Conclusion

The described synthesis is a new metal-free route towards branched polyphenylsilanes. 2D NMR spectroscopy revealed a branched and highly substituted structure of the resulting polymer. This novel synthesis of polysilanes holds great potential for the rational synthesis of branched as well as of linear polysilanes by optimizing the catalyst and the monomer substrate.

### References:

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### Acknowledgement

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