

# 9H-9-Borafluorene

## Preparation and utilization in hydroboration reactions

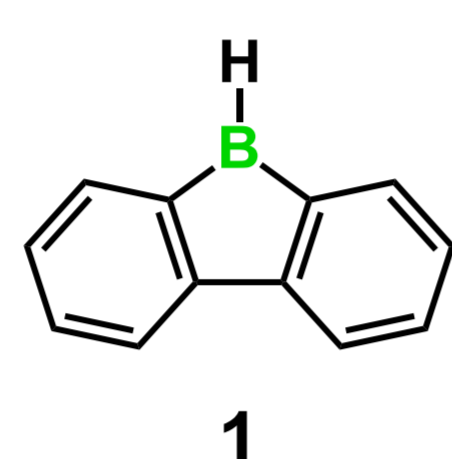
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### Introduction

The photophysical properties of  $\pi$ -conjugated materials can be tuned extensively by the incorporation of boron atoms into the organic framework.<sup>[1]</sup> Given this background, our group is interested in the development of novel boron-containing building blocks for luminescent organoboron compounds.

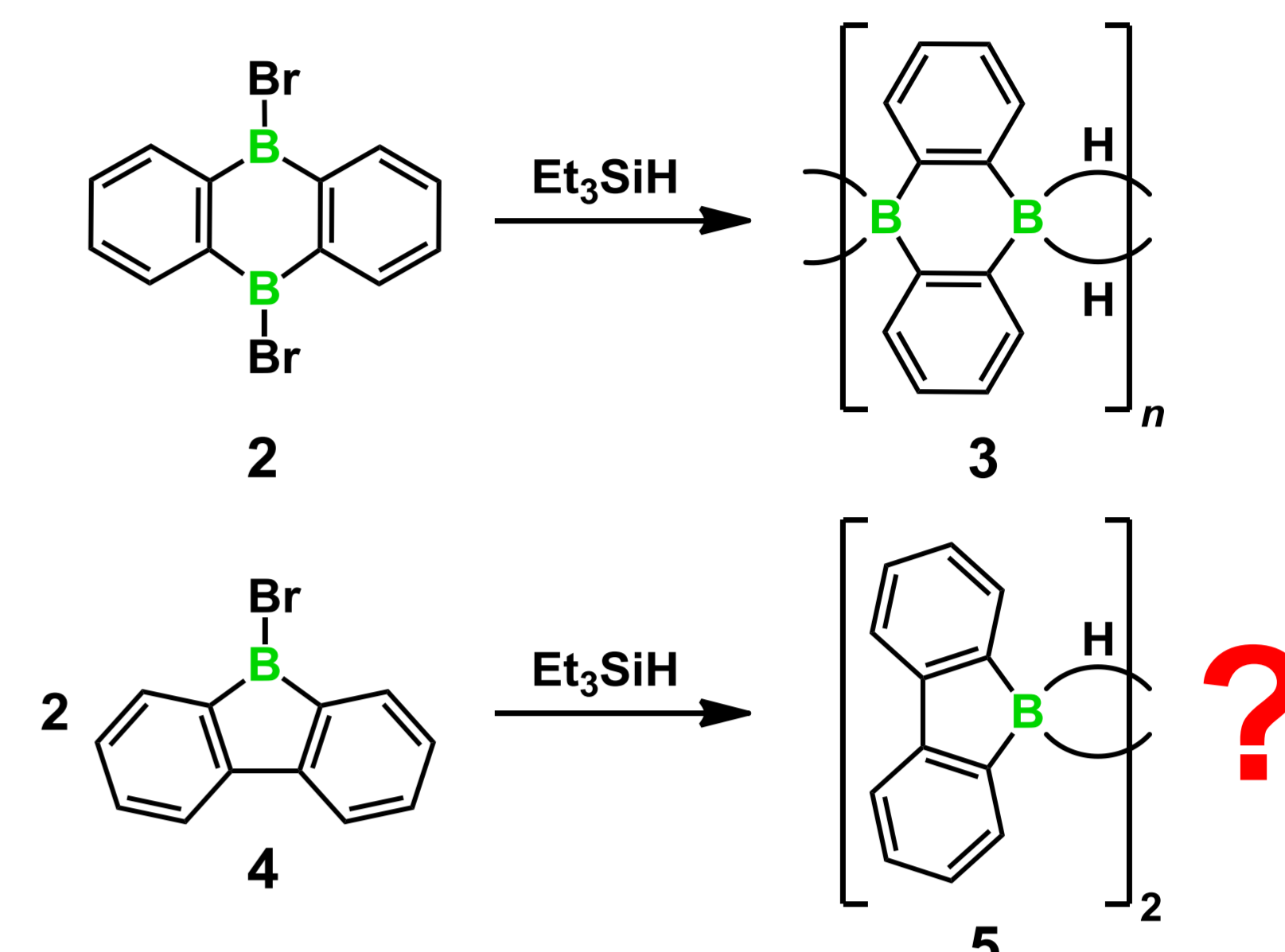
We therefore decided to prepare 9H-9-borafluorene (**1**), which had so far remained elusive, and investigated its suitability for hydroboration reactions.



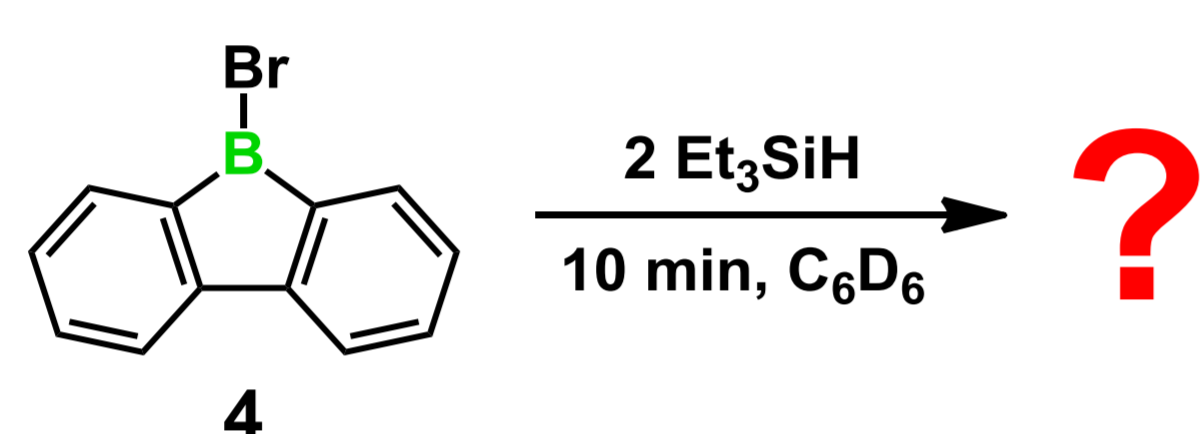
### Concept

The ditopic analogue of **1**, 9,10-dihydro-9,10-diboraanthracene (**3**), is accessible from the bromo derivative **2** and  $\text{Et}_3\text{SiH}$  as a hydride source.<sup>[2]</sup> We thus decided to prepare 9H-9-borafluorene (**1**) in a similar reaction by treating 9Br-9-borafluorene (**4**) with  $\text{Et}_3\text{SiH}$ .

**3** forms a B–H–B bridged coordination polymer in the solid state.<sup>[2]</sup> Consequently, we expected **1** to form a highly symmetric dimer **5**.



### The reaction product and its structure



NMR spectroscopic results 10 min after  $\text{Et}_3\text{SiH}$  addition:<sup>[3]</sup>

- The  $^1\text{H}$  NMR spectrum revealed a complete conversion of the starting material and 16 well-resolved multiplets, all of them possessing the same integral value.
- The  $^{13}\text{C}$  NMR spectrum showed 24 resonances, four of them were severely broadened (Fig. 1).
- Two-dimensional NMR techniques indicated that all resonances arise from only four different *o*-phenylene moieties. One of these rings shows very unusual chemical shift values (cf. selected signals marked in green; Fig. 1).
- These initially observed NMR patterns change gradually with time.

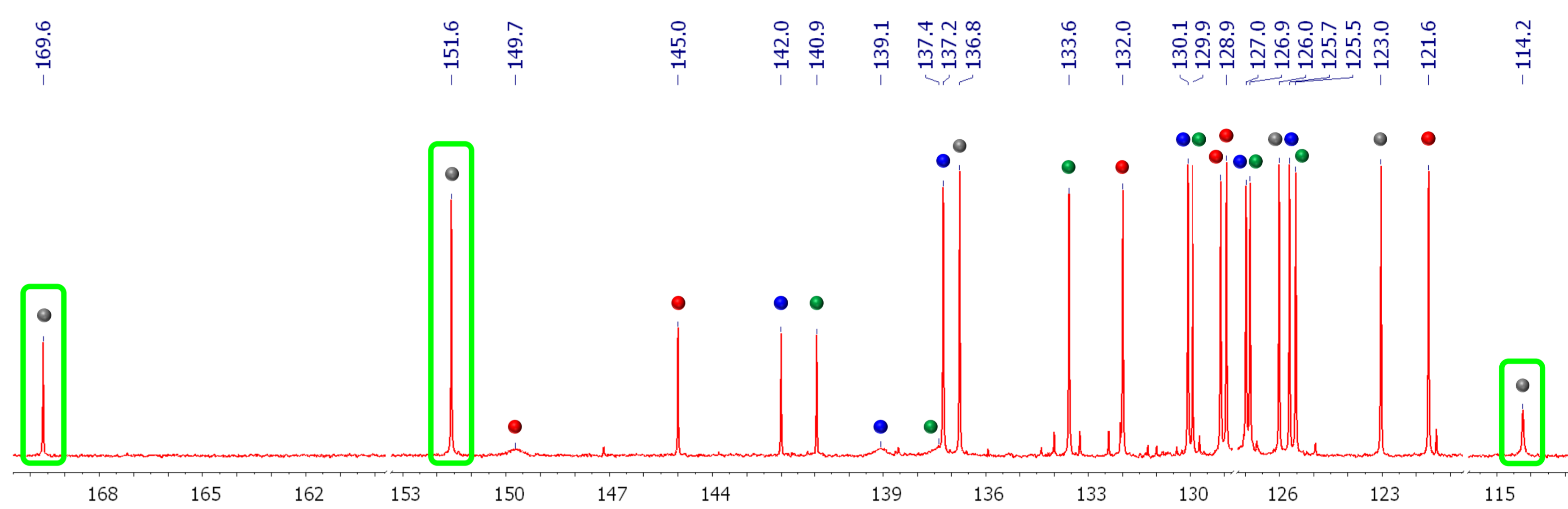


Figure 1:  $^{13}\text{C}$  NMR spectrum 10 min after the addition of  $\text{Et}_3\text{SiH}$ . The colors blue, green, red, and grey refer to four different *o*-phenylene rings.

Results of trapping experiments performed 10 min after  $\text{Et}_3\text{SiH}$  addition:

- After addition of pyridine or dimethyl sulfide (DMS), the corresponding adducts of **1** were isolated in quantitative yields (cf. Fig. 2).
- Addition of *t*BuCCH provided a mixture of the di- and monohydroboration products **6** and **7** (Fig. 2).

Conclusions:

- The initially observed primary product reacts like **1**.
- The NMR resonance patterns are in accord with a dimeric form of **1** possessing  $C_1$ -symmetry. Consequently, the initially proposed structure **5** can be excluded.

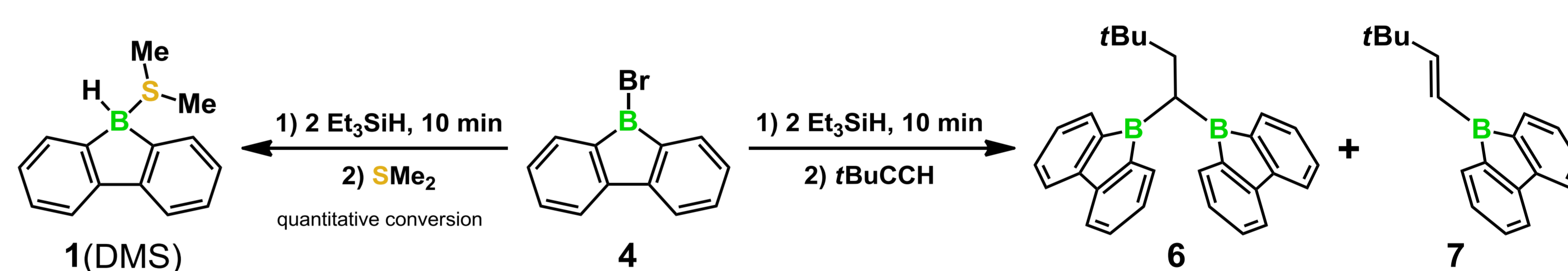
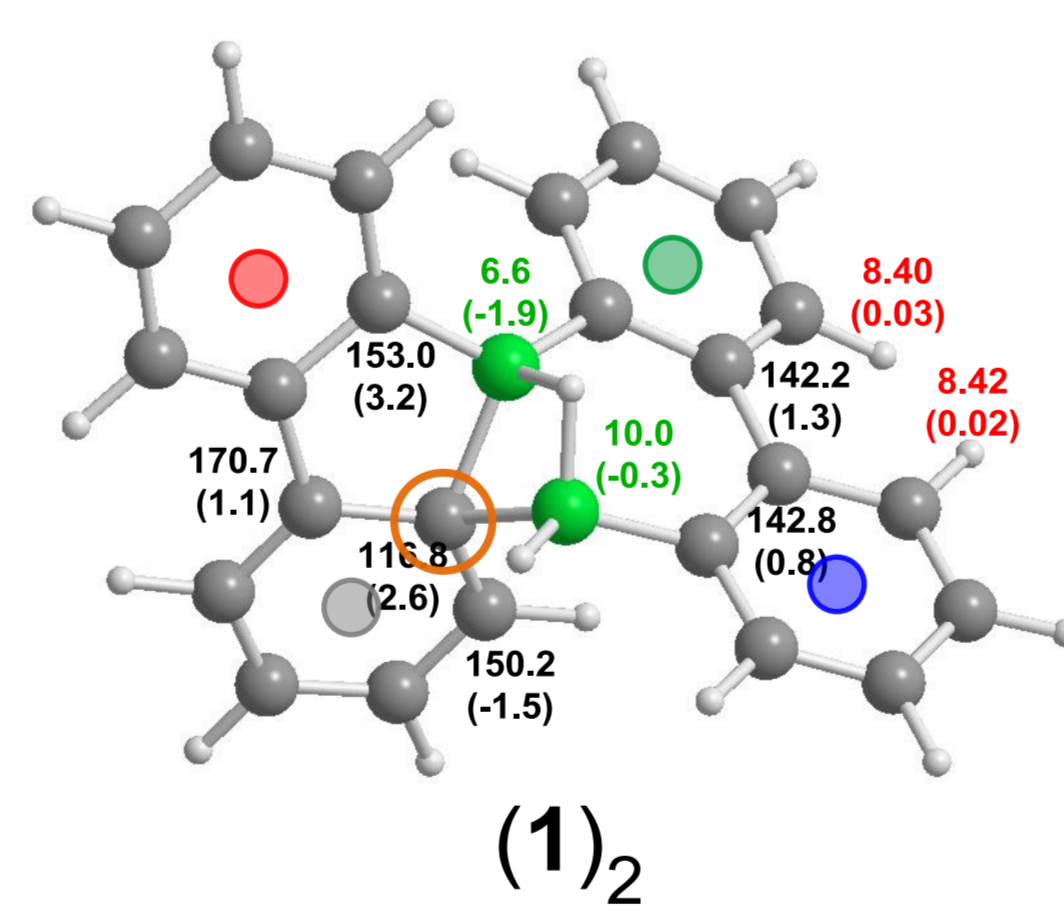


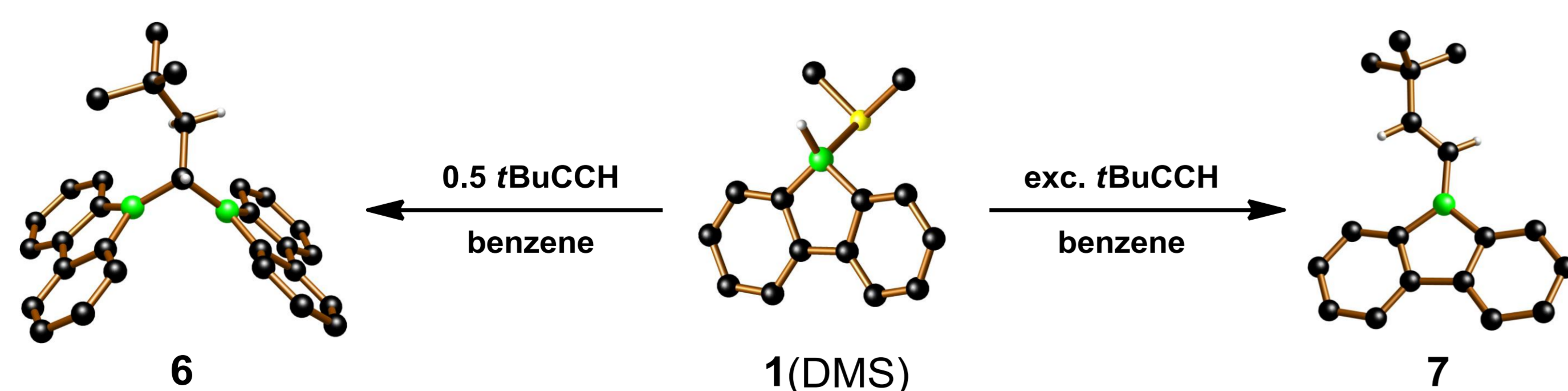
Figure 2: The in situ generated product of the conversion of **4** with  $\text{Et}_3\text{SiH}$  exclusively reacts as the target compound 9H-9-borafluorene (**1**).

Results of quantum-chemical calculations on various conceivable isomers of dimeric **1**:<sup>[3]</sup>



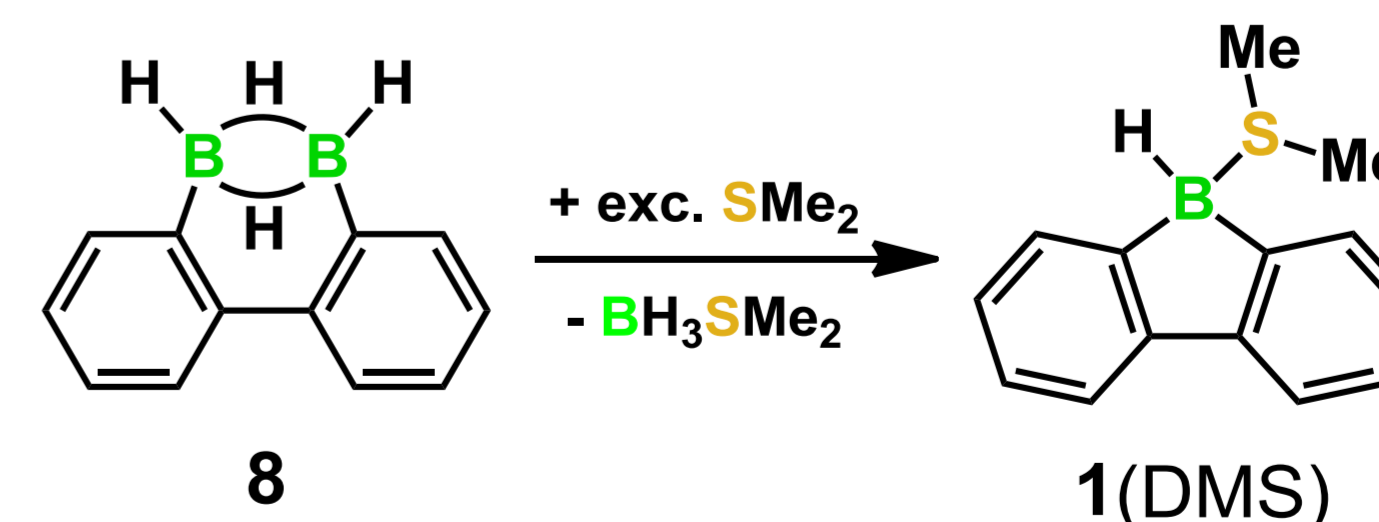
- Compound (**1**)<sub>2</sub> is the thermodynamically most favourable isomer.
- All calculated chemical shift values of (**1**)<sub>2</sub> ( $^1\text{H}$ ,  $^{13}\text{C}$ ,  $^{11}\text{B}$ ) are in perfect agreement with the experimentally determined data. This is not the case for any of the other computed dimers.
- (**1**)<sub>2</sub> contains a unique boron-bridging *o*-phenylene ring, which is responsible for the peculiarities of the  $^{13}\text{C}$  NMR spectrum (cf. Fig. 1).
- (**1**)<sub>2</sub> consists of one 9-borafluorene fragment and one 1,2-(2,2'-biphenylene)diborane(6)-type moiety.

### Selective mono- and dihydroboration with 1(DMS)



The 9H-9-borafluorene dimethyl sulfide adduct **1(DMS)** is a crystalline storage form of unstable (**1**)<sub>2</sub> and can be used for the selective mono- or dihydroboration of terminal alkynes.

### Modeling the reactivity of (**1**)<sub>2</sub>



In order to understand the reactivity of (**1**)<sub>2</sub> toward Lewis bases, we added DMS to a  $\text{C}_6\text{D}_6$  solution of 1,2-(2,2'-biphenylene)diborane(6) (**8**), a model system of the partially ring-opened half of (**1**)<sub>2</sub>.

The immediate and quantitative formation of **1(DMS)** (together with  $\text{BH}_3\text{SMe}_2$ ) provides further evidence that (**1**)<sub>2</sub> can act as a direct source of **1**.

[1] (a) C. D. Entwistle, T. B. Marder, *Angew. Chem. Int. Ed.* **2002**, 41, 2927. (b) C. D. Entwistle, T. B. Marder, *Chem. Mater.* **2004**, 16, 4574. (c) S. Yamaguchi, A. Wakamiya, *Pure Appl. Chem.* **2006**, 78, 1413. (d) F. Jäkle, *Coord. Chem. Rev.* **2006**, 250, 1107. (e) F. Jäkle, *Chem. Rev.* **2010**, 110, 3985.

[2] A. Lorbach, M. Bolte, H. Li, H.-W. Lerner, M. C. Holthausen, F. Jäkle, M. Wagner, *Angew. Chem. Int. Ed.* **2009**, 48, 4584.

[3] A. Hübner, Z.-W. Qu, U. Englert, M. Bolte, H.-W. Lerner, M. C. Holthausen, M. Wagner, *J. Am. Chem. Soc.* **2011**, 133, 4596.