

Reactivity of (dibromoboryl)arenes toward triethylsilane

Facile access to boron-bridged π -electron systems

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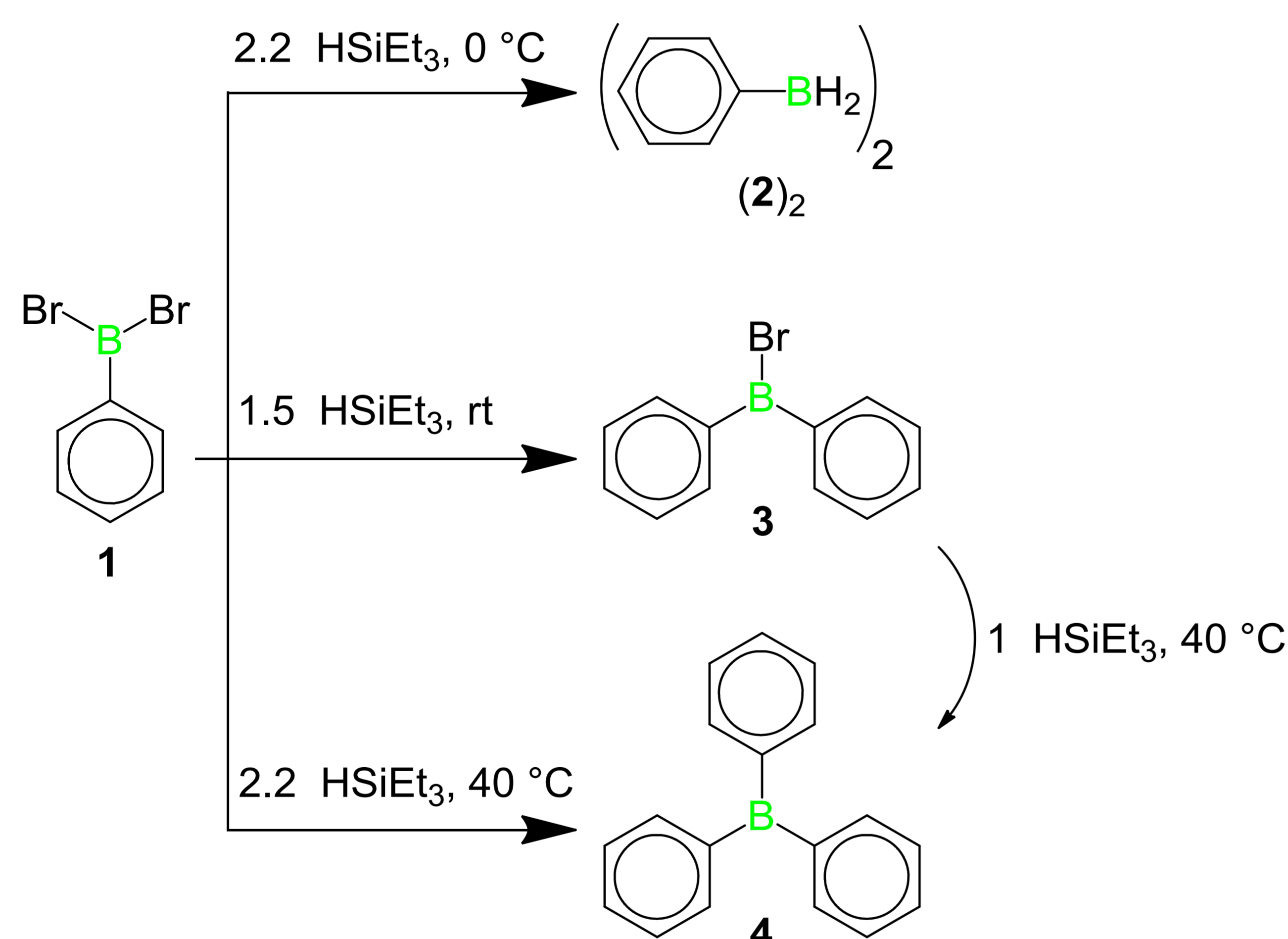
Introduction

Organoboranes have received increasing interest during the last years due to a great variety of applications as catalysts, sensor systems, and luminescent materials.^[1-3] This property spectrum can be expanded even further by the incorporation of transition metal ions into the boron-containing framework.

In cooperation with F. Jäkle, our group has recently developed a novel synthetic route to boron-bridged poly(ferrocenylene)s **B** via a triethylsilane-induced condensation reaction starting from 1,1'-bis(dibromoboryl)ferrocene **A**.^[4-6] We are currently examining the scope of the reaction by trying to couple a broad selection of (hetero)arylboranes **C** to di((hetero)aryl)boranes **D**.

Different reaction pathways

Depending on the temperature and the amount of triethylsilane employed, the reaction of PhBBr₂ **1** can be driven to give either [PhBH₂]₂ (**2**)₂, or Ph₂BBr **3**, or Ph₃B **4**.^[7]

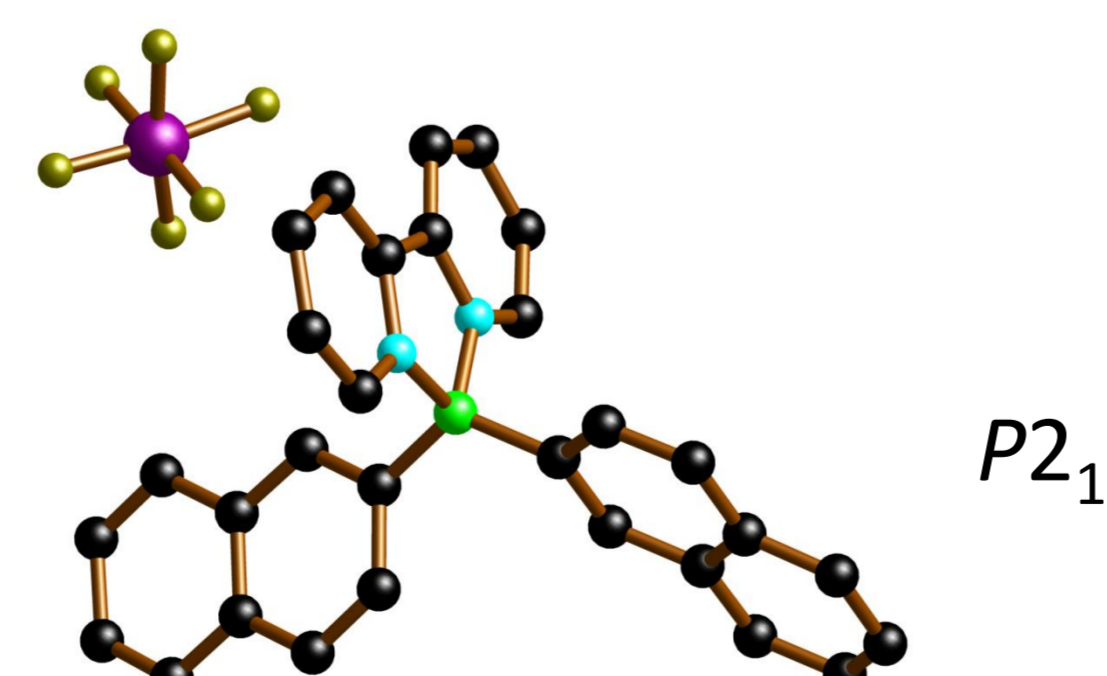
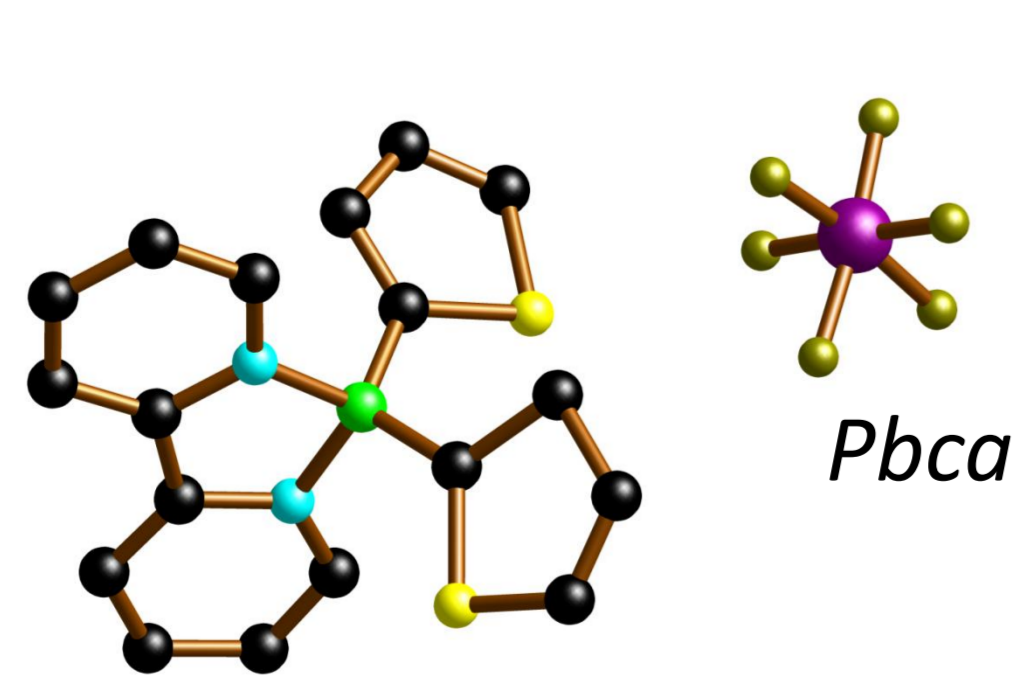
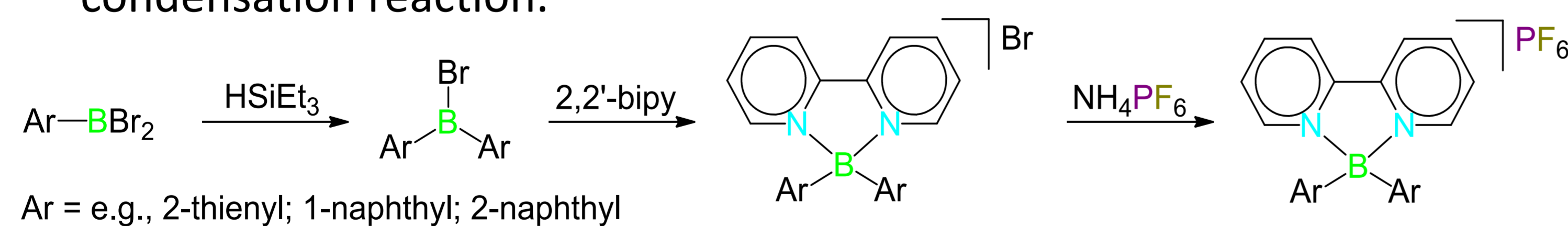


The advantages of the triethylsilane-induced coupling reaction are:

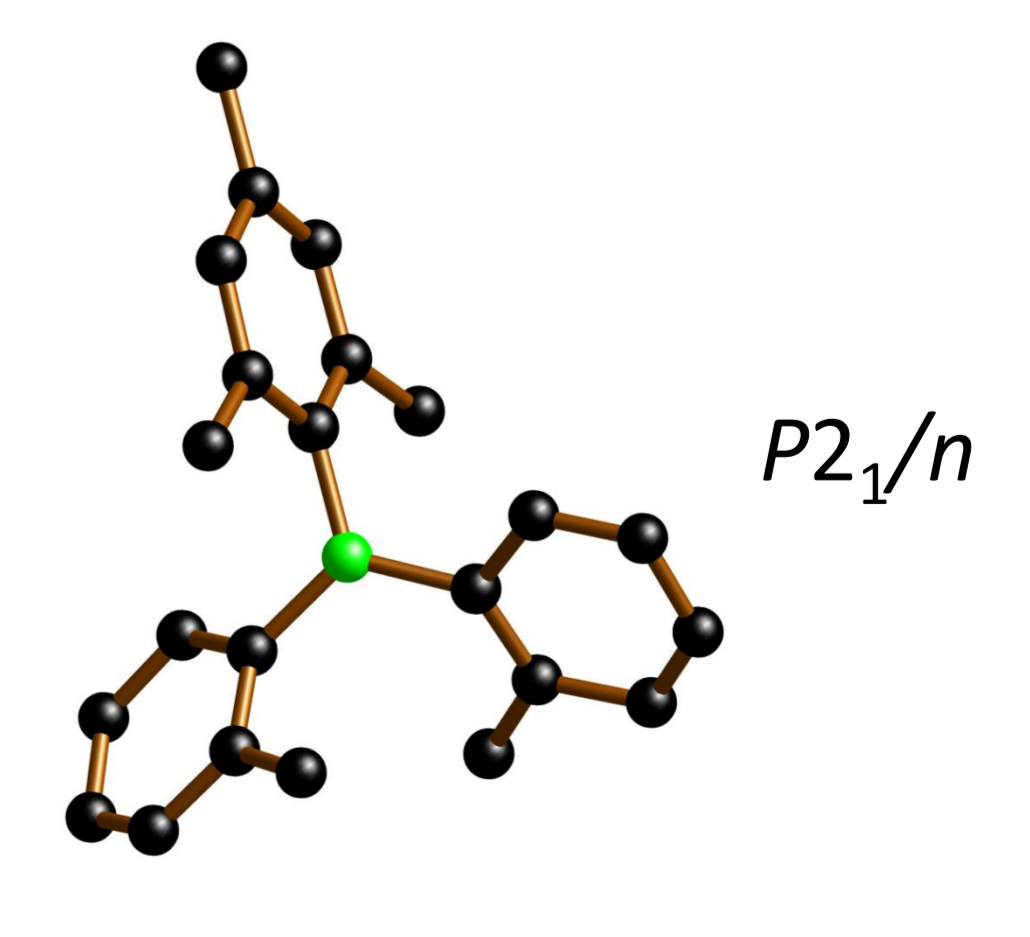
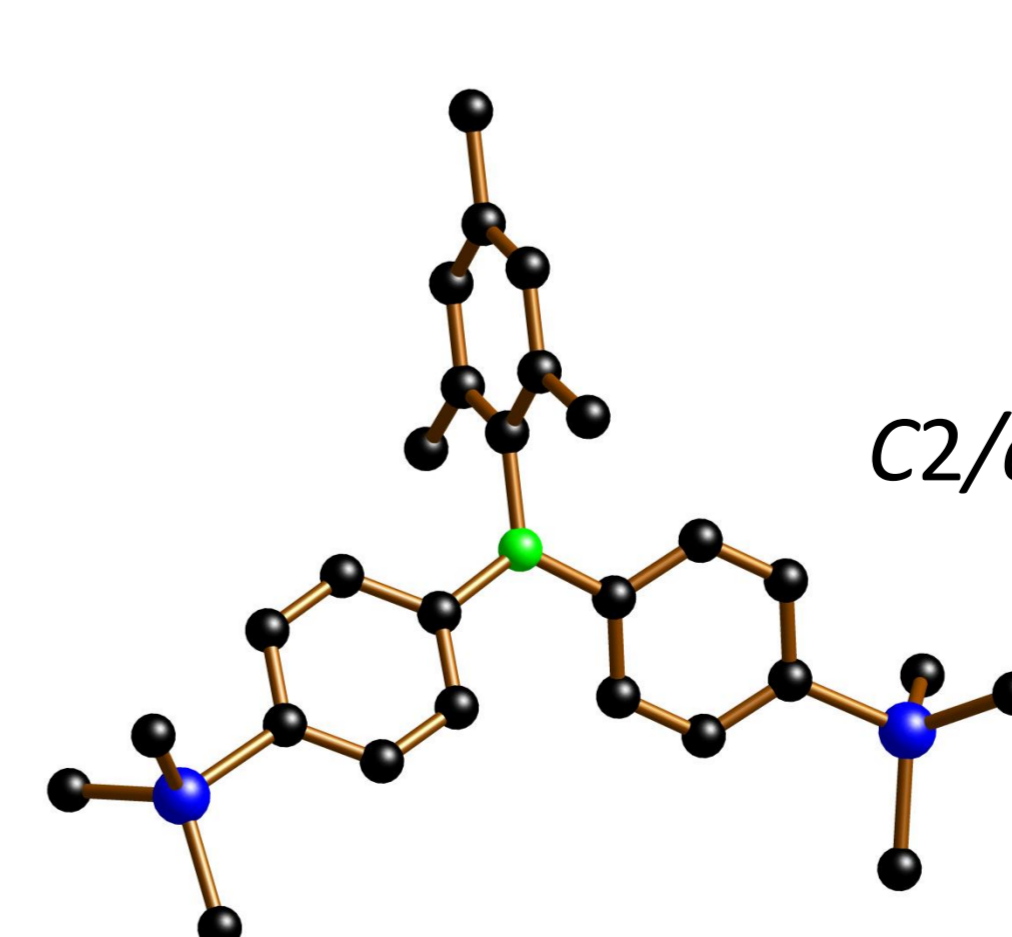
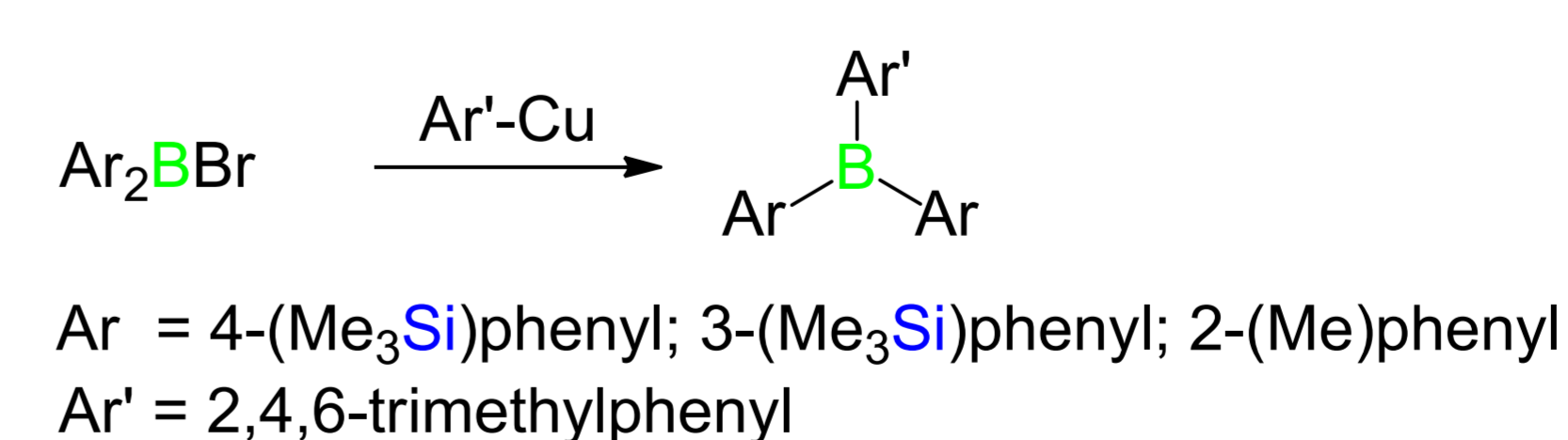
- use of non-donor solvents
- one-step reaction
- volatile by-products
- smooth reaction

Scope

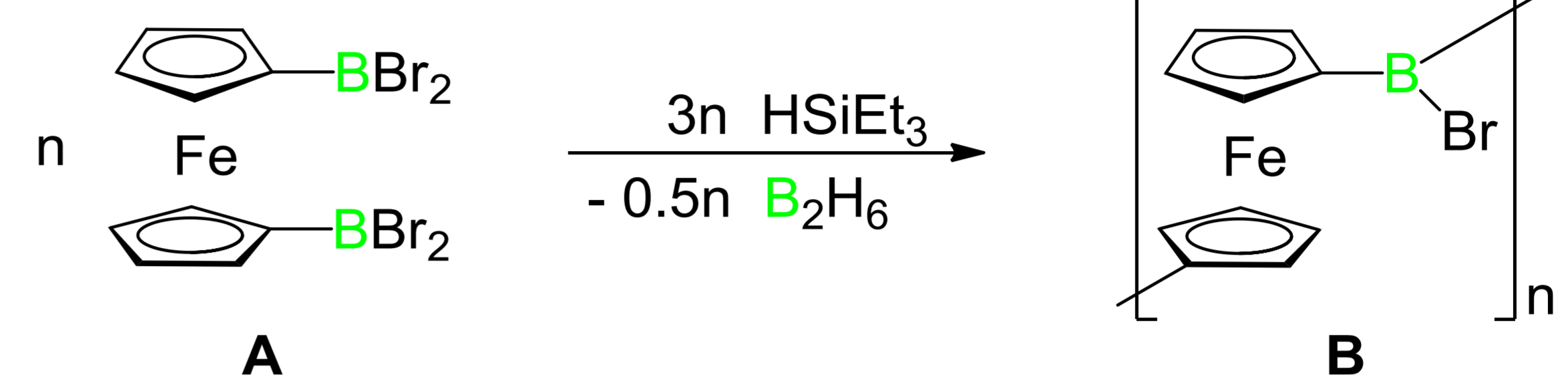
➤ We found that various other (dibromoboryl)arenes also undergo the condensation reaction.



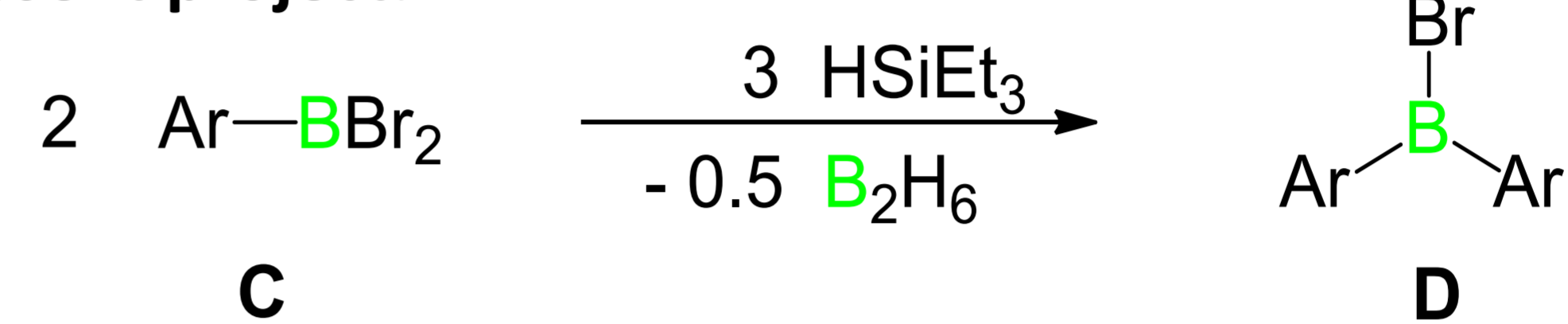
➤ It is possible to synthesize triarylboranes of the type Ar₂Ar'B starting from Ar₂BBr and Ar'-M (M = Cu, Li, MgBr).



Previous project:

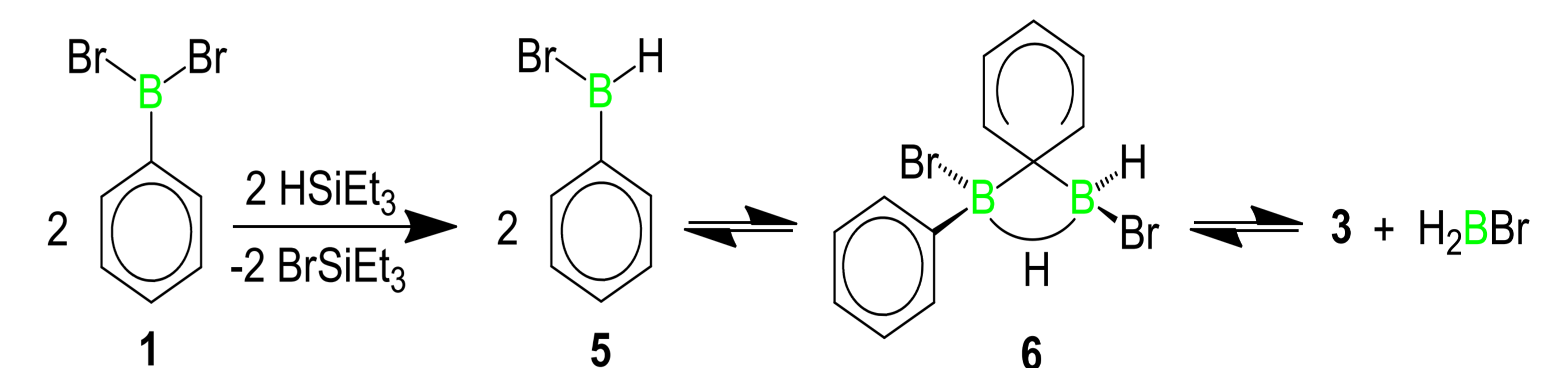


Present project:

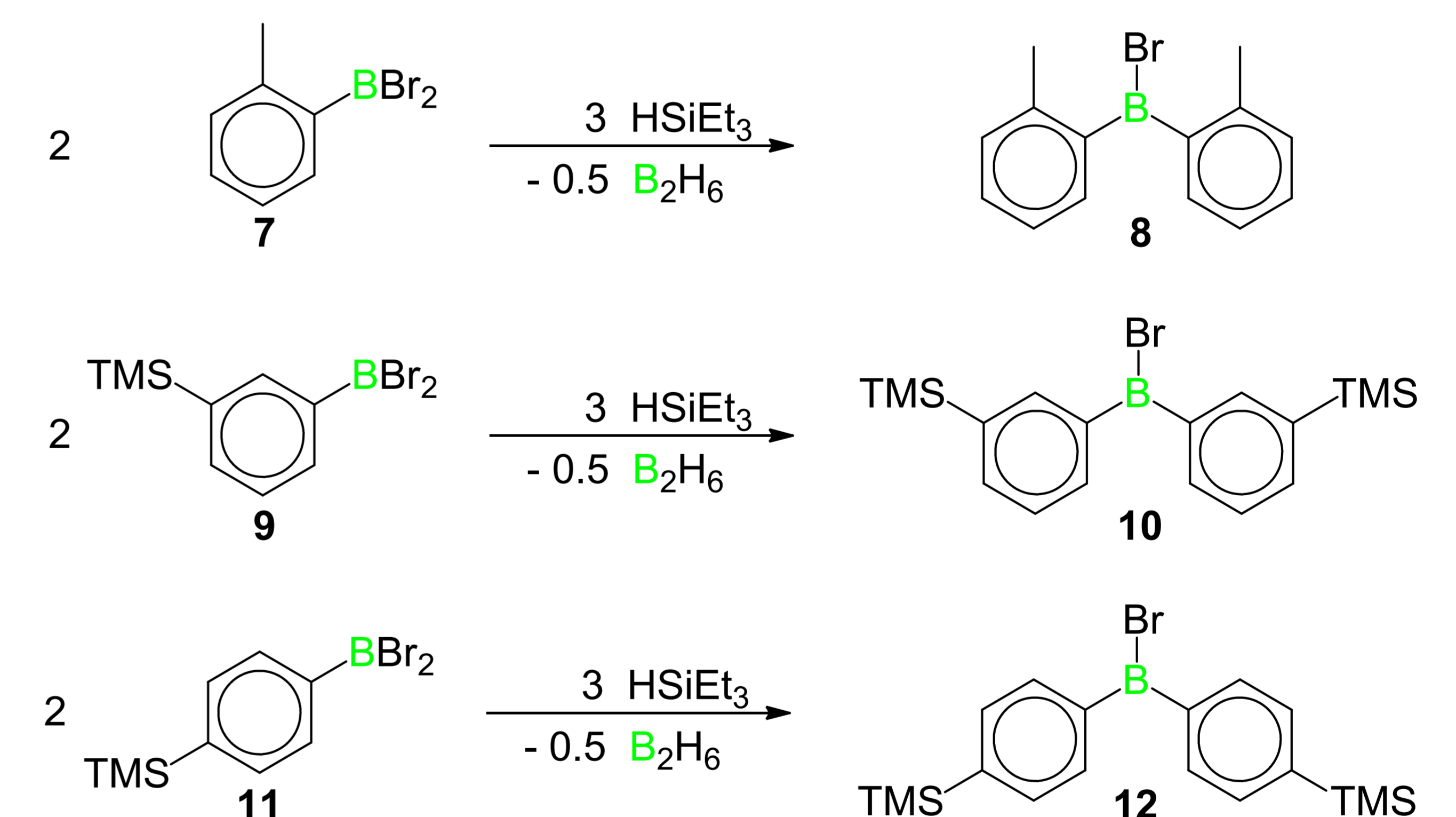


Mechanism and regioselectivity

An investigation of the potential energy surface by DFT calculations shows that the key step following hydride transfer is the formation of the (μ -H)-(μ -C)-bridged intermediate **6**.



Using 2-(Me)phenyl, 3-(TMS)phenyl, and 4-(TMS)phenyl substituents, it has been shown that the coupling reaction proceeds with perfect regioselectivity.



[1] F. Jäkle, *Chem. Rev.* **2010**, *110*, 3985.

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[4] M. Scheibitz, H. Li, J. Schnorr, A. S. Perucha, M. Bolte, H.-W. Lerner, F. Jäkle, M. Wagner, *J. Am. Chem. Soc.* **2009**, *131*, 16319.

[5] J. B. Heilmann, M. Scheibitz, Y. Qin, A. Sundararaman, F. Jäkle, T. Kretz, M. Bolte, H.-W. Lerner, M. C. Holthausen, M. Wagner, *Angew. Chem. Int. Ed.* **2006**, *45*, 920.

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[7] U. D. Eckensberger, *Ph.D. thesis*, Goethe-University Frankfurt am Main, **2009**.

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