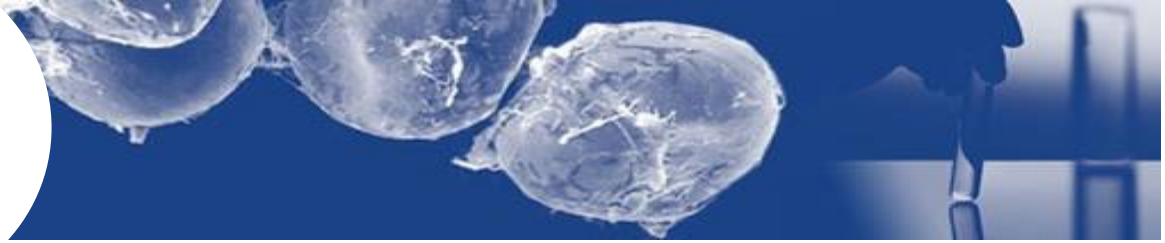


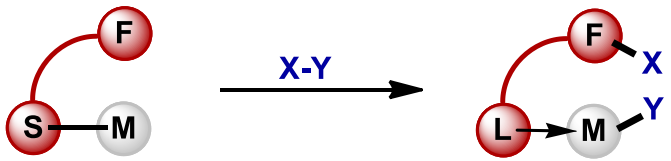
An Overview of Boron-Ligand-Cooperation: Concept and Application

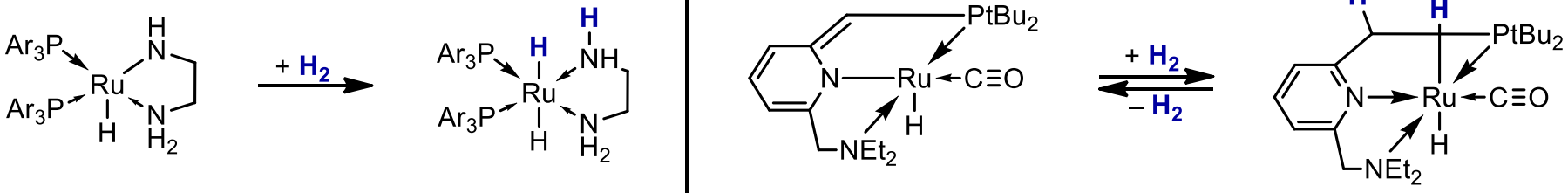
Max Hasenbeck

AG Gellrich

Institute for Organic Chemistry
Justus-Liebig University, Giessen

Metal-Ligand Cooperation





R. Noyori; T. Okhuma, *Angew. Chem. Int. Ed.* **2001**, *40*, 40–73.
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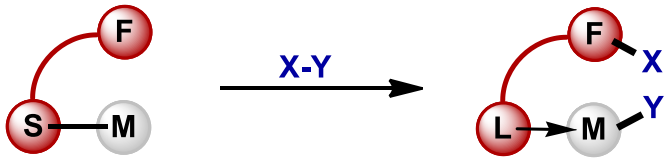
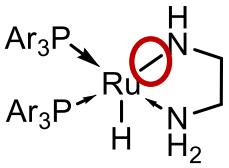
Metal-Ligand Cooperation

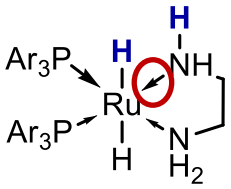


covalent bond

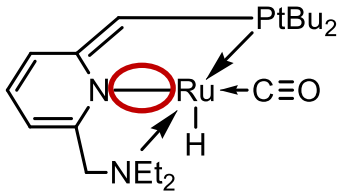


+ H_2

dative bond



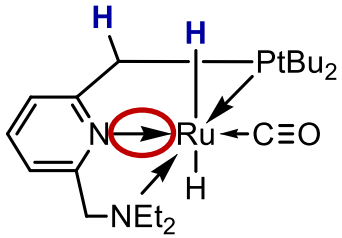
covalent bond



+ H_2

– H_2

dative bond



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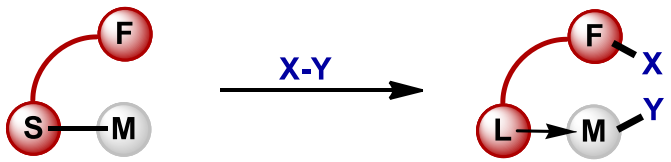
J. Zhang; G. Leitus, Y. Ben-David, D. Milstein, *J. Am. Chem. Soc.* **2005**, *127*, 10840–10841.

Criteria for Metal-Ligand Cooperation



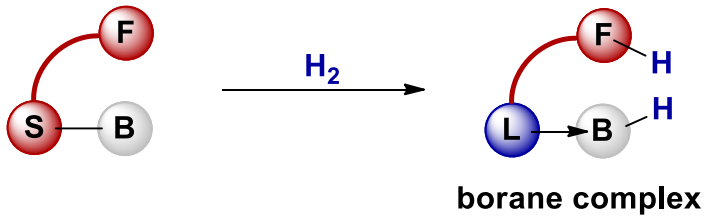
1) Metal and ligand participate in the bond activation

2) Metal and ligand are chemically modified during bond activation.

3) The coordination mode of the ligand undergoes significant changes as a result of bond activation.

J. R. Khusnutdinova, D. Milstein, *Angewandte Chemie International Edition* **2015**, *54*, 12236-12273.

Criteria for Boron-Ligand-Cooperation



1) A covalently bound substituent and the borane are involved in the bond activation

2) As a result of the bond activation, the covalently bound substituent becomes a datively bound ligand

Dative bounds

dative bond

Online use...

https://doi.org/10.1351/goldbook.D01523

The coordination bond formed upon interaction between molecular species, one of which serves as a donor and the other as an acceptor of the electron pair to be shared in the complex formed, *e.g*, the N→B bond in $H_3N{\rightarrow}BH_3$. In spite of the analogy of dative bonds with covalent bonds, in that both types imply sharing a common electron pair between two vicinal atoms, the former are distinguished by their significant polarity, lesser strength, and greater length. The distinctive feature of dative bonds is that their minimum-energy rupture in the gas phase or in inert solvent follows the heterolytic bond cleavage path.

Source:

PAC, 1999, *71*, 1919. (*Glossary of terms used in theoretical organic chemistry*) on page 1933 [Terms] [Paper]

Cite as: *IUPAC. Compendium of Chemical Terminology, 2nd ed. (the "Gold Book"). Compiled by A. D. McNaught and A. Wilkinson. Blackwell Scientific Publications, Oxford (1997). Online version (2019-) created by S. J. Chalk. ISBN 0-9678550-9-8. https://doi.org/10.1351/goldbook.*

Div. III PDF Text JSON History Feedback

Last revised: February 24, 2014

Dative bounds

dative bond

Online use...

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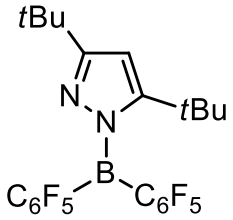
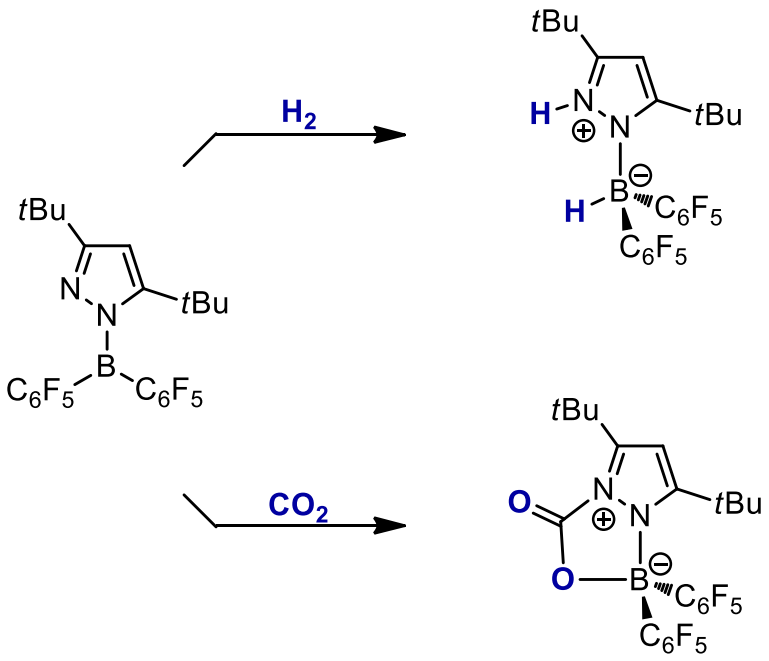
Boron-Ligand Cooperation: Early examples



E. Theuergarten, D. Schluns, J. Grunenberg, C. G. Daniliuc, P. G. Jones, M. Tamm, *Chemical Communications* **2010**, *46*, 8561-8563.
E. Theuergarten, J. Schlösser, D. Schlüns, M. Freytag, C. G. Daniliuc, P. G. Jones, M. Tamm, *Dalton Transactions* **2012**, *41*, 9101-9110.

Boron-Ligand Cooperation: Early examples



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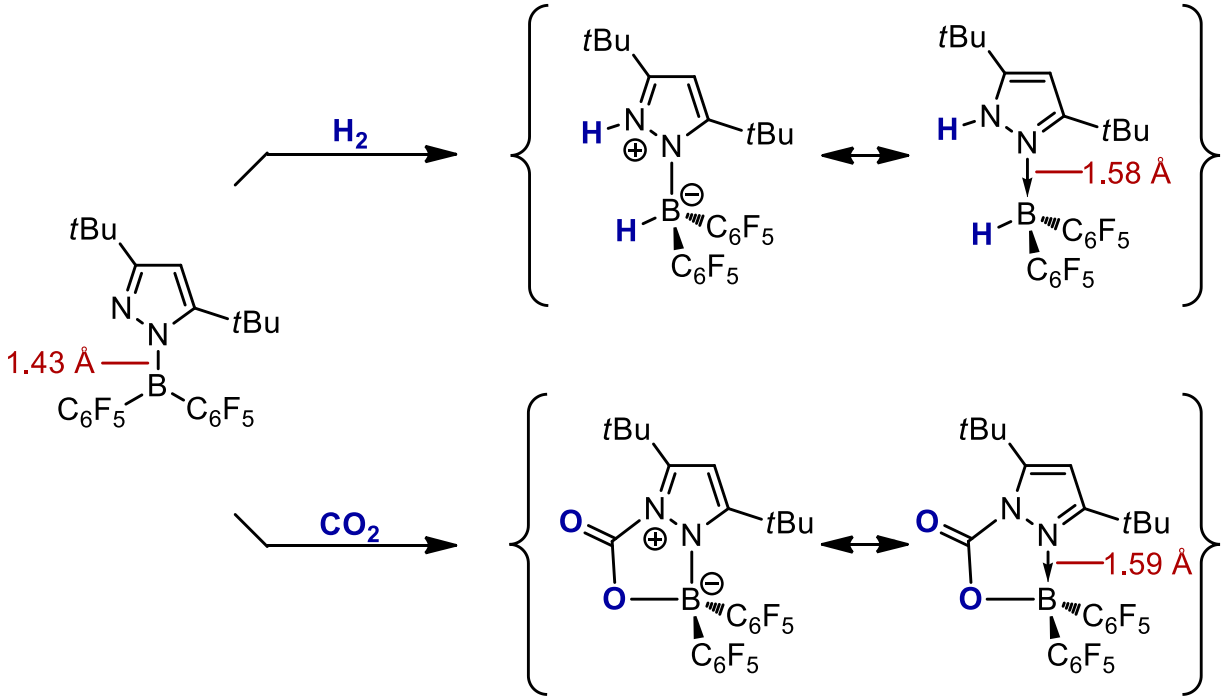

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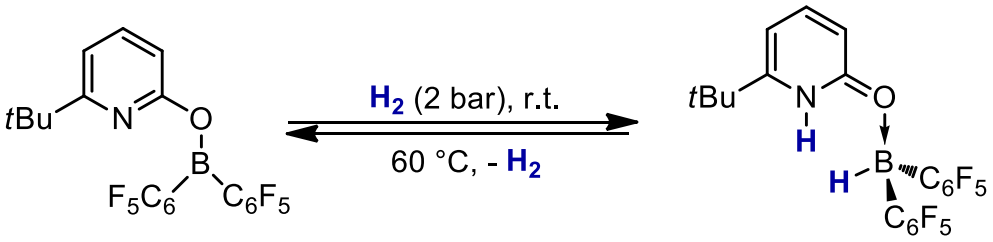
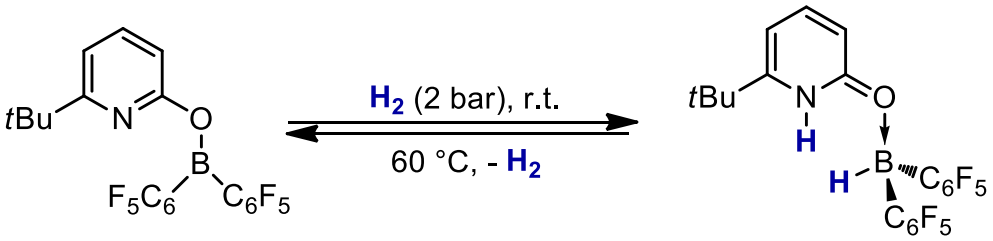
Boron-Ligand Cooperation using Aromatization

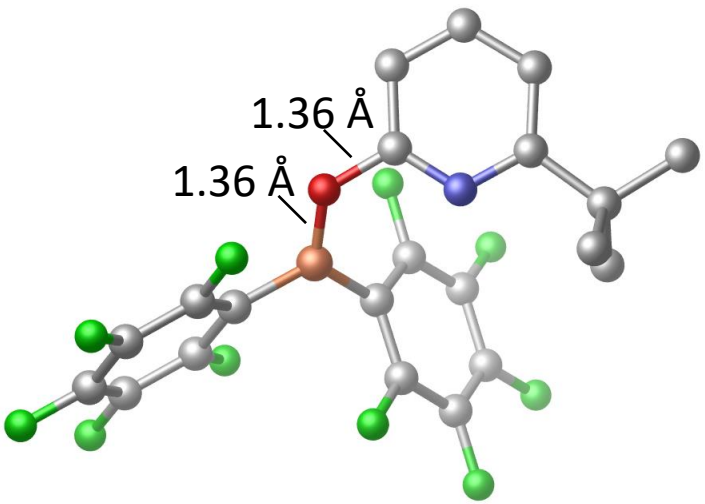


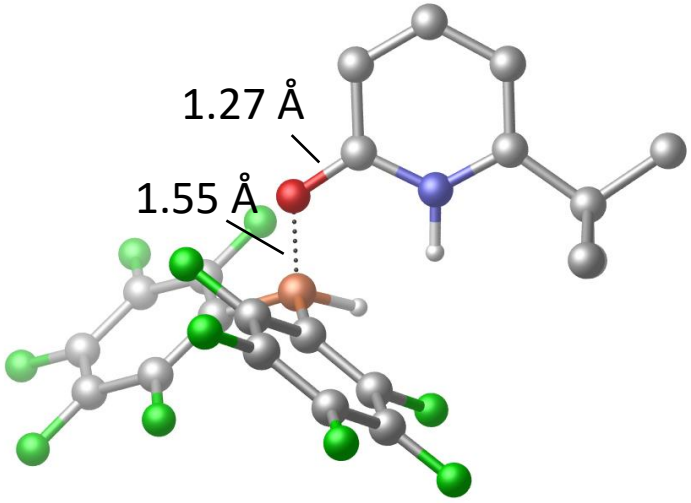
U. Gellrich, *Angewandte Chemie International Edition* **2018**, *57*, 4779-4782.

Boron-Ligand Cooperation using Aromatization



$\tilde{\nu}$ (C=O) = 1643 cm^{-1} (exp.)

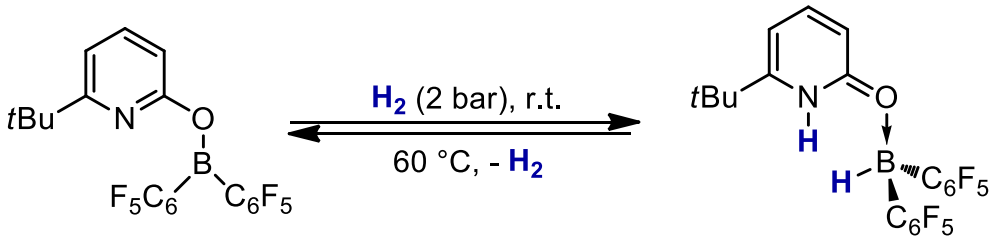


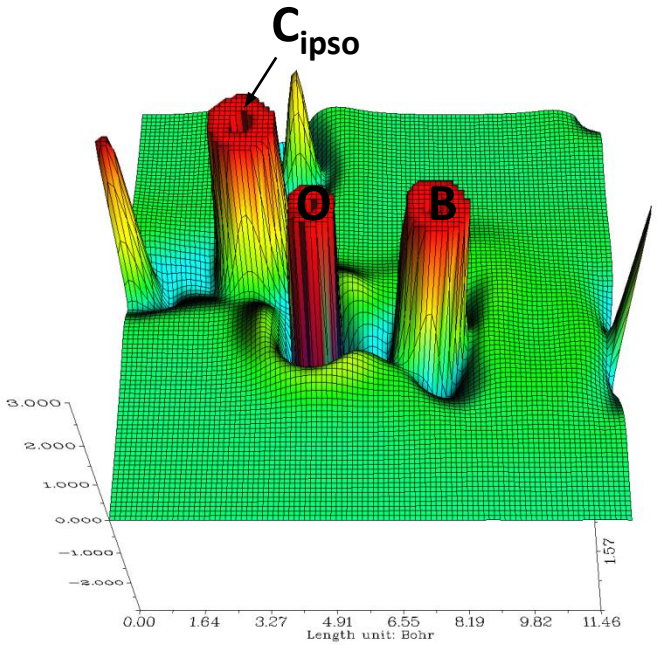


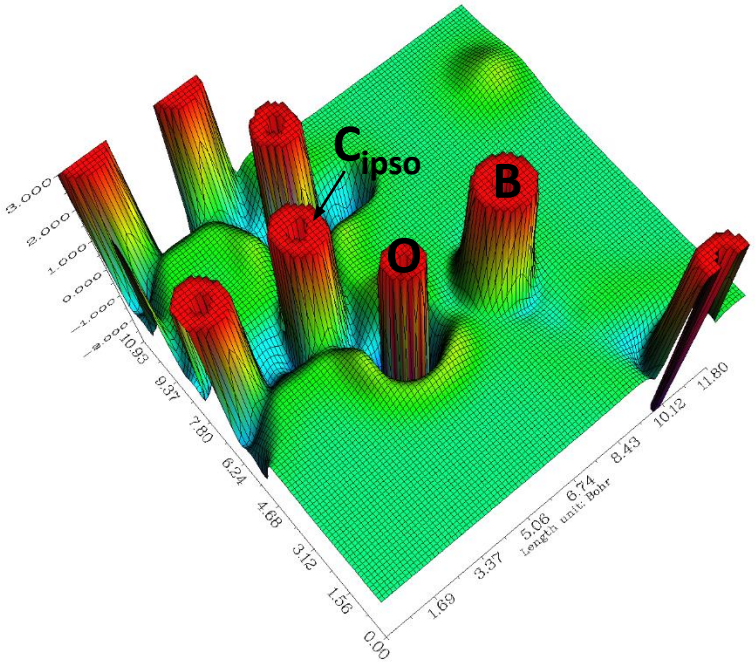
PBE0-D3(BJ)/def2-TZVP

U. Gellrich, *Angewandte Chemie International Edition* **2018**, *57*, 4779-4782.

Boron-Ligand Cooperation using Aromatization







$$\nabla^2\left(n_e(\vec{r})\right)$$

PBE0-D3(BJ)/def2-TZVP

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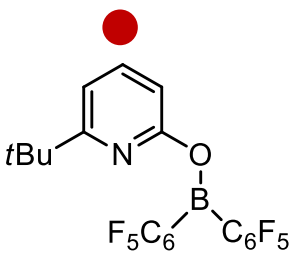
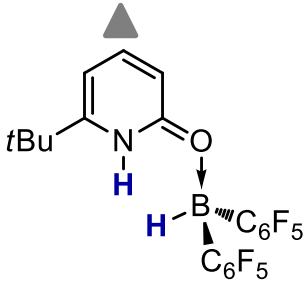
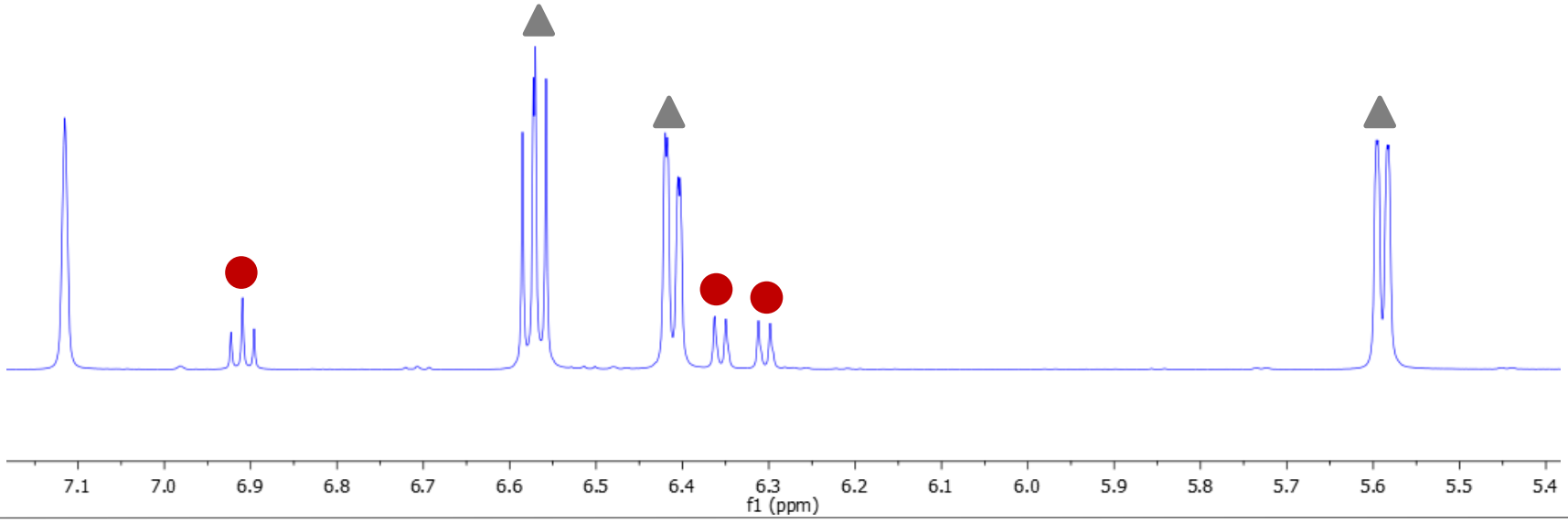
Boron-Ligand Cooperation using Aromatization



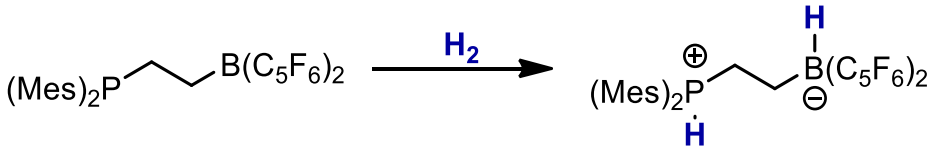


NICS (1_{zz}) = -9.4 -6.8

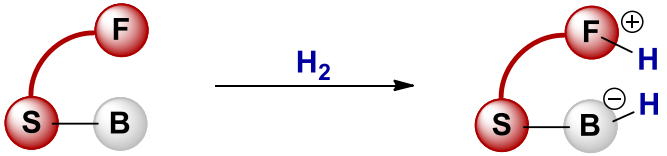


U. Gellrich, *Angewandte Chemie International Edition* **2018**, *57*, 4779-4782., J. I. Wu, J. E. Jackson, P. v. R. Schleyer, *Journal of the American Chemical Society* **2014**, *136*, 13526-13529.

Boron-Ligand Cooperation using Aromatization



Classic FLPs

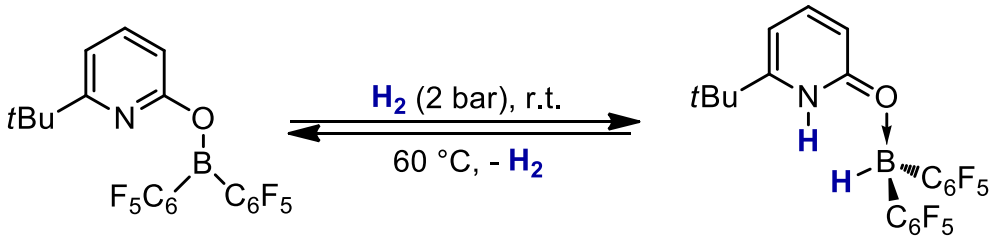


borohydride

U. Gellrich, *Angewandte Chemie International Edition* **2018**, *57*, 4779-4782.

P. Spies, G. Erker, G. Kehr, K. Bergander, R. Fröhlich, S. Grimme, D. W. Stephan, *Chemical Communications* **2007**, 5072-5074.

Boron-Ligand Cooperation using Aromatization



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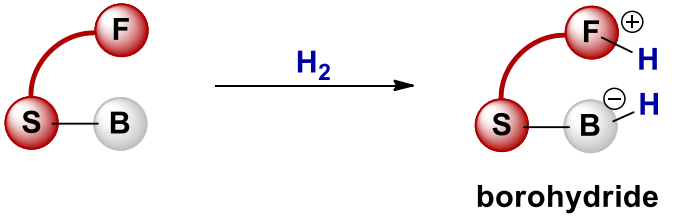
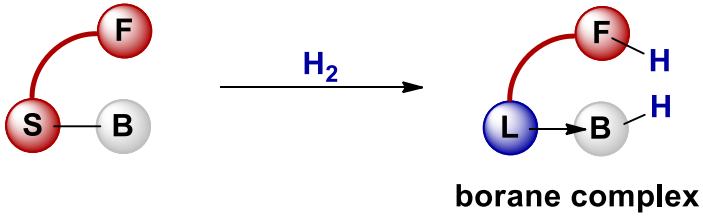


Boron-Ligand-Cooperation



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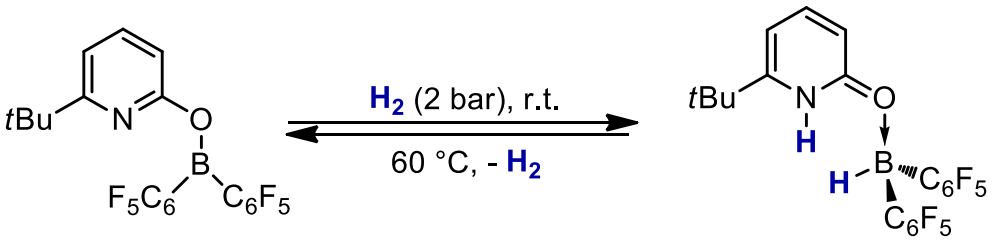

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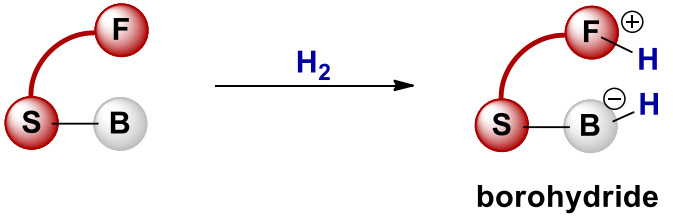

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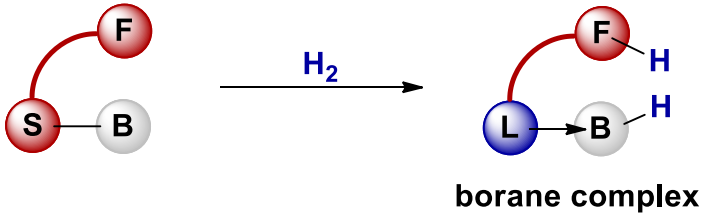

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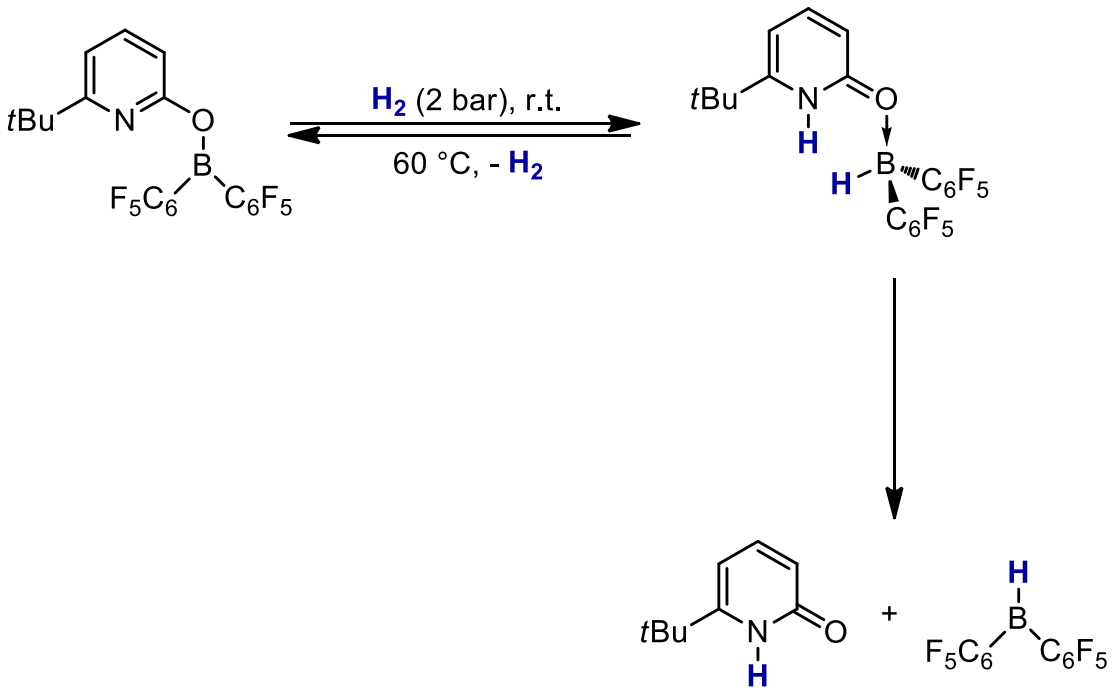
A. Haaland, *Angewandte Chemie International Edition in English* **1989**, *28*, 992-1007.

Boron-Ligand Cooperation using Aromatization



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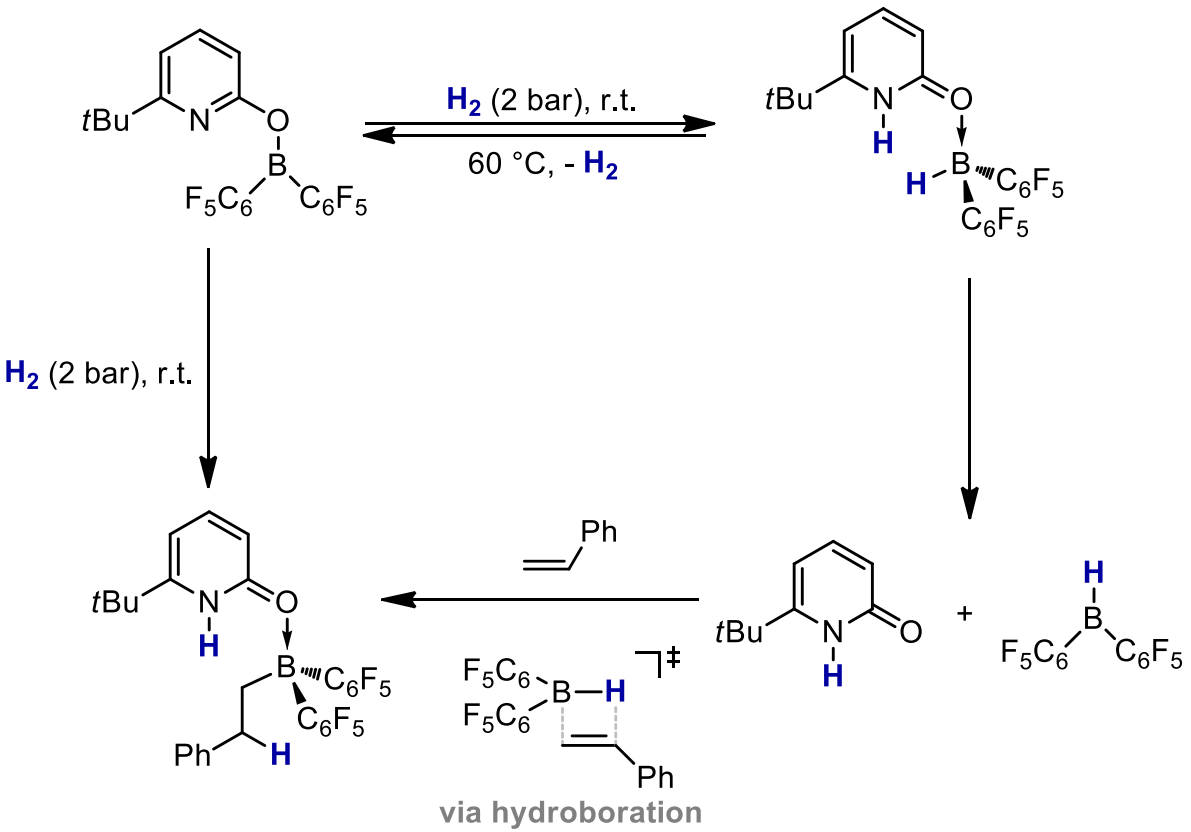
F. Wech, M. Hasenbeck, U. Gellrich, *Chemistry – A European Journal* **2020**, DOI: 10.1002/chem.202001276

Boron-Ligand Cooperation using Aromatization



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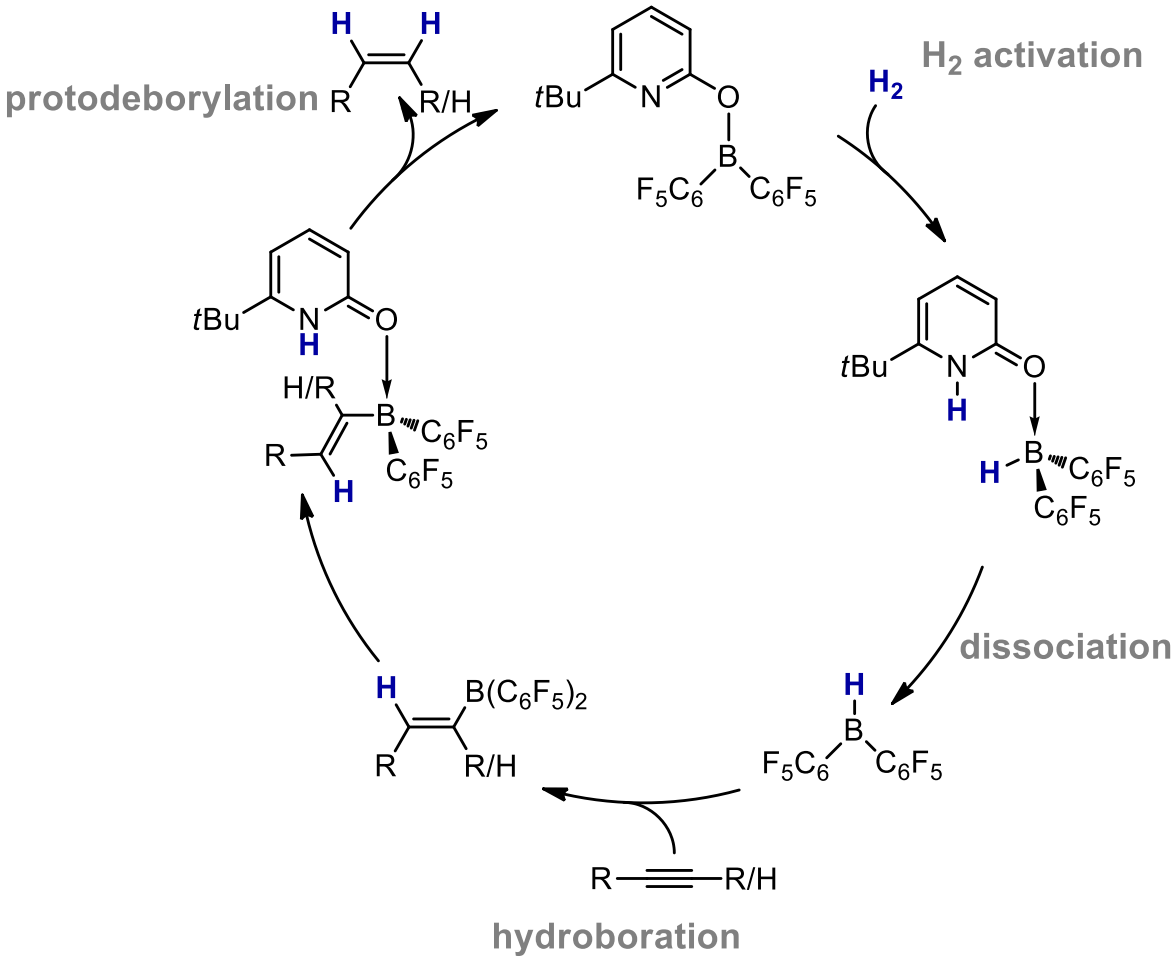
Boron-Ligand Cooperation: Hydrogenations



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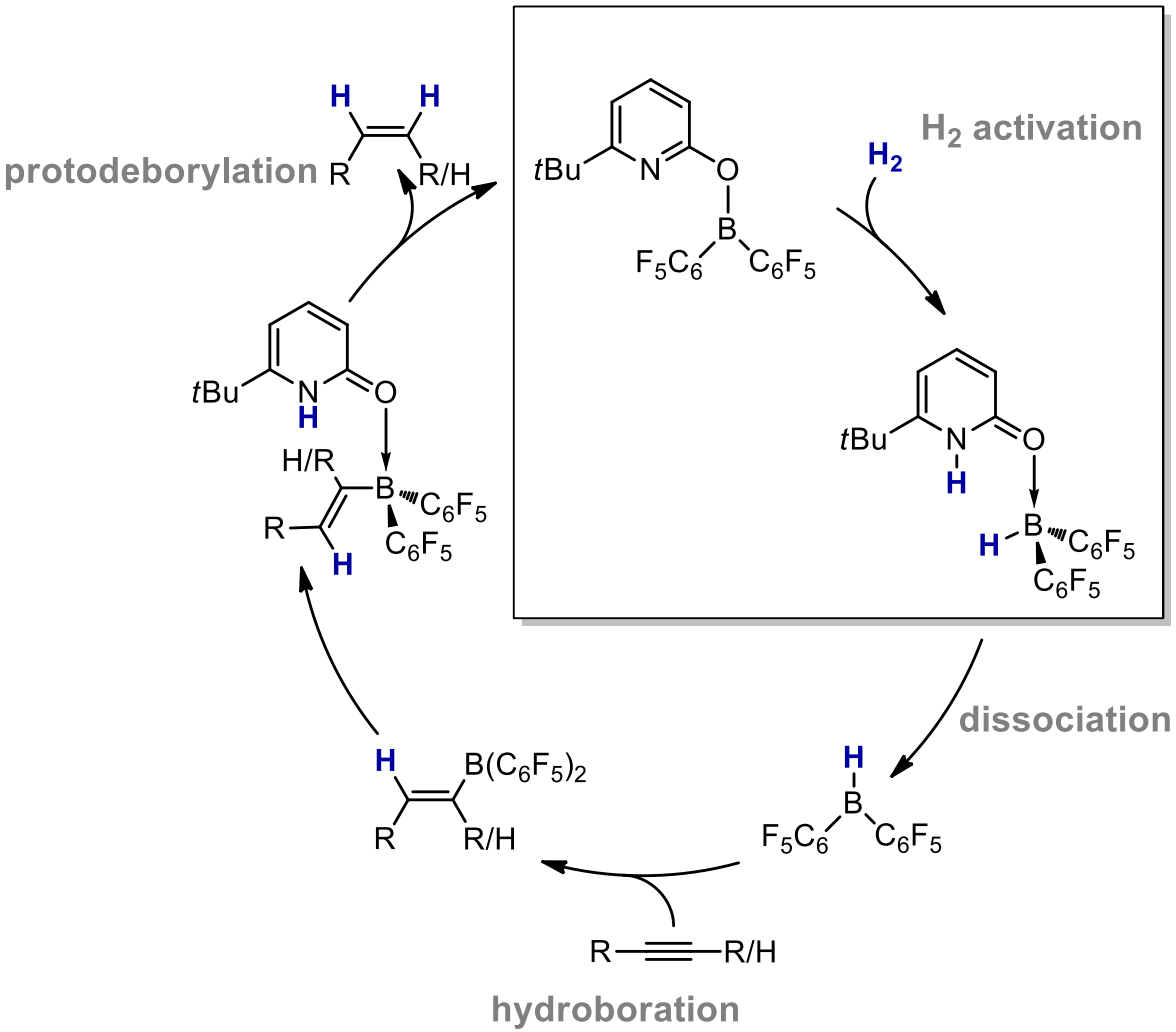
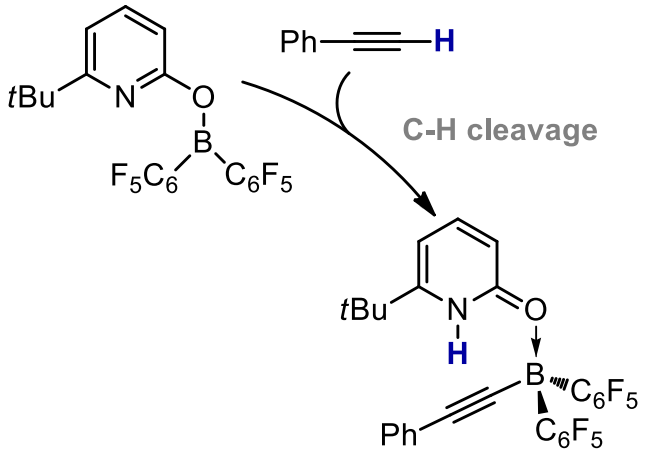


12 examples, 47-95% yield

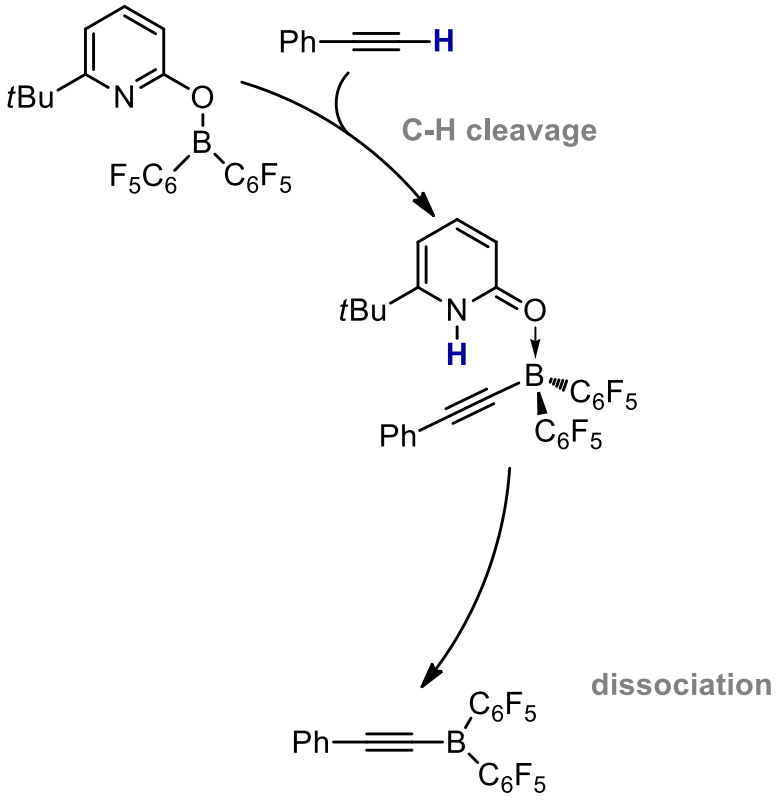
F. Wech, M. Hasenbeck, U. Gellrich, *Chemistry – A European Journal* **2020**, DOI: 10.1002/chem.202001276

Boron-Ligand Cooperation: Carboboration



M. Hasenbeck, T. Müller, U. Gellrich, *Catalysis Science & Technology* **2019**, *9*, 2438-2444.

Boron-Ligand Cooperation: Carboboration



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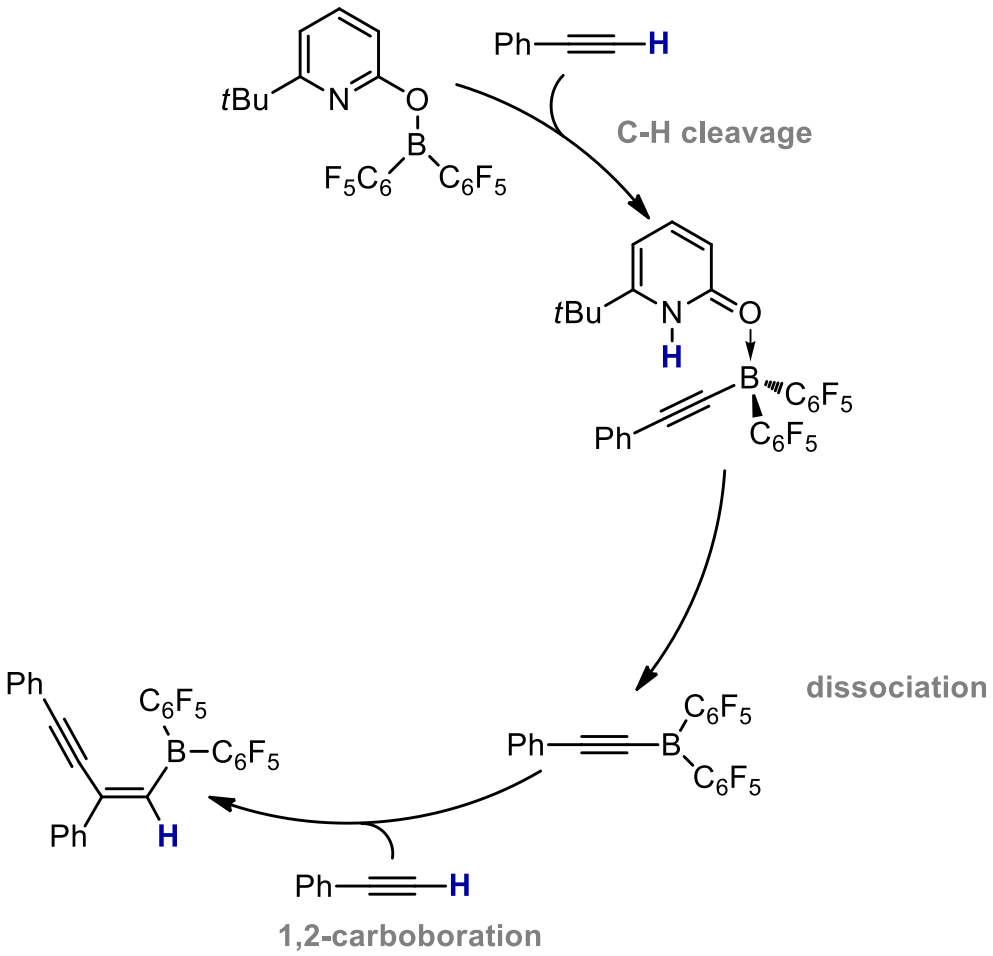

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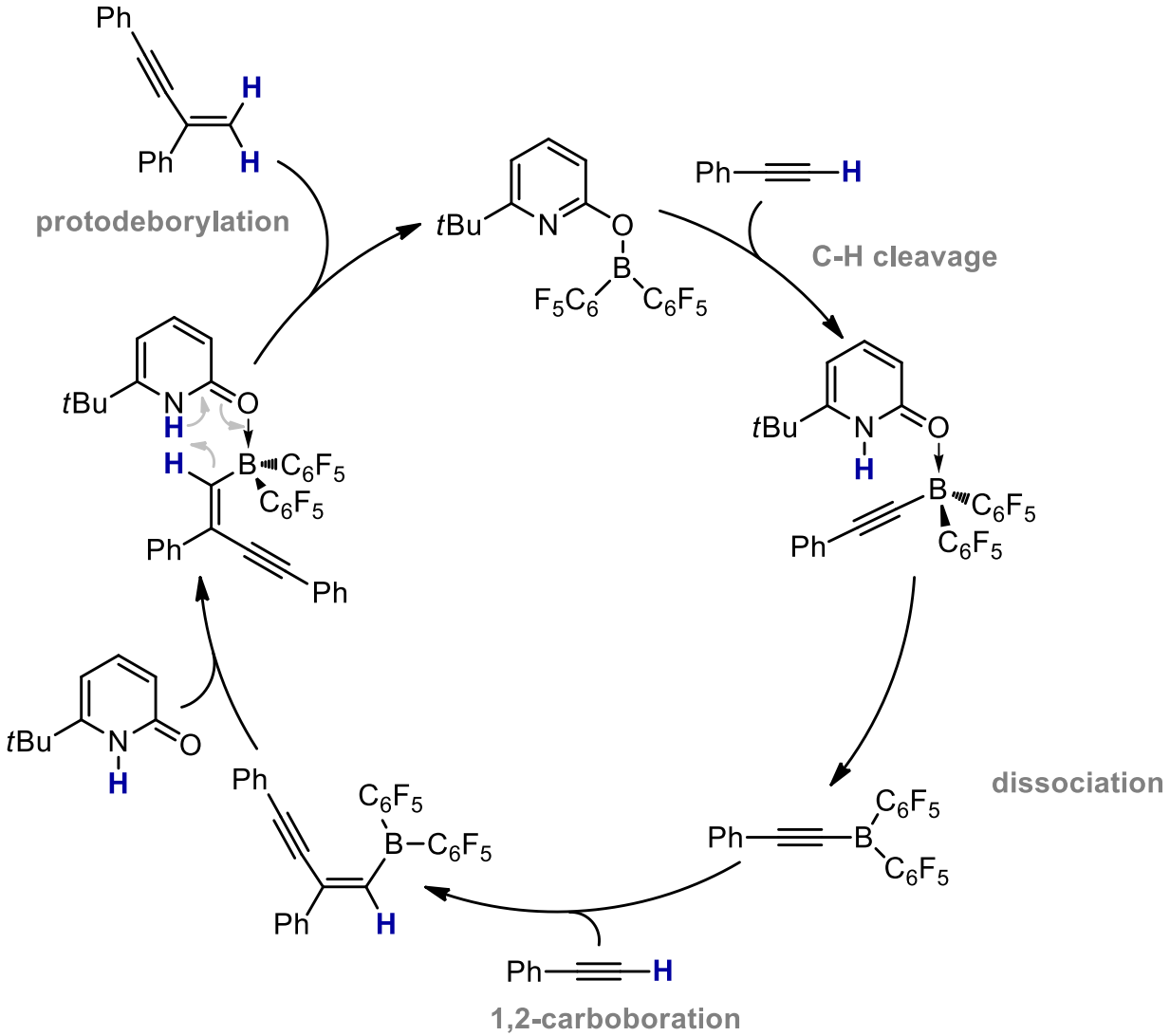

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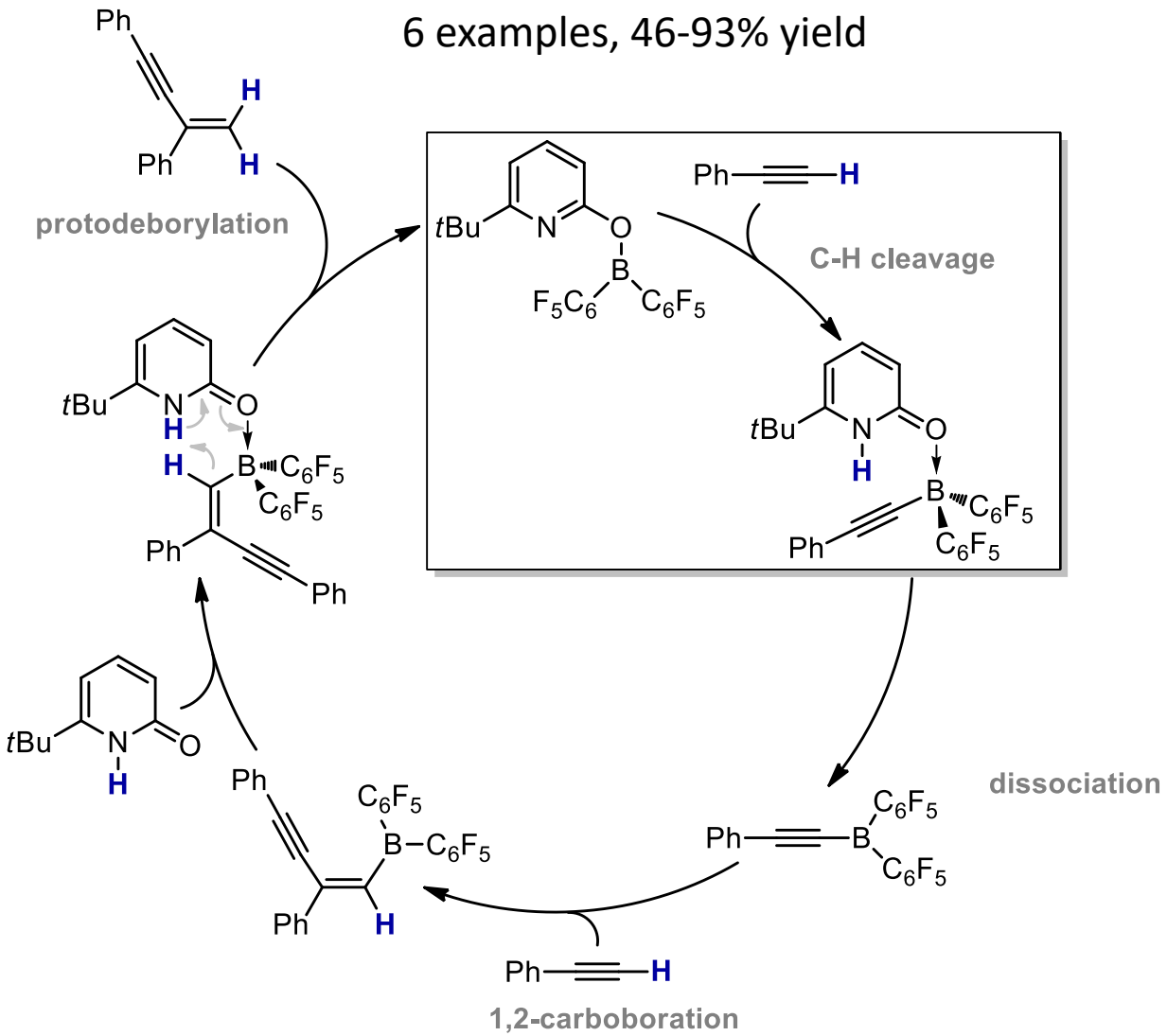

M. Hasenbeck, T. Müller, U. Gellrich, *Catalysis Science & Technology* **2019**, *9*, 2438-2444.

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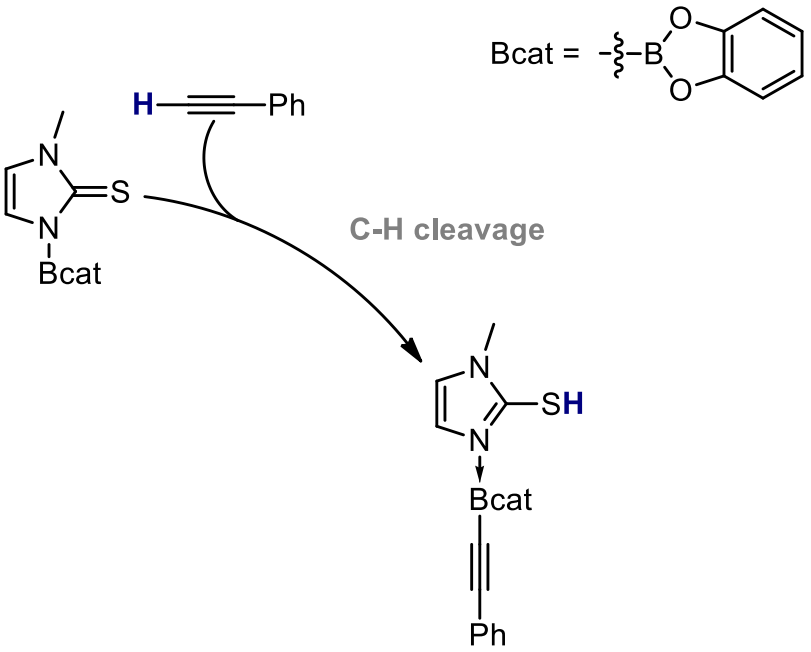
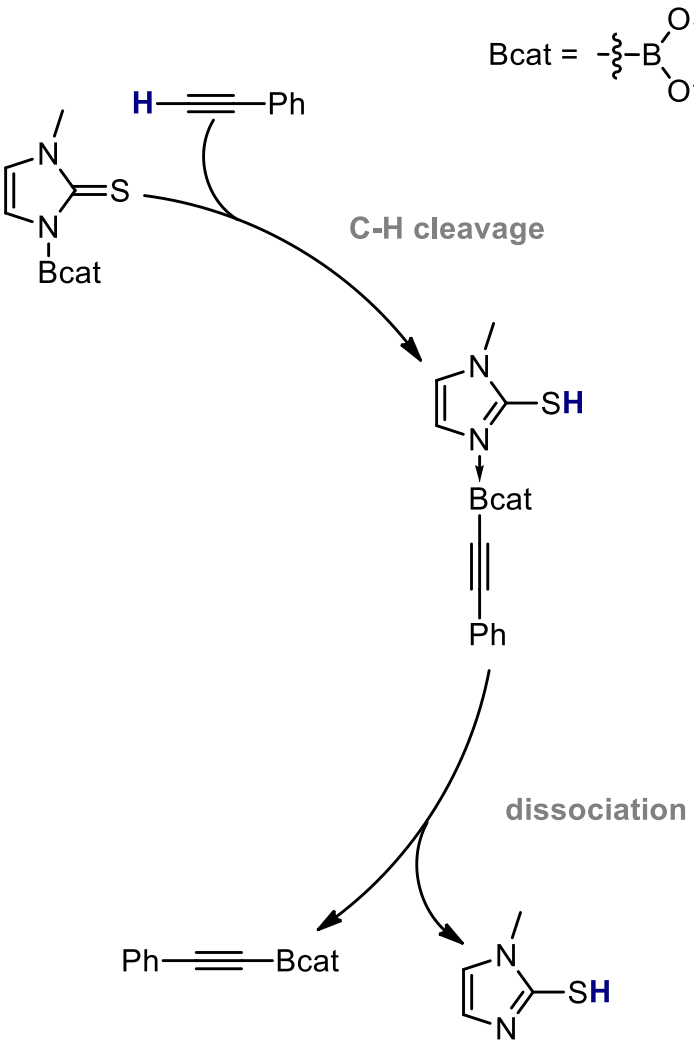


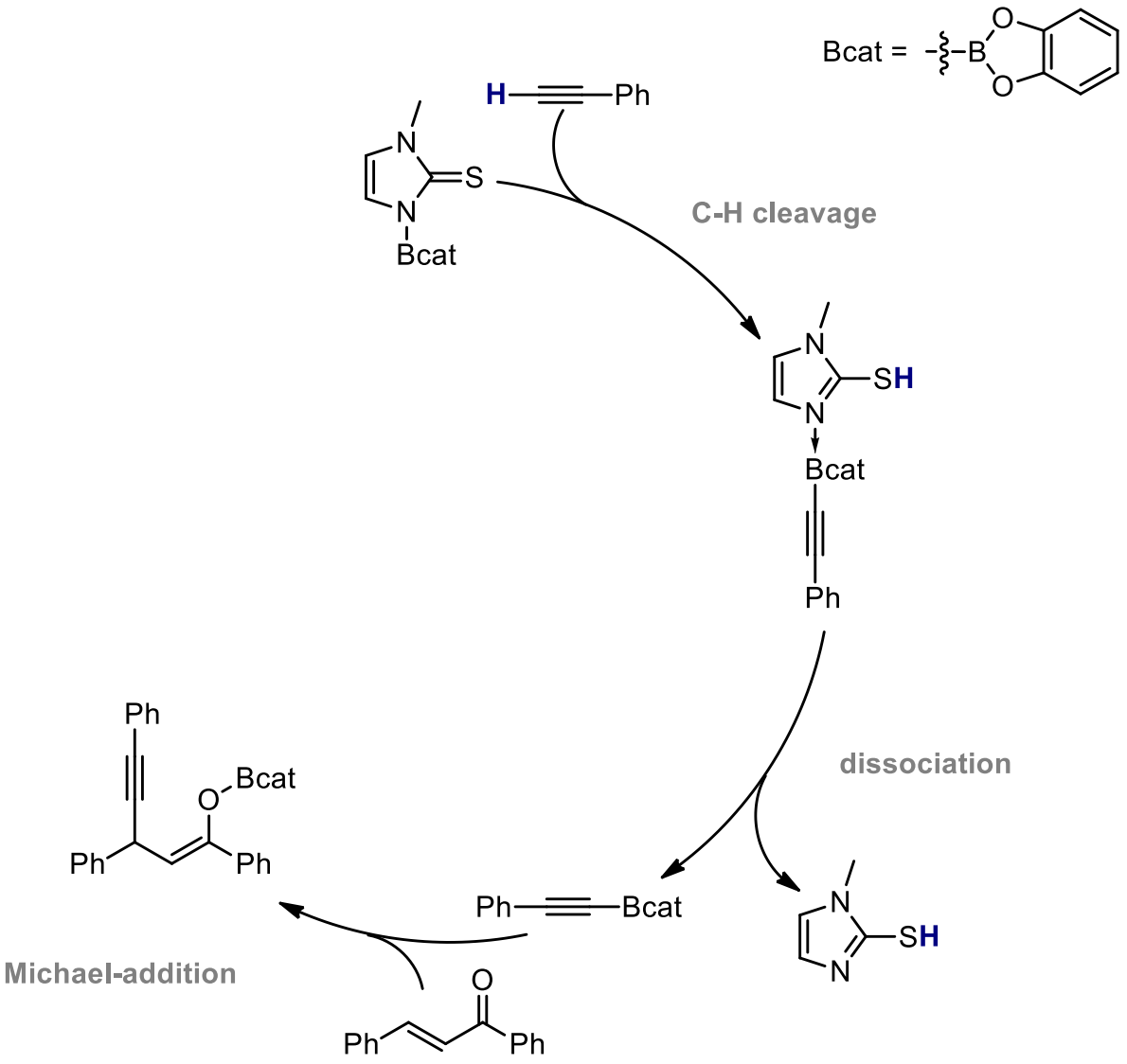
V. Desrosiers, C. Z. Garcia, F.-G. Fontaine, *ACS Catalysis* **2020**, 11046-11056.

Boron-Ligand Cooperation: Carboboration



V. Desrosiers, C. Z. Garcia, F.-G. Fontaine, *ACS Catalysis* **2020**, 11046-11056.

Boron-Ligand Cooperation: Carboboration



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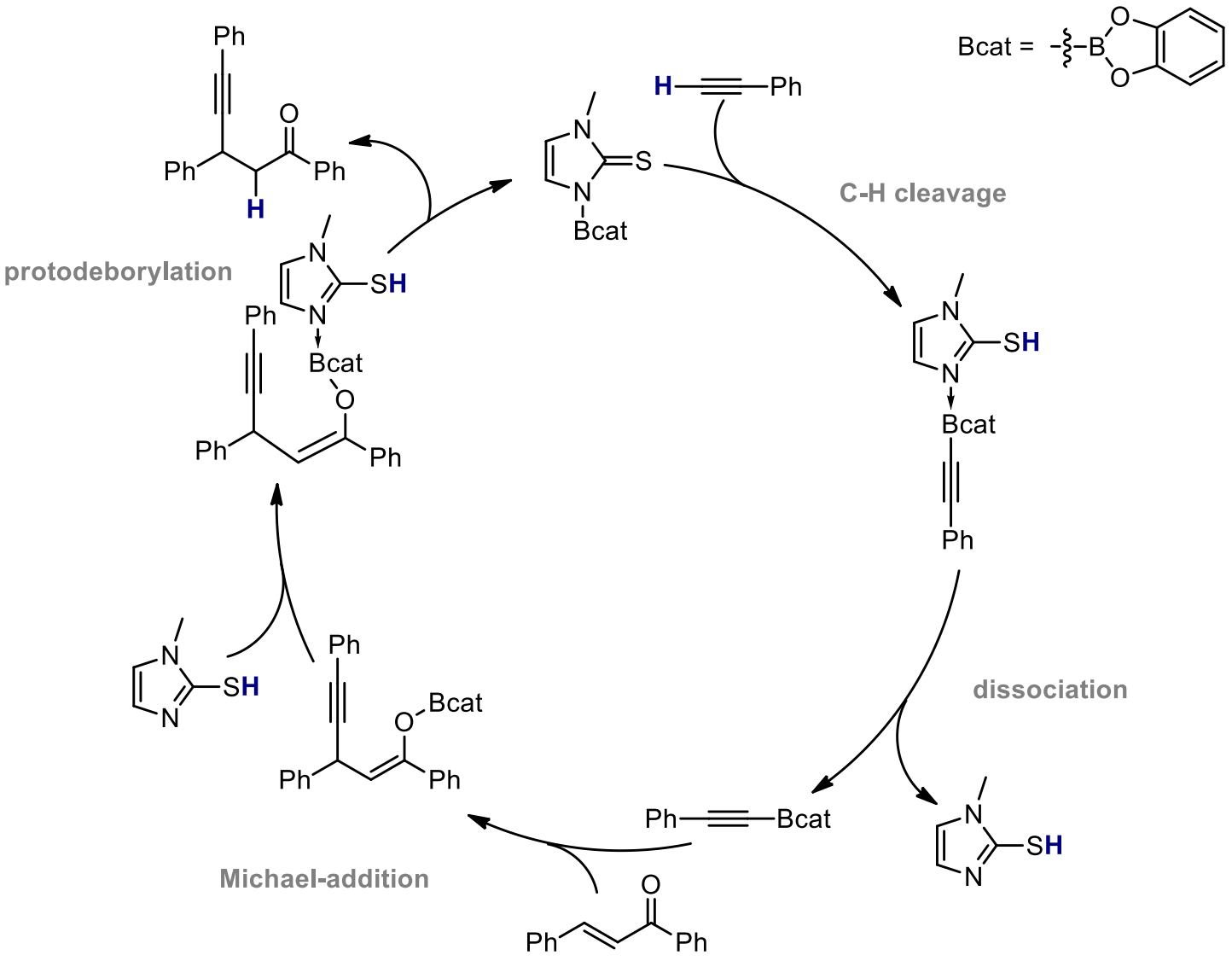
Boron-Ligand Cooperation: Carboboration



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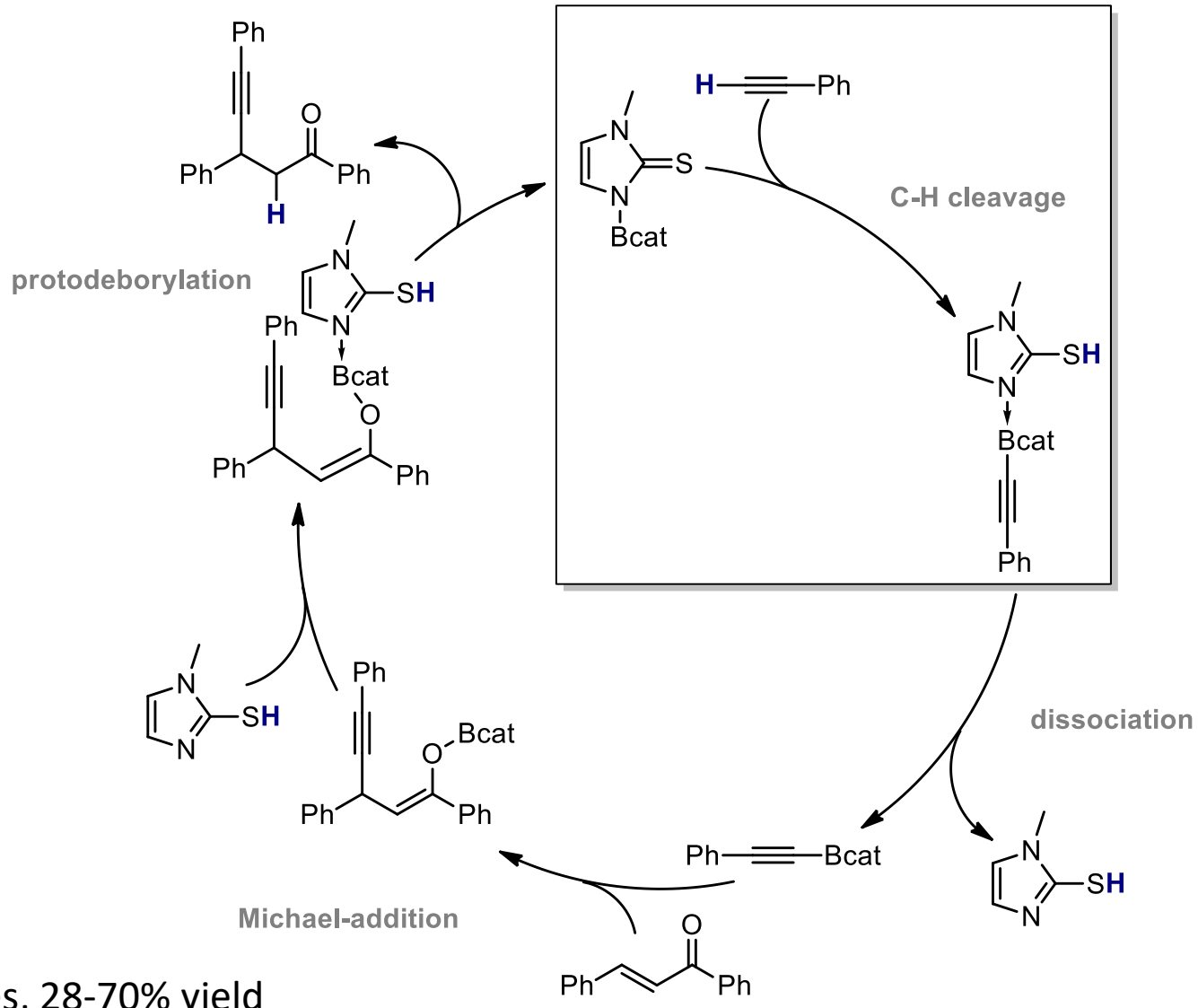
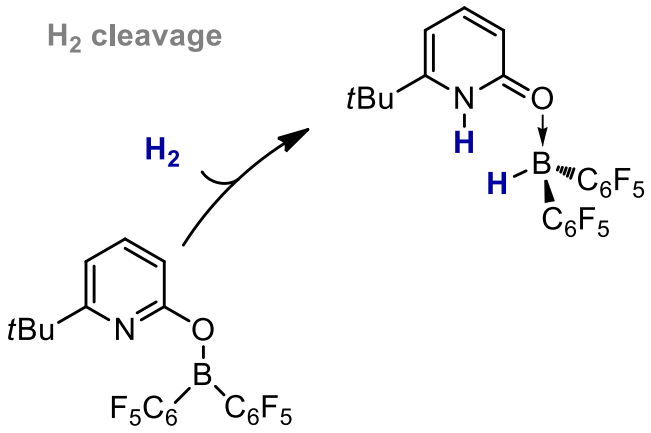
Boron-Ligand Cooperation: Carboboration



12 examples, 28-70% yield

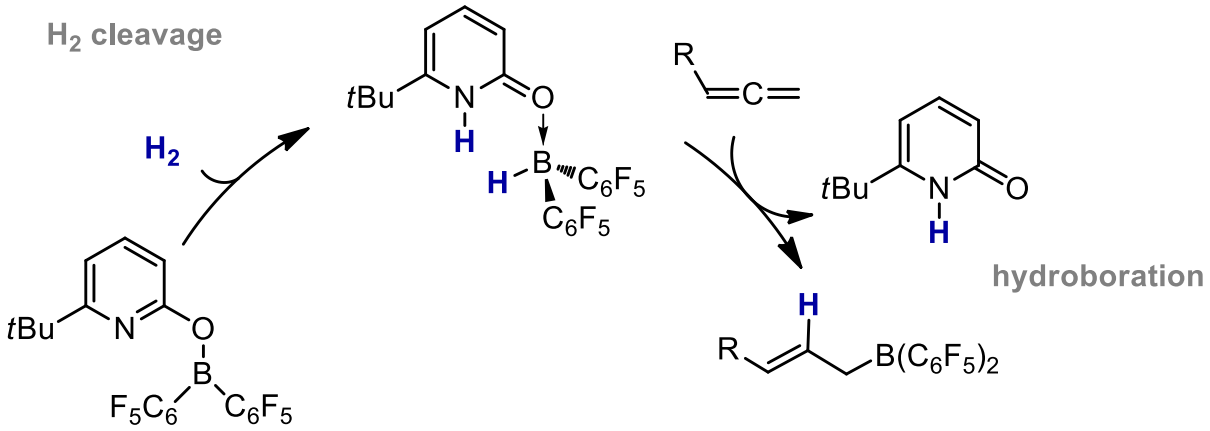
V. Desrosiers, C. Z. Garcia, F.-G. Fontaine, *ACS Catalysis* **2020**, 11046-11056.

Boron-Ligand Cooperation: Allylation



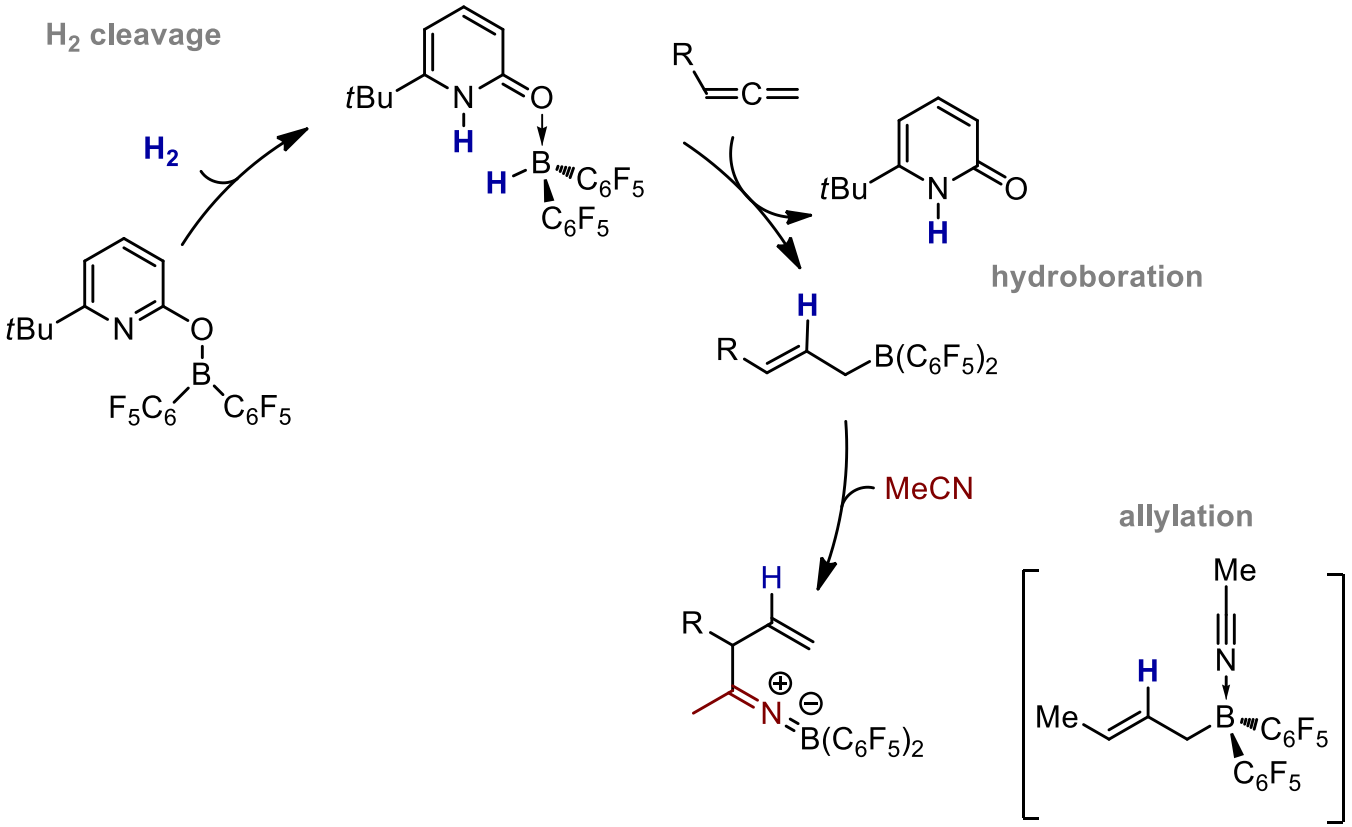
U. Gellrich, M. Hasenbeck, S. Ahles, A. Averdunk, J. Becker, *Angewandte Chemie International Edition* **2020**, DOI: 10.1002/anie.202011790

Boron-Ligand Cooperation: Allylation



U. Gellrich, M. Hasenbeck, S. Ahles, A. Averdunk, J. Becker, *Angewandte Chemie International Edition* **2020**, DOI: 10.1002/anie.202011790

Boron-Ligand Cooperation: Allylation



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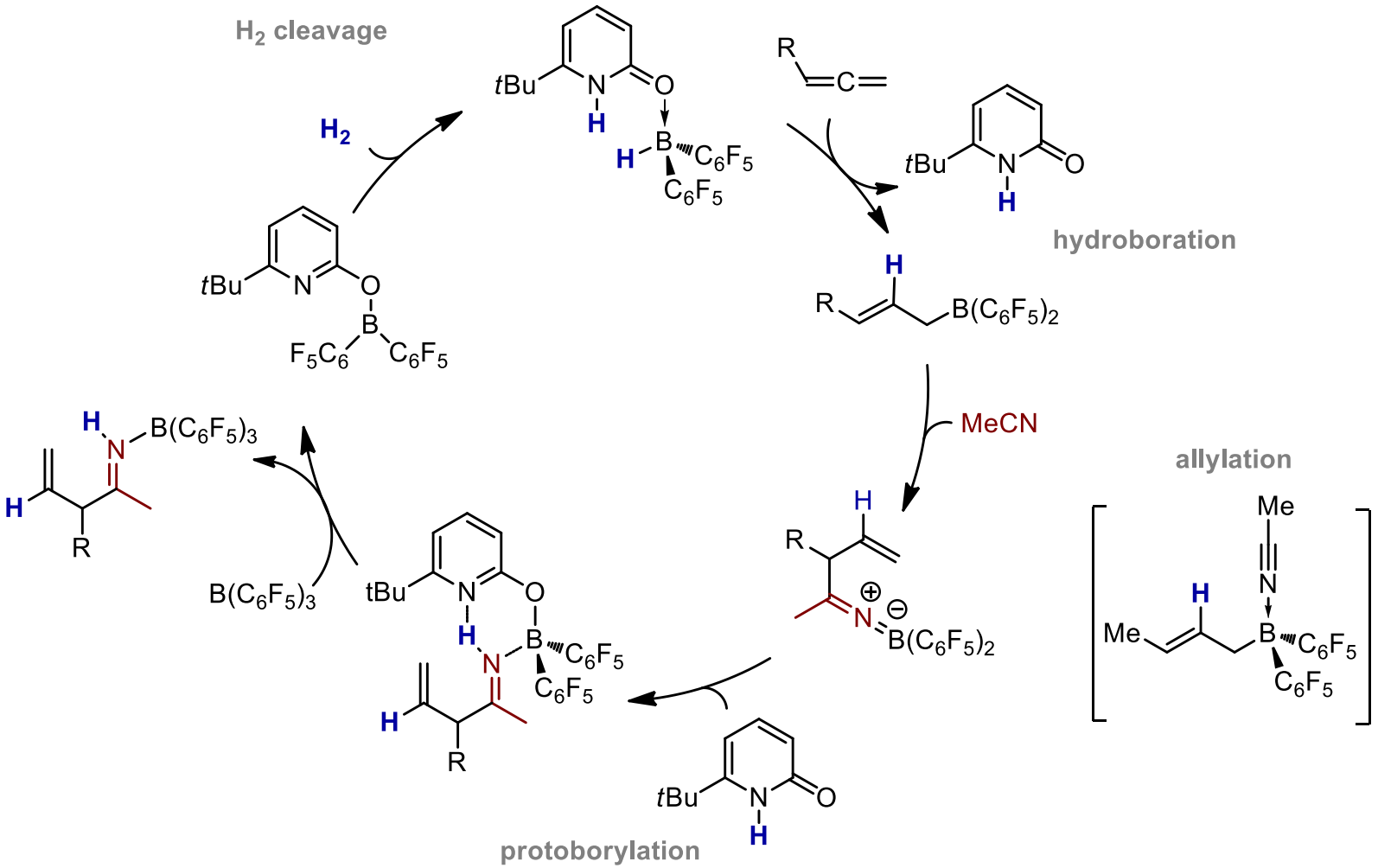
Boron-Ligand Cooperation: Allylation



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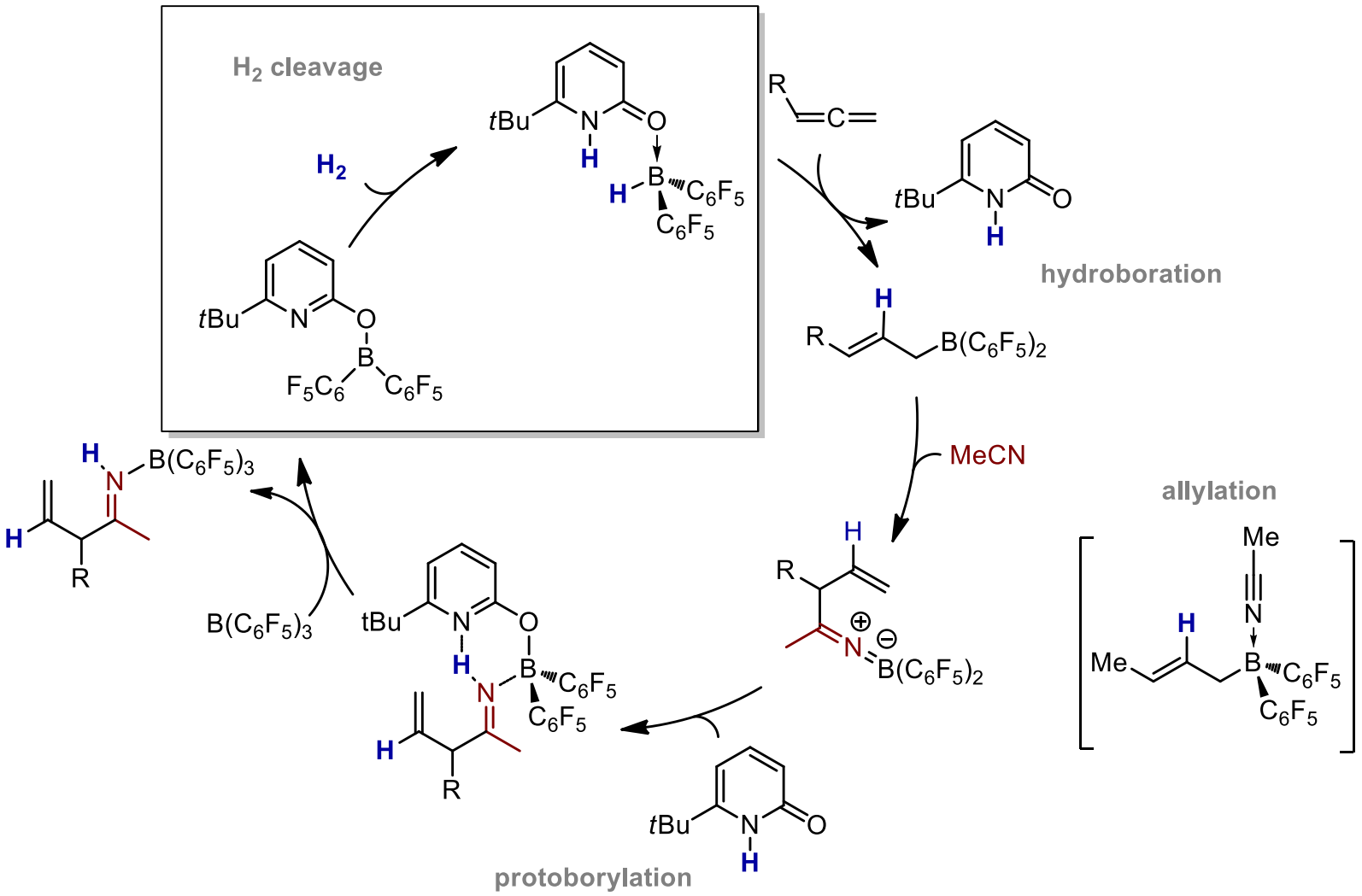
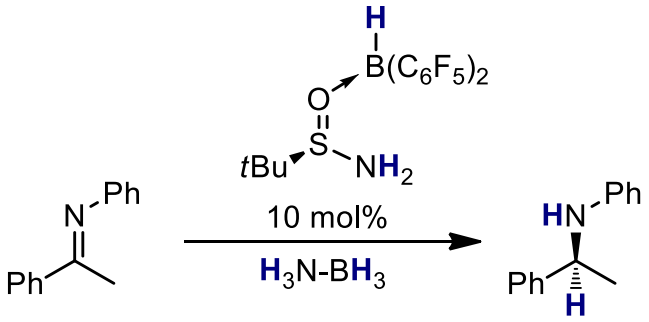
Boron-Ligand Cooperation: Allylation



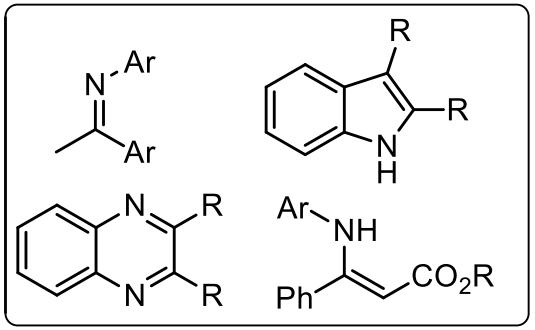
7 examples, 49-90% yield

U. Gellrich, M. Hasenbeck, S. Ahles, A. Averdunk, J. Becker, *Angewandte Chemie International Edition* **2020**, DOI: 10.1002/anie.202011790

Boron-Ligand Cooperation: Transferhydrogenation

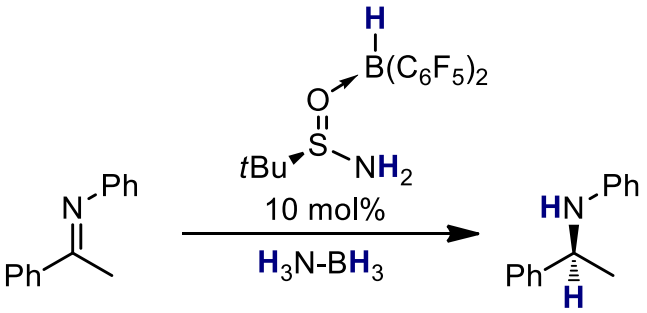


Suitable substrates

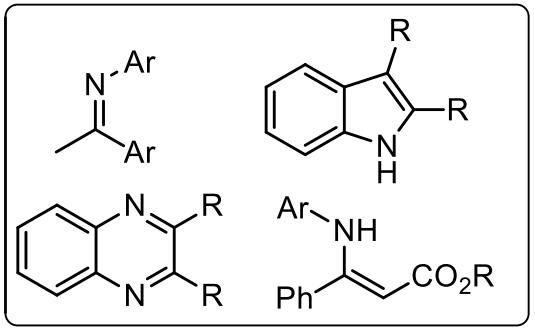


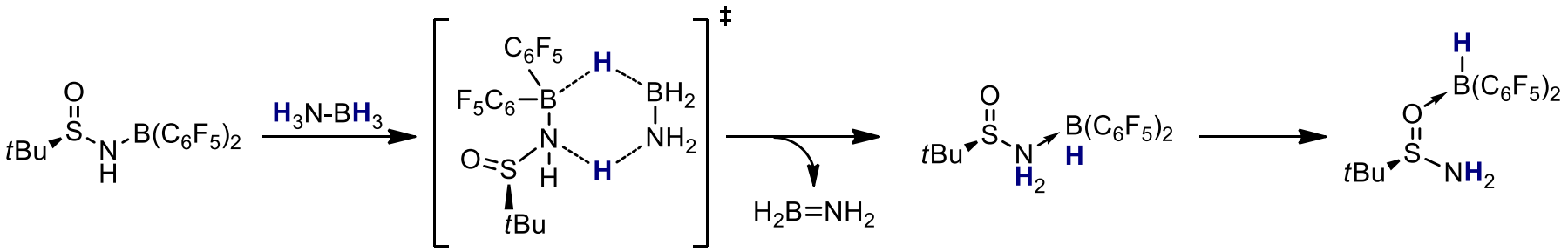
S. Li, G. Li, W. Meng, H. Du, *Journal of the American Chemical Society* **2016**, *138*, 12956-12962., W. Zhao, Z. Zhang, X. Feng, J. Yang, H. Du, *Organic Letters* **2020**, *22*, 5850-5854., S. Li, W. Meng, H. Du, *Organic Letters* **2017**, *19*, 2604-2606., W. Zhao, X. Feng, J. Yang, H. Du, *Tetrahedron Letters* **2019**, *60*, 1193-1196.

Boron-Ligand Cooperation: Transferhydrogenation



Suitable substrates





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Acknowledgement

- Dr. Urs Gellrich
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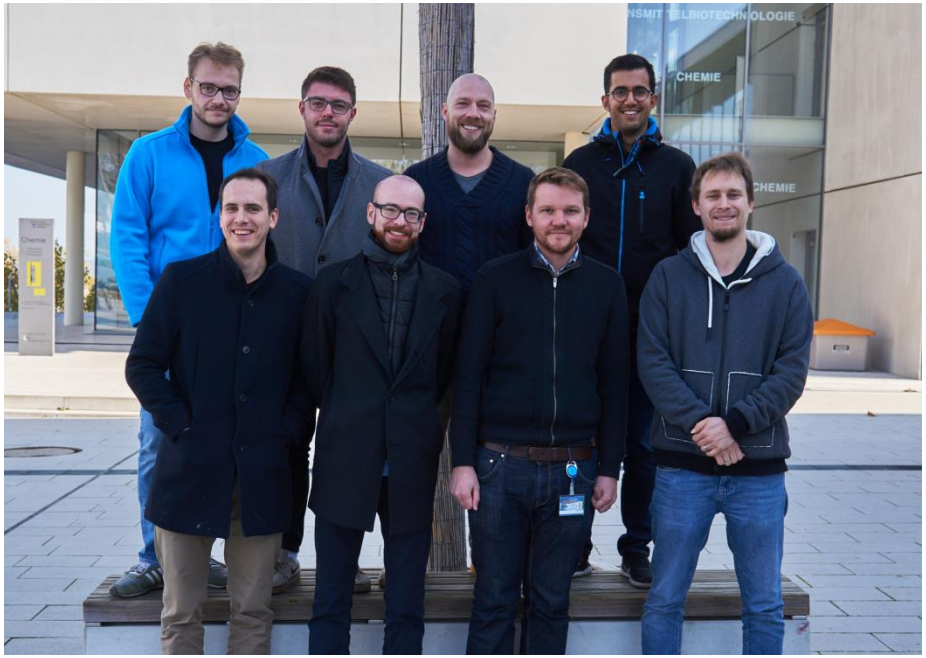
- Gellrich Group
- Organic Chemistry Department



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