Organoboron Compounds: Prevalent and Novel Applications

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Contents

Characteristics of Boron[1]

Table: Atomic Radii

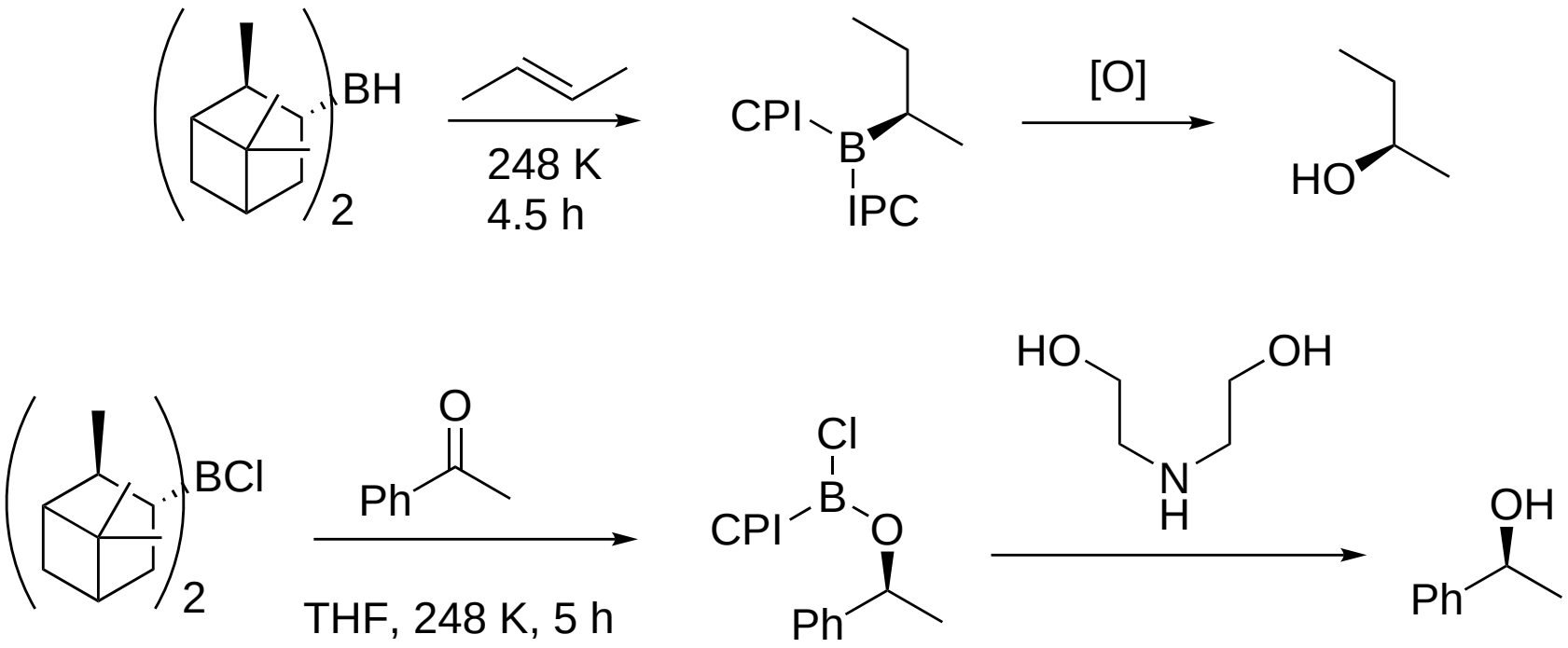
	B	C
r_{vdw}(Å)		1.70
r_{cov}(Å)	0.83	0.68

Table: Bond Dissociation Energy

Bonds	$D^{\circ}_{298K}\ (kJ \cdot mol^{-1})$
B – B	290
B – H	345.2 ± 2.5
C – C	618 ± 15.4
C – H	318.4 ± 1.2
B – C	448 ± 29

[1] David R. Lide. *CRC Handbook of Chemistry and Physics*. 90th Edition (CD-ROM Version 2010). Boca Raton, FL.: CRC Press/Taylor and Francis.

Asymmetric Reduction of C=C[2] and C=O[3] Bonds



[2] Herbert C. Brown, Manoj C. Desai, and Prabhakar K. Jadhav. "Hydroboration. 61. Diisopinocampheylborane of high optical purity. Improved preparation and asymmetric hydroboration of representative cis-disubstituted alkenes". In: *The Journal of Organic Chemistry* 47.26 (1982). DOI: 10.1021/jo00147a004.

[3] Herbert C. Brown, J. Chandrasekharan, and P. V. Ramachandran. "Chiral synthesis via organoboranes. 14. Selective reductions. 41. Diisopinocampheylchloroborane, an exceptionally efficient chiral reducing agent". In: *Journal of the American Chemical Society* 110.5 (1988). DOI: 10.1021/ja00213a030.

Diastereoselective Allylboration[4]

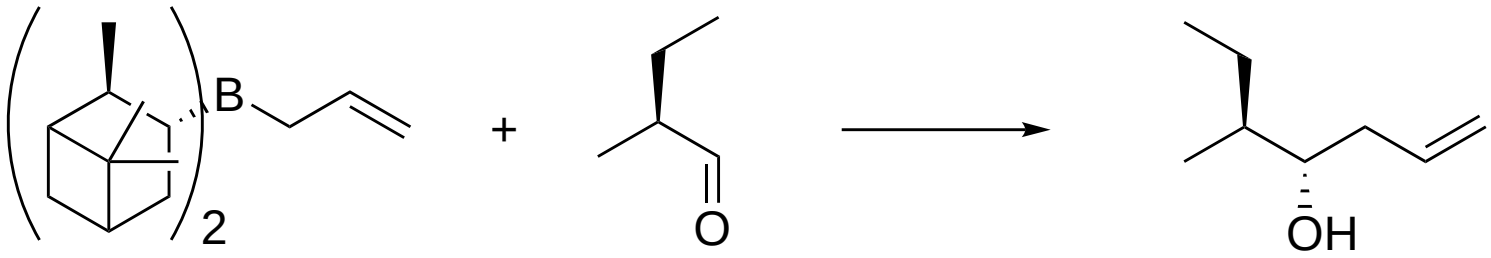
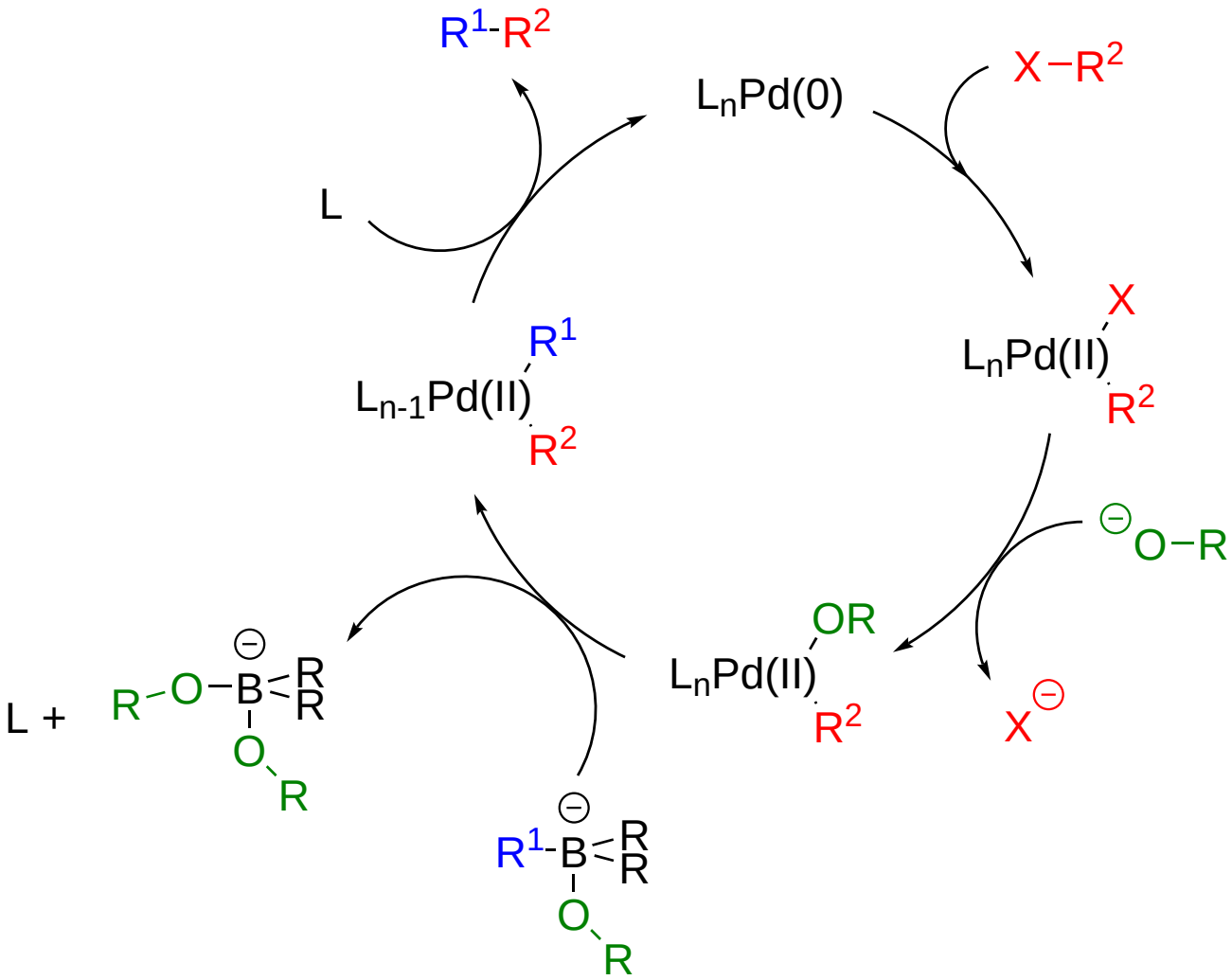


Figure: Diastereoselective Allylboration

[4] Herbert C. Brown, Krishna S. Bhat, and Ramnarayan S. Randad. "β-Allyldiisopinocampheylborane: a remarkable reagent for the diastereoselective allylboration of α-substituted chiral aldehydes". In: *The Journal of Organic Chemistry* 52.2 (1987), pp. 319–320. ISSN: 0022-3263. DOI: 10.1021/jo00378a042. URL: https://doi.org/10.1021/jo00378a042.

Suzuki-Miyaura Cross-Coupling



Tandem Diels-Alder Cycloaddition

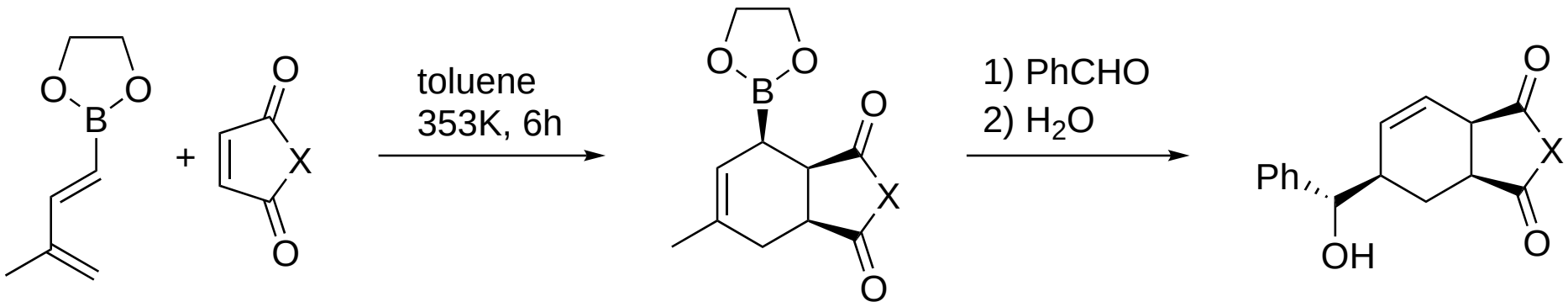
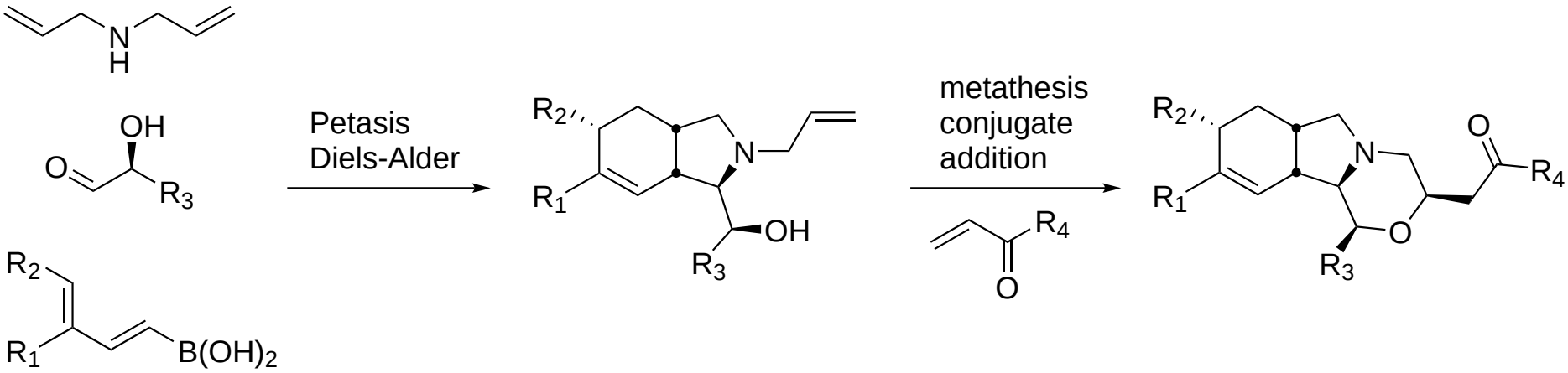


Figure: A Module Figure

The diastereoselectivity of this two-step process is very high, that is why this process is very important for generating multiple stereocentres from rather simple starting materials.[5]

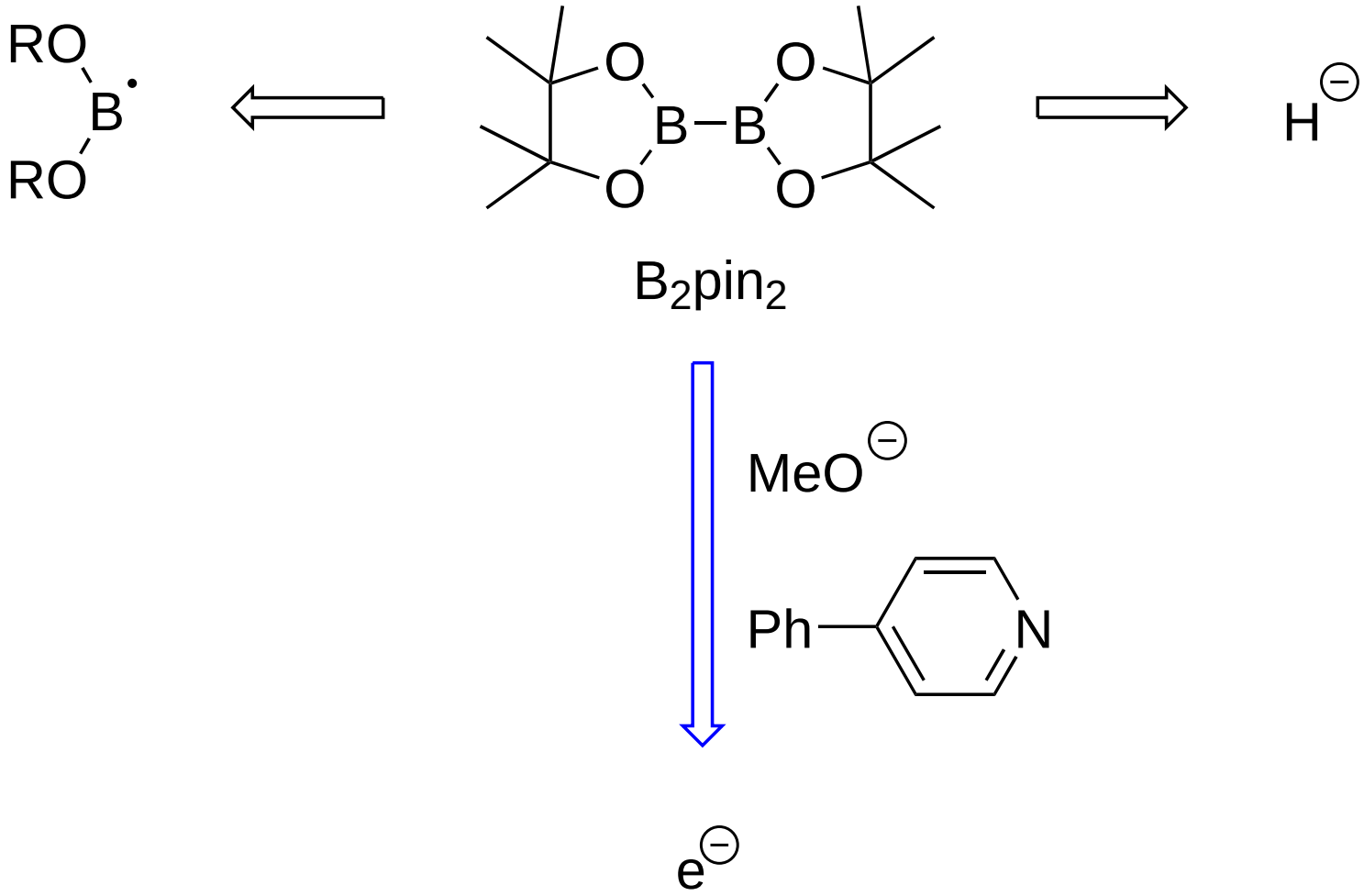
[5] Jadwiga Pyziak, Jędrzej Walkowiak, and Bogdan Marciniec. "Recent Advances in Boron-Substituted 1,3-Dienes Chemistry: Synthesis and Application". In: 23.15 (2017). DOI: 10.1002/chem.201602124.

A Synthetic Example[6]



[6] Alexandre Cannillo et al. "Fast Synthesis of Complex Enantiopure Heterocyclic Scaffolds by a Tandem Sequence of Simple Transformations on -Hydroxyaldehydes". In: *Chemistry – A European Journal* 19.28 (2013). DOI: 10.1002/chem.201301712.

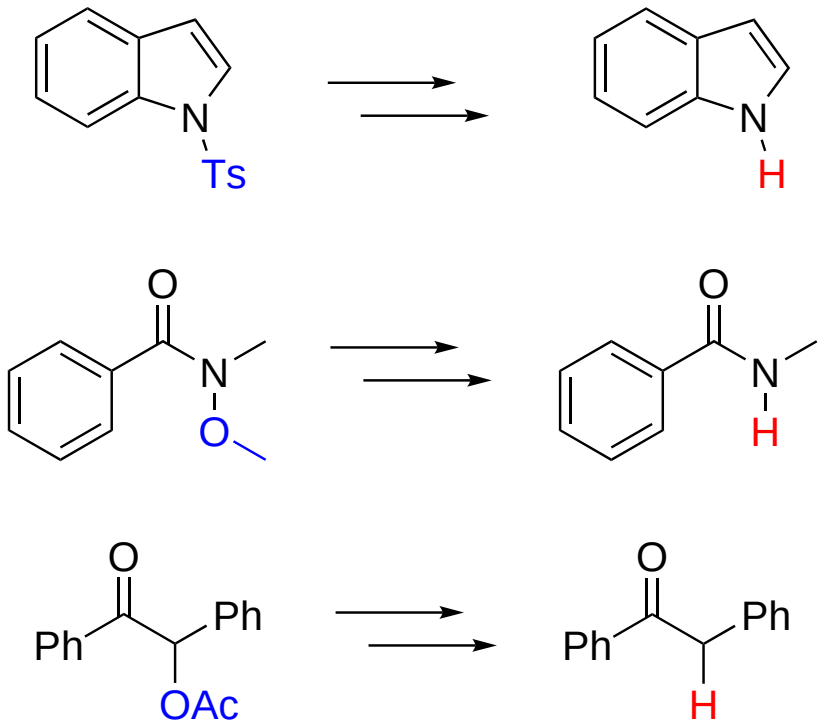
Latest application of B_2pin_2[7]



[7] Li Zhang and Lei Jiao. "Super electron donors derived from diboron". In: *Chemical Science* 9.10 (2018). DOI: 10.1039/C8SC00008E.

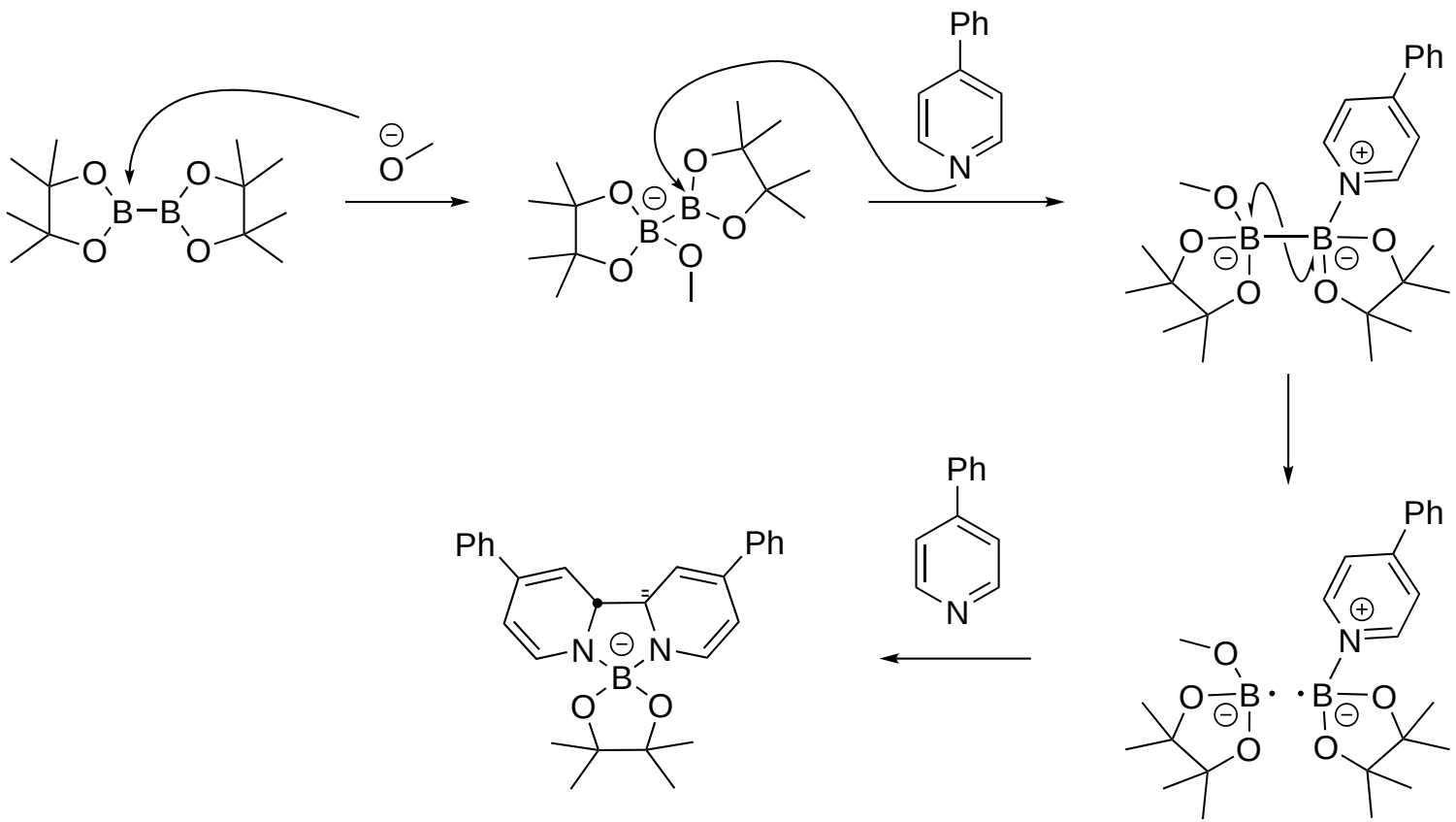
Synthetic Applications of the New Method

When applied with B_2pin_2, p-PhPy, MeOK, the following reactions can take place[8]:

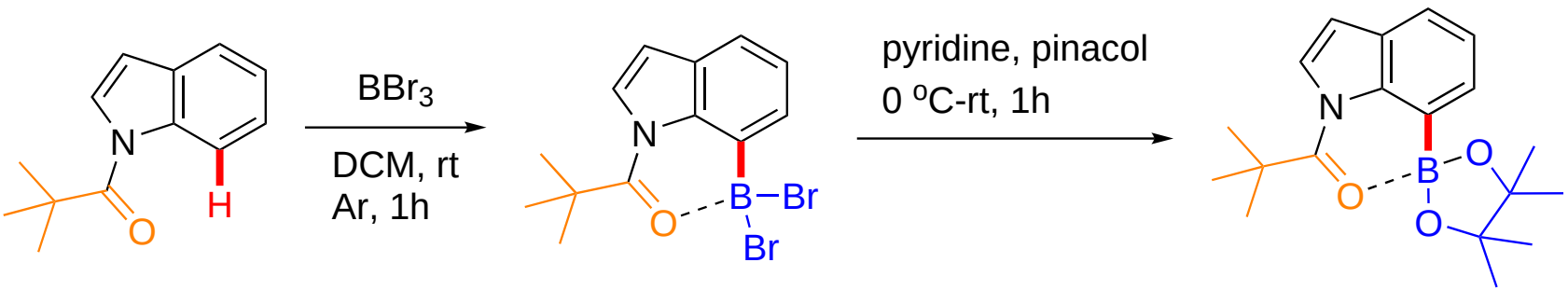


[8] Li Zhang and Lei Jiao. "Pyridine-Catalyzed Radical Borylation of Aryl Halides". In: *Journal of the American Chemical Society* 139.2 (2017). DOI: 10.1021/jacs.6b11813.

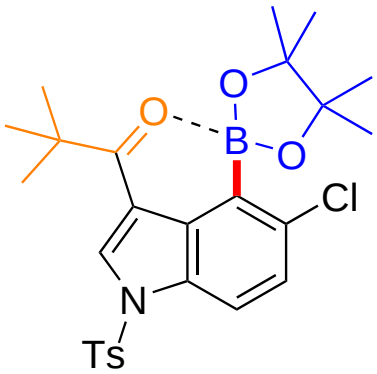
Mechanisms of this Method



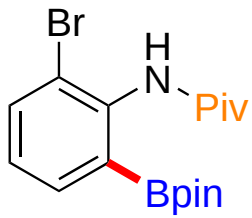
Metal-Free Directed C—H Borylation[9]



yield: 78%



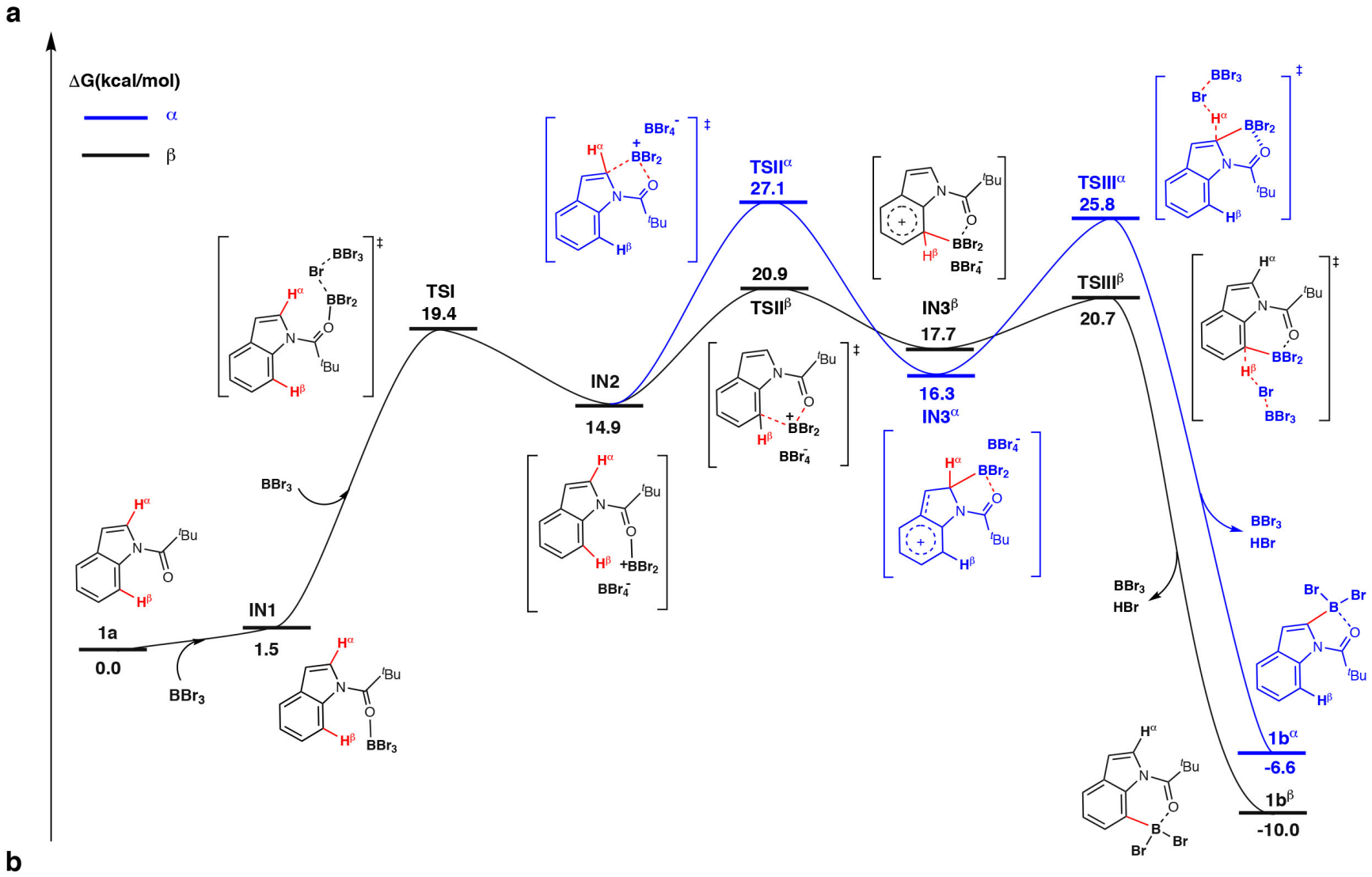
yield: 91%



yield: 99%

[9] Jiahang Lv et al. "Metal-free directed C–H bond activation and borylation". In: *Nature* (2019). DOI: 10.1038/s41586-019-1640-2.

Mechanism of this Reaction



Acknowledgments

- Associate Prof. Jiao
- Associate Prof. Chen
- Authors of the brilliant works mentioned above

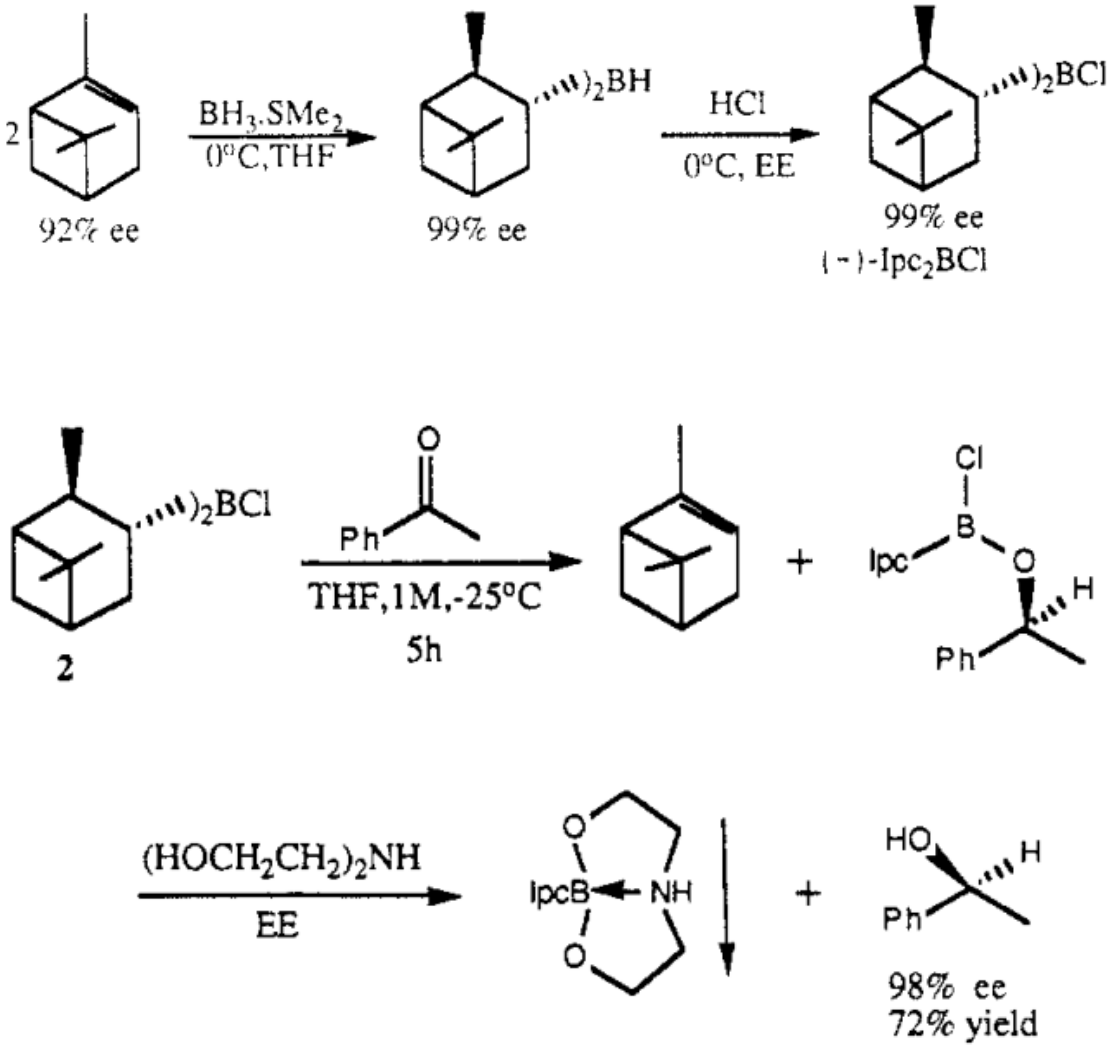
Annex

This slide and articles cited in the slide can be found here:

https://github.com/Alexander-Qi/organoboron/releases/tag/1.1

Or Scan this QRcode:

IPC_2B-Cl Related Information



Boryl–pyridine species and their interconversion