XU GROUP

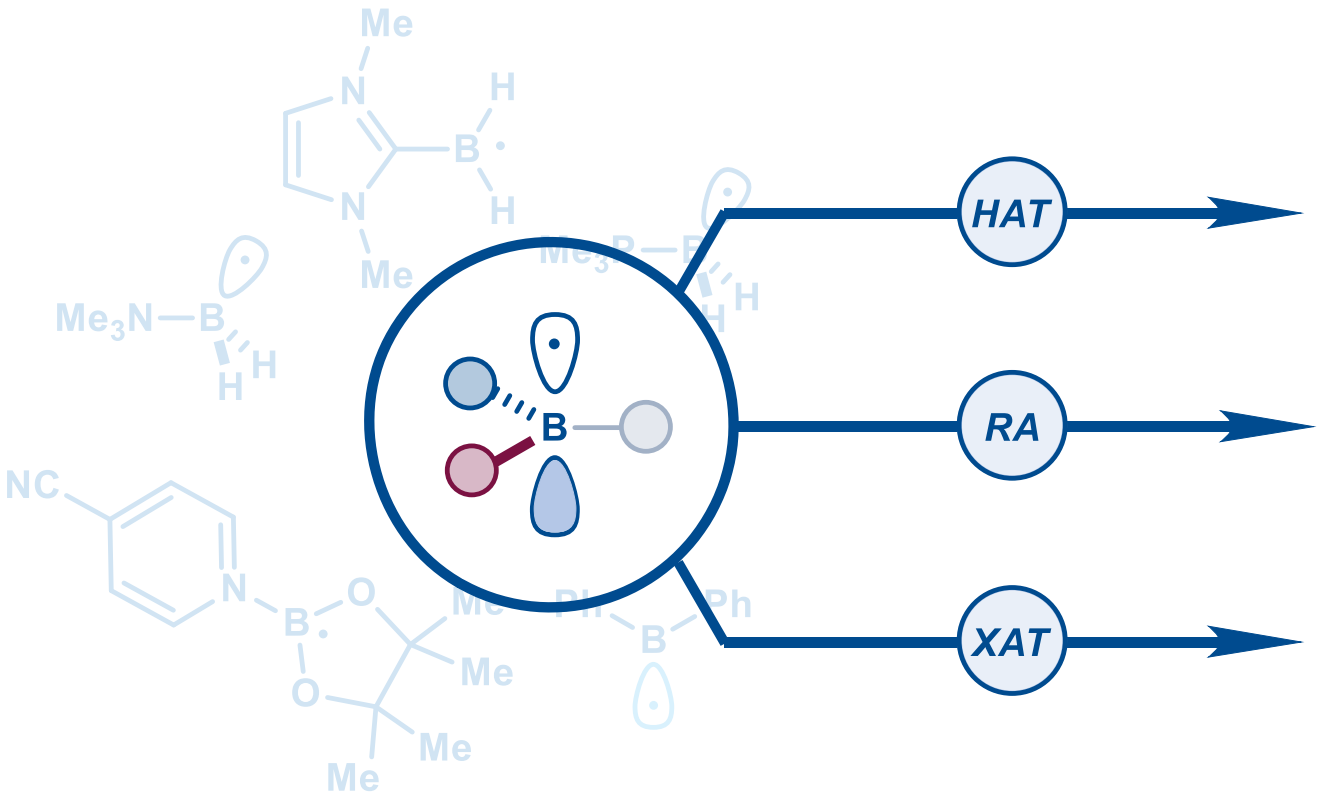
Department of Chemistry, Peking University

Selected Weekly Literature Presentations

Disclaimer:

These slides contain personal interpretations and may include errors or subjective views.

Boryl Radicals in Organic Synthesis



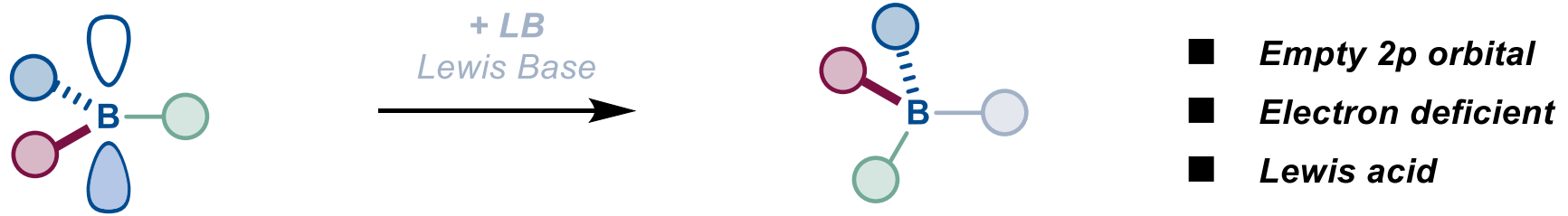
Reporter: Peijie Luo

Adviser: Yan Xu

2025.11.28

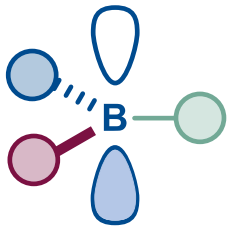
Content

Introduction of Boryl Radicals

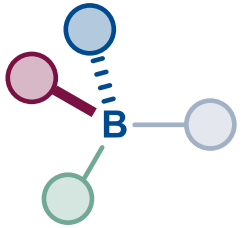


- ***Empty 2p orbital***
- ***Electron deficient***
- ***Lewis acid***

Introduction of Boryl Radicals



+ LB
Lewis Base



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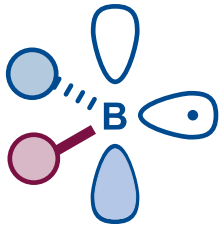

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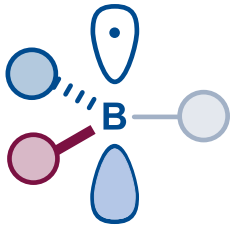


Ligated Boryl Radicals (LBRs)

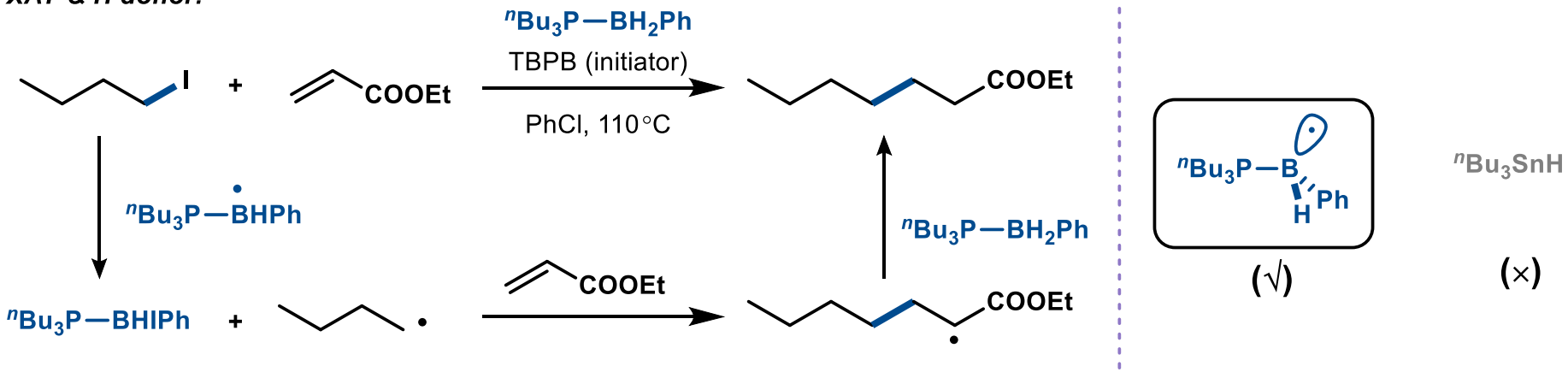
3 center - 5 electron (3c-5e)
highly electron deficient
unstable

4 center - 7 electron (4c-7e)
tunable strics and electronics
isolatable

Development History

Roberts et al. (1980's)

XAT & H donor:



Roberts, B. P. *et al. J. Chem. Soc., Chem. Commun.*, **1983**, 1224 – 1226.

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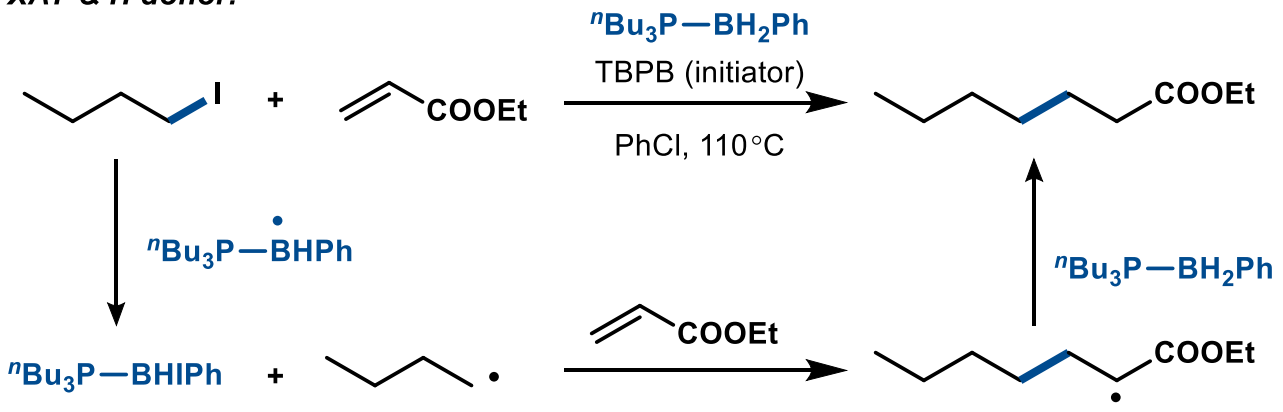
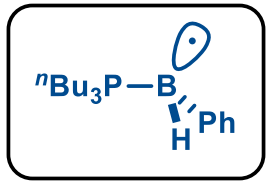


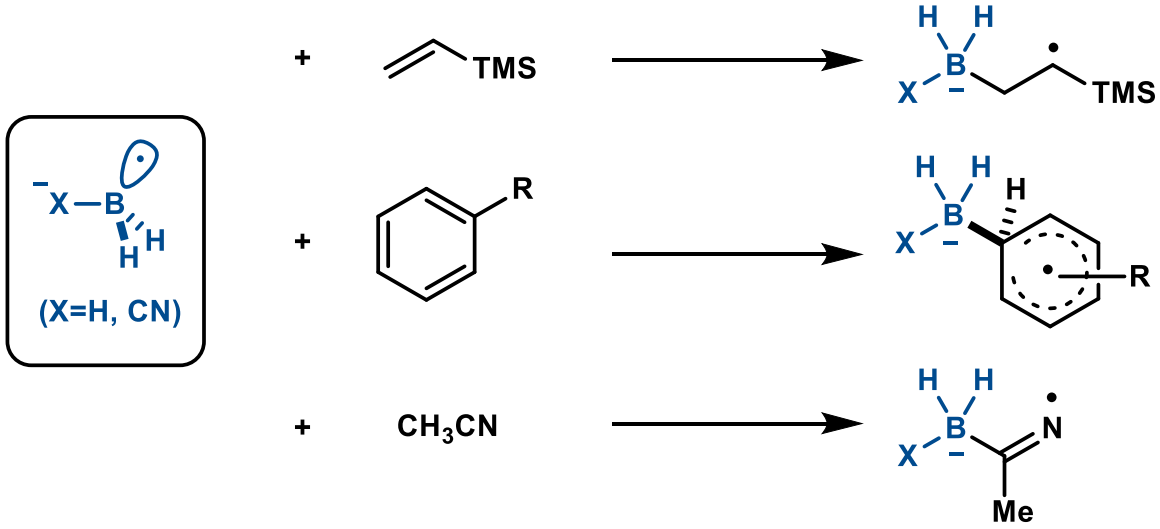


(√)

$^{n}Bu_3SnH$

(×)

Radical Addition:



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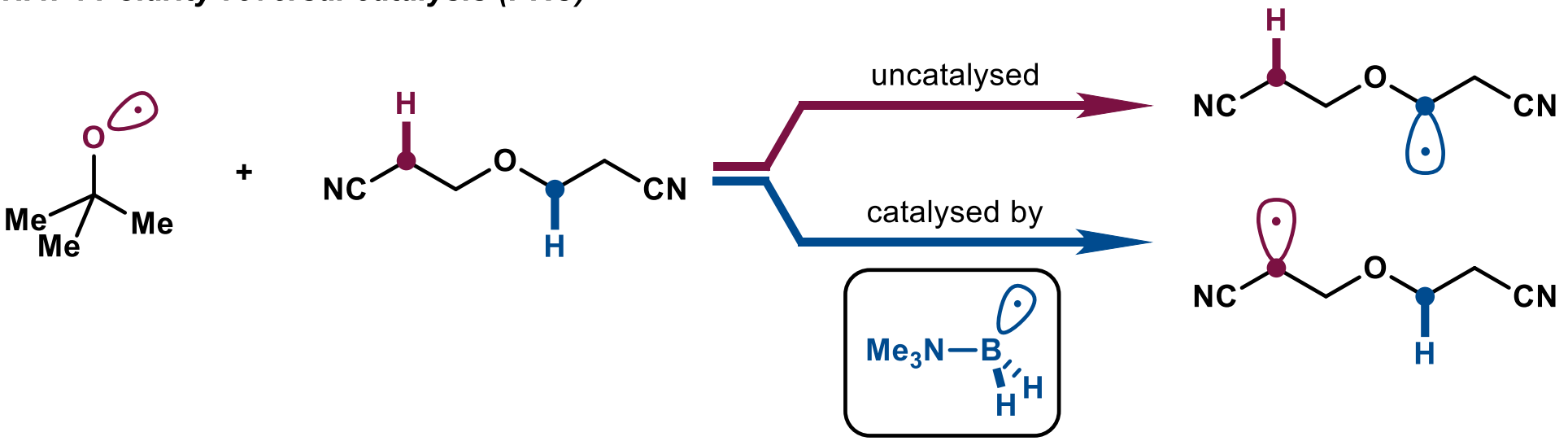
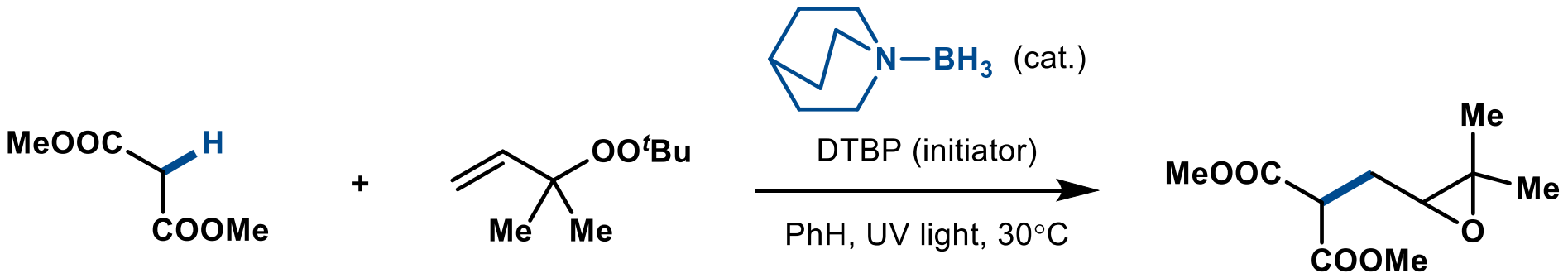
Development History

Roberts et al. (1980's)

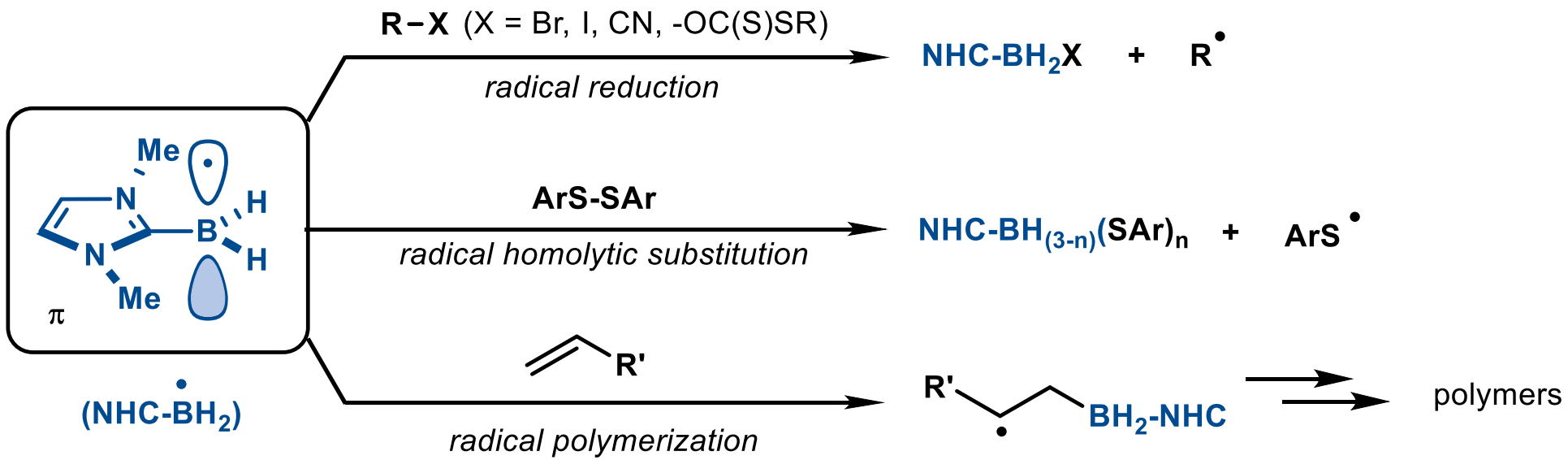
HAT : Polarity-reversal catalysis (PRC)





Development History

Curran and coworkers (2008-2015)



Curran, D. P. *et al. J. Am. Chem. Soc.*, **2008**, 130, 10082 – 10083.
Lalevee, J. *et al. J. Phys. Org. Chem.*, **2009**, 22, 986 – 993.
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Development History

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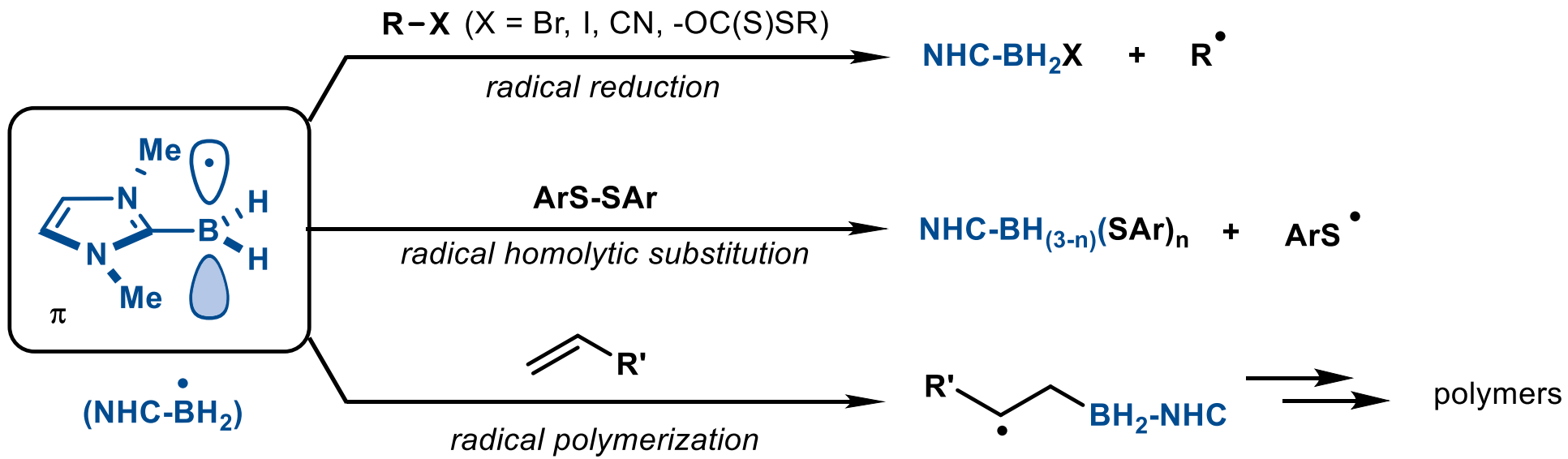
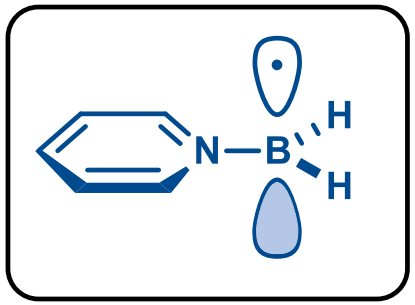
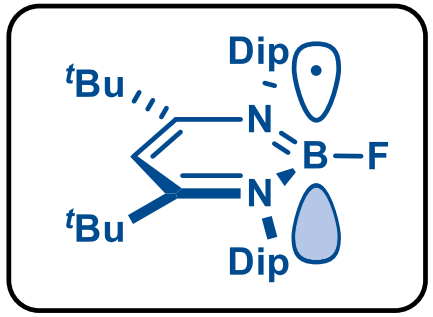


Lalevee et al. 2009





Nozaki et al. 2009

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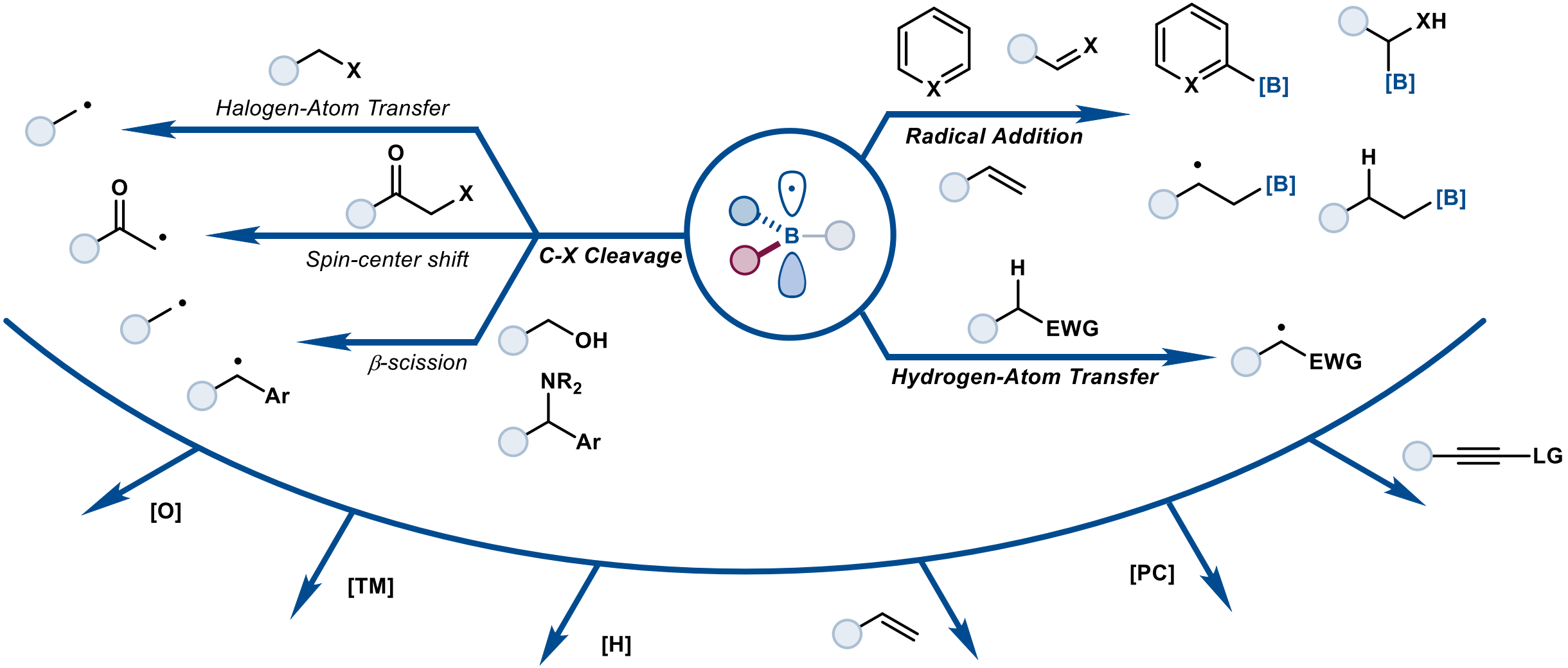
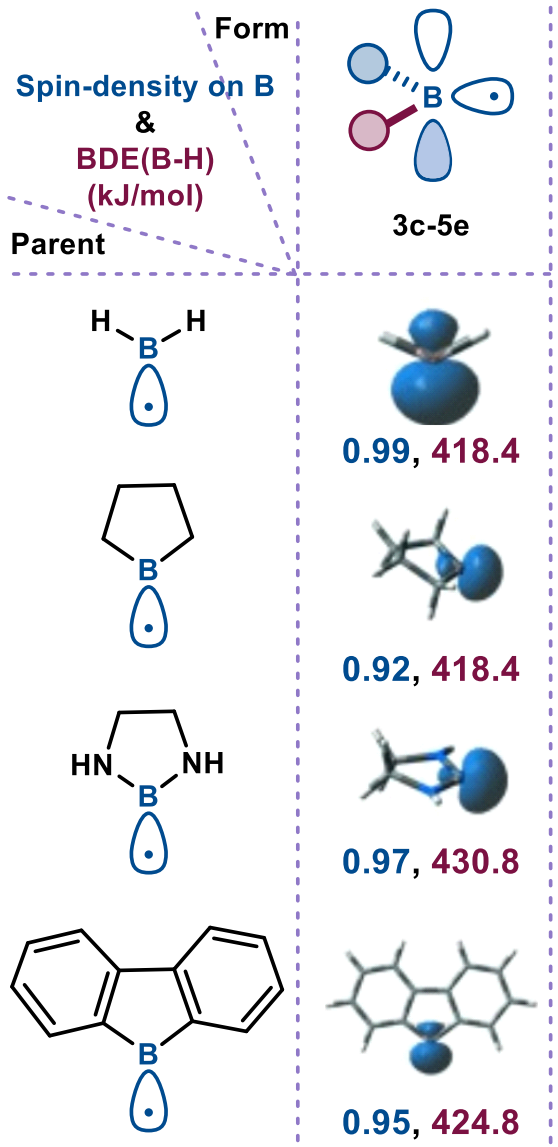
Reactivity


X
Halogen-Atom Transfer
O
X
O
Spin-center shift
β-scission
OH
Ar
NR2
Ar
C-X Cleavage
B
X
X
[B]
Radical Addition
XH
[B]
[B]
H
[B]
H
EWG
EWG
Hydrogen-Atom Transfer
LG
[O]
[TM]
[H]
[PC]

Content

- *Introduction of Boryl Radicals*
- *Structures, Properties and Reactivity*
  - *Structure*
  - *Spin-density Distribution, Stability and BDE(B-H)*
  - *Electrophilicity and Nucleophilicity*
  - *Reactivity*
- *Application of Boryl Radicals in Organic Chemistry*
- *Outlook*

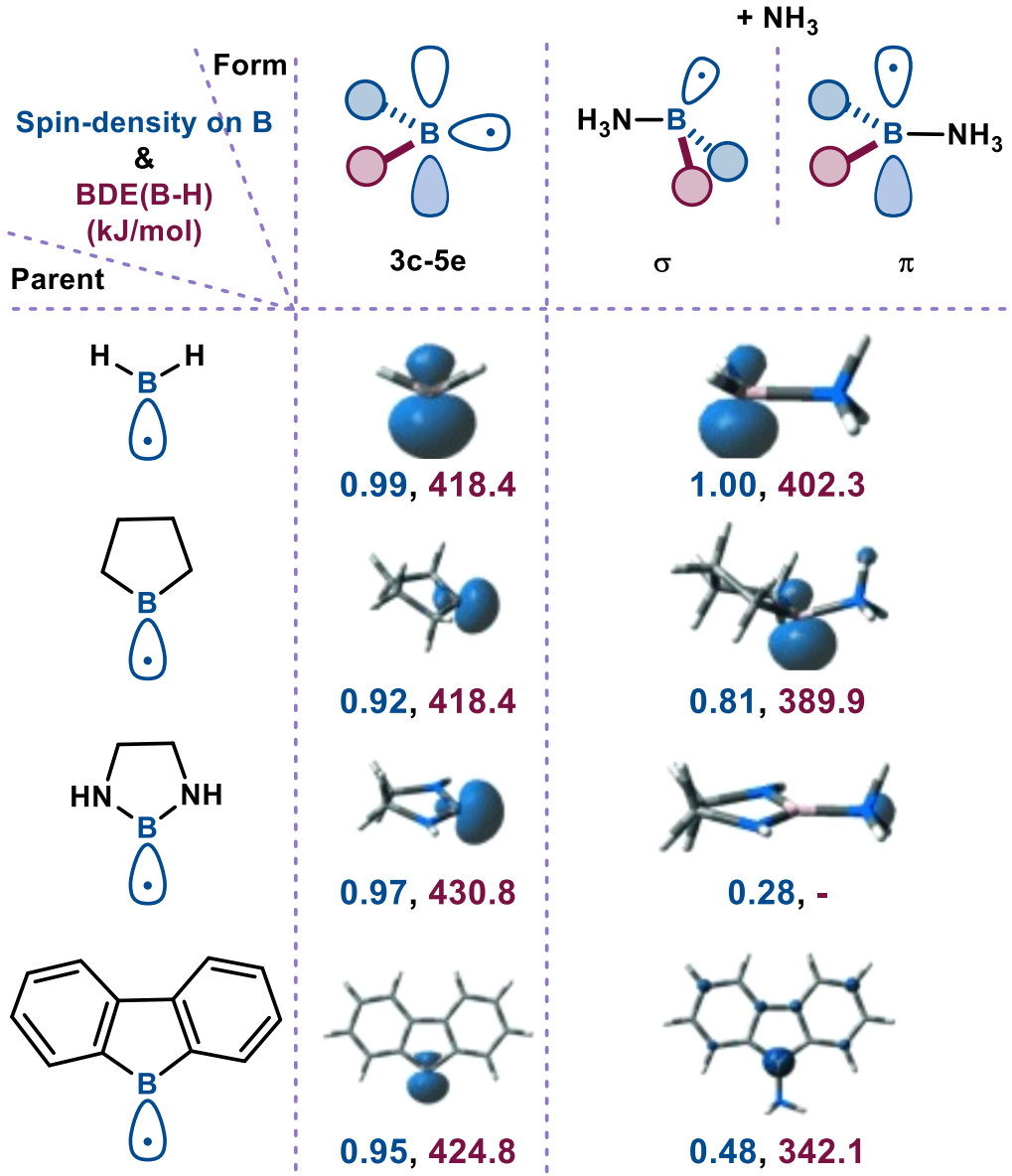
Structures and Properties



- Py vs. NHC
- BDE(B-LB):
  - NHC > Py > NH_3
- BDE(B-H):
  - ~ spin-density
- Stablity:
  - Py > NHC > NH_3
  - Captodative effect
- 3c-5e vs. 4c-7e

Li, P. F. *et al. Chem. Eur. J.*, **2014**, *20*, 1630 – 1637.

Structures and Properties



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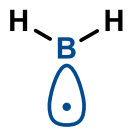
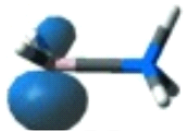
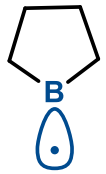
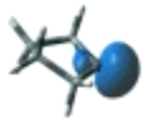
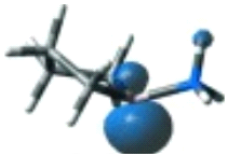
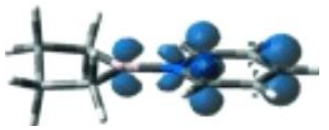
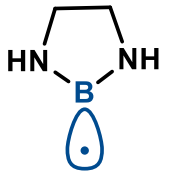
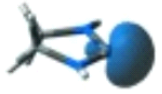
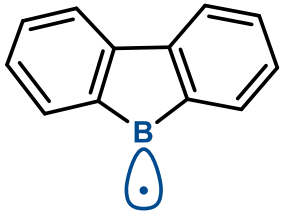
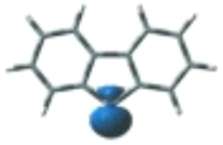
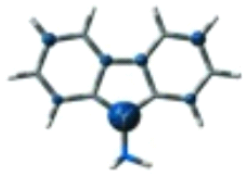
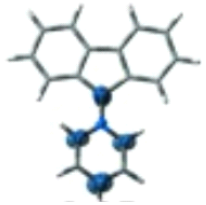
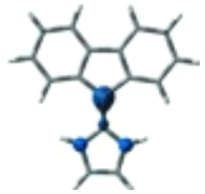
Structures and Properties

Form / Spin-density on B & BDE(B-H) (kJ/mol) / Parent	3c-5e	+ NH_3 σ	+ NH_3 π	+ Py π	+ NHC π
	 0.99, 418.4	 1.00, 402.3		 0.32, 278.0	 0.54, 304.2
	 0.92, 418.4	 0.81, 389.9		 0.20, 238.4	 0.41, 276.2
	 0.97, 430.8	 0.28, -		 0.05, 203.0	 0.13, 245.2
	 0.95, 424.8	 0.48, 342.1		 0.25, 263.3	 0.36, 271.7

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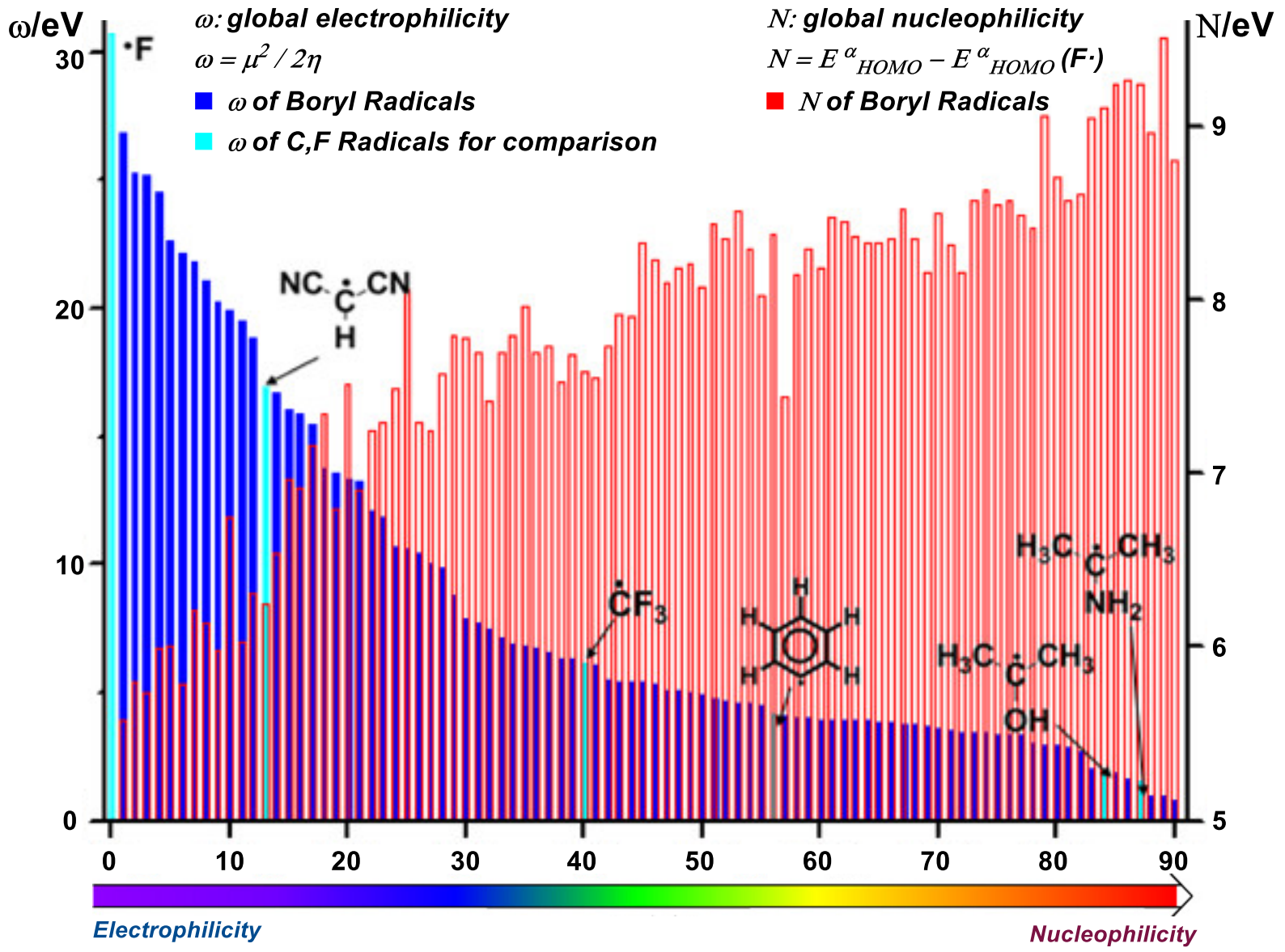
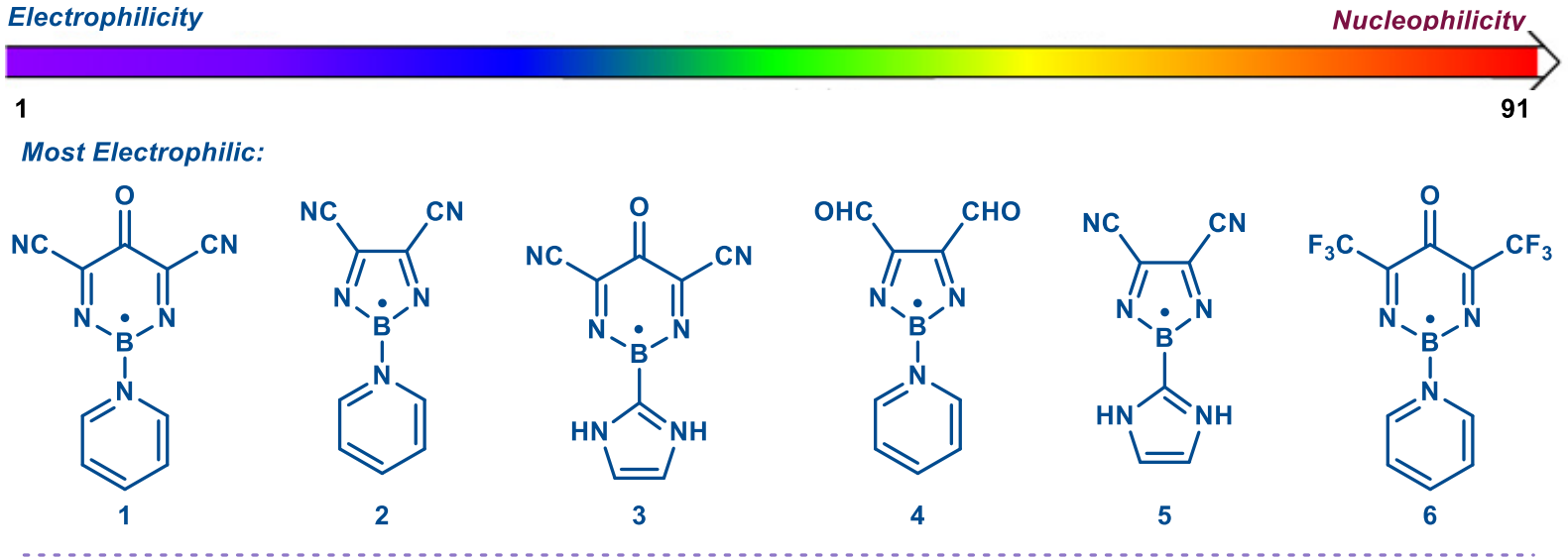
Electrophilicity and Nucleophilicity



- Boryl vs. Carbon
- Major: Nucleophilicity
- Minor: Electrophilicity
  - Structure
  - Spin-density
- Substituent on LB:

Li, P. F. *et al. J. Org. Chem.*, **2017**, *82*, 2898 – 2905.

Electrophilicity and Nucleophilicity



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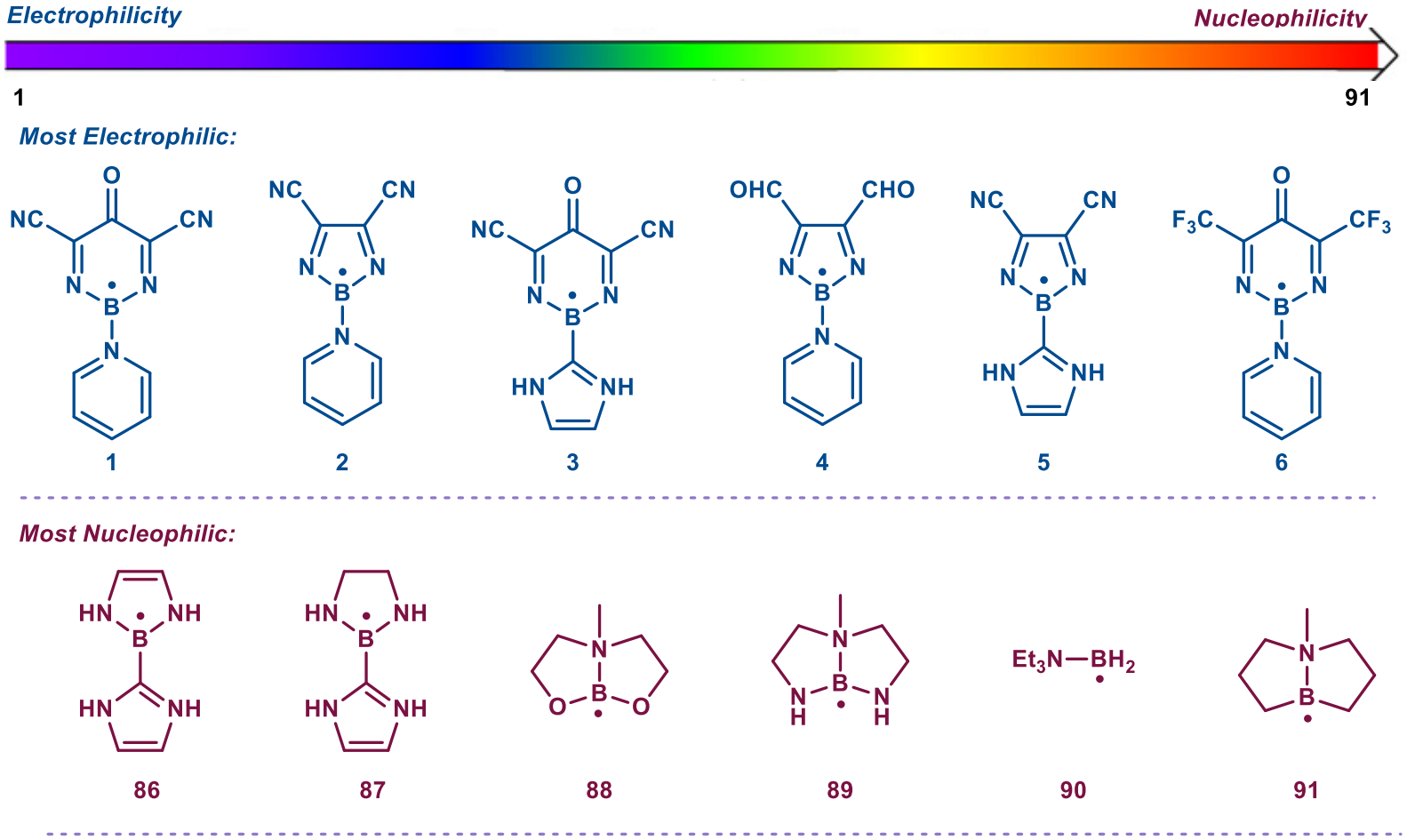

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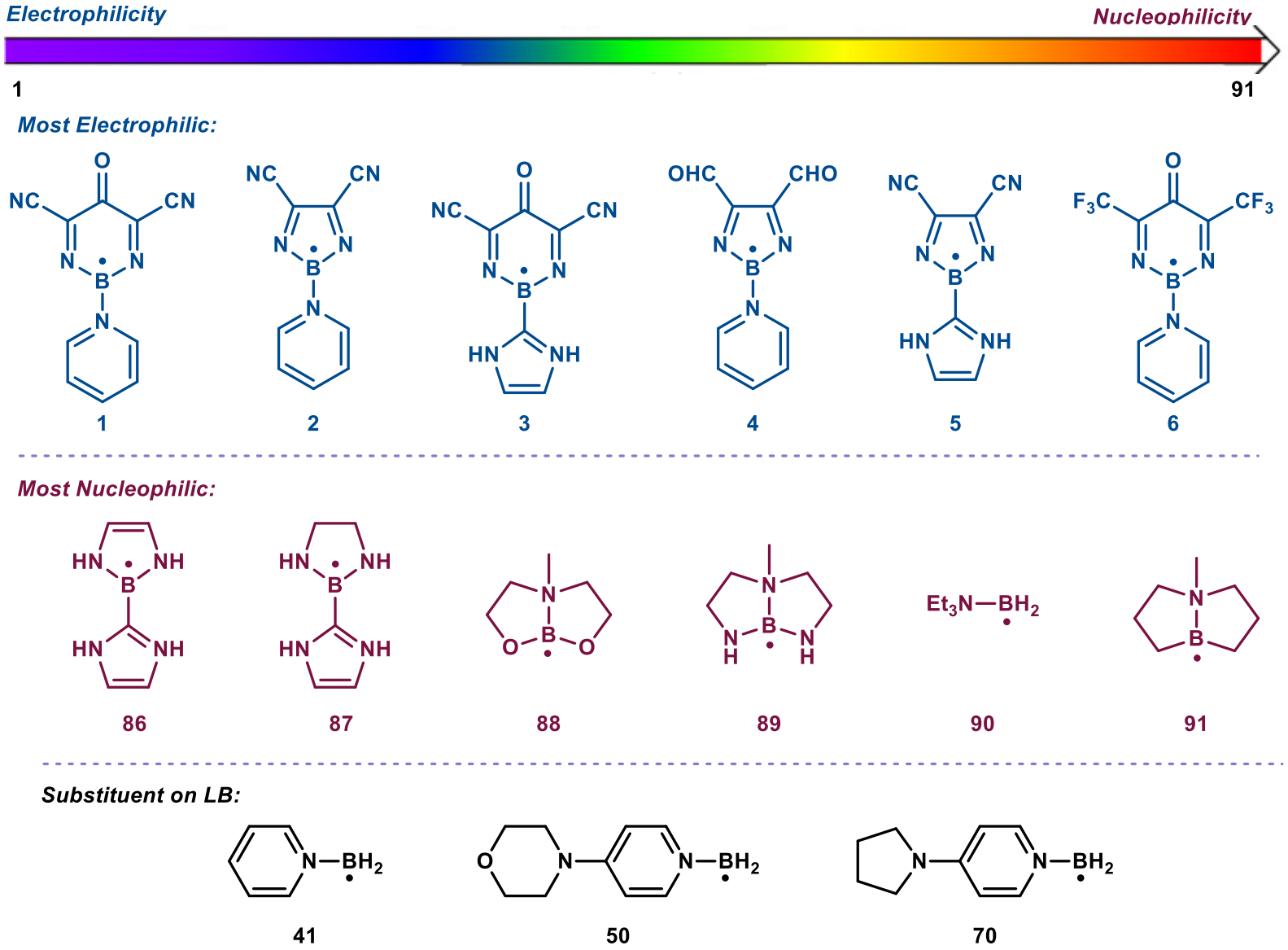

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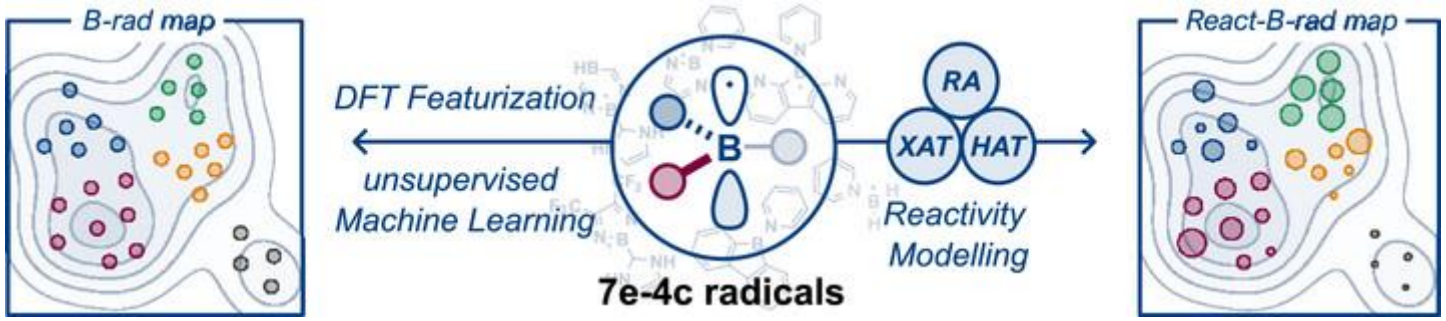
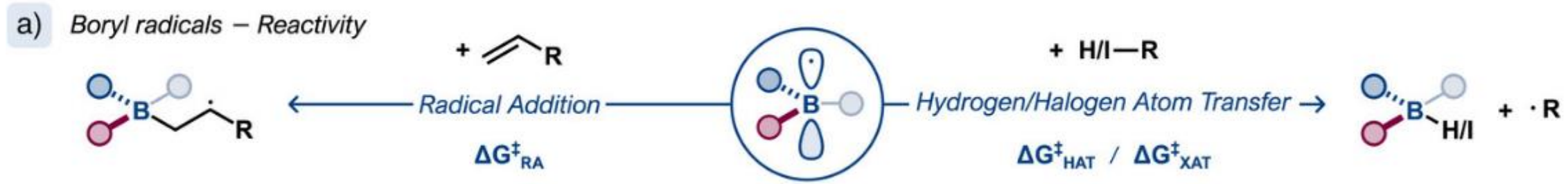
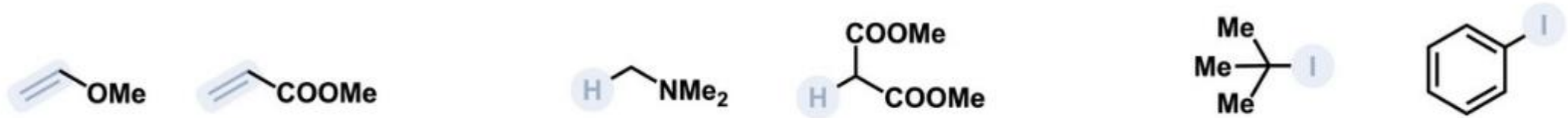
Reactivity



Boryl Radical Reactivity Mapping (React-B-rad maps) ■ *5 clusters, 6 benchmark reactions*



Investigation Scope



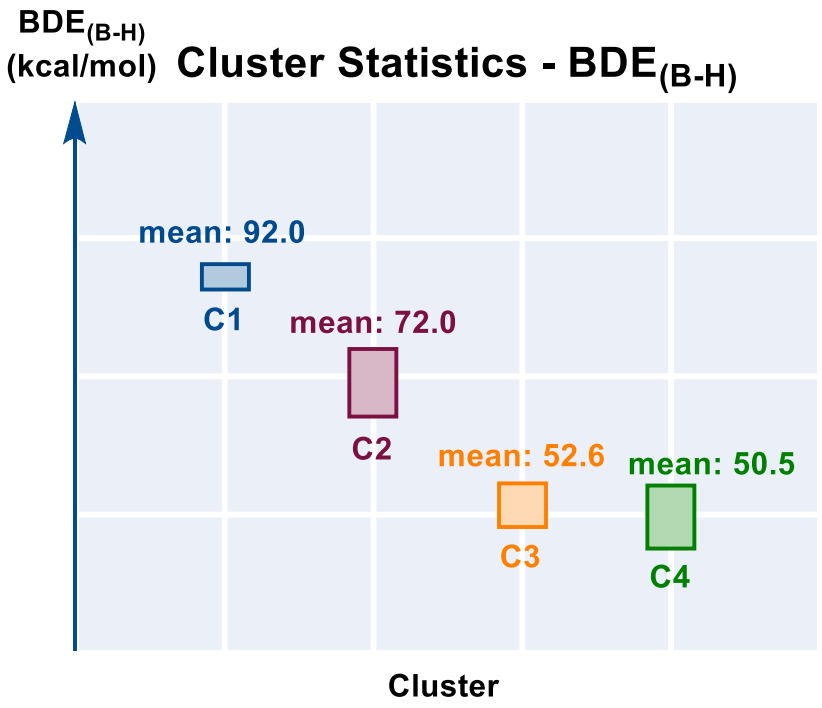
Ia *electron rich* **Ib** *electron poor* — ***Radical Addition (RA)***

IIa *electron rich* **IIb** *electron poor* — ***Hydrogen Atom Transfer (HAT)***

IIIa *alkyl* **IIIb** *aryl* — ***Halogen Atom Transfer (XAT)***

Ardoiz, I. F. *et al. Angew. Chem. Int. Ed.*, **2025**, e202511509.

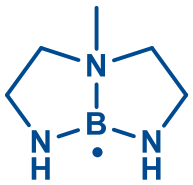
Reactivity



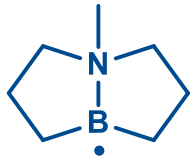
BDE: C1 > C2 > C3, C4

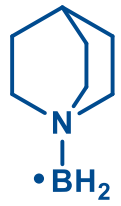
- *HAA: **C1**: high reactivity (hard to generate)*
- *HAD: **C2**: high reactivity (chain reaction)*
- *Reactivity: **C1** > **C2***

C1

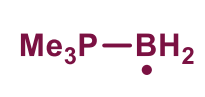


$BDE_{(B-H)}$: 100.5 kcal/mol

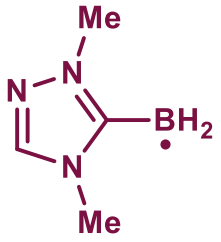


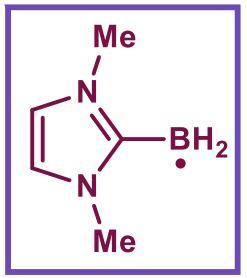


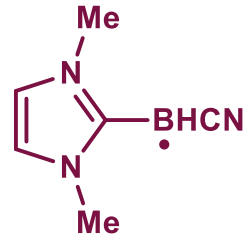
C2



$BDE_{(B-H)}$(calculated): 61.23 kcal/mol

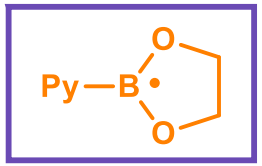


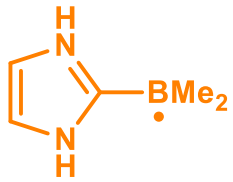




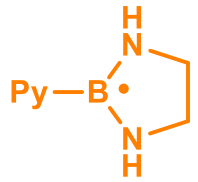
$BDE_{(B-H)}$: 82.3 kcal/mol

C3

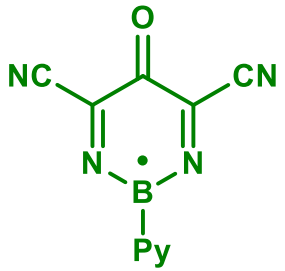


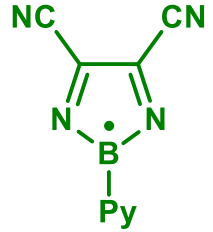


$BDE_{(B-H)}$(calculated): 46.93 kcal/mol

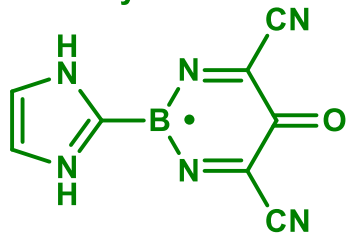


C4

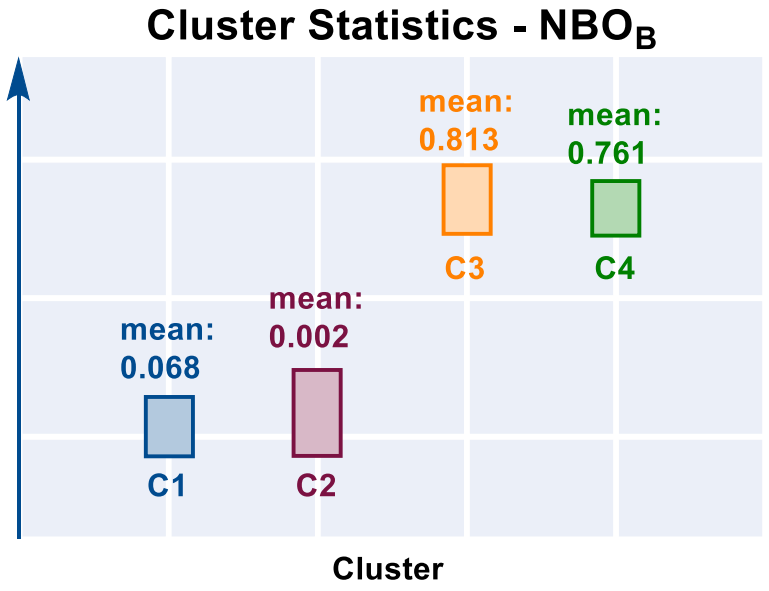


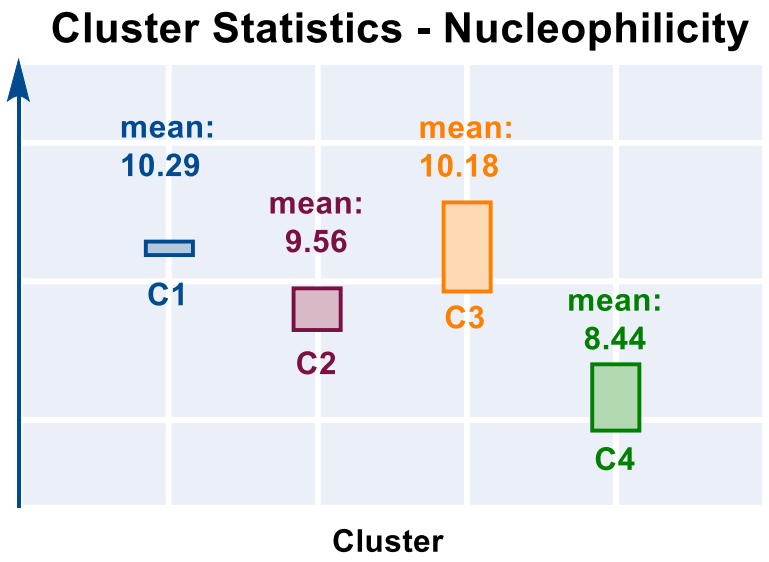


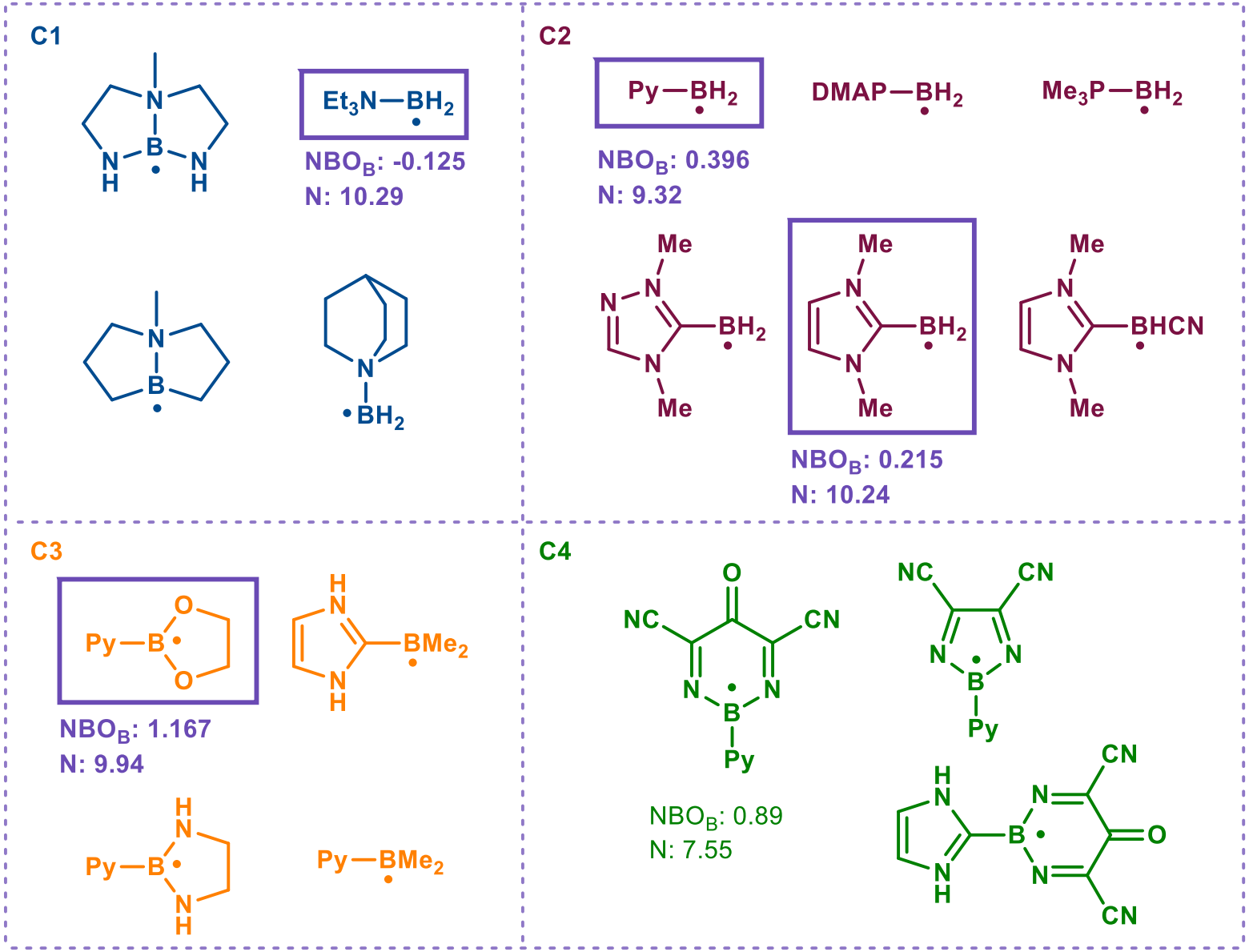
$BDE_{(B-H)}$(calculated): 43.81 kcal/mol



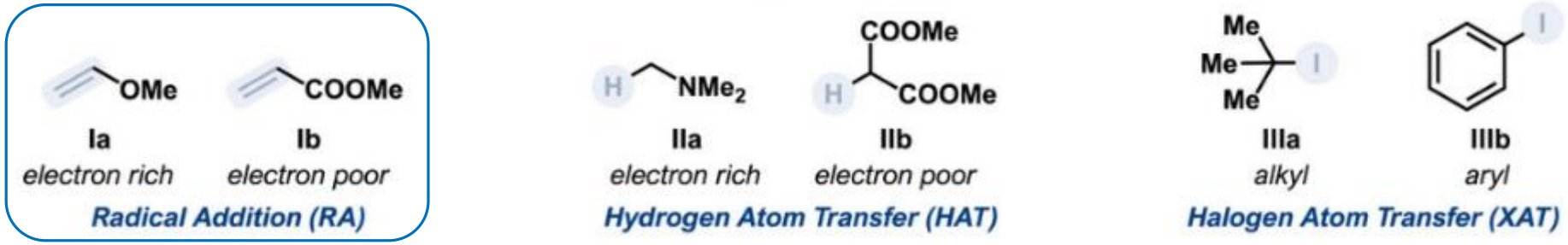
Reactivity


Cluster Statistics - NBO$_B$
mean: 0.813
mean: 0.761
mean: 0.068
mean: 0.002
C3
C4
C1
C2
Cluster

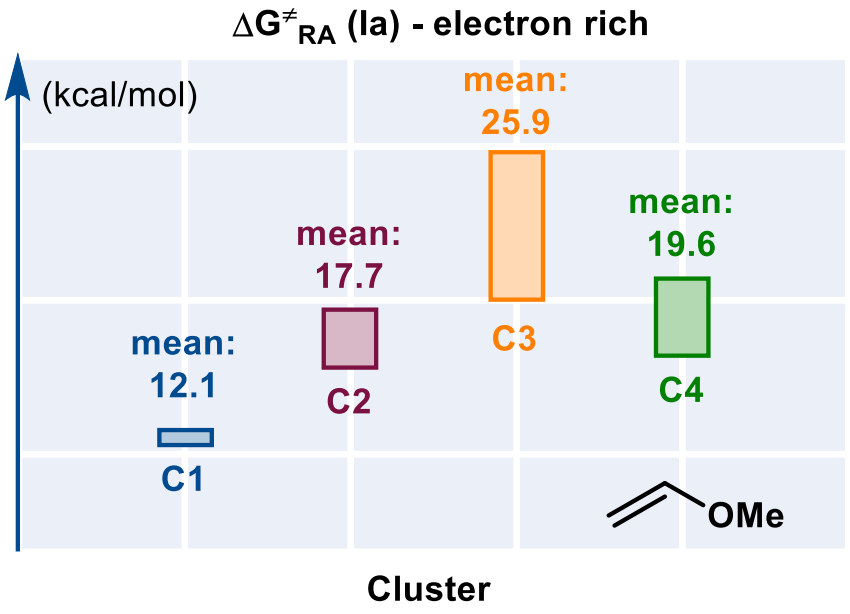

Cluster Statistics - Nucleophilicity
mean: 10.29
mean: 10.18
mean: 9.56
mean: 8.44
C1
C2
C3
C4
Cluster

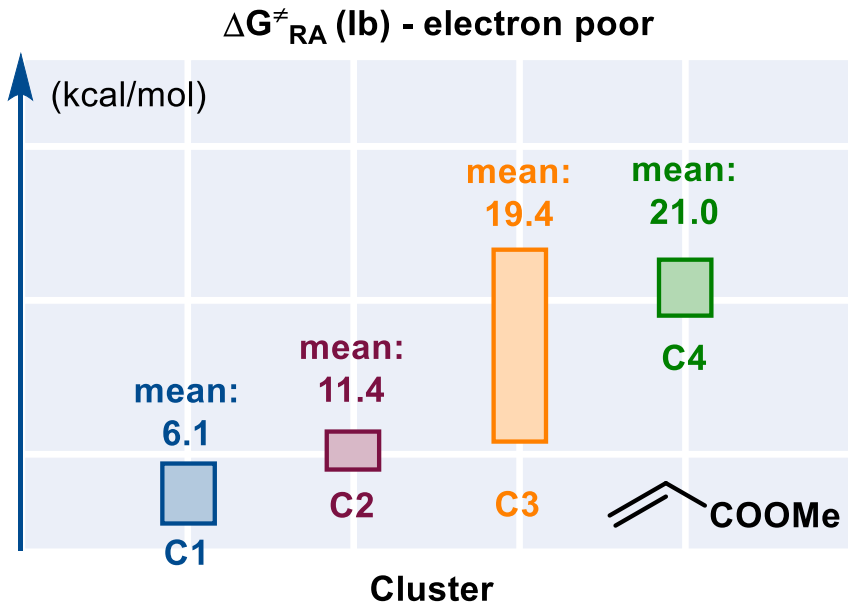

C1
Et$_3$N—BH$_2$
NBO$_B$: -0.125
N: 10.29
•BH$_2$
C2
Py—BH$_2$
DMAP—BH$_2$
Me$_3$P—BH$_2$
NBO$_B$: 0.396
N: 9.32
BHCN
NBO$_B$: 0.215
N: 10.24
C3
Py—B
BMe$_2$
NBO$_B$: 1.167
N: 9.94
Py—BMe$_2$
C4
NBO$_B$: 0.89
N: 7.55

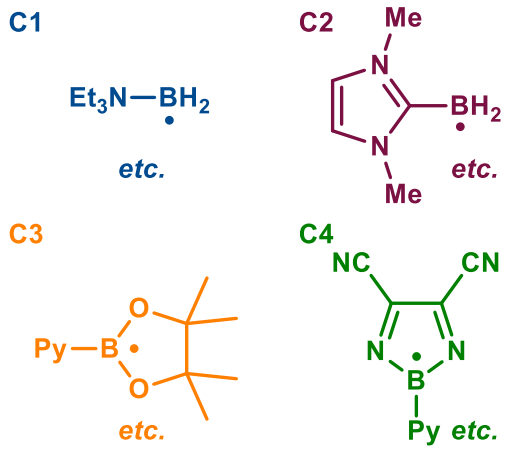
Reactivity



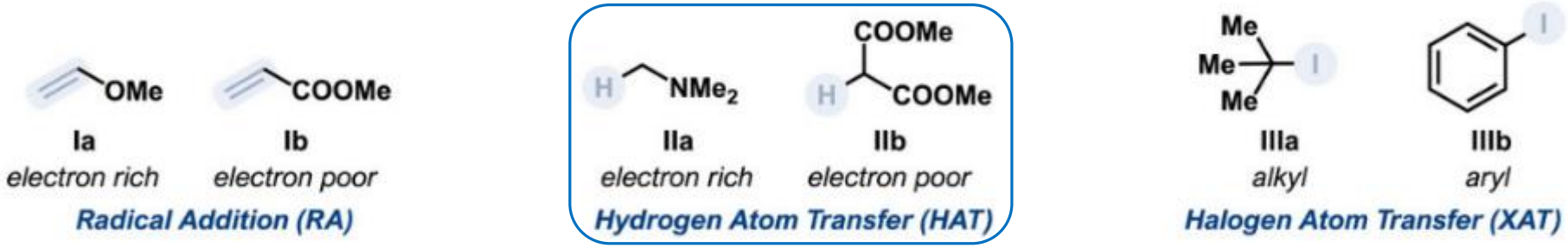
- ***RA-electron rich:***
  *fast: **C1** > **C2***
  *slow: **C3**, **C4***
- ***RA-electron poor:***
  fast: C1** > **C2** > **C3
  *slow: **C4***



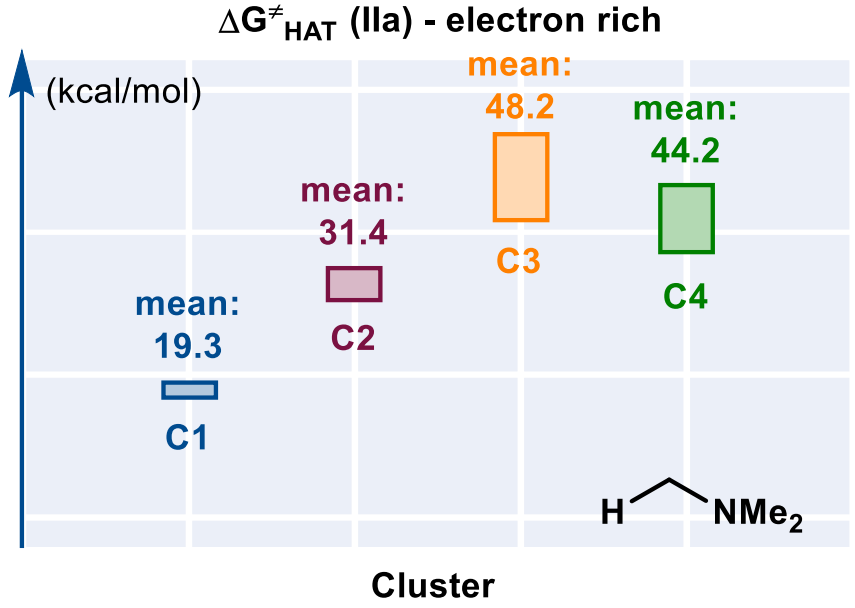


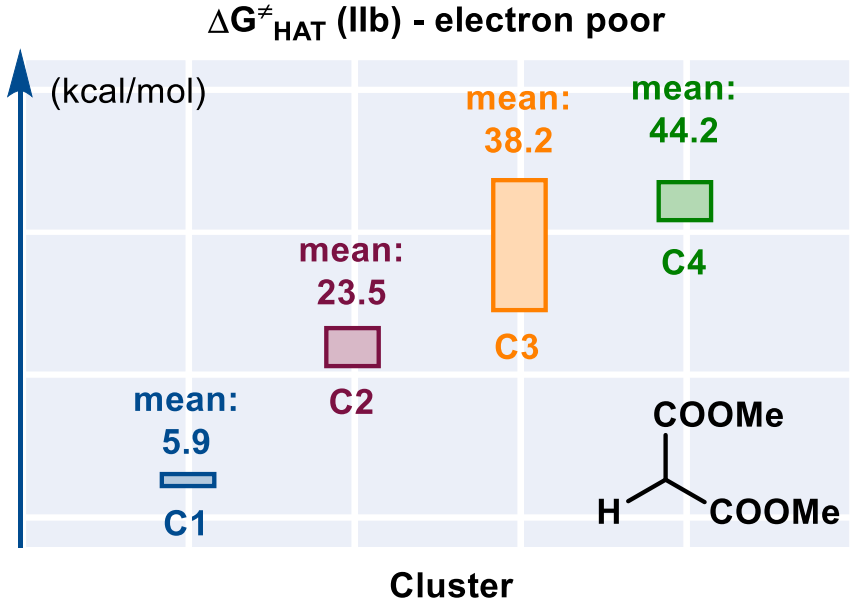


Reactivity

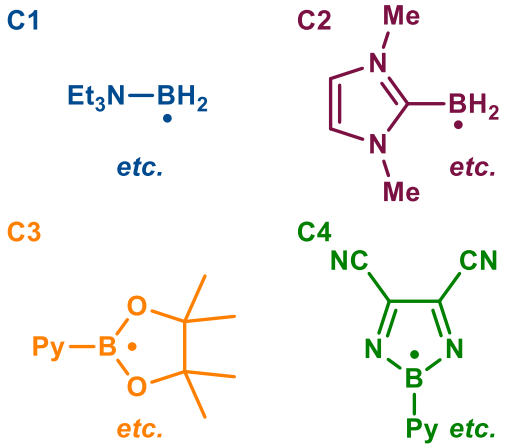


- ***RA-electron rich:***
  *fast: **C1** > **C2***
  *slow: **C3**, **C4***
- ***RA-electron poor:***
  fast:** **C1** > **C2** > **C3
  *slow: **C4***

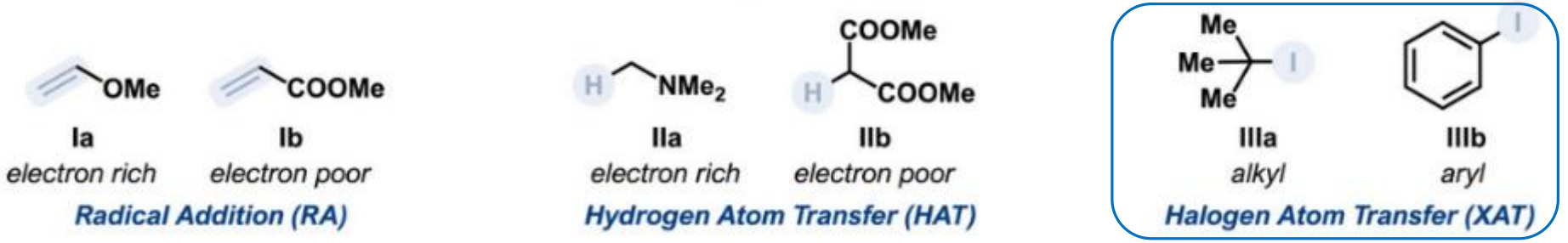


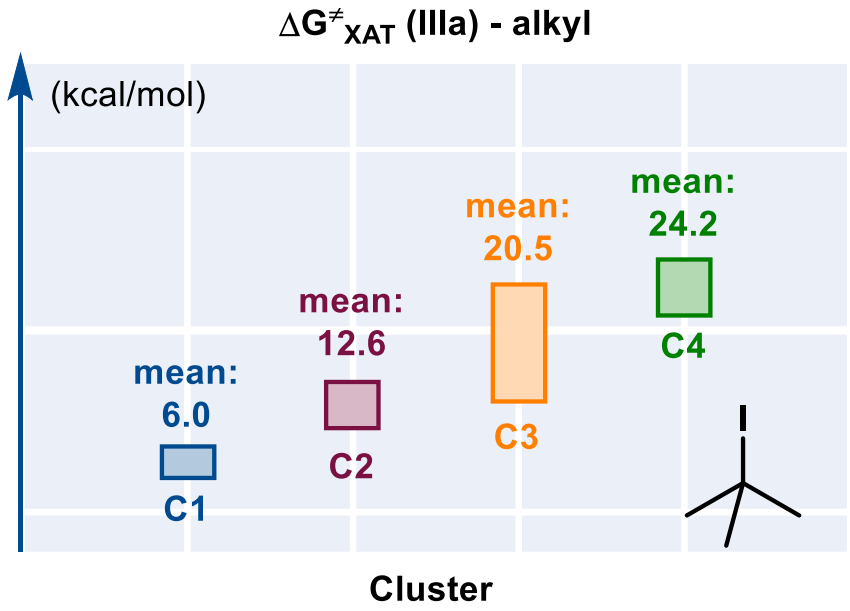


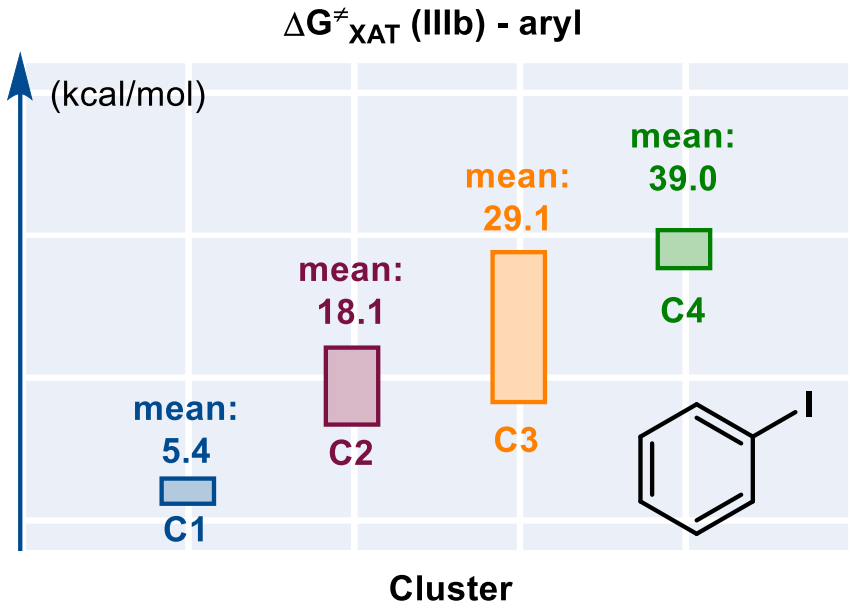
- ***HAT-electron rich:***
  *slow: **C1**, **C2**, **C4**, **C3***
- ***HAT-electron poor:***
  *fast: **C1***
  *slow: **C2**, **C3**, **C4***



Reactivity







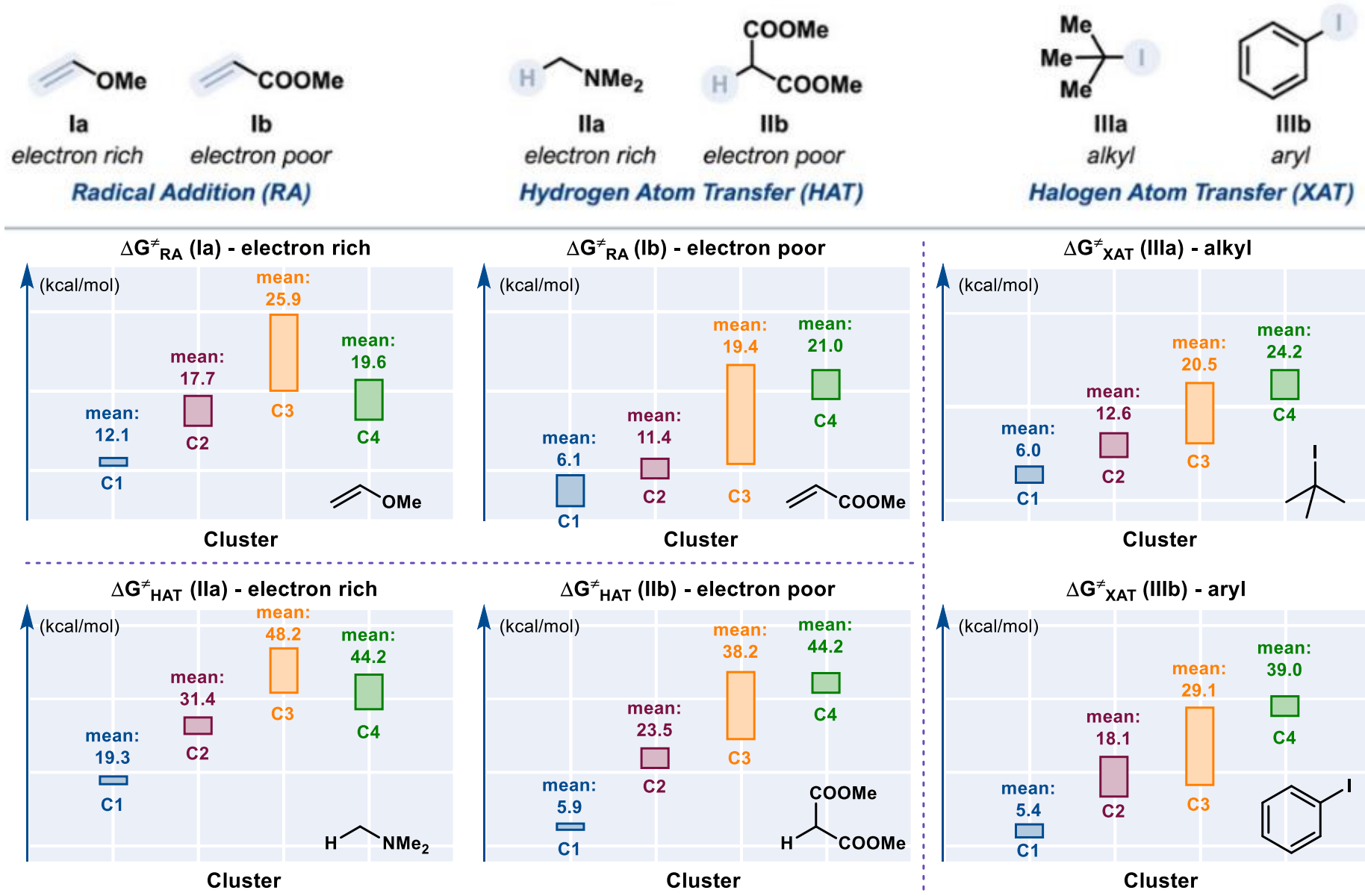
- ***RA-electron rich:***
  *fast: **C1** > **C2***
  *slow: **C3**, **C4***
- ***RA-electron poor:***
  fast:** **C1** > **C2** > **C3
  *slow: **C4***

- ***HAT-electron rich:***
  *slow: **C1**, **C2**, **C4**, **C3***
- ***HAT-electron poor:***
  *fast: **C1***
  *slow: **C2**, **C3**, **C4***

- ***XAT-alkyl:***
  *fast: **C1** > **C2***
  *slow: **C3**, **C4***
- ***XAT-aryl:***
  *fast: **C1***
  *slow: **C2**, **C3**, **C4***

Ardoiz, I. F. *et al. Angew. Chem. Int. Ed.*, **2025**, e202511509.

Reactivity



- ***RA-electron rich:***
  *fast: **C1** > **C2***
  *slow: **C3**, **C4***
- ***RA-electron poor:***
  fast: C1** > **C2** > **C3
  *slow: **C4***

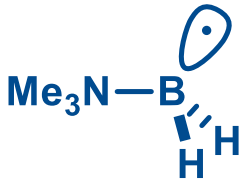
- ***HAT-electron rich:***
  *slow: **C1**, **C2**, **C4**, **C3***
- ***HAT-electron poor:***
  *fast: **C1***
  *slow: **C2**, **C3**, **C4***

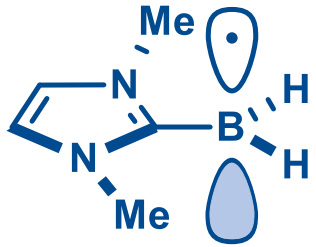
- ***XAT-alkyl:***
  *fast: **C1** > **C2***
  *slow: **C3**, **C4***
- ***XAT-aryl:***
  *fast: **C1***
  *slow: **C2**, **C3**, **C4***

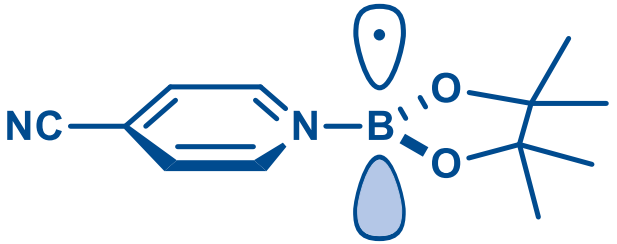
Ardoiz, I. F. *et al. Angew. Chem. Int. Ed.*, **2025**, e202511509.

Reactivity

- **Reaction Type: XAT > RA ≫ HAT**







- ***High reactivity***
  Moderate selectivity
- ***HAA (√)***
  Chain reaction (×)
- ***Difficult RA***
  Difficult XAT
- ***Mild reactivity***
  Tunable selectivity
- ***HAD (√)***
  Chain reaction (√)
- ***Commonly used in RA***
  Easy XAT
- ***Low reactivity***
  High stability
- ***Boryl radical shuttle***
- ***React at LB***

Content

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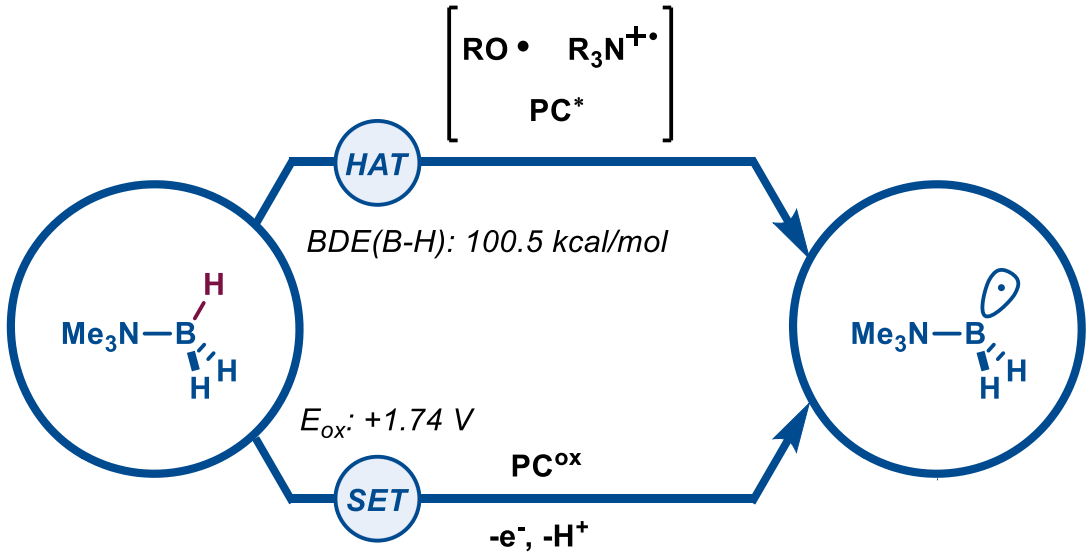
  - *C-X Cleavage*
- *Outlook*

Content

Generation of Boryl Radical

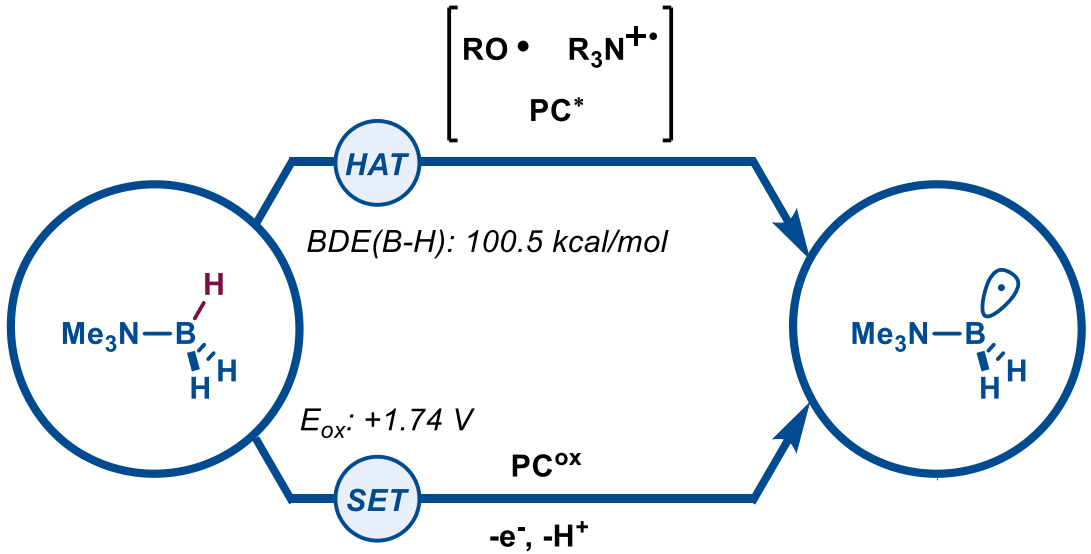


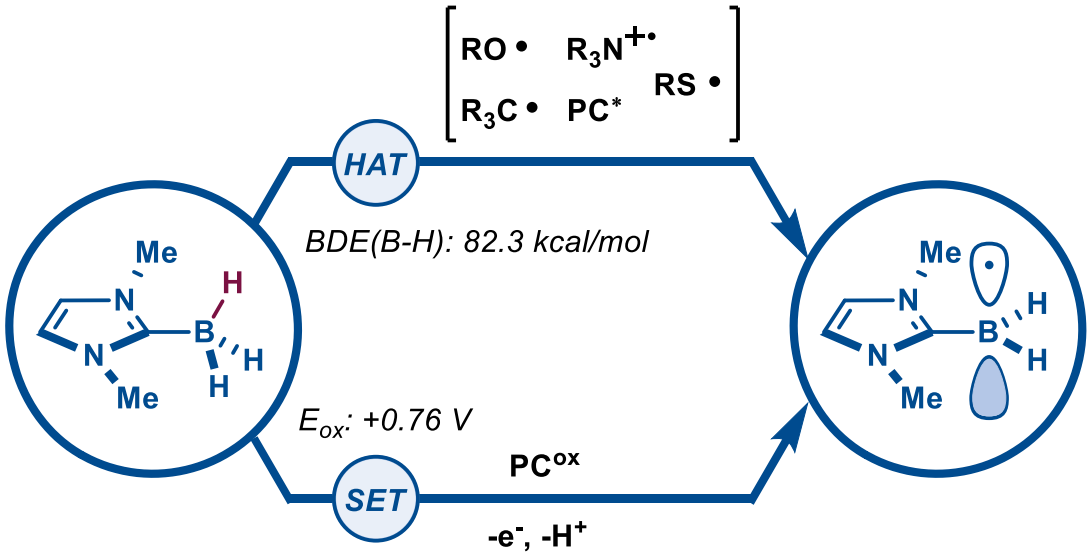
Noel, T. *et al. J. Am. Chem. Soc.*, **2023**, *145*, 991 – 999.

Leonori, D. *et al. J. Am. Chem. Soc.*, **2024**, 146, 24042 – 24052.

Xu, P. F. *et al. Org. Lett.*, **2024**, 26, 9282 – 9287.

Generation of Boryl Radical





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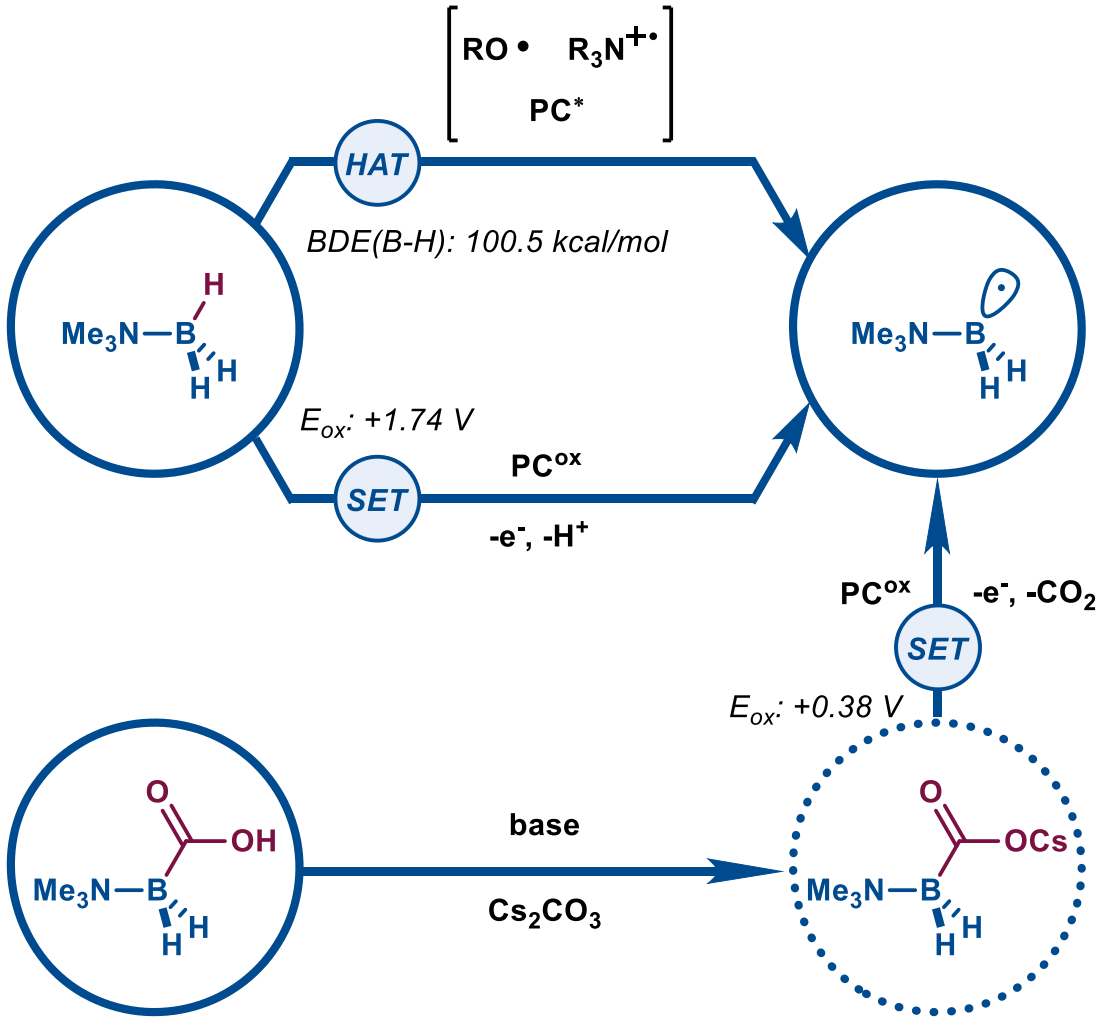
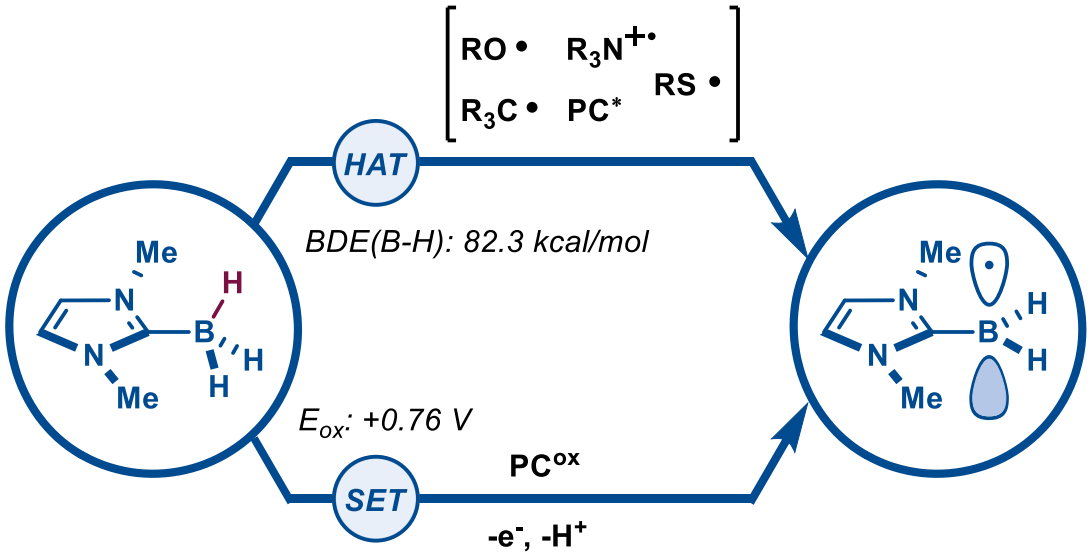
Generation of Boryl Radical





- Preparation without column chromatography
- Long-term storage
- Air stable

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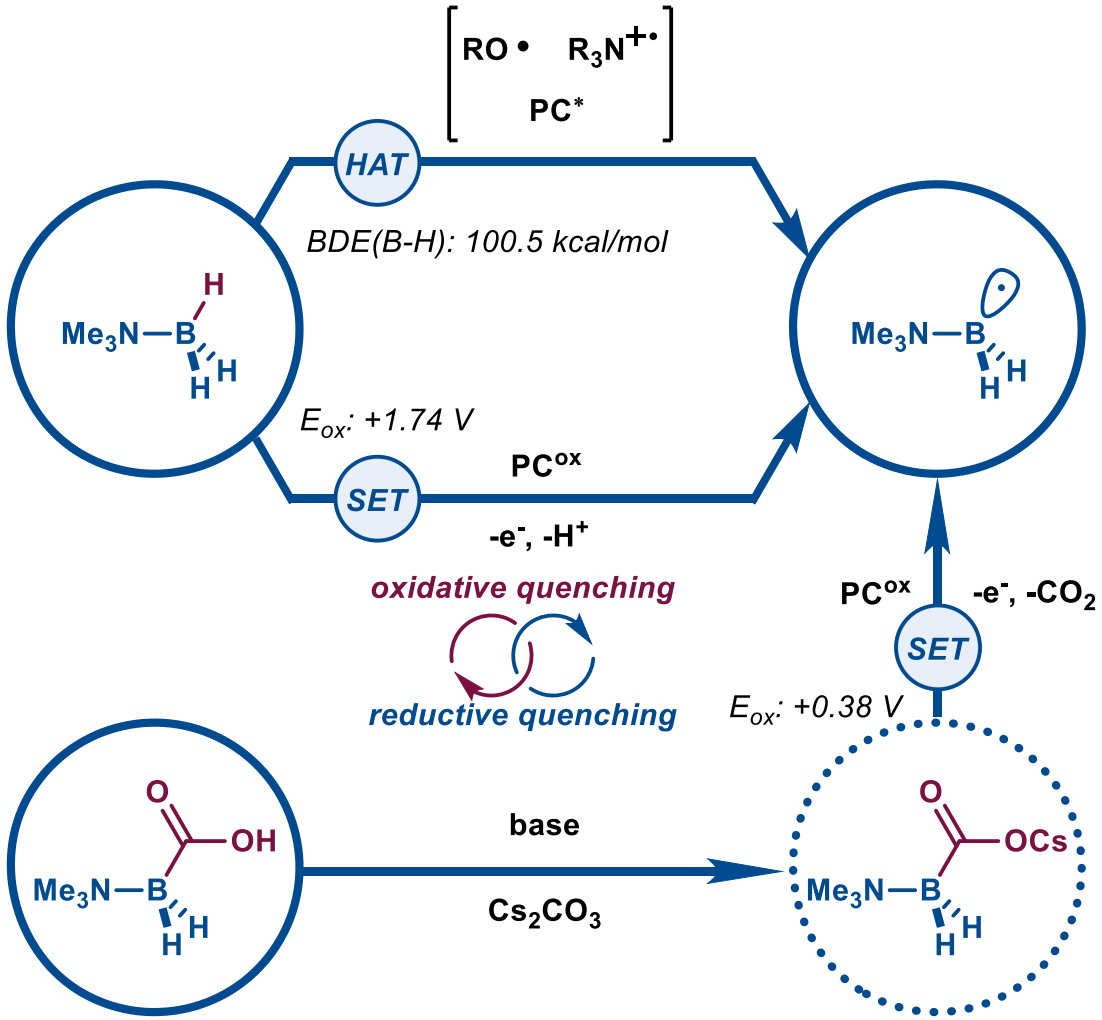
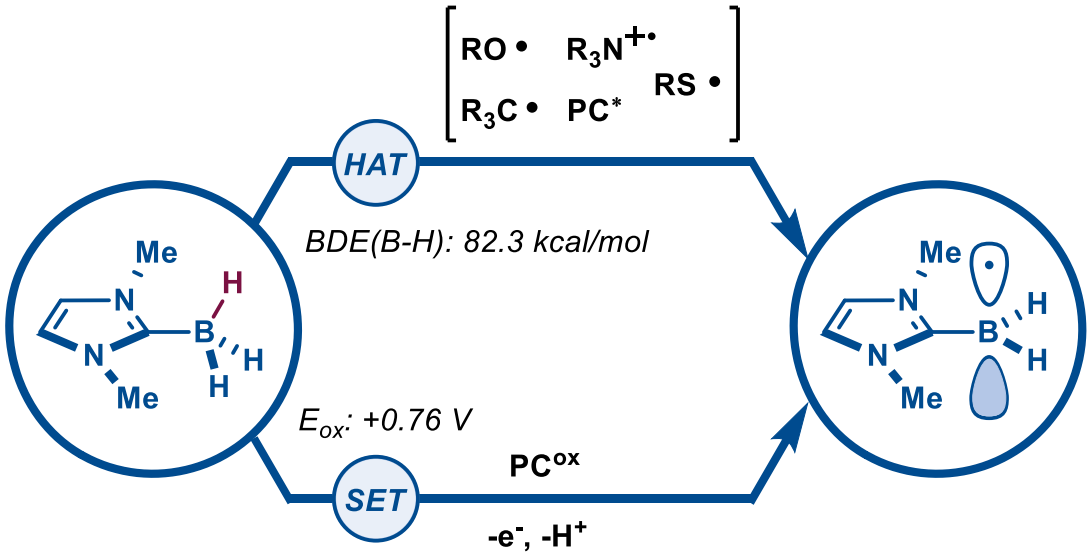
Generation of Boryl Radical





- Preparation without column chromatography
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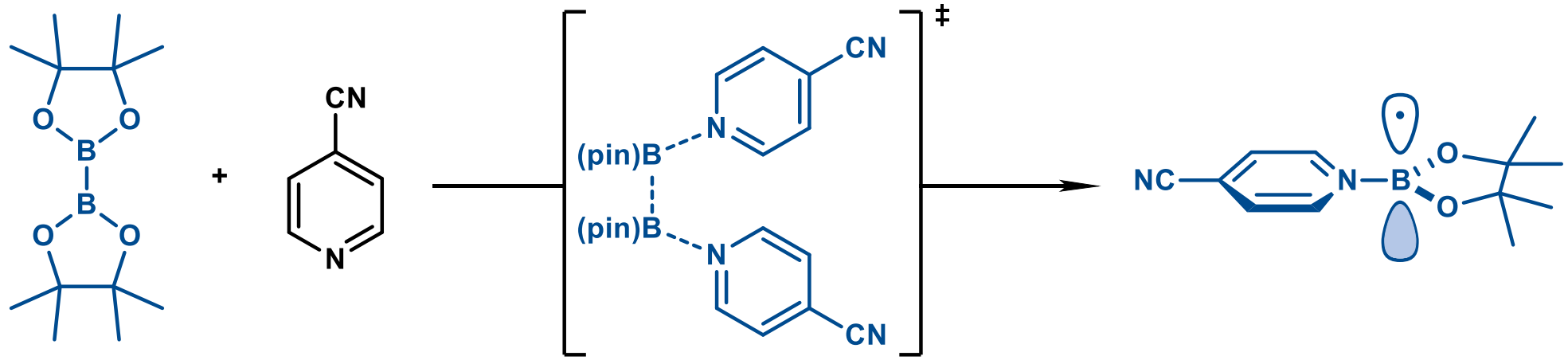
Xu, P. F. *et al. Org. Lett.*, **2024**, 26, 9282 – 9287.

Generation of Boryl Radical

- *via homolytic cleavage of the B-B bond in $B_2(OR)_4$*

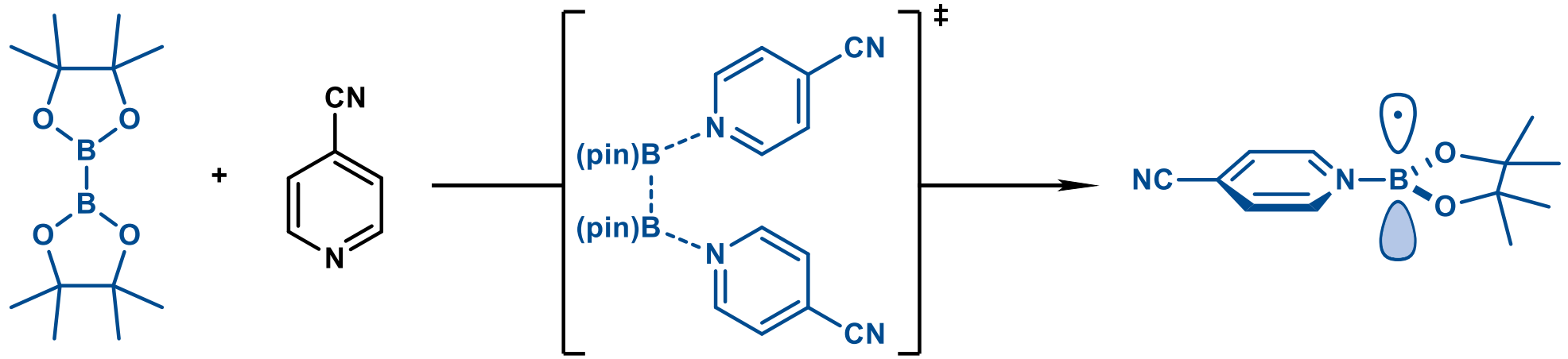


Li, S. H. *et al. Angew. Chem. Int. Ed.*, **2016**, 55, 5985 – 5989.

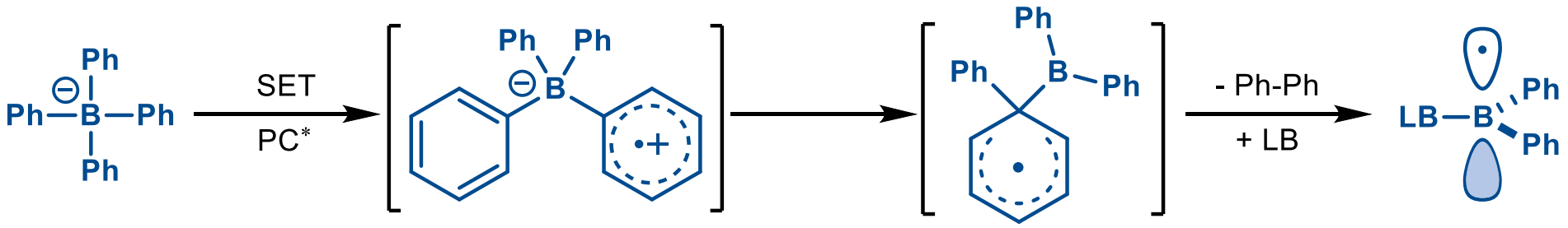
Xia, J. B. *et al. J. Am. Chem. Soc.*, **2022**, *144*, 8551 – 8559.

Generation of Boryl Radical

- *via homolytic cleavage of the B-B bond in $B_2(OR)_4$*



- *via SET and Aryl Migration from $NaBAr_4$*



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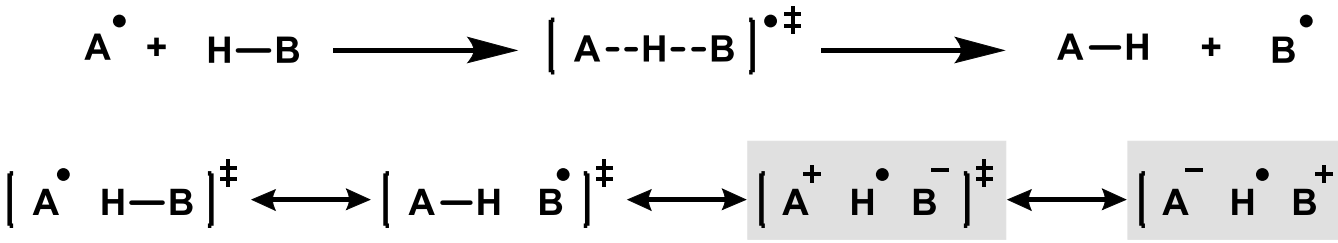
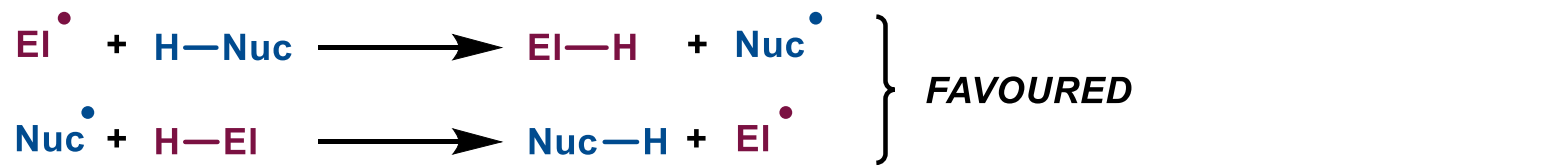
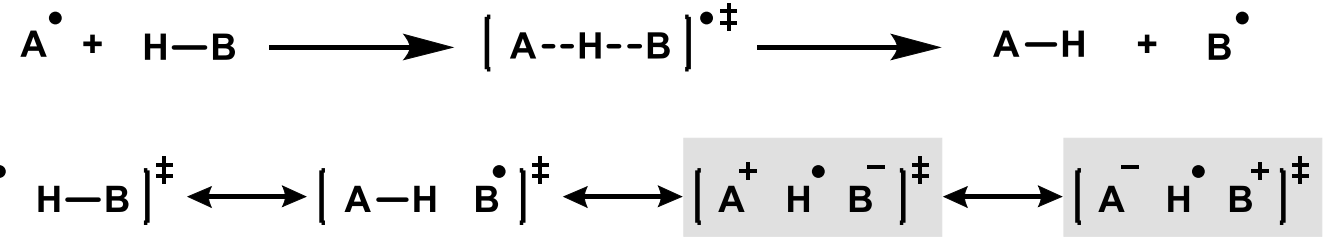
Hydrogen-Atom Transfer (HAT)

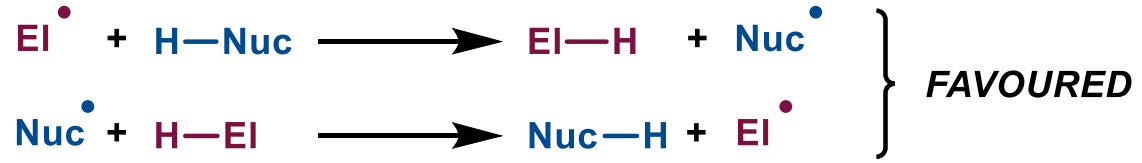




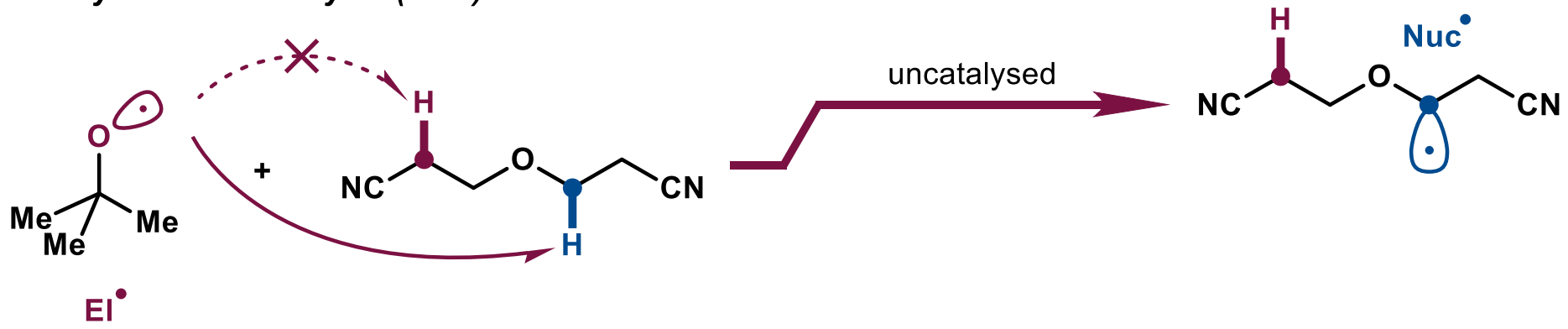
Roberts, B. P. *et al. Chem. Soc. Rev.*, **1999**, 28, 25 – 35.

Hydrogen-Atom Transfer (HAT)





Polarity-reversal catalysis (PRC)



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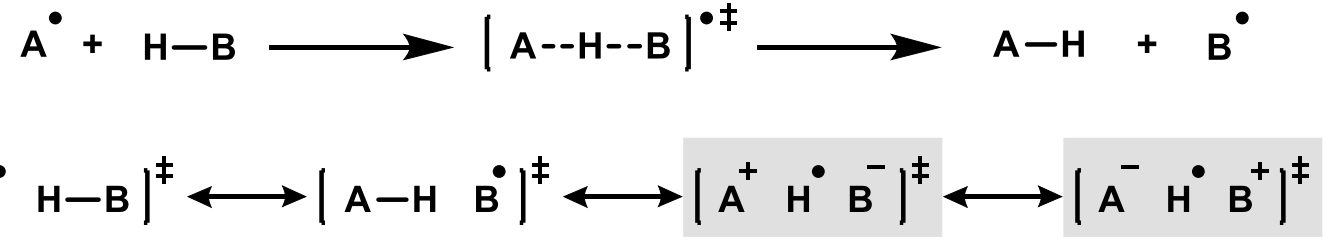
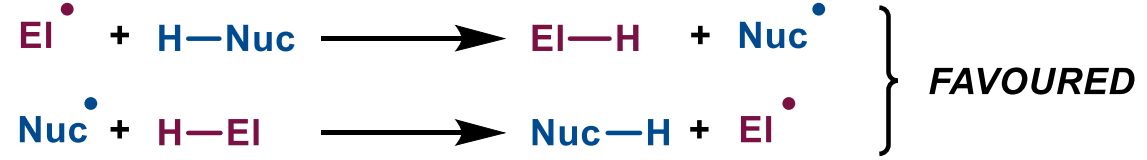
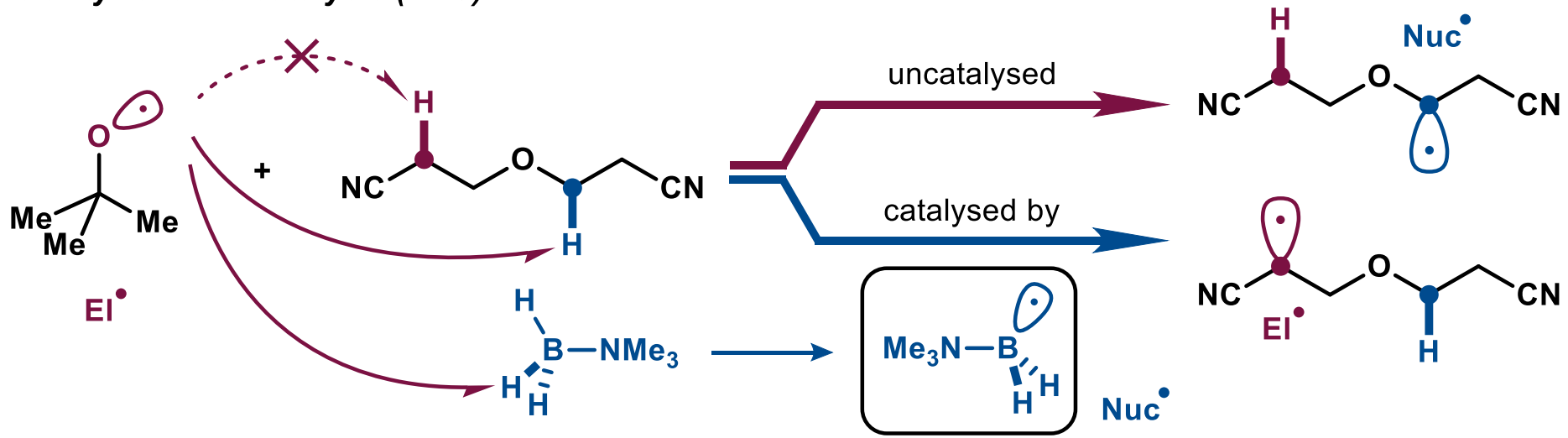
Hydrogen-Atom Transfer (HAT)



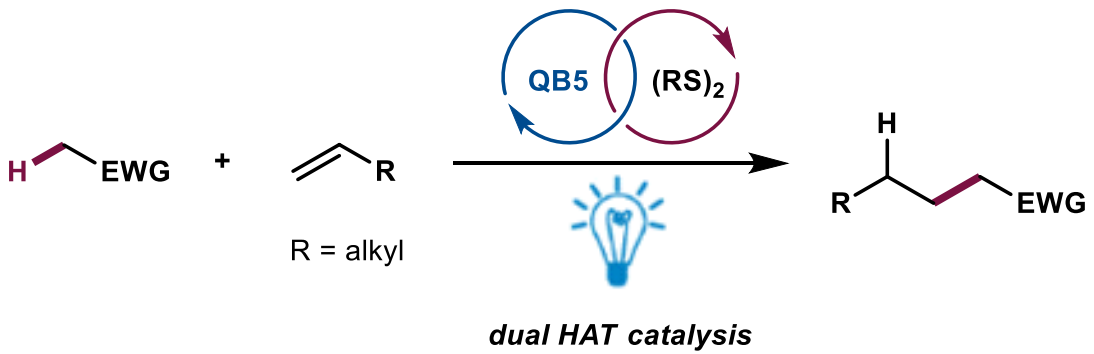


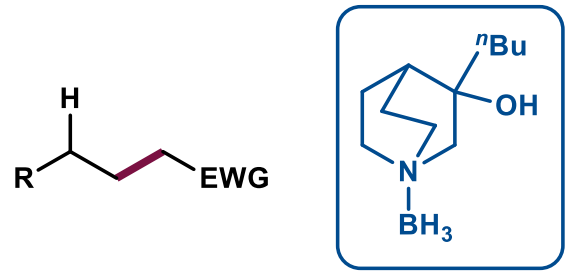
Polarity-reversal catalysis (PRC)

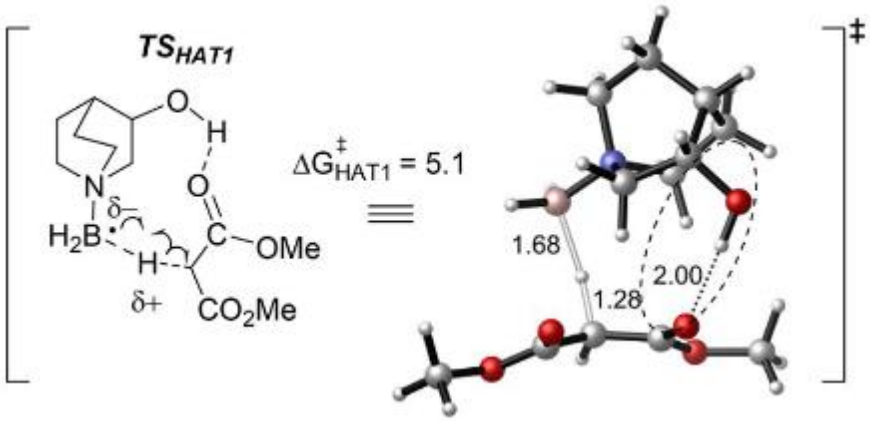


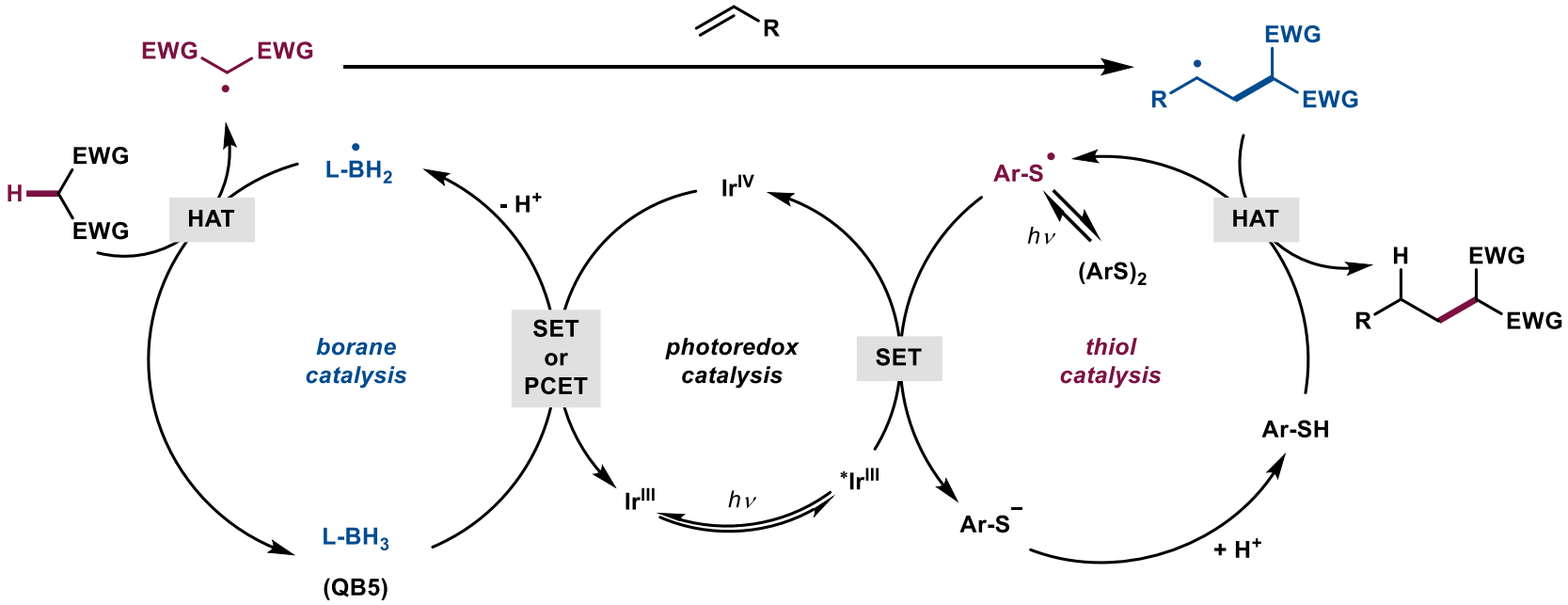
Roberts, B. P. *et al. Chem. Soc. Rev.*, **1999**, 28, 25 – 35.

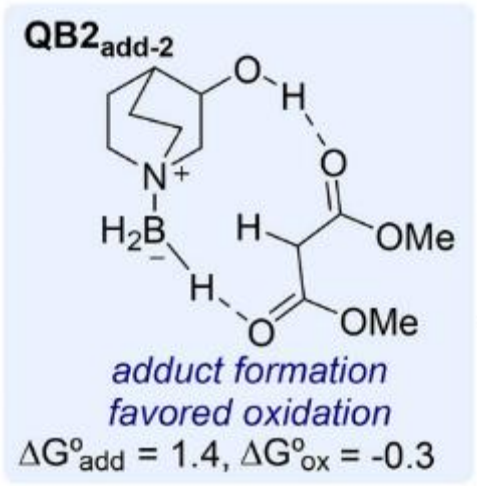
Hydrogen-Atom Transfer (HAT)









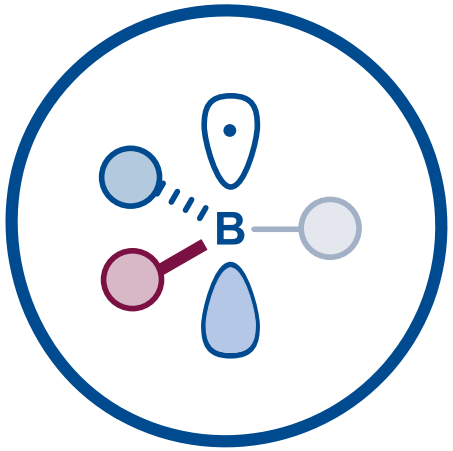


Ye, J. T. *et al. J. Am. Chem. Soc.*, **2021**, *143*, 11251 – 11261.

Content

- *Introduction of Boryl Radicals*
- *Structures, Properties and Reactivity*
- *Application of Boryl Radicals in Organic Chemistry*
  - *Generation of Boryl Radical*
  - *Hydrogen-Atom Transfer (HAT)*
  - *Radical Addition (RA)*
  - *C-X Cleavage*
- *Outlook*

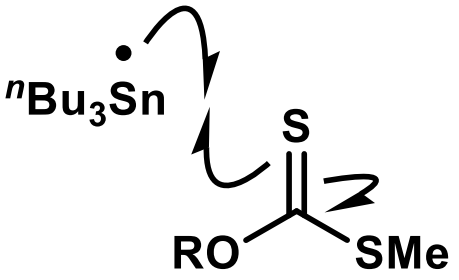
Radical Addition

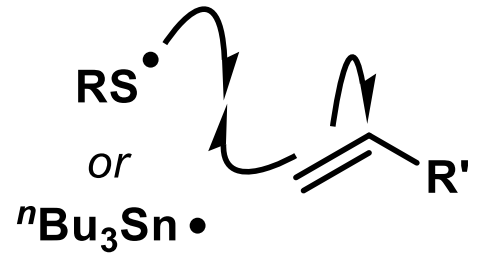


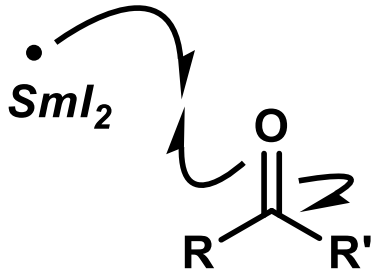
vs.

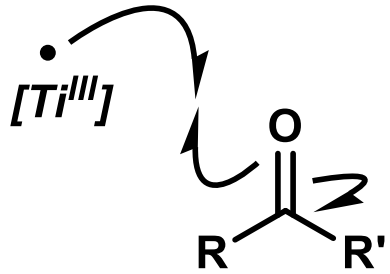
- *Low-cost*
- *Low-toxicity*
- *Diverse structures*
- *Metal-free*
- *Nucleophilic (complementary to thio radicals)*
- *Versatile in post-synthetic modification*

Sn *S* *Sm* *Ti* .....

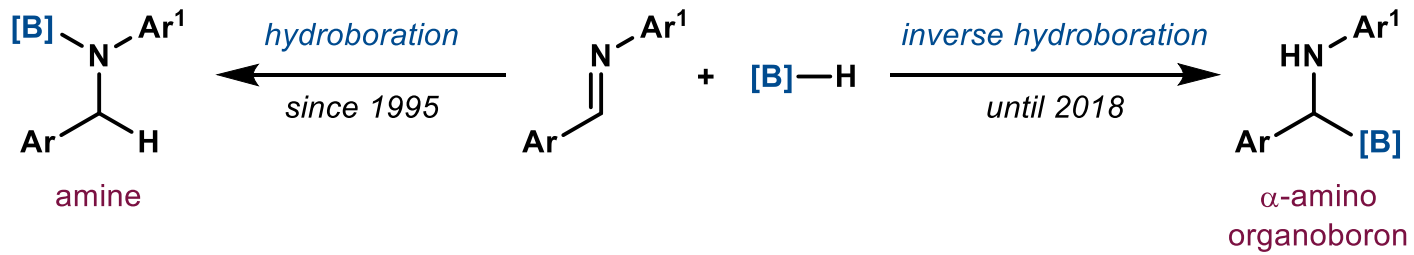


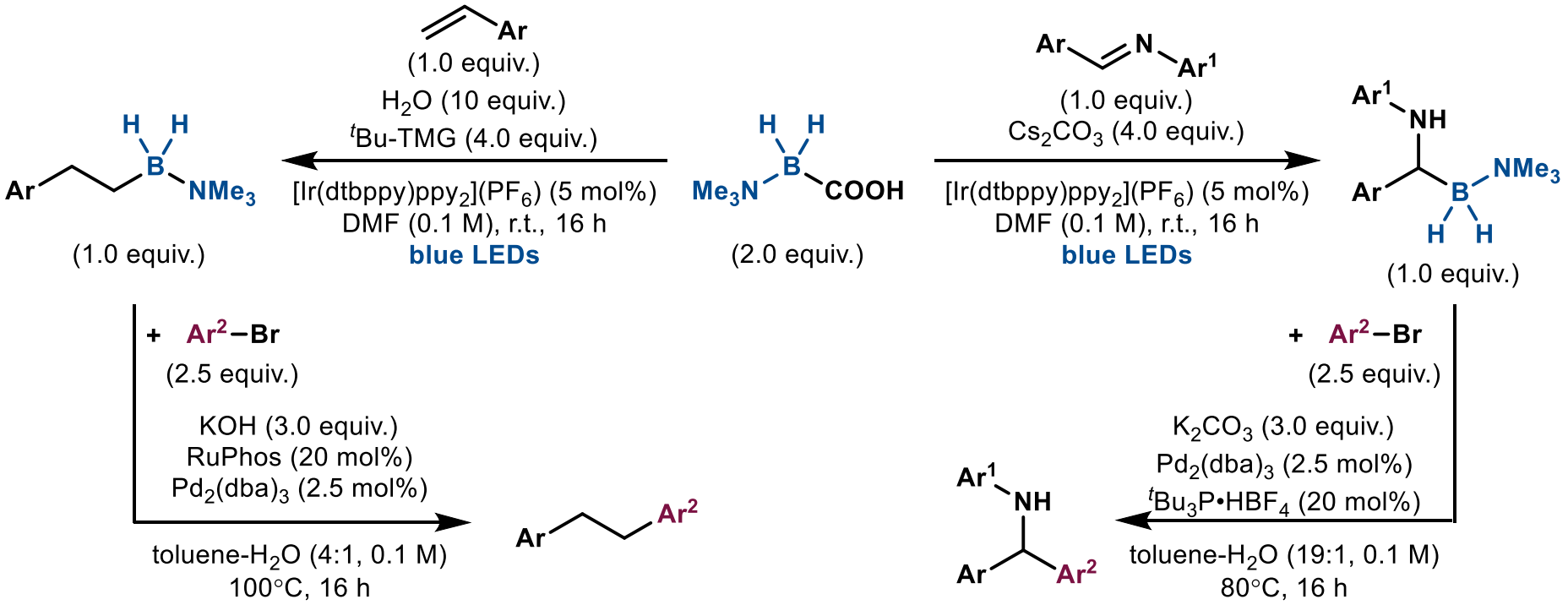






Radical Addition – C=N

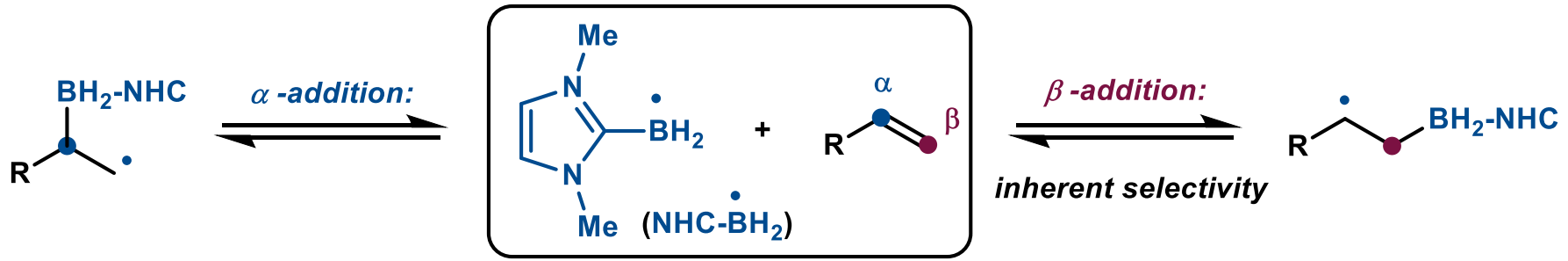


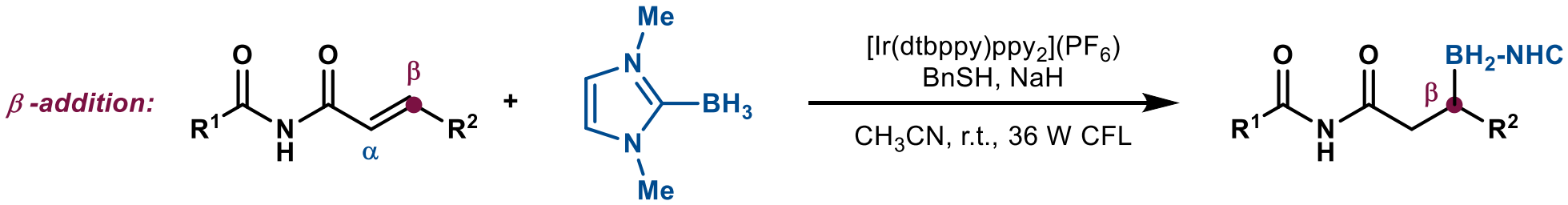


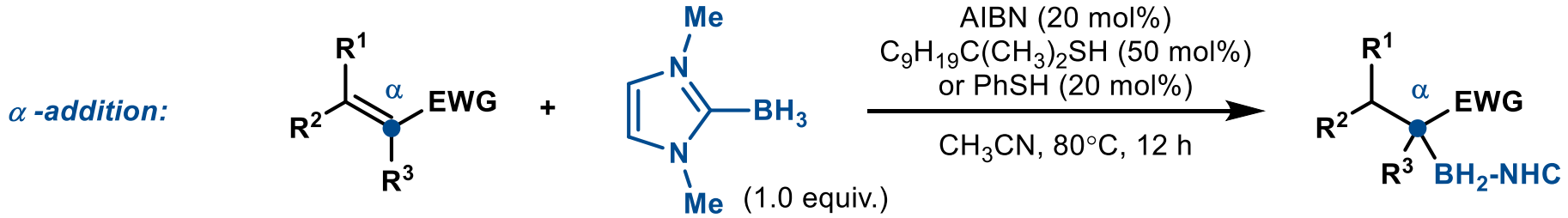
Zhu, C. J. *et al. Angew. Chem. Int. Ed.*, **2018**, 57, 3990 – 3994.

Leonori, D. *et al. J. Am. Chem. Soc.*, **2024**, 146, 24042 – 24052.

Radical Addition – C=C







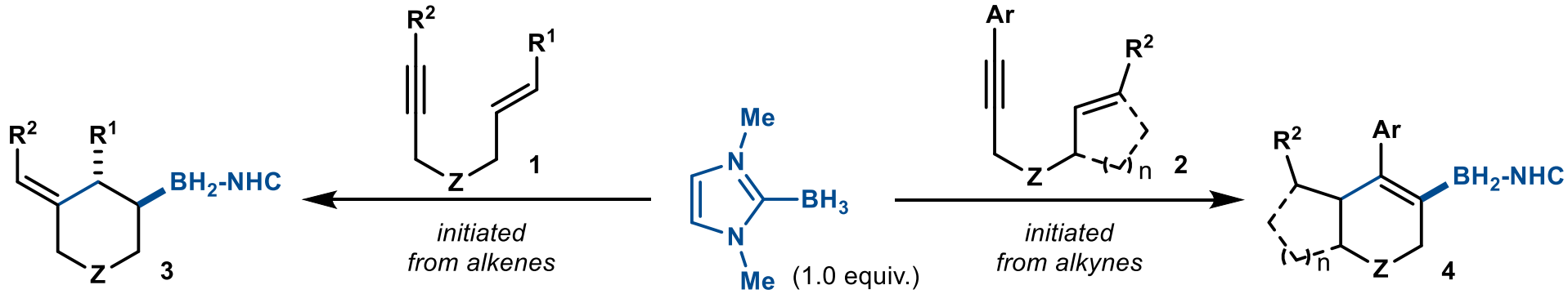
Key Determinants: ■ ***Stability of the Intermediate*** ■ ***Polarity-Matched HAT*** ■ ***Steric Effects***

Liu, P. *et al. Adv. Synth. Catal.*, **2020**, 362, 2990 – 2996.

Wang, Y. F. *et al. Nat. Commun.*, **2019**, 10, 1934 .

Radical Addition – C=C

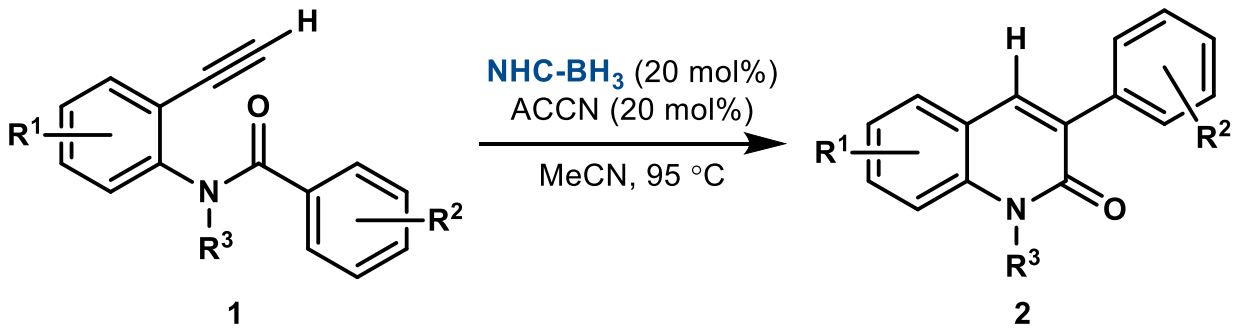
■ **Borylation / Cyclization Cascades**

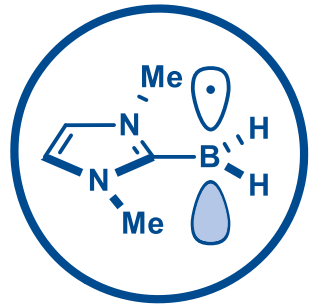


conditions: AIBN (20 mol%), $C_9H_{19}C(CH_3)_2SH$ (50 mol%)
MeCN, 80 °C, 2-12 h

R^1 = Ar, COOMe, Z = NTs, $C(COOEt)_2$, n = 1, 2, 3

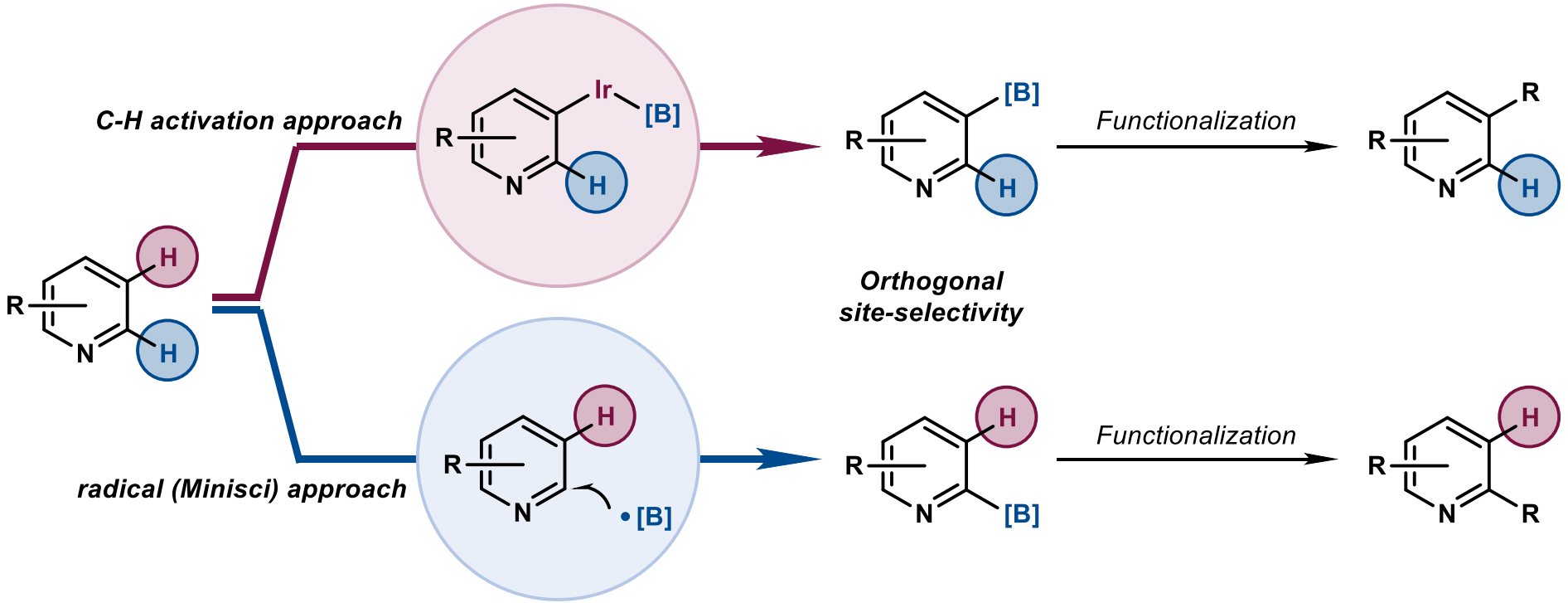
■ **Radical-catalyzed addition / elimination**

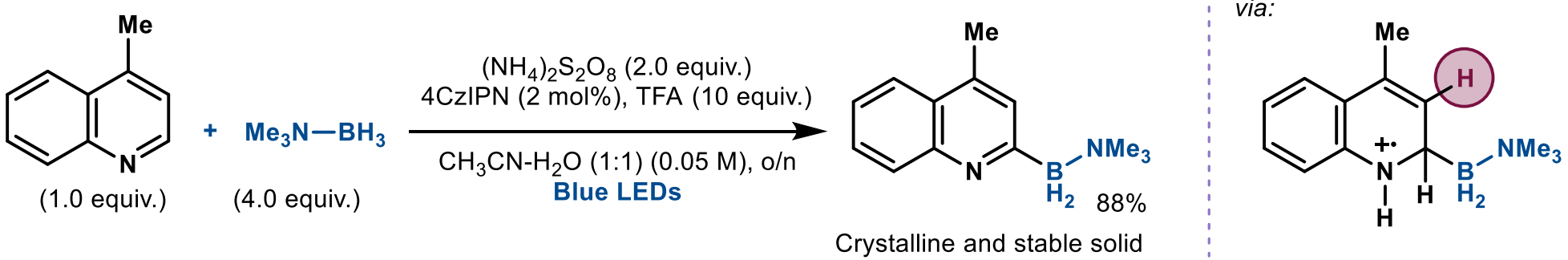




Wang. Y. F. *et al. J. Am. Chem. Soc.*, **2017**, *139*, 6050 – 6053.
Wang. Y. F. *et al. CCS Chem.*, **2019**, *1*, 504.

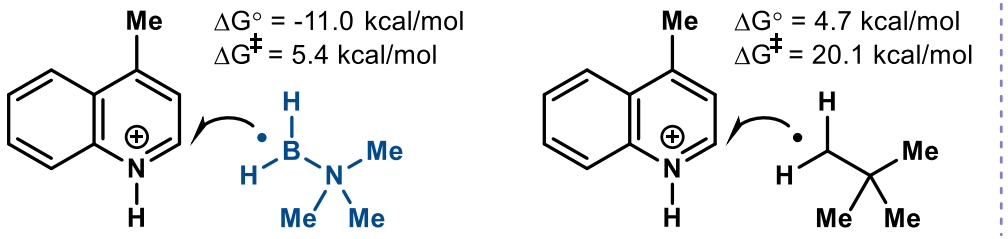
Radical Addition - Arene



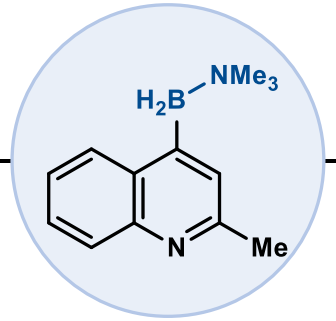


Leonori. D. *et al. Nature*, **2021**, *595*, 677 – 683.

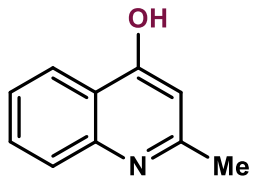
Radical Addition - Arene



$Me_3N—BH_3$	$Me_3P—BH_3$	NHC—BH_3
(√)	(×)	(×)

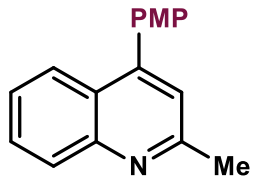


Oxone (8.0 equiv.)
THF-H_2SO_4 (1:3) (0.025 M)
40 °C, air, o/n



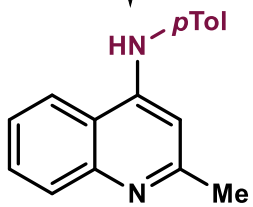
85%
Oxidation to phenol

4-OMe-C_6H_4-I (2.0 equiv.)
$Pd_2(dppf)Cl_2$ (10 mol%)
Na_2CO_3 (5.0 equiv.)
MeOH (0.05 M), 40 °C, o/n



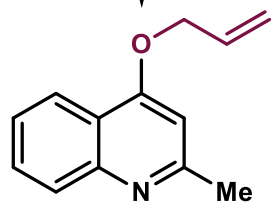
75%
Suzuki-Miyaura cross-couoling

4-OMe-C_6H_4-NH_2 (4.0 equiv.)
Cu(OAc) (1.0 equiv.), Et_3N (10.0 equiv.)
4 A MS, O_2 (ballon)
CH_2Cl_2 (0.05 M), 50 °C, o/n



24%
Chan-Lam amination

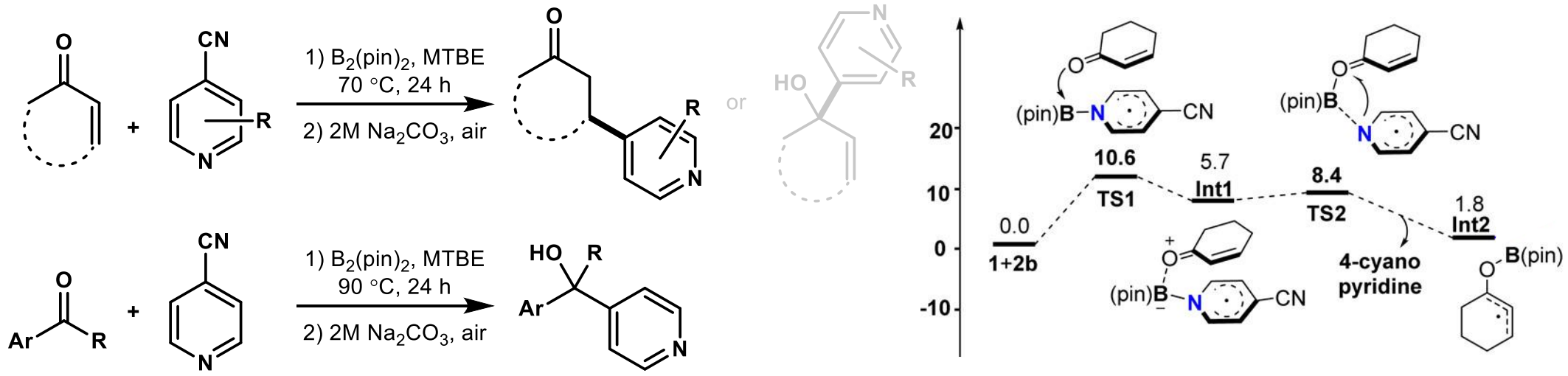
Cu(OAc) (1.0 equiv.),4 A MS
allyl-OH (solv.)
55 °C, o/n

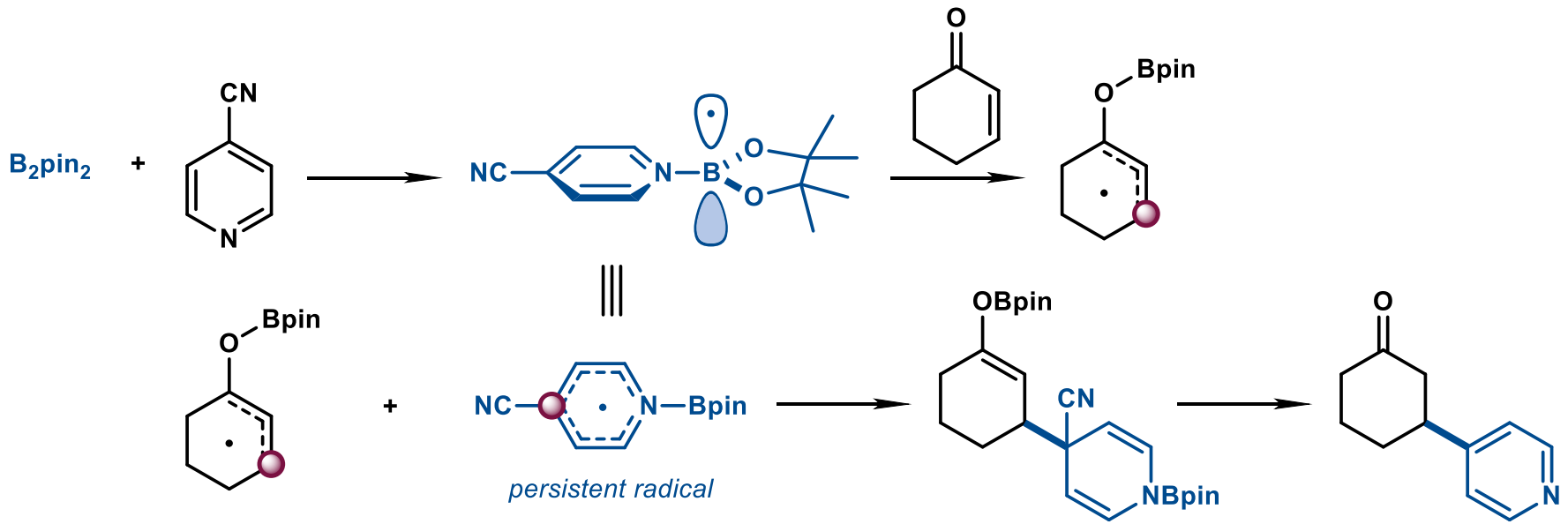


92% (81%)
Chan-Lam etherification

Leonori. D. *et al. Nature*, **2021**, *595*, 677 – 683.

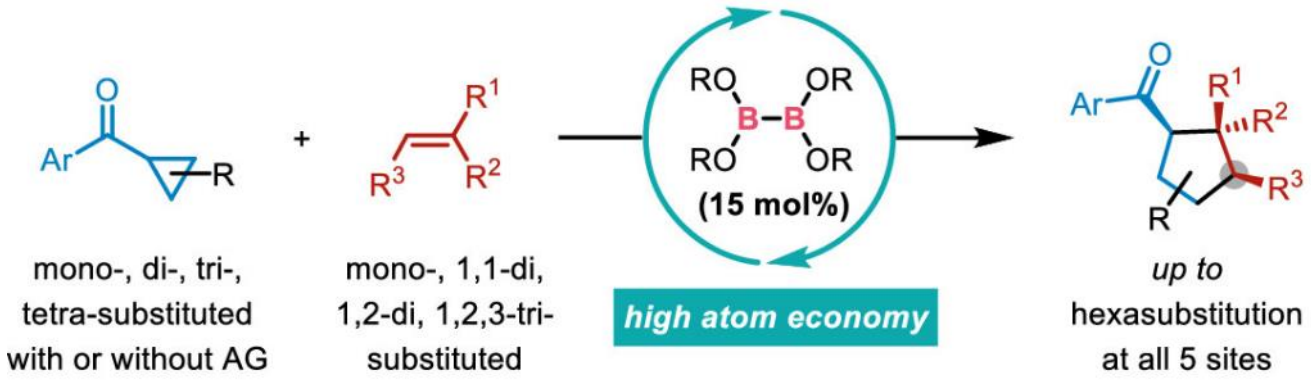
Radical Addition – C=O

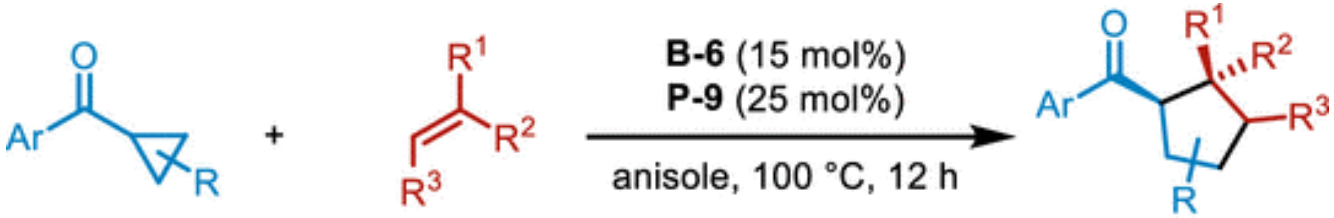


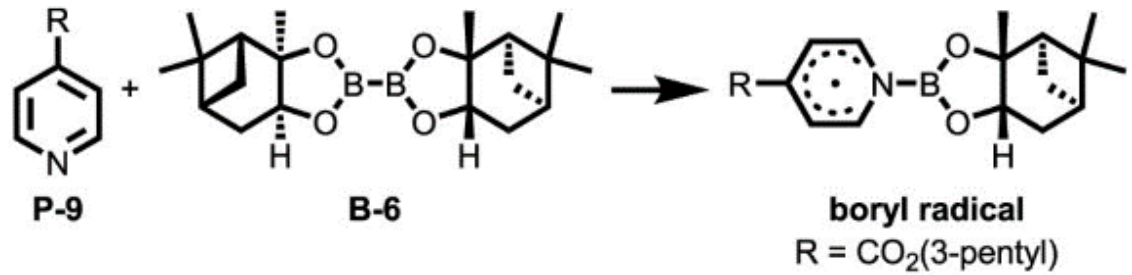


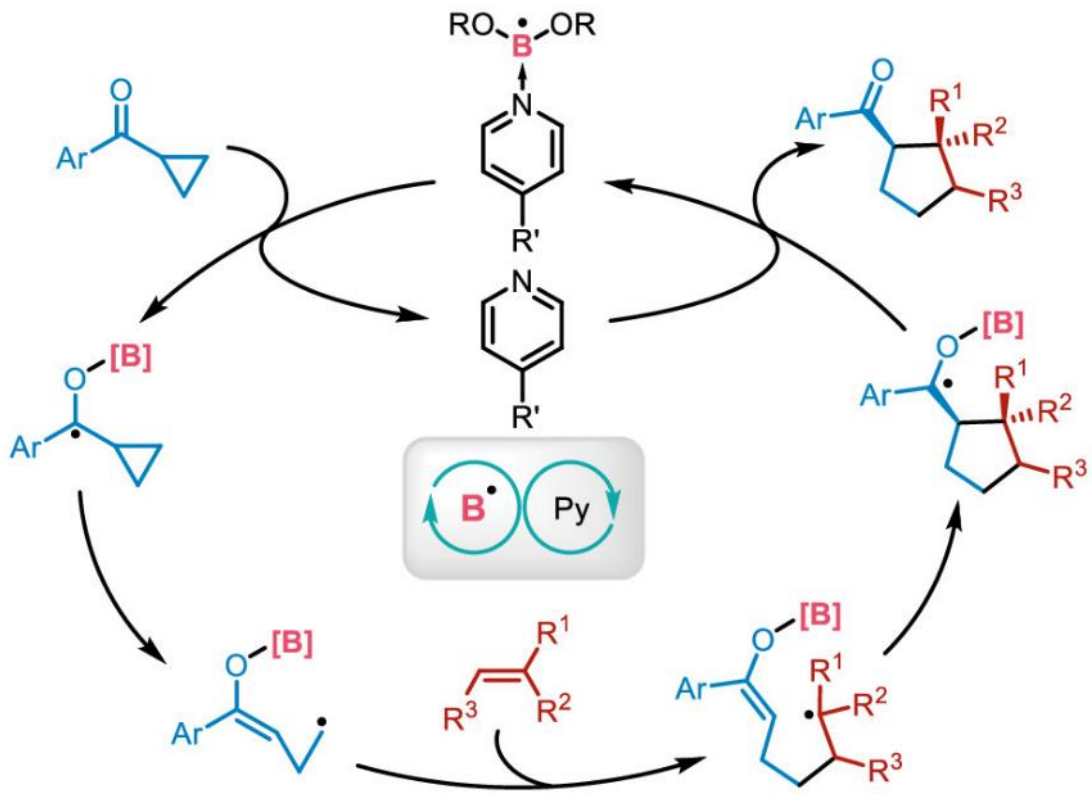
Li. S. H. *et al. J. Am. Chem. Soc.*, **2017**, *139*, 3904 – 3910.C

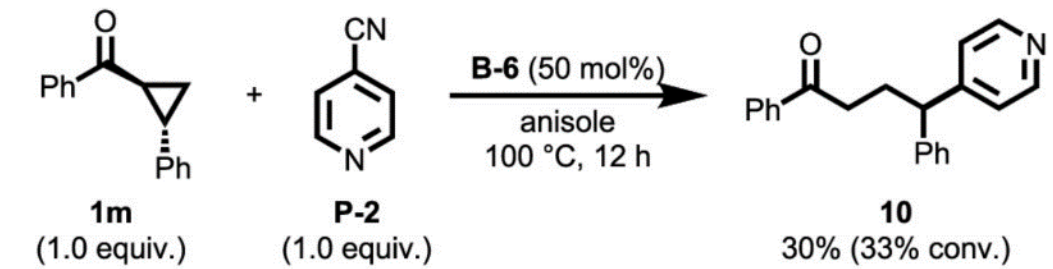
Radical Addition – C=O





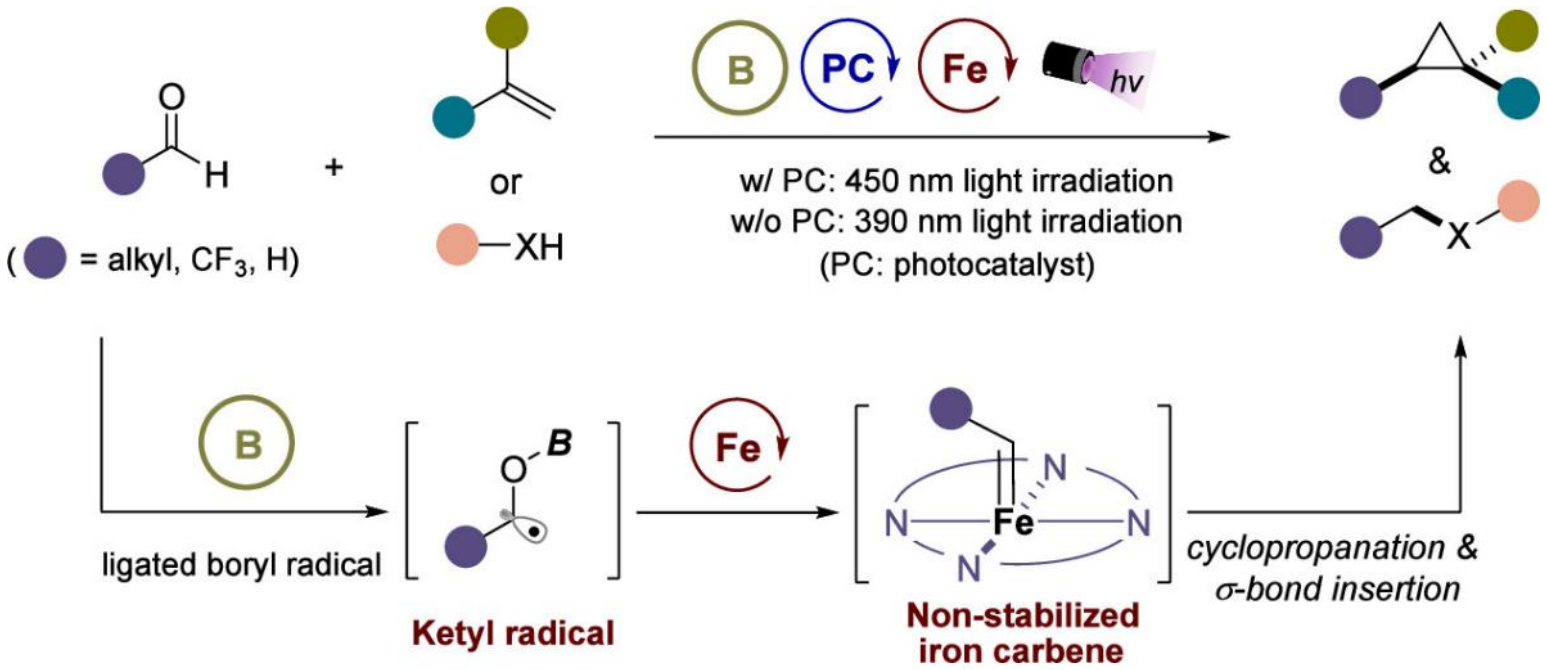


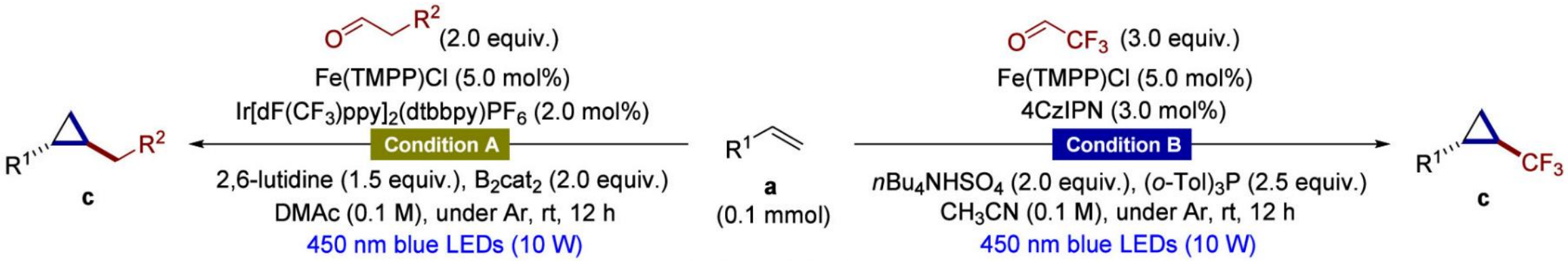




Li. P. F. *et al. J. Am. Chem. Soc.*, **2022**, *144*, 8870 – 8882.

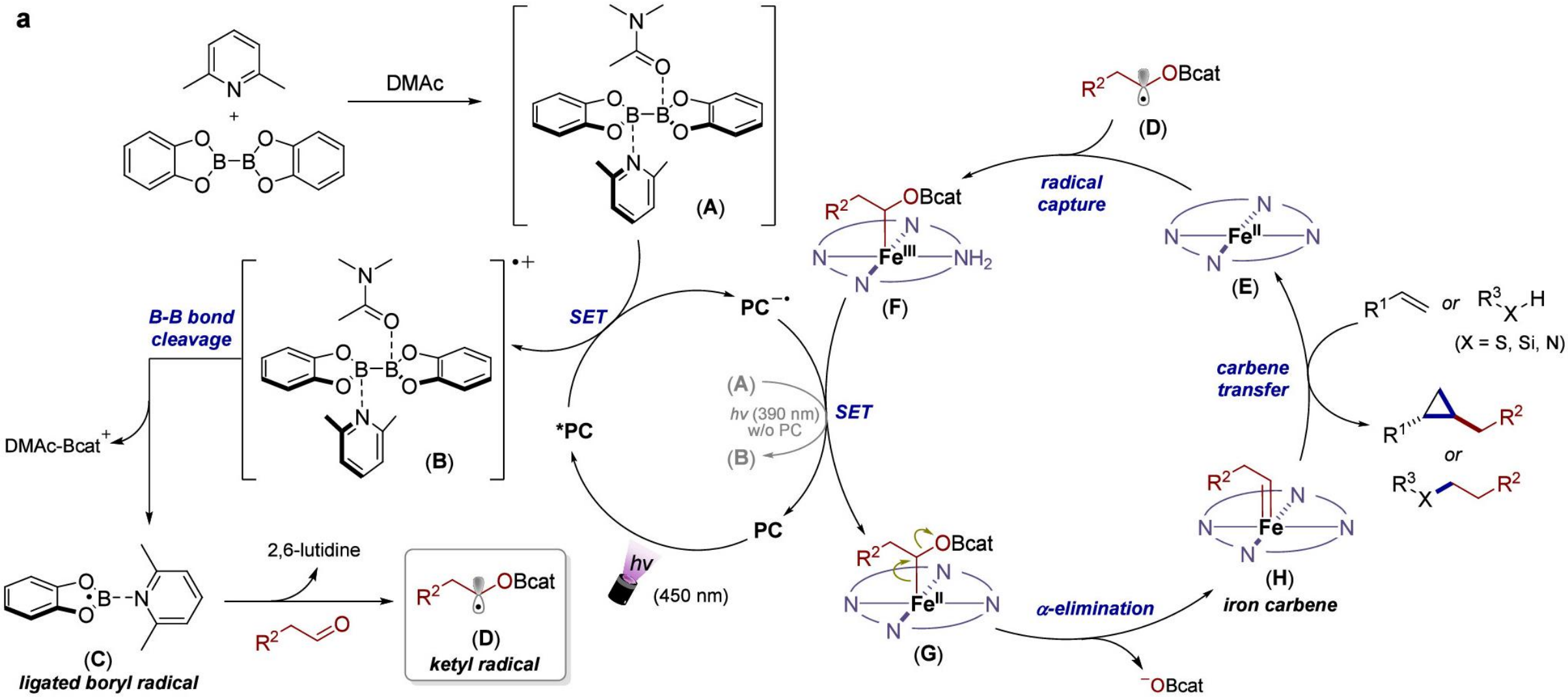
Radical Addition – C=O





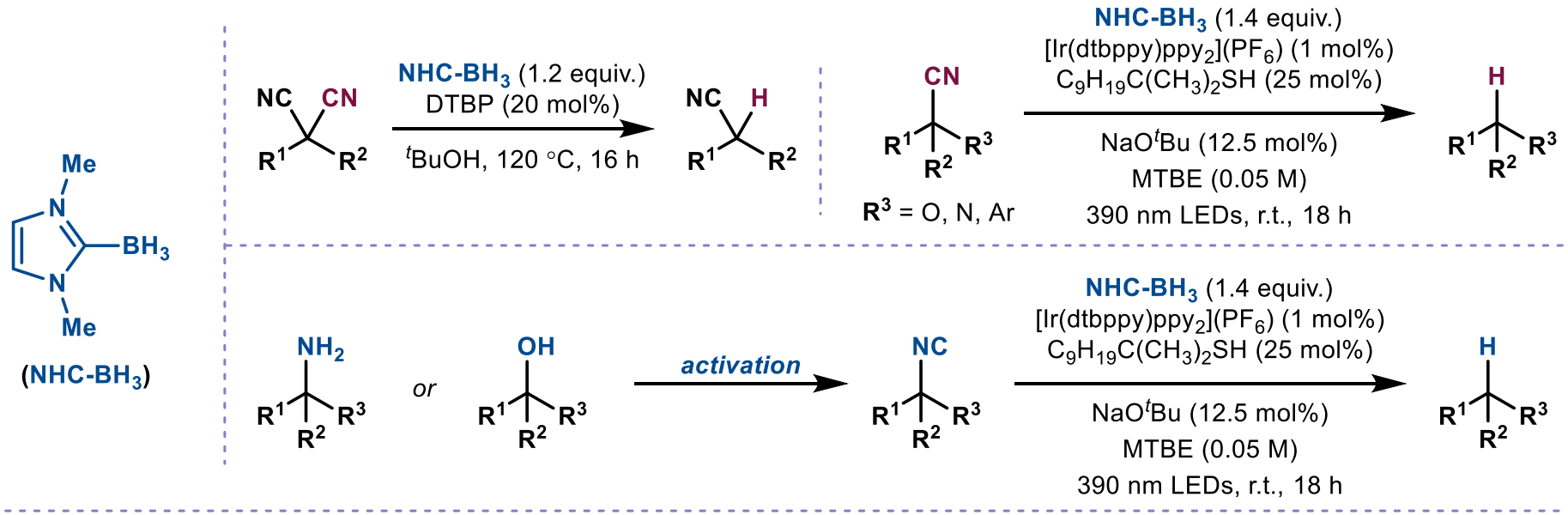
Guo. L. *et al. J. Am. Chem. Soc.*, **2025**, *147*, 36781 – 36792.

Radical Addition – C=O



Guo. L. *et al. J. Am. Chem. Soc.*, **2025**, *147*, 36781 – 36792.

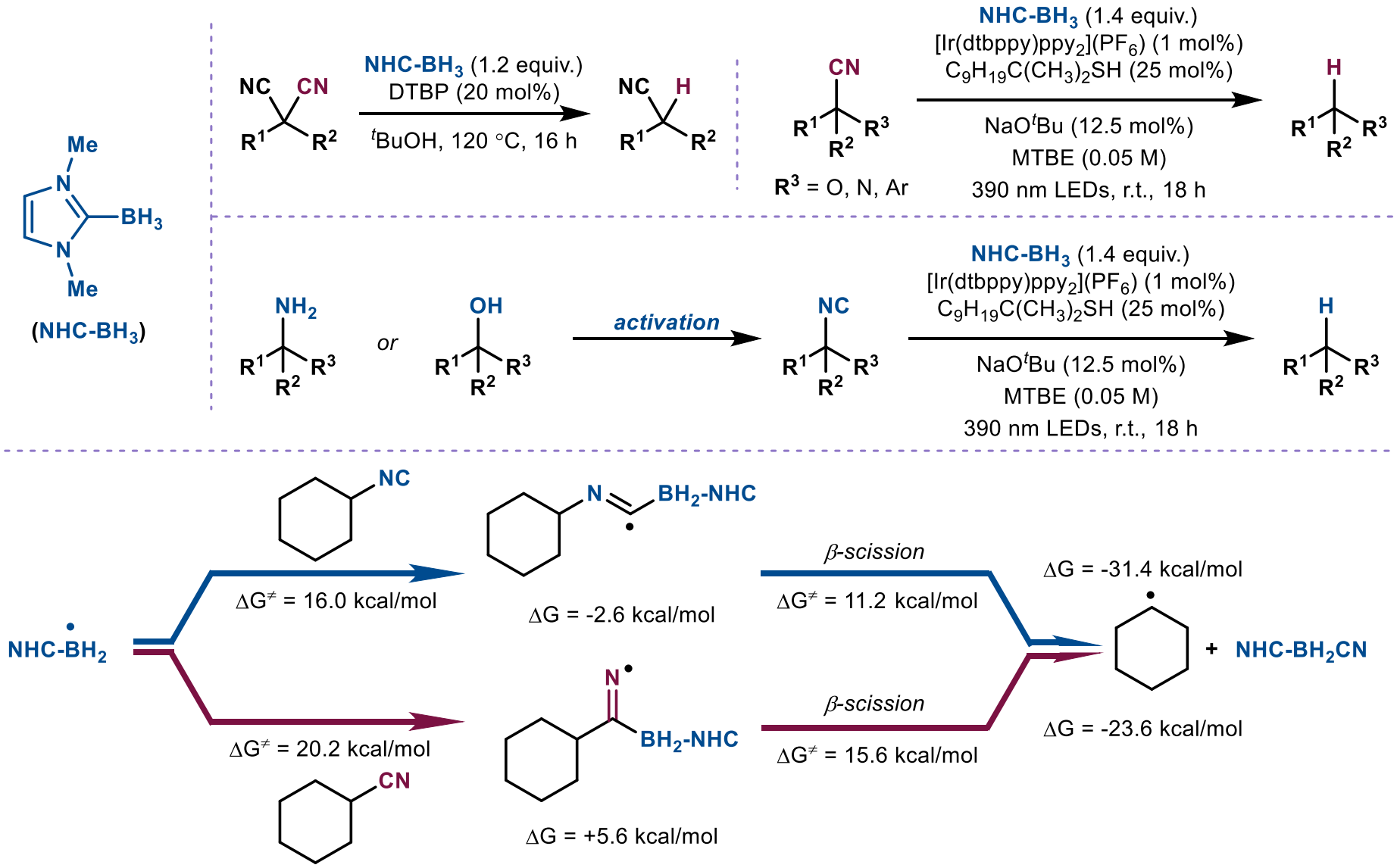
Radical Addition – CN & NC



Curran, D. P. *et al. J. Am. Chem. Soc.*, **2015**, 137, 8617 – 8622.

Schuppe, A. W. *et al. Angew. Chem. Int. Ed.*, **2024**, 63, e202405779.

Radical Addition – CN & NC

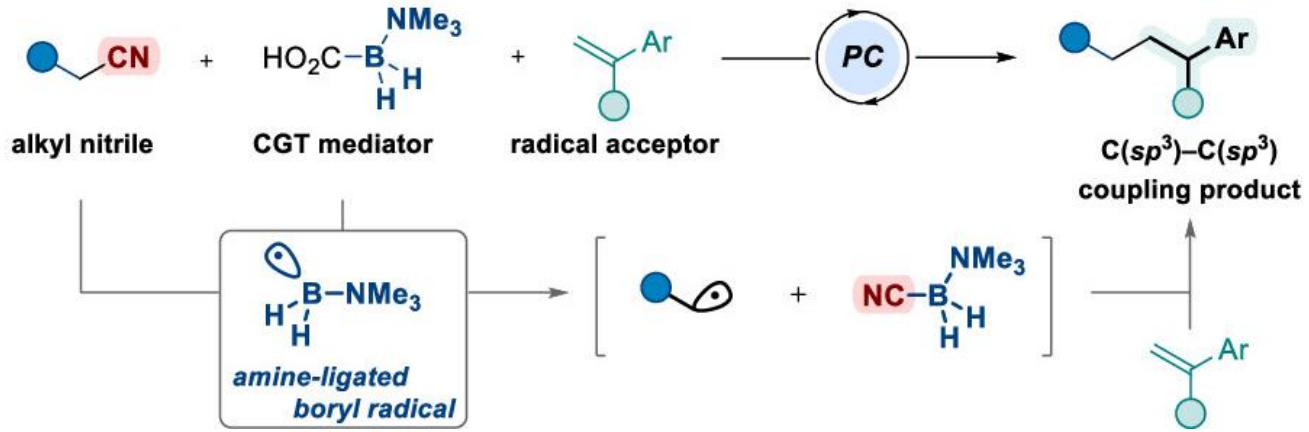


Curran, D. P. *et al. J. Am. Chem. Soc.*, **2015**, 137, 8617 – 8622.

Schuppe, A. W. *et al. Angew. Chem. Int. Ed.*, **2024**, 63, e202405779.

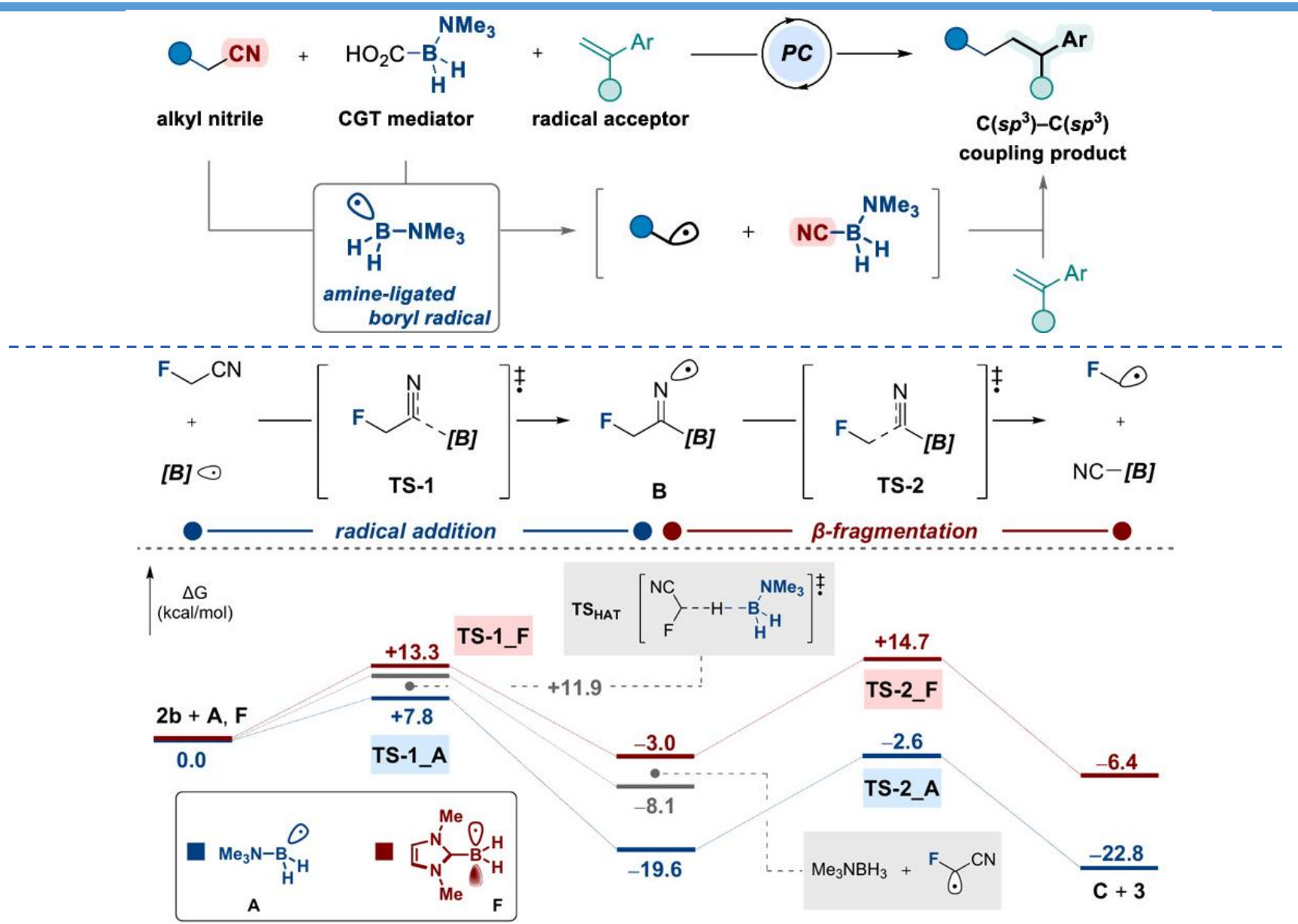
Radical Addition – CN & NC

- α substituent : X



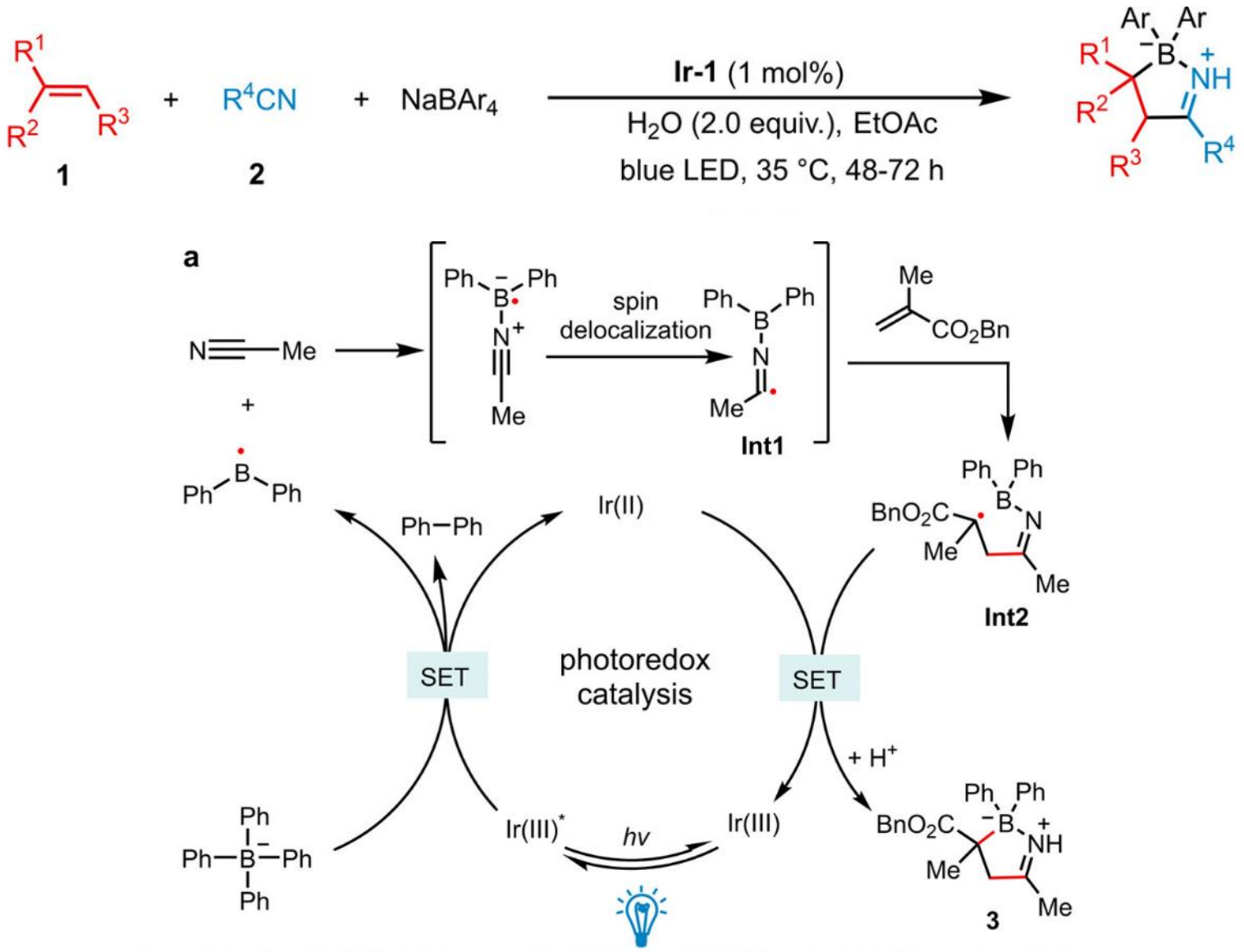
Radical Addition – CN & NC

- α substituent : X



Yasukawa, N. *et al. Org. Lett.*, **2025**, 27, 7236 – 7241.

Radical Addition – CN & NC



Ye, J. T. *et al. J. Am. Chem. Soc.*, **2025**, *147*, 25397 – 25406.

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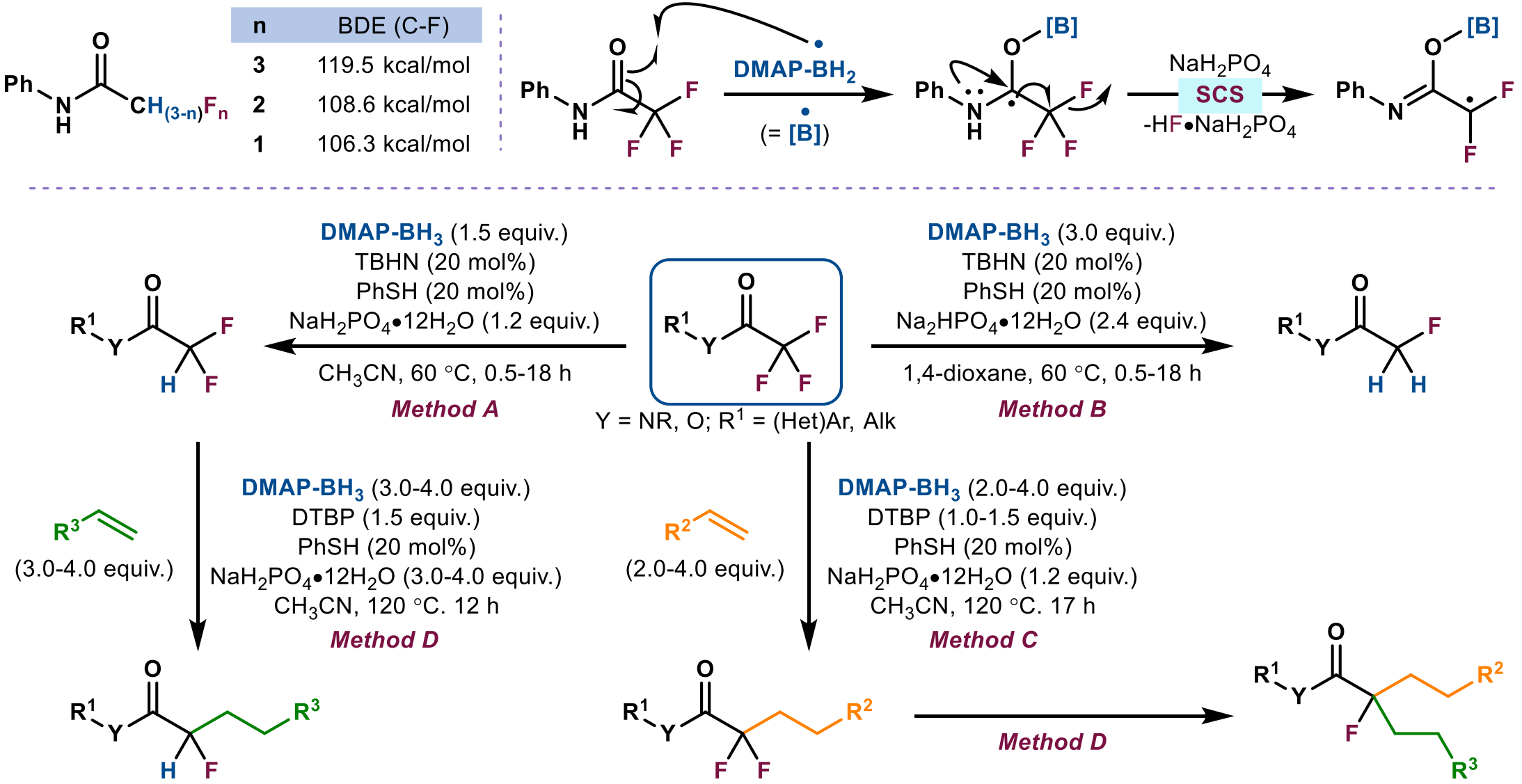
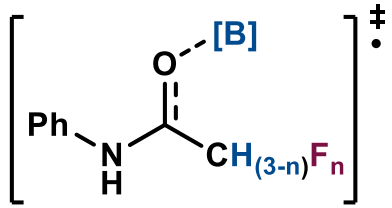
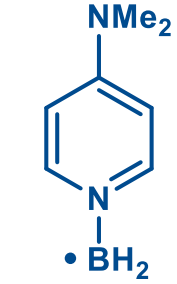
Spin-center shift



Spin-center shift

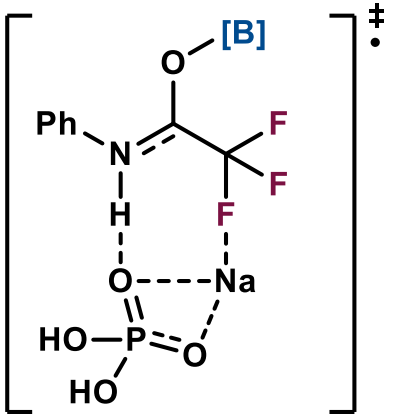


n	ΔG≠
3	7.9 kcal/mol
2	9.2 kcal/mol
1	11.1 kcal/mol

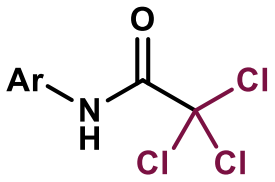


SOMO -4.25 eV

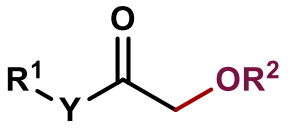
n	SOMO/LUMO gap
3	4.03 eV
2	4.14 eV
1	4.45 eV



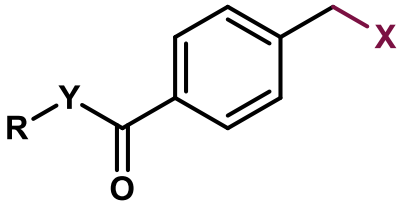
ΔG≠ = 9.6, ΔG = -5.2



step-1: XAT
step-2: SCS
step-3: SCS



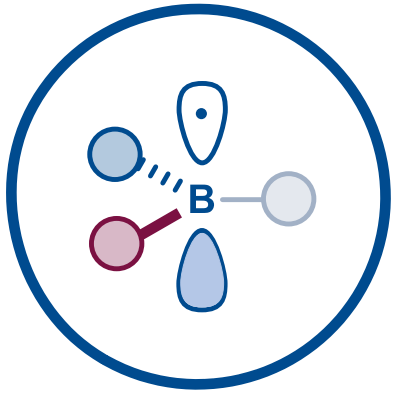
R^2 = Ac, Ms



X = OH or NHMs

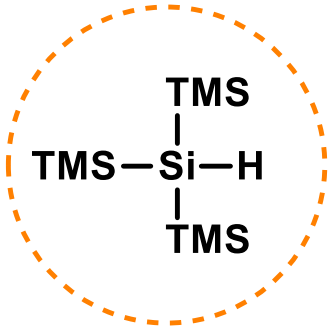
Wang. Y. F. *et al. Science*, **2021**, *371*, 1232 – 1240.
Wang. Y. F. *et al. J. Am. Chem. Soc.*, **2022**, *144*, 15275 – 15285.
Wang. Y. F. *et al. Angew. Chem. Int. Ed.*, **2022**, e202201329.
Wang. Y. F. *et al. Angew. Chem. Int. Ed.*, **2025**, 64, e202506771.

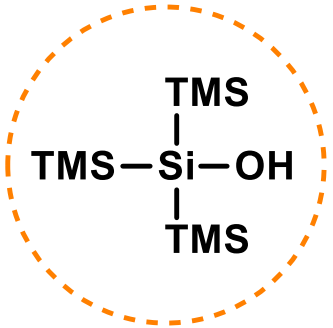
Halogen-Atom Transfer (XAT)



vs.

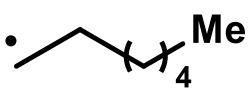
.....





- *Low-cost*
- *Low-toxicity*
- *Diverse structures*
- *Metal-free*
- *Compatible with metals*

- *High-cost*
- *High MW*
- *Low atom economy*
- *Limited structures*
- *Sterically sensitive*

$Me_3N\text{-}BH_2^{\bullet} \approx Et_3Si^{\bullet} > (TMS)_3Si^{\bullet} \approx Bu_3Sn^{\bullet} \approx Bu_3Ge^{\bullet} > NHC\text{-}BH_2^{\bullet} >$  $>$ 

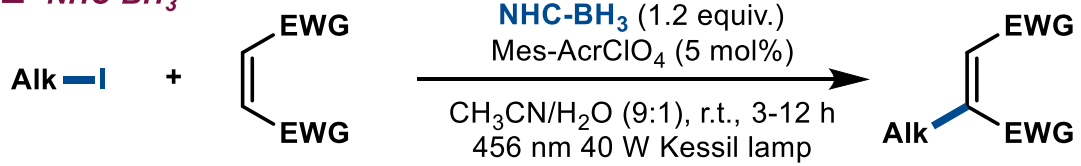
enthalpic effects ***polar effects***

R-X BDE *Y-X BDE* *R• stability* *Y• nucleophilic character* *R electrophilicity*

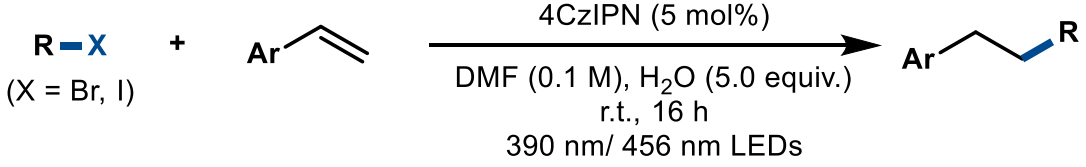
Leonori, D. *et al. Chem. Rev.*, **2022**, 122, 2292 – 2352.

Halogen-Atom Transfer (XAT)

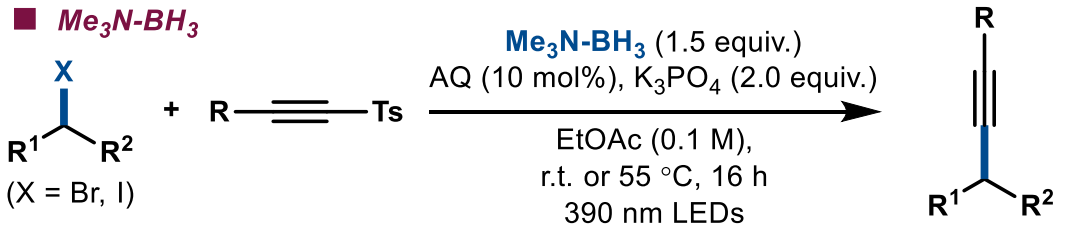
■ *NHC-BH$_3$*



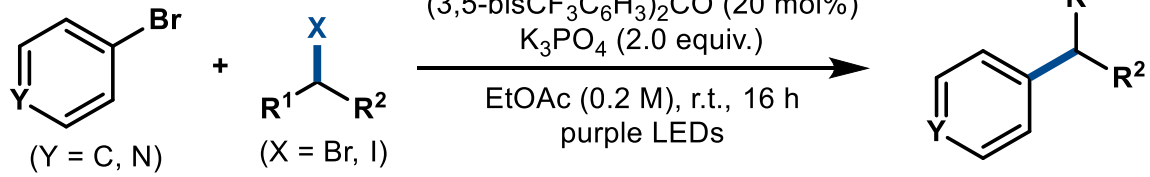
■ *NaBPh$_4$*



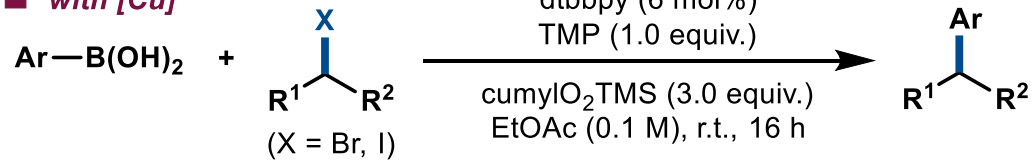
■ *Me$_3$N-BH$_3$*



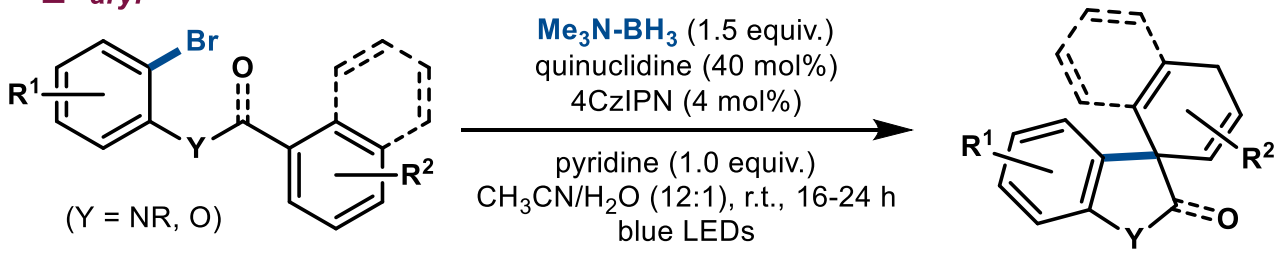
■ *with [Ni]*



■ *with [Cu]*



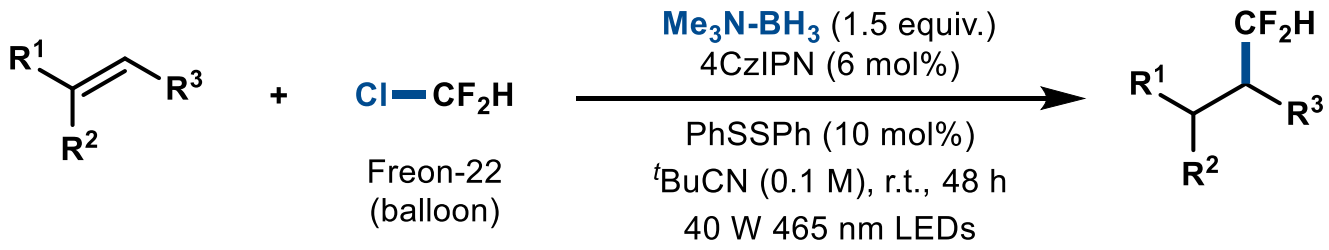
■ *aryl*



Noel, T. *et al. J. Am. Chem. Soc.*, **2023**, *145*, 991 – 999.
Sharma. K. *et al. Chem. Sci.*, **2024**, *15*, 8813 – 8819.
Leonori. D. *et al. Chem. Sci.*, **2024**, *15*, 19113 – 19118.
Leonori. D. *et al. Nat. Synth.*, **2024**, *3*, 1221 – 1230.
Liu. P. J. *et al. ACS Catal.*, **2025**, *15*, 1294 – 1304.

Halogen-Atom Transfer (XAT)

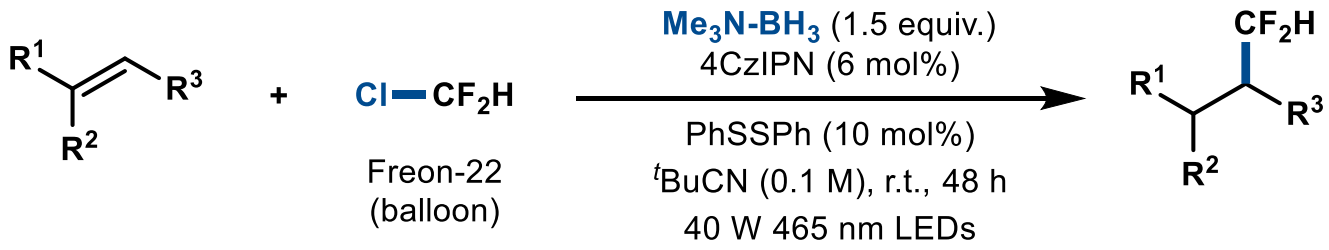
- *activated C-Cl*



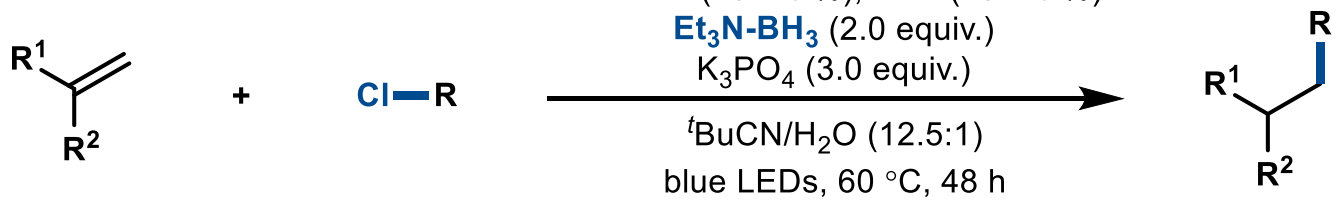
Wu, J. *et al. J. Am. Chem. Soc.*, **2022**, 144, 14288 – 14296.
Chen, X. Y. *et al. J. Am. Chem. Soc.*, **2024**, 146, 26574 – 26584.

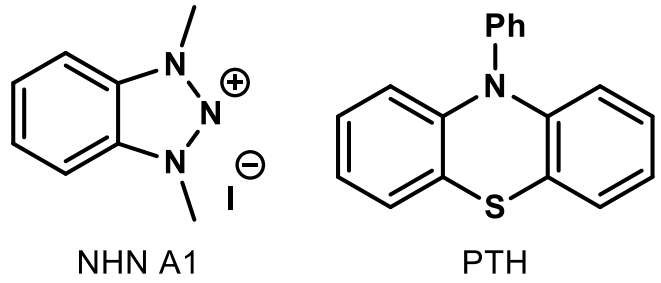
Halogen-Atom Transfer (XAT)

■ *activated C-Cl*

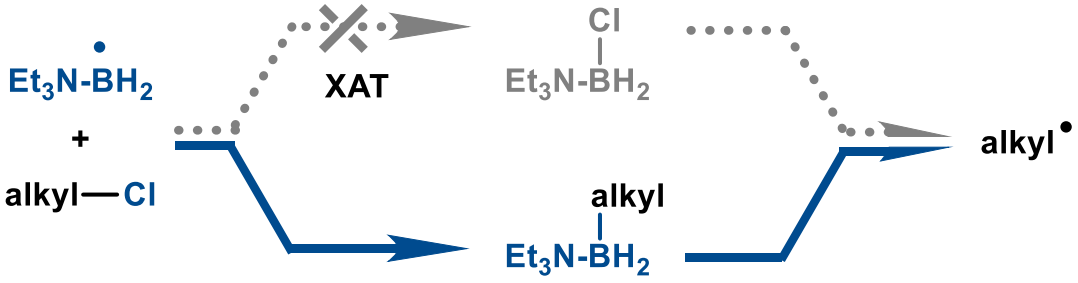


■ *unactivated C-Cl*

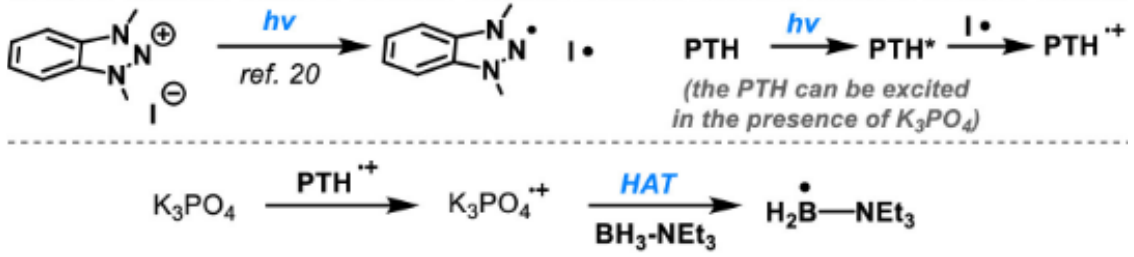




■ *radical replacement*



■ *generation of LBR*

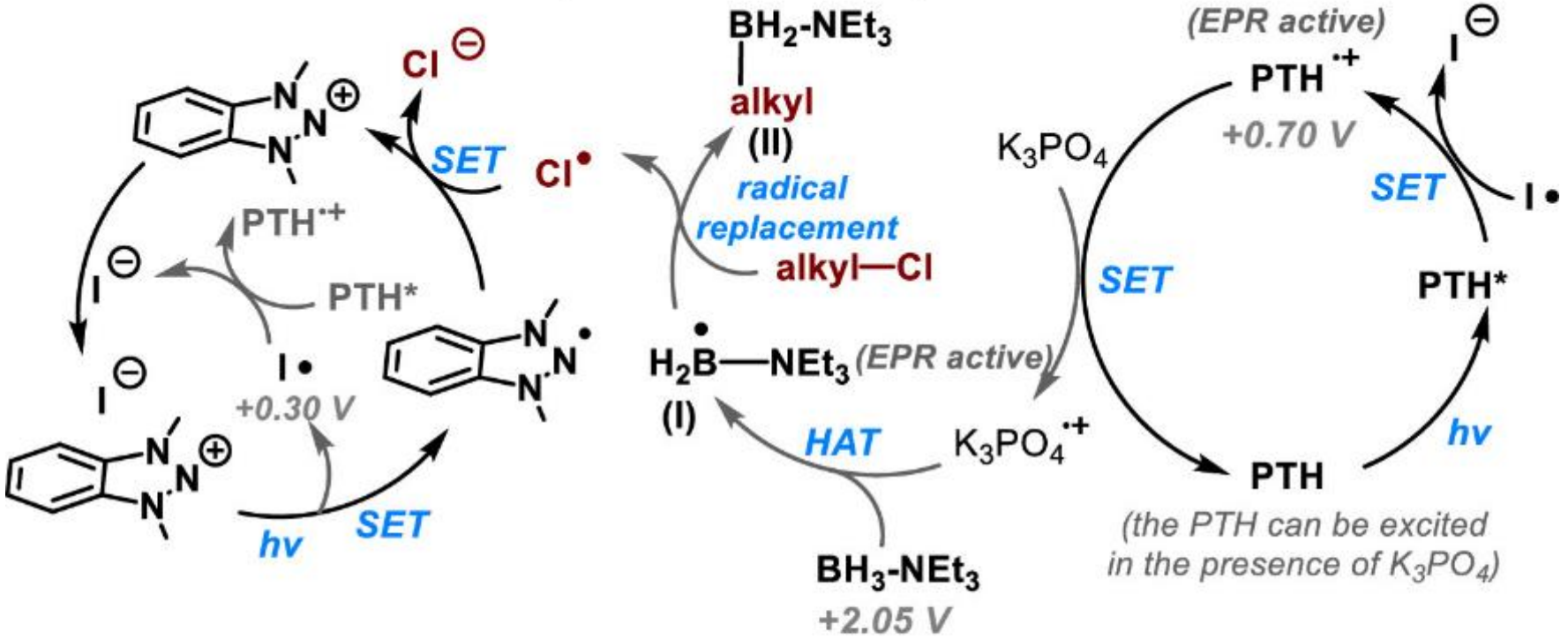


Wu, J. *et al. J. Am. Chem. Soc.*, **2022**, 144, 14288 – 14296.

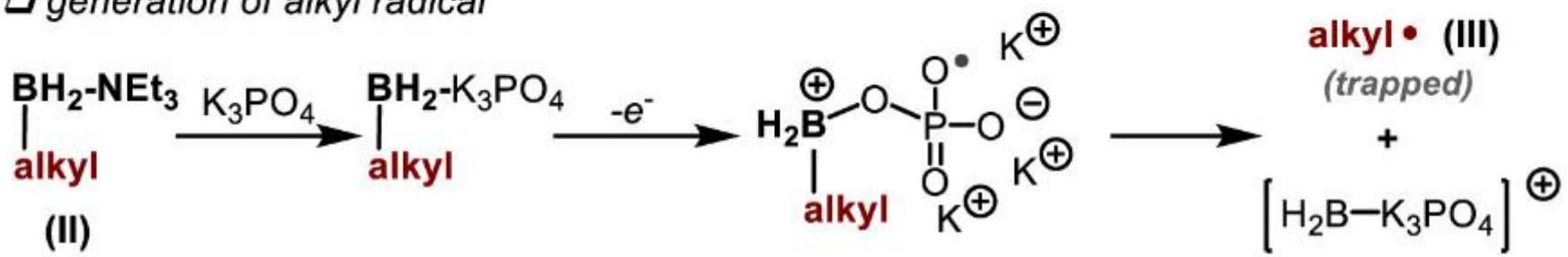
Chen, X. Y. *et al. J. Am. Chem. Soc.*, **2024**, 146, 26574 – 26584.

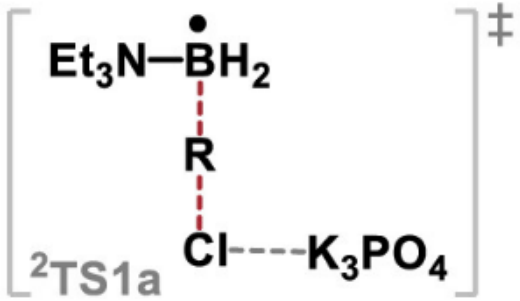
Halogen-Atom Transfer (XAT)

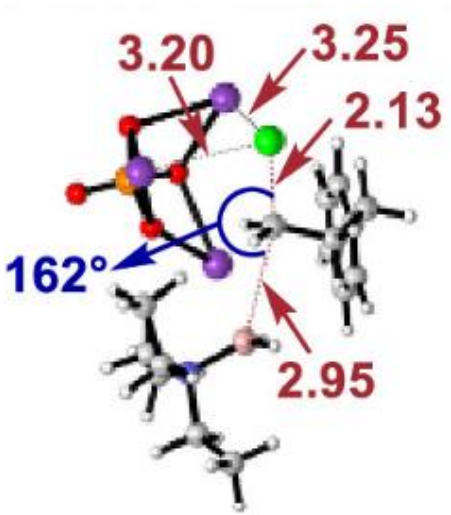
❑ activation of alkyl chlorides (detected via ^{11}B-NMR)



❑ generation of alkyl radical

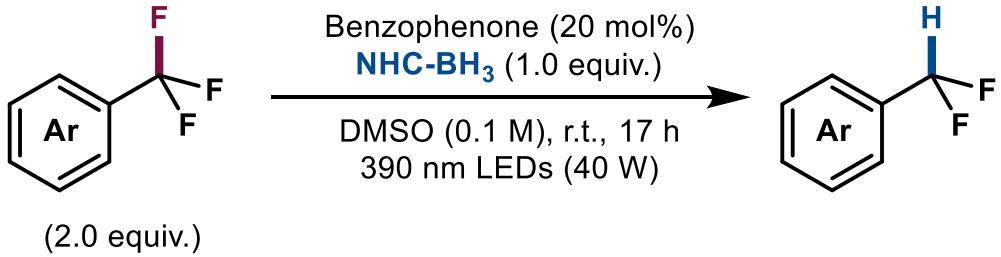






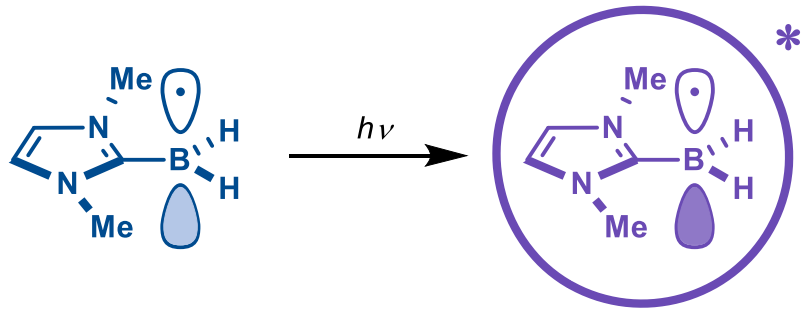
Chen, X. Y. *et al. J. Am. Chem. Soc.*, **2024**, 146, 26574 – 26584.

Halogen-Atom Transfer (XAT)

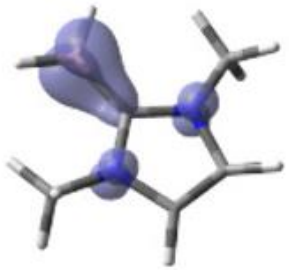


8 examples
32%-86%

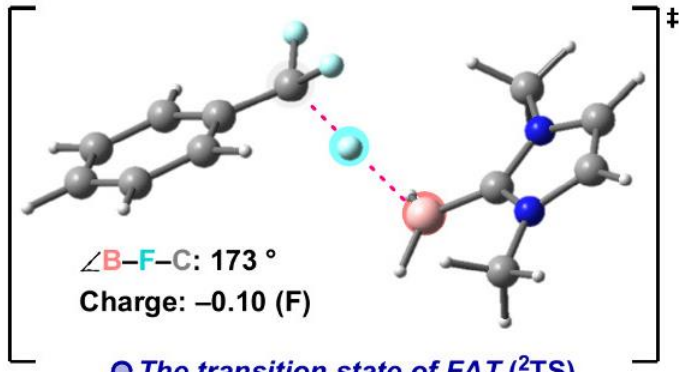
■ ***Excited-State NHC-LBR***



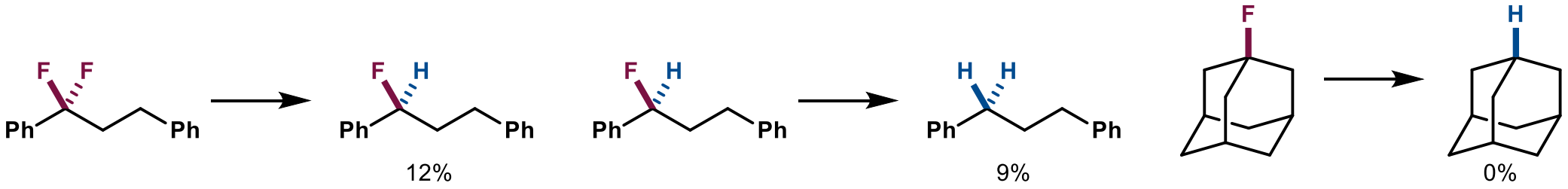
absorb: 300-420 nm



spin-density
0.51 (B)

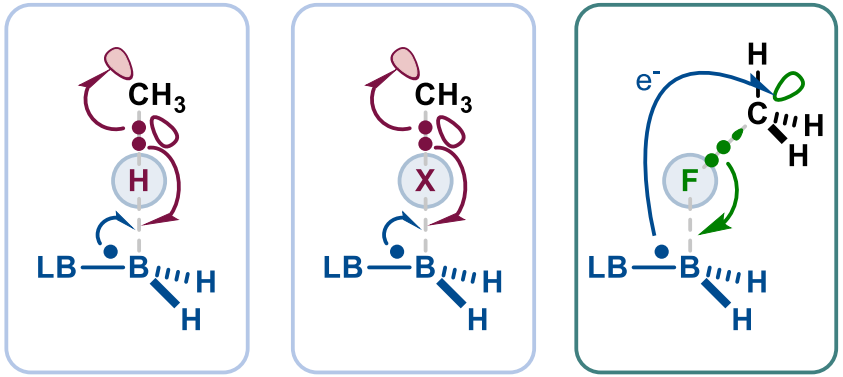


The transition state of FAT (²TS)



Lee, H. G. *et al. J. Am. Chem. Soc.*, **2024**, 146, 22874 – 22880.

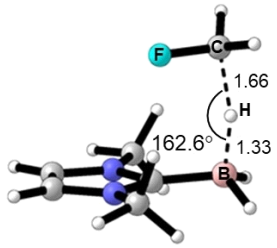
Halogen-Atom Transfer (XAT)



H
HAT

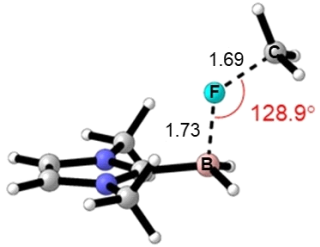
X = Cl, Br, I
XAT

F
cEF^{-}T



TS-BR3-H-CH_2F

$\Delta G^{\ddagger}$ = 34.7 kcal/mol

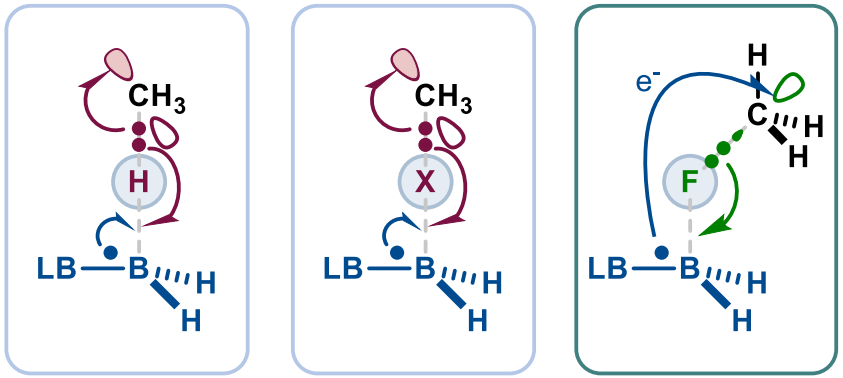


TS-BR3-F-CH_3

$\Delta G^{\ddagger}$ = 39.2 kcal/mol

Xue, X. S. *et al. Angew. Chem. Int. Ed.*, **2025**, 64, e202415715.

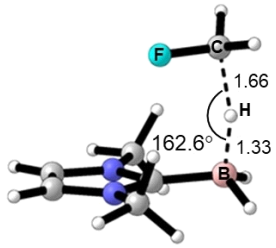
Halogen-Atom Transfer (XAT)



H
HAT

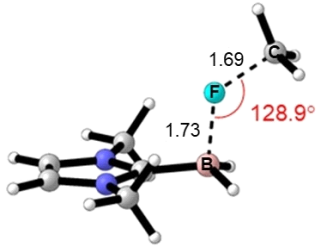
X = Cl, Br, I
XAT

F
cEF⁻T



TS-BR3-H-CH_2F

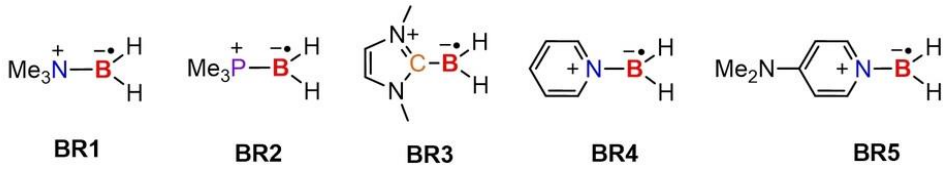
$\Delta G^{\ddagger}$ = 34.7 kcal/mol



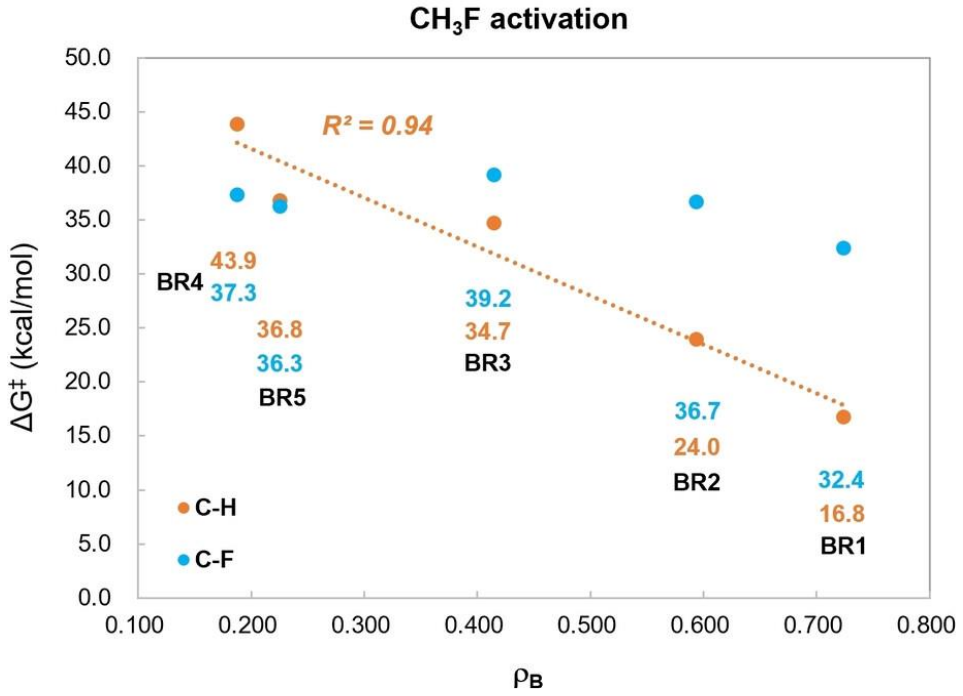
TS-BR3-F-CH_3

$\Delta G^{\ddagger}$ = 39.2 kcal/mol

■ *cEF⁻T vs. HAT*



BR1 BR2 BR3 BR4 BR5

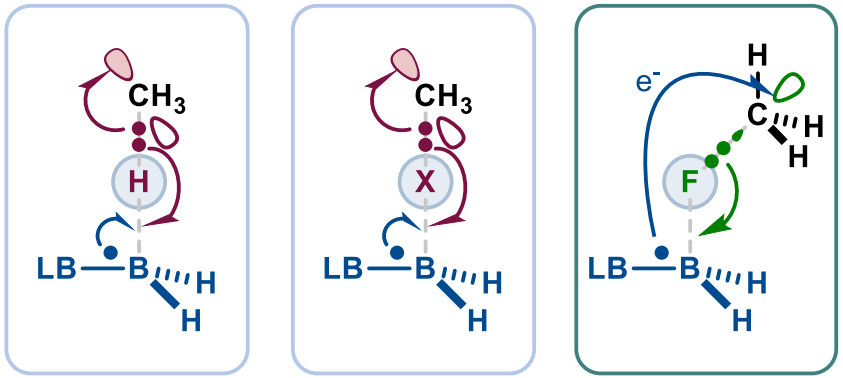


■ *σ donor* ↑: $\Delta G^{\neq}$(cEF⁻T) ↓ $\Delta G^{\neq}$(HAT) ↓

■ *π acceptor* ↑: cEF⁻T ↑ HAT ↓

Xue, X. S. *et al. Angew. Chem. Int. Ed.*, **2025**, 64, e202415715.

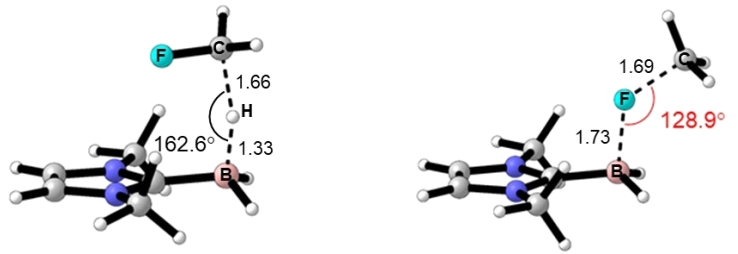
Halogen-Atom Transfer (XAT)



H
HAT

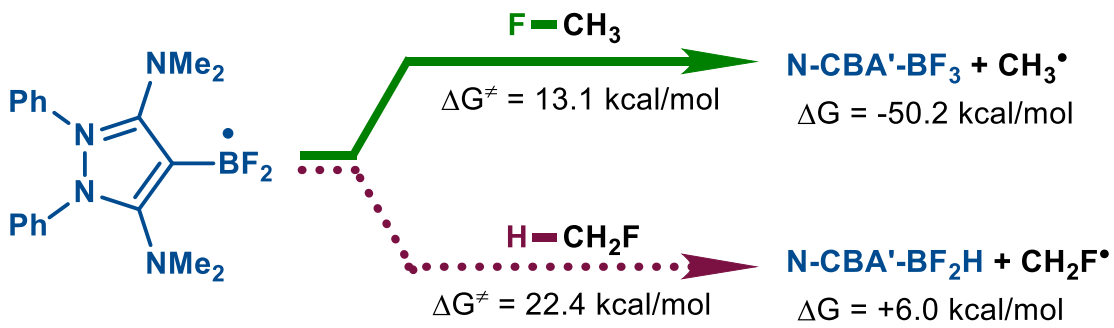
X = Cl, Br, I
XAT

F
cEF⁻T

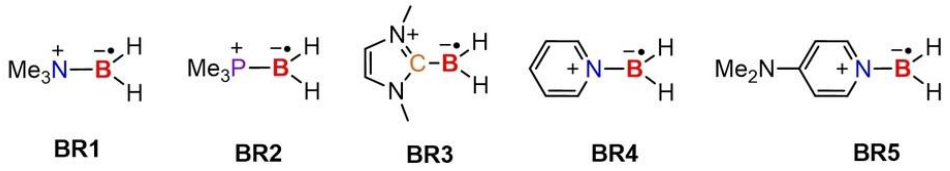


TS-BR3-H-CH_2F
$\Delta G^{\ddagger}$ = 34.7 kcal/mol

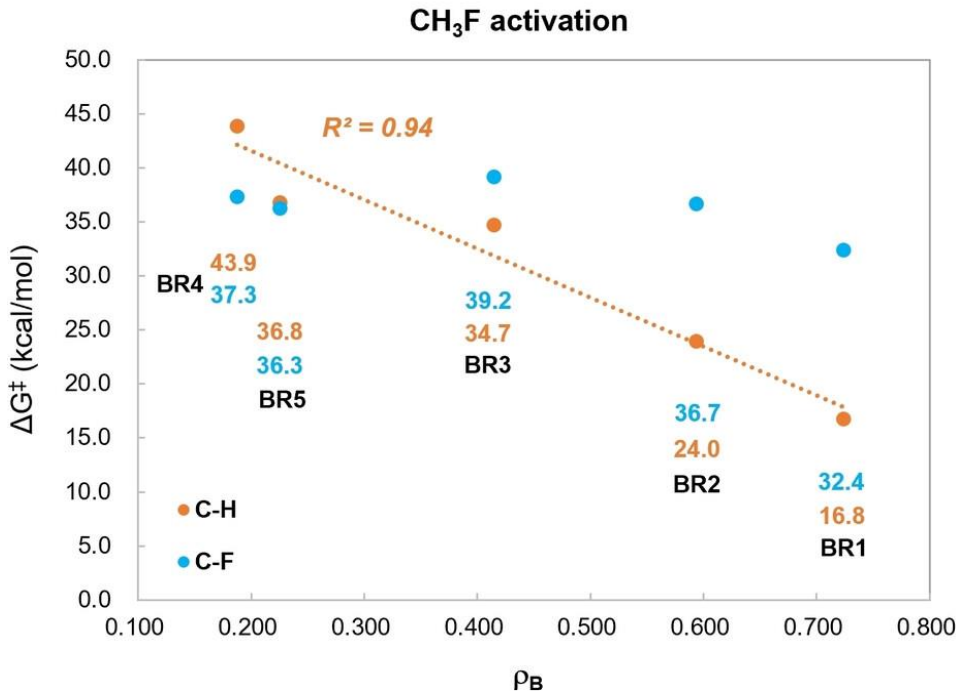
TS-BR3-F-CH_3
$\Delta G^{\ddagger}$ = 39.2 kcal/mol



■ *cEF⁻T vs. HAT*



BR1 BR2 BR3 BR4 BR5



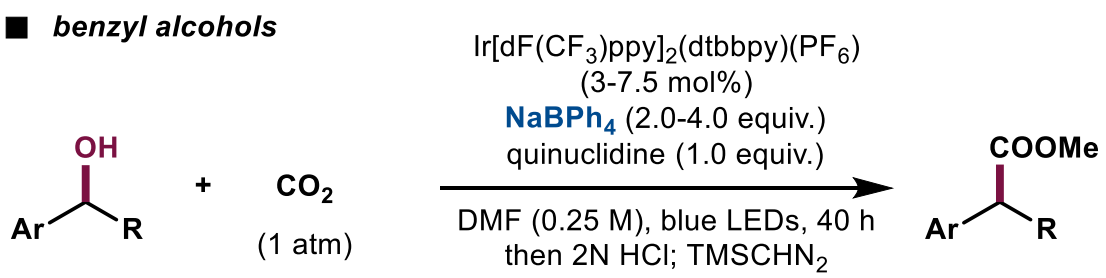
■ *σ donor* ↑: $\Delta G^{\neq}$(cEF⁻T) ↓ $\Delta G^{\neq}$(HAT) ↓

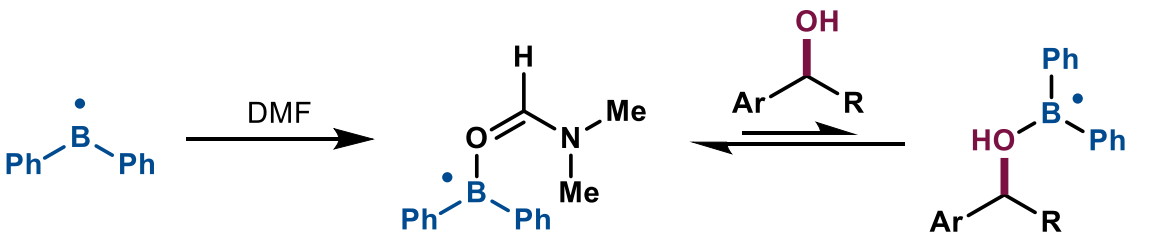
■ *π acceptor* ↑: cEF⁻T ↑ HAT ↓

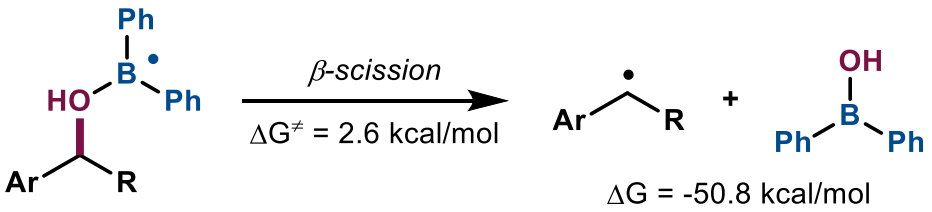
Xue, X. S. *et al. Angew. Chem. Int. Ed.*, **2025**, 64, e202415715.

C-O Cleavage

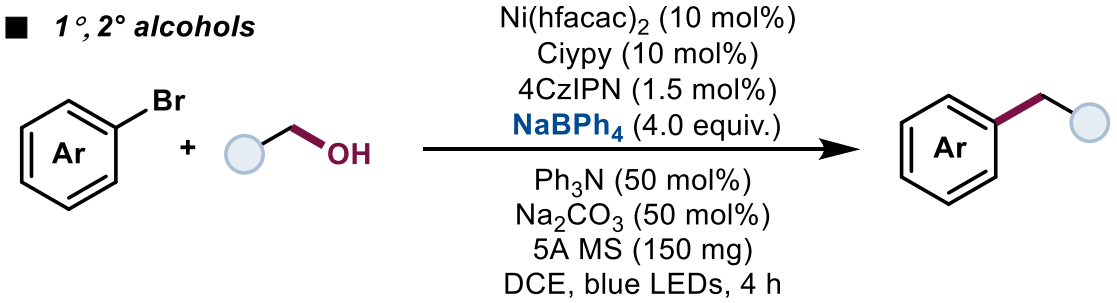
■ ***benzyl alcohols***

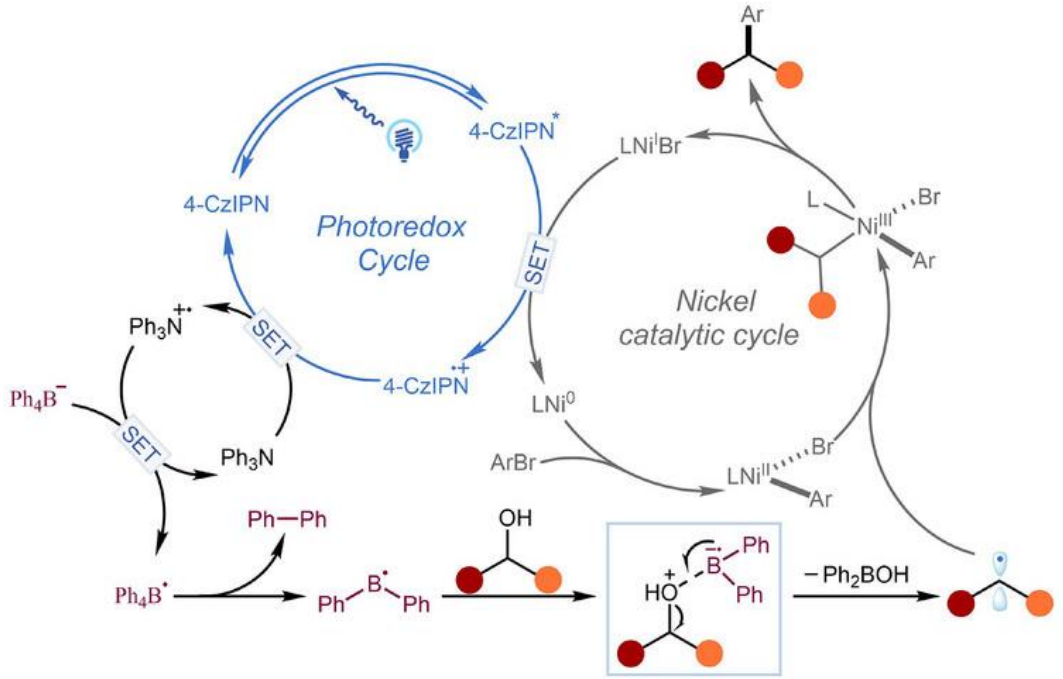






■ ***1°, 2° alcohols***

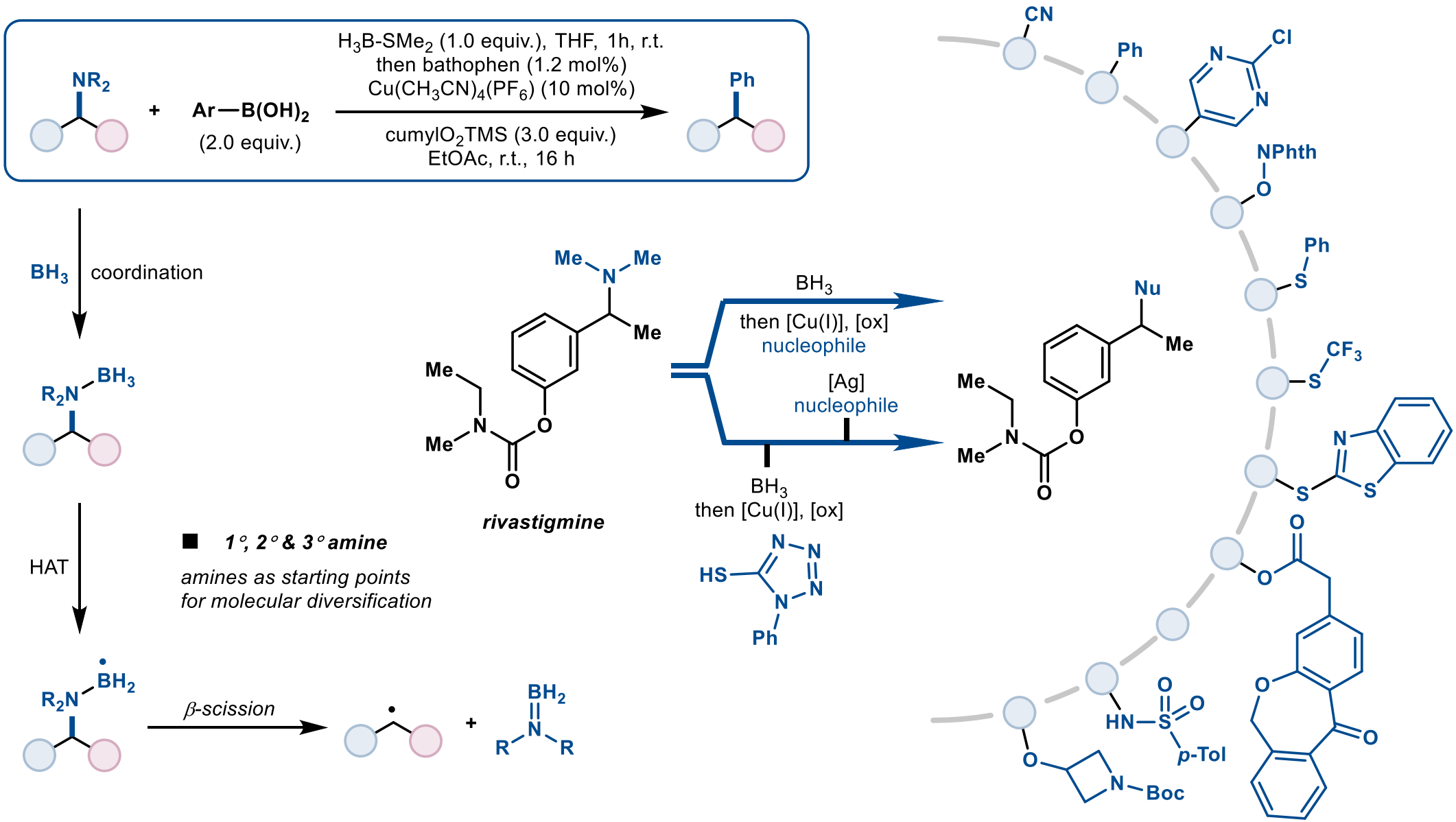




Xia, J. B. *et al. J. Am. Chem. Soc.*, **2022**, *144*, 8551 – 8559.

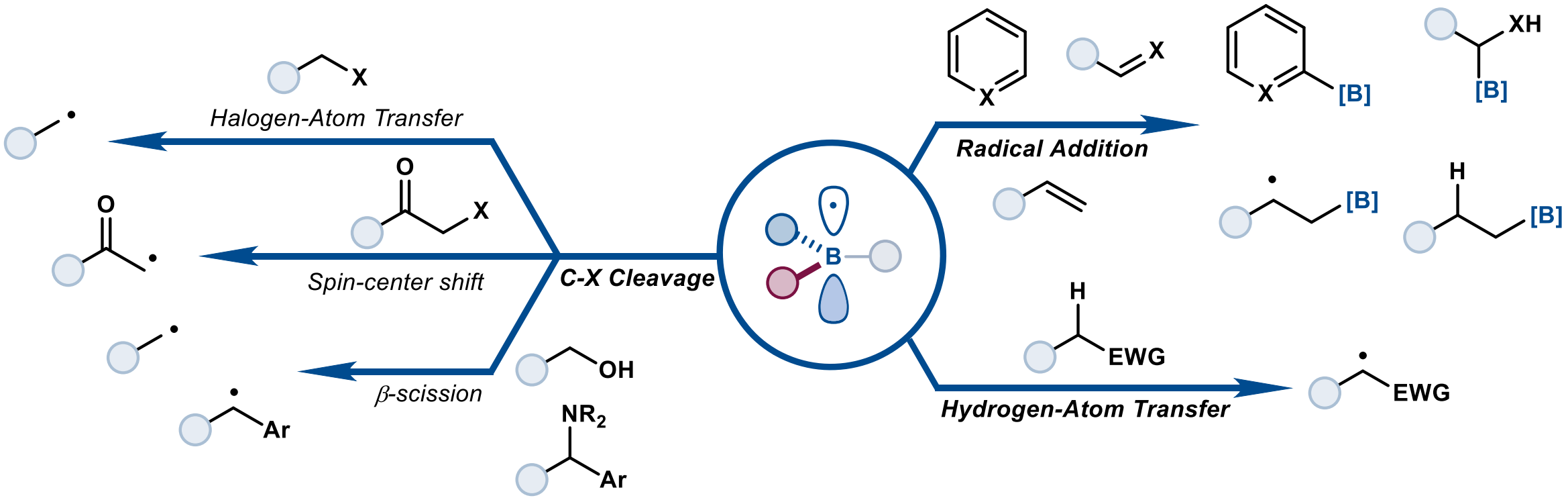
Chen, Y. G. *et al. Angew. Chem. Int. Ed.*, **2025**, e20148.

C-N Cleavage

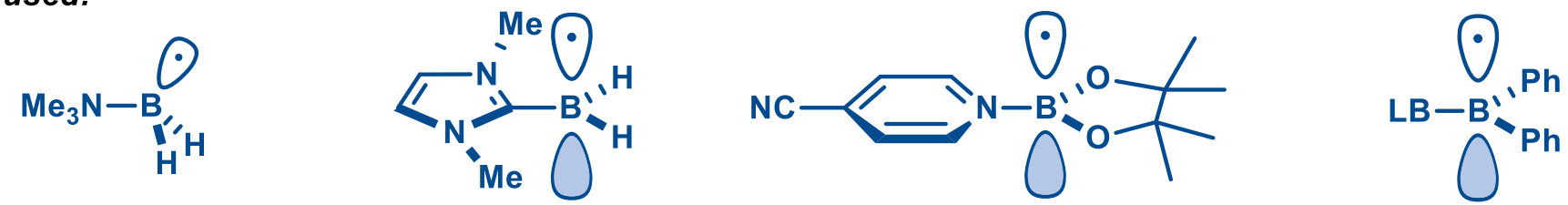


Leonori. D. *et al. Nature*, **2025**, *595*, 10.1038/s41586-025-09725-1.

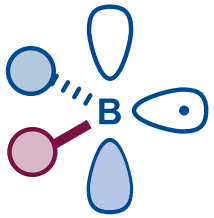
Outlook



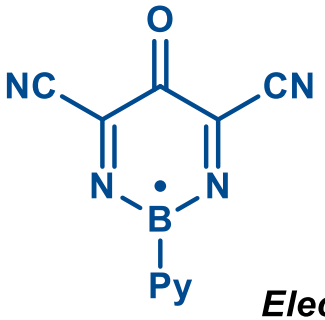
■ ***Most widely used:***



Outlook

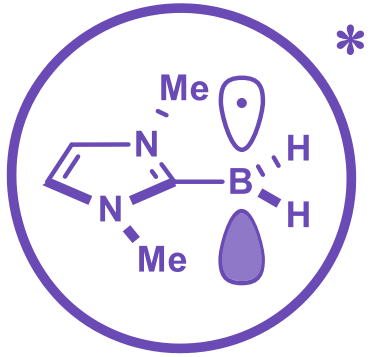


3 center - 5 electron
(3c-5e)



- *Low spin-density on B*
- *Low reactivity*
- *Different reactivity ?*

Electrophilic LBR

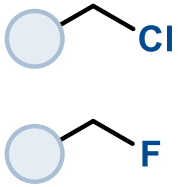


Excited-State LBR

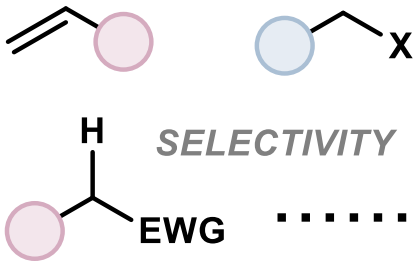
HAT (PRC)

vs.

XAT, RA.....



unactivated
C-X



SELECTIVITY

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- *Everyone here*