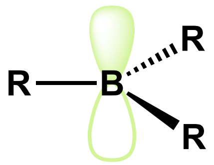
Neutral Boryl Radicals
~ Characteristics and Synthetic Applications ~

Literature Seminar #2
2025/06/19
M1 Yusuke Nakamura

Contents

Closed-Shell Borane Species

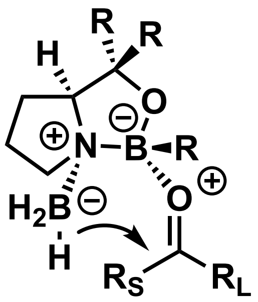


Trivalent boron

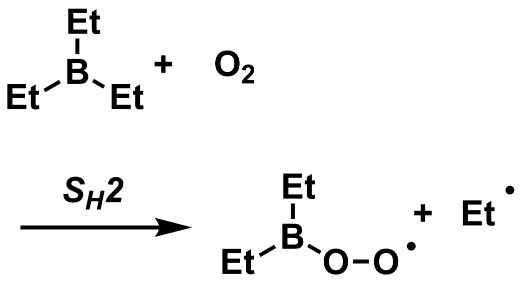
- **Empty p orbital**
→ Electron deficient
(Lewis acid)

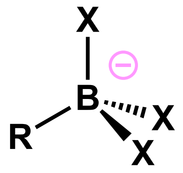
Examples

1. CBS reduction
(activation of carbonyls)



2. Radical initiation



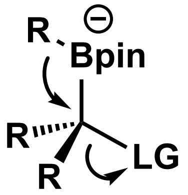


Tetravalent boron

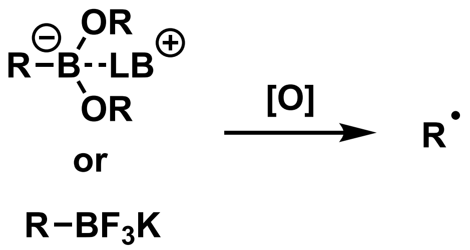
- **Negatively charged**
→ Electron rich
(Lewis base)

Examples

1. Matteson reaction
(source of $R^{\ominus}$)



2. Radical precursors

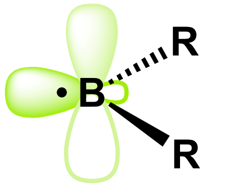


B-based closed-shell species are well studied and utilized many kinds of reactions.

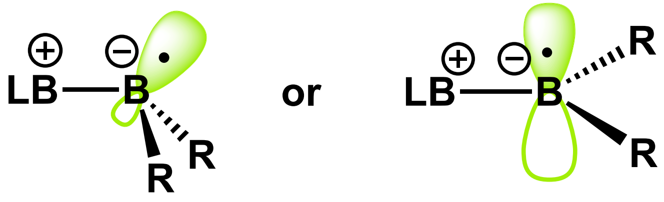
Ravelli, D. *et al. Chem Catalysis*, **2022**, *2*, 957.
Huang, Y. Y. *et al. Adv. Synth. Catal.* **2020**, *362*, 2778.

Opened-Shell Borane Species

Boryl Radicals



Ligated Boryl Radicals (LBRs)



σ-type
(LB = R_3N)

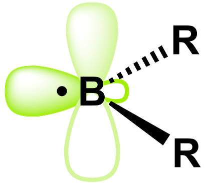
π-type
(LB = R_3P, NHC, pyridine etc.)

- In the 1980s, Roberts and co-workers discovered relatively stable 4-center–7-electron type Lewis base–boryl radicals (LBRs).
- In 2008, Curran and co-workers achieved a breakthrough with the discovery of *N*-heterocyclic carbene (NHC)–boryl radicals.
- Due to their unique reactivity, they are currently being studied extensively.

Ravelli, D. *et al*. *Chem Catalysis*, **2022**, *2*, 957.

Boryl Radicals

Boryl Radicals

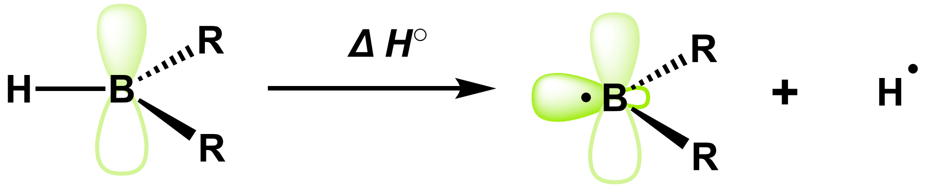


3-center-5-electron spiecies

- Low energy level SOMO & Empty p-orbital
→ unstable (electron deficient)

- Synthetic application is limited. (Detected in MS)

Fehlner, T. P., & Koski, W. S. *J. Am. Chem. Soc*, **1964**, *86*, 2733.

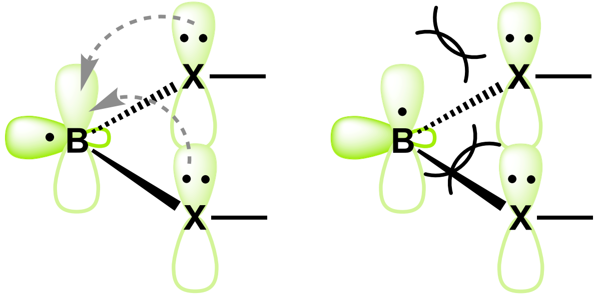


Entry	Bond	BDE$_{298K}$(kcal/mol)
1	H_2B-H	105.5
2	$BHCH_3$-H	104.6
3	$B(CH_3)_2$-H	103.8
4	$PhBCH_3$-H	105.4
5	CH_3CH_2-H	101.7

BDE calculated by CBS-4

- High BDE … difficult to generate (high reactivity)

- Few delocalization effect
(Orbitals are orthogonal to each other.)

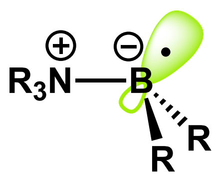


Due to the electronic repulsion, unpaired electron cannot exist in the p_z orbital of B.

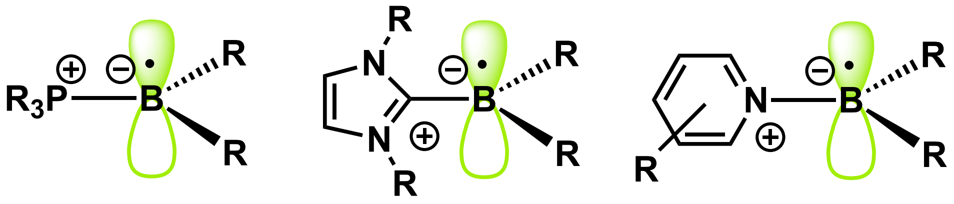
Rablen, P. R., & Hartwig, J. F. *J. Am. Chem. Soc*, **1996**, *118*, 4648.
Zipse, H. *et al. Chem. Eur. J*, **2010**, *16*, 6861.

Ligated Boryl Radicals (LBRs)

Ligated Boryl Radicals (LBRs)

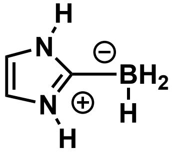


σ-type (pyramidal)



π-type (planar)

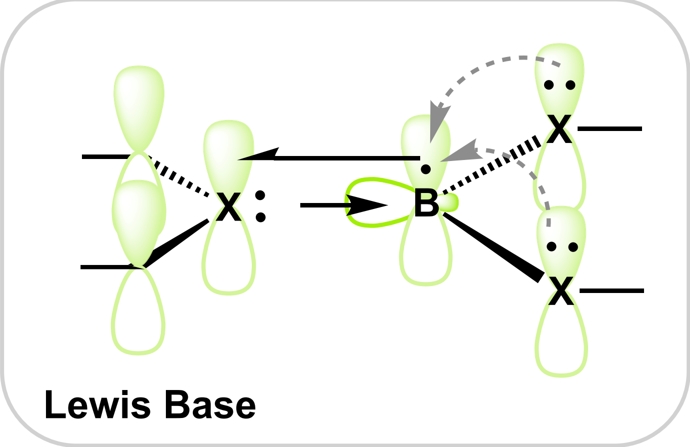
4-center-7-electron spiecies

Entry	Bond	BDE$_{0K}$(kcal/mol)
1	H_2B-H	105.5
2	NH_3BH_2-H	102.1
3	PH_3BH_2-H	92.4
4	pyridine-BH_2-H	70.9
5		80.0

at G3(MP2)-RAD level

- By coordination of LB, BDE is decreased.

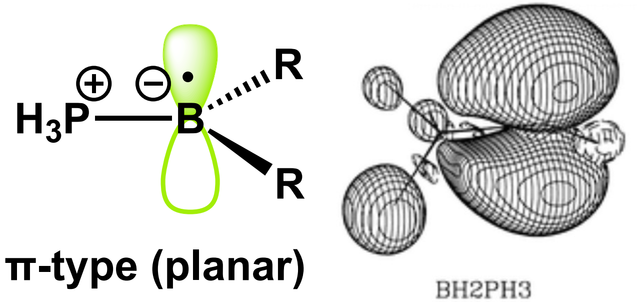
→ **Synergistic Effects of Lewis Bases and Substituents**



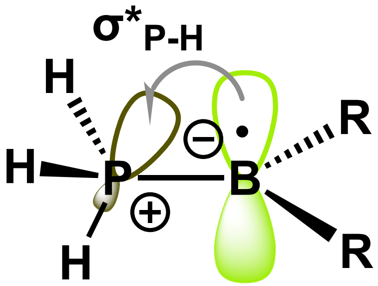
Lewis base
→ σ donor & π acceptor
(“**push-pull**”)

Zipse, H. *et al. Chem. Eur. J*, **2010**, *16*, 6861.
Rablen, P. R. *J. Am. Chem. Soc*, **1997**, *119*, 8350.
Li, P. *et al. Chem. Eur. J*, **2014**, *20*, 1630.

Geometry of LBRs and Localization of Spin Density



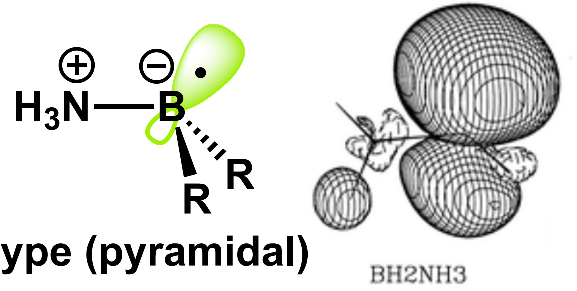
π-type (planar)



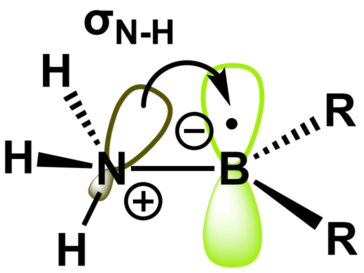
SOMO stabilized by $\sigma^*_{P\text{-}H}$ (and d orbital)
"Anti" P-H bond 0.02 Å longer than other P-H bonds.

Spin denisity by AIM … BH_2 0.658, PH_3 0.342
Cf. hyperfine splitting(G) … $Et_3P\text{-}BH_2$ a(^{11}B) = 17.6 at 183 K

- -



σ-type (pyramidal)



Higher energy level of π* ($\sigma^*_{N\text{-}H}$) orbital
& electron negativity N > H > P
→ Less stabilization effect
& strong distabilization by hyperconjugation
(plannar geometry → unfavorable)

Spin denisity by AIM … BH_2 0.898, NH_3 0.102 (more localized at B atom)
Cf. hyperfine splitting(G) … $Et_3N\text{-}BH_2$ a(^{11}B) = 47.5 at 193 K

Rablen, P. R. *J. Am. Chem. Soc*, **1997**, *119*, 8350.
Baban, J. A., & Roberts, B. P. *J. Chem. Soc, Perkin. Trans. 2,* **1984**, 10, 1717.

Reactivity of LBRs

Index of Radical Polarity

$$\omega = \frac{\chi^2}{2\eta} = \frac{1}{8}\frac{(I+A)^2}{(I-A)}$$

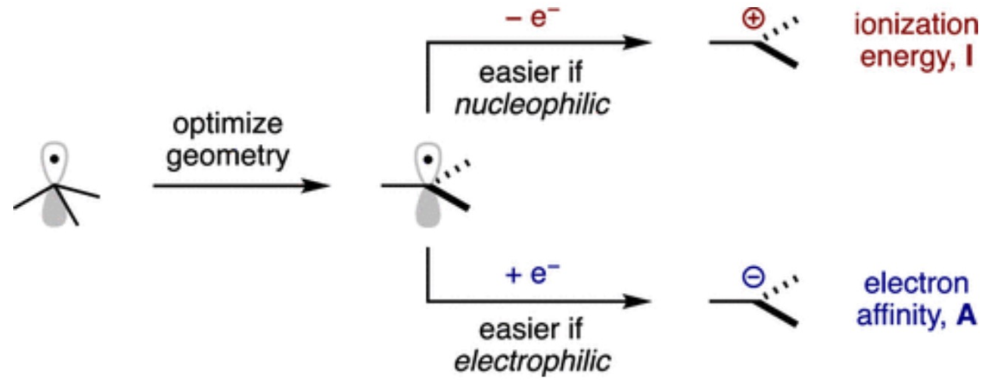
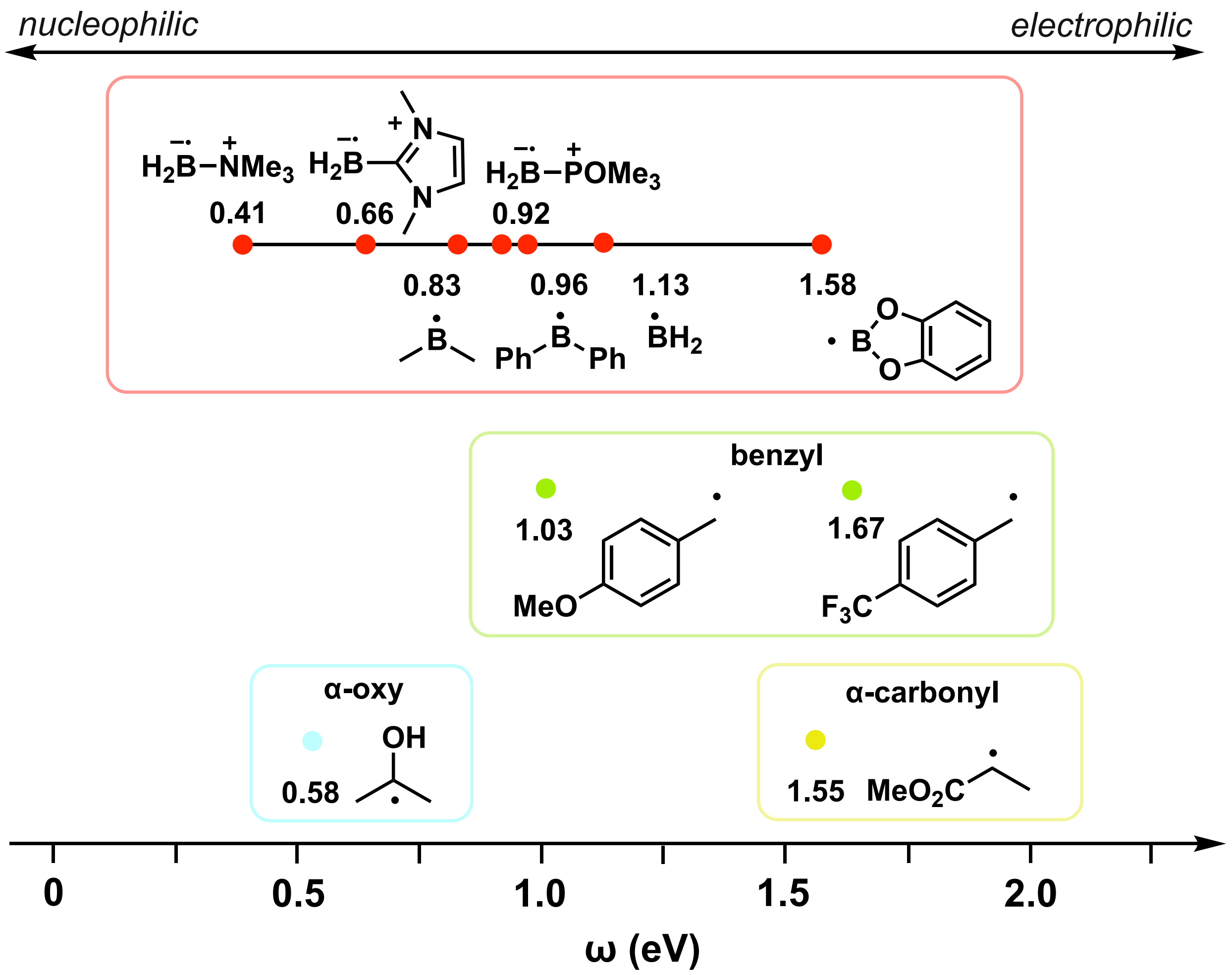


Figure 3. Computational workflow (B3LYP-D3/6-311 + G**).

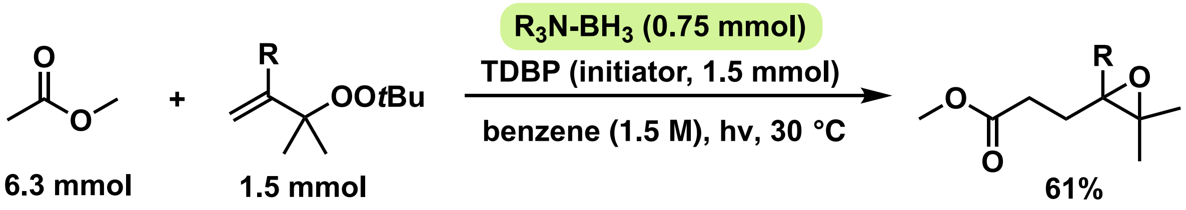


Nagib, D. A. *et al. J. Am. Chem. Soc*, **2024**, *146*, 28034.

Reaction Examples

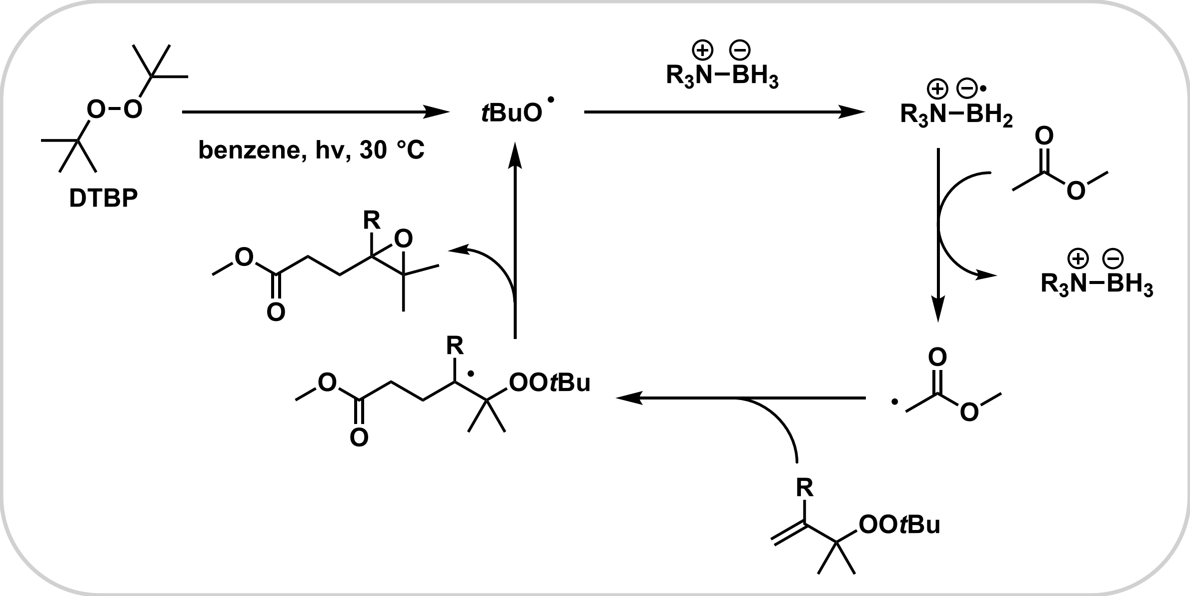
- Radical chain reactions

Ex1. HAT from α- position of carbonyls (Polarity reversal)

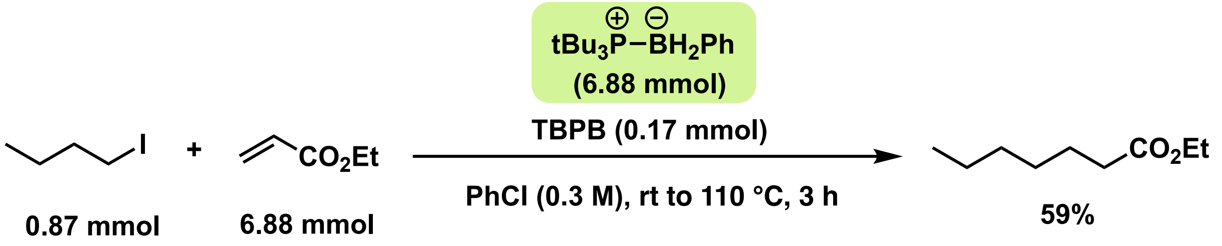


R_3N-BH_3 (0.75 mmol)
TDBP (initiator, 1.5 mmol)
benzene (1.5 M), hv, 30 °C

6.3 mmol
1.5 mmol
61%

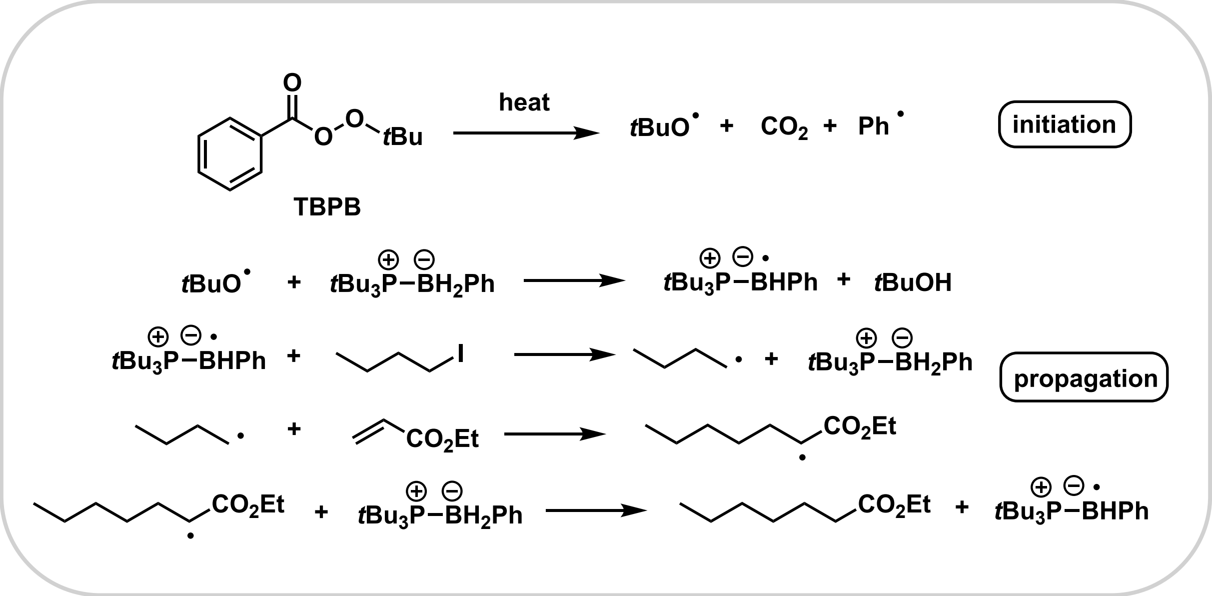


Ex2. XAT from R – X



$\overset{\oplus\ \ominus}{tBu_3P-BH_2Ph}$
(6.88 mmol)
TBPB (0.17 mmol)
PhCl (0.3 M), rt to 110 °C, 3 h

0.87 mmol
6.88 mmol
59%

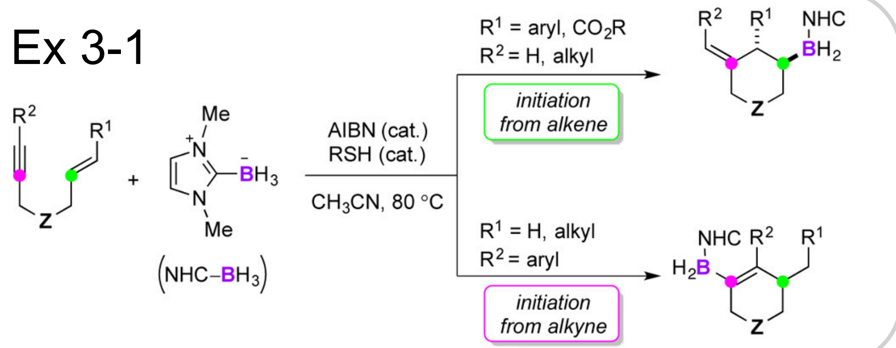


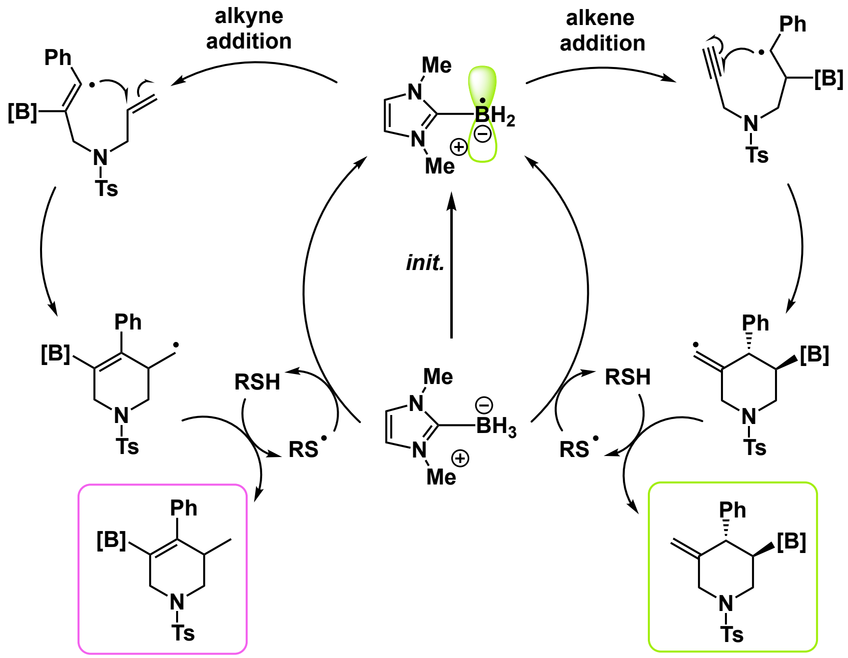
Roberts, B. P. *Chem. Soc. Rev*, **1999**, *28*, 25.
Dang, H. S., & Roberts, B. P. *J. Chem. Soc. Perkin Trans 1*, **1993**, 8, 891.
Baban, J. A., & Roberts, B. P. *J. Chem. Soc. Perkin Trans. 2*, **1988**, 7, 1195.

Reaction Examples

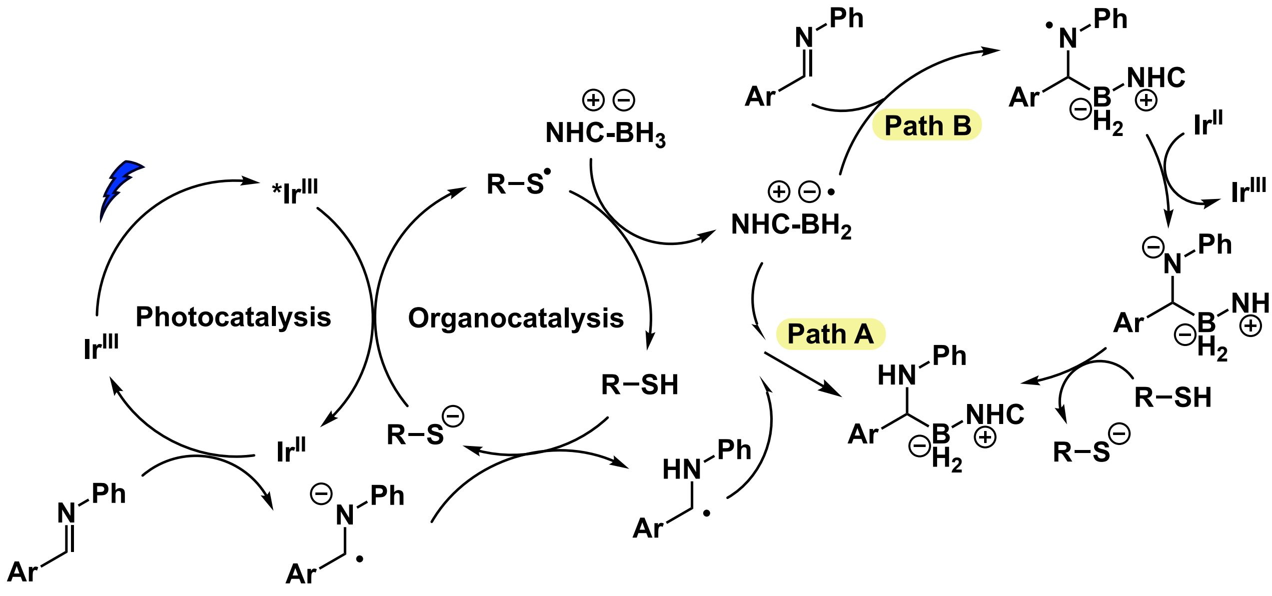
Ex 3. Radical addition

Ex 3-1



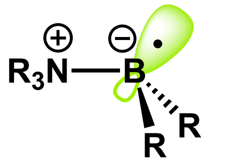
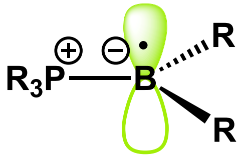
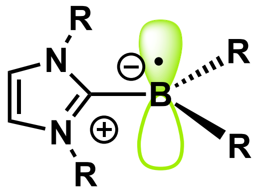
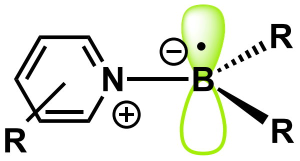


Ex 3-2 (Inverse Hydroboration)



Wang, Y. F. *et al. J. Am. Chem. Soc*, **2017**, *139*, 6050.
Zhu, C. *et al. Angew. Chem*, **2018**, *130*, 4054.

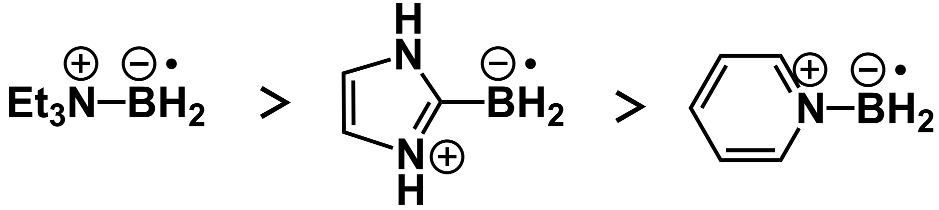
Summery of LBRs Reactivity (Synthetic Applications)

	HAT	XAT	Radical Addition
	✓	✓ Ex. Alkyl - Cl, Br, I Aryl - Br	✓ Ex. Michael acceptor imine, Het-Ar
	?	✓ Ex. Alkyl - Br, I	✓ Ex. Barton-MaCombie type deoxygenation
	? (weak BDE)	✓ Ex. Alkyl - F, Br, I Aryl - I	✓ Ex. Michael acceptor imine
	? (weak BDE)	✓ Ex. Ar-SO_2-F	✓ Ex. Carbonyls

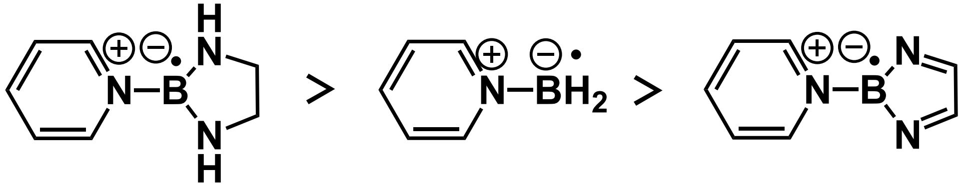
(New types of reactions are being found constantly.
This table is just a guide. There are some examples in Appendix.)

- Reactivity also changes depending on R. (Tunable by Lewis bases and substituents)

Ex1. effect of Lewis bases (Nucleophilicity)



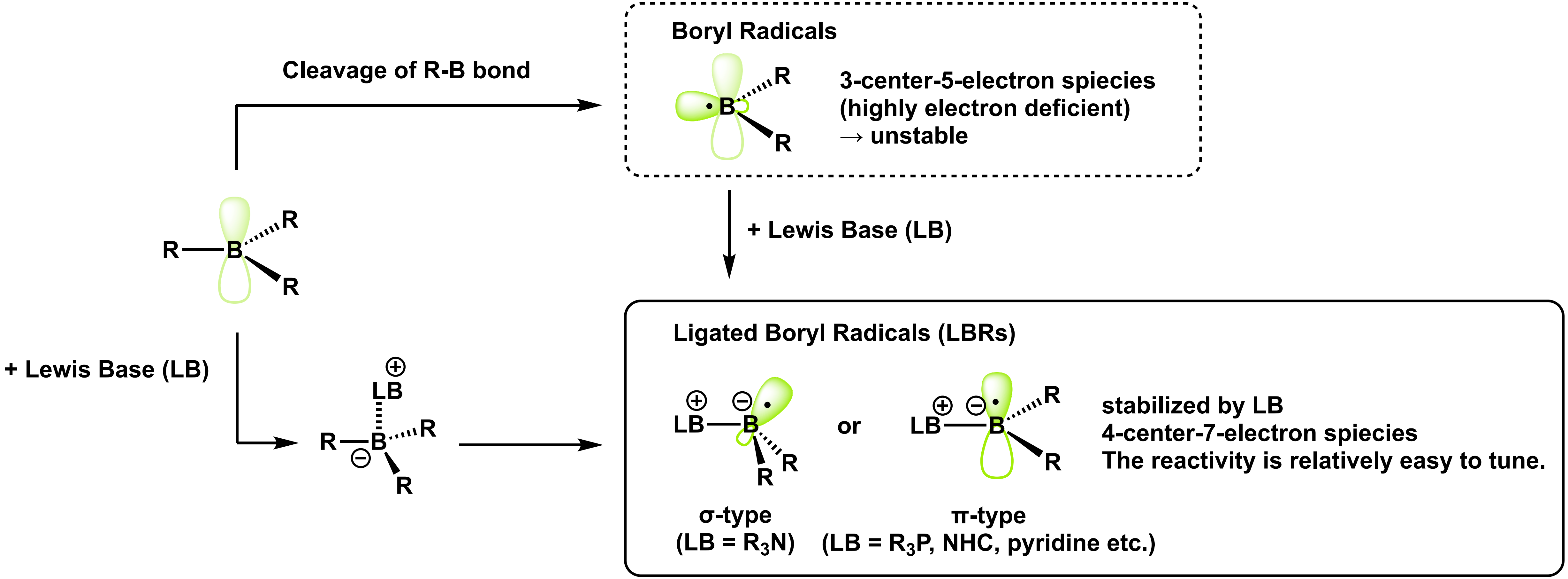
Ex2. effect of substituents (Nucleophilicity)



- Steric effects also exist.

Lu, D. *et al. J. Org. Chem*, **2017**, *82*, 2898.

Short Summary



Cleavage of R-B bond

Boryl Radicals

3-center-5-electron spiecies
(highly electron deficient)
→ unstable

+ Lewis Base (LB)

+ Lewis Base (LB)

Ligated Boryl Radicals (LBRs)

σ-type
(LB = R_3N)

π-type
(LB = R_3P, NHC, pyridine etc.)

stabilized by LB
4-center-7-electron spiecies
The reactivity is relatively easy to tune.

Ravelli, D. *et al*. *Chem Catalysis*, **2022**, *2*, 957
Lu, D. *et al. J. Org. Chem*, **2017**, *82*, 2898.

Contents

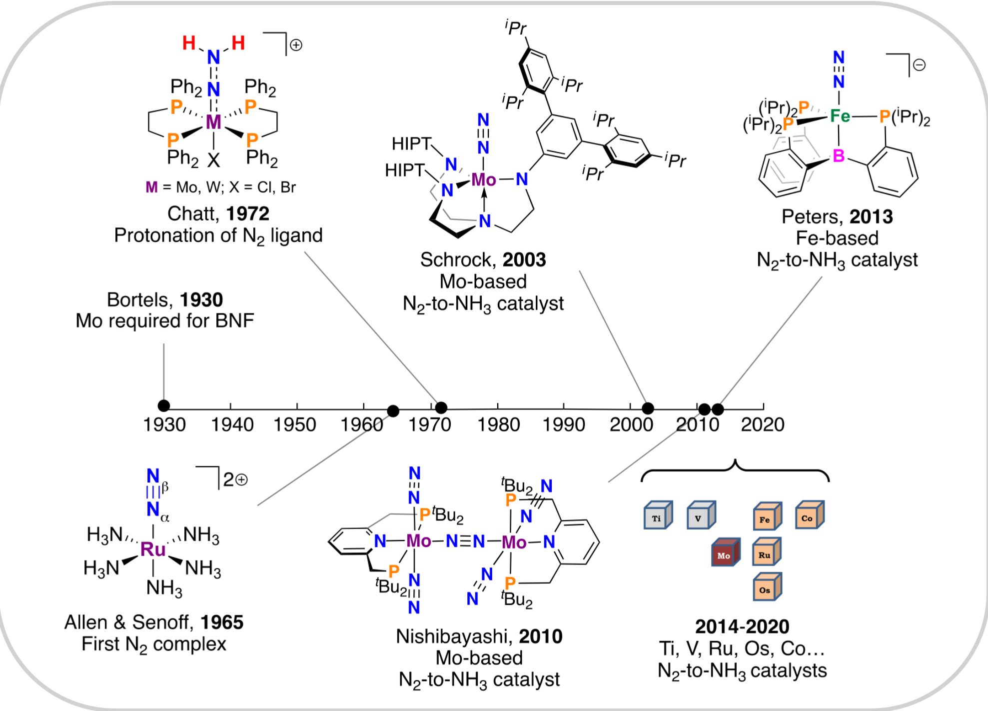
Ammonia Synthesis (N_2 Fixation)

- Harber – Bosch process

High temperature & High pressure
1.4% of the world's CO_2 emissions

$$N_2 + 3H_2 \xrightarrow[\text{400-500 °C, 150-250 bar}]{\text{Metal cat.}} 2NH_3$$

- Transition metal approach



Chatt, **1972**
Protonation of N_2 ligand

Schrock, **2003**
Mo-based
N_2-to-NH_3 catalyst

Peters, **2013**
Fe-based
N_2-to-NH_3 catalyst

Bortels, **1930**
Mo required for BNF

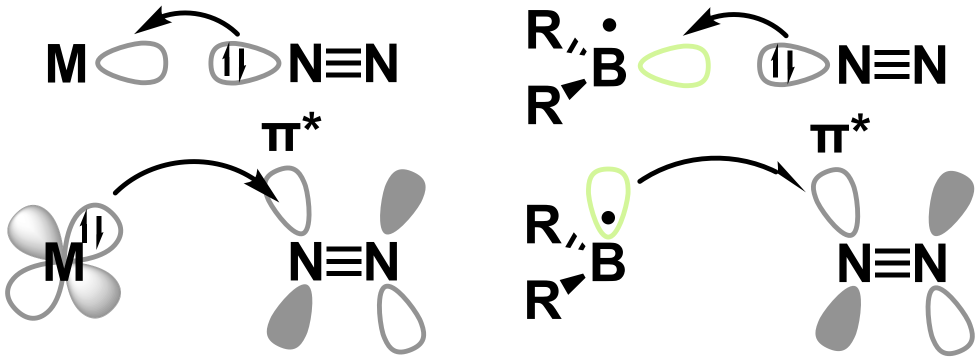
Allen & Senoff, **1965**
First N_2 complex

Nishibayashi, **2010**
Mo-based
N_2-to-NH_3 catalyst

2014-2020
Ti, V, Ru, Os, Co…
N_2-to-NH_3 catalysts

- This work

High energy boryl radical can mimic transition metals?

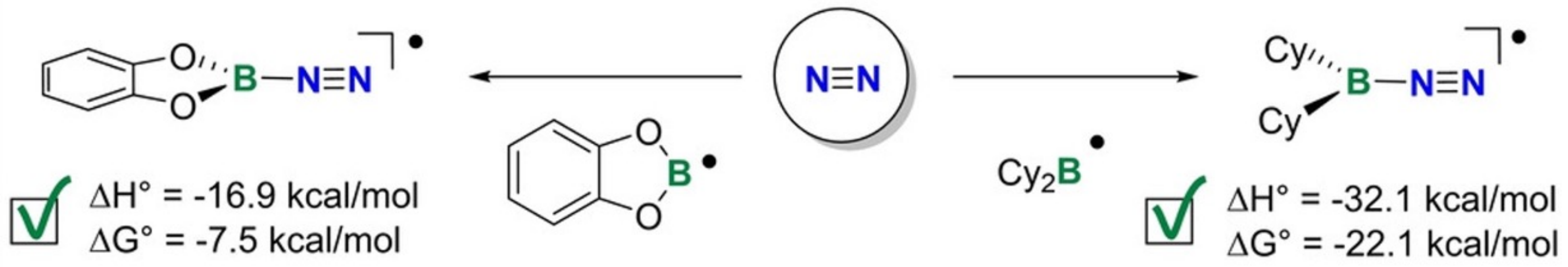


(weaken the strong N≡N bond by back donation?)

Mézailles, N. *et al. Angew. Chem. Int. Ed*, **2023**, *62*, e202209102.
Peters, J. C. *et al. Chem. Rev.* **2020**, 120, 5582.

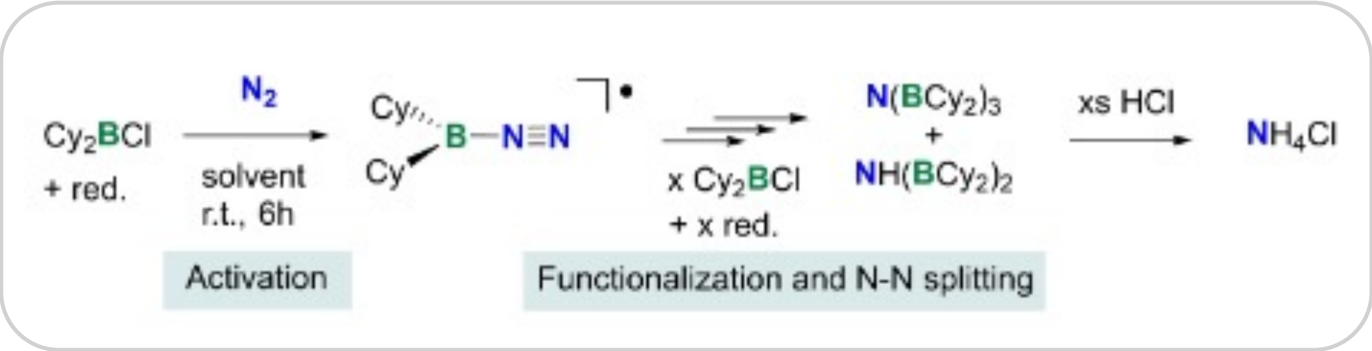
Predictive DFT and Selection of B Radical Source

- DFT calculation



DFT → B radicals are promising candidates for N_2 activation.

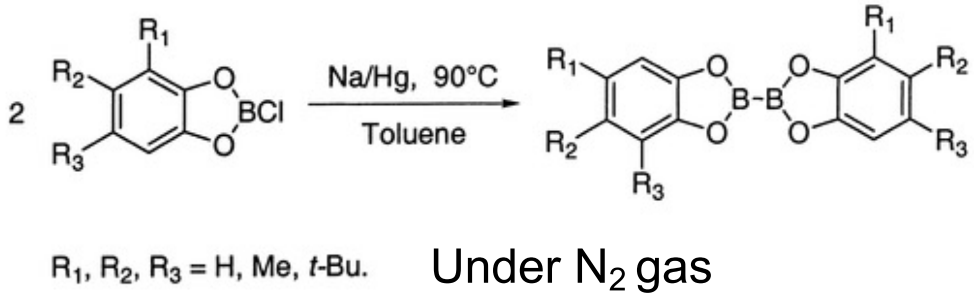
- They chose **R_2B-Cl + reductant** for generating corresponding boryl radicals.



Consideration
- B radicals are highly unstable.
- B-B bond formation is favorable especially when B substituents have donor atom.

→ They decided to use **Cy_2B-Cl** as precursor.

Cf.



Under N_2 gas

Mézailles, N. *et al*. *Angew. Chem. Int. Ed*, **2023**, *62*, e202209102.
Hartwig, J. F. *et al*. *Organometallics*, **2003**, *22*, 365.

Optimization

$$Cy_2B\text{-}Cl \xrightarrow[N_2\text{, rt, 6 h}]{\text{Reducing reagent}} \xrightarrow{\text{excess HCl}} NH_4Cl$$

Entry	$[R_2B\text{-}Cl]$ (mol/L)	Solvent	Reducing agent	Stoich. Red	PN_2 (bar)	Yield
1	0.04	THF	K	1, 2.5	1	7, 41
2	0.04	MeTHF, Pentane, Toluene, Et_2O, Dioxane	K	2.5 or 3.3	1	0 (dioxane → Trace)
3	0.04	THF	Na, Na/Hg, Na/naphtalene, KC_8, SmI_2	2.5	1	0
4[a]	0.04	THF	K	2.5	1	56
5	0.04	THF	K	2.5	20, 40, 80	60, 76, 94
6[b]	0.08	THF	K	2.5	1	38
7[c]	0.04	THF	K	2.5	1	0
8 CatB-Cl	0.04	THF	K	2.5	1	0

a … K was cut into 5 pieces.
b … 100 times scale
c … 60 °C or -70 °C

- THF was the best.
- Reducing reagents other than K failed while B-H bond formation was observed.
- 2.5 eq of K was needed.
- High N_2 pressure improved yield.
- Alkyl substituents → subsequent study

* Yields were calculated by $3 \times (NH_4^+)/Cy_2BCl \times 100$.

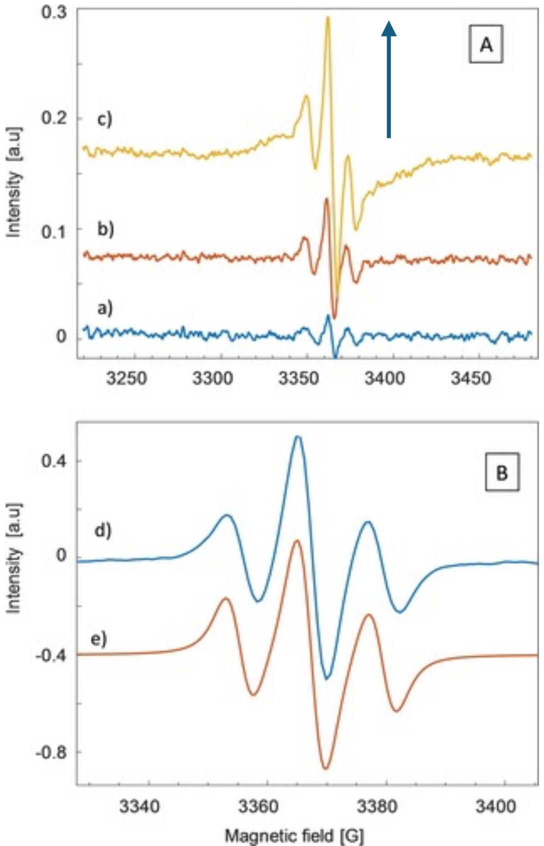
Mézailles, N. *et al*. *Angew. Chem. Int. Ed*, **2023**, *62*, e202209102.
Hartwig, J. F. *et al*. *Organometallics*, **2003**, *22*, 365

NMR analysis and EPR Monitoring

- NMR analysis (prior to hydrolysis)

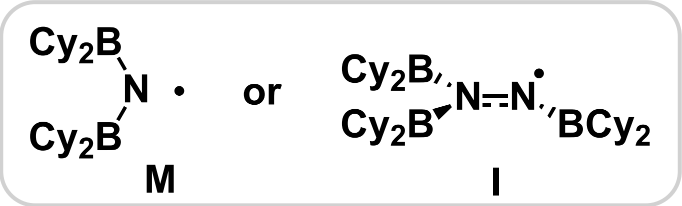
① ^{11}B NMR → Side products ($Cy_2BH_2^-$ and Cy_2BH) could be observed.
(Cf. B-N bond containing species were not observed. Due to peak broadening by B-N coupling ?)

② ^{1}H, ^{15}N, ^{15}N-^{1}H HMBC → $NH(BCy_2)_2$ was observed. $N(BCy_2)_3$ was not detected. Considering NH_4Cl yield, $NH(BCy_2)_2 : N(BCy_2)_3 = 7:93$.



- EPR analysis

At least 2 kinds of radicals were detected.



① Triplet (1:1:1) at g = 2.0036
→ ^{14}N (I = 1) - centered radical. $a_N = 11.8$ G and unresolved interaction(< 1 G) with surrounding H atoms.

② Singlet at g = 2.0034
→ C or B (^{11}B I = 3/2 or ^{10}B I = 5/2) centered radical (hypothetical) with unresolved hyperfine constant. (Cf. This peak was also detected under Ar atmosphere.)

Mézailles, N. *et al*. *Angew. Chem. Int. Ed*, **2023**, *62*, e202209102.

DFT Calculations

Lowest energy pathway leading to $N(BCy_2)_3$

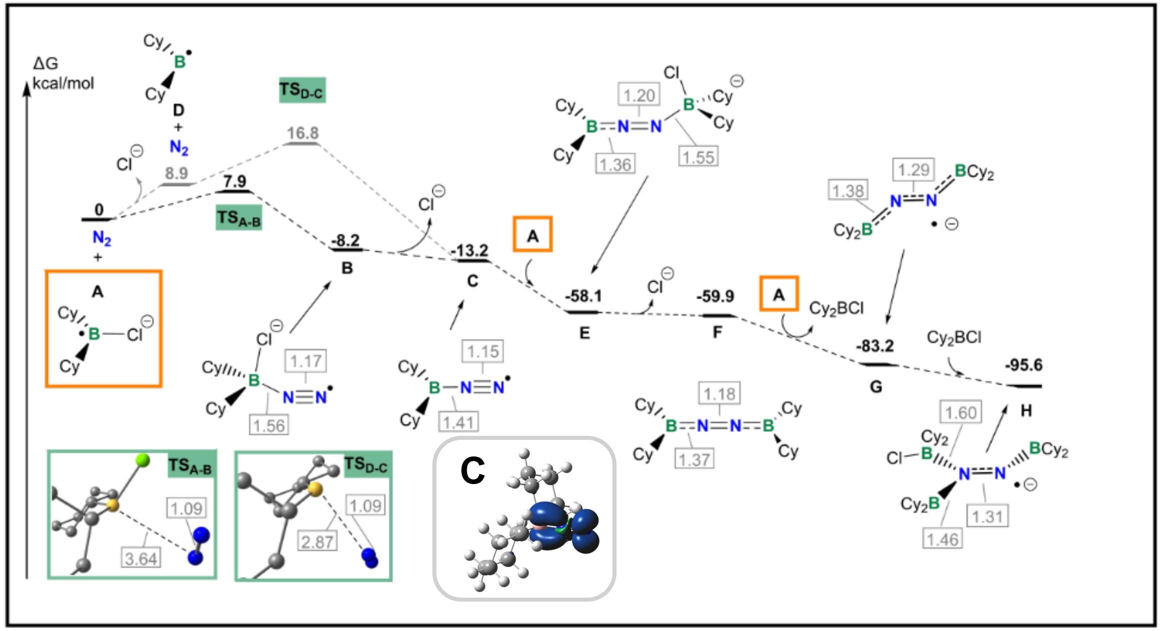


Figure 3. Computed pathway: the energies are relative to "6 A + N_2". Addition of **A** ($Cy_2BCl^{•-}$) to N_2 up to the formation of three N–B bonds (compound **H**, three-electron reduction of N_2). Note that the energy positioning of the various species does not take into account any potential stabilizing interactions developing between K^+ and Cl^- in the experimental situation.

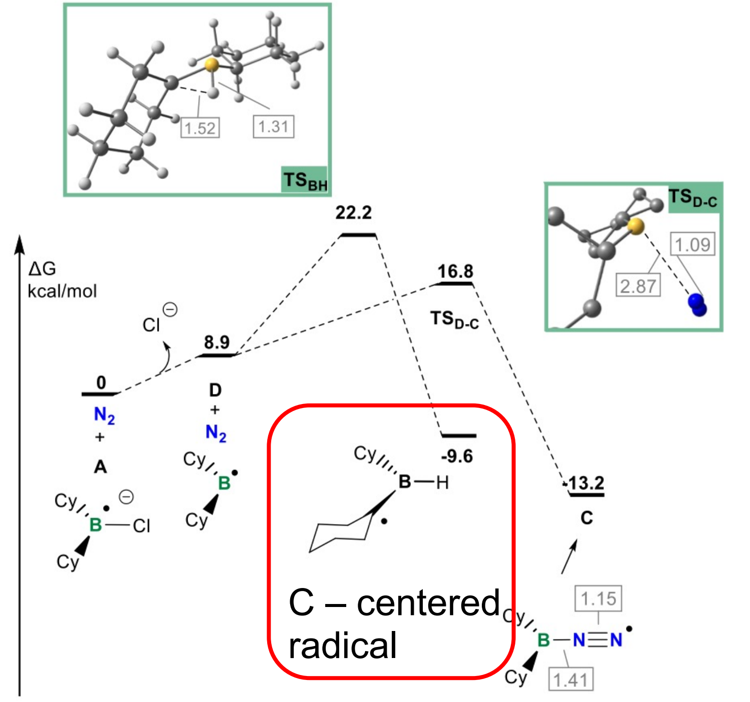
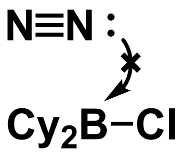


Figure S33. Comparison between the calculated pathways for N_2 coordination to $Cy_2B^•$ and intramolecular HAT between the ipso-carbon and boron.

- Boryl radical generating pathway is reasonable.
- Radical anion B indicates boryl radical weakens N-N bond. (1.097Å→ 1.174Å)
- **C** was kinetically and thermodynamically preferred.

But C - centered radical is lower energy than **B.** Kinetic control is important.

Cf.



Mézailles, N. *et al*. *Angew. Chem. Int. Ed*, **2023**, *62*, e202209102.

DFT Calculations

Lowest energy pathway leading to $N(BCy_2)_3$

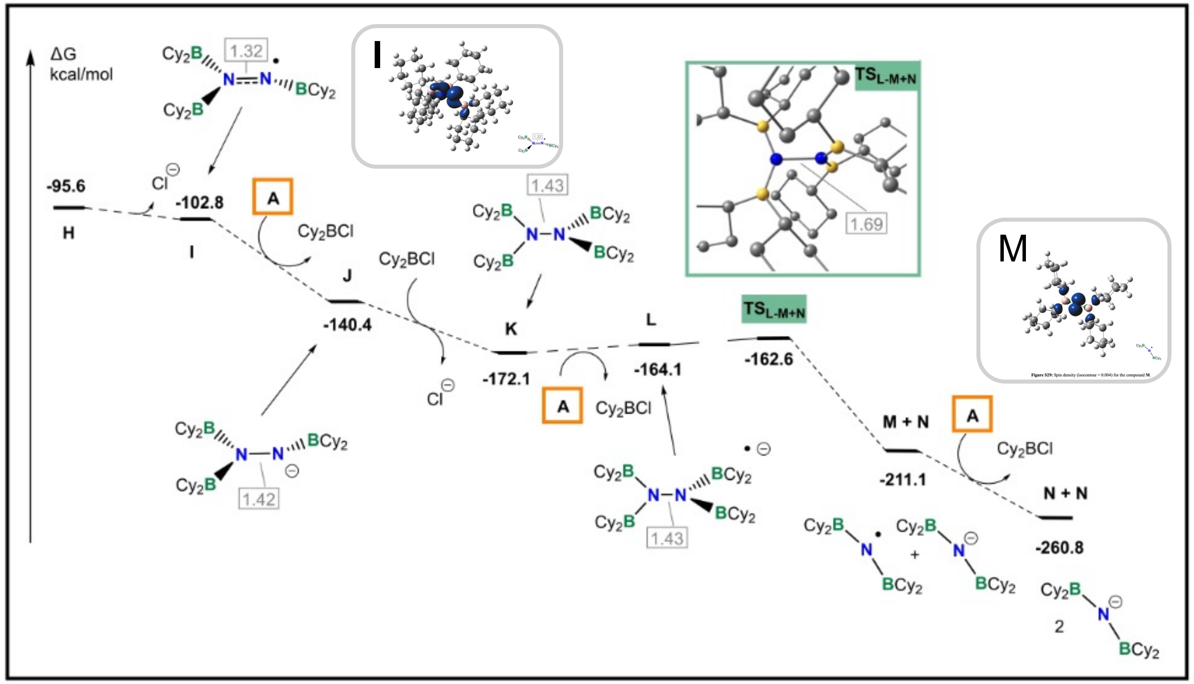


Figure 4. Computed pathway: the energies are relative to “6 A + N_2”. Functionalization to the hydrazine $(Cy_2B)_2NN(BCy_2)_2$ derivative (**K**) followed by reductive NN bond splitting process leading to bis-borylamide **N**.

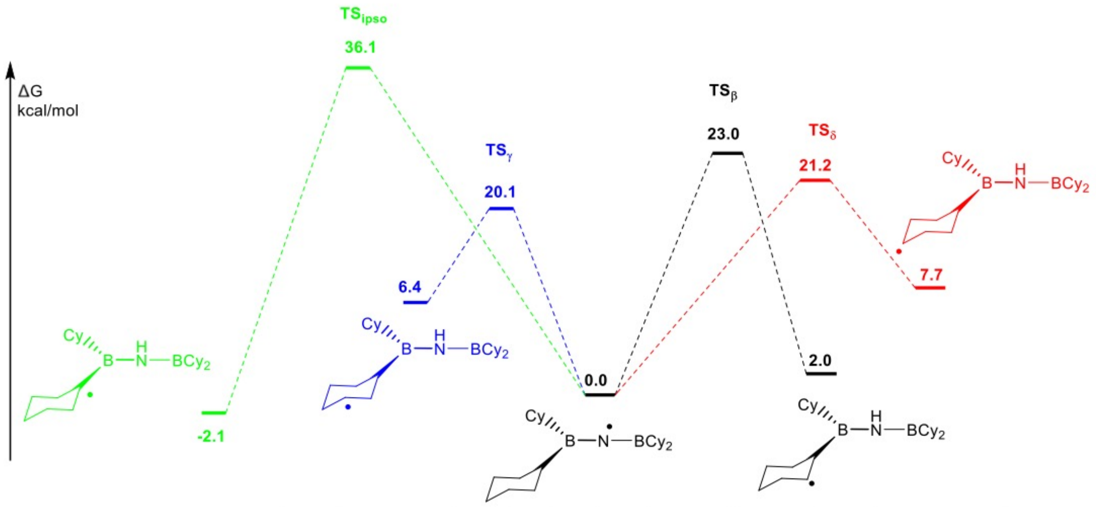
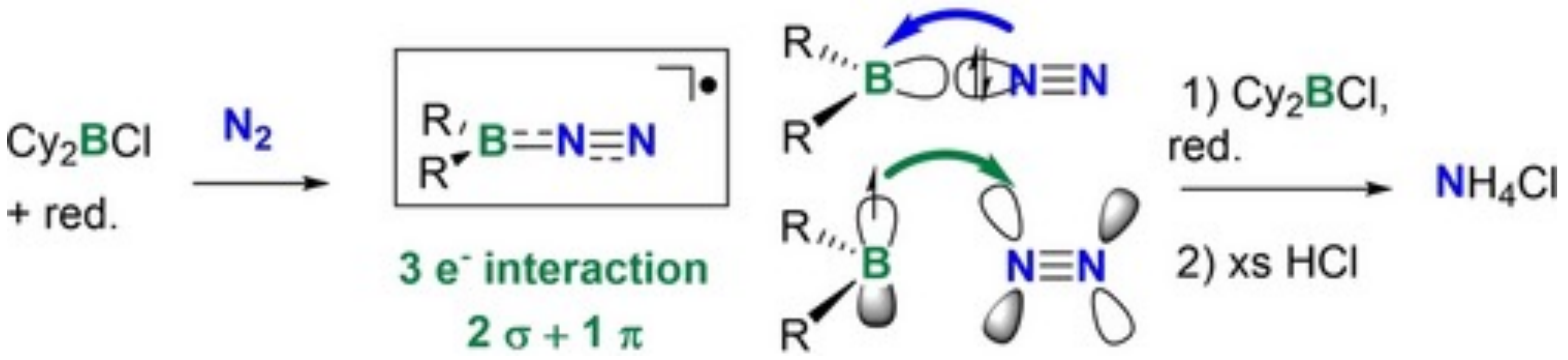


Figure S34. Comparison between the calculated pathways for H migration (HAT) from radical **M** $(Cy_2B)_2N^{\cdot}$ to C centered radicals rationalizing the formation of $(Cy_2B)_2NH$.

- N-N bond (46.1 kcal/mol) cleavage → endoergic (8.0 kcal/mol)
- M+N → N+N strongly exoergic (- 49.7 kcal/mol)
- N-H product might be formed by HAT from solvent.

Mézailles, N. *et al*. *Angew. Chem. Int. Ed*, **2023**, *62*, e202209102.

Short Summery



A new strategy for N_2 fixation utilizing boryl radical was developed.

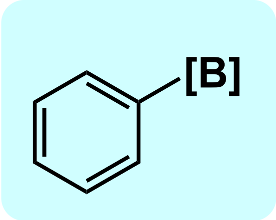
○ At room temperature (& at atmospheric pressure)
○ No use of transition metals

△ Scalability (0.16 mmol scale reaction.)
△ Not catalytic, use of strong reducing agent

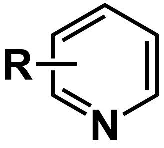
Mézailles, N. *et al*. *Angew. Chem. Int. Ed*, **2023**, *62*, e202209102.

Contents

Synthesis of Boryl Aromatics



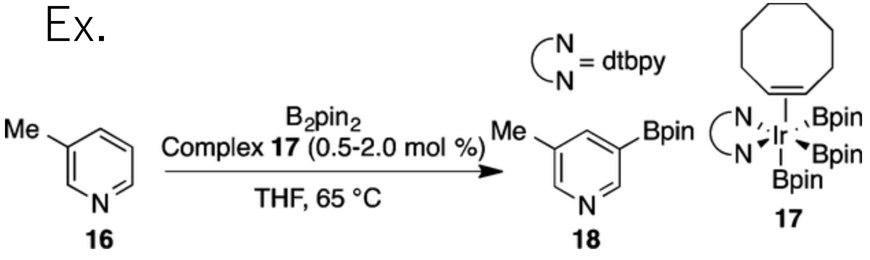
Borylayted aromatics are used for many kinds of reactions.
And this is synthesized by ① borylation of Ar – X and ② **C-H activation**



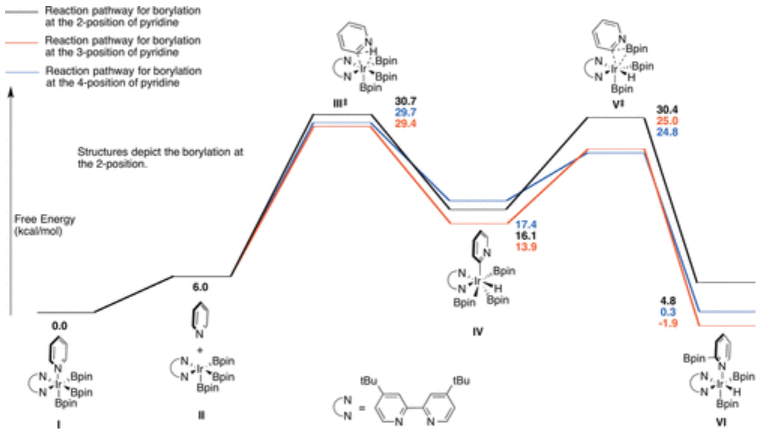
Azines

Borylation of azines via C-H activation → functionalize distal from nitrogen atoms

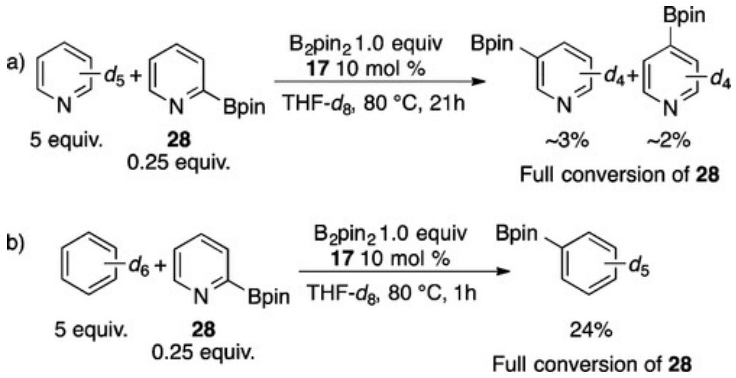
Ex.



① High activation barrier



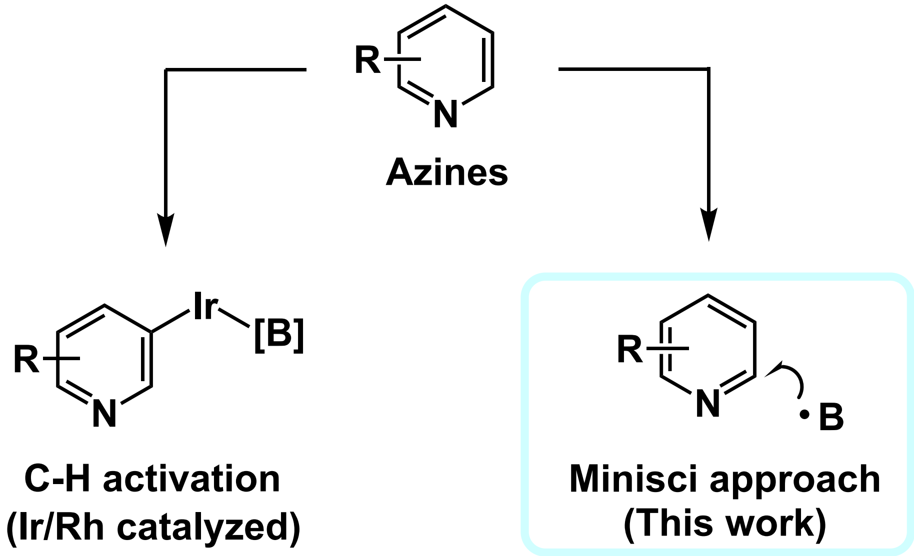
② Instability



Larsen, M. A., & Hartwig, J. F. *J. Am. Chem. Soc*, **2014,** *136*, 4287.

Minisci Reaction by Amine - Boryl Radical

- **Direct azine borylation**



Azines

C-H activation (Ir/Rh catalyzed)

Minisci approach (This work)

Orthogonal reactivity can be realized?

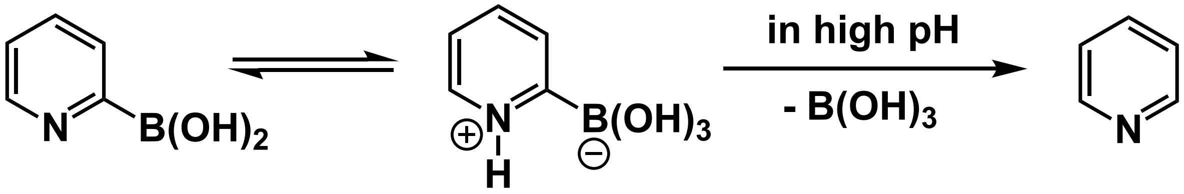
- **Minisci approach by boryl radical.**

This approach needs
① Stability of borylating reagent
② Boryl radical with nucleophilicity
③ Borylated product is stable while amenable to further functionalization.

They chose amine - boryl radical.

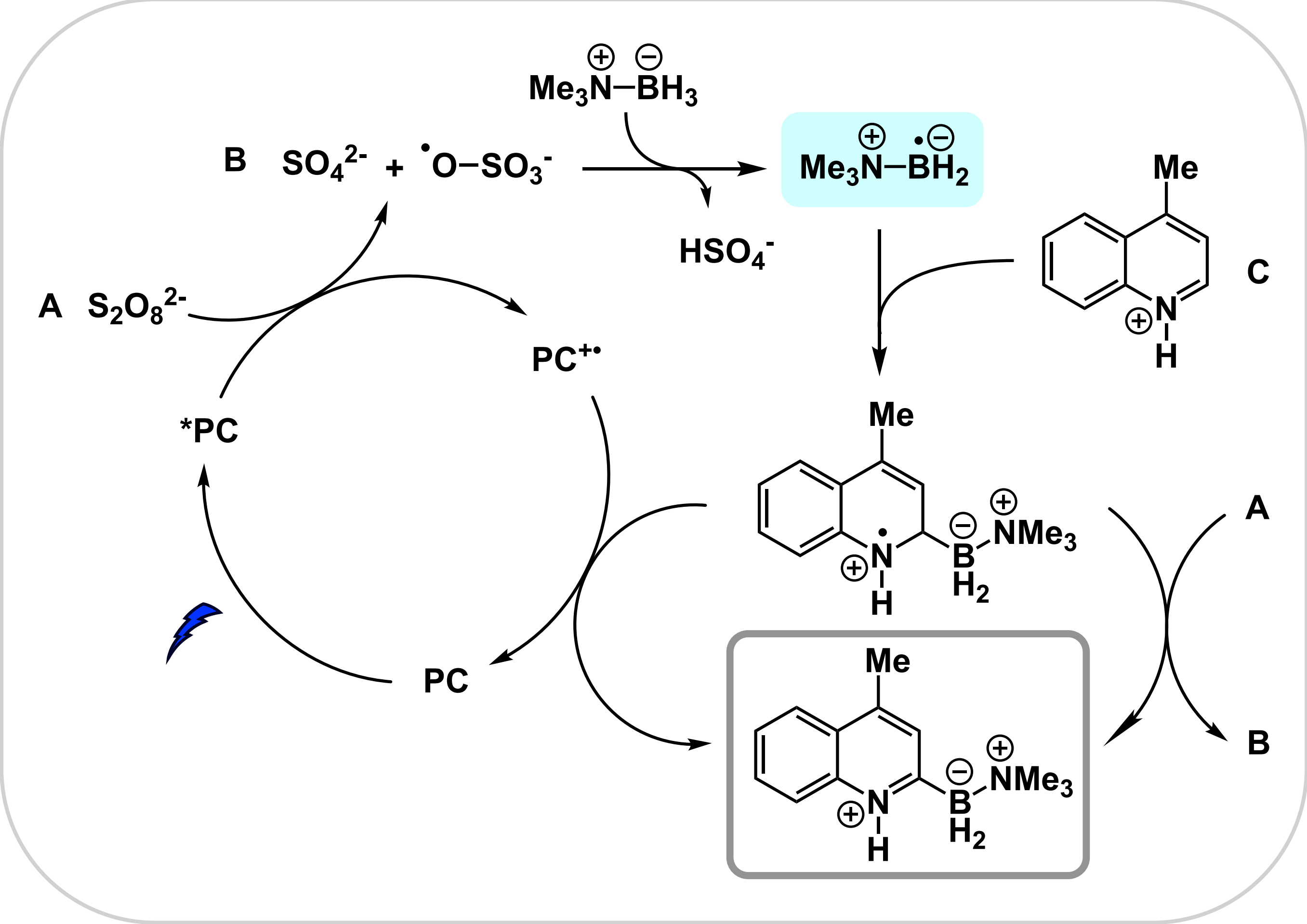
① **Highly nucleophilic** ② Stable ③ Inexpensive

Cf.



Leonori, D. *et al. Nature*, **2021**, *595*, 677.
Larsen, M. A., & Hartwig, J. F. *J. Am. Chem. Soc*, **2014,** *136*, 4287.
Willis, M. C. *et al. Angew. Chem*, **2021**, *133*, 11168.

Reaction Design

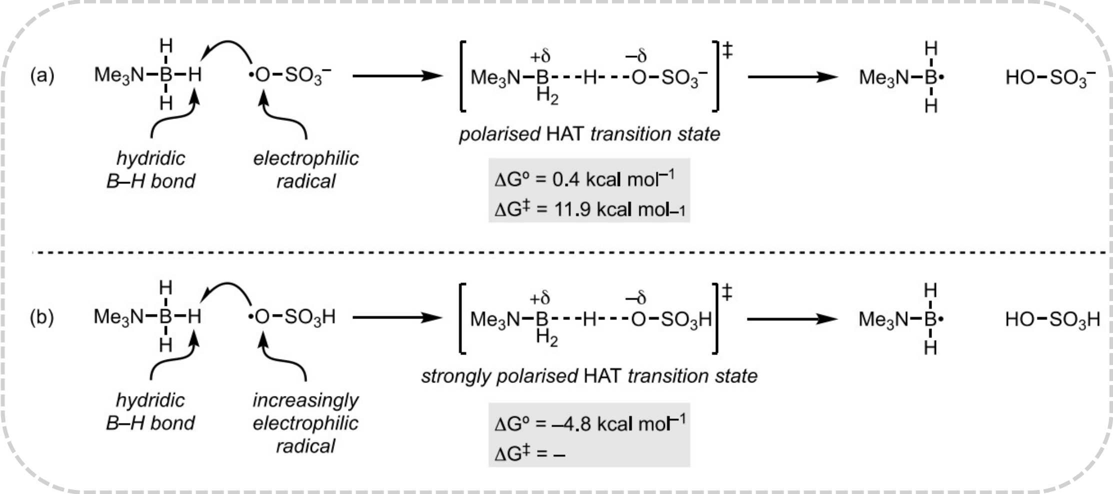


- HAT by electrophilic radical
- Brønsted acid is required.

① Facilitate the SET reduction of **A**

$(NH_4)_2S_2O_8$ … $E_{1/2}^{red}$ = -2.85 V vs SCE
$(NH_4)_2S_2O_8$ +TFA … $E_{1/2}^{red}$ = -1.29 V vs SCE

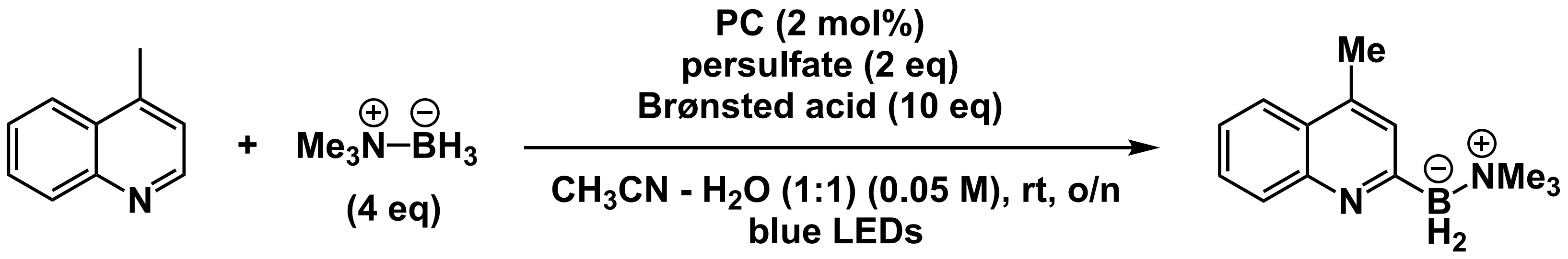
② Amplify the electrophilic character of **B**



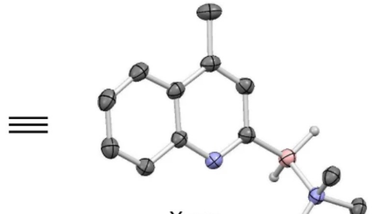
③ Activation of azines **C** by protonation
& prevent undesired HAT from product

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

Optimization



Crystalline and stable solid

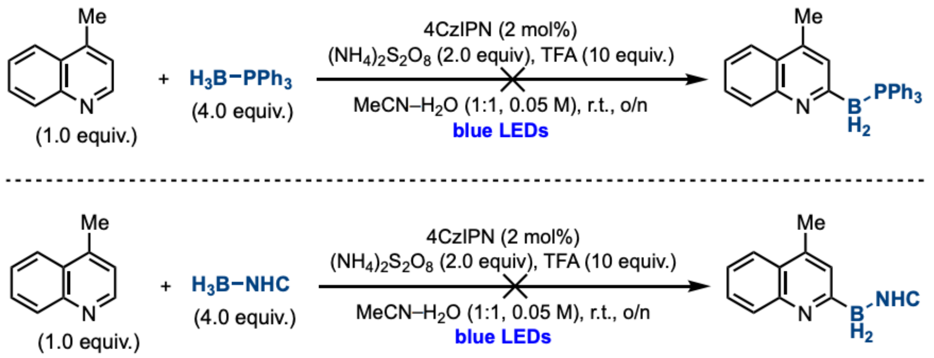


X-ray structure

Entry	PC	Persulfate	Brønsted acid	Yield
1	–	$K_2S_2O_8$	TFA	45
2	4CzIPN	$K_2S_2O_8$	TFA	74
3	$[Ir(ppy)_2(dtbbpy)]PF_6$	$K_2S_2O_8$	TFA	61
4	*fac*-$Ir(ppy)_3$	$K_2S_2O_8$	TFA	62
5	$Ru(bpy)_3(PF_6)_2$	$K_2S_2O_8$	TFA	60
6	Mes-Acr(ClO_4)	$K_2S_2O_8$	TFA	54
7	4CzIPN	$(NH_4)_2S_2O_8$	TFA	88
8	4CzIPN	$(NH_4)_2S_2O_8$	AcOH	78

- Without PC, reaction proceeded. But this condition cannot be improved and be applied to most of the substrates.

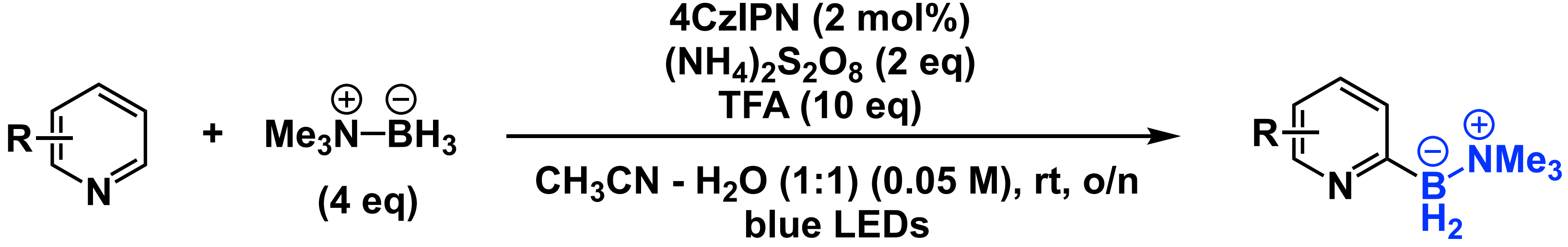
- Amine – borane was the best boryl radical source.



Scheme S1.

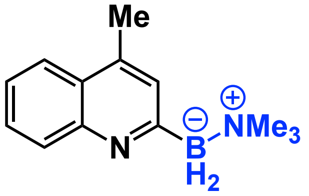
Leonori, D. *et al. Nature*, **2021**, *595*, 677.

Substrates Scope

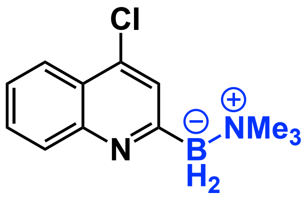


4CzIPN (2 mol%)
$(NH_4)_2S_2O_8$ (2 eq)
TFA (10 eq)

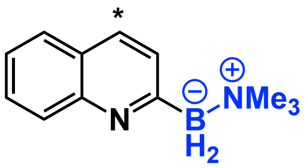
$CH_3CN - H_2O$ (1:1) (0.05 M), rt, o/n
blue LEDs



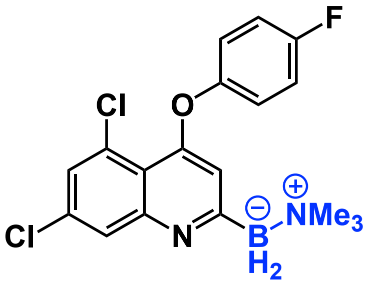
88%
(Gram-scale)



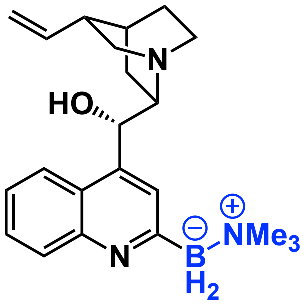
50%
$K_2S_2O_8$ was used.



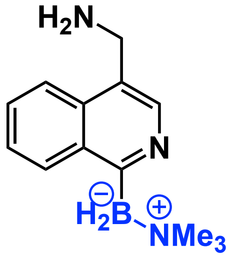
63% (3:1)



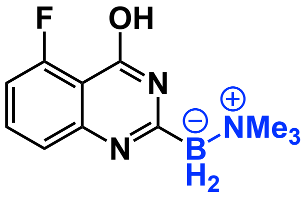
Quinoxyfen
44%
$K_2S_2O_8$ was used.



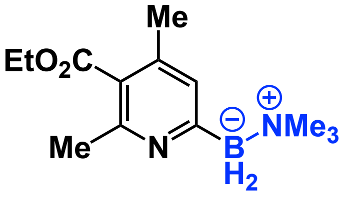
Cinchonidine
35% (Gram scale)
$Ru(bpy)_3PF_6$ was used.



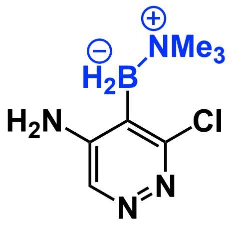
67%



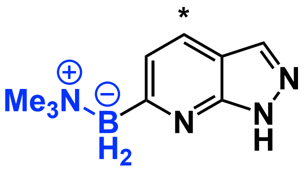
91%



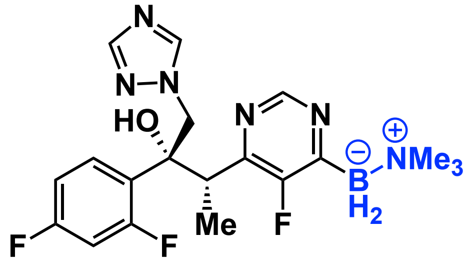
63%



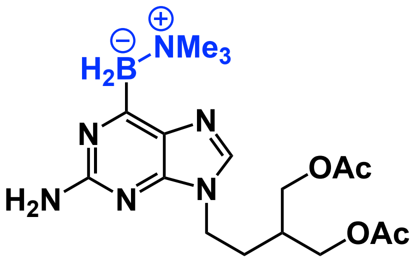
31%



61% (1.7:1)
$(n\text{-}Bu_4N)_2S_2O_8$ was used.



Voriconazole
46% (Gram scale)
AcOH and $Ru(bpy)_3PF_6$ were used.



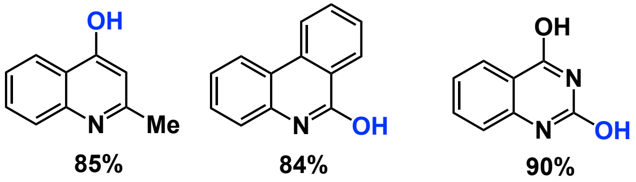
Famciclovir
51%
AcOH was used.

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

Synthetic Applications

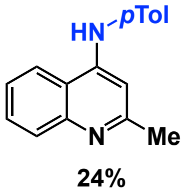
Oxidation to phenol

Oxone (8 eq)
THF - H_2SO_4 (1:3) (0.025 M)
40 °C, air, o/n



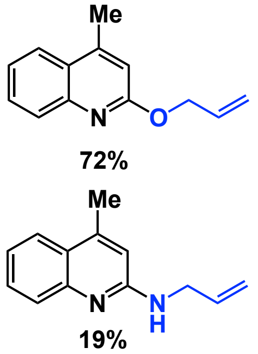
Chan-Lam amination

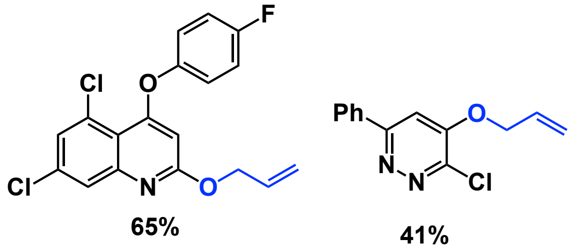
Amine (4 eq)
Cu(OAc) (1 eq) , Et_3N (10.0 eq)
4 Å MS, O_2, DCM (0.05 M), 50 °C, o/n



Chan-Lam etherification

Cu(OAc) (1 eq) , 4 Å MS, air,
allyl - OH or allyl amine (solv. 0.05 M), 55 °C, o/n

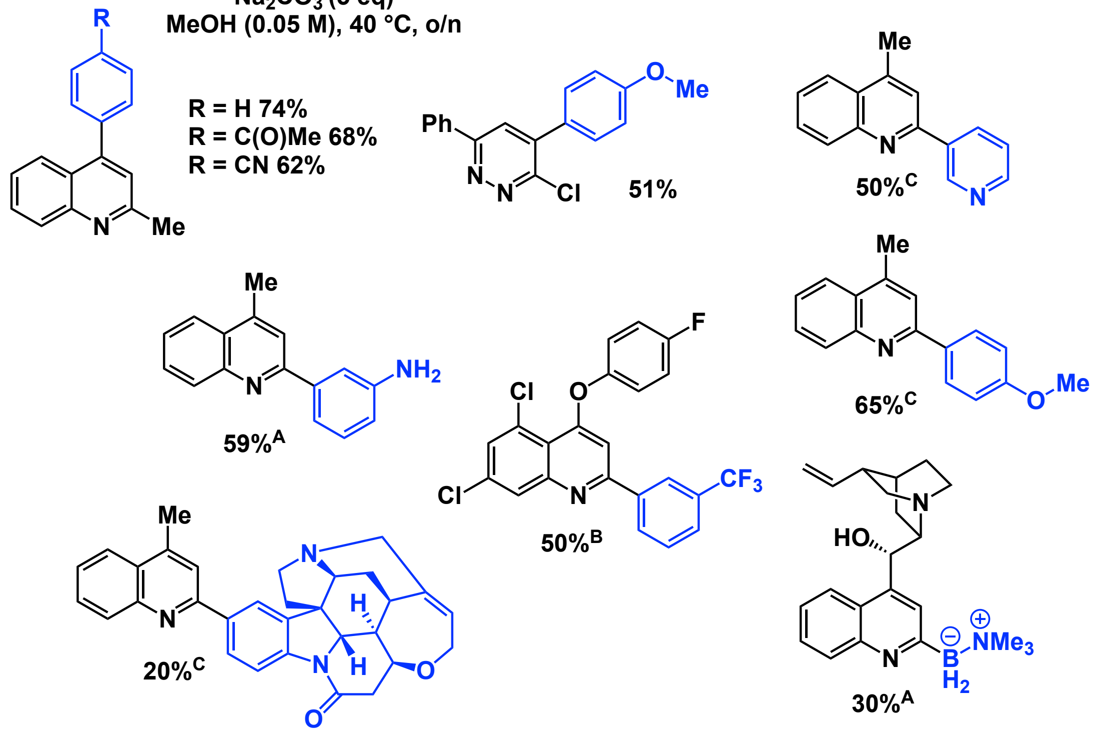




Suzuki-Miyaura cross-coupling

Ar-I (2 eq)
Pd(dppf)Cl_2 (10 mol%)
Na_2CO_3 (5 eq)
MeOH (0.05 M), 40 °C, o/n

Cf. Amine … High RSE p. 41



R = H 74%
R = C(O)Me 68%
R = CN 62%

For α - N - borylated azines

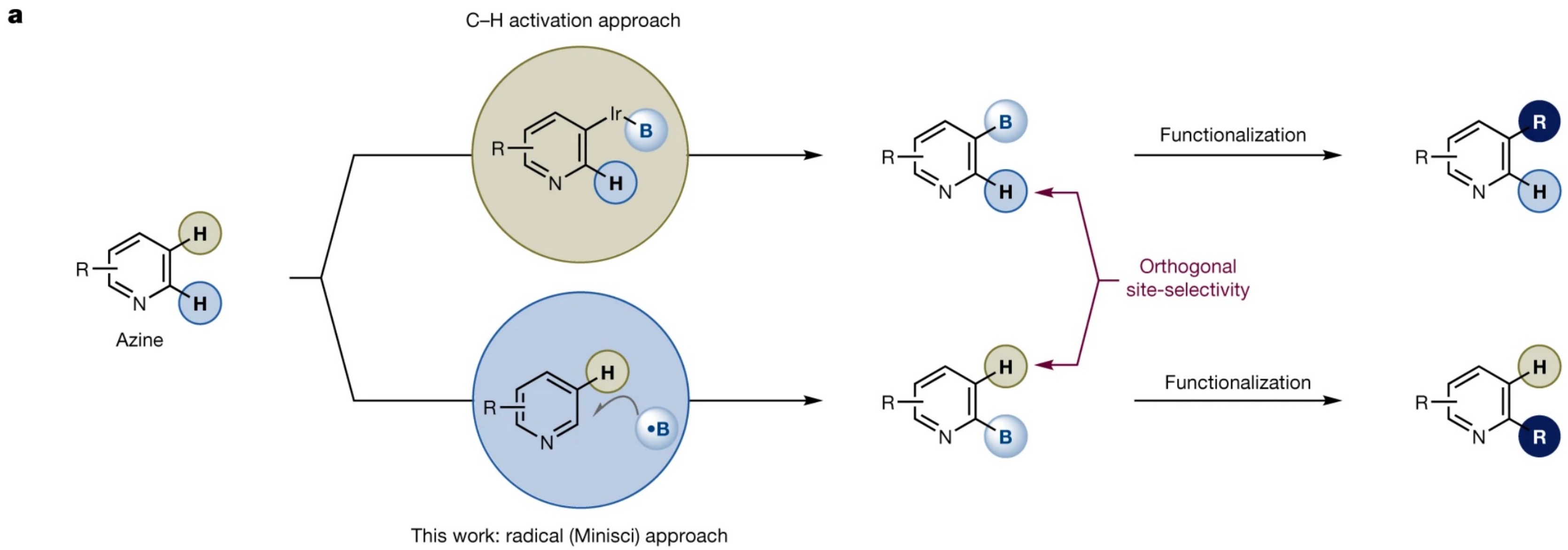
A
Ar-Br (4 eq)
Pd(dppf)Cl_2 (10 mol%)
NaOH (6 eq, 10 M in H_2O)
EtOH (0.05 M), 45 °C, 16 h

B
Ar-Br (2 eq)
$Pd_2(dba)_3Cl_2$ (2.5 mol%)
dpp-pent (5 mol%), LiOH (5 eq)
THF-H_2O (5.5:1, 0.05 M), 55 °C, 18 h

C
Ar-Br/I (2 eq)
$Pd_2(dba)_3$ (2.5 mol%)
XPhos (12 mol%), LiOH (5 eq)
THF-H_2O (5.5:1, 0.05 M), 55 °C, 24 h

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

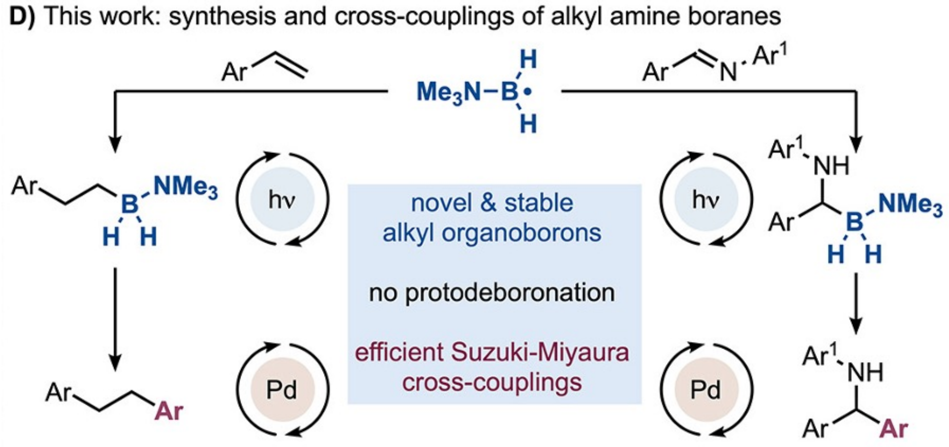
Short Summery



- By utilizing amine - boryl radical, Minisci reactivity was realized.

○ Gram scale
○ Further functionalization

Cf



← Michael acceptors, imines

Leonori, D. *et al. Nature*, **2021**, *595*, 677.
Leonori, D. *et al. J. Am. Chem. Soc*, **2024**, *146*, 24042.

Contents

1. Introduction

2. Ammonia synthesis at RT by Boryl radical

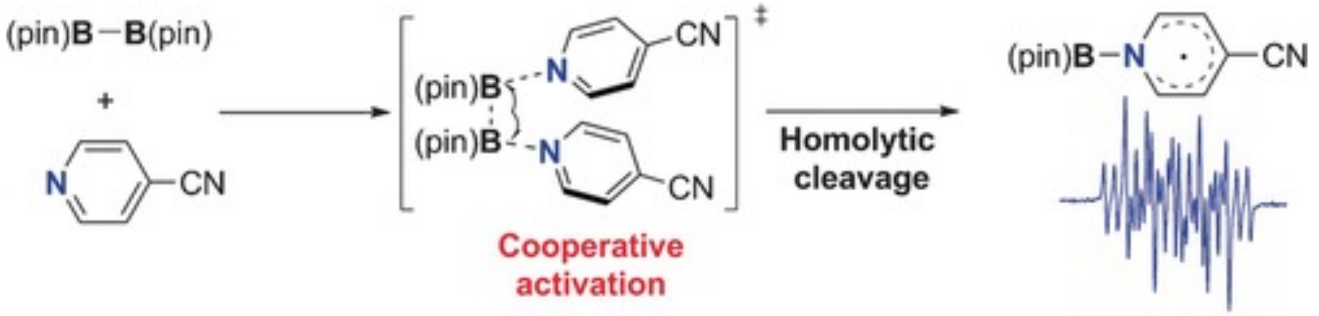
3. Radical addition of amine – boryl radical

4. **Utilizing pyridine – boryl radical for construction of bicyclic ring**

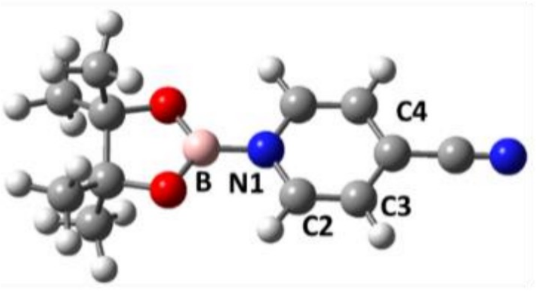
5. Summary

Pyridine – Boryl Radical

- Generated by B-B cleavage by pyridine derivatives



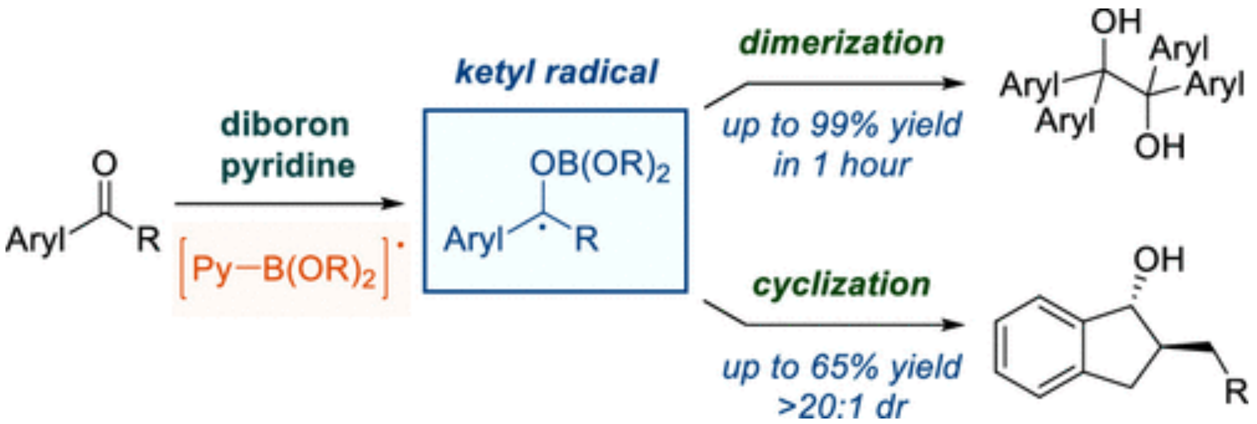
High spin density at C4 atom



1

	Spin density
B	**0.048**
N1	0.139
C2	0.218
C3	-0.084
C4	**0.448**

- Ketyl radical formation by pyridine – boryl radical

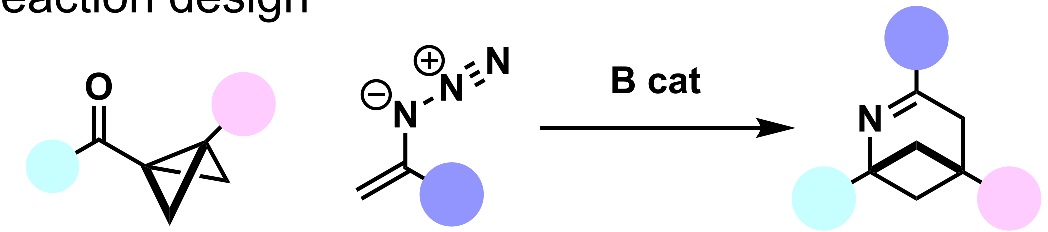


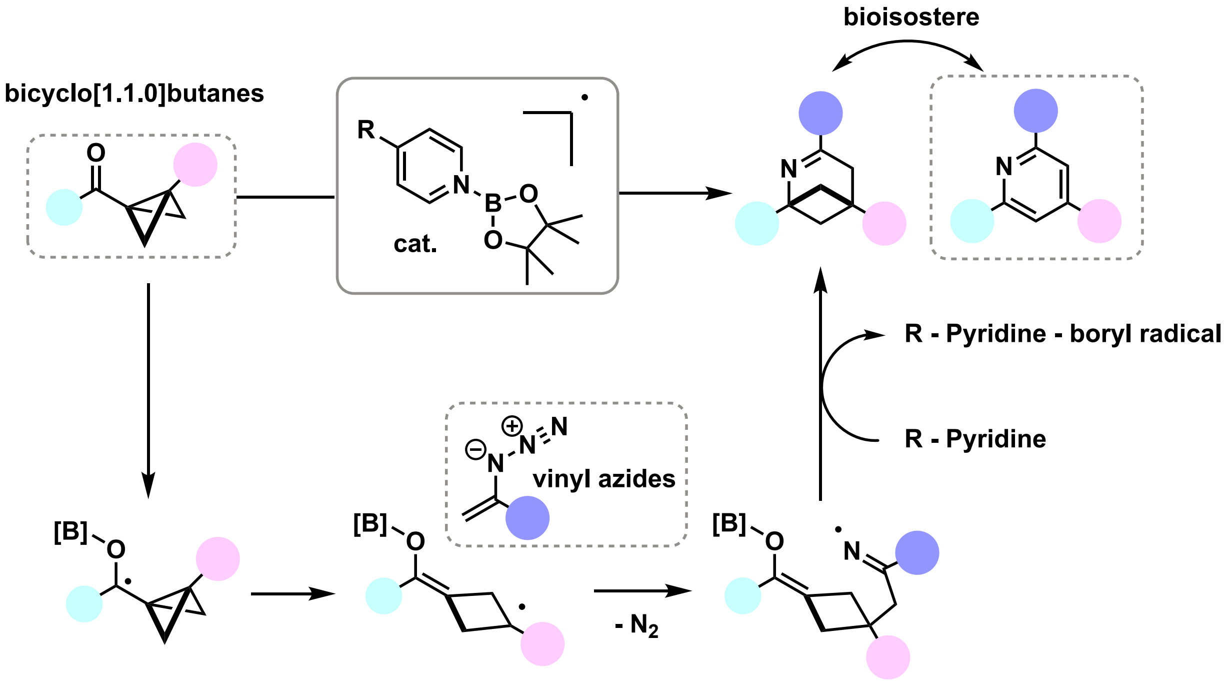
- Electrophilic pyridine - boryl radical can generate ketyl radical from carbonyls.

Li, S. *et al. Angew. Chem*, **2016**, *128*, 6089.
Li, S. *et al. J. Am. Chem. Soc,* **2017,** *139*, 3904.
Chung, W. J. *et al. Org. Chem*, **2024**, *89*, 8985.

[3π + 2σ] Cycloaddition for the Synthesis of Pyridine Isosteres

Reaction design

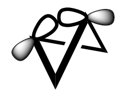




Bicyclo[1,1,0]butane (2σ) + vinyl azide (3π) cycloaddition

- Points

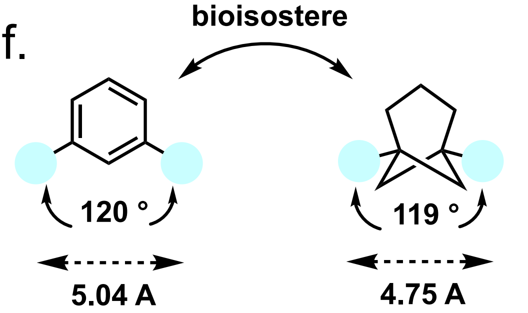
① Bicyclo[1,1,0]butane → significant strain (behave like biradical)
② vinyl azide → 3π radical acceptor



63.9 kcal/mol
strain energy

- 2-azabicyclo[3.1.1]heptene
→ bioisostere of pyridine
(similar basicity of pyridine and geometry)

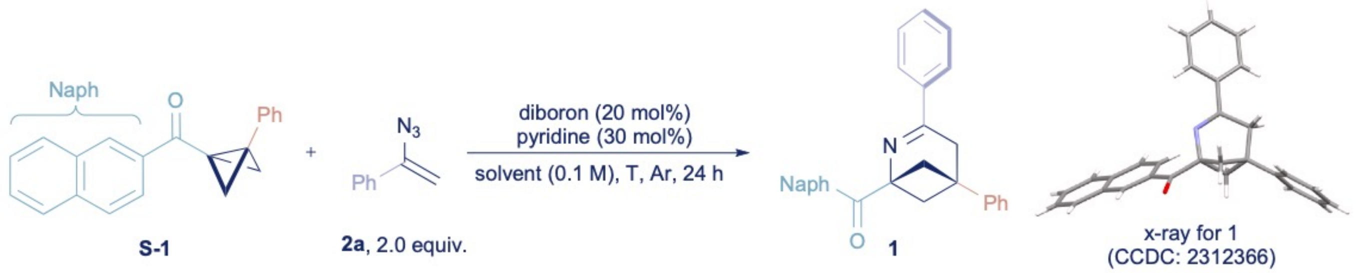
Cf.



Structural Simmilarity

Wang, H. *et al. Chem*, **2024**, *10*, 3699.
Molander, G. A. *et al. J. Am. Chem. Soc*, **2022**, *144*, 23685.

Optimization



entry	solvent	boron	T (°C)	pyridine	Yield
1	toluene	B1	25 °C	P1	50%
2	toluene	B1	25 °C	P2-P6	0
3	toluene	B3	25 °C	P1	70%
4	toluene	B4, B5	25 °C	P1	0
5	toluene	B2	25 °C	P4	75%
6	toluene	B2	25 °C	P2	83%
7	**anisole**	**B2**	**25 °C**	**P2**	**91%/96%[b]**
8[c]	anisole	B2	45 °C	P2	84%
9	anisole	-	25 °C	P2	0
10	anisole	B2	25 °C	-	0
11[d]	anisole	B2	25 °C	P2	0

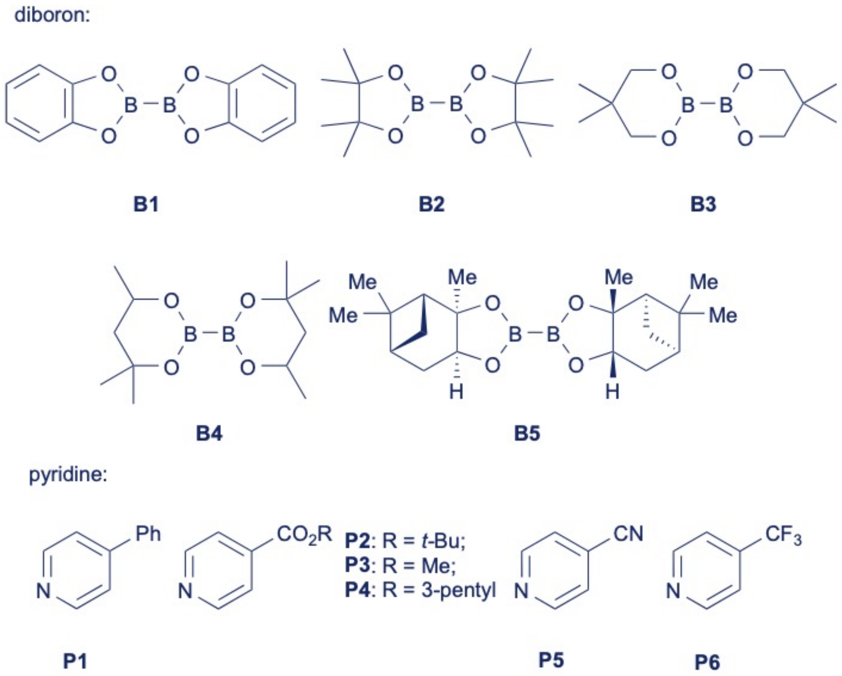


Figure 1. Reaction optimization

[a]Reaction conditions: S-1 (0.1 mmol), 2a (0.2 mmol), B$_2$pin$_2$ (20 mol %), 4-CO$_2$*t*-Bu-pyridine (30 mol %), solvent (1.0 mL), Ar atmosphere, and 30 h.

[b]Yield of isolated product.

[c]B$_2$pin$_2$ (10 mol %), 4-CO$_2$*t*-Bu-pyridine (15 mol %) and 48 h.

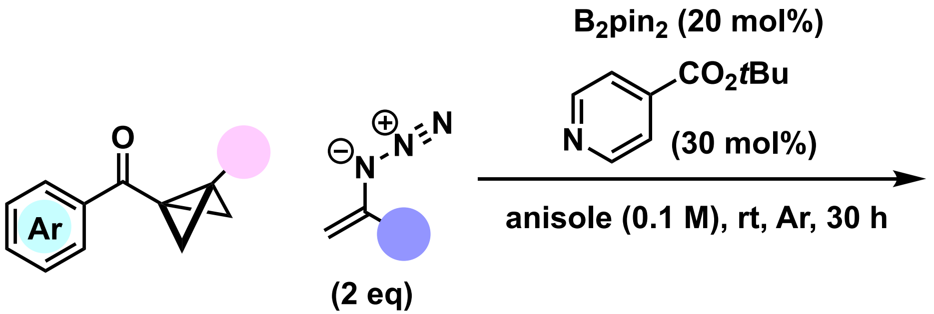
[d]Reaction as in entry 7 but in the presence of 3.0 equiv of TEMPO.

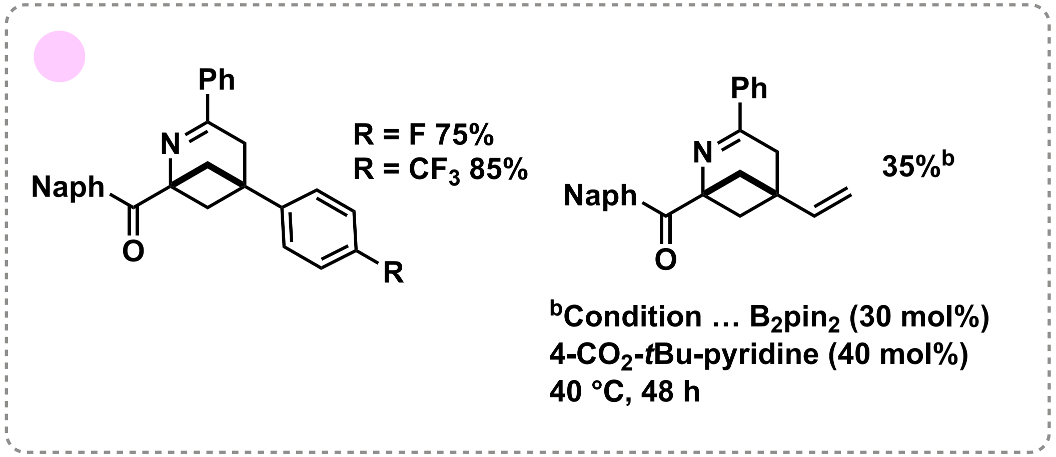
- The combination of B2/P2 gave the highest yield (entry 6).

- Anisol was optimal solvent.
(*n*-hexane, DMF, THF, DCM → 0% yield)

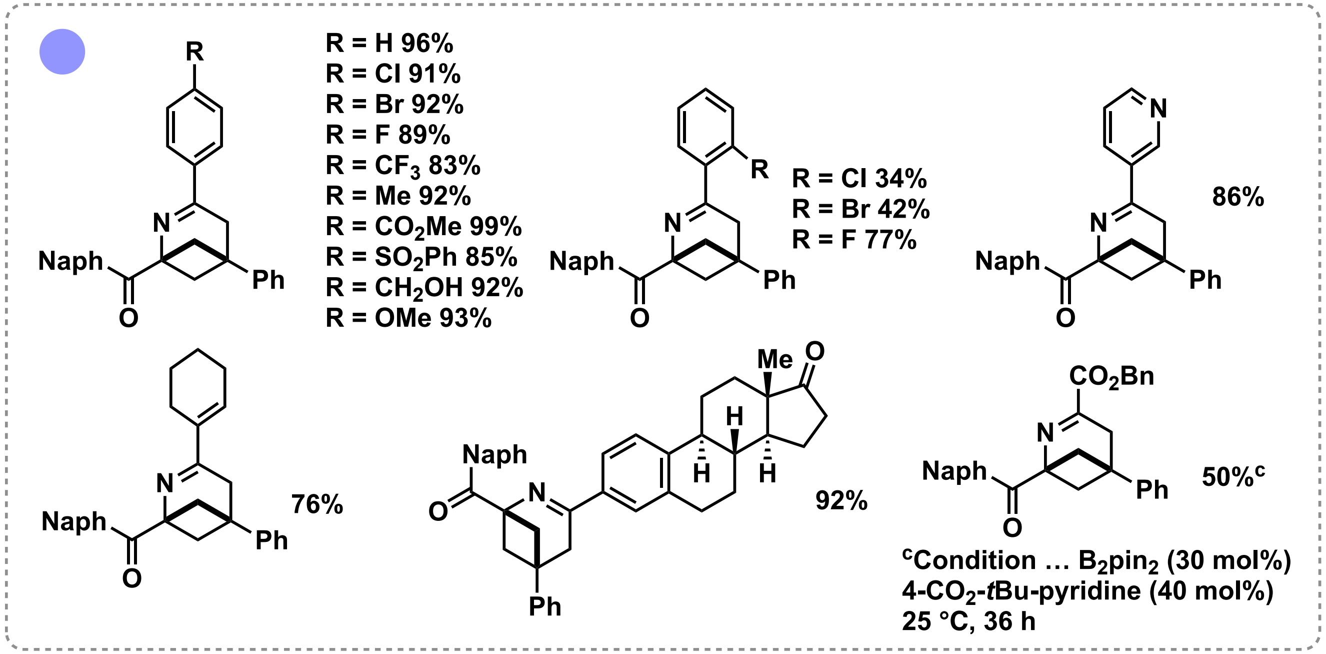
Wang, H. *et al. Chem*, **2024**, *10*, 3699.

Substrates Scope

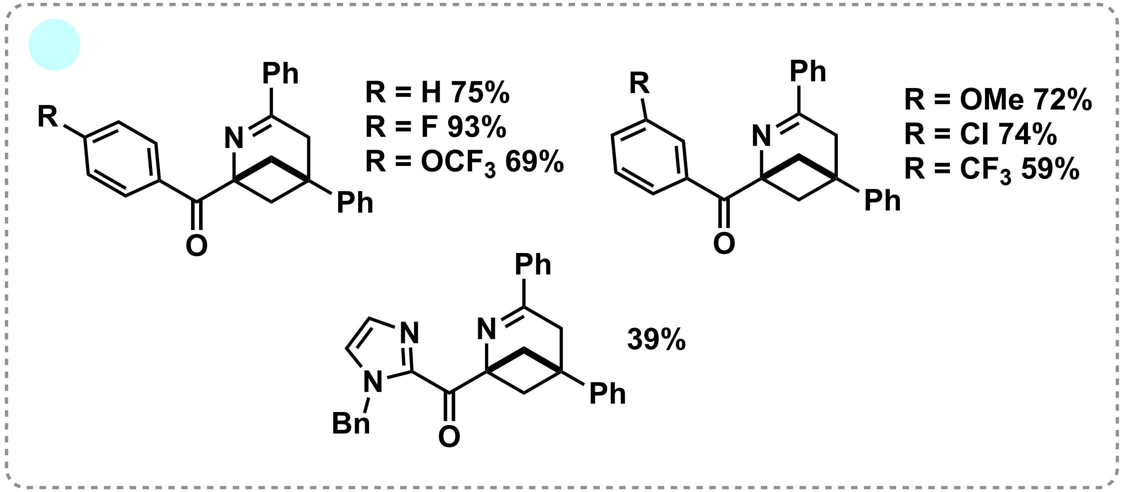




[b]Condition … B$_2$pin$_2$ (30 mol%)
4-CO$_2$-*t*Bu-pyridine (40 mol%)
40 °C, 48 h



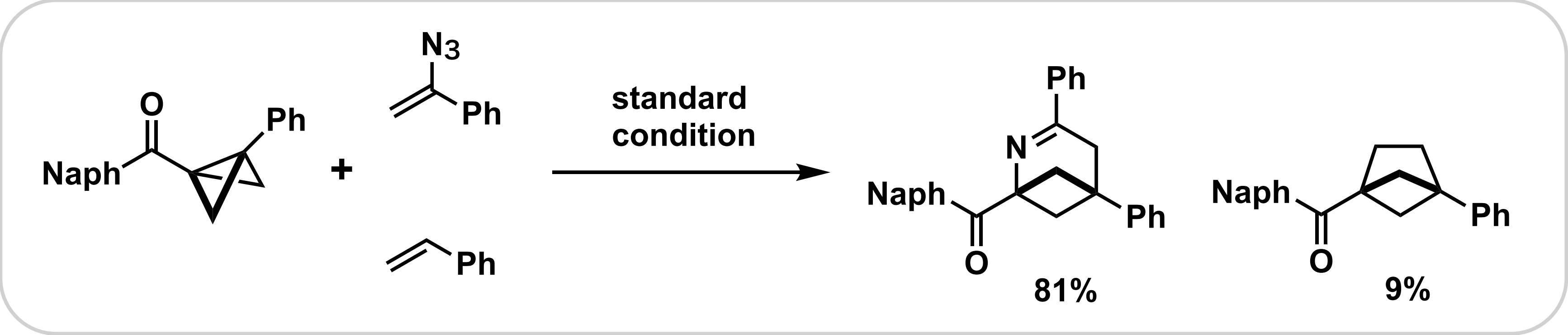
[c]Condition … B$_2$pin$_2$ (30 mol%)
4-CO$_2$-*t*Bu-pyridine (40 mol%)
25 °C, 36 h



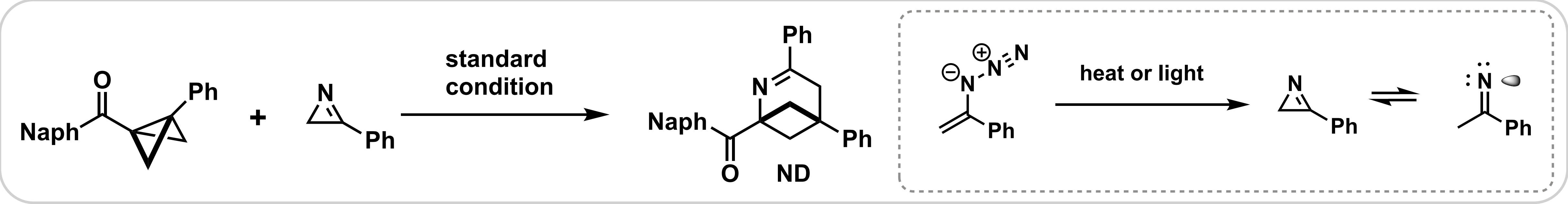
Wang, H. *et al. Chem*, **2024**, *10*, 3699.

Mechanistic Studies

- Competition experiment … azide → activating role

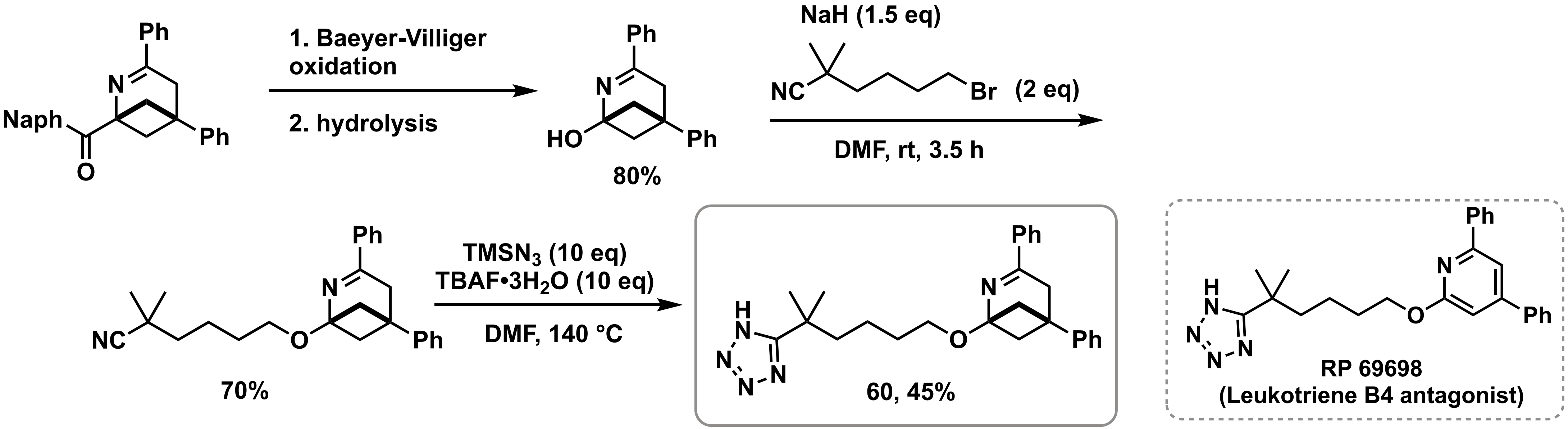


- 2H-azirine is not an intermediate

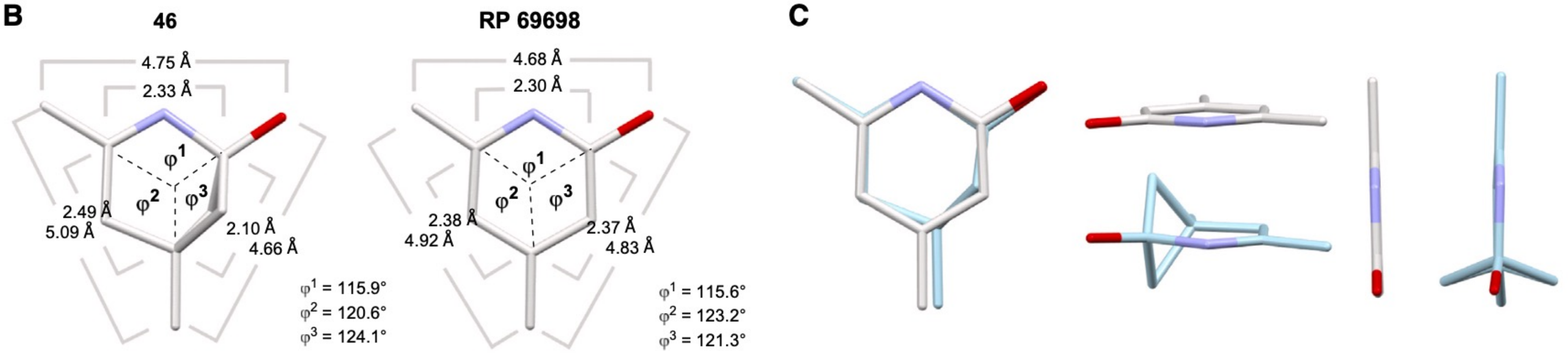


Wang, H. *et al. Chem*, **2024**, *10*, 3699.

Isostere Analysis



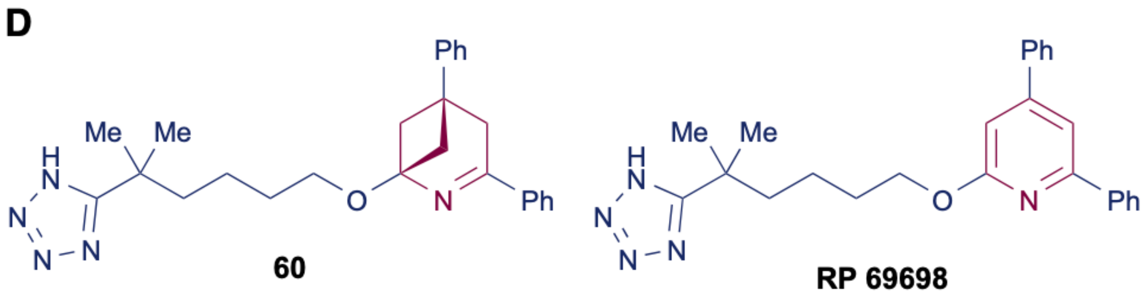
- X-ray



Wang, H. *et al. Chem*, **2024**, *10*, 3699.

Isostere Analysis

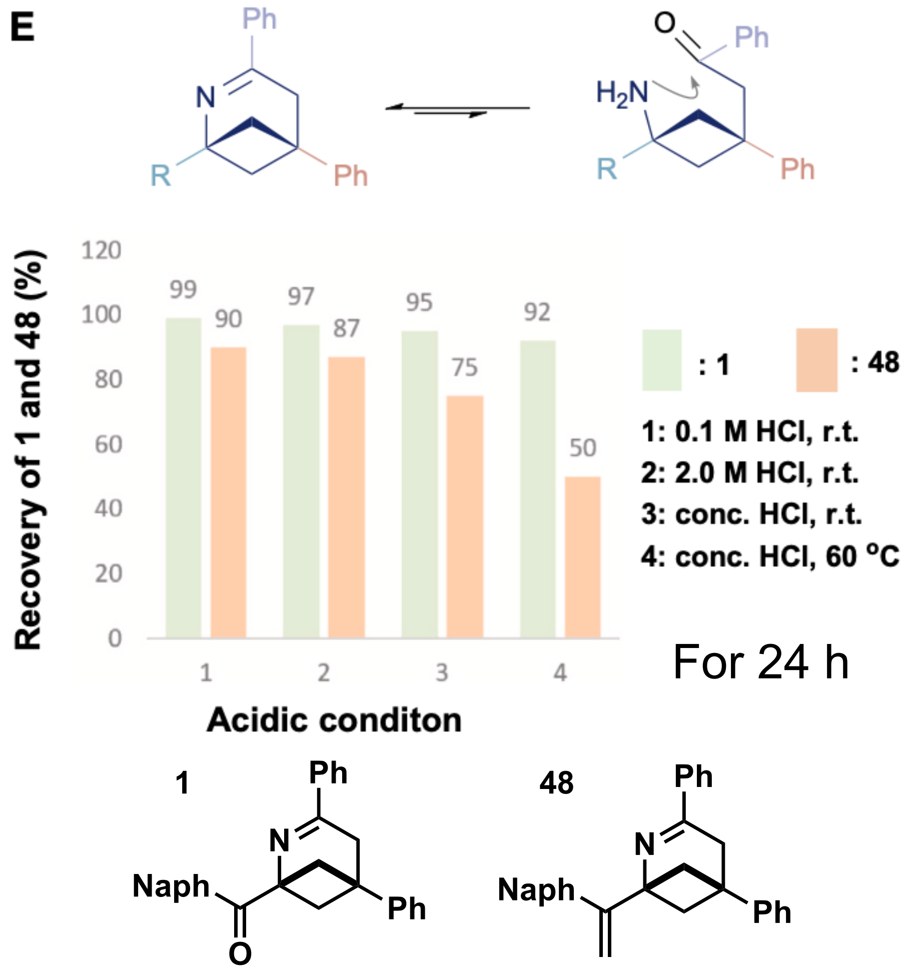
- Metabolic stability in human liver microsomes



Compound	cpK_a	cLogP	LogD (7.4)	CL_{int}	$t_{1/2}$
RP 69698	7.34	6.28	4.97	0.0146	94.9
60	6.09	5.01	3.14	0.0072	>120

- Replacing pyridine with the scaffold decreases the compound lipophilicity (*c*logP, LogD(7.4)).
- Introducing a 3D scaffold enhances the metabolic stability. (CL_{int}, $t_{1/2}$)
- Binding affinity to the receptor was not observed.

- Stability of 2-azabicyclo[3.1.1]heptenes In acidic conditions



For 24 h

Wang, H. *et al. Chem*, **2024**, *10*, 3699.

Contents

1. Introduction

2. Ammonia synthesis at RT by Boryl radical

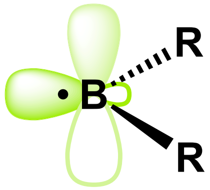
3. Radical addition of amine – boryl radical

4. Utilizing pyridine – boryl radical for construction of bicyclic ring

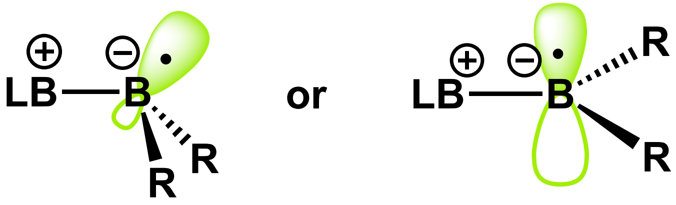
5. Summary

Summery

Boryl Radicals



Ligated Boryl Radicals (LBRs)



σ-type
(LB = R_3N)

π-type
(LB = R_3P, NHC, pyridine etc.)

- Various unique transformations were realized utilizing reactivity of boryl radicals

Perspectives

① Selectivity control (Ex. Radical addition or XAT, regioselectivity, asymmetric reaction etc …)
② Investigation of new reactivity (including new ligands)

Appendix

EPR spectrum

$Me_3N\text{-}\dot{B}H_2$

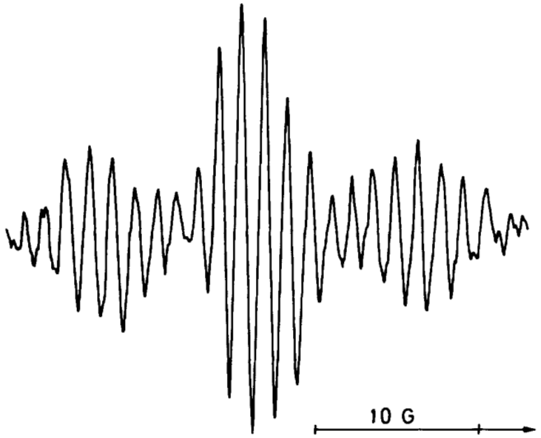
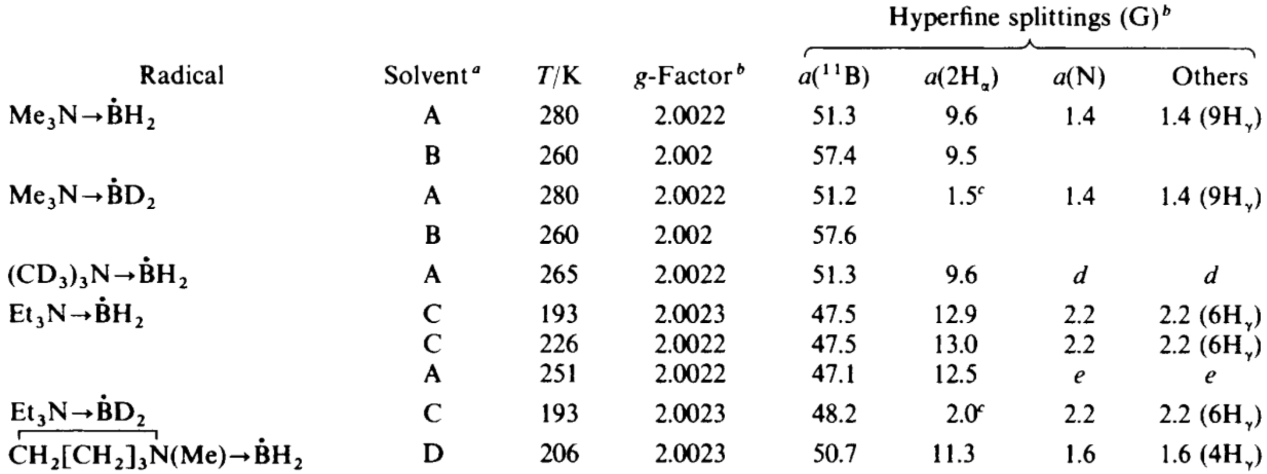
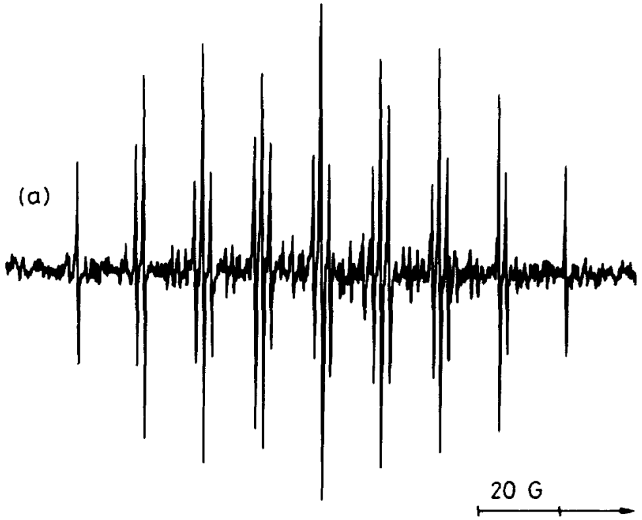


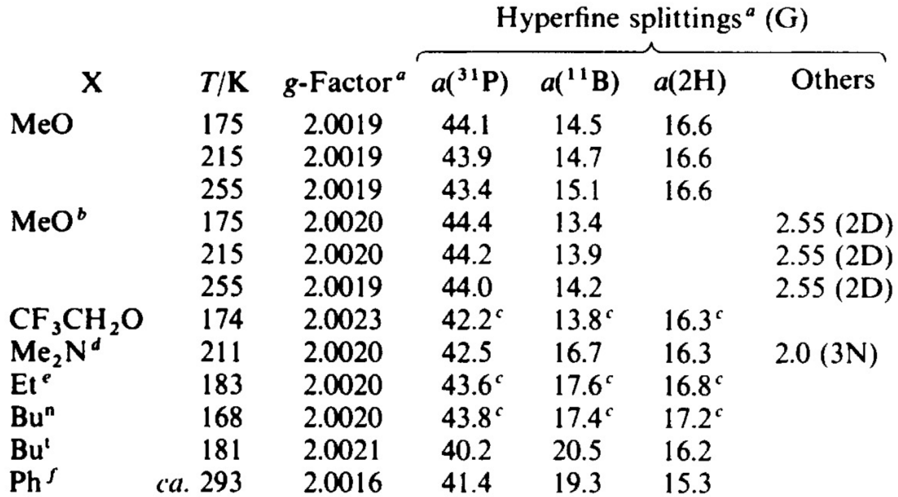
Figure 1. Lowest-field $[I(^{11}B) + 3/2]$ multiplet from the e.s.r. spectrum of the trimethylamine–boryl radical (**1**; R = Me) in Bu^{t}OH–Me$_2$O (4:1 v/v) at 280 K



Radical	Solvent[a]	T/K	g-Factor[b]	Hyperfine splittings (G)[b]			
				$a(^{11}B)$	$a(2H_\alpha)$	a(N)	Others
$Me_3N\rightarrow\dot{B}H_2$	A	280	2.0022	51.3	9.6	1.4	1.4 ($9H_\gamma$)
	B	260	2.002	57.4	9.5		
$Me_3N\rightarrow\dot{B}D_2$	A	280	2.0022	51.2	1.5[c]	1.4	1.4 ($9H_\gamma$)
	B	260	2.002	57.6			
$(CD_3)_3N\rightarrow\dot{B}H_2$	A	265	2.0022	51.3	9.6	*d*	*d*
$Et_3N\rightarrow\dot{B}H_2$	C	193	2.0023	47.5	12.9	2.2	2.2 ($6H_\gamma$)
	C	226	2.0022	47.5	13.0	2.2	2.2 ($6H_\gamma$)
	A	251	2.0022	47.1	12.5	*e*	*e*
$Et_3N\rightarrow\dot{B}D_2$	C	193	2.0023	48.2	2.0[c]	2.2	2.2 ($6H_\gamma$)
$CH_2[CH_2]_3N(Me)\rightarrow\dot{B}H_2$	D	206	2.0023	50.7	11.3	1.6	1.6 ($4H_\gamma$)

$(MeO)_3P\text{-}\dot{B}H_2$





X	T/K	g-Factor[a]	Hyperfine splittings[a] (G)			
			$a(^{31}P)$	$a(^{11}B)$	a(2H)	Others
MeO	175	2.0019	44.1	14.5	16.6	
	215	2.0019	43.9	14.7	16.6	
	255	2.0019	43.4	15.1	16.6	
MeO[b]	175	2.0020	44.4	13.4		2.55 (2D)
	215	2.0020	44.2	13.9		2.55 (2D)
	255	2.0019	44.0	14.2		2.55 (2D)
CF_3CH_2O	174	2.0023	42.2[c]	13.8[c]	16.3[c]	
Me_2N[d]	211	2.0020	42.5	16.7	16.3	2.0 (3N)
Et[e]	183	2.0020	43.6[c]	17.6[c]	16.8[c]	
Bu^n	168	2.0020	43.8[c]	17.4[c]	17.2[c]	
Bu^t	181	2.0021	40.2	20.5	16.2	
Ph[f]	*ca.* 293	2.0016	41.4	19.3	15.3	

Baban, J. A., & Roberts, B. P. *J. Chem. Soc, Perkin. Trans. 2,* **1984***,* 10, 1717.
Roberts, B. P. *et al*. *J. Chem. Soc, Perkin Trans. 2*, **1985**, 11, 1723.

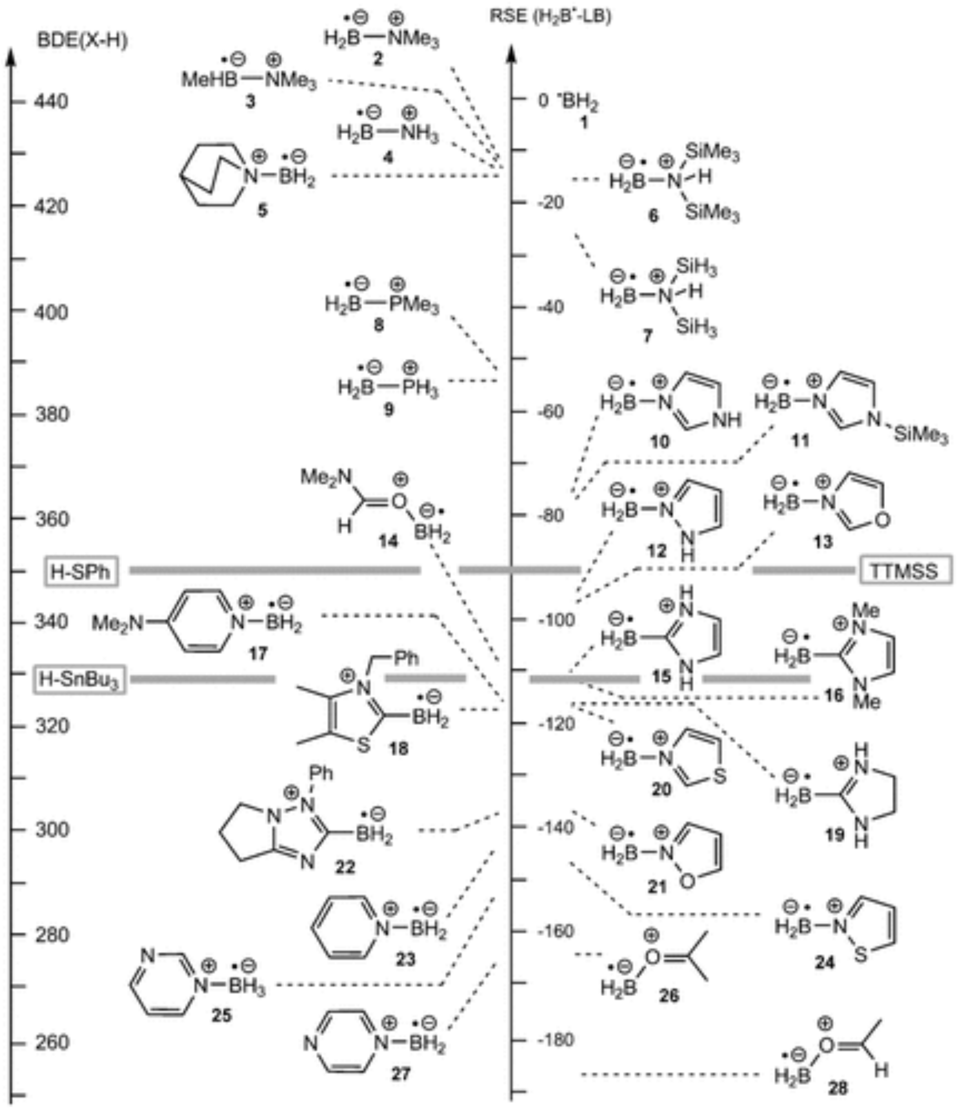
Calculation of BDEs

$$\underset{\mathbf{1}}{H_2B^\bullet} + \overset{\ominus\ \ \oplus}{H_3B-LB} \xrightarrow{RSE} \underset{\mathbf{1H}}{BH_3} + \overset{\ominus\ \ \oplus}{H_2B^\bullet-LB}$$

$$BDE(LB-BH_2-H) = -E_c(LB-BH_3) + BDE(BH_2-H) + E_c(LB-BH_2^\bullet)$$

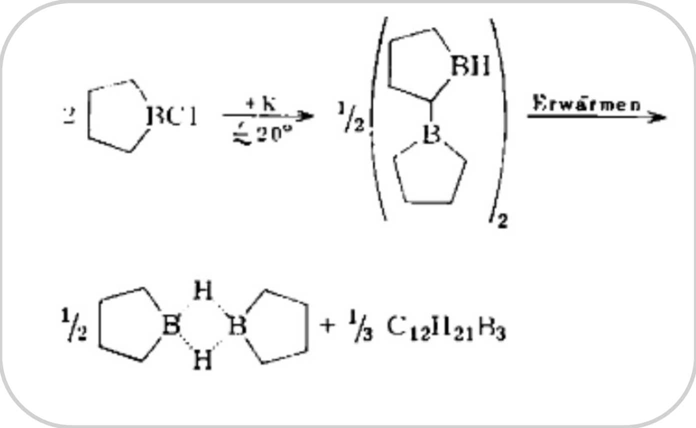
$$RSE(LB-BH_2^\bullet) = E_c(LB-BH_2^\bullet) - E_c(LB-BH_3)$$

$$\begin{tikzcd}
\overset{\oplus\ \ \ominus}{LB-BH_3} \arrow[r, "BDE(LB\text{-}BH_2\text{-}H)"] \arrow[d, "-LB"', "-E_c(LB\text{-}BH_3)"] & \overset{\oplus\ \ \ominus}{LB-BH_2^\bullet} + H^\bullet \arrow[d, "-LB"', "-E_c(LB\text{-}BH_2^\bullet)"] \\
\underset{\mathbf{1H}}{BH_3} \arrow[r, "BDE(BH_2\text{-}H)"] & \underset{\mathbf{1}}{{}^\bullet BH_2} + H^\bullet
\end{tikzcd}$$



Zipse, H. *et al. Chemistry–A European Journal*, **2010**, *16*, 6861.

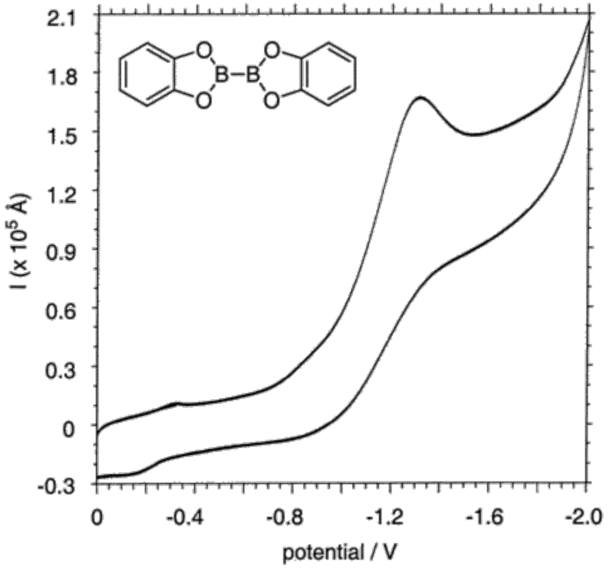
Supplemental Information

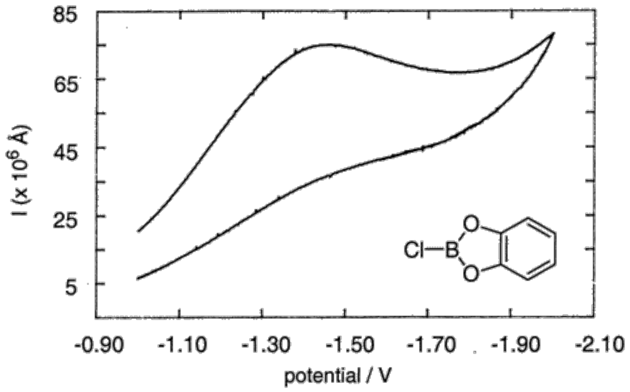


Boryl radical

Low concentration → cannot react with N_2 and dimerize?
(reducing reagent other than K)

Reduction potential





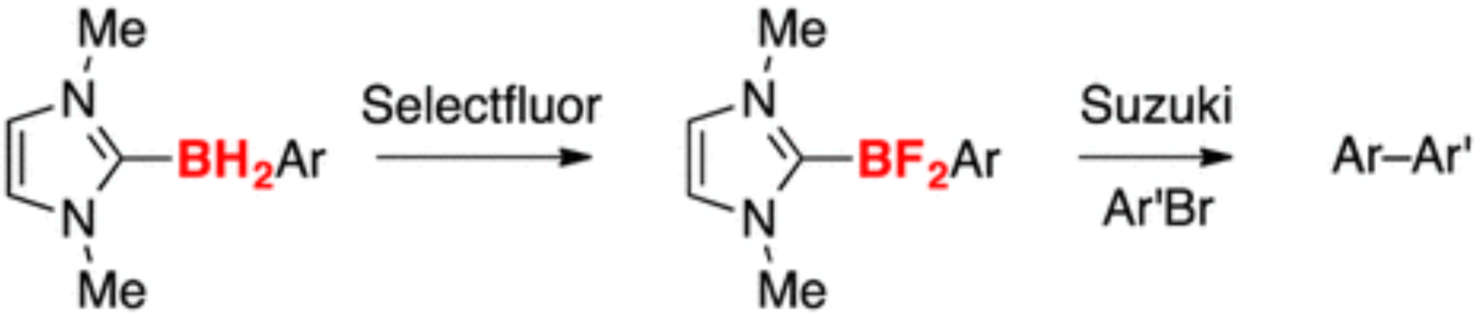
Vs Ag/AgCl

Koester, R., & Benedikt, G. *Angew. Chem*, **1963,** *75*, 346.

Hartwig, J. F. *et al*. *Organometallics*, **2003**, *22*, 365.

NHC – Boryl Radical for Suzuki Miyaura Coupling

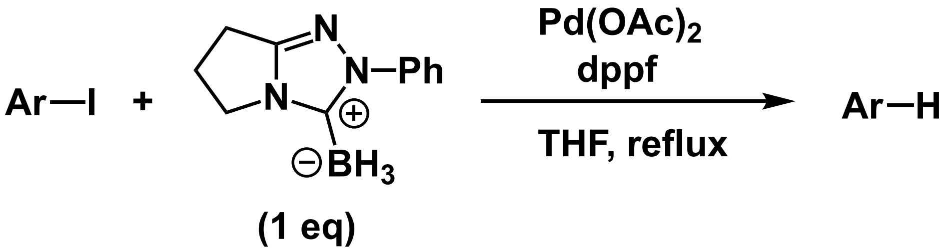
- Boronic acid equivalent synthesis from NHC – borane.



NHC-Arylboranes

NHC-Difluoro(aryl)boranes
neutral, stable

Cf. LB – Borane can reduce Ar-X as hydryde doner.

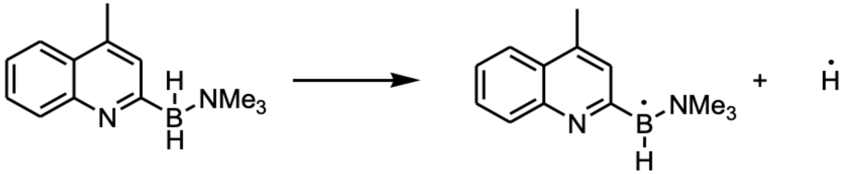
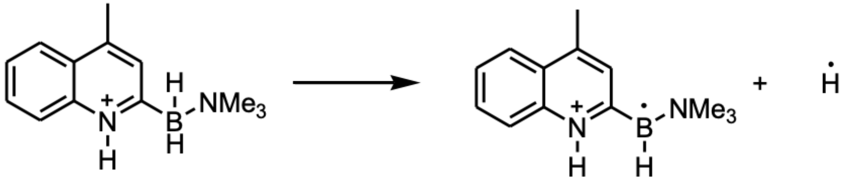


Lacôte, E. *et al. Chem. Eur. J*, **2009**, *15*, 12937
Nerkar, S., & Curran, D. P. *Org. Lett*, **2015,** *17*, 3394.

DFT Calculations

8.2 Bond Dissociation Enthalpies (BDE)

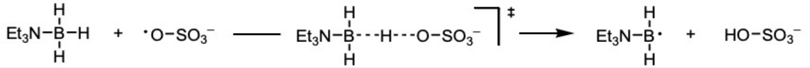
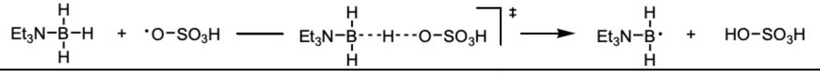
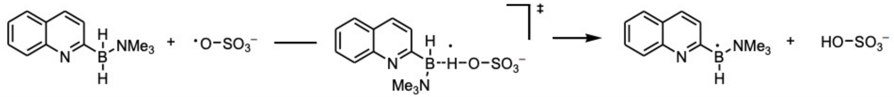
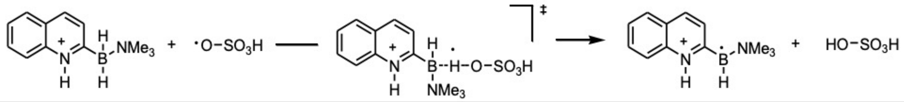
DFT Method: UB3LYP/6-31+G(d)

Reaction	BDE (Kcal mol^{-1})
 $Me_3N-\overset{H}{B}H_2 \longrightarrow Me_3N-\dot{B}H_2 + \dot{H}$	100.7
	97.3
	80.6

8.5 Activation Energy (ΔG‡) and Reaction Energy (ΔG^{o}) for HAT Reactions

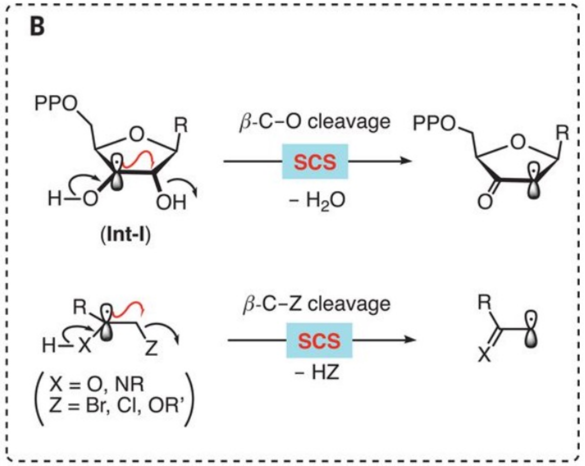
DFT Method: UB3LYP/6-31+G(d) [values are in Kcal mol^{-1}]

Solvent: CH_3CN and values in parenthesis are related to the corresponding gaseous phase calculations

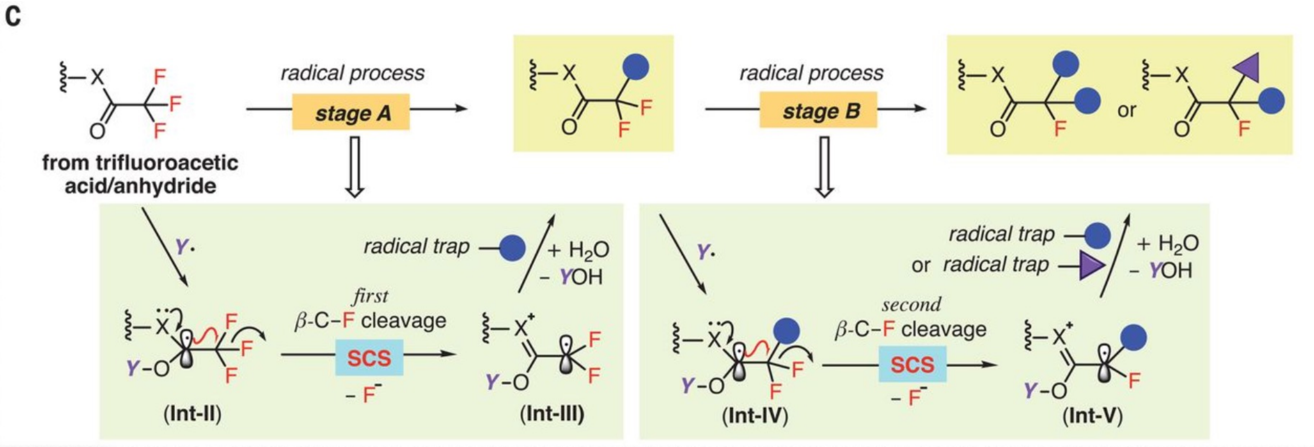
HAT Reactions	ΔG‡	ΔG^{o}
	11.9 (19.0)	0.4 (5.8)
	-7.8 (-3.9)	-4.8 (-0.5)
	10.4 (12.5)	-15.8 (-7.7)
	2.5	-25.0 (-19.9)

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

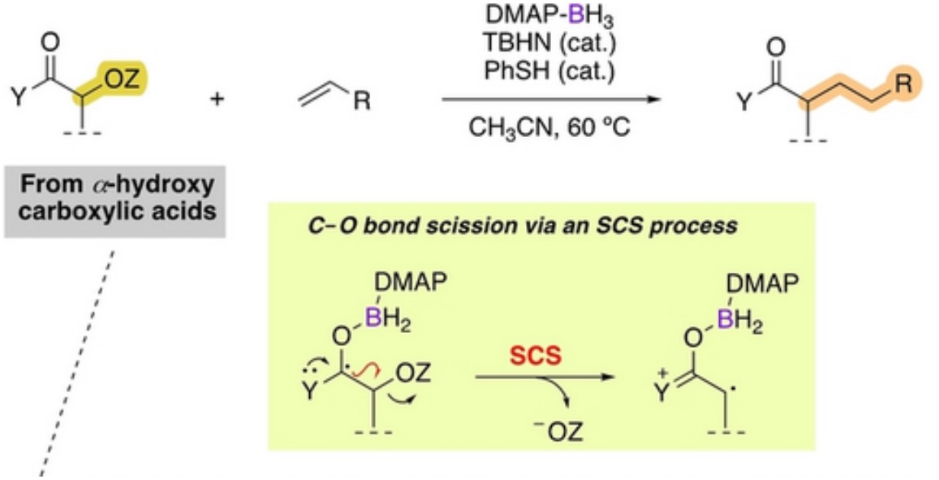
Spin Center Shift (SCS) by Pyridine – Boryl Radical



- C-F activation (DMAP – boryl radical)



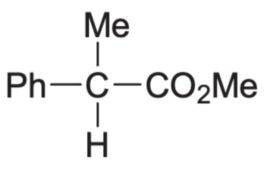
- C-O activation (DMAP – boryl radical)



Wang, Y. F. *et al. Science*, **2021**, *371*, 1232.

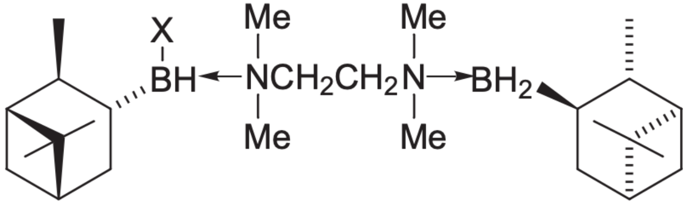
Wang, Y. F. *et al. Angew. Chem. Int. Ed*, **2022**, *61*, e202201329.

Asymmetric Reactions



$Ph-C(Me)(H)-CO_2Me$

45



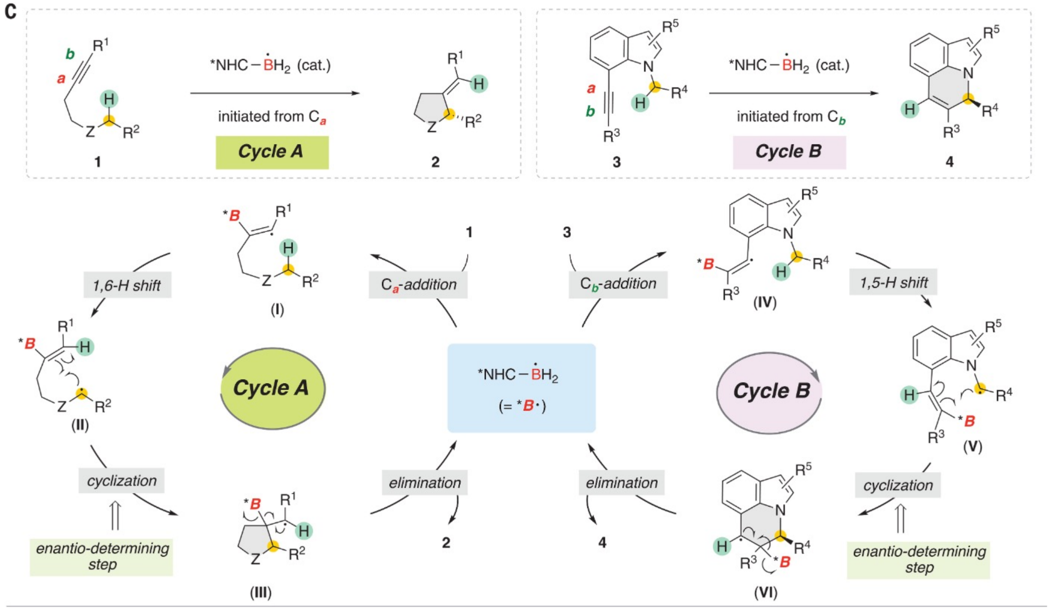
46 X = H

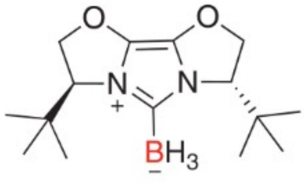
47 X = unpaired electron

Using 47, (*R*) – 45 is 2.4 times more reactive than (*S*) – 45.

Mok, P. L., & Roberts, B. P. *J. Chem. Soc., Chem. Commun*, **1991**, 3, 150.
Roberts, B. P. *Chem. Soc. Rev*, **1999**, *28*, 25.

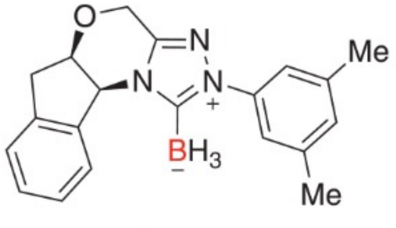
- Assymmetric cyclization





B-1

For cycle A

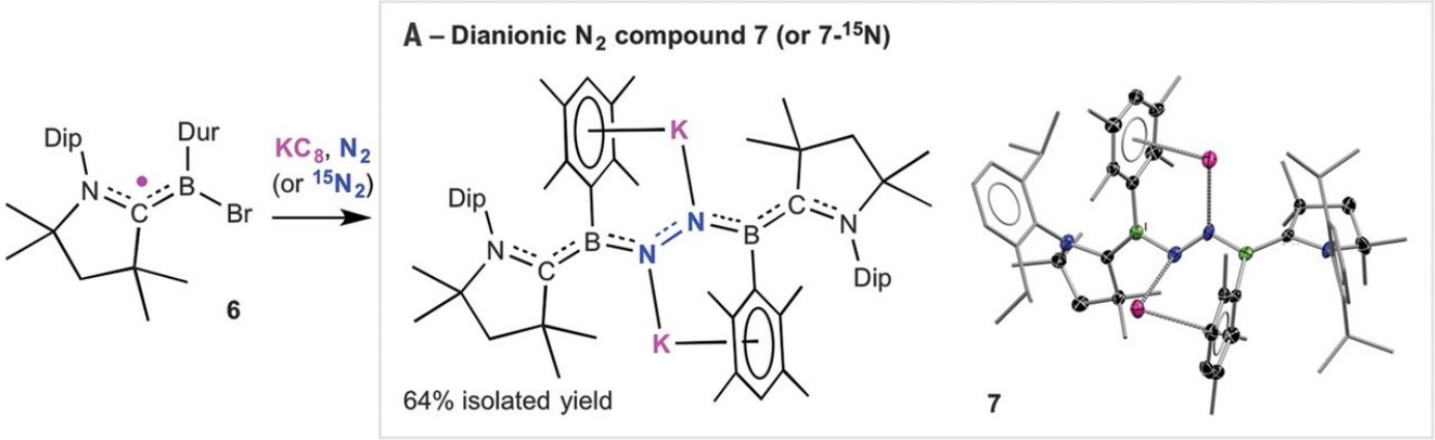


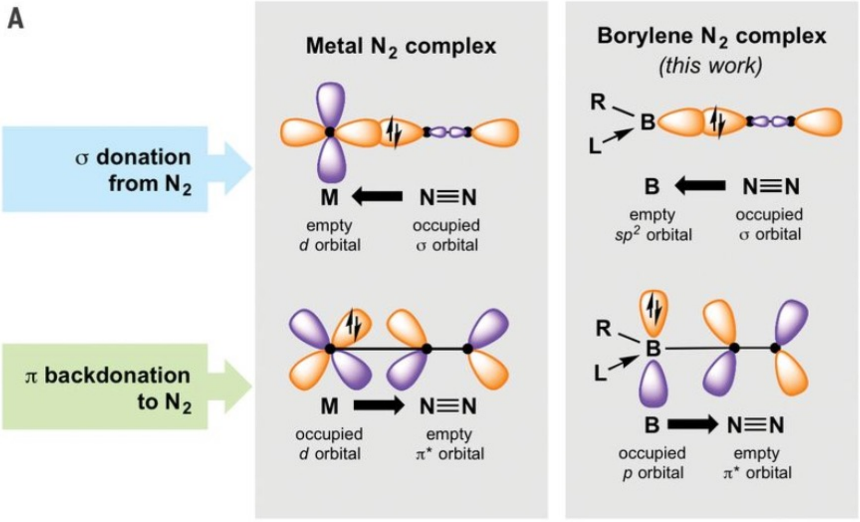
B-5

For cycle B

Wang, Y. F. *et al. Science*, **2023**, *382*, 1056.

N_2 Fixation by Bolyrene

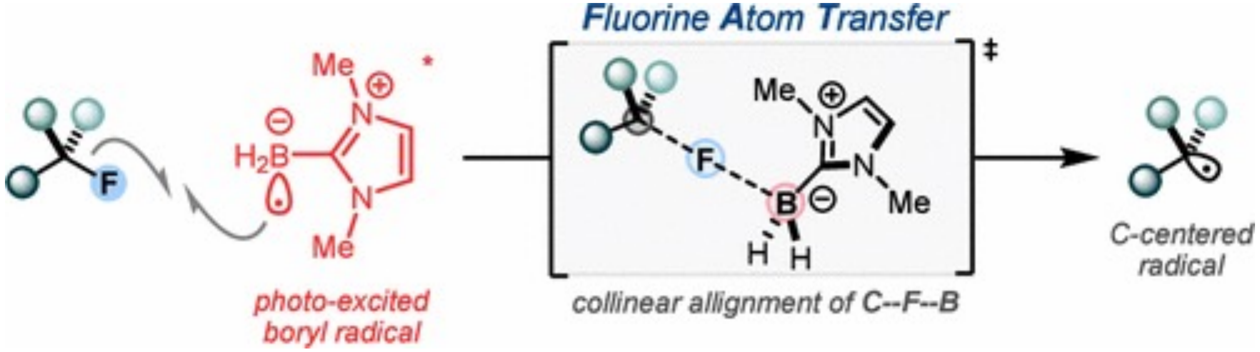


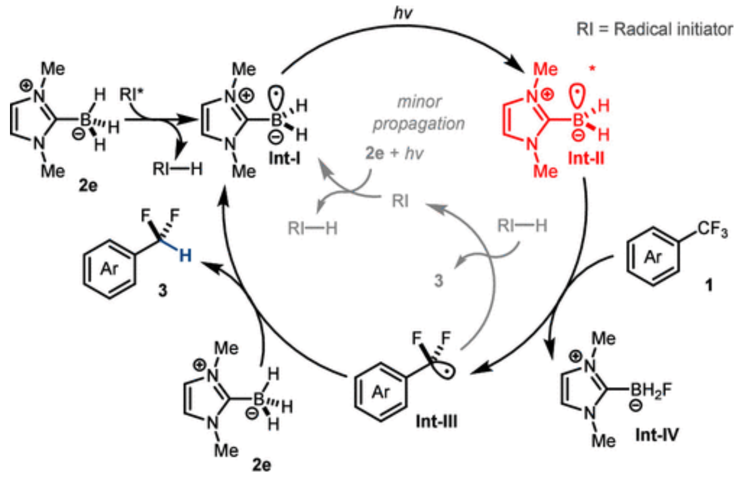


Braunschweig, H. *et al*. *Science*, **2018**, *359*, 896.

FAT

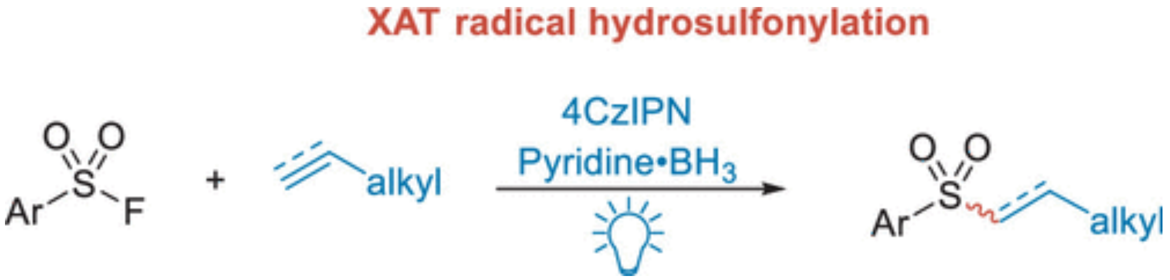
- Excited NHC – boryl radical

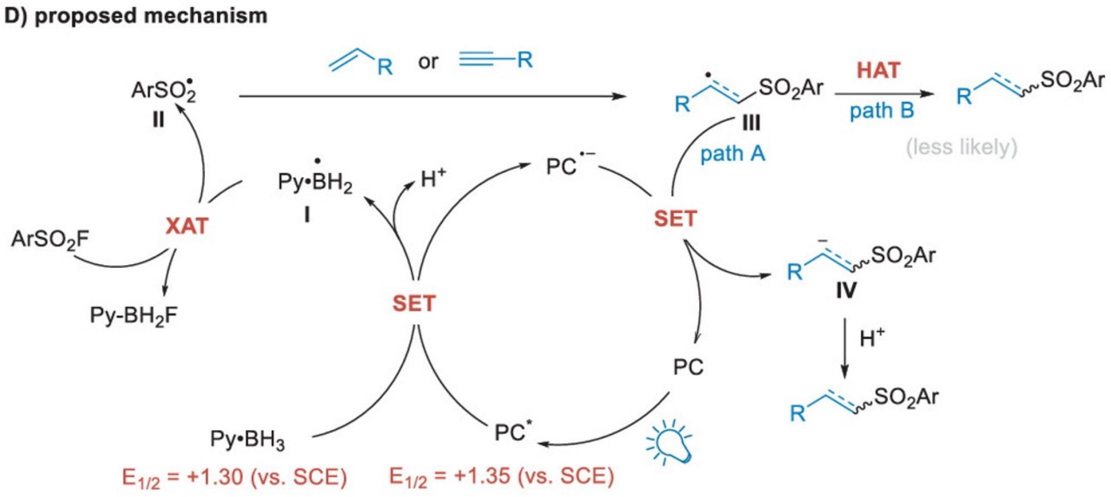




Lee, H. G. *et al. J. Am. Chem. Soc*, **2024**, *146*, 22874.

- Pyridine – boryl radical

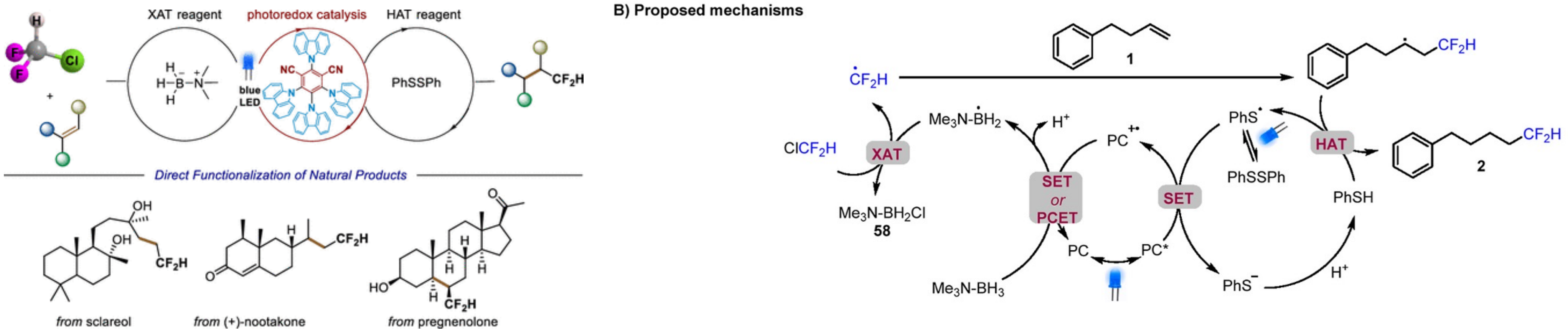




Wu, X., & Gao, B. *Org. Lett*, **2023**, *25*, 8722.

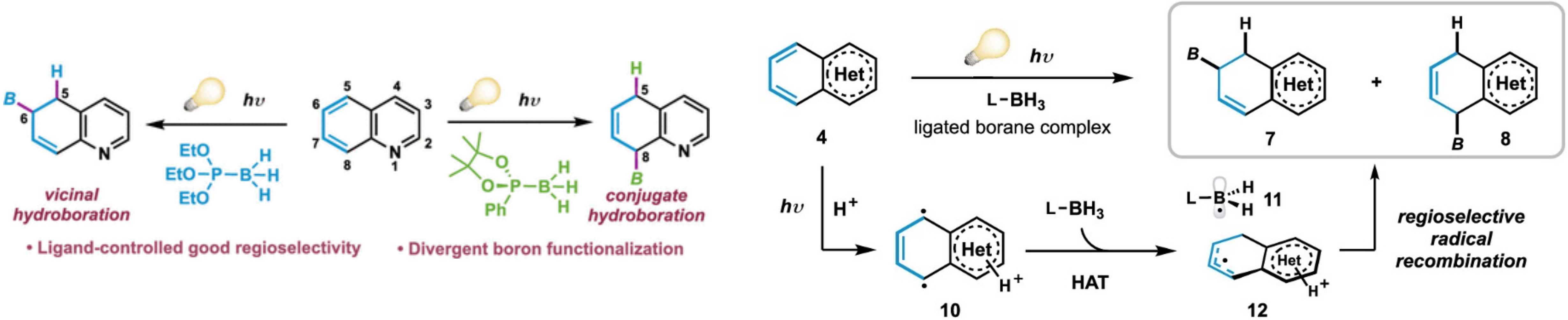
Other Examples

- C-Cl bond cleavage by amine – boryl radical



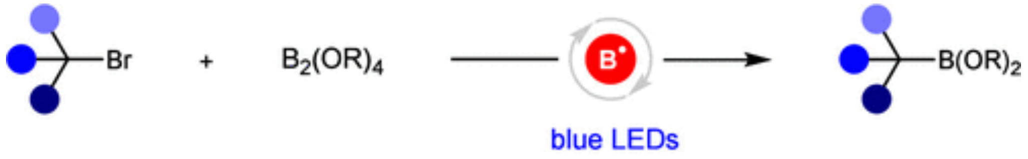
Wu, J. *et al. J. Am. Chem. Soc*, **2022**, *144*, 14288.

- Dearomative hydroboration by phosphine – boryl radical



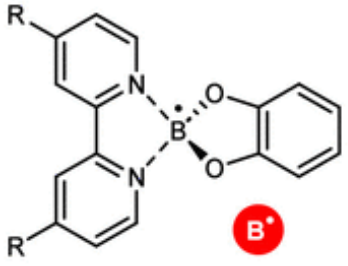
Qin, T. *et al. J. Am. Chem. Soc*, **2025**, *147*, 11906.

New Type of Boryl Radical ?

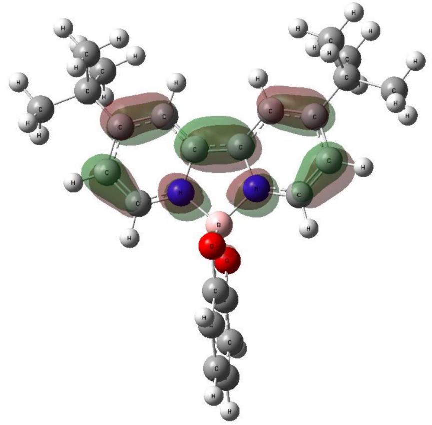


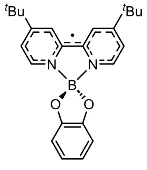
Boryl Radical Photocatalysis

- Long-lived persistent radical generated in situ
- Powerful excited state reductant (*E* < –3.4 V)

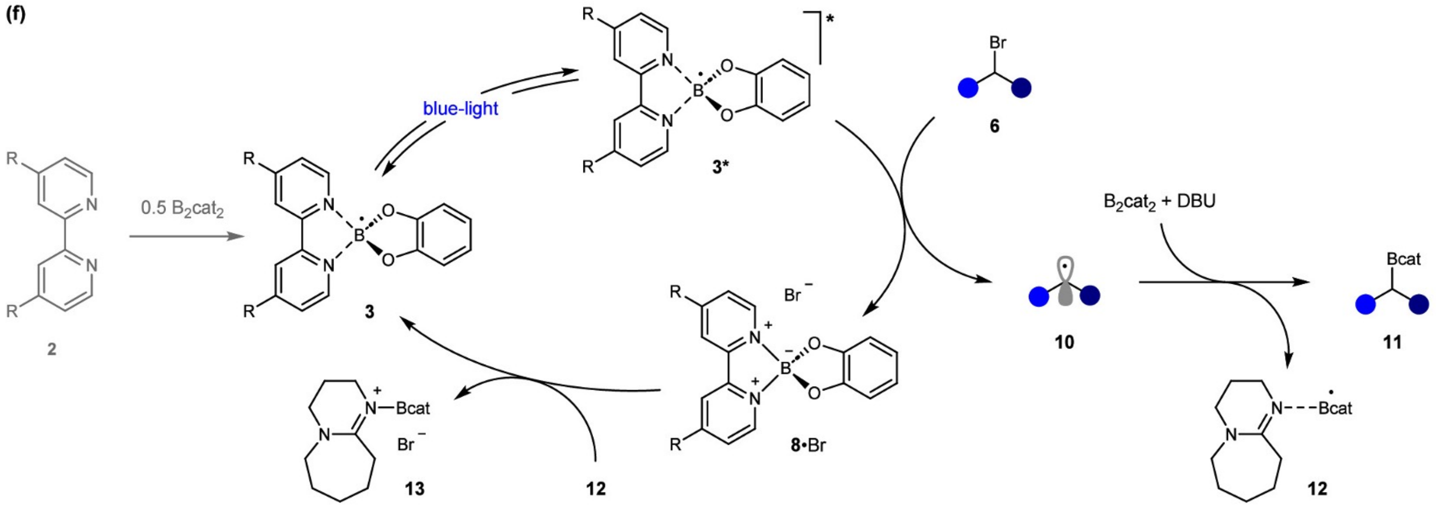


SOMO ··· localized on bipyridyl





3a



Aggarwal, V. K. *et al. J. Am. Chem. Soc*, **2025**