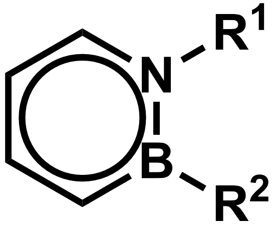
Chemistry of Azaborine family
–focusing on Shih–Yuan Liu’s work–

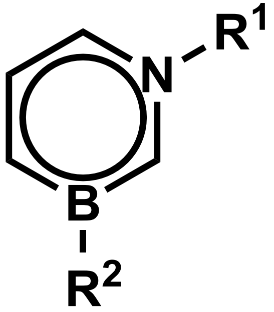
Literature Seminar

2015/3/19 (Thu.)

Hideoki NAGAI (M1)



1,2-Azaborine



1,3-Azaborine

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1. Introduction of B-N chemistry
2. Characteristics of aromatized B-N compounds
3. Hydrogen storage
4. Perspective

1. Introduction of B-N chemistry

1-1. The Nobel Prize in Boron chemistry

1-2. BN/CC isosterism

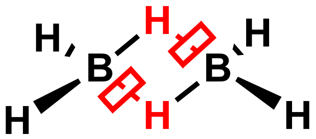
1-3. The differences in BN/CC molecular properties

1-4. Aromaticity of Borazine

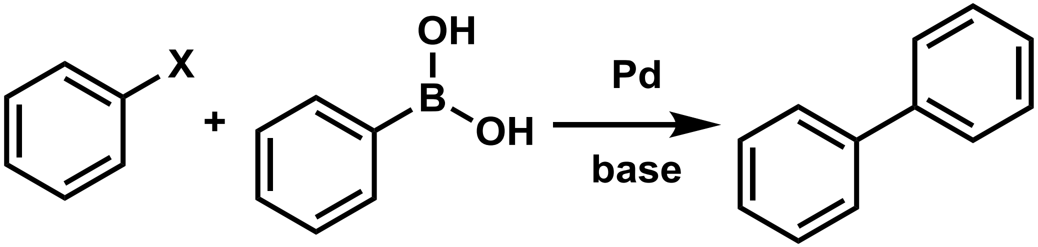
1-5. Shih-Yuan Liu & Azaborine family

1-1. The Nobel Prize in Boron chemistry

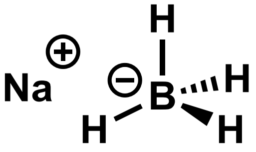
William N. Lipscomb (1976)
"The structure of boranes illuminating problems of chemical bonding"



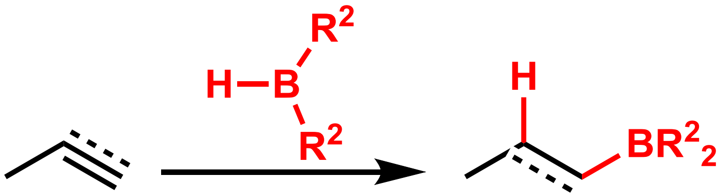
Akira Suzuki (2010)
"Cross-Coupling Reaction of organoboranes"



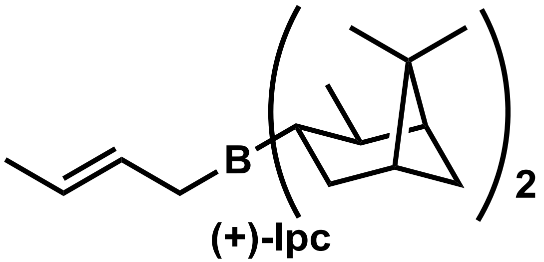
Herbert C. Brown (1979)
"The use of boron-containing compounds"



-Brown Hydroboration-



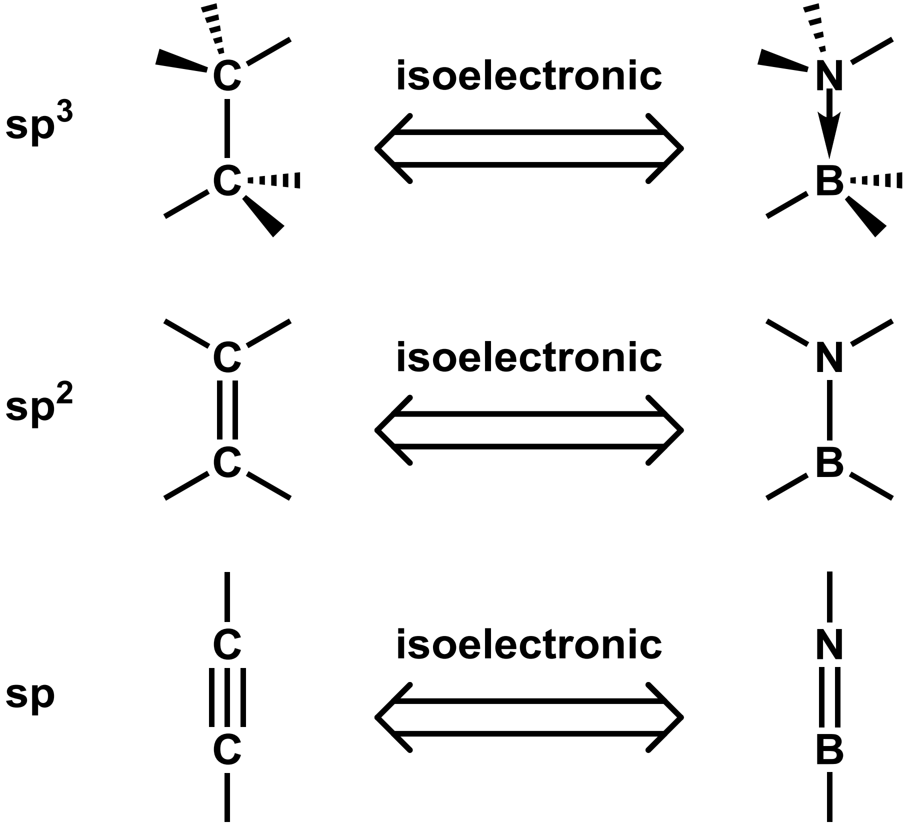
-Asymmetric Allylboration-



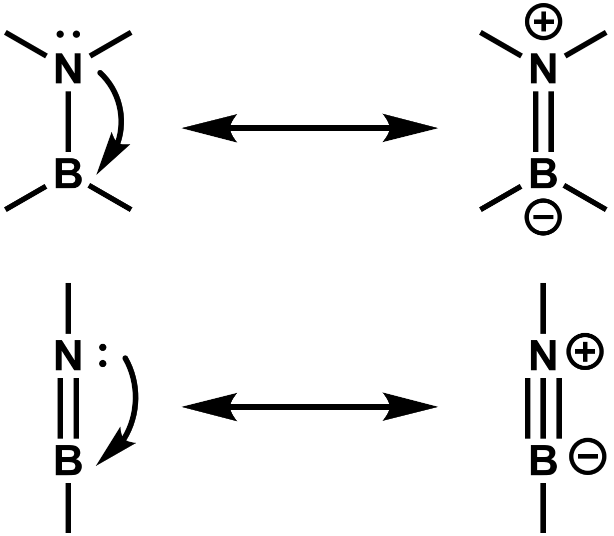
William N. Lipscomb, *Angew. Chem. Int. Ed.* **1977**, *89*, 685.
Akira Suzuki, *Angew. Chem. Int. Ed.* **2011**, *50*, 6722.
von Herbert C. Brown, *Angew. Chem. Int. Ed.* **1980**, *92*, 675.

1-2. BN/CC isosterism

-The substitution of a C=C bond with an isoelectronic and isosteric B-N unit (BN/CC isosterism)-



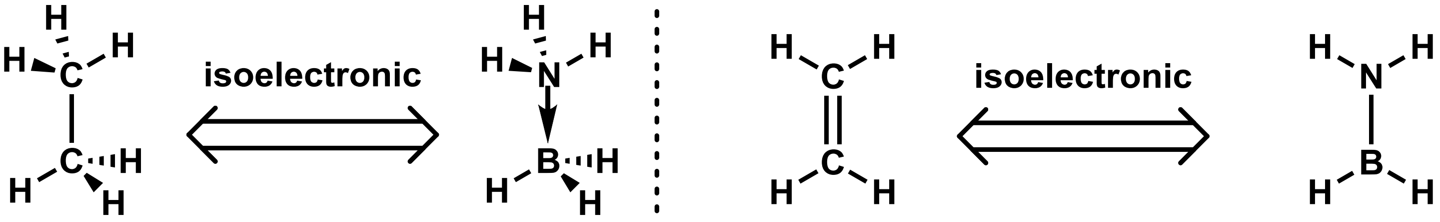
element	B	C	N
Valence electrons	3	4	5



A BN unit has the same total valence electron count as a corresponding C=C unit.

Shi-Yuan Liu, *et al.*, *Angew. Chem. Int. Ed.* **2012**, *51*, 6074.

1-3. The differences in BN/CC molecular properties



	ethane	ammonia borane	ethene	aminoborane
bp (°C)	-89	104	-104	- (a strong tendency to polymerize)
BDE (kcal mol^{-1})	90.1	27.2	174.1 (= 109.1 σ + 65.0 π)	139.7 (= 109.8 σ + 29.9 π)
dipole moment (Debye)	0	5.216	0	1.844

* BDE : bond dissociation energy

Robert H. Pritchard, C. W. Kern, *J. Am. Chem. Soc.* **1969**, *91*, 1631.
Stephen J. Blanksby, G. Barney Ellison, *J. Am. Chem. Soc.* **2003**, *36*, 255.
L. R. Thorne, *et al.*, *J. Chem. Phys.* **1983**, *78*, 167.
David A. Dixon, *et al.*, *J. Phys. Chem. A.* **2006**, *110*, 12955.
Jose Elguero, *et al.*, *Structual Chemistry* **1998**, *9*, 59.
Chi Matsumura, *et al.*, *Chemical Physics Letters* **1979**, *64*, 573.
Shi-Yuan Liu, *et al.*, *Angew. Chem. Int. Ed.* **2012**, *51*, 6074.

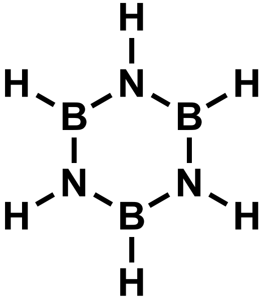
1-4. Aromaticity of Borazine

"The sp^2-type BN/CC isosterism associated with conjugated aromatic systems has most attention."

Because of....

- **the ubiquity and wide utility of arene-containing compounds**
- **the increased stability of the corresponding BN-containing isosteres compounds to sp$_3$-type BN isosteres**

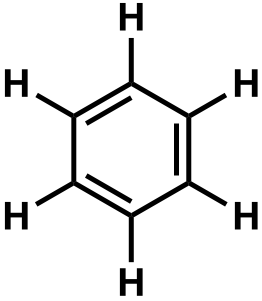
Alfred Stock (1926)



Borazine

- **Inorganic benzene**
- **The aromatic character**

Faraday (1825)



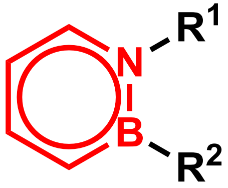
Benzene

→ **Potential to dramatically increase the diversity of aromatic structures**

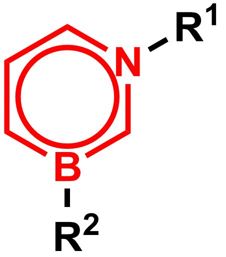
Alfred Stock, Erich Pohland, *Ber. Dtsch. Chem. Ges.* **1926**, *59*, 2210.
David E. Bean, Patrick W. Fowler, *J. Phys. Chem. A.* **2011**, *115*, 13649.

1-5. Shih-Yuan Liu & Azaborine family

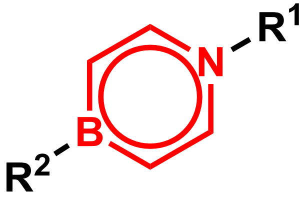
Shih-Yuan Liu



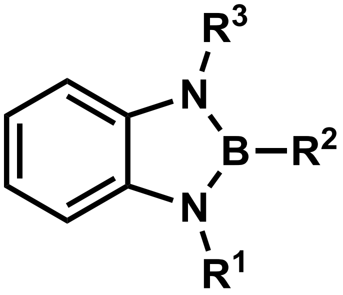
1,2-**Azaborine**



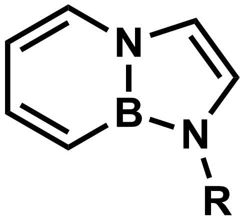
1,3-**Azaborine**



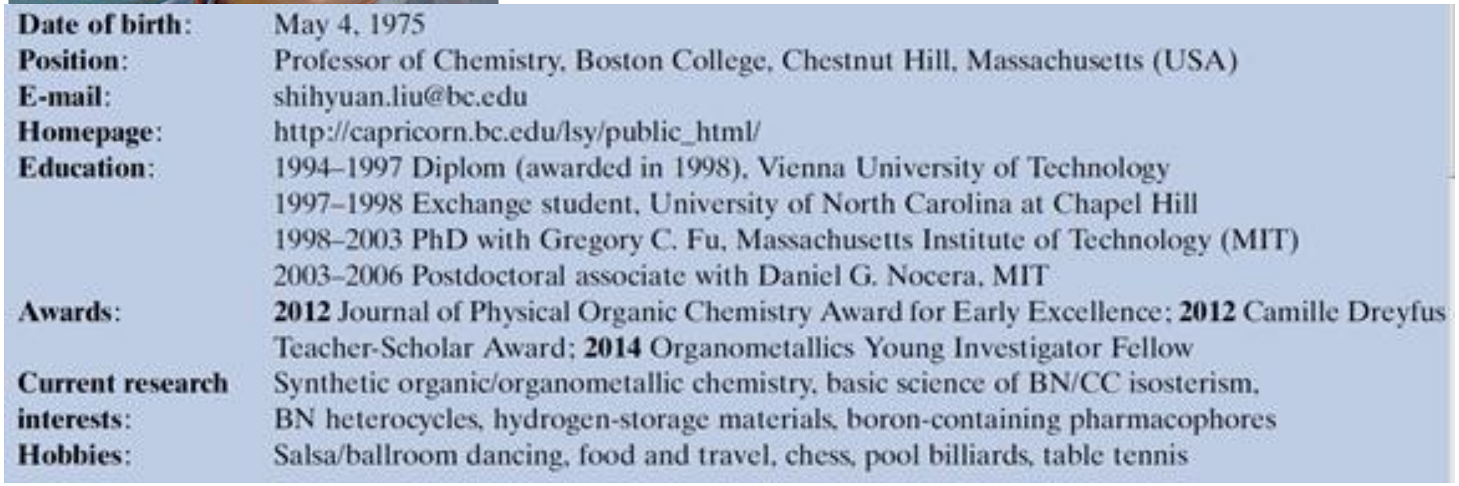
1,4-**Azaborine**



"External" BN indole



"Fused" BN indole



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Homepage:	http://capricorn.bc.edu/lsy/public_html/
Education:	1994–1997 Diplom (awarded in 1998), Vienna University of Technology 1997–1998 Exchange student, University of North Carolina at Chapel Hill 1998–2003 PhD with Gregory C. Fu, Massachusetts Institute of Technology (MIT) 2003–2006 Postdoctoral associate with Daniel G. Nocera, MIT
Awards:	**2012** Journal of Physical Organic Chemistry Award for Early Excellence; **2012** Camille Dreyfus Teacher-Scholar Award; **2014** Organometallics Young Investigator Fellow
Current research interests:	Synthetic organic/organometallic chemistry, basic science of BN/CC isosterism, BN heterocycles, hydrogen-storage materials, boron-containing pharmacophores
Hobbies:	Salsa/ballroom dancing, food and travel, chess, pool billiards, table tennis

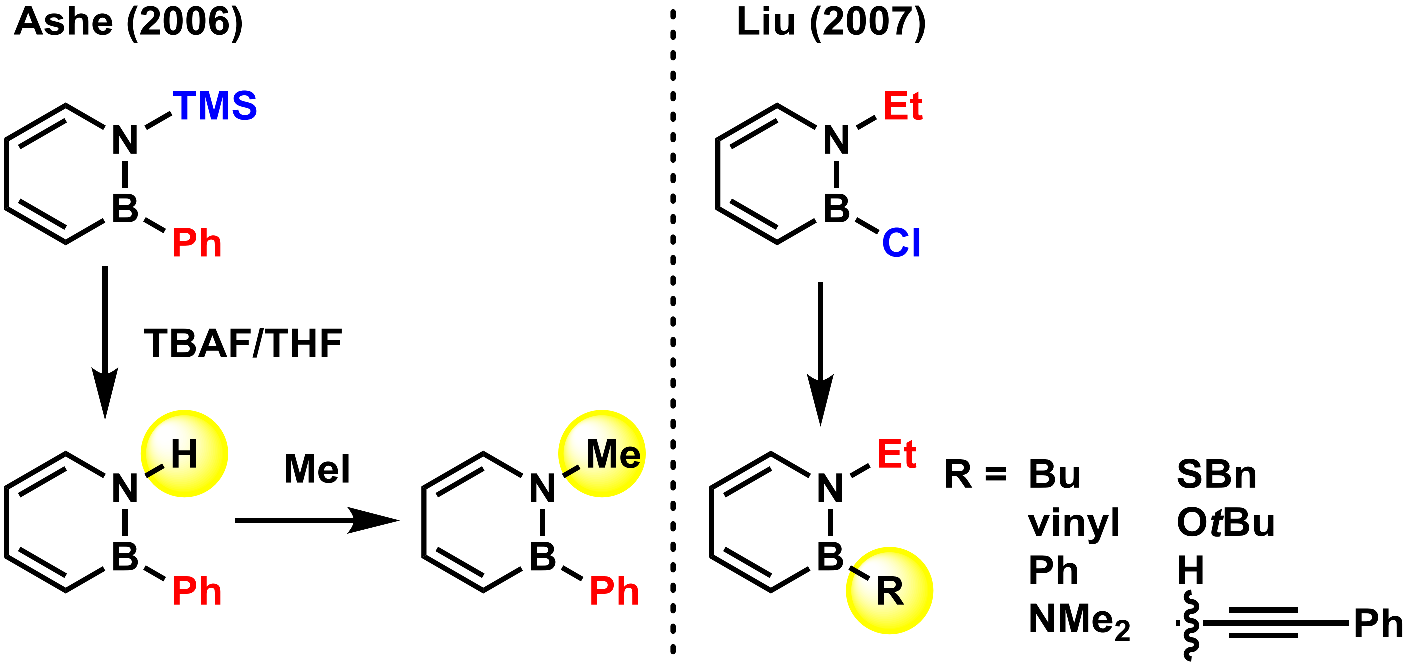
Author Profile, *Angew. Chem. Int. Ed.* **2015**, *54*, 726.

2. Characteristics of aromatized B-N compounds

- 2-1. 1,2-Azaborine
  - -1. Synthesis method
  - -2. Evidence of aromaticity
  - -3. Reactivity
- 2-2. 1,3-Azaborine
- 2-3. BN indole
  - -1. Synthesis method
  - -2. Reactivity

2-1-1. Synthesis method

-1,2-Azaborine synthons-

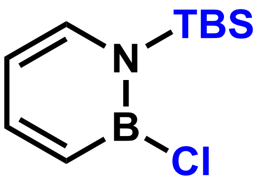


* **Nonremovable** groups are labeled red.
Removable and **functionalizable** groups are labeled green.

- Synthetic limitation is remained.
- The method for substitution of both N- and B- was not developed.

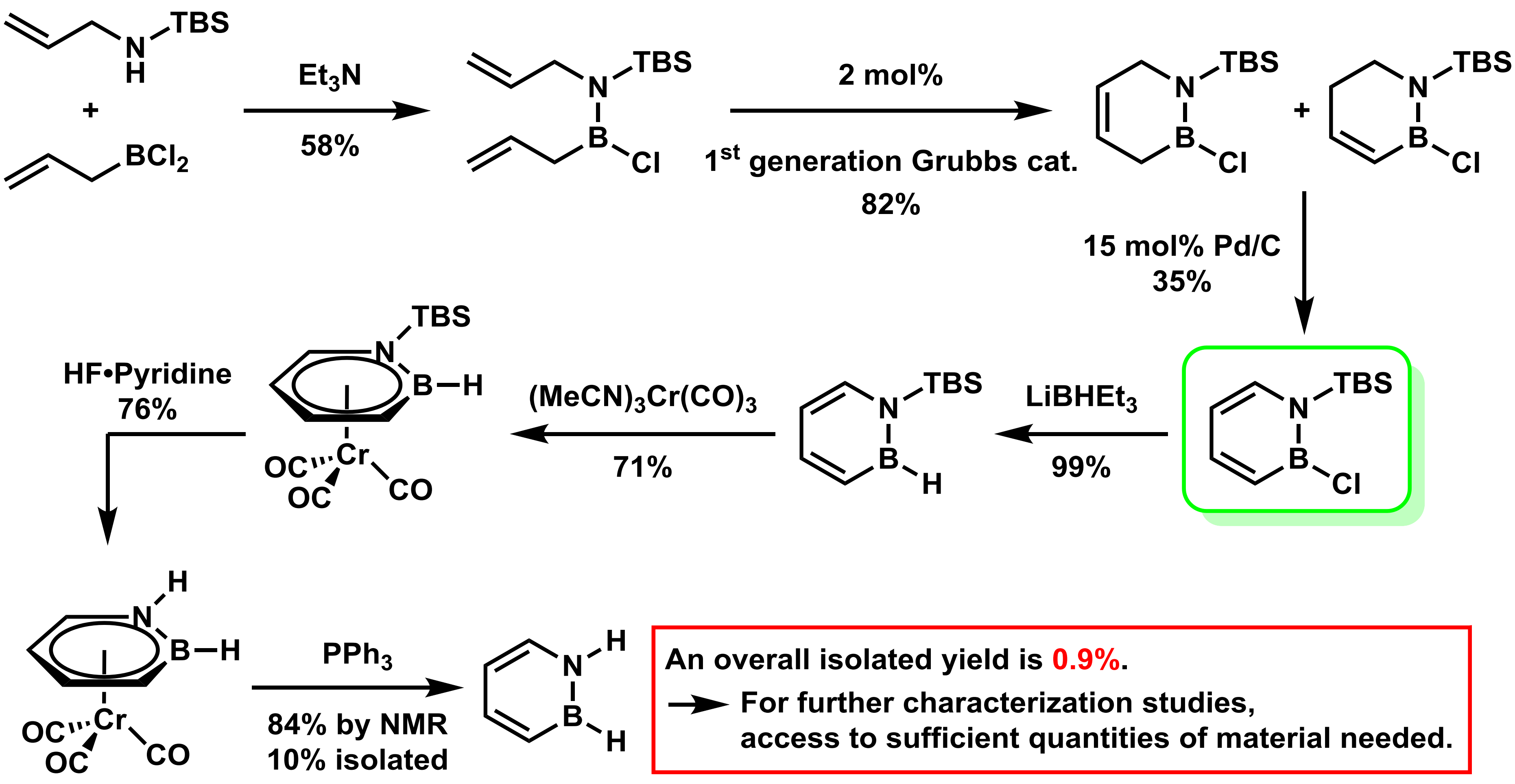
Arthur J. Ache, *et al.*, *Organometallics* **2004**, *23*, 5626.
Shih-Yuan Liu, *et al.*, *Org. Lett.* **2007**, *9*, 4905.
Shih-Yuan Liu, *et al.*, *J. Am. Chem. Soc.* **2013**, *135*, 12908.

Liu (2007)



2-1-1. Synthesis method

-Synthesis of 1,2-Azaborine (protecting group)-



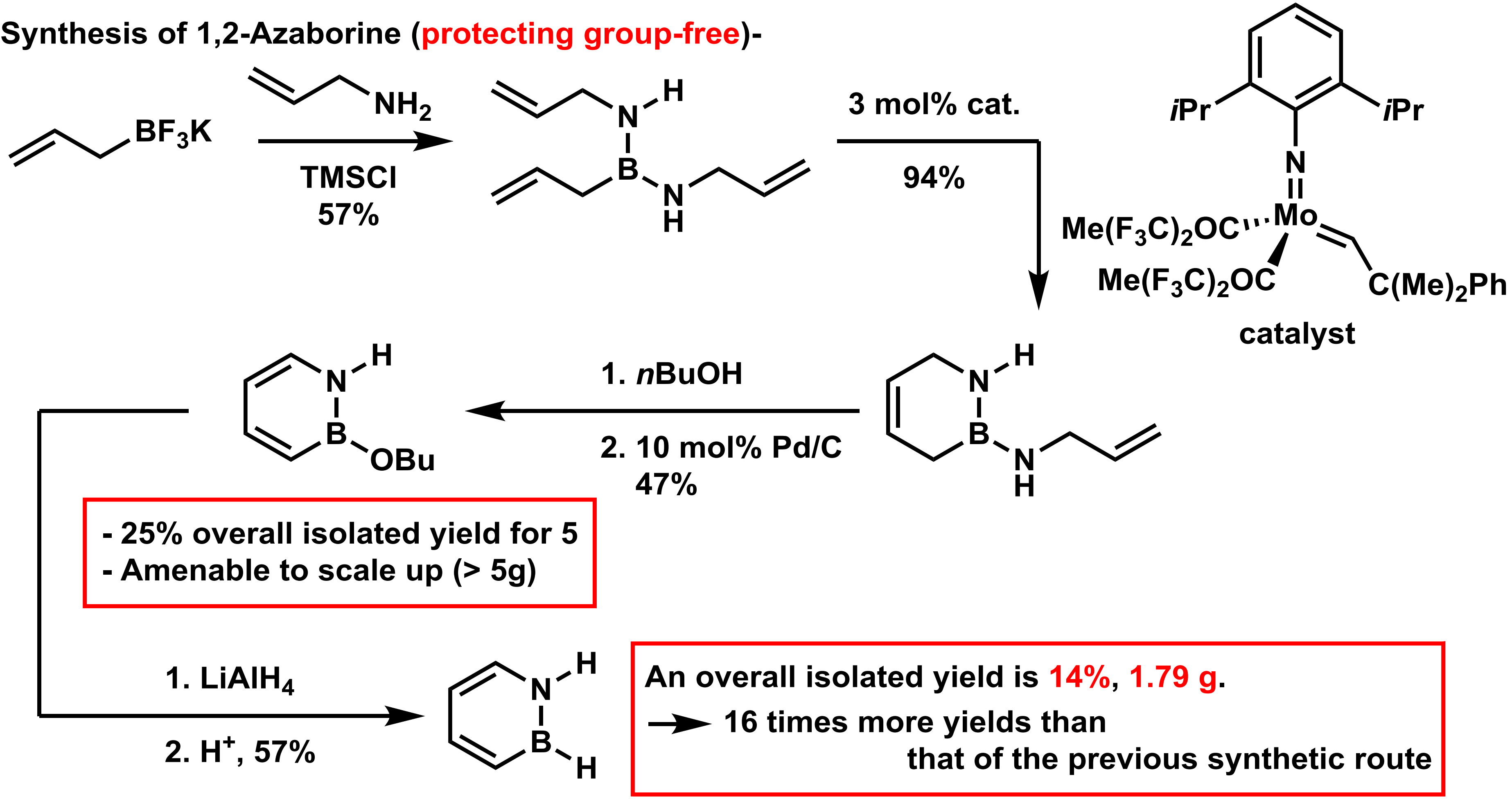
An overall isolated yield is 0.9%.

**→ For further characterization studies,
access to sufficient quantities of material needed.**

Shih-Yuan Liu, *et al.*, *Angew. Chem. Int. Ed*. **2009**, *48*, 973.

2-1-1. Synthesis method

-Synthesis of 1,2-Azaborine (protecting group-free)-



- **25% overall isolated yield for 5**
- **Amenable to scale up (> 5g)**

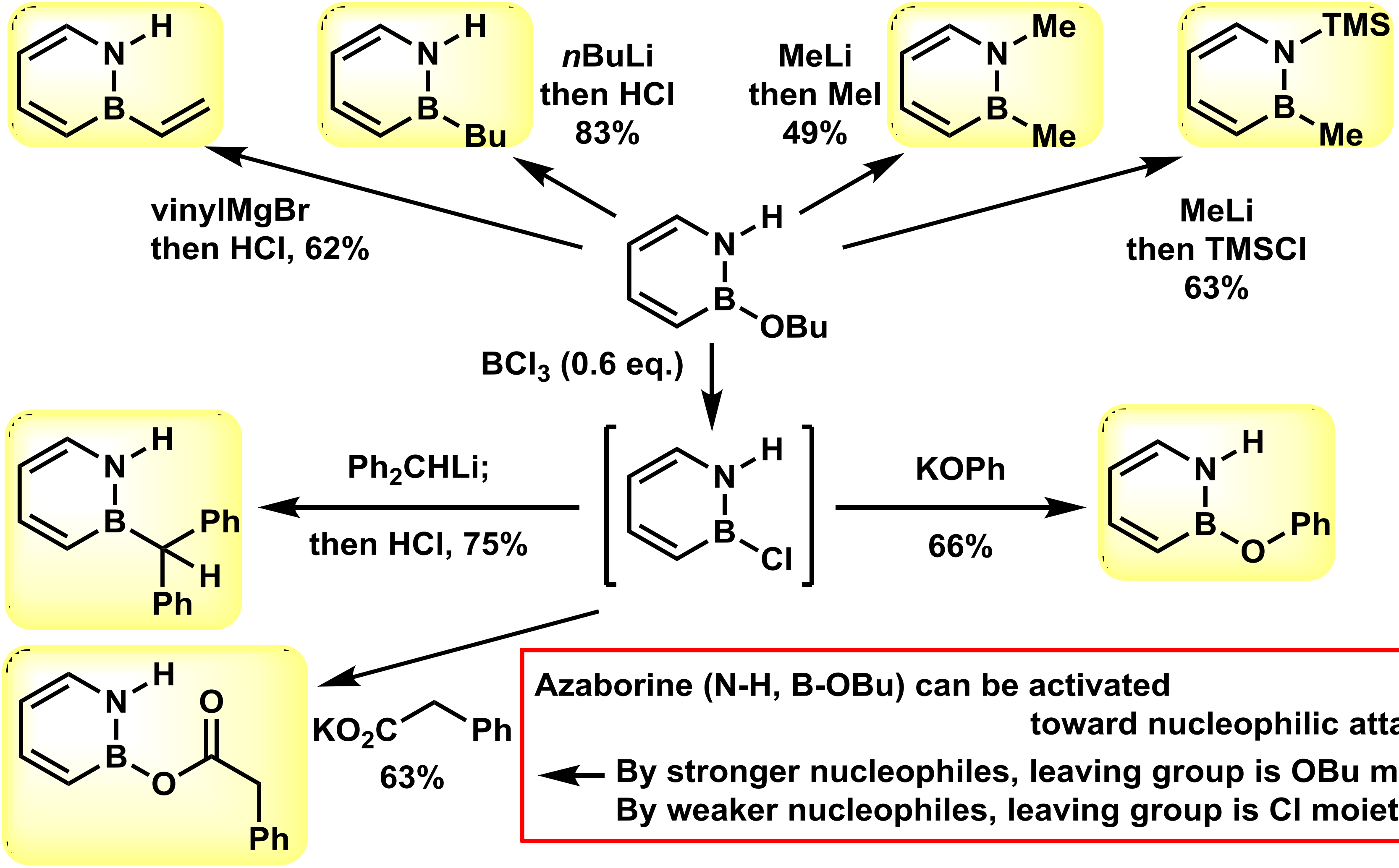
An overall isolated yield is 14%, 1.79 g.

→ 16 times more yields than that of the previous synthetic route

Shih-Yuan Liu, *et al.*, *J. Am. Chem. Soc.* **2013**, *135*, 12908.

2-1-1. Synthesis method

-Functionalization of 1,2-Azaborine-



Azaborine (N-H, B-OBu) can be activated toward nucleophilic attack.

← By stronger nucleophiles, leaving group is OBu moiety.
By weaker nucleophiles, leaving group is Cl moiety.

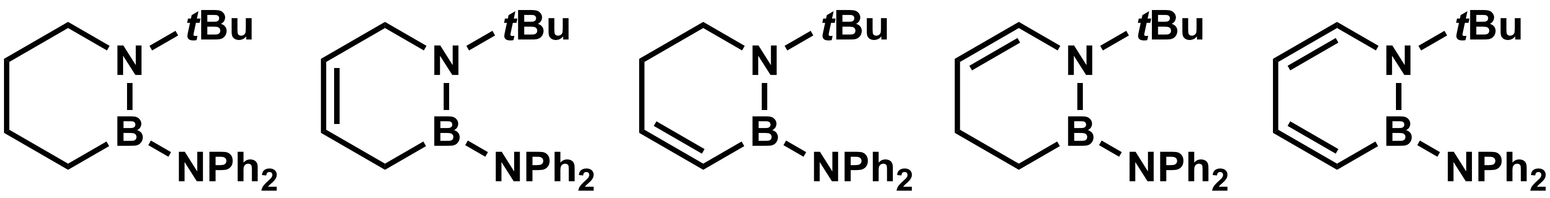
Shih-Yuan Liu, *et al.*, *J. Am. Chem. Soc.* **2013**, *135*, 12908.

2-1-2. Evidence of aromaticity

-The conditions for aromaticity-

1. **Cyclic -- The molecule must be a cyclic polyene**
2. **Planar -- The geometry of the cyclic part must be planar**
3. **Each atom in the cyclic system must have a p orbital perpendicular to the ring.**
4. **The cyclic system has 4n+2 π electrons.**

-Azaborine can meet all of the conditions?-



planarity[a]	**0.226**	**0.164**	**0.199**	**0.183**	**0.048**

* Structual data for all five heterocycles was obtained via single crystal X-ray diffraction.

[a] Root mean square deviation of intra-ring atoms from the least-squares plane (in Å)

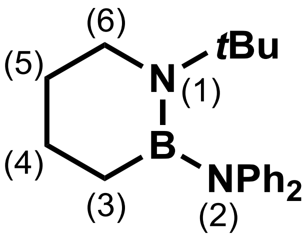
→ **All conditions for aromaticity are met in Azaborine structure.**

Shih-Yuan Liu, *et al.*, *J. Am. Chem. Soc.* **2008**, *130*, 7250.

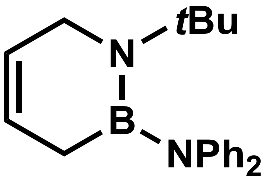
2-1-2. Evidence of aromaticity

-Supporting data for aromaticity of Azaborine-

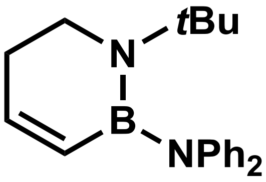
1. Bond distances



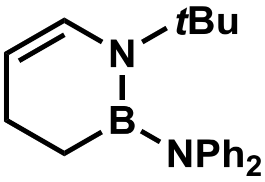
1



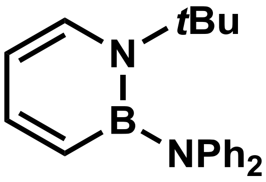
2



3



4



5

		1	2	3	4	5
N(1)**-B**	(Å)	**1.403(2)**	**1.405(2)**	**1.407(2)**	**1.417(3)**	**1.446(2)**
B-C(3)		**1.584(3)**	**1.590(2)**	**1.559(2)**	**1.579(4)**	**1.518(2)**
C(3)**-C**(4)		**1.511(3)**	**1.493(2)**	**1.338(2)**	**1.504(4)**	**1.363(2)**
C(4)**-C**(5)		**1.511(3)**	**1.319(2)**	**1.479(2)**	**1.494(4)**	**1.412(2)**
C(5)**-C**(6)		**1.508(3)**	**1.493(2)**	**1.503(2)**	**1.319(3)**	**1.356(2)**
C(6)**-N**(1)		**1.479(2)**	**1.477(2)**	**1.479(2)**	**1.432(3)**	**1.383(2)**
B-N(2)		**1.488(2)**	**1.478(2)**	**1.483(2)**	**1.480(3)**	**1.486(2)**

* Structual data gor all five heterocycles was obtained via single crystal X-ray diffraction.

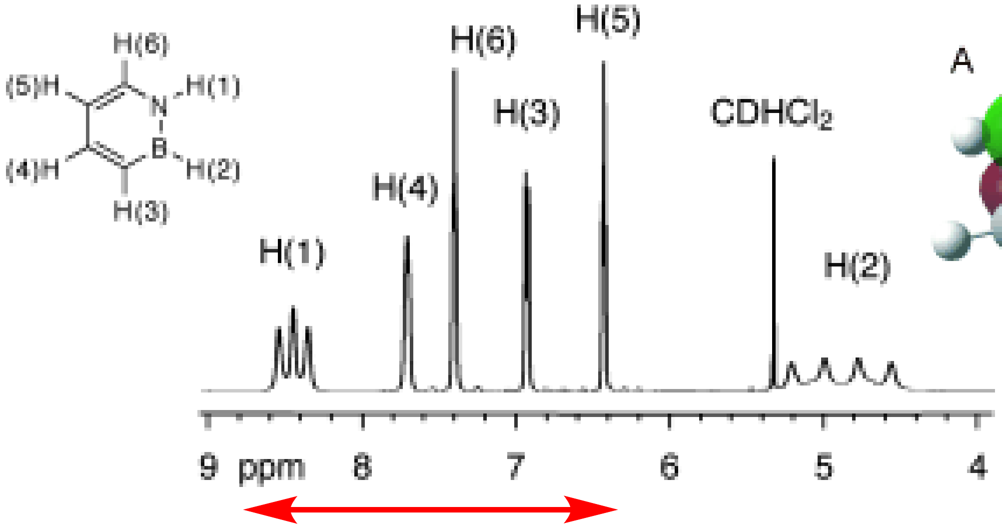
- **All nonaromatic structures (1-4) have B-N bond distances consistent with significant double bond character (~1.41 Å), which lengthen to 1.45 Å after oxidation to 5.**
- **Formal C=C double bonds in 2,3 and 4 lengthen significantly upon aromatization.**
- **All formal single bonds shorten upon aromatization.**

Shih-Yuan Liu, *et al.*, *J. Am. Chem. Soc.* **2008**, *130*, 7250.

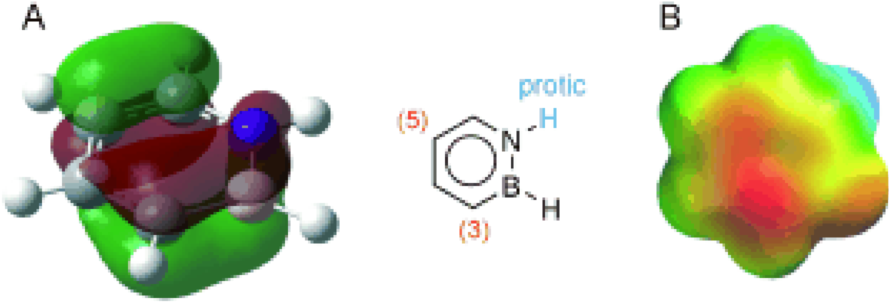
2-1-2. Evidence of aromaticity

-Supporting data for aromaticity of Azaborine-

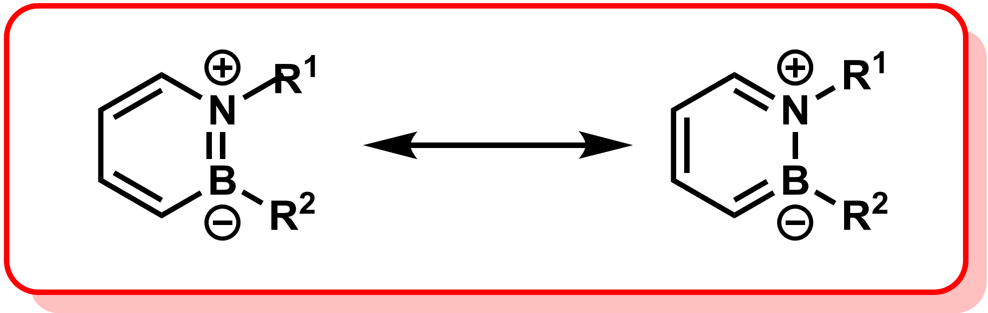
2. ^{1}H NMR



chemical shift for aromatic H



A) HOMO of 1,2-Azaborine
B) Electrostatic potential surface

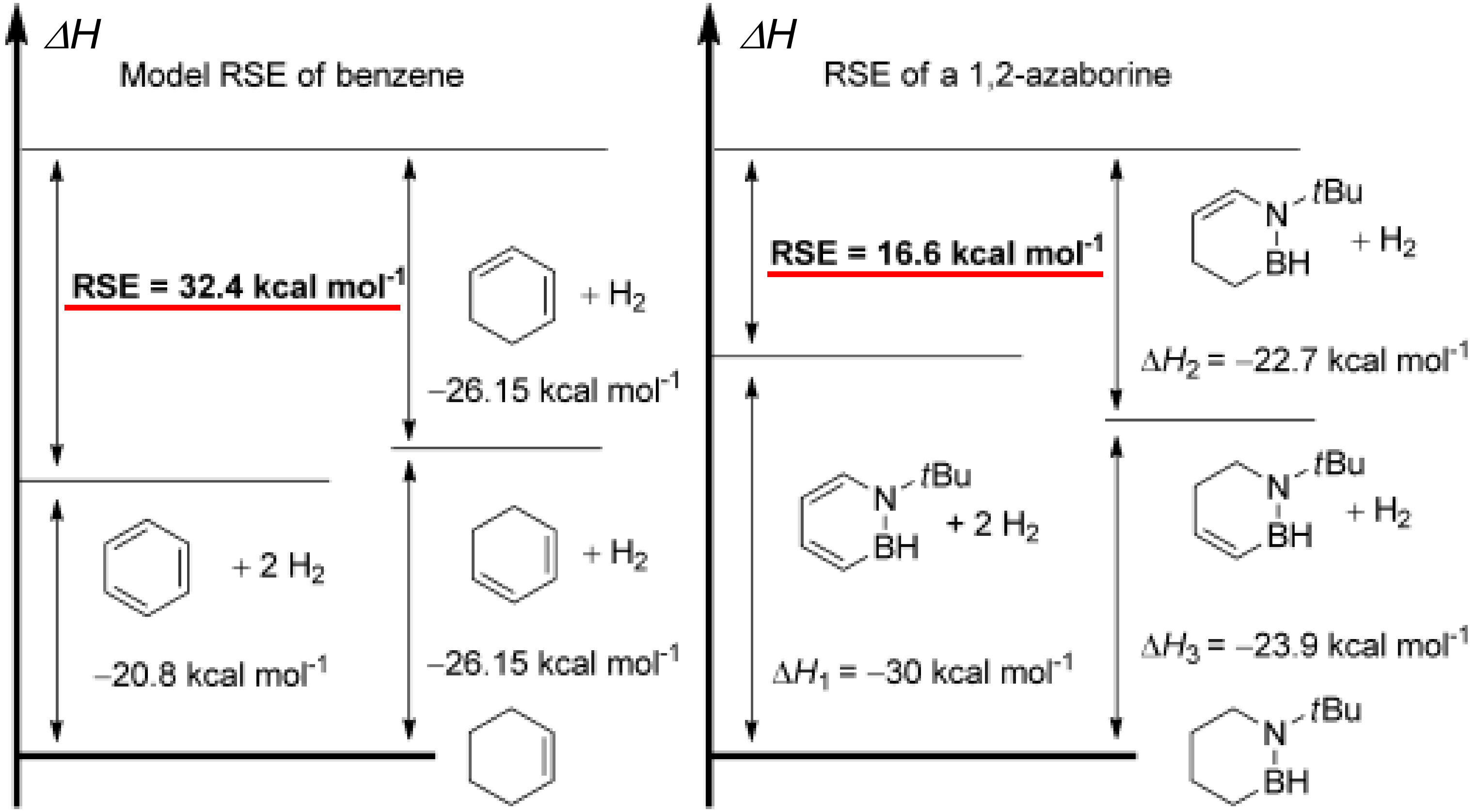


Shih-Yuan Liu, *et al.*, *J. Am. Chem. Soc.* **2008**, *130*, 7250.

2-1-2. Evidence of aromaticity

-Supporting data for aromaticity of Azaborine-

3. The resonance stabilization energy (RSE)



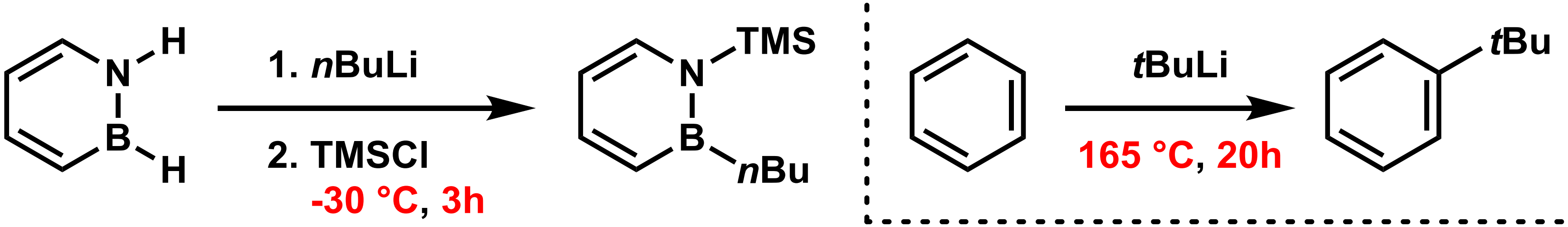
- **Significant additional stability by 6-π-electron delocalization**
- **1,2-Azaborines are less aromatic than their all-carbon counterparts.**

Shih-Yuan Liu, *et al.*, *J. Am. Chem. Soc.* **2010**, *132*, 18048.

2-1-3. Reactivity

-Nucleophilic Aromatic Substitution Reaction (SNArR)-

"What is the fundamental reactivity differences between Azaborine and benzene?"



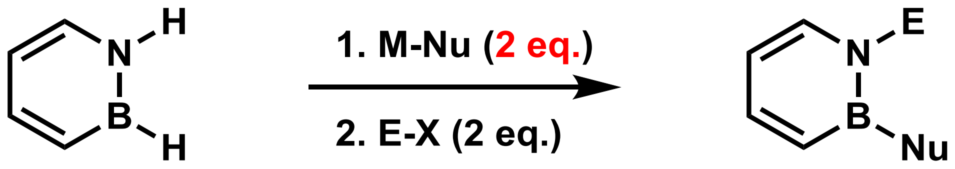
entry	*n*BuLi (eq.)	yield (%)
1	1	17
2	2	94
3	3	71

- The ease with which this substitution occurs is distinct from the reactivity of benzene.
- 2 equivalents of *n*BuLi is needed to achieve a high yield.

J. A. Dixon, D. H. Fishman, *J. Am. Chem. Soc.* **1963**, *85*, 1356.
Shih-Yuan Liu, *et al.*, *Angew. Chem. Int. Ed.* **2011**, *50*, 8157.

2-1-3. Reactivity (SNArR substrate scope)

-Substrate scope of SNAr reaction-



entry	M-Nu	E-X	yield (%)
1	Na-O*t*Bu	H-Cl	63
2	K-Oallyl	H-Cl	79
3	Li-*t*Bu	H-Cl	81
4	Li-*n*Bu	H-Cl	80
5	Li-Ph	H-Cl	98
6	BrMg-vinyl	H-Cl	59
7	BrMg$-\equiv-$Ph	H-Cl	71
8	Li-*n*Bu	TMS-Cl	89
9	Li-*n*Bu	Me-I	67
10	Li-*n*Bu	Bn-Cl	60

- Oxygen-based nucleophiles are suitable. (entry 1,2)

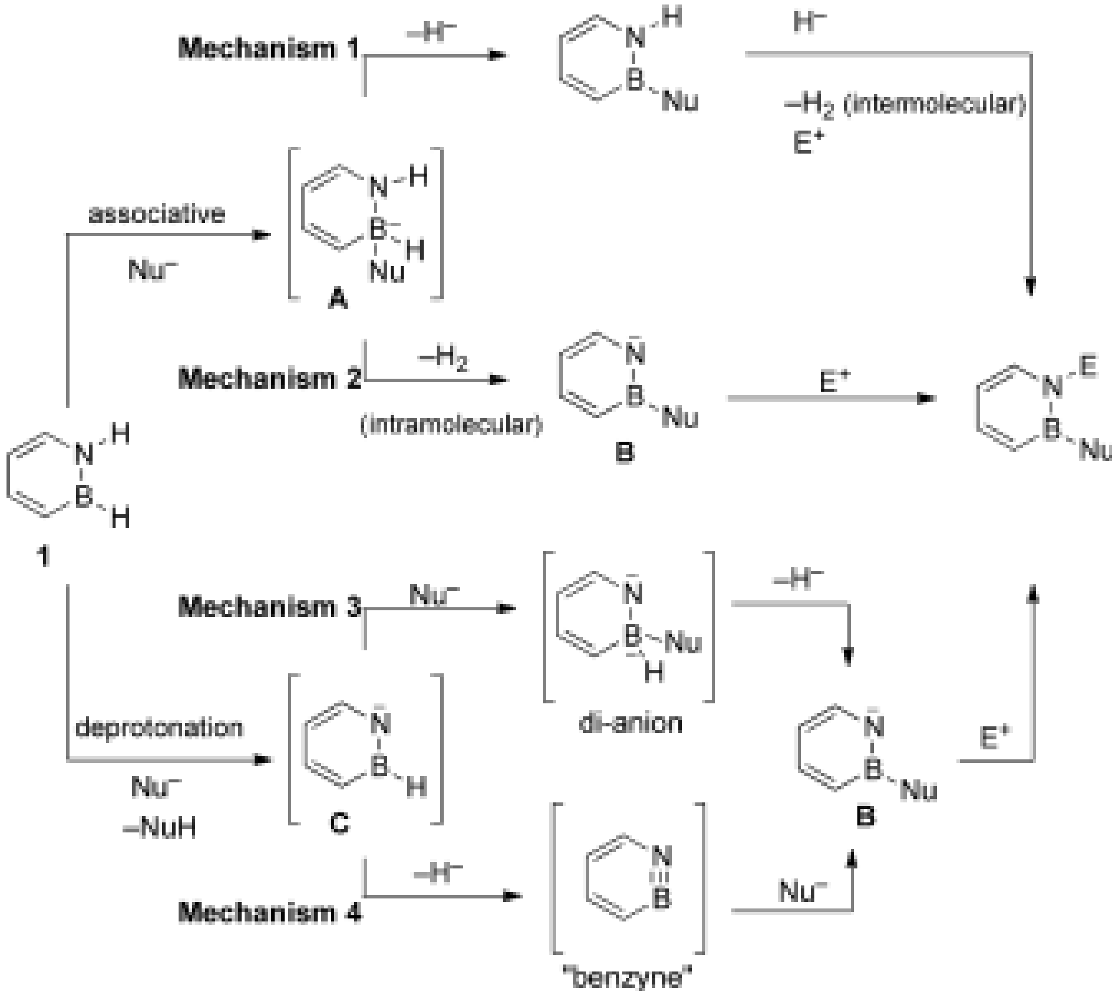
- Carbon nucleophiles are effective partners.
  hindered branched (entry 3)
  less-hindered linear (entry 4)
  sp^2-hybridized (entry 5)
  Grignard reagents (entry 6,7)

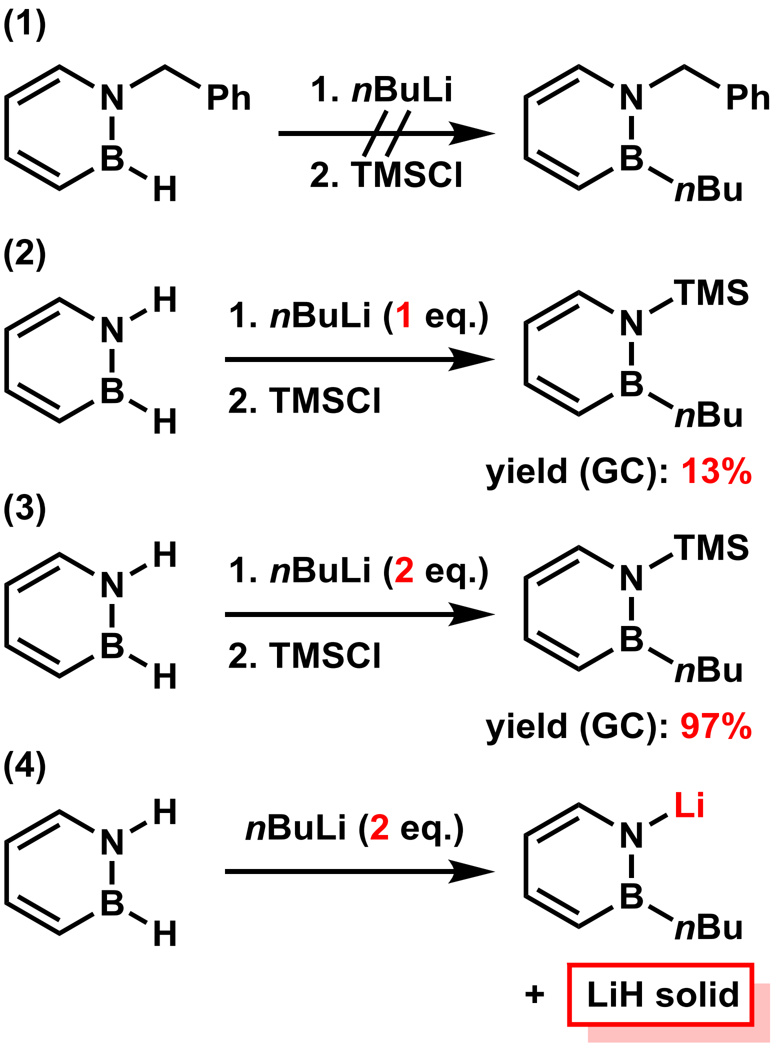
- Electrophiles at N position (entry 8,9,10)

Shih-Yuan Liu, *et al.*, *Angew. Chem. Int. Ed.* **2011**, *50*, 8157.

2-1-3. Reactivity (SNArR mechanism)

-Possible reaction pathways of SNAr reaction-





(1) -- not mechanism1
(2) vs (3) -- not mechanism2
(4) -- not mechanism1, 2

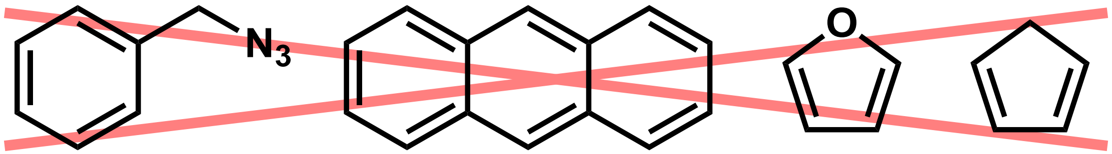
→ **mechanism3 or 4**

Shih-Yuan Liu, *et al.*, *Angew. Chem. Int. Ed.* **2011**, *50*, 8157.

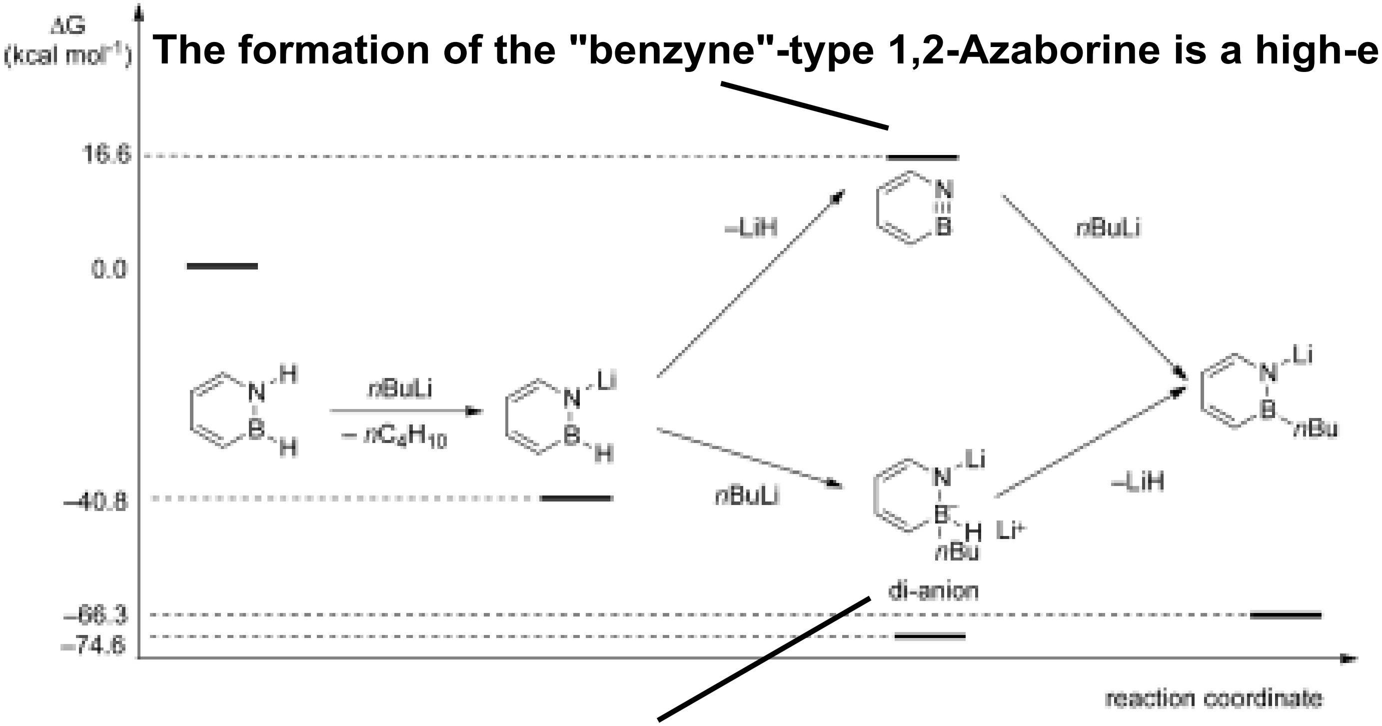
2-1-3. Reactivity (SNArR mechanism)

-Mechanism3 or 4-

Not successful in trapping the "benzyne"-type 1,2-Azaborine intermediate.



-The computationally determined energy diagram-



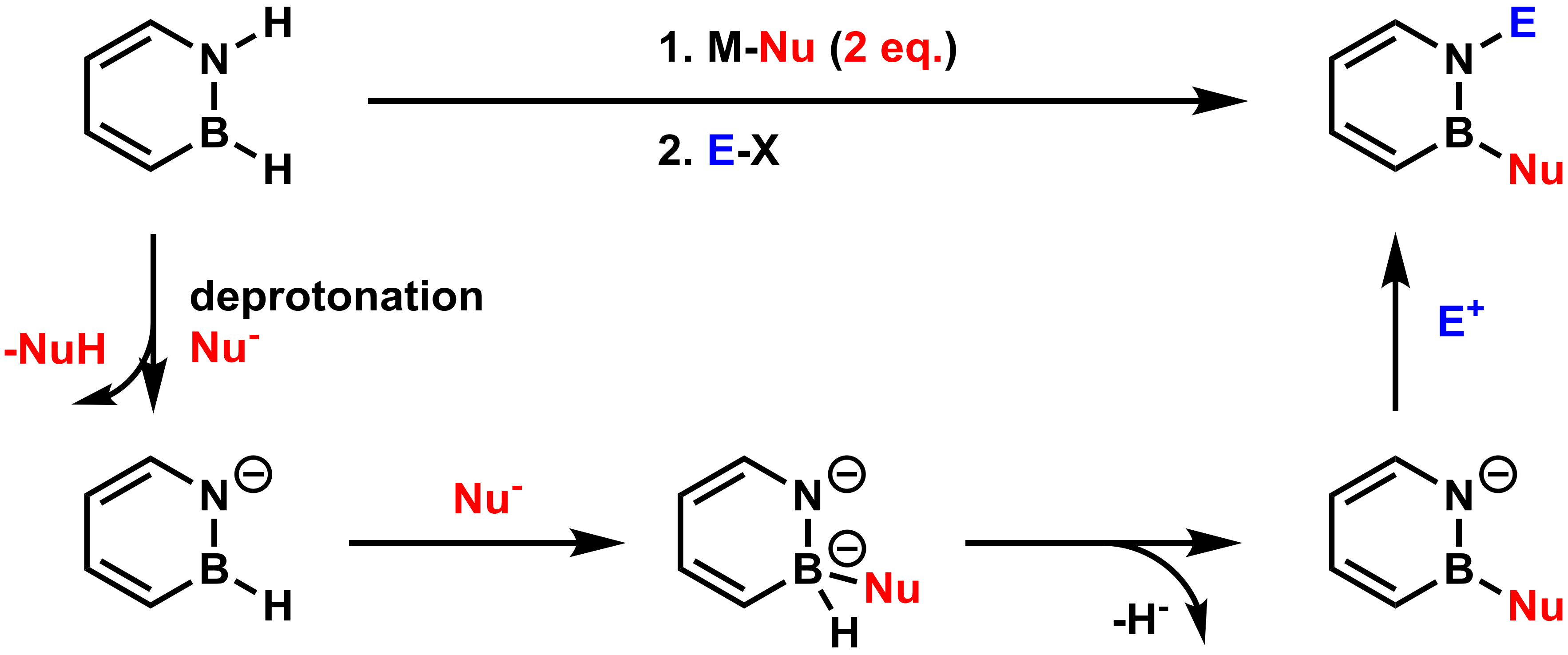
The formation of the "benzyne"-type 1,2-Azaborine is a high-energy process.

The formation of the "di-anion"intermediate is energetically very favorable.

Shih-Yuan Liu, *et al.*, *Angew. Chem. Int. Ed.* **2011**, *50*, 8157.

2-1-3. Reactivity (SNArR mechanism)

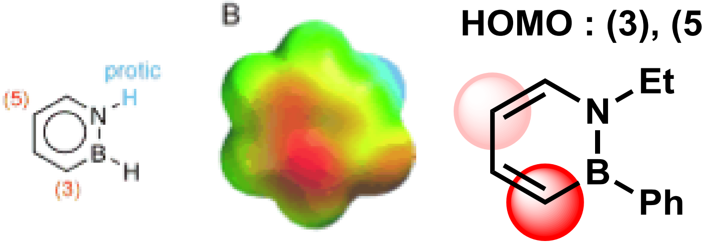
Mechanism3 is the most likely mechanism.



Shih-Yuan Liu, *et al.*, *Angew. Chem. Int. Ed.* **2011**, *50*, 8157.

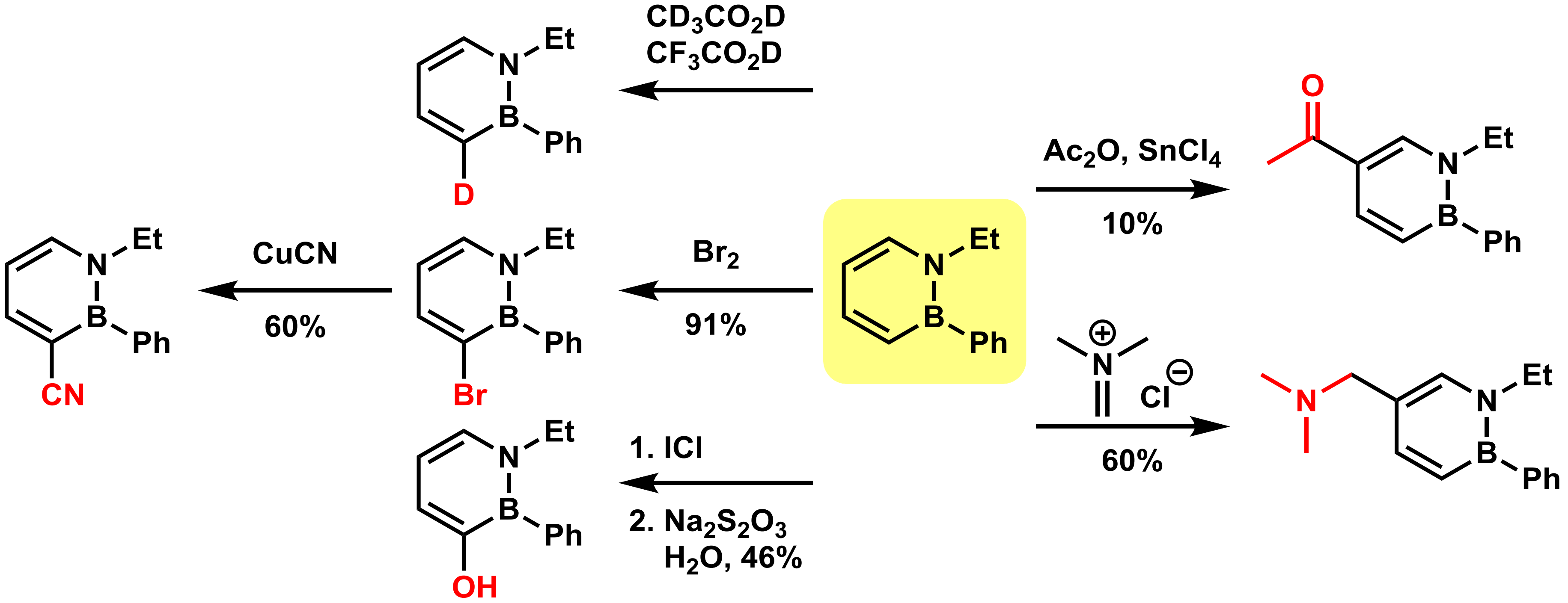
2-1-3. Reactivity (EASR)

-Electrophilic Aromatic Substitution Reaction (EASR)-



-Reaction at (3)-

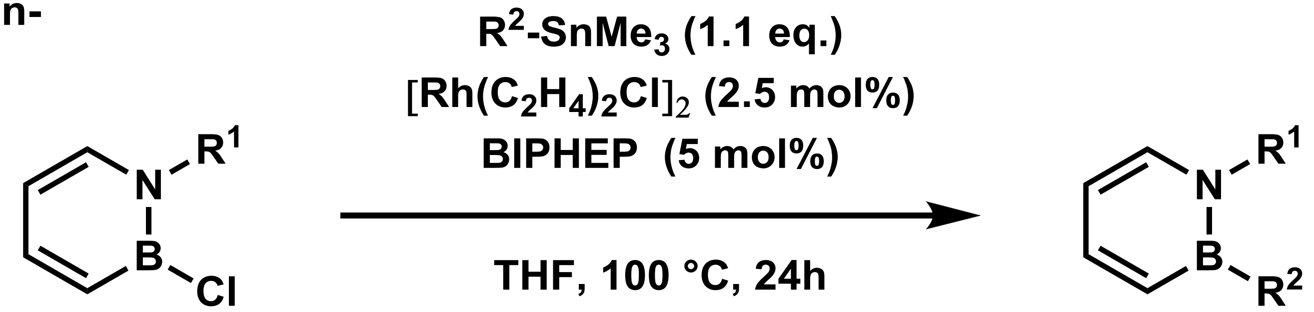
-Reaction at (5)-

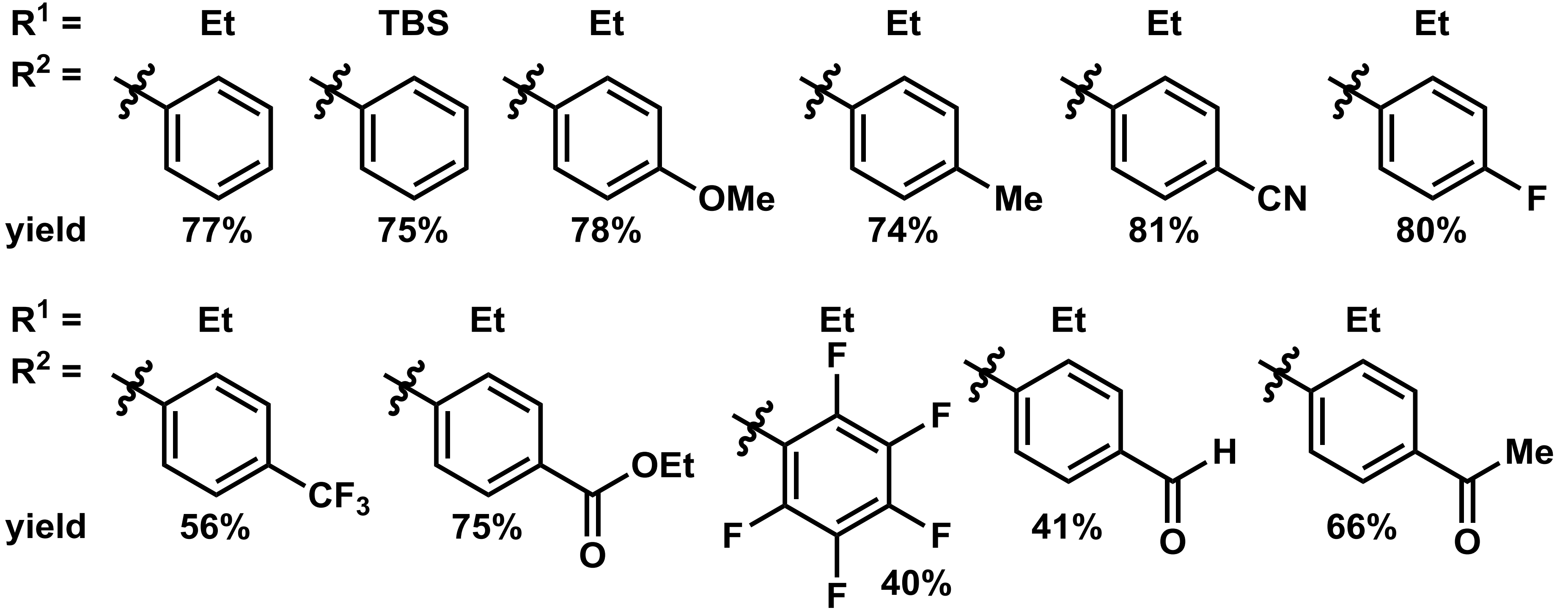


Shih-Yuan Liu, *et al.*, *J. Am. Chem. Soc.* **2008**, *130*, 7250.
Arthur J. Ashe, *et al.*, *Org. Lett.* **2007**, *9*, 679.
Shih-Yuan Liu, *et al.*, *J. Am. Chem. Soc.* **2011**, *133*, 20152.

2-1-3. Reactivity (B- functionalization)

-Boron Arylation-

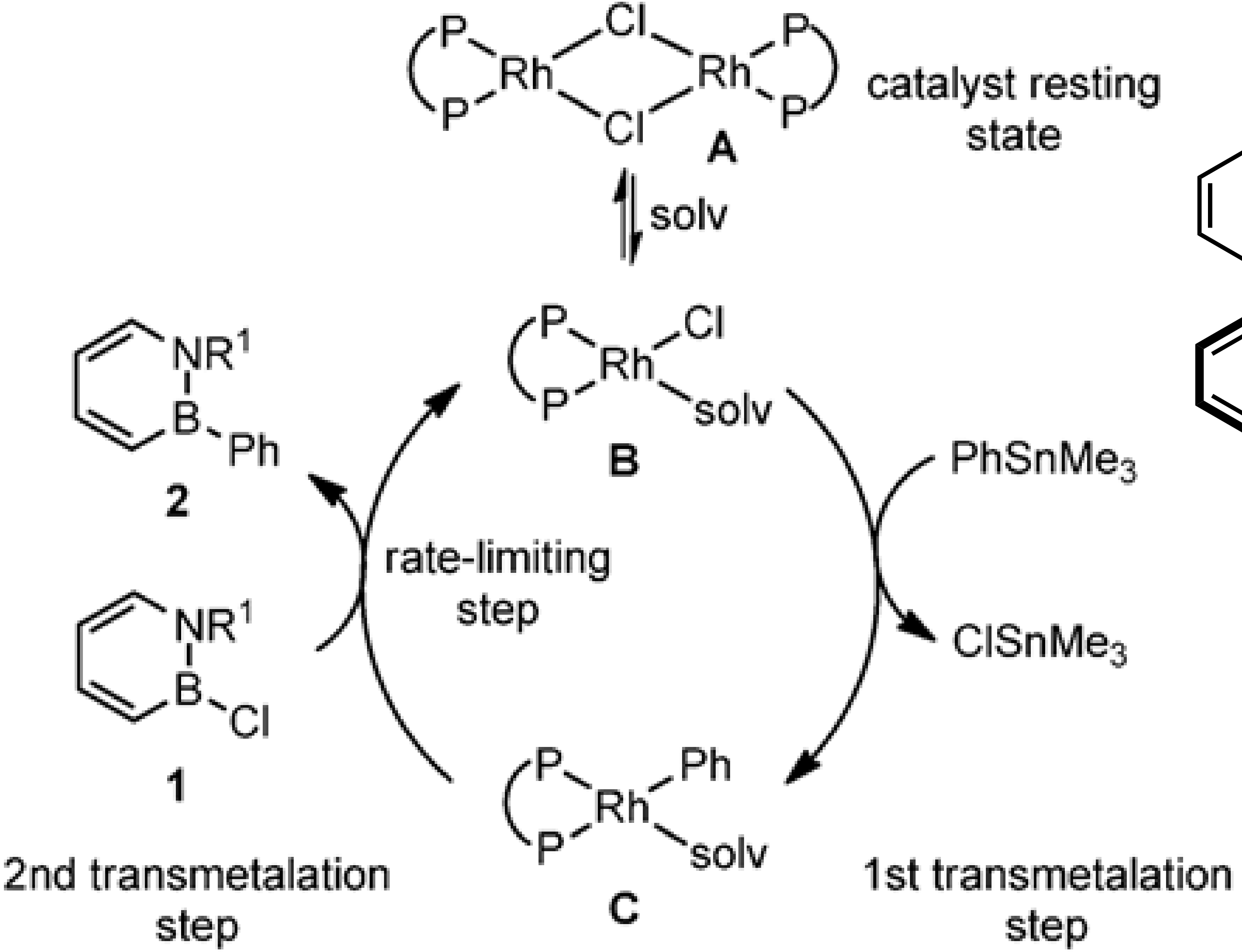

R^2-$SnMe_3$ (1.1 eq.)
$[Rh(C_2H_4)_2Cl]_2$ (2.5 mol%)
BIPHEP (5 mol%)
THF, 100 °C, 24h

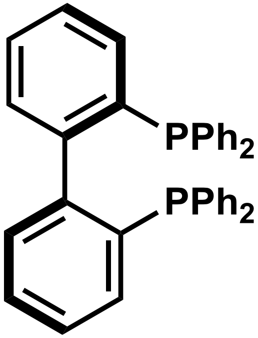


Shih-Yuan Liu, *et al.*, *Angew. Chem. Int. Ed.* **2013**, *52*, 9316.

Appendix 1

-Mechanism of Boron Arylation-



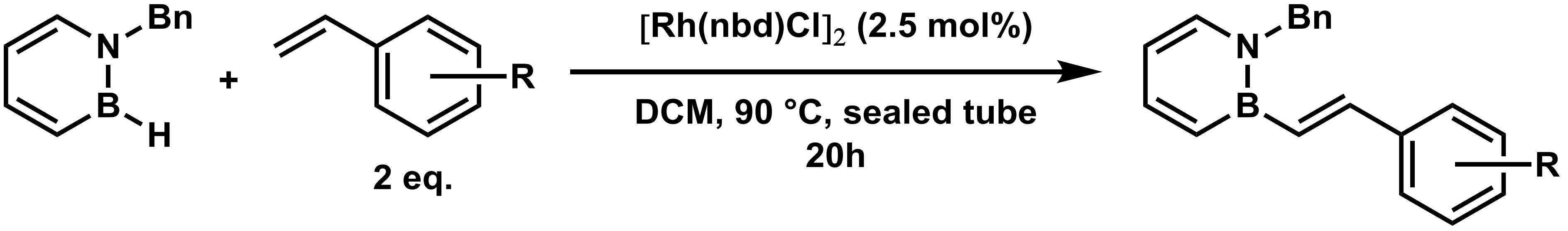


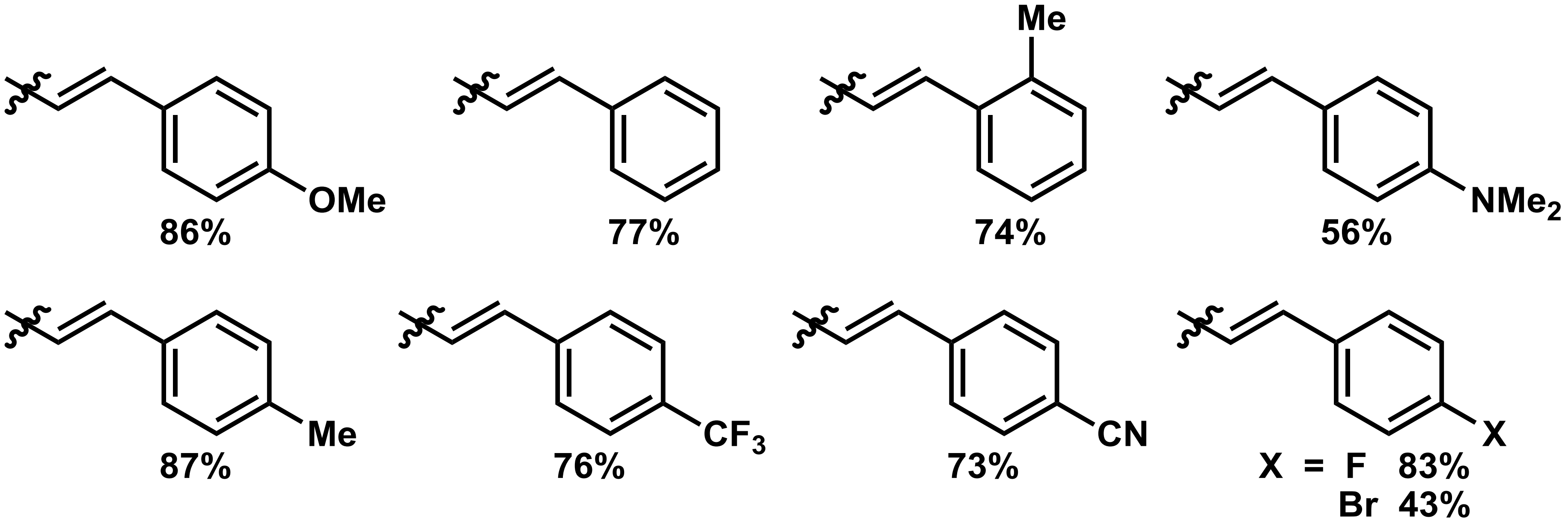
BIPHEP

Shih-Yuan Liu, *et al.*, *Angew. Chem. Int. Ed.* **2013**, *52*, 9316.

2-1-3. Reactivity (B- functionalization)

-B-H activation toward BN isosteres of Stilbenes-

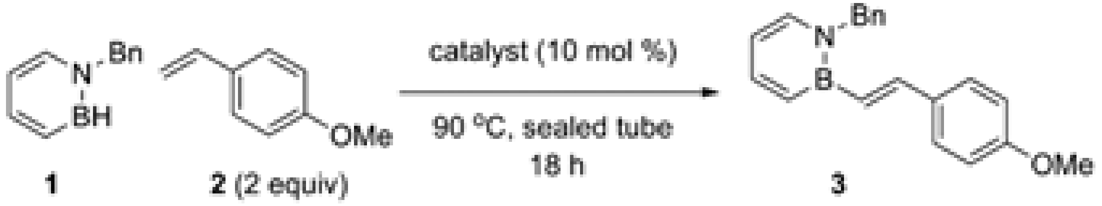


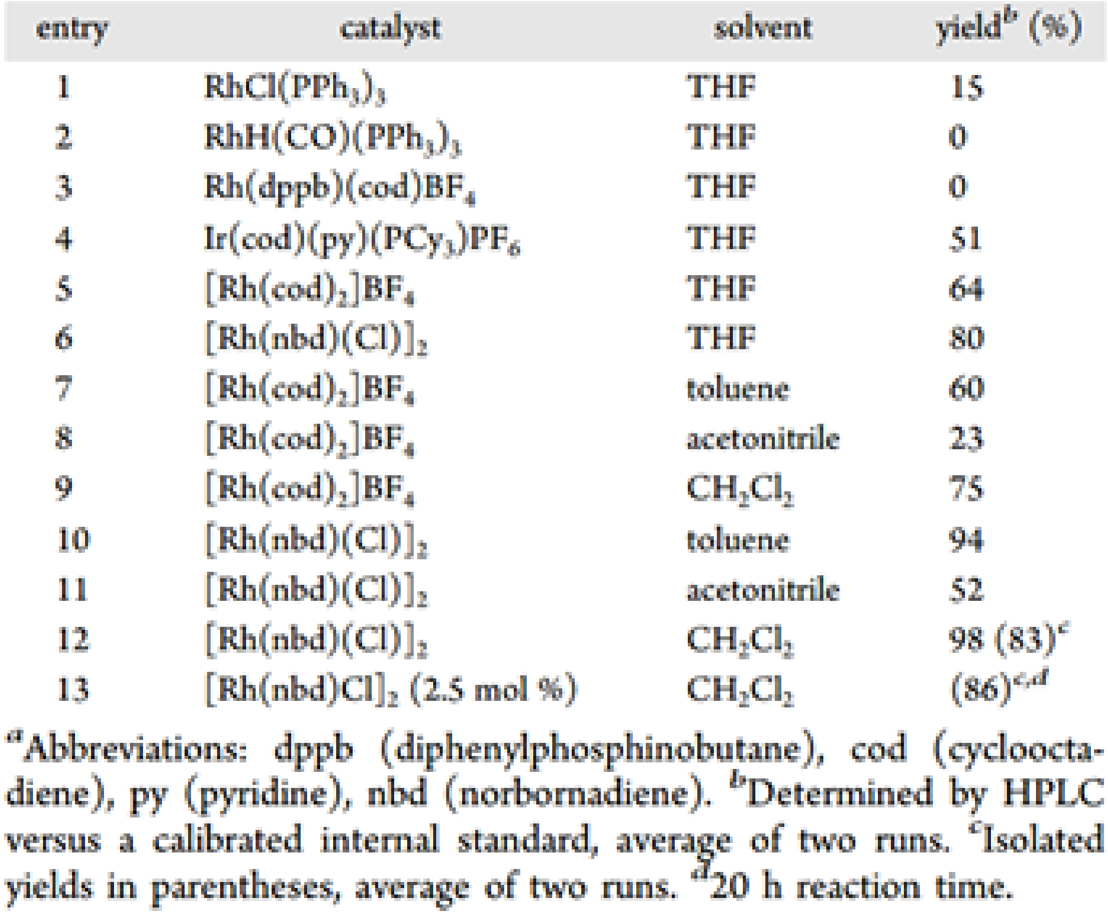


Shih-Yuan Liu, *et al.*, *Org. Lett.* **2014**, *16*, 3340.

Appendix 2

-Dehydrogenative Borylation Reaction-





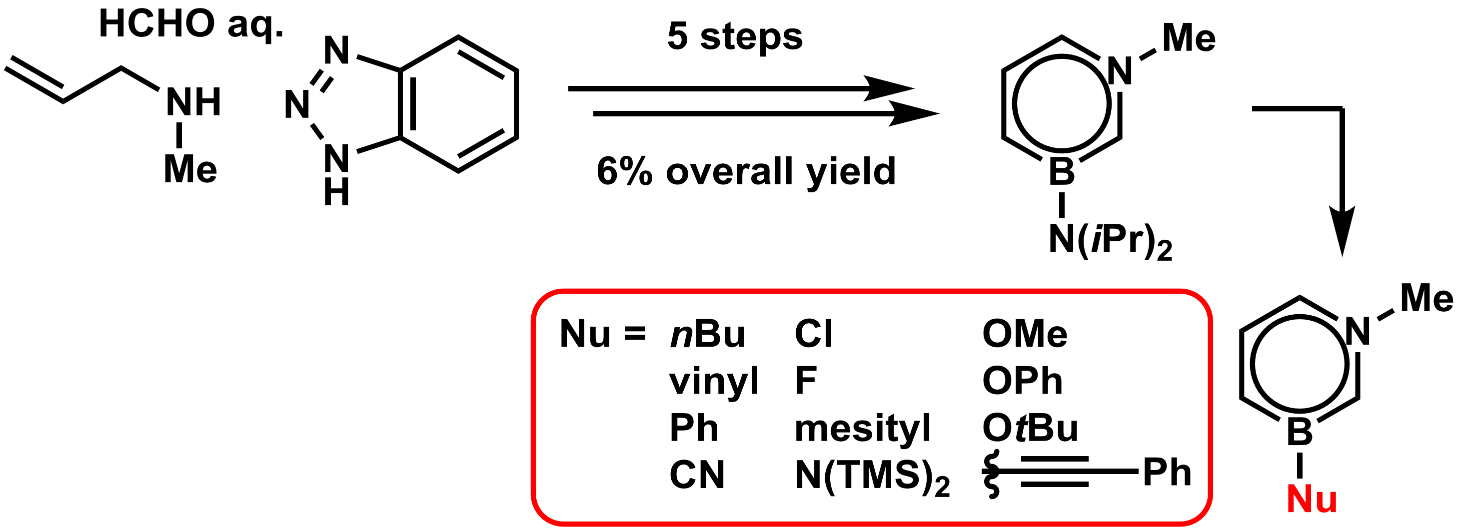
entry	catalyst	solvent	yield[b] (%)
1	$RhCl(PPh_3)_3$	THF	15
2	$RhH(CO)(PPh_3)_3$	THF	0
3	$Rh(dppb)(cod)BF_4$	THF	0
4	$Ir(cod)(py)(PCy_3)PF_6$	THF	51
5	$[Rh(cod)_2]BF_4$	THF	64
6	$[Rh(nbd)(Cl)]_2$	THF	80
7	$[Rh(cod)_2]BF_4$	toluene	60
8	$[Rh(cod)_2]BF_4$	acetonitrile	23
9	$[Rh(cod)_2]BF_4$	CH_2Cl_2	75
10	$[Rh(nbd)(Cl)]_2$	toluene	94
11	$[Rh(nbd)(Cl)]_2$	acetonitrile	52
12	$[Rh(nbd)(Cl)]_2$	CH_2Cl_2	98 (83)[c]
13	$[Rh(nbd)Cl]_2$ (2.5 mol %)	CH_2Cl_2	(86)[c,d]

[a] Abbreviations: dppb (diphenylphosphinobutane), cod (cyclooctadiene), py (pyridine), nbd (norbornadiene). [b] Determined by HPLC versus a calibrated internal standard, average of two runs. [c] Isolated yields in parentheses, average of two runs. [d] 20 h reaction time.

Shih-Yuan Liu, *et al.*, *Org. Lett.* **2014**, *16*, 3340.

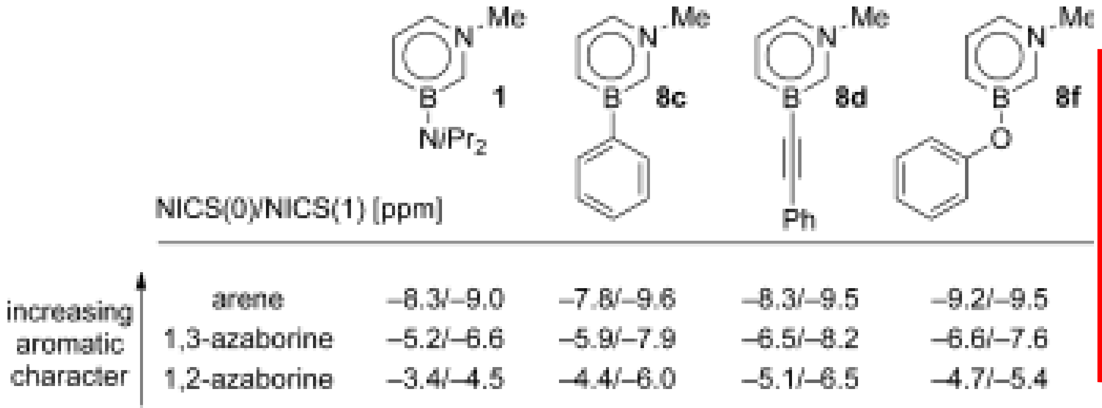
2-2. 1,3-Azaborine

-Reactivity-



Nu = *n*Bu, vinyl, Ph, CN, Cl, F, mesityl, N(TMS)$_2$, OMe, OPh, O*t*Bu, ≀—≡—Ph

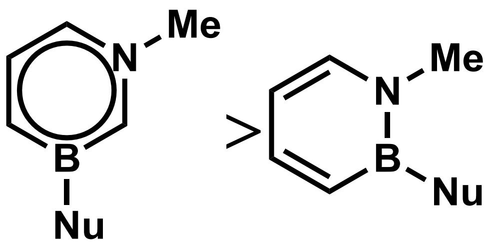
-Evaluation of Aromaticity-



NICS(0)/NICS(1) [ppm]	1	8c	8d	8f
arene	−8.3/−9.0	−7.8/−9.6	−8.3/−9.5	−9.2/−9.5
1,3-azaborine	−5.2/−6.6	−5.9/−7.9	−6.5/−8.2	−6.6/−7.6
1,2-azaborine	−3.4/−4.5	−4.4/−6.0	−5.1/−6.5	−4.7/−5.4

1,3-Azaborine 1, 8c, 8d, 8f and their corresponding 1,2-Azaborine and carbonaceous (arene) counterparts.

aromaticity



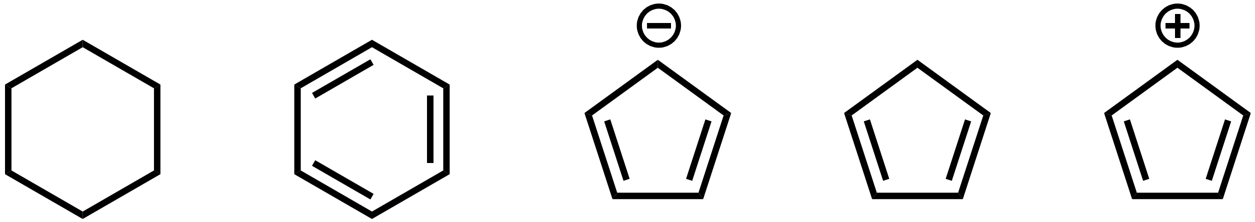
Shih-Yuan Liu, *et al.*, *J. Am. Chem. Soc.* **2011**, *133*, 20152.
Shih-Yuan Liu, *et al.*, *Angew. Chem. Int. Ed.* **2013**, *52*, 7527.

Appendix 4

-NICS (nucleus-independent chemical shift)-

The absolute magnetic shieldings at the center of the ring

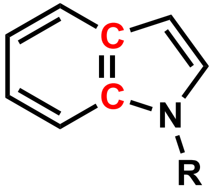
NICS $<$ 0 : aromaticity
NICS $>$ 0 : antiaromaticity



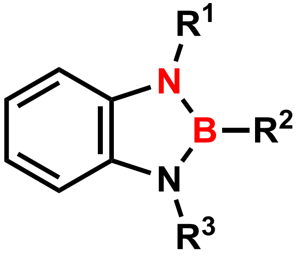
P. v. R. Schleyer, *et al.*, *J. Am. Chem. Soc.* **1996**, *118*, 6317.
K. Yamamoto, *Lit. Sem.* **2011**.

2-3-1. Synthesis method

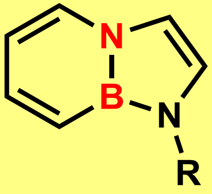
-BN indole family-



Indole

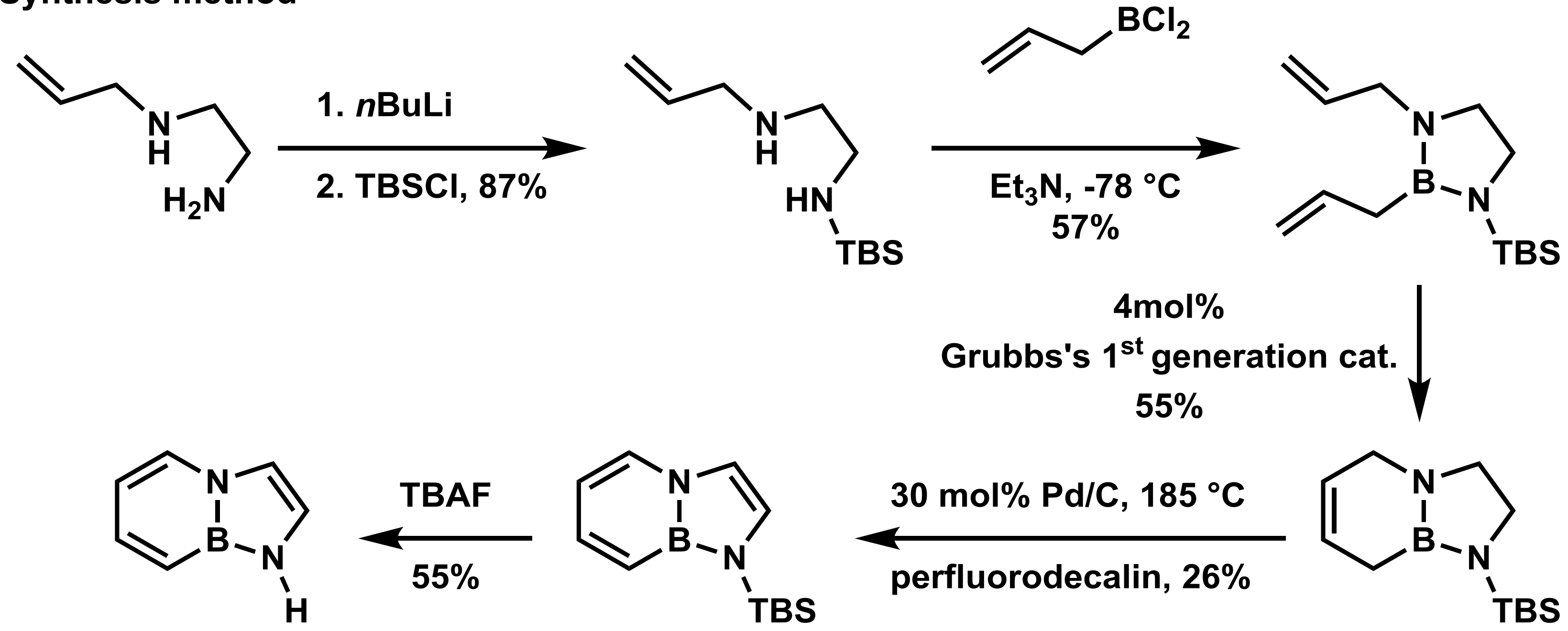


"External" BN indole



"Fused" BN indole

-Synthesis method-

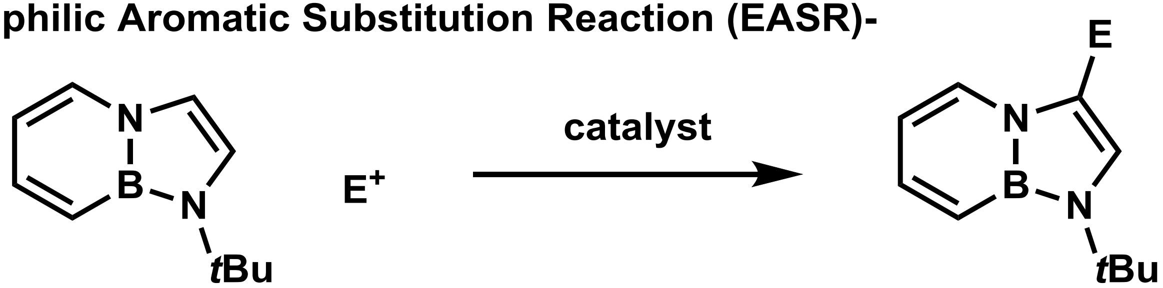


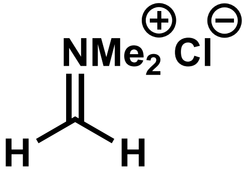
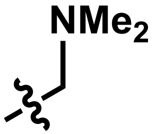
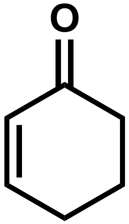
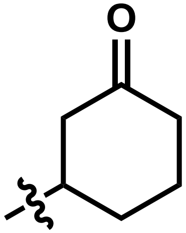
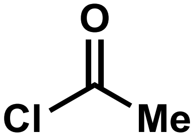
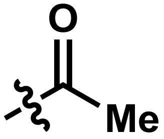
3.9% overall isolated yield

Shih-Yuan Liu, *et al.*, *J. Am. Chem. Soc.* **2011**, *133*, 11508.
Eric R. Abbey, Shih-Yuan Liu, *Org. Biomol. Chem.* **2013**, *11*, 2060.

2-3-2. Reactivity (EASR)

-Electrophilic Aromatic Substitution Reaction (EASR)-

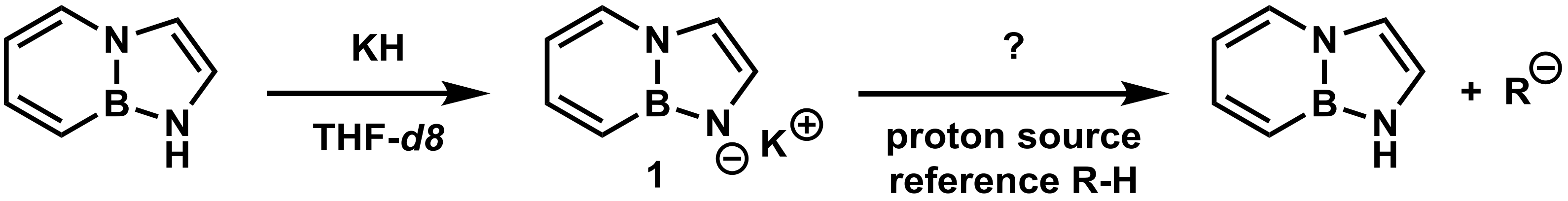


entry	electrophile (E^+)	catalyst	3-substituent (E)	yield (%)
1	Br_2	-	Br	39
2		-		53
3		$ZrCl_4$		57
4	CD_3OD/D_2O	-	D	39
5		Et_2AlCl		23

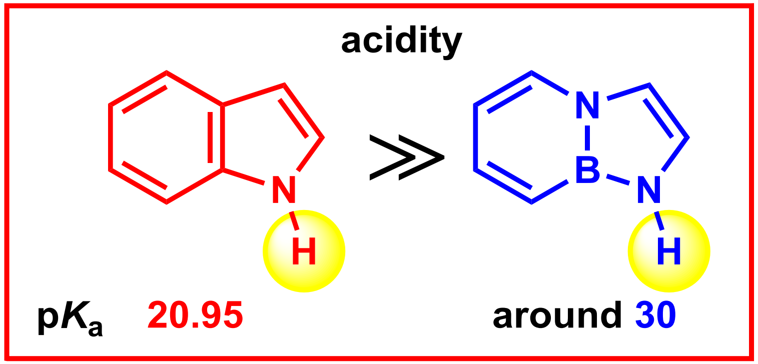
Shih-Yuan Liu, *et al.*, *J. Am. Chem. Soc.* **2010**, *132*, 16340.

2-3-2. Reactivity (p*K*a and BN vs natural)

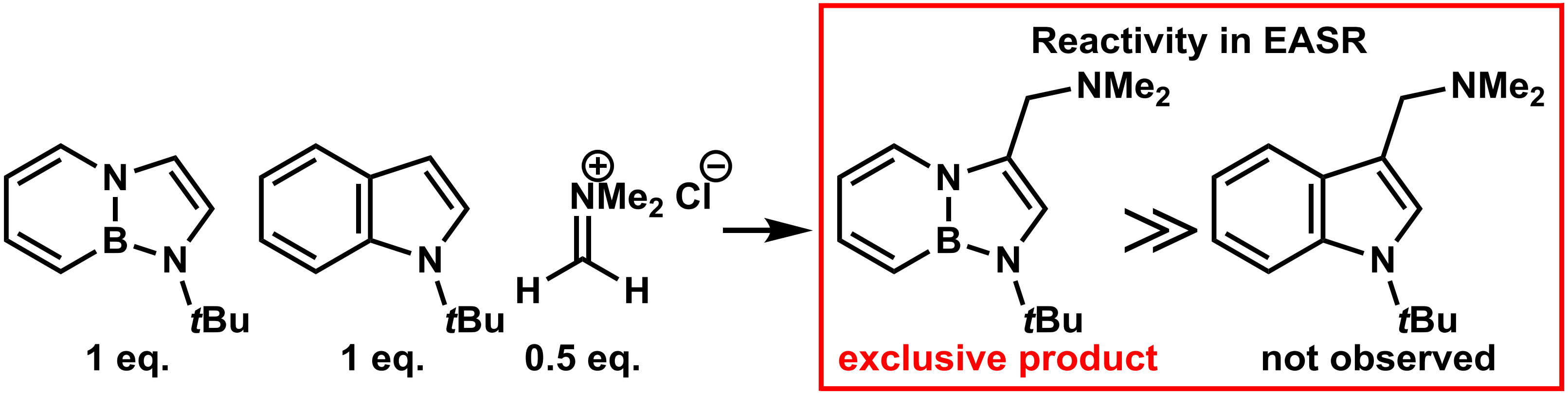
-pK_a for N-H of B-N indole-



R-H	pK_a (DMSO)	deprotonated by 1
Indole	20.95	yes
Ph_2NH	25	yes
PhCCH	28.8	yes
Ph_3H	30.6	trace
CH_3CN	31.3	no



-Competition in reactivity between "BN" indole and "natural" indole-



Frederick G. Bordwell, *Acc. Chem. Res.* **1988**, *21*, 456.
Shih-Yuan Liu, *et al.*, *J. Am. Chem. Soc.* **2011**, *133*, 11508.
Eric R. Abbey, Shih-Yuan Liu, *Org. Biomol. Chem.* **2013**, *11*, 2060.

3. Hydrogen storage

3-1. Availability of B-N compounds for HS

3-2. “Fully charged” fuel

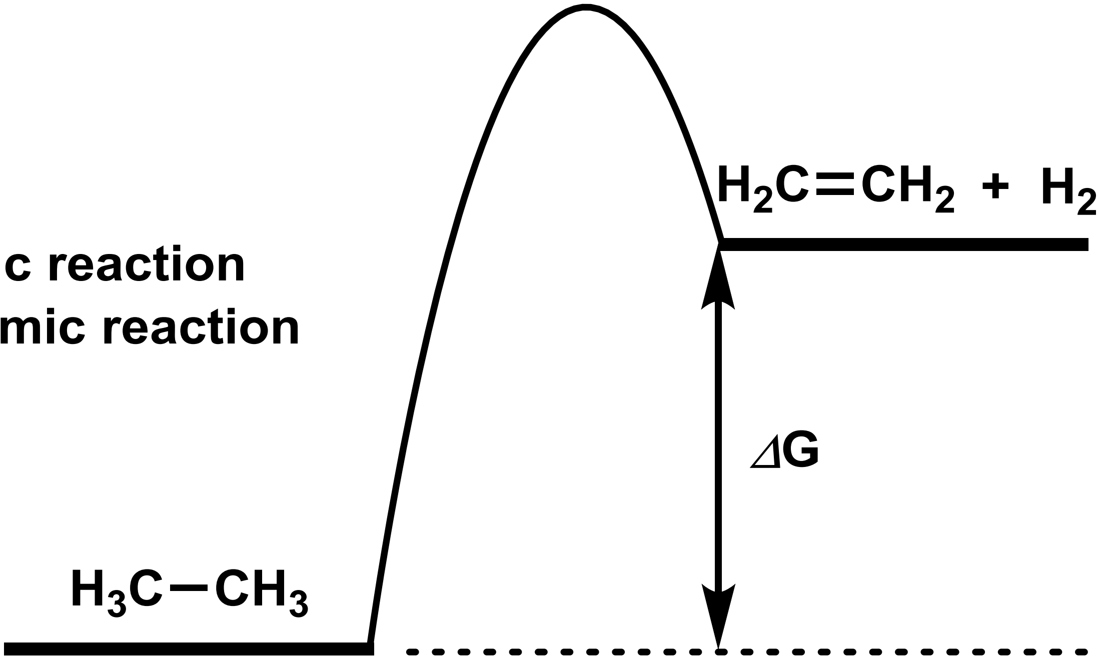
3-3. Process to release H_2

3-4. The leading-edge HS material

Appendix 5

- $\Delta G = \Delta H - T\Delta S$ -

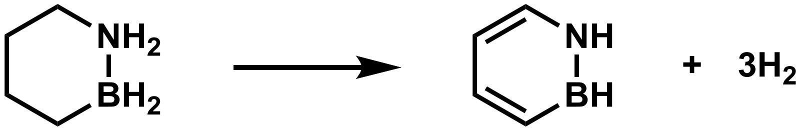
$\Delta H < 0$: exothemic reaction
$\Delta H > 0$: endothermic reaction

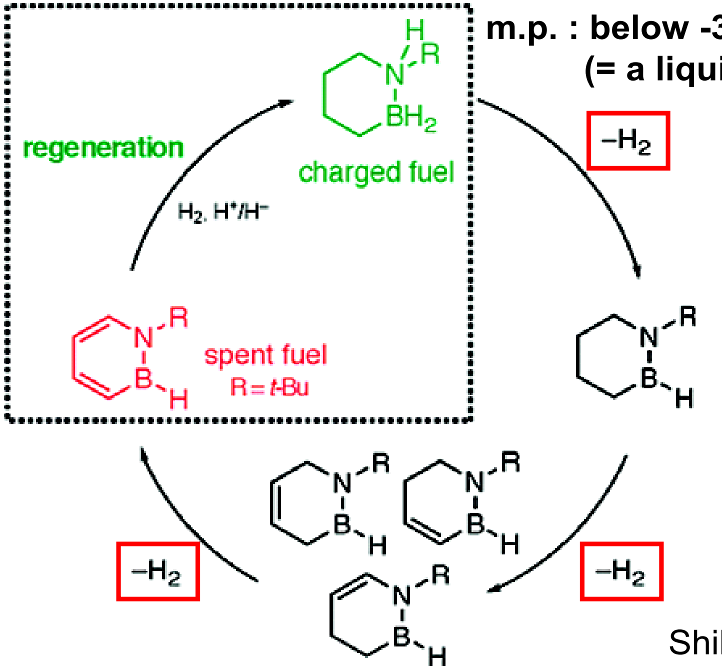


3-1. Availability of B-N compounds for HS

"Why have boron- and nirtogen-containing chemical hydrides attracted much attention currently?"

- **High gravimetric hydrogen densities**
- **Kinetics of hydrogen release**

	ΔH (kcal/mol)	ΔG (kcal/mol)	gravimetric density
$H_3N{-}BH_3 \longrightarrow H_2N{-}BH_2 + H_2$	-5.1	-13.6	19.6 wt.% H_2
$H_3C{-}CH_3 \longrightarrow H_2C{=}CH_2 + H_2$	32.6	23.9	-
	27.9	$\boxed{1.9}$	7.1 wt.% H_2



m.p. : below -30 °C
(= a liquid at operating temprature)

ΔG ≈ 0

Overall thermodynamics conducive to reversible H_2 uptake/release

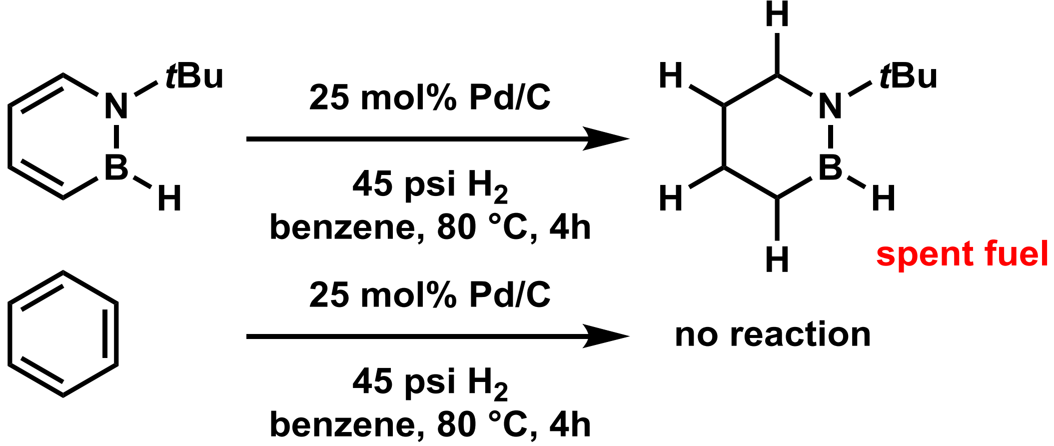
↓

A potentially viable H_2 storage platform

Shih-Yuan Liu, *et al.*, *J. Am. Chem. Soc.* **2010**, *132*, 3289.

3-2. “Fully charged” fuel

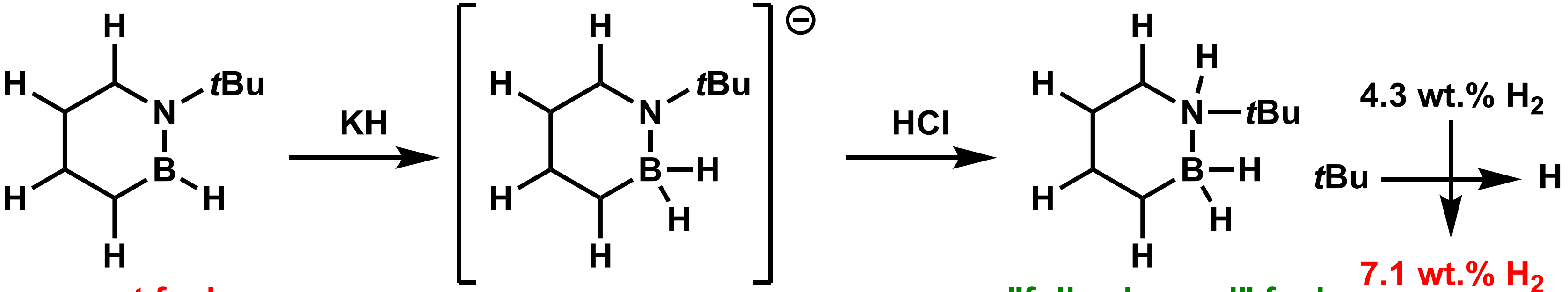
-Hydrogenation reactivity compared with benzene-



spent fuel

no reaction

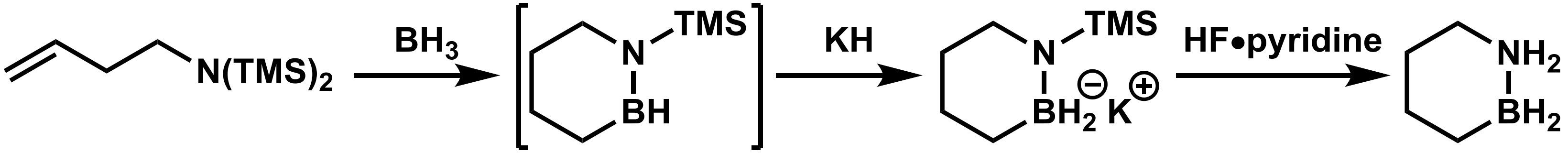
-Synthesis of "fully charged" fuel-



spent fuel

"fully charged" fuel

-Synthesis of ideal "fully charged" fuel-



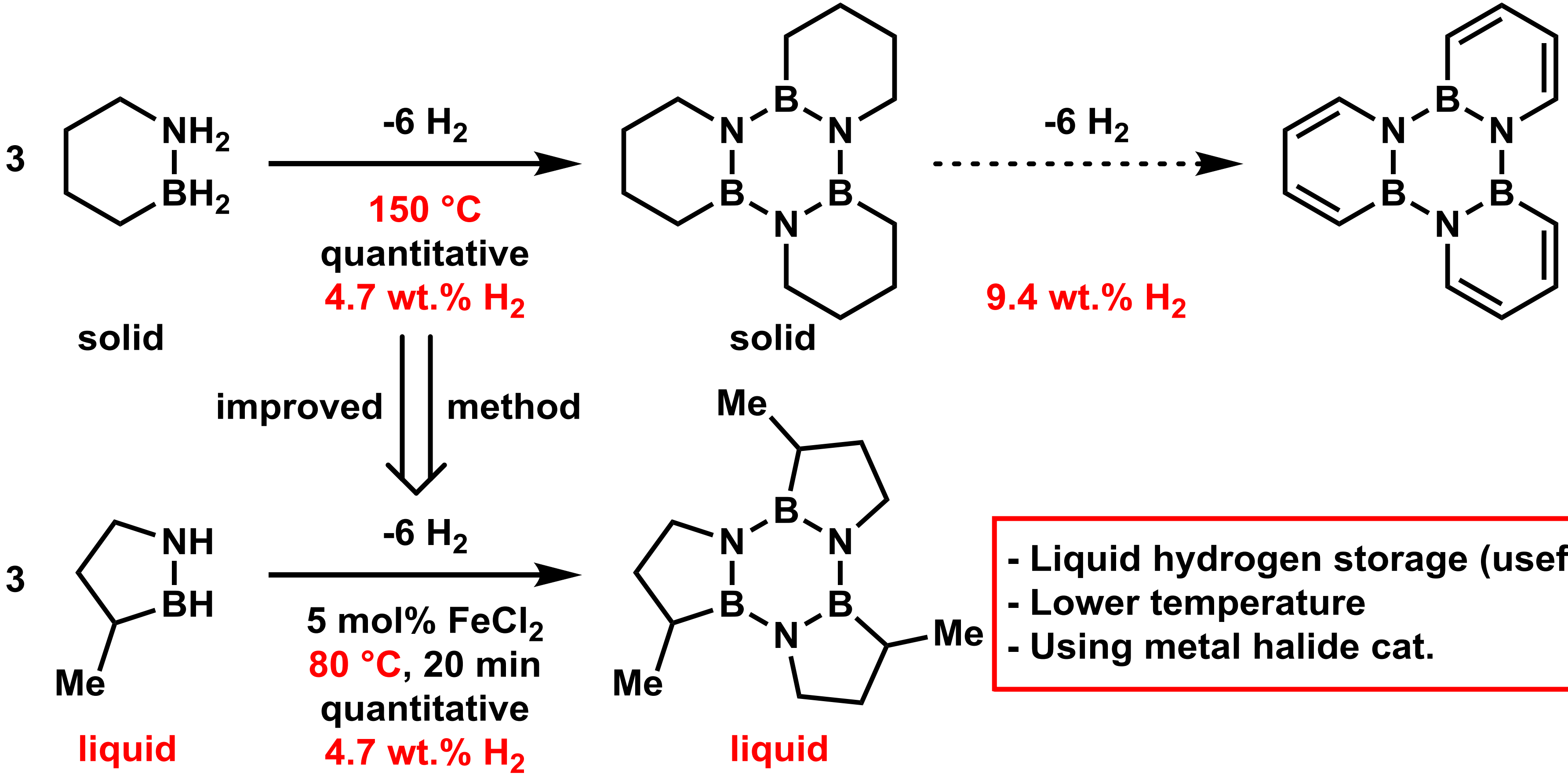
62%

58% overall yield

Shih-Yuan Liu, *et al.*, *J. Am. Chem. Soc.* **2010**, *132*, 3289.
Shih-Yuan Liu, *et al.*, *J. Am. Chem. Soc.* **2011**, *133*, 13006.

3-3. Process to release H_2

-Process to release H_2-



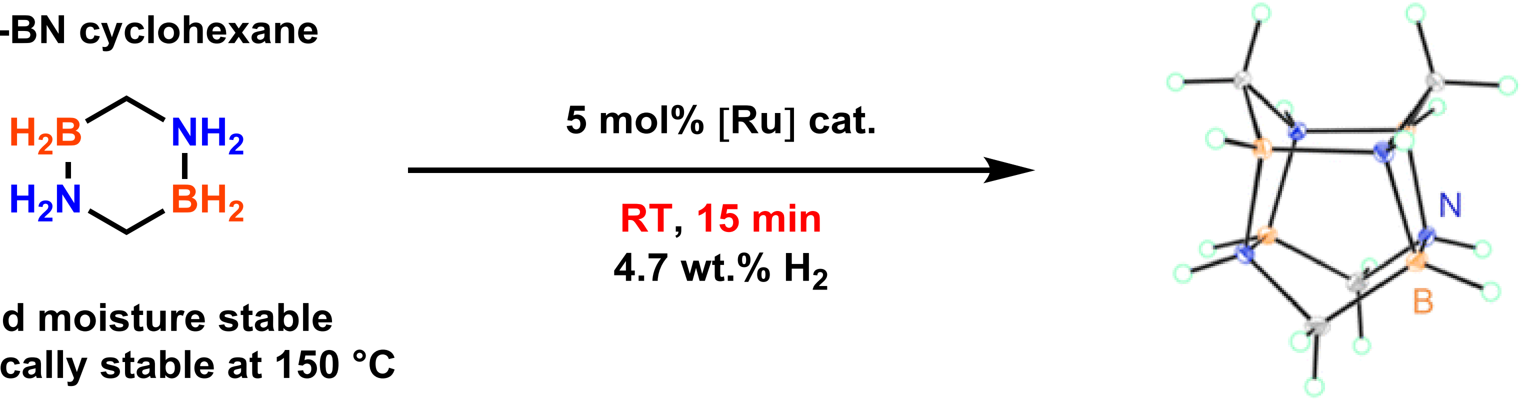
- **Liquid hydrogen storage (useful)**
- **Lower temperature**
- **Using metal halide cat.**

Shih-Yuan Liu, *et al.*, *Angew. Chem. Int. Ed.* **2012**, *51*, 6074.
Shih-Yuan Liu, *et al.*, *J. Am. Chem. Soc.* **2011**, *133*, 13006.

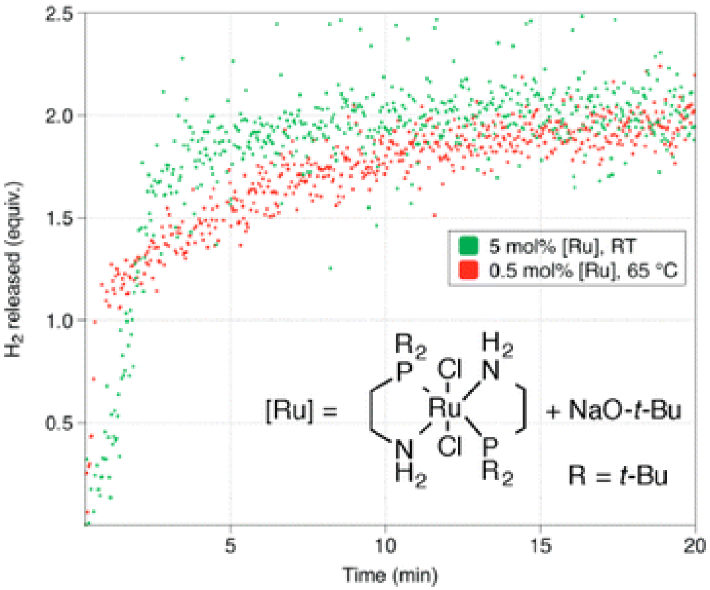
3-4. The leading-edge HS material

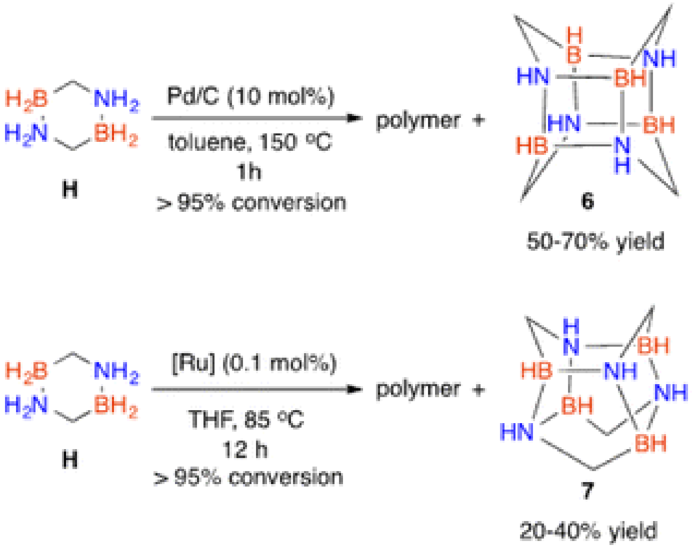
-The leading-edge hydrogen storage material-

Bis-BN cyclohexane



- **Air and moisture stable**
- **Kinetically stable at 150 °C**





G3MP2 energies
at 298K

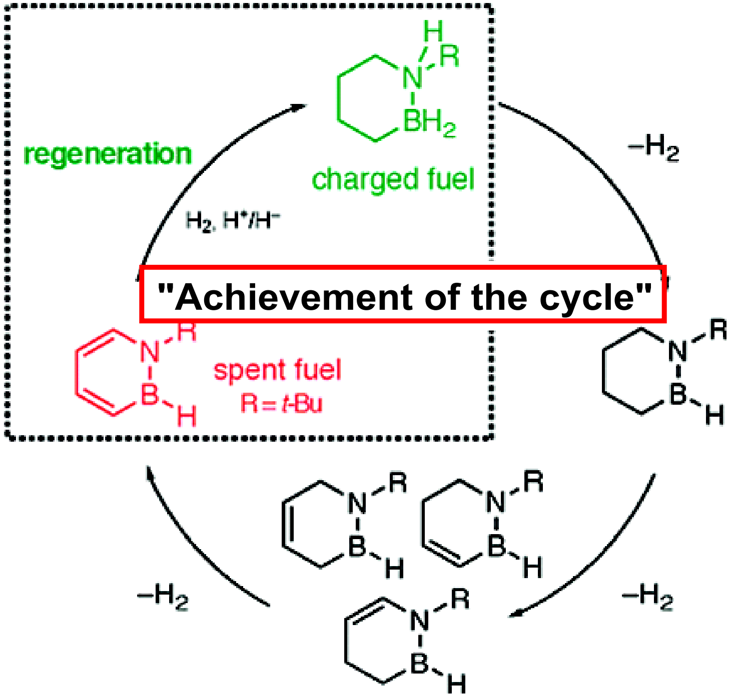
ΔH = -38.8 kcal/mol
ΔG = -56.0 kcal/mol

ΔH = -48.2 kcal/mol
ΔG = -64.3 kcal/mol

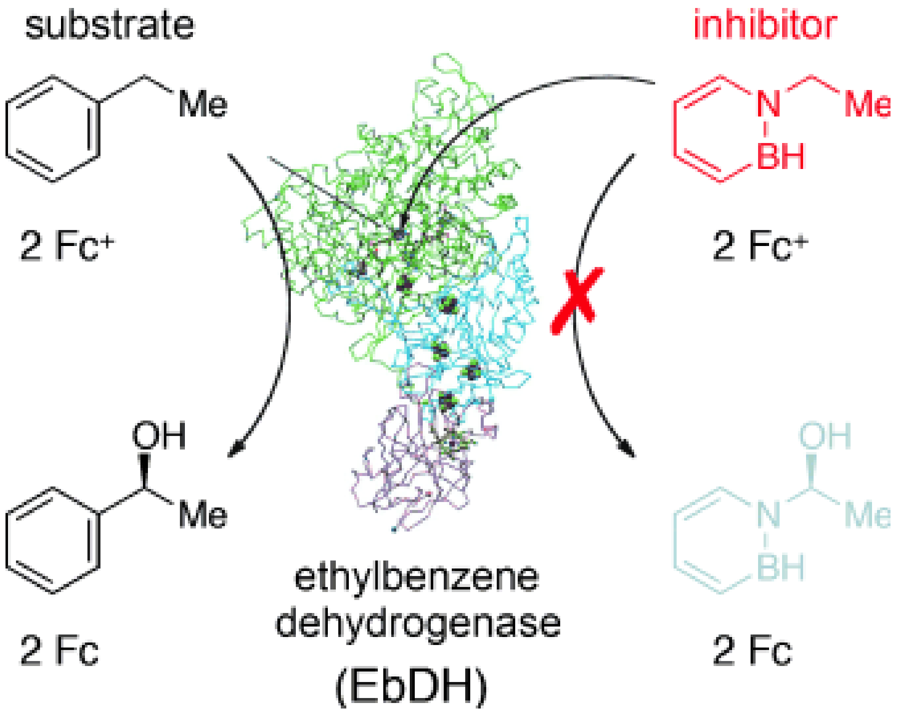
Shih-Yuan Liu, *et al.*, *J. Am. Chem. Soc.* **2015**, *137*, 134.

4. Perspective

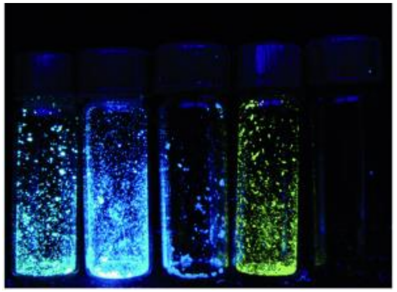
-Hydrogen storage material-

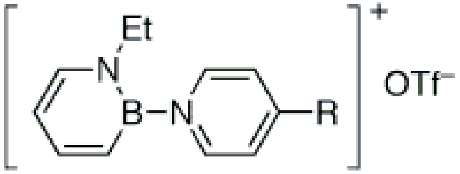


-BN/CC isosteric compound as enzyme inhibitor-



-Fluorence material-



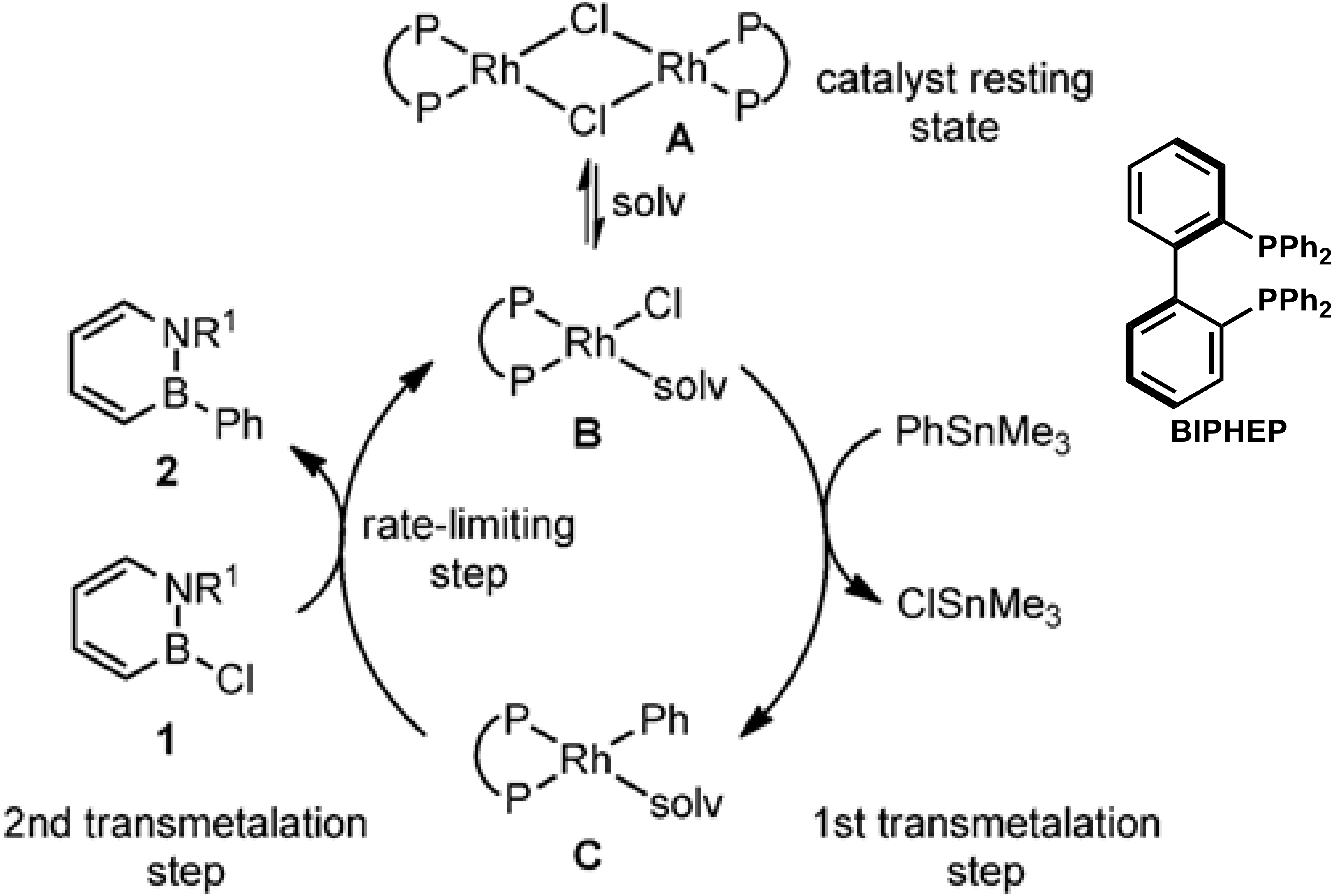


R = Me, Ph, H, CF_3, NMe_2

Shih-Yuan Liu, *et al.*, *J. Am. Chem. Soc.* **2010**, *132*, 3289.
Shih-Yuan Liu, *et al.*, *Angew. Chem. Int. Ed.* **2013**, *52*, 2599.
Shih-Yuan Liu, *et al.*, *Angew. Chem. Int. Ed.* **2010**, *49*, 7444.

Appendix 1

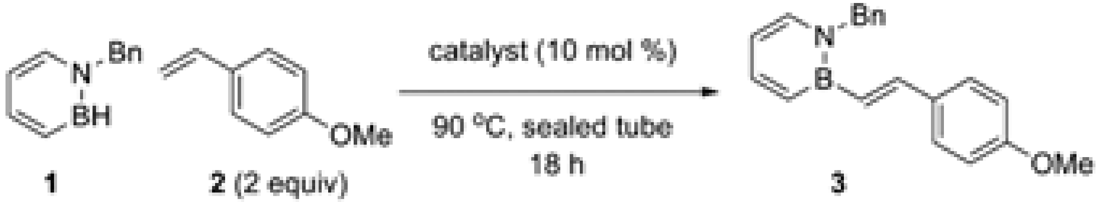
-Mechanism of Boron Arylation-

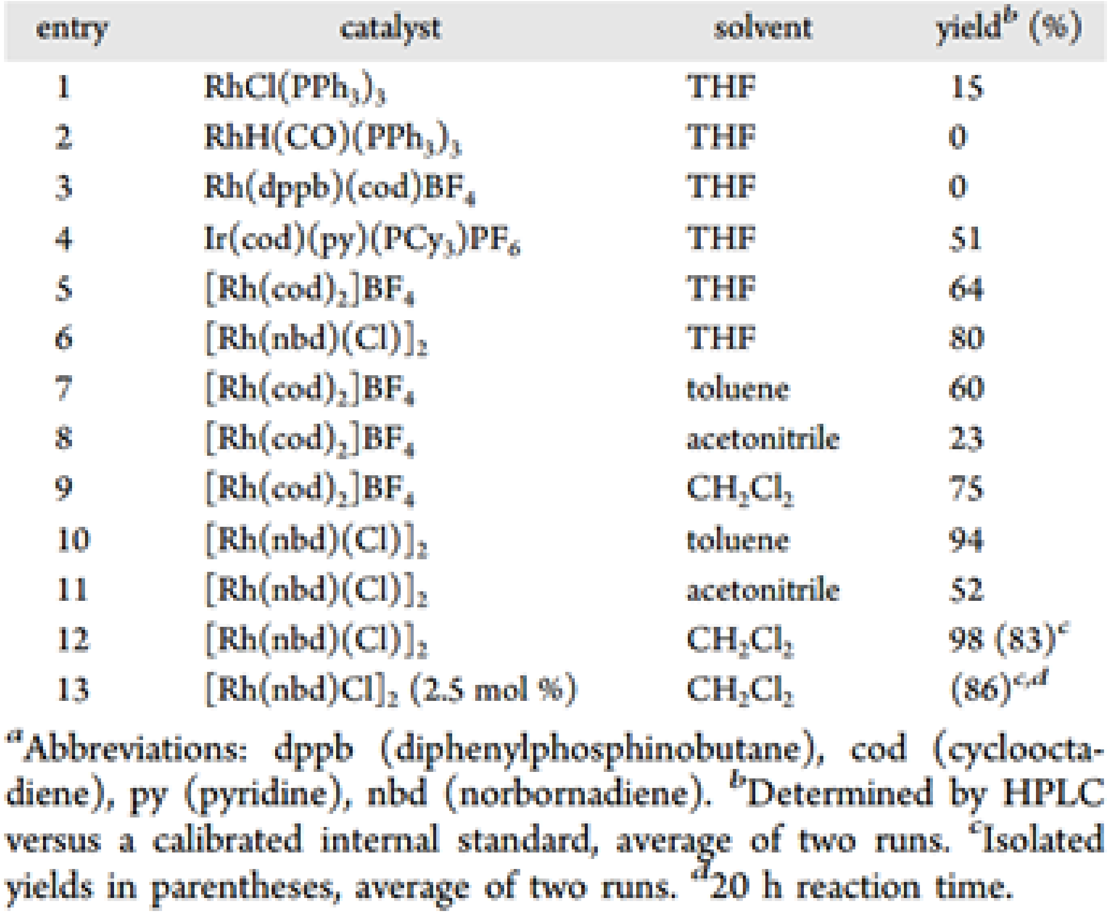


Shih-Yuan Liu, *et al.*, *Angew. Chem. Int. Ed.* **2013**, *52*, 9316.

Appendix 2

-Dehydrogenative Borylation Reaction-





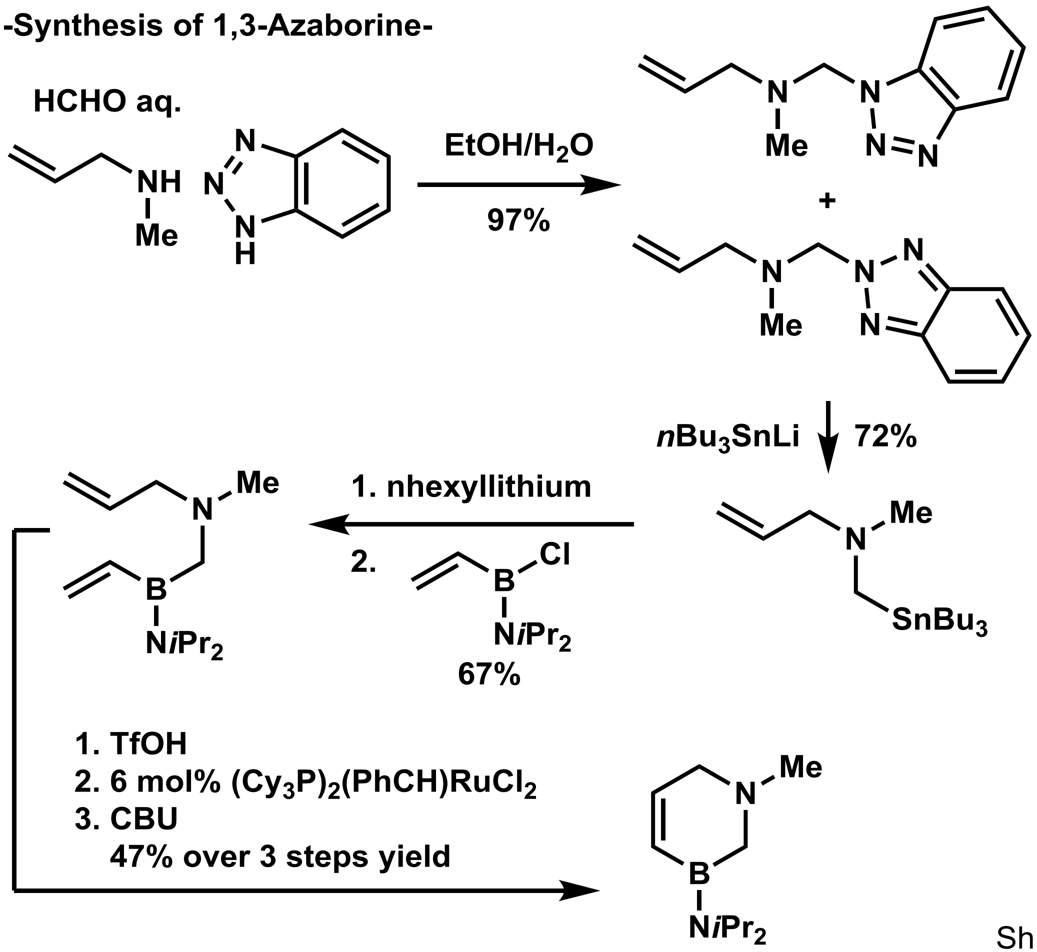
entry	catalyst	solvent	yield^b (%)
1	$RhCl(PPh_3)_3$	THF	15
2	$RhH(CO)(PPh_3)_3$	THF	0
3	$Rh(dppb)(cod)BF_4$	THF	0
4	$Ir(cod)(py)(PCy_3)PF_6$	THF	51
5	$[Rh(cod)_2]BF_4$	THF	64
6	$[Rh(nbd)(Cl)]_2$	THF	80
7	$[Rh(cod)_2]BF_4$	toluene	60
8	$[Rh(cod)_2]BF_4$	acetonitrile	23
9	$[Rh(cod)_2]BF_4$	CH_2Cl_2	75
10	$[Rh(nbd)(Cl)]_2$	toluene	94
11	$[Rh(nbd)(Cl)]_2$	acetonitrile	52
12	$[Rh(nbd)(Cl)]_2$	CH_2Cl_2	98 (83)^c
13	$[Rh(nbd)Cl]_2$ (2.5 mol %)	CH_2Cl_2	(86)^{c,d}

[a] Abbreviations: dppb (diphenylphosphinobutane), cod (cyclooctadiene), py (pyridine), nbd (norbornadiene). [b] Determined by HPLC versus a calibrated internal standard, average of two runs. [c] Isolated yields in parentheses, average of two runs. [d] 20 h reaction time.

Shih-Yuan Liu, *et al.*, *Org. Lett.* **2014**, *16*, 3340.

Appendix 3

-Synthesis of 1,3-Azaborine-



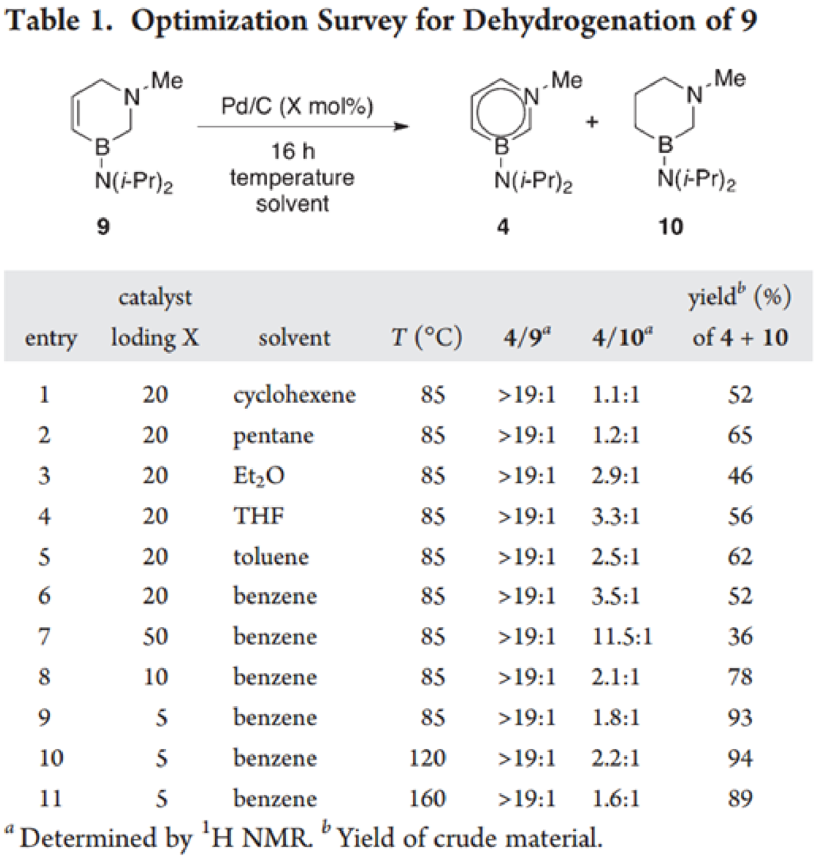


Table 1. Optimization Survey for Dehydrogenation of 9

entry	catalyst loding X	solvent	T (°C)	$4/9^a$	$4/10^a$	yield^b (%) of 4 + 10
1	20	cyclohexene	85	>19:1	1.1:1	52
2	20	pentane	85	>19:1	1.2:1	65
3	20	Et_2O	85	>19:1	2.9:1	46
4	20	THF	85	>19:1	3.3:1	56
5	20	toluene	85	>19:1	2.5:1	62
6	20	benzene	85	>19:1	3.5:1	52
7	50	benzene	85	>19:1	11.5:1	36
8	10	benzene	85	>19:1	2.1:1	78
9	5	benzene	85	>19:1	1.8:1	93
10	5	benzene	120	>19:1	2.2:1	94
11	5	benzene	160	>19:1	1.6:1	89

[a] Determined by ^{1}H NMR. [b] Yield of crude material.

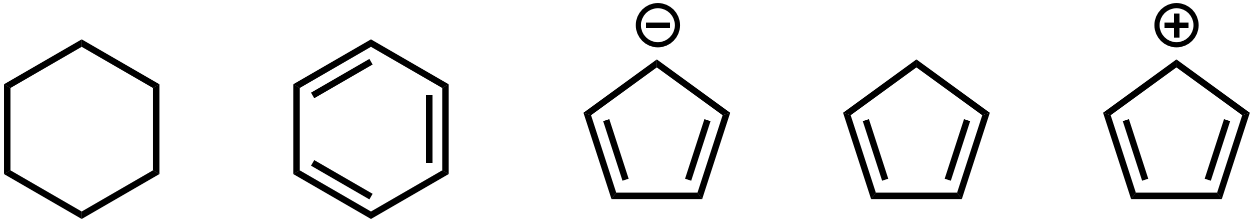
Shih-Yuan Liu, *et al.*, *J. Am. Chem. Soc.* **2011**, *133*, 20152.

Appendix 4

-NICS (nucleus-independent chemical shift)-

The absolute magnetic shieldings at the center of the ring

NICS $<$ 0 : aromaticity
NICS $>$ 0 : antiaromaticity



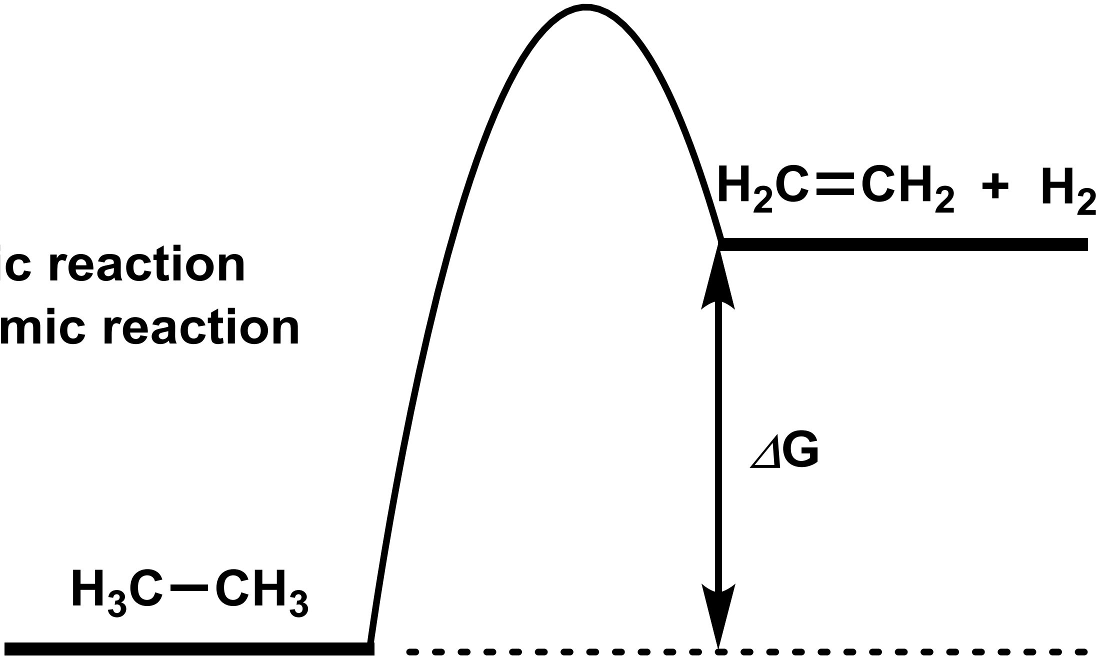
-2.2 -9.7 -14.3 -3.2 54.2

P. v. R. Schleyer, *et al.*, *J. Am. Chem. Soc.* **1996**, *118*, 6317.
K. Yamamoto, *Lit. Sem.* **2011**.

Appendix 5

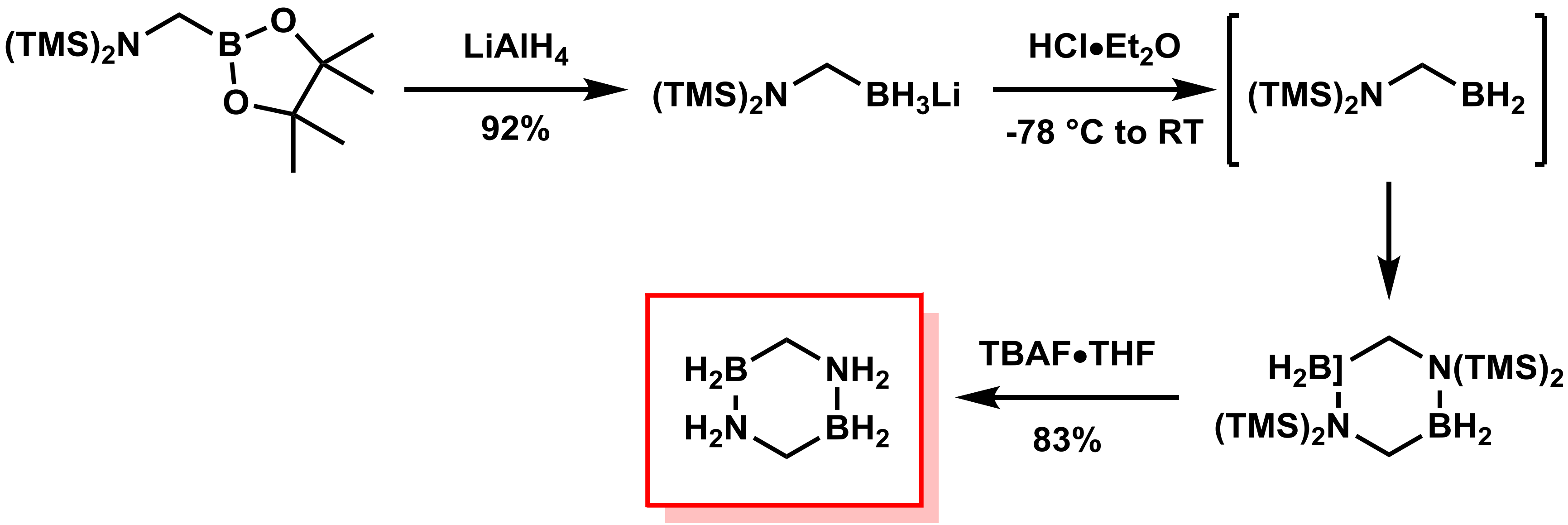
- $\Delta G = \Delta H - T\Delta S$ -

$\Delta H < 0$: exothemic reaction
$\Delta H > 0$: endothermic reaction



Appendix 6

-Synthesis of bis-BN cyclohexane-



Shih-Yuan Liu, *et al.*, *J. Am. Chem. Soc.* **2015**, *137*, 134.