Bidentate Boryl Ligand-Supported Complexes and Their Catalytic Applications

MR July 15th 2023

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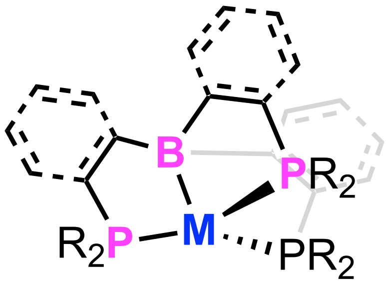
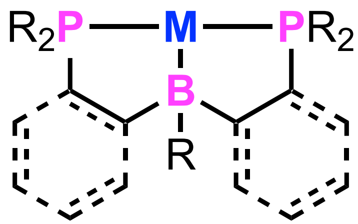
D2

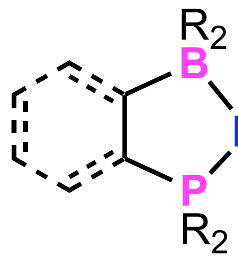
Background

2013 (Keisuke Takahashi, MR)

Mono-, Bis-, and Tris(phosphine)/Borane-Ligated Complexes



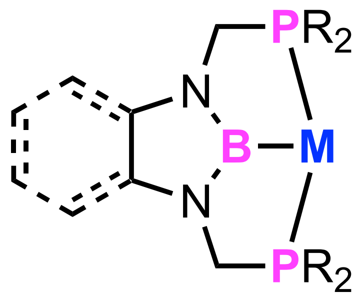




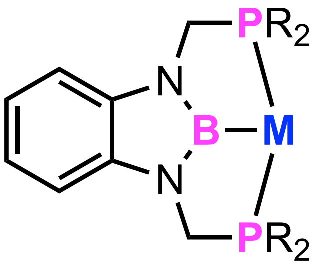
“PBP” Pincer Ligand-Supported Complexes

Our group’s works

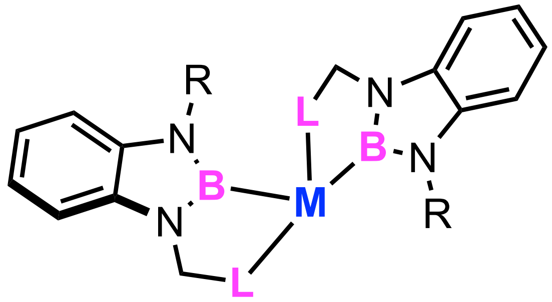
(and Thakun’s current research topic)



“PBP” pincer ligand vs. bidentate boryl ligand



(**M** = Ir, Rh, Pt, Ru, Co, Ni)



(**M** = Ir, Pt)

PBP pincer ligand

bidentate boryl ligand

rigid coordination sphere

more stable boryl group

applications in catalysis: many

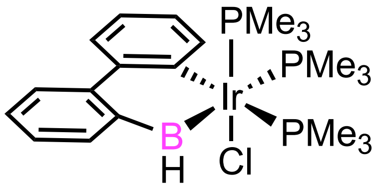
more flexible coordination sphere

potentially less stable boryl group

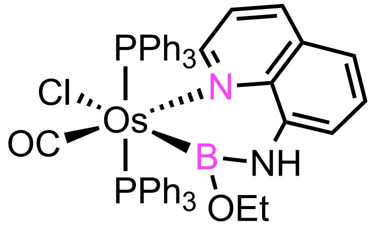
application in catalysis: rare

Mostly borylation

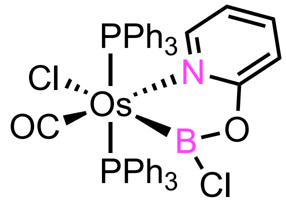
Reported examples



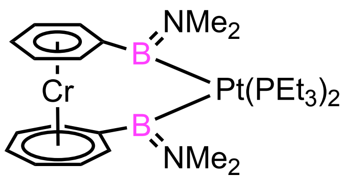
By Eisenstein & Crabtree
Organometallics **1995**, *14*, 1168.



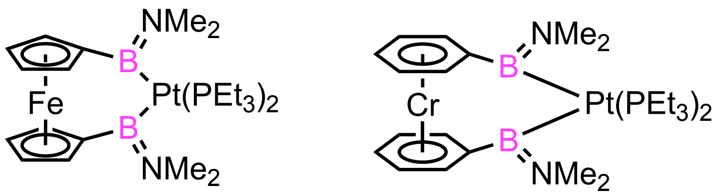
By Roper & Wright
Angew. Chem. Int. Ed. **2000**, *39*, 948.



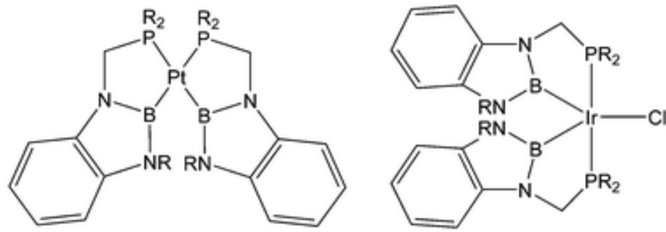
By Roper & Wright
Organometallics **2002**, *21*, 1714.



By Braunschweig,
Angew. Chem. Int. Ed. **2005**, *44*, 5647.



By Braunschweig,
Angew. Chem. Int. Ed. **2006**, *45*, 8048.

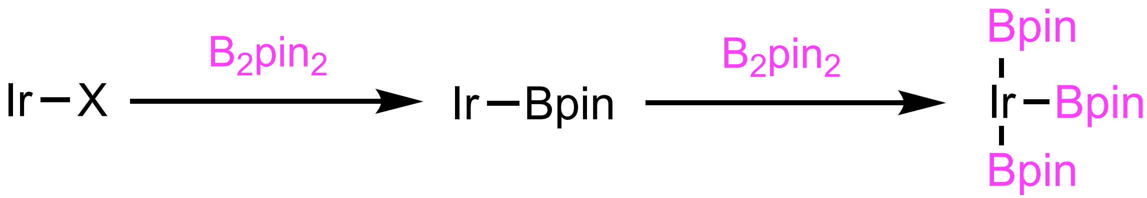


By Wesemann,
Chem. Commun. **2014**, *50*, 2738.

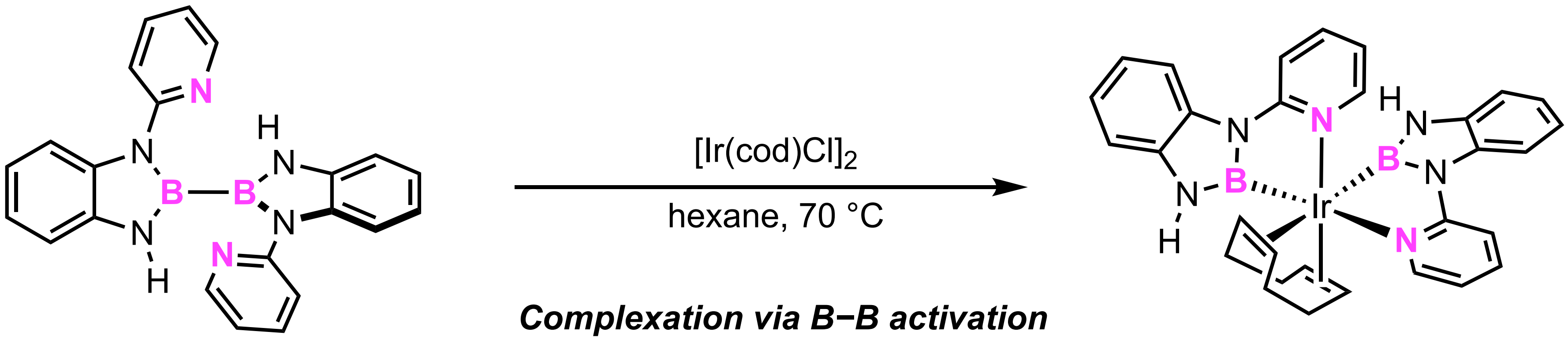
No catalytic reaction developed by above ones

Inspiration of ligand

Iridium's reactivity towards B–B bond

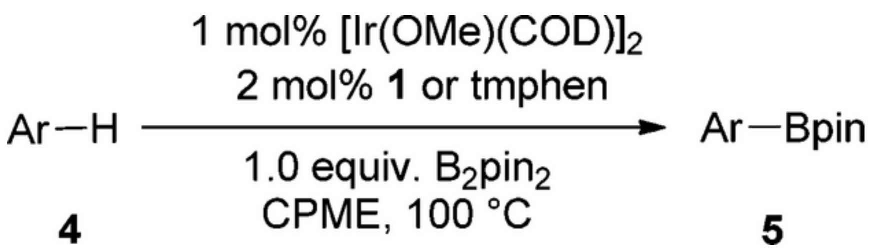


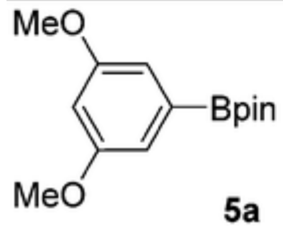
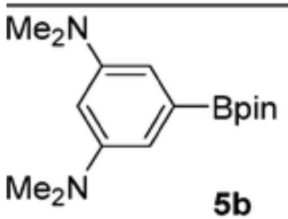
Synthesis of N,B-bidentate ligand (via B–B activation)



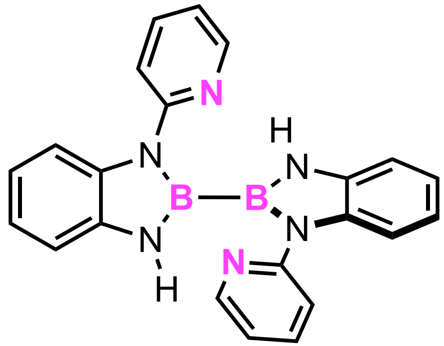
J. Am. Chem. Soc. **2015**, *137*, 8058.

Comparison with tmphen ligand

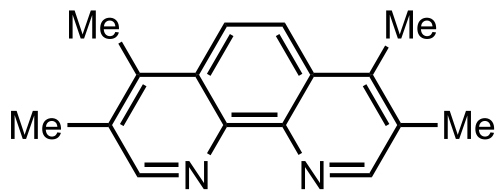


Product	Preligand **1**		tmphen	
	Conv. (%)[b]	Yield (%)[b,c]	Conv. (%)[b]	Yield (%)[b,c]
 **5a**	98	98 (95)	94	81 (78)
 **5b**	94	94 (93)	50	50 (49)

ligand



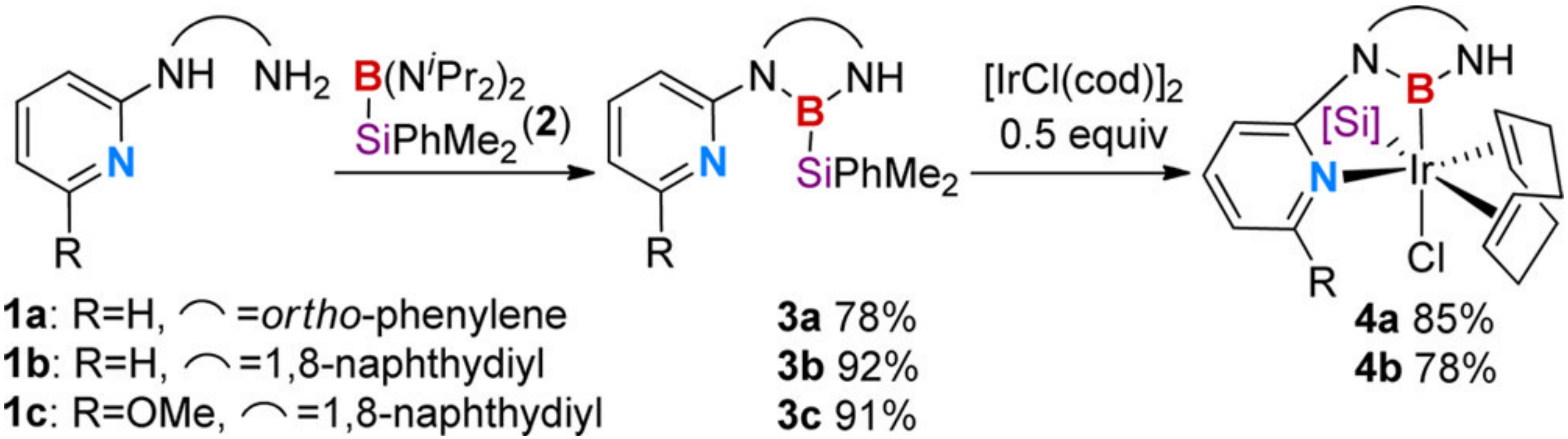
1

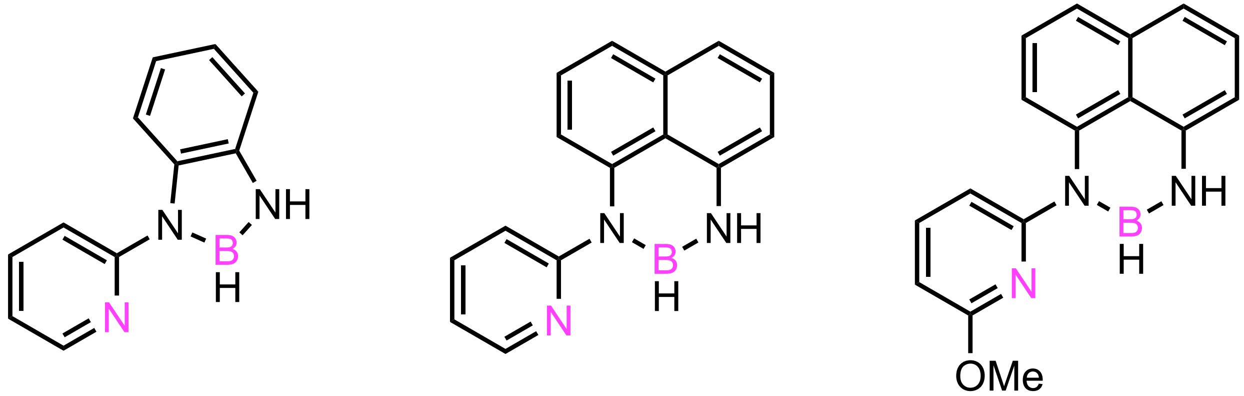


tmphen

J. Am. Chem. Soc. **2015**, *137*, 8058.

Synthesis of Complex (via B–Si activation)

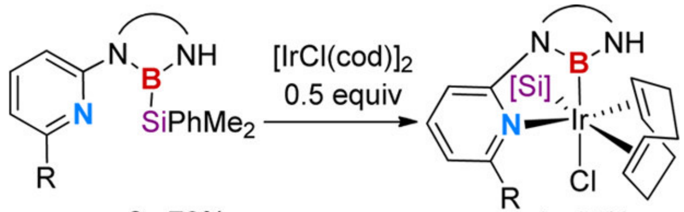




3a **3b** **3c**

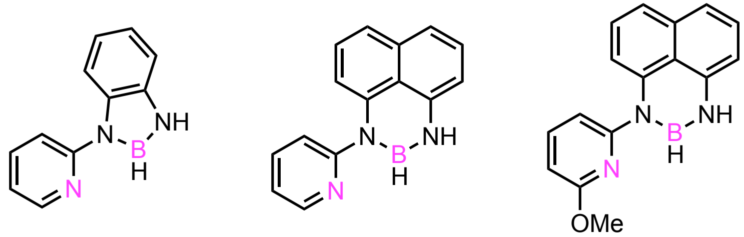
J. Am. Chem. Soc. **2015**, *139*, 91.

Optimization of conditions

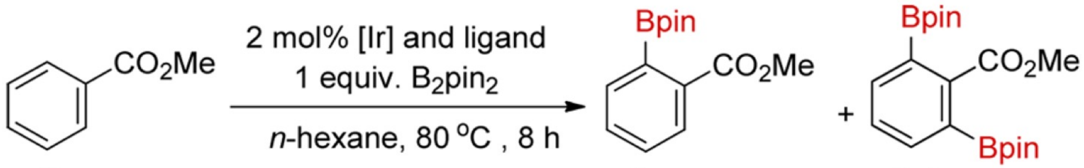


3a 78%
3b 92%
3c 91%

a: R=H, ⌒ =*ortho*-phenylene
b: R=H, ⌒ =1,8-naphthydiyl
c: R=OMe, ⌒ =1,8-naphthydiyl



3a **3b** **3c**



entry	precatalyst	conv. (%)[b]	yield (%)[b]	Ratio of $o/(m + p)$[b]
1	**3a**/[Ir(OMe)(cod)]$_2$	89	4 (**6a**)	5:95
2	**3a**/[IrCl(cod)]$_2$	7	–	–
3	complex **4a**	4	–	–
4	**3b**/[Ir(OMe)(cod)]$_2$	58	36 (**6a**) + 4 (**6a′**)	69:31
5	**3b**/ [IrCl(cod)]$_2$	22	19 (**6a**) + 1 (**6a′**)	91:9
6	complex **4b**	43	35 (**6a**) + 3 (**6a′**)	91:9
7	**3c**/[IrCl(cod)]$_2$	84	70 (**6a**) + 13 (**6a′**)	>99:1
8	**3c**/[Ir(OMe)(cod]$_2$	20	7 (**6a**)	35:65

Negative selectivity

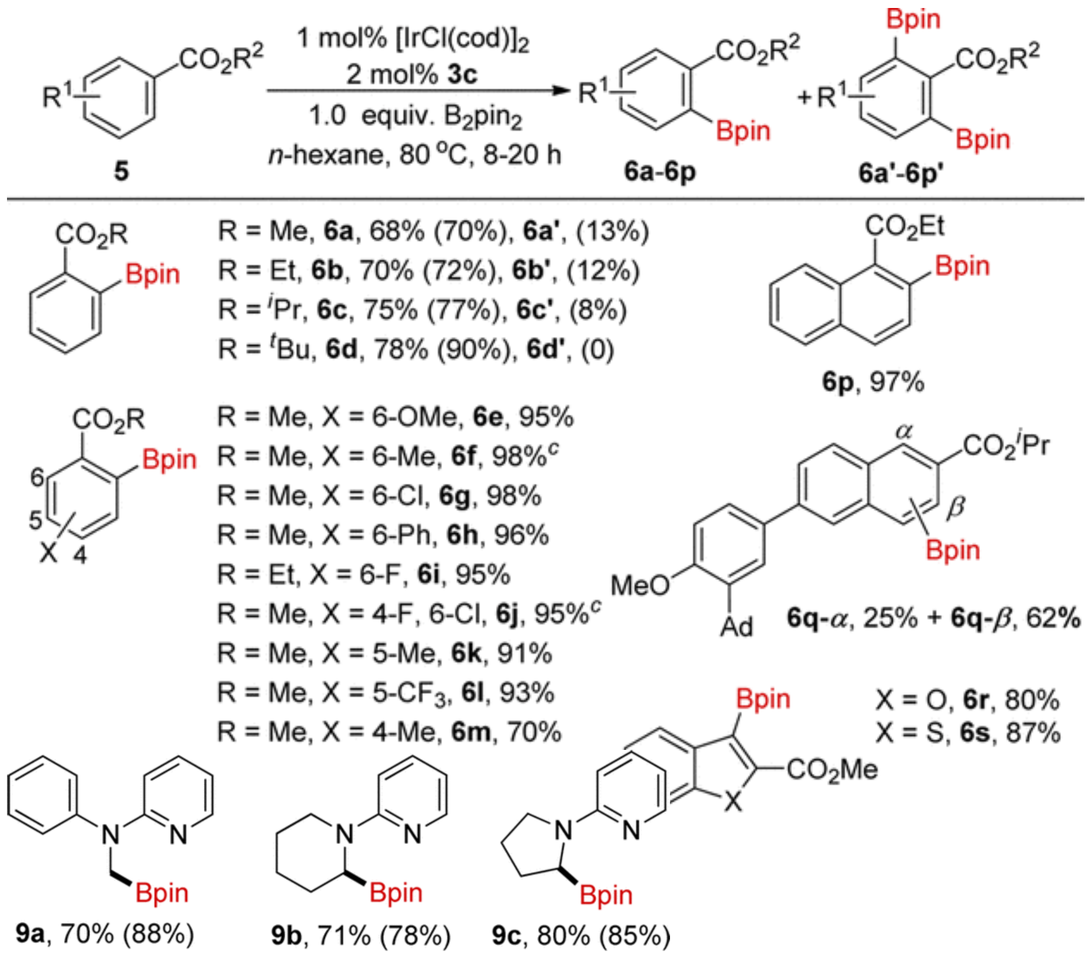
Negative reactivity

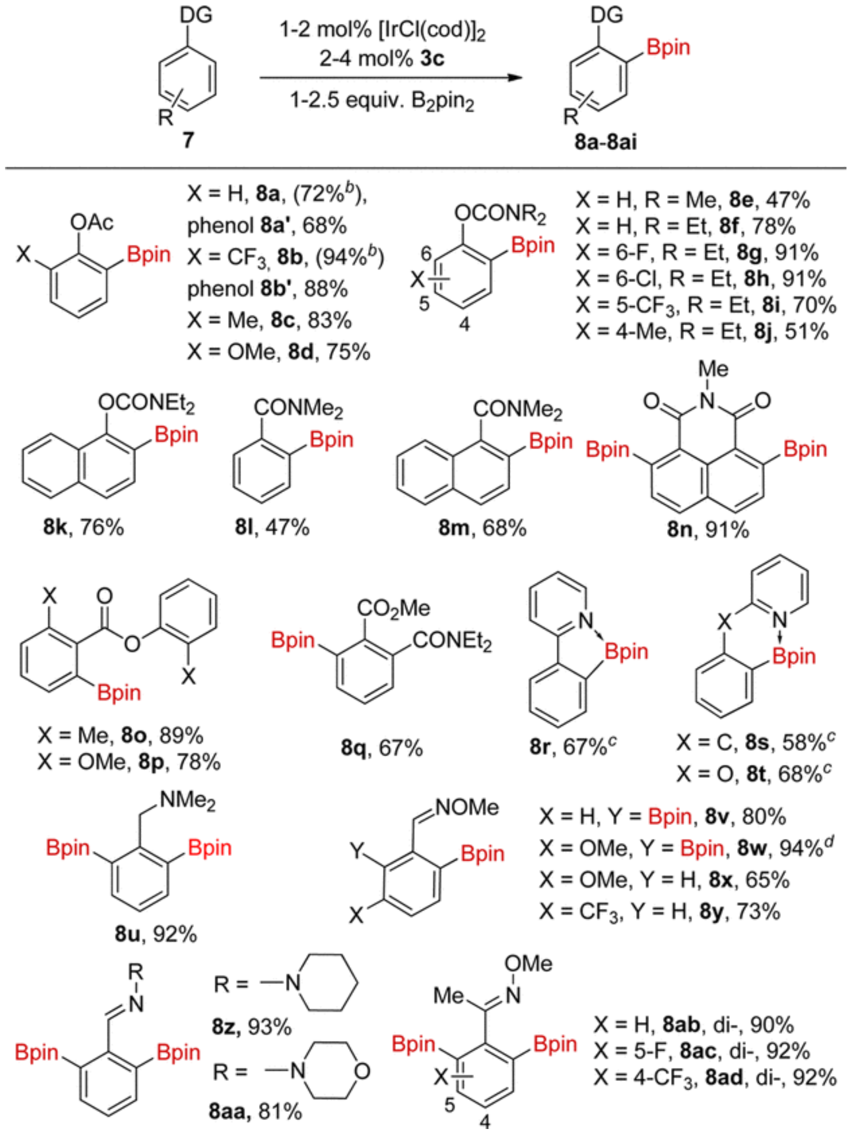
[a]Reaction conditions: methyl benzoate **5a** (0.5 mmol), B_2pin_2 (0.5 mmol), [Ir(X) (cod)]$_2$ (0.005 mmol), preligand (0.01 mmol) or complex (0.01 mmol) in 1.0 mL of *n*-hexane, 80 °C, 8 h. [b]Conversions, yields, and ratio were based on ^{1}H NMR analyses of the crude products with **5a** as the limiting reagent.

J. Am. Chem. Soc. **2015**, *139*, 91.

B,N-type Boryl Ligand Directed C–H Borylation (Li, 2017)

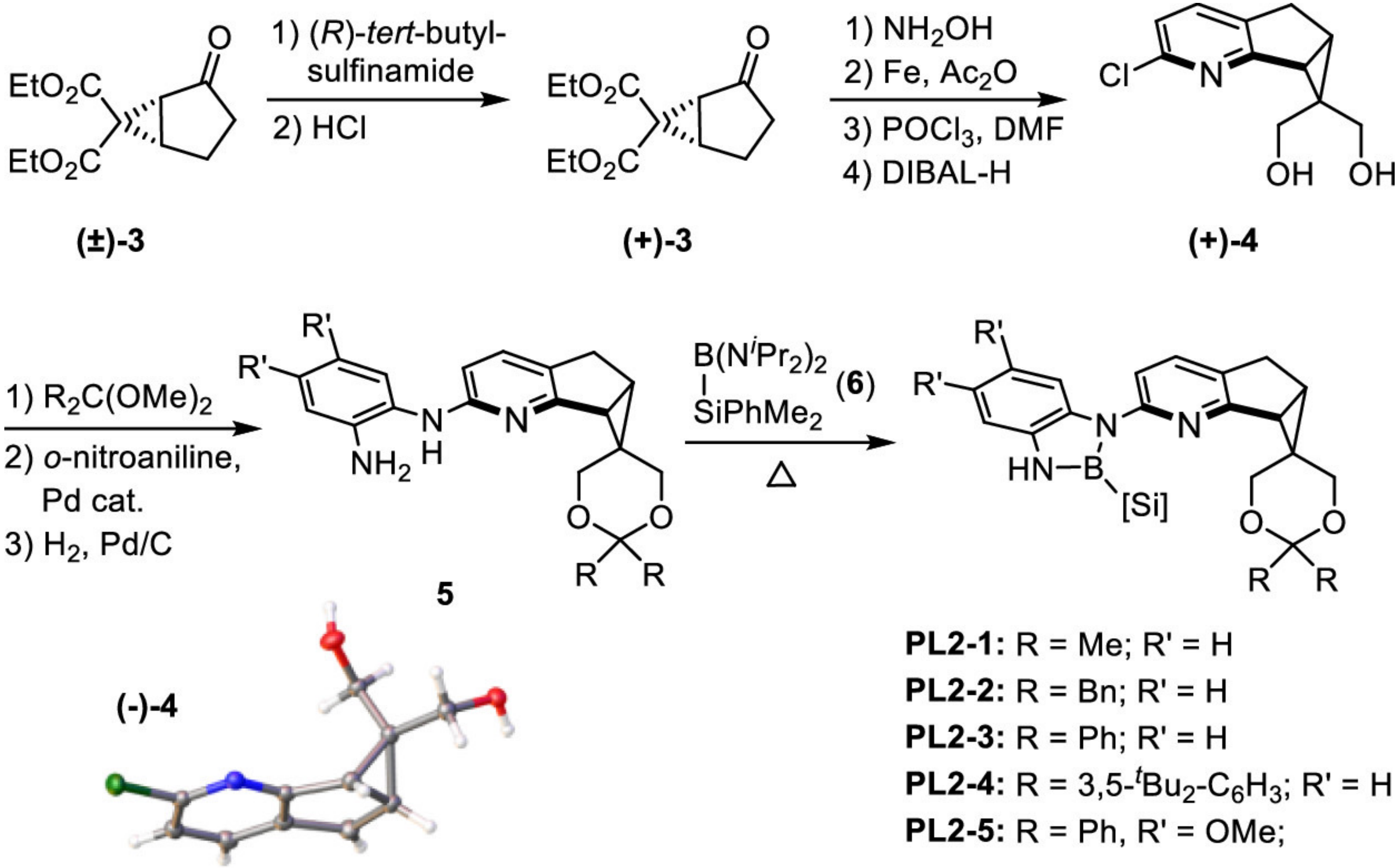
Compatibility





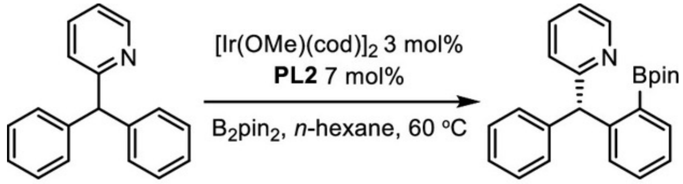
J. Am. Chem. Soc. **2015**, *139*, 91.

Synthesis of chiral ligand



ACS Catal. **2021**, *11*, 7339.

Ligand optimization



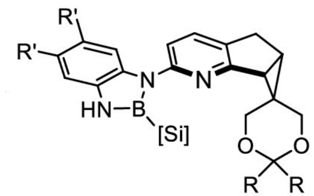
1a **2a**

entry	ligand	yield (%)[b]	ee (%)[c]
1	**PL2-1**	85	45
2	**PL2-2**	79	62
3	**PL2-3**	89	84
4	**PL2-4**	92	83
5	**PL2-5**	54	83
6[d]	**PL2-3**	93	94
7[e]	**PL2-3**	58	76
8	**PL3**	86	35
9	**PL4**	79	6
10	**PL5**	83	−5
11	**PL6**	70	10
12	**PL7**	trace	
13	**PL8**	trace	

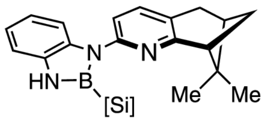
Low ee

Low yield

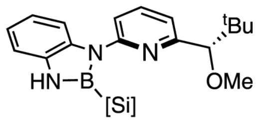
[a]Unless otherwise noted, all of the reactions were carried out with **1a** (0.1 mmol), $[Ir(OMe)(cod)]_2$ (0.003 mmol), **PL** (0.007 mmol), and B_2pin_2 (0.15 mmol) in *n*-hexane (1.0 mL) at 60 °C for 6 h. [b]Yield of **2a** was determined by ^{1}H NMR using 1,3,5-trimethoxybenzene as the internal standard. [c]After an oxidative workup, the corresponding phenol was isolated and the enantiomeric excess was determined by HPLC on a chiral AD-H column. [d]The reaction was carried out in a solvent mixture containing *n*-hexane and 2-MeTHF (5:1, v/v). [e]$[IrCl(cod)]_2$ was used.



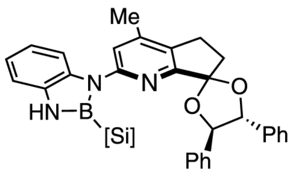
PL2-1: R = Me; R' = H
PL2-2: R = Bn; R' = H
PL2-3: R = Ph; R' = H
PL2-4: R = 3,5-^{t}Bu$_2$-C_6H_3; R' = H
PL2-5: R = Ph, R' = OMe;



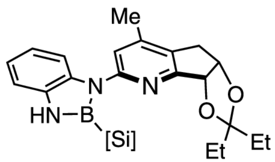
PL3



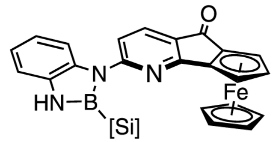
PL4



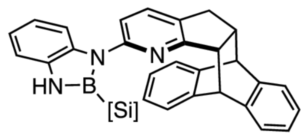
PL5



PL6

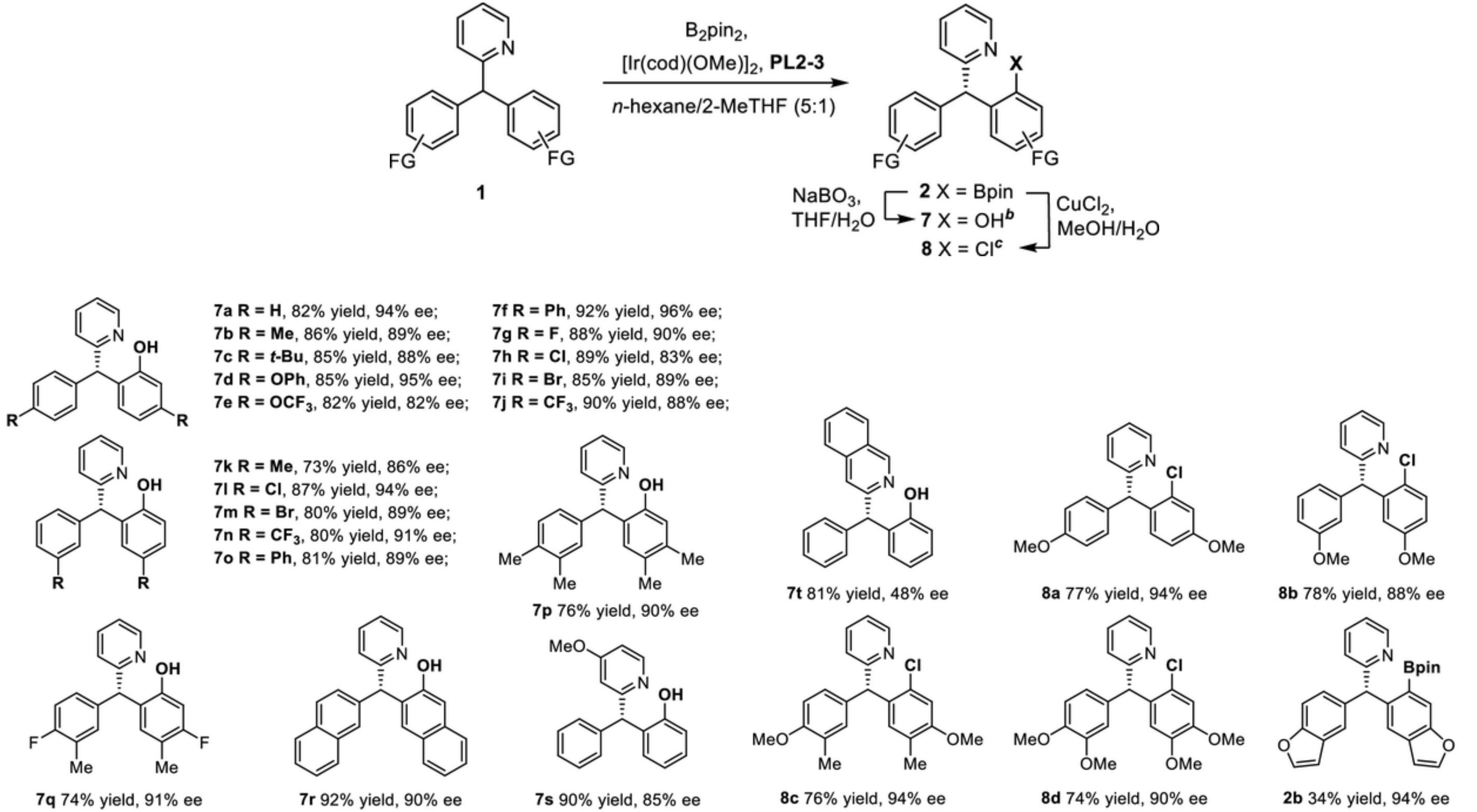


PL7



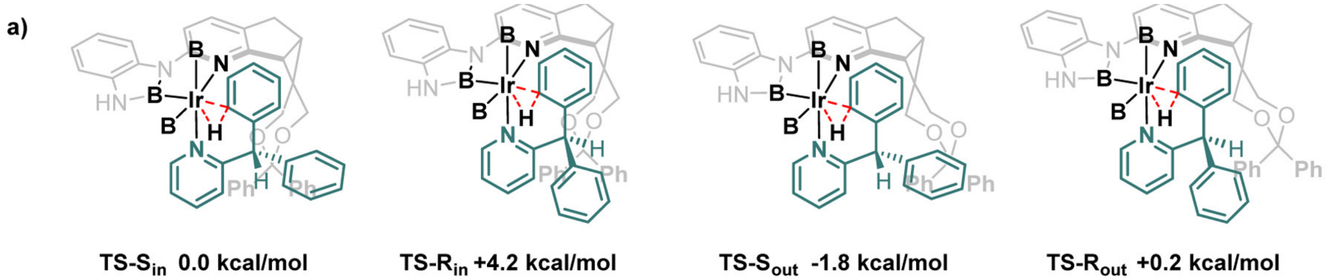
PL8

Compatibility

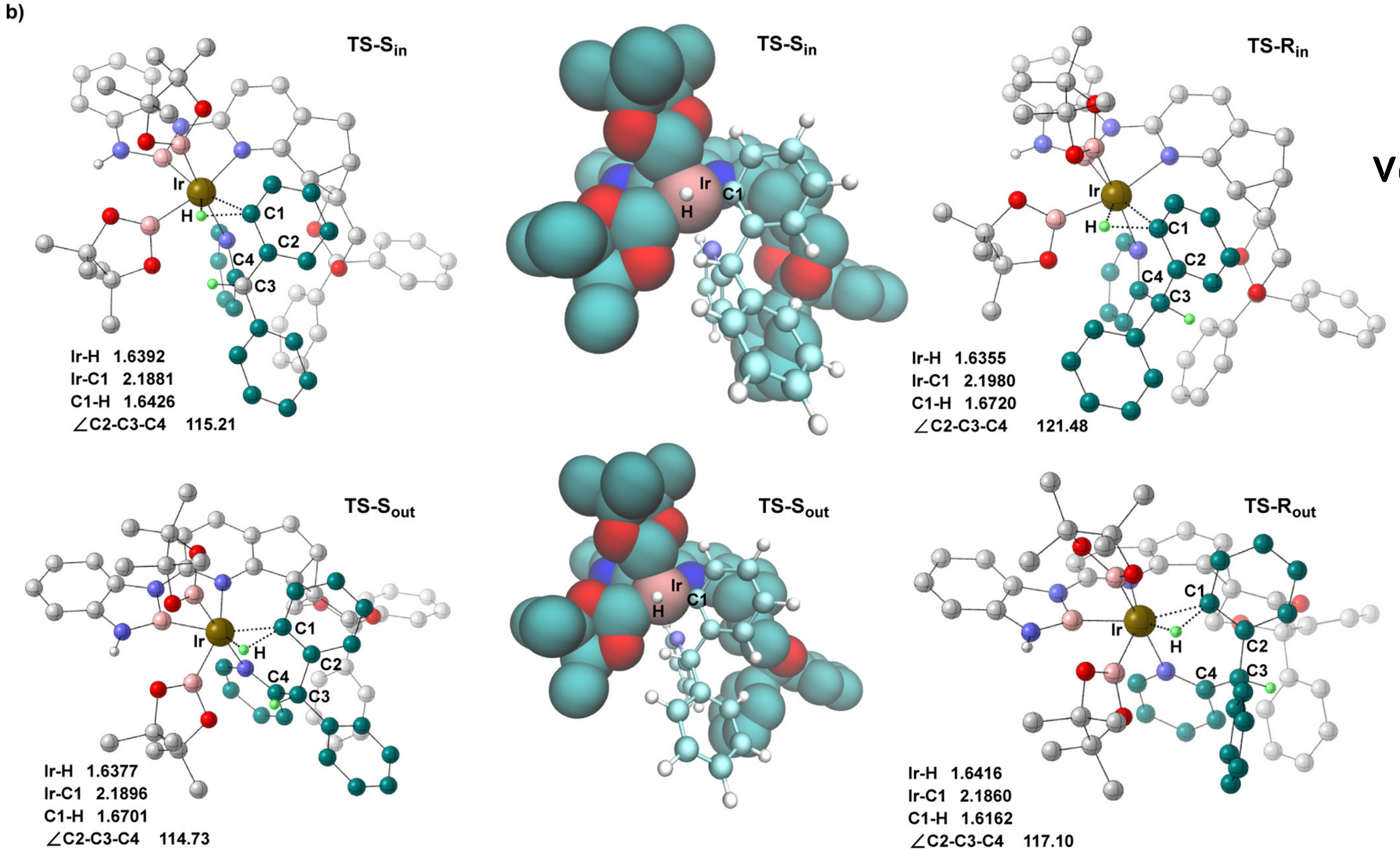


ACS Catal. **2021**, *11*, 7339.

TS for C–H activation step



TS-S_{out}: most feasible



Very similar parameters

Ir-H length

Ir-C1 length

Different parameters

C1-H length

∠C2–C3–C4

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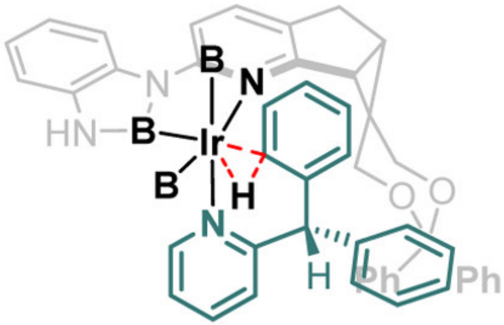
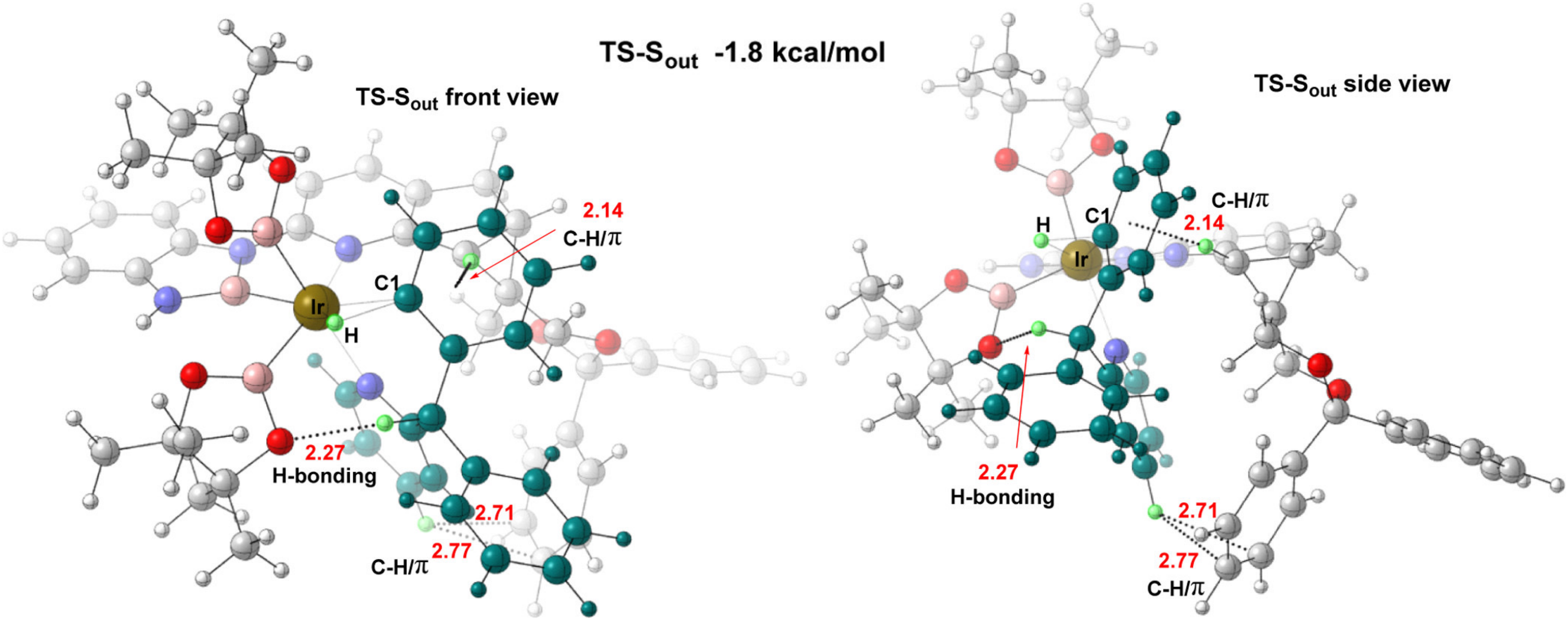
TS-S_{out}: A weak interaction

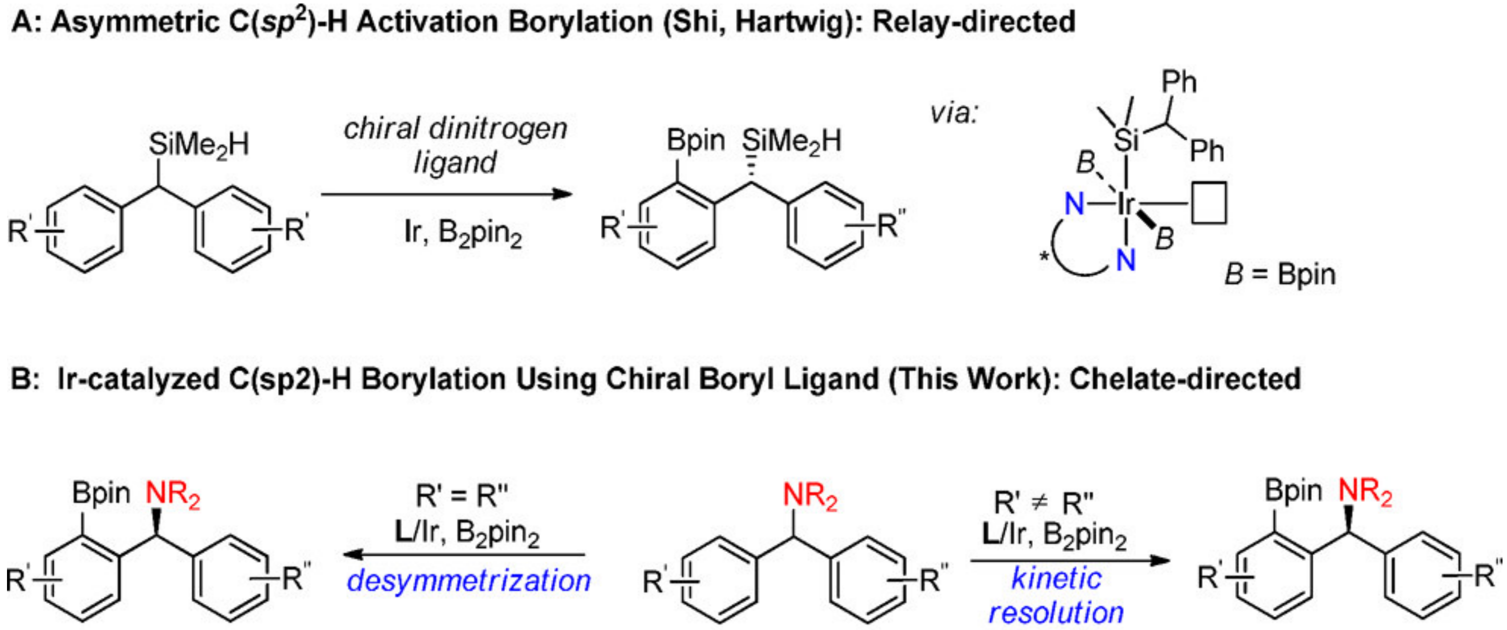




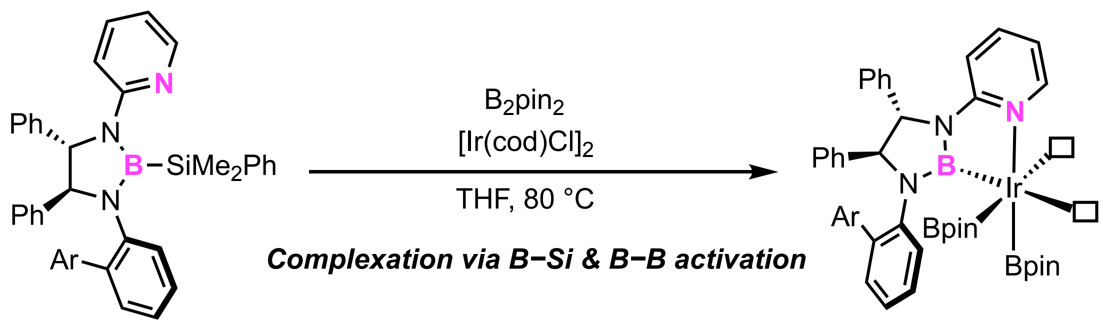
ACS Catal. **2021**, *11*, 7339.

B,N-type Boryl Ligand | Asymmetric C–H Borylation (Ke & Xu, 2019)

Introduction

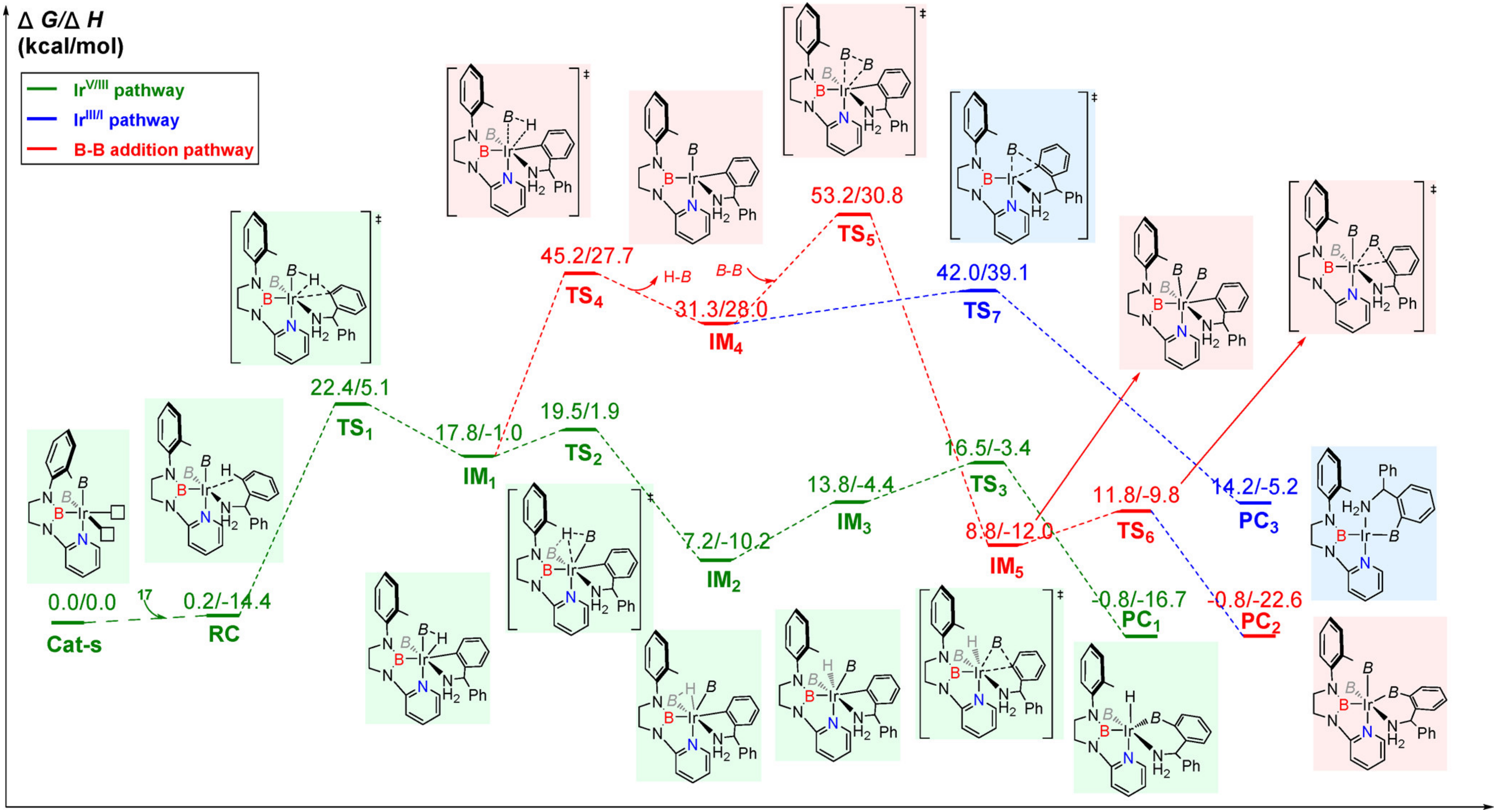


In-situ generation of active species



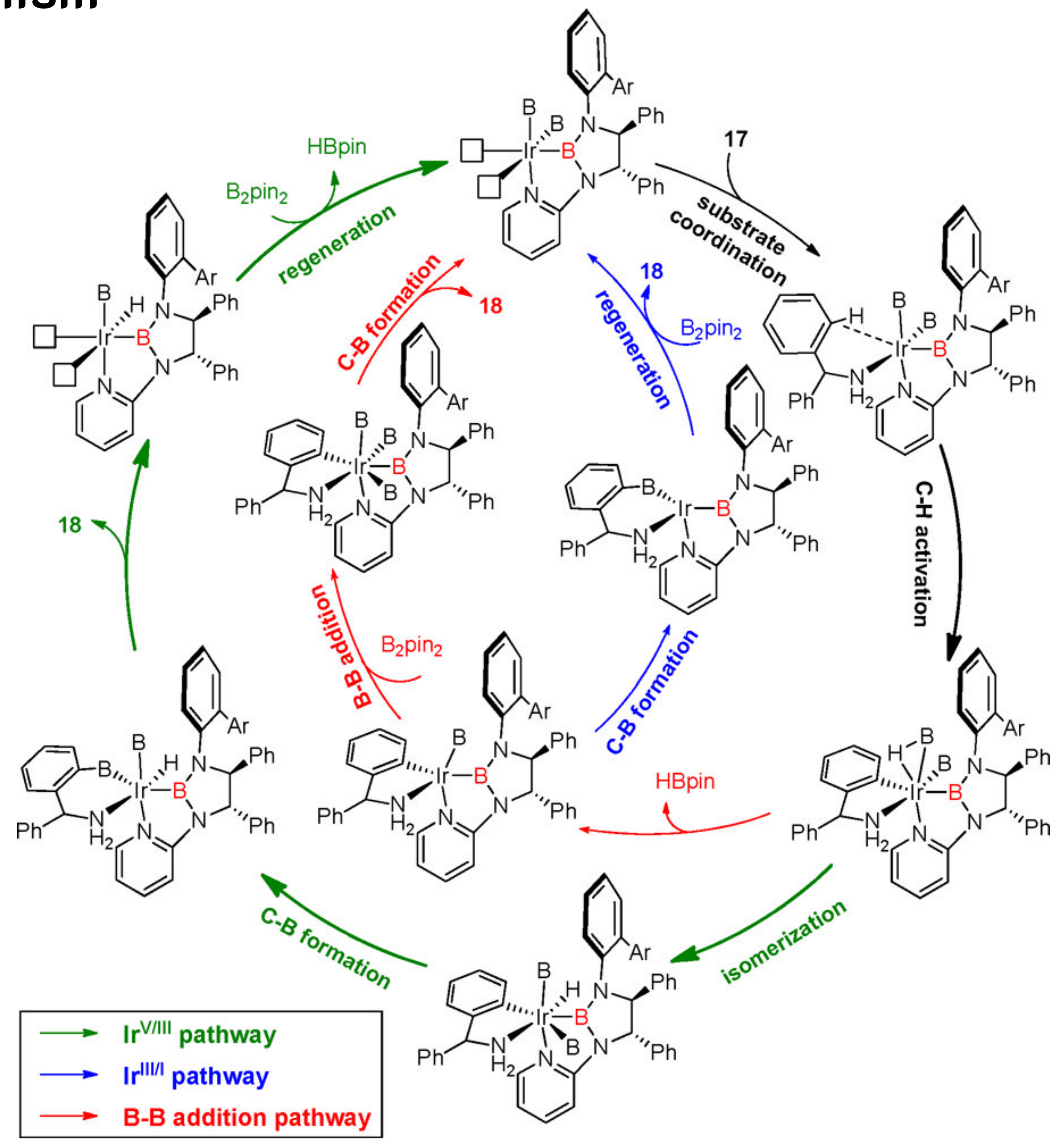
J. Am. Chem. Soc. **2019**, *141*, 5334.

Computational study on mechanism



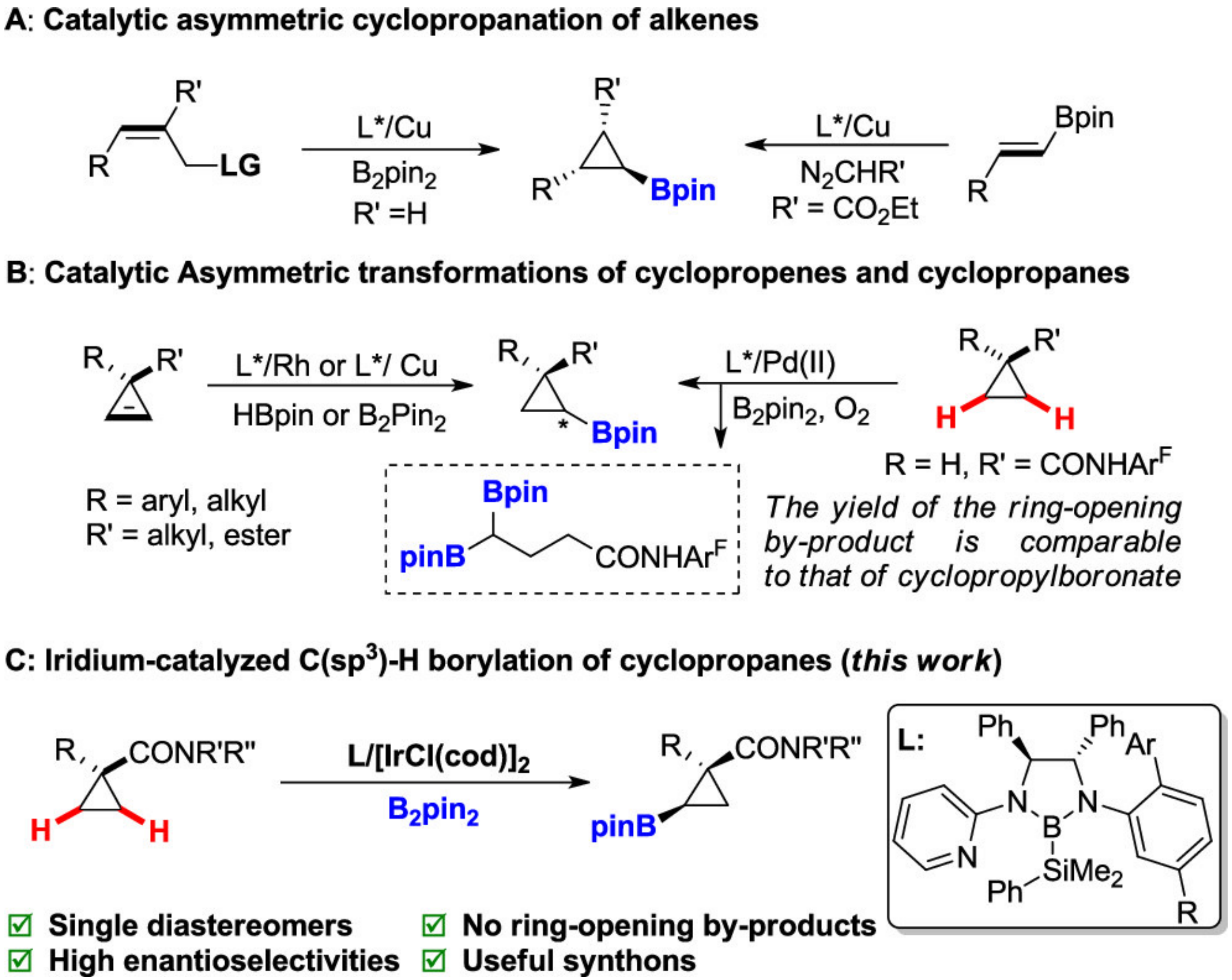
J. Am. Chem. Soc. **2019**, *141*, 5334.

Proposed mechanism



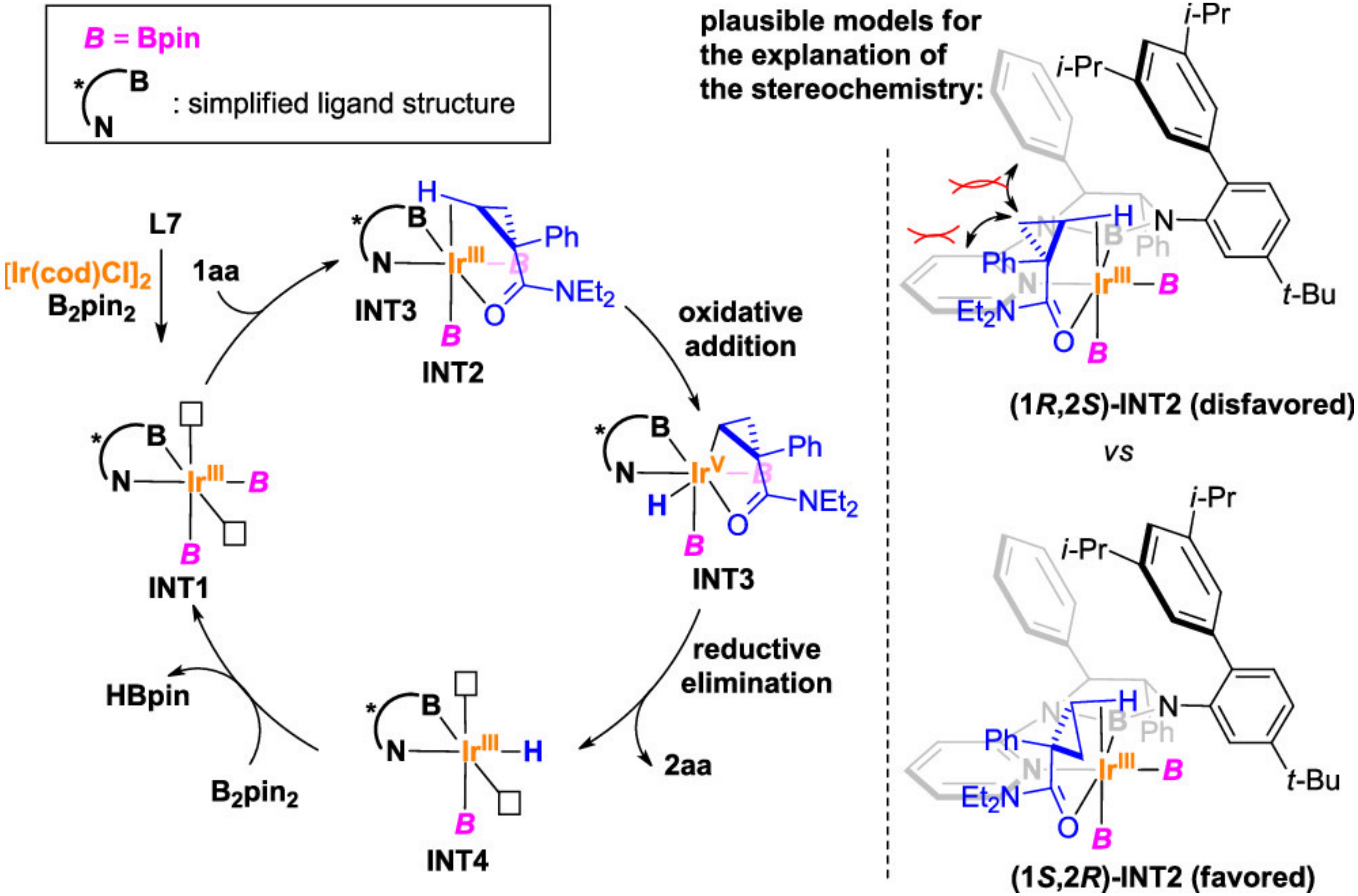
J. Am. Chem. Soc. **2019**, *141*, 5334.

Asymmetric C–H borylation of cyclopropanes



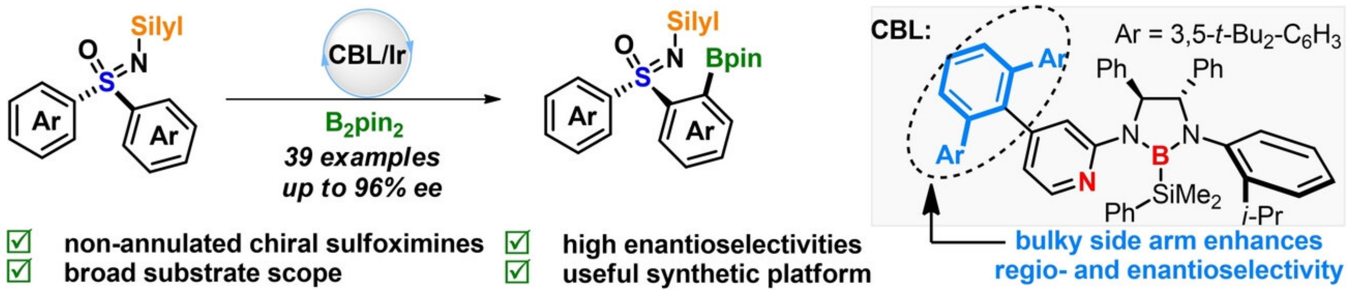
J. Am. Chem. Soc. **2019**, *141*, 10599.

Proposed mechanism

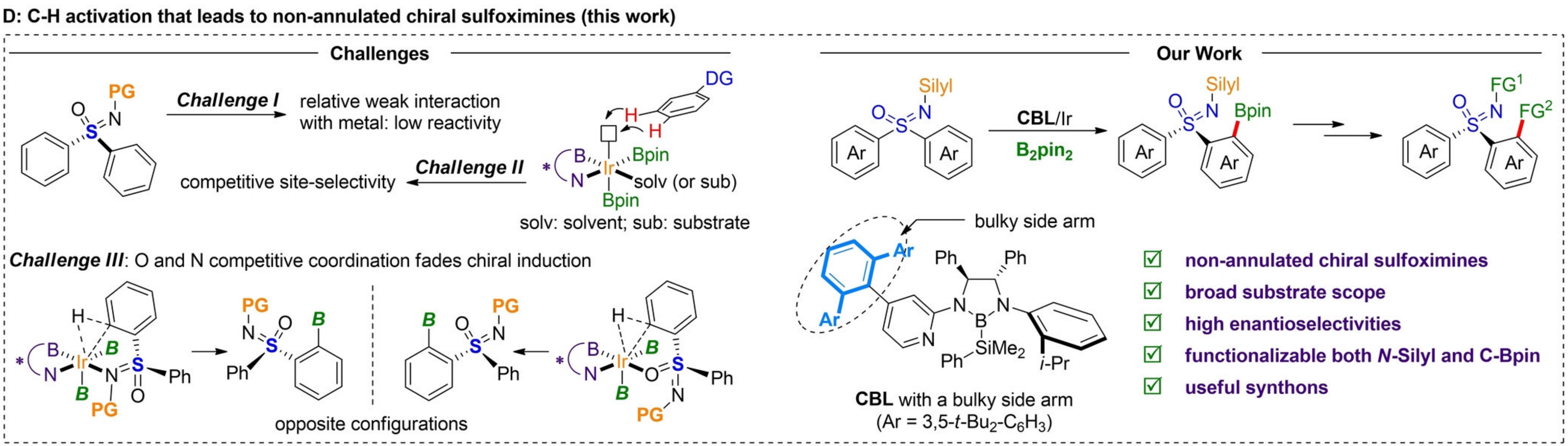


J. Am. Chem. Soc. **2019**, *141*, 10599.

Regio- and enantioselective C–H borylation of sulfoximine



Challenges on the substrate



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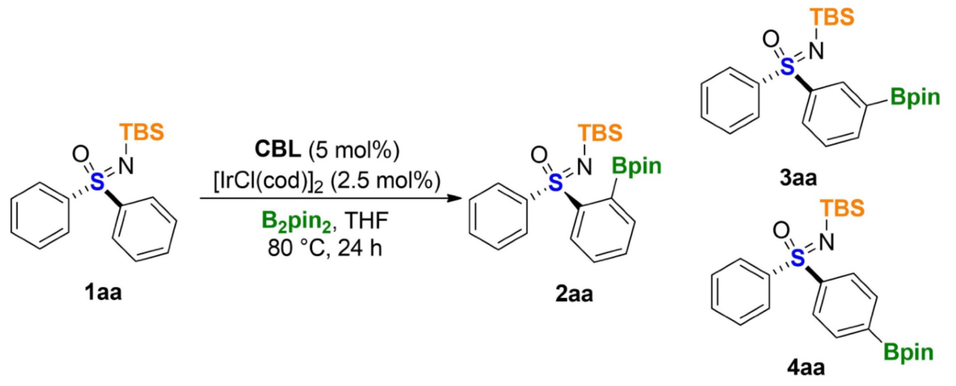
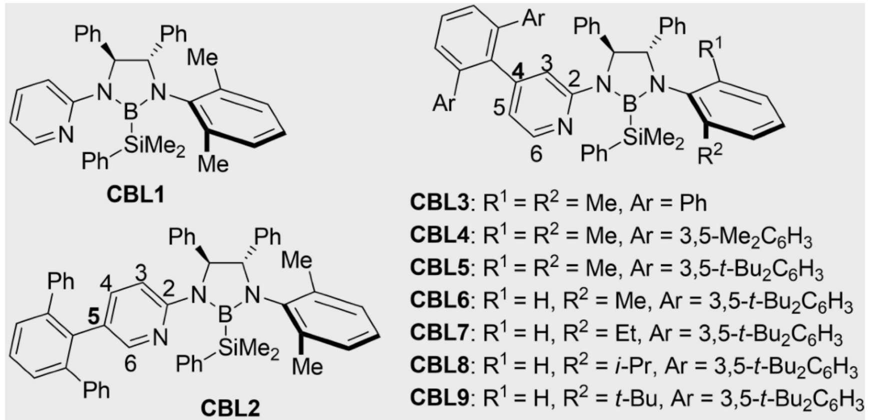
Ligand optimization





rr = **2aa/3aa+4aa**

Entry[a]	CBL	*rr*[b]	Yield [%][c]	ee [%][d]
1	**CBL1**	81:19	60	–26 (Inverse *ee*)
2	**CBL2**	29:71 (Inverse *rr*)	19	66
3	**CBL3**	69:31	52	66
4	**CBL4**	83:17	63	83
5	**CBL5**	54:46	41	91
6	**CBL6**	61:39	50	91
7	**CBL7**	71:29	56	91
8	**CBL8**	81:19	64	90
9	**CBL9**	62:38	51	82
10[e]	**CBL8**	95:5	74	89
11[f]	**CBL8**	88:12	65	90
12[e–g]	**CBL8**	96:4	79	93

[a] Unless otherwise noted, all the reactions were carried out with **1aa** (0.20 mmol), B_2pin_2 (0.30 mmol), **CBL** (0.01 mmol), and $[IrCl(cod)]_2$ (0.005 mmol) in THF (2.0 mL) at 80 °C for 24 h. [b] The *rr* values were determined by gas chromatography (GC) analysis. [c] Isolated yield of **2aa**. [d] Enantiomeric excess (ee) was determined by HPLC on a chiral stationary IC column. [e] *n*-hexane (2.0 mL) as the solvent. [f] $[Ir(OMe)(cod)]_2$ in lieu of $[IrCl(cod)]_2$. [g] The reaction was carried out at 60 °C for 36 h.

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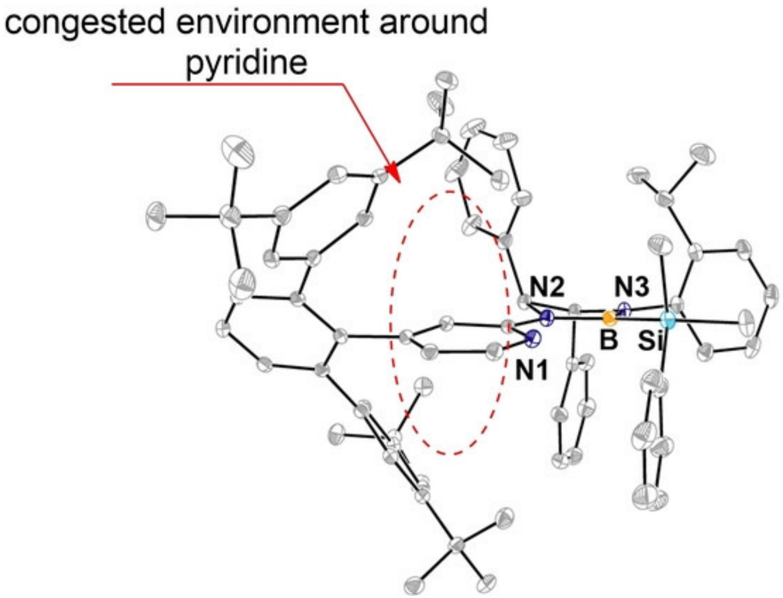
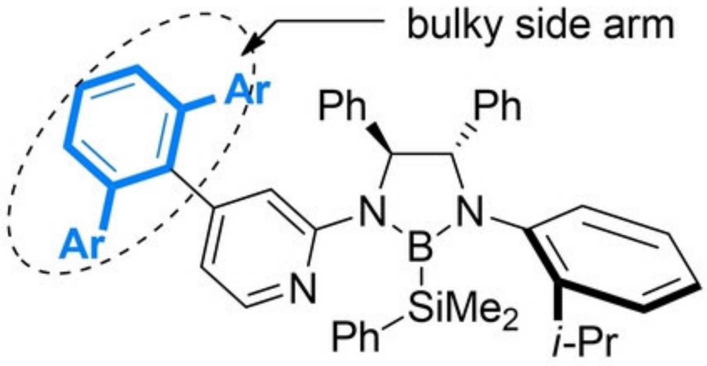
Optimized ligand (CBL8)

Side arms on pyridine clearly show steric effect





CBL with a bulky side arm
(Ar = 3,5-*t*-Bu_2-C_6H_3)

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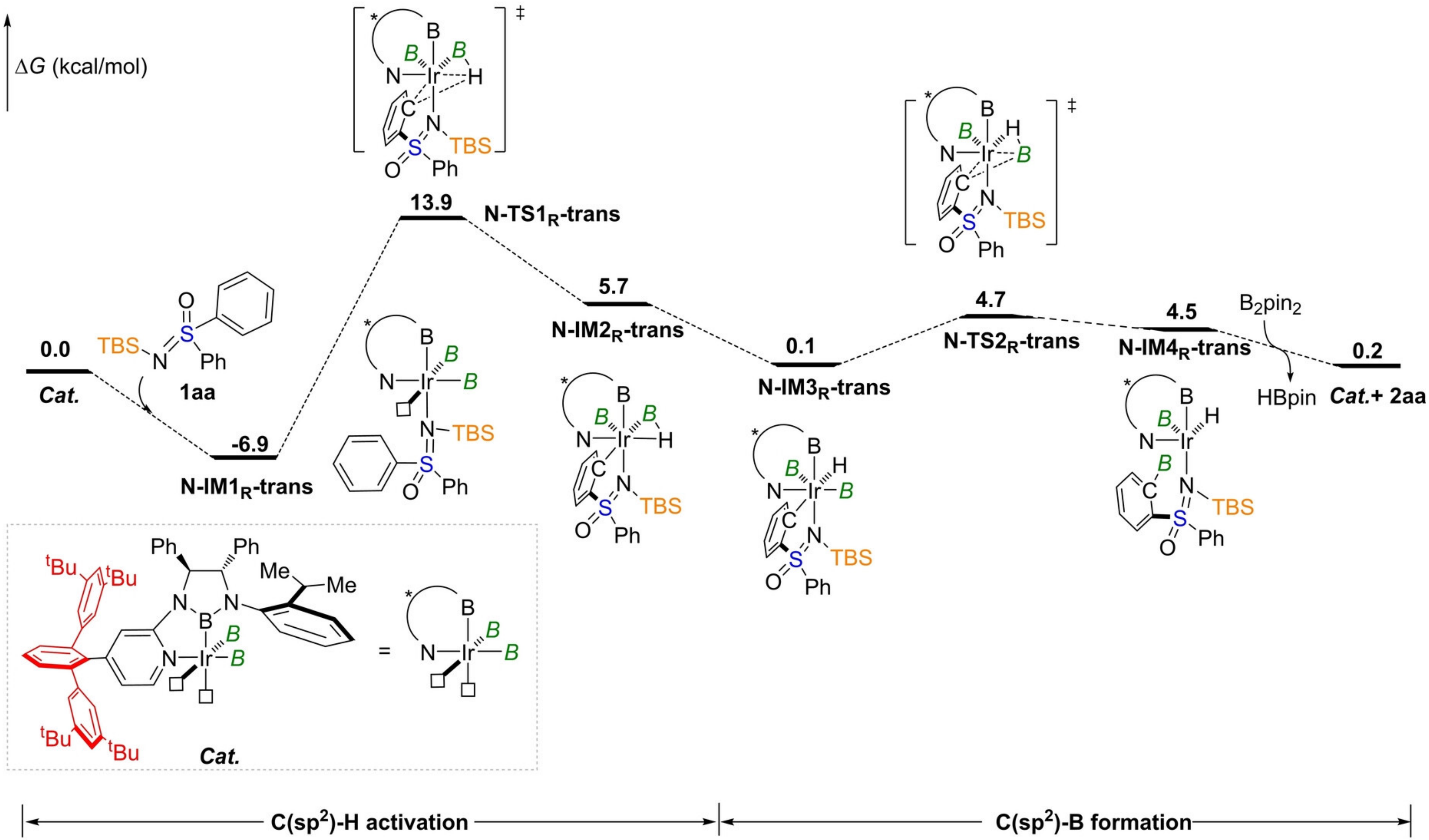
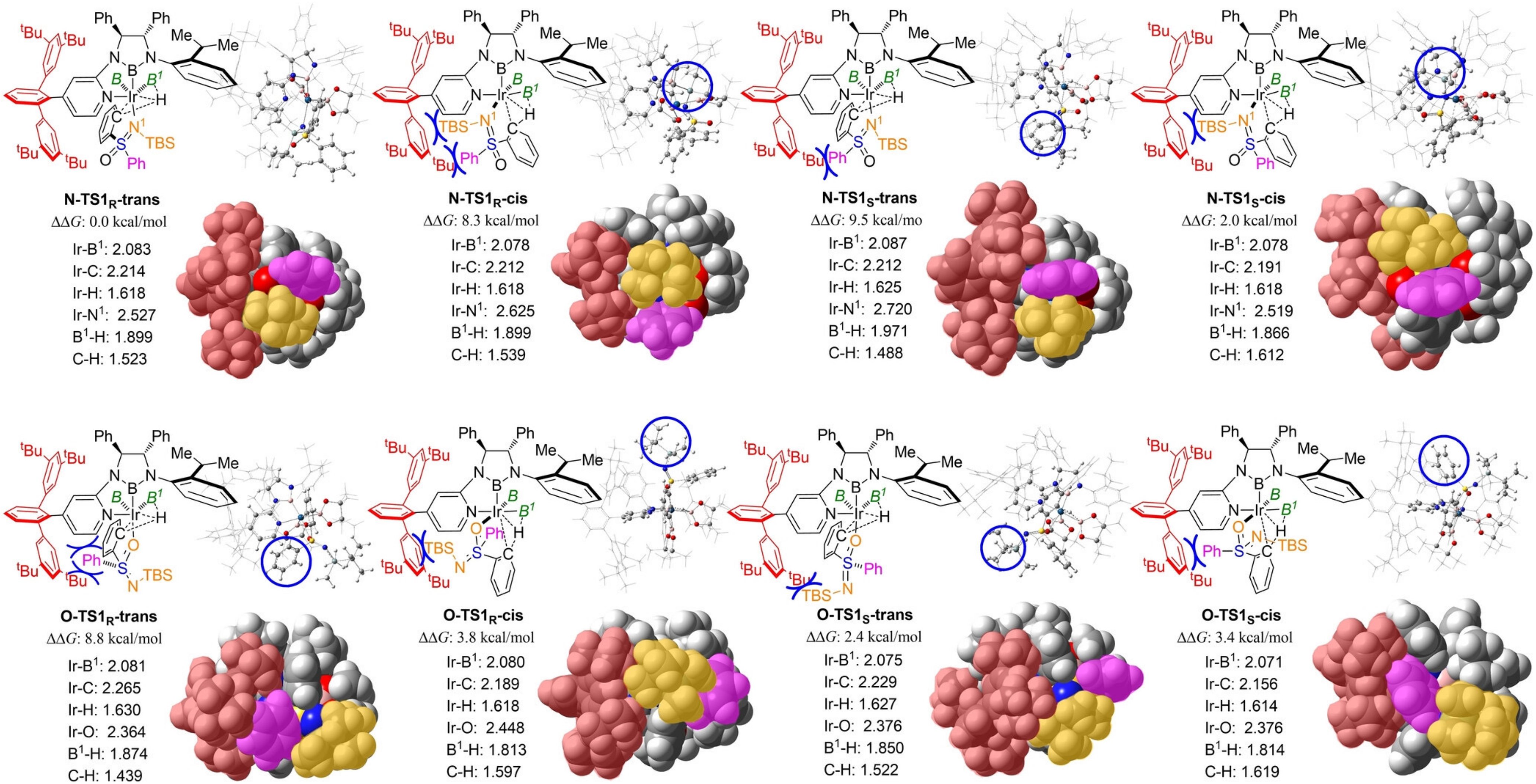
Computational study



Angew. Chem. Int. Ed. **2023**, *62*, e202217130.

Discussion on TS1 (OA of C–H bond is the enantio-determining step)

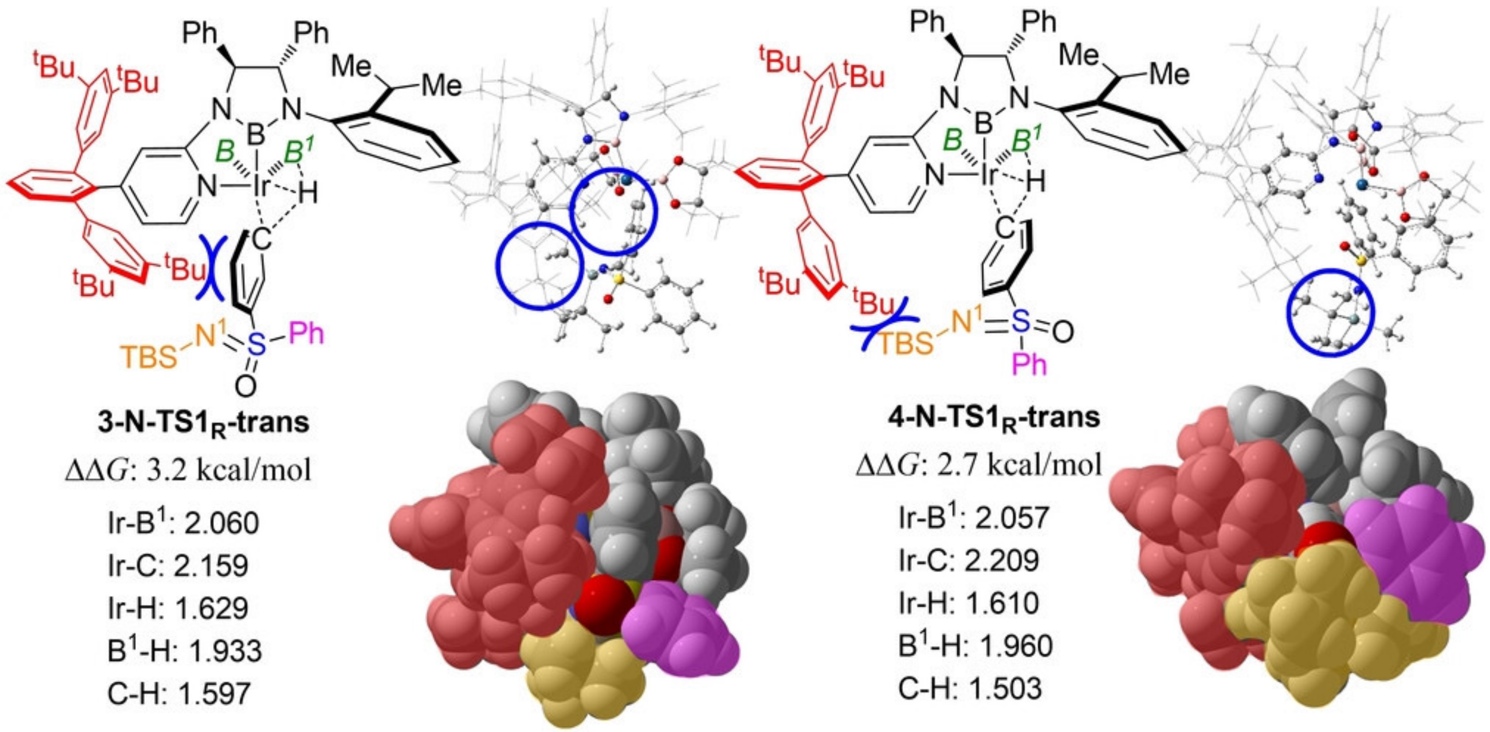
Selectivity on **1)** N-/O-atom; **2)** *trans-/cis-* of C/B; **3)** R/S of sulfoximine



Angew. Chem. Int. Ed. **2023**, *62*, e202217130.

Discussion on *ortho-* and *para-*borylation

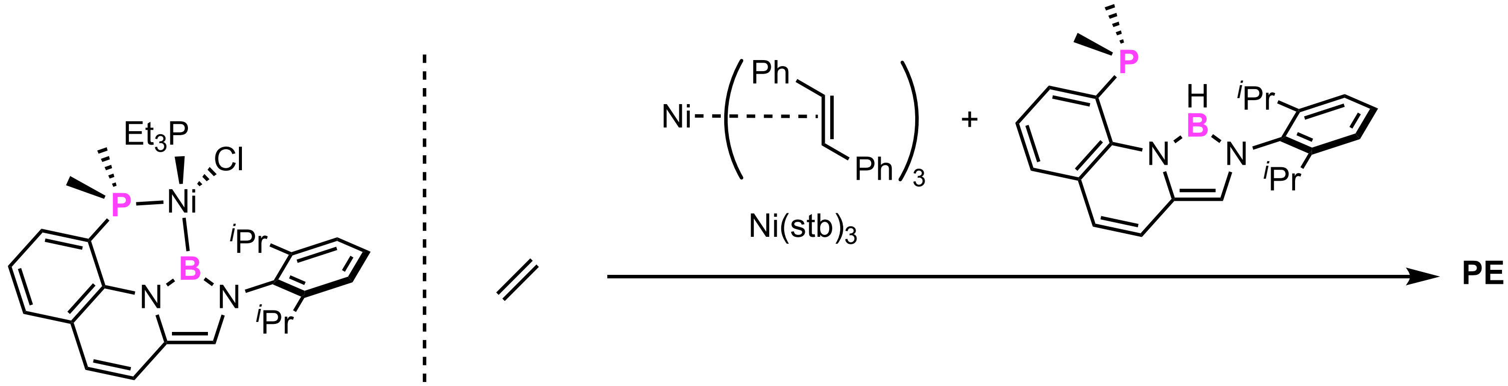
Selectivity on **1)** N-/O-atom; **2)** *trans-/cis-* of C/B; **3)** R/S of sulfoximine



Angew. Chem. Int. Ed. **2023**, *62*, e202217130.

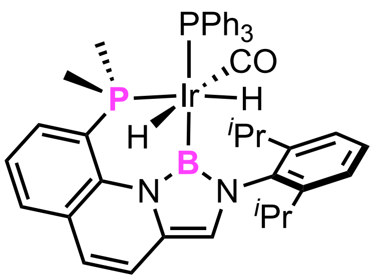
B,P-type Boryl Ligand | Ethylene Polymerization (Nozaki, 2022)

B,P-type ligand-supported Ni complex (Nozaki, 2022)

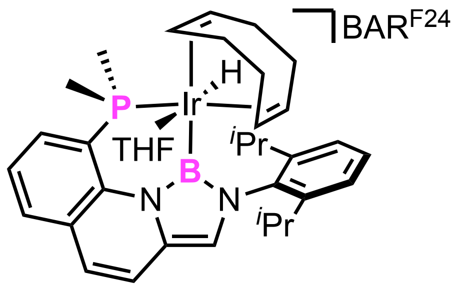


Angew. Chem. Int. Ed. **2022**, *61*, e202111691.

B,P-type ligand-supported Ir complexes (Nozaki, 2022)



neutral



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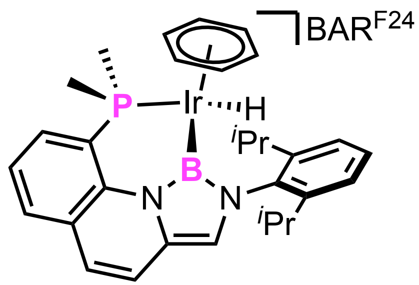

cationic

Organometallics **2022**, *41*, 1063.

Conclusion

Flexible coordination

Nature of bidentate ligand enables various stereo structures, where the rational choice of substituent could direct the reaction process selectively.

Limited reaction variety

Most developed examples were C–H borylation (racemic of enantioselective borylation).

More catalytic applications are expected.

THANK YOU FOR YOUR PATIENCE