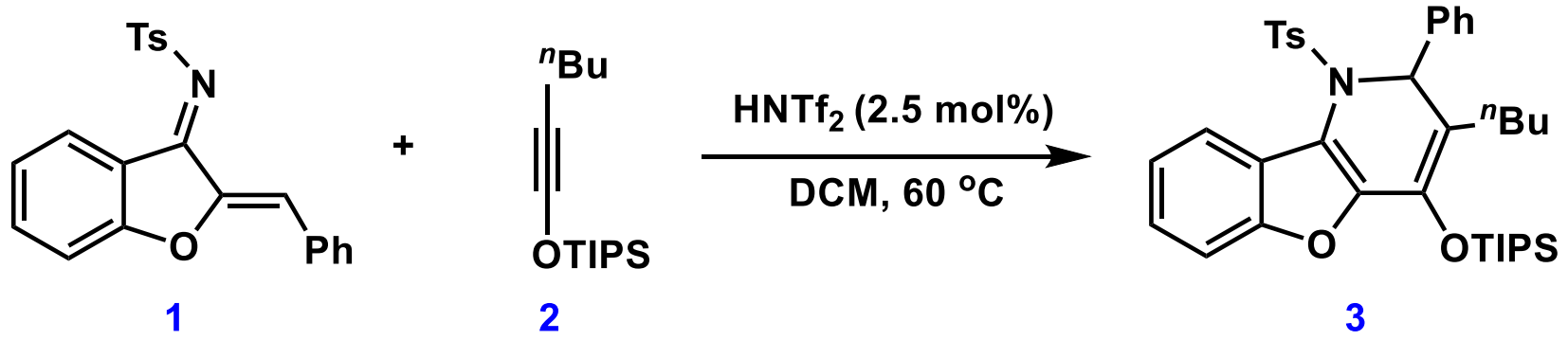
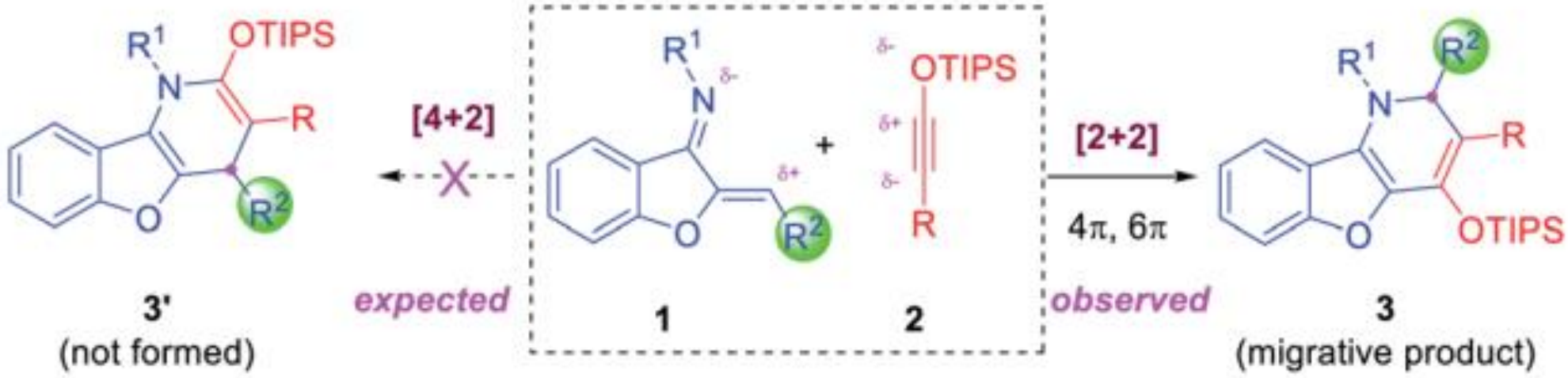
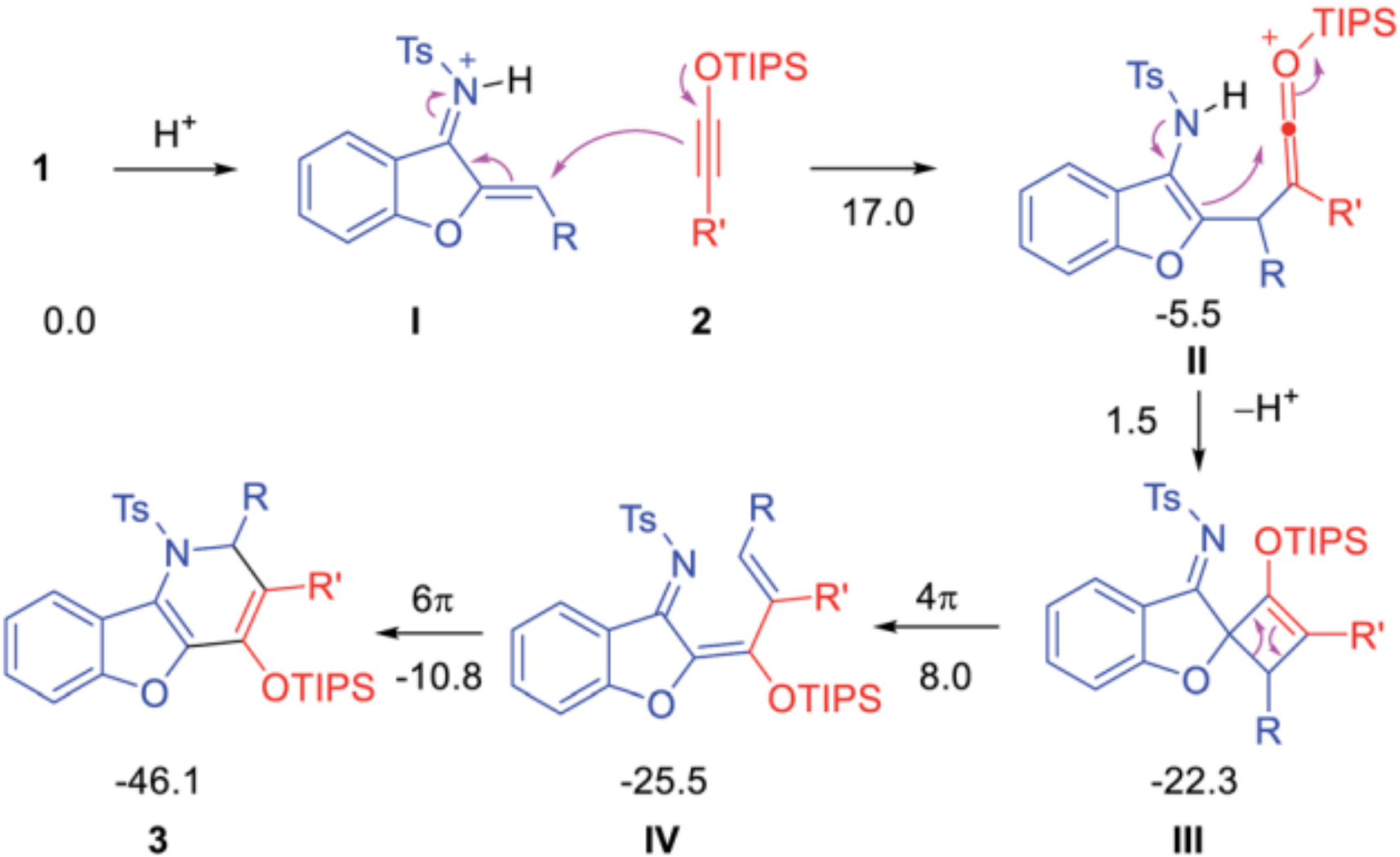
1.

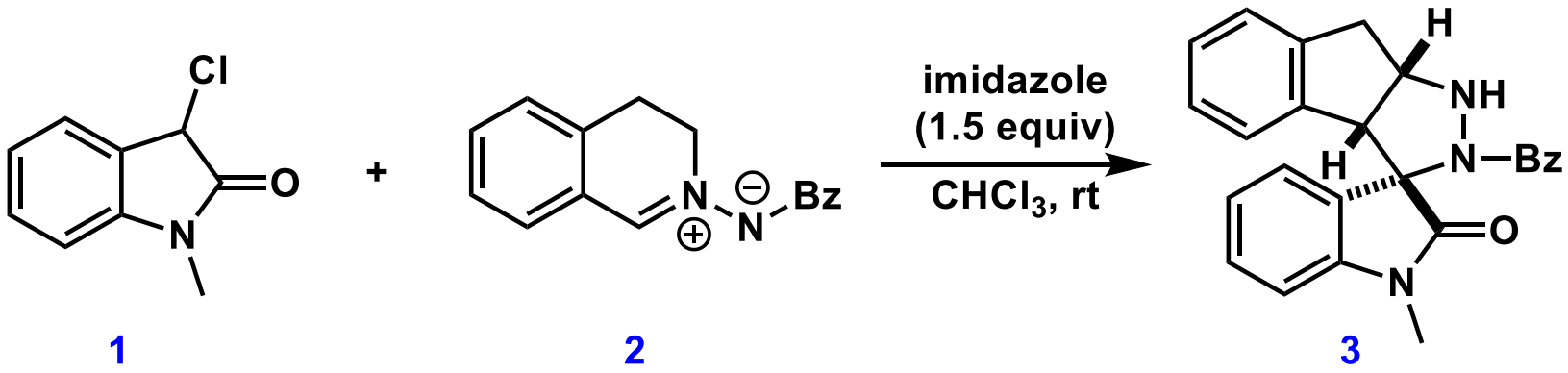


Chem. Sci. **2021**, *12*, 7953.



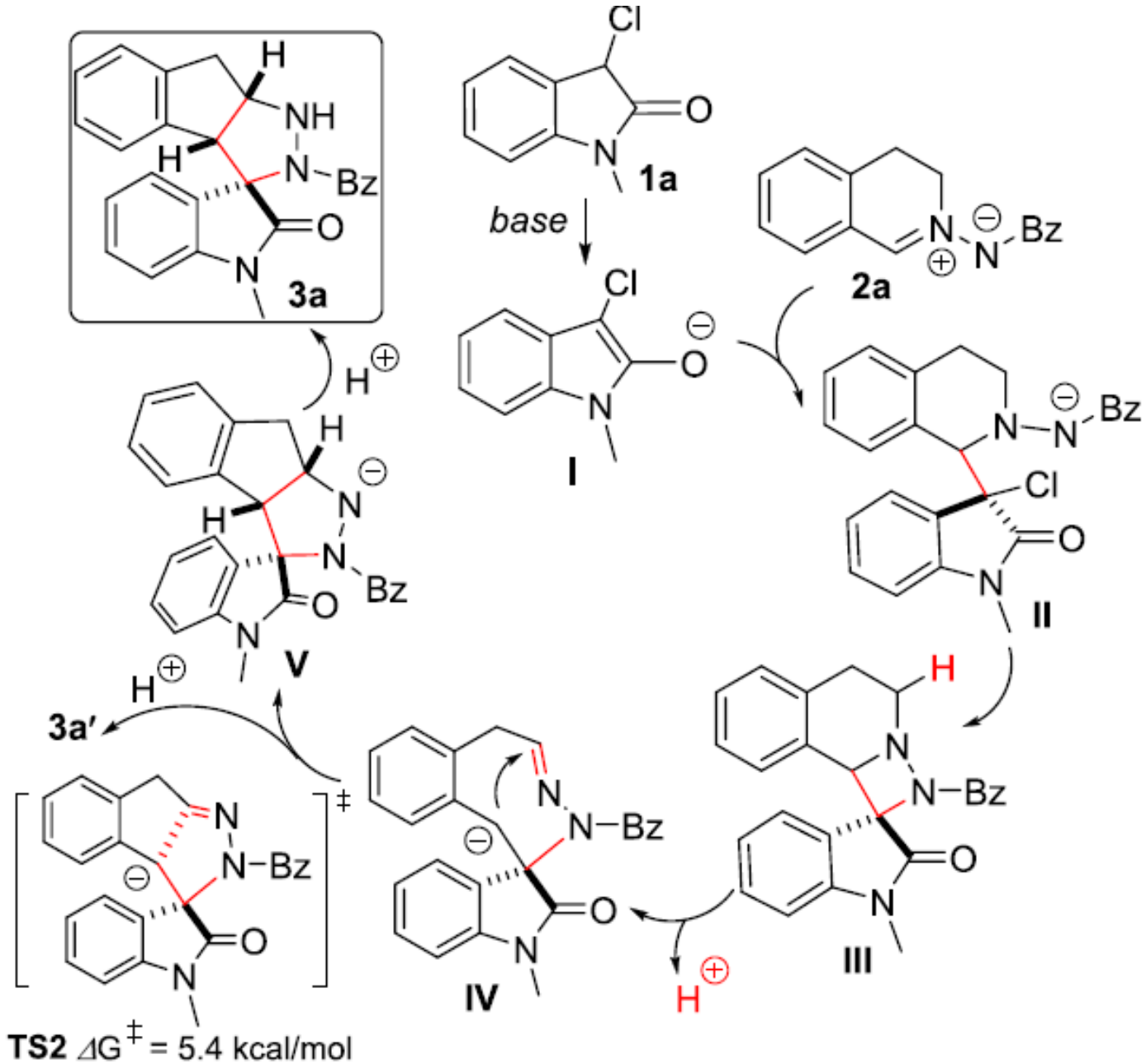

1
H+
0.0
Ts
N
H
R
O
I
OTIPS
R'
2
17.0
TIPS
-5.5
II
1.5
–H+
-22.3
III
4π
8.0
-25.5
IV
6π
-10.8
-46.1
3

2.

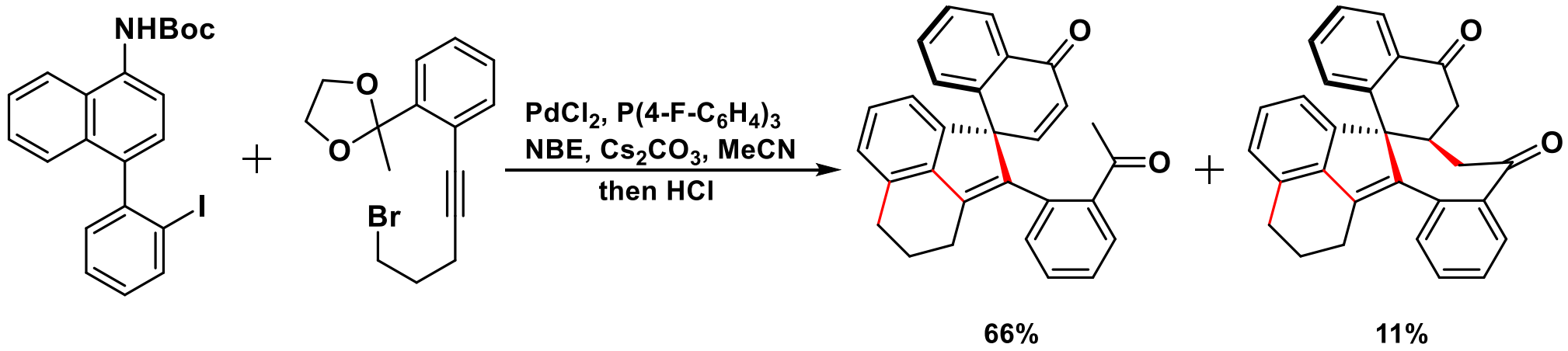


1 2 3

Org. Lett. **2019**, *21*, 10052.

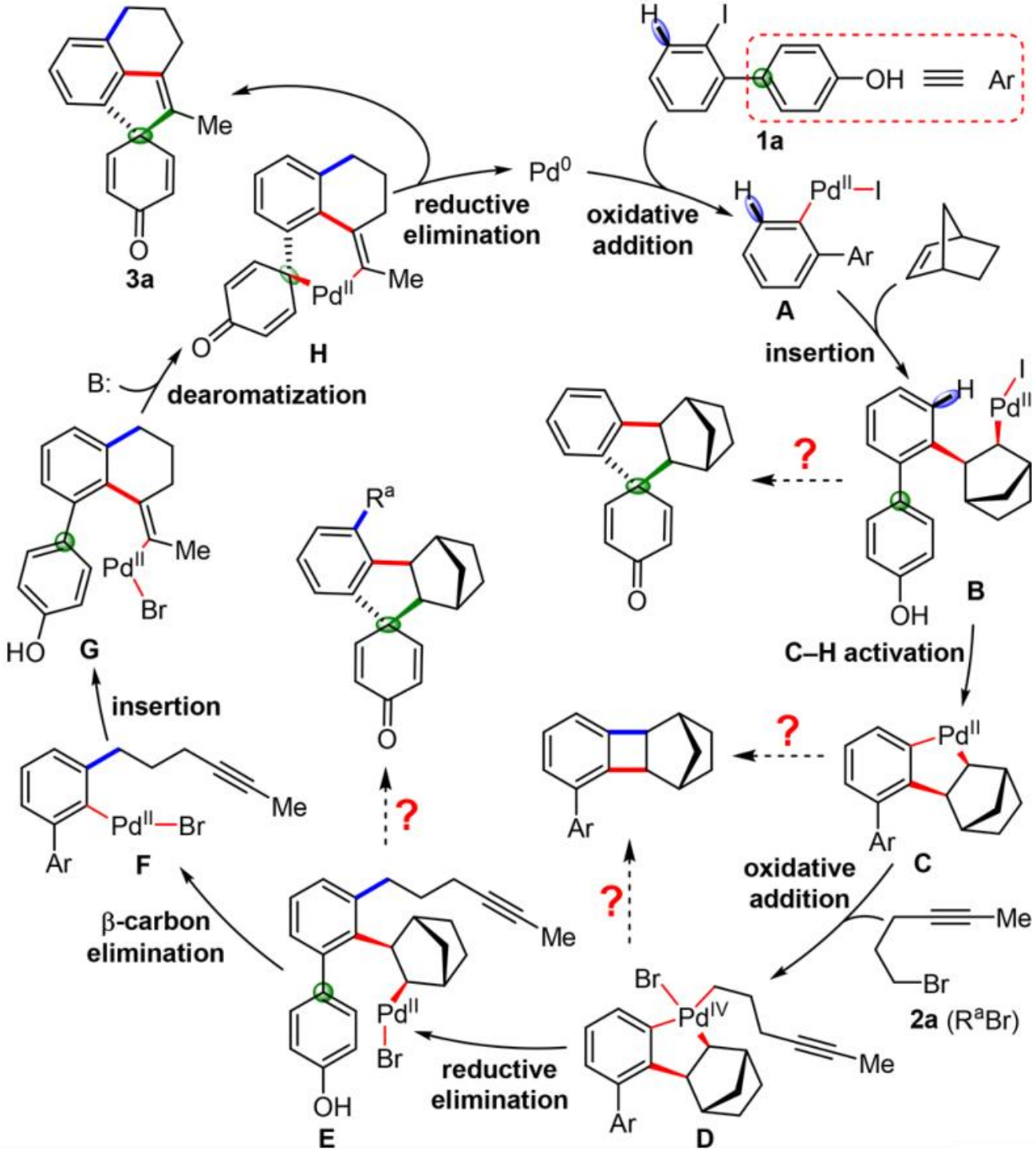

Cl
O
N
1a
base
Cl
O
N
I
2a
N
N
Bz
Cl
O
N
II
H
N
N–Bz
O
N
III
N
N–Bz
O
N
IV
H
H
N
N–Bz
O
N
V
H
H
NH
N–Bz
O
N
3a
H
3a′
TS2 ΔG‡ = 5.4 kcal/mol

3.

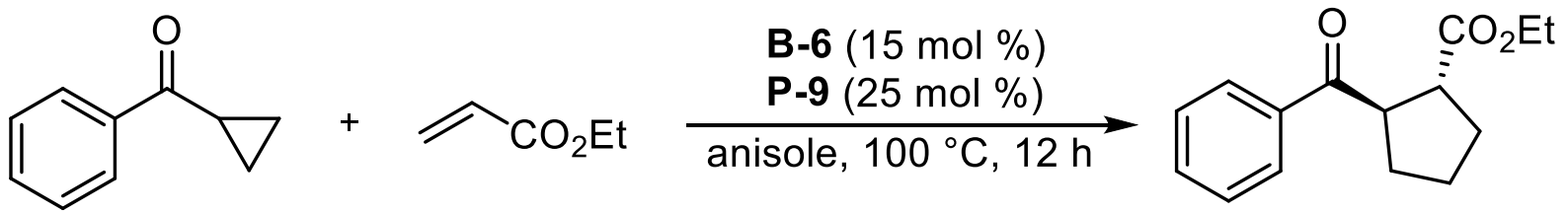


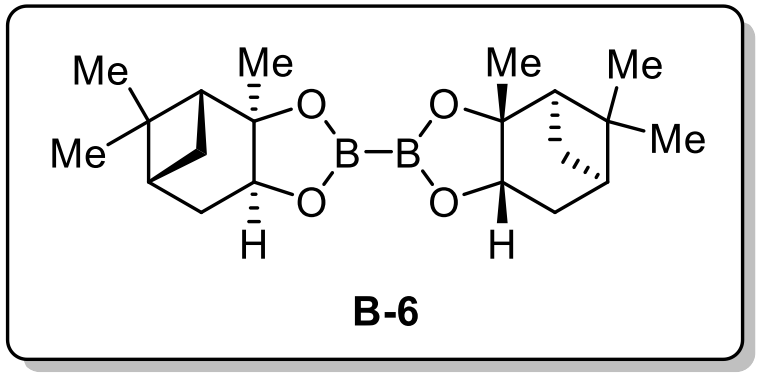
66% 11%

J. Am. Chem. Soc., **2021**, *143*, 21270.

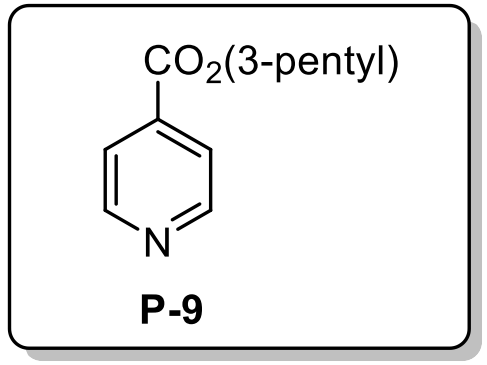

1a
Pd0
oxidative addition
reductive elimination
A
insertion
B
C–H activation
C
oxidative addition
2a (RaBr)
D
reductive elimination
E
β-carbon elimination
F
insertion
G
dearomatization
H
3a
B:
Me
Ar
OH
HO
Br
O
?

4.





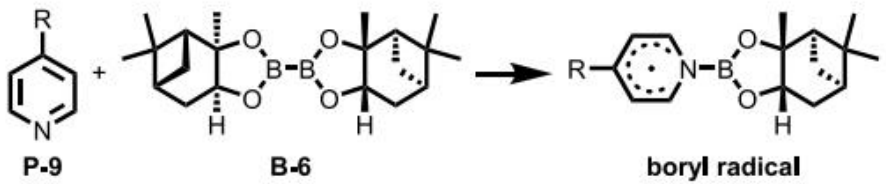
B-6



P-9

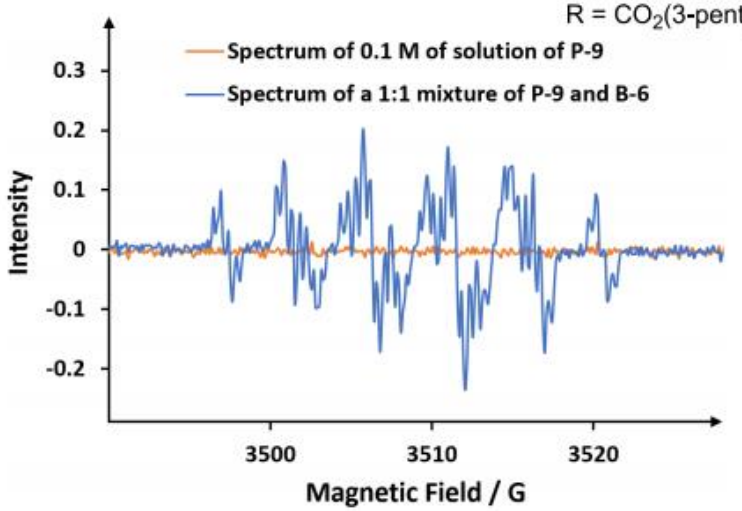
DOI:10.1021/jacs.2c03673.

A. electron paramagnetic resonance (EPR) experiments

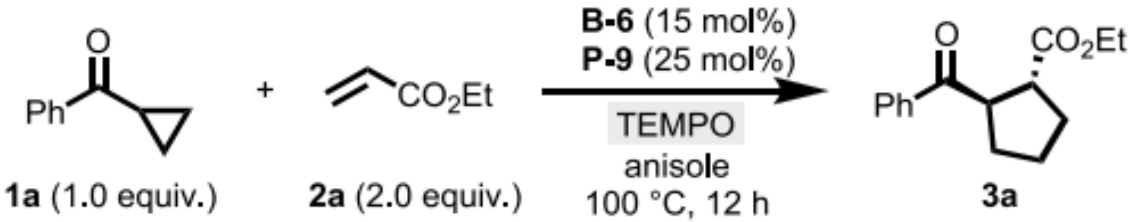


P-9 B-6 boryl radical

R = CO_2(3-pentyl)



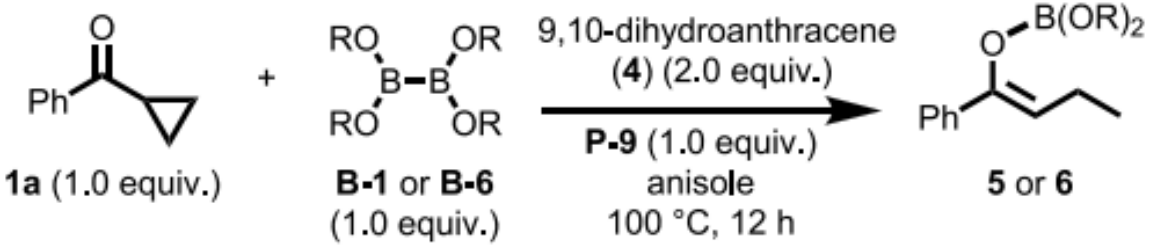
B. TEMPO stoichiometrically inhibited the catalyst



1a (1.0 equiv.) **2a** (2.0 equiv.) **3a**

TEMPO 10 mol%, **3a** 73% (77% conv.)
TEMPO 10 mol%, no reaction.

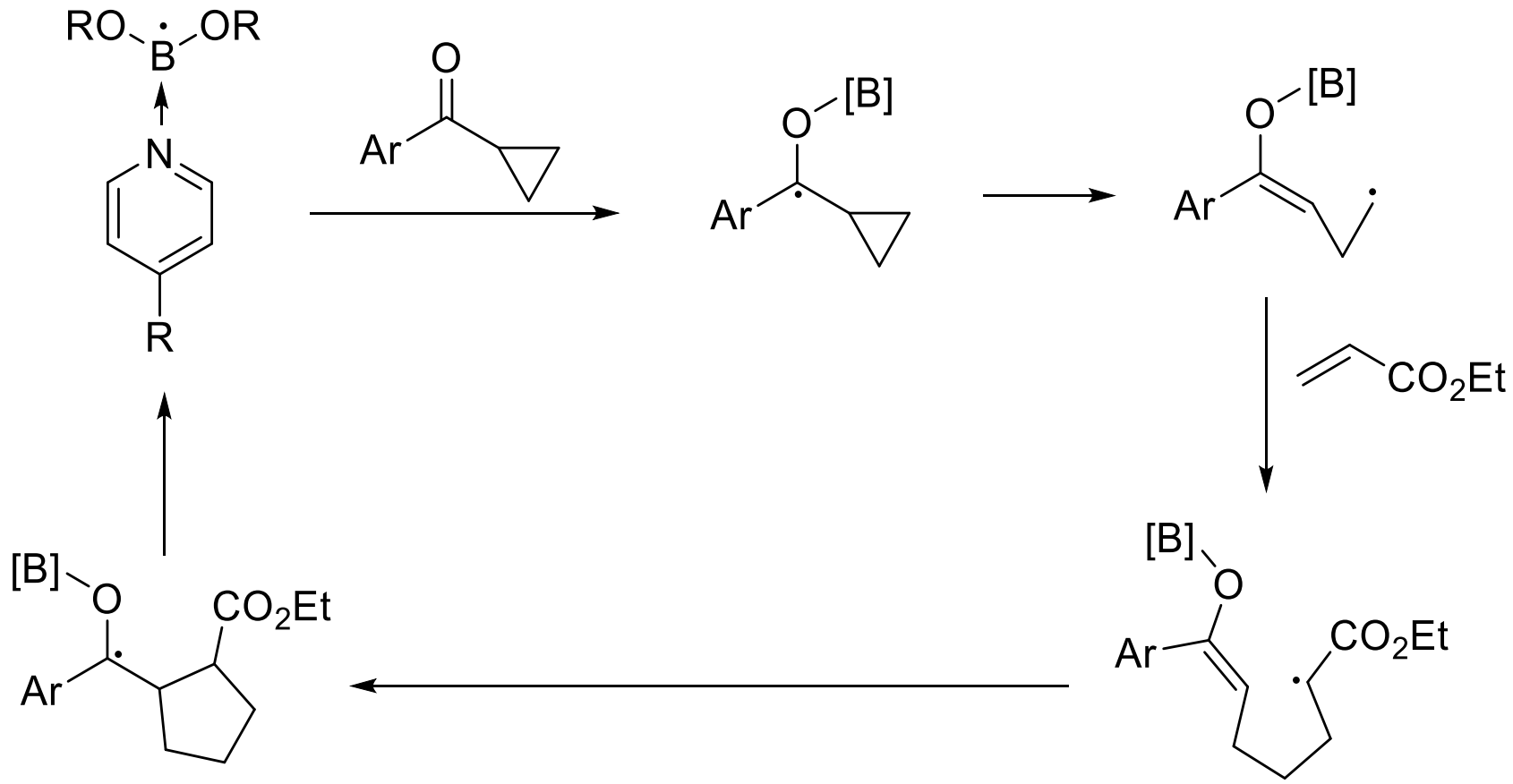
C. interception with a hydrogen donor led to ring-opened boron enolate

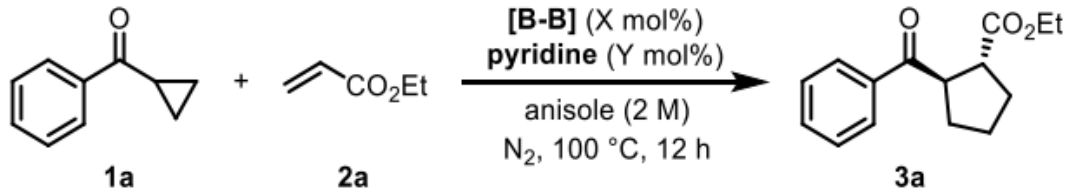


1a (1.0 equiv.) **B-1** or **B-6** (1.0 equiv.) **5** or **6**

5 (using **B-1**) 21% (38% conv.)
6 (using **B-6**) 59% (87% conv.)

by ^{1}H, ^{13}C NMR, COSY and HRMS

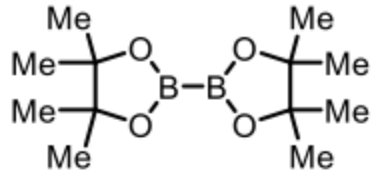

RO
B
OR
N
R
O
Ar
[B]
O
Ar
[B]
O
Ar
CO2Et
[B]
O
Ar
CO2Et
[B]
O
Ar
CO2Et



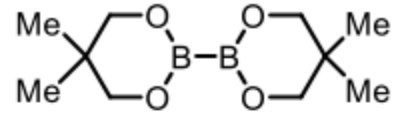
1a 2a 3a

entry	[B–B] (*X* mol %)	pyridine (*Y* mol %)	conversion (%)	yield (%)
1	**B-1** (15)	**P-1** (25)	32	28
2	**B-2** (15)	**P-1** (25)	7	<5
3	**B-3** (15)	**P-1** (25)	12	<5
4	**B-4** (15)	**P-1** (25)	38	37
5	**B-5** (15)	**P-1** (25)	50	48
6	**B-6** (15)	**P-1** (25)	87	86
7	**B-6** (15)	**P-2** (25)	66	65
8	**B-6** (15)	**P-3** (25)	5	<5
9	**B-6** (15)	**P-4** (25)	7	<5
10	**B-6** (15)	**P-5** (25)	0	0
11	**B-6** (15)	**P-6** (25)	0	0
12	**B-6** (15)	**P-7** (25)	86	83
13	**B-6** (15)	**P-8** (25)	79	76
14	**B-6** (15)	**P-9** (25)	92	90(87[b])
15	**B-6** (10)	**P-9** (25)	83	80
16	**B-6** (5)	**P-9** (25)	<5	<5
17	**B-6** (15)	**P-9** (50)	70	68
18	**B-6** (15)	**P-9** (10)	67	65
19		**P-9** (25)	0	0
20	**B-6** (15)		0	0

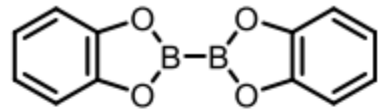
[a]Reactions were run on 0.3 mmol scale in 0.15 mL of anisole at 100 °C for 12 h. Conversion and yield were determined by ^{1}H NMR using 1,3,5-trimethoxybenzene as an internal standard. [b]Isolated yield.



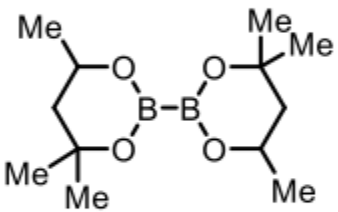
B-1



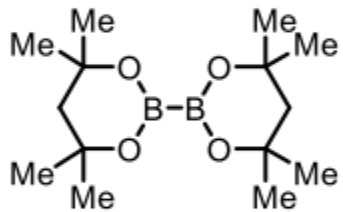
B-2



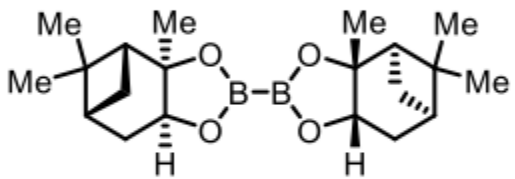
B-3



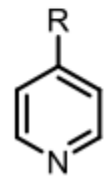
B-4



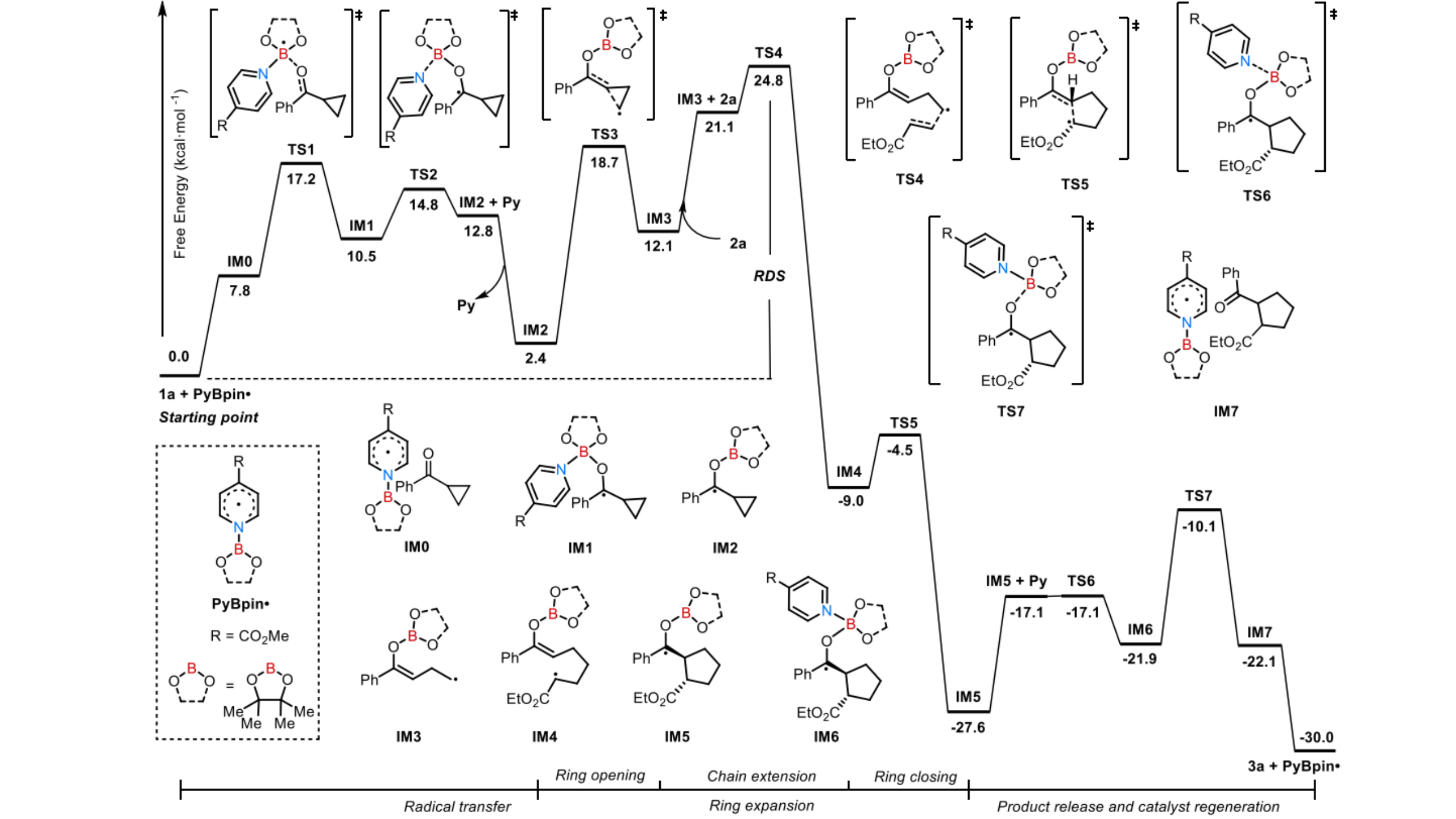
B-5



B-6



P-1: R = CO_2Et
P-2: R = CN
P-3: R = CF_3
P-4: R = Ph
P-5: R = ^{t}Bu
P-6: R = NMe_2
P-7: R = CO_2Me
P-8: R = $CO_2{}^t$Bu
P-9: R = CO_2(3-pentyl)


Free Energy (kcal·mol⁻¹)
0.0
1a + PyBpin•
Starting point
IM0
7.8
TS1
17.2
IM1
10.5
TS2
14.8
IM2 + Py
12.8
Py
IM2
2.4
TS3
18.7
IM3
12.1
IM3 + 2a
21.1
2a
TS4
24.8
RDS
IM4
-9.0
TS5
-4.5
IM5
-27.6
IM5 + Py
-17.1
TS6
-17.1
IM6
-21.9
TS7
-10.1
IM7
-22.1
3a + PyBpin•
PyBpin•
R = CO2Me
IM0
IM1
IM2
IM3
IM4
IM5
IM6
TS4
TS5
TS6
TS7
IM7
Ring opening
Chain extension
Ring closing
Radical transfer
Ring expansion
Product release and catalyst regeneration