Recent Advances in Transition-Metal-Catalyzed C−X Activation

Reporter: Songbai Wu

Supervisor: Prof. Jing Zhao

Dr. Mei Hong

2014.06.08

Contents

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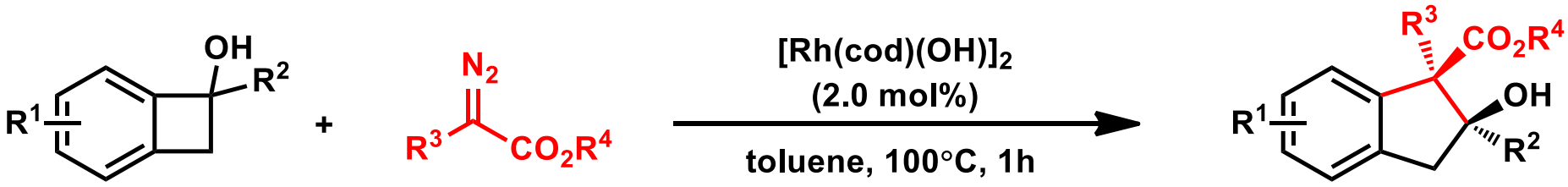
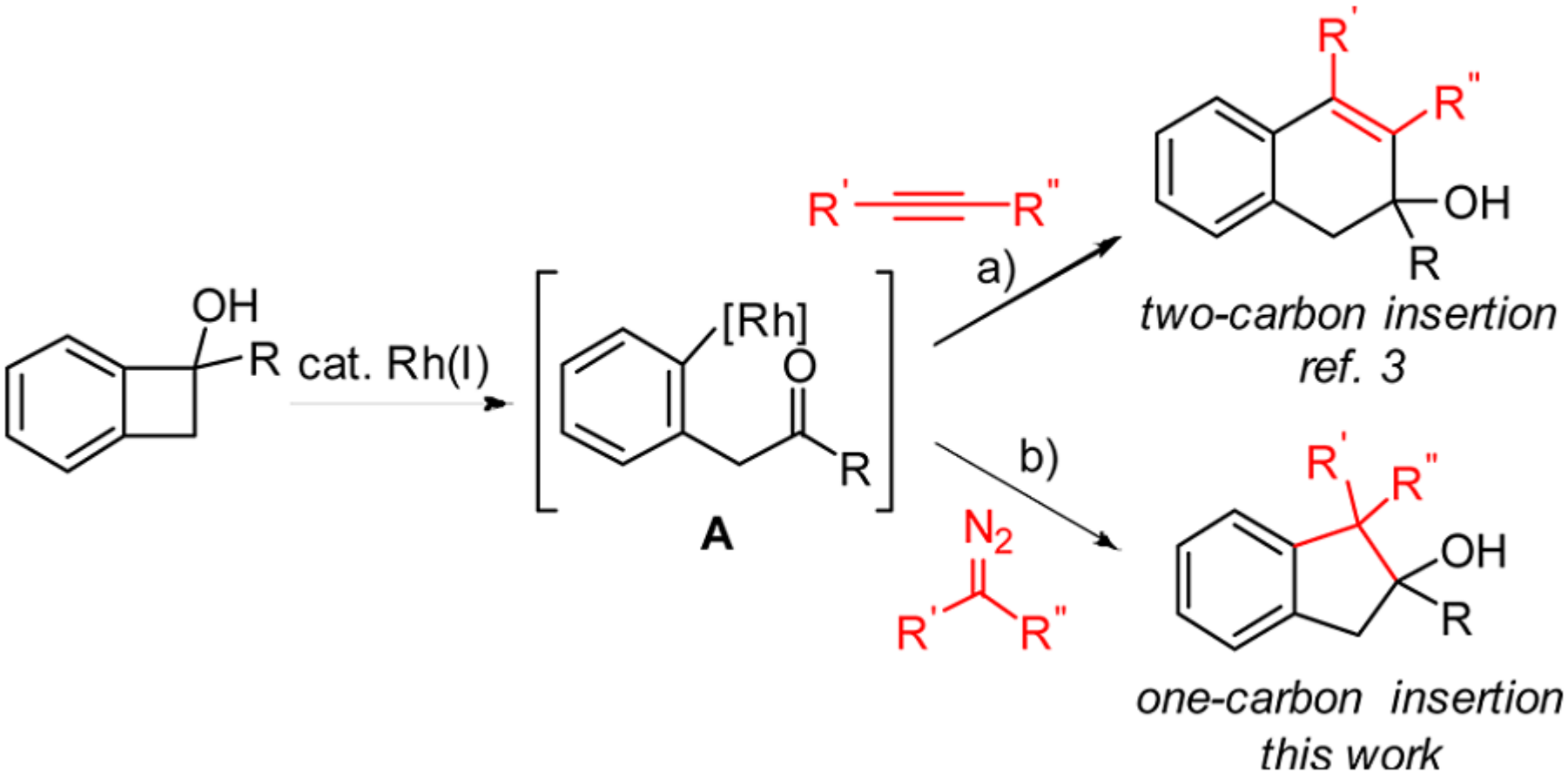
Formal Carbene Insertion into C–C Bond: Rh(I)-Catalyzed Reaction of Benzocyclobutenols with Diazoesters

Ying Xia, Zhenxing Liu, Zhen Liu, Rui Ge, Fei Ye, Mohammad Hossain, Yan Zhang, and Jianbo Wang*



Y. Xia, Z. Liu, Z Liu, R. Ge, F. Ye, M. Hossain, Y. Zhang and J. Wang, *J. Am. Chem. Soc*., 2014, **136**, 3013.

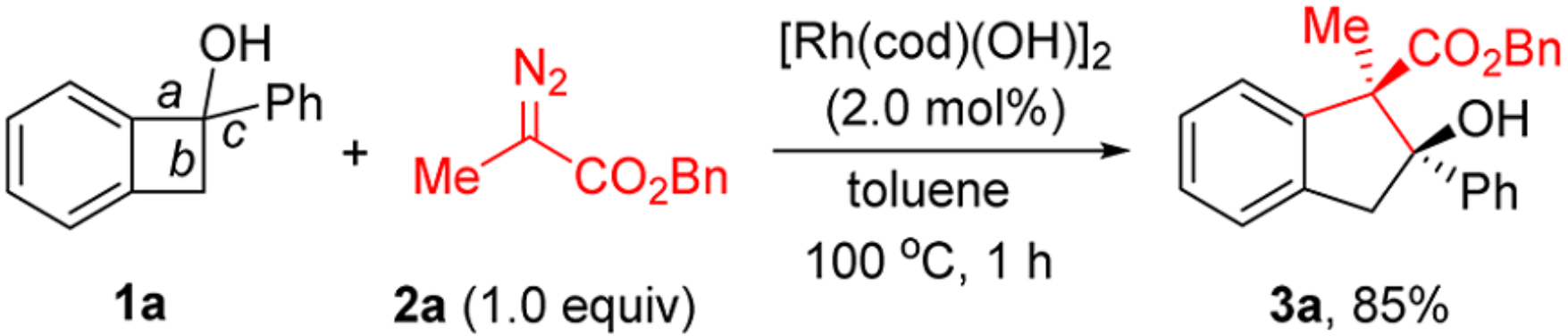
Origin of the Idea



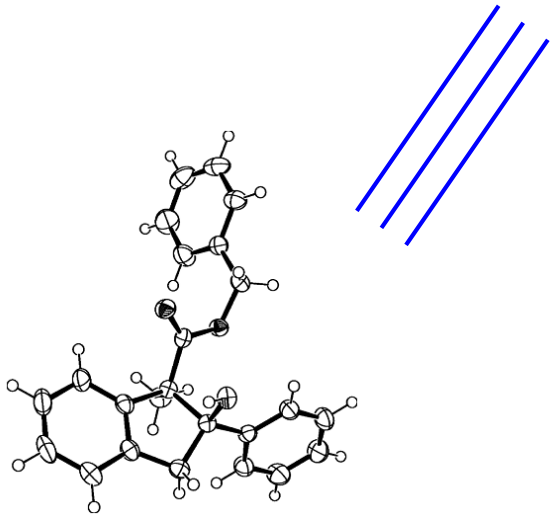
a) Ishida. N, Nakanishi and Y, Murakami. M, *J. Am. Chem. Soc*., 2012, **134**, 19103.

b) Y. Xia, Z. Liu, Z Liu, R. Ge, F. Ye, M. Hossain, Y. Zhang and J. Wang, *J. Am. Chem. Soc*., 2014, **136**, 3013.

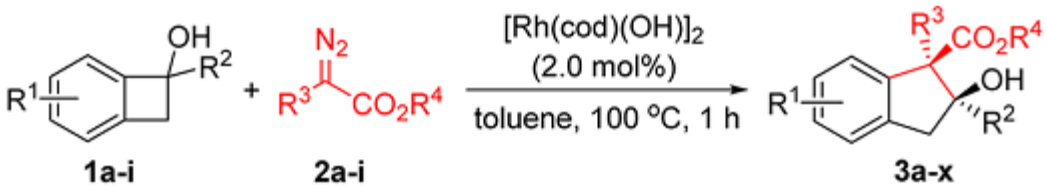
Screening of the Reaction Conditions



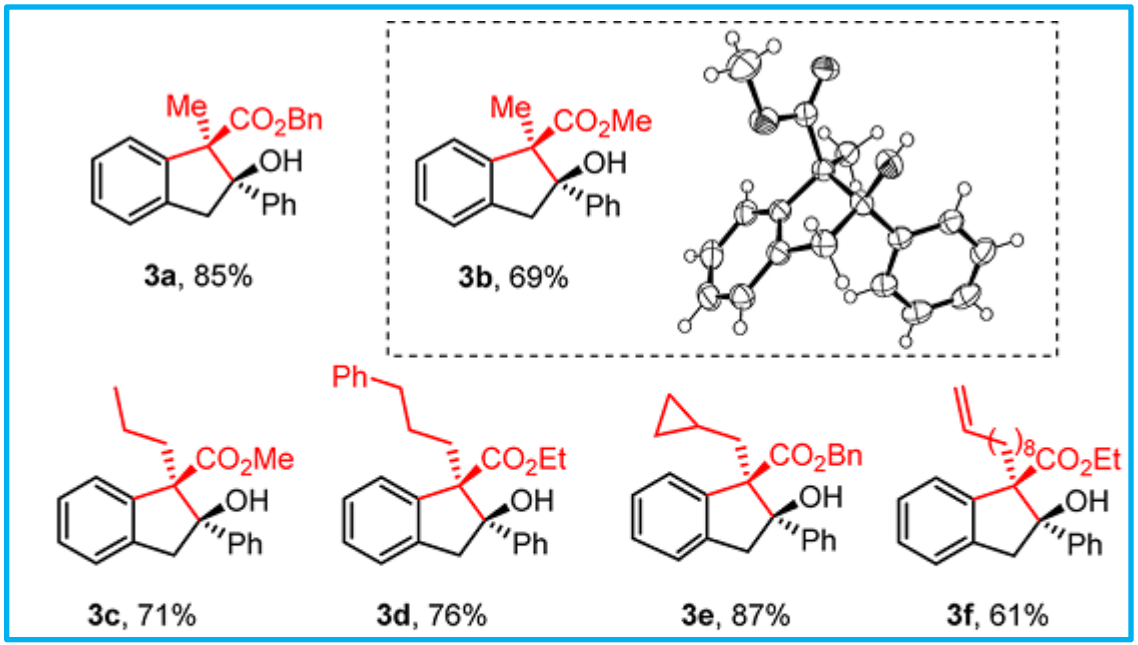
1a **2a** (1.0 equiv) **3a**, 85%

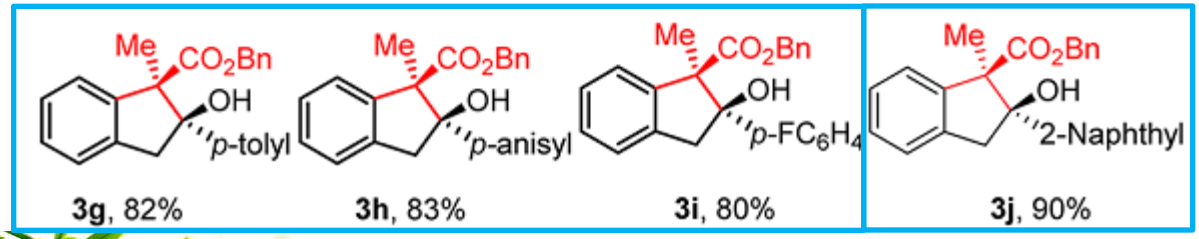


Scope of Substrates



1a-i **2a-i** **3a-x**





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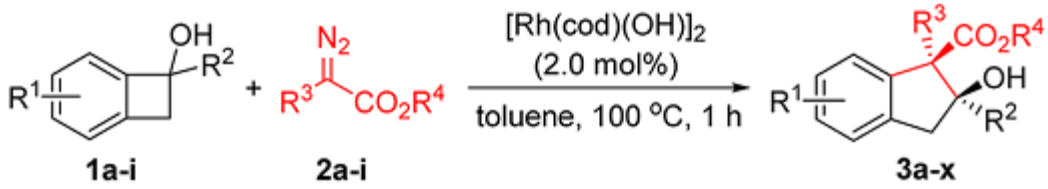
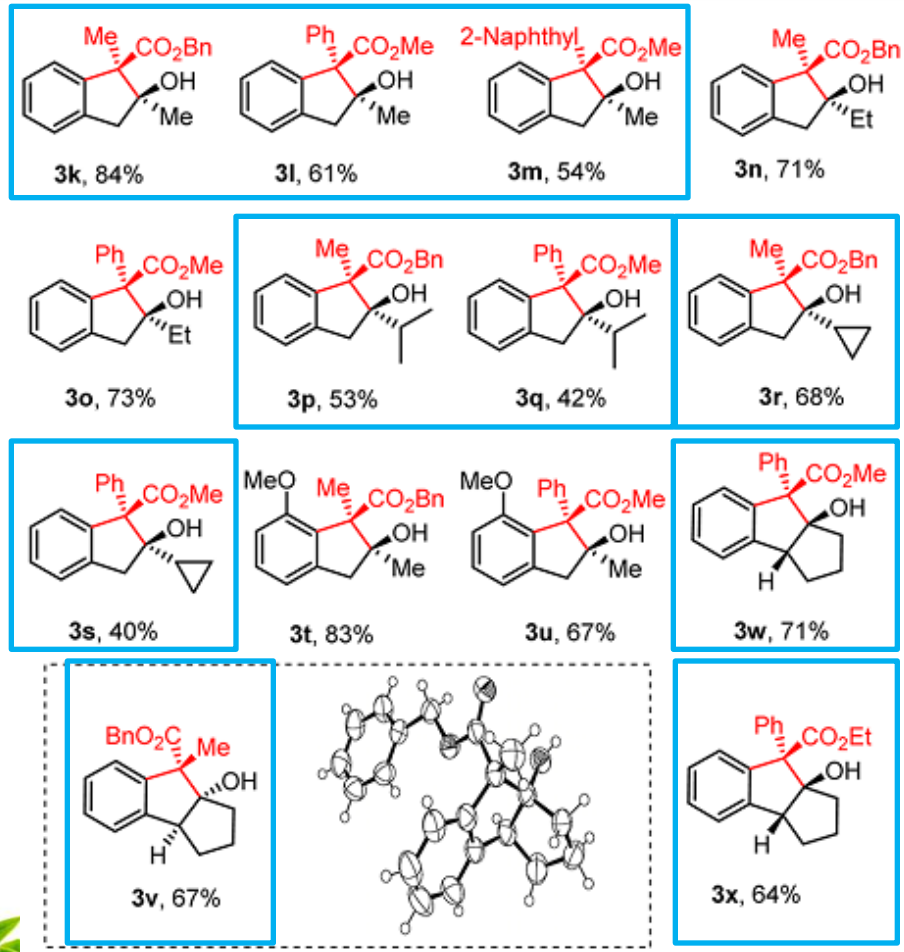
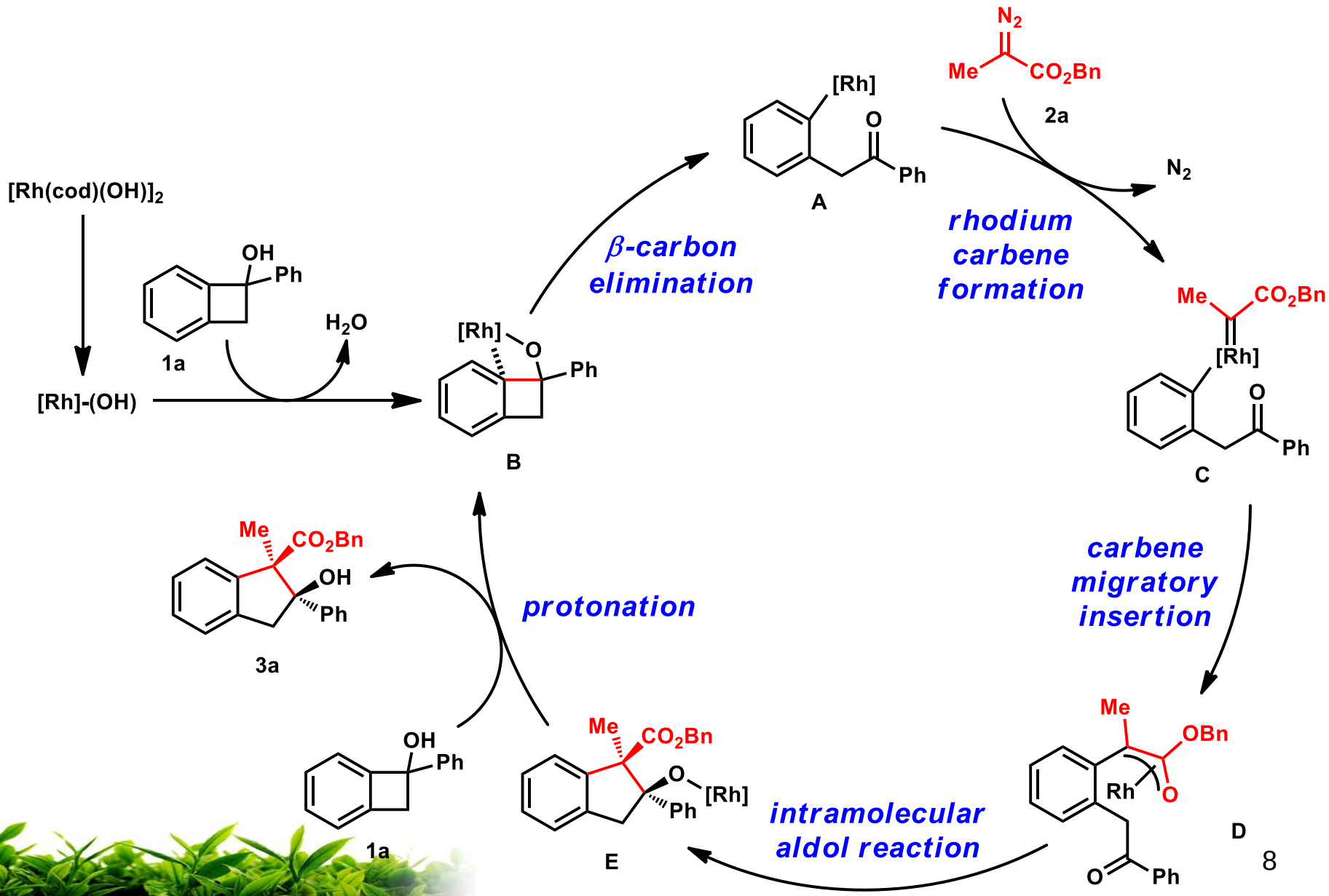


1a-i 2a-i 3a-x



Proposed Mechanism



Summary-1

A Rh(I)-catalyzed formal C-C bond carbene insertion reaction between benzocyclobutenols and diazoesters

Selective cleavage of C-C bond, Rh(I) carbene insertion, and intramolecular aldol reaction

Excellent regioselectivity and diastereoselectivity under mild reaction conditions, all-carbon quaternary center

Chemical Science

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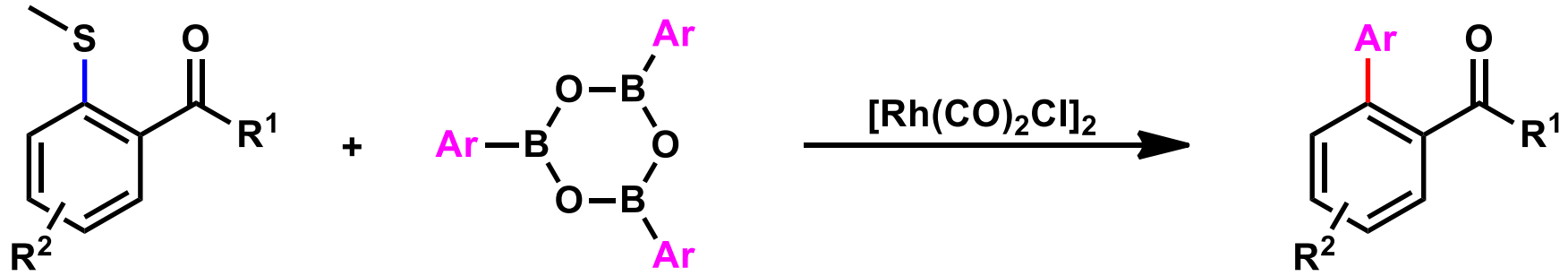
Cross coupling of thioethers with aryl boroxines to construct biaryls *via* Rh catalyzed C–S activation†

Cite this: *Chem. Sci.*, 2013, **4**, 1573

Fei Pan,[a] Hui Wang,[b] Peng-Xiang Shen,[a] Jing Zhao[b] and Zhang-Jie Shi*[ac]



F. Pan, H. Wang, P. Shen, J. Zhao and Z. Shi, *Chem. Sci*., 2013, **4**, 1573.

Origin of the Idea

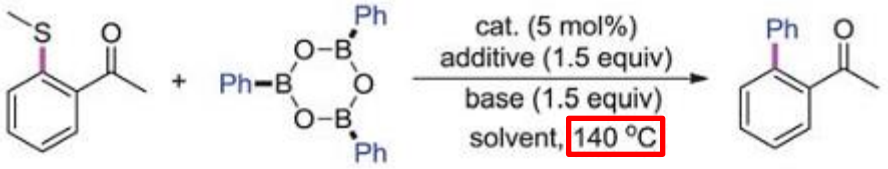
Traditional Methods

X=I, Br, Cl, OMe, OTf, OTs, etc

New Method

a) N. Miyaura, K. Yamada and A. Suzuki, *Tetrahedron Lett*., 1979, **20**, 3437.
b) F. Pan, H. Wang, P. Shen, J. Zhao and Z. Shi, *Chem. Sci*., 2013, **4**, 1573.

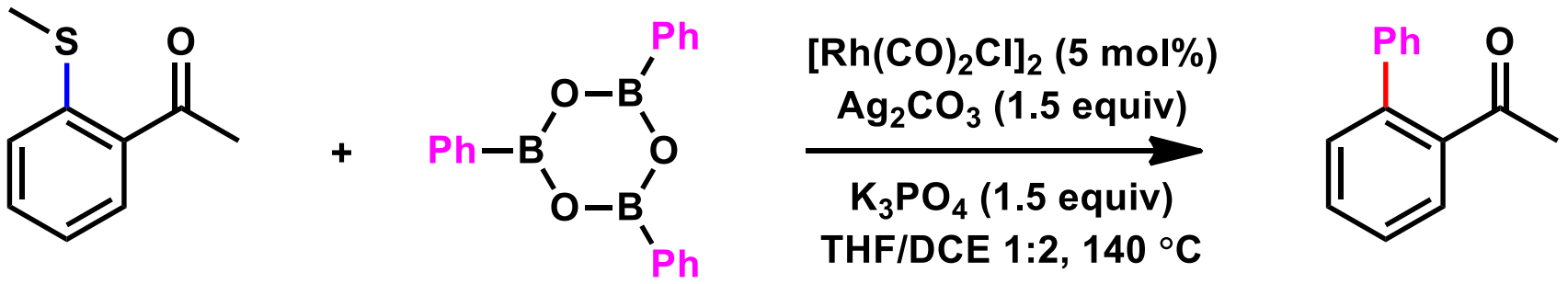
Screening of the Reaction Conditions



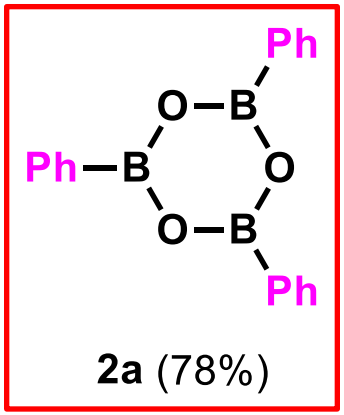
1a 2a 3aa

Entry	Catalyst	Additive	Base	Solvent	3aa[b] (%)
1	$Rh(CO)_2Cl_2$	Ag_2CO_3	K_3PO_4	Toluene	38%
2	$Rh(CO)_2Cl_2$	Ag_2CO_3	K_3PO_4	Dioxane	48%
3	$Rh(CO)_2Cl_2$	Ag_2CO_3	K_3PO_4	THF	53%
4	$Rh(CO)_2Cl_2$	Ag_2CO_3	K_3PO_4	DCE	56%
5	$Rh(CO)_2Cl_2$	Ag_2CO_3	K_3PO_4	THF–DCE 1 : 1	59%
6	$Rh(CO)_2Cl_2$	Ag_2CO_3	K_3PO_4	THF–DCE 1 : 2	83%
7	$Rh(COD)Cl_2$	Ag_2CO_3	K_3PO_4	THF–DCE 1 : 2	42%
8	$Rh(acac)_3$	Ag_2CO_3	K_3PO_4	THF–DCE 1 : 2	0
9	$Pd(OAc)_2$	Ag_2CO_3	K_3PO_4	THF–DCE 1 : 2	62%
10	$Ni(PCy_3)_2Cl_2$	Ag_2CO_3	K_3PO_4	THF–DCE 1 : 2	5%
11	$Ru(COD)Cl_2$	Ag_2CO_3	K_3PO_4	THF–DCE 1 : 2	47%
12	CuI	Ag_2CO_3	K_3PO_4	THF–DCE 1 : 2	0
13	$Rh(CO)_2Cl_2$	Ag_2O	K_3PO_4	THF–DCE 1 : 2	17%
14	$Rh(CO)_2Cl_2$	$Cu(OAc)_2$	K_3PO_4	THF–DCE 1 : 2	26%
15	$Rh(CO)_2Cl_2$	Ag_2CO_3	K_2CO_3	THF–DCE 1 : 2	46%
16	$Rh(CO)_2Cl_2$	Ag_2CO_3	Na_3PO_4	THF–DCE 1 : 2	18%
17	$Rh(CO)_2Cl_2$	Ag_2CO_3	CsOAc	THF–DCE 1 : 2	29%
18	$Rh(CO)_2Cl_2$	Ag_2CO_3	—	THF–DCE 1 : 2	19%
19	$Rh(CO)_2Cl_2$	—	K_3PO_4	THF–DCE 1 : 2	16%
20	—	Ag_2CO_3	K_3PO_4	THF–DCE 1 : 2	0
21[c]	$Rh(CO)_2Cl_2$	Ag_2CO_3	K_3PO_4	THF–DCE 1 : 2	88% (78%)

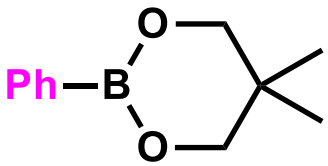
Screening of the Reaction Conditions



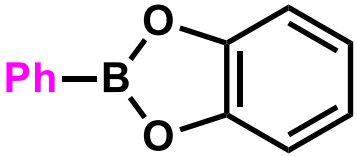
1a + **2** → **3aa**



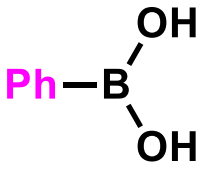
2a (78%)



2b (21%)



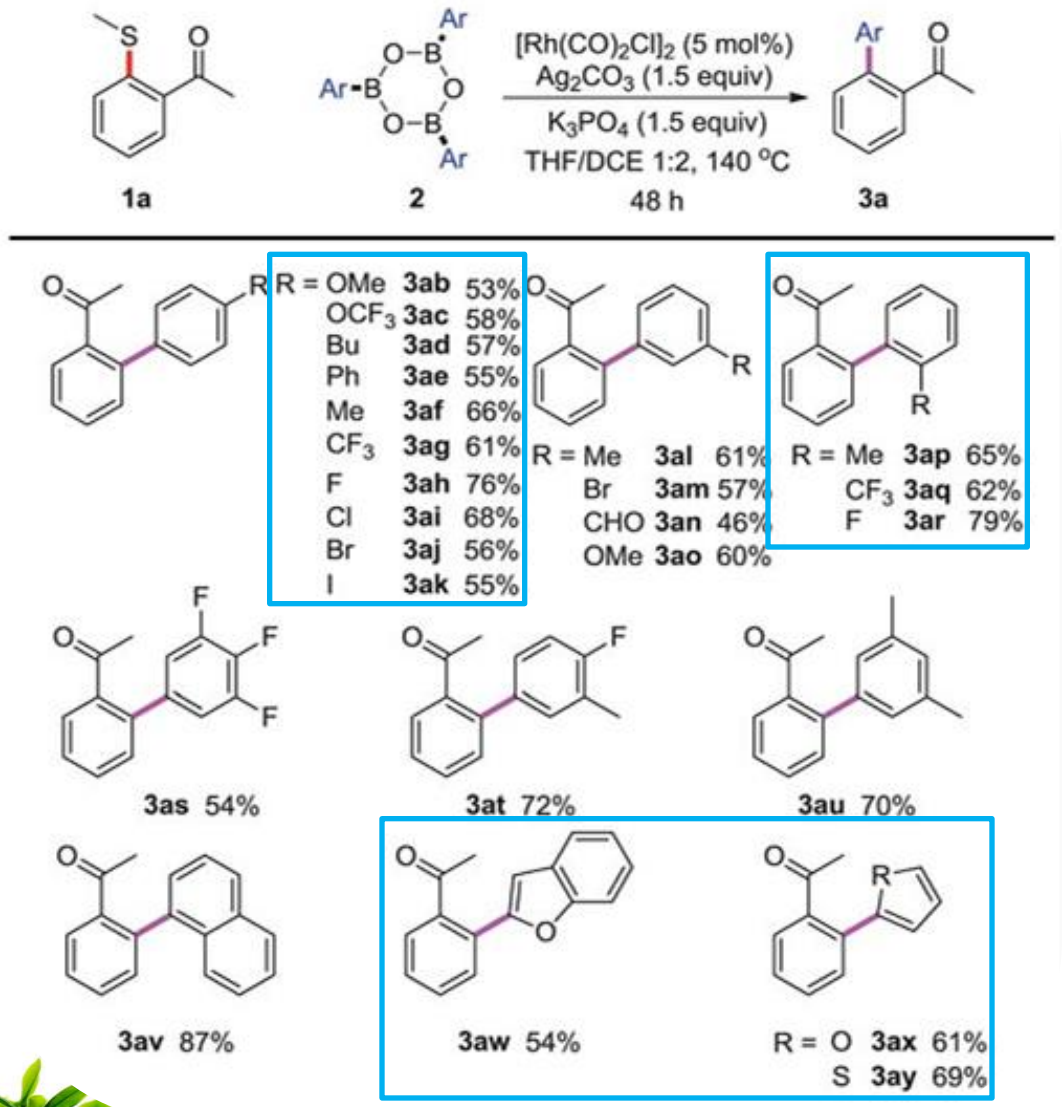
2c (35%)



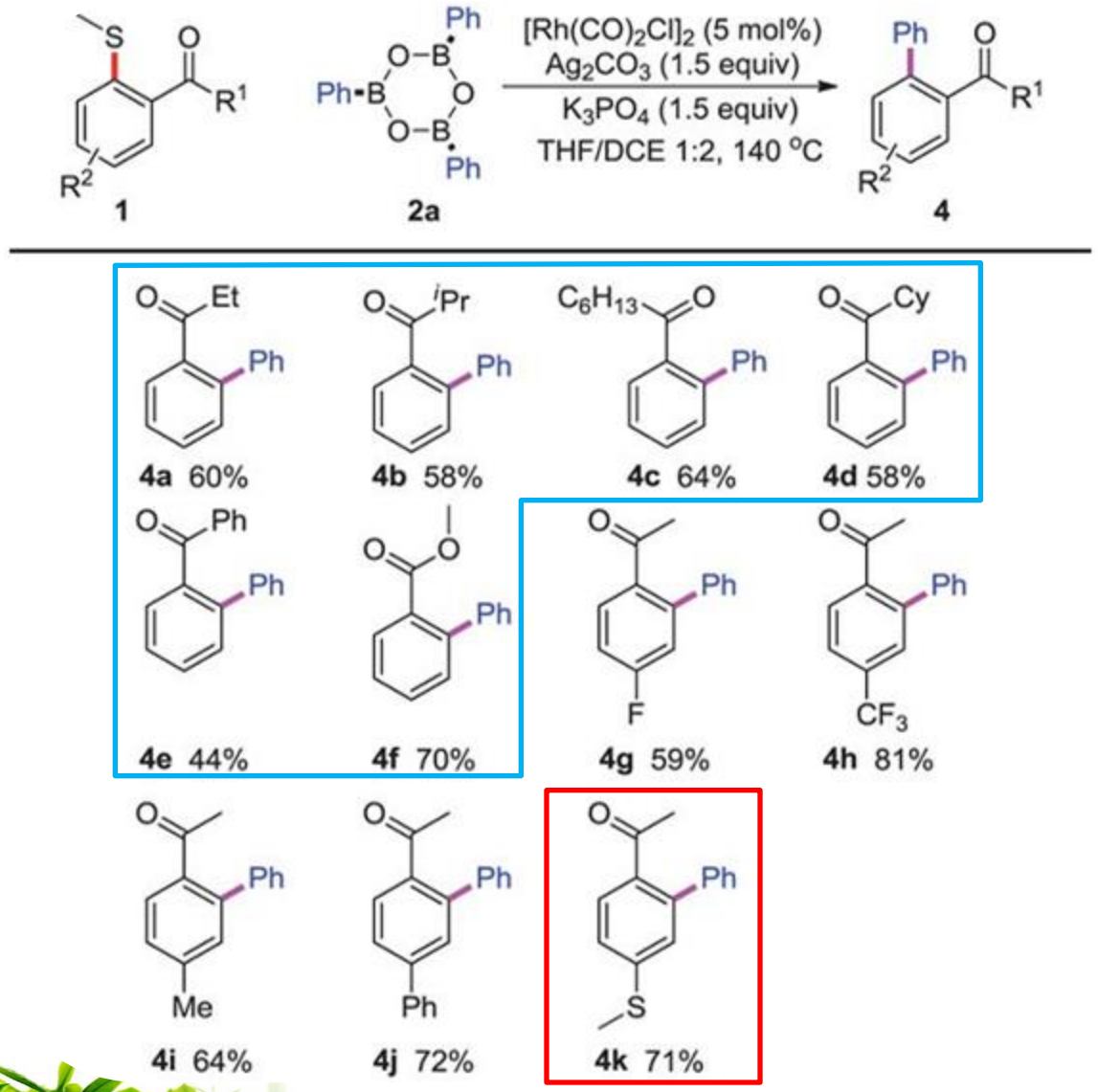
2d (49%)

2e (0%)

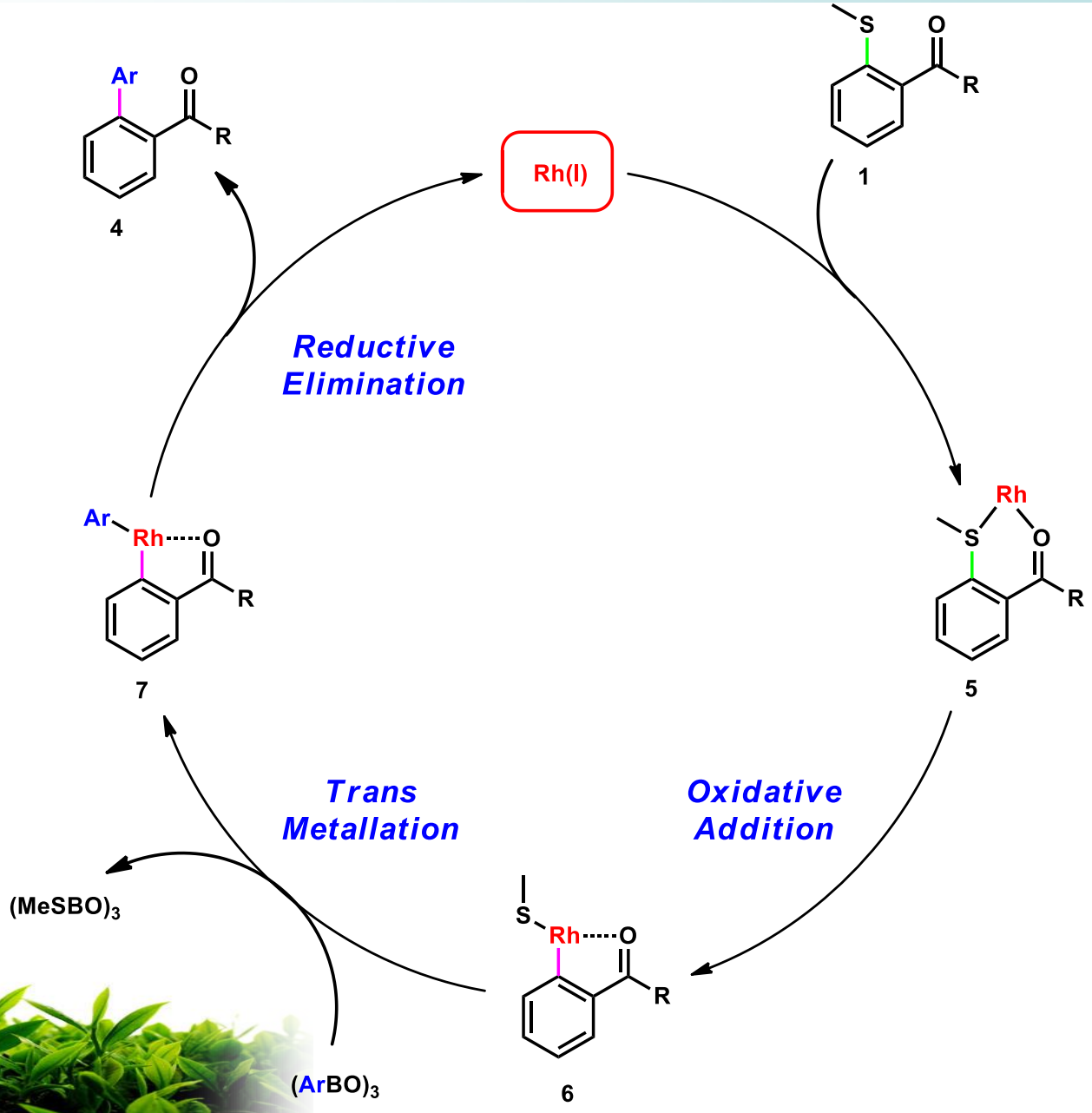
Scope of Aryl Boroxines



Scope of Thioethers



Proposed Mechanism



Summary-2

Rhodium-catalyzed C–C bond formation through unreactive aryl C–S bond cleavage

A supplement to the traditional Suzuki–Miyaura coupling

Broad substrate scope and good to excellent yields

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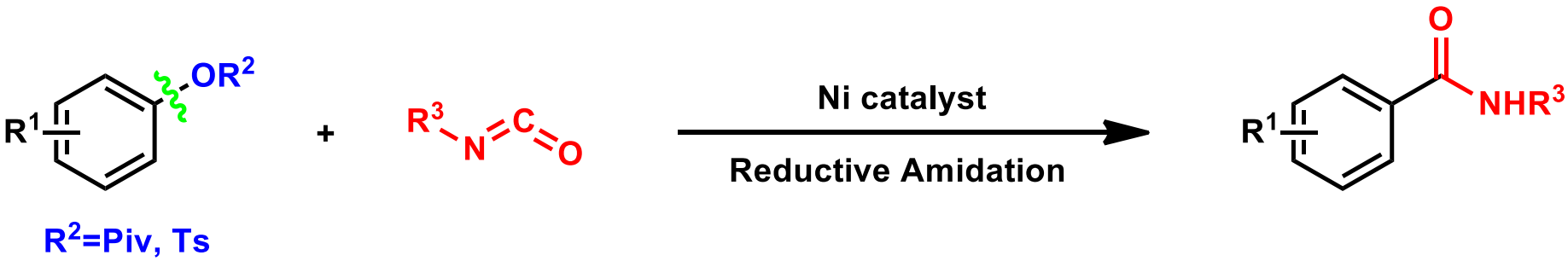
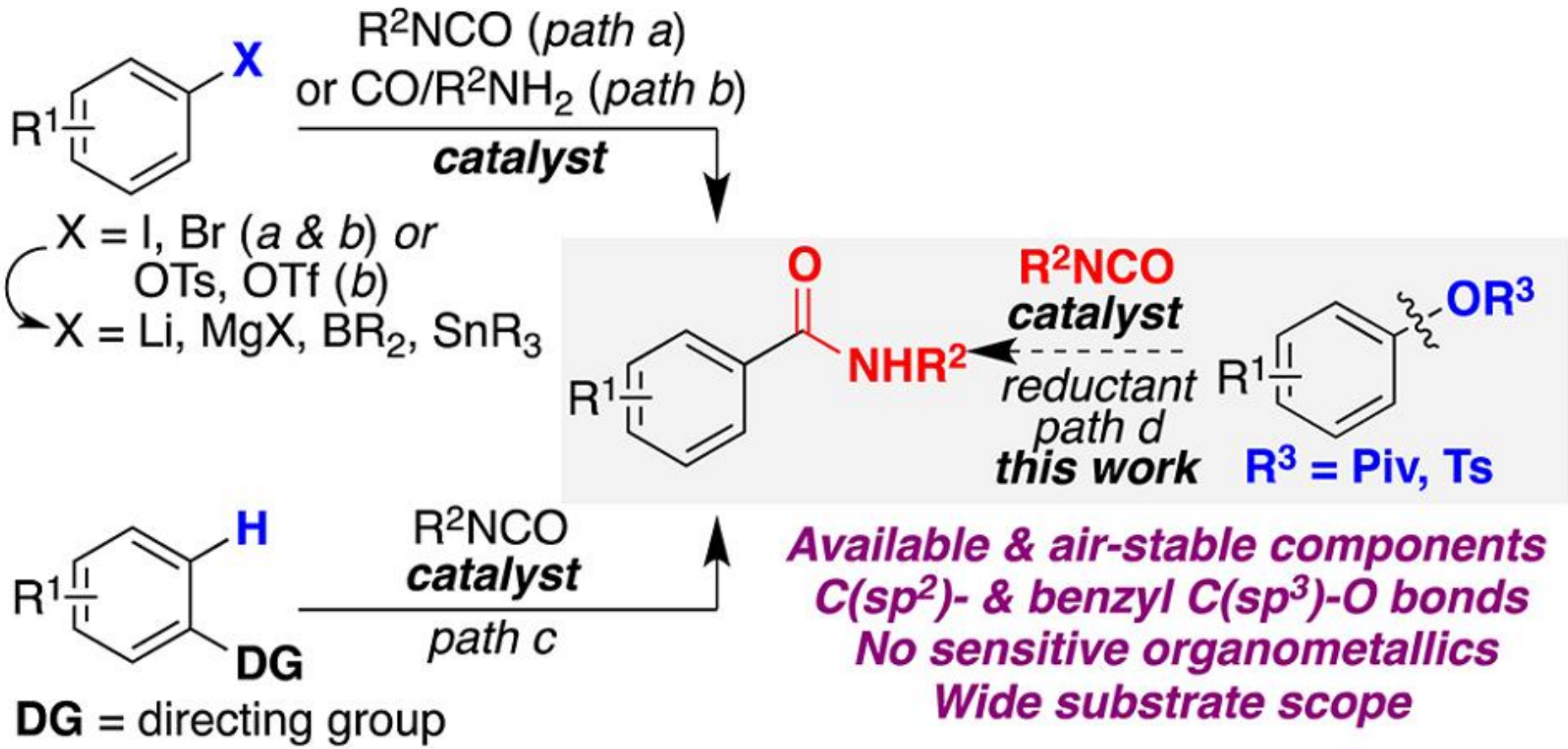
Ni-Catalyzed Direct Reductive Amidation via C–O Bond Cleavage

Arkaitz Correa† and Ruben Martin*,†,§

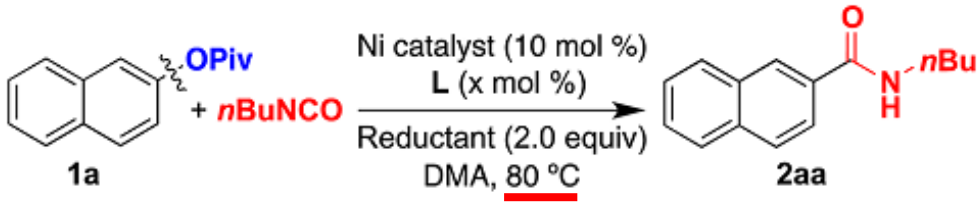


A. Correa and R. Martin, *J. Am. Chem. Soc.*, 2014, **136**, 7253.

Origin of the Idea



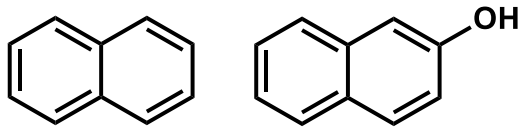
Screening of the Reaction Conditions



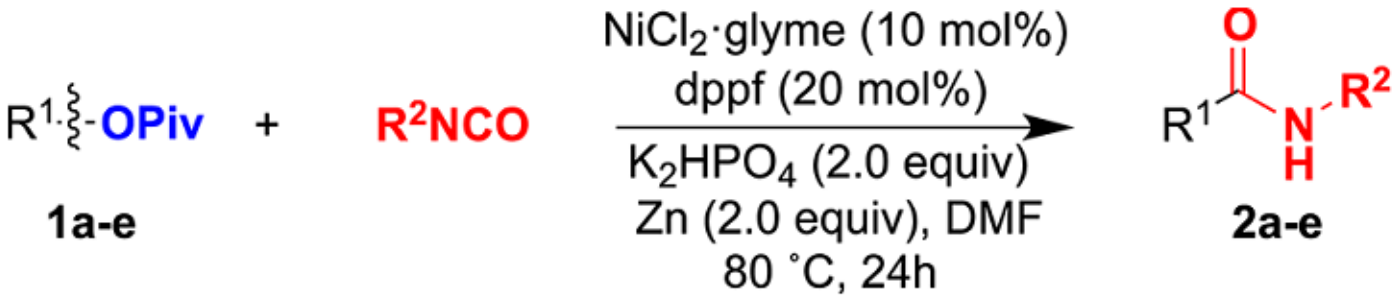
1a 2aa

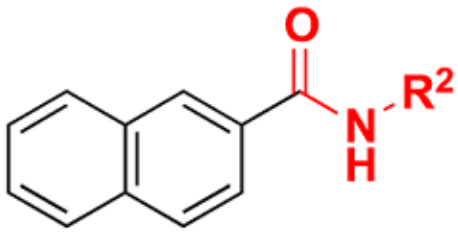
entry	Ni catalyst	L (x mol%)	reductant	yield **2aa** (%)[b]
1	$NiCl_2(dppf)$	dppf (10)	Mn	18
2	$NiCl_2(dppp)$	dppp (10)	Mn	0
3	$NiCl_2(PMe_3)_2$	PMe_3 (10)	Mn	0
4	$NiCl_2(PPh_3)_2$	PPh_3 (10)	Mn	0
5	$NiBr_2(bpy)_2$	bpy (10)	Mn	0
6	$NiCl_2(dppf)$	dppf (10)	Zn	38
7	$Ni(acac)_2$	dppf (20)	Zn	28
8	$Ni(OTf)_2$	dppf (20)	Zn	21
9	$NiBr_2$·glyme	dppf (20)	Zn	46
10	$NiBr_2 \cdot H_2O$	dppf (20)	Zn	42
11	$NiCl_2$·glyme	dppf (20)	Zn	55
12	$NiCl_2$·glyme	dppf (10)	Zn	4
13[c,d]	$NiCl_2$·glyme	dppf (20)	Zn	70[f]
14[d,e]	***$NiCl_2$·glyme***	***dppf (20)***	***Zn***	***81***[f]

[a]Reaction conditions: **1a** (0.50 mmol), *n*BuNCO (2.0 equiv), [Ni] (10 mol%), **L** (x mol%), reductant (2.0 equiv), DMA (0.25 M) at 80 °C for 24 h. [b]HPLC yield using anisole as internal standard. [c]K_2HPO_4 (1.0 equiv) was added. [d]DMF as solvent. [e]K_2HPO_4 (2.0 equiv) was added. [f]Isolated yield.

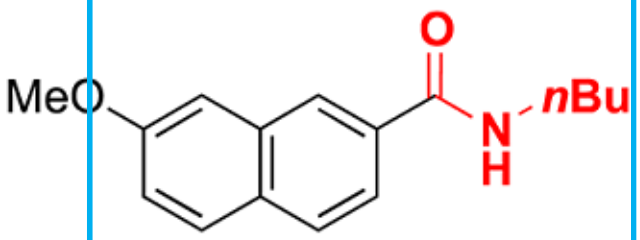


Scope of Isocyanates

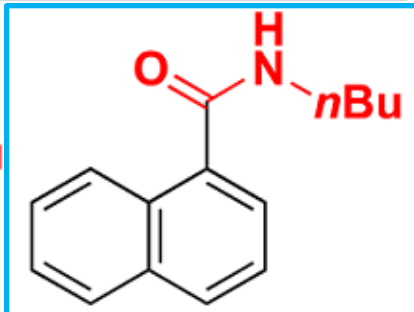




81%, 85%[c] (R^2 = *n*Bu, **2aa**)

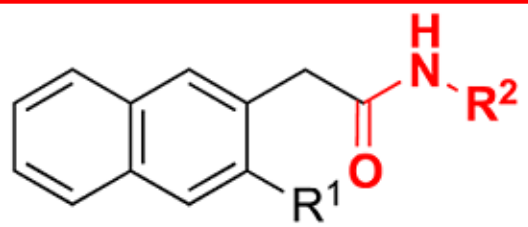


67% **(2b)**



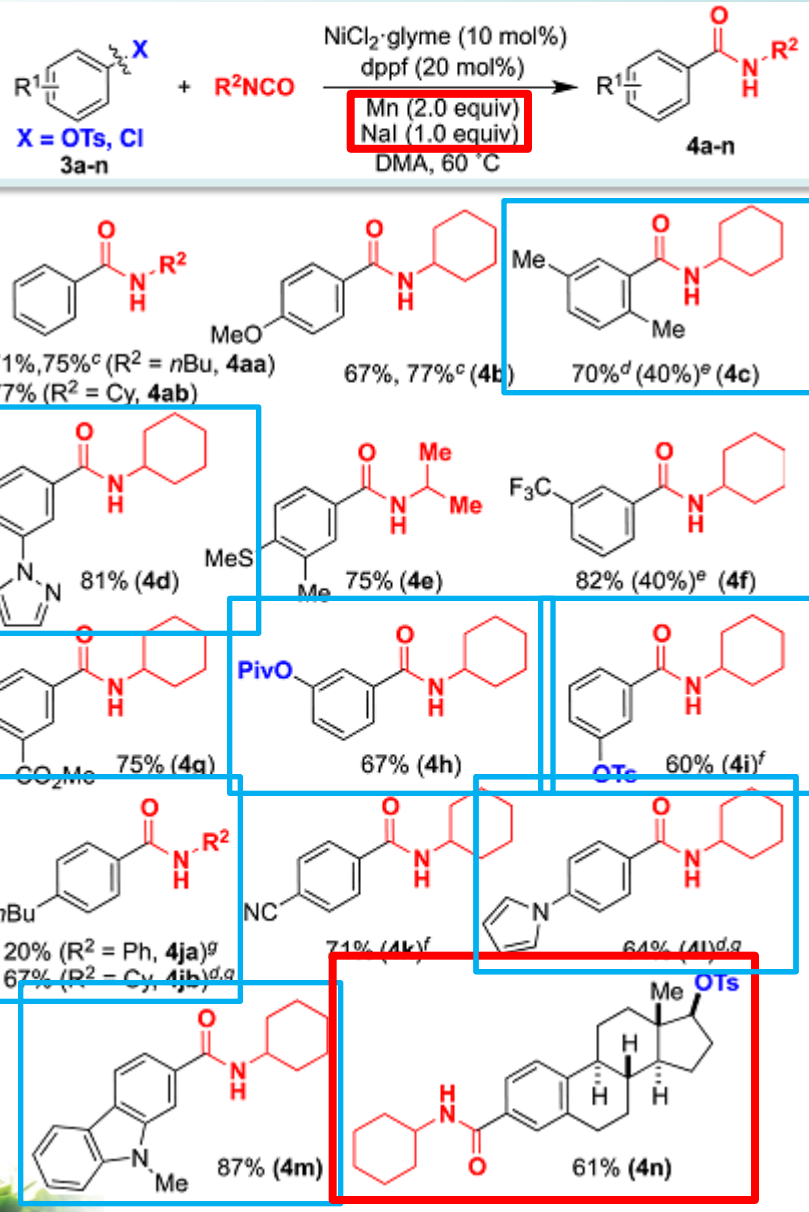
48%[d] **(2c)**

55% (R^2 = Et, **2ab**)
63% (R^2 = *n*Hex, **2ac**)
56% (R^2 = Bn, **2ad**)[d]
54% (R^2 = $(CH_2)_2Ph$, **2ae**)[d]
64% (R^2 = *i*Pr, **2af**)[d]
78% (R^2 = Cy, **2ag**)



56%, 64%[c] (R^1 = H; R^2 = *n*Bu, **2d**)[e]
61% (R^1 = **OPiv**; R^2 = Cy, **2e**)[e]

Scope of Aryl Tosylates



Summary-3

A novel Ni-catalyzed reductive amidation of aryl C(sp^2)-O and C(sp^3)-O eletrophiles with isocyanates

C-C bond formation through C-O bond cleavage

A complement to existing methodologies to prepare benzamide derivatives

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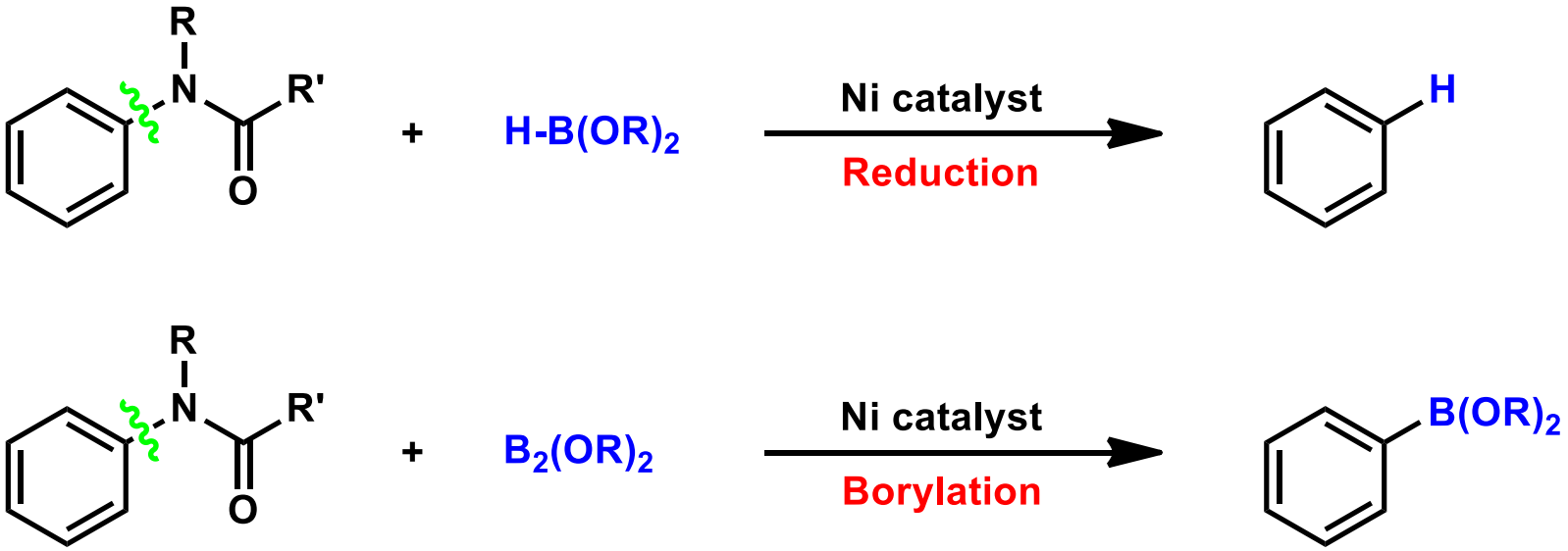
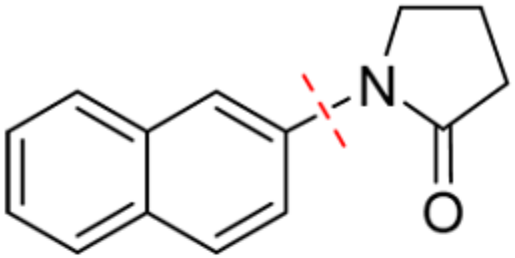
Nickel-Catalyzed Reductive and Borylative Cleavage of Aromatic Carbon–Nitrogen Bonds in N-Aryl Amides and Carbamates

Mamoru Tobisu,*[,†,‡,§] Keisuke Nakamura,[†] and Naoto Chatani*[,†]



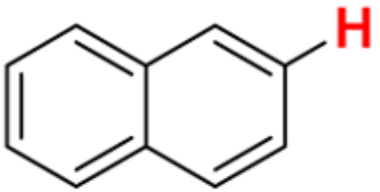
M. Tobisu, K. Nakamura and N. Chatani, *J. Am. Chem. Soc.*, 2014, **136**, 5587.

Screening of the Reaction Conditions



1a

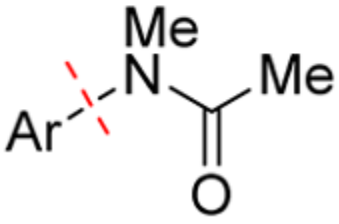
H-M (2 equiv.)
$Ni(cod)_2$ (10 mol%)
PCy_3 (20 mol%)
toluene
70 °C, 20 h



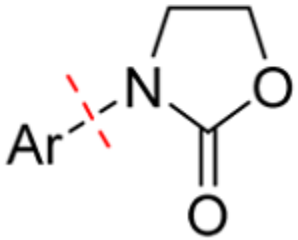
2

(Ar = 2-naphthyl)

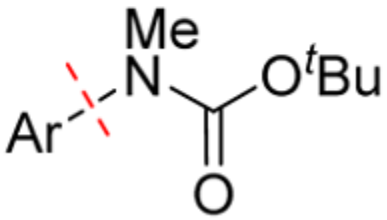
H-M	GC yield
H-SiMe(OMe)$_2$	7%
H-B(pin)	61%



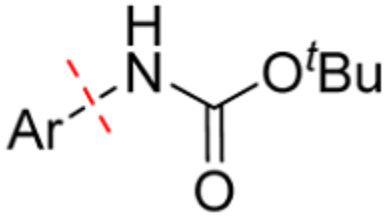
1b 8%



1c 71%

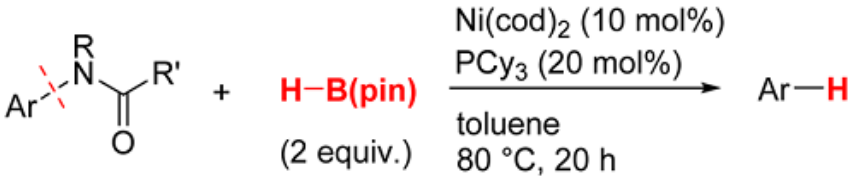


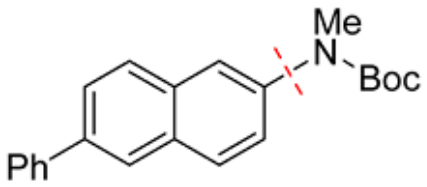
1d 65%



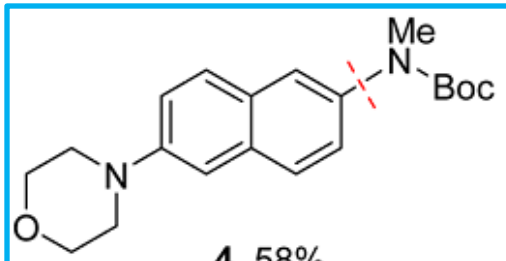
1e 0%

Scope of Substrates

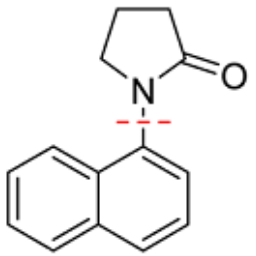




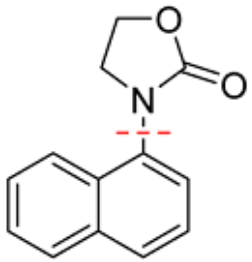
3 72%



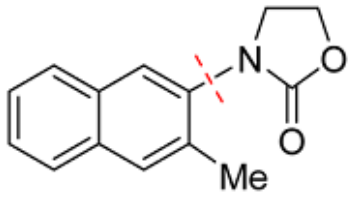
4 58%



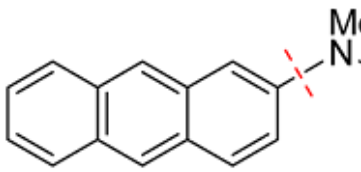
5 60%[b]



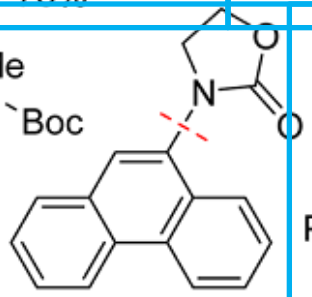
6 78%[b,c]



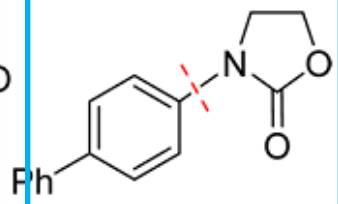
7 71%[b]



8 52%

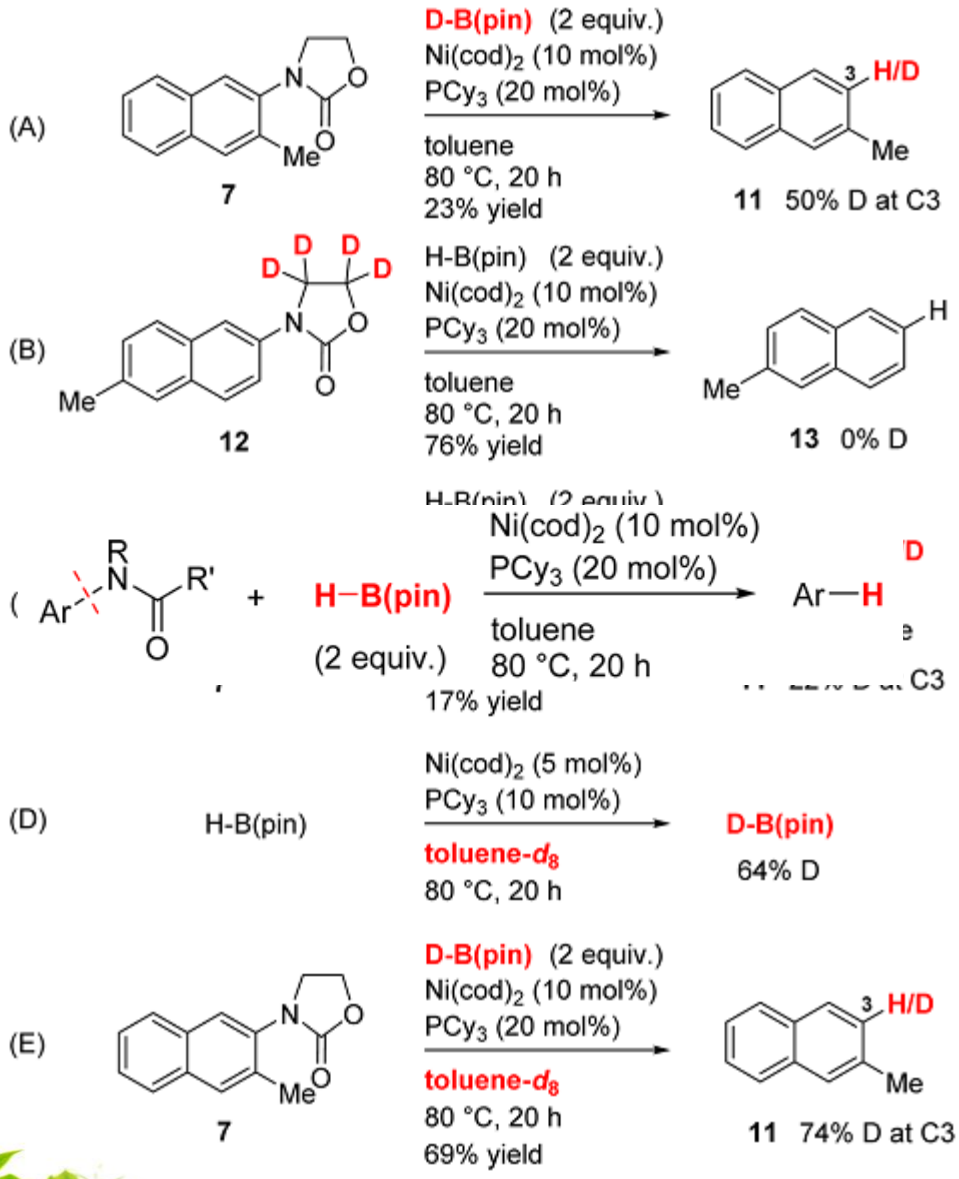


9 64%

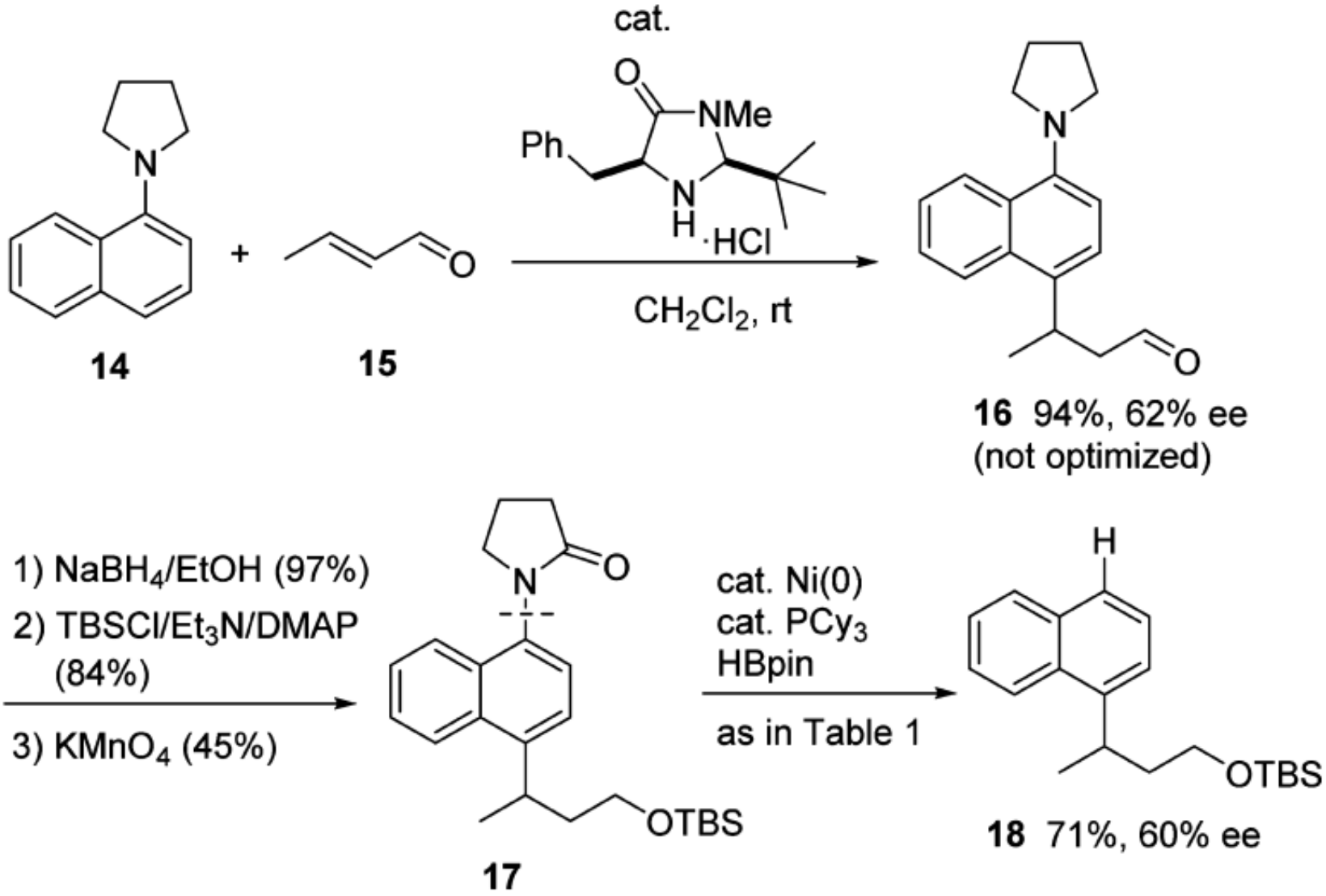


10 25%[d]

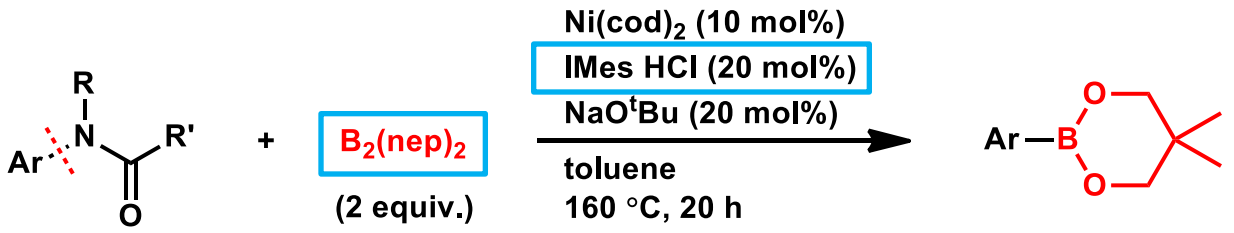
Labeling Studies

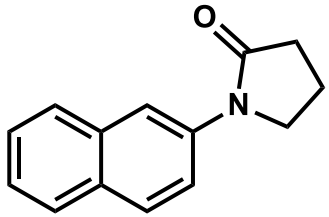


Synthetic Applications

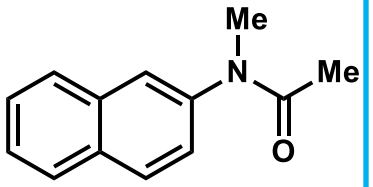


Scope of Substrates

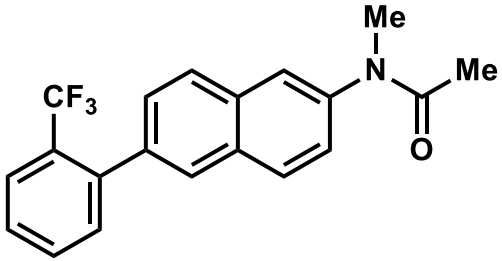




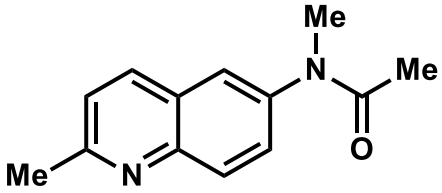
1a (55%)



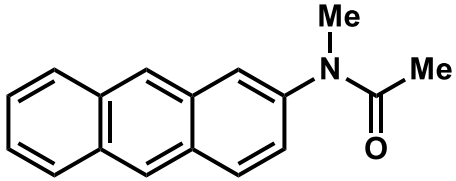
1b (72%)



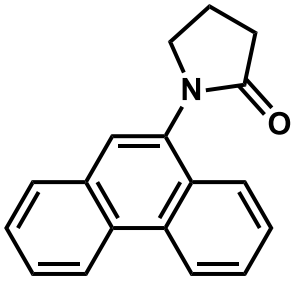
20 (51%)



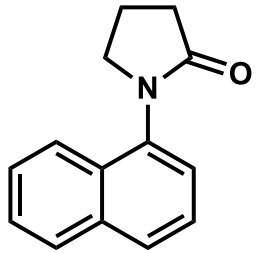
22 (72%)



24 (72%)



26 (76%)



5 (17%)

Summary-4

A novel Ni-catalyzed C(aryl)-N bond cleavage reaction

C-H and C-B bond formation through C-N bond cleavage, respectively

In the absense of an *ortho* directing group

Thank you!