芳基C-H键与硅烷的脱氢偶联反应

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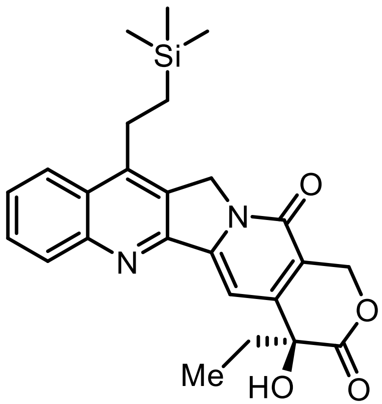
导 师： 关冰涛 研究员

日 期： 2022-11-18

目 录

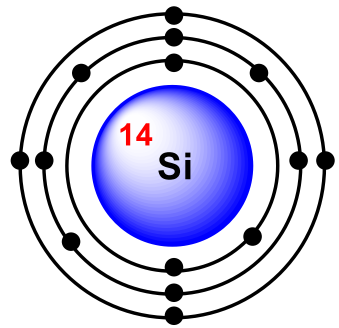
目 录

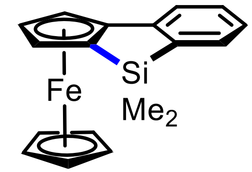
背景

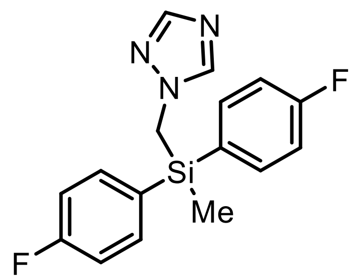


BNP 1350

BNP-1350是一种拓扑异构酶I
抑制剂，具有强大的抗癌活性



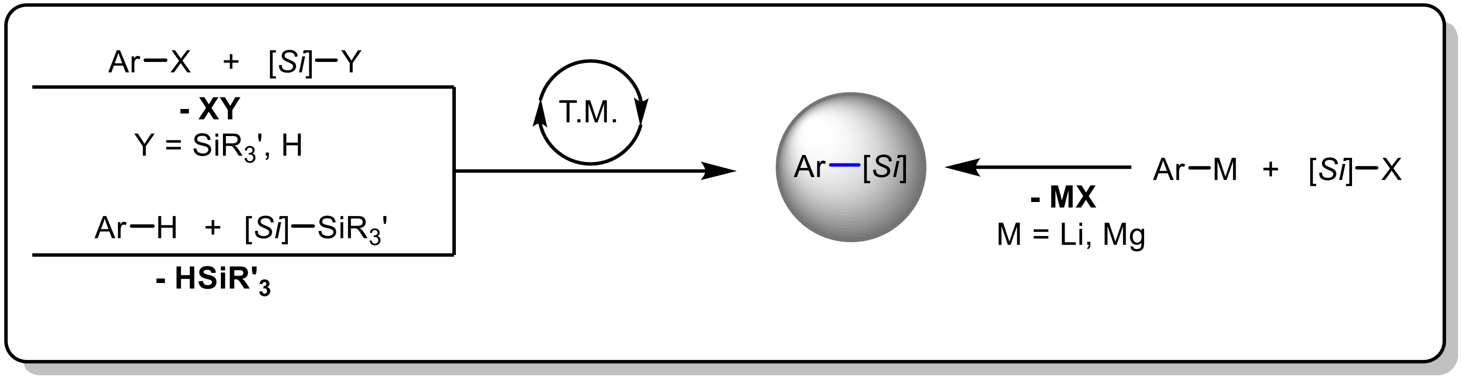


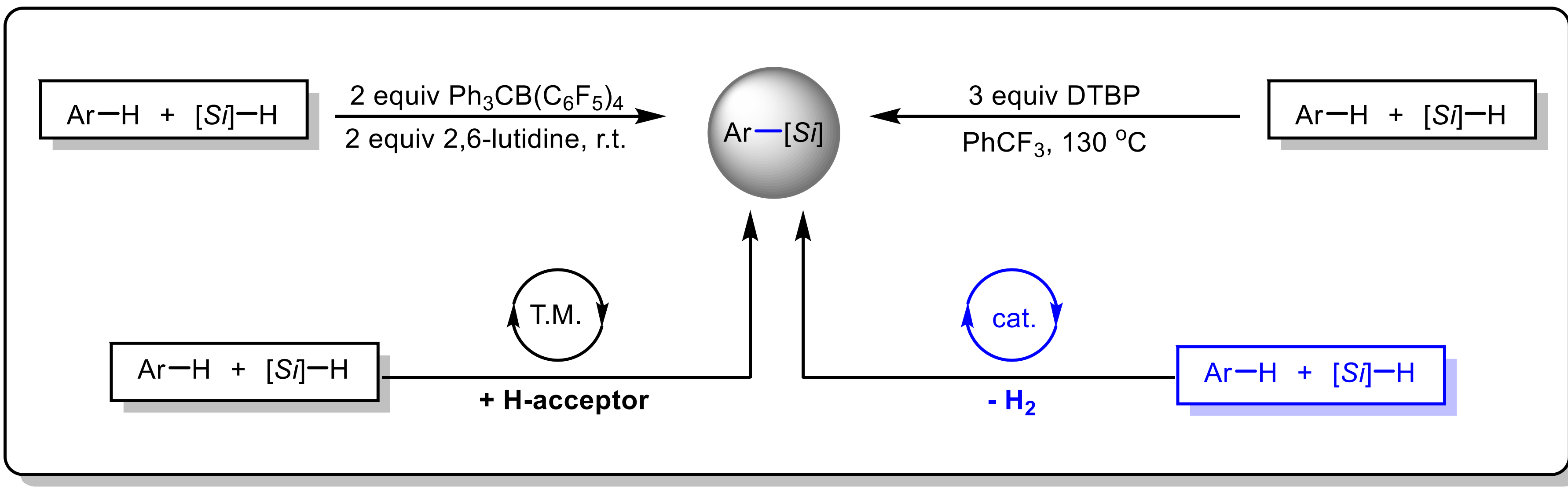


flusilazole

Annaliese K. Franz, *et al*. *J. Med. Chem.* **2013**, *56*, 388.
Kazuhiko Takai, *et al*. *Org. Lett.* **2015**, *17*, 3102.

背景



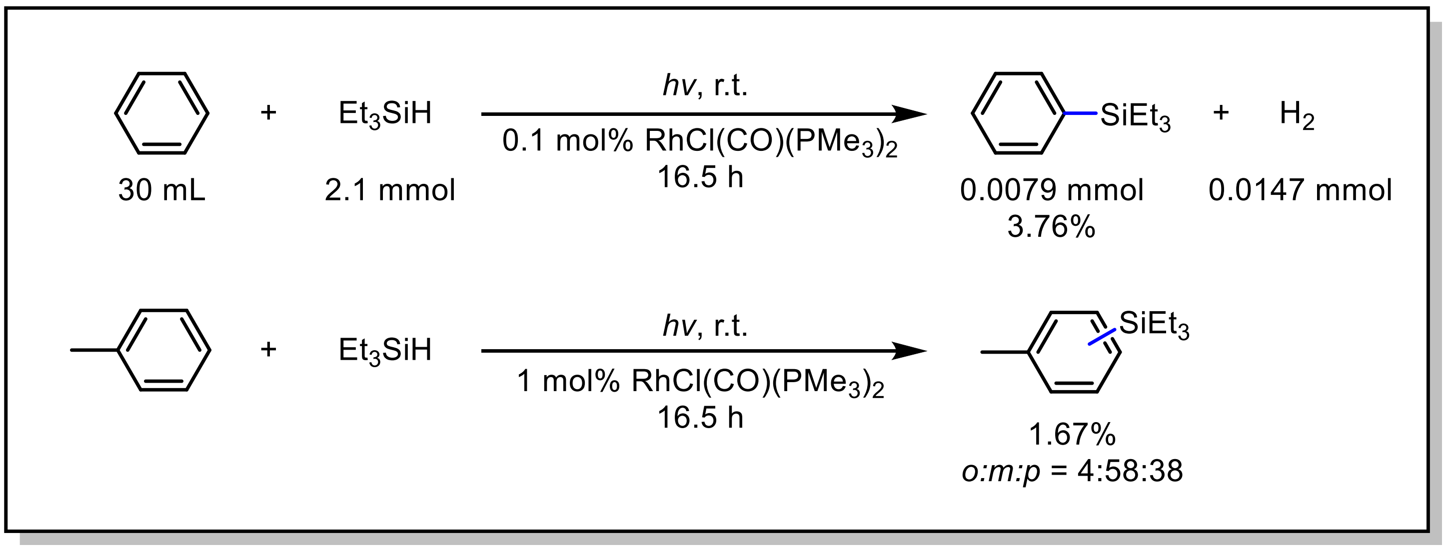


Chinmoy K. Hazra, *et al*. *Asian J. Org. Chem.* **2021**, *10*, 334.
Congyang Wang, *et al*. *Sci. China. Chem.* **2015**, 58, 1266.

目 录

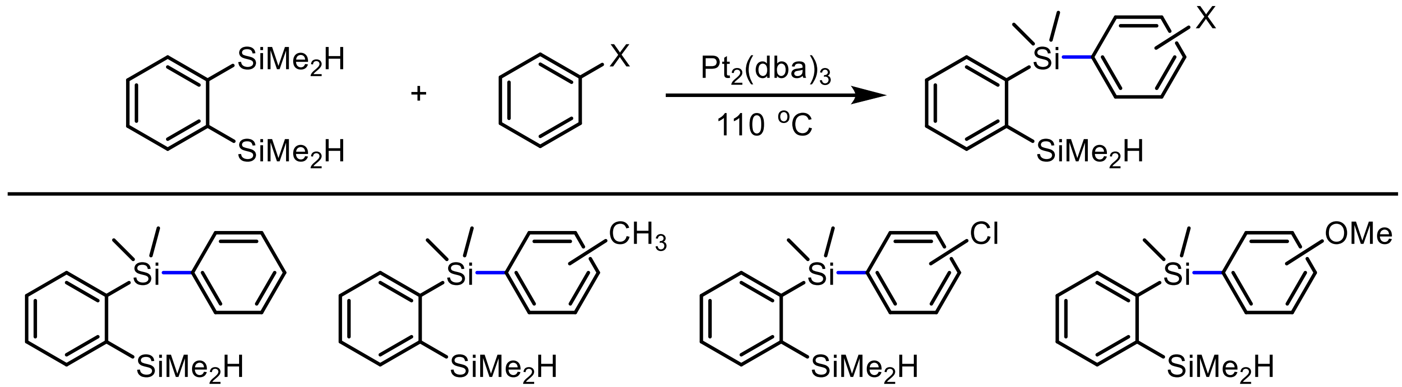
过渡金属催化芳基C-H键与硅烷的脱氢偶联

$Me_3SiOSiMe_2H \xrightarrow[\text{Benzene, 60 °C, } N_2]{\text{2 mol\% } (PPh_3)_2(CO)IrCl}$ $Me_3SiOSi(H)MeOSiMe_3$ (75%) + $Me_3SiOSiMe_2OSiMe_3$ (5%) + $Me_3Si(OSiMe_2)OSiMe_3$ (4%) + $\boxed{PhMe_2SiOSiMe_3 \text{ 2\%}}$ + $PhMe_2SiOSiMe_2H$ (1-2%)



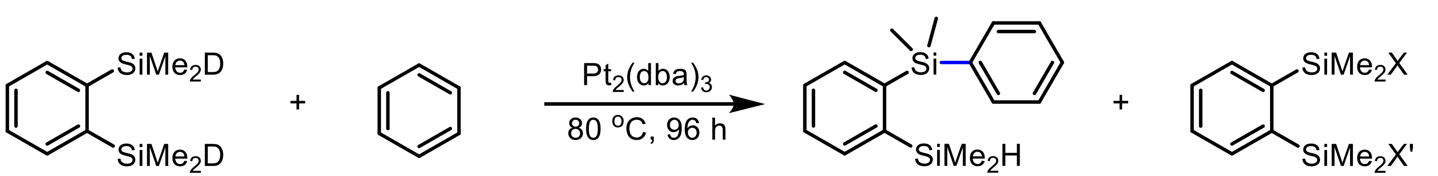
M. David Curtis, *et al*. *Organometallics* **1982**, *1*, 884.
Masato Tanaka, *et al*. *Chem. Lett.* **1987**, *16*, 2375.

过渡金属催化芳基C-H键与硅烷的脱氢偶联



87% | 84%, *o*:*m*:*p* = 18:54:28 | 81%, *o*:*m*:*p* = 59:30:11 | 84%, *o*:*m*:*p* = 87:10:3

机理实验



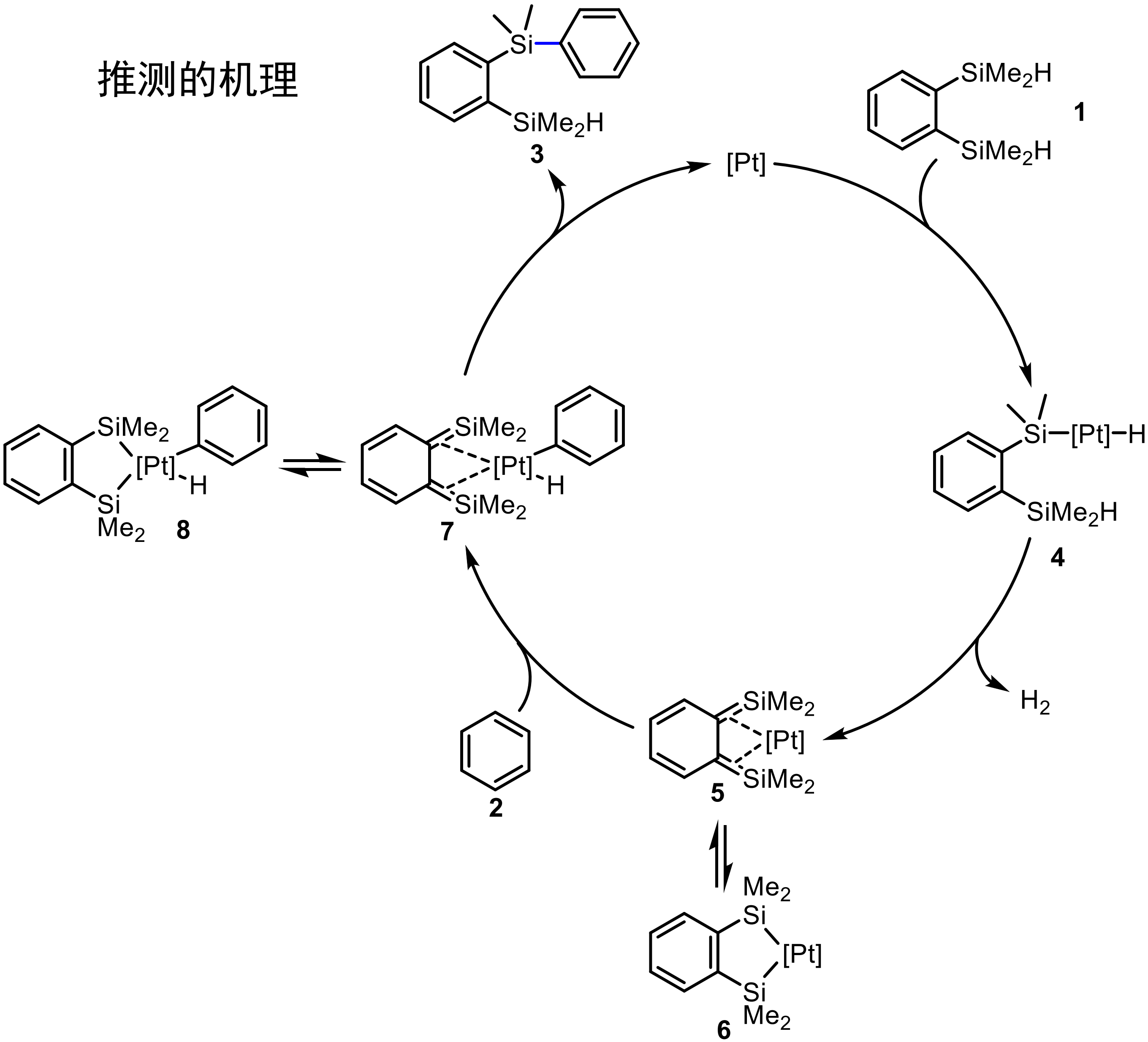
56%

11: X = X' = D
12: X = D, X' = H
1: X = X' = H

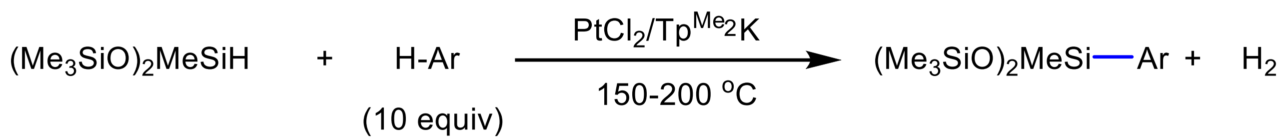
Masato Tanaka, *et al*. *Organometallics* **1993**, *12*, 2065.

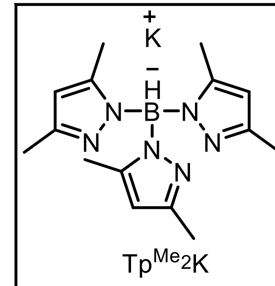
过渡金属催化芳基C-H键与硅烷的脱氢偶联

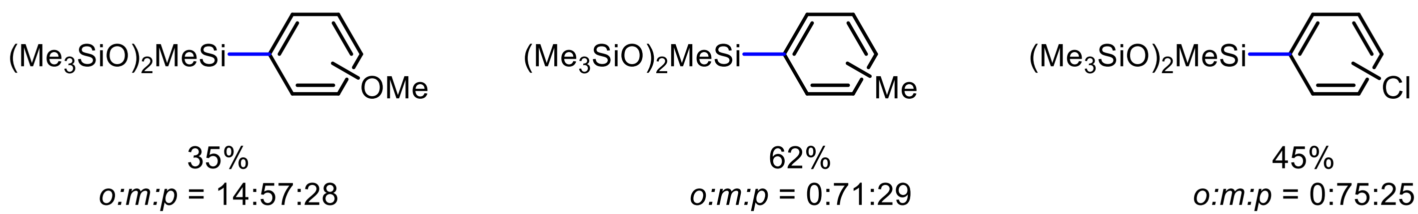
推测的机理

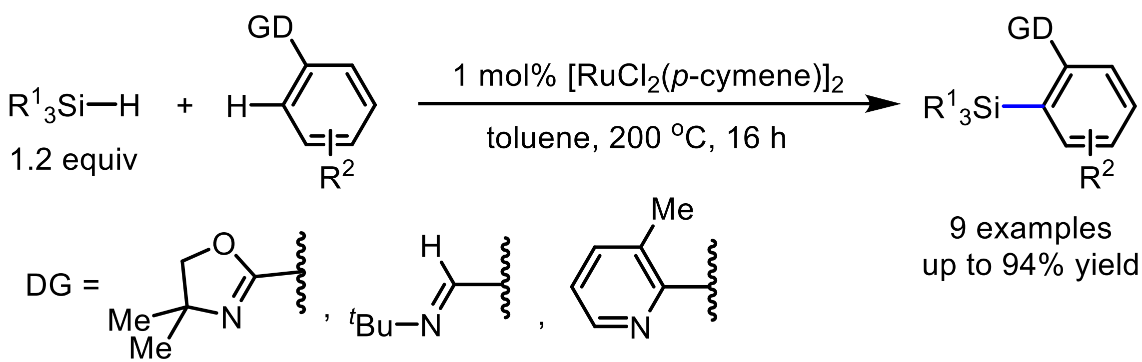


过渡金属催化芳基C-H键与硅烷的脱氢偶联



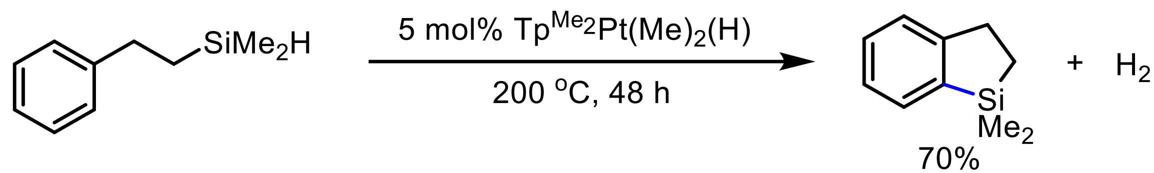


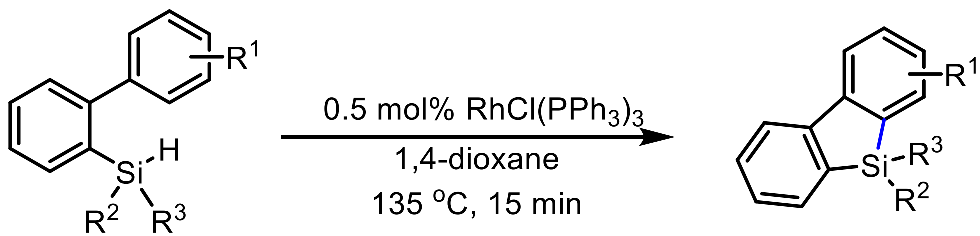




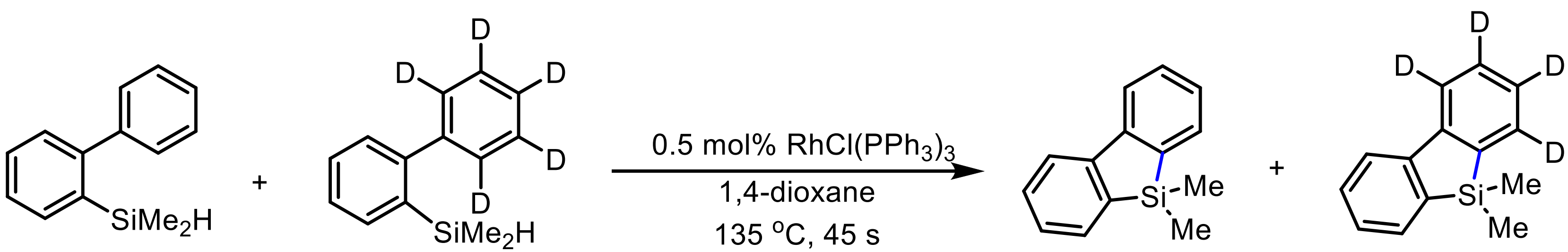
Miki Murata, *et al*. *Chem. Lett.* **2007**, *36*, 910.
Miki Murata, *et al*. *Chem Lett.* **2012**, *41*, 374.

过渡金属催化芳基C-H键与硅烷的脱氢偶联





15 examples
up to 96% yield



1a **1a-*d*** **2a** **2a-*d***

2a + **2a-*d*** 9% [**2a**:**2a-*d*** = 87:13]
KIE = 6.8

John F. Hartwig, *et al*. *J. Am. Chem. Soc.* **2005**, *127*, 5022.
Kazuhiko Takai, *et al*. *J. Am. Chem. Soc.* **2010**, *132*, 14324.

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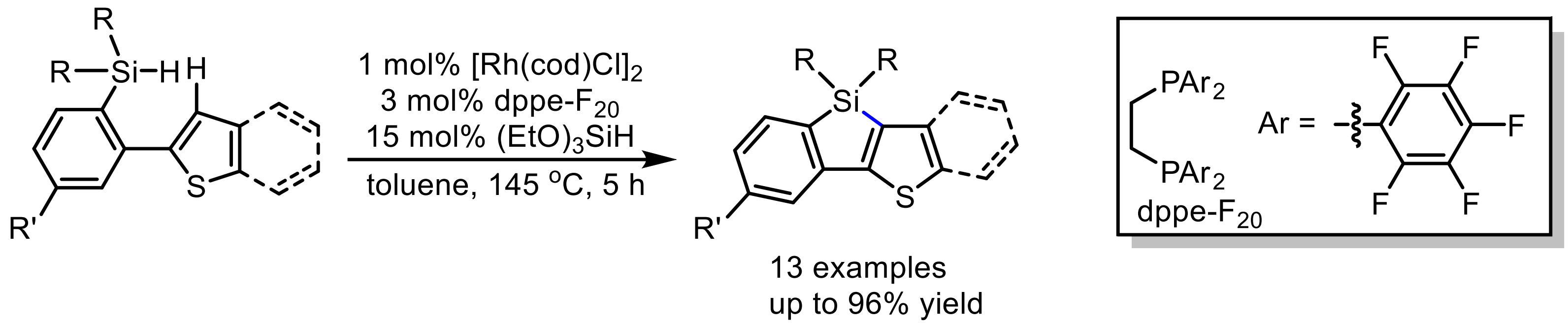

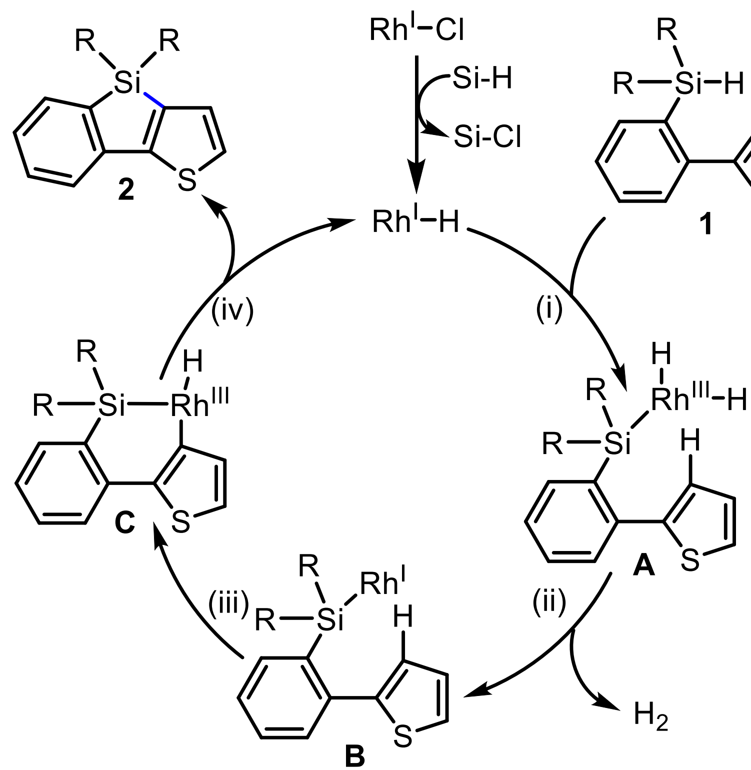

Seiji Suga, *et al*. *Org. Lett.* **2017**, *19*, 2564.

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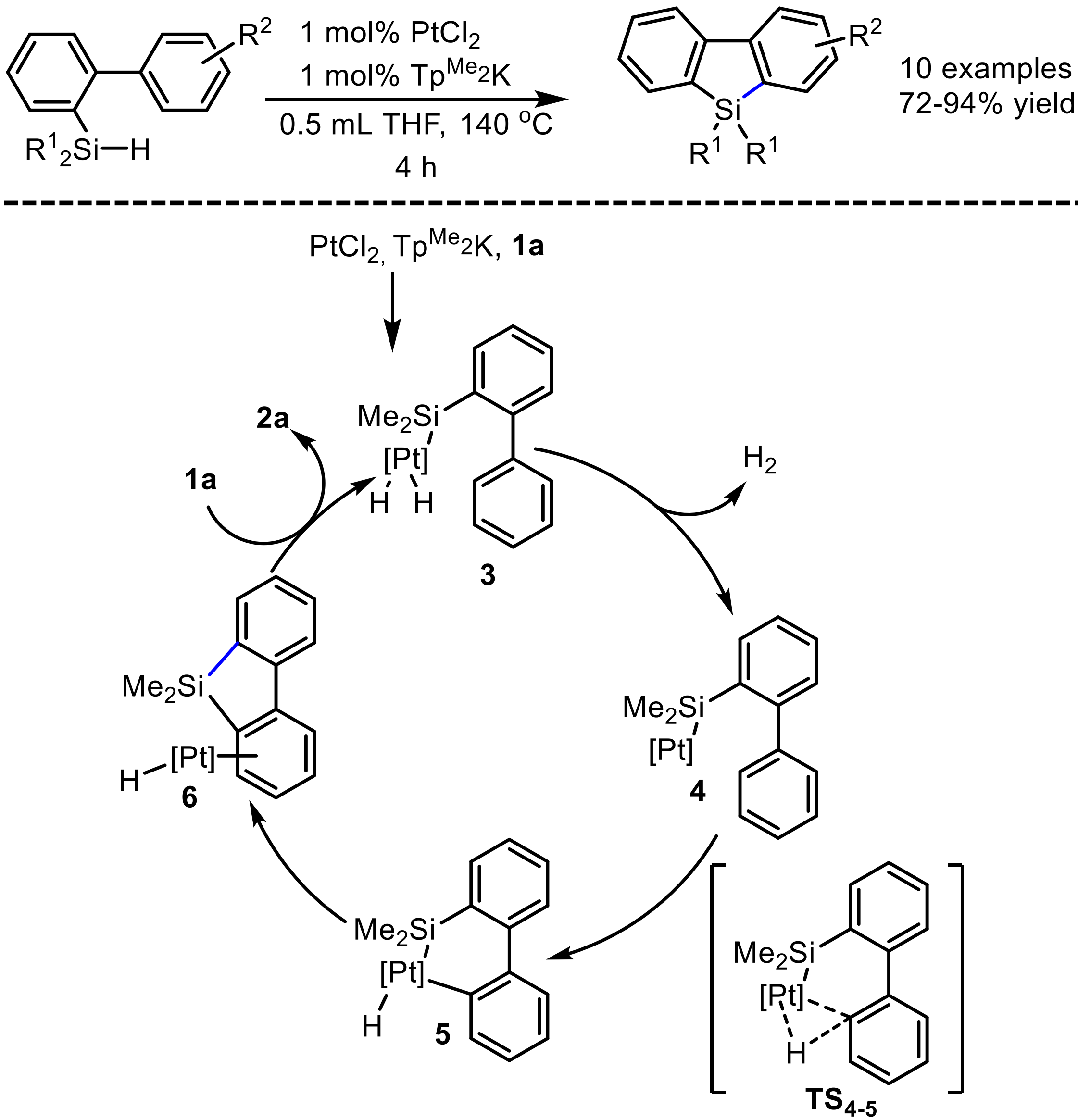

Miki Murata, *et al*. *Chem. Lett.* **2016**, *45*, 857.

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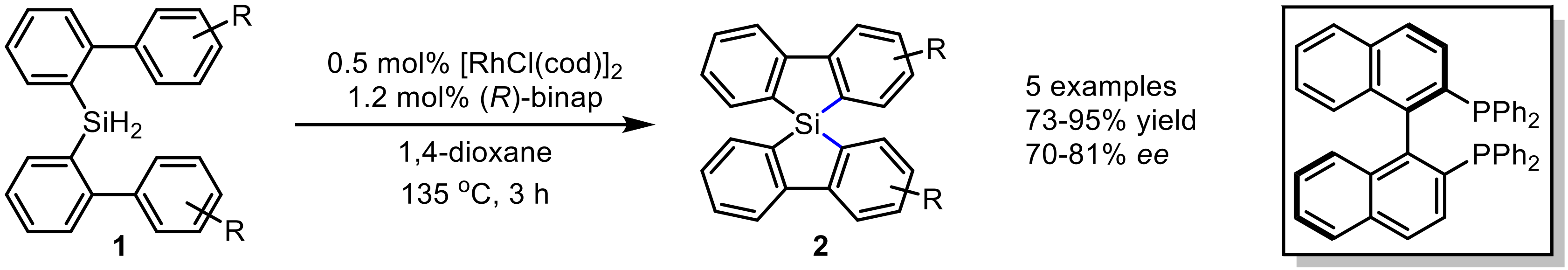

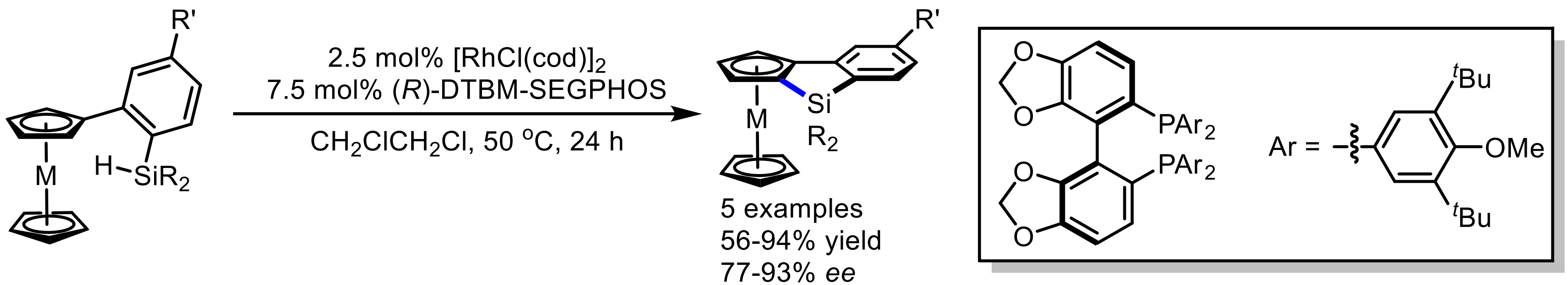

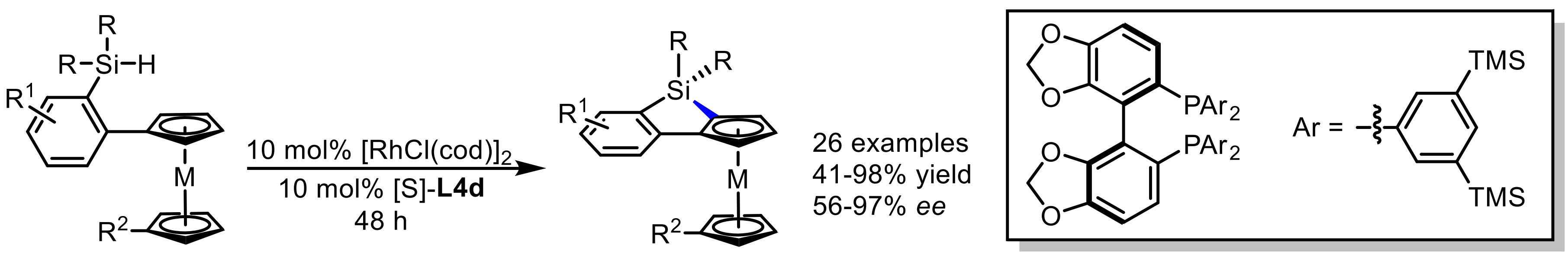

Kazuhiko Takai, *et al*. *Angew. Chem. Int. Ed.* **2013**, *52*, 1520.
Kazuhiko Takai, *et al*. *Org. Lett.* **2015**, *17*, 3102.
Wei He, *et al*. *Angew. Chem. Int. Ed.* **2015**, *54*, 6918.

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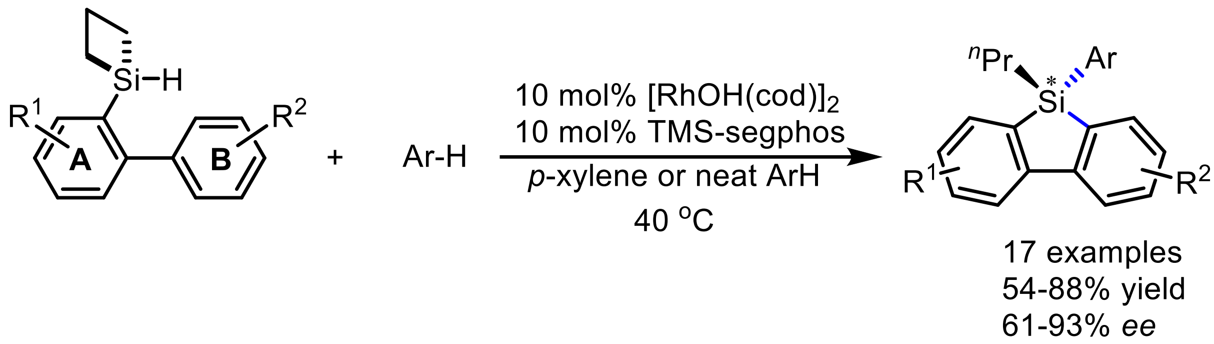

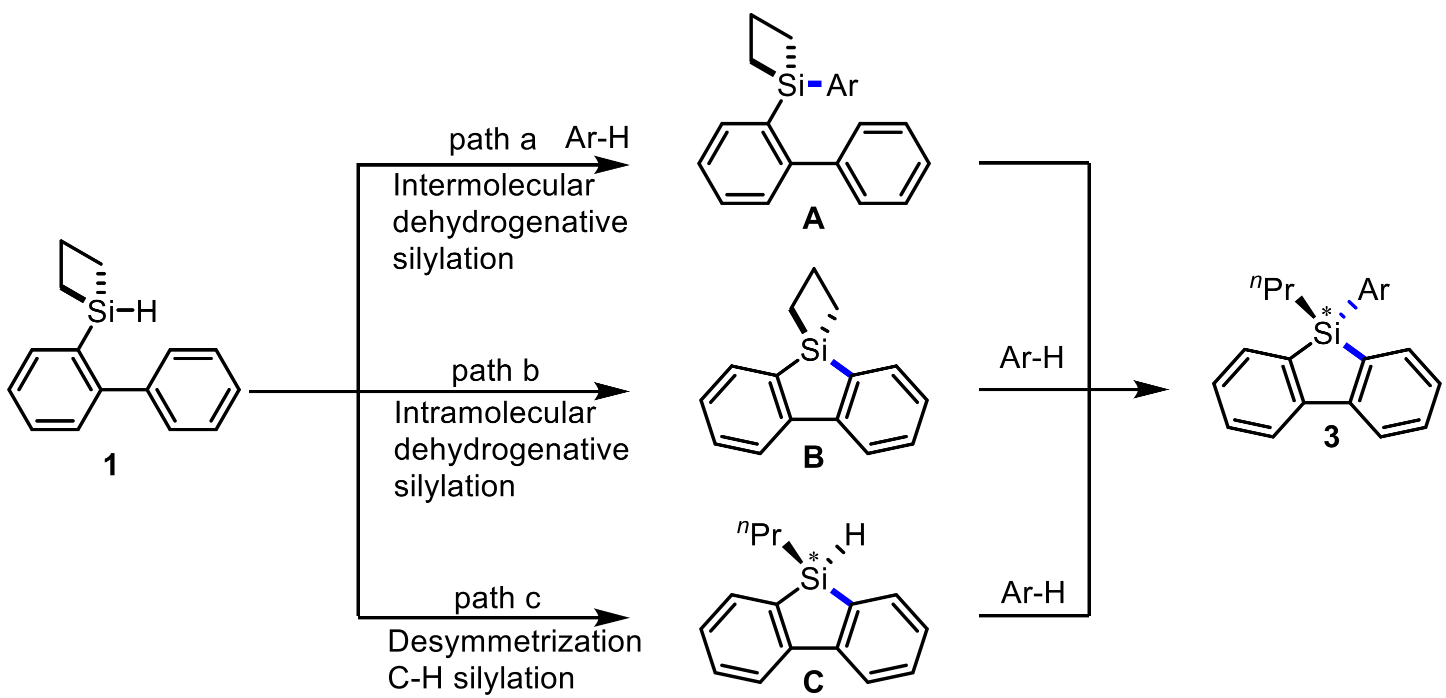

Wei He, *et al*. *Angew. Chem. Int. Ed.* **2017**, *56*, 1125.

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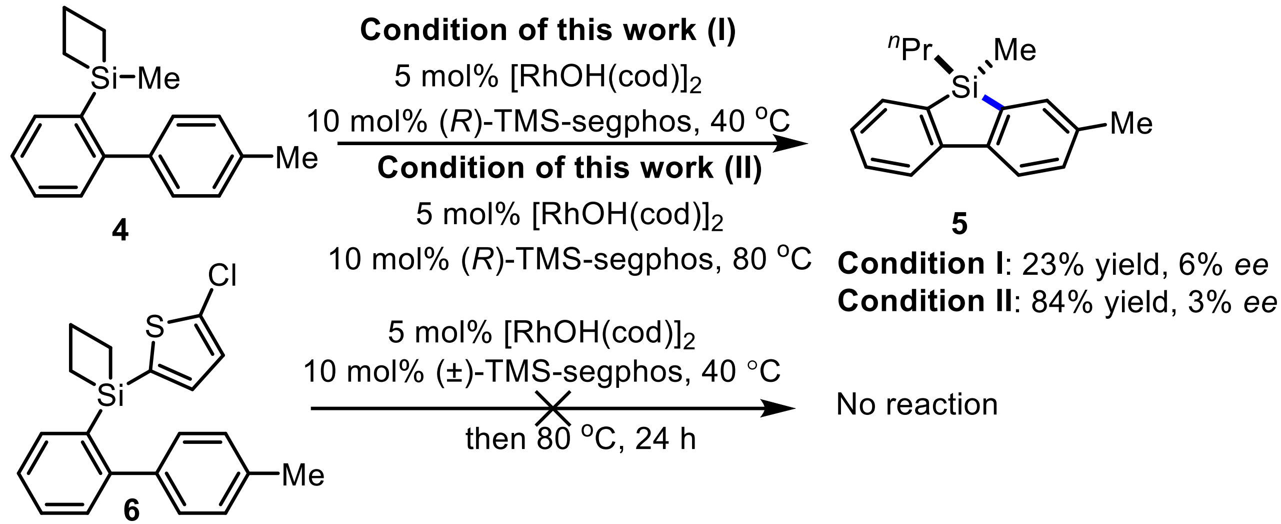

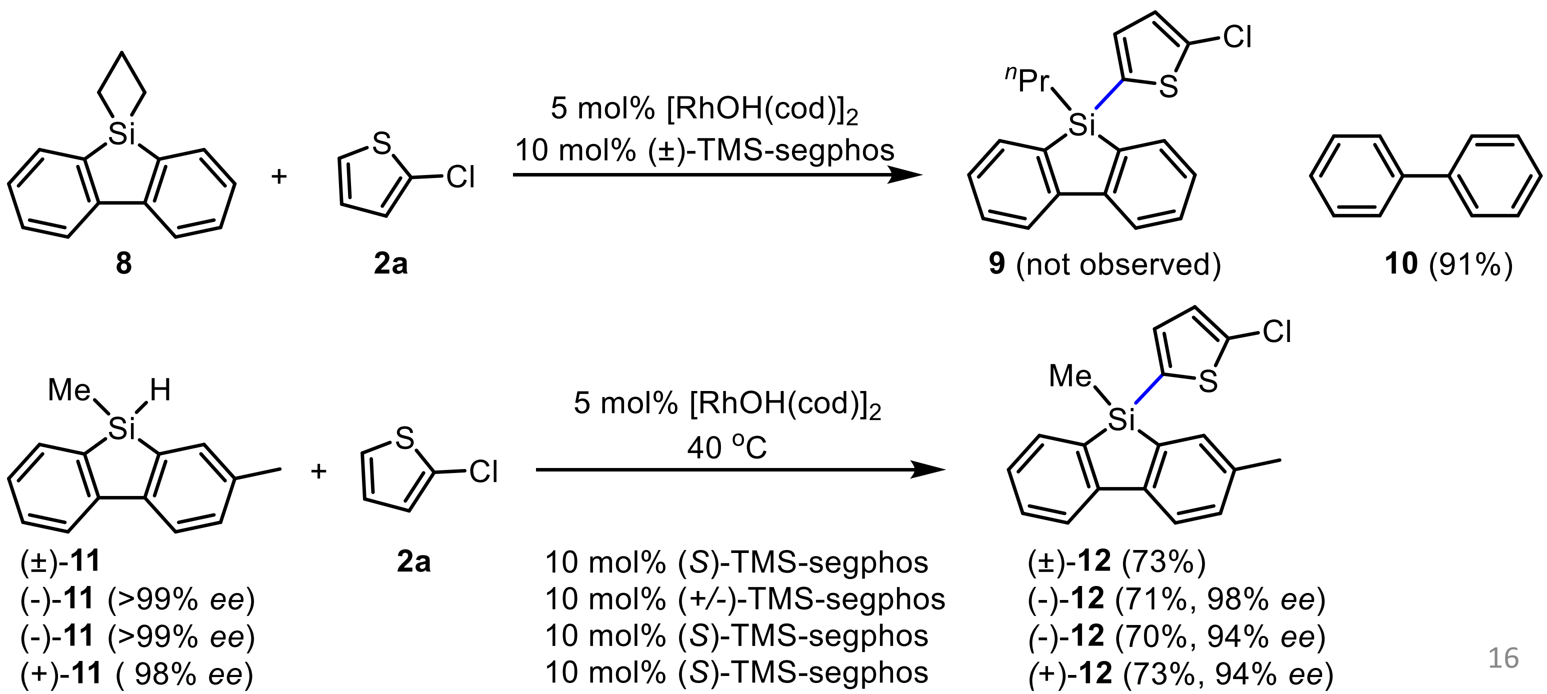

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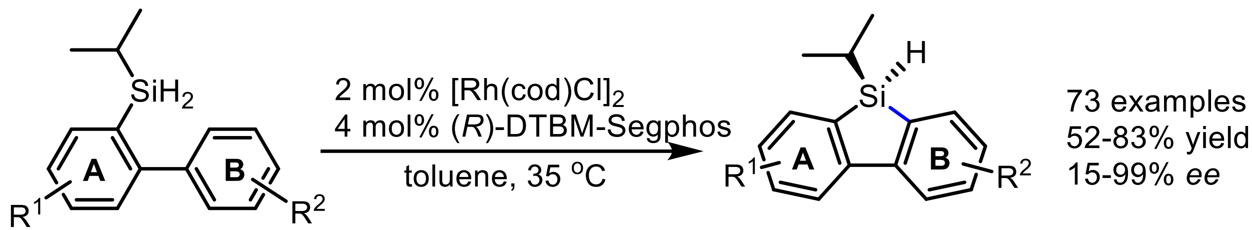

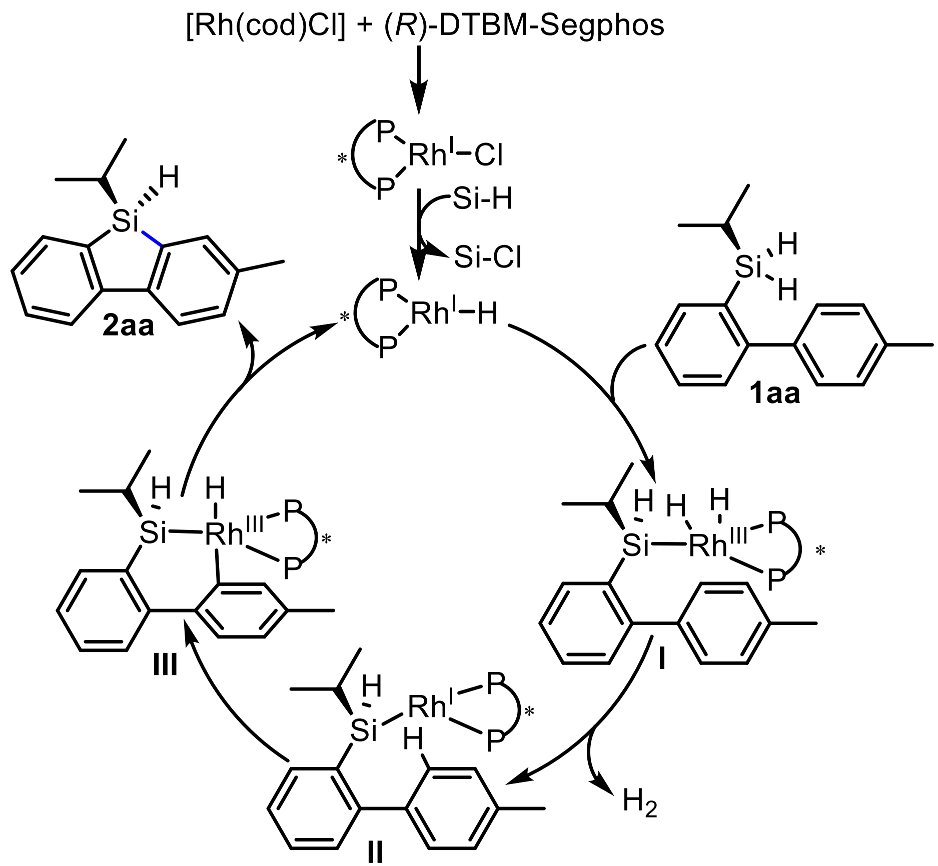

Wei He, *et al*. *Angew. Chem. Int. Ed.* **2021**, *60*, 4245.

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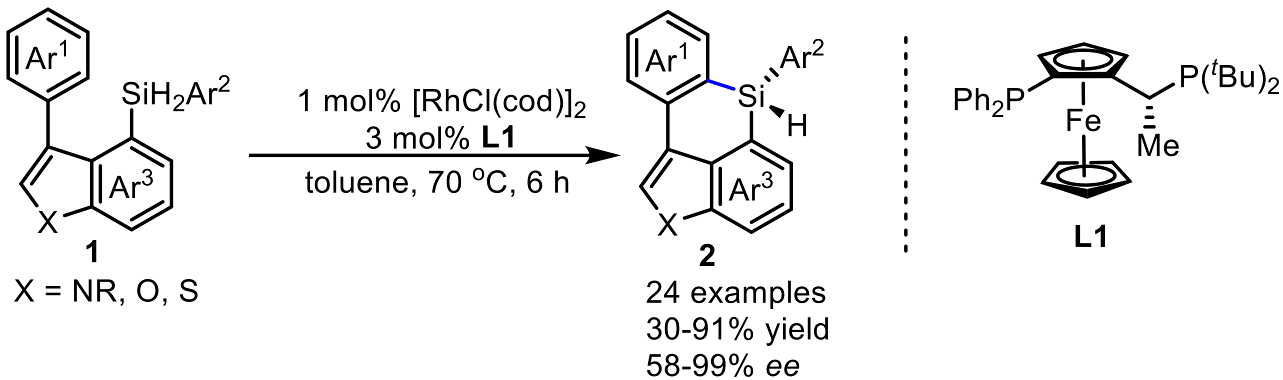
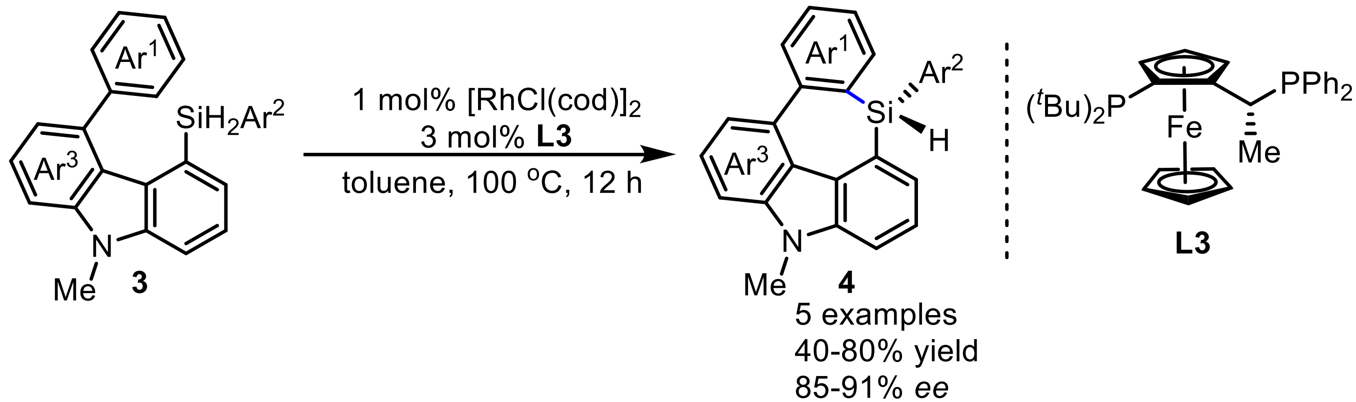
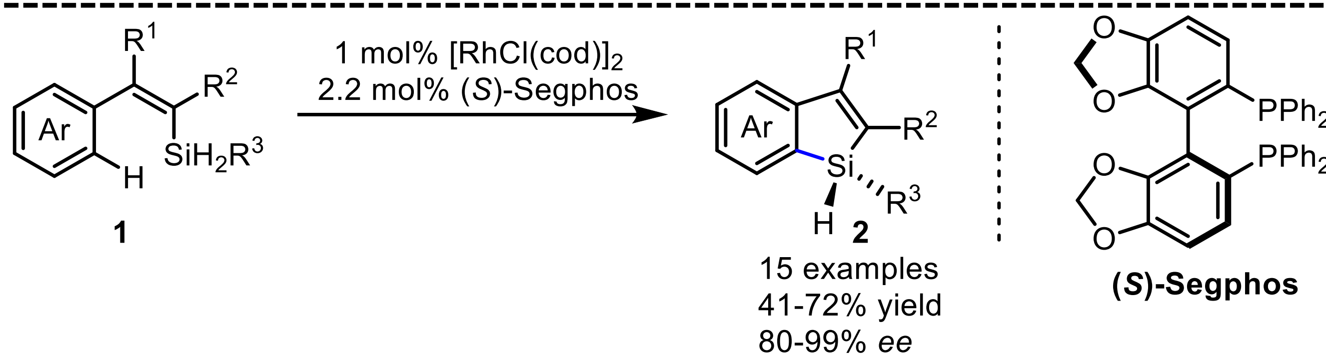


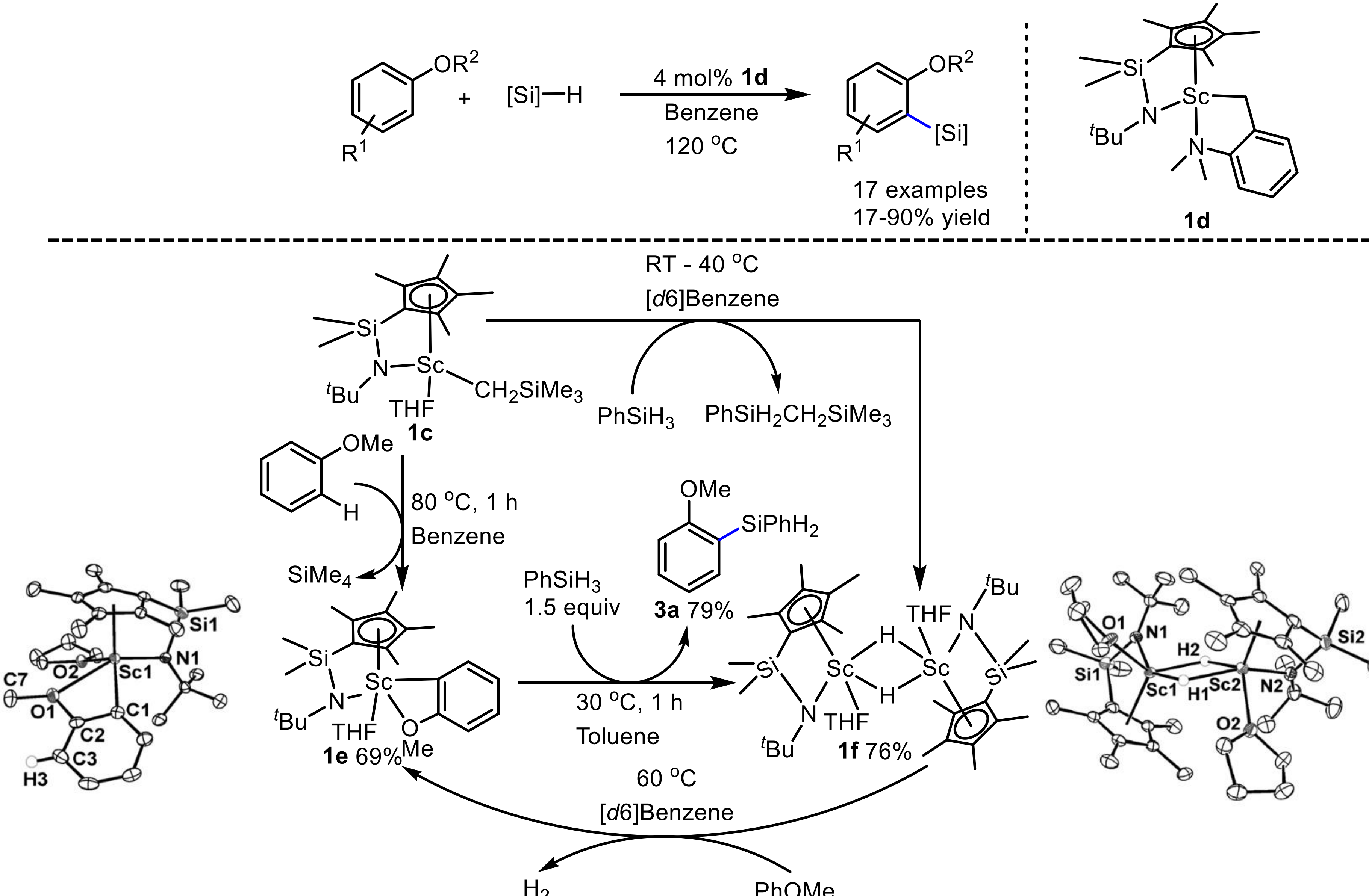




Chuan He, *et al*. *Nat. Commun.* **2021**, *12*, 1249.
Chuan He, *et al*. *Org. Lett.* **2021**, *23*, 1367.

目 录

稀土、碱土、碱金属催化芳基C-H键与硅烷的脱氢偶联



Zhaomin Hou, *et al*. *Angew. Chem. Int. Ed.* **2011,** *50*, 10720.

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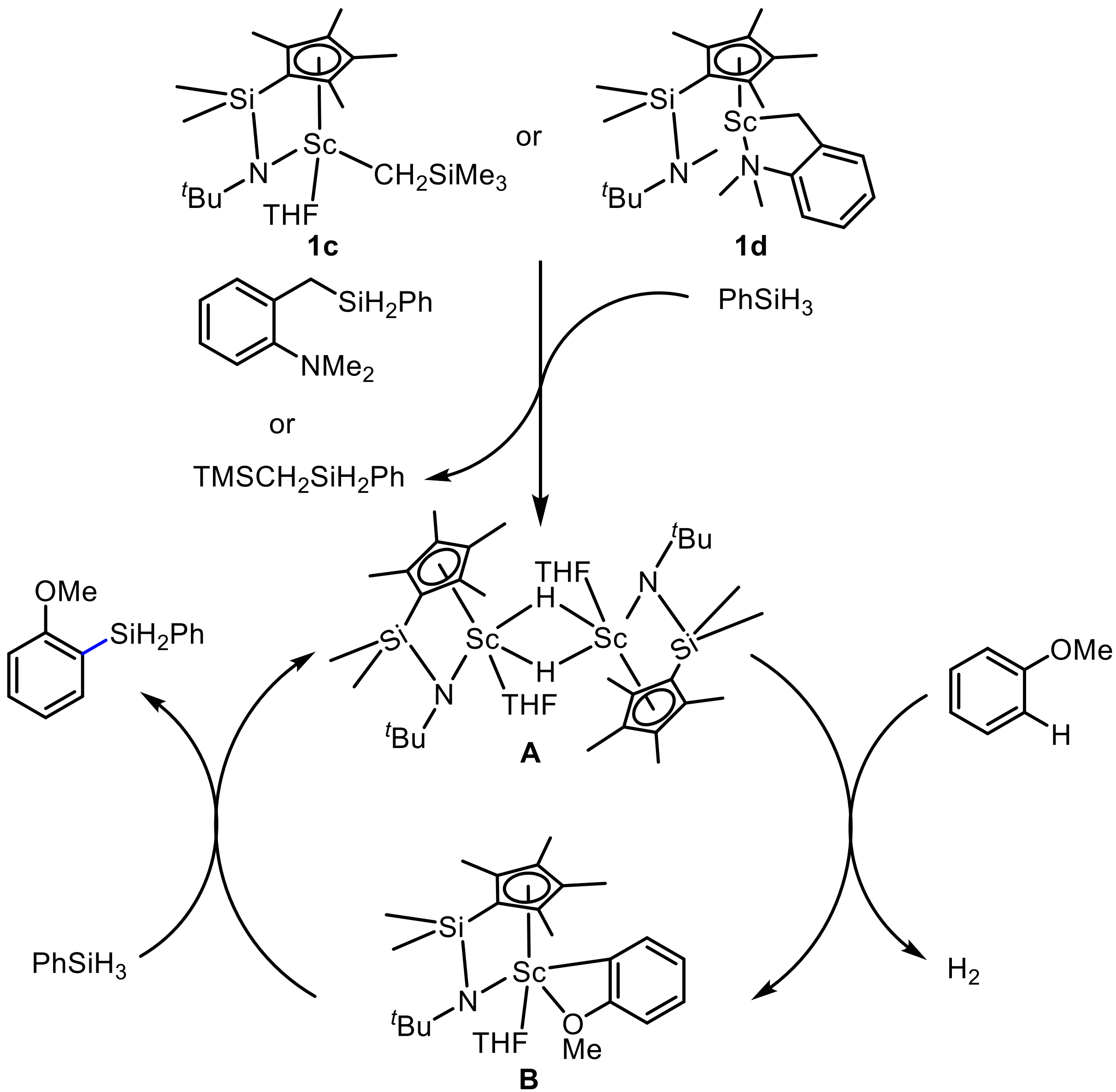

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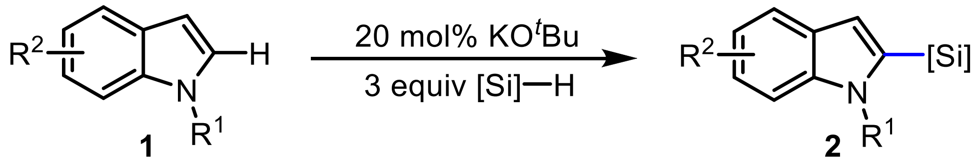
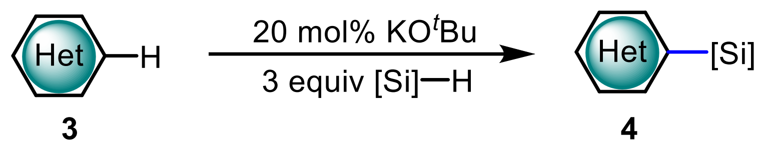
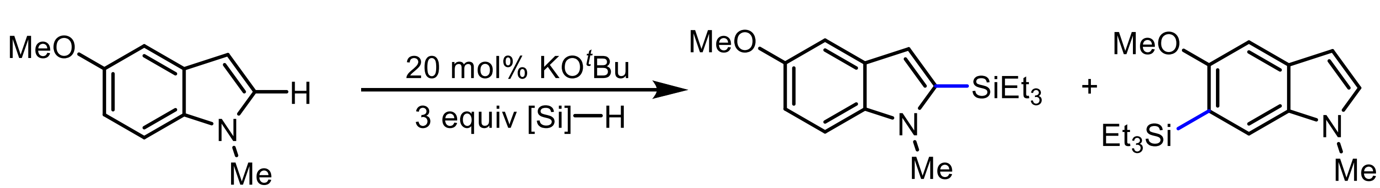


24 examples
45-83% yield

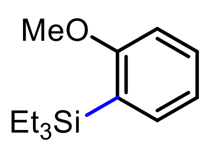


23 examples
31-95% yield

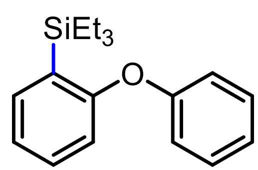


64%

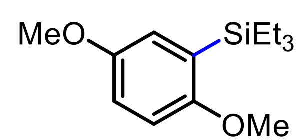
9%



o:(*m* + *p*) > 20:1
43% yield



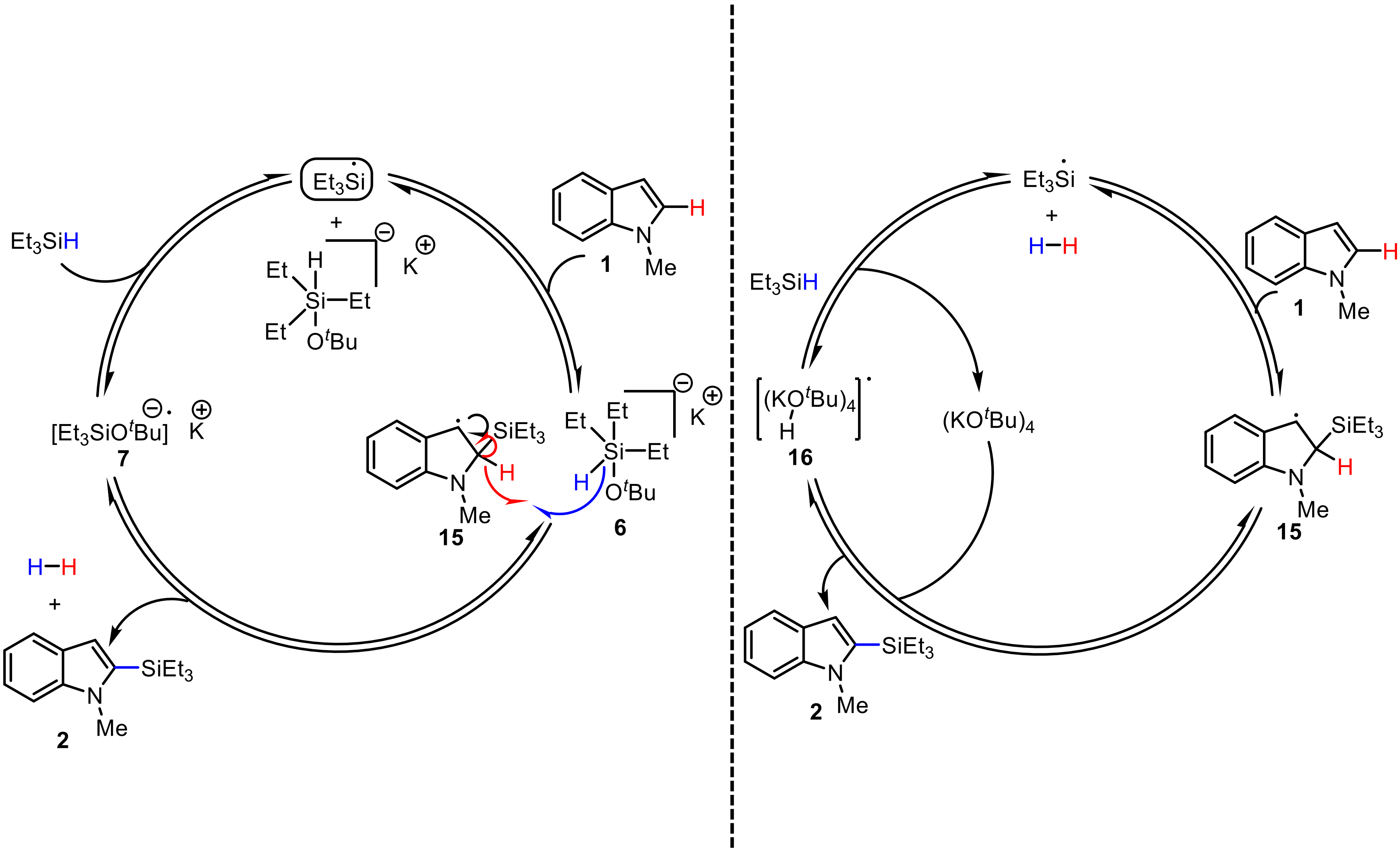
o:(*m* + *p*) > 20:1
55% yield



mono:2,5-bis = 5:1
42% (mono) + 8% (bis)

Robert H. Grubbs, *et al*. *Nature* **2015,** *518*, 80.

稀土、碱土、碱金属催化芳基C-H键与硅烷的脱氢偶联



Robert H. Grubbs, *et al*. *J. Am. Chem. Soc.* **2017**, *139*, 6867.

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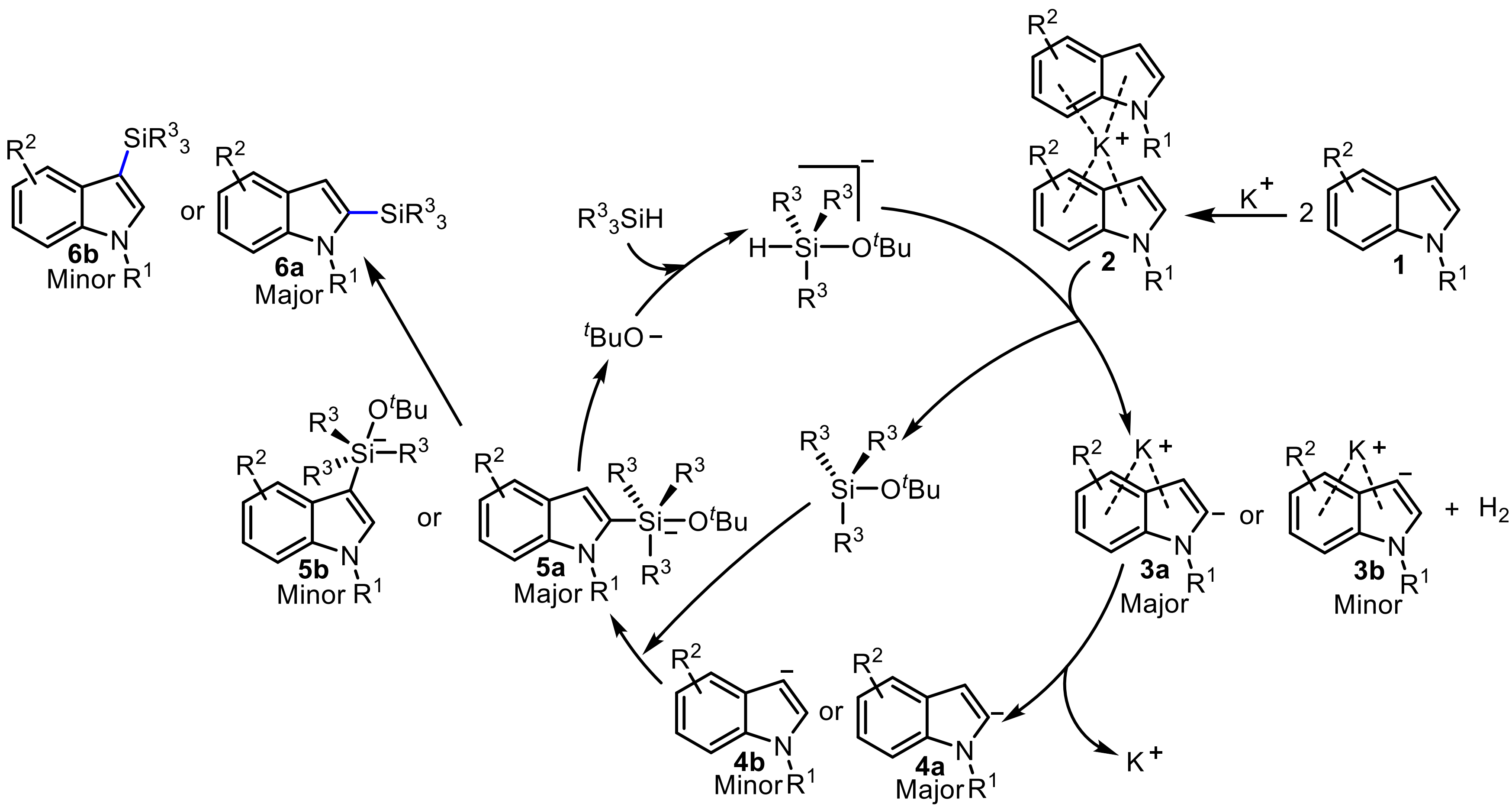

Anton A. Toutov, *et al*. *J. Am. Chem. Soc.* **2017**, *139*, 6880.

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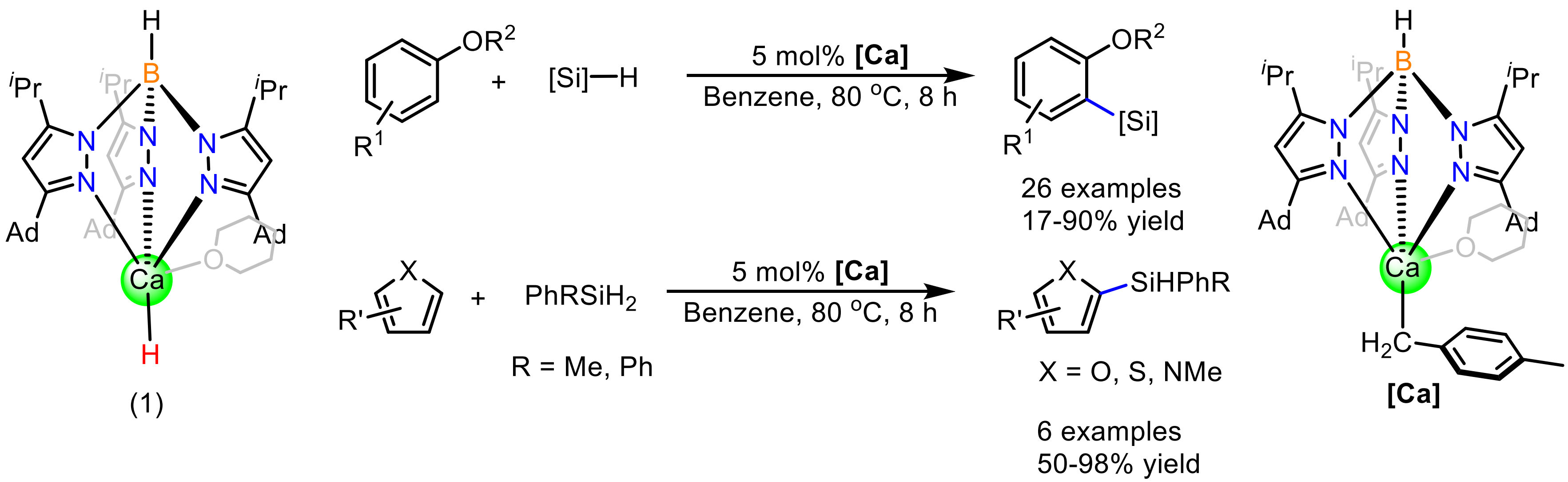

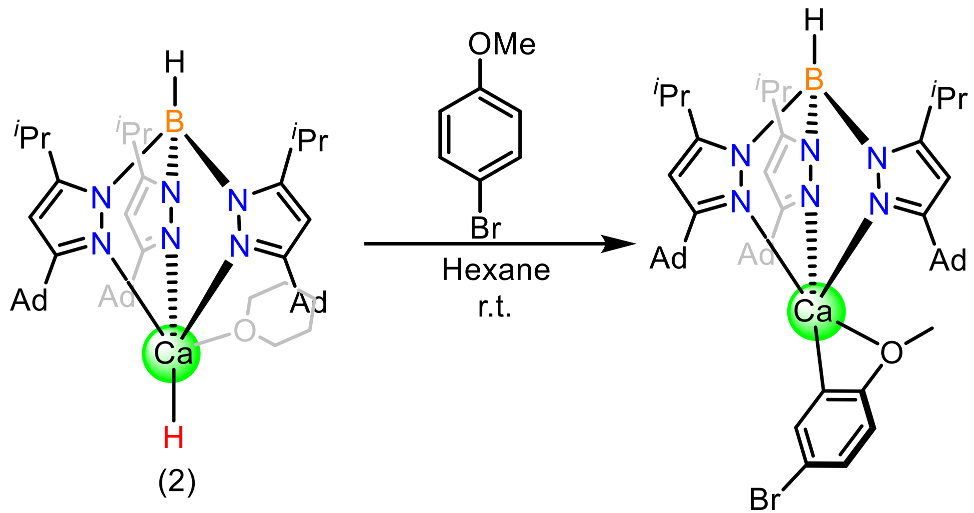

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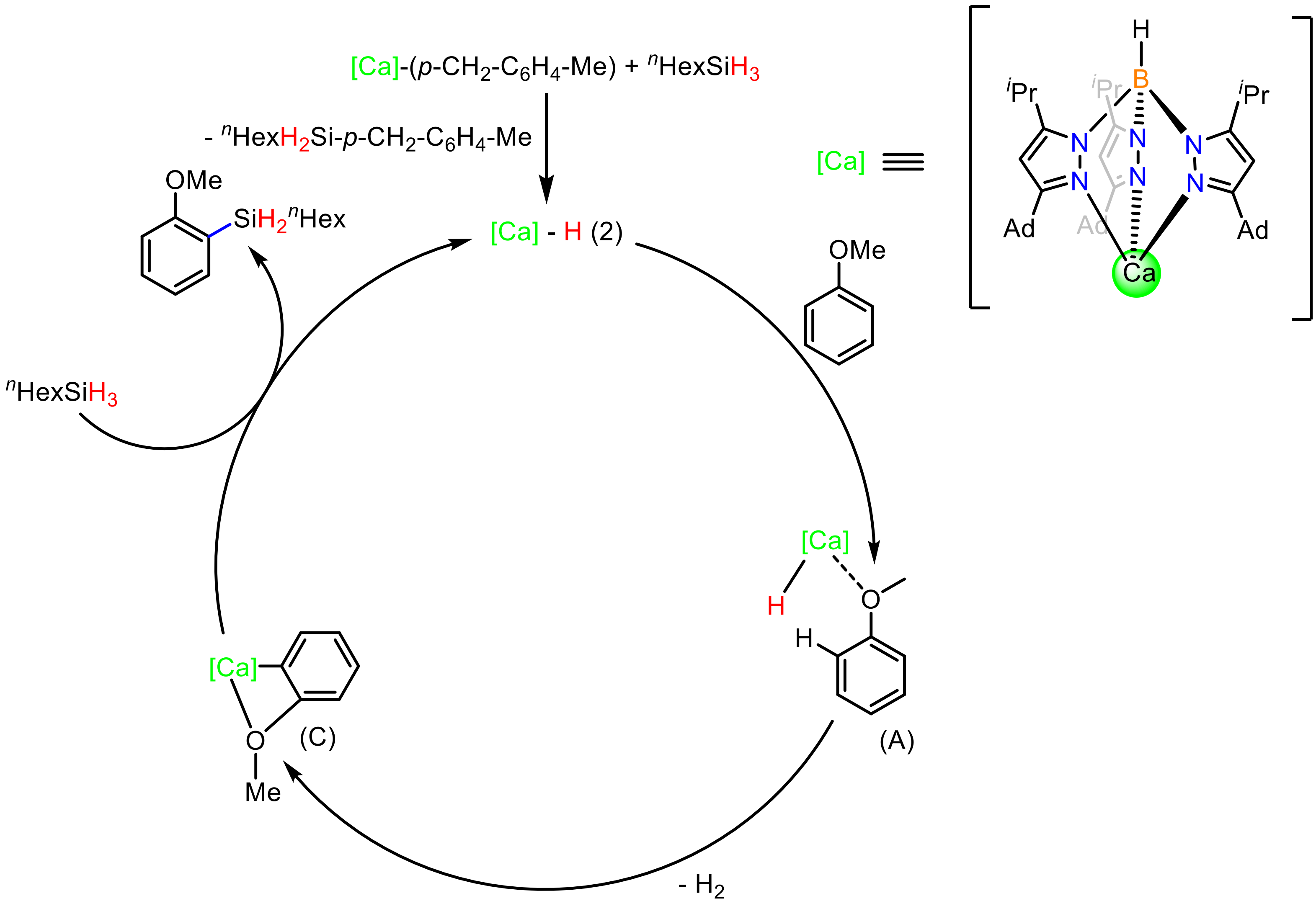
Jianhua Cheng, *et al*. *ACS Catal.* **2021**, *11*, 2041.
Jianhua Cheng, *et al*. *ChemCatChem* **2022**, *14*, e20220006.

稀土、碱土、碱金属催化芳基C-H键与硅烷的脱氢偶联



目 录

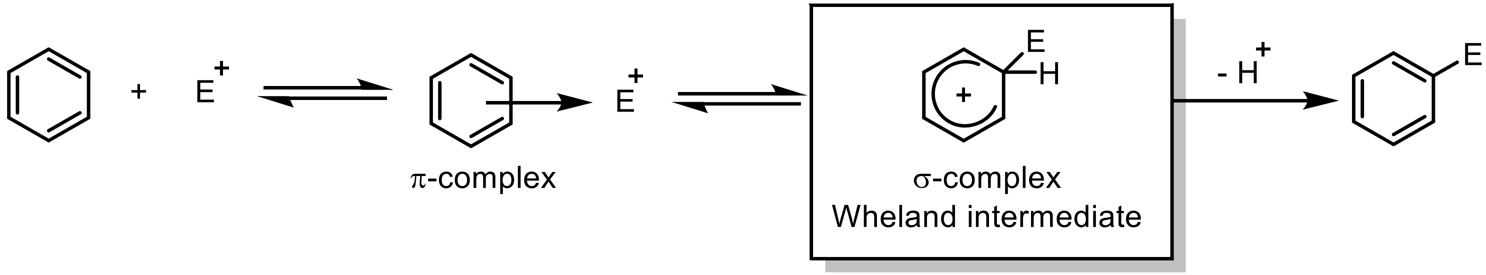
一 背景

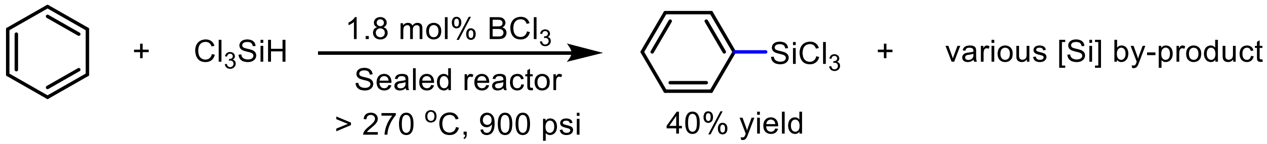
二 芳基C-H键与硅烷的脱氢偶联

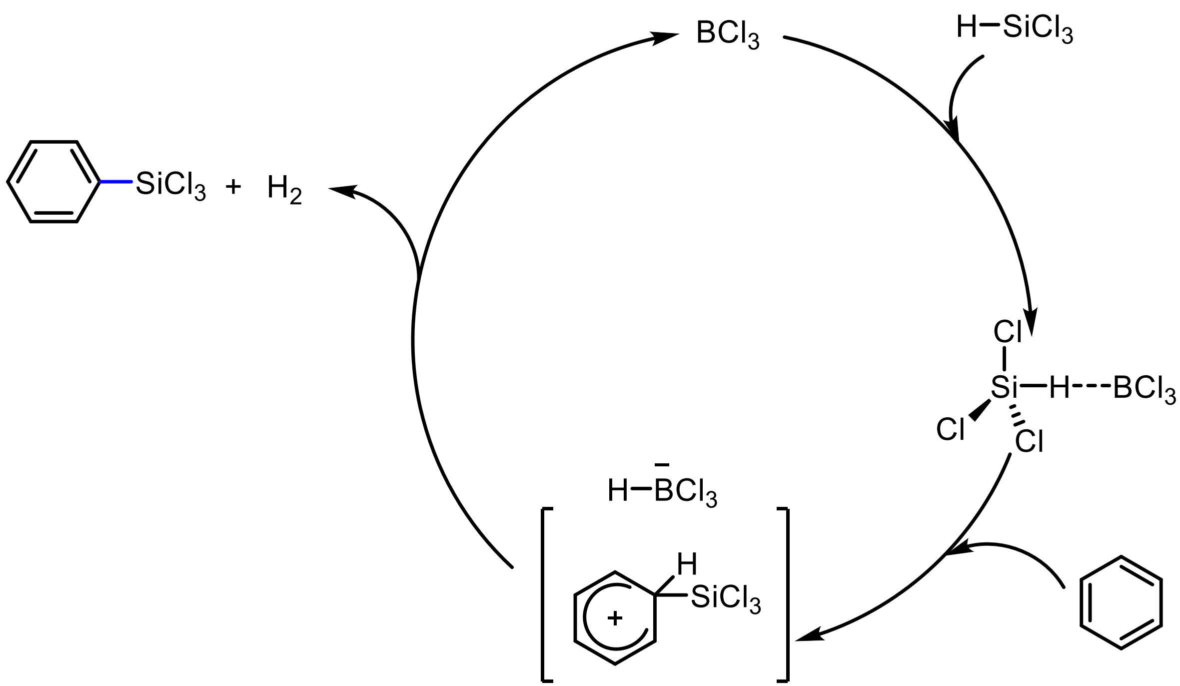
- 过渡金属催化芳基C-H键与硅烷的脱氢偶联
- 稀土、碱土、碱金属催化芳基C-H键与硅烷的脱氢偶联
- **Lewis酸催化芳基C-H键与硅烷的脱氢偶联**

三 总结与展望

Lewis酸催化芳基C-H键与硅烷的脱氢偶联

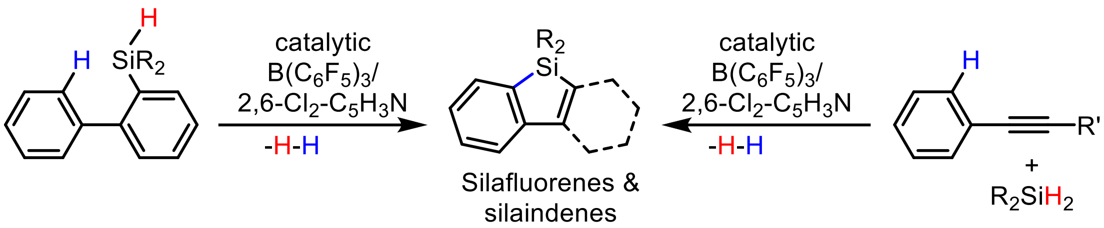


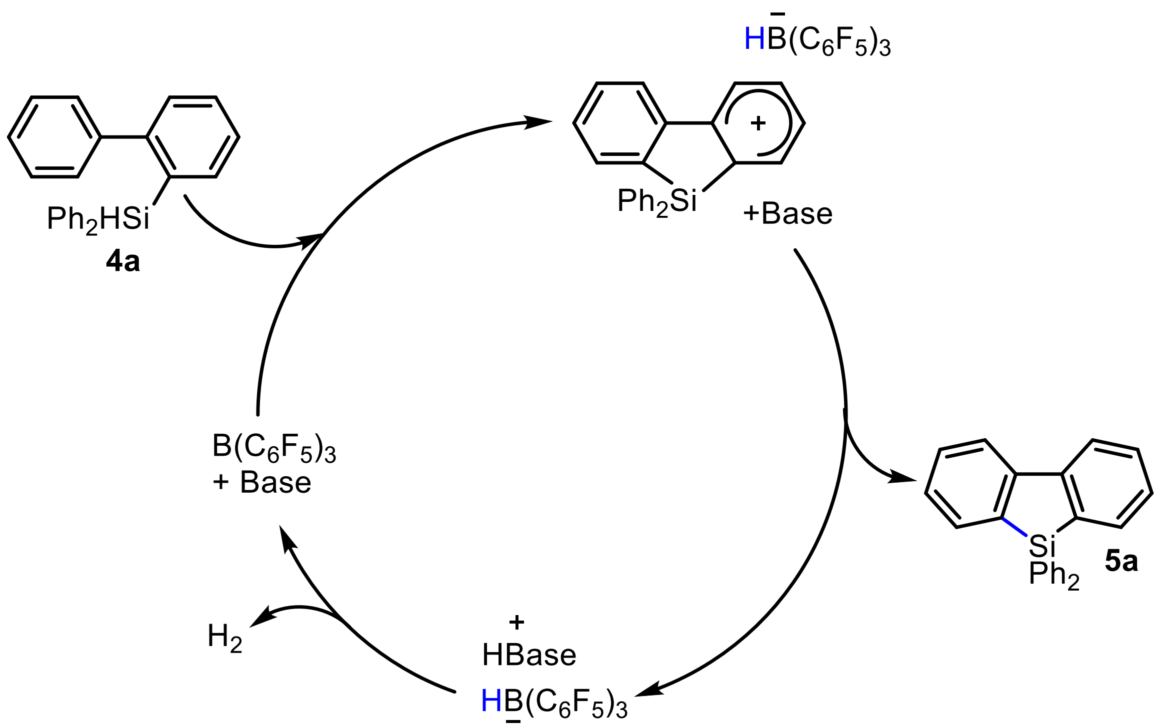




Jay K. Kochi, *et al*. *J. Am. Chem. Soc.* **2000**, *122*, 8279.
D. E. Hook, *et al*. *Ind. Eng. Chem. Res.* **1959**, *51*, 131.

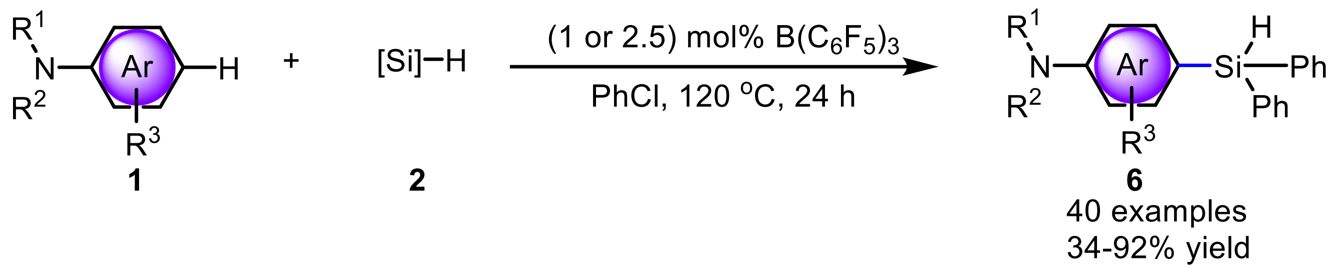
Lewis酸催化芳基C-H键与硅烷的脱氢偶联

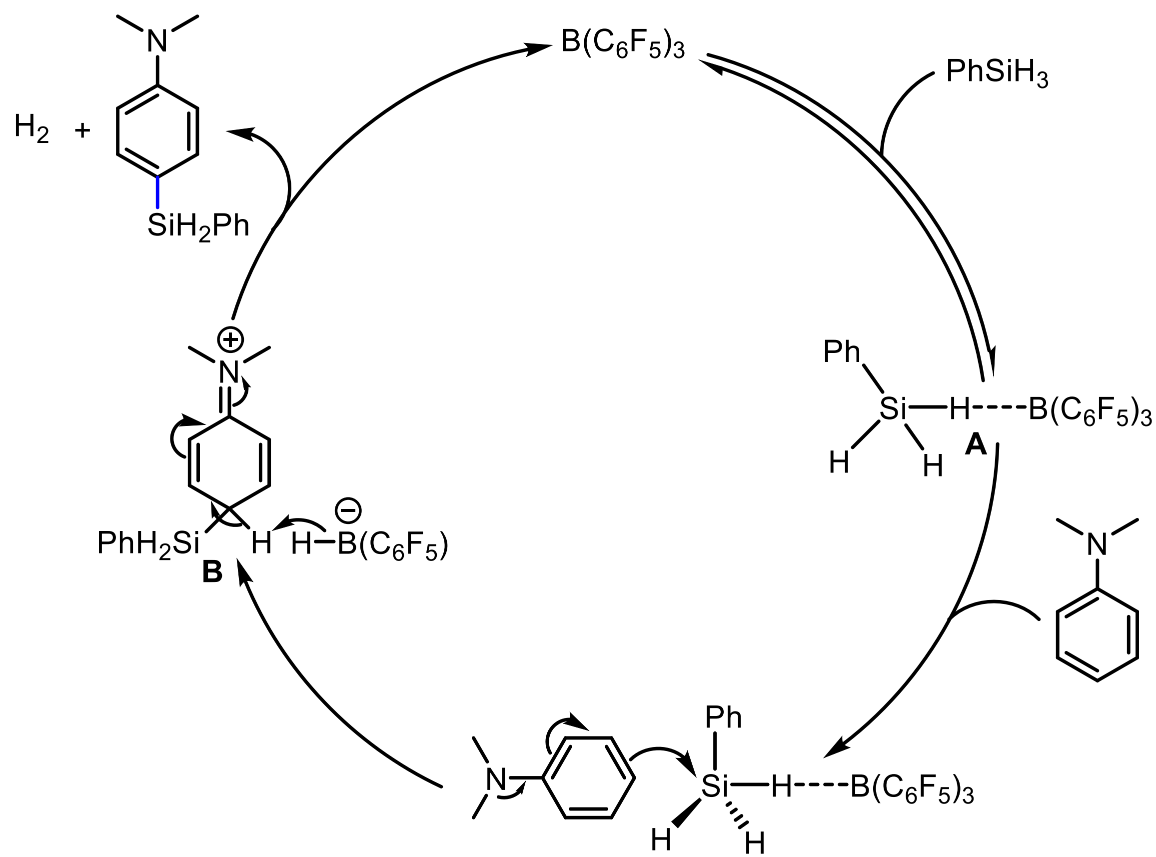




Michael J. Ingleson, *et al*. *Organometallics* **2014**, *33*, 7241.

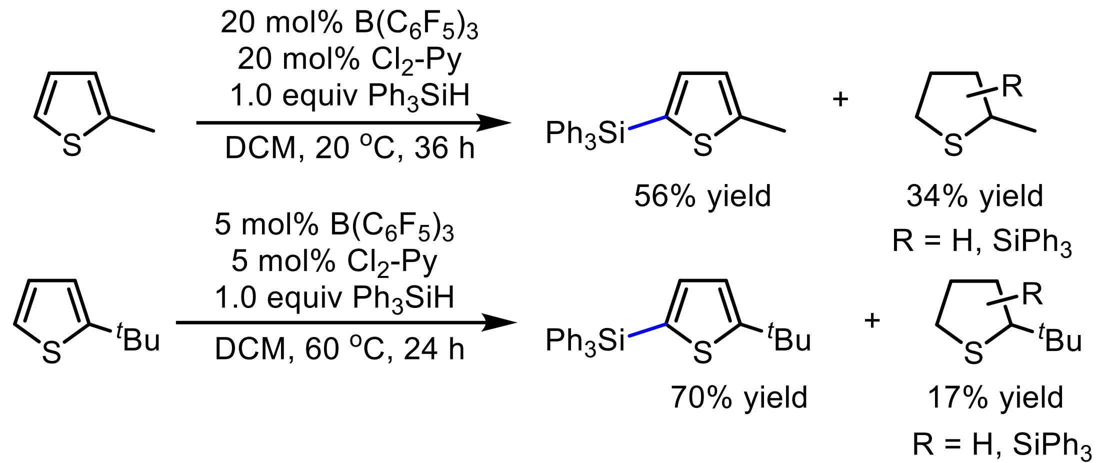
Lewis酸催化芳基C-H键与硅烷的脱氢偶联

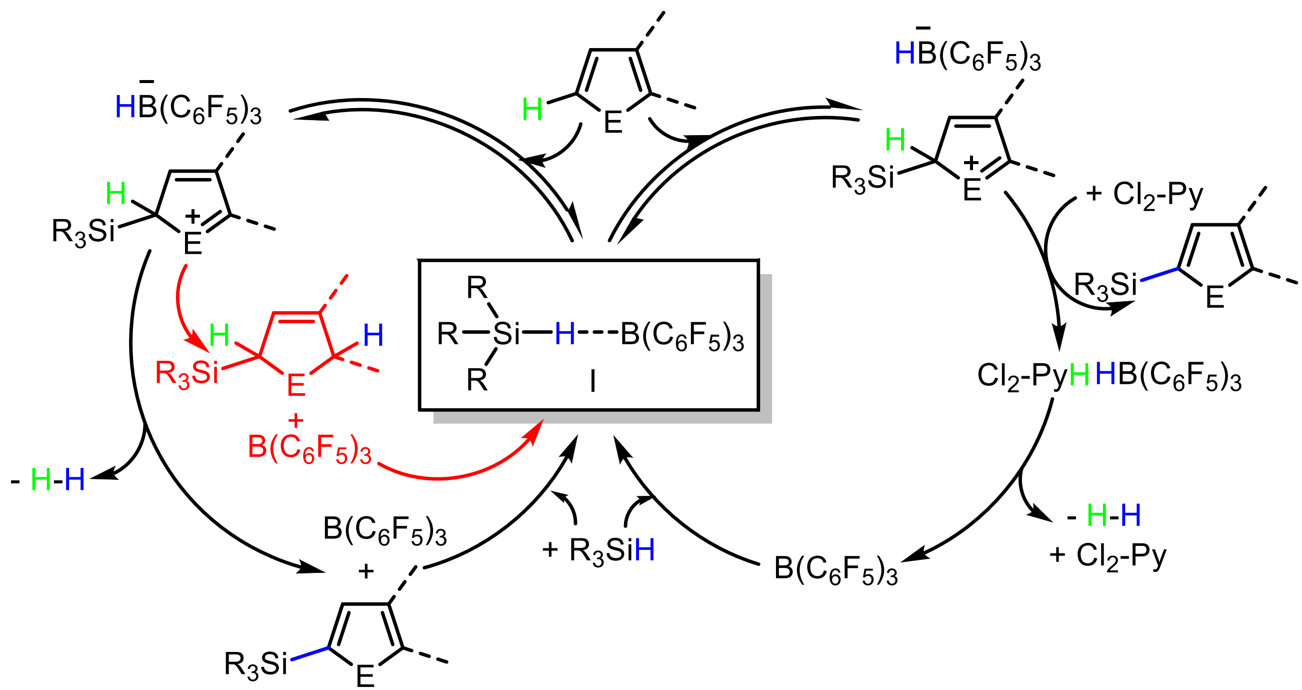




Zhaomin Hou, *et al*. *J. Am. Chem. Soc.* **2016**, *138*, 3663.

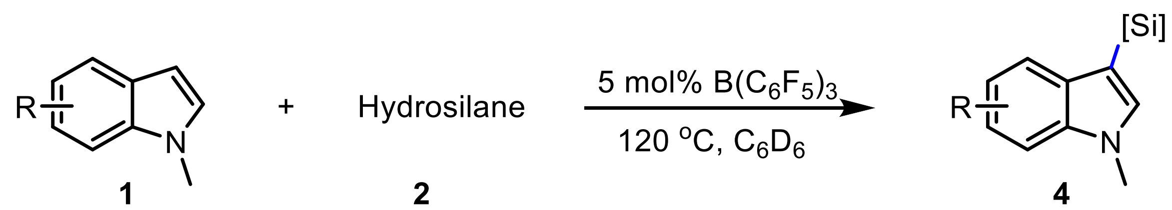
Lewis酸催化芳基C-H键与硅烷的脱氢偶联

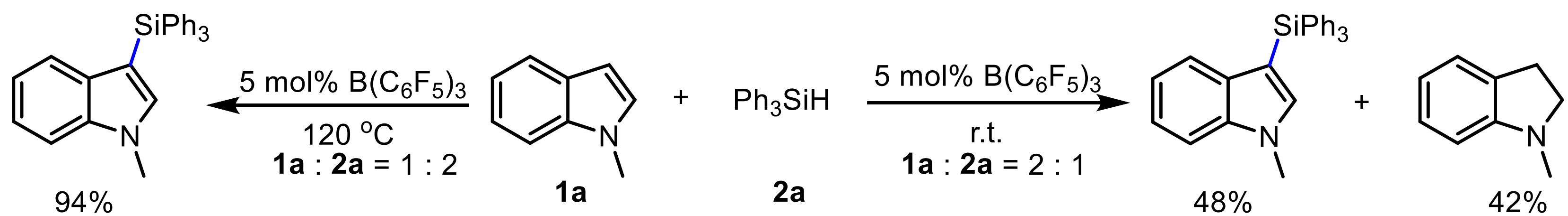




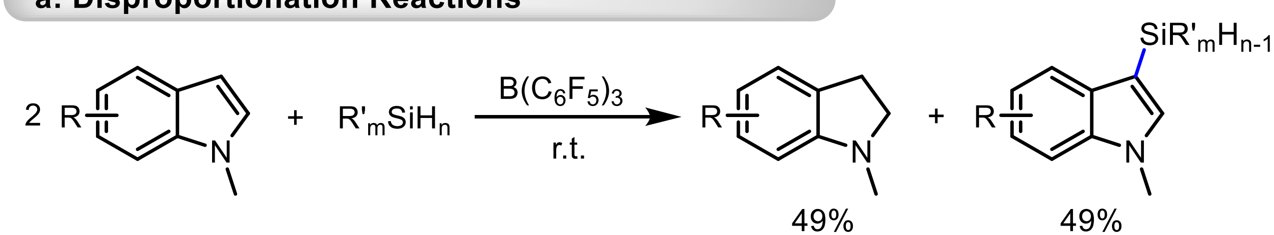
Michael J. Ingleson, *et al*. *Chem. Commun.* **2014**, 50, 5270.

Lewis酸催化芳基C-H键与硅烷的脱氢偶联

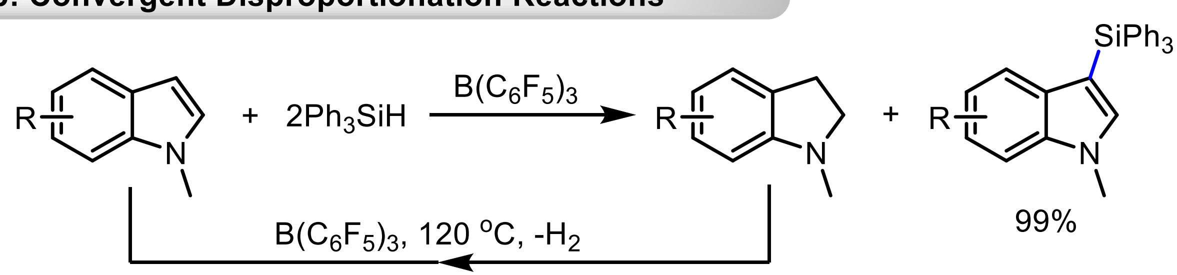




a: Disproportionation Reactions

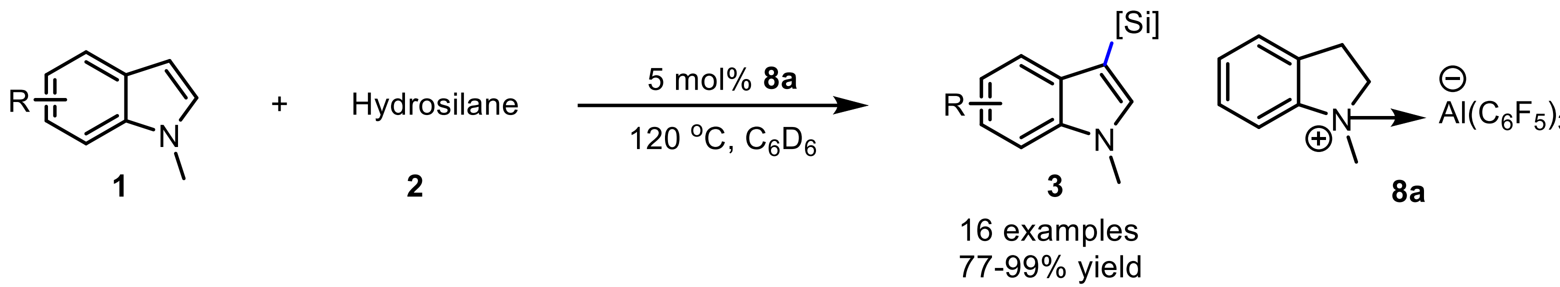


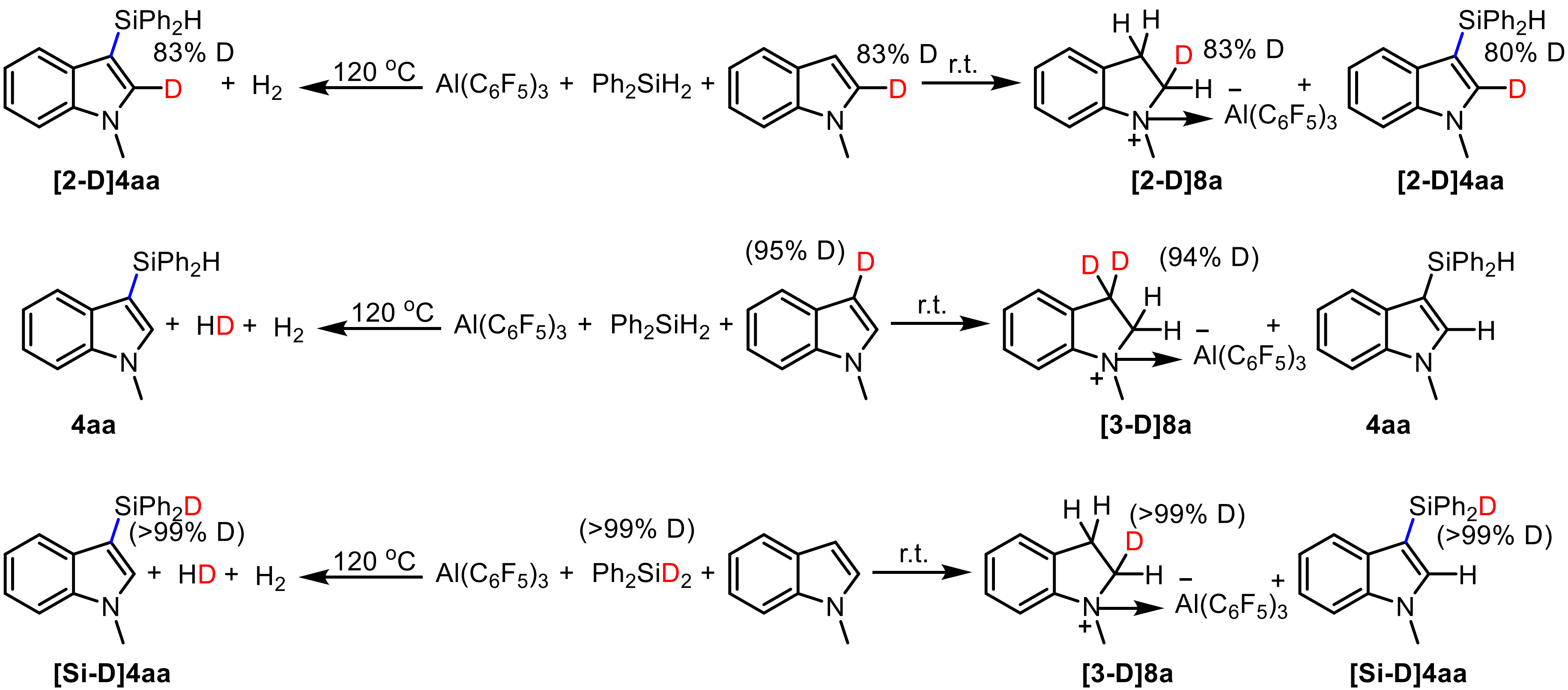
b: Convergent Disproportionation Reactions



Yuetao Zhang, *et al*. *J. Am. Chem. Soc.* **2017**, *139*, 7399.

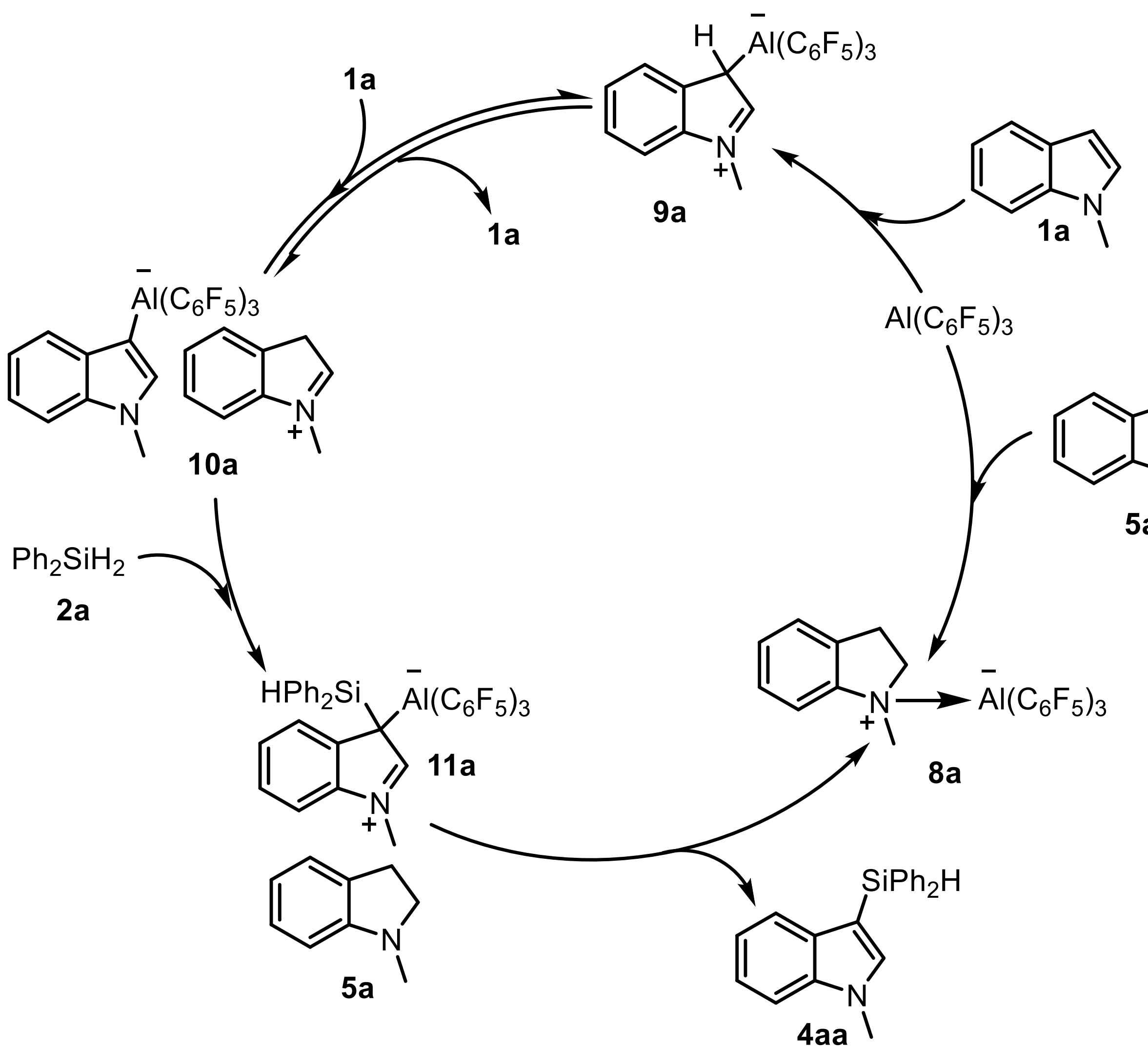
Lewis酸催化芳基C-H键与硅烷的脱氢偶联

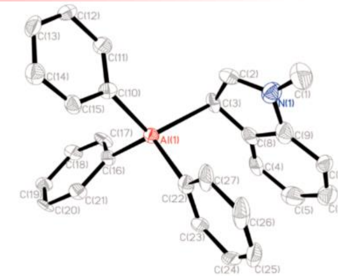




Yuetao Zhang, *et al*. *ACS Catal.* **2018**, *8*, 8765.

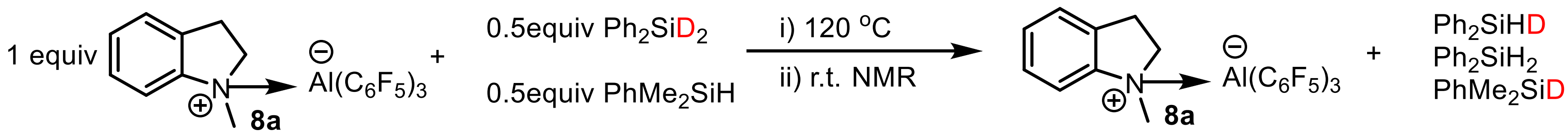
Lewis酸催化芳基C-H键与硅烷的脱氢偶联

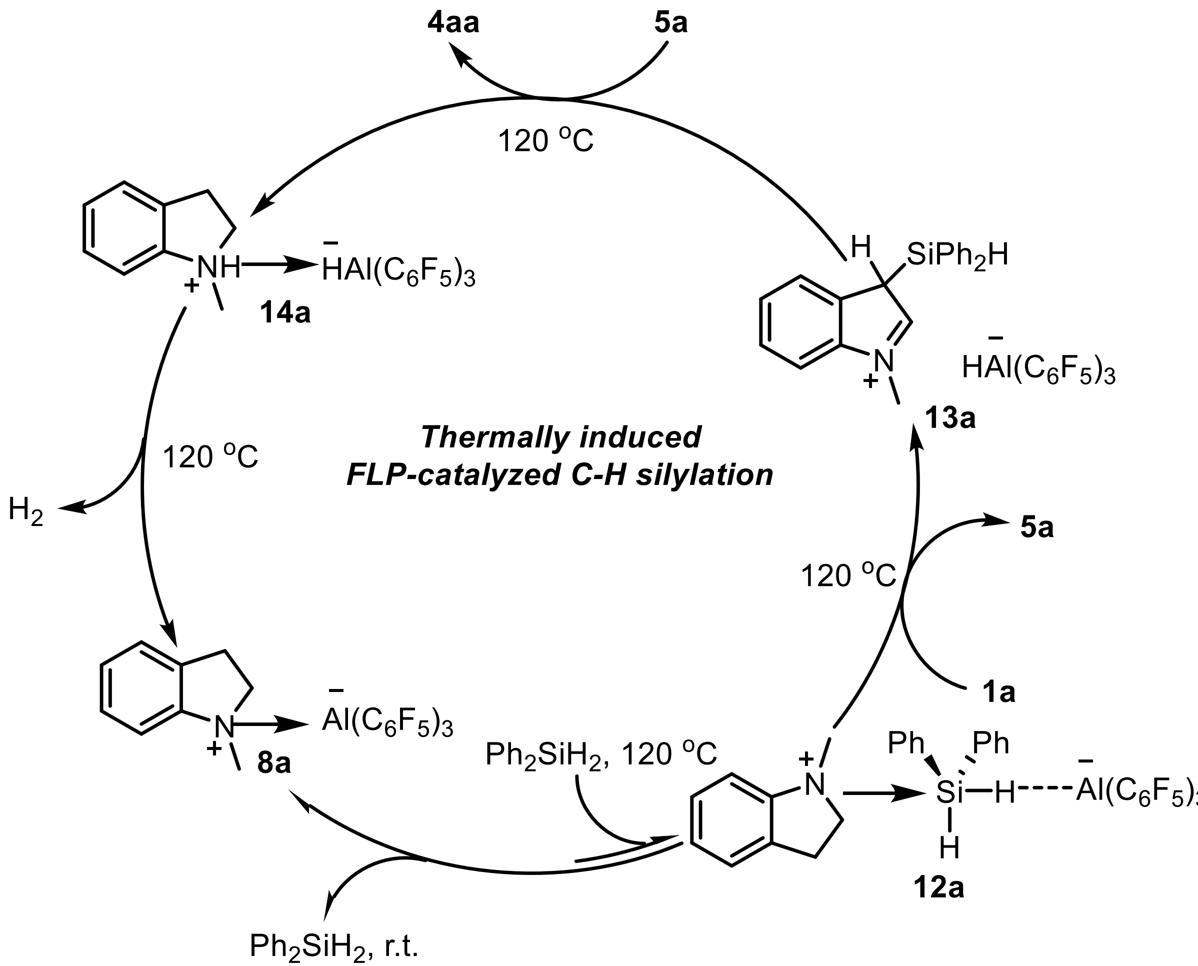




9a

Lewis酸催化芳基C-H键与硅烷的脱氢偶联





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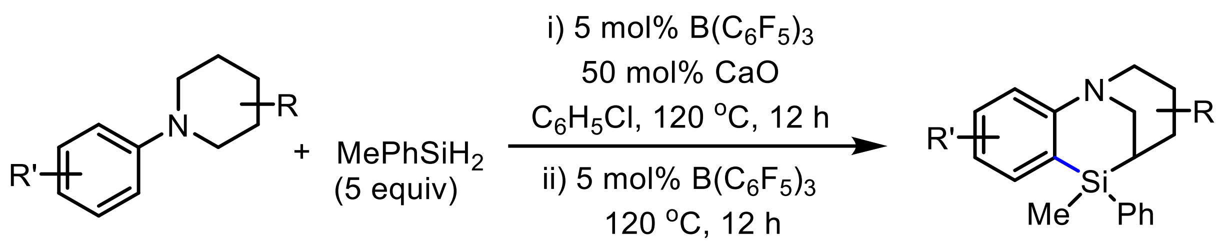
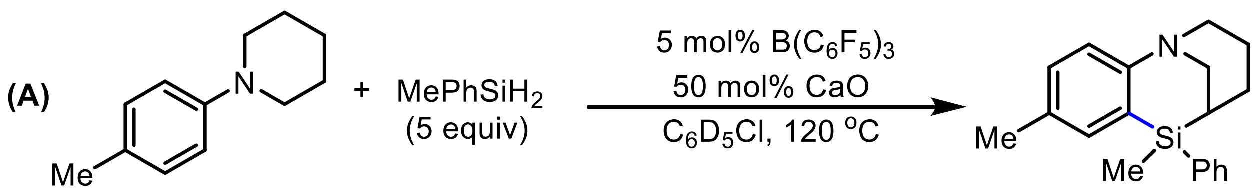
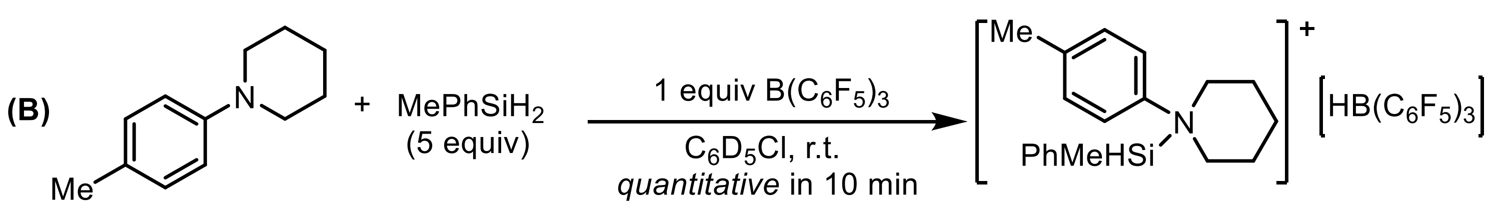




time (h)	conv. (%)	yield (%)
6	40	33
12	55	40
24	61	43

$\left[[Si]\text{-}\overset{+}{N}_{piperidine}\ H\overset{-}{B}(C_6F_5)_3\right]$ - major species detected by NMR

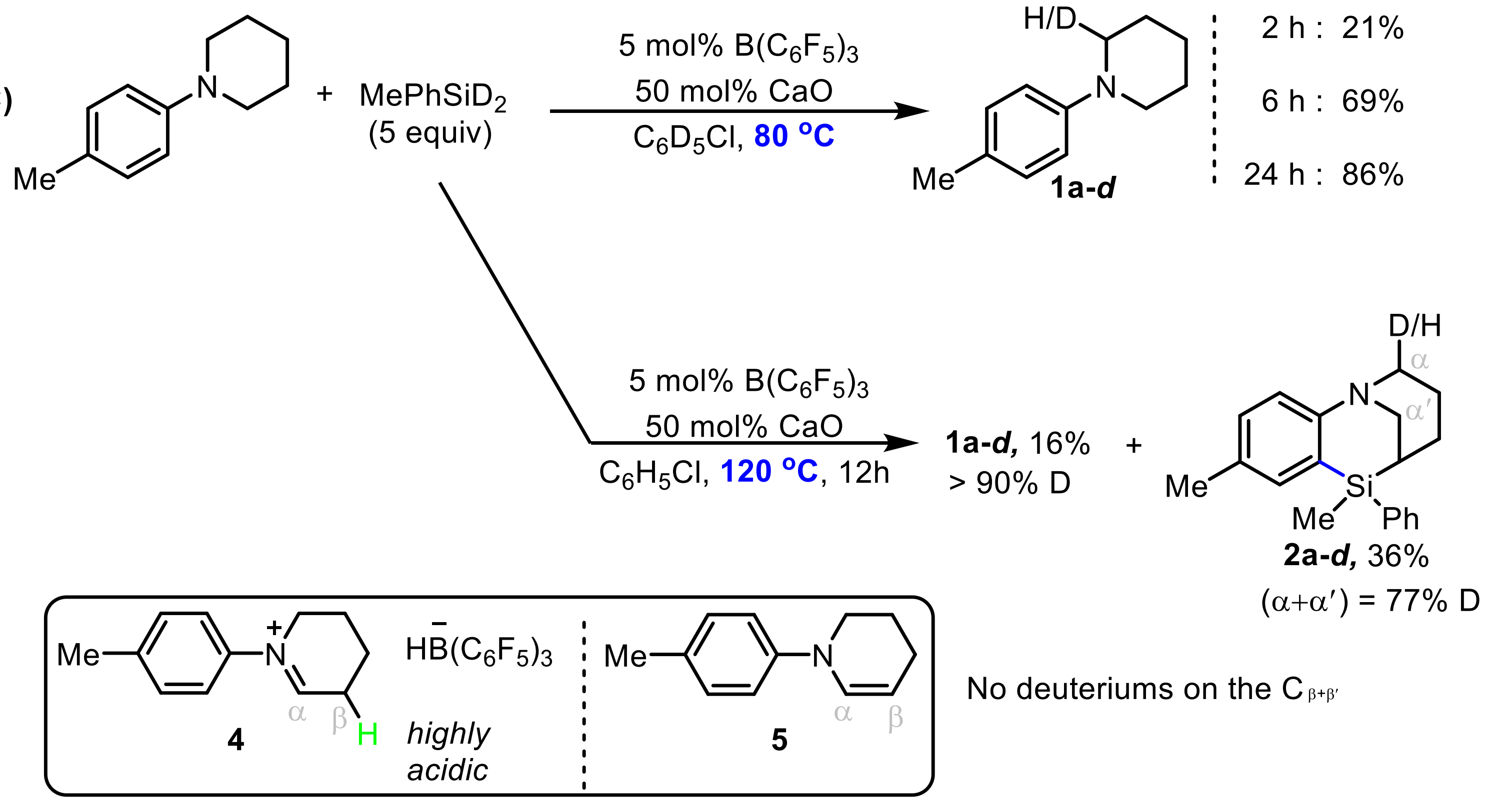


3

Sukbok Chang, *et al*. *J. Am. Chem. Soc.* **2018**, *140*, 13209.

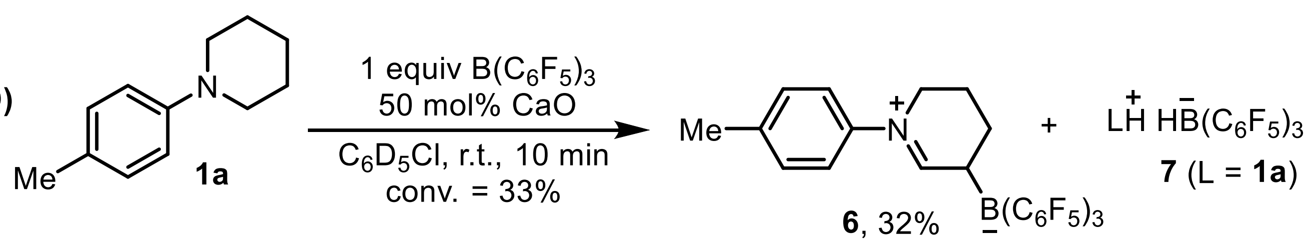
Lewis酸催化芳基C-H键与硅烷的脱氢偶联

(C)



No deuteriums on the $C_{\beta+\beta'}$

(D)



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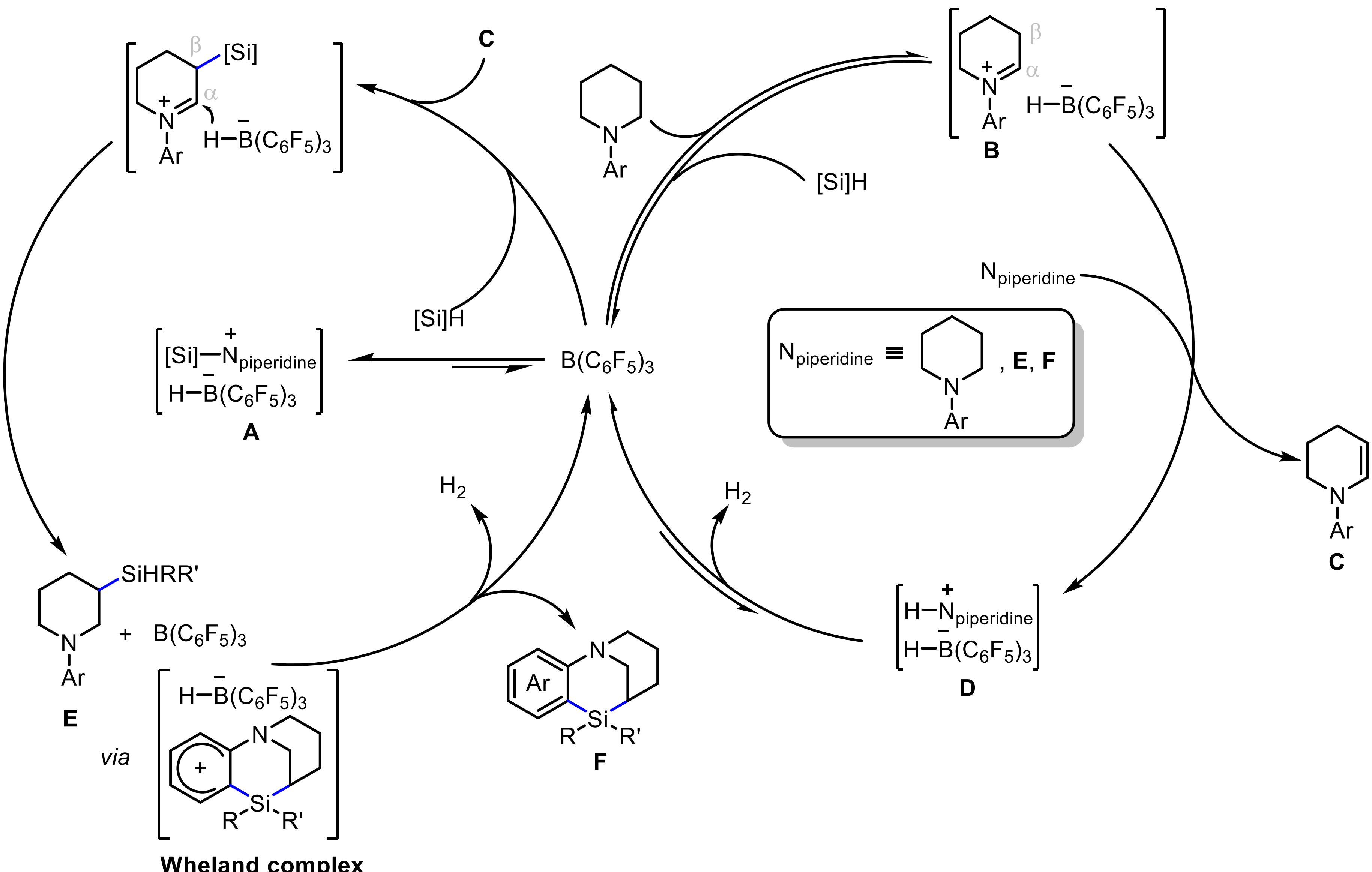

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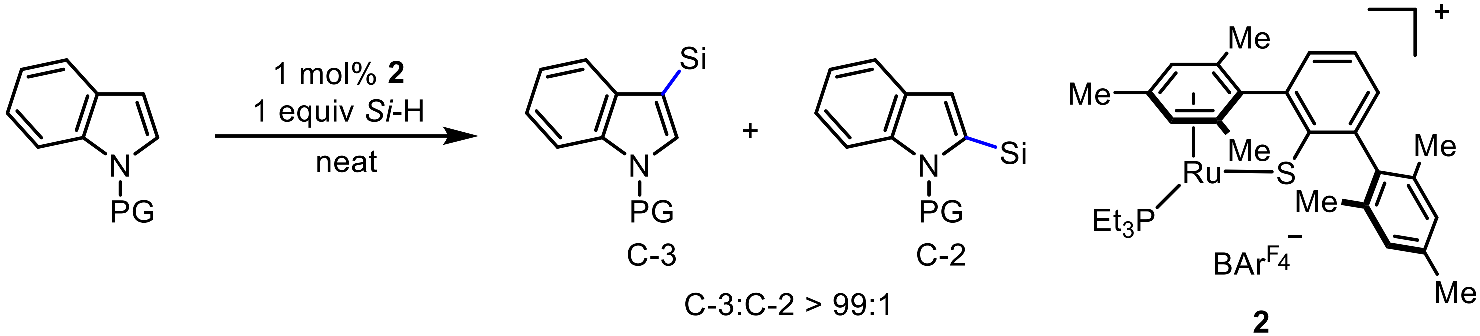

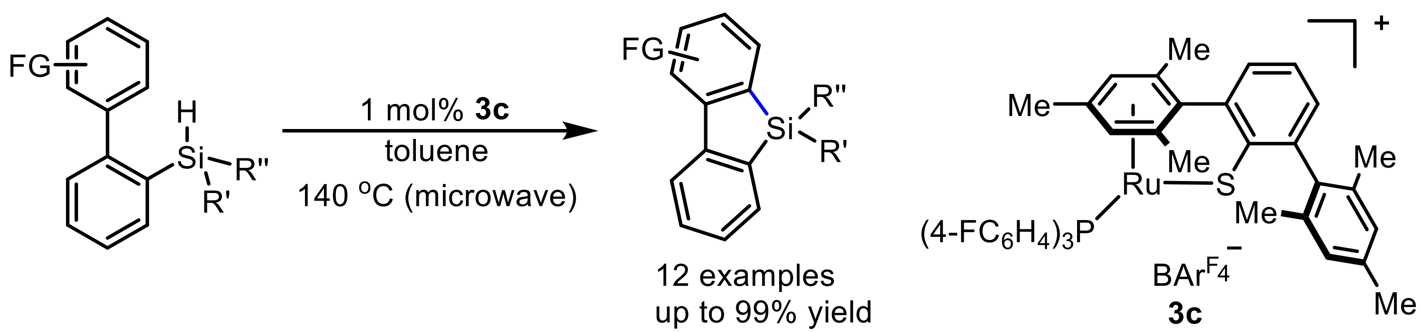

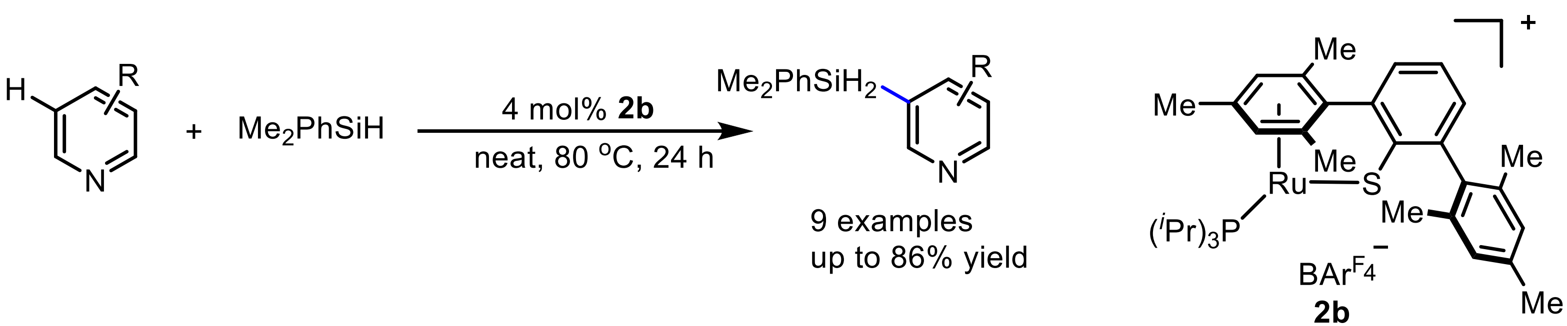

Martin Oestreich, *et al*. *J. Am. Chem. Soc.* **2011**, *133*, 3312.
Martin Oestreich, *et al*. *Angew. Chem. Int. Ed.* **2015**, *54*, 10276.
Martin Oestreich, *et al*. *Angew. Chem. Int. Ed.* **2015**, *54*, 15876.

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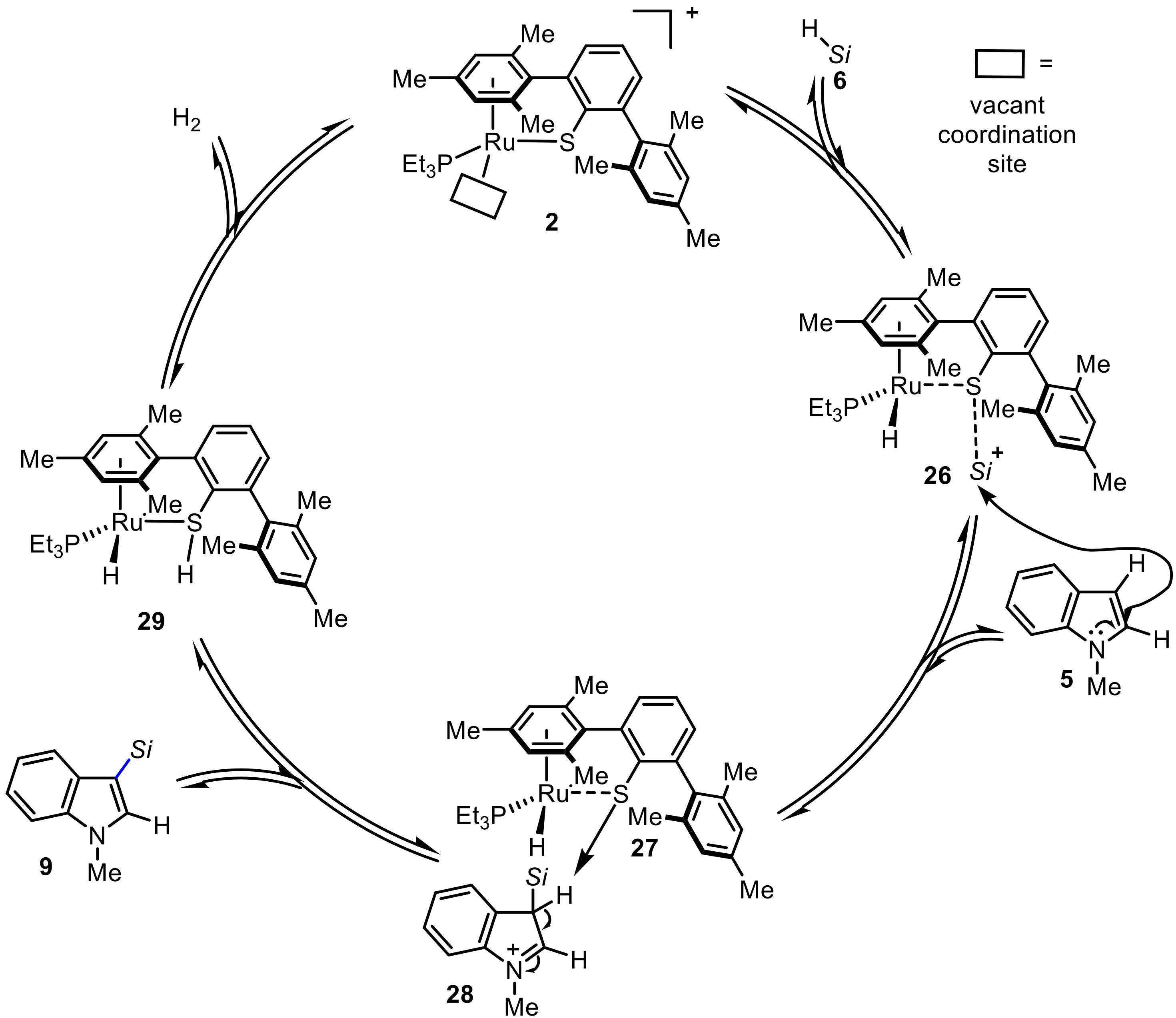

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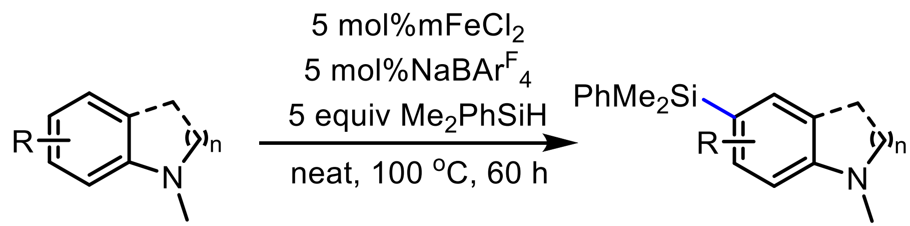


17 examples
up to 95% yield

Entry	Metal salt	*p:o*	Conv.[%]
1	Sc(OTf)$_3$	97:3	68
2	CoCl$_2$	98:2	87
3	NiCl$_2$	97:3	74
4	CuCl$_2$	95:5	55
5	Zn(OTf)$_2$	97:3	88
6	AlCl$_3$	98:2	77
7	Y(OTf)$_3$	98:2	46
8	Ce(Cl)$_3$	96:4	72
9	Sm(OTf)$_3$	99:1	74
10	ZnCl$_2$	99:1	79
11	InCl$_3$	98:2	88
12	FeBr$_2$	98:2	90
13	Fe(OAc)$_2$	99:1	35
14	FeCl$_3$	97:3	83
15	FeCl$_2$	95:5	90

Martin Oestreich, *et al*. *Angew. Chem. Int. Ed.* **2016**, *55*, 3204.

目 录

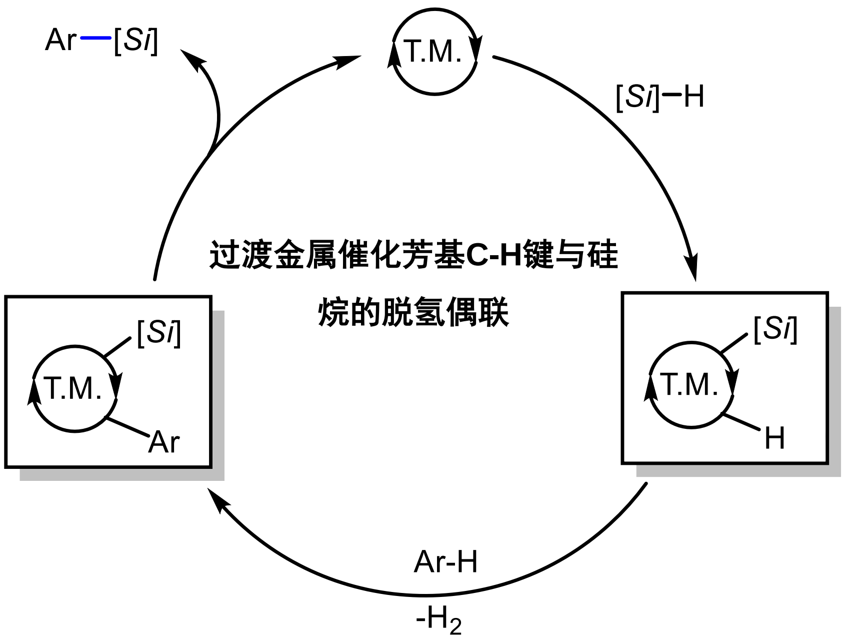
一 背景

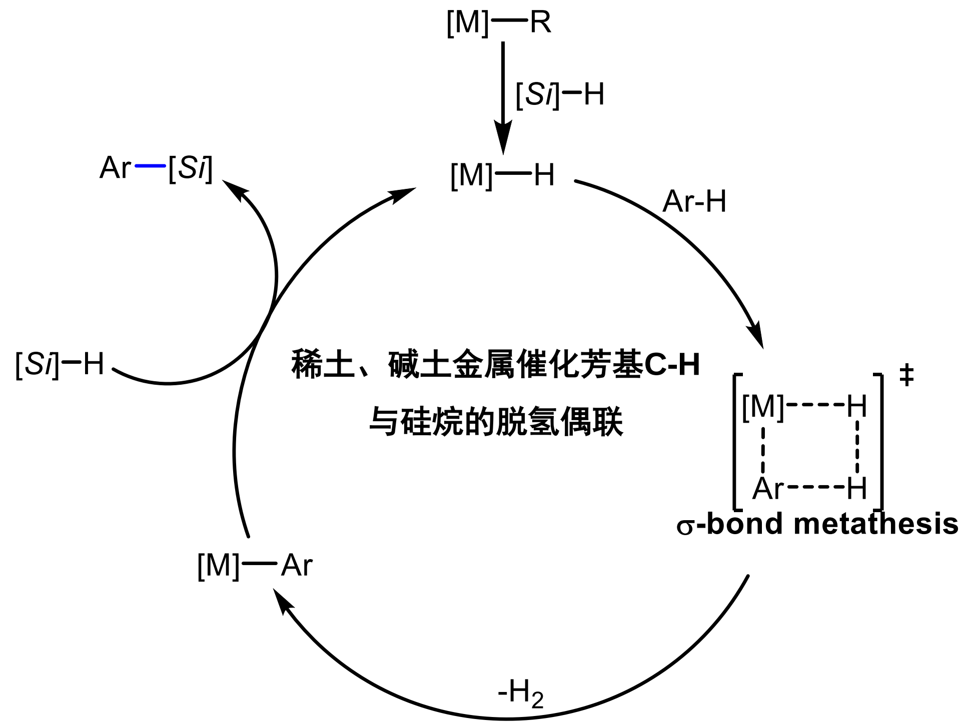
二 芳基C-H键与硅烷的脱氢偶联

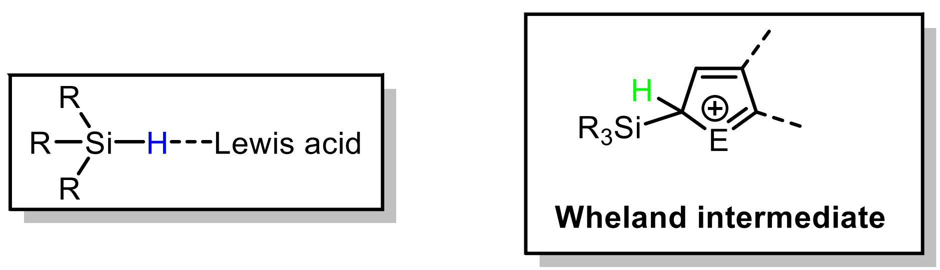
- 过渡金属催化芳基C-H键与硅烷的脱氢偶联
- 稀土、碱土、碱金属催化芳基C-H键与硅烷的脱氢偶联
- Lewis酸催化芳基C-H键与硅烷的脱氢偶联

三 总结与展望

总结



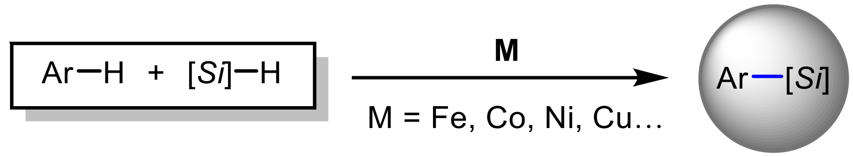




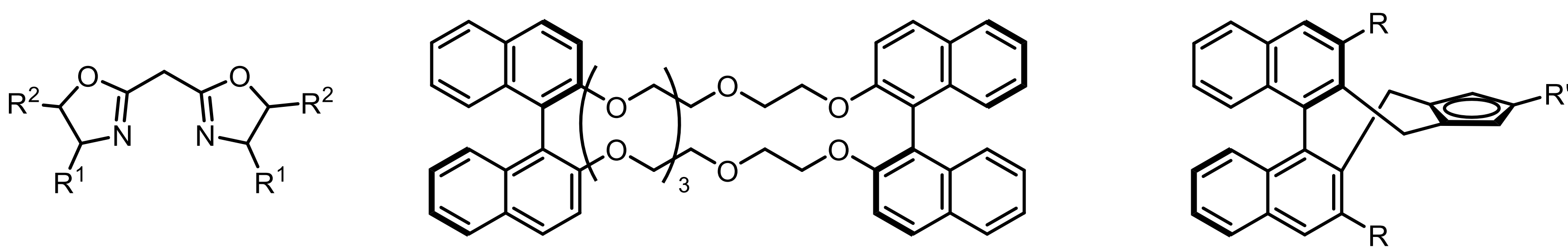
Lewis酸催化芳基C-H与硅烷的脱氢偶联

展望

过渡金属催化芳基C-H键与硅烷的脱氢偶联



稀土、碱土、碱金属催化芳基C-H键与硅烷的脱氢偶联



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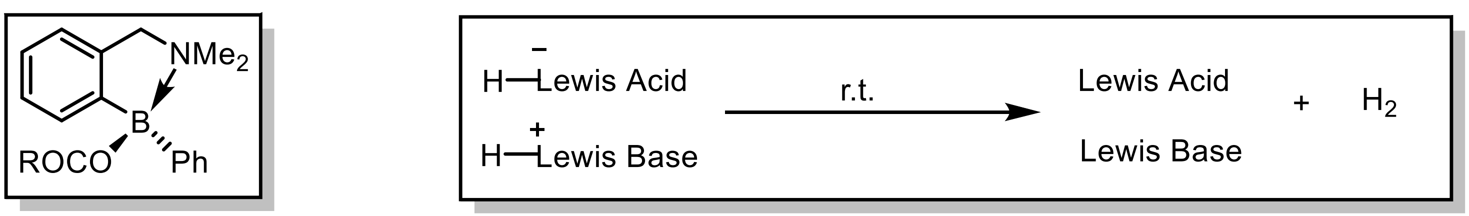

请老师与同学们批评指正！
谢谢！