C-Si键偶联

汇报时间：2023.10.13

报告人：李蔚鹏

Part 1. 背景介绍

何川

2004-2008 武汉大学，理学学士 导师：雷爱文

2008-2013 武汉大学，理学博士 导师：雷爱文

2013-2017 剑桥大学，博士后/玛丽居里研究员

合作导师：Matthew Gaunt

2018-至今 南方科技大学，副教授/研究员

研究方向：

手性有机硅化学　电催化杂原子化学

手性有机硼化学　手性有机功能材料

Part 1. 背景介绍

舒兴中

2001-2005 B.S. — Shaoxing University

2005-2010 Ph.D. — Lanzhou University Advisor: Prof. Yong-Min Liang

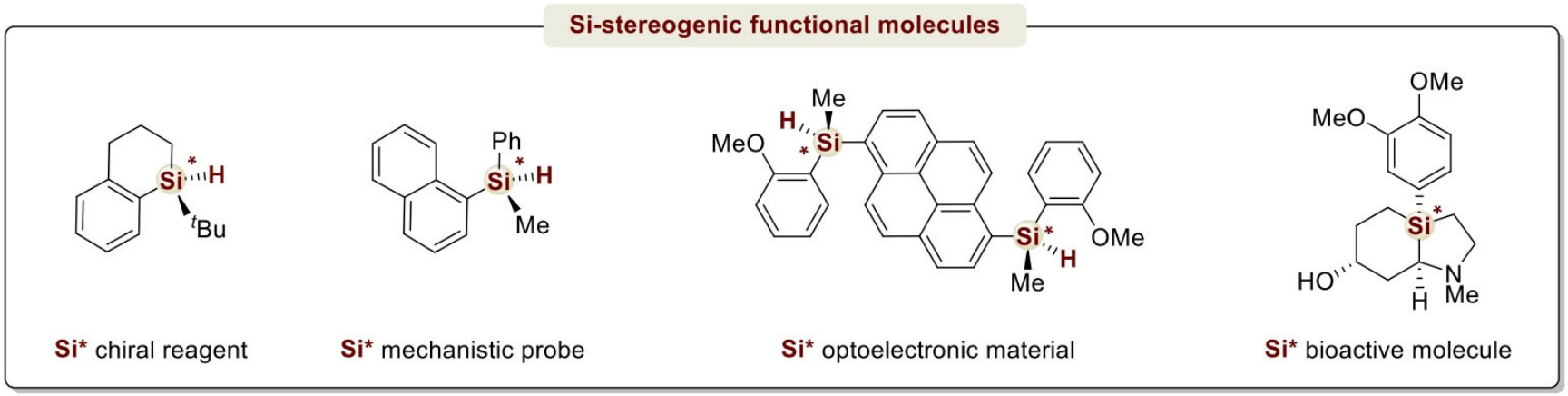
2010-2012 Postdoc — University of Wisconsin-Madison Advisor: Prof. Weiping Tang

2012-2015 Postdoc — University of California, Berkeley & Lawrence Berkeley National Laboratory Advisor: Prof. F. Dean Toste and Prof. Paul Alivisatos

研究方向：

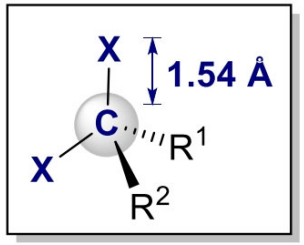
还原偶联反应　不对称催化　有机硅化学

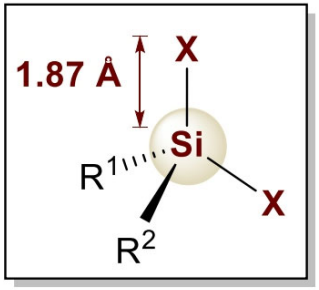
Part 1. 背景介绍



手性试剂　　机械探针　　光电材料　　生物活性分子

Part 1. 背景介绍

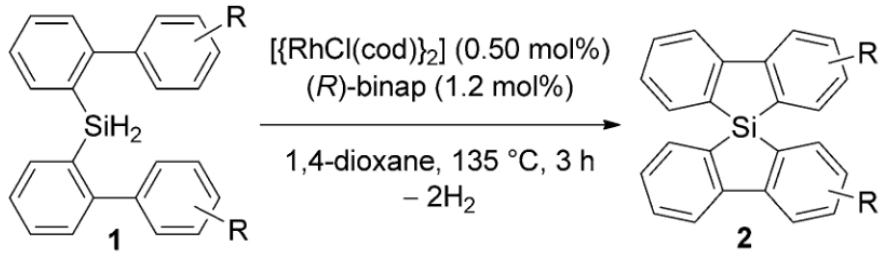




硅的原子半径较大（C 77 pm vs. Si 117 pm），其 pπ-pπ 作用弱，导致硅的多重键不稳定

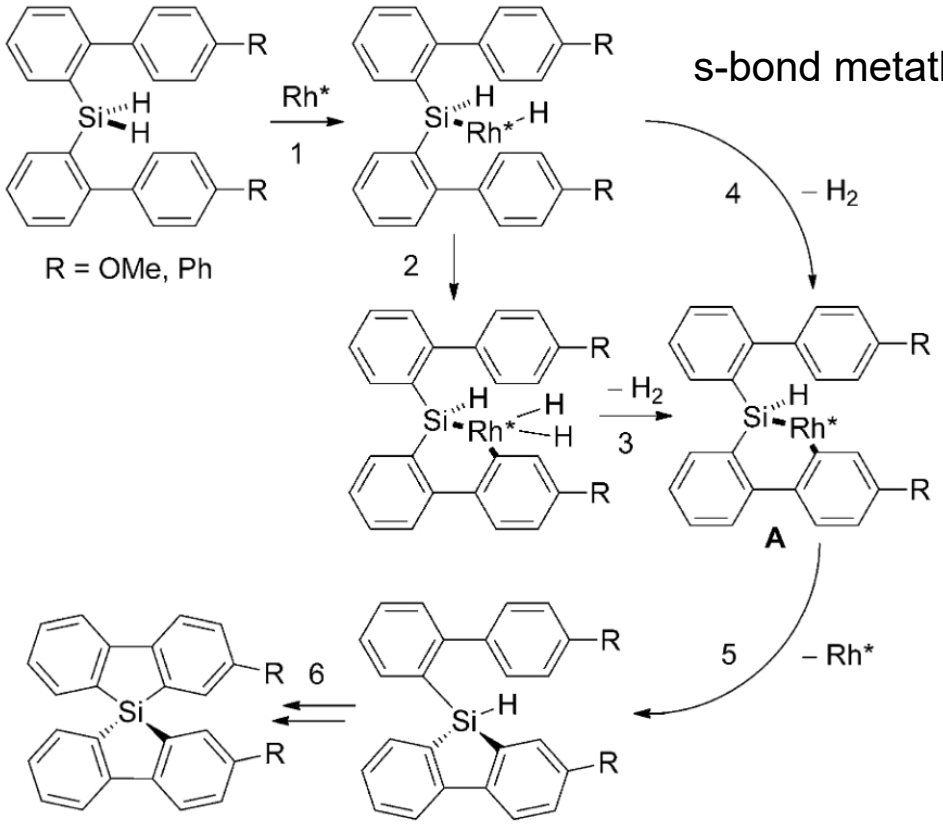
碳–硅键较长（C–Si bond vs. C–C bond: 1.87 Å vs. 1.54 Å），不容易形成紧凑的过渡态，导致其手性的识别和控制困难

Part 2.不对称脱氢偶联串联策略构筑四取代硅中心手性有机硅烷



Entry	R	Yield [%][a]	*ee* [%][b]	Major enantiomer	
1	4-MeO (**1b**)	95 (**2b**)	81	(+)	*S*
2	4-*t*Bu (**1c**)	94 (**2c**)	78	(+)	–[c]
3[d]	4-CF_3 (**1d**)	90 (**2d**)	75	(–)	–[c]
4	4-Ph (**1e**)	90 (**2e**)	70	(+)	*S*
5	2-MeO (**1f**)	73 (**2f**)	77	(–)	–[c]

适用范围小



s-bond metathesis

Kuninobu Y, Yamauchi K, Tamura N, Seiki T, Takai K. Rhodium-Catalyzed Asymmetric Synthesis of Spirosilabifluorene Derivatives. Angewandte Chemie International Edition. 2013;52(5):1520-2.

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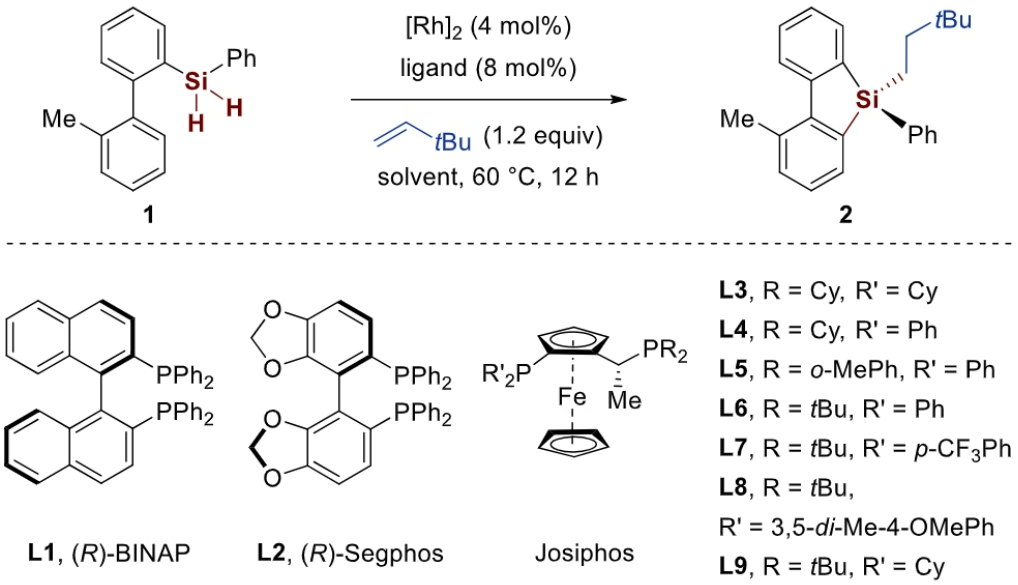
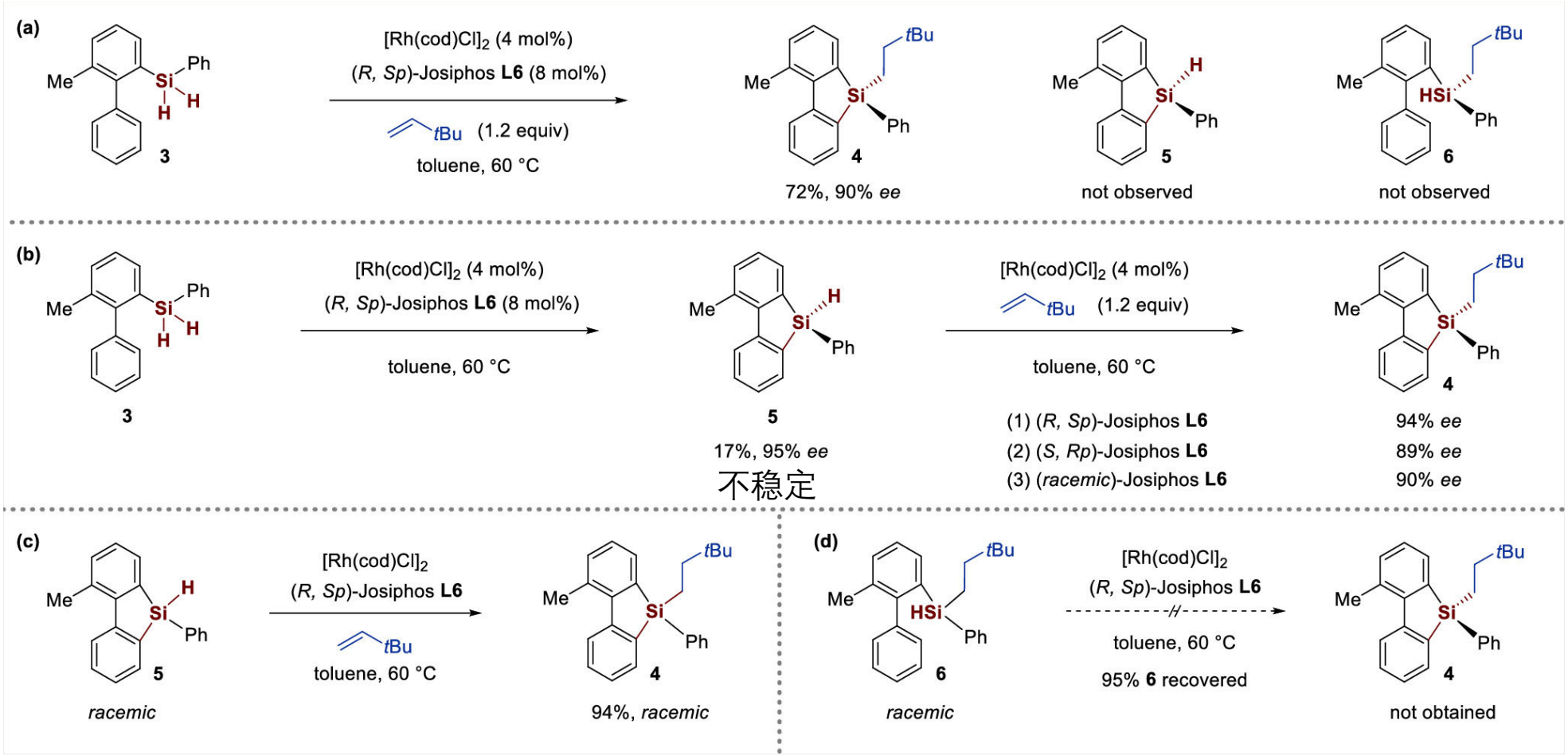


entry	[Rh]	ligand	solvent	yield (%)	*ee* (%)
1	$[Rh(cod)Cl]_2$	**L1**	toluene	10	75
2	$[Rh(cod)Cl]_2$	**L2**	toluene	8	60
3	$[Rh(cod)Cl]_2$	**L3**	toluene	49	91
4	$[Rh(cod)Cl]_2$	**L4**	toluene	13	70
5	$[Rh(cod)Cl]_2$	**L5**	toluene	3	32
6	$[Rh(cod)Cl]_2$	**L6**	toluene	77 (75)	91
7	$[Rh(cod)Cl]_2$	**L7**	toluene	62	82
8	$[Rh(cod)Cl]_2$	**L8**	toluene	68	70
9	$[Rh(cod)Cl]_2$	**L9**	toluene	26	77
10	$[Rh(cod)OH]_2$	**L6**	toluene	44	55
11	$[Rh(nbd)Cl]_2$	**L6**	toluene	18	91
12	$[Rh(CO)_2Cl]_2$	**L6**	toluene	57	70
13	$[Rh(cod)Cl]_2$	**L6**	THF	70	86
14	$[Rh(cod)Cl]_2$	**L6**	DCE	47	87
15	$[Rh(cod)Cl]_2$	**L6**	Et_2O	73	85

Mu D, Yuan W, Chen S, Wang N, Yang B, You L, et al. Streamlined Construction of Silicon-Stereogenic Silanes by Tandem Enantioselective C–H Silylation/Alkene Hydrosilylation. Journal of the American Chemical Society. 2020;142(31):13459-68.

Part 2.不对称脱氢偶联串联策略构筑四取代硅中心手性有机硅烷



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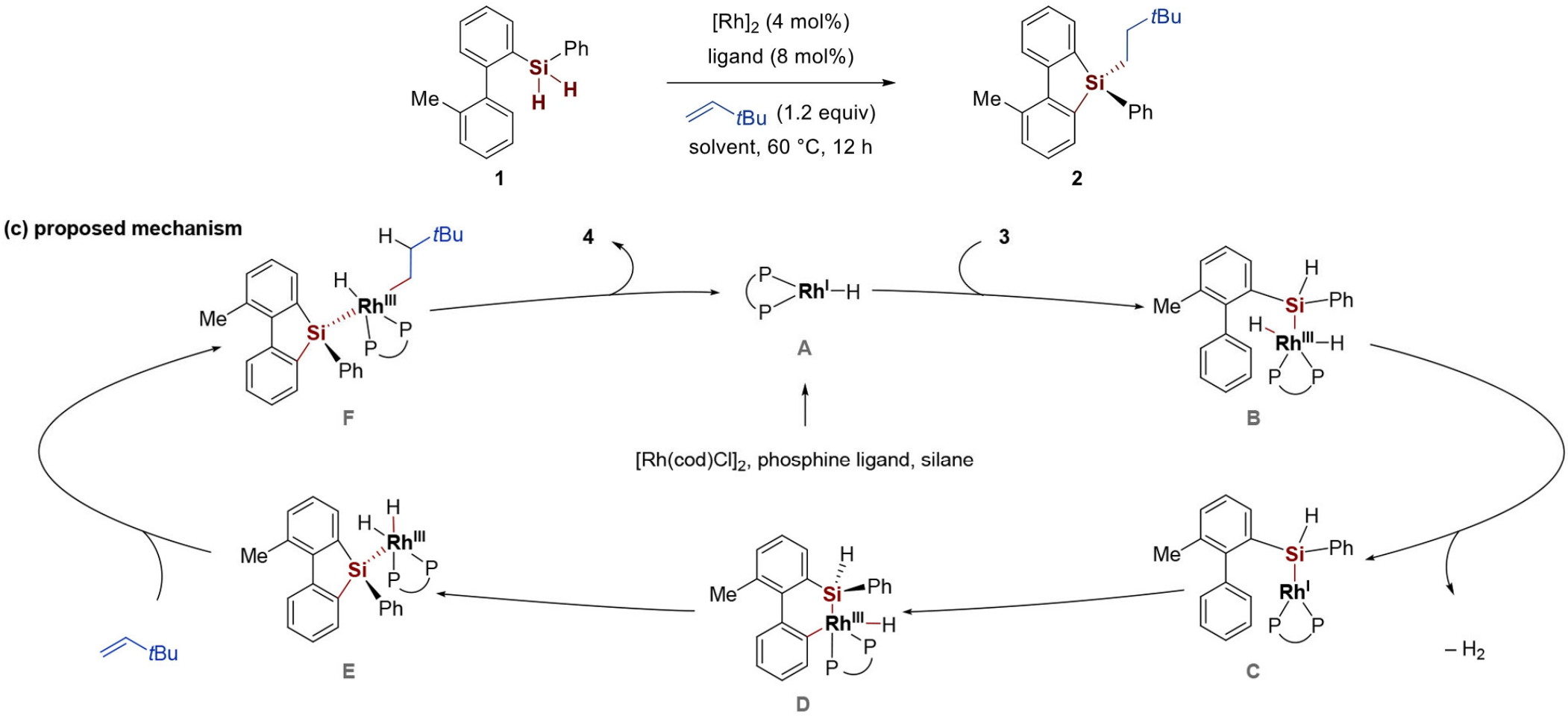

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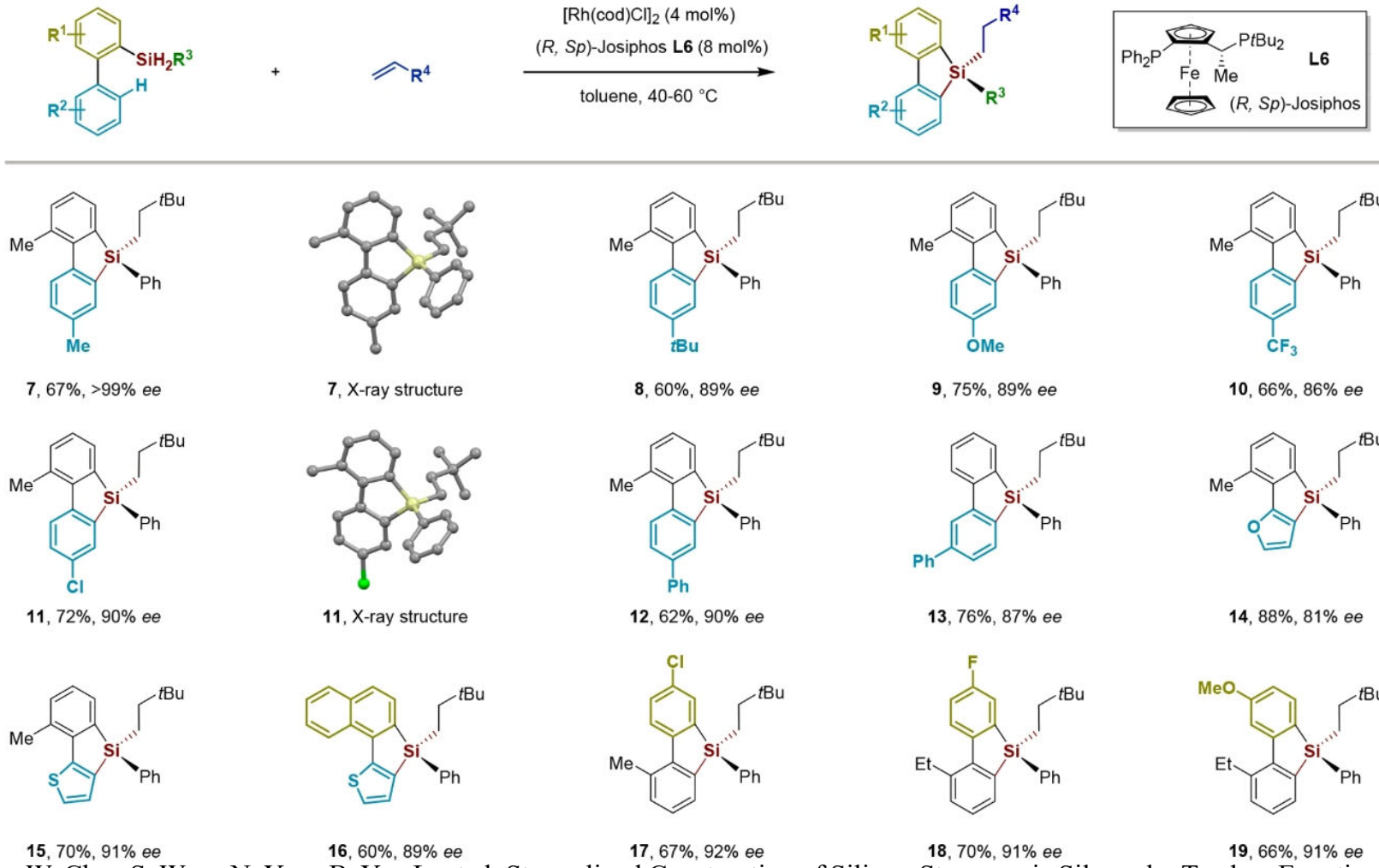

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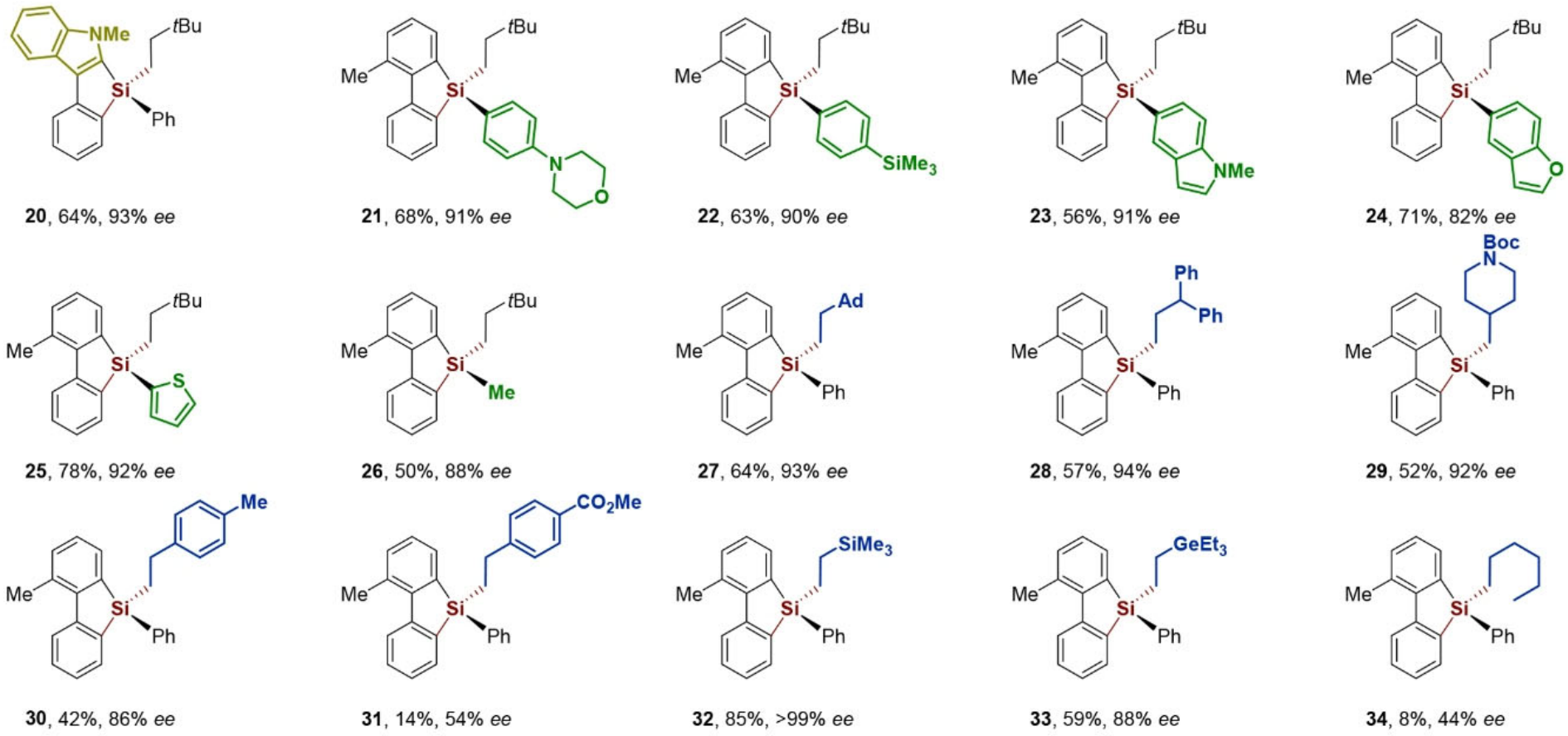

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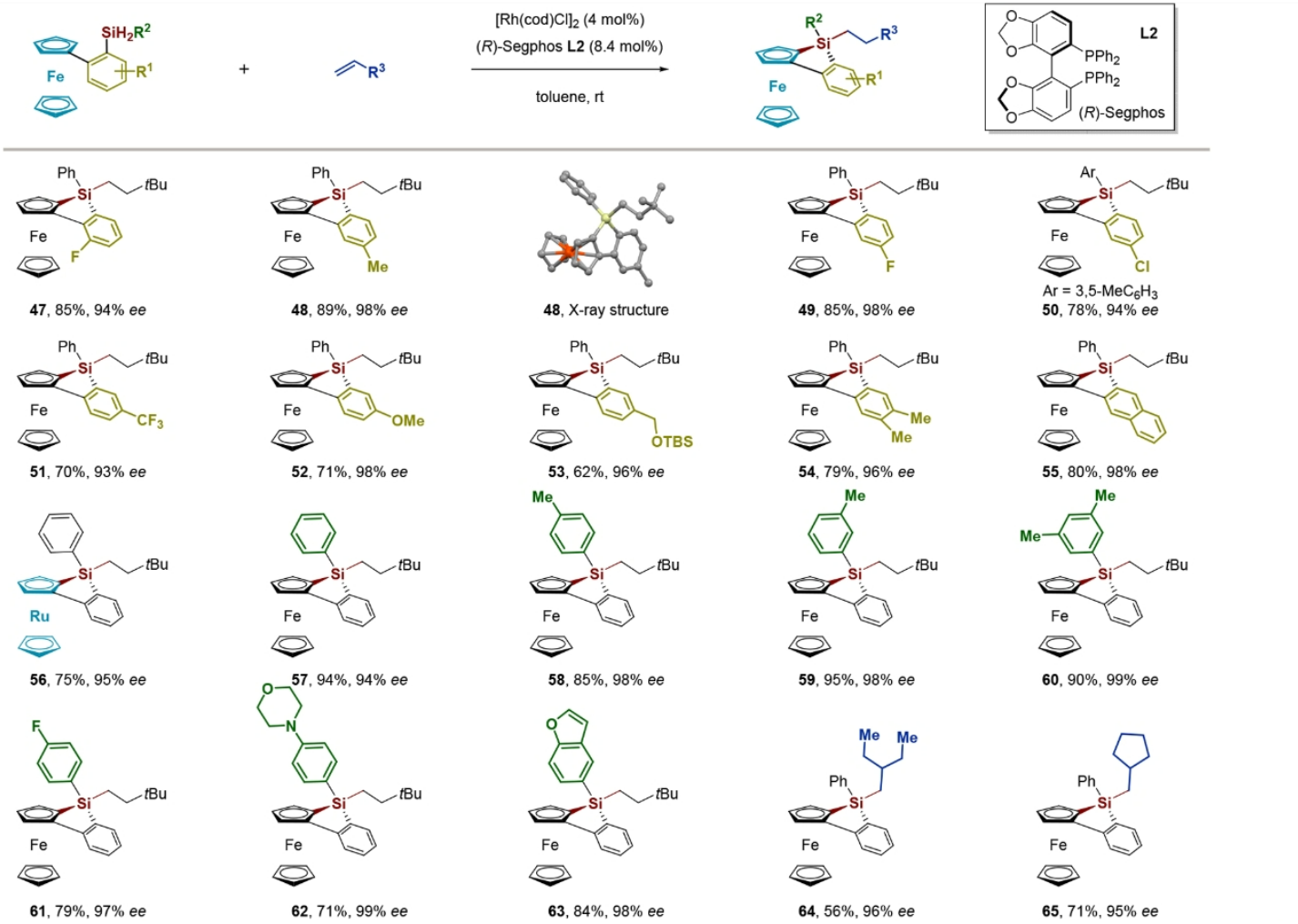

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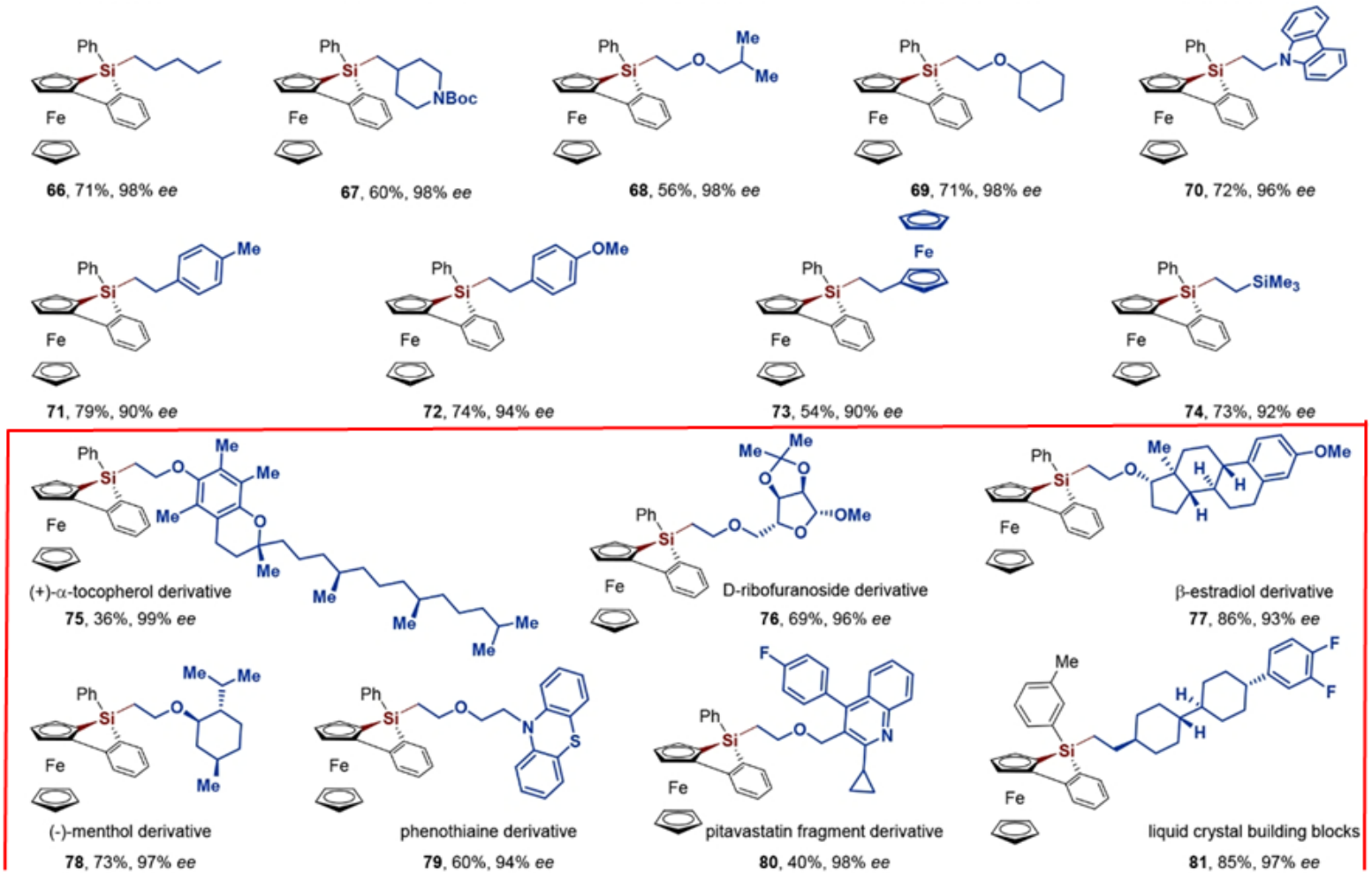

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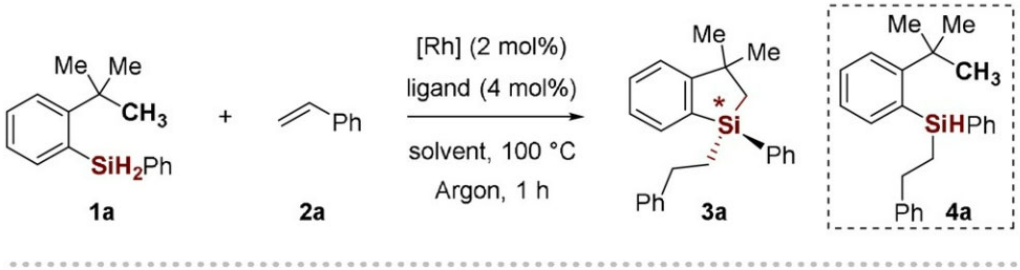
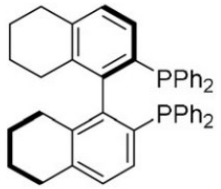
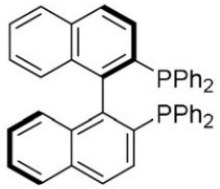
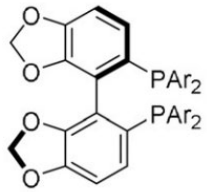




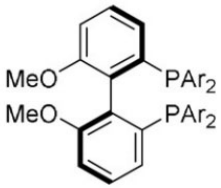
L1, (*R*)-H_8-BINAP



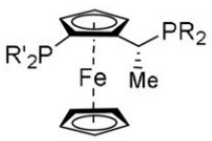
L2, (*R*)-BINAP



L3, Ar = Ph
L4, Ar = 3,5-*di*-Me-4-OMePh



L5, Ar = 3,5-*di*-Me-Ph



Josiphos

L6, R = Cy, R' = Ph
L7, R = *t*Bu, R' = Ph
L8, R = *t*Bu, R' = *p*-CF_3Ph
L9, R = *t*Bu, R' = 3,5-*di*-Me-4-OMePh
L10, R = *o*-MePh, R' = *t*Bu
L11, R = 3,5-*di*-MePh, R' = Ph

Entry	[Rh]	Ligand	Solvent	Yield [%]	*ee* [%]
1	$[Rh(cod)Cl]_2$	**L1**	toluene	67	25
2	$[Rh(cod)Cl]_2$	**L2**	toluene	61	25
3	$[Rh(cod)Cl]_2$	**L3**	toluene	66	33
4	$[Rh(cod)Cl]_2$	**L4**	toluene	69	3
5	$[Rh(cod)Cl]_2$	**L5**	toluene	72	30
6	$[Rh(cod)Cl]_2$	**L6**	toluene	54	35
7	$[Rh(cod)Cl]_2$	**L7**	toluene	77	85
8	$[Rh(cod)Cl]_2$	**L8**	toluene	78	84
9	$[Rh(cod)Cl]_2$	**L9**	toluene	76	83
10	$[Rh(cod)Cl]_2$	**L10**	toluene	17	18
11	$[Rh(cod)Cl]_2$	**L11**	toluene	71	1
12	$[Rh(cod)Cl]_2$	**L7**	dioxane	71	83
13	$[Rh(cod)Cl]_2$	**L7**	DCE	78 (75)	92
14	$[Rh(cod)Cl]_2$	**L7**	*n*-hexane	75	79
15	$[Rh(cod)OH]_2$	**L7**	DCE	67	86
16	$[Rh(nbd)Cl]_2$	**L7**	DCE	72	89

Yang B, Yang W, Guo Y, You L, He C. Enantioselective Silylation of Aliphatic C−H Bonds for the Synthesis of Silicon-Stereogenic Dihydrobenzosiloles. Angewandte Chemie International Edition. 2020;59(49):22217-22.

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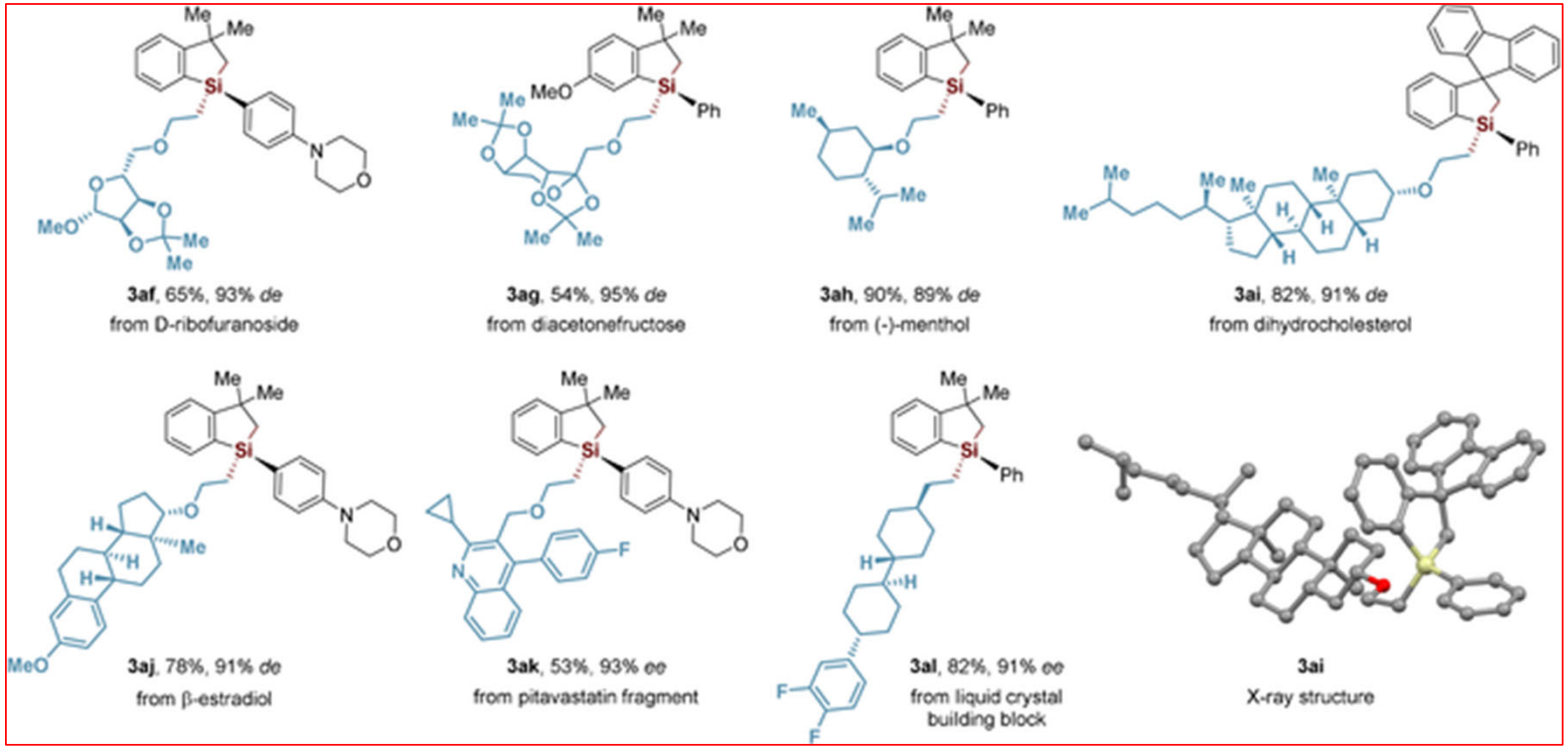

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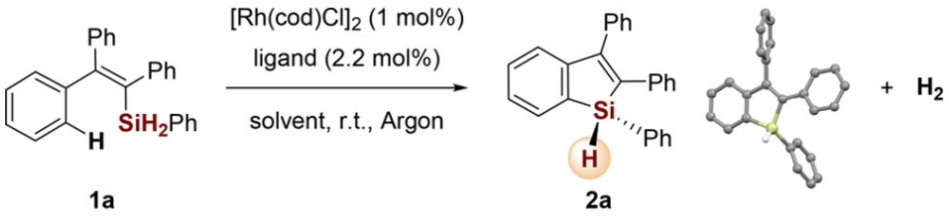

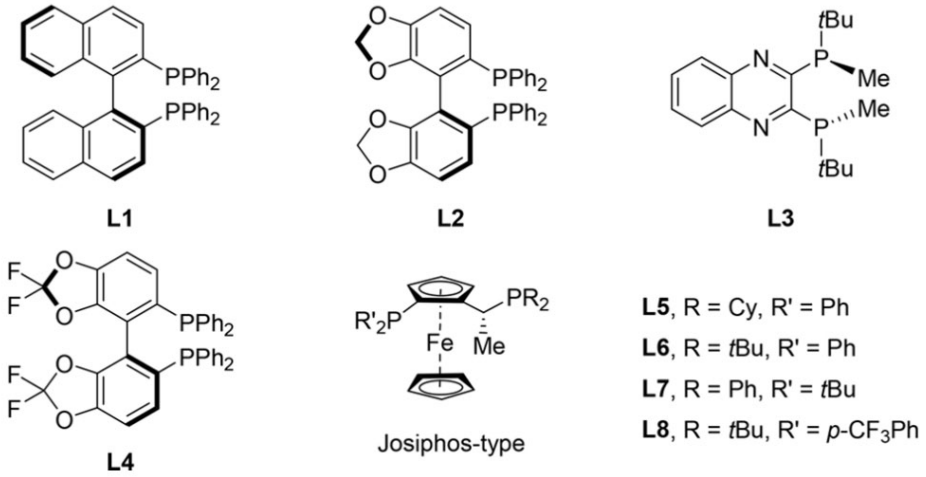

降低催化剂浓度，稳定单H硅烷

entry	ligand	solvent	yield of **2a** (%)	ee of **2a** (%)
1	**L1**	DCE	74	38
2	**L2**	DCE	67	82
3	**L3**	DCE	16	−44
4	**L4**	DCE	81 (71)	87
5	**L5**	DCE	5	−49
6	**L6**	DCE	22	4
7	**L7**	DCE	23	−48
8	**L8**	DCE	47	53
9	**L4**	$CHCl_3$	25	99
10	**L4**	THF	(60)	90
11	**L4**	THF/$CHCl_3$ (19/1)	51	97
12	**L2**	$CHCl_3$	14	99
13	**L2**	1,4-dioxane	83	85
14	**L2**	1,4-dioxane/$CHCl_3$ (19/1)	(60)	94

Yuan W, You L, Lin W, Ke J, Li Y, He C. Asymmetric Synthesis of Silicon-Stereogenic Monohydrosilanes by Dehydrogenative C–H Silylation. Organic Letters. 2021;23(4):1367-72.

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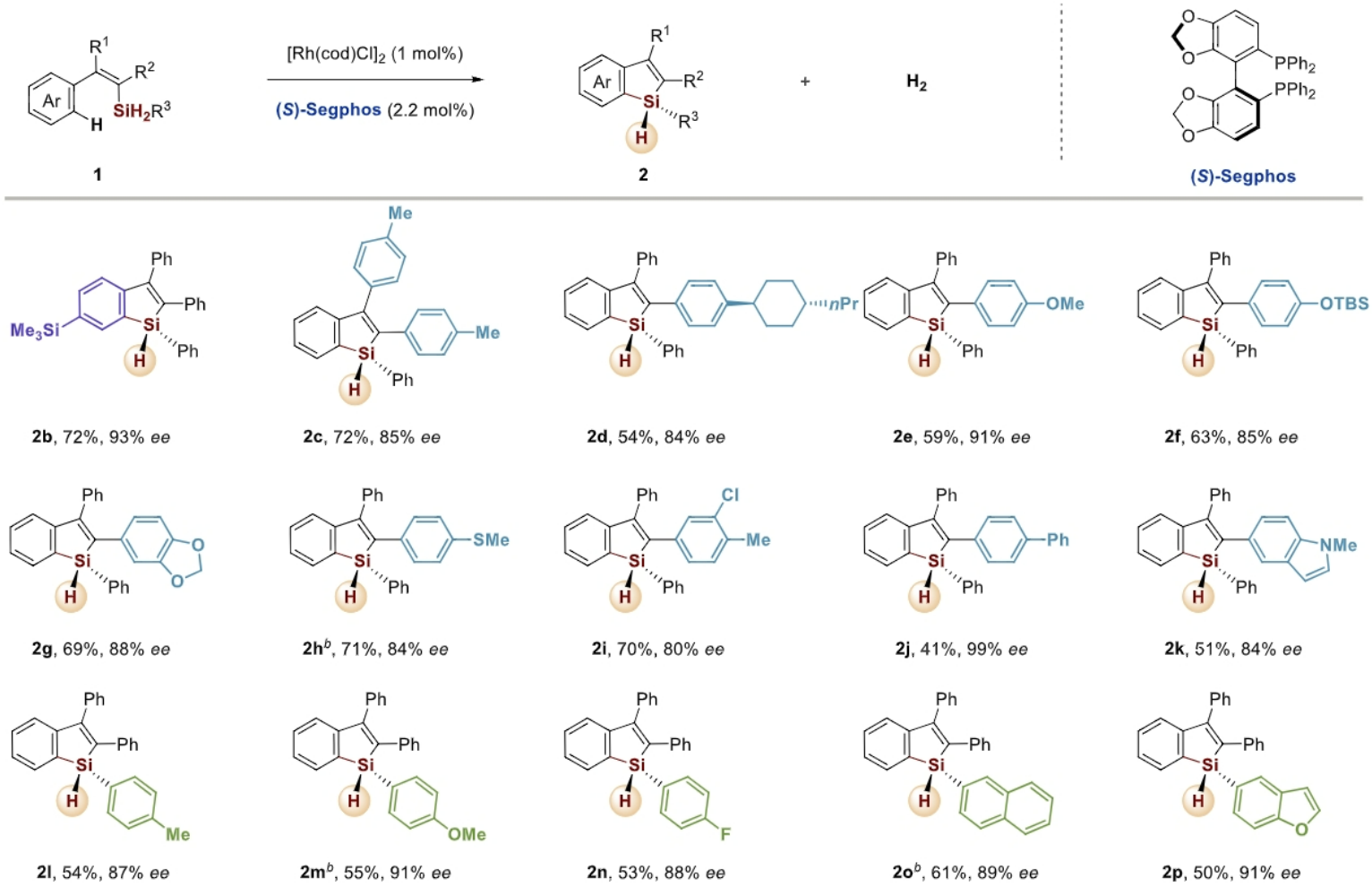

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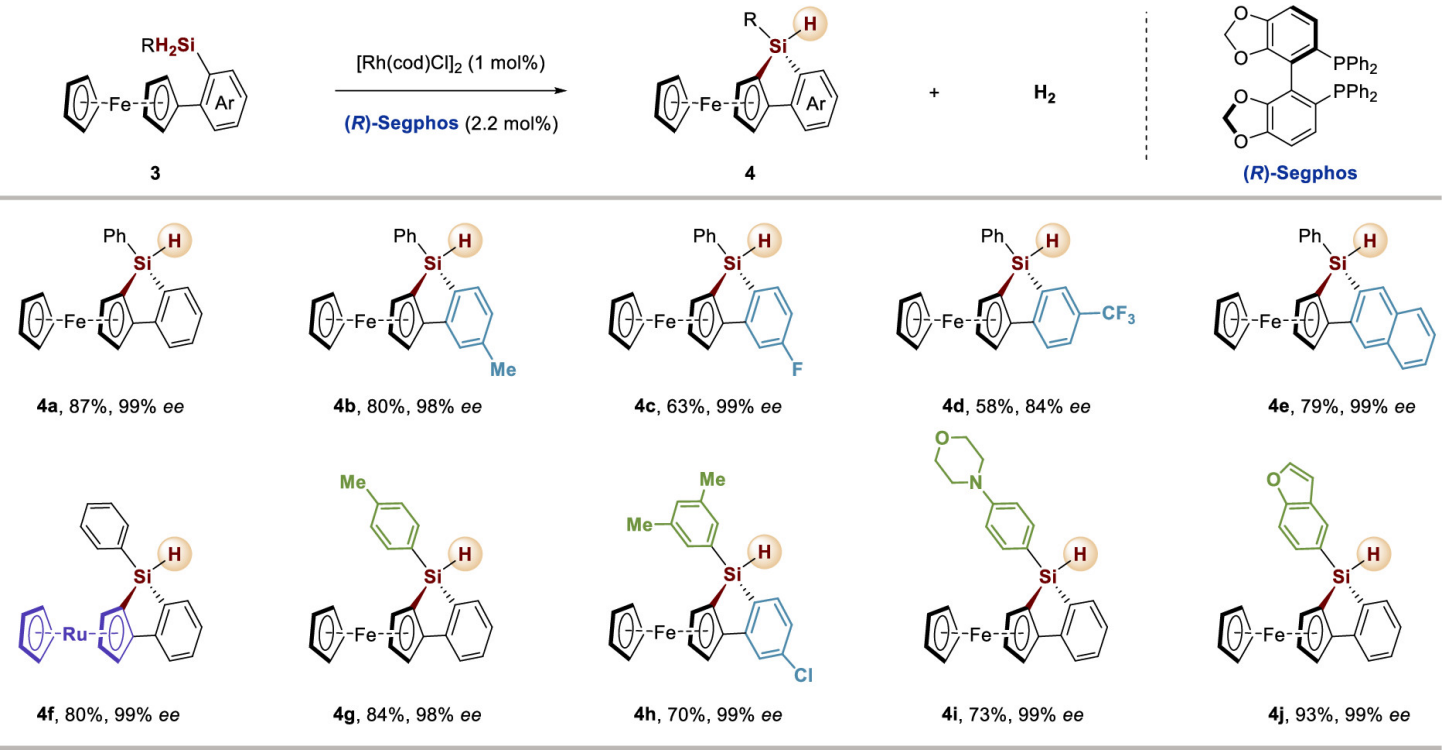

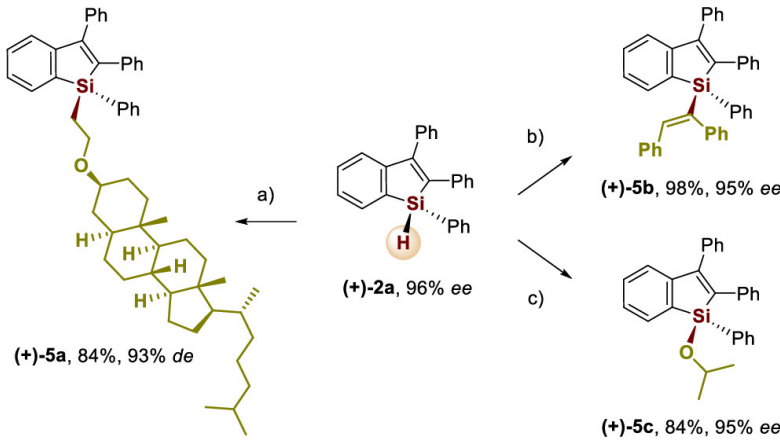

进一步转化

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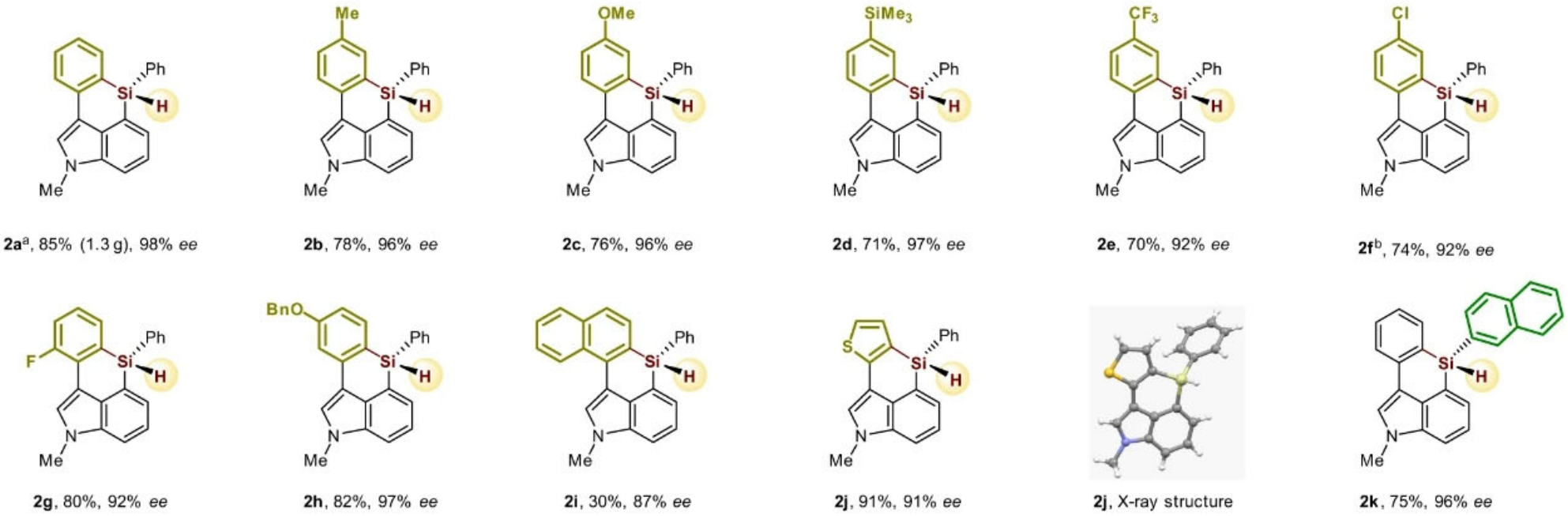

Chen S, Mu D, Mai P-L, Ke J, Li Y, He C. Enantioselective construction of six- and seven-membered triorgano-substituted silicon-stereogenic heterocycles. Nature Communications. 2021;12(1).

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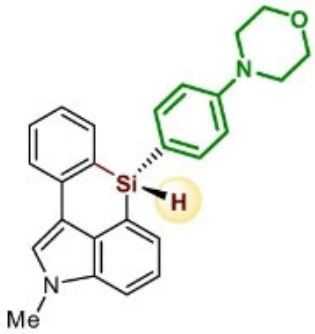
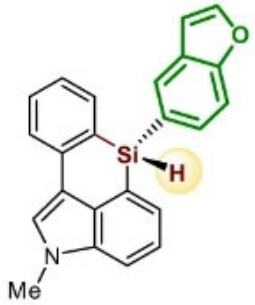


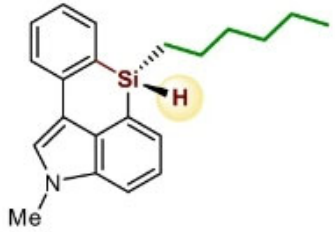
2l, 78%, 93% *ee*

2m, 24%, 90% *ee*

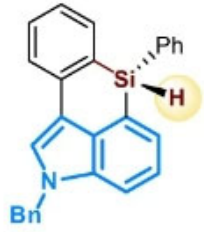


2n, 50%, 94% *ee*

2o, 62%, 90% *ee*

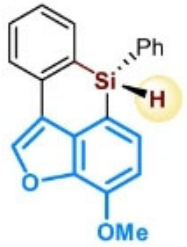


2p, 80%, 98% *ee*



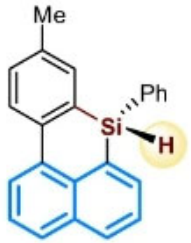
2q, 74%, 91% *ee*

2r, 72%, 95% *ee*

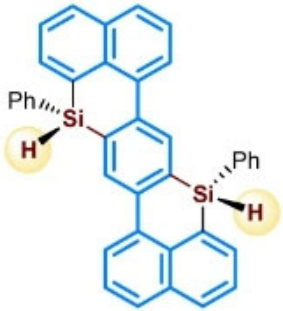


2s, 60%, 95% *ee*

R = OMe, **2t**[c], 53%, 94% *ee*
R = OTBS, **2u**, 61%, 95% *ee*



2v[d], 76%, 97% *ee*



2w[e], 42%, 99% *ee*

纯六元双硅立体杂环，硅桥梯形π共轭体系

2x[f], 45%, 58% *ee*

具有独特光学和电子性质的硅基立体苯胺(硅桥二苯胺)衍生物

Chen S, Mu D, Mai P-L, Ke J, Li Y, He C. Enantioselective construction of six- and seven-membered triorgano-substituted silicon-stereogenic heterocycles. Nature Communications. 2021;12(1).

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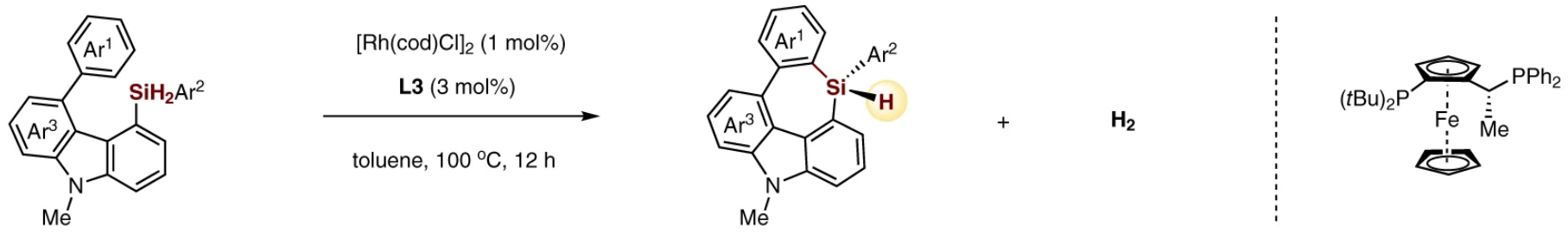
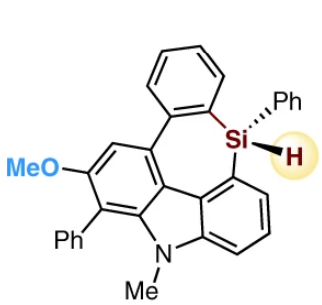
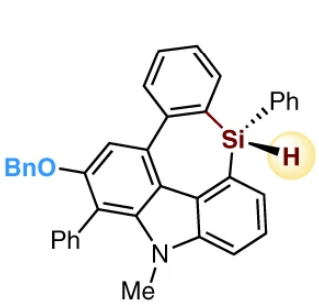
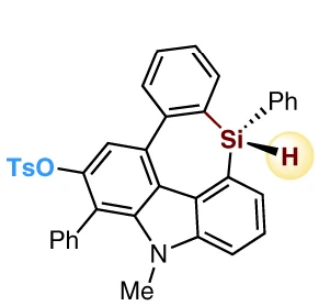




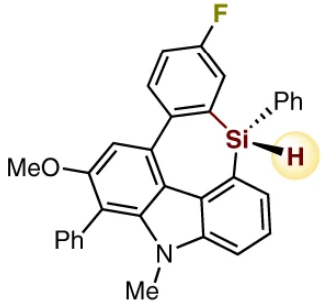
4a, 78%, 90% *ee*



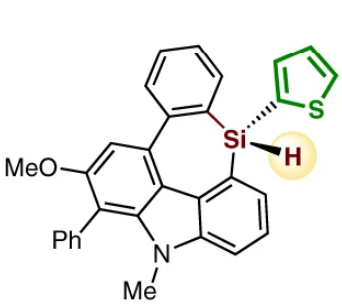
4b, 55%, 85% *ee*



4c, 68%, 90% *ee*



4d, 80%, 91% *ee*



4e, 40%, 86% *ee*

构筑七元硅环

Chen S, Mu D, Mai P-L, Ke J, Li Y, He C. Enantioselective construction of six- and seven-membered triorgano-substituted silicon-stereogenic heterocycles. Nature Communications. 2021;12(1).

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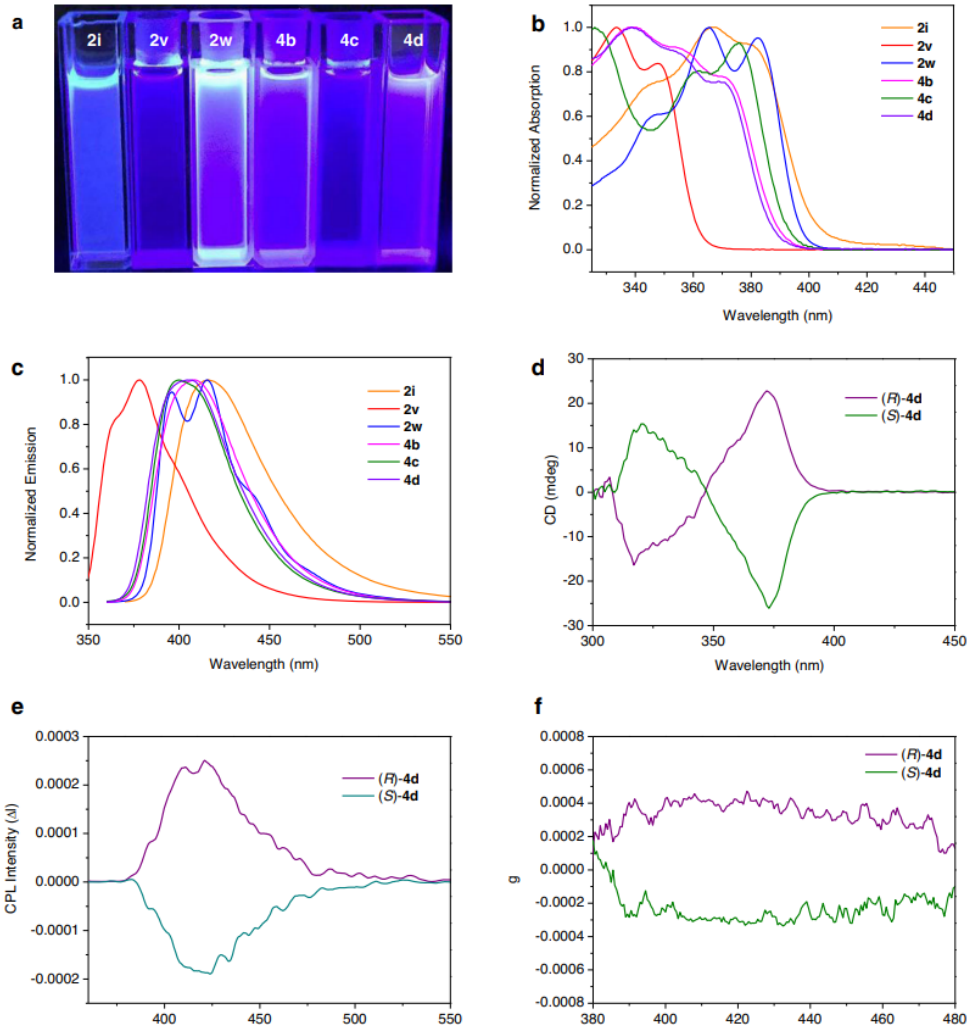

可能具有优秀的光学性能

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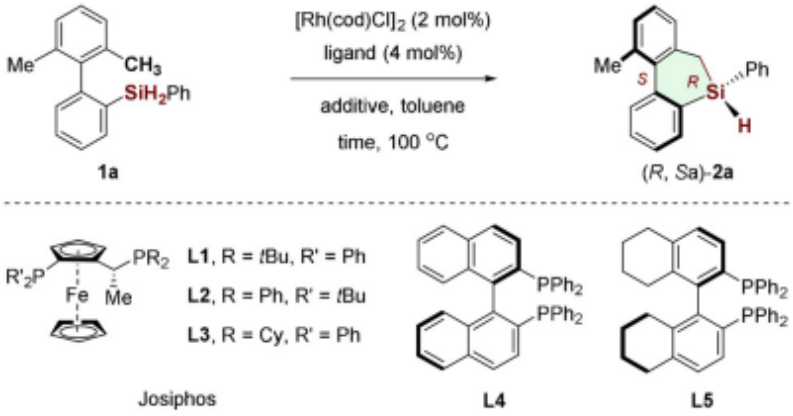
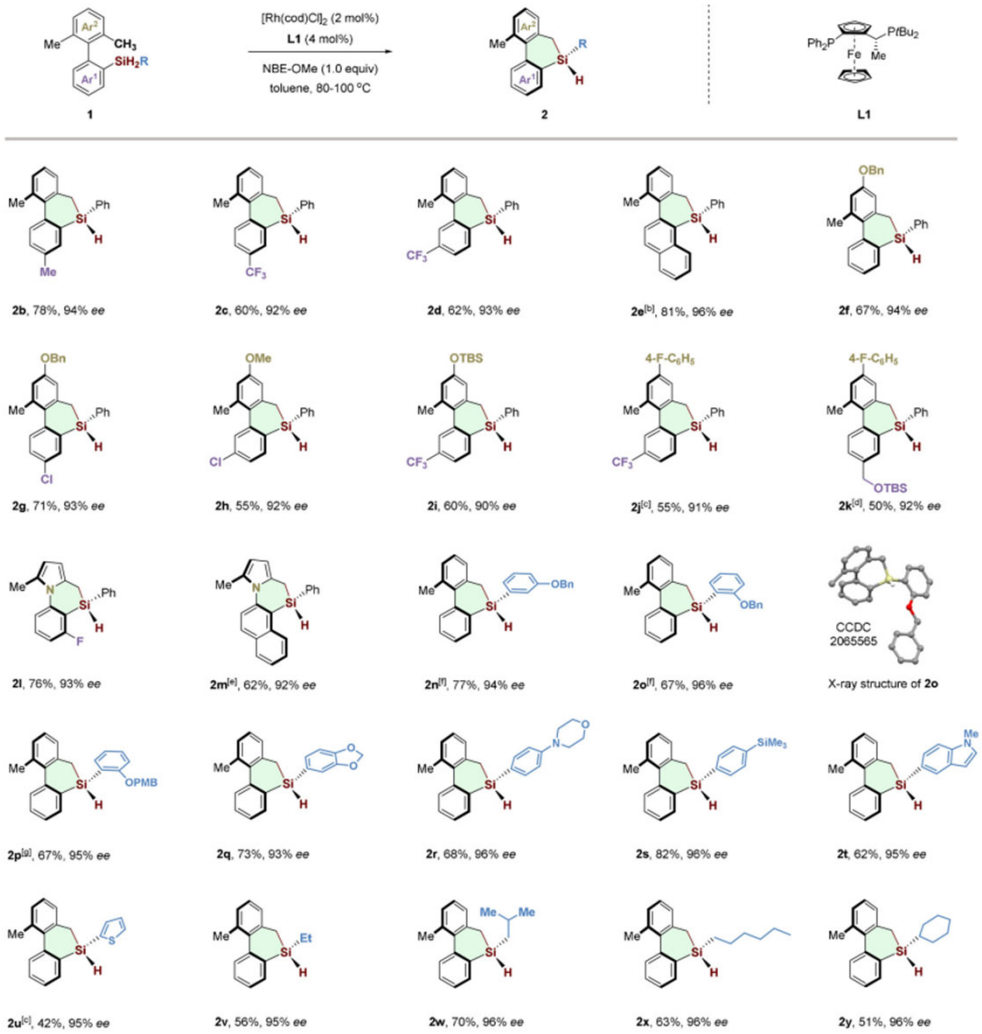


Entry	Ligand	Additive	t	Yield [%]	ee [%]
1	L1	–	15 min	21	95
2	L1	–	5 h	76	0
3	L1	NBE	15 min	84	94
4	L2	NBE	15 min	35	94
5	L3	NBE	15 min	12	60
6	L4	NBE	15 min	28	30
7	L5	NBE	15 min	trace	–
8	L1	NBE-OMe	15 min	79(70)	96

延长时间，ee值大幅下降
加入NBE作为氢受体加快反应速率



Yuan W, Zhu X, Xu Y, He C. Synthesis of Si-Stereogenic Silanols by Catalytic Asymmetric Hydrolytic Oxidation. Angewandte Chemie International Edition. 2022;61(31).

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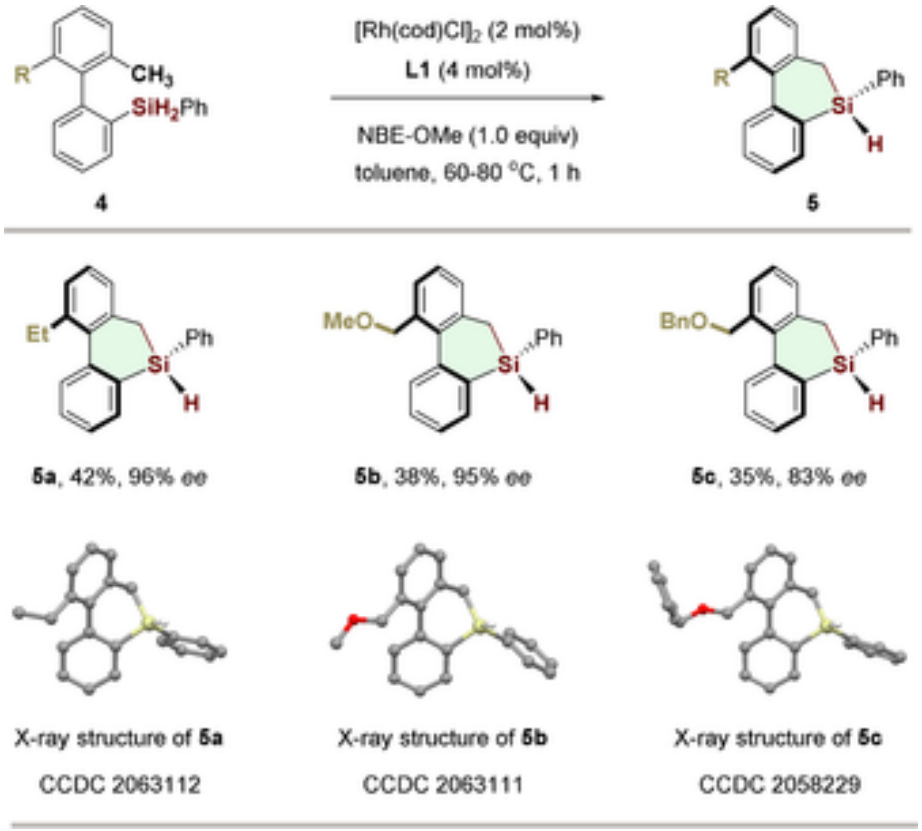

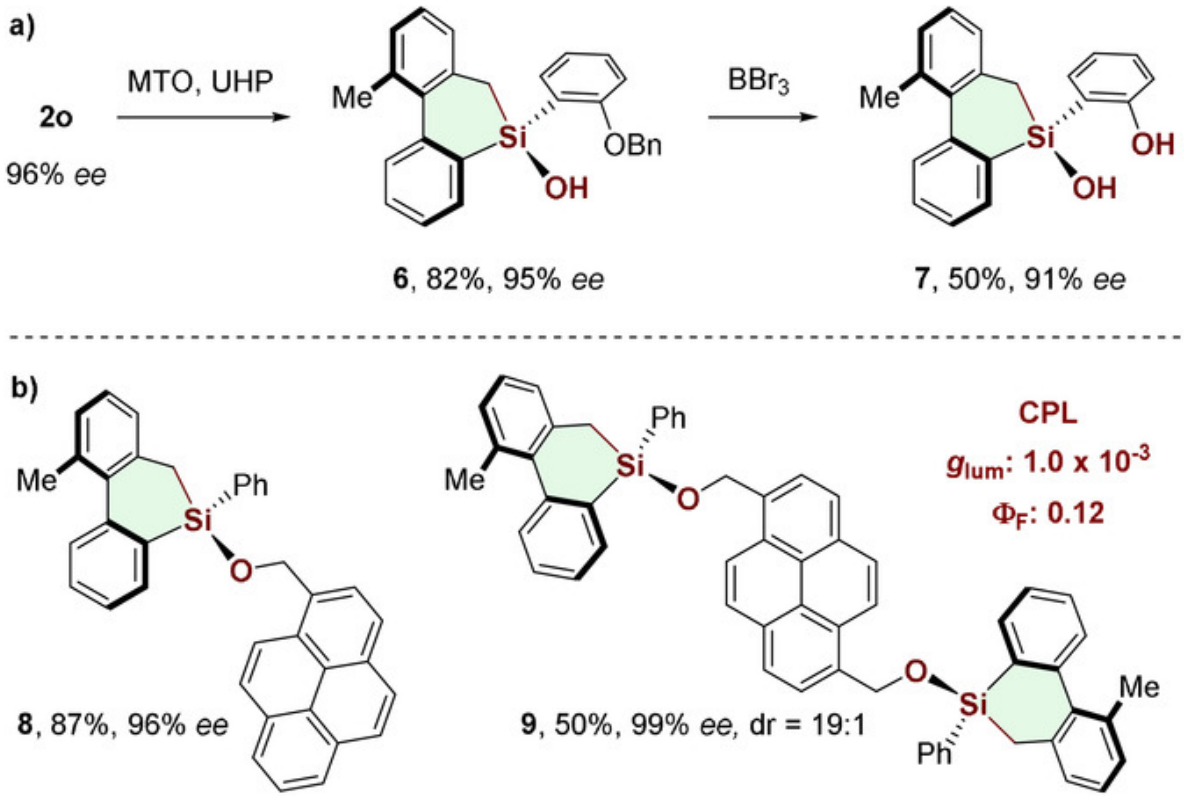

后续进一步转化

Yuan W, Zhu X, Xu Y, He C. Synthesis of Si-Stereogenic Silanols by Catalytic Asymmetric Hydrolytic Oxidation. Angewandte Chemie International Edition. 2022;61(31).

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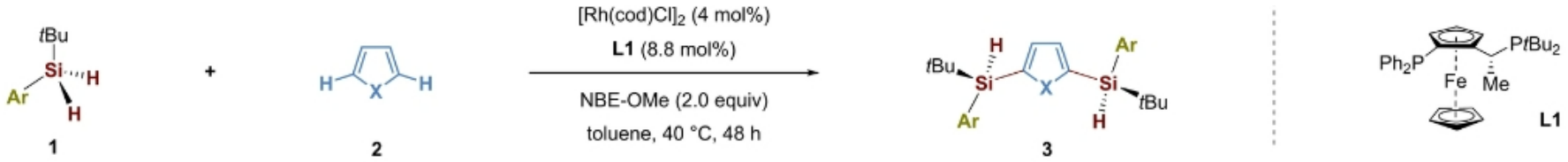
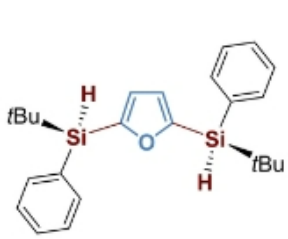
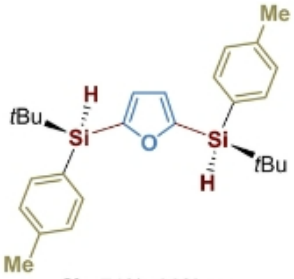
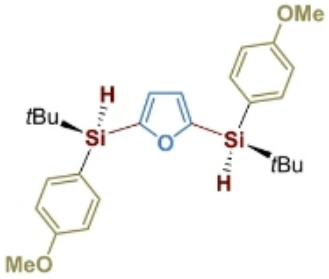




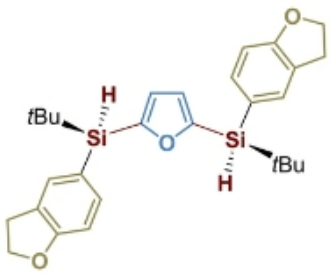
3a,76%, 99% *ee*



3b, 71%, 98% *ee*

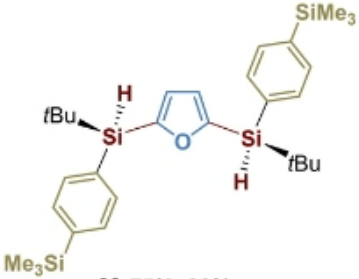


3c, 70%, 98% *ee*



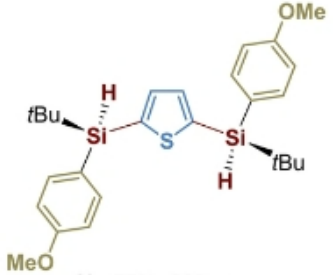
3d, 68%, 98% *ee*

3e, 74%, 97% *ee*



3f, 75%, 98% *ee*

3g, 71%, 99% *ee*



3h, 57%, 99% *ee*

Chen S, Zhu J, Ke J, Li Y, He C. Enantioselective Intermolecular C−H Silylation of Heteroarenes for the Synthesis of Acyclic Si-Stereogenic Silanes. Angewandte Chemie International Edition. 2022;61(21).

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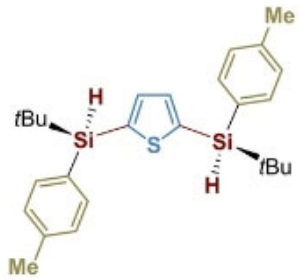
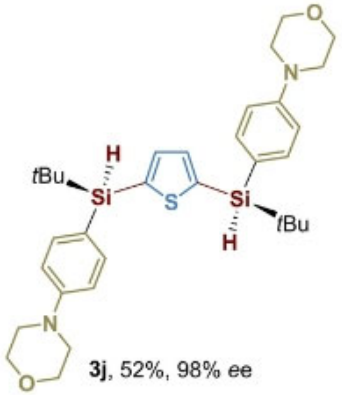
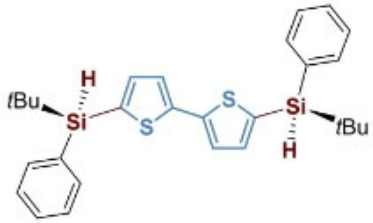


3i, 57%, 96% *ee*

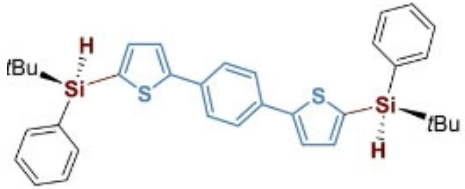


3j, 52%, 98% *ee*

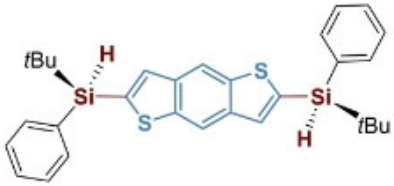
3k, 63%, 95% *ee*



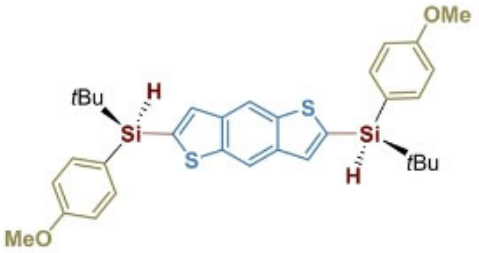
3l, 23%, 95% *ee*



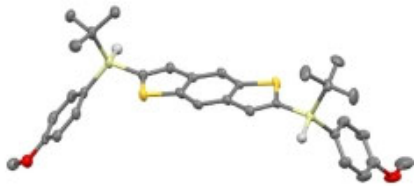
3m, 45%, 97% *ee*



3n, 56%, 97% *ee*



3o, 50%, 97% *ee*



CCDC 2092185

3o, X-ray structure

Chen S, Zhu J, Ke J, Li Y, He C. Enantioselective Intermolecular C−H Silylation of Heteroarenes for the Synthesis of Acyclic Si-Stereogenic Silanes. Angewandte Chemie International Edition. 2022;61(21).

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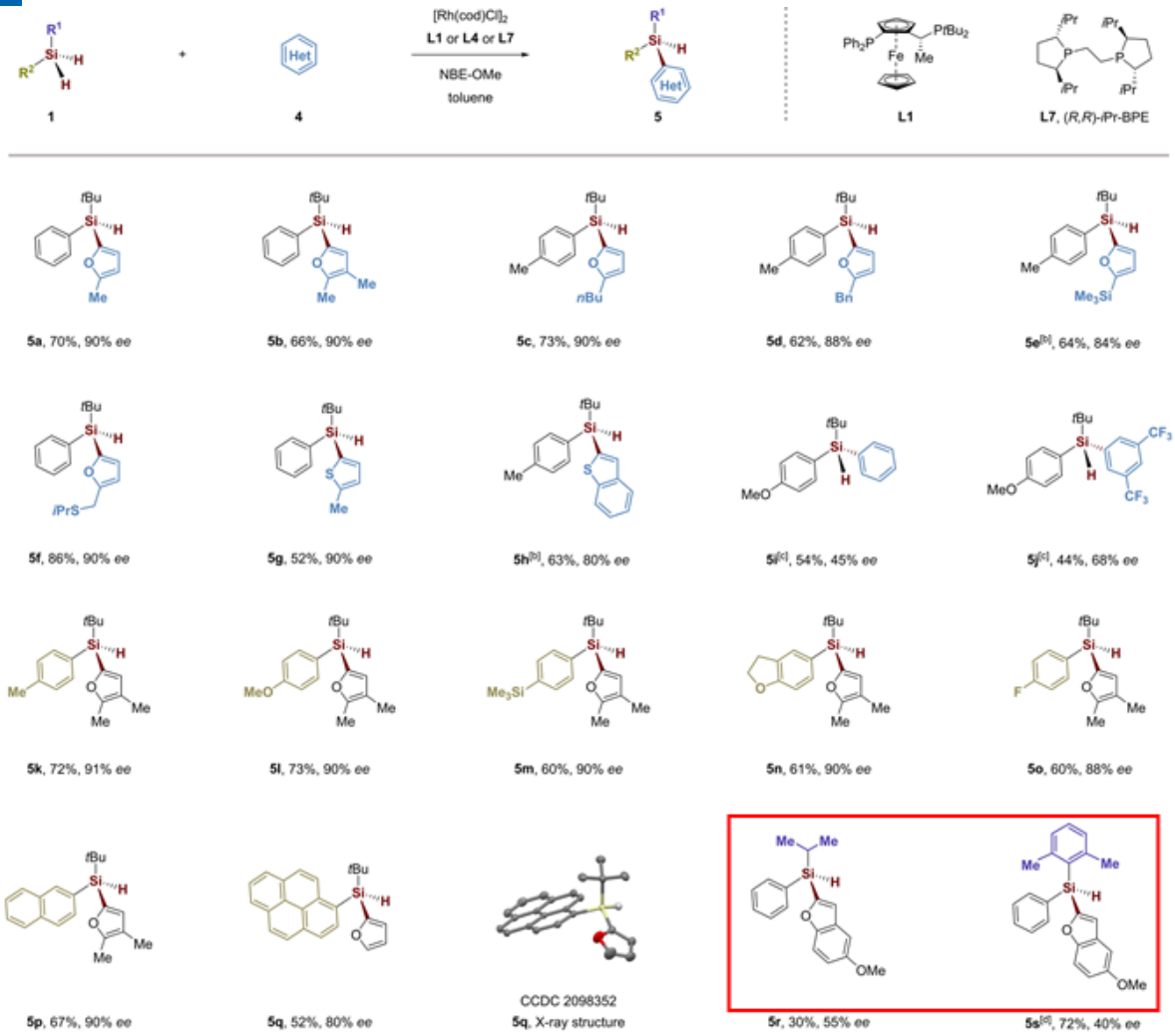

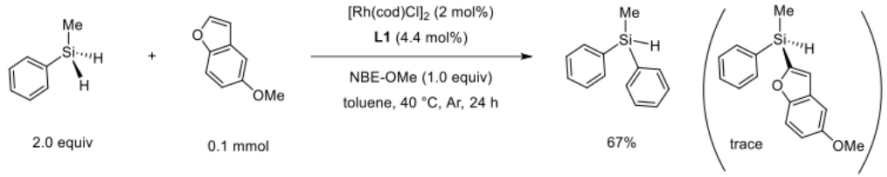

二氢硅烷重排

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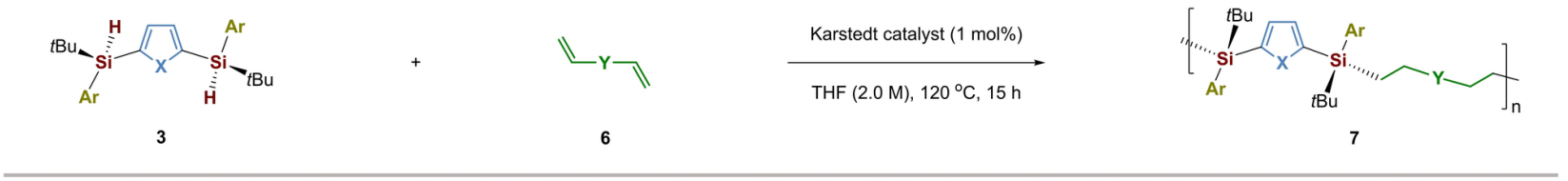


3 + 6 → 7

7a

M_n = 4.7 kg mol^{-1}, M_w = 9.0 kg mol^{-1}, PDI = 1.9
75% yield

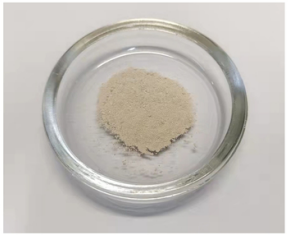
7b

M_n = 5.5 kg mol^{-1}, M_w = 12.1 kg mol^{-1}, PDI = 2.2
88% yield

7c

M_n = 3.7 kg mol^{-1}, M_w = 5.5 kg mol^{-1}, PDI = 1.5
62% yield

形成多聚体



7a

7d

M_n = 5.9 kg mol^{-1}, M_w = 14.6 kg mol^{-1}, PDI = 2.5
86% yield

7e

M_n = 6.2 kg mol^{-1}, M_w = 16.2 kg mol^{-1}, PDI = 2.6
91% yield

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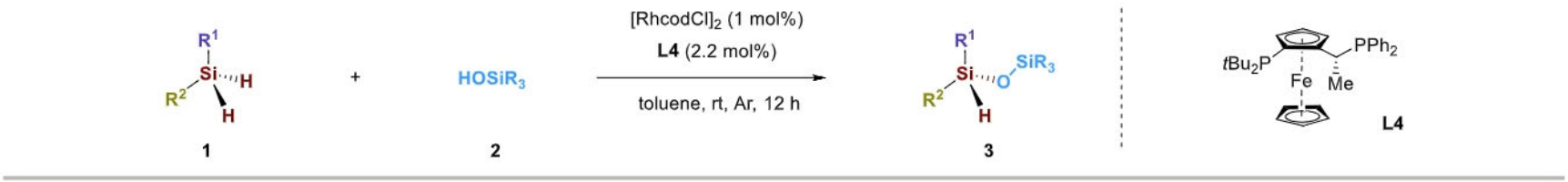

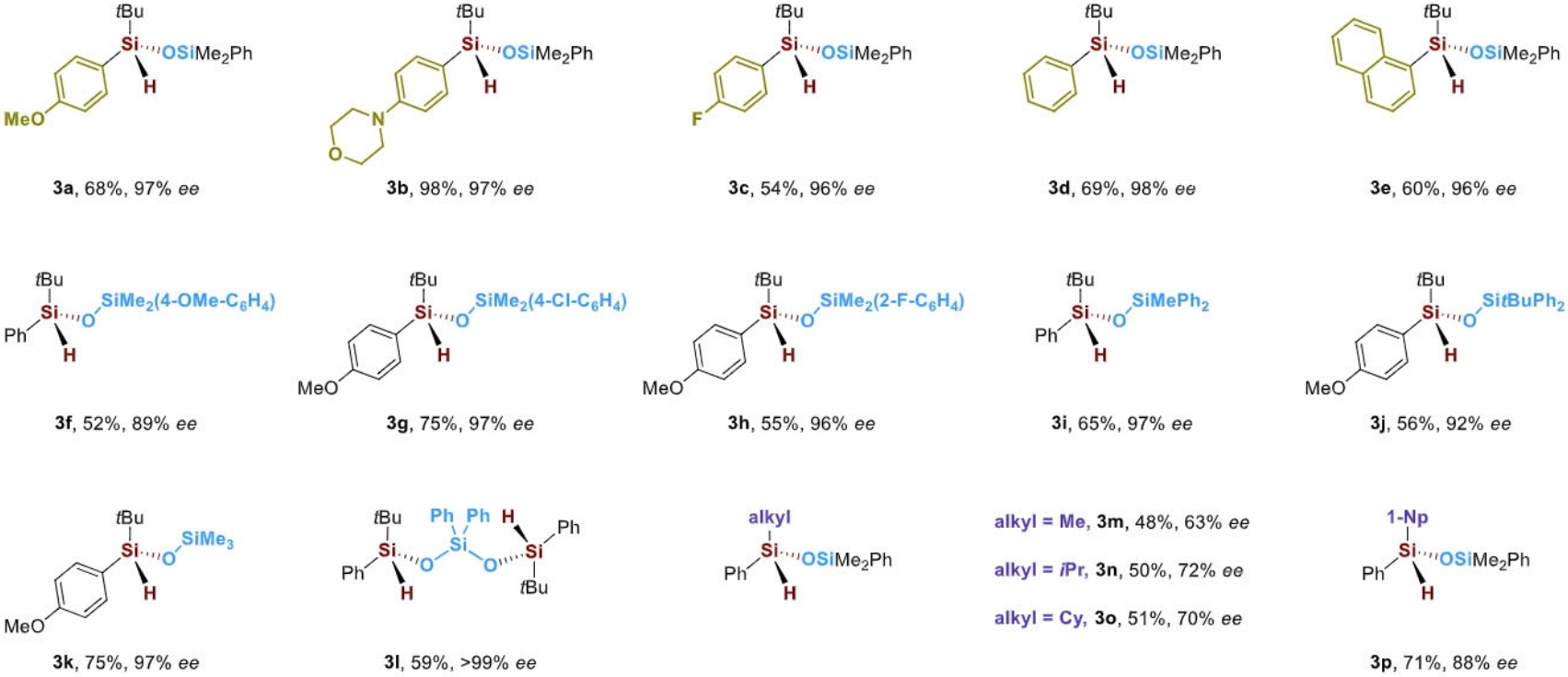

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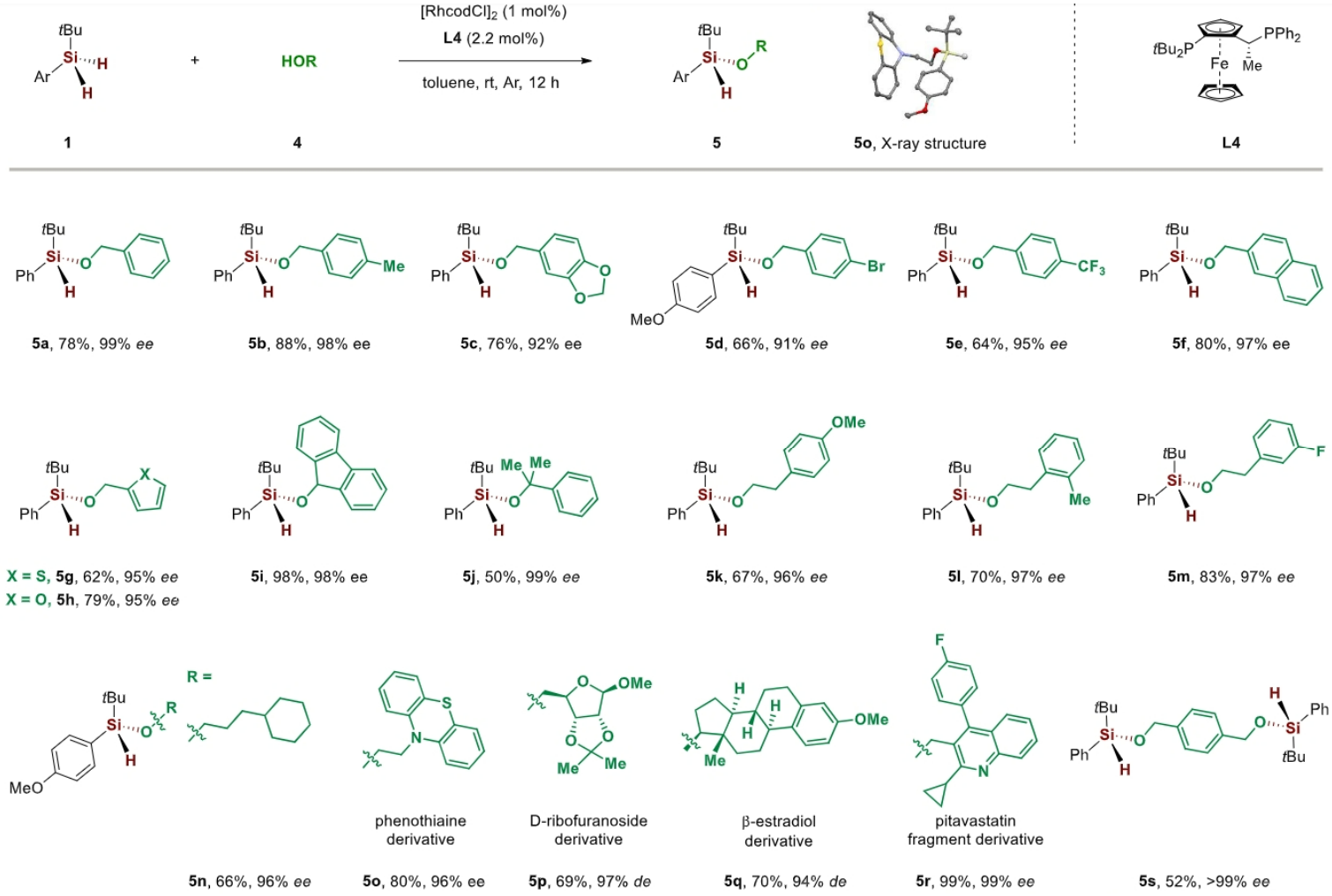

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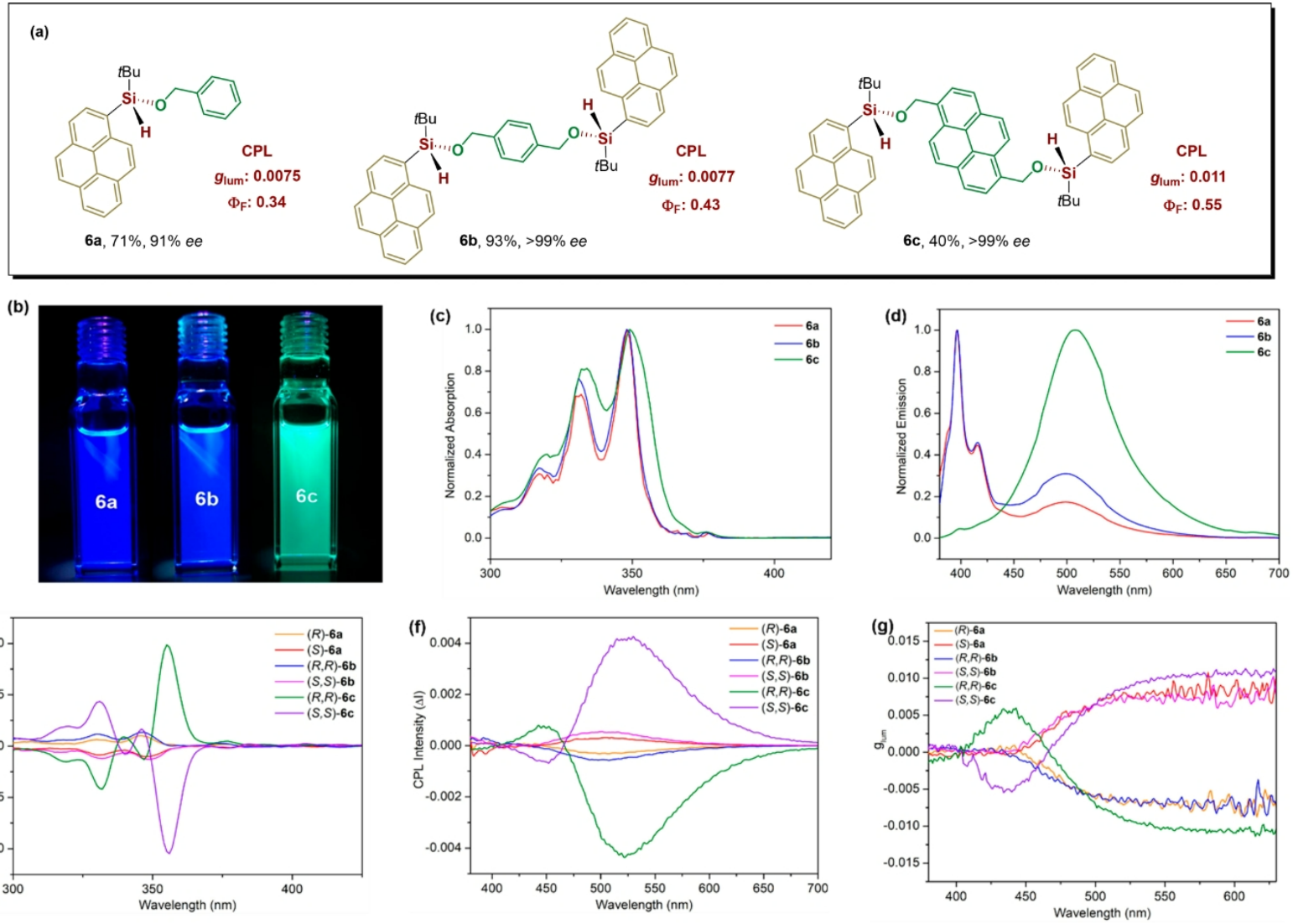

光响应良好，具有光电材料的潜力

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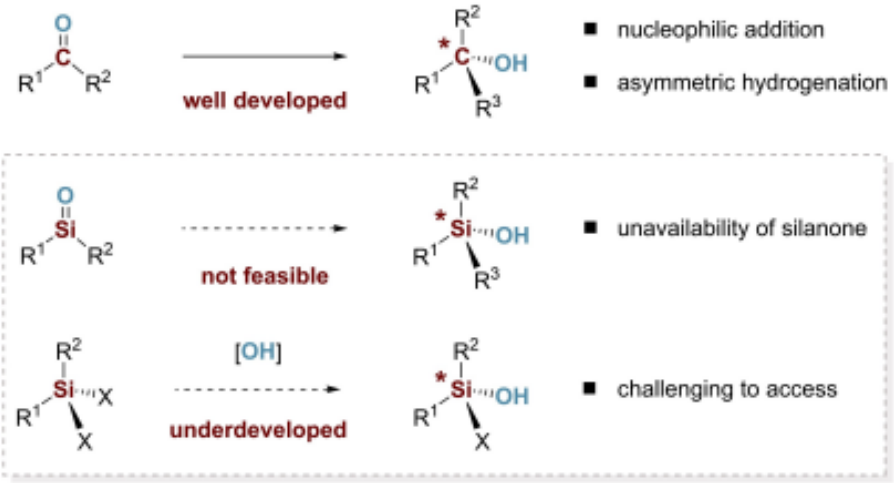
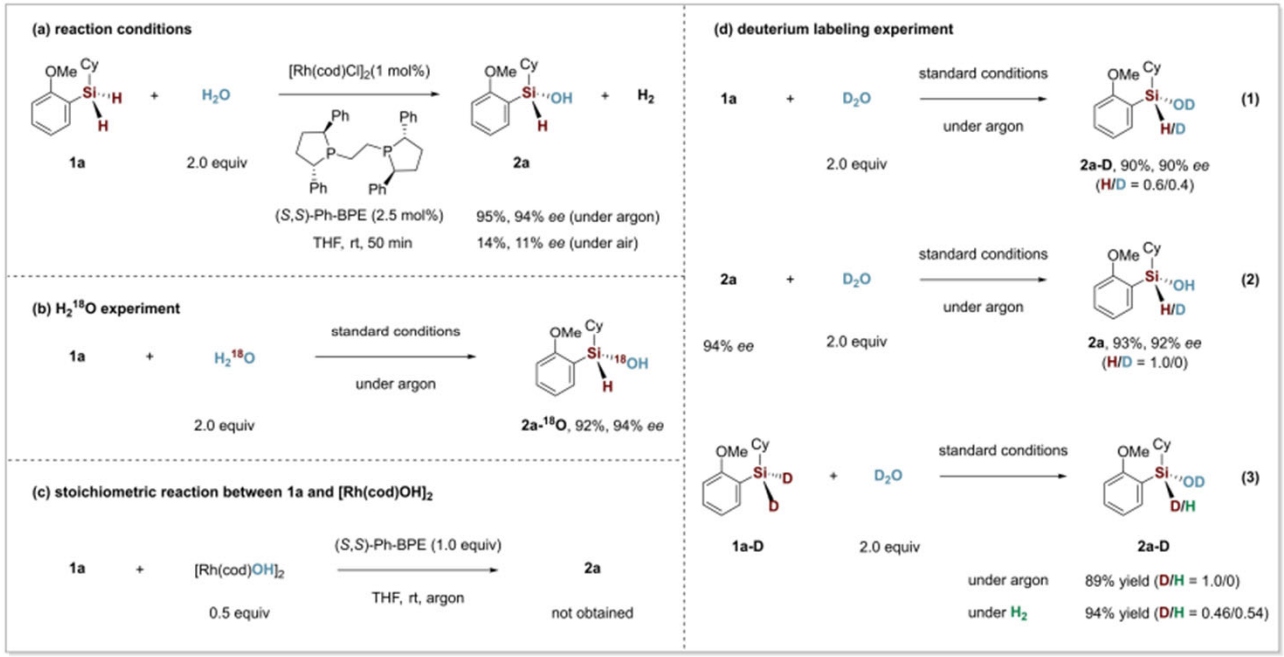


硅的原子半径较大（C 77 pm vs. Si 117 pm），其 pπ-pπ 作用弱，导致硅的多重键不稳定

探究反应机理



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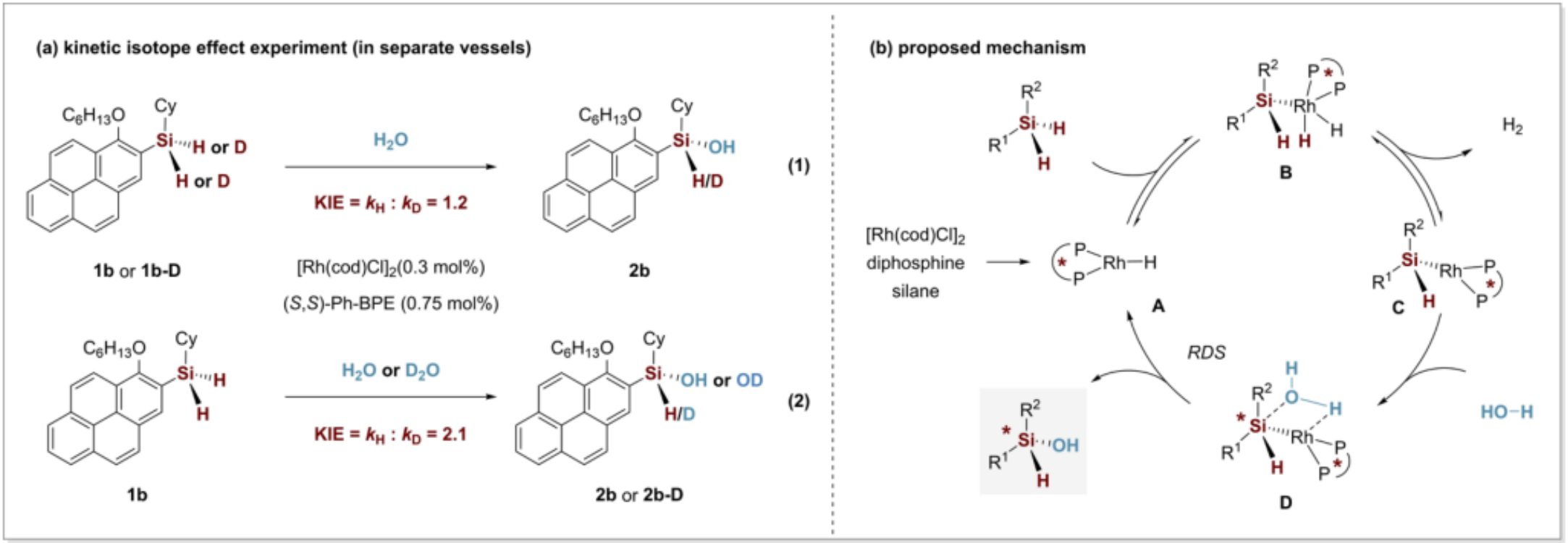

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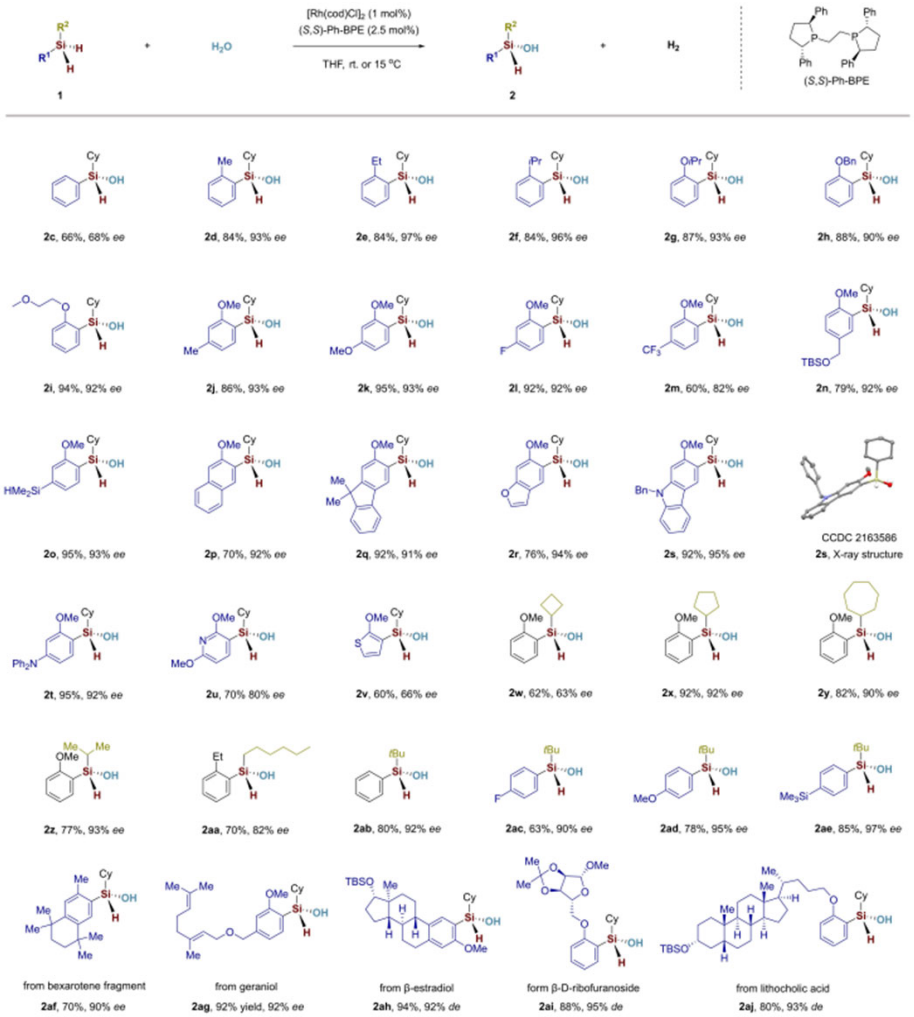

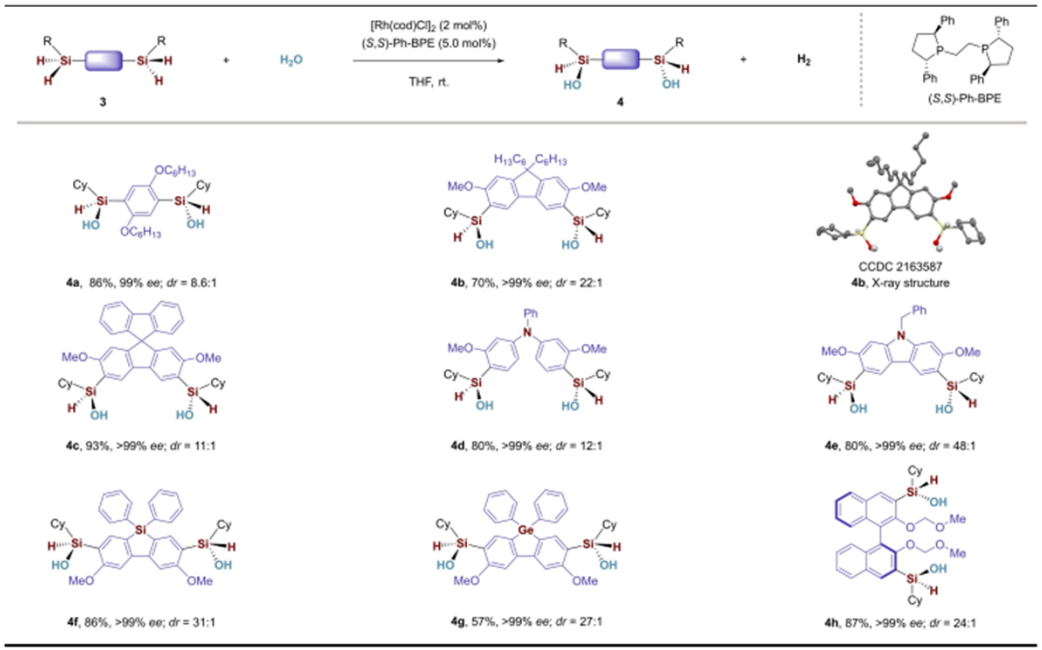

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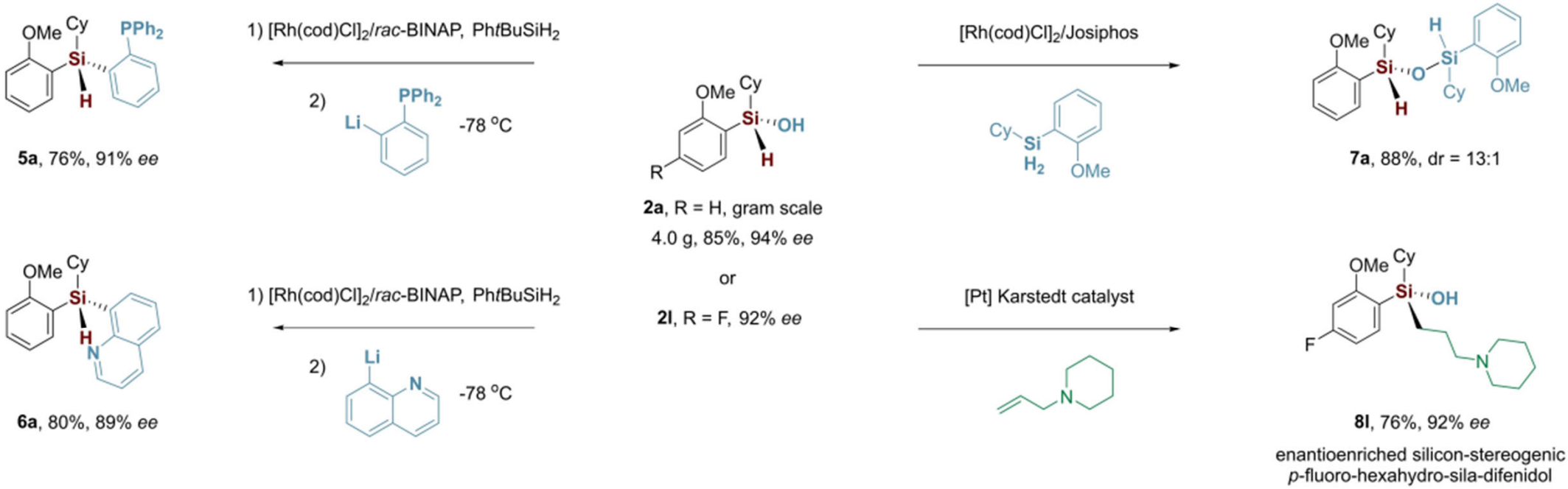
进一步反应



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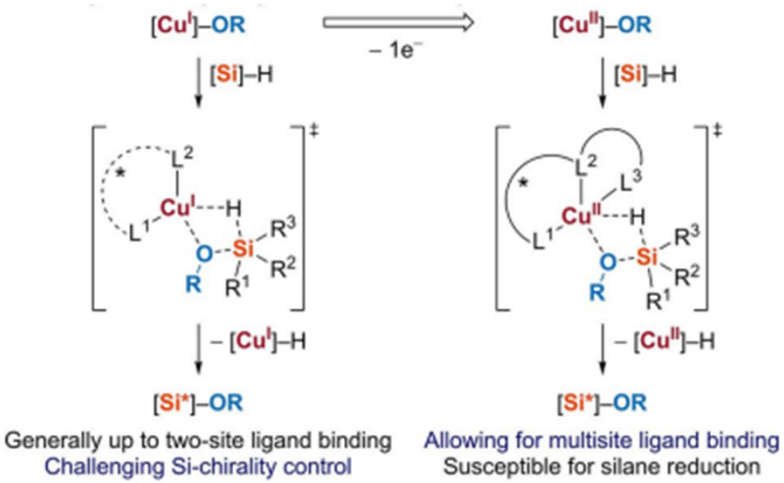
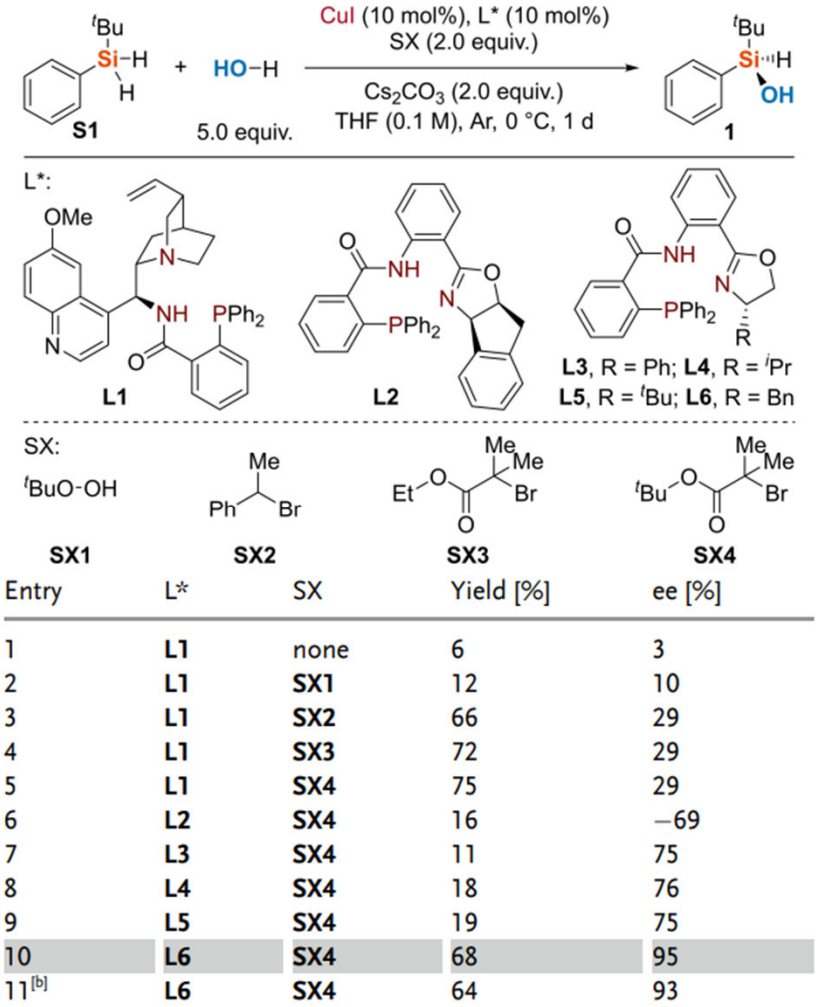


二价铜对手性控制更有利



Entry	L*	SX	Yield [%]	ee [%]
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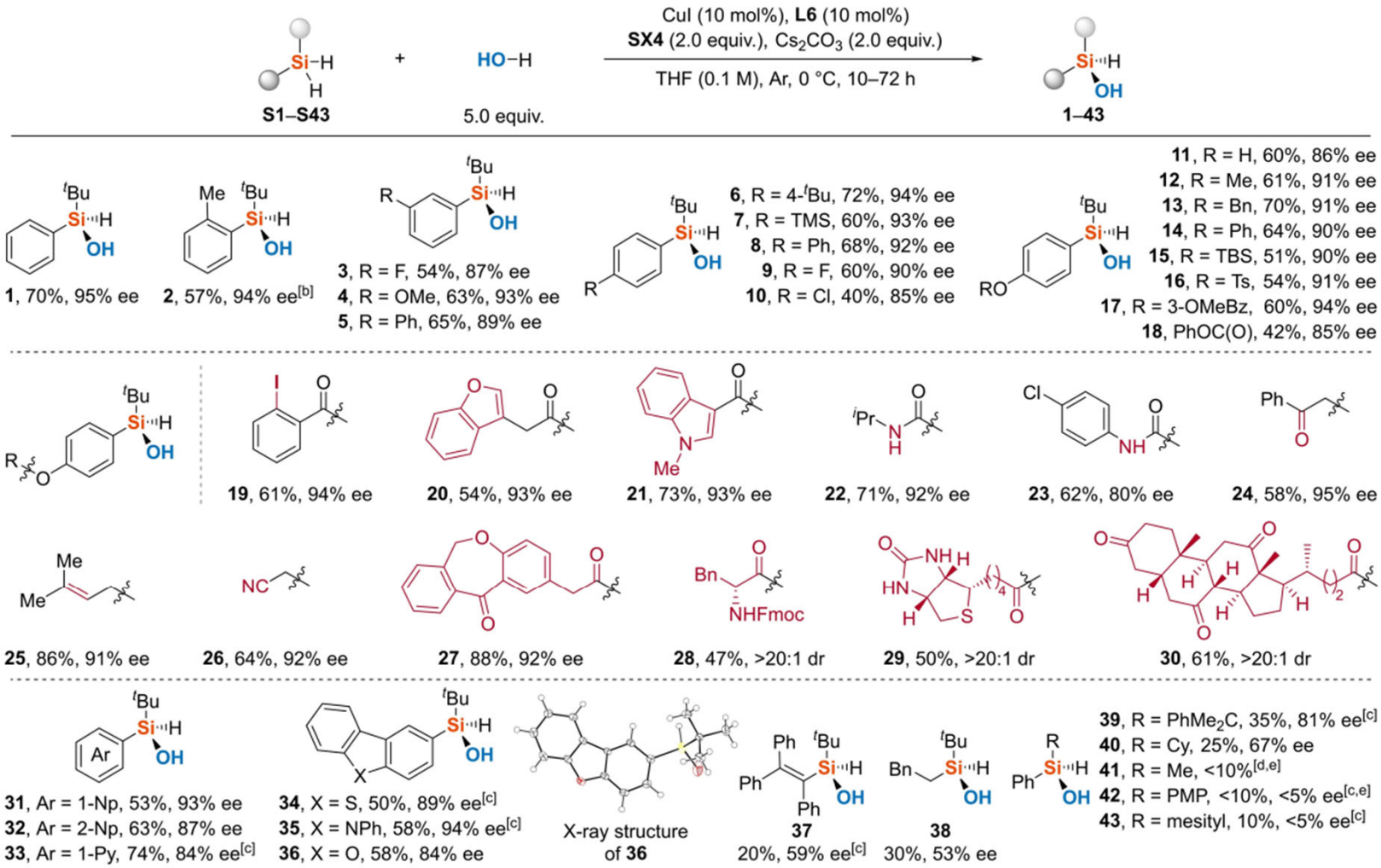
2	L1	SX1	12	10
3	L1	SX2	66	29
4	L1	SX3	72	29
5	L1	SX4	75	29
6	L2	SX4	16	–69
7	L3	SX4	11	75
8	L4	SX4	18	76
9	L5	SX4	19	75
10	L6	SX4	68	95
11[b]	L6	SX4	64	93

Yang W, Liu L, Guo J, Wang SG, Zhang JY, Fan LW, et al. Enantioselective Hydroxylation of Dihydrosilanes to Si-Chiral Silanols Catalyzed by In Situ Generated Copper(II) Species. Angewandte Chemie International Edition. 2022;61(32)

Part 4.分子间 Si–H/X–H 脱氢偶联构筑非环状多样化的硅中心手性硅烷



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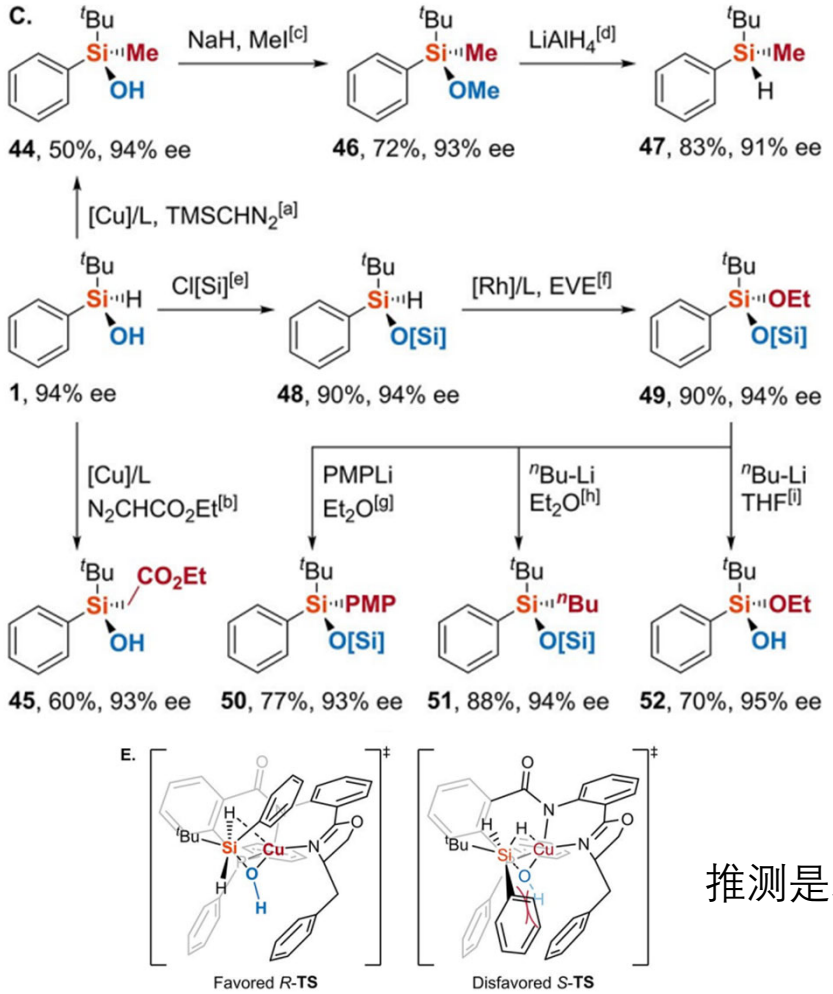

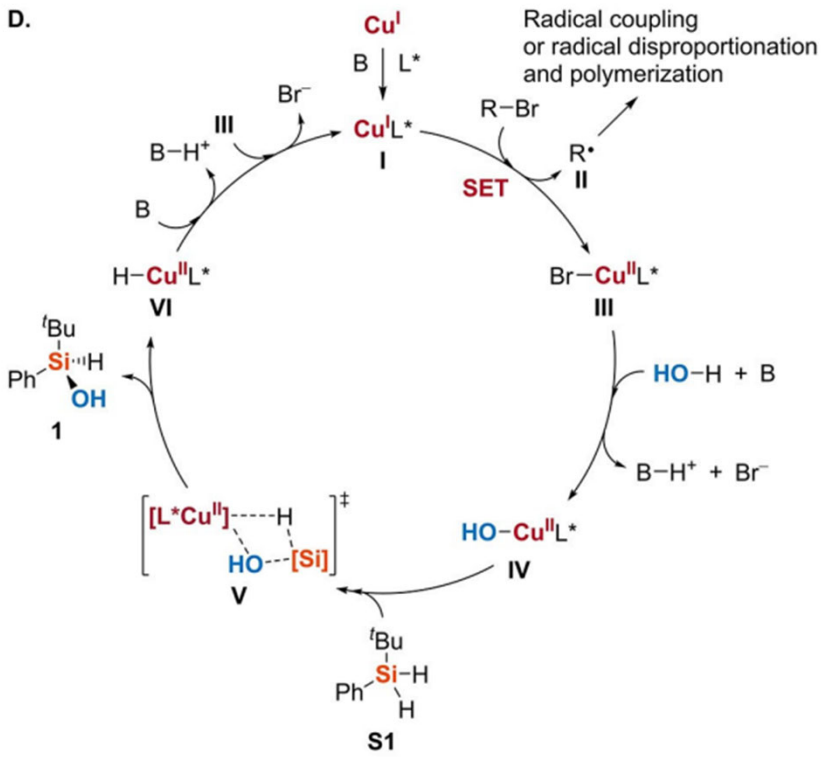

推测是苯基和羟基的冲突导致手性控制

Yang W, Liu L, Guo J, Wang SG, Zhang JY, Fan LW, et al. Enantioselective Hydroxylation of Dihydrosilanes to Si-Chiral Silanols Catalyzed by In Situ Generated Copper(II) Species. Angewandte Chemie International Edition. 2022;61(32)

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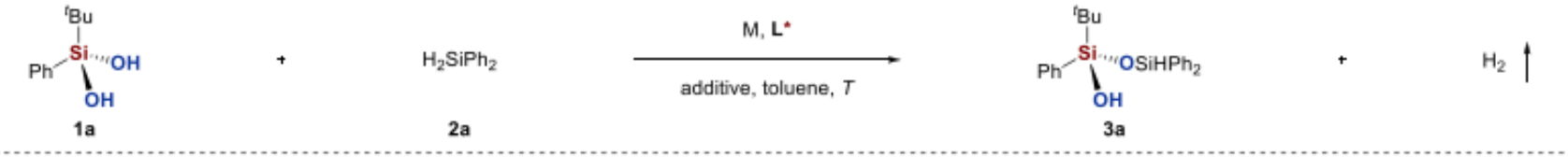

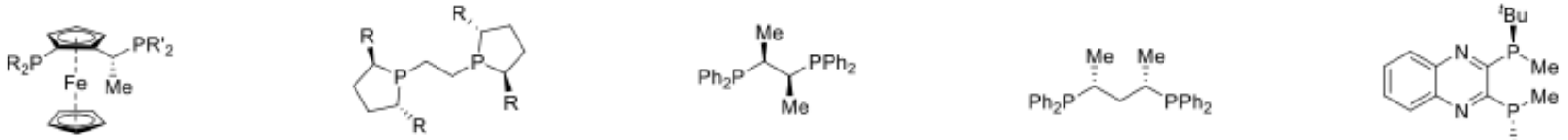

entry	catalyst	ligand	additive	T [°C]	yield [%]	ee [%]
1	$[Rh(cod)Cl]_2$	**L1**	-	RT	83	6
2	$[Rh(cod)Cl]_2$	**L2**	-	RT	51	4
3	$[Rh(cod)Cl]_2$	**L3**	-	RT	53	4
4	$Cu(MeCN)_4PF_6$	**L3**	-	RT	86	78
5	$Cu(MeCN)_4PF_6$	**L4**	-	RT	57	75
6	$Cu(MeCN)_4PF_6$	**L5**	-	RT	56	28
7	$Cu(MeCN)_4PF_6$	**L6**	-	RT	49	6
8	$Cu(MeCN)_4PF_6$	**L7**	-	RT	48	10
9	$Cu(MeCN)_4PF_6$	**L3**	-	0	82	83
10	$Cu(MeCN)_4PF_6$	**L3**	-	−15	84	85
11	$Cu(MeCN)_4PF_6$	**L3**	-	−35	NR	-
12	$Cu(MeCN)_4PF_6$	**L3**	^{t}BuOK	−35	58	70
13	$Cu(MeCN)_4PF_6$	**L3**	^{t}BuONa	−35	62	77
14	$Cu(MeCN)_4PF_6$	**L3**	^{t}BuOLi	−35	81(72)	90

Gao J, Mai P-L, Ge Y, Yuan W, Li Y, He C. Copper-Catalyzed Desymmetrization of Prochiral Silanediols to Silicon-Stereogenic Silanols. ACS Catalysis. 2022;12(14):8476-83.

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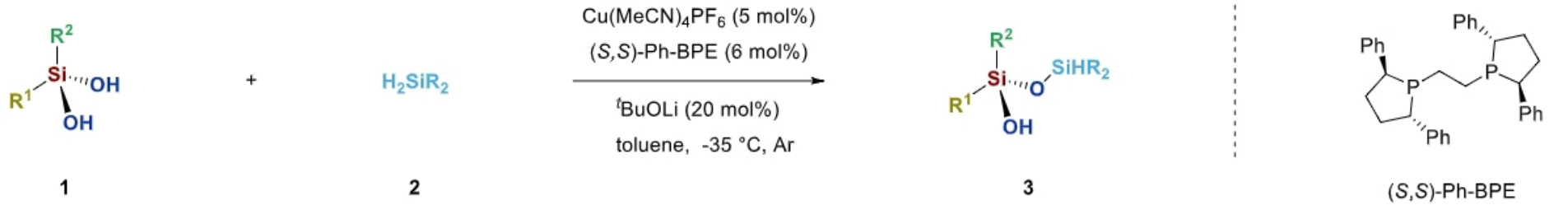
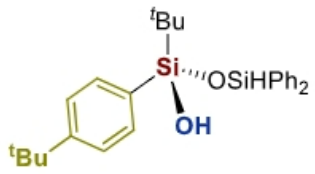
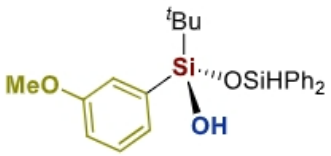


1 2 3 (*S*,*S*)-Ph-BPE

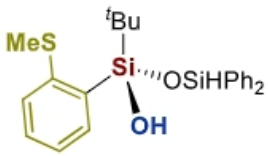


3b, 79%, 94% *ee*

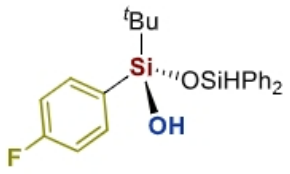
3c, 52%, 88% *ee*



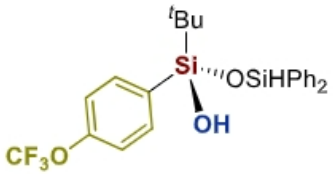
3d, 61%, 90% *ee*



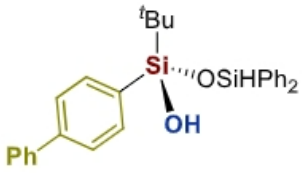
3e, 63%, 80% *ee*



3f, 62%, 85% *ee*

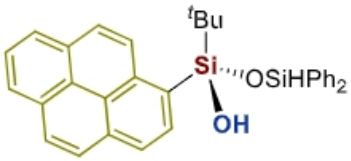


3g, 70%, 90% *ee*



3h, 83%, 94% *ee*

3i, 81%, 92% *ee*



3j, 65%, 96% *ee*

3k, 66%, 92% *ee*

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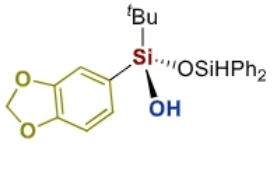
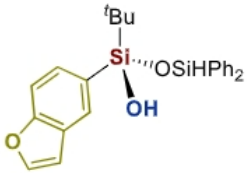
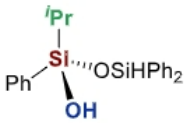


3l, 63%, 90% *ee*

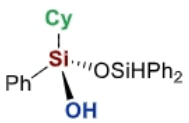


3m, 68%, 90% *ee*

3n, 59%, 96% *ee*



3o, 68%, 79% *ee*



3p, 72%, 63% *ee*

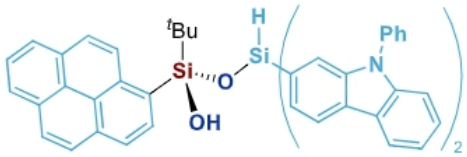
3q, 75%, 74% *ee*

3r, 62%, 83% *ee*

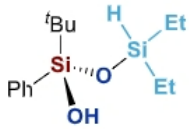
3s, 80%, 90% *ee*

Ar = 4-^{t}Bu-C_6H_4
3t, 54%, 90% *ee*

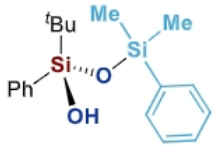
Ar = 4-^{t}Bu-C_6H_4
3u, 58%, 88% *ee*



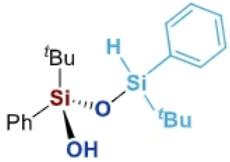
3v, 59%, 96% *ee*



3w[b], 52%, 72% *ee*



3x[b], 63%, 67% *ee*



3y[c], 58% (dr = 2.7 :1)
86% *ee*, 94% *ee*

3z[c], 53% (dr = 1.5:1)
84% *ee*, 89% *ee*

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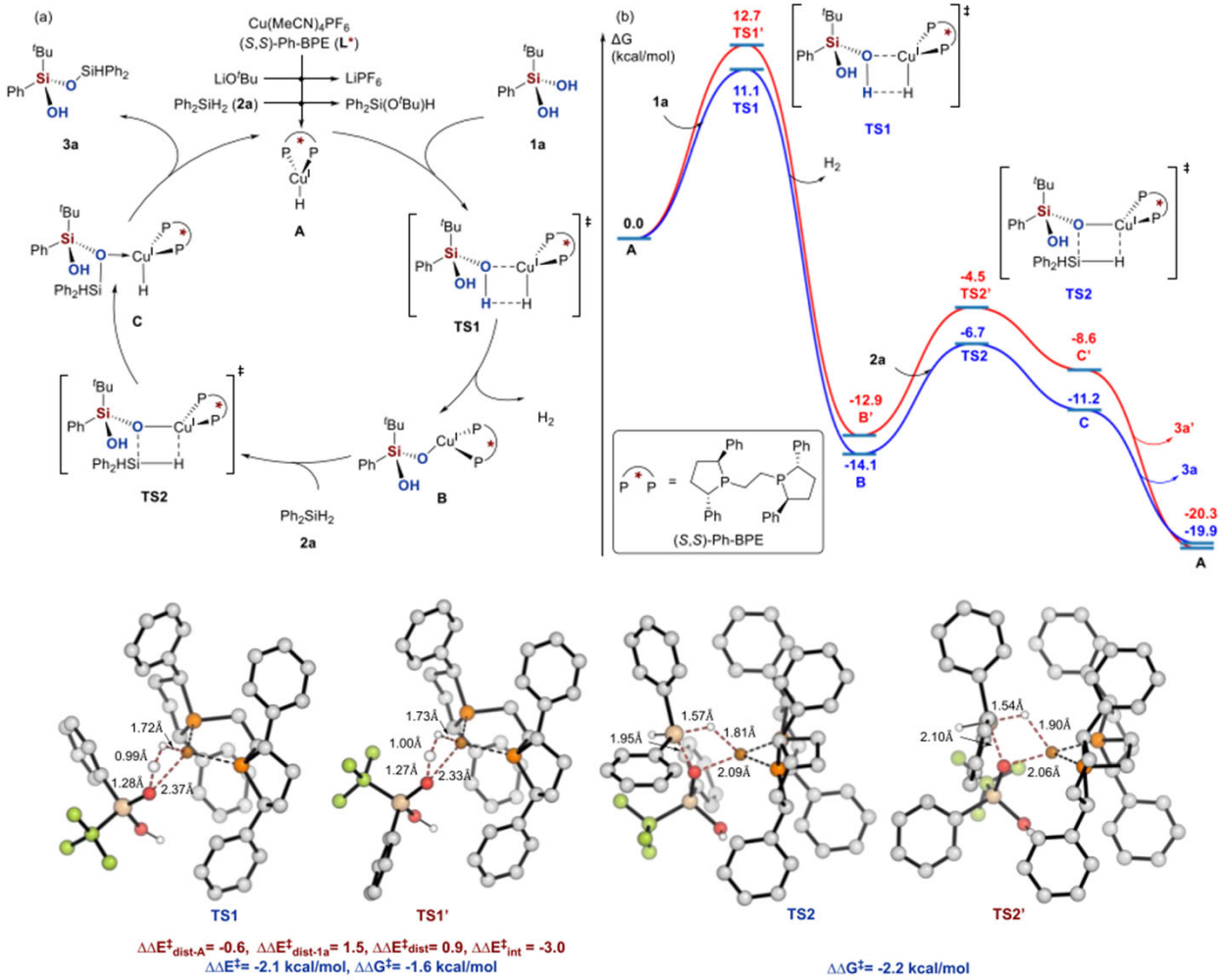

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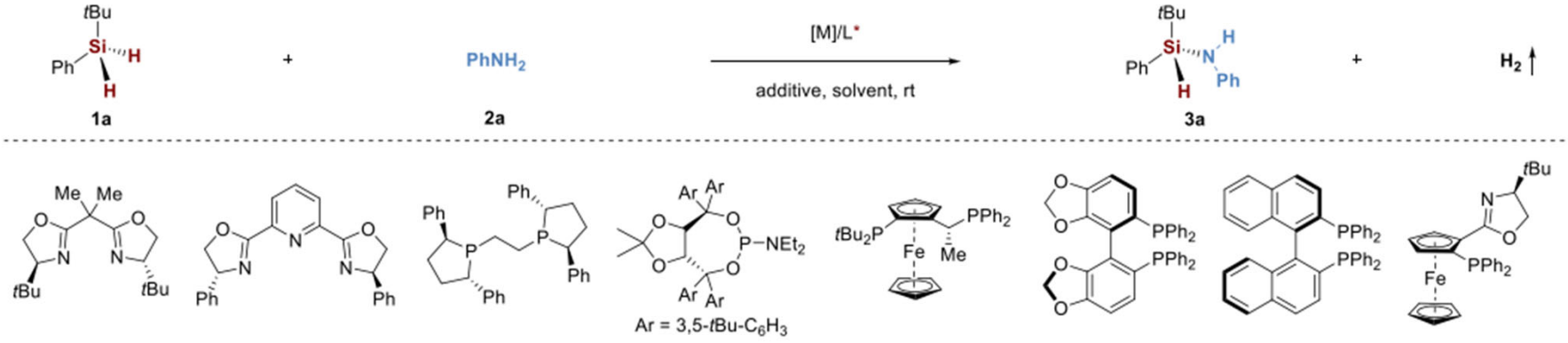

entry	[M]	ligand	additive	solvent	yield [%]	*ee* [%]
1[b]	$CpMn(CO)_3$	**L1**	*t*BuOK	toluene	trace	
2[b]	$CpMn(CO)_3$	**L2**	*t*BuOK	toluene	0	
3[b]	$FeCl_2$	**L1**	*t*BuOK	toluene	trace	
4[b]	$FeCl_2$	**L2**	*t*BuOK	toluene	0	
5[b]	CuCl	**L2**	*t*BuONa	toluene	0	
6[c]	CuCl	**L3**	*t*BuONa	toluene	89	51
7	$[Rh(cod)Cl]_2$	**L3**		toluene	82	85
8[c]	$Pd_2(dba)_3$	**L4**	Et_3N	THF	trace	
9[d]	$[Rh(cod)Cl]_2$	**L5**		toluene	92	98
10	$[Rh(cod)Cl]_2$	**L6**		toluene	90	87
11	$[Rh(cod)Cl]_2$	**L7**		toluene	88	73
12	$[Rh(cod)Cl]_2$	**L8**		toluene	45	20

Liu M-M, Xu Y, He C. Catalytic Asymmetric Dehydrogenative Si–H/N–H Coupling: Synthesis of Silicon-Stereogenic Silazanes. Journal of the American Chemical Society. 2023.

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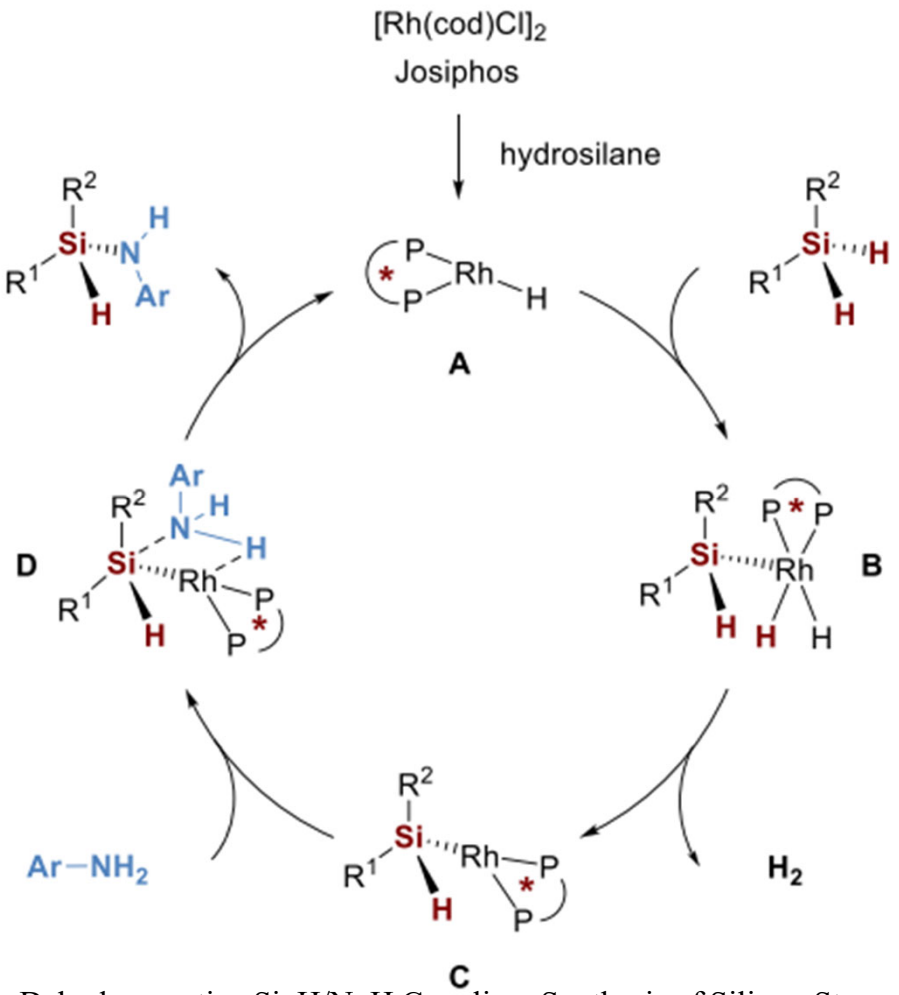

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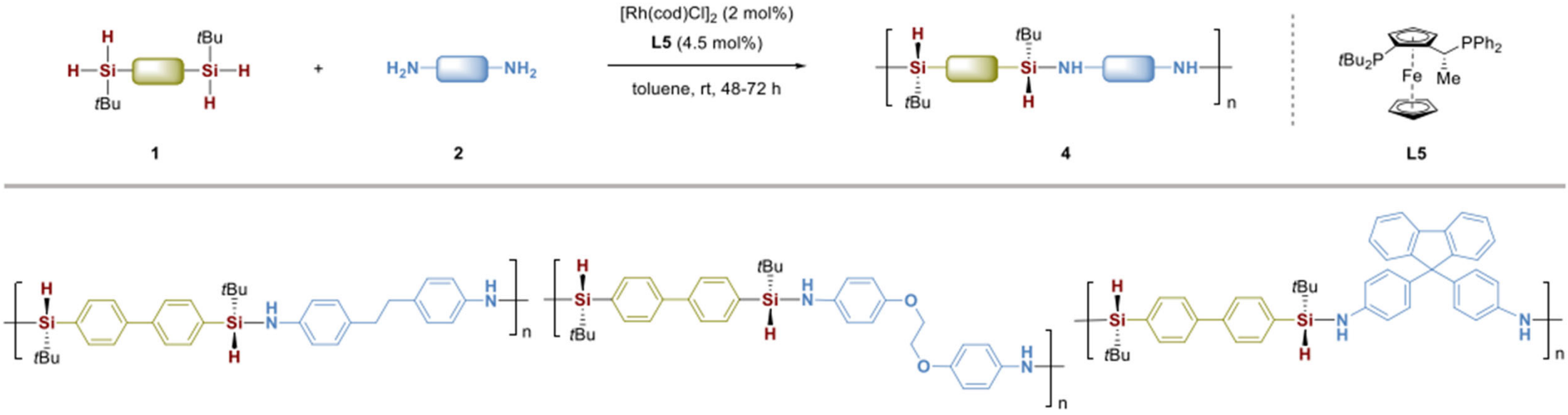
发生缩聚反应



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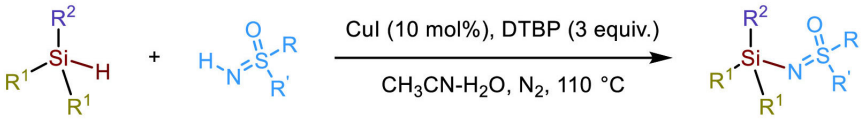
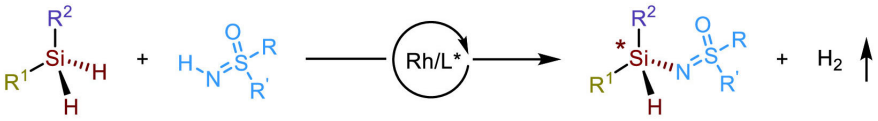
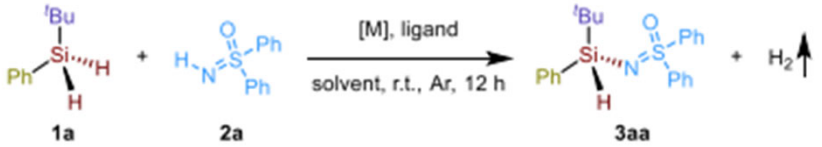
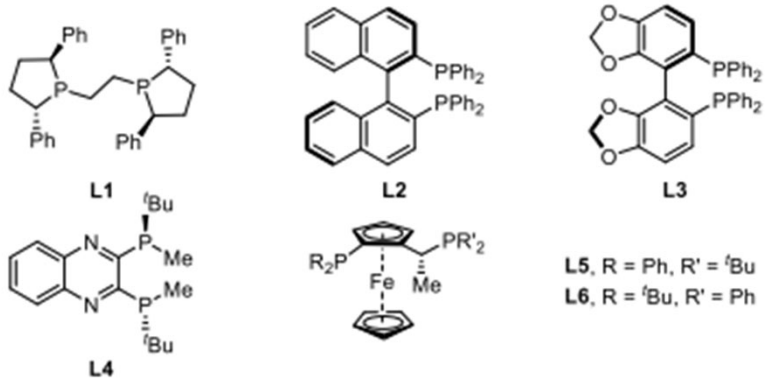
(b) Cu-catalyzed *N*-silylation of sulfoximines



(c) This work: the first enantioselective *N*-silylation of sulfoximines







Entry	[M] (x mol%)	Ligand (x mol%)	Solvent	Yield (%)	*ee* (%)
1	$Cu(OAc)_2$ (5)	**L1** (6)	THF	88	30
2	$Cu(OAc)_2$ (5)	**L6** (6)	THF	86	15
3	$[Rh(cod)Cl]_2$ (1)	**L1** (2.2)	Toluene	75	1
4	$[Rh(cod)Cl]_2$ (1)	**L2** (2.2)	Toluene	42	62
5	$[Rh(cod)Cl]_2$ (1)	**L3** (2.2)	Toluene	71	10
6	$[Rh(cod)Cl]_2$ (1)	**L4** (2.2)	Toluene	12	0
7	$[Rh(cod)Cl]_2$ (1)	**L5** (2.2)	Toluene	73	78
8	$[Rh(cod)Cl]_2$ (1)	**L6** (2.2)	Toluene	98	98
9	$[Rh(cod)Cl]_2$ (1)	**L6** (2.2)	THF	60	95
10	$[Rh(cod)Cl]_2$ (1)	**L6** (2.2)	DCE	50	85
11	$[Rh(cod)Cl]_2$ (1)	-	Toluene	96	0

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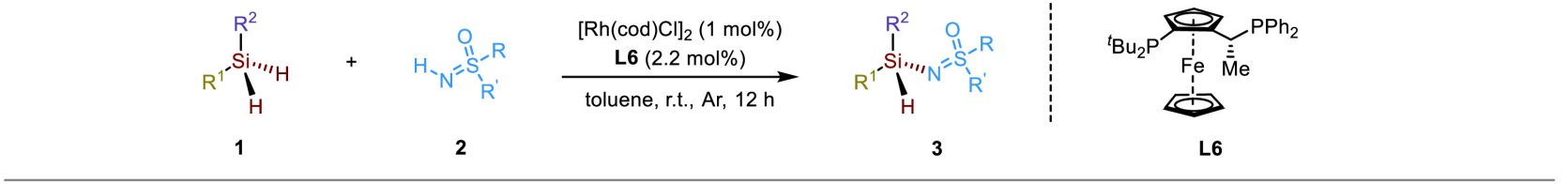
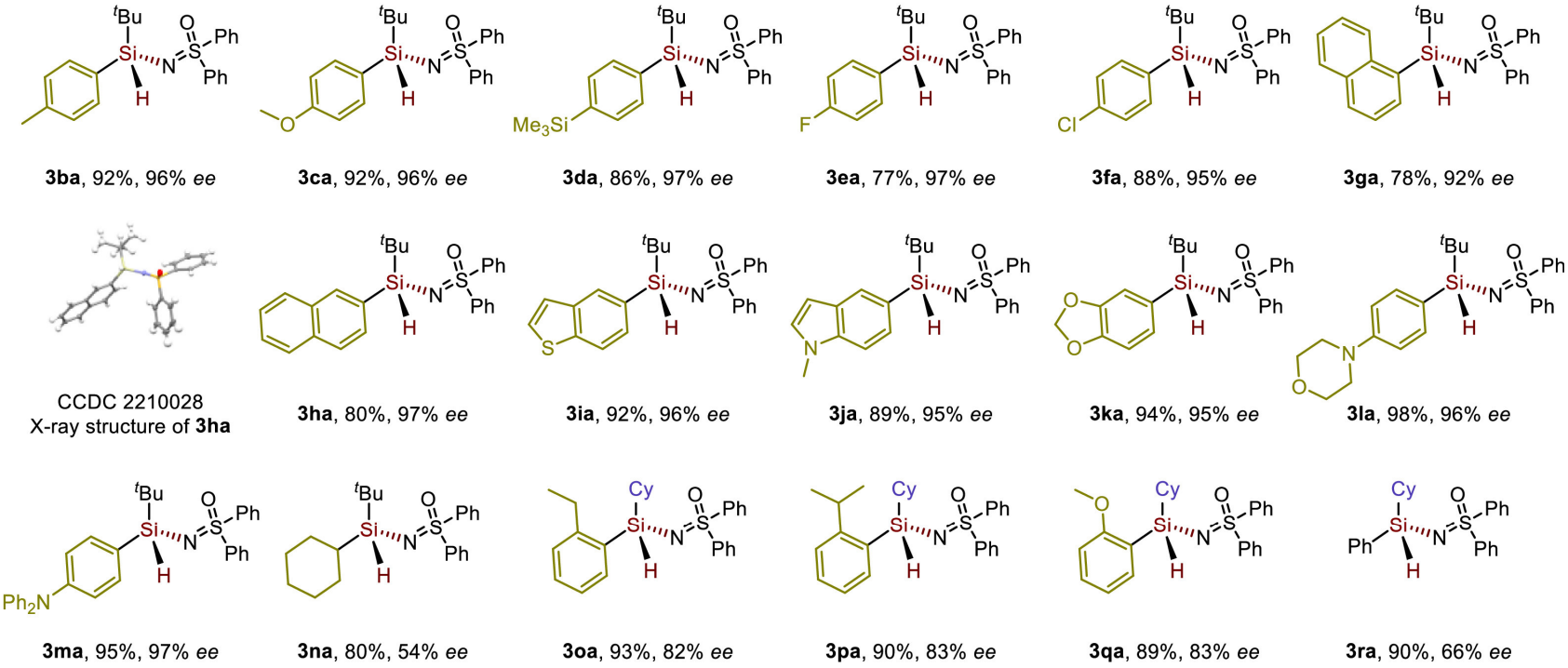


1 + 2 → 3 (L6)



3ba, 92%, 96% *ee*

3ca, 92%, 96% *ee*

3da, 86%, 97% *ee*

3ea, 77%, 97% *ee*

3fa, 88%, 95% *ee*

3ga, 78%, 92% *ee*

CCDC 2210028
X-ray structure of **3ha**

3ha, 80%, 97% *ee*

3ia, 92%, 96% *ee*

3ja, 89%, 95% *ee*

3ka, 94%, 95% *ee*

3la, 98%, 96% *ee*

3ma, 95%, 97% *ee*

3na, 80%, 54% *ee*

3oa, 93%, 82% *ee*

3pa, 90%, 83% *ee*

3qa, 89%, 83% *ee*

3ra, 90%, 66% *ee*

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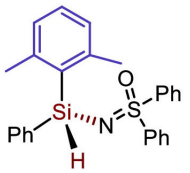
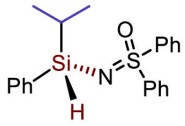
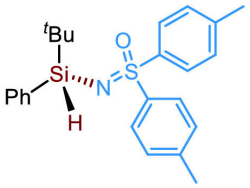


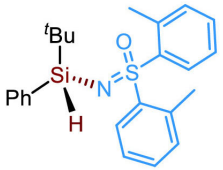
3sa, 85%, 16% *ee*



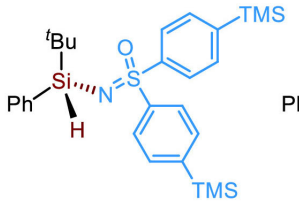
3ta, 83%, 65% *ee*



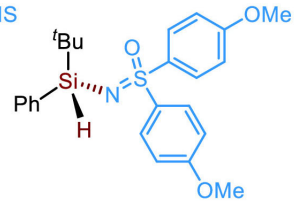
3ab, 88%, 97% *ee*



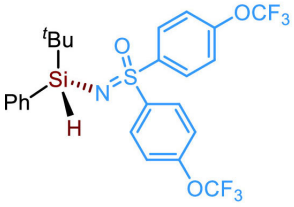
3ac, 95%, 97% *ee*



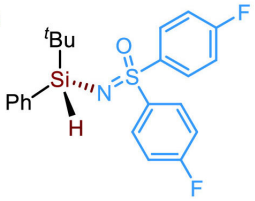
3ad, 87%, 95% *ee*



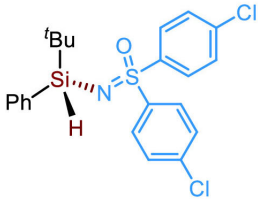
3ae, 80%, 96% *ee*



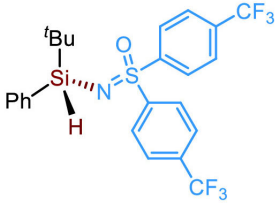
3af, 93%, 96% *ee*



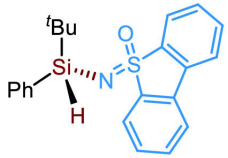
3ag, 86%, 97% ee



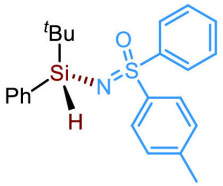
3ah, 91%, 97% *ee*



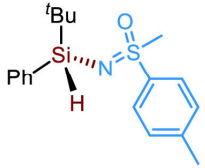
3ai, 70%, 94% *ee*



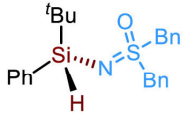
3aj, 85%, 96% *ee*



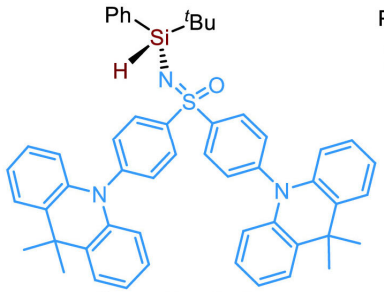
3ak, 92%, 98% *ee*, 96% *ee*, 1:1 *dr*



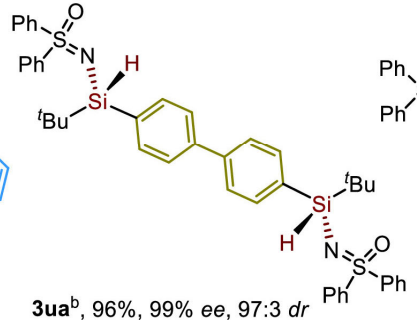
3al, 89%, 95% *ee*, 95% *ee*, 1:1 *dr*



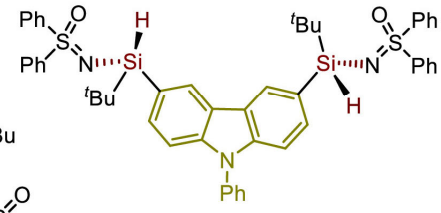
3am[a], 89%, 80% *ee*



3an, 91%, 97% *ee*



3ua[b], 96%, 99% *ee*, 97:3 *dr*

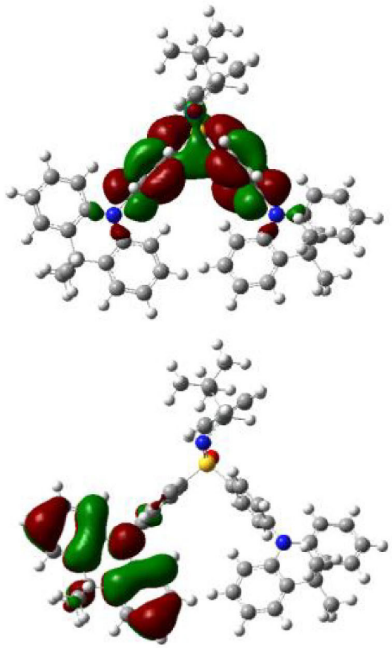


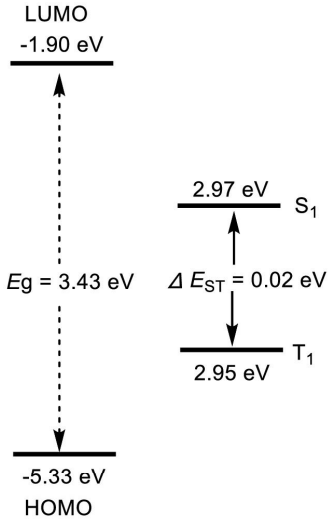
3va[b], 99%, 99% *ee*, 96:4 *dr*

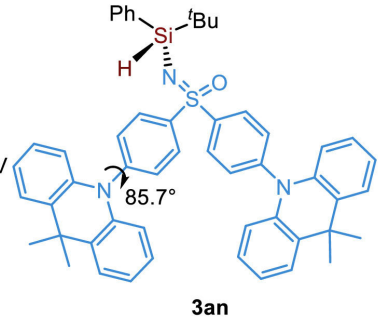
Huang X, Zhu J, He C. Catalytic enantioselective N-silylation of sulfoximine. Chinese Chemical Letters. 2023.

Part 4.分子间 Si–H/X–H 脱氢偶联构筑非环状多样化的硅中心手性硅烷

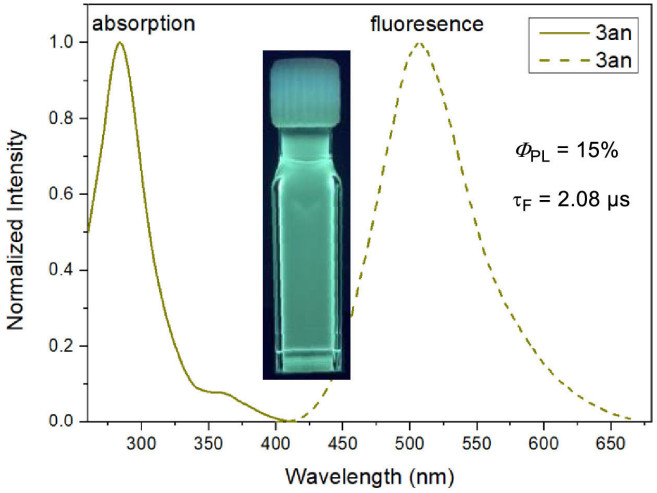
这些特性显示了该产物在TADF材料中应用的潜在可能性



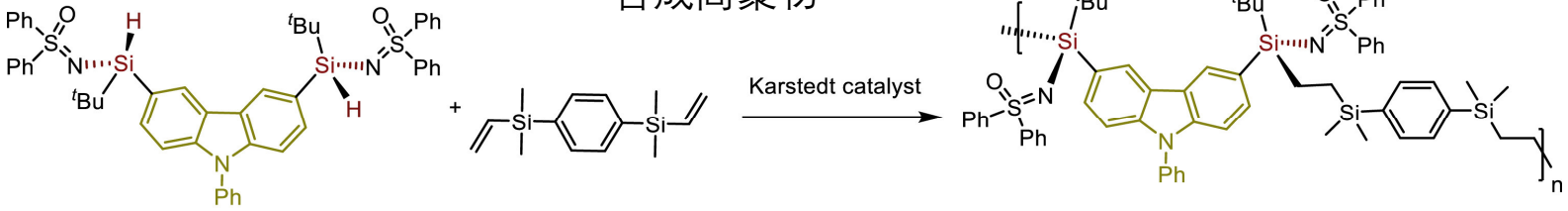




3an



合成高聚物

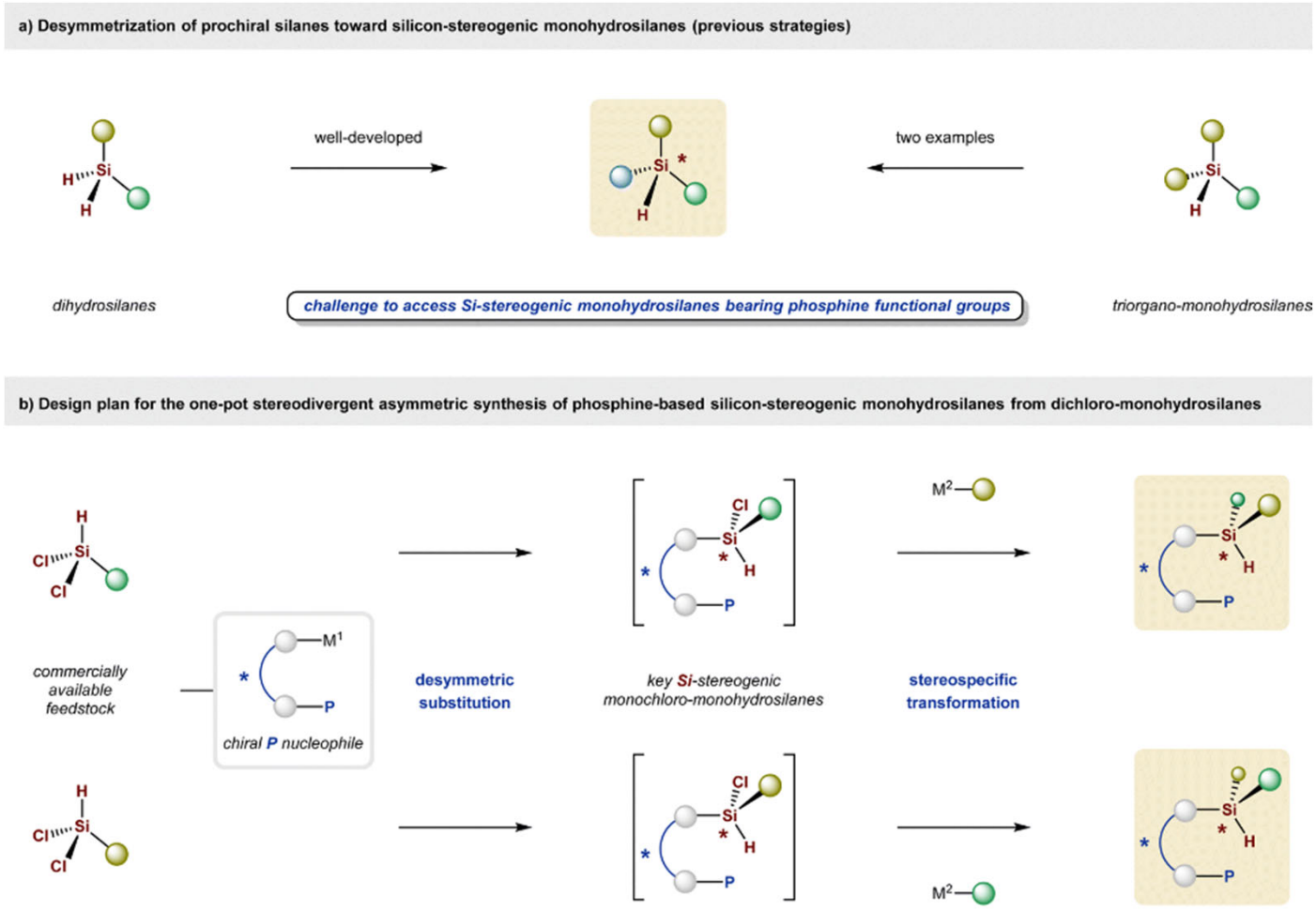


3va, 99% *ee*, 96:4 *dr*

4va, 75%, Mn = 7.3 kg/mol, PDI = 1.1

Huang X, Zhu J, He C. Catalytic enantioselective N-silylation of sulfoximine. Chinese Chemical Letters. 2023.

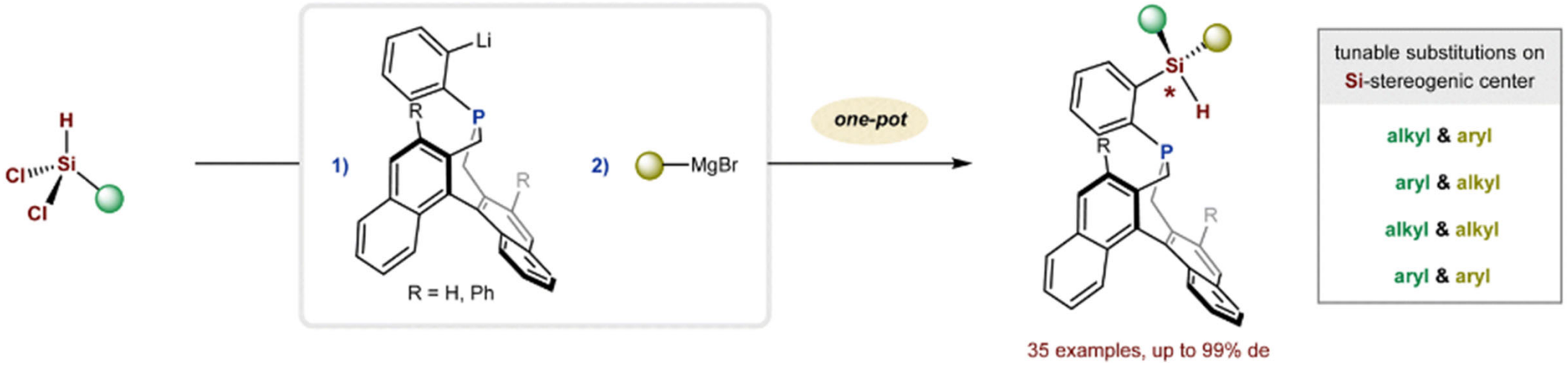
Part 5.分子间 Si–X/C–X 偶联构筑硅中心手性硅烷



Yang B, Tan X, Ge Y, Li Y, He C. Stereodivergent asymmetric synthesis of P-atropisomeric Si-stereogenic monohydrosilanes. Organic Chemistry Frontiers. 2023;10(19):4862-70.

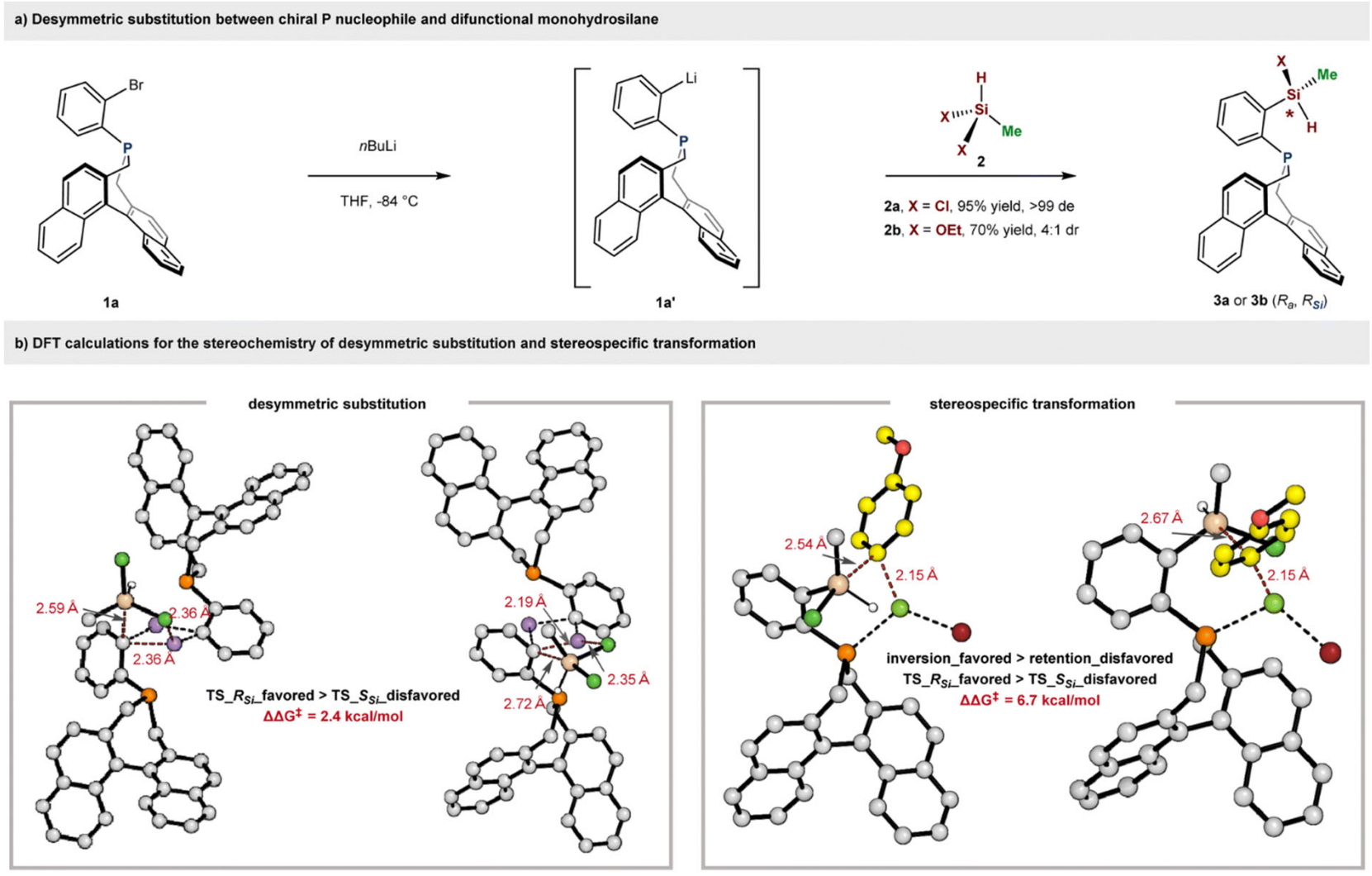
Part 5.分子间 Si–X/C–X 偶联构筑硅中心手性硅烷

c) Stereodivergent asymmetric synthesis of P-atropisomeric Si-stereogenic monohydrosilanes (this work)



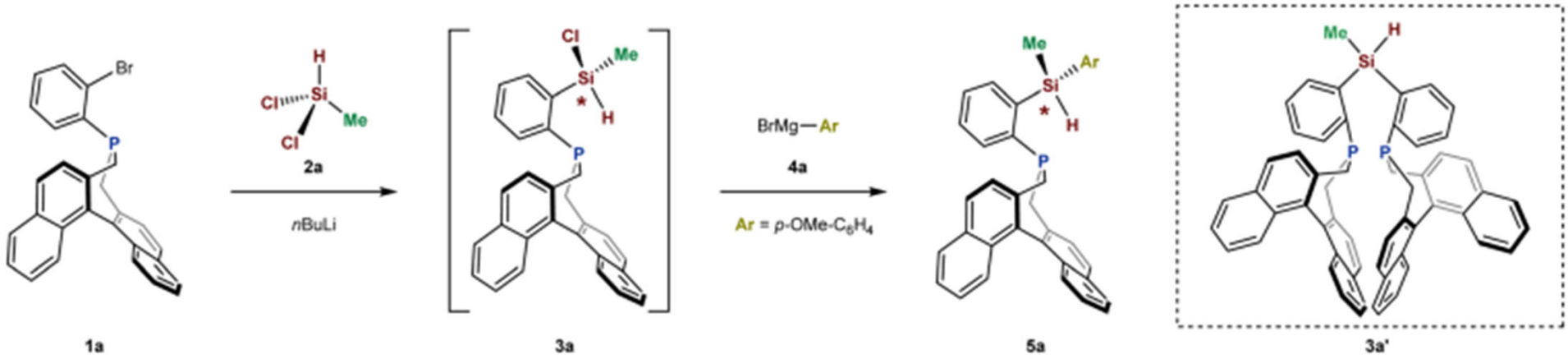
Yang B, Tan X, Ge Y, Li Y, He C. Stereodivergent asymmetric synthesis of P-atropisomeric Si-stereogenic monohydrosilanes. Organic Chemistry Frontiers. 2023;10(19):4862-70.

Part 5.分子间 Si–X/C–X 偶联构筑硅中心手性硅烷



Yang B, Tan X, Ge Y, Li Y, He C. Stereodivergent asymmetric synthesis of P-atropisomeric Si-stereogenic monohydrosilanes. Organic Chemistry Frontiers. 2023;10(19):4862-70.

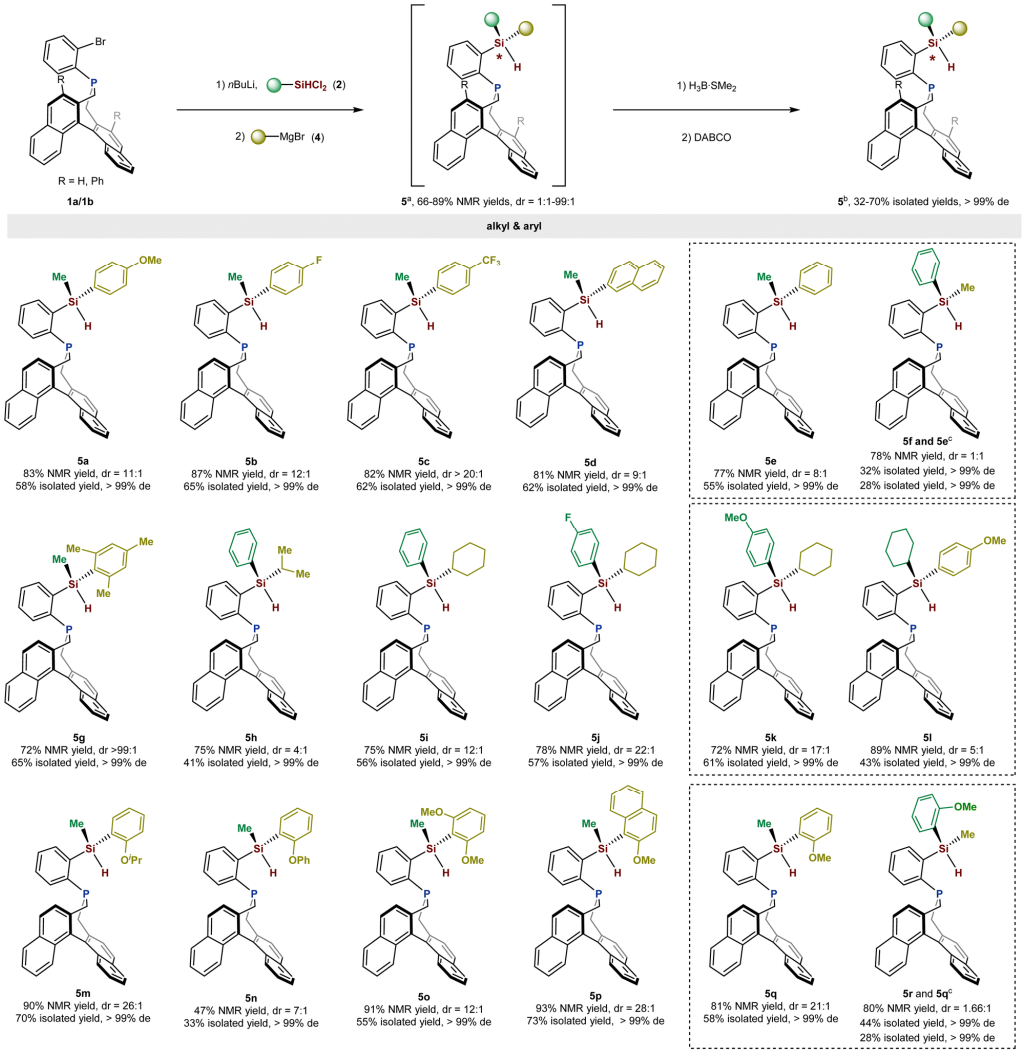
Part 5.分子间 Si–X/C–X 偶联构筑硅中心手性硅烷



Entry	2a (equiv.)	ArMgBr (equiv.)	Solvent	Temperature (°C)	5a/3a′ [a]	5a yield [b] (%)	5a dr [a] (%)
1	1.1 equiv.	1.5 equiv.	THF	−84 (°C)	1 : 1.7	33	7 : 1
2	2.0 equiv.	3.5 equiv.	THF	−84 (°C)	5.5 : 1	66	5.6 : 1
3	2.0 equiv.	3.5 equiv.	Et_2O	−84 (°C)	nd [c]	—	—
4	2.0 equiv.	3.5 equiv.	THF/Et_2O (1 : 1)	−84 (°C)	8.3 : 1	66	4.5 : 1
5	2.0 equiv.	3.5 equiv.	THF/Et_2O (1 : 1)	−116 (°C)	>40 : 1	83	11 : 1
6	2.0 equiv.	3.5 equiv.	THF/Et_2O (2 : 1)	−116 (°C)	>40 : 1	79	10 : 1
7	2.0 equiv.	3.5 equiv.	THF/Et_2O (1 : 2)	−116 (°C)	>40 : 1	77	7.2 : 1
8 [d]	2.0 equiv.	3.5 equiv.	THF/Et_2O (1 : 1)	−116 (°C)	>40 : 1	58 [e]	>99 : 1

Yang B, Tan X, Ge Y, Li Y, He C. Stereodivergent asymmetric synthesis of P-atropisomeric Si-stereogenic monohydrosilanes. Organic Chemistry Frontiers. 2023;10(19):4862-70.

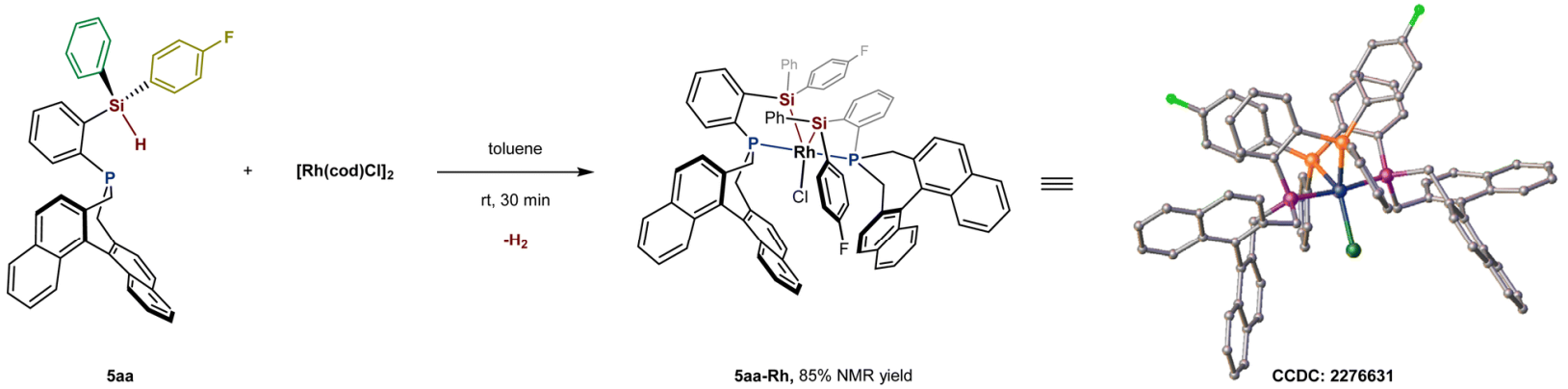
Part 5.分子间 Si–X/C–X 偶联构筑硅中心手性硅烷



Yang B, Tan X, Ge Y, Li Y, He C. Stereodivergent asymmetric synthesis of P-atropisomeric Si-stereogenic monohydrosilanes. Organic Chemistry Frontiers. 2023;10(19):4862-70.

Part 5.分子间 Si–X/C–X 偶联构筑硅中心手性硅烷

a) Synthesis of chiral silyl Rh(III) complex

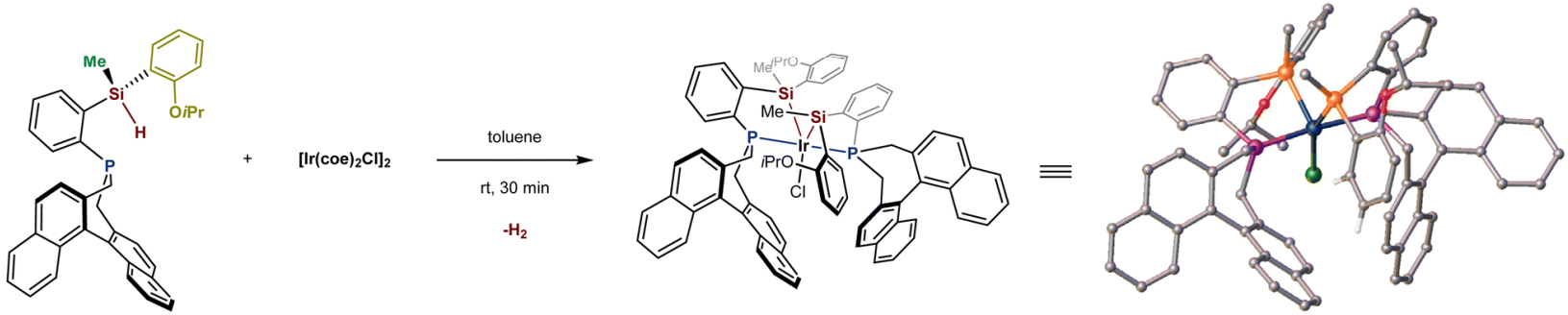


5aa

5aa-Rh, 85% NMR yield

CCDC: 2276631

b) Synthesis of chiral silyl Ir(III) complex



5m

5m-Ir, 93% NMR yield

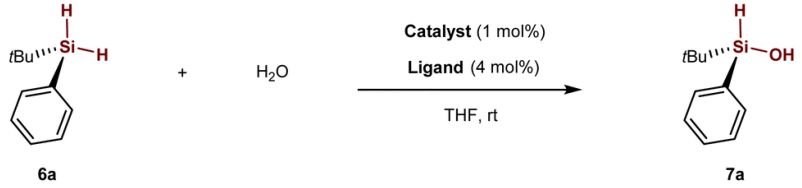
CCDC: 2276694

可以和金属发生稳定配位

Yang B, Tan X, Ge Y, Li Y, He C. Stereodivergent asymmetric synthesis of P-atropisomeric Si-stereogenic monohydrosilanes. Organic Chemistry Frontiers. 2023;10(19):4862-70.

Part 5.分子间 Si–X/C–X 偶联构筑硅中心手性硅烷

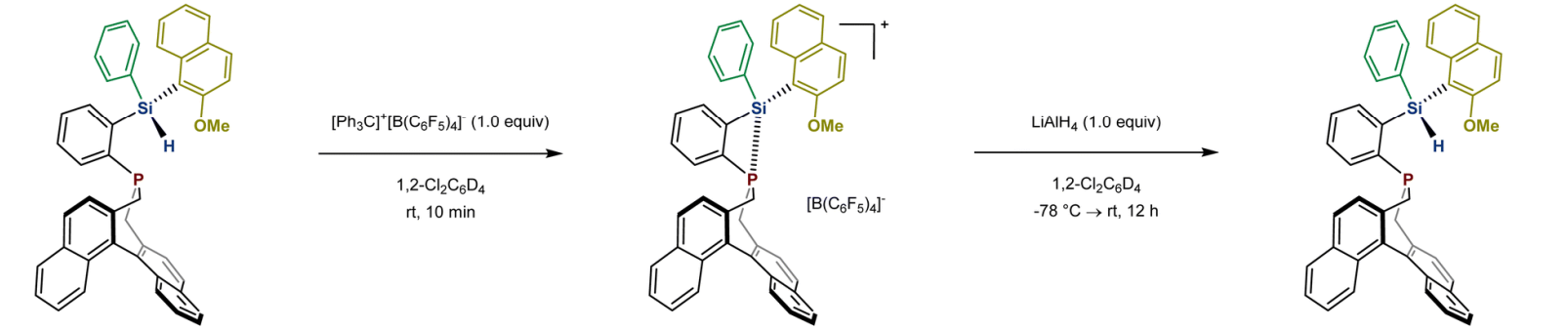
c) Chiral silyl metal complexes or silyl ligands enabled asymmetric hydrolytic oxidation of dihydrosilane



6a 7a

Entry	Catalyst	Ligand	Yield (%)	ee (%)
1	**5aa-Rh**	-	99	-19
2	**5m-Ir**	-	98	-17
3	$[Rh(cod)_2]BF_4$	**5u**	99	-72
4	$[Rh(cod)_2]BF_4$	**5q**	99	22
5	$[Rh(cod)_2]BF_4$	**5r**	99	-2

d) Synthesis of chiral silylium ions and preliminary chiral memory study



(R_{Si})-5af, dr = 97:3

δ (^{31}P) -2.6 (minor), -3.3 (major) ppm
δ (^{29}Si) -34.1 [d, J(^{31}P-^{29}Si) = 25.1 Hz] ppm

(R_{Si})-9, dr = 90:10

δ (^{31}P) 35.7 (minor), 29.1 (major) ppm
δ (^{29}Si) 8.5 [d, J(^{31}P-^{29}Si) = 48.7 Hz] ppm

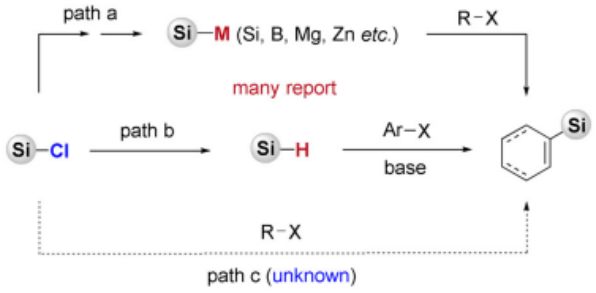
(R_{Si})-5af, dr = 86:14

δ (^{31}P) -2.6 (minor), -3.3 (major) ppm
δ (^{29}Si) -34.3 [d, J(^{31}P-^{29}Si) = 24.2 Hz] ppm

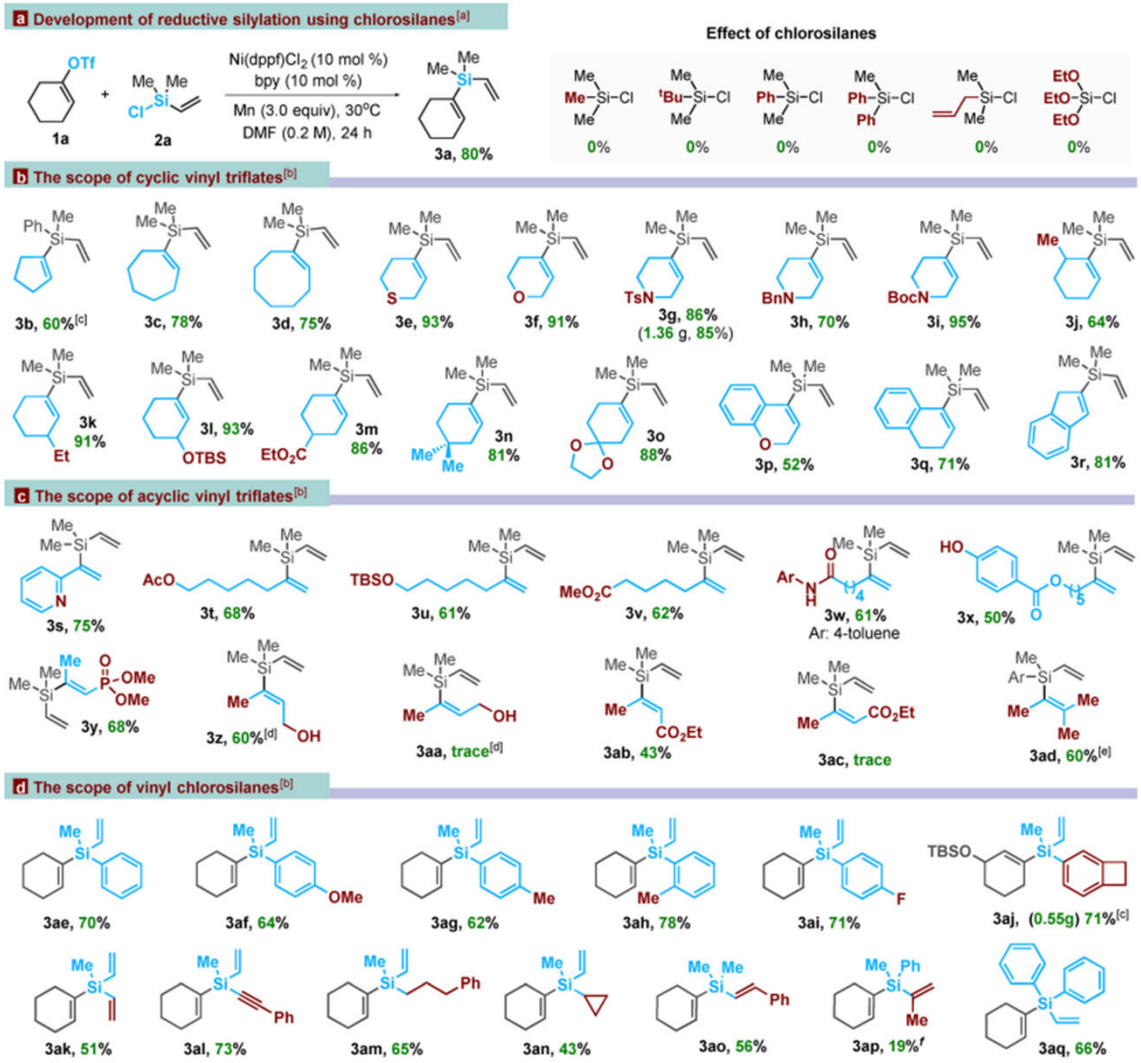
可以形成稳定Si离子手性中心

Yang B, Tan X, Ge Y, Li Y, He C. Stereodivergent asymmetric synthesis of P-atropisomeric Si-stereogenic monohydrosilanes. Organic Chemistry Frontiers. 2023;10(19):4862-70.

Part 6.交叉亲电试剂C-Si偶联反应

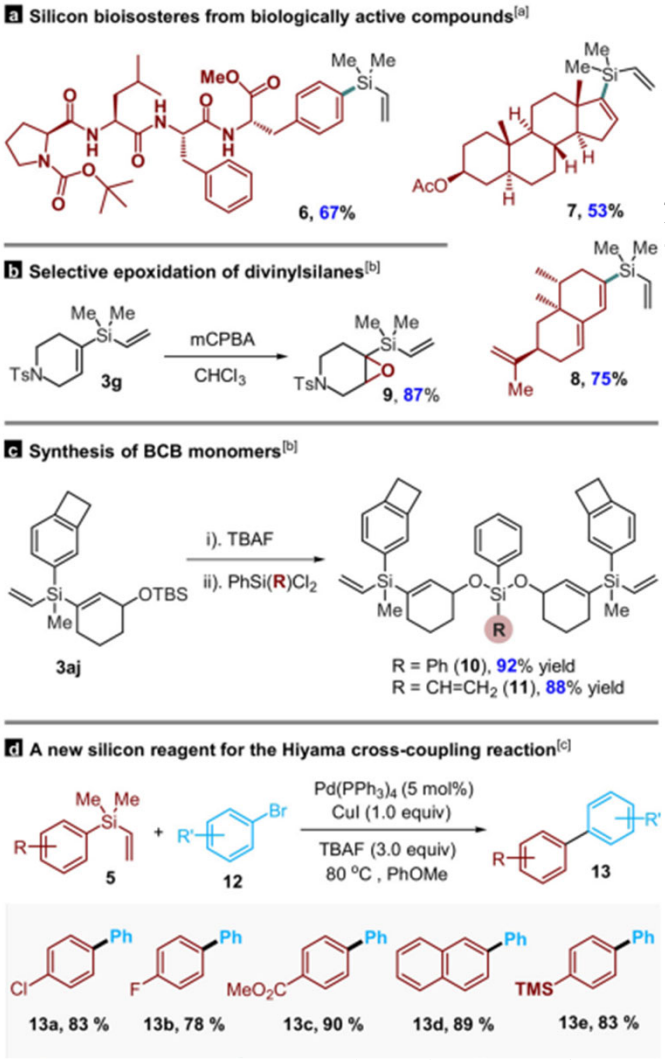


第一例交叉亲电试剂
C-Si偶联反应



Duan J, Wang K, Xu GL, Kang S, Qi L, Liu XY, et al. Cross-Electrophile C(sp2)−Si Coupling of Vinyl Chlorosilanes. Angewandte Chemie International Edition. 2020;59(51):23083-8.

Part 6.交叉亲电试剂C-Si偶联反应

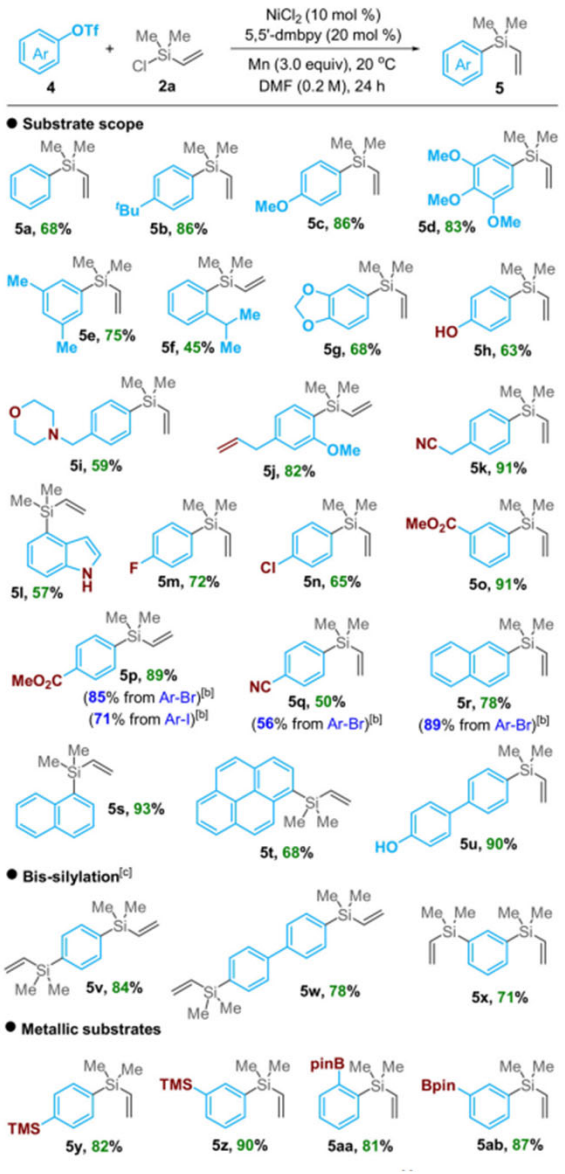


适配天然药物分子

烯烃基团可以进一步反应

新的苯并环丁烯单体

Hiyama偶联

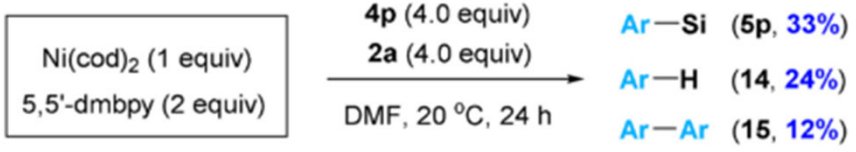


Duan J, Wang K, Xu GL, Kang S, Qi L, Liu XY, et al. Cross-Electrophile C(sp2)−Si Coupling of Vinyl Chlorosilanes. Angewandte Chemie International Edition. 2020;59(51):23083-8.

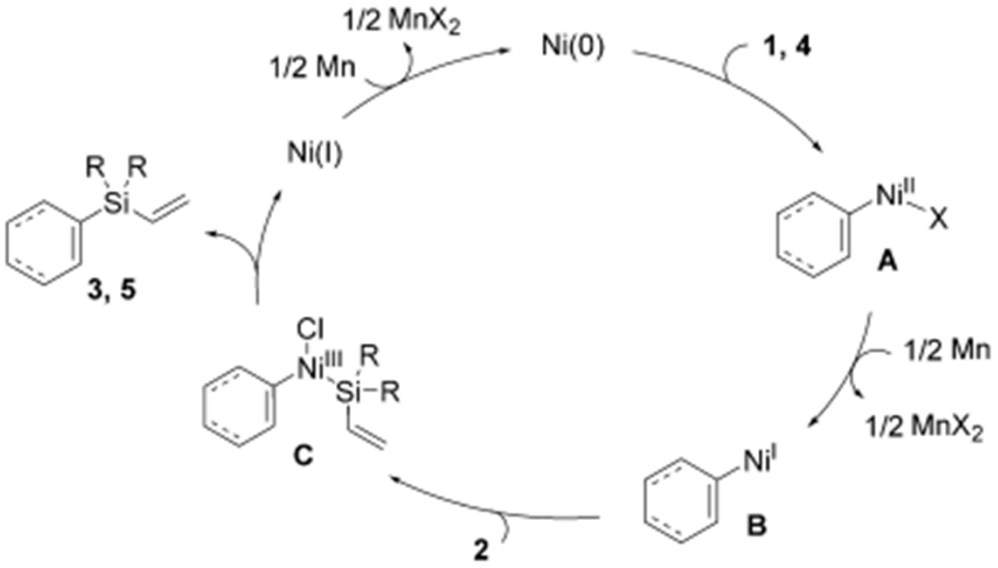
Part 6.交叉亲电试剂C-Si偶联反应

镍更倾向于和C亲电试剂反应

(a) The selectivity of 4p and 2a in the initial reaction with Ni(0)[a]



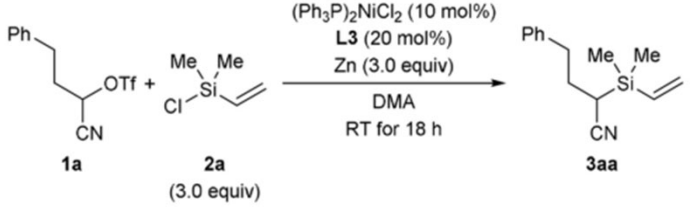
(b) Stoichiometric reaction of Ar-Ni(II) (16) with chlorosilane 2a

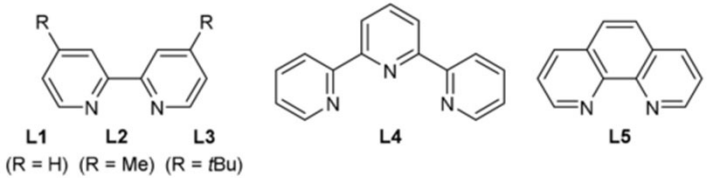


证明确实是生成了Ar-Ni(II)
并且经过Ni(I)过程

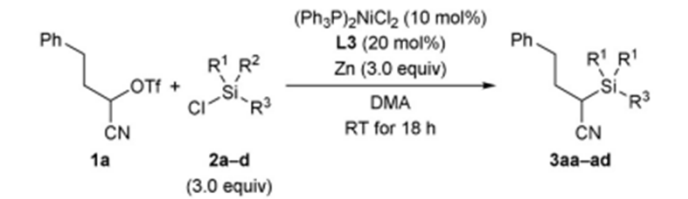
Duan J, Wang K, Xu GL, Kang S, Qi L, Liu XY, et al. Cross-Electrophile C(sp2)−Si Coupling of Vinyl Chlorosilanes. Angewandte Chemie International Edition. 2020;59(51):23083-8.

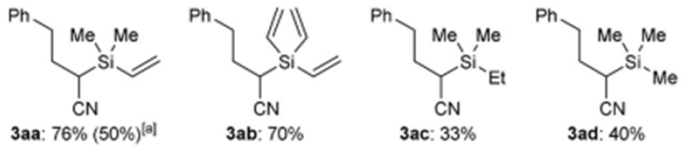
Part 6.交叉亲电试剂C-Si偶联反应



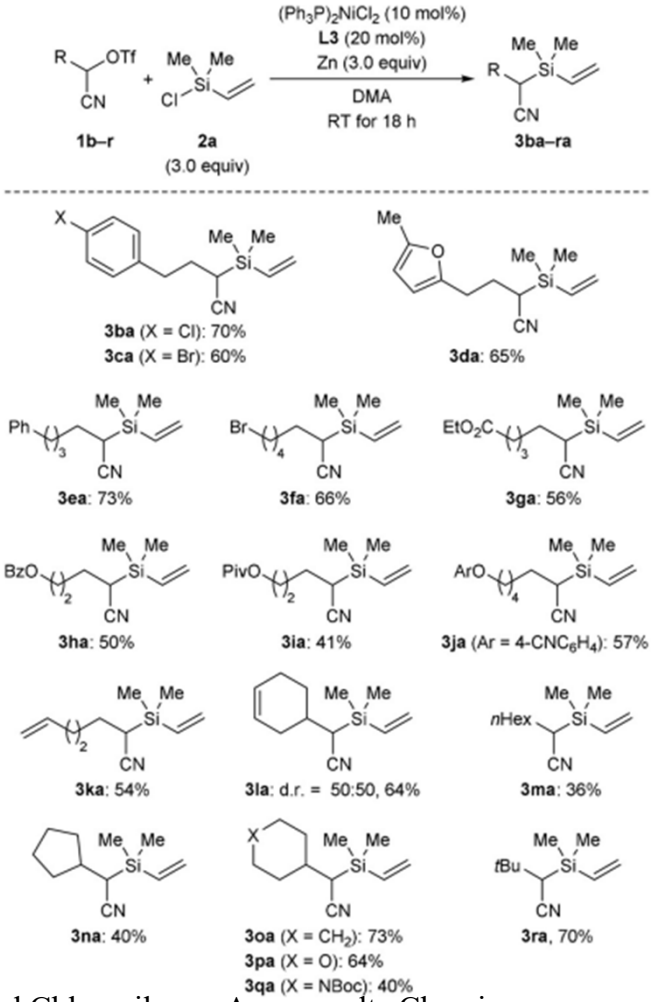


Entry	Variation	Yield [%][b]
1	None	90 (76)[c]
2	w/o Zn	0
3	w/o $(Ph_3P)_2NiCl_2$	0
4	w/o **L3**	70
5	**L1** instead of **L3**	85
6	**L2** instead of **L3**	80
7	**L4** instead of **L3**	76
8	**L5** instead of **L3**	5
9	Mn instead of Zn	54
10	Cl instead of OTf	80
11	Br instead of OTf	75
12	0 °C instead of RT	83
13	40 °C instead of RT	81



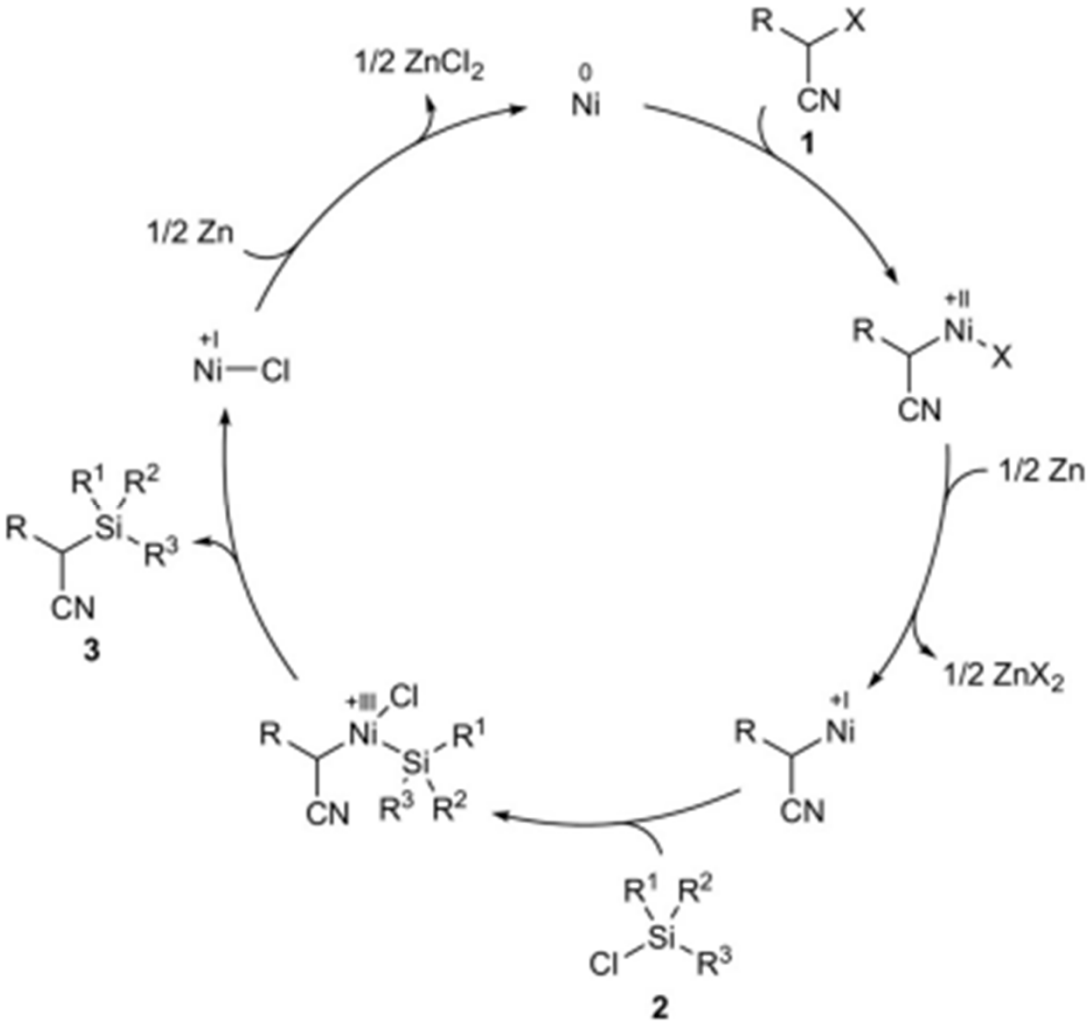


带有苯基和叔丁基不反应



Zhang L, Oestreich M. Nickel-Catalyzed, Reductive C(sp3)−Si Cross-Coupling of α-Cyano Alkyl Electrophiles and Chlorosilanes. Angewandte Chemie International Edition. 2021;60(34):18587-90.

Part 6.交叉亲电试剂C-Si偶联反应



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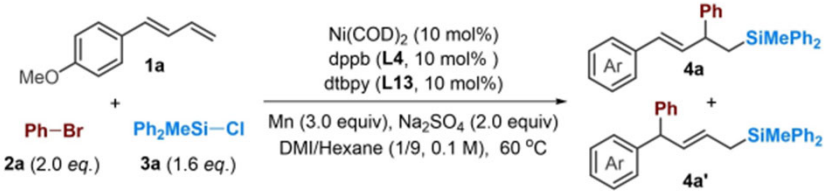
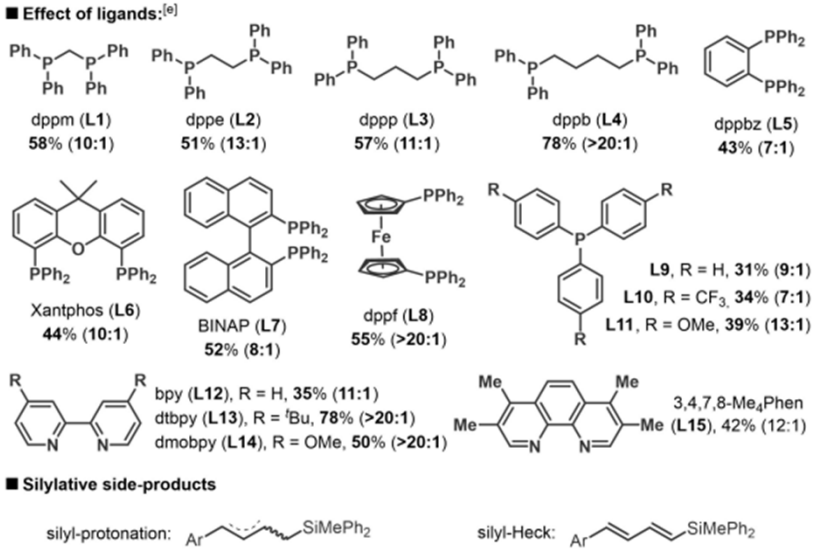
Part 6.交叉亲电试剂C-Si偶联反应



entry	change of conditions	4a (%)	4a/4a'
1	none	78 (74)[b]	>20:1
2	$NiCl_2$	58	5:1
3	$NiBr_2$	56	4:1
4[c]	no dtbpy	31	8:1
5[d]	no dppb	5	-
6	hexane	0	-
7	DMI	45	16:1
8	no Na_2SO_4	70	>20:1
9	Zn instead of Mn	55	15:1
10	no Ni or Mn	0	-
11	Ph-Cl instead of PhBr	36	15:1
12	Ph-I instead of PhBr	34	8:1
13	Ph-OTf instead of PhBr	42	6:1



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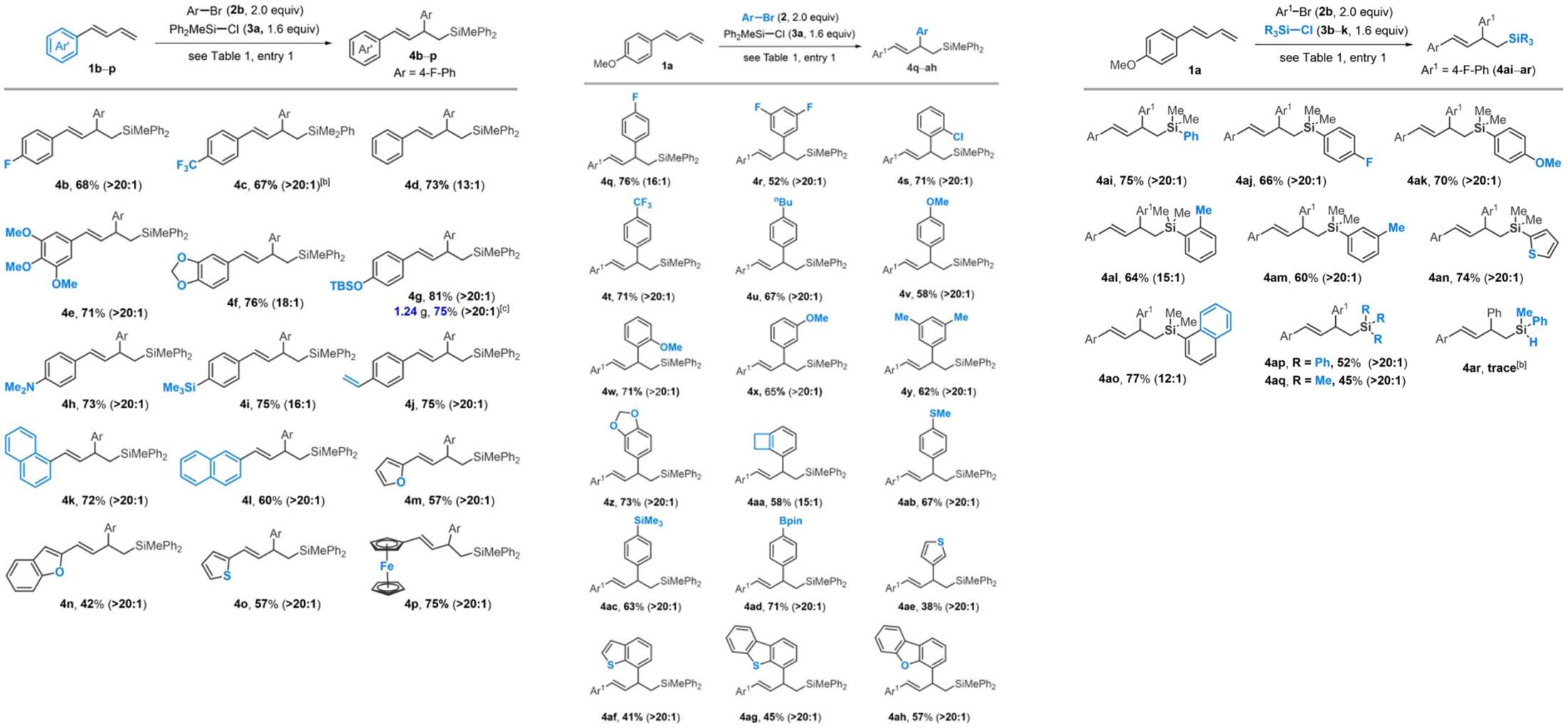
Part 6.交叉亲电试剂C-Si偶联反应



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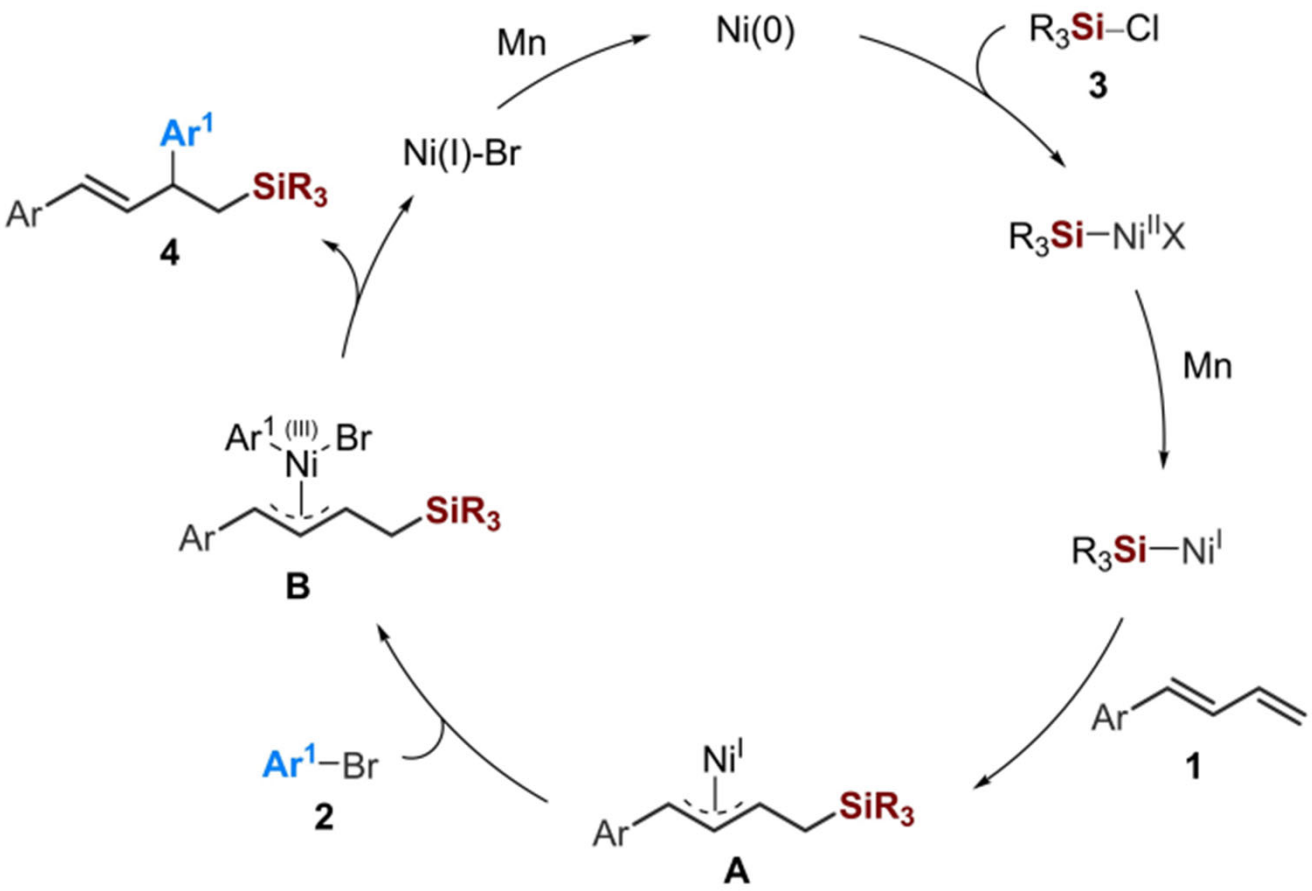

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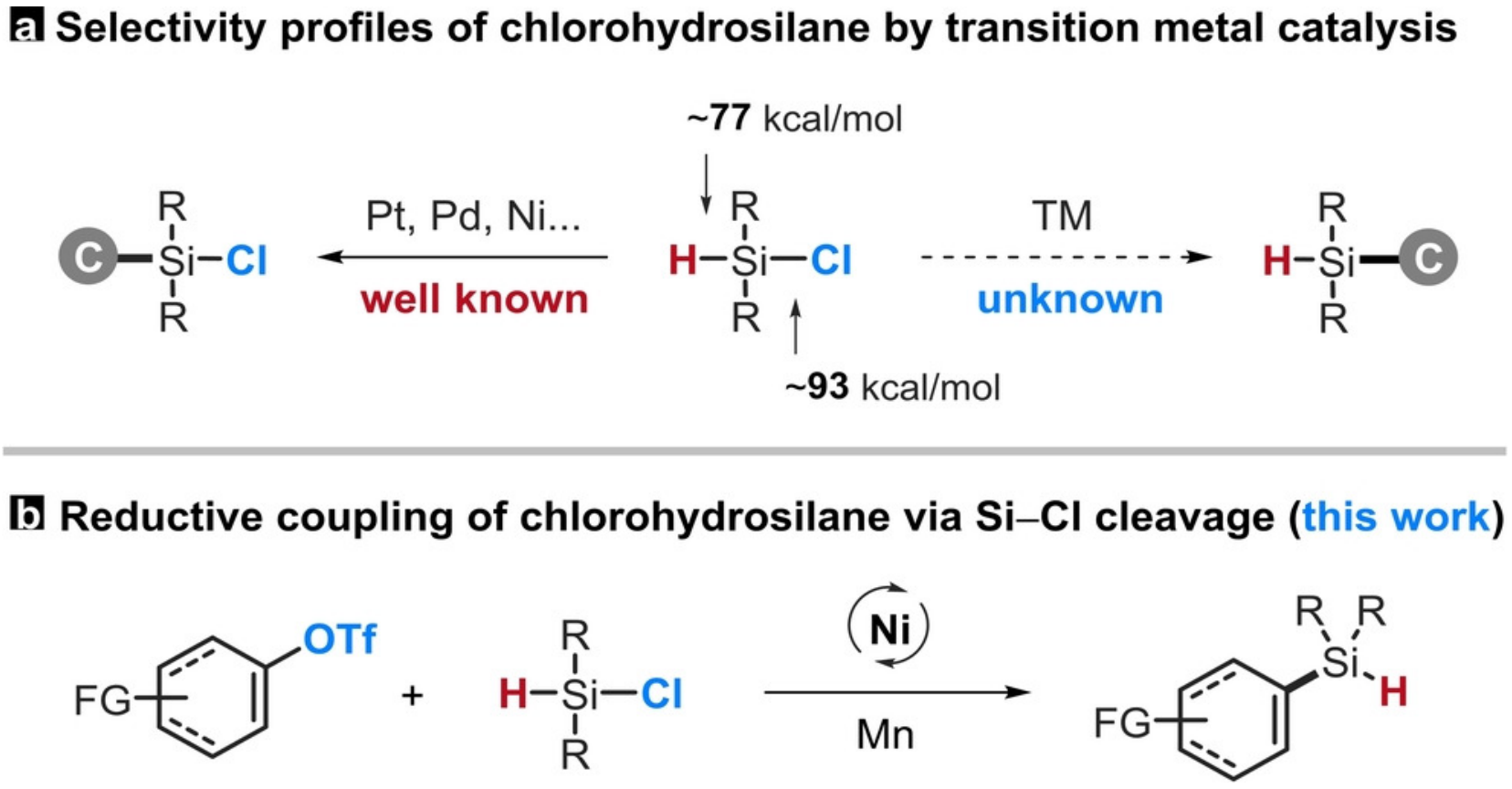

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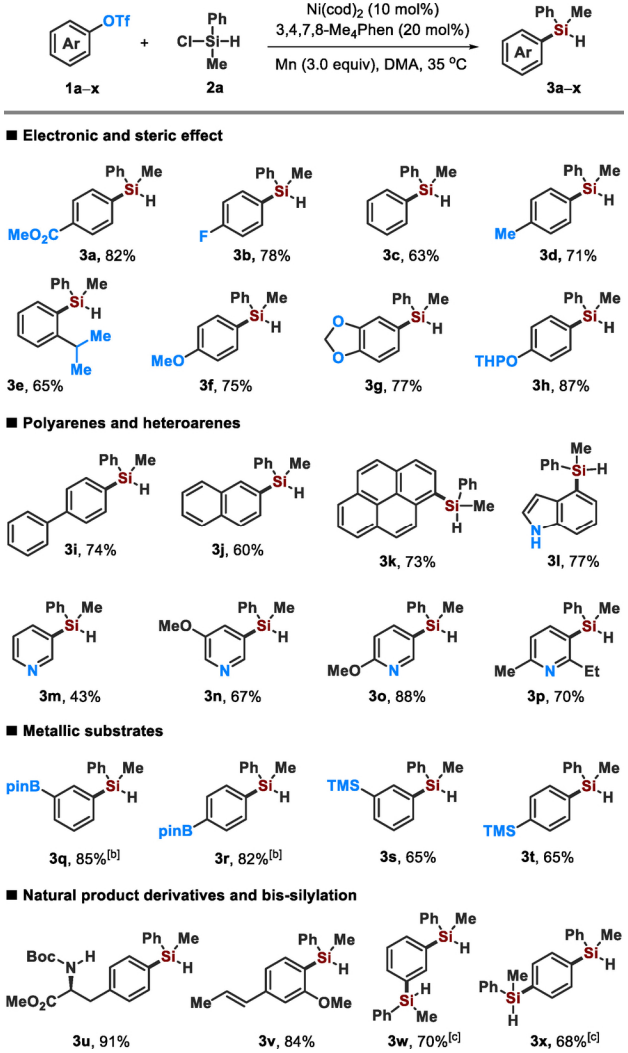

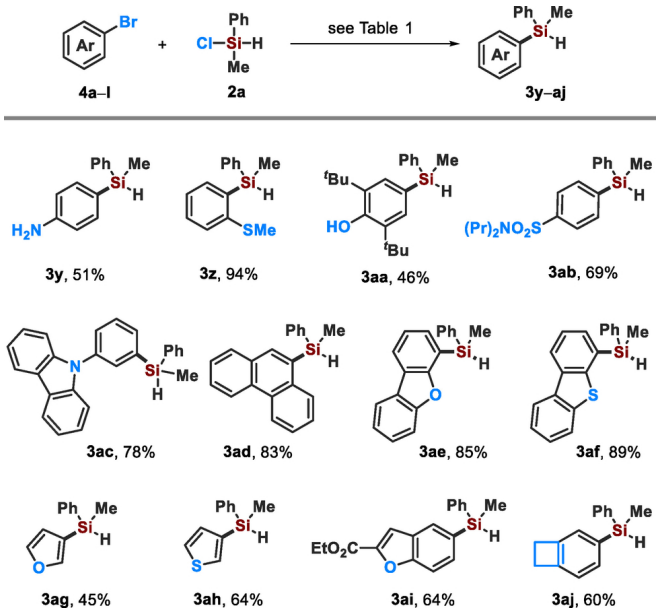

Si无需烯丙基即可反应

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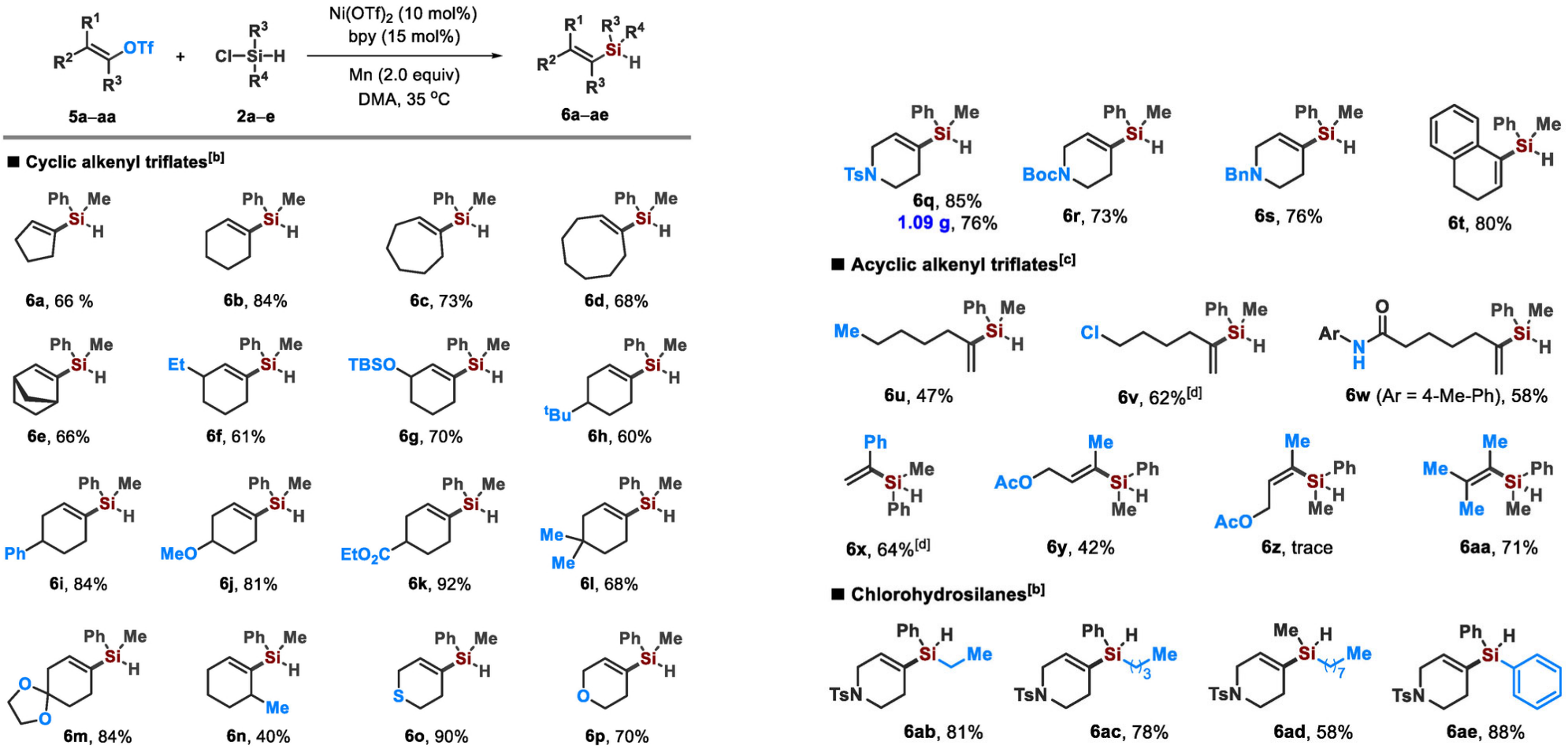

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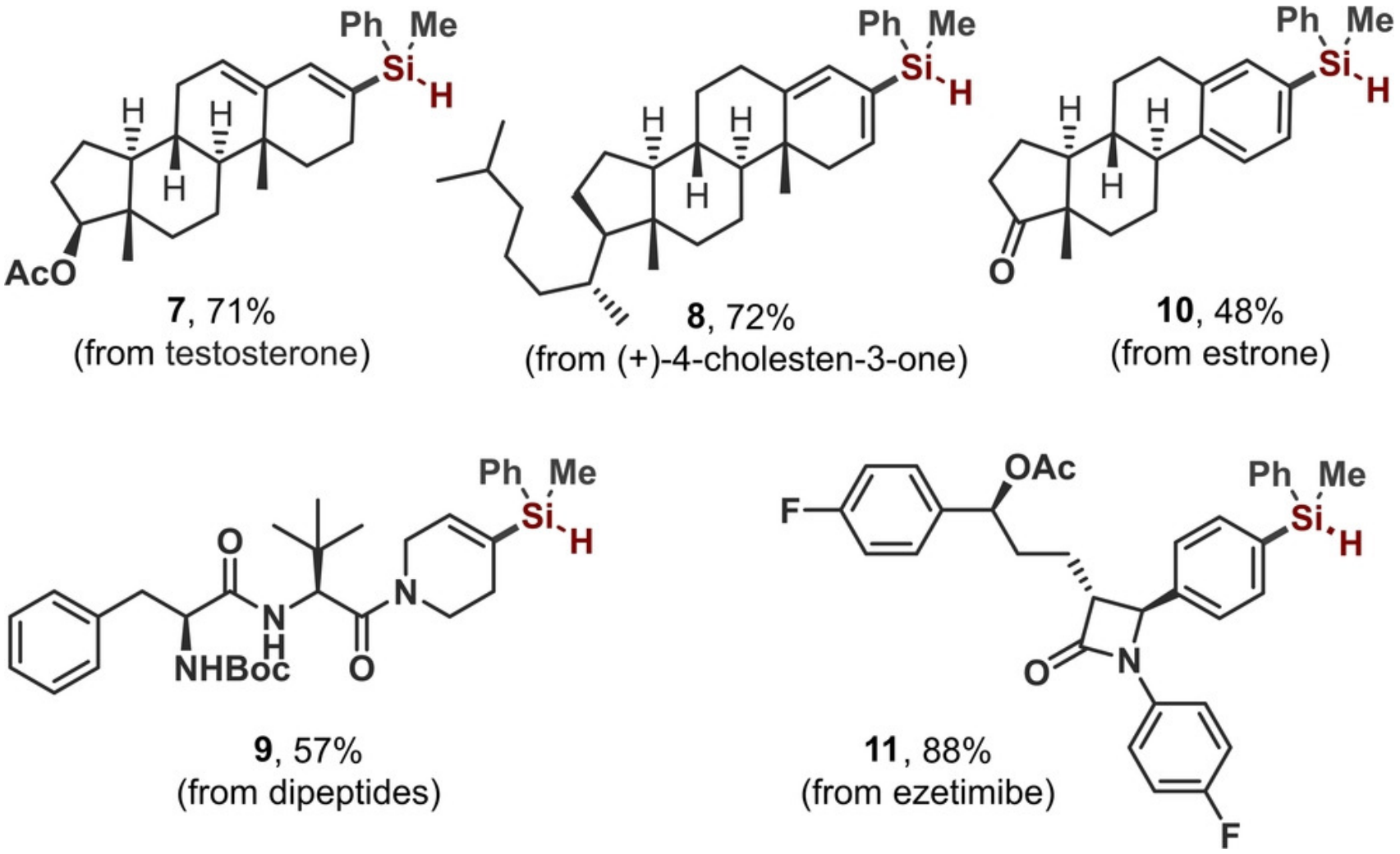

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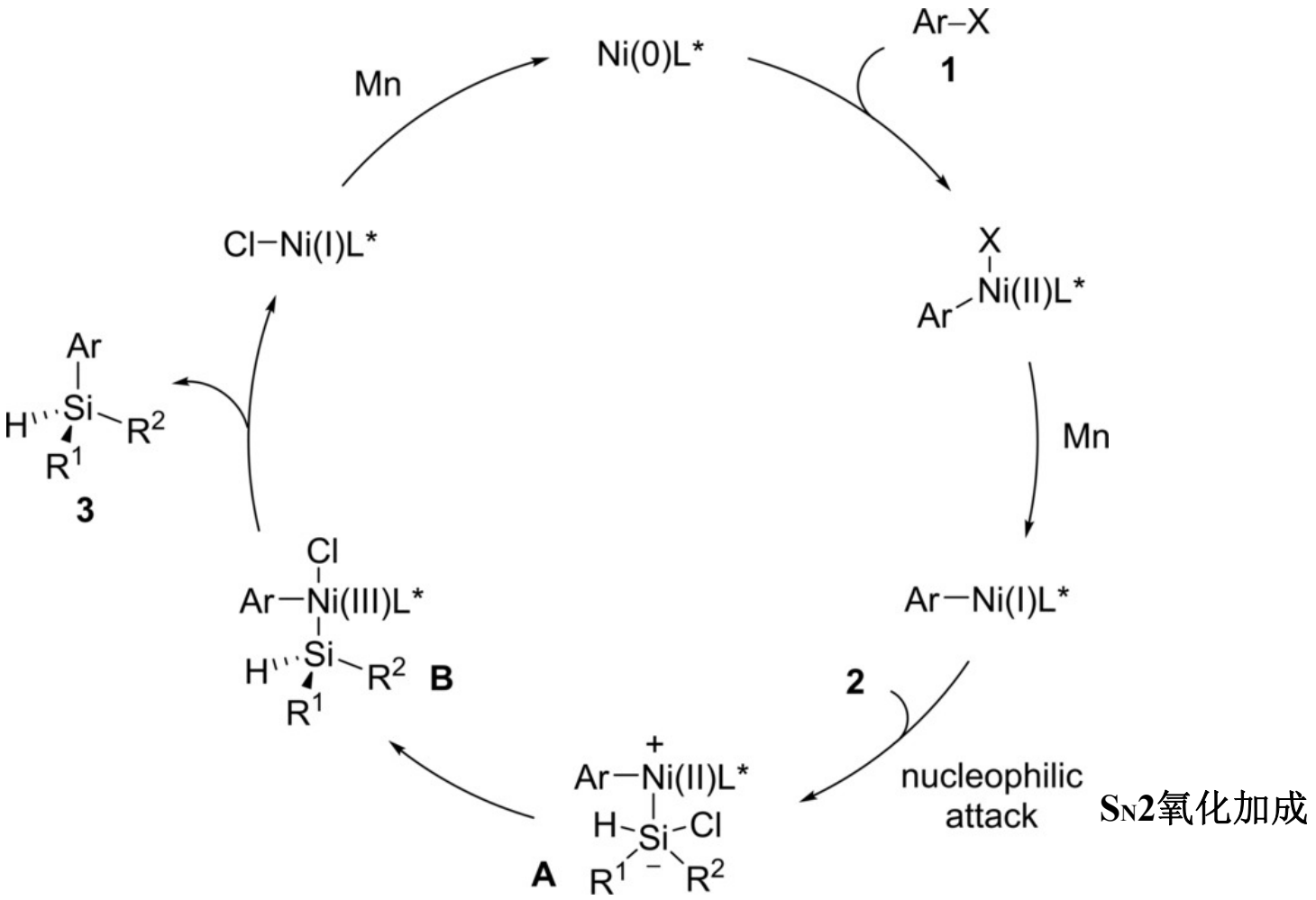

S_N2氧化加成

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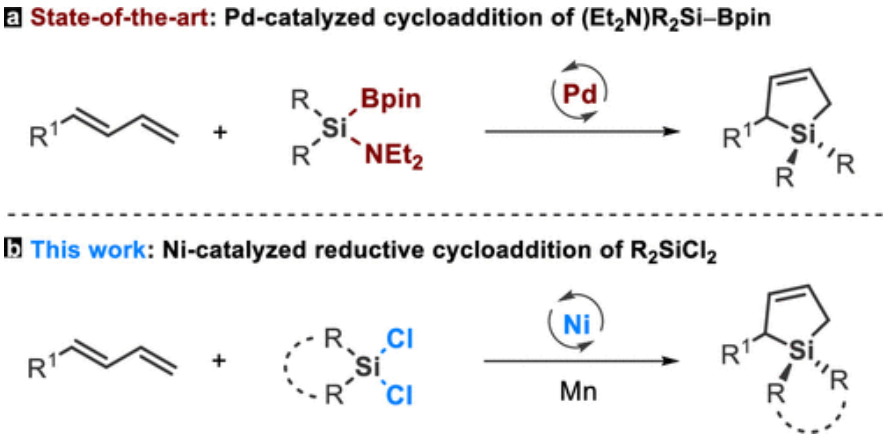

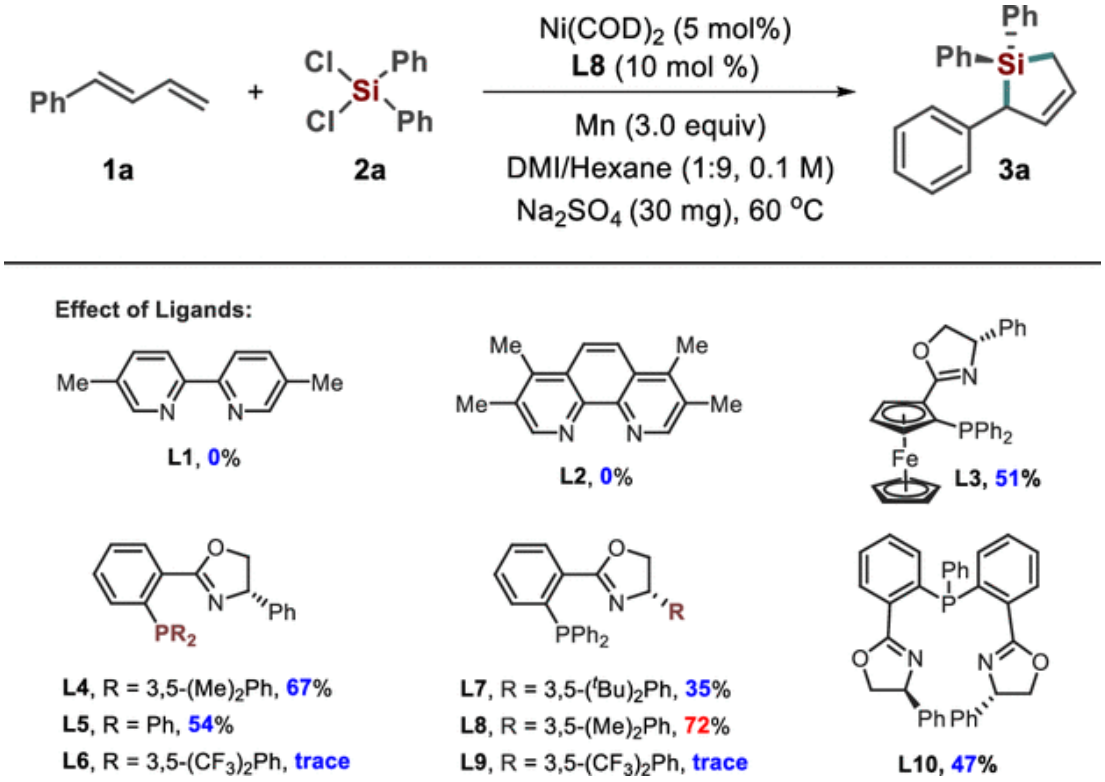

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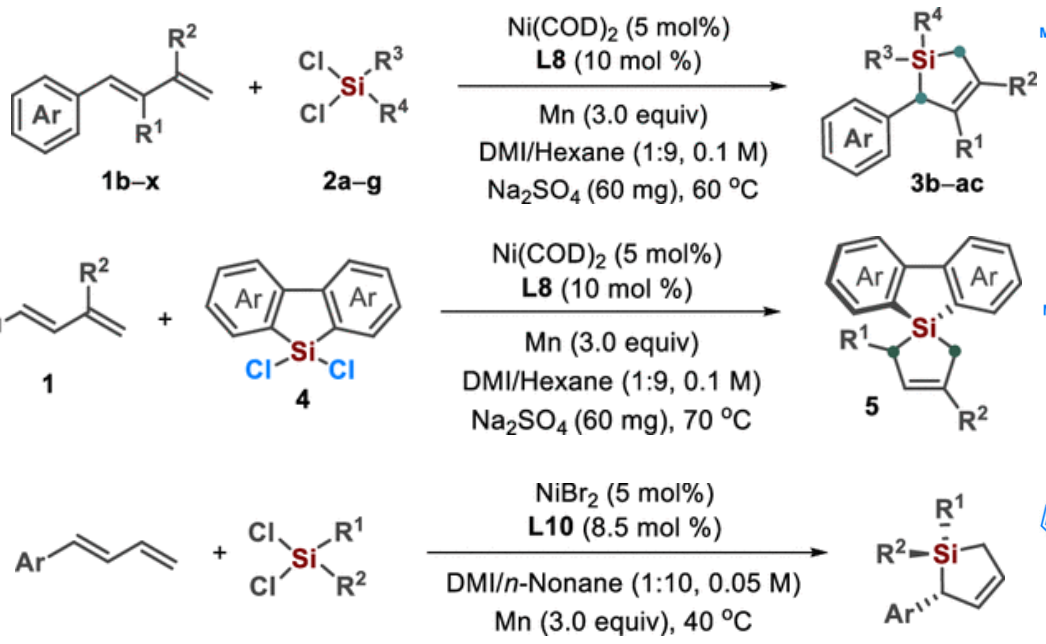

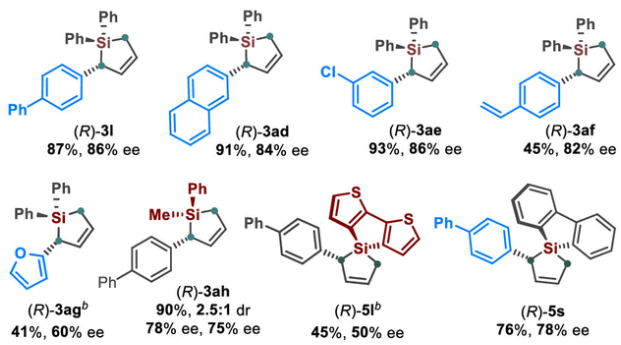

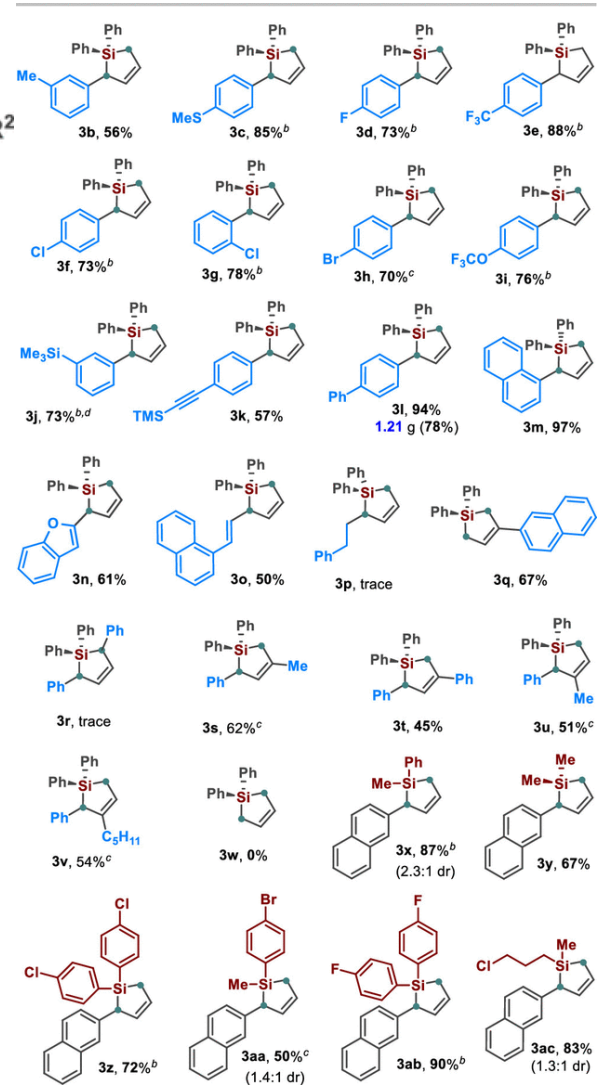

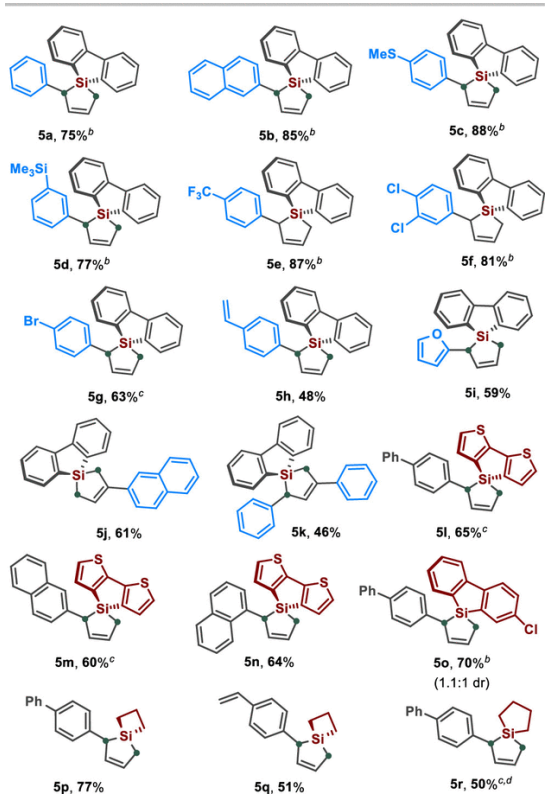

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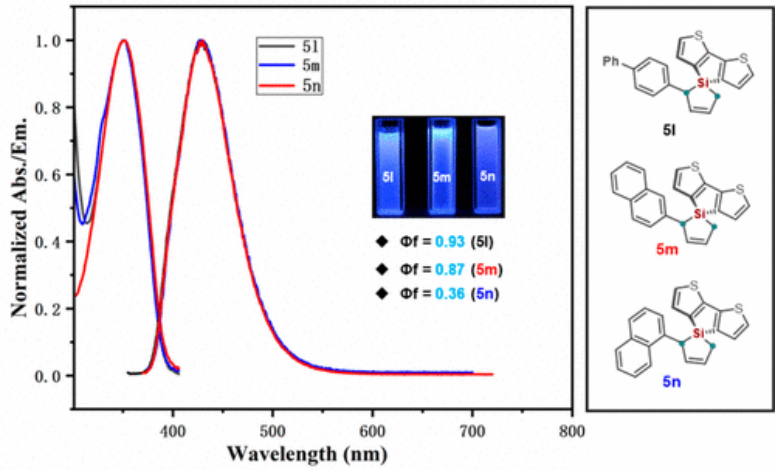

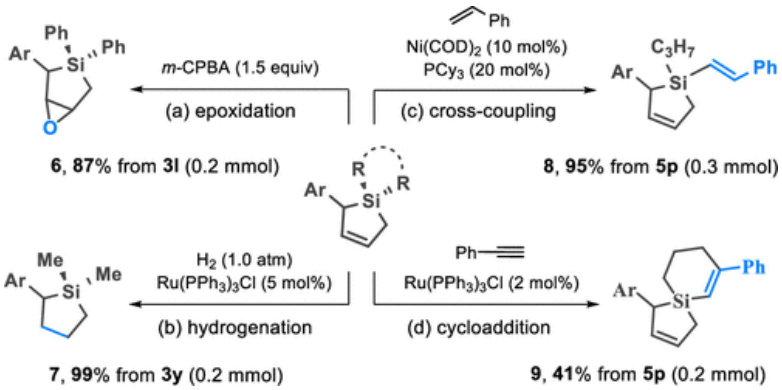

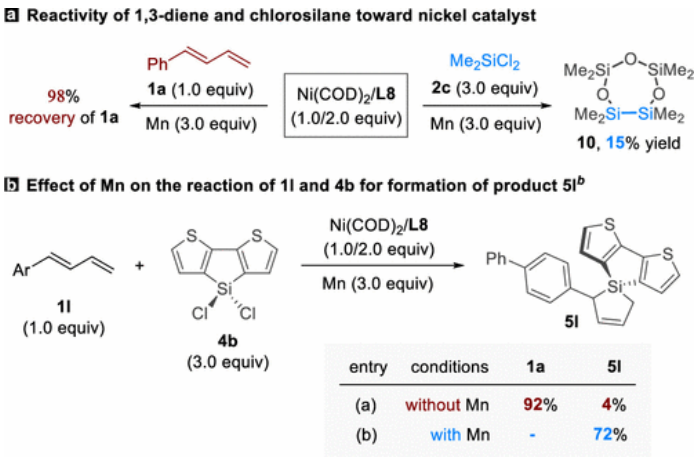

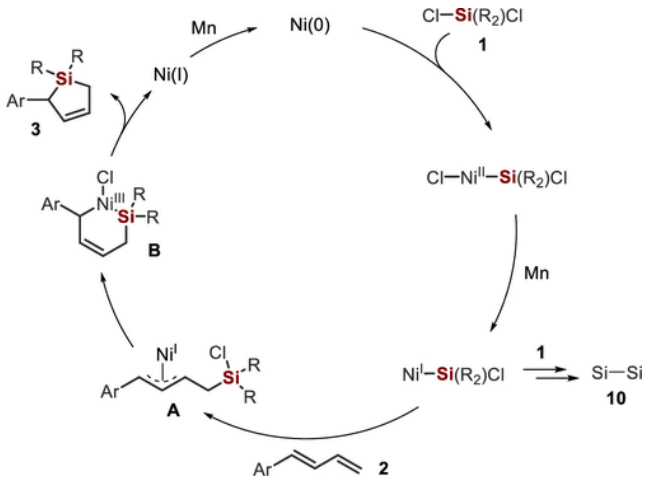

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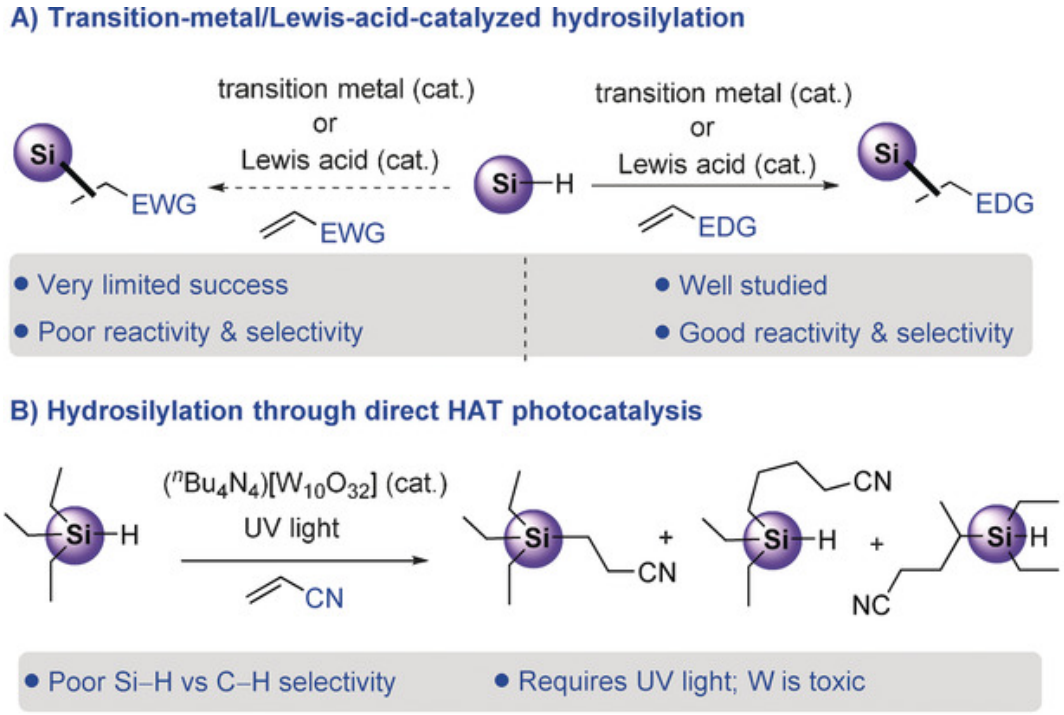
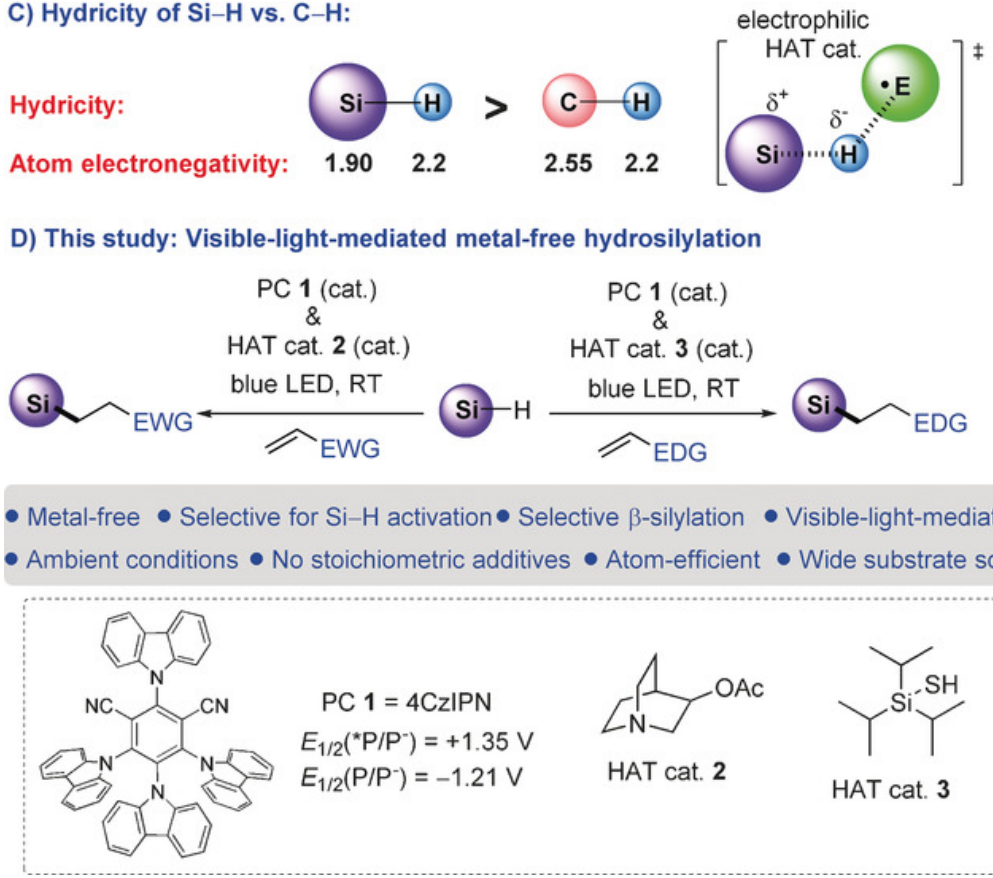
Part 7.光催化产生Si自由基与C（sp2）偶联

富电子烯烃能反应，缺电子烯烃很难反应



选择性差



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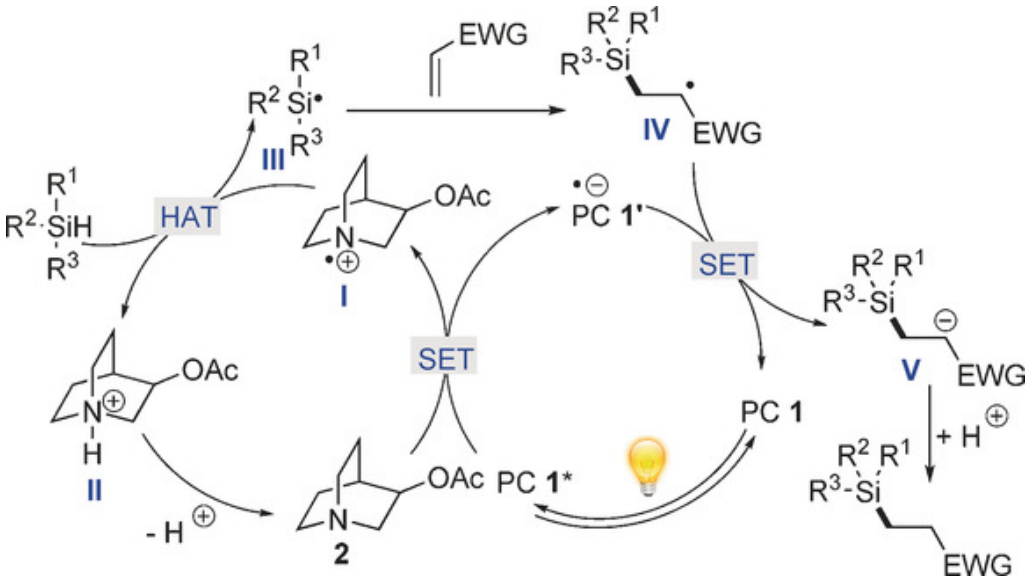

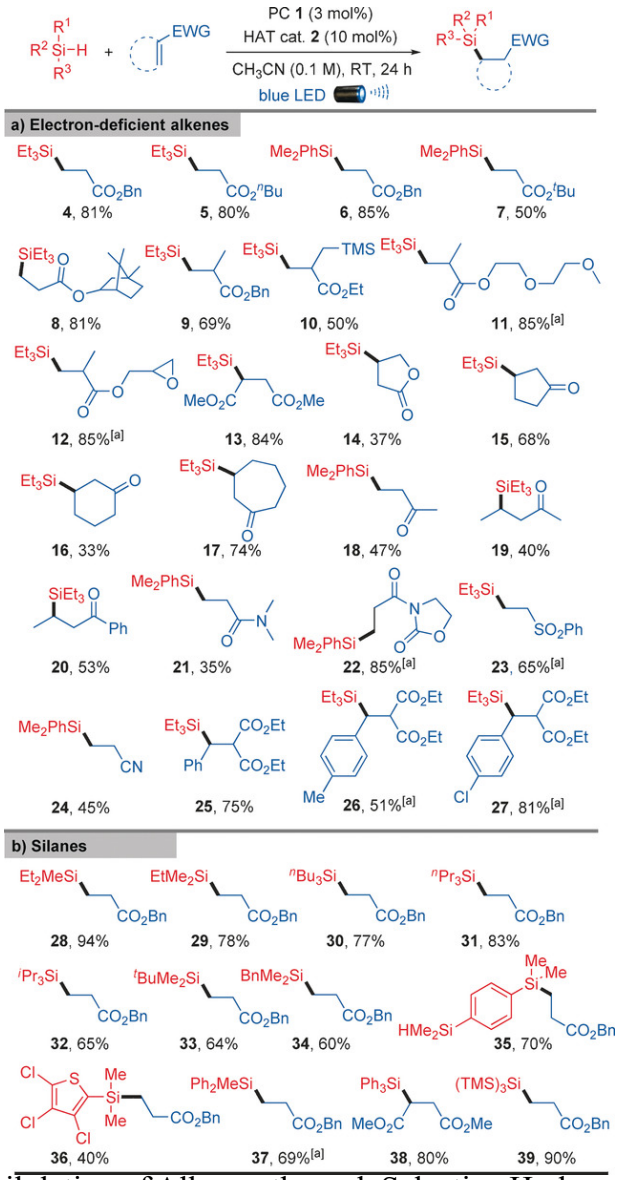

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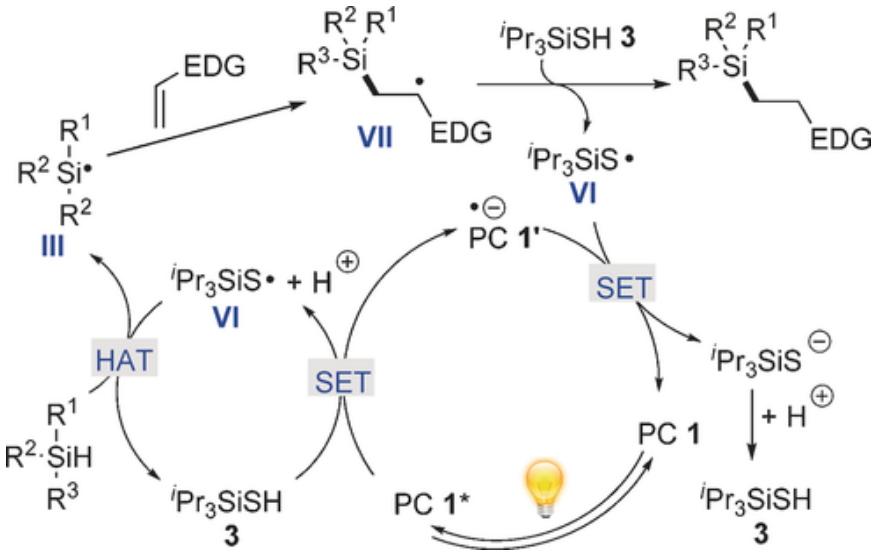

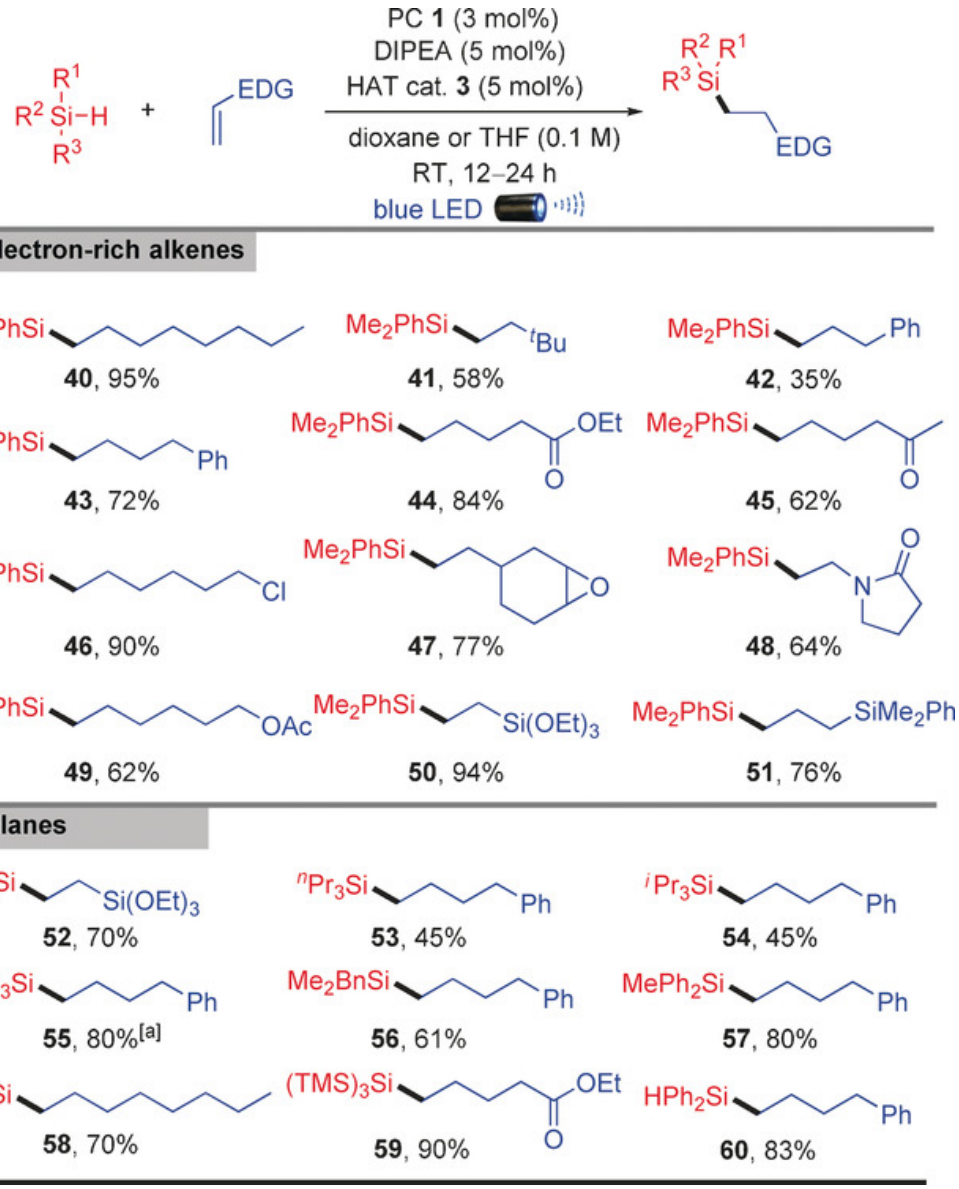

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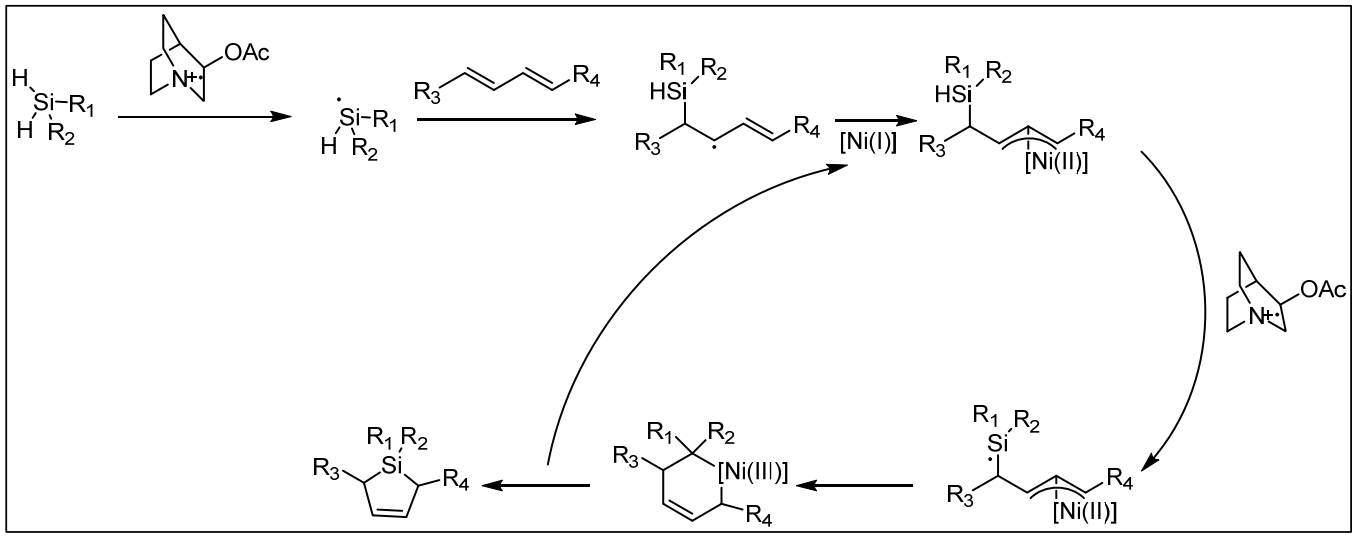
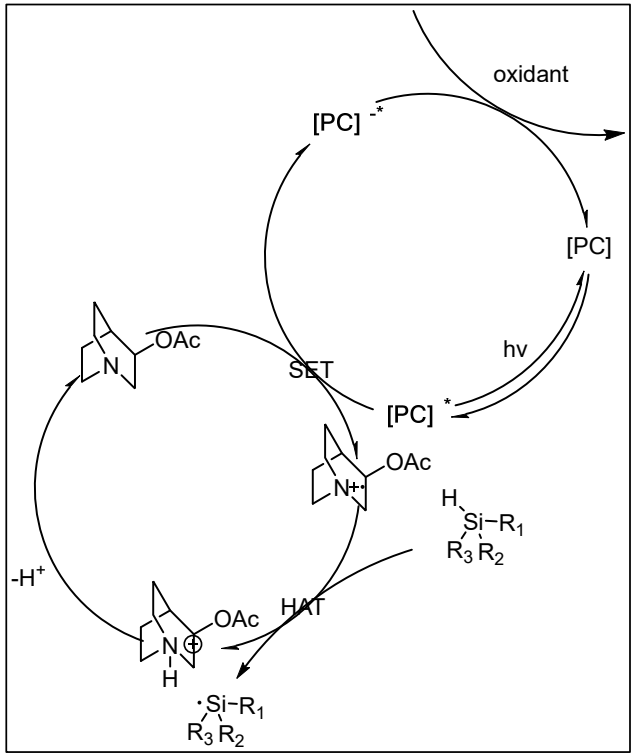
Part 8.proposal





Thanks For Listening