Desymmetrical Synthesis of Chiral Silicon Compounds Catalyzed by Transition Metal

Reporter：Sanliang Li
Supervisor: Dr. Junliang Zhang

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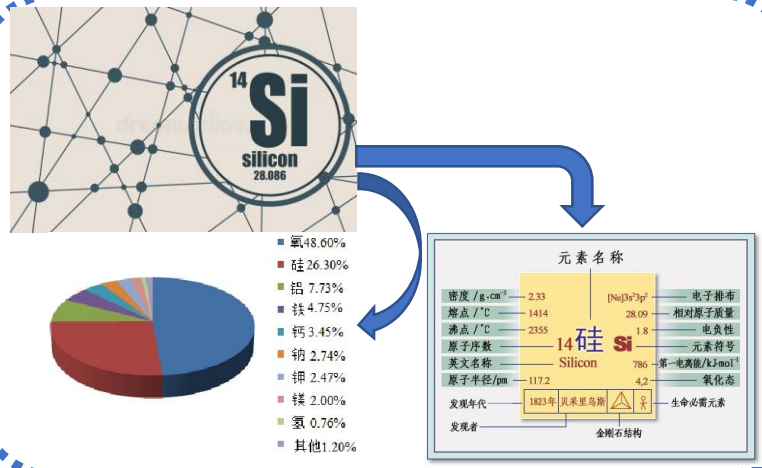
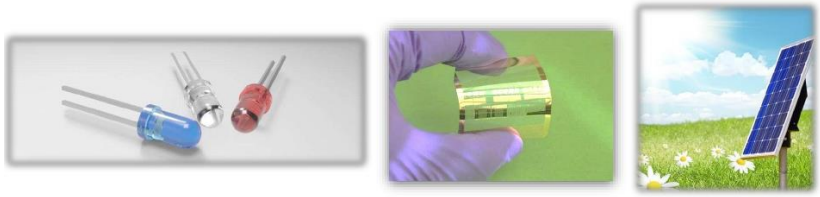
Introduction



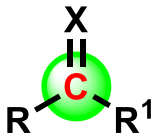


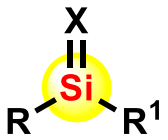
Achiral aryl silicon material

Chiral organic silicon material ⇨ **Circularly polarized luminescence (CPL) spectrum**

Other applications remain to be developed

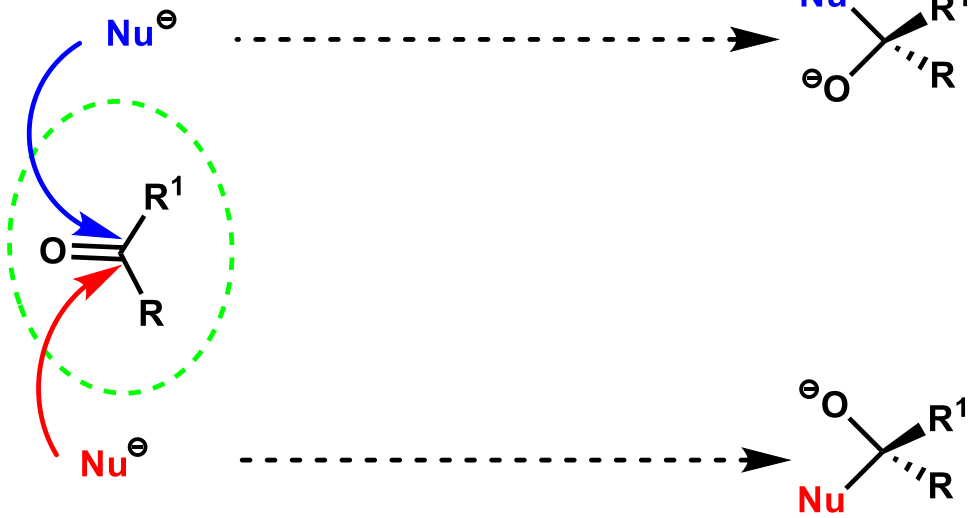
Difficulties in Synthesising Chiral Silicon Compounds





X = C, N, O, P, S

Atomic radium:	117 pm	77 pm
Electronegativity:	1.90	2.55
	stable	unstable



C. Strohmann, et al. *Eur. J. Inorg. Chem*. **2016**, 2868

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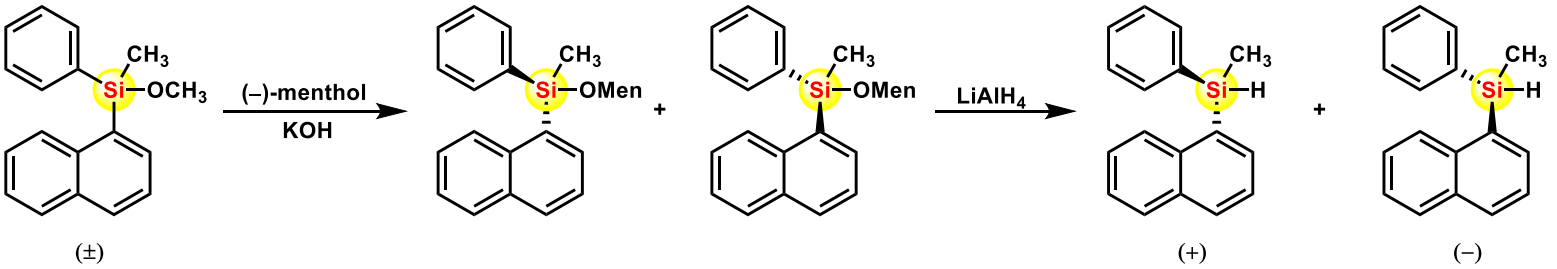
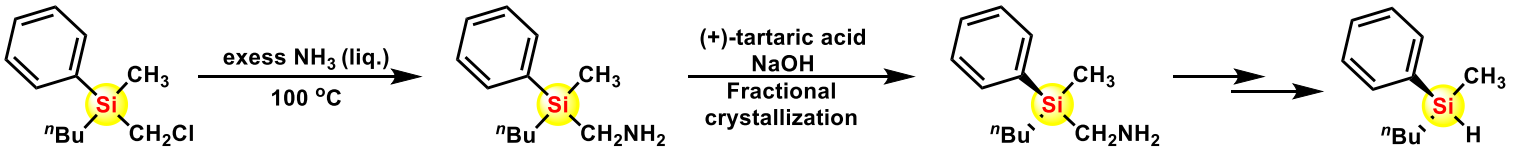
Chiral Resolution



K. W. Michael, et al. *J. Am. Chem. Soc.* **1964**, *86*, 3271



H. Nohira, Bull. et al. *Chem. Soc. Jpn*. **1980**, *53*, 789

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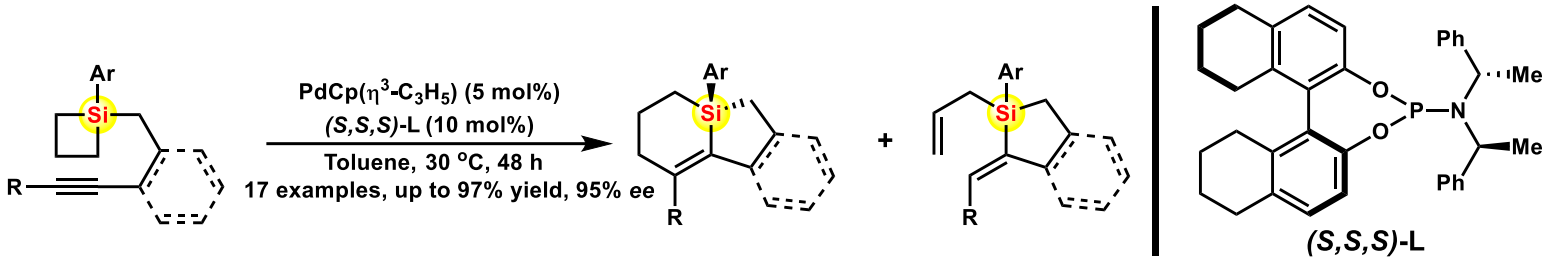
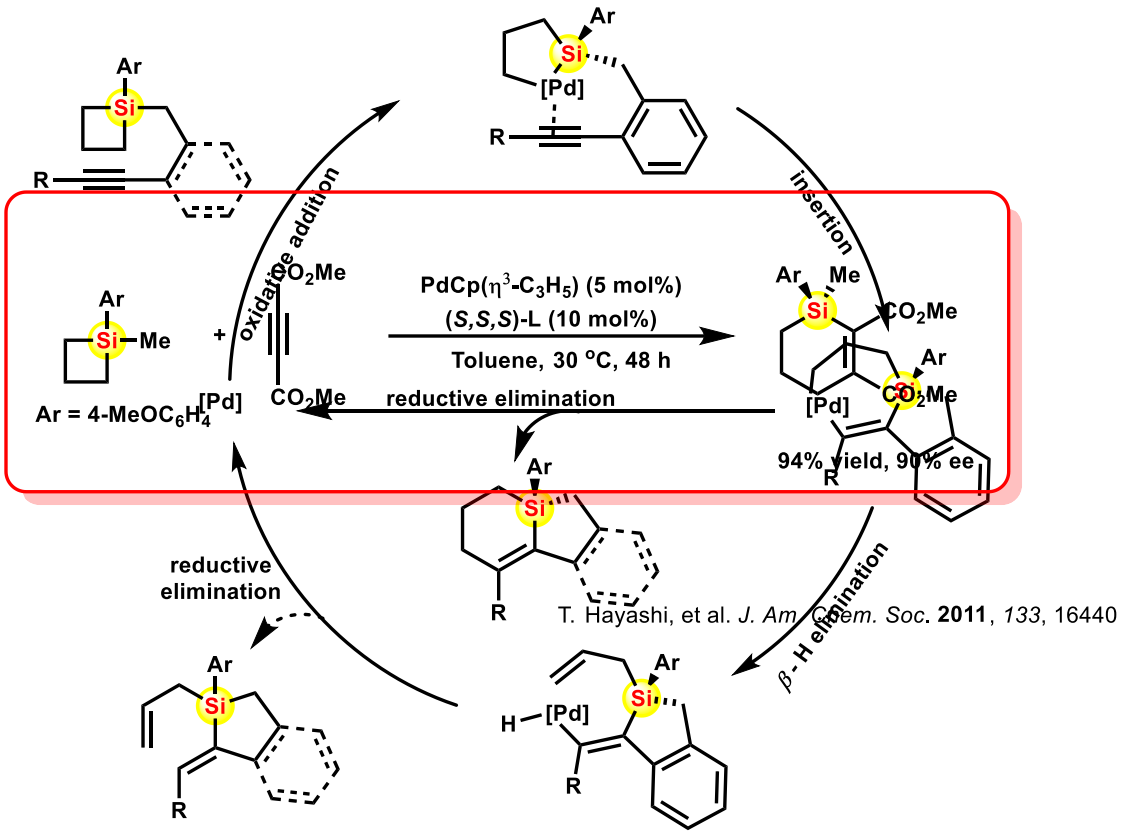
Desymmetrical Reaction of Non-dihydrosilane

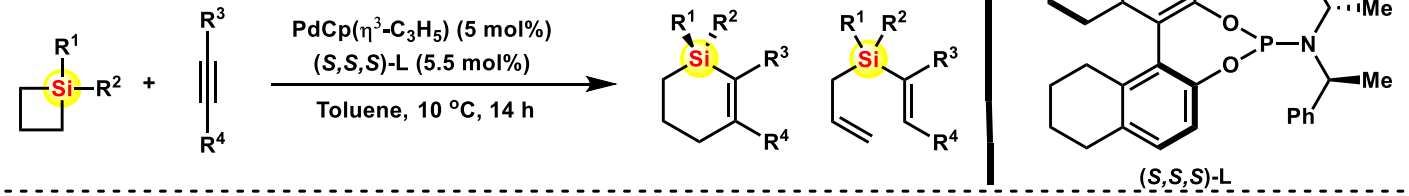


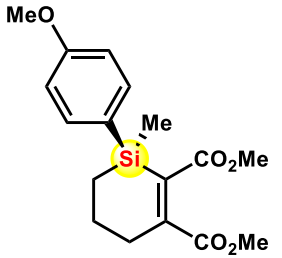


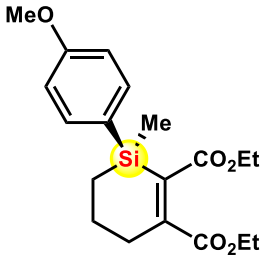
T. Hayashi, et al. *J. Am. Chem. Soc.* **2011**, *133*, 16440

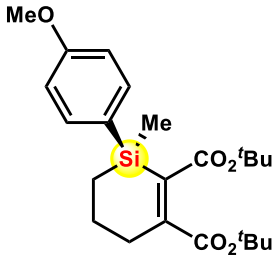
T. Hayashi, et al. *J. Am. Chem. Soc.* **2011**, *133*, 16440

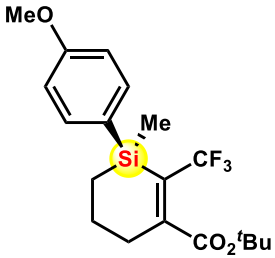
Desymmetrical Reaction of Non-dihydrosilane

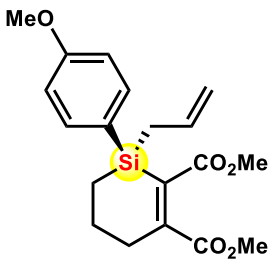


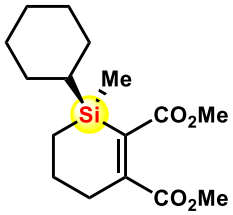

95%, 92% *ee*

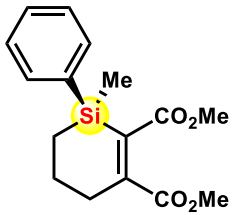

90%, 90% *ee*

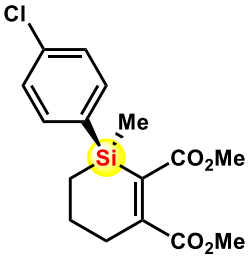

85%, 91% *ee*

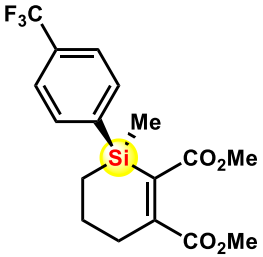

70%, 88% *ee*

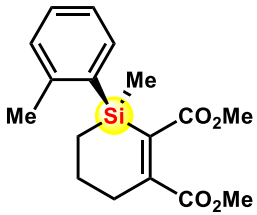

91%, 94% *ee*

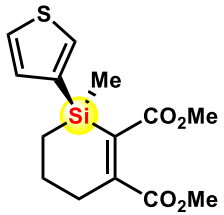

83%, 84% *ee*

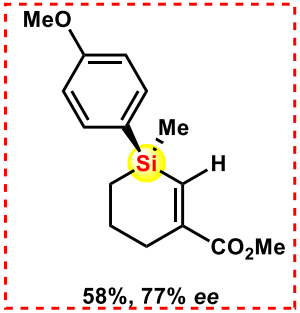

95%, 92% *ee*


97%, 92% *ee*


95%, 92% *ee*

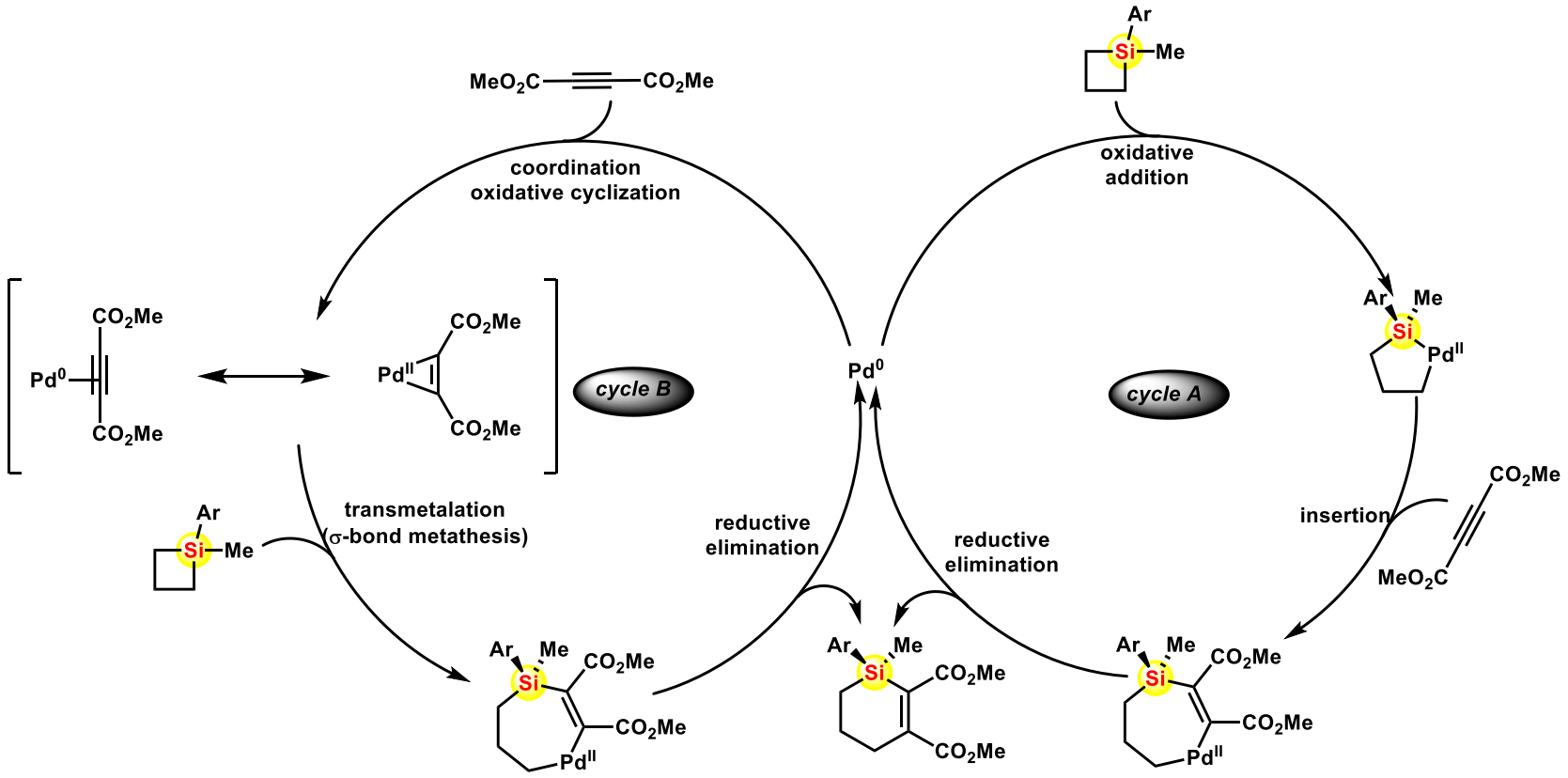

89%, 90% *ee*

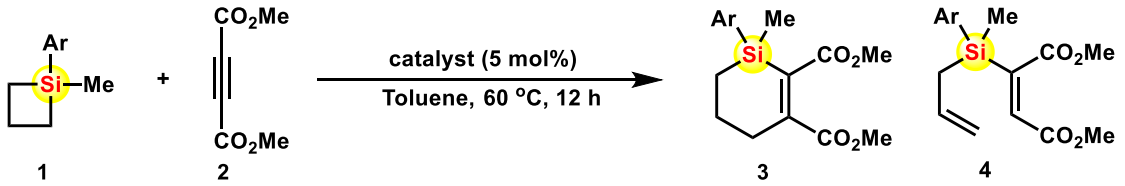

95%, 91% *ee*


58%, 77% *ee*

T. Hayashi, et al. *Org. Lett.* **2012**, *14*, 2902

Desymmetrical Reaction of Non-dihydrosilane





catalyst	3/4	yield of 3
$Pd(PPh_3)_4$	86/14	74%
$Pd(PPh_3)_2(2)$	84/16	82%

T. Hayashi, et al. *Org. Lett*. **2012**, *14*, 2902

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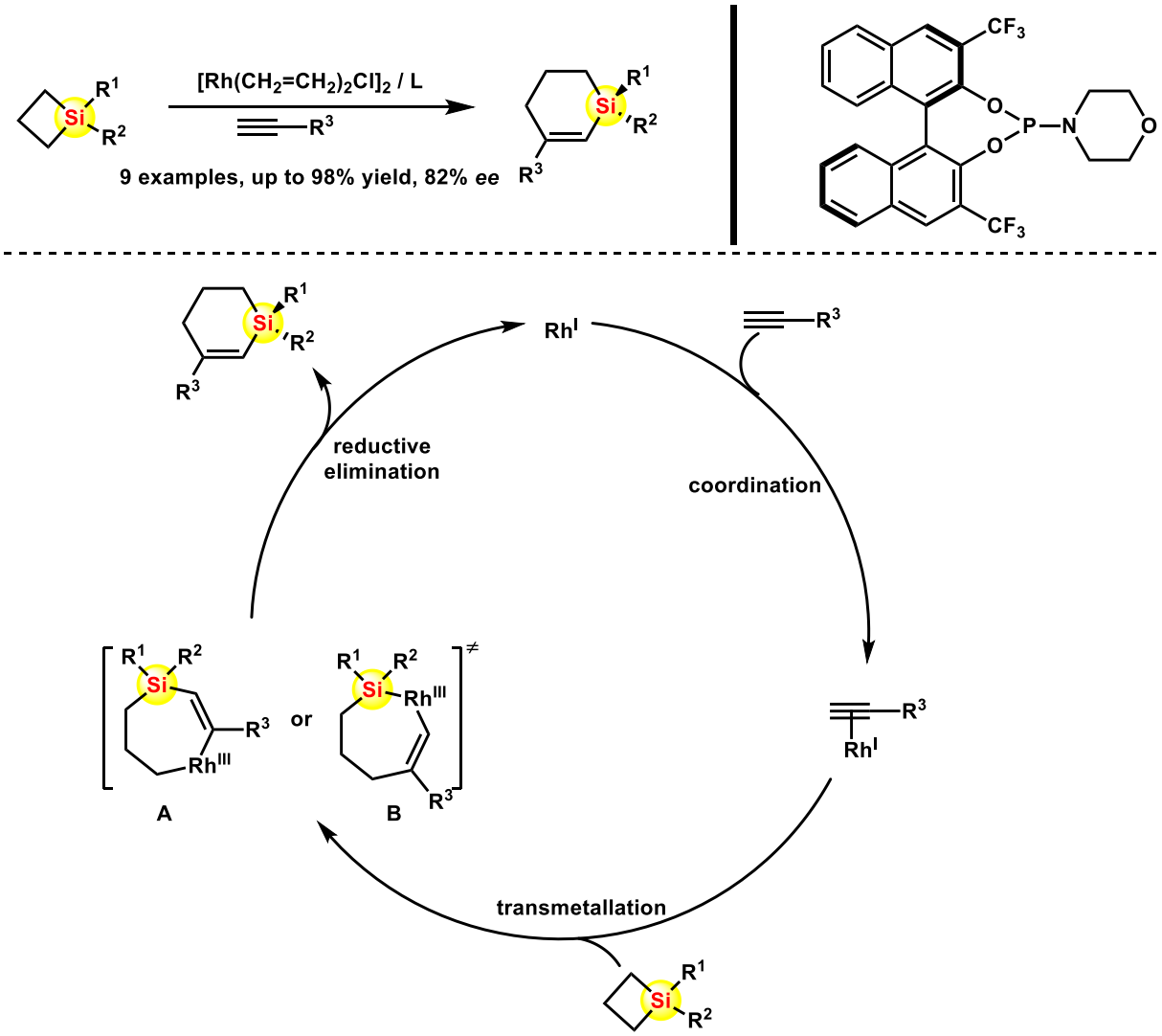
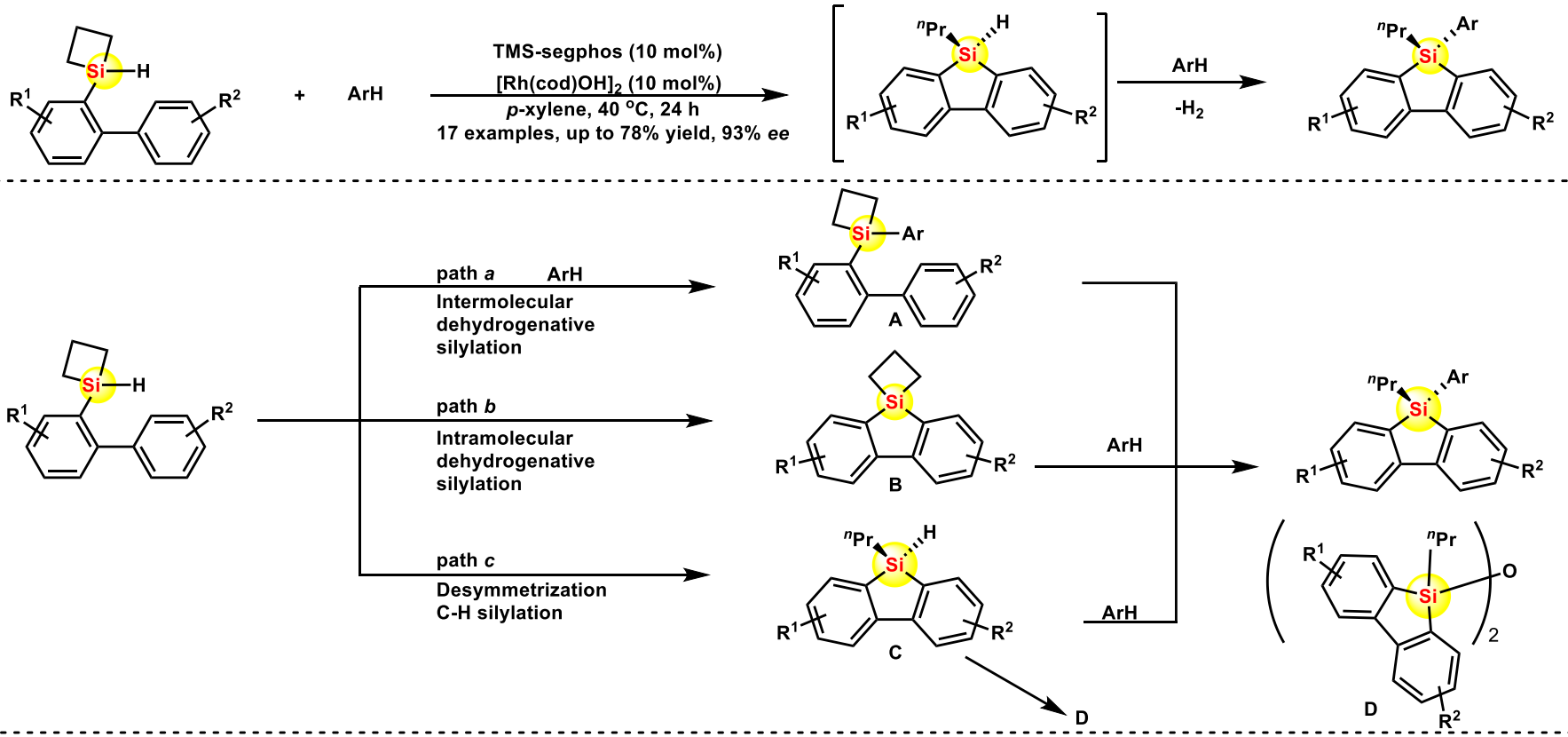
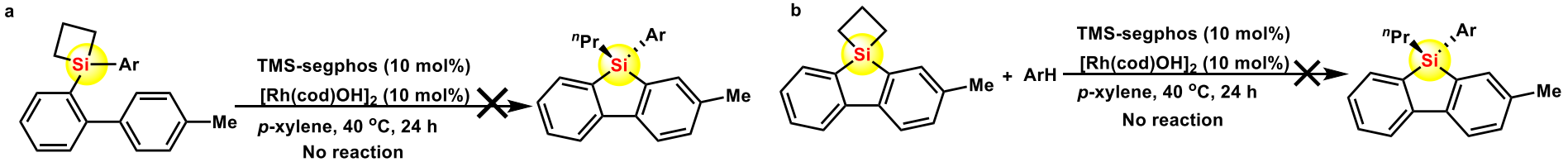
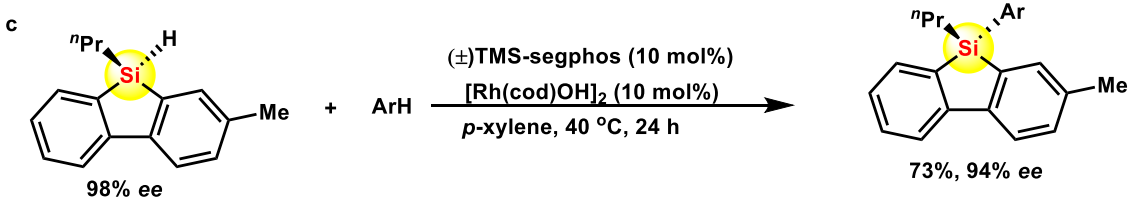


Z. L. Song, et al. *Angew. Chem. Int. Ed*. **2019**, *58*, 4695

Desymmetrical Reaction of Non-dihydrosilane

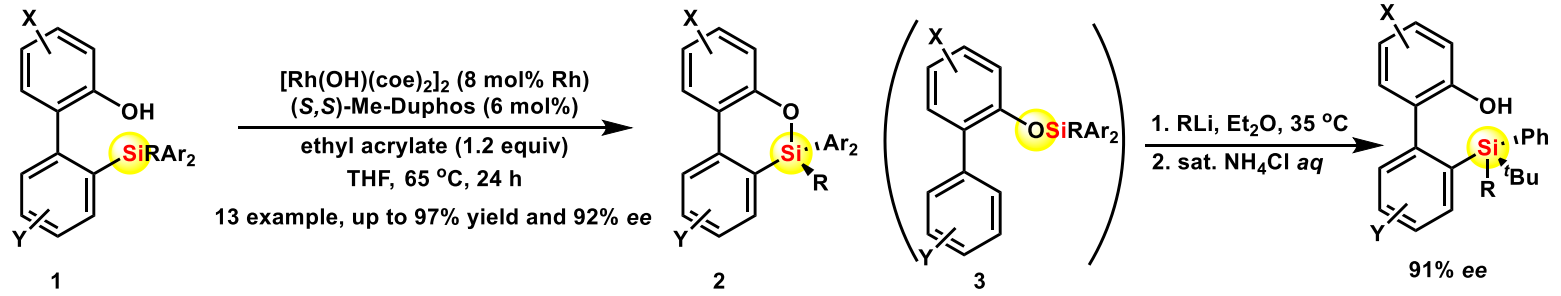




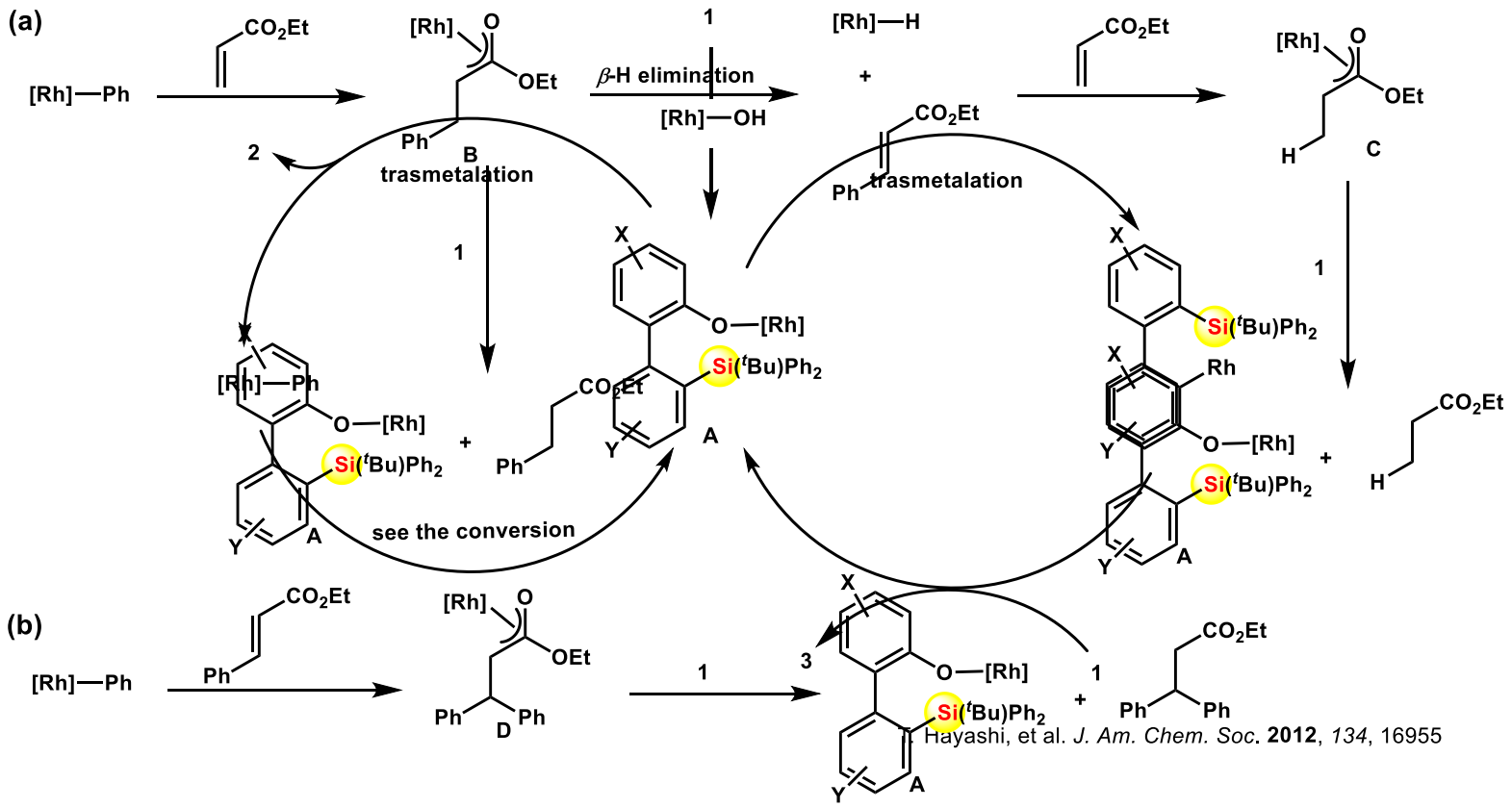


W. He, et al. *Angew. Chem. Int. Ed.* **2016**, *56*, 1125

Desymmetrical Reaction of Non-dihydrosilane



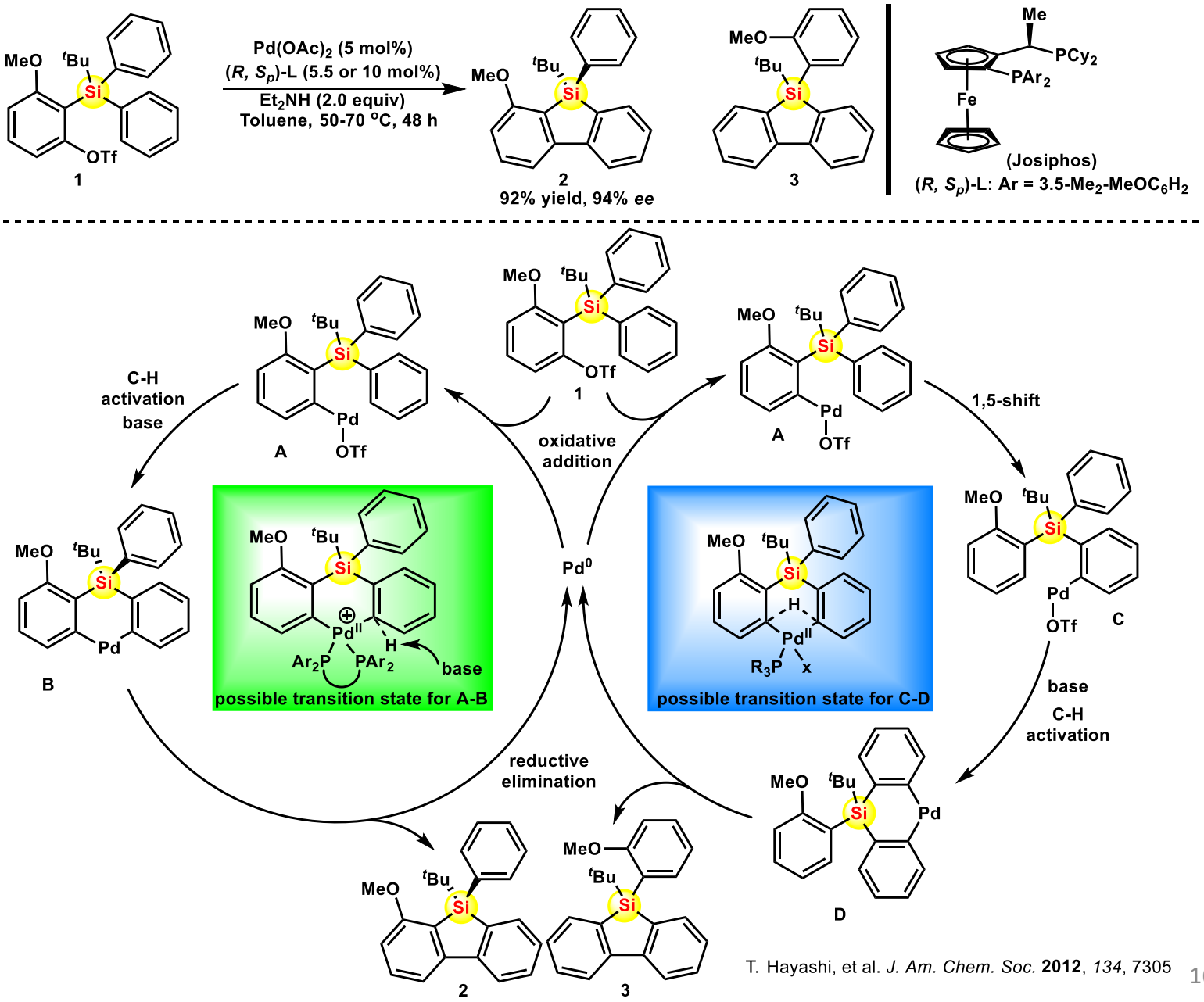
Conversion



Hayashi, et al. *J. Am. Chem. Soc.* **2012**, *134*, 16955

T. Hayashi, et al. *J. Am. Chem. Soc.* **2012**, *134*, 16955

Desymmetrical Reaction of Non-dihydrosilane



T. Hayashi, et al. *J. Am. Chem. Soc.* **2012**, *134*, 7305

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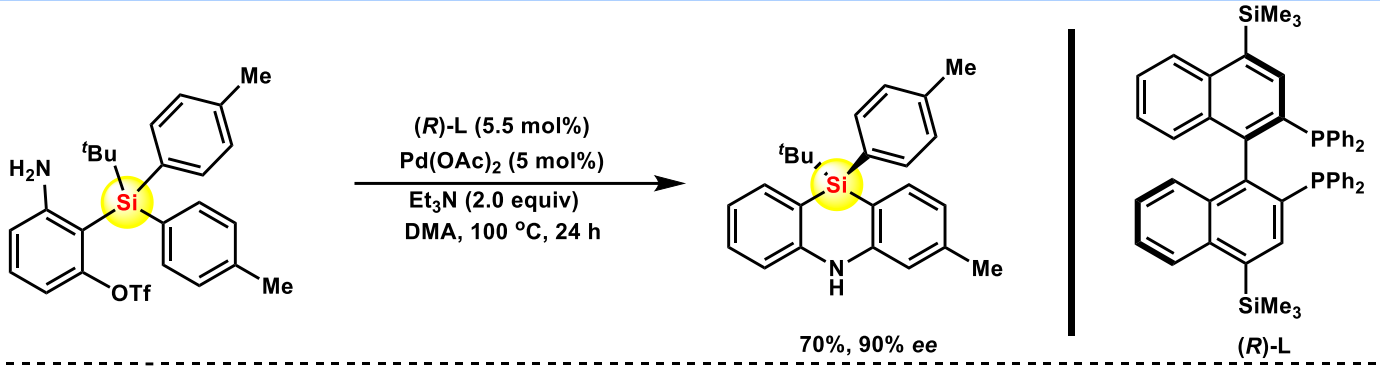

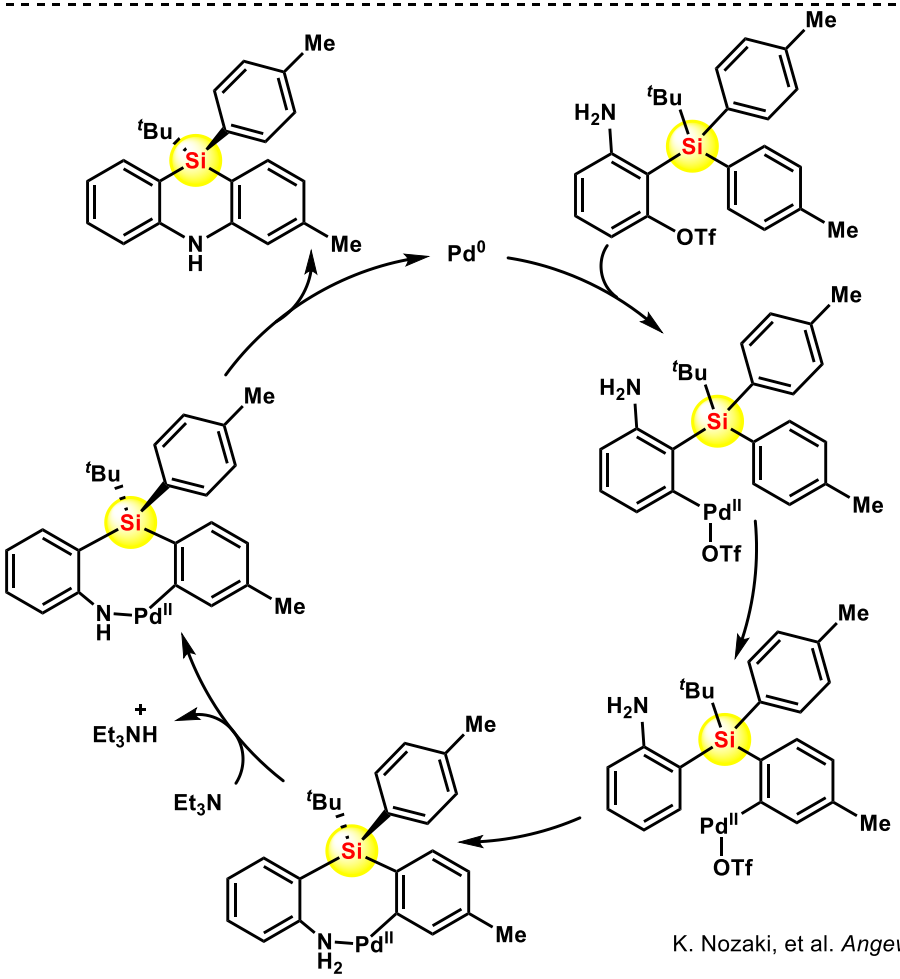

K. Nozaki, et al. *Angew. Chem. Int. Ed.* **2017**, *56*, 9211

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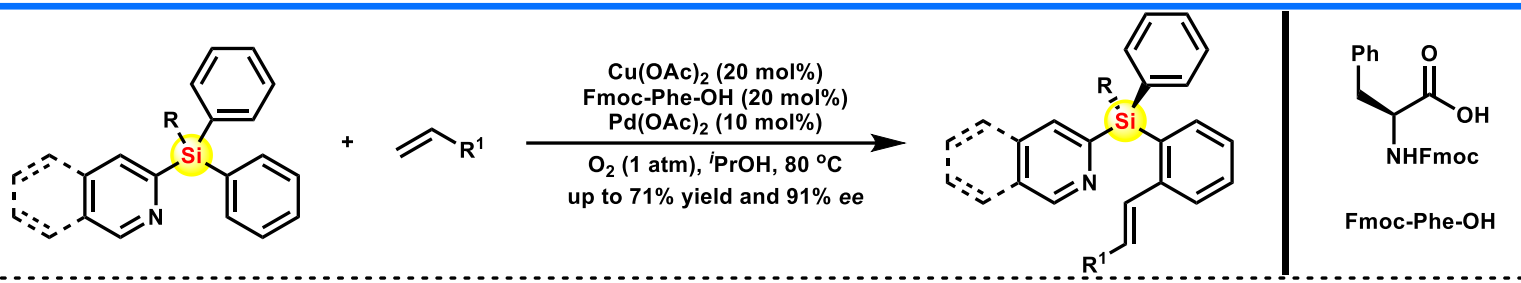

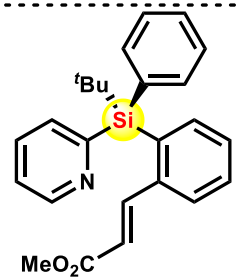

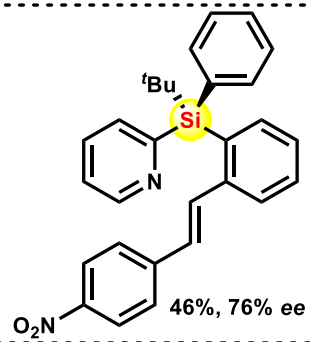

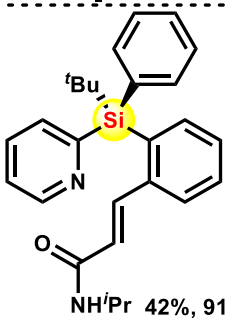

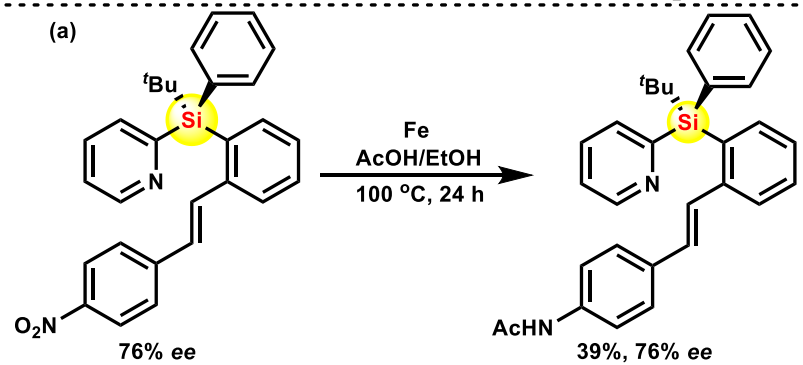

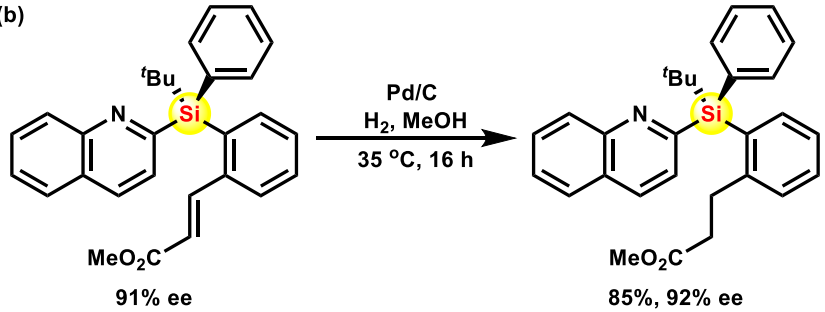

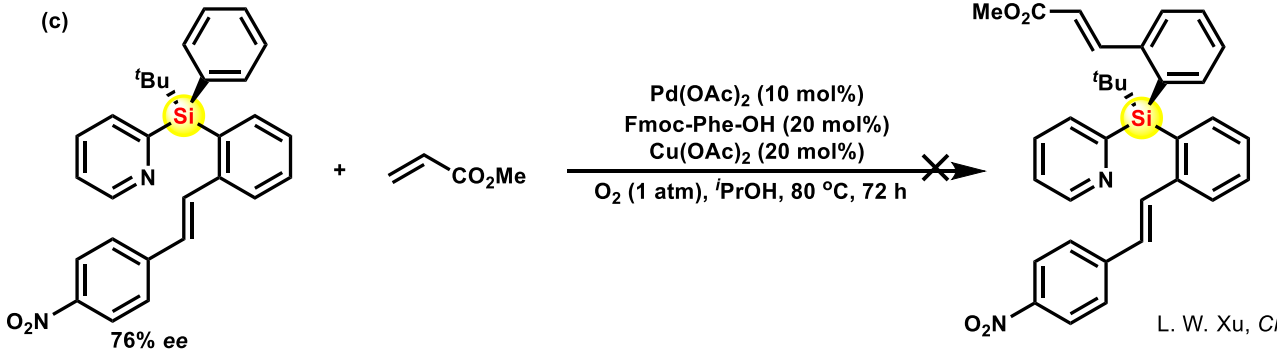

L. W. Xu, *Chem. Asian J.* **2019**, *14*, 2082

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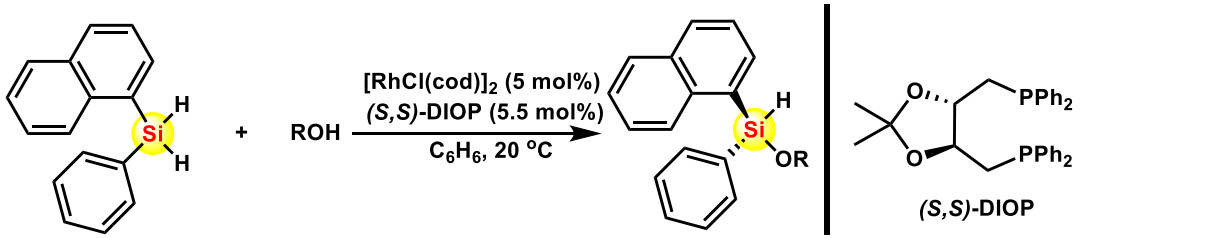
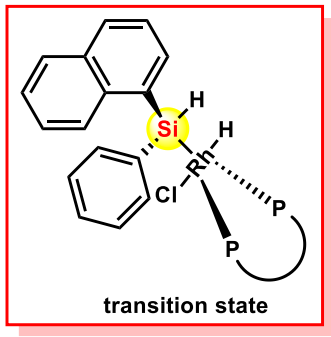
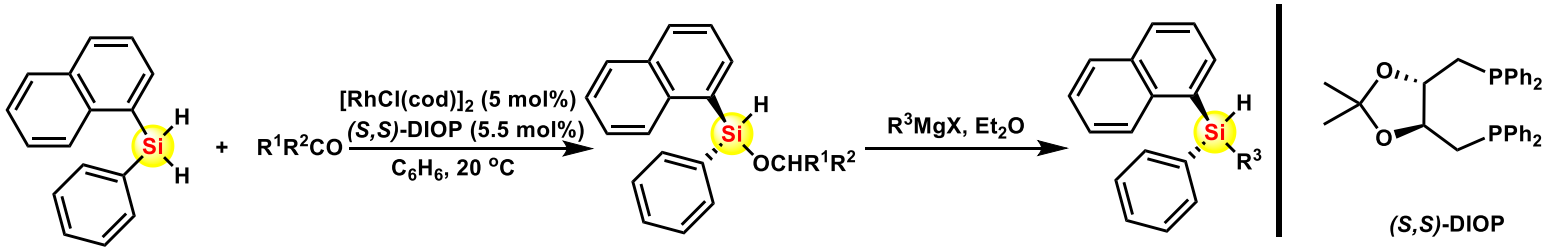


MeOH 3% *ee* ^{t}BuOH 7% *ee* ^{i}PrOH 8% *ee* Ph_2CHOH 19% *ee* cyclohexanol 17% *ee*

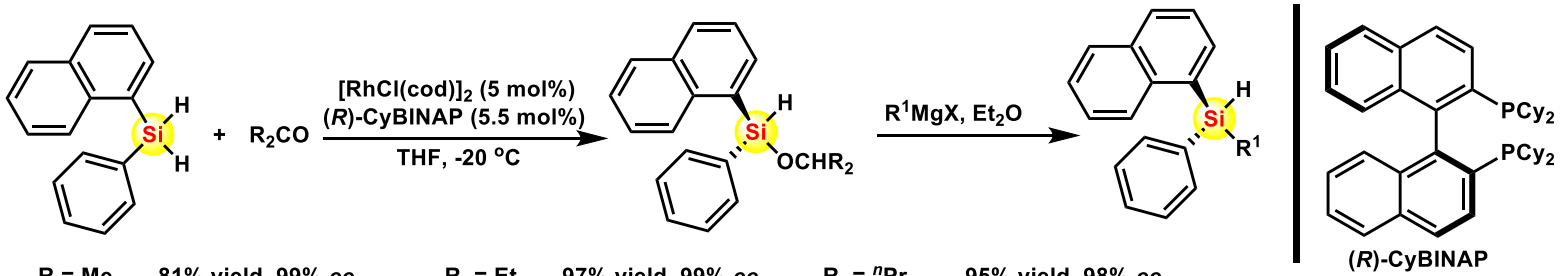


R. J. P. Corriu, et al. *Tetrahedron Lett*. **1973**, *45*, 44



$R^1 = R^2 = Me$ 30% *ee* $R^1 = R^2 = {}^{n}Pr$ 39% *ee* $R^1 = R^2 = Et$ 46% *ee* $R^1 = R^2 = Ph$ 31% *ee* $R^1 = Me, R^2 = Et$ 42% *ee* $R^1 = Ph, R^2 = Me$ 55% *ee* $R^1 = Ph, R^2 = Et$ 42% *ee*

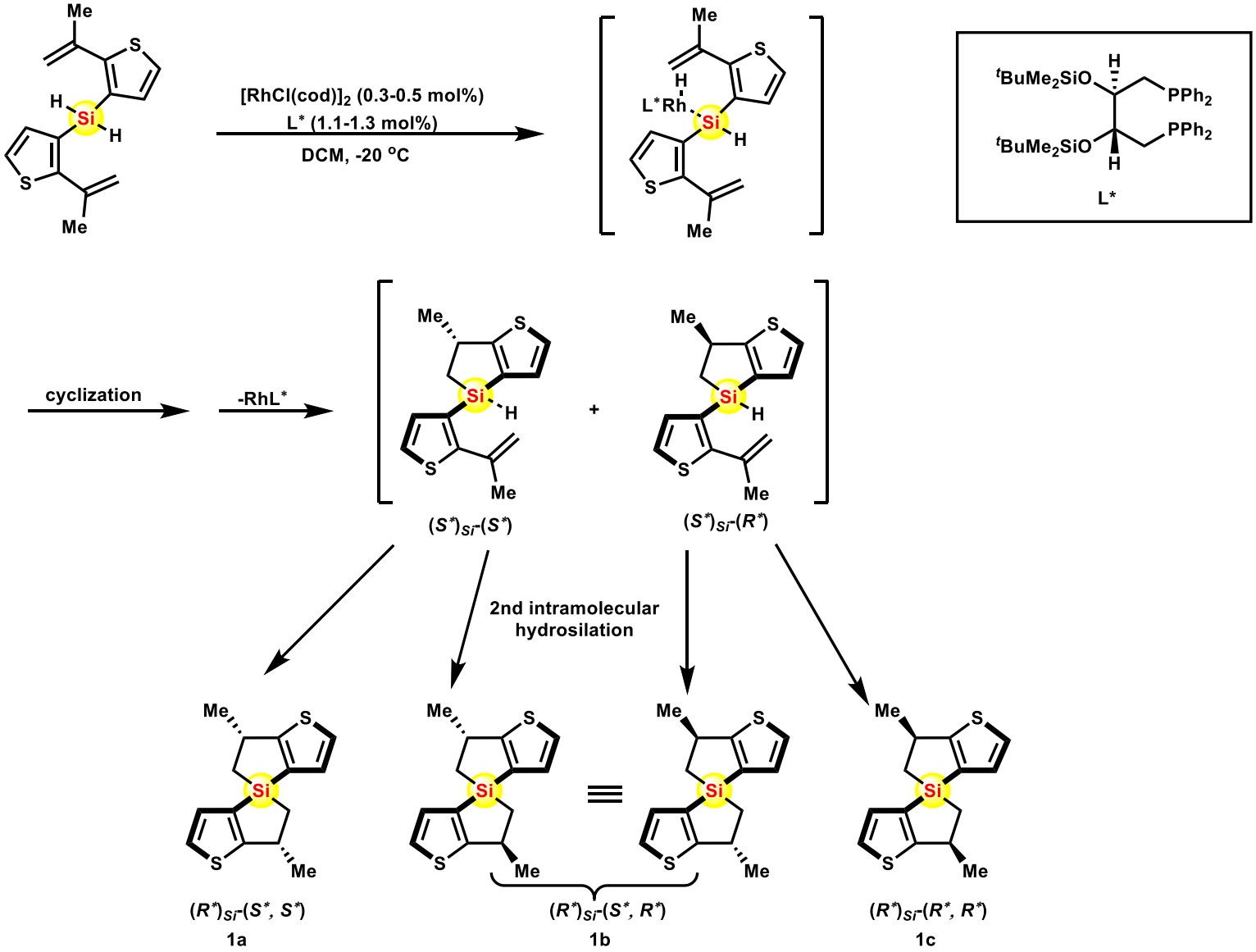
R. J. P. Corriu, et al. *J. Organometallic. Chem*. **1974**, *64*, C51



R = Me 81% yield, 99% *ee* R = Et 97% yield, 99% *ee* R = ^{n}Pr 95% yield, 98% *ee*

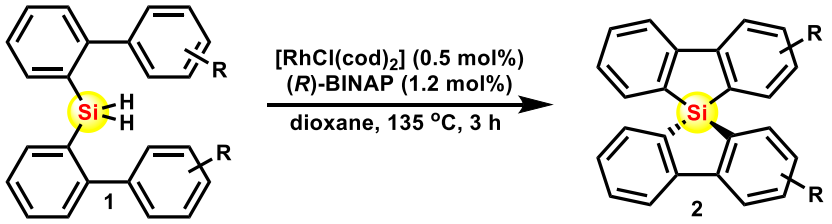
H. Takaya, et al. *J. Chem. Soc*. **1994**, 2525

Desymmetrical Reaction of Dihydrosilane

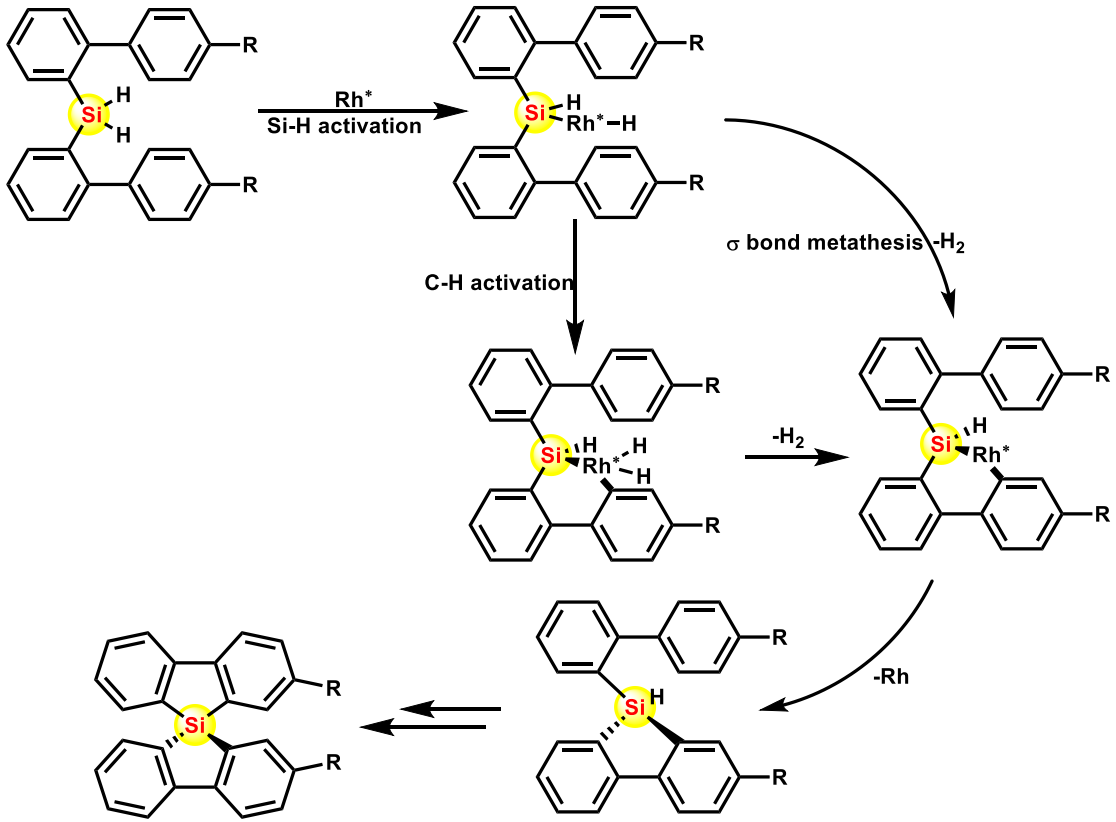


K. Tamao, et al. *J. Am. Chem. Soc.* **1996**, *118*, 12469

Desymmetrical Reaction of Dihydrosilane

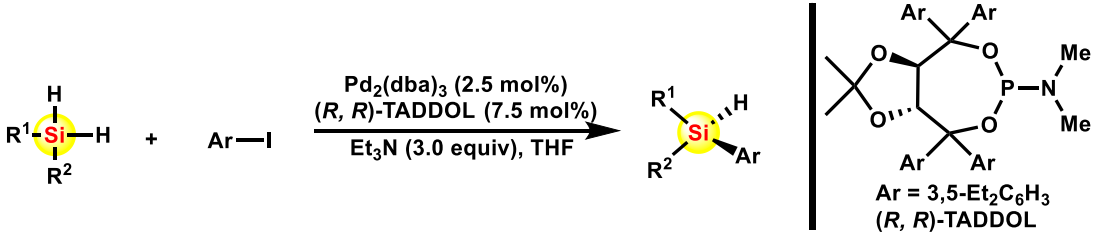


entry	R	yield (%)	ee (%)
1	4-MeO	95	81
2	4-^{t}Bu	94	78
3	4-CF_3	90	75
4	2-MeO	73	77

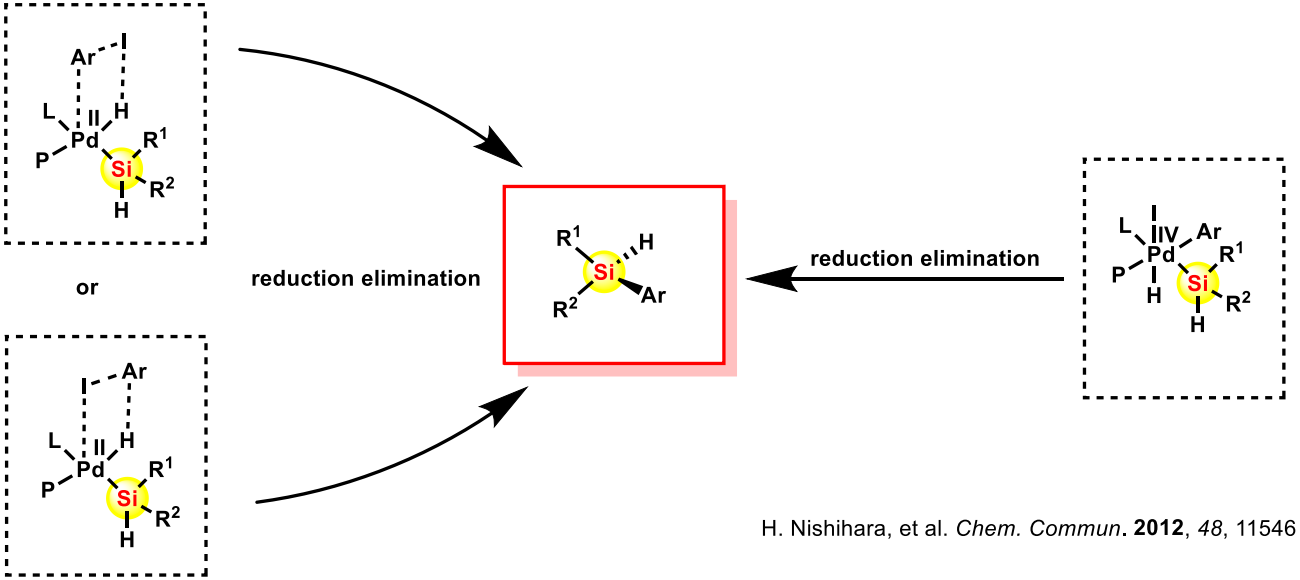


K. Takai, et al. *Angew. Chem. Int. Ed*. **2013**, *52*, 1520

Desymmetrical Reaction of Dihydrosilane



entry	R^1	R^2	Ar	Temp / °C	yield (%)	ee (%)
1	Ph	Me	2-$MeOC_6H_4$	-40	57	61
2	Ph	Me	3-$MeOC_6H_4$	-40	29	23
3	Ph	Me	3-$MeOC_6H_4$	-40	16	8
4	Ph	Me	2-MeC_6H_4	-40	44	58
5	Ph	Me	1-Np	20	58	51
6	Ph	^{n}Pr	2-$MeOC_6H_4$	-40	73	70
7	Ph	^{i}Pr	2-$MeOC_6H_4$	-40	73	76



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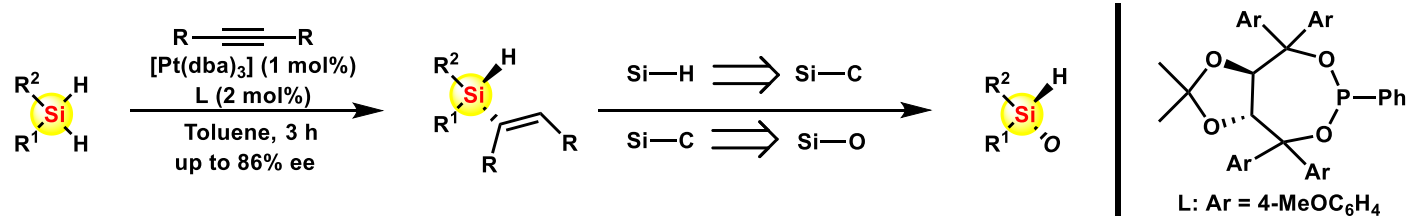
Desymmetrical Reaction of Dihydrosilane



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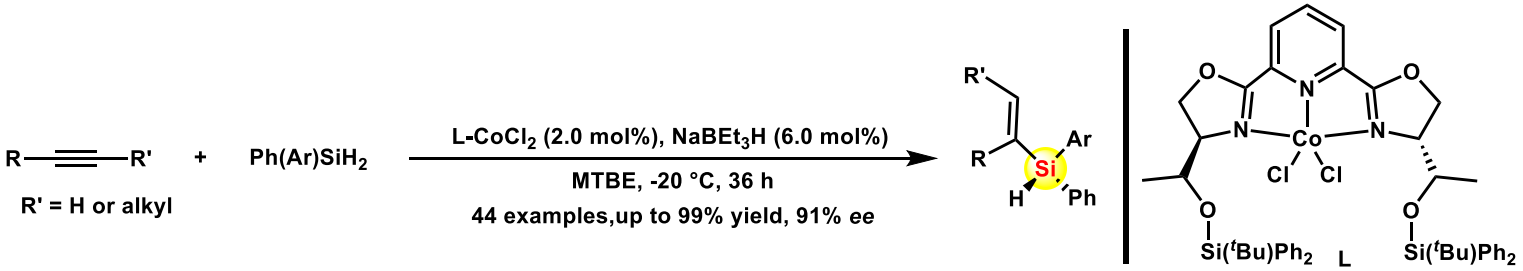
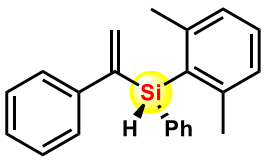
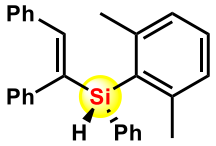
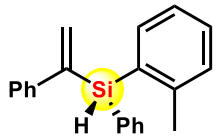




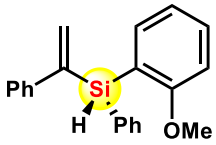
98%, 91% *ee*



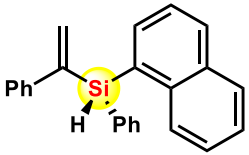
98%, 63% *ee*



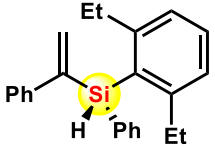
91%, 6% *ee*



98%, 9% *ee*

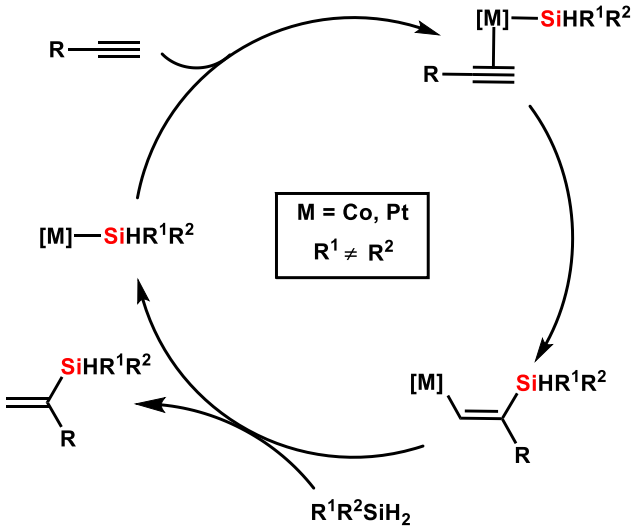


93%, 11% *ee*

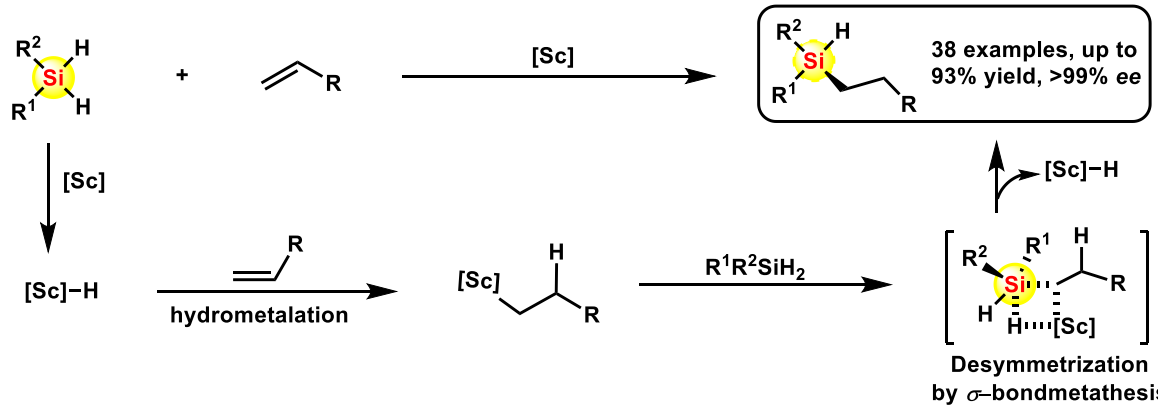


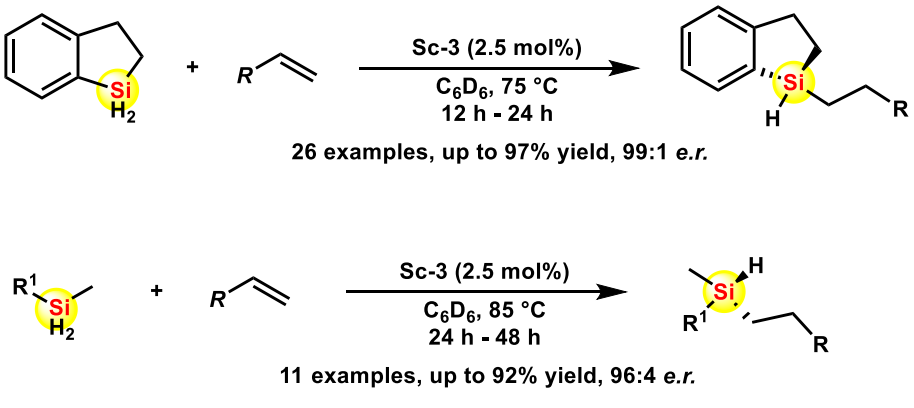
< 10%

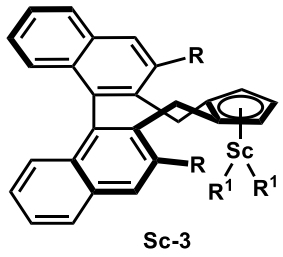
Z. M. Hou, et al. *Angew. Chem. Int. Ed.* **2018**, *57*, 12342

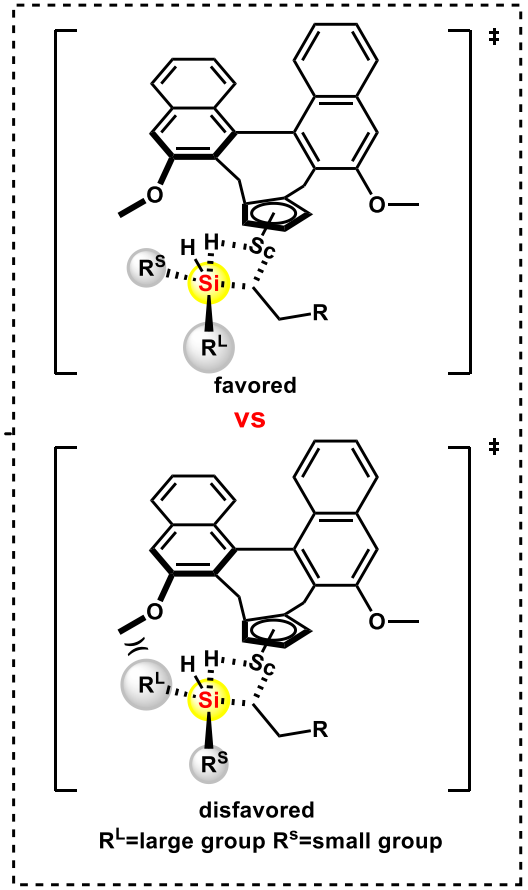


Desymmetrical Reaction of Dihydrosilane









Z. Huang, et al. *Angew. Chem. Int. Ed.* **2018**, *57*, 6319

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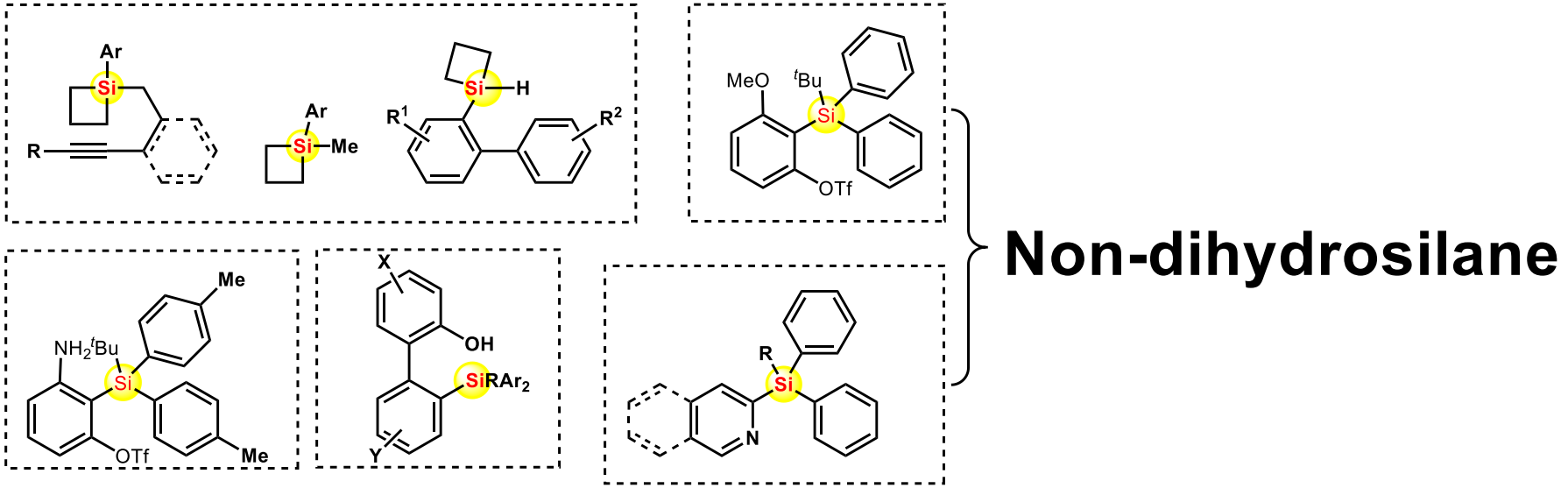
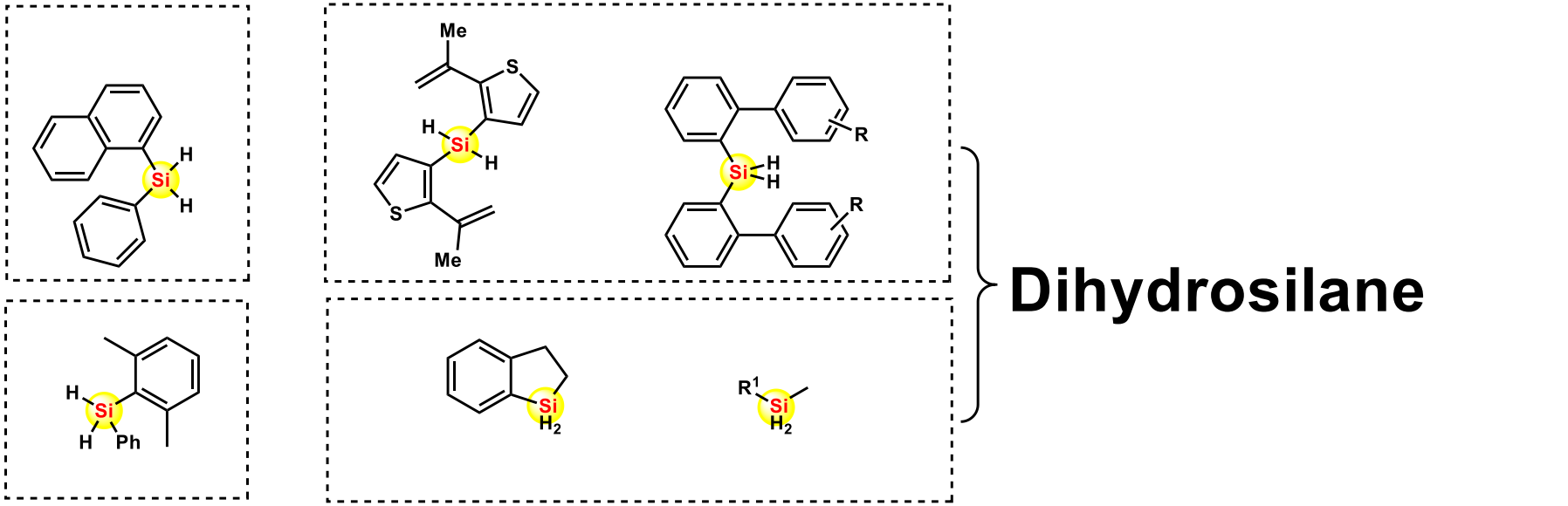
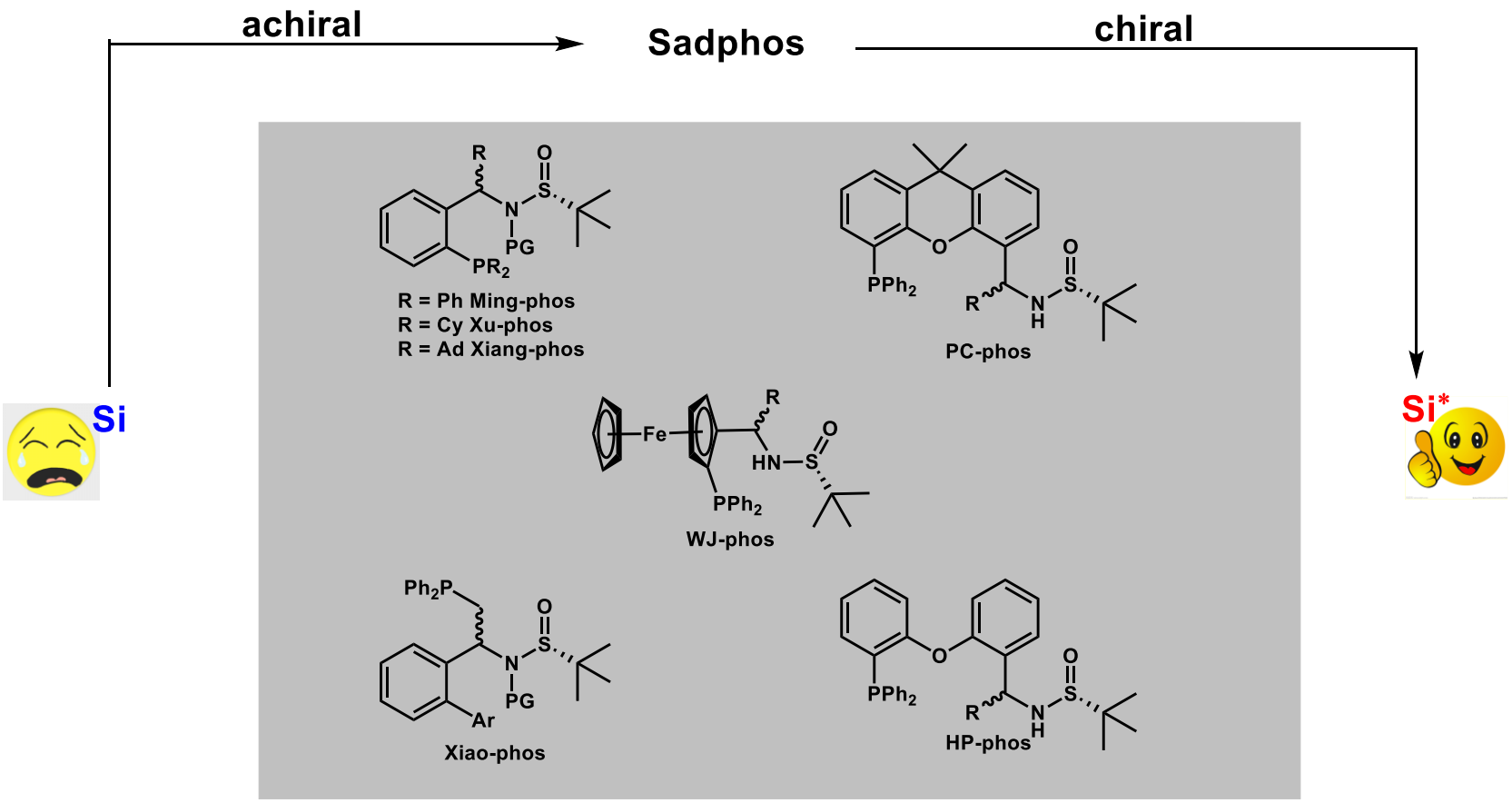
Summary





Summary

1. At present, there are only a few strategies for directly and efficiently synthesizing chiral silanes of silicon atoms. It is still in the preliminary stage of development.
2. The future research direction will be to realize the synthesis of diverse chiral compounds based on silicon atoms and to explore their applications in the field of materials science.



Thanks for your attention!