有机化学 DOI: 10.6023/cjoc202304035 研究论文
Chinese Journal of Organic Chemistry ARTICLE

镍催化苯并硅杂环丁烷与酰基硅烷的[4＋2]环化反应

张维露[a,b] 陈绍维[a,b] 沈 晓*[,a,b]
([a]武汉大学高等研究院 武汉 430072)
([b]有机硅化合物及材料教育部工程研究中心 武汉 430072)

摘要 报道了镍催化苯并硅杂环丁烷与酰基硅烷的[4＋2]环化反应, 合成了环状双硅化合物. 该反应条件温和, 表现出较好的底物普适性, 产物还可以通过一步转化合成单醇或二醇化合物.
关键词 镍催化; 苯并硅杂环丁烷; 酰基硅烷; 环加成反应; 碳硅键活化

Nickel-Catalyzed [4＋2] Cyclization of Benzosilacyclobutenes and Acylsilanes

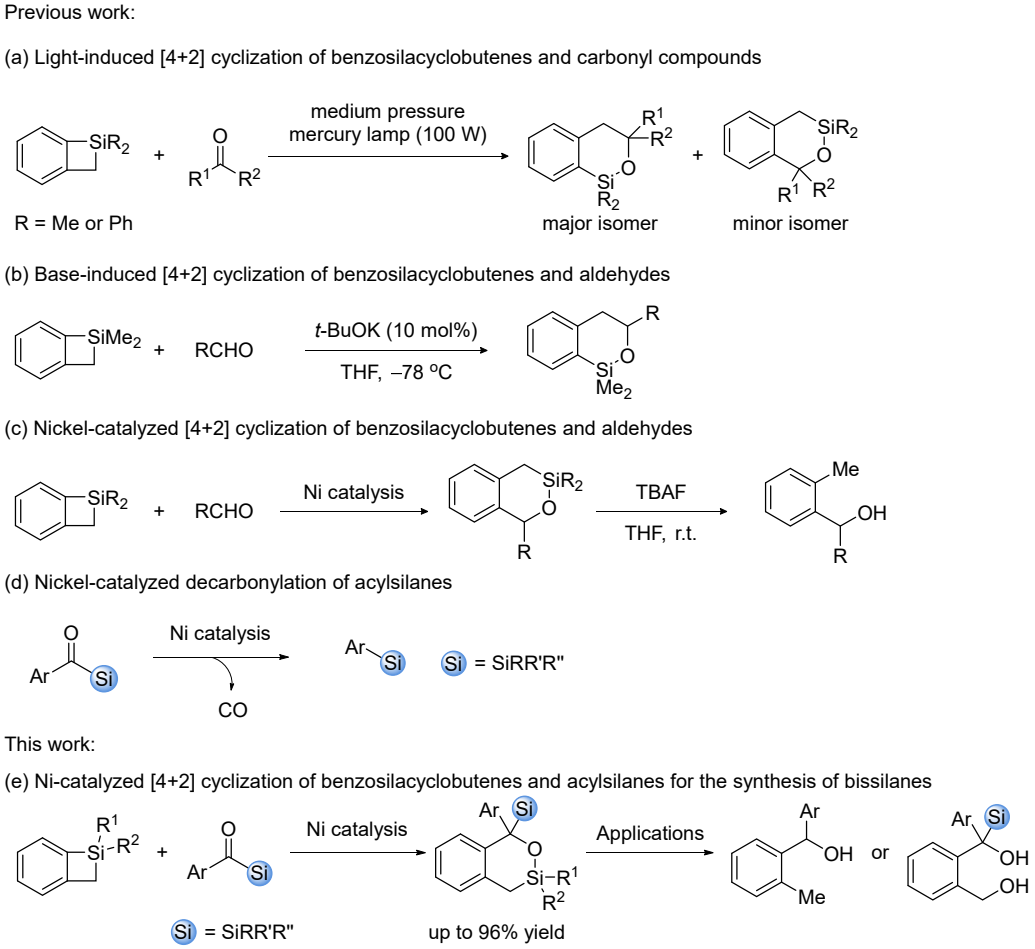
Zhang, Weilu[a,b] Chen, Shaowei[a,b] Shen, Xiao*[,a,b]
([a] *Institute for Advanced Studies*, *Wuhan University*, *Wuhan 430072*)
([b] *Engineering Research Center of Organosilicon Compounds & Materials*, *Ministry of Education*, *Wuhan 430072*)

Abstract A nickel-catalyzed [4＋2] cyclization reaction between benzosilacyclobutenes and acylsilanes for the synthesis of cyclic bissilanes is reported. The mild reaction showes good substrate scope and the products can be transformed to monoaclohols or diols via one-step down-stream transformations.
Keywords nickel catalysis; benzosilacyclobutene; acylsilane; cycloaddition; C—Si bond activation

1 Introduction

Organosilicon compounds are widely used in synthetic chemistry and material science.[1] Among various organosilicon compounds, benzosilacyclobutenes (BSCBs) are of particular importance, due to the unique properties induced by the Lewis acidity and high ring-strain (150 kJ/mol).[2] Therefore, various ring-opening and ring-expansion transformations have been developed.[3] For examples, the [4＋2] cyclization reactions of BSCBs and carbonyl compounds have been developed for the synthesis of six-membered oxasilacycles.[3] In 1981, Okazaki and co-workers[4] developed a light-induced ring-expansion reaction of BSCBs through diradical S_H2 (bimolecular homolytic substitution) process, but mixtures of regio-isomers were obtained (Scheme 1, a). In 1990, Utimoto and co-workers[5] reported a base-induced [4＋2] cyclization reactions of BSCBs and aldehydes for the synthesis of oxasilacycles, in which good regioselectivity was observed (Scheme 1, b). In 2006, Oshima and co-workers[6] developed the first nickel-catalyzed ring-expansion reaction between BSCBs with aldehydes to give oxasilacyclohexenes (Scheme 1, c). In 2022, Xu and co-workers[7] successfully achieved asymmetric synthesis of oxasilacyclohexenes through the reaction of BSCBs and aldehydes (Scheme 1, c). However, the [4＋2] cyclization reaction of silacyclobutenes (SCBs) with acylsilanes has not been reported, probably because of the low stability of acylsilanes under light-irradiation, base treatment or Ni-catalyzed conditions. Acylsilanes are known to be able to decompose through generation of carbenes even under blue light.[8] Moreover, arylacylsilanes could undergo C—Si bond cleavage under basic conditions to generate acyl anions.[9] Recently, Tobisu and co-workers[10] found that decarbonylation of acylsilanes would happen under nickel catalyzed conditions (Scheme 1, d). Herein, we reported the first nickel-catalyzed [4＋2] cycloaddition of BSCBs with acylsilanes for the synthesis of bissilanes (Scheme 1, e). The mild reaction showes good substrate scope and the products can be transformed to monoaclohols or diols via one-step down-stream transformations.

* Corresponding author. E-mail: xiaoshen@whu.edu.cn
Received April 28, 2023; revised June 24, 2023; published online July 12, 2023.
Project supported by the National Key R&D Program of China (No. 2022YFA1506100), the Fundamental Research Funds for the Central Universities (Nos. 2042023kf1010, 2042023kf0202) and the National Natural Science Foundation of China (No. 21901191).
国家重点研究发展计划(No. 2022YFA1506100)、中央高校基本科研基金(Nos. 2042023kf1010, 2042023kf0202)和国家自然科学基金(No. 21901191)资助项目.



Scheme 1 Background and our work on the Ni-catalyzed [4+2] cyclization of benzosilacyclobutenes and acylsilanes

2 Results and discussion

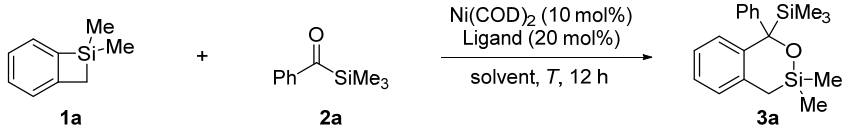
We began our study by examining reaction conditions with 1,1-dimethylbenzosilacyclobutene (**1a**) and acylsilane (**2a**) as the model substrates and 10 mol% $Ni(COD)_2$ (COD = cycloocta-1,5-diene) as the catalyst (Table 1). However, when bis(diphenylphosphino)methane (DPPM) was used as the ligand, the reaction in toluene at 100 ℃ gave desired [4+2] cyclization product **3a** in less than 5% yield (Table 1, Entry 1). Fortunately, when $P(^{p}MeC_6H_4)_3$ was used as the ligand, 32% yield was obtained for compound **3a** (Table 1, Entry 2). Further investigation of monophosphine ligands led to the finding of $P(^{n}Bu)_3$ as the optimal ligand (Table 1, Entries 3～8). Increasing the loading of **1a** to 2.5 equiv. further improved the yield of **3a** to 97% (Table 1, Entry 9). The reaction at 80 ℃ afforded **3a** in 96% isolated yield, but further lowering the reaction temperature resulted in decreased yield of **3a** (Table 1, Entries 10～13). Lowering the catalyst loading to 5 mol% also resulted in lower yield (72%, Table 1, Entry 14). Other solvents such as CH_3CN, 1,2-dichloroethane (DCE), dichloromethane (DCM) and *tert*-butyl methyl ether (MTBE) were found to be less efficient solvent than toluene (Table 1, Entries 15～18). Some commercially available chiral ligands were also tested to probe the asymmetric [4+2] cyclization, but no desired product was observed when **L1**～**L6** were used (Table 1, Entries 19～24). When **L7** was used, no enantioselectivity was observed, albeit there was 7% yield of **3a** was obtained (Table 1, Entries 25).

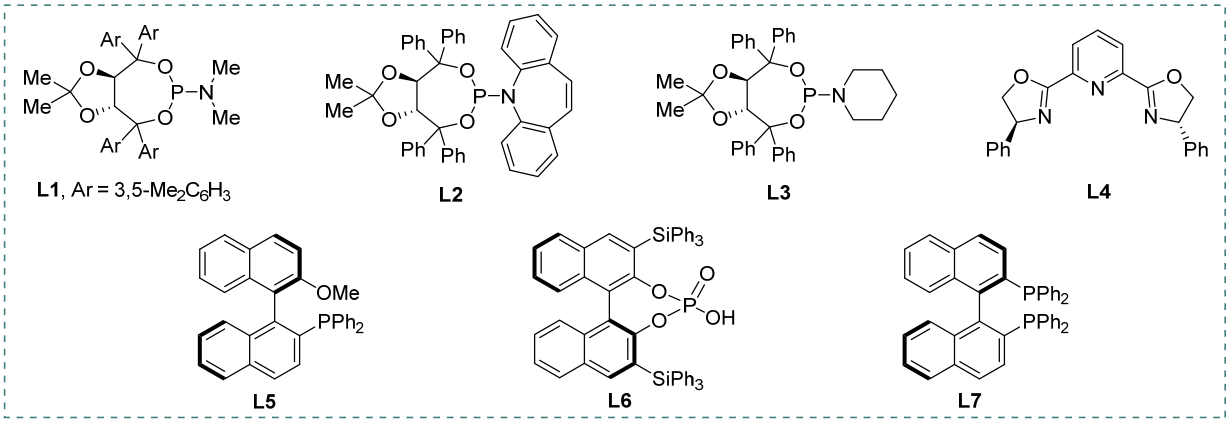
With the optimized conditions in hand, the substrate scope of the Ni-catalyzed [4+2] cyclization was then investigated (Table 2). Various benzosilacyclobutenes could be employed as substrates, affording bissilanes **3a**～**3j** in 55%～96% yields. The reaction of sterically hindered 7,7-diphenyl benzosilacyclobutane (**1c**) proceeded smoothly to afford the corresponding ring-expanded product **3c** in 91% yield, although 7-ethyl-7-methyl-ben-zosilacyclobutene (**1e**) only afforded product **3e** in 57% yield with 3∶2 *dr*. Subsequently, the scope of acylsilanes **2** was examined. As shown in Table 2, a wide range of acylsilanes with various substituents on aryl including Me, Ph, ^{t}Bu, F and Cl were suitable substrates, providing the desired oxasilacyclohexene products **3p**～**3t** and **3n** in 41%～82 % yields. Even the sterically hindered $^{t}BuMe_2Si$-contaning acylsilane could also gave product **3m** in 58% yield. Moreover, a naphthyl group-containing product **3o** was also successfully synthesized in 84% yield.

In order to probe possible mechanism of the reaction, several control experiments have been performed (Scheme 2). Firstly, the catalyst, ligand and substrate **1a** were premixed and heated at 80 ℃ for 15 min and then acylsilane **2a**

was added, after which the resulting mixture was stirred for 12 h, and only 16% yield of **3a** was detected by ^{1}H NMR (Scheme 2, a). In this reaction, we assume that intermediate **A** might be formed, although we have not been able to isolate this compound.[7] Secondly, acylsilane **2a**, catalyst and ligand were mixed together at 80 ℃ for 15 min and then **1a** add added, compound **3a** was formed in 95% yield (Scheme 2, b). When both **1a** and **2a** were mixed with catalyst and ligand together at the same time, 93% yield of **3a** was obtained (Scheme 2, c). These experimental data suggests that intermediate **Int-1** might be generated in the reaction. Although further investigations are needed, based on

Table 1 Optimization of reaction conditions[a]

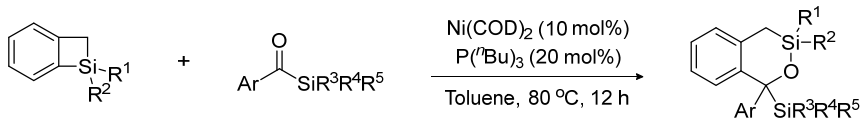




Entry	Ligand	**1a**/**2a**	Solvent	*T*/℃	Yield/%
1	DPPM	1∶1	Toluene	100	<5
2	P(*p*-MeC$_6$H$_4$)$_3$	1∶1	Toluene	100	32
3	P(^{n}Bu)Ad$_2$	1∶1	Toluene	100	16
4	PPh$_2$Vi	1∶1	Toluene	100	32
5	PPhCy$_2$	1∶1	Toluene	100	60
6	PPh$_2$Cy	1∶1	Toluene	100	53
7	PCy$_3$	1∶1	Toluene	100	42
8	P(^{n}Bu)$_3$	1∶1	Toluene	100	56
9	P(^{n}Bu)$_3$	2.5∶1	Toluene	100	97
10[b]	P(^{n}Bu)$_3$	2.5∶1	Toluene	80	99 (96)
11	P(^{n}Bu)$_3$	2.5∶1	Toluene	60	76
12	P(^{n}Bu)$_3$	2.5∶1	Toluene	40	23
13	P(^{n}Bu)$_3$	2.5∶1	Toluene	25	9
14[c]	P(^{n}Bu)$_3$	2.5∶1	Toluene	80	72
15	P(^{n}Bu)$_3$	2.5∶1	MeCN	80	12
16	P(^{n}Bu)$_3$	2.5∶1	DCE	80	44
17	P(^{n}Bu)$_3$	2.5∶1	DCM	80	57
18	P(^{n}Bu)$_3$	2.5∶1	MTBE	80	trace
19	**L1**	2.5∶1	Toluene	80	ND
20	**L2**	2.5∶1	Toluene	80	ND
21	**L3**	2.5∶1	Toluene	80	ND
22	**L4**	2.5∶1	Toluene	80	ND
23	**L5**	2.5∶1	Toluene	80	ND
24	**L6**	2.5∶1	Toluene	80	ND
25[d]	**L7**	2.5∶1	Toluene	80	7

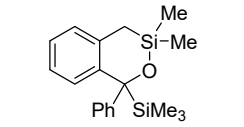
[a] The reactions were carried out using Ni(COD)$_2$ (10 mol%), ligand (20 mol%), benzosilacyclobutene (**1a**) and acylsilane (**2a**) (0.2 mmol) in dry toluene (1.0 mL) under N_2 protection, yield was determined by ^{1}H NMR analysis with 1,2-dibromoethane as an internal standard. [b] Isolated yield is given in the parenthesis. [c] The reactions were carried out using Ni(COD)$_2$ (5 mol%), ligand (10 mol%), silacyclobutene **1a** (0.5 mmol), and acylsilane (**2a**) (0.2 mmol) in dry toluene (1.0 mL) under N_2 atmosphere. [d] 0% *ee* of **3a** was determined through chiral HPLC. Cy: cyclohexyl, Ad: adamantyl, Vi: vinyl, ND: not detected.

Table 2 Substrates scope of silacyclobutenes with acylsilanes[a]

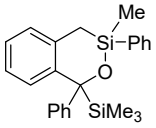


1 2 3

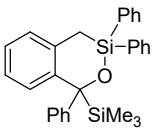
(A) Scope of benzosilacyclobutenes



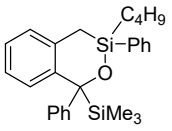
3a, 96%



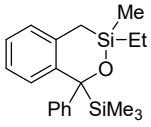
3b, 57%, *dr* = 3:2



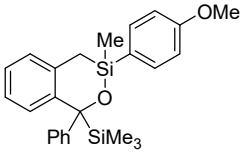
3c, 91%



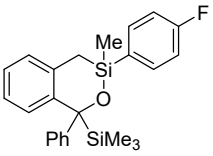
3d, 90%, *dr* = 2:1



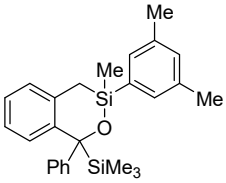
3e, 57%, *dr* = 3:2



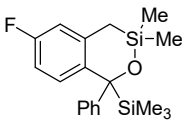
3f, 91%, *dr* = 3:2



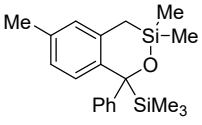
3g, 87%, *dr* = 3:2



3h, 65%, *dr* = 3:1

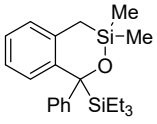


3i, 55%

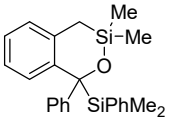


3j, 84%

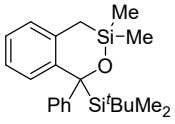
(B)Scope of acylsilanes



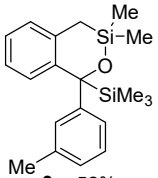
3k, 76%



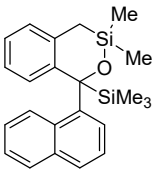
3l, 76%



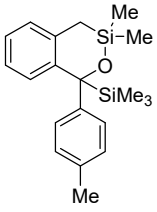
3m, 58%



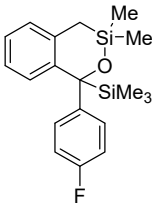
3n, 52%



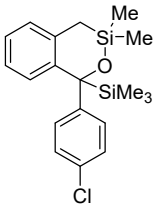
3o, 84%



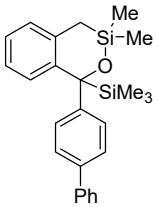
3p, 76%



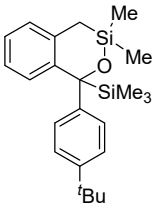
3q, 82%



3r, 41%

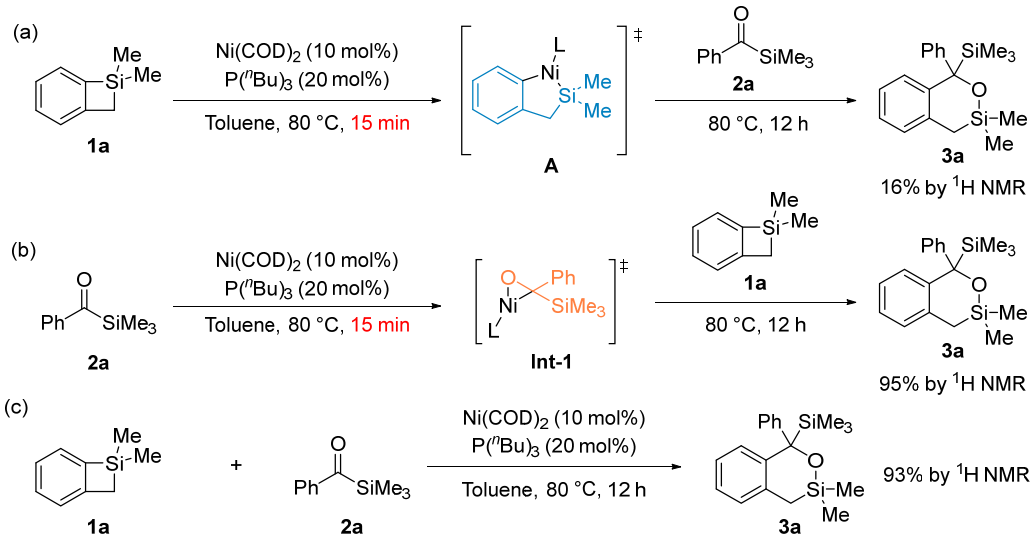


3s, 80%



3t, 70%

[a] The reactions were carried out using $Ni(COD)_2$ (10 mol%), ligand (20 mol%), benzosilacyclobutene **1** (0.5 mmol) and acylsilane **2** (0.2 mmol) in dry toluene (1.0 mL) under N_2 protection; isolated yield is given.



Scheme 2 Mechanism study

the above results and reported literature,[7] we propose a possible mechanism for the current [4+2] reaction (Scheme 3). The nickel(0) species **I** might initially react with acylsilane via oxidative cyclometalation to generate nickelacycle species **Int-1**, and then **Int-1** undergoes transmetalation with benzosilacyclobutene **1a** to form Ni(II) complexes **Int-2**. Finally, reductive elimination from complex **Int-2** would give product **3a** and regenerate Ni(0) species **I**.

Subsequently, we explored a gram-scale synthesis and down-stream transformations of oxasilacyclohexene **3a** to show the synthetic potential of the reaction (Scheme 4). Compound **3a** was successfully prepared in 1.58 g (97% yield) on 5 mmol scale of acylsilane **2a**. We found that when **3a** was treated with TBAF in THF at 60 ℃, both silyl group would be removed, affording monoalcohols **4a** in 82% yield. However, Rubottom oxidation conditions could transform **3a** to diol **5a** in 78% yield, which is difficult to prepare by other method.

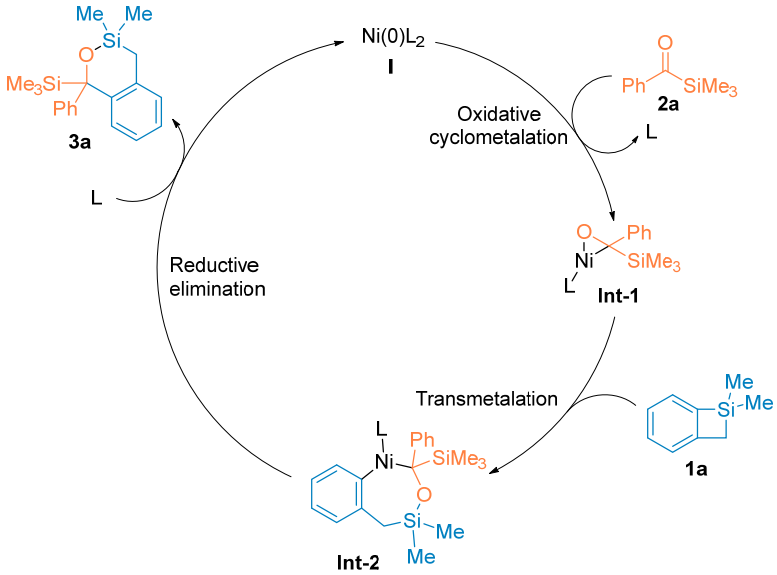
3 Conclusions

In summary, a nickel-catalyzed [4+2] cyclization of benzosilacyclobutenes and acylsilanes are developed, which afford bissilanes as the products. The mild reaction showed good substrate scope and the products can be transformed to monoaclohols or diols via one-step down-stream transformations.

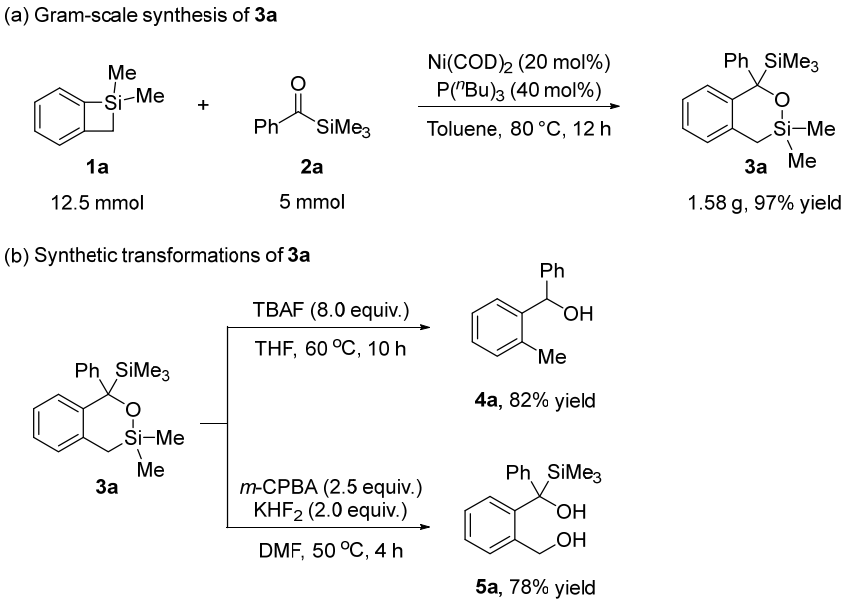
4 Experimental section

4.1 General experimental information

Chromatography: Hai Lang Silica Flash P60 size 40～63



Scheme 3 Proposed reaction mechanism



Scheme 4 Gram-scale synthesis and down-stream transformations of **3a**

μm (200～300 mesh). Thin layer chromatography (TLC): HaiLang silica gel 60 (0.25 mm). Visualization of the chromatogram was performed by UV, phosphomolybdic acid and 2,4-dinitrophenylhydrazine. ^{1}H NMR, ^{19}F NMR spectra were recorded on JNM-ECZ 400 MHz or Bruker AVANCE NEO 600 MHz, and ^{13}C NMR, ^{29}Si NMR were recorded on Bruker AVANCE NEO 151 MHz or 119 MHz using $CDCl_3$ as solvent and tetramethylsilane (TMS) as the internal standard. Chemical shift values are reported with the solvent resonance as the internal standard ($CDCl_3$ δ 7.26 for ^{1}H NMR, δ 77.16 for ^{13}C NMR). Infrared spectra were recorded on an Agilent Technologies Cary 630 FTIR. Melting point was measured by INESA SGW X-4. Mass spectra were recorded on a Bruker UltiMate 3000. All reagents were purchased from commercial suppliers (TCI, Aldrich, Alfa, Adamas, Energy Chemical, Bidepharm) and used without further purification, and solvents were dried and degassed according to standard procedure.

4.2 Synthesis of the products **3a**～**3r**

In a glovebox, to an oven-dried 10 mL Schlenk-tube equipped with a magnetic stir bar were added $Ni(COD)_2$ (5.6 mg, 10 mol%), $P(^nBu)_3$ (8.0 mg, 20 mol%) and dry toluene (1.0 mL). The mixture was stirred for 30 min, and then to the mixture were added **1** (0.50 mmol) and **2** (0.20 mmol) at room temperature, sequentially. The reaction mixture was stirred at 80 ℃ for 12 h. After the reaction, the mixture was quenched with water (30 mL) and then extracted by CH_2Cl_2 (10 mL×3). The organic layers were collected, dried with anhydrous Na_2SO_4 and concentrated under reduced pressure. The crude product was purified with flash column chromatography on silica gel (200～300 mesh) with petroleum ether as eluent to afford the title compound **3** as a colorless oil.

3,3-Dimethyl-1-phenyl-1-(trimethylsilyl)-3,4-dihydro-1*H*-benzo[*d*][1,2]oxasilane (**3a**): 57.1 mg, colorless oil, 87% yield, major. R_f=0.80 (petroleum ether). ^{1}H NMR (400 MHz, $CDCl_3$, 25 ℃) δ: 7.50～7.46 (m, 1H), 7.23～7.15 (m, 4H), 7.14～7.03 (m, 4H), 1.77 (d, J=14.5 Hz, 1H), 1.51 (d, J=14.5 Hz, 1H), 0.39 (s, 3H), 0.08 (s, 9H), −0.12 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$, 25 ℃) δ: 145.8, 143.2, 137.5, 131.9, 128.1, 127.4, 127.2, 125.6, 125.1, 124.1, 80.8, 21.3, 0.9, 0.6, −2.1; ^{29}Si NMR (119 MHz, $CDCl_3$, 25 ℃) δ: 14.7, 4.8; IR (ATR) ν: 3060, 3091, 2959, 2900, 1593, 1476, 1446, 1249, 1010, 950, 839, 813 cm^{-1}; HRMS (ESI-FTMS) calcd for $C_{19}H_{27}OSi_2$ $(M+H)^+$ 327.1595, found 327.1594.

3-Methyl-1,3-diphenyl-1-(trimethylsilyl)-3,4-dihydro-1*H*-benzo[*d*][1,2]oxasiline (**3b**): 43.3 mg, colorless oil, 57% yield, *dr*=2∶3. R_f=0.80 (petroleum ether). ^{1}H NMR (400 MHz, $CDCl_3$, 25 ℃) δ: 7.74～7.66 (m, 1H), 7.56～7.54 (m, 1H), 7.49～7.44 (m, 1H), 7.29～7.01 (m, 11H), 2.00 (d, J=14.9 Hz, 1H), 1.99 (d, J=14.9 Hz, 1H'), 1.96(d, J=14.9 Hz, 1H) 1.64 (d, J=14.9 Hz, 1H'), 0.14～0.12 (m, 12H, H+H'); ^{13}C NMR (151 MHz, $CDCl_3$, 25 ℃) δ: 145.7, 145.4, 143.7, 143.1, 138.0, 137.2, 136.8, 133.9, 133.7, 132.4, 132.3, 130.0, 129.6, 128.3, 128.2, 128.1, 127.6, 127.5, 127.4, 127.3, 125.9, 125.8, 125.4, 125.2, 124.4, 124.3, 81.6, 81.5, 20.8, 19.7, −0.3, −1.9, −2.0, −2.0; ^{29}Si NMR (119 MHz, $CDCl_3$, 25 ℃) δ: 4.9, 4.6, 3.5, 2.5; IR (ATR) ν: 3056, 3012, 2956, 2896, 1953, 1480, 1446, 1394, 1249, 1118, 1006, 947, 835 cm^{-1}; HRMS (APCI-FTMS) calcd for $C_{24}H_{29}OSi_2$ $(M+H)^+$ 389.1751, found 389.1757.

1,3,3-Triphenyl-1-(trimethylsilyl)-3,4-dihydro-1*H*-benzo[*d*][1,2]oxasiline (**3c**): 82.0 mg, colorless oil, 91% yield, major. R_f=0.70 (petroleum ether). ^{1}H NMR (400 MHz, $CDCl_3$, 25 ℃) δ: 7.66～7.63 (m, 2H), 7.60～7.55 (m, 1H), 7.53～7.41 (m, 3H), 7.29～7.27 (m, 1H), 7.26～7.13 (m, 6H), 7.12～7.09 (m, 1H), 7.07～7.04 (m, 5H), 2.25 (d, J=14.9 Hz, 1H), 2.06 (d, J=14.8 Hz, 1H), 0.16 (s, 9H); ^{13}C NMR (151 MHz, $CDCl_3$, 25 ℃) δ: 145.2, 143.8, 136.3, 136.0, 135.7, 134.7, 134.7, 132.7, 130.1, 129.8, 128.2, 128.1, 127.6, 127.5, 127.4, 126.1, 125.3, 124.5, 82.3, 18.9, −1.8; ^{29}Si NMR (119 MHz, $CDCl_3$, 25 ℃) δ: 5.1, −7.7; IR (ATR) ν: 3068, 3019, 2956, 1595, 1480, 1428, 1249, 1111, 995, 939, 831, 701 cm^{-1}; HRMS (ESI-FTMS) calcd for $C_{29}H_{31}OSi_2$ $(M+H)^+$ 451.1908, found 451.1914.

3-Butyl-1,3-diphenyl-1-(trimethylsilyl)-3,4-dihydro-1*H*-benzo[*d*][1,2]oxasiline (**3d**): 81.8 mg, colorless oil, 90% yield, *dr*=2∶1. R_f=0.60 (petroleum ether). ^{1}H NMR (400 MHz, $CDCl_3$, 25 ℃) δ: 7.74～7.59 (m, 1H), 7.56～7.41 (m, 2H), 7.33～7.20 (m, 5H), 7.19～7.10 (m, 3H), 7.10～6.88 (m, 3H), 2.10 (d, J=14.8 Hz, 1H), 2.00 (d, J=14.8 Hz, 1H'), 1.87 (d, J=14.8 Hz 1H), 1.84 (d, J=14.8 Hz 1H'), 1.61～1.54 (m, 1H), 1.53～1.35 (m, 2H), 1.17～1.07 (m, 2H), 0.95～0.72 (m, 3H), 0.68～0.55 (m, 1H), 0.13 (s, 9H); ^{13}C NMR (151 MHz, $CDCl_3$, 25 ℃) δ: 145.8, 145.3, 143.5, 143.5, 137.2, 136.9, 136.9, 136.8, 133.8, 133.8, 132.3, 132.2, 129.8, 129.4, 128.2, 128.2, 128.0, 127.6, 127.5, 127.4, 127.3, 127.3, 125.9, 125.8, 125.4, 125.1, 124.4, 124.2, 81.6, 81.4, 26.6, 26.3, 25.3, 25.0, 19.7, 18.5, 16.0, 14.8, 13.9, 13.8, −1.8, −1.9; IR (ATR) ν: 3068, 3019, 2956, 1595, 1480, 1428, 1249, 1111, 995, 939, 831, 701 cm^{-1}; HRMS (ESI-FTMS) calcd for $C_{27}H_{35}OSi_2$ $(M+H)^+$ 431.2221, found 431.2234.

3-Ethyl-3-methyl-1-phenyl-1-(trimethylsilyl)-3,4-dihydro-1*H*-benzo[*d*][1,2]oxasiline (**3e**): 38.6 mg, colorless oil, 57% yield, *dr*=2∶3. R_f=0.60 (petroleum ether). ^{1}H NMR (400 MHz, $CDCl_3$, 25 ℃) δ: 7.50～7.48 (m, 1H), 1.86 (d, J=14.6 Hz, 1H), 1.81 (d, J=14.6 Hz, 1H'), 1.53 (d, J=14.6 Hz, 1H), 1.49 (d, J=14.6 Hz, 1H'), 1.14～1.09 (m, 1H), 0.98～0.66 (m, 3H, H+H'), 0.36 (s, 3H), 0.11 (s, 9H), 0.10 (s, 9H'), −0.14 (s, 1H); ^{13}C NMR (151 MHz, $CDCl_3$, 25 ℃) δ: 145.8, 145.8, 143.4, 143.1, 137.7, 137.5, 132.0, 131.9, 128.2, 127.4, 127.4, 127.2, 127.1, 125.7, 125.6, 125.1, 125.1, 124.1, 124.0, 80.8, 80.5, 20.0, 19.9, 9.1, 8.1, 6.8, 6.6, −1.2, −2.0, −2.1, −3.1; ^{29}Si NMR (119 MHz, $CDCl_3$, 25 ℃) δ: 15.1, 14.6 (Si'), 4.4, 0.0 (Si'); IR (ATR) ν: 3064, 3019, 2959, 1595, 1480, 1446, 1249, 1014, 950, 839, 787, 705 cm^{-1}; HRMS (ESI-FTMS) calcd for $C_{20}H_{29}OSi_2$ $(M+H)^+$ 341.1751, found 341.1739.

3-(4-Methoxyphenyl)-3-methyl-1-phenyl-1-(trimethylsilyl)-3,4-dihydro-1H-benzo[*d*][1,2]oxasiline (**3f**): 65.0 mg, colorless oil, 91% yield, *dr*=3∶2. R_f=0.60 (petroleum

ether). ^{1}H NMR (400 MHz, $CDCl_3$, 25 ℃) δ: 7.65～7.52 (m, 3H), 7.28～7.23 (m, 4H), 7.23～7.11 (m, 10H), 7.07～6.99 (m, 2H), 6.82～6.74 (m, 2H), 3.89 (s, 3H'), 3.76 (s, 3H), 1.99 (d, J=14.6 Hz, 1H'), 1.95 (d, J=14.4 Hz, 1H), 1.94 (d, J=15.0 Hz, 1H'), 1.68 (d, J=14.5 Hz, 1H), 0.68 (s, 3H), 0.15 (s, 9H), 0.14 (s, 3H'), 0.13 (s, 9H'); ^{13}C NMR (151 MHz, $CDCl_3$, 25 ℃) δ: 161.2, 160.8, 145.7, 145.6, 143.7, 143.0, 137.4, 137.1, 135.6, 135.3, 132.3, 132.2, 129.0, 128.2, 128.1, 127.5, 127.4, 127.3, 127.3, 125.9, 125.8, 125.4, 125.2, 124.4, 124.2, 113.8, 113.4, 81.5, 81.4, 55.2, 55.0, 21.1, 19.9, −0.3, −1.9, −2.0, −2.0; ^{29}Si NMR (119 MHz, $CDCl_3$, 25 ℃) δ: 4.8, 4.5, 3.5, 2.4; IR (ATR) ν: 3053, 3019, 2963, 2911, 1595, 1502, 1446, 1249, 1118, 1006, 947, 839, 786 cm^{-1}; HRMS (ESI-FTMS) calcd for $C_{25}H_{31}O_2Si_2$ $(M+H)^+$ 419.1857, found 419.1860.

3-(4-Fluorophenyl)-3-methyl-1-phenyl-1-(trimethylsilyl)-3,4-dihydro-1*H*-benzo[*d*][1,2]oxasiline (**3g**): 71.0 mg, colorless oil, 87% yield, *dr*=3∶2, major. R_f=0.60 (petroleum ether). ^{1}H NMR (400 MHz, $CDCl_3$, 25 ℃) δ: 7.64～7.50 (m, 1H), 7.24～7.21 (m, 2H), 7.20～7.10 (m, 6H), 7.07～6.98 (m, 2H), 6.94～6.85 (m, 2H), 1.94 (d, J=15.0 Hz, 1H), 1.64 (d, J=15.0 Hz, 1H), 0.65 (s, 3H), 0.11 (s, 9H); ^{13}C NMR (151 MHz, $CDCl_3$, 25 ℃) δ: 145.6, 143.6, 136.0, 136.0, 135.7, 135.7, 132.3, 128.3, 127.5, 127.5, 125.8, 125.8, 125.5, 125.3, 124.5, 124.4, 114.9, 114.7, 81.6, 20.9, 0.4, −1.9; ^{29}Si NMR (119 MHz, $CDCl_3$, 25 ℃) δ: 4.9, 2.4; IR (ATR) ν: 3060, 3026, 2959, 2900, 1588, 1498, 1446, 1249, 1163, 1003, 939, 839, 786, 704 cm^{-1}; HRMS (ESI-FTMS) calcd for $C_{24}H_{28}OFSi_2$ $(M+H)^+$ 407.1657, found 407.1652.

3-(3,5-Dimethylphenyl)-3-methyl-1-phenyl-1-(trimethylsilyl)-3,4-dihydro-1*H*-benzo[*d*][1,2]oxasil-ine (**3h**): 54.1 mg, colorless oil, 65% yield, *dr*=3∶1. R_f=0.40 (petroleum ether). ^{1}H NMR (400 MHz, $CDCl_3$, 25 ℃) δ: 7.54～7.51 (m, 1H), 7.29～7.27 (m, 1H), 7.24～7.11 (m, 10H), 7.01～6.99 (m, 1H), 6.92～6.91 (m, 1H), 6.80～6.79 (m, 2H), 2.38 (s, 6H'), 2.29～2.27 (m, 2H'), 2.18 (s, 6H), 1.94 (d, J=14.7 Hz, 1H), 1.67 (d, J=14.7 Hz, 1H), 0.64 (s, 3H), 0.14 (s, 9H), 0.12 (s, 3H'), 0.11 (s, 9H'); ^{13}C NMR (151 MHz, $CDCl_3$, 25 ℃) δ: 145.8, 145.6, 143.6, 143.0, 137.7, 137.5, 137.3, 137.0, 136.8, 136.8, 132.4, 132.2, 131.8, 131.8, 131.6, 131.3, 128.2, 127.5, 127.3, 127.3, 127.3, 126.0, 125.9, 125.3, 125.2, 124.3, 124.1, 81.5, 81.4, 21.6, 21.4, 21.0, 19.9, −0.3, −1.9, −2.0, −2.2; ^{29}Si NMR (119 MHz, $CDCl_3$, 25 ℃) δ: 4.86, 4.52, 3.72, 2.39; IR (ATR) ν: 3056, 3019, 2959, 2915, 1595, 1480, 1446, 1401, 1249, 1141, 1006, 835 cm^{-1}; HRMS (ESI-FTMS) calcd for $C_{26}H_{33}OSi_2$ $(M+H)^+$ 417.2065, found 417.2071.

6-Fluoro-3,3-dimethyl-1-phenyl-1-(trimethylsilyl)-3,4-dihydro-1*H*-benzo[*d*][1,2]oxasiline (**3i**): 38.0 mg, colorless oil, 55% yield. R_f=0.80 (petroleum ether). ^{1}H NMR (400 MHz, $CDCl_3$, 25 ℃) δ: 7.45～7.41 (m, 1H), 7.24～7.17 (m, 2H), 7.13～7.05 (m, 3H), 6.89～6.85 (m, 1H), 6.81～6.77 (m, 1H), 1.75 (d, J=14.7 Hz, 1H), 1.53 (d, J=14.5 Hz, 1H), 0.39 (s, 3H), 0.08 (s, 9H), −0.11 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$, 25 ℃) δ: 162.5, 160.9, 145.6, 140.6, 140.5, 139.0, 139.0, 129.3, 129.3, 127.5, 125.6, 125.3, 118.4, 118.3, 110.7, 110.5, 80.3, 21.7, −2.2; ^{29}Si NMR (119 MHz, $CDCl_3$, 25 ℃) δ: 13.8, 4.4; IR (ATR) ν: 3071, 2959, 2896, 1584, 1483, 1252, 1163, 1014, 839, 805, 704 cm^{-1}; HRMS (APCI-FTMS) calcd for $C_{19}H_{26}OFSi_2$ $(M+H)^+$ 345.1501, found 345.1504.

3,3,6-Trimethyl-1-phenyl-1-(trimethylsilyl)-3,4-dihydro-1*H*-benzo[*d*][1,2]oxasiline (**3j**): 57.4 mg, colorless oil, 84% yield. R_f=0.80 (petroleum ether). ^{1}H NMR (400 MHz, $CDCl_3$, 25 ℃) δ: 7.37～7.36 (m, 1H), 7.26～7.17 (m, 2H), 7.15～7.05 (m, 3H), 7.02～6.96 (m, 1H), 6.91～6.87 (m, 1H), 2.32 (s, 3H), 1.72 (d, J=14.5 Hz, 1H), 1.49 (d, J=14.5 Hz, 1H), 0.39 (s, 3H), 0.08 (s, 9H), −0.11 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$, 25 ℃) δ: 146.0, 140.3, 137.3, 136.6, 132.7, 128.0, 127.4, 125.6, 125.0, 124.8, 80.5, 21.2, 21.1, 0.9, −0.5, −2.1; ^{29}Si NMR (119 MHz, $CDCl_3$, 25 ℃) δ: 13.9, 4.1; IR (ATR) ν: 2963, 2930, 1248, 1163, 1014, 842, 809, 701 cm^{-1}; HRMS (APCI-FTMS) calcd for $C_{20}H_{29}OSi_2$ $(M+H)^+$ 341.1751, found 341.1753.

3,3-Dimethyl-1-phenyl-1-(triethylsilyl)-3,4-dihydro-1*H*-benzo[*d*][1,2]oxasiline (**3k**): 56.2 mg, colorless oil, 76% yield, major. R_f=0.60 (petroleum ether). ^{1}H NMR (400 MHz, $CDCl_3$, 25 ℃) δ: 7.53～7.44 (m, 1H), 7.22～7.14 (m, 4H), 7.14～7.05 (m, 4H), 1.76 (d, J=14.7 Hz, 1H), 1.45 (d, J=14.7 Hz, 1H), 0.91～0.86 (m, 9H), 0.76～0.70 (m, 6H), 0.37 (s, 3H), −0.10 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$, 25 ℃) δ: 146.4, 143.6, 137.2, 132.0, 128.2, 127.5, 127.1, 125.7, 125.2, 123.9, 82.4, 21.2, 8.2, 3.7, 1.2, −0.3; ^{29}Si NMR (119 MHz, $CDCl_3$, 25 ℃) δ: 13.9, 6.3; IR (ATR) ν: 3060, 3019, 2952, 2877, 1595, 1476, 1252, 1006, 865, 813, 704 cm^{-1}; HRMS (ESI-FTMS) calcd for $C_{22}H_{33}OSi_2$ $(M+H)^+$ 369.2064, found 369.2050.

1-(Dimethyl(phenyl)silyl)-3,3-dimethyl-1-phenyl-3,4-dihydro-1*H*-benzo[*d*][1,2]oxasiline (**3l**): 58.8 mg, colorless oil, 76% yield, major. R_f=0.50 (petroleum ether). ^{1}H NMR (400 MHz, $CDCl_3$, 25 ℃) δ: 7.47～7.40 (m, 1H), 7.33～7.26 (m, 3H), 7.25～7.19 (m, 2H), 7.18～7.10 (m, 4H), 7.08～6.97 (m, 4H), 1.76 (d, J=14.7 Hz, 1H), 1.50 (d, J=15.0 Hz, 1H), 0.38 (s, 6H), 0.33 (s, 3H), −0.08 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$, 25 ℃) δ: 145.4, 142.9, 138.0, 137.2, 135.3, 131.9, 129.0, 128.6, 127.3, 127.1, 126.1, 125.4, 124.1, 81.0, 21.2, 1.0, −0.5, −3.1, −4.1; ^{29}Si NMR (119 MHz, $CDCl_3$, 25 ℃) δ: 14.6, −3.3; IR (ATR) ν: 3064, 3015, 2959, 1595, 1480, 1446, 1252, 1111, 1006, 865, 812, 701 cm^{-1}; HRMS (ESI-FTMS) calcd for $C_{24}H_{29}OSi_2$ $(M+H)^+$ 389.1751, found 389.1764.

1-(*tert*-Butyldimethylsilyl)-3,3-dimethyl-1-phenyl-3,4-dihydro-1*H*-benzo[*d*][1,2]oxasiline (**3m**): 43.1 mg, colorless oil, 58% yield, major. R_f=0.60 (petroleum ether). ^{1}H NMR (400 MHz, $CDCl_3$, 25 ℃) δ: 7.62～7.53 (m, 1H), 7.23～7.13 (m, 6H), 7.11～6.99 (m, 2H), 1.76 (d, J=14.7 Hz, 1H), 1.47 (d, J=14.7 Hz, 1H), 0.88 (s, 9H), 0.43 (s, 3H), 0.14 (s, 3H), 0.00 (s, 3H), −0.06 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$, 25 ℃) δ: 146.0, 143.9, 136.8, 132.0, 128.9, 127.2, 127.1, 126.2, 125.1, 123.7, 83.5, 29.2, 21.1, 19.2, 1.2, 0.0, −3.8, −4.7; ^{29}Si NMR (119 MHz, $CDCl_3$, 25 ℃) δ: 13.8, 6.1; IR (ATR) ν: 3060, 3019, 2959, 2855, 1595, 1476, 1252, 1010, 939, 865, 809, 704 cm^{-1}; HRMS

(ESI-FTMS) calcd for $C_{22}H_{33}OSi_2$ $(M+H)^+$ 369.2064, found 369.2050.

3,3-Dimethyl-1-(*m*-tolyl)-1-(trimethylsilyl)-3,4-dihydro-1*H*-benzo[*d*][1,2]oxasiline (**3n**): 35.3 mg, colorless oil, 52% yield, major. R_f=0.60 (petroleum ether). ^{1}H NMR (400 MHz, $CDCl_3$, 25 ℃) δ: 7.51～7.44 (m, 1H), 7.23～7.14 (m, 2H), 7.11～7.03 (m, 2H), 6.98～6.93 (m, 1H), 6.91～6.87 (m, 2H), 2.27 (s, 3H), 1.78 (d, J=14.5 Hz, 1H), 1.54 (d, J=4.5 Hz, 1H), 0.40 (s, 3H), 0.09 (s, 9H), −0.12 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$, 25 ℃) δ: 145.6, 143.3, 137.5, 136.7, 131.9, 128.1, 127.3, 127.1, 126.4, 125.8, 124.1, 122.8, 80.8, 21.8, 21.3, 1.0, 0.6, −2.0; ^{29}Si NMR (119 MHz, $CDCl_3$, 25 ℃) δ: 14.1, 4.0; IR (ATR) ν: 3060, 3019, 2959, 2900, 1602, 1476, 1249, 1144, 1014, 939, 839, 813, 738 cm^{-1}; HRMS (ESI-FTMS) calcd for $C_{20}H_{29}OSi_2$ $(M+H)^+$ 341.1752, found 341.1740.

3,3-Dimethyl-1-(naphthalen-1-yl)-1-(trimethylsilyl)-3,4-dihydro-1*H*-benzo[*d*][1,2]oxasiline (**3o**): 63.0 mg, colorless oil, 84% yield. R_f=0.50 (petroleum ether). ^{1}H NMR (400 MHz, $CDCl_3$, 25 ℃) δ: 7.77～7.73 (m, 2H), 7.68～7.60 (m, 2H), 7.58～7.56 (m, 1H), 7.45～7.36 (m, 2H), 7.26～7.20 (m, 3H), 7.09～7.03 (m, 1H), 1.76 (d, J=14.7 Hz, 1H), 1.50 (d, J=14.5 Hz, 1H), 0.45 (s, 3H), 0.11 (s, 9H), −0.09 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$, 25 ℃) δ: 143.5, 143.0, 137.7, 133.1, 132.0, 131.7, 128.2, 128.0, 127.6, 127.3, 126.9, 125.8, 125.1, 124.9, 124.2, 123.7, 81.0, 21.3, 1.0, 0.6, −2.0; ^{29}Si NMR (119 MHz, $CDCl_3$, 25 ℃) δ: 14.4, 4.8; IR (ATR) ν: 3056, 3019, 2959, 2900, 1632, 1595, 1506, 1446, 1248, 1017, 842, 812, 741 cm^{-1}; HRMS (ESI-FTMS) calcd for $C_{23}H_{29}OSi_2$ $(M+H)^+$ 377.1751, found 377.1747.

3,3-Dimethyl-1-(*p*-tolyl)-1-(trimethylsilyl)-3,4-dihydro-1*H*-benzo[*d*][1,2]oxasiline (**3p**): 52.0 mg, colorless oil, 76% yield, major. R_f=0.60 (petroleum ether). ^{1}H NMR (400 MHz, $CDCl_3$, 25 ℃) δ: 7.48～7.44 (m, 1H), 7.20～7.14 (m, 2H), 7.09～7.02 (m, 1H), 6.99 (s, 4H), 2.28 (s, 3H), 1.77 (d, J=14.7 Hz, 1H), 1.53 (d, J=14.4 Hz, 1H), 0.38 (s, 3H), 0.08 (s, 9H), −0.13 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$, 25 ℃) δ: 143.3, 142.7, 137.5, 134.4, 131.9, 128.1, 128.0, 127.0, 125.6, 124.1, 80.7, 21.3, 21.1, 1.0, 0.6, −2.0; ^{29}Si NMR (119 MHz, $CDCl_3$, 25 ℃) δ: 13.9, 3.9; IR (ATR) ν: 3060, 3019, 2956, 2903, 1506, 1446, 1249, 1141, 1010, 865, 839, 790, 742 cm^{-1}; HRMS (ESI-FTMS) calcd for $C_{20}H_{29}OSi_2$ $(M+H)^+$ 341.1752, found 341.1753.

1-(4-Fluorophenyl)-3,3-dimethyl-1-(trimethylsilyl)-3,4-dihydro-1*H*-benzo[*d*][1,2]oxasiline (**3q**): 56.6 mg, colorless oil, 82% yield, major. R_f=0.60 (petroleum ether). ^{1}H NMR (400 MHz, $CDCl_3$, 25 ℃) δ: 7.49～7.42 (m, 1H), 7.22～7.15 (m, 2H), 7.09～7.03 (m, 3H), 6.93～6.83 (m, 2H), 1.79 (d, J=14.7 Hz, 1H), 1.50 (d, J=14.5 Hz, 1H), 0.37 (s, 3H), 0.08 (s, 9H), −0.13 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$, 25 ℃) δ: 161.8, 160.2, 142.9, 141.6, 141.6, 137.4, 132.1, 128.0, 127.3, 127.0, 127.0, 124.3, 114.2, 114.1, 80.3, 21.3, 0.9, −0.6, −2.1; ^{29}Si NMR (119 MHz, $CDCl_3$, 25 ℃) δ: 14.3, 4.3; IR (ATR) ν: 2960, 2907, 1599, 1502, 1252, 1159, 1018, 865, 846, 805, 745 cm^{-1}; HRMS (APCI-FTMS) calcd for $C_{19}H_{26}FOSi_2$ $(M+H)^+$ 345.1501, found 345.1499.

1-(4-Chlorophenyl)-3,3-dimethyl-1-(trimethylsilyl)-3,4-dihydro-1*H*-benzo[*d*][1,2]oxasiline (**3r**): 29.1 mg, colorless oil, 41% yield, major. R_f=0.80 (petroleum ether). ^{1}H NMR (400 MHz, $CDCl_3$, 25 ℃) δ: 7.49～7.42 (m, 1H), 7.23～7.13 (m, 4H), 7.11～7.00 (m, 3H), 1.79 (d, J=14.5 Hz, 1H), 1.53～1.45 (m, 1H), 0.38 (s, 3H), 0.08 (s, 9H), −0.13 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$, 25 ℃) δ: 144.6, 142.7, 137.4, 132.1, 130.9, 128.0, 127.6, 127.4, 127.0, 124.3, 80.4, 21.3, 0.9, 0.7, −2.1; ^{29}Si NMR (119 MHz, $CDCl_3$, 25 ℃) δ: 14.5, 4.6; IR (ATR) ν: 3064, 3019, 2956, 2900, 1484, 1450, 1398, 1249, 1092, 1006, 926, 839, 753 cm^{-1}; HRMS (ESI-FTMS) calcd for $C_{19}H_{26}ClOSi_2$ $(M+H)^+$ 361.1205, found 361.1191.

1-([1,1'-Biphenyl]-4-yl)-3,3-dimethyl-1-(trimethylsilyl)-3,4-dihydro-1*H*-benzo[*d*][1,2]oxasiline (**3s**): 63.6 mg, colorless oil, 80% yield, major. R_f=0.50 (petroleum ether). ^{1}H NMR (400 MHz, $CDCl_3$, 25 ℃) δ: 7.60～7.54 (m, 2H), 7.53～7.49 (m, 1H), 7.46～7.38 (m, 4H), 7.32～7.27 (m, 1H), 7.22～7.15 (m, 4H), 7.11～7.07 (m, 1H), 1.80 (d, J=14.5 Hz, 1H), 1.59 (d, J=14.5 Hz, 1H), 0.42 (s, 3H), 0.12 (s, 9H), −0.11 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$, 25 ℃) δ: 145.0, 143.1, 141.1, 137.7, 137.6, 132.0, 128.8, 128.1, 127.2, 127.0, 127.0, 126.1, 126.0, 124.2, 80.7, 21.4, 0.9, 0.6, −2.0; ^{29}Si NMR (119 MHz, $CDCl_3$, 25 ℃) δ: 14.3, 4.4; IR (ATR) ν: 3060, 3030, 2959, 2903, 1599, 1483, 1446, 1401, 1252, 1014, 842, 760, 697 cm^{-1}; HRMS (ESI-FTMS) calcd for $C_{25}H_{31}OSi_2$ $(M+H)^+$ 403.1908, found 403.1895.

1-(4-Methoxyphenyl)-3,3-dimethyl-1-(trimethylsilyl)-3,4-dihydro-1*H*-benzo[*d*][1,2]oxasiline (**3t**): 53.2 mg, colorless oil, 70% yield. R_f=0.80 (petroleum ether). ^{1}H NMR (400 MHz, $CDCl_3$, 25 ℃) δ: 7.50～7.42 (m, 1H), 7.20～7.14 (m, 4H), 7.07～7.03 (m, 1H), 7.02～6.98 (m, 2H), 1.76 (d, J=14.5 Hz, 1H), 1.55 (d, J=14.5 Hz, 1H), 1.26 (s, 9H), 0.39 (s, 3H), 0.08 (s, 9H), −0.13 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$, 25 ℃) δ: 147.7, 143.4, 142.4, 137.5, 131.9, 128.0, 127.0, 125.2, 124.2, 124.1, 80.7, 34.3, 31.6, 21.3, 0.9, −0.5, −2.0; ^{29}Si NMR (119 MHz, $CDCl_3$, 25 ℃) δ: 13.7, 3.9; IR (ATR) ν: 3063, 3030, 2959, 2900, 1505, 1450, 1394, 1249, 1006, 865, 842, 809 cm^{-1}; HRMS (APCI-FTMS) calcd for $C_{23}H_{35}OSi_2$ $(M+H)^+$ 383.2221, found 383.2219.

4.3 Applications of product **3a**

4.3.1 Synthesis of phenyl(*o*-tolyl) methanol (**4a**)

In air condition, to 20 mL vail equipped with a magnetic stir bar were added **3a** (32.6 mg, 0.1 mmol), TBAF (0.8 mL, 1 mol/L in THF), and THF (0.5 mL). The mixture was stirred at 60 ℃ for 10 h with TLC monitor. After reaction finished, the mixture was quenched with water (20 mL) and then extracted by CH_2Cl_2 (10 mL×3). The organic layers were collected, dried with anhydrous Na_2SO_4 and concentrated under reduced pressure. The crude product was purified with flash column chromatography on silica gel (200～300 mesh) with petroleum ether as eluent to afford the title compound as a colorless solid **4a** (16.3 mg, 82% yield). The product was according to literature.[6] R_f=0.50 (petroleum ether/ethyl acetate, V∶V=10∶1). ^{1}H NMR (400 MHz, $CDCl_3$, 25 ℃) δ: 7.55～7.50 (m, 1H), 7.34～7.32 (m, 4H), 7.30～7.20 (m, 3H), 7.16～7.14 (m, 1H), 6.01 (s, 1H), 2.26

(s, 3H), 2.20 (s, 1H).

4.3.2 Synthesis of (2-(hydroxymethyl)phenyl)(phenyl)(trimethylsilyl)methanol (**5a**)

In air condition, to 20 mL Schlenk-tube equipped with a magnetic stir bar were added **3a** (32.6 mg, 0.1 mmol), *m*-chloroperoxybenzoic acid (*m*-CPBA) (62.0 mg, 0.25 mmol), KHF_2 (15.6 mg, 0.2 mmol) and *N*,*N*-dimethylformamide (DMF) (0.3 mL). The mixture was stirred at 50 ℃ for 4 h. After reaction finished, the mixture was quenched with water (20 mL) and then extracted by CH_2Cl_2 (10 mL×3). The organic layers were collected, dried with anhydrous Na_2SO_4 and concentrated under reduced pressure. The crude product was purified with flash column chromatography on silica gel (200～300 mesh) with petroleum ether/ethyl acetate (V∶V=5∶1) as eluent to afford the title compound **5a** (23.0 mg, 77% yield) as a colorless solid. m.p. 133～135 ℃; R_f = 0.50 (petroleum ether/ethyl acetate, V∶V=5∶1). ^{1}H NMR (400 MHz, $CDCl_3$, 25 ℃) δ: 7.69～7.57 (m, 1H), 7.36～7.33 (m, 1H), 7.31～7.27 (m, 2H), 7.26～7.20 (m, 2H), 7.16 (dt, J=8.1, 1.5 Hz, 3H), 4.14 (d, J=2.3 Hz, 2H), 3.38 (s, 1H), 0.16 (s, 9H); ^{13}C NMR (151 MHz, $CDCl_3$, 25 ℃) δ: 146.0, 145.9, 140.5, 133.2, 130.2, 128.0, 127.8, 127.7, 125.6, 125.5, 77.4, 64.9, −1.9; IR (ATR) ν: 1688, 1569, 1476, 1416, 1301, 1260, 1141, 895, 850, 745 cm^{-1}; HRMS (APCI-FTMS) calcd for $C_{17}H_{21}OSi$ $(M-OH)^-$ 269.1356, found 269.1357.

Supporting Information Experimental procedures, condition screening table, characterization data, and copies of NMR spectra for all new products. The Supporting Information is available free of charge via the Internet at http://sioc-journal.cn.

References

[1] (a) Lee, V. Y. *Organosilicon Compounds*, Elsevier Ltd, England, **2017**.
(b) Hiyama, T.; Oestreich, M. *Organosilicon Chemistry*: *Novel Approaches and Reactions*, Wiley, Germany, **2020**.
(c) Huang, J.; Liu, F.; Wu, X.; Chen, J.-Q.; Wu, J. *Org. Chem. Front.* **2022**, *9*, 2840.
(d) Zhai, X. Y.; Wang, X. Q.; Bo, W.; Zhou, Y.-G. *Chin. J. Chem.* **2022**, *40*, 21.
(e) Liu, Y.; Zhan, M.; Li, P. F. *Chin. J. Chem.* **2022**, *40*, 1028.
(f) An, K.; He, W. *Chin. J. Org. Chem.* **2022**, *42*, 918 (in Chinese).
(安坤, 何伟, 有机化学, **2022**, *42*, 918.)

[2] (a) Raabe, G.; Michl, J. *Chem. Rev.* **1985**, *85*, 419.
(b) Auner, V. N.; Grobe, J. *Anorg. Allg. Chem.* **1983**, *500*, 132.
(c) Gor-don, M. S.; Boatz, J. A.; Walsh, R. J. *Phys. Chem.* **1989**, *93*, 1584.

[3] (a) Yuan, W.; Smirnov, P.; Oestreich, M. *Chem* **2018**, *4*, 1443.
(b) Zhang, L.; An, K.; Wang, Y.; Wu, Y. D.; Zhang, X.; Yu, Z. X.; He, W. *J. Am. Chem. Soc.* **2021**, *143*, 3571.
(c) Wang, X. B.; Zheng, Z. J.; Xie, J. L.; Gu, X. W.; Mu, Q. C.; Yin, G. W.; Ye, F.; Xu, Z.; Xu, L. W. *Angew. Chem.*, *Int. Ed.* **2020**, *59*, 790.
(d) Chen, H.; Chen, Y.; Tang, X.; Liu, S.; Wang, R.; Hu, T.; Gao, L.; Song, Z. *Angew. Chem.*, *Int. Ed.* **2019**, *58*, 4695.
(e) Zhao, W.-T.; Gao, F.; Zhao, D. *Angew. Chem.*, *Int. Ed.* **2018**, *57*, 6329.
(f) Mu, Q.-C.; Chen, J.; Xia, C.-G.; Xu, L.-W. *Coord. Chem. Rev.* **2018**, *374*, 93.
(e) Huang, W-S.; Wang, Q.; Yang, H.; Xu, L. W. *Synthesis* **2022**, *54*, 5400.
(f) Chen, S.; He, X.; Jin, C.; Zhang, W.-L.; Yang, Y.; Liu, S.; Lan, Y.; Houk, K. N.; Shen, X. *Angew. Chem.*, *Int. Ed.* **2022**, *61*, e202213431.
(g) Okumura, S.; Sun, F.; Ishida, N.; Murakami, M. *J. Am. Chem. Soc.* **2017**, *139*, 12414.
(h) Uenishi, K.; Imae, I.; Shirakawa, E.; Kawakami, Y. *Macromolecules* **2002**, *35*, 2455.
(i) Shintani, R.; Moriya, K.; Hayashi, T. *J. Am. Chem. Soc.* **2011**, *133*, 16440.

[4] Okazaki, R.; Kang, K.-T.; Inamoto, N. *Tetrahedron Lett.* **1981**, *22*, 235.

[5] Takeyama, Y.; Oshima, K.; Utimoto, K. *Tetrahedron Lett.* **1990**, *31*, 6059.

[6] Hirano, K.; Yorimitsu, H.; Oshima, K. *Org. Lett.* **2006**, *8*, 483.

[7] Wang, Q.; Zhang, K.-B.; Xu, H.; Li, S.-N.; Zhu, W.-K.; Ye, F.; Xu, Z.; Lan, Y.; Xu, L.-W. *ACS Catal.* **2022**, *12*, 4571.

[8] (a) Zhou, G.; Guo, Z.; Shen, X. *Angew. Chem.*, *Int. Ed.* **2023**, *62*, e202217189.
(b) Priebbenow, D. L. *Adv. Synth. Catal.* **2020**, *362*, 1927.
(c) Zhu, Z.; Zhang, W.; Zhang, Y.; Liu, S.; Shen, X. *CCS Chem.* **2023**, *5*, 325.
(d) Zhang, Y.; Zhou, G.; Gong, X.; Guo, Z.; Qi, X.; Shen, X. *Angew. Chem.*, *Int. Ed.* **2022**, *61*, e202202175.
(e) Zhou, G.; Shen, X. *Angew. Chem.*, *Int. Ed.* **2022**, *61*, e202115334.
(f) Zhang, Y.; Zhang, Y.; Ye, C.; Qi, X.; Wu, L.-Z.; Shen, X. *Nat. Commun.* **2022**, *13*, 6111.
(g) Zhang, Y.; Niu, Y.; Guo, Y.; Wang, J.; Liu, S.; Shen, X. *Angew. Chem.*, *Int. Ed.* **2022**, *61*, e202212201.
(h) Ye, J.-H.; Quach, L.; Paulisch, T.; Glorius, F. *J. Am. Chem. Soc.* **2019**, *141*, 16227.
(i) Zheng, L.; Guo, X.; Li, Y.; Wu, Y.; Xue, X.; Wang, P. *Angew. Chem.*, *Int. Ed.* **2023**, *62*, e202216373.
(i) Ito, K.; Tamashima, H.; Iwasawa, N.; Kusama, H. *J. Am. Chem. Soc.* **2011**, *133*, 3716.
(j) Dalton, J. C.; Bourque, R. A. *J. Am. Chem. Soc.* **1981**, *103*, 699.

[9] (a) Ricci, A.; Fiorenza, M.; Degl'Innocenti, A.; Seconi, G.; Dembech, P.; Witzgall, K.; Bestmann, H. J. *Angew. Chem.*, *Int. Ed.* **1985**, *24*, 2534.
(b) Xin, L. H.; Johnson, J. S. *Angew. Chem.*, *Int. Ed.* **2003**, *42*, 1068.
(c) Xin, L. H.; Potnick, J. R.; Johnson, J. S. *J. Am. Chem. Soc.* **2004**, *126*, 3070.

[10] Nakatani, S.; Ito, Y.; Sakurai, S.; Kodama, T.; Tobisu, M. *J. Org. Chem.* **2020**, *85*, 7588.

(Zhao, C.)

