Supporting Information

Electrochemical oxidative dehydrogenation of hydrosilanes to generate silyl radicals: An efficient method for construction

Si-O/Si-Si bonds utilizing recyclable ionic liquid catalyst

Zhaoxin Wei^a, Ziren Chen^a, Fei Xue^a, Yuancheng Yue^a, Shaofeng Wu^a, Yonghong Zhang^a, Bin Wang^a, Yu Xia^a, Weiwei Jin^b and Chenjiang Liu^{*a}

^aState Key Laboratory of Chemistry and Utilization of Carbon Based Energy Resources, Key Laboratory of Oil and Gas Fine Chemicals, Ministry of Education & Xinjiang Uygur Autonomous Region, Urumqi Key Laboratory of Green Catalysis and Synthesis Technology, College of Chemistry, Xinjiang University, Urumqi 830017, P. R. China

E-mail: pxylcj@126.com

^bKey Laboratory of Specialty Agri-product Quality and Hazard Controlling Technology of Zhejiang Province, College of Life Sciences, China Jiliang University, Hangzhou 310018, P. R. China

Table of Contents

1. Materials and methods	S2
2. Experimental procedures	S3
2.1 Preparation of the starting silanes	S3
2.2 Optimization of reaction conditions	S4
2.3 General procedure for the synthesis of products	S4
2.4 General procedure for the ionic liquid recycling experiment	S 7
2.5 Gram-scale synthesis	S7
3. Mechanistic studies	S 8
3.1 On-off electric experiment	S 8
3.2 Radical trapping experiments	S 8
3.3 Parallel kinetic isotope effect experiments	S9
3.4 H ₂ detection experiment	S10
4. Analytical data	S10
5. References	S27
6. Copies of NMR spectra	S28

1. General consideration

¹H and ¹³C NMR spectra were recorded on a Varian Inova-400 or 600 MHz spectrometers. ¹H and ¹³C NMR chemical shifts were determined relative to internal standard TMS at δ 0.0 or CDCl₃ (δ (¹H), 7.26 ppm; δ (¹³C), 77.16 ppm). Chemical shifts (δ) were reported in ppm, and coupling constants (J) are in Hertz (Hz). The following abbreviations were used to explain the multiplicities: s = singlet, d =doublet, t = triplet, q = quartet, m = multiplet, br = broad. The HRMS analysis was obtained on a Agilent 6540 UHD Q-TOF mass spectrometer. The melting point was recorded on BÜCHI (M-560) and uncorrected. Analytical thin layer chromatography (TLC) was performed on 0.25 mm silica gel 60 F254 plates and viewed by UV light (254 nm). Column chromatographic purification was performed using 200-300 mesh silica gel. Electrochemical reactions were performed on DC Power Supply (GPD-2303S). The H₂ was detected by a gaschromatograph (SHIMADZU GC-2014 C) and analyzed by a thermal conductivity detector (TCD, 5A molecular sieve column) with column diameter (2 m \times 4 mm) and argon as the carrier gas. Cyclic voltammetry (CV) was carried out on a CHI660E electrochemical workstation (CH Instruments, Ins). All commercial reagents and solvents were purchased from commercial sources and used as received unless otherwise indicated.

2. Experimental procedures

2.1 Preparation of the starting silanes

2.1.1 General procedure for the preparation of starting materials of products 9-21, 23, 24^[1]



In a 100 mL round-bottom flask, aryl bromides (5.0 mmol, 1.0 equiv.) in THF (10 mL) was cooled to -78 °C. *n*-BuLi (3.2 mL,1.6 M in THF, 6.0 mmol, 1.2 equiv.) was added dropwise slowly over 30 min. The resulting mixture was stirred at -78 °C for 2 h before the dropwise addition of chlorodiphenylsilane (6.0 mmol, 1.2 equiv.). The reaction was allowed to warm to room temperature and stirred for 8 h. The reaction mixture was quenched with NH₄Cl (15 mL, saturated aqueous solution) and the mixture was extracted with *tert*-Butyl methyl ether (3×15 mL). The combined organic layer was washed with water (20 mL), brine (20 mL), dried over anhydrous Na₂SO₄, and then concentrated under reduced pressure. The residue was purified by flash silica gel column chromatography to afford the hydrosilanes.

2.1.2 General procedure for the preparation of starting materials of product 22^[1]

$$\begin{array}{c} \begin{array}{c} Ph \\ I \\ + CI - Si - H \\ Ph \end{array} \xrightarrow{i - PrMgCI, - 78 \circ C} Ph \xrightarrow{Ph} \\ \hline THF \\ Ph \end{array} \xrightarrow{Ph} Ph \xrightarrow{Ph} Ph \xrightarrow{Ph} \\ \end{array}$$

In a 100 mL round-bottom flask, 4-iodo-1,1'-biphenyl (5.0 mmol, 1.0 equiv.) in THF (10 mL) was cooled to -78 °C. *i*-PrMgCl (3 mL, 2.0 M in THF, 6.0 mmol, 1.2 equiv.) was added dropwise slowly over 15 min. The resulting mixture was allowed to warm to -40 °C in 2 h and maintained at -40 °C for another 2 h before the dropwise addition of chlorodiphenylsilane (6.0 mmol, 1.2 equiv.). The reaction was allowed to warm to room temperature and stirred for 8 h. The reaction mixture was quenched with NH₄Cl (15 mL, saturated aqueous solution) and the mixture was extracted with CH₂Cl₂ (3×15 mL). The combined organic layer was washed with water (20 mL), brine (20 mL), dried over anhydrous Na₂SO₄, and then concentrated under reduced pressure. The residue was purified by flash silica gel column chromatography to afford the [1,1'-biphenyl]-4-yldiphenylsilane.

2.2 Optimization of reaction conditions

Table S1. Optimization of reaction conditions^a

	F Ph-S F 1	Ph electr Si-H + MeOH——— Ph ai Ph und	ode, current <u>cat.</u> ➤ Pt r, rt, time ivided cell	Ph n-Si - OMe + H ₂ Ph 2	
Entry	Electrode	Cat. (mol%)	Current (mA)	Time (h)	Conv. ^{<i>b</i>} (%)
1	Pt(+)/C(-)	TBAI (50)	15	1	99
2	Pt(+)/C(-)	TBAI (10)	15	1	95
3	Pt(+)/C(-)	TBAI (5)	15	1	43
4	Pt(+)/C(-)	TBAB (10)	15	1	98
5	Pt(+)/C(-)	TBAClO ₄ (10)	15	1	n.d
6	Pt(+)/C(-)	$\text{TBAPF}_6(10)$	15	1	n.d
7	Pt(+)/C(-)	TBACl (10)	15	1	50
8	C(+)/C(-)	TBAB (10)	15	1	96
9	Pt(+)/Pt(-)	TBAB (10)	15	1	90
10	C(+)/Pt(-)	TBAB (10)	15	1	98
11	C(+)/Ni(-)	TBAB (10)	15	1	95
12	C(+)/C(-)	TBAB (10)	12	1	85
13	C(+)/C(-)	TBAB (10)	18	1	98
14	C(+)/C(-)	TBAB (10)	15	0.5	56
15	C(+)/C(-)	TBAB (10)	15	1.5	98
16	C(+)/C(-)	PmimBr (10)	15	1	96
17	C(+)/C(-)	[Bmpyrr]Br (10)	15	1	99 (95) ^c
18	C(+)/C(-)	BzmimBr (10)	15	1	35
19	C(+)/C(-)	AmimBr (10)	15	1	59
20	C(+)/C(-)	HmmimBr (10)	15	1	90
21	C(+)/C(-)	[C4MPd]Br (10)	15	1	91
22	C(+)/C(-)	[Bmpyrr]BF ₄ (10)	15	1	n.d
23^d	C(+)/C(-)	[Bmpyrr]Br (10)	15	1	85
24	C(+)/C(-)		15	1	n.d
25	C(+)/C(-)	[Bmpyrr]Br (10)	0	1	n.d

^{*a*} Standard reaction conditions: electrodes, constant current, **1** (0.24 mmol), catalyst, MeOH (5.0 mL), room temperature, time, undivided cell, under air. ^{*b*} conv. determined by GC. ^{*c*} Yield of isolated product. ^{*d*} MeOH = 3 mL. n.d. = not detected.

2.3 General procedure for the synthesis of products

2.3.1 General procedure for the synthesis of alkoxysilane (taking 2 as an example)



Under air, a mixture of triphenylsilane 1 (63 mg, 0.24 mmol), [Bmpyrr]Br (5 mg, 0.024 mmol) and MeOH (5.0 mL) were added in an oven-dried undivided bottle (10 mL). The bottle was equipped with graphite plates (10 mm × 15 mm × 2 mm) as anode and cathode. The resulting mixture was stirred and electrolyzed at a constant current of 15 mA at ambient temperature for 1 h. When the reaction was finished, the resulting mixture was evaporated under reduced pressure. The resultant residue was purified by silica gel column chromatography (eluent: petroleum ether/EtOAc = 80:1, v/v) to afford the desired product **2** as a colorless liquid (66 mg, 95% yield).



Fig. S1 Experimental facility

2.3.2 General procedure for the synthesis of aryloxysilanes (taking 45 as an example)



Under air, a mixture of *tert*-butyldimethylsilane (120 μ L, 0.72 mmol, 3.0 equiv.), [BMpyrr]Br (27 mg, 0.12 mmol, 0.5 equiv.), 4-ethylphenol (29 μ L, 0.24 mmol, 1.0 equiv.) and MeCN (5 mL) were added in an oven-dried undivided bottle (10 mL). The bottle was equipped with graphite plate (10 mm × 10 mm × 2 mm) as anode and nickel plate (10 mm × 10 mm × 0.1 mm) as cathode. The resulting mixture was stirred

and electrolyzed at a constant current of 15 mA at ambient temperature for 1.5 h. When the reaction was finished, the resulting mixture was evaporated under reduced pressure. The resultant residue was purified by silica gel column chromatography (eluent: petroleum ether/EtOAc = 30:1, v/v) to afford the desired product **45** as a colorless liquid (47 mg, 83%).

2.3.3 General procedure for the synthesis of silanol (taking 60 as an example)

$$\begin{array}{c} Ph \\ Ph-Si-H \\ Ph \\ Ph \\ Ph \\ 1 \end{array} + \begin{array}{c} C(+)/Ni(-), I = 15 \text{ mA} \\ [Bmpyrr]Br (50 \text{ mol}\%) \\ air, rt, 1.5 \text{ h} \\ undivided cell \\ 1 \end{array} + \begin{array}{c} Ph \\ Ph-Si-OH \\ Ph \\ 0 \end{array}$$

Under air, a mixture of triphenylsilane **1** (63 mg, 0.24 mmol), [Bmpyrr]Br (26 mg, 0.12 mmol), H₂O (0.5 mL)and MeCN (5.0 mL) were added in an oven-dried undivided bottle (10 mL). The bottle was equipped with graphite plate (10 mm × 10 mm × 2 mm) as anode and nickel plate (10 mm × 10 mm × 0.1 mm) as cathode. The resulting mixture was stirred and electrolyzed at a constant current of 15 mA at ambient temperature for 1.5 h. When the reaction was finished, the resulting mixture was evaporated under reduced pressure. The resultant residue was purified by silica gel column chromatography (eluent: petroleum ether/EtOAc = 30:1, v/v) to afford the desired product **60** as a white solid (59 mg, 89% yield).

2.3.4 General procedure for the synthesis of 1,2-dimethyl-1,1,2,2-tetraphenyldisilane

$$\begin{array}{c} \mathsf{Ph-} \overset{|}{\mathsf{Si-H}} & \begin{array}{c} \mathsf{C(+)/C(-), I=5 \ mA} \\ \hline [\mathsf{C4MPd}]\mathsf{Br} \ (30 \ mol\%) \\ \hline \mathsf{MeCN} \ (4 \ mL), \ air, \ rt, \ 1 \ h \\ undivided \ cell \end{array} \end{array} \xrightarrow{} \begin{array}{c} \mathsf{Ph-} \overset{|}{\mathsf{Si-}\mathsf{Ph}} + \mathsf{H}_2 \\ \hline \mathsf{H} \overset{|}{\mathsf{C4MPd}} \end{array}$$

Under air, a mixture of methyldiphenylsilane (40 mg, 0.2 mmol, 1.0 equiv.), [C4MPd]Br (14 mg, 0.06 mmol, 0.3 equiv), and MeCN (4.0 mL) were added in an oven-dried undivided bottle (10 mL). The bottle was equipped with graphite plates (10 mm × 15 mm × 2 mm) as anode and cathode. The resulting mixture was stirred and electrolyzed at a constant current of 5 mA at ambient temperature for 1 h. When the reaction was finished, the resulting mixture was evaporated under reduced pressure. The resultant residue was purified by silica gel column chromatography (eluent: petroleum ether/EtOAc = 80:1, v/v) to afford the desired product 1,2-dimethyl-1,1,2,2-tetraphenyldisilane as a colorless liquid (37 mg, 93%).

2.3.5 Unreactive substrates



Fig. S2 Unreactive substrates

We utilized the aforementioned *O*-nucleophiles as substrates (Fig. S2), yet none of them exhibited reactivity.

2.4 General procedure for the ionic liquid recycling experiment



Under air, triphenylsilane 1 (63 mg, 0.24 mmol), [Bmpyrr]Br (5 mg, 0.024 mmol) and MeOH (5.0 mL) were added in an oven-dried undivided bottle (10 mL). The bottle was equipped with graphite plates (10 mm \times 15 mm \times 2 mm) as anode and cathode. The resulting mixture was stirred and electrolyzed at a constant current of 15 mA under room temperature for 1 h. When the reaction was finished, the resulting mixture was evaporated under reduced pressure. Next, water (10 mL) and ethyl acetate (10 mL) were added, the organic phase was extracted three times with water (3×10 mL) and all the water phase was combined. Then, [Bmpyrr]Br was recovered from the aqueous layer and recycled for the next reaction after being dried to constant weight under vacuum at 80 °C.

2.5 Gram-scale synthesis

2.5.1 Gram-scale synthesis of alkoxysilane 2



Under air, a mixture of triphenylsilane 1 (1.04 g, 4 mmol), [Bmpyrr]Br (89 mg, 0.4 mmol) and MeOH (10.0 mL) were added in a bottle (50 mL). The bottle was equipped with graphite plates (10 mm \times 40 mm \times 2 mm) as anode and cathode, The resulting mixture was stirred and electrolyzed at a constant current of 40 mA at ambient temperature for 4 h. When the reaction was finished, the resulting mixture

was evaporated under reduced pressure. The resultant residue was purified by silica gel column chromatography (eluent: petroleum ether/EtOAc = 120:1, v/v) to afford the desired product **2** as a colorless liquid (1.12 g, 97% yield).



Fig. S3 A device for gram-scale experiment

2.5.2 Gram-scale synthesis of silanol 60



Under air, a mixture of triphenylsilane 1 (1.30 g, 5 mmol), [Bmpyrr]Br (111 mg, 0.5 mmol), H₂O (5.0 mL)and CH₃CN (25.0 mL) were added in an oven-dried undivided bottle (10 mL). The bottle was equipped with graphite plate (10 mm × 40 mm × 1 mm) as anode and nickel plate (10 mm × 40 mm × 0.1 mm) as cathode. The resulting mixture was stirred and electrolyzed at a constant current of 40 mA at ambient temperature for 8 h. When the reaction was finished, the resulting mixture was evaporated under reduced pressure. The resultant residue was purified by silica gel column chromatography (eluent: petroleum ether/EtOAc = 30:1, v/v) to afford the desired product **60** as a white solid (1.24 g, 90% yield).

2.5.3 Gram-scale synthesis of tertmethyldiphenyldisilane



Under air, a mixture of dimethylphenylsilane (2.04 g, 15 mmol), [C4MPd]Br

(1.06 g, 4.5 mmol) and CH₃CN (30.0 mL) were added in an oven-dried undivided bottle (100 mL). The bottle was equipped with graphite plates (10 mm × 40 mm × 2 mm) as anode and cathode. The resulting mixture was stirred and electrolyzed at a constant current of 5 mA at ambient temperature for 46 h. When the reaction was finished, the resulting mixture was evaporated under reduced pressure. The resultant residue was purified by silica gel column chromatography (eluent: petroleum ether/EtOAc = 80:1, v/v) to afford the desired product as a colourless liquid (1.08 g, 95% yield).

3. Mechanistic studies

3.1 On-off electric experiment



3.2 Radical trapping experiments^a

Ph Ph-Si-H Ph 1	C(+)/C(-), I = 15 mA [Bmpyrr]Br (10 mol%) + MeOH air, rt, 1 h undivided cell	Ph - Ph−Si <mark>=OMe</mark> + H ₂ Ph 2
Entry	Radical scavenger	Yield of $2 (\%)^b$
1	none	95%
2	TEMPO (1 equiv.)	26%
3	TEMPO (2 equiv.)	10%

^{*a*} Standard reaction conditions: graphite plate anode (10 mm × 15 mm × 0.2 mm), graphite plate cathode (10 mm × 15 mm × 0.2 mm), constant current = 15 mA, **1** (0.24 mmol), [BMPyrr]Br (10

mol%), MeOH (5.0 mL), room temperature, 1 h, undivided cell, under air. ^bYield of isolated product.

When 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO, 2.0 equiv.) was introduced into the model reactions, the desired triphenylsiloxane was isolated in 26% yield after column chromatography separation. Next, the TEMPO was improving to 2 equiv. at the standard condition the isolated yield of **2** reduced from 95% to 10%. These results suggest the involvement of radical process in this transformation.

3.3 Parallel kinetic isotope effect experiments



Under air, a mixture of 1 (63 mg, 0.24 mmol, 1 equiv.) or [D]-1 (63 mg, 0.24 mmol, 1 equiv.), [Bmpyrr]Br (5 mg, 0.024 mmol) and MeOH (5.0 mL) were added in two oven-dried undivided bottles (10 mL). The bottles were equipped with graphite plates (10 mm x 10 mm x 2 mm) as anode and cathode. The resulting mixture was stirred and electrolyzed at a constant current of 15 mA at ambient temperature for 1 h. The two reaction mixtures were separately isolated by silica gel column chromatography (petroleum ether/EtOAc = 80/1) (95% and 0%). The result indicate that Si-H bond cleavage is involved in the rate-determining step of this electrochemical reaction.

3.4 H₂ detection experiment





Fig. S4 H₂ detection experiment by GC

In order to demonstrate the H_2 evolution during this procedure, the model reaction of triphensilane (1) with methanol was detected by GC under standard conditions. As a standard, we first tested the retention time of a mixture of hydrogen, oxygen, and nitrogen at 1.351, 2.052, and 2.754 min, respectively (Fig. S4).

4. Analytical data

Ph Ph Si Ph O

.**Methoxytriphenylsilane** (2)^[1]: 66 mg, 95% yield. Colorless liquid. ¹H NMR (600 MHz, CDCl₃) δ 7.63-7.62 (m, 6H), 7.44-7.41 (m, 3H), 7.39-7.36(m, 6H), 3.64(s, 3H). ¹³C NMR (150 MHz, CDCl₃) δ 135.5, 134.0, 130.2, 128.04, 52.0.



(2-chlorophenyl)(methoxy)diphenylsilane (9)^[21]: 71 mg, 91% yield. Colorless liquid. ¹H NMR (600 MHz, CDCl₃) δ 7.73-7.72 (m, 4H), 7.51-7.39 (m, 9H), 7.34-7.32 (m, 1H), 3.69(s, 3H). ¹³C NMR (150 MHz, CDCl₃) δ 141.1, 138.2, 135.5, 133.7, 133.4, 131.9, 130.2, 129.7, 128.0, 126.2, 52.1. HRMS (ESI) m/z Calcd for C₁₄H₁₂FNOS [M+H]⁺: 325.0810; Found: 325.0809.

Ph Ph Si O Cl

(3-chlorophenyl)(methoxy)diphenylsilane (10)^[2]: 68 mg, 87% yield. Colorless liquid. ¹H NMR (600 MHz, CDCl₃) δ 7.53-7.51 (m, 5H), 7.41-7.36 (m, 3H), 7.33-7.31 (m, 5H), 7.24 (t, J = 7.6 Hz, 1H), 3.56 (s, 3H). ¹³C NMR (150 MHz, CDCl₃)

δ 137.0, 135.48, 135.0, 134.6, 133.4, 133.2, 130.5, 130.3, 129.6, 128.2, 52.1. **HRMS** (ESI) m/z Calcd for C₁₄H₁₂FNOS [M+H]⁺: 325.0810; Found: 325.0810.



(4-chlorophenyl)(methoxy)diphenylsilane (11)^[2]: 56 mg, 72% yield. Colorless liquid. ¹H NMR (600 MHz, CDCl₃) δ 7.63-7.61 (m, 4H), 7.58-7.56 (m, 2H), 7.49-7.46 (m, 2H), 7.43-7.39 (m, 6H), 3.65 (s, 3H). ¹³C NMR (150 MHz, CDCl₃) δ 136.9, 136.7, 135.5, 134.8, 133.5, 132.5, 130.4, 128.4, 128.2, 52.0.



(2-fluorophenyl)(methoxy)diphenylsilane (12): 53 mg, 72% yield. Colorless liquid. ¹H NMR (600 MHz, CDCl₃) δ 7.68-7.65 (m, 4H), 7.50-7.40 (m, 8H), 7.19 (t, J = 11.0 Hz, 1H), 7.07 (t, J = 12.5 Hz, 1H), 3.69 (s, 3H). ¹³C NMR (150 MHz, CDCl₃) δ 167.3 (d, J = 241.5 Hz), 137.3 (d, J = 9.0 Hz), 135.3, 133.5, 132.8 (d, J = 9.0 Hz), 130.3, 128.1, 124.2, 121.0 (d, J = 28.5 Hz), 115.2 (d, J = 24.0 Hz), 52.1. HRMS (ESI) m/z Calcd for C₁₄H₁₂FNOS [M+H]⁺: 309.1105; Found: 309.1108.



(3-fluorophenyl)(methoxy)diphenylsilane (13): 52 mg, 70% yield. Colorless liquid. ¹H NMR (600 MHz, CDCl₃) δ 7.50-7.47 (m, 4H), 7.35-7.32 (m, 2H), 7.29-7.22 (m, 6H), 7.18 (dd, J = 2.6 Hz, 8.7 Hz, 1H),7.01-6.97 (m, 1H), 3.52(s, 3H). ¹³C NMR (150 MHz, CDCl₃) δ 162.7 (d, J = 247.5 Hz), 137.3 (d, J = 4.5 Hz), 135.5, 133.3, 131.0 (d, J = 3.0 Hz), 130.5, 129.9 (d, J = 30.0 Hz), 128.2, 121.7 (d, J = 72.0Hz), 117.2 (d, J = 72.0 Hz), 52.1. HRMS (ESI) m/z Calcd for C₁₄H₁₂FNOS [M+H]⁺: 309.1105; Found: 309.1103.

F Ph Ph Ph

(4-fluorophenyl)(methoxy)diphenylsilane (14): 50 mg, 68% yield. Colorless liquid. ¹H NMR (600 MHz, CDCl₃) δ 7.50-7.47 (m, 4H), 7.35-7.32 (m, 2H),

7.29-7.22 (m, 6H), 7.18 (dd, J = 2.6 Hz, 8.7 Hz, 1H), 7.01-6.97 (m, 1H), 3.52(s, 3H). ¹³C NMR (150 MHz, CDCl₃) δ 162.7 (d, *J* = 247.5 Hz), 137.3 (d, *J* = 4.5 Hz), 135.5, 133.3, 131.0 (d, *J* = 3.0 Hz), 130.5, 129.9 (d, *J* = 30.0 Hz), 128.2, 121.7 (d, *J* = 72.0 Hz), 117.2 (d, *J* = 72.0 Hz), 52.1. HRMS (ESI) m/z Calcd for C₁₄H₁₂FNOS [M+H]⁺: 309.1105; Found:309.1103.



Methoxydiphenyl(*o*-tolyl)silane (15)^[3]: 56 mg, 77% yield. Colorless liquid. ¹H NMR (400 MHz, CDCl₃) δ 7.66-7.63 (m, 4H), 7.57 (d, J = 7.5Hz, 1H), 7.49-7.36 (m, 7H), 7.23-7.19 (m, 2H), 3.67 (s, 3H), 2.33 (s, 3H). ¹³C NMR (150 MHz, CDCl₃,) δ 145.0, 137.0, 135.5, 134.5, 132.6, 130.5, 130.2, 130.1, 128.1, 150.0, 51.9, 23.2.



Methoxydiphenyl(*m*-tolyl)silane (16): 59 mg, 81% yield. Colorless liquid. ¹H NMR (600 MHz, CDCl₃) δ 7.74-7.71 (m, 4H), 7.56-7.55 (m, 1H), 7.53-7.44 (m, 7H), 7.37-7.32 (m, 2H), 3.73(s, 3H), 2.42(s, 3H). ¹³C NMR (150 MHz, CDCl₃) δ 137.4, 136.0, 135.5, 134.2, 133.8, 132.6, 131.1, 130.2, 128.0, 128.0, 52.0, 21.7. HRMS (ESI) m/z Calcd for C₂₀H₂₀OSi [M+H]⁺: 305.1356; Found: 305.1355.

Ph Ph Si O

Methoxydiphenyl(*p*-tolyl)silane (17): 70 mg, 96% yield. Colorless liquid. ¹H NMR (400 MHz, CDCl₃) δ 7.72-7.69 (m, 4H), 7.61-7.59 (d, J = 7.9 Hz, 2H), 7.52-7.42 (m, 6H), 7.29-7.27 (d, J = 7.9 Hz, 2H), 3.71 (s, 3H), 2.44 (s, 3H). ¹³C NMR (150 MHz, CDCl₃) δ 140.2, 135.6, 135.5, 134.3, 130.3, 130.1, 128.9, 128.0, 52.0, 21.7.



(4-(*tert*-butyl)phenyl)(methoxy)diphenylsilane (18): 71 mg, 86% yield. Colorless liquid. ¹H NMR (400 MHz, CDCl₃) δ 7.63 (d, J = 4.6 Hz, 4H), 7.55 (d, J = 5.3 Hz, 2H), 7.43-7.37 (m, 8H), 3.63 (s, 3H), 1.32 (s,9H). ¹³C NMR (150 MHz, CDCl₃) δ 153.2, 135.5, 135.4, 134.3, 130.4, 130.1, 128.0, 150.0, 52.0, 34.9, 31.4. HRMS (ESI) m/z Calcd for C₂₃H₂₆OSi [M+H]⁺: 347.1826; Found: 347.1822.



Methoxydiphenyl(4-(trimethylsilyl)phenyl)silane (19): 51 mg, 60% yield. Colorless liquid. ¹H NMR (600 MHz, CDCl₃) δ 7.69-7.67 (m, 4H), 7.62-7.60 (m, 2H), 7.47-7.45 (m, 4H), 7.43-7.41 (m, 4H), 3.68 (s, 3H), 1.37 (s, 9H). ¹³C NMR (150 MHz, CDCl₃) δ 142.7, 135.5, 134.7, 134.4, 134.1, 132.9, 130.2, 128.0, 52.0, -1.1. HRMS (ESI) m/z Calcd for C₂₂H₂₆OSi₂ [M+H]⁺: 363.1595; Found: 363.1593.



Methoxydiphenyl(4-(trifluoromethyl)phenyl)silane (**20**)^[4]: 52 mg, 61% yield. Colorless liquid. ¹**H NMR** (600 MHz, CDCl₃) δ 7.81-7.78 (m, 2H), 7.68 (d, J = 1.26 Hz, 1H), 7.67-7.64 (m, 5H), 7.52-7.48 (m, 2H), 7.46-7.42 (m, 4H), 3.69 (s, 3H). ¹³**C NMR** (150 MHz, CDCl₃) δ 139.3, 135.8, 135.5, 134.8, 133.1, 132.0 (d, J = 31.5 Hz), 130.6, 128.2, 124.6 (t, J = 3.0 Hz), 52.1.



Methoxy(4-methoxyphenyl)diphenylsilane (**21**): 58 mg, 76% yield. Colorless liquid. ¹**H NMR** (600 MHz, CDCl₃) δ 7.55-7.54 (m, 4H), 7.48-7.46 (m, 2H), 7.37-7.34 (m, 2H), 7.32-7.29 (m, 4H), 6.87-6.84 (m, 2H), 3.74 (s, 3H), 3.55 (s, 3H). ¹³**C NMR** (150 MHz, CDCl₃) δ 161.4, 137.2, 135.5, 134.4, 130.1, 128.1, 124.8, 113.8, 55.2, 51.9. **HRMS** (ESI) m/z Calcd for C₂₀H₂₀O₂Si [M+H]⁺: 321.1305; Found: 321.1308.



[1,1'-biphenyl]-4-yl(methoxy)diphenylsilane (22): 59 mg, 57% yield. White solid. ¹H NMR (600 MHz, CDCl₃) δ 7.74-7.64 (m, 10H), 7.51-7.46 (m, 5H),

7.44-7.37 (m, 4H). ¹³C NMR (150 MHz, CDCl₃) 142.9, 141.1, 136.0, 135.5, 134.0, 132.7, 130.3, 128.9, 128.1, 127.7, 127.3, 126.8, 52.0. HRMS (ESI) m/z Calcd for C₂₅H₂₂OSi [M+H]⁺: 367.1513; Found: 367.1512.



Ethyl 4-(methoxydiphenylsilyl)benzoate (23)^[21]: 72 mg, 82% yield. Colorless liquid. ¹H NMR (600 MHz, CDCl₃) δ 7.97 (d, J = 7.9 Hz, 2H), 7.64 (d, J = 7.9 Hz, 2H), 7.53 (d, J = 7.6 Hz, 4H), 7.39-7.37 (m, 2H), 7.33-7.31 (m, 4H), 4.30 (q, J = 7.1, 2H), 3.57 (s, 3H), 1.31 (t, J = 7.1 3H). ¹³C NMR (150 MHz, CDCl₃) δ 166.8, 140.1, 135.5, 135.4, 133.3, 131.9, 130.5, 128.7, 128.2, 61.2, 52.1, 14.5. HRMS (ESI) m/z Calcd for C₂₂H₂₂O₃Si [M+H]⁺: 363.1411; Found: 363.1408.



Methoxy(naphthalen-1-yl)diphenylsilane (24)^[5]: 71 mg, 88% yield. Colorless liquid. ¹H NMR (400 MHz, CDCl₃) δ 8.25 (d, *J* = 8.1 Hz, 1H), 7.99 (d, *J* = 8.2 Hz, 1H), 7.92 (d, *J* = 8.1 Hz, 1H), 7.79 (dd, *J* = 6.8 Hz, 1.2Hz, 1H), 7.72-7.69 (m, 4H), 7.52-7.47 (m, 4H), 7.44-7.40 (m, 5H), 3.75(s, 3H). ¹³C NMR (150 MHz, CDCl₃) δ 137.6, 137.0, 135.6, 134.6, 133.6, 131.9, 131.2, 130.2, 129.1, 128.9, 128.1, 126.3, 125.8, 125.2, 52.2.



Methoxydiphenyl(thiophen-2-yl)silane (25): 41 mg, 58% yield. Colorless liquid. ¹H NMR (600 MHz, CDCl3) δ 7.65 (d, J = 4.6 Hz, 1H), 7.59 (d, J = 7.0 Hz, 4H), 7.39-7.36 (m, 2H), 7.33-7.31 (m, 5H), 7.18-7.16 (m, 1H), 3.58 (s, 3H). ¹³C NMR (150 MHz, CDCl₃) δ 138.1, 135.3, 133.9, 133.2, 132.7, 130.5, 128.4, 128.1, 52.0. HRMS (ESI) m/z Calcd for C₁₇H₁₆OSSi [M+Na]⁺: 319.0583; Found: 319.0586.

Ph Si-Ó Ph

Tribenzyl(methoxy)silane (26)^[6]: 73 mg, 91% yield. Colorless liquid. ¹H NMR

(600 MHz, CDCl₃) δ 7.12 (t, J = 7.7 Hz, 6H), 7.01 (t, J = 7.4 Hz, 3H), 6.92 (d, J = 7.4 Hz, 6H), 3.27 (s, 3H), 2.07 (s, 6H). ¹³C NMR (150 MHz, CDCl₃) δ 138.2, 128.9, 128.5, 124.6, 51.6, 22.7.

Ph Ph Si O

Butyl(methoxy)diphenylsilane (27)^[7]: 73 mg, 91% yield. Colorless liquid. ¹H NMR (600 MHz, CDCl₃) δ 7.66-7.64 (m, 4H), 7.49-7.44 (m, 4H), 7.43-7.40 (m, 2H), 3.59 (s, 3H), 1.51-1.37 (m, 4H), 1.24-1.20 (m, 2H), 0.93 (t, *J* = 21.3, 10.6 Hz, 3H). ¹³C NMR (150 MHz, CDCl₃) 135.0, 134.8, 129.9, 128.0, 51.5, 26.6, 25.3, 13.8, 13.4.



Tert-butyl(methoxy)diphenylsilane (**28**)^[8]: 59 mg, 90% yield. Colorless liquid. **¹H NMR** (600 MHz, CDCl₃) δ 7.61-7.60 (m, 4H), 7.35-7.29 (m, 6H), 3.45 (s, 3H), 0.96 (s, 9H). ¹³C NMR (150 MHz, CDCl₃) δ 135.7, 133.7, 129.8, 127.8, 52.3, 26.9, 19.3.

Ph Ph Si O

Ethoxytriphenylsilane (29)^[1]: 67 mg, 92% yield. White solid. ¹H NMR (400 MHz, CDCl₃) δ 7.65-7.59 (m, 6H), 7.46-7.41 (m, 3H), 7.41-7.36 (m, 6H), 3.88 (q, J = 7.0 Hz, 2H), 1.24 (t, J = 7.0 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 135.5, 134.6, 130.1, 128.0, 59.9, 18.5.

$Ph Ph Si O^{+}_{2}$

Triphenyl(propoxy)silane (**30**)^[1]: 71 mg, 93% yield. White solid. ¹**H NMR** (400 MHz, CDCl₃) δ 7.65-7.58 (m, 6H), 7.46-7.42 (m, 3H), 7.41-7.37 (m, 6H), 3.77(t, J = 6.6 Hz, 2H), 1.65-1.60 (m, 2H), 0.92 (t, J = 7.4 Hz, 3H). ¹³**C NMR** (CDCl₃, 100 MHz) δ 135.5, 134.6, 130.1, 128.0, 65.8, 25.9, 10.5.

Butoxytriphenylsilane (31)^[1]: 72 mg, 90% yield. White solid. ¹H NMR (400 MHz, CDCl₃) δ 7.76-7.64 (m, 6H), 7.51-7.47 (m, 3H), 7.46-7.41 (m, 6H), 3.88(t, J =

6.5 Hz, 2H), 1.69-1.62 (m, 2H), 1.50-1.43 (m, 2H), 0.93 (t, *J* = 7.4 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 135.5, 134.6, 130.1, 128.0, 63.8, 34.8, 19.1, 14.0.

Ph Ph Si O

Pentyloxytriphenylsilane (**32**)^[1]: 74 mg, 89% yield. White solid. ¹**H NMR** (400 MHz, CDCl₃) δ 7.65-7.62 (m, 6H), 7.47-7.42 (m, 3H), 7.41-7.37 (m, 6H), 3.80 (t, J = 6.6 Hz, 2H), 1.64-1.57 (m, 2H), 1.37-1.32 (m, 2H), 1.29-1.23 (m, 2H), 0.87 (t, J = 7.1 Hz, 3H). ¹³**C NMR** (150 MHz, CDCl₃) δ 135.5, 134.6, 130.1, 128.0, 64.2, 32.4, 28.1, 22.6, 14.2.

PhPhSiO6

Heptyloxytriphenylsilane (33)^[21]: 71 mg, 79% yield. White solid. ¹H NMR (400 MHz, CDCl₃) δ 7.65-7.62 (m, 5H), 7.46 (d, J = 4.1Hz, 1H), 7.43-7.41 (m, 2H), 7.39-7.35 (m, 6H), 7.25-7.23 (m, 1H), 3.78(t, J = 4.4 Hz, 2H), 1.60-1.55 (m, 2H), 1.34-1.29 (m, 2H), 1.27-1.20 (m, 6H), 0.85 (t, J = 4.6 Hz, 3H). ¹³C NMR (150 MHz, CDCl₃) δ 135.5, 134.6, 130.1, 129.00, 64.1, 32.7, 32.0, 29.2, 25.9, 22.8, 14.3. Ph, Ph, Si.O

Isopropoxytriphenylsilane (**34**)^[1]: 67 mg, 87% yield. Colorless liquid. ¹**H NMR** (600 MHz, CDCl₃) δ 7.56-7.55 (m, 6H), 7.35-7.32 (m, 3H), 7.29-7.27 (m, 6H), 4.11-4.08 (m, 1H), 1.53 (d, J = 6.1 Hz, 6H). ¹³**C NMR** (150 MHz, CDCl₃) δ 135.6, 135.1, 130.0, 127.9, 66.5, 25.8.

Ph Si Ph

Cyclobutoxytriphenylsilane (**36**)^[1]: 62 mg, 78% yield. Colorless liquid. ¹**H NMR** (600 MHz, CDCl₃) δ 7.55-7.53 (m, 6H), 7.36-7.33 (m, 3H), 7.31-7.28 (m, 6H), 4.33-4.28 (m, 1H), 2.03-1.96 (m, 4H), 1.54-1.48 (m, 1H), 1.25-1.18 (m, 1H). ¹³**C NMR** (150 MHz, CDCl₃) δ 135.5, 134.8, 130.1, 127.9, 68.2, 33.9, 12.3.

Ph Ph Ph Si O

Cyclohexyloxytriphenylsilane (37)^[1]: 65 mg, 76% yield. Colorless liquid. ¹H

NMR (600 MHz, CDCl₃) δ 7.55-7.54 (m, 6H), 7.33-7.30 (m, 3H), 7.27-7.24 (m, 6H), 3.77-3.73 (m, 1H), 1.67-1.58 (m, 4H), 1.39-1.33 (m, 3H), 1.13-1.02 (m, 3H). ¹³C NMR (150 MHz, CDCl₃) δ 135.6, 135.3, 129.9, 127.9, 71.9, 35.7, 25.8, 24.1.

PhPhSiO4

(hex-5-en-1-yloxy)triphenylsilane (38)^[1]: 53 mg, 62% yield. Colorless liquid. ¹H NMR (600 MHz, CDCl₃) δ 7.55-7.54 (m, 6H), 7.37-7.34 (m, 3H), 7.31-7.29 (m, 6H), 5.72-5.66 (m, 1H), 4.90-4.86 (m, 1H), 4.85-4.83 (m, 1H), 3.72 (t, *J* = 6.5 Hz, 2H), 1.96-1.92 (m, 2H), 1.55-1.51 (m, 2H), 1.41-1.36 (m, 2H). ¹³C NMR (150 MHz, CDCl₃) δ 139.0, 135.5, 134.6, 130.1, 128.0, 114.5, 63.9, 33.6, 32.1, 25.2. HRMS (ESI) m/z Calcd for C₂₄H₂₆OSi [M+H]⁺: 359.1826; Found: 359.1823.



((2,3-dihydro-1*H*-inden-1-yl)oxy)triphenylsilane (39)^[10]: 46 mg, 49% yield. Yellow liquid. ¹H NMR (600 MHz, CDCl₃) δ 7.61-7.60 (m, 6H), 7.36-7.33 (m, 3H), 7.31-7.28 (m, 6H), 711-7.03 (m, 4H), 5.38 (t, J = 6.5 Hz, 1H), 2.93-2.88 (m, 1H), 2.63-2.57 (m, 1H), 2.20-2.14 (m, 1H), 2.01-1.96 (m, 1H). ¹³C NMR (150 MHz, CDCl₃) δ 145.2, 143.0, 135.7, 135.3, 134.8, 130.2, 128.0, 126.5, 124.8, 124.6, 77.6, 36.4, 29.9.

Ph Ph Si O

(benzyloxy)triphenylsilane (40)^[11]: 66 mg, 74% yield. Colorless liquid. ¹H NMR (600 MHz, CDCl₃) δ 7.58-7.56 (m, 6H), 7.36-7.33 (m, 3H), 7.30-7.28 (m, 6H), 7.26-7.25 (m, 2H), 7.23-7.21 (m, 2H), 7.16-7.14 (m, 1H), 4.81 (s, 2H). ¹³C NMR (150 MHz, CDCl₃) δ 140.7, 135.6, 134.1, 130.23, 128.4, 128.1, 127.2, 126.5, 65.7.

Ph.Ph Ph.Si.O

Triphenyl(1-phenylethoxy)silane (41)^[11]: 60 mg, 66% yield. Colorless liquid. ¹H NMR (600 MHz, CDCl₃) δ 7.52-7.50 (m, 6H), 7.33-7.30 (m, 3H), 7.26-7.22 (m, 8H), 7.19-7.16 (m, 2H), 7.13-7.10 (m, 1H), 4.95 (q, *J* = 6.4 Hz, 1H), 1.34 (d, *J* = 6.4 Hz, 3H). ¹³C NMR (150 MHz, CDCl₃) δ 146.1, 135.6, 134.7, 130.1, 128.3, 127.9, 127.0, 125.7, 72.2, 27.0.



(benzyloxy)triethylsilane (42)^[12]: 45 mg, 84% yield. Colorless liquid. ¹H NMR (600 MHz, CDCl₃) δ 7.27-7.24 (m, 4H), 7.18-7.15 (m, 1H), 4.66 (s, 2H), 0.91 (t, *J* = 7.9 Hz, 9H), 0.58 (q, *J* = 7.9 Hz, 6H). ¹³C NMR (150 MHz, CDCl₃) δ 141.5, 128.4, 127.1, 126.4, 64.9, 6.9, 4.7.

Ph Ph O^{Si}O

Diisopropoxydiphenylsilane (43)^[1]: 33 mg, 46% yield. Colorless liquid. ¹H NMR (600 MHz, CDCl₃) δ 7.67-7.65 (m, 4H), 7.41-7.38 (m, 2H), 7.36-7.33 (m, 4H), 4.24-4.18 (m, 2H), 1.34 (d, *J* = 6.1 Hz, 12H). ¹³C NMR (150 MHz, CDCl₃) δ 135.2, 134.4, 130.1, 127.8, 77.2, 65.8, 25.8.



Diphenyldipropoxysilane (44)^[1]: 37 mg, 51% yield. Colorless liquid. ¹H NMR (600 MHz, CDCl₃) δ 7.67-7.66 (m, 4H), 7.43-7.40 (m, 2H), 7.37-7.35 (m, 4H), 3.74 (t, J = 6.6 HZ, 4H), 1.65-1.59 (m, 4H), 0.93 (t, J = 7.4 Hz, 6H). ¹³C NMR (150 MHz, CDCl₃) δ 135.1, 133.5, 130.3, 127.9, 65.0, 25.8, 10.4.



Tert-butyl(4-ethylphenoxy)dimethylsilane (45)^[14]: 47 mg, 83% yield. Colorless liquid. ¹H NMR (600 MHz, CDCl₃) δ 7.05 (d, J = 8.5 HZ, 2H), 6.77-6.75 (m, 2H), 2.59 (q, J = 7.6 HZ, 2H), 1.21 (t, J = 7.6 HZ, 3H), 0.99 (s, 9H), 0.19 (s, 6H). ¹³C NMR (150 MHz, CDCl₃) δ 153.6, 137.1, 128.8, 119.9, 28.2, 25.9, 18.3, 15.9, -4.3.



Tert-butyl(4-(*tert*-butyl)phenoxy)dimethylsilane (46)^[15]: 48 mg, 76% yield. Colorless liquid. ¹H NMR (600 MHz, CDCl₃) δ 7.06-7.04 (m, 2H), 6.60-6.57 (m, 2H), 1.1 (s, 9H), 0.81 (s, 9H), 0.02 (s, 6H). ¹³C NMR (150 MHz, CDCl₃) δ 153.3, 143.9, 126.3, 119.4, 34.3, 31.7, 25.9, 18.3, -4.3

Tert-butyl(4-methoxyphenoxy)dimethylsilane (47)^[15]: 40 mg, 70% yield. Colorless liquid. ¹H NMR (600 MHz, CDCl₃) δ 6.77 (s, 4H), 3.76 (s, 3H), 0.98 (s, 9H), 0.17 (s, 6H). ¹³C NMR (150 MHz, CDCl₃) δ 154.2, 149.5, 120.8, 114.7, 55.8, 25.9, 18.3, -4.4.

Tert-butyl(4-chlorophenoxy)dimethylsilane (48)^[15]: 47 mg, 81% yield. Colorless liquid. ¹H NMR (600 MHz, CDCl₃) δ 6.99-6.96 (m, 2H), 6.57-6.55 (m, 2H), 0.78 (s, 9H), 0.01 (s, 6H). ¹³C NMR (150 MHz, CDCl₃) δ 154.5, 129.5, 126.4, 121.5, 25.8, 18.3, -4.4.



(4-bromophenoxy)(tert-butyl)dimethylsilane (49)^[15]: 50 mg, 73% yield. Colorless liquid. ¹H NMR (600 MHz, CDCl₃) δ 7.23-7.21 (m, 2H), 6.63-6.60 (m, 2H), 0.88 (s, 9H), 0.09 (s, 6H). ¹³C NMR (CDCl₃, 125 MHz) δ 155.0, 132.4, 122.1, 113.8, 25.8, 18.3, -4.3.



4-((tert-butyldimethylsilyl)oxy)benzonitrile (**50**)^[15]: 39 mg, 70% yield. Colorless liquid. ¹**H NMR** (600 MHz, CDCl₃) δ 7.55-7.52 (m, 2H), 6.90-6.87 (m, 2H), 0.98 (s, 9H), 0.23 (s, 6H). ¹³**C NMR** (150 MHz, CDCl₃) δ 159.8, 134.1, 121.0, 119.4, 104.8, 25.7, 18.4, -4.3.



1-(4-((tert-butyldimethylsilyl)oxy)phenyl)ethan-1-one (**51**)^[15]: 38 mg, 64% yield. Colorless liquid. ¹H NMR (600 MHz, CDCl₃) δ 7.89-7.87 (m, 2H), 6.88-6.86 (m, 2H), 2.55(s, 3H), 0.99 (s, 9H), 0.23 (s, 6H). ¹³C NMR (150 MHz, CDCl₃) δ 197.0, 160.4, 131.0, 130.9, 120.0, 26.5, 25.6, 18.4, -4.2.



Methyl 4-((tert-butyldimethylsilyl)oxy)benzoate (52)^[16]: 58 mg, 91% yield. Colorless liquid. ¹H NMR (600 MHz, CDCl₃) δ 7.95-7.92 (m, 2H), 6.86-6.84 (m, 2H), 3.87 (s, 3H), 0.98 (s, 9H), 0.22 (s, 6H). ¹³C NMR (150 MHz, CDCl₃) δ 167.0, 160.2, 131.7, 123.3, 119.9, 51.9, 25.7, 18.3, -4.3.

N-(4-((tert-butyldimethylsilyl)oxy)phenyl)acetamide (53)^[16]: 27 mg, 42% yield. Colorless liquid. ¹H NMR (600 MHz, CDCl₃) δ 7.50 (s, 1H), 7.34-7.32 (m, 2H), 6.78-6.75 (m, 2H), 2.12 (s, 3H), 0.97 (s, 9H), 0.17 (s, 6H). ¹³C NMR (150 MHz, CDCl₃) δ 168.5, 152.5, 131.7, 121.8, 120.4, 25.8, 24.4, 18.3, -4.4.



([1,1'-biphenyl]-4-yloxy)(tert-butyl)dimethylsilane (54)^[15]: 60 mg, 88% yield. Colorless liquid. ¹H NMR (600 MHz, CDCl₃) δ 7.55-7.53 (s, 2H), 7.47-7.44 (m, 2H), 7.40 (t, *J* = 7.8 Hz, 2H), 7.28 (t, *J* = 7.8 Hz, 1H), 6.91-6.89 (m, 2H), 1.00 (s, 9H), 0.23 (s, 6H). ¹³C NMR (150 MHz, CDCl₃) δ 155.4, 141.1, 134.5, 128.8, 128.2, 126.9, 126.8, 120.5, 25.9, 18.4, -4.2.



Tert-butyl(2-chlorophenoxy)dimethylsilane (55)^[15]: 35 mg, 60% yield. Colorless liquid. ¹H NMR (600 MHz, CDCl3) δ 7.35-7.34 (m, 1H), 7.14-7.11 (m, 1H), 6.90-6.88 (m, 2H), 105 (s, 9H), 0.24 (s, 6H). ¹³C NMR (150 MHz, CDCl₃) δ 151.8, 130.5, 127.6, 125.8, 122.2, 121.0, 25.8, 18.5, -4.2.



(2-allylphenoxy)(tert-butyl)dimethylsilane (56)^[18]: 40 mg, 67% yield. Colorless liquid. ¹H NMR (600 MHz, CDCl₃) δ 7.13 (d, J = 7.8 Hz, 1H), 7.10-7.07 (m, 1H), 6.90-6.88 (m, 1H), 6.79 (d, J = 7.8 Hz, 1H), 6.00-6.94 (m, 1H), 5.05-5.02 (m, 2H), 3.37 (d, J = 6.6 Hz, 2H), 1.01 (s, 9H), 0.23 (s, 6H). ¹³**C NMR** (150 MHz, CDCl₃) δ 153.5, 137.2, 130.8, 130.3, 127.2, 121.2, 118.6, 115.6, 34.6, 26.0, 18.4, -4.0.



Tert-butyl(4-chloro-3,5-dimethylphenoxy)dimethylsilane (57)^[19]: 43 mg, 62% yield. Colorless liquid. ¹H NMR (600 MHz, CDCl₃) δ 6.58 (s, 2H), 2.32 (s, 6H), 0.99 (s, 9H), 0.15 (s, 6H). ¹³C NMR (150 MHz, CDCl₃) δ 153.6, 137.1, 127.0, 120.1, 25.8, 20.9, 18.3, -4.3.



Tert-butyldimethyl(naphthalen-1-yloxy)silane (58)^[15]: 32 mg, 52% yield. Colorless liquid. ¹H NMR (600 MHz, CDCl₃) δ 8.22-8.19 (m, 1 H), 7.82-7.78 (m, 1H), 7.49-7.46 (m, 3H), 7.33 (t, J = 15.7, 7.8 Hz, 1H), 6.88 (dd, J = 7.6, 1.1 Hz, 1H), 1.12 (s, 9H), 0.31 (s, 6H). ¹³C NMR (150 MHz, CDCl₃) δ 151.8, 135.1, 128.1, 127.7, 126.3, 126.0, 125.2, 122.7, 121.0, 112.7, 26.1, 18.6, -4.1.



((1-bromonaphthalen-2-yl)oxy)(*tert*-butyl)dimethylsilane (59)^[20]: 54 mg, 67% yield. Colorless liquid. ¹H NMR (600 MHz, CDCl3) δ 8.24 (d, J = 8.4 Hz, 1H), 7.78 (d, J = 8.2 Hz, 1H), 7.71 (d, J = 8.8 Hz, 1H),7.58-7.55 (m, 1H), 7.42-7.39 (m, 1H), 7.14 (d, J = 8.8 Hz, 1H), 1.12 (s, 9H), 0.32 (s, 6H). ¹³C NMR (150 MHz, CDCl₃) δ 150.8, 133.6, 130.2, 128.6, 128.1, 127.6, 126.6, 124.5, 121.2, 112.3, 26.0, 18.6, -3.8. Ph Ph Ph

Triphenylsilanol (**60**)^[21]: 59 mg, 89% yield. White solid. ¹**H NMR** (400 MHz, CDCl₃) δ 7.66-7.64 (m, 6H), 7.49-7.44 (m, 3H), 7.42-7.38 (m, 6H), 2.68(s, 1H). ¹³**C NMR** (150 MHz, CDCl₃) δ 135.3, 135.1, 130.3, 128.1.



Diphenyl(p-tolyl)silanol (**61**)^[21]: 56 mg, 80% yield. Colorless liquid. ¹**H NMR** (600 MHz, CDCl₃) δ 7.55-7.52 (m, 4H), 7.42 (d, *J* = 7.8 Hz, 2H), 7.34-7.32 (m, 2H), 7.29-7.26 (m, 4H), 7.11 (d, *J* = 7.9 Hz, 2H), 2.55 (s, 1H), 2.27 (s, 3H). ¹³**C NMR** (150 MHz, CDCl₃) δ 140.3, 135.5, 135.2, 135.1, 131.7, 130.2, 128.9, 128.0, 21.7.



(4-(*tert***-butyl)phenyl)diphenylsilanol (62)**^[21]: 50 mg, 63% yield. Colorless liquid. ¹H NMR (600 MHz, CDCl₃) δ 7.67-7.65 (m, 4H), 7.59-7.57 (m, 2H), 7.46-7.38 (m, 8H), 2.32 (s, 6H), 1.34 (s, 9H). ¹³C NMR (150 MHz, CDCl₃) δ 153.3, 135.5, 135.1, 135.1, 131.7, 130.2, 128.1, 125.1, 34.9, 31.3.



Diphenyl(4-(trimethylsilyl)phenyl)silanol (**63**)^[21]: 41 mg, 49% yield. Colorless liquid. ¹**H NMR** (600 MHz, CDCl₃) δ 7.47-7.45 (m, 4H), 7.43 (d, *J* = 6.5 Hz, 2H), 7.36 (d, *J* = 7.7 Hz, 2H), 7.27-7.24 (m, 2H), 7.21-7.19 (m, 4H), 2.52 (s, 1H), 0.10 (s, 9H). ¹³**C NMR** (150 MHz, CDCl₃) δ 142.8, 135.6, 135.3, 135.1, 134.3, 132.9, 130.2, 128.1, -1.1.

Ph'

[1,1'-biphenyl]-4-yldiphenylsilanol (64)^[21]: 45 mg, 54% yield. Colorless liquid.
¹H NMR (600 MHz, CDCl₃) δ 7.74-7.72 (m, 2H), 7.69 (dd, J = 8.0 Hz,1.3 Hz, 4H), 7.65-7.63 (m, 4H), 7.50-7.46 (m, 4H), 7.44-7.41 (m, 4H), 7.40-7.37 (m, 1H), 2.73 (s, 1H).
¹³C NMR (150 MHz, CDCl₃) δ 142.9, 141.0, 135.6, 135.3, 135.1, 134.0, 130.3, 128.9, 128.1, 127.7, 127.3, 126.8.



Diphenyl(*m*-tolyl)silanol (65)^[21]: 40 mg, 58% yield. Colorless liquid. ¹H NMR (600 MHz, CDCl₃) δ 7.53-7.52 (m, 4H), 7.36-7.31 (m, 4H), 7.29-7.26 (m, 4H), 7.19-7.15 (m, 2H), 2.59 (s, 1H), 2.23 (s, 3H). ¹³C NMR (150 MHz, CDCl₃) δ 137.5, 135.6, 135.4, 135.1, 132.2, 131.0, 130.2, 128.9, 128.0, 128.0, 21.6.



(2-fluorophenyl)diphenylsilanol (66)^[21]: 29 mg, 41% yield. Colorless liquid. ¹H NMR (600 MHz, CDCl₃) δ 7.56-7.55 (m, 4H), 7.38-7.35 (m, 3H), 7.33-7.30 (m, 5H), 7.06 (t, *J* = 7.3 Hz, 1H), 6.97 (t, *J* = 8.4 Hz, 1H), 2.68 (s, 1H). ¹³C NMR (150 MHz, CDCl₃) δ 167.5 (d, *J* = 238.5 Hz), 136.9 (d, *J* = 10.5 Hz), 135.0, 134.6, 132.8 (d, *J* = 8.6 Hz), 130.5, 128.1, 124.3, 122.0 (d, *J* = 28.5 Hz), 115.2 (d, *J* = 24.0 Hz). Ph_Ph

Methyldiphenylsilanol (67)^[21]: 40 mg, 78% yield. Colorless liquid. ¹H NMR (600 MHz, CDCl₃) δ 7.63-7.61 (m, 4H), 7.45-7.42 (m, 2H), 7.40-7.38 (m, 4H), 2.32 (s, 1H), 0.68 (s, 3H). ¹³C NMR (150 MHz, CDCl₃) δ 137.2, 135.1, 134.1, 130.0, 128.0, -1.1.



Butyldiphenylsilanol (**68**)^[1]: 46 mg, 75% yield. White solid. ¹H NMR (600 MHz, CDCl₃) δ 7.62-7.61 (m, 4H), 7.45-7.42 (m, 2H), 7.40-7.38 (m, 4H), 2.27 (s, 1H), 1.48-1.43 (m, 2H), 1.41-1.36 (m, 2H), 1.18-1.15 (m, 2H), 0.89(t, *J* = 7.2 Hz, 3H). ¹³C NMR (150 MHz, CDCl₃) δ 136.5, 134.3, 130.0, 128.0, 26.6, 25.3, 15.0, 13.8.

```
Ph Ph
Si OH
```

Tert-butyldiphenylsilanol (69)^[21]: 49 mg, 80% yield. Colorless liquid. ¹H NMR (600 MHz, CDCl₃) δ 7.76-7.74 (m, 4H), 7.46-7.43 (m, 2H), 7.42-7.39 (m, 4H), 2.39 (s, 1H), 1.11 (s, 9H). ¹³C NMR (150 MHz, CDCl₃) δ 135.3, 135.0, 129.8, 127.9, 26.7, 19.1.

```
PhPh
Ph-Si-Si-Ph
I I
```

1,2-dimethyl-1,1,2,2-tetraphenyldisilane^[22]: 37 mg, 93% yield. Colorless liquid.

¹**H NMR** (600 MHz, CDCl₃) δ 7.44-7.42 (m, 8H), 7.28-7.25 (m, 4H), 7.22-7.19 (m, 8H), 0.48 (s, 6H). ¹³**C NMR** (150 MHz, CDCl₃) δ 137.7, 134.1, 129.7, 127.9, -0.4.



1,2-dimethyl-1,2-diphenyl-1,2-di*p*-tolyldisilane^[22]: 83 mg, 76% yield. Colorless liquid. ¹H NMR (600 MHz, CDCl₃) δ 7.54-7.52 (m, 8H), 7.44-7.38 (m, 8H), 7.31-7.28 (m, 8H), 7.13 (d, J = 7.6 Hz, 4H), 2.38 (s, 6H). ¹³C NMR (150 MHz, CDCl₃) δ 139.8, 135.9, 135.4, 135.3, 132.1, 129.8, 128.7, 127.8, 21.7. Ph-si-si-Ph

1,2-dimethyl-1,1,2,2-tetraphenyldisilane^[22]: 49 mg, 91% yield. Colorless liquid. **¹H NMR** (600 MHz, CDCl₃) δ 7.49-7.48 (m, 4H), 7.31-7.27 (m, 6H), 0.27 (s, 12H). **¹³C NMR** (150 MHz, CDCl₃) δ 140.0, 133.2, 129.4, 127.9, 1.0.



1,2-dibutyl-1,1,2,2-tetraphenyldisilane^[22]: 41 mg, 85% yield. Colorless liquid. **¹H NMR** (600 MHz, CDCl₃) δ 7.55-7.51 (m, 8H), 7.41-7.38 (m, 4H), 7.34-7.29 (m, 8H), 1.34-1.25 (m, 8H), 1.10-1.07 (m, 4H), 0.80 (t, *J* = 14.4, 7.1 Hz, 6H). ¹³C NMR (150 MHz, CDCl₃) δ 137.0, 134.5, 129.6, 127.8, 26.6, 25.3, 15.5, 13.7.

5. References

- Cao, J.; Yang, X.; Ma, L.; Lu, K.; Zhou, R., Metal-free Hydrogen Evolution Cross-coupling Enabled by Synergistic Photoredox and Polarity Reversal Catalysis. *Green Chem.* 2021, 23 (22), 8988-8994.
- [2] Bazant, V.; Cerny, M., Organosilicon compounds. CXVIII. Synthesis of P-chlorophenyldiphenylsilanes and Unsymmetrical P-bissilylarylenes from P-dichlorobenzene and P-bromochlorobenzene by the Grignard reaction. Collect. Czech. Chem. Commun. 1974, 39 (7), 1880.
- [3] Kang, K. T.; Yoon, U. C.; Seo, H. C.; Kim, K. N.; Song, H. Y.; Lee, J. C., Thermal and Photochemical Reactions of Benzosilacyclobutenes with Alcohols. Intermediacy of *O*-silaquinone Methide in the Photochemical Reactions. *Bull.*

Korean Chem. Soc. 1991, 12 (1), 57-60.

- [4] Xu, D.; Huang, S.; Hu, F.; Peng, L.; Jia, S.; Mao, H.; Gong, X.; Li, F.; Qin, W.;
 Yan, H., Diversity-Oriented Enantioselective Construction of Atropisomeric Heterobiaryls and N Aryl Indoles via Vinylidene Ortho-Quinone Methides. CCS Chem. 2022, 4 (8), 2686-2697.
- [5] Harland, J. J.; Payne, J. S.; Day, R. O.; Holmes, R. R., Pentacoordinated Molecules. 70. Steric hindrance in Pentacoordinated Fluorosilicates. Synthesis and molecular Structure of the Diphenyl-1-naphthyldifluorosilicate Anion and the Phenylmethyltrifluorosilicate Anion. *Inorg. Chem.* **1987**, *26* (5), 760-765.
- [6] Dickstein, Joshua S.; Qin, Zengquan. Producing High Cis-1,4-polydiene and Lanthanide-based Catalyst Compositions. WO2018022994.
- [7] Liu, Y.; Holder, A. J., A Quantum Mechanical Quantitative Structure-property Relationship Study of the Melting Point of a Variety of Organosilicons. J. Mol. Graphics Modell. 2011, 31, 57-64.
- [8] Savela, R.; Zawartka, W.; Leino, R., Iron-Catalyzed Chlorination of Silanes. Organometallics 2012, 31 (8), 3199-3206.
- [9] United Kingdom, GB971598 1964-09-30.
- [10] Sheppard, C. I.; Taylor, J. L.; Wiskur, S. L., Silylation-Based Kinetic Resolution of Monofunctional Secondary Alcohols. Org. Lett. 2011, 13 (15), 3794-3797.
- [11] Chang, A. S.-m.; Kawamura, K. E.; Henness, H. S.; Salpino, V. M.; Greene, J. C.; Zakharov, L. N.; Cook, A. K., (NHC)Ni(0)-Catalyzed Branched-Selective Alkene Hydrosilylation with Secondary and Tertiary Silanes. ACS Catal. 2022, 12 (18), 11002-11014.
- [12] Lamac, M.; Urban, B.; Horacek, M.; Buzek, D.; Leonova, L.; Styskalik, A.;
 Vykydalova, A.; Skoch, K.; Kloda, M.; Mahun, A.; Kobera, L.; Lang, K.;
 Londesborough, M. G. S.; Demel, J., "Activated Borane"- A Porous Borane Cluster
 Polymer as an Efficient Lewis Acid-based Catalyst. ACS Catal. 2023, 13 (22), 14614-14626.
- [13] Sorribes, I.; Ventura-Espinosa, D.; Assis, M.; Martin, S.; Concepcion, P.; Bettini,J.; Longo, E.; Mata, J. A.; Andres, J., Unraveling a Biomass-Derived Multiphase

Catalyst for the Dehydrogenative Coupling of Silanes with Alcohols under Aerobic Conditions. *ACS Sustainable Chem. Eng.* **2021**, *9* (7), 2912-2928.

- [14] Li, Y.; Guo, S.; Li, Q.-H.; Zheng, K., Metal-free Photoinduced C(sp3)-H/C(sp3)-H Cross-coupling to Access α-tertiary amino acid derivatives. *Nat. Commun.* 2023, 14 (1), 6225.
- [15] Pein, W. L.; Wiensch, E. M.; Montgomery, J., Nickel-Catalyzed Ipso-Borylation of Silyloxyarenes via C-O Bond Activation. Org. Lett. 2021, 23 (12), 4588-4592.
- [16] Han, B.; Ren, C.; Jiang, M.; Wu, L., Titanium-Catalyzed Exhaustive Reduction of Oxo-Chemicals. Angew. Chem., Int. Ed. 2022, 61 (46), e202209232.
- [17] Wiensch, E. M.; Todd, D. P.; Montgomery, J., Silyloxyarenes as Versatile Coupling Substrates Enabled by Nickel-Catalyzed C-O Bond Cleavage. *ACS Catal.* **2017**, 7 (9), 5568-5571.
- [18] Iwamoto, H.; Tsuruta, T.; Ogoshi, S., Development and Mechanistic Studies of (E)-Selective Isomerization/Tandem Hydroarylation Reactions of Alkenes with a Nickel(0)/Phosphine Catalyst. ACS Catal. 2021, 11 (11), 6741-6749.
- [19] Lazzaroni, S.; Protti, S.; Fagnoni, M.; Albini, A., Photoinduced Three-Component Reaction: A Convenient Access to 3-Arylacetals or 3-Arylketals. *Org. Lett.* 2009, *11* (2), 349-352.
- [20] Sarvi Beigbaghlou, S.; Yafele, R. S.; Kalek, M., Electrochemical Dearomatizing Spirolactonization and Spiroetherification of Naphthols and Phenols. *Synthesis* 2023, *55 (24)*, 4173-4180.
- [21] Liang, H.; Wang, L. J.; Ji, Y. X.; Wang, H.; Zhang, B., Selective Electrochemical Hydrolysis of Hydrosilanes to Silanols via Anodically Generated Silyl Cations. *Angew. Chem., Int. Ed.* 2020, 60 (4), 1839-1844.
- [22] Guan, W.; Lu, L.; Jiang, Q.; Gittens, A. F.; Wang, Y.; Novaes, L. F. T.; Klausen, R. S.; Lin, S., An Electrochemical Strategy to Synthesize Disilanes and Oligosilanes from Chlorosilanes. *Angew. Chem., Int. Ed.* 2023, *62 (26)*, e202303592.

6. Copies of NMR spectra ¹H NMR of product 2 in CDCl₃ (600 MHz)



¹H NMR of product 9 in CDCl₃ (600 MHz)



¹³C NMR of product 9 in CDCl₃ (150 MHz)



¹H NMR of product 10 in CDCl₃ (600 MHz)



¹H NMR of product 11 in CDCl₃ (600 MHz)



¹³C NMR of product 11 in CDCl₃ (150 MHz)



¹H NMR of product 12 in CDCl₃ (400 MHz)



¹H NMR of product 13 in CDCl₃ (600 MHz)



¹³C NMR of product 13 in CDCl₃ (150 MHz)



¹H NMR of product 14 in CDCl₃ (600 MHz)



¹H NMR of product 15 in CDCl₃ (400 MHz)



¹H NMR of product 16 in CDCl₃ (400 MHz)


¹H NMR of product 17 in CDCl₃ (400 MHz)



¹³C NMR of product 17 in CDCl₃ (150 MHz)



¹H NMR of product 18 in CDCl₃ (600 MHz)



¹H NMR of product 19 in CDCl₃ (600 MHz)







¹H NMR of product 20 in CDCl₃ (400 MHz)



¹³C NMR of product 20 in CDCl₃ (150 MHz)



¹H NMR of product 21 in CDCl₃ (600 MHz)



¹H NMR of product 22 in CDCl₃ (400 MHz)

f1 (ppm) 80 70 60 50 40 30 20 10 0 -10



¹³C NMR of product 22 in CDCl₃ (100 MHz)



¹H NMR of product 23 in CDCl₃ (600 MHz)



¹H NMR of product 24 in CDCl₃ (400 MHz)



¹³C NMR of product 24 in CDCl₃ (150 MHz)



¹H NMR of product 25 in CDCl₃ (400 MHz)



¹³C NMR of product 25 in CDCl₃ (150 MHz)



¹H NMR of product 26 in CDCl₃ (600 MHz)



¹³C NMR of product 26 in CDCl₃ (150 MHz)



¹H NMR of product 27 in CDCl₃ (400 MHz)



¹³C NMR of product 27 in CDCl₃ (150 MHz)



¹H NMR of product 28 in CDCl₃ (600 MHz)





¹H NMR of product 29 in CDCl₃ (400 MHz)



¹³C NMR of product 29 in CDCl₃ (150 MHz)



¹H NMR of product 30 in CDCl₃ (400 MHz)



¹H NMR of product 31 in CDCl₃ (400 MHz)



¹³C NMR of product 31 in CDCl₃ (150 MHz)



¹H NMR of product 32 in CDCl₃ (400 MHz)



¹H NMR of product 33 in CDCl₃ (400 MHz)



¹³C NMR of product 33 in CDCl₃ (150 MHz)



¹H NMR of product 34 in CDCl₃ (600 MHz)



¹H NMR of product 36 in CDCl₃ (600 MHz)



¹³C NMR of product 36 in CDCl₃ (150 MHz)



¹H NMR of product 37 in CDCl₃ (600 MHz)



¹³C NMR of product 37 in CDCl₃ (150 MHz)



¹H NMR of product 38 in CDCl₃ (600 MHz)



¹³C NMR of product 38 in CDCl₃ (150 MHz)



¹H NMR of product 39 in CDCl₃ (600 MHz)



¹³C NMR of product 39 in CDCl₃ (150 MHz)



¹H NMR of product 40 in CDCl₃ (600 MHz)



¹³C NMR of product 40 in CDCl₃ (150 MHz)



¹H NMR of product 41 in CDCl₃ (600 MHz)



¹H NMR of product 42 in CDCl₃ (600 MHz)



¹³C NMR of product 42 in CDCl₃ (150 MHz)



¹H NMR of product 43 in CDCl₃ (600 MHz)



¹H NMR of product 44 in CDCl₃ (600 MHz)



¹³C NMR of product 44 in CDCl₃ (150 MHz)



¹H NMR of product 45 in CDCl₃ (600 MHz)



¹H NMR of product 46 in CDCl₃ (600 MHz)



¹³C NMR of product 46 in CDCl₃ (150 MHz)



¹H NMR of product 47 in CDCl₃ (600 MHz)



¹³C NMR of product 47 in CDCl₃ (150 MHz)



¹H NMR of product 48 in CDCl₃ (600 MHz)



¹H NMR of product 49 in CDCl₃ (600 MHz)



¹H NMR of product 50 in CDCl₃ (600 MHz)



¹H NMR of product 51 in CDCl₃ (600 MHz)



¹H NMR of product 52 in CDCl₃ (600 MHz)



¹H NMR of product 53 in CDCl₃ (600 MHz)


¹H NMR of product 54 in CDCl₃ (600 MHz)



¹H NMR of product 55 in CDCl₃ (600 MHz)





¹H NMR of product 56 in CDCl₃ (600 MHz)





¹H NMR of product 57 in CDCl₃ (600 MHz)



¹H NMR of product 58 in CDCl₃ (600 MHz)



¹³C NMR of product 58 in CDCl₃ (150 MHz)



¹H NMR of product 59 in CDCl₃ (600 MHz)







¹H NMR of product 60 in CDCl₃ (400 MHz)



¹³C NMR of product 60 in CDCl₃ (150 MHz)



¹H NMR of product 61 in CDCl₃ (600 MHz)



¹³C NMR of product 61 in CDCl₃ (150 MHz)



¹H NMR of product 62 in CDCl₃ (600 MHz)







¹H NMR of product 63 in CDCl₃ (600 MHz)







¹H NMR of product 64 in CDCl₃ (600 MHz)



¹³C NMR of product 64 in CDCl₃ (150 MHz)



¹H NMR of product 65 in CDCl₃ (600 MHz)



¹³C NMR of product 65 in CDCl₃ (150 MHz)



¹H NMR of product 66 in CDCl₃ (600 MHz)







¹H NMR of product 67 in CDCl₃ (600 MHz)



¹³C NMR of product 67 in CDCl₃ (150 MHz)



¹H NMR of product 68 in CDCl₃ (600 MHz)







¹H NMR of product 69 in CDCl₃ (600 MHz)





¹H NMR of product 1,2-dimethyl-1,2-diphenyl-1,2-di-*p*-tolyldisilane in CDCl₃ (600 MHz)

¹³C NMR of product 1,2-dimethyl-1,2-diphenyl-1,2-di-*p*-tolyldisilane in CDCl₃ (150 MHz)



¹H NMR of product 1,2-dimethyl-1,1,2,2-tetraphenyldisilane in CDCl₃ (600 MHz)



¹³C NMR of product 1,2-dimethyl-1,1,2,2-tetraphenyldisilane in CDCl₃ (150 MHz)



¹H NMR of product 1,1,2,2-tetramethyl-1,2-diphenyldisilane in CDCl₃ (600 MHz)



¹³C NMR of product 1,1,2,2-tetramethyl-1,2-diphenyldisilane in CDCl₃ (150 MHz)



¹H NMR of product 1,2-dibutyl-1,1,2,2-tetraphenyldisilane in CDCl₃ (600 MHz)



¹³C NMR of product 1,2-dibutyl-1,1,2,2-tetraphenyldisilane in CDCl₃ (150 MHz)

