

Electrochemical strategies for NaX-mediated hydrolysis and alcoholysis of hydrosilanes under mild conditions

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1. General considerations

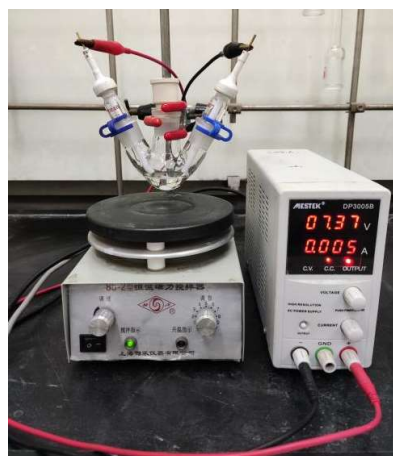
The compounds of **1b-1i** were prepared following literature procedures,¹ all other reagents were commercially available and used as received unless otherwise noted. The instrument for electrolysis is Adjustable DC Power Supply (DP3005B) (made in China). Column chromatography was performed on silica gel 300-400 mesh. The yields reported are the isolated yields and the average of two runs. ¹H, ¹³C and ¹⁹F NMR spectra of all compounds were recorded at 400, 100 and 376 MHz with CDCl₃ or d₆-DMSO as solvent respectively. All coupling constants (*J* values) were reported in Hertz (Hz). Cyclic voltammograms were obtained on a IVIUMSTAT potentiostat. The amount of electrocatalytic hydrogen evolution was measured on a gas chromatography (Kexiao, GC-1690 China) (TCD detector, 13X molecular sieve column, N₂ gas carrier).

2. Experimental procedures

(A) Procedure A, electrochemical NaCl-mediated hydrolysis of hydrosilanes: silane (0.2 mmol), NaCl (6 mg, 0.1 mmol, 0.5 equiv.) and CH₃CN/H₂O (4:1, 5 mL) were combined and added into oven-dried three-necked flask (25 mL) equipped with a stir bar. The flask was equipped with two platinum electrodes (1.0 × 1.0 cm²) as the anode and cathode. The reaction mixture was stirred and electrolyzed under room temperature and air conditions at a constant current of 5 mA for 3 hours. After 3 h, the reaction was washed with EtOAc and concentrated in vacuo. The resulting residue was purified by flash chromatography on silica gel to provide corresponding product.

(B) Procedure B, electrochemical NaBr-promoted alcoholysis of hydrosilanes: unless otherwise noted, silane (0.2 mmol), NaBr (10.3 mg, 0.1 mmol, 0.5 equiv.) and alcohol were combined and added into oven-dried three-necked flask (25 mL) equipped with two platinum electrodes (1.0 × 1.0 cm²) as the anode and cathode as well as a stir bar, the reaction mixture was stirred and electrolyzed under room temperature and air conditions at a constant current of 5 mA for 3 hours. After 3 h, the reaction was washed with EtOAc and concentrated in vacuo. The resulting residue was purified by flash chromatography on silica gel to provide corresponding product.

(C) Procedure C, electrochemical TBAB-promoted alcoholysis of hydrosilanes: unless otherwise noted, silane (0.2 mmol), TBAB (33 mg, 0.1 mmol, 0.5 equiv.) and alcohol were combined and added into oven-dried three-necked flask (25 mL) equipped with two platinum electrodes (1.0 × 1.0 cm²) as the anode and cathode as well as a stir bar, the reaction mixture was stirred and electrolyzed under room temperature and air conditions at a constant current of 5 mA for 3 hours. After 3 h, the reaction was washed with EtOAc and concentrated in vacuo. The resulting residue was purified by flash chromatography on silica gel to provide corresponding product.



Triphenylsilanol (**3a**)

Procedure A was followed using triphenylsilane (52.1 mg, 0.2 mmol), NaCl (6.0 mg, 0.1 mmol, 0.5 equiv.) and CH₃CN/H₂O (4:1, 5 mL). The crude reaction mixture was purified by flash silica gel column chromatography (petroleum ether: EtOAc = 9:1) to afford the desired product **3a** as white solid (51.4 mg, 93%). Exhibited spectral data in accordance with previous report.¹ ¹H NMR (400 MHz, CDCl₃) δ 7.68 - 7.62 (m, 6H), 7.51 - 7.44 (m, 3H), 7.43 - 7.36 (m, 6H), 2.79 (s, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 135.1, 135.0, 130.1, 127.9.

Diphenyl(*o*-tolyl)silanol (**3b**)

Procedure A was followed using diphenyl(*o*-tolyl)silane (54.9 mg, 0.2 mmol), NaCl (6.0 mg, 0.1 mmol, 0.5 equiv.) and CH₃CN/H₂O (4:1, 5 mL). The crude reaction mixture was purified by flash silica gel column chromatography (petroleum ether: EtOAc = 9:1) to afford the desired product **3b** as white solid (45.9 mg, 79%). Exhibited spectral data in accordance with previous report.¹ ¹H NMR (400 MHz, CDCl₃) δ 7.63 - 7.58 (m, 4H), 7.47 - 7.33 (m, 8H), 7.23 - 7.14 (m, 2H), 2.56 (s, 1H), 2.33 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 144.6, 136.6, 135.7, 134.7, 133.5, 130.5, 130.1, 130.0, 128.0, 124.9, 23.3.

Diphenyl(*p*-tolyl)silanol (**3c**)

Procedure A was followed using diphenyl(*p*-tolyl)silane (54.9 mg, 0.2 mmol), NaCl (6.0 mg, 0.1 mmol, 0.5 equiv.) and CH₃CN/H₂O (4:1, 5 mL). The crude reaction mixture was purified by flash silica gel column chromatography (petroleum ether: EtOAc = 9:1) to afford the desired product **3c** as white solid (52.3 mg, 90%). Exhibited spectral data in accordance with previous report.¹ ¹H NMR (400 MHz, CDCl₃) δ 7.67 - 7.62 (m, 4H), 7.56 - 7.50 (m, 2H), 7.47 - 7.35 (m, 6H), 7.22 (d, *J* = 7.6 Hz, 2H), 2.54 (s, 1H), 2.38 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 140.2, 135.4, 135.0, 134.9, 131.5, 130.0, 128.8, 127.9, 21.6.

(4-Methoxyphenyl)diphenylsilane (**3d**)

Procedure A was followed using (4-methoxyphenyl)diphenylsilane (58.1 mg, 0.2 mmol), NaCl (6.0 mg, 0.1 mmol, 0.5 equiv.) and CH₃CN/H₂O (4:1, 5 mL). The crude reaction mixture was purified by flash silica gel column chromatography (petroleum

ether: EtOAc = 9:1) to afford the desired product **3d** as white solid (52.1 mg, 85%). Exhibited spectral data in accordance with previous report.¹ ¹H NMR (400 MHz, CDCl₃) δ 7.65 - 7.59 (m, 4H), 7.58 - 7.52 (m, 2H), 7.46 - 7.34 (m, 6H), 6.95 - 6.90 (m, 2H), 3.82 (s, 3H), 2.50 (s, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 161.2, 136.6, 135.6, 134.9, 130.0, 127.9, 126.0, 113.7, 55.0.

(4-Chlorophenyl)diphenylsilanol (**3e**)

Procedure A was followed using (4-chlorophenyl)diphenylsilane (59.0 mg, 0.2 mmol), NaCl (6.0 mg, 0.1 mmol, 0.5 equiv.) and CH₃CN/H₂O (4:1, 5 mL). The crude reaction mixture was purified by flash silica gel column chromatography (petroleum ether: EtOAc = 9:1) to afford the desired product **3e** as white solid (46.6 mg, 75%). Exhibited spectral data in accordance with previous report.¹ ¹H NMR (400 MHz, CDCl₃) δ 7.62 - 7.58 (m, 4H), 7.57 - 7.53 (m, 2H), 7.47 - 7.34 (m, 9H), 2.91 (s, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 136.6, 136.3, 134.9, 134.6, 133.5, 130.3, 128.2, 128.0.

(4-Fluorophenyl)diphenylsilanol (**3f**)

Procedure A was followed using (4-fluorophenyl)diphenylsilane (55.7 mg, 0.2 mmol), NaCl (6.0 mg, 0.1 mmol, 0.5 equiv.) and CH₃CN/H₂O (4:1, 5 mL). The crude reaction mixture was purified by flash silica gel column chromatography (petroleum ether: EtOAc = 9:1) to afford the desired product **3f** as white solid (44.7 mg, 76%). Exhibited spectral data in accordance with previous report.² ¹H NMR (400 MHz, CDCl₃) δ 7.64 - 7.58 (m, 6H), 7.48 - 7.36 (m, 6H), 7.08 (t, *J* = 8.8 Hz, 2H), 2.66 (s, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 165.6, 163.1, 137.1 (d, *J* = 7.7 Hz), 134.9, 130.8, 130.2, 128.0, 115.2 (d, *J* = 19.8 Hz). ¹⁹F NMR (376 MHz, CDCl₃) δ -110.0.

Diphenyl(4-(trifluoromethyl)phenyl)silanol (**3g**)

Procedure A was followed using diphenyl(4-(trifluoromethyl)phenyl)silane (65.7 mg, 0.2 mmol), NaCl (6.0 mg, 0.1 mmol, 0.5 equiv.) and CH₃CN/H₂O (4:1, 5 mL). The crude reaction mixture was purified by flash silica gel column chromatography (petroleum ether: EtOAc = 9:1) to afford the desired product **3g** as white solid (49.6 mg, 72%). Exhibited spectral data in accordance with previous report.¹ ¹H NMR (400 MHz, CDCl₃) δ 7.79 - 7.73 (m, 2H), 7.65 - 7.58 (m, 6H), 7.49 - 7.37 (m, 6H), 2.77 (s, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 140.1, 135.2, 134.9, 134.2, 131.9 (q, *J* = 32.3 Hz), 130.5, 128.1, 124.4 (q, *J* = 3.8 Hz), 124.1 (q, *J* = 272.3 Hz). ¹⁹F NMR (376 MHz, CDCl₃) δ -63.05.

(4-Dibenzofuranyl)diphenylsilanol (**3h**)

Procedure A was followed using (4-dibenzofuranyl)diphenylsilane (76.1 mg, 0.2 mmol), NaCl (6.0 mg, 0.1 mmol, 0.5 equiv.) and CH₃CN/H₂O (4:1, 5 mL). The crude reaction mixture was purified by flash silica gel column chromatography (petroleum ether: EtOAc = 9:1) to afford the desired product **3h** as white solid (57.2 mg, 78%). Exhibited spectral data in accordance with previous report.¹ ¹H NMR (400 MHz, CDCl₃) δ 8.05 (d, *J* = 7.6 Hz, 1H), 7.97 (d, *J* = 7.6 Hz, 1H), 7.74 - 7.69 (m, 4H), 7.53 - 7.48 (m, 2H), 7.47 - 7.32 (m, 9H), 3.32 (s, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 160.8, 155.9,

135.1, 134.7, 134.2, 130.3, 127.9, 127.1, 123.9, 123.2, 122.9, 122.8, 122.7, 120.7, 118.2, 111.8.

(4-Dibenzothienyl)diphenylsilanol (**3i**)

Procedure A was followed using (4-dibenzothienyl)diphenylsilane (79.3 mg, 0.2 mmol), NaCl (6.0 mg, 0.1 mmol, 0.5 equiv.) and CH₃CN/H₂O (4:1, 5 mL). The crude reaction mixture was purified by flash silica gel column chromatography (petroleum ether: EtOAc = 9:1) to afford the desired product **3i** as white solid (58.9 mg, 77%). Exhibited spectral data in accordance with previous report.¹ ¹H NMR (400 MHz, CDCl₃) δ 8.25 (dd, *J* = 7.9, 1.2 Hz, 1H), 8.18 - 8.14 (m, 1H), 7.75 (dd, *J* = 7.7, 1.4 Hz, 1H), 7.72 - 7.66 (m, 4H), 7.62 (dd, *J* = 7.1, 1.2 Hz, 1H), 7.50 - 7.36 (m, 9H), 2.88 (s, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 145.8, 139.7, 135.2, 134.95, 134.8, 134.0, 130.5, 128.1, 126.7, 124.3, 123.8, 123.5, 122.6, 121.4.

Methyldiphenylsilanol (**3j**)

Procedure A was followed using methyldiphenylsilane (39.7 mg, 0.2 mmol), NaCl (6.0 mg, 0.1 mmol, 0.5 equiv.) and CH₃CN/H₂O (4:1, 5 mL). The crude reaction mixture was purified by flash silica gel column chromatography (petroleum ether: EtOAc = 9:1) to afford the desired product **3j** as white solid (39.4 mg, 92%). Exhibited spectral data in accordance with previous report.¹ ¹H NMR (400 MHz, CDCl₃) δ 7.65 - 7.60 (m, 4H), 7.47 - 7.36 (m, 6H), 2.65 (s, 1H), 0.68 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 137.1, 134.0, 129.9, 127.9, -1.3.

Tribenzylsilanol (**3k**)

Procedure A was followed using tribenzylsilane (60.5 mg, 0.2 mmol), NaCl (6.0 mg, 0.1 mmol, 0.5 equiv.) and CH₃CN/H₂O (4:1, 5 mL). The crude reaction mixture was purified by flash silica gel column chromatography (petroleum ether: EtOAc = 9:1) to afford the desired product **3k** as white solid (41.4 mg, 65%). Exhibited spectral data in accordance with previous report.³ ¹H NMR (400 MHz, CDCl₃) δ 7.25 - 7.19 (m, 6H), 7.15 - 7.06 (m, 3H), 7.02 - 6.96 (m, 6H), 2.17 (s, 6H), 1.70 (s, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 137.9, 128.5, 124.6, 24.1.

Benzyl dimethylsilanol (**3l**)

Procedure A was followed using benzyl dimethylsilane (30.1 mg, 0.2 mmol), NaCl (6.0 mg, 0.1 mmol, 0.5 equiv.) and CH₃CN/H₂O (4:1, 5 mL). The crude reaction mixture was purified by flash silica gel column chromatography (petroleum ether: EtOAc = 9:1) to afford the desired product **3l** as white solid (20.5 mg, 66%). Exhibited spectral data in accordance with previous report.⁴ ¹H NMR (400 MHz, CDCl₃) δ 7.26 - 7.21 (m, 2H), 7.12 - 7.04 (m, 3H), 2.18 (s, 2H), 1.94 (s, 1H), 0.14 (s, 6H). ¹³C NMR (100 MHz, CDCl₃) δ 139.0, 128.4, 128.2, 124.3, 28.1, -0.7.

Methoxytriphenylsilane (**4a**)

Procedure B was followed using triphenylsilane (52.1 mg, 0.2 mmol), NaBr (10.3 mg, 0.1 mmol, 0.5 equiv.) and CH₃OH (5 mL). The crude reaction mixture was purified

by flash silica gel column chromatography (petroleum ether: EtOAc = 95:5) to afford the desired product **4a** as white solid (53.4 mg, 92%).

Procedure C was followed using triphenylsilane (52.1 mg, 0.2 mmol), TBAB (33 mg, 0.1 mmol, 0.5 equiv.) and CH₃OH (5 mL). The crude reaction mixture was purified by flash silica gel column chromatography (petroleum ether: EtOAc = 95:5) to afford the desired product **4a** as white solid (55.2 mg, 95%).

Exhibited spectral data in accordance with previous report.⁴ ¹H NMR (400 MHz, CDCl₃) δ 7.68 - 7.58 (m, 6H), 7.49 - 7.34 (m, 9H), 3.66 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 135.4, 133.9, 130.0, 127.9, 51.8.

Ethoxytriphenylsilane (**5a**)

Procedure B was followed using triphenylsilane (52.1 mg, 0.2 mmol), NaBr (10.3 mg, 0.1 mmol, 0.5 equiv.) and ethanol (5 mL). The crude reaction mixture was purified by flash silica gel column chromatography (petroleum ether: EtOAc = 95:5) to afford the desired product **5a** as white solid (53.5 mg, 88%).

Procedure C was followed using triphenylsilane (52.1 mg, 0.2 mmol), TBAB (33 mg, 0.1 mmol, 0.5 equiv.) and ethanol (5 mL). The crude reaction mixture was purified by flash silica gel column chromatography (petroleum ether: EtOAc = 95:5) to afford the desired product **5a** as white solid (56.6 mg, 93%).

Exhibited spectral data in accordance with previous report.⁴ ¹H NMR (400 MHz, CDCl₃) δ 7.71 - 7.61 (m, 6H), 7.52 - 7.36 (m, 9H), 3.91 (q, *J* = 6.0, 5.0 Hz, 2H), 1.27 (t, *J* = 7.0 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 135.4, 134.4, 130.0, 127.9, 59.8, 18.4.

Propoxytriphenylsilane (**6a**)

Procedure B was followed using triphenylsilane (52.1 mg, 0.2 mmol), NaBr (10.3 mg, 0.1 mmol, 0.5 equiv.) and *n*-propanol (5 mL). The crude reaction mixture was purified by flash silica gel column chromatography (petroleum ether: EtOAc = 95:5) to afford the desired product **6a** as white solid (45.2 mg, 71%).

Procedure C was followed using triphenylsilane (52.1 mg, 0.2 mmol), TBAB (33 mg, 0.1 mmol, 0.5 equiv.) and *n*-propanol (5 mL). The crude reaction mixture was purified by flash silica gel column chromatography (petroleum ether: EtOAc = 95:5) to afford the desired product **6a** as white solid (52.9 mg, 83%).

Exhibited spectral data in accordance with previous report.⁴ ¹H NMR (400 MHz, CDCl₃) δ 7.71 - 7.65 (m, 6H), 7.51 - 7.39 (m, 9H), 3.81 (t, *J* = 6.6 Hz, 2H), 1.72 - 1.60 (m, 2H), 0.95 (t, *J* = 7.4 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 135.4, 134.5, 130.0, 127.8, 65.7, 25.8, 10.4.

Butoxytriphenylsilane (**7a**)

Procedure B was followed using triphenylsilane (52.1 mg, 0.2 mmol), NaBr (10.3 mg, 0.1 mmol, 0.5 equiv.) and *n*-butanol (5 mL). With stirring, the reaction mixture was performed at a constant current of 5 mA under nitrogen atmosphere at room temperature for 3 hours. The crude reaction mixture was purified by flash silica gel column chromatography (petroleum ether: EtOAc = 95:5) to afford the desired product **7a** as

white solid (35.9 mg, 54%).

Procedure C was followed using triphenylsilane (52.1 mg, 0.2 mmol), TBAB (33 mg, 0.1 mmol, 0.5 equiv.) and *n*-butanol (5 mL). With stirring, the reaction mixture was performed at a constant current of 5 mA under nitrogen atmosphere at room temperature for 3 hours. The crude reaction mixture was purified by flash silica gel column chromatography (petroleum ether: EtOAc = 95:5) to afford the desired product **7a** as white solid (51.9 mg, 78%).

Exhibited spectral data in accordance with previous report.⁴ ¹H NMR (400 MHz, CDCl₃) δ 7.70 - 7.58 (m, 6H), 7.48 - 7.32 (m, 9H), 3.82 (t, *J* = 6.4 Hz, 2H), 1.65 - 1.56 (m, 2H), 1.46 - 1.35 (m, 2H), 0.89 (t, *J* = 7.4 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 135.4, 134.5, 130.0, 127.8, 63.7, 34.7, 19.0, 13.9.

Pentyloxytriphenylsilane (**8a**)

Procedure B was followed using triphenylsilane (52.1 mg, 0.2 mmol), NaBr (10.3 mg, 0.1 mmol, 0.5 equiv.) and acetonitrile/*n*-amyl alcohol (4.9:0.1, 5 mL). With stirring, the reaction mixture was performed at a constant current of 5 mA under nitrogen atmosphere at room temperature for 3 hours. The crude reaction mixture was purified by flash silica gel column chromatography (petroleum ether: EtOAc = 95:5) to afford the desired product **8a** as white solid (33.2 mg, 48%).

Procedure C was followed using triphenylsilane (52.1 mg, 0.2 mmol), TBAB (33 mg, 0.1 mmol, 0.5 equiv.) and acetonitrile/*n*-amyl alcohol (4.9:0.1, 5 mL). With stirring, the reaction mixture was performed at a constant current of 5 mA under nitrogen atmosphere at room temperature for 3 hours. The crude reaction mixture was purified by flash silica gel column chromatography (petroleum ether: EtOAc = 95:5) to afford the desired product **8a** as white solid (52.3 mg, 74%).

Exhibited spectral data in accordance with previous report.⁸ ¹H NMR (400 MHz, CDCl₃) δ 7.67 - 7.63 (m, 6H), 7.47 - 7.37 (m, 9H), 3.81 (t, *J* = 6.6 Hz, 2H), 1.67 - 1.57 (m, 2H), 1.38 - 1.25 (m, 4H), 0.88 (t, *J* = 7.0 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 135.4, 134.5, 129.9, 127.8, 64.0, 32.3, 28.0, 22.4, 14.1.

iso-Propoxytriphenylsilane (**9a**)

Procedure B was followed using triphenylsilane (52.1 mg, 0.2 mmol), NaBr (10.3 mg, 0.1 mmol, 0.5 equiv.) and acetonitrile/*iso*-propanol (4.9:0.1, 5 mL). With stirring, the reaction mixture was performed at a constant current of 5 mA under nitrogen atmosphere at room temperature for 3 hours. The crude reaction mixture was purified by flash silica gel column chromatography (petroleum ether: EtOAc = 95:5) to afford the desired product **9a** as white solid (36.9 mg, 58%).

Procedure C was followed using triphenylsilane (52.1 mg, 0.2 mmol), TBAB (33 mg, 0.1 mmol, 0.5 equiv.) and acetonitrile/*iso*-propanol (4.9:0.1, 5 mL). With stirring, the reaction mixture was performed at a constant current of 5 mA under nitrogen atmosphere at room temperature for 3 hours. The crude reaction mixture was purified by flash silica gel column chromatography (petroleum ether: EtOAc = 95:5) to afford the desired product **9a** as white solid (47.8 mg, 75%).

Exhibited spectral data in accordance with previous report.⁴ ¹H NMR (400 MHz,

CDCl₃) δ 7.66 - 7.61 (m, 6H), 7.44 - 7.34 (m, 9H), 4.23 - 4.13 (m, 1H), 1.18 (d, J = 6.0 Hz, 6H). ¹³C NMR (100 MHz, CDCl₃) δ 135.4, 135.0, 129.8, 127.7, 66.3, 25.7.

sec-Butoxytriphenylsilane (**10a**)

Procedure B was followed using triphenylsilane (52.1 mg, 0.2 mmol), NaBr (10.3 mg, 0.1 mmol, 0.5 equiv.) and acetonitrile/*sec*-butyl alcohol (4.9:0.1, 5 mL). With stirring, the reaction mixture was performed at a constant current of 5 mA under nitrogen atmosphere at room temperature for 3 hours. The crude reaction mixture was purified by flash silica gel column chromatography (petroleum ether: EtOAc = 95:5) to afford the desired product **10a** as white solid (34.5 mg, 52%).

Procedure C was followed using triphenylsilane (52.1 mg, 0.2 mmol), TBAB (33 mg, 0.1 mmol, 0.5 equiv.) and acetonitrile/*sec*-butyl alcohol (4.9:0.1, 5 mL). With stirring, the reaction mixture was performed at a constant current of 5 mA under nitrogen atmosphere at room temperature for 3 hours. The crude reaction mixture was purified by flash silica gel column chromatography (petroleum ether: EtOAc = 95:5) to afford the desired product **10a** as white solid (45.9 mg, 69%).

Exhibited spectral data in accordance with previous report.⁷ ¹H NMR (400 MHz, CDCl₃) δ 7.72 - 7.67 (m, 6H), 7.50 - 7.38 (m, 9H), 4.04 - 3.95 (m, 1H), 1.68 - 1.48 (m, 2H), 1.21 (d, J = 6.0 Hz, 3H), 0.89 (t, J = 7.4 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 135.5, 135.2, 129.8, 127.8, 71.2, 32.2, 22.9, 9.8.

Cyclohexyloxytriphenylsilane (**11a**)

Procedure B was followed using triphenylsilane (52.1 mg, 0.2 mmol), NaBr (10.3 mg, 0.1 mmol, 0.5 equiv.) and acetonitrile/cyclohexanol (4.9:0.1, 5 mL). With stirring, the reaction mixture was performed at a constant current of 5 mA under nitrogen atmosphere at room temperature for 3 hours. The crude reaction mixture was purified by flash silica gel column chromatography (petroleum ether: EtOAc = 95:5) to afford the desired product **11a** as white solid (35.1 mg, 49%).

Procedure C was followed using triphenylsilane (52.1 mg, 0.2 mmol), TBAB (33 mg, 0.1 mmol, 0.5 equiv.) and acetonitrile/cyclohexanol (4.9:0.1, 5 mL). With stirring, the reaction mixture was performed at a constant current of 5 mA under nitrogen atmosphere at room temperature for 3 hours. The crude reaction mixture was purified by flash silica gel column chromatography (petroleum ether: EtOAc = 95:5) to afford the desired product **11a** as white solid (40.9 mg, 57%).

Exhibited spectral data in accordance with previous report.⁷ ¹H NMR (400 MHz, CDCl₃) δ 7.74 - 7.58 (m, 6H), 7.48 - 7.32 (m, 9H), 3.91 - 3.79 (m, 1H), 1.84 - 1.65 (m, 4H), 1.50 - 1.43 (m, 2H), 1.33 - 1.09 (m, 4H). ¹³C NMR (100 MHz, CDCl₃) δ 135.4, 135.2, 129.8, 127.7, 71.8, 35.6, 25.6, 23.9.

tert-Butoxytriphenylsilane (**12a**)

Procedure B was followed using triphenylsilane (52.1 mg, 0.2 mmol), NaBr (10.3 mg, 0.1 mmol, 0.5 equiv.) and acetonitrile/*tert*-butanol (4.9:0.1, 5 mL). With stirring, the reaction mixture was performed at a constant current of 5 mA under nitrogen atmosphere at room temperature for 3 hours. The crude reaction mixture was purified

by flash silica gel column chromatography (petroleum ether: EtOAc = 95:5) to afford the desired product **12a** as white solid (28.6 mg, 43%).

Procedure C was followed using triphenylsilane (52.1 mg, 0.2 mmol), TBAB (33 mg, 0.1 mmol, 0.5 equiv.) and acetonitrile/*tert*-butanol (4.9:0.1, 5 mL). With stirring, the reaction mixture was performed at a constant current of 5 mA under nitrogen atmosphere at room temperature for 3 hours. The crude reaction mixture was purified by flash silica gel column chromatography (petroleum ether: EtOAc = 95:5) to afford the desired product **12a** as white solid (42.6 mg, 64%).

¹H NMR (400 MHz, CDCl₃) δ 7.70 - 7.66 (m, 6H), 7.41 - 7.32 (m, 9H), 1.27 (s, 9H). ¹³C NMR (100 MHz, CDCl₃) δ 135.5, 129.5, 127.6, 74.1, 32.1. HRMS (ESI) calculated for C₂₂H₂₄NaOSi [M+Na]⁺ m/z 355.1494, found 355.1484.

tert-Pentoxytriphenylsilane (**13a**)

Procedure B was followed using triphenylsilane (52.1 mg, 0.2 mmol), NaBr (10.3 mg, 0.1 mmol, 0.5 equiv.) and acetonitrile/*tert*-amyl alcohol (4.9:0.1, 5 mL). With stirring, the reaction mixture was performed at a constant current of 5 mA under nitrogen atmosphere at room temperature for 3 hours. However, none of desired product was observed via TLC (thin-layer chromatography).

Procedure C was followed using triphenylsilane (52.1 mg, 0.2 mmol), TBAB (33 mg, 0.1 mmol, 0.5 equiv.) and acetonitrile/*tert*-amyl alcohol (4.9:0.1, 5 mL). With stirring, the reaction mixture was performed at a constant current of 5 mA under nitrogen atmosphere at room temperature for 3 hours. The crude reaction mixture was purified by flash silica gel column chromatography (petroleum ether: EtOAc = 95:5) to afford the desired product **13a** as white solid (36.7 mg, 53%).

¹H NMR (400 MHz, DMSO-*d*₆) δ 7.61 - 7.56 (m, 6H), 7.47 - 7.38 (m, 9H), 1.47 (q, *J* = 7.4 Hz, 2H), 1.15 (s, 6H), 0.89 (t, *J* = 7.4 Hz, 3H). ¹³C NMR (100 MHz, DMSO-*d*₆) δ 135.8, 134.7, 129.6, 127.7, 75.7, 36.5, 28.9, 8.5. HRMS (ESI) calculated for C₂₃H₂₆NaOSi [M+Na]⁺ m/z 369.1651, found 369.1639.

Methoxydiphenyl(*o*-tolyl)silane (**4b**)

Procedure B was followed using diphenyl(*o*-tolyl)silane (54.9 mg, 0.2 mmol), NaBr (10.3 mg, 0.1 mmol, 0.5 equiv.) and CH₃OH (5 mL). The crude reaction mixture was purified by flash silica gel column chromatography (petroleum ether: EtOAc = 95:5) to afford the desired product **4b** as white solid (49.9 mg, 82%).

Procedure C was followed using diphenyl(*o*-tolyl)silane (54.9 mg, 0.2 mmol), TBAB (33 mg, 0.1 mmol, 0.5 equiv.) and CH₃OH (5 mL). The crude reaction mixture was purified by flash silica gel column chromatography (petroleum ether: EtOAc = 95:5) to afford the desired product **4b** as white solid (48.1 mg, 79%).

¹H NMR (400 MHz, CDCl₃) δ 7.67 - 7.63 (m, 4H), 7.58 (d, *J* = 6.6 Hz, 1H), 7.48 - 7.35 (m, 7H), 7.28 - 7.17 (m, 2H), 3.67 (s, 3H), 2.33 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 144.9, 136.8, 135.3, 134.4, 132.5, 130.4, 130.1, 129.9, 127.9, 124.9, 51.8, 23.1. HRMS (ESI) calculated for C₂₀H₂₀NaOSi [M+Na]⁺ m/z 327.1181, found 327.1175.

Methoxydiphenyl(*p*-tolyl)silane (**4c**)

Procedure B was followed using diphenyl(*p*-tolyl)silane (54.9 mg, 0.2 mmol), NaBr (10.3 mg, 0.1 mmol, 0.5 equiv.) and CH₃OH (5 mL). The crude reaction mixture was purified by flash silica gel column chromatography (petroleum ether: EtOAc = 95:5) to afford the desired product **4c** as white solid (52.3 mg, 86%).

Procedure C was followed using diphenyl(*p*-tolyl)silane (54.9 mg, 0.2 mmol), TBAB (33 mg, 0.1 mmol, 0.5 equiv.) and CH₃OH (5 mL). The crude reaction mixture was purified by flash silica gel column chromatography (petroleum ether: EtOAc = 95:5) to afford the desired product **4c** as white solid (53.6 mg, 88%).

¹H NMR (400 MHz, CDCl₃) δ 7.67 - 7.63 (m, 4H), 7.57 - 7.53 (m, 2H), 7.47 - 7.38 (m, 6H), 7.26 - 7.22 (m, 2H), 3.66 (s, 3H), 2.40 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 140.1, 135.5, 135.4, 134.2, 130.2, 130.0, 128.8, 127.9, 51.8, 21.6. HRMS (ESI) calculated for C₂₀H₂₀NaOSi [M+Na]⁺ m/z 327.1181, found 327.1175.

Methoxy(4-methoxyphenyl)diphenylsilane (**4d**)

Procedure B was followed using (4-methoxyphenyl)diphenylsilane (58.1 mg, 0.2 mmol), NaBr (10.3 mg, 0.1 mmol, 0.5 equiv.) and CH₃OH (5 mL). The crude reaction mixture was purified by flash silica gel column chromatography (petroleum ether: EtOAc = 95:5) to afford the desired product **4d** as white solid (53.8 mg, 84%).

Procedure C was followed using (4-methoxyphenyl)diphenylsilane (58.1 mg, 0.2 mmol), TBAB (33 mg, 0.1 mmol, 0.5 equiv.) and CH₃OH (5 mL). The crude reaction mixture was purified by flash silica gel column chromatography (petroleum ether: EtOAc = 95:5) to afford the desired product **4d** as white solid (48.1 mg, 75%).

¹H NMR (400 MHz, CDCl₃) δ 7.65 - 7.60 (m, 4H), 7.58 - 7.54 (m, 2H), 7.47 - 7.36 (m, 6H), 6.97 - 6.92 (m, 2H), 3.83 (s, 3H), 3.64 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 157.3, 133.1, 131.4, 130.3, 126.0, 123.9, 120.8, 109.7, 51.1, 47.8. HRMS (ESI) calculated for C₂₀H₂₀NaO₂Si [M+Na]⁺ m/z 343.1130, found 343.1122.

Methoxy(4-chlorophenyl)diphenylsilane (**4e**)

Procedure B was followed using (4-chlorophenyl)diphenylsilane (59.0 mg, 0.2 mmol), NaBr (10.3 mg, 0.1 mmol, 0.5 equiv.) and CH₃OH (5 mL). The crude reaction mixture was purified by flash silica gel column chromatography (petroleum ether: EtOAc = 95:5) to afford the desired product **4e** as white solid (55.1 mg, 85%).

Procedure C was followed using (4-chlorophenyl)diphenylsilane (59.0 mg, 0.2 mmol), TBAB (33 mg, 0.1 mmol, 0.5 equiv.) and CH₃OH (5 mL). The crude reaction mixture was purified by flash silica gel column chromatography (petroleum ether: EtOAc = 95:5) to afford the desired product **4e** as white solid (52.6 mg, 81%).

¹H NMR (400 MHz, CDCl₃) δ 7.65 - 7.61 (m, 4H), 7.60 - 7.56 (m, 2H), 7.48 - 7.38 (m, 8H), 3.66 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 136.7, 136.6, 135.3, 133.4, 132.4, 130.3, 128.2, 128.0, 51.9. HRMS (ESI) calculated for C₁₉H₁₇ClNaOSi [M+Na]⁺ m/z 347.0635, found 347.0625.

Methoxy(4-fluorophenyl)diphenylsilane (**4f**)

Procedure B was followed using (4-fluorophenyl)diphenylsilane (55.7 mg, 0.2

mmol), NaBr (10.3 mg, 0.1 mmol, 0.5 equiv.) and CH₃OH (5 mL). The crude reaction mixture was purified by flash silica gel column chromatography (petroleum ether: EtOAc = 95:5) to afford the desired product **4f** as white solid (49.9 mg, 81%).

Procedure C was followed using (4-fluorophenyl)diphenylsilane (55.7 mg, 0.2 mmol), TBAB (33 mg, 0.1 mmol, 0.5 equiv.) and CH₃OH (5 mL). The crude reaction mixture was purified by flash silica gel column chromatography (petroleum ether: EtOAc = 95:5) to afford the desired product **4f** as white solid (48.7 mg, 79%).

¹H NMR (400 MHz, CDCl₃) δ 7.65 - 7.58 (m, 6H), 7.48 - 7.38 (m, 6H), 7.13 - 7.06 (m, 2H), 3.64 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 165.6, 163.1, 137.4 (d, *J* = 8.0 Hz), 135.3, 133.6, 130.2, 128.0, 115.2 (d, *J* = 8.0 Hz), 51.82. ¹⁹F NMR (376 MHz, CDCl₃) δ -110.19. HRMS (ESI) calculated for C₁₉H₁₇FNaOSi [M+Na]⁺ *m/z* 331.0930, found 331.0923.

Methoxydiphenyl(4-(trifluoromethyl)phenyl)silane (**4g**)

Procedure B was followed using diphenyl(4-(trifluoromethyl)phenyl)silane (65.7 mg, 0.2 mmol), NaBr (10.3 mg, 0.1 mmol, 0.5 equiv.) and CH₃OH (5 mL). The crude reaction mixture was purified by flash silica gel column chromatography (petroleum ether: EtOAc = 95:5) to afford the desired product **4g** as white solid (55.1 mg, 77%).

Procedure C was followed using diphenyl(4-(trifluoromethyl)phenyl)silane (65.7 mg, 0.2 mmol), TBAB (33 mg, 0.1 mmol, 0.5 equiv.) and CH₃OH (5 mL). The crude reaction mixture was purified by flash silica gel column chromatography (petroleum ether: EtOAc = 95:5) to afford the desired product **4g** as white solid (53.0 mg, 74%).

¹H NMR (400 MHz, CDCl₃) δ 7.81 - 7.78 (m, 2H), 7.68 - 7.63 (m, 6H), 7.51 - 7.41 (m, 6H), 3.69 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 139.1, 135.6, 135.3, 132.9, 131.85 (q, *J* = 32.3 Hz), 130.7 (q, *J* = 228.9 Hz), 130.4, 128.1, 124.41 (q, *J* = 3.8 Hz), 51.9. ¹⁹F NMR (376 MHz, CDCl₃) δ -63.05. HRMS (ESI) calculated for C₂₀H₁₇F₃NaOSi [M+Na]⁺ *m/z* 381.0893, found 381.0884.

Methoxy(4-dibenzofuranyl)diphenylsilane (**4h**)

Procedure B was followed using (4-dibenzofuranyl)diphenylsilane (76.1 mg, 0.2 mmol), NaBr (10.3 mg, 0.1 mmol, 0.5 equiv.) and CH₃OH (5 mL). The crude reaction mixture was purified by flash silica gel column chromatography (petroleum ether: EtOAc = 95:5) to afford the desired product **4h** as white solid (66.9 mg, 88%).

Procedure C was followed using (4-dibenzofuranyl)diphenylsilane (76.1 mg, 0.2 mmol), TBAB (33 mg, 0.1 mmol, 0.5 equiv.) and CH₃OH (5 mL). The crude reaction mixture was purified by flash silica gel column chromatography (petroleum ether: EtOAc = 95:5) to afford the desired product **4h** as white solid (61.6 mg, 81%).

¹H NMR (400 MHz, CDCl₃) δ 8.06 (d, *J* = 7.6 Hz, 1H), 7.96 (d, *J* = 7.8 Hz, 1H), 7.73 - 7.68 (m, 4H), 7.58 (d, *J* = 7.2 Hz, 1H), 7.48 - 7.30 (m, 10H), 3.76 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 160.8, 156.0, 135.4, 134.8, 133.7, 130.1, 127.9, 127.0, 124.0, 123.2, 123.0, 122.6, 120.5, 117.2, 111.8, 52.2. HRMS (ESI) calculated for C₂₅H₂₀NaO₂Si [M+Na]⁺ *m/z* 403.1130, found 403.1124.

Methoxy(4-dibenzothieryl)diphenylsilane (**4i**)

Procedure B was followed using (4-dibenzothieryl)diphenylsilane (79.3 mg, 0.2 mmol), NaBr (10.3 mg, 0.1 mmol, 0.5 equiv.) and CH₃OH (5 mL). The crude reaction mixture was purified by flash silica gel column chromatography (petroleum ether: EtOAc = 95:5) to afford the desired product **4i** as white solid (68.1 mg, 86%).

Procedure C was followed using (4-dibenzothieryl)diphenylsilane (79.3 mg, 0.2 mmol), TBAB (33 mg, 0.1 mmol, 0.5 equiv.) and CH₃OH (5 mL). The crude reaction mixture was purified by flash silica gel column chromatography (petroleum ether: EtOAc = 95:5) to afford the desired product **4i** as white solid (66.6 mg, 84%).

¹H NMR (400 MHz, CDCl₃) δ 8.26 (dd, *J* = 7.9, 1.2 Hz, 1H), 8.19 - 8.15 (m, 1H), 7.80 - 7.77 (m, 1H), 7.75 - 7.70 (m, 4H), 7.68 (dd, *J* = 7.0, 1.2 Hz, 1H), 7.51 - 7.39 (m, 9H), 3.76 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 146.2, 140.1, 135.6, 135.2, 135.0, 134.9, 132.8, 130.4, 128.0, 126.6, 124.1, 123.8, 123.5, 122.5, 121.4, 52.0. HRMS (ESI) calculated for C₂₅H₂₀NaOSSi [M+Na]⁺ *m/z* 419.0902, found 419.0897.

Methoxymethyldiphenylsilane (**4j**)

Procedure B was followed using methyldiphenylsilane (39.7 mg, 0.2 mmol), NaBr (10.3 mg, 0.1 mmol, 0.5 equiv.) and CH₃OH (5 mL). The crude reaction mixture was purified by flash silica gel column chromatography (petroleum ether: EtOAc = 95:5) to afford the desired product **4j** as colorless oil (36.5 mg, 80%).

Procedure C was followed using methyldiphenylsilane (39.7 mg, 0.2 mmol), TBAB (33 mg, 0.1 mmol, 0.5 equiv.) and CH₃OH (5 mL). The crude reaction mixture was purified by flash silica gel column chromatography (petroleum ether: EtOAc = 95:5) to afford the desired product **4j** as colorless oil (43.4 mg, 95%).

Exhibited spectral data in accordance with previous report.⁴ ¹H NMR (400 MHz, CDCl₃) δ 7.65 - 7.59 (m, 4H), 7.47 - 7.37 (m, 6H), 3.57 (s, 3H), 0.67 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 135.7, 134.3, 129.9, 127.9, 51.3, -3.6.

Tribenzyl(methoxy)silane (**4k**)

Procedure B was followed using tribenzylsilane (60.5 mg, 0.2 mmol), NaBr (10.3 mg, 0.1 mmol, 0.5 equiv.) and CH₃OH (5 mL). The crude reaction mixture was purified by flash silica gel column chromatography (petroleum ether: EtOAc = 95:5) to afford the desired product **4k** as white solid (59.1 mg, 89%).

Procedure C was followed using tribenzylsilane (60.5 mg, 0.2 mmol), TBAB (33 mg, 0.1 mmol, 0.5 equiv.) and CH₃OH (5 mL). The crude reaction mixture was purified by flash silica gel column chromatography (petroleum ether: EtOAc = 95:5) to afford the desired product **4k** as white solid (56.5 mg, 85%).

¹H NMR (400 MHz, CDCl₃) δ 7.27 - 7.21 (m, 6H), 7.15 - 7.10 (m, 3H), 7.06 - 7.02 (m, 6H), 3.39 (s, 3H), 2.19 (s, 6H). ¹³C NMR (100 MHz, CDCl₃) δ 138.1, 128.8, 128.4, 124.5, 51.5, 22.6. HRMS (ESI) calculated for C₂₂H₂₄NaOSi [M+Na]⁺ *m/z* 355.1494, found 355.1480.

Benzyl(methoxy)dimethylsilane (**4l**)

Procedure B was followed using benzyldimethylsilane (30.1 mg, 0.2 mmol), NaBr

(10.3 mg, 0.1 mmol, 0.5 equiv.) and CH₃OH (5 mL). The crude reaction mixture was purified by flash silica gel column chromatography (petroleum ether: EtOAc = 95:5) to afford the desired product **4l** as colorless oil (19.5 mg, 54%).

Procedure C was followed using benzyldimethylsilane (30.1 mg, 0.2 mmol), TBAB (33 mg, 0.1 mmol, 0.5 equiv.) and CH₃OH (5 mL). The crude reaction mixture was purified by flash silica gel column chromatography (petroleum ether: EtOAc = 95:5) to afford the desired product **4l** as colorless oil (26.3 mg, 73%).

Exhibited spectral data in accordance with previous report.⁵ ¹H NMR (400 MHz, CDCl₃) δ 7.22 (t, *J* = 7.6 Hz, 2H), 7.11 - 7.04 (m, 3H), 3.42 (s, 3H), 2.19 (s, 2H), 0.09 (s, 6H). ¹³C NMR (100 MHz, CDCl₃) δ 139.0, 128.3, 128.2, 124.2, 50.6, 26.2, -3.0.

Tri(*iso*-propyl)(methoxy)silane (**4m**)

Procedure B was followed using tri(*iso*-propyl)silane (31.7 mg, 0.2 mmol), NaBr (10.3 mg, 0.1 mmol, 0.5 equiv.) and CH₃OH (5 mL). The crude reaction mixture was purified by flash silica gel column chromatography (petroleum ether: EtOAc = 95:5) to afford the desired product **4m** as colorless oil (13.5 mg, 36%).

Procedure C was followed using tri(*iso*-propyl)silane (31.7 mg, 0.2 mmol), TBAB (33 mg, 0.1 mmol, 0.5 equiv.) and CH₃OH (5 mL). The crude reaction mixture was purified by flash silica gel column chromatography (petroleum ether: EtOAc = 95:5) to afford the desired product **4m** as colorless oil (15.4 mg, 41%).

Exhibited spectral data in accordance with previous report.⁶ ¹H NMR (400 MHz, CDCl₃) δ 3.53 (s, 3H), 1.07 (s, 21H). ¹³C NMR (100 MHz, CDCl₃) δ 51.6, 17.9, 11.8.

Dimethoxydiphenylsilane (**4n**)

Procedure B was followed using diphenylsilane (36.9 mg, 0.2 mmol), NaBr (10.3 mg, 0.1 mmol, 0.5 equiv.) and CH₃OH (5 mL). The crude reaction mixture was purified by flash silica gel column chromatography (petroleum ether: EtOAc = 95:5) to afford the desired product **4n** as colorless oil (34.2 mg, 70%).

Procedure C was followed using diphenylsilane (36.9 mg, 0.2 mmol), TBAB (33 mg, 0.1 mmol, 0.5 equiv.) and CH₃OH (5 mL). The crude reaction mixture was purified by flash silica gel column chromatography (petroleum ether: EtOAc = 95:5) to afford the desired product **4n** as colorless oil (33.2 mg, 68%).

Exhibited spectral data in accordance with previous report.⁴ ¹H NMR (400 MHz, CDCl₃) δ 7.67 - 7.63 (m, 4H), 7.45 - 7.35 (m, 6H), 3.63 (s, 6H). ¹³C NMR (100 MHz, CDCl₃) δ 134.8, 132.2, 130.3, 127.9, 50.9.

3. Scale-up synthesis of triphenylsilanol (**3a**) and methoxytriphenylsilane (**4a**)

Synthesis of triphenylsilanol (**3a**): an undivided three-necked bottle (250 mL) equipped with triphenylsilane (5 mmol), NaCl (150 mg, 2.5 mmol, 0.5 equiv.), CH₃CN/H₂O (4:1, 100 mL) and a stir bar. The bottle was equipped with a platinum electrode (1.0 × 1.0 cm²) anode and cathode. The reaction mixture was stirred and electrolyzed at a constant current of 15 mA under air conditions at room temperature for 18 h. After 18 h, the reaction was washed with EtOAc and the combined organic layers were concentrated with a rotary evaporator, subsequently, the pure product was

obtained by flash column chromatography on silica gel (9:1, petroleum ether: EtOAc) to afford 1.29 g (93%) of the **3a**.

Synthesis of methoxytriphenylsilane (**4a**): an undivided three-necked bottle (250 mL) equipped with triphenylsilane (5 mmol), NaBr (257.5 mg, 2.5 mmol, 0.5 equiv.), methanol (100 mL) and a stir bar. The bottle was equipped with a platinum electrode ($1.0 \times 1.0 \text{ cm}^2$) anode and cathode. The reaction mixture was stirred and electrolyzed at a constant current of 15 mA under air conditions at room temperature for 16 h. After 16 h, the reaction was diluted with EtOAc and the combined organic layers were concentrated with a rotary evaporator, subsequently, the pure product was obtained by flash column chromatography on silica gel (95: 5, petroleum ether: EtOAc) to afford 1.31 g (90%) of the **4a**.



4. General procedure for CV (cyclic voltammetry)

Cyclic voltammetry was performed in a three-electrode cell connected to a schlenk line under room temperature. Glassy carbon electrode was used as working electrode, and platinum electrode was employed as counter electrode and Ag/AgCl electrode was used as reference electrode. The mixture of acetonitrile (8 mL) and H₂O (2 mL) containing 20 mM *n*Bu₄NBF₄ was poured into the electrochemical cell in all experiments. The scan rate was 100 mV/s ranging from -0.5 to 3.0 V.

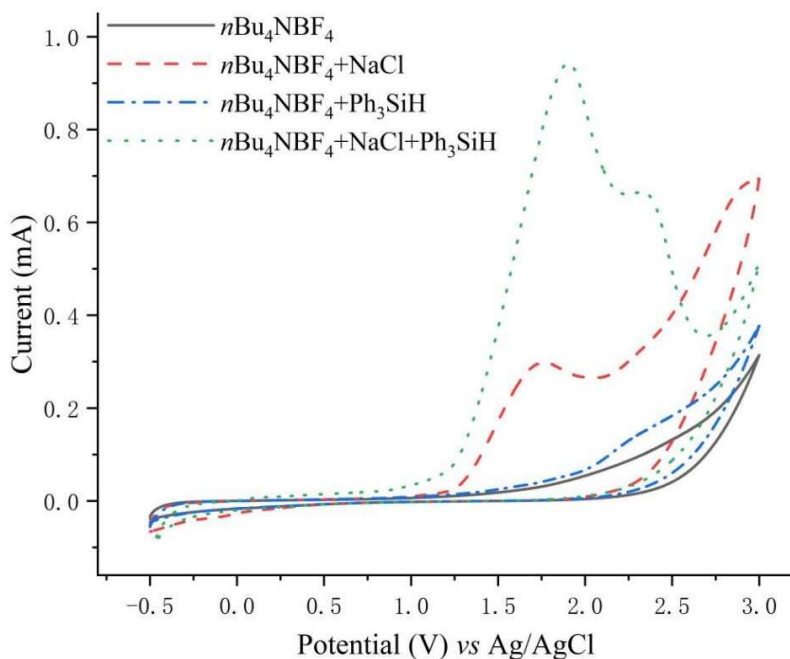


Fig. 1 Cyclic voltammetry of reactants and mixtures in 20 mM $n\text{Bu}_4\text{NBF}_4$ MeCN/ H_2O (4:1) solution using a glassy carbon as working electrode, Pt as counter electrode, Ag/AgCl as reference electrode, at 100 mV/s scan rate: background ($n\text{Bu}_4\text{NBF}_4$ 20 mM in MeCN/ H_2O); NaCl (20 mM); triphenylsilane **1a** (20 mM); NaCl (20 mM) + triphenylsilane (20 mM).

5. Isotope water experiment for the model electrochemical hydrolysis of triphenylsilane (**1a**)

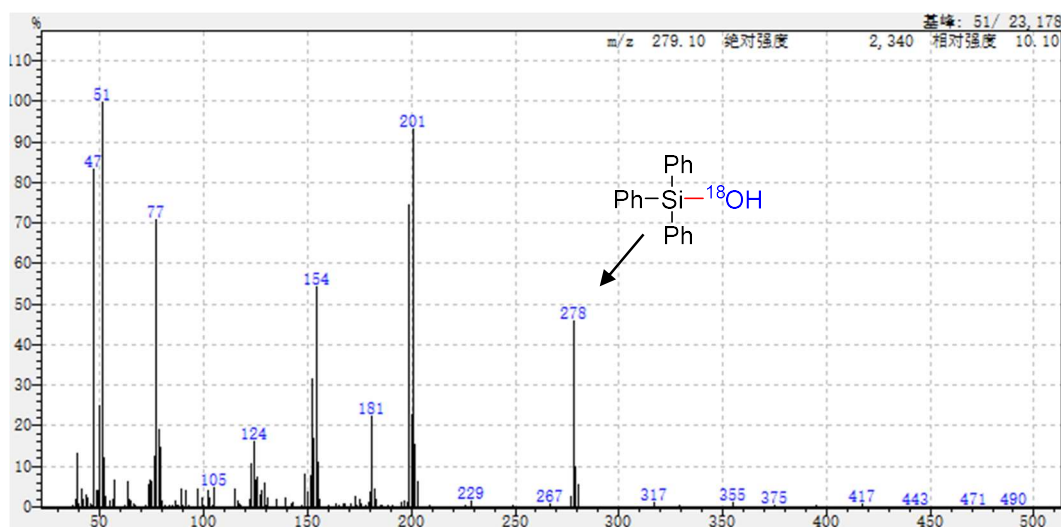
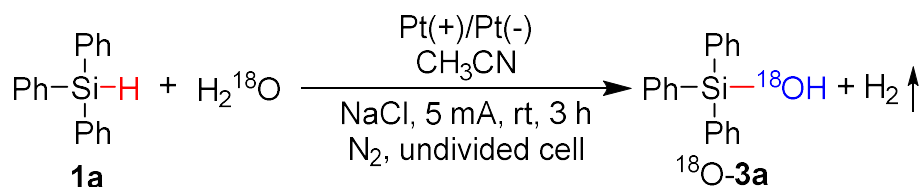


Fig. 2 GC-MS of the ^{18}O -triphenylsilanol ($^{18}\text{O-3a}$)

6. Hydrogen detection experiment

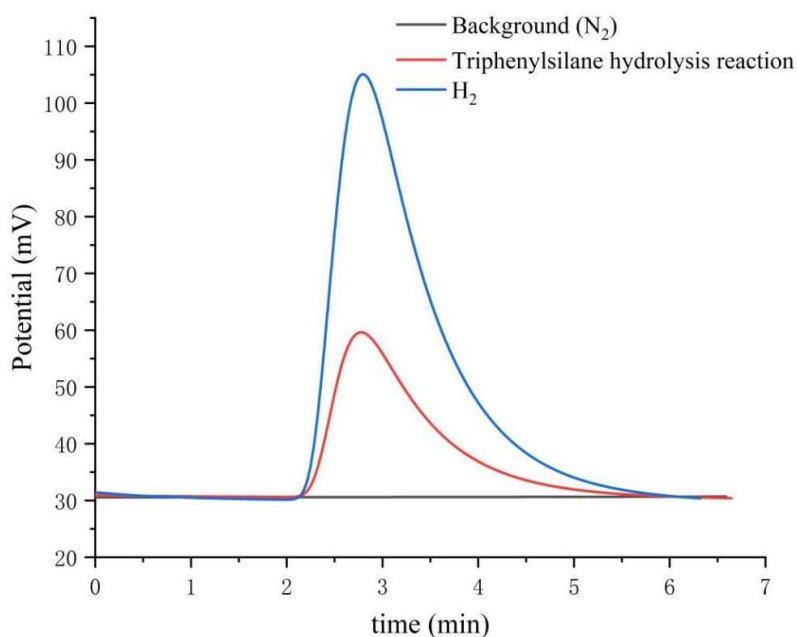
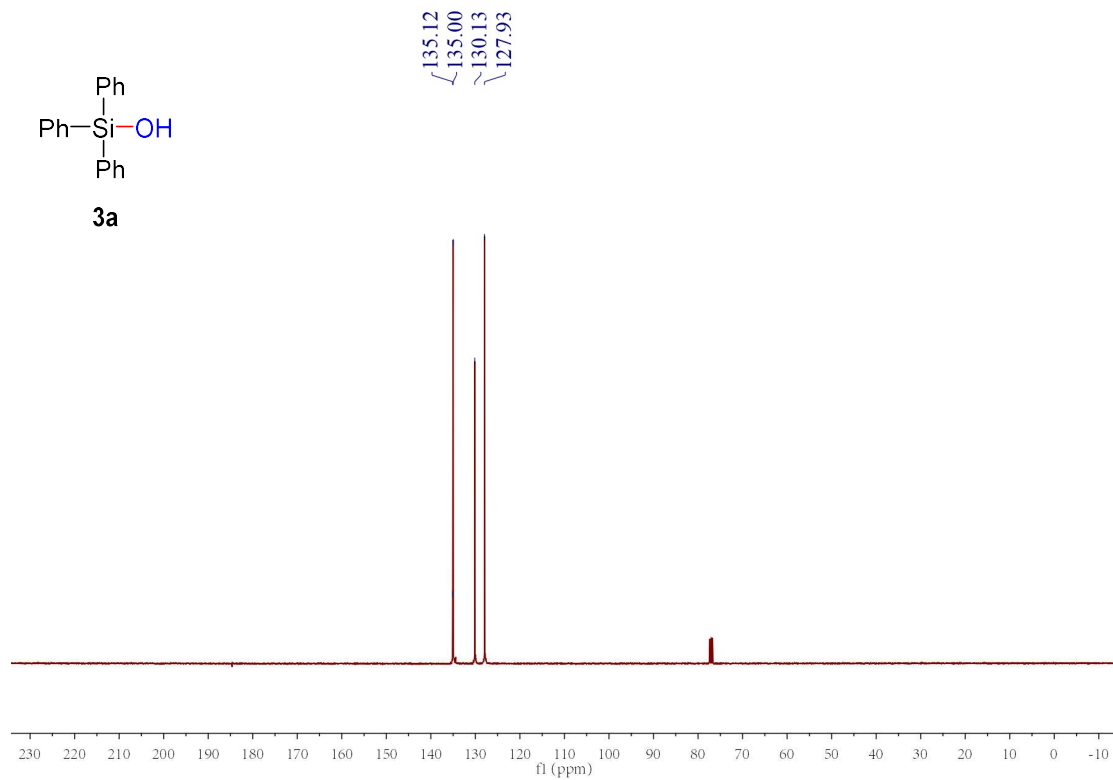
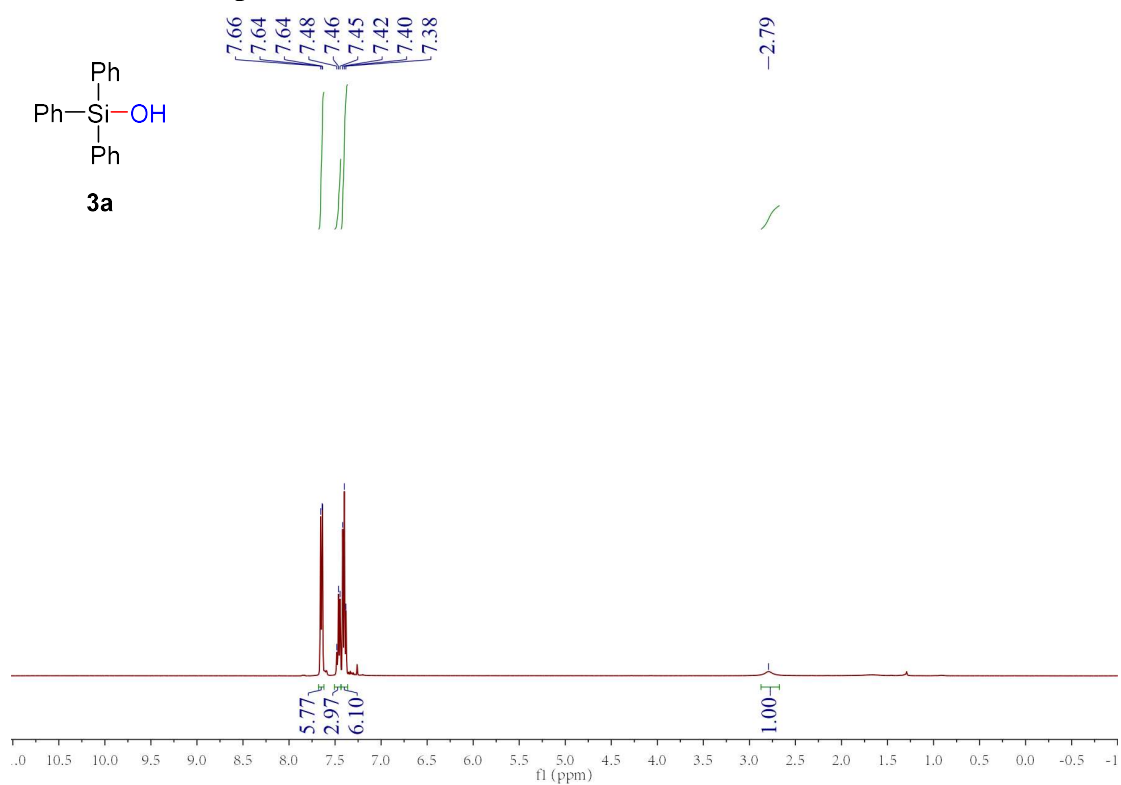


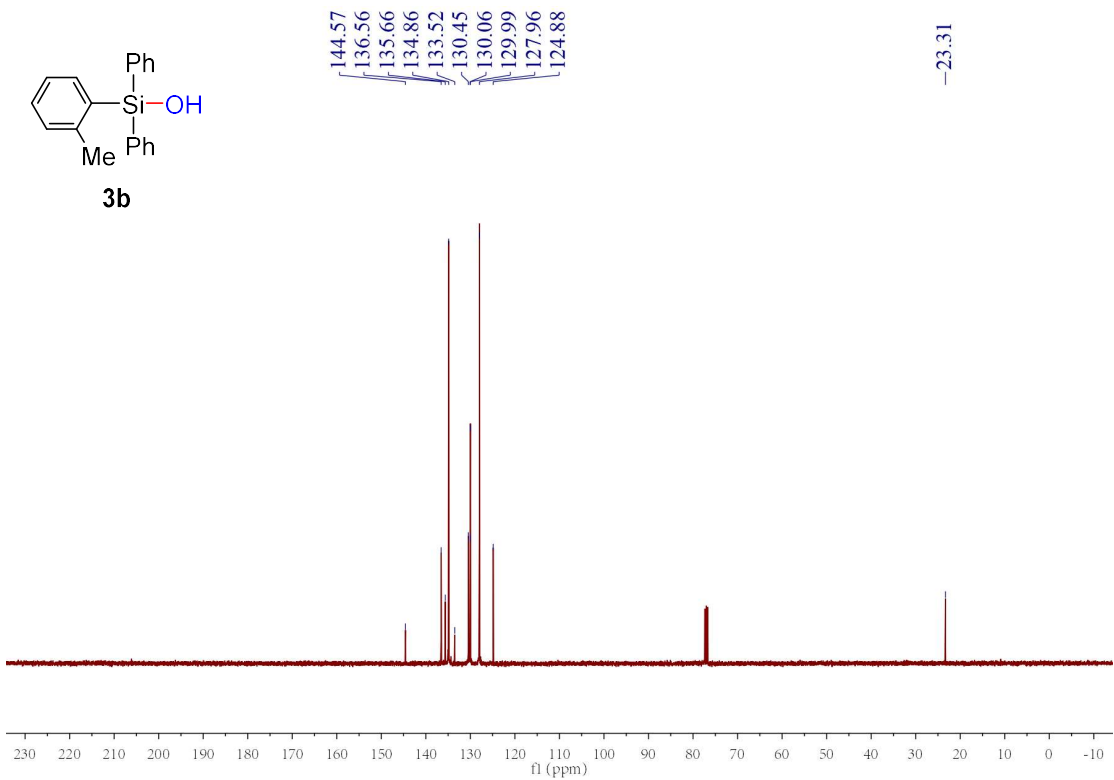
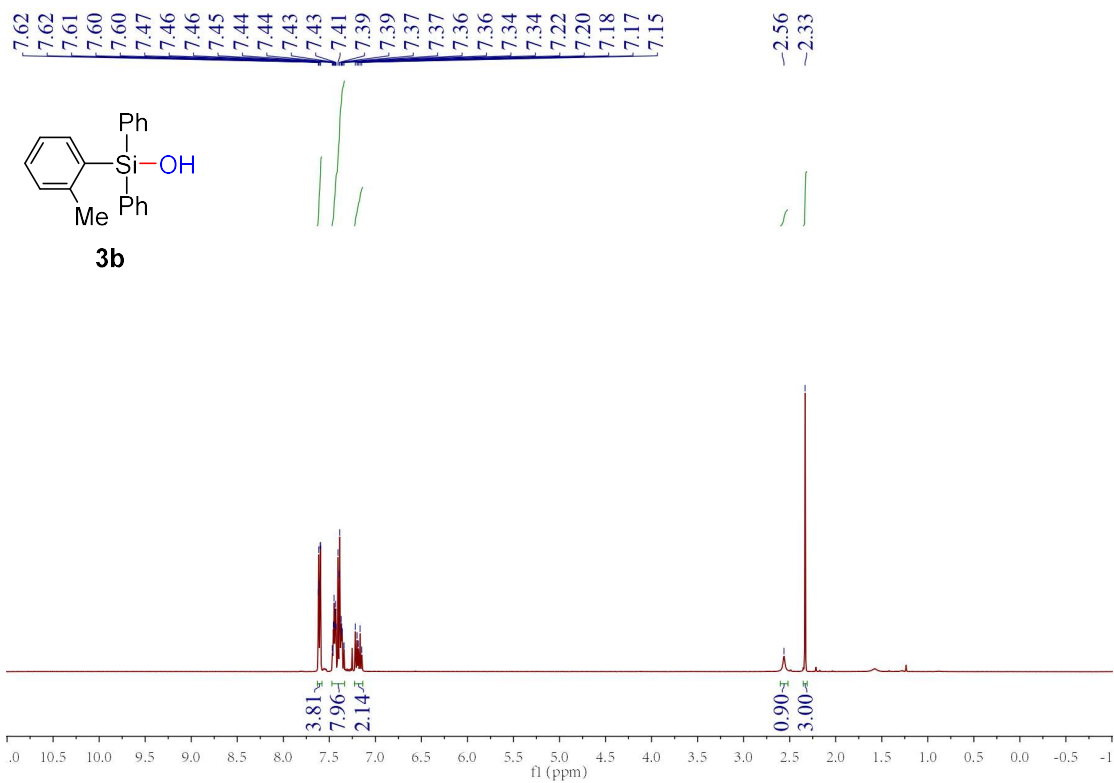
Fig. 3 The observation of H₂ gas liberation on cathode was confirmed via GC (KeXiao GC1690) during electrolysis.

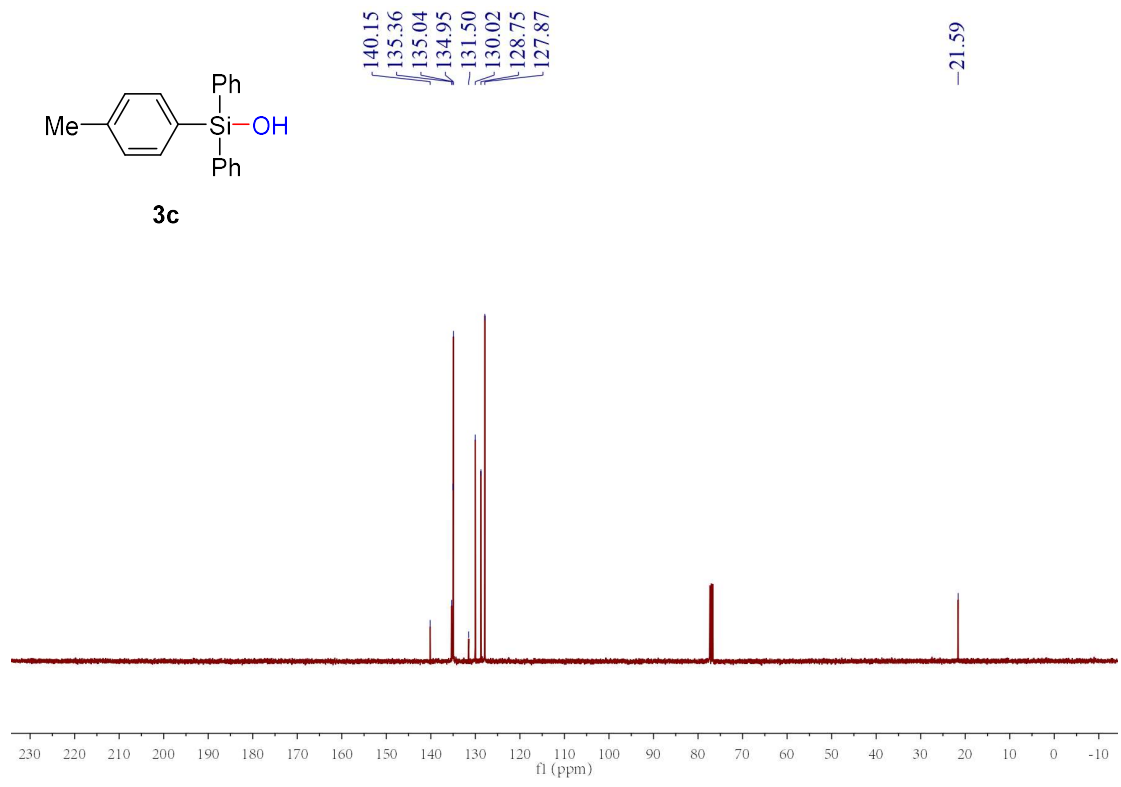
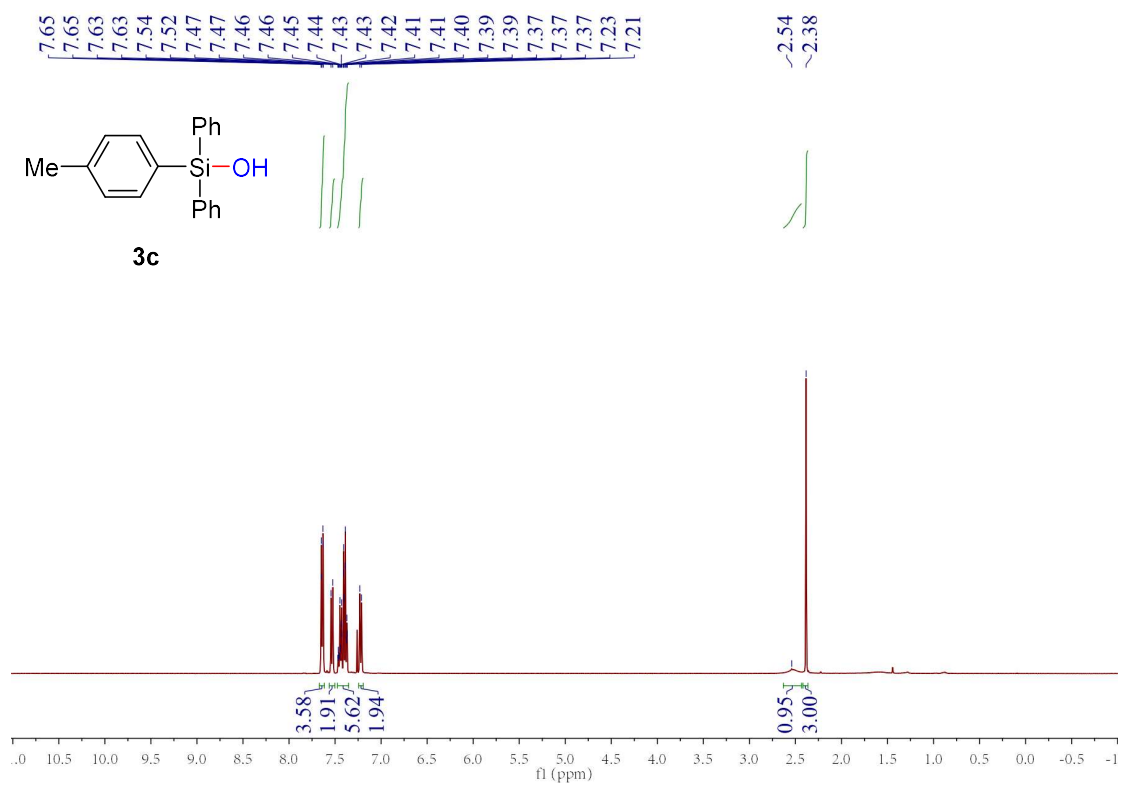
7. References

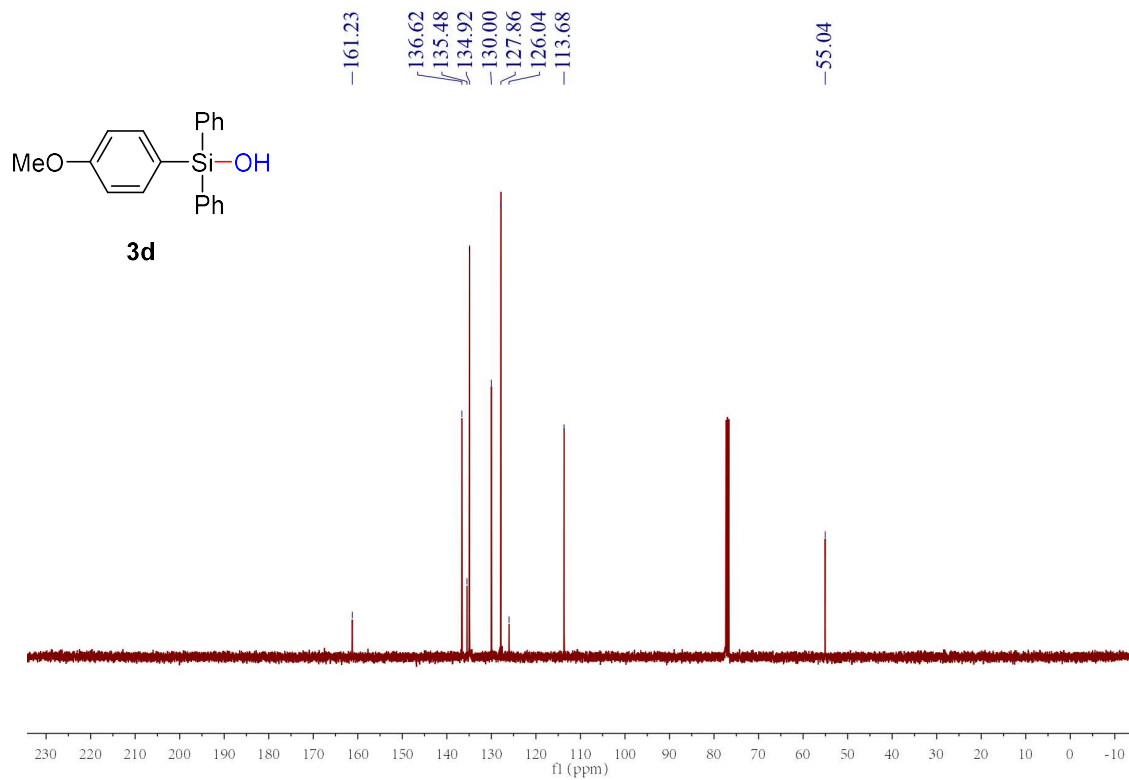
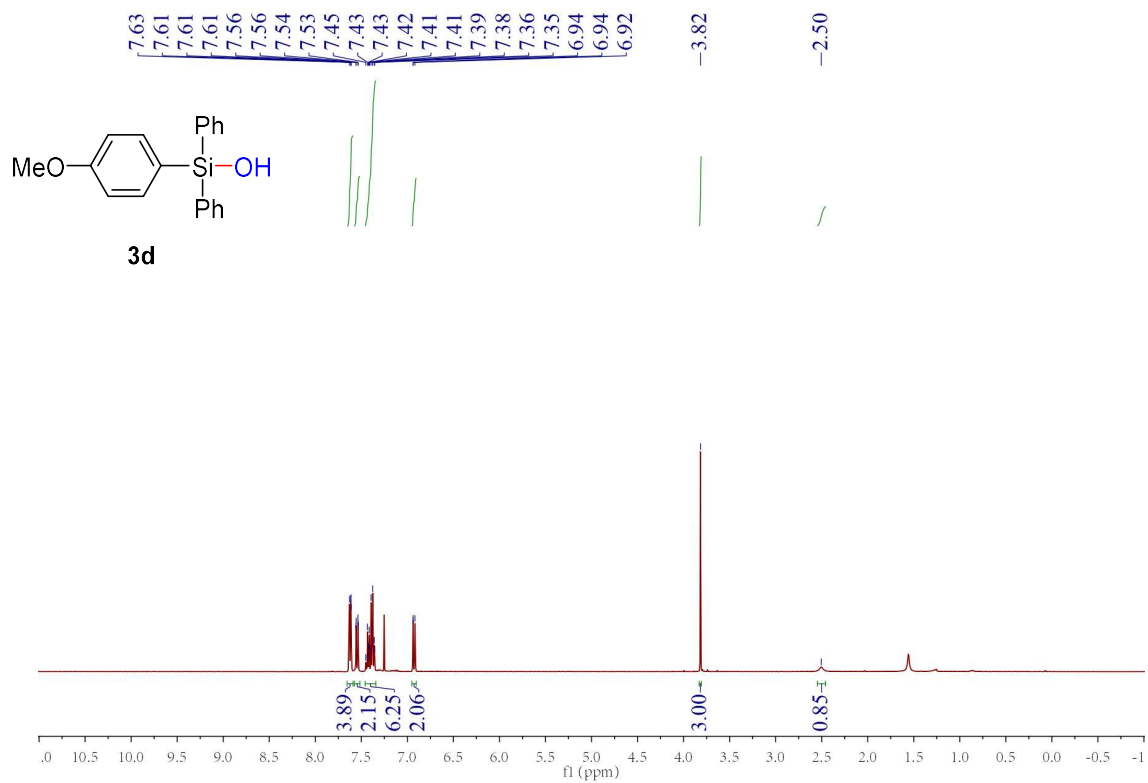
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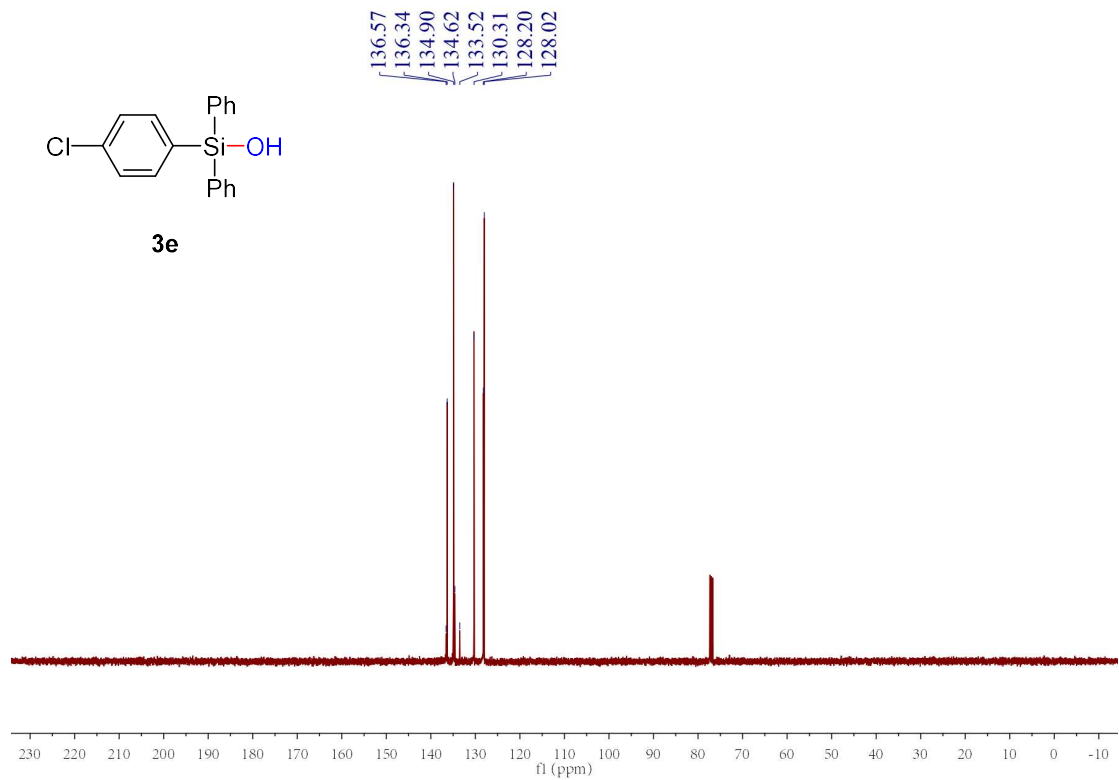
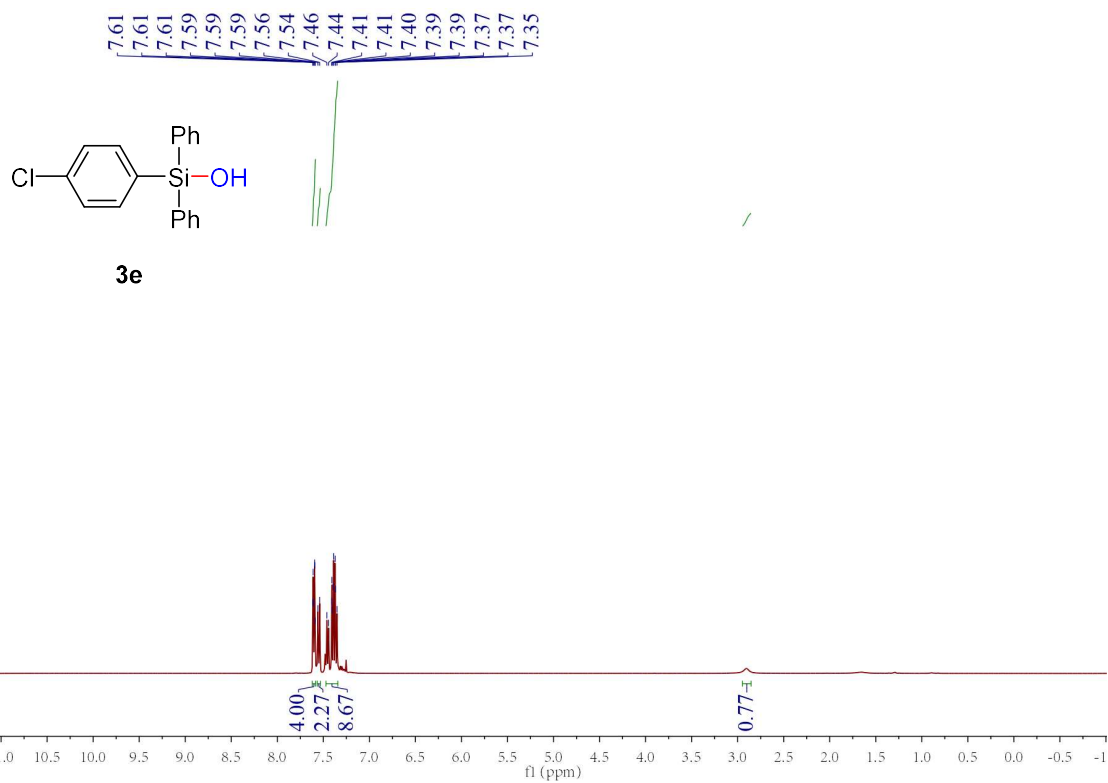
8. ^1H , ^{13}C and ^{19}F spectra

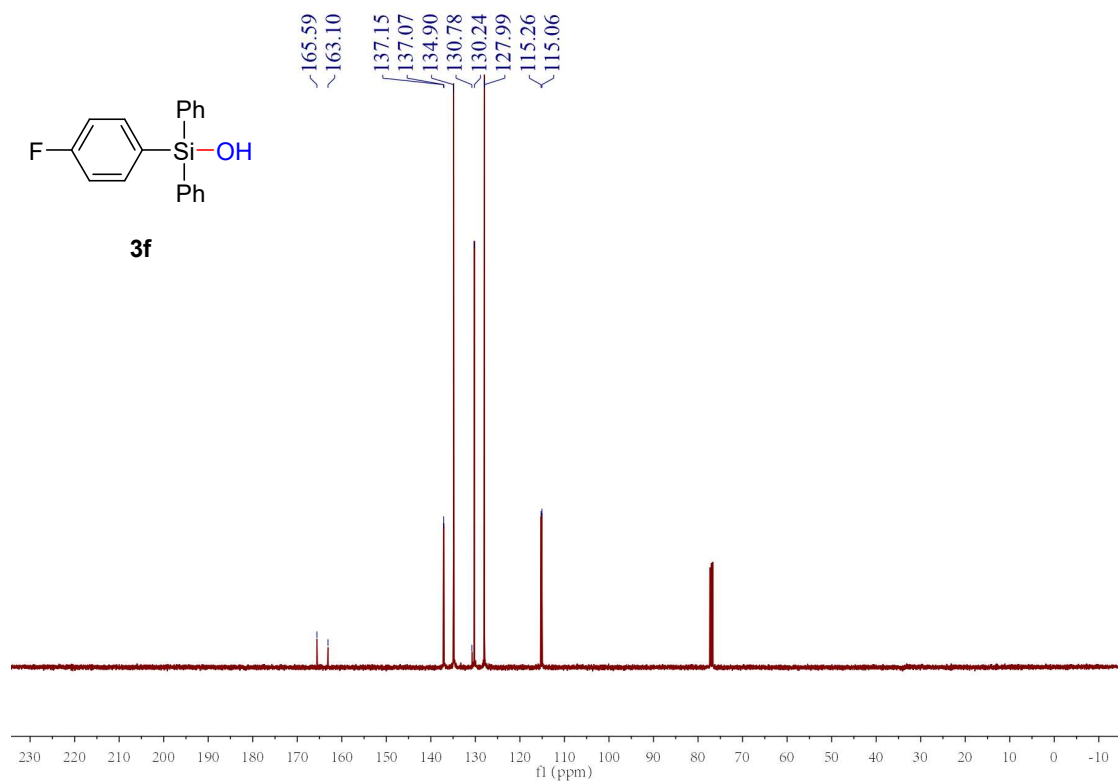
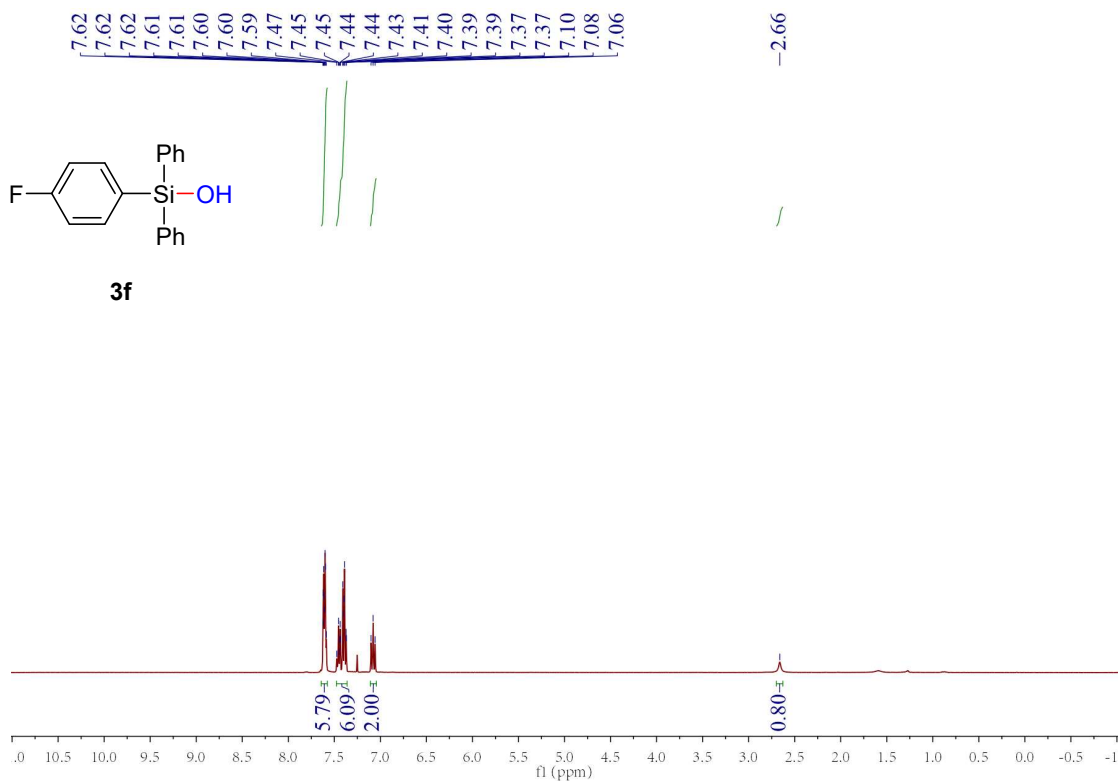


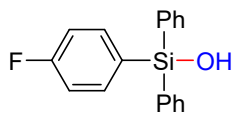




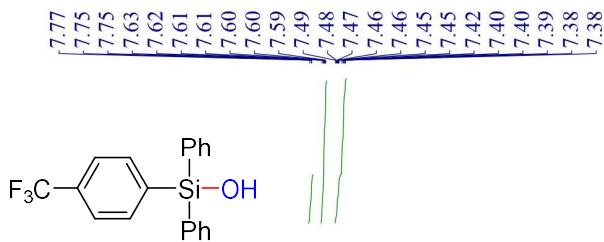
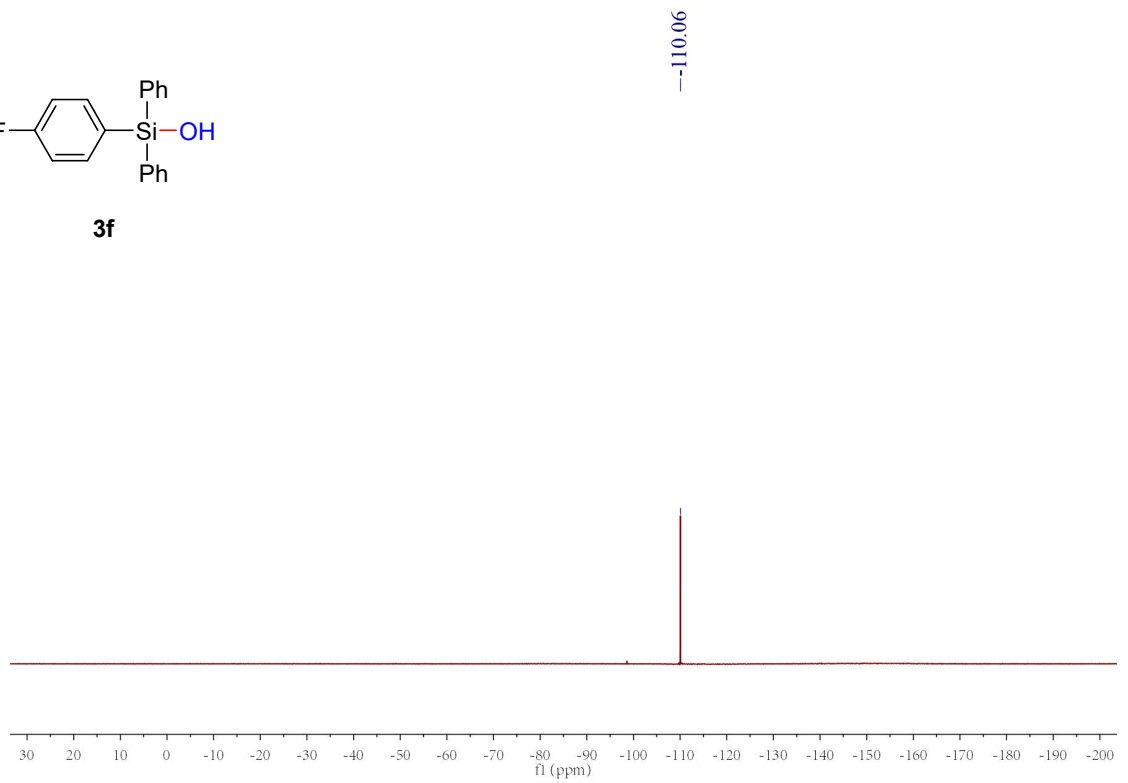








3f



3g

