Photocatalyzed Cross-Dehydrogenative Coupling of Silanes with Alcohols and Water

Haiping Lv,^a Ronibala Devi Laishram,^a Jingchao Chen, ^{*a} Ruhima Khan,^a Yuanbin Zhu,^b Shiyuan Wu,^b Jianqiang Zhang,^c Xingyuan Liu,^c and Baomin Fan^{*a}

- a Key Laboratory of Chemistry in Ethnic Medicinal Resources, Yunnan Minzu University, Yuehua Street, Kunming, 650500, China. E-mail: chenjingchao84@163.com (Jingchao Chen); FanBM@ynni.edu.cn (Baomin Fan)
- Yunnan Tiefeng High Tech Mining Chemicals. Co. Ltd, Qingfeng industrial park, Lufeng,
 651200, Yunnan Province, China
- c College of Biology and Chemistry, Puer University, Puer 665000, Yunnan, China.

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1. General Information

All commercially available reagents were obtained from commercial suppliers and used without further purification. All catalytic experiments were carried out using standard techniques. Chromatography was carried out over silica gel (Innochem 200–300 mesh) and TLC was performed using silica gel 60 F254 (Merck) plates. ¹H NMR (400 MHz) and ¹³C NMR (100 MHz) spectra were recorded on a Bruker NMR spectrometer in CDCl₃ using TMS as an internal reference with chemical shift values reported in ppm. Abbreviations used in the NMR follow-up experiments: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet. The LEDs were used as a visible light source. Steady-state fluorescence measurements were performed with Cary Eclipse Fluorescence Spectrophotometer NO. G9800A of Agilent technologies. High-resolution mass spectra (HRMS) were obtained by fast atom bombardment (FAB) using a double focusing magnetic sector mass spectrometer and electron impact (EI) ionization technique.

2. Procedure for the cross-dehydrogenative coupling of silanes with alcohols

In an oven-dried reaction tube containing a magnetic stirring bar was charged with a solution of Tris(2,2'-bipyridine)ruthenium dichloride (0.5 mol%) in MeCN (1 mL) followed by the addition of dimethylphenylsilane **1** (1.0 mmol) and 2-(p-Methylphenyl)ethanol **2** (0.2 mmol). The reaction mixture was stirred under the irradiation of 20 W LED at room temperature. After completion of the reaction (indicated by TLC), the solution was concentrated in vacuum. The residue was purified by column chromatography using a mixture of petroleum ether and ethyl acetate as eluent to give the desired product **3** (53.2 mg, 99%).

3. Procedure for the cross-dehydrogenative coupling of silanes with water

In an oven-dried reaction tube containing a magnetic stirring bar was charged with a solution of Tris(2,2'-bipyridine)ruthenium dichloride (0.5 mol%) in MeCN (1 mL) followed by the addition of dimethylphenylsilane1 (0.2 mmol) and water (1.0 mmol). The reaction mixture was stirred under the irradiation of 20 W LED at room temperature. After completion of the reaction (indicated by GC), the solution was concentrated in vacuum. The residue was purified by column chromatography using a mixture of

petroleum ether and ethyl acetate as eluent to give the desired product 76 (27.9 mg, 92%).

4. Optimization of the reaction conditions

4.1 Screening of photosensitizer for the cross-dehydrogenative coupling of silanes with alcohols^a



Entry	Photosensitizer	Time (h)	Yield ^b
1	Anthraquinone	72	21%
2	1,4-Dicyanobenzene	72	9%
3	9-Fluorenone	72	57%
4	Methylene Blue	72	11%
5	TPP	72	30%
6	Acriflavine	72	35%
7	Fluorescein	72	10%
8	Eosin Y	72	38%
9	Rose Bengal	72	17%
10	Riboflavin	72	36%
11	Rhodamine B	72	16%
12	10-Methylacridinium Perchlorate	72	33%
13	Fac-Ir(ppy) ₃	3	97%
14	Ru(bpy) ₃ Cl ₂	3	98%

Table S1 Optimization of the reaction conditions

^aReaction conditions: Reactions were conducted with 1(1.0 mmol), 2(0.2 mmol), photosensitizer (5 mol%), in dry MeCN (1 mL) at room temperature in argon under a 20 W blue LED (460-470 nm) irradiation, unless otherwise noted. ^bYields were determined by analysis of the crude 1H NMR using 1,3-Benzodioxole as an internal standard.

4.2 Screening of solvent for the cross-dehydrogenative coupling of silanes with alcohols^a



Entry	Solvent	Time(h)	Yield ^b
1	MeCN	3	98%
2	DCE	18	81%
3	CHCl ₃	18	87%
4	Toluene	72	NR
5	THF	72	NR
6	1,4-dioxane	72	NR
7	Acetone	72	31%
8	EtOAc	72	Trace
9	DMSO	12	91%
10	DMF	5	92%

 Table S2 Optimization of the reaction conditions

^aReaction conditions: Reactions were conducted with **1** (1.0 mmol), **2** (0.2mmol), $Ru(bpy)_3Cl_2$ (5 mol%), in dry solvent (1 mL) at room temperature in argon under a 20 W blue LED(460-470 nm) irradiation, unless otherwise noted. NR= no reaction. ^bYields were determined by analysis of the crude ¹H NMR using 1,3-Benzodioxole as an internal standard.

4.3 Screening of light sourcefor the cross-dehydrogenative coupling of silanes with alcohols^a



Entry	Light source	Time(h)	Yield ^b
1	460-470 nm(blue)	2	99%
2	395-405 nm(purple)	24	82%
3	410-420 nm(purple)	6	93%
4	450-455 nm(blue)	3	98%
5	490-495 nm(green)	4	89%
6	520-530 nm(green)	4	92%
7	620-630 nm(red)	72	26%
8	6000-6500K(white)	4	93%

Table S3 Optimization of the reaction conditions

^aReaction conditions: Reactions were conducted with 1 (1.0 mmol), 2 (0.2 mmol), Ru(bpy)₃Cl₂ (0.5 mol%), in dry MeCN (1 mL) at room temperature in argon under a 20 W LEDirradiation, unless

otherwise noted. NR= no reaction. ^bYields were determined by analysis of the crude 1H NMR using 1,3-Benzodioxole as an internal standard.

4.4 Screening of different amounts of photosensitizer^a



Entry	Loading	Time(h)	Yield ^b
1	5%	3	98%
2	3%	2	98%
3	1%	2	97%
4	0.5%	1.5	99%
5	0.1%	6	93%

Table S4 Optimization of the reaction conditions

^aReaction conditions: Reactions were conducted with **1** (1.0 mmol), **2** (0.2mmol), $Ru(bpy)_3Cl_2$ (x mol%), in dry MeCN (1 mL) at room temperature in argon under a 20 W blue LED(460-470 nm), unless otherwise noted. NR= no reaction. b: Yields were determined by analysis of the crude ¹H NMR using 1,3-Benzodioxole as an internal standard.

4.5 Screening of different amounts of silane^a



Table S5	Optimization	of the	reaction	conditions
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Entry	1a:1b	Time(h)	Yield ^b
1	5:1	1.5	99%
2	4:1	2	96%
3	3:1	4	89%
4	2:1	36	64%

^aReaction conditions: Reactions were conducted with 1(x mmol), 2 (0.2 mmol), $Ru(bpy)_3Cl_2 (0.5 \text{ mol}\%)$, in dry MeCN (1 mL) at room temperature in argon under a 20 W blue LED (460-470 nm), unless otherwise noted. NR= no reaction. ^bYields were determined by analysis of the crude ¹H NMR using 1,3-Benzodioxole as an internal standard.

5. Emission Spectrum of blue LED Strip

Figure s1. Emission spectrum of 20 W blue LED strip

6. The gram scale reaction



In an oven-dried reaction tube containing a magnetic stirring bar was charged with a solution of Tris(2,2'-bipyridine)ruthenium dichloride (0.5 mol%) in MeCN (30 mL) followed by the addition of dimethylphenylsilane1 (30.0 mmol) and 2-(p-Methylphenyl)ethanol 2 (6.0 mmol). The reaction mixture was stirred under the irradiation of 20 W LED at room temperature for 8 h. After completion of the reaction (indicated by TLC), the solution was concentrated in vacuum. The residue was purified by column chromatography using a mixture of petroleum ether and ethyl acetate as eluent to give the desired product 3 (1.498 g, 92%).

In an oven-dried reaction tube containing a magnetic stirring bar was charged with a solution of Tris(2,2'-bipyridine)ruthenium dichloride (0.5 mol%) in MeCN (30 mL) followed by the addition of dimethylphenylsilane**1** (6.0 mmol) and H₂O (60.0 mmol).

The reaction mixture was stirred under the irradiation of 20 W LED at room temperature for 24 h. After completion of the reaction (indicated by TLC), the solution was concentrated in vacuum. The residue was purified by column chromatography using a mixture of petroleum ether and ethyl acetate as eluent to give the desired product **76** (0.798 g, 88%).

7. Mechanistic Investigation

7.1. Control experiments



In an oven-dried reaction tube containing a magnetic stirring bar was charged with a solution of Tris(2,2'-bipyridine)ruthenium dichloride (0.5 mol%) in MeCN (1 mL) followed by the addition of dimethylphenylsilane1 (1.0 mmol) and 2-(p-Methylphenyl)ethanol 2 (0.2 mmol). The reaction mixture was stirred under dark at room temperature for 1.5 h. After completion of the reaction (indicated by TLC), the solution was concentrated in vacuum. The residue was purified by column chromatography using a mixture of petroleum ether and ethyl acetate as eluent to give the desired product **3**.



In an oven-dried reaction tube containing a magnetic stirring bar was charged with a solution of2-(p-Methylphenyl)ethanol2 (0.2 mmol) in MeCN (1 mL) followed by the addition of dimethylphenylsilane1 (1.0 mmol). The reaction mixture was stirred under the irradiation of 20 W LED at room temperature for 1.5 h. After completion of the reaction (indicated by TLC), the solution was concentrated in vacuum. The residue was purified by column chromatography using a mixture of petroleum ether and ethyl acetate as eluent to give the desired product 3.

7.2. Light/Dark experiment



In an oven-dried reaction tube containing a magnetic stirring bar was charged with a solution of Tris(2,2'-bipyridine)ruthenium dichloride (0.5 mol%) in MeCN (1 mL) followed by the addition of dimethylphenylsilane1 (1.0 mmol) and 2-(p-Methylphenyl)ethanol 2 (0.2 mmol). The reaction mixture was stirred under the irradiation of 20 W LED at room temperature. Fifteen minutes later, the light was turned off. The reaction mixture was taken and concentrated in vacuum. The residue was purified by column chromatography using a mixture of petroleum ether and ethyl acetate as eluent to give the desired product 3. After another 15 minutes, the light was turned on and the reaction mixture was taken again and purified to give the desired product 2a. The procedure wasrepeated four times and generated the profile of the reaction under the light off/on over time.



Figure S2. On/Off LED irradiation experiment for the synthesis of 3.

7.3. Rate experiment



In an oven-dried reaction tube containing a magnetic stirring bar was charged with a solution of Tris(2,2'-bipyridine)ruthenium dichloride (0.5 mol%) in MeCN (1 mL) followed by the addition of dimethylphenylsilane1 (1.0 mmol) and 2-(p-Methylphenyl)ethanol 2 (0.2 mmol). The reaction mixture was stirred under the irradiation of 20 W LED at room temperature. Ten minutes later, The reaction mixture was taken and concentrated in vacuum. The residue was purified by column

chromatography using a mixture of petroleum ether and ethyl acetate as eluent to give the desired product **3**.



Figure S3.Rate experiment for the synthesis of 3

7.4. MS data of ¹⁸O labeling experiments



In an oven-dried reaction tube containing a magnetic stirring bar was charged with a solution of Tris(2,2'-bipyridine)ruthenium dichloride (0.5 mol%) in MeCN (1 mL) followed by the addition of dimethylphenylsilane1 (0.2 mmol) and H_2O^{18} (1.0 mmol). The reaction mixture was stirred under the irradiation of 20 W LED at room temperature. After completion of the reaction (indicated by GC), the solution was concentrated in vacuum. The residue was purified by column chromatography using a mixture of petroleum ether and ethyl acetate as eluent to give the desired product O^{18} -**76** (27.9 mg, 92%).



Figure S4. The HRMS data (m/z:154) of ¹⁸O-76, which demonstrated water rather than the molecule oxygen served as the oxygen source.

7.5. Qualitative hydrogen gas detection



In an oven-dried reaction tube containing a magnetic stirring bar was charged with a solution of Tris(2,2'-bipyridine)ruthenium dichloride (0.5 mol%) in MeCN (1 mL) followed by the addition of dimethylphenylsilane **1** (1.0 mmol) and 2-(p-Methylphenyl)ethanol **2** (0.2 mmol). The reaction mixture was stirred under the irradiation of 20 W LED at room temperature. After completion of the reaction (indicated by TLC), the hydrogen gas evolved during the photocatalytic aceptorless dehydrogenation was qualitatively detected in GC (Figure S3).



Figure S5. GC analysis of the gases reaction mixture (after reaction).



In an oven-dried reaction tube containing a magnetic stirring bar was charged with a solution of Tris(2,2'-bipyridine)ruthenium dichloride (0.5 mol%) in MeCN (1 mL) followed by the addition of dimethylphenylsilane**1** (0.2 mmol) and water (1.0 mmol). The reaction mixture was stirred under the irradiation of 20 W LED at room

temperature. After completion of the reaction (indicated by GC), the hydrogen gas evolved during the photocatalytic aceptorless dehydrogenation was qualitatively detected in GC (Figure S3).



Figure S6. GC analysis of the gases reaction mixture (after reaction).

7.6. Radical-trapping experiment with TEMPO

In an oven-dried reaction tube containing a magnetic stirring bar was charged with a solution of Tris(2,2'-bipyridine)ruthenium dichloride (0.5 mol%) in MeCN (1 ml) followed by the addition of dimethylphenylsilane1 (1.0 mmol), 2-(p-Methylphenyl)ethanol 2 (0.2 mmol) and TEMPO (313 mg, 2 mmol, 10.0 equiv). The reaction mixture was stirred under the irradiation of 20 W LED at room temperature for 1.5 h. No product 3 were found and only 93 was detected in GC-MS.



Figure S7. Radical-trapping experiment with TEMPO

8. Characterization data for the products

Triethyl(phenoxy)silane (4)

Colorless liquid; 94% yield; ¹H NMR (400 MHz, Chloroform-d) δ 7.25 – 7.21 (m, 2H), 6.97 – 6.93 (m, 1H), 6.88 – 6.84 (m, 2H), 1.01 (t, J = 7.9 Hz, 9H), 0.78 – 0.72 (m, 6H); ¹³C NMR (101 MHz, Chloroform-d) δ 155.7, 129.5, 121.4, 120.1, 6.8, 5.1; HRMS-EI⁺ (m/z) [M]⁺calcd for C₁₂H₂₀OSi 208.1283, found 208.1281.

Triethyl(o-tolyloxy)silane (5)

Colorless liquid; 78% yield; ¹H NMR (400 MHz, Chloroform-d) δ 7.15 – 7.13 (m, 1H), 7.06 (td, J = 7.5, 1.3 Hz, 1H), 6.86 (td, J = 7.4, 1.1 Hz, 1H), 6.79 – 6.77 (m, 1H), 2.23 (s, 3H), 1.01 (t, J = 7.9 Hz, 9H), 0.78 (q, J = 7.5 Hz, 6H); ¹³C NMR (101 MHz, Chloroform-d) δ 154.1, 131.0, 128.9, 126.7, 121.1, 118.5, 16.8, 6.8, 5.5; HRMS-EI⁺ (m/z) [M]⁺calcd for C₁₃H₂₂OSi 222.1440, found 222.1434.

Triethyl(m-tolyloxy)silane (6)

Colorless liquid; 84% yield;¹H NMR (400 MHz, Chloroform-d) δ 7.11 (t, J = 7.7 Hz, 1H), 6.77 (d, J = 7.5 Hz, 1H), 6.69 – 6.65 (m, 2H), 2.31 (s, 3H), 1.01 (t, J = 7.9 Hz, 9H), 0.75 (q, J = 7.6 Hz, 6H); ¹³C NMR (101 MHz, Chloroform-d) δ 155.6, 139.5, 129.2, 122.2, 120.9, 117.0, 21.5, 6.8, 5.1; HRMS-EI⁺ (m/z) [M]⁺calcd for C₁₃H₂₂OSi 222.1440, found 222.1436.

Triethyl(p-tolyloxy)silane (7)



Colorless liquid; 96% yield;¹H NMR (400 MHz, Chloroform-d) δ 7.04 – 7.01 (m, 2H), 6.78 – 6.74 (m, 2H), 2.29 (s, 3H), 1.01 (t, J = 7.9 Hz, 9H), 0.74 (q, J = 7.6 Hz, 6H); ¹³C NMR (101 MHz, Chloroform-d) δ 153.4, 130.6, 123.0, 119.8, 20.7, 6.8, 5.1; HRMS-EI⁺ (m/z) [M]⁺calcd for C₁₃H₂₂OSi 222.1440, found 222.1439.

Triethyl(4-ethylphenoxy)silane (8)



Colorless liquid; 96% yield; ¹H NMR (400 MHz, Chloroform-d) δ 7.06 – 7.03 (m, 2H), 6.79 – 6.76 (m, 2H), 2.58 (q, J = 7.6 Hz, 2H), 1.21 (t, J = 7.6 Hz, 3H), 1.00 (t, J = 7.9 Hz, 9H), 0.74 (q, J = 7.6 Hz, 6H); ¹³C NMR (101 MHz, Chloroform-d) δ 153.5, 137.0, 128.8, 119.8, 28.2, 15.9, 6.8, 5.1; HRMS-EI⁺ (m/z) [M]⁺calcd for C₁₄H₂₄OSi 236.1596, found 236.1597.

(4-(tert-butyl)phenoxy)triethylsilane (9)



Colorless liquid; 96% yield; ¹H NMR (400 MHz, Chloroform-d) δ 7.25 – 7.22 (m, 2H), 6.81 – 6.77 (m, 2H), 1.30 (s, 9H), 1.02 (t, J = 7.9 Hz, 9H), 0.75 (q, J = 7.6 Hz, 6H); ¹³C NMR (101 MHz, Chloroform-d) δ 153.3, 143.9, 126.3, 119.3, 34.2, 31.7, 6.8, 5.1; HRMS-EI⁺ (m/z) [M]⁺calcd for C₁₆H₂₈OSi 264.1909, found 264.1908.

([1,1'-biphenyl]-4-yloxy)triethylsilane (10)



Colorless liquid; 92% yield; ¹H NMR (400 MHz, Chloroform-d) δ 7.58 (dt, J = 8.2, 1.7 Hz, 2H), 7.51 – 7.47 (m, 2H), 7.45 – 7.41 (m, 2H), 7.34 – 7.30 (m, 1H), 6.97 – 6.93 (m, 2H), 1.05 (t, J = 7.9 Hz, 9H), 0.83 – 0.77 (m, 6H); ¹³C NMR (101 MHz, Chloroform-d) δ 155.4, 141.0, 134.4, 128.8, 128.2, 126.9, 126.8, 120.3, 6.8, 5.2; HRMS-EI⁺ (m/z) [M]⁺calcd for C₁₈H₂₄OSi 284.1596, found 284.1595.

Triethyl(4-fluorophenoxy)silane (11)



Colorless liquid; 92% yield; ¹H NMR (400 MHz, Chloroform-d) δ 6.94 – 6.88 (m, 2H), 6.82 – 6.77 (m, 2H), 1.01 (t, J = 7.9 Hz, 9H), 0.74 (q, J = 7.6 Hz, 6H); ¹³C NMR (101 MHz, Chloroform-d) δ 157.6 (d, J = 237.0 Hz), 151.7 (d, J = 2.4 Hz), 120.9 (d, J = 8.1 Hz), 115.9 (d, J = 22.8 Hz), 6.70, 5.05; ¹⁹F NMR (376 MHz, Chloroform-d) δ -123.35 (tt, J = 8.3, 4.6 Hz); HRMS-EI⁺ (m/z) [M]⁺calcd for C₁₂H₁₉OFSi 226.1189, found 226.1191.

(4-chlorophenoxy)triethylsilane (12)

Colorless liquid; 98% yield; ¹H NMR (400 MHz, Chloroform-d) δ 7.20 – 7.16 (m, 1H), 6.80 – 6.76 (m, 1H), 0.99 (t, J = 7.9 Hz, 5H), 0.73 (q, J = 7.5 Hz, 3H); ¹³C NMR (101

MHz, Chloroform-d) δ 154.4, 129.5, 126.3, 121.3, 6.7, 5.0; HRMS-EI⁺ (m/z) [M]⁺calcd for C₁₂H₁₉OSiCl 242.0894, found 242.0897.

(4-bromophenoxy)triethylsilane (13)

Colorless liquid; 99% yield; ¹H NMR (400 MHz, Chloroform-d) δ 7.34 – 7.30 (m, 2H), 6.75 – 6.72 (m, 2H), 0.99 (t, J = 7.9 Hz, 9H), 0.73 (q, J = 7.5 Hz, 6H); ¹³C NMR (101 MHz, Chloroform-d) δ 154.9, 132.4, 121.9, 113.7, 6.7, 5.0; HRMS-EI⁺ (m/z) [M]⁺calcd for C₁₂H₁₉OBrSi 286.0389, found 286.0931.

(2-bromophenoxy)triethylsilane (14)



Colorless liquid; 86% yield; ¹H NMR (400 MHz, Chloroform-d) δ 7.51 (dd, J = 7.9, 1.6 Hz, 1H), 7.16 (ddd, J = 8.1, 7.4, 1.7 Hz, 1H), 6.88 (dd, J = 8.1, 1.5 Hz, 1H), 6.84 – 6.80 (m, 1H), 1.02 (t, J = 7.9 Hz, 9H), 0.80 (q, J = 7.4 Hz, 6H); ¹³C NMR (101 MHz, Chloroform-d) δ 152.8, 133.4, 128.4, 122.5, 120.4, 115.5, 6.8, 5.4; HRMS-EI⁺ (m/z) [M]⁺calcd for C₁₂H₁₉OBrSi 286.0389, found 286.0381.

(3-bromophenoxy)triethylsilane (15)

Br O Si Et

Colorless liquid; 96% yield; ¹H NMR (400 MHz, Chloroform-d) δ 7.11 – 7.06 (m, 2H), 7.03 – 7.02 (m, 1H), 6.81 – 6.76 (m, 1H), 1.00 (t, J = 7.9 Hz, 9H), 0.75 (q, J = 7.5 Hz, 6H);

¹³C NMR (101 MHz, Chloroform-d) δ 156.7, 130.6, 124.6, 123.5, 122.6, 118.79, 6.7, 5.0; HRMS-EI⁺ (m/z) [M]⁺calcd for C₁₂H₁₉OBrSi 286.0389, found 286.0391.

Triethyl(4-(trifluoromethyl)phenoxy)silane (16)

Colorless liquid; 96% yield;¹H NMR (400 MHz, Chloroform-d) δ 7.49 (d, J = 8.4 Hz, 2H), 6.92 (d, J = 8.3 Hz, 2H), 1.01 (t, J = 7.9 Hz, 9H), 0.77 (q, J = 7.5 Hz, 6H); ¹³C NMR (101 MHz, Chloroform-d) δ 158.7 (d, J = 1.2 Hz), 127.0 (q, J = 3.7 Hz), 124.7 (q, J = 269.6 Hz), 123.5 (q, J = 32.3 Hz), 120.1, 6.7, 5.1; ¹⁹F NMR (376 MHz, Chloroform-d) δ -62.30; HRMS-EI⁺ (m/z) [M]⁺calcd for C₁₃H₁₉OSiF₃ 276.1157, found 276.1165.

4-((triethylsilyl)oxy)aniline (17)



Colorless liquid; 85% yield; ¹H NMR (400 MHz, Chloroform-d) δ 6.70 – 6.66 (m, 2H), 6.59 – 6.55 (m, 2H), 3.32 (brs, 2H), 0.99 (t, J = 7.9 Hz, 9H), 0.74 – 0.68 (m, 6H).¹³C NMR (101 MHz, Chloroform-d) δ 148.2, 140.4, 120.6, 116.4, 6.8, 5.0; HRMS-ESI(m/z) [M + H]+calcd for C₁₂H₂₁NOSi 224.1465, found 224.1470.

Triethyl(4-methoxyphenoxy)silane (18)



Colorless liquid; 94% yield; ¹H NMR (400 MHz, Chloroform-d) δ 6.81 – 6.75 (m, 4H), 3.76 (s, 3H), 1.00 (t, J = 7.9 Hz, 9H), 0.72 (q, J = 7.9 Hz, 6H); ¹³C NMR (101 MHz, Chloroform-d) δ 154.2, 149.4, 120.6, 114.6, 55.7, 6.8, 5.1; HRMS-EI⁺ (m/z) [M]⁺calcd for C₁₃H₂₂O₂Si 238.1389, found 238.1388.

Triethyl(4-phenoxyphenoxy)silane (19)

Colorless liquid; 93% yield; ¹H NMR (400 MHz, Chloroform-d) δ 7.34 – 7.28 (m, 2H), 7.07 – 7.03 (m, 1H), 6.97 – 6.90 (m, 4H), 6.86 – 6.82 (m, 2H), 1.02 (t, J = 7.9 Hz, 9H), 0.79 – 0.73 (m, 6H); ¹³C NMR (101 MHz, Chloroform-d) δ 158.5, 151.8, 150.7, 129.7, 122.6, 121.0, 120.7, 117.8, 6.8, 5.1; HRMS-EI⁺ (m/z) [M]⁺calcd for C₁₈H₂₄O₂Si 300.1546, found 300.1542.

Triethyl(4-nitrophenoxy)silane (20)



Colorless liquid; 91% yield; ¹H NMR (400 MHz, Chloroform-d) δ 8.17 – 8.13 (m, 2H), 6.92 – 6.88 (m, 2H), 1.01 (t, J = 7.9 Hz, 9H), 0.79 (q, J = 7.4 Hz, 6H); ¹³C NMR (101 MHz, Chloroform-d) δ 161.8, 142.0, 126.0, 120.0, 6.6, 5.1; HRMS-EI⁺ (m/z) [M]⁺calcd for C₁₂H₁₉NO₃Si 253.1134, found 253.1136.

4-((triethylsilyl)oxy)benzonitrile (21)



Colorless liquid; 69% yield; ¹H NMR (400 MHz, Chloroform-d) δ 7.55 – 7.51 (m, 2H), 6.91 – 6.87 (m, 2H), 0.99 (t, J = 7.9 Hz, 9H), 0.76 (q, J = 7.5 Hz, 6H); ¹³C NMR (101 MHz, Chloroform-d) δ 159.81, 134.13, 120.77, 119.35, 104.66, 6.60, 5.09; HRMS-EI⁺ (m/z) [M]⁺calcd for C₁₃H₁₉NOSi 233.1236, found 233.1239. (2,3-dimethylphenoxy)triethylsilane (22)



Colorless liquid; 96% yield; ¹H NMR (400 MHz, Chloroform-d) δ 6.95 (t, J = 7.8 Hz, 1H), 6.78 (d, J = 7.5 Hz, 1H), 6.67 (d, J = 8.0 Hz, 1H), 2.27 (s, 3H), 2.15 (s, 3H), 1.02 (t, J = 7.9 Hz, 9H), 0.78 (q, J = 7.9 Hz, 6H); ¹³C NMR (101 MHz, Chloroform-d) δ 153.8, 138.3, 127.4, 125. 7, 122.7, 116.2, 20.5, 12.4, 6.9, 5.4; HRMS-EI⁺ (m/z) [M]⁺calcd for C₁₄H₂₄OSi 236.1596, found 236.1597.

(2,6-dimethylphenoxy)triethylsilane (23)



Colorless liquid; 95% yield; ¹H NMR (400 MHz, Chloroform-d) δ 7.02 (d, J = 7.6 Hz, 1H), 6.69 (d, J = 7.6 Hz, 1H), 6.61 (s, 1H), 2.29 (s, 3H), 2.19 (s, 3H), 1.03 (t, J = 7.9 Hz, 9H), 0.78 (q, J = 7.5 Hz, 6H); ¹³C NMR (101 MHz, Chloroform-d) δ 153.9, 136.4, 130.6, 125.6, 121.8, 119.4, 21.3, 16.4, 6.9, 5.5; HRMS-EI⁺ (m/z) [M]⁺calcd for C₁₃H₂₂OSi 236.1596, found 236.1602.

(2,6-dichlorophenoxy)triethylsilane (24)



Colorless liquid; 96% yield; ¹H NMR (400 MHz, Chloroform-d) δ 7.25 (s, 1H), 7.23 (s, 1H), 6.82 (t, J = 8.0 Hz, 1H), 1.02 – 0.98 (m, 9H), 0.88 – 0.82 (m, 6H); ¹³C NMR (101 MHz, Chloroform-d) δ 149.1, 128.7, 127.0, 122.2, 6.8, 5.7; HRMS-ESI (m/z) [M - H]⁻calcd for C₁₂H₁₈Cl₂OSi275.0431, found 275.0435.

Triethyl(naphthalen-1-yloxy)silane (25)



Colorless liquid; 94% yield; ¹H NMR (400 MHz, Chloroform-d) δ 8.26 – 8.22 (m, 1H), 7.85 – 7.81 (m, 1H), 7.52 – 7.47 (m, 3H), 7.37 – 7.33 (m, 1H), 6.91 (dd, J = 7.5, 0.9 Hz, 1H), 1.07 (t, J = 7.9 Hz, 9H), 0.89 (q, J = 7.3 Hz, 6H); ¹³C NMR (101 MHz, Chloroform-d) δ 151.83, 135.06, 127.96, 127.70, 126.26, 126.05, 125.21, 122.66, 120.99, 112.45, 6.92, 5.37; HRMS-EI⁺ (m/z) [M]⁺calcd for C₁₆H₂₂OSi258.1440, found 258.1444.

Triethyl(naphthalen-2-yloxy)silane (26)



Colorless liquid; 96% yield; ¹H NMR (400 MHz, Chloroform-d) δ 7.79 (d, J = 8.2 Hz, 1H), 7.75 (d, J = 9.0 Hz, 1H), 7.72 (d, J = 8.3 Hz, 1H), 7.45 (ddd, J = 8.2, 6.9, 1.3 Hz, 1H), 7.36 (ddd, J = 8.1, 6.9, 1.2 Hz, 1H), 7.24 (d, J = 2.3 Hz, 1H), 7.13 (dd, J = 8.8, 2.4 Hz, 1H), 1.06 (t, J = 7.9 Hz, 9H), 0.83 (q, J = 7.5 Hz, 6H); ¹³C NMR (101 MHz, Chloroform-d) δ 153.5, 134.8, 129.5, 129.4, 127.8, 126.8, 126.2, 123.9, 122.1, 114.8, 6.8, 5.2; HRMS-EI⁺ (m/z) [M]⁺calcd for C₁₆H₂₂OSi258.1440, found 258.1443.

1,2-bis((triethylsilyl)oxy)benzene (27)



Colorless liquid; 89% yield; ¹H NMR (400 MHz, Chloroform-d) δ 6.87 – 6.79 (m, 4H), 1.01 (t, J = 7.9 Hz, 18H), 0.78 (q, J = 8.0 Hz, 12H); ¹³C NMR (101 MHz,

Chloroform-d) δ 147.1, 121.6, 120. 8, 6.8, 5.3; HRMS-ESI (m/z) [M + H]⁺calcd for C₁₈H₃₄O₂Si₂ 339.2170, found 339.2171.

1,3-bis((triethylsilyl)oxy)benzene (28)



Colorless liquid; 89% yield; ¹H NMR (400 MHz, Chloroform-*d*) δ 7.05 (t, *J* = 8.0 Hz, 1H), 6.48 (dd, *J* = 8.1, 2.3 Hz, 2H), 6.39 (t, *J* = 2.3 Hz, 1H), 1.00 (t, *J* = 7.9 Hz, 18H), 0.73 (q, *J* = 7.9 Hz, 12H); ¹³C NMR (101 MHz, Chloroform-*d*) δ 156.7, 129.7, 113.4, 112.1, 6.8, 5.1; HRMS-EI⁺ (m/z) [M]⁺calcd for C₁₈H₃₄O₂Si₂ 338.2097, found 338.2099.

1,4-bis((triethylsilyl)oxy)benzene (29)



Colorless liquid; 91% yield; ¹H NMR (400 MHz, Chloroform-*d*) δ 6.70 (s, 4H), 0.98 (t, J = 8.0 Hz, 18H), 0.71 (q, J = 8.0 Hz, 12H); ¹³C NMR (101 MHz, Chloroform-*d*) δ 149.8, 120.6, 6.8, 5.1; HRMS-EI⁺ (m/z) [M]⁺calcd for C₁₈H₃₄O₂Si₂ 338.2097, found 338.2099.

2,2'-bis((triethylsilyl)oxy)-1,1'-biphenyl (30)



Colorless liquid; 98% yield; ¹H NMR (400 MHz, Chloroform-*d*) δ 7.27 (d, *J* = 1.8 Hz, 1H), 7.25 (d, *J* = 1.8 Hz, 1H), 7.18 (td, *J* = 7.8, 1.8 Hz, 2H), 6.96 (td, *J* = 7.5, 1.1 Hz, 2H), 6.87 (dd, *J* = 8.1, 1.0 Hz, 2H), 0.82 (t, *J* = 7.9 Hz, 18H), 0.56 (q, *J* = 7.9 Hz, 12H);

¹³C NMR (101 MHz, Chloroform-*d*) δ 153.3, 132.0, 130.7, 128.1, 120.5, 119.3, 6.7,
5.2; HRMS-ESI (m/z) [M]⁺calcd for C₂₄H₃₉O₂Si₂ 415.2489, found 415.2485.

(8R,9S,13S,14S)-13-methyl-3-((triethylsilyl)oxy)-6,7,8,9,11,12,13,14,15,16-decahyd ro-17H-cyclopenta[a]phenanthren-17-one (31)



White solid; m.p. 87 – 88 °C; 85% yield; ¹H NMR (400 MHz, Chloroform-*d*) δ 7.12 (d, J = 8.4 Hz, 1H), 6.64 (dd, J = 8.4, 2.6 Hz, 1H), 6.58 (d, J = 2.5 Hz, 1H), 2.92 – 2.80 (m, 2H), 2.50 (dd, J = 18.8, 8.6 Hz, 1H), 2.40 – 2.33 (m, 1H), 2.24 (td, J = 10.8, 4.0 Hz, 1H), 2.19 – 2.10 (m, 1H), 2.08 – 1.93 (m, 3H), 1.67 – 1.37 (m, 6H), 1.00 (t, J = 7.9 Hz, 9H), 0.91 (s, 3H), 0.73 (q, J = 7.8 Hz, 6H); ¹³C NMR (101 MHz, Chloroform-*d*) δ 153.5, 137.7, 132.5, 126.3, 120.0, 117.3, 50.6, 48.2, 44.2, 38.4, 36.0, 31.7, 29.6, 26.7, 26.0, 21.7, 14.0, 6.8, 5.1; HRMS-EI⁺ (m/z) [M]⁺calcd for C₁₈H₃₄O₂Si 384.2485, found 384.2490.

Dimethyl(phenethoxy)(phenyl)silane (59)



Colorless liquid; 94% yield; ¹H NMR (400 MHz, Chloroform-d) δ 7.57 – 7.54 (m, 2H), 7.44 – 7.36 (m, 3H), 7.30 (ddd, J = 7.5, 6.3, 1.2 Hz, 2H), 7.25 – 7.18 (m, 3H), 3.82 (t, J = 7.2 Hz, 2H), 2.87 (t, J = 7.2 Hz, 2H), 0.36 (s, 6H); ¹³C NMR (101 MHz, Chloroform-d) δ 139.0, 137.9, 133.6, 129.7, 129.2, 128.4, 128.0, 126.3, 64.5, 39.5, -1.7; HRMS-EI⁺ (m/z) [M]⁺calcd for C₁₆H₂₀OSi 256.1283, found 256.1281.

(4-fluorophenethoxy)dimethyl(phenyl)silane (32)



Colorless liquid; 97% yield; ¹H NMR (400 MHz, Chloroform-d) δ 7.56 – 7.53 (m, 2H), 7.45 – 7.37 (m, 3H), 7.14 (ddd, J = 8.4, 5.3, 2.5 Hz, 2H), 7.01 – 6.95 (m, 2H), 3.81 (t, J = 7.0 Hz, 2H), 2.83 (t, J = 7.0 Hz, 2H), 0.36 (s, 6H); ¹³C NMR (101 MHz, Chloroform-d) δ 131.7 (d, J = 24.2 Hz), 137.8, 134.8 (d, J = 3.1 Hz), 133.6, 130.6 (d, J = 7.9 Hz), 129.7, 128.0, 115.1 (d, J = 20.9 Hz), 64.3 (d, J = 1.5 Hz), 38.6, -1.8; ¹⁹F NMR (376 MHz, Chloroform-d) δ -117.25; HRMS-EI⁺ (m/z) [M]⁺calcd for C₁₆H₁₉OSiF 274.1189, found 274.1184.

(4-chlorophenethoxy)dimethyl(phenyl)silane (33)



Colorless liquid; 97% yield; ¹H NMR (400 MHz, Chloroform-d) δ 7.60 – 7.48 (m, 2H), 7.47 – 7.31 (m, 3H), 7.30 – 7.21 (m, 2H), 7.16 – 7.07 (m, 2H), 3.80 (t, J = 6.9 Hz, 2H), 2.82 (t, J = 6.9 Hz, 2H), 0.36 (s, 6H); ¹³C NMR (101 MHz, Chloroform-d) δ 137.7, 137.6, 133.6, 132.1, 130.6, 129.8, 128.5, 128.0, 64.0, 38.7, -1.8; HRMS-EI⁺ (m/z) [M]⁺calcd for C₁₆H₁₉OSiCl 290.0894, found 290.0891.

(4-bromophenethoxy)dimethyl(phenyl)silane (34)



Colorless liquid; 95% yield;¹H NMR (400 MHz, Chloroform-d) δ 7.42 – 7.40 (m, 2H), 7.32 – 7.26 (m, 5H), 6.97 – 6.93 (m, 2H), 3.68 (t, J = 6.9 Hz, 2H), 2.69 (t, J = 6.9 Hz, 2H), 0.24 (s, 6H); ¹³C NMR (101 MHz, Chloroform-d) δ 138.1, 137.7, 133.6, 131.4, 131.0, 129.8, 128.0, 120.1, 64.0, 38.7, -1.8; HRMS-EI⁺ (m/z) [M]⁺calcd for C₁₆H₁₉OSiBr 334.0389, found 334.0390.

Dimethyl(phenyl)(4-(trifluoromethyl)phenethoxy)silane (35)



Colorless liquid; 82% yield; ¹H NMR (400 MHz, Chloroform-d) δ 7.53 (d, J = 8.0 Hz, 2H), 7.50 – 7.48 (m, 2H), 7.43 – 7.34 (m, 3H), 7.28 (d, J = 8.0 Hz, 2H), 3.83 (t, J = 6.8 Hz, 2H), 2.89 (t, J = 6.8 Hz, 2H), 0.34 (s, 6H); ¹³C NMR (101 MHz, Chloroform-d) δ 143.4 (d, J = 1.6 Hz), 137.6, 133.5, 129.8, 129.6, 128.7 (d, J = 32.1 Hz), 128.0, 125.2 (d, J = 3.7 Hz), 124.4 (d, J = 270.2 Hz), 63.8, 39.2, -1.8; ¹⁹F NMR (376 MHz, Chloroform-d) δ -62.670; HRMS-EI⁺ (m/z) [M]⁺calcd for C₁₇H₁₉OSiF₃ 324.1157, found 324.1161.

(4-methoxyphenethoxy)dimethyl(phenyl)silane (36)



Colorless liquid; 98% yield; ¹H NMR (400 MHz, Chloroform-d) δ 7.58 – 7.55 (m, 2H), 7.44 – 7.37 (m, 3H), 7.13 – 7.09 (m, 2H), 6.86 – 6.83 (m, 2H), 3.81 – 3.77 (m, 5H), 2.81 (t, J = 7.3 Hz, 2H), 0.37 (s, 6H); ¹³C NMR (101 MHz, Chloroform-d) δ 158.2, 138.0, 133.6, 131.1, 130.1, 129.7, 127.9, 113.8, 64.7, 55.4, 38.6, -1.7; HRMS-EI⁺ (m/z) [M]⁺calcd for C₁₇H₂₂O₂Si 286.1389, found 286.1383. 4-(2-((dimethyl(phenyl)silyl)oxy)ethyl)-N,N-dimethylaniline (37)



Colorless liquid; 93% yield; ¹H NMR (400 MHz, Chloroform-d) δ 7.68 – 7.54 (m, 2H), 7.51 – 7.35 (m, 3H), 7.09 (d, J = 8.7 Hz, 2H), 6.73 (d, J = 8.7 Hz, 2H), 3.85 – 3.76 (m, 2H), 2.95 (s, 6H), 2.81 (t, J = 7.5 Hz, 2H), 0.41 (s, 6H); ¹³C NMR (101 MHz, Chloroform-d) δ 149.5, 138.1, 133.6, 129.8, 129.6, 127.9, 126.9, 113.1, 64.9, 41.0, 38.5, -1.7; HRMS-EI⁺ (m/z) [M]⁺calcd for C₁₈H₂₅NOSi 299.1705, found 299.1706.

(4-(tert-butyl)phenethoxy)dimethyl(phenyl)silane (38)



Colorless liquid; 98% yield; ¹H NMR (400 MHz, Chloroform-d) δ 7.63 – 7.60 (m, 2H), 7.49 – 7.41 (m, 3H), 7.39 – 7.36 (m, 2H), 7.18 (d, J = 8.4 Hz, 2H), 3.87 (t, J = 7.4 Hz, 2H), 2.90 (t, J = 7.4 Hz, 2H), 1.39 (s, 9H), 0.42 (s, 6H); ¹³C NMR (101 MHz, Chloroform-d) δ 149.1, 138.0, 135.9, 133.6, 129.7, 128. 9, 128.0, 125.3, 64.6, 39.0, 34.5, 31.5, -1.7; HRMS-EI⁺ (m/z) [M]⁺calcd for C₁₈H₂₈OSi 312.1909, found 312.1909.

Dimethyl(3-methylphenethoxy)(phenyl)silane (39)



Colorless liquid; 97% yield; ¹H NMR (400 MHz, Chloroform-*d*) δ 7.59 (dq, *J* = 6.3, 2.1 Hz, 2H), 7.47 – 7.39 (m, 3H), 7.21 (t, *J* = 7.5 Hz, 1H), 7.08 – 7.01 (m, 3H), 3.84 (t, *J* = 7.3 Hz, 2H), 2.86 (t, *J* = 7.3 Hz, 2H), 2.37 (s, 3H), 0.39 (s, 6H); ¹³C NMR (101 MHz, Chloroform-*d*) δ 138.9, 138.0, 137.9, 133.6, 130.0, 129.7, 128.3, 128.0, 127.0, 126.2,

64.5, 39.4, 21.5, -1.7; HRMS-EI⁺ (m/z) [M]⁺calcd for $C_{17}H_{22}O_2Si$ 270.1440, found 270.1440.

Dimethyl(2-methylphenethoxy)(phenyl)silane (40)



Colorless liquid; 98% yield; ¹H NMR (400 MHz, Chloroform-*d*) δ 7.59 (dq, J = 6.2, 2.2 Hz, 2H), 7.47 – 7.39 (m, 3H), 7.17 – 7.12 (m, 4H) , 3.81 (t, J = 7.6 Hz, 2H), 2.92 (t, J = 7.6 Hz, 2H), 2.30 (s, 3H), 0.41 (s, 6H); ¹³C NMR (101 MHz, Chloroform-*d*) δ 137.8, 137.0, 136.5, 133.6, 130.3, 130.0, 129.7, 128.0, 126.5, 126.0, 63. 3, 36.6, 19.4, -1.9; HRMS-EI⁺ (m/z) [M]⁺calcd for C₁₇H₂₂O₂Si 270.1440, found 270.1441.

Dimethyl(phenyl)(3-phenylpropoxy)silane (41)



Colorless liquid; 88% yield; ¹H NMR (400 MHz, Chloroform-d) δ 7.64 – 7.61 (m, 2H), 7.46 – 7.39 (m, 3H), 7.31 – 7.27 (m, 2H), 7.22 – 7.17 (m, 3H), 3.67 (t, J = 6.4 Hz, 2H), 2.69 (t, J = 8.0 Hz, 2H), 1.92 – 1.85 (m, 2H), 0.42 (s, 6H); ¹³C NMR (101 MHz, Chloroform-d) δ 142.2, 138.1, 133.6, 129.7, 128.6, 128.4, 128.0, 125.8, 62.5, 34.3, 32.2, -1.6; HRMS-ESI (m/z) [M + H]⁺calcd for C₁₇H₂₂OSi 271.1513, found 271.1505.

(Benzyloxy)dimethyl(phenyl)silane (42)



Colorless liquid; 82% yield; ¹H NMR (400 MHz, Chloroform-d) δ 7.58 – 7.55 (m, 2H), 7.42 – 7.31 (m, 4H), 7.30 – 7.27 (m, 2H), 7.25 – 7.17 (m, 2H), 4.65 (s, 2H), 0.37 (s, 6H);

¹³C NMR (101 MHz, Chloroform-d) δ 140.8, 137.7, 133.7, 129.8, 128.4, 128.0, 127.2, 126.7, 65.1, -1.6; HRMS-EI⁺ (m/z) [M]⁺calcd for C₁₅H₁₈OSi 242.1127, found 242.1129.

Butoxydimethyl(phenyl)silane (43)



Colorless liquid; 83% yield; ¹H NMR (400 MHz, Chloroform-d) δ 7.63 – 7.57 (m, 2H), 7.44 – 7.37 (m, 3H), 3.62 (t, J = 6.6 Hz, 2H), 1.60 – 1.48 (m, 2H), 1.42 – 1.30 (m, 2H), 0.91 (t, J = 7.4 Hz, 3H), 0.40 (s, 6H);¹³C NMR (101 MHz, Chloroform-d) δ 138.3, 133.6, 129.6, 127.9, 63.0, 34.9, 19.1, 14.0, -1.6; HRMS-EI⁺ (m/z) [M]⁺calcd for C₁₂H₂₀OSi 208.1283, found 208.1287.

Dimethyl(octyloxy)(phenyl)silane (44)



Colorless liquid; 88% yield; ¹H NMR (400 MHz, Chloroform-d) δ 7.70 – 7.51 (m, 2H), 7.49 – 7.30 (m, 3H), 3.60 (t, J = 6.7 Hz, 2H), 1.53 (q, J = 7.0 Hz, 2H), 1.35 – 1.17 (m, 10H), 0.89 (t, J = 6.9 Hz, 3H), 0.39 (s, 6H); ¹³C NMR (101 MHz, Chloroform-d) δ 138.3, 133.6, 129.6, 127.9, 63.4, 32.8, 32.0, 29.5, 29.4, 25.9, 22.8, 14.3, -1.6; HRMS-EI⁺ (m/z) [M]⁺calcd for C₁₅H₂₆OSi 250.1753, found 250.1752.

(Decyloxy)dimethyl(phenyl)silane (45)



Colorless liquid; 92% yield; ¹H NMR (400 MHz, Chloroform-d) δ 7.62 – 7.57 (m, 2H), 7.44 – 7.36 (m, 3H), 3.60 (t, J = 6.7 Hz, 2H), 1.54 (p, J = 6.8 Hz, 2H), 1.34 – 1.27 (m,

14H), 0.90 (t, J = 6.9 Hz, 3H), 0.40 (s, 6H); ¹³C NMR (101 MHz, Chloroform-d) δ 138.3, 133.6, 129.6, 127.9, 63.4, 32.8, 32.1, 29.8, 29.7, 29.6, 29.5, 25.9, 22.8, 14.3, -1.6; HRMS-EI⁺ (m/z) [M]⁺calcd for C₁₈H₃₂OSi 292.2222, found 292.2215

Isopropoxydimethyl(phenyl)silane (46)



Colorless liquid; 78% yield; ¹H NMR (400 MHz, Chloroform-d) δ 7.64 – 7.58 (m, 2H), 7.43 – 7.34 (m, 3H), 4.00 (hept, J = 6.1 Hz, 1H), 1.16 (s, 3H), 1.14 (s, 3H), 0.40 (s, 6H); ¹³C NMR (101 MHz, Chloroform-d) δ 138.7, 133.6, 129.6, 127.9, 65.4, 25.8, -1.0; HRMS-EI⁺ (m/z) [M]⁺calcd for C₁₁H₁₈OSi 194.1127, found 194.1125.

Cyclobutoxydimethyl(phenyl)silane (47)



Colorless liquid; 79% yield; ¹H NMR (400 MHz, Chloroform-d) δ 7.60 – 7.55 (m, 2H), 7.43 – 7.35 (m, 3H), 4.18 (ttd, J = 8.0, 6.9, 1.0 Hz, 1H), 2.13 (dddd, J = 10.7, 6.9, 4.8, 2.7 Hz, 2H), 2.01 – 1.90 (m, 2H), 1.63 – 1.54 (m, 1H), 1.40 – 1.26 (m, 1H), 0.37 (s, 6H); ¹³C NMR (101 MHz, Chloroform-d) δ 138.29, 133.60, 129.68, 127.93, 67.35, 33.94, 12.42, -1.14; HRMS-EI⁺ (m/z) [M]⁺calcd for C₁₂H₁₈OSi 206.1127, found 206.1131.

(Cyclopentyloxy)dimethyl(phenyl)silane (48)

`o^{_`Si}↓

Colorless liquid; 83% yield; ¹H NMR (400 MHz, Chloroform-d) δ 7.61 – 7.58 (m, 2H), 7.41 – 7.36 (m, 3H), 4.27 – 4.22 (m, 1H), 1.79 – 1.65 (m, 2H), 1.61 – 1.44 (m, 4H), 0.39 (s, 6H); ¹³C NMR (101 MHz, Chloroform-d) δ 138.9, 133.6, 129.5, 127.9, 74.9, 35.7, 23.3, -0.9; HRMS-EI⁺ (m/z) [M]⁺calcd for C₁₃H₂₀OSi 220.1283, found 220.1280.

(Cyclohexyloxy)dimethyl(phenyl)silane (49)



Colorless liquid; 87% yield; ¹H NMR (400 MHz, Chloroform-d) δ 7.61 – 7.57 (m, 2H), 7.42 – 7.35 (m, 3H), 3.60 (ddd, J = 13.7, 9.6, 4.0 Hz, 1H), 1.78 – 1.68 (m, 4H), 1.51 – 1.10 (m, 6H), 0.38 (s, 6H); ¹³C NMR (101 MHz, Chloroform-d) δ 139.0, 133.6, 129.5, 127.9, 71.5, 36.0, 25.7, 24.5, -0.8; HRMS-EI⁺ (m/z) [M]⁺calcd for C₁₄H₂₂OSi 234.1440, found 234.1439.

(Cycloheptyloxy)dimethyl(phenyl)silane (50)



Colorless liquid; 79% yield; ¹H NMR (400 MHz, Chloroform-d) δ 7.63 – 7.60 (m, 2H), 7.41 – 7.36 (m, 3H), 3.84 (tt, J = 8.2, 4.3 Hz, 1H), 1.84 – 1.77 (m, 2H), 1.67 – 1.51 (m, 8H), 1.32 (tt, J = 10.6, 5.1 Hz, 2H), 0.39 (s, 6H); ¹³C NMR (101 MHz, Chloroform-d) δ 138.9, 133.6, 129.5, 127.9, 73.8, 37.9, 28.2, 22.8, -0.9; HRMS-EI⁺ (m/z) [M]⁺calcd for C₁₅H₂₄OSi 248.1596, found 248.1592.

Dimethyl(phenyl)((tetrahydro-2H-pyran-4-yl)oxy)silane (51)



Colorless liquid; 81% yield; ¹H NMR (400 MHz, Chloroform-d) δ 7.61 – 7.56 (m, 2H), 7.43 – 7.36 (m, 3H), 3.87 (ddt, J = 25.5, 13.0, 4.4 Hz, 3H), 3.38 (ddd, J = 11.9, 9.6, 2.8 Hz, 2H), 1.77 – 1.71 (m, 2H), 1.64 – 1.55 (m, 2H), 0.39 (s, 6H); ¹³C NMR (101 MHz, Chloroform-d) δ 138.4, 133.6, 129.8, 128.0, 67.8, 65.7, 35.9, -0.9; HRMS-EI⁺ (m/z) [M]⁺calcd for C₁₃H₂₀O₂Si 236.1233, found 236.1235.

Dimethyl(phenyl)((1-phenylpropan-2-yl)oxy)silane (52)



Colorless liquid; 92% yield; ¹H NMR (400 MHz, Chloroform-d) δ 7.55 – 7.53 (m, 2H), 7.46 – 7.37 (m, 3H), 7.32 (ddd, J = 7.4, 6.2, 1.3 Hz, 2H), 7.28 – 7.23 (m, 1H), 7.19 – 7.17 (m, 2H), 4.03 (dt, J = 7.0, 6.0 Hz, 1H), 2.84 – 2.69 (m, 2H), 1.20 (d, J = 6.1 Hz, 3H), 0.29 (d, J = 7.4 Hz, 6H); ¹³C NMR (101 MHz, Chloroform-d) δ 139.4, 138.3, 133.7, 129.8, 129.6, 128.2, 127.9, 126.2, 70.5, 46. 4, 23.6, -1.2, -1.5; HRMS-ESI (m/z) [M + H]⁺calcd for C₁₇H₂₂OSi 271.1513, found 271.1511.

Dimethyl(phenyl)(1-(p-tolyl)ethoxy)silane (53)



Colorless liquid; 88% yield; ¹H NMR (400 MHz, Chloroform-d) δ 7.65 – 7.61 (m, 2H), 7.48 – 7.40 (m, 3H), 7.27 (d, J = 8.1 Hz, 2H), 7.17 (d, J = 7.9 Hz, 2H), 4.89 (q, J = 6.4 Hz, 1H), 2.39 (s, 3H), 1.48 (d, J = 6.4 Hz, 3H), 0.38 (d, J = 19.3 Hz, 6H); ¹³C NMR (101 MHz, Chloroform-d) δ 143.4, 138.4, 136.5, 133.7, 129.6, 129.0, 127.9, 125.5, 71.1, 27.0, 21.2, -1.2; HRMS-EI⁺ (m/z) [M]⁺calcd for C₁₇H₂₂OSi 270.1440, found 270.1442.

((2,3-dihydro-1H-inden-1-yl)oxy)dimethyl(phenyl)silane (54)



Colorless liquid; 93% yield; ¹H NMR (400 MHz, Chloroform-d) δ 7.68 – 7.63 (m, 2H), 7.42 – 7.36 (m, 3H), 7.24 (dt, J = 6.3, 2.9 Hz, 1H), 7.19 – 7.15 (m, 3H), 5.24 (t, J = 6.6 Hz, 1H), 2.97 (ddd, J = 15.8, 8.7, 3.6 Hz, 1H), 2.70 (dt, J = 15.9, 8.0 Hz, 1H), 2.30 (dddd, J = 12.7, 8.0, 6.9, 3.6 Hz, 1H), 1.98 – 1.89 (m, 1H), 0.47 (d, J = 3.2 Hz, 6H); ¹³C NMR (101 MHz, Chloroform-d) δ 145.2, 142.8, 138.3, 133.7, 129.8, 128.0, 127.9, 126.6, 124.8, 124.4, 76.8, 36.3, 29.9, -0.8, -0.9; HRMS-EI⁺ (m/z) [M]⁺calcd for C₁₇H₂₀OSi 268.1283, found 268.1289.

(Benzhydryloxy)dimethyl(phenyl)silane (55)



Colorless liquid; 89% yield; ¹H NMR (400 MHz, Chloroform-d) δ 7.63 – 7.60 (m, 2H), 7.49 – 7.33 (m, 11H), 7.30 – 7.26 (m, 2H), 5.83 (s, 1H), 0.37 (s, 6H); ¹³C NMR (101 MHz, Chloroform-d) δ 144.8, 137.9, 133.7, 129.7, 128.3, 127.9, 127.2, 126.7, 77.0, -0.9; HRMS-EI⁺ (m/z) [M]⁺calcd for C₂₁H₂₂OSi 318.1440, found 318.1445.

2,9-dimethyl-2,9-diphenyl-3,8-dioxa-2,9-disiladecane (56)



Colorless liquid; 72% yield; ¹H NMR (400 MHz, Chloroform-*d*) δ 7.61 – 7.58 (m, 4H), 7.45 – 7.37 (m, 6H), 3.63 – 3.59 (m, 4H), 1.63 – 1.56 (m, 4H), 0.39 (s, 12H); ¹³C NMR

(101 MHz, Chloroform-*d*) δ 138.1, 133.6, 129.7, 127.9, 63.0, 29.1, -1.7; HRMS-EI⁺ (m/z) [M]⁺calcd for C₂₀H₃₀O₂Si₂ 358.1777, found 358.1784.

1,4-bis(((dimethyl(phenyl)silyl)oxy)methyl)benzene (57)



Colorless liquid; 85% yield;¹H NMR (400 MHz, Chloroform-d) δ 7.62 – 7.58 (m, 4H), 7.44 – 7.37 (m, 6H), 7.26 (s, 4H), 4.68 (s, 4H), 0.41 (s, 12H); ¹³C NMR (101 MHz, Chloroform-d) δ 139.8, 137.8, 133.7, 129.8, 128.0, 126.7, 65.0, -1.5; HRMS-EI⁺ (m/z) [M]⁺calcd for C₂₄H₃₀O₂Si₂ 406.1780, found 406.1784.

(8R,9S,10R,13S,14S,17S)-10,13-dimethyl-17-((triethylsilyl)oxy)-1,2,6,7,8,9,10,11,12 ,13,14,15,16,17-tetradecahydro-3H-cyclopenta[a]phenanthren-3-one (58)



White solid; m.p. 117 - 118 °C; 78% yield; ¹H NMR (400 MHz, Chloroform-*d*) δ 5.71 (s, 1H), 3.54 (t, *J* = 8.3 Hz, 1H), 2.45 - 2.22 (m, 4H), 2.01 (ddd, *J* = 13.4, 4.9, 3.3 Hz, 1H), 1.94 - 1.76 (m, 3H), 1.66 (td, *J* = 13.9, 4.9 Hz, 1H), 1.60 - 1.35 (m, 5H), 1.27 (tt, *J* = 11.8, 6.0 Hz, 1H), 1.17 (s, 3H), 1.03 - 0.85 (m, 13H), 0.74 (s, 3H), 0.53 (q, *J* = 7.6 Hz, 6H); ¹³C NMR (101 MHz, Chloroform-*d*) δ 199.7, 171.6, 123.9, 81.5, 54.2, 50.3, 43.3, 38.8, 36.9, 35.8, 35.8, 34.1, 33.0, 31.7, 31.1, 23.6, 20.8, 17.5, 11.4, 7.0, 5.0; HRMS-ESI (m/z) [M + H]⁺calcd for C₂₄H₃₉O₂Si 403.3027, found 403.3026.

Dimethyl(4-methylphenethoxy)(phenyl)silane (3)



Colorless liquid; 99% yield; ¹H NMR (400 MHz, Chloroform-*d*) δ 7.56 (dq, *J* = 6.4, 2.1 Hz, 2H), 7.44 – 7.36 (m, 3H), 7.12 – 7.07 (m, 4H), 3.80 (t, *J* = 7.4 Hz, 2H), 2.83 (t, *J* = 7.4 Hz, 2H), 2.34 (s, 3H), 0.37 (s, 6H); ¹³C NMR (101 MHz, Chloroform-*d*) δ 138.0, 135.8, 135.8, 133.6, 129.7, 129.1, 128.0, 64.6, 39.1, 21.2, -1.7; HRMS-EI⁺ (m/z) [M]⁺calcd for C₁₇H₂₂OSi 270.1440, found 270.1440.

(4-methoxyphenyl)dimethyl(4-methylphenethoxy)silane (60)



Colorless liquid; 93% yield; ¹H NMR (400 MHz, Chloroform-d) δ 7.49 – 7.46 (m, 2H), 7.11 – 7.05 (m, 4H), 6.92 (d, J = 8.6 Hz, 2H), 3.83 (s, 3H), 3.76 (t, J = 7.4 Hz, 2H), 2.80 (t, J = 7.4 Hz, 2H), 2.33 (s, 3H), 0.33 (s, 6H); ¹³C NMR (101 MHz, Chloroform-d) δ 160.9, 135.9, 135.7, 135.2, 129.1, 129.0, 113.7, 64.5, 55.2, 39.1, 21.2, -1.6; HRMS-ESI (m/z) [M + H]⁺calcd for C₁₈H₂₄O₂Si 301.1618 found 301.1615.

Dimethyl(4-methylphenethoxy)(p-tolyl)silane (61)



Colorless liquid; 95% yield; ¹H NMR (400 MHz, Chloroform-d) δ 7.47 (d, J = 7.9 Hz, 2H), 7.24 – 7.22 (m, 2H), 7.09 (dd, J = 7.3, 4.9 Hz, 4H), 3.80 (t, J = 7.4 Hz, 2H), 2.84 (t, J = 7.4 Hz, 2H), 2.40 (s, 3H), 2.35 (s, 3H), 0.37 (s, 6H); ¹³C NMR (101 MHz, 2H), 2.40 (s, 3H), 2.35 (s, 3H), 0.37 (s, 6H); ¹³C NMR (101 MHz, 2H), 2.40 (s, 3H), 2.35 (s, 3H), 0.37 (s, 6H); ¹³C NMR (101 MHz, 2H), 2.40 (s, 3H), 2.35 (s, 3H), 0.37 (s, 6H); ¹³C NMR (101 MHz, 2H), 2.40 (s, 3H), 2.35 (s, 3H), 0.37 (s, 6H); ¹³C NMR (101 MHz, 2H), 2.40 (s, 3H), 2.35 (s, 3H), 0.37 (s, 6H); ¹³C NMR (101 MHz, 2H), 2.40 (s, 3H), 2.35 (s, 3H), 0.37 (s, 6H); ¹³C NMR (101 MHz, 2H), 2.40 (s, 3H), 2.35 (s, 3H), 0.37 (s, 6H); ¹³C NMR (101 MHz, 2H), 2.40 (s, 3H), 2.35 (s, 3H), 0.37 (s, 6H); ¹³C NMR (101 MHz, 2H), 2.40 (s, 3H), 2.35 (s, 3H), 0.37 (s, 6H); ¹³C NMR (101 MHz, 2H), 2.40 (s, 3H), 2.35 (s, 3H), 0.37 (s, 6H); ¹³C NMR (101 MHz, 2H), 2.40 (s, 3H), 2.35 (s, 3H), 2.35 (s, 2H), 2.40 (s, 2H), 2.40

Chloroform-d) δ 139.6, 135.9, 135.7, 134.3, 133.7, 129.1, 129.1, 128.8, 64.6, 39.1, 21.7, 21.2, -1.7; HRMS-ESI (m/z) [M + H]⁺calcd for C₁₈H₂₄OSi 285.1669 found 285.1668.

Dimethyl(4-methylphenethoxy)(o-tolyl)silane (62)



Colorless liquid; 91% yield; ¹H NMR (400 MHz, Chloroform-*d*) δ 7.54 (dd, *J* = 7.7, 1.2 Hz, 1H), 7.37 – 7.32 (m, 1H), 7.22 (t, *J* = 6.9 Hz, 2H), 7.14 – 7.10 (m, 4H), 3.81 (t, *J* = 7.4 Hz, 2H), 2.88 (t, *J* = 7.4 Hz, 2H), 2.51 (s, 3H), 2.36 (s, 3H), 0.43 (s, 6H); ¹³C NMR (101 MHz, Chloroform-*d*) δ 143.8, 136.3, 135.8, 135.8, 134.7, 130.0, 129.9, 129.1, 129.1, 125.0, 64.5, 39.0, 22.6, 21.2, -0.7; HRMS-ESI (m/z) [M + H]⁺calcd for C₁₈H₂₄OSi 285.1669 found 285.1672.

Dimethyl(4-methylphenethoxy)(m-tolyl)silane (63)



Colorless liquid; 94% yield; ¹H NMR (400 MHz, Chloroform-d) δ 7.36 – 7.35 (m, 2H), 7.28 (t, J = 7.5 Hz, 1H), 7.23 (d, J = 7.4 Hz, 1H), 7.12 – 7.07 (m, 4H), 3.79 (t, J = 7.4 Hz, 2H), 2.83 (t, J = 7.4 Hz, 2H), 2.38 (s, 3H), 2.34 (s, 3H), 0.35 (s, 6H);¹³C NMR (101 MHz, Chloroform-d) δ 137.8, 137.3, 135.9, 135.8, 134.3, 130.7, 130.5, 129.1, 129.1, 127.9, 64.6, 39.1, 21.7, 21.2, -1.7; HRMS-ESI (m/z) [M + H]⁺calcd for C₁₈H₂₄OSi 285.1669 found 285.1667.

(4-ethylphenyl)dimethyl(4-methylphenethoxy)silane (64)



Colorless liquid; 98% yield; ¹H NMR (400 MHz, Chloroform-*d*) δ 7.51 (d, *J* = 7.7 Hz, 2H), 7.26 (d, *J* = 7.6 Hz, 2H), 7.14 – 7.09 4H), 3.81 (t, *J* = 7.4 Hz, 2H), 2.85 (t, *J* = 7.4 Hz, 2H), 2.70 (q, *J* = 7.6 Hz, 2H), 2.36 (s, 3H), 1.30 (t, *J* = 7.6 Hz, 3H), 0.38 (s, 6H); ¹³C NMR (101 MHz, Chloroform-*d*) δ 145.9, 135.8, 135.7, 134.6, 133.7, 129.1, 129.1, 127.6, 64.6, 39.1, 29.0, 21.2, 15.6, -1.7; HRMS-ESI (m/z) [M + H]⁺calcd for C₁₉H₂₆OSi 299.1826 found 299.1822.

(3,5-dimethylphenyl)dimethyl(4-methylphenethoxy)silane (65)



Colorless liquid; 98% yield; ¹H NMR (400 MHz, Chloroform-d) δ 7.18 – 7.17 (m, 2H), 7.14 – 7.07 (m, 5H), 3.81 (t, J = 7.3 Hz, 2H), 2.85 (t, J = 7.3 Hz, 2H), 2.36 (s, 9H), 0.37 (s, 6H); ¹³C NMR (101 MHz, Chloroform-d) δ 137.7, 137.2, 135.9, 135.7, 131.5, 131.3, 129.1, 129.1, 64.6, 39.1, 21.5, 21.2, -1.6; HRMS-ESI (m/z) [M + H]⁺calcd for C₁₉H₂₆OSi 299.1826 found 299.1824.

(4-(tert-butyl)phenyl)dimethyl(4-methylphenethoxy)silane (66)



Colorless liquid; 97% yield; ¹H NMR (400 MHz, Chloroform-*d*) δ 7.53 (d, *J* = 8.3 Hz, 2H), 7.45 (d, *J* = 8.2 Hz, 2H), 7.14 – 7.09 (m, 4H), 3.81 (t, *J* = 7.4 Hz, 2H), 2.85 (t, *J* = 7.4 Hz, 2H), 2.36 (s, 3H), 1.38 (s, 9H), 0.38 (s, 6H); ¹³C NMR (101 MHz, Chloroform-*d*) δ

152.7, 135.9, 135.7, 134.4, 133.5, 129.1, 129.1, 124.9, 64.6, 39.1, 34.8, 31.4, 21.2, -1.7; HRMS-ESI (m/z) $[M + H]^+$ calcd for C₂₁H₃₀OSi 327.2139 found 327.2143.

(4-chlorophenyl)dimethyl(4-methylphenethoxy)silane (67)



Colorless liquid; 92% yield; ¹H NMR (400 MHz, Chloroform-*d*) δ 7.45 (d, *J* = 8.3 Hz, 2H), 7.35 (d, *J* = 8.3 Hz, 2H), 7.09 (q, *J* = 8.1 Hz, 4H), 3.78 (t, *J* = 7.2 Hz, 2H), 2.82 (t, *J* = 7.2 Hz, 2H), 2.35 (s, 3H), 0.35 (s, 6H); ¹³C NMR (101 MHz, Chloroform-*d*) δ 136.2, 136.0, 135.8, 135.7, 135.0, 129.1, 129.1, 128.2, 64.6, 39.0, 21.2, -1.7; HRMS-ESI (m/z) [M + Na]⁺calcd for C₁₇H₂₁ClOSi 327.0942 found 327.0947.

(4-bromophenyl)dimethyl(4-methylphenethoxy)silane (68)



Colorless liquid; 87% yield; ¹H NMR (400 MHz, Chloroform-d) δ 7.51 (dd, J = 8.2, 1.7 Hz, 2H), 7.38 (dd, J = 8.2, 1.8 Hz, 2H), 7.10 (q, J = 8.0 Hz, 4H), 3.79 (t, J = 7.2 Hz, 2H), 2.83 (t, J = 7.2 Hz, 2H), 2.36 (s, 3H), 0.35 (s, 6H); ¹³C NMR (101 MHz, Chloroform-d) δ 136.7, 135.8, 135.7, 135.2, 131.1, 129.1, 129.1, 124.5, 64.6, 39.0, 21.2, -1.8; HRMS-EI⁺ (m/z) [M]⁺calcd for C₁₇H₂₁BrOSi 348.0550, found 348.0545.

4-(dimethyl(4-methylphenethoxy)silyl)benzonitrile (69)



Colorless liquid; 88% yield; ¹H NMR (400 MHz, Chloroform-*d*) δ 7.62 – 7.55 (m, 4H), 7.07 (q, *J* = 8.0 Hz, 4H), 3.78 (t, *J* = 7.1 Hz, 2H), 2.80 (t, *J* = 7.1 Hz, 2H), 2.33 (s, 3H),

0.34 (s, 6H); ¹³C NMR (101 MHz, Chloroform-*d*) δ 144.6, 135.9, 135.6, 134.0, 131.2, 129.1, 129.1, 119.1, 113.1, 64.7, 38.9, 21.2, -1.9; HRMS-ESI (m/z) [M + Na]⁺calcd for C₁₈H₂₁NOSi 318.1285 found 318.1285.

Dimethyl(4-methylphenethoxy)(naphthalen-1-yl)silane (70)



Colorless liquid; 93% yield; ¹H NMR (400 MHz, Chloroform-d) δ 8.32 – 8.28 (m, 1H), 7.91 – 7.86 (m, 2H), 7.72 (dd, J = 6.8, 1.3 Hz, 1H), 7.53 – 7.45 (m, 3H), 7.08 – 7.03 (m, 4H), 3.81 (t, J = 7.3 Hz, 2H), 2.85 (t, J = 7.3 Hz, 2H), 2.32 (s, 3H), 0.52 (s, 6H); ¹³C NMR (101 MHz, Chloroform-d) δ 137.0, 135.9, 135.8, 135.7, 133.9, 133.4, 130.6, 129.1, 129.0, 128.4, 126.1, 125.6, 125.1, 64.6, 39.0, 21.2, 0.5; HRMS-ESI (m/z) [M + H]⁺calcd for C₂₁H₂₄OSi 321.1669 found 321.1663.

Methyl(4-methylphenethoxy)diphenylsilane (71)



Colorless liquid; 89% yield; ¹H NMR (400 MHz, Chloroform-d) δ 7.62 – 7.58 (m, 4H), 7.48 – 7.39 (m, 6H), 7.12 (dd, J = 7.4, 5.0 Hz, 4H), 3.93 (t, J = 7.3 Hz, 2H), 2.90 (t, J = 7.3 Hz, 2H), 2.37 (s, 3H), 0.64 (s, 3H); ¹³C NMR (101 MHz, Chloroform-d) δ 136.2, 135.8, 135.8, 134.5, 129.9, 129.2, 129.1, 128.0, 65.0, 39.0, 21.2, -3.0; HRMS-ESI (m/z) [M + Na]⁺calcd for C₂₂H₂₄OSi 355.1489 found 355.1492.

(4-methylphenethoxy)triphenylsilane (72)


Colorless liquid; 81% yield; ¹H NMR (400 MHz, Chloroform-*d*) δ 7.83 – 7.66 (m, 6H), 7.60 – 7.42 (m, 9H), 7.23 – 7.10 (m, 4H), 4.11 (t, *J* = 7.2 Hz, 2H), 2.99 (t, *J* = 7.2 Hz, 2H), 2.43 (s, 3H); ¹³C NMR (101 MHz, Chloroform-*d*) δ 135.8, 135.7, 135.5, 134.4, 130.1, 129.2, 129.1, 128.0, 65.4, 39.0, 21.2; HRMS-ESI (m/z) [M + K]⁺calcd for C₂₇H₂₆OSi 433.1385 found 433.1383.

Triethyl(4-methylphenethoxy)silane (73)



Colorless liquid; 98% yield; ¹H NMR (400 MHz, Chloroform-*d*) δ 7.11 (s, 4H), 3.79 (t, *J* = 7.6 Hz, 2H), 2.83 (t, *J* = 7.6 Hz, 2H), 2.33 (s, 3H), 0.96 (t, *J* = 7.9 Hz, 9H), 0.60 (q, *J* = 7.9 Hz, 6H); ¹³C NMR (101 MHz, Chloroform-*d*) δ 135.9, 135.8, 129.1, 129.1, 64.6, 39.4, 21.2, 6.9, 4.5; HRMS-ESI (m/z) [M + Na]⁺calcd for C₁₅H₂₆OSi 273.1645 found 273.1644.

Tributyl(4-methylphenethoxy)silane (74)



Colorless liquid; 95% yield; ¹H NMR (400 MHz, Chloroform-d) δ 7.02 (s, 4H), 3.68 (t, J = 7.4 Hz, 2H), 2.72 (t, J = 7.4 Hz, 2H), 2.24 (s, 3H), 1.28 – 1.15 (m, 12H), 0.80 (t, J = 6.9 Hz, 9H), 0.50 – 0.46 (m, 6H); ¹³C NMR (101 MHz, Chloroform-d) δ 136.06, 135.73, 129.12, 129.09, 64.55, 39.39, 26.77, 25.53, 21.16, 13.92, 13.45; HRMS-EI⁺ (m/z) [M]⁺calcd for C₂₁H₃₈OSi 334.2680, found 334.2692.

Benzyldimethyl(4-methylphenethoxy)silane (75)



Colorless liquid; 98% yield; ¹H NMR (400 MHz, Chloroform-d) δ 7.24 – 7.20 (m, 2H), 7.14 – 7.07 (m, 5H), 7.05 – 7.03 (m, 2H), 3.74 (t, J = 7.3 Hz, 2H), 2.78 (t, J = 7.3 Hz, 2H), 2.33 (s, 3H), 2.15 (s, 2H), 0.05 (s, 6H);¹³C NMR (101 MHz, Chloroform-d) δ 139.2, 135.9, 135.8, 129.1, 129.1, 128.5, 128.4, 124.3, 64.5, 39.1, 26.8, 21.2, -2.4; HRMS-ESI (m/z) [M + Na]⁺calcd for C₁₈H₂₄OSi 307.1489 found 307.1485.

Dimethyl(phenyl)silanol (76)



Colorless liquid; 92% yield; ¹H NMR (400 MHz, Chloroform-d) δ 7.61 – 7.59 (m, 2H), 7.42 – 7.37 (m, 3H), 2.33 (brs, 1H), 0.41 (s, 6H); ¹³C NMR (101 MHz, Chloroform-d) δ 139.2, 133.2, 129.8, 128.0, 0.1; HRMS-EI⁺ (m/z) [M]⁺calcd for C₈H₁₂OSi 152.0658, found 152.0657.

Dimethyl(p-tolyl)silanol (77)



Colorless liquid; 84% yield; ¹H NMR (400 MHz, Chloroform-d) δ 7.51 (d, J = 8.0 Hz, 2H), 7.22 (d, J = 7.5 Hz, 2H), 2.47 (brs, 1H), 2.39 (s, 3H), 0.40 (s, 6H); ¹³C NMR (101 MHz, Chloroform-d) δ 139.4, 135.4, 133.0, 128.6, 21.4, 0.1; HRMS-EI⁺ (m/z) [M]⁺calcd for C₉H₁₄OSi 166.0813, found 166.0814.

(4-ethylphenyl)dimethylsilanol (78)



Colorless liquid; 89% yield; ¹H NMR (400 MHz, Chloroform-d) δ 7.51 (d, J = 8.0 Hz, 2H), 7.22 (d, J = 8.2 Hz, 2H), 2.65 (q, J = 7.6 Hz, 2H), 2.23 (brs, 1H), 1.24 (t, J = 7.6 Hz, 3H), 0.38 (s, 6H); ¹³C NMR (101 MHz, Chloroform-d) δ 146.0, 136.0, 133.3, 127.7, 29.0, 15.6, 0.1; HRMS-EI⁺ (m/z) [M]⁺calcd for C₁₀H₁₆OSi 180.0971, found 180.0970.

Dimethyl(o-tolyl)silanol (79)



Colorless liquid; 87% yield; ¹H NMR (400 MHz, Chloroform-*d*) δ 7.57 – 7.55 (m, 1H), 7.32 (td, *J* = 7.5, 1.6 Hz, 1H), 7.20 (t, *J* = 7.9 Hz, 2H), 2.52 (s, 3H), 2.16 (brs, 1H), 0.45 (s, 6H); ¹³C NMR (101 MHz, Chloroform-*d*) δ 143.4, 137.5, 134.2, 130.0, 123.0, 125.1, 22.9, 1.2; HRMS- ESI (m/z) [M - H]⁻calcd for C₉H₁₄OSi 165.0741, found 165.0736.

Dimethyl(m-tolyl)silanol (80)



Colorless liquid; 76% yield; ¹H NMR (400 MHz, Chloroform-d) δ 7.42 – 7.10 (m, 2H), 7.30 (t, J = 7.3 Hz, 1H), 7.25 – 7.23 (m, 1H), 2.38 (s, 3H), 2.33 (brs, 1H), 0.40 (s, 6H); ¹³C NMR (101 MHz, Chloroform-d) δ 139.1, 137.4, 133.8, 130.5, 130.2, 128.0, 21.6, 0.1; HRMS- ESI (m/z) [M - H]⁻calcd for C₉H₁₄OSi 165.0741, found 165.0737.

(3,5-dimethylphenyl)dimethylsilanol (81)



Colorless liquid; 87% yield; ¹H NMR (400 MHz, Chloroform-d) δ 7.22 (s, 1H), 7.06 (s, 1H), 2.35 (s, 1H), 2.09 (s, 1H), 0.40 (s, 6H); ¹³C NMR (101 MHz, Chloroform-d) δ 139.0, 137.4, 131.5, 130.9, 21.5, 0.2; HRMS-EI⁺ (m/z) [M]⁺calcd for C₁₀H₁₆OSi 180.0975, found 180.0970.

(4-methoxyphenyl)dimethylsilanol (82)



Colorless liquid; 89% yield; ¹H NMR (400 MHz, Chloroform-*d*) δ 7.51 – 7.49 (m, 2H), 6.92 – 6.89 (m, 2H), 3.80 (s, 3H), 2.73 (brs, 1H), 0.35 (s, 6H); ¹³C NMR (101 MHz, Chloroform-*d*) δ 160.8, 134.7, 130.3, 113.6, 55.1, 0.1. HRMS-EI⁺ (m/z) [M]⁺calcd for C₉H₁₄O₂Si 182.0761, found 182.0763.

(4-chlorophenyl)dimethylsilanol (83)

Colorless liquid; 83% yield; ¹H NMR (400 MHz, Chloroform-*d*) δ 7.51 – 7.48 (m, 2H), 7.36 – 7.33 (m, 2H), 2.52 (s, 1H), 0.37 (s, 6H); ¹³C NMR (101 MHz, Chloroform-*d*) δ 137.4, 136.0, 134.6, 128.2, 0.1; HRMS- ESI (m/z) [M - H]⁻calcd for C₈H₁₁ClOSi 185.0195, found 185.0195.

(4-bromophenyl)dimethylsilanol(84)



Colorless liquid; 86% yield; ¹H NMR (400 MHz, Chloroform-*d*) δ 7.53 – 7.50 (m, 2H), 7.45 – 7.43 (m, 2H), 2.18 (s, 1H), 0.38 (s, 6H); ¹³C NMR (101 MHz, Chloroform-*d*) δ 137.9, 134.8, 131.2, 124.6, 0.1; HRMS-EI⁺ (m/z) [M]⁺calcd for C₈H₁₁BrOSi 229.9763, found 229.9763.

(4-(tert-butyl)phenyl)dimethylsilanol (85)



White solid; m.p. 89 – 90 °C; 81% yield; ¹H NMR (400 MHz, Chloroform-*d*) δ 7.58 – 7.56 (m, 2H), 7.45 – 7.43 (m, 2H), 2.22 (brs, 1H), 1.35 (s, 9H), 0.41 (s, 6H); ¹³C NMR

(101 MHz, Chloroform-*d*) δ 152.8, 135.8, 133.2, 125.0, 34.8, 31.4, 0.1; HRMS-ESI (m/z) [M + Na]⁺calcd for C₁₀H₂₀OSi 231.1176, found 231.1173.

4-(hydroxydimethylsilyl)benzonitrile (86)



Colorless liquid; 72% yield; ¹H NMR (400 MHz, Chloroform-*d*) δ 7.69 – 7.67 (m, 2H), 7.62 – 7.60 (m, 2H), 2.74 (brs, 1H), 0.40 (s, 6H); ¹³C NMR (101 MHz, Chloroform-*d*) δ 146.0, 133.7, 131.2, 119.0, 113.0, 0; HRMS- ESI (m/z) [M - H]⁻calcd for C₉H₁₁NOSi 176.0537, found 176.0536.

Dimethyl(naphthalen-1-yl)silanol (87)



White solid; m.p. 76 – 77 °C; 89% yield; ¹H NMR (400 MHz, Chloroform-d) δ 8.28 (dt, J = 7.4, 1.0 Hz, 1H), 7.92 – 7.87 (m, 2H), 7.75 (dd, J = 6.8, 1.3 Hz, 1H), 7.56 – 7.46 (m, 3H), 2.27 (brs, 1H), 0.59 (s, 6H); ¹³C NMR (101 MHz, Chloroform-d) δ 136.9, 136.6, 133.4, 133.3, 130.5, 129.1, 128.2, 126.1, 125.6, 125.1, 1.4; HRMS-EI⁺ (m/z) [M]⁺calcd for C₁₂H₁₄OSi 202.0815, found 202.0814.

Methyldiphenylsilanol (88)



Colorless liquid; 93% yield; ¹H NMR (400 MHz, Chloroform-d) δ 7.62 (dt, J = 6.6, 1.5 Hz, 4H), 7.47 – 7.38 (m, 6H), 2.82 (s, 1H), 0.67 (s, 3H); ¹³C NMR (101 MHz,

Chloroform-d) δ 137.1, 134.1, 123.0, 128.0, -1.2; HRMS- ESI (m/z) [M - H]⁻calcd for C₁₃H₁₄OSi 213.0741, found 213.0741.

Triphenylsilanol (89)



White solid; m.p. 150 – 151 °C; 87% yield; ¹H NMR (400 MHz, Chloroform-*d*) δ 7.65 (dt, J = 6.7, 1.5 Hz, 6H), 7.49 – 7.38 (m, 9H), 2.77 (brs, 1H); ¹³C NMR (101 MHz, Chloroform-*d*) δ 135.2, 135.1, 130.3, 128.1; HRMS- ESI (m/z) [M - H]⁻calcd for C1₈H₁₆OSi 275.0898, found 275.0899.

Benzyldimethylsilanol (90)

.si OH

Colorless liquid; 84% yield; ¹H NMR (400 MHz, Chloroform-*d*) δ 7.28 – 7.24 (m, 2H), 7.13 – 7.07 (m, 3H), 2.19 (s, 2H), 1.92 (s, 1H), 0.15 (s, 6H); ¹³C NMR (101 MHz, Chloroform-*d*) δ 139.1, 128.6, 128.3, 124.4, 28.2, 0.6; HRMS- ESI (m/z) [M - H]⁻calcd for C₉H₁₄OSi 165.0741, found 165.0742.

Trihexylsilanol (91)



Colorless liquid; 85% yield; ¹H NMR (400 MHz, Chloroform-*d*) δ 1.37 (brs, 1H),1.34 – 1.27 (m, 24H), 0.91 – 0.87(m, 9H), 0.61 – 0.57 (m, 6H); ¹³C NMR (101 MHz,

Chloroform-*d*) δ 33.4, 31.7, 23.2, 22.7, 15.2, 14.3; HRMS-EI⁺ (m/z) [M]⁺calcd for C₁₈H₄₀OSi 299.2776, found 299.2768.

1,4-phenylenebis(dimethylsilanol) (92)

Colorless liquid; 85% yield; ¹H NMR (400 MHz, Chloroform-d) δ 7.61 (s, 4H), 2.05 (s, 2H), 0.41 (s, 12H); ¹³C NMR (101 MHz, Chloroform-d) δ 140.8, 132.6, 0.1; HRMS-EI⁺ (m/z) [M]⁺calcd for C₁₀H₁₈O₂Si₂ 225.0773, found 225.0768.

9. NMR spectra of for the products





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210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 fl (ppm)













 $210\ 200\ 190\ 180\ 170\ 160\ 150\ 140\ 130\ 120\ 110\ 100\ 90\ 80\ 70\ 60\ 50\ 40\ 30\ 20\ 10\ 0\ -10\ fl\ (ppm)$











210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 fl (ppm)



0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -2⁻¹ fl (ppm)















210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 fl (ppm)





220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 fl (ppm)









210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 fl (ppm)




















210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 fl (ppm)







210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 fl (ppm)



10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 fl (ppm)







^{210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10} fl (ppm)





s81







s84





222333777777777228990 669402877586660 769402877586660

1,921,921,901,901,901,901,901,901,901,83 1,83

7.64 7.63 7.62 7.62





210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 fl (ppm)





s89















210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 fl (ppm) 40 30 20





210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 fl (ppm)





s100





7.30 7.3






























^{210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10} fl (ppm)



210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 fl (ppm)











210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 fl (ppm)









210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 fl (ppm)



s128

















210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 fl (ppm)











