Supporting Information

A Free-Radical-Promoted Site-Selective C-H Silylation of Arenes by Using Hydrosilanes

Zhengbao Xu, Li Chai, Zhong-Quan Liu*

State Key Laboratory of Applied Organic Chemistry, Lanzhou University, Lanzhou 730000, P. R	
China E-mail: <u>liuzhq@lzu.edu.cn</u>	
General Information	1
Representative procedure	1-2
Modification of the reaction conditions	.2-6
Transformation of the arylsiane products6	5-10
Confirmation of isomers structure10)-14
Physical data and references for the following products15	-35
Copies of the ¹ H NMR, ¹⁹ F NMR, ¹³ C NMR spectra30	6-98

General Information

¹H, ¹⁹F and ¹³C NMR spectra were recorded on a Bruker advance III 400 spectrometer in CDCl₃ with TMS as internal standard. Mass spectra were determined on a Hewlett Packard 5988A spectrometer by direct inlet at 70 eV. High-resolution mass spectral analysis (HRMS) data were measured on a Bruker Apex II. All products were identified by ¹H and ¹³C NMR, MS, and HRMS. The starting materials were purchased from Aldrich, Acros Organics, J&K Chemicals or TCI and used without further purification.

Representative procedure:

Procedure A (0.1 mmol scale): A mixture of *N*-phenylacetamide (1 equiv, 0.1 mmol), silanes (18 equiv, 1.8 mmol), $Cu_2O(5 \text{ mol}\%, 0.005 \text{ mmol})$, DTBP (12 equiv, 1.2 mmol) and *t*-BuOH (0.5 mL) was head at 120 °C in a sealed tube (5 mL). After 12 h, the reaction mixture was treated with an additional portion of silanes (18 equiv, 1.8 mmol), DTBP (12 equiv, 1.2 mmol), the resulting mixture was stirred for another 12 h. After the reaction finished, the mixture was evaporated under vacuum and purified by column chromatography to afford the desired product **1** (petroleum ether/ethyl acetate = 3/1; 15.4 mg;

62% isolated yield).

Procedure B (1 mmol scale): A mixture of *N*-phenylacetamide (1 equiv, 1.0 mmol), silanes (18 equiv, 18.0 mmol), Cu₂O (5 mol%, 0.05 mmol), DTBP (12 equiv, 12.0 mmol) and *t*-BuOH (5 mL) was heated at 120 °C in a sealed tube (25 mL). After 12 h, the reaction mixture was treated with an additional portion of silanes (18 equiv, 18.0 mmol), DTBP (12 equiv, 12.0 mmol), the resulting mixture was stirred for another 12 h. After the reaction finished, the mixture was evaporated under vacuum and purified by column chromatography to afford the desired product **1** (petroleum ether/ethyl acetate = 3/1; 87.2 mg; 35% isolated yield).

The modification of the reaction condition



Entry	S ₂ (equiv)	Initiator	Catalyst	Solvent (mL)	T(°C)	t (h)	Yield(%)
1	8	4 equiv DTBP	5% CuF ₂	2	130	12	19
2	6	4 equiv DTBP	5% CuF ₂	2	130	12	23
3	4	4 equiv DTBP	5% CuF ₂	2	130	12	18
4	10	4 equiv DTBP	5% CuF ₂	2	130	12	20
5	6	4 equiv DTBP	-	2	130	12	trace
6	6	4 equiv DTBP	5% Cu	2	130	12	20
7	6	4 equiv DTBP	5% CuCl	2	130	12	6
8	6	4 equiv DTBP	5% CuBr	2	130	12	8
9	6	4 equiv DTBP	5% Cul	2	130	12	8
10	6	4 equiv DTBP	5% Cu ₂ O	2	130	12	28
11	6	4 equiv	5% CuCl ₂	2	130	12	9

S1:1 equiv (0.2 mmol)

		DTBP					
12	6	4 equiv	5% CuBr ₂	2	130	12	trace
		DTBP	_				
13	6	4 equiv	5%	2	130	12	7
		DTBP	Mn(OAc) ₂	_			
14	6	4 equiv DTBP	5% PdCl ₂	2	130	12	trace
15	6	4 equiv	5%	2	130	12	trace
		DTBP	Fe(OAc) ₂				
16	6	4 equiv DTBP	5% NiCl ₂	2	130	12	NR
		4 equiv					
17	6	DTBP	5% <i>t</i> -Bu₄NI	2	130	12	trace
18	6	4 equiv DTBP	5% AgNO ₃	2	130	12	NR
19	6	4 equiv DTBP	5% Cu(OAc)₂	2	130	12	25
20	6	4 equiv DTBP	5% Cu(acac)₂	2	130	12	NR
21	6	4 equiv DTBP	5% Cu(OTf) ₂	2	130	12	NR
22	6	4 equiv DTBP	5% CuSO ₄ 5 H ₂ O	2	130	12	trace
23	6	4 equiv DTBP	5% FeCl ₂	2	130	12	trace
24	6	4 equiv DTBP	5% Co(OAc)₂	2	130	12	trace
25	6	4 equiv DTBP	5% FeCl ₃	2	130	12	12
26	6	4 equiv TBHP	5% Cu ₂ O	2	130	12	trace
27	6	4 equiv TBPA	5% Cu ₂ O	2	130	12	8
28	6	4 equiv DCP	5% Cu ₂ O	2	130	12	NR
29	6	4 equiv BPO	5% Cu ₂ O	2	130	12	trace
30	6	4 equiv TBCP	5% Cu ₂ O	2	130	12	NR
31	6	4 equiv K ₂ S ₂ O ₈	5% Cu ₂ O	2	130	12	NR
32	6	4 equiv DTBP	5% Cu ₂ O	2	130	6	14

33	6	4 equiv DTBP	5% Cu ₂ O	2	130	18	25
34	6	4 equiv DTBP	5% Cu₂O	2 mL Ph	130	12	trace
35	6	4 equiv DTBP	5% Cu ₂ O 2 mL ethanol		130	12	18
36	6	4 equiv DTBP	5% Cu ₂ O	2 mL propan-2 -ol	130	12	NR
37	6	4 equiv DTBP	5% Cu ₂ O	2 mL cyclohex ane	130	12	NR
38	6	4 equiv DTBP	5% Cu ₂ O	2 mL tetrahyd rofuran	130	12	NR
39	6	4 equiv DTBP	5% Cu₂O	2mL DMF	130	12	NR
40	6	4 equiv DTBP	5% Cu ₂ O	2 mL DMSO	130	12	NR
41	6	4 equiv DTBP	5% Cu₂O	2 mL TFE	130	12	NR
42	6	4 equiv DTBP	5% Cu ₂ O	2mL ethyl acetate	130	12	NR
43	6	4 equiv DTBP	5% Cu₂O	2 mL 1,2-dichl oroethan e	130	12	NR
44	6	4 equiv DTBP	5% Cu ₂ O	2mL toluene	130	12	NR
45	6	4 equiv DTBP	5% Cu2O	2 mL bromobe nzene	130	12	NR
46	6	4 equiv DTBP	5% Cu ₂ O	0.5	130	12	23
47	6	4 equiv DTBP	5% Cu ₂ O	1	130	15	28
48	6	4 equiv DTBP	5% Cu ₂ O	3	130	12	15
49	6	4 equiv DTBP	5% Cu ₂ O	5	130	12	trace
50	6	4 equiv DTBP	5% Cu ₂ O	1	90	12	trace
51	6	4 equiv	5% Cu ₂ O	1	110	12	16

		DTBP					
50	0	4 equiv		1	160	12	trace
52	0	DTBP	5% Cu ₂ O				
	6	4 equiv		1	130	12	10
53		DTBP	5% Cu₂O				
		0.5 equiv					
		<i>t</i> -BuOK					
	6	4 equiv	5% Cu₂O	1	130	12	trace
54		DTBP					
		0.5 equiv					
		CF ₃ COOH					

S1:1 equiv (0.1 mmol)

Entry	$S_2(\text{equiv})$	Initiator	Catalyst	Solvent	Т	t	Yield(%)
		(equiv)		(mL)	(°C)	(h)	
1	12	2×8	10%	0.5	130	12	52
			Cu ₂ O				
2	12	2×8	10%	1	130	12	27
			Cu ₂ O				
3	12	2×8	10%	2	130	12	18
			Cu ₂ O				
4	12	2×4	10%	0.5	130	12	24
			Cu ₂ O				
5	12	2×6	10%	0.5	130	12	33
			Cu ₂ O				
6	12	2×10	10%	0.5	130	12	46
			Cu ₂ O				
7	12	2×12	10%	0.5	130	12	38
			Cu ₂ O				
8	12	2×15	10%	0.5	130	12	39
			Cu ₂ O				
9	8	2×8	10%	0.5	130	12	34
			Cu ₂ O				
10	16	2×8	10%	0.5	130	12	37
			Cu ₂ O				
11	24	2×8	10%	0.5	130	12	45
			Cu ₂ O				
12	36	2×8	10%	0.5	130	12	46
			Cu ₂ O				
13	12	2×8	10%	0.5	140	12	44
			Cu ₂ O				
14	12	2×8	10%	0.5	150	12	40
			Cu ₂ O				
15	12	2×8	10%	0.5	120	12	21

			Cu ₂ O				
16	2×12	2×8	10%	0.5	130	2×12	34
			Cu ₂ O				
17	2×18	2×12	10%	0.5	130	2×12	49
			Cu ₂ O				
18	2×18	2×12	10%	0.5	120	2×12	56
			Cu ₂ O				
19	2×18	2×12		0.5	120	2×12	Trace
20	2×18	2×12	10%	0.5	120	2×12	42
			Cu				
21	2×18	2×12	10% CuBr	0.5	120	2×12	14
22	2×18	2×12	10%	0.5	120	2×12	trace
			Fe(OAc) ₂				
23	2×18	2×12	10%	0.5	120	2×12	NR
			Cu ₂ O	DMF			
24	2×18	2×12	10%	0.5	120	2×12	NR
			Cu ₂ O	DMSO			
25	2×18	2×12	10%	0.5	120	2×12	NR
			Cu ₂ O	TFE			
26	2×18	2×12	10%	0.5	120	2×12	NR
			Cu ₂ O	Ph			
27	2×18	2×12	10%	0.5	120	2×12	trace
		DCP	Cu ₂ O				
28	2×18	2×12	10%	0.5	120	2×12	trace
		BPO	Cu ₂ O				
29	2×18	2×12	5%	0.5	120	2×12	62
			Cu ₂ O				
30	2×18	2×12	2%	0.5	120	2×12	51
			Cu ₂ O				

Transformation of the arylsilane products.

(1)



1 equiv (0.25 mmol) 5 equiv

An oven-dried 5 mL screw-capped test tube containing a stirring bar was charged

with *N*-(4-(triethylsilyl)phenyl)acetamide (62 mg, 0.25 mmol) and NCS (168 mg, 5 equiv.). The test tube was evacuated and back-filled with dry argon (this sequence was repeated three times). Dry acetonitrile (3 mL) was then added into the tube by syringe through the septum under a positive pressure of argon and the resulting mixture was stirred at 40 °C for 24 h. Then the mixture was concentrated and purified by column chromatography in silica gel (Hexanes/AcOEt = 5/1) to yield the title product *N*-(2,4-dichlorophenyl)acetamide (Yield: 85%, 43 mg, colorless liquid).

¹**H NMR (400 MHz, CDCl₃):** δ 8.33 (d, *J* = 8.8 Hz, 1H), 7.56 (s, 1H), 7.37 (d, *J* = 2.4 Hz, 1H), 7.24 (dd, *J* = 8.8, 2.4 Hz, 1H), 2.24 (s, 3H).

¹³C NMR (101 MHz, CDCl₃): δ 168.2, 133.3, 129.0, 128.6, 127.9, 122.9, 122.2, 24.8.

MS(EI): *m/z*(%): 207(2.5), 205(12.0), 203(18.9), 168(24.1), 161(100.0)







An oven-dried 5 mL screw-capped test tube containing a stirring bar was charged with *N*-(4-(triethylsilyl)phenyl)acetamide (62 mg, 0.25 mmol) and NBS (222 mg, 5 equiv.). The test tube was evacuated and back-filled with dry argon (this sequence was repeated three times). Dry acetonitrile (3 mL) was then added into the tube by syringe through the septum under a positive pressure of argon and the resulting mixture was stirred at room temperature for 24 h. Then the mixture was concentrated and purified by column chromatography in silica gel (Hexanes/AcOEt = 5/1) to yield the title product *N*-(4-bromophenyl)acetamide (Yield: 88%, 47mg, white solid).

¹**H NMR (400 MHz, DMSO):** δ 10.07 (s, 1H), 7.55 (d, *J* = 8.8 Hz, 2H), 7.46 (d, *J* = 8.8 Hz, 2H), 2.04 (s, 3H).

¹³C NMR (101 MHz, DMSO): δ 168.6, 138.9, 131.6, 120.9, 114.6, 24.1.

MS(EI): *m/z*(%): 215(24.8), 213(26.5), 173(98.2), 171(100.0), 105(45.0), 92(38.8). (3)



1 equiv (0.25 mmol) 5 equiv

An oven-dried 5 mL screw-capped test tube containing a stirring bar was charged with *N*-(4-(triethylsilyl)phenyl)acetamide (61 mg, 0.25 mmol) and N-iodosuccinimide (281 mg, 5 equiv.). The test tube was evacuated and back-filled with dry argon (this sequence was repeated three times). Dry acetonitrile (3 mL) was then added into the tube by syringe through the septum under a positive pressure of argon and the resulting mixture was stirred at room temperature for 24 h. Then the mixture was concentrated and purified by column chromatography in silica gel (Hexanes/AcOEt = 5/1) to yield the title product *N*-(4-iodophenyl)acetamide (Yield: 67%, 44 mg, white solid).

¹**H NMR (400 MHz, DMSO):** δ 10.04 (s, 1H), 7.61 (d, *J* = 8.8 Hz, 2H), 7.42 (d, *J* = 8.8 Hz, 2H), 2.03 (s, 3H).

¹³C NMR (101 MHz, DMSO): δ 168.6, 139.2, 137.4, 121.2, 86.4, 24.2.
MS(EI): m/z(%): 261(46.4), 219(100.0), 92(42.2).
(4)



A 5 mL glass vial was charged with PdCl₂(MeCN)₂ (6.5 mg, 5 mol %, 0.025 mmol), CuCl₂ (134.5 mg, 1.0 mmol), and benzo[b]thiophene (0.5 mmol). The vial was

evacuated and refilled with N_2 through a MininertTM valve. Then, 0.5 mL of dried toluene and N-(4-(triethylsilyl)phenyl)acetamide (1.0 mmol) were added, and the resulting mixture was stirred at 100 °C for 24 h. The reaction mixture was cooled to room temperature, and passed through a silica gel short column (dichloromethane). After the volatile was removed in vacuo, the residue was purified by silica gel flash column chromatography to give the corresponding cross-coupling product (Yield: 62%, 83 mg, white solid).

¹**H NMR (400 MHz, CDCl₃):** δ 7.93 – 7.86 (m, 2H), 7.68 (s, 1H), 7.63 (d, *J* = 8.8 Hz, 2H), 7.53 (d, *J* = 8.4 Hz, 2H), 7.39 – 7.36 (m, 2H), 7.34 (s, 1H), 2.22 (s, 3H).

¹³C NMR (101 MHz, CDCl₃): δ 168.6, 140.6, 137.8, 137.4, 137.3, 132.0, 129.2, 124.4, 124.3, 123.1, 122.9, 122.8, 120.2, 24.6.

HRMS (ESI, m/z): Calculated for C₁₆H₁₃NOS (M+H)⁺ 268.0791, found 268.0792. (5)



A mixture of methyl 4-(triethylsilyl)benzoate (0.4 mmol), PhI(OAc)₂ (0.6 mmol), and Pd(OAc)₂ (0.02 mmol) in AcOH (1 mL) was stirred at 100 $^{\circ}$ C for 24 h. To the reaction mixture, then, was added water (1 mL) and the mixture was stirred at 100 $^{\circ}$ C for 3 h. The reaction mixture was poured into aqueous NaHCO₃ solution and extract with CH₂Cl₂ (20 mL × 3). The combined organic extract was dried over anhydrous Na₂SO₄, and concentrated under a reduced pressure. The product was separated by column chromatography on silica gel with hexane/AcOEt eluent (Yield: 53%, 32 mg, white solid).

¹**H NMR (400 MHz, CDCl3):** δ 7.96 (d, J = 8.8 Hz, 2H), 6.86 (d, J = 8.8 Hz, 2H), 5.56 (s, 1H), 3.89 (s, 3H).

¹³C NMR (101 MHz, CDCl3): δ 166.9, 159.7, 131.9, 122.7, 115.2, 51.9.

(6)



Naphthalene (0.5 mmol), aryltrimethylsilanes (1.0 mmol), CuCl₂ (269.0 mg, 2.0 mmol), and PdCl₂ (4.4 mg, 0.025 mmol) in 0.5 mL of dried 1.2-dichloroethane was stirred at 120 $^{\circ}$ C for 24 h. The reaction mixture was cooled to room temperature and passed through a silica gel short column (dichloroethane). After the volatile was removed in vacuo, the residue was purified by silica gel flash chromatography (hexane) to give the cross-coupling product (Yield: 35%, 59 mg, white solid).

¹**H NMR (400 MHz, CDCl₃):** δ 8.10 (d, J = 8.4 Hz, 1H), 8.00 (d, J = 7.6 Hz, 1H), 7.95 (d, J = 8.4 Hz, 1H), 7.80 (d, J = 8.4 Hz, 2H), 7.72 (d, J = 8.4 Hz, 2H), 7.65 (d, J= 8.0 Hz, 2H), 7.62 – 7.51 (m, 6H), 1.48 (s, 9H).

¹³C NMR (101 MHz, CDCl₃): δ 150.3, 139.9, 139.9, 139.4, 137.9, 133.8, 131.6, 130.4, 128.3, 127.6, 126.9, 126.8, 126.7, 126.0, 125.8, 125.4, 34.5, 31.4.

MS(EI): *m/z*(%): 336(83.2), 322(25.5), 321(100.0), 146(30.9).

Confirmation of isomer structure

(1) Mixture of isomers(GC-MS):



methyl 3-(triethylsilyl)benzoate (MS)





xuzhengbao170314-01 #1981-1983 RT: 13.97-13.98 AV: 3 SB: 34 13.34-13.46 , 13.69-13.75 NL: 4.35E7 T: + c Full ms [35.00-650.00]



Mixture of isomers (¹H NMR)



From these spectra, we can know that the mixture of isomers are *para*-isomer and *meta*- isomer, the ratio of the isomers: p: m = 4: 1.

(2) Mixture of isomers(GC-MS):



3-(triethylsilyl)benzamide (MS)



Mixture of isomers (¹H NMR)



From these spectra, we can know that the mixture of isomers are *para*-isomer and *meta*- isomer, the ratio of the isomers: p: m = 2: 1.

Physical data and references for the following products

All known compounds are determined by ¹H NMR, ¹⁹F NMR and ¹³C NMR, MS analysis and compared with which were cited in the following references, and the new compounds were further confirmed by HRMS and/or element analysis.

References:

- 1. L. Zhang, Z. Hang, Z.-Q. Liu, Angew. Chem. Int. Ed. 2016, 55, 236-239.
- 2. K. Funaki, T. Sato, S. Qi, Org. Lett. 2012, 14, 6186-6189.
- 3. K. Gondo, J. Oyamada, T. Kitamura, Org. Lett. 2015, 17, 4778-4781.
- 4. K. Funaki, H. Kawai, T. Sato, S. Qi, Chem. Lett.. 2011, 40, 1050-1052.
- T. Komiyama, Y. Minami, T. Hiyama, Angew. Chem. Int. Ed. 2016, 55, 15787-15791.

1. N-(4-(triethylsilyl)phenyl)acetamide

A yellow solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 3/1; 62%, 15.4 mg)



¹H NMR (400 MHz, CDCl₃): δ 7.49 (d, J = 8.4 Hz, 2H), 7.47(s, 1H), 7.43 (d, J = 8.0 Hz, 2H), 2.16 (s, 3H), 0.95 (t, J = 8.0 Hz, 9H), 0.76 (q, J = 8.0 Hz, 6H). ¹³C NMR (101 MHz, CDCl₃): δ 168.4, 138.4, 134.9, 132.9, 119.0, 24.6, 7.3, 3.4.

HRMS (ESI, m/z): Calculated for $C_{14}H_{23}NOSi (M+H)^+ 250.1622$, found 250.1620.

2. N-(4-(triethylsilyl)phenyl)butyramide

A colorless liquid after purification by flash column chromatography (petroleum ether/ethyl acetate = 3/1; 53%, 14.7 mg)



¹**H** NMR (400 MHz, CDCl₃): δ 7.50 (d, J = 8.0 Hz, 2H), 7.43 (d, J = 8.4 Hz, 2H), 7.21 (s, 1H), 2.33 (t, J = 7.6 Hz, 2H), 1.80 – 1.71 (m, 2H), 1.00 (t, J = 7.2 Hz, 3H), 0.95 (t, J = 7.6 Hz, 9H), 0.77 (q, J = 7.6 Hz, 6H).

¹³C NMR (101 MHz, CDCl₃): δ 171.2, 138.4, 135.0, 132.8, 118.9, 39.8, 19.1, 13.7, 7.3, 3.4.

HRMS (ESI, m/z): Calculated for $C_{16}H_{27}NOSi (M+H)^+ 278.1935$, found 278.1936.

3. N-(4-(triethylsilyl)phenyl)pivalamide

A colorless liquid after purification by flash column chromatography (petroleum ether/ethyl acetate = 3/1; 59%, 17.2 mg)



¹**H** NMR (400 MHz, CDCl₃): δ 7.52 (d, J = 8.4 Hz, 2H), 7.44 (d, J = 8.4 Hz, 2H), 7.31 (s, 1H), 1.31 (s, 3H), 0.94 (t, J = 7.6 Hz, 9H), 0.77 (q, J = 7.6 Hz, 6H). ¹³C NMR (101 MHz, CDCl₃): δ 176.5, 138.5, 134.9, 132.8, 119.1, 39.6, 27.6, 7.3, 3.4.

HRMS (ESI, m/z): Calculated for $C_{17}H_{29}NOSi (M+H)^+ 292.2091$, found 292.2092.

4. N-(4-(triethylsilyl)phenyl)cyclohexanecarboxamide

A colorless liquid after purification by flash column chromatography (petroleum ether/ethyl acetate = 3/1; 50%, 15.9 mg)



¹**H NMR (400 MHz, CDCl₃):** δ 7.54 (d, *J* = 8.0 Hz, 2H), 7.46 (s, 1H), 7.42 (d, *J* = 8.0 Hz, 2H), 2.24 (tt, *J* = 11.6, 3.2 Hz, 1H), 1.93 (d, *J* = 12.8 Hz, 1H), 1.81 (dd, *J* = 9.6, 3.2 Hz, 2H), 1.68 (d, *J* = 8.0 Hz, 1H), 1.52 (dt, *J* = 12.0, 7.6 Hz, 2H), 1.32 – 1.21 (m, 3H), 0.94 (t, *J* = 8.0 Hz, 9H), 0.76 (q, *J* = 8.0 Hz, 6H).

¹³C NMR (101 MHz, CDCl₃): δ 174.5, 138.6, 134.9, 132.5, 118.9, 46.5, 32.0, 29.6, 25.6, 7.3, 3.3.

HRMS (ESI, m/z): Calculated for $C_{19}H_{31}NOSi (M+H)^+ 318.2248$, found 318.2253.

5. 1-(4-(triethylsilyl)phenyl)pyrrolidin-2-one

A white solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 5/1; 51%, 14.0 mg)



¹**H** NMR (400 MHz, CDCl₃): δ 7.59 (d, J = 8.8 Hz, 2H), 7.49 (d, J = 8.8 Hz, 2H), 3.85 (t, J = 6.8 Hz, 2H), 2.59 (t, J = 8.0 Hz, 2H), 2.18 – 2.10 (m, 2H), 0.95 (t, J = 7.6 Hz, 9H), 0.78 (q, J = 7.6 Hz, 6H).

¹³C NMR (101 MHz, CDCl₃): δ 174.1, 139.8, 134.7, 133.1, 119.0, 48.5, 32.7, 18.0, 7.3, 3.3.

HRMS (ESI, m/z): Calculated for $C_{16}H_{25}NOSi (M+H)^+ 276.1778$, found 276.1777.

6. N-(2-methyl-4-(triethylsilyl)phenyl)acetamide

A colorless liquid after purification by flash column chromatography (petroleum

ether/ethyl acetate = 3/1; 62%, 16.3 mg)



¹**H** NMR (400 MHz, CDCl₃): δ 7.77 (d, J = 8.0 Hz, 1H), 7.32 (d, J = 8.0 Hz, 1H), 7.28 (s, 1H), 7.08 (s, 1H), 2.26 (s, 3H), 2.19 (s, 3H), 0.95 (t, J = 8.0 Hz, 9H), 0.77 (q, J = 8.0 Hz, 6H).

¹³C NMR (101 MHz, CDCl₃): δ 168.2, 136.3, 136.2, 134.0, 132.8, 127.8, 122.2, 24.3, 17.8, 7.3, 3.3.

HRMS (ESI, m/z): Calculated for $C_{15}H_{25}NOSi (M+H)^+ 264.1778$, found 264.1776.

7. N-(2-isopropyl-4-(triethylsilyl)phenyl)acetamide

A white solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 3/1; 60%, 17.5 mg)



¹**H** NMR (400 MHz, CDCl₃): δ 7.63 (d, J = 7.6 Hz, 1H), 7.38 (s, 1H), 7.32 (dd, J = 7.6, 1.2 Hz, 1H), 7.08 (s, 1H), 3.03 (dt, J = 13.6, 6.8 Hz, 1H), 2.20 (s, 3H), 1.25 (d, J = 6.8 Hz, 6H), 0.96 (t, J = 7.6 Hz, 9H), 0.77 (q, J = 7.6 Hz, 6H).

¹³C NMR (101 MHz, CDCl₃): δ 168.6, 139.1, 134.9, 134.5, 132.3, 131.4, 123.9, 27.9, 24.3, 23.1, 7.4, 3.4.

HRMS (ESI, m/z): Calculated for $C_{17}H_{29}NOSi (M+H)^+ 292.2091$, found 292.2094.

8. N-(2-fluoro-4-(triethylsilyl)phenyl)acetamide

A colorless liquid after purification by flash column chromatography (petroleum ether/ethyl acetate = 3/1; 63%, 16.8 mg)



¹**H NMR (400 MHz, CDCl₃):** δ 8.27 (t, *J* = 8.0 Hz, 1H), 7.39 (s, 1H), 7.22 (d, *J* = 8.0 Hz, 1H), 7.17 (d, *J* = 11.2 Hz, 1H), 2.22 (s, 3H), 0.94 (t, *J* = 8.0 Hz, 9H), 0.76 (q, *J* = 8.0 Hz, 6H).

¹⁹F NMR (**376** MHz, CDCl₃): δ -133.04 – -133.10 (m, 1F).

¹³C NMR (101 MHz, CDCl₃): δ 168.2, 152.0 (d, J = 246.0 Hz), 134.2, 130.4 (d, J = 3.6 Hz), 126.6 (d, J = 9.7 Hz), 121.0, 119.7 (d, J = 16.8 Hz), 24.6, 7.2, 3.3.

HRMS (ESI, m/z): Calculated for $C_{14}H_{22}FNOSi (M+H)^+ 268.1527$, found 268.1528.

9. N-(2-chloro-4-(triethylsilyl)phenyl)acetamide

A colorless liquid after purification by flash column chromatography (petroleum ether/ethyl acetate = 3/1; 43%, 12.2 mg)



¹**H NMR (400 MHz, CDCl₃):** δ 8.33 (d, *J* = 8.0 Hz, 1H), 7.63 (s, 1H), 7.43 (d, *J* = 1.2 Hz, 1H), 7.36 (dd, *J* = 8.0, 1.2 Hz, 1H), 2.23 (s, 3H), 0.95 (t, *J* = 8.4 Hz, 9H), 0.77 (q, *J* = 8.4 Hz, 6H).

¹³C NMR (101 MHz, CDCl₃): δ 168.2, 134.8, 134.5,134.3, 133.6, 122.4, 120.9, 24.8, 7.2, 3.2.

HRMS (ESI, m/z): Calculated for $C_{14}H_{22}CINOSi (M+H)^+ 284.1232$, found 284.1230.

10. N-(3-methoxy-4-(triethylsilyl)phenyl)acetamide

A white solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 3/1; 72%, 20.1 mg)



¹**H NMR (400 MHz, CDCl₃):** δ 8.00 (s, 1H), 7.33 (d, *J* = 0.8 Hz, 1H), 7.23 (d, *J* = 8.0 Hz, 1H), 6.90 (d, *J* = 7.6 Hz, 1H), 3.71 (s, 3H), 2.16 (s, 3H), 0.91 (t, *J* = 7.6 Hz, 9H), 0.78 (q, *J* = 7.6 Hz, 6H).

¹³C NMR (101 MHz, CDCl₃): δ 168.8, 165.1, 140.4, 136.1, 120.4, 111.2, 101.7, 54.8, 24.5, 7.5, 3.4.

HRMS (ESI, m/z): Calculated for $C_{15}H_{25}NO_2Si (M+H)^+ 280.1727$, found 280.1726.

11. N-(3,5-dimethoxy-4-(triethylsilyl)phenyl)acetamide

A white solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 3/1; 76%, 23.5 mg)



¹**H NMR (400 MHz, CDCl₃):** δ 8.05 (s, 1H), 6.76 (s, 2H), 3.65 (s, 6H), 2.16 (s, 3H), 0.90 (t, *J* = 7.6 Hz, 9H), 0.79 (q, *J* = 7.6 Hz, 6H).

¹³C NMR (101 MHz, CDCl₃): δ 168.8, 166.1, 141.0, 107.4, 95.3, 54.9, 24.6, 7.8, 5.1.

HRMS (ESI, m/z): Calculated for $C_{16}H_{27}NO_3Si(M+H)^+ 310.1833$, found 310.1832.

12. [1,1'-biphenyl]-4-yltriethylsilane

A colorless liquid after purification by flash column chromatography (petroleum ether; 32%, 8.6 mg)



¹**H** NMR (400 MHz, CDCl₃): δ 7.62 (d, *J* = 7.6 Hz, 2H), 7.59 (dt, *J* = 8.4, 1.6 Hz, 4H), 7.45 (t, *J* = 7.6 Hz, 2H), 7.35 (t, *J* = 7.2 Hz, 1H), 1.01 (t, *J* = 7.6 Hz, 9H), 0.84 (q, *J* = 7.6 Hz, 6H).

¹³C NMR (101 MHz, CDCl₃): δ 141.4, 141.2, 136.2, 134.7, 128.7, 127.3, 127.1, 126.4, 7.4, 3.4.

MS(EI): *m/z*(%): 268(23.2), 239(68.1), 211(89.4), 183(100.0), 181(50.3).

12^c. 4,4'-bis(triethylsilyl)-1,1'-biphenyl

A colorless liquid after purification by flash column chromatography (petroleum ether; 14%, 5.4 mg)



¹**H** NMR (400 MHz, CDCl₃): δ 7.58 (q, J = 8.4 Hz, 8H), 1.00 (t, J = 7.6 Hz, 18H), 0.83 (q, J = 7.6 Hz, 12H).

¹³C NMR (101 MHz, CDCl₃): δ 141.4, 136.3, 134.6, 126.3, 7.4, 3.4 MS(EI): *m/z*(%): 382(24.0), 353(72.9), 325(47.0), 297(100.0), 212(49.7), 134(41.9), 120(43.7), 106(75.7).

13. (4'-(tert-butyl)-[1,1'-biphenyl]-4-yl)triethylsilane

A colorless liquid after purification by flash column chromatography (petroleum ether; 51%, 16.5 mg)



¹**H NMR (400 MHz, CDCl₃):** δ 7.61 – 7.55 (m, 6H), 7.48 (d, J = 8.4 Hz, 2H), 1.39 (s, 9H), 1.02 (t, J = 8.0 Hz, 9H), 0.85 (q, J = 8.0 Hz, 6H).

¹³C NMR (101 MHz, CDCl₃): δ 150.2, 141.3, 138.3, 135.8, 134.6, 126.7, 126.2, 125.7, 34.5, 31.4, 7.4, 3.4.

MS(EI): *m/z*(%): 324(23.0), 295(54.7), 267(48.8), 239(100.0), 112(38.8), 98(38.1).

14. N-(4'-(triethylsilyl)-[1,1'-biphenyl]-4-yl)acetamide

A white solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 3/1; 43%, 14.0 mg)



¹**H** NMR (400 MHz, CDCl₃): δ 7.56 (d, J = 7.6 Hz, 8H), 7.45 (s, 1H), 2.20 (s, 3H), 0.99 (t, J = 7.6 Hz, 9H), 0.82 (q, J = 7.6 Hz, 6H).

¹³C NMR (101 MHz, CDCl₃): δ 168.3, 140.6, 137.2, 137.1, 136.1, 134.7, 127.5, 126.0, 120.1, 24.6, 7.41, 3.4.

HRMS (ESI, m/z): Calculated for $C_{20}H_{27}NOSi (M+H)^+$ 326.1935, found 326.1942.

15. N-(4-methoxy-3-(triethylsilyl)phenyl)acetamide

A white solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 3/1; 42%, 11.7 mg)



¹**H NMR (400 MHz, CDCl₃):** δ 7.63 (dd, *J* = 8.8, 2.8 Hz, 1H), 7.48 (s, 1H), 7.22 (d, *J* = 2.8 Hz, 1H), 6.76 (d, *J* = 8.8 Hz, 1H), 3.75 (s, 3H), 2.13 (s, 3H), 0.92 (t, *J* = 7.6 Hz, 9H), 0.79 (q, *J* = 7.6 Hz, 6H).

¹³C NMR (101 MHz, CDCl₃): δ 168.3, 161.3, 130.7, 128.1, 125.7, 123.0, 109.6, 55.2, 24.2, 7.5, 3.4.

HRMS (ESI, m/z): Calculated for $C_{15}H_{25}NO_2Si (M+H)^+ 280.1727$, found 280.1725.

16. N-(2,4-dimethoxy-5-(triethylsilyl)phenyl)acetamide

A white solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 3/1; 36%, 11.1 mg)



¹**H NMR (400 MHz, CDCl₃):** δ 8.26 (s, 1H), 7.47 (s, 1H), 6.42 (s, 1H), 3.88 (s, 3H), 3.77 (s, 3H), 2.16 (s, 3H), 0.93 (t, *J* = 7.6 Hz, 9H), 0.79 (q, *J* = 7.6 Hz, 6H).

¹³C NMR (101 MHz, CDCl₃): δ 167.8, 161.4, 150.2, 127.7, 120.7, 115.7, 93.9, 55.5, 55.3, 24.6, 7.6, 3.6.

HRMS (ESI, m/z): Calculated for $C_{16}H_{27}NO_3Si(M+H)^+ 310.1833$, found 310.1836.

17. (3,6-dimethoxy-1,2-phenylene)bis(triethylsilane)

A white solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 100/1; 52%, 19.1 mg)



¹**H NMR (400 MHz, CDCl₃):** δ 6.83 (s, 2H), 3.76 (s, 6H), 0.97 (t, *J* = 8.0 Hz, 18H), 0.84 (q, *J* = 8.0 Hz, 12H).

¹³C NMR (101 MHz, CDCl₃): δ 158.5, 127.2, 117.0, 55.6, 7.6, 3.6. MS(EI): *m/z*(%): 366(57.6), 337(42.4), 309(54.1), 251(28.9), 235(100.0), 126(25.6).

18. (2,6-dimethoxyphenyl)triethylsilane

A colorless liquid after purification by flash column chromatography (petroleum ether/ethyl acetate = 100/1; 41%, 10.3 mg)



¹**H** NMR (400 MHz, CDCl₃): δ 7.28 (t, J = 8.0 Hz, 1H), 6.50 (d, J = 8.0 Hz, 2H), 3.75 (s, 6H), 0.94 (t, J = 6.8 Hz, 9H), 0.85 (q, J = 7.6 Hz, 6H).

¹³C NMR (101 MHz, CDCl₃): δ 165.9, 131.1, 112.0, 103.3, 55.0, 7.8, 5.3.

HRMS (ESI, m/z): Calculated for $C_{14}H_{24}O_2Si (M+H)^+ 253.1618$, found 253.1624.

19. 4-(triethylsilyl)benzamide

A white solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 5/1; 35%, 8.2 mg)



¹H NMR (400 MHz, CDCl₃): δ 7.77 (d, J = 7.6 Hz, 2H), 7.57 (d, J = 8.0 Hz, 2H), 6.13 (d, J = 32.4 Hz, 1H), 0.95 (t, J = 7.6 Hz, 9H), 0.80 (q, J = 7.6 Hz, 6H). ¹³C NMR (101 MHz, CDCl₃): δ 169.7, 142.9, 134.4, 133.4, 126.2, 7.3, 3.2.

HRMS (ESI, m/z): Calculated for $C_{13}H_{21}NOSi (M+H)^+ 236.1465$, found 236.1467.

20. N-methyl-4-(triethylsilyl)benzamide

A white solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 5/1; 71%, 17.7 mg)



¹**H NMR (400 MHz, CDCl₃):** δ 7.71 (d, J = 8.0 Hz, 2H), 7.53 (d, J = 8.0 Hz, 3H), 6.30 (s, 1H), 3.00 (d, J = 4.8 Hz, 3H), 0.95 (t, J = 8.0 Hz, 9H), 0.79 (q, J = 8.0 Hz, 6H).

¹³C NMR (101 MHz, CDCl₃): δ 168.4, 141.9, 134.7, 134.3, 125.8, 26.8, 7.3, 3.2.

HRMS (ESI, m/z): Calculated for $C_{14}H_{23}NOSi (M+H)^+ 250.1622$, found 250.1626.

21. methyl 4-(triethylsilyl)benzoate

A colorless liquid after purification by flash column chromatography (petroleum ether/ethyl acetate = 100/1; 75%, 18.8 mg)



¹**H** NMR (400 MHz, CDCl₃): δ 7.99 (d, J = 8.0 Hz, 2H), 7.57 (d, J = 8.0 Hz, 2H), 3.91 (s, 3H), 0.96 (t, J = 7.6 Hz, 9H), 0.81 (q, J = 7.6 Hz, 6H).

¹³C NMR (101 MHz, CDCl₃): δ 167.3, 144.0, 134.1, 130.2, 128.4, 52.0, 7.3, 3.2.

HRMS (ESI, m/z): Calculated for $C_{14}H_{22}O_2Si(M+H)^+ 251.1462$, found 215.1461.

22. ethyl 4-(triethylsilyl)benzoate

A colorless liquid after purification by flash column chromatography (petroleum ether/ethyl acetate = 100/1; 76%, 20.1 mg)



¹**H** NMR (400 MHz, CDCl₃): δ 8.00 (d, J = 8.0 Hz, 2H), 7.56 (d, J = 8.0 Hz, 2H), 4.38 (q, J = 6.8 Hz, 2H), 1.39 (t, J = 6.8 Hz, 3H), 0.96 (t, J = 7.6 Hz, 9H), 0.81 (q, J = 7.6 Hz, 6H).

¹³C NMR (101 MHz, CDCl₃): δ 166.8, 143.9, 134.1, 130.6, 128.3, 60.8, 14.3, 7.3, 3.2.

HRMS (ESI, m/z): Calculated for $C_{15}H_{24}O_2Si (M+H)^+ 265.1618$, found 265.1617.

23. isopropyl 4-(triethylsilyl)benzoate

A colorless liquid after purification by flash column chromatography (petroleum ether/ethyl acetate = 100/1; 70%, 19.5 mg)



¹**H NMR (400 MHz, CDCl₃):** δ 7.99 (d, J = 8.0 Hz, 2H), 7.56 (d, J = 8.4 Hz, 2H), 5.30 - 5.21 (m, 1H), 1.36 (d, J = 6.4 Hz, 6H), 0.96 (t, J = 7.6 Hz, 9H), 0.81 (q, J = 7.6 Hz, 6H).

¹³C NMR (101 MHz, CDCl₃): δ 166.3, 143.7, 134.1, 131.0, 128.3, 68.2, 21.9, 7.3, 3.2.

HRMS (ESI, m/z): Calculated for $C_{16}H_{26}O_2Si(M+H)^+$ 279.1775, found 279.1776.

24. tert-butyl 4-(triethylsilyl)benzoate

A colorless liquid after purification by flash column chromatography (petroleum ether/ethyl acetate = 100/1; 67%, 19.6 mg)



¹H NMR (400 MHz, CDCl₃): δ 7.95 (d, J = 8.4 Hz, 2H), 7.55 (d, J = 8.4 Hz, 2H), 1.59 (s, 9H), 0.95 (t, J = 7.6 Hz, 9H), 0.80 (q, J = 7.6 Hz, 6H). ¹³C NMR (101 MHz, CDCl₃): δ 166.0, 143.3, 134.0, 132.1, 128.2, 28.2, 7.3, 3.2. **HRMS (ESI, m/z):** Calculated for $C_{17}H_{28}O_2Si (M+Na)^+ 315.1751$, found 315.1750.

25. cyclohexyl 4-(triethylsilyl)benzoate

A colorless liquid after purification by flash column chromatography (petroleum ether/ethyl acetate = 100/1; 65%, 20.7 mg)



¹**H** NMR (400 MHz, CDCl₃): δ 8.01 (d, J = 8.0 Hz, 2H), 7.57 (d, J = 8.0 Hz, 2H), 5.07 - 5.00 (m, 1H), 1.93 (d, J = 8.4 Hz, 2H), 1.81 - 1.78 (m, 2H), 1.63 - 1.55 (m, 4H), 1.49 - 1.43 (m, 2H), 0.96 (t, J = 7.6 Hz, 9H), 0.81 (q, J = 7.6 Hz, 6H).

¹³C NMR (101 MHz, CDCl₃): δ 166.2, 143.7, 134.1, 131.1, 128.3, 72.9, 31.6, 25.5, 23.6, 7.3, 3.2.

HRMS (ESI, m/z): Calculated for $C_{19}H_{30}O_2Si (M+Na)^+ 341.1907$, found 341.1906.

26. (tetrahydrofuran-2-yl)methyl 4-(triethylsilyl)benzoate

A colorless liquid after purification by flash column chromatography (petroleum ether/ethyl acetate = 100/1; 68%, 21.8 mg)



¹**H** NMR (400 MHz, CDCl₃): δ 8.01 (d, J = 7.6 Hz, 2H), 7.56 (d, J = 7.6 Hz, 2H), 4.39 – 4.35 (m, 1H), 4.33 – 4.25 (m, 2H), 3.93 (dd, J = 14.8, 6.4 Hz, 1H), 3.83 (dd, J = 14.8, 6.4 Hz, 1H), 2.11 – 2.03 (m, 1H), 2.01 – 1.89 (m, 2H), 1.79 – 1.69 (m, 1H), 0.95 (t, J = 7.6 Hz, 9H), 0.81 (q, J = 7.6 Hz, 6H).

¹³C NMR (101 MHz, CDCl₃): δ 166.8, 144.1, 134.1, 130.2, 128.5, 76.6, 68.5, 66.8, 28.1, 25.8, 7.3, 3.2.

HRMS (ESI, m/z): Calculated for $C_{18}H_{28}O_3Si(M+H)^+ 321.1880$, found 321.1879.

27. 3,5-dimethoxy-4-(triethylsilyl)benzamide

A white solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 5/1; 60%, 17.7 mg)



¹H NMR (400 MHz, CDCl₃): δ 6.90 (s, 2H), 6.46 (s, 2H), 3.75 (s, 6H), 0.90 (t, J =

8.0 Hz, 9H), 0.82 (q, J = 8.0 Hz, 6H). ¹³C NMR (101 MHz, CDCl₃): δ 170.1, 165.8, 136.4, 116.9, 102.1, 55.2, 7.7, 5.0. HRMS (ESI, m/z): Calculated for C₁₅H₂₅NO₃Si (M+H)⁺ 296.1676, found 296.1675.

28. 3,5-dimethoxy-N-propyl-4-(triethylsilyl)benzamide

A white solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 5/1; 84%, 28.4 mg)



¹**H** NMR (400 MHz, CDCl₃): δ 6.86 (s, 2H), 6.51 (s, 1H), 3.74 (s, 6H), 3.37 (dd, J = 13.2, 6.4 Hz, 2H), 1.65 – 1.56 (m, 2H), 0.94 (t, J = 7.6 Hz, 3H), 0.89 (t, J = 7.6 Hz, 9H), 0.81 (q, J = 7.6 Hz, 6H).

¹³C NMR (101 MHz, CDCl₃): δ 167.8, 165.8, 138.0, 115.8, 101.8, 55.1, 41.7, 22.9, 11.4, 7.7, 5.0.

HRMS (ESI, m/z): Calculated for $C_{18}H_{31}NO_3Si(M+H)^+$ 338.2146, found 338.2145.

29. 3-methoxy-N-propyl-4-(triethylsilyl)benzamide

A white solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 5/1; 80%, 24.6 mg)



¹**H NMR** (**400 MHz**, **CDCl**₃): δ 7.35 (d, J = 7.6 Hz, 1H), 7.31 (d, J = 0.8 Hz, 1H), 7.20 (dd, J = 7.6, 0.8 Hz, 1H), 6.34 (s, 1H), 3.81 (s, 3H), 3.40 (dd, J = 13.6, 6.4 Hz, 2H), 1.66 – 1.57 (m, 2H), 0.96 (t, J = 7.2 Hz, 3H), 0.91 (t, J = 7.6 Hz, 9H), 0.80 (q, J = 7.6 Hz, 6H).

¹³C NMR (101 MHz, CDCl₃): δ 167.7, 164.8, 137.1, 135.8, 129.4, 117.6, 108.3, 55.0, 41.7, 22.9, 11.4, 7.5, 3.3.

HRMS (ESI, m/z): Calculated for $C_{17}H_{29}NO_2Si (M+H)^+ 308.2040$, found 308.2045.

30. methyl 3-methoxy-4-(triethylsilyl)benzoate

A white solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 100/1; 85%, 23.8 mg)



¹**H** NMR (400 MHz, CDCl₃): δ 7.61 (dd, J = 7.6, 1.2 Hz, 1H), 7.45 (d, J = 1.2 Hz, 1H), 7.41 (d, J = 7.6 Hz, 1H), 3.91 (s, 3H), 3.84 (s, 3H), 0.93 (t, J = 7.6 Hz, 9H), 0.83 (q, J = 7.6 Hz, 6H).

¹³C NMR (101 MHz, CDCl₃): δ 167.2, 164.4, 135.9, 132.1, 131.7, 121.4, 109.6, 55.05, 52.0, 7.5, 3.3.

HRMS (ESI, m/z): Calculated for $C_{15}H_{24}O_3Si(M+H)^+ 281.1567$, found 281.1572.

31. methyl 5-methoxy-2-methyl-4-(triethylsilyl)benzoate

A colorless liquid after purification by flash column chromatography (petroleum ether/ethyl acetate = 100/1; 82%, 24.1 mg)



¹**H NMR (400 MHz, CDCl₃):** δ 7.33 (s, 1H), 7.18 (s, 1H), 3.90 (s, 3H), 3.80 (s, 3H), 2.52 (s, 3H), 0.93 (t, *J* = 7.6 Hz, 9H), 0.82 (q, *J* = 7.6 Hz, 6H).

¹³C NMR (101 MHz, CDCl₃): δ 168.2, 162.4, 139.3, 131.3, 130.8, 130.7, 110.5, 55.1, 51.8, 20.9, 7.5, 3.3.

HRMS (ESI, m/z): Calculated for $C_{16}H_{26}O_3Si(M+H)^+$ 295.1724, found 295.1728.

32. methyl 2,3-dimethoxy-4-(triethylsilyl)benzoate

A colorless liquid after purification by flash column chromatography (petroleum ether/ethyl acetate = 100/1; 45%, 14.0 mg)



¹**H** NMR (400 MHz, CDCl₃): δ 7.44 (d, J = 7.6 Hz, 1H), 7.11 (d, J = 7.6 Hz, 1H), 3.91 (s, 3H), 3.89 (s, 3H), 3.87 (s, 3H), 0.94 (t, J = 7.6 Hz, 9H), 0.82 (q, J = 7.6 Hz,6H).

¹³C NMR (101 MHz, CDCl₃): δ 166.7, 158.6, 151.6, 136.4, 130.3, 127.2, 125.0, 61.0, 60.2, 52.2, 7.5, 3.5.

HRMS (ESI, m/z): Calculated for $C_{16}H_{26}O_4Si (M+H)^+ 311.1673$, found 311.1678.

33. methyl 3,5-dimethoxy-4-(triethylsilyl)benzoate

A white solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 100/1; 86%, 26.7 mg)



¹**H NMR (400 MHz, CDCl₃):** δ 7.14 (s, 2H), 3.91 (s, 3H), 3.79 (s, 6H), 0.91 (t, *J* = 6.4 Hz, 9H), 0.84 (q, *J* = 7.2 Hz, 6H).

¹³C NMR (101 MHz, CDCl₃): δ 167.1, 165.7, 132.8, 118.2, 104.1, 55.2, 52.1, 7.8, 5.0.

HRMS (ESI, m/z): Calculated for $C_{16}H_{26}O_4Si (M+H)^+ 311.1673$, found 311.1676.

34. methyl 3-fluoro-4-(triethylsilyl)benzoate

A colorless liquid after purification by flash column chromatography (petroleum ether/ethyl acetate = 100/1; 63%, 16.9 mg)



¹**H** NMR (400 MHz, CDCl₃): δ 7.78 (d, J = 7.6 Hz, 1H), 7.61 (dd, J = 8.8, 0.8 Hz, 1H), 7.45 (dd, J = 7.6, 5.2 Hz, 1H), 3.92 (s, 3H), 0.95 (t, J = 7.6 Hz, 9H), 0.86 (q, J = 7.6 Hz, 6H).

¹⁹F NMR (376 MHz, CDCl₃): δ -99.17 – -99.60 (m, 1F).

¹³C NMR (101 MHz, CDCl₃): δ 167.3 (d, J = 218.2 Hz), 166.0, 136.1 (d, J = 11.9 Hz), 133.1 (d, J = 8.1 Hz), 129.7 (d, J = 32.0 Hz), 124.6 (d, J = 2.8 Hz), 115.5 (d, J = 28.8 Hz), 52.3, 7.2, 3.2.

HRMS (ESI, m/z): Calculated for $C_{14}H_{21}FO_2Si (M+H)^+ 269.1368$, found 269.1369.

35. methyl 3-cyano-4-(triethylsilyl)benzoate

A colorless liquid after purification by flash column chromatography (petroleum ether/ethyl acetate = 100/1; 38%, 10.4 mg)



¹**H** NMR (400 MHz, CDCl₃): δ 8.32 (d, J = 0.8 Hz, 1H), 8.15 (dd, J = 8.0, 1.6 Hz, 1H), 7.67 (d, J = 8.0 Hz, 1H), 3.95 (s, 3H), 1.02 - 0.94 (m, 15H).

¹³C NMR (101 MHz, CDCl₃): δ 165.4, 148.1, 136.0, 134.3, 131.8, 131.0, 119.2, 118.1, 52.6, 7.26, 2.8.

HRMS (ESI, m/z): Calculated for $C_{15}H_{21}NO_2Si (M+H)^+ 276.1414$, found 276.1419.

36. dimethyl 4-(triethylsilyl)phthalate

A colorless liquid after purification by flash column chromatography (petroleum ether/ethyl acetate = 100/1; 70%, 21.6 mg)



¹**H** NMR (400 MHz, CDCl₃): δ 7.79 (s, 1H), 7.68 (d, J = 7.6 Hz, 1H), 7.63 (dd, J = 7.6, 0.8 Hz, 1H), 3.89 (s, 3H), 3.88 (s, 3H), 0.93 (t, J = 7.6 Hz, 9H), 0.80 (q, J = 7.6 Hz, 6H).

¹³C NMR (101 MHz, CDCl₃): δ 168.5, 168.1, 142.4, 136.8, 134.1, 131.7, 130.9, 127.7, 52.5, 52.5, 7.1, 3.0.

HRMS (ESI, m/z): Calculated for $C_{16}H_{24}O_4Si (M+H)^+ 309.1517$, found 309.1516.

37. 4-methoxy-N-propyl-3-(triethylsilyl)benzamide

A white solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 5/1; 48%, 14.7 mg)



¹**H NMR (400 MHz, CDCl₃):** δ 7.77 - 7.74 (m, 2H), 6.81 (d, *J* = 8.4 Hz, 1H), 6.13 (s, 1H), 3.81 (s, 3H), 3.39 (dd, *J* = 14.0, 6.8 Hz, 2H), 1.67 - 1.58 (m, 2H), 0.97 (t, *J* = 7.6 Hz, 3H), 0.91 (t, *J* = 7.6 Hz, 9H), 0.82 (q, *J* = 7.6 Hz, 6H).

¹³C NMR (101 MHz, CDCl₃): δ 167.6, 166.8, 134.8, 129.8, 126.7, 125.4, 108.8, 55.1, 41.6, 23.0, 11.4, 7.5, 3.3.

HRMS (ESI, m/z): Calculated for $C_{17}H_{29}NO_2Si (M+H)^+ 308.2040$, found 308.2043.

38. methyl 4-methoxy-3-(triethylsilyl)benzoate

A colorless liquid after purification by flash column chromatography (petroleum ether/ethyl acetate = 100/1; 51%, 14.3 mg)



¹**H NMR (400 MHz, CDCl₃):** δ 8.05 – 8.03 (m, 2H), 6.83 (d, *J* = 8.0 Hz, 1H), 3.88 (s, 3H), 3.84 (s, 3H), 0.93 (t, *J* = 7.6 Hz, 9H), 0.83 (q, *J* = 7.6 Hz, 6H).

¹³C NMR (101 MHz, CDCl₃): δ 168.1, 167.2, 137.8, 133.0, 125.4, 122.2, 108.8, 55.1, 51.8, 7.5, 3.3.

HRMS (ESI, m/z): Calculated for $C_{15}H_{24}O_3Si(M+H)^+ 281.1567$, found 281.1568.

39. triethyl(3-methylbenzofuran-2-yl)silane

A colorless liquid after purification by flash column chromatography (petroleum ether; 76%, 18.7 mg)



¹**H** NMR (400 MHz, CDCl₃): δ 7.53 (dd, J = 7.6, 0.4 Hz, 1H), 7.47 (d, J = 8.0 Hz, 1H), 7.30 – 7.26 (m, 1H), 7.24 – 7.20 (m, 1H), 2.34 (s, 3H), 1.04 (t, J = 7.6 Hz, 9H), 0.92 (q, J = 7.6 Hz, 6H).

¹³C NMR (101 MHz, CDCl₃): δ 157.7, 156.0, 129.9, 126.0, 124.0, 121.6, 119.1, 111.1, 8.9, 7.3, 3.4.

MS(EI): *m/z*(%): 246(38.1), 217(45.9), 189(100.0), 161(44.5), 115(26.3).

40. triethyl(3-phenylbenzofuran-2-yl)silane

A colorless liquid after purification by flash column chromatography (petroleum ether; 71%, 21.9 mg)



¹**H NMR (400 MHz, CDCl₃):** δ 7.61 (d, *J* = 8.4 Hz, 1H), 7.55 – 7.45 (m, 6H), 7.37 (t, *J* = 7.2 Hz, 1H), 7.27 (t, *J* = 7.2 Hz, 1H), 0.99 (t, *J* = 8.0 Hz, 9H), 0.82 (q, *J* = 8.0 Hz, 6H).

¹³C NMR (101 MHz, CDCl₃): δ 157.7, 157.0, 133.2, 133.2, 129.8, 129.0, 128.2, 127.6, 124.4, 122.2, 120.0, 111.2, 7.3, 3.6.

HRMS (ESI, m/z): Calculated for $C_{20}H_{24}OSi (M+H)^+$ 309.1669, found 309.1671.

41. triethyl(3-methylbenzo[b]thiophen-2-yl)silane

A colorless liquid after purification by flash column chromatography (petroleum ether; 72%, 18.9 mg)



¹**H** NMR (400 MHz, CDCl₃): δ 7.87 (d, J = 8.0 Hz, 1H), 7.75 (d, J = 7.6 Hz, 1H), 7.39 (t, J = 7.6 Hz, 1H), 7.34 (t, J = 7.6 Hz, 1H), 2.52 (s, 3H), 1.04 (t, J = 7.6 Hz, 9H), 0.95 (q, J = 7.6 Hz, 6H).

¹³C NMR (101 MHz, CDCl₃): δ 143.1, 141.8, 139.0, 132.0, 123.9, 123.5, 122.1, 121.6, 14.6, 7.5, 4.5.

MS(EI): *m/z*(%): 262(51.8), 233(62.5), 205(100.0), 177(97.7).

42. triethyl(3-phenylbenzo[b]thiophen-2-yl)silane

A colorless liquid after purification by flash column chromatography (petroleum ether; 70%, 22.7 mg)



¹**H** NMR (400 MHz, CDCl₃): δ 7.97 (d, J = 7.6 Hz, 1H), 7.51 (d, J = 7.2 Hz, 4H), 7.45 (dd, J = 7.4, 2.4 Hz, 2H), 7.42 – 7.38 (m, 1H), 7.37 – 7.33 (m, 1H), 0.98 (t, J = 8.0 Hz, 9H), 0.72 (q, J = 8.0 Hz, 6H).

¹³C NMR (101 MHz, CDCl₃): δ 145.6, 142.9, 141.8, 137.6, 134.9, 130.1, 128.0, 127.6, 124.2, 123.8, 123.1, 121.8, 7.4, 4.5.

HRMS (ESI, m/z): Calculated for $C_{20}H_{24}SSi(M+H)^+$ 325.1441, found 325.1439.

43. triethyl(3-phenylthiophen-2-yl)silane

A colorless liquid after purification by flash column chromatography (petroleum ether; 35%, 9.6 mg)



¹**H NMR (400 MHz, CDCl₃):** δ 7.59 (d, J = 4.4 Hz, 1H), 7.37 – 7.34 (m, 5H), 7.17 (d, J = 4.4 Hz, 1H), 0.87 (t, J = 8.0 Hz, 9H), 0.64 (q, J = 8.0 Hz, 6H).

¹³C NMR (101 MHz, CDCl₃): δ 150.9, 139.3, 131.9, 131.2, 129.8, 129.1, 127.8, 127.1, 7.3, 4.8.

HRMS (ESI, m/z): Calculated for $C_{16}H_{22}SSi(M+H)^+ 275.1284$, found 275.1278.

43^c. (3-phenylthiophene-2,5-diyl)bis(triethylsilane)

A colorless liquid after purification by flash column chromatography (petroleum ether; 12%, 4.7 mg)



¹**H NMR (400 MHz, CDCl₃):** δ 7.37 – 7.32 (m, 5H), 7.26 (s, 1H), 1.03 (t, *J* = 8.0 Hz,

9H), 0.87 (t, *J* = 8.0 Hz, 9H), 0.83 (q, *J* = 8.0 Hz, 6H), 0.65 (t, *J* = 8.0 Hz, 6H). ¹³C NMR (101 MHz, CDCl₃): δ 151.7, 141.8, 139.5, 138.5, 137.8, 129.1, 127.7, 127.0, 7.4, 7.4, 4.9, 4.6.

HRMS (ESI, m/z): Calculated for $C_{22}H_{36}SSi_2(M+H)^+$ 389.2149, found 389.2146.

44. 1-(3-(triethylsilyl)-1H-indol-1-yl)ethanone

A colorless liquid after purification by flash column chromatography (petroleum ether/ethyl acetate = 60/1; 30%, 8.2 mg)



¹**H NMR (400 MHz, CDCl₃):** δ 8.44 (d, J = 8.4 Hz, 1H), 7.62 (d, J = 7.6 Hz, 1H), 7.38 (s, 1H), 7.36 – 7.32 (m, 1H), 7.29 – 7.25 (m, 1H), 2.67 (s, 3H), 1.00 (t, J = 7.6 Hz, 9H), 0.90 (q, J = 7.6 Hz, 6H).

¹³C NMR (101 MHz, CDCl₃): δ 168.3, 136.8, 134.7, 131.8, 124.8, 123.4, 121.9, 116.5, 115.6, 24.1, 7.5, 3.8.

HRMS (ESI, m/z): Calculated for $C_{16}H_{23}NOSi (M+H)^+ 274.1622$, found 274.1621.

45. 2-phenyl-5-(triethylsilyl)pyridine

A colorless liquid after purification by flash column chromatography (petroleum ether/ethyl acetate = 40/1; 32%, 8.6 mg)



¹**H NMR (400 MHz, CDCl₃):** δ 8.76 (s, 1H), 8.02 (d, *J* = 8.0 Hz, 2H), 7.84 (d, *J* = 7.6 Hz, 1H), 7.71 (d, *J* = 7.6 Hz, 1H), 7.48 (t, *J* = 7.6 Hz, 2H), 7.41 (t, *J* = 7.2 Hz, 1H), 1.00 (t, *J* = 7.6 Hz, 9H), 0.85 (q, *J* = 7.6Hz, 6H).

¹³C NMR (101 MHz, CDCl₃): δ 157.3, 154.6, 142.8, 139.4, 130.3, 129.0, 128.7, 126.8, 119.8, 7.3, 3.2.

HRMS (ESI, m/z): Calculated for $C_{17}H_{23}NSi (M+H)^+ 270.1673$, found 270.1671.

46. 5-(triethylsilyl)-2,2'-bipyridine

A colorless liquid after purification by flash column chromatography (petroleum ether/ethyl acetate = 5/1; 40%, 10.8 mg)



¹**H** NMR (400 MHz, CDCl₃): δ 8.74 (dd, J = 1.6, 0.8 Hz, 1H), 8.70 – 8.66 (m, 1H), 8.40 (d, J = 8.0 Hz, 1H), 8.35 (dd, J = 8.0, 0.8 Hz, 1H), 7.90 (dd, J = 8.0, 1.6 Hz, 1H), 7.81 (td, J = 7.6, 2.0 Hz, 1H), 7.30 (ddd, J = 7.6, 4.8, 1.2 Hz, 1H), 0.99 (t, J = 7.6 Hz, 9H), 0.85 (q, J = 7.6 Hz, 6H).

¹³C NMR (101 MHz, CDCl₃): δ 156.2, 156.0, 154.0, 149.2, 143.0, 136.9, 132.5, 123.7, 121.0, 120.3, 7.2, 3.1.

HRMS (ESI, m/z): Calculated for $C_{16}H_{22}N_2Si(M+H)^+ 271.1625$, found 271.1623.

47. 1-phenyl-3-(triethylsilyl)-1H-pyrrole

A colorless liquid after purification by flash column chromatography (petroleum ether/ethyl acetate = 100/1; 62%, 15.9 mg)



¹**H NMR (400 MHz, CDCl₃):** δ 7.42 – 7.41 (m, 4H), 7.26 – 7.22 (m, 1H), 7.18 (t, J = 2.4 Hz, 1H), 7.10 (t, J = 1.6 Hz, 1H), 6.41 – 6.40 (m, 1H), 1.02 (t, J = 7.6 Hz, 9H), 0.75 (q, J = 7.6 Hz, 6H).

¹³C NMR (101 MHz, CDCl₃): δ 140.6, 129.4, 125.5, 125.2, 120.5, 120.4, 116.5, 115.9, 7.6, 4.3.

HRMS (ESI, m/z): Calculated for $C_{16}H_{23}NSi (M+H)^+ 258.1673$, found 258.1676.

48. N-(4-(tert-butyldimethylsilyl)phenyl)acetamide

A white solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 3/1; 61%, 15.2 mg)



¹H NMR (400 MHz, CDCl₃): δ 7.49 (d, J = 8.4 Hz, 2H), 7.45 (d, J = 8.4 Hz, 2H),

7.40 (s, 1H), 2.17 (s, 3H), 0.86 (s, 9H), 0.25 (s, 6H). ¹³C NMR (101 MHz, CDCl₃): δ 168.4, 138.4, 135.2, 133.3, 118.8, 26.4, 24.6, 16.9, -6.2.

HRMS (ESI, m/z): Calculated for $C_{14}H_{23}NOSi (M+H)^+ 250.1622$, found 250.1623.

49. N-(4-(trihexylsilyl)phenyl)acetamide

A colorless liquid after purification by flash column chromatography (petroleum ether/ethyl acetate = 3/1; 56%, 23.4 mg)



¹**H** NMR (400 MHz, CDCl₃): δ 7.48 (d, J = 8.0 Hz, 2H), 7.42 (d, J = 8.4 Hz, 2H), 7.40 (s, 1H), 2.17 (s, 3H), 1.30 – 1.24 (m, 24H), 0.87 (t, J = 6.4 Hz, 9H), 0.77 – 0.73 (m, 6H).

¹³C NMR (101 MHz, CDCl₃): δ 168.3, 138.2, 134.9, 133.8, 119.0, 33.4, 31.5, 24.6, 23.7, 22.6, 14.1, 12.5.

HRMS (ESI, m/z): Calculated for $C_{26}H_{47}NOSi (M+H)^+ 435.3765$, found 435.3764.

50. methyl 3,5-dimethoxy-4-(2-(trimethylsilyl)propan-2-yl)benzoate

A colorless liquid after purification by flash column chromatography (petroleum ether/ethyl acetate = 100/1; 83%, 25.7 mg)



¹**H NMR (400 MHz, CDCl₃):** δ 7.14 (s, 2H), 3.92 (s, 3H), 3.77 (s, 6H), 0.87 (s, 9H), 0.29 (s, 6H).

¹³C NMR (101 MHz, CDCl₃): δ 167.0, 165.6, 132.9, 118.8, 104.2, 55.1, 52.2, 26.9, 18.2, -1.8.

HRMS (ESI, m/z): Calculated for $C_{16}H_{26}O_4Si(M+H)^+$ 311.1673, found 311.1674.

51. methyl 3,5-dimethoxy-4-(trihexylsilyl)benzoate

A colorless liquid after purification by flash column chromatography (petroleum ether/ethyl acetate = 100/1; 80%, 38.2 mg)



¹**H NMR (400 MHz, CDCl₃):** δ 7.14 (s, 2H), 3.91 (s, 3H), 3.79 (s, 6H), 1.27 – 1.23 (m, 24H), 0.86 (t, *J* = 6.4 Hz, 9H), 0.82 – 0.80 (m, 6H).

¹³C NMR (101 MHz, CDCl₃): δ 167.1, 165.5, 132.7, 119.0, 104.2, 55.2, 52.1, 33.6, 31.6, 24.1, 22.6, 14.2, 14.1.

HRMS (ESI, m/z): Calculated for $C_{28}H_{50}O_4Si (M+H)^+ 479.3551$, found 479.3550.

52. methyl 3,5-dimethoxy-4-(triisopropylsilyl)benzoate

A colorless liquid after purification by flash column chromatography (petroleum ether/ethyl acetate = 100/1; 48%, 16.9 mg)



¹**H NMR (400 MHz, CDCl₃):** δ 7.16 (s, 2H), 3.92 (s, 3H), 3.78 (s, 6H), 1.54 - 1.46 (m, 3H), 1.02 (d, *J* = 7.2 Hz, 18H).

¹³C NMR (101 MHz, CDCl₃): δ 167.1, 165.7, 132.7, 117.4, 103.9, 54.8, 52.1, 19.0, 13.0.

HRMS (ESI, m/z): Calculated for $C_{19}H_{32}O_4Si (M+H)^+ 353.2143$, found 353.2152.

53. methyl 4-(dimethyl(phenyl)silyl)-3,5-dimethoxybenzoate

A colorless liquid after purification by flash column chromatography (petroleum ether/ethyl acetate = 100/1; 67%, 22.1 mg)



¹**H NMR (400 MHz, CDCl₃):** δ 7.56 – 7.54 (m, 2H), 7.34 – 7.31 (m, 3H), 7.18 (s, 2H), 3.94 (s, 3H), 3.72 (s, 6H), 0.62 (s, 6H).

¹³C NMR (101 MHz, CDCl₃): δ 166.9, 165.4, 140.4, 133.5, 133.3, 128.2, 127.4, 127.3, 127.3, 118.4, 104.6, 55.3, 52.2, 0.3.

HRMS (ESI, m/z): Calculated for $C_{18}H_{22}O_4Si (M+H)^+ 331.1360$, found 331.1359.

54. methyl 4-((4-(dimethylsilyl)phenyl)dimethylsilyl)-3,5-dimethoxybenzoate

A colorless liquid after purification by flash column chromatography (petroleum

ether/ethyl acetate = 100/1; 51%, 19.8 mg)



¹**H** NMR (400 MHz, CDCl₃): δ 7.53 (d, J = 7.8 Hz, 1H), 7.48 (d, J = 7.9 Hz, 1H), 7.15 (s, 1H), 4.45 – 4.35 (m, 1H), 3.92 (s, 1H), 3.72 (s, 2H), 0.58 (s, 2H), 0.33 (d, J = 3.7 Hz, 3H).

¹³C NMR (101 MHz, CDCl₃): δ 167.0, 165.4, 141.5, 137.2, 133.3, 133.0, 132.9, 118.3, 104.6, 55.3, 52.2, 0.3, -3.9.

HRMS (ESI, m/z): Calculated for $C_{20}H_{28}O_4Si_2(M+H)^+$ 389.1599, found 389.1607.

Copies of the ¹H NMR, ¹⁹F NMR, ¹³C NMR spectra





1.¹³C NMR
















































 12^{c} .¹H NMR


































































































































43^{c} .¹H NMR

























$49.^{1}$ H NMR















































