Supplementary Information

for

Nickel/copper-cocatalyzed decarbonylative silylation of acyl fluorides

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1. General

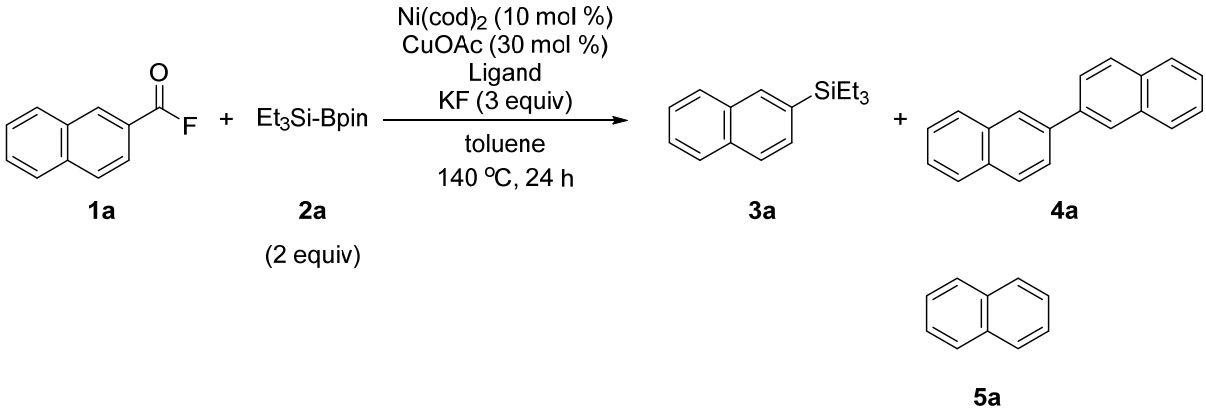
Unless otherwise noted, all the reactions were carried out under an Argon atmosphere using standard Schlenk techniques. Glassware was dried in an oven (150 ºC) and heated under reduced pressure prior to use. Solvents were employed as eluents for all other routine operation, as well as dehydrated solvents were purchased from commercial suppliers and employed without any further purification. For thin layer chromatography (TLC) analyses throughout this work, Merck precoated TLC plates (silica gel 60 GF254, 0.25 mm) were used. Silica gel column chromatography was carried out using silica gel 60 N (spherical, neutral, 40-100 μm) from Kanto Chemicals Co., Ltd. NMR spectra (^{1}H, ^{13}C{^{1}H} and ^{19}F{^{1}H}) were recorded on Varian INOVA-600 (600 MHz) or Mercury-400 (400 MHz) spectrometers. Chemical shifts (δ) are in parts per million related to $CDCl_3$ at 7.26 ppm for ^{1}H and at 77.16 ppm for ^{13}C{^{1}H}. The ^{19}F{^{1}H} NMR spectra were measured by using CCl_3F (δ = 0.00 ppm) as an external standard. The GC yields were determined by GC analysis of the crude mixture, using *n*-dodecane as an internal standard. GC analyses were performed on a Shimadzu GC-14A equipped with a flame ionization detector using Shimadzu Capillary Column (CBP1-M25-025) and Shimadzu C-R6A-Chromatopac integrator. Infrared spectra were recorded on a SHIMADZU IRP restige-21 spectrophotometer. HRMS analyses were obtained by using a double focusing magnetic sector mass spectrometer (JEOL JMS-700 MStation). Elemental analyses were carried out with a Perkin-Elmer 2400 CHN elemental analyzer at Okayama University.

Chemicals

Unless otherwise noted, materials obtained from commercial suppliers were used without further purification. Bis(1,5-cyclooctadiene)nickel was purchased from Merck. Triphenylphosphine and potassium fluoride (purity > 95%) were obtained from Nacalai Tesque. *n*-Dodecane (purity > 99%) was purchased from Kanto Chemical Co. Acyl fluorides **1a**-**1v**[1,2] and silylboranes **2a**-**2e**[3,4] were prepared according to the literatures and showed the identical spectra reported.

2. Optimization Details for Decarbonylative Silylation

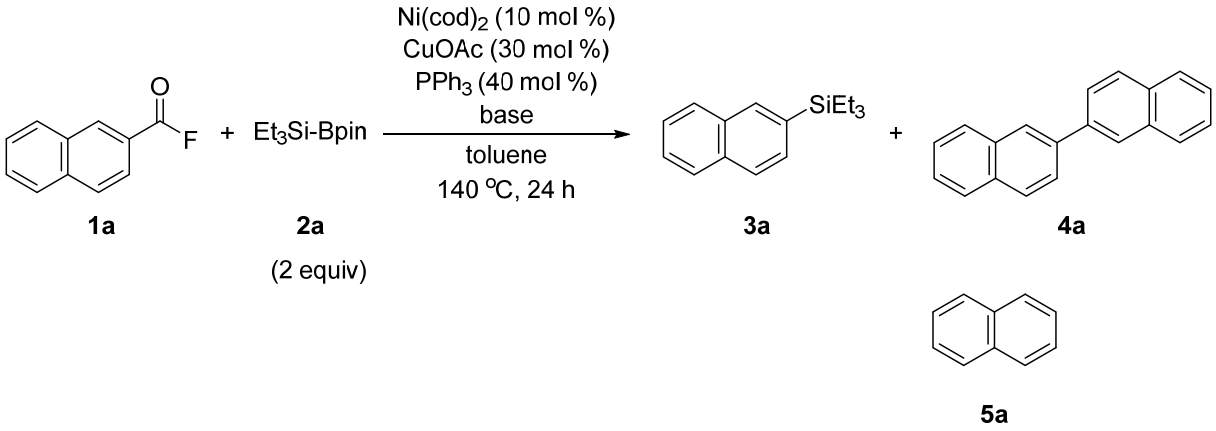
Table S1. Optimization of Ligand in Ni/Cu-Cocatalyzed Decarbonylative Silylation of 1a[a]



entry	ligand (mol %)	**1a** (%)[b]	**2a** (%)[b]	**3a** (%)[b]	**4a** (%)[b]	**5a** (%)[b]
1	dcype (20)	0	0	50	0	16
2	PCy_3 (40)	0	0	50	4	14
3	P^nBu_3 (40)	0	0	32	0	7
4	$P(OPh)_3$ (40)	0	66	11	0	26
5	**PPh_3 (40)**	**0**	**63**	**85**	**0**	**10**
6	PPh_3 (30)	0	0	53	0	11
7	PPh_3 (20)	0	41	49	6	15
8	PPh_3 (10)	12	68	48	6	10

[a] Reaction conditions: **1a** (0.2 mmol), **2a** (0.4 mmol), $Ni(cod)_2$ (0.02 mmol), CuOAc (0.06 mmol) and KF (0.6 mmol) in toluene (1.0 mL) at 140 °C for 24 h. [b] Determined by GC analysis of the crude mixture using *n*-dodecane as an internal standard.

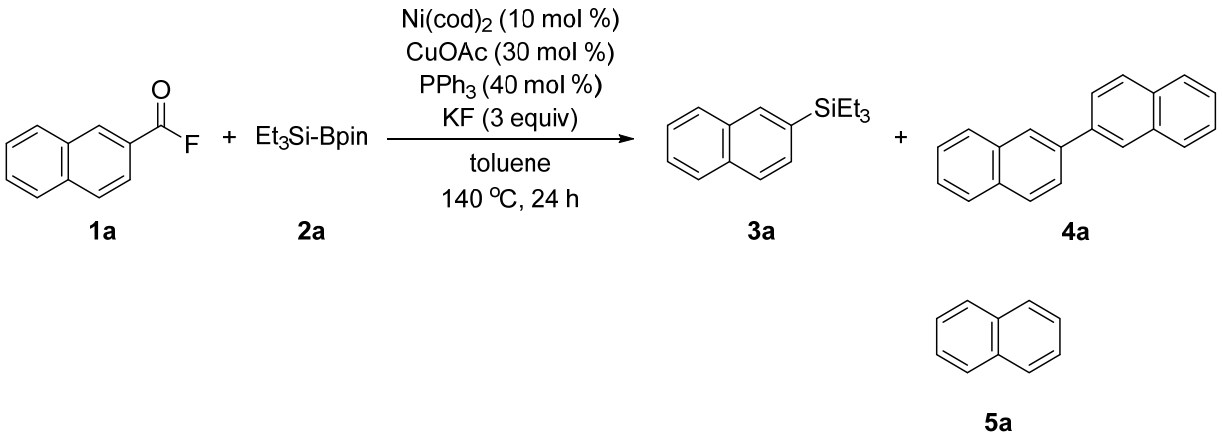
Table S2. Optimization of Base[a]



entry	base (equiv)	**1a** (%)[b]	**2a** (%)[b]	**3a** (%)[b]	**4a** (%)[b]	**5a** (%)[b]
1	LiF (3)	0	14	45	0	0
2	NaF (3)	0	0	49	0	0
3	**KF (3)**	**0**	**63**	**85**	**0**	**10**
4	CsF (3)	0	0	18	0	8
5	KOAc (3)	0	0	71	6	5
6	KO^{t}Bu (3)	0	18	0	0	6
7	KF (2)	0	27	68	6	13
8	KF (1)	0	0	42	16	16

[a] Reaction conditions: **1a** (0.2 mmol), **2a** (0.4 mmol), $Ni(cod)_2$ (0.02 mmol), CuOAc (0.06 mmol) and PPh_3 (0.08 mmol) in toluene (1.0 mL) at 140 °C for 24 h. [b] Determined by GC analysis of the crude mixture using *n*-dodecane as an internal standard.

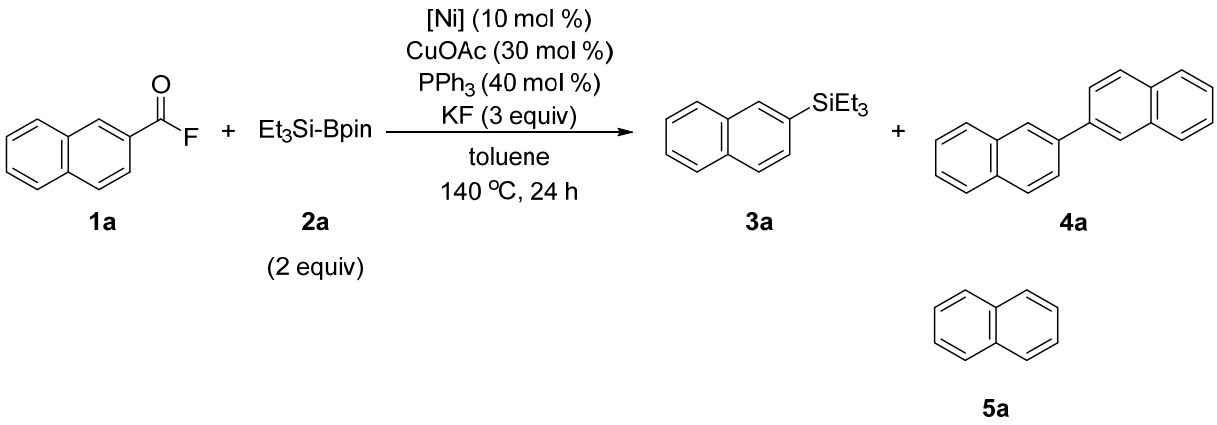
Table S3. Optimization the Amount of Silylborane 2a[a]



entry	**2a** (equiv)	**1a** (%)[b]	**2a** (%)[b]	**3a** (%)[b]	**4a** (%)[b]	**5a** (%)[b]
1	1	0	0	28	6	5
2	1.5	0	0	37	4	12
3	**2**	**0**	**63**	**85**	**0**	**10**

[a] Reaction conditions: **1a** (0.2 mmol), $Ni(cod)_2$ (0.02 mmol), CuOAc (0.06 mmol), PPh_3 (0.08 mmol) and KF (0. 6 mmol) in toluene (1.0 mL) at 140 °C for 24 h. [b] Determined by GC analysis of the crude mixture using *n*-dodecane as an internal standard.

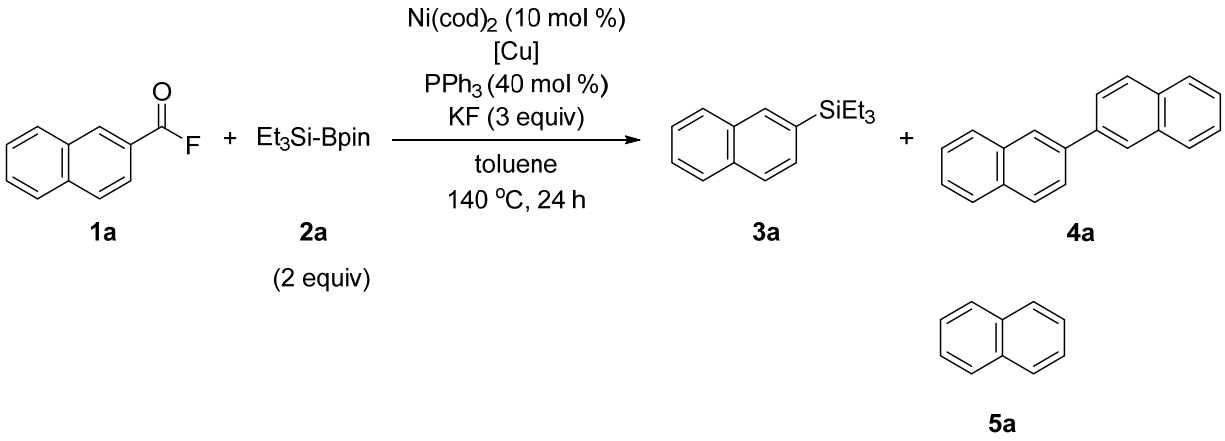
Table S4. Optimization of Nickel Catalyst[a]



entry	Ni catalyst	**1a** (%)[b]	**2a** (%)[b]	**3a** (%)[b]	**4a** (%)[b]	**5a** (%)[b]
1	**$Ni(cod)_2$**	**0**	**63**	**85**	**0**	**10**
2[c]	$NiCl_2$	0	0	25	0	9
3[c]	$Ni(OAc)_2·4H_2O$	0	0	8	7	7

[a] Reaction conditions: **1a** (0.2 mmol), **2a** (0.4 mmol), CuOAc (0.06 mmol), PPh_3 (0.08 mmol) and KF (0.6 mol) in toluene (1.0 mL) at 140 °C for 24 h. [b] Determined by GC analysis of the crude mixture using *n*-dodecane as an internal standard. [c] Average values in three runs.

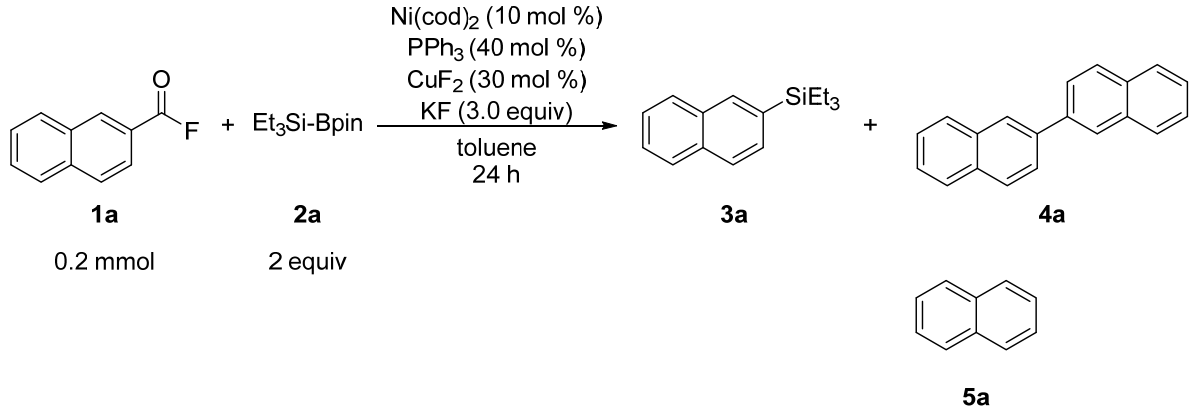
Table S5. Optimization of Copper Salt[a]



entry	[Cu] (mol %)	**1a** (%)[b]	**2a** (%)[b]	**3a** (%)[b]	**4a** (%)[b]	**5a** (%)[b]
1	CuF_2 (30)	0	60	77	0	6
2[c]	$CuCl_2$ (30)	57	99	0	9	8
3[c]	$Cu(OTf)_2$ (30)	0	0	5	2	16
4	$Cu(OAc)_2$ (30)	0	0	31	0	0
5	CuI (30)	60	148	15	0	0
6	CuOAc (30)	0	63	85	0	10
7	AgOAc (30)	0	38	13	10	3
8	KOH (30)	0	40	0	0	0
9	TBAT (30)	0	131	31	0	19
10	TBAF (30)	43	132	9	0	0
11[d]	CuOAc (30)	0	0	53	6	15
12[d]	**CuF_2 (30)**	**0**	**19**	**89**	**0**	**5**

[a] Reaction conditions: **1a** (0.2 mmol), **2a** (0.4 mmol), $Ni(cod)_2$ (0.02 mmol), PPh_3 (0.08 mmol) and KF (0. 6 mmol) in toluene (1.0 mL) at 140 °C for 24 h. [b] Determined by GC analysis of the crude mixture using *n*-dodecane as an internal standard. [c] Average values in three runs. [d] 150 °C.

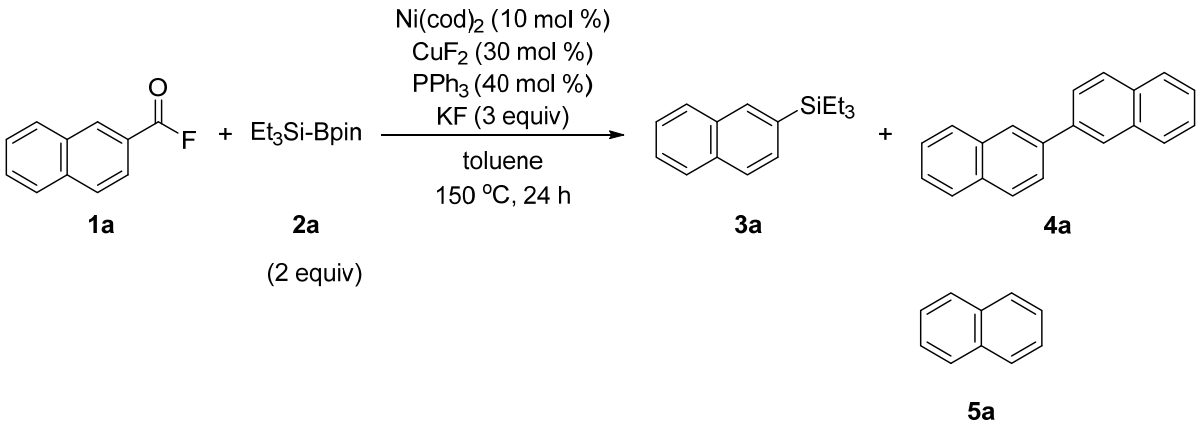
Table S6. Screening of the reaction temperature[a]



entry[a]	**temp.** (°C)	**1a**[b] (%)	**2a**[b] (%)	**3a**[b] (%)	**4a**[b] (%)	**5a**[b] (%)
1	80	62	135	0	14	0
2	100	58	119	13	14	0
3	120	45	82	21	13	0
4	140	0	60	77	0	6
5	**150**	**0**	**19**	**89 (85)**	**0**	**5**

[a]**1a** (0.2 mmol), **2a** (0.4 mmol), $Ni(cod)_2$ (0.02 mmol), PPh_3 (0.08 mmol), CuF_2 (0.06 mmol) and KF (0.6 mmol) in toluene (1.0 mL) for 24 h. [b]Determined by GC analysis of the crude mixture, using *n*-dodecane as an internal standard.

Table S7. Control Experiments[a]

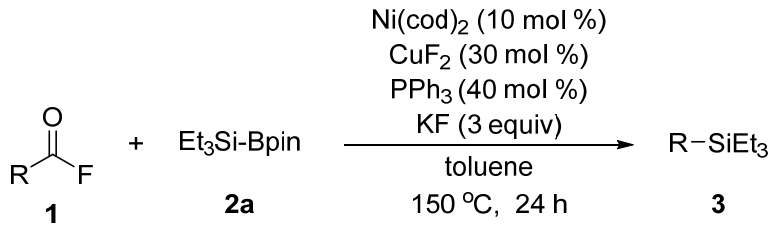


1a **2a** **3a** **4a** **5a**

entry	deviation from standard conditions	**1a** (%)[b]	**2a** (%)[b]	**3a** (%)[b]	**4a** (%)[b]	**5a** (%)[b]
1	**none**	**0**	**19**	**89 (85)**	**0**	**5**
2	without $Ni(cod)_2$	0	3	0	0	0
3	without CuF_2	0	119	5	58	22
4	without PPh_3	0	31	<1	0	8
5	without KF	0	23	46	4	11
6	2-naphthoyl chloride instead of **1a**	nd	186	0	0	5

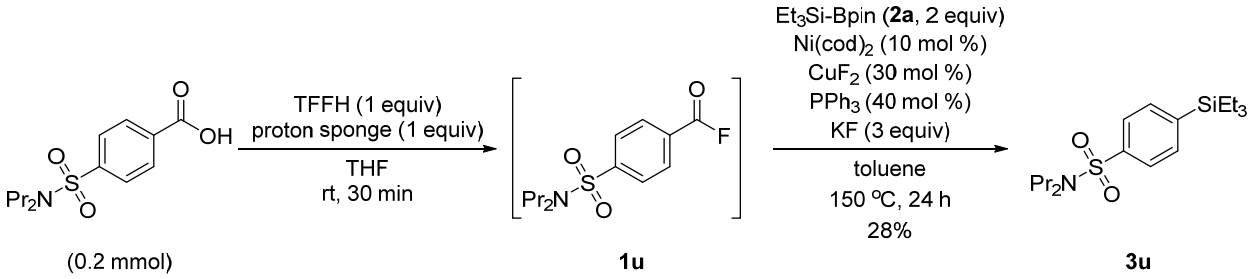
[a] Reaction conditions: **1a** (0.2 mmol), **2a** (0.4 mmol), $Ni(cod)_2$ (0.02 mmol), CuF_2 (0.06 mmol), PPh_3 (0.08 mmol) and KF (0.6 mol) in toluene (1.0 mL) at 150 °C for 24 h. [b] Determined by GC analysis of the crude mixture using *n*-dodecane as an internal standard. An isolated yield is given in parentheses.

Scheme S1. Scope for Alkenyl and Alkyl Acyl Fluorides in Ni/Cu-Cocatalyzed Decarbonylative Silylation[a]



[a] Reaction conditions: **1** (0.2 mmol), **2a** (0.4 mmol), $Ni(cod)_2$ (0.02 mmol), CuF_2 (0.06 mol), PPh_3 (0.08 mmol), and KF (0.6 mmol) in toluene (1 mL) at 150 ºC for 24 h.

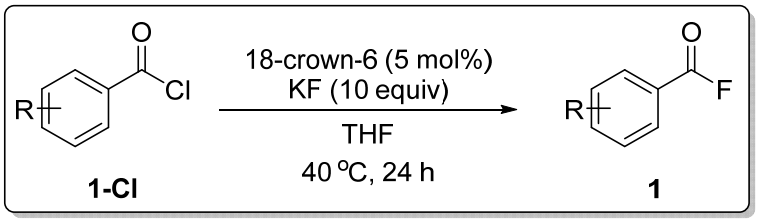
Scheme S2. One-Pot Reaction from Probenecid without Isolating Aroyl Fluoride 1u



To a 20 mL of Schlenk tube charged with a magnetic stirrer bar, were successively added probenecid (0.2 mmol, 57.1 mg), TFFH (0.2 mmol, 1 equiv, 52.8 mg), proton sponge (0.2 mmol, 1 equiv, 42.9 mg) and THF (0.4 mL). After the reaction mixture was stirred at room temperature for 30 min, a pre-mixed solution of $Ni(cod)_2$ (0.02 mmol, 10 mol %, 5.5 mg), PPh_3 (0.08 mmol, 40 mol %, 21.0 mg) in toluene (1 mL) was added. Successively, KF (0.6 mmol, 3 equiv, 36.6 mg), Et_3Si-Bpin (**2a**) (0.4 mmol, 2 equiv, 96.9 mg) and CuF_2 (0.06 mmol, 30 mol %, 6.1 mg) were added. The mixture was heated at 150 ºC with stirring. After 24 h, *n*-dodecane was added as an internal standard and the mixture was stirred vigorously. Take a portion of the mixture, diluted by Et_2O (2 mL), GC analysis was conducted using resulting organic phase, which indicated the formation of **3u** in 28% yield.

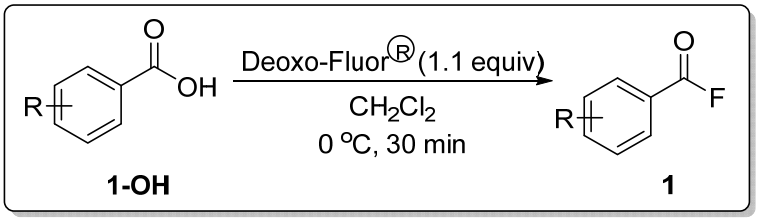
3. Synthesis and Characterization of Starting Materials

3.1 Representative Procedure for the Synthesis of Acyl Fluorides from Acyl Chlorides[1]



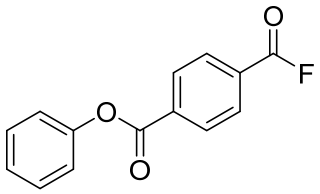
To a 50 mL of Schlenk tube charged with a magnetic stirrer bar, were successively added acyl chloride **1-Cl** (4.0 mmol), 18-crown-6 (0.2 mmol, 5 mol %, 52.9 mg), KF (40 mmol, 10 equiv, 2.32 g) and THF (20 mL). After the reaction was stirred at 40 ºC for 24 h, the insoluble inorganic solid (KF or KCl) was filtered, and the volatiles were concentrated using a rotary evaporator. The crude product was purified by bulb-to-bulb distillation to afford the corresponding acyl fluorides **1**.

3.2 Representative Procedure for the Synthesis of Acyl Fluorides from Carboxylic Acids[2]



To a 20 mL of Schlenk tube charged with a magnetic stirrer bar, were successively added carboxylic acid **1-OH** (3.0 mmol) and CH_2Cl_2 (15 mL). After the mixture was stirred at 0 ºC, Deoxo-Fluor® reagent (3.3 mmol, 1.1 equiv, 608 μL) was slowly added to the reaction mixture. After the reaction mixture was stirred at 0 ºC for 30 min, the solution was slowly poured into saturated $NaHCO_3$, and after CO_2 evolution ceased it was extracted into CH_2Cl_2 (3 × 15 mL), and dried over $MgSO_4$. The crude product was purified by flash chromatography to afford the corresponding acyl fluorides **1**.

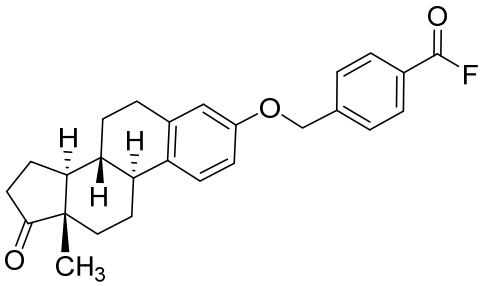
Phenyl 4-(fluorocarbonyl)benzoate (**1n**)



Purification: column chromatography (*n*-hexane/EtOAc = 10:1, R_f = 0.39). White solid. Isolated yield: 63% (461.6 mg). Melting point: 120-121 °C. ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.22-7.24 (m, 2H), 7.28-7.33 (m, 1H), 7.43-7.47 (m, 2H), 8.19-8.22 (m, 2H), 8.27-8.36 (m, 2H). ^{13}C{^{1}H} NMR

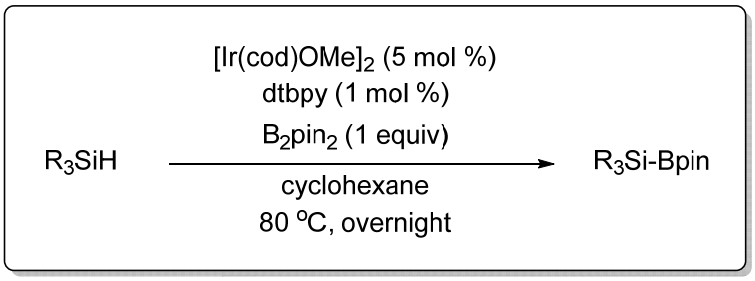
(151 MHz, $CDCl_3$): δ 121.6, 126.5, 129.3 (d, J = 61.9 Hz), 129.8, 130.8, 131.7 (d, J = 3.5 Hz), 135.7, 150.7, 156.6 (d, J = 345.9 Hz), 163.9. $^{19}F\{^1H\}$ NMR (376 MHz, $CDCl_3$): δ 20.3. FT-IR (neat): 689, 718, 1013, 1082, 1192, 1225, 1240, 1267, 1410, 1491, 1740, 1817 cm^{-1}. Anal. Calcd for $C_{14}H_9FO_3$: C, 68.57; H, 3.42%. Found: C, 68.85; H, 3.71%. HRMS (FAB^+): Calcd for $C_{14}H_9FO_3$: 244.0536. Found: 244.0532.

4-((((8*R*,9*S*,13*S*,14*S*)-13-Methyl-17-*oxo*-7,8,9,11,12,13,14,15,16,17-decahydro-6*H*-cyclopenta[a]phenanthren-3-yl)oxy)methyl)benzoyl fluoride (1v)



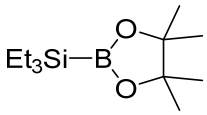
Purification: column chromatography (*n*-hexane/EtOAc = 5:1, R_f = 0.40). White solid. Isolated yield: 53% (646.3 mg). ^1H NMR (400 MHz, $CDCl_3$): δ 0.91 (s, 3H), 1.39-1.49 (m, 2H), 1.53-1.68 (m, 6H), 1.94-2.19 (m, 4H), 2.22-2.28 (m, 1H), 2.37-2.42 (m, 1H), 2.47-2.54 (m, 1H), 2.88-2.92 (m, 2H), 5.14 (s, 2H), 6.72 (d, J = 2.8 Hz, 1H), 6.77 (dd, J = 8.6, 2.8 Hz, 1H), 7.22 (dd, J = 8.4, 3.2 Hz, 1H), 7.58-7.60 (m, 2H), 8.05 (d, J = 8.4 Hz, 2H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 13.9, 21.7, 26.0, 26.6, 29.7, 31.7, 35.9, 38.4, 44.1, 48.1, 50.5, 69.0, 112.4, 115.0, 124.3 (J = 61.3 Hz), 126.6, 127.4, 131.8 (J = 3.8 Hz), 133.0, 138.1, 145.6, 156.35, 157.3 (J = 345.6 Hz), 220.9. $^{19}F\{^1H\}$ NMR (376 MHz, $CDCl_3$): δ 18.3. FT-IR (KBr): 741, 1001, 1032, 1061, 1159, 1240, 1375, 1456, 1495, 1612, 1734, 1734, 2857, 2924 cm^{-1}. HRMS (FAB^+): Calcd for $C_{26}H_{27}FO_3$: 406.1944. Found: 406.1915.

3.3 Representative Procedure for the Synthesis of Silylboranes from Silanes[3]



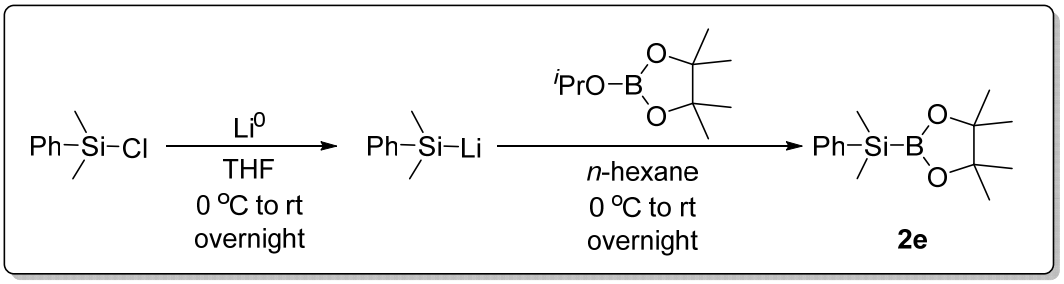
To a 20 mL of Schlenk tube charged with a magnetic stirrer bar, were successively added $[Ir(cod)OMe]_2$ (0.5 mol %, 13.2 mg), 4,4'-di-*tert*-butyl-2,2'-bipyridyl (dtbpy) (1 mol %, 10.8 mg), bis(pinacolato)diboron (B_2pin_2; 4.0 mmol, 1.02 g), cyclohexane (1.0 mL) and the hydorosilane (4 equiv, 16.0 mmol). The resulting dark brown solution was heated at 80 °C overnight. After being cooled to room temperature, the crude reaction mixture was concentrated under reduced pressure, and the residue was purified by flash column chromatography to afford the corresponding silylboranes **2a**-**2d** in 30-60% yields.

Triethyl(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)silane (2a)[3]



Purification: column chromatography (*n*-hexane, R_f = 0.39). Colorless oil. Isolated yield: 60% (581.4 mg). ^{1}H NMR (600 MHz, $CDCl_3$): δ 0.59 (q, J = 7.8 Hz, 6H), 0.96 (t, J = 7.8 Hz, 9H), 1.22 (s, 12H). $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$): δ 3.1, 8.5, 25.2, 83.0. $^{11}B\{^1H\}$ NMR (192 MHz, $CDCl_3$): δ 35.1.

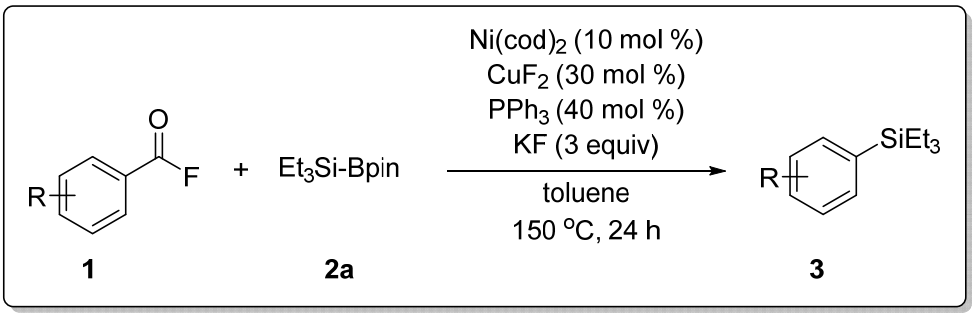
3.4 Representative Procedure for the Synthesis of Silylborane 2e[4]



Metallic lithium (120 mmol, 826 mg) was added to THF (30 mL) under an argon flow. The flask was placed in an ice bath and dimethylphenyl(chloro)silane (30 mmol, 5 mL) was added dropwise. The red mixture was vigorously stirred overnight and added dropwise to a solution of 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (60 mmol, 12.2 mL) in *n*-hexane (30 mL). The mixture was stirred at room temperature overnight, and the volatile materials were removed under reduced pressure. The residue was extracted with *n*-hexane (30 mL) and filtered through Celite under argon (Celite was dried under reduced pressure before use). The solvent was removed under reduced pressure and the product was purified by bulb-to-bulb distillation (bp = 120 °C at 0.1 mbar).

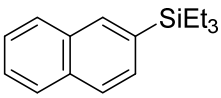
4. Decarbonylative Silylation of Acyl Fluorides

4.1 Representative Procedure for Decarbonylative Silylation of Acyl Fluorides 1 with Silylborane 2a



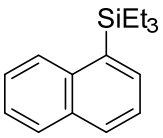
A 20 mL dried Schlenk tube containing a stirrer bar and KF (0.6 mmol, 3 equiv, 36.6 mg) was dried with a heat gun under reduced pressure and filled with argon after cooling to room temperature. To this vessel, were added $Ni(cod)_2$ (0.02 mmol, 10 mol %, 5.5 mg), PPh_3 (0.08 mmol, 40 mol %, 21.0 mg,), toluene (1 mL), acyl fluoride (**1**, 0.2 mmol), triethyl(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)silane (**2a**, 0.4 mmol, 2 equiv, 96.9 mg), and CuF_2 (0.06 mmol, 30 mol %, 6.1 mg). The mixture was heated at 150 ºC with stirring for 24 h. The solution was then cooled to room temperature, and the solvent was removed under vacuum. The decarbonylative silylation product **3** was purified by flash column chromatography on silica gel.

Triethyl(naphthalen-2-yl)silane (3a)[3]



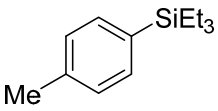
Purification: column chromatography (*n*-hexane, R_f = 0.65). Colorless oil. Isolated yield: 85% (41.2 mg). ^{1}H NMR (600 MHz, $CDCl_3$): δ 0.89 (qd, J = 7.8, 1.2 Hz, 6H), 1.00-1.03 (m, 9H), 7.47-7.50 (sext, J = 3.0 Hz, 2H), 7.59 (dd, J = 8.4, 1.2 Hz, 1H), 7.82-7.86 (m, 3H), 8.00 (s, 1H).

Triethyl(naphthalen-1-yl)silane (3b)[3]



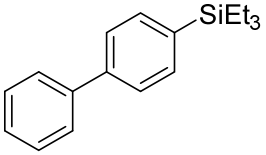
Purification: column chromatography (*n*-hexane, R_f = 0.63). Colorless oil. Isolated yield: 82% (39.8 mg). ^{1}H NMR (600 MHz, $CDCl_3$): δ 0.97-1.00 (m, 9H), 1.02-1.06 (m, 6H), 7.45-7.52 (m, 3H), 7.68 (dd, J = 7.2, 1.8 Hz, 1H), 7.86-7.88 (m, 2H), 8.10-8.12 (m, 1H).

Triethyl(*p*-tolyl)silane (3c)[3]



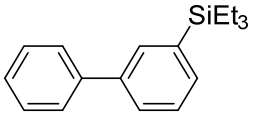
Purification: column chromatography (*n*-hexane, R_f = 0.70). Colorless oil. Isolated yield: 85% (35.0 mg). ^{1}H NMR (600 MHz, $CDCl_3$): δ 0.76-0.80 (m, 6H), 0.96 (t, J = 8.4 Hz, 9H), 2.35 (s, 3H), 7.18 (d, J = 7.2 Hz, 2H), 7.39 (d, J = 7.8 Hz, 2H).

[1,1'-Biphenyl]-4-yltriethylsilane (3d)[3]



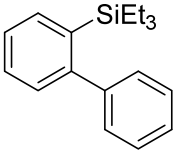
Purification: column chromatography (*n*-hexane, R_f = 0.60). Colorless oil. Isolated yield: 81% (43.5 mg). ^{1}H NMR (600 MHz, $CDCl_3$): δ 0.83-0.87 (m, 6H), 1.02 (t, J = 7.8 Hz, 9H), 7.35-7.37 (m, 1H), 7.44-7.47 (m, 2H), 7.58-7.64 (m, 6H).

[1,1'-Biphenyl]-3-yltriethylsilane (3e)[3]



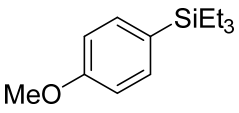
Purification: column chromatography (*n*-hexane, R_f = 0.60). Colorless oil. Isolated yield: 70% (37.6 mg). ^{1}H NMR (600 MHz, $CDCl_3$): δ 0.82-0.86 (m, 6H), 1.00 (t, J = 6.0 Hz, 9H), 7.36 (dt, J = 7.8, 7.2, 1.2 Hz, 1H), 7.42-7.49 (m, 4H), 7.57-7.61 (m, 3H), 7.70 (dt, J = 1.8, 0.6 Hz, 1H).

[1,1'-Biphenyl]-2-yltriethylsilane (3f)[3]



Purification: column chromatography (*n*-hexane, R_f = 0.68). Colorless oil. Isolated yield: 61% (32.8 mg). ^{1}H NMR (600 MHz, $CDCl_3$): δ 0.46 (q, J = 7.8 Hz, 6H), 0.81 (t, J = 7.8 Hz, 9H), 7.21-7.22 (m, 1H), 7.27-7.29 (m, 2H), 7.32-7.39 (m, 5H), 7.56-7.57 (m, 1H).

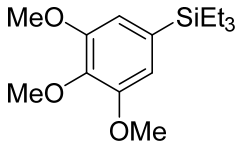
Triethyl(4-methoxyphenyl)silane (3g)[5]



Purification: column chromatography (*n*-hexane/EtOAc = 50:1, R_f = 0.38). Colorless oil. Isolated yield:

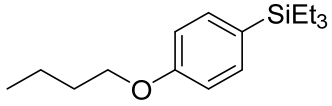
62% (27.6 mg). ^{1}H NMR (600 MHz, $CDCl_3$): δ 0.76 (qd, J = 7.8, 0.6 Hz, 6H), 0.95 (t, J = 7.8 Hz, 9H), 3.81 (s, 3H), 6.90-6.92 (m, 2H), 7.40-7.43 (m, 2H).

Triethyl(3,4,5-trimethoxyphenyl)silane (3h)



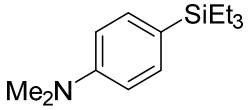
Purification: column chromatography (*n*-hexane/EtOAc = 20:1, R_f = 0.53). Colorless oil. Isolated yield: 52% (29.4 mg). ^{1}H NMR (600 MHz, $CDCl_3$): δ 0.76-0.80 (m, 6H), 0.98 (t, J = 7.8 Hz, 9H), 3.86 (s, 3H), 3.87 (s, 6H), 6.67 (s, 2H). $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$): δ 3.6, 7.6, 56.3, 60.9, 110.9, 132.6, 139.0, 153.0. FT-IR (neat, cm^{-1}): 696 (s), 719 (s), 1003 (s), 1126 (s), 1306 (s), 1395 (s), 1464 (s), 1504 (s), 1570 (s), 2876 (s), 2911 (s), 2938 (s), 3019 (s). HRMS (FAB^+): Calcd for $C_{15}H_{26}O_3Si$: 282.1651. Found: 282.1679

(4-Butoxyphenyl)triethylsilane (3i)



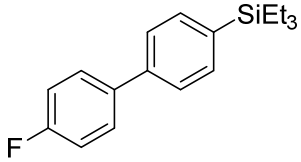
Purification: column chromatography (*n*-hexane, R_f = 0.50). Colorless oil. Isolated yield: 50% (26.4 mg). ^{1}H NMR (600 MHz, $CDCl_3$): δ 0.74-0.78 (m, 6H), 0.94-1.00 (m, 12H), 1.47-1.53 (m, 2H), 1.75-1.79 (m, 2H), 3.97 (t, J = 6.6 Hz, 2H), 6.89-6.91 (m, 2H), 7.39-7.41 (m, 2H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 3.7, 7.6, 14.0, 19.4, 31.5, 67.5, 114.1, 128.0, 135.7, 159.9. FT-IR (neat, cm^{-1}): 714 (s), 1007 (s), 1109 (s), 1182 (s), 1225 (s), 1244 (m), 1273 (s), 1503 (s), 1593 (s), 2873 (s), 2957 (s). HRMS (FAB^+): Calcd for $C_{16}H_{28}OSi$: 264.1909. Found: 264.1895.

***N,N*-Dimethyl-4-(triethylsilyl)aniline (3j)**[3]



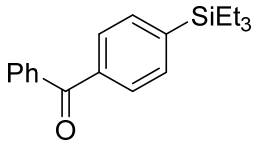
Purification: column chromatography (*n*-hexane/EtOAc = 20:1, R_f = 0.63). Colorless oil. Isolated yield: 50% (23.5 mg). ^{1}H NMR (600 MHz, $CDCl_3$): δ 0.74-0.78 (m, 6H), 0.97 (t, J = 8.4 Hz, 9H), 2.97 (s, 6H), 6.76 (d, J = 8.4 Hz, 2H), 7.37 (d, J = 8.4 Hz, 2H).

Triethyl(4'-fluoro-[1,1'-biphenyl]-4-yl)silane (3k)[3]



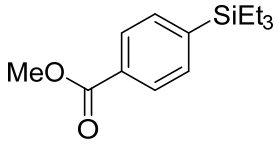
Purification: column chromatography (*n*-hexane, R_f = 0.63). Colorless oil. Isolated yield: 66% (37.8 mg). ^{1}H NMR (600 MHz, $CDCl_3$): δ 0.81-0.85 (m, 6H), 1.00 (t, J = 8.4 Hz, 9H), 7.12-7.15 (m, 2H), 7.53-7.58 (m, 6H). ^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$): δ -115.8.

Phenyl(4-(triethylsilyl)phenyl)methanone (3l)



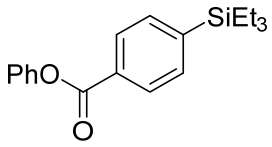
Purification: column chromatography (*n*-hexane/EtOAc = 20:1, R_f = 0.67). Colorless oil. Isolated yield: 53% (31.4 mg). ^{1}H NMR (600 MHz, $CDCl_3$): δ 0.82-0.86 (m, 6H), 0.97-1.00 (m, 9H), 7.47-7.50 (m, 2H), 7.58-7.62 (m, 3H), 7.75-7.77 (m, 2H), 7.81-7.83 (m, 2H). ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$): δ 3.4, 7.5, 128.4, 129.1, 130.2, 132.5, 134.2, 137.8, 143.7, 197.1. FT-IR (neat, cm^{-1}): 660 (s), 702 (s), 924 (s), 1283 (s), 1317 (s), 1655 (m), 2913 (s), 2957 (s), 3013 (s). HRMS (FAB$^+$): Calcd for $C_{19}H_{24}OSi$: 296.1596. Found: 296.1604.

Methyl 4-(triethylsilyl)benzoate (3m)[3]



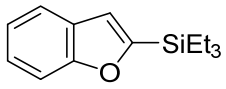
Purification: column chromatography (*n*-hexane/EtOAc = 20:1, R_f = 0.70). Colorless oil. Isolated yield: 63% (31.6 mg). ^{1}H NMR (600 MHz, $CDCl_3$): δ 0.79-0.83 (m, 6H), 0.96 (t, J = 7.2 Hz, 9H), 3.91 (s, 3H), 7.56-7.58 (m, 2H), 7.98-8.00 (m, 2H).

Phenyl 4-(triethylsilyl)benzoate (3n)[3]



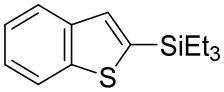
Purification: column chromatography (*n*-hexane/EtOAc = 20:1, R_f = 0.70). Colorless oil. Isolated yield: 60% (37.5 mg). ^{1}H NMR (600 MHz, $CDCl_3$): δ 0.83-0.87 (m, 6H), 0.97-1.00 (m, 9H), 7.21-7.23 (m, 2H), 7.27-7.29 (m, 1H), 7.42-7.45 (m, 2H), 7.64-7.66 (m, 2H), 8.16-8.18 (m, 2H).

Benzofuran-2-yltriethylsilane (3o)[3]



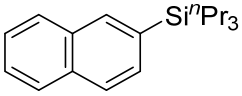
Purification: column chromatography (*n*-hexane, R_f = 0.65). Colorless oil. Isolated yield: 71% (33.0 mg). ^{1}H NMR (600 MHz, $CDCl_3$): δ 0.84-0.88 (m, 6H), 1.03 (t, J = 7.2 Hz, 9H), 6.99 (d, J = 0.6 Hz, 1H), 7.19-7.21 (m, 1H), 7.26-7.28 (m, 1H), 7.50-7.52 (m, 1H), 7.57-7.59 (m, 1H).

Benzo[*b*]thiophen-2-yltriethylsilane (3p)[3]



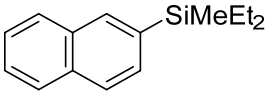
Purification: column chromatography (*n*-hexane, R_f = 0.66). Colorless oil. Isolated yield: 65% (32.3 mg). ^{1}H NMR (600 MHz, $CDCl_3$): δ 0.86-0.90 (m, 6H), 1.04 (t, J = 7.8 Hz, 9H), 7.30-7.36 (m, 2H), 7.47 (d, J = 0.6 Hz, 1H), 7.82-7.83 (dd, J = 6.6, 0.6 Hz, 1H), 7.89 (d, J = 8.4 Hz, 1H).

Naphthalen-2-yltripropylsilane (3q)[3]



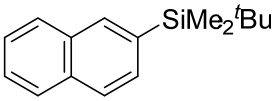
Purification: column chromatography (*n*-hexane, R_f = 0.67). Colorless oil. Isolated yield: 64% (36.4 mg). ^{1}H NMR (600 MHz, $CDCl_3$): δ 0.89-0.92 (m, 6H), 1.01 (t, J = 7.2 Hz, 9H), 1.39-1.46 (m, 6H), 7.49-7.51 (m, 2H), 7.60 (dd, J = 8.4, 1.2 Hz, 1H), 7.83-7.88 (m, 3H), 8.00 (s, 1H).

Diethyl(methyl)(naphthalen-2-yl)silane (3r)[3]



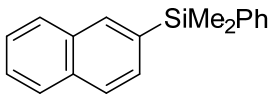
Purification: column chromatography (*n*-hexane, R_f = 0.68). Colorless oil. Isolated yield: 63% (28.8 mg). ^{1}H NMR (600 MHz, $CDCl_3$): δ 0.33 (s, 3H), 0.83-0.87 (m, 4H), 0.99 (t, J = 7.8 Hz, 6H), 7.47-7.50 (m, 2H), 7.59 (dd, J = 7.8, 1.2 Hz, 1H), 7.83 (dd, J = 7.8, 4.2 Hz, 2H), 7.85 (dd, J = 6.0, 3.6 Hz, 1H), 8.00 (s, 1H).

***Tert*-butyldimethyl(naphthalen-2-yl)silane (3s)**[3]



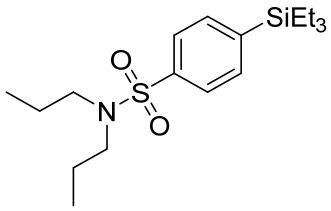
Purification: column chromatography (*n*-hexane, R_f = 0.66). Colorless oil. Isolated yield: 85% (41.2 mg). ^{1}H NMR (600 MHz, $CDCl_3$): δ 0.40 (s, 6H), 0.95 (s, 9H), 7.49-7.52 (m, 2H), 7.63 (dd, J = 8.4, 1.2 Hz, 1H), 7.83-7.89 (m, 3H), 8.03 (s, 1H).

Dimethyl(naphthalen-2-yl)(phenyl)silane (3t)[3]



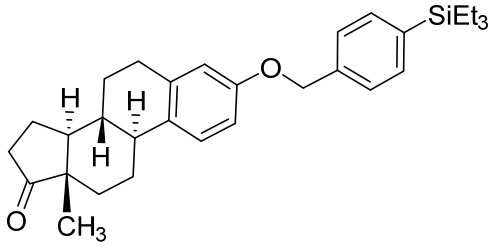
Purification: column chromatography (*n*-hexane, R_f = 0.47). White solid. Isolated yield: 96% (50.4 mg). ^{1}H NMR (600 MHz, $CDCl_3$): δ 0.68 (s, 6H), 7.38-7.42 (m, 3H), 7.50-7.54 (m, 2H), 7.60-7.64 (m, 3H), 7.85-7.87 (m, 3H), 8.08 (s, 1H).

_N,N_-Dipropyl-4-(triethylsilyl)benzenesulfonamide (3u)



Purification: column chromatography (*n*-hexane/EtOAc = 20:1, R_f = 0.60). Colorless solid. Isolated yield: 72% (51.9 mg). ^{1}H NMR (600 MHz, $CDCl_3$): δ 0.79-0.83 (m, 6H), 0.86 (t, J = 7.8 Hz, 6H), 0.94-0.97 (m, 9H), 1.54-1.57 (m, 4H), 3.07-3.09 (m, 4H), 7.59-7.60 (m, 2H), 7.74-7.75 (m, 2H). ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$): δ 3.3, 7.4, 11.3, 22.3, 50.2, 126.0, 134.7, 140.3, 143.6. FT-IR (neat, cm^{-1}): 608 (s), 721 (s), 999 (s), 1109 (s), 1157 (s), 1225 (m), 1337 (s), 2876 (s), 2959 (s), 3028 (s). Anal. Calcd for $C_{18}H_{33}NO_2SSi$: C, 60.80; H, 9.35; N, 3.94%. Found: C, 60.89; H, 9.60; N, 3.76%.

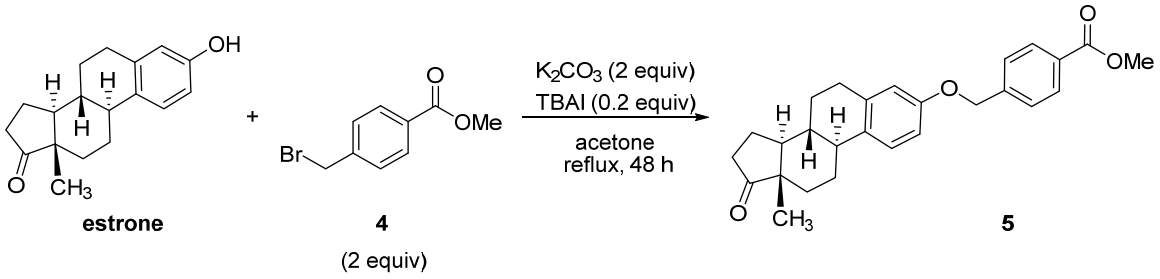
(8R,9S,13S,14S)-13-methyl-3-((4-(triethylsilyl)benzyl)oxy)-6,7,8,9,11,12,13,14,15,16-decahydro-17H-cyclopenta[*a*]phenanthren-17-one (3v)



Purification: column chromatography (*n*-hexane/EtOAc = 10:1, R_f = 0.34). Colorless oil. Isolated yield: 75% (71.2 mg). ^{1}H NMR (600 MHz, $CDCl_3$): δ 0.80 (qd, J = 7.8, 0.9 Hz, 6H), 0.92 (s, 3H), 0.97 (t, J = 8.4 Hz, 9H), 1.41-1.60 (m, 5H), 1.63-1.67 (m, 1H), 1.95-1.97 (m, 1H), 1.99-2.08 (m, 2H), 2.12-2.18 (m, 1H), 2.25-2.29 (m, 1H), 2.39-2.42 (m, 1H), 2.49-2.53 (m, 1H), 2.90-2.93 (m, 2H), 5.03 (s, 2H), 6.75 (d, J = 2.4 Hz, 1H), 6.81 (dd, J = 8.4, 3.0 Hz, 1H), 7.21 (dd, J = 8.4, 1.2 Hz, 1H), 7.42 (d, J = 7.8 Hz, 2H), 7.51 (d, J = 7.8 Hz, 2H). ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$): δ 3.3, 7.4, 13.9, 21.6, 25.9, 26.6, 29.7, 31.6, 35.9, 38.4, 44.0, 48.0, 50.4, 70.0, 112.3, 114.8, 126.4, 126.8, 132.3, 134.5, 137.1, 137.6, 137.8, 156.9, 221.0. FT-IR (KBr):

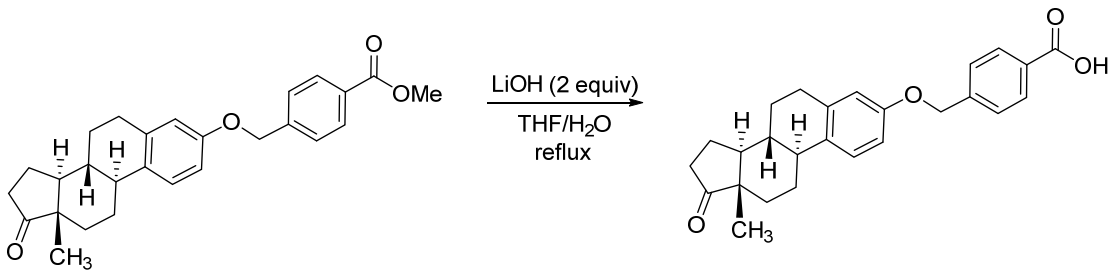
669, 752, 770, 895, 930, 1007, 1055, 1101, 1163, 1215, 1499, 1607, 1734, 2344, 2363, 2399, 2876, 2913, 2936, 2955, 3019 cm^{-1}. HRMS (FAB^+): Calcd for $C_{31}H_{42}O_2Si$: 474.2954. Found: 474.2931.

4.2 Synthesis of Methyl 4-((((8R,9S,13S,14S)-13-methyl-17-*oxo*-7,8,9,11,12,13,14,15,16,17-decahydro-6*H*-cyclopenta[*a*]phenanthren-3-yl)oxy)methyl)benzoate (5)



Compound **5** was synthesized according to a modified procedure.[6] An oven-dried 50 mL of Schlenk tube containing a stirrer bar was charged with estrone (270 mg, 1 mmol), ester **4** (458.2 mg, 2 mmol, 2 equiv), K_2CO_3 (276.4 mg, 2 mmol, 2 equiv), TBAI (73.9 mg, 0.2 mmol, 0.2 equiv), and acetone (10 mL). After the reaction mixture was heated to reflux for 48 h, the solvent was removed under vacuum. The crude mixture was extracted with dichloromethane (10 mL × 3) and organic layers were combined, dried over Na_2SO_4, filtered. The solvent was removed under reduced pressure. The crude product was purified by column chromatography (hexane:EtOAc = 5:1) to afford **5** quantitatively (418 mg) as white solid. ^1H NMR (600 MHz, $CDCl_3$): δ 0.91 (s, 3H), 1.39-1.65 (m, 6H), 1.93-1.97 (m, 1H), 1.98-2.08 (m, 2H), 2.14 (dt, J = 19.0, 8.8 Hz, 1H), 2.23-2.28 (m, 1H), 2.37-2.41 (m, 1H), 2.50 (dd, J = 19.0, 8.8 Hz, 1H), 2.88-2.91 (m, 2H), 3.92 (s, 3H), 5.10 (s, 2H), 6.72 (d, J = 2.6 Hz, 1H), 6.77 (dd, J = 8.6, 3.0 Hz, 1H), 7.21 (d, J = 8.4 Hz, 1H), 7.50 (d, J = 8.4 Hz, 2H), 8.05 (dd, J = 7.2, 1.8 Hz, 2H). $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$): δ 14.0, 21.7, 26.0, 26.6, 29.8, 31.7, 36.0, 38.4, 44.1, 48.1, 50.5, 52.3, 69.4, 112.4, 115.0, 126.5, 127.0, 129.6, 130.0, 132.7, 138.0, 142.6, 156.6, 167.0, 221.1. FT-IR (KBr): 1036, 1109, 1175, 1236, 1254, 1279, 1414, 1437, 1499, 1454, 1605, 1719, 1734, 1734, 2859, 2910, 2934 cm^{-1}. Anal. Calcd for $C_{27}H_{30}O_4$: C, 77.48; H, 7.23%. Found: C, 77.41; H, 7.25%. HRMS (FAB^+): Calcd for $C_{27}H_{30}O_4$: 418.2144. Found: 418.2150.

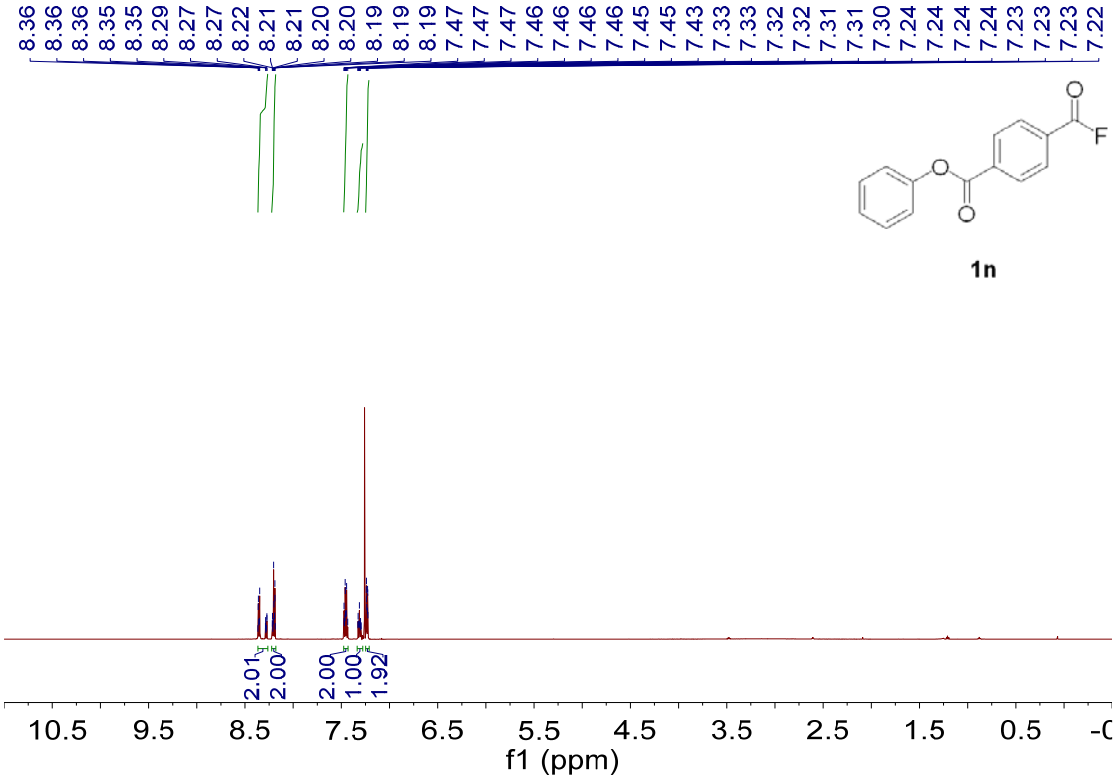
4.3 Synthesis of 4-((((8R,9S,13S,14S)-13-Methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[*a*]phenanthren-3-yl)oxy)methyl)benzoic acid (6)[7]

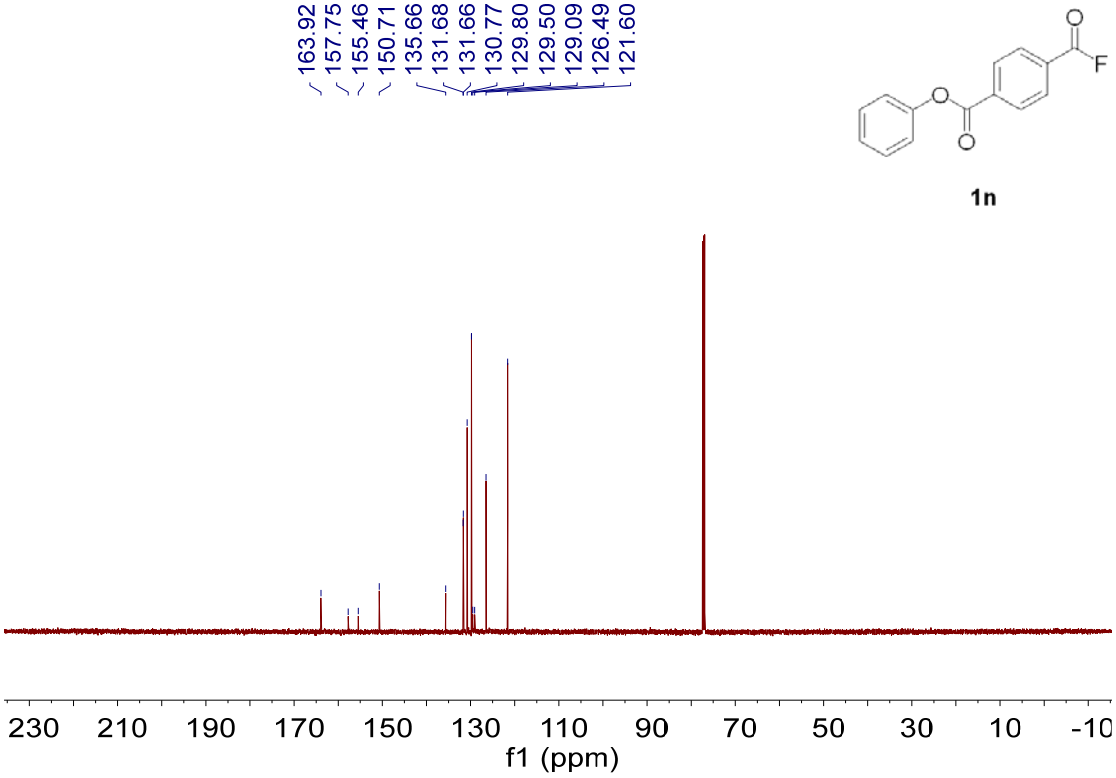


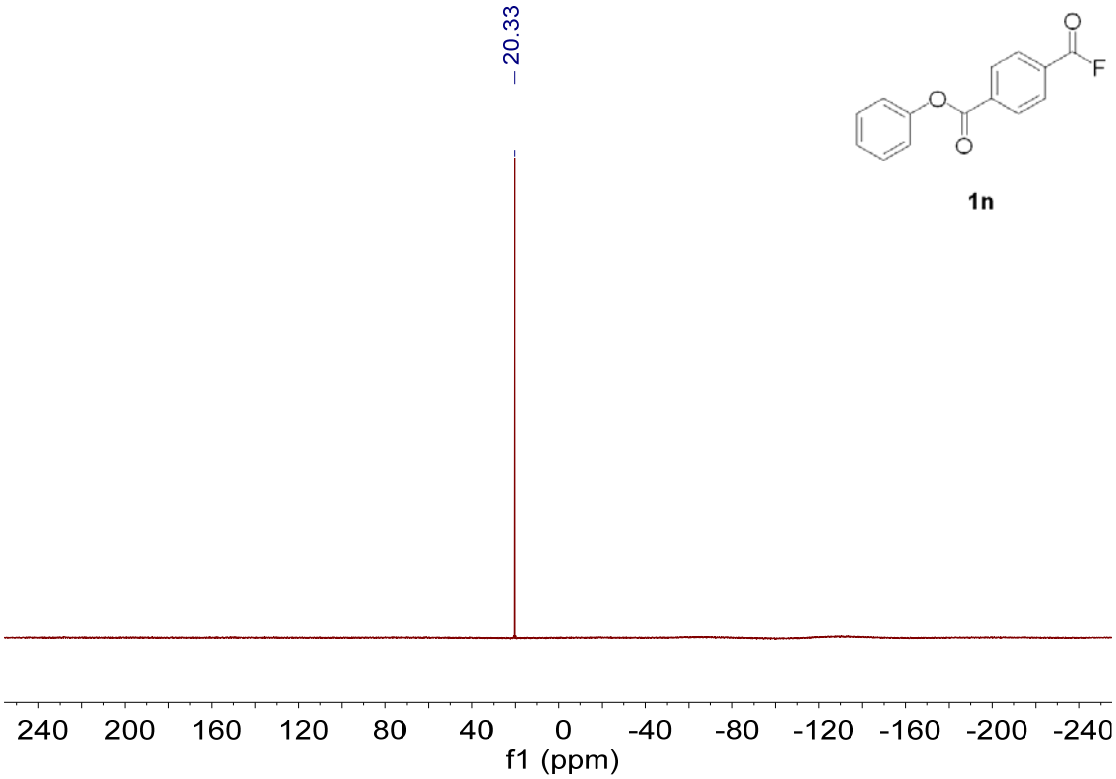
5 **6**

Compound **5** was subjected to hydrolysis according to the reported method.[8] A solution of ester **5** (418 g, 1 mmol) and lithium hydroxide monohydrate (84 mg, 2 mmol) in tetrahydrofuran (2 mL) and water (2 mL) was refluxed at 100 °C. After 4 h, the solvent was evaporated, and concentrated HCl was added to the residue. The precipitate was filtrated, washed with water, dried under vacuum to give a white solid (388.3 mg, 96%). ^{1}H NMR (600 MHz, $(CD_3)_2SO$): δ 0.81 (s, 3H), 1.30-1.39 (m, 3H), 1.44-1.57 (m, 3H), 1.72-1.77 (m, 1H), 1.89-1.96 (m, 2H), 2.05 (dt, J = 18.5, 8.5 Hz, 1H), 2.14-2.18 (m, 1H), 2.29-3.35 (m, 1H), 2.43 (dd, J = 18.5, 8.5 Hz, 1H), 2.79-2.82 (m, 2H), 3.36 (brs, 1H), 5.14 (s, 2H), 6.72 (d, J = 2.8 Hz, 1H), 6.76 (dd, J = 8.6, 2.8 Hz, 1H), 7.17 (d, J = 8.6 Hz, 1H), 7.52 (d, J = 8.0 Hz, 2H), 7.95 (d, J = 8.0 Hz, 2H); ^{13}C{^{1}H} NMR (151 MHz, $(CD_3)_2SO$): δ 13.6, 21.2, 25.5, 26.1, 29.2, 31.4, 35.4, 37.8, 43.5, 47.4, 49.6, 68.4, 112.3, 114.6, 126.4, 127.2, 129.5, 130.3, 132.2, 137.6, 142.4, 156.0, 167.2, 219.8. FT-IR (KBr): 860, 1005, 1057, 1159, 1254, 1425, 1425, 1611, 1678, 1734, 2876, 2932 cm^{-1}. Anal. Calcd for $C_{26}H_{28}O_4$: C, 77.20; H, 6.98%. Found: C, 77.03; H, 6.80%.

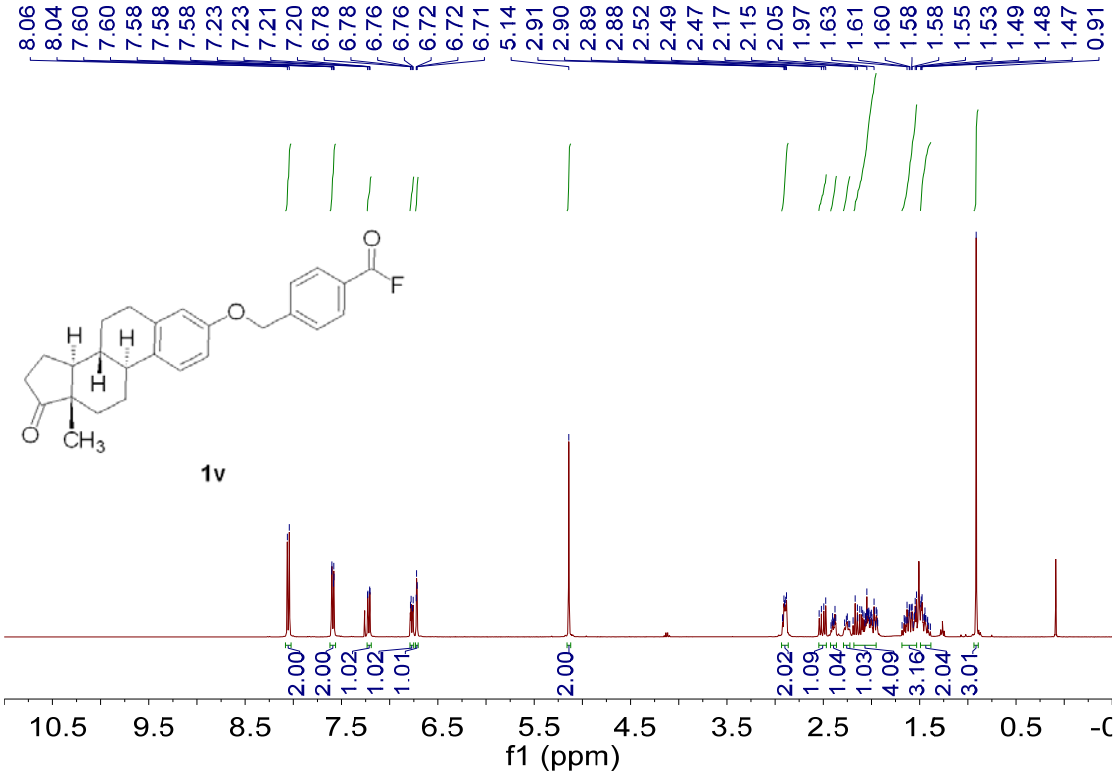
5. Copies of NMR Charts for Products

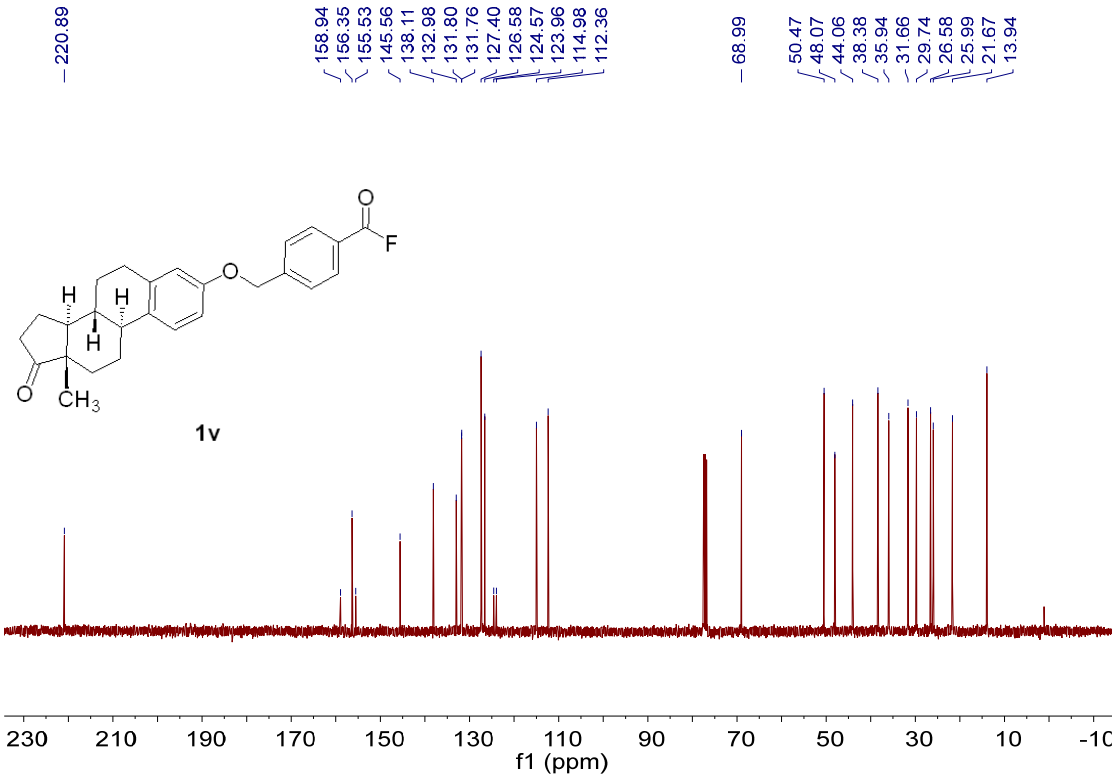


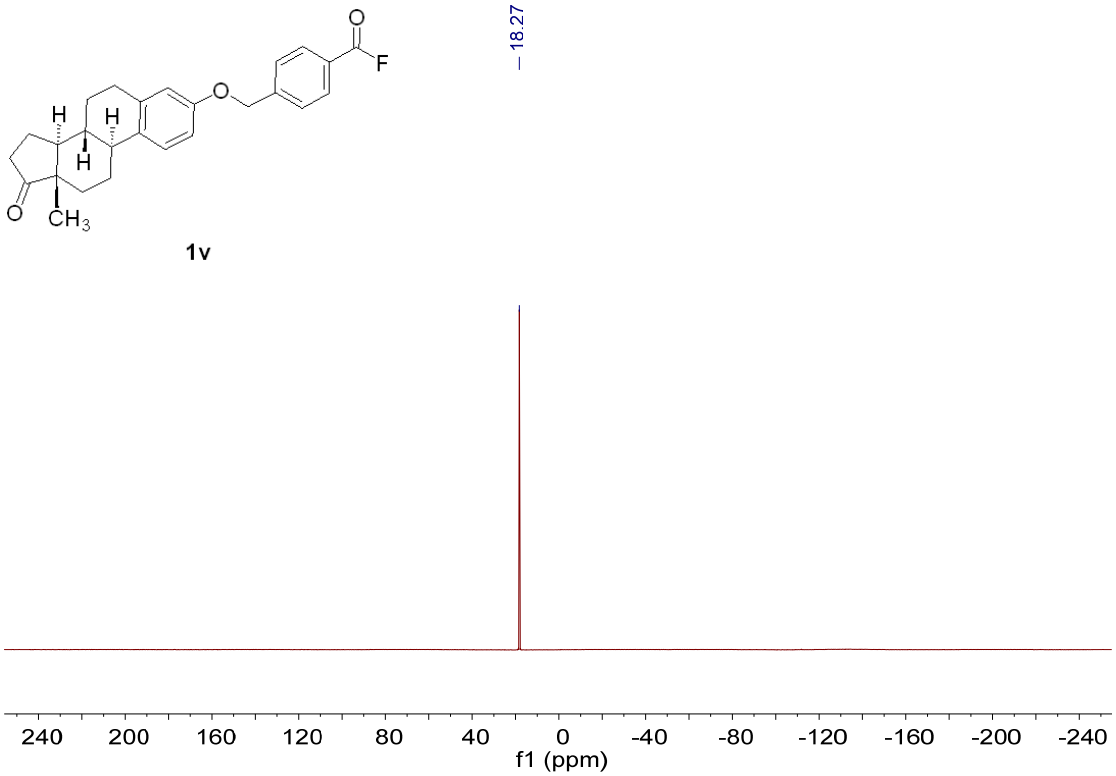




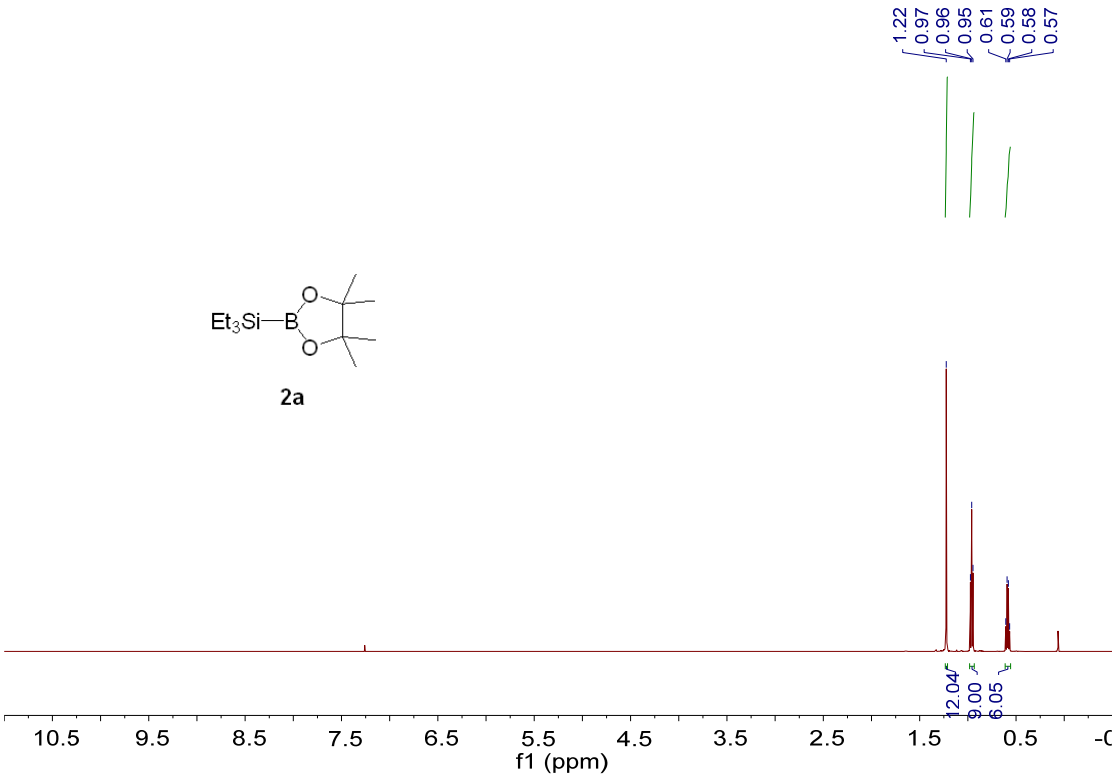
^{1}H NMR (600 MHz), ^{13}C{^{1}H} NMR (151 MHz), and ^{19}F{^{1}H} NMR (376 MHz) spectra of **1n** ($CDCl_3$, rt).



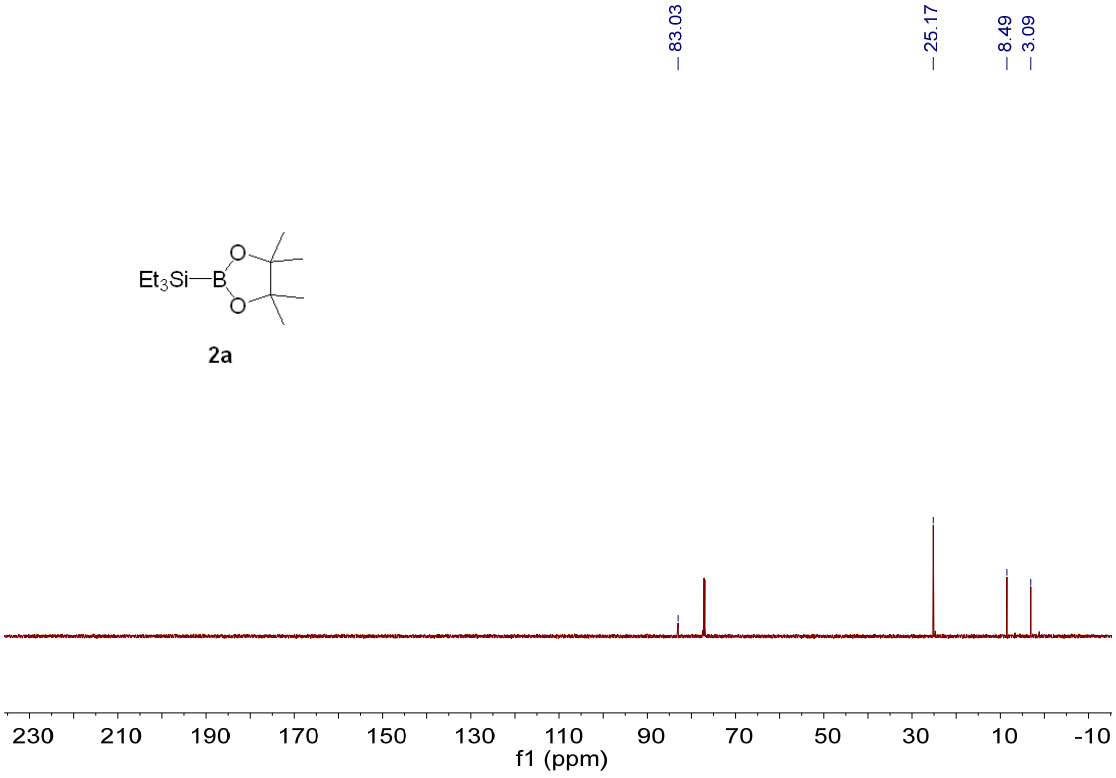




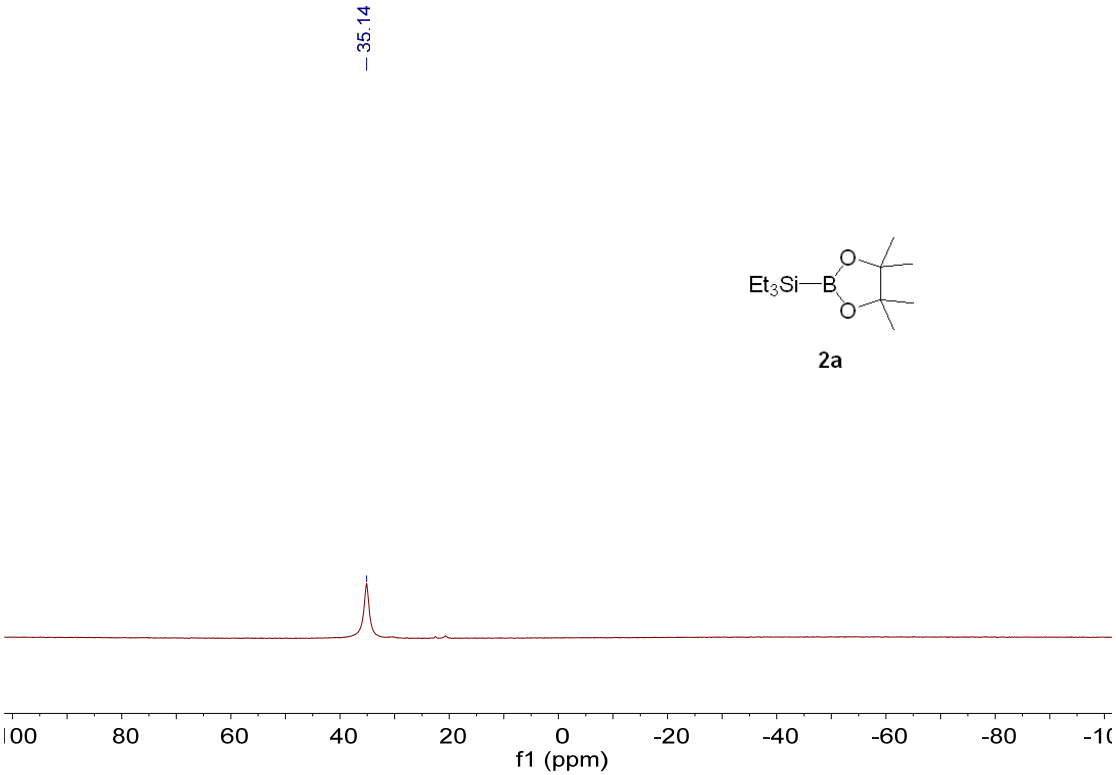
^{1}H NMR (400 MHz), ^{13}C{^{1}H} NMR (101 MHz), and ^{19}F{^{1}H} NMR (376 MHz) spectra of **1v** (rt., $CDCl_3$)


1.22
0.97
0.96
0.95
0.61
0.59
0.58
0.57
Et3Si—B
O
O
12.04
9.00
6.05
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
f1 (ppm)

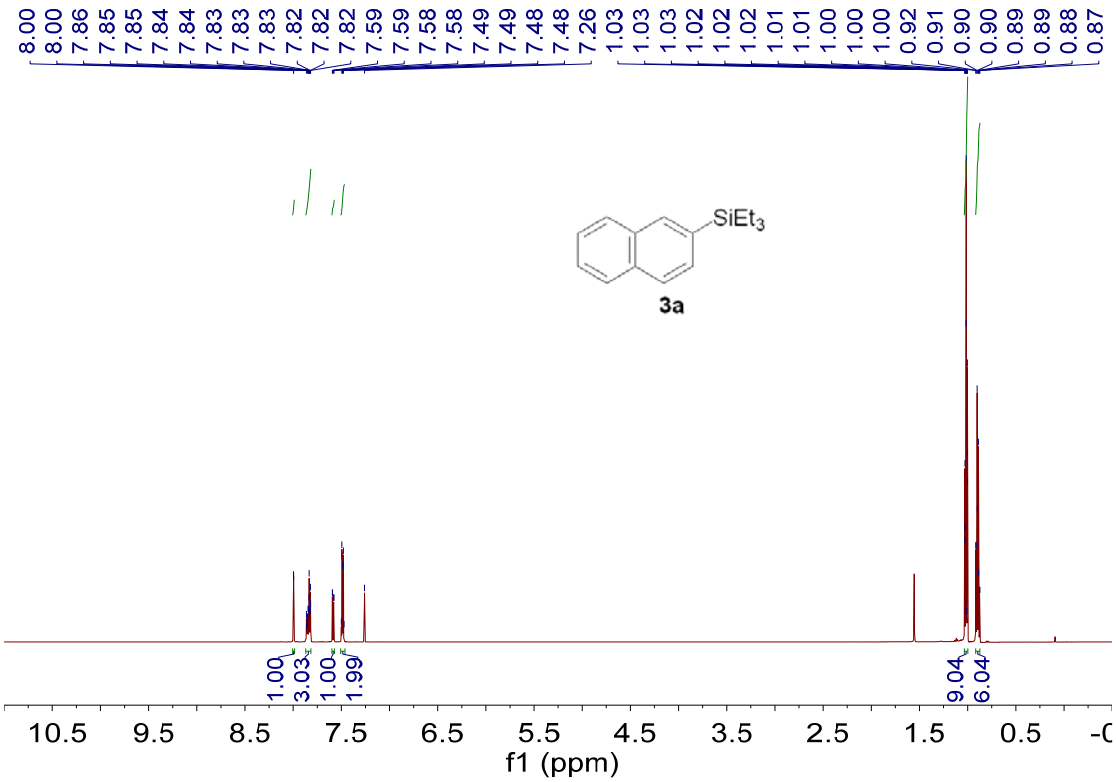
2a


83.03
25.17
8.49
3.09
Et3Si—B
O
O
230
210
190
170
150
130
110
90
70
50
30
10
-10
f1 (ppm)

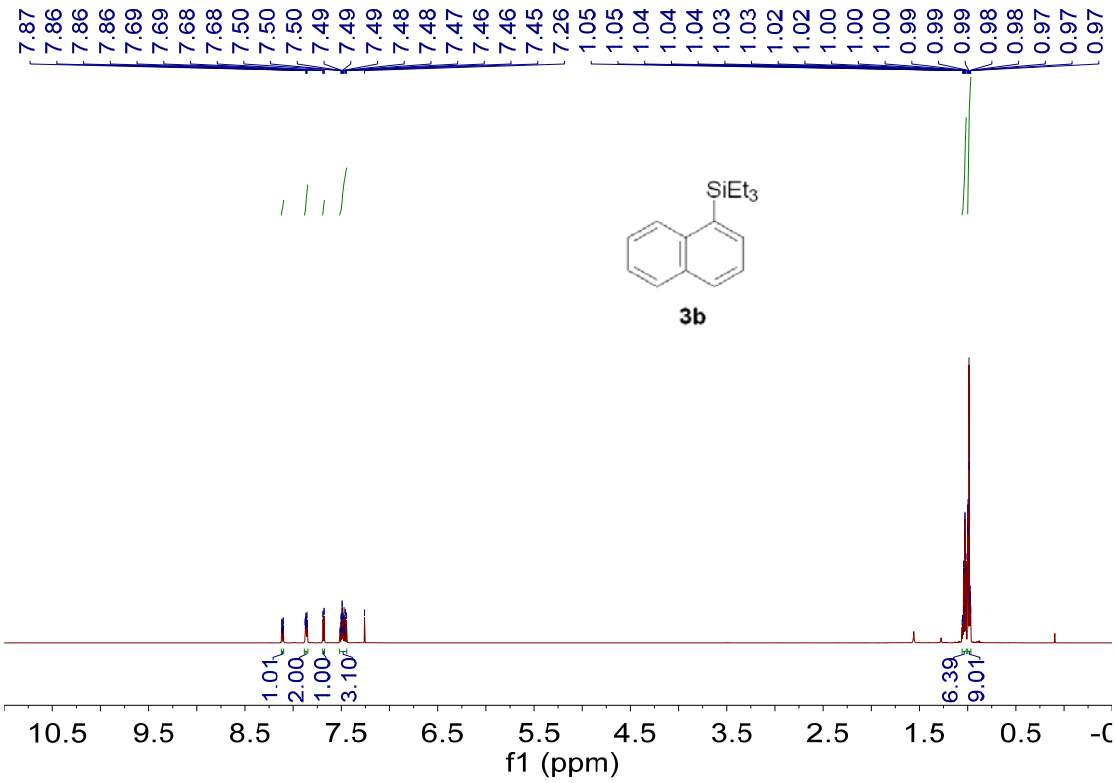
2a



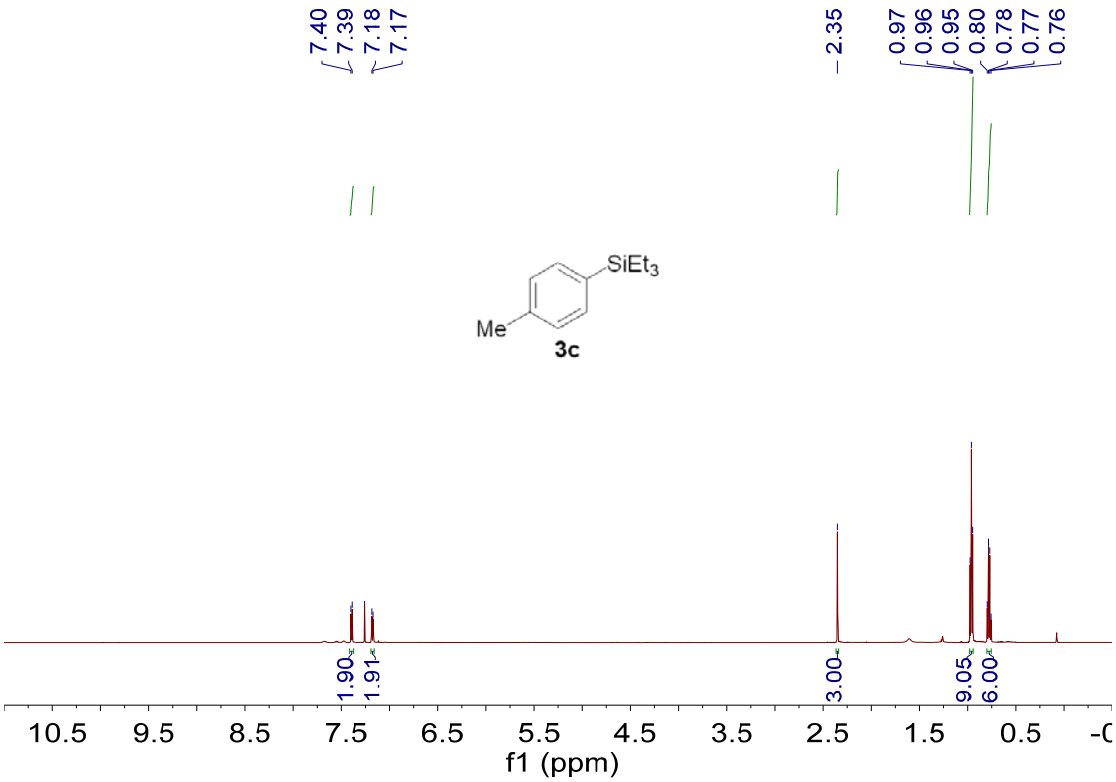
^{1}H NMR (600 MHz), ^{13}C{^{1}H} NMR (151 MHz), and ^{11}B{^{1}H} NMR (192 MHz) spectra of **2a** ($CDCl_3$, rt).



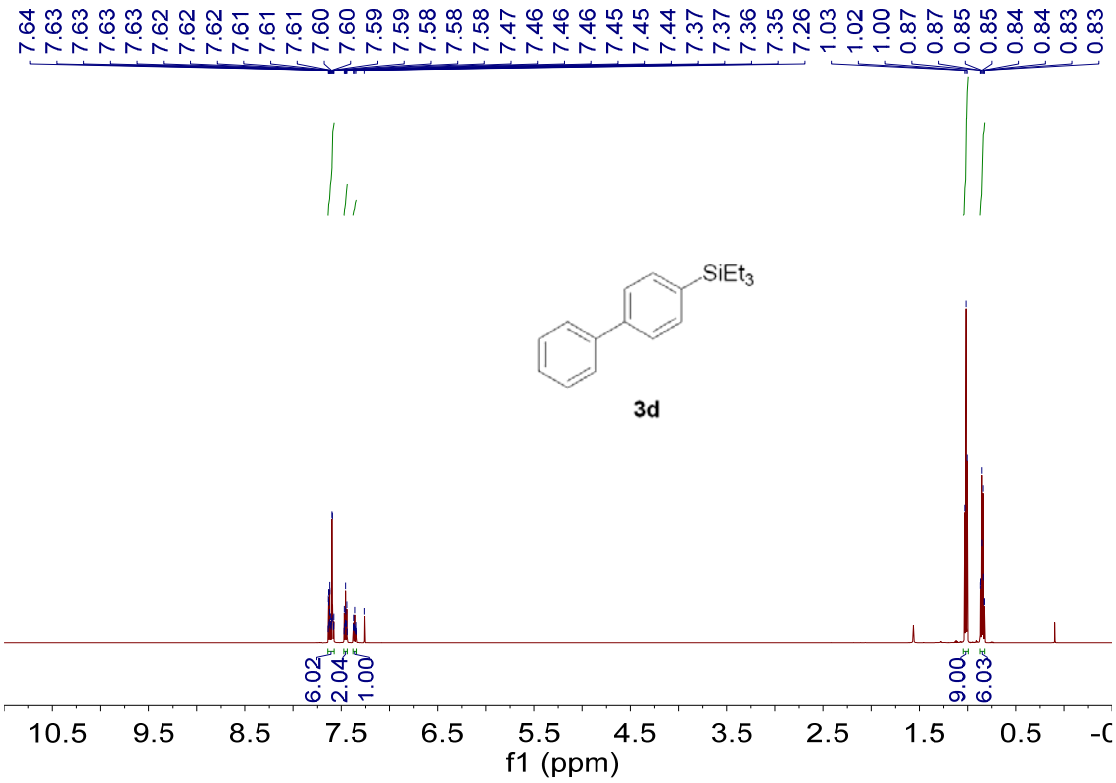
^{1}H NMR (600 MHz) spectrum of **3a** ($CDCl_3$, rt).



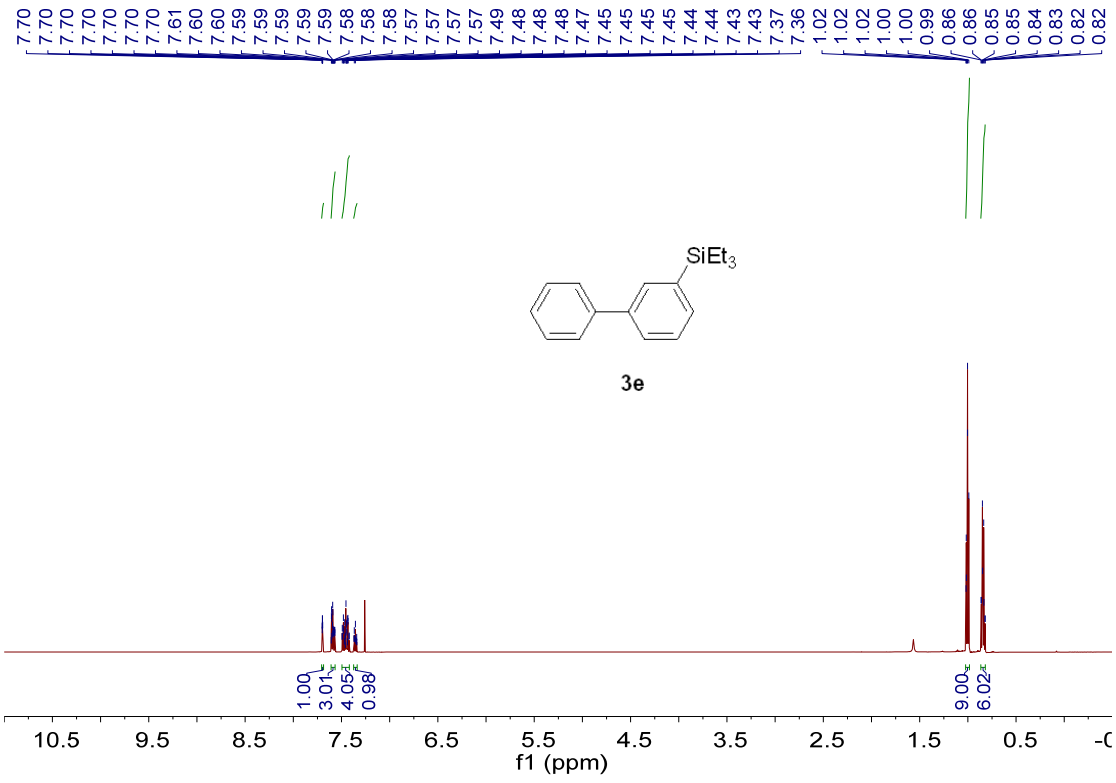
^{1}H NMR (600 MHz) spectrum of **3b** ($CDCl_3$, rt).



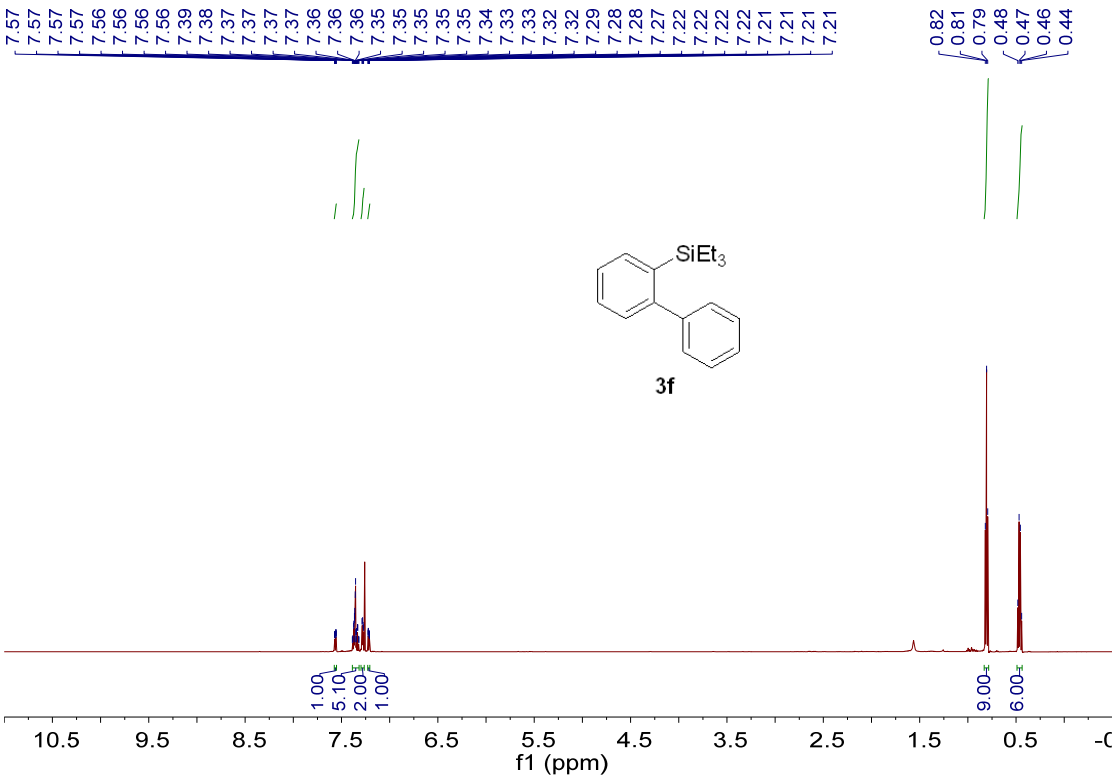
^{1}H NMR (600 MHz) spectrum of **3c** ($CDCl_3$, rt).



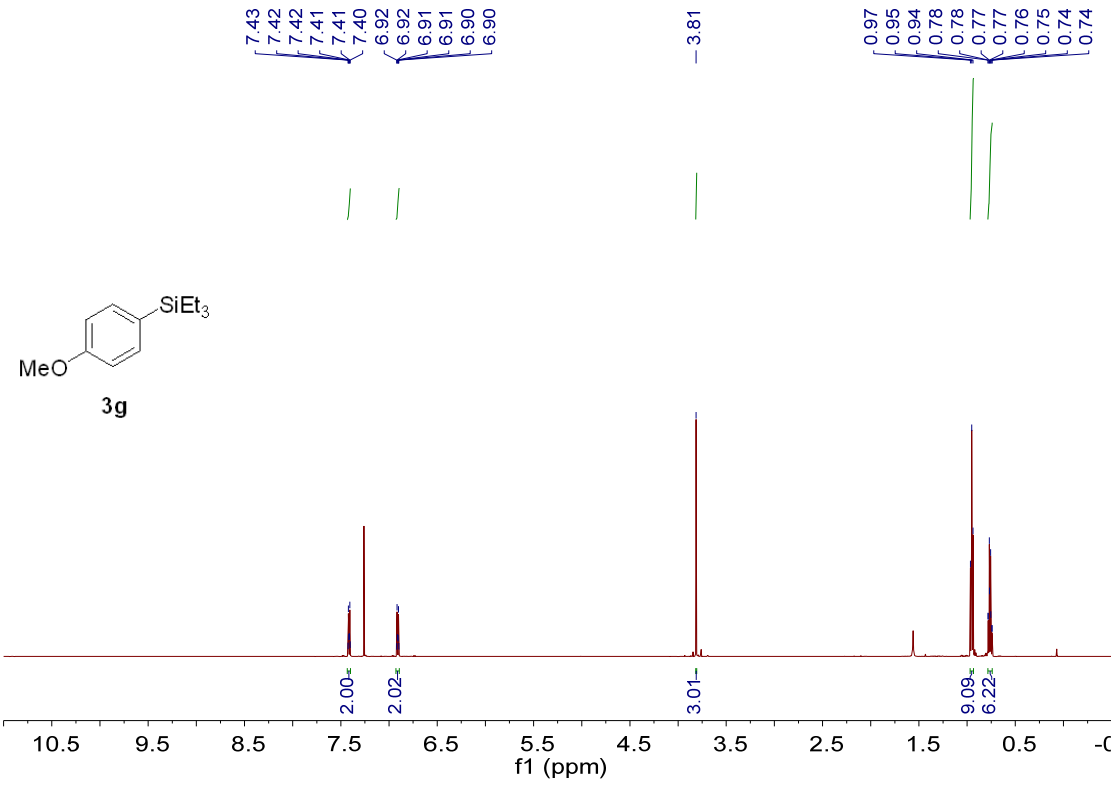
^{1}H NMR (600 MHz) spectrum of **3d** ($CDCl_3$, rt).



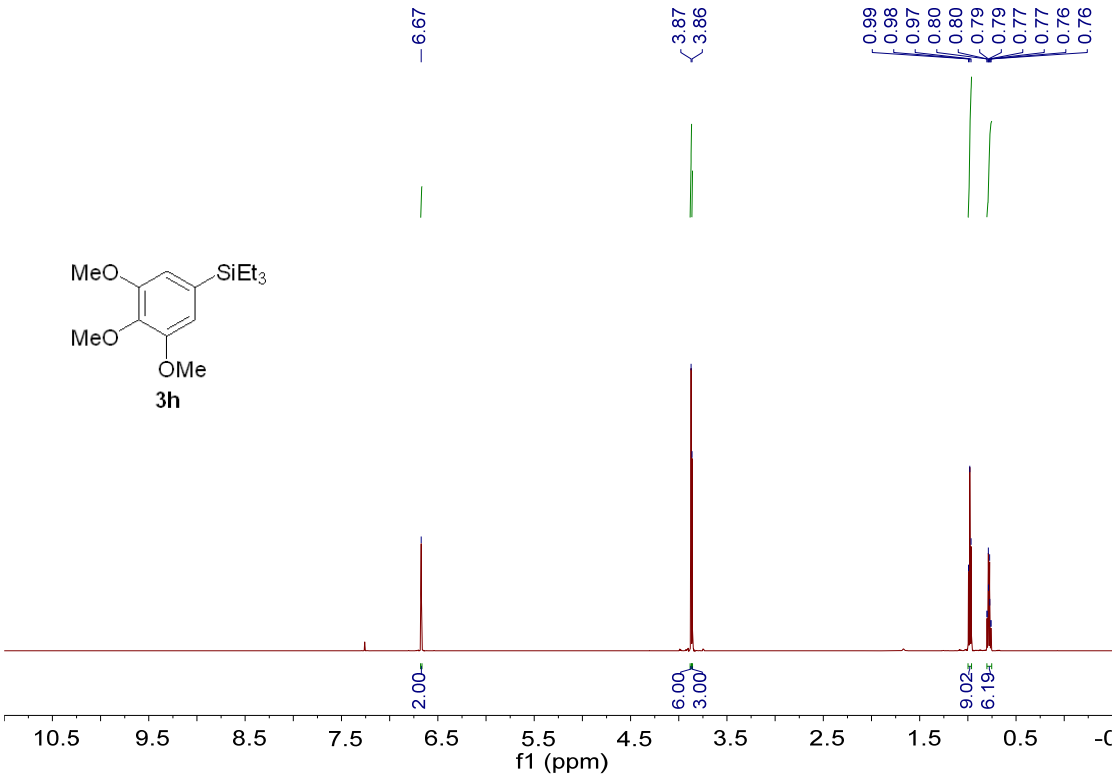
^{1}H NMR (600 MHz) spectrum of **3e** ($CDCl_3$, rt).

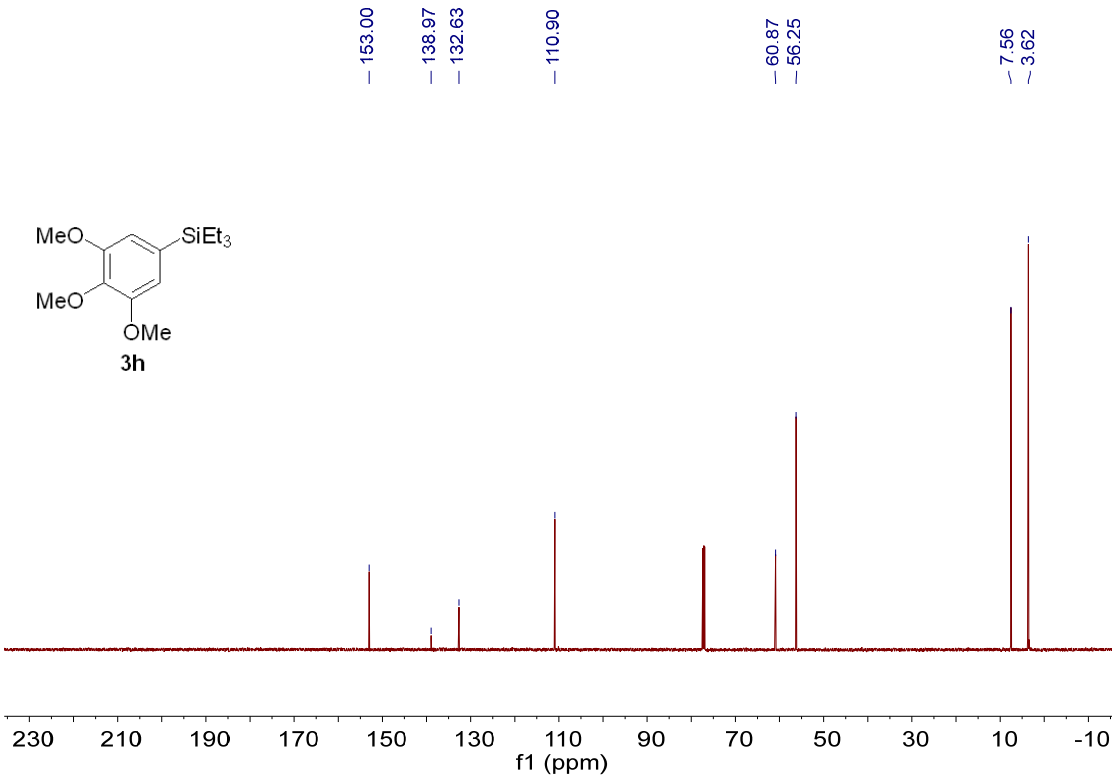


^{1}H NMR (600 MHz) spectrum of **3f** ($CDCl_3$, rt).

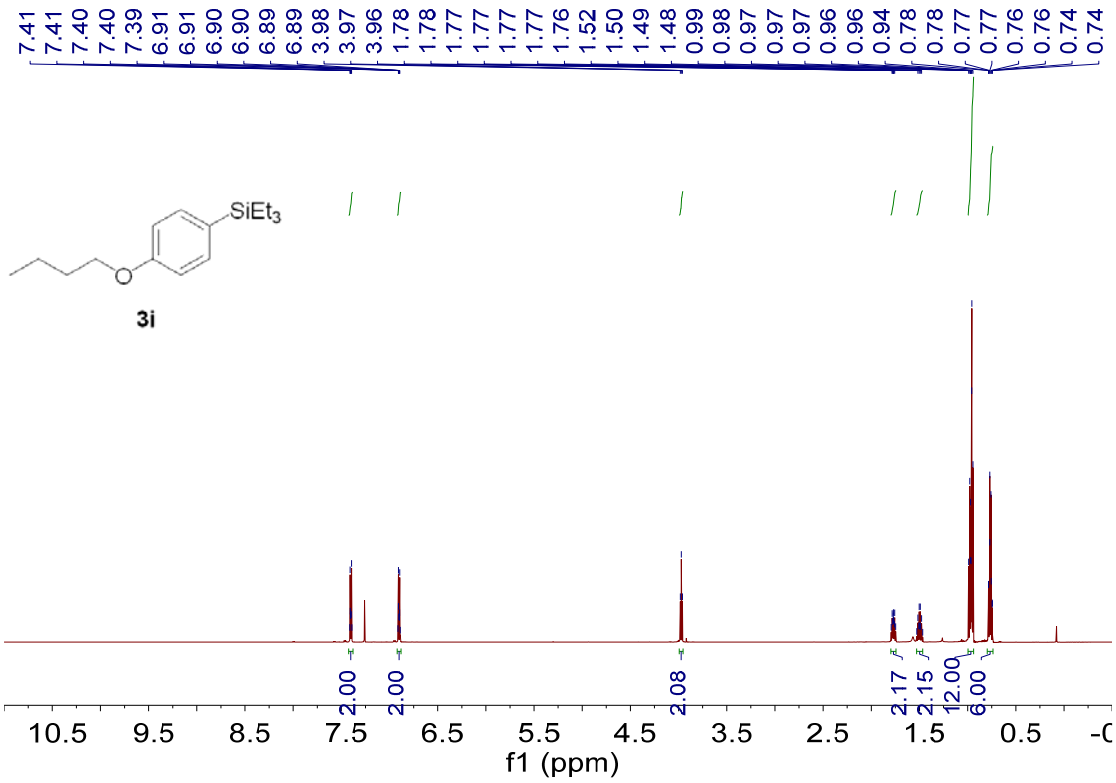


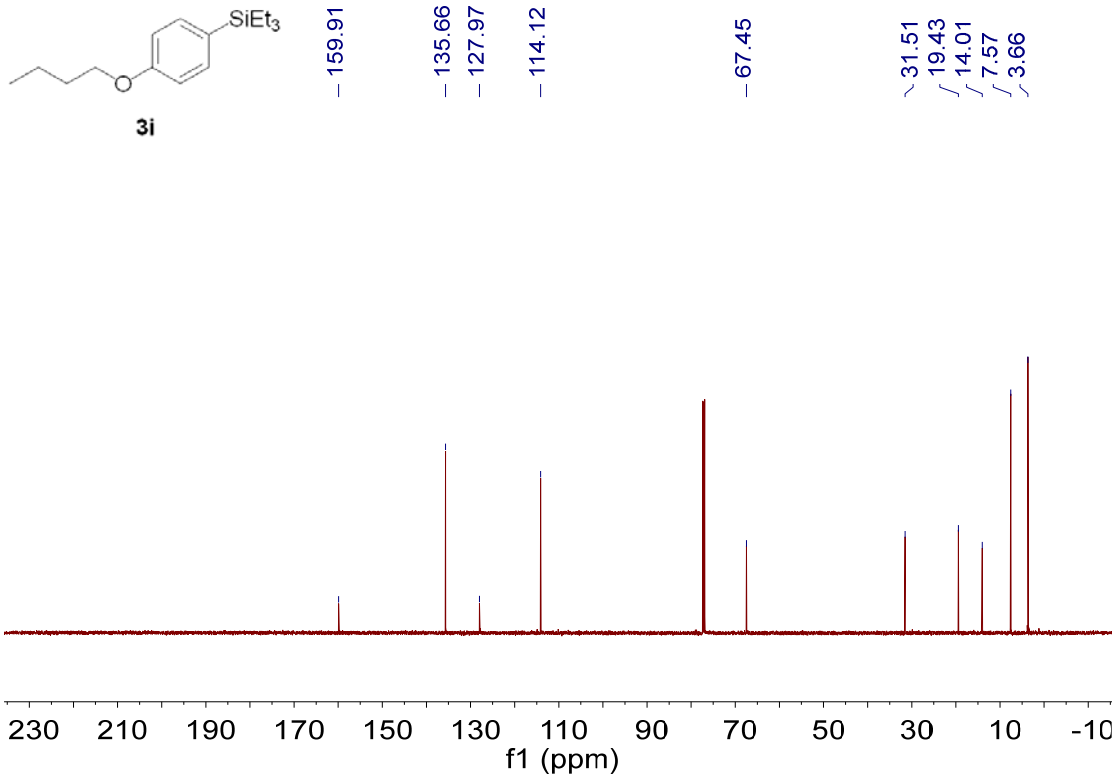
^{1}H NMR (600 MHz) spectrum of **3g** ($CDCl_3$, rt).



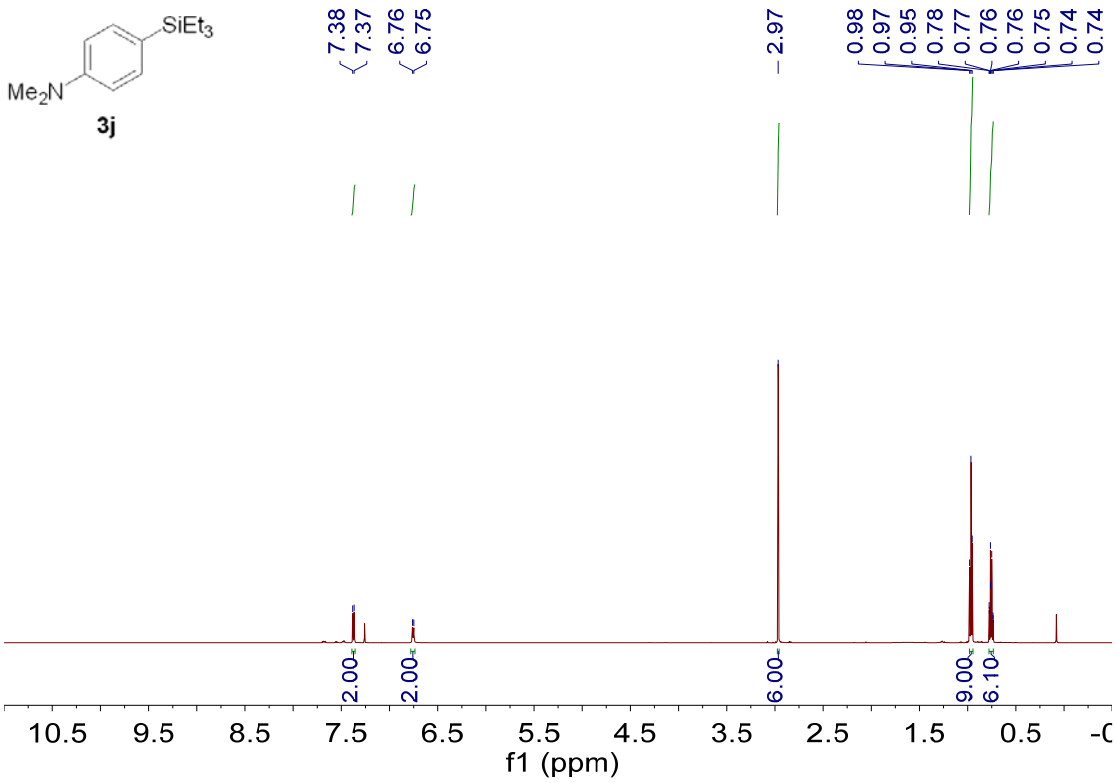


^{1}H NMR (600 MHz) and ^{13}C{^{1}H} NMR (151 MHz) spectra of **3h** ($CDCl_3$, rt).

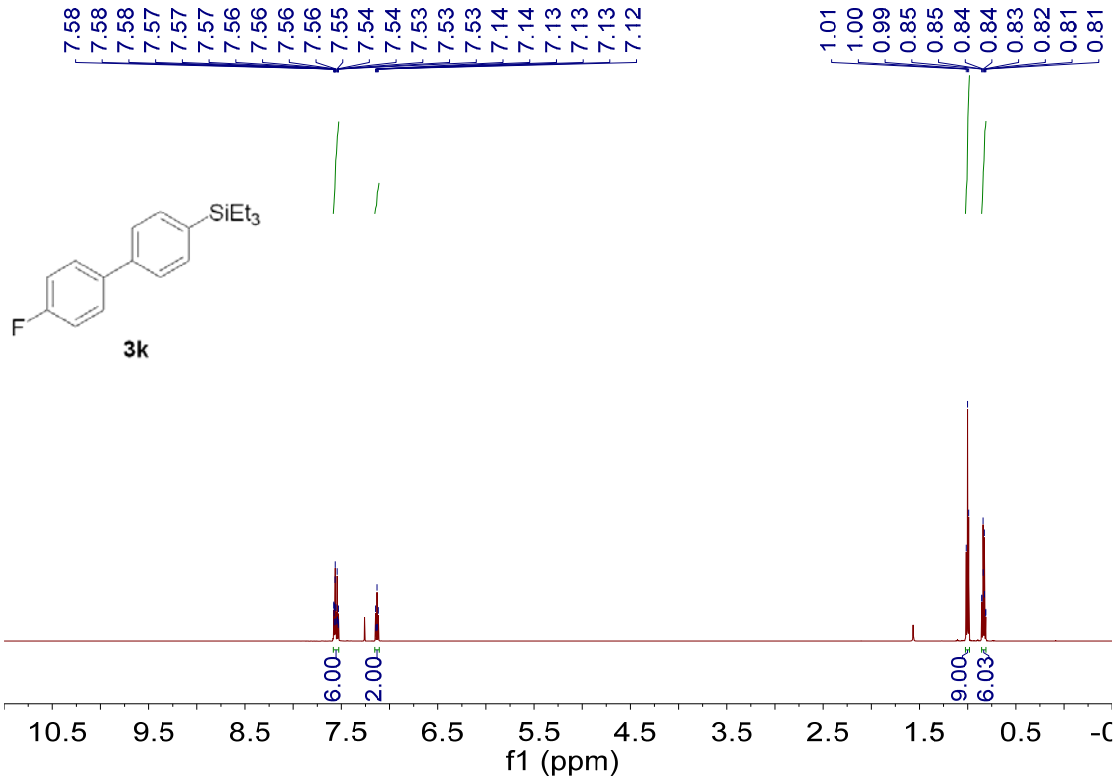


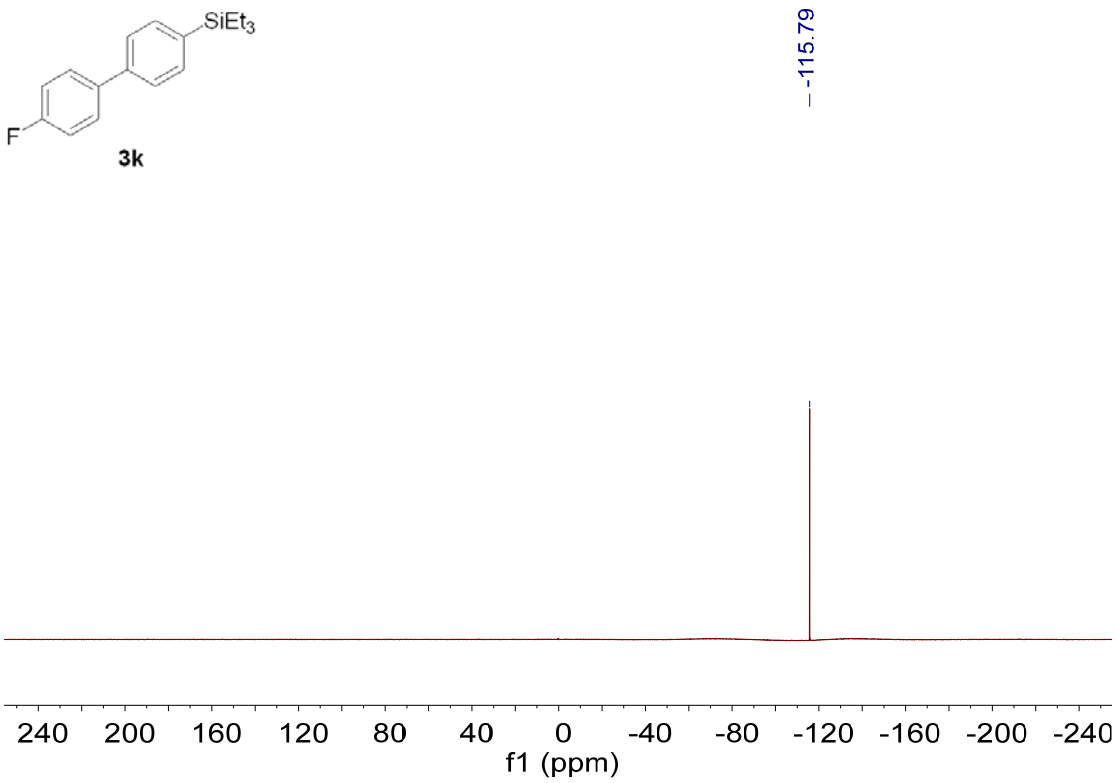


^{1}H NMR (600 MHz) and ^{13}C{^{1}H} NMR (151 MHz) spectra of **3i** ($CDCl_3$, rt).

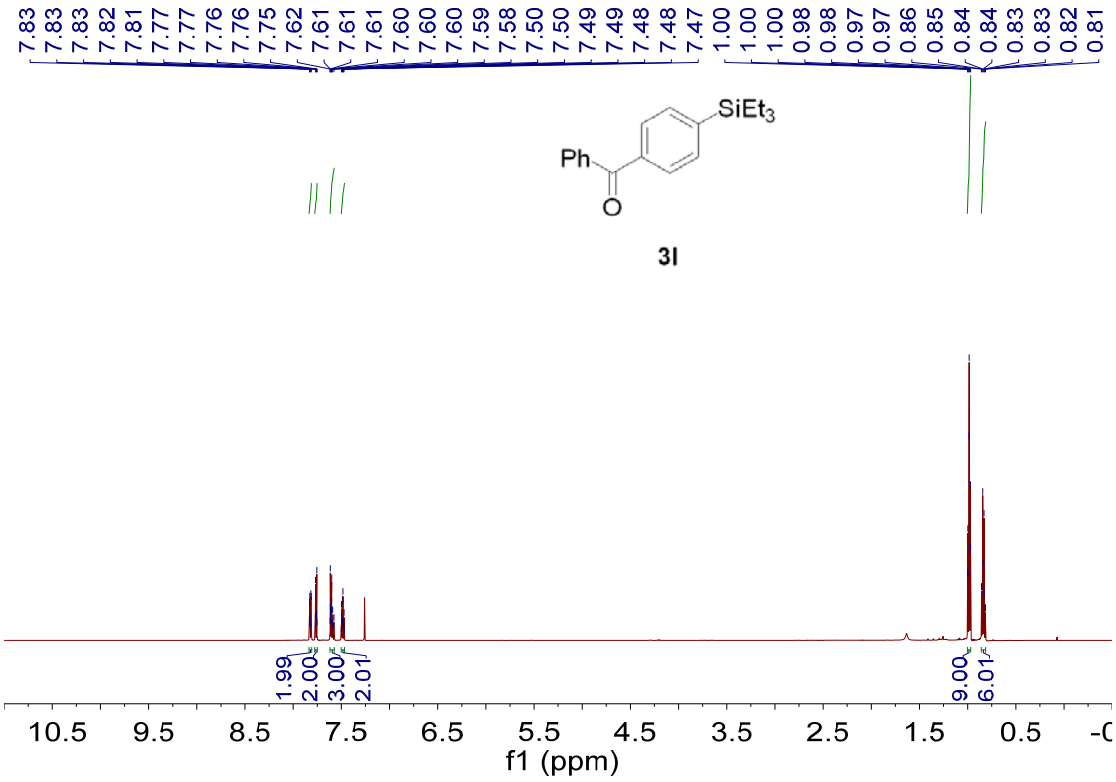


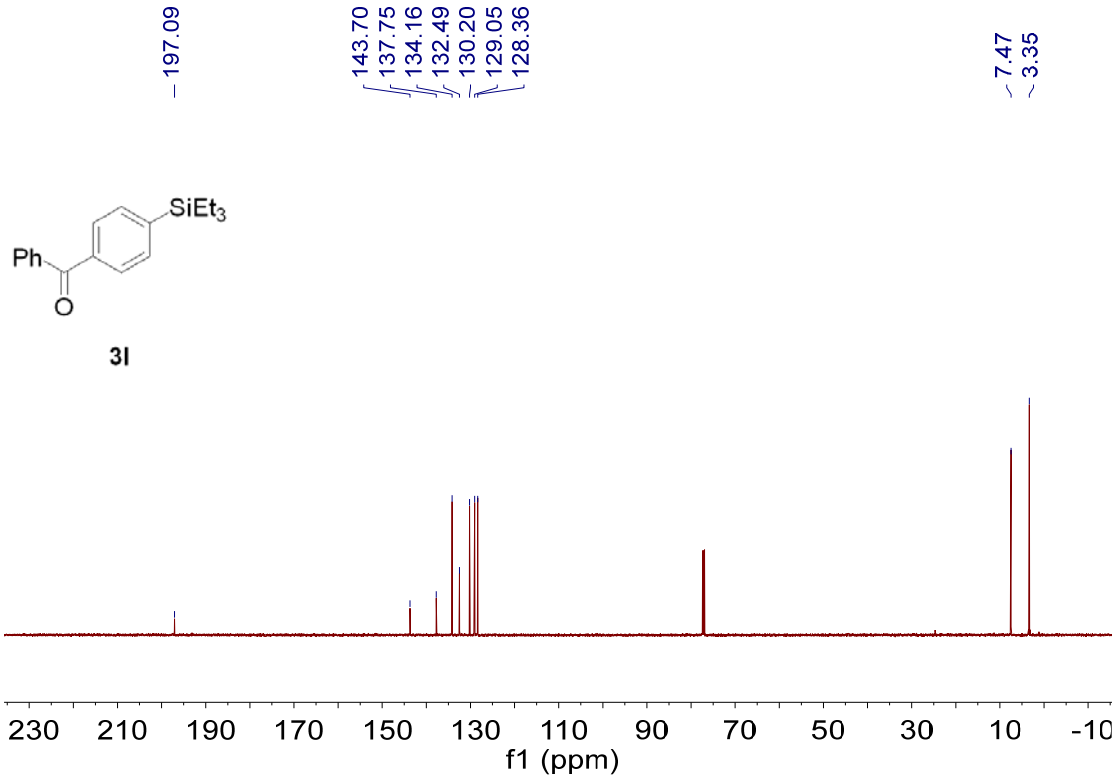
^{1}H NMR (600 MHz) spectrum of **3j** ($CDCl_3$, rt).



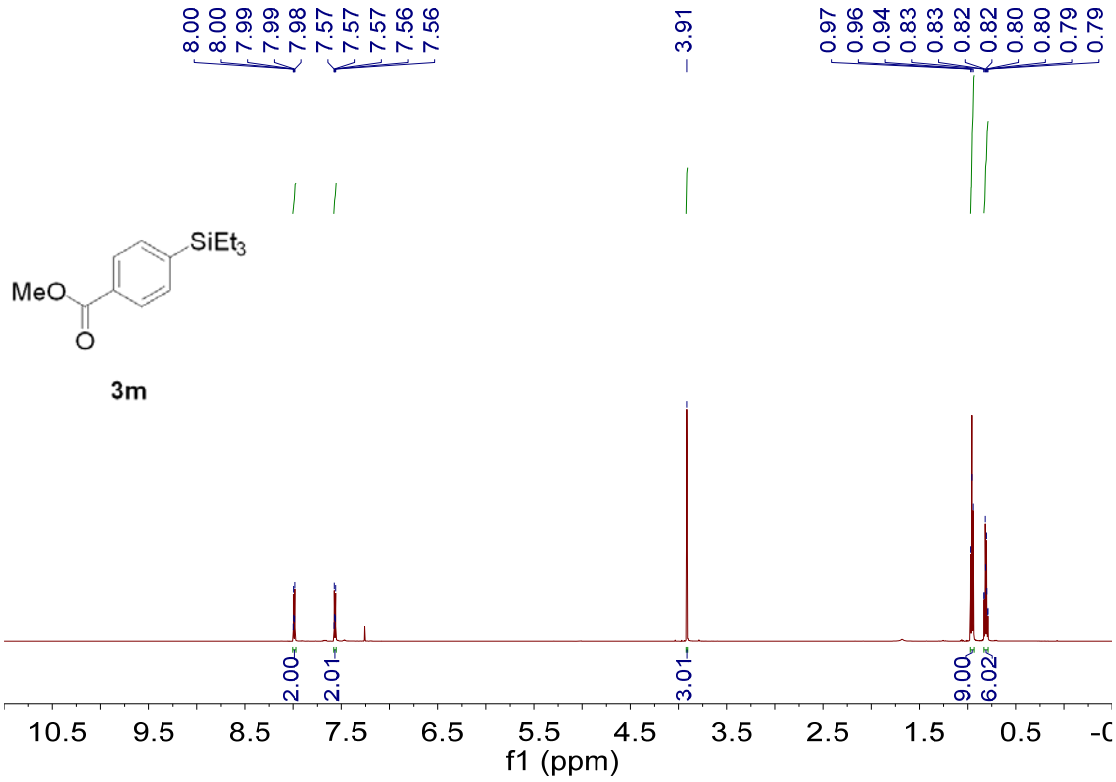


^{1}H NMR (600 MHz) and ^{19}F{^{1}H} NMR (376 MHz) spectra of **3k** ($CDCl_3$, rt).

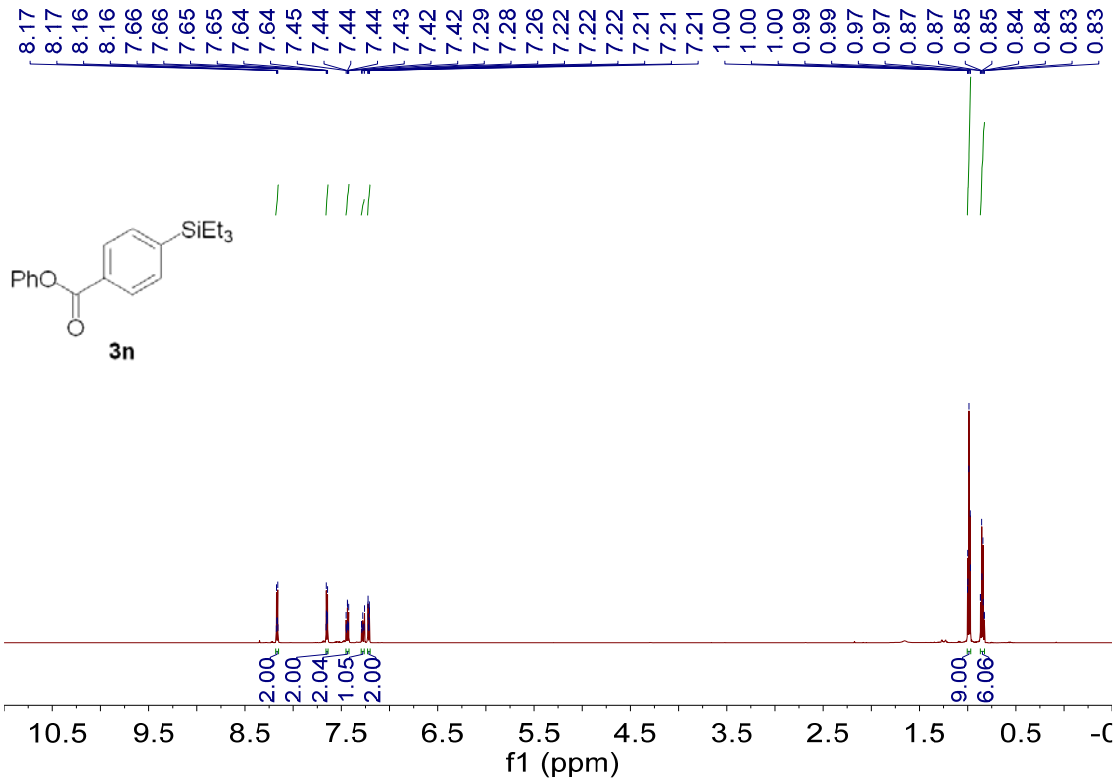




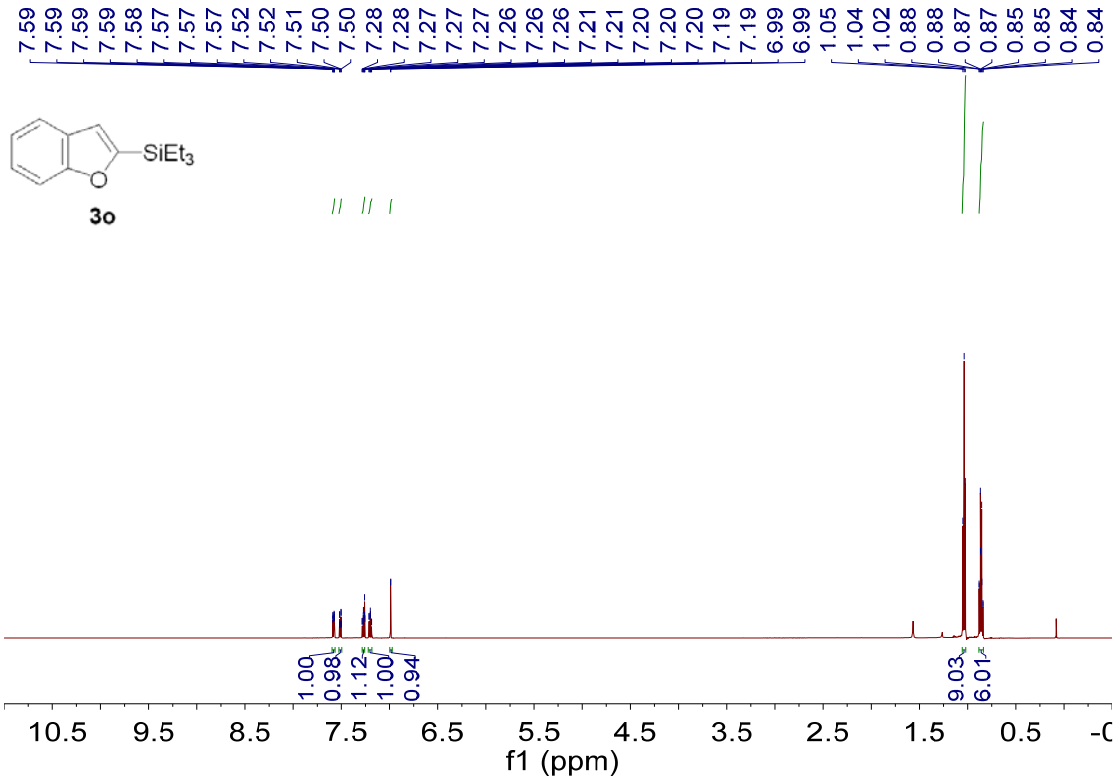
^{1}H NMR (600 MHz) and ^{13}C{^{1}H} NMR (151 MHz) spectra of **3l** ($CDCl_3$, rt).



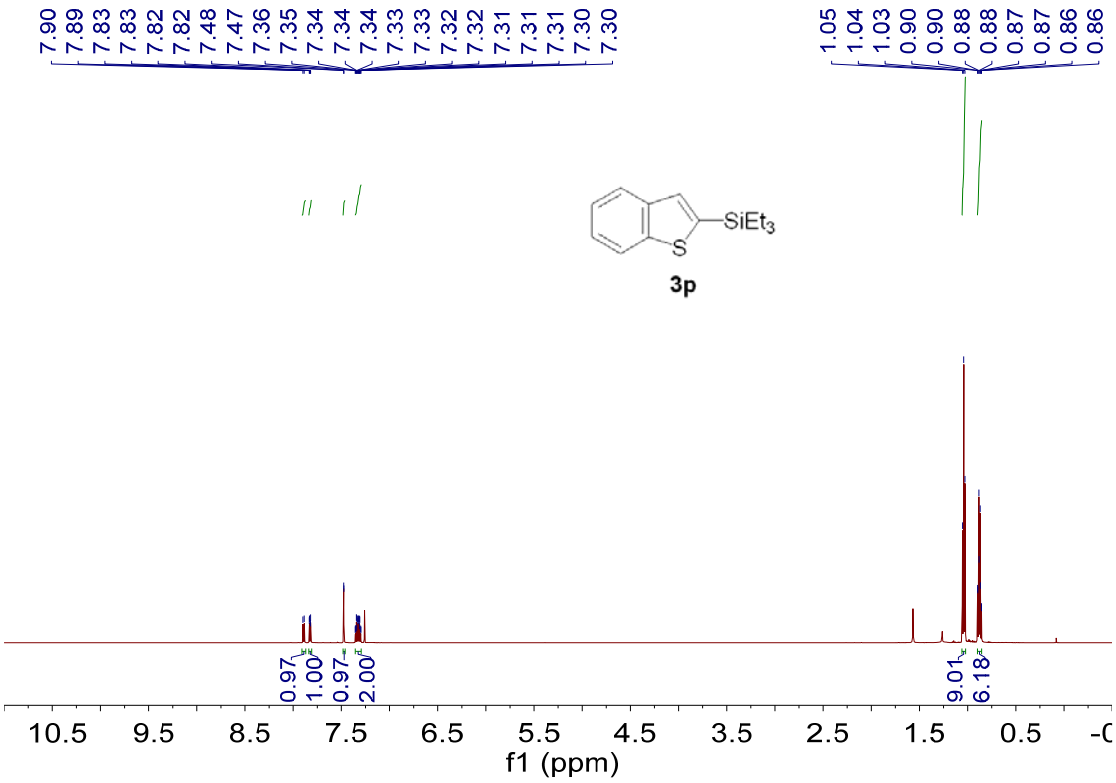
^{1}H NMR (600 MHz) spectrum of **3m** ($CDCl_3$, rt).



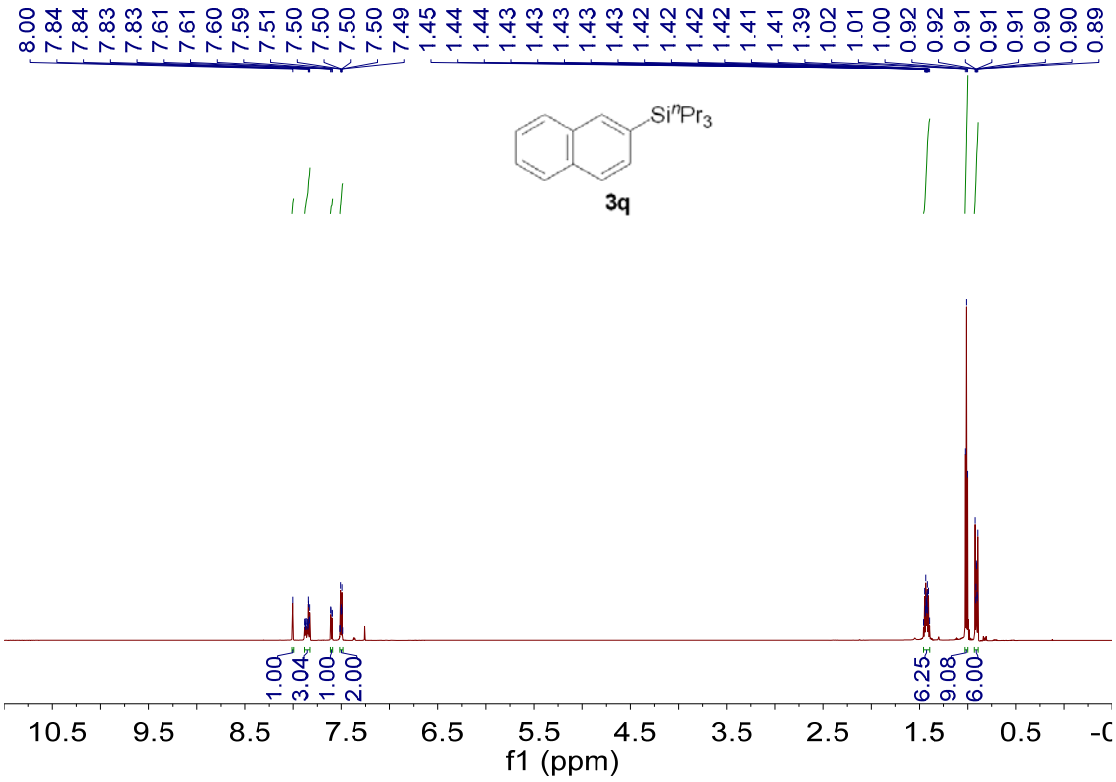
^{1}H NMR (600 MHz) spectrum of **3n** ($CDCl_3$, rt).



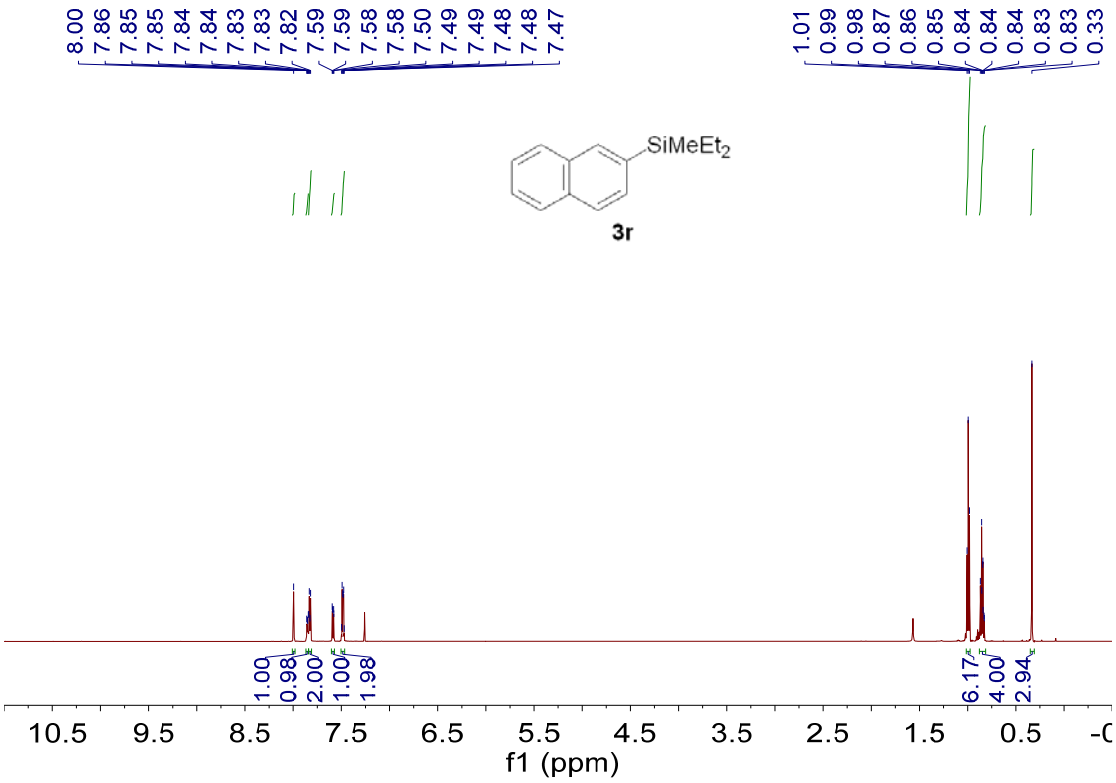
^{1}H NMR (600 MHz) spectrum of **3o** ($CDCl_3$, rt).



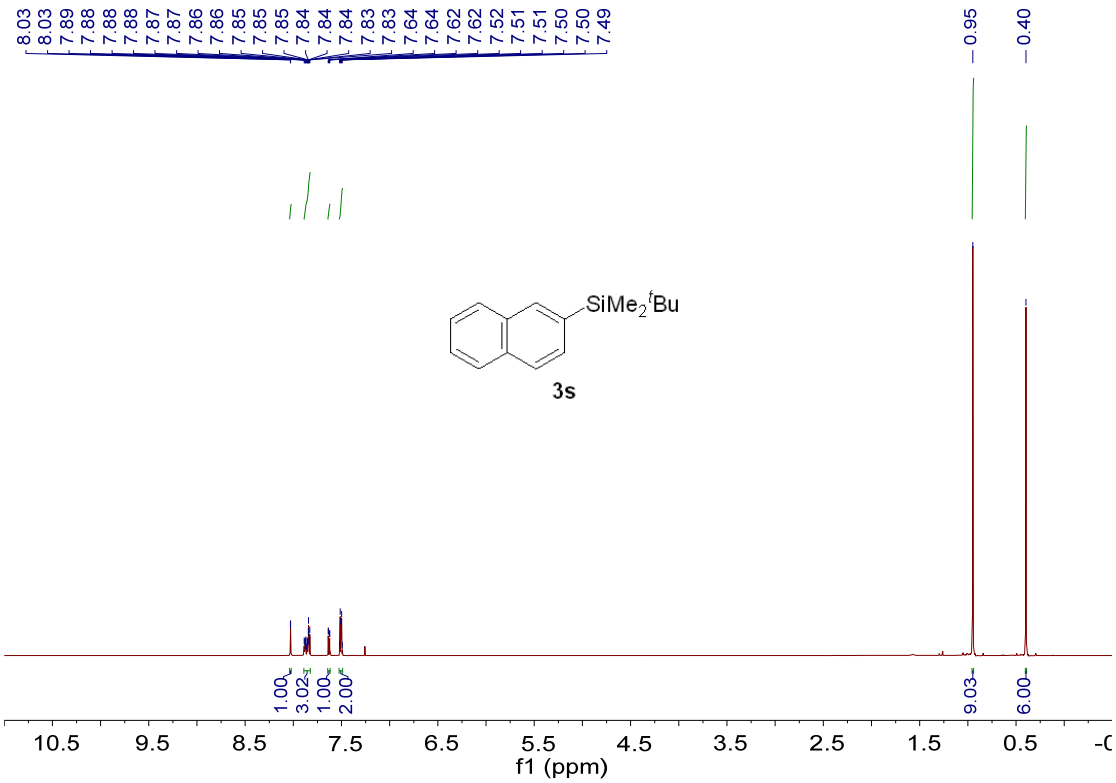
^{1}H NMR (600 MHz) spectrum of **3p** ($CDCl_3$, rt).



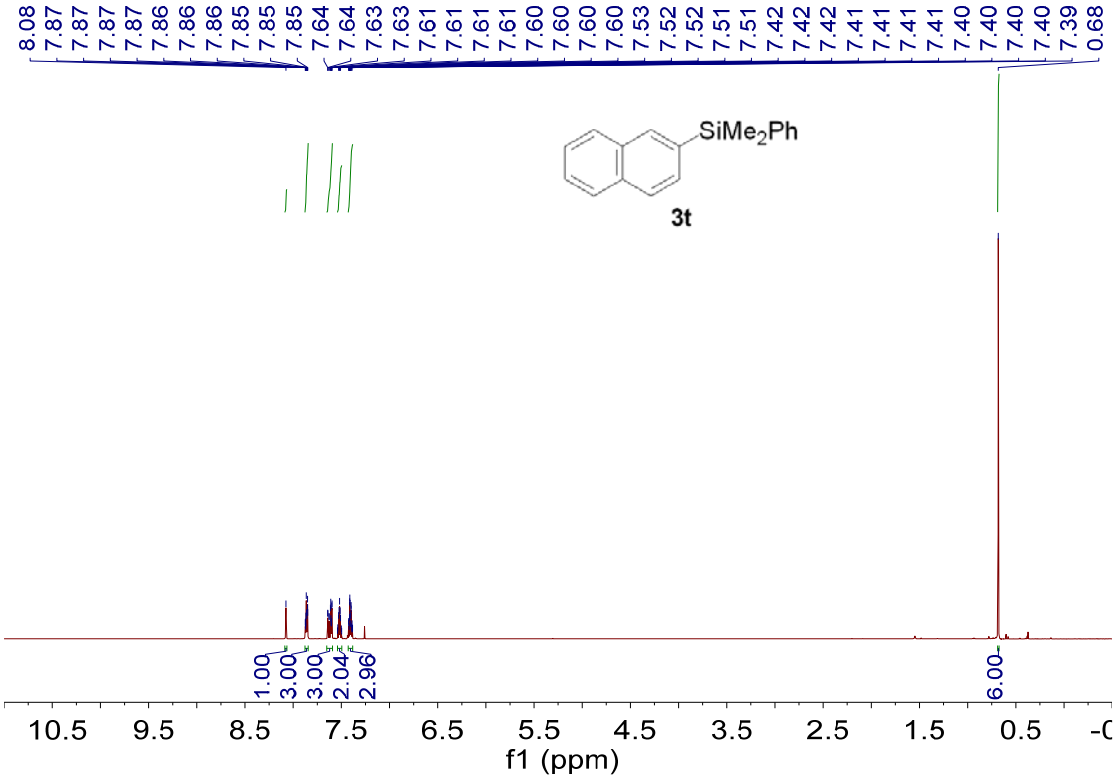
^{1}H NMR (600 MHz) spectrum of **3q** ($CDCl_3$, rt).



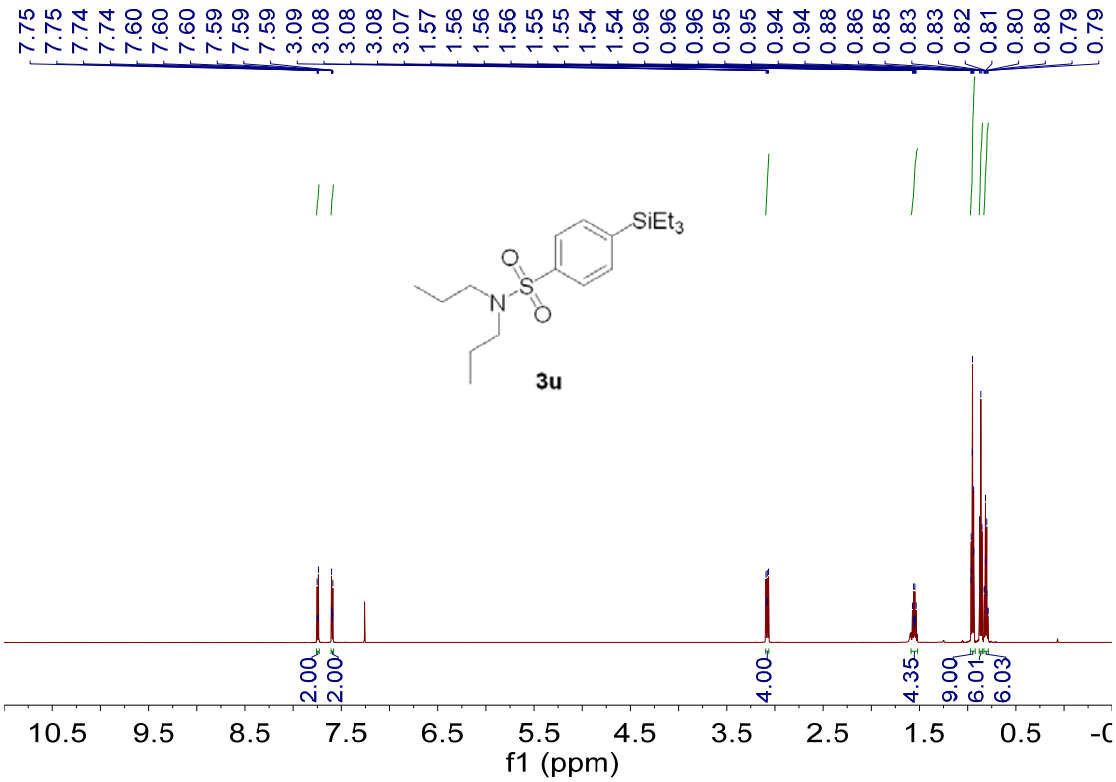
^{1}H NMR (600 MHz) spectrum of **3r** ($CDCl_3$, rt).

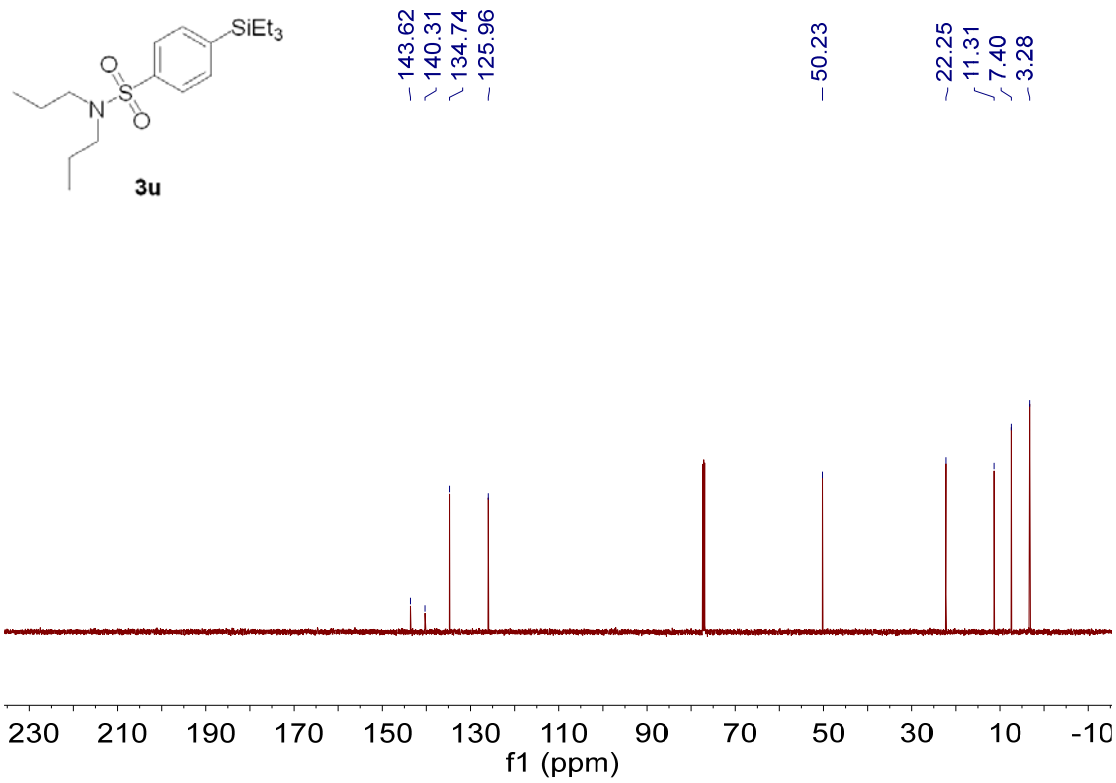


^{1}H NMR (600 MHz) spectrum of **3s** ($CDCl_3$, rt).

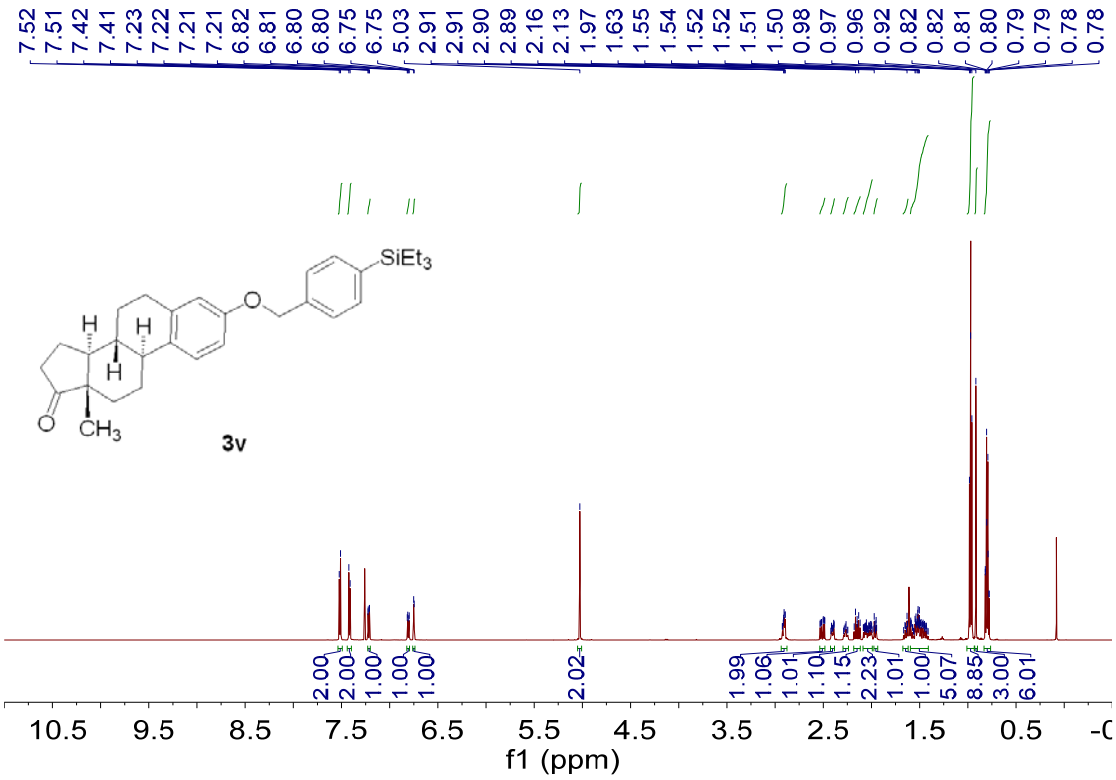


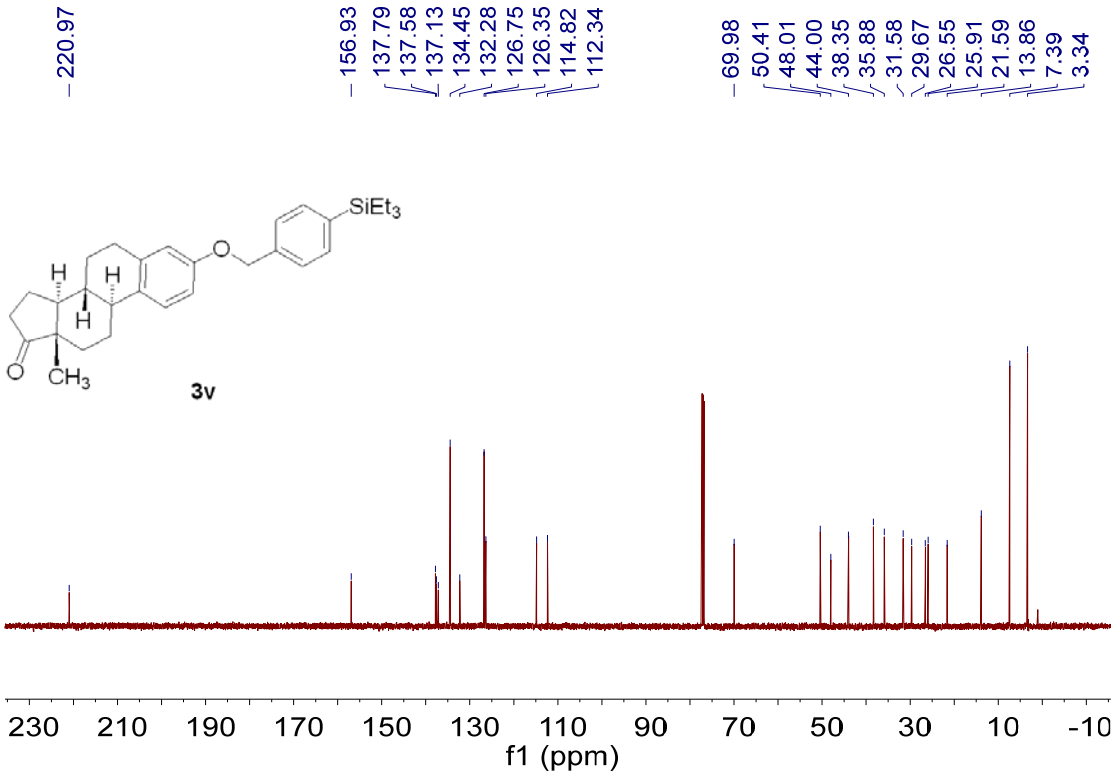
^{1}H NMR (600 MHz) spectrum of **3t** ($CDCl_3$, rt).



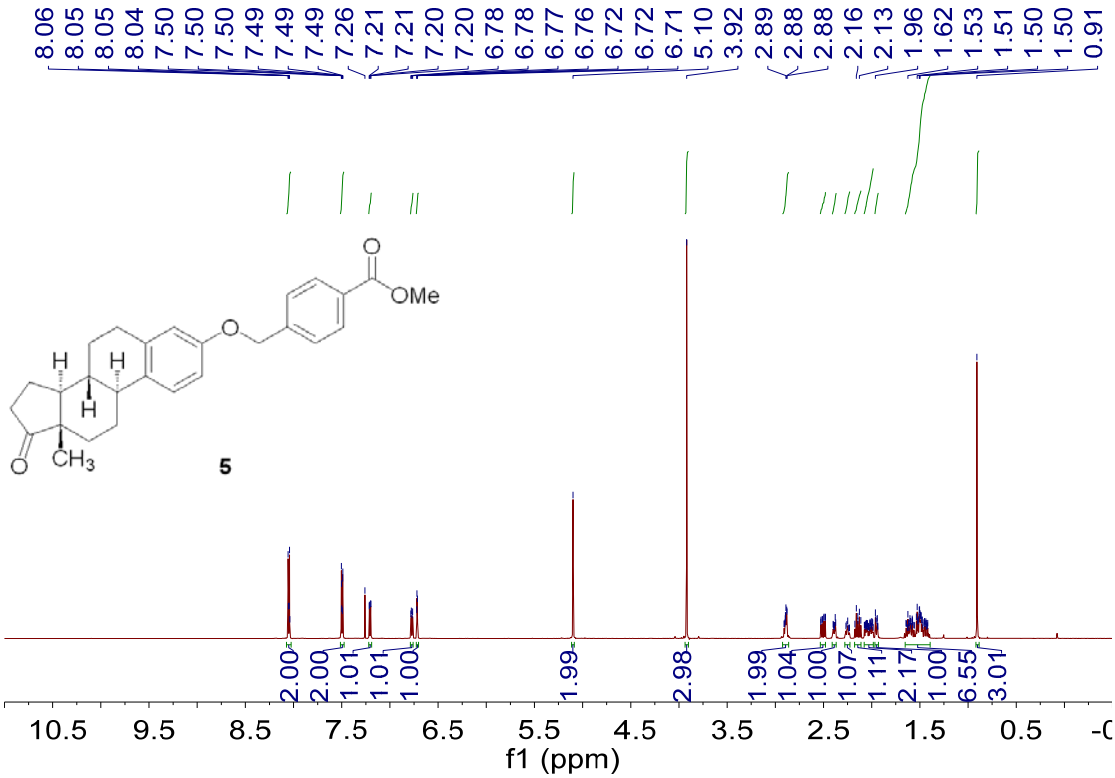


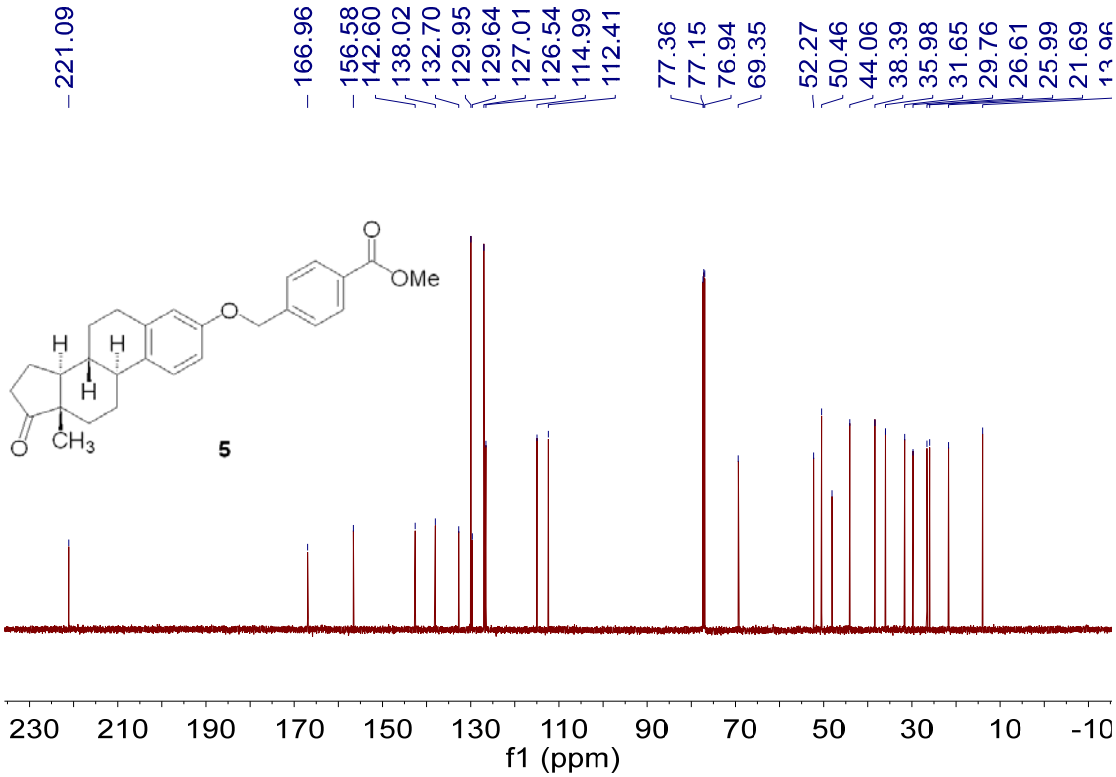
^{1}H NMR (600 MHz) and ^{13}C{^{1}H} NMR (151 MHz) spectra of **3u** ($CDCl_3$, rt).



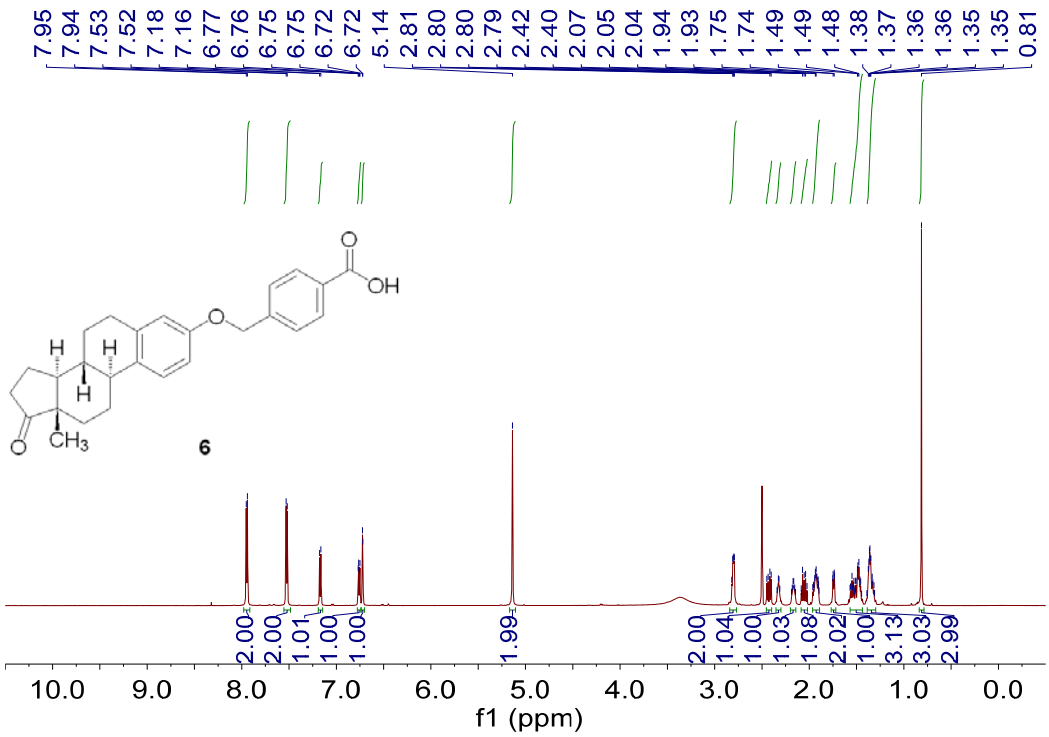


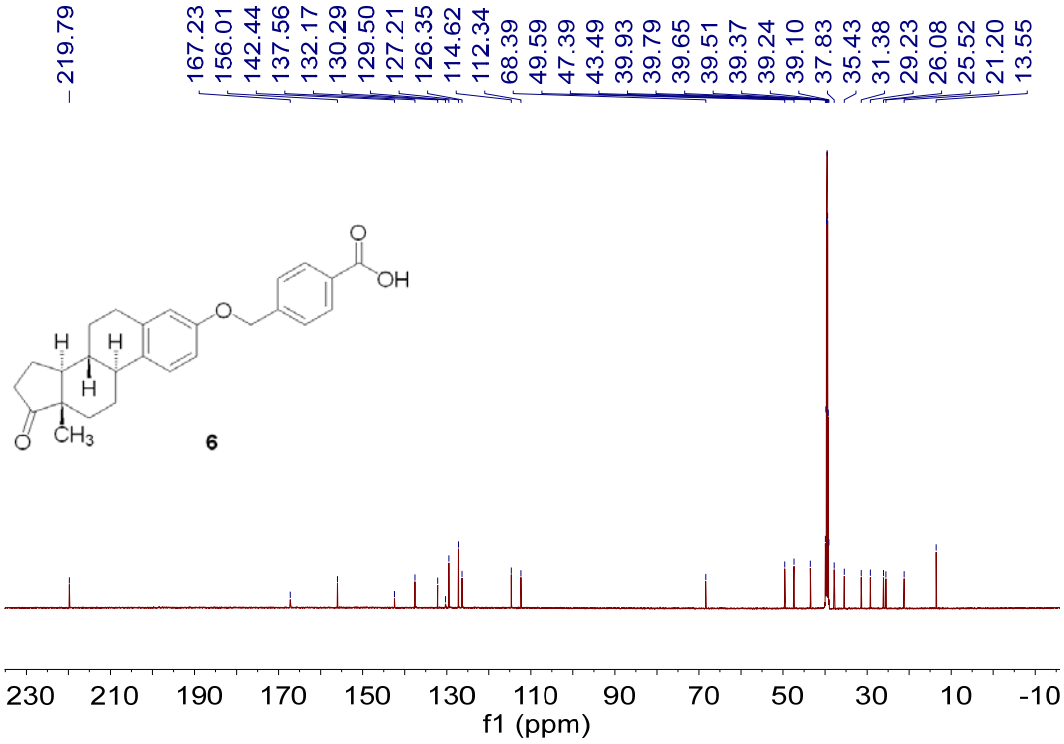
^{1}H NMR (600 MHz) and ^{13}C{^{1}H} NMR (151 MHz) spectra of **3v** ($CDCl_3$, rt).





^{1}H NMR (600 MHz) and ^{13}C NMR (151 MHz) spectra of **5** ($CDCl_3$, rt).





^{1}H NMR (600 MHz) and ^{13}C NMR (151 MHz) spectra of **6** ($(CD_3)_2SO$, rt).

6. References

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