Supporting Information

Palladium-Catalyzed C−Si bond Formation via Denitrative Cross-Coupling of Nitroarenes with Hexamethyldisilane

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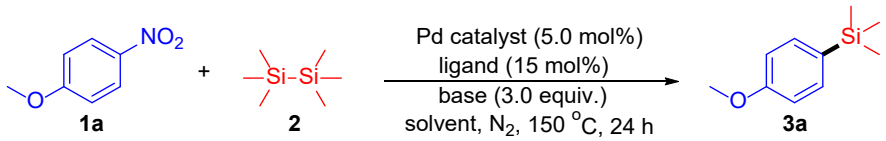
1. General Information

^{1}H NMR spectra were recorded on Bruker 500 MHz spectrometer and the chemical shifts were reported in parts per million (δ) relative to internal solvent signal (7.261 ppm in $CDCl_3$). The peak patterns are indicated as follows: s, singlet; d, doublet; dd, doublet of doublet; t, triplet; q, quartet; m, multiplet. The coupling constants, J, are reported in Hertz (Hz). ^{13}C NMR spectra were obtained at Bruker 126 MHz and referenced to the internal solvent signals (central peak is 77.000 ppm in $CDCl_3$). $CDCl_3$ was used as the NMR solvent. APEX II (Bruker Inc.) was used for HR-MS and APCI-MS.

Unless otherwise noted, all reagents were purchased from commercial suppliers (Energy-Chemical, Bidepharm, Heowns, or TCI) and used without further purification. Flash column chromatography was performed over silica gel 200-300. The reagents were weighed and handled in a glove box. All reactions were heated by metal sand bath (WATTCAS, LAB-500, https://www.wattcas.com).

2. Optimization of the Reaction Conditions

Table S1. Optimization of the reaction conditions [a,b]



entry	catalyst	ligand	base	solvent	**3a**/yield/%
1	$Pd(acac)_2$	BrettPhos	KF	$PhCF_3$	0
2	$Pd(acac)_2$	BrettPhos	CsF	$PhCF_3$	0
3	$Pd(acac)_2$	BrettPhos	K_3PO_4	$PhCF_3$	53
4	$Pd(acac)_2$	BrettPhos	$K_3PO_4{\cdot}3H_2O$	$PhCF_3$	55
5	$Pd(acac)_2$	BrettPhos	Li_2CO_3	$PhCF_3$	0
6	$Pd(acac)_2$	BrettPhos	K_2CO_3	$PhCF_3$	32
7	$Pd(acac)_2$	BrettPhos	Rb_2CO_3	$PhCF_3$	45
8	$Pd(acac)_2$	BrettPhos	Cs_2CO_3	$PhCF_3$	69
9	$Pd(acac)_2$	BrettPhos	KOH	$PhCF_3$	0
10	$Pd(acac)_2$	BrettPhos	^{t}BuOLi	$PhCF_3$	trace
11	$Pd(acac)_2$	BrettPhos	AcOK	$PhCF_3$	0
12	$Pd(acac)_2$	BrettPhos	Cs_2CO_3	PhF	48
13	$Pd(acac)_2$	BrettPhos	Cs_2CO_3	*n*-heptane	20
14	$Pd(acac)_2$	BrettPhos	Cs_2CO_3	toluene	40
15	$Pd(acac)_2$	BrettPhos	Cs_2CO_3	*p*-xylene	22
16	$Pd(acac)_2$	BrettPhos	Cs_2CO_3	*m*-xylene	30
17	$Pd(acac)_2$	BrettPhos	Cs_2CO_3	1,4-dioxane	0
18	$Pd(acac)_2$	BrettPhos	Cs_2CO_3	DMF	0
19	$Pd(acac)_2$	BrettPhos	Cs_2CO_3	DMSO	0
20	$Pd(TFA)_2$	BrettPhos	Cs_2CO_3	$PhCF_3$	30
21	$Pd(OAc)_2$	BrettPhos	Cs_2CO_3	$PhCF_3$	25
22	$Pd_2(dba)_3$	BrettPhos	Cs_2CO_3	$PhCF_3$	0
23	$Pd(dba)_2$	BrettPhos	Cs_2CO_3	$PhCF_3$	0
24	$[Pd(allyl)Cl]_2$	BrettPhos	Cs_2CO_3	$PhCF_3$	trace
25	$Pd(acac)_2$	^{t}BuBrettPhos	Cs_2CO_3	$PhCF_3$	8
26	$Pd(acac)_2$	XantPhos	Cs_2CO_3	$PhCF_3$	0
27	$Pd(acac)_2$	DPPF	Cs_2CO_3	$PhCF_3$	0

28	$Pd(acac)_2$	^{t}BuXPhos	Cs_2CO_3	$PhCF_3$	15
29 [c]	$Pd(acac)_2$	BrettPhos	Cs_2CO_3	$PhCF_3$	72
30 [d]	$Pd(acac)_2$	BrettPhos	Cs_2CO_3	$PhCF_3$	77
31 [e]	$Pd(acac)_2$	BrettPhos	Cs_2CO_3	$PhCF_3$	69
32 [d, f]	$Pd(acac)_2$	BrettPhos	Cs_2CO_3	$PhCF_3$	66
33 [d, g]	$Pd(acac)_2$	BrettPhos	Cs_2CO_3	$PhCF_3$	71
34 [d, h]	$Pd(acac)_2$	BrettPhos	Cs_2CO_3	$PhCF_3$	83(78)[i]
35 [d, j]	$Pd(acac)_2$	BrettPhos	Cs_2CO_3	$PhCF_3$	67
36 [d, h, k]	$Pd(acac)_2$	BrettPhos	Cs_2CO_3	$PhCF_3$	82
37 [d, h, l]	$Pd(acac)_2$	BrettPhos	Cs_2CO_3	$PhCF_3$	75
38 [d, h, m]	$Pd(acac)_2$	BrettPhos	Cs_2CO_3	$PhCF_3$	27

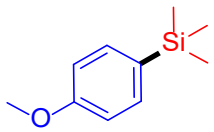
[a] Reaction conditions: 4-nitroanisole **1a** (0.30 mmol), hexamethyldisilane **2** (0.20 mmol), catalyst (5.0 mol%), ligand (15 mol%) and base (3.0 equiv.) in $PhCF_3$ (1.5 mL) at 150 °C for 24 hours under N_2; [b] The yields of 3**a** were determined by ^{1}H NMR using 1,3,5-trimethoxybenzene as an internal standard; [c] $PhCF_3$ (0.5 mL), [d] $PhCF_3$ (1.0 mL), [e] $PhCF_3$ (2.0 mL); [f] Cs_2CO_3 (1.0 equiv.), [g] Cs_2CO_3 (2.0 equiv.), [h] Cs_2CO_3 (4.0 equiv.), [j] Cs_2CO_3 (5.0 equiv.); [i] Isolated yield; [k] Additive (H_2O, 2.0 equiv.), [l] Additive ($CaSO_4$, 2.0 equiv.); [m] In air.

3. General Procedure for Product 3

In a glovebox, a flame-dried reaction tube (35 mL) equipped with a magnetic stir bar was charged with $Pd(acac)_2$ (3.1 mg, 5 mol%), BrettPhos (16.1 mg, 15 mol%), 1-methoxy-4-nitrobenzene **1a** (0.3 mmol), hexamethyldisilane **2** (0.2 mmol) and Cs_2CO_3 (0.8 mmol) before being sealed with a rubber septum. The reaction mixture was stirred at 150 °C for 24 hours. After the mixture was cooled to room temperature, the resulting solution was directly filtered. The solvent was evaporated in vacuo to give the crude products. The residue was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate) to give the desired product **3**.

4. Characterization Data of Products

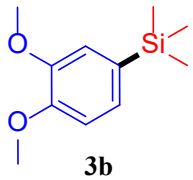
(4-Methoxyphenyl)trimethylsilane (3a)



3a

Following the general procedure, the title compound was isolated by flash column chromatography on silica gel (petroleum ether/EtOAc=50:1) as a colourless oil in (78 %, 28.1 mg) yield. The spectral data were in accordance with those reported in the literature[1]. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.49 (d, *J* = 8.6 Hz, 2H), 6.95 (d, *J* = 8.6 Hz, 2H), 3.84 (s, 3H), 0.29 (s, 9H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 160.2, 134.7, 131.2, 113.5, 54.9, -1.0.

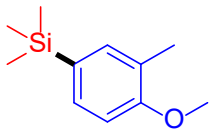
(3,4-Dimethoxyphenyl)trimethylsilane (3b)



3b

Following the general procedure, the title compound was isolated by flash column chromatography on silica gel (petroleum ether/EtOAc=50:1) as a colourless oil in (86 %, 36.2 mg) yield; The spectral data were in accordance with those reported in the literature[2]. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.09 (dd, *J* = 7.8, 1.2 Hz, 1H), 7.01 (s, 1H), 6.90 (d, *J* = 7.8 Hz, 1H), 3.91 (s, 3H), 3.89 (s, 3H), 0.27 (s, 9H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 149.7, 148.5, 131.8, 126.4, 115.7, 110.9, 55.817, 55.7, -1.0.

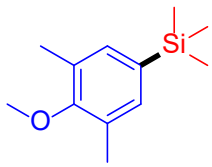
(4-Methoxy-3-methylphenyl)trimethylsilane (3c)



3c

Following the general procedure, the title compound was isolated by flash column chromatography on silica gel (petroleum ether) as a colourless oil in (56 %, 27.1 mg) yield. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.38 (dd, *J* = 8.0, 1.4 Hz, 1H), 7.33 (s, 1H), 6.88 (d, *J* = 8.0 Hz, 1H), 3.87 (s, 3H), 2.29 (s, 3H), 0.30 (s, 9H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 158.5, 135.7, 132.3, 130.8, 126.0, 109.45, 55.1, 16.2, -0.9. **HRMS** (APCI) calcd for $C_{11}H_{18}OSi$ [M + H^+], 195.1200; found: 195.1198.

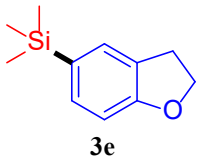
(4-Methoxy-3,5-dimethylphenyl)trimethylsilane (3d)



3d

Following the general procedure, the title compound was isolated by flash column chromatography on silica gel (petroleum ether/EtOAc=50:1) as a colourless oil in (74 %, 30.8 mg) yield; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.21 (s, 2H), 3.78 (s, 3H), 2.35 (s, 6H), 0.30 (s, 9H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 157.7, 135.3, 134.1, 130.1, 59.5, 16.1, -1.0. **HRMS** (APCI) calcd for $C_{12}H_{20}OSi$ [M + H^+], 209.1356; found: 209.1355.

(2,3-Dihydrobenzofuran-5-yl)trimethylsilane (3e)

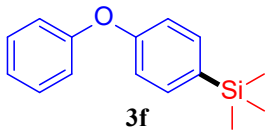


3e

Following the general procedure, the title compound was isolated by flash column chromatography on silica gel (petroleum ether) as a colourless oil in (75 %, 28.8 mg) yield. **^{1}H NMR** (500 MHz, $CDCl_3$) δ

7.39 (d, J = 0.6 Hz, 1H), 7.33 – 7.29 (m, 1H), 6.84 (d, J = 7.8 Hz, 1H), 4.58 (t, J = 8.7 Hz, 2H), 3.24 (t, J = 8.7 Hz, 2H), 0.28 (s, 9H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 160.9, 133.4, 131.1, 129.8, 126.6, 109.1, 71.0, 29.5, -0.8. **HRMS** (APCI) calcd for $C_{11}H_{16}OSi$ [M + H^+], 193.1043; found: 193.1042.

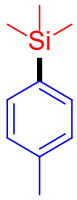
Trimethyl(4-phenoxyphenyl)silane (3f)



3f

Following the general procedure, the title compound was isolated by flash column chromatography on silica gel (petroleum ether) as a colourless oil in (56 %, 27.1 mg) yield. The spectral data were in accordance with those reported in the literature[3]. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.55 – 7.50 (m, 2H), 7.38 (dd, J = 8.6, 7.4 Hz, 2H), 7.15 (s, 1H), 7.09 – 7.03 (m, 4H), 0.32 (s, 9H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 158.1, 156.9, 134.9, 134.4, 129.7, 123.4, 119.2, 118.0, -1.0.

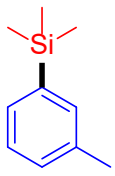
Trimethyl(p-tolyl)silane (3g)



3g

Following the general procedure, the title compound was isolated by flash column chromatography on silica gel (petroleum ether) as a colourless oil in (55 %, 18.1 mg) yield. The spectral data were in accordance with those reported in the literature[4]. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.44 (d, J = 7.7 Hz, 2H), 7.19 (d, J = 7.5 Hz, 2H), 2.36 (s, 3H), 0.26 (s, 9H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 138.6, 136.8, 133.3, 128.6, 21.4, -1.1.

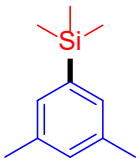
Trimethyl(m-tolyl)silane (3h)



3h

Following the general procedure, the title compound was isolated by flash column chromatography on silica gel (petroleum ether) as a colourless oil in (58 %, 19.1 mg) yield. The spectral data were in accordance with those reported in the literature[4]. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.33 (d, J = 6.3 Hz, 2H), 7.26 (t, J = 7.6 Hz, 1H), 7.19 – 7.16 (m, 1H), 2.37 (s, 3H), 0.27 (s, 9H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 140.5, 137.2, 134.1, 130.5, 129.7, 127.8, 21.7, -1.0.

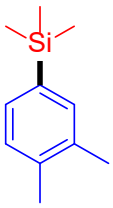
(3,5-Dimethylphenyl)trimethylsilane (3i)



3i

Following the general procedure, the title compound was isolated by flash column chromatography on silica gel (petroleum ether) as a colourless oil in (56 %, 20.0 mg) yield. The spectral data were in accordance with those reported in the literature[5]. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.16 (s, 2H), 7.03 (s, 1H), 2.35 (s, 6H), 0.28 (s, 9H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 140.2, 137.0, 131.0, 130.6, 21.4, -1.1.

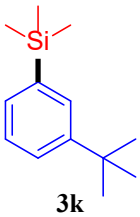
(3,4-Dimethylphenyl)trimethylsilane (3j)



3j

Following the general procedure, the title compound was isolated by flash column chromatography on silica gel (petroleum ether) as a colourless oil in (56 %, 20.0 mg) yield. The spectral data were in accordance with those reported in the literature[6]. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.31 (d, J = 10.4 Hz, 2H), 7.17 (d, J = 7.3 Hz, 1H), 2.32 (s, 3H), 2.30 (s, 3H), 0.29 (s, 9H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 137.4, 137.3, 135.8, 134.6, 131.0, 129.2, 19.7, -1.0.

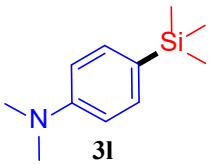
(3-(*tert*-Butyl)phenyl)trimethylsilane (3k)



3k

Following the general procedure, the title compound was isolated by flash column chromatography on silica gel (petroleum ether) as a colourless oil in (44 %, 18.2 mg) yield. The spectral data were in accordance with those reported in the literature[7]. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.60 (d, J = 0.9 Hz, 1H), 7.48 – 7.31 (m, 3H), 1.38 (s, 9H), 0.32 (s, 9H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 150.0, 139.9, 130.5, 129.9, 127.4, 125.89, 34.7, 31.4, -1.0.

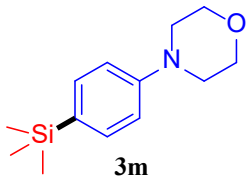
***N,N*-Dimethyl-4-(trimethylsilyl)aniline (3l)**



3l

Following the general procedure, the title compound was isolated by flash column chromatography on silica gel (petroleum ether/EtOAc=40:1) as a colourless oil in (73 %, 28.2 mg) yield. The spectral data were in accordance with those reported in the literature[1]. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.46 (d, *J* = 8.6 Hz, 2H), 6.80 (d, *J* = 8.6 Hz, 2H), 3.01 (s, 6H), 0.29 (s, 9H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 151.1, 134.5, 125.8, 112.1, 40.4, -0.7.

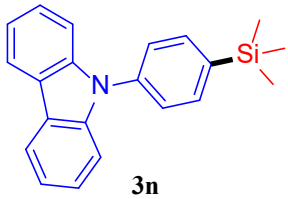
4-(4-(Trimethylsilyl)phenyl)morpholine (3m)



3m

Following the general procedure, the title compound was isolated by flash column chromatography on silica gel (petroleum ether/EtOAc=20:1) as a white solid in (84 %, 39.5 mg) yield; The spectral data were in accordance with those reported in the literature[8]. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.54 (d, *J* = 8.6 Hz, 2H), 7.00 (d, *J* = 8.6 Hz, 2H), 3.95 – 3.91 (m, 4H), 3.28 – 3.24 (m, 4H), 0.35 (s, 9H); **^{13}C NMR** ^{13}C NMR (126 MHz, $CDCl_3$) δ 151.5, 134.3, 129.8, 114.7, 66.7, 48.7, -1.0.

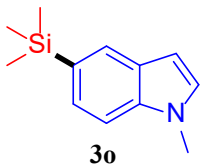
9-(4-(Trimethylsilyl)phenyl)-9*H*-carbazole (3n)



3n

Following the general procedure, the title compound was isolated by flash column chromatography on silica gel (petroleum ether) as a white solid in (32 %, 20.2 mg) yield; The spectral data were in accordance with those reported in the literature[9]. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.17 (d, *J* = 7.7 Hz, 2H), 7.79 – 7.75 (m, 2H), 7.60 – 7.57 (m, 2H), 7.48 (d, *J* = 8.2 Hz, 2H), 7.43 (dt, *J* = 8.2, 4.1 Hz, 2H), 7.33 – 7.29 (m, 2H), 0.40 (s, 9H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 140.8, 139.8, 138.1, 134.8, 126.2, 125.9, 123.4, 120.3, 119.9, 109.9, -1.1.

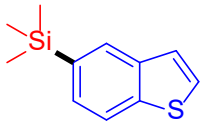
1-Methyl-5-(trimethylsilyl)-1*H*-indole (3o)



3o

Following the general procedure, the title compound was isolated by flash column chromatography on silica gel (petroleum ether) as a colourless oil in (95 %, 38.6 mg) yield; The spectral data were in accordance with those reported in the literature[10]; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.90 (s, 1H), 7.45 (d, *J* = 8.1 Hz, 1H), 7.40 (d, *J* = 8.1 Hz, 1H), 7.08 (d, *J* = 3.1 Hz, 1H), 6.56 (d, *J* = 3.1 Hz, 1H), 3.82 (s, 3H), 0.39 (s, 9H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 137.3, 129.3, 128.8, 128.6, 126.5, 126.3, 109.0, 101.1, 32.7, -0.5.

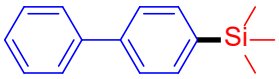
Benzo[b]thiophen-5-yltrimethylsilane (3p)



3p

Following the general procedure, the title compound was isolated by flash column chromatography on silica gel (petroleum ether) as a colourless oil in (33 %, 13.6 mg) yield; The spectral data were in accordance with those reported in the literature[11] **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.02 (s, 1H), 7.91 (d, *J* = 8.0 Hz, 1H), 7.50 (d, *J* = 8.5 Hz, 1H), 7.44 (d, *J* = 5.4 Hz, 1H), 7.36 (d, *J* = 5.4 Hz, 1H), 0.35 (s, 9H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 140.6, 139.4, 135.7, 128.9, 128.9, 126.1, 124.0, 122.0, -0.8.

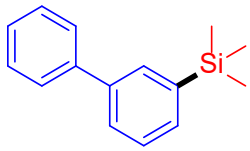
[1,1'-Biphenyl]-4-yltrimethylsilane (3q)



3q

Following the general procedure, the title compound was isolated by flash column chromatography on silica gel (petroleum ether) as a white solid in (58 %, 26.3 mg) yield; The spectral data were in accordance with those reported in the literature[12]. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.65 – 7.60 (m, 6H), 7.46 (t, *J* = 7.7 Hz, 2H), 7.39 – 7.35 (m, 1H), 0.33 (s, 9H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 141.8, 141.3, 139.4, 134.0, 128.9, 127.5, 127.3, 126.6, -0.9.

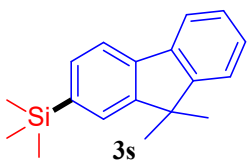
[1,1'-Biphenyl]-3-yltrimethylsilane (3r)



3r

Following the general procedure, the title compound was isolated by flash column chromatography on silica gel (petroleum ether) as a colourless oil in (58 %, 26.3 mg) yield. The spectral data were in accordance with those reported in the literature[13]. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.78 (s, 1H), 7.66 – 7.61 (m, 3H), 7.56 (dd, *J* = 4.8, 3.6 Hz, 1H), 7.49 (dt, *J* = 7.2, 5.3 Hz, 3H), 7.40 (d, *J* = 7.4 Hz, 1H), 0.37 (s, 9H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 141.6, 141.0, 140.5, 132.2, 132.1, 128.7, 128.1, 127.7, 127.3, 127.2, -1.1.

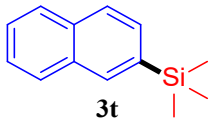
(9,9-Dimethyl-9*H*-fluoren-2-yl)trimethylsilane (3s)



3s

Following the general procedure, the title compound was isolated by flash column chromatography on silica gel (petroleum ether) as a colourless oil in (56 %, 29.8 mg) yield; The spectral data were in accordance with those reported in the literature[13]. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.78 – 7.74 (m, 2H), 7.62 (s, 1H), 7.55 (dd, *J* = 7.4, 0.9 Hz, 1H), 7.49 – 7.46 (m, 1H), 7.38 – 7.34 (m, 2H), 1.54 (s, 6H), 0.37 (s, 9H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 153.8, 152.7, 139.9, 139.4, 139.1, 132.1, 127.4, 127.2, 126.9, 122.6, 120.1, 119.3, 46.8, 27.2, -0.8.

Trimethyl(naphthalen-2-yl)silane (3t)

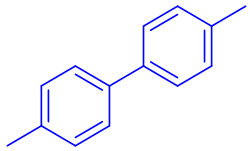


3t

Following the general procedure, the title compound was isolated by flash column chromatography on silica gel (petroleum ether) as a colourless oil in (40 %, 16.0 mg) yield; The spectral data were in accordance with those reported in the literature[1]; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.03 (s, 1H), 7.85 (ddd, *J* = 11.7, 5.9, 3.2 Hz, 3H), 7.62 (dd, *J* = 8.1, 1.1 Hz, 1H), 7.51 – 7.47 (m, 2H), 0.37 (s, 9H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 137.9, 133.7, 133.6, 132.9, 129.8, 128.0, 127.7, 126.9, 126.2, 125.8, -1.1.

5. Derivatizations of Products and Characterization Data of Derivatives

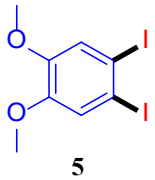
(4-Methoxy-3,5-dimethylphenyl)trimethylsilane (4)



4

In a glovebox, a flame-dried reaction tube (35 mL) equipped with a magnetic stir bar was charged with **3g** (57.0 μL, 0.3 mmol), $Pd(MeCN)_4(BF_4)_2$ (3.3 mg, 2.5 mol%), *o*-chloranil (55.3 mg, 0.225 mmol), $CHCl_3$ (1.5 mL) before being sealed with a rubber septum. The reaction mixture was stirred at 60 °C for 10 hours. After the mixture was cooled to room temperature, the resulting solution was directly filtered. The solvent was evaporated in vacuo to give the crude products. The residue was purified by flash column chromatography on silica gel (petroleum ether) to give the desired product **4** (23.4 mg, 86%); The spectral data were in accordance with those reported in the literature[14]; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.40 (d, *J* = 8.1 Hz, 4H), 7.15 (d, *J* = 7.9 Hz, 4H), 2.31 (s, 6H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 138.3, 136.7, 129.4, 126.8, 21.1.

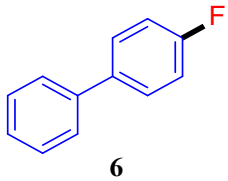
1,2-Diiodo-4,5-dimethoxybenzene (5)



5

In air, a flame-dried reaction tube (35 mL) equipped with a magnetic stir bar was charged with **3b** (42.1 mg, 0.2 mmol), I_2 (50.8mg,0.2mmol),1-chloromethyl-4-fluoro-1,4-diazabicyclo [2.2.2] octane di(tetrafluoroborate) salt (142.0 mg, 0.4 mmol), CH_3CN (1.5 mL) before being sealed with a rubber septum. The reaction mixture was stirred at room temperature for 1 hour. The solvent was evaporated in vacuo to give the crude products. The residue was purified by flash column chromatography on silica gel (petroleum ether) to give the desired product **5** (50.0 mg, 65%); The spectral data were in accordance with those reported in the literature[15]; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.23 (s, 2H), 3.83 (s, 6H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 149.6, 121.6, 96.0, 56.1.

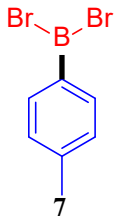
4-Fluoro-1,1'-biphenyl (6)



6

In a glovebox, a flame-dried reaction tube (35 mL) equipped with a magnetic stir bar was charged with **3q** (45.3 mg, 0.2 mmol), $Pb(OAc)_4$ (106.4 mg, 0.24 mmol), BF_3·Et_2O (5.0 mL) before being sealed with a rubber septum. The reaction mixture was stirred overnight at room temperature, the resulting solution was directly filtered . The solvent was evaporated in vacuo to give the crude products. The residue was purified by flash column chromatography on silica gel (petroleum ether) to give the desired product **6** (31.0 mg, 90%); The spectral data were in accordance with those reported in the literature[16]; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.57 (ddd, J = 5.2, 3.5, 2.5 Hz, 4H), 7.49 – 7.44 (m, 2H), 7.37 (ddd, J = 7.5, 3.9, 1.0 Hz, 1H), 7.18 – 7.12 (m, 2H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 162.4 (d, $J_{C\text{-}F}$ = 246.2 Hz), 140.2, 137.3 (d, $J_{C\text{-}F}$ = 3.2 Hz), 128.8, 128.7 (d, $J_{C\text{-}F}$ = 8.0 Hz), 127., 127.0, 115.6 (d, $J_{C\text{-}F}$ = 21.4 Hz); **^{19}F NMR** (471 MHz, $CDCl_3$) δ -115.8.

Dibromo(p-tolyl)borane (7)

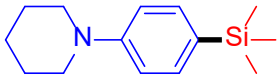


7

In a glovebox, a flame-dried reaction tube (35 mL) equipped with a magnetic stir bar was charged with **3g** (57.0 µL, 0.3 mmol), BBr_3 (32.0 µL, 0.33 mmol), pentane (0.25 mL) before being sealed with a rubber septum. The resulting mixture was stirred at 50 °C for 5 h. After the mixture was cooled to room temperature, the solvent was evaporated in vacuo to give the product **7** (57.0 mg, 73%); The spectral data were in accordance with those reported in the literature[17]; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.13 (d, J = 7.7 Hz, 2H), 7.32 (d, J = 7.6 Hz, 2H), 2.45 (s, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 142.9, 135.7, 128.8, 21.9.

6. The Selective Transformations of the C–Br and C–NO_2 Bonds

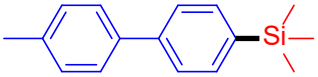
1-(4-(trimethylsilyl)phenyl)piperidine (8)



8

In a glovebox, a flame-dried reaction tube (35 mL) equipped with a magnetic stir bar was charged with 1-bromo-4-nitrobenzene (60.6 mg, 0.3 mmol), piperidine (30 μL, 0.3 mmol), $Pd(acac)_2$ (5.0 mol%), BrettPhos (15 mol%), Cs_2CO_3(3.0 equiv.), $PhCF_3$ (1.0 mL) before being sealed with a rubber septum. The reaction mixture was stirred at 100 °C for 24 hours. After through flash column chromatography on silica gel (petroleum ether/EtOAc=50:1) to give the intermediate product, then the reaction was carried out according to the standard conditions of denitrative silylation to afford the **8** in 82% yield. The spectral data were in accordance with those reported in the literature[18]; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.41 (d, *J* = 8.6 Hz, 2H), 6.93 (d, *J* = 8.6 Hz, 2H), 3.24 – 3.16 (m, 4H), 1.70 (dt, *J* = 11.3, 5.7 Hz, 4H), 1.60 (dd, *J* = 11.3, 5.8 Hz, 2H), 0.24 (s, 9H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 152.4, 134.3, 128.6, 115.4, 50.0, 25.8, 24.4, -0.9.

Trimethyl(4'-methyl-[1,1'-biphenyl]-4-yl)silane(9).



9

In a glovebox, a flame-dried reaction tube (35 mL) equipped with a magnetic stir bar was charged with 1-bromo-4-nitrobenzene (60.6 mg, 0.3 mmol), p-tolylboronic acid (40.8mg, 0.3 mmol), $Pd(acac)_2$ (5.0 mol%), BrettPhos (15 mol%), Cs_2CO_3(3.0 equiv.), $PhCF_3$ (1.0 mL) before being sealed with a rubber septum. The reaction mixture was stirred at 100 °C for 24 hours. After through flash column chromatography on silica gel (petroleum ether/EtOAc=100:1) to give the intermediate product, then the reaction was carried out according to the standard conditions of denitrative silylation to afford the **9** in 63% yield. The spectral data were in accordance with those reported in the literature[19]; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.68 – 7.56 (m, 4H), 7.53 (d, *J* = 8.1 Hz, 2H), 7.32 – 7.17 (m, 2H), 2.43 (s, 3H), 0.33 (s, 9H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 141.5, 138.8, 138.3, 137.1, 133.8, 129.5, 127.0, 126.3, 21.1, -1.1.

7. 1 mmol Scale Experiments

In a glovebox, a flame-dried reaction tube (35 mL) equipped with a magnetic stir bar was charged with $Pd(acac)_2$ (15.5 mg, 5 mol%), BrettPhos (80.5 mg, 15 mol%), 1-methoxy-4-nitrobenzene **1a** (1.5 mmol) or 1-methyl-4-nitrobenzene or 1,2-dimethoxy-4-nitrobenzene, hexamethyldisilane **2** (1.0 mmol) and Cs_2CO_3 (4.0 mmol) before being sealed with a rubber septum. The reaction mixture was stirred at 150 °C for 24 hours. After the mixture was cooled to room temperature, the resulting solution was directly filtered . The solvent was evaporated in vacuo to give the crude products. The residue was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate) to give the desired product **3a** (170.0 mg, 94%), **3g** (113.0 mg, 69%), and **3b** (185.0 mg, 88%).

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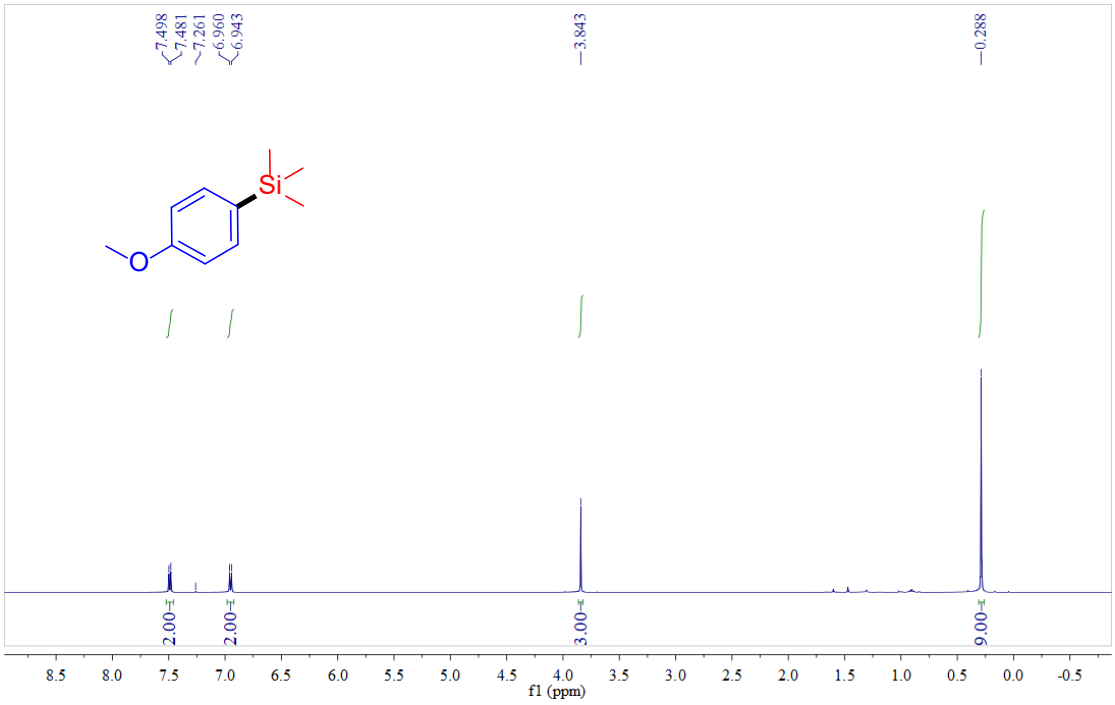
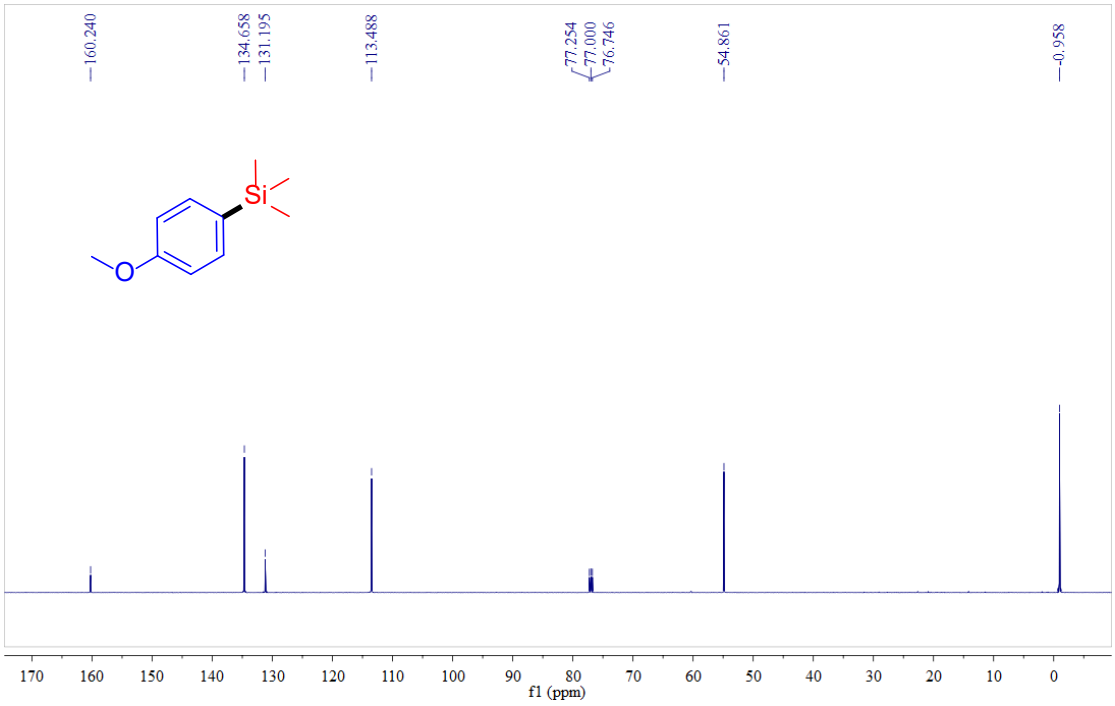
9. NMR Spectra of Products and Derivatives

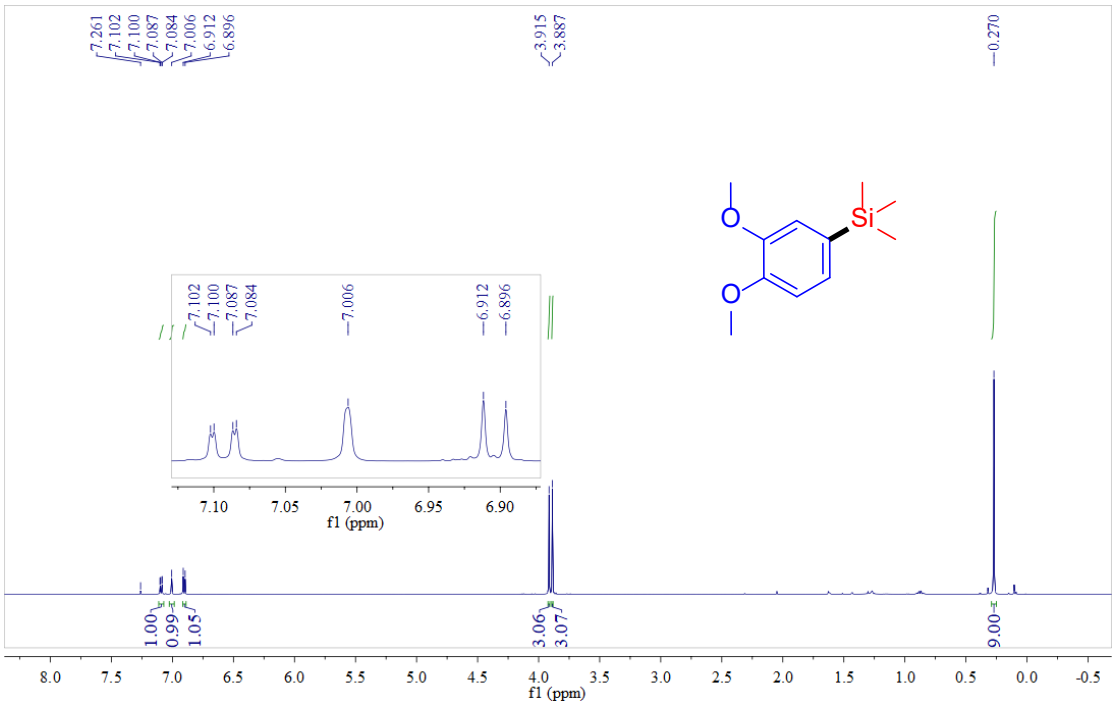
^{1}H NMR Spectrum of **3a**



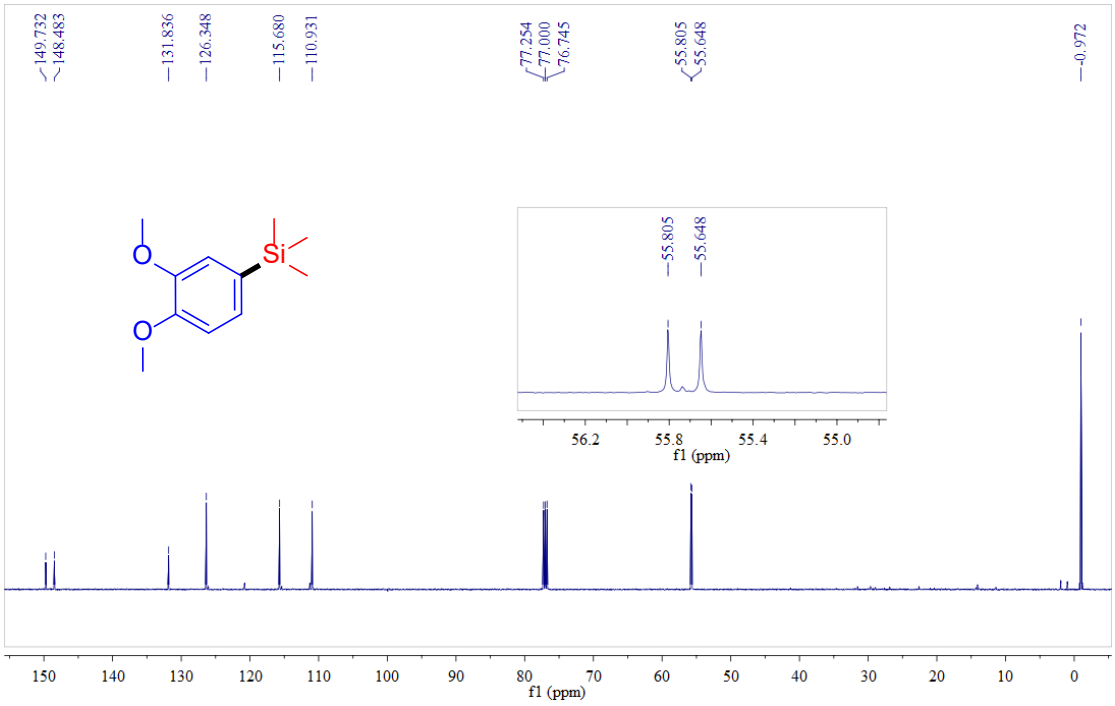
^{13}C NMR Spectrum of **3a**



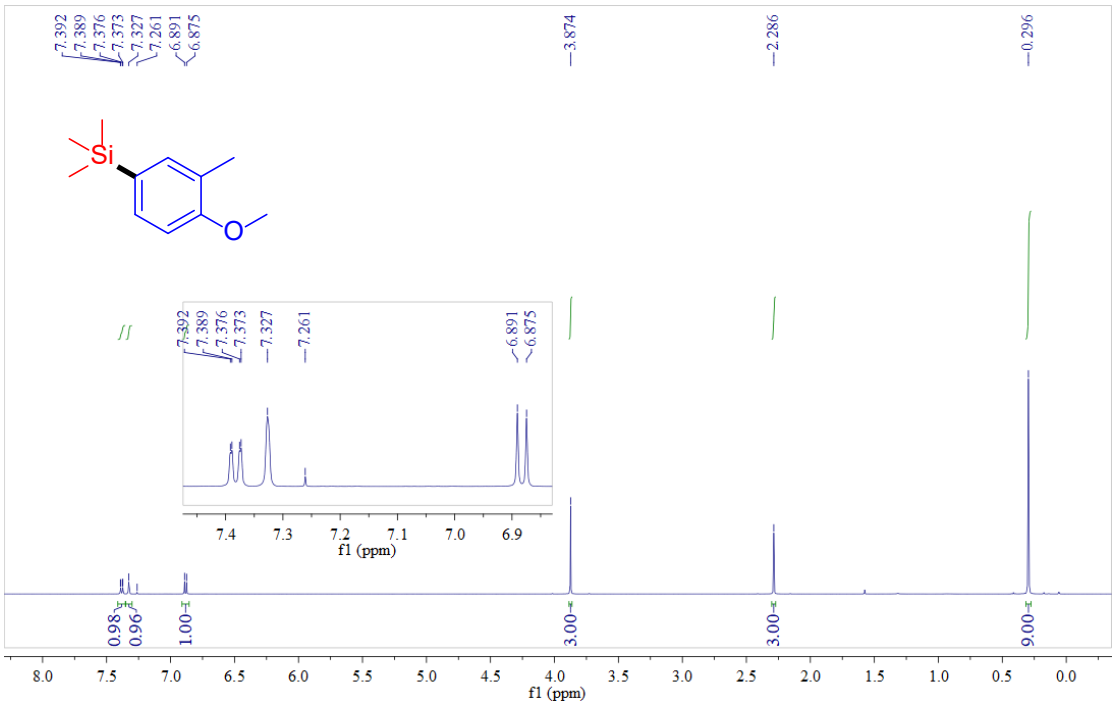
^{1}H NMR Spectrum of **3b**



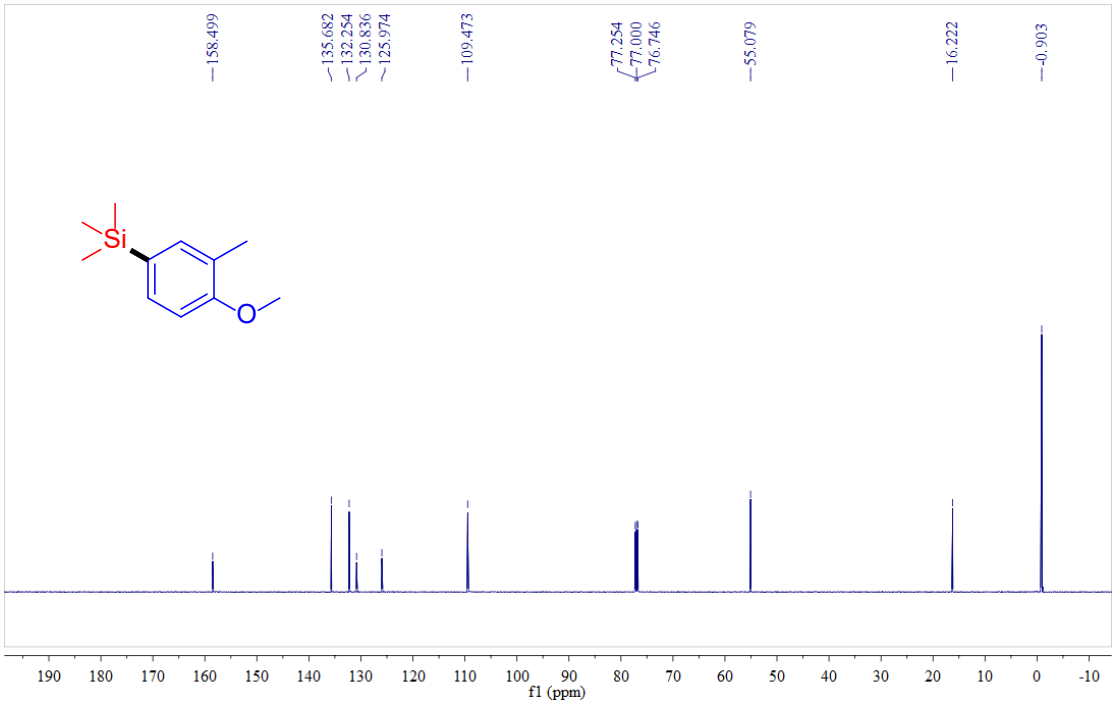
^{13}C NMR Spectrum of **3b**



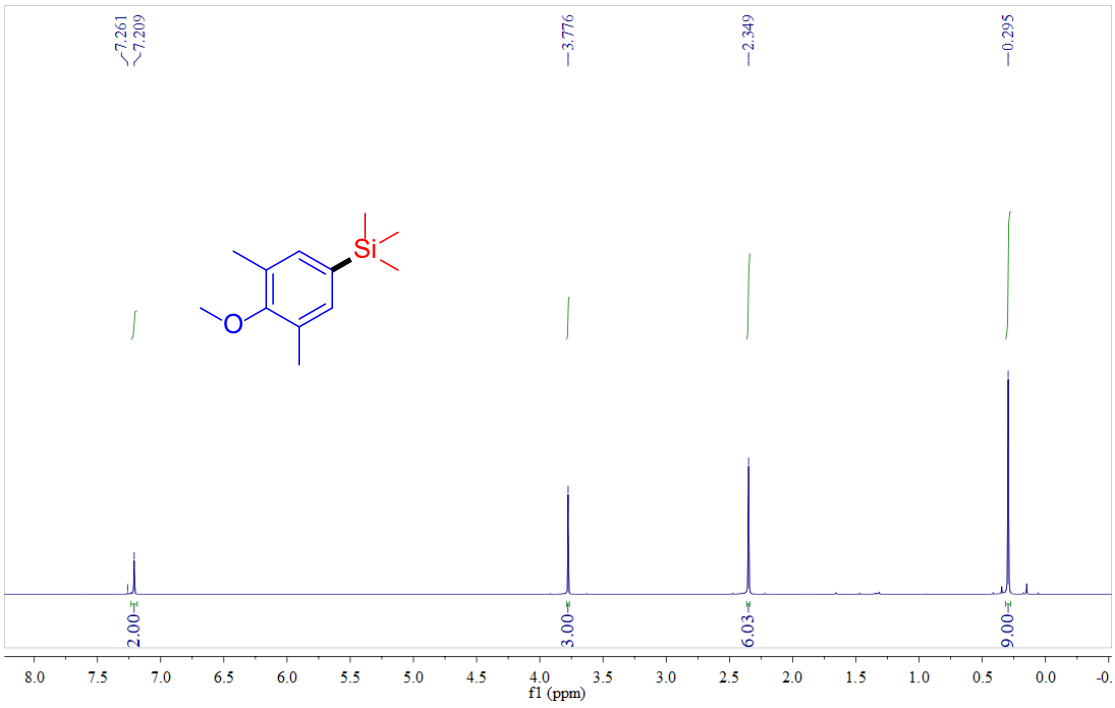
^{1}H NMR Spectrum of **3c**



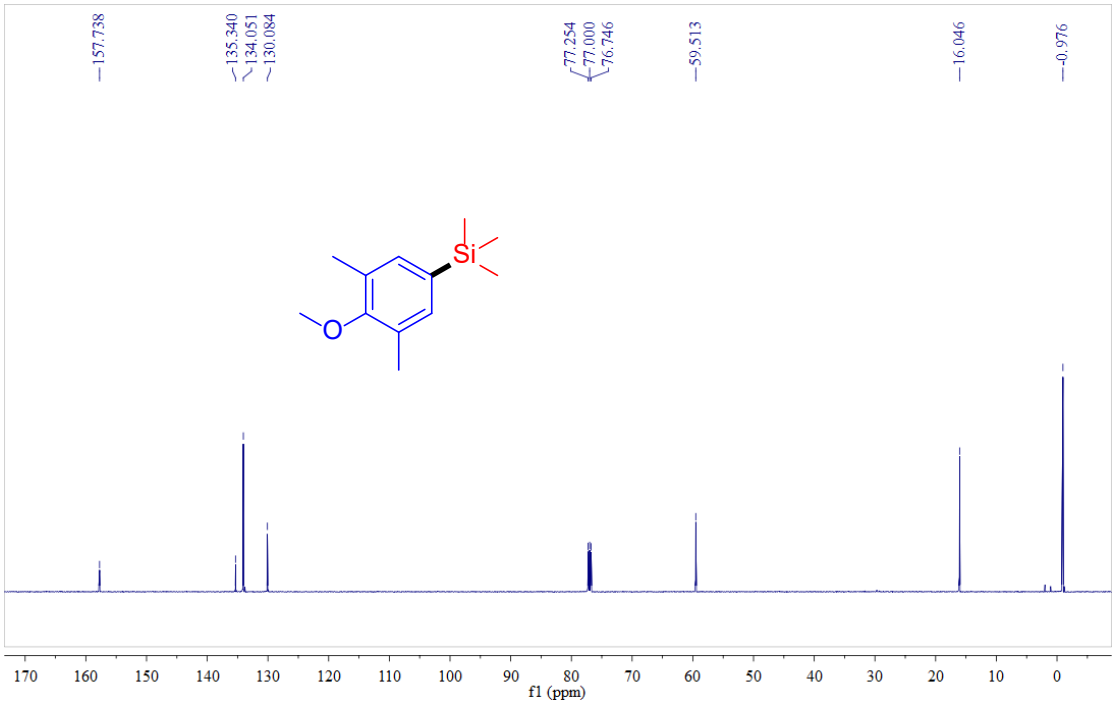
^{13}C NMR Spectrum of **3c**



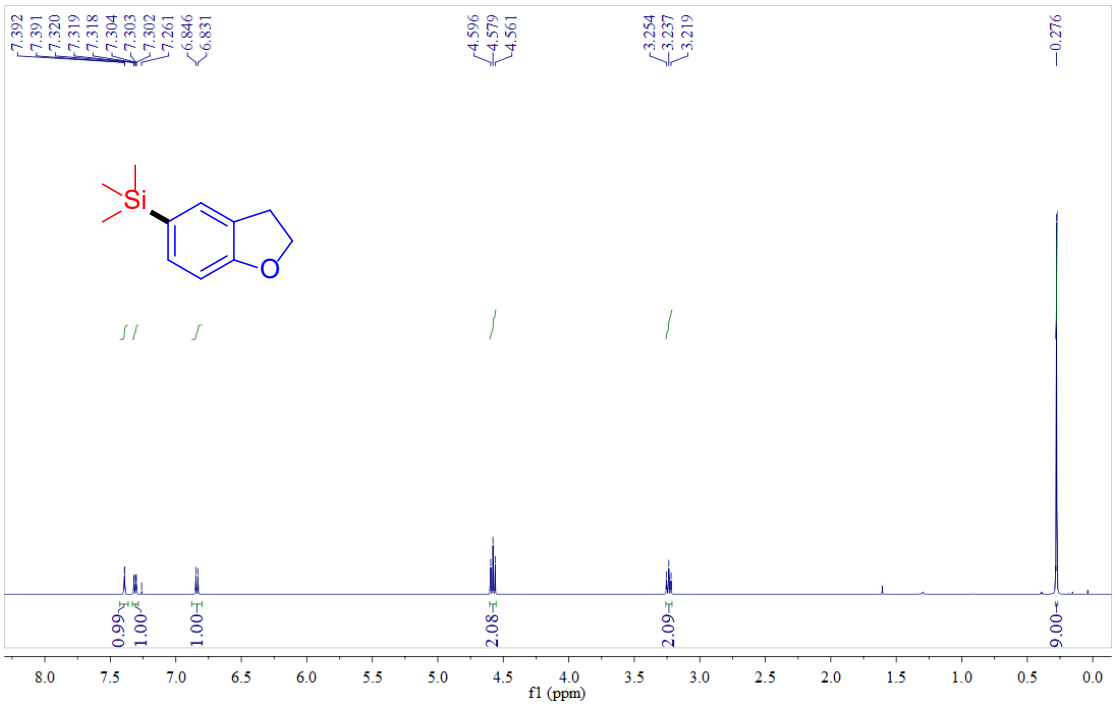
^{1}H NMR Spectrum of **3d**



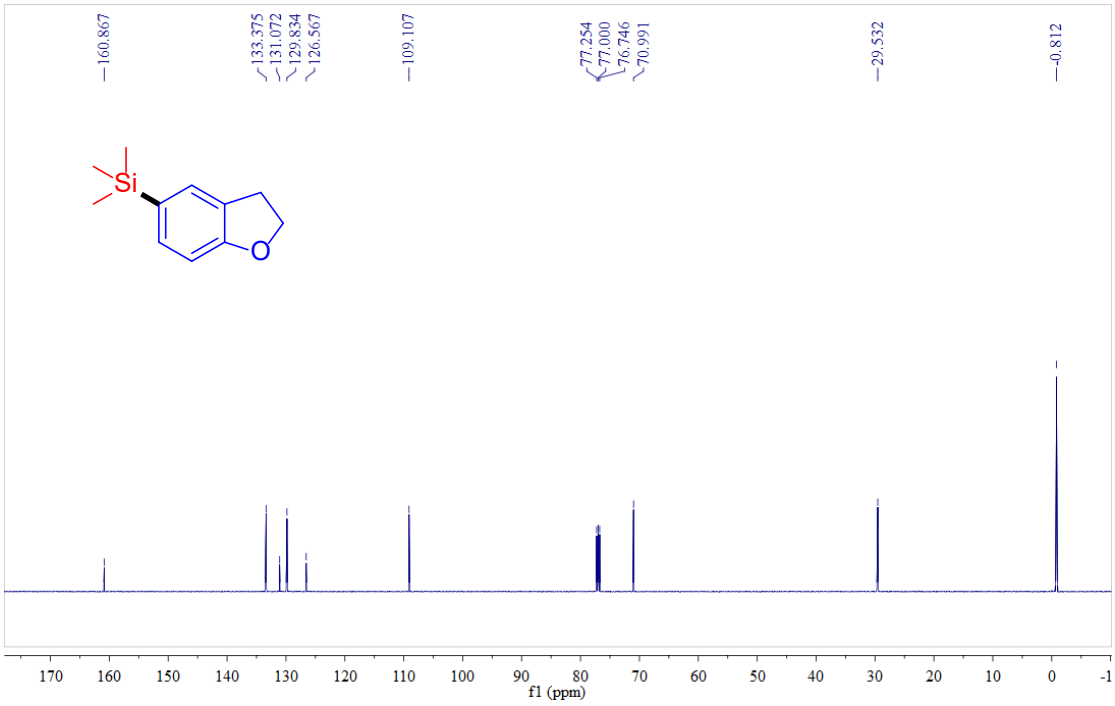
^{13}C NMR Spectrum of **3d**



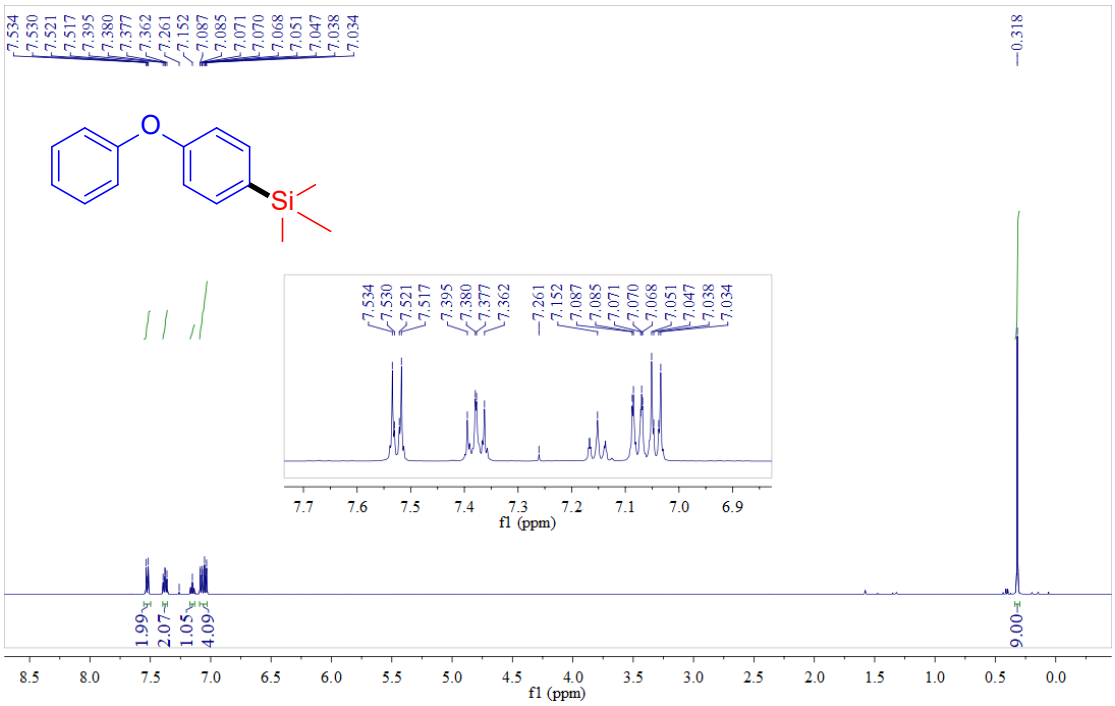
^{1}H NMR Spectrum of **3e**



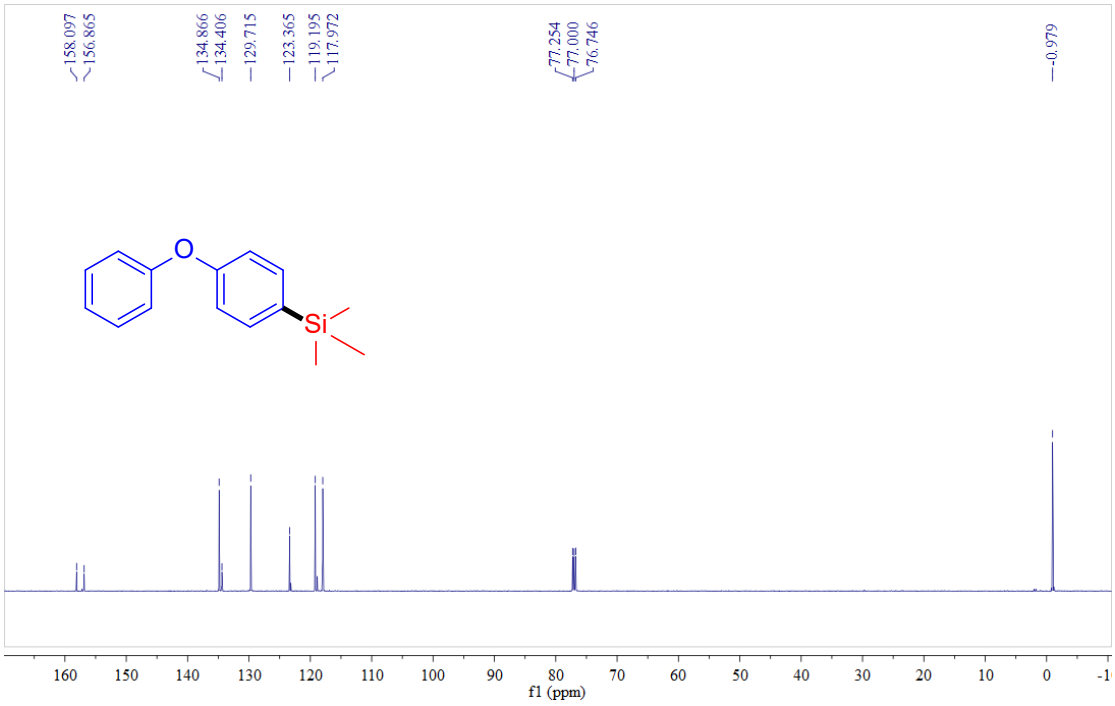
^{13}C NMR Spectrum of **3e**



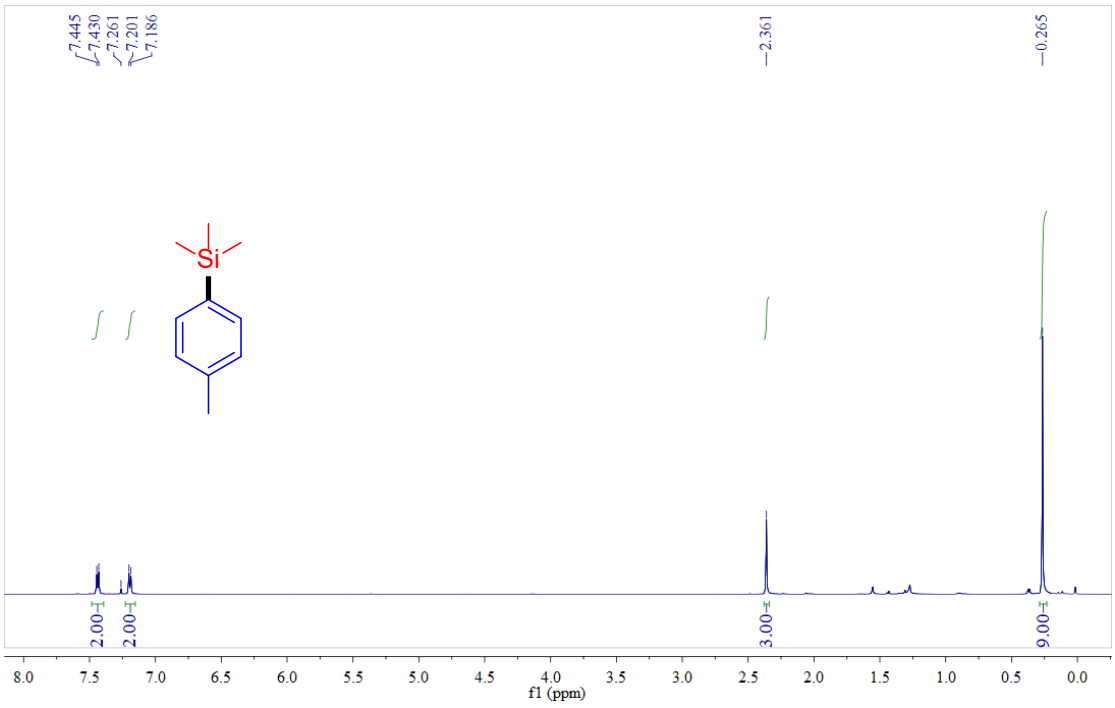
^{1}H NMR Spectrum of **3f**



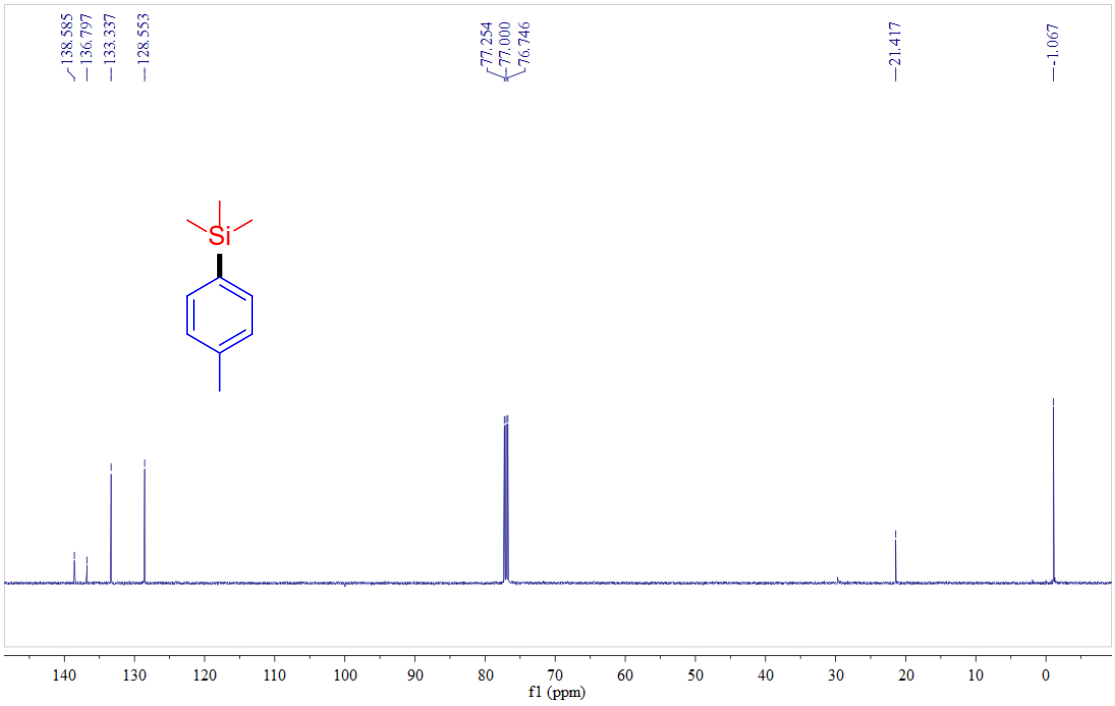
^{13}C NMR Spectrum of **3f**



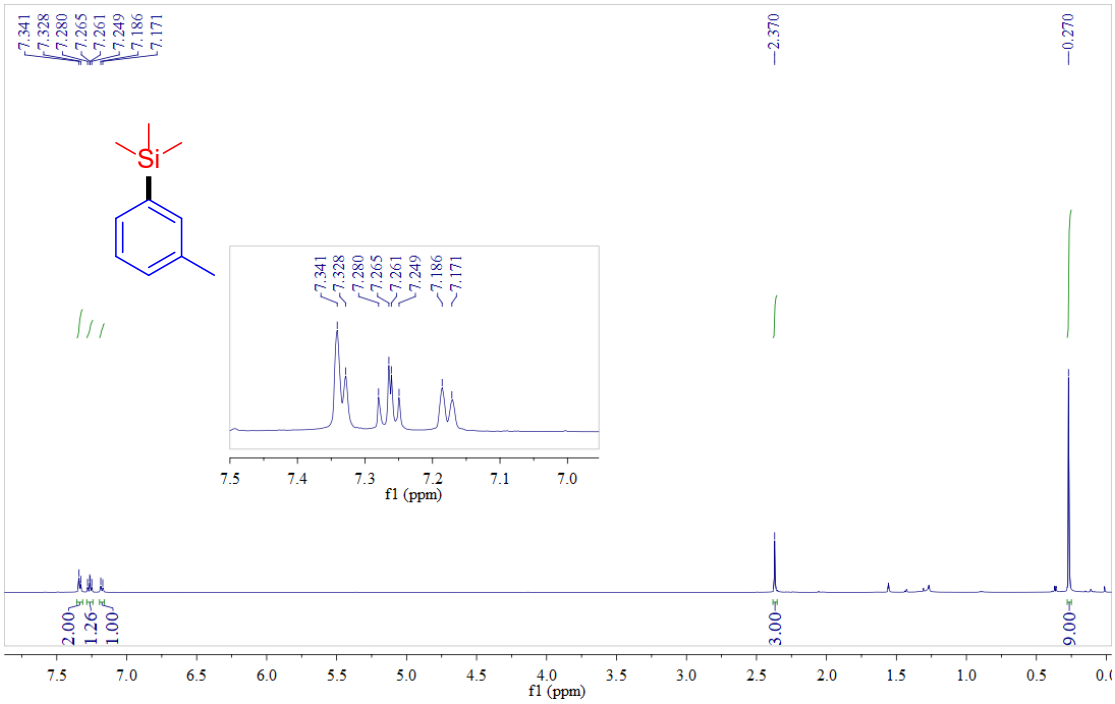
^{1}H NMR Spectrum of **3g**



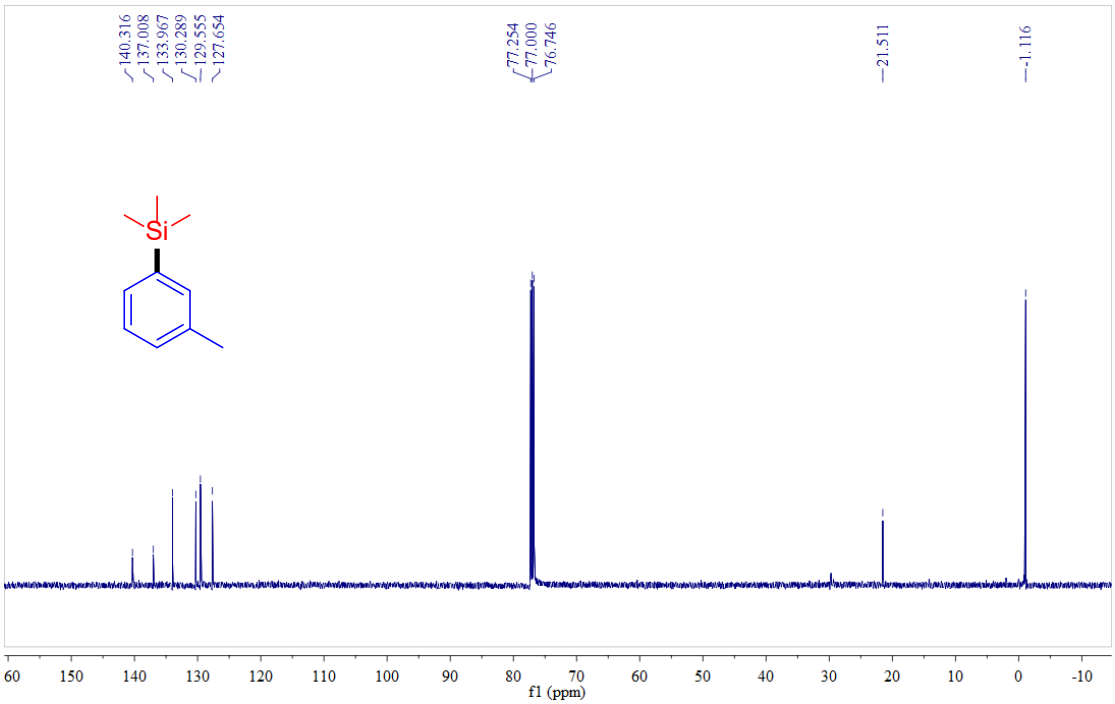
^{13}C NMR Spectrum of **3g**



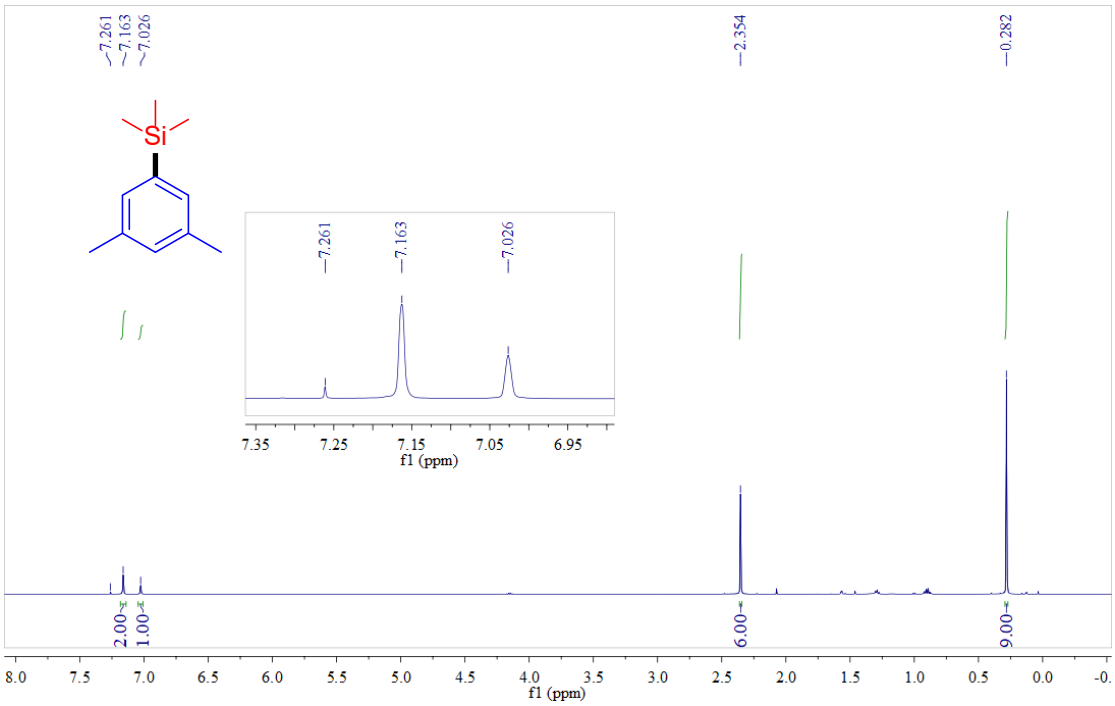
^{1}H NMR Spectrum of **3h**



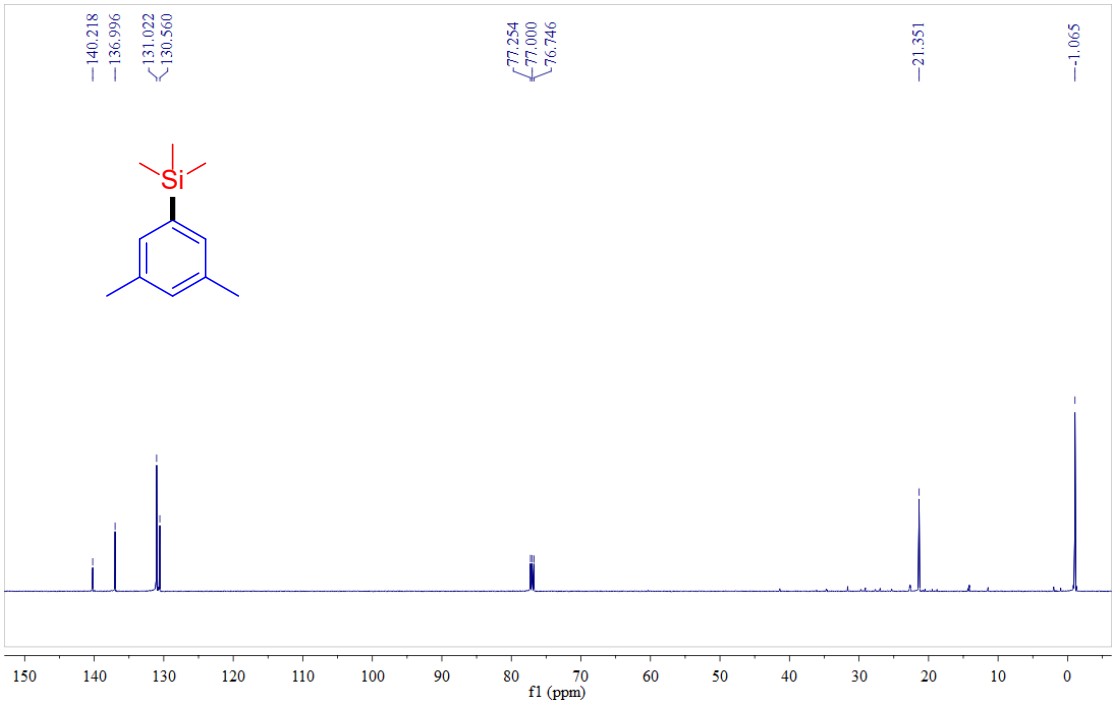
^{13}C NMR Spectrum of **3h**



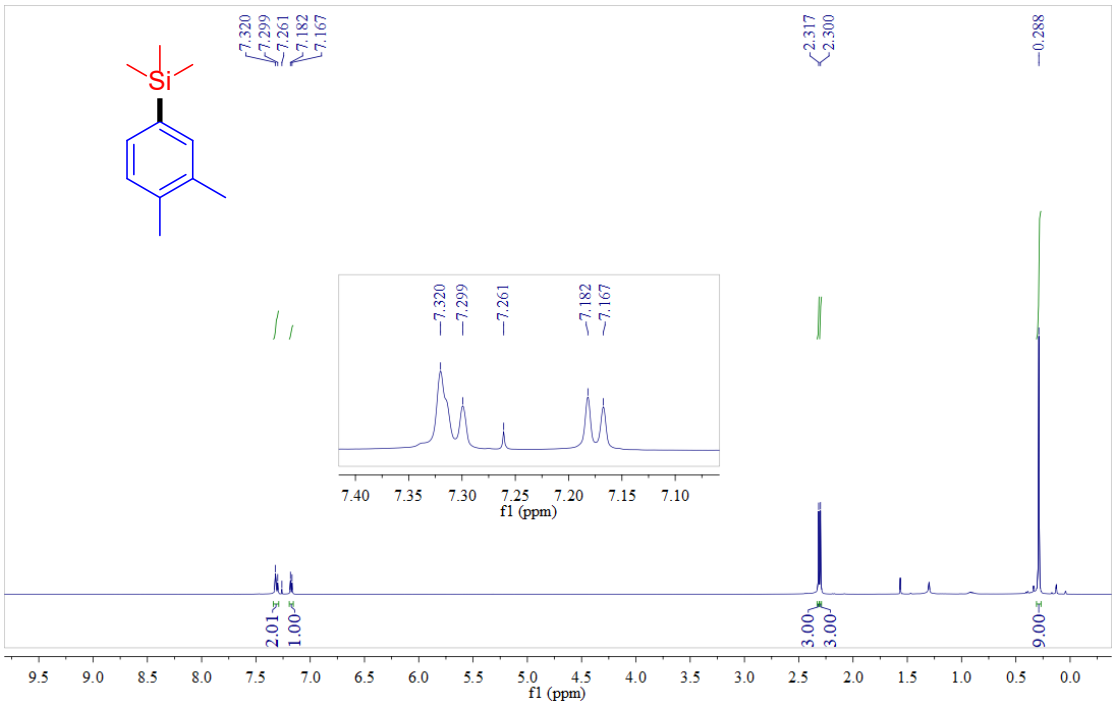
^{1}H NMR Spectrum of **3i**



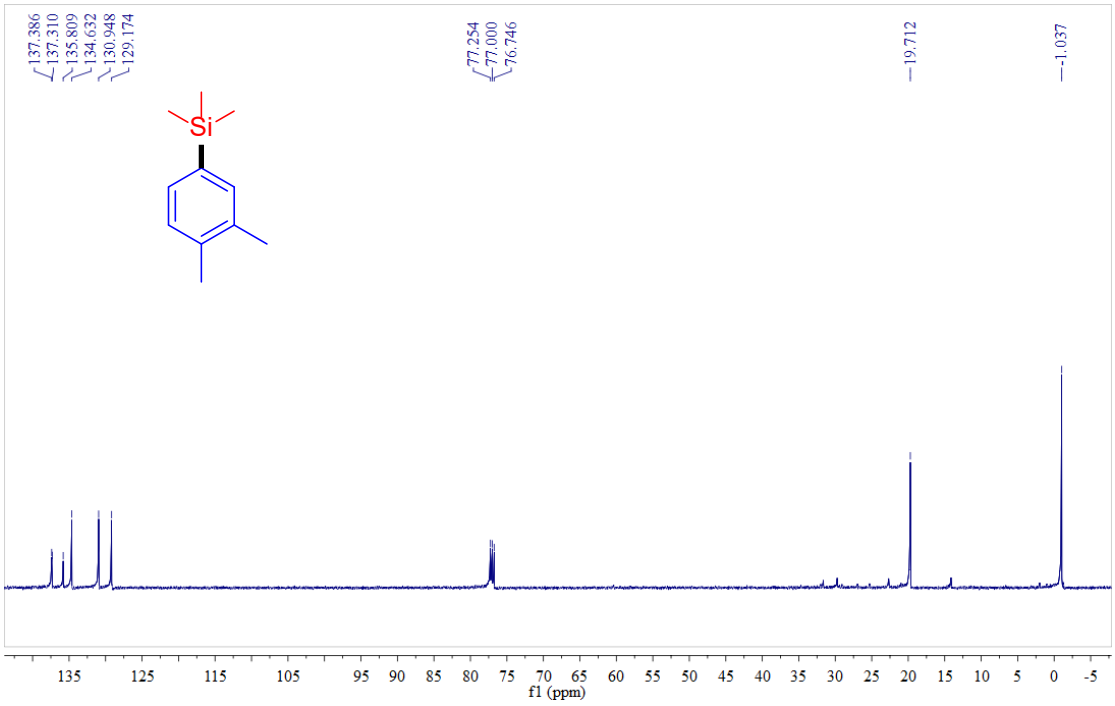
^{13}C NMR Spectrum of **3i**



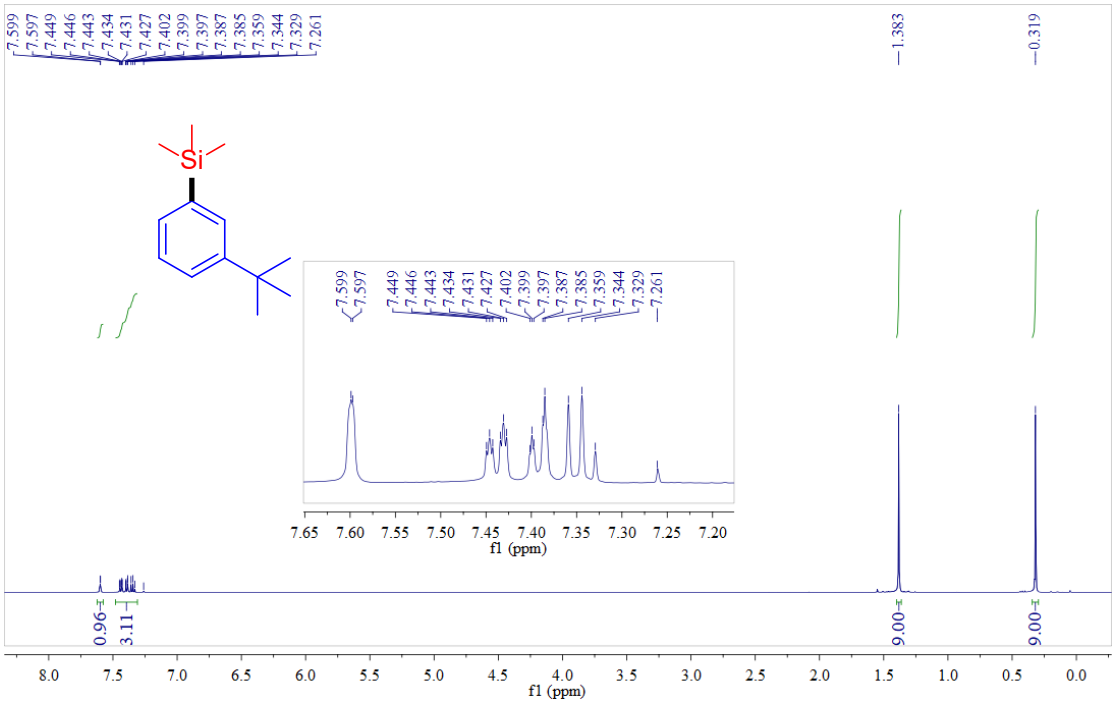
^{1}H NMR Spectrum of **3j**



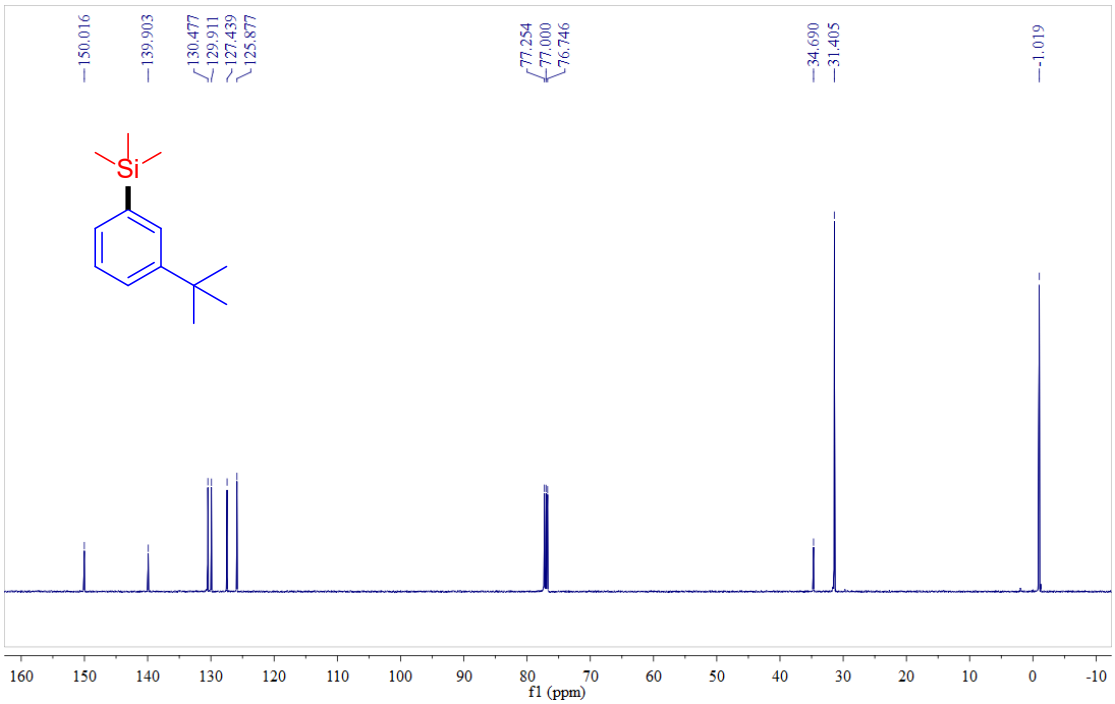
^{13}C NMR Spectrum of **3j**



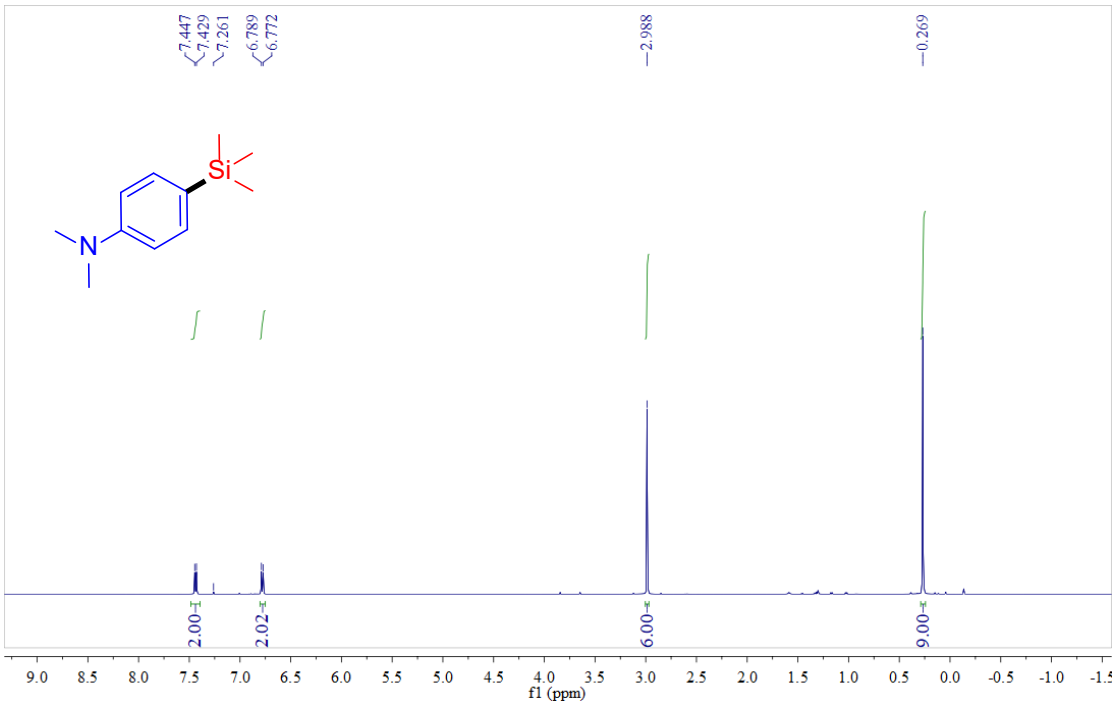
^{1}H NMR Spectrum of **3k**



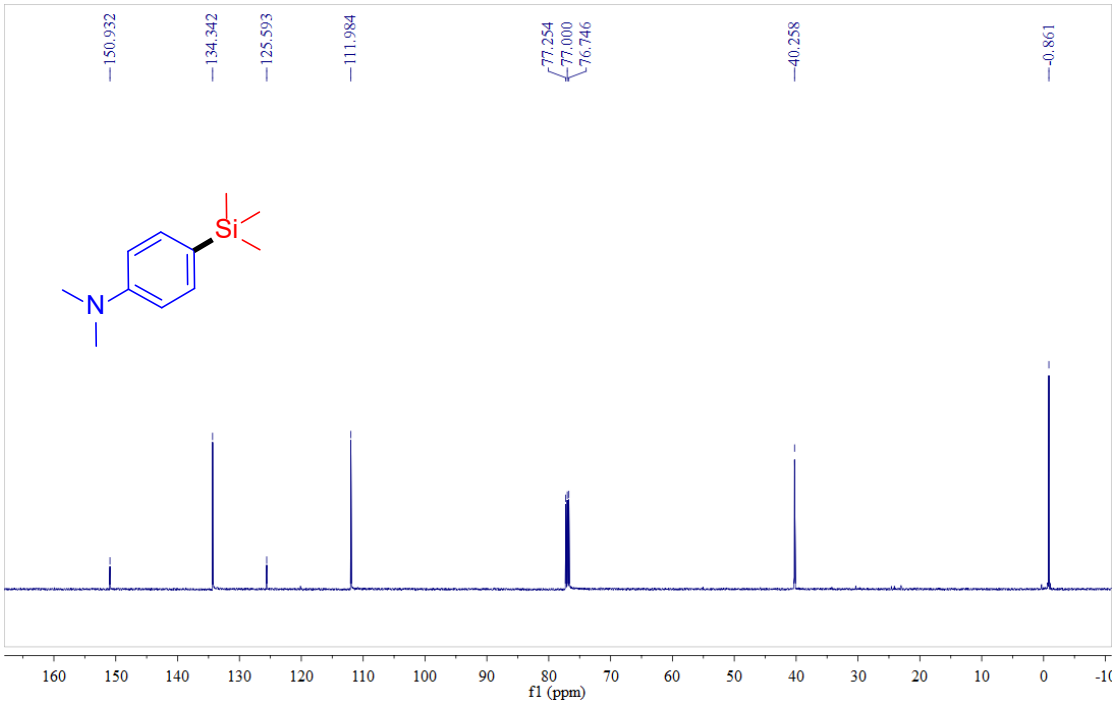
^{13}C NMR Spectrum of **3k**



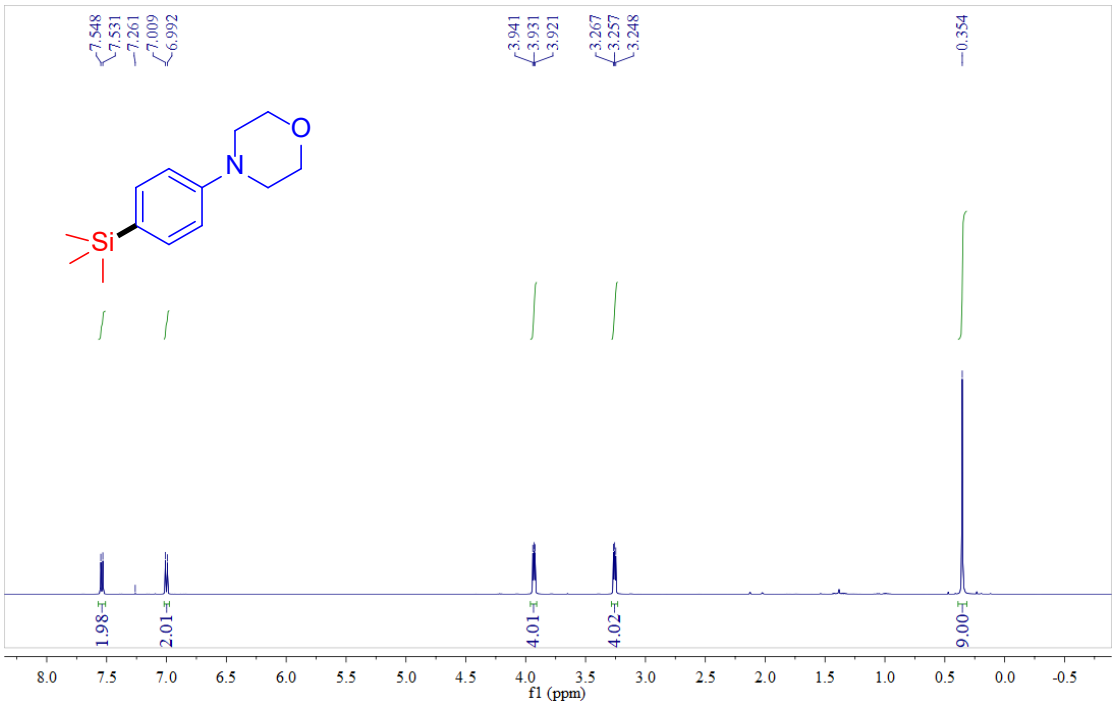
^{1}H NMR Spectrum of **3l**



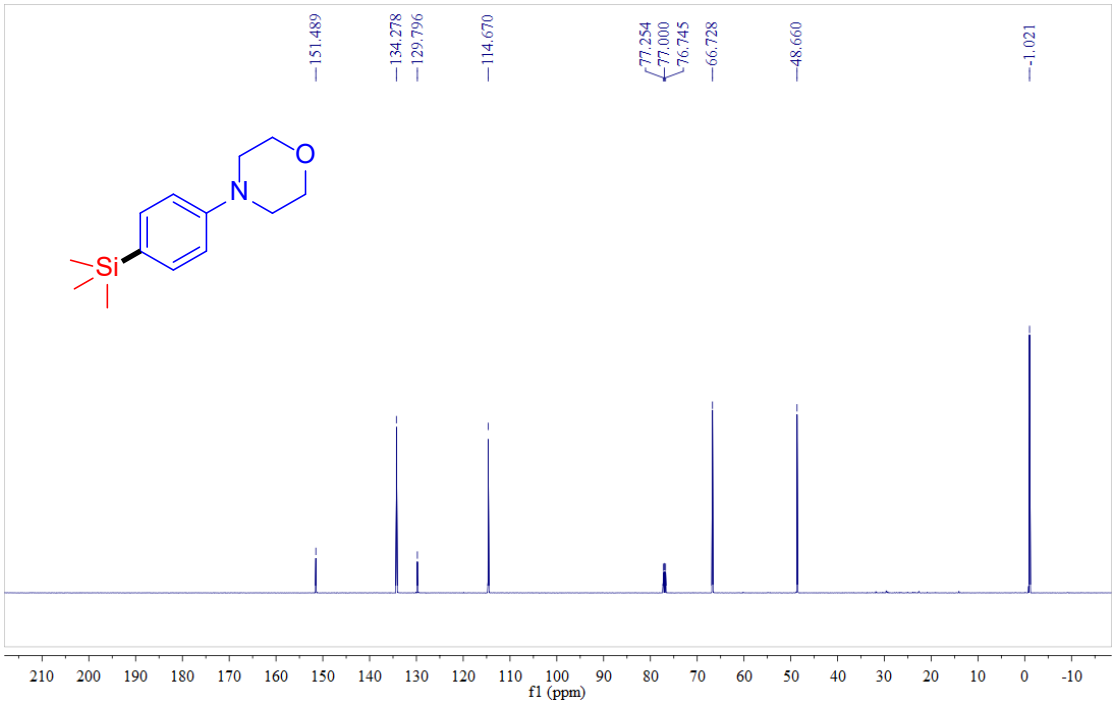
^{13}C NMR Spectrum of **3l**



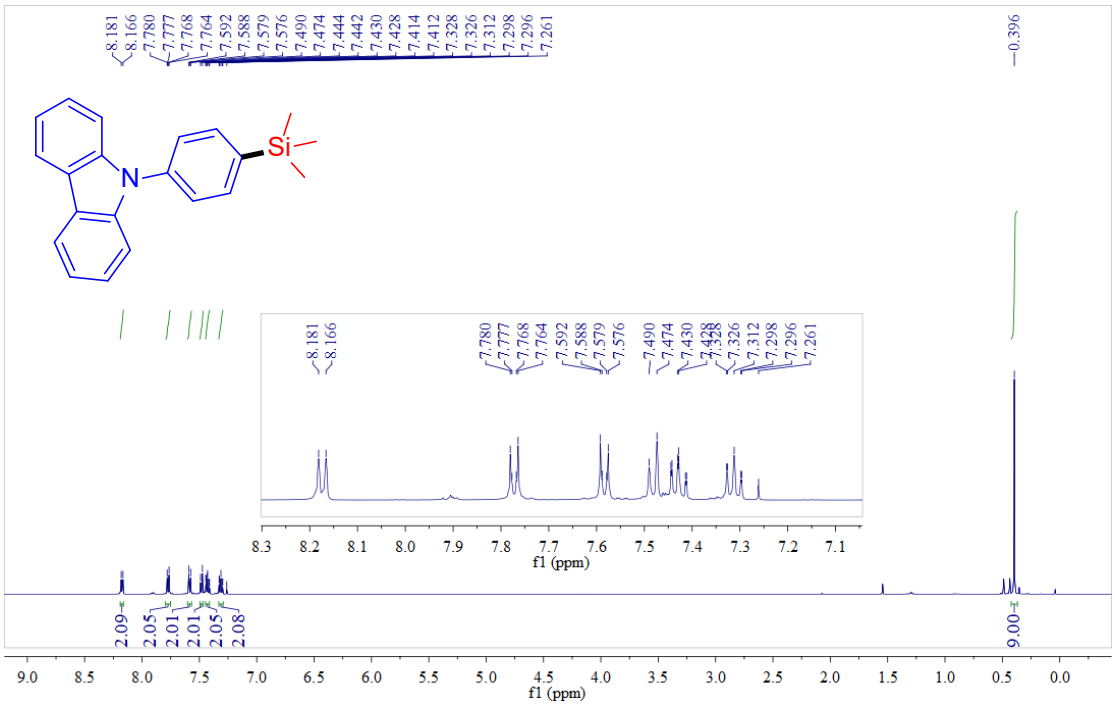
^{1}H NMR Spectrum of **3m**



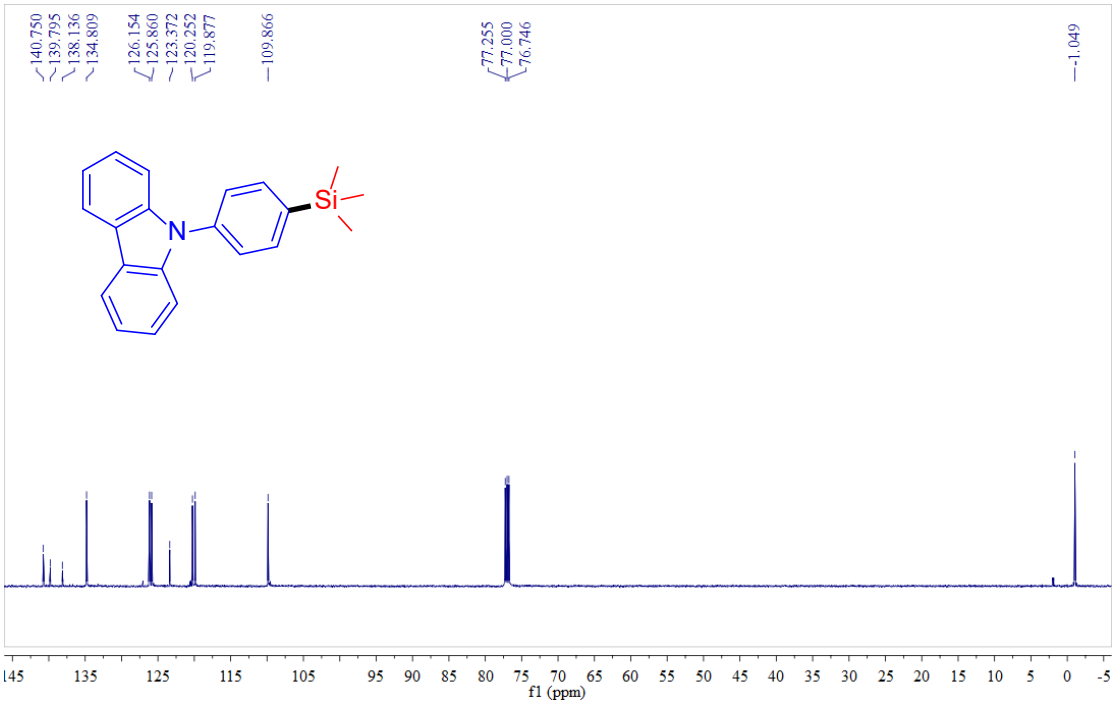
^{13}C NMR Spectrum of **3m**



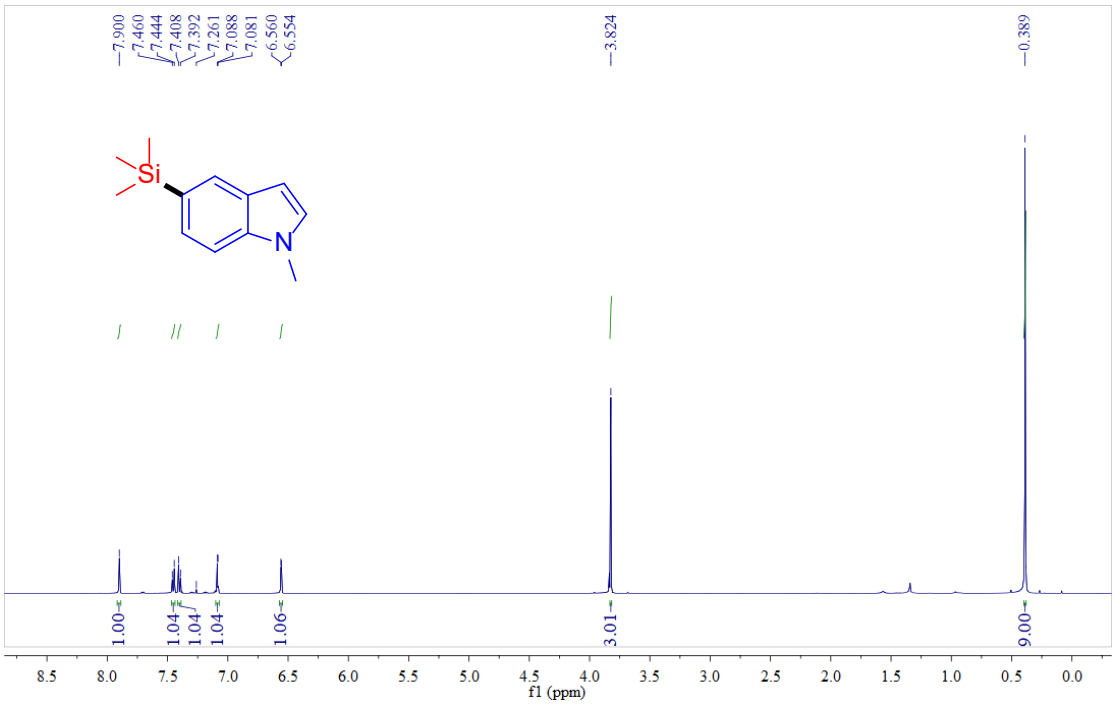
^{1}H NMR Spectrum of **3n**



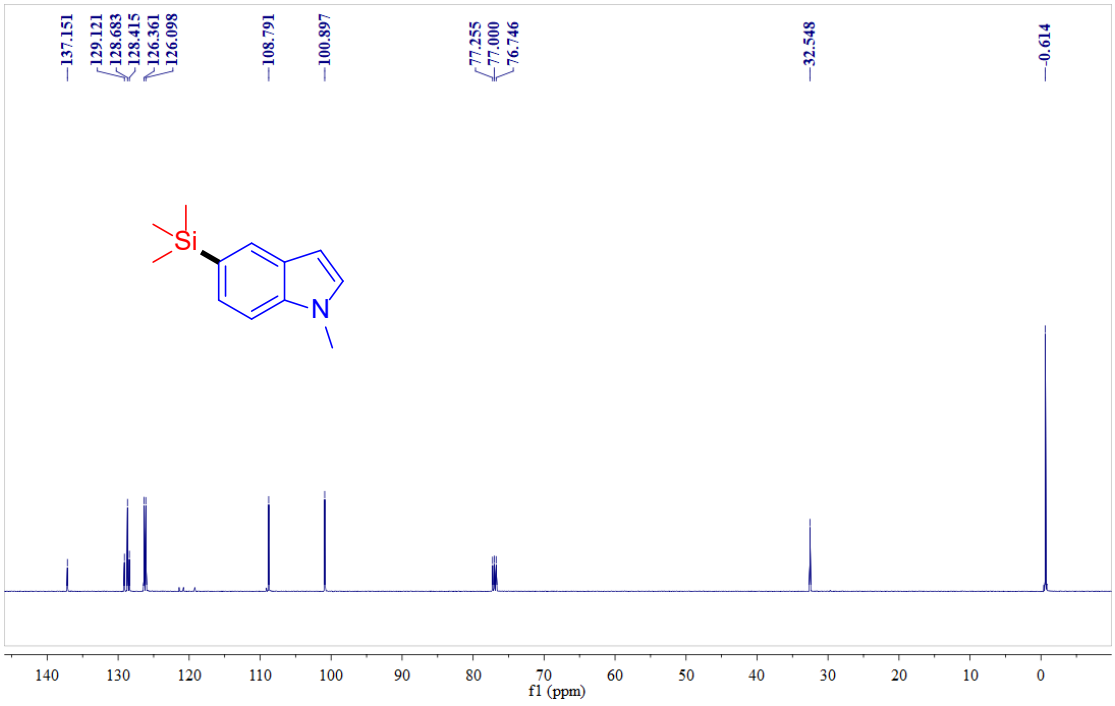
^{13}C NMR Spectrum of **3n**



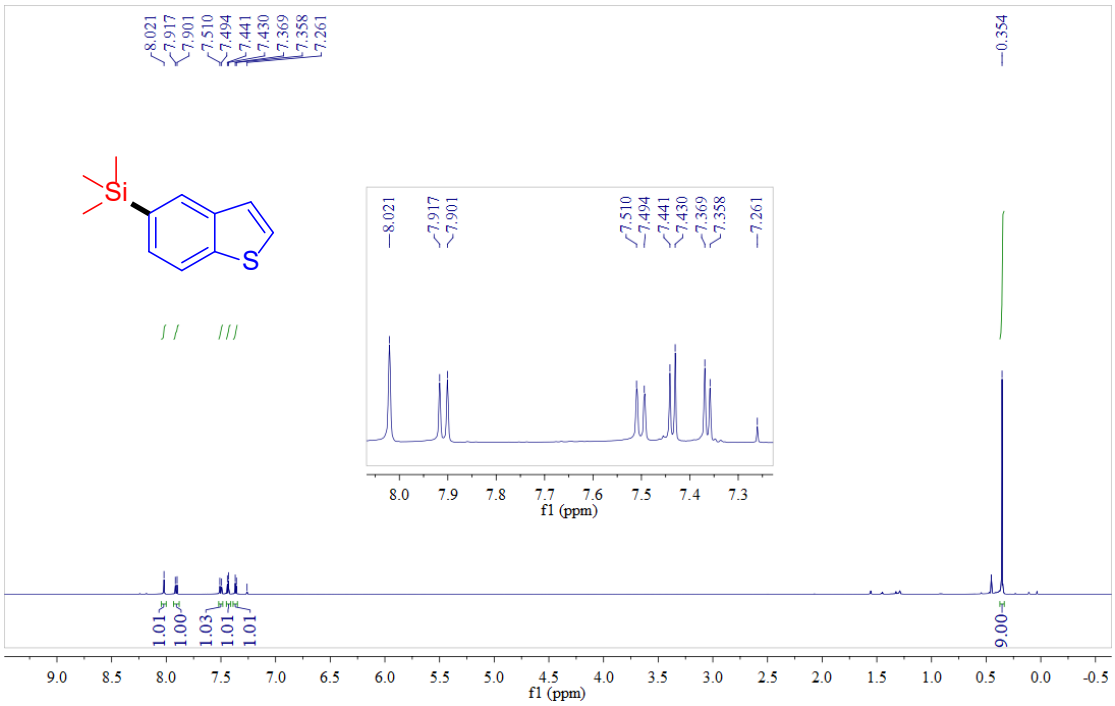
^{1}H NMR Spectrum of **3o**



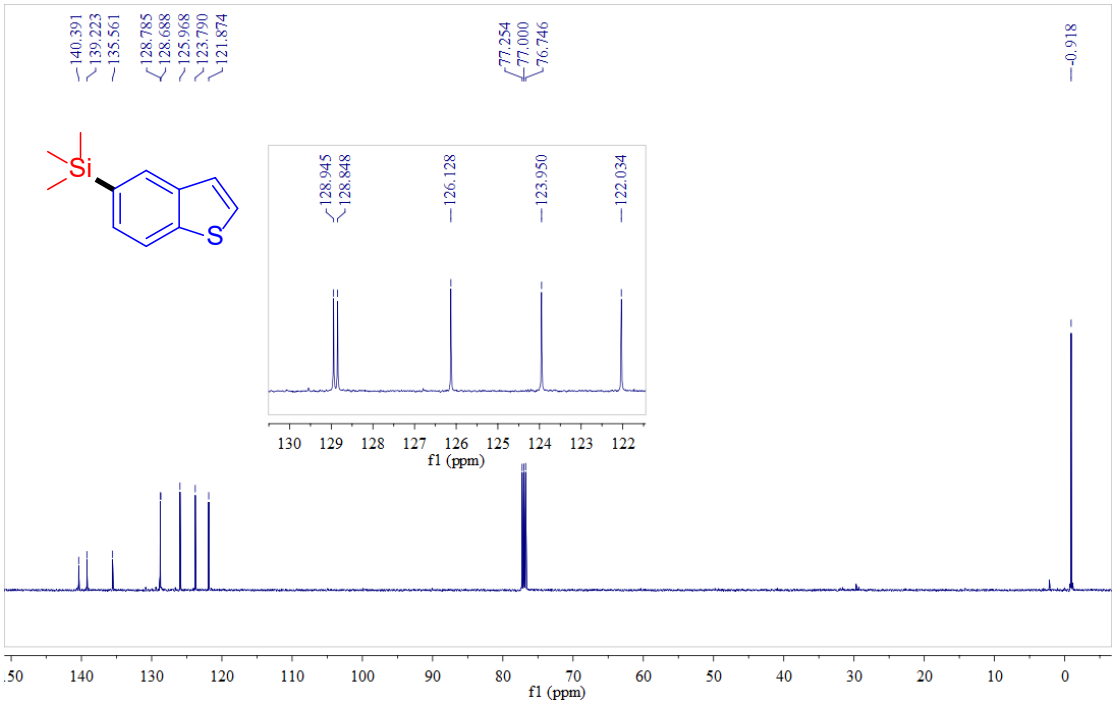
^{13}C NMR Spectrum of **3o**



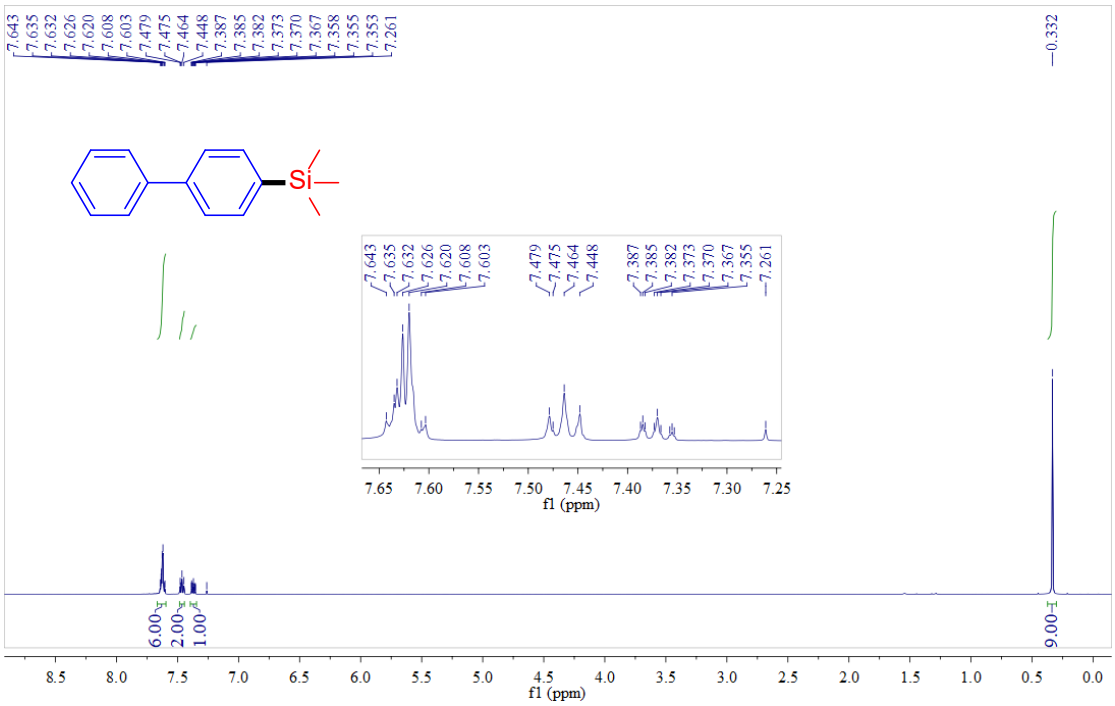
^{1}H NMR Spectrum of **3p**



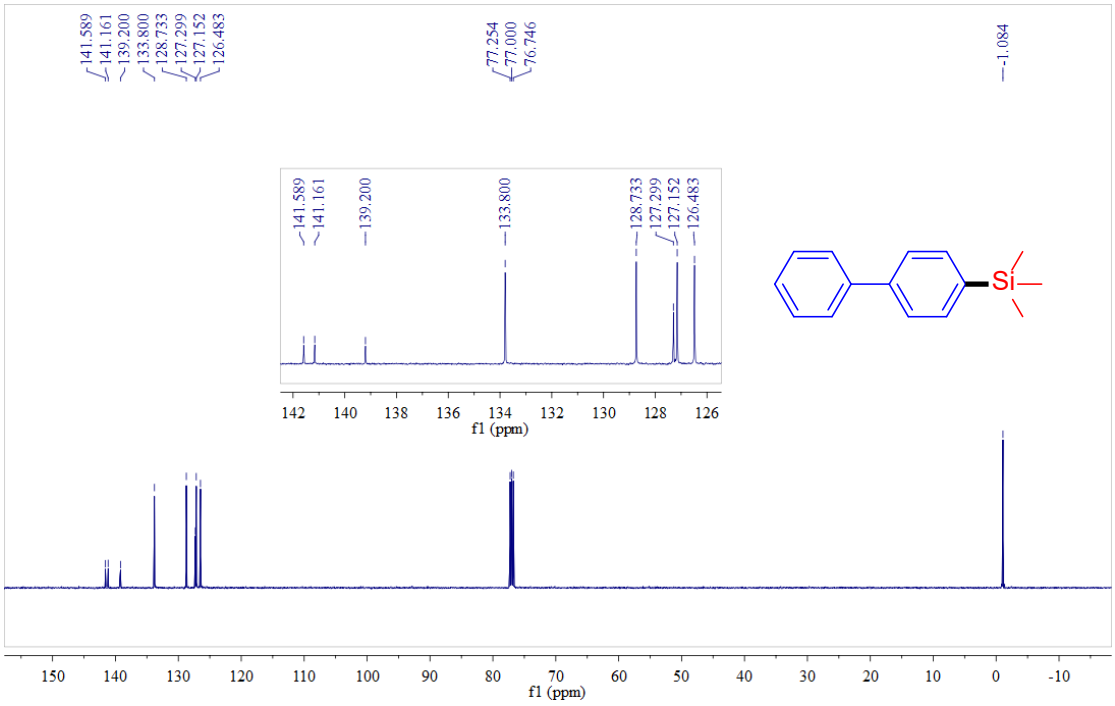
^{13}C NMR Spectrum of **3p**



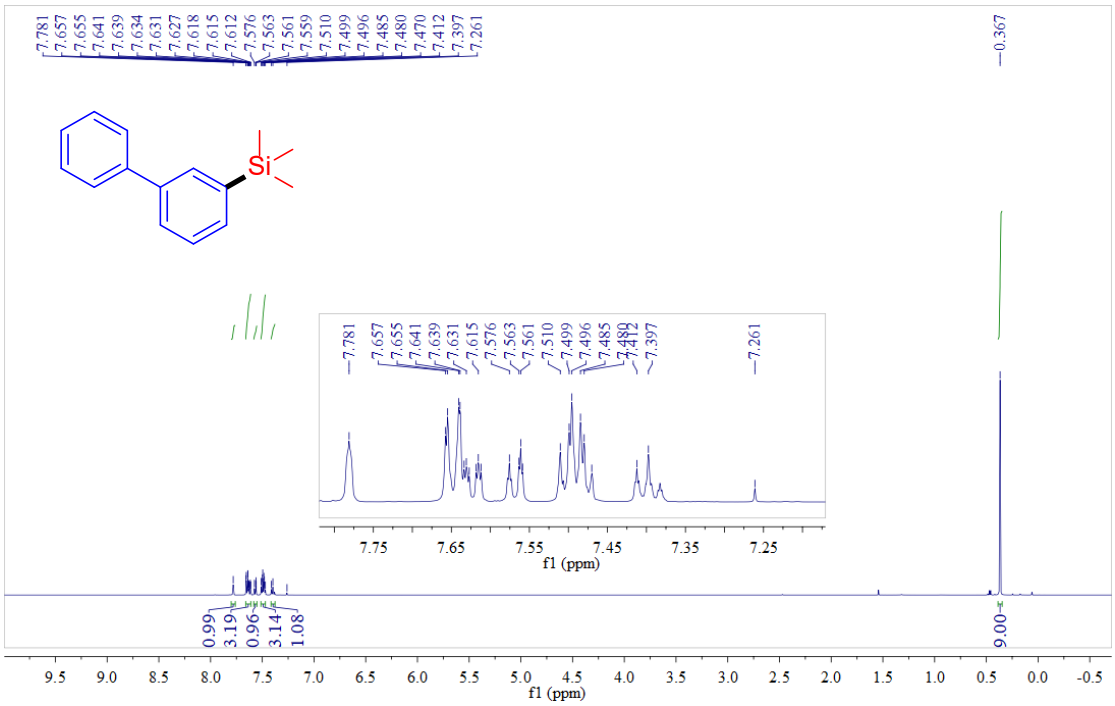
^{1}H NMR Spectrum of **3q**



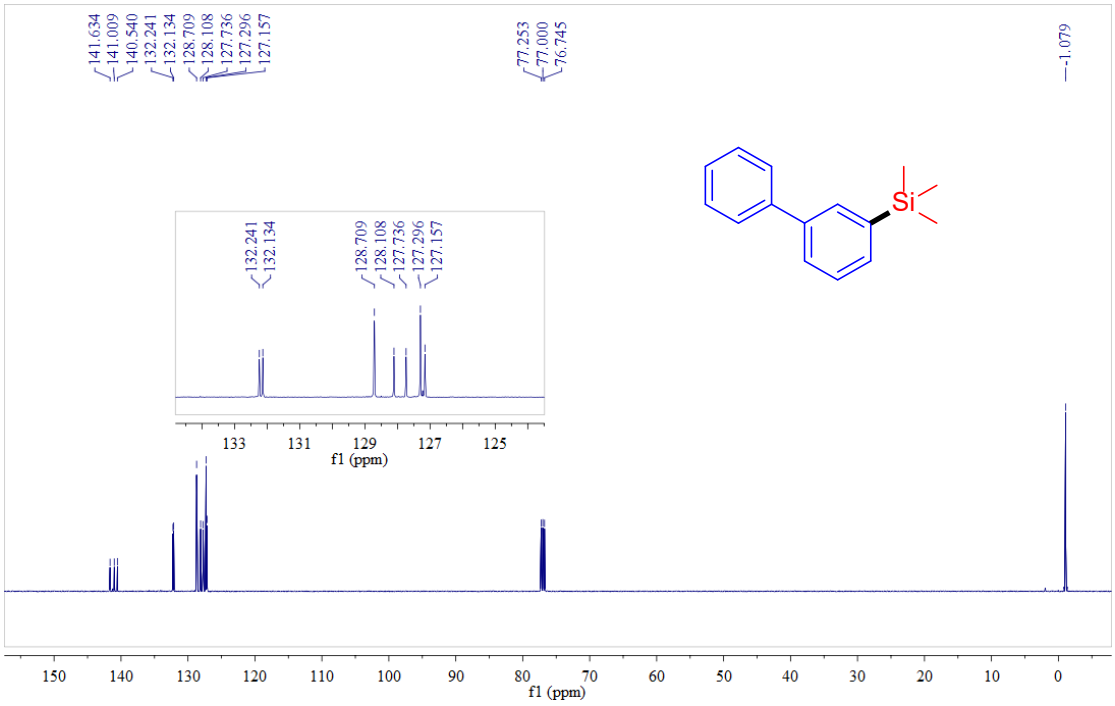
^{13}C NMR Spectrum of **3q**



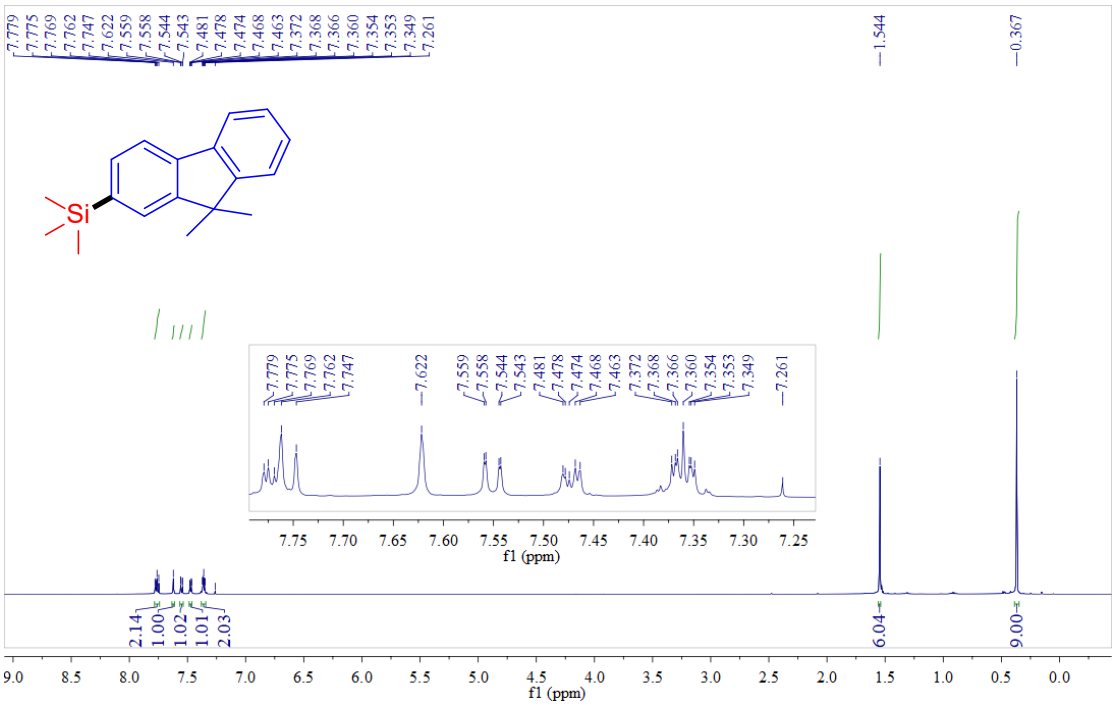
^{1}H NMR Spectrum of **3r**



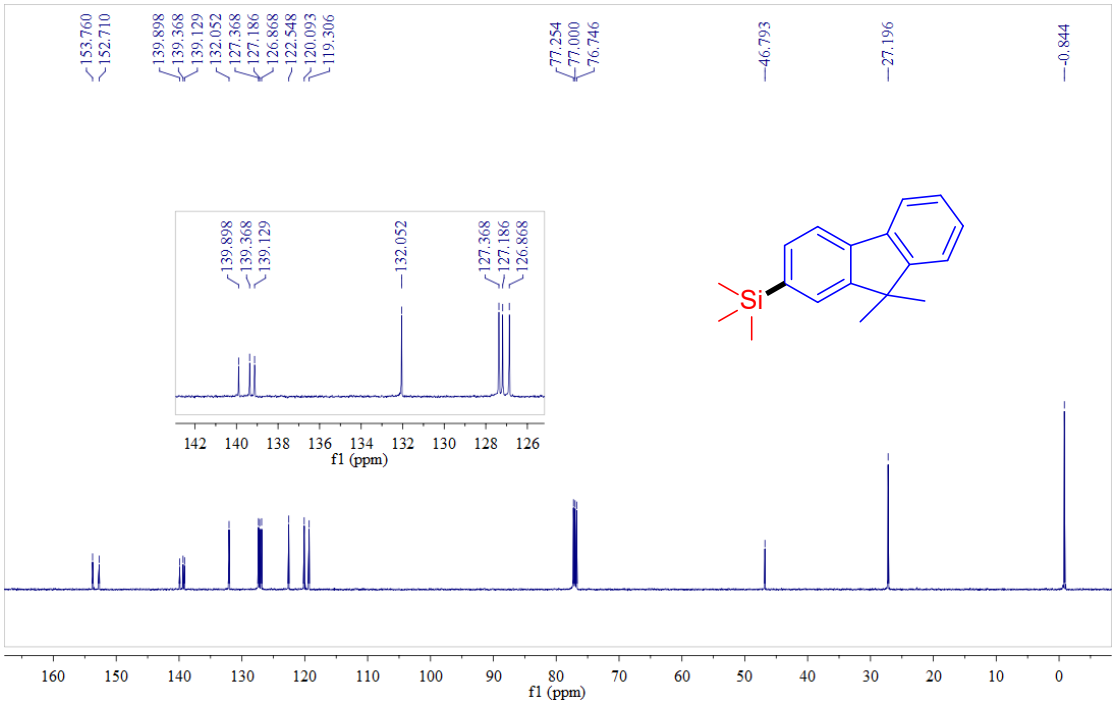
^{13}C NMR Spectrum of **3r**



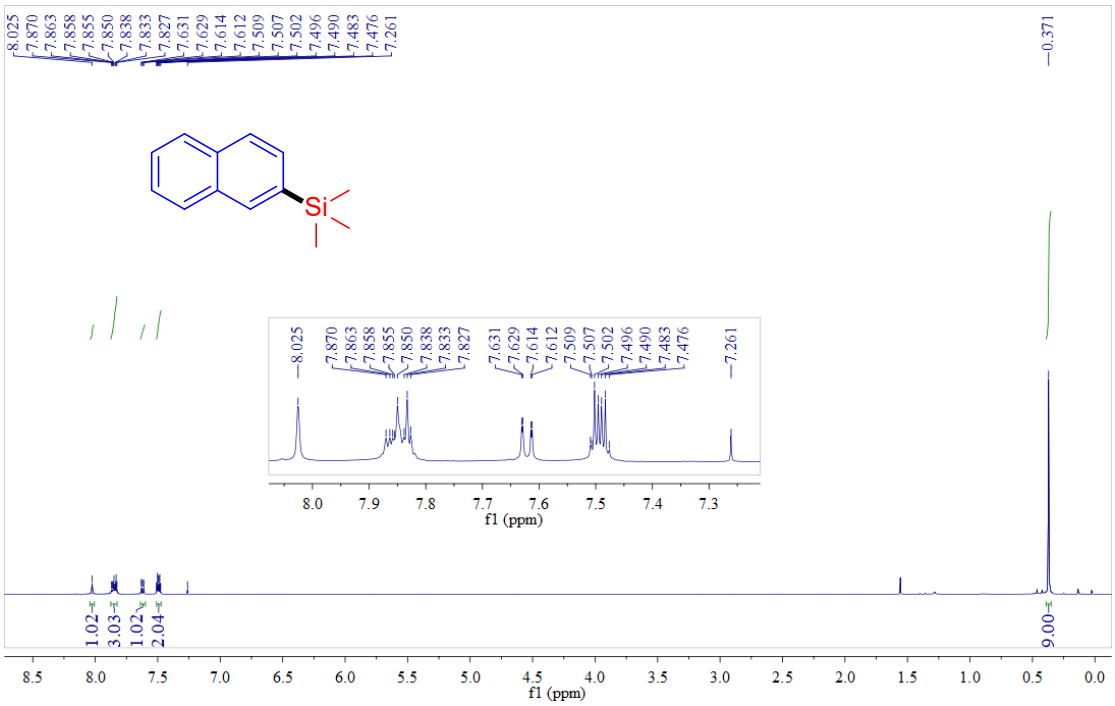
^{1}H NMR Spectrum of **3s**



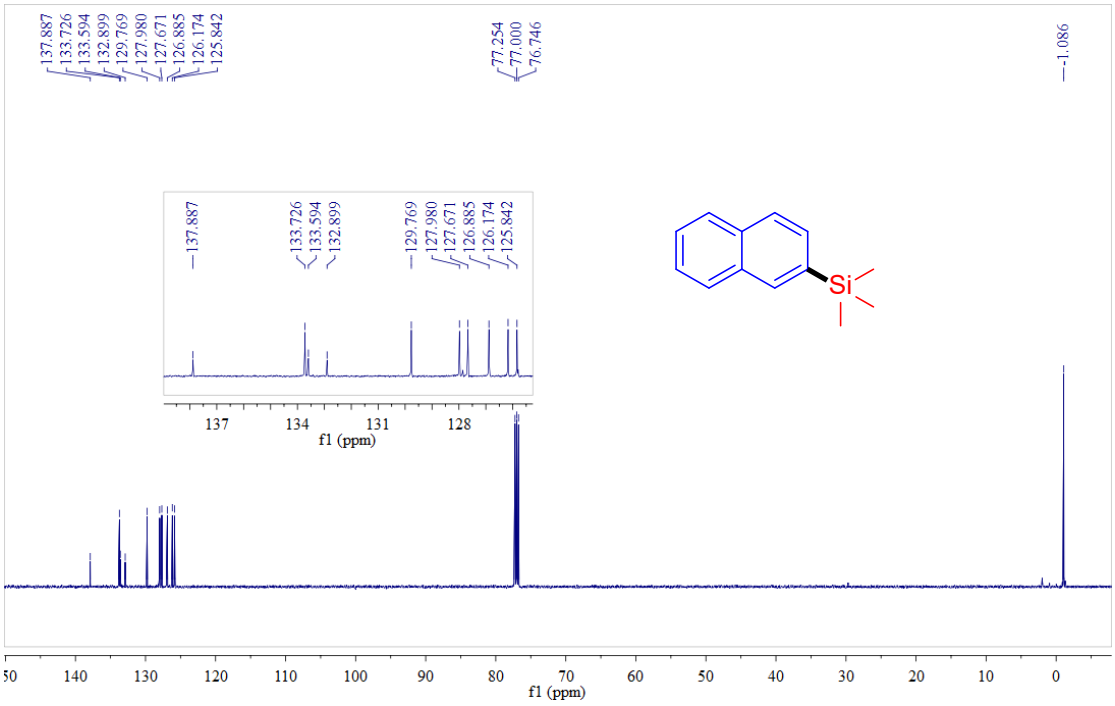
^{13}C NMR Spectrum of **3s**



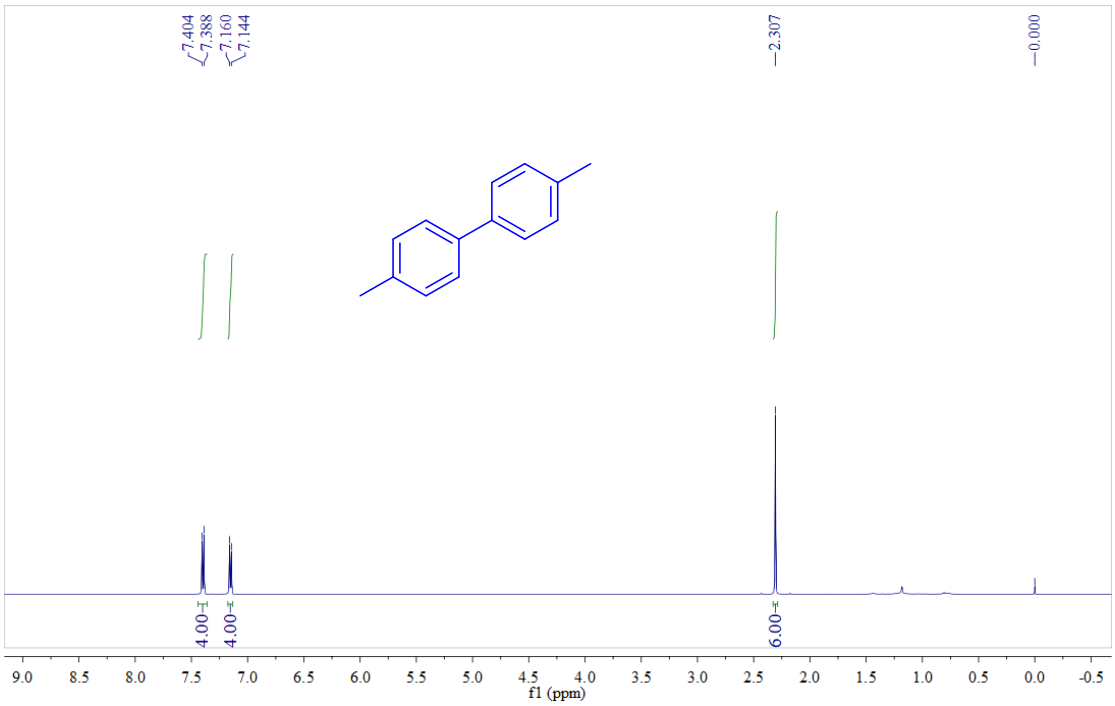
^{1}H NMR Spectrum of **3t**



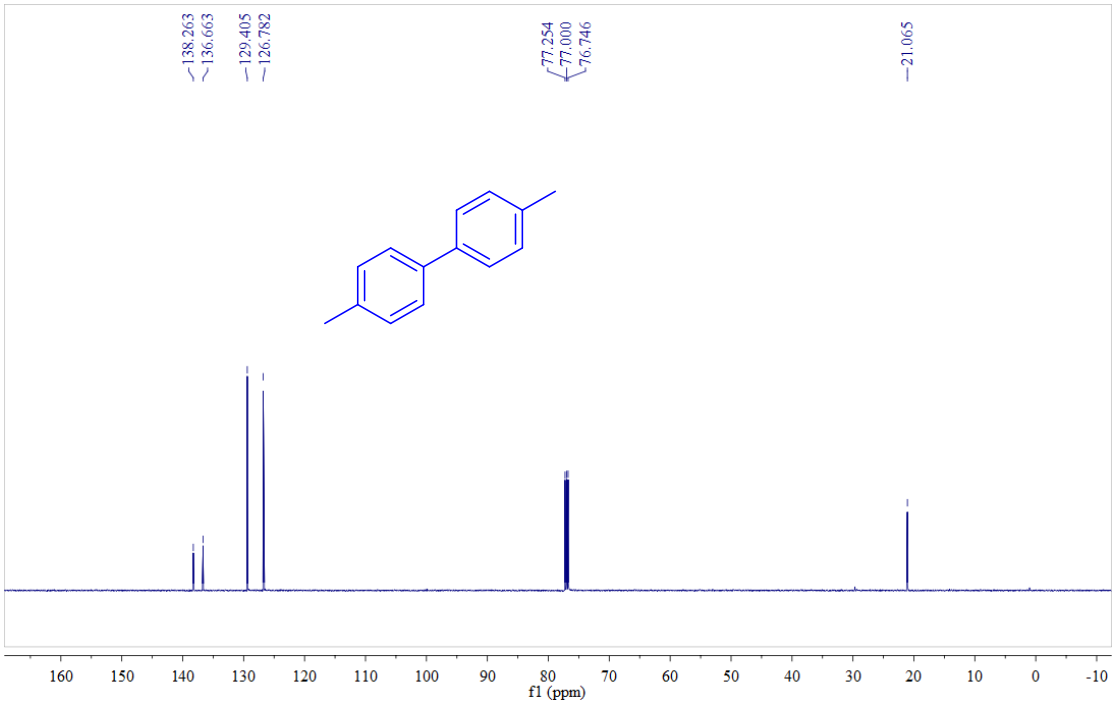
^{13}C NMR Spectrum of **3t**



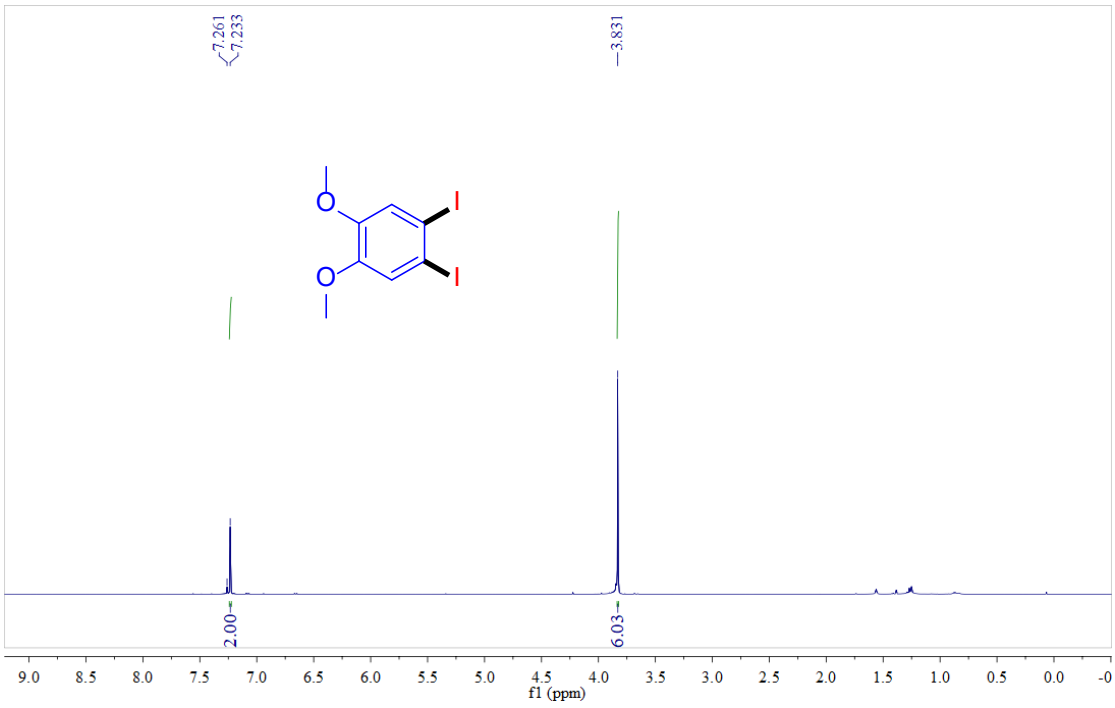
^{1}H NMR Spectrum of **4**



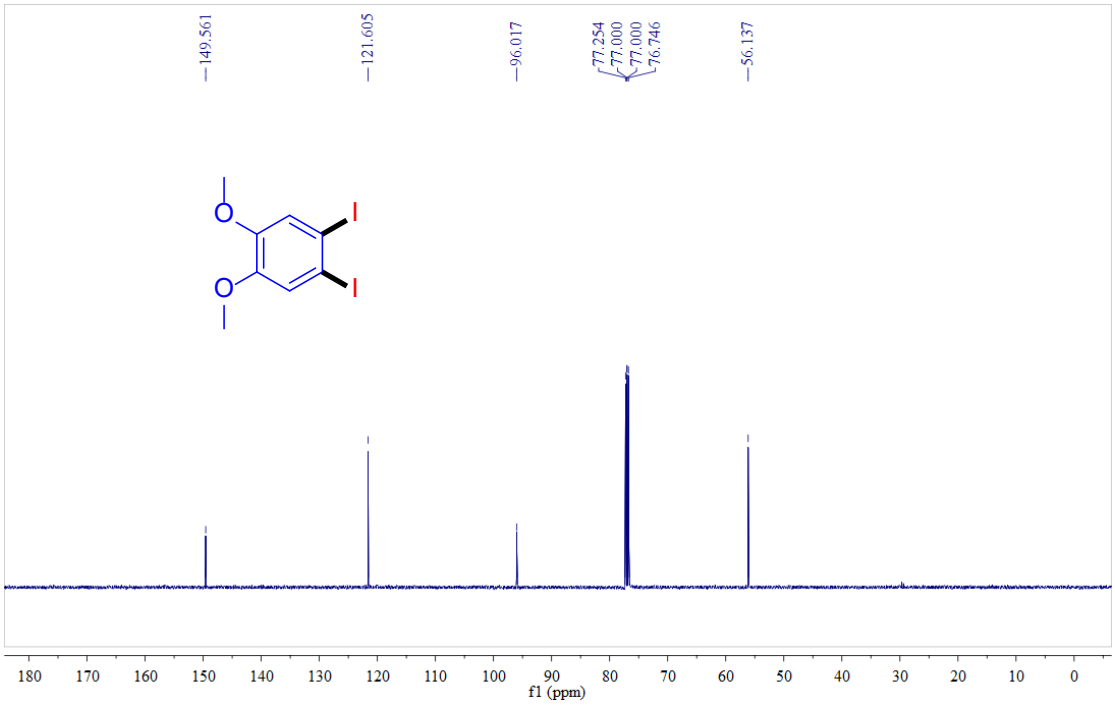
^{13}C NMR Spectrum of **4**



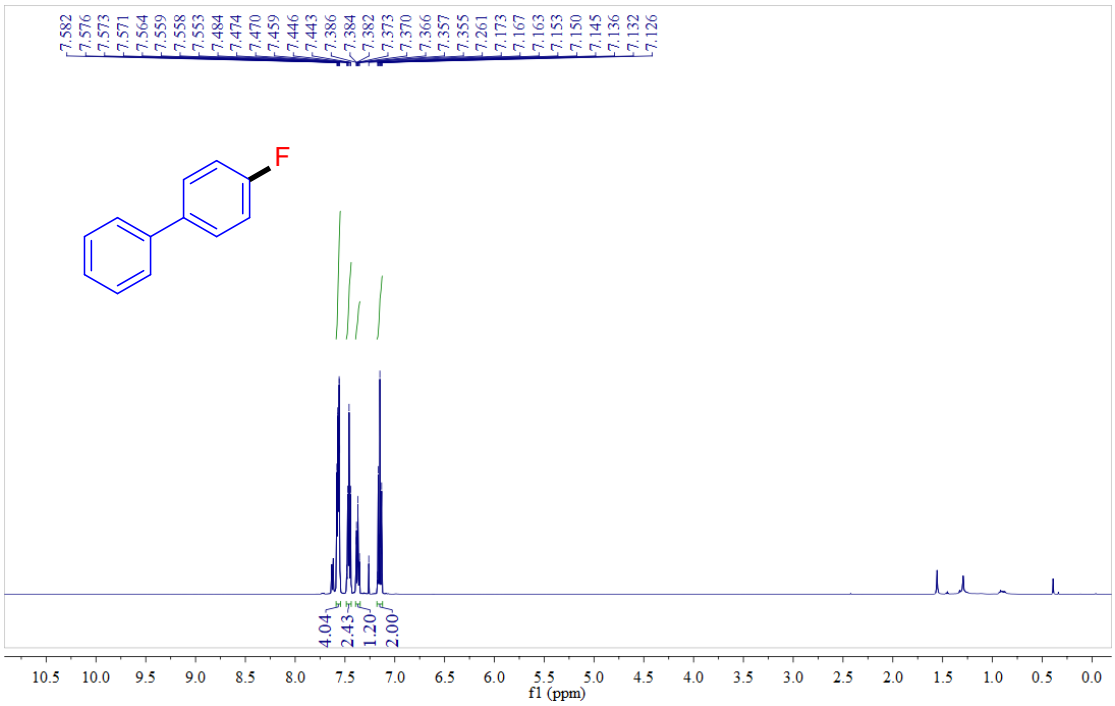
^{1}H NMR Spectrum of **5**



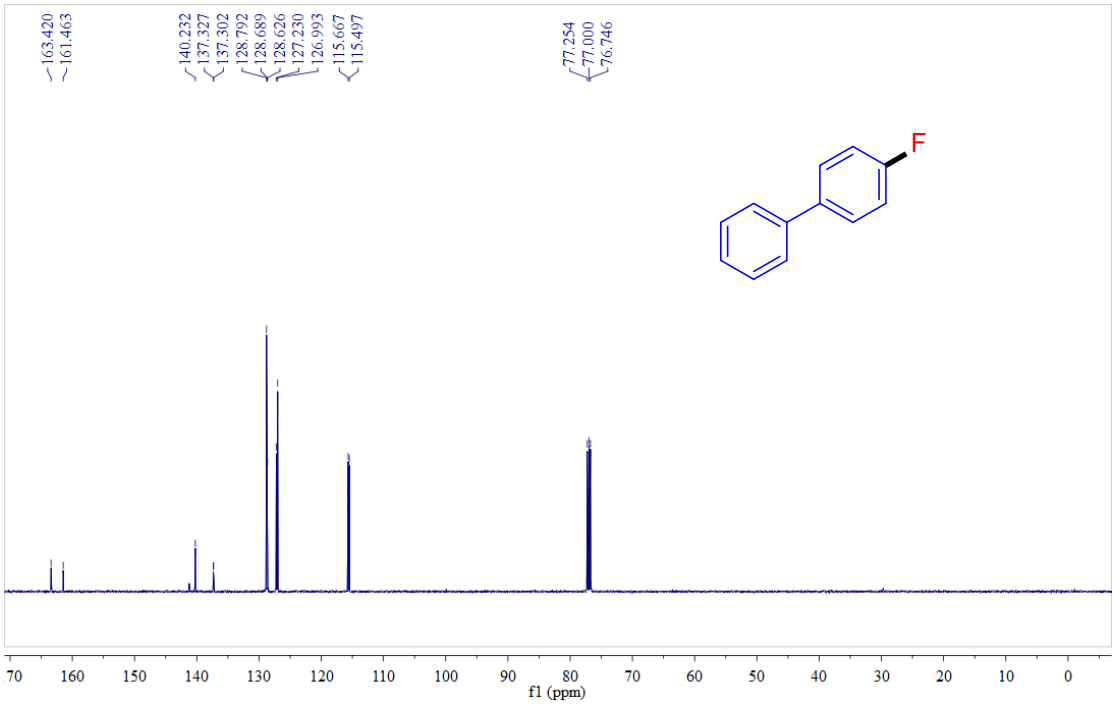
^{13}C NMR Spectrum of **5**



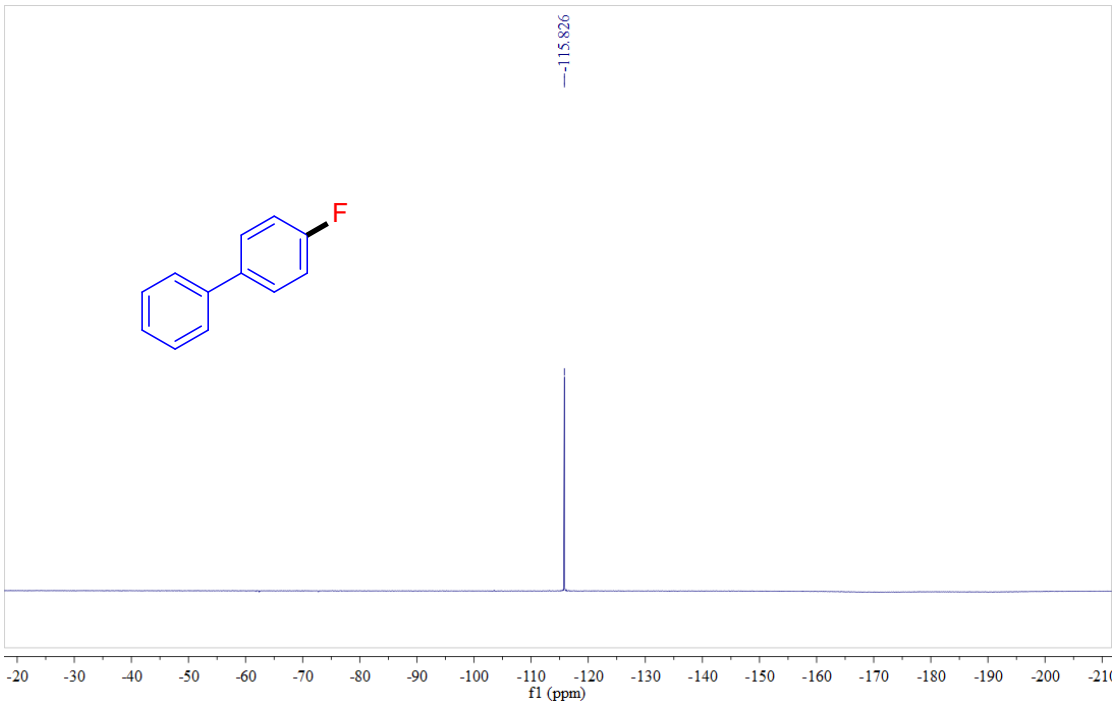
^{1}H NMR Spectrum of **6**



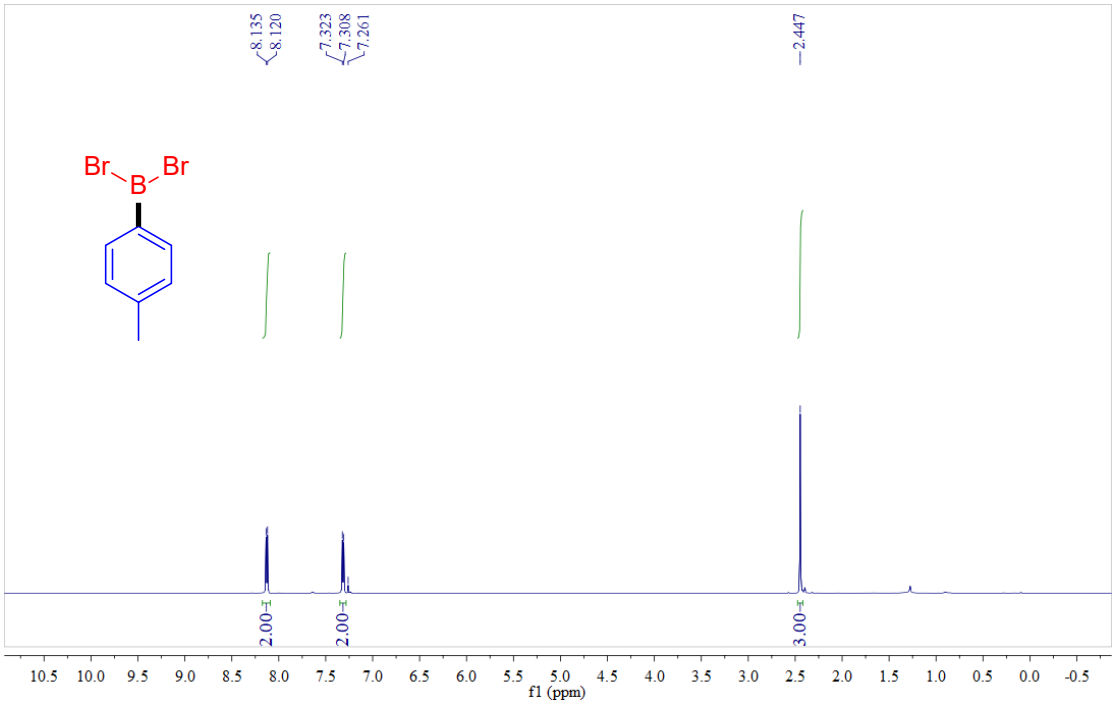
^{13}C NMR Spectrum of **6**



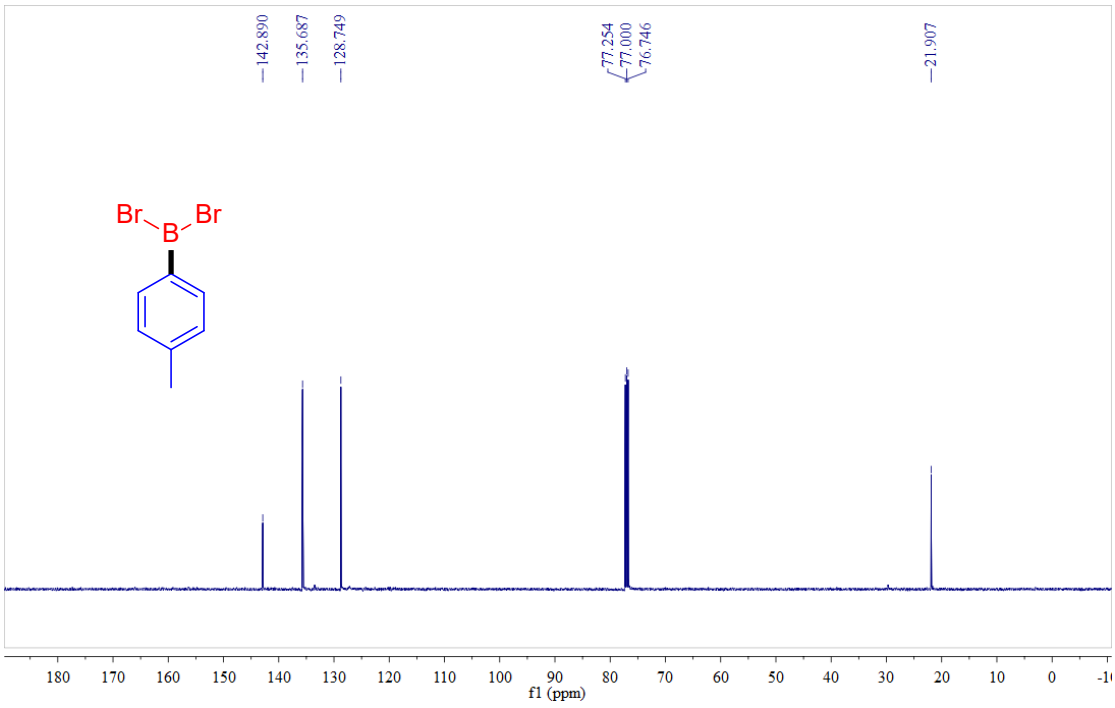
^{19}F NMR Spectrum of **6**



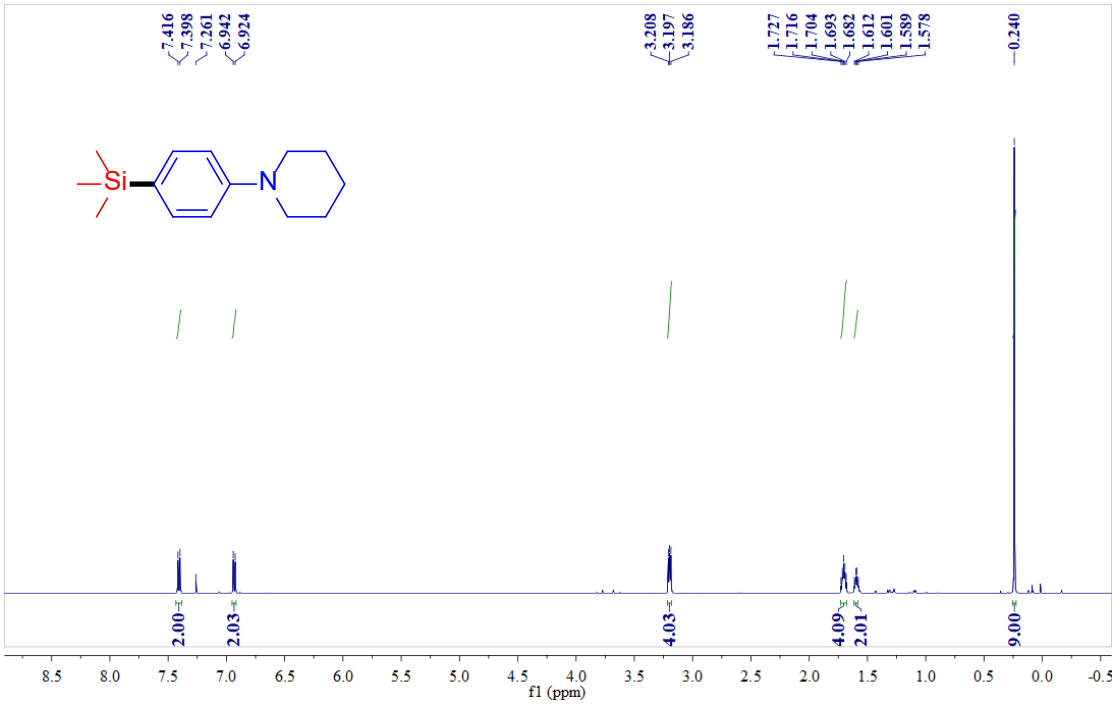
^{1}H NMR Spectrum of **7**



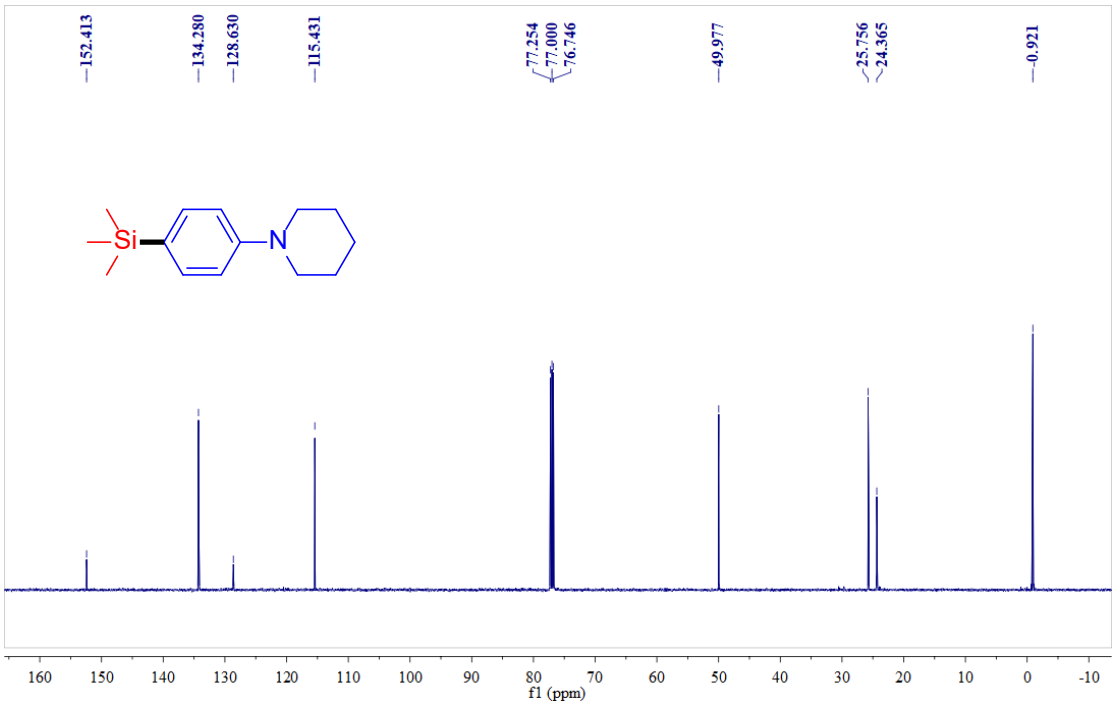
^{13}C NMR Spectrum of **7**



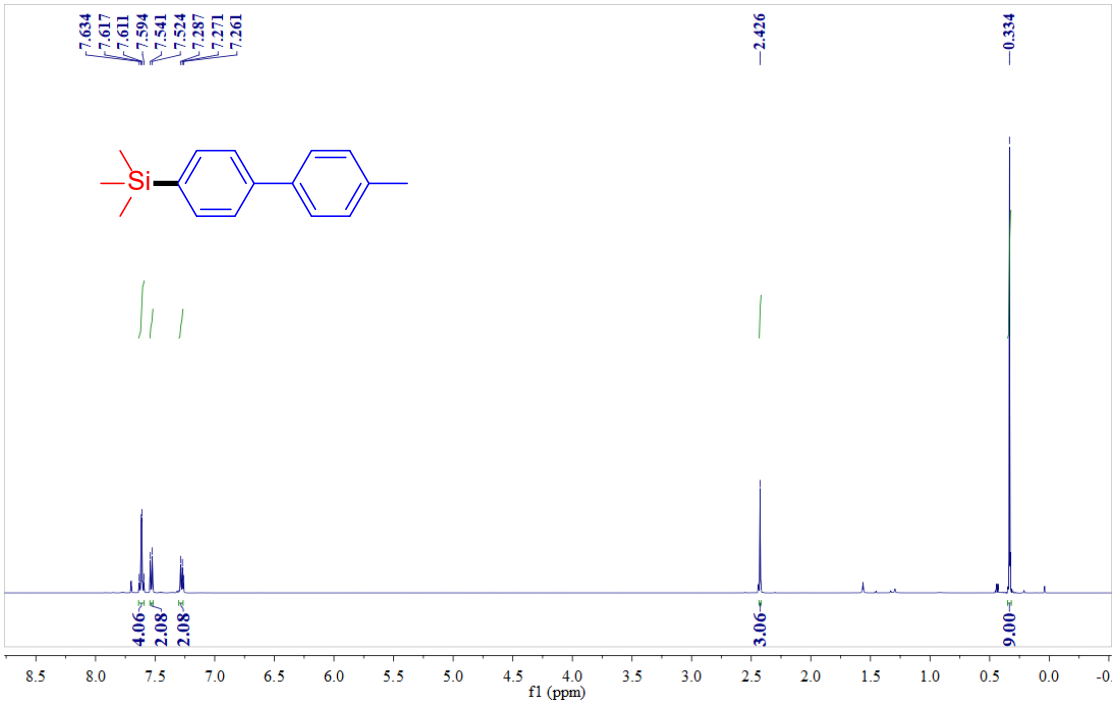
^{1}H NMR Spectrum of **8**



^{13}C NMR Spectrum of **8**



^{1}H NMR Spectrum of **9**



^{13}C NMR Spectrum of **9**