

Supporting Information for

**“N-Heterocyclic Carbene Catalysed Trimethylsilylation of
Terminal Acetylenes and Indoles with Ruppert’s Reagent
under Solvent Free Conditions”**

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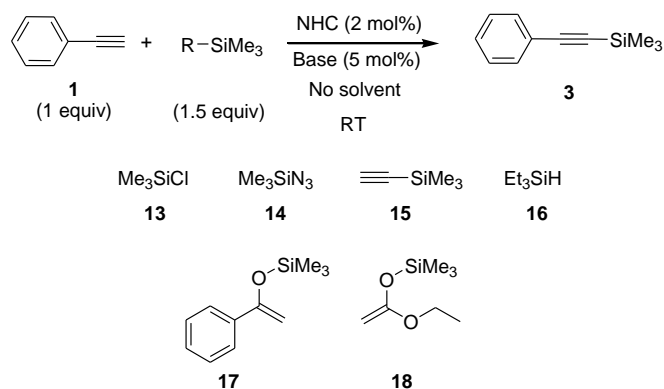
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General Methods: All reactions were carried out under Argon atmosphere. All the reagents including *N*-heterocyclic carbene precursors used were purchased from commercial sources and used as such. ^1H , ^{13}C , ^{19}F and ^{29}Si NMR spectra were recorded in CDCl_3 using 400 MHz Bruker FT-NMR spectrometer. Chemical shifts values are reported in parts per million relative to TMS and $\text{BF}_3\text{Et}_2\text{O}$. High-resolution mass spectroscopy was performed on a Waters Q-TOF Premier-HAB213 spectrometer. FTIR spectra were recorded on a Bruker FTIR spectrometer equipped with a PIKE MIRacle ATR and Perkin Elmer FTIR spectrometer. Thin layer chromatography was performed on Merck Silica gel 60 F₂₅₄ TLC plates using Hexane/EtOAc mixture as an eluent. Column chromatography was carried out through silica gel (100-200 mesh) and neutral alumina.

General procedure for the silylation of terminal acetylenes: Trifluoromethyl trimethylsilane (0.45 mmol) was added to a mixture of **5** (0.006 mmol), Sodium hydride (0.015 mmol) and terminal acetylene (0.3 mmol) and the resulting suspension was stirred for few minutes at room temperature until the terminal acetylene was completely consumed. The reaction mixture was diluted with hexane (2 mL) and passed through a silica gel column at ambient temperature. Removal of volatiles under vacuum furnished the pure trimethylsilyl acetylene derivative.

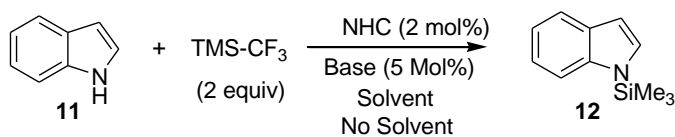
Table 1 Optimisation with different silyl pronucleophiles



S. No	Catalyst	Me ₃ SiR	Base	Solvent	Time [h]	Yield [%] ^a
1	5	13	NaH	--	12	--
2	5	14	NaH	--	12	--
3	5	15	NaH	--	12	--
4	5	16	NaH	--	12	--
5	5	16	NaH	THF	12	--
6	5	17	NaH	--	12	--
7	5	17	NaH	THF	12	--
8	5	18	NaH	--	12	--
9	5	18	NaH	THF	12	--

^a Isolated yield; RT = 31 - 33 °C

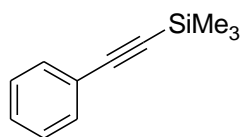
Table 2 Optimisation table: Silylation of Indoles



S. No	Catalyst	Base	Solvent	Time [h]	Yield [%] ^a
1 ^b	5	NaH	THF	12	--
2 ^b	5	NaH	DMF	12	--
3 ^b	5	NaH	Dioxane	12	--
4	5	NaH	--	3	93
5	5	DBU	--	6	9
6	4	NaH	--	6	63
7	6	NaH	--	6	75
8	7	NaH	--	6	78
9	8	NaH	--	6	17

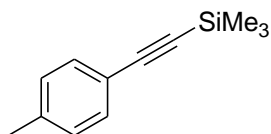
^a Isolated yield; RT = 31 - 33 °C, ^b Reactions tried with 11h.

Trimethyl(2-phenylethynyl)silane (3):¹



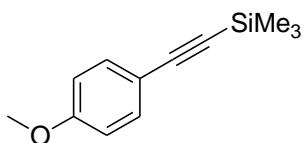
98% Yield. Colourless liquid; FT IR (ATR) = 2160, cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.51 – 7.49 (m, 2H), 7.35 – 7.31 (m, 3H), -0.29 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3) δ 132.0, 128.5, 128.2, 123.2, 105.2, 94.1, 0.01.

Trimethyl(2-*p*-tolylethynyl)silane (10a):¹



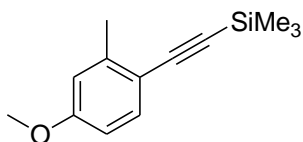
97% Yield. Colourless liquid; FT IR (ATR) = 2151 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.32 (d, J = 8.1 Hz, 2H), 7.05 (d, J = 8.1 Hz, 2H), 2.31 (s, 3H), 0.21 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3) δ 138.6, 131.9, 128.9, 120.1, 105.4, 93.2, 21.5, 0.05.

(2-(4-methoxyphenyl)ethynyl)trimethylsilane (10b):¹



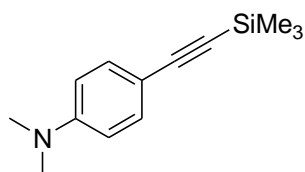
99% Yield. Colourless liquid; FT IR (ATR) = 2155 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.30 (d, J = 8.8 Hz, 2H), 6.84 (d, J = 8.8 Hz, 2H), 3.83 (s, 3H), 0.26 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3) δ 159.7, 133.5, 115.2, 113.8, 105.2, 92.4, 55.3, 0.08.

(2-(4-methoxy-2-methylphenyl)ethynyl)trimethylsilane (10c):



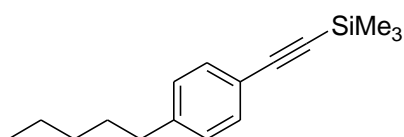
99% Yield. Light yellow liquid; FT IR (ATR) = 2148 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.38 (d, J = 8.5 Hz, 1H), 6.75 (d, J = 2.3 Hz, 1H), 6.68 (dd, J = 8.5, 2.3 Hz, 1H), 3.81 (s, 3H) 2.44 (s, 3H), 0.27 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3) δ 159.6, 142.5, 133.5, 115.2, 114.9, 111.1, 104.2, 96.4, 55.2, 20.9, 0.17; HRMS (ESI): m/z calcd for $\text{C}_{13}\text{H}_{18}\text{OSi}$ 218.1127; found 218.1125.

***N,N*-dimethyl-4-(2-(trimethylsilyl)ethynyl)benzenamine (10d):**²



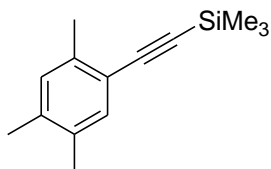
90% Yield. Brown solid; mp 87 – 90 °C; FT IR (ATR) = 2140 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.33 (d, J = 8.8 Hz, 2H), 6.58 (d, J = 8.9 Hz, 2H), 2.96 (s, 6H), 0.23 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3) δ 150.2, 133.1, 111.7, 109.8, 106.5, 91.2, 40.2, 0.24.

Trimethyl(2-(4-pentylphenyl)ethynyl)silane (10e):



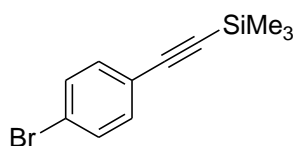
99% Yield. Colourless liquid; FT IR (ATR) = 2158 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.40 (d, J = 8.3 Hz, 2H), 7.13 (d, J = 8.4 Hz, 2H), 2.61 (t, J = 7.6 Hz, 2H), 1.65 – 1.58 (m, 2H), 1.38 – 1.28 (m, 4H), 0.91 (t, J = 6.7, 3H), 0.27 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3) δ 143.7, 131.9, 128.3, 120.2, 105.4, 93.3, 35.9, 31.4, 30.9, 22.5, 14.1, 0.06; HRMS (ESI): m/z calcd for $\text{C}_{16}\text{H}_{24}\text{Si}$ 244.1647; found 244.1647.

Trimethyl(2-(2,4,5-trimethylphenyl)ethynyl)silane (10f):



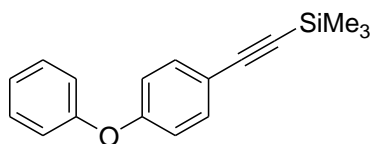
99% Yield. White solid; mp 57 – 59°C; FT IR (ATR) = 2147 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.23 (s, 1H), 6.97 (s, 1H), 2.38 (s, 3H), 2.24 (s, 3H), 2.20 (s, 3H), 0.27 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3) δ 137.9, 137.3, 133.6, 133.1, 130.8, 120.0, 104.5, 96.9, 20.0, 19.7, 19.0, 0.15; HRMS (ESI): m/z calcd for $\text{C}_{14}\text{H}_{20}\text{Si}$ 216.1334; found 216.1338.

(2-(4-bromophenyl)ethynyl)trimethylsilane (10g):³



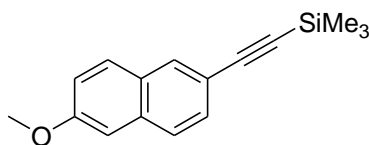
99% Yield. White solid; mp 64 – 66 °C; FT IR (ATR) = 2158 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.45 (d, *J* = 8.7 Hz, 2H), 7.34 (d, *J* = 8.7 Hz, 2H), 0.27 (s, 9H); ¹³C NMR (100 MHz, CDCl₃) δ 133.4, 131.5, 122.8, 122.1, 103.9, 95.6, -0.10.

Trimethyl(2-(4-phenoxyphenyl)ethynyl)silane (10h):



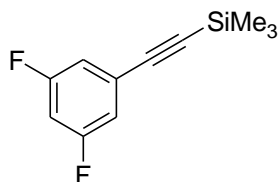
99% Yield. Light yellow liquid; FT IR (ATR) = 2157 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.44 (d, *J* = 8.8 Hz, 2H), 7.39 (t, *J* = 7.8 Hz, 2H), 7.17 (t, *J* = 7.6 Hz, 1H), 7.04 (d, *J* = 7.6 Hz, 2H), 6.94 (d, *J* = 8.7 Hz, 2H), 0.28 (s, 9H); ¹³C NMR (100 MHz, CDCl₃) δ 157.7, 156.4, 133.6, 129.9, 123.9, 119.4, 118.2, 117.7, 104.7, 93.4, 0.05; HRMS (ESI): *m/z* calcd for C₁₇H₁₈OSi 266.1127; found 266.1128.

(2-(2-methoxynaphthalen-6-yl)ethynyl)trimethylsilane (10i):⁴



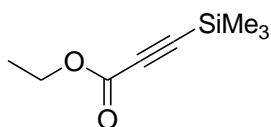
90% Yield. White solid; mp 105 – 107 °C; FT IR (ATR) = 2154 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.95 (s, 1H), 7.71 – 7.66 (m, 2H), 7.51 – 7.48 (m, 1H), 7.18 – 7.15 (m, 1H), 7.11 (d, *J* = 2.5 Hz, 1H), 3.94 (s, 3H), 0.30 (s, 9H); ¹³C NMR (100 MHz, CDCl₃) δ 158.4, 134.2, 131.9, 129.4, 129.2, 128.3, 126.7, 119.4, 118.0, 105.8, 105.7, 93.7, 55.4, 0.08.

(2-(3,5-difluorophenyl)ethynyl)trimethylsilane (10j):



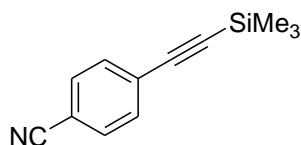
95% Yield. Yellow liquid; FT IR (ATR) = 2360 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.02–6.96 (m, 2H), 6.83 – 6.78 (m, 1H), 0.27 (s, 9H); ¹³C NMR (100 MHz, CDCl₃) δ 162.6 (dd, ¹*J*_{C-F} = 247.2, 13.2 Hz, 2C), 125.8, 114.9 (d, *J*_{C-F} = 26.2 Hz, 1C), 104.7 (t, *J*_{C-F} = 25.5 Hz, 1C), 102.4, 96.8, -0.25; HRMS (ESI): *m/z* calcd for C₁₁H₁₂F₂Si 210.0676; found 210.0677.

Ethyl 3-(trimethylsilyl)propiolate (10k):⁵



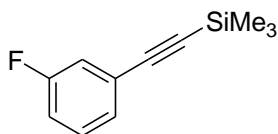
95% Yield. Colourless liquid; FT IR (ATR) = 2183, 1713 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 4.22 (q, $J = 7.1$, Hz, 2H), 1.31 (t, $J = 7.2$ Hz, 3H) 0.24 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3) δ 153.0, 94.7, 93.6, 62.0, 14.0, -0.88.

4-(2-(trimethylsilyl)ethynyl)benzonitrile (10l):¹



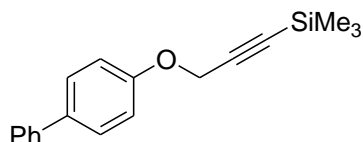
99% Yield. White solid; mp 102–104 $^{\circ}\text{C}$; FT IR (ATR) = 2234, 2157 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.61 (d, $J = 8.6$ Hz, 2H), 7.55 (d, $J = 8.7$ Hz, 2H) 0.28 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3) δ 132.5, 131.9, 118.5, 111.8, 103.0, 99.6, 92.3, -0.26.

(2-(3-fluorophenyl)ethynyl)trimethylsilane (10m):



99% Yield. Yellow liquid; FT IR (ATR) = 2190 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.31 – 7.25 (m, 2H), 7.20 – 7.16 (m, 1H), 7.07 – 7.02 (m, 1H), 0.28 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3) δ 162.2 (d, $^1J_{\text{C-F}} = 245.0$ Hz, 1C), 129.8 (d, $J_{\text{C-F}} = 8.8$ Hz, 1C), 127.8 (d, $J_{\text{C-F}} = 3.0$ Hz, 1C), 124.9 (d, $J_{\text{C-F}} = 9.5$ Hz, 1C), 118.8 (d, $J_{\text{C-F}} = 22.6$ Hz, 1C), 115.8 (d, $J_{\text{C-F}} = 21.0$ Hz, 1C), 103.6 (d, $J_{\text{C-F}} = 3.7$ Hz, 1C), 95.4, -0.12; HRMS (ESI): m/z calcd for $\text{C}_{11}\text{H}_{13}\text{FSi}$ 192.0771; found 192.0770.

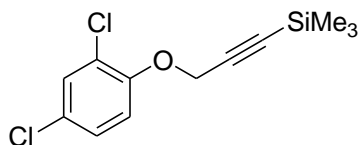
(3-(4-phenylphenoxy)prop-1-ynyl)trimethylsilane (10n):



99% Yield. White solid; mp 65 – 67 $^{\circ}\text{C}$; FT IR (ATR) = 2174 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.60 – 7.55 (m, 4H), 7.47 – 7.43 (m, 2H), 7.36 – 7.32 (m, 1H), 7.08 (d, $J = 8.8$ Hz, 2H), 4.74 (s, 2H), 0.21 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3) δ 157.4,

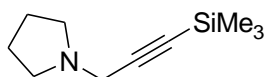
148.1, 140.7, 134.5, 128.8, 128.1, 126.8, 115.3, 100.0, 92.9, 56.9, -0.26; HRMS (ESI): m/z calcd for $C_{11}H_{13}FSi$ 280.1283; found 280.1287.

3-(2,4-dichlorophenoxy)prop-1-ynyltrimethylsilane (10o):



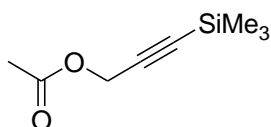
99% Yield. White solid; mp 68 – 70 °C; FT IR (ATR) = 2170 cm^{-1} ; 1H NMR (400 MHz, $CDCl_3$) δ 7.40 (d, J = 2.5 Hz, 1H), 7.21 (dd, J = 8.8, 2.5 Hz, 1H), 7.05 (d, J = 8.8 Hz, 1H), 4.76 (s, 2H), 0.18 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.1, 130.1, 127.4, 126.7, 124.2, 115.6, 99.0, 94.1, 58.1, -0.37.

1-(3-(trimethylsilyl)prop-2-ynyl)pyrrolidine (10p):⁶



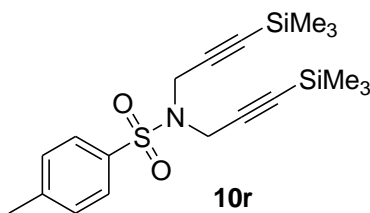
96% Yield. Yellow liquid; FT IR (ATR) = 2167 cm^{-1} ; 1H NMR (400 MHz, $CDCl_3$) δ 3.42 (s, 2H), 2.63 – 2.60 (m, 4H), 1.83 – 1.80 (m, 4H), 0.17 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 101.9, 88.8, 52.6, 44.1, 23.7, 0.04.

3-(trimethylsilyl)prop-2-ynyl acetate (10q):¹



99% Yield. Colourless liquid; FT IR (ATR) = 2186, 1750 cm^{-1} ; 1H NMR (400 MHz, $CDCl_3$) δ 4.69 (s, 2H), 2.13 (s, 3H) 0.20 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.3, 98.9, 92.1, 52.8, 20.8, -0.30.

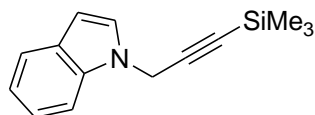
3-(trimethylsilyl)-N-tosylprop-2-yn-1-amine (10r):



99% Yield. Light yellow solid; mp 59 – 61 °C; FT IR (ATR) = 2174 cm^{-1} ; 1H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, J = 8.3 Hz, 2H), 7.30 (d, J = 8.5 Hz, 2H), 4.17 (s, 4H),

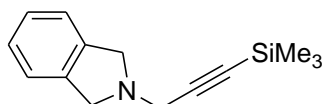
2.44 (s, 3H), 0.08 (s, 18H); ^{13}C NMR (100 MHz, CDCl_3) δ 143.7, 135.4, 129.6, 127.9, 97.7, 91.0, 37.2, 21.6, -0.34; HRMS (ESI): m/z calcd for $\text{C}_{19}\text{H}_{29}\text{NO}_2\text{SSi}_2\text{H}$ 392.1536; found 392.1540.

1-(3-(trimethylsilyl)prop-2-ynyl)-1H-indole (10s):



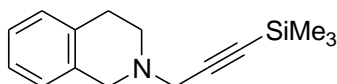
99% Yield. Yellow liquid; FT IR (ATR) = 2181 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.69 – 7.67 (m, 1H), 7.45 – 7.43 (m, 1H), 7.30 – 7.26 (m, 2H), 7.19 – 7.15 (m, 1H), 6.57 – 6.56 (m, 1H), 4.92 (s, 2H), 0.21 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3) δ 135.8, 128.8, 127.2, 121.7, 121.0, 119.7, 109.4, 101.8, 99.1, 90.7, 36.8, -0.22.

2-(3-(trimethylsilyl)prop-2-ynyl)isoindoline (10t):



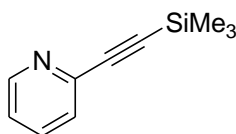
95% Yield. Light brown liquid; FT IR (ATR) = 2158, cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.25 – 7.21 (m, 4H), 4.08 (s, 4H), 3.67 (s, 2H) 0.18 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3) δ 140.0, 126.8, 122.4, 101.2, 90.8, 57.3, 43.8, 0.03.

1,2,3,4-tetrahydro-2-(3-(trimethylsilyl)prop-2-ynyl)isoquinoline (10u):



93% Yield. Yellow liquid; FT IR (ATR) = 2163 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.18 – 7.07 (m, 4H), 3.80 (s, 2H), 3.56 (s, 2H), 2.98 (t, J = 6.0 Hz, 2H), 2.86 (t, J = 6.0 Hz, 2H), 0.20 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3) δ 134.4, 133.7, 128.7, 126.6, 126.2, 125.7, 100.4, 90.4, 54.2, 49.6, 47.7, 29.1, 0.04.

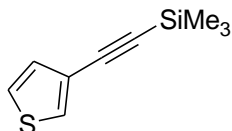
2-(2-(trimethylsilyl)ethynyl)pyridine (10v):⁷



90% Yield. Yellow liquid; FT IR (ATR) = 2166 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 8.59 – 8.57 (m, 1H), 7.67 – 7.63 (m, 1H), 7.48 – 7.45 (m, 1H), 7.29 – 7.22 (m, 1H),

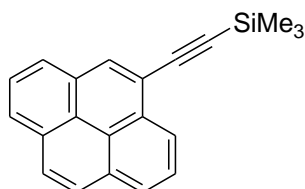
0.28 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3) δ 149.9, 143.0, 136.1, 127.3, 123.1, 103.6, 94.8, -0.27.

Trimethyl(2-(thiophen-3-yl)ethynyl)silane (10w):⁷



99% Yield. Yellow liquid; FT IR (ATR) = 2154, cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.51 (dd, $J = 3.0, 1.2$ Hz, 1H), 7.26 (dd, $J = 5.0, 3.0$ Hz, 1H), 7.15 (dd, $J = 5.0, 1.1$ Hz, 1H), 0.27 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3) δ 130.1, 129.6, 125.2, 122.3, 99.9, 93.9, -0.28.

Trimethyl(2-(pyren-4-yl)ethynyl)silane (10x):⁸



90% Yield. Yellow solid, mp 104 – 106 $^\circ\text{C}$; FT IR (ATR) = 2150 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 8.60 (d, $J = 9.1$ Hz, 1H), 8.25 – 8.18 (m, 4H), 8.11 – 8.02 (m, 4H), 0.46 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3) δ 132.3, 131.4, 131.2, 131.0, 129.9, 128.4, 128.2, 127.2, 126.2, 125.7, 125.6, 125.5, 124.4, 124.3, 124.2, 117.6, 104.2, 100.2, 0.28.

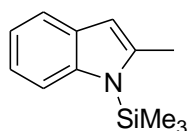
General procedure for the silylation of indoles: Trifluoromethyl trimethylsilane (0.7 mmol) was added to a mixture of **5** (0.007 mmol), Sodium hydride (0.017 mmol) and indole (0.35 mmol) and the resulting suspension was stirred for few minutes at room temperature until the indole was completely consumed. The reaction mixture was diluted with hexane (2 mL) and passed through a neutral alumina column at ambient temperature. Removal of volatiles under vacuum furnished the pure trimethylsilyl indole derivative.

1-(trimethylsilyl)-1H-indole (12a):⁹



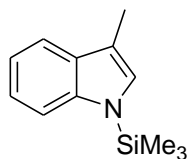
93% Yield. Colourless liquid; FT IR = 2959, 1452 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.73 – 7.70 (m, 1H), 7.58–7.54 (m, 1H), 7.27 – 7.17 (m, 3H), 6.66 (d, J = 3.2 Hz, 1H), 0.60 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3) δ 140.2, 131.6, 129.9, 121.4, 120.9, 119.9, 112.9, 104.6, -0.06.

2-methyl-1-(trimethylsilyl)-1H-indole (12b):



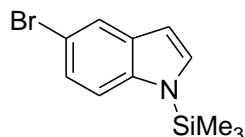
96% Yield. Colourless liquid; FT IR = 2958, 1455 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.60 – 7.57 (m, 2H), 7.19–7.16 (m, 2H), 6.40 (s, 1H), 2.56 (d, J = 1.0 Hz, 3H) 0.68 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3) δ 141.7, 141.4, 131.5, 120.5, 119.8, 119.5, 113.1, 105.6, 17.1, 2.33.

3-methyl-1-(trimethylsilyl)-1H-indole (12c):



97% Yield. Colourless liquid; FT IR = 2958, 1452 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.66 (d, J = 8.2 Hz, 1H), 7.54 (d, J = 8.4 Hz, 1H), 7.27 – 7.23 (m, 2H), 7.02 (s, 1H), 2.40 (s, 3H), 0.60 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3) δ 140.6, 132.0, 127.2, 121.4, 119.3, 119.1, 113.5, 112.9, 9.7, 0.04.

5-bromo-1-(trimethylsilyl)-1H-indole (12d):



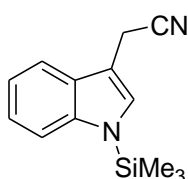
51% Yield. Yellow liquid; FT IR = 2958, 1444 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.79 (d, J = 2.0 Hz, 1H), 7.398 – 7.36 (m, 1H), 7.29 – 7.26 (m, 1H), 7.19 (d, J = 3.2 Hz, 1H), 6.55 (d, J = 3.2 Hz, 1H), 0.56 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3) δ 138.8, 133.6, 131.1, 124.2, 123.3, 114.2, 113.3, 104.1, -0.15.

7-ethyl-1-(trimethylsilyl)-1H-indole (12e) :



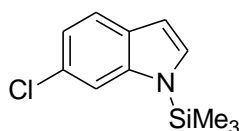
90% Yield. Colourless liquid; FT IR = 2965, 1413 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.59 – 7.55 (m, 1H), 7.33 (d, J = 3.3 Hz, 1H), 7.23 – 7.09 (m, 2H), 6.66 (d, J = 3.3 Hz, 1H), 3.14 (q, J = 7.4 Hz, 2H), 1.41 (t, J = 7.4 Hz, 3H), 0.65 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3) δ 139.2, 132.9, 131.8, 128.8, 122.0, 120.7, 118.4, 105.0, 26.0, 15.9, 2.68.

2-(1-(trimethylsilyl)-1H-indol-3-yl)acetonitrile (12f):



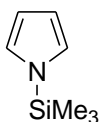
65% Yield. Colourless liquid; FT IR = 2959, 2254, 1455 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.66 (d, J = 8.2 Hz, 1H), 7.54 (d, J = 8.4 Hz, 1H), 7.27 – 7.23 (m, 2H), 7.02 (s, 1H), 3.85 (s, 3H), 0.60 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3) δ 140.6, 129.5, 128.4, 122.3, 120.3, 118.3, 118.2, 113.3, 106.4, 14.4, -0.08.

6-chloro-1-(trimethylsilyl)-1H-indole (12g):



95% Yield. Colourless liquid; FT IR = 2961, 1460 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.59 (d, J = 8.4 Hz, 1H), 7.50 (s, 1H), 7.20 (d, J = 3.2 Hz, 1H), 7.16 – 7.13 (m, 1H), 6.61 (d, J = 8.4 Hz, 1H), 0.59 (s, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 140.6, 130.6, 130.1, 127.3, 121.5, 120.6, 112.8, 104.6, -0.10.

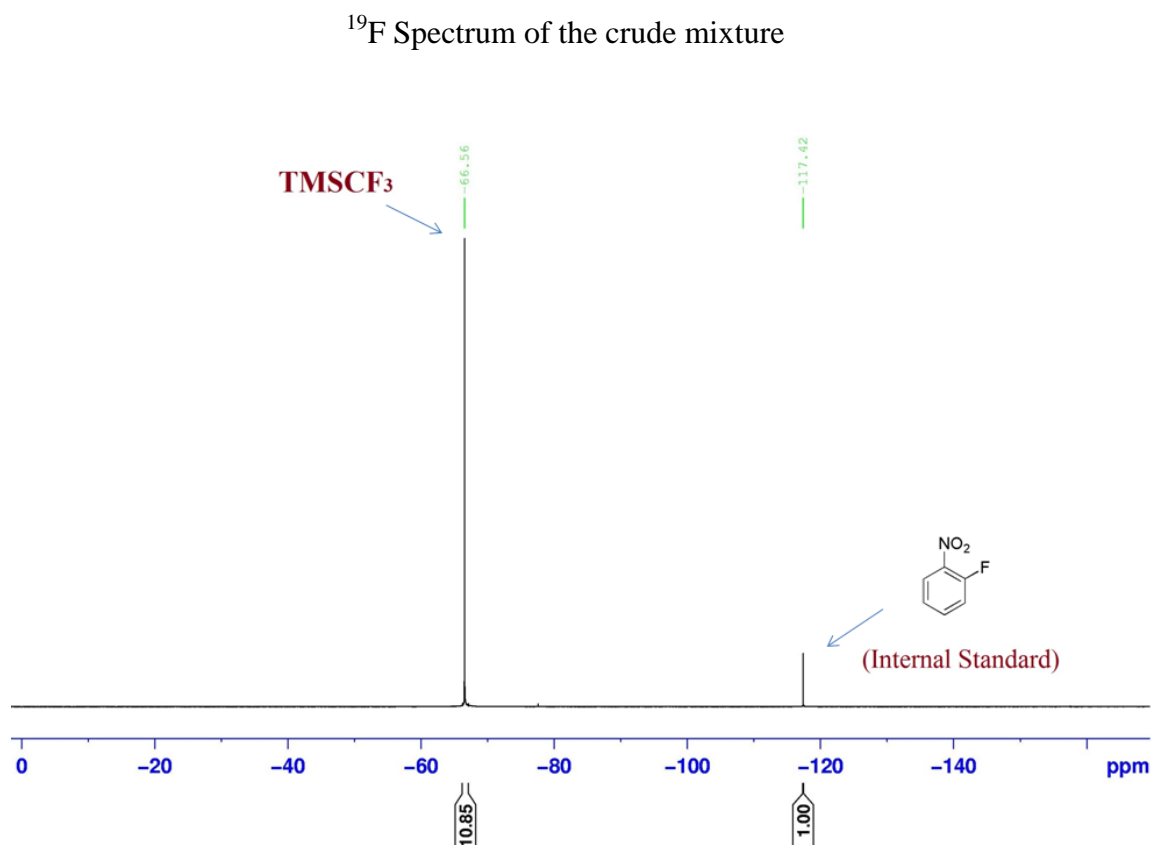
1-(trimethylsilyl)-1H-pyrrole (12i):⁹



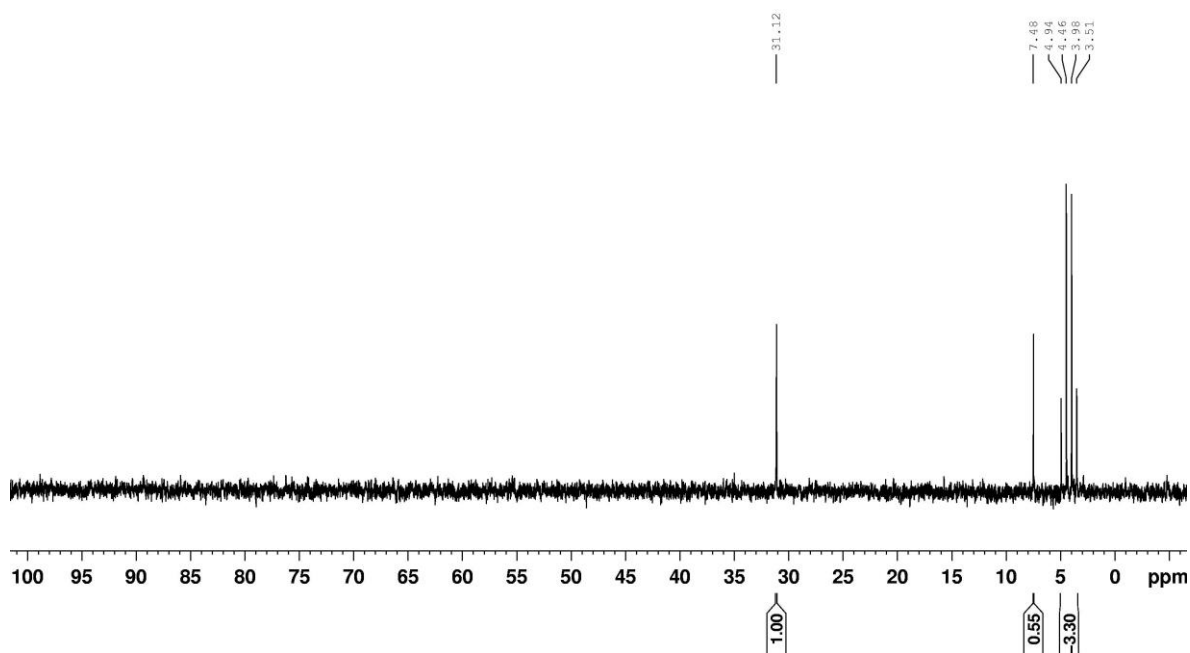
76% Yield. Colourless liquid; FT IR = 2960, 1472 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ , 6.87 (t, J = 2.0 Hz, 2H), 6.39 (t, J = 2.0 Hz, 2H), 0.47 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3) δ 123.0, 110.8, -0.26.

Procedure for the regeneration of Me_3SiCF_3 from CHF_3 :¹⁰ Trifluoromethyl trimethylsilane (490 μL , 3.3 mmol) was added to a mixture of **5** (20.0 mg, 0.044 mmol), Sodium hydride [8.0 mg (55% suspension in mineral oil), 0.11 mmol] and phenylacetylene (490 μL , 2.2 mmol) and the resulting suspension was stirred for few minutes at room temperature. During the reaction CHF_3 (approx. 2.2 mmol) was generated. It was passed through cannula to another reaction flask containing potassium hexamethyldisilazide [0.5 M in toluene] (0.2 mL, 1 mmol) and chlorotrimethylsilane (108 μL , 1 mmol) at -85°C for 30 minutes. Resulting mixture was stirred vigorously at -85°C for 5 hours. The reaction mixture was then slowly warmed to room temperature and stirred for 3 hours. *o*-Fluoro nitrobenzene (45 mg, 0.32 mmol) was added as an internal standard to the crude mixture and it was analysed by ^{29}Si and ^{19}F NMR (Figure 1). Yield 58% (by ^{19}F NMR); ^{19}F NMR (376.5 MHz, CDCl_3) δ -66.6 (s); ^{29}Si NMR (79.5 MHz, CDCl_3) δ 4.22 (q, $J_{\text{Si-F}} = 38.0$ Hz, 1Si).

Figure 1:



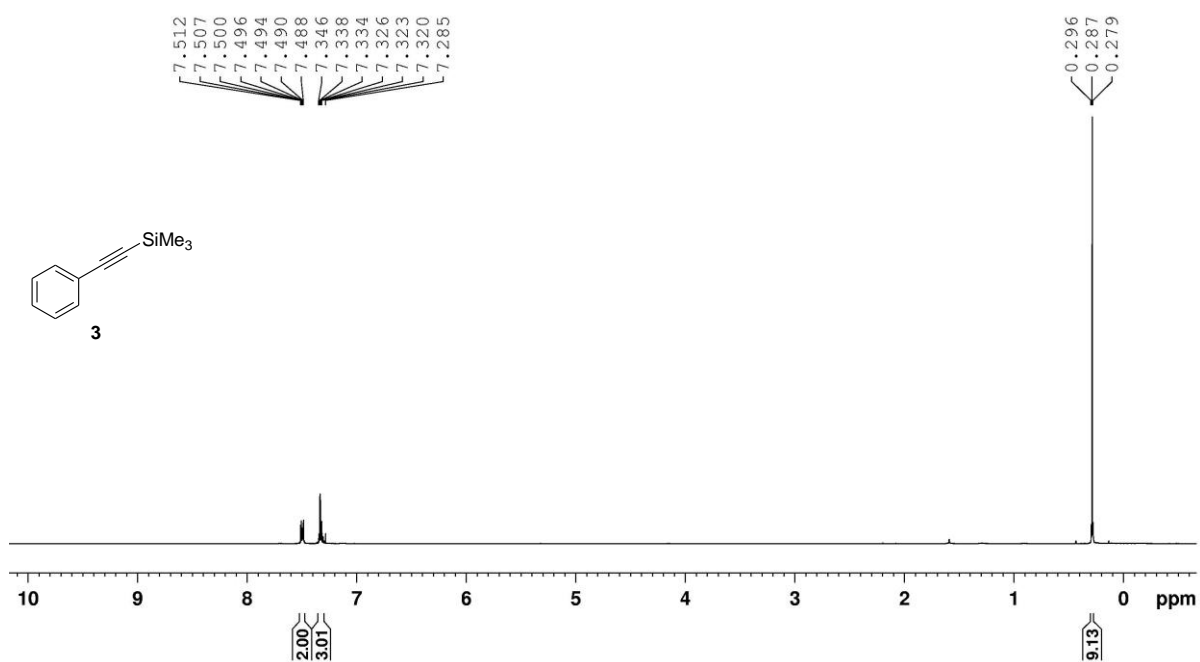
^{29}Si Spectrum of the crude mixture



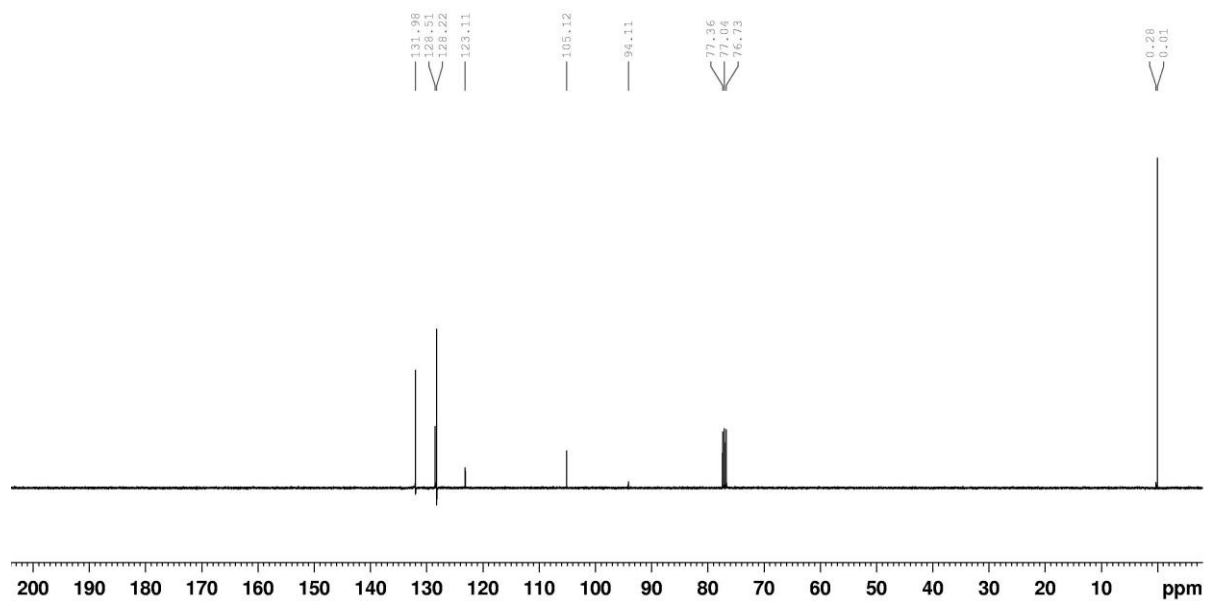
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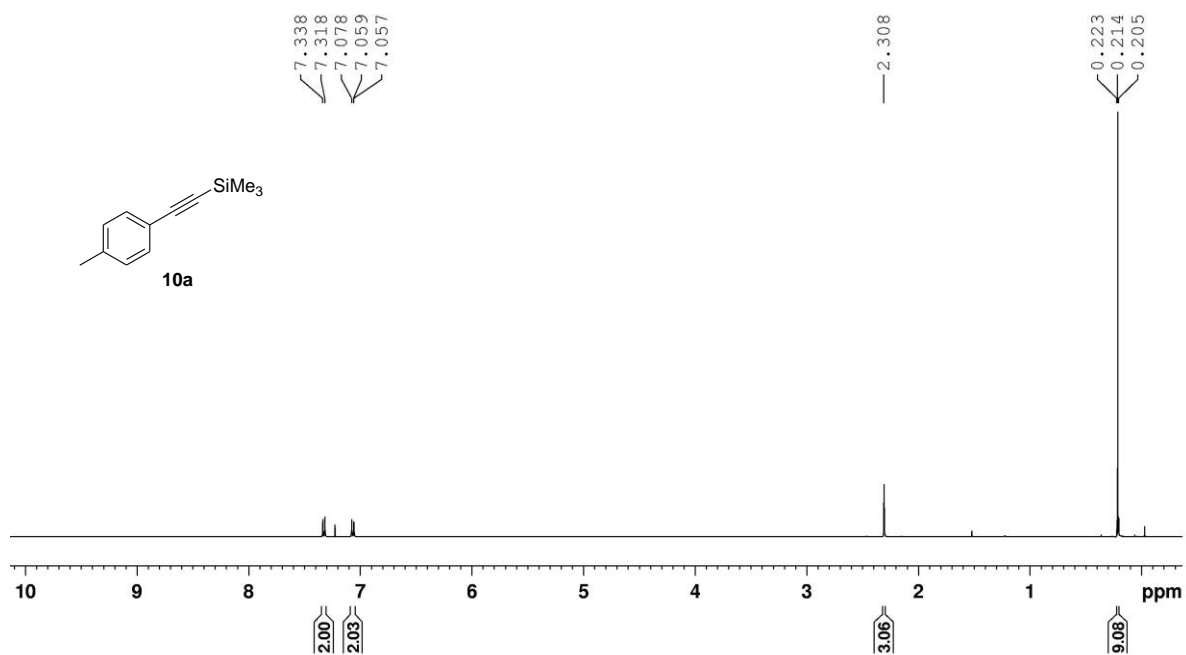
^1H NMR Spectrum of **3**



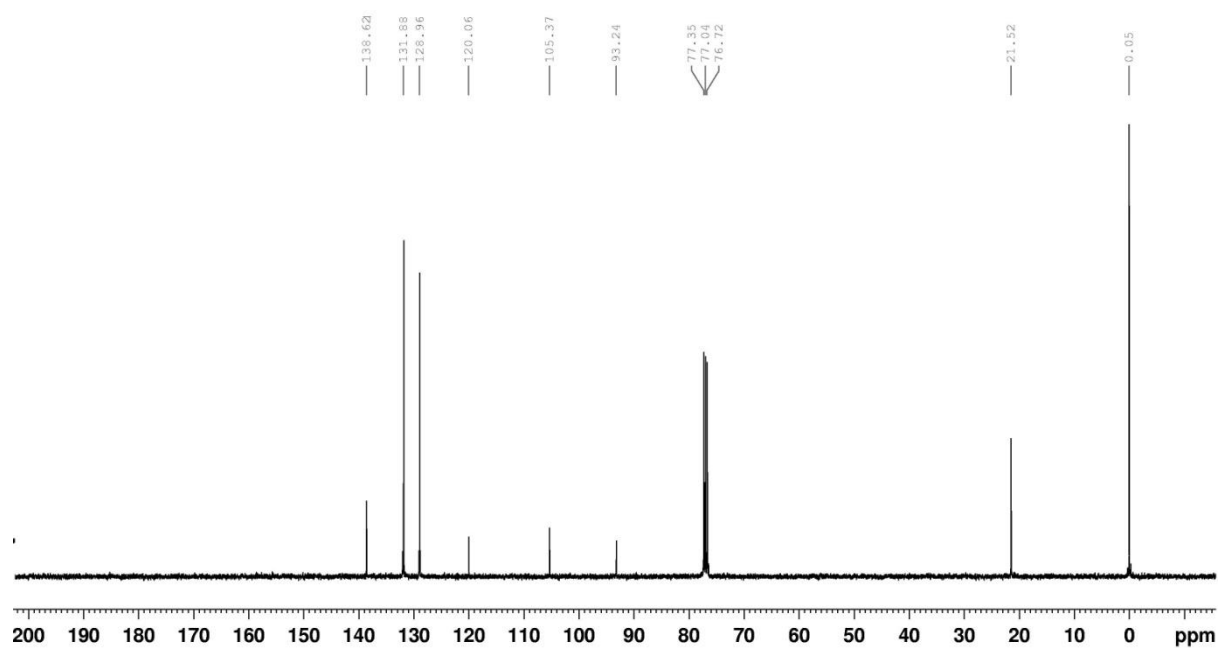
^{13}C NMR Spectrum of **3**



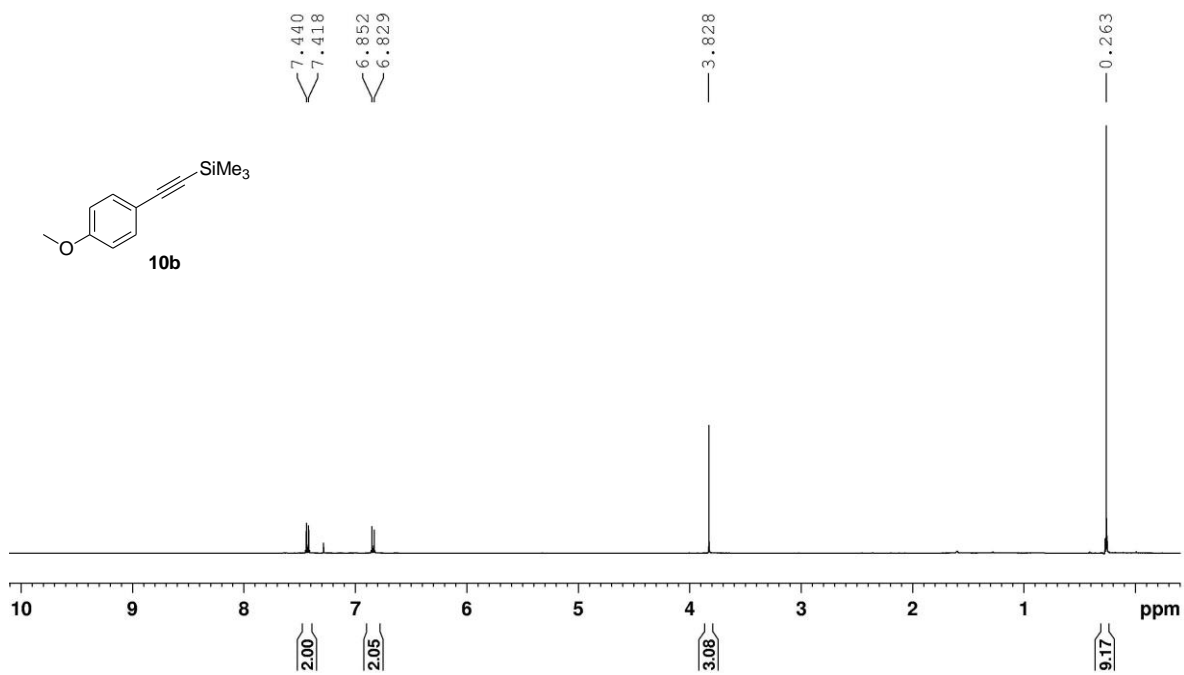
¹H NMR Spectrum of 10a



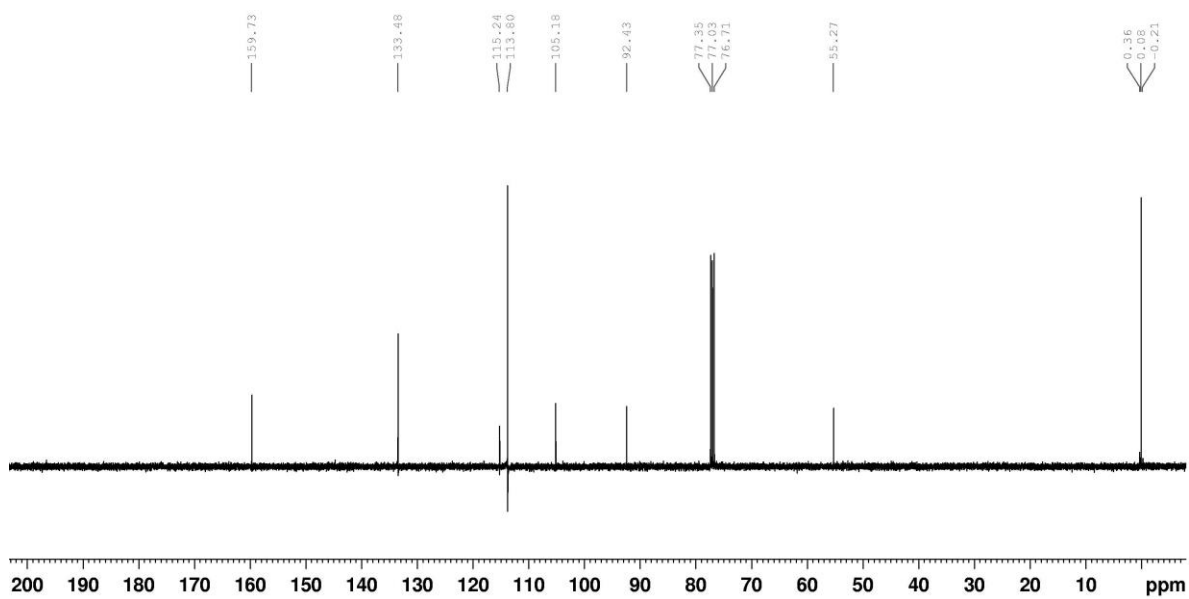
¹³C NMR Spectrum of 10a



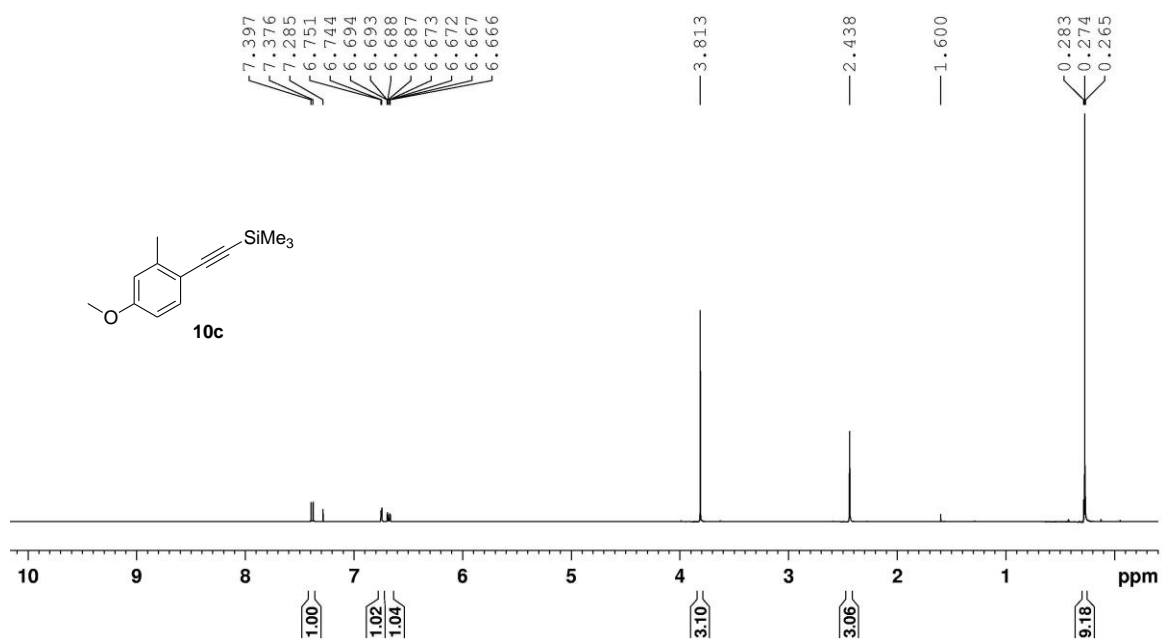
¹H NMR Spectrum of **10b**



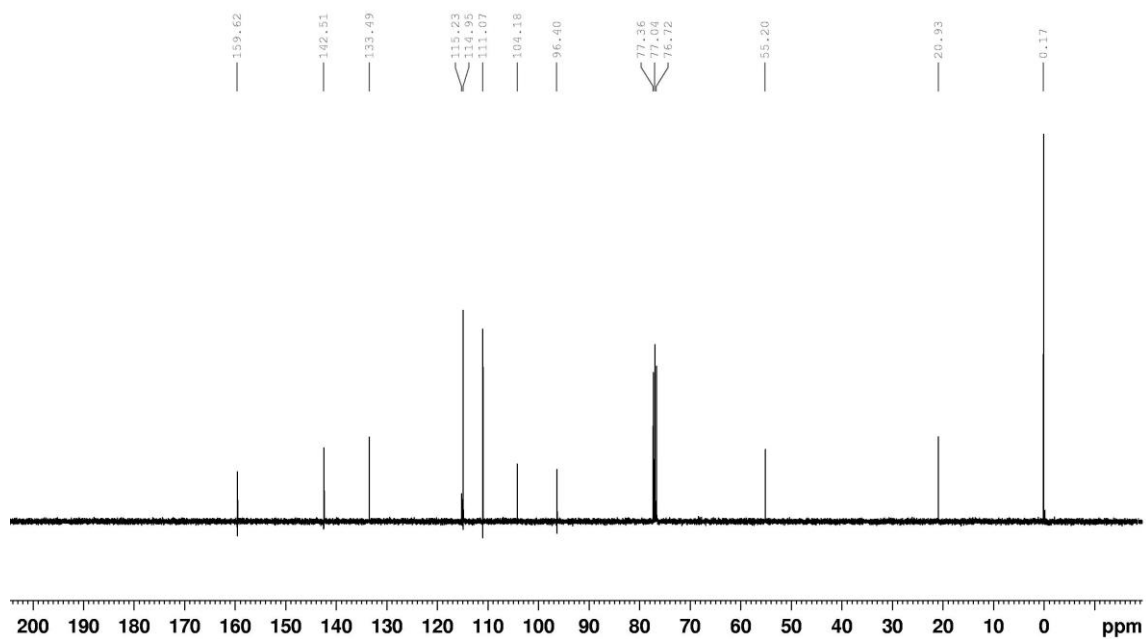
¹³C NMR Spectrum of **10b**



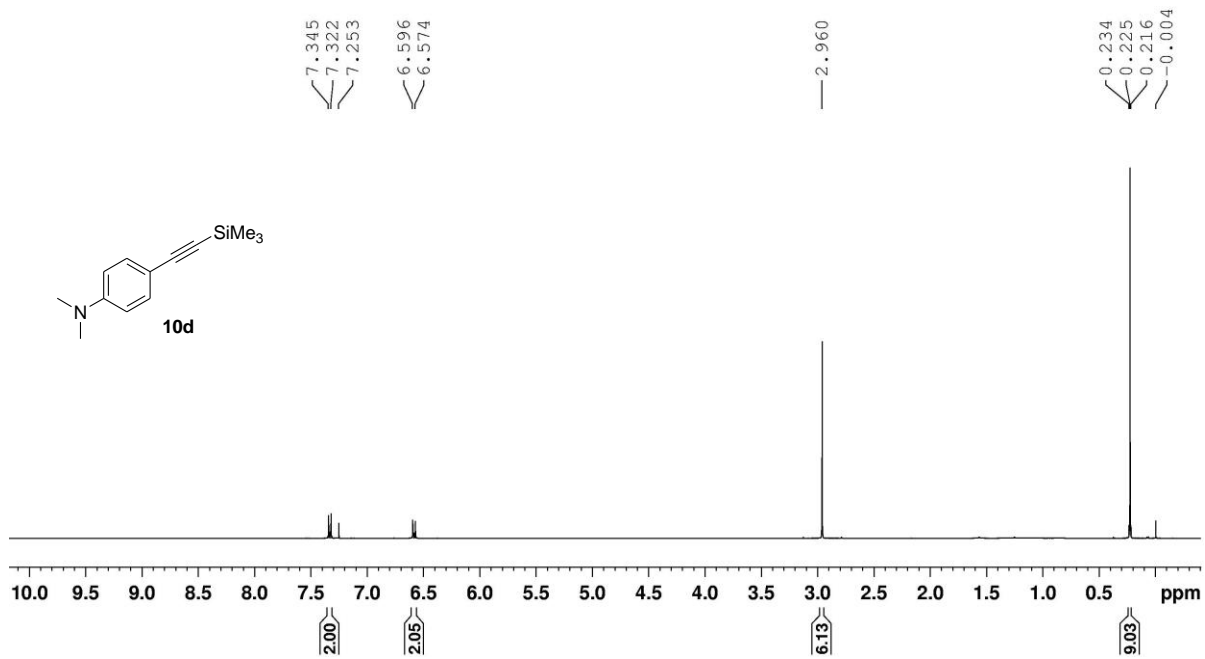
^1H NMR Spectrum of **10c**



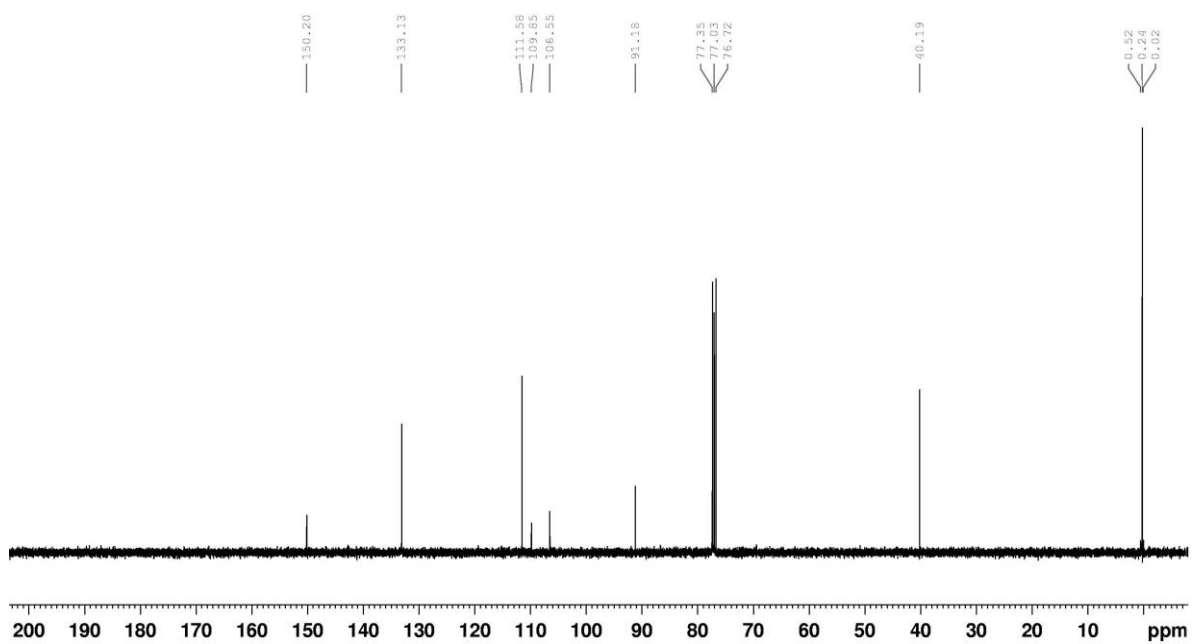
^{13}C NMR Spectrum of **10c**



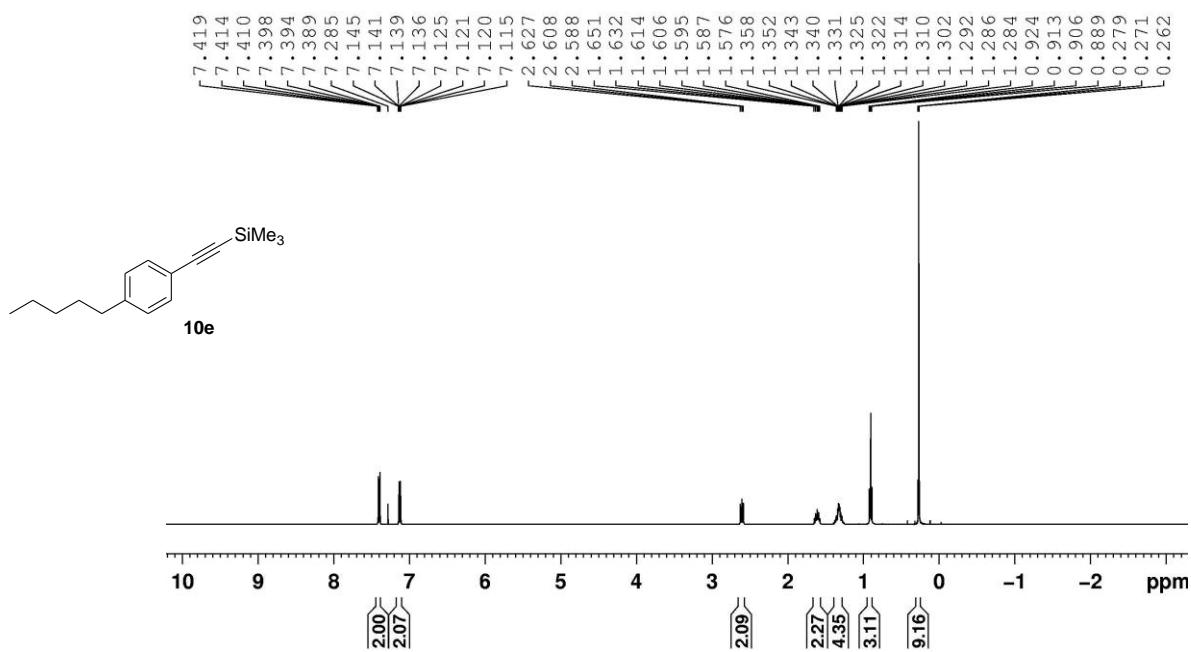
^1H NMR Spectrum of **10d**



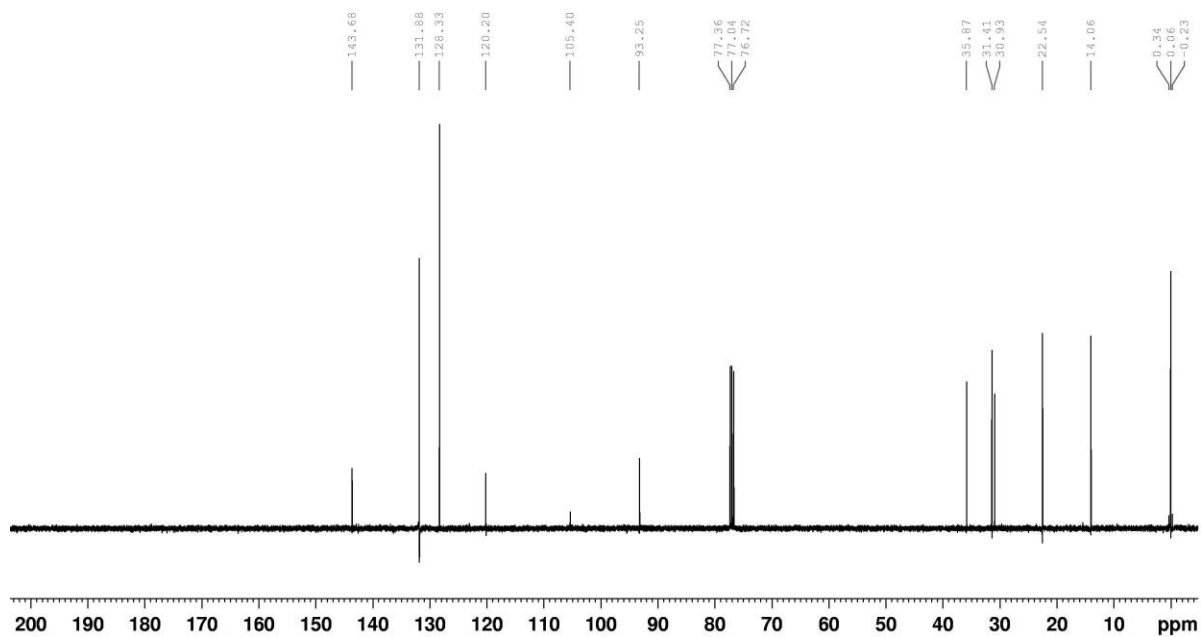
^{13}C NMR Spectrum of **10d**



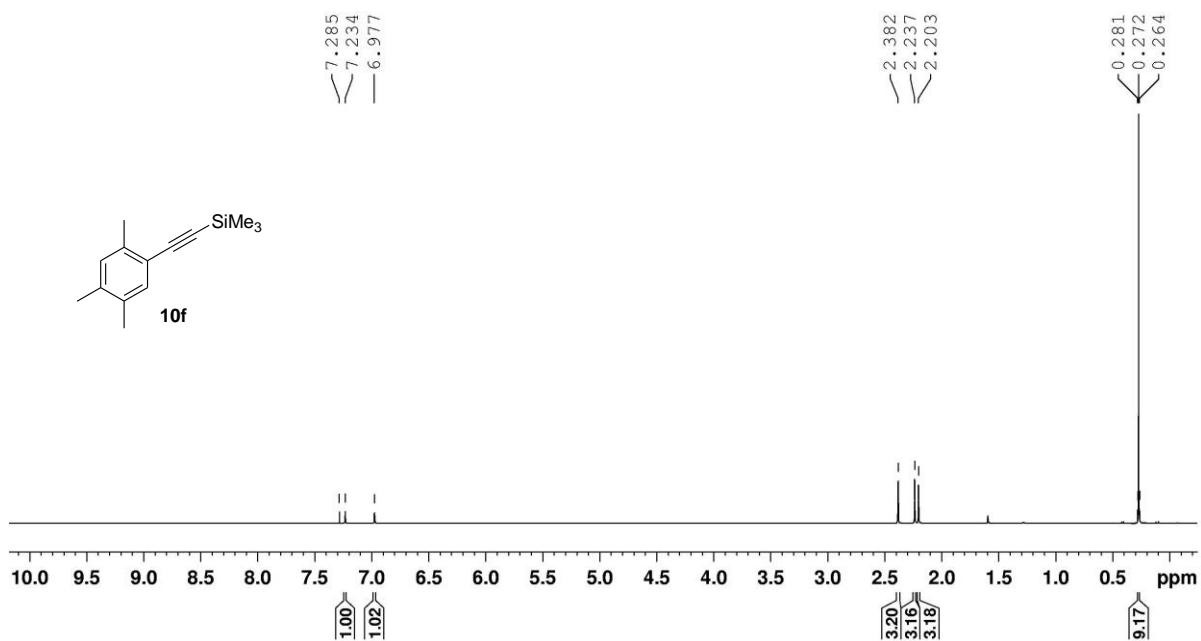
¹H NMR Spectrum of 10e



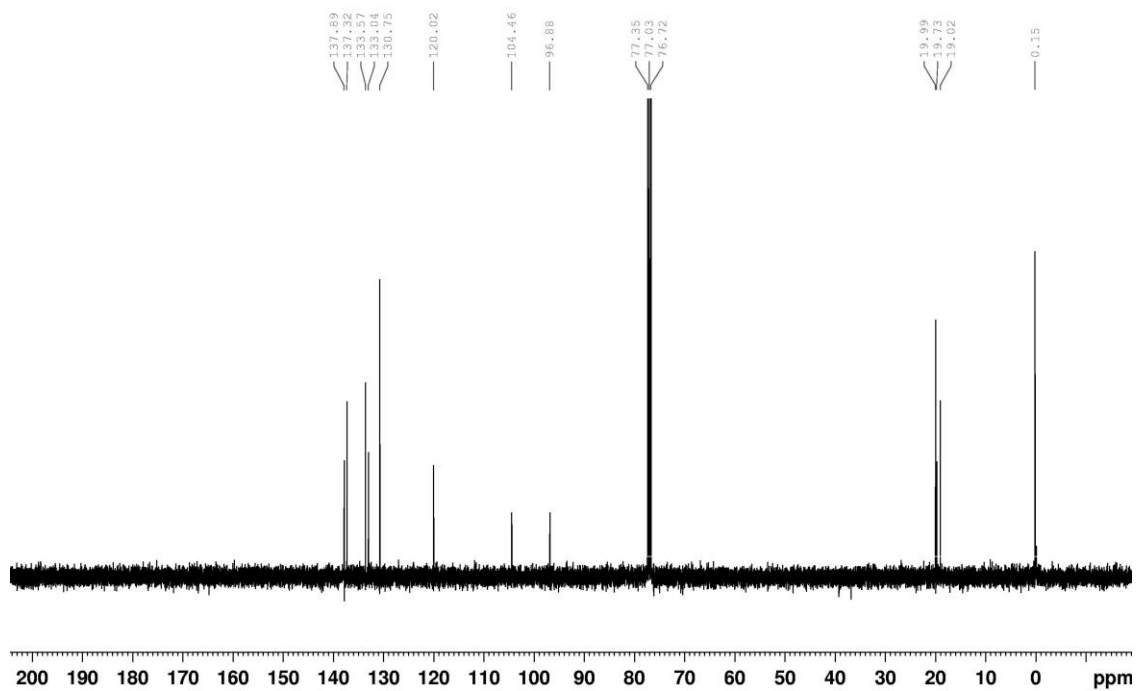
¹³C NMR Spectrum of 10e



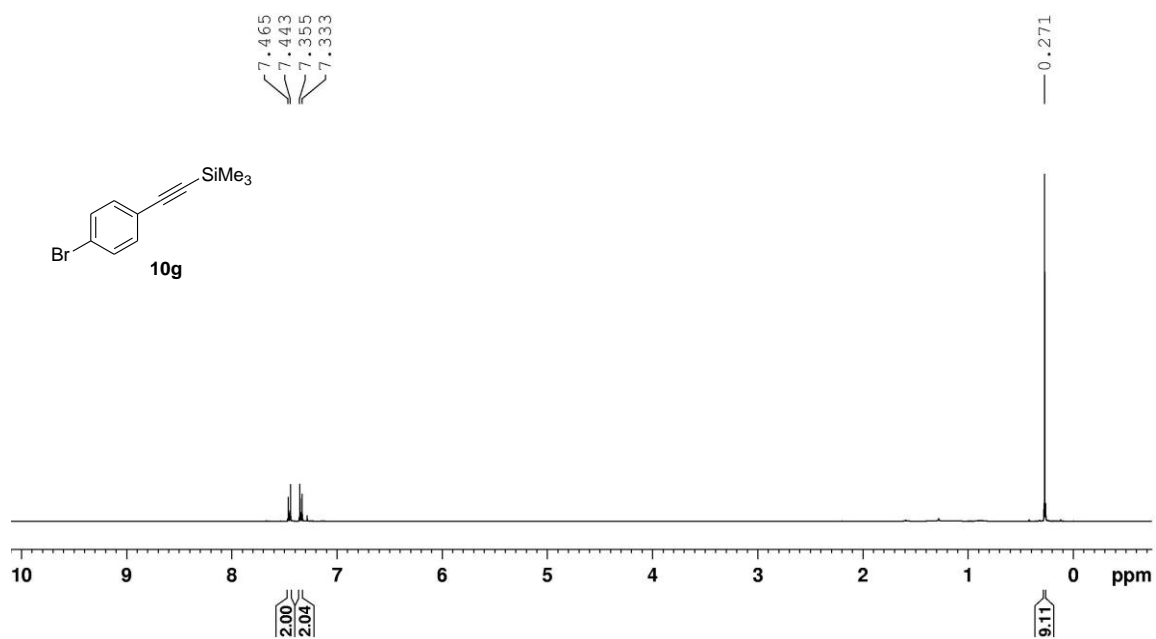
¹H NMR Spectrum of **10f**



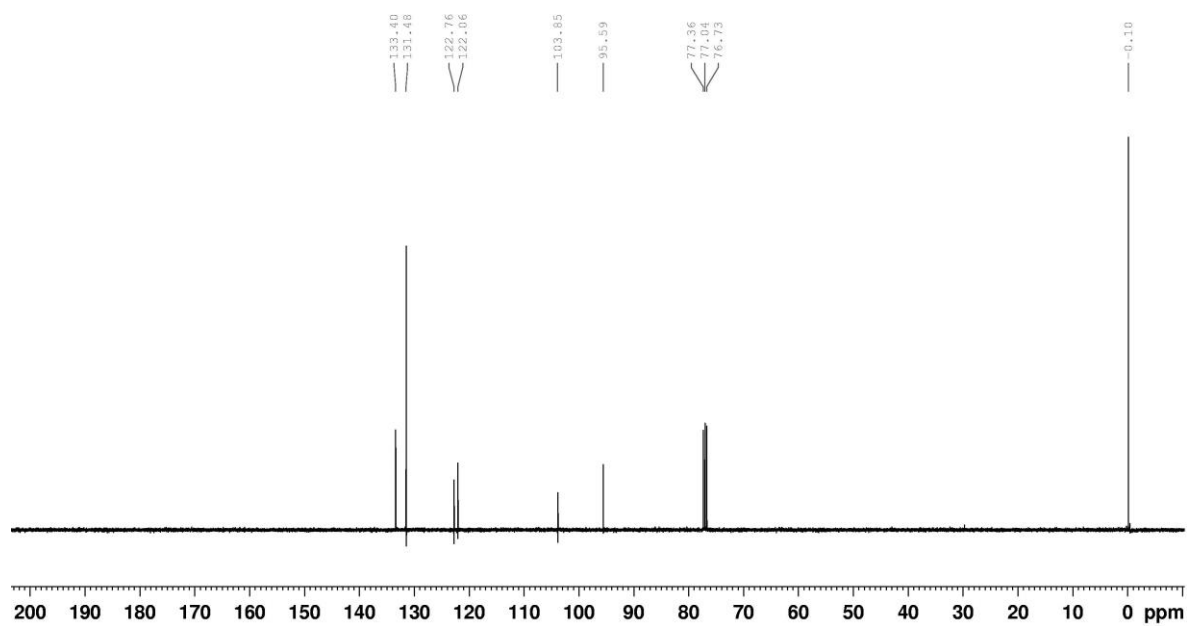
¹³C NMR Spectrum of **10f**



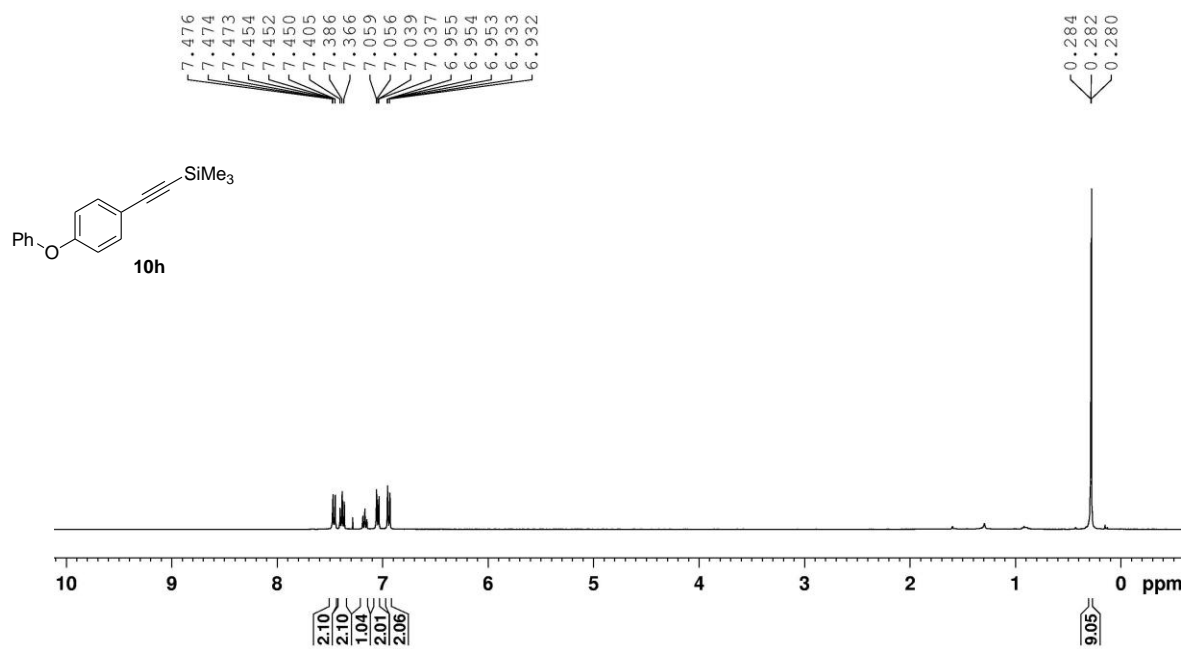
^1H NMR Spectrum of **10g**



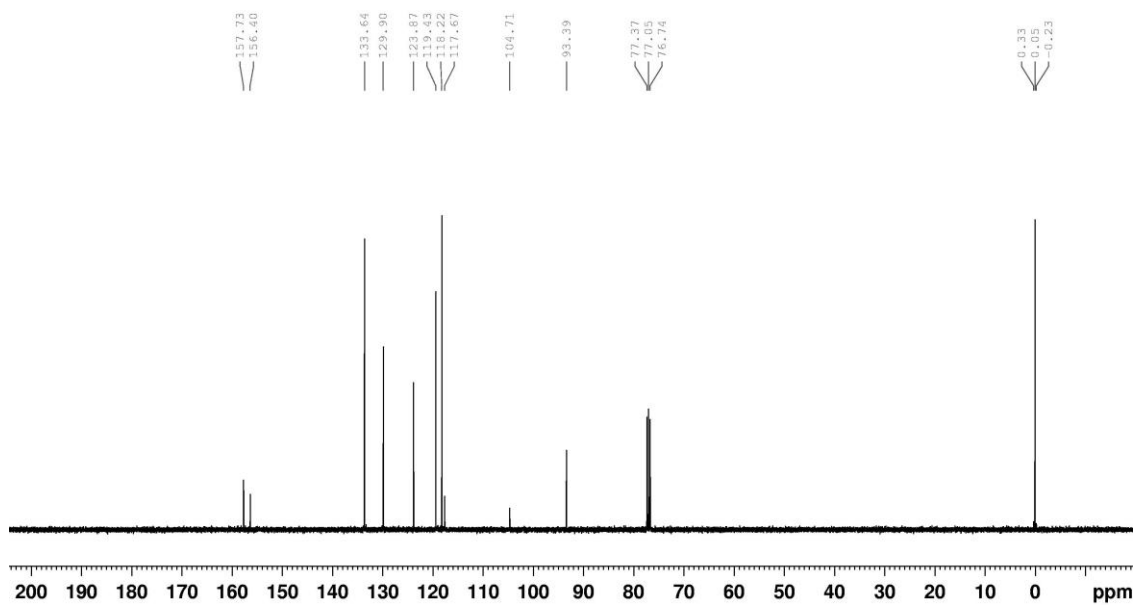
^{13}C NMR Spectrum of **10g**



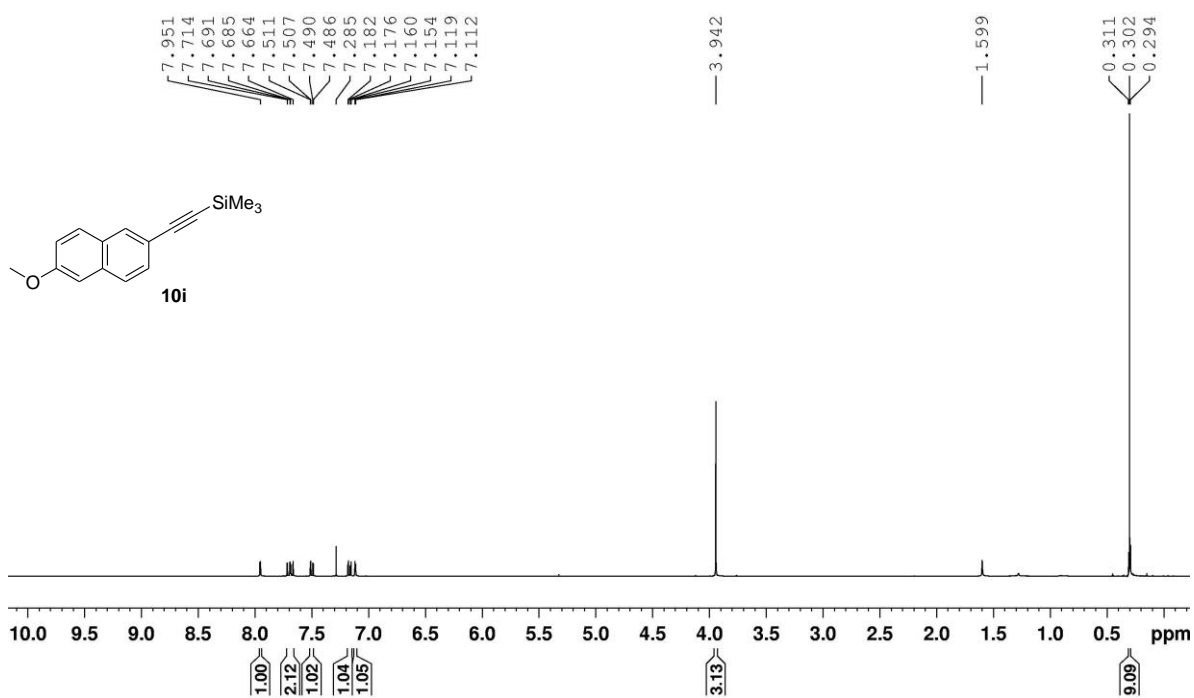
^1H NMR Spectrum of **10h**



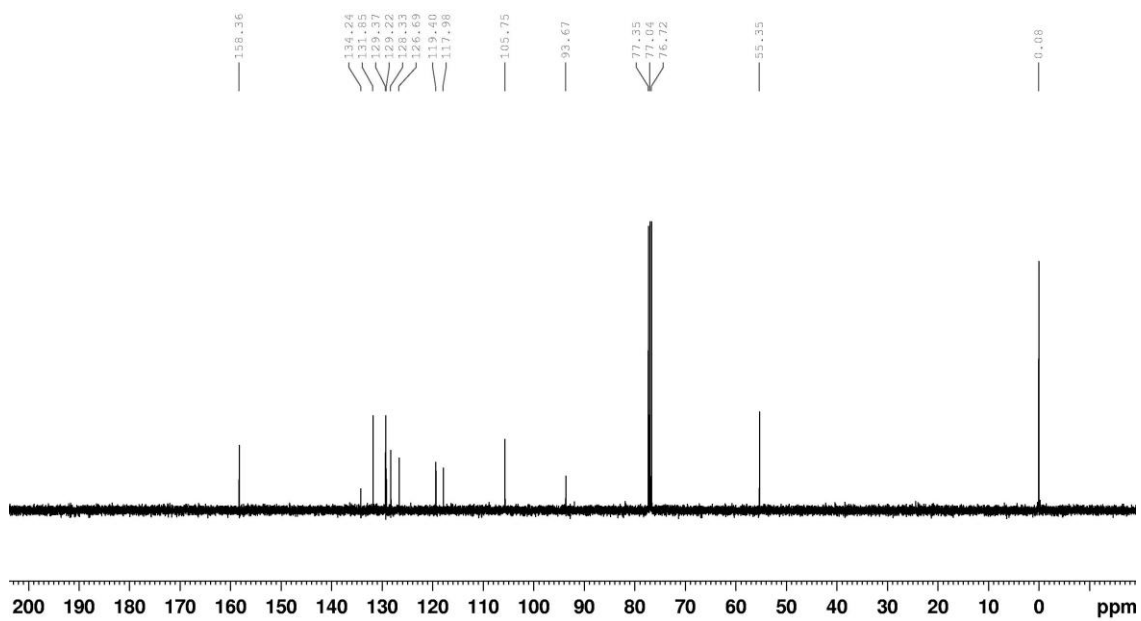
^{13}C NMR Spectrum of **10h**



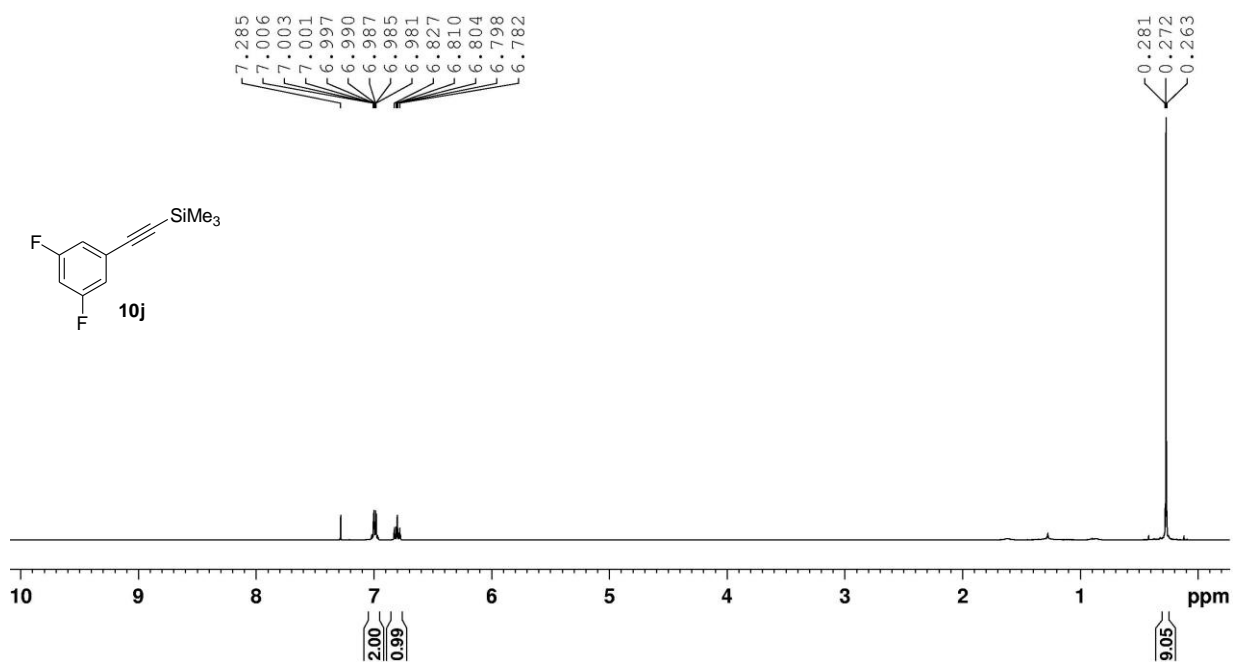
¹H NMR Spectrum of **10i**



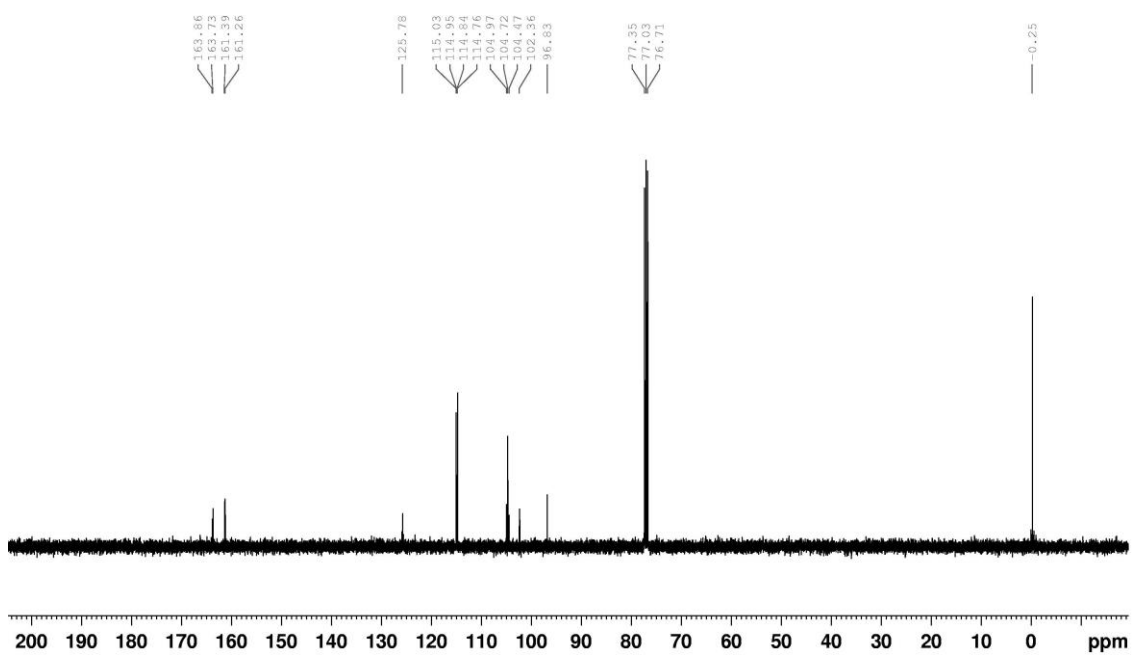
¹³C NMR Spectrum of **10i**



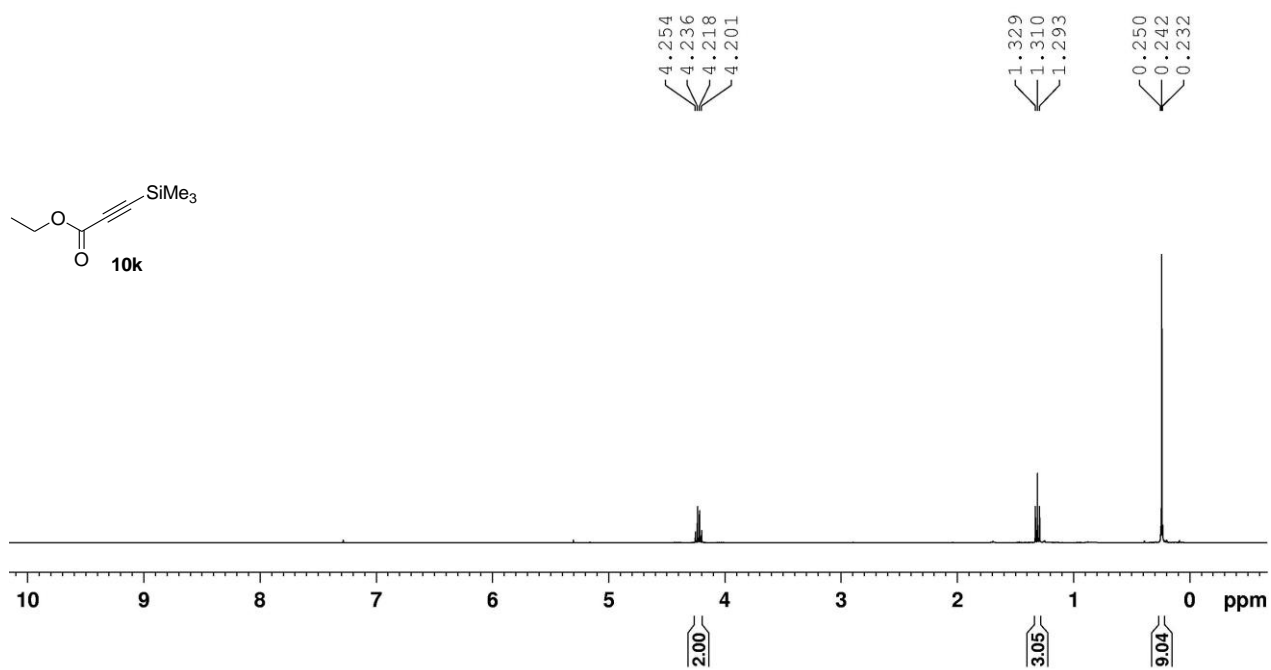
¹H NMR Spectrum of 10j



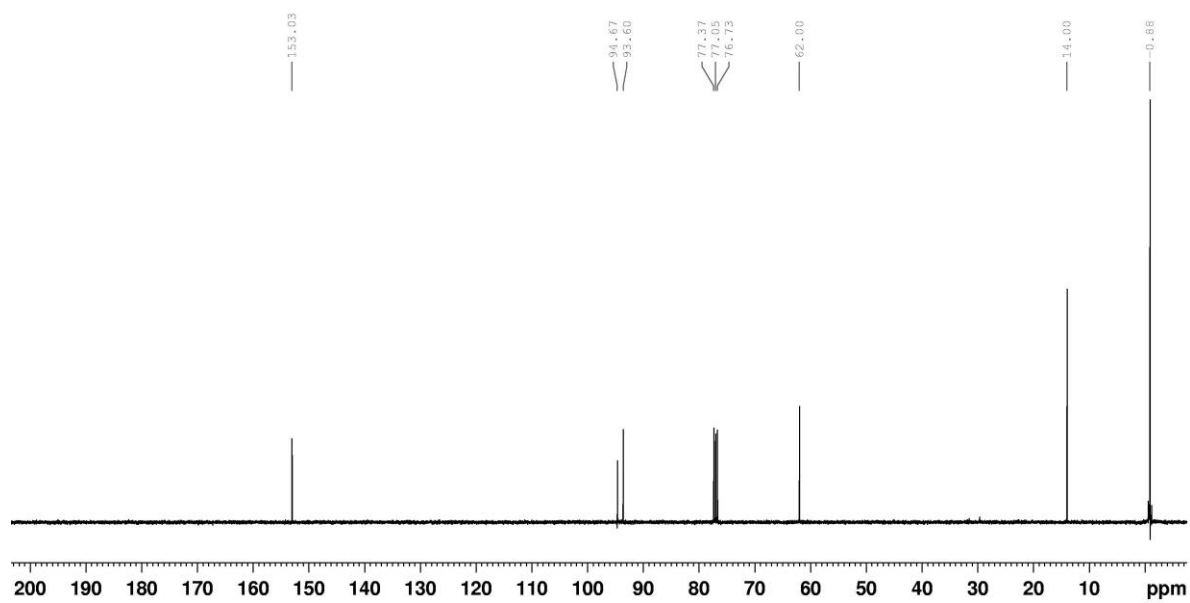
¹³C NMR Spectrum of 10j



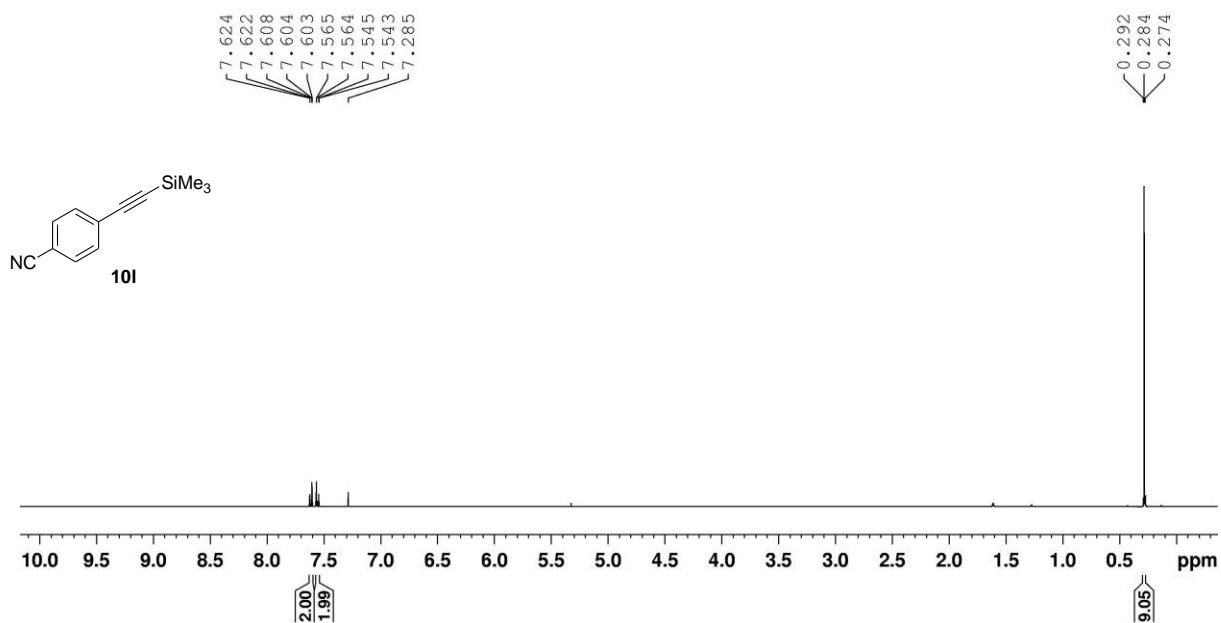
¹H NMR Spectrum of **10k**



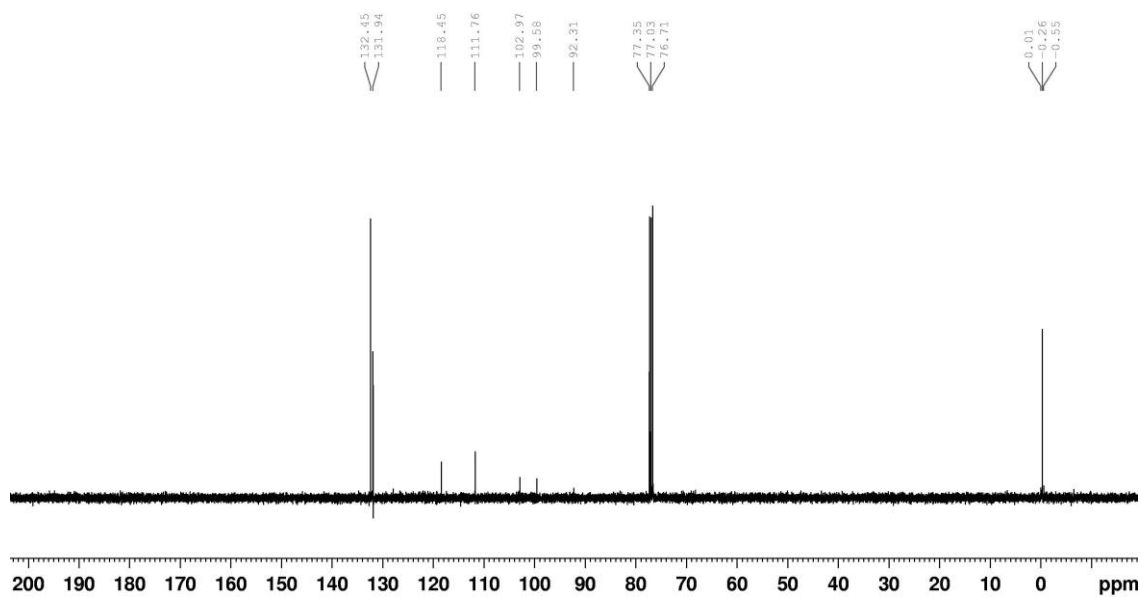
¹³C NMR Spectrum of **10k**



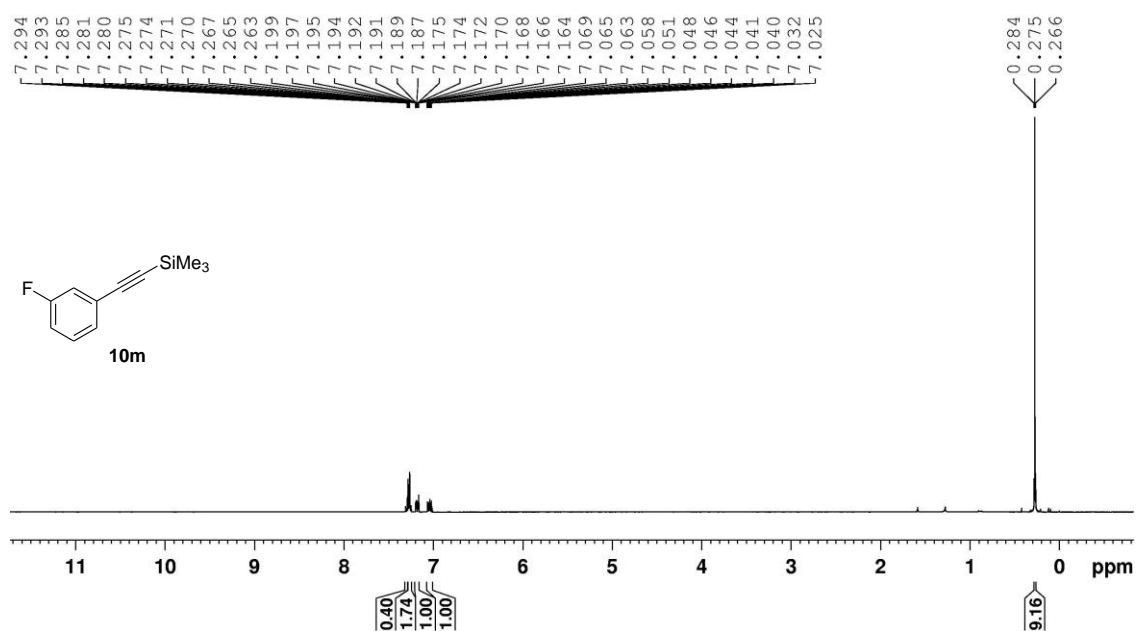
¹H NMR Spectrum of **101**



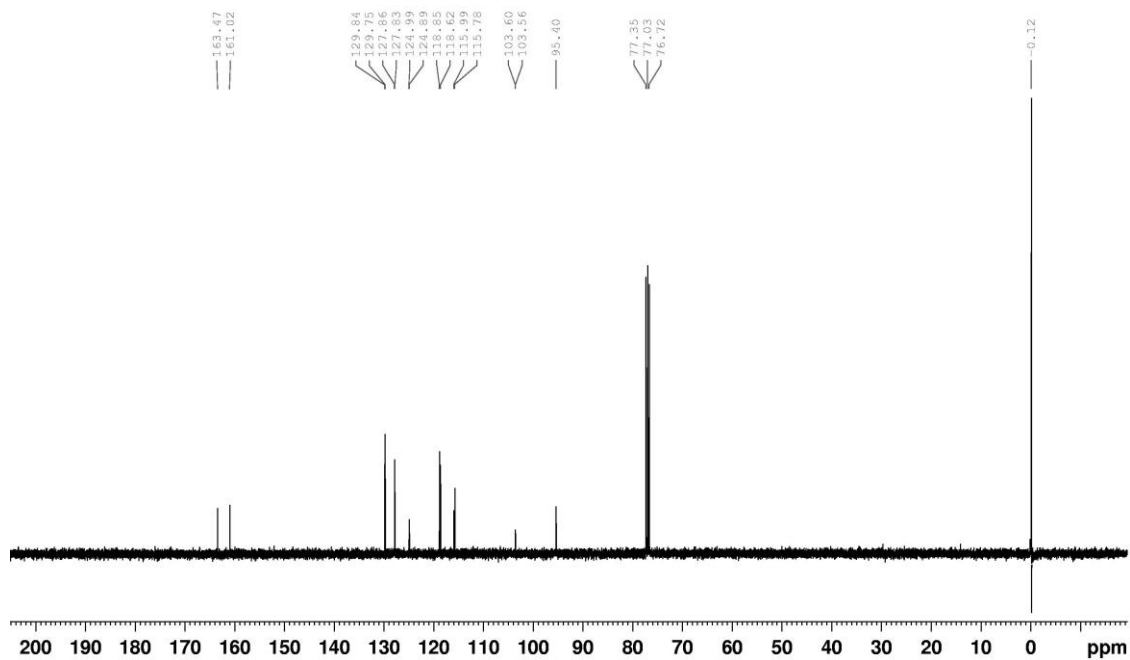
¹³C NMR Spectrum of **101**



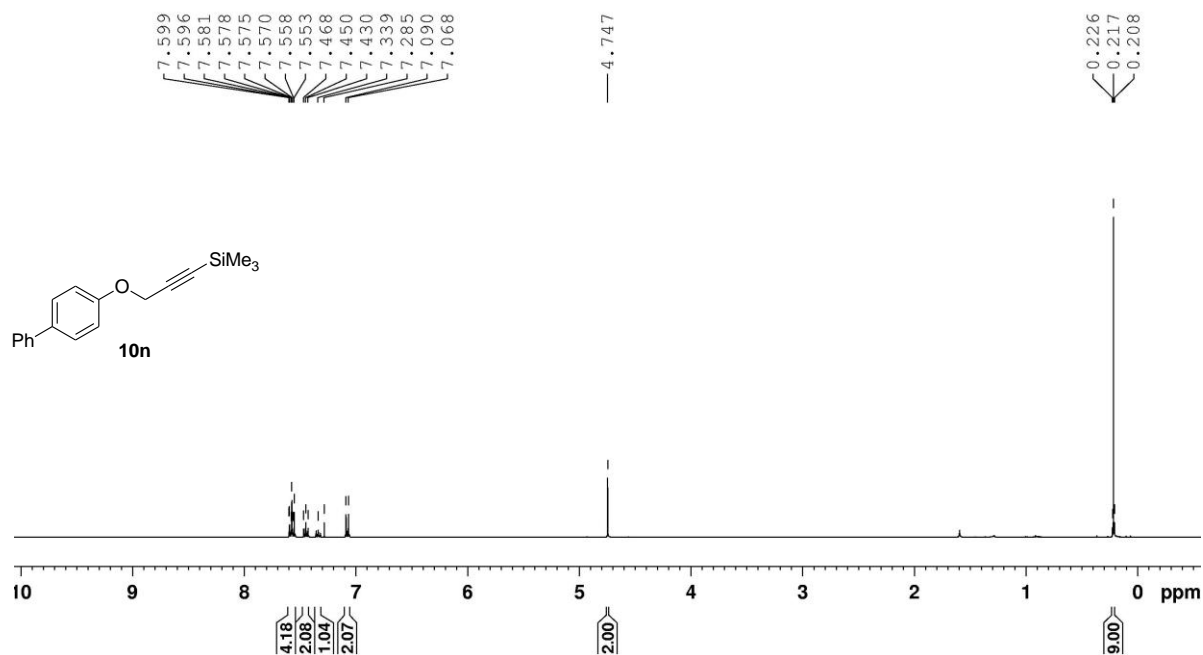
^1H NMR Spectrum of **10m**



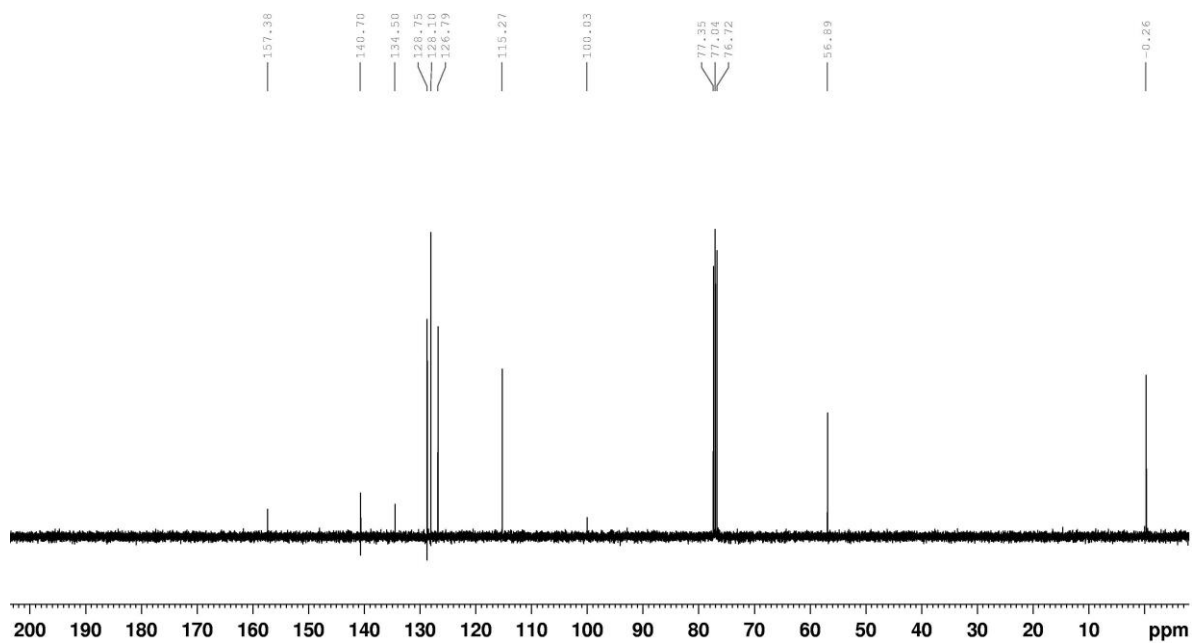
^{13}C NMR Spectrum of **10m**



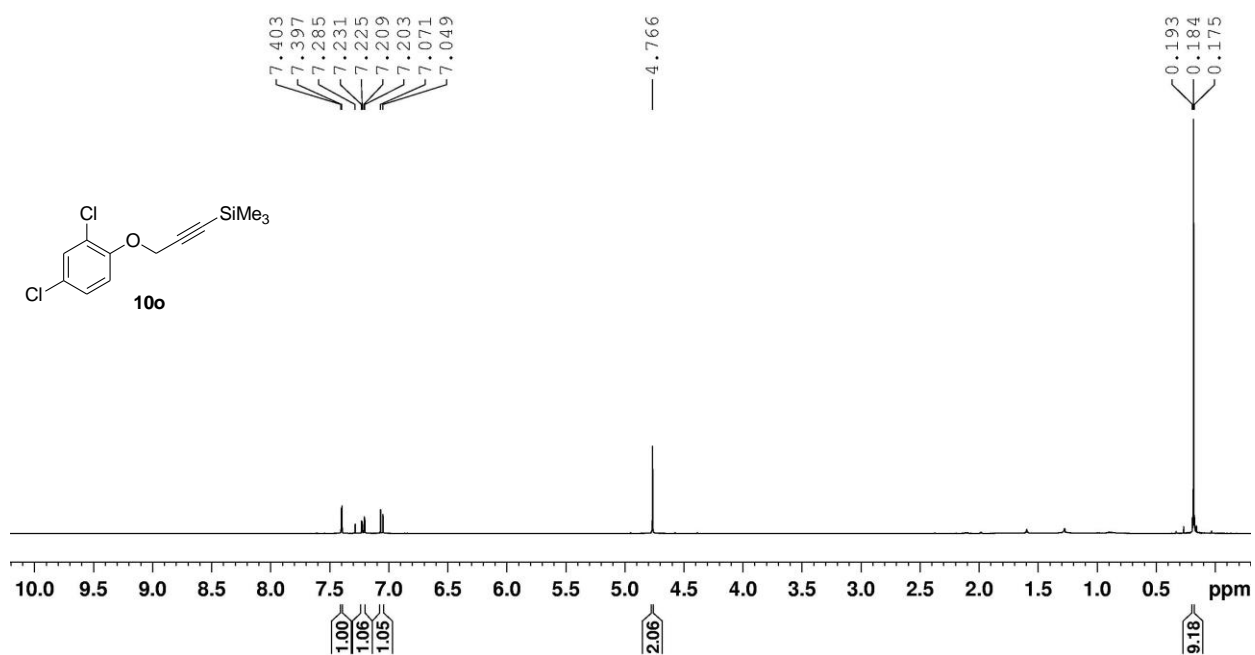
¹H NMR Spectrum of 10n



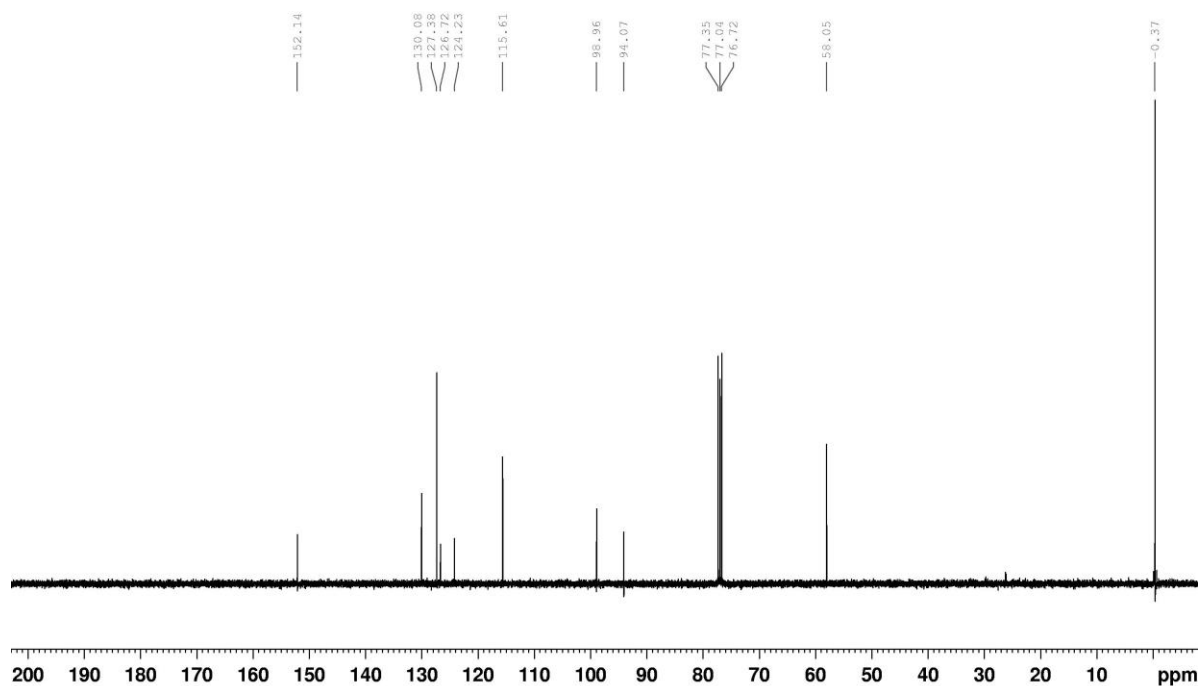
¹³C NMR Spectrum of 10n



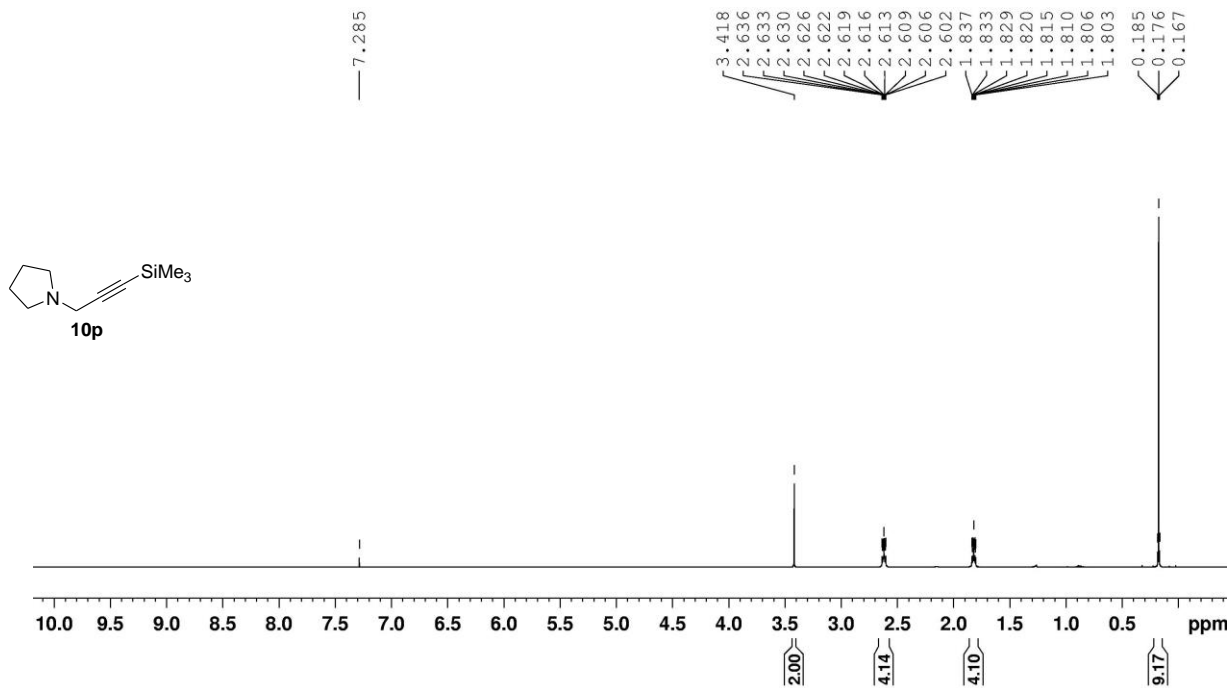
¹H NMR Spectrum of **10o**



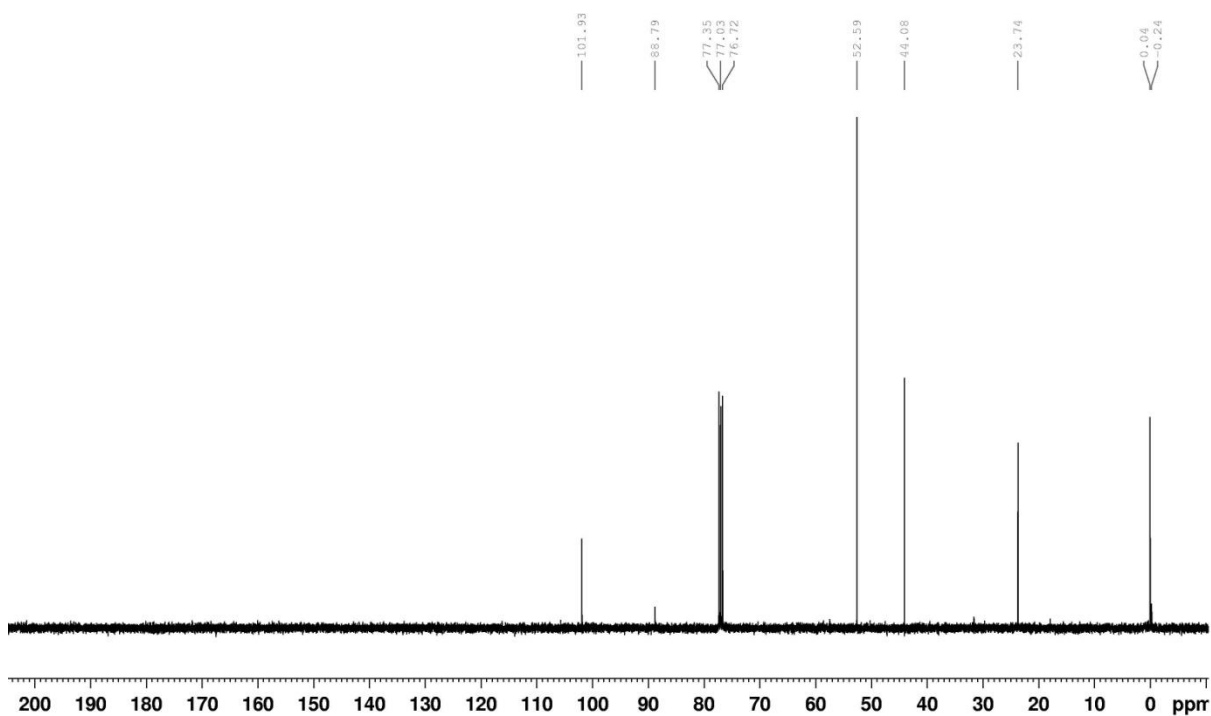
¹³C NMR Spectrum of **10o**



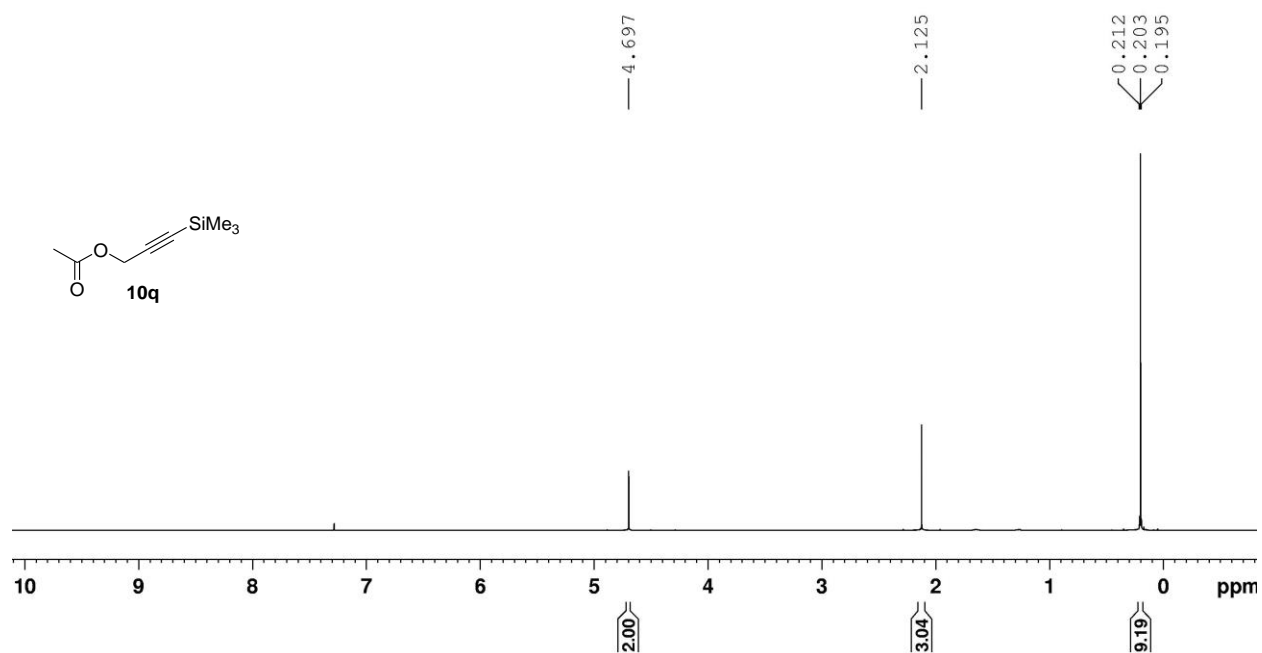
^1H NMR Spectrum of **10p**



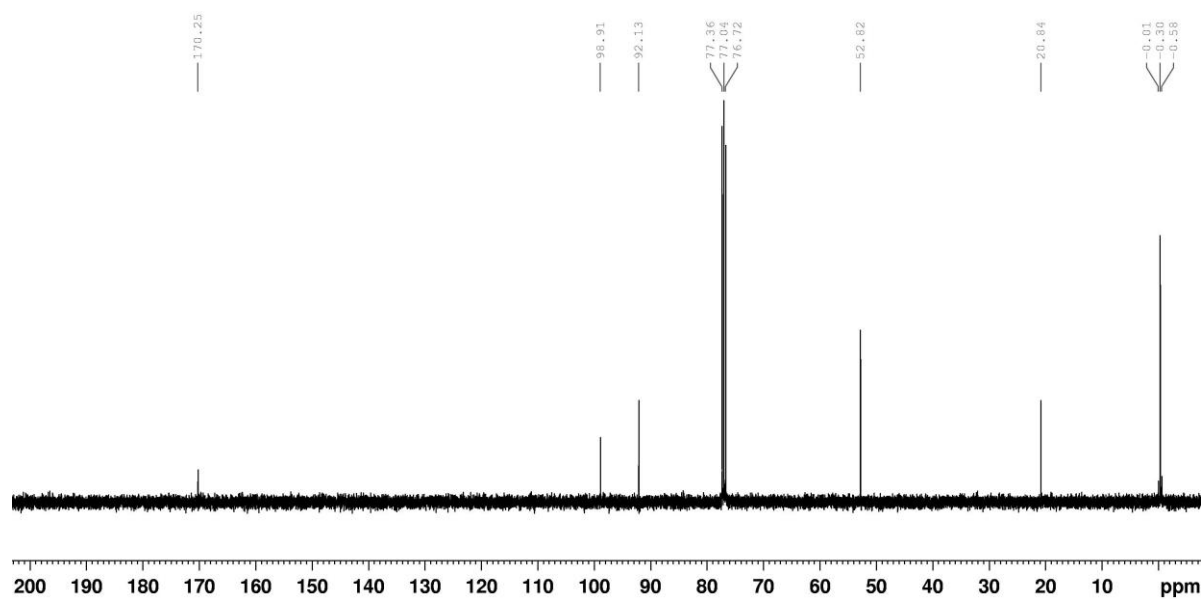
^{13}C NMR Spectrum of **10p**



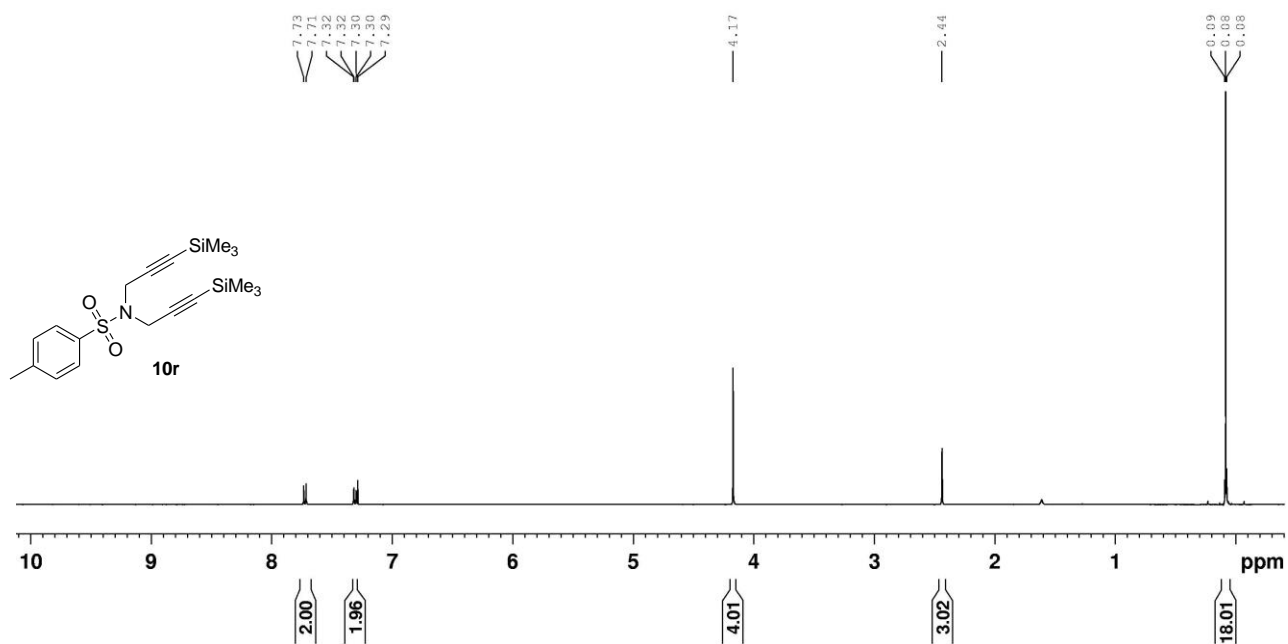
¹H NMR Spectrum of 10q



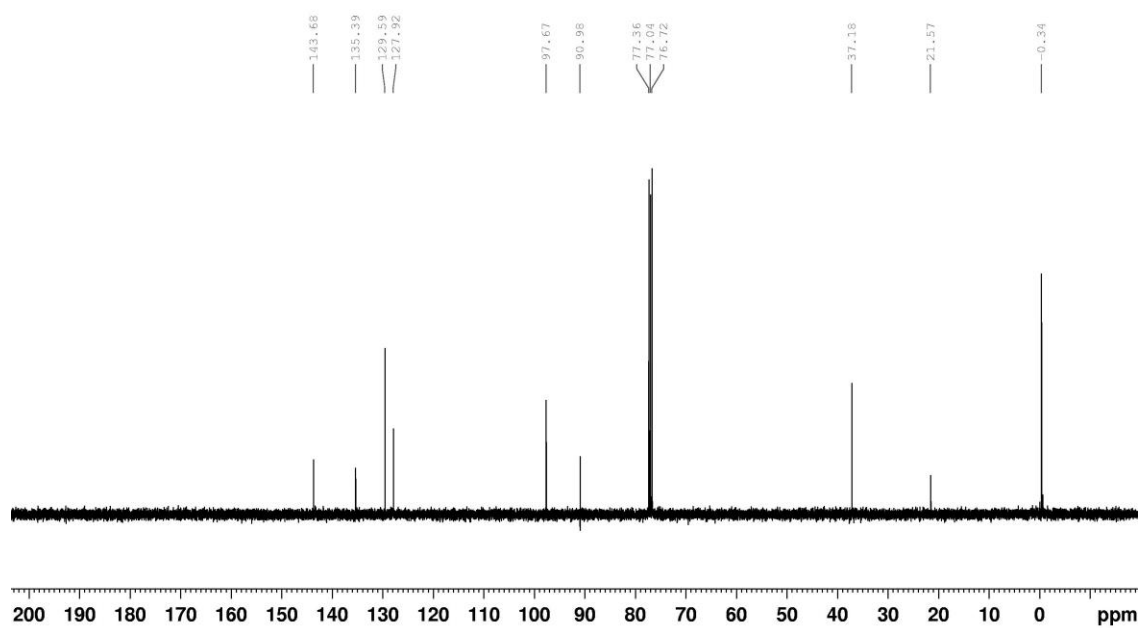
¹³C NMR Spectrum of 10q



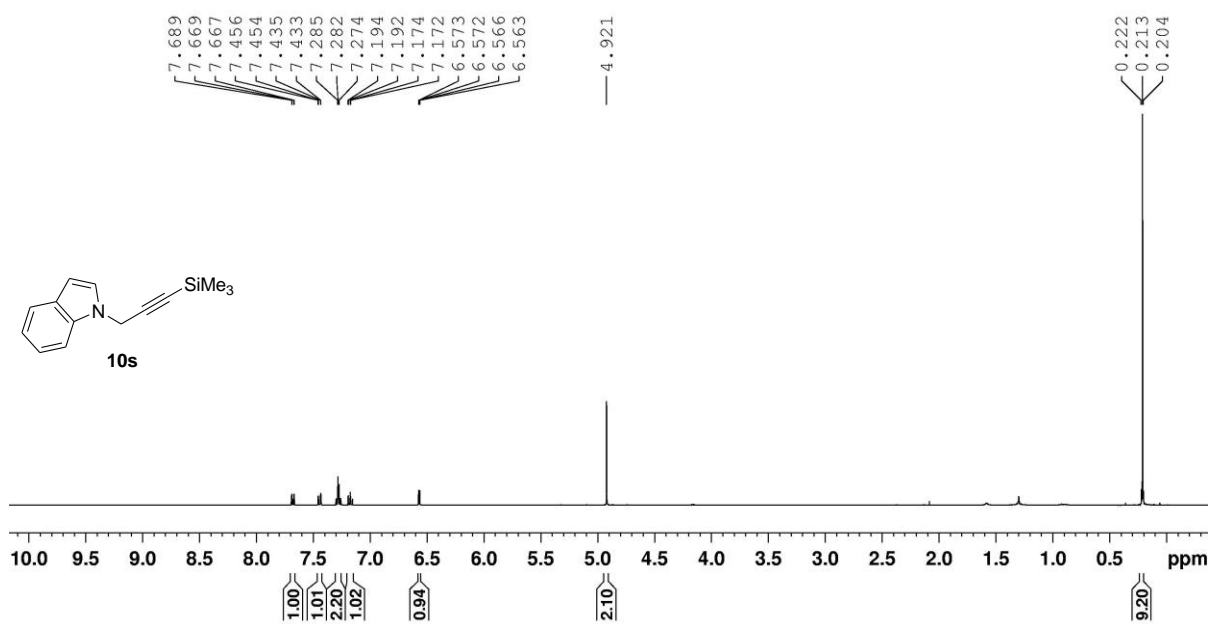
^1H NMR Spectrum of **10r**



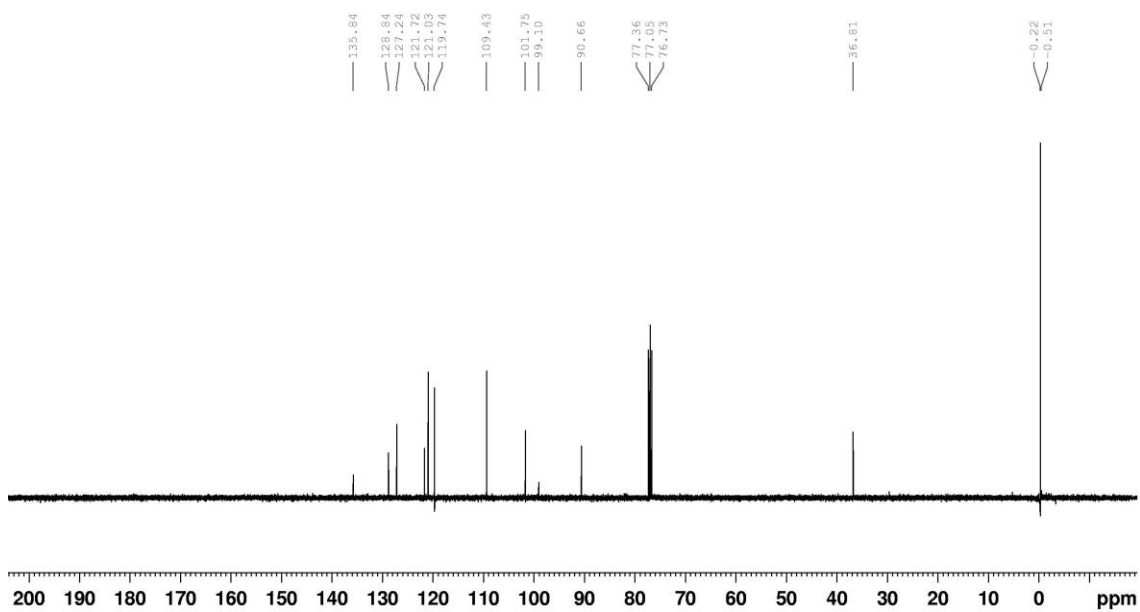
^{13}C NMR Spectrum of **10r**



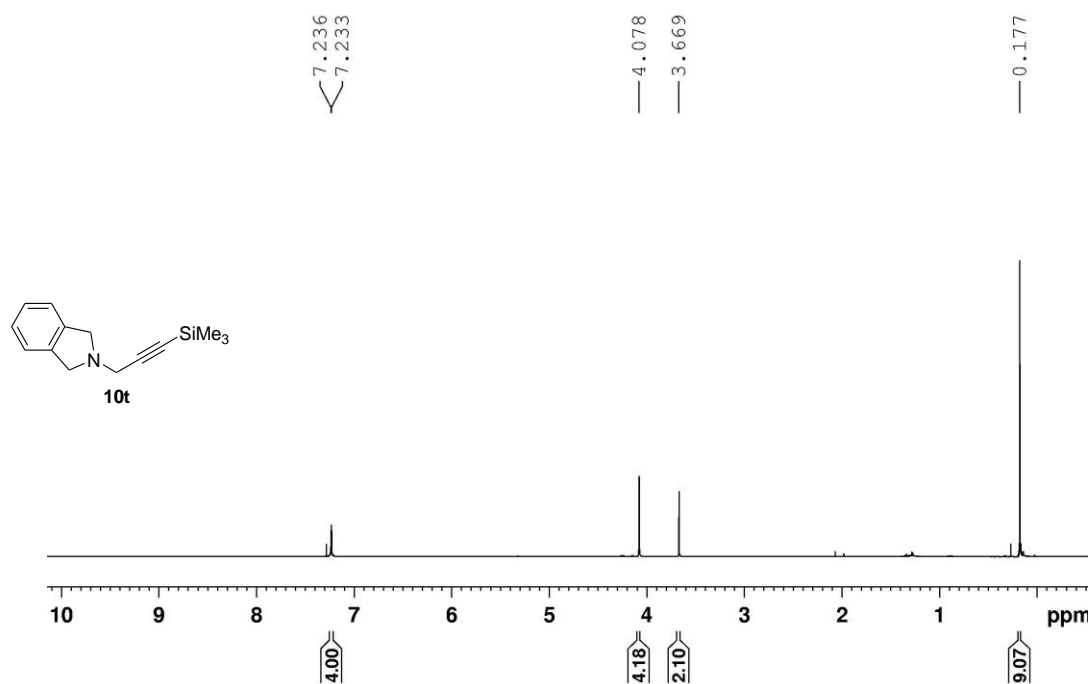
¹H NMR Spectrum of 10s



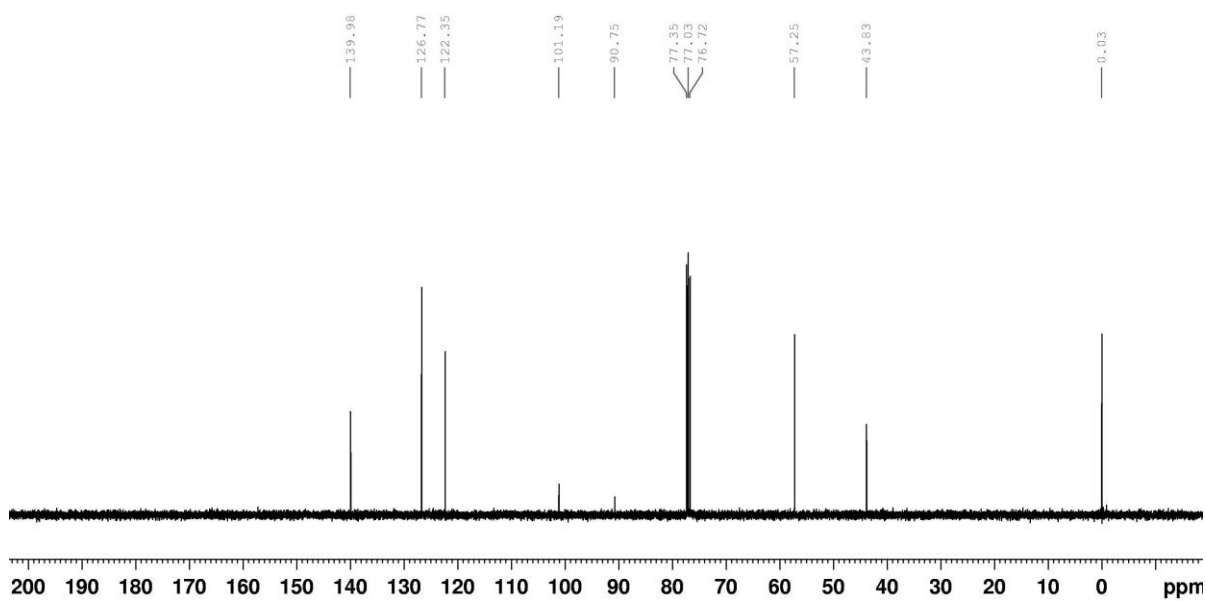
¹³C NMR Spectrum of 10s



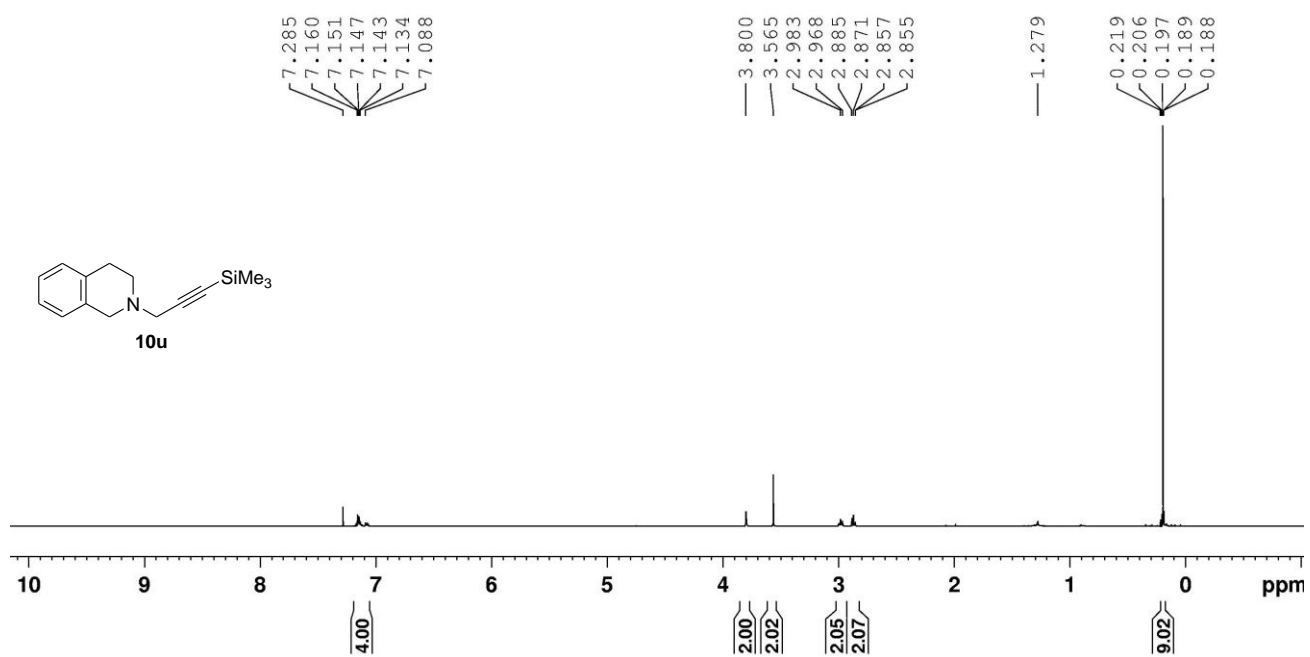
¹H NMR Spectrum of **10t**



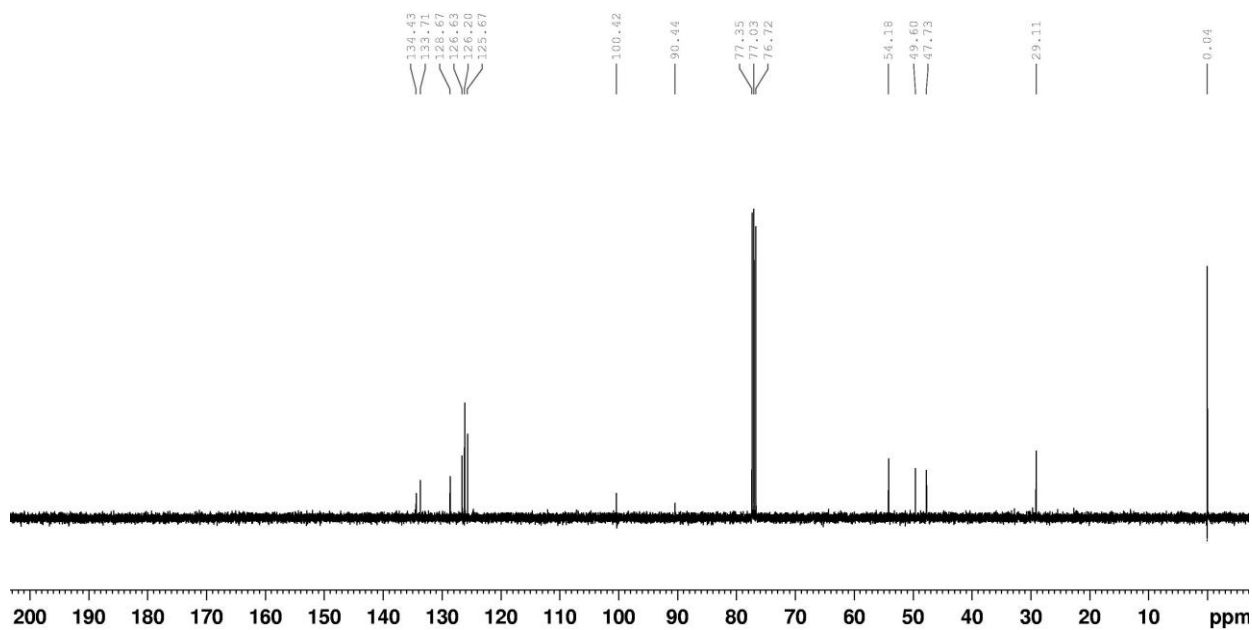
¹³C NMR Spectrum of **10t**



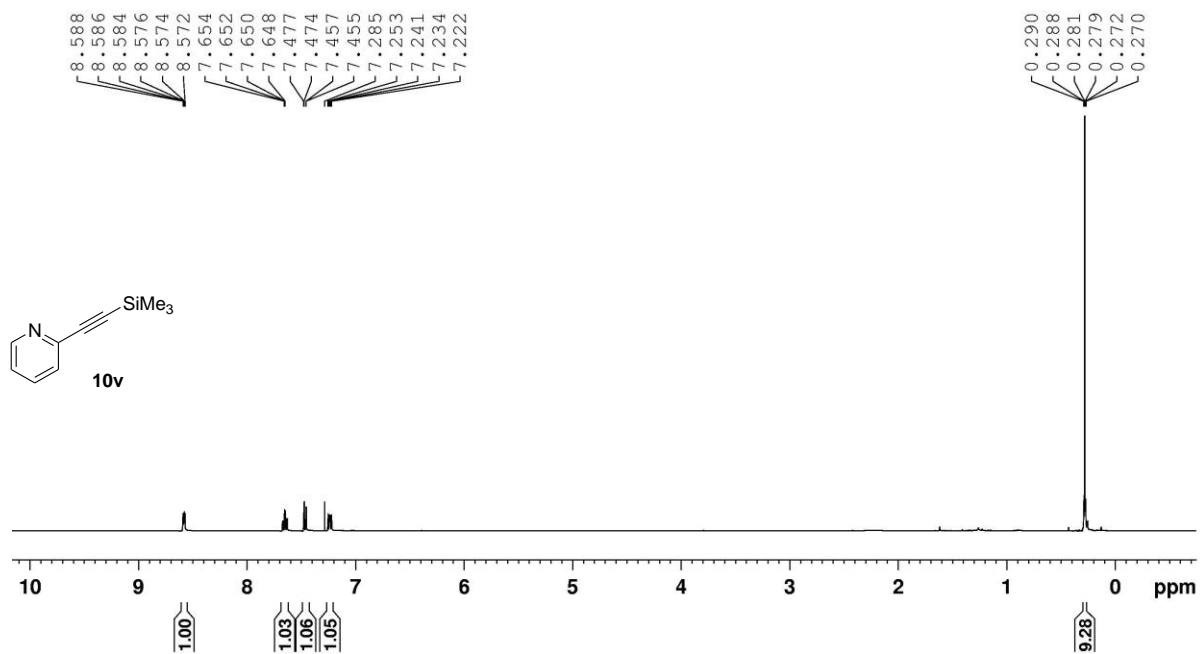
^1H NMR Spectrum of **10u**



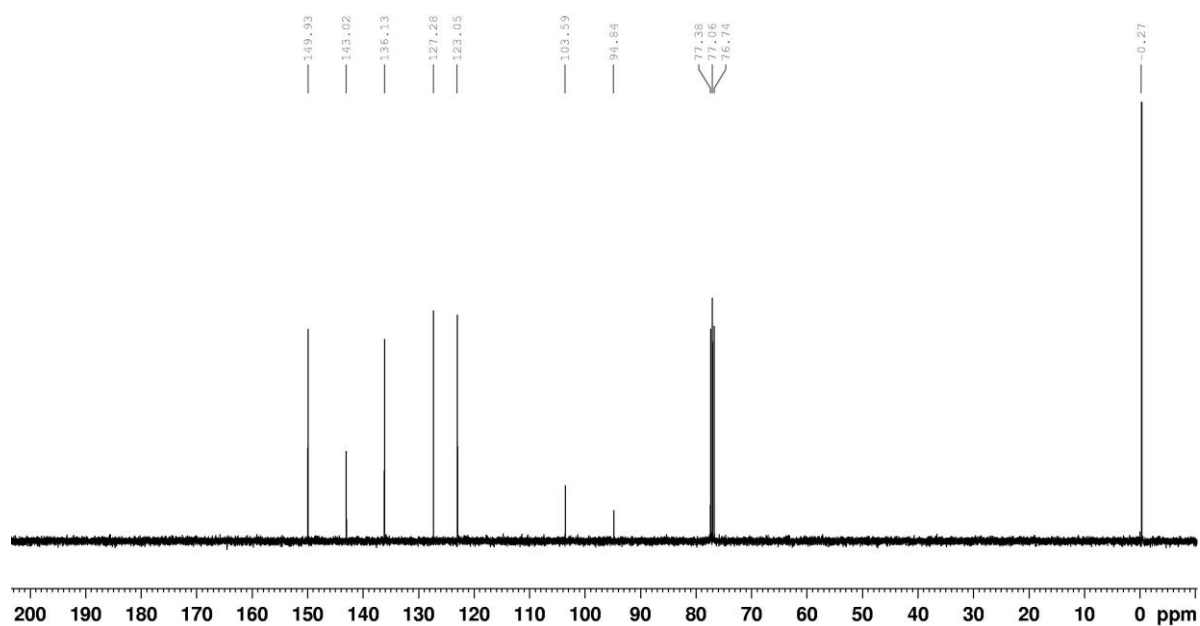
^{13}C NMR Spectrum of **10u**



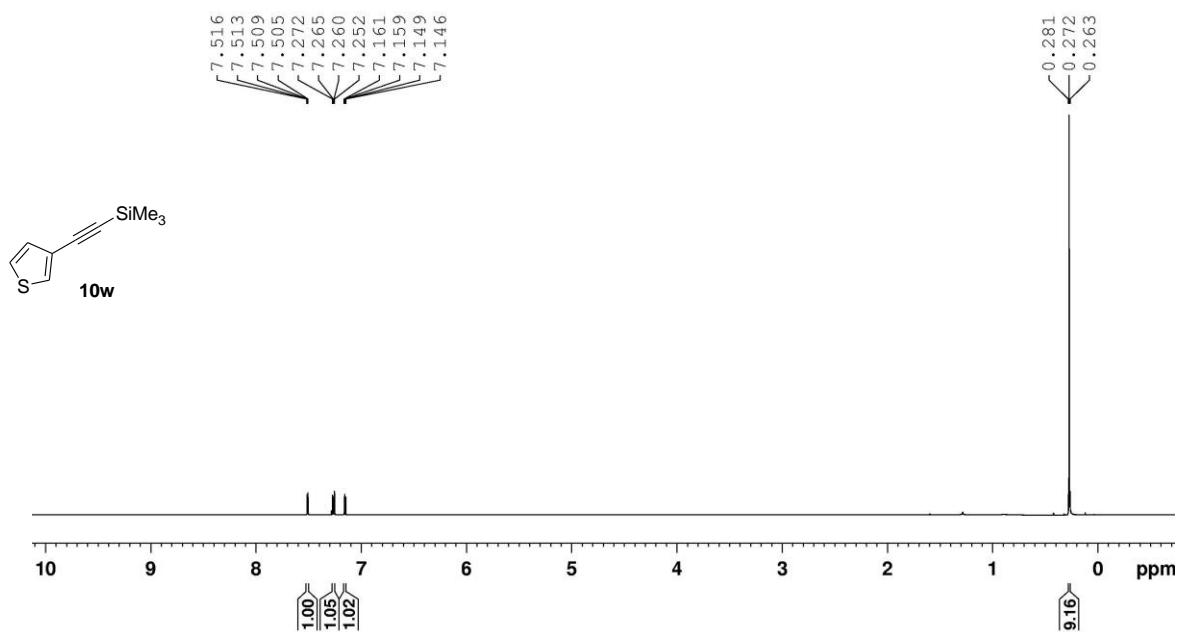
¹H NMR Spectrum of 10v



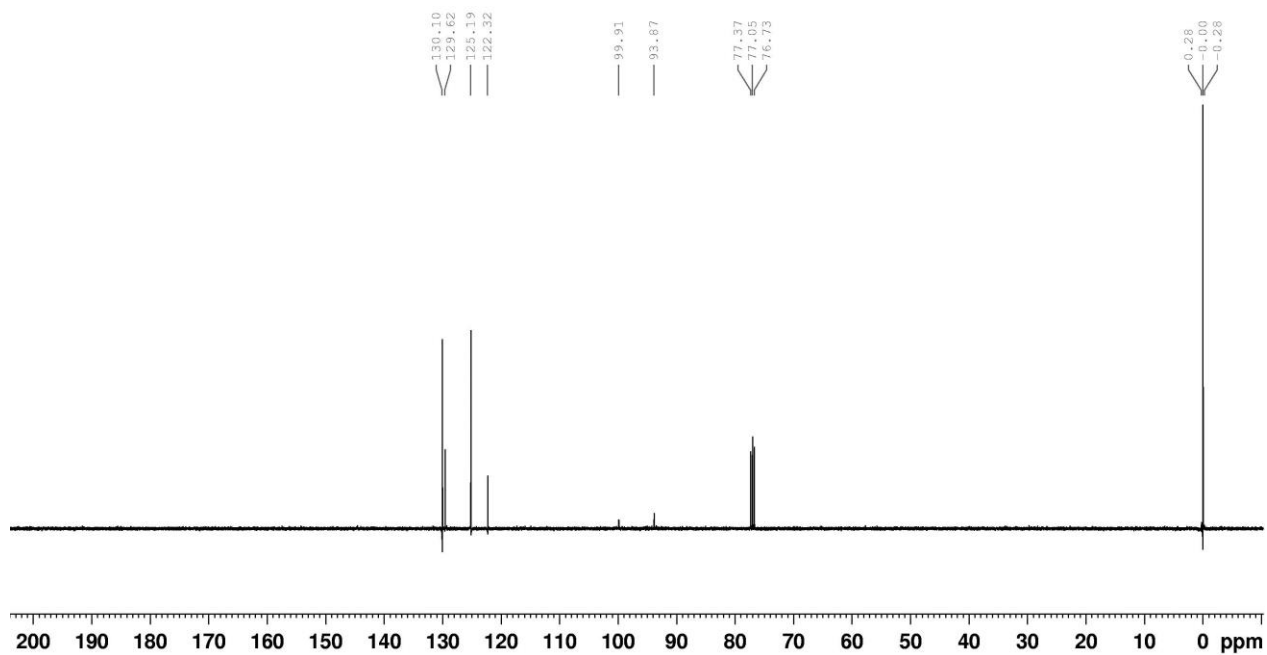
¹³C NMR Spectrum of 10v



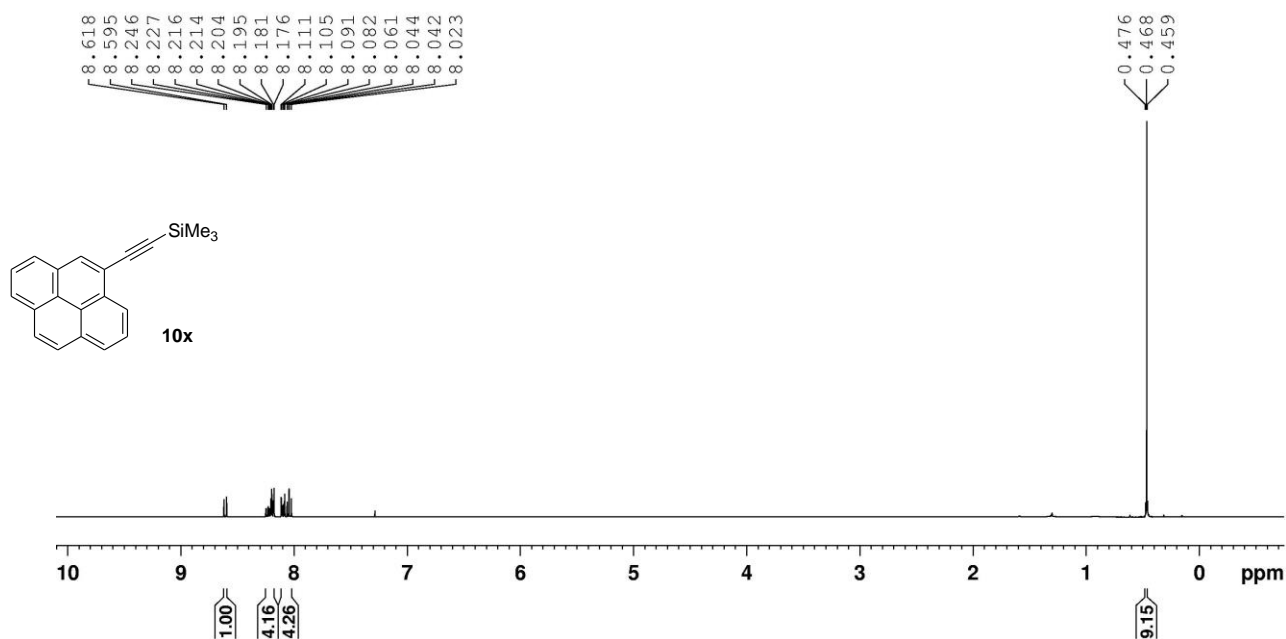
^1H NMR Spectrum of **10w**



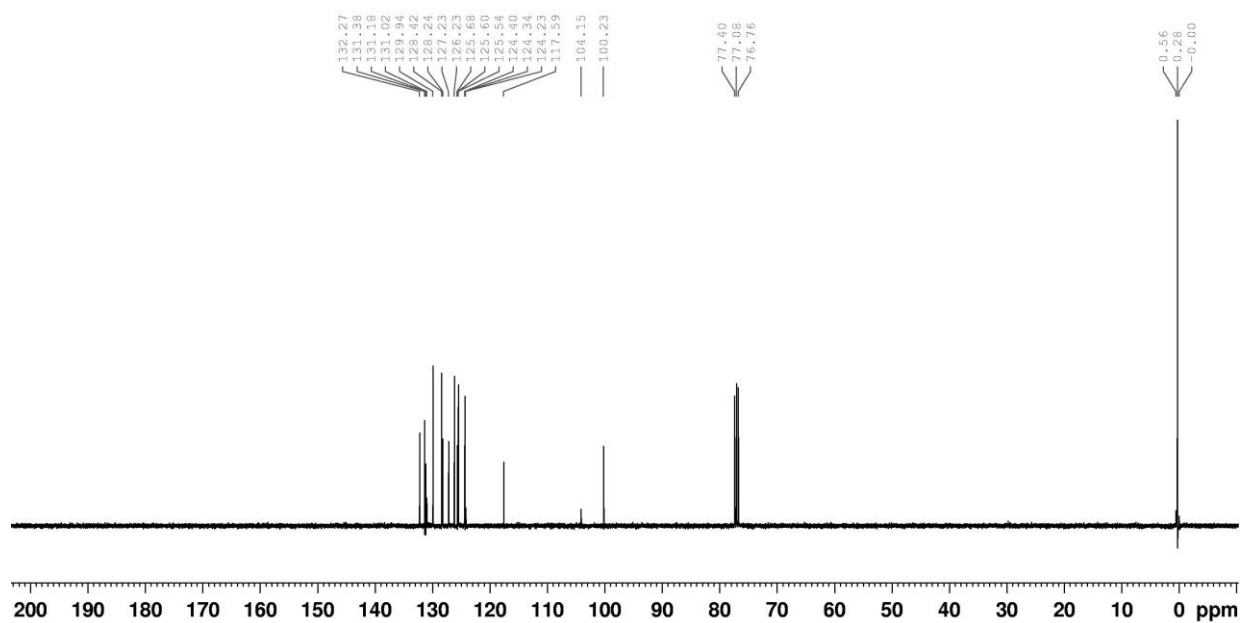
^{13}C NMR Spectrum of **10w**



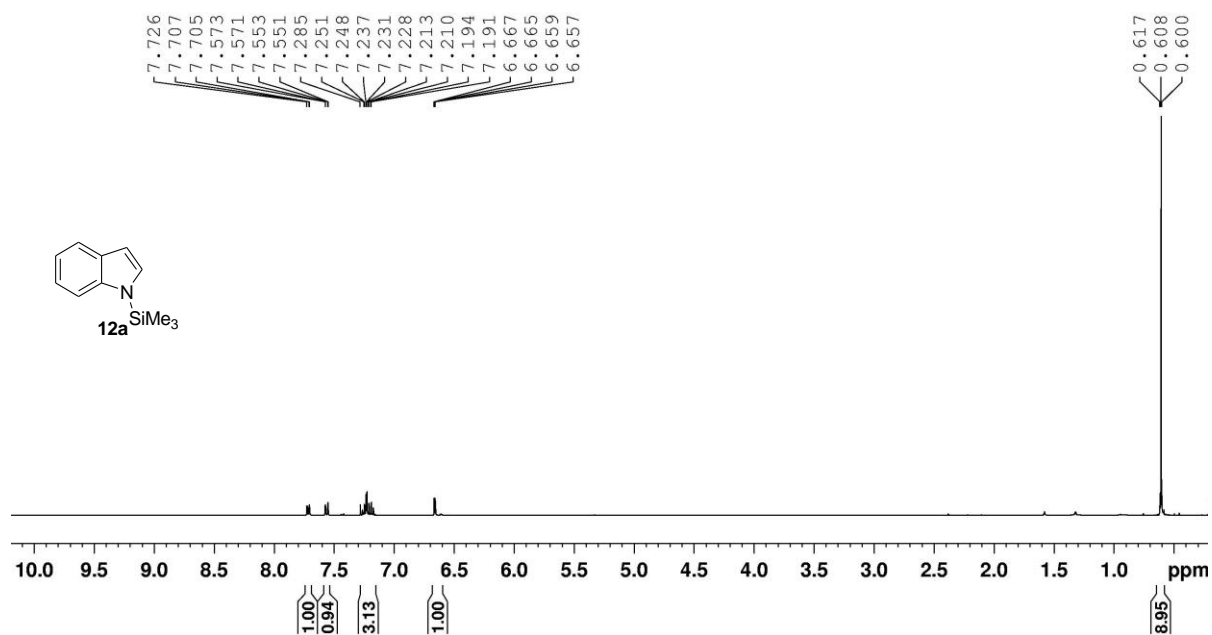
¹H NMR Spectrum of 10x



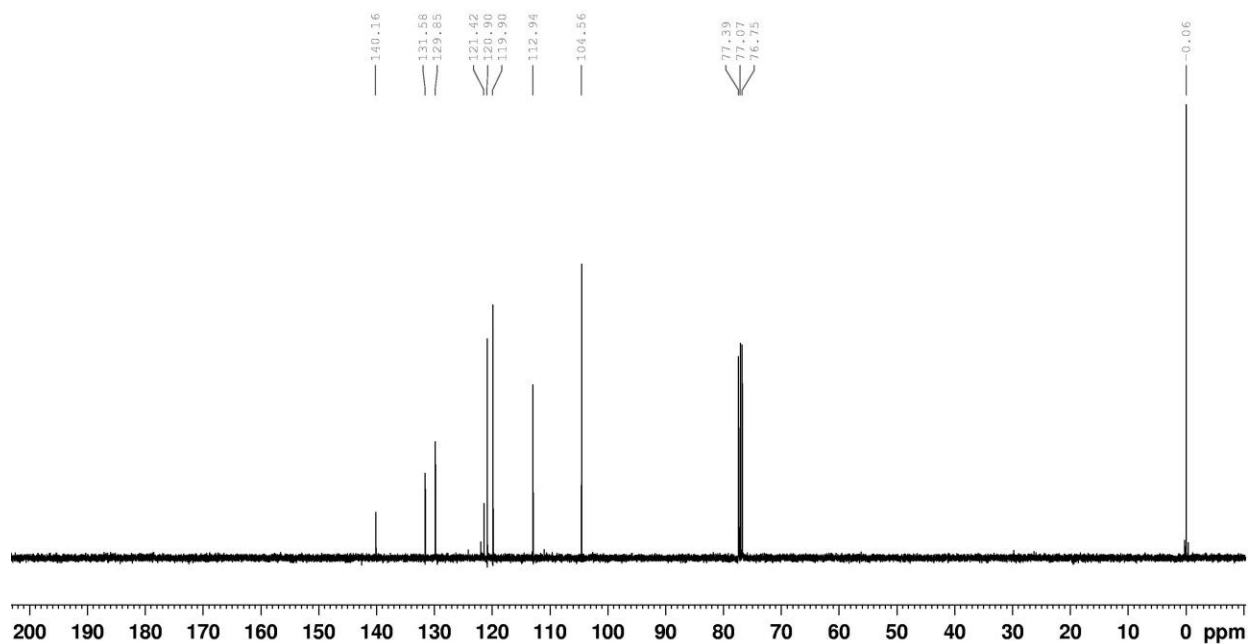
¹³C NMR Spectrum of 10x



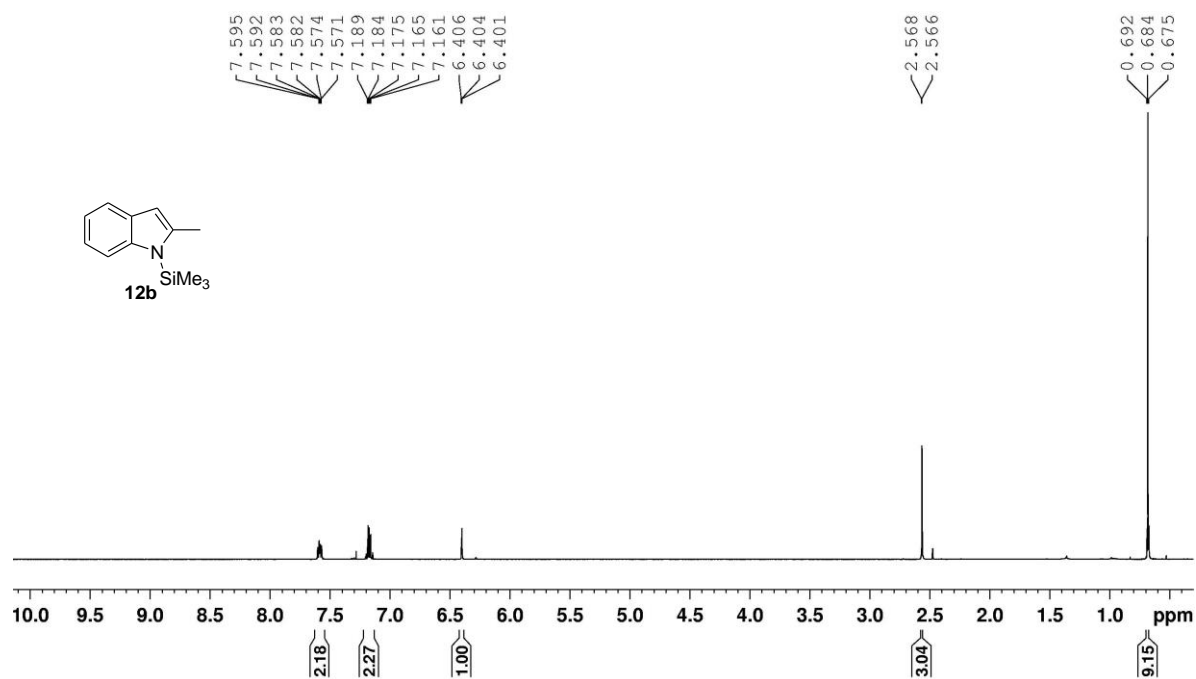
¹H NMR Spectrum of **12a**



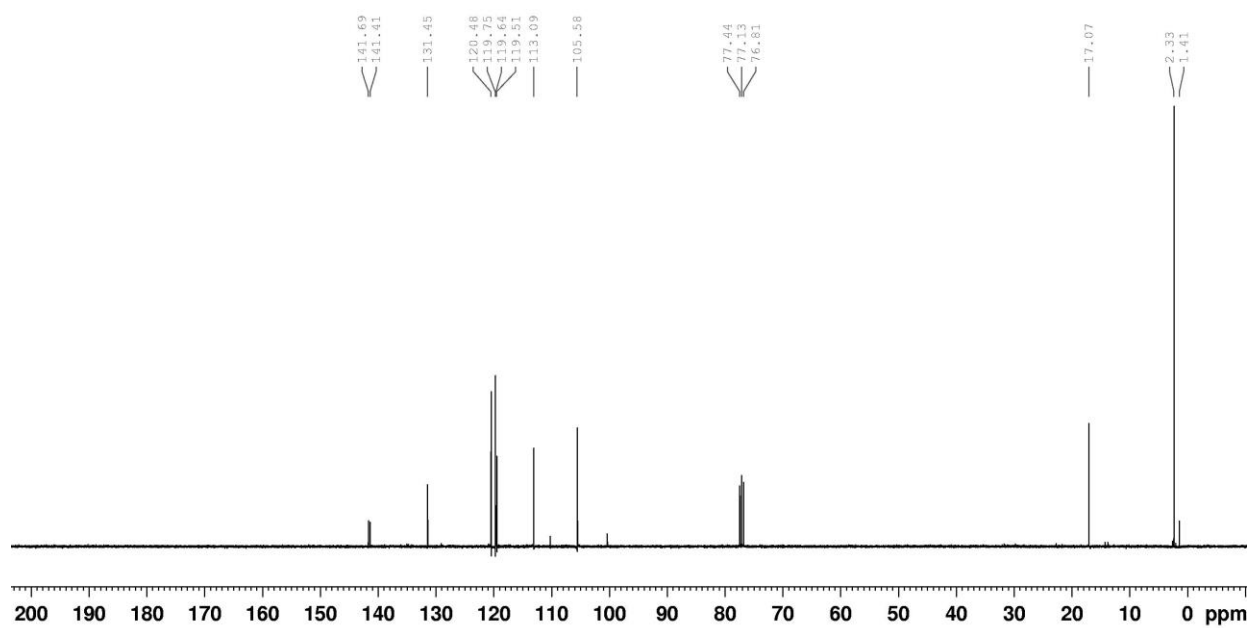
¹³C NMR Spectrum of **12a**



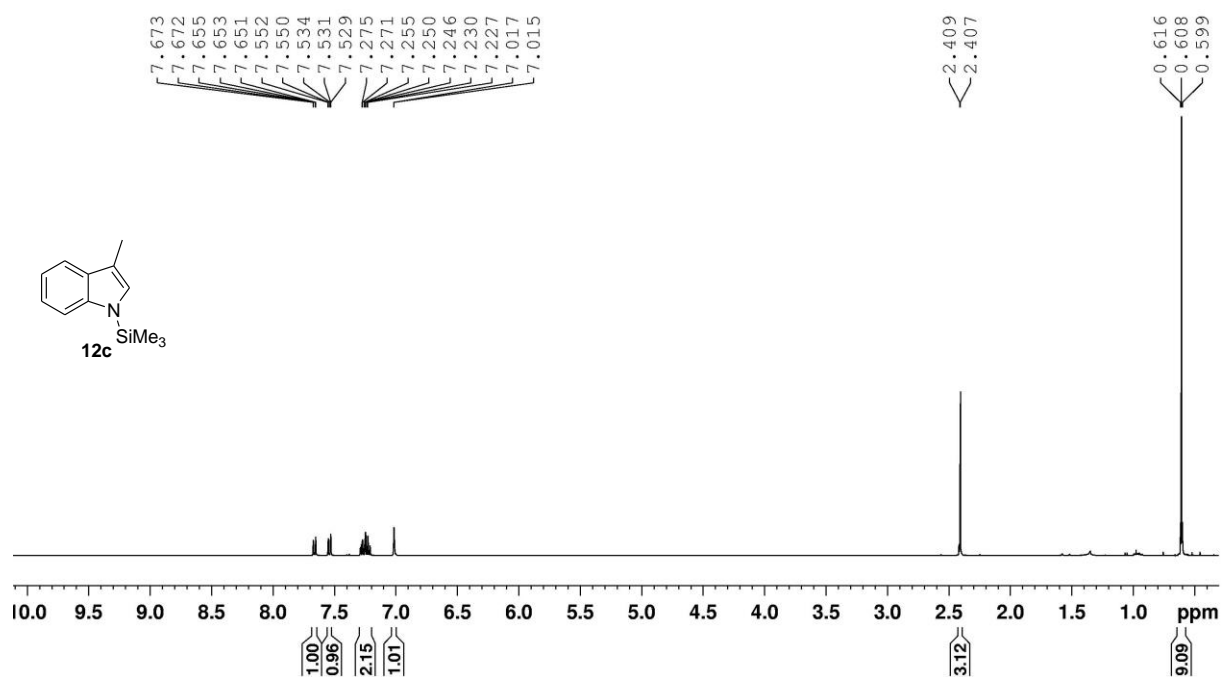
¹H NMR Spectrum of **12b**



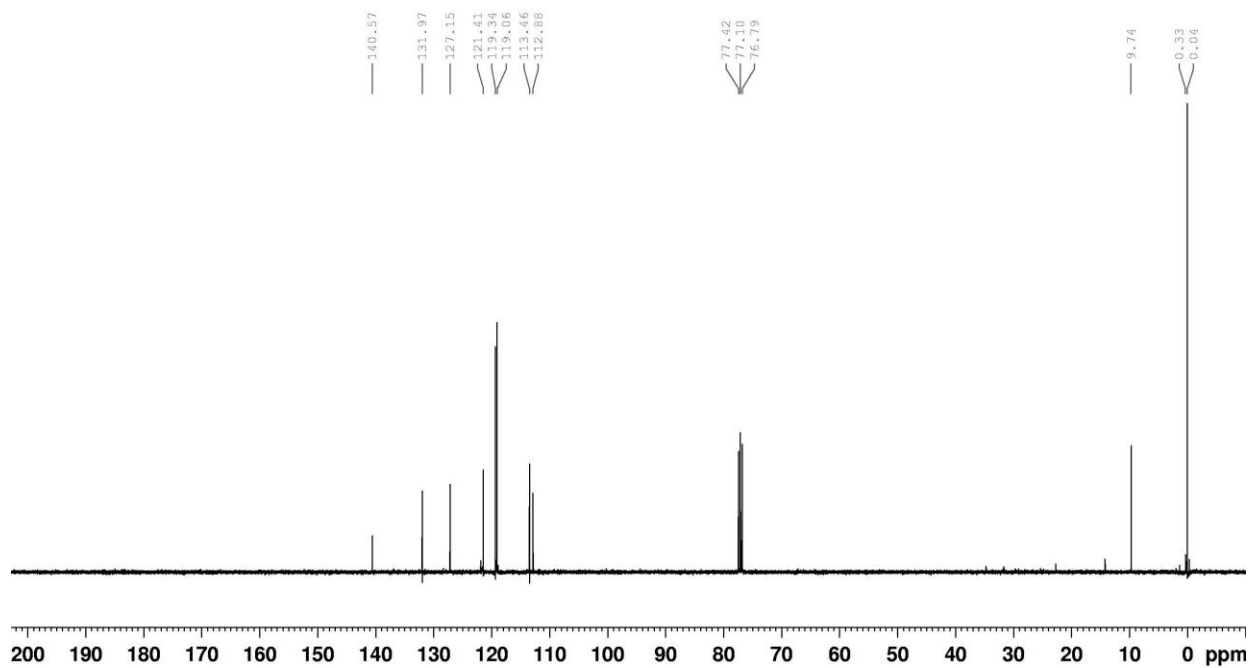
¹³C NMR Spectrum of **12b**



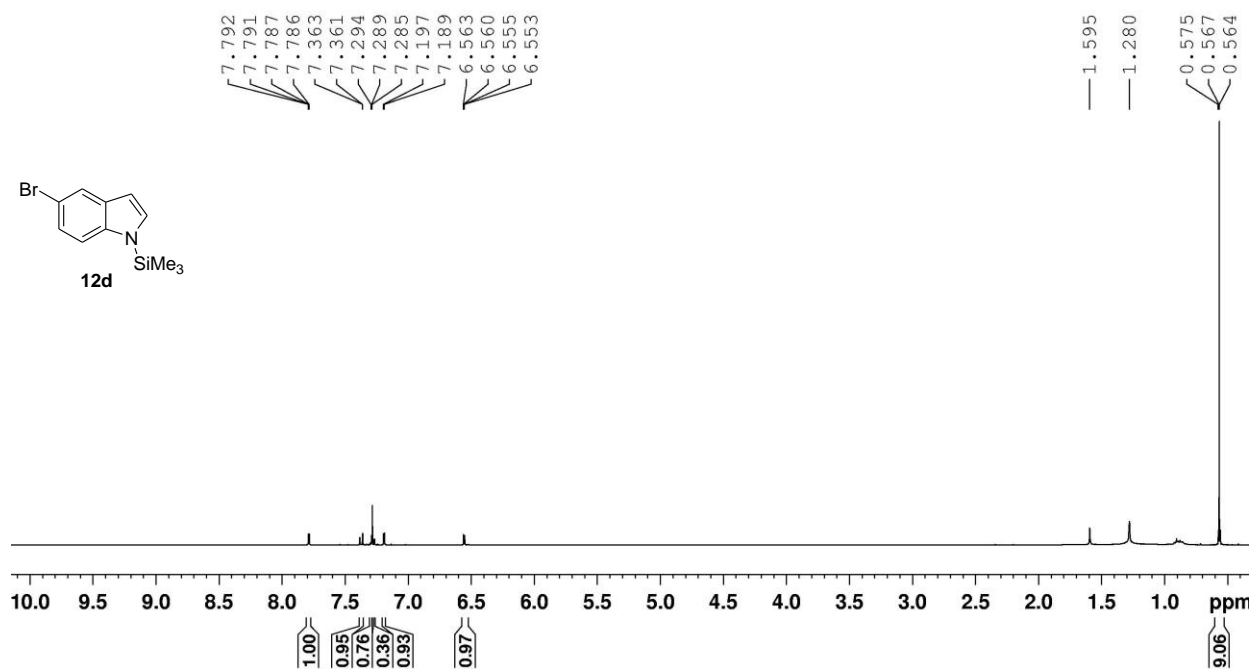
^1H NMR Spectrum of **12c**



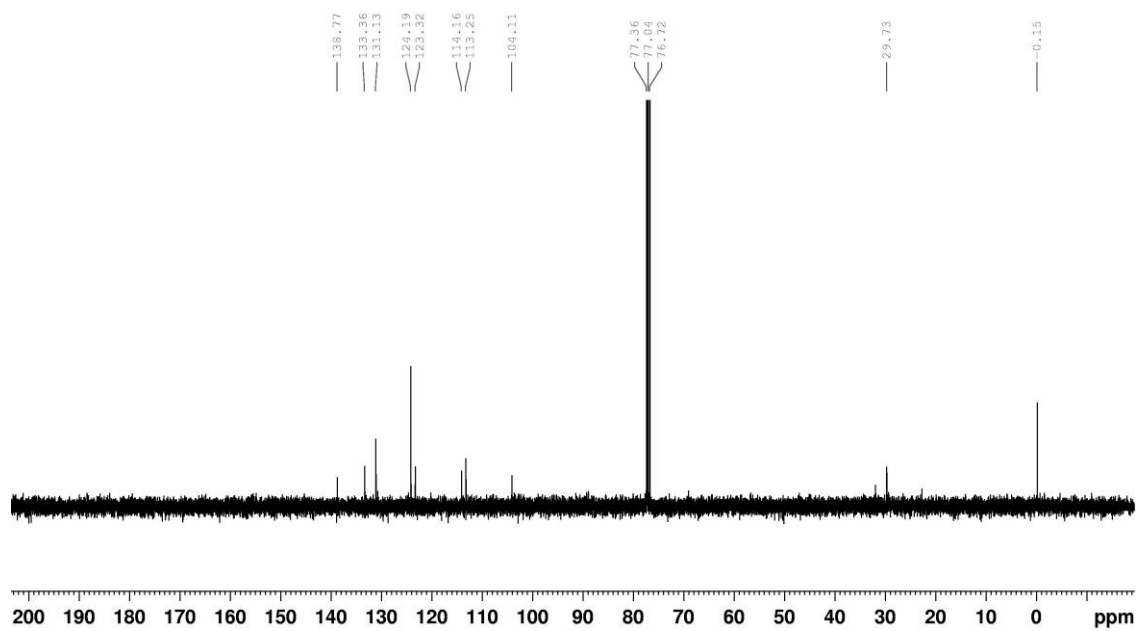
^{13}C NMR Spectrum of **12c**



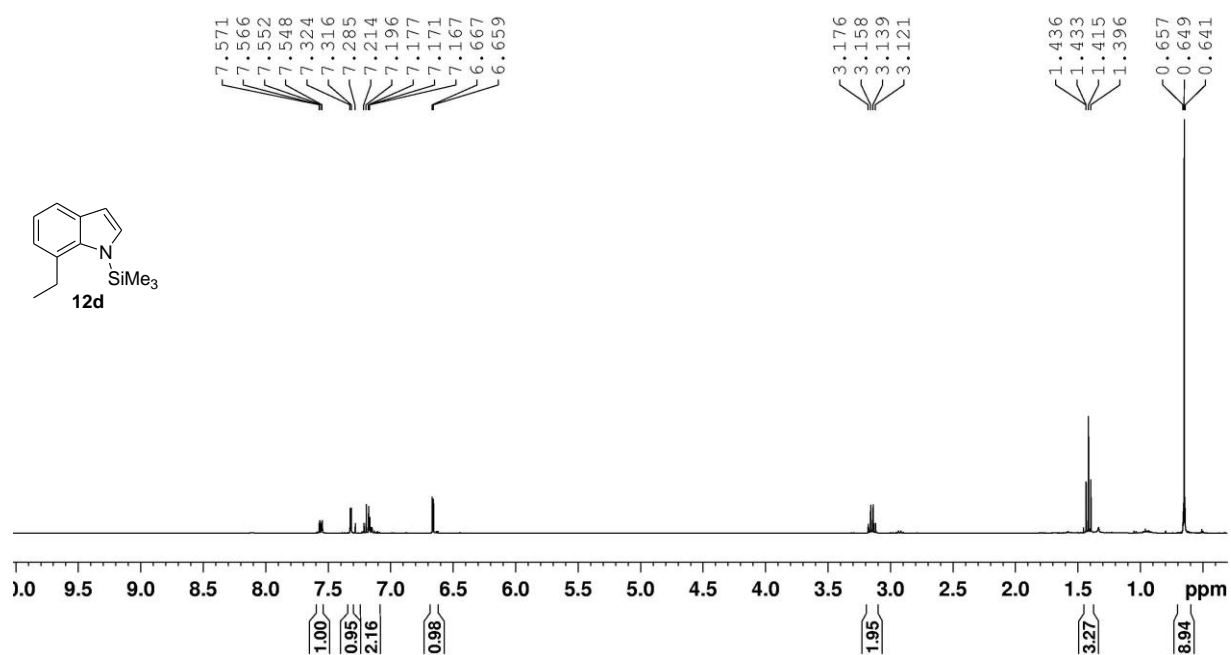
¹H NMR Spectrum of 12d



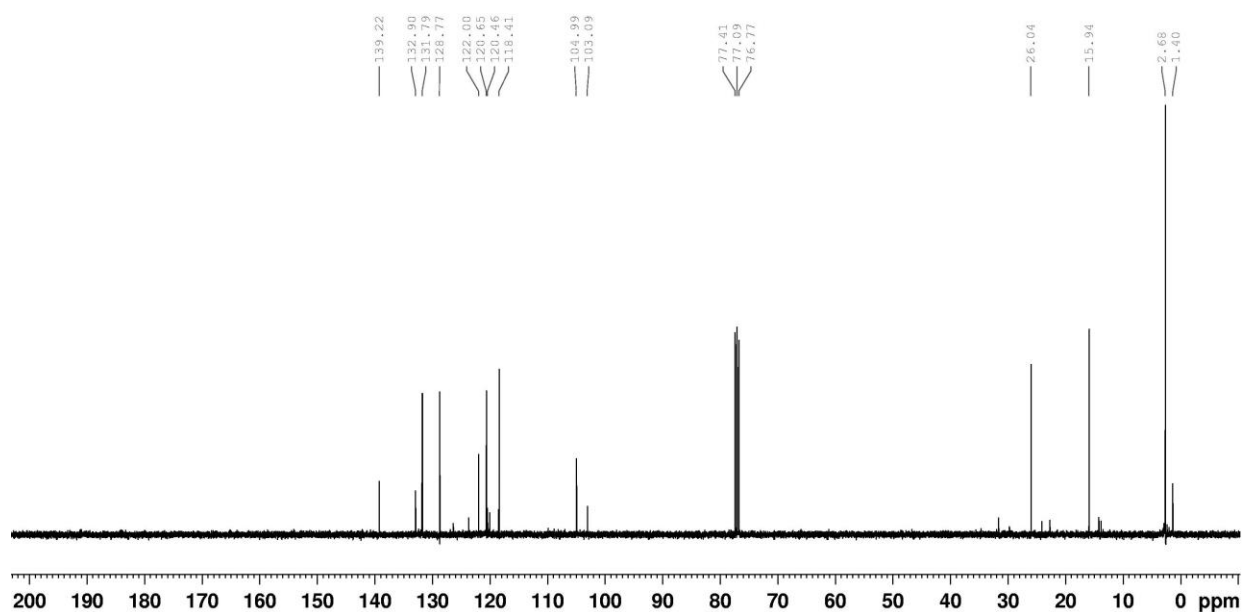
¹³C NMR Spectrum of 12d



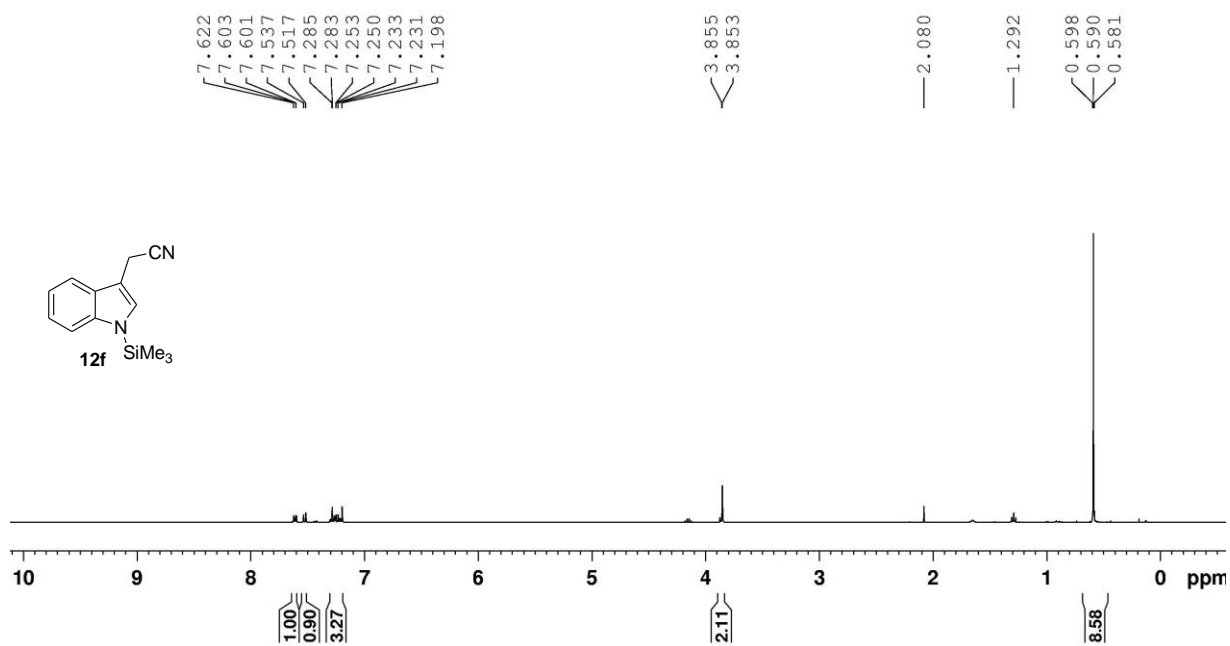
¹H NMR Spectrum of 12e



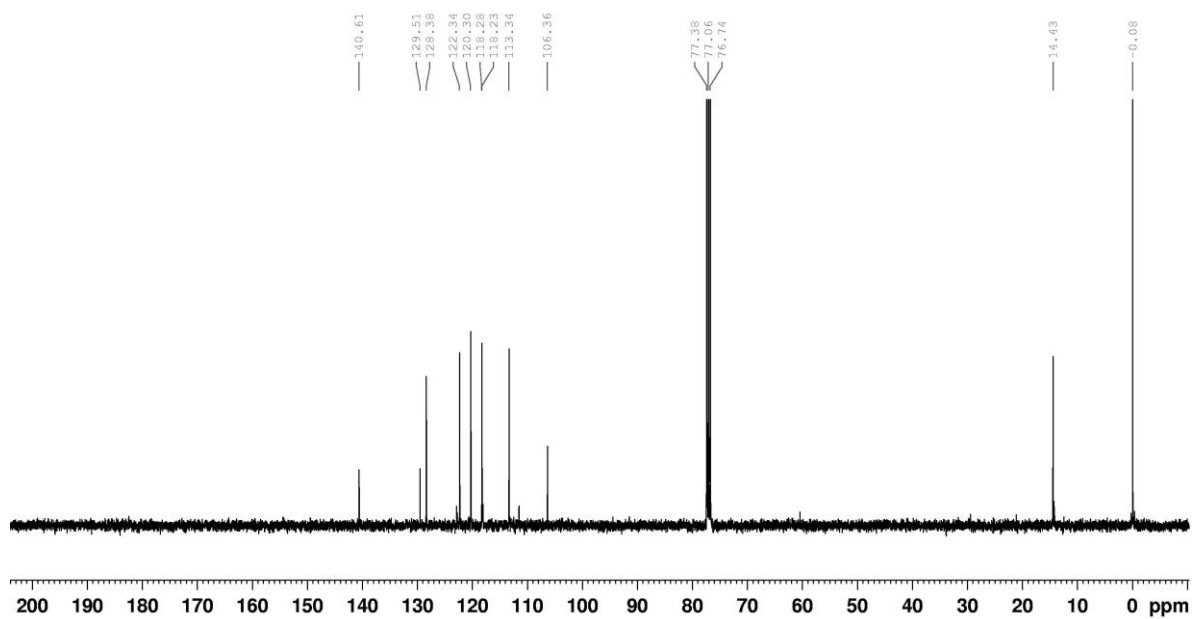
¹³C NMR Spectrum of 12e



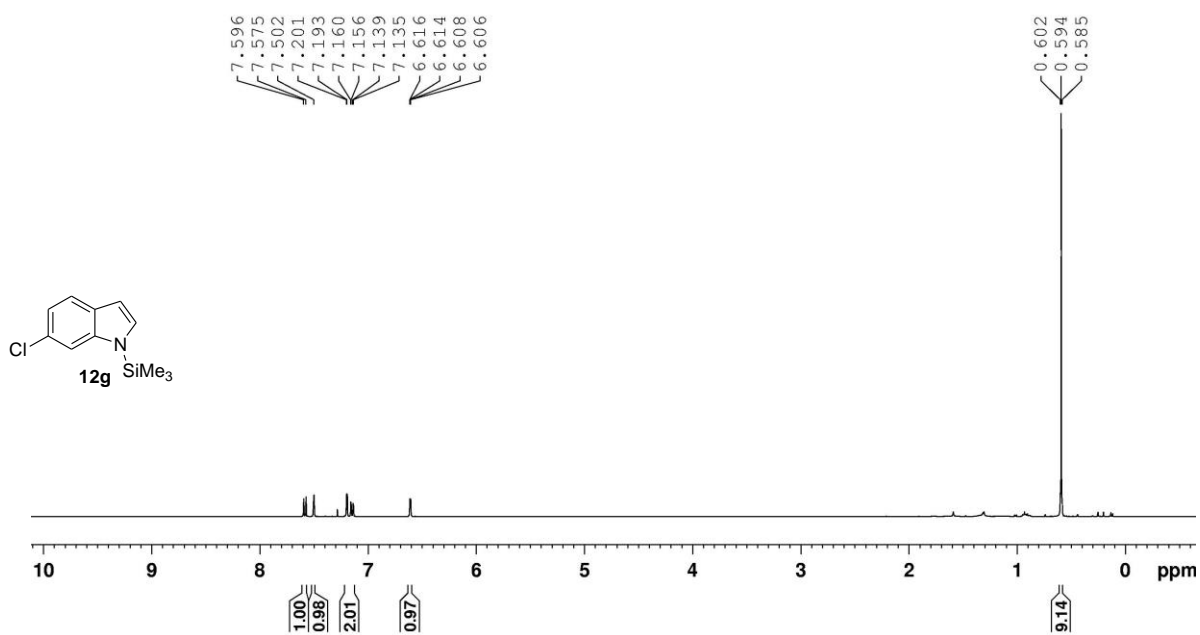
¹H NMR Spectrum of **12f**



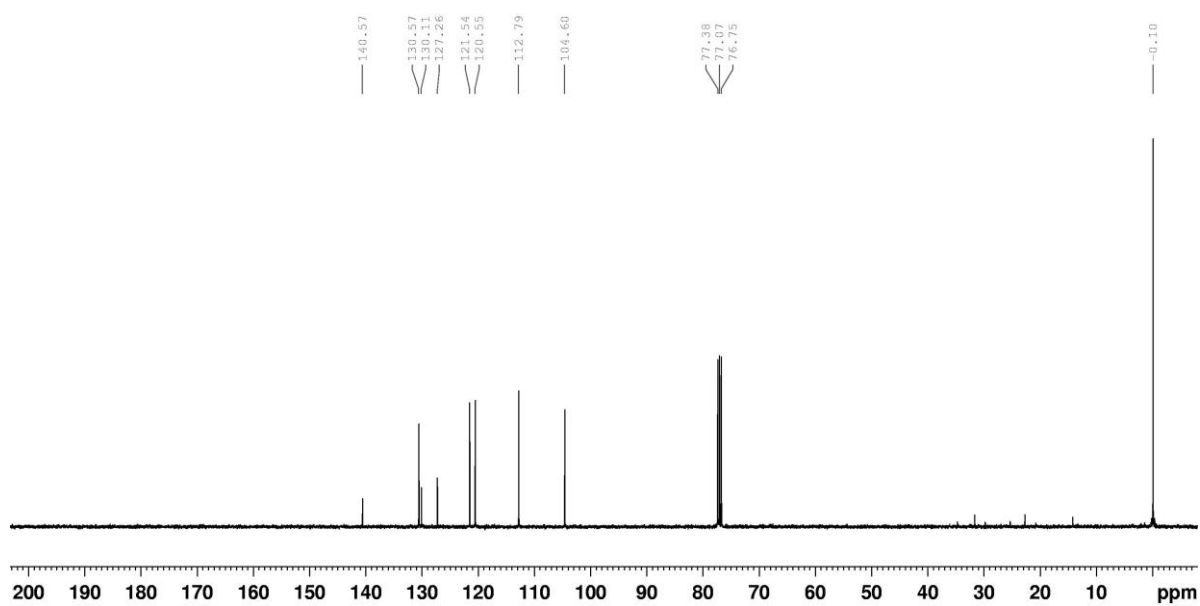
¹³C NMR Spectrum of **12f**



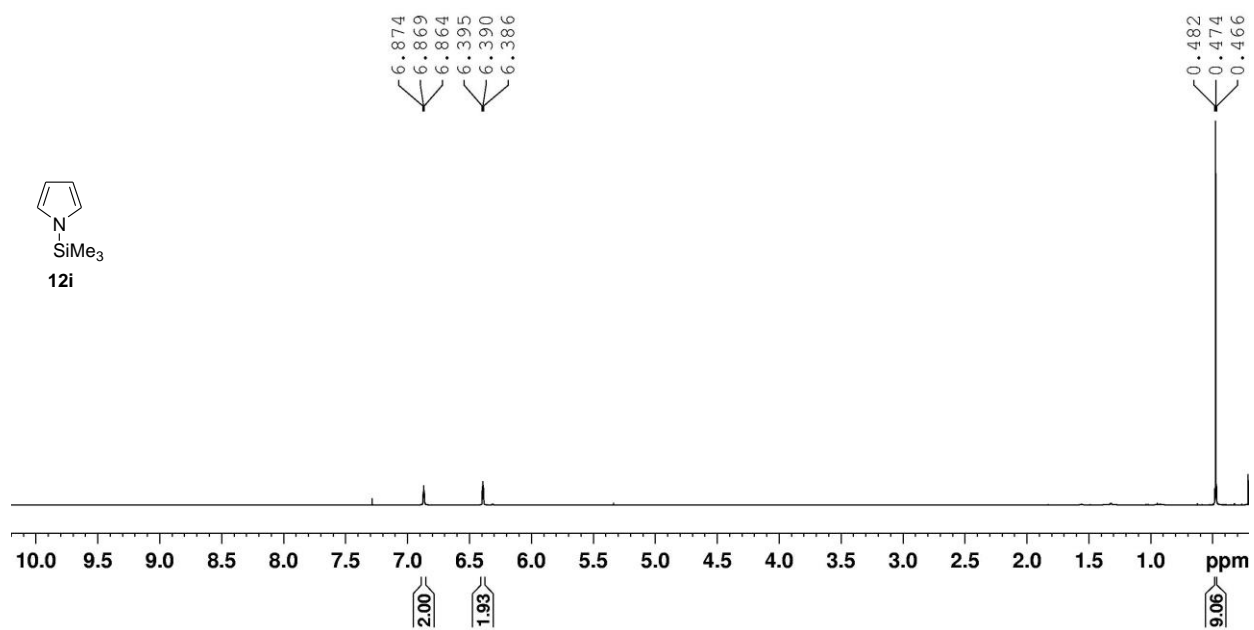
¹H NMR Spectrum of **12g**



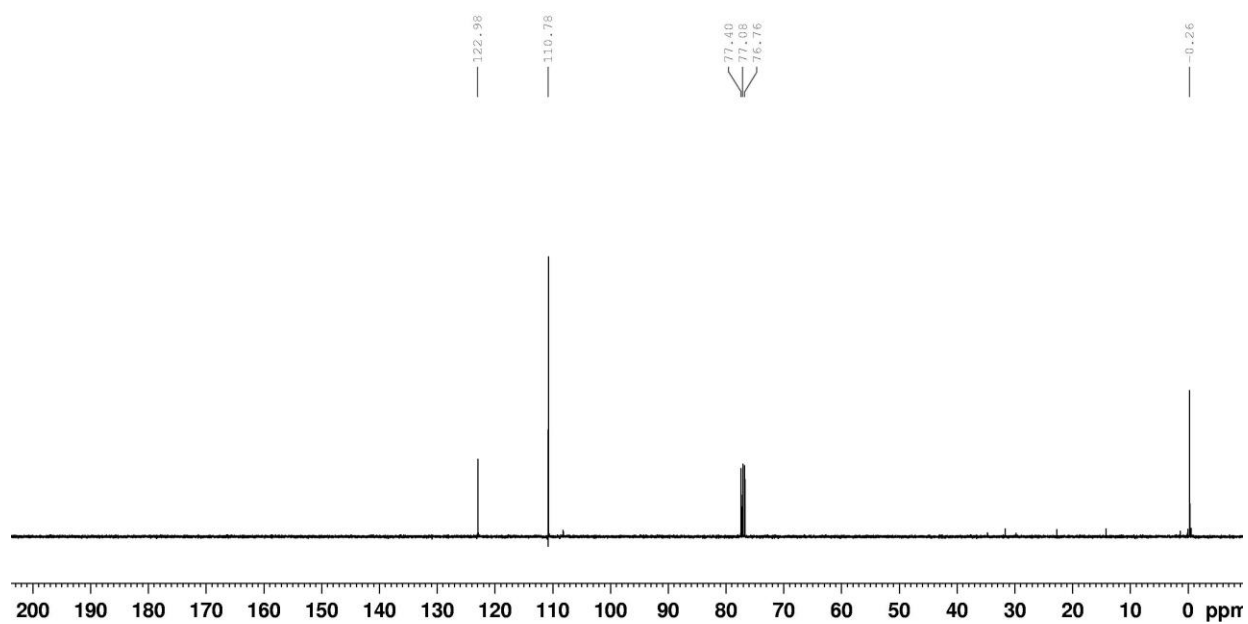
¹³C NMR Spectrum of **12g**



¹H NMR Spectrum of **12i**



¹³C NMR Spectrum of **12i**



^{19}F Spectrum the reaction mixture (entry 4 in Table 1)

