Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Synthesis of topologically constrained naphthalimide appended Palladium(II)-N-Heterocyclic carbene complexes - Insights into additive controlled product selectivity

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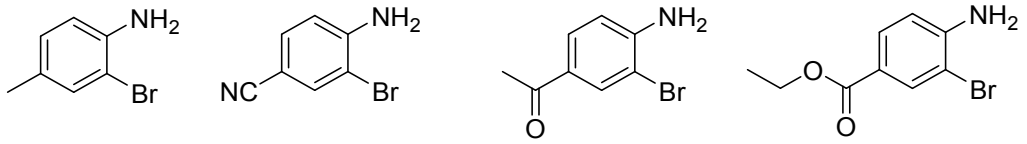
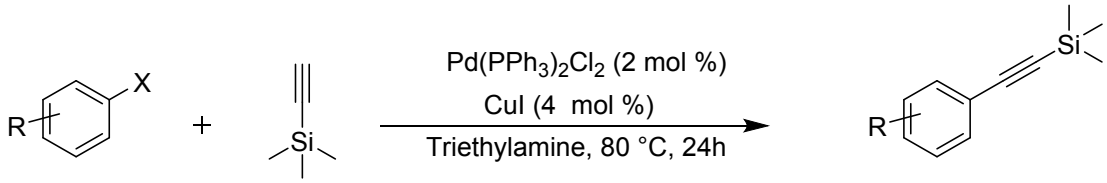
1. General synthetic procedure for *o*-bromoanilines and silyl protected acetylenes

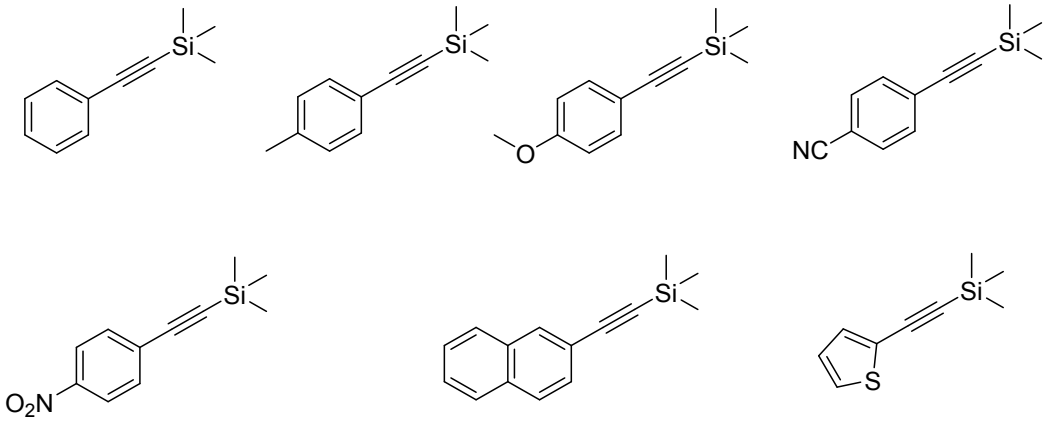
o-bromoanilines are synthesized following the reported literature[1] and scheme shows the the representative examples of *o*-haloanilines used in the study.



1.1 Typical procedure for the synthesis of silyl protected acetylenes:[2]



To a solution of aryl halide (1 equiv), copper iodide (4 mol %) and $Pd(PPh_3)_2Cl_2$ (2 mol %) in triethylamine (5 mL) was added trimethylsilylacetylene (1.2 equiv) dropwise under inert atmosphere. The mixture was heated under inert atmosphere at 80 °C for 24 h. After completion of reaction, it was filtered and the filtrate was treated with water and extracted with DCM (3 x 15 mL). The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4 and concentrated under vacuum to yield the crude product. The crude product was purified by column chromatography (100 - 200 silica mesh) using hexane/ethyl acetate as the eluent to give silyl protected acetylene derivatives.

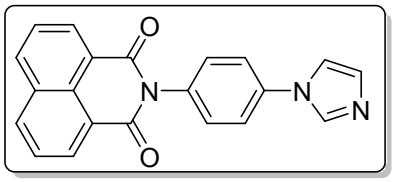


2. Typical Procedure for the Synthesis of Precursors (3, 4 & 10)

To a stirred suspension of 1,8-naphthalic anhydride (1 equiv) and amine derivatives of heterocycles (**1**, **2** & **9**) (1 equiv) in ethanol, triethylamine (2 equiv) was charged. After stirring for 24 h at 90 °C, the mass was cooled to room temperature and the solids formed were filtered and washed with a minimum quantity of ethanol to washout the unwanted impurities. The solids were dried under vacuum and used without further purification.

Compound **3**:

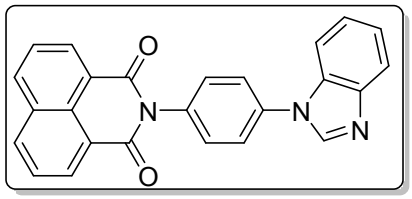
Yield: 82%; Light yellow coloured solid. R_f=0.45 (MeOH/DCM 3:97). Purified by column chromatography on silica gel (DCM/Methanol = 98/2).



^{1}H NMR (400 MHz, DMSO-d$_6$) δ 8.54 – 8.52 (d, *J* = 7.72 Hz, 4H), 8.37 (s, 1H), 7.95 – 7.91 (t, *J* = 7.76 Hz, 2H), 7.86 (s, 1H), 7.83 (d, *J* = 8.52 Hz, 2H), 7.59 (d, *J* = 8.48 Hz, 2H), 7.17 (s, 1H); **^{13}C NMR (100 MHz, DMSO-d$_6$)** 164.21, 137.08, 136.24, 135.03, 134.99, 131.94, 131.26, 131.14, 130.49, 128.36, 127.74, 123.09, 121.26, 118.67; **HRMS** [M+H$^+$] Calcd. for $C_{21}H_{14}N_3O_2$: 340.1086, found: 340.1092.

Compound **4**:

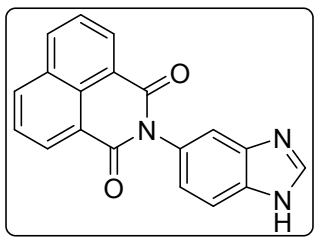
Yield: 71%; White coloured solids. TLC: R_f=0.40 (MeOH/DCM 3:97). Purified by column chromatography on silica gel (DCM/Methanol = 97/3).



^{1}H NMR (400 MHz, DMSO-d$_6$) δ 8.75 (s, 1H), 8.61 – 8.58 (dd, *J* = 2.24, 7.2 Hz, 4H), 8.00 – 7.96 (t, *J* = 7.76 Hz, 2H), 7.94 (d, *J* = 8.64 Hz, 2H), 7.89 – 7.87 (dd, *J* = 1.64, 7.2 Hz, 1H), 7.81 – 7.79 (dd, *J* = 1.12, 6.88 Hz, 1H), 7.76 – 7.74 (m, 2H), 7.46 – 7.38 (m, 2H); **^{13}C NMR (100 MHz, DMSO-d$_6$)** 164.25, 144.41, 143.90, 136.22, 135.75, 135.01, 133.43, 131.96, 131.42, 131.27, 128.39, 127.74, 124.37, 124.10, 123.11, 123.07, 120.51, 111.26; **HRMS** [M+H$^+$] Calcd. for $C_{25}H_{16}N_3O_2$: 390.1243, found: 390.1237.

Compound **10**:

Yield: 71%; Yellow coloured solid. TLC R_f=0.40 (MeOH/DCM 3:97). Purified by column chromatography on silica gel (DCM/Methanol = 97/3).



^{1}H NMR (400 MHz, DMSO-d$_6$) δ 8.51 – 8.48 (t, *J* = 6.64 Hz, 4H), 8.37 (s, 1H), 7.91 – 7.87 (t, *J* = 7.74 Hz, 2H), 7.72 (d, *J* = 8.44 Hz, 1H), 7.67 (s, 1H), 7.22 – 7.19 (dd, *J* = 1.68, 8.4 Hz, 1H); **^{13}C NMR (100**

MHz, DMSO-d_6) 164.51, 143.48, 138.74, 137.98, 134.77, 131.89, 131.15, 130.59, 128.31, 127.66, 123.48, 123.22, 116.71, 115.54; **HRMS** [M+H$^+$] Calcd. for $C_{19}H_{12}N_3O_2$: 314.0930, found: 314.0931.

3. General Procedure for the regioselective heteroannulation of *o*-haloanilines with internal alkynes

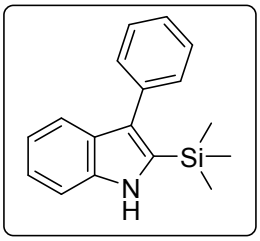
A flame dried reaction tube was charged with *o*-haloaniline (1 mmol), Pd-NHC (0.04 mmol), TBAB or LiBr (2.2 mmol or 1 mmol respectively), anhydrous K_2CO_3 (2.0 mmol), internal alkyne (2.0 mmol) and 1,4-dioxane (2 mL). The tube was capped and stirred at 120 °C for 8 h. On completion of the reaction, the mixture was cooled to room temperature, diluted with 15 mL of ethyl acetate and filtered through a short plug of celite. The organic layers were washed with water, dried over sodium sulphate and concentrated in *vacuo*. The crude mixture was then purified by column chromatography to afford the desired products.

3.1 General Procedure for the synthesis of 2-trimethylsilyl-3-aryl indoles (23)

The general procedure mentioned above **3** was applied with *o*-haloaniline (1 mmol), **16** (0.04 mmol), LiBr (1 mmol), anhydrous K_2CO_3 (2 mmol), TMS protected alkynes (2 mmol) and 1,4-dioxane (2 mL) to yield the desired products in excellent yields.

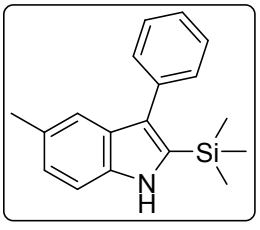
3-Phenyl-2-(trimethylsilyl)-1*H*-indole (23a)

White solid; 188 mg (71% yield). TLC R_f=0.70 (EtOAc/Hexane 1:49). Purified by column chromatography on silica gel (EtOAc/Hexane = 1/49).



^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (br, 1H), 7.56 (d, *J* = 7.96 Hz, 1H), 7.48 - 7.40 (m, 5H), 7.36 - 7.32 (m, 1H), 7.23 - 7.19 (m, 1H), 7.11 - 7.07 (m, 1H), 0.22 (s, 9H); **^{13}C NMR (100 MHz, $CDCl_3$)** 137.98, 136.65, 134.19, 130.49, 128.72, 128.19, 127.93, 126.69, 122.82, 120.01, 119.69, 110.90, -0.27. The data obtained are in accordance with those reported in the literature.[3]

5-Methyl-3-phenyl-2-(trimethylsilyl)-1*H*-indole (23b)



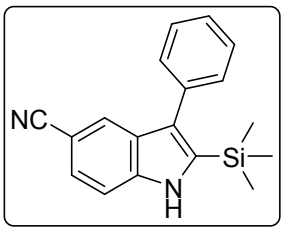
Light brown solid; 204 mg (73% yield). TLC R_f=0.65 (EtOAc/Hexane 1:49). Purified by column chromatography on silica gel (EtOAc/Hexane = 1/49).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (br, 1H), 7.47 - 7.40 (m, 4H), 7.36 - 7.30 (m, 3H), 7.05 -7.03 (dd, *J* = 1.28, 8.16 Hz, 1H), 2.40 (s, 3H), 0.20 (s,

9H); **^{13}C NMR (100 MHz, $CDCl_3$)** 136.86, 136.38, 134.29, 130.53, 129.32, 129.02, 128.85, 128.17, 127.66, 127.44, 126.61, 124.52, 119.12, 110.54, 21.57, -0.26; **HRMS** [M+H$^+$] Calcd. for $C_{18}H_{22}NSi$: 280.1522, found: 280.1520.

3-Phenyl-2-(trimethylsilyl)-1*H*-indole-5-carbonitrile (23c)

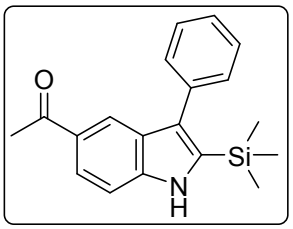
White solid; 176 mg (61 % yield). TLC R_f=0.35 (EtOAc/Hexane 3:47). Purified by column chromatography on silica gel (EtOAc/Hexane = 4/46).



^{1}H NMR (400 MHz, $CDCl_3$) δ 8.45 (br, 1H), 7.88 (s, 1H), 7.48 – 7.44 (m, 4H), 7.41 – 7.39 (m, 3H), 0.24 (s, 9H); **^{13}C NMR (100 MHz, $CDCl_3$)** 139.46, 137.14, 135.07, 130.34, 128.72, 128.51, 127.45, 125.66, 125.46, 120.91, 111.83, 103.05, -0.45; **HRMS** [M+H$^+$] Calcd. for $C_{18}H_{19}N_2Si$: 291.1318, found: 291.1323.

1-(3-Phenyl-2-(trimethylsilyl)-1*H*-indol-5-yl)ethanone (23d)

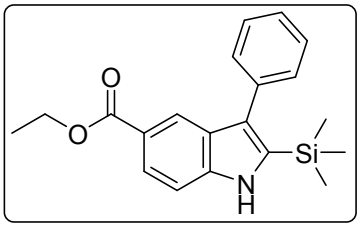
Light yellow solid; 200 mg (65% yield). TLC R_f=0.40 (EtOAc/Hexane 4:46). Purified by column chromatography on silica gel (EtOAc/Hexane = 3/47).



^{1}H NMR (400 MHz, $CDCl_3$) δ 8.36 (br, 1H), 8.17 (m, 1H), 7.92 – 7.89 (dd, J = 1.64, 8.64 Hz, 1H), 7.48 – 7.43 (m, 5H), 7.41 – 7.37 (m, 1H), 2.60 (s, 3H), 0.23 (s, 9H); **^{13}C NMR (100 MHz, $CDCl_3$)** 198.47, 140.48, 136.26, 135.75, 130.48, 130.31, 129.57, 128.47, 128.43, 127.20, 123.06, 122.07, 110.85, 26.80, -0.39; **HRMS** [M+H$^+$] Calcd. for $C_{19}H_{22}NOSi$: 308.1471, found: 308.1468.

Ethyl 3-phenyl-2-(trimethylsilyl)-1*H*-indole-5-carboxylate (23e)

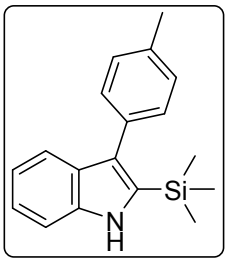
White solid; 202 mg (60% yield). TLC R_f=0.40 (EtOAc/Hexane 5:45). Purified by column chromatography on silica gel (EtOAc/Hexane = 4/46).



^{1}H NMR (400 MHz, $CDCl_3$) δ 8.32 (br, 1H), 8.29 (s, 1H), 7.95 – 7.92 (dd, J = 1.56, 8.6 Hz, 1H), 7.46 – 7.45 (m, 4H), 7.43 – 7.41 (m, 1H), 7.40 – 7.37 (m, 1H), 4.38 – 4.33 (q, J = 7.12 Hz, 2H), 1.39 – 1.35 (t, J = 7.08 Hz, 3H), 0.22 (s, 9H); **^{13}C NMR (100 MHz, $CDCl_3$)** 167.86, 140.40, 135.90, 135.85, 130.53, 129.28, 128.50, 128.35, 127.08, 124.14, 122.79, 122.55, 110.53, 60.70, 14.60, -0.37; **HRMS** [M+H$^+$] Calcd. for $C_{20}H_{24}NO_2Si$: 338.1576, found: 338.1580.

3-(*p*-tolyl)-2-(trimethylsilyl)-1*H*-indole (23f)

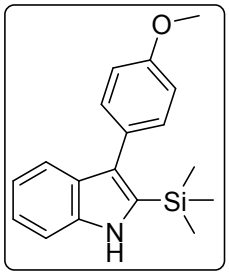
White solid; 198 mg (71% yield). TLC R_f=0.65 (EtOAc/Hexane 1:49). Purified by column chromatography on silica gel (EtOAc/Hexane = 1/49).



^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (br, 1H), 7.56 (d, *J* = 7.96, 1H), 7.42 (d, *J* = 8.16, 1H), 7.36 - 7.34 (m, 2H), 7.24 - 7.19 (m, 3H), 7.11 - 7.06 (m, 1H), 2.42 (s, 3H), 0.22 (s, 9H); **^{13}C NMR (100 MHz, $CDCl_3$)** 137.99, 136.22, 134.00, 133.56, 130.33, 128.92, 128.83, 127.88, 122.76, 119.92, 119.75, 110.87, 21.41, -0.24; **HRMS** [M+H$^+$] Calcd. for $C_{18}H_{22}NSi$: 280.1522, found: 280.1519.

3-(4-Methoxyphenyl)-2-(trimethylsilyl)-1*H*-indole (23g)

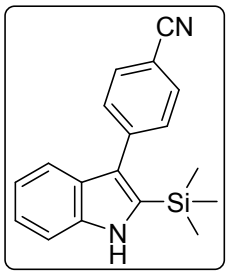
White solid; 203 mg (69% yield). TLC R_f=0.50 (EtOAc/Hexane 2:48). Purified by column chromatography on silica gel (EtOAc/Hexane = 3/47).



^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (br, 1H), 7.53 (d, *J* = 7.8 Hz, 1H), 7.42 (d, *J* = 8.16 Hz, 1H), 7.39 - 7.35 (m, 2H), 7.22 - 7.18 (m, 1H), 7.10 - 7.06 (m, 1H), 6.99 - 6.95 (m, 2H), 3.87 (s, 3H), 0.21 (s, 9H); **^{13}C NMR (100 MHz, $CDCl_3$)** 158.62, 137.94, 134.01, 131.50, 128.97, 128.95, 128.77, 127.52, 122.75, 119.90, 119.68, 113.64, 110.87, 55.42, -0.25; **HRMS** [M+H$^+$] Calcd. for $C_{18}H_{22}NOSi$: 296.1471, found: 296.1469.

4-(2-(Trimethylsilyl)-1*H*-indol-3-yl)benzonitrile (23h)

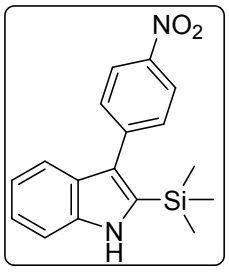
White solid; 182 mg (63% yield). TLC R_f=0.40 (EtOAc/Hexane 4:46). Purified by column chromatography on silica gel (EtOAc/Hexane = 4/46).



^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26 (br, 1H), 7.73 - 7.71 (m, 2H), 7.60 - 7.57 (m, 2H), 7.53 (d, *J* = 7.32 Hz, 1H), 7.46 (d, *J* = 8.2 Hz, 1H), 7.27 - 7.23 (m, 1H), 7.15 - 7.11 (m, 1H), 0.25 (s, 9H); **^{13}C NMR (100 MHz, $CDCl_3$)** 142.14, 138.07, 135.32, 132.13, 130.86, 128.06, 125.92, 123.34, 120.68, 119.40, 119.10, 111.21, 110.16, -0.21; **HRMS** [M+H$^+$] Calcd. for $C_{18}H_{19}N_2Si$: 291.1318, found: 291.1324.

3-(4-Nitrophenyl)-2-(trimethylsilyl)-1*H*-indole (23i)

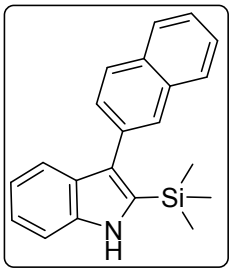
Light yellow solid; 183 mg (59% yield). TLC R_f=0.50 (EtOAc/Hexane 5:45). Purified by column chromatography on silica gel (EtOAc/Hexane = 4/46).



^{1}H NMR (400 MHz, $CDCl_3$) δ 8.32 - 8.29 (m, 3H), 7.66 - 7.63 (m, 2H), 7.56 (d, *J* = 7.72 Hz, 1H), 7.47 (d, *J* = 8.16 Hz, 1H), 7.29 - 7.26 (m, 1H), 7.17 - 7.13 (m, 1H), 0.27 (s, 9H); **^{13}C NMR (100 MHz, $CDCl_3$)** 146.57, 144.33,

138.12, 135.70, 130.73, 128.03, 125.52, 123.70, 123.44, 120.84, 119.09, 111.27, -0.17; **HRMS** [M+H$^+$] Calcd. for $C_{17}H_{19}N_2O_2Si$: 311.1216, found: 311.1215.

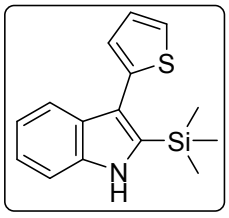
3-(Naphthalen-2-yl)-2-(trimethylsilyl)-1*H*-indole (23j)



White solid; 215 mg (68% yield). TLC R_f=0.70 (EtOAc/Hexane 2:48). Purified by column chromatography on silica gel (EtOAc/Hexane = 3/97). **^{1}H NMR (400 MHz, $CDCl_3$) δ** 8.22 (br, 1H), 7.92 - 7.89 (m, 3H), 7.88 - 7.86 (m, 1H), 7.66 - 7.60 (m, 2H), 7.53 - 7.49 (m, 2H), 7.47 (d, *J* = 8.2 Hz, 1H), 7.27 - 7.23 (m, 1H), 7.14 - 7.10 (m, 1H), 0.24 (s, 9H); **^{13}C NMR (100 MHz, $CDCl_3$)** 138.07, 134.59, 134.29, 133.61, 132.50, 129.12, 128.86, 128.81, 127.98, 127.89, 127.77, 127.67, 126.16, 125.65, 122.93, 120.16, 119.70, 110.99, -0.19; **HRMS** [M+H$^+$] Calcd. for $C_{21}H_{22}NSi$: 316.1522, found: 316.1520.

3-(Thiophen-2-yl)-2-(trimethylsilyl)-1*H*-indole (23k)

Yellow semisolid; 168 mg (62% yield). TLC R_f=0.40 (EtOAc/Hexane 4:46). Purified by column chromatography on silica gel (EtOAc/Hexane = 4/46).



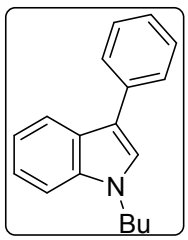
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.2 (br, 1H), 7.67 (d, *J* = 7.92 Hz, 1H), 7.41 - 7.39 (d, *J* = 8.12 Hz, 1H), 7.35 - 7.34 (m, 1H), 7.24 - 7.20 (m, 1H), 7.14 - 7.10 (m, 2H), 7.08 - 7.07 (m, 1H), 0.28 (s, 9H); **^{13}C NMR (100 MHz, $CDCl_3$)** 137.83, 137.72, 136.16, 129.25, 127.13, 126.93, 124.99, 123.04, 120.34, 119.79, 119.49, 110.93, -0.48; **HRMS** [M+H$^+$] Calcd. for $C_{15}H_{18}NSSi$: 272.0929, found: 272.0933.

3.2 General Procedure for the synthesis of *N*-alkyl-3-arylindoles (25)

The general procedure mentioned above **3** was applied with *o*-bromoaniline (1 mmol), **16** (0.04 mmol), TBAB (2.2 mmol), anhydrous K_2CO_3 (2 mmol), TMS protected alkynes (2 mmol) and 1,4-dioxane (2 mL) to yield the desired products in excellent yields.

1-Butyl-3-phenyl-1*H*-indole (25a)

Brown liquid; 162 mg (65%). TLC R_f=0.60 (100% hexane). Purified by column chromatography on silica gel (100% Hexane).

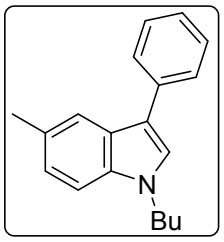


^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, *J* = 7.96 Hz, 1H), 7.66 (d, *J* = 7.72 Hz, 2H), 7.43 – 7.40 (t, *J* = 7.62 Hz, 2H), 7.38 (d, *J* = 8.2 Hz, 1H), 7.26 (s, 1H), 7.24 – 7.22 (m, 2H), 7.18 – 7.14 (m, 1H), 4.16 – 4.13 (t, *J* = 7.10 Hz, 2H), 1.89 – 1.81 (m, 2H), 1.42 – 1.32 (m, 2H), 0.96 – 0.92 (t, *J* = 7.32 Hz, 3H); **^{13}C NMR (100**

MHz, $CDCl_3$) 136.93, 135.91, 128.86, 127.46, 126.37, 125.78, 125.73, 121.91, 120.13, 119.91, 116.76, 109.85, 46.32, 32.44, 20.37, 13.86; **HRMS** [M+H$^+$] Calcd. for $C_{18}H_{20}N$: 250.1596, found: 250.1600.

1-Butyl-5-methyl-3-phenyl-1*H*-indole (25b)

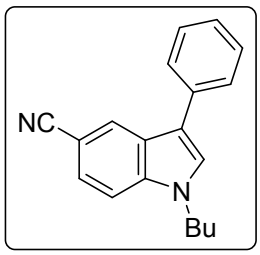
Colorless oil; 175 mg (67%). TLC R_f=0.70 (EtOAc/Hexane 1:49). Purified by column chromatography on silica gel (EtOAc/Hexane = 1/99).



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (s, 1H), 7.67 – 7.64 (dd, *J* = 1.24, 8.28 Hz, 2H), 7.46 – 7.42 (m, 2H), 7.29 – 7.26 (m, 2H), 7.24 (s, 1H), 7.10 – 7.08 (dd, *J* = 1.28, 8.32 Hz, 1H), 4.16 – 4.12 (t, *J* = 7.06 Hz, 2H), 2.49 (s, 3H), 1.89 – 1.82 (m, 2H), 1.42 – 1.33 (m, 2H), 0.97 – 0.93 (t, *J* = 7.36 Hz, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)** 136.08, 135.32, 129.21, 128.83, 127.44, 126.58, 125.85, 125.66, 123.50, 119.74, 116.20, 109.55, 46.36, 32.45, 21.71, 20.36, 13.86; **HRMS** [M+H$^+$] Calcd. for $C_{19}H_{22}N$: 264.1752, found: 264.1750.

1-Butyl-3-phenyl-1*H*-indole-5-carbonitrile (25c)

Brown coloured semi solid; 160 mg (58%). TLC R_f=0.60 (EtOAc/Hexane 3:47). Purified by column chromatography on silica gel (EtOAc/Hexane = 5:95).

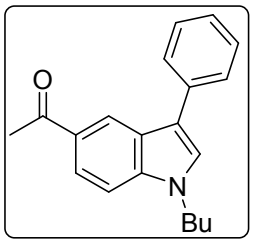


^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (m, 1H), 7.50 – 7.45 (m, 5H), 7.44 – 7.41 (m, 2H), 6.58 (m, 1H), 4.19 – 4.15 (t, *J* = 7.56 Hz, 2H), 1.69 – 1.61 (m, 2H), 1.22 – 1.13 (m, 2H), 0.82 – 0.78 (t, *J* = 7.36 Hz, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)** 143.81, 138.93, 132.25, 129.58, 128.82, 128.79, 128.02, 126.15, 124.53, 121.03, 110.92, 102.86, 102.81, 44.10, 32.15, 20.03, 13.67; **HRMS** [M+H$^+$] Calcd. for $C_{19}H_{19}N_2$: 275.1548, found: 275.1545.

1-(1-Butyl-3-phenyl-1*H*-indol-5-yl)ethanone (25d)

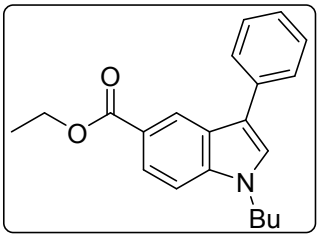
Yellow coloured liquid; 175 mg (60%). TLC R_f=0.50 (EtOAc/Hexane 5:95). Purified by column chromatography on silica gel (EtOAc/Hexane = 5/95).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.57 (d, *J* = 1.28 Hz, 1H), 7.95 – 7.92 (dd, *J* = 1.64, 8.72 Hz, 1H), 7.67 – 7.65 (dd, *J* = 1.24, 8.28 Hz, 2H), 7.50 – 7.46 (m, 2H), 7.41 (d, *J* = 8.72 Hz, 1H), 7.35 - 7.30 (m, 2H), 4.21 – 4.17 (t, *J* = 7.10 Hz, 2H), 2.68 (s, 3H), 1.92 – 1.84 (m, 2H), 1.43 – 1.36 (m, 2H), 0.98 – 0.95 (t, *J* = 7.36 Hz, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)** 198.23, 139.24, 134.78, 129.93, 128.97, 127.58, 126.91, 126.33, 125.83, 122.30, 122.20, 118.76, 109.55, 46.44, 32.32, 26.70, 20.19, 13.70; **HRMS** [M+H$^+$] Calcd. for $C_{20}H_{22}NO$: 292.1701, found: 292.1700.



Ethyl 1-butyl-3-phenyl-1*H*-indole-5-carboxylate (25e)

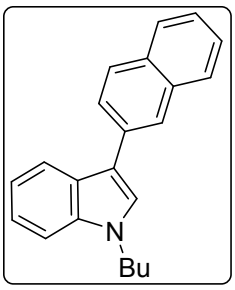
Yellow colored liquid; 183 mg (57%). TLC R_f=0.40 (EtOAc/Hexane 3:47). Purified by column chromatography on silica gel (EtOAc/Hexane = 7/93).



^{1}H NMR (400 MHz, $CDCl_3$) δ 8.67 (d, *J* = 1.28 Hz, 1H), 7.97 – 7.94 (dd, *J* = 1.56, 8.72 Hz, 1H), 7.67 – 7.64 (dd, *J* = 1.24, 8.28 Hz, 2H), 7.47 – 7.42 (m, 2H), 7.38 – 7.36 (d, *J* = 8.72 Hz, 1H), 7.31 – 7.28 (m, 2H), 4.42 – 4.36 (q, *J* = 7.12 Hz, 2H), 4.19 – 4.15 (t, *J* = 7.10 Hz, 2H), 1.90 – 1.83 (m, 2H), 1.42 – 1.35 (m, 5H), 0.97 – 0.93 (t, *J* = 7.36 Hz, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)** 167.88, 139.34, 135.02, 129.02, 127.70, 126.82, 126.33, 125.99, 123.35, 123.20, 122.37, 118.50, 109.40, 60.73, 46.54, 32.45, 20.33, 14.65, 13.83; **HRMS** [M+H$^+$] Calcd. for $C_{21}H_{24}NO_2$: 322.1807, found: 322.1805.

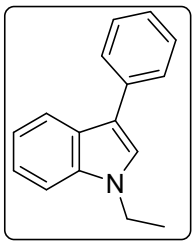
1-Butyl-3-(naphthalen-2-yl)-1*H*-indole (25f)

Light yellow liquid; 165 mg (55%). TLC R_f=0.60 (EtOAc/Hexane 1:49). Purified by column chromatography on silica gel (EtOAc/Hexane = 1/49).



^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (s, 1H), 8.08 (d, *J* = 7.88 Hz, 1H), 7.91 – 7.80 (m, 4H), 7.51 – 7.41 (m, 4H), 7.31 – 7.27 (m, 1H), 7.24 – 7.20 (m, 1H), 4.22 – 4.19 (t, *J* = 7.10 Hz, 2H), 1.94 – 1.87 (m, 2H), 1.47 – 1.37 (m, 2H), 1.00 – 0.96 (t, *J* = 7.36 Hz, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)** 136.96, 134.09, 133.30, 131.93, 128.22, 127.74, 127.70, 126.49, 126.39, 126.10, 126.05, 125.09, 124.92, 121.95, 120.12, 119.97, 116.57, 109.83, 46.29, 32.36, 20.29, 13.75; **HRMS** [M+H$^+$] Calcd. for $C_{22}H_{22}N$: 300.1752, found: 300.1754.

1-Ethyl-3-phenyl-1*H*-indole (26a)

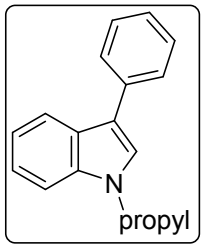


Colourless sticky liquid; 133 mg (60%). TLC R_f=0.70 (EtOAc/Hexane 1:49). Purified by column chromatography on silica gel (EtOAc/Hexane = 1/99).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, *J* = 8.04 Hz, 1H), 7.63 (d, *J* = 7.2 Hz, 2H), 7.41 (d, *J* = 7.48 Hz, 2H), 7.37 – 7.34 (m, 1H), 7.24 – 7.20 (m, 3H), 7.16 – 7.12 (m, 1H), 4.21 – 4.15 (q, *J* = 7.28 Hz, 2H), 1.49 – 1.46 (t, *J* = 7.20 Hz, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)** 136.67, 135.91, 128.87, 127.48, 126.47, 125.81, 124.93, 121.97, 120.19, 119.98, 116.98, 109.72, 41.18, 15.60; **HRMS** [M+H$^+$] Calcd. for $C_{16}H_{16}N$: 222.1283, found: 222.1287.

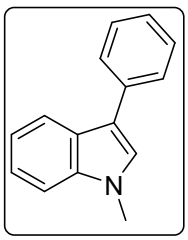
1-Propyl-3-phenyl-1*H*-indole (27a)

Colourless liquid; 120 mg (51%). TLC R_f=0.70 (EtOAc/Hexane 1:99). Purified by column chromatography on silica gel (EtOAc/Hexane = 1/99).



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, *J* = 7.96 Hz, 1H), 7.68 (d, *J* = 7.44 Hz, 2H), 7.46 (t, *J* = 7.66 Hz, 2H), 7.40 (d, *J* = 8.2 Hz, 1H), 7.29 – 7.28 (m, 2H), 7.24 (s, 1H), 7.20 – 7.16 (m, 1H), 4.15 – 4.12 (t, *J* = 7.08 Hz, 2H), 1.97 – 1.88 (m, 2H), 1.00 – 0.96 (t, *J* = 7.4 Hz, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)** 137.06, 136.00, 128.94, 127.55, 126.49, 125.87, 122.00, 120.22, 120.00, 116.85, 109.94, 48.36, 23.75, 11.81; **HRMS** [M+H$^+$] Calcd. for $C_{17}H_{18}N$: 236.1439, found: 236.1443.

1-Methyl-3-phenyl-1*H*-indole (28a)



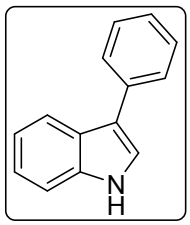
Colourless liquid; 48 mg (23%). TLC R_f=0.70 (EtOAc/Hexane 1:99). Purified by column chromatography on silica gel (EtOAc/Hexane = 1/99).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, *J* = 7.96 Hz, 1H), 7.67 (d, *J* = 8 Hz, 2H), 7.46 – 7.42 (t, *J* = 7.66 Hz, 2H), 7.38 (d, *J* = 8.16 Hz, 1H), 7.30 – 7.29 (m, 2H), 7.24 (s, 1H), 7.21 – 7.17 (m, 1H), 3.85 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)** 137.72, 135.89, 128.95, 127.56, 126.75, 126.41, 125.92, 122.19, 120.16, 120.11, 116.99, 109.23, 33.09

The obtained data are in accordance with the literature report.[4]

Synthesis of 3-Phenyl-1*H*-indole 24

To a solution of indole **23a** (100 mg) in methanol, was added 3N HCl solution and the reaction mixture was stirred at room temperature until the completion of reaction as shown by thin layer chromatography. The reaction mass was diluted with ethyl acetate and the organic layer was washed with water and dried over sodium sulphate. The residue was then purified by silica gel chromatography to afford the desired 2**4** in good yields. Yield: 73 mg (89%). TLC R_f=0.50 (EtOAc/Hexane 1:49). Purified by column chromatography on silica gel (EtOAc/Hexane = 2:48).



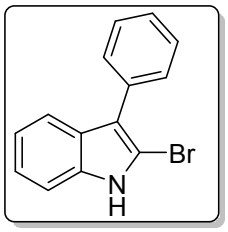
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.25 (br, 1H), 7.97 (d, *J* = 7.92 Hz, 1H), 7.70 – 7.67 (m, 2H), 7.48 – 7.43 (m, 3H), 7.38 (d, *J* = 2.52 Hz, 1H), 7.32 – 7.28 (m, 1H), 7.25 – 7.18 (m, 2H); **^{13}C NMR (100 MHz, $CDCl_3$)** 136.80, 135.69, 128.89, 127.64, 126.12, 125.90, 122.56, 121.88, 120.46, 119.97, 118.54, 111.52.

The obtained data are in accordance with the literature report.[5]

Synthesis of 2-Bromo-3-phenyl-1*H*-indole 29[6]

A solution of **23a** (1 mmol) in dichloromethane (10 mL) was allowed to cool to -5 °C and stirred for 5 min. NBS (1.1 mmol) was dissolved in dichloromethane and was added drop-wise and the reaction was stirred at room temperature for 12 h and the residue was purified over silica gel chromatography to afford in good yields.

white coloured solids; Yield: 65 mg (64%). TLC R_f=0.70 (EtOAc/Hexane 1:49). Purified by column chromatography on silica gel (EtOAc/Hexane = 1/49).

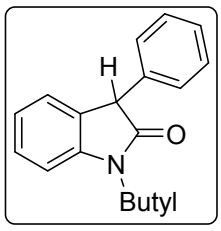


^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (br, 1H), 7.55 – 7.51 (m, 3H), 7.43 – 7.39 (m, 2H), 7.31 – 7.26 (m, 2H), 7.16 – 7.12 (m, 1H), 7.10 – 7.06 (m, 1H); **^{13}C NMR (100 MHz, $CDCl_3$)** 135.86, 134.04, 133.38, 130.05, 128.82, 127.75, 127.33, 122.32, 119.54, 118.99, 110.67, 108.72; **HRMS** [M+H$^+$] Calcd. for $C_{14}H_{11}BrN$: 272.0075, found: 272.0071.

Synthesis of 1-Butyl-3-phenylindolin-2-one 30[7]

To a solution of **25a** (100 mg) in acetonitrile (5 mL), selectfluor (1.2 equiv.) was added in one-portion and the reaction mixture was stirred at room temperature for overnight (monitored by TLC). The residue was then concentrated and the crude was purified by silica gel column chromatography to afford the pure compound **30** in good yields.

Colourless liquid; Yield: 75 mg (71%). TLC R_f=0.40 (EtOAc/Hexane 3:47). Purified by column chromatography on silica gel (EtOAc/Hexane = 4/46).

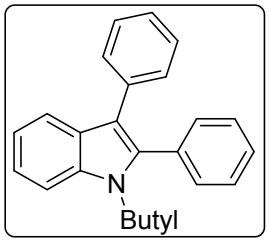


^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 – 7.28 (m, 3H), 7.24 (d, J = 7.92 Hz, 1H), 7.17 – 7.12 (m, 3H), 7.03 – 6.99 (m, 1H), 6.89 (d, J = 7.84 Hz, 1H), 4.56 (s, 1H), 3.78 – 3.65 (m, 2H), 1.69 – 1.63 (m, 2H), 1.42 – 1.32 (m, 2H), 0.94 – 0.91 (t, J = 7.34 Hz, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)** 175.90, 143.96, 136.89, 129.16, 128.88, 128.41, 128.30, 127.50, 125.18, 122.45, 108.44, 52.07, 39.96, 29.53, 20.19, 13.78; **HRMS** [M+H$^+$] Calcd. for $C_{18}H_{20}NO$: 266.1545, found: 266.1550.

Synthesis of 1-Butyl-2,3-diphenyl-1*H*-indole 31[8]

A reaction vial equipped with a magnetic stir bar was charged with **25a** (100 mg) palladium acetate (5 mol %), Cy_2P-*o*-biphenyl (10 mol %), sodium carbonate (2 equiv) and chlorobenzene (5 equiv) in DMA as solvent. The vial was place in a preheated oil bath at 120 °C for 36 h. The reaction mass was then allowed to cool to room temperature, diluted with ethyl acetate and filtered through celite bed. The organic layer was then washed with water and concentrated under reduced pressure. The crude was then purified using column chromatography to afford compound **31**.

White coloured solid; 88 mg (68%). TLC R_f=0.70 (EtOAc/Hexane 1:99). Purified by column chromatography on silica gel (EtOAc/Hexane = 1:99).



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, *J* = 7.96 Hz, 1H), 7.47 (d, *J* = 8.2 Hz, 1H), 7.41 – 7.39 (m, 3H), 7.37 – 7.33 (m, 3H), 7.31 – 7.28 (m, 4H), 7.22 – 7.16 (m, 2H), 4.13 – 4.09 (t, *J* = 7.6 Hz, 2H), 1.73 – 1.66 (m, 2H), 1.27 – 1.17 (m, 2H), 0.83 – 0.80 (t, *J* = 7.34 Hz, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)** 137.57, 136.44, 135.28, 132.34, 131.21, 129.88, 128.40, 128.11, 128.06, 127.21, 125.41, 121.98, 120.06, 119.75, 115.25, 110.00, 43.65, 32.13, 20.06, 13.64; The obtained data is in accordance with the reported literature.[8]

4. X-ray crystallography of compound 7

Single crystal X-ray structural data of the compounds **7** were collected on a CMOS based Bruker D8 Venture PHOTON 100 diffractometer equipped with a INCOATEC micro-focus source with graphite monochromated Mo Kα radiation (λ = 0.71073 Å) operating at 50 kV and 30 mA. The SAINT[9] program was used for the integration of diffraction profiles and absorption correction was applied with the SADABS[10] program. Both the structures were initially solved by SIR 92[11] and refined by the full matrix least squares method using SHELXL-2013[12] and WinGX system, Ver2013.3.[13] The non-hydrogen atoms in both the structures were located using the difference Fourier map and refined anisotropically. The hydrogen atoms were fixed by HFIX and placed in ideal positions and included in the refinement process using a riding model with isotropic thermal parameters.

Complex	**7**
CCDC No.	CCDC 1584103
Empirical formula	$C_{30}H_{26}Br_2N_4O_2Pd$
Formula weight	740.77
Temperature/K	293(2)
Crystal system	orthorhombic
Wavelength	0.71073Å
Space group	*Pca 2$_1$*
a/Å	40.319(5)
b/Å	8.136(5)
c/Å	8.974(5)

α/°	90.000(5)
β/°	90.000(5)
ϒ/°	90.000(5)
Volume	2944(2)
Z	4
Calculated density g/cm^3	1.671
Absorption coefficient (μ/mm^{-1})	3.379
F(000)	1464
Index ranges	-53<h<53, -10<k<10, -11<l<12
Reflections collected	82760
Independent reflections	7309
Data/restraint/parameters	7309/1/352
Goodness of fit on F^2	1.075
Final R indices[I>2σ(I)]	R1 = 0.0342 wR2 = 0.0708
Final R indices [all data]	R1 = 0.0421 wR2 = 0.0738

4.1 Bond distances of 7

Atom1	Atom2	Length		Atom1	Atom2	Length
Pd1	Br2	2.423(1)		C22	H22B	0.97
Pd1	Br1	2.430(1)		C22	C23	1.56(1)
Pd1	N4	2.093(5)		C3	C2	1.461(8)
Pd1	C20	1.950(5)		C3	C12	1.378(9)
N2	C18	1.436(6)		C3	C4	1.391(9)
N2	C19	1.386(7)		C16	H16	0.93
N2	C20	1.354(7)		C7	H7	0.928
N1	C13	1.449(7)		C7	C6	1.40(1)
N1	C2	1.397(7)		C7	C8	1.36(1)
N1	C1	1.408(7)		C12	H12	0.93
N3	C22	1.454(8)		C12	C11	1.40(1)
N3	C20	1.355(6)		C23	H23A	0.97
N3	C21	1.371(7)		C23	H23B	0.971
C18	C17	1.364(7)		C23	C24	1.47(1)
C18	C16	1.368(8)		C4	C9	1.437(9)

O1	C2	1.214(7)		C9	C10	1.40(1)
C14	H14	0.931		C9	C8	1.42(1)
C14	C17	1.378(8)		C11	H11	0.93
C14	C13	1.377(8)		C11	C10	1.35(1)
O2	C1	1.200(8)		C6	H6	0.93
N4	C27	1.333(7)		C24	H24A	0.97
N4	C25	1.330(9)		C24	H24B	0.97
C17	H17	0.93		C24	C32	1.50(1)
C5	C4	1.416(8)		C29	H29	0.93
C5	C6	1.371(8)		C29	C28	1.37(1)
C5	C1	1.468(8)		C10	H10	0.931
C30	H30	0.931		C27	H27	0.929
C30	C29	1.35(1)		C25	H25	0.93
C30	C27	1.37(1)		C25	C28	1.36(1)
C15	H15	0.93		C21	H21	0.93
C15	C13	1.341(8)		C28	H28	0.931
C15	C16	1.387(9)		C8	H8	0.93
C19	H19	0.93		C32	H32A	0.96
C19	C21	1.318(8)		C32	H32B	0.96
C22	H22A	0.97		C32	H32C	0.96

4.2 Bond angles of 7

Atom1	Atom2	Atom3	Angle		Atom1	Atom2	Atom3	Angle
Br2	Pd1	Br1	175.65(3)		C3	C12	H12	120.2
Br2	Pd1	N4	92.3(1)		C3	C12	C11	119.6(7)
Br2	Pd1	C20	89.1(2)		H12	C12	C11	120.2
Br1	Pd1	N4	91.5(1)		C22	C23	H23A	109.1
Br1	Pd1	C20	87.2(2)		C22	C23	H23B	109.2
N4	Pd1	C20	177.3(2)		C22	C23	C24	112.3(6)
C18	N2	C19	123.3(4)		H23A	C23	H23B	107.9
C18	N2	C20	126.6(4)		H23A	C23	C24	109.1
C19	N2	C20	110.1(4)		H23B	C23	C24	109
C13	N1	C2	117.3(4)		C5	C4	C3	121.8(5)
C13	N1	C1	117.4(4)		C5	C4	C9	118.6(5)
C2	N1	C1	125.3(5)		C3	C4	C9	119.6(5)
C22	N3	C20	124.8(5)		C4	C9	C10	117.3(6)
C22	N3	C21	124.8(5)		C4	C9	C8	118.0(6)
C20	N3	C21	110.3(4)		C10	C9	C8	124.6(7)
N2	C18	C17	121.1(5)		C12	C11	H11	119.7
N2	C18	C16	118.3(5)		C12	C11	C10	120.5(8)
C17	C18	C16	120.5(5)		H11	C11	C10	119.8
H14	C14	C17	119.9		C5	C6	C7	120.3(6)
H14	C14	C13	119.7		C5	C6	H6	119.9

C17	C14	C13	120.4(5)		C7	C6	H6	119.9
Pd1	N4	C27	121.3(4)		C23	C24	H24A	109.1
Pd1	N4	C25	121.5(4)		C23	C24	H24B	109.3
C27	N4	C25	117.1(5)		C23	C24	C32	112.0(8)
C18	C17	C14	119.5(5)		H24A	C24	H24B	107.9
C18	C17	H17	120.3		H24A	C24	C32	109.3
C14	C17	H17	120.2		H24B	C24	C32	109.1
C4	C5	C6	121.0(5)		C30	C29	H29	121.2
C4	C5	C1	119.5(5)		C30	C29	C28	117.6(8)
C6	C5	C1	119.5(5)		H29	C29	C28	121.2
H30	C30	C29	120.1		C9	C10	C11	122.2(8)
H30	C30	C27	120.1		C9	C10	H10	118.9
C29	C30	C27	119.8(7)		C11	C10	H10	118.9
H15	C15	C13	119.4		Pd1	C20	N2	129.4(4)
H15	C15	C16	119.4		Pd1	C20	N3	125.7(4)
C13	C15	C16	121.2(6)		N2	C20	N3	104.7(4)
N2	C19	H19	126.5		N4	C27	C30	122.9(6)
N2	C19	C21	107.0(5)		N4	C27	H27	118.5
H19	C19	C21	126.5		C30	C27	H27	118.6
N3	C22	H22A	109.3		N4	C25	H25	118.9
N3	C22	H22B	109.3		N4	C25	C28	122.2(7)
N3	C22	C23	111.9(5)		H25	C25	C28	118.9
H22A	C22	H22B	107.9		N3	C21	C19	107.9(5)
H22A	C22	C23	109.2		N3	C21	H21	126.1
H22B	C22	C23	109.2		C19	C21	H21	126
N1	C13	C14	119.6(5)		C29	C28	C25	120.3(9)
N1	C13	C15	121.0(5)		C29	C28	H28	120
C14	C13	C15	119.4(5)		C25	C28	H28	119.7
C2	C3	C12	119.0(5)		N1	C1	O2	119.9(6)
C2	C3	C4	120.1(5)		N1	C1	C5	116.3(5)
C12	C3	C4	120.8(6)		O2	C1	C5	123.8(6)
C18	C16	C15	119.0(6)		C7	C8	C9	121.8(7)
C18	C16	H16	120.6		C7	C8	H8	119.1
C15	C16	H16	120.5		C9	C8	H8	119.1
H7	C7	C6	119.8		C24	C32	H32A	109.4
H7	C7	C8	119.9		C24	C32	H32B	109.5
C6	C7	C8	120.3(7)		C24	C32	H32C	109.6
N1	C2	O1	119.9(5)		H32A	C32	H32B	109
N1	C2	C3	116.8(5)		H32A	C32	H32C	109
O1	C2	C3	123.2(5)		H32B	C32	H32C	109

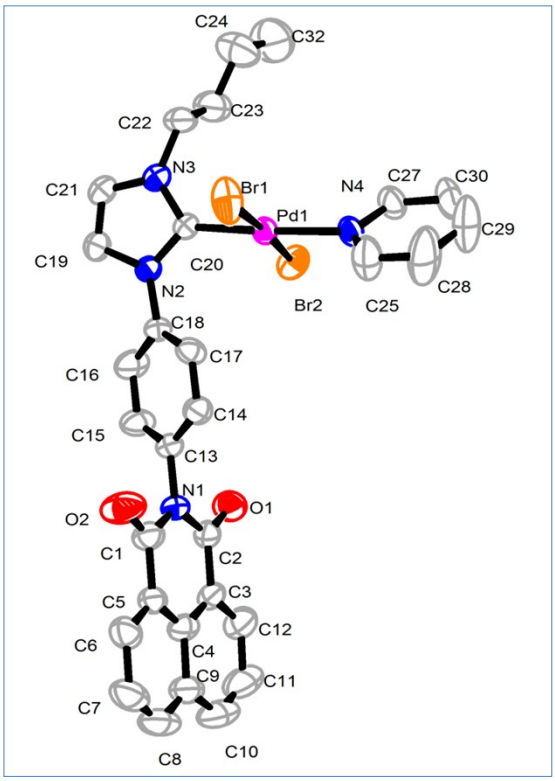


Fig.1 ORTEP representation of **7**

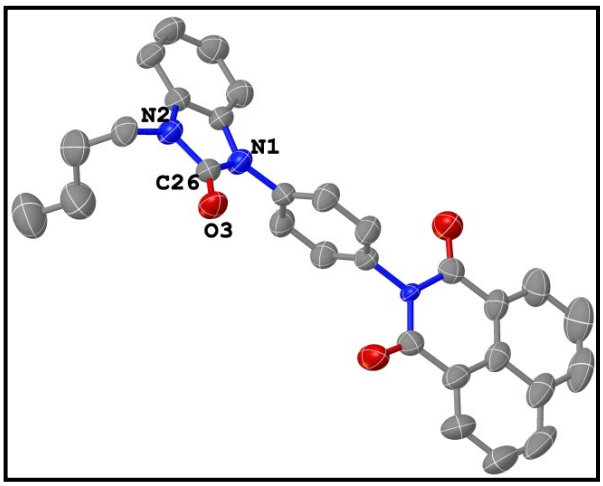


Fig.2 ORTEP representation of cyclic urea impurity

5. UV-Visible spectrophotometric studies:

We envision that the polyaromatic naphthalimide unit in the Pd-NHC engages in the π-stacking interactions with the aromatic reactants and thus results in the enhanced activity which was established in our previous work[14] and also by Peris *et al.*[15] To further confirm, interactions of Pd-NHCs **7** & **13** with pyrene and anthracene are studied using UV-Visible absorption spectrophotometric experiments in dichloromethane at room temperature. The absorption of anthracene and pyrene was enhanced upon increasing the concentration of Pd-NHC complexes (**7** & **13**). The above preliminary study indicates the interactions between complexes and the π-stacking additives.

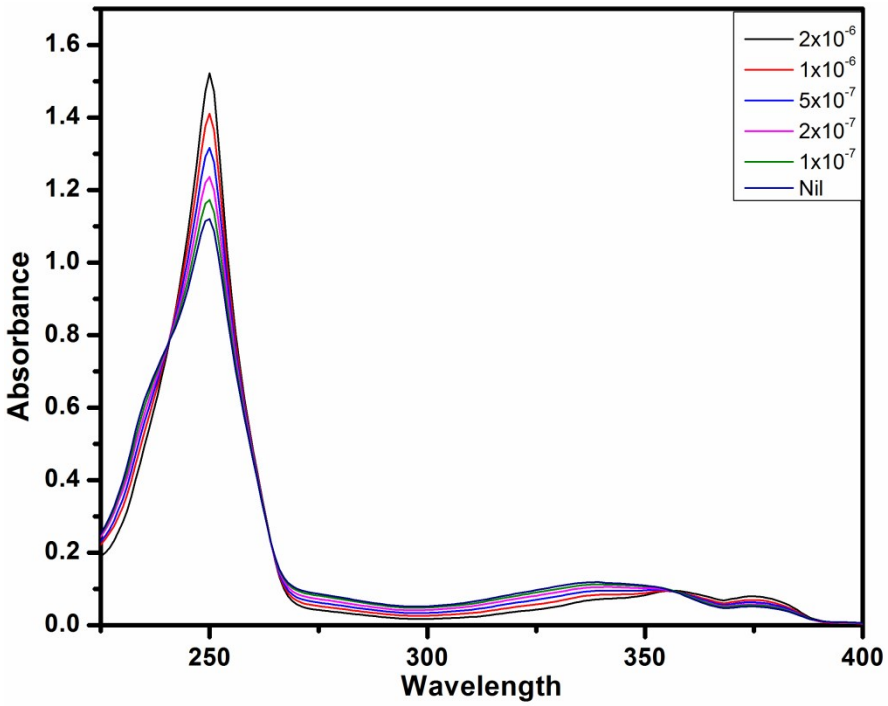


Figure 5.1 Enhancement in the intensity of electronic absorption of anthracene ($8x10^{-6}$ M) with increasing concentration of **7** in dichloromethane at 25 °C.

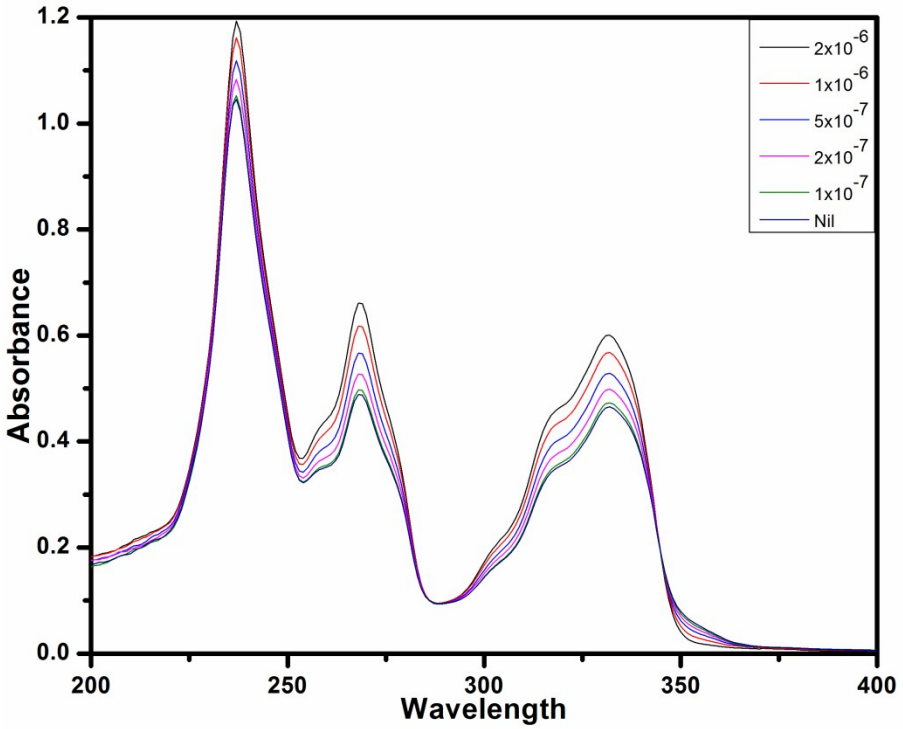


Figure 5.2 Enhancement in the intensity of electronic absorption of pyrene ($8x10^{-6}$ M) with increasing concentration of **7** in dichloromethane at 25 ^{o}C.

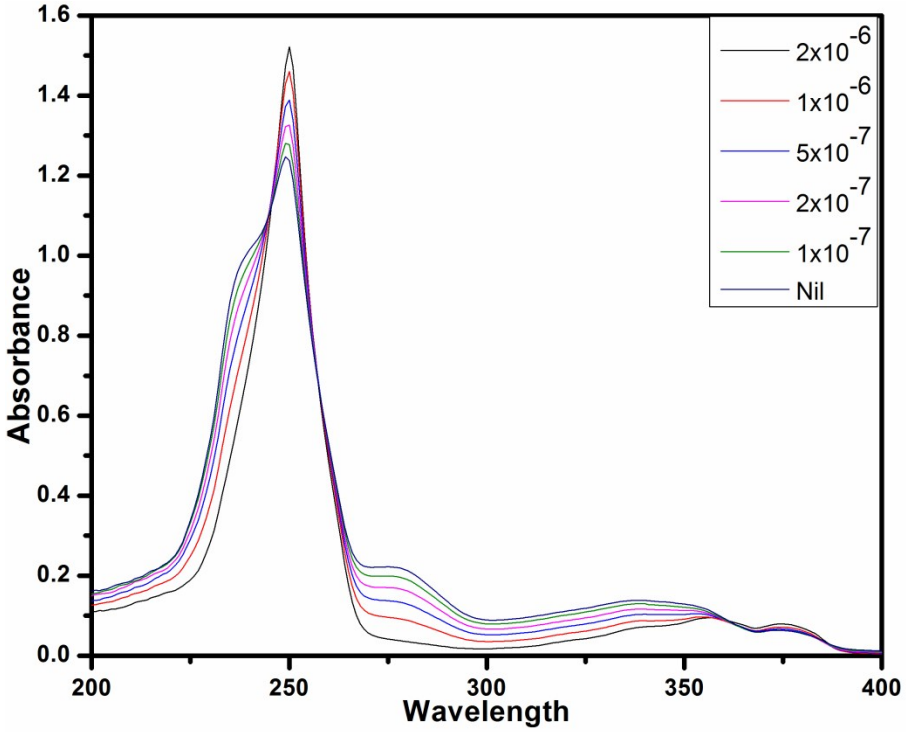


Figure 5.3 Enhancement in the intensity of electronic absorption of anthracene ($8x10^{-6}$ M) with increasing concentration of **13** in dichloromethane at 25 ^{o}C.

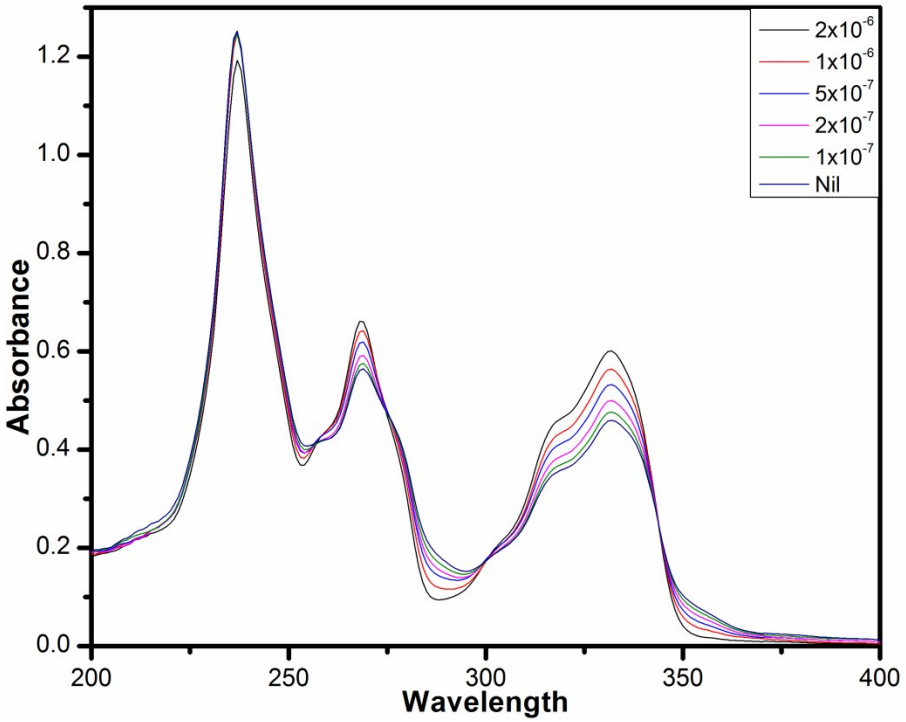
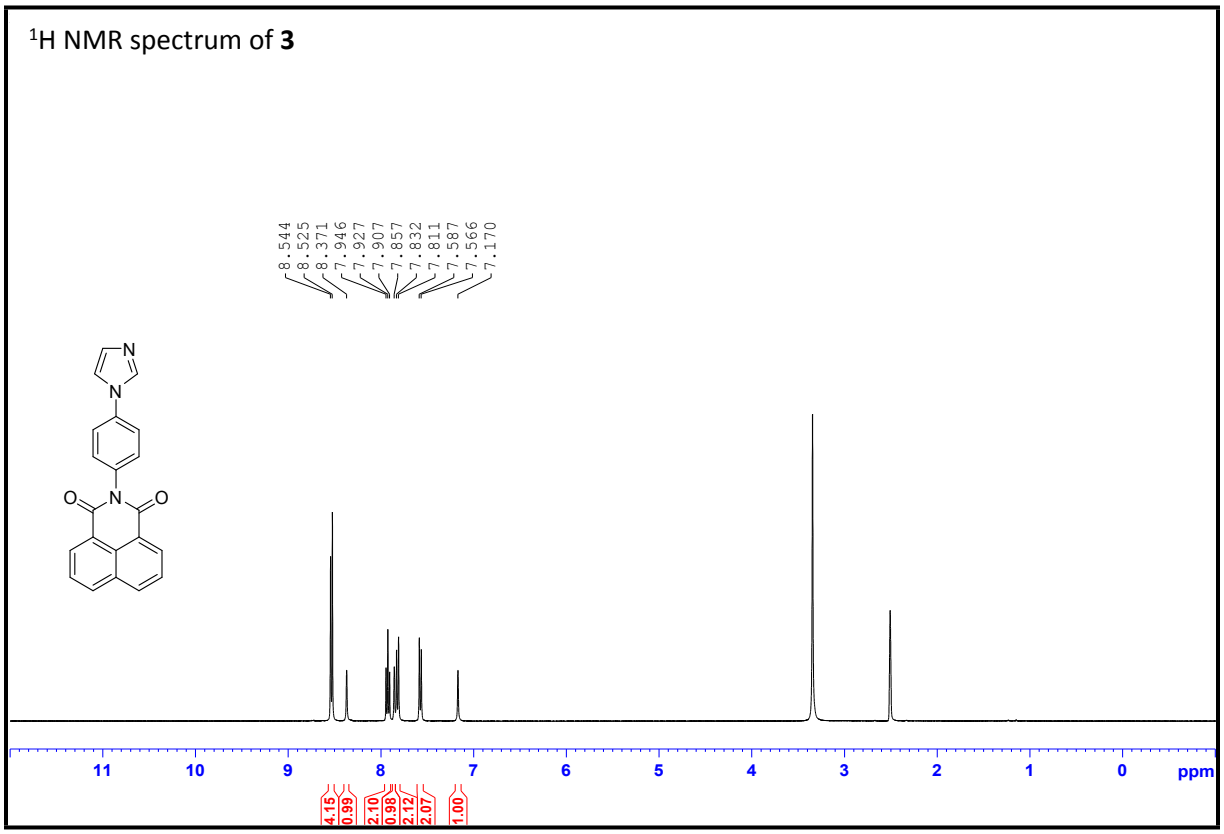
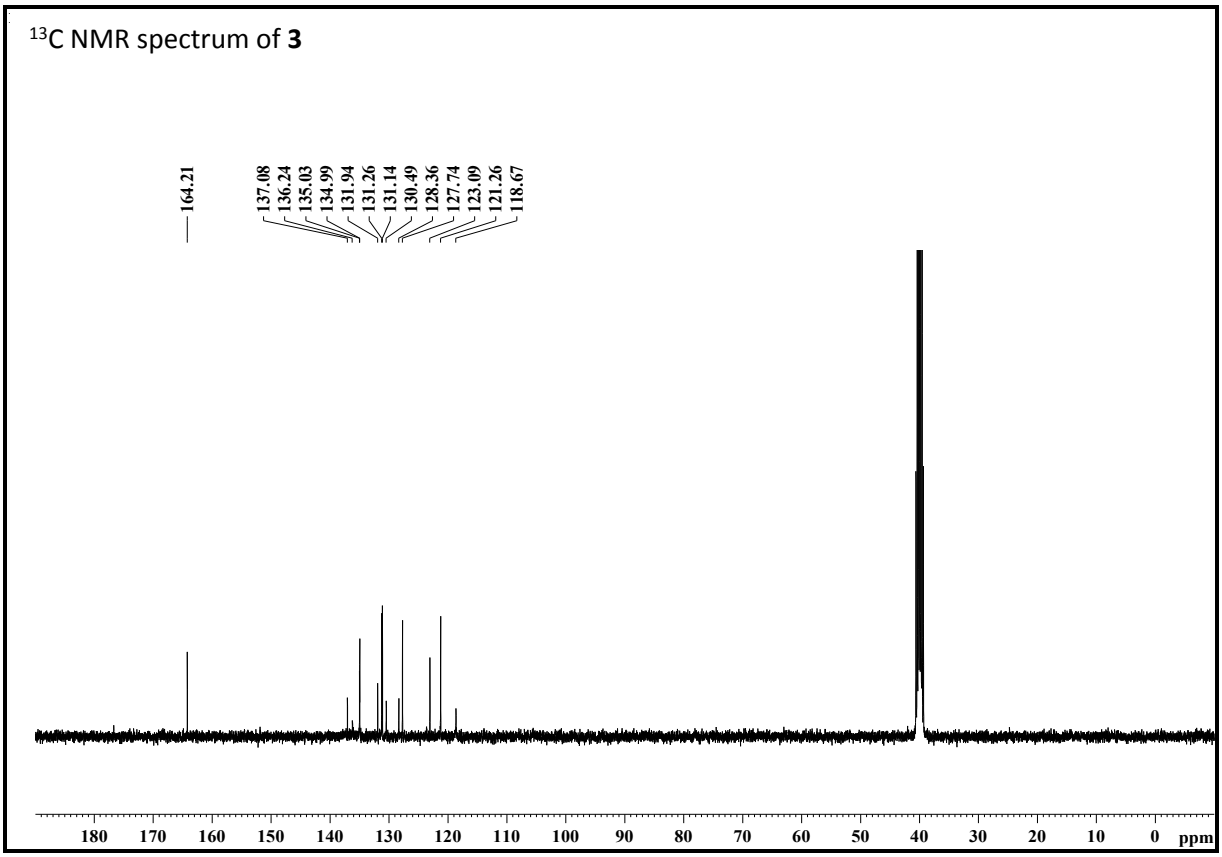


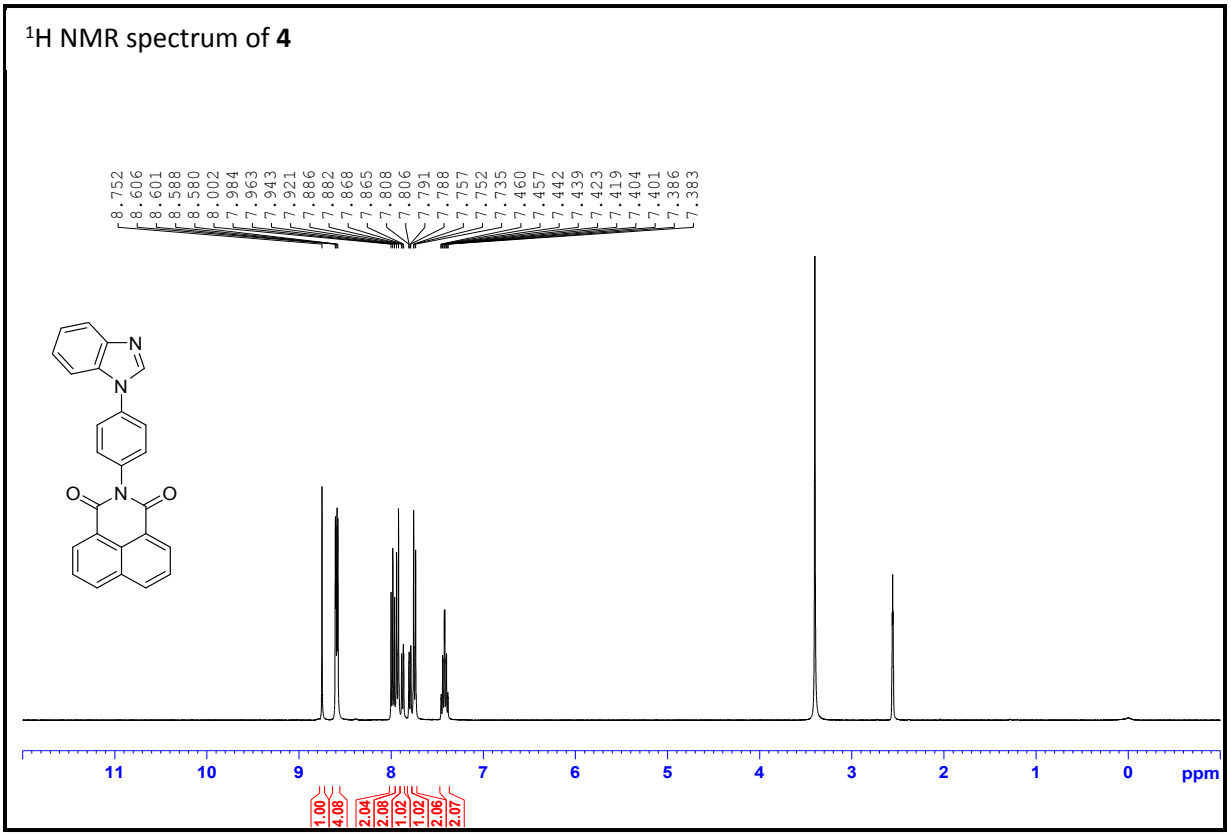
Figure 5.4 Enhancement in the intensity of electronic absorption of pyrene ($8x10^{-6}$ M) with increasing concentration of **13** in dichloromethane at 25 ^{o}C.



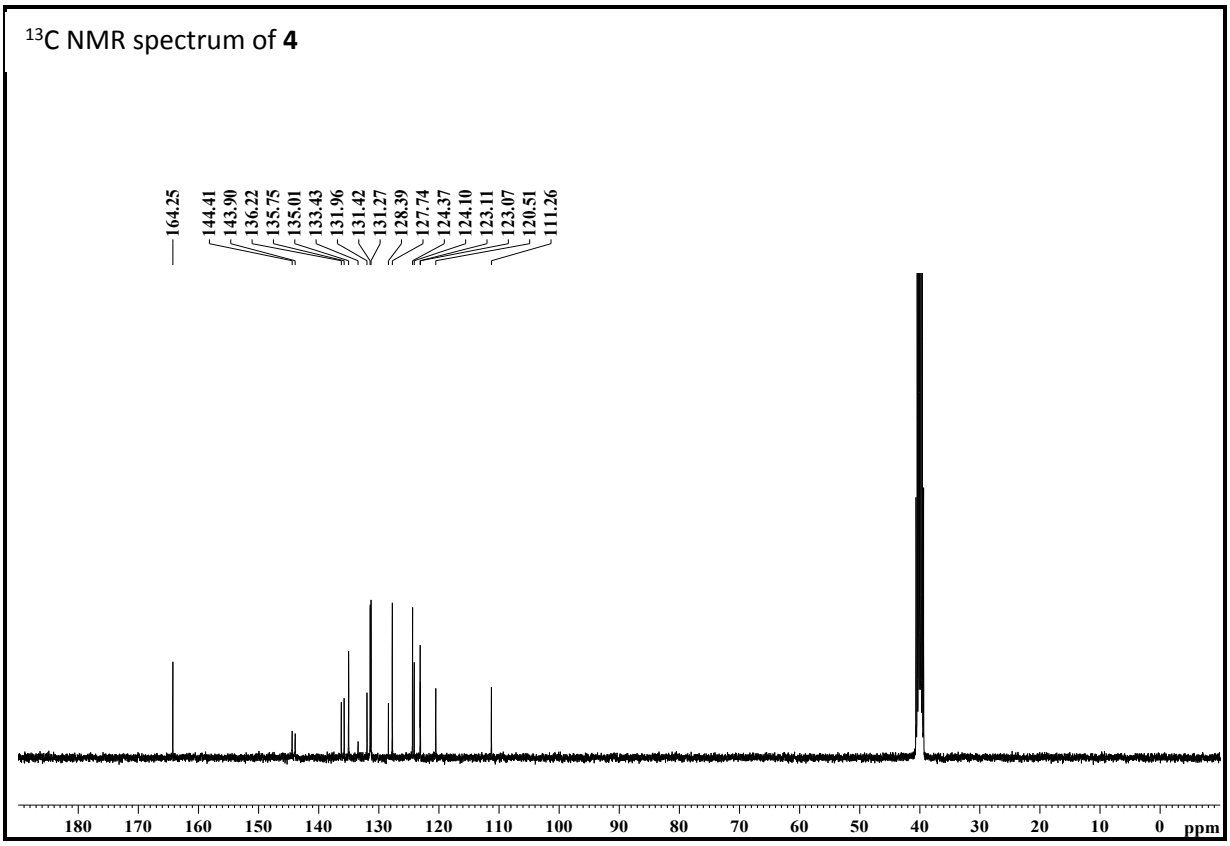
^{13}C NMR spectrum of **3**



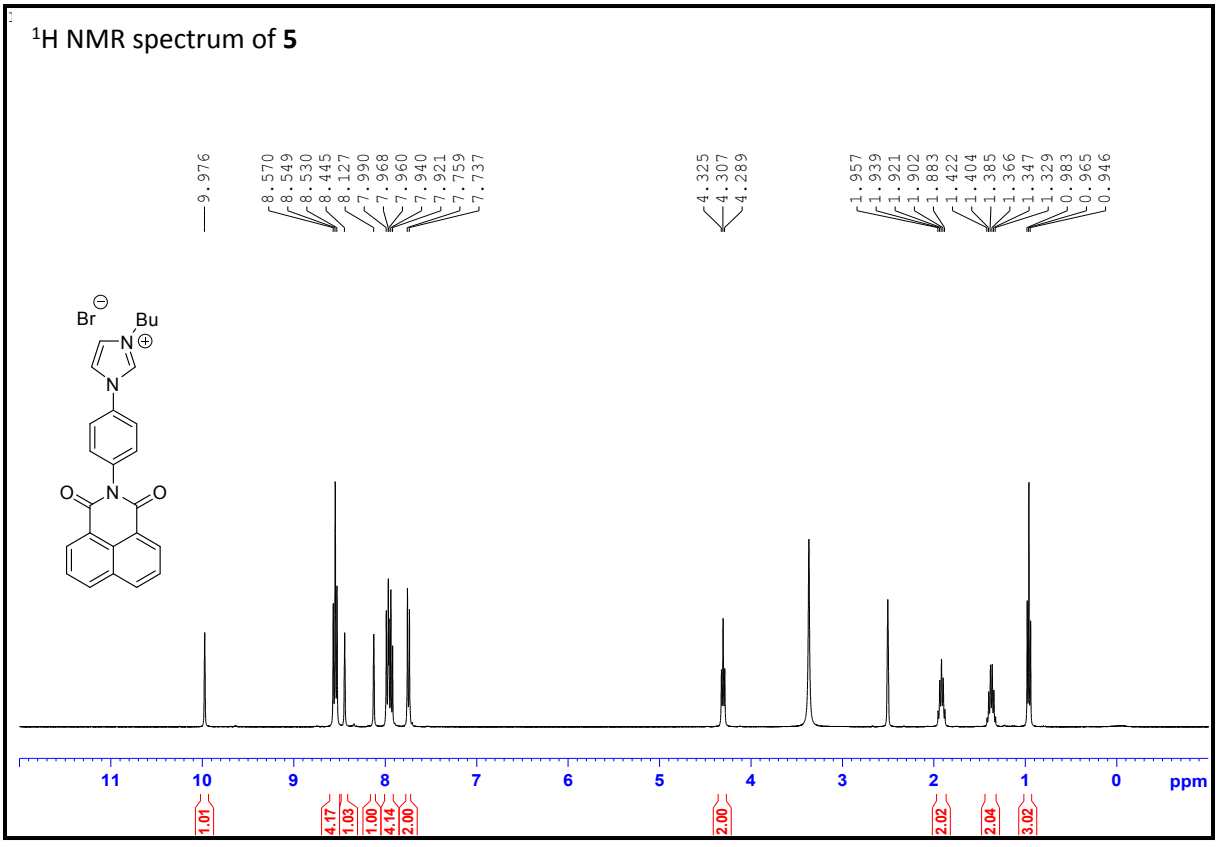
^{1}H NMR spectrum of **4**



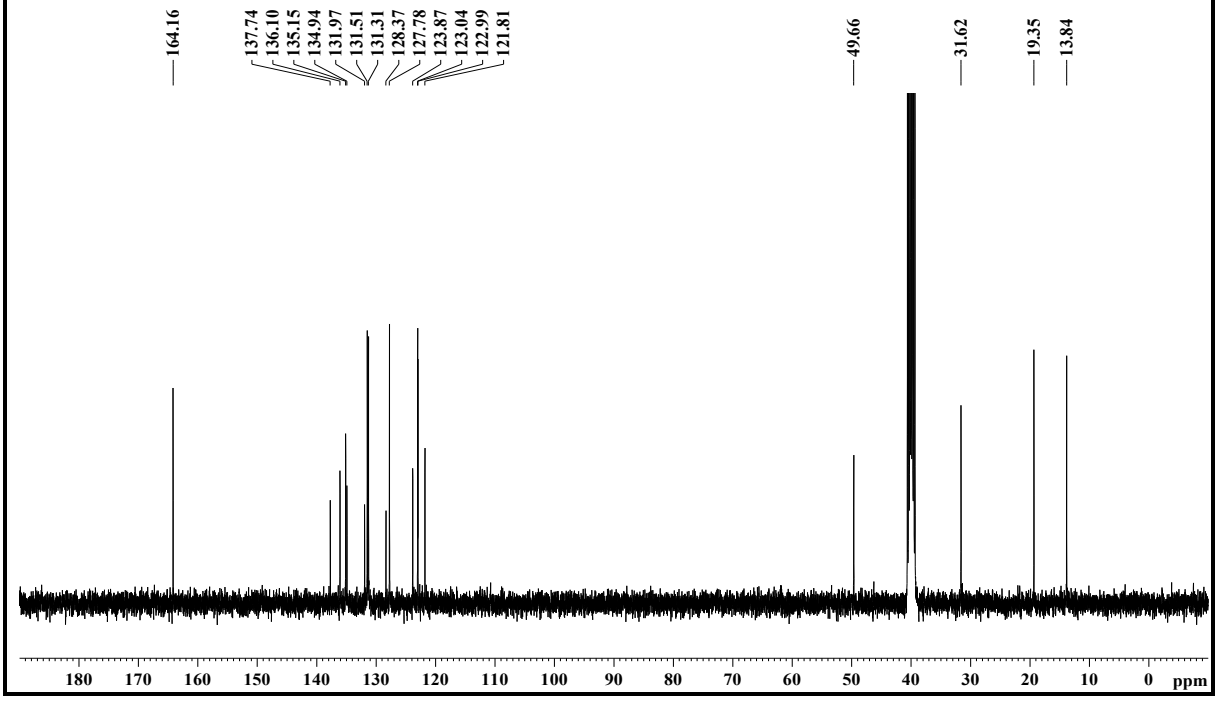
^{13}C NMR spectrum of **4**



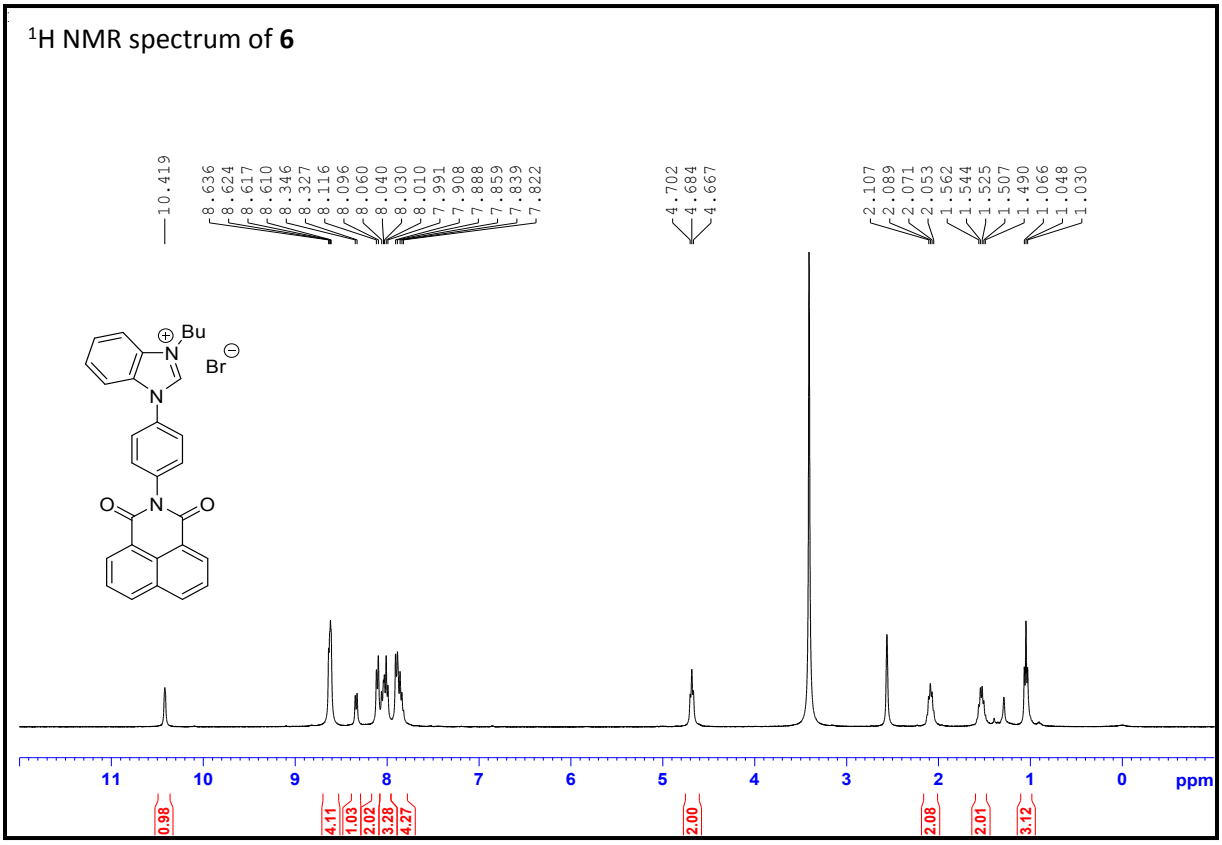
^{1}H NMR spectrum of **5**



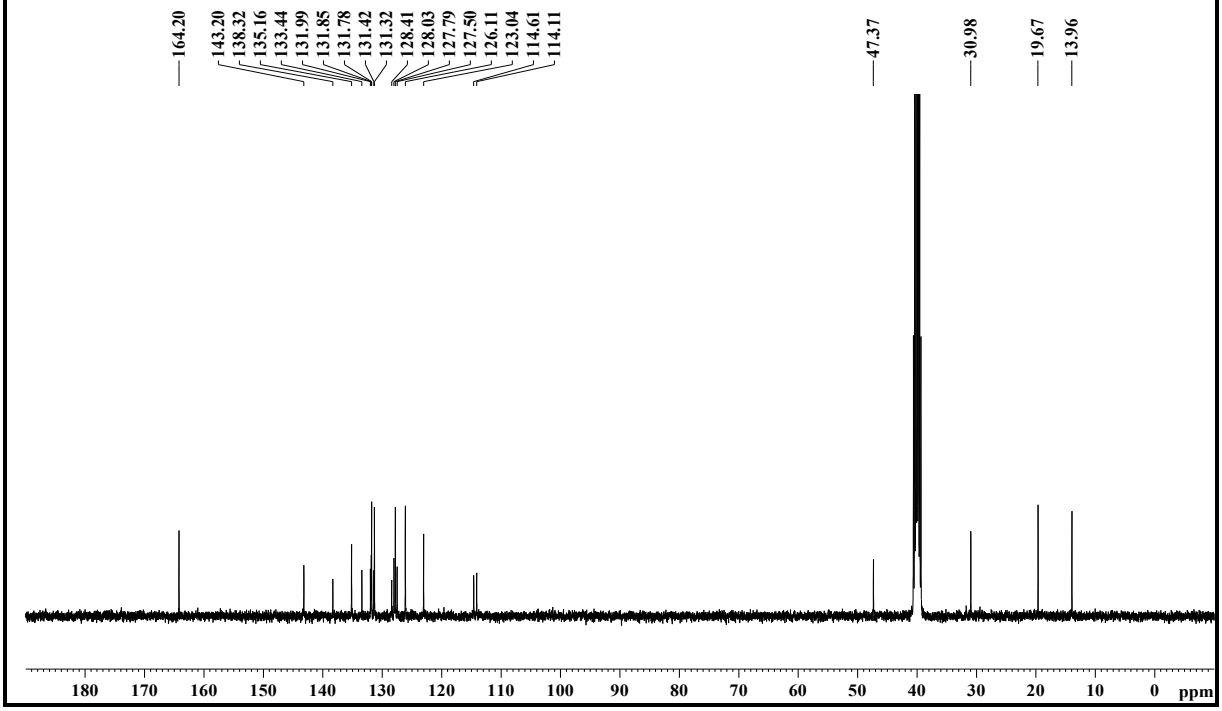
^{13}C NMR spectrum of **5**



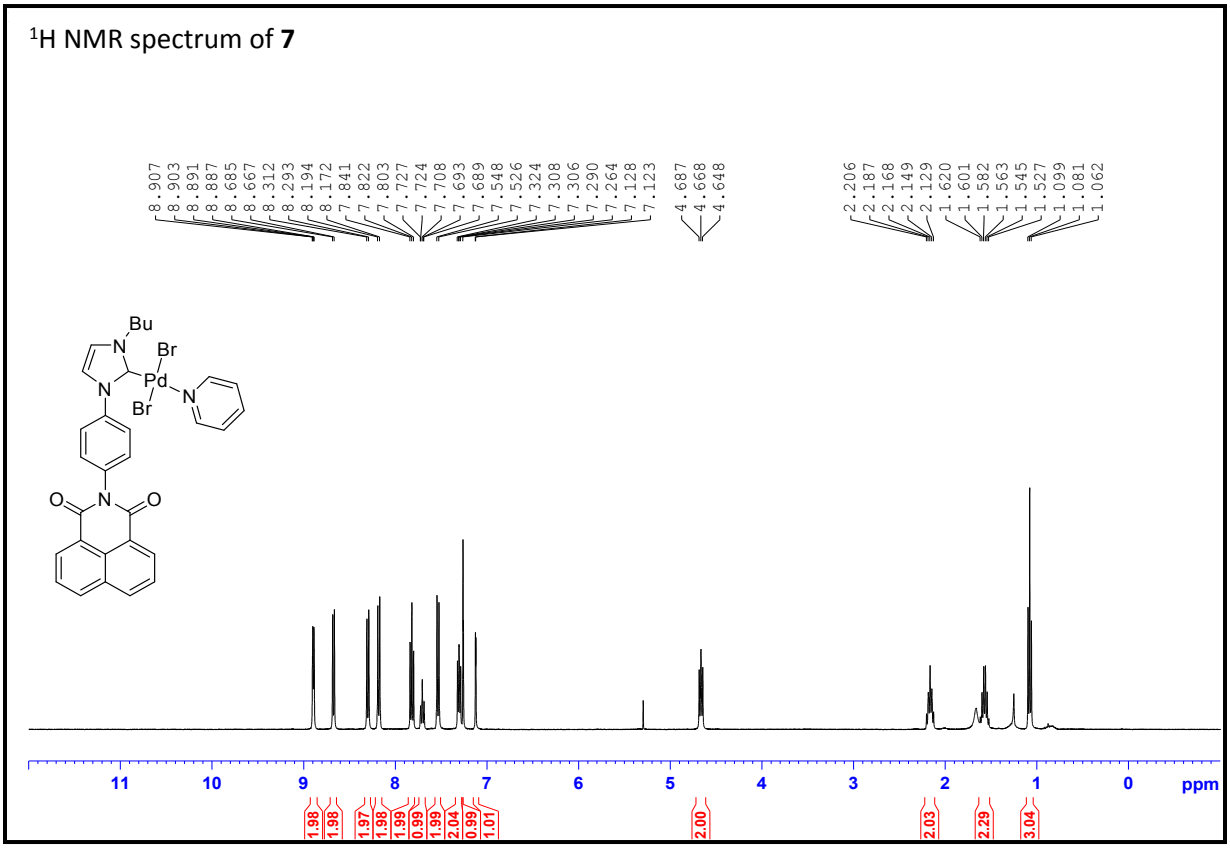
^{1}H NMR spectrum of **6**



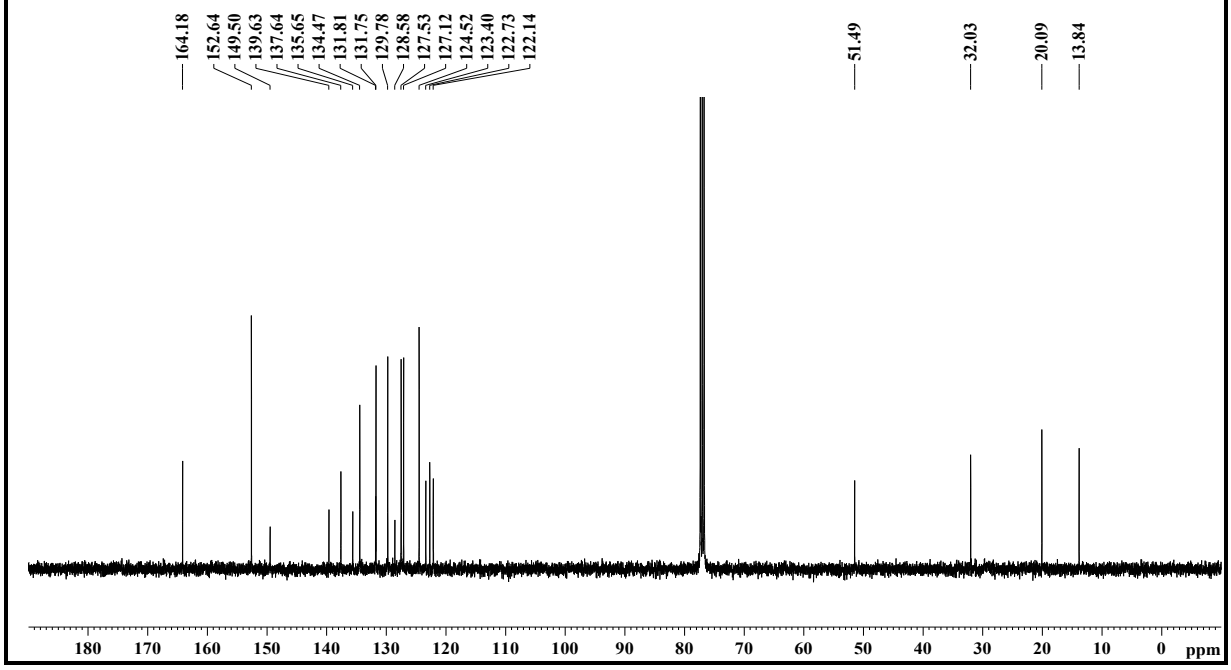
^{13}C NMR spectrum of **6**



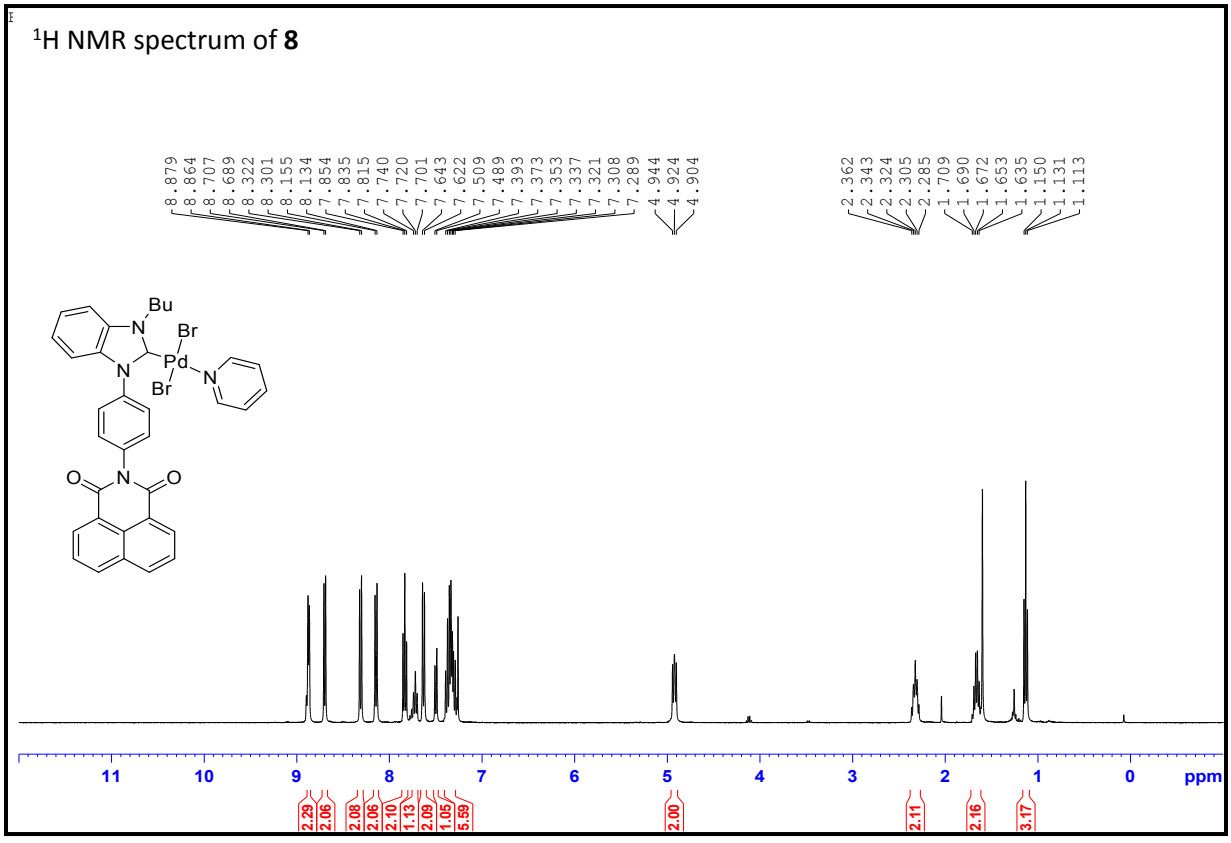
^{1}H NMR spectrum of **7**



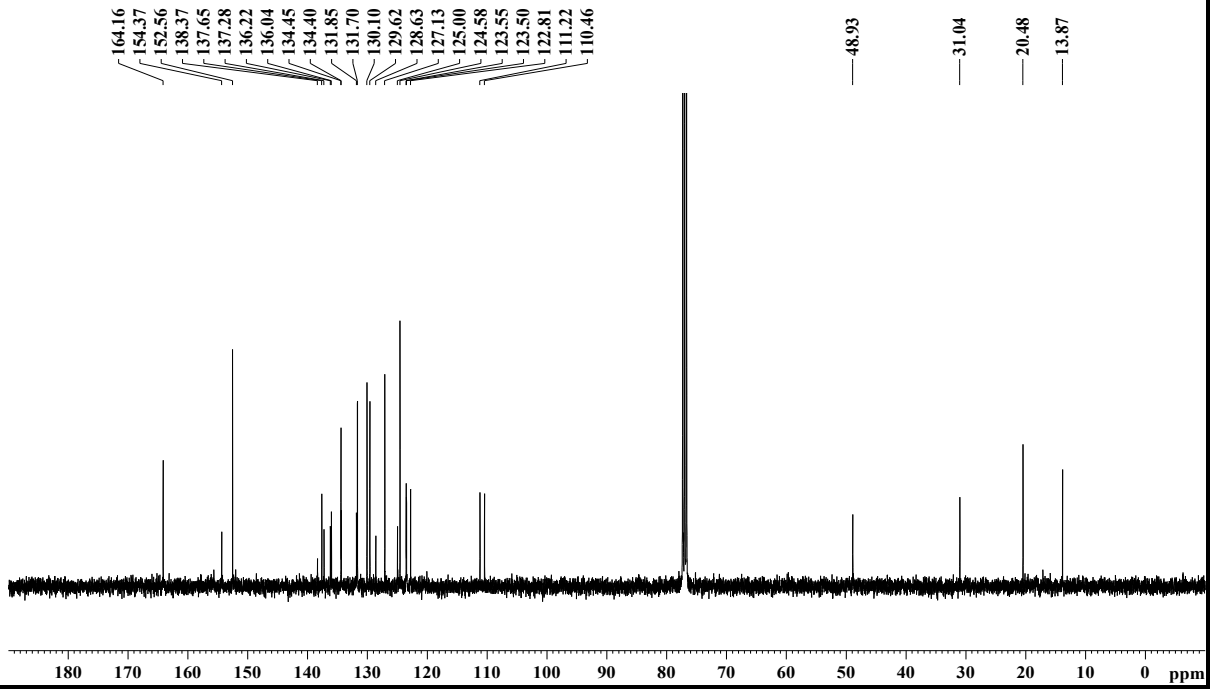
^{13}C NMR spectrum of **7**



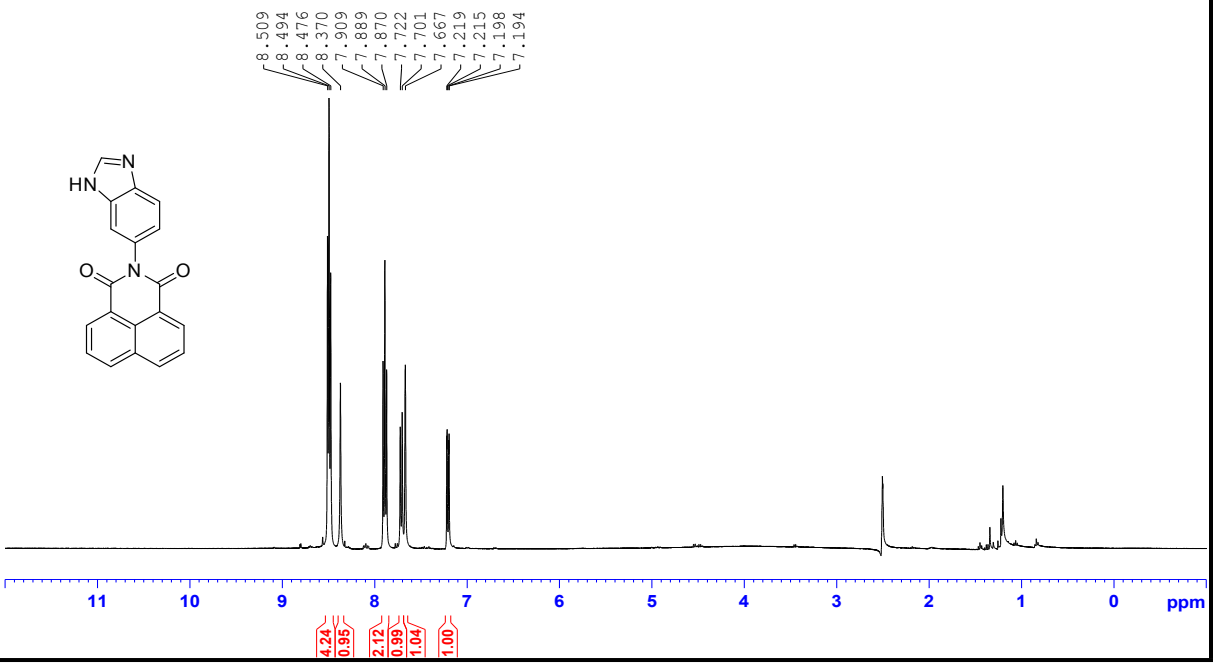
^{1}H NMR spectrum of **8**



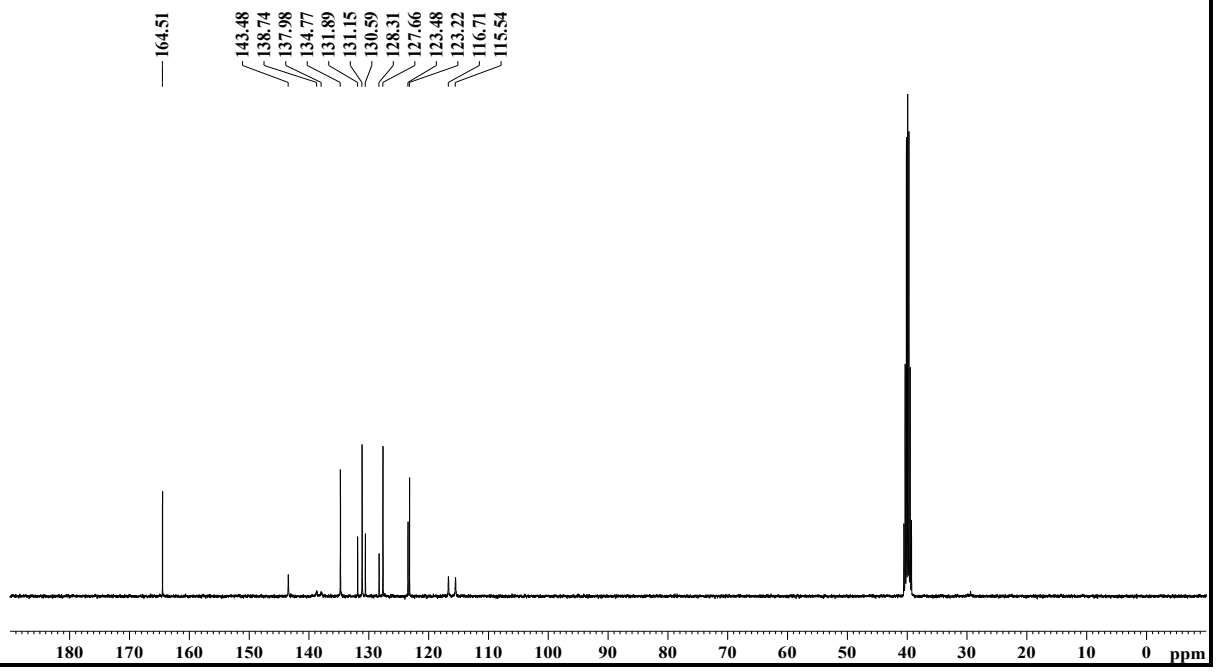
^{13}C NMR spectrum of **8**



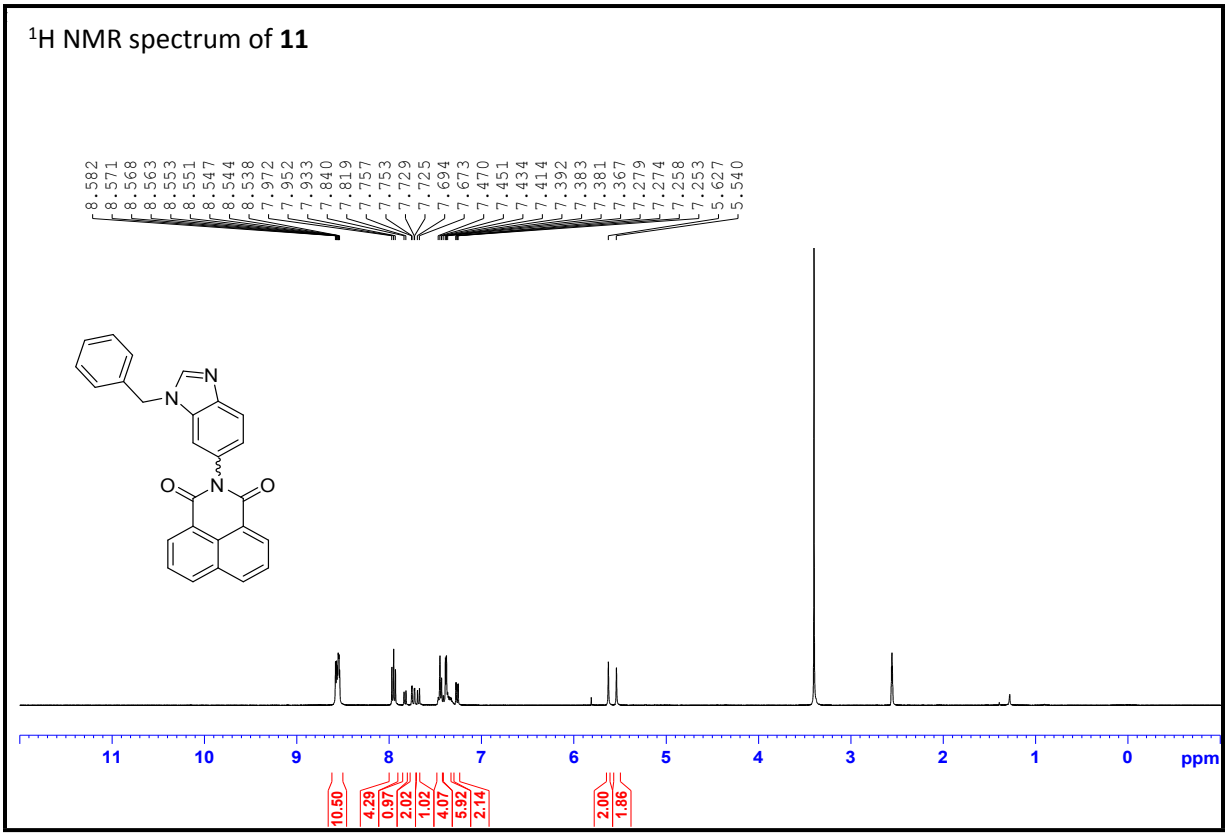
^{1}H NMR spectrum of **10**



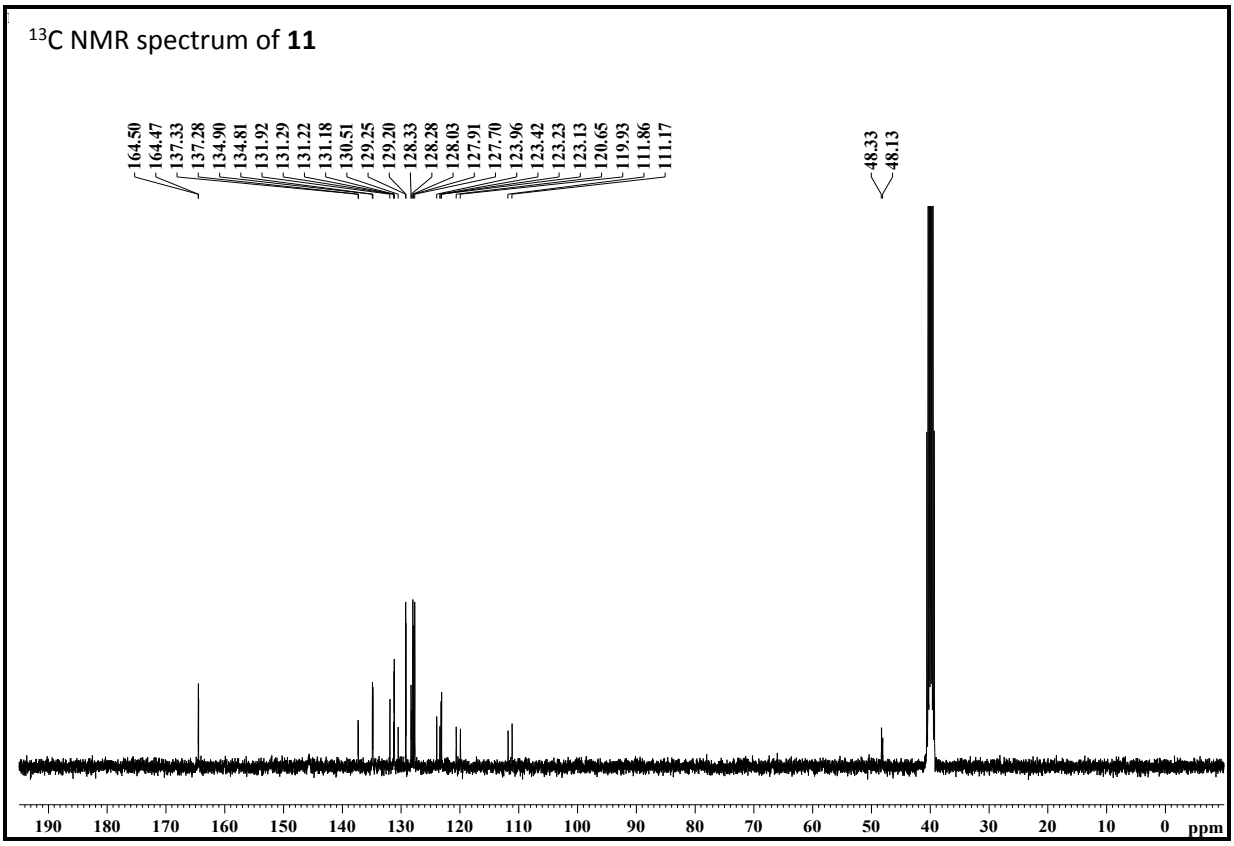
^{13}C NMR spectrum of **10**



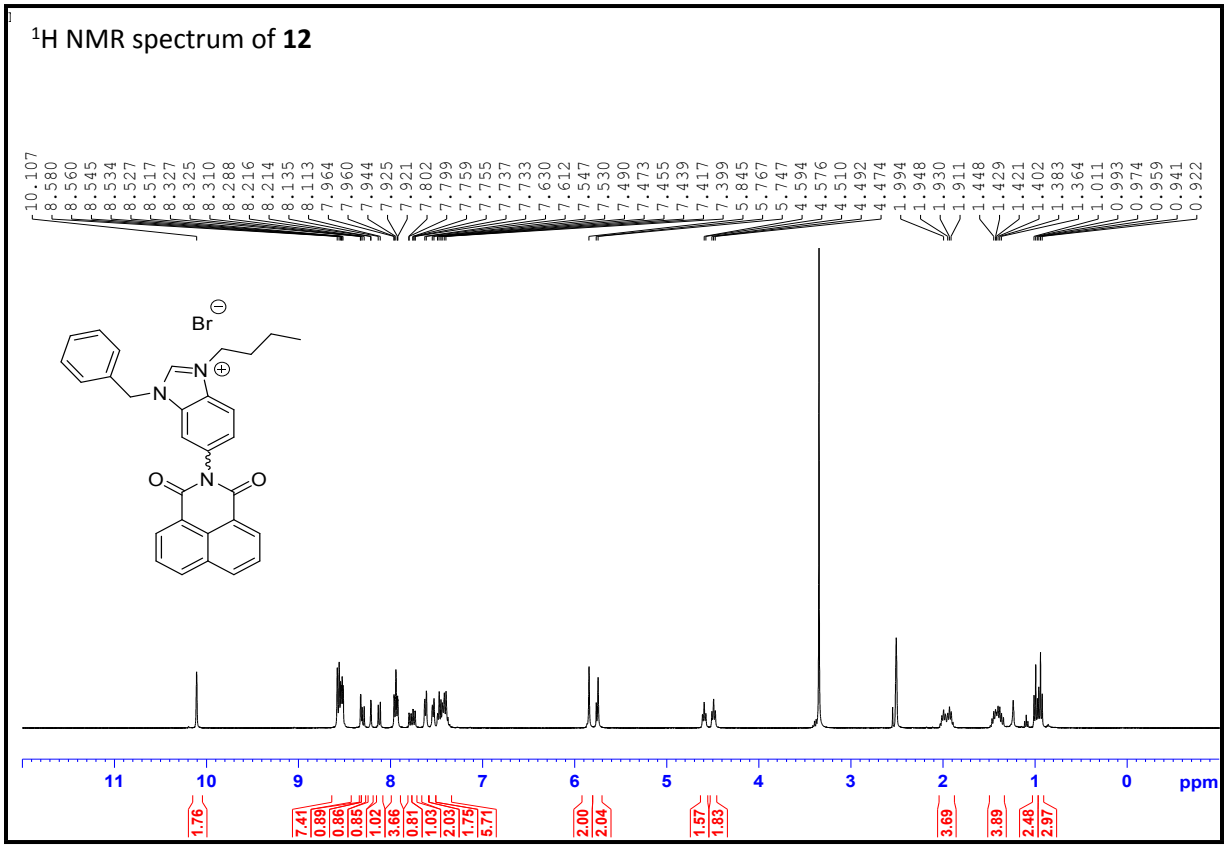
^{1}H NMR spectrum of **11**



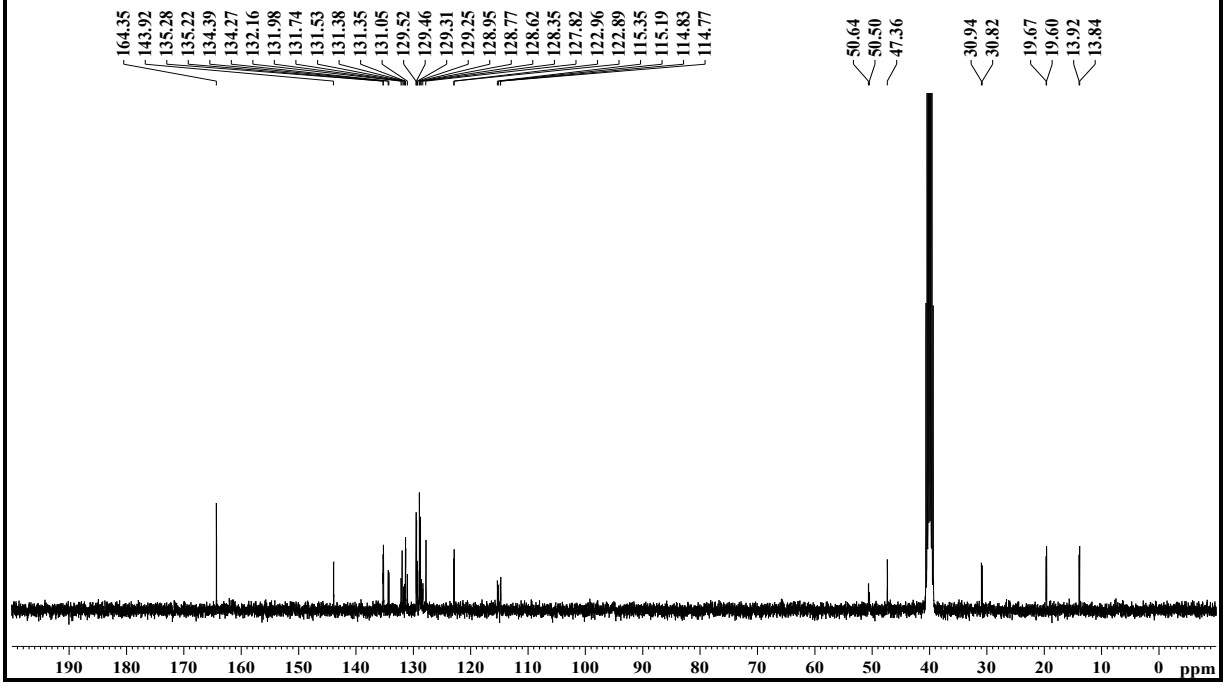
^{13}C NMR spectrum of **11**



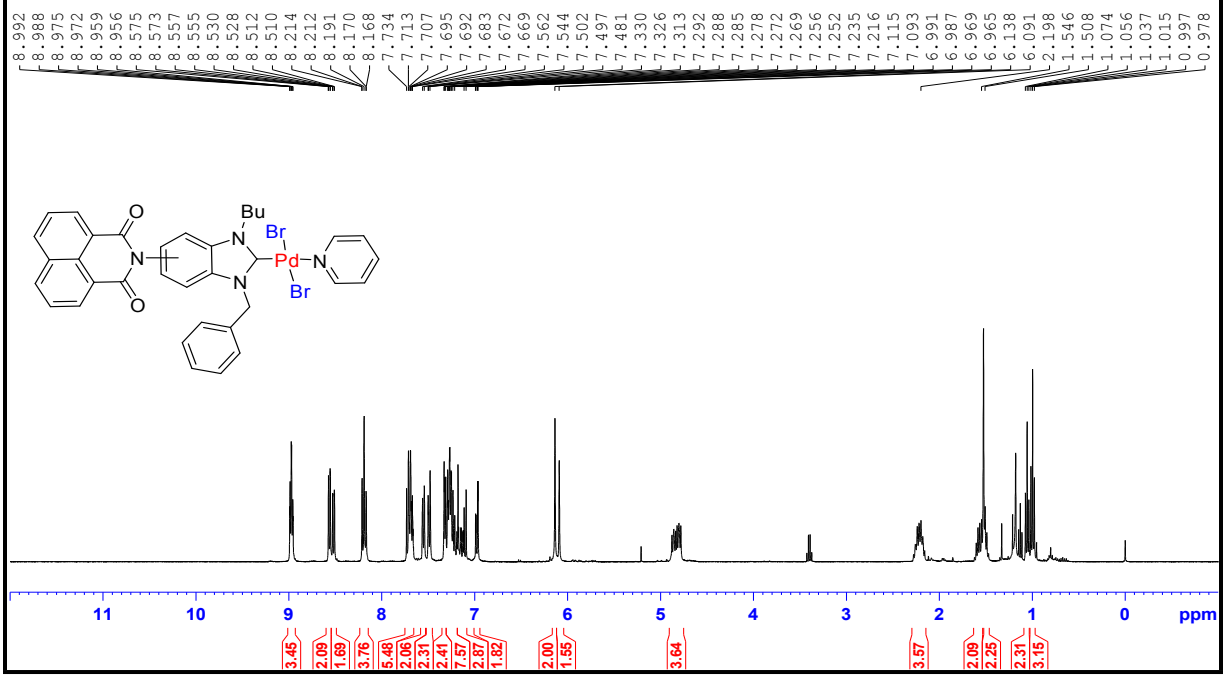
^{1}H NMR spectrum of **12**



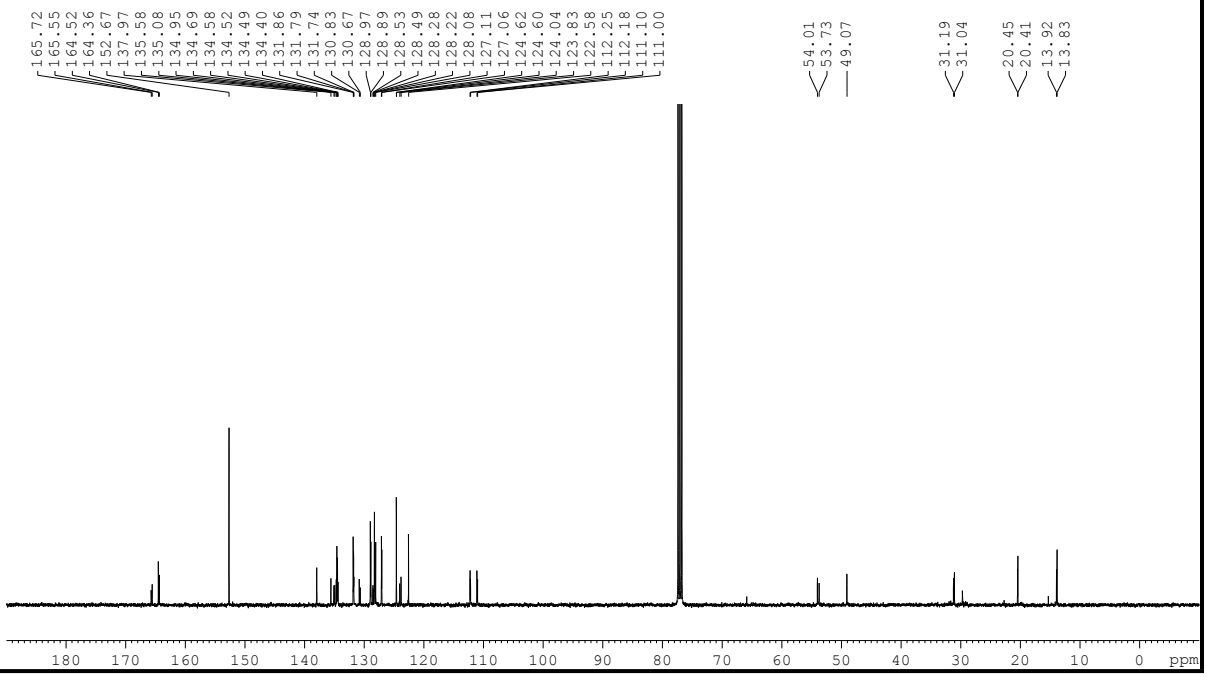
^{13}C NMR spectrum of 12



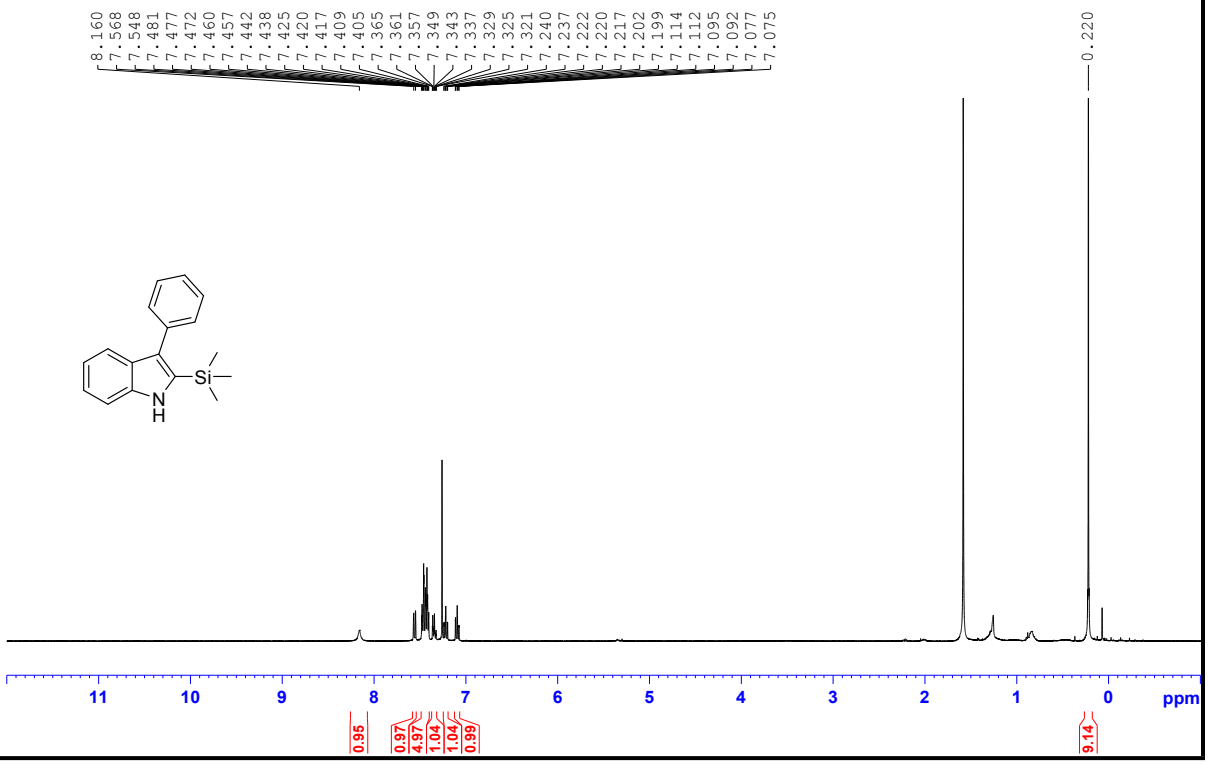
^{1}H NMR spectrum of **13**



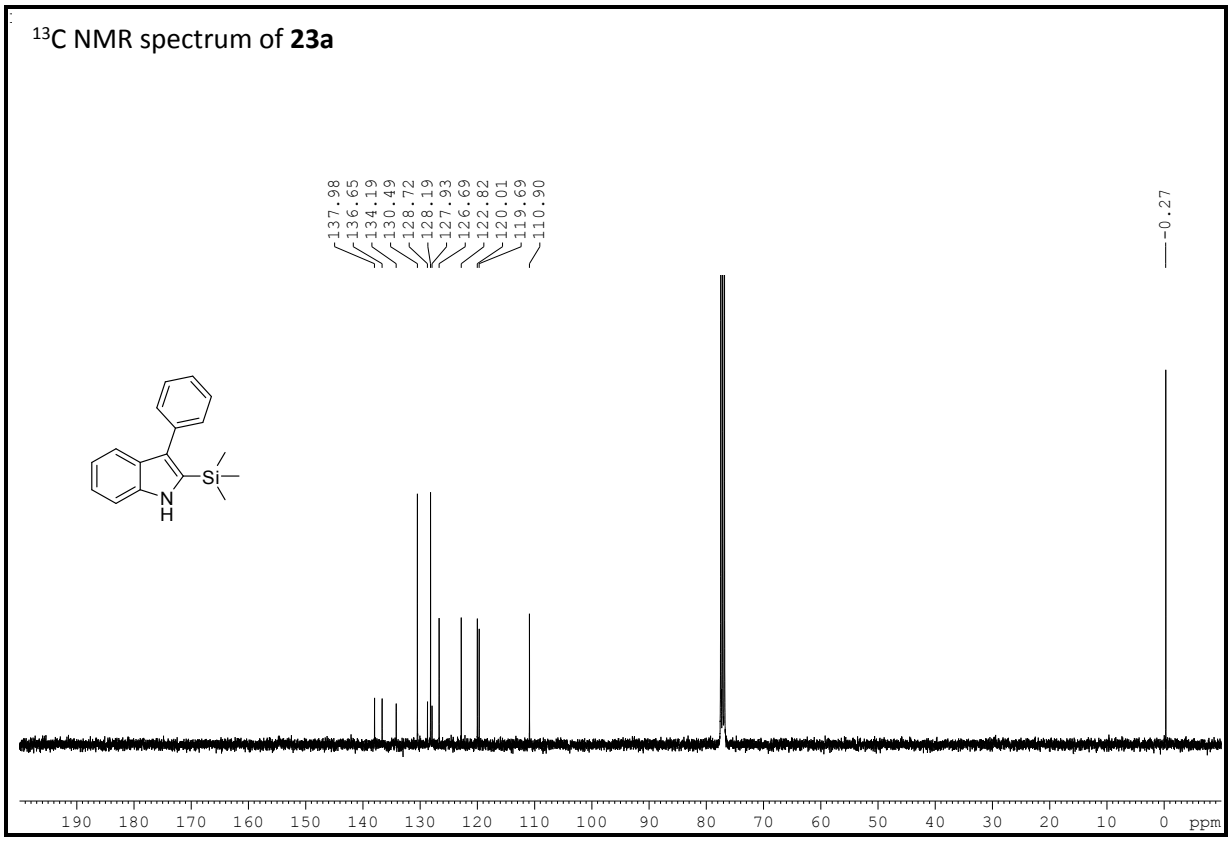
^{13}C NMR spectrum of **13**



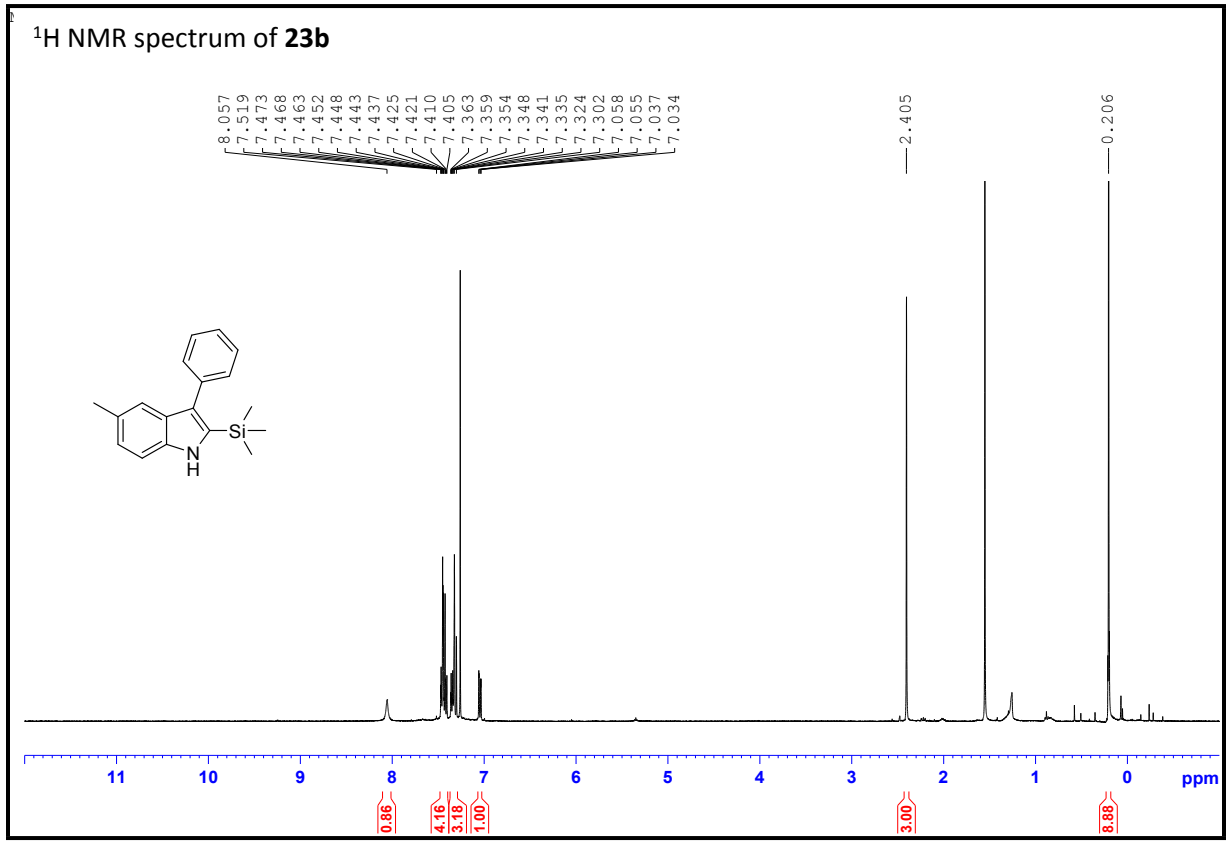
^{1}H NMR spectrum of **23a**



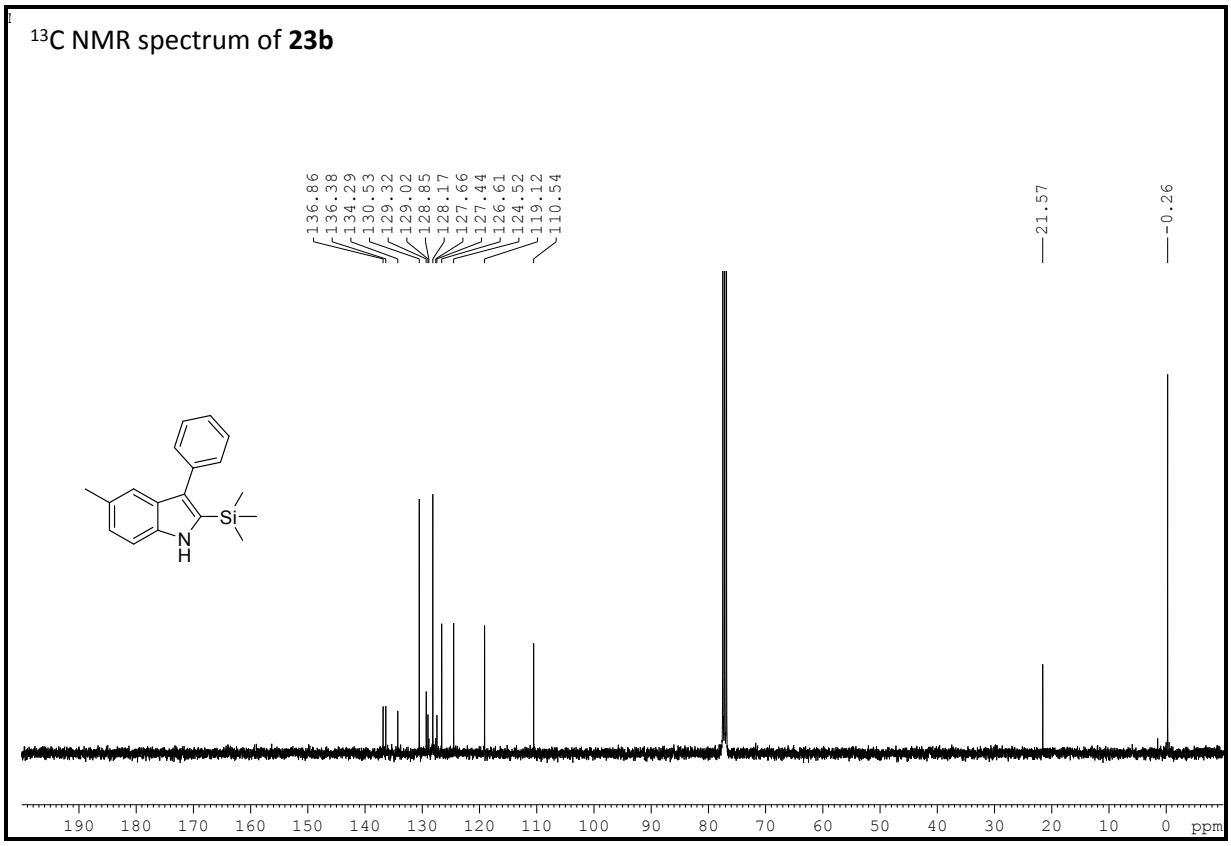
^{13}C NMR spectrum of **23a**



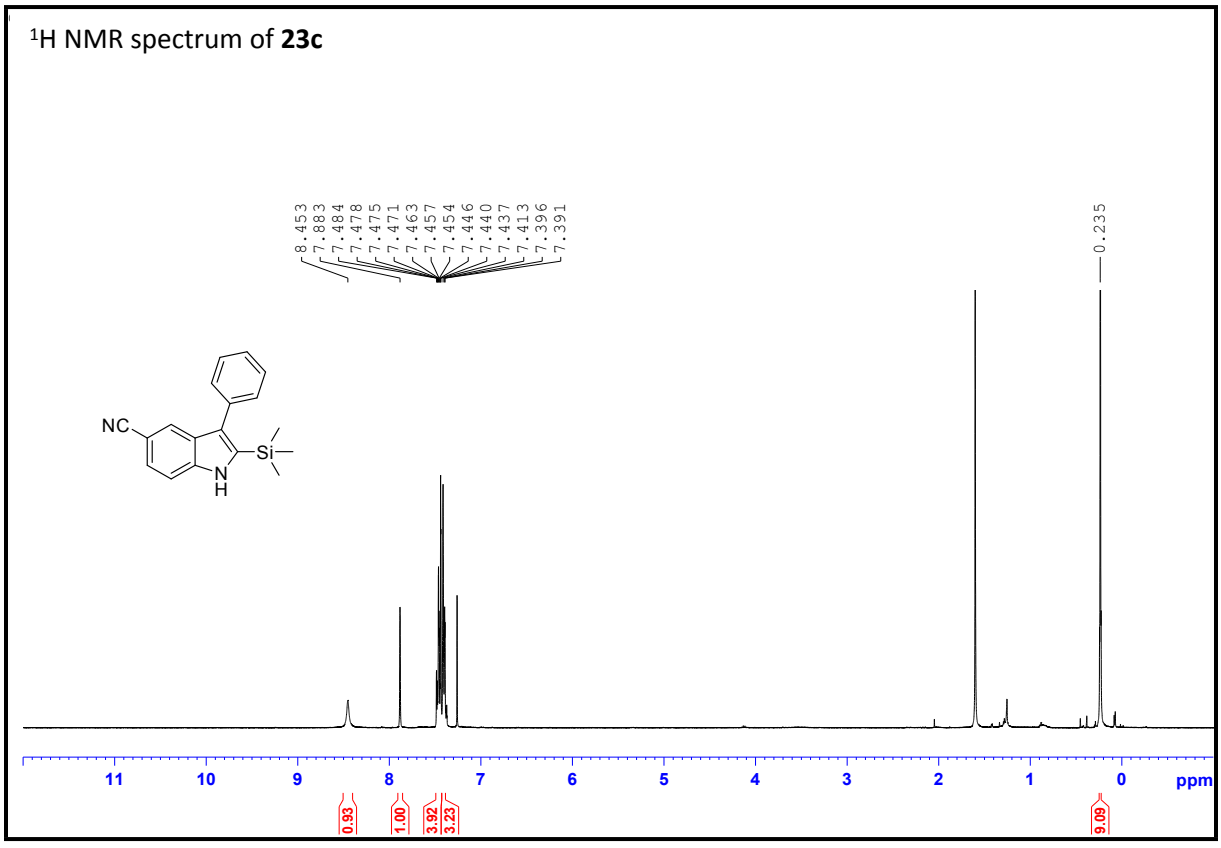
^{1}H NMR spectrum of **23b**



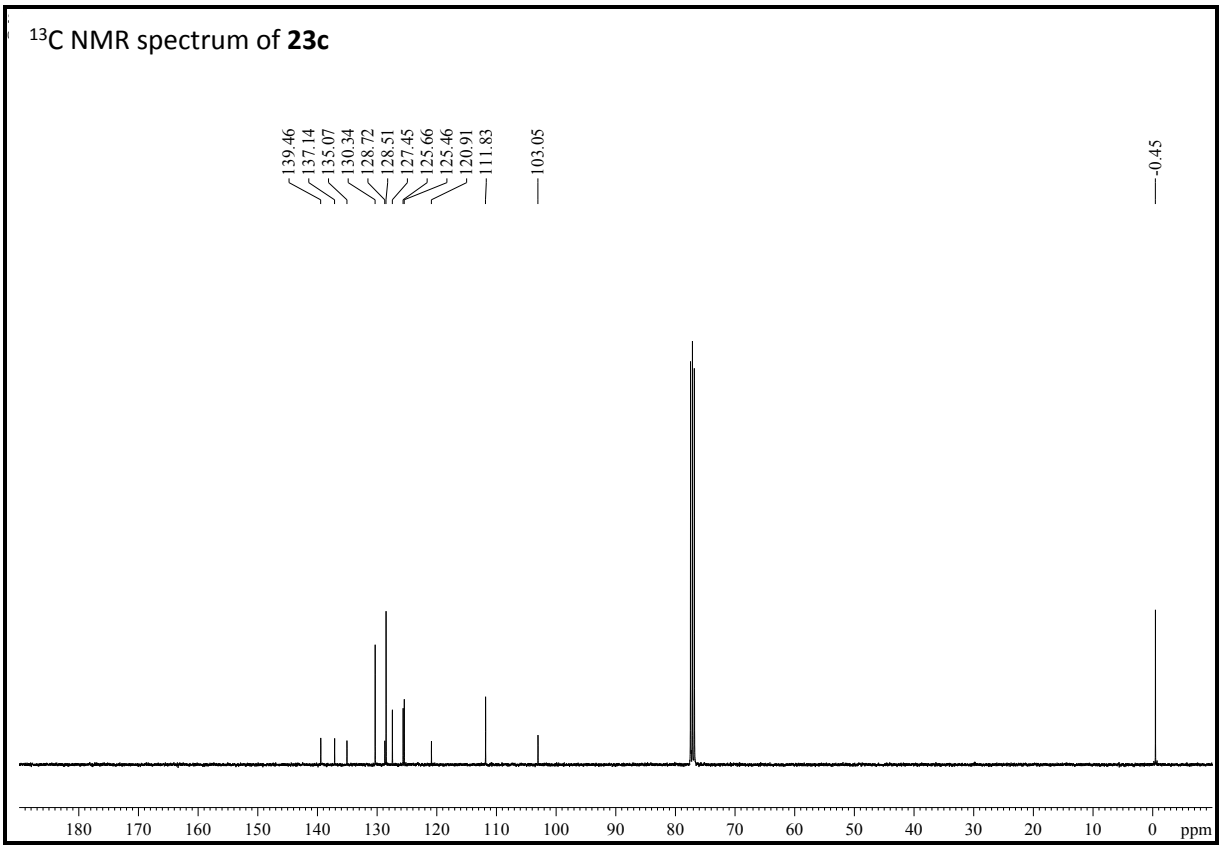
^{13}C NMR spectrum of **23b**



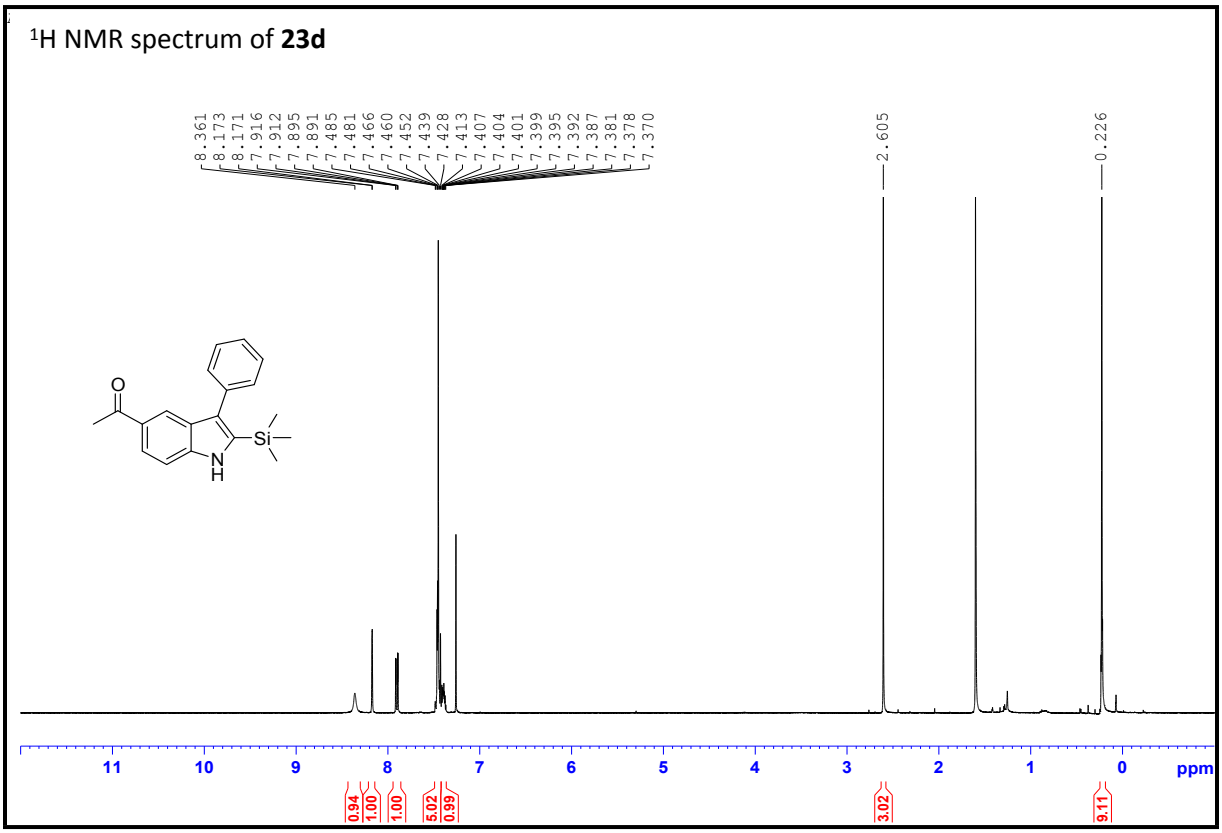
^{1}H NMR spectrum of **23c**



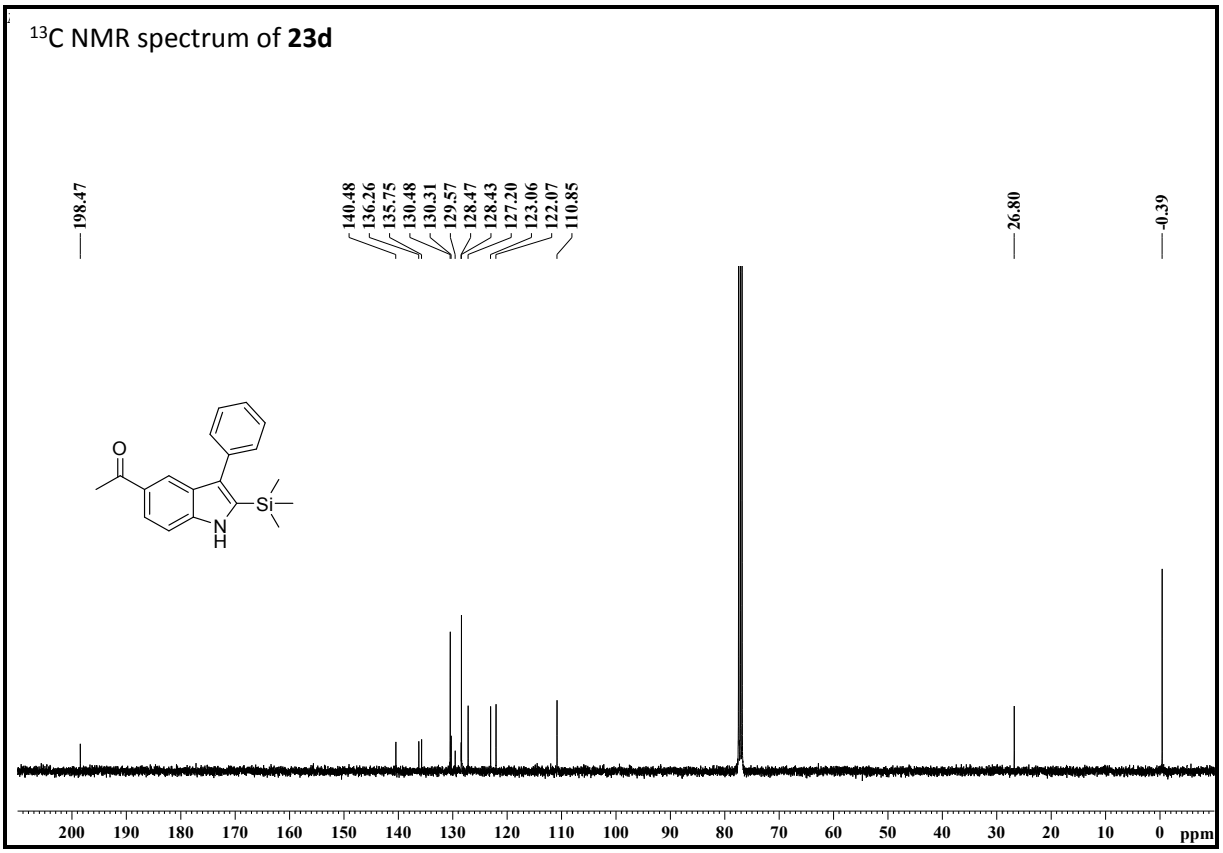
^{13}C NMR spectrum of **23c**



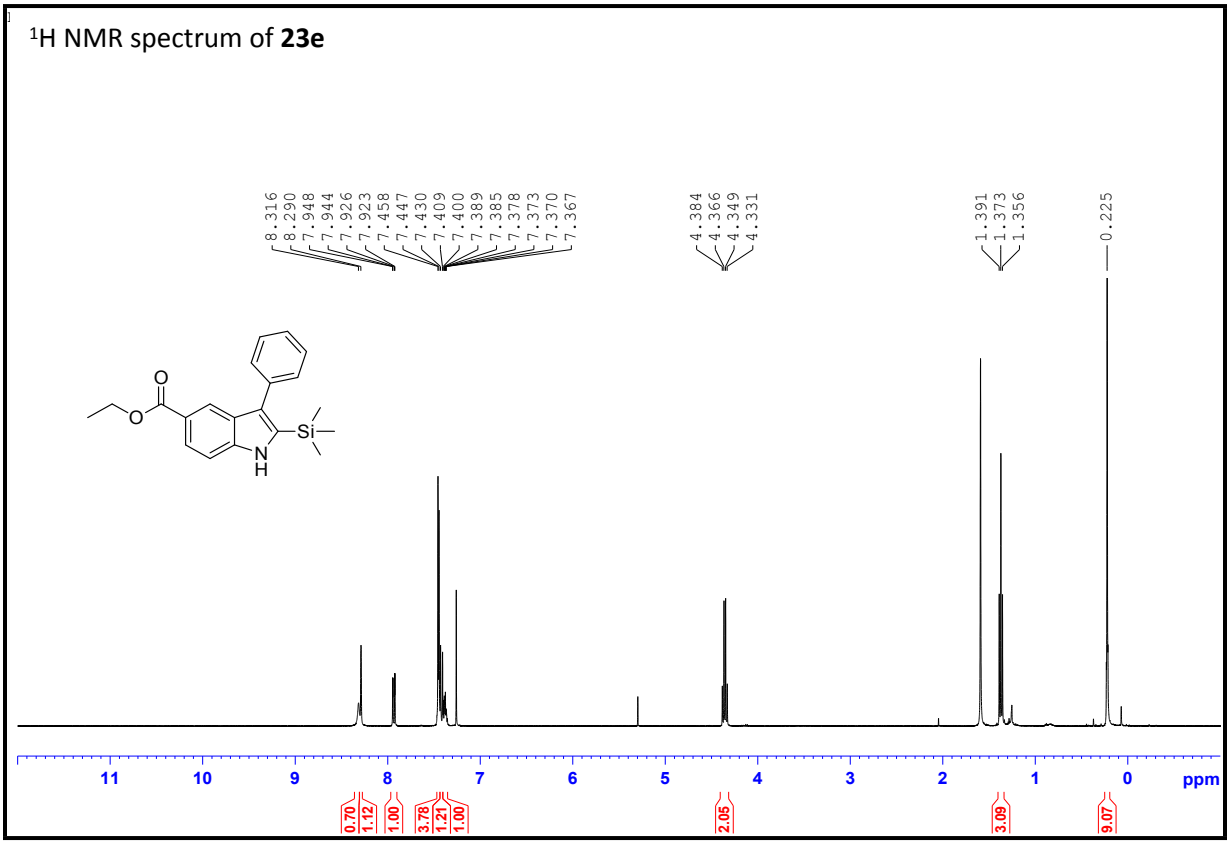
^{1}H NMR spectrum of **23d**



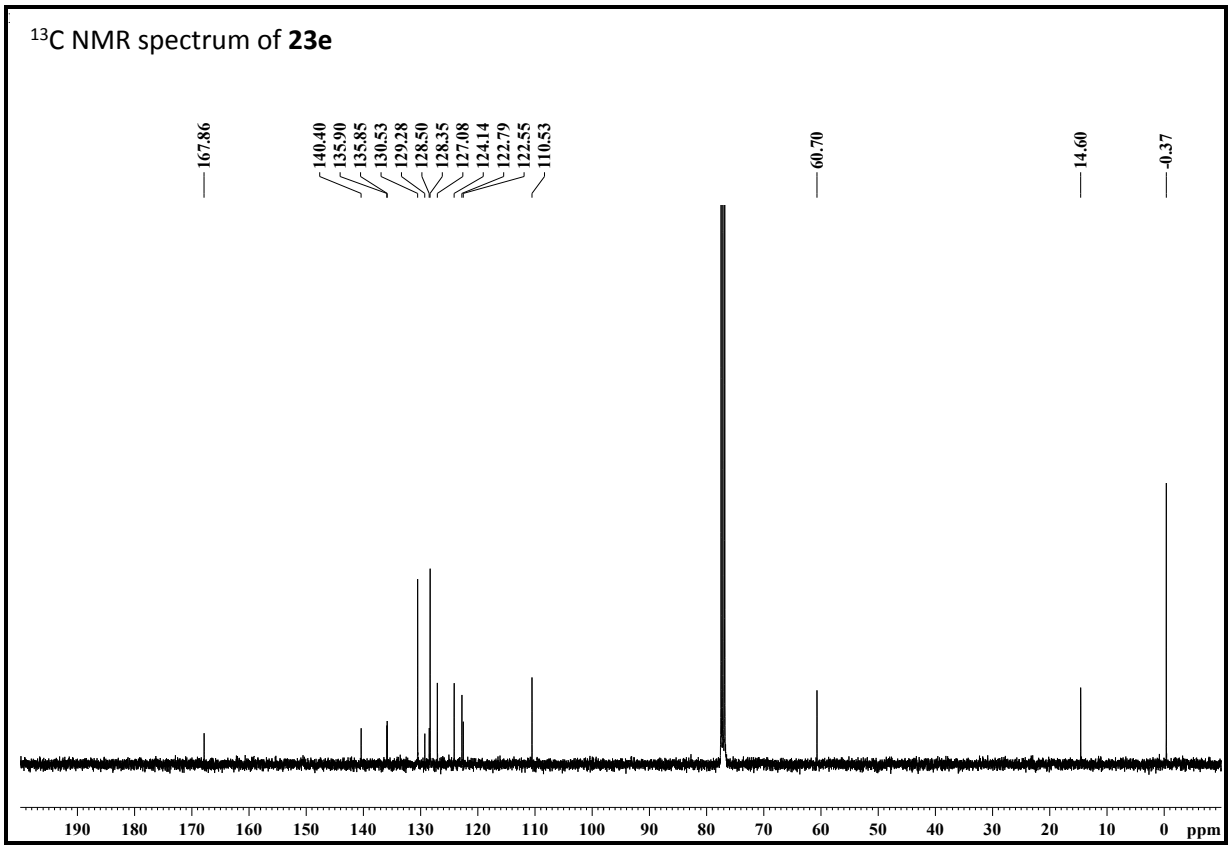
^{13}C NMR spectrum of **23d**



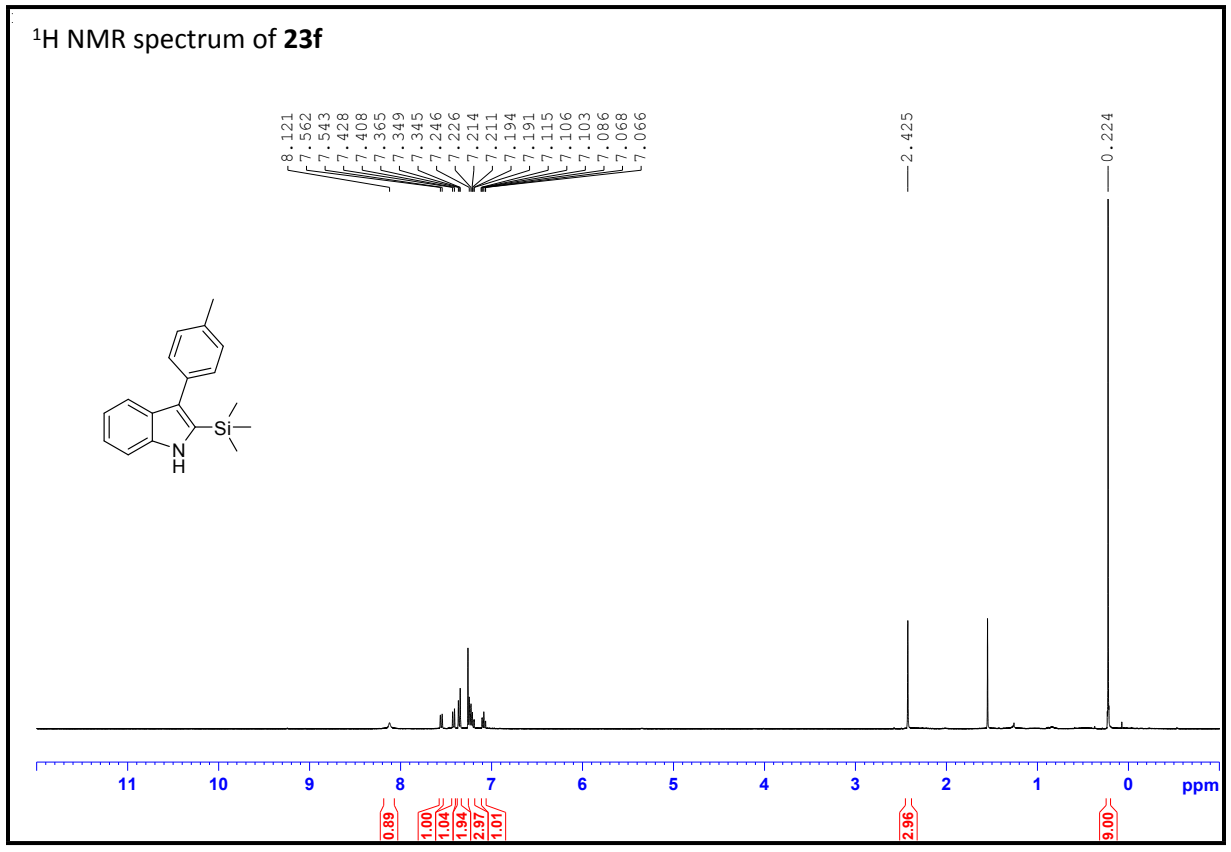
^{1}H NMR spectrum of **23e**



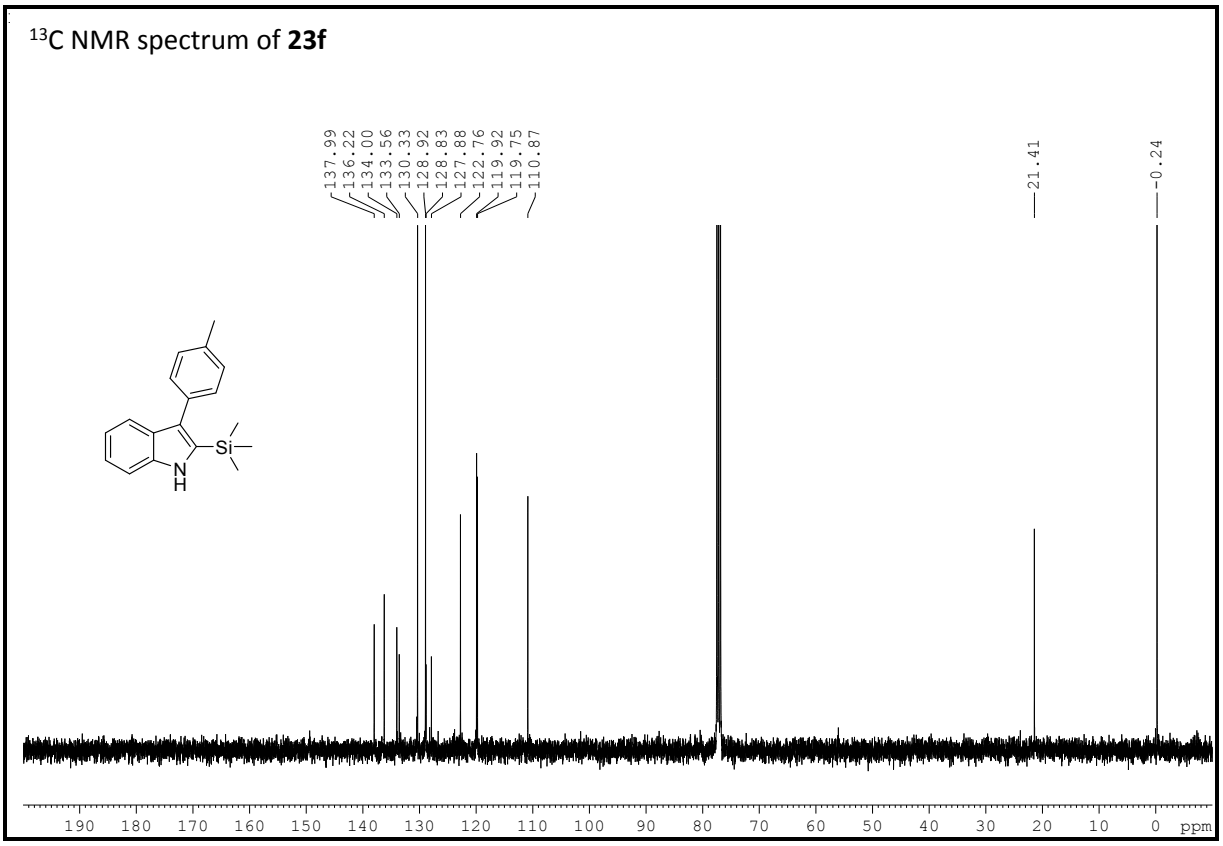
^{13}C NMR spectrum of **23e**



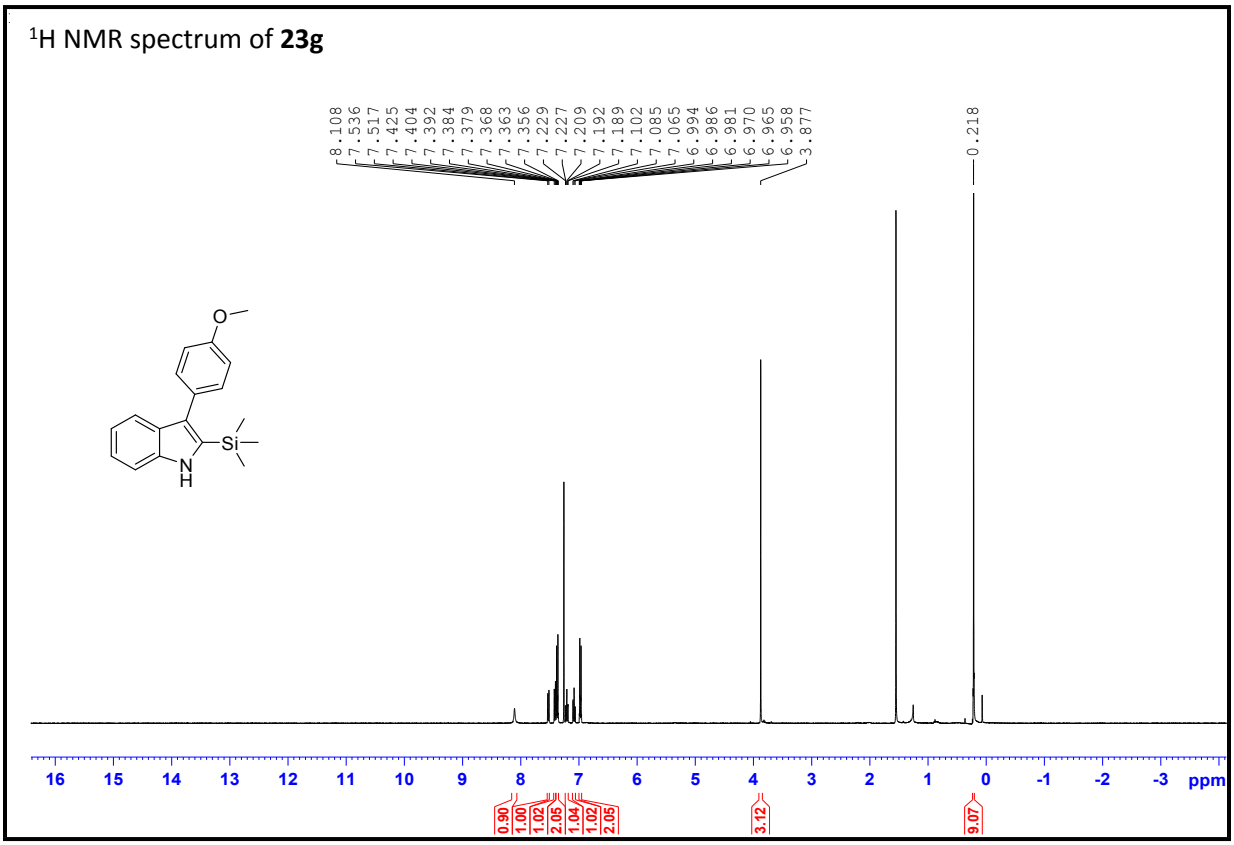
^{1}H NMR spectrum of **23f**



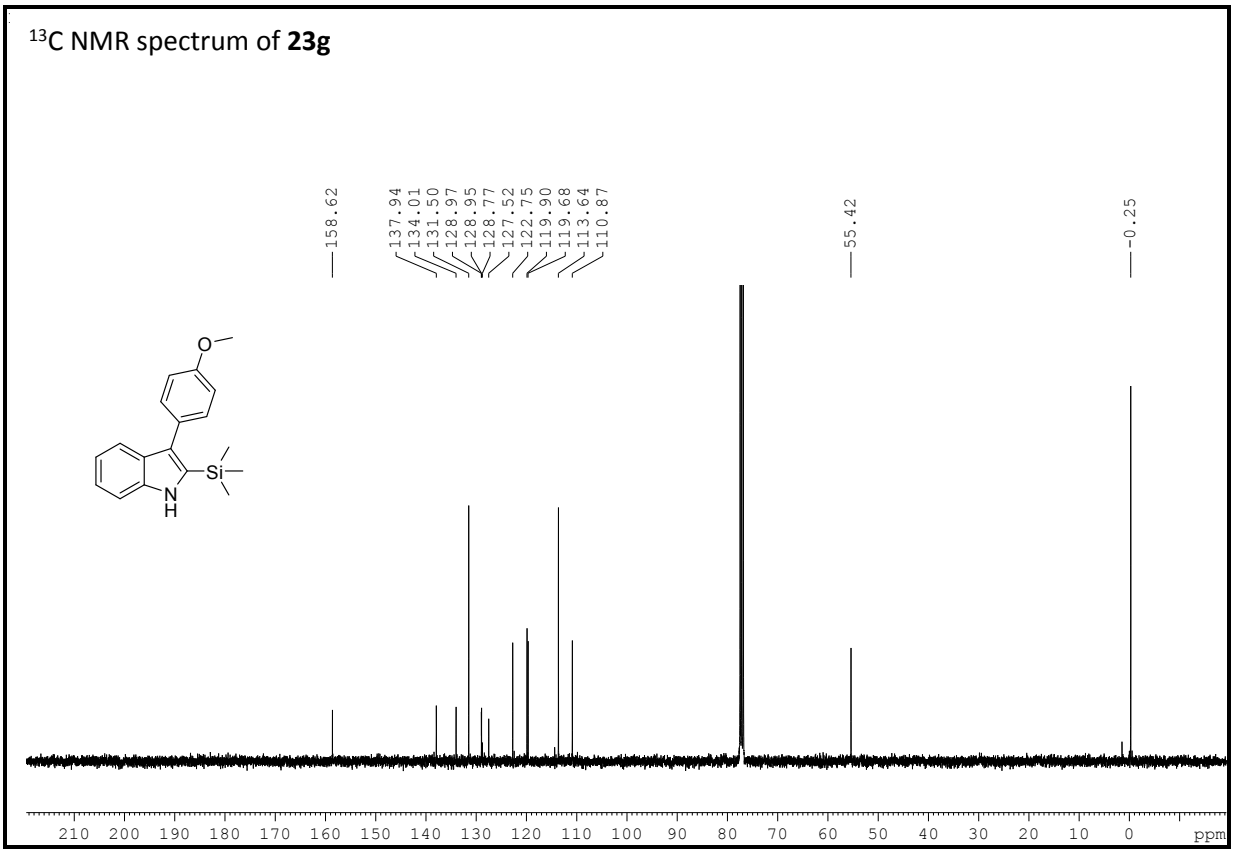
^{13}C NMR spectrum of **23f**



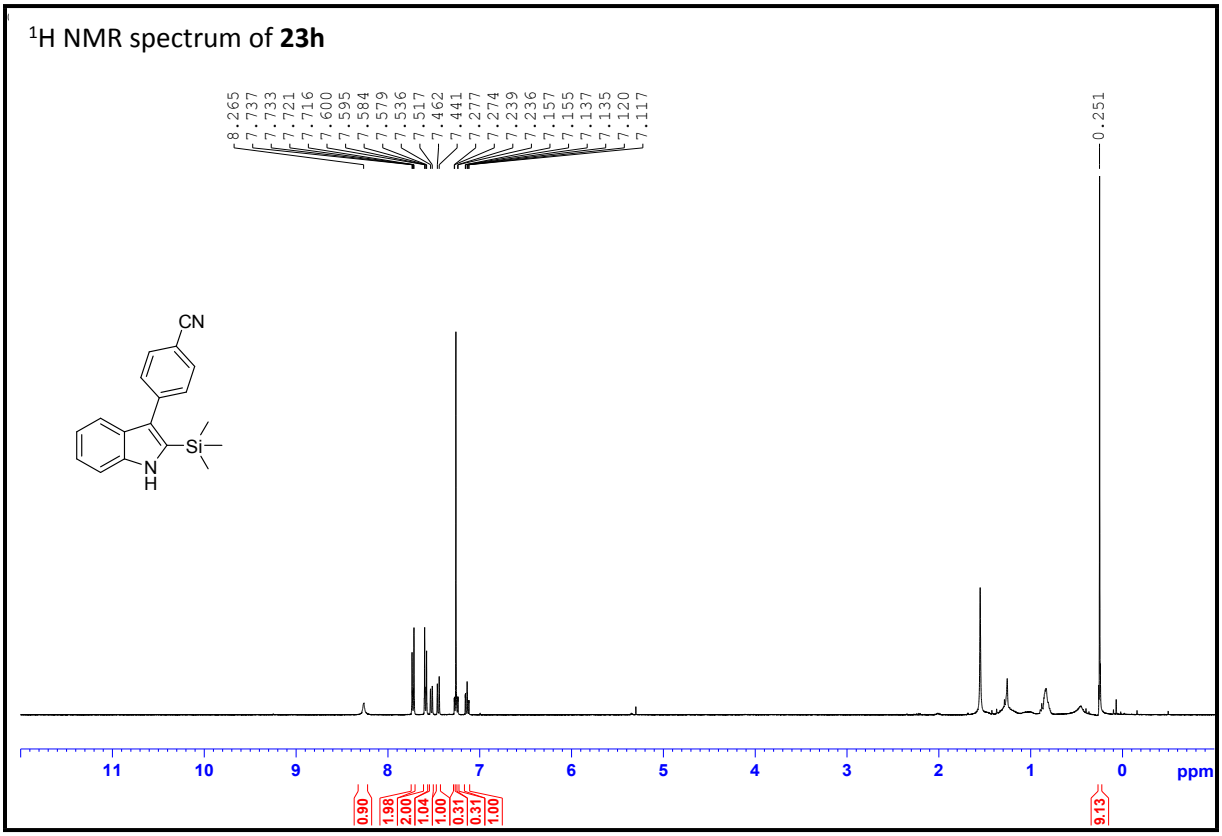
^{1}H NMR spectrum of **23g**



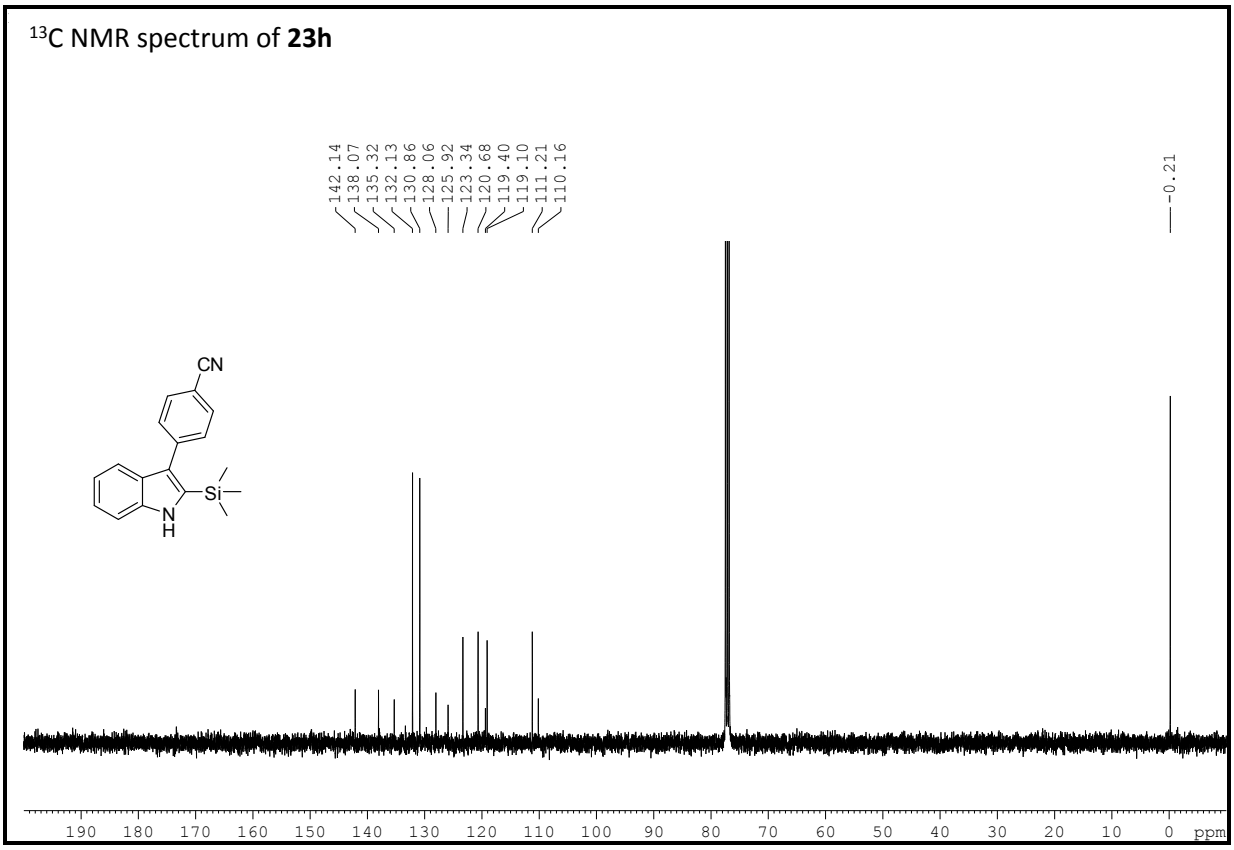
^{13}C NMR spectrum of **23g**



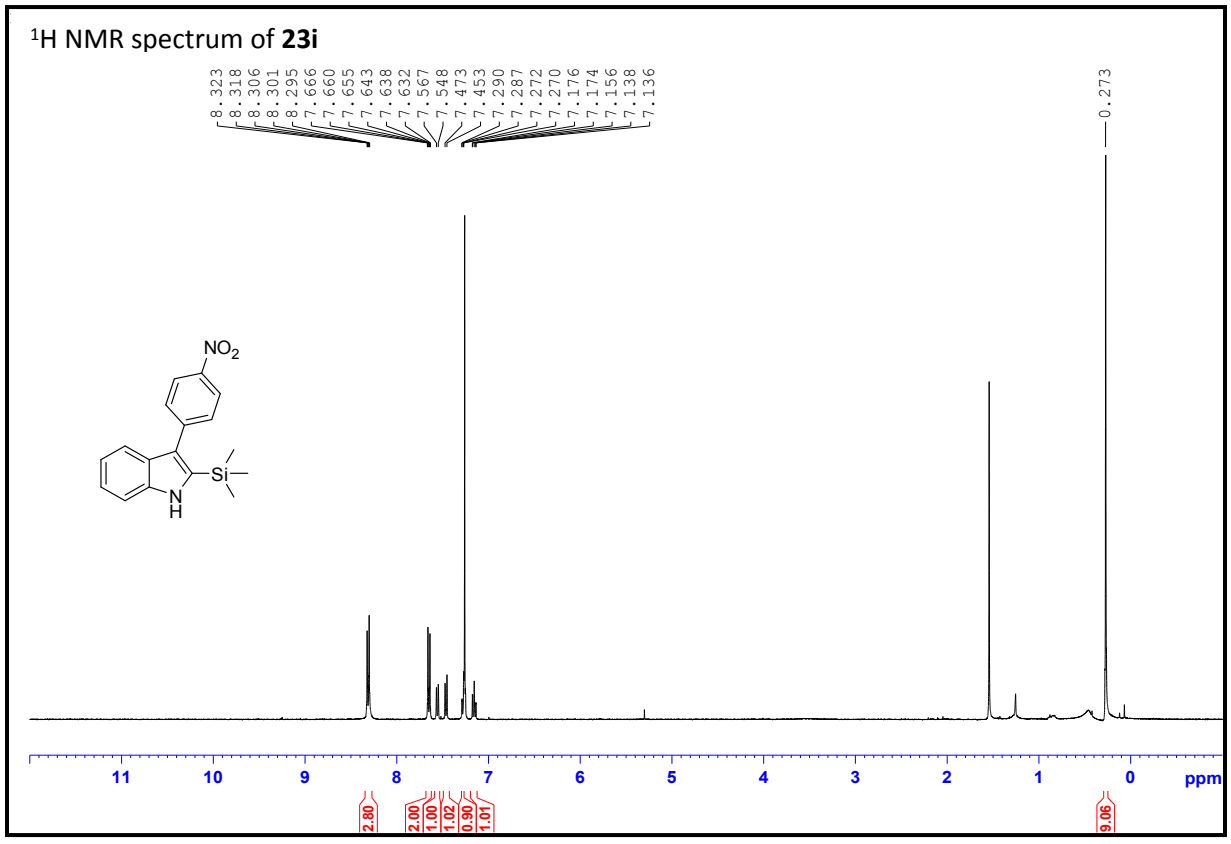
^{1}H NMR spectrum of **23h**



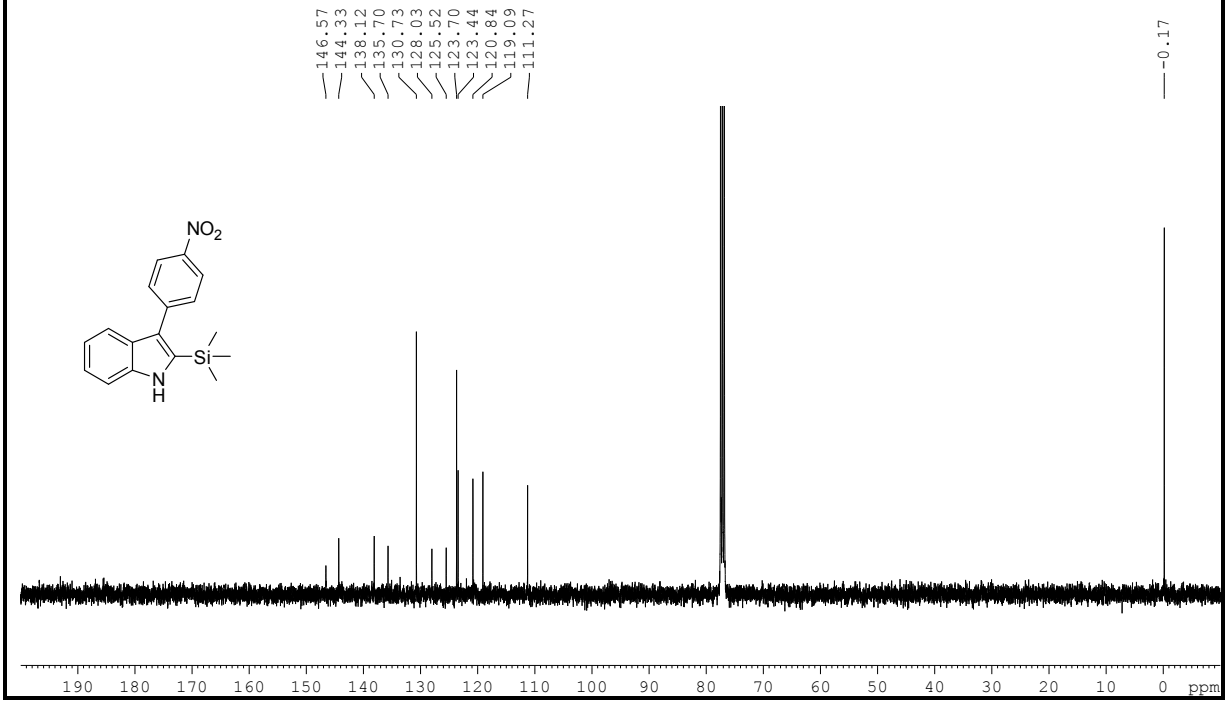
^{13}C NMR spectrum of **23h**



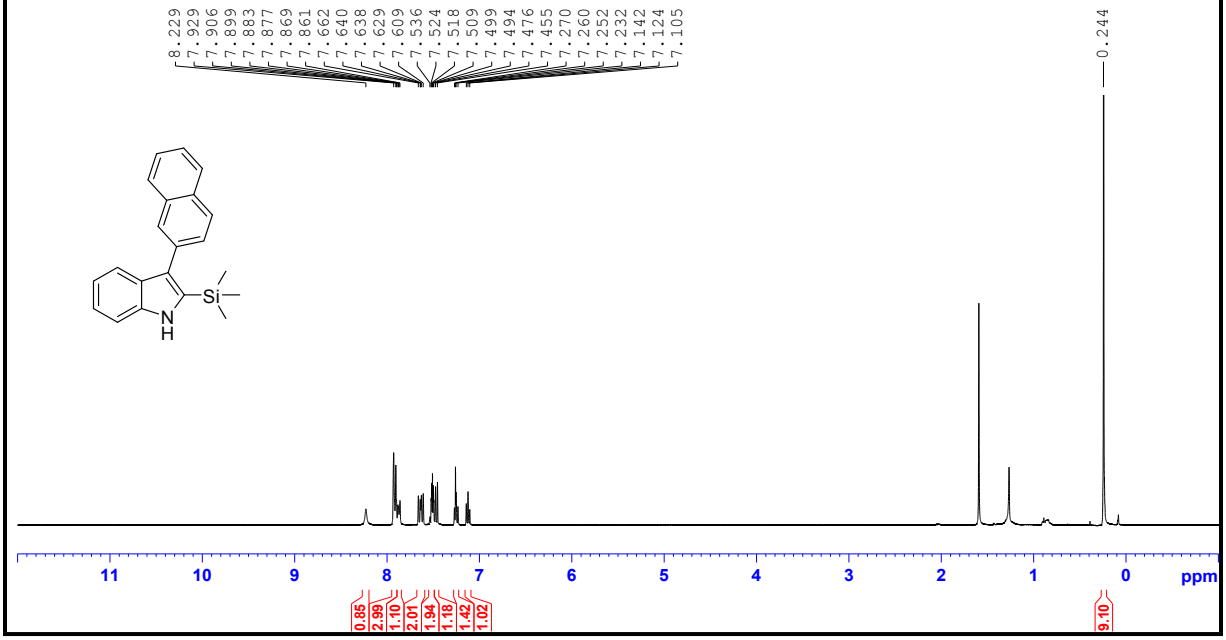
^{1}H NMR spectrum of **23i**



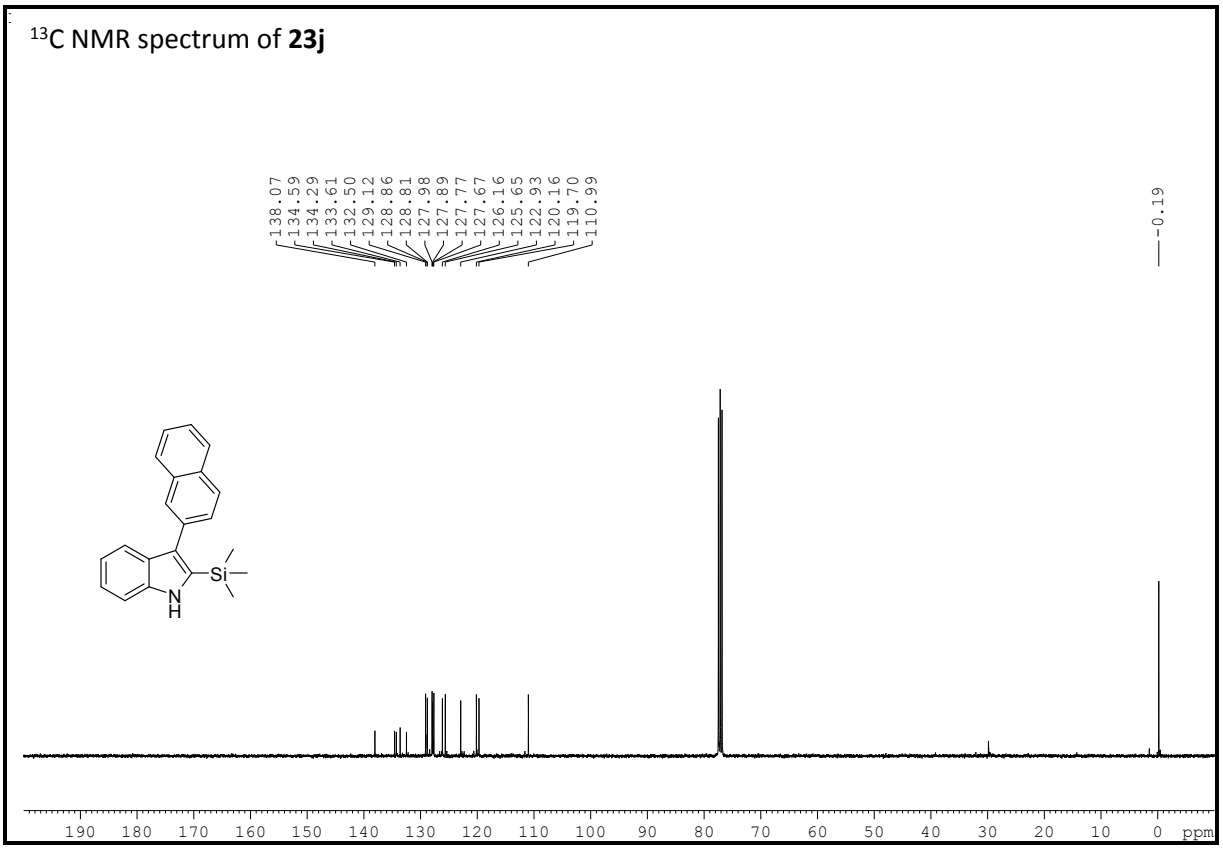
^{13}C NMR spectrum of **23i**



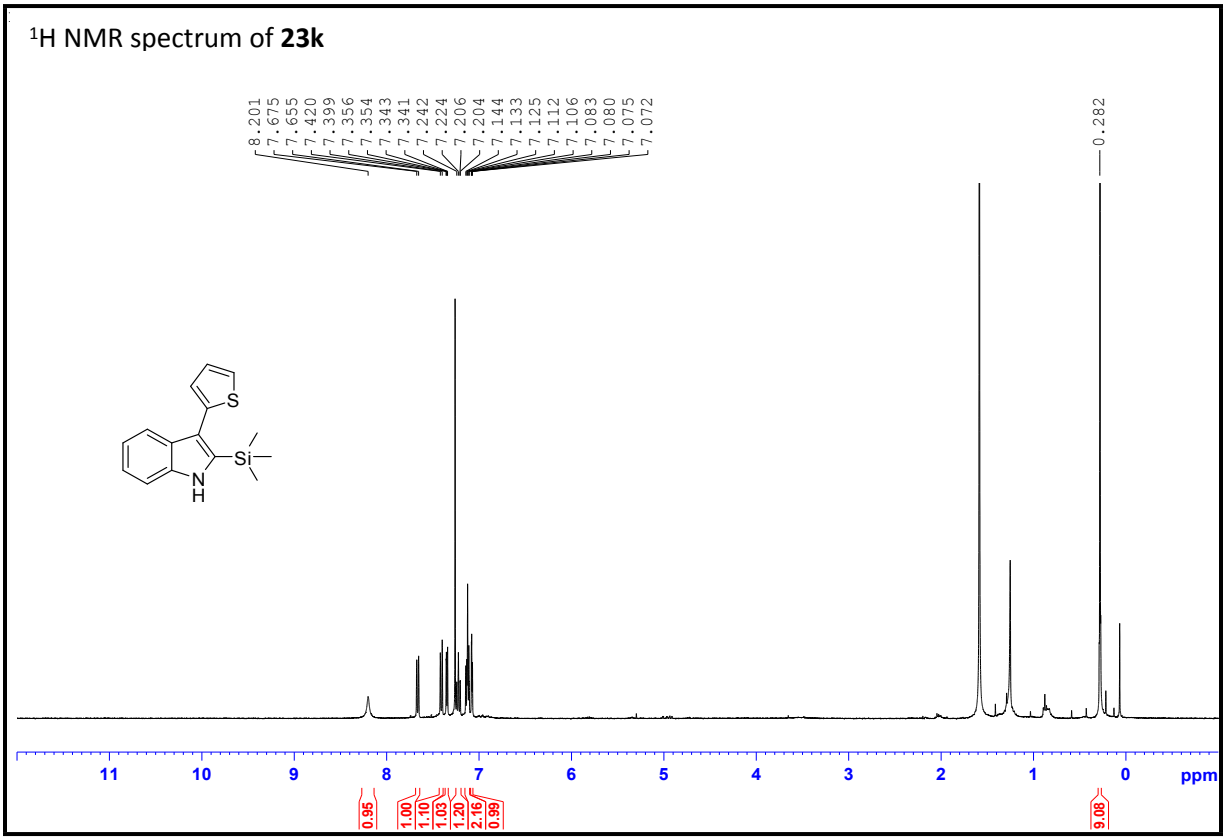
^{1}H NMR spectrum of **23j**



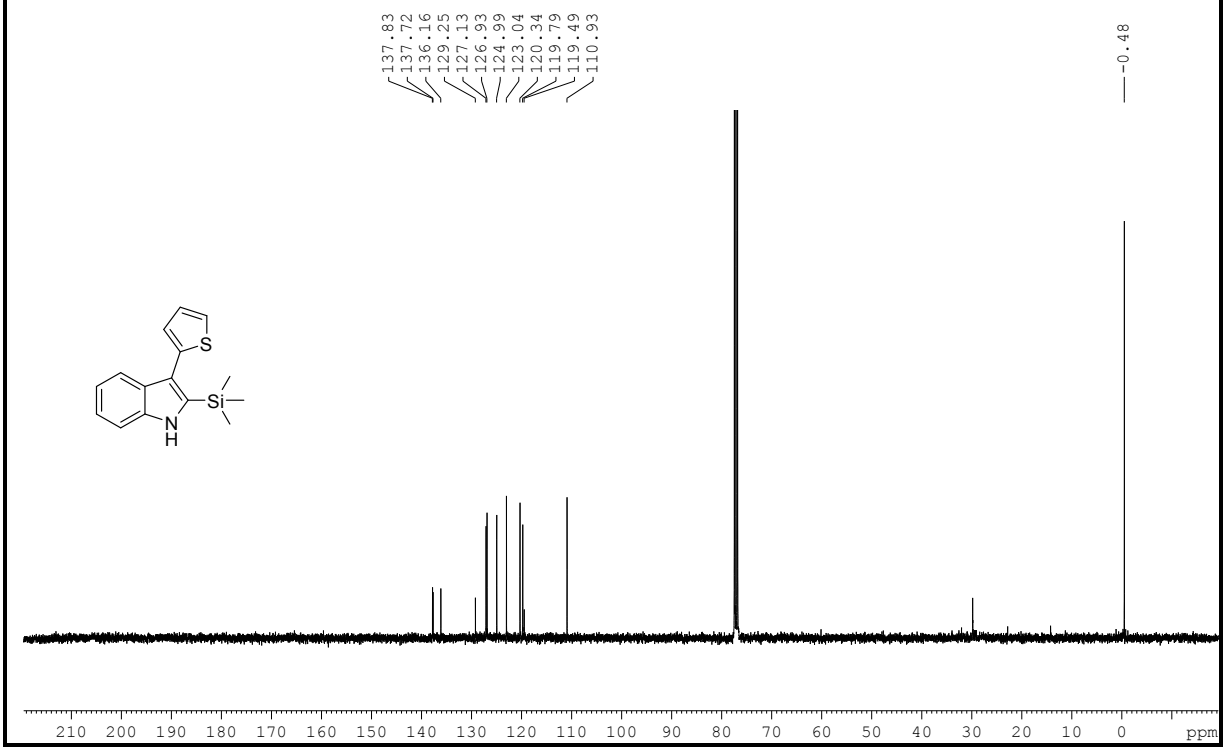
^{13}C NMR spectrum of **23j**



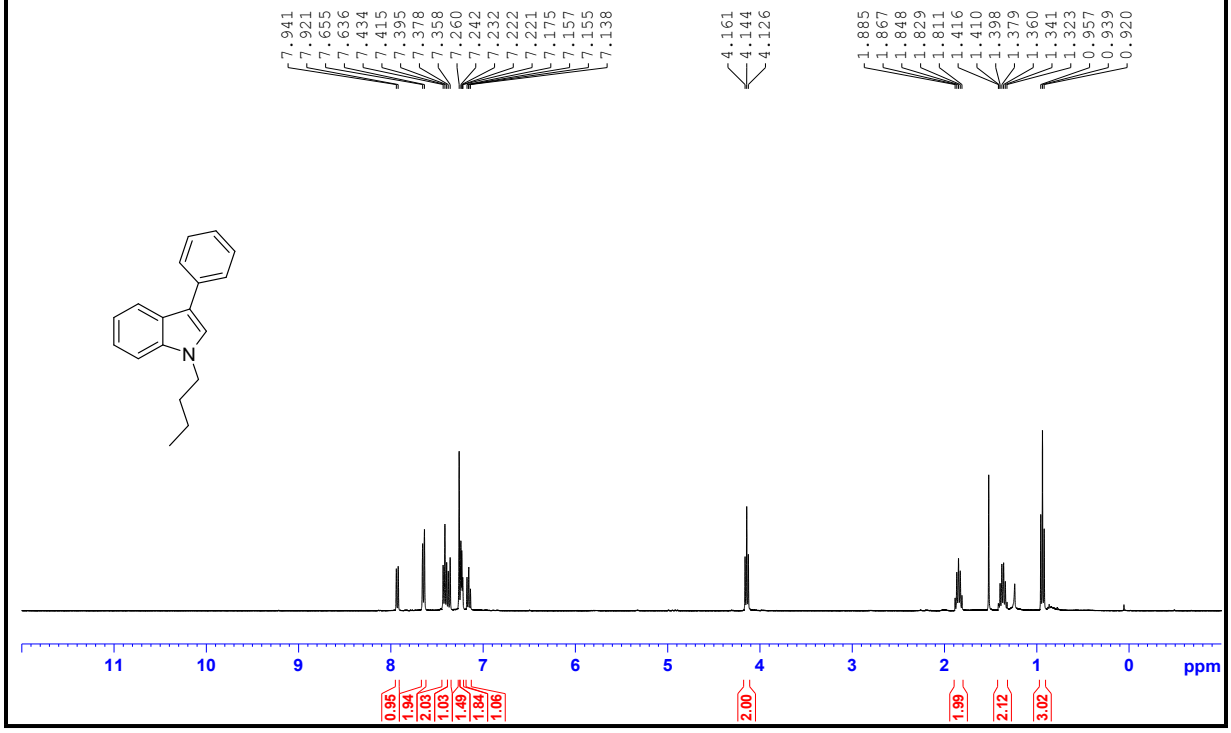
^{1}H NMR spectrum of **23k**



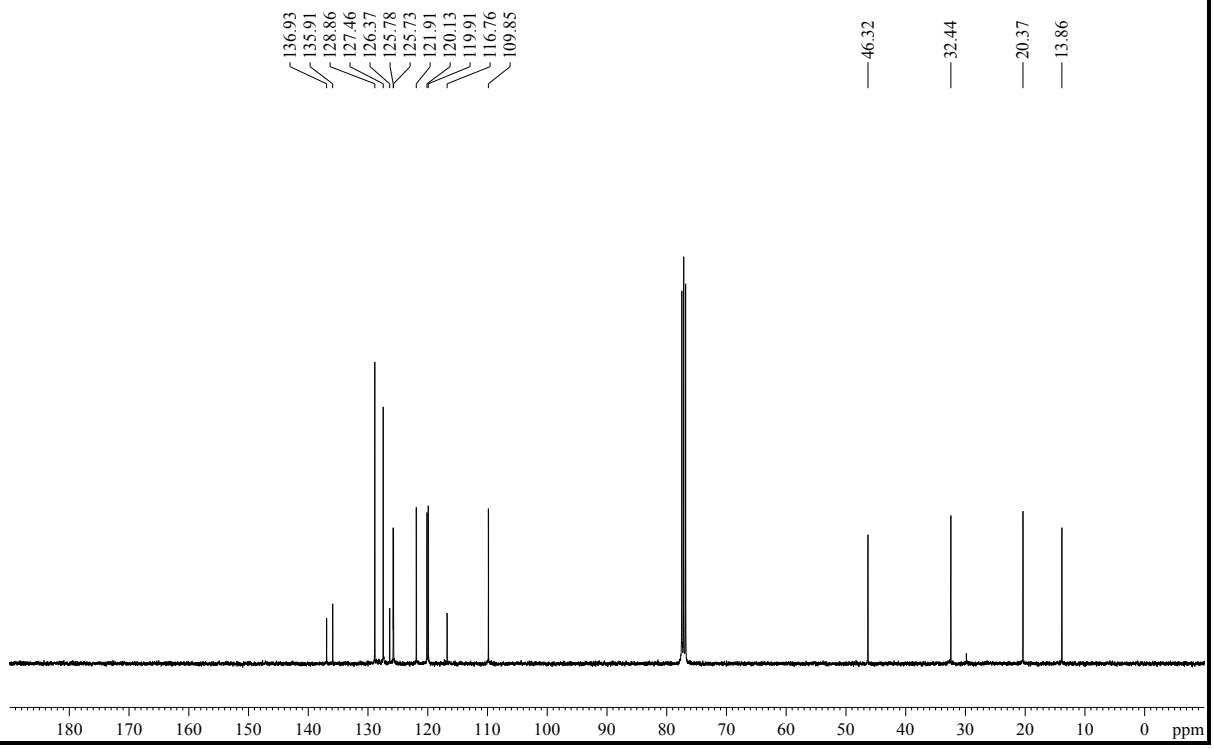
^{13}C NMR spectrum of **23k**



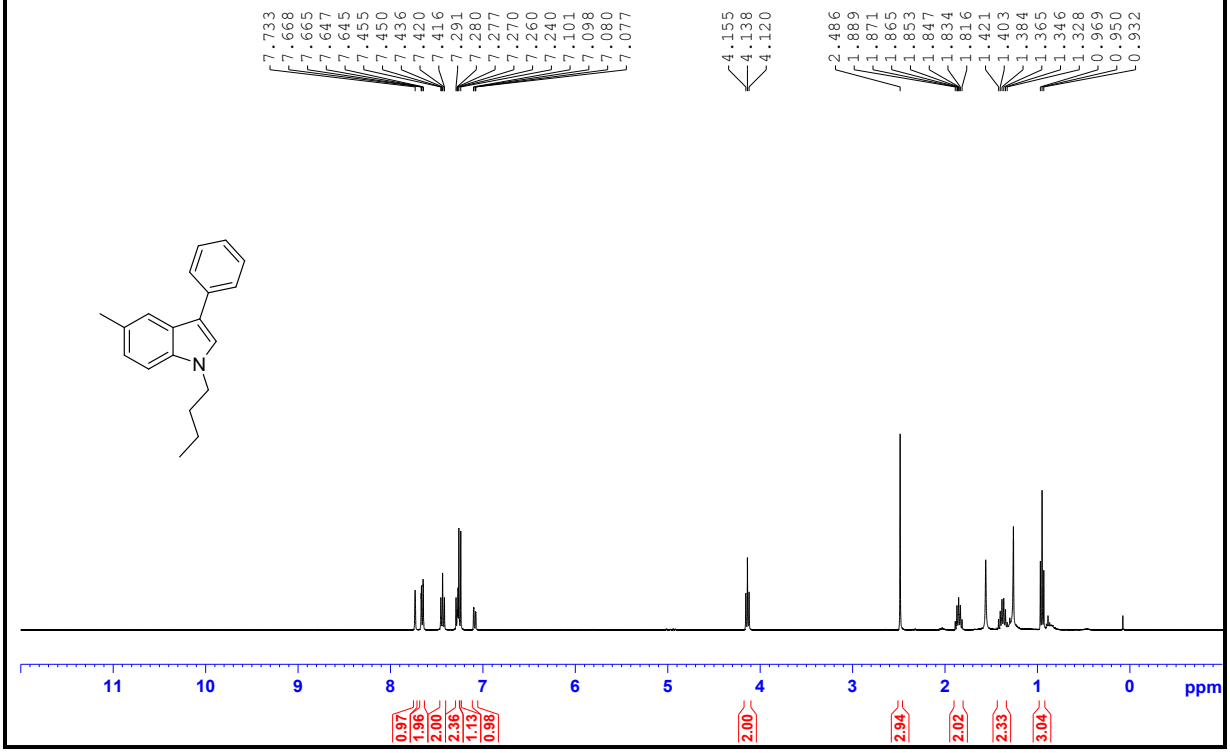
^{1}H NMR spectrum of **25a**



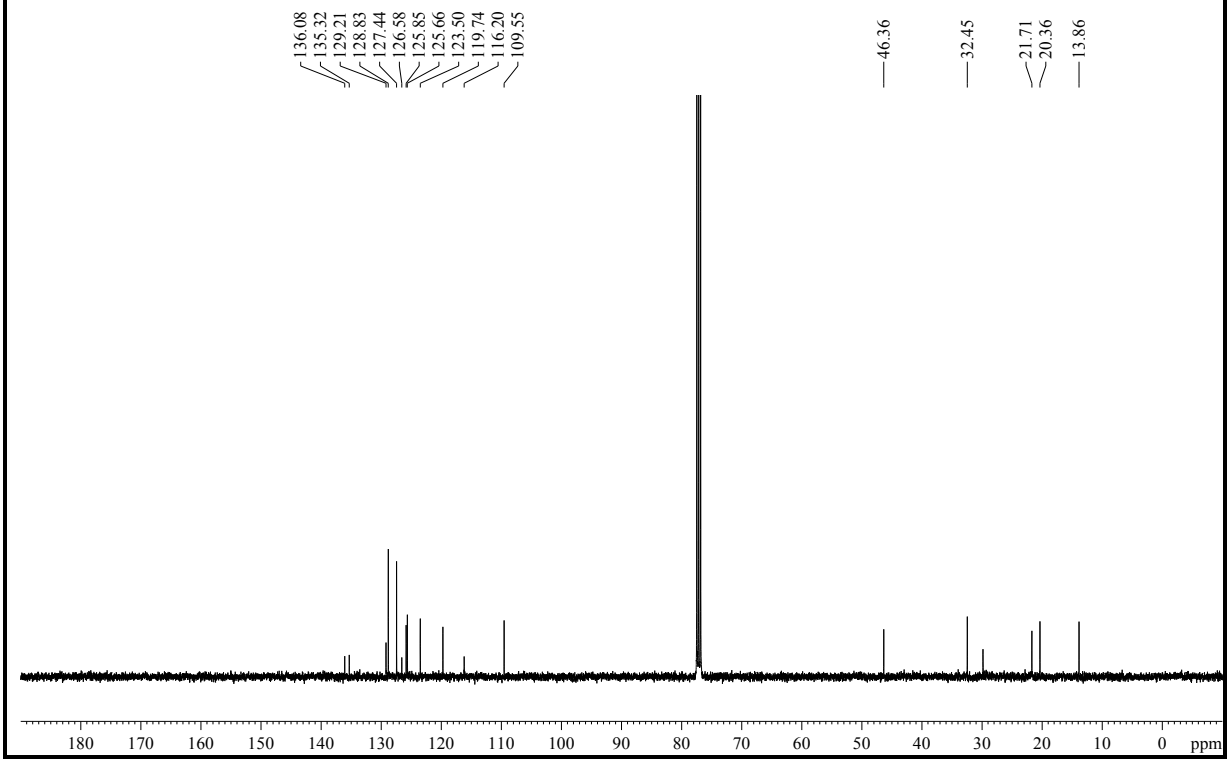
^{13}C NMR spectrum of **25a**



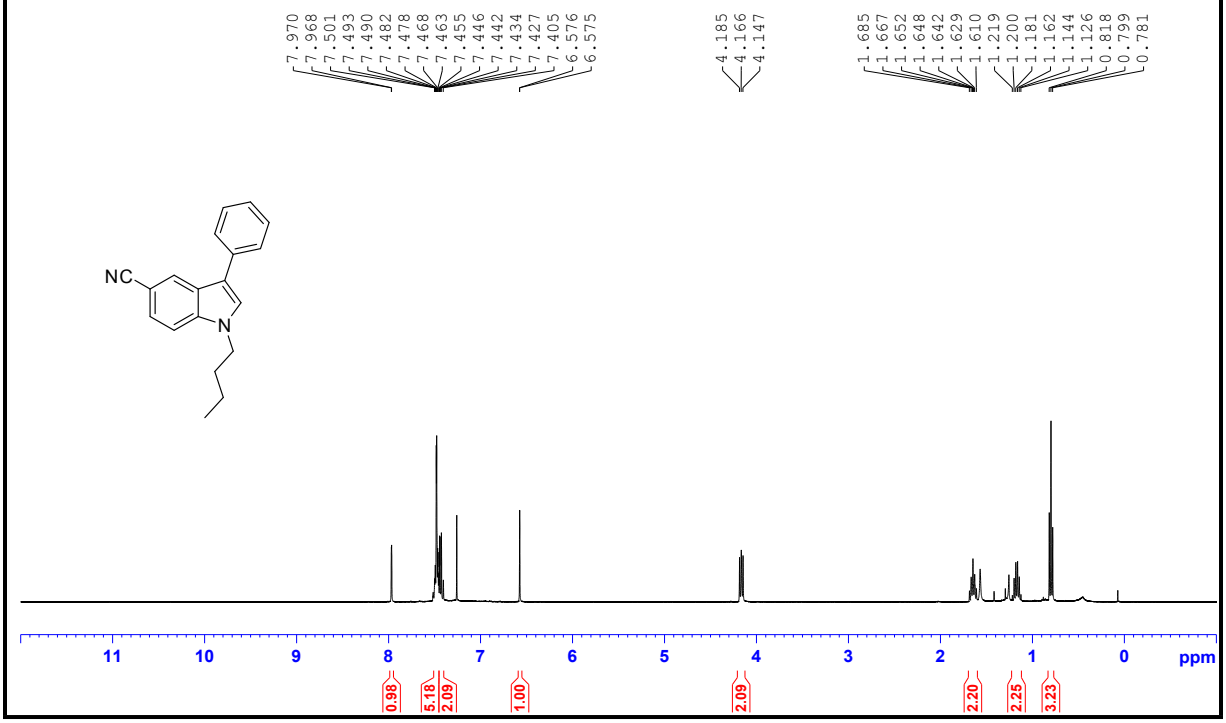
^{1}H NMR spectrum of **25b**



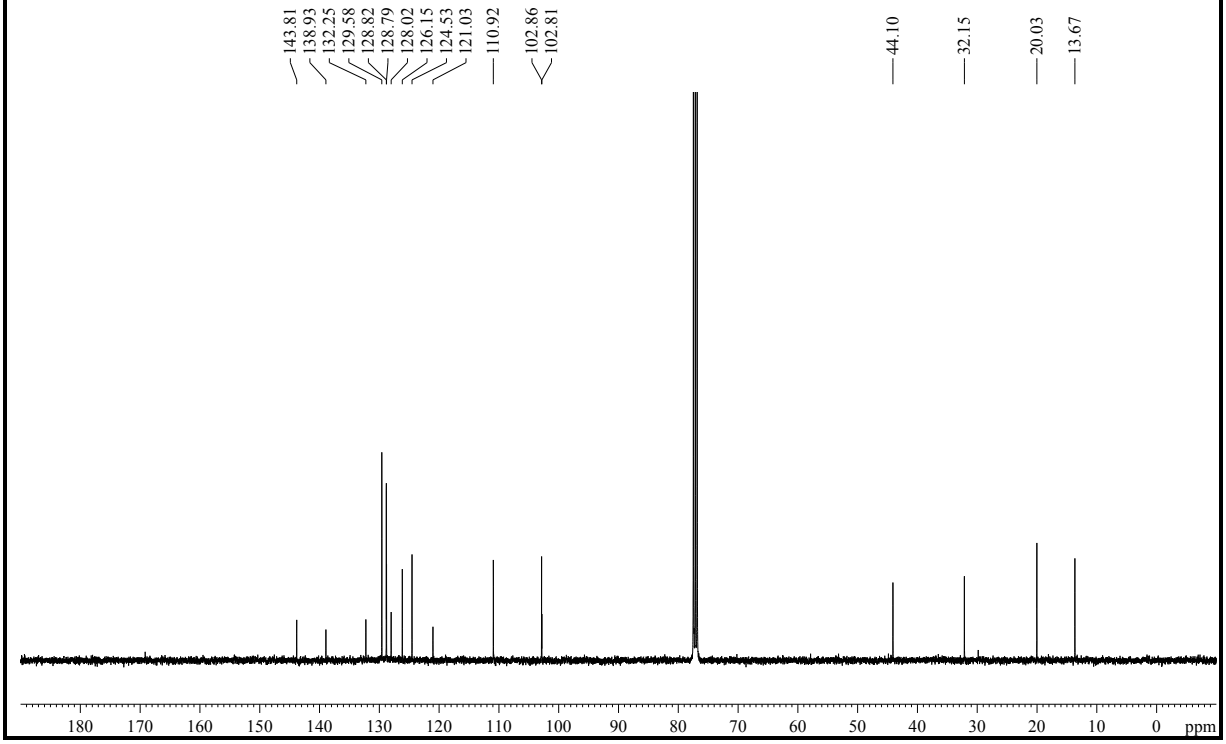
^{13}C NMR spectrum of **25b**



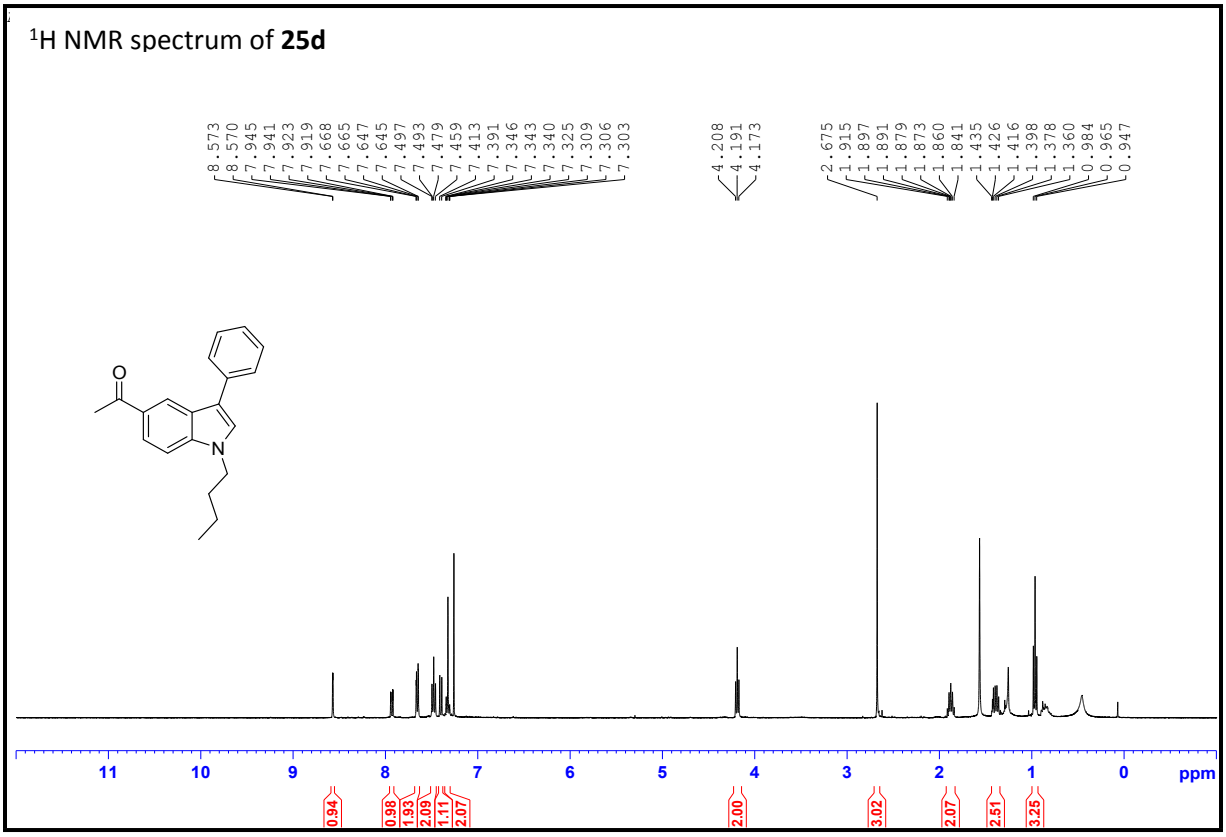
^{1}H NMR spectrum of **25c**



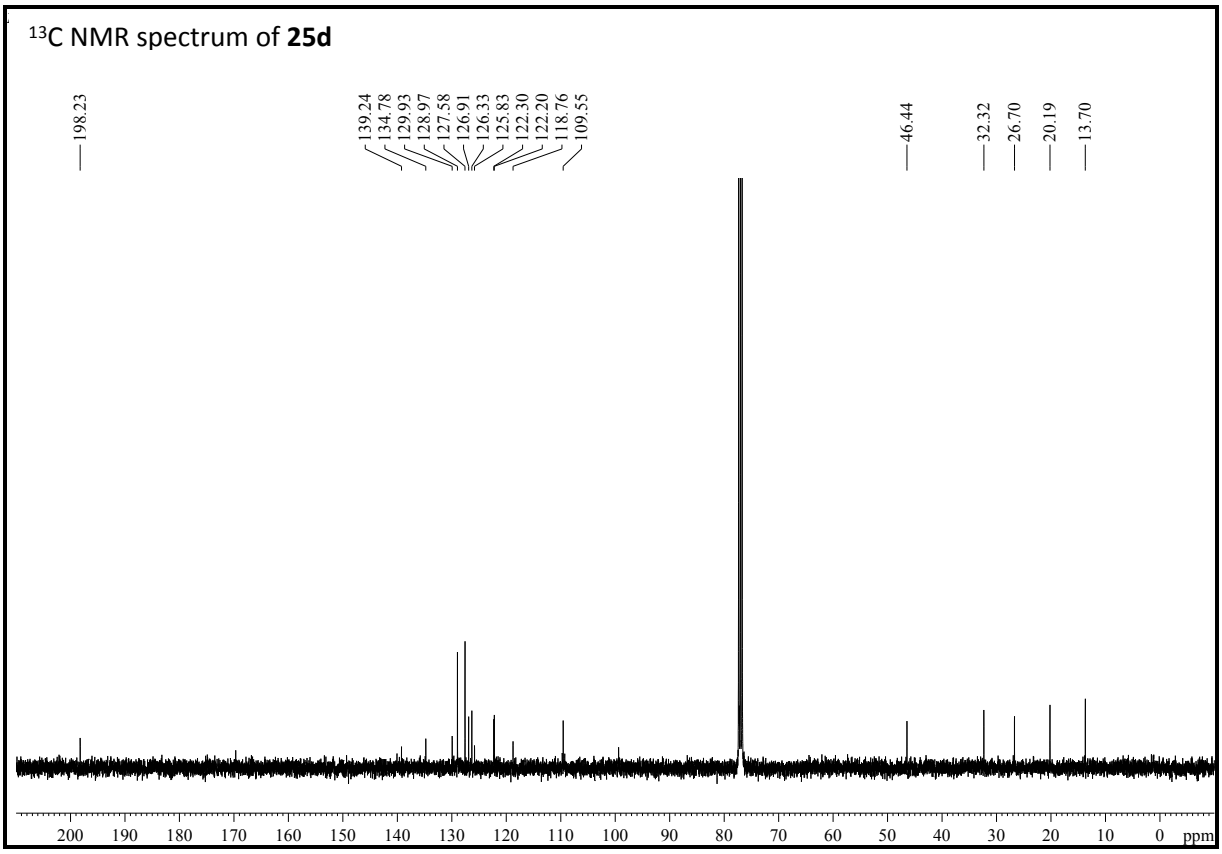
^{13}C NMR spectrum of **25c**



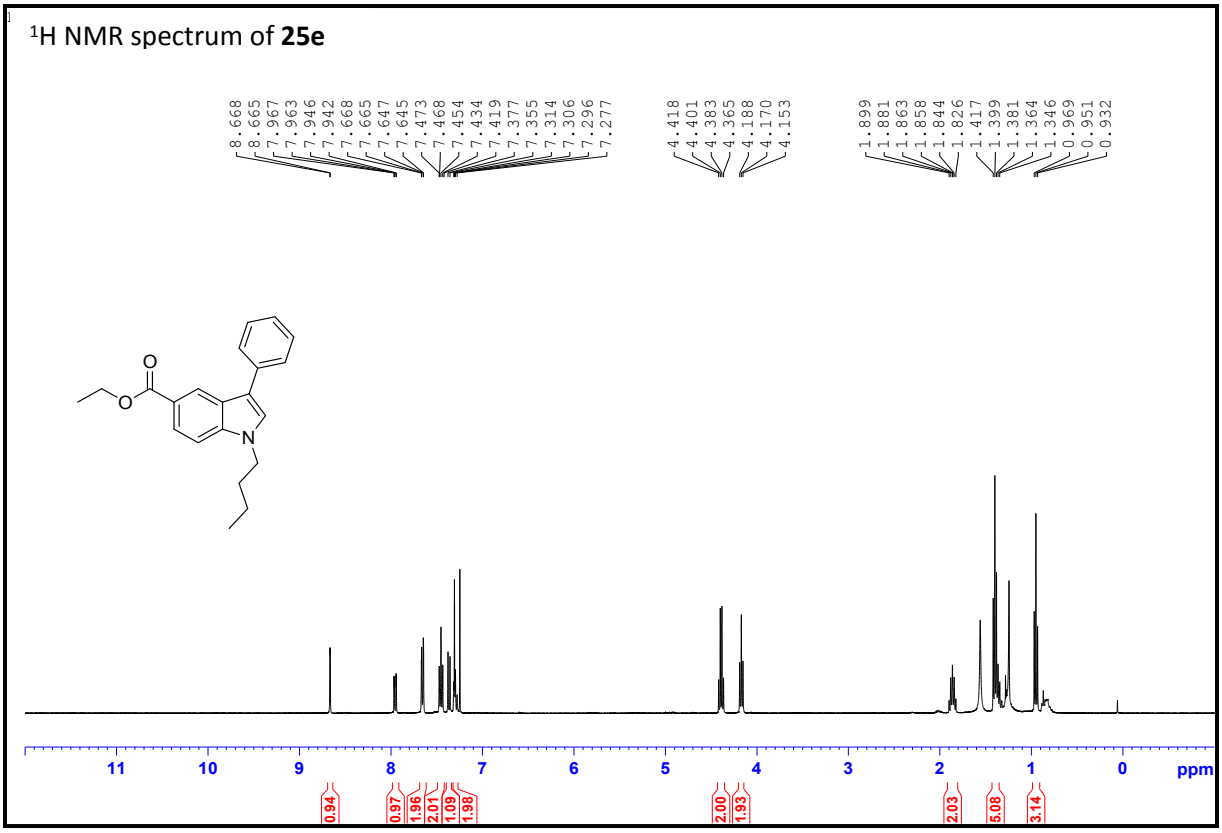
^{1}H NMR spectrum of **25d**



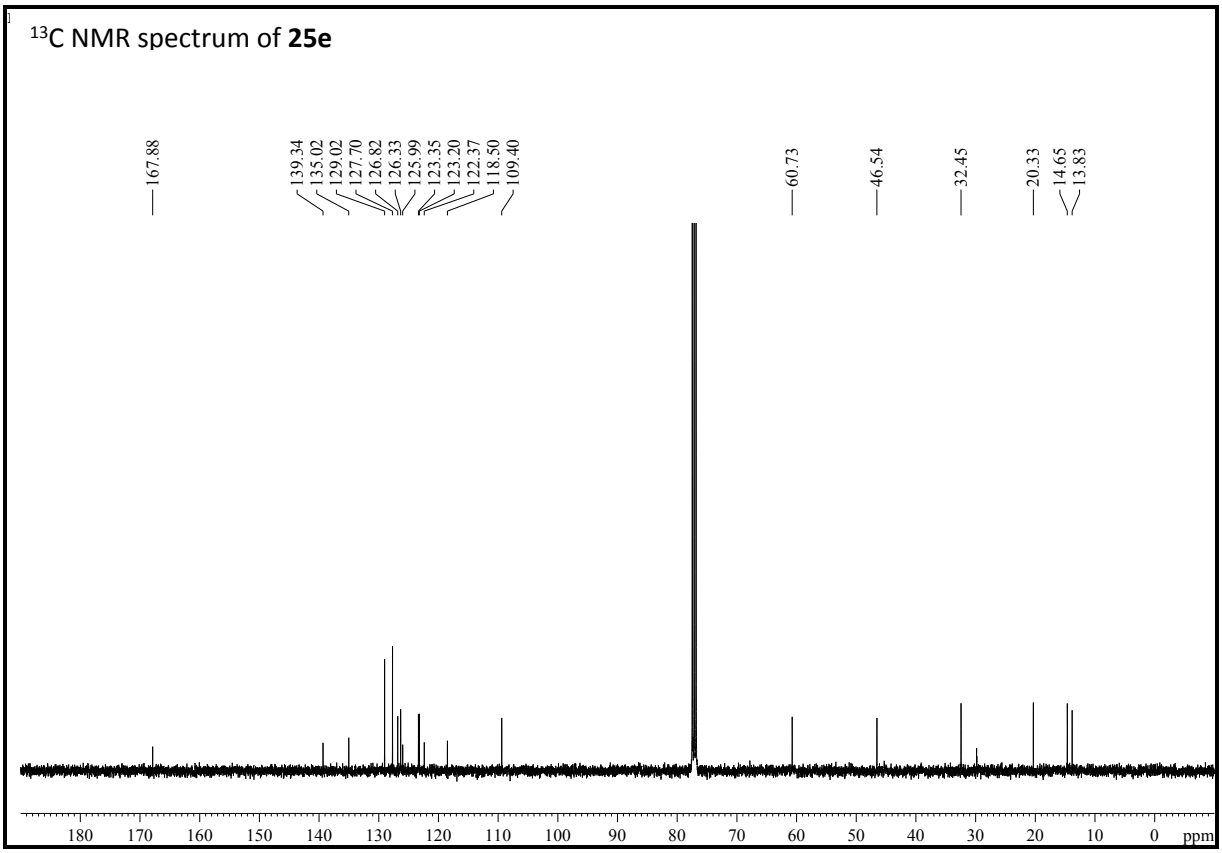
^{13}C NMR spectrum of **25d**



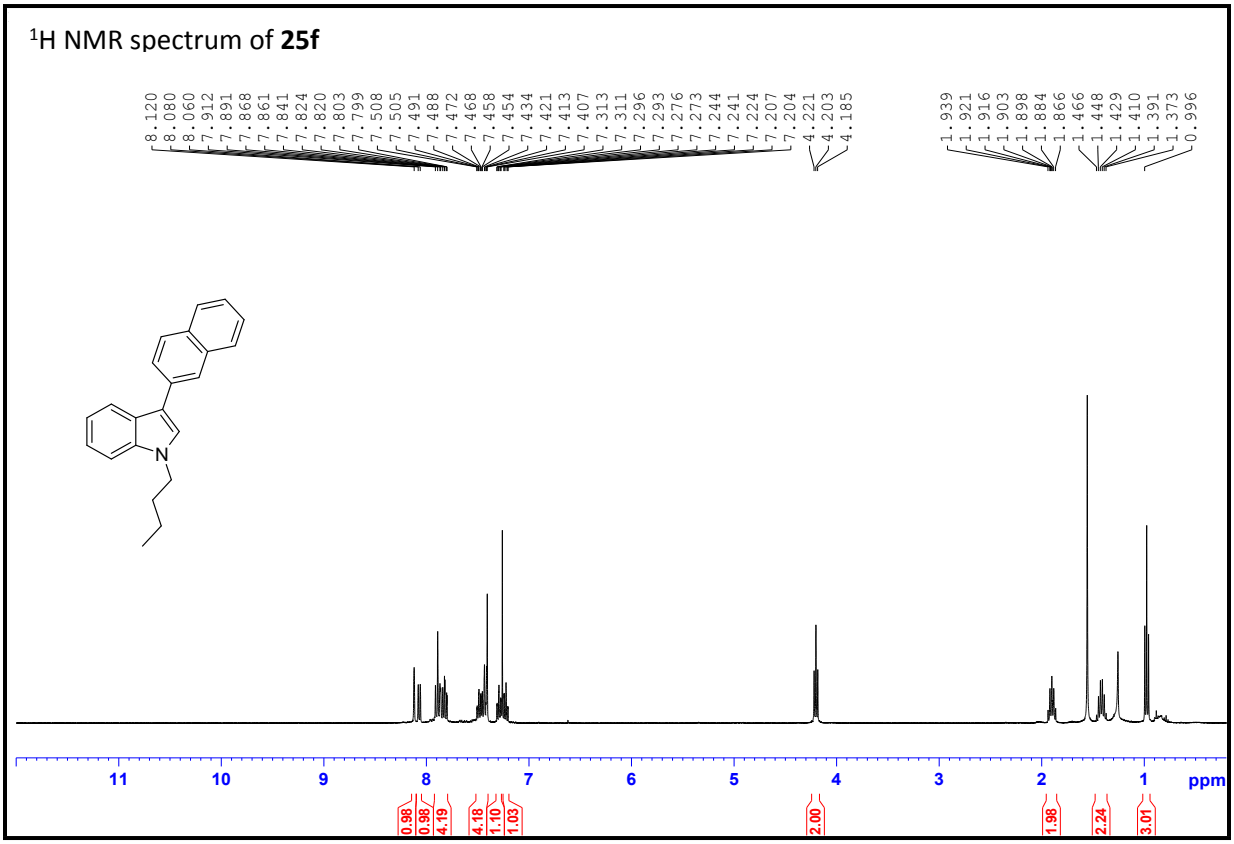
^{1}H NMR spectrum of **25e**



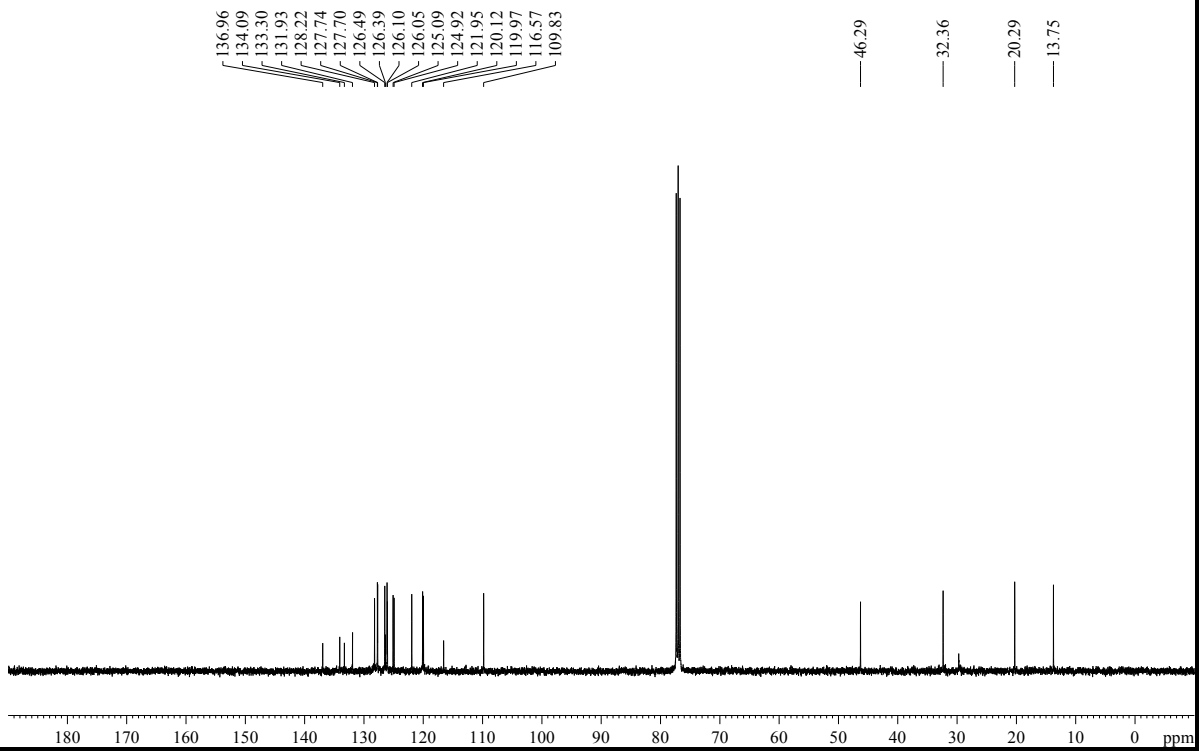
^{13}C NMR spectrum of **25e**



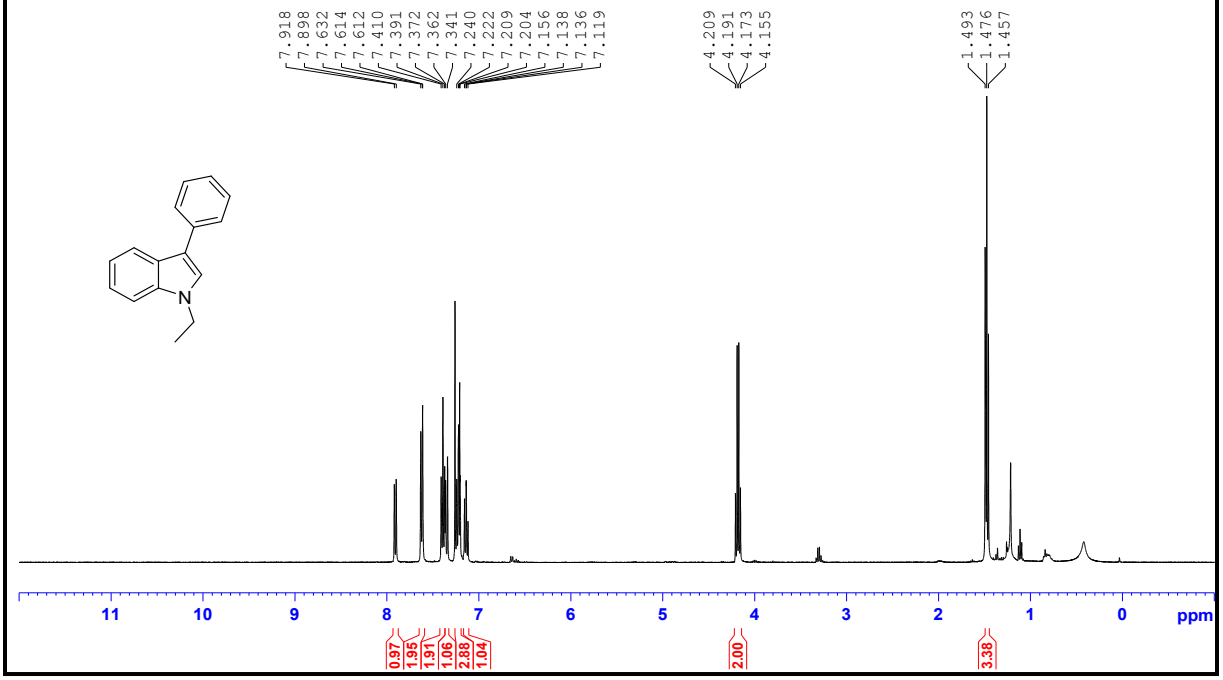
^{1}H NMR spectrum of **25f**



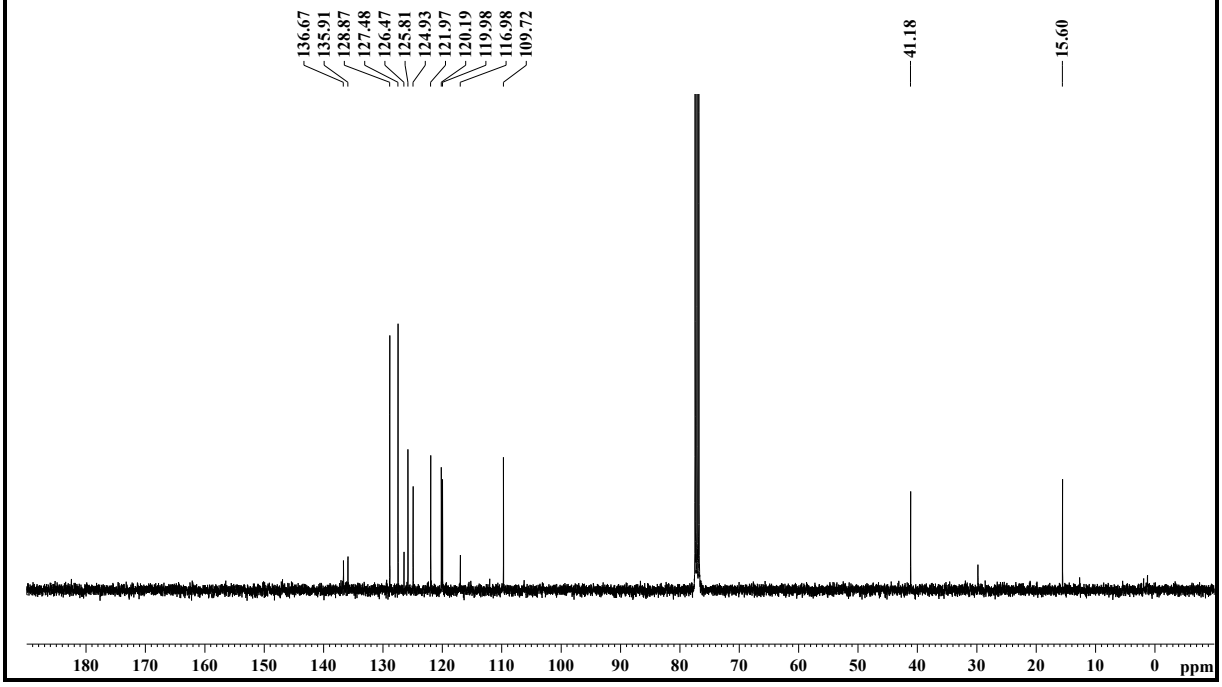
^{13}C NMR spectrum of **25f**



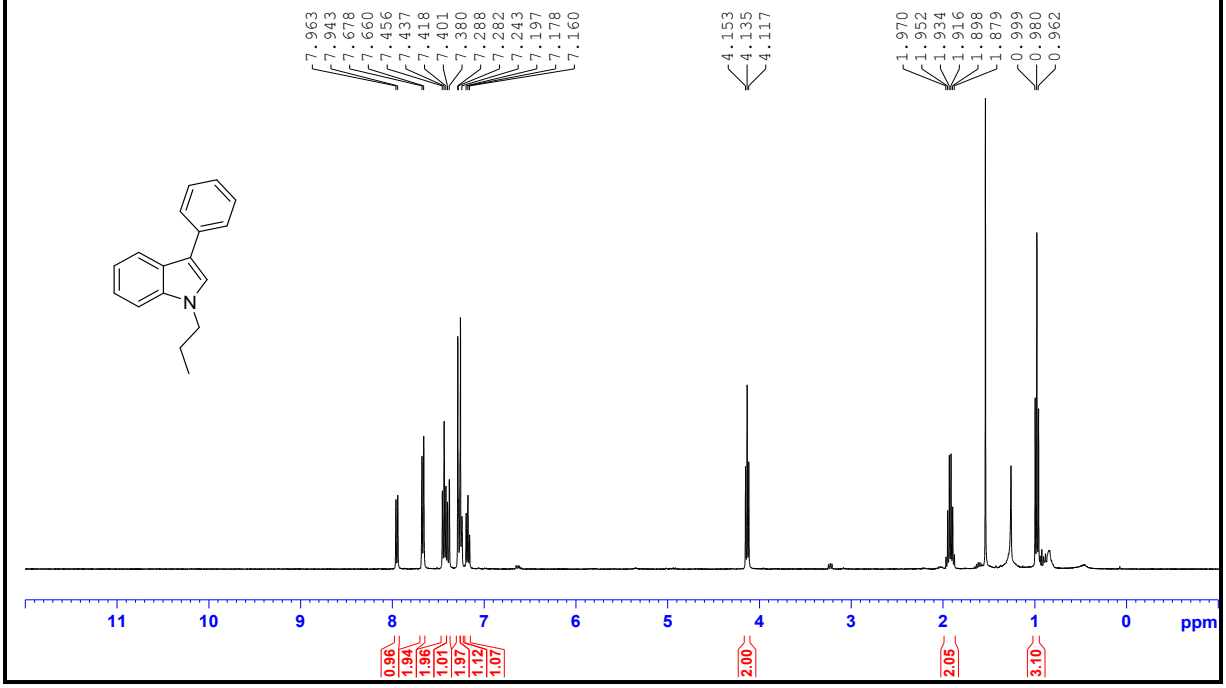
^{1}H NMR spectrum of **26a**



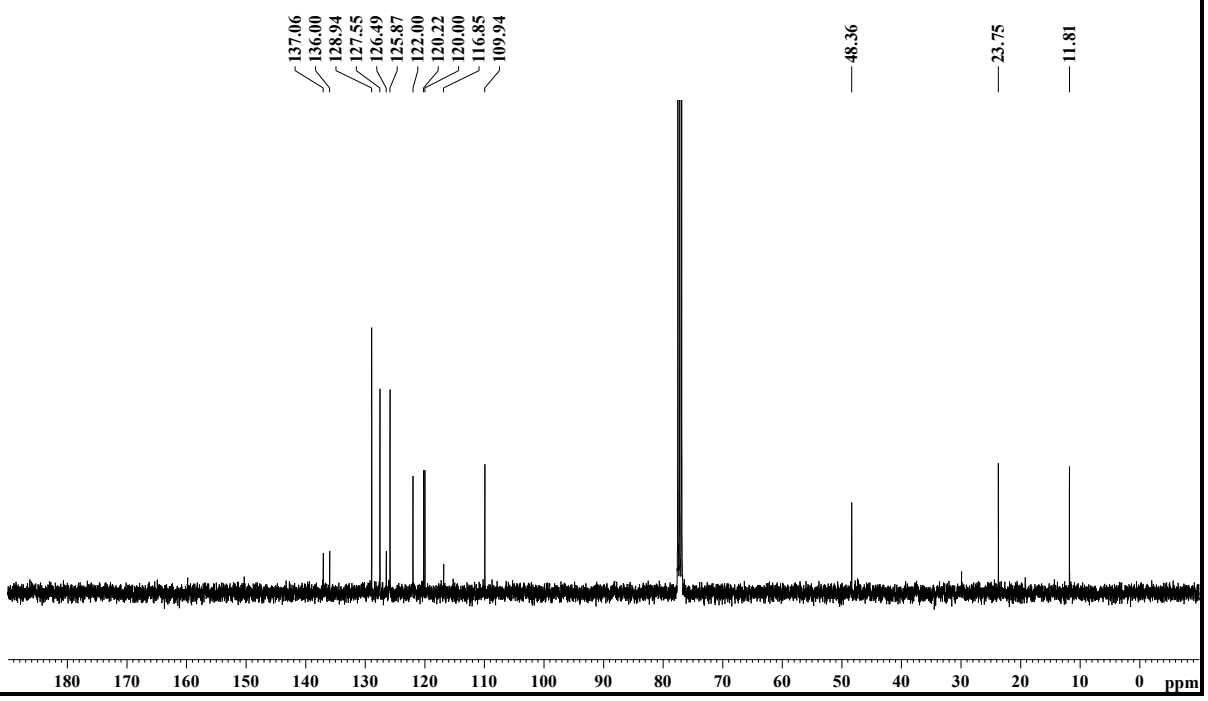
^{13}C NMR spectrum of **26a**



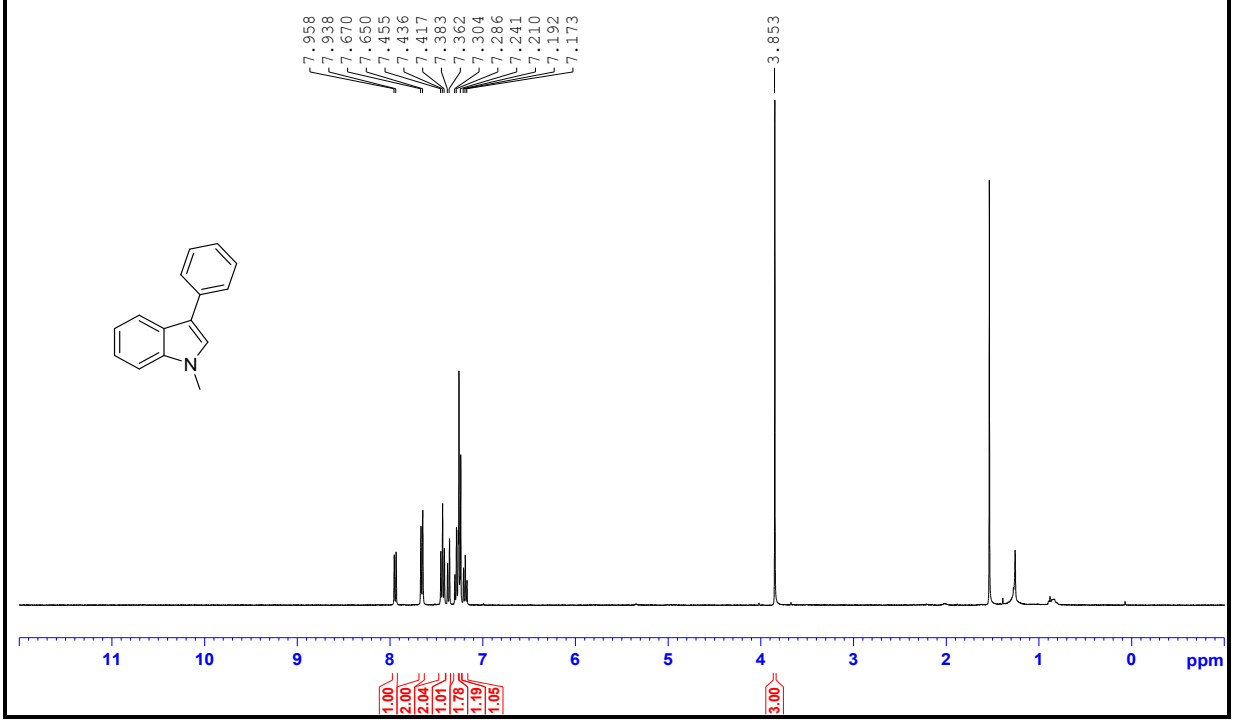
^{1}H NMR spectrum of **27a**



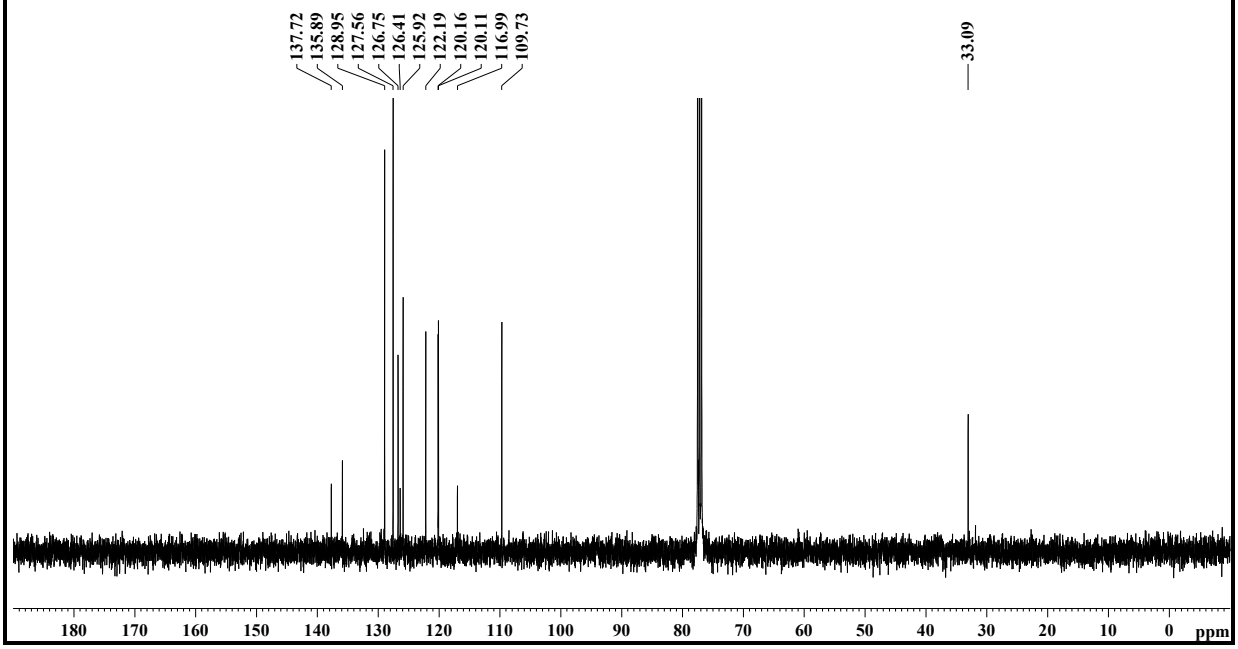
^{13}C NMR spectrum of **27a**



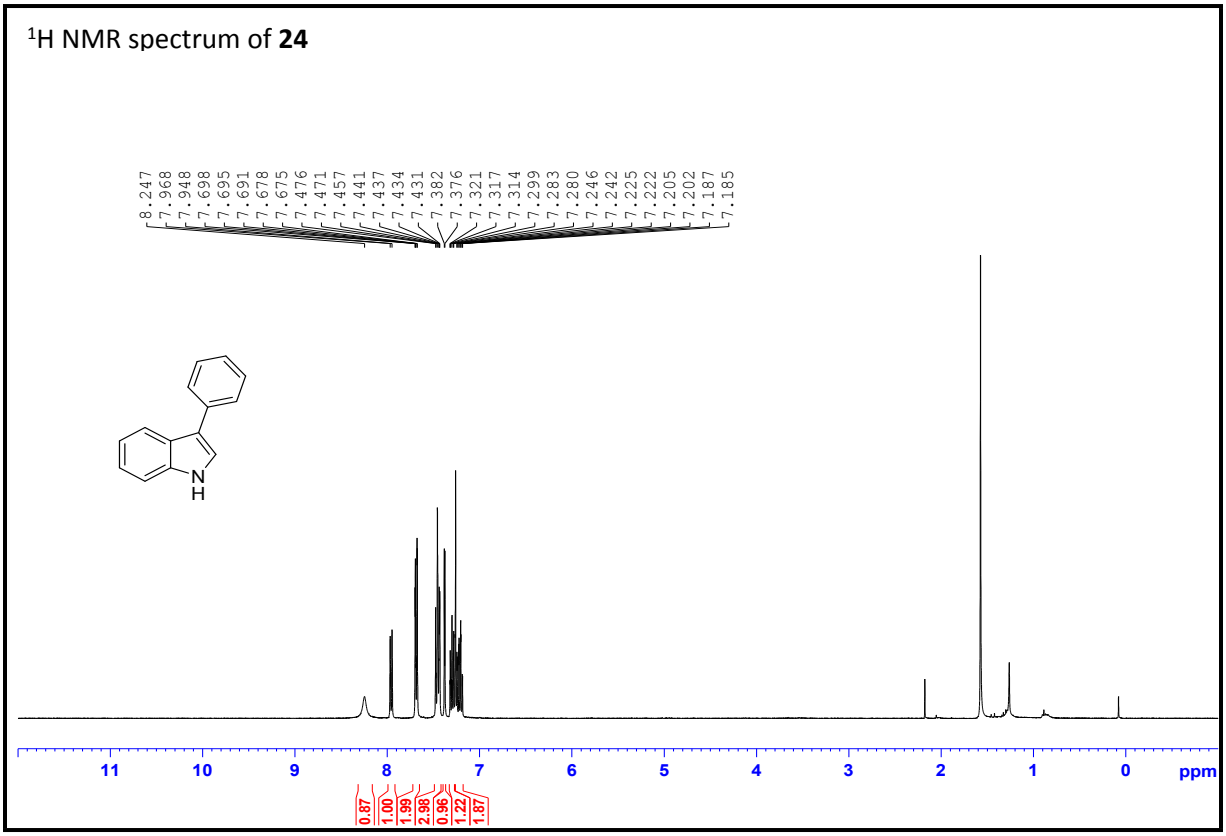
^{1}H NMR spectrum of **28a**



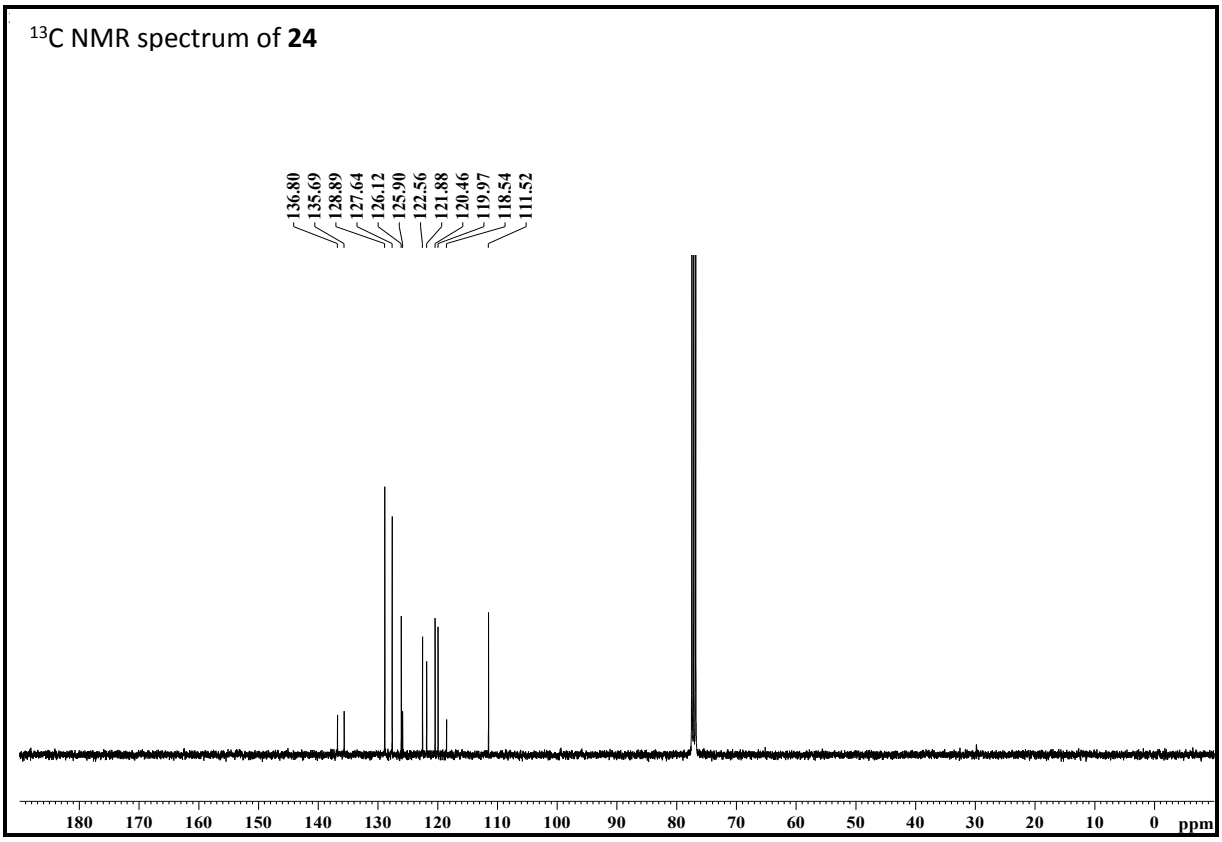
^{13}C NMR spectrum of **28a**



^{1}H NMR spectrum of **24**

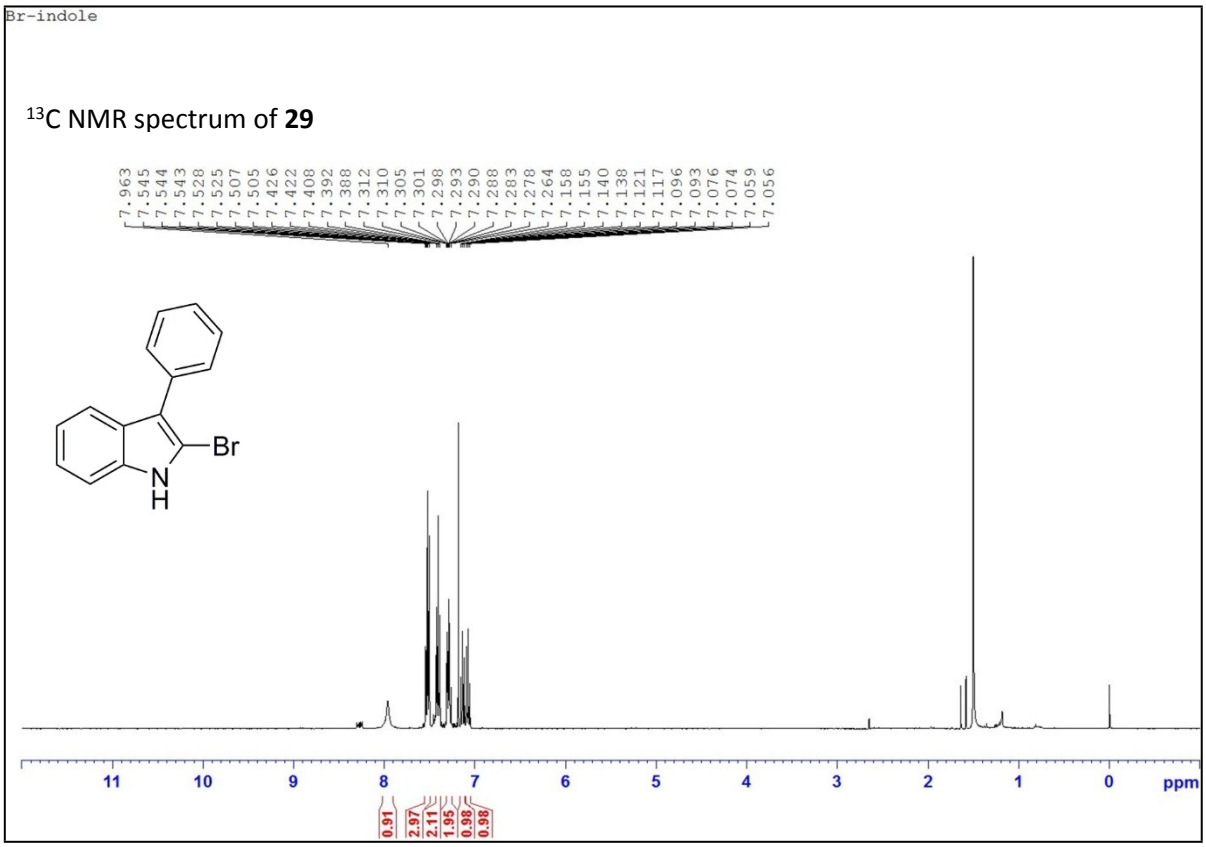


^{13}C NMR spectrum of **24**

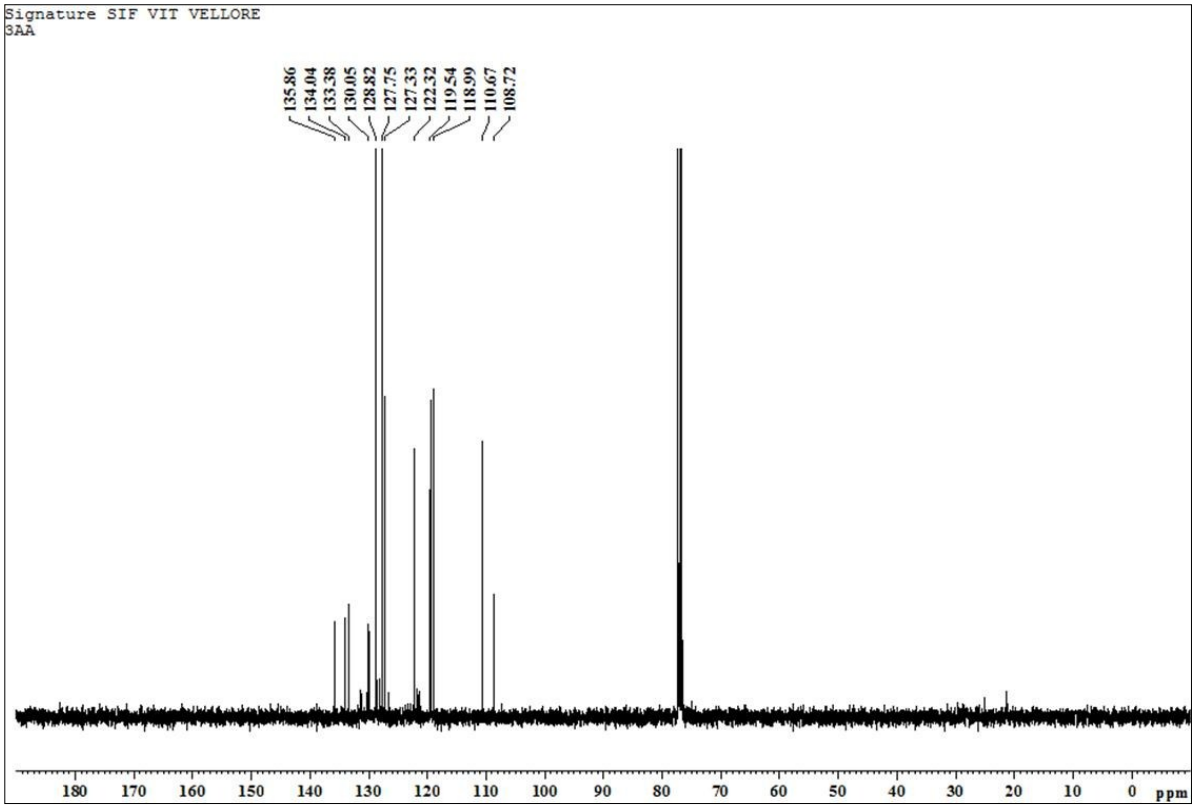


Br-indole

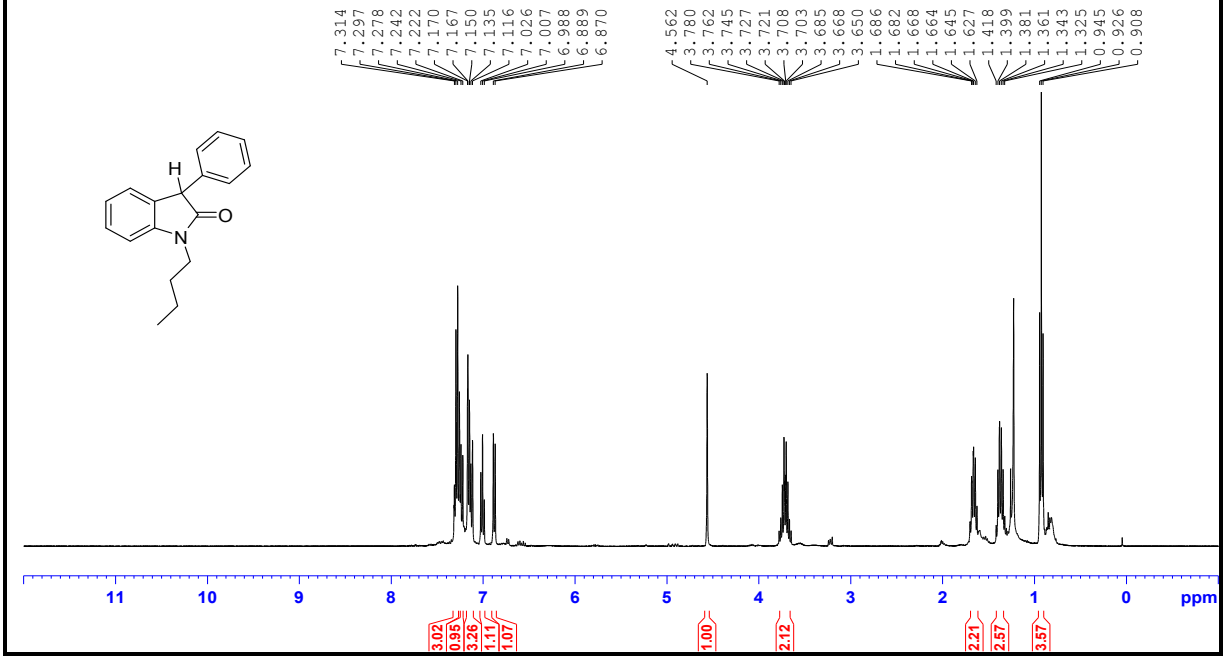
^{13}C NMR spectrum of **29**



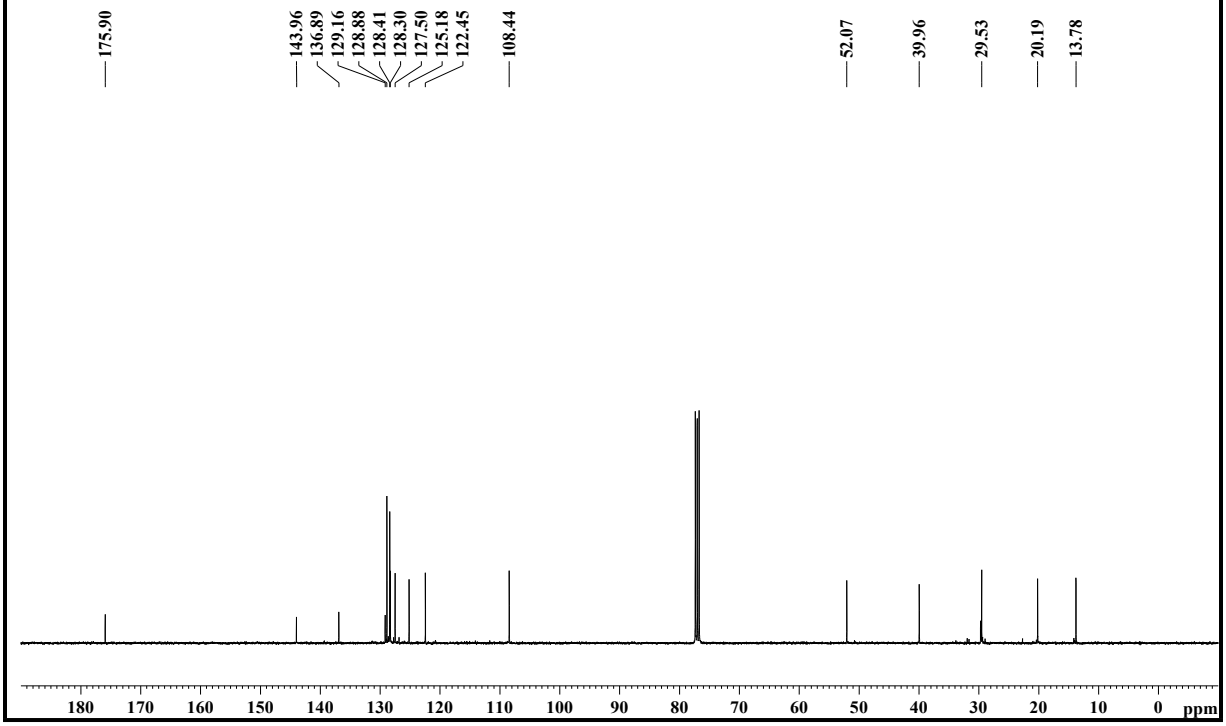
Signature SIF VIT VELLORE
3AA



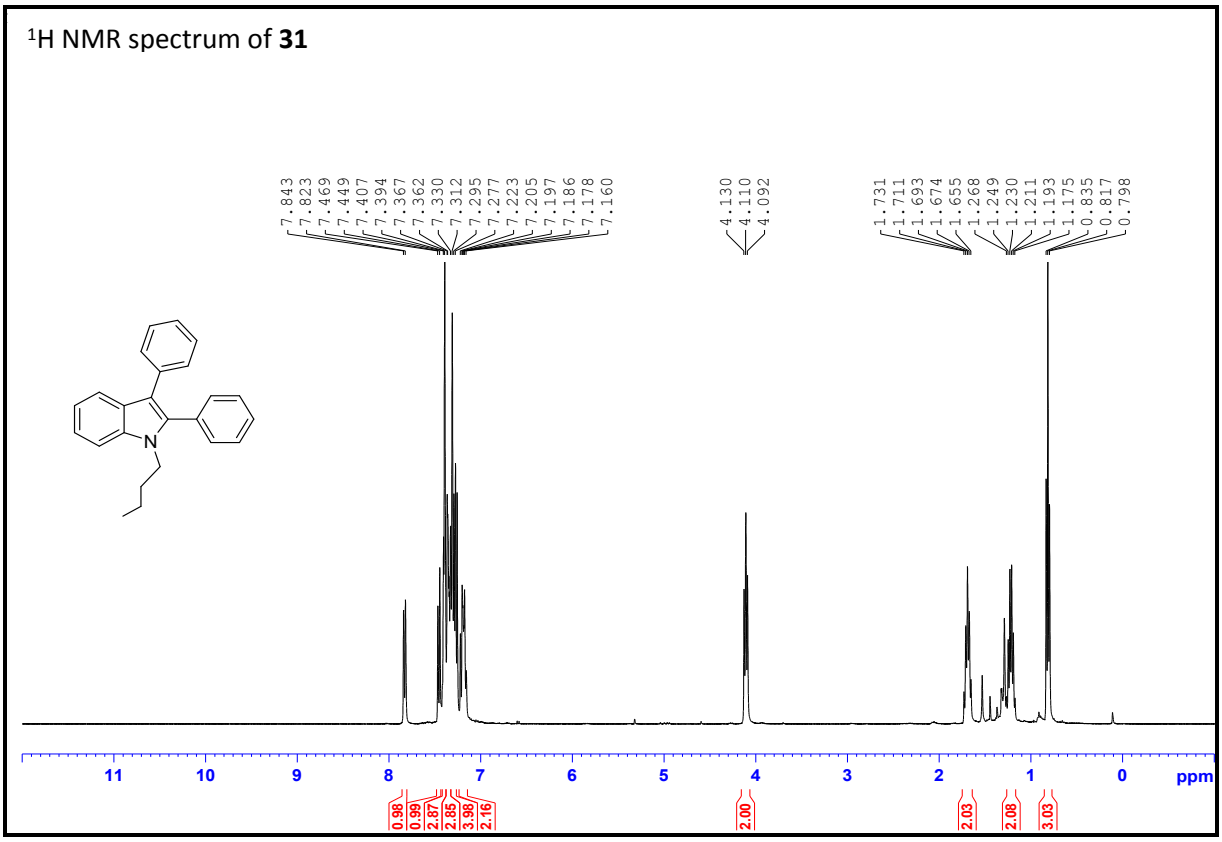
^{1}H NMR spectrum of **30**



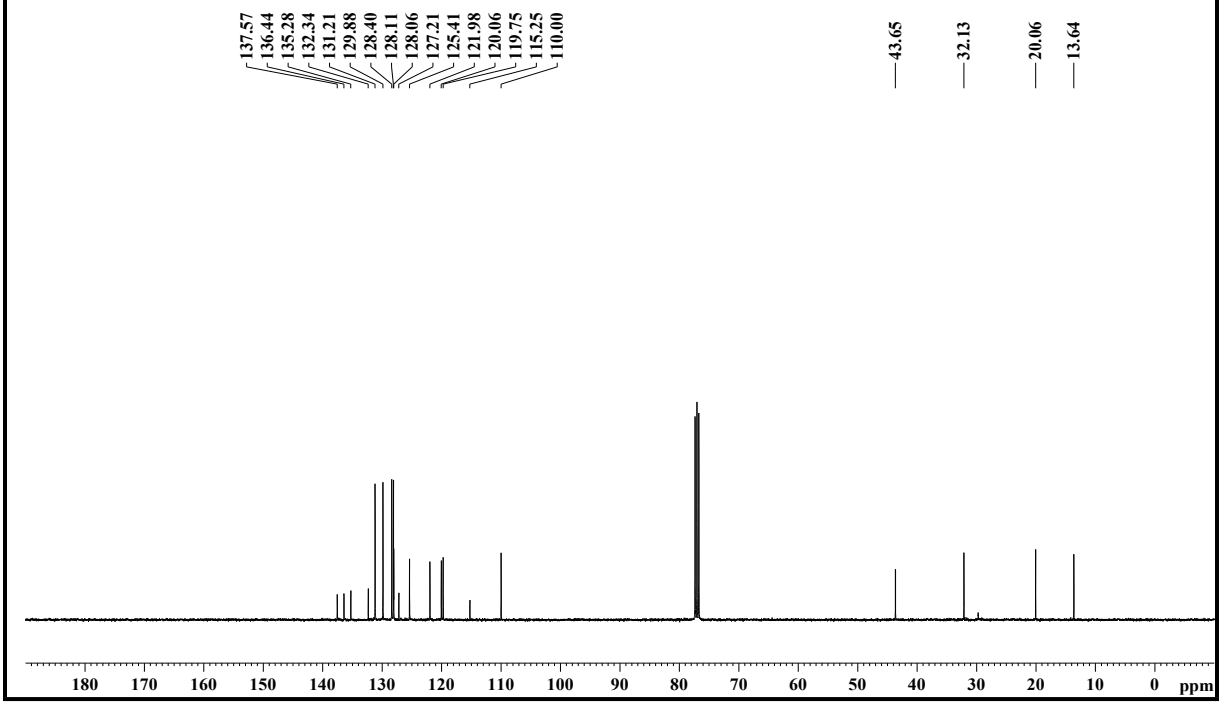
^{13}C NMR spectrum of **30**

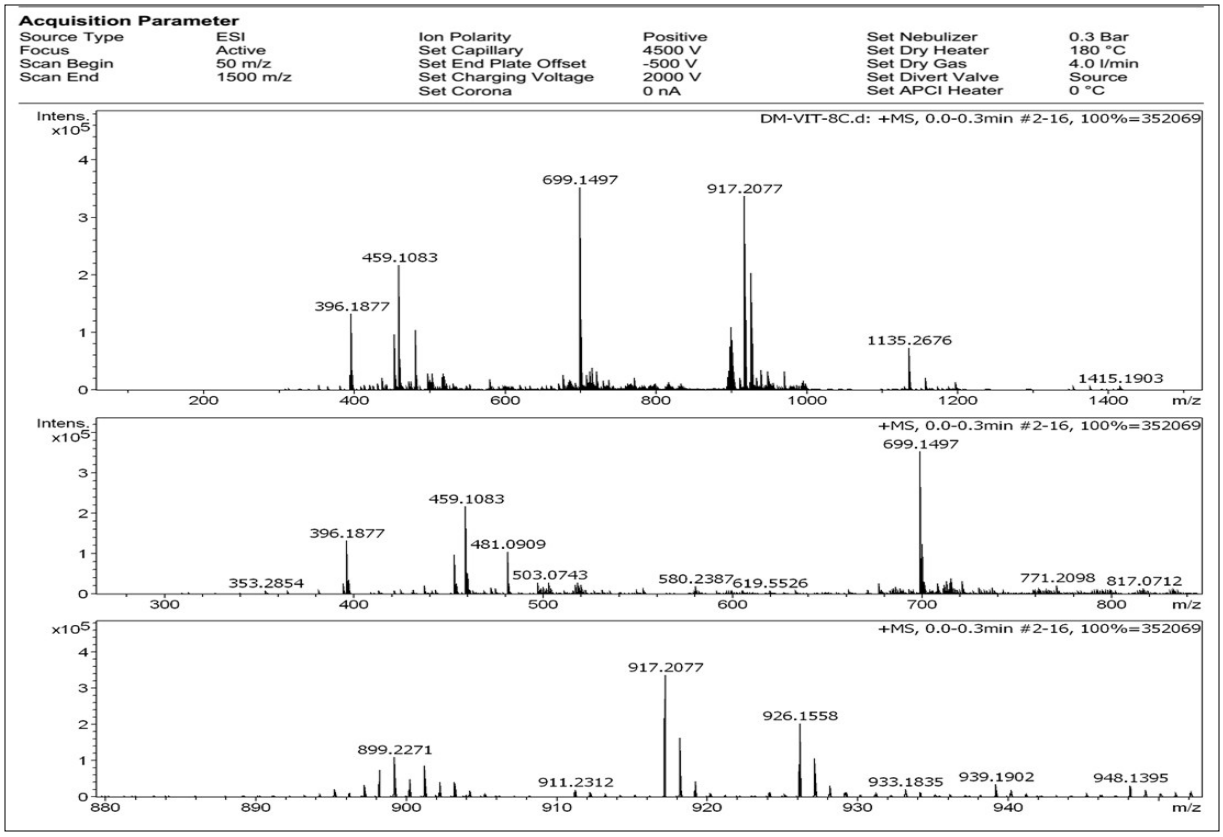


^{1}H NMR spectrum of **31**

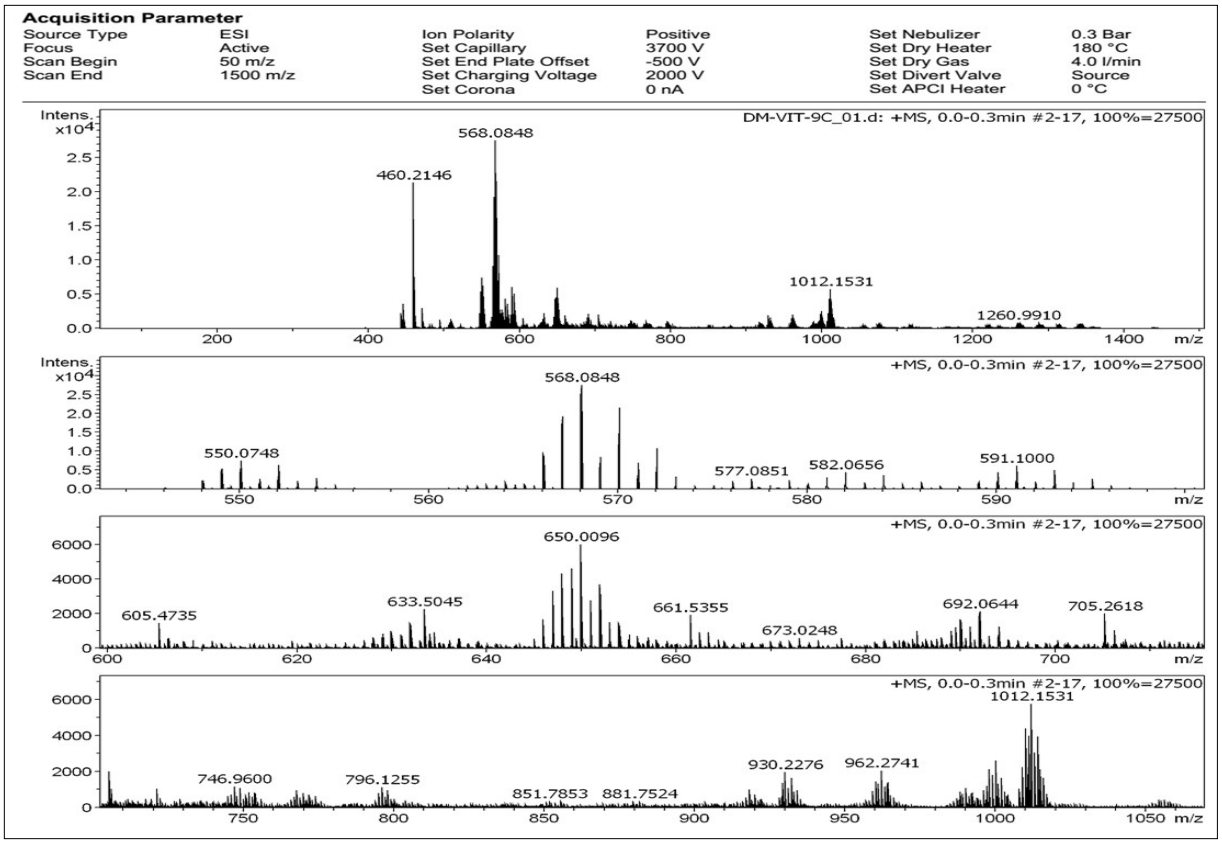


^{13}C NMR spectrum of **31**

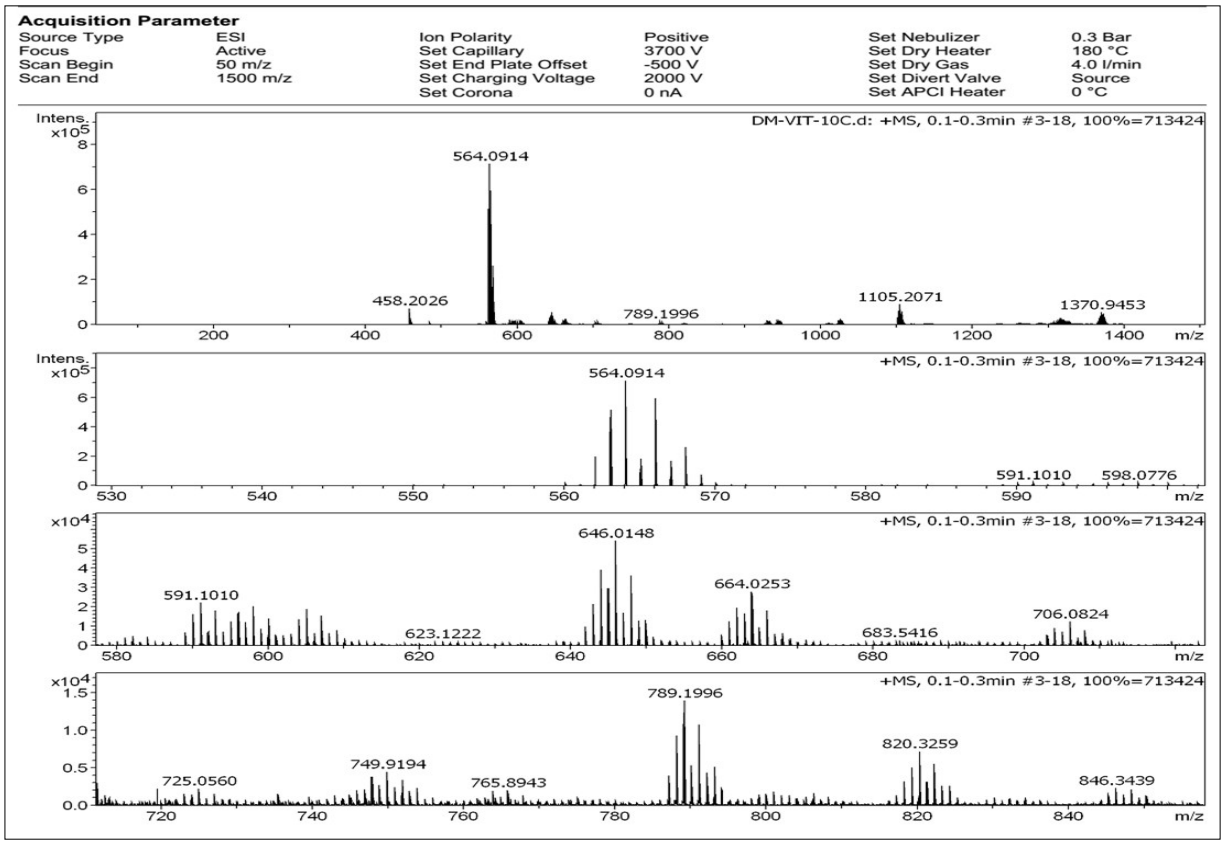




ESI-MS Spectrum of **7**



ESI-MS Spectrum of **8**



ESI-MS Spectrum of **13**

7. References:

[1] Y. Tobe, N. Utsumi, K. Kawabata, A. Nagano, K. Adachi, S. Araki, M. Sonoda, K. Hirose, K. Naemura, *J. Am. Chem. Soc.* 2002, **124**, 5350-5364.

[2] A. Nandakumar, K. Balakrishnan, P. T. Perumal, *Synlett* 2011, 2733-2739.

[3] R. C. Larock, E. K. Yum, M. D. Refvik, *J. Org. Chem.* 1998, **63**, 7652-7662.

[4] Y. Nakao, K. S. Kanyiva, S. Oda, T. Hiyama, *J. Am. Chem. Soc.* 2006, **128**, 8146-8147.

[5] S. Chen, Y. Liao, F. Zhao, H. Qi, S. Liu, G.-J. Deng, *Org. Lett.* 2014, **16**, 1618-1621.

[6] P. Tao, J. Liang, Y. Jia, *Eur. J. Org. Chem.* 2014, **2014**, 5735-5748.

[7] X. Jiang, J. Yang, F. Zhang, P. Yu, P. Yi, Y. Sun, Y. Wang, *Org. Lett.* 2016, **18**, 3154-3157.

[8] E. T. Nadres, A. Lazareva, O. Daugulis, *J. Org. Chem.* 2011, **76**, 471-483.

[9] SMART (V 5.628), SAINT (V 6.45a), XPREP, SHELXTL; Bruker AXS Inc., Madison, Wisconsin, USA, 2004.

[10] Sheldrick, G.M.; Siemens Area Detector Absorption Correction Program. University of Göttingen, Göttingen, Germany 2004.

[11] A. Altomare, G. Cascarano, C. Giacovazzo, A. Guagliardi, *J. Appl. Crystallogr.* 1993, **26**, 343.

[12] Sheldrick, G. M.;SHELXL-2014, Program for Crystal Structure Solution and Refinement; University of Göttingen, Göttingen, Germany, 2014.

[13] L. J. Farrugia, WinGX-A Windows Program for Crystal Structure Analysis, *J. Appl. Crystallogr.* 2012, **45**, 849.

[14] P. K. R. Panyam, T. Gandhi, *Adv. Synth. Catal.* 2017, **359**, 1144-1151

[15] S. Ruiz-Botella, E. Peris, *Organometallics* 2014, **33**, 5509-5516.