Electronic Supplementary Information (ESI)

A facile synthesis of 2*H*-indazoles under neat conditions and further transformation into aza-*γ*-carboline alkaloid analogues in a tandem one-pot fashion

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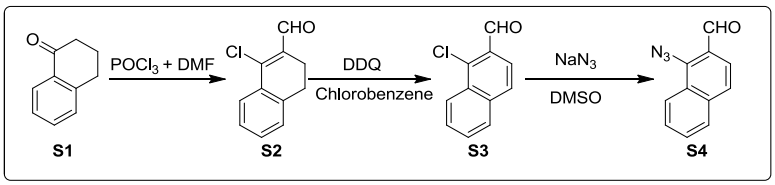
Experimental Section

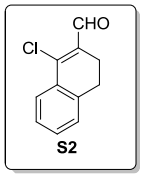
General: IR spectra were recorded on a Bruker Tensor 37 (FTIR) spectrophotometer. ^{1}H NMR spectra were recorded on Bruker Avance 400 (400 MHz) spectrometer at 295 K in $CDCl_3$; chemical shifts (δ in ppm) and coupling constants (J in Hz) are reported in standard fashion with reference to either internal standard tetramethylsilane (TMS) (δ_H = 0.00 ppm) or $CHCl_3$ (δ_H = 7.25 ppm). ^{13}C NMR spectra were recorded on Bruker Avance 400 (100 MHz) spectrometer at RT in $CDCl_3$; chemical shifts (δ in ppm) are reported relative to $CHCl_3$ (δ_C = 77.00 ppm). In the ^{1}H-NMR, the following abbreviations are used throughout: s = singlet, d = doublet, t = triplet, q = quartet, qui = quintet, m = multiplet and br s = broad singlet, sept = septet. The assignment of signals were confirmed by ^{1}H and ^{13}C spectral data. High-resolution mass spectra (HR-MS) were recorded on an Agilent 6538 UHD Q-TOF using multimode source. Microwave experiments were carried out with CEM Discover Labmate^{TM} instrument in 10 ml vial, closed vessel, Power: 250W, Temperature: 60 °C-100 ^{o}C for 50-100 minutes. Melting points were determined using melting point apparatus manufactured by GUNA enterprises, India and are uncorrected. All small scale reactions were carried out using standard syringe-septum technique. Reactions were monitored by TLC on silica gel using a combination of hexane and ethyl acetate as eluents. Solvents were distilled prior to use. We gave all spectral data for known and unknown compounds.

(A) General procedure for 2-azidoaldehyde preparation:[1]

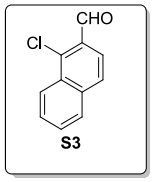
(B) General procedure for the synthesis of 1-azido-2-naphthaldehyde (S4):[1b]

All 2-azidobenzaldehydes were prepared by using literature known methods except **S4**



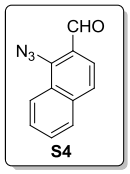


1-Chloro-2-naphthaldehyde S2: The general procedure was followed using 1.33 mL of α-tetralone (10.0 mmol), 1.9 mL of $POCl_3$ (20.0 mmol), and 4.0 ml of DMF. Purification by column chromatography with hexane:EtOAc/20:1 afforded **S2** as a slightly yellow oil (70-75%). (**Caution**: Reaction should be carried at room temperature as the product is volatile). For spectral data see reference 1.



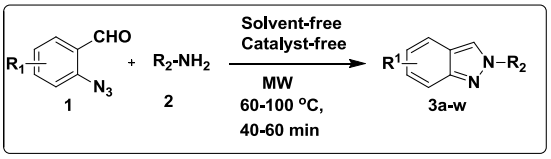
1-Chloro-2-napthaldehyde S3: The general procedure was followed using 1.465 g of chloroalkenal (7.57 mmol), DDQ (15.15 mmol), and 60 ml of chlorobenzene. The reaction mixture was refluxed at 130 °C for 72 h. It was then poured into saturated aqueous $NaHCO_3$ solution and extracted with ethyl acetate (3 × 20 mL). The ethyl acetate extract was dried over Na_2SO_4. Evaporation of the solvent and purification of the residue over a silicagel column using hexane:ethyl acetate/99:1 as eluent furnished the saturated chloroaldehyde **S3** (1.0 g, 95%) as a pale yellow solid. IR (MIR-ATR, 4000–600 cm^{-1}): υ_{max} = 3059, 2867, 2746, 1683, 1650, 1618, 1594, 1557, 1455, 1318, 1218, 993, 894, 812, 754. ^1H NMR ($CDCl_3$, 400 MHz): δ_H = 10.74 (s, 1H), 8.48-8.44 (m, 1H), 7.92 (d, 1H, J = 8.8 Hz), 7.88-7.85 (m, 1H), 7.79 (d, 1H, J = 8.8 Hz),

7.70-7.65 (m, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ_C = 190.4, 138.8, 137.0, 130.8, 129.7, 129.6, 128.4, 127.0, 125.4, 123.3. HR-MS (ESI+) m/z calculated for $[C_{11}H_8ClO]^+ = [M+H]^+$: 191.0258; found: 191.0262.



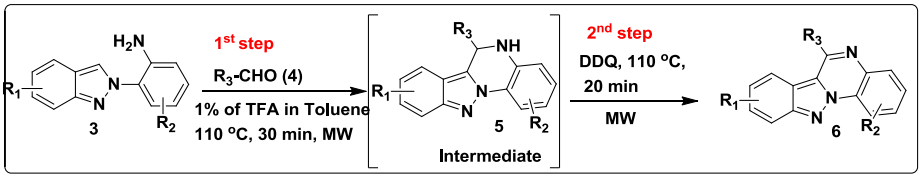
1-Azido-2-naphthaldehyde S4: To a solution of 1-chloro-2-napthaldehyde (2.0 mmol, 1.0 equiv) in 3.0 mL of DMSO was added NaN_3 (2.4 mmol, 1.2 equiv). The mixture was stirred at ambient temperature and monitored by TLC. Once the starting material disappeared, the reaction mixture was poured in ice cold water (30.0 mL) and extracted with dichloromethane (10 mL×2). The DCM layer was washed with water (10 mL×2), brine (20 mL×1). The organic layer was dried over Na_2SO_4, filtered and concentrated to afford the crude product. Purification by column chromatography with hexane/EtOAc afforded the final analytically pure product. IR (MIR-ATR, 4000–600 cm^{-1}): υ_{max} = 3041, 2865, 2110, 2027, 1984, 1926, 1684, 1618, 1592, 1455, 1377, 1330, 1258, 1217, 812, 752. ^{1}H NMR ($CDCl_3$, 400 MHz): δ_H = 10.25 (s, 1H), 8.48-8.46 (m, 1H), 7.94 (d, 1H, J = 8.3 Hz), 7.90-7.87 (m, 1H), 7.81 (d, 1H, J = 8.3 Hz), 7.71-7.66 (m, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ_C = 193.6, 129.7, 129.5, 128.7, 125.6, 121.8, 116.2. HR-MS (ESI+) m/z calculated for $[C_{13}H_{11}N_2]^+ = [M+H]^+$: 198.0662; found: 198.0661.

(C) General procedure for the synthesis of 2*H*-indazole (3a-x):



2-Azidobenzaldehyde **1** (1 mmol), amine **2** (1 mmol) were taken in a 10 mL microwave vessel and sealed with microwave septum. It was then placed in to CEM Discover system under the irradiation conditions: 3-5 min run time with high stirring. Maximum power and maximum pressure were set at 250 W and 300 psi respectively, with a set temperature of 60-100 ^{o}C for 50-100 min (hold time) depending on the components. After completion, the mixture was cooled to room temperature. The reaction mixture was diluted with EtOH and slight amount of charcoal was added, filtered, dried in vacuo and recrystallized using ethanol and few of them are purified on a silica gel column chromatography (hexane/ethylacetate 90:10 to 85:15). All the compounds were confirmed by FTIR, ^{1}H NMR, ^{13}C NMR and HR-MS Spectral analyses and **3k** was further confirmed by XRD. Among 24 compounds, 10 (**3b, 3c, 3n, 3p, 3s-3x**) are unknown and 14 (**3a, 3d-3m, 3o, 3q and 3r**) are known.

(D) General procedure for the synthesis of indazolo[2,3-*a*]quinoxalines (6a-i) in stepwise:

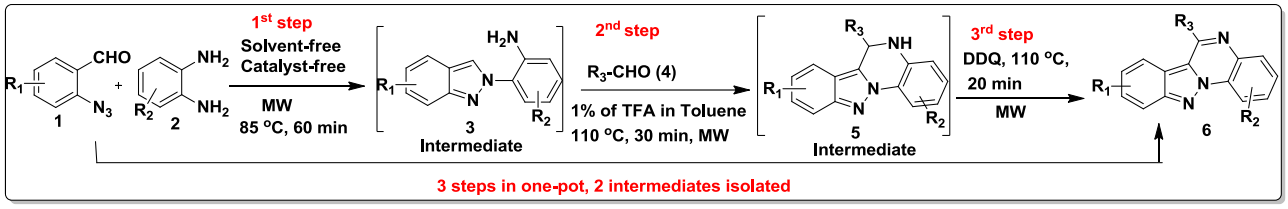


2*H*-indazole **3** (1 mmol) and aldehyde **4** (1 mmol) were taken in 10 mL microwave vessel and added 1% TFA in toluene, sealed with microwave septum. It was then placed in to CEM Discover system under the irradiation conditions: 3-5 min run time with high stirring. Maximum power and maximum pressure were set at 250 W and 300 psi respectively, with a set temperature of 110 ^{o}C for 30 min (hold time). After completion, the mixture was cooled to room temperature. Then 0.5 equivalent of DDQ was added and treated under the same conditions as above for 15 min. On cooling to room temperature, the reaction mixture was quenched with $NaHCO_3$, extracted with ethylacetate, dried over Na_2SO_4 and was purified on a silica gel column chromatography (hexane/ethylacetate 90:10) which furnished the respective solids (**6a-i**). All the compounds were confirmed by FTIR, ^{1}H NMR, ^{13}C NMR and HR-MS spectral analyses.

Table 1: Screening of %TFA and its solvent for Pictet-Spengler strategy:

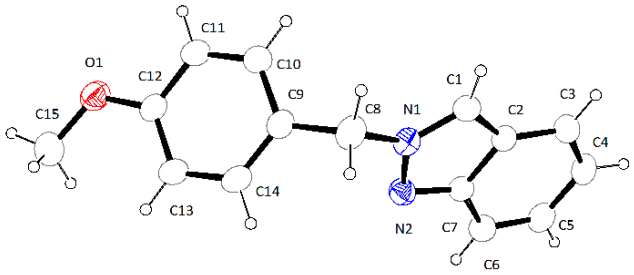
S.no	% TFA in solvent	Temperature (^{o}C)	Yield (%)
1	50% TFA in DCE	85	97
2	40% TFA in DCE	85	97
3	20% TFA in DCE	85	94
4	10% TFA in DCE	85	92
5	5% TFA in DCE	85	85
6	5% TFA in toluene	110	97
7	**1% TFA in toluene**	**110**	**96**
8	Toluene	110	15

(E) General procedure for sequential one-pot synthesis of indazolo[2,3-*a*]quinoxaline (6a-i):



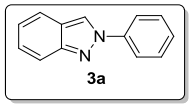
2-Azidobenzaldehyde **1** (1 mmol), diamine **2** (1 mmol) were taken in a 10 mL microwave vessel and sealed with microwave septum. It was then placed in to CEM Discover system under the irradiation conditions: 3-5 min run time with high stirring. Maximum power and maximum pressure were set at 250 W and 300 psi respectively, with a set temperature of 85 ^{o}C for 60 min (hold time). Once indazole formation was confirmed by TLC, aldehyde **4** and 1% TFA in toluene were added and treated under the microwave condition: 3-5 min run time with high stirring. Maximum power and maximum pressure were set at 250 W and 300 psi respectively, with a set temperature of 110 ^{o}C for 30 min (hold time). After completion, the mixture was cooled to room temperature. Then 0.5 equivalent of DDQ was added and treated under the same conditions as above for 15 min. On cooling to room temperature, the reaction mixture was quenched with $NaHCO_3$, extracted with ethylacetate, dried over Na_2SO_4 and was purified on a silica gel column chromatography (hexane/ethylacetate 90:10) furnished the respective solids (**6a-i**). All the compounds were confirmed by FTIR, ^{1}H NMR, ^{13}C NMR and HR-MS spectral analyses.

(G) X-ray crystal structure data for 2-(4-Methoxybenzyl)-2*H*-indazole (3k) CCDC 994876:

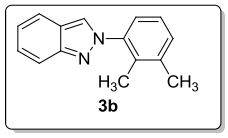


Operator	K. Ravikumar
Diffractometer	Oxford Super Nova
Empirical formula	$C_{15}H_{14}N_2O$
Formula weight	238.28
Temperature/K	293(2)
Wavelength/A	1.54184
Crystal system	Monoclinic
Space group	P 21
a/Å	9.4150(16)
b/Å	5.6395(9)
c/Å	12.3566(18)
α/°	90
β/°	110.273(18)
γ/°	90
Volume/Å^3	615.44 (18)
Z	2
ρ_{calc}mg/mm^3	1.286
m/mm^{-1}	0.652
F(000)	252
Crystal size/mm^3	0.18 x 0.16 x 0.12
2Θ range for data collection	3.814 to 70.672
Index ranges	-11<=h<=10, -6<=k<=3, -14<=l<=15
Reflections collected	2239
Independent reflections	1654 [R (int) = 0.0200]
Data/restraints/parameters	1654 / 1 / 165
Goodness-of-fit on F^2	1.091
Final R indexes [I>=2σ (I)]	R1 = 0.0386, wR2 = 0.0975
Final R indexes [all data]	R1 = 0.0463, wR2 = 0.1079
Largest diff. peak/hole / e Å^{-3}	0.146 and -0.128

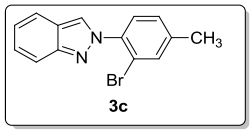
Spectral data of all compounds (3a-x), 5 and (6a-i):



2-Phenyl-2*H*-indazole (3a):[2] Reaction time = 50 min; Cream solid (94%), Mp 74–76 ^{o}C. IR (MIR-ATR, 4000–600 cm^{-1}): υ_{max} = 3128, 3055, 2923, 2852, 1628, 1595, 1519, 1496, 1379, 1314, 1204, 1046, 780, 751. ^{1}H NMR ($CDCl_3$, 400 MHz): δ_H = 8.42 (s, 1H), 7.92 (d, 2H, J = 7.3 Hz), 7.82 (d, 1H, J = 8.8 Hz), 7.72 (d, 1H, J = 8.3 Hz), 7.54 (t, 2H, J = 7.8 Hz), 7.43-7.40 (m, 1H), 7.36-7.32 (m, 1H), 7.13 (dd, 1H, J_a = 7.8 and J_b = 6.8 Hz). ^{13}C NMR ($CDCl_3$, 100 MHz): δ_C = 149.8, 140.6, 129.6, 127.9, 126.9, 122.8, 122.5, 121.0, 120.5, 120.4, 118.0. HR-MS (ESI+) m/z calculated for $[C_{13}H_{11}N_2]^+$ = $[M+H]^+$: 195.0917; found: 195.0908.

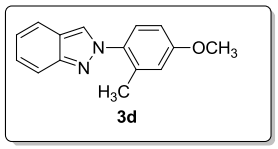


2-(2,3-dimethylphenyl)-2*H*-indazole (3b): Reaction time = 50 min; Brown solid (97%), Mp 68–70 ^{o}C. IR (MIR-ATR, 4000–600 cm^{-1}): υ_{max} = 3052, 2945, 2921, 1625, 1583, 1515, 1482, 1387, 1346, 1265, 1192, 1110, 1081, 1029, 957, 780, 755, 713, 662. ^{1}H NMR ($CDCl_3$, 400 MHz): δ_H = 8.05 (s, 1H), 7.79 (d, 1H, J = 8.8 Hz), 7.72 (d, 1H, J = 8.3 Hz), 7.34-7.27 (m, 2H), 7.21 (m, 2H), 7.14-7.11 (m, 1H), 2.35 (s, 3H), 2.03 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ_C = 149.2, 140.5, 138.5, 133.0, 130.7, 126.3, 125.9, 124.7, 124.5, 122.1, 121.9, 120.3, 117.9, 20.3, 14.3. HR-MS (ESI+) m/z calculated for $[C_{15}H_{15}N_2]^+$ = $[M+H]^+$: 223.1230; found: 223.1221.



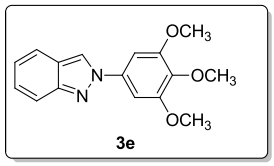
3c

2-(2-Bromo-4-methylphenyl)-2*H*-indazole (3c): Reaction time = 50 min; Brown solid (90%), Mp 66–68 ^{o}C. IR (MIR-ATR, 4000–600 cm^{-1}): υ_{max} = 3057, 2921, 1521, 1500, 1386, 1200, 1070, 1030, 954, 820, 784, 755, 646. ^{1}H NMR ($CDCl_3$, 400 MHz): δ_H = 8.25 (s, 1H), 7.8 (d, 1H, *J* = 8.8 Hz), 7.74 (d, 1H, *J* = 8.3 Hz), 7.57 (s, 1H), 7.49 (d, 1H, *J* = 7.8 Hz), 7.37-7.33 (m, 1H), 7.26 (d, 1H, *J* = 7.3 Hz), 7.16-7.12 (m, 1H), 2.43 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ_C = 149.3, 141.0, 137.8, 134.0, 129.0, 128.4, 126.8, 125.2, 122.3, 121.9, 120.5, 118.5, 118.0, 20.9. HR-MS (ESI+) m/z calculated for $[C_{14}H_{12}BrN_2]^+ = [M+H]^+$: 287.0178; found: 287.0168.



3d

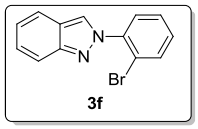
2-(4-Methoxy-2-methylphenyl)-2*H*-indazole (3d):[3] Reaction time = 50 min; Brown solid (92%), Mp 82–84 ^{o}C. IR (MIR-ATR, 4000–600 cm^{-1}) υ_{max} = 2923, 2854, 1612, 1568, 1545, 1452, 1409, 1264, 1153, 1094, 1004, 806, 748, 696. ^{1}H NMR ($CDCl_3$, 400 MHz): δ_H = 8.06 (s, 1H), 7.80 (d, 1H, *J* = 8.8 Hz), 7.74 (d, 1H, *J* = 8.3 Hz), 7.36-7.33 (m, 2H), 7.17-7.13 (m, 1H), 6.88-6.83 (m, 2H), 3.87 (s, 3H), 2.2 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ_C = 159.9, 149.1, 135.5, 133.7, 127.7, 126.3, 124.6, 122.0, 122.0, 120.2, 117.9, 116.1, 111.6, 55.5, 18.0. HR-MS (ESI+) m/z calculated for $[C_{15}H_{15}N_2O]^+ = [M+H]^+$: 239.1179; found: 239.1188.



3e

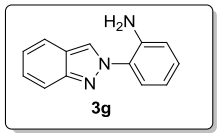
2-(3,4,5-trimethoxyphenyl)-2*H*-indazole (3e):[4] Reaction time = 50 min; Brown solid (90%), Mp 82–84 ^{o}C. IR (MIR-ATR, 4000–600 cm^{-1}): υ_{max} = 3124, 2937, 2830, 1599, 1518, 1504, 1467, 1423, 1319, 1225, 1122, 1072, 998, 830, 753, 729. ^{1}H NMR ($CDCl_3$, 400 MHz): δ_H = 8.36 (s,

1H), 7.78 (d, 1H, J = 8.8 Hz), 7.69 (d, 1H, J = 8.3 Hz), 7.32 (dd, 1H, J_a = 8.3 and J_b = 7.3 Hz), 7.13-7.09 (m, 3H), 3.96-3.95 (m, 6H), 3.90 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ_C = 153.8, 137.9, 136.6, 126.9, 122.7, 122.5, 120.7, 120.3, 117.8, 98.9, 61.0, 56.4. HR-MS (ESI+) m/z calculated for $[C_{16}H_{17}N_2O_3]^+ = [M+H]^+$: 285.1234; found: 285.1224.



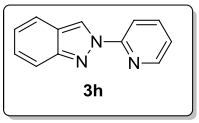
3f

2-(2-Bromophenyl)-2*H*-indazole (3f):[5] Reaction time = 50 min; Brown solid (86%), Mp 82–84 ^{o}C. IR (MIR-ATR, 4000–600 cm^{-1}): υ_{max} = 3429, 3063, 3031, 2927, 2852, 1660, 1578, 1562, 1475, 1346, 1147, 938, 765, 695. ^{1}H NMR ($CDCl_3$, 400 MHz): δ_H = 8.13 (br s, 1H), 7.83 (d, 1H, J = 8.8 Hz), 7.76 (d, 2H, J = 7.8 Hz), 7.63-7.56 (m, 1H), 7.50-7.48 (m, 1H), 7.36-7.35 (m, 2H), 7.16 (t, 1H, J = 7.6 Hz). ^{13}C NMR ($CDCl_3$, 100 MHz): δ_C = 149.4, 140.3, 133.8, 130.5, 128.9, 128.3, 126.9, 125.2, 122.5, 121.9, 120.6, 118.9, 118.0. HR-MS (ESI+) m/z calculated for $[C_{13}H_{10}BrN_2]^+ = [M+H]^+$: 285.1234; found: 285.1224

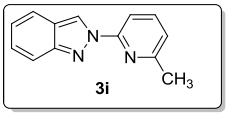


3g

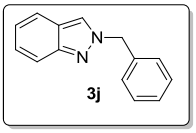
2-(2*H*-Indazol-2-yl)aniline (3g):[6] Reaction time = 60 min; Off white (86%), Mp 76–78 ^{o}C. IR (MIR-ATR, 4000–600 cm^{-1}): υ_{max} = 3438, 3330, 3056, 1615, 1516, 1502, 1464, 1385, 1349, 1314, 1248, 1193, 1144, 1048, 954, 787, 744. ^{1}H NMR ($CDCl_3$, 400 MHz): δ_H = 8.16 (s, 1H), 7.72 (dd, 2H, J = 19.1 and J = 8.8 Hz), 7.33-7.27 (m, 2H), 7.21-7.15 (m, 1H), 7.12-7.08 (m, 1H), 6.79 (m, 2H).^{13}C NMR ($CDCl_3$, 100 MHz): δ_C = 149.5, 141.5, 129.5, 126.8, 126.5, 125.0, 123.7, 122.2, 121.9, 120.4, 118.0, 117.5, 117.5. HR-MS (ESI+) m/z calculated for $[C_{13}H_{12}N_3]^+ = [M+H]^+$: 210.1026; found: 210.1018.



2-(Pyridin-2-yl)-2*H*-indazole (3h):[2] Reaction time = 50 min; Cream solid (88%), Mp 104–106 ^{o}C. IR (MIR-ATR, 4000–600 cm^{-1}): υ_{max} = 3396, 3149, 3057, 3010, 2926, 1627, 1591, 1573, 1516, 1472, 1376, 1201, 1144, 1056, 954, 778, 756, 734. ^{1}H NMR ($CDCl_3$, 400 MHz): δ_H = 9.1 (s, 1H), 8.49 (d, 1H, J = 3.4 Hz), 8.27 (d, 1H, J = 8.3 Hz), 7.89-7.85 (m, 1H), 7.76-7.71 (m, 2H), 7.34-7.26 (m, 2H), 7.11-7.07 (m, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ_C = 151.8, 150.3, 148.3, 138.9, 127.6, 122.8, 122.7, 122.4, 121.2, 120.6, 118.0, 114.1. HR-MS (ESI+) m/z calculated for $[C_{12}H_{10}N_3]^+ = [M+H]^+$: 196.0869; found: 196.0862.

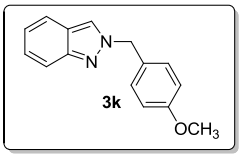


2-(6-methylpyridin-2-yl)-2*H*-indazole (3i):[1b&2] Reaction time = 50 min; Pale yellow solid (89%), Mp 106–108 ^{o}C. IR (MIR-ATR, 4000–600 cm^{-1}): υ_{max} = 3156, 3051, 2925, 1627, 1603, 1570, 1518, 1474, 1428, 1374, 1329, 1207, 1072, 910, 787, 756. ^{1}H NMR ($CDCl_3$, 400 MHz): δ_H = 9.14 (s, 1H), 8.07 (d, 1H, J = 8.3 Hz), 7.78-7.72 (m, 3H), 7.33 (dd, 1H, J_a = 7.8 and J_b = 6.8 Hz), 7.15-7.10 (m, 2H), 2.62 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ_C = 157.8, 151.2, 150.2, 139.0, 127.4, 122.5, 122.3, 122.2, 122.0, 120.6, 118.0, 110.9, 24.2. HR-MS (ESI+) m/z calculated for $[C_{13}H_{12}N_3]^+ = [M+H]^+$: 210.1026; found: 210.1021.

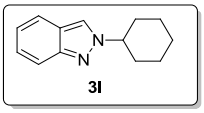


2-Benzyl-2*H*-indazole (3j):[1b&2] Reaction time = 50 min; Brown solid (94%), Mp 44–46 ^{o}C. IR (MIR-ATR, 4000–600 cm^{-1}): υ_{max} = 3060, 3031, 2936, 1627, 1514, 1495, 1469, 1422, 1309, 1153, 1135, 1009, 981, 907, 838, 782, 754, 703, 643. ^{1}H NMR ($CDCl_3$, 400 MHz): δ_H = 7.86 (s, 1H), 7.73 (d, 1H), 7.61 (d, 1H), 7.35-7.24 (m, 6H), 7.08-7.04 (m, 1H), 5.57 (s, 2H).^{13}C NMR

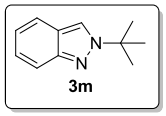
($CDCl_3$, 100 MHz): δ_C = 149.0, 135.8, 129.0, 128.4, 128.0, 126.0, 122.9, 122.1, 121.8, 120.2, 117.6. 57.5. HR-MS (ESI+) m/z calculated for $[C_{14}H_{13}N_2]^+$ = $[M+H]^+$: 209.1073; found: 209.1073.



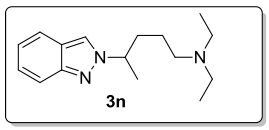
2-(4-Methoxybenzyl)-2*H*-indazole (3k):[7] Reaction time = 50 min; Off white solid (96%), Mp 114–118 ^oC. IR (MIR-ATR, 4000–600 cm^{-1}): υ_{max} = 3121, 2930, 2835, 1993, 1611, 1513, 1453, 1390, 1247, 1178, 1028, 814, 792, 759. ^1H NMR ($CDCl_3$, 400 MHz): δ_H = 7.83 (s, 1H), 7.72 (d, 1H, *J* = 8.8 Hz), 7.6 (d, 1H, *J* = 8.3 Hz), 7.29-7.24 (m, 3H), 7.07-7.04 (m, 1H), 6.88 (m, 2H, *J* = 8.8 Hz), 5.52 (s, 2H), 3.78 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ_C = 159.7, 148.9, 129.6, 127.7, 125.9, 122.5, 122.0, 121.7, 120.1, 117.5, 114.3, 57.0, 55.3. HR-MS (ESI+) m/z calculated for $[C_{15}H_{15}N_2O]^+$ = $[M+H]^+$: 239.1179; found: 239.1188.



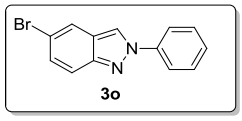
2-Cyclohexyl-2*H*-indazole (3l):[2] Reaction time = 50 min; Peach solid (92 %), Mp 80-82 ^oC. IR (MIR-ATR, 4000–600 cm^{-1}): υ_{max} = 3395, 3150, 3047, 2935, 2849, 1621, 1509, 1449, 1373, 1306, 1227, 1148, 976, 895, 751, 727, 647. ^1H NMR ($CDCl_3$, 400 MHz): δ_H = 7.94 (s, 1H), 7.72 (d, 1H, *J* = 8.8 Hz), 7.67 (d, 1H, *J* = 8.8 Hz), 7.31-7.27 (m, 1H), 7.10-7.07 (m, 1H), 4.42 (tt, 1H, J_a = 11.7 Hz and J_b = 3.5 Hz), 2.29 (d, 2H, *J* = 10.8 Hz), 1.99-1.95 (m, 3H), 1.92-1.86 (m, 1H), 1.82-1.74 (m, 1H), 1.57-1.45 (m, 2H), 1.40-1.30 (m, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ_C = 148.2, 125.6, 121.4, 121.4, 120.1, 117.4, 62.9, 34.0, 25.5, 25.8. HR-MS (ESI+) m/z calculated for $[C_{13}H_{17}N_2]^+$ = $[M+H]^+$: 201.1386; found: 201.1385.



2-(*Tert*-butyl)-2*H*-indazole (3m):[2&8] Reaction time = 50 min; Dark brown solid (91%), Mp 115–118 ^{o}C. IR (MIR-ATR, 4000–600 cm^{-1}): υ_{max} = 3395, 3150, 3037, 2935, 2846, 1621, 1519, 1446, 1373, 1250, 1227, 1148, 972, 891, 751, 713, 643. ^{1}H NMR ($CDCl_3$, 400 MHz): δ_H = 8.0 (s, 1H), 7.73 (d, 1H, J = 8.8 Hz), 7.62 (d, 1H, J = 8.3 Hz), 7.26-7.22 (m, 1H), 7.04-7.01 (m, 1H), 1.71 (s, 9H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ_C = 148.3, 125.6, 121.4, 121.3,120.2, 119.3, 117.5, 60.0, 30.2. HR-MS (ESI+) m/z calculated for $[C_{11}H_{15}N_2]^+$ = $[M+H]^+$: 175.1230; found: 175.1230.

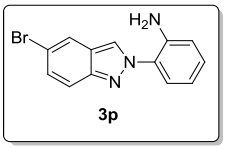


***N*,*N*-diethyl-4-(2*H*-indazol-2-yl)pentan-1-amine (3n)**: Reaction time = 50 min; Brown liquid (95%). IR (MIR-ATR, 4000–600 cm^{-1}): υ_{max} = 3058, 2968, 2933, 287, 2800, 1627, 1513, 1454, 1382, 1291, 1200, 1138, 1069, 972, 754, 665. ^{1}H NMR ($CDCl_3$, 400 MHz): δ_H = 7.92 (s, 1H), 7.71 (d, 1H, J = 8.3 Hz), 7.64 (d, 1H, J = 8.3 Hz), 7.27-7.23 (m, 1H), 7.07-7.03 (m, 1H), 4.63-4.54 (m, 1H), 2.59-2.31 (m, 6H), 2.07 (ddt, 1H, J_a = 19, J_b = 8.7 and J_c = 5.3 Hz), 1.93-1.84 (m, 1H), 1.64 (d, 3H, J = 6.8 Hz), 1.46-1.36 (m, 1H), 1.29-1.21 (m, 1H), 1.01-.93 (m, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ_C = 148.4, 125.6, 121.5, 121.4, 120.8, 120.1, 117.5, 60.1, 52.4, 46.7, 35.4, 23.8, 21.9, 11.5. HR-MS (ESI+) m/z calculated for $[C_{16}H_{26}N_3]^+$ = $[M+H]^+$: 260.2121; found: 260.2125.

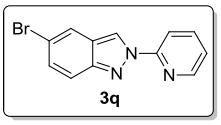


5-Bromo-2-phenyl-2*H*-indazole (3o):[2] Reaction time = 50 min; Cream solid (90%), Mp 126–128 ^{o}C. IR (MIR-ATR, 4000–600 cm^{-1}): υ_{max} = 3745, 3127, 2920, 2849, 1597, 1509, 1463, 1371,

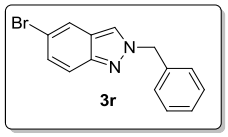
1199, 1039, 872, 807, 753, 727. ^{1}H NMR ($CDCl_3$, 400 MHz): δ_H = 8.36-8.34 (m, 1H), 7.88 (d, 3H, J = 8.3 Hz), 7.68 (d, 1H, J = 9.3 Hz), 7.53 (t, 2H, J = 7.6 Hz), 7.44-7.37 (m, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ_C = 148.3, 140.2, 130.5, 129.7, 128.3, 123.9, 122.5, 121.0, 119.9, 119.7, 116.0. HR-MS (ESI+) m/z calculated for $[C_{13}H_{10}BrN_2]^+ = [M+H]^+$: 273.0022; found: 273.0016.



2-(5-Bromo-2*H*-indazole-2-yl)aniline (3p): Reaction time = 60 min; Pale brown solid (87%), Mp 88–90 ^{o}C. IR (MIR-ATR, 4000–600 cm^{-1}): υ_{max} = 3746, 3457, 3336, 2923, 2853, 2312, 1993, 1618, 1510, 1454, 1367, 1188, 1037, 802, 749. ^{1}H NMR ($CDCl_3$, 400 MHz): δ_H = 8.17 (s, 1H), 7.9 (d, 1H, J = 1 Hz), 7.65 (d, 1H, J = 8.8 Hz), 7.4 (dd, 1H, J_a = 9 and J_b = 1.7 Hz), 7.33-7.31 (m, 1H), 7.27-7.22 (m, 1H), 6.90-6.82 (m, 2H), 4.87 (br s, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ_C = 147.8, 141.3, 130.3, 129.7, 126.1, 124.9, 123.1, 123.0, 122.5, 119.2, 118.2, 117.6. HR-MS (ESI+) m/z calculated for $[C_{13}H_{10}BrN_3]^+ = [M+H]^+$: 288.0131; found: 288.0131.

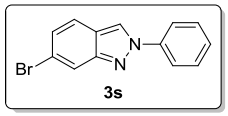


5-Bromo-2-(pyridine-2-yl)-2*H*-indazole (3q):[9] Reaction time = 60 min; Yellow solid (89%), Mp 176–178 ^{o}C. IR (MIR-ATR, 4000–600 cm^{-1}): υ_{max} = 3143, 2921, 2851, 1621, 1592, 1502, 1431, 1368, 1194, 1056, 1035, 802, 776. ^{1}H NMR ($CDCl_3$, 400 MHz): δ_H = 9.05 (s, 1H), 8.52-8.51 (m, 1H), 8.26 (d, 1H, J = 8.3 Hz), 7.93-7.88 (m, 2H), 7.64 (d, 1H, J = 8.8 Hz), 7.39-7.27 (m, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ_C = 151.5, 148.9, 148.4, 139.0, 131.2, 123.5, 123.2, 123.1, 120.0, 119.8, 116.8, 114.1. HR-MS (ESI+) m/z calculated for $[C_{12}H_9BrN_3]^+ = [M+H]^+$: 273.9974; found: 273.9964.



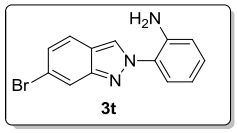
3r

2-Benzyl-5-bromo-2*H*-indazole (3r):[7] Reaction time = 50 min; Brown solid (93%), Mp 52–54 ^{o}C. IR (MIR-ATR, 4000–600 cm^{-1}): υ_{max} = 3063, 3031, 2934, 1730, 1500, 1454, 1342, 1141, 1039, 803, 706. ^{1}H NMR ($CDCl_3$, 400 MHz): δ_H = 7.82 (s, 1H), 7.77 (d, 1H, J = 1 Hz), 7.6 (d, 1H, J = 8.8 Hz), 7.38-7.31 (m, 4H), 7.27-7.25 (m, 2H), 5.56 (s, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ_C = 147.3, 135.4, 129.6, 129.0, 128.6, 128.0, 123.3, 122.4, 122.3, 119.3, 115.3, 57.7. HR-MS (ESI+) m/z calculated for $[C_{14}H_{11}BrN_2]^+$ = $[M+H]^+$: 287.0178; found: 287.0170.



3s

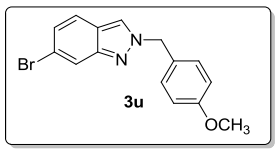
6-Bromo-2-phenyl-2*H*-indazole (3s): Reaction time = 50 min; Peach solid (86%), Mp 102–104 ^{o}C. IR (MIR-ATR, 4000–600 cm^{-1}): υ_{max} = 3126, 3080, 3056, 1620, 1594, 1536, 1506, 1462, 1375, 1203, 1034, 920, 808, 758, 685. ^{1}H NMR ($CDCl_3$, 400 MHz): δ_H = 8.39 (s, 1H), 7.99 (s, 1H), 7.89 (d, 2H, J = 7.8 Hz), 7.61-7.52 (m, 3H), 7.45-7.41 (m, 1H), 7.22 (dd, 1H, J_a = 9.3 and J_b = 1.5 Hz). ^{13}C NMR ($CDCl_3$, 100 MHz): δ_C = 150.4, 140.2, 129.7, 128.2, 126.3, 121.8, 121.3, 121.0, 120.9, 120.8, 120.3. HR-MS (ESI+) m/z calculated for $[C_{13}H_{10}BrN_2]^+$ = $[M+H]^+$: 273.0022; found: 273.0011.



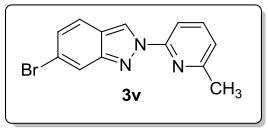
3t

2-(6-Bromo-2*H*-indazol-2-yl)aniline (3t): Reaction time = 60 min; Pale yellow solid (84%), Mp 176–178 ^{o}C. IR (MIR-ATR, 4000–600 cm^{-1}): υ_{max} = 3457, 3336, 2923, 2853, 2312, 1993, 1618, 1510, 1454, 1367, 1188, 1037, 802, 749. ^{1}H NMR ($CDCl_3$, 400 MHz): δ_H = 8.2 (s, 1H), 7.95 (s, 1H), 7.62 (d, 1H, J = 8.8 Hz), 7.33-7.22 (m, 4H), 6.96-6.80 (m, 2H), 4.86 (br s, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ_C = 150.1, 148.5, 141.3, 129.7, 127.7, 126.2, 126.2, 124.9, 121.8,

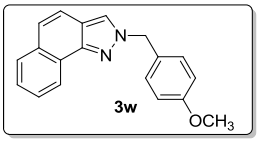
120.8, 120.4, 119.9, 119.6, 118.2, 117.9, 110.7. HR-MS (ESI+) m/z calculated for $[C_{13}H_{10}BrN_3]^+$ = $[M+H]^+$: 288.0131; found: 288.0131.



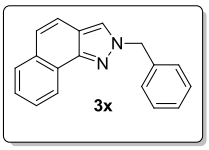
6-Bromo-2-(4-methoxybenzyl)-2*H*-indazole (3u): Reaction time = 50 min; Pale yellow solid (90%), Mp 88–90 ^oC. IR (MIR-ATR, 4000–600 cm^{-1}): υ_{max} = 3124, 2933, 2835, 1612, 1513, 1248, 1176, 1035, 911, 807, 735, 593. ^1H NMR ($CDCl_3$, 400 MHz): δ_H = 7.9 (s, 1H), 7.82 (s, 1H), 7.48 (d, 1H, J = 8.8 Hz), 7.26 (d, 2H, J = 8.8 Hz), 7.14 (dd, 1H, J_a = 8.8 and J_b = 1.5 Hz), 6.9 (d, 2H, J = 8.3 Hz), 5.5 (s, 2H), 3.8 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ_C = 159.8, 149.6, 129.7, 127.3, 125.4, 123.0, 121.6, 120.6, 120.0, 114.4, 57.1, 55.3. HR-MS (ESI+) m/z calculated for $[C_{15}H_{14}BrN_2O]^+$ = $[M+H]^+$: 317.0284; found: 317.0275.



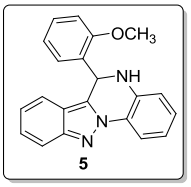
6-Bromo-2-(6-methylpyridin-2-yl)-2*H*-indazole (3v): Reaction time = 70 min; Cream solid (87%), Mp 110–112 ^oC.IR (MIR-ATR, 4000–600 cm^{-1}): υ_{max} = 3164, 3040, 2918, 1621, 1630, 1577, 1497, 1477, 1455, 1371, 1266, 1209, 1077, 1034, 989, 922, 844, 790, ^1H NMR ($CDCl_3$, 400 MHz): δ_H = 9.12 (s, 1H), 8.04 (d, 1H, J = 8.3 Hz), 7.94 (s, 1H), 7.78 (t, 1H, J = 7.8 Hz), 7.6 (d, 1H, J = 8.8 Hz), J = 7.17 (d, 2H, J = 7.3 Hz), 2.62 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ_C = 157.9, 150.9, 150.7, 139.0, 126.4, 122.6, 122.5, 121.5, 121.1, 120.8, 120.4, 110.9, 24.24. HR-MS (ESI+) m/z calculated for $[C_{13}H_{11}BrN_3]^+$ = $[M+H]^+$: 288.0131; found: 288.0130.



2-(4-methoxybenzyl)-2*H*-benzo[*g*]indazole (3w): Reaction time = 90 min; Brown solid (75%), Mp 110–112 ^{o}C. IR (MIR-ATR, 4000–600 cm^{-1}): υ_{max} = 3050, 2930, 2835, 1612, 1512, 1460, 1247, 1177, 1032, 955, 813, 746, 697. ^{1}H NMR ($CDCl_3$, 400 MHz): δ_H = 8.59 (d, 1H, *J* = 7.8 Hz), 7.79-7.75 (m, 2H), 7.58-7.49 (m, 2H), 7.46 (d, 1H, *J* = 9.3 Hz), 7.33 (d, 1H, *J* = 8.8 Hz), 7.25 (d, 2H, *J* = 8.8 Hz), 6.87 (d, 2H, *J* = 8.8 Hz), 5.55 (s, 2H), 3.77 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ_C = 159.6, 146.3, 132.4, 129.6, 128.3, 128.1, 126.5, 125.5, 123.6, 123.5, 122.3, 119.1, 118.4, 114.3, 56.7, 55.3. HR-MS (ESI+) m/z calculated for $[C_{19}H_{17}N_2O]^+$ = $[M+H]^+$: 289.1335; found: 289.1329.



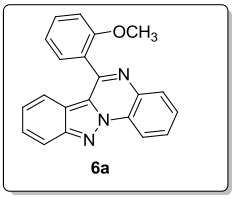
2-Benzyl-2*H*-benzo[*g*]indazole (3x): Reaction time = 100 min; Olive green solid (68 %), Mp 50–52 ^{o}C. IR (MIR-ATR, 4000–600 cm^{-1}): υ_{max} = 3481, 3308, 3052, 3030, 2929, 1651, 1613, 1546, 1456, 1426, 1326, 1143, 1101, 812, 739, 696,562. ^{1}H NMR ($CDCl_3$, 400 MHz): δ_H = 8.61 (d, 1H, *J* = 7.8 Hz), 7.81-7.79 (m, 2H), 7.60-7.52 (m, 2H), 7.51-7.45 (m, 1H), 7.37-7.31 (m, 4H), 7.29-7.24 (m, 2H), 5.63 (s, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ_C = 146.4, 136.2, 132.2, 129.6, 128.9, 128.6, 128.3, 128.2, 127.9, 126.5, 125.6, 123.9, 123.7, 122.4, 121.8, 119.1, 118.4, 116.1, 57.2. HR-MS (ESI+) m/z calculated for $[C_{18}H_{15}N_2]^+$ = $[M+H]^+$: 259.1230; found: 259.12403.



5

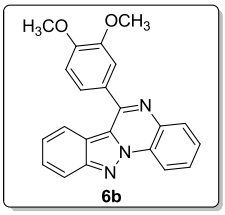
Isolated intermediate (5) and its spectral data:

6-(2-methoxyphenyl)-5,6-dihydroindazolo[2,3-*a*]quinoxaline (5): lemon yellow solid (99%), Mp 48–50 ^{o}C. IR (MIR-ATR, 4000–600 cm^{-1}): υ_{max} = 3271, 3064, 2935, 2835, 1602, 1583, 1494, 1464, 1359, 1250, 1102, 744, 677. ^{1}H NMR ($CDCl_3$, 400 MHz): δ_H = 8.16 (d, 1H, J = 7.8 Hz), 7.77 (d, 1H, J = 8.8 Hz), 7.29-7.25 (m, 2H), 7.2 (d, 1H, J = 8.8 Hz), 7.06 (td, 1H, J_a = 7.7 and J_b = 1.2 Hz), 6.96-6.86 (m, 3H), 6.80-6.74 (m, 2H), 6.68 (d, J = 7.3 Hz), 6.61 (s, 1H), 4.78 (br.s, 1H), 3.92 (s, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ_C = 156.3, 149.4, 136.5, 129.6, 128.9, 128.4, 128.1, 127.8, 126.8, 124.7, 121.6, 120.9, 119.5, 119.1, 119.0, 117.5, 117.4, 114.8, 110.6, 55.5, 49.2. HR-MS (ESI+) m/z calculated for $[C_{21}H_{18}N_3O]^+$ = $[M+H]^+$: 328.1444; found: 328.1432.

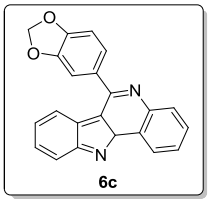


6a

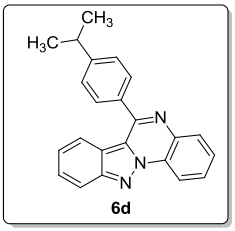
6-(2-Methoxyphenyl)indazolo[2,3-*a*]quinoxaline (6a): Yellow color solid (96%), Mp 140-144 ^{o}C. IR (MIR-ATR, 4000–600 cm^{-1}): υ_{max} = 3064, 2929, 2836, 1602, 1581, 1465, 1359, 1250, 1161, 1024, 952, 745, 677. ^{1}H NMR ($CDCl_3$, 400 MHz): δ_H = 8.9 (dd, 1H, J_a = 8.3 and J_b = 1Hz), 8.3 (dd, 1H, J_a = 7.8 and J_b = 1Hz), 8.07 (s, 1H), 7.82-7.81 (m, 2H), 7.61-7.56 (m, 3H), 7.27-7.15 (m, 4H), 3.36 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ_C = 157.4, 152.2, 149.2, 138.2, 131.5, 130.4, 129.1, 128.1, 128.0, 126.8, 123.0, 121.3, 120.8, 117.6, 117.2, 116.4, 111.2, 55.5. HR-MS (ESI+) m/z calculated for $[C_{21}H_{16}N_3O]^+$ = $[M+H]^+$: 326.1288; found: 326.1292.



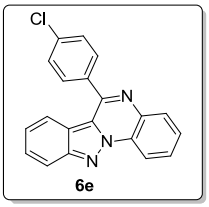
6-(3,4-Dimethoxyphenyl)indazolo[2,3-*a*]quinoxaline (6b): Off white solid (96%), Mp 168-170 ^{o}C. IR (MIR-ATR, 4000–600 cm^{-1}): υ_{max} = 3064, 2993, 2835, 1603, 1578, 1502, 1432, 1260, 1138, 1025, 950, 760, 674. ^{1}H NMR ($CDCl_3$, 400 MHz): δ_H = 8.80 (d, 1H, J = 7.8 Hz), 8.19 (d, 1H, J = 7.3 Hz), 8.00 (d, 1H, J = 8.3 Hz), 7.72-7.65 (m, 3H), 7.52-7.47 (m, 3H), 7.20-7.17 (m, 1H), 7.09 (d, 1H, J = 8.3 Hz), 4.01 (s, 3H), 3.96 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ_C = 153.7, 150.8, 149.2, 138.0, 130.4, 129.7, 128.8, 128.1, 128.0, 127.7, 125.7, 122.9, 121.9, 121.4, 117.4, 117.2, 116.4, 111.9, 111.1, 56.1, 56.0. HR-MS (ESI+) m/z calculated for $[C_{22}H_{18}N_3O_2]^+$ = $[M+H]^+$: 356.1394; found: 356.1396.



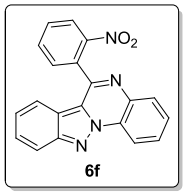
6-(Benzo[*d*][1,3]dioxol-5-yl)indazolo[2,3-*a*]quinoxaline (6c): Pale yellow solid (97%), Mp 216-218 ^{o}C. IR (MIR-ATR, 4000–600 cm^{-1}): υ_{max} = 3065, 2955, 2923, 2853, 1607, 1577, 1499, 1445, 1358, 1247, 1038, 933, 739, 673. ^{1}H NMR ($CDCl_3$, 400 MHz): δ_H = 8.86 (dd, 1H, J_a = 8.3 and J_b = 1.5 Hz), 8.23 (dd, 1H, J_a = 7.6 and J_b = 1.2 Hz), 8.07 (d, 1H, J = 8.8 Hz), 7.80-7.73 (m, 3H), 7.58 (t, 1H, J = 7.6 Hz), 7.48-7.43 (m, 2H), 7.29-7.25 (m, 1H), 7.07 (d, 1H, J = 7.8 Hz), 6.13 (s, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ_C = 153.8, 149.9, 149.6, 148.5, 138.3, 132.0, 130.1, 129.2, 128.5, 128.4, 128.0, 126.0, 123.6, 123.4, 121.6, 109.7, 108.9, 101.9. HR-MS (ESI+) m/z calculated for $[C_{21}H_{14}N_3O_2]^+$ = $[M+H]^+$: 340.1081; found: 340.1081.



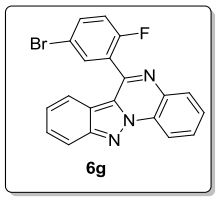
6-(4-Isopropylphenyl)indazolo[2,3-*a*]quinoxaline (6d): Pale yellow solid (95%), Mp 172-174 ^{o}C. IR (MIR-ATR, 4000–600 cm^{-1}): υ_{max} = 3063, 2958, 2868, 1609, 1577, 1478, 1358, 1227, 1105, 954, 831, 759, 744. ^{1}H NMR ($CDCl_3$, 400 MHz): δ_H = 8.84 (d, 1H, J = 7.3 Hz), 8.23 (d, 1H, J = 7.8 Hz), 8.03 (d, 1H, J = 8.3 Hz), 2.07 (d, 2H, J = 8.3 Hz), 7.75- 7.69 (m, 3H), 7.54-7.49 (m, 3H), 7.21 (t, 1H, J = 7.1 Hz), 3.09 (dt, 1H, J_a = 13.7 and J_b = 6.8 Hz), 1.39 (d, 6H, J = 6.8 Hz). ^{13}C NMR ($CDCl_3$, 100 MHz): δ_C = 154.2, 151.3, 149.3, 138.1, 135.8, 129.9, 128.9, 128.1, 128.0, 127.7, 127.0, 125.8, 123.0, 121.4, 117.4, 117.2, 116.4, 34.3, 24.0. HR-MS (ESI+) m/z calculated for $[C_{23}H_{20}N_3]^+$ = $[M+H]^+$: 338.1652; found: 338.1643.



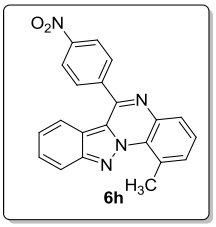
6-(4-Chlorophenyl)indazolo[2,3-*a*]quinoxaline (6e): Off white solid (92%), Mp 168-170 ^{o}C. IR (MIR-ATR, 4000–600 cm^{-1}): υ_{max} = 3396, 2954, 2922, 2852, 1659, 1550, 1478, 1360, 1227, 1160, 1091, 950, 830, 758, 739. ^{1}H NMR ($CDCl_3$, 400 MHz): δ_H = 8.86 (dd, 1H, J_a = 8.3 and J_b = 1.5 Hz), 8.82 (dd, 1H, J_a = 8.1 and J_b = 1.2 Hz), 8.05 (d, 1H, J = 8.8 Hz), 7.88 (d, 2H, J = 8.3 Hz), 7.80-7.71 (m, 2H), 7.63-7.60 (m, 3H), 7.58-7.54 (m, 1H), 7.27-7.23 (m, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ_C = 152.8,149.3, 138.0, 136.4, 130.3, 129.9, 129.3, 129.2, 128.3, 128.2, 127.8, 125.5, 123.4, 121.0, 117.6, 117.0, 116.5. HR-MS (ESI+) m/z calculated for $[C_{20}H_{13}ClN_3]^+$ = $[M+H]^+$: 330.0793; found: 330.0793.



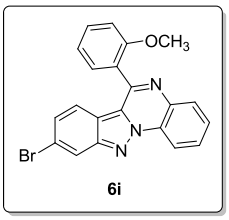
6-(2-Nitophenyl)indazolo[2,3-*a*]quinoxaline (6f): Light brown solid (89%), Mp 178-180 ^{o}C.IR (MIR-ATR, 4000–600 cm^{-1}): υ_{max} = 3065, 2923, 2853, 1608, 1526, 1429, 1345, 1228, 1160, 1088, 950, 757, 742, 704. ^{1}H NMR ($CDCl_3$, 400 MHz): δ_H = 8.89 (d, 1H, *J* = 8.3 Hz), 8.38 (d, 1H, *J* = 8.3 Hz), 8.2 (d, 1H, *J*=7.8 Hz), 8.06 (d, 1H, *J* = 8.8 Hz), 7.91-7.88 (m, 1H), 7.84-7.72 (m, 4H), 7.54 (t, 1H, *J* = 7.6 Hz), 7.17 (t, 1H, *J* = 7.3 Hz), 7.02 (d, 1H, *J* = 8.3 Hz).^{13}C NMR ($CDCl_3$, 100 MHz): δ_C = 150.7, 149.2, 148.0, 137.8, 132.9, 131.4, 130.9, 130.0, 129.7, 128.3, 128.1, 125.6, 125.3, 123.7, 119.5, 117.7, 116.9, 116.5. HR-MS (ESI+) m/z calculated for $[C_{20}H_{13}N_4O_2]^+$ = $[M+H]^+$: 341.1033; found: 341.1038.



6-(5-Bromo-2-fluorophenyl)indazolo[2,3-*a*]quinoxaline (6g): Lemon yellow solid (86%), Mp 214-217 ^{o}C. IR (MIR-ATR, 4000–600 cm^{-1}): υ_{max} = 3066, 2920, 2851, 1607, 1575, 1477, 1358, 1210, 1102, 961, 812, 757, 742, 685. ^{1}H NMR ($CDCl_3$, 400 MHz): δ_H = 8.86 (d, 1H, *J* = 8.3 Hz), 8.24 (dd, 1H, *J* = 8.3 Hz), 8.05 (d, 1H,*J* = 8.3 Hz), 7.90 (dd, 1H, J_a = 5.9 and J_b = 2.4 Hz), 7.83-7.79 (m, 1H), 7.76-7.71 (m, 2H), 7.57 (t, 1H, *J* = 7.6 Hz), 7.39 (d, 1H, *J* = 8.3 Hz), 7.27-7.24 (m, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ_C = 160.6, 158.1, 149.2, 147.3, 137.8, 134.9, 133.9, 133.8, 130.1, 129.8, 128.4, 128.3, 127.7, 127.6, 125.9, 123.7, 120.2, 120.1, 118.3, 118.1, 117.6, 117.5, 117.0, 116.5. HR-MS (ESI+) m/z calculated for $[C_{20}H_{12}BrFN_3]^+$ = $[M+H]^+$: 392.0193; found: 392.0197.

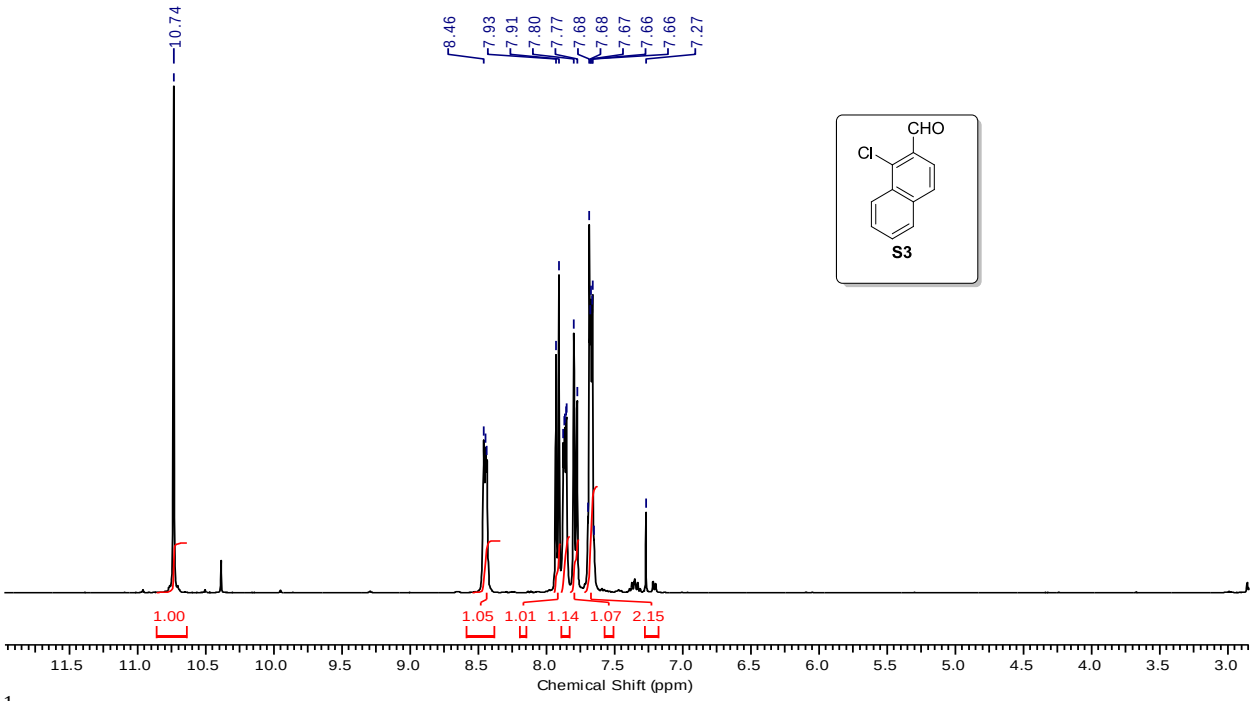


1-Methyl-6-(4-nitrophenyl)indazolo[2,3-*a*]quinoxaline (6h): Golden yellow (89%), Mp 236-238 ^{o}C. IR (MIR-ATR, 4000–600 cm^{-1}): υ_{max} = 3020, 2921, 1624, 1529, 1415, 1345, 1297, 1128, 935, 746, 687. ^{1}H NMR ($CDCl_3$, 400 MHz): δ_H = 8.83 (d, 1H, J = 7.3 Hz), 8.48 (d, 1H, J = 8.3 Hz), 7.98-7.89 (m, 3H), 7.80-7.70 (m, 3H), 7.26-7.24 (m, 1H), 6.97 (t, 1H, J = 7.8 Hz), 6.08 (d, 1H, J = 8.3 Hz), 2.82 (s, 3H).^{13}C NMR ($CDCl_3$, 100 MHz): δ_C = 147.1, 146.8, 145.3, 143.8, 142.1, 135.0, 131.8, 131.7, 131.2, 130.6, 129.9, 128.5, 128.4, 128.1, 126.0, 125.4, 124.5, 122.9, 118.9, 109.5, 17.1. HR-MS (ESI+) m/z calculated for $[C_{21}H_{15}N_4O_2]^+$ = 355.1190 $[M+H]^+$; found: 355.1183.

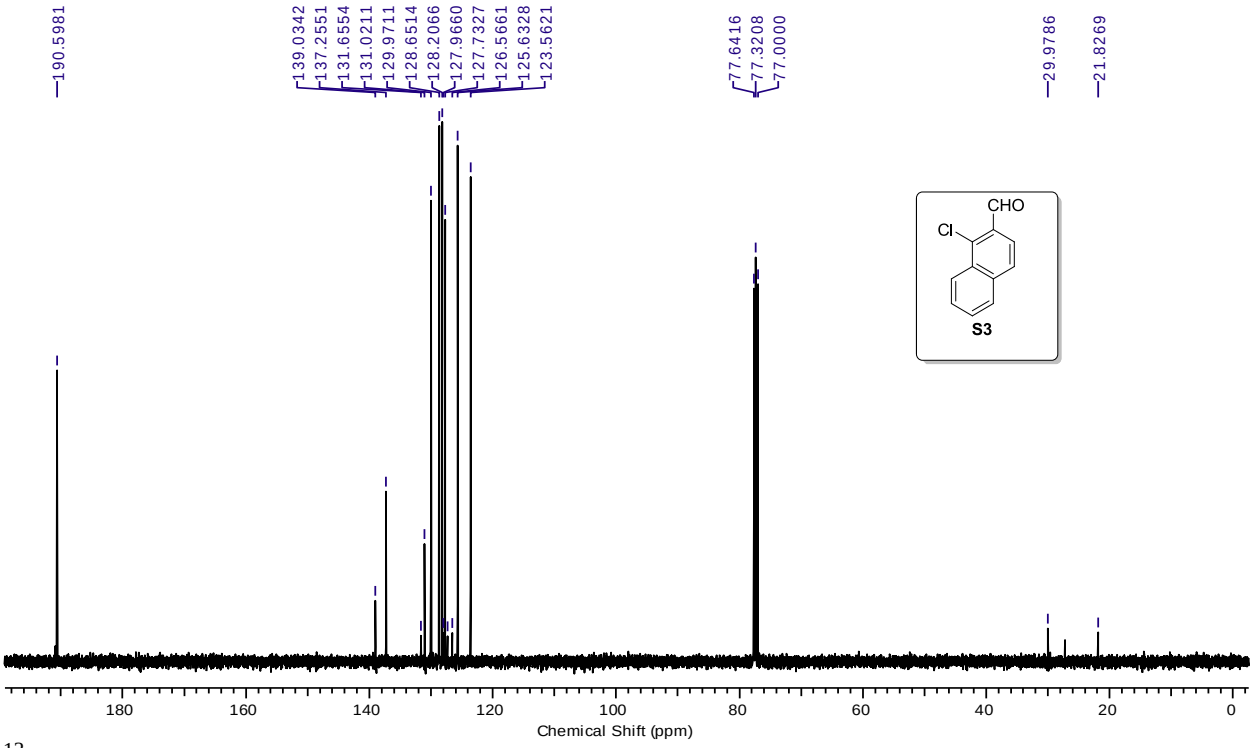


9-Bromo-6-(2-methoxyphenyl)indazolo[2,3-*a*]quinoxaline (6i): Yellow solid (90%), Mp 180-182 ^{o}C. IR (MIR-ATR, 4000–600 cm^{-1}): υ_{max} = 3067, 2998, 2955, 1600, 1580, 1462, 1279, 1247, 1103, 1024, 931, 751, 682. ^{1}H NMR ($CDCl_3$, 400 MHz): δ_H = 8.85 (dd, 1H, J_a= 8.3 and J_b = 1Hz), 8.29 (dd, 1H, J_a = 7.8 and J_b = 1Hz), 7.92 (d, 1H, J = 9.3 Hz), 7.84-7.74 (m, 2H), 7.66-7.59 (m, 3H), 7.35 (d, 1H, J = 1.5 Hz), 7.26-7.22 (m, 1H), 7.18 (d, 1H, J = 8.3 Hz), 3.32 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ_C = 157.2, 152.0, 147.5, 138.3, 131.9, 131.5, 130.5, 130.2, 129.3, 128.4, 127.9, 126.4, 126.1, 123.3, 121.5, 118.8, 118.7, 116.4, 116.3, 111.2, 55.5. HR-MS (ESI+) m/z calculated for $[C_{21}H_{15}BrN_3O]^+$ = $[M+H]^+$: 404.0393; found: 404.0398.

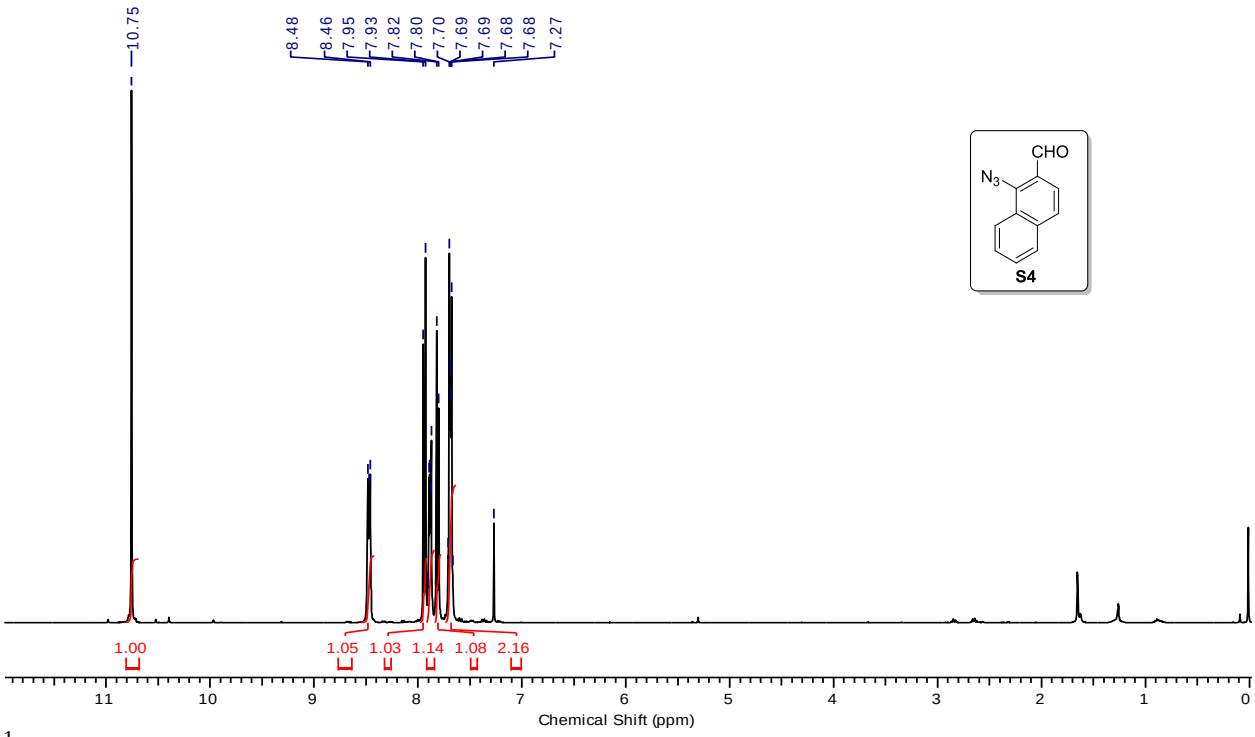
Copies of ^{1}H, ^{13}C NMR Spectra of all Compounds (S3, S4, 3a-w, 5 and 6a-i):



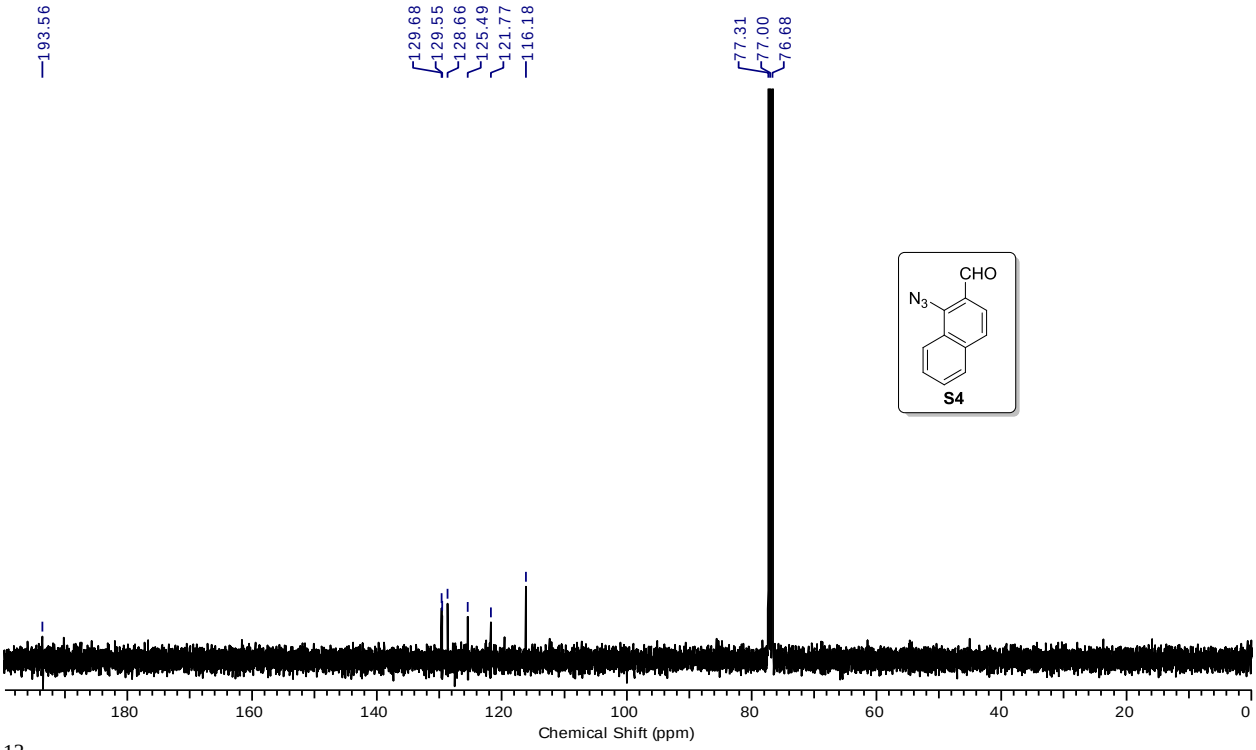
^{1}H NMR (400 MHz) spectrum of compound **S3** in $CDCl_3$



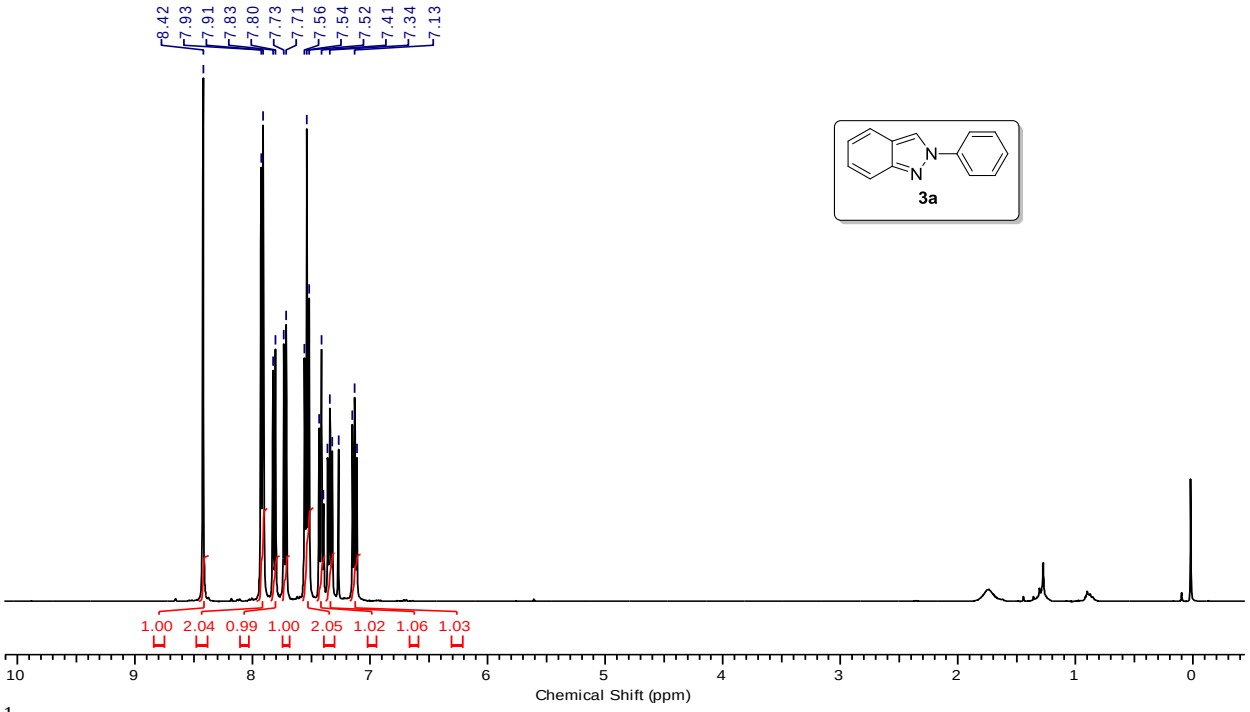
^{13}C NMR (100 MHz) spectrum of compound **S3** in $CDCl_3$



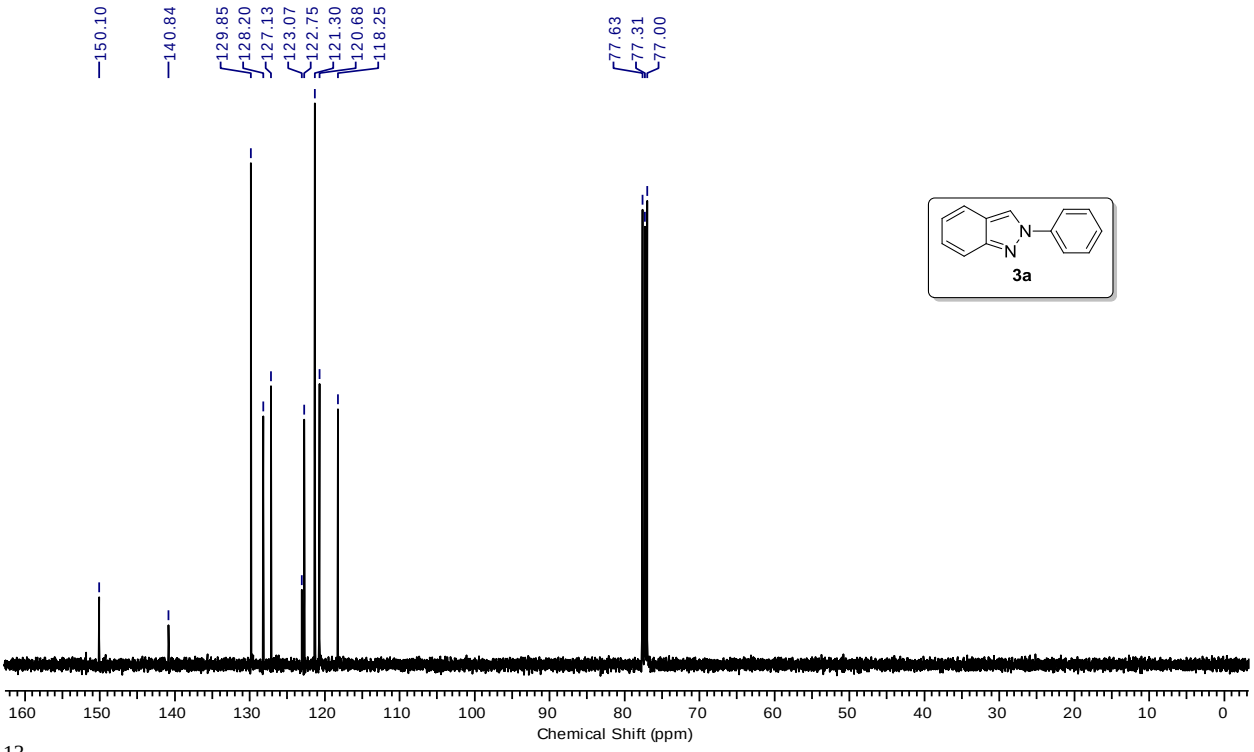
^{1}H NMR (400 MHz) spectrum of compound **S4** in $CDCl_3$



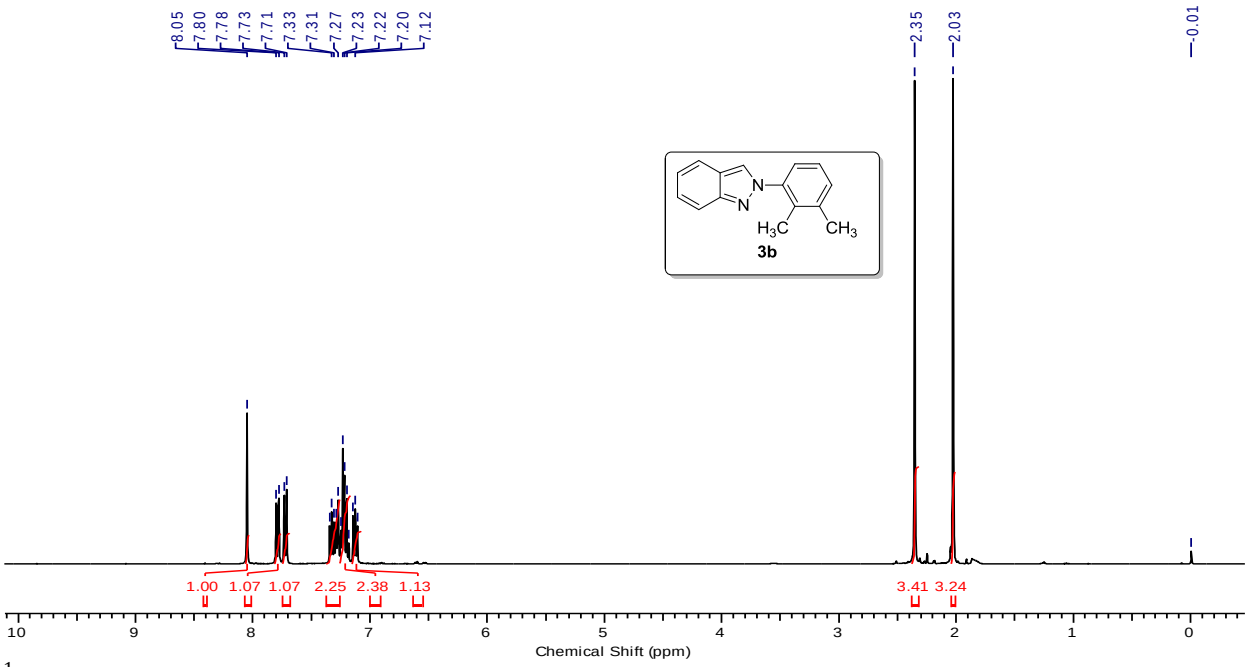
^{13}C NMR (100 MHz) spectrum of compound **S4** in $CDCl_3$



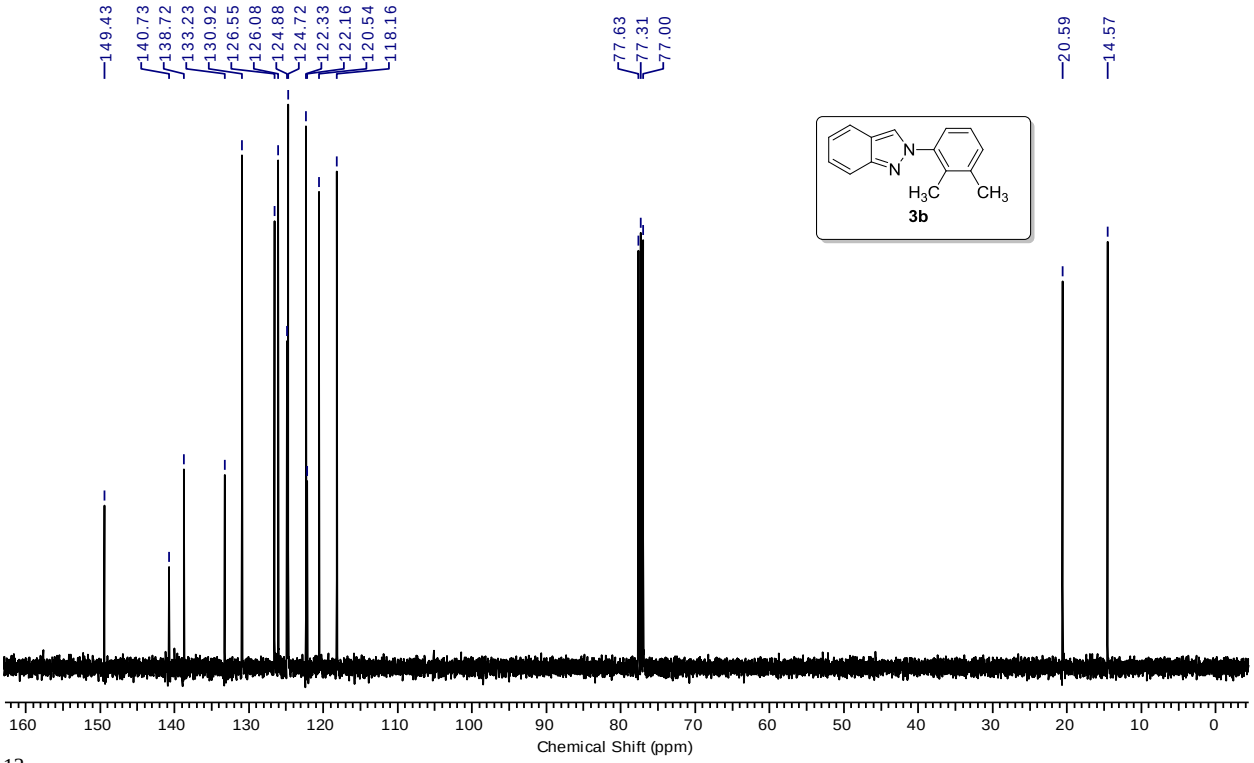
^{1}H NMR (400 MHz) spectrum of compound **3a** in $CDCl_3$



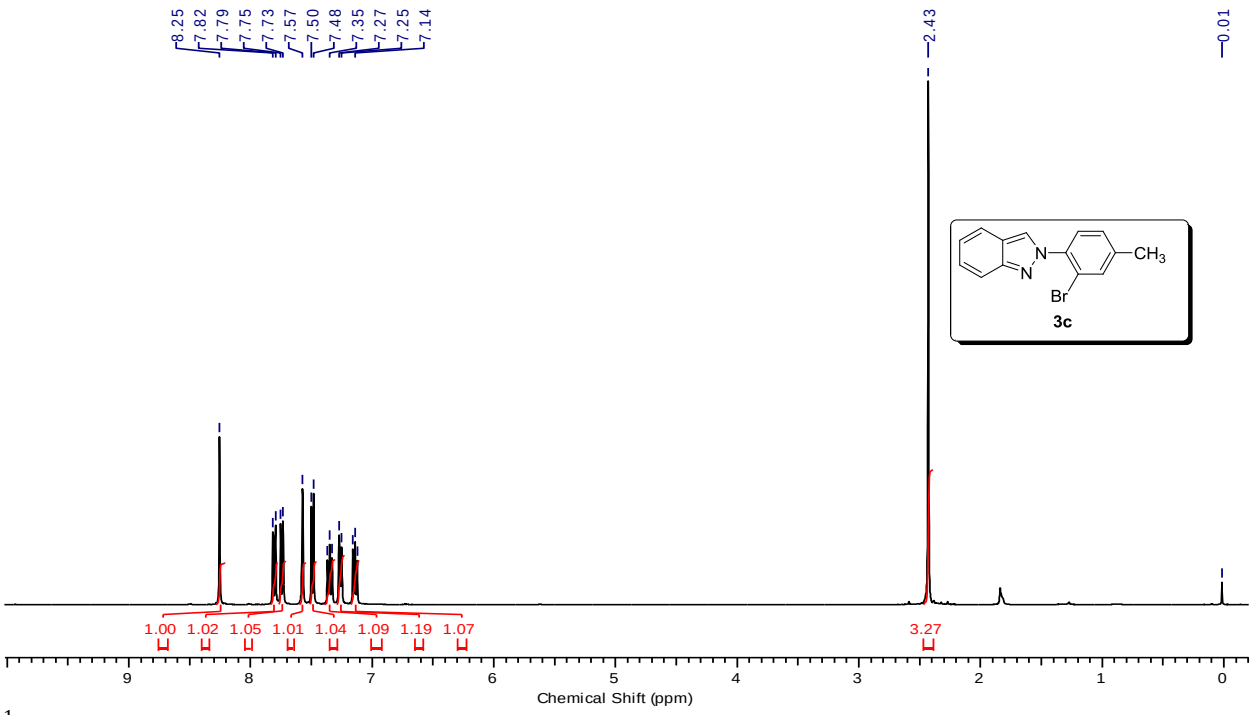
^{13}C NMR (100 MHz) spectrum of compound **3a** in $CDCl_3$



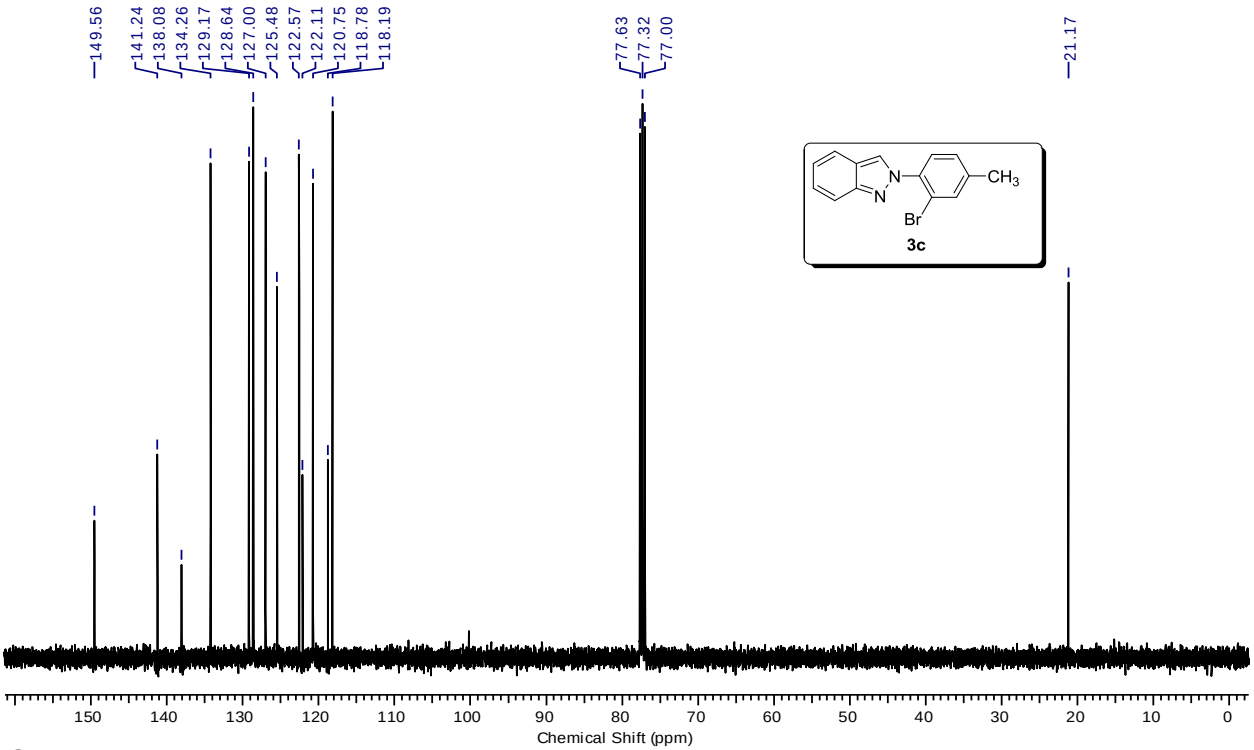
^{1}H NMR (400 MHz) spectrum of compound **3b** in $CDCl_3$



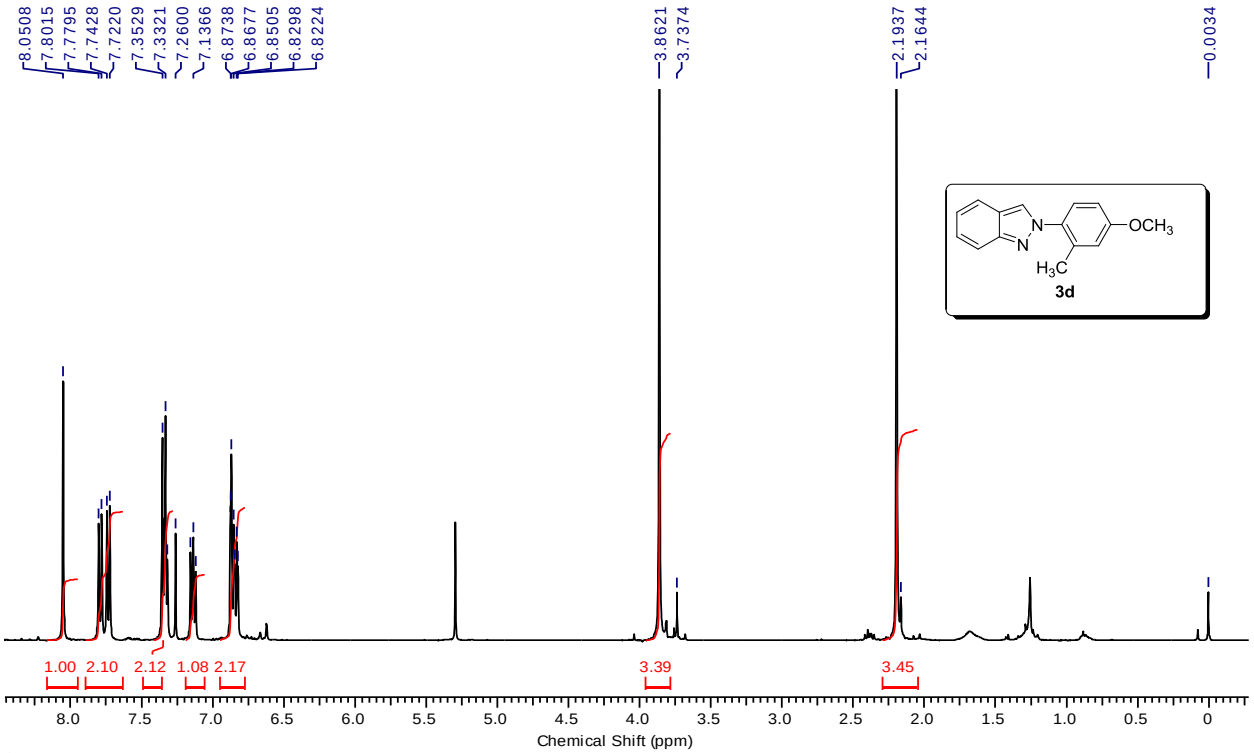
^{13}C NMR (100 MHz) spectrum of compound **3b** in $CDCl_3$



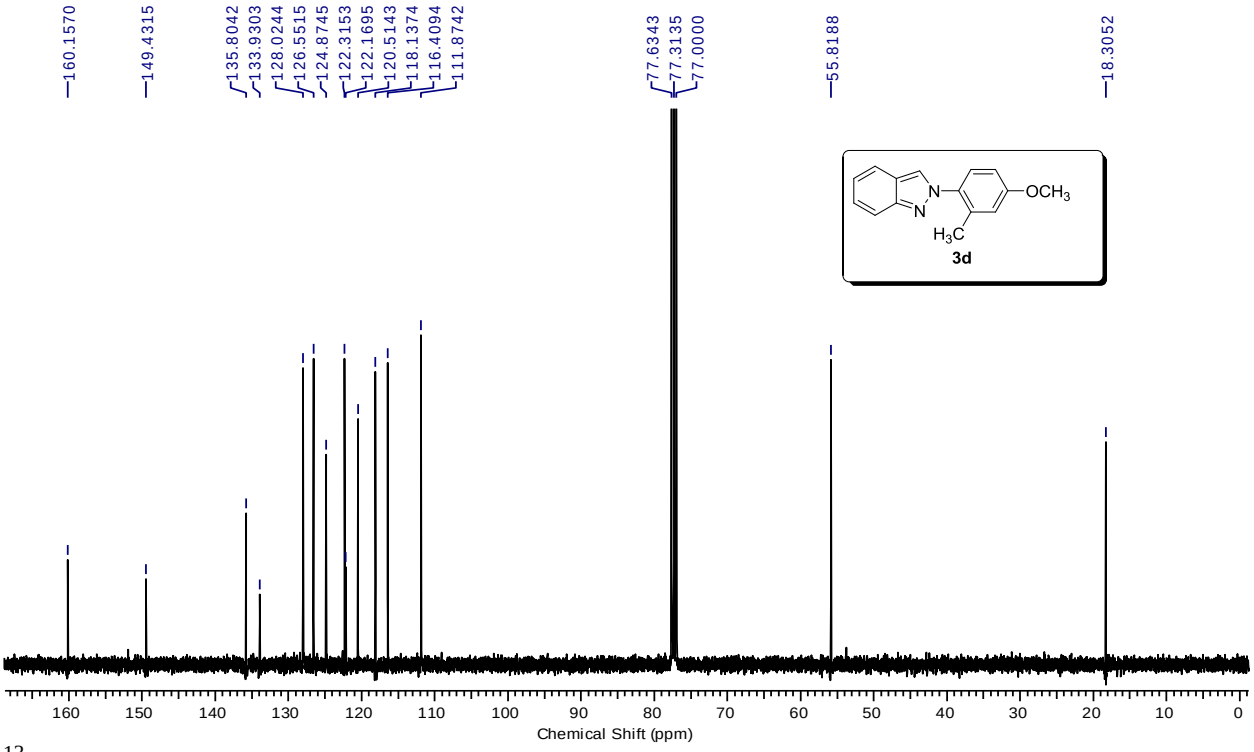
^{1}H NMR (400 MHz) spectrum of compound **3c** in $CDCl_3$



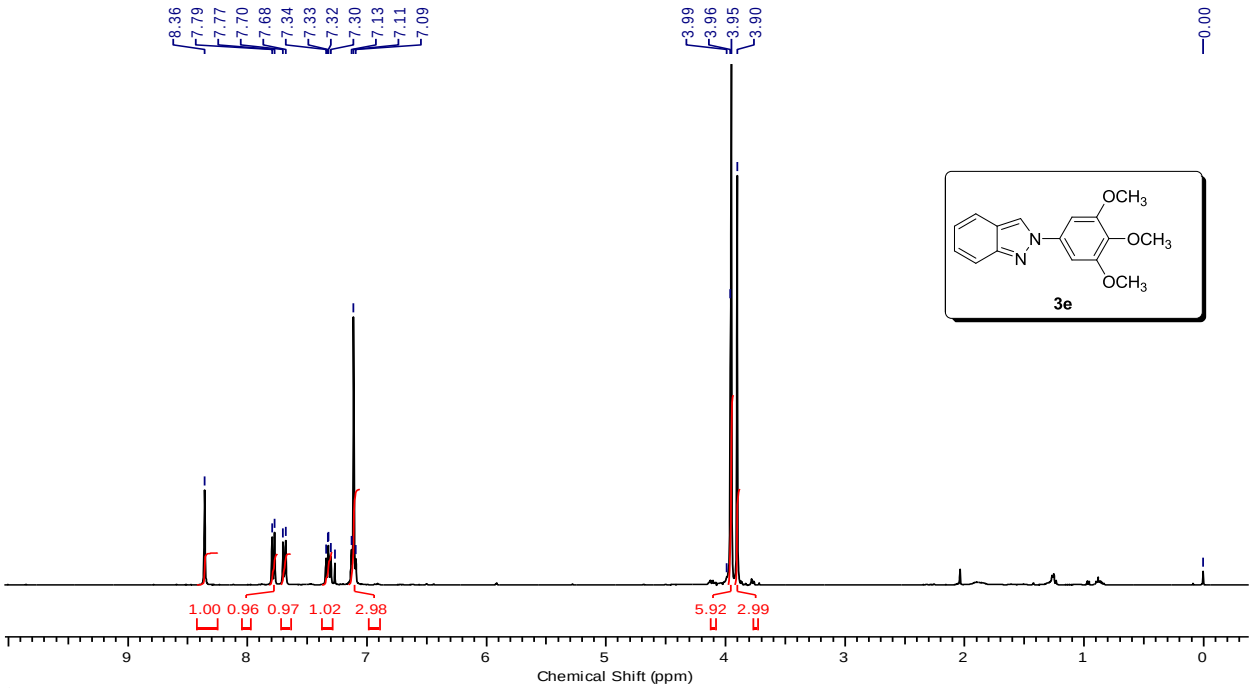
^{13}C NMR (100 MHz) spectrum of compound **3c** in $CDCl_3$



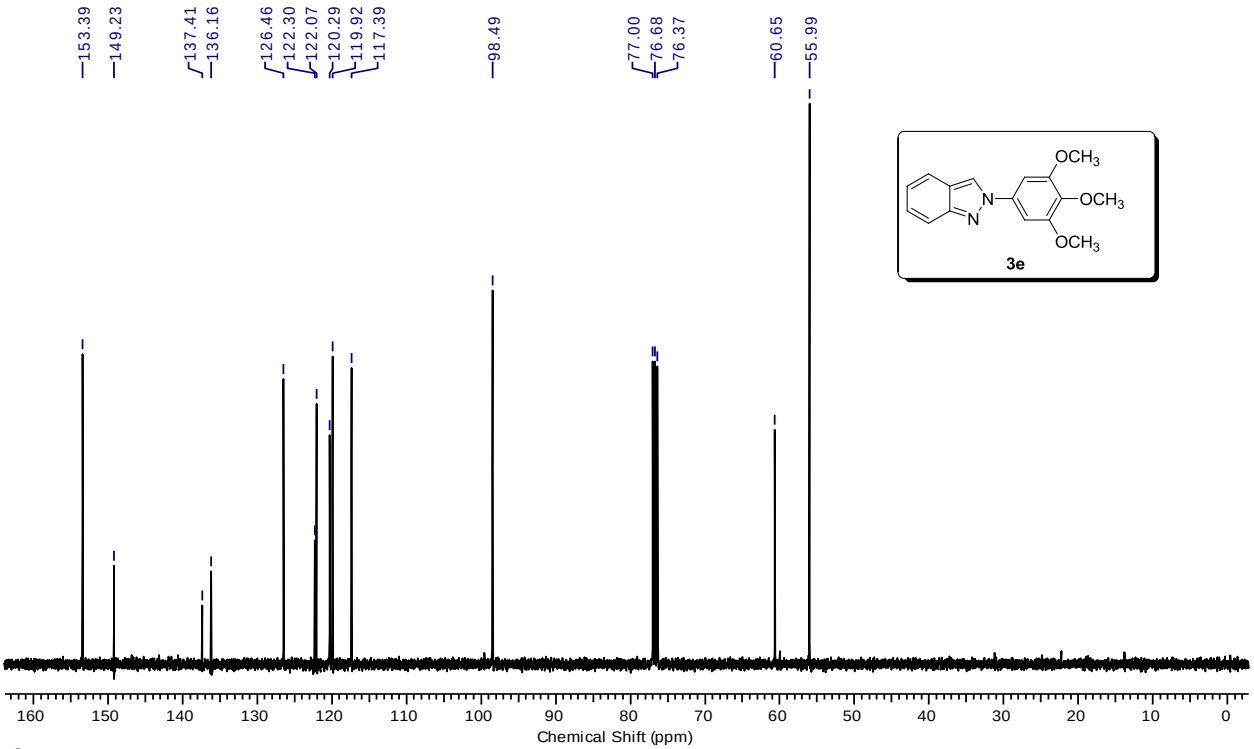
^{1}H NMR (400 MHz) spectrum of compound **3d** in $CDCl_3$



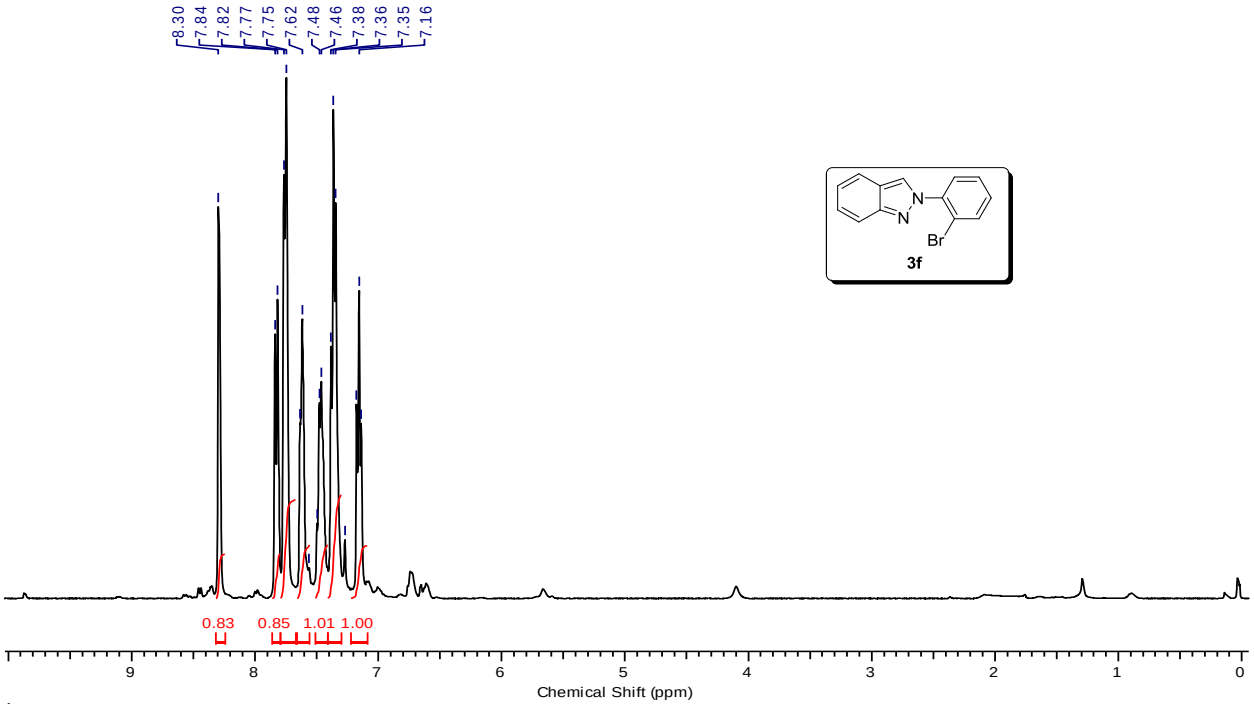
^{13}C NMR (100 MHz) spectrum of compound **3d** in $CDCl_3$



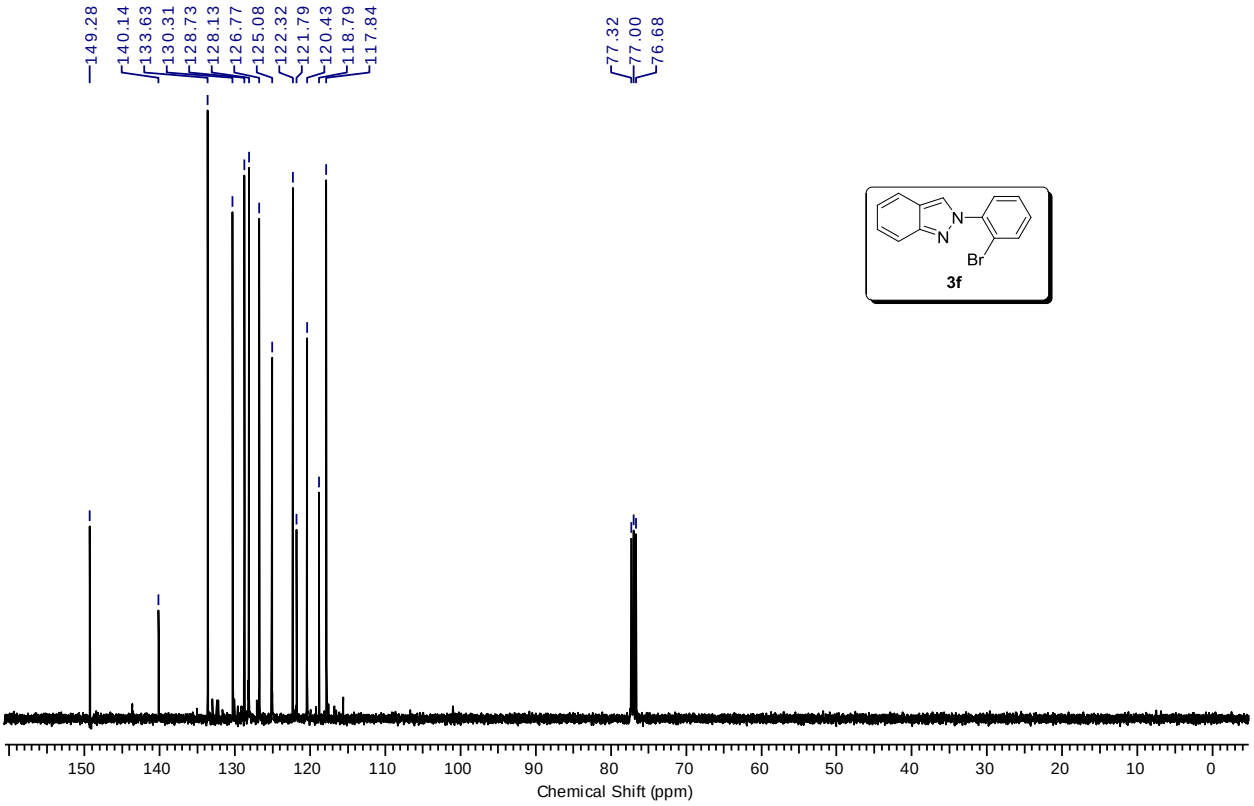
^{1}H NMR (400 MHz) spectrum of compound **3e** in $CDCl_3$

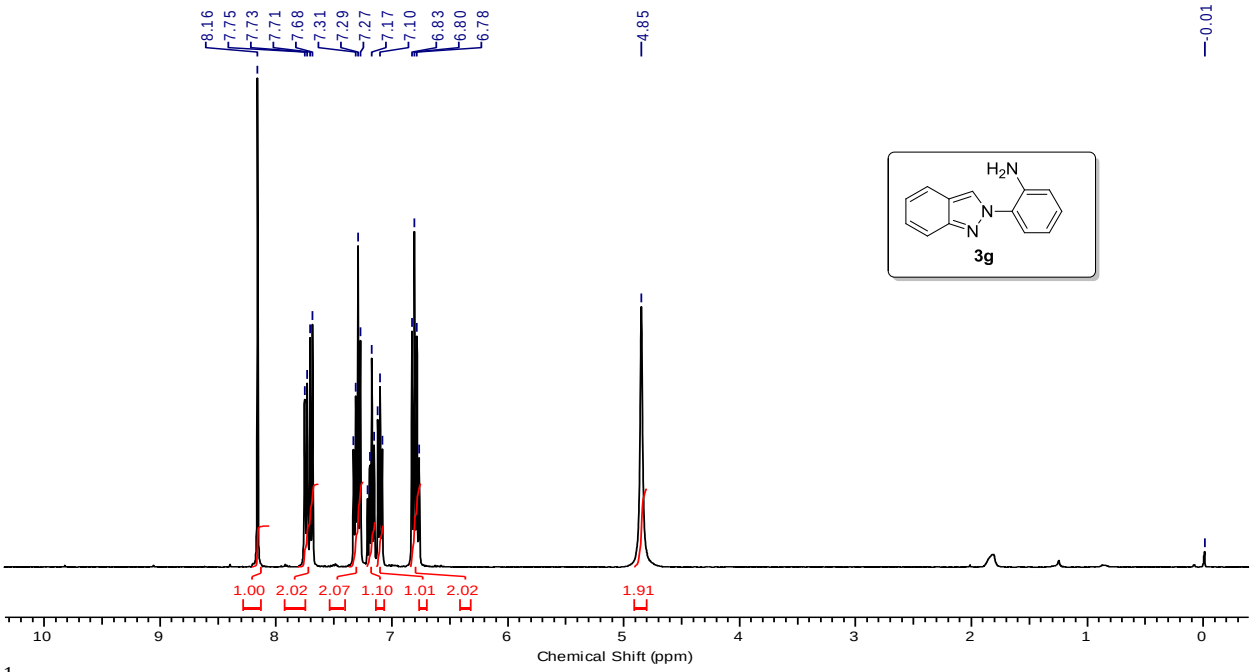


^{13}C NMR (100 MHz) spectrum of compound **3e** in $CDCl_3$

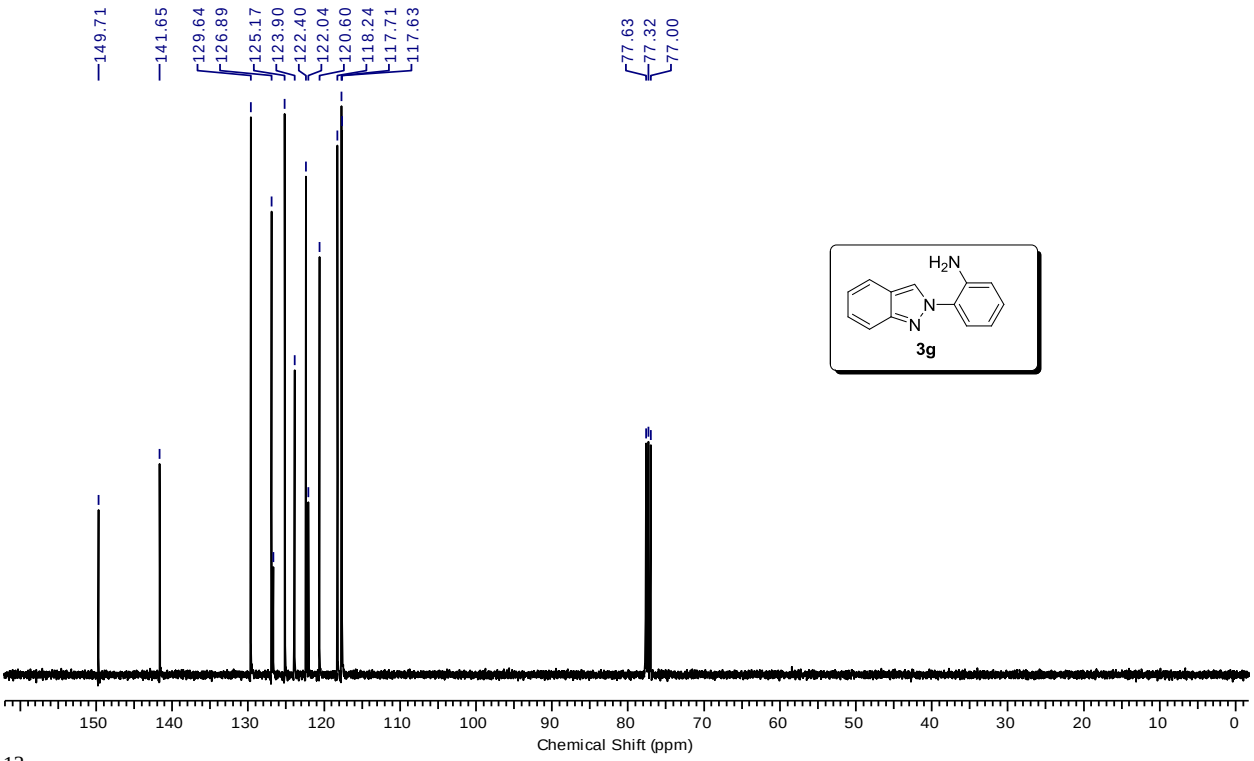


^{1}H NMR (400 MHz) spectrum of compound **3f** in $CDCl_3$

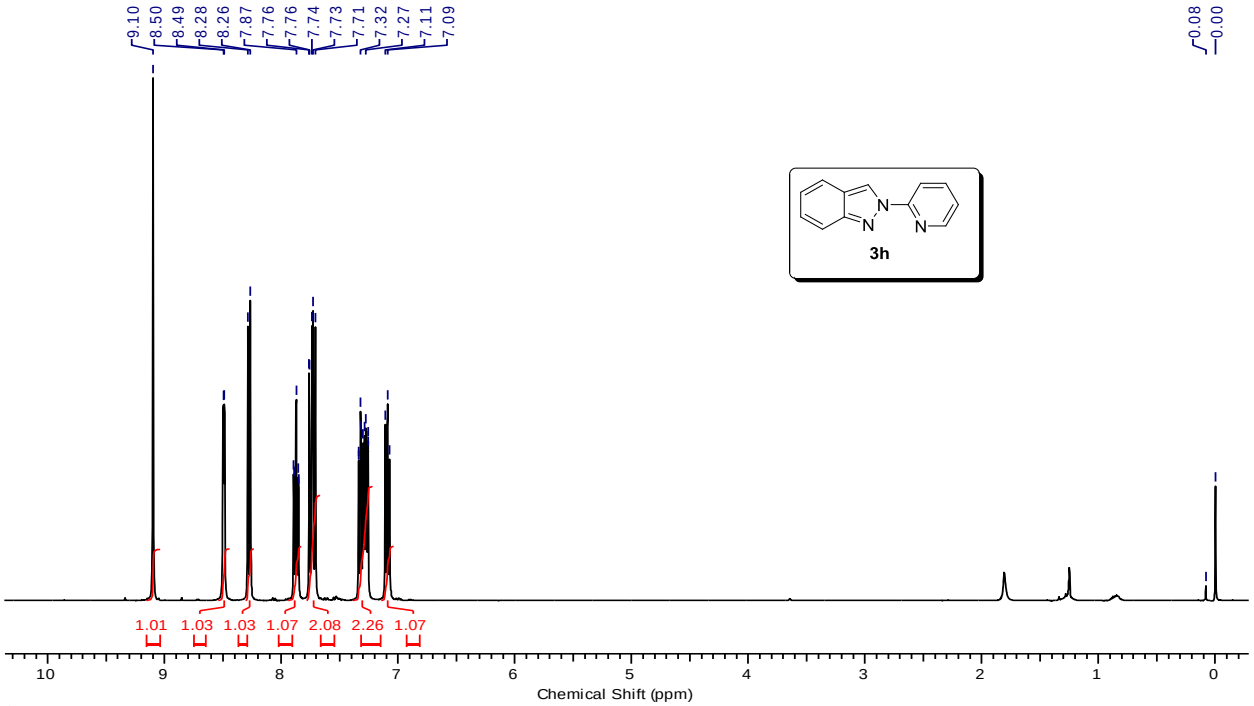




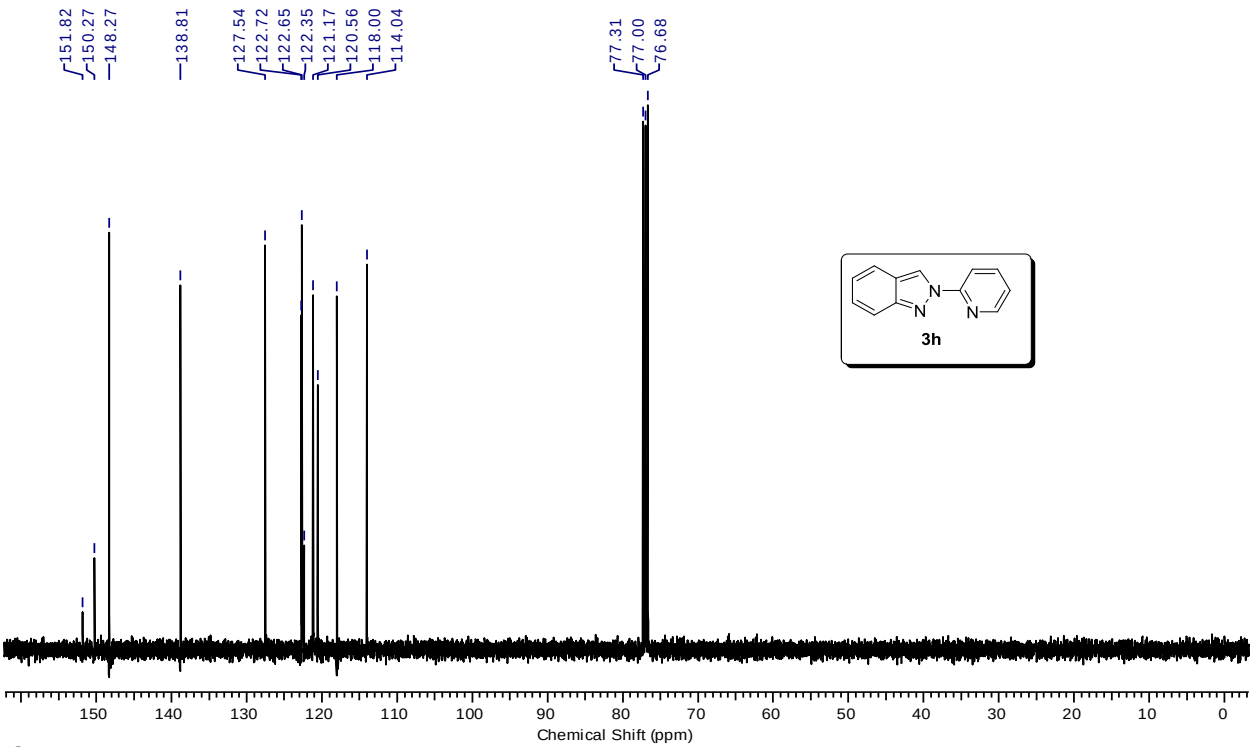
^{1}H NMR (400 MHz) spectrum of compound **3g** in $CDCl_3$



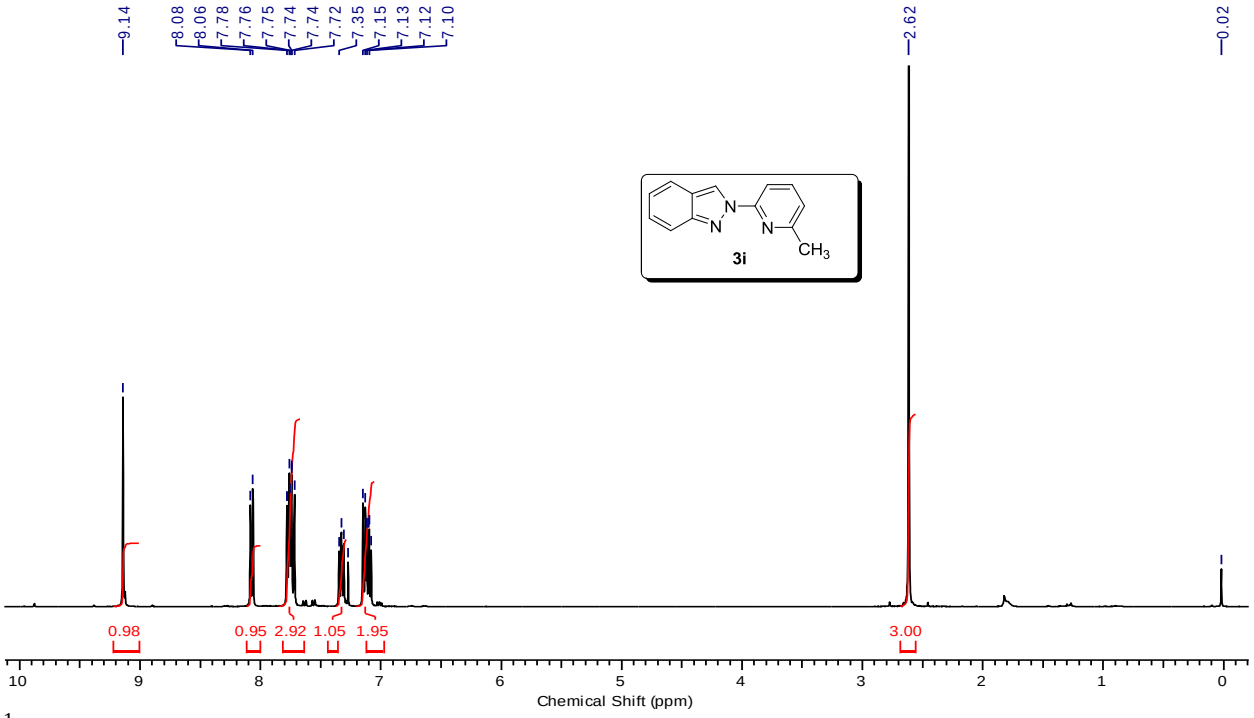
^{13}C NMR (100 MHz) spectrum of compound **3g** in $CDCl_3$



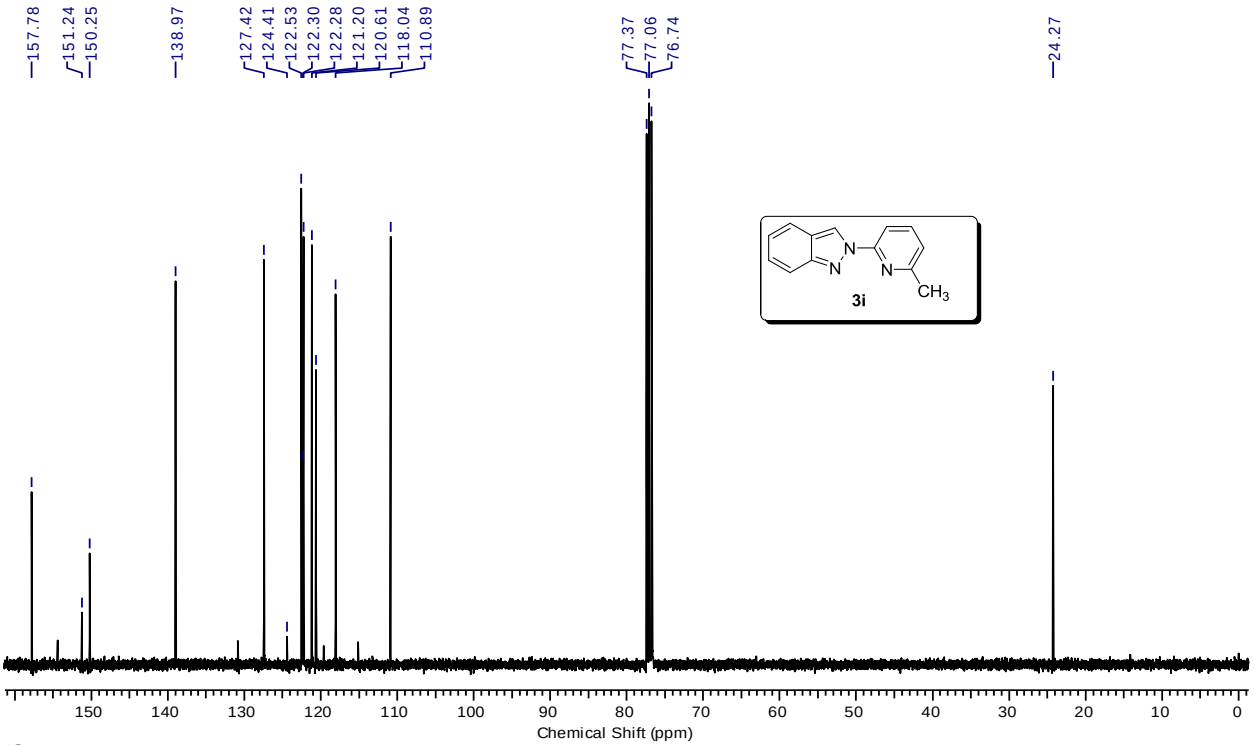
^{1}H NMR (400MHz) spectrum of compound **3h** in $CDCl_3$



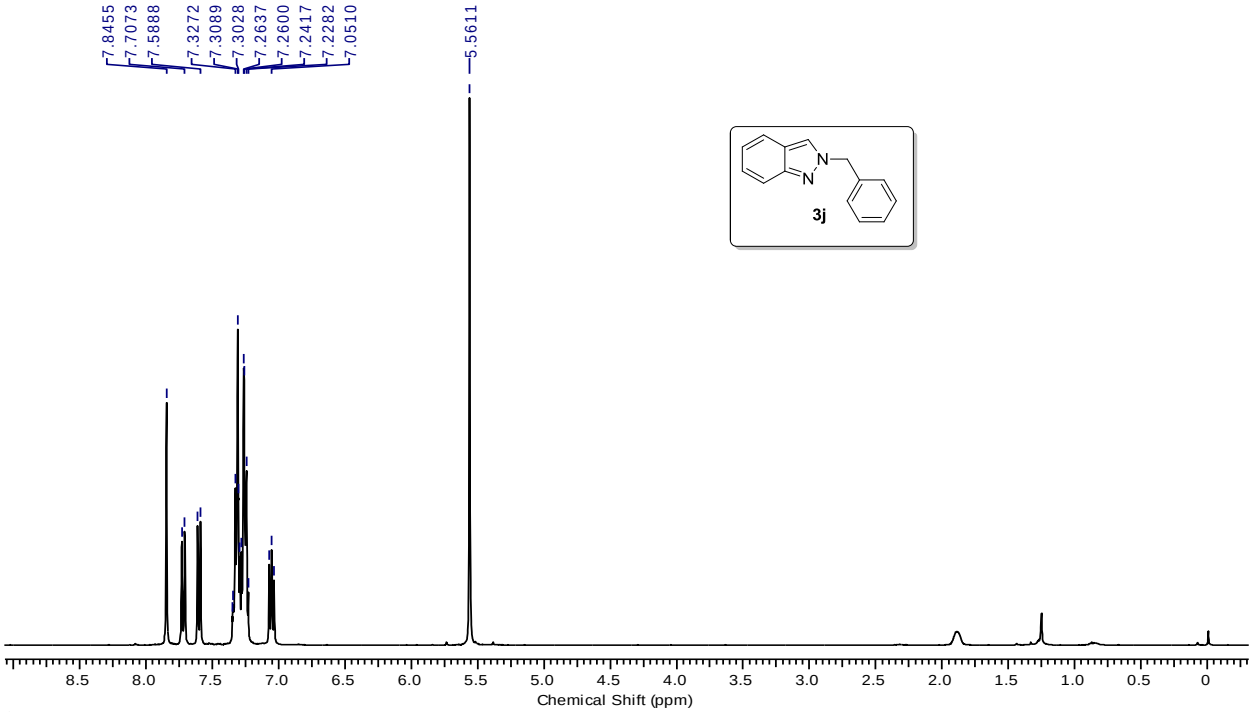
^{13}C NMR (100MHz) spectrum of compound **3h**in $CDCl_3$



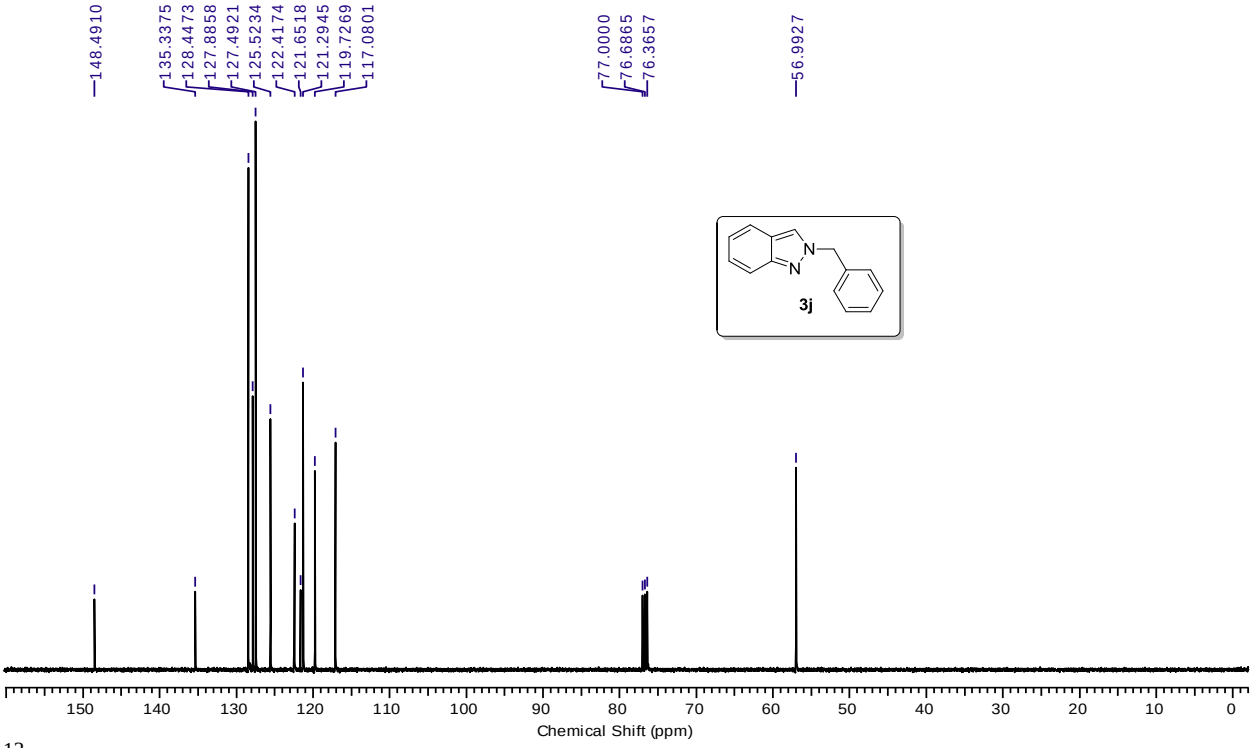
^{1}H NMR (400 MHz) spectrum of compound **3i** in $CDCl_3$



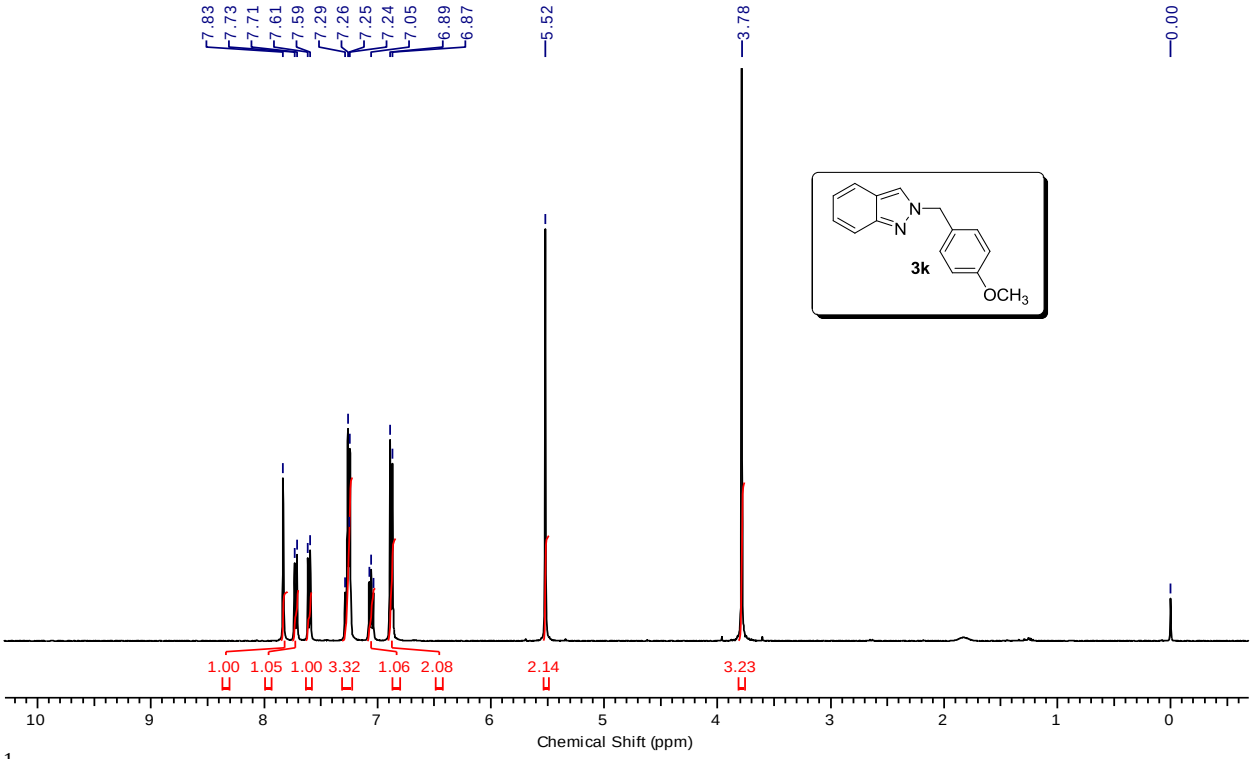
^{13}C NMR (100 MHz) spectrum of compound **3i** in $CDCl_3$



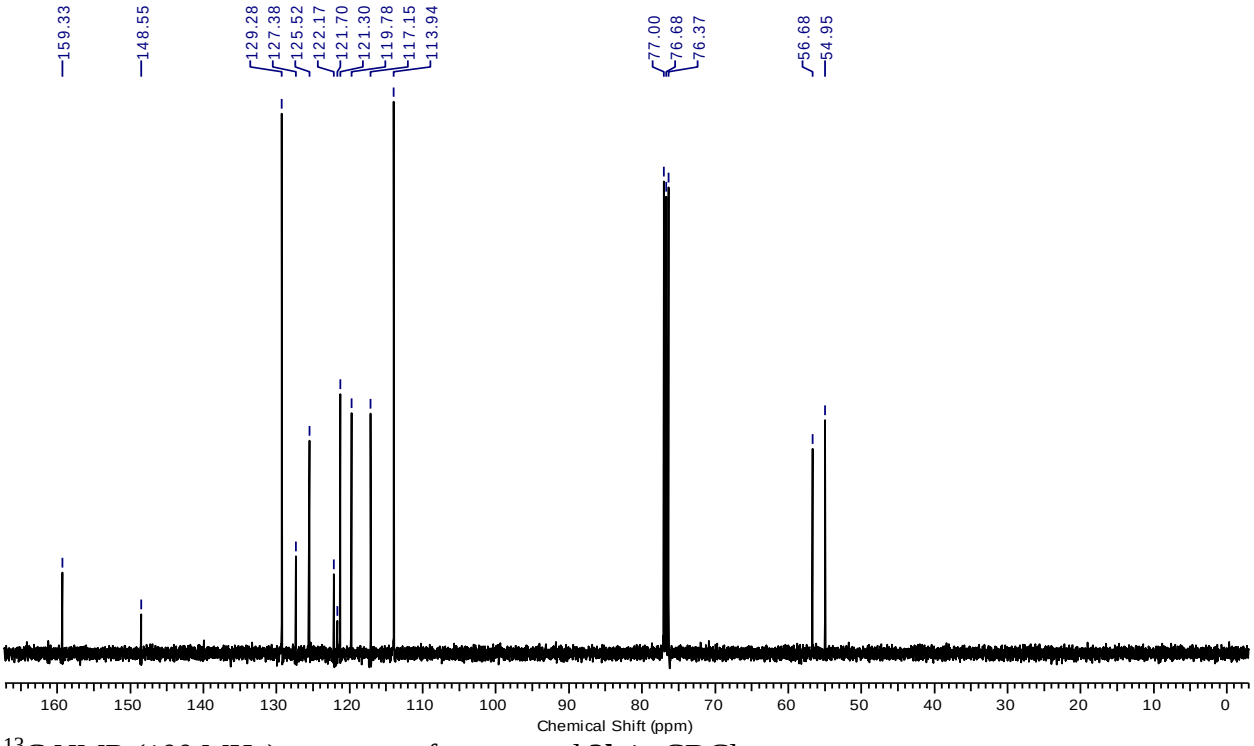
^{1}H NMR (400 MHz) spectrum of compound **3j** in $CDCl_3$



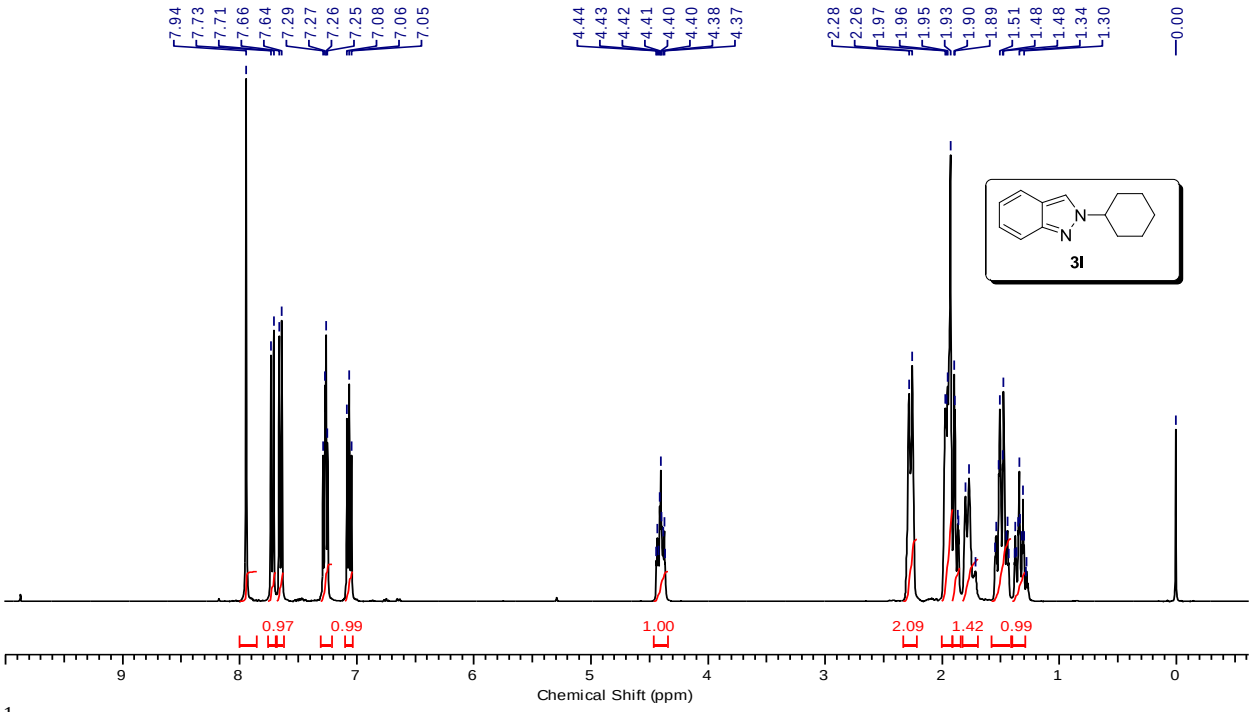
^{13}C NMR (100 MHz) spectrum of compound **3j** in $CDCl_3$



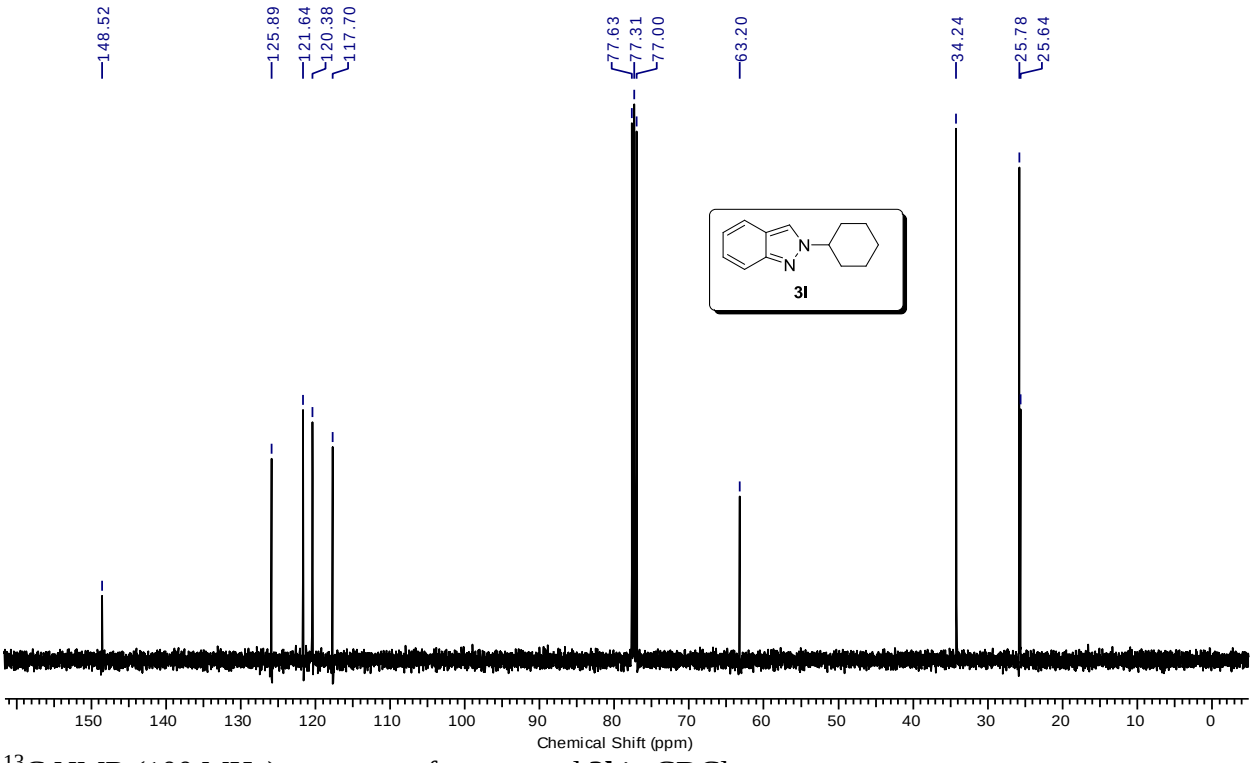
^{1}H NMR (400 MHz) spectrum of compound **3k** in $CDCl_3$



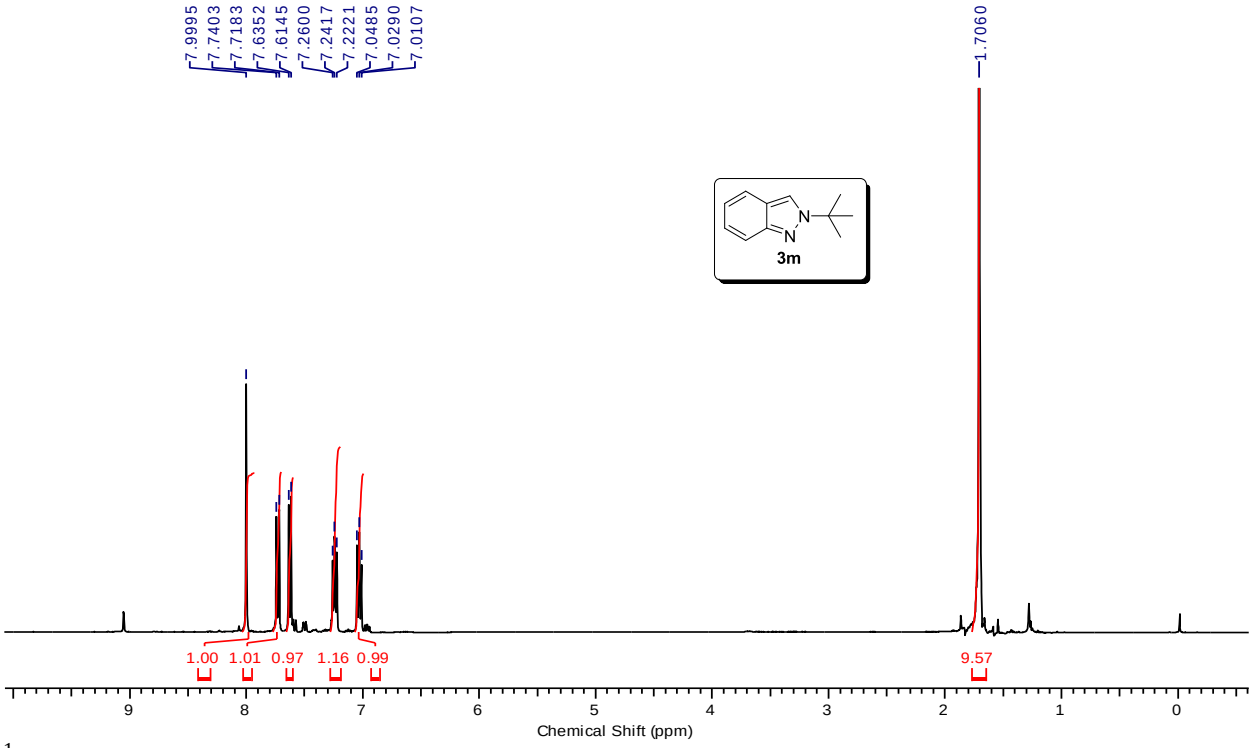
^{13}C NMR (100 MHz) spectrum of compound **3k** in $CDCl_3$



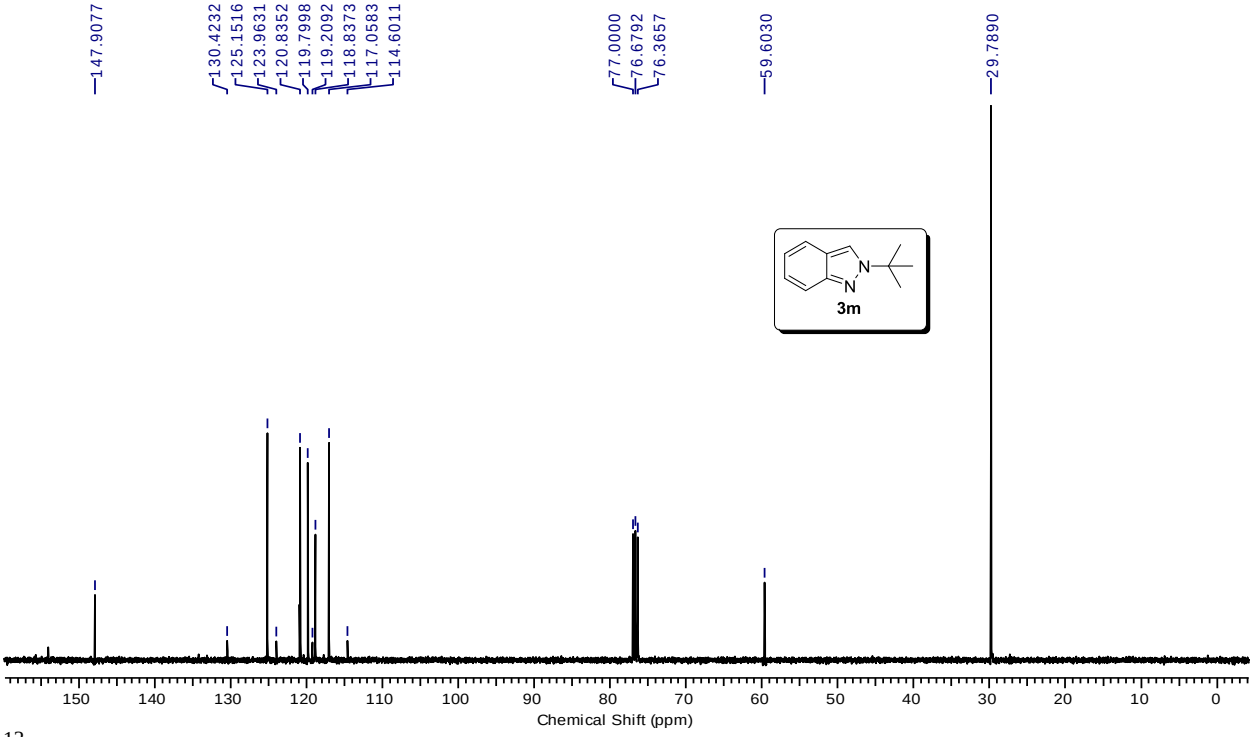
^{1}H NMR (400 MHz) spectrum of compound **3l** in $CDCl_3$



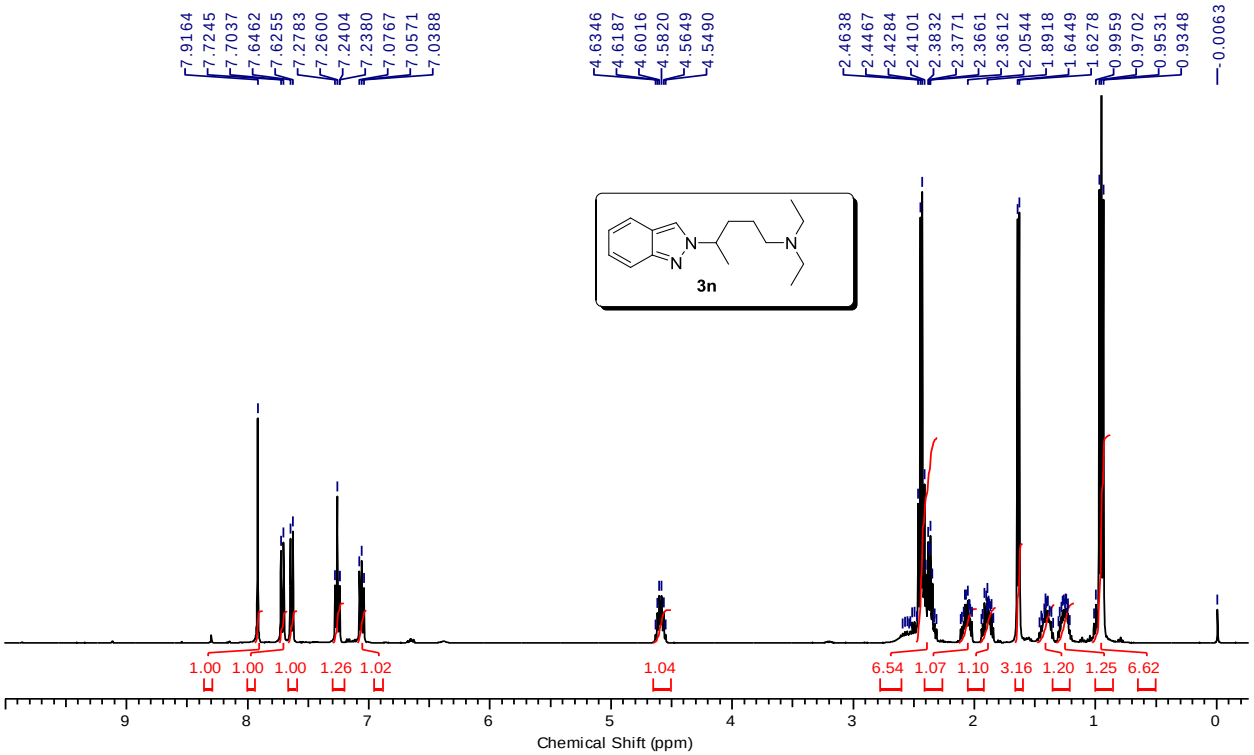
^{13}C NMR (100 MHz) spectrum of compound **3l** in $CDCl_3$



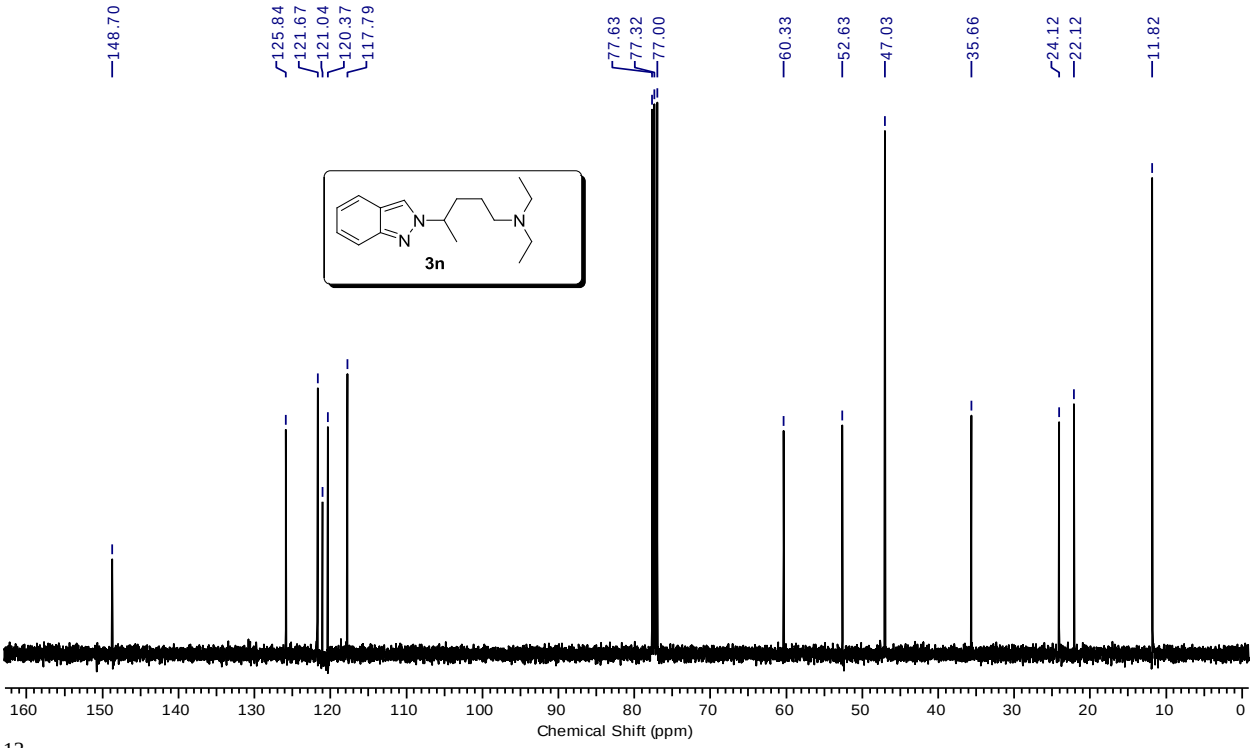
^{1}H NMR (400 MHz) spectrum of compound **3m** in $CDCl_3$



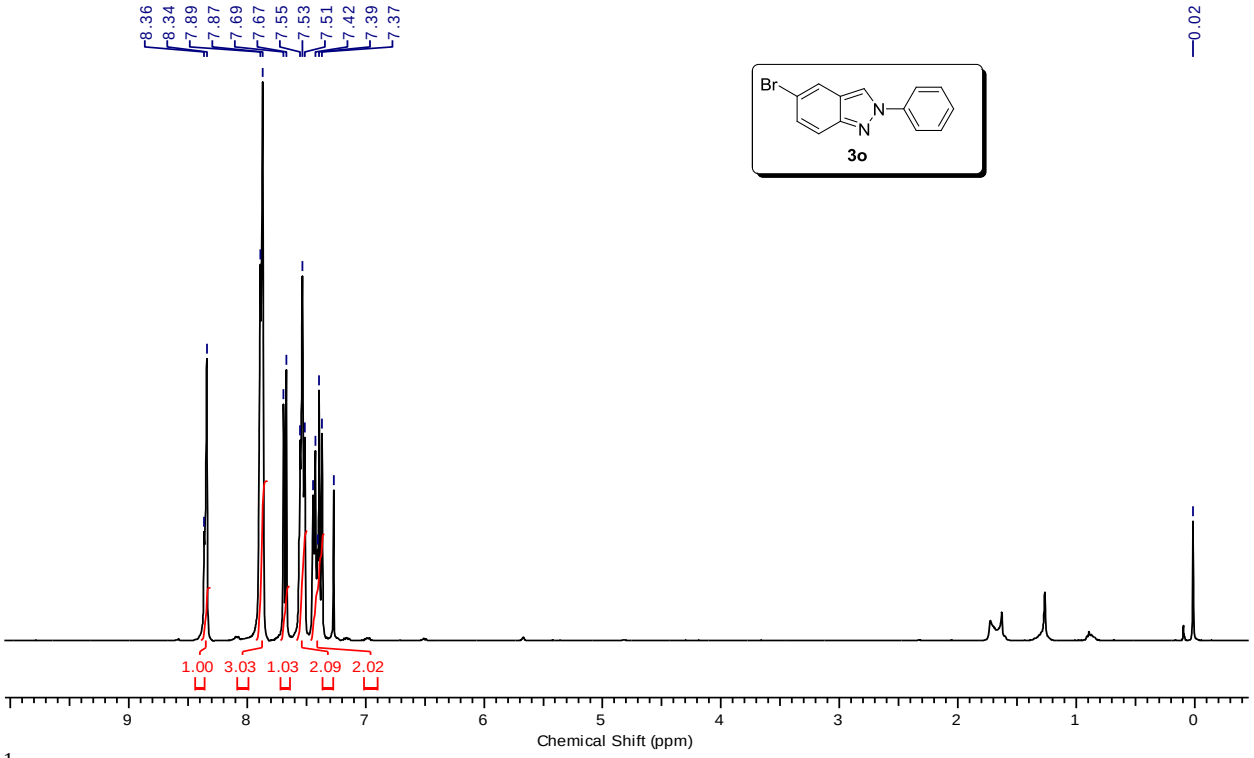
^{13}C NMR (100 MHz) spectrum of compound **3m** in $CDCl_3$



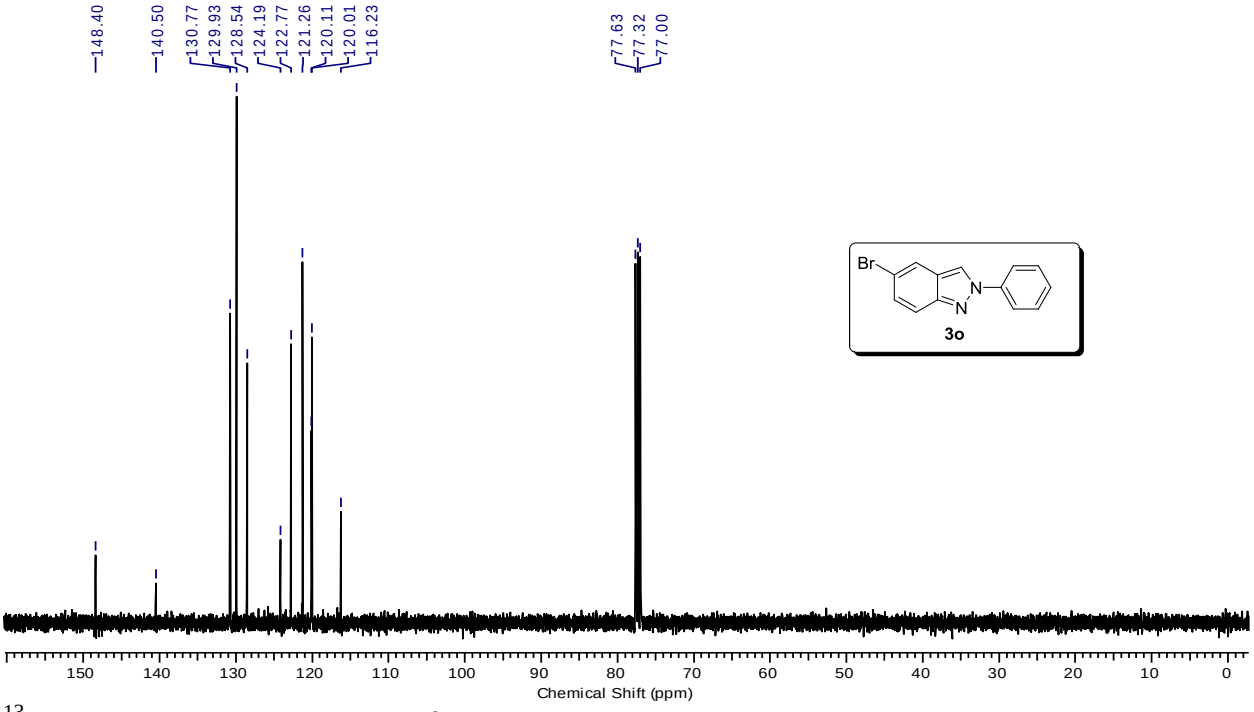
^{1}H NMR (400 MHz) spectrum of compound **3n** in $CDCl_3$



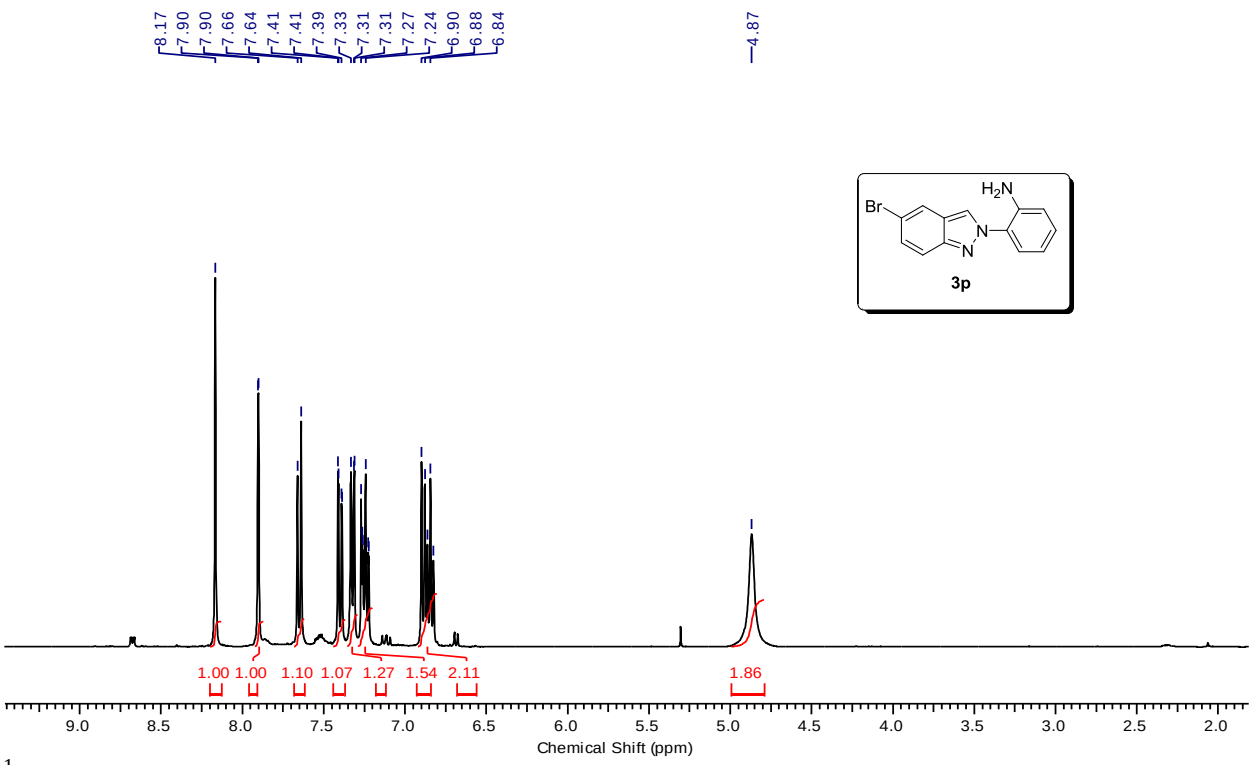
^{13}C NMR (100 MHz) spectrum of compound **3n** in $CDCl_3$



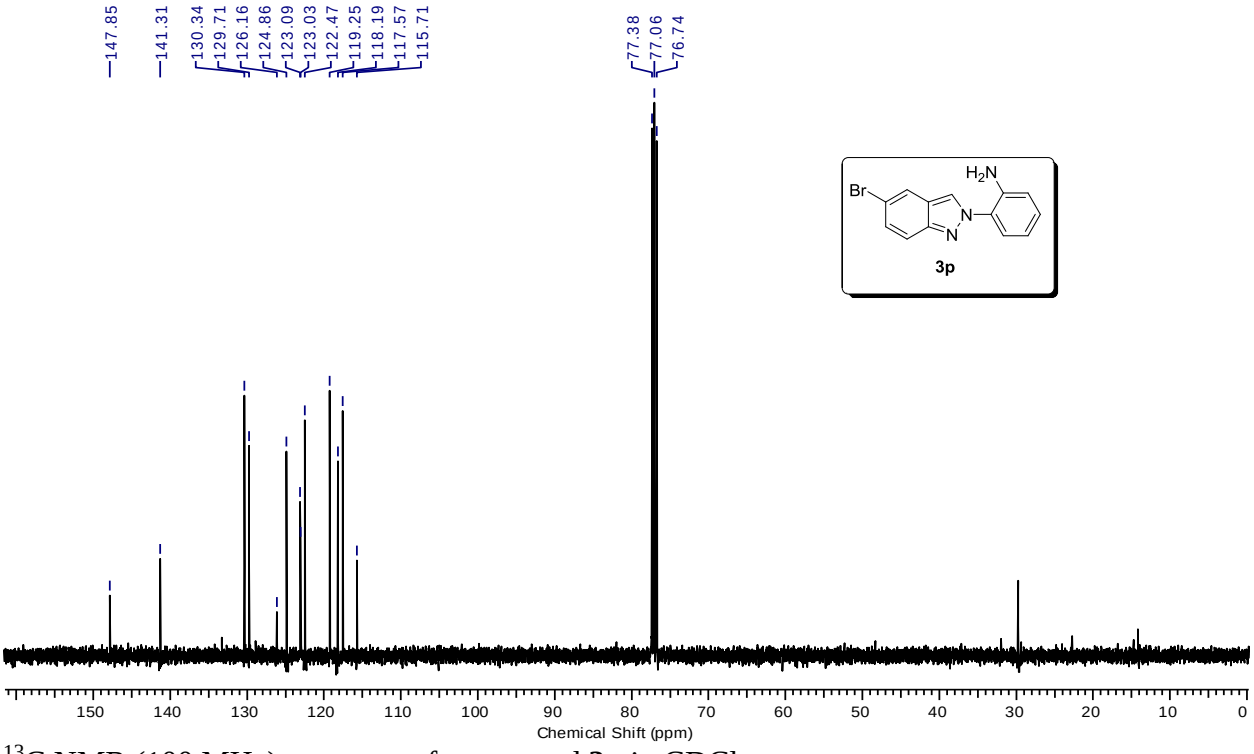
^{1}H NMR (400 MHz) spectrum of compound **3o** in $CDCl_3$



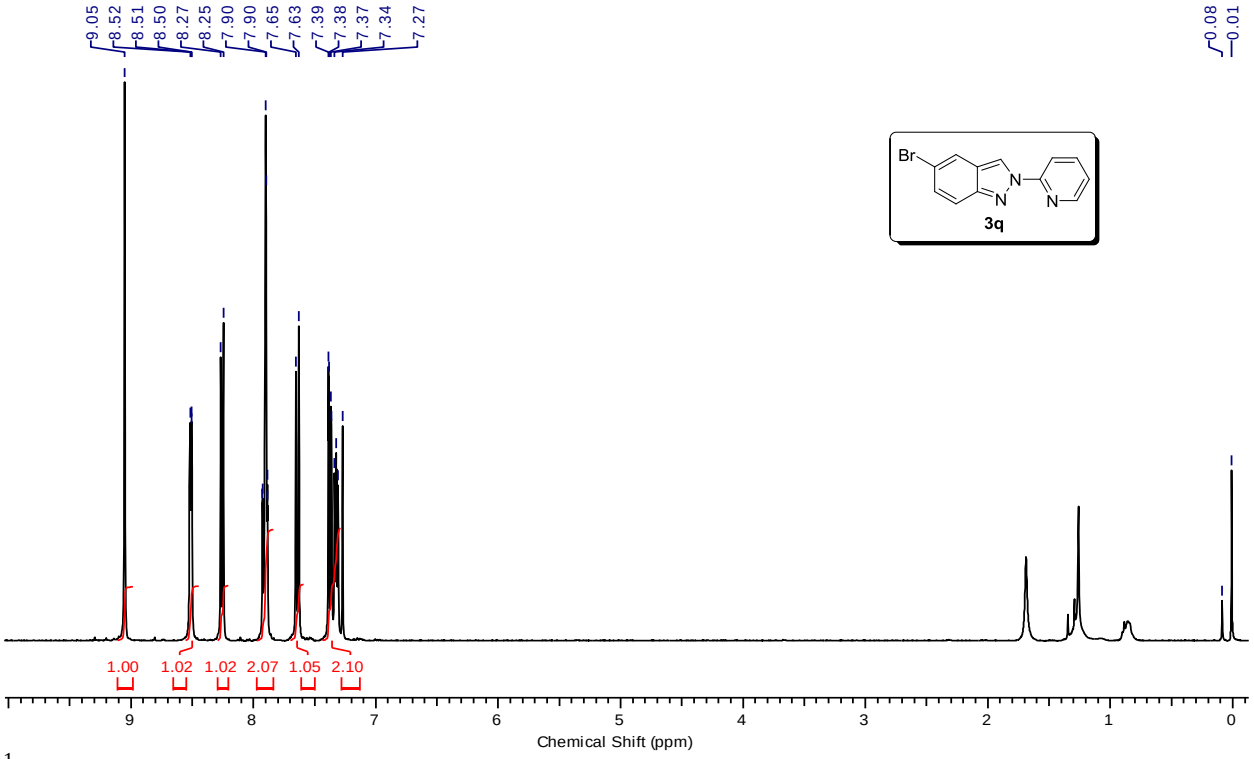
^{13}C NMR (100 MHz) spectrum of compound **3o** in $CDCl_3$



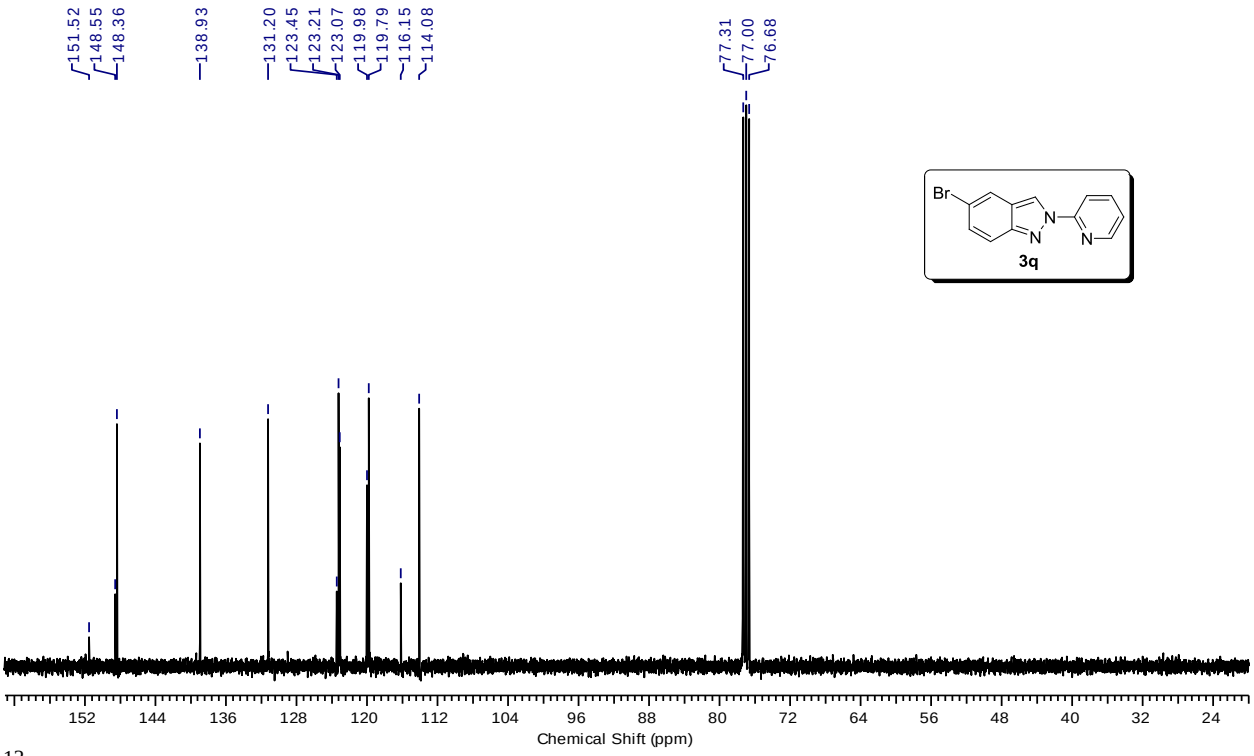
^{1}H NMR (400 MHz) spectrum of compound **3p** in $CDCl_3$



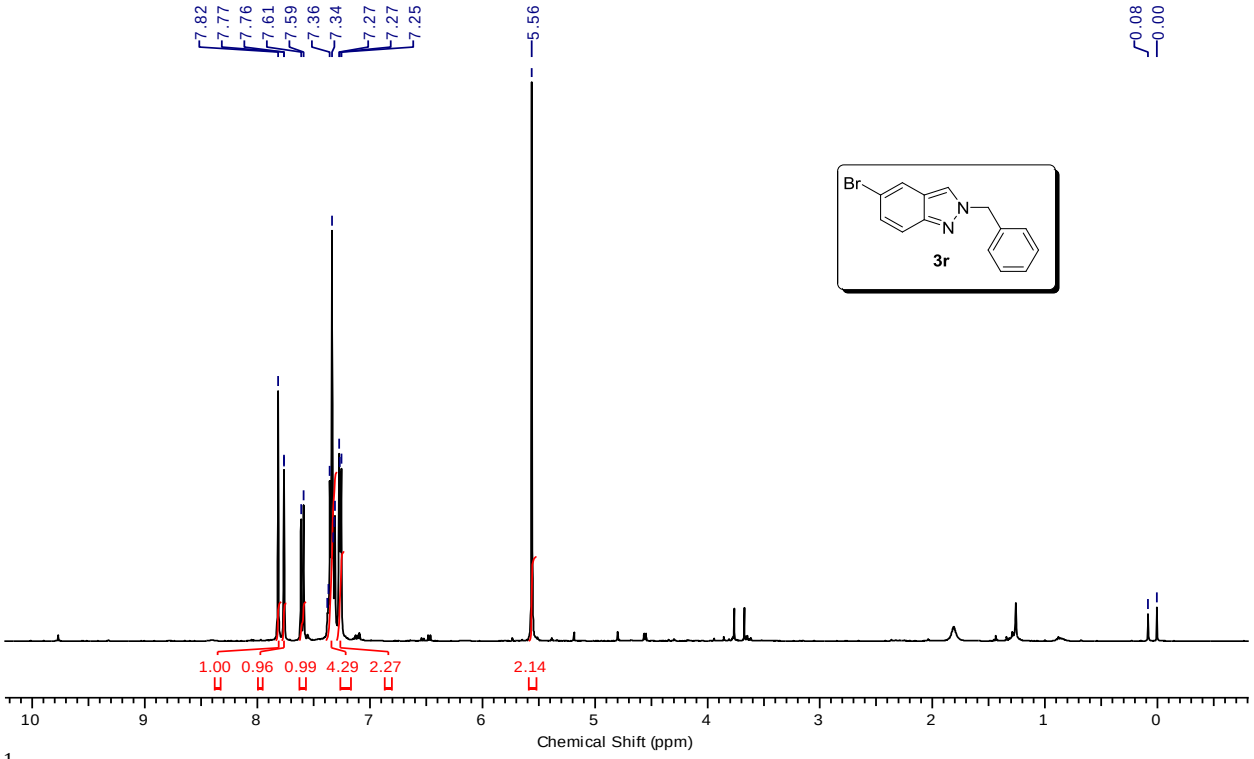
^{13}C NMR (100 MHz) spectrum of compound **3p** in $CDCl_3$



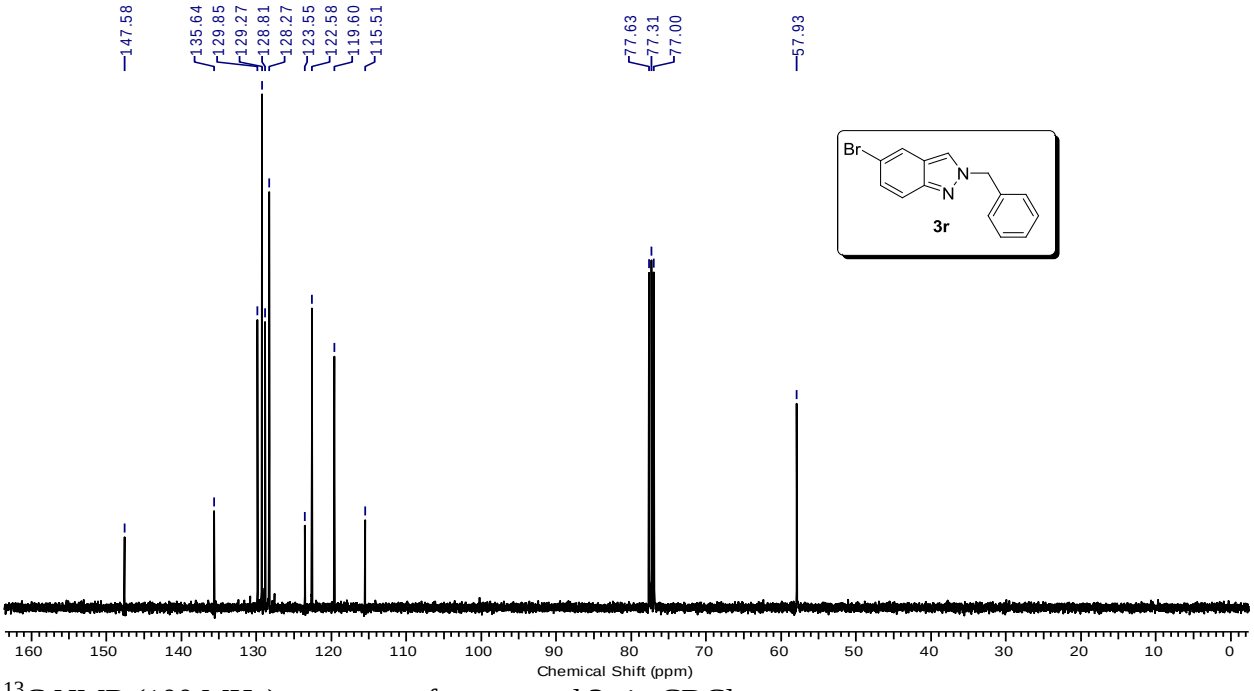
^{1}H NMR (400 MHz) spectrum of compound **3q** in $CDCl_3$



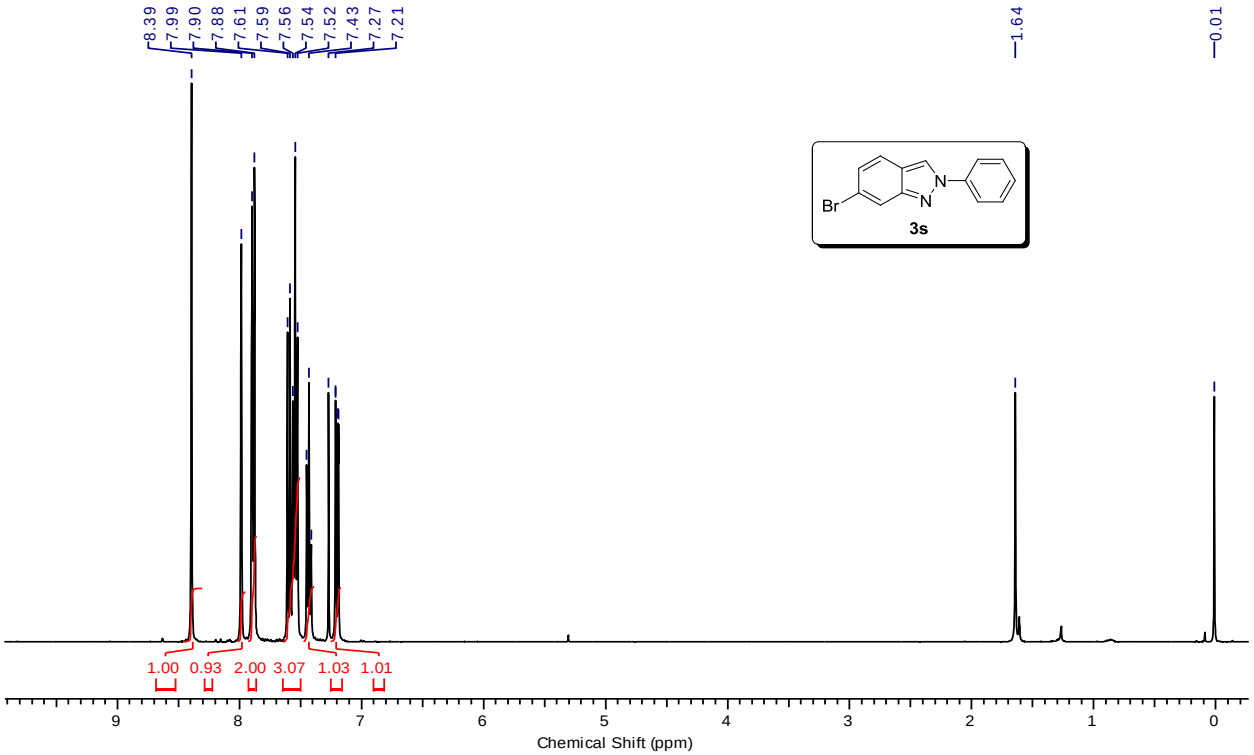
^{13}C NMR (100 MHz) spectrum of compound **3q** in $CDCl_3$



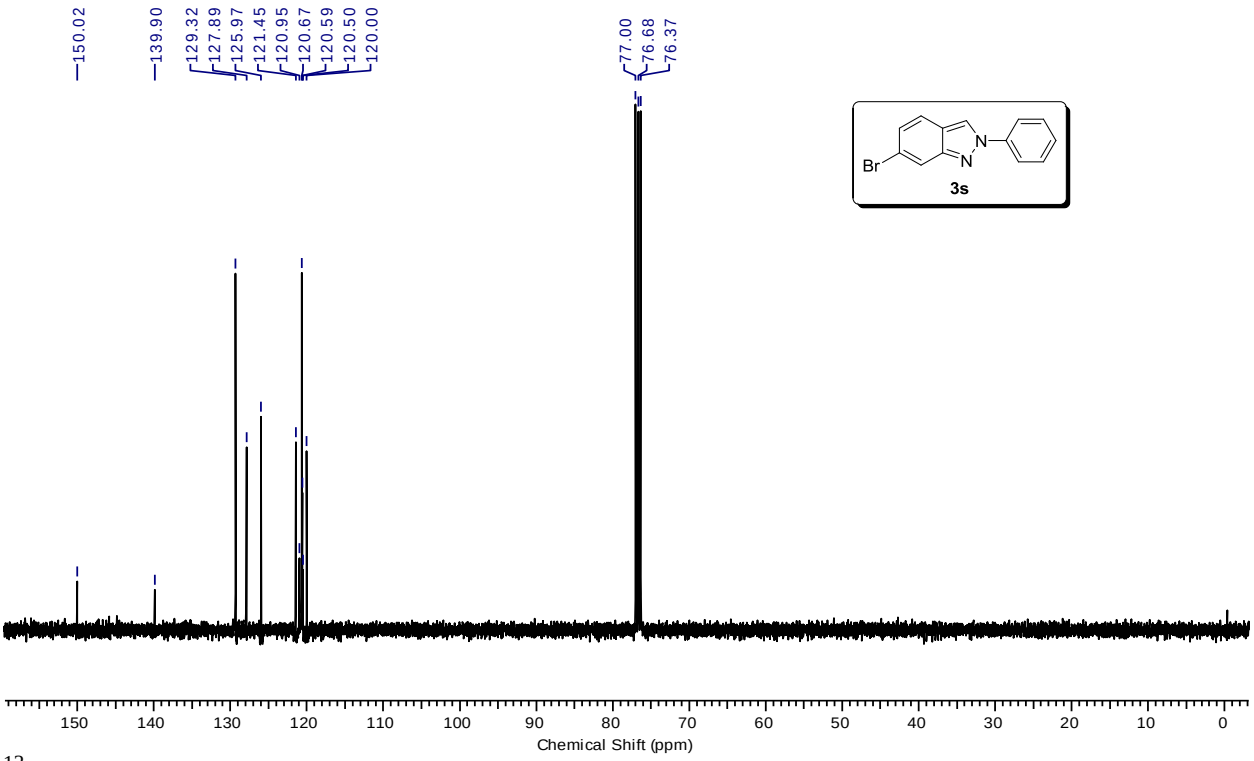
^{1}H NMR (400 MHz) spectrum of compound **3r** in $CDCl_3$



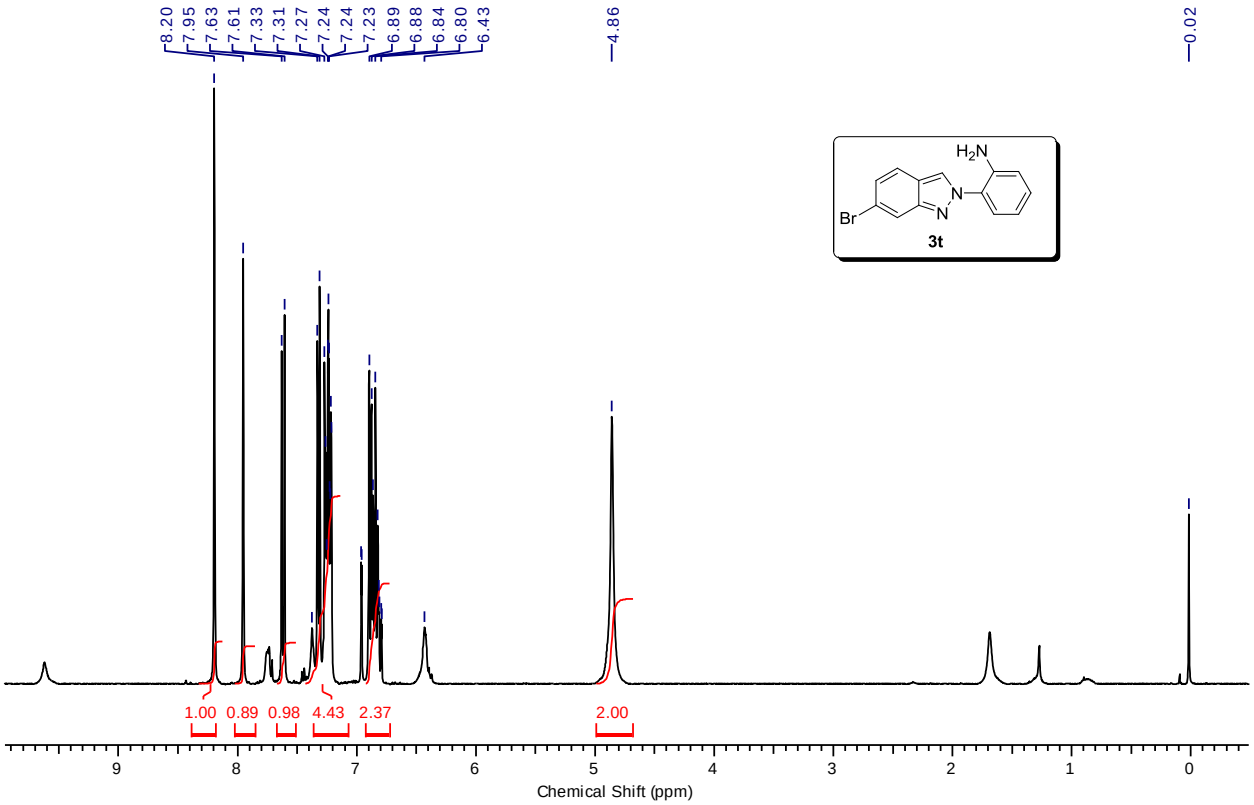
^{13}C NMR (100 MHz) spectrum of compound **3r** in $CDCl_3$



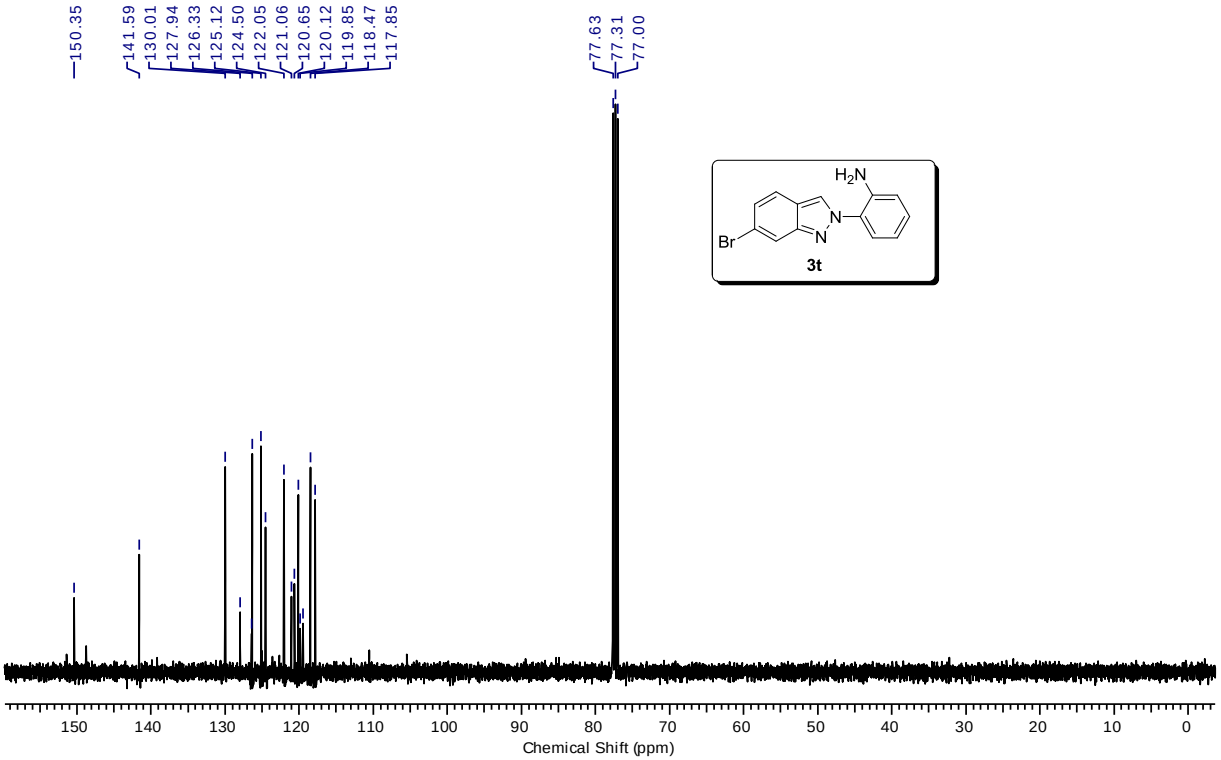
^{1}H NMR (400 MHz) spectrum of compound **3s** in $CDCl_3$



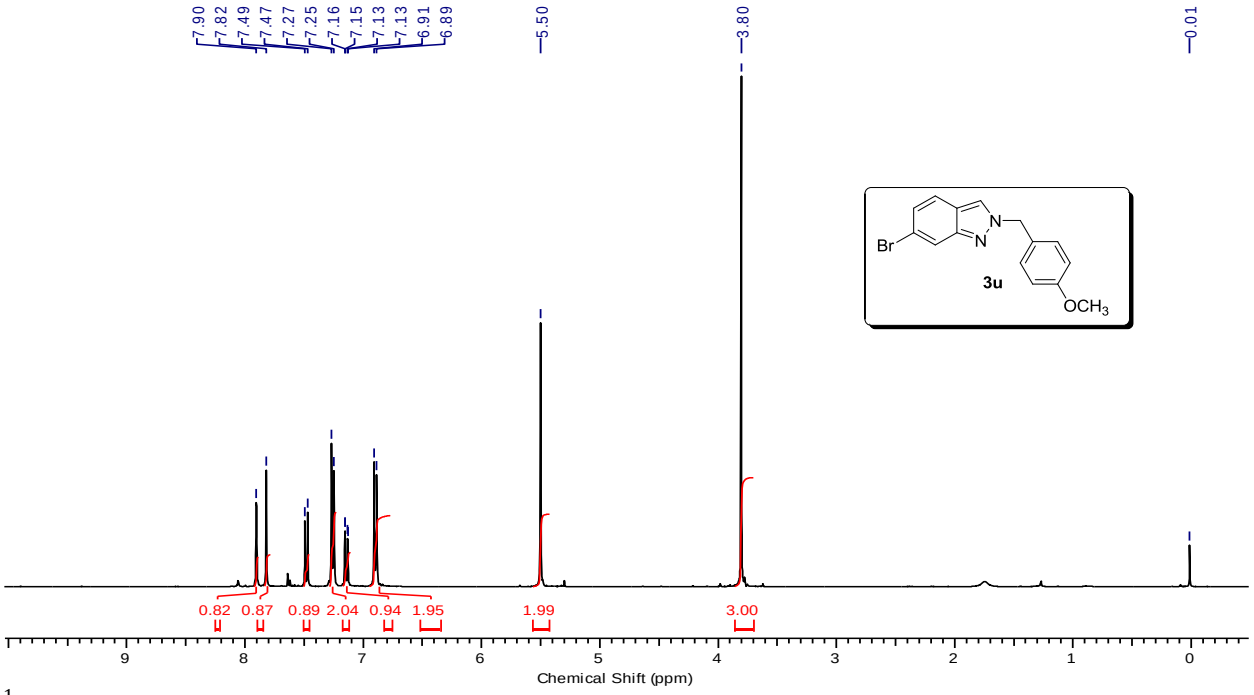
^{13}C NMR (100 MHz) spectrum of compound **3s** in $CDCl_3$



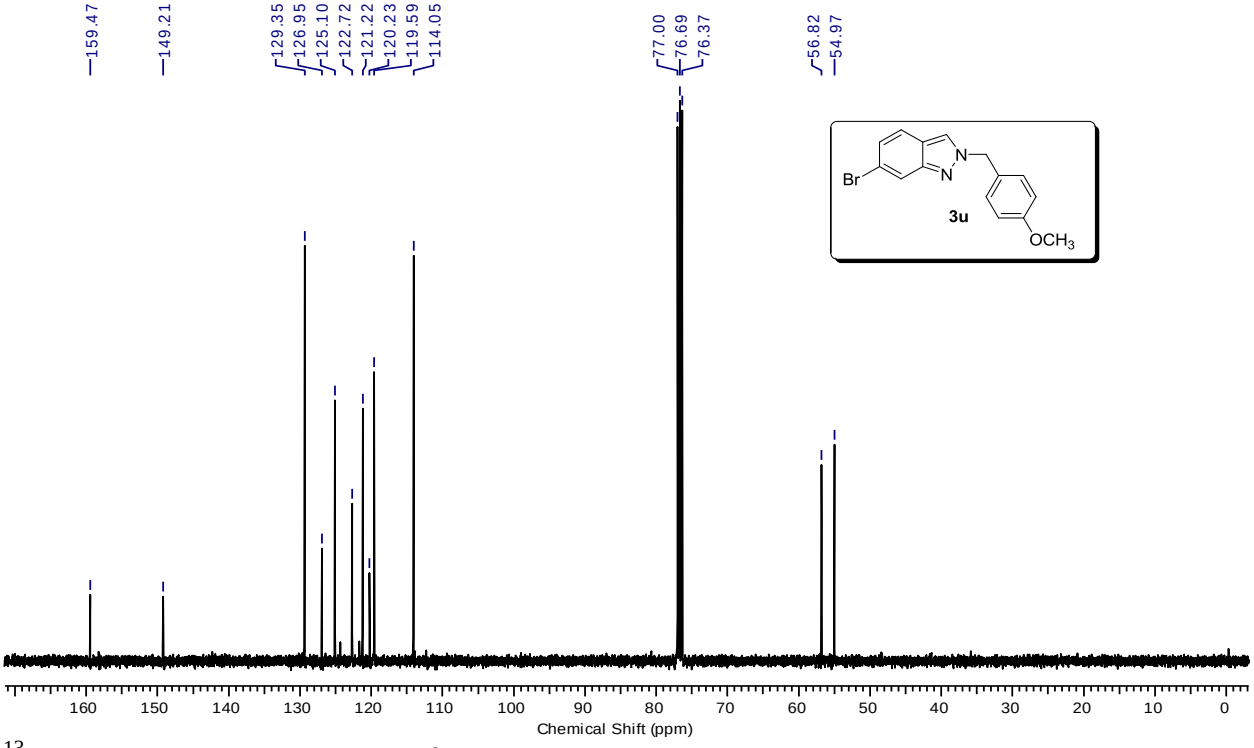
^{1}H NMR (400 MHz) spectrum of compound **3t** in $CDCl_3$



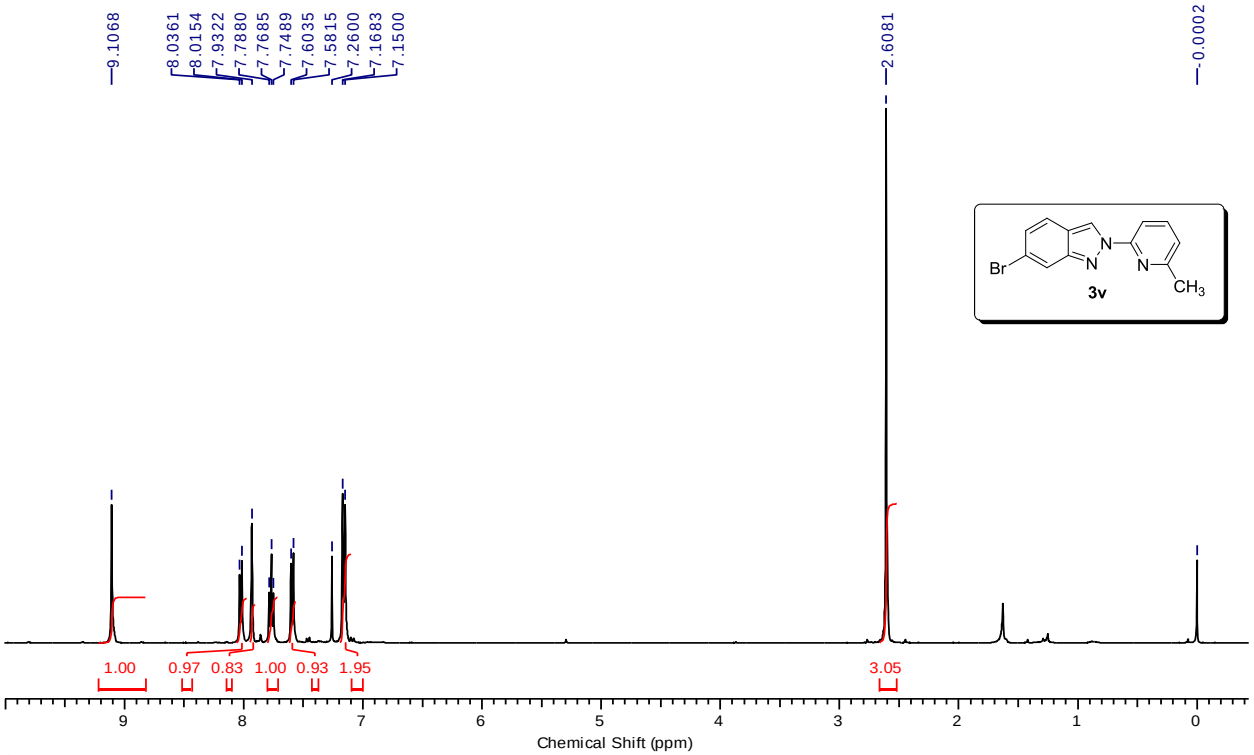
^{13}C NMR (100 MHz) spectrum of compound **3t** in $CDCl_3$



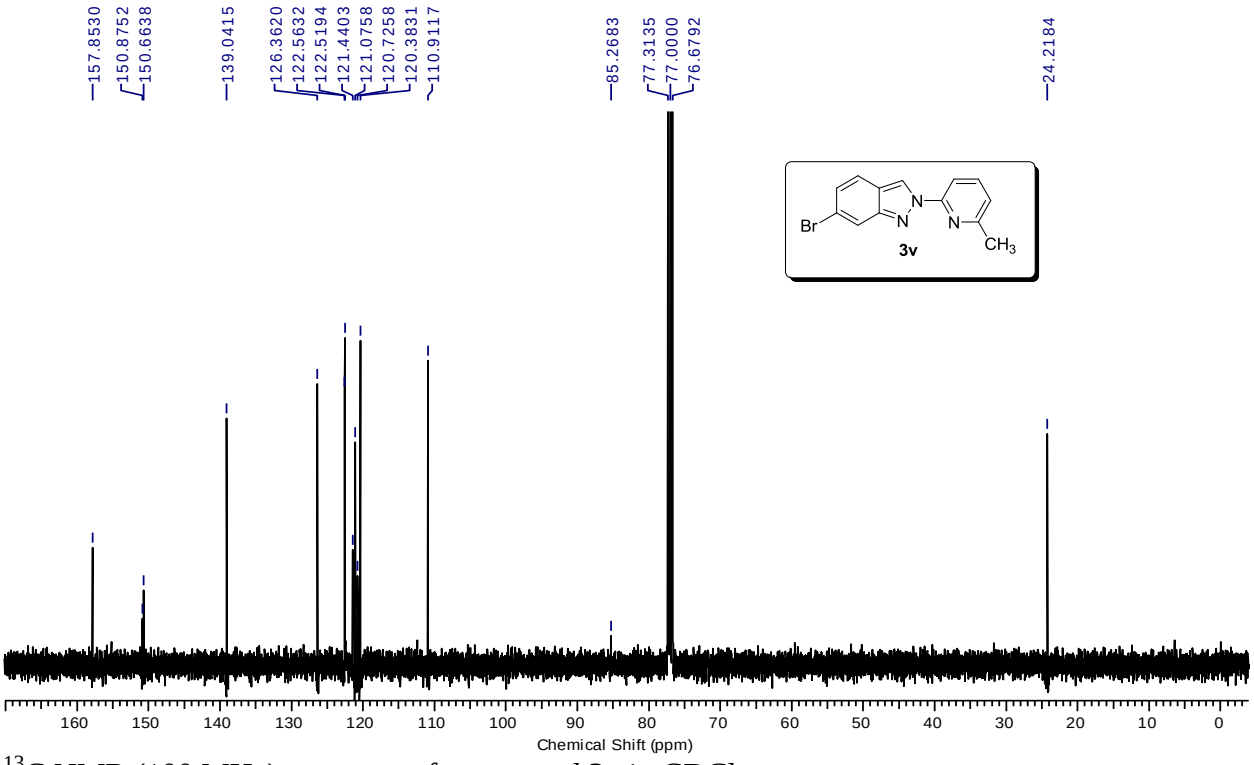
^{1}H NMR (400 MHz) spectrum of compound **3u** in $CDCl_3$



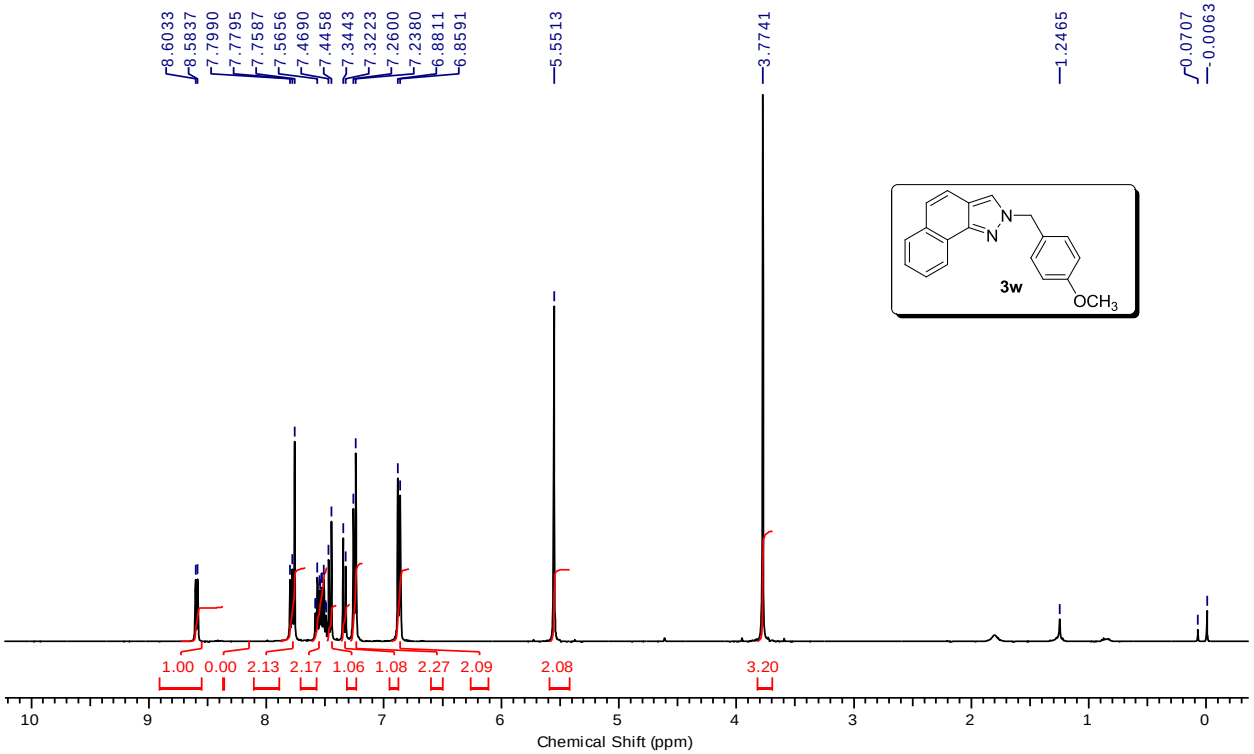
^{13}C NMR (100 MHz) spectrum of compound **3u** in $CDCl_3$



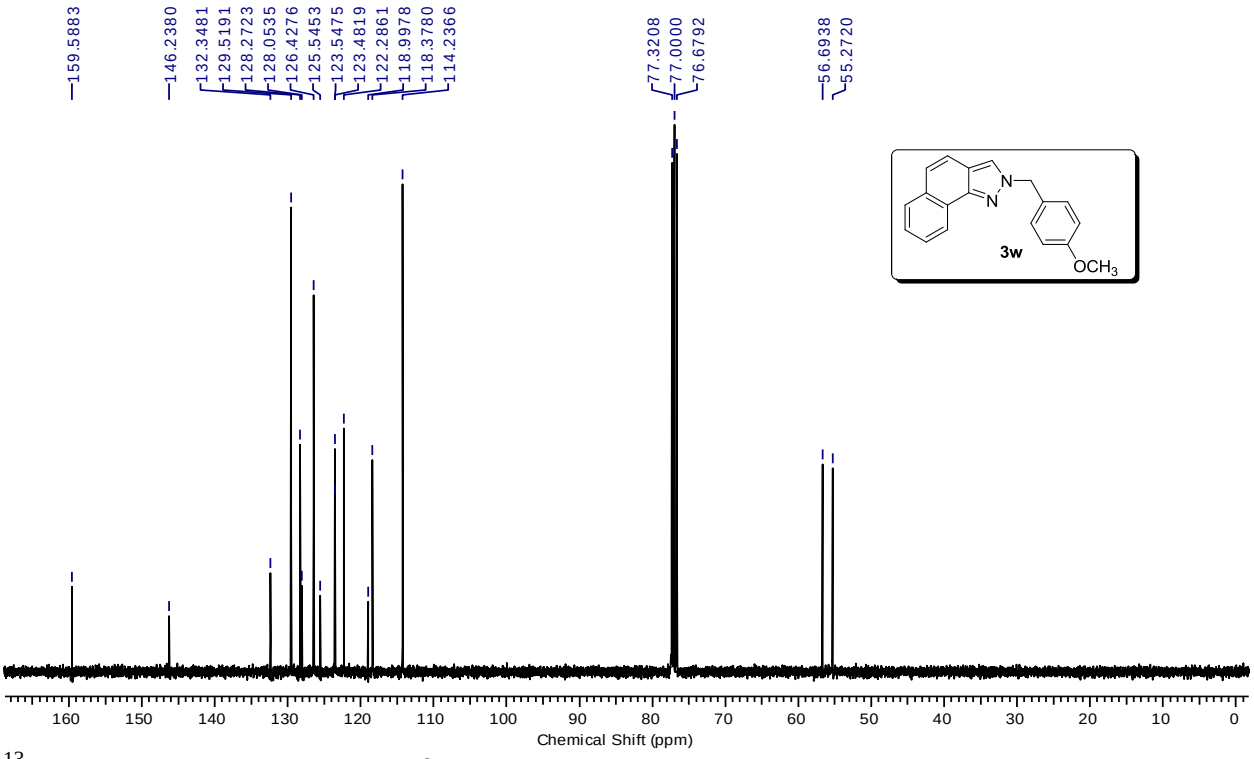
^{1}H NMR (400 MHz) spectrum of compound **3v** in $CDCl_3$



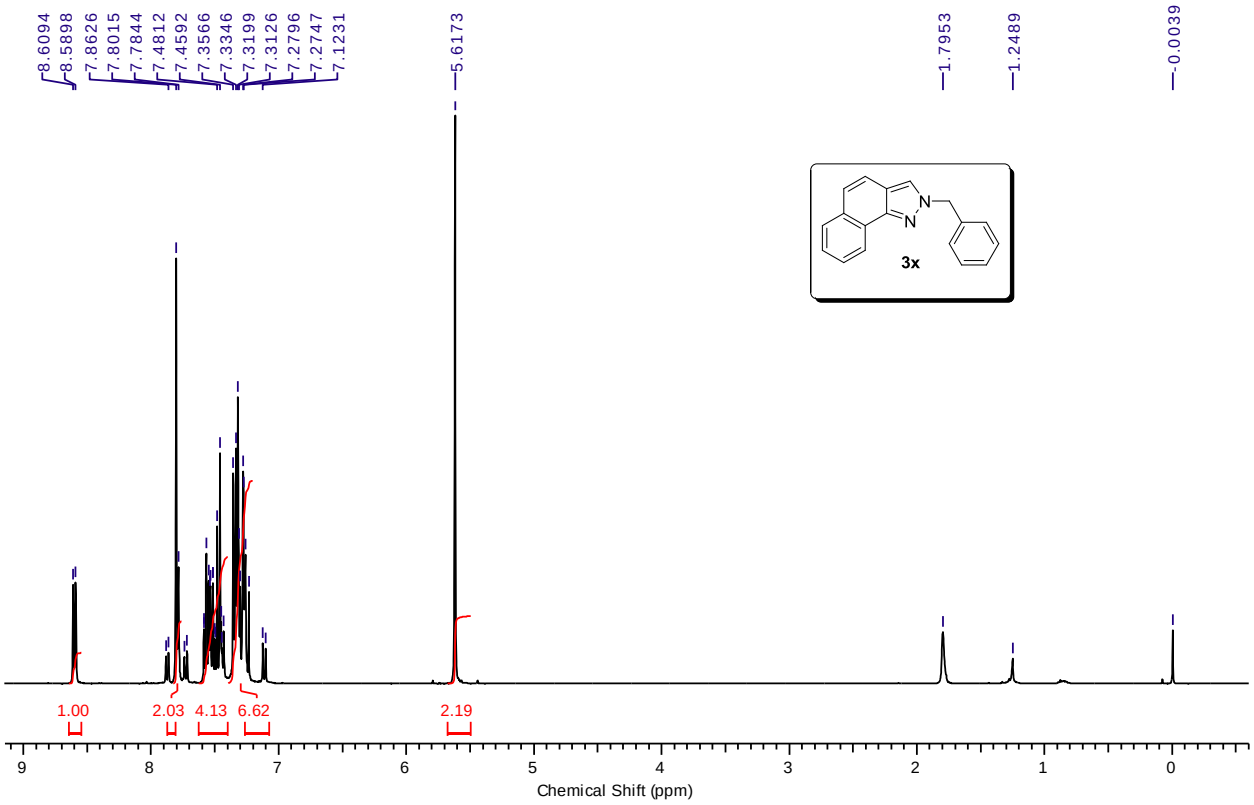
^{13}C NMR (100 MHz) spectrum of compound **3v** in $CDCl_3$



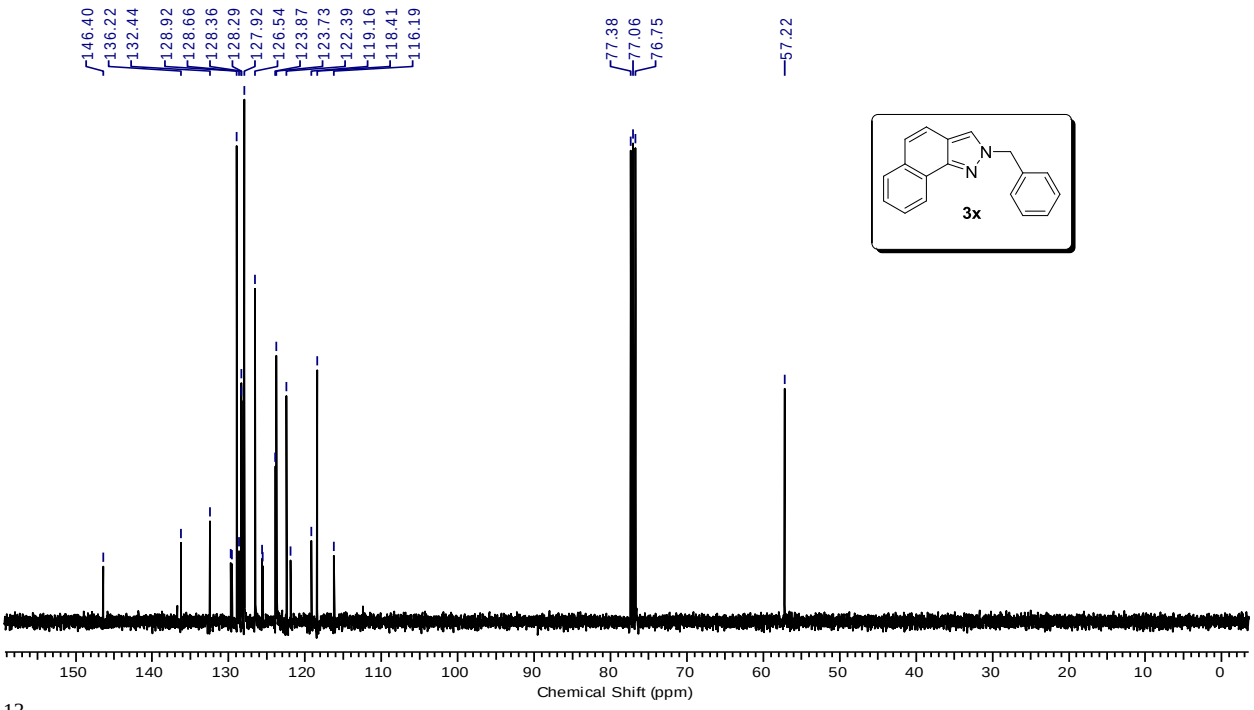
^{1}H NMR (400 MHz) spectrum of compound **3w** in $CDCl_3$



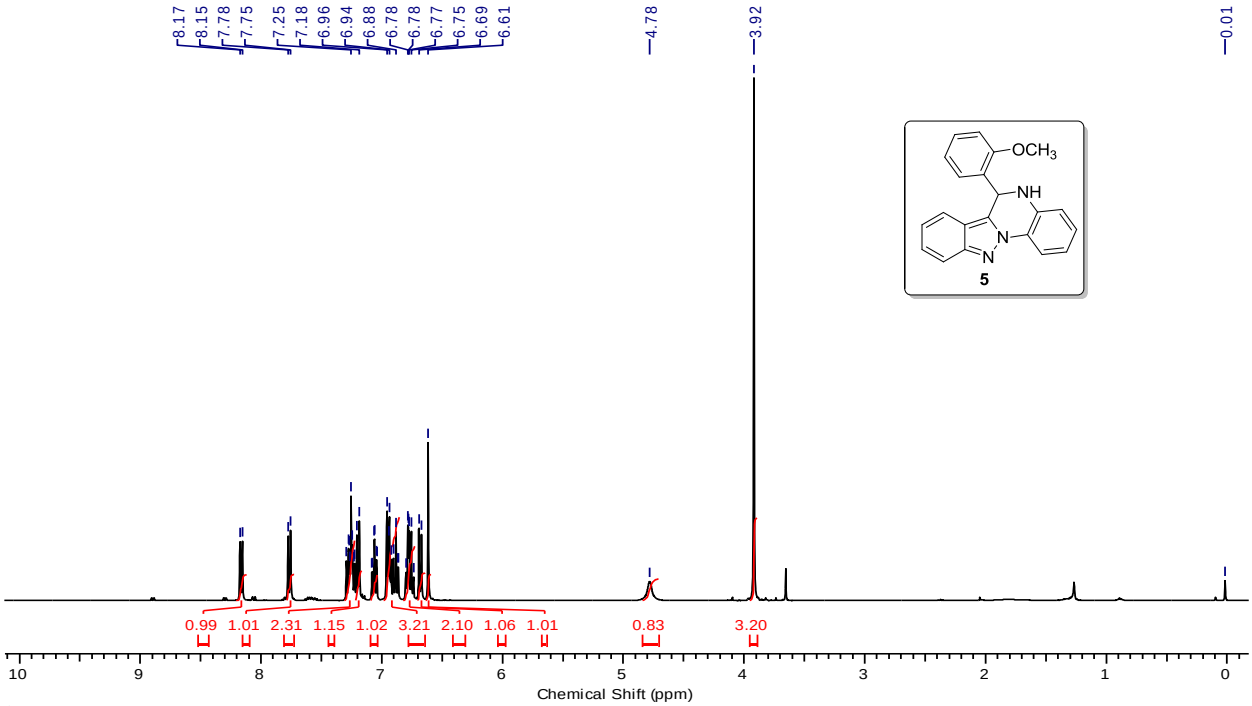
^{13}C NMR (100MHz) spectrum of compound **3w**in $CDCl_3$



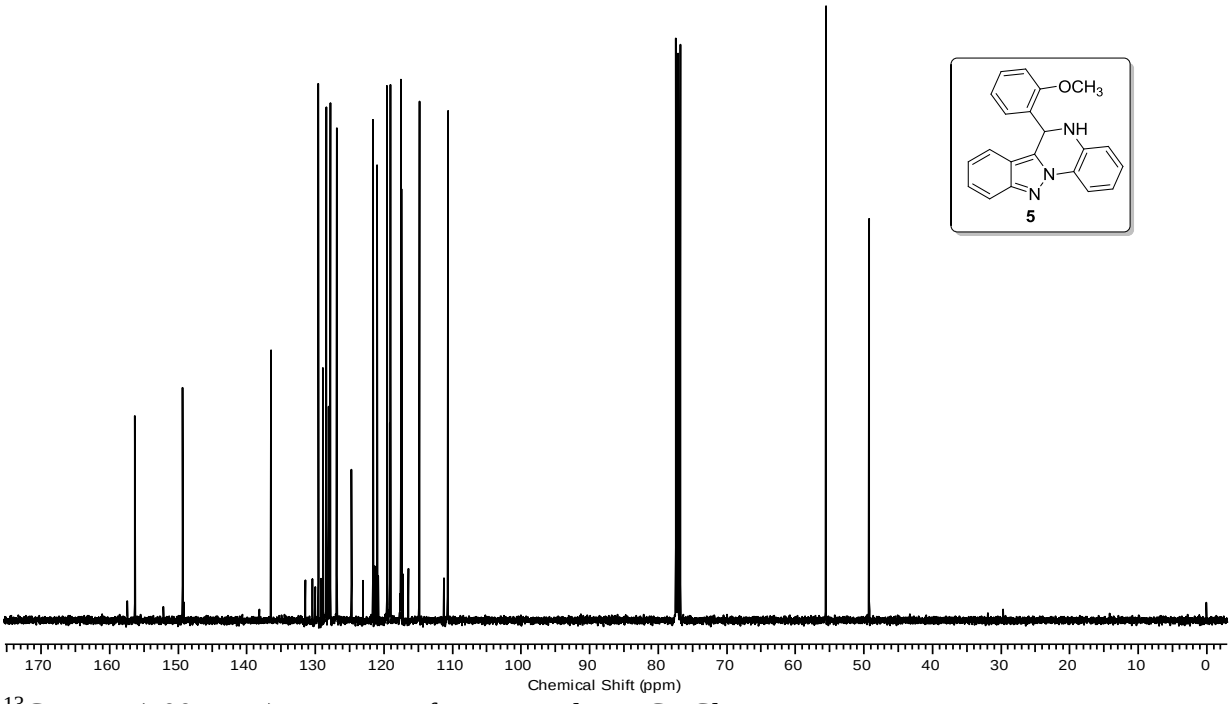
^{1}H NMR (400 MHz) spectrum of compound **3x** in $CDCl_3$



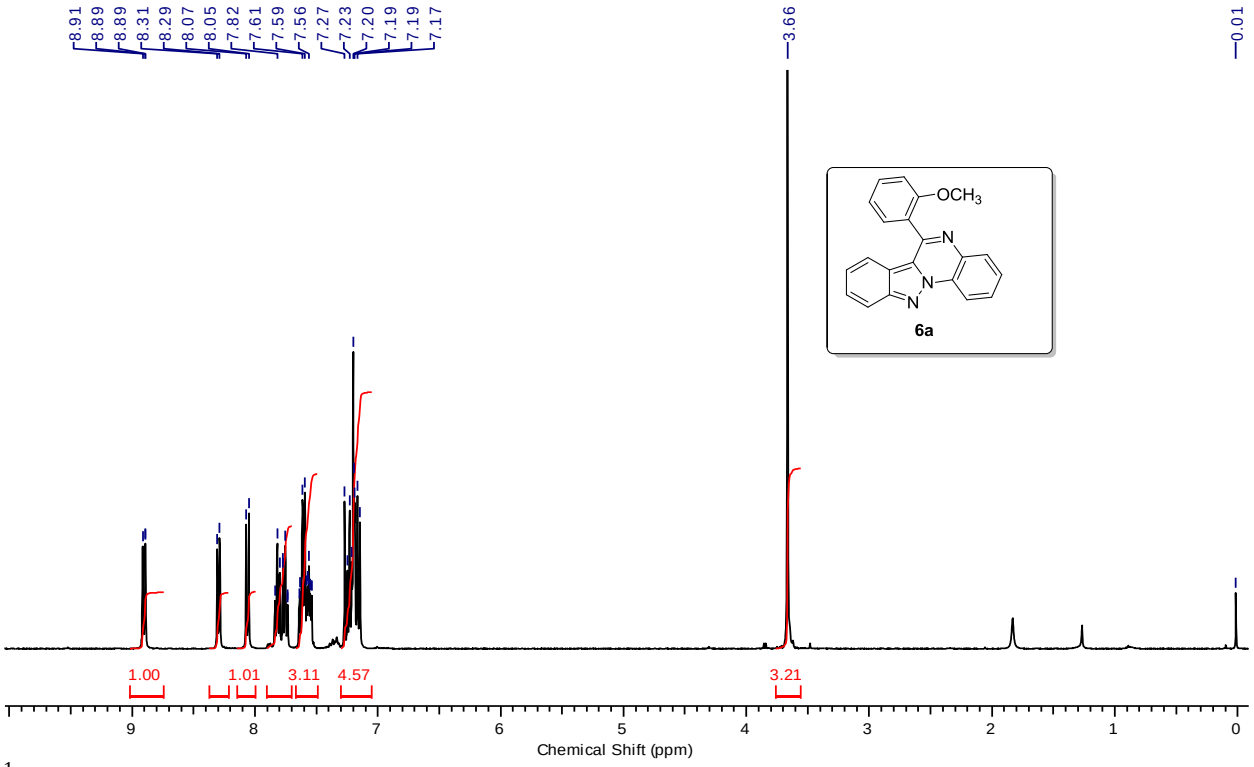
^{13}C NMR (100 MHz) spectrum of compound **3x** in $CDCl_3$



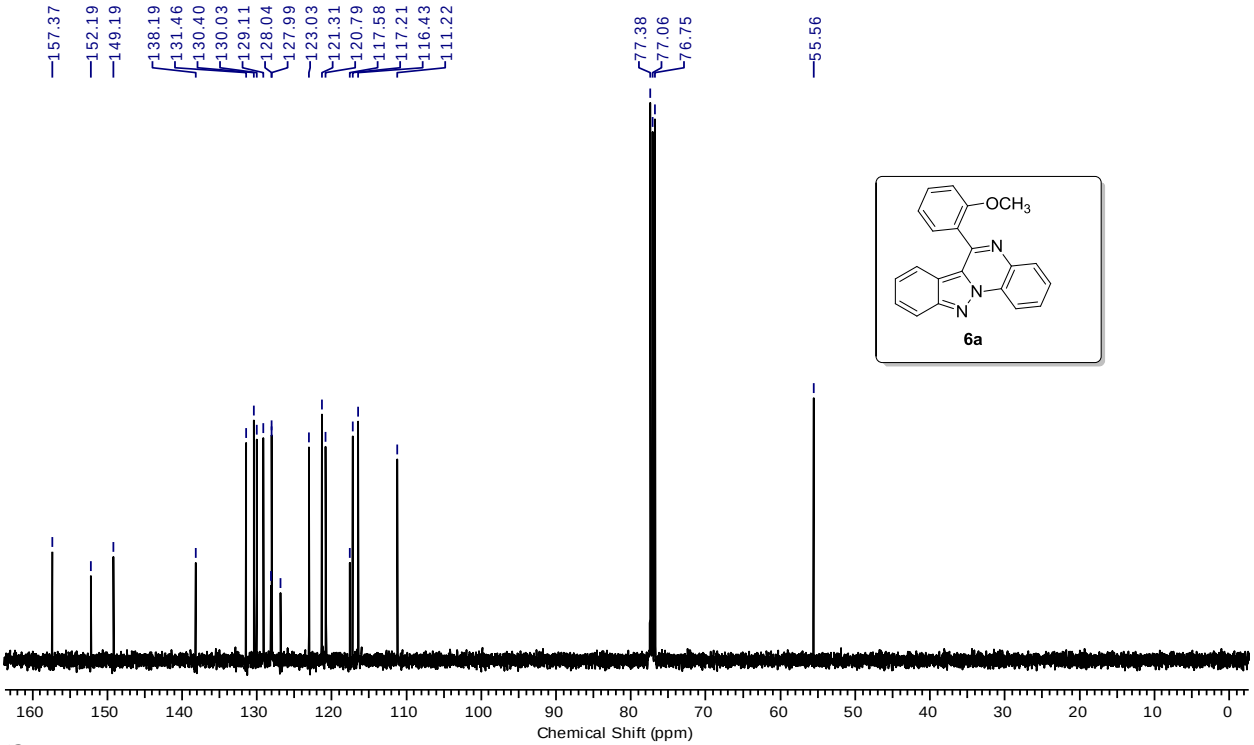
^{1}H NMR (400 MHz) spectrum of compound **5** in $CDCl_3$



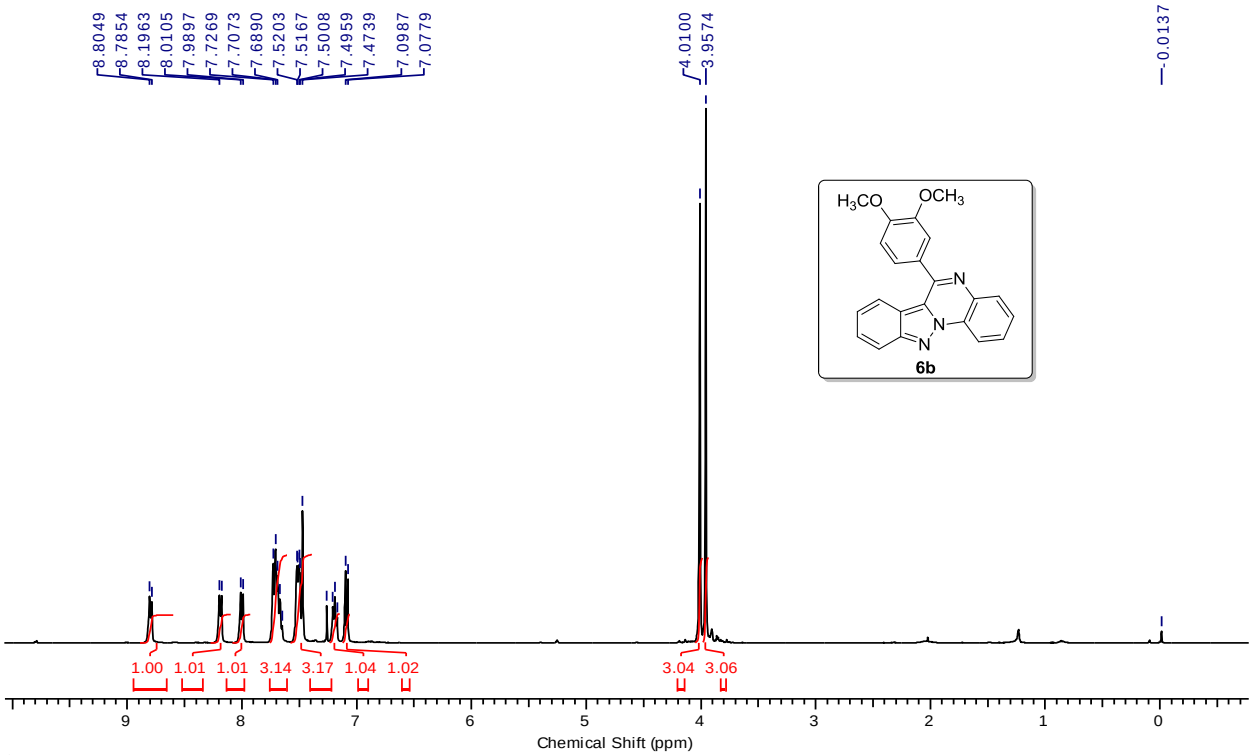
^{13}C NMR (100 MHz) spectrum of compound **5** in $CDCl_3$



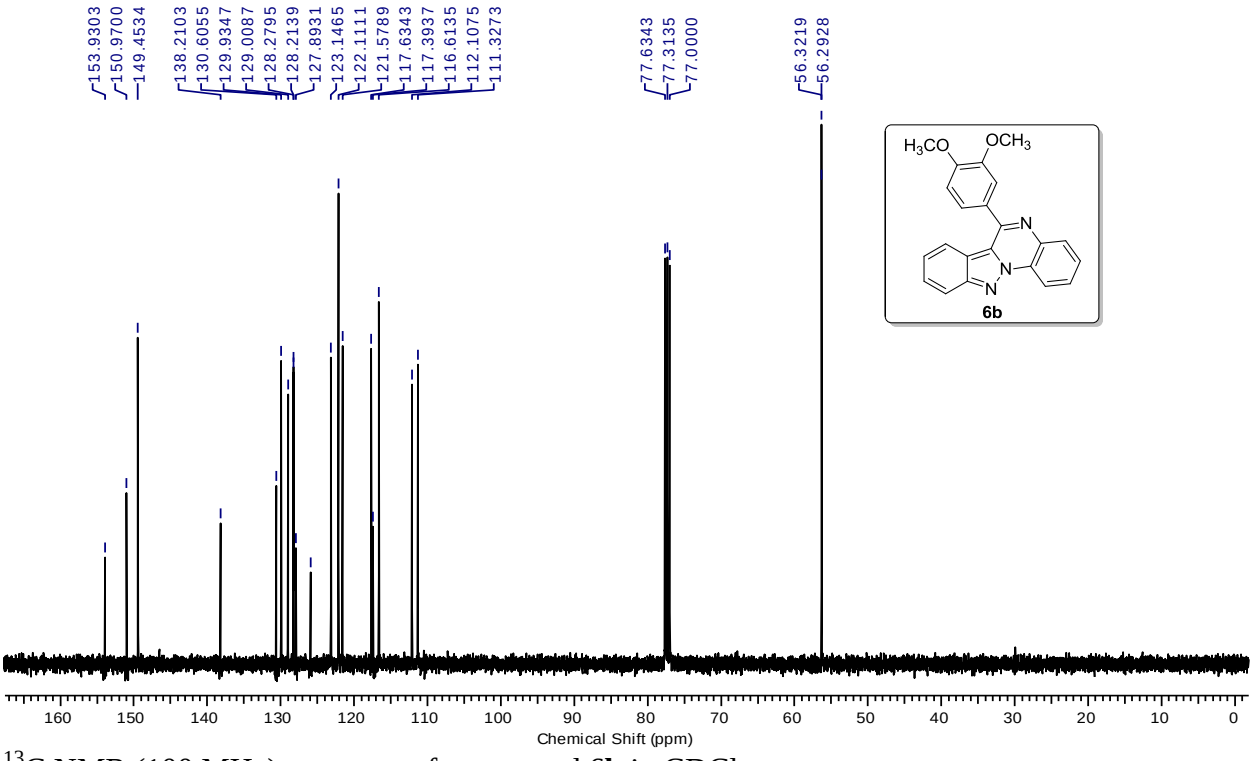
^{1}H NMR (400 MHz) spectrum of compound **6a** in $CDCl_3$



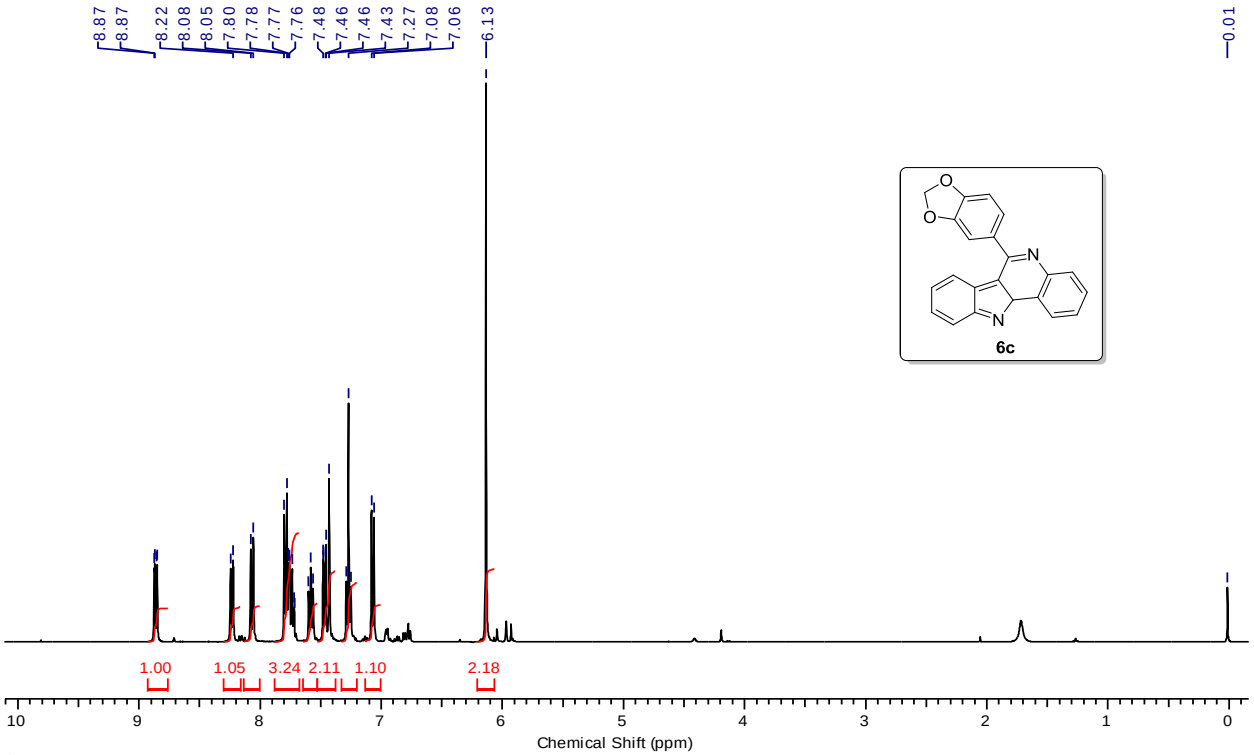
^{13}C NMR (100 MHz) spectrum of compound **6a** in $CDCl_3$



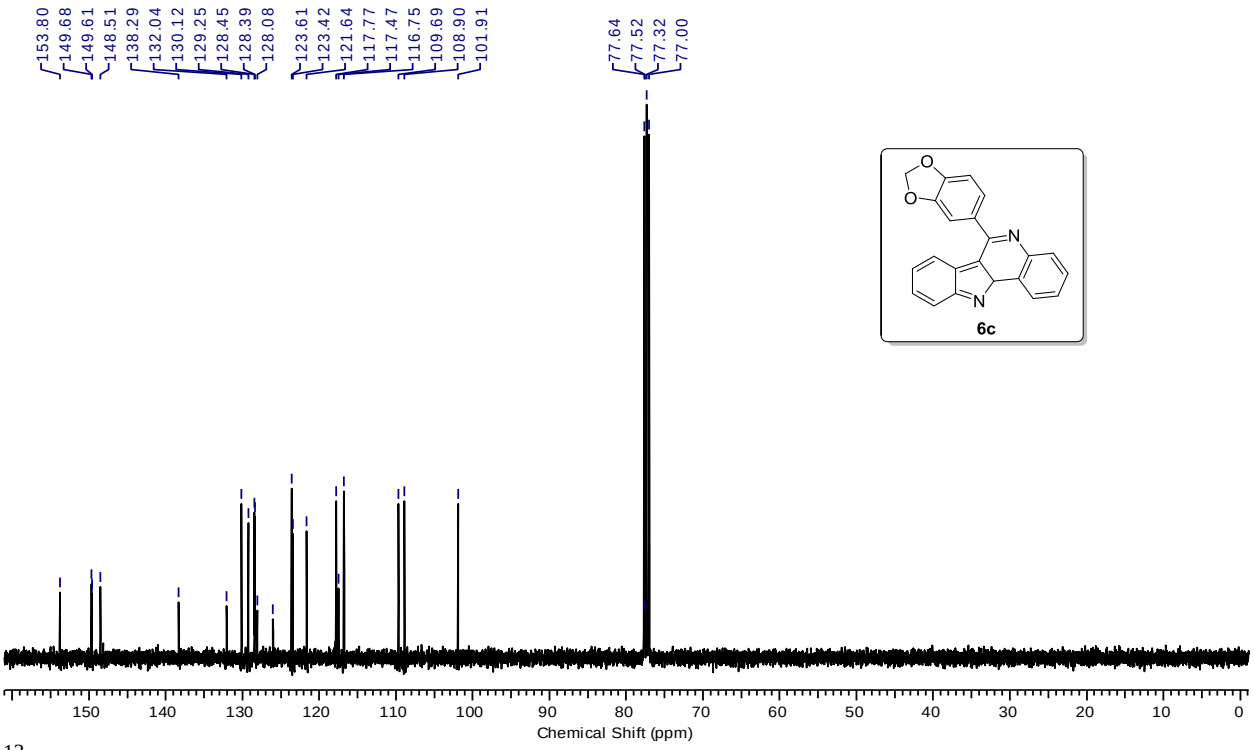
^{1}H NMR (400 MHz) spectrum of compound **6b** in $CDCl_3$



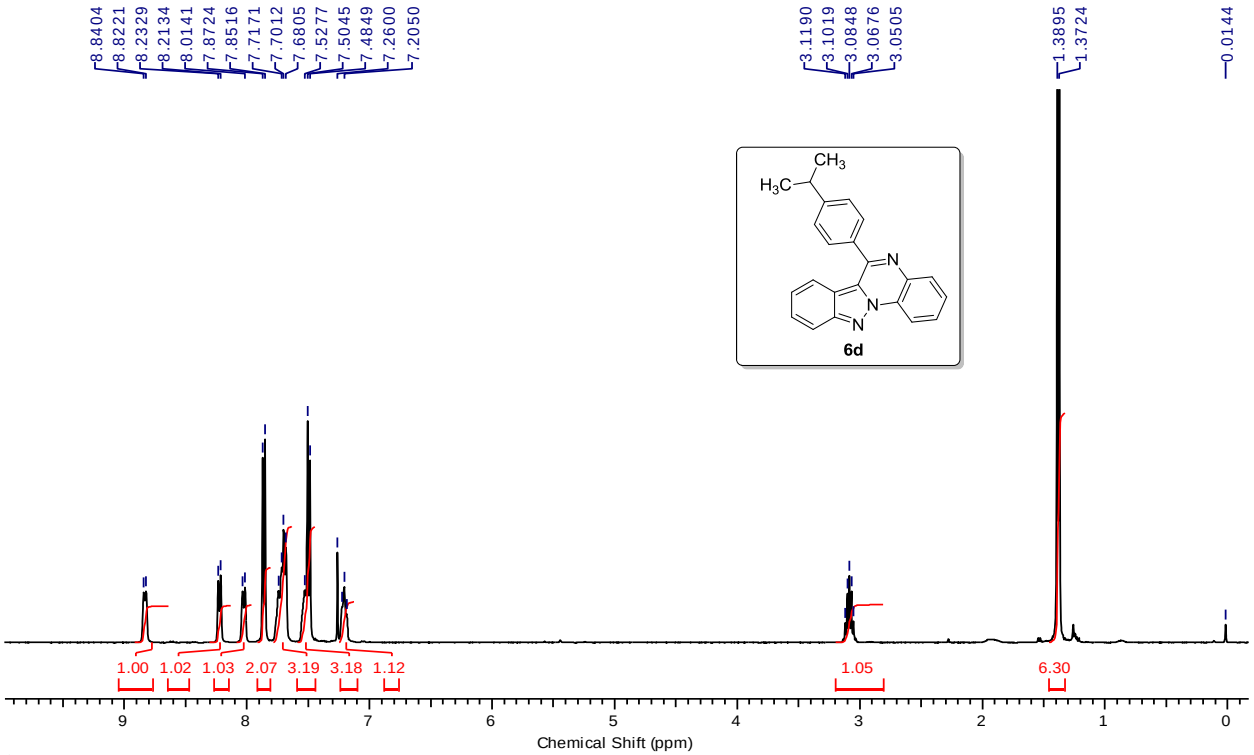
^{13}C NMR (100 MHz) spectrum of compound 6**b** in $CDCl_3$



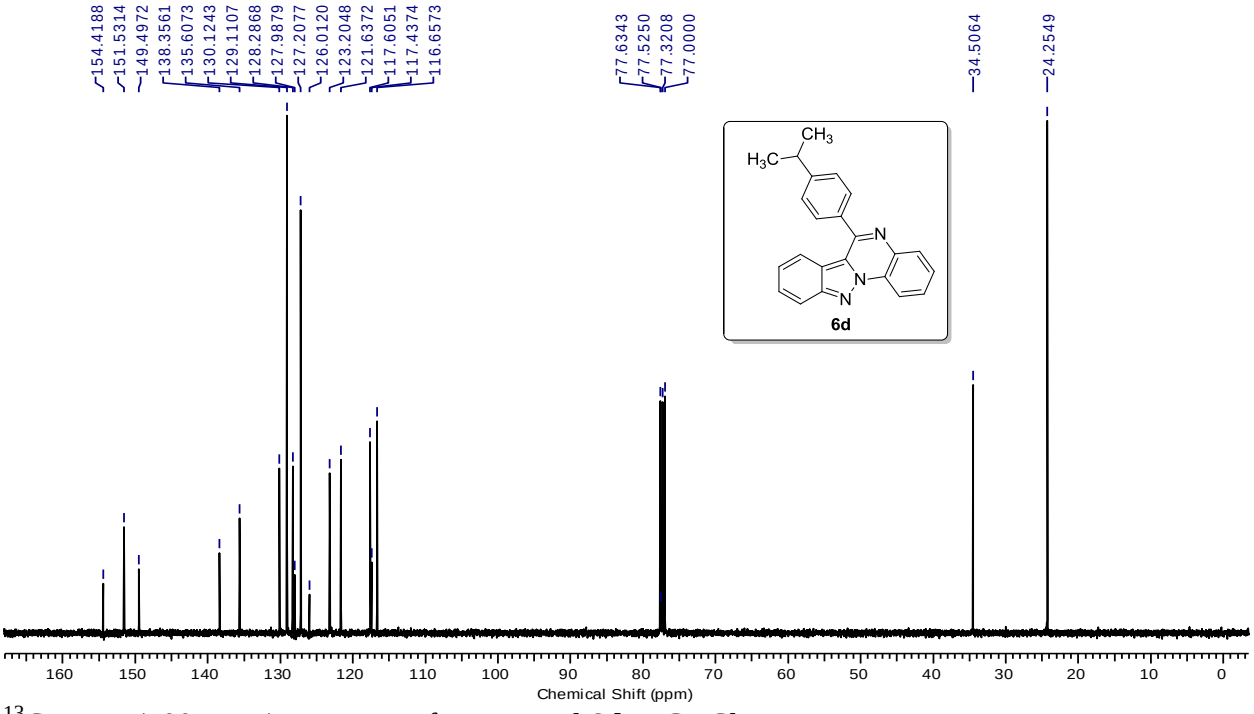
^{1}H NMR (400 MHz) spectrum of compound **6c** in $CDCl_3$



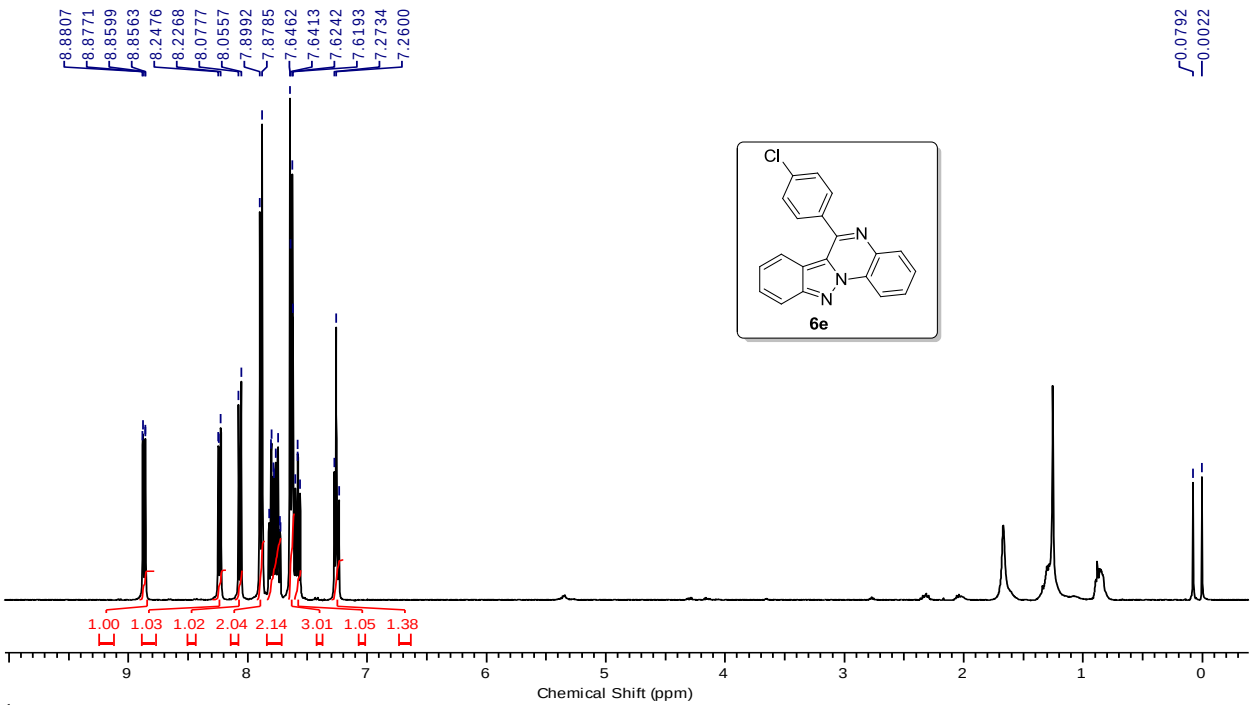
^{13}C NMR (100 MHz) spectrum of compound **6c** in $CDCl_3$



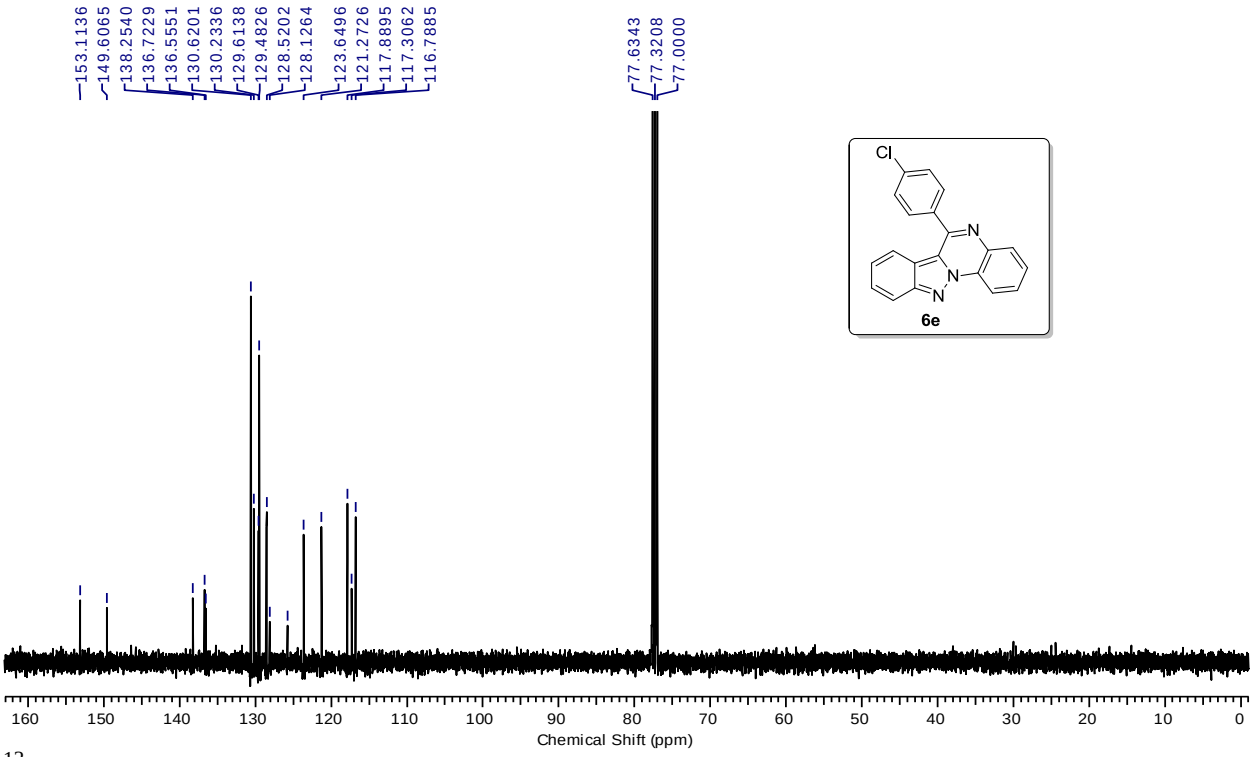
^{1}H NMR (400 MHz) spectrum of compound **6d** in $CDCl_3$



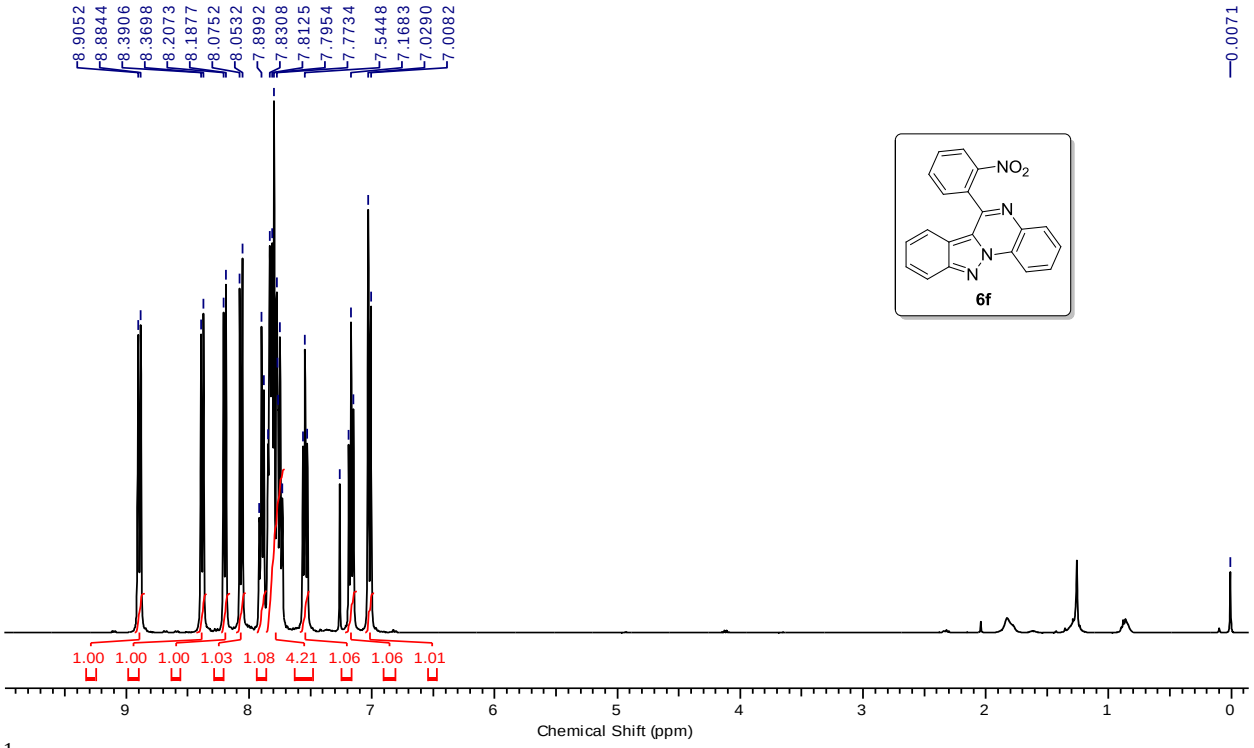
^{13}C NMR (100 MHz) spectrum of compound **6d** in $CDCl_3$



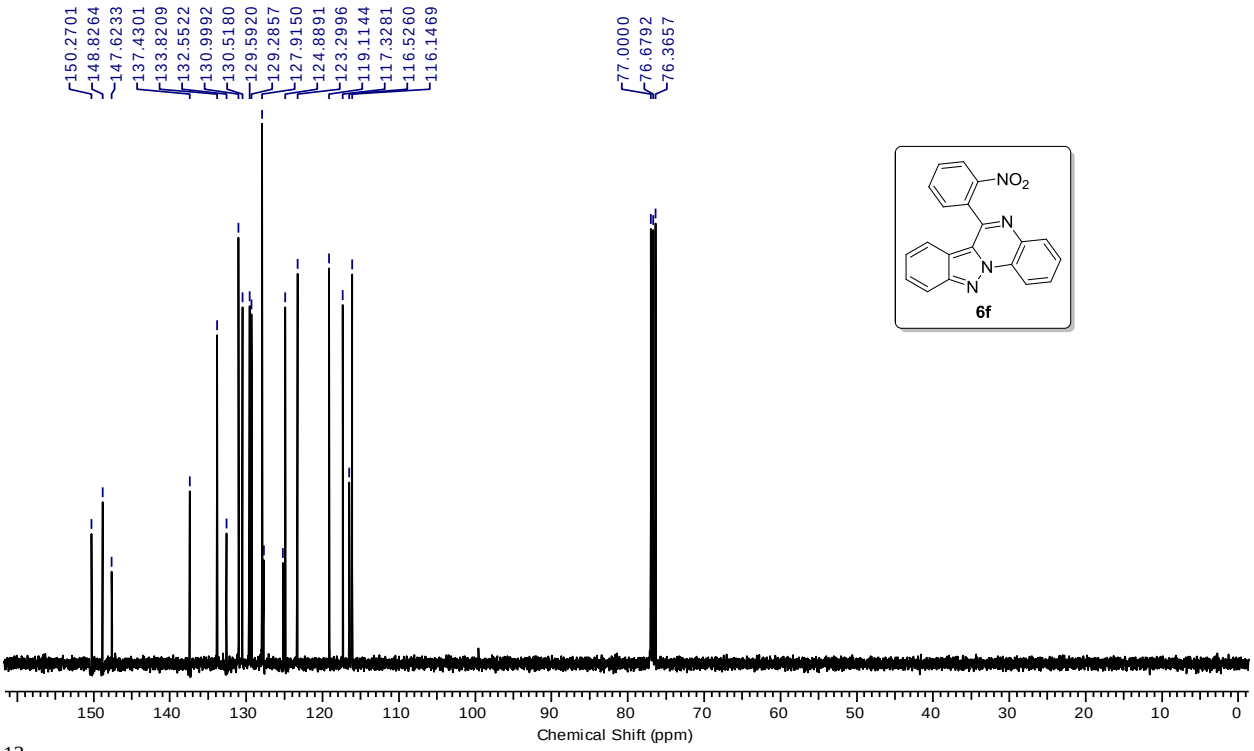
^{1}H NMR (400 MHz) spectrum of compound **6e** in $CDCl_3$



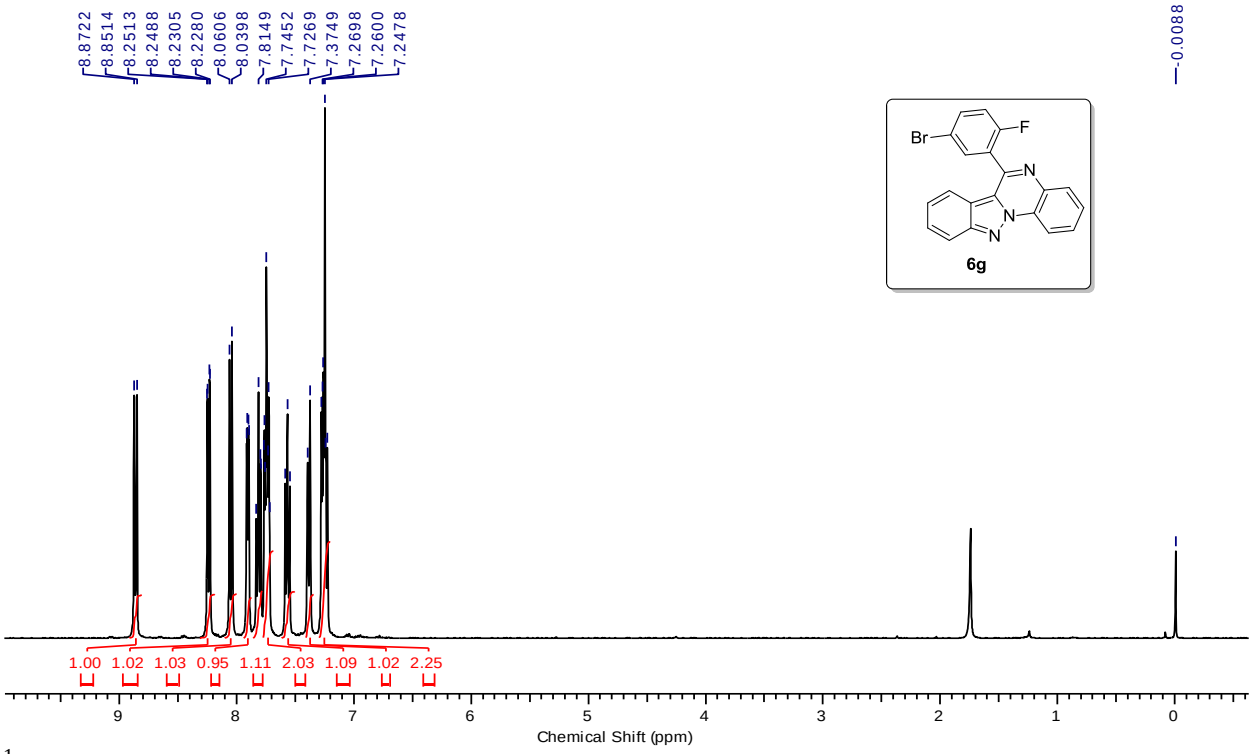
^{13}C NMR (100 MHz) spectrum of compound **6e** in $CDCl_3$



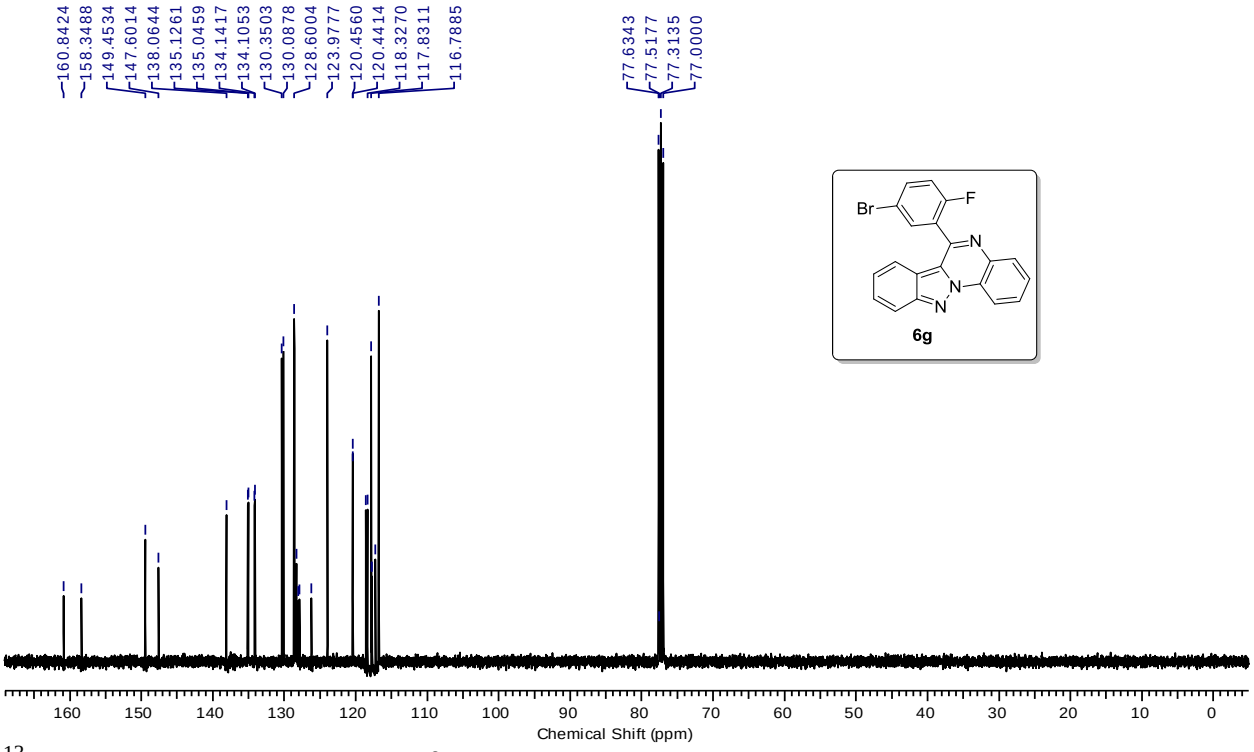
^{1}H NMR (400 MHz) spectrum of compound **6f** in $CDCl_3$



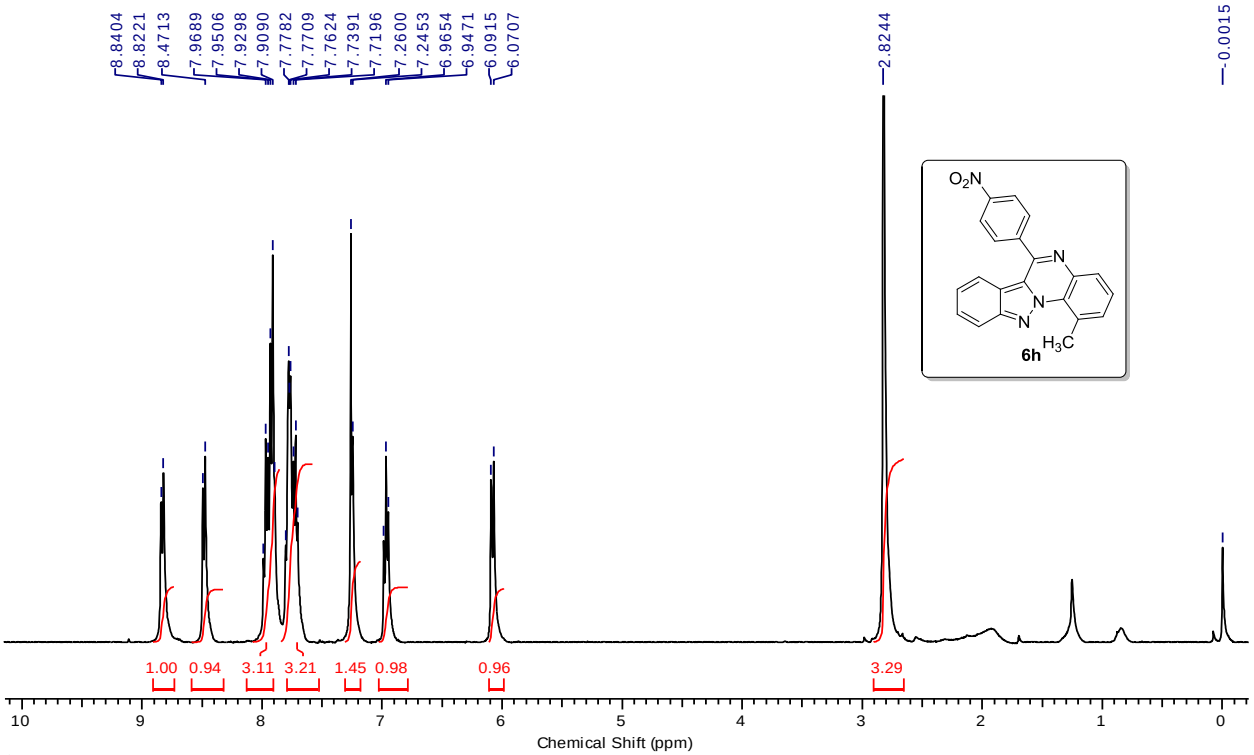
^{13}C NMR (100 MHz) spectrum of compound **6f** in $CDCl_3$



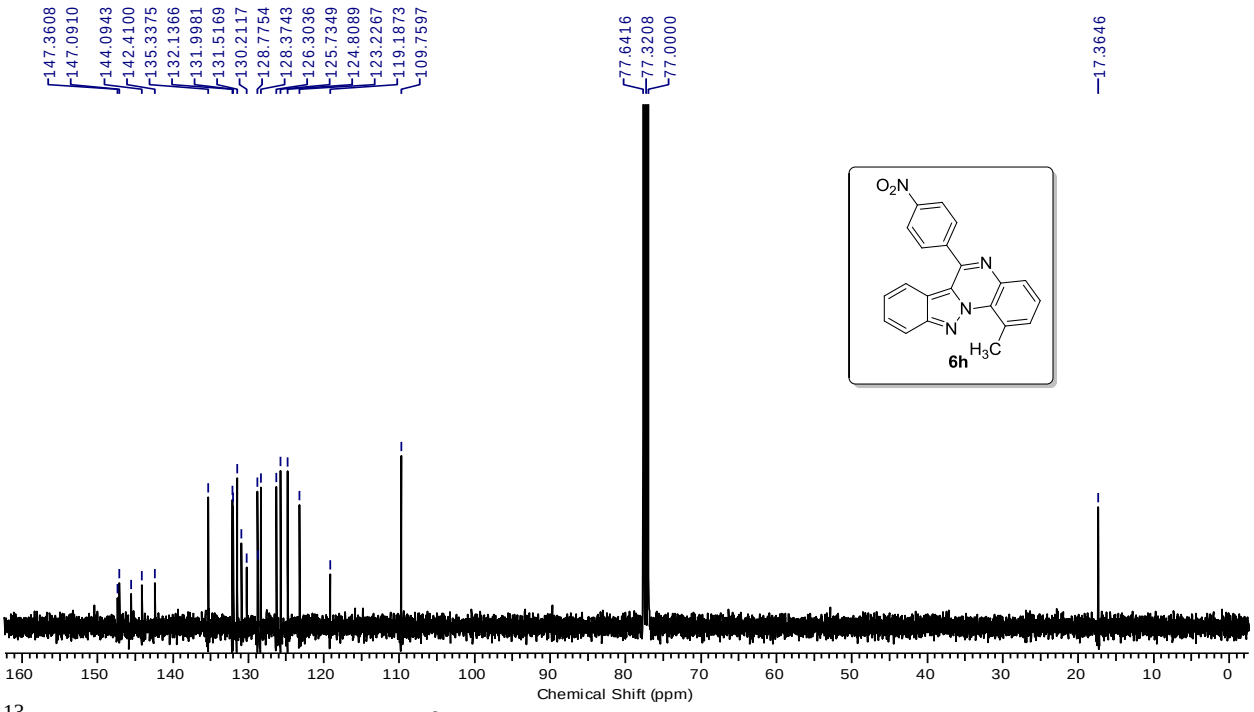
^{1}H NMR (400 MHz) spectrum of compound **6g** in $CDCl_3$



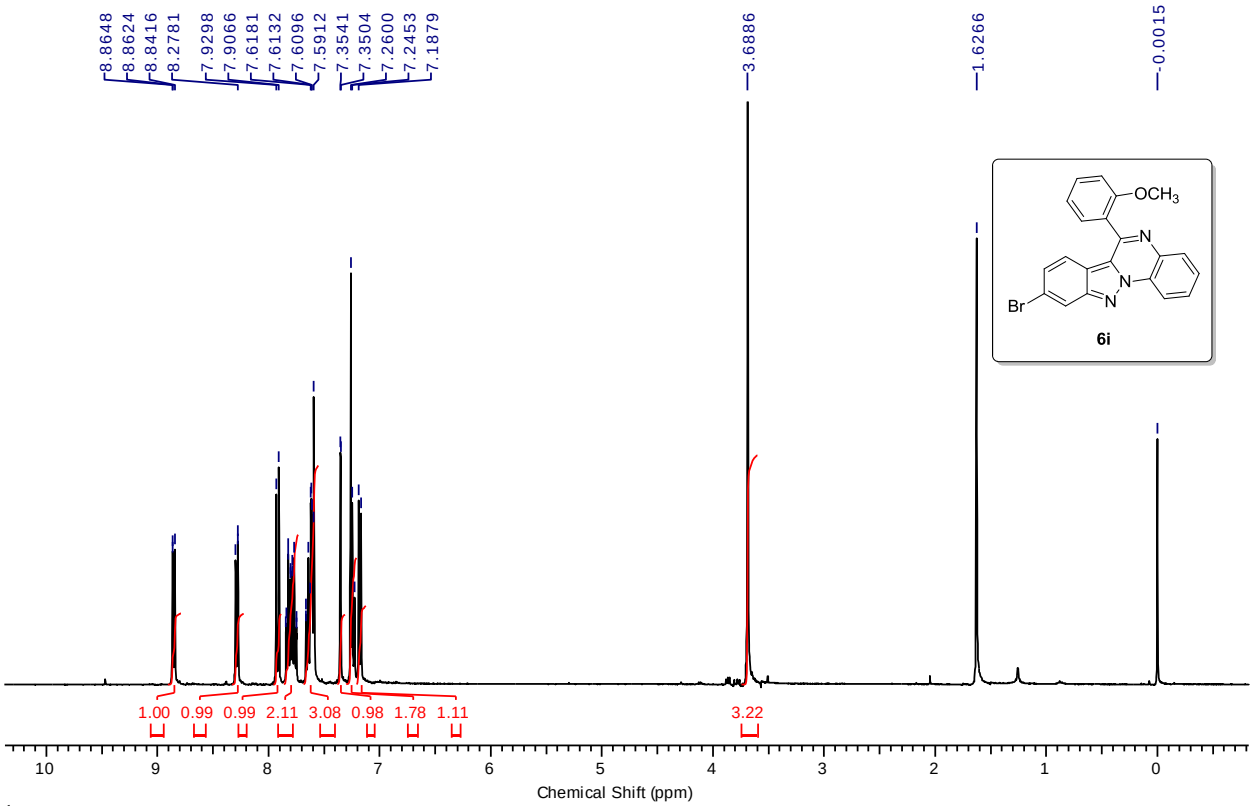
^{13}C NMR (100 MHz) spectrum of compound 6**g** in $CDCl_3$



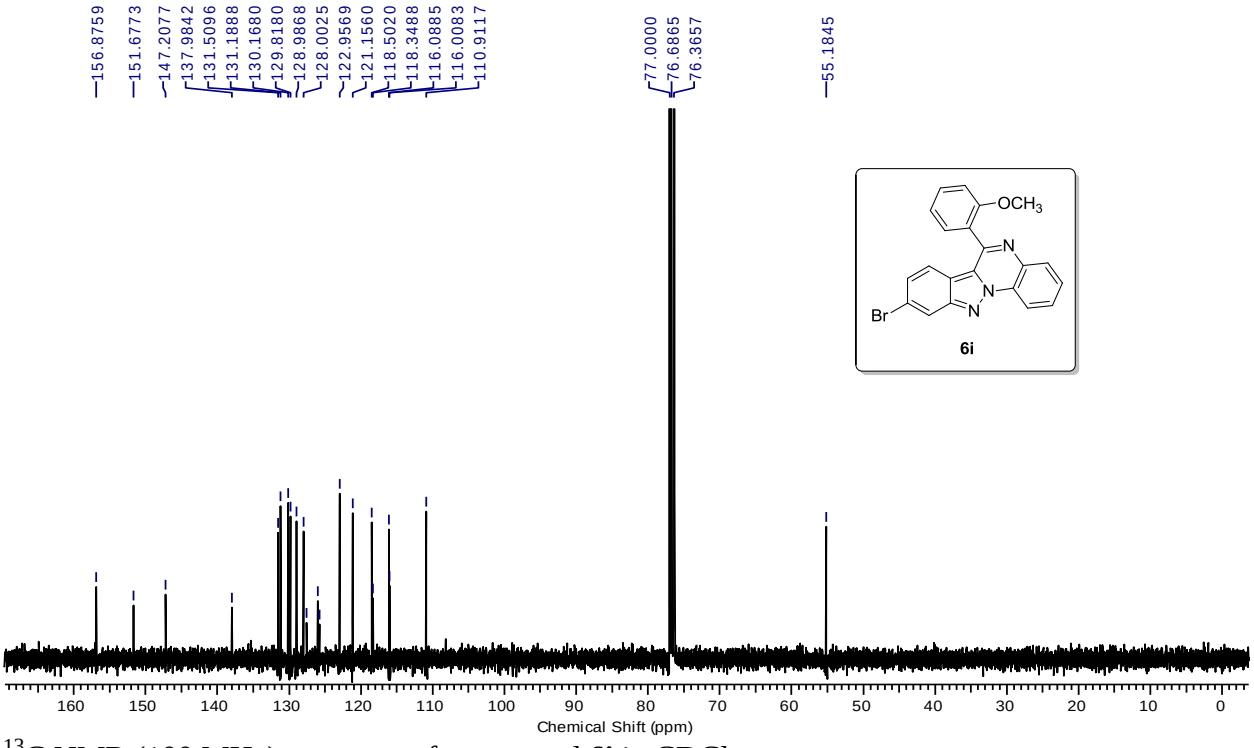
^{1}H NMR (400 MHz) spectrum of compound **6h** in $CDCl_3$



^{13}C NMR (100 MHz) spectrum of compound 6**h** in $CDCl_3$



^{1}H NMR (400 MHz) spectrum of compound **6i** in $CDCl_3$



^{13}C NMR (100 MHz) spectrum of compound 6**i** in $CDCl_3$

References:

1. (*a*) M. Shen and T. G. Driver, *Org Lett*, 2010, **12,** 2884; (*b*) J. Hu, Y. Cheng, Y. Yang, and Y. Rao, *Chem.Commun*., 2011, **47**, 10133.
2. N. E. Genung, L. Wei, and G. E. Aspnes, *Org. Lett.*, 2014, **16**, 3114; (*b*) M. R. Kumar, A. Park, N. Park, and S. Lee, *Org. Lett.*, 2011, **13**, 3542.
3 A. G. Erik, D. M. Theresa, F. K. James, G-P. Angel, L. E. Cheng Yin, P. J. Allen, S. B. Dawson, T. M. Mike., Appl. Publ. (2012), US 20120202834 A1 20120809.
4. A. Taher, S. Ladwa, S. Thirumalai Rajan, and G. W. Weaver, *Tetrahedron Letters*, 2000, **41**, 9893.
5. A. H. Moustafa, C. C. Malakar, N. Aljaar, E. Merisor, J. Conrad, U. Beifuss, *Synlett*, 2013, 24, 1573
6. J. C. Antilla, J. M. Baskin, T. E. Barder, and S. L. Buchwald, *J. Org. Chem.*, 2004, **69**, 5578.
7. D. J. Slade, N. F. Pelz, W. Bodnar, J. W. Lampe, and P. S. Watson, *J. Org. Chem.*, 2009, **74**, 6331.
8. M. Akazome, T. Kondo, and Y. Watanabe, *J. Org. Chem.*, 1994, **59**, 3375.
9. H. L. Gaetan, J. B. Michael, C. W. Wai, B. Donald, PCT Int. Appl. (2003), WO 2003027094 A2 20030403.