Electronic Supplementary Information

Copper Catalyzed *N*-Arylation of 5-Aminopyrazoles: A Simple Route to Pyrazolo[3, 4-*b*]indoles

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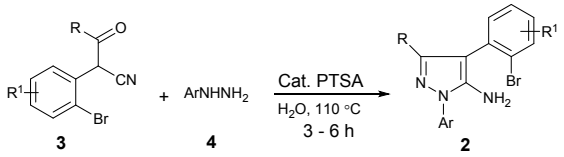
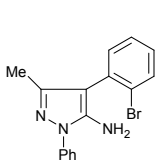
Table S1. Synthesis of 5-amino-4-(2-bromoaryl)pyrazoles **2**.[a]

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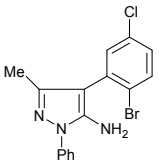
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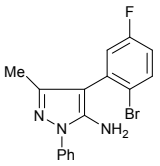
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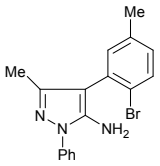
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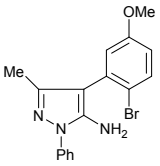
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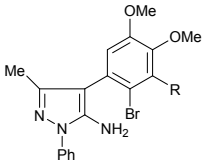
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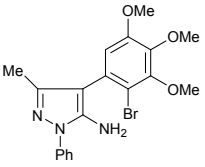
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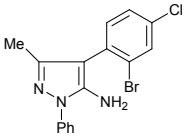
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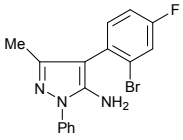
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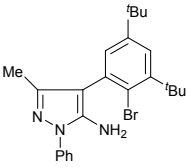
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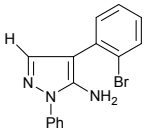
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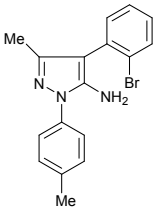
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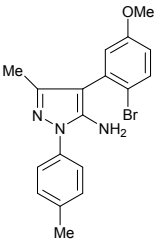
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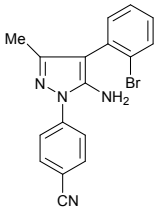
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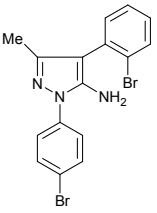
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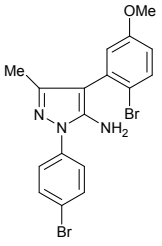
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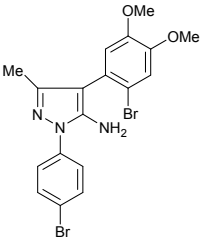
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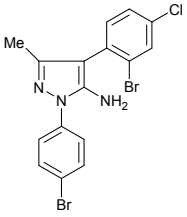
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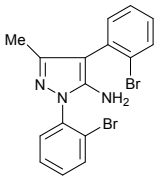
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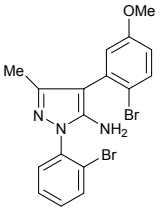
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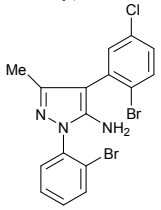
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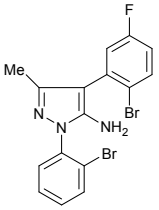
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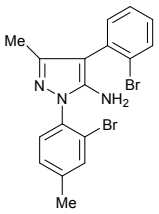
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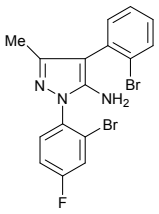
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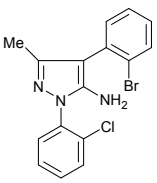
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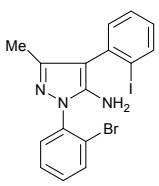
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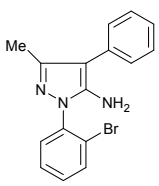
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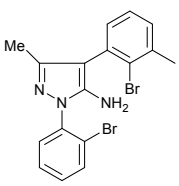
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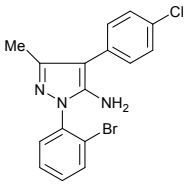
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[a]Isolated yields

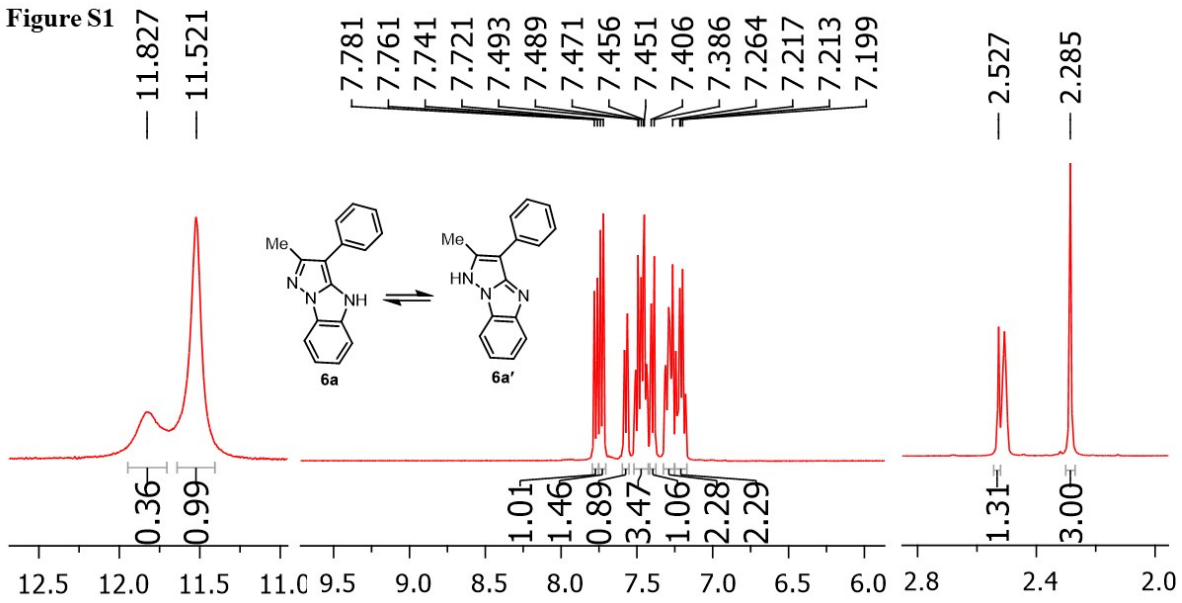


Figure S1. [1]H NMR spectra of **6a** & **6a'**

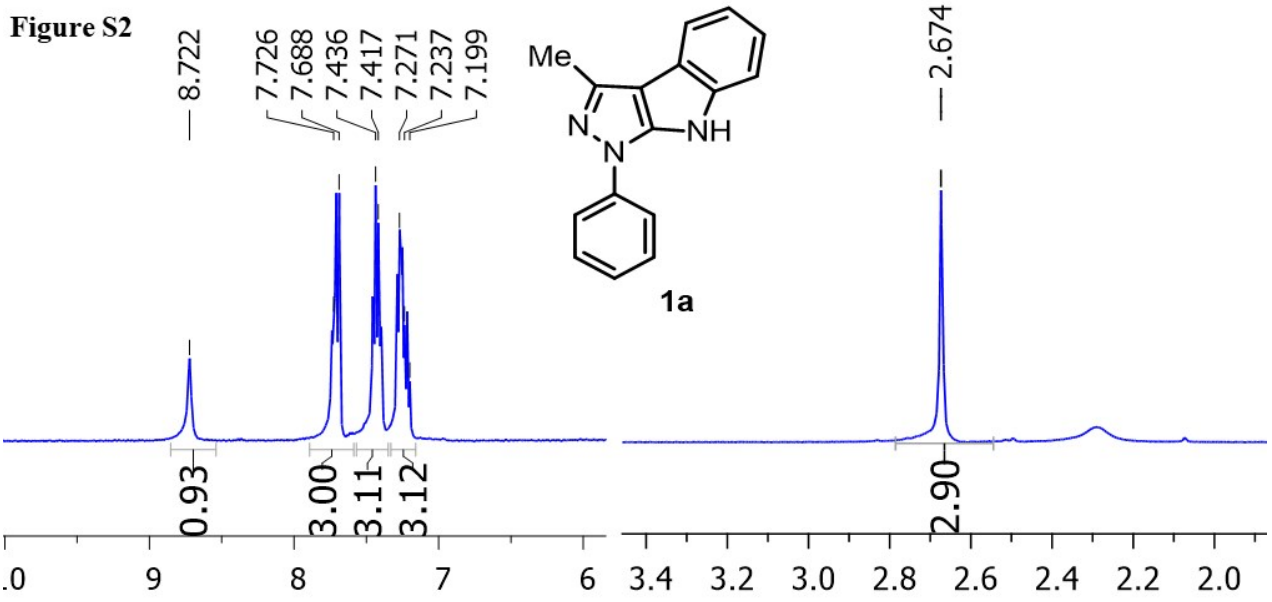


Figure S2. [1]H NMR spectra of **1a**

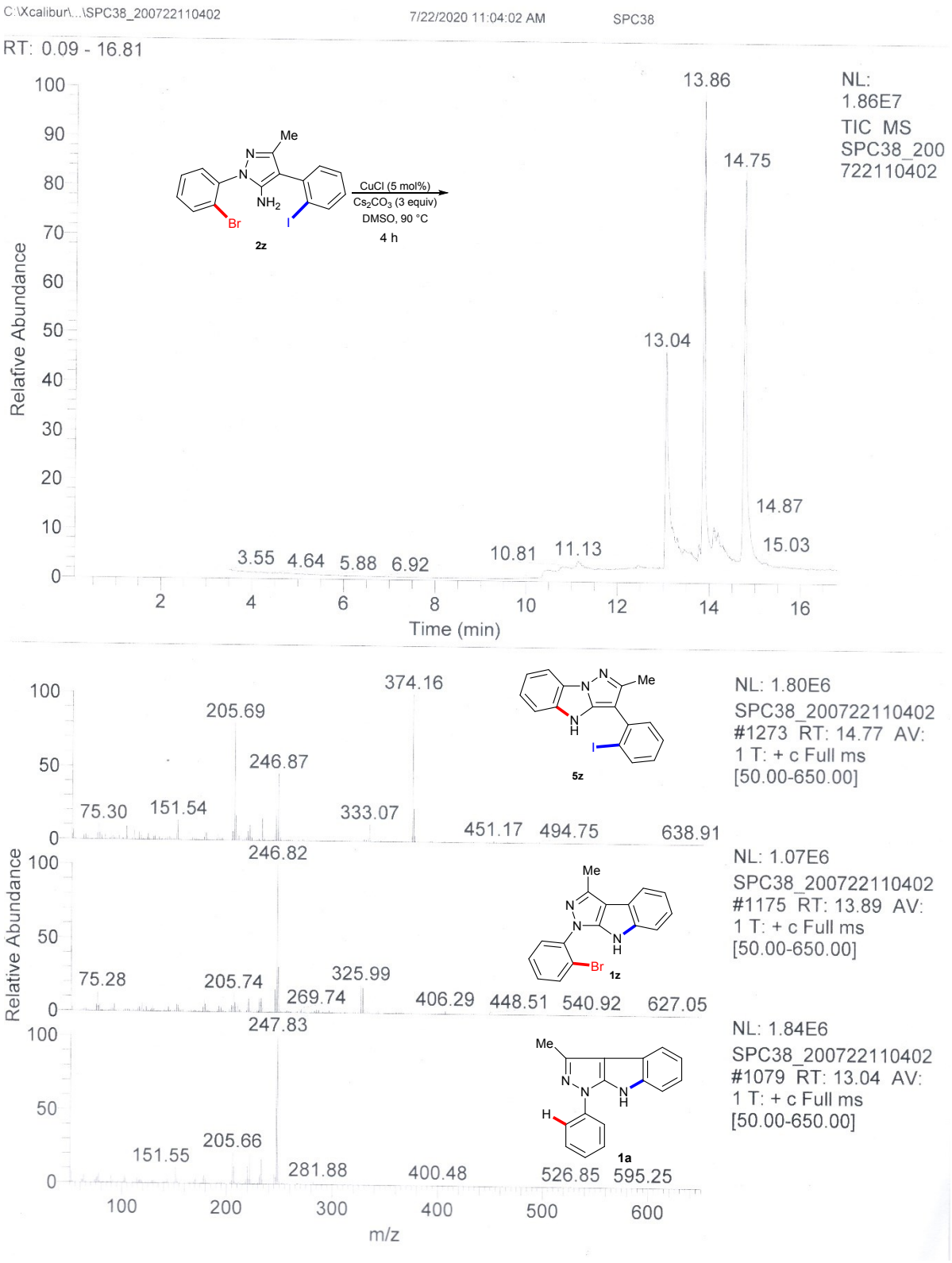


Figure S3. GCMS Analysis of crude reaction mixture of **2z**

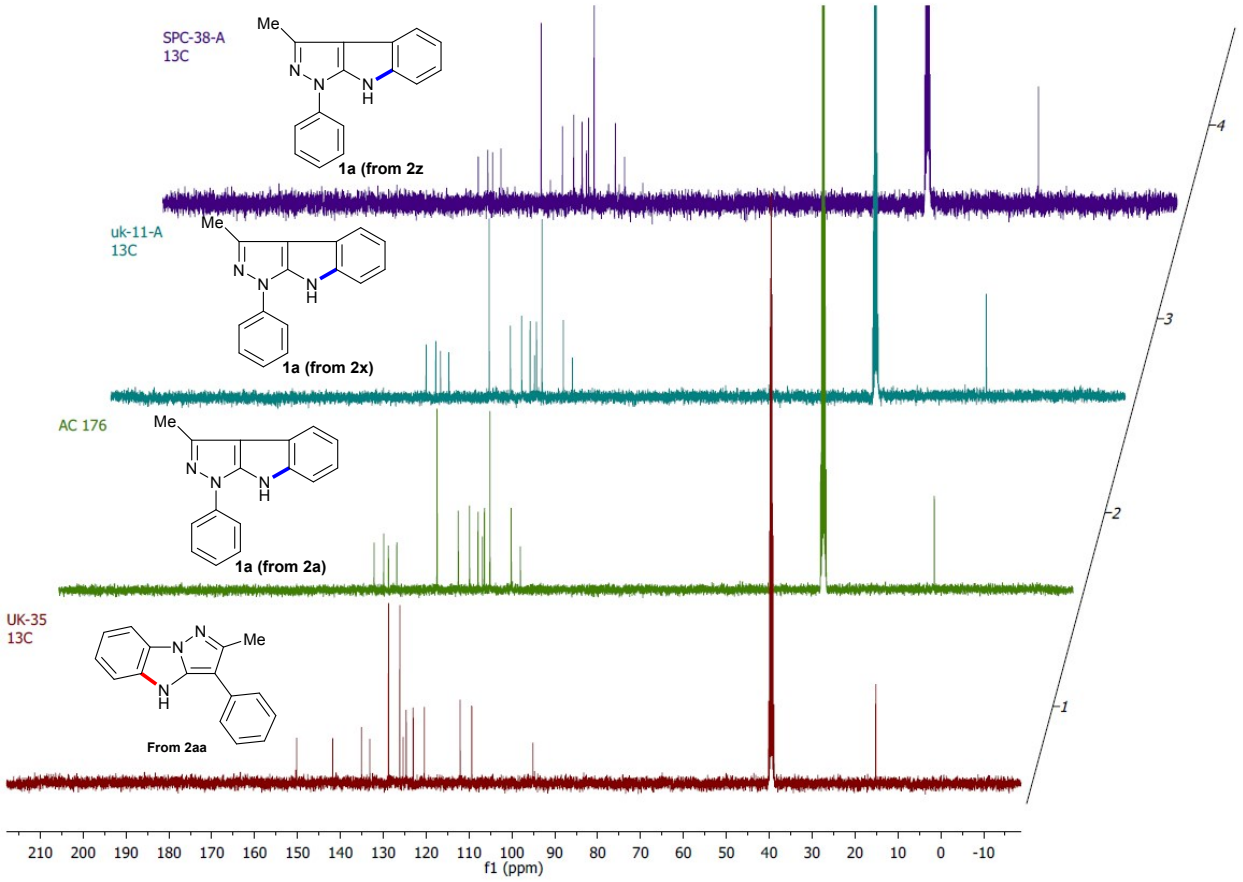


Figure S4. Assignment of Dehalogenated products from controlled experiments

General Information

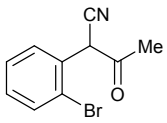
All reactions were performed by using a standard vial technique with a rubber septum. All solids were weighed in air. Dioxane, DMF, DMSO, Cs_2CO_3, K_2CO_3, and KO^{t}Bu, PTSA were purchased from Aldrich, Acros, Merck, Spectrochem, or Alfa-Aesar and used as received. CuI, CuBr, CuCl, and $Cu(OAc)_2{\cdot}H_2O$ were purchased from Aldrich. Aryl hydrazines and 1,10-Phenanthroline were purchased from Spectrochem and Aldrich respectively. All other reagents were purchased from standard suppliers and used without further purification. Flash chromatography was performed using Merck Silica gel(230-400 mesh). Fractions were monitored by thin-layer chromatography on precoated silica gel $60F_{254}$ plates (Merck & co.) and were

visualized by UV. NMR data were recorded on Bruker ARX 400 & 700 and Jeol 400 spectrometers. ^{1}H, ^{13}C NMR, and ^{19}F spectra were recorded in $CDCl_3$ and DMSO-d_6 referenced according to signals of deuterated solvents. ESI HR-MS measurements were performed on Bruker micro TOF-Q-II mass-spectro.

General Procedure for the Synthesis *β*-Ketonitriles 3a-j:[1]

To a stirred solution of 2-bromobenzyl cyanide (1 eqiuv, 5 mmol) in EtOAc (20 mL) sodium metal (1.5 equiv) was added by portion at room temperature. When sodium metal was completely dissolved in the reaction mixture, then the reaction mixture was refluxed. The reaction was monitored by TLC. Then it was quenched with ice cooled water and followed by neutralization with 3N HCl. The reaction mixture was extracted with ethyl acetate. The combined organic layer was washed brine solution, dried over Na_2SO_4, and concentrated under reduced pressure. The crude was purified through column chromatography using ethyl acetate and hexane as eluent.

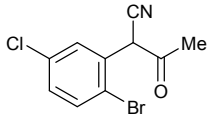
2-(2-Bomophenyl)-3-oxobutanenitrile (3a):[2] Reaction time: 3 h; Yield: 88% (1.04 g); Keto:enol



tautomer(4:1); Orange color gel; R_f = 0.15 in 20% EtOAc in hexane; IR (KBr, ν cm^{-1}): 3437, 2206, 1731, 1644, 1615, 1470, 1433, 1386, 1050, 1027, 755; ^{1}H NMR (400 MHz, $CDCl_3$, Keto isomer) δ 7.65 (d, J = 8.0 Hz, 1H), 7.50 (d, J = 7.6 Hz, 1H), 7.42 (t, J = 7.6, 1H), 7.29 (t, J = 8.4,1H), 5.27 (s, 1H) , 2.32(s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, Keto isomer) δ 195.5, 133.5, 130.8, 130.14, 130.10, 128.5, 123.7, 115.4, 50.6, 27.8.; HRMS (ESI – TOF), m/z $[M + H]^+$ Cal for $C_{10}H_8BrNO$: 237.9862 & 239.9842; Found: 237.9853 & 239.9866.

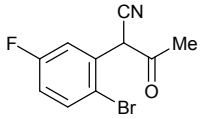
2-(2-Bromo-5-chlorophenyl)-3-oxobutanenitrile (3b): Reaction time: 3 h; Yield: 82% (1.11 g); Keto:enol tautomer(4:1); White color solid; R_f = 0.13 in 20% EtOAc in hexane; m.p = 125 °C; IR

(KBr, ν cm^{-1}): 3431, 2205, 1645, 1457, 1339, 1270, 1096, 1019, 815; ^{1}H NMR (400 MHz, $CDCl_3$,



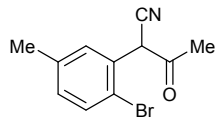
Keto isomer) δ 7.58 (d, *J* = 8.8 Hz, 1H), 7.48 (s, 1H), 7.27 (d, *J* = 8.8 Hz, 1H) , 5.17 (s, 1H), 2.35 (s, 3H).; ^{13}C NMR (175 MHz, $CDCl_3$, Keto isomer) δ 194.4, 134.9, 134.6, 131.9, 131.2, 130.3, 121.8, 115.1, 50.4, 28.4.; HRMS (ESI – TOF), m/z $[M + H]^+$ Cal for $C_{10}H_7BrClNO$: 271.9472 & 273.945; Found: 271.9480 & 273.9457.

2-(2-Bromo-5-fluorophenyl)-3-oxobutanenitrile (3c): Reaction time: 3 h; Yield: 80% (1.02 g);



Keto:enol tautomer(4:1); White color solid; R_f = 0.13 in 20% EtOAc in hexane; m.p = 138 °C; IR (KBr, ν cm^{-1}): 3421, 2207, 1699, 1652, 1471, 1386, 1187; ^{1}H NMR (400 MHz, $CDCl_3$, Keto isomer) δ 7.63 (dd, *J* = 8.8, 5.2 Hz, 1H), 7.27 (dd, *J* = 8.8, 2.8 Hz, 1H), 7.06 (td, *J* = 8, 2.8 Hz, 1H), 5.21 (s, 1H), 2.38 (s, 3H).; ^{13}C NMR (175 MHz, $CDCl_3$, Keto isomer) δ 194.5, 162.9 (d, *J* =248.5), 135.0(d, *J* = 8.7), 132.1 (d, *J* = 7), 118.5 (d, *J* = 21), 118.2 (d, *J* = 3.5), 117.7 (d, *J* =24.5), 115.1, 50.6, 28.3.; ^{19}F NMR (376 MHz, $CDCl_3$) δ -112.34, -113.54; HRMS (ESI – TOF), m/z $[M + H]^+$ Cal for $C_{10}H_7BrFNO$: 255.9768 & 257.9748; Found: 255.9754 & 257.9753.

2-(2-Bromo-5-methylphenyl)-3-oxobutanenitrile (3d): Reaction time: 3 h; Yield: 81% (1.02 g);



Keto:enol tautomer(4.7:1); White color solid; R_f = 0.16 in 20% EtOAc in hexane; m.p = 121°C; IR (KBr, ν cm^{-1}): 3437, 2204, 1732, 1646, 1506,1475, 1358, 1165,1025,813; ^{1}H NMR (400 MHz, $CDCl_3$, Keto isomer) δ 7.51 (d, *J* = 8 Hz, 1H), 7.09 (s, 1H), 7.1 (d, *J* = 8 Hz, 1H), 5.22 (s, 1H), 2.34 (s, 3H), 2.30 (s, 3H); ^{13}C NMR (175 MHz, $CDCl_3$, Keto isomer) δ 195.5, 139.2, 133.4, 132.0, 130.7, 129.9, 120.6, 115.8, 50.7, 28.1, 21.0; HRMS (ESI – TOF), m/z $[M + H]^+$ Cal for $C_{11}H_{10}BrNO$: 252.0019 & 253.9998; Found: 252.0042 & 254.0055.

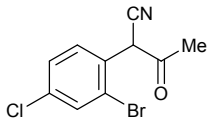
2-(2-Bromo-5-methoxyphenyl)-3-oxobutanenitrile (3e): Reaction time: 3 h; Yield: 82% (1.09 g); Keto:enol tautomer(6:1); White color solid; R_f = 0.16 in 20% EtOAc in hexane; m.p = 97 °C; IR (KBr, ν cm^{-1}): 3437, 2837, 2205, 1731, 1643, 1594, 1570, 1475, 1414, 1289, 1242, 1055, 1019, 812 ; ^{1}H NMR (400 MHz, $CDCl_3$, Keto isomer) δ 7.51 (d, *J* = 9.2 Hz, 1H), 7.00 (d, *J* = 2.8 Hz, 1H), 6.83 (dd, *J* = 2.8, 8.8, 1H), 5.21 (s, 1H), 3.81 (s, 3H), 2.30 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, Keto isomer) δ 195.2, 159.8, 134.3, 131.0, 117.1, 115.6, 115.4, 114.1, 55.8, 50.9, 28.1; HRMS (ESI – TOF), m /z $[M + H]^+$ Cal for $C_{11}H_{10}BrNO_2$: 267.9968 & 269.9948; Found: 267.9954 & 269.9935.

2-(2-Bromo-4, 5-dimethoxyphenyl)-3-oxobutanenitrile (3f): Reaction time: 3 h; Yield: 80% (1.19 g); Keto:enol tautomer(1.5:1); White color solid; R_f = 0.17 in 20% EtOAc in hexane; m.p = 115 °C; IR (KBr, ν cm^{-1}): 3437, 2202, 1730, 1643, 1503, 1440, 1380, 1261, 1210, 1169, 1024, 860; ^{1}H NMR (400 MHz, $CDCl_3$, Keto isomer) δ 7.05 (s, 1H), 6.86 (s, 1H), 5.19 (s, 1H), 3.87 (s, 3H), 3.86 (s, 3H), 2.26 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, Keto isomer) δ 195.9, 150.4, 149.4, 121.7, 115.8, 115.7, 114.3, 111.5, 56.4, 56.3, 50.5, 27.9; HRMS (ESI – TOF), m/z $[M + H]^+$ Cal for $C_{12}H_{12}BrNO_3$: 298.0073 & 300.0053; Found: 298.0061 & 300.0041.

2-(2-Bromo-3, 4, 5-trimethoxyphenyl)-3-oxobutanenitrile (3g): Reaction time: 3 h; Yield: 80% (1.31 g); Keto:enol tautomer(10:1); White color solid; R_f = 0.17 in 20% EtOAc in hexane; m.p = 118 °C; IR (KBr, ν cm^{-1}): 3437, 2940, 2206, 1730, 1642, 1484, 1428, 1392, 1338, 1246, 1106, 1005, 926; ^{1}H NMR (400 MHz, $CDCl_3$, Keto isomer) δ 6.79 (s, 1H), 5.29 (s, 1H), 3.91 (s, 3H), 3.90 (s, 3H), 3.87 (s, 3H), 2.31 (s, 3H); ^{13}C NMR (175 MHz, $CDCl_3$, Keto isomer) δ 195.5, 153.8, 151.7, 144.0, 125.3, 115.8, 111.1,

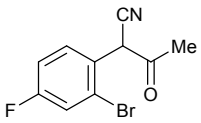
108.3, 61.3, 61.3, 56.5, 50.8, 28.1.; HRMS (ESI – TOF), m /z $[M + H]^+$ Cal for $C_{13}H_{14}BrNO_4$: 349.9998 & 351.9979; Found: 349.9970 & 351.9949.

2-(2-Bromo-4-chlorophenyl)-3-oxobutanenitrile (3h): Reaction time: 3 h; Yield: 78% (1.06 g);



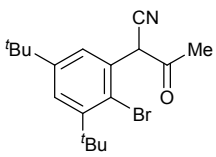
Keto:enol tautomer(3:1); White color solid; R_f = 0.13 in 20% EtOAc in hexane; m.p = 137 °C; IR (KBr, ν cm^{-1}): 3406, 2227, 1603, 1517, 1392, 1370, 1059, 1022, 845, 757; ^1H NMR (400 MHz, $CDCl_3$, Keto isomer) δ 7.67 (s, 1H), 7.45-7.40 (m, 2H), 5.19 (s, 1H), 2.36 (s, 3H).; ^{13}C NMR (175 MHz, $CDCl_3$, Keto isomer) δ 194.6, 136.4, 133.3, 131.0, 129.1, 128.9, 124.4, 115.3, 50.1, 28.3.; HRMS (ESI – TOF), m/z $[M + H]^+$ Cal for $C_{10}H_7BrClNO$: 271.9472 & 273.9451; Found: 271.9491 & 273.9495.

2-(2-Bromo-4-fluorophenyl)-3-oxobutanenitrile (3i): Reaction time: 3 h; Yield: 75% (0.960 g);



Keto:enol tautomer(10:1); White color solid; R_f = 0.13 in 20% EtOAc in hexane; m.p = 136 °C; IR (KBr, ν cm^{-1}): 3421, 2220, 1634, 1573, 1465, 1332, 1280, 1259, 1195, 959, 876; 1H NMR (400 MHz, $CDCl_3$, Keto isomer) δ 7.49 (dd, J = 8.4, 5.6 Hz, 1H), 7.40 (dd, J = 7.9, 2.4 Hz, 1H), 7.15 (td, J = 8, 2.4 Hz, 1H), 5.18 (s, 1H), 2.36 (s, 3H); ^{13}C NMR (175 MHz, $CDCl_3$, Keto isomer) δ 194.9, 163.4 (d, J = 252), 131.4 (d, J = 8.75), 126.5 (d, J = 3.5), 124.4 (d, J = 10.5), 121.2 (d, J = 24.5), 116.2 (d, J = 21), 115.5, 49.9, 28.2; HRMS (ESI – TOF), m/z $[M + H]^+$ Cal for $C_{10}H_7BrFNO$: 255.9768 & 257.9748; Found: 255.9747 & 257.9753.

2-(2-Bromo-3,5-di-tert-butylphenyl)-3-oxobutanenitrile (3j): Reaction time : 3 h; Yield: 80%



(1.4 g); Keto:enol tautomer(10:1); white color solid; R_f = 0.26 in 20% EtOAc in hexane; m.p = 128 °C; IR (KBr, ν cm^{-1}): 3441, 2966, 1733, 1652, 1634, 1539, 1363, 1265, 1017, 739; ^1H NMR (700 MHz, $CDCl_3$, keto isomer) δ 7.55 (d, J = 2.1 Hz, 1H), 7.33 (d, J = 2.8 Hz, 1H), 5.46 (s, 1H), 2.30 (s, 3H), 1.54 (s, 9H), 1.31 (s, 9H);

^{13}C NMR (175 MHz, $CDCl_3$, Keto isomer) δ 196.19, 151.26, 149.29, 131.96, 126.79, 125.51, 121.53, 116.31, 52.44, 37.84, 35.10, 31.27, 30.16, 28.17.; HRMS (ESI – TOF), m/z $[M + H]^+$ Cal for $C_{18}H_{24}BrNO$: 350.1095 & 352.1075; Found: 350.1114 & 352.1094.

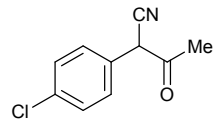
2-(2-Iodophenyl)-3-oxobutanenitrile (3k): Reaction time: 3 h ; Yield: 52% (0.741 g); Keto:enol tautomer(2:1); Orange viscous liquid ; R_f = 0.13 in 20% EtOAc in hexane; IR (KBr, ν cm^{-1}): 2920, 2205, 1730, 1646, 1465, 1277, 1014, 918, 757; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, J = 8.0 Hz, 1H), 7.39-7.46 (m, 2H), 7.10-7.13 (m,1H) 5.23 (s, 1H), 2.30 (s, 3H).; ^{13}C NMR (100 MHz, $CDCl_3$, Keto isomer) δ 195.6, 140.5, 133.6, 132.0, 131.0, 129.6, 129.4, 115.7, 55.1, 28.4.; HRMS (ESI – TOF), m/z $[M + H]^+$ Cal for $C_{10}H_8INO$: 285.9723; Found: 285.9704.

2-Phenyl-3-oxobutanenitrile (3l); Reaction time: 3h ; Yield: 65% (0.517 g); Keto:enol tautomer(4.2:1); Pale yellow colour solid ; R_f = 0.1 in 20% EtOAc in hexane; m.p = 112 °C; IR (KBr, ν cm^{-1}): 3536, 2372, 2217, 1869, 1635, 754, 688; ^{1}H NMR (700 MHz, $CDCl_3$) δ 7.49 (d, J = 7 Hz, 2H), 7.42 (t, J = 7.7, 2H), 7.32 (t, J = 7.7 Hz, 1H), 7.07 (s, 1H), 2.36 (s, 3H).; ^{13}C NMR (175 MHz, $CDCl_3$, Keto isomer) δ 196.6, 129.8, 129.5, 128.4, 128.3, 119.8, 51.6, 27.0; HRMS (ESI – TOF), m/z $[M + Na]^+$ Cal for $C_{10}H_9NO$: 182.0576; Found: 182.0580.

2-(3-Methylphenyl)-3-oxobutanenitrile (3m): Reaction time: 5 h ; Yield: 53% (0.461 g); Keto:enol tautomer(10:1); Pale yellow colour solid; R_f = 0.17 in 20% EtOAc in hexane; m.p = 110 °C; IR (KBr, ν cm^{-1}): 3567, 2364, 2205, 1729, 1635, 1343, 1278, 1199, 785; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 (t, J = 7.2 Hz, 1H), 7.18 (t, J = 8.4 Hz, 3H), 4.63 (s, 1H), 2.25 (s, 3H).; ^{13}C NMR (100 MHz, $CDCl_3$, Keto isomer) δ 196.7,

130.2, 129.6, 129.6, 128.6, 116.4, 51.6, 27.0; HRMS (ESI – TOF), m/z [M + Na]$^+$ Cal for $C_{11}H_{11}NO$: 196.0733; Found: 196.0735.

2-(4-Chlorophenyl)-3-oxobutanenitrile (3n): Reaction time: 4 h ; Yield: 65% (0.627 g);

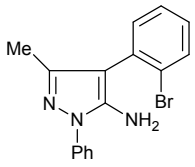


Keto:enol tautomer(4:1); Yellow colour solid; R_f = 0.07 in 20% EtOAc in hexane; m.p = 118 °C; IR (KBr, ν cm^{-1}): 3567, 3109, 2368, 2221, 1700, 1653, 1491, 1353, 1271, 1008, 827, 780; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (d, J = 8.4 Hz , 2H), 7.33 (d, J = 8.4 Hz, 2H), 4.64 (s, 1H), 2.29 (s, 3H).; ^{13}C NMR (100 MHz, $CDCl_3$, Keto isomer) δ 195.9, 135.7, 129.9, 129.6, 129.3, 115.9, 50.7, 27.1; HRMS (ESI – TOF), m/z [M + Na]$^+$ Cal for $C_{11}H_{11}NO$: 216.0187; Found: 216.0192.

General Procedure for the Synthesis of 5-Amino-4-arylpyrazoles 2a-x & 2aa-ac:

A round bottom flask was charged with *β*-ketonitrile (1 equiv, 1 mmol), aryl hydrazine (1.1 equiv, 1.1 mmol) and PTSA (cat.) in water, which was heated at 105 °C for 3-6 h. The reaction was monitored by TLC. After disappearance of the starting material, the reaction mixture was then cooled to room temperature and was extracted with ethyl acetate trice. The combined organic layer was washed with brine solution (25 mL), dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The crude products were purified through flash column chromatography using 20% ethyl acetate in hexane as eluent.

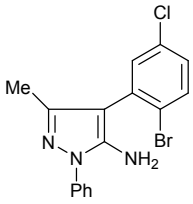
5-Amino-4-(2-bromophenyl)-3-methyl-1-phenyl-*1H*-pyrazole (2a): Reaction time: 3 h; Yield:



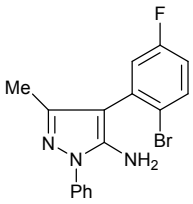
98% (0.328 g); White color solid; R_f = 0.2 in 20% EtOAc in hexane; m.p = 100 °C; IR (KBr, ν cm^{-1}): 3339,1652, 1569, 1512, 1498, 1322, 1023, 1006, 755; ^{1}H NMR (400 MHz, DMSO) δ 7.72 (d, J = 8 Hz, 1H), 7.64 (d, J = 7.6 Hz, 2H), 7.49-7.40 (m, 3H), 7.35 – 7.25 (m, 3H), 4.93 (s, 2H), 1.98 (s, 3H); ^{13}C NMR (100 MHz, DMSO) δ

146.3, 143.7, 139.2, 133.9, 133.2, 132.7, 129.0, 128.9, 127.7, 125.9, 125.3, 122.6, 104.2, 12.9; HRMS (ESI – TOF), m/z $[M + H]^+$ Cal for $C_{16}H_{14}BrN_3$: 328.0444 & 330.0424; Found: 328.0438 & 330.0417.

5-Amino-4-(2-bromo-5-chlorophenyl)-3-methyl-1-phenyl-*1H*-pyrazole (2b): Reaction time: 3 h; Yield: 87 % (0.362 g); White color solid; R_f = 0.33 in 20% EtOAc in hexane; m.p = 138 °C; IR (KBr, ν cm^{-1}): 3437, 1621, 1596, 1515, 1453, 1397, 1318, 1264, 1093, 1012, 810; 1H NMR (400 MHz, $CDCl_3$) δ 7.62 – 7.60 (m, 3H), 7.48 (t, *J* = 7.6 Hz, 2H), 7.36-7.33 (m, 2H), 7.18 (dd, *J* = 8.8, 2.4 Hz, 1H), 3.75 (s, 2H), 2.16 (s, 3H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 147.6, 142.3, 138.6, 135.7, 134.3, 133.5, 132.7, 129.6, 129.1, 127.4, 124.0, 123.4, 104.3, 13.0; HRMS (ESI – TOF), m/z $[M + H]^+$ Cal for $C_{16}H_{13}BrClN_3$: 362.0054 & 364.0033; Found: 362.0046 & 364.0025.

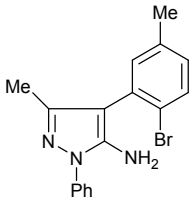


5-Amino-4-(2-bromo-5-fluorophenyl)-3-methyl-1-phenyl-*1H*-pyrazole (2c): Reaction time: 3 h; Yield: 72% (0.249 g); White color solid; R_f = 0.31 in 20% EtOAc in hexane; m.p = 98 °C; IR (KBr, ν cm^{-1}): 3437, 2064, 1634, 1515, 1455, 1404, 1256, 1185, 1018 ; ^1H NMR (400 MHz, $CDCl_3$) δ 7.66 – 7.60 (m, 3H), 7.49 (t, *J* = 7.6 Hz, 2H), 7.35 (t, *J* = 7.2 Hz, 1H), 7.07 (dd, *J* = 9.2, 3.2 Hz, 1H), 6.95 (td, *J* = 8.0, 3.2 Hz, 1H), 3.76 (s, 2H), 2.17 (s, 3H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 161.9 (d, *J* = 246.7 Hz), 147.6, 146.9, 142.3, 138.6, 135.9 (d, *J* = 8.7 Hz), 134.4 (d, *J* = 8.7 Hz) , 129.6, 127.4, 124.0, 119.8 (d, *J* = 28 Hz), 119.6 (d, *J* = 3.5 Hz), 116.3 (d, *J* = 28 Hz), 104.5, 13.0; ^{19}F (376 MHz,$CDCl_3$): δ -115.6; HRMS (ESI – TOF), m/z $[M + H]^+$ Cal for $C_{16}H_{13}BrFN_3$: 346.0350 & 348.0330; Found: 346.0361 & 348.0343.

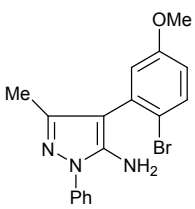


5-Amino-4-(2-bromo-5-methylphenyl)-3-methyl-1-phenyl-*1H*-pyrazole (2d): Reaction time: 3 h ; Yield: 95 % (0.325 g); White color solid; R_f = 0.26 in 20% EtOAc in hexane; m.p = 135 °C; IR

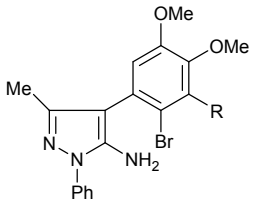
(KBr, ν cm^{-1}): 3437, 1634, 1558, 1455, 1398, 1017, 667; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (d, *J* = 7.6 Hz, 2H), 7.55 (d, *J* = 7.6 Hz, 1H), 7.48 (t, *J* = 7.2 Hz, 2H), 7.33 (t, *J* = 6.8 Hz, 1H), 7.15 (s, 1H), 7.02 (d, *J* = 8 Hz, 1H), 3.72 (s, 2H), 2.34 (s, 3H), 2.17 (s, 3H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 147.8, 142.2, 138.9, 137.6, 133.7, 133.6, 132.9, 130.0, 129.5, 127.2, 123.8, 122.1, 105.5, 21.0, 13.0; HRMS (ESI – TOF), m/z $[M + H]^+$ Cal for $C_{17}H_{16}BrN_3$: 342.0600 & 344.0580; Found: 342.0619 & 344.0600.



5-Amino-4-(2-bromo-5-methoxyphenyl)-3-methyl-1-phenyl-*1H*-pyrazole (2e): Reaction time: 3 h ; Yield: 95% (0.340 g); White color solid; R_f = 0.26 in 20% EtOAc in hexane; m.p = 148 °C; IR (KBr, ν cm^{-1}): 3422, 1618, 1570, 1513, 1434, 1323, 1282, 1221, 1178, 1028, 1010, 817, 762; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (d, *J* = 7.6, 2H), 7.55 (d, *J* = 8.8 Hz, 1H), 7.47 (t, *J* = 7.6 Hz, 2H), 7.33 (t, *J* = 7.6 Hz, 1H),6.87 (d, *J* = 2.8 Hz, 1H),6.77 (dd, *J* = 8.8, 2.8 Hz, 1H), 3.80 (s, 3H), 3.84 (brs, 2H) 2.17 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.0, 147.6, 142.3, 138.6, 134.6, 133.7, 129.5, 127.2, 123.8, 118.0, 115.8, 115.1, 105.3, 55.6, 12.9; HRMS (ESI – TOF), m/z $[M + H]^+$ Cal for $C_{17}H_{16}BrN_3O$: 358.0550 & 360.0530; Found: 358.0512 & 360.0494.

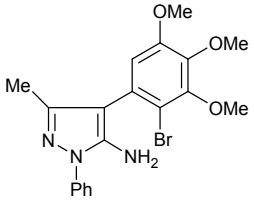


5-Amino-4-(2-bromo-4,5-dimethoxyphenyl)-3-methyl-1-phenyl-*1H*-pyrazole (2f): Reaction time: 3 h; Yield: 98 % (0.380 g); White color solid; R_f = 0.16 in 20% EtOAc in hexane; m.p = 162-164 °C; IR (KBr, ν cm^{-1}): 3430, 2304, 1618, 1507, 1463, 1264, 1208, 1174, 1064, 896, 785; ^{1}H NMR (700 MHz, $CDCl_3$) δ 7.62 (d, *J* = 7.7 Hz, 2H), 7.47 (t, *J* = 7.7 Hz, 2H), 7.33 (t, *J* = 7.7 Hz, 1H), 7.14 (s, 1H), 6.82 (s, 1H), 3.90 (s, 3H), 3.87 (s, 3H), 3.73 (s, 2H), 2.17 (s, 3H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 149.1, 148.5, 147.9, 142.3, 138.9, 129.6, 127.1, 125.7, 123.8, 115.7, 115.6, 115.1, 105.3, 56.3, 56.2, 13.0;



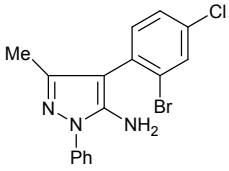
HRMS (ESI – TOF), m /z $[M + H]^+$ Cal for $C_{18}H_{18}BrN_3O_2$: 388.0655 & 390.0635; Found: 388.0677 & 390.0656.

5-Amino-4-(2-bromo-3,4,5-trimethoxyphenyl)-3-methyl-1-phenyl-*1H*-pyrazole (2g): Reaction



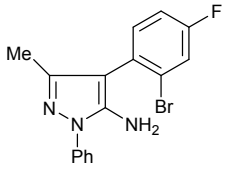
time: 3 h; Yield: 95% (0.389 g); pale brown color solid; R_f = 0.16 in 20% EtOAc in hexane; m.p = 128 °C; IR (KBr, ν cm^{-1}): 3422, 1638, 1513, 1452, 1379, 1342, 1243, 1105, 1008, 758; ^{1}H NMR (400 MHz, DMSO) δ 7.62 (d, J = 8 Hz, 2H), 7.47 (t, J = 7.6 Hz, 2H), 7.29 (t, J = 7.6 Hz, 1H), 6.78 (s, 1H), 4.94 (s, 2H), 3.82 (s, 3H), 3.81 (brs, 6H), 1.99 (s, 3H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 152.8, 151.5, 147.7, 142.6, 142.2, 138.8, 129.6, 129.4, 127.2, 123.8, 111.8, 111.3, 105.4, 61.2, 61.1, 56.3, 13.1; HRMS (ESI – TOF), m/z $[M + H]^+$ Cal for $C_{19}H_{20}BrN_3O_3$: 418.0761 & 420.0741; Found: 418.0769 & 420.0750.

5-Amino-4-(2-bromo-4-chlorophenyl)-3-methyl-1-phenyl-*1H*-pyrazole (2h): Reaction time: 6



h; Yield: 95% (0.392 g); White color solid; R_f = 0.3 in 20% EtOAc in hexane; m.p = 139 °C; IR (KBr, ν cm^{-1}): 3053, 2986, 1617, 1597, 1546, 1513, 1421, 1265, 1055, 1005, 895, 739 ; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, J = 2.4 Hz, 1H), 7.61 (d, J = 7.6 Hz, 2H), 7.48 (t, J = 7.6 Hz, 2H), 7.37-7.32 (m, 2H), 7.28 – 7.26 (m, 1H), 3.72 (s, 2H), 2.14 (s, 3H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 147.6, 142.3, 138.6, 134.0, 133.6, 132.9, 132.5, 129.6, 128.1, 127.4, 125.8, 123.9, 104.2, 12.9; HRMS (ESI – TOF), m/z $[M + H]^+$ Cal for $C_{16}H_{13}BrClN_3$: 362.0054, 364.0033; Found: 362.0025, 364.0022.

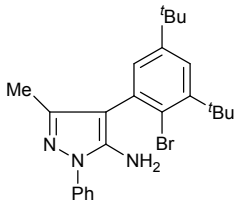
5-Amino-4-(2-bromo-4-fluorophenyl)-3-methyl-1-phenyl-*1H*-pyrazole (2i): Reaction time: 3



h; Yield: 67% (0.236 g); White color solid; R_f = 0.33 in 20% EtOAc in hexane; m.p = 106 °C; IR (KBr, ν cm^{-1}): 3424, 1616, 1652, 1575, 1539, 15151, 1453, 1256, 1199, 1071, 870, 762; ^{1}H NMR (700 MHz, $CDCl_3$) δ 7.61 (d, J = 7.7 Hz, 2H), 7.48 (t, J = 7.7 Hz, 2H), 7.44 (dd, J = 8.4, 2.8 Hz, 1H), 7.35 – 7.30 (m, 2H),

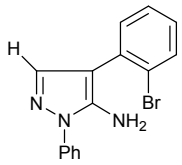
7.10 (td, J = 8.4, 2.8 Hz, 1H), 3.70 (s, 2H), 2.14 (s, 3H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 162.62 (d, J = 250.2), 147.89, 142.43, 138.77, 133.94 (d, J = 8.7), 130.08 (d, J = 3.5), 129.65, 127.36, 125.86 (d, J = 8.7), 123.92, 120.51 (d, J = 22.7) , 115.1 (d, J = 21), 104.3, 12.9; ^{19}F NMR (376 MHz, DMSO) δ -114.7. HRMS (ESI – TOF), m/z $[M + H]^+$ Cal for $C_{16}H_{13}BrFN_3$: 346.0350 & 348.0330; Found: 346.0349 & 348.0331.

5-Amino-4-(2-bromo-3,5-di-tert-butylphenyl)-3-methyl-1-phenyl-*1H*-pyrazole (2j): Reaction



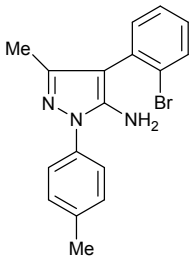
time: 3 h; Yield: 78 % (0.343 g); White color solid; R_f = 0.3 in 20% EtOAc in hexane; m.p = 209 °C; IR (KBr, ν cm^{-1}): 3437, 2064, 1622, 1515, 1455, 1393, 1362, 1264, 1013, 737; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (d, J = 7.6 Hz, 2H), 7.49-7.46 (m, 3H), 7.32 (t, J = 7.2 Hz, 1H), 7.20 (d, J = 2 Hz, 1H), 3.69 (s, 2H), 2.14 (s, 3H), 1.59 (s, 9H), 1.33 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.8, 148.2, 148.0, 142.1, 139.0, 135.6, 129.5, 128.0, 127.0, 124.8, 123.7, 123.0, 108.2, 37.6, 34.9, 31.4, 30.3, 13.0, 1.1; HRMS (ESI – TOF), m/z $[M + H]^+$ Cal for $C_{24}H_{30}BrN_3$: 440.1696 & 442.1677; Found: 440.1658 & 442.1633.

5-Amino-4-(2-bromophenyl)-1-phenyl-*1H*-pyrazole (2k): Reaction time: 6 h; Yield: 90 %



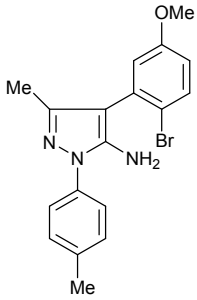
(0.314 g); Pale yellow color solid; R_f = 0.3 in 20% EtOAc in hexane; m.p = 125 °C; IR (KBr, ν cm^{-1}): 3429, 1686, 1656, 1619, 1555, 1497, 1410, 1376, 1023, 1013, 939, 762. ; ^{1}H NMR (700 MHz, $CDCl_3$) δ 7.68 (d, J = 7.7 Hz, 1H), 7.65-7.63 (m, 3H), 7.51 (t, J = 7.7 Hz, 2H),7.44 – 7.33 (m, 3H), 7.17 (t, J = 7.3 Hz, 1H), 3.93 (s, 2H).; ^{13}C NMR (175 MHz, $CDCl_3$) δ 141.9, 140.5, 138.6, 133.7, 133.5, 131.7, 129.7, 128.5, 127.8, 127.7, 124.1, 123.9, 105.6.; HRMS (ESI – TOF), m /z $[M + H]^+$ Cal for $C_{15}H_{12}BrN_3$: 314.0287 & 316.0267; Found: 314.0288 & 316.0270.

5-Amino-4-(2-bromophenyl)-3-methyl-1-(4-tolyl)-*1H*-pyrazole (2l): Reaction time: 3 h; Yield:



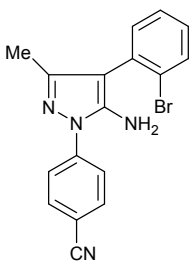
93% (0.318 g); Pale pink color solid; R_f = 0.28 in 20% EtOAc in hexane; m.p = 119 °C; IR (KBr, ν cm^{-1}): 3438, 1655, 1619, 1571, 1519, 1393, 1059, 1019, 821,755; ^{1}H NMR (400 MHz, DMSO) δ 7.72 (d, *J* = 7.2 Hz, 1H), 7.51 (d, *J* = 8.4 Hz, 2H), 7.42 (t, *J* = 6.8 Hz, 1H), 7.33 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.29 - 7.24(m, 3H), 4.89 (s, 2H), 2.34 (s, 3H), 1.97 (s, 3H); ^{13}C NMR (100 MHz, DMSO) δ 146.0, 143.6, 136.8, 135.2, 134.0, 133.2, 132.7, 129.5, 128.9, 127.8, 125.3, 122.7, 104.0, 20.6, 12.9; HRMS (ESI – TOF), m /z $[M + H]^+$ Cal for $C_{17}H_{16}BrN_3$: 342.0600 & 344.0580; Found: 342.0580 & 344.0557.

5-Amino-4-(2-bromo-5-methoxyphenyl)-3-methyl-1-(4-tolyl)-*1H*-pyrazole (2m): Reaction



time: 3 h; Yield: 95% (0.353 g); White color solid; R_f = 0.3 in 20% EtOAc in hexane; m.p = 140 °C; IR (KBr, ν cm^{-1}): 3438, 1655, 1619, 1571, 1519, 1393, 1059, 1019, 821, 755; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, *J* = 8.8 Hz, 1H), 7.48 (d, *J* = 8 Hz, 2H),7.27 (d, *J* = 8.4 Hz, 2H), 6.87 (d, *J* = 2.8 Hz, 1H), 6.77 (dd, *J* = 8.8, 2.8 Hz, 1H), 3.81 (s, 3H), 3.73 (s, 2H), 2.39 (s, 3H), 2.18 (s, 3H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 159.1,152.0, 147.4, 142.3, 137.3, 136.16, 134.8, 133.8, 130.1, 123.9, 115.8, 115.1, 105.2, 55.6, 21.2, 13.0; HRMS (ESI – TOF), m/z $[M + H]^+$ Cal for $C_{18}H_{18}BrN_3O$: 372.0706 & 374.0686; Found: 372.0722 & 374.0703.

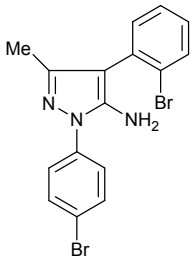
5-Amino-4-(5-amino-4-(2-bromophenyl)-3-methyl-*1H*-pyrazol-1-yl)benzonitrile (2n):



Reaction time: 2 h; Yield: 92% (0.324 g); Pale yellow color solid; R_f = 0.26 in 20% EtOAc in hexane; m.p = 130 °C; IR (KBr, ν cm^{-1}): 3422, 2070, 1627, 1517, 1413, 1391, 1059, 1003, 755; ^{1}H NMR (400 MHz, DMSO) δ 7.92 (brs, 4H), 7.73 (d, *J* = 7.6 Hz, 1H), 7.43 (t, *J* = 7.2 Hz, 1H), 7.34 – 7.29 (m, 2H), 5.25 (s, 2H), 1.98 (s, 3H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 149.5, 142.8, 142.6, 133.5, 133.4, 133.0, 132.9,

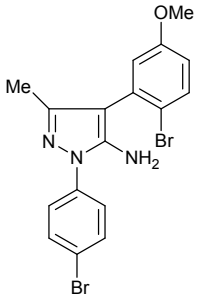
129.5, 127.9, 125.5, 122.6, 118.6, 109.6, 107.4, 13.0; HRMS (ESI – TOF), m/z $[M + H]^+$ Cal for $C_{17}H_{13}BrN_4$: 353.0396 & 355.0376; Found: 353.0415 & 355.0393.

5-Amino-4-(2-bromophenyl)-1-(4-bromophenyl)-3-methyl-*1H*-pyrazole (2o): Reaction time: 5

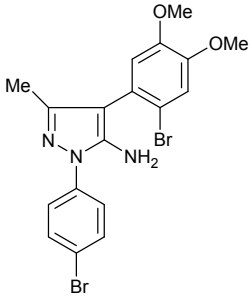


h; Yield: 95% (0.386 g); Yellow color solid; R_f = 0.36 in 20% EtOAc in hexane; m.p = 138 °C; IR (KBr, ν cm^{-1}): 3424, 1655, 1649, 1590, 1510, 1493, 1484, 1391, 1069, 1009, 829, 755; ^1H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, J = 8.0 Hz, 1H), 7.61-7.54 (m, 4H), 7.39-7.30 (m, 2H), 7.22 (t, J = 7.2 Hz, 1H), 3.70 (s, 2H), 2.17 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.2, 142.3, 137.7, 133.4, 133.3, 133.0, 132.6, 129.2, 127.8, 125.5, 125.1, 120.6, 105.9, 12.9; HRMS (ESI – TOF), m/z $[M + H]^+$ Cal for $C_{16}H_{13}Br_2N_3$: 405.9549, 407.9529 & 409.9509; Found: 405.9560, 407.9494 & 409.9523.

5-Amino-4-(2-bromo-5-methoxyphenyl)-1-(4-bromophenyl)-3-methyl-*1H*-pyrazole (2p):



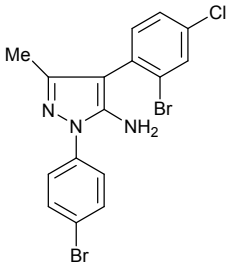
Reaction time: 3 h; Yield: 95% (0.415 g); Pale orange color; R_f = 0.26 in 20% EtOAc in hexane; m.p = 169 °C; IR (KBr, ν cm^{-1}): 3415, 1624, 1510, 1492, 1461, 1217, 1027, 1010, 821; ^1H NMR (400 MHz, $CDCl_3$) δ 7.61 – 7.53 (m, 5H), 6.85 (d, J = 2.9 Hz, 1H), 6.79 (dd, J = 8.8, 2.9 Hz, 1H), 3.81 (s, 3H), 3.72 (s, 2H), 2.16 (s, 3H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 159.1, 148.2, 142.3, 137.9, 134.4, 133.8, 132.6, 125.1, 120.6, 118.1, 115.8, 115.3, 106.0, 55.6, 13.0. HRMS (ESI – TOF), m/z $[M + H]^+$ Cal for $C_{17}H_{15}Br_2N_3O$: 435.9655, 437.9635 & 439.9614; Found: 435.9662, 437.9613 & 439.9624.



5-Amino-4-(2-bromo-4,5-dimethoxyphenyl)-1-(4-bromophenyl)-3-methyl-*1H*-pyrazole (2q): Reaction time: 3 h ; Yield: 98% (0.457 g); white color solid; R_f = 0.25 in 20% EtOAc in hexane; m.p = 128-130 °C; IR (KBr, ν cm^{-1}): 3415, 1624, 1621, 1591, 1510, 1503, 1396, 1234, 1208, 1173, 832;

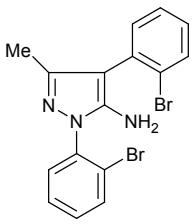
^{1}H NMR (700 MHz, $CDCl_3$) δ 7.60 - 7.54 (m, 4H), 7.14 (s, 1H), 6.80 (s, 1H), 3.91 (s, 3H), 3.86 (s, 3H), 3.69 (s, 2H), 2.15 (s, 3H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 149.2, 148.6, 148.4, 142.3, 138.0, 132.6, 125.4, 125.0, 120.5, 115.8, 115.6, 115.0, 105.9, 56.3, 56.2, 13.0; HRMS (ESI – TOF), m/z $[M + H]^+$ Cal for $C_{18}H_{17}Br_2N_3O_2$: 465.9760, 467.9741 & 469.9720; Found: 465.9769, 467.9722 & 469.9735.

5-Amino-4-(2-bromo-4-chlorophenyl)-1-(4-bromophenyl)-3-methyl-*1H*-pyrazole (2r):



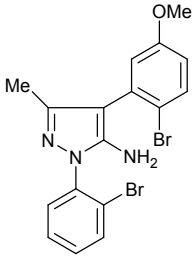
Reaction time: 4 h; Yield: 94% (0.415 g); White color solid; R_f = 0.63 in 20% EtOAc in hexane; m.p = 122 °C; IR (KBr, ν cm^{-1}): 3431, 2054, 1616, 1569, 1506, 1456, 1403, 1264, 1010, 832, 738; ^{1}H NMR (700 MHz, $CDCl_3$) δ 7.73 (s, 1H), 7.61 (d, J = 8.4 Hz, 2H),7.54 (d, J = 7.7 Hz, 2H), 7.37 (d, J = 7.7 Hz, 1H), 7.27 – 7.26 (m, 1H), 3.71 (s, 2H), 2.14 (s, 3H); ^{13}C NMR (176 MHz, $CDCl_3$) δ 148.1, 142.3, 137.7, 134.3, 133.6, 132.9, 132.7, 132.2, 128.1, 125.8, 125.1, 120.7, 104.7, 12.9; HRMS (ESI – TOF), m/z $[M + H]^+$ Cal for $C_{16}H_{12}Br_2ClN_3$: 439.9159, 441.9138 & 443.9118; Found: 439.9156, 441.9132 & 443.9112.

5-Amino-1, 4-bis(2-bromophenyl)-3-methyl-*1H*-pyrazole (2s): Reaction time: 3 h; Yield: 84%



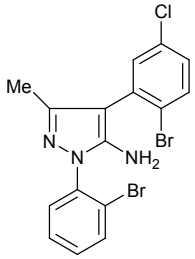
(0.341 g); White color solid; R_f = 0.2 in 20% EtOAc in Hexane; m.p = 120-122 °C; IR (KBr, ν cm^{-1}): 3355, 1617, 1515, 1390, 1318, 1264, 1028, 1005, 737, 448; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94-7.67 (m, 2H), 7.65-7.46 (m, 2H), 7.48-7.05 (m, 4H), 3.61 (s, 2H), 2.23 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.0, 143.5, 137.5, 133.9, 133.6, 133.1, 133.0, 130.8, 130.6, 129.0, 128.6, 127.6, 125.4, 122.4, 104.9, 13.0; HRMS (ESI-TOF), m/z $[M+H]^+$ Cal for $C_{16}H_{13}Br_2N_3$: 405.9549, 407.9529 & 409.9509. Found: 405.9576, 407.9567 & 409.9546.

5-Amino-4-(2-bromo-5-methoxyphenyl)-1-(2-bromophenyl)-3-methyl-*1H*-pyrazole (2t):



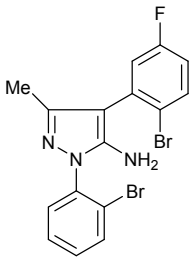
Reaction time: 3 h; Yield: 76% (0.332 g); White color solid; R_f = 0.16 in 20% EtOAc in Hexane; m.p = 106 °C; IR (KBr, ν cm^{-1}): 3307, 2062, 1630, 1536, 1461, 1384, 1283, 1219, 1027, 704; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 -7.28 (m, 5H), 7.19 - 6.52 (m, 2H), 3.82 (s, 3H), 3.57 (s, 2H), 2.19 (s, 3H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 159.1, 148.1, 143.5, 137.7, 134.8, 133.8, 133.7, 130.9, 130.7, 128.7, 122.5, 118.2, 115.9, 115.1, 105.1, 55.7, 13.1; HRMS (ESI-TOF), m/z $[M+H]^+$ Cal for $C_{17}H_{15}Br_2N_3O$: 435.9655, 437.9635 & 439.9614; Found: 435.9711, 437.9695 & 439.9673.

5-Amino-4-(2-bromo-5-chlorophenyl)-1-(2-bromophenyl)-3-methyl-*1H*-pyrazole (2u):



Reaction time: 3 h; Yield: 75% (0.331 g); White color solid; R_f = 0.3 in 20% EtOAc in Hexane; m.p = 135-137 °C; IR (KBr, ν cm^{-1}): 3436, 1617, 1585, 1517, 1442, 1311, 1264, 1094, 1012, 737; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, J = 8 Hz, 1H), 7.61 (d, J = 8.8 Hz, 1H), 7.46 (t, J = 7.6 Hz, 1H), 7.73(d, J = 7.6 Hz, 1H), 7.32-7.34 (m, 2H), 7.19 (d, J = 8.4 Hz, 1H), 3.56 (s, 2H), 2.17 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.0, 143.5, 137.5, 135.8, 134.2, 133.7, 133.5, 132.8, 131.0, 130.7, 129.1, 128.8, 123.5, 122.5, 103.9, 13.1; HRMS (ESI-TOF), m/z $[M+H]^+$ Cal for $C_{16}H_{12}Br_2ClN_3$: 439.9159, 441.9138 & 443.9118; Found: 439.9186, 441.9175 & 443.9148.

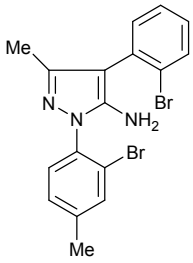
5-Amino-4-(2-bromo-5-fluorophenyl)-1-(2-bromophenyl)-3-methyl-*1H*-pyrazole (2v):



Reaction time: 3 h; Yield: 73% (0.310 g); White color solid; R_f = 0.26 in 20% EtOAc in Hexane; m.p = 115 °C; IR (KBr, ν cm^{-1}): 3202, 2067, 1619, 1513, 1312, 1186, 1055, 1016, 765; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, J = 8 Hz, 1H), 7.68 – 7.58 (m, 1H), 7.58 – 7.40 (m, 2H), 7.34 (t, J = 7.4 Hz, 1H), 7.08 (d, J = 7.6 Hz, 1H), 6.94 (t, J = 6.8 Hz, 1H), 3.57 (s, 2H), 2.17 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ

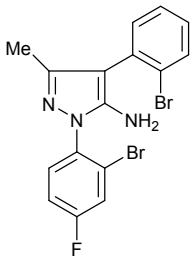
161.9 (d, J = 246.6 Hz), 147.9, 143.5, 137.5, 135.7 (d, J = 8.7 Hz), 134.3 (d, J = 8.5 Hz), 133.7, 130.9, 130.6, 128.8, 122.4, 119.8 (d, J = 21.6 Hz), 119.6 (d, J = 3.5 Hz), 116.2 (d, J = 22.4 Hz), 13.1; ^{19}F (376 MHz,$CDCl_3$): δ -115.9; HRMS (ESI-TOF), m/z $[M+H]^+$ Cal for $C_{16}H_{12}Br_2FN_3$: 423.9455, 425.9435 & 427.9414; Found: 423.9469, 425.9455, 427.9428.

5-Amino-4-(2-bromo-5-methylphenyl)-1-(2-bromophenyl)-3-methyl-*1H*-pyrazole (2w):



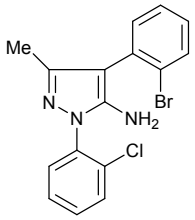
Reaction time: 6 h; Yield: 70% (0.294 g); White color solid; R_f = 0.25 in 20% EtOAc in Hexane; m.p = 188 °C; IR (KBr, ν cm^{-1}): 3402, 3267, 2074, 1621, 1528, 1316, 1265, 1026, 828, 755; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, J = 8.0 Hz, 1H), 7.56 (s, 1H), 7.48 – 7.32 (m, 3H), 7.29 – 7.18 (m, 2H), 3.54 (s, 2H), 2.42 (s, 3H), 2.19 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.9, 143.5, 141.4, 135.0, 134.1, 134.0, 133.2, 133.1, 130.2, 129.4, 128.9, 127.6, 125.5, 122.1, 104.8, 21.1, 13.1; HRMS (ESI-TOF), m/z $[M+H]^+$ Cal for $C_{17}H_{15}Br_2N_3$: 419.9705, 421.9686 & 423.9665; Found: 419.9681, 421.9646 & 423.9637.

5-Amino-1-(2-bromo-4-fluorophenyl)-4-(2-bromophenyl)-3-methyl-*1H*-pyrazole (2x):



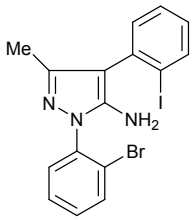
Reaction time: 3 h; Yield: 72% (0.306 g); White color solid; R_f = 0.3 in 20% EtOAc in Hexane; m.p = 170-172 °C; IR (KBr, ν cm^{-1}): 3053, 2986, 2303, 1517, 1421, 1265, 1204, 895, 739, 705; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, J = 8.0 Hz, 1H), 7.53 (dd, J = 8.6, 5.6 Hz, 1H), 7.6 (dd, J = 7.8, 2.4 Hz, 1H), 7.42 - 7.28 (m, 2H), 7.25 – 7.10 (m, 2H), 3.51 (s, 2H), 2.15 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.5 (d, J = 252.3 Hz), 148.3, 143.6, 134.1 (d, J = 3.5 Hz), 133.8, 133.2, 133.0, 131.8 (d, J = 9.2 Hz), 129.1, 127.7, 125.5, 123.4 (d, J = 10.2 Hz), 120.8 (d, J = 25.3 Hz), 115.8 (d, J = 22.1 Hz), 105.1, 13.1; ^{19}F (376 MHz, DMSO): δ -111.6; HRMS (ESI-TOF), m/z $[M+H]^+$ Cal for $C_{16}H_{12}Br_2FN_3$: 423.9455, 425.9435 & 427.9414; Found: 423.9444, 425.9413 & 427.9404.

5-Amino-1-(2-chlorophenyl)-4-(2-bromophenyl)-3-methyl-*1H*-pyrazole (2y): Reaction time: 4



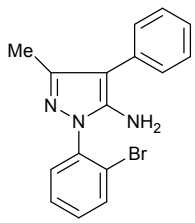
h; Yield: 40% (0.181 g); Orange viscous liquid; R_f = 0.11 in 20% EtOAc in hexane; IR (KBr, ν cm^{-1}): 2924, 2194, 1731, 1494, 1390, 1264, 1005, 756; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (d, *J* = 8.0 Hz, 1H), 7.57 - 7.51 (m, 2H), 7.44 – 7.32 (m, 4H), 7.24 - 7.15 (m, 1H), 3.57 (s, 2H), 2.16 (s, 3H).; ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.3, 143.7, 136.0, 133.8, 133.2, 133.1, 132.2, 130.5(2C), 130.4, 129.0, 128.1, 127.7, 125.4, 104.9, 13.1.; HRMS (ESI – TOF), m/z $[M + H]^+$ Cal for $C_{16}H_{13}BrClN_3$:362.0054, 364.0033; Found: 362.0044, 364.0021.

5-Amino-1-(2-bromophenyl)-4-(2-iodophenyl)-3-methyl-*1H*-pyrazole (2z): Reaction time: 5



h; Yield: 80% (1.82 g); Pale yellow colour solid ; R_f = 0.1 in 20% EtOAc in hexane; m.p = 150 °C; IR (KBr, ν cm^{-1}): 2920, 2668, 1615, 1516, 1491, 1389, 1250, 1002, 755; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 7.6 Hz, 1H), 7.73 (d, *J* = 7.6 Hz, 1H), 7.55 (d, *J* = 7.6 Hz, 1H), 7.51 – 7.38 (m, 2H), 7.37 - 7.30 (m, 2H), 7.05 (t, *J* = 7.2 Hz, 1H), 3.52 (s, 2H), 2.15 (s, 3H).; ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.9, 143.2, 139.5, 137.9, 137.4, 133.7, 132.4, 131.0, 130.7, 129.4, 128.8, 128.6, 122.4, 108.7, 102.8, 13.1.; HRMS (ESI – TOF), m/z $[M + H]^+$ Cal for $C_{16}H_{13}BrIN_3$: 453.9410, 455.9390; Found: 453.9400, 455.9375.

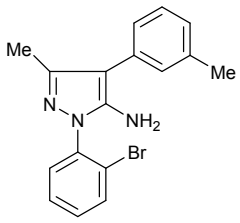
5-Amino-1-(2-bromophenyl)-4-phenyl-3-methyl-*1H*-pyrazole (2aa): Reaction time: 3 h; Yield:



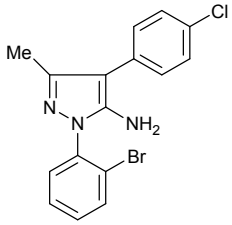
70% (1.15 g); Pale yellow colour solid ; R_f = 0.1 in 20% EtOAc in hexane; m.p = 218 °C; IR (KBr, ν cm^{-1}): 3056, 2923, 1576, 1437, 1320, 1265, 1027, 759; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.71 (dd, *J* = 8.0, 1.1 Hz, 1H), 7.51 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.47 – 7.36 (m, 5H), 7.32 (td, *J* = 7.9, 1.6 Hz, 1H), 7.30 – 7.21 (m, 1H), 3.73 (s, 2H), 2.31 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.6, 143.4, 133.7, 133.4,

130.9, 130.6, 129.0, 128.7, 128.6, 126.1, 122.3, 104.3, 13.3; HRMS (ESI – TOF), m/z $[M + H]^+$ Cal for Cal for $C_{16}H_{15}N_3Br$: 328.0444, 330.0424; Found: 328.0439, 330.0421.

5-Amino-1-(2-bromophenyl)-4-(3-methylphenyl)-3-methyl-*1H*-pyrazole (2ab): Reaction time: 4 h ; Yield: 67% (1.15 g); Pale yellow colour solid ; R_f = 0.1 in 20% EtOAc in hexane; m.p = 186 °C; IR (KBr, ν cm^{-1}): 2624, 1844, 1267, 764,; ^1H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, *J* = 8.0 Hz, 1H), 7.53 (d, *J* = 7.6 Hz, 1H), 7.46 (t, *J* = 7.2 Hz, 1H), 7.39 - 7.30 (m, 2H), 7.24 - 7.15 (m, 2H), 7.10 (d, *J* = 7.6 Hz, 1H), 3.76 (s, 2H), 2.41 (s, 3H), 2.33 (s, 3H).; ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.6, 143.5, 138.7, 133.8(2C), 133.2, 131.0, 130.7, 129.4, 129.0, 128.8, 127.1, 125.8, 122.4, 104.5, 21.7, 13.3.; HRMS (ESI – TOF), m/z $[M + H]^+$ Cal for $C_{17}H_{17}N_3Br$: 342.0600, 344.0580; Found: 342.0596, 344.0576.



5-Amino-1-(2-bromophenyl)-4-(4-chlorophenyl)-3-methyl-*1H*-pyrazole (2ac): Reaction time: 3 h ; Yield: 72% (1.30 g) ; Yellow viscous liquid; R_f = 0.13 in 20% EtOAc in hexane; IR (KBr, ν cm^{-1}): 3433, 3350, 3190, 3059, 1616, 1442, 1394, 1264, 1006, 822, 765; ^1H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, *J* = 8.0 Hz, 1H), 7.54 – 7.44 (m, 2H), 7.43 – 7.38 (m, 2H), 7.37 - 7.30 (m, 3H), 3.73 (s, 2H), 2.30 (s, 3H).; ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.5, 143.5, 137.2, 133.8, 132.0, 131.9, 131.1, 130.6, 129.9, 129.3, 128.9, 122.3, 103.3, 13.2.; HRMS (ESI – TOF), m/z $[M + H]^+$ Cal for $C_{16}H_{14}N_3BrCl$: 362.0054, 364.0033; Found: 362.0033, 364.0012



Procedure for Optimization of the *N*-Arylation 5-Amino-4-arylpyrazole 2a:

An oven dried 8 mL reaction vial was charged with copper-salt (5 mol %), ligand (10 mol %) and base (3 equiv), the respective 5-amino-4-(2-bromophenyl)pyrazole **2a** (0.5 mmol) in

solvent (2.0 mL) was stirred at rt-120 °C for 3 – 24 h. The reaction mixture was monitored by TLC. After the starting material had been completely consumed, the reaction mixture was purified by flash chromatography using hexane and EtOAc as eluent.

References:

1 J. M. McCall, R. C. Kelly and D. L. Romero, *PCT Int. Appl.*, WO 2012/149157 A2.

2 N. Hisano, Y. Kamei, Y. Kansaku, M. Yamanaka and K. Mor, *Org. Lett*., 2018, **20**, 4223.

Crystal Data for **5s** $C_{16}H_{12}BrN_3$ (M =326.20 g/mol): monoclinic, space group $P2_1/n$ (no. 14), a = 7.1264(10) Å, b = 19.8670(19) Å, c = 19.419(3) Å, β = 94.326(14)°, V = 2741.5(6) Å^3, Z = 8, T = 293(2) K, μ(MoKα) = 2.991 mm^{-1}, *Dcalc* = 1.581 g/cm^3, 27049 reflections measured (6.582° ≤ 2Θ ≤ 49.998°), 4819 unique (R_{int} = 0.2166, R_{sigma} = 0.1452) which were used in all calculations. The final R_1 was 0.0994 (I > 2σ(I)) and wR_2 was 0.2384 (all data).

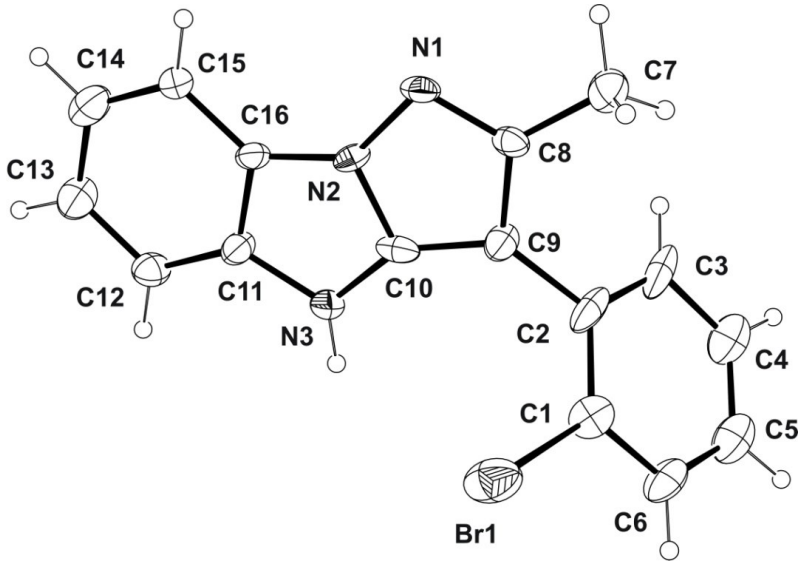
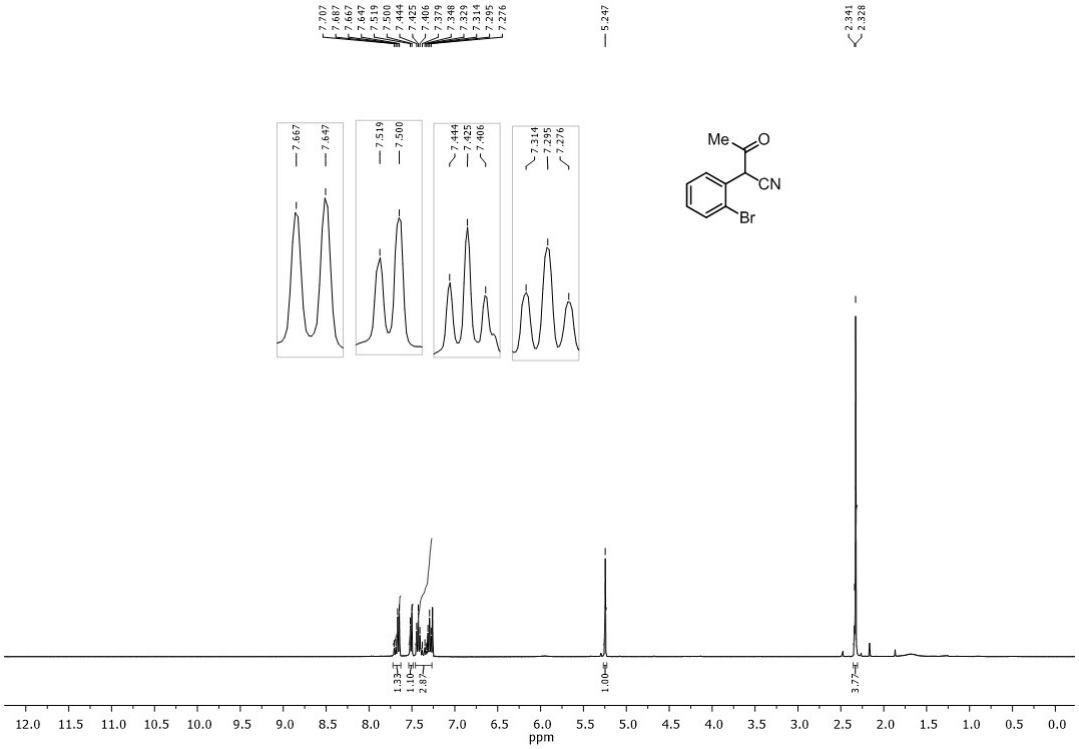
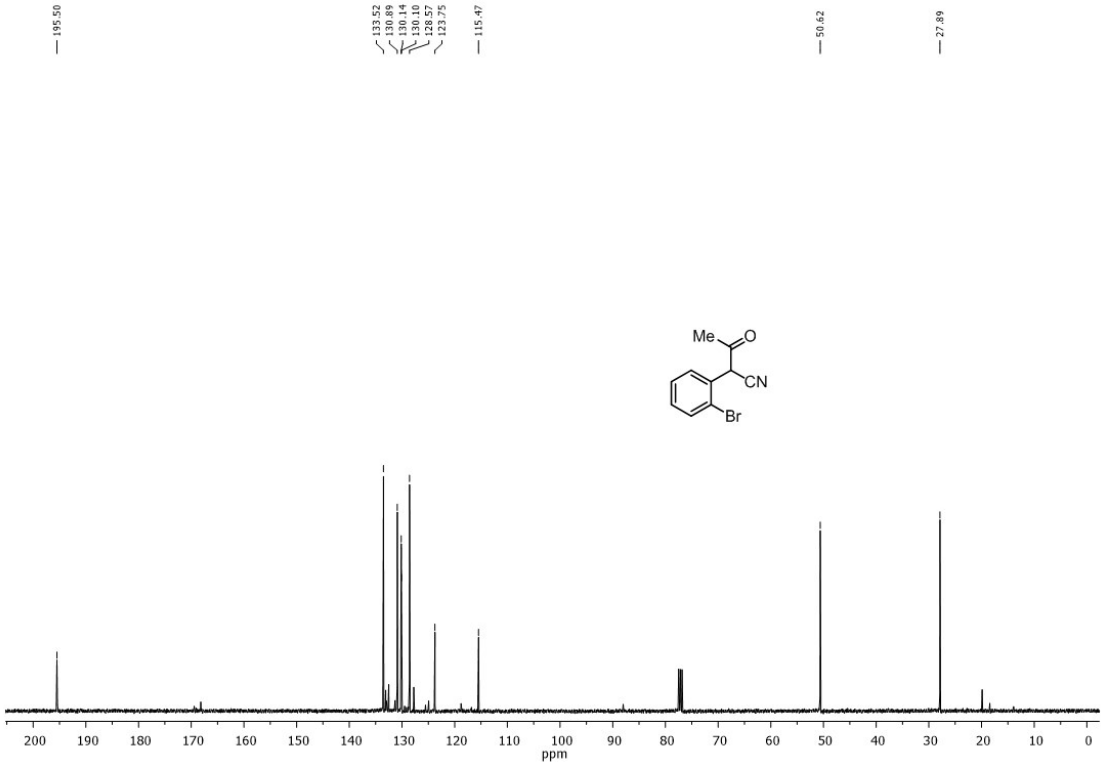


Figure S3. Molecular structure of compound **5s** at 30% probability of thermal ellipsoids.

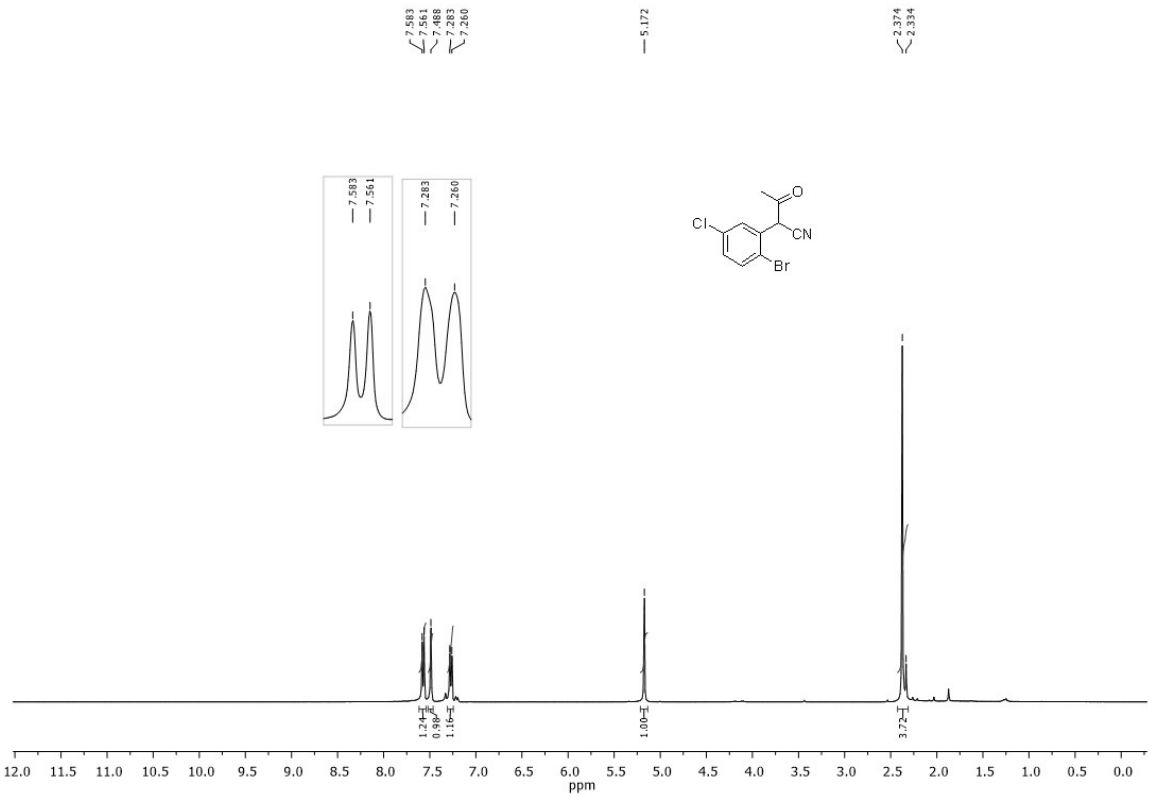
^{1}H & ^{13}C NMR of β-Ketonitriles (**3a-n**):



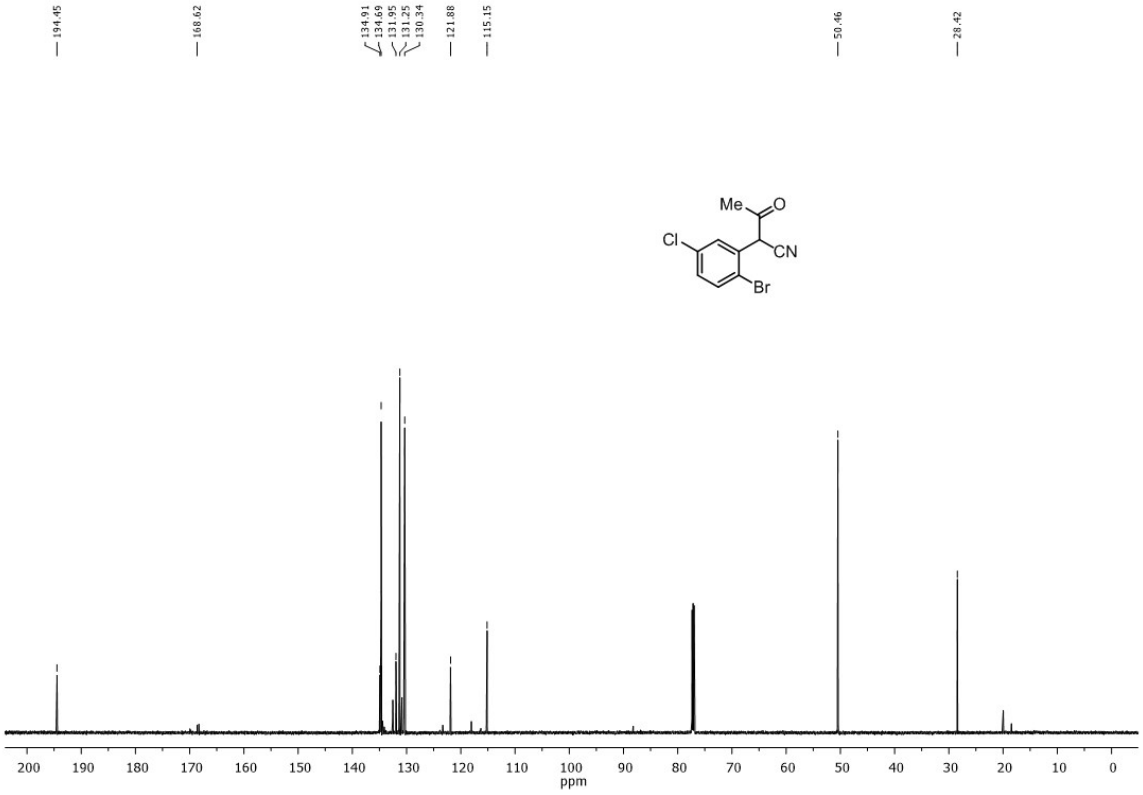
^{1}H Spectra of compound **3a** in $CDCl_3$ (400MHz)



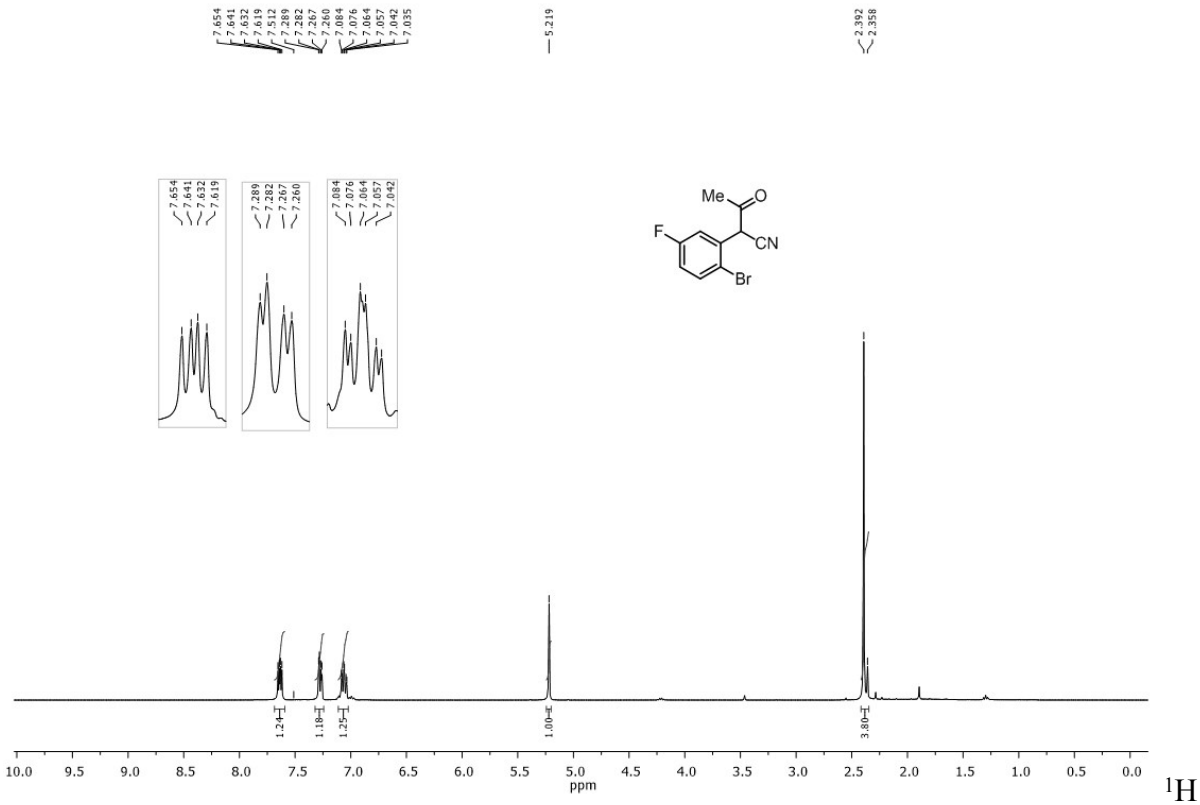
^{13}C Spectra of compound **3a** in $CDCl_3$ (100 MHz)



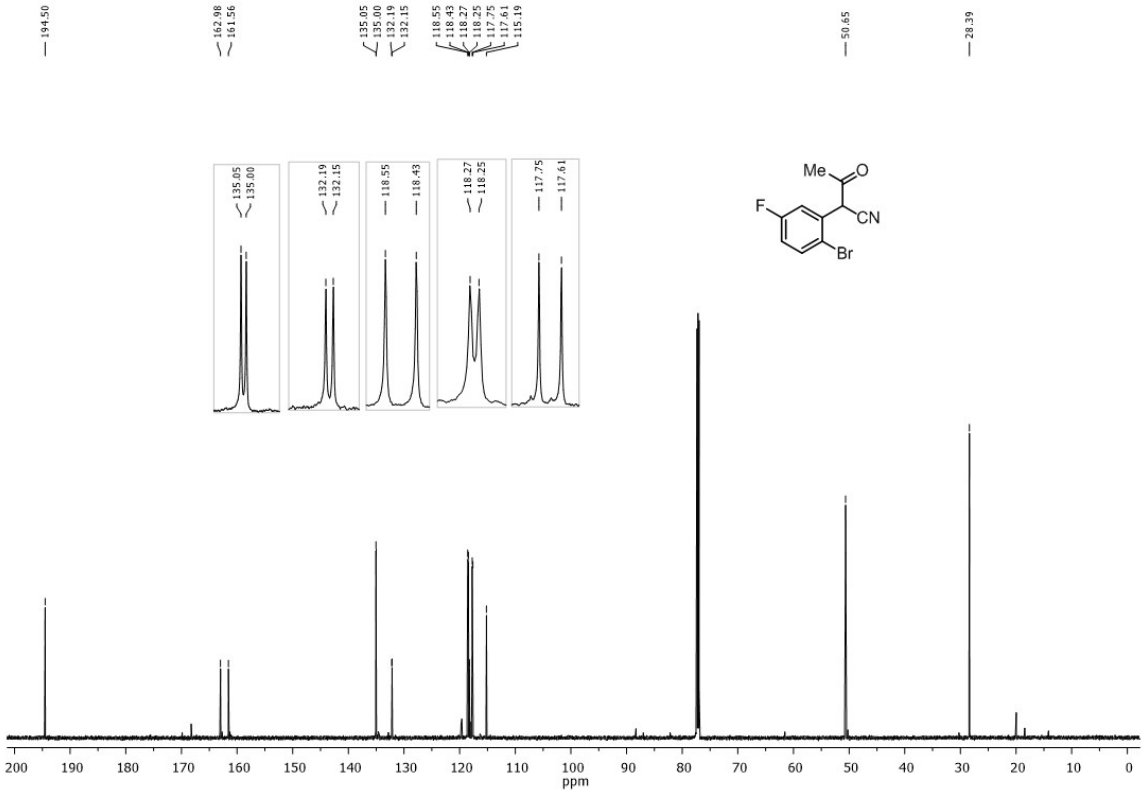
^{1}H Spectra of compound **3b** in $CDCl_3$ (400 MHz)



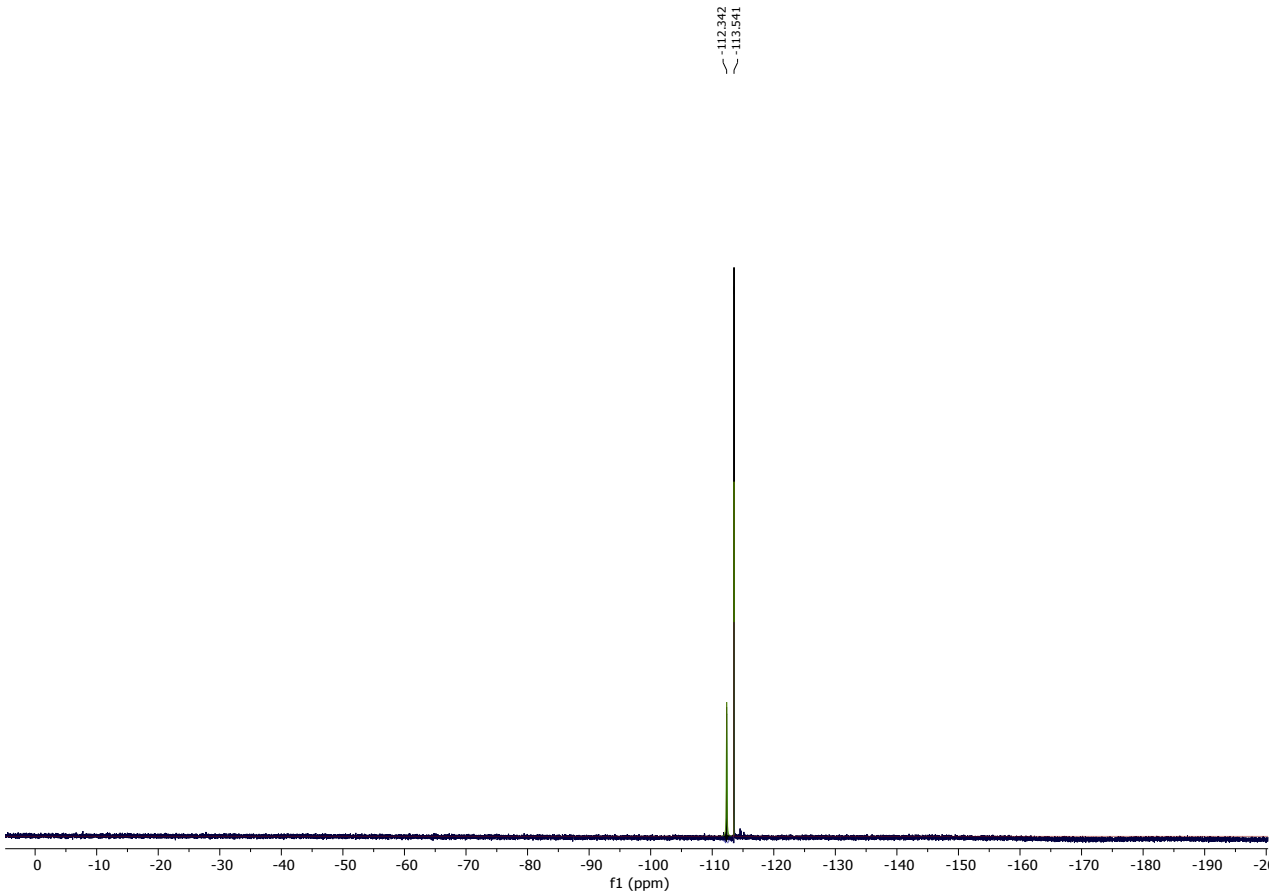
^{13}C Spectra of compound **3b** in $CDCl_3$ (175 MHz)



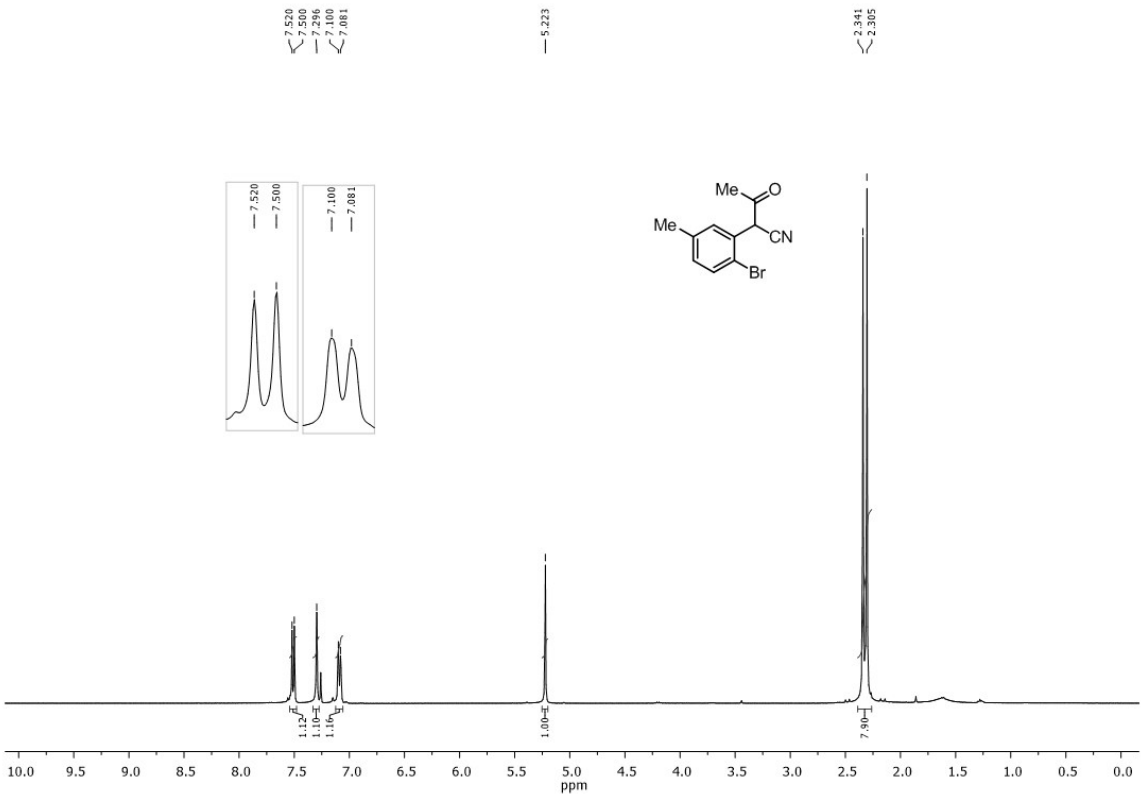
^{1}H Spectra of compound **3c** in $CDCl_3$ (400 MHz)



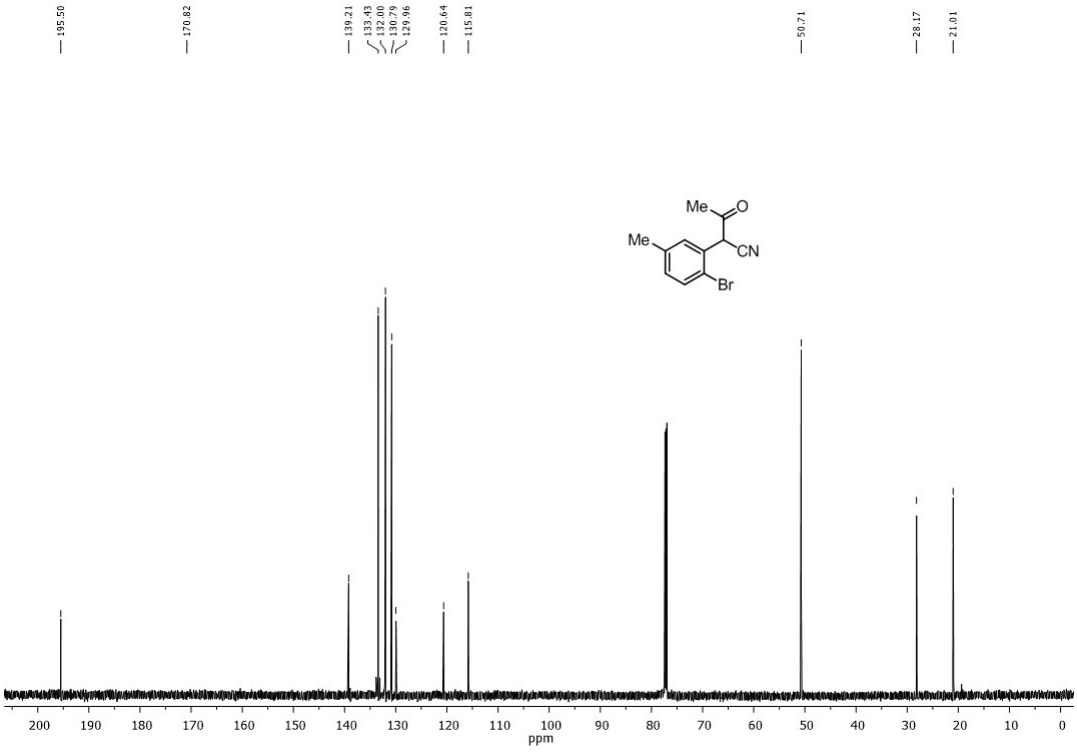
^{13}C Spectra of compound **3c** in $CDCl_3$ (175 MHz)



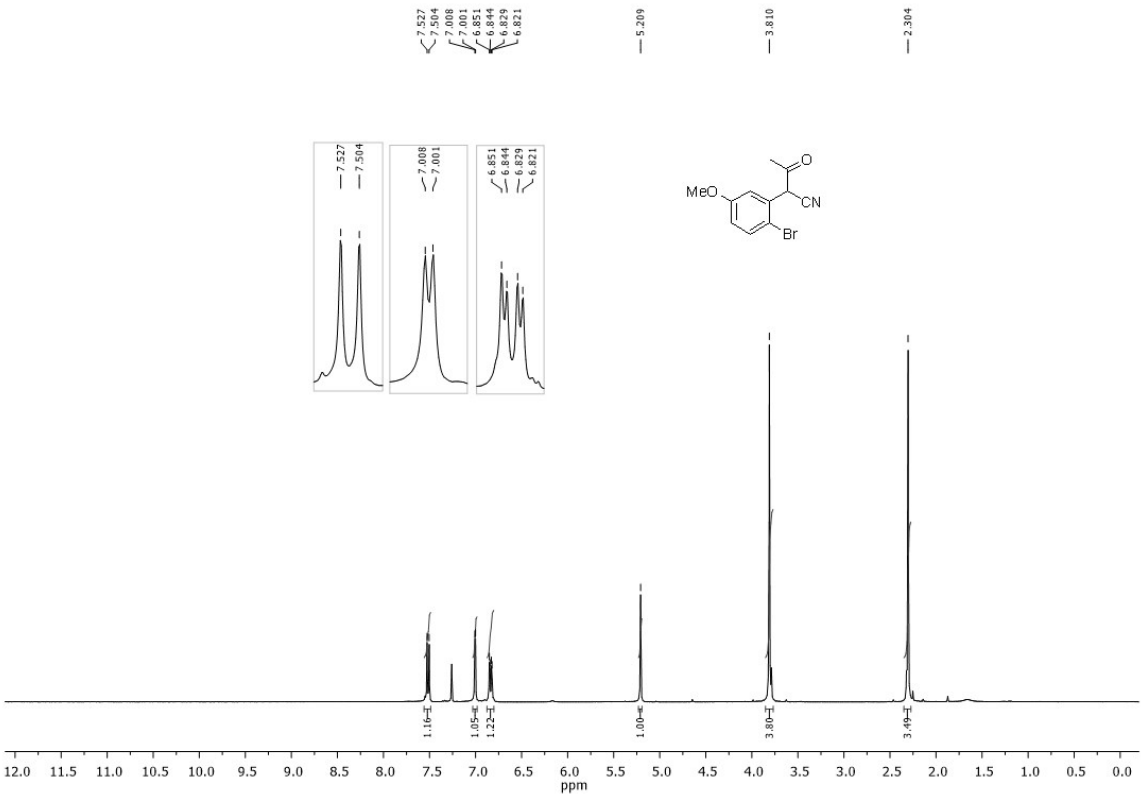
^{19}F Spectra of compound **3c** in $CDCl_3$ (376 MHz)



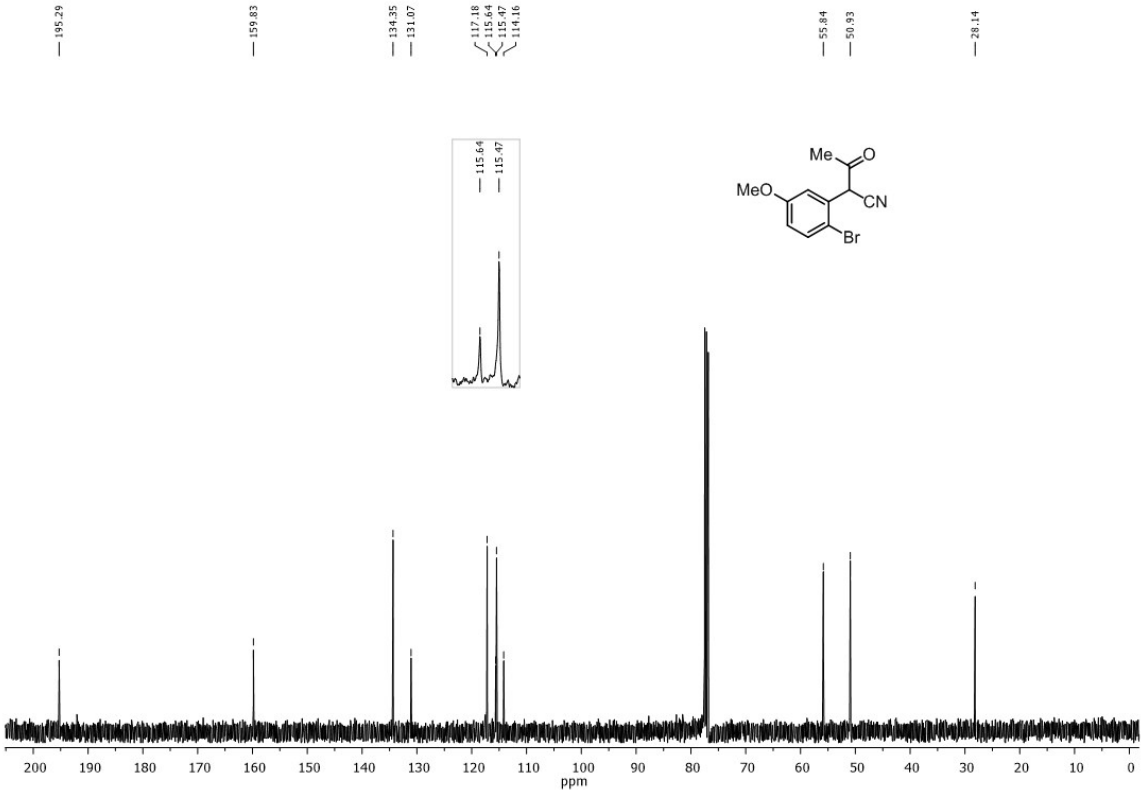
^{1}H Spectra of compound **3d** in $CDCl_3$ (400 MHz)



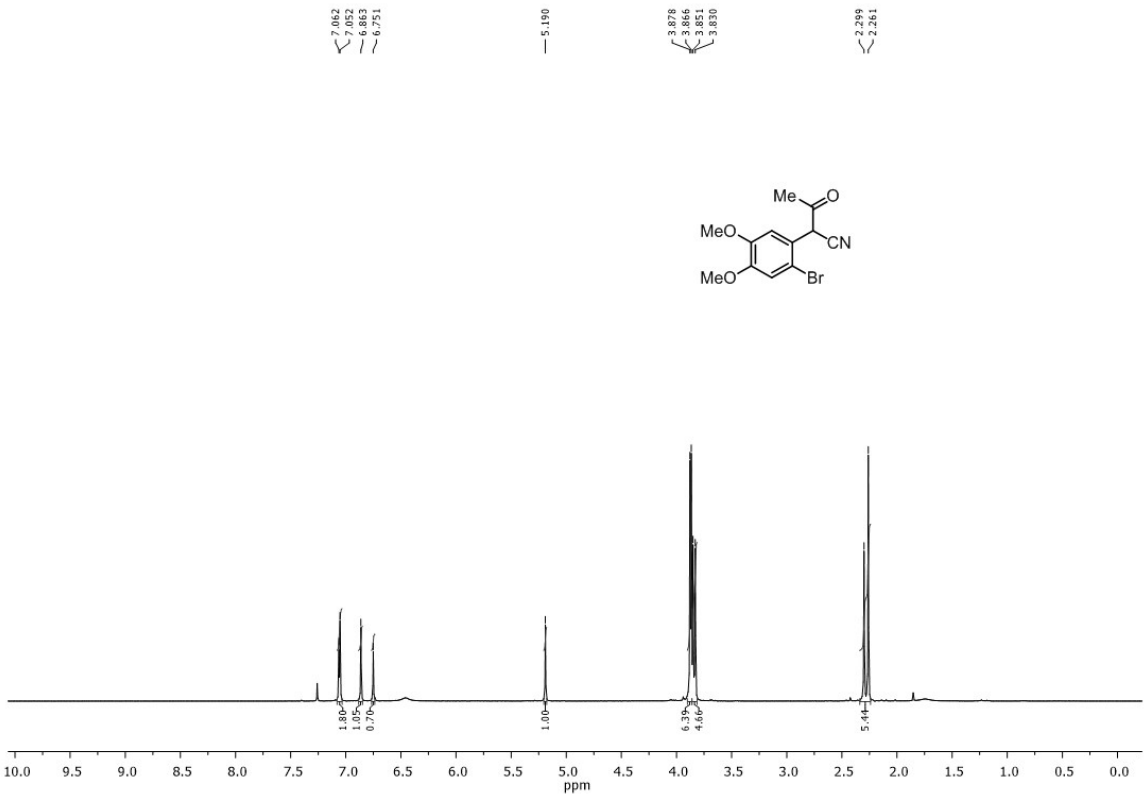
^{13}C Spectra of compound **3d** in $CDCl_3$ (175 MHz)



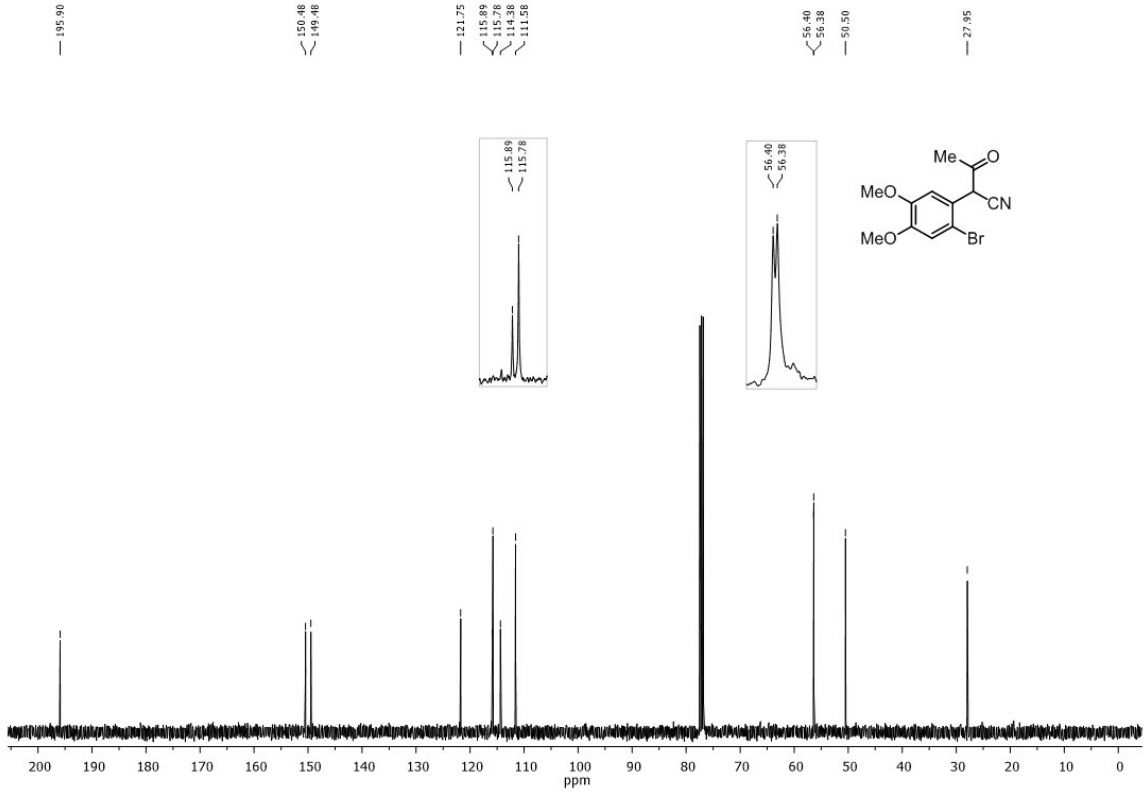
^{1}H Spectra of compound **3e** in $CDCl_3$ (400 MHz)



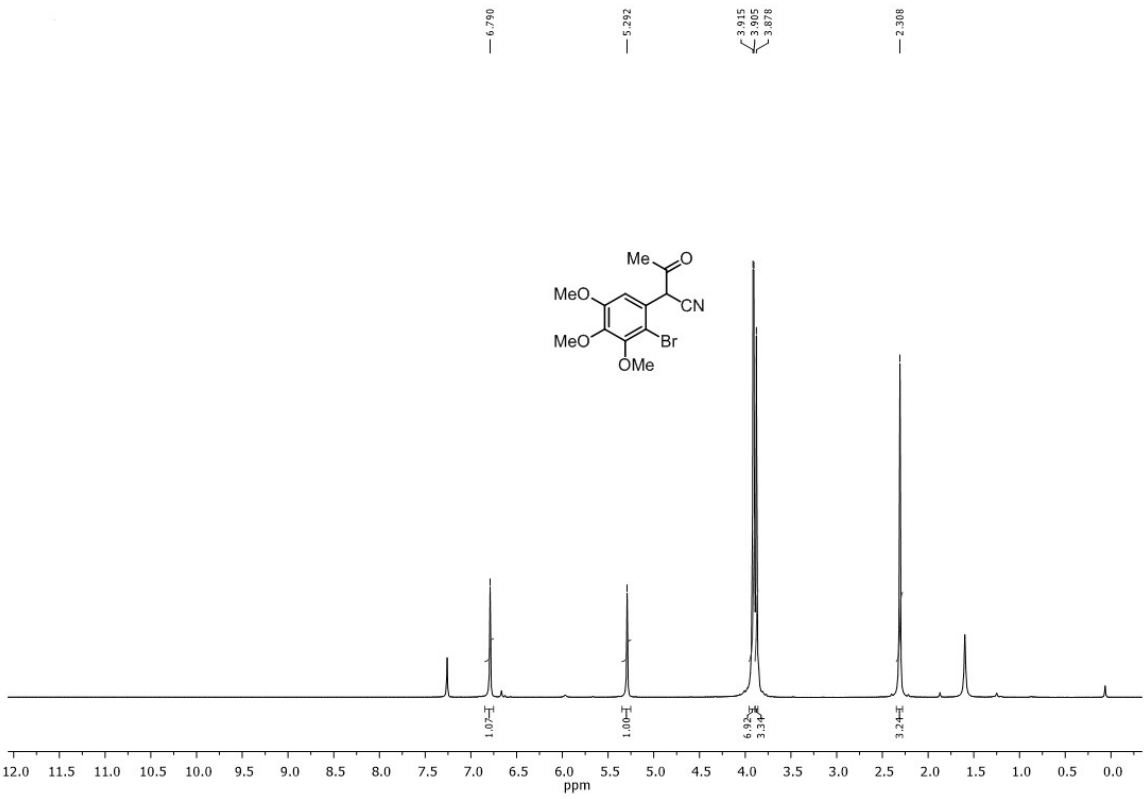
^{13}C Spectra of compound **3e** in $CDCl_3$ (100 MHz)



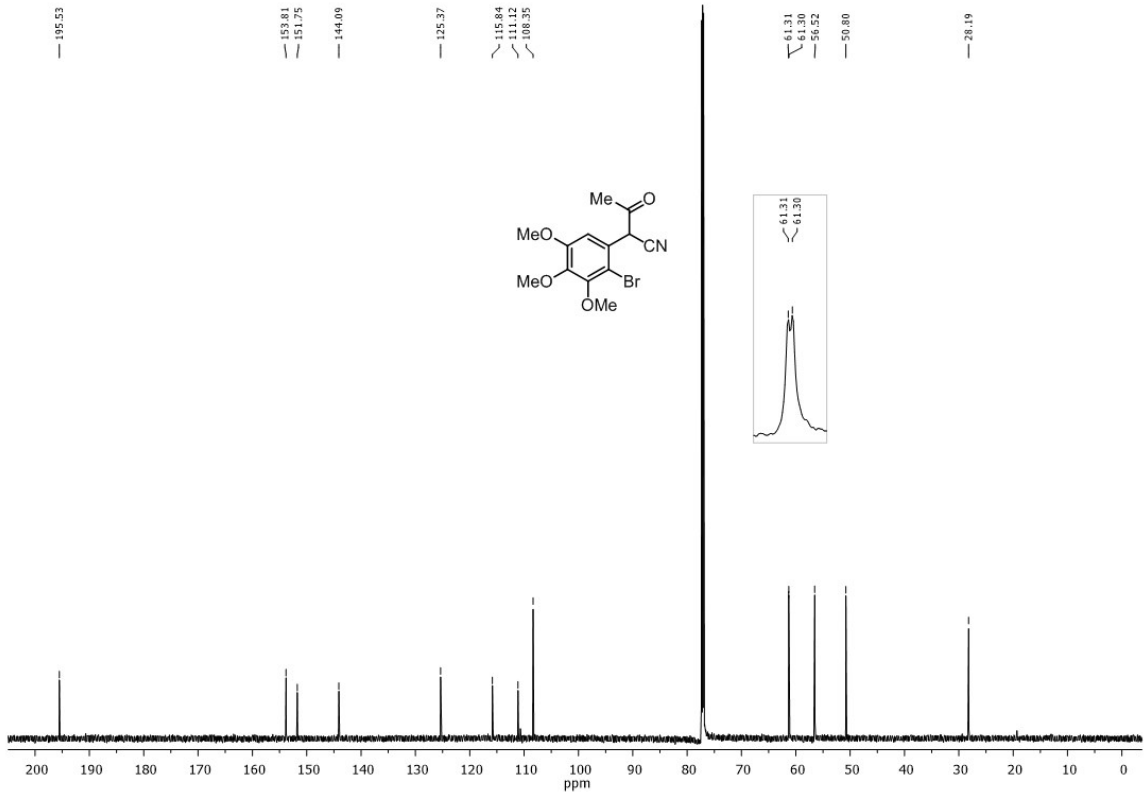
^{1}H Spectra of compound **3f** in $CDCl_3$ (400 MHz)



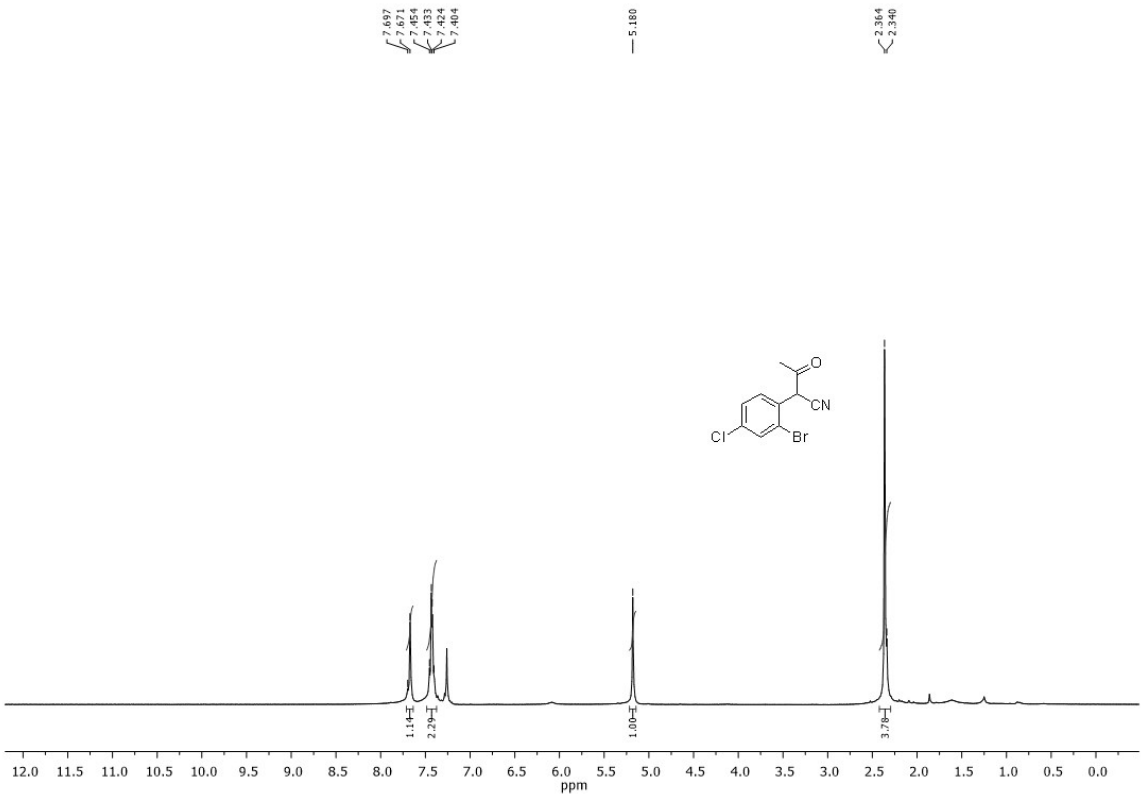
^{13}C Spectra of compound **3f** in $CDCl_3$ (100 MHz)



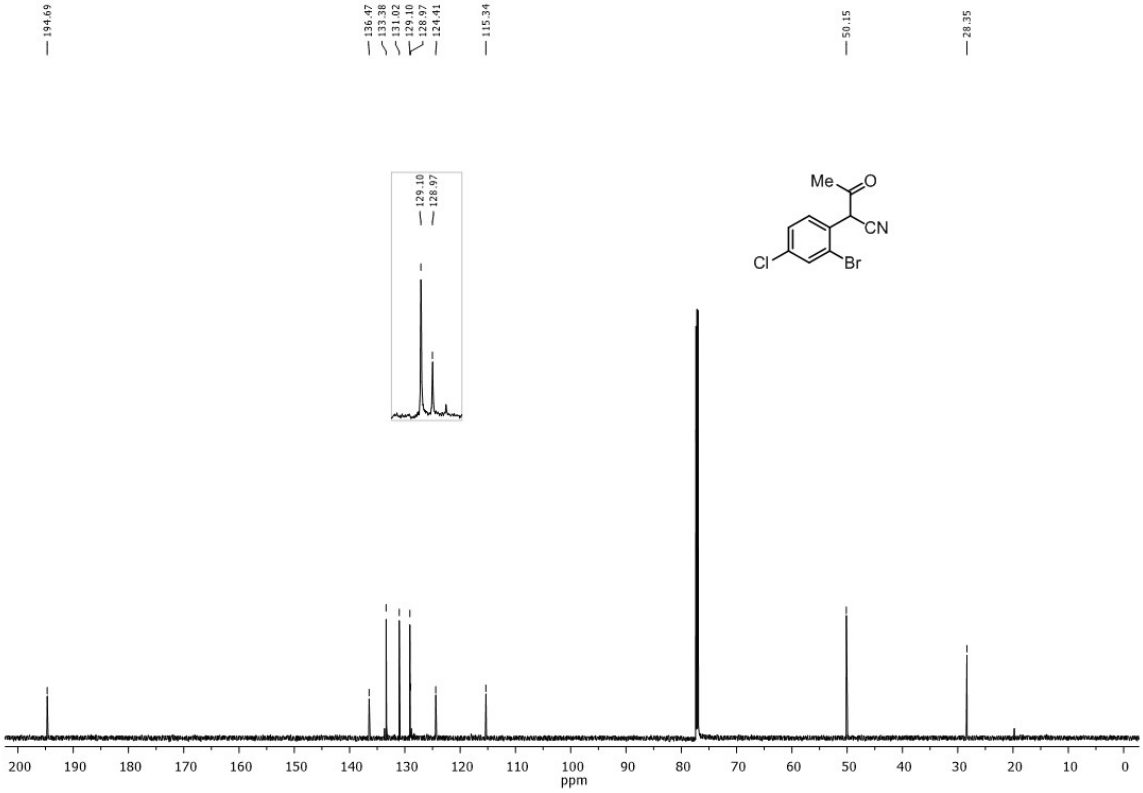
^{1}H Spectra of compound **3g** in $CDCl_3$ (400 MHz)



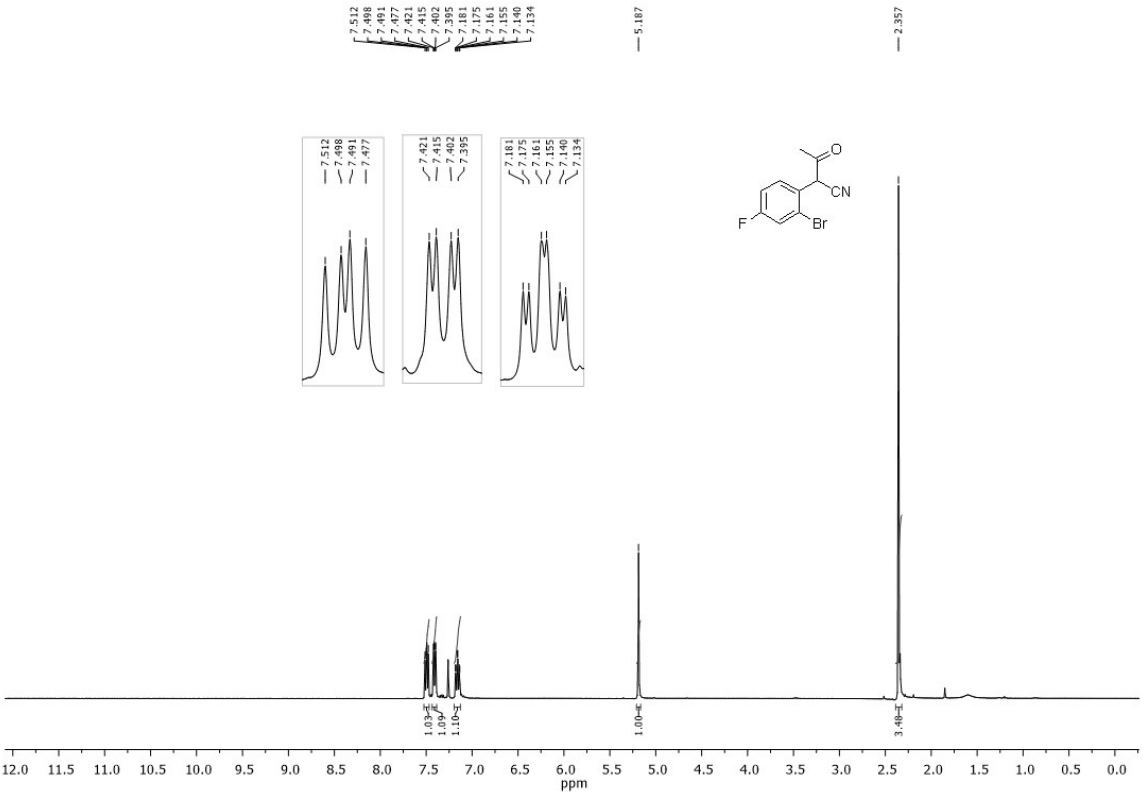
^{13}C Spectra of compound **3g** in $CDCl_3$ (175 MHz)



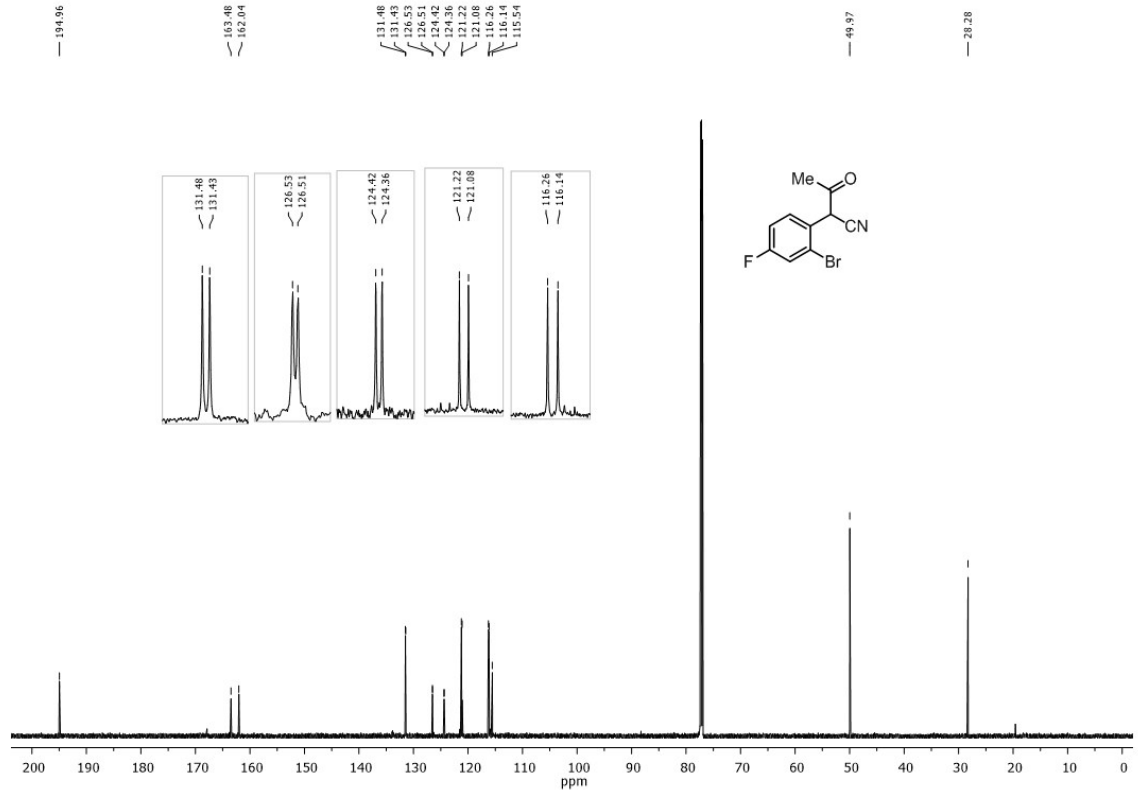
^{1}H Spectra of compound **3h** in $CDCl_3$ (400 MHz)



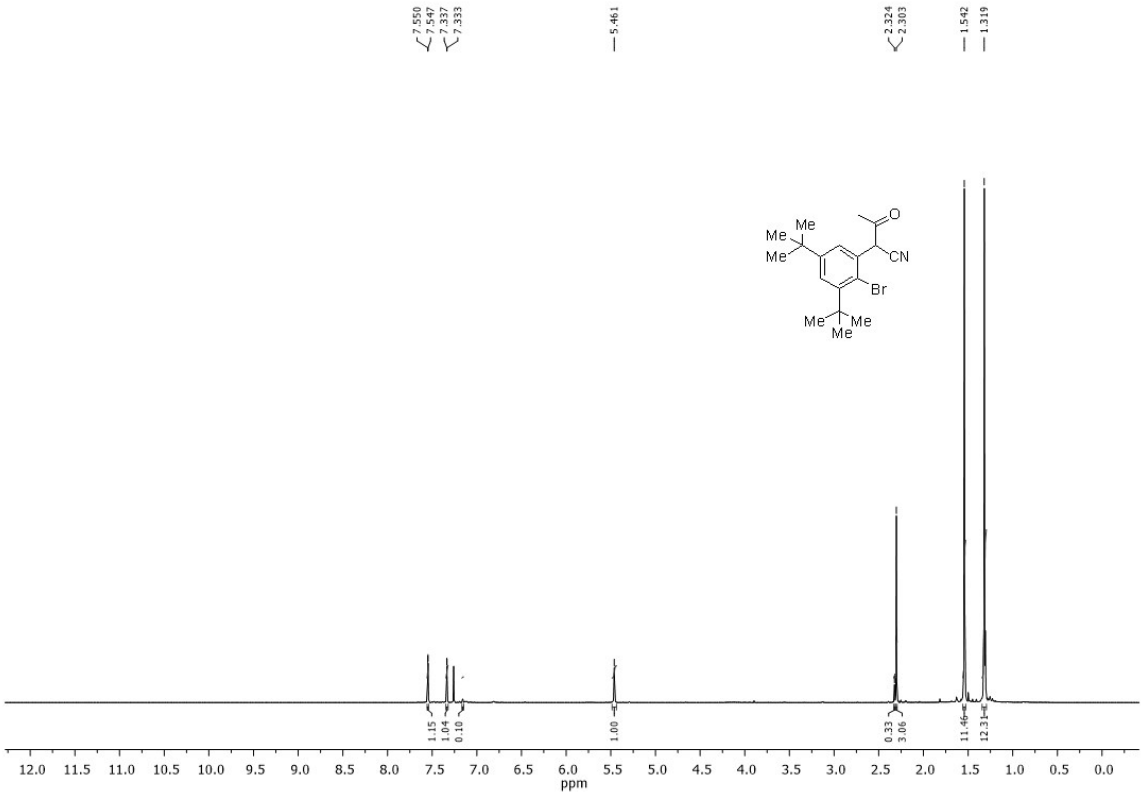
^{13}C Spectra of compound **3h** in $CDCl_3$ (175 MHz)



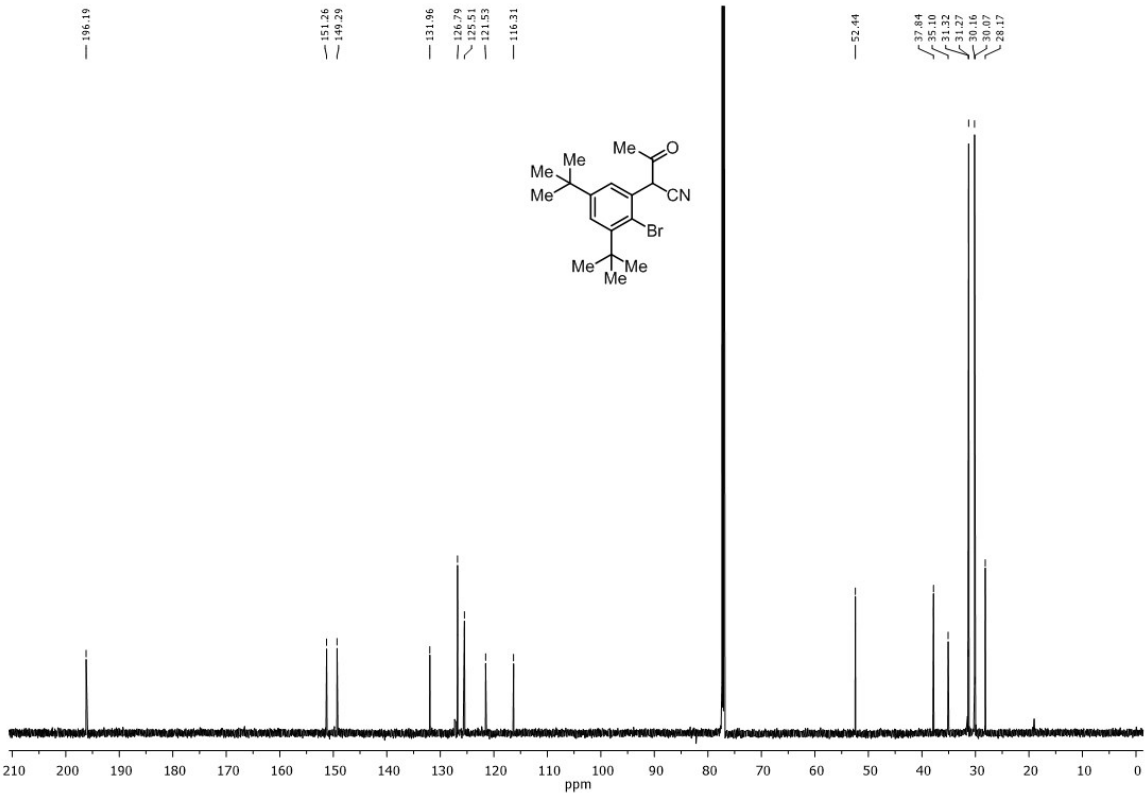
^{1}H Spectra of compound **3i** in $CDCl_3$ (400 MHz)



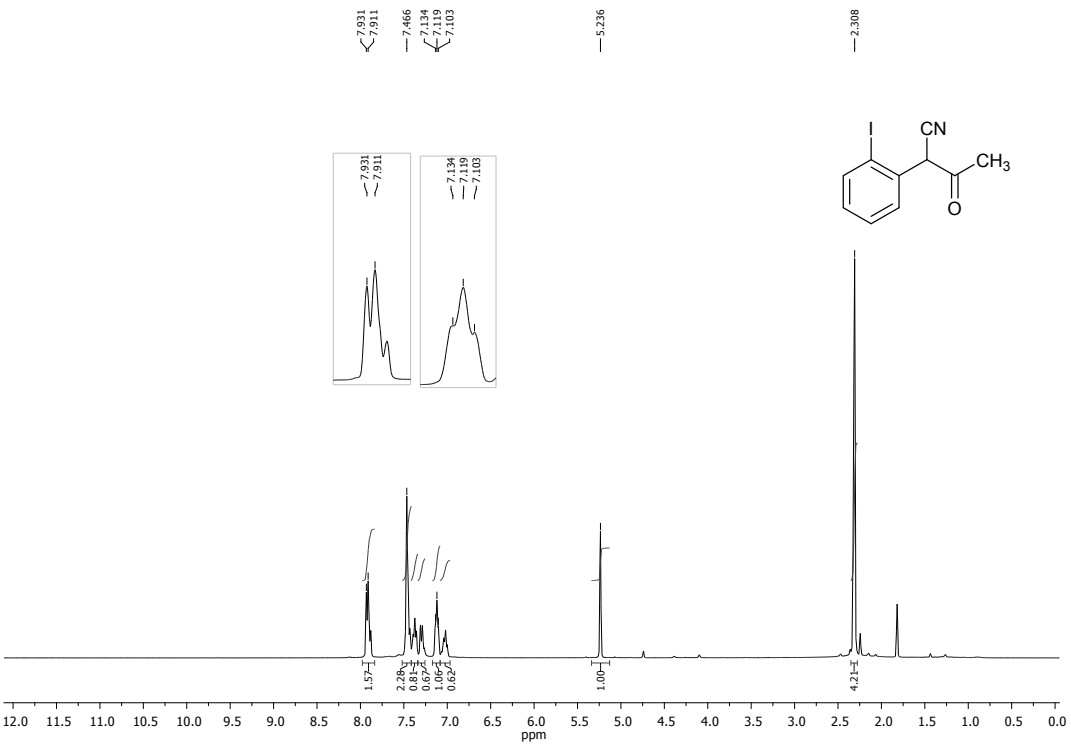
^{13}C Spectra of compound **3i** in $CDCl_3$ (175 MHz)



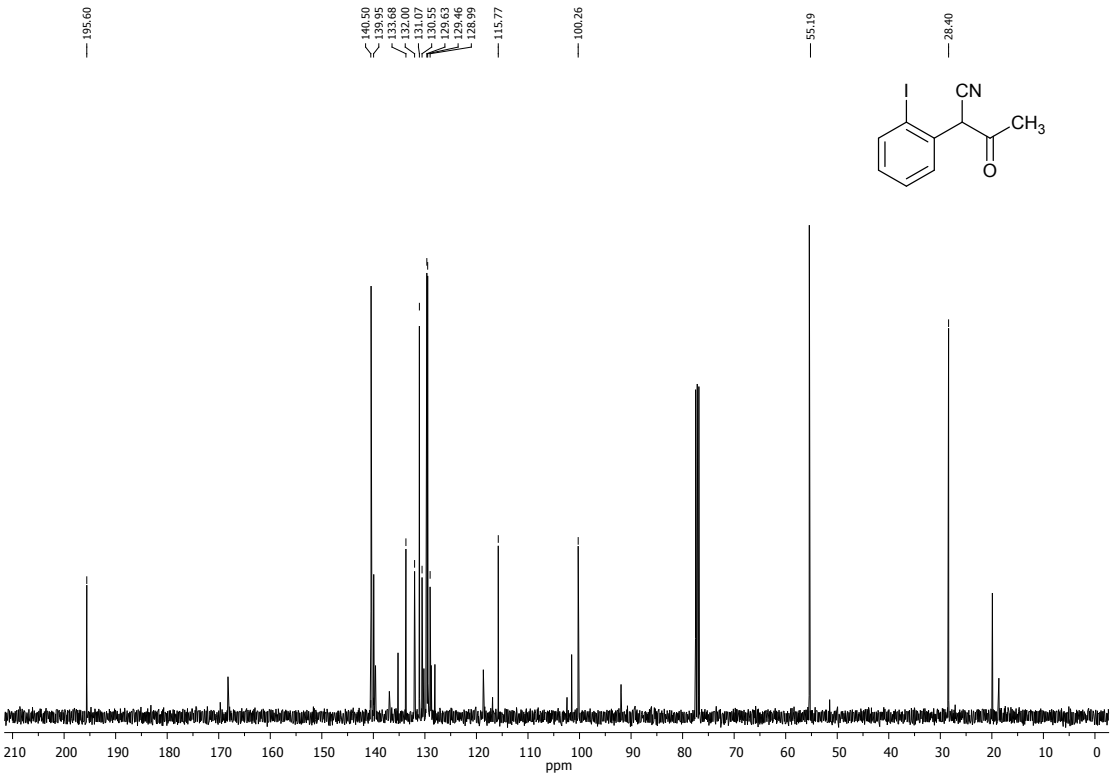
^{1}H Spectra of compound **3j** in $CDCl_3$ (700 MHz)



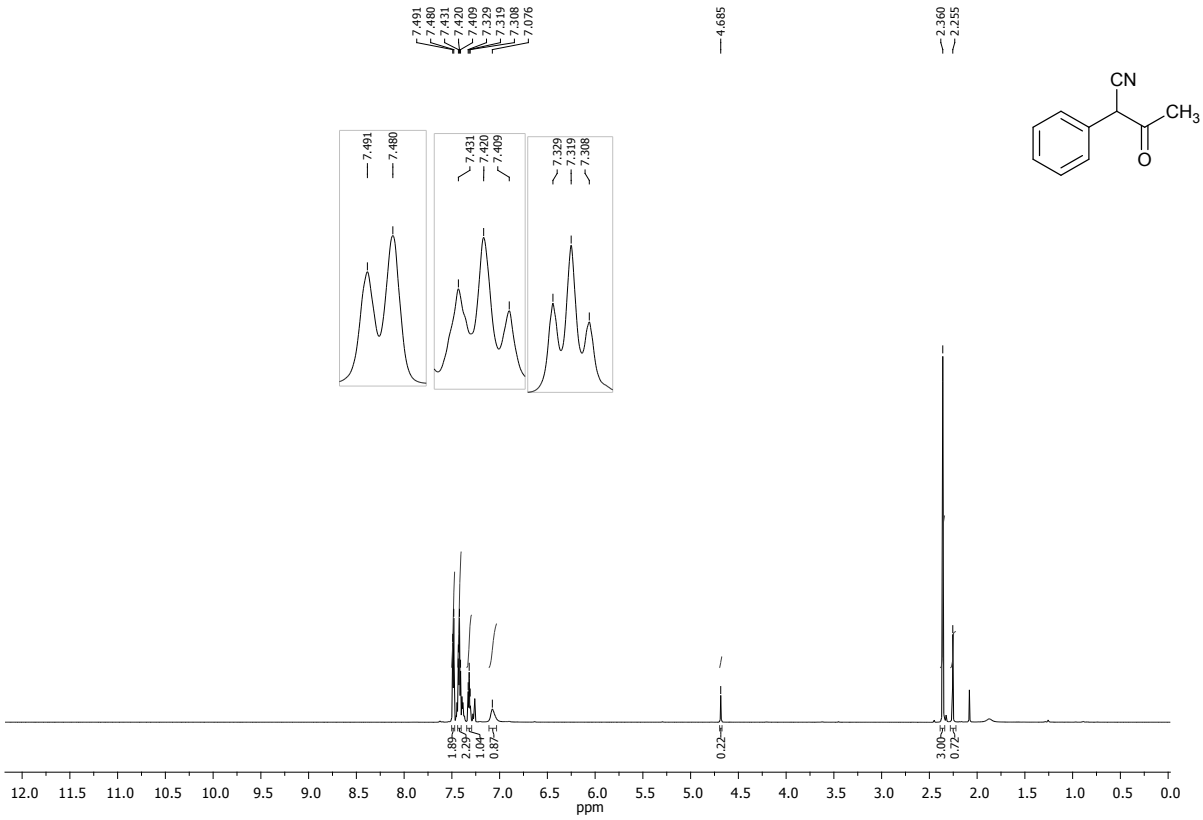
^{13}C Spectra of compound **3j** in $CDCl_3$ (175 MHz)



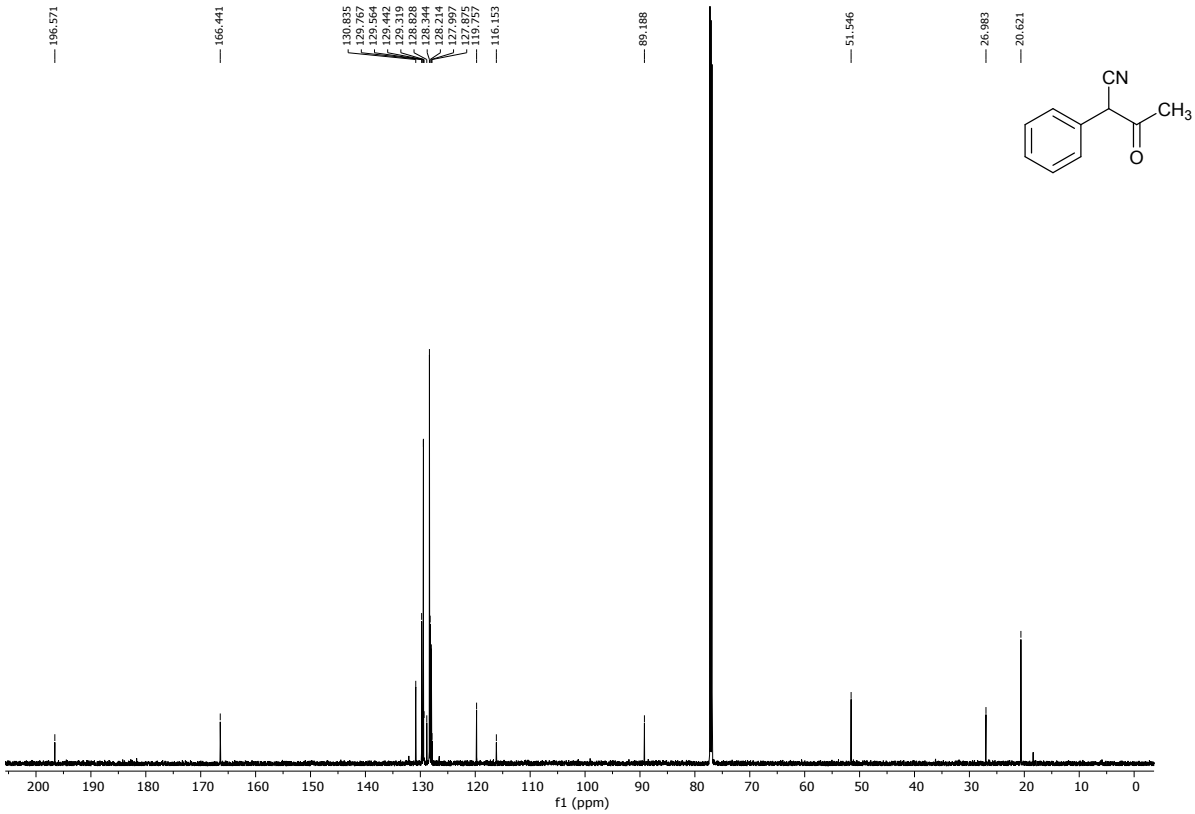
^{1}H Spectra of compound **3k** in $CDCl_3$ (400 MHz)



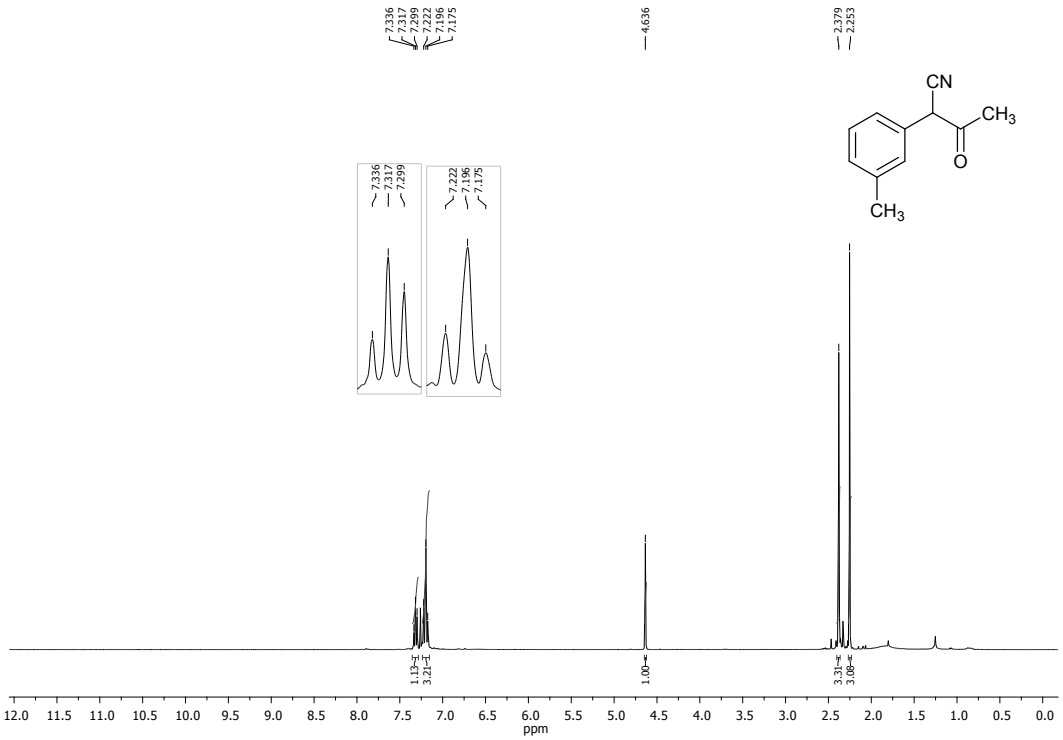
^{13}C Spectra of compound **3k** in $CDCl_3$ (100 MHz)



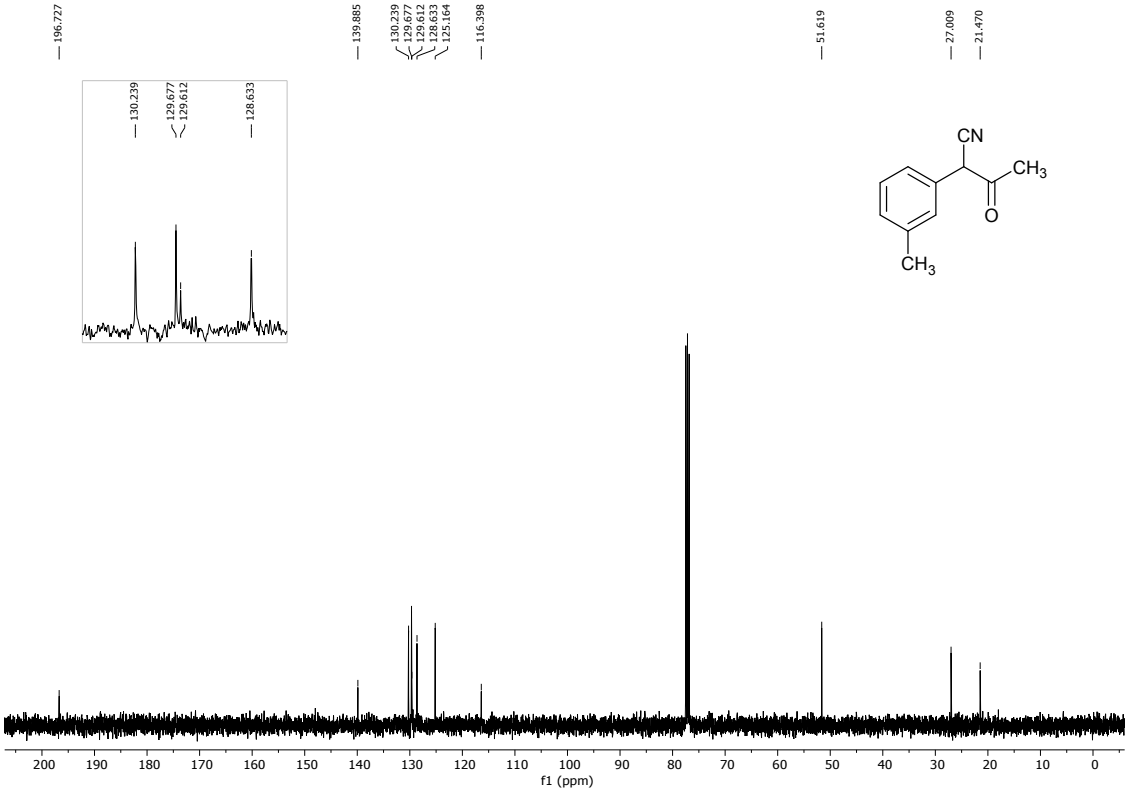
^{1}H Spectra of compound **3l** in $CDCl_3$ (400 MHz)



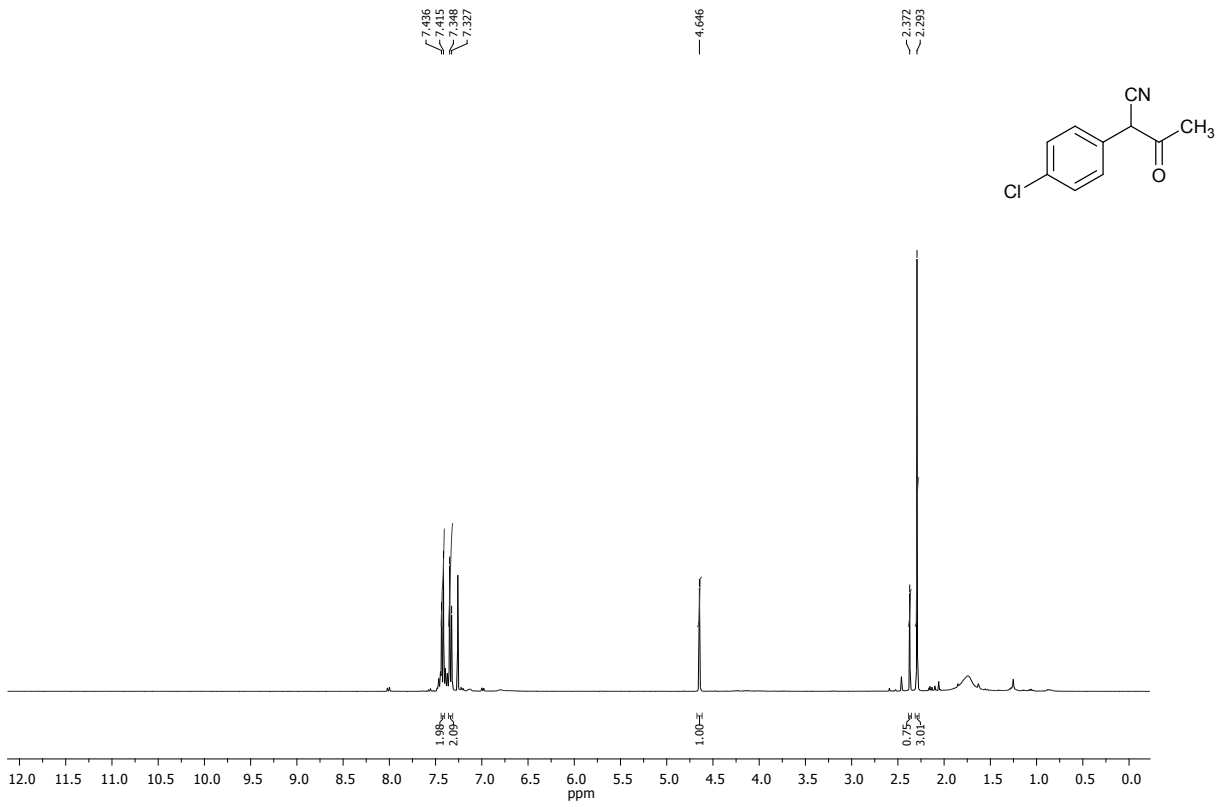
^{13}C Spectra of compound **3l** in $CDCl_3$ (100 MHz)



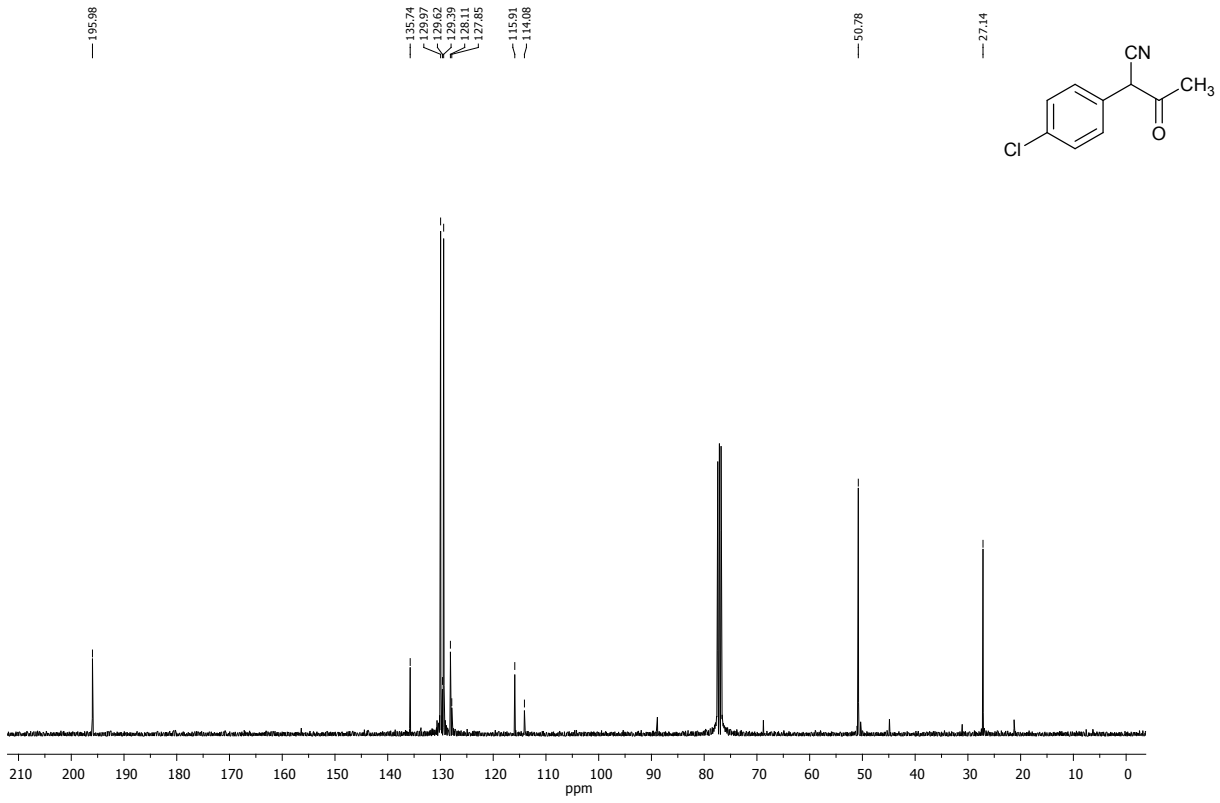
^{1}H Spectra of compound **3m** in $CDCl_3$ (400 MHz)



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

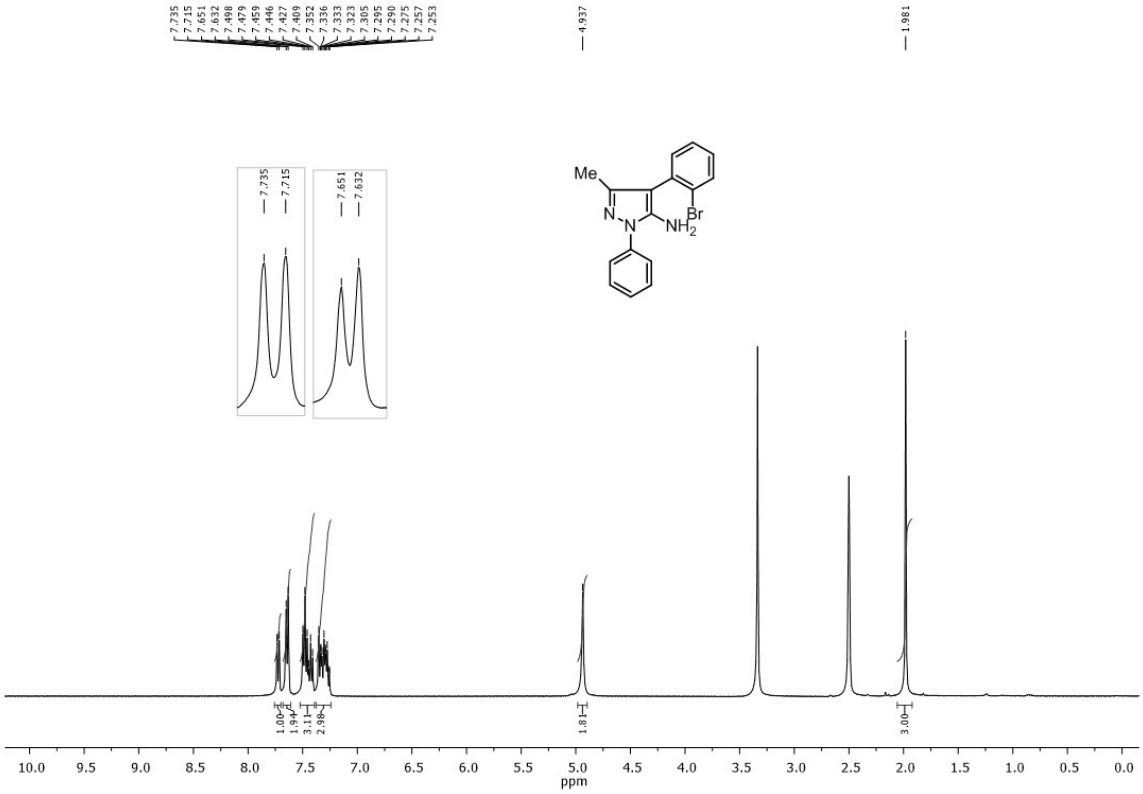


^{1}H Spectra of compound **3n** in $CDCl_3$ (400 MHz)

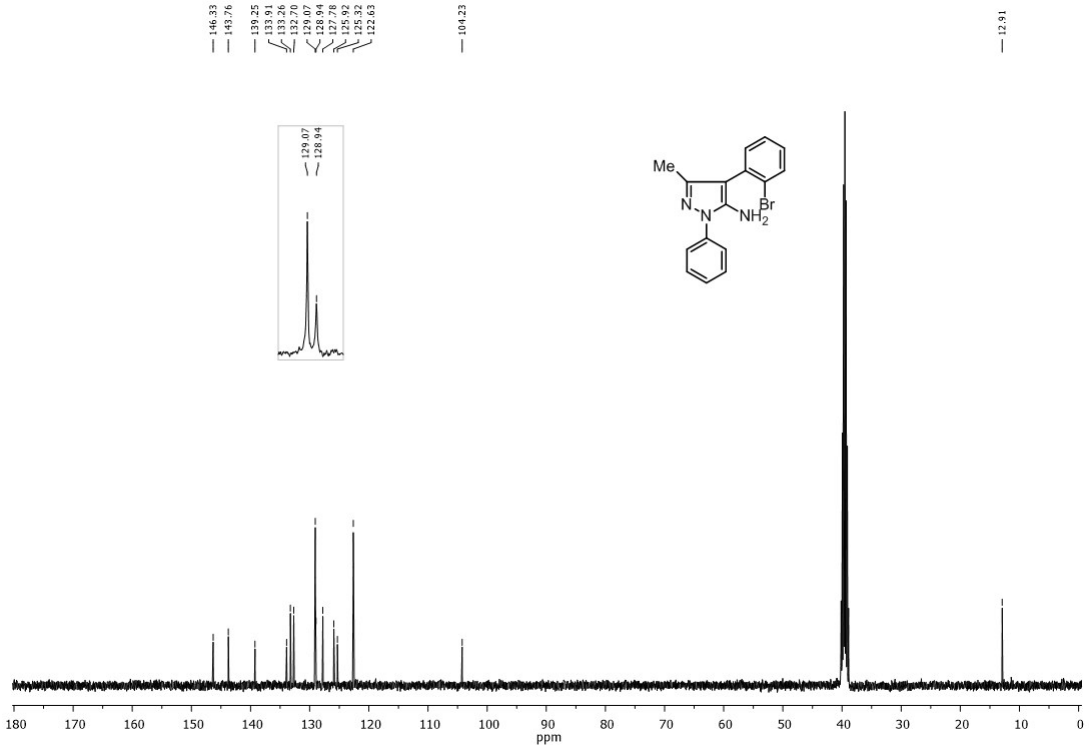


^{13}C Spectra of compound **3n** in $CDCl_3$ (100 MHz)

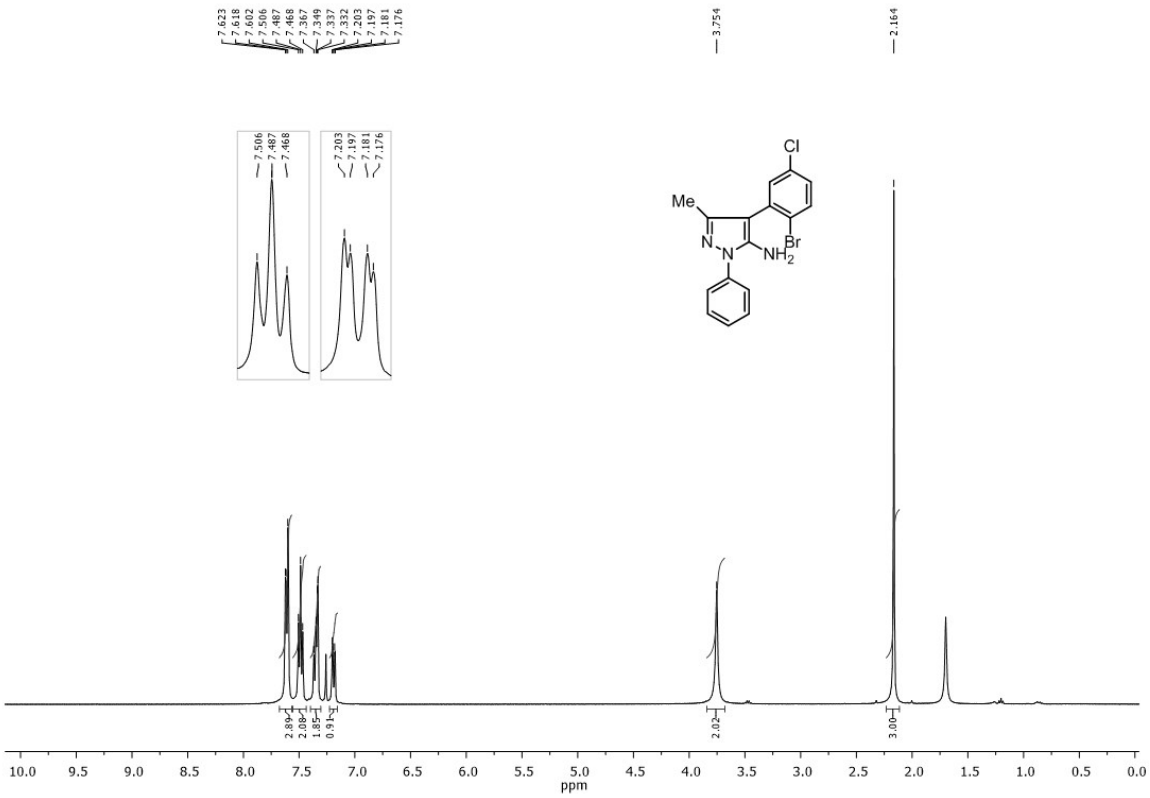
^{1}H & ^{13}C NMR of 5-Aminopyrazoles (**2a-x**):



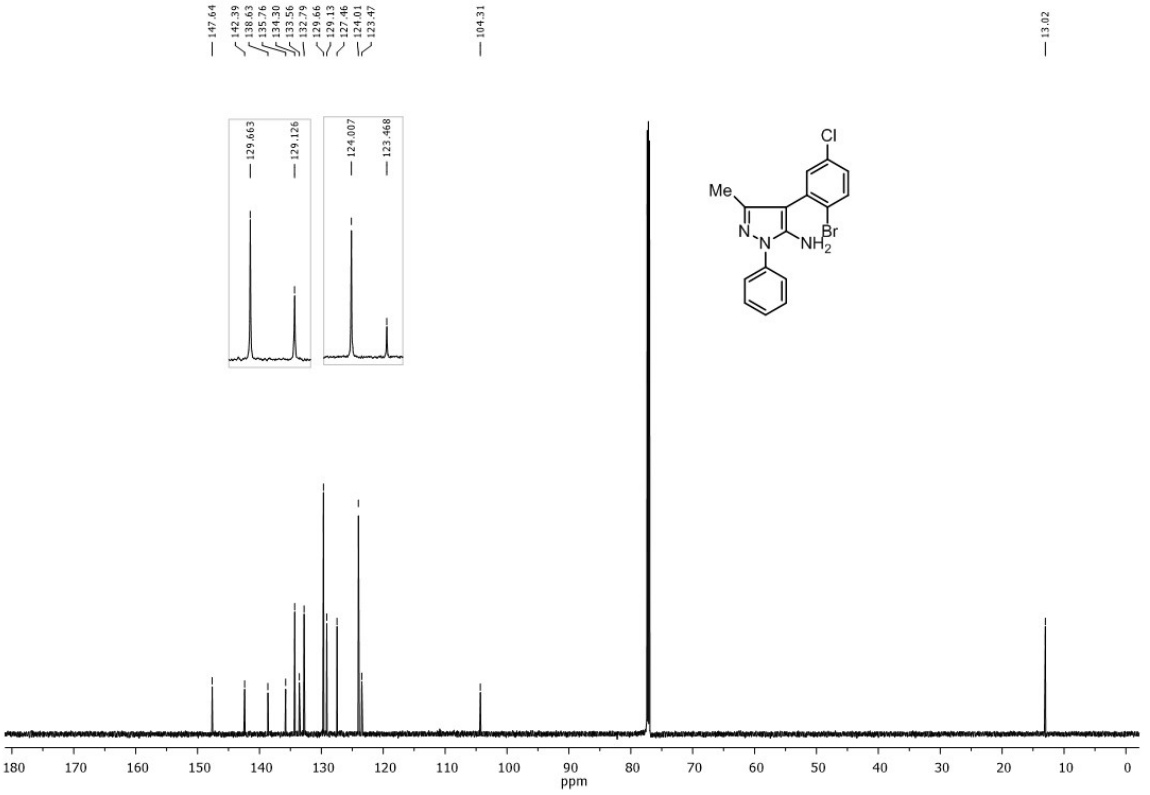
^{1}H Spectra of compound **2a** in $CDCl_3$ (400 MHz)



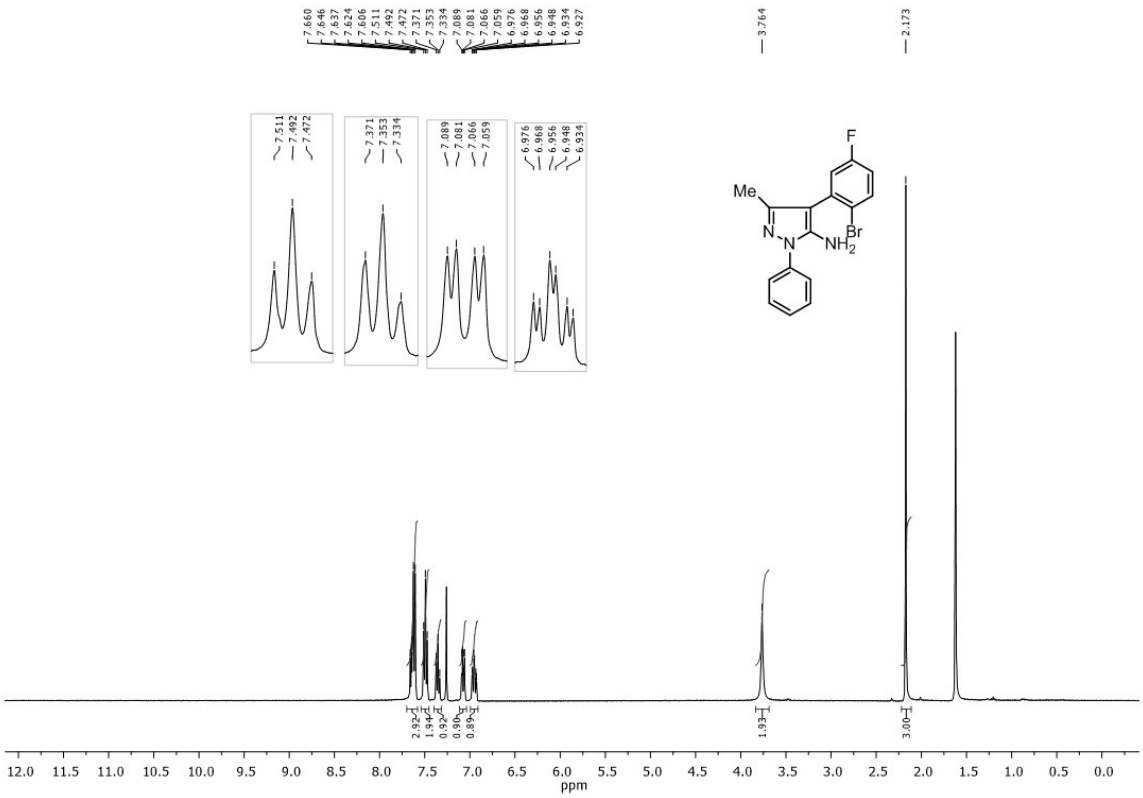
^{13}C Spectra of compound **2a** in $CDCl_3$ (100 MHz)



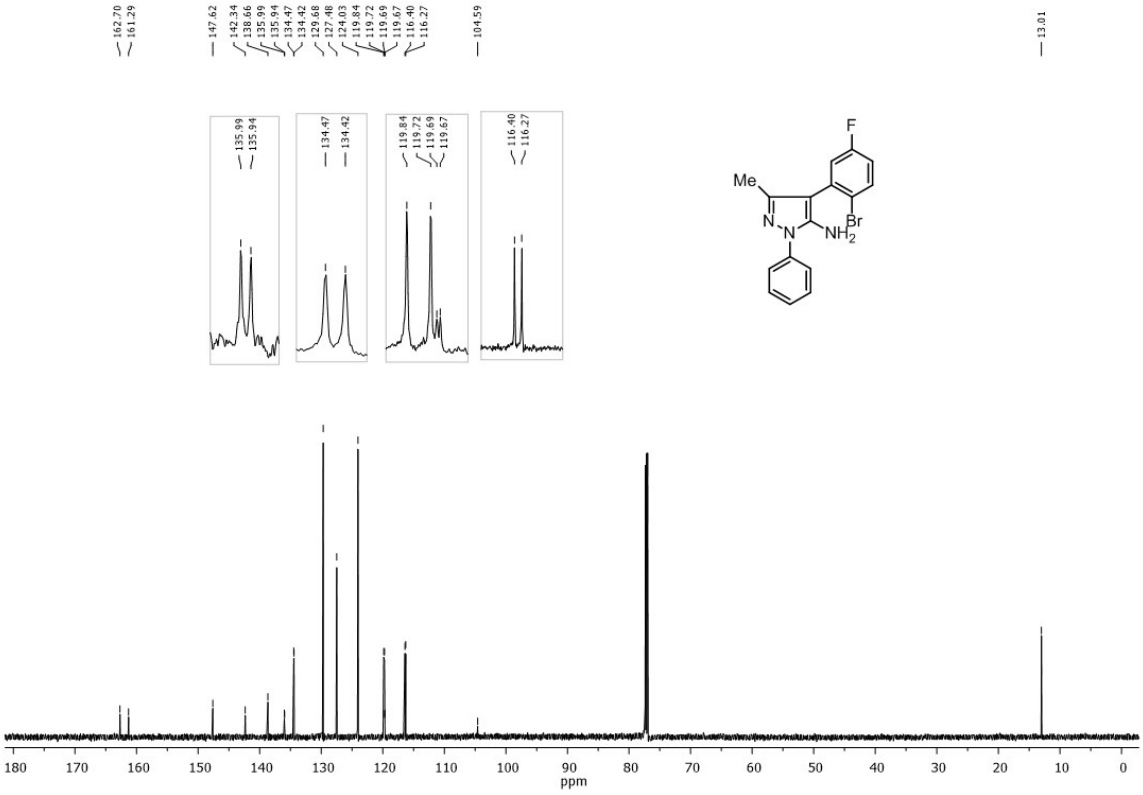
^{1}H Spectra of compound **2b** in $CDCl_3$ (400 MHz)



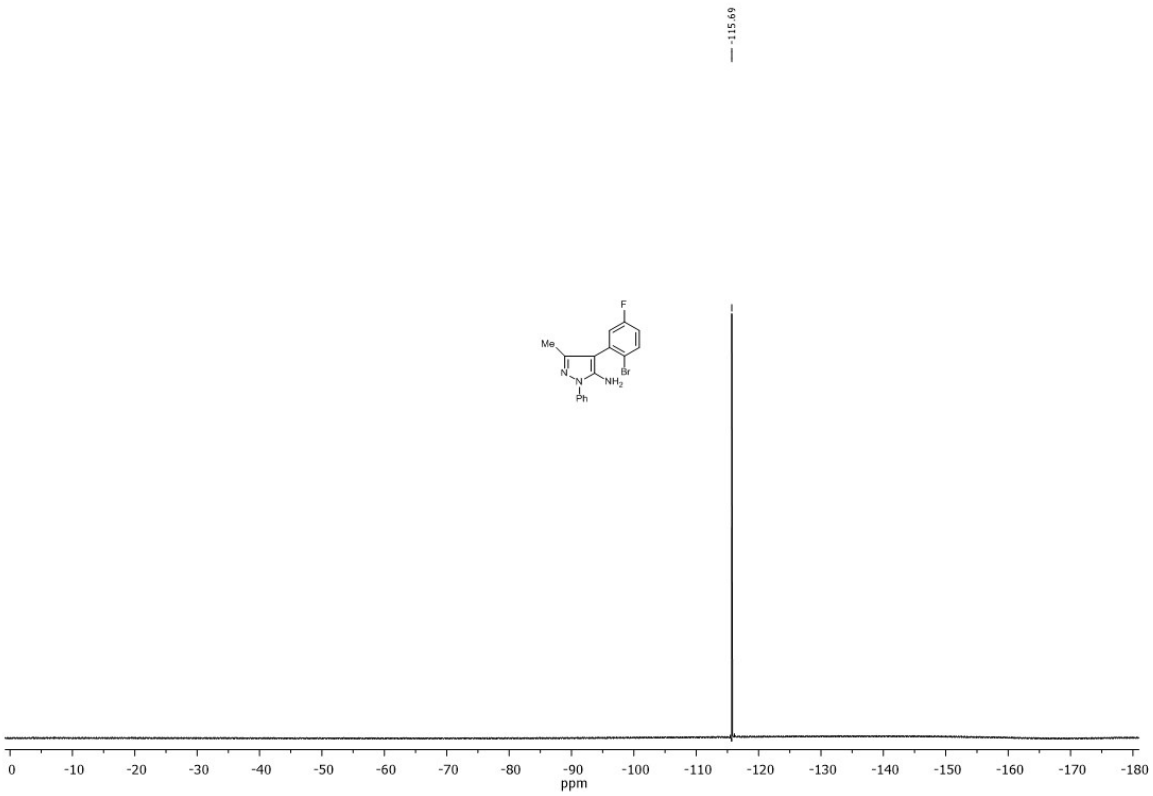
^{13}C Spectra of compound **2b** in $CDCl_3$ (175 MHz)



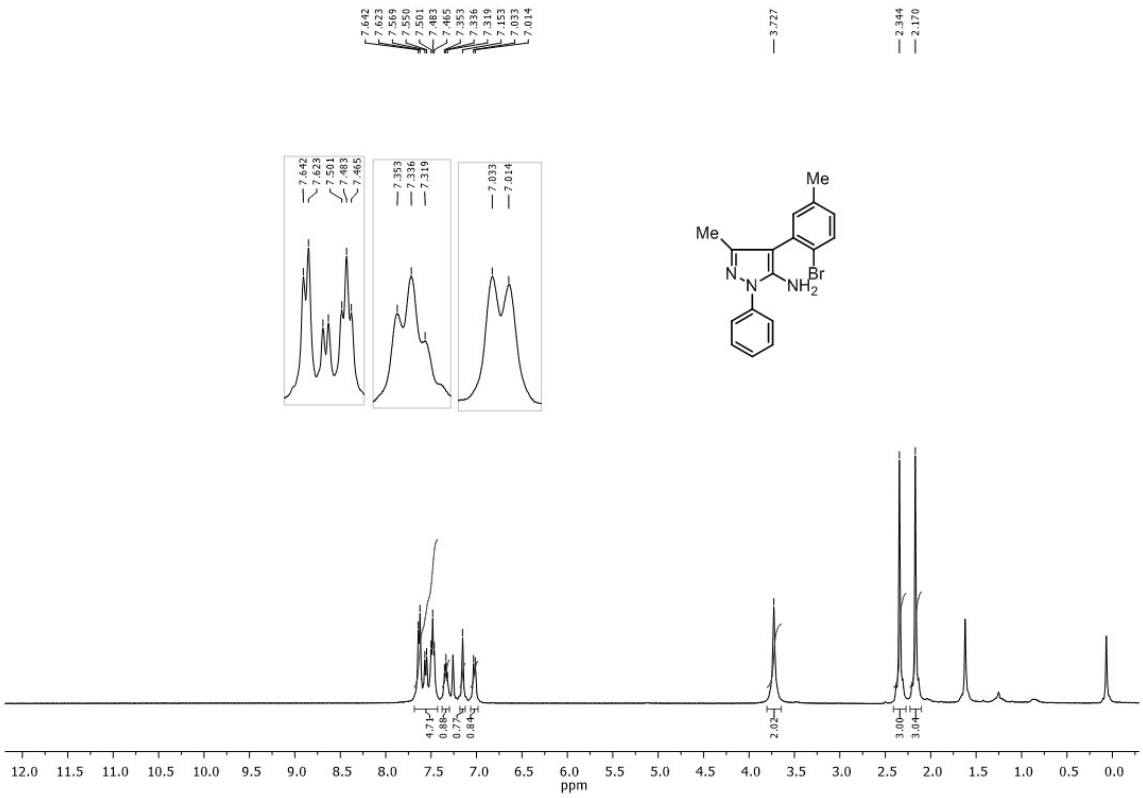
^{1}H Spectra of compound **2c** in $CDCl_3$ (400 MHz)



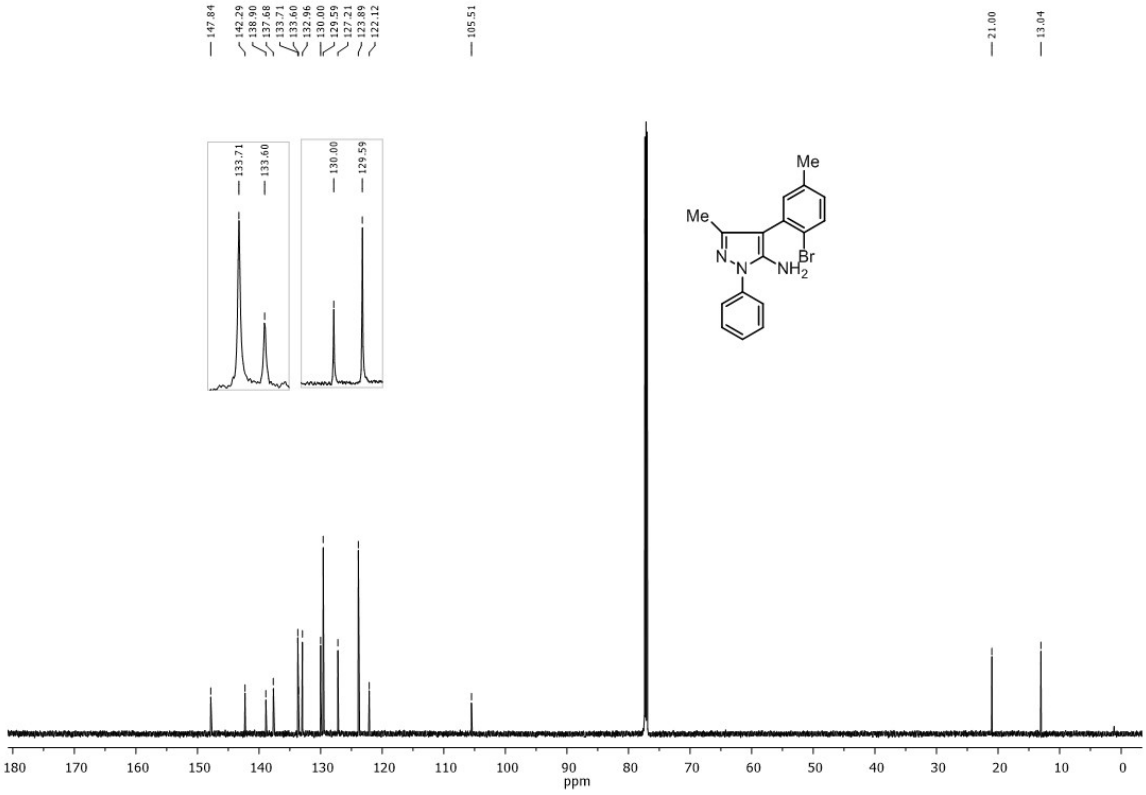
^{13}C Spectra of compound **2c** in $CDCl_3$ (175 MHz)



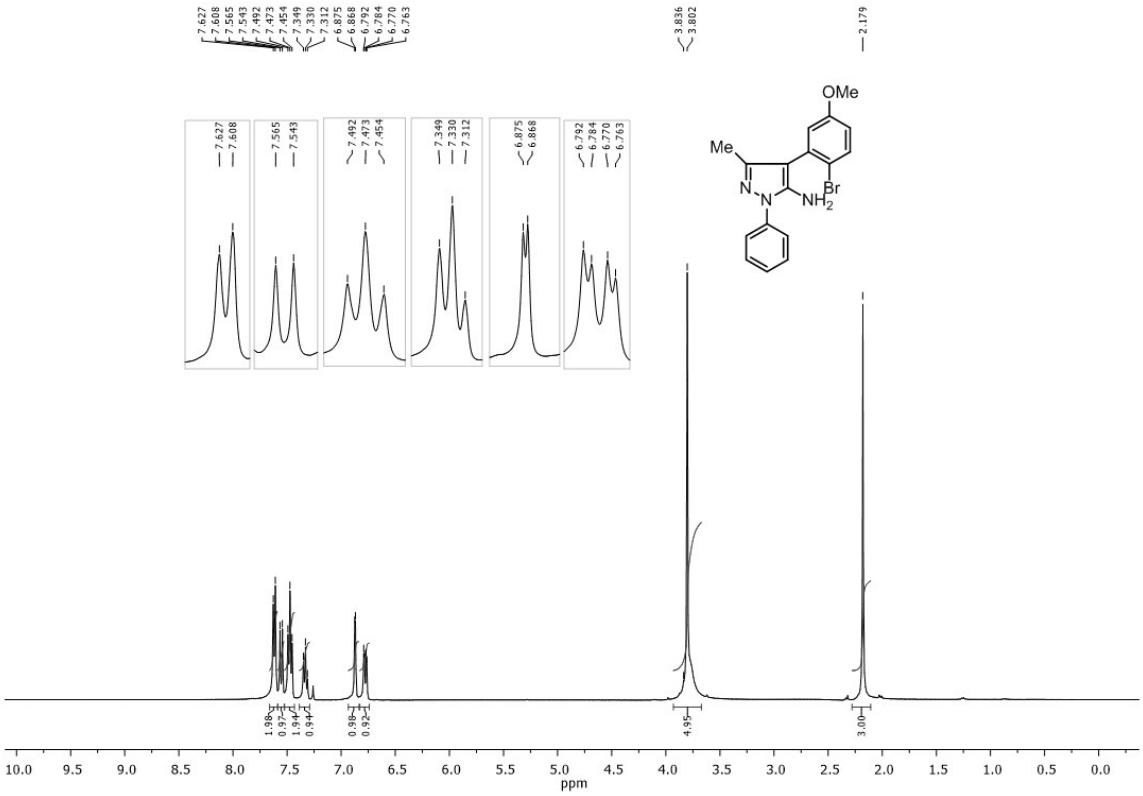
^{19}F Spectra of compound **2c** in $CDCl_3$ (377 MHz)



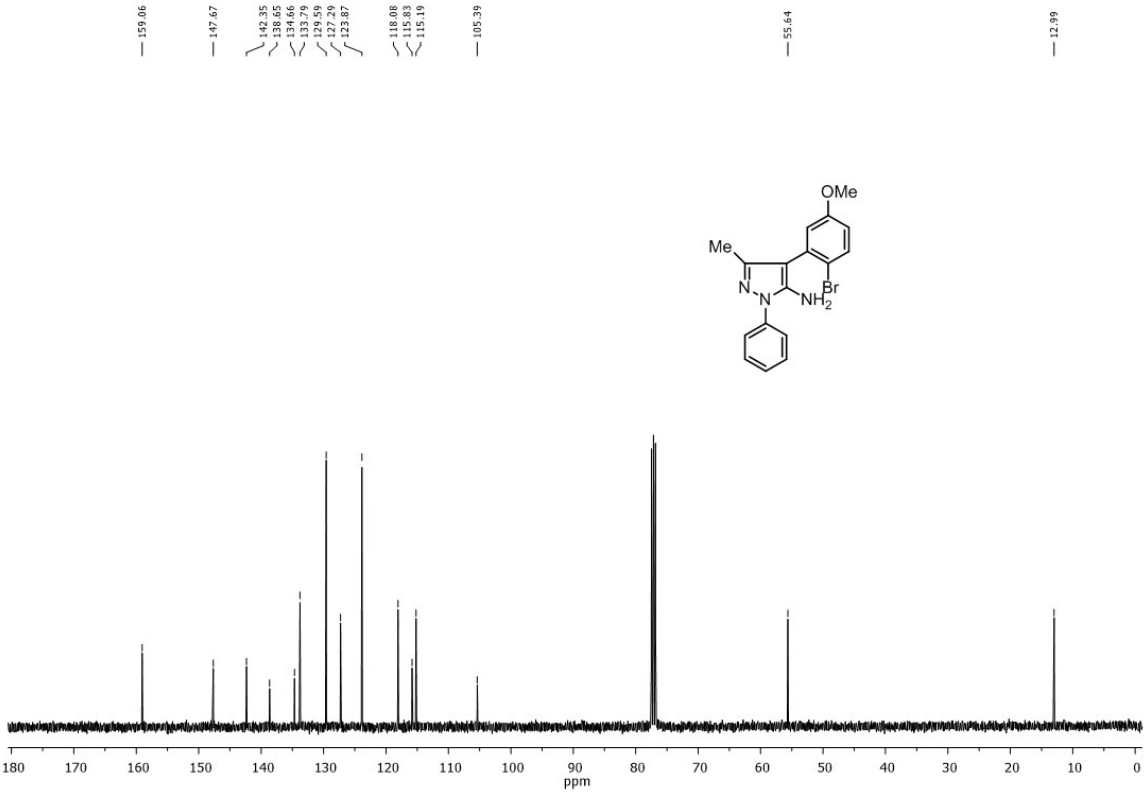
^{1}H Spectra of compound **2d** in $CDCl_3$ (400 MHz)



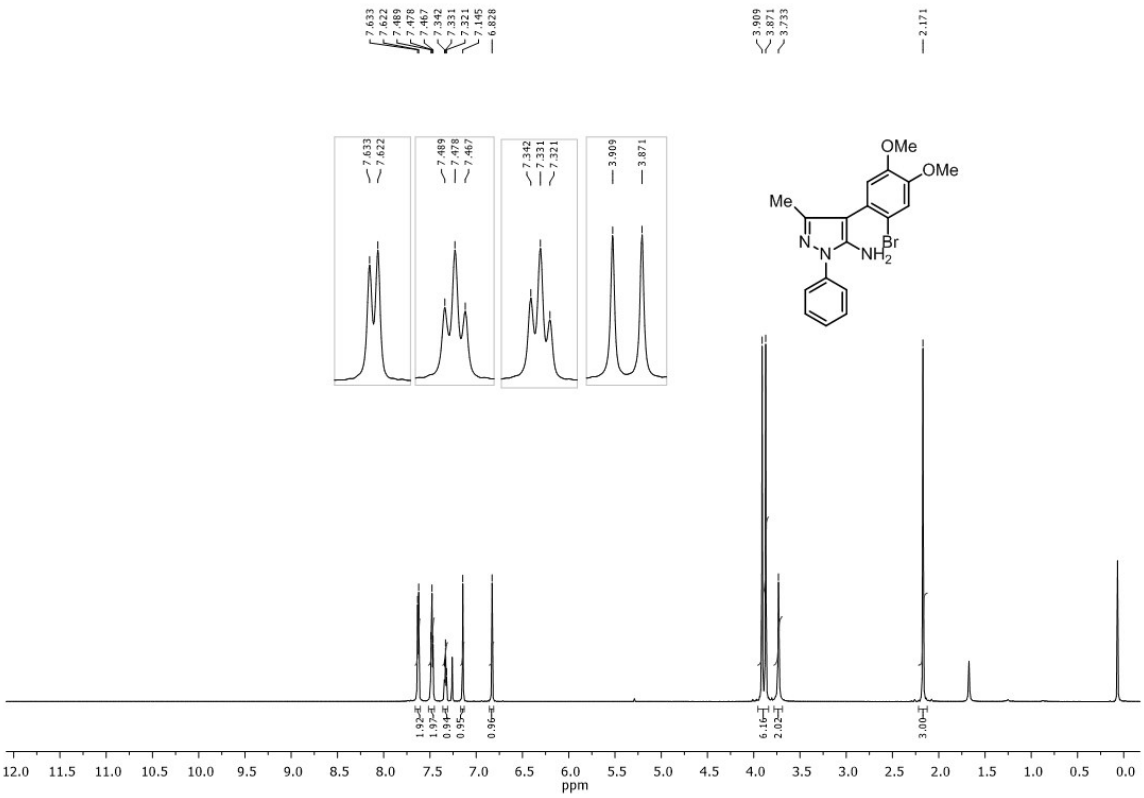
^{13}C Spectra of compound **2d** in $CDCl_3$ (175 MHz)



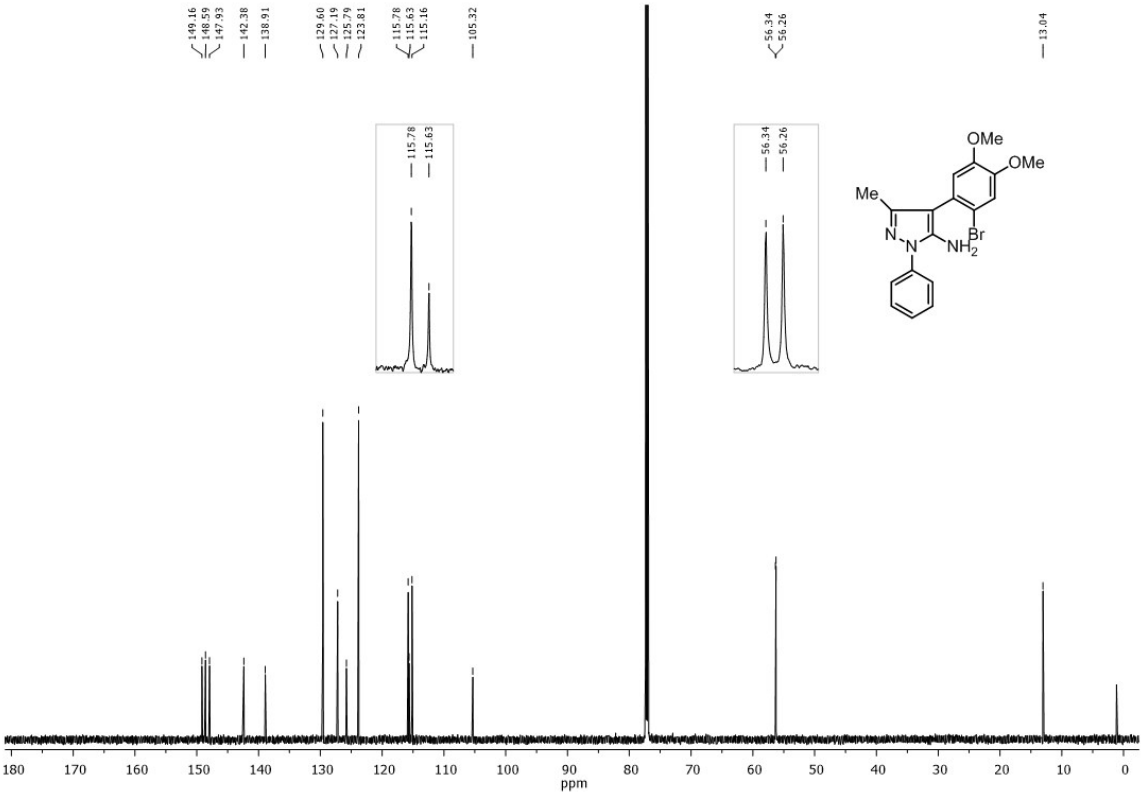
^{1}H Spectra of compound **2e** in $CDCl_3$ (400 MHz)



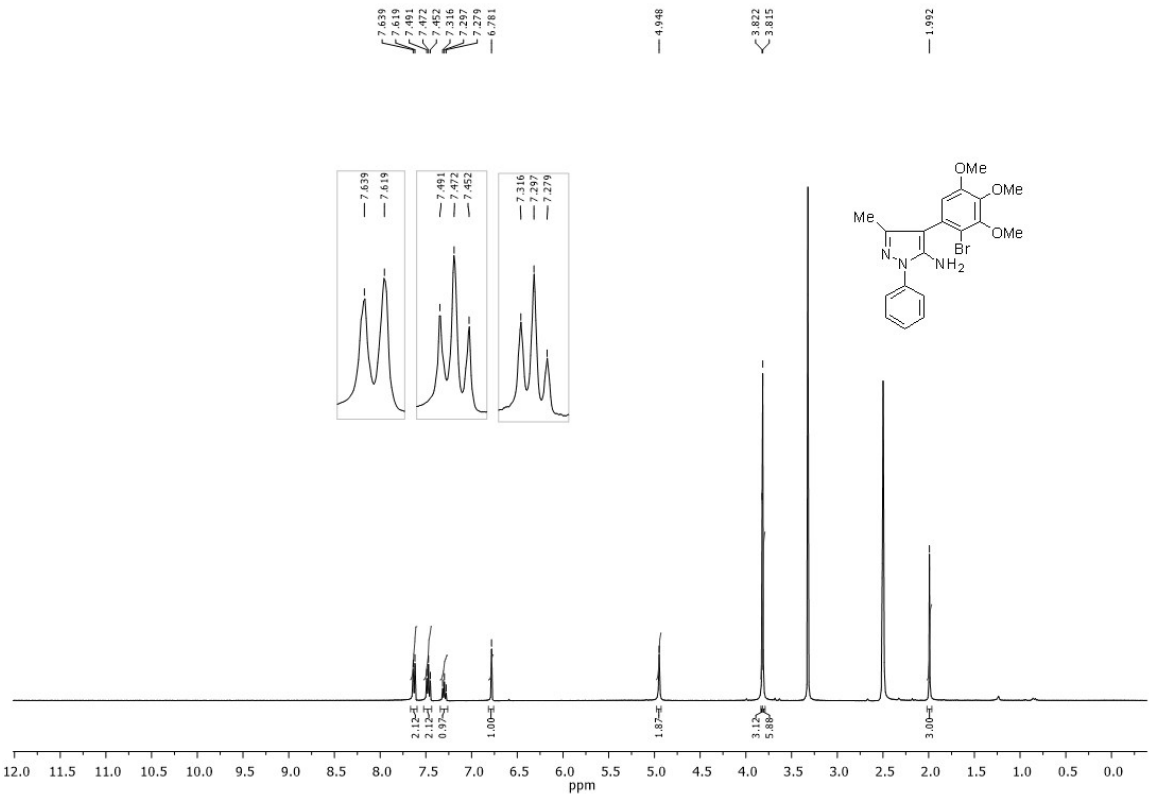
^{13}C Spectra of compound **2e** in $CDCl_3$ (100 MHz)



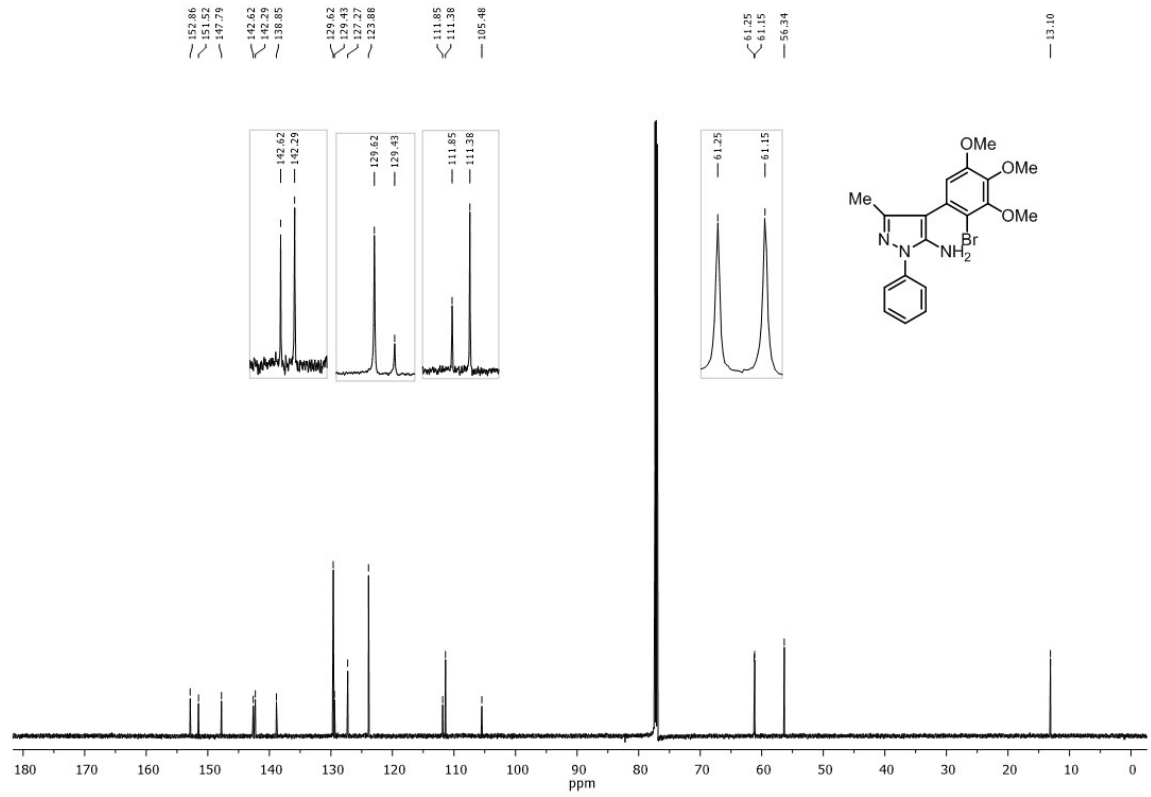
^{1}H Spectra of compound **2f** in $CDCl_3$ (700 MHz)



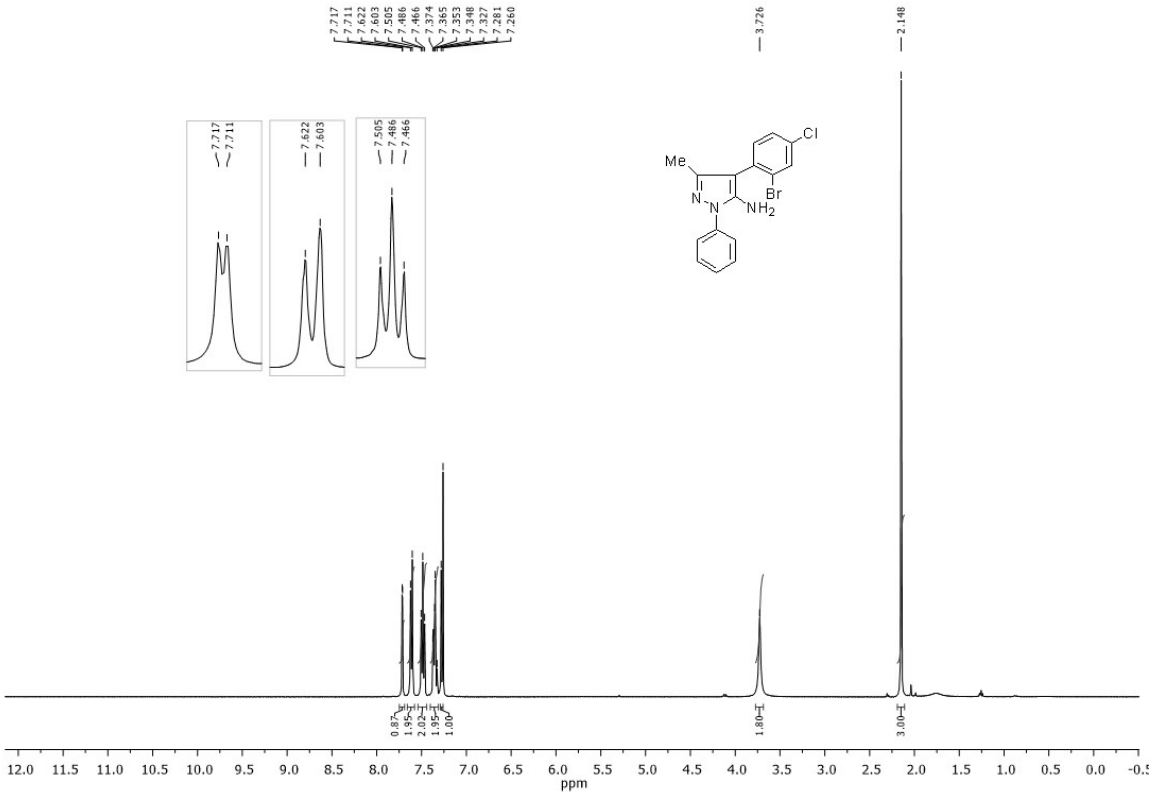
^{13}C Spectra of compound **2f** in $CDCl_3$ (175 MHz)



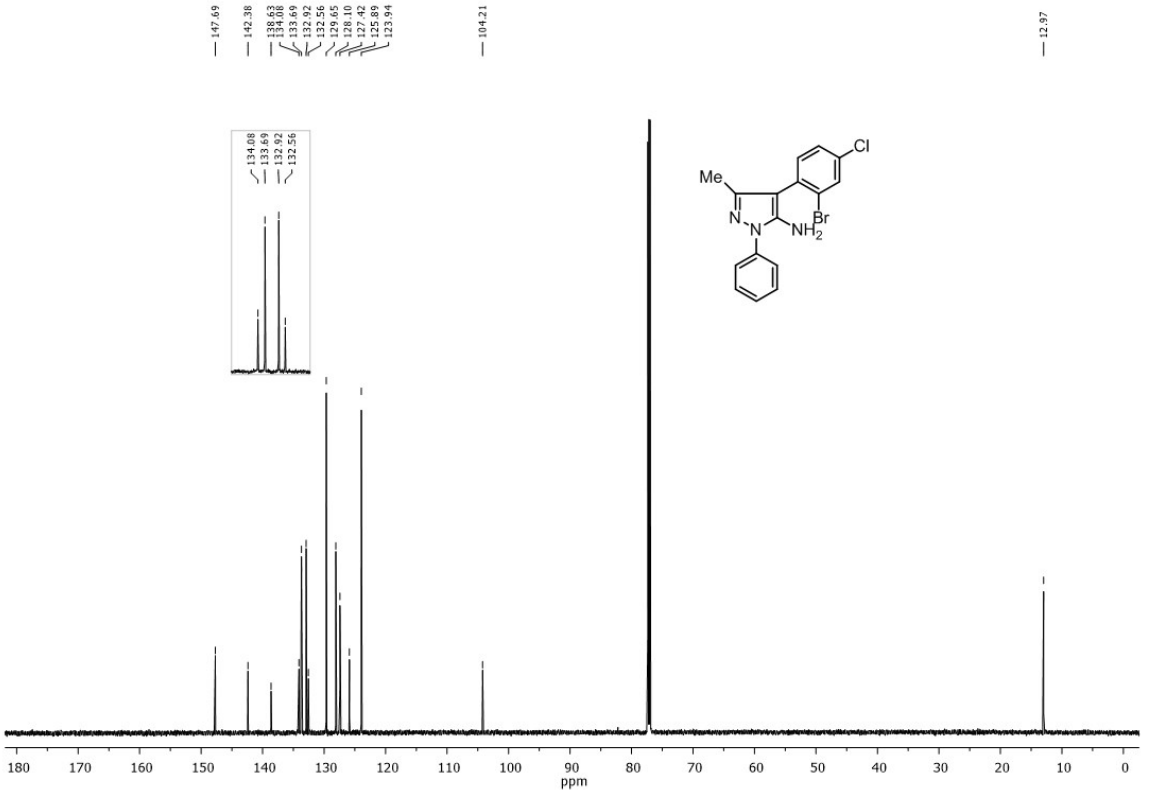
^{1}H Spectra of compound **2g** in DMSO-d_6 (400 MHz)



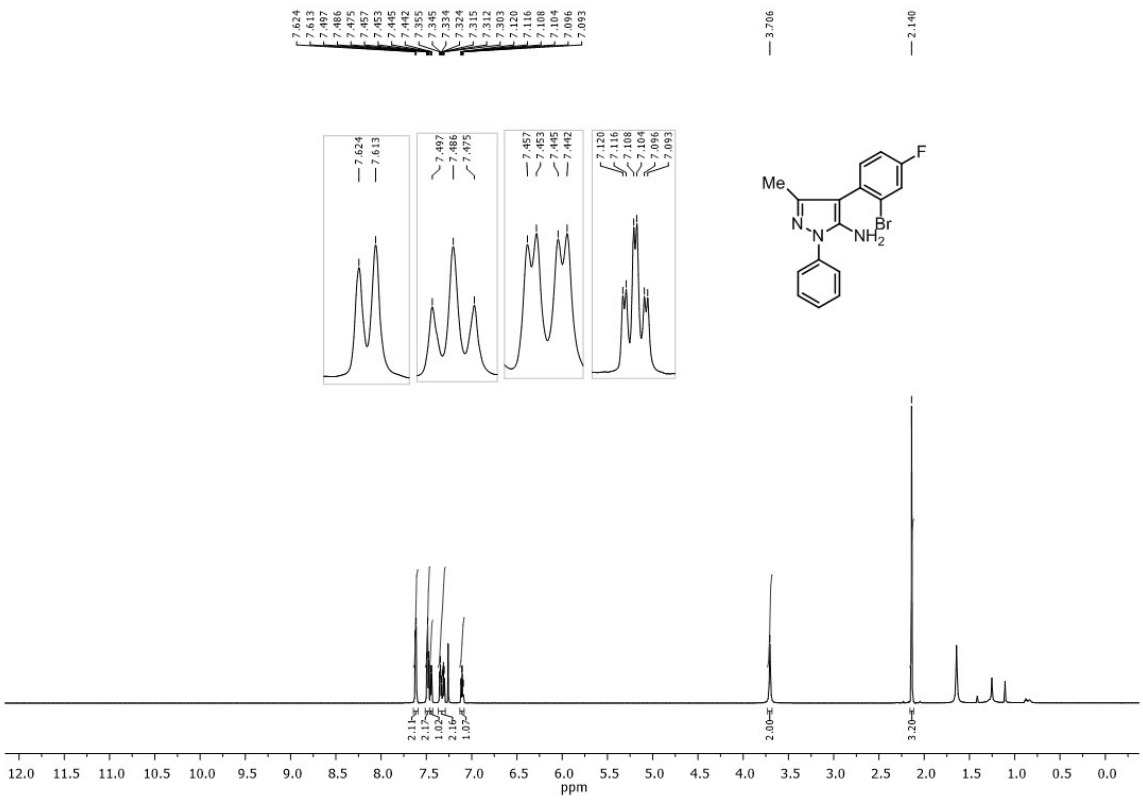
^{13}C Spectra of compound **2g** in $CDCl_3$ (175 MHz)



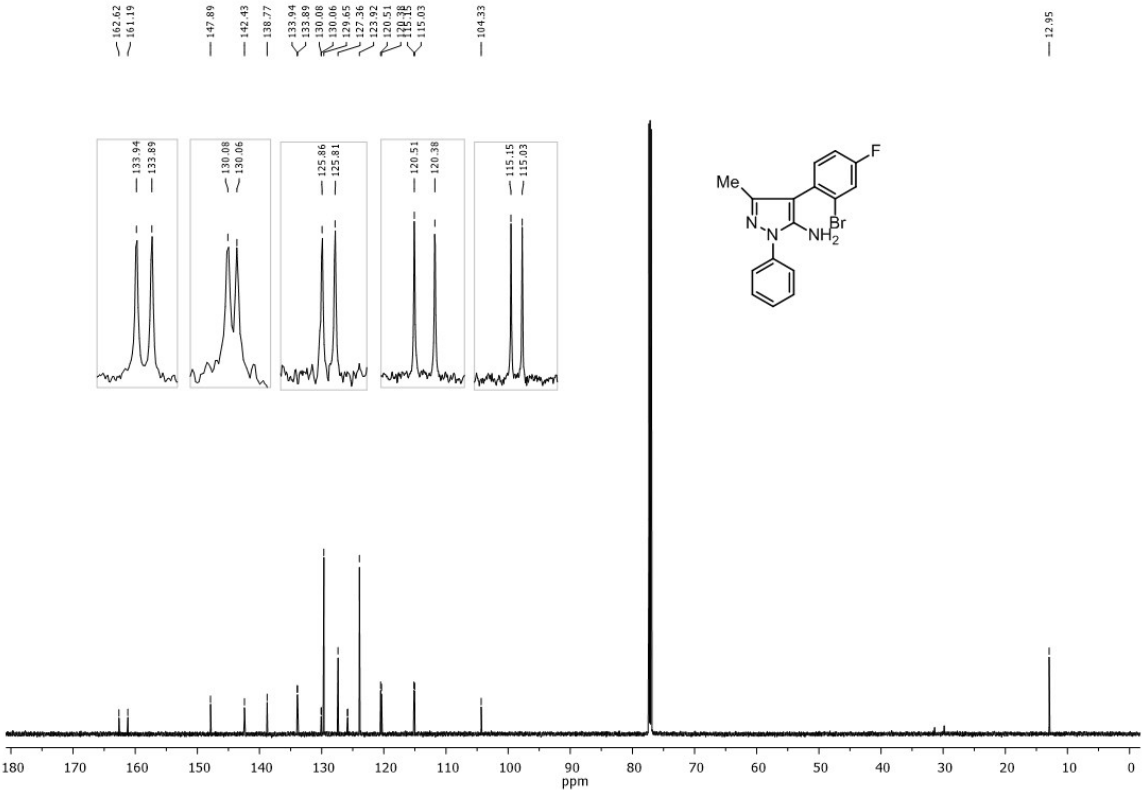
^{1}H Spectra of compound **2h** in $CDCl_3$ (400 MHz)



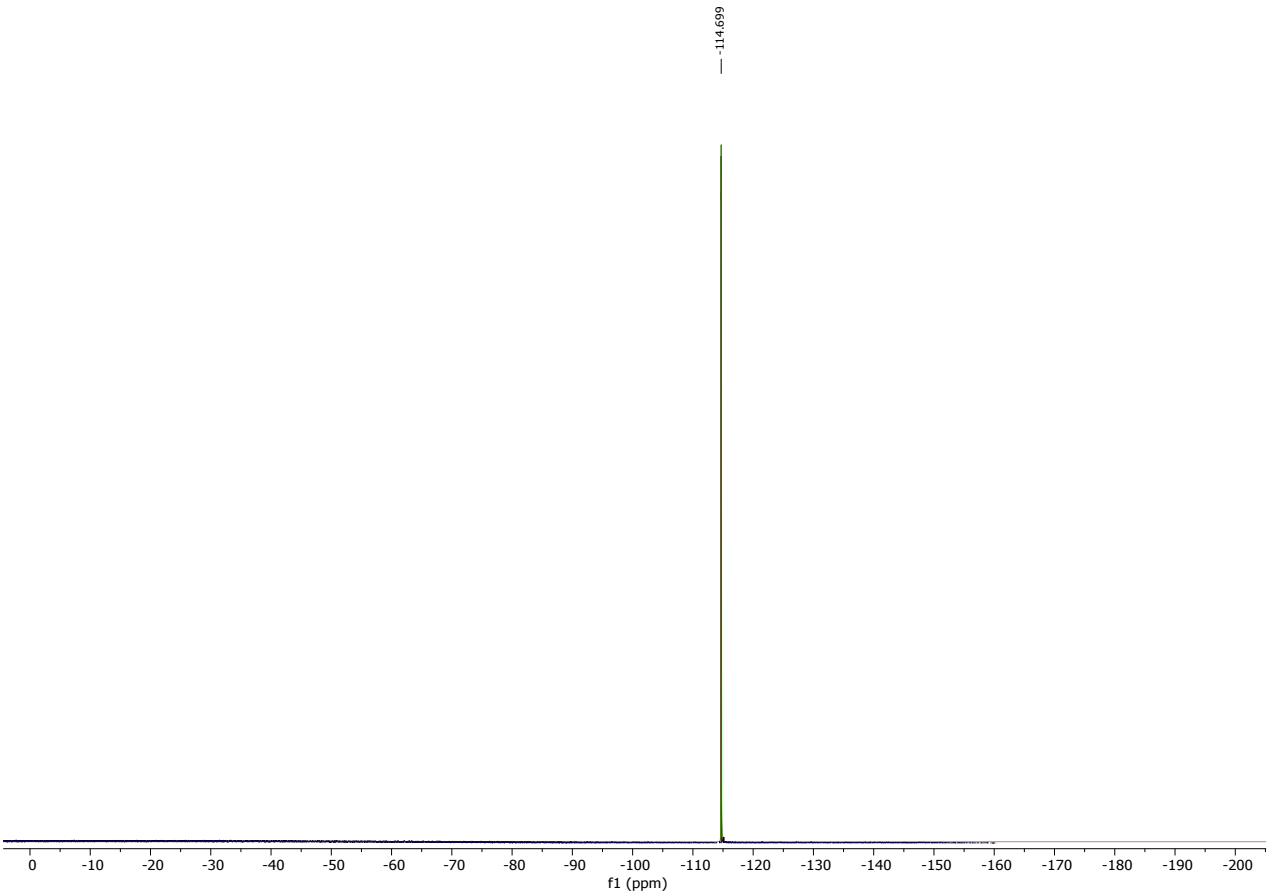
^{13}C Spectra of compound **2h** in $CDCl_3$ (175 MHz)



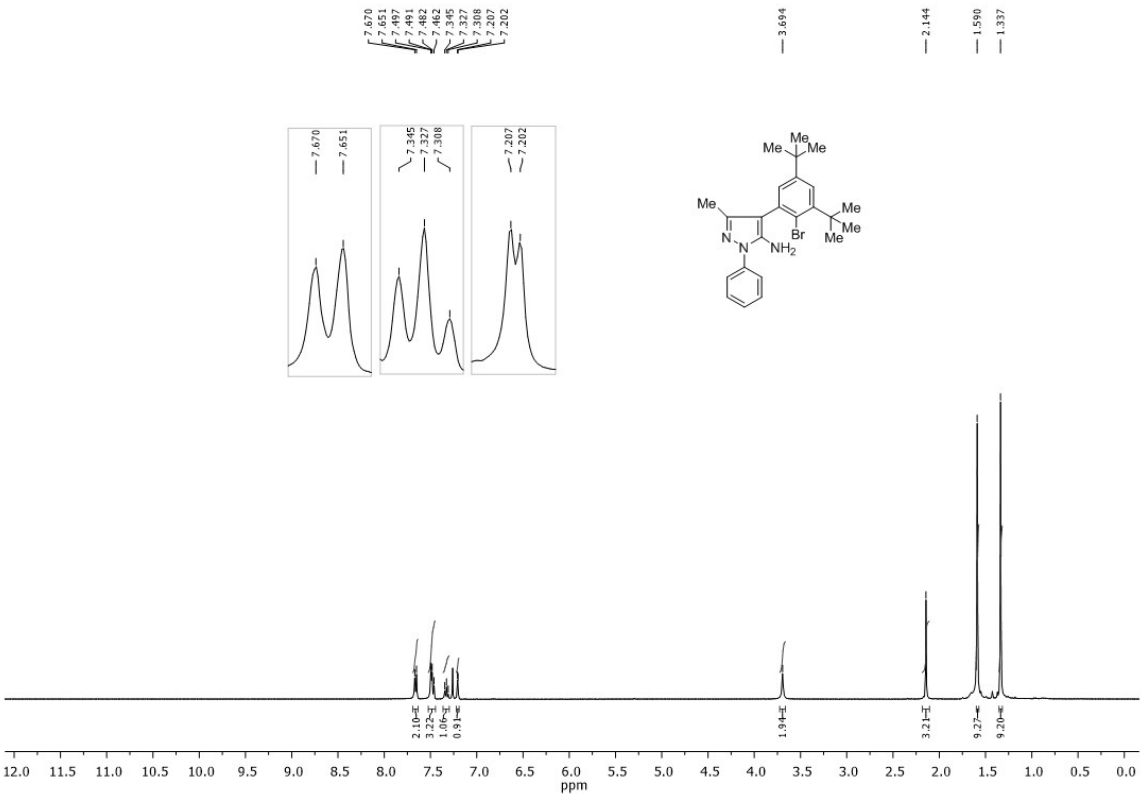
^{1}H Spectra of compound **2i** in $CDCl_3$ (700 MHz)



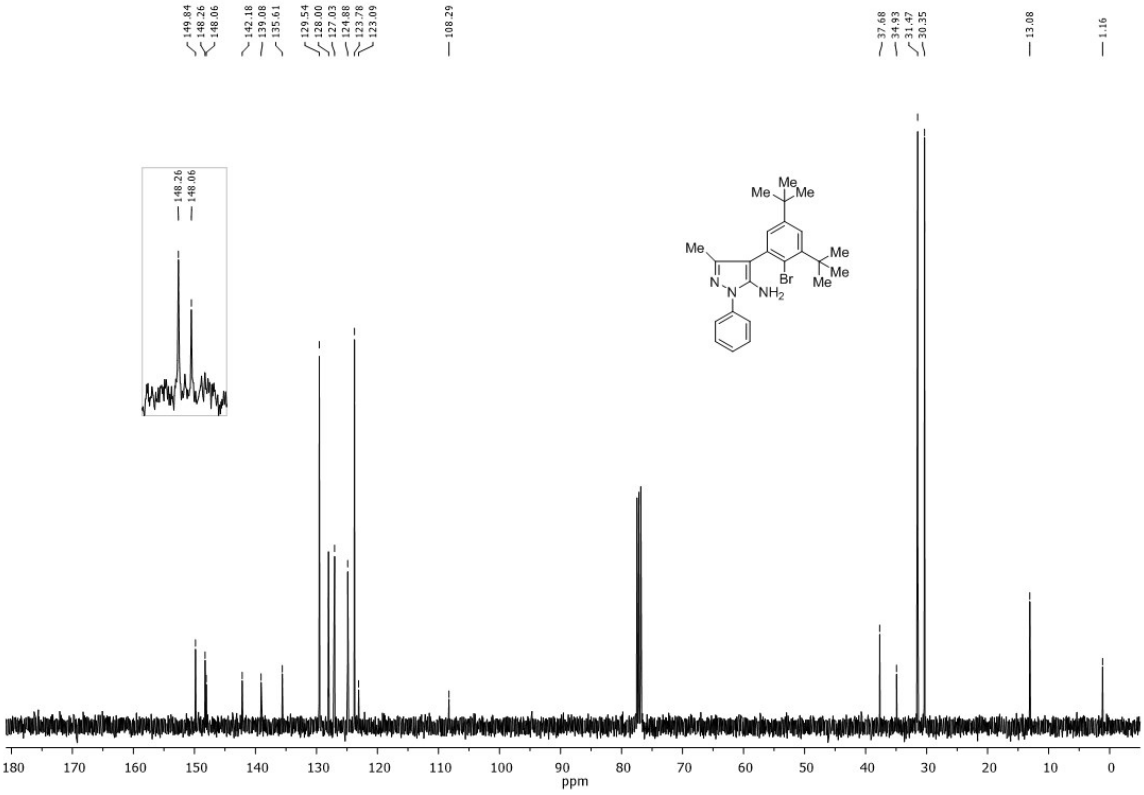
^{13}C Spectra of compound **2i** in $CDCl_3$ (175 MHz)



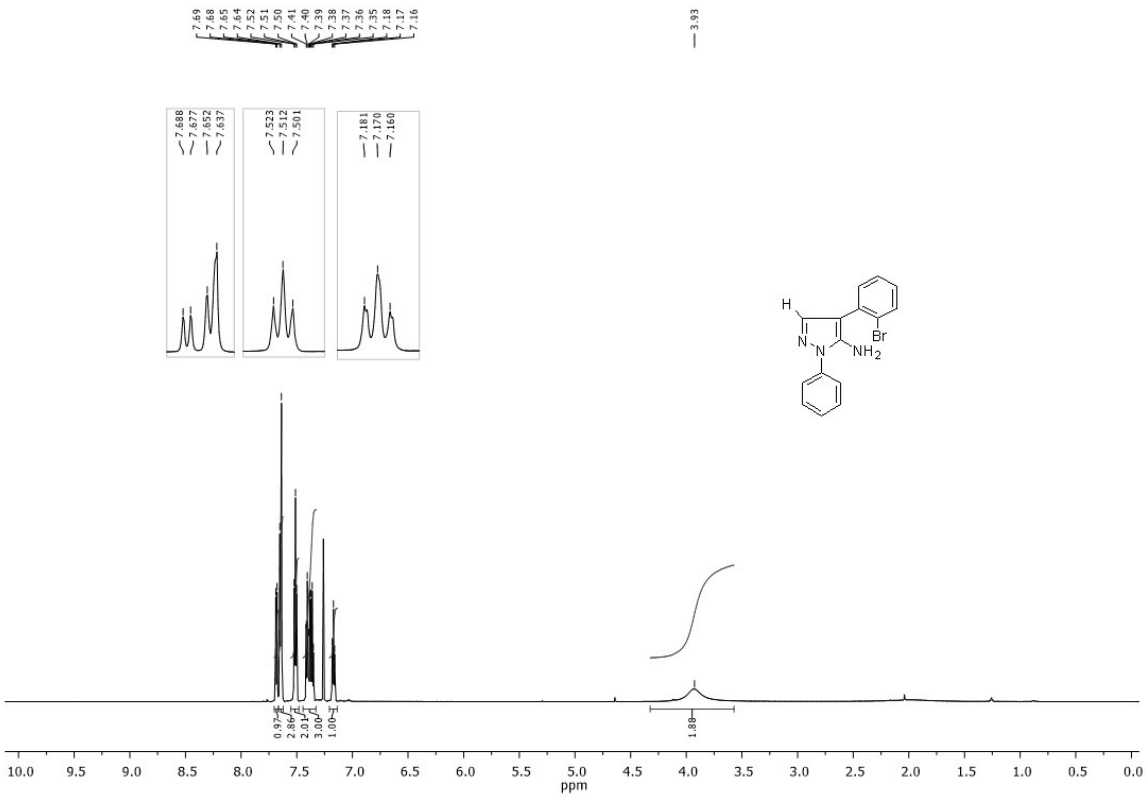
^{19}F Spectra of compound **2i** in DMSO-d_6 (376 MHz)



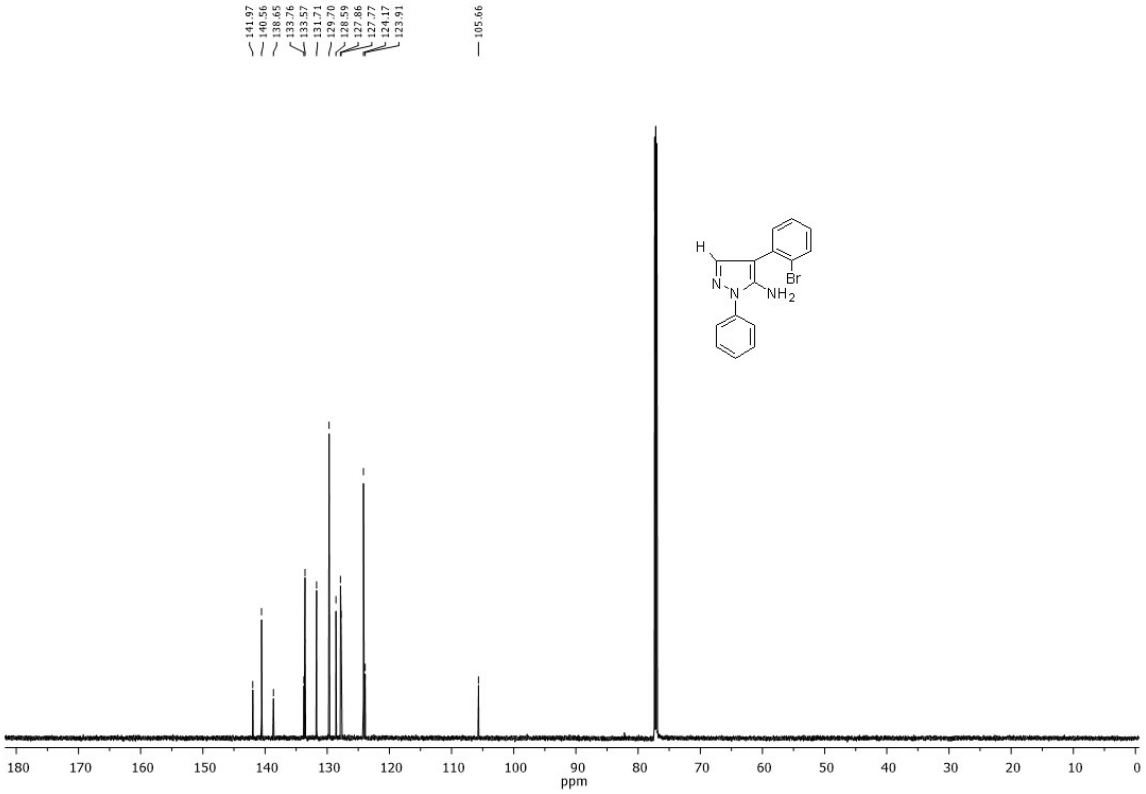
^{1}H Spectra of compound **2j** in $CDCl_3$ (400 MHz)



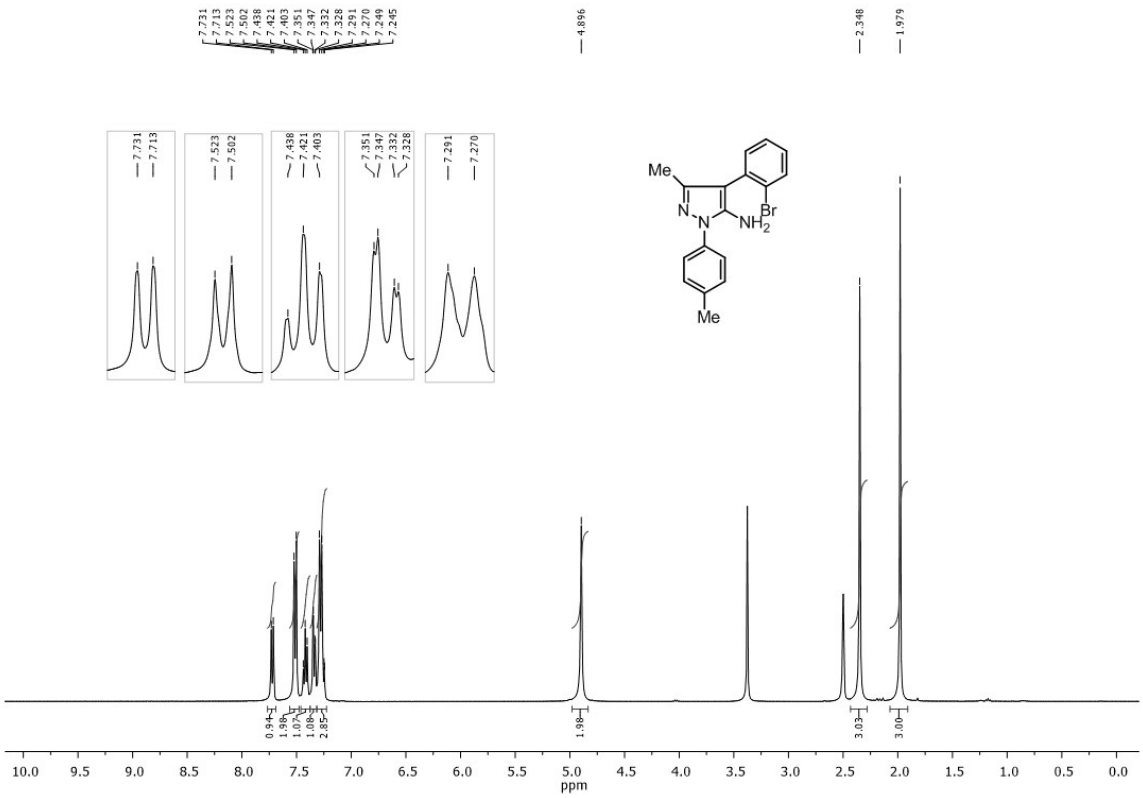
^{13}C Spectra of compound **2j** in $CDCl_3$ (100 MHz)



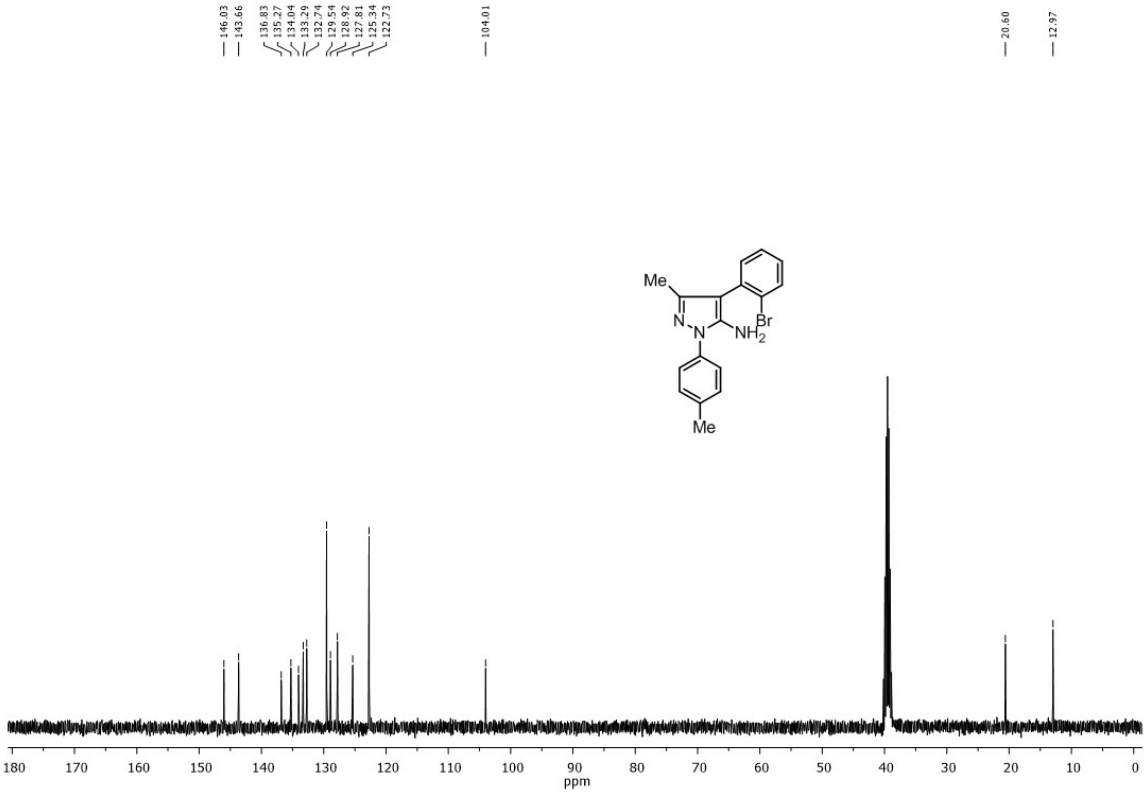
^{1}H Spectra of compound **2k** in $CDCl_3$ (700 MHz)



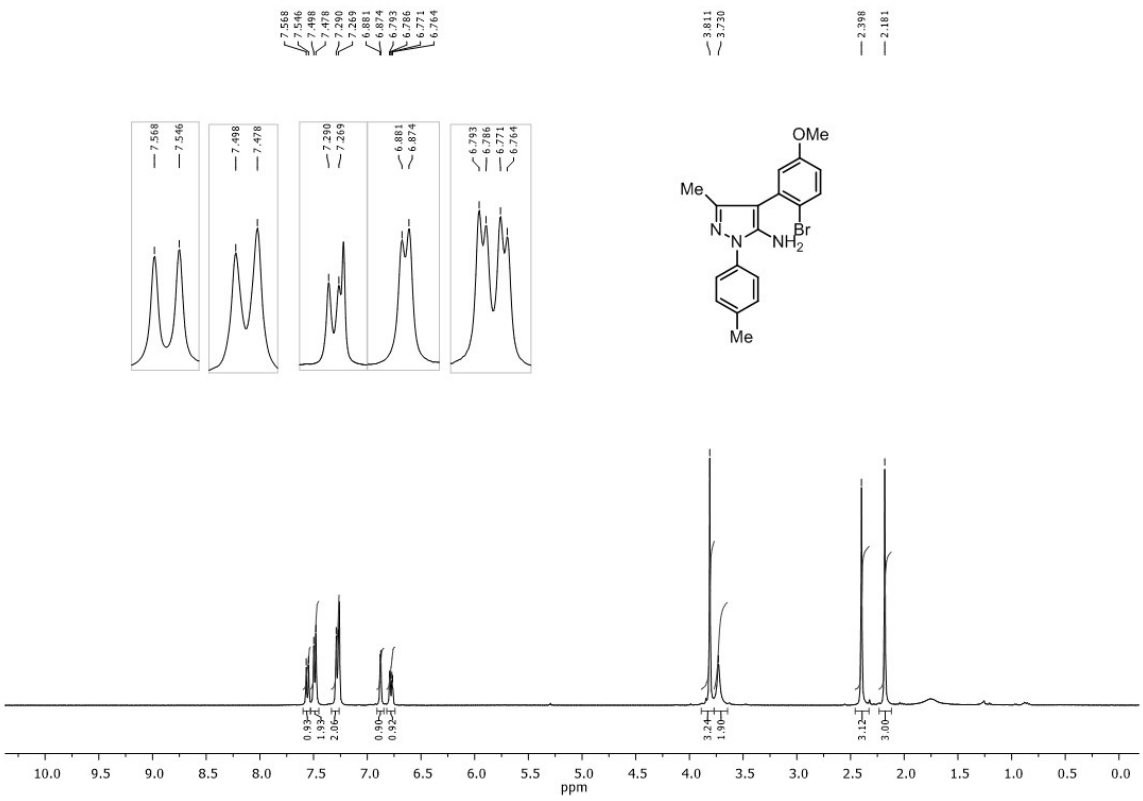
^{13}C Spectra of compound **2k** in $CDCl_3$ (175 MHz)



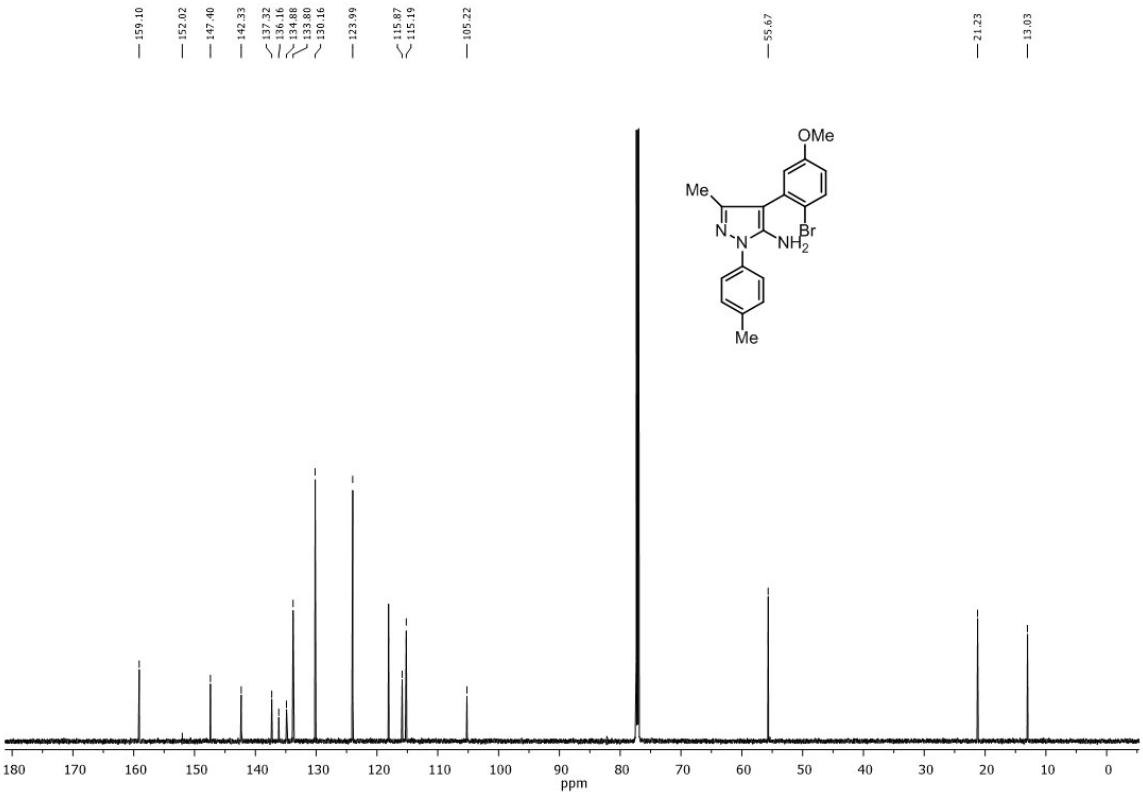
^{1}H Spectra of compound **2l** in DMSO-d_6 (400 MHz)



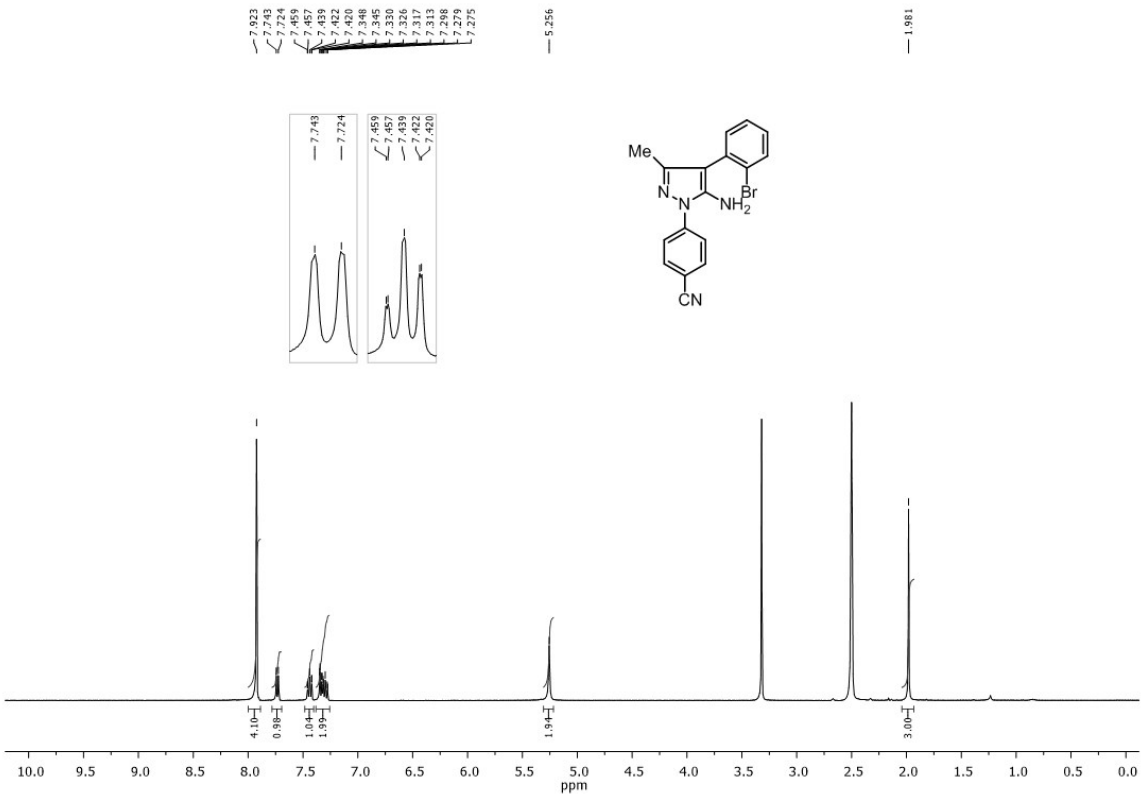
^{13}C Spectra of compound **2l** in DMSO-d_6 (100 MHz)



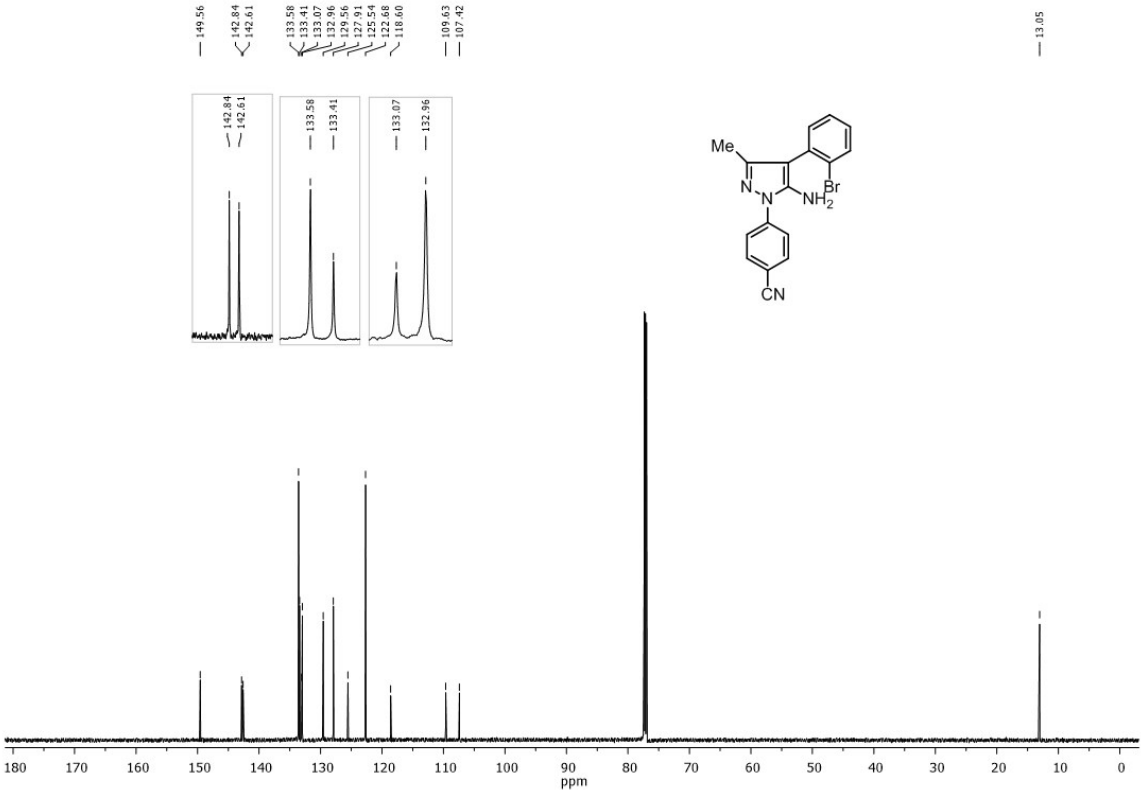
^{1}H Spectra of compound **2m** in $CDCl_3$ (400 MHz)



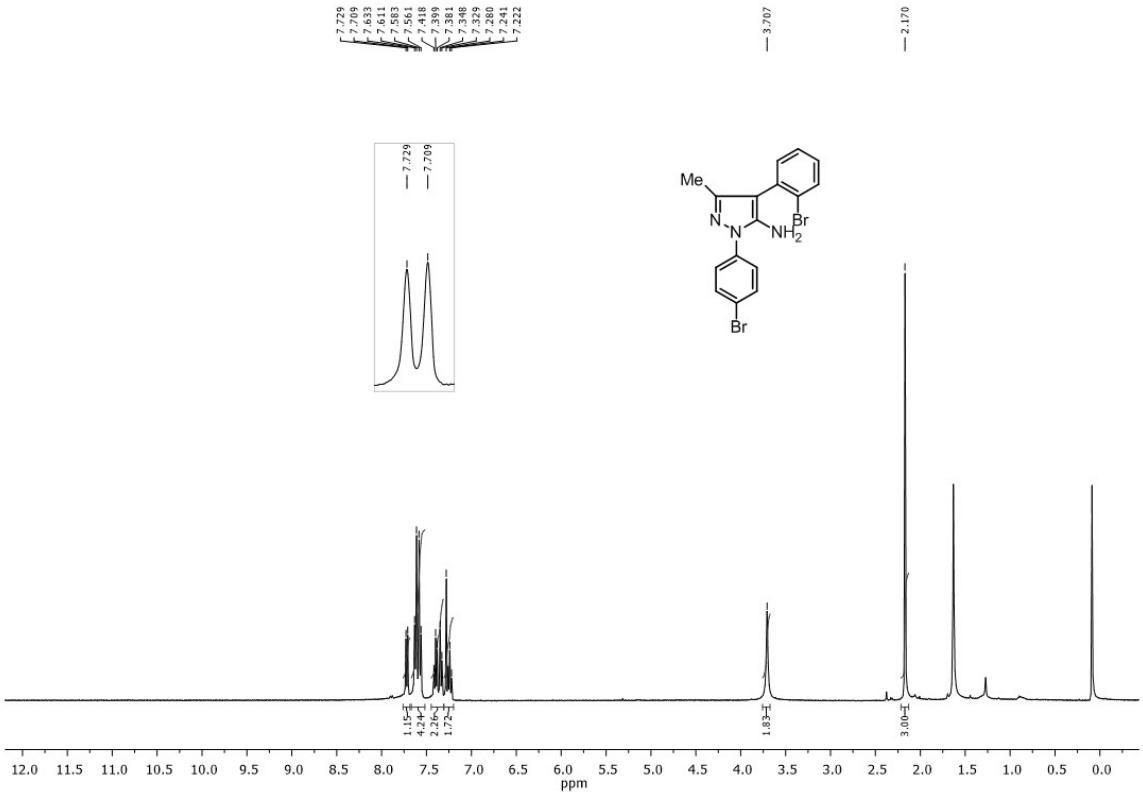
^{13}C Spectra of compound **2m** in $CDCl_3$ (175 MHz)



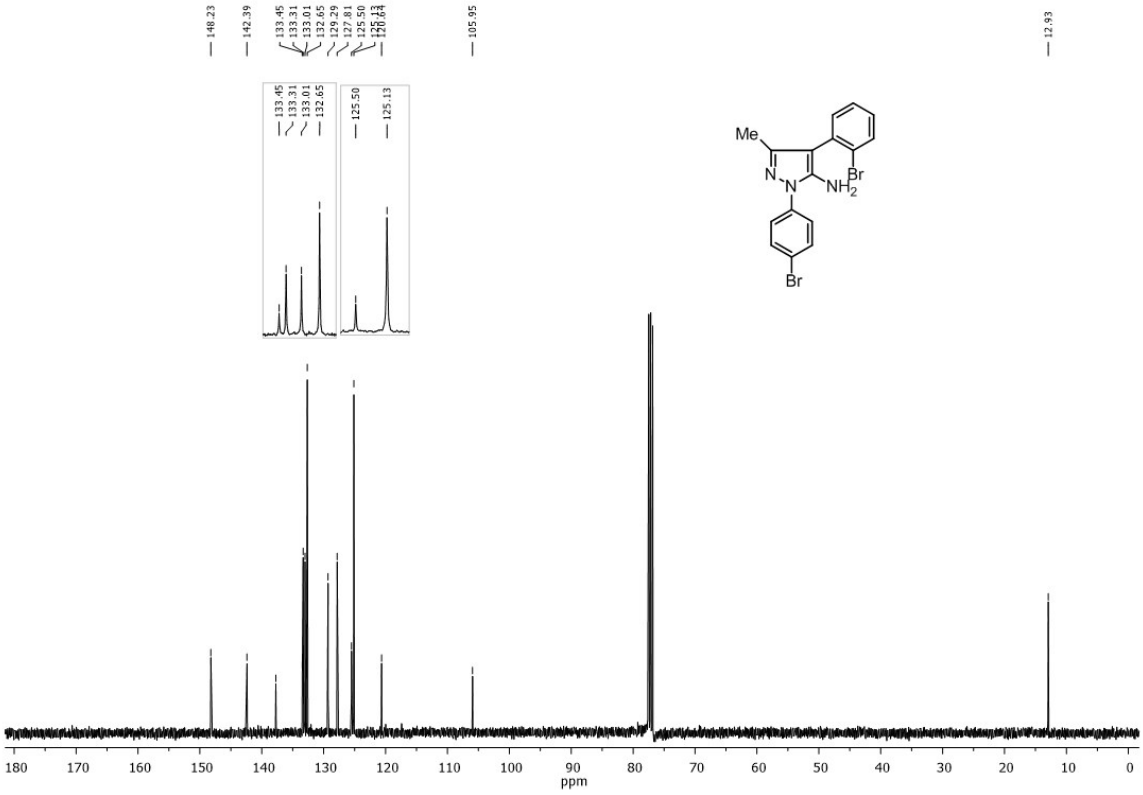
^{1}H Spectra of compound **2n** in DMSO-d_6 (400 MHz)



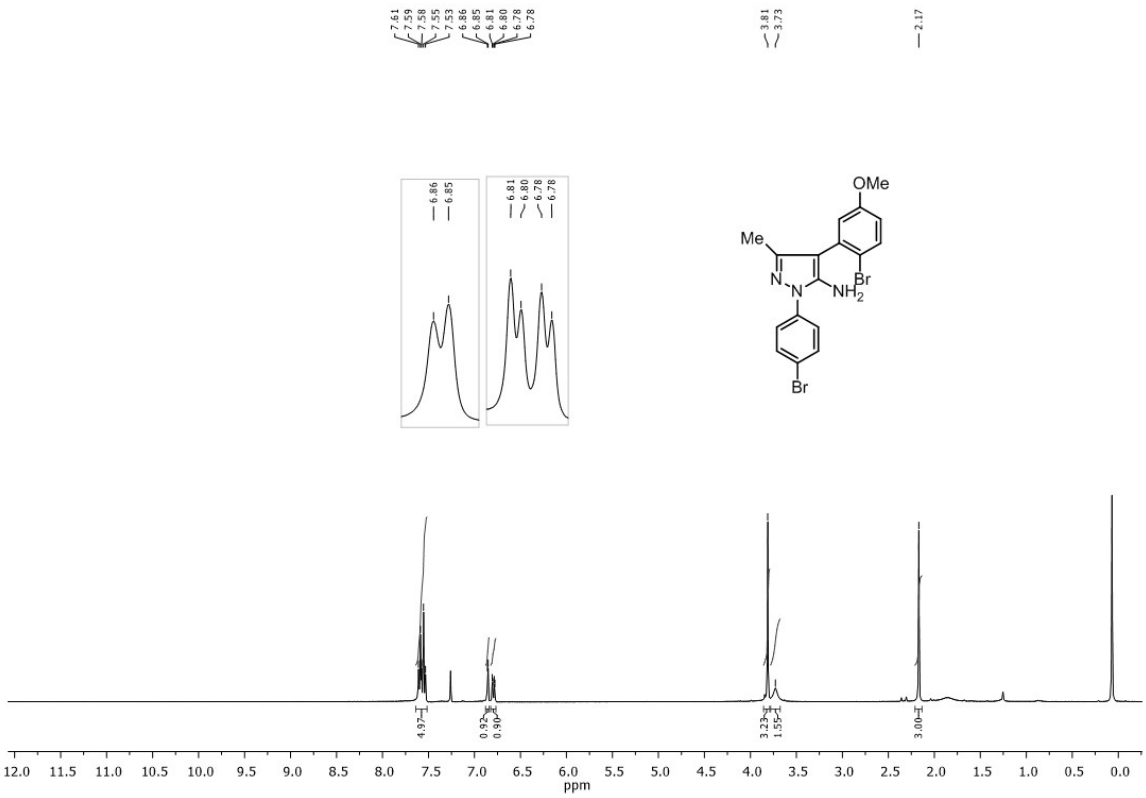
^{13}C Spectra of compound **2n** in $CDCl_3$ (175 MHz)



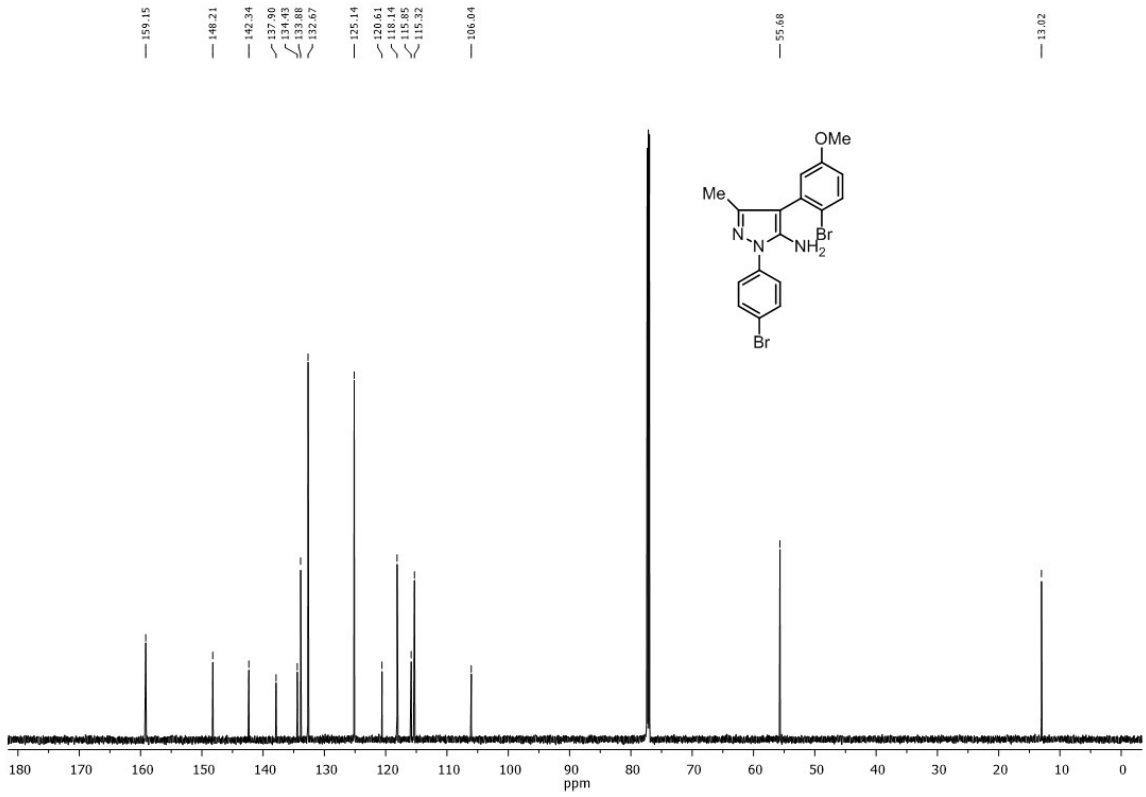
^{1}H Spectra of compound **2o** in $CDCl_3$ (400 MHz)



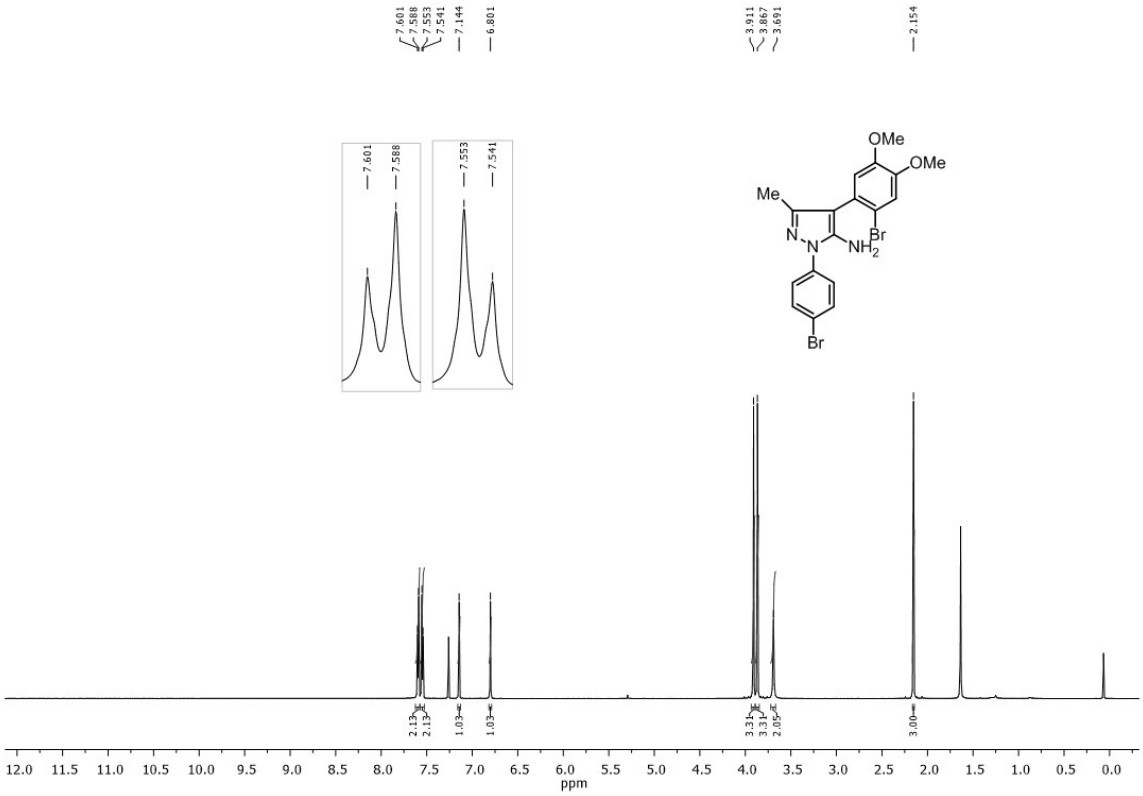
^{13}C Spectra of compound **2o** in $CDCl_3$ (100 MHz)



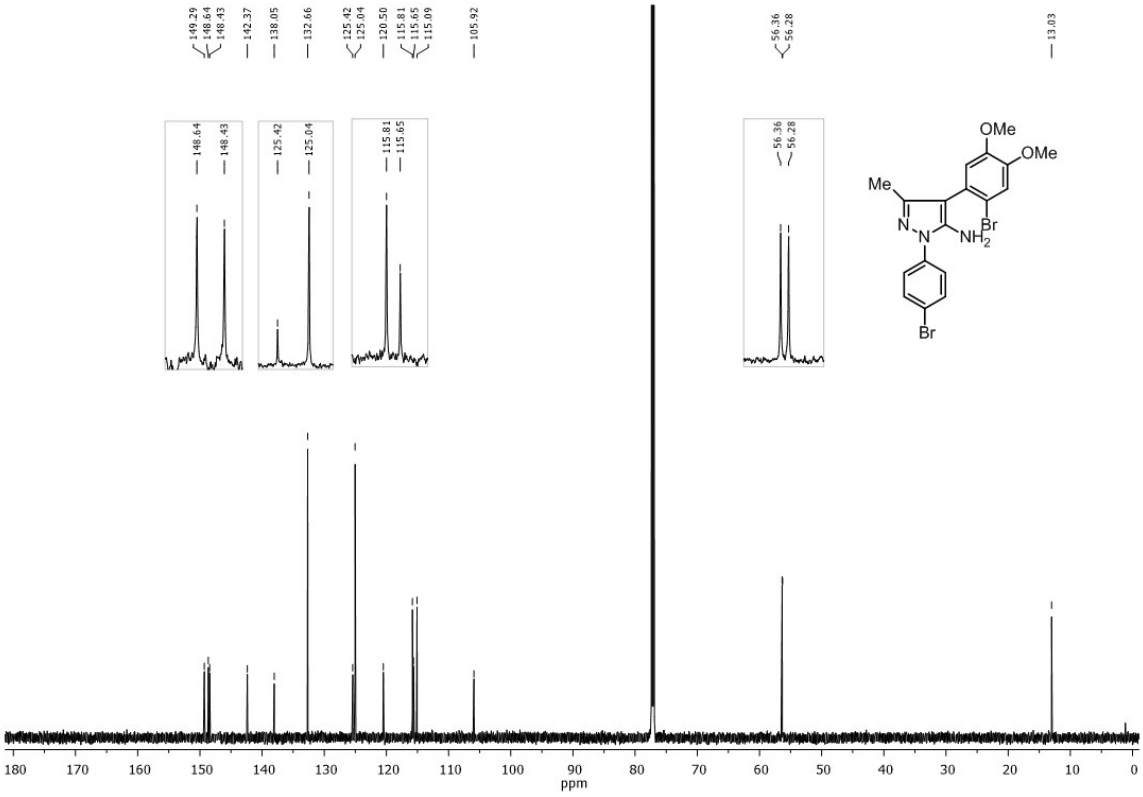
^{1}H Spectra of compound **2p** in $CDCl_3$ (400 MHz)



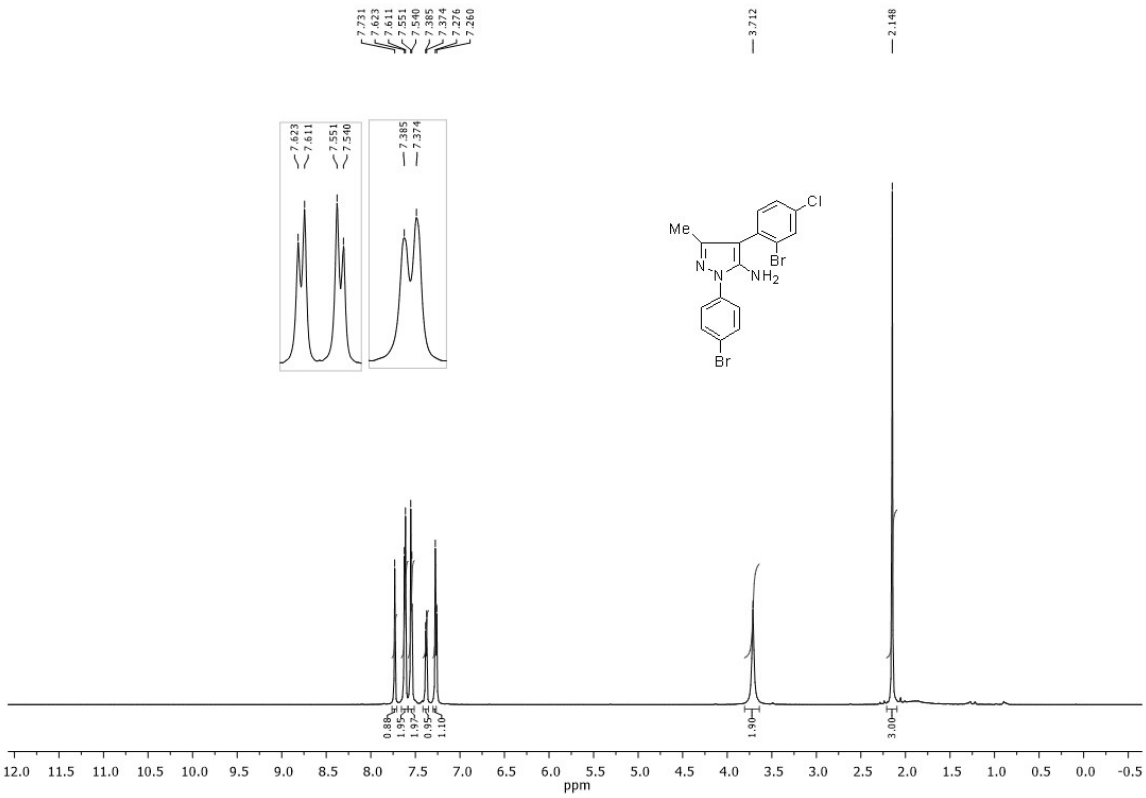
^{13}C Spectra of compound **2p** in $CDCl_3$ (175 MHz)



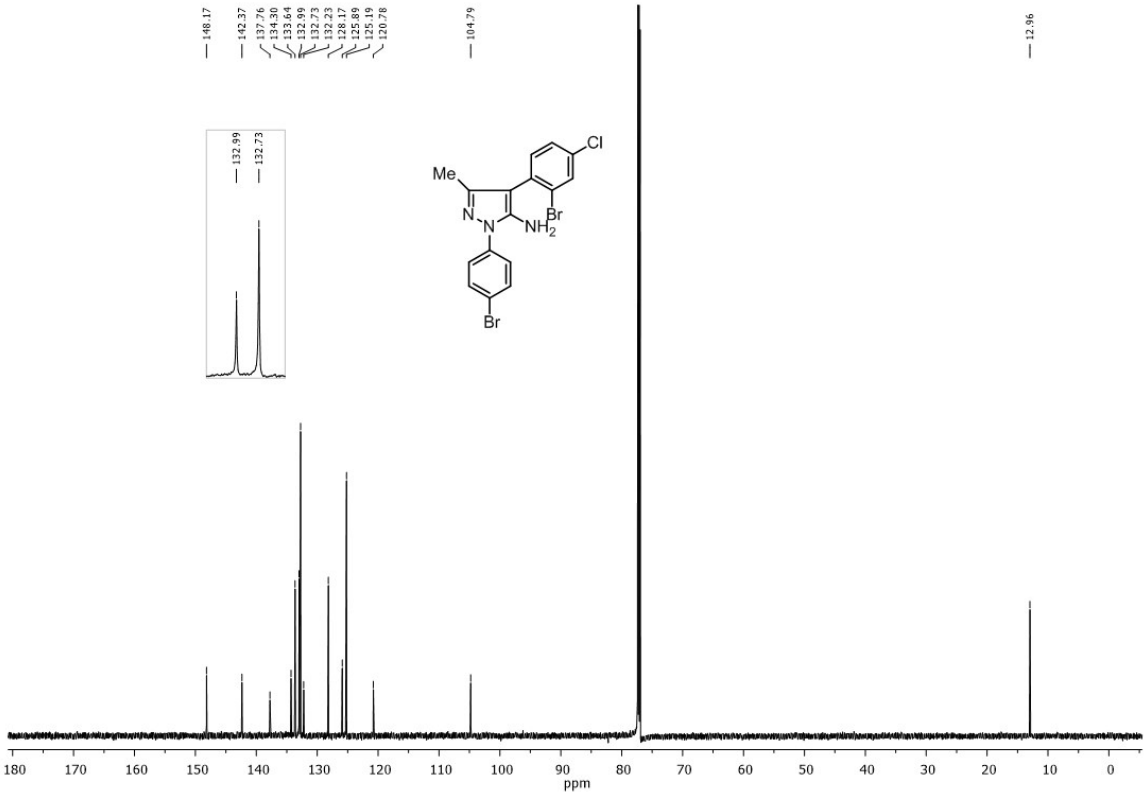
^{1}H Spectra of compound **2q** in $CDCl_3$ (700 MHz)



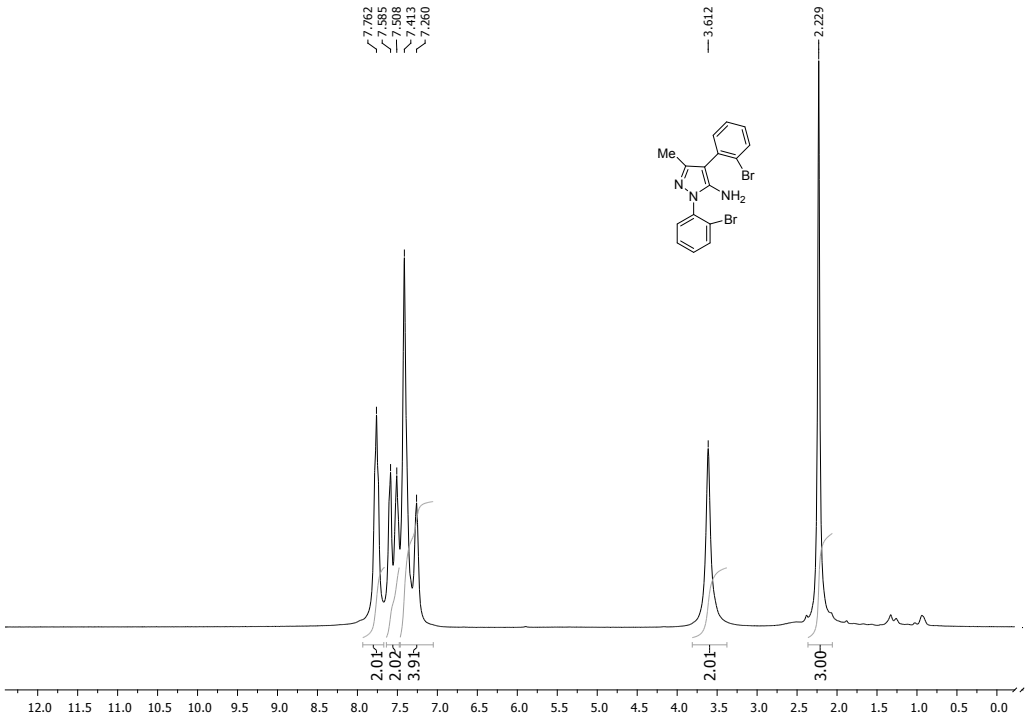
^{13}C Spectra of compound **2q** in $CDCl_3$ (175 MHz)



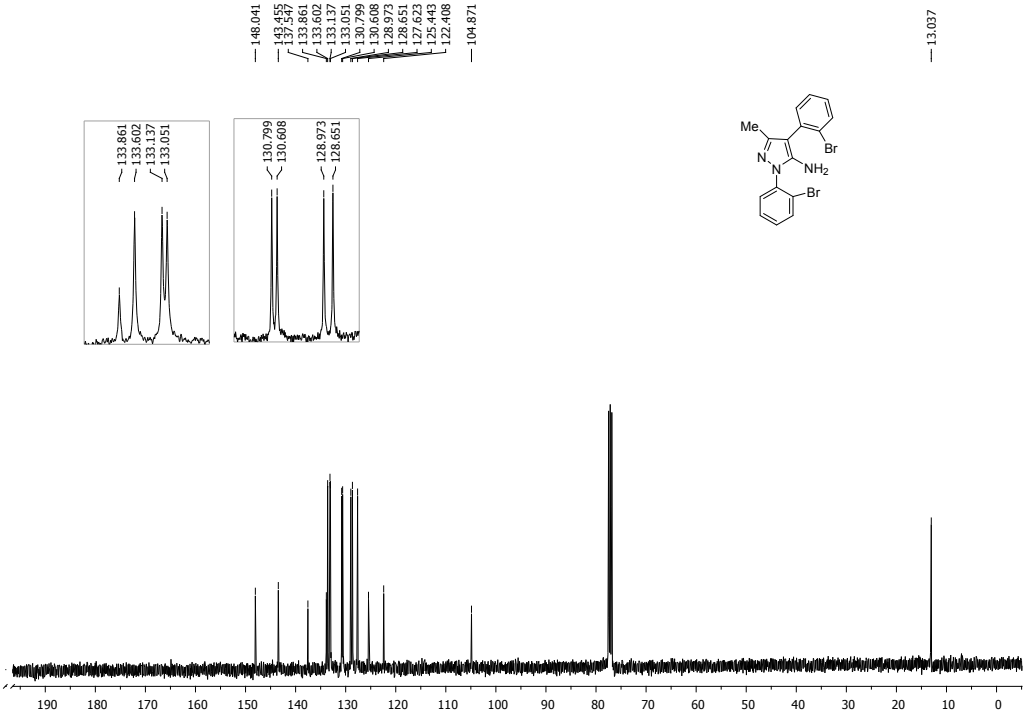
^{1}H Spectra of compound **2r** in $CDCl_3$ (700 MHz)



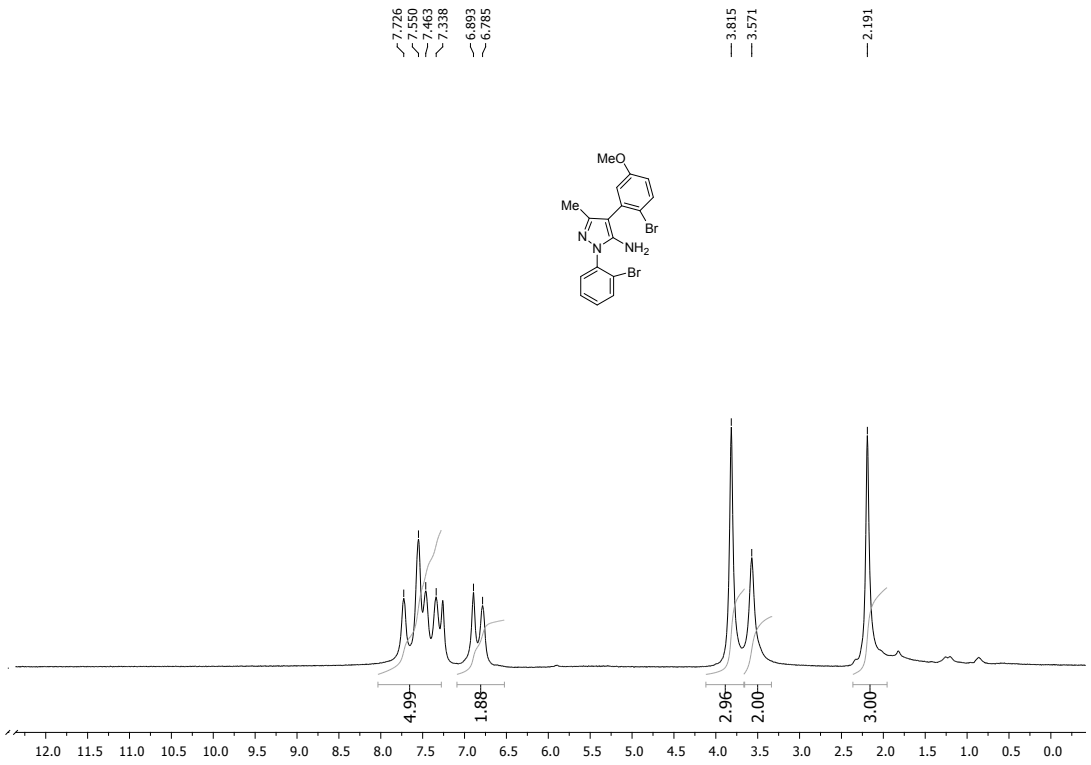
^{13}C Spectra of compound **2r** in $CDCl_3$ (175 MHz)



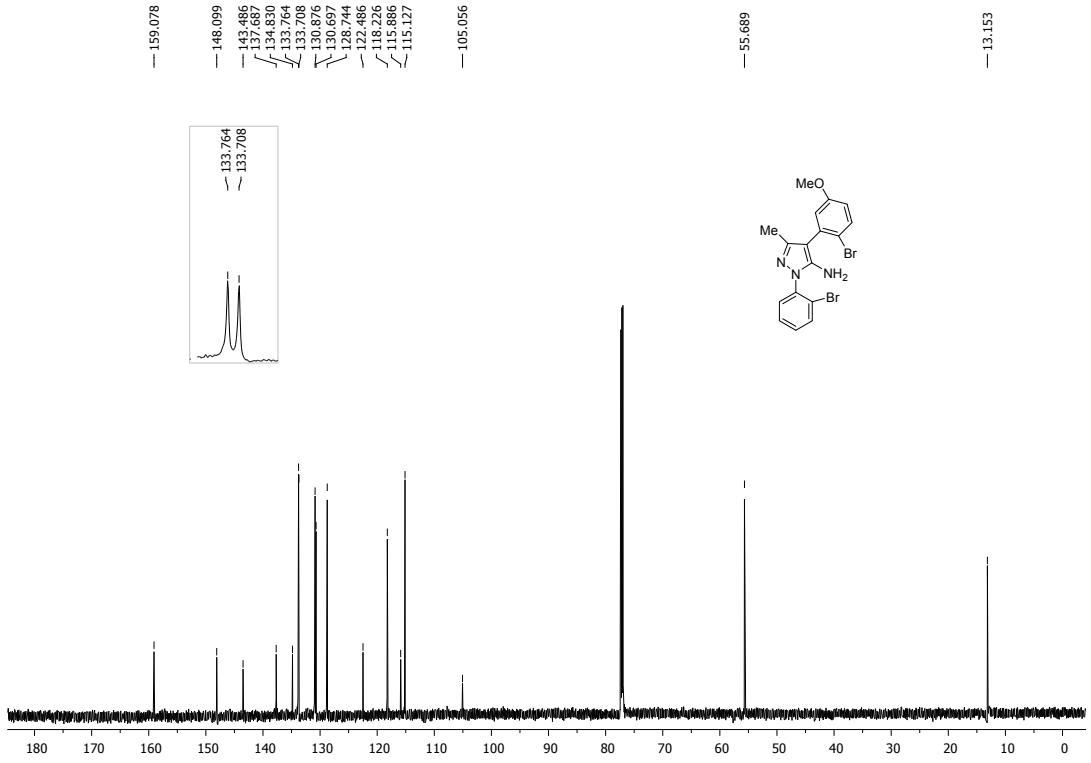
^{1}H Spectra of compound **2s** in $CDCl_3$ (400 MHz)



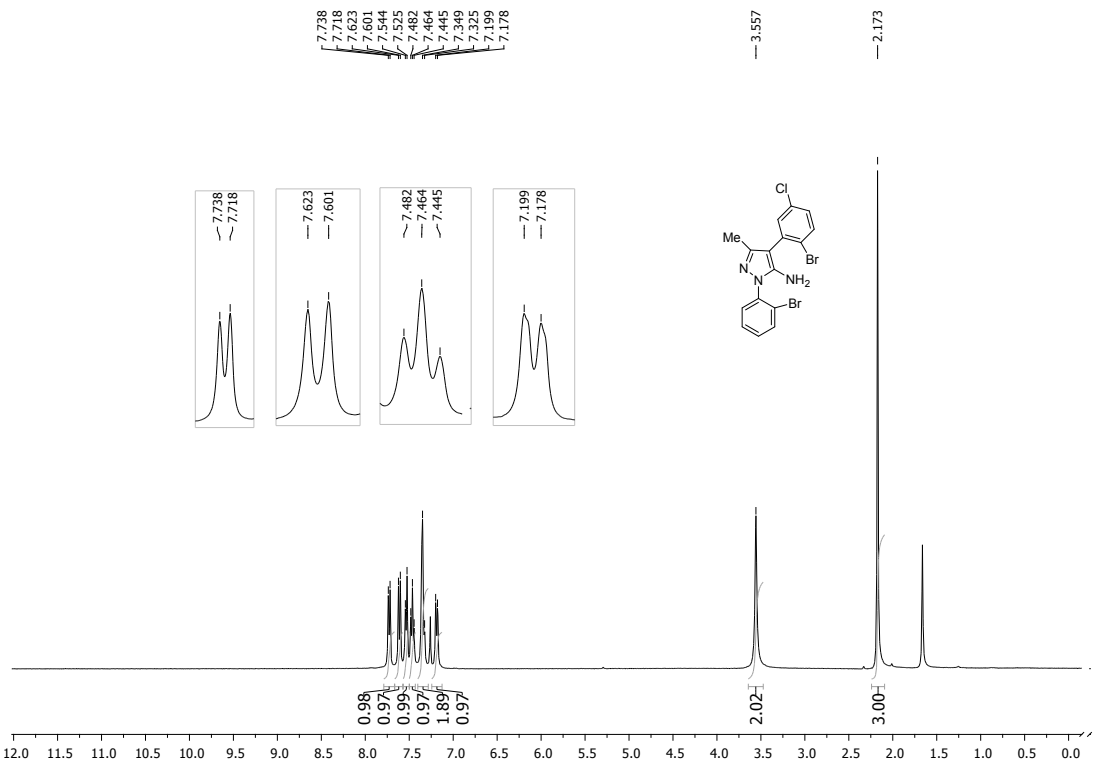
^{13}C Spectra of compound **2s** in $CDCl_3$ (100 MHz)



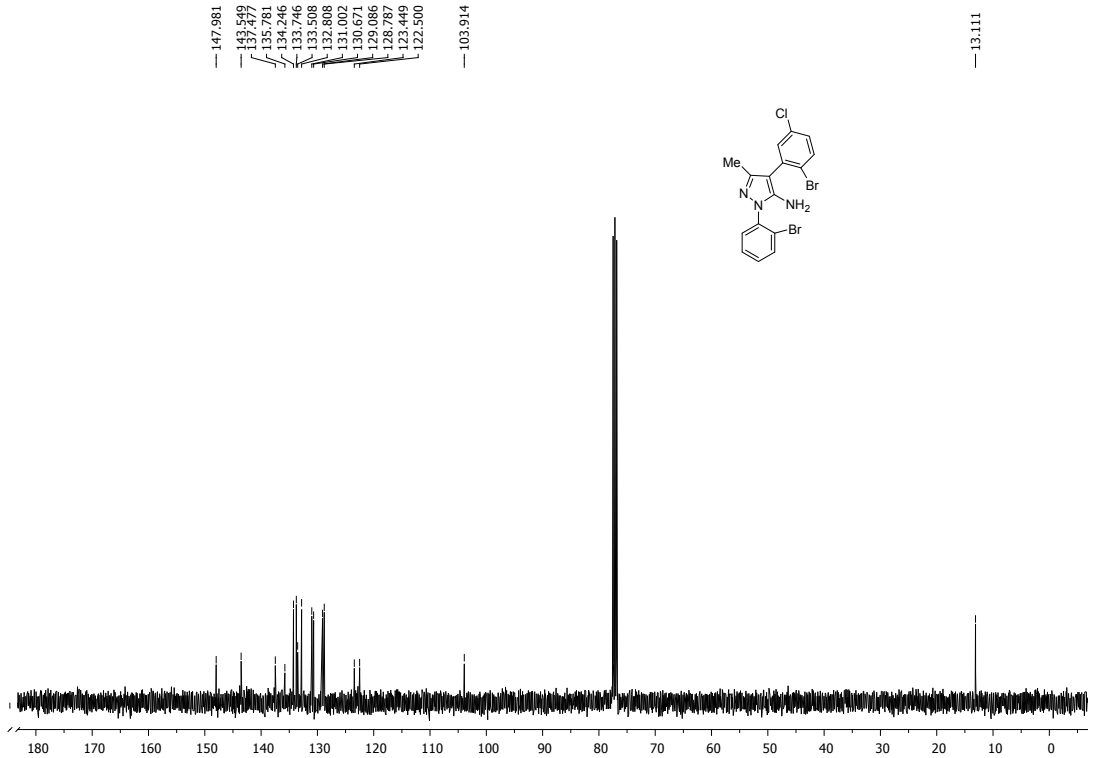
^{1}H Spectra of compound **2t** in $CDCl_3$ (400 MHz)



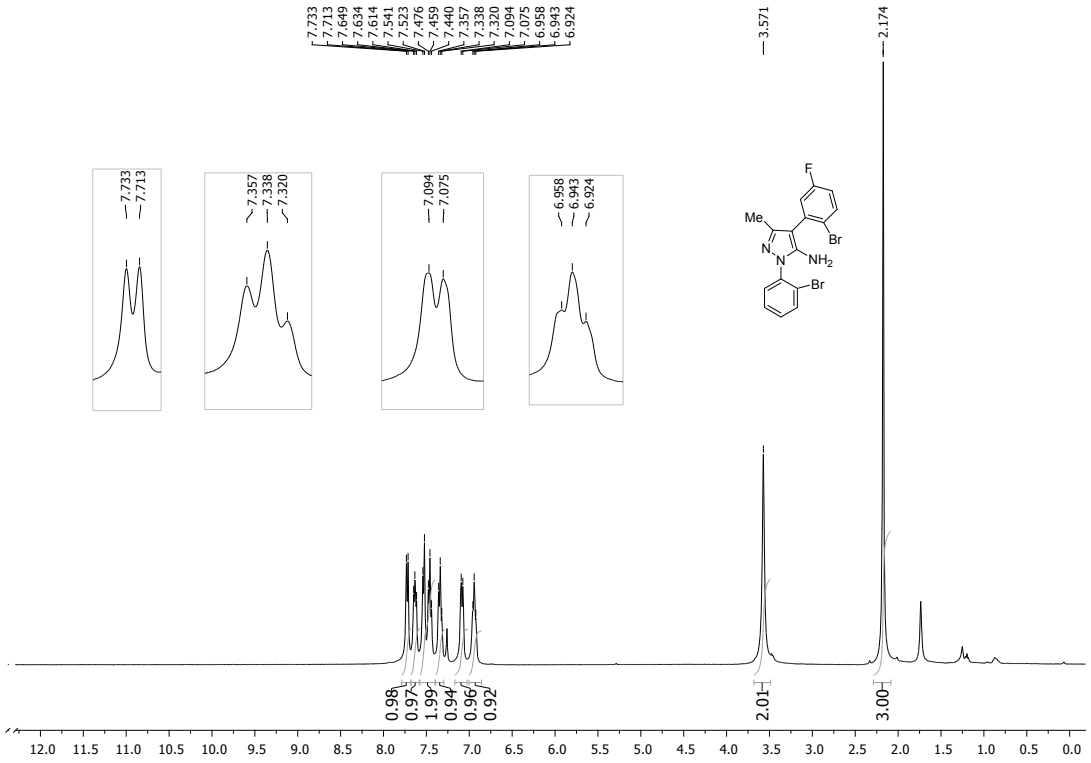
^{13}C Spectra of compound **2t** in $CDCl_3$ (175 MHz)



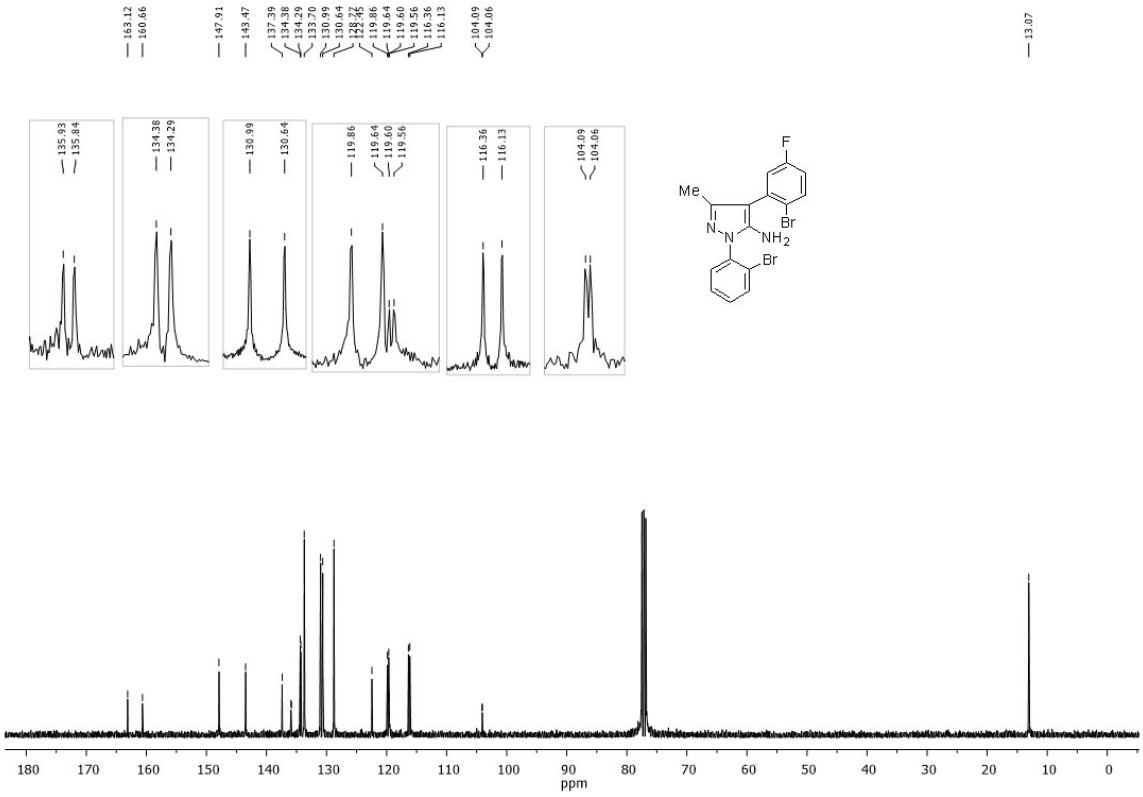
^{1}H Spectra of compound **2u** in $CDCl_3$ (400 MHz)



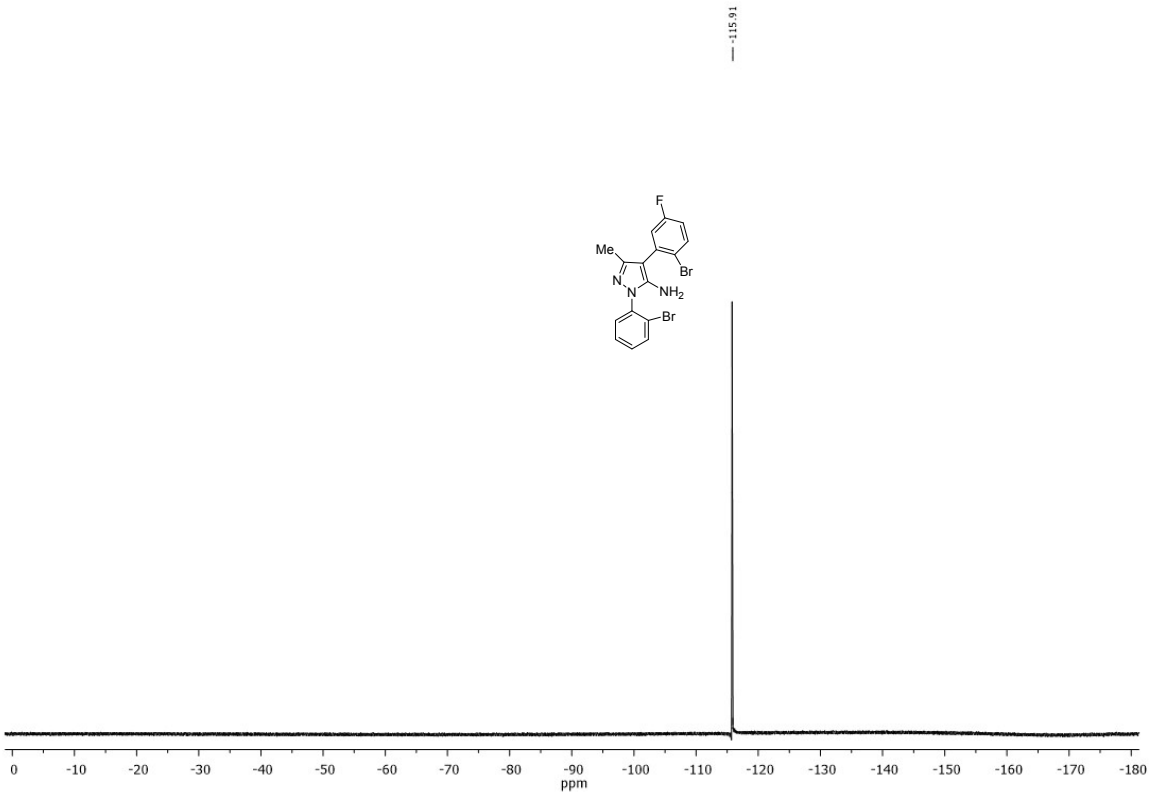
^{13}C Spectra of compound **2u** in $CDCl_3$ (100 MHz)



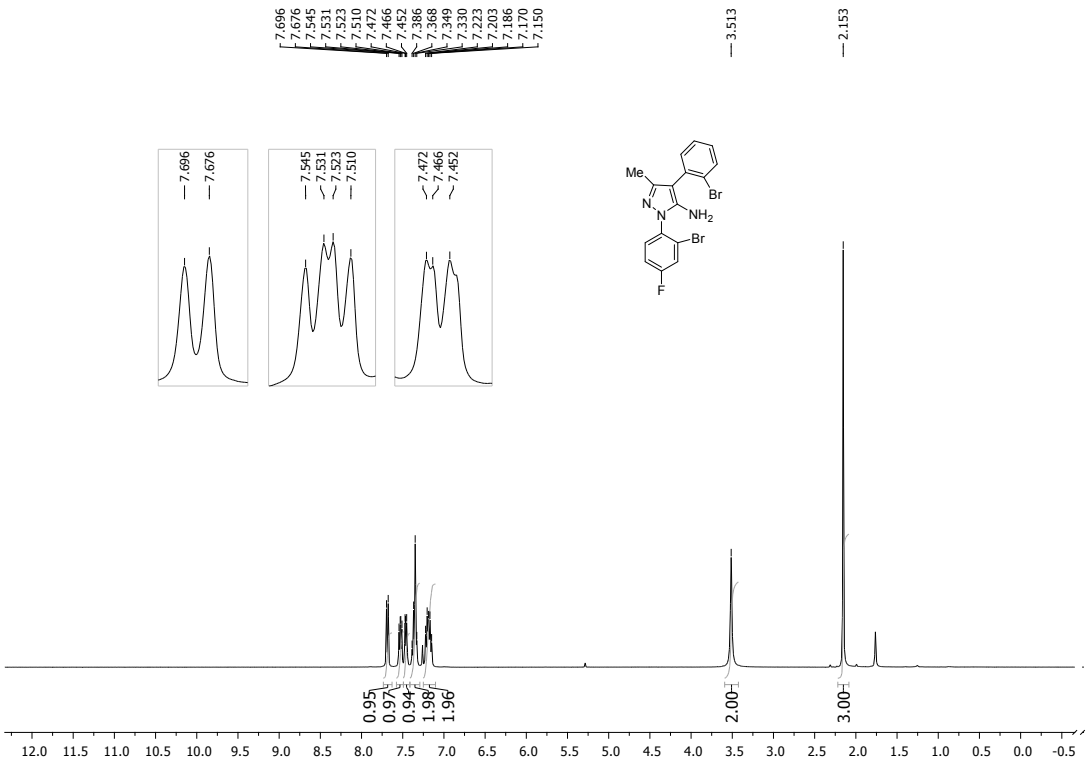
^{1}H Spectra of compound **2v** in $CDCl_3$ (400 MHz)



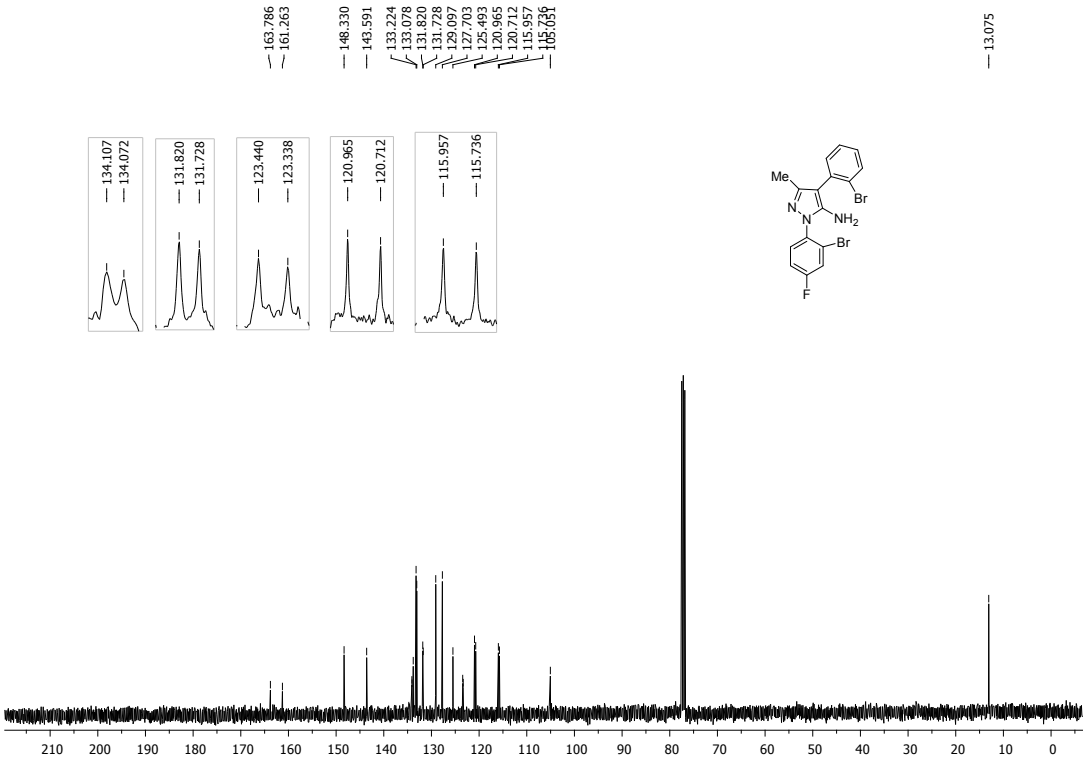
^{13}C Spectra of compound **2v** in $CDCl_3$ (100 MHz)



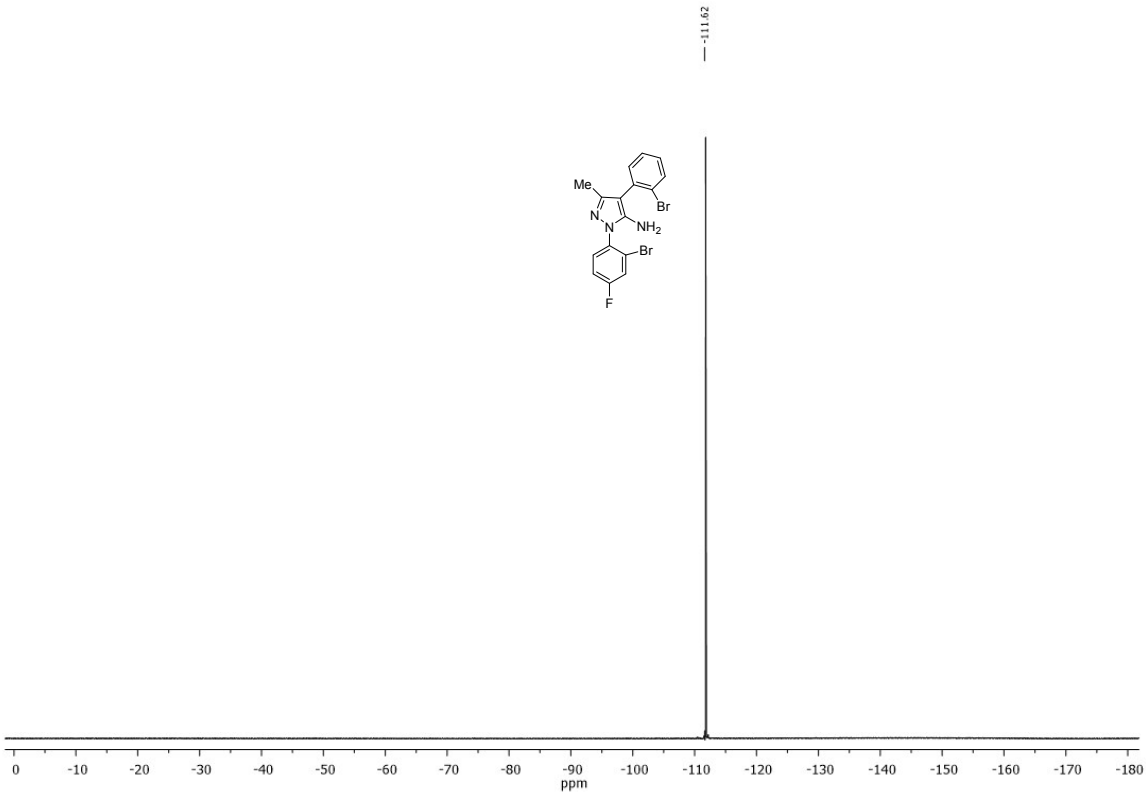
^{19}F Spectra of Compound **2v** in DMSO-d_6 (377MHz)



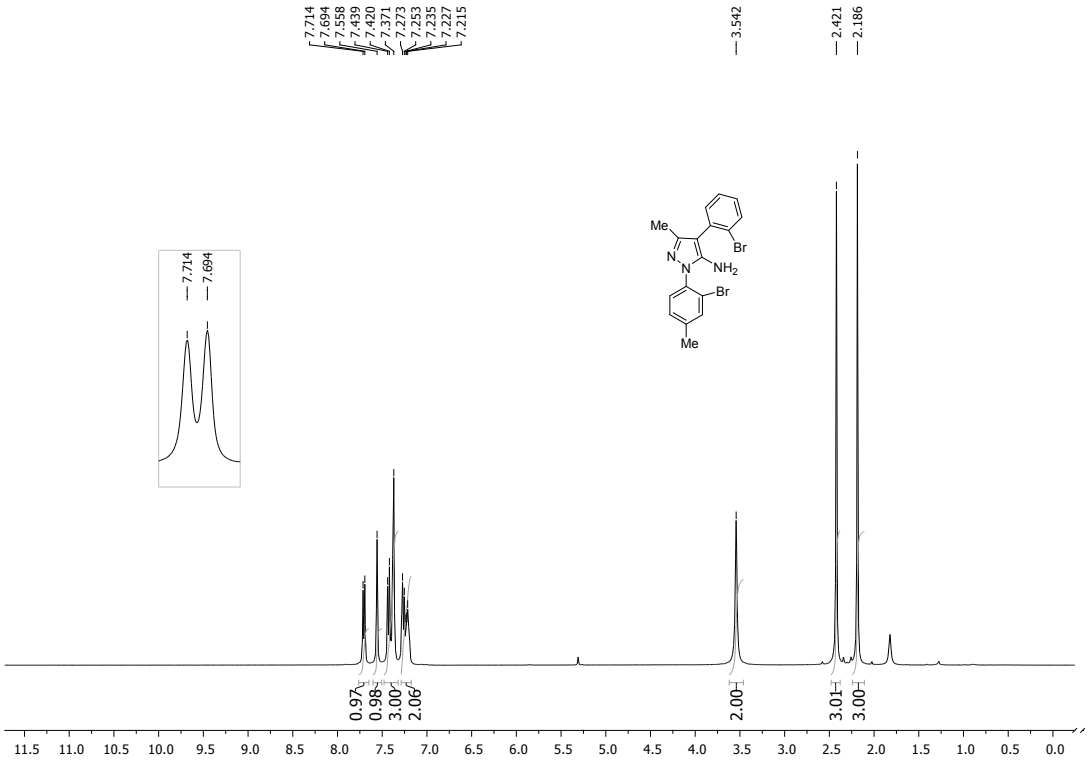
^{1}H Spectra of compound **2w** in $CDCl_3$ (400 MHz)



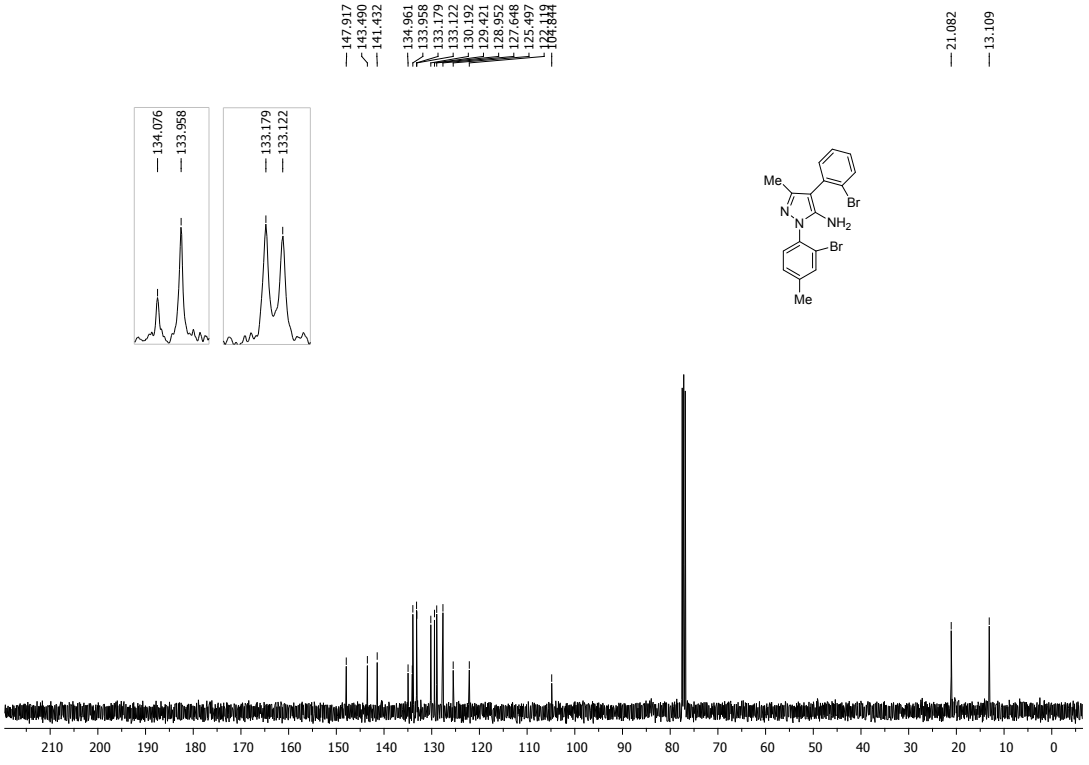
^{13}C Spectra of compound **2w** in $CDCl_3$ (100 MHz)



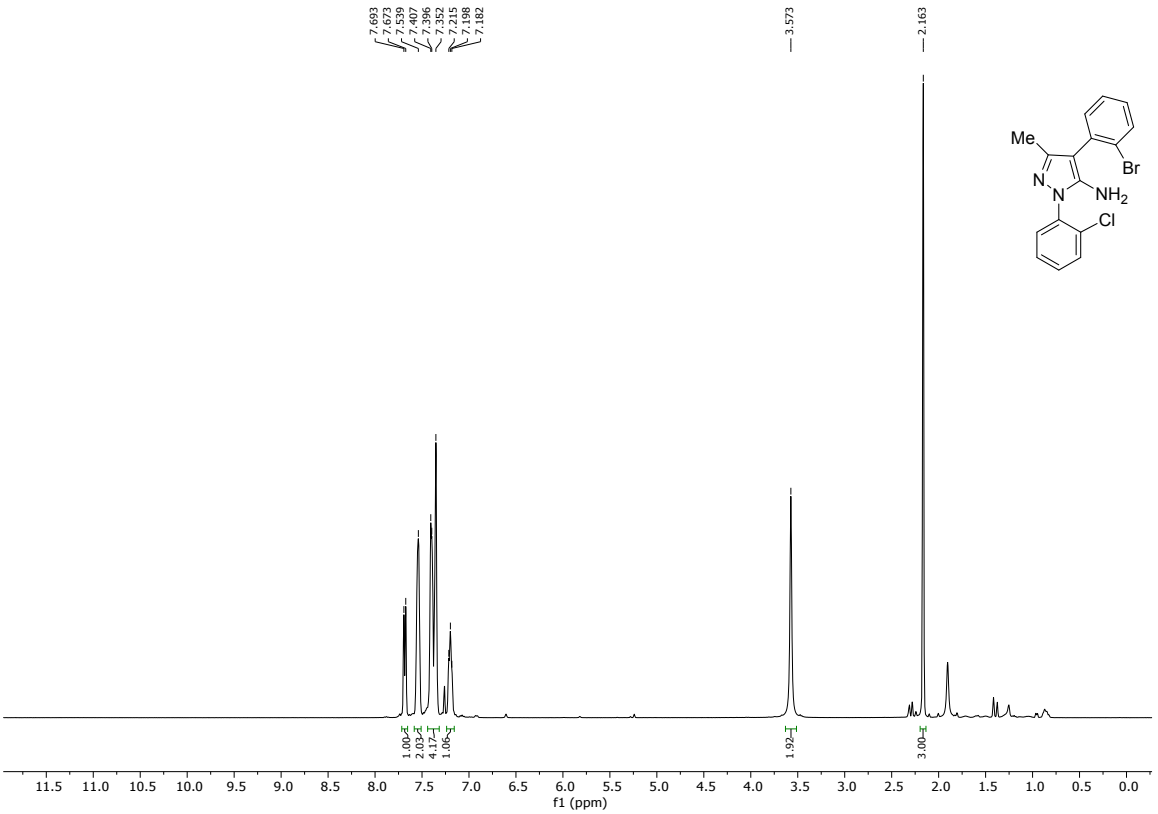
^{19}F Spectra of Compound **2w** in DMSO-d_6 (376 MHz)



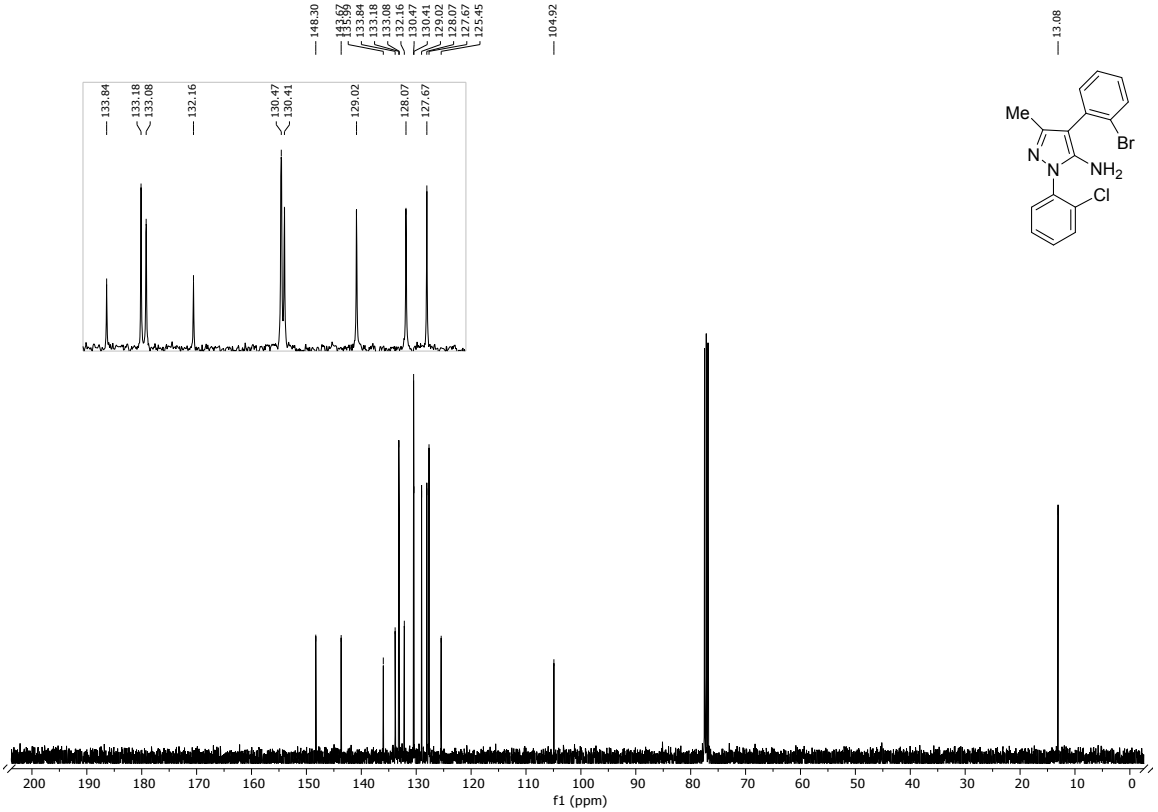
^{1}H Spectra of compound **2x** in $CDCl_3$ (400 MHz)



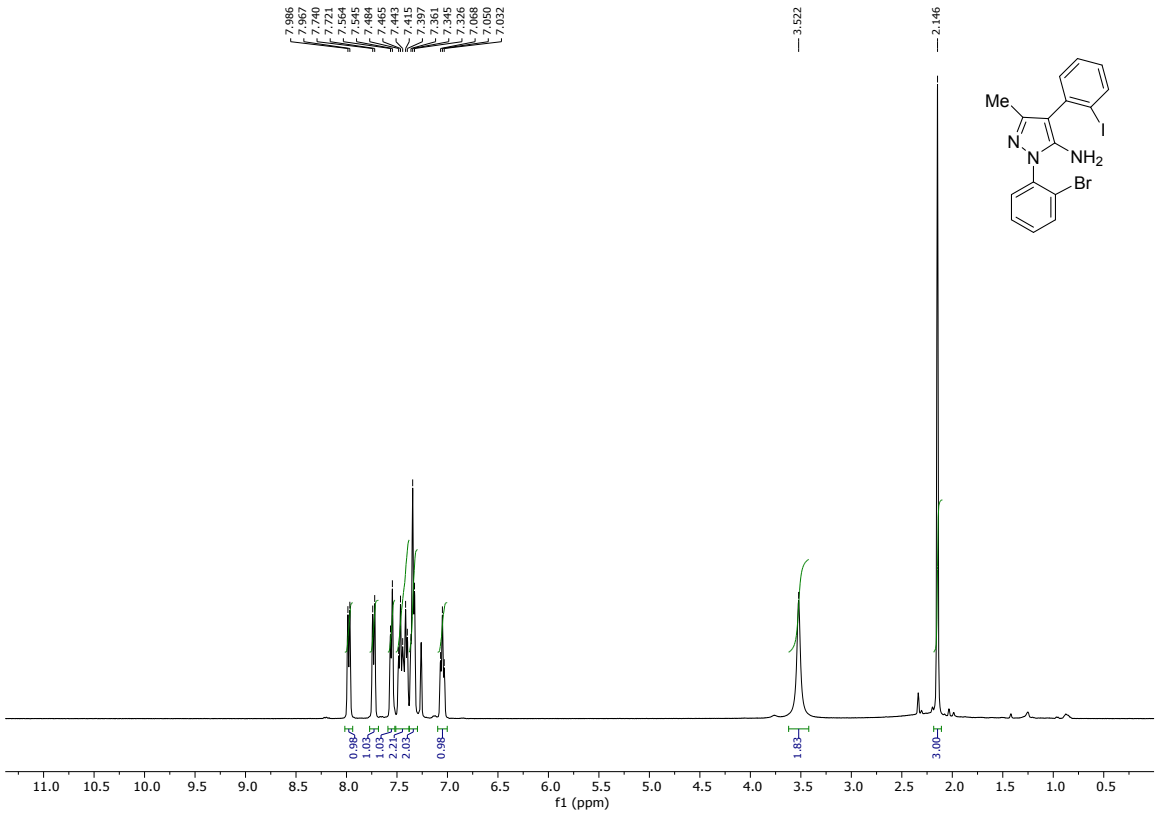
^{13}C Spectra of compound **2x** in $CDCl_3$ (100 MHz)



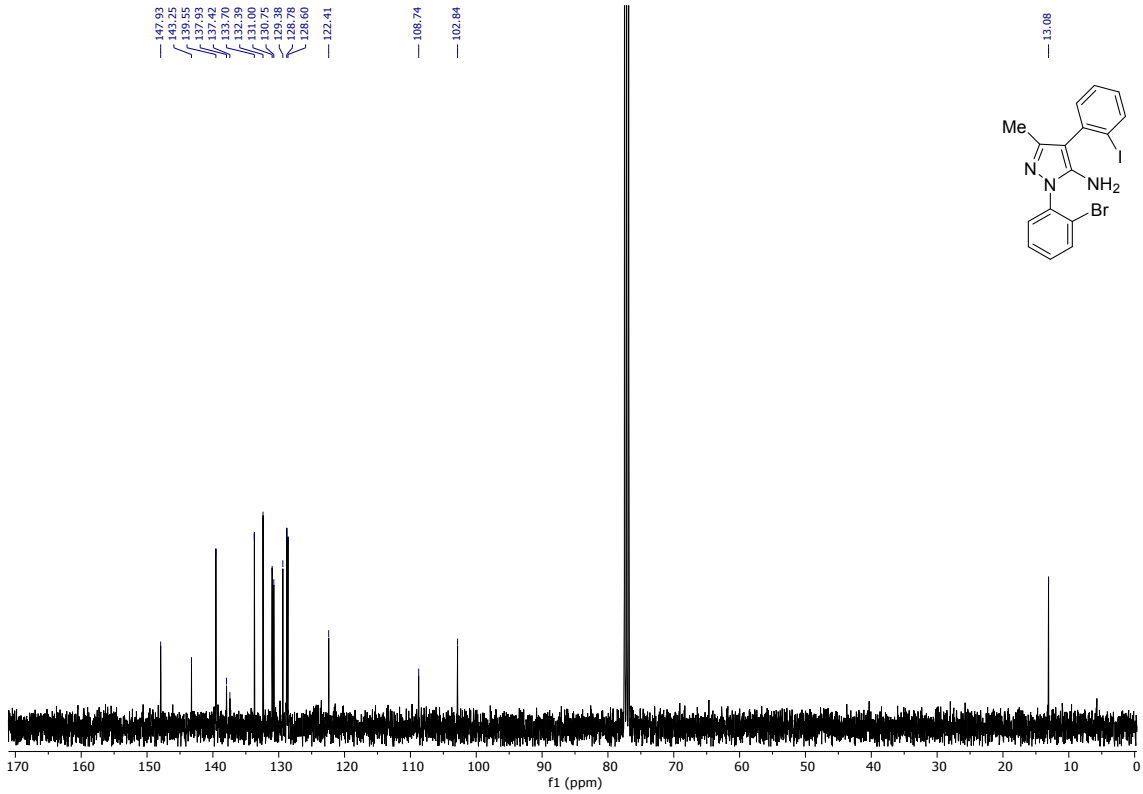
^{1}H Spectra of compound **2y** in $CDCl_3$ (400 MHz)



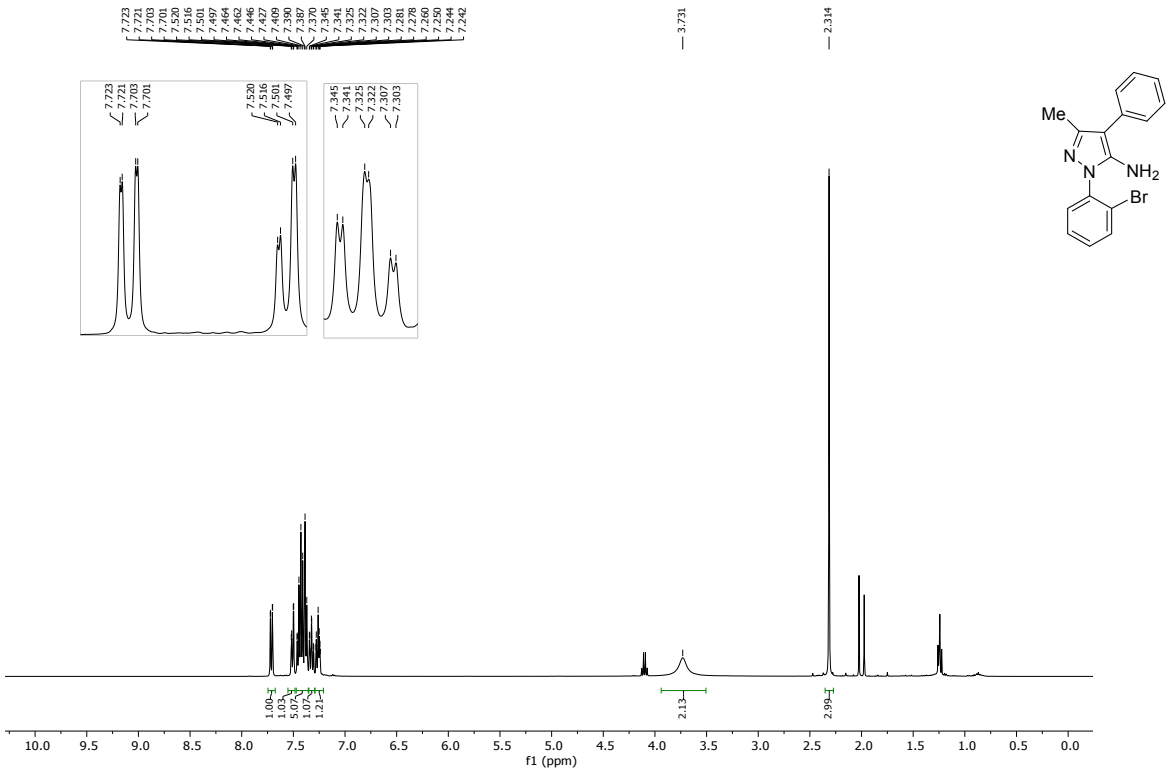
^{13}C Spectra of compound **2y** in $CDCl_3$ (100 MHz)



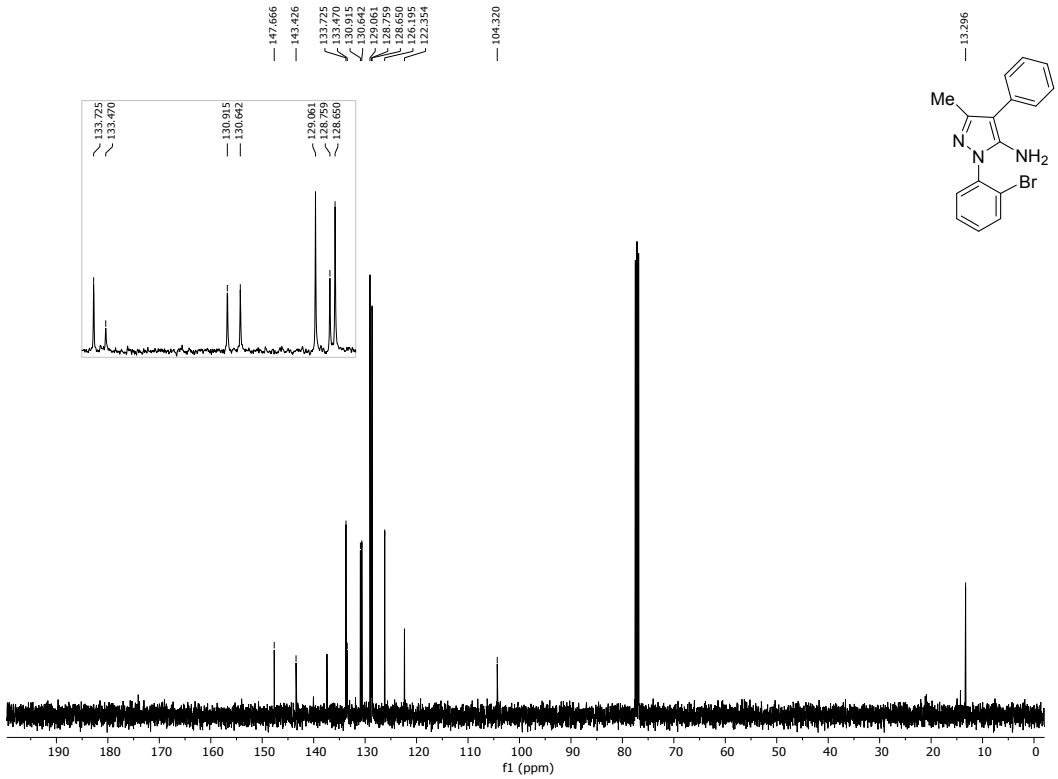
^{1}H Spectra of compound **2z** in $CDCl_3$ (400 MHz)



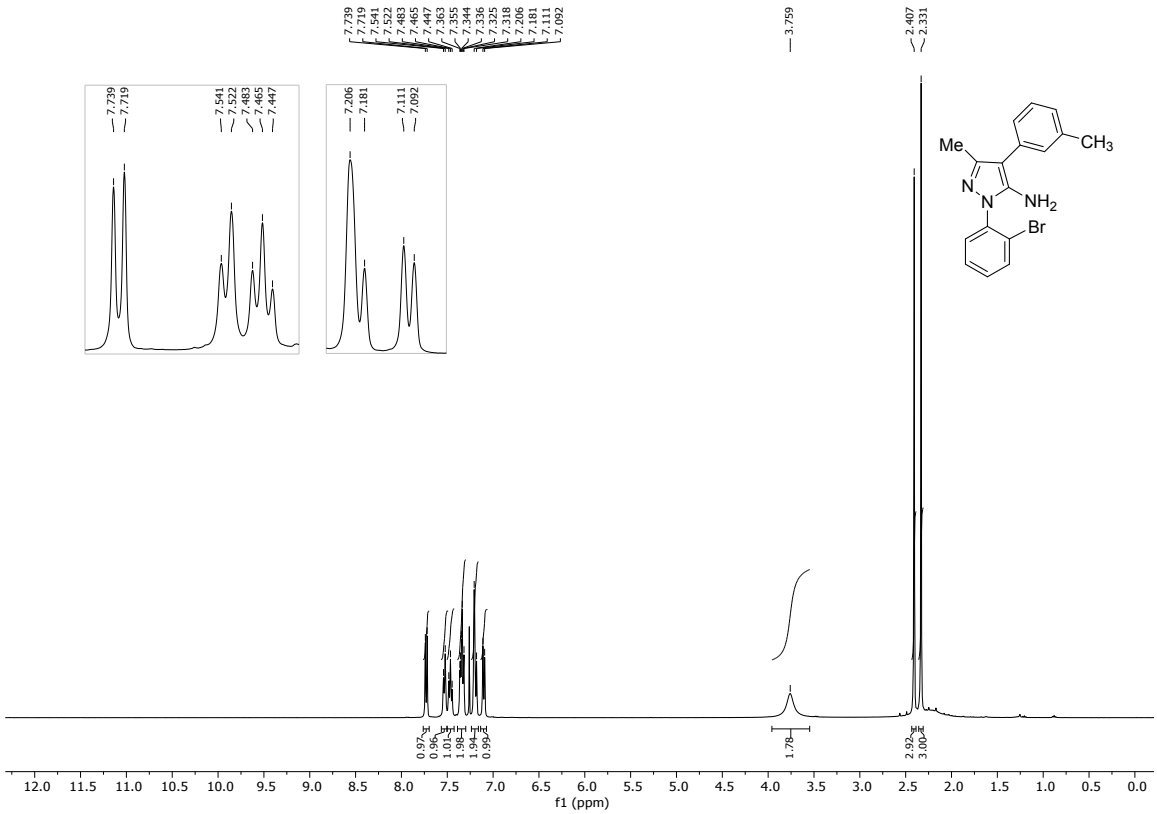
^{13}C Spectra of compound **2z** in $CDCl_3$ (100 MHz)



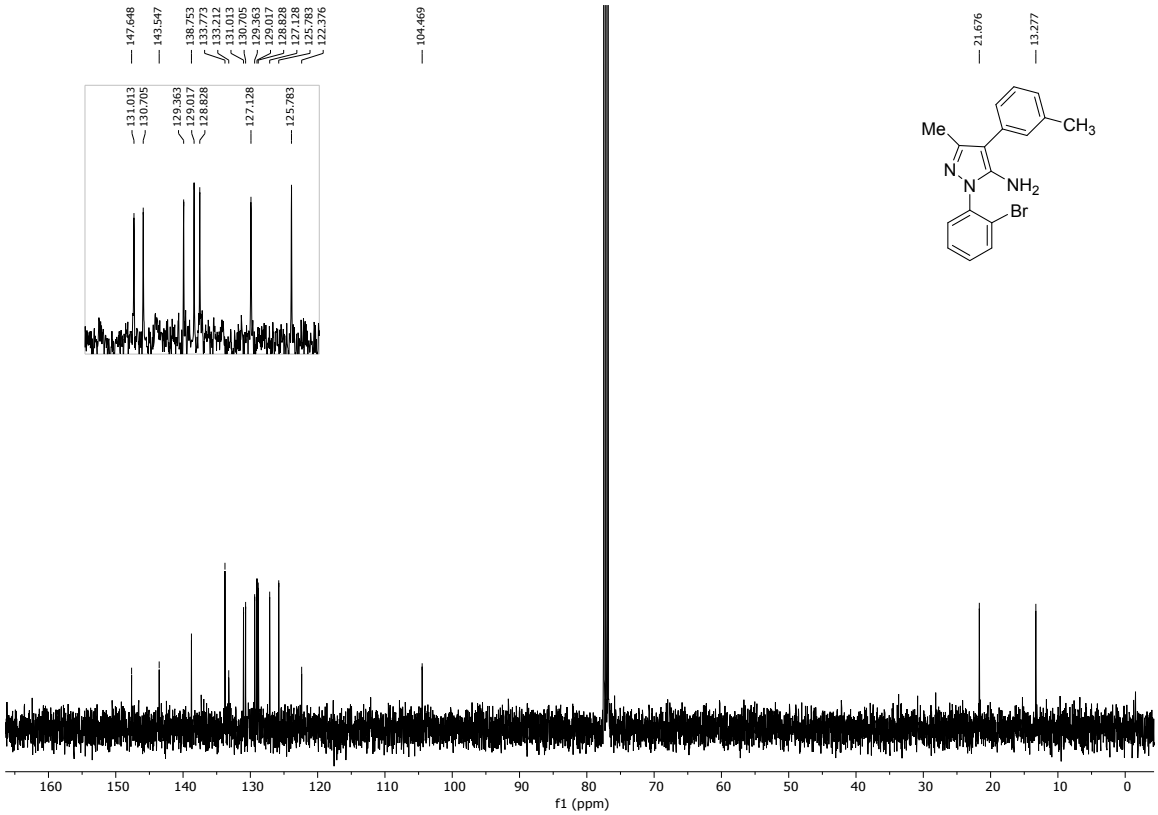
^{1}H Spectra of compound **2aa** in $CDCl_3$ (400 MHz)



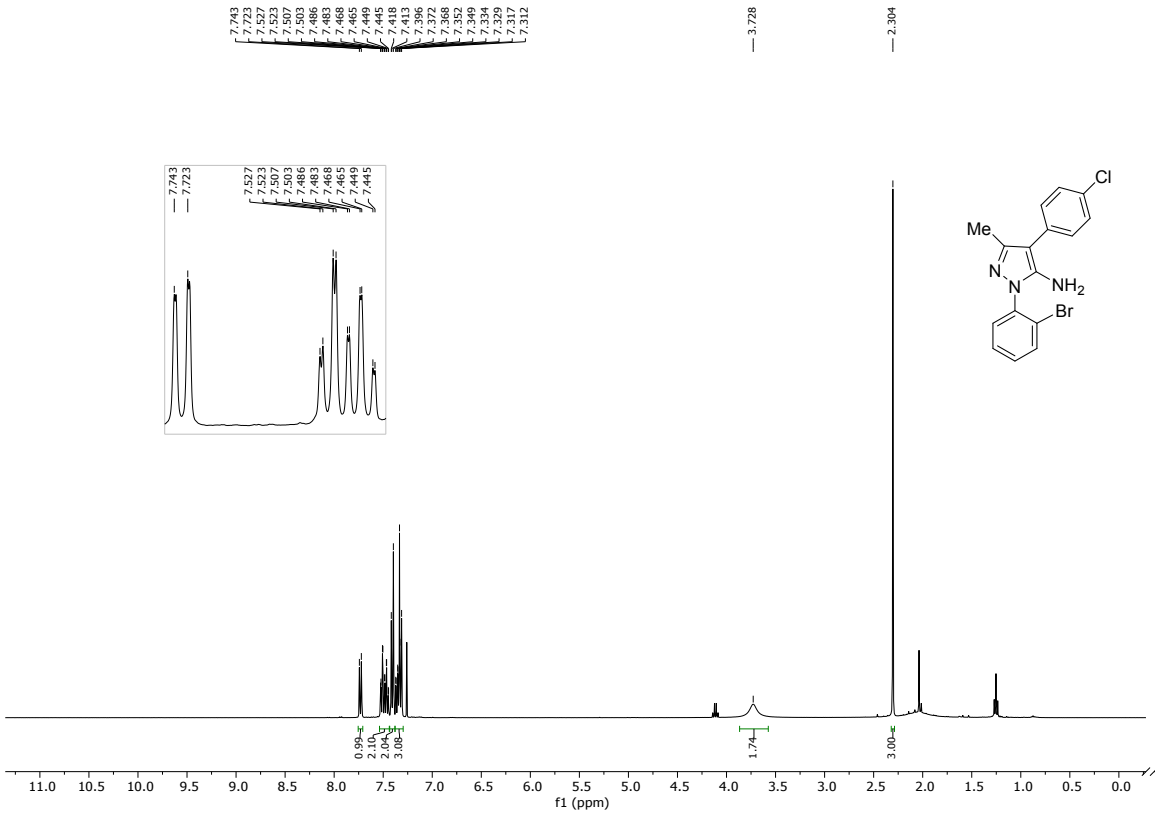
^{13}C Spectra of compound **2aa** in $CDCl_3$ (100 MHz)



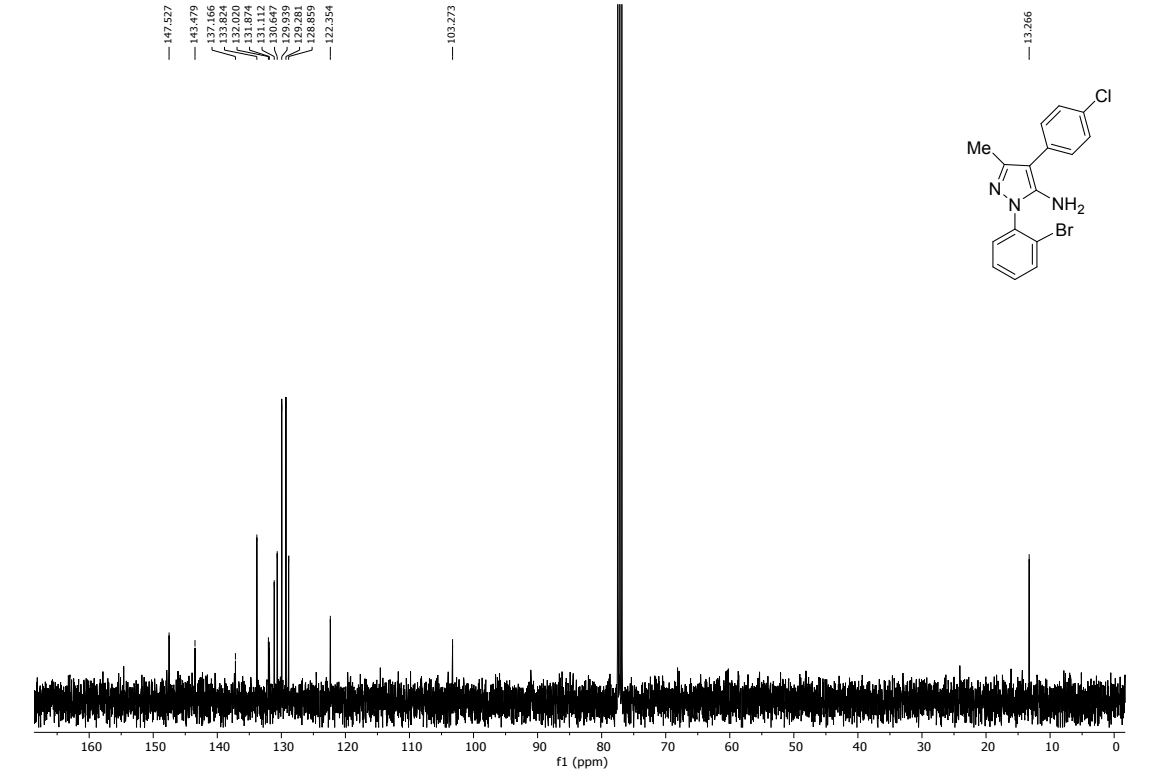
^{1}H Spectra of compound **2ab** in $CDCl_3$ (400 MHz)



^{13}C Spectra of compound **2ab** in $CDCl_3$ (100 MHz)

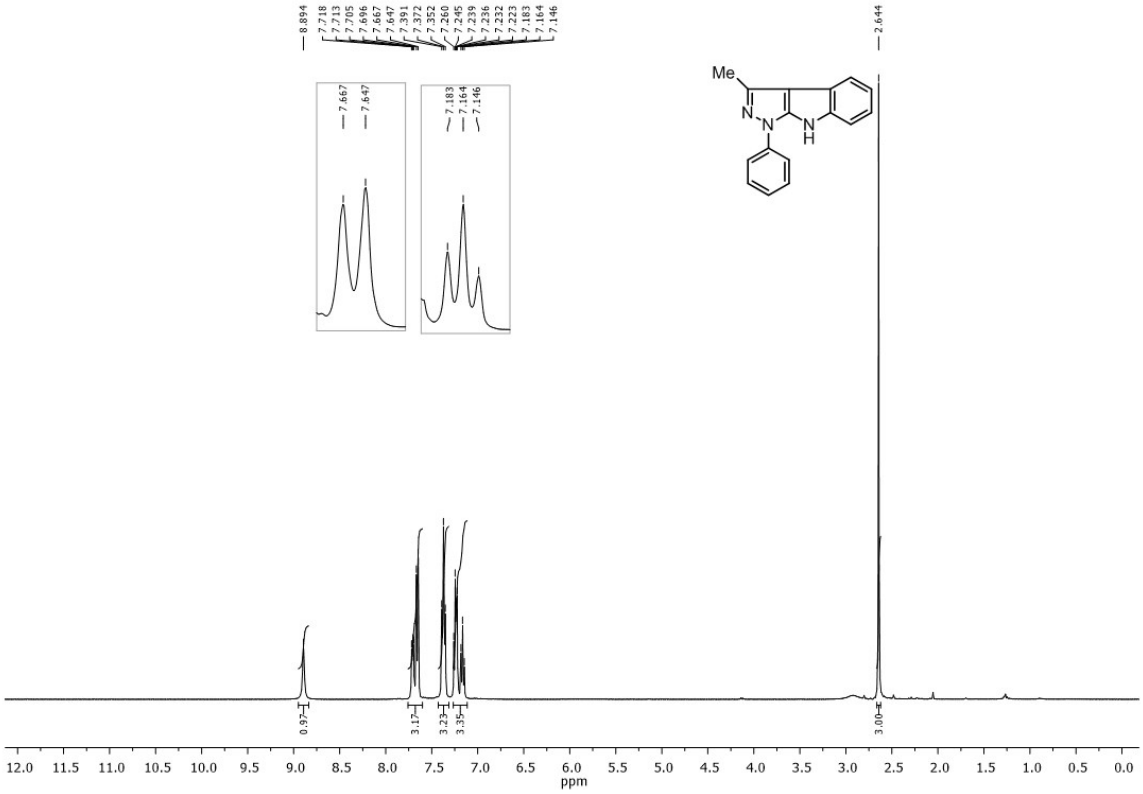


^{1}H Spectra of compound **2ac** in $CDCl_3$ (400 MHz)

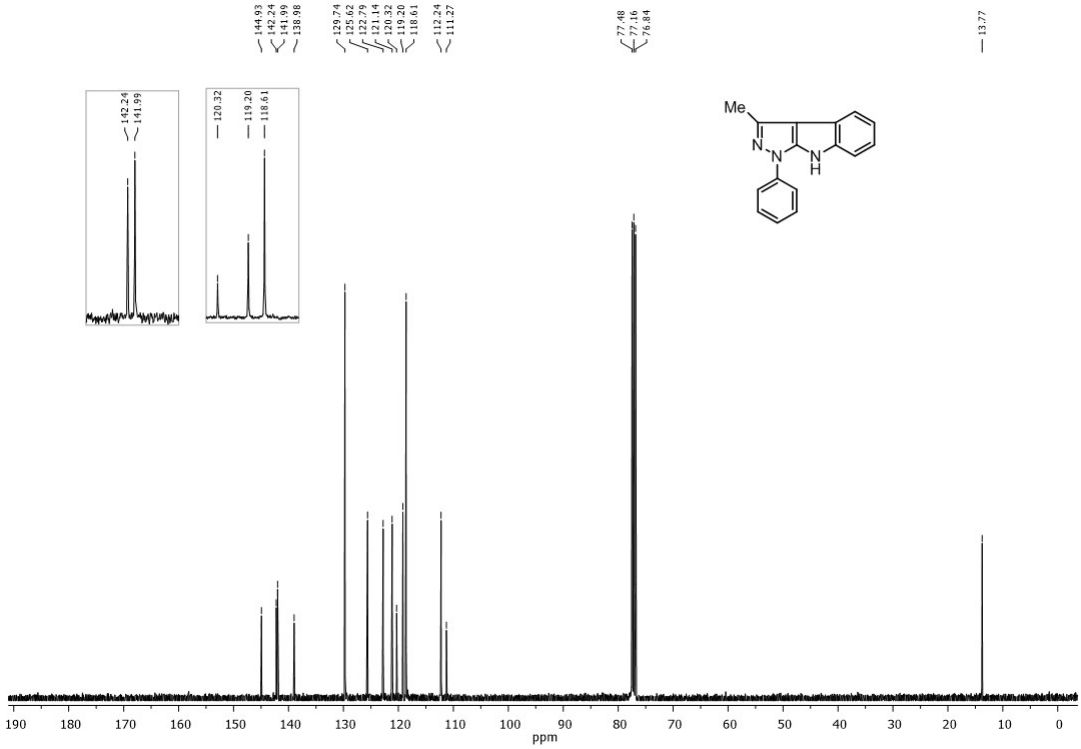


^{13}C Spectra of compound **2ac** in $CDCl_3$ (100 MHz)

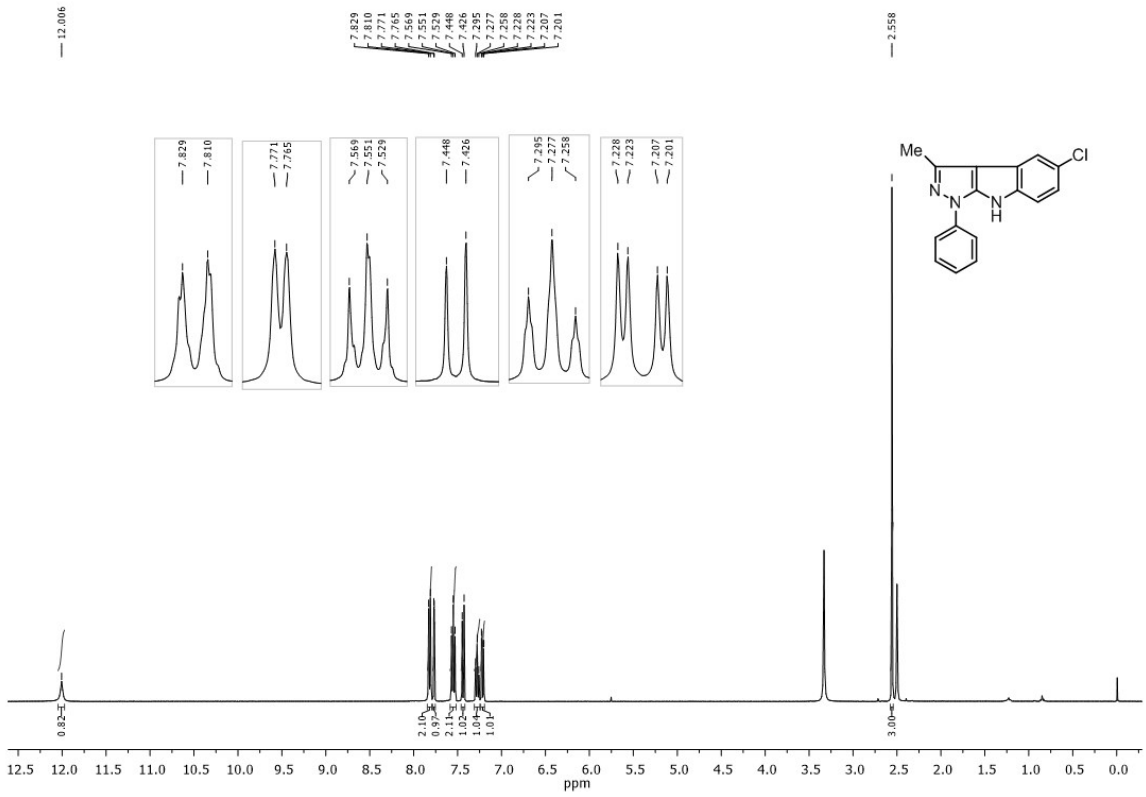
^{1}H & ^{13}C NMR of Pyrazolo[3,4-*b*]indole (**1a-1q**)



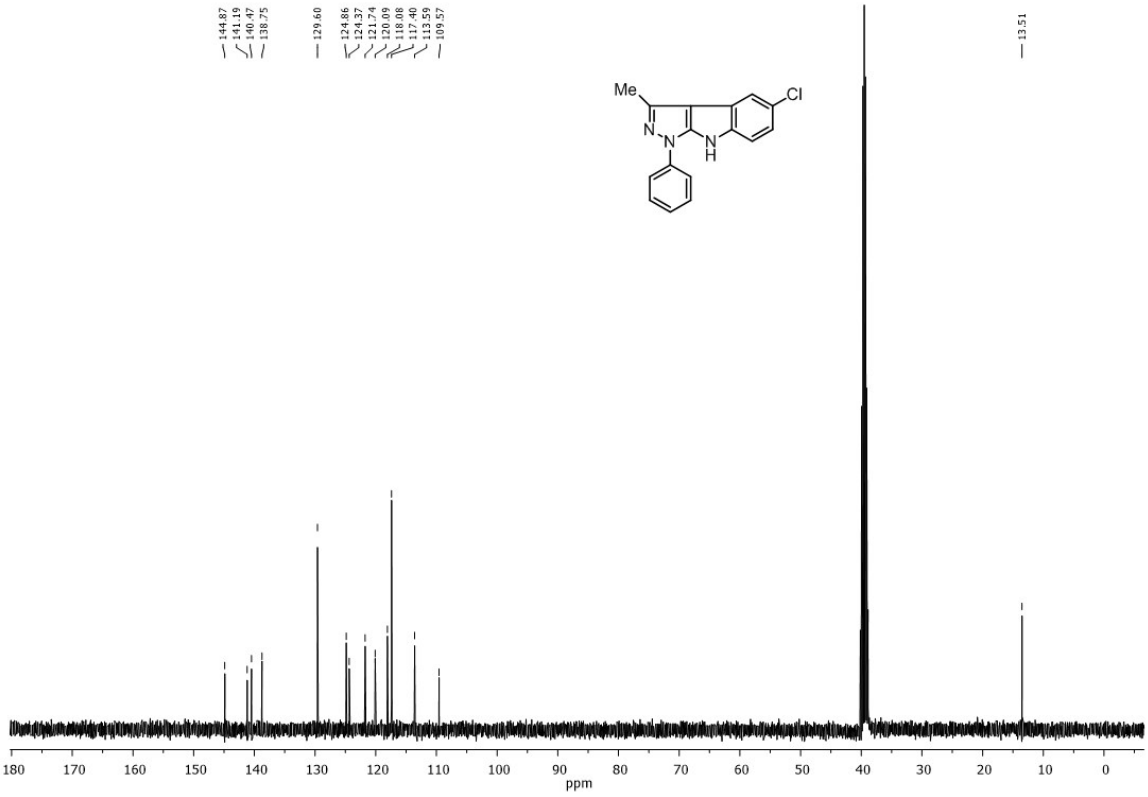
^{1}H Spectra of compound **1a** in $CDCl_3$ (400 MHz)



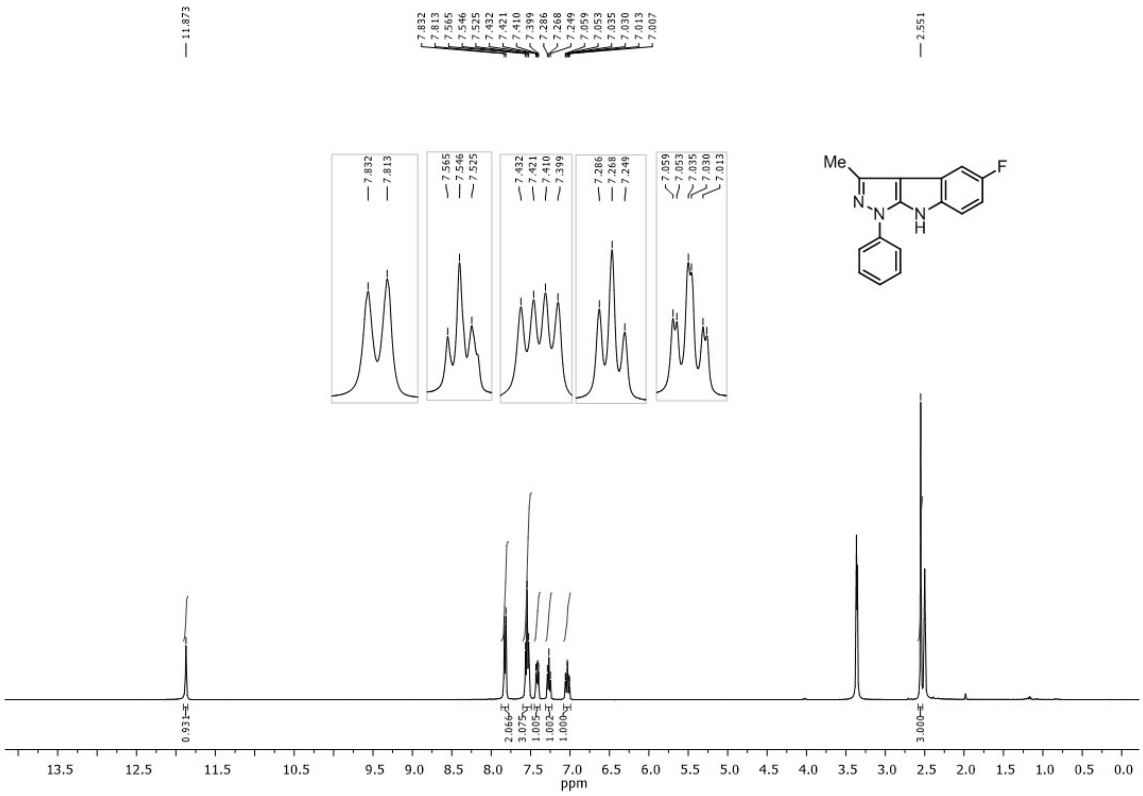
^{13}C Spectra of compound **1a** in $CDCl_3$ (100 MHz)



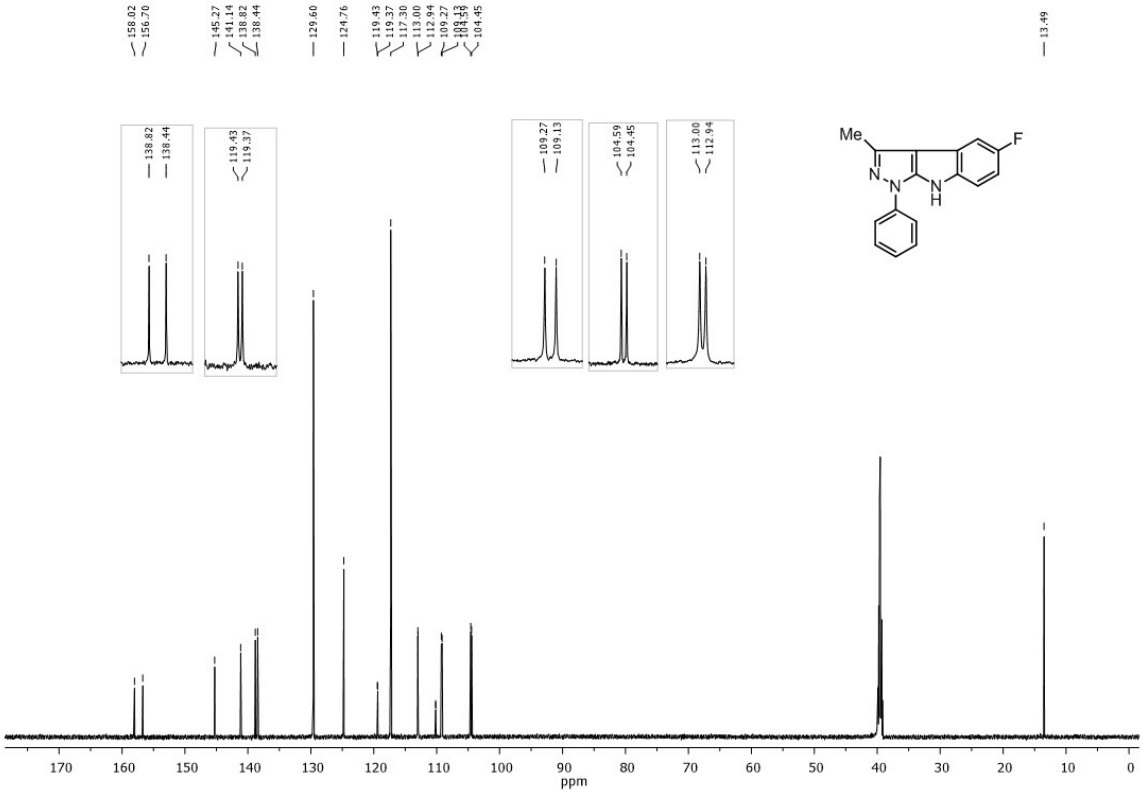
^{1}H Spectra of compound **1b** in DMSO-d_6 (400 MHz)



^{13}C Spectra of compound **1b** in DMSO-d_6 (100 MHz)

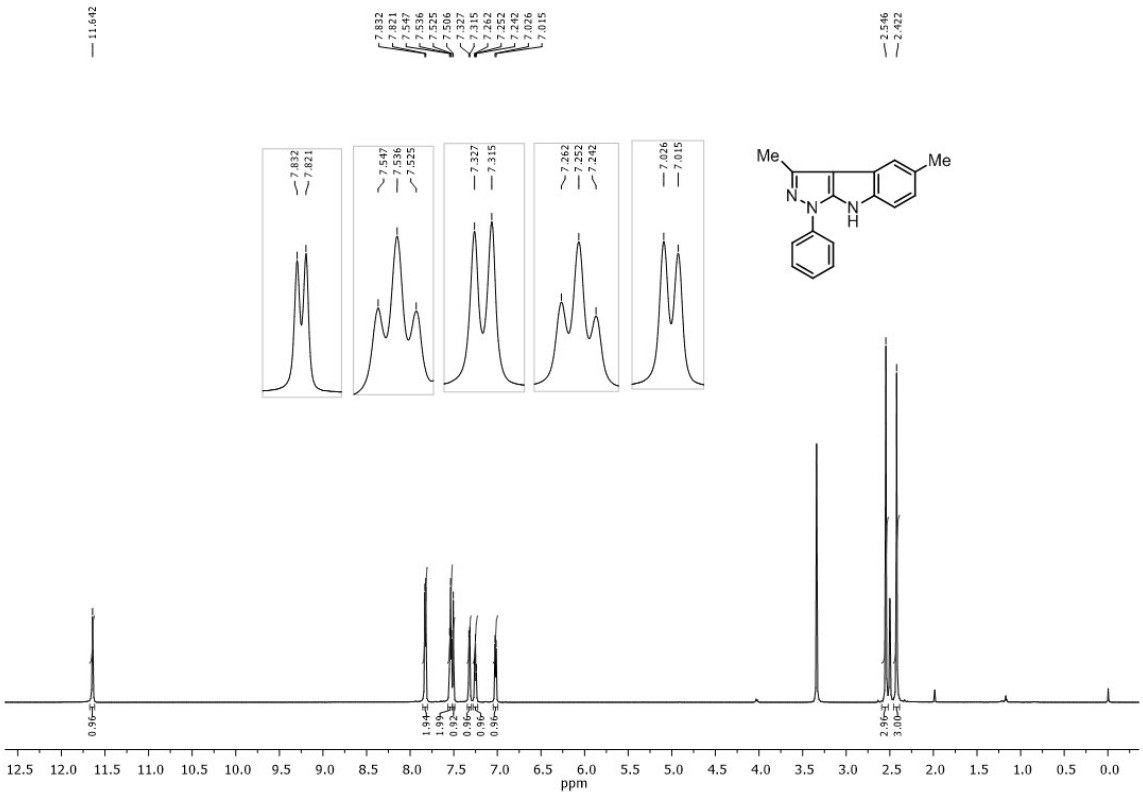


^{1}H Spectra of compound **1c** in DMSO-d_6 (400 MHz)

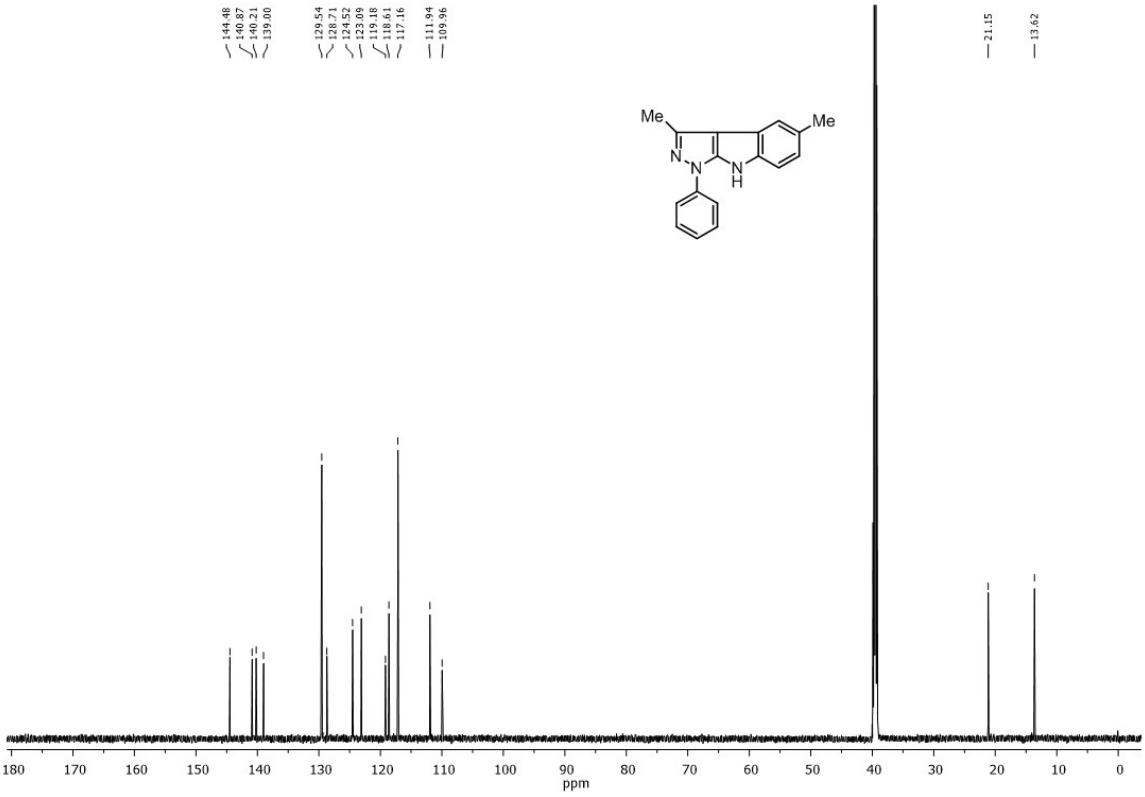


^{13}C Spectra of compound **1c** in DMSO-d_6 (175 MHz)

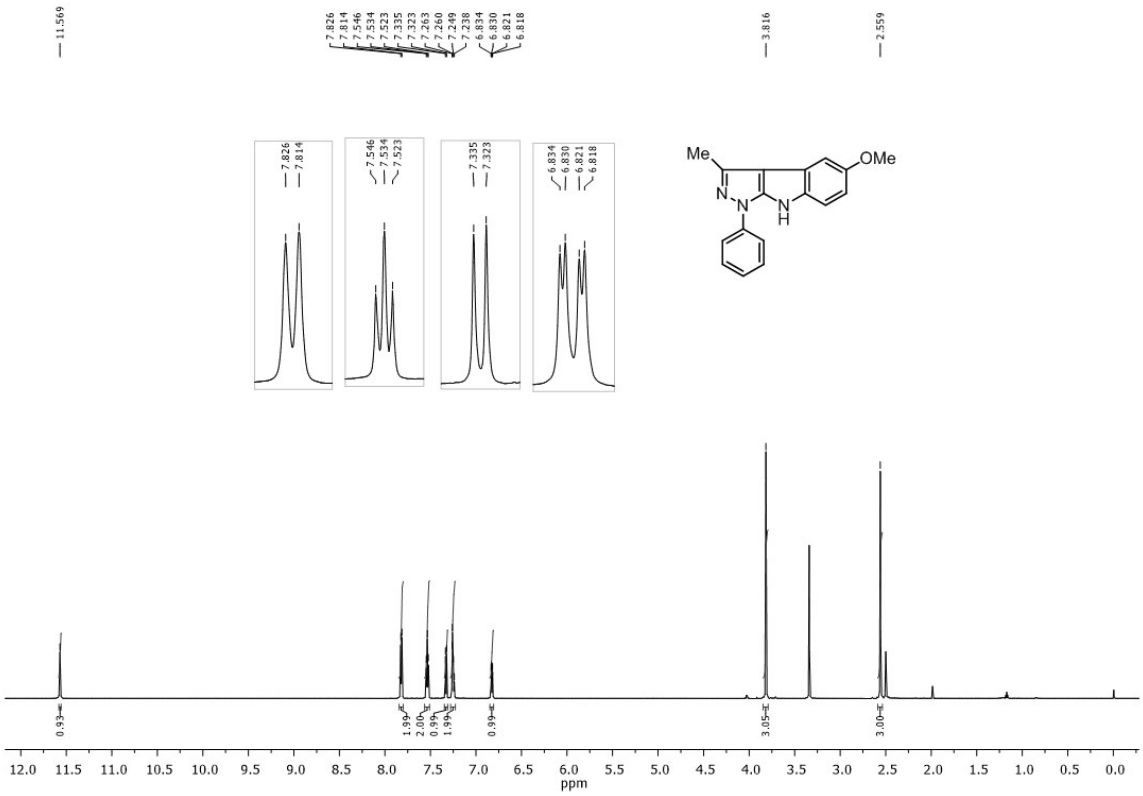
^{19}F Spectra of Compound **1c** in DMSO-d_6 (376 MHz)



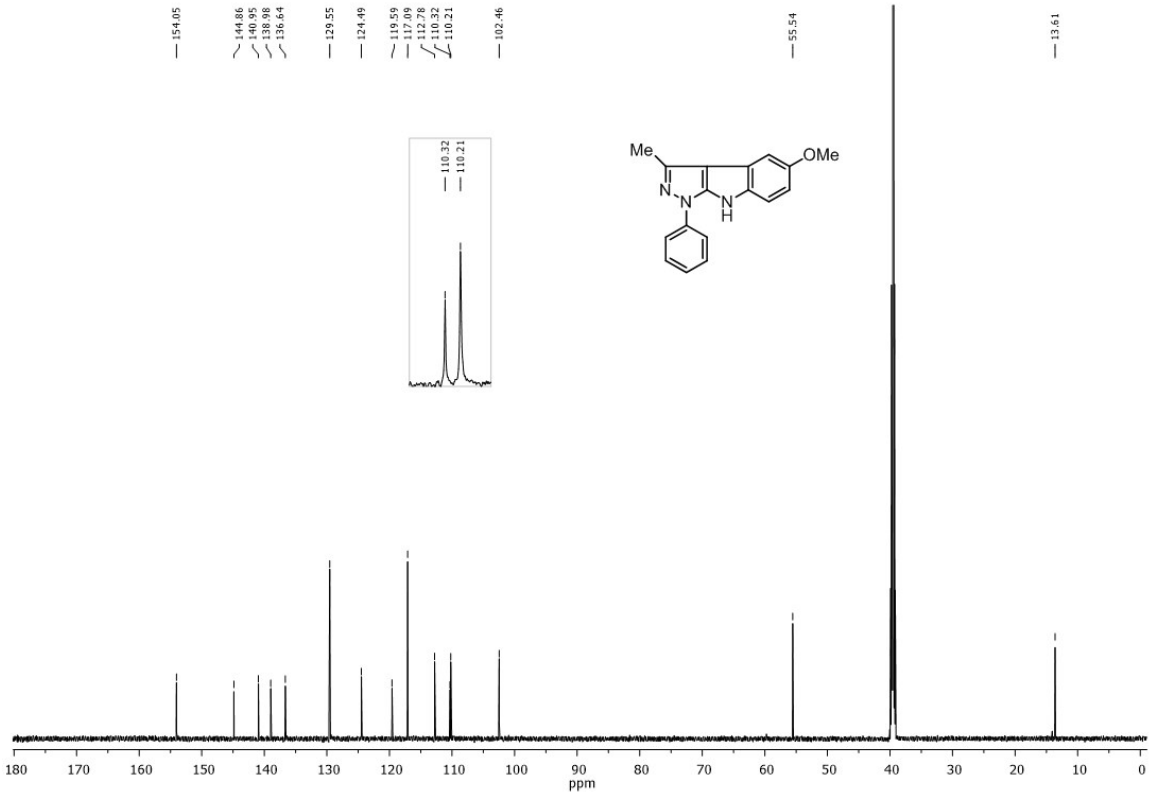
^{1}H Spectra of compound **1d** in DMSO-d_6 (700 MHz)



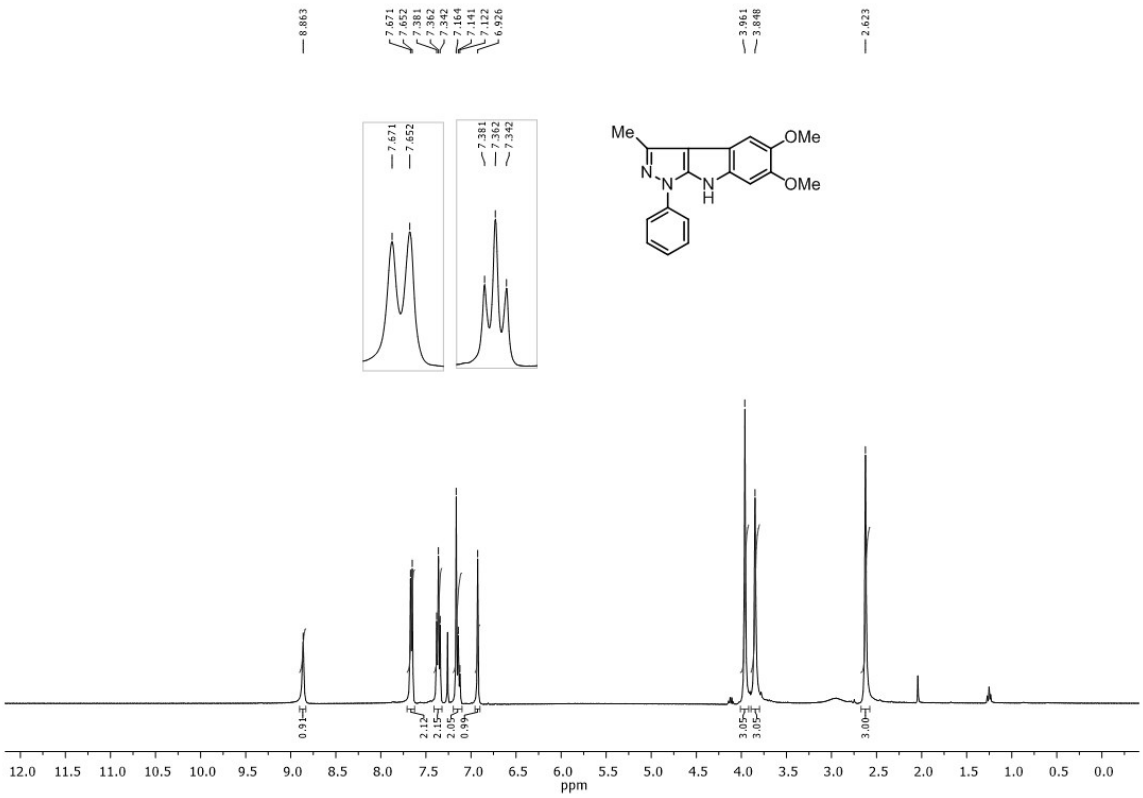
^{13}C Spectra of compound **1d** in DMSO-d_6 (100 MHz)



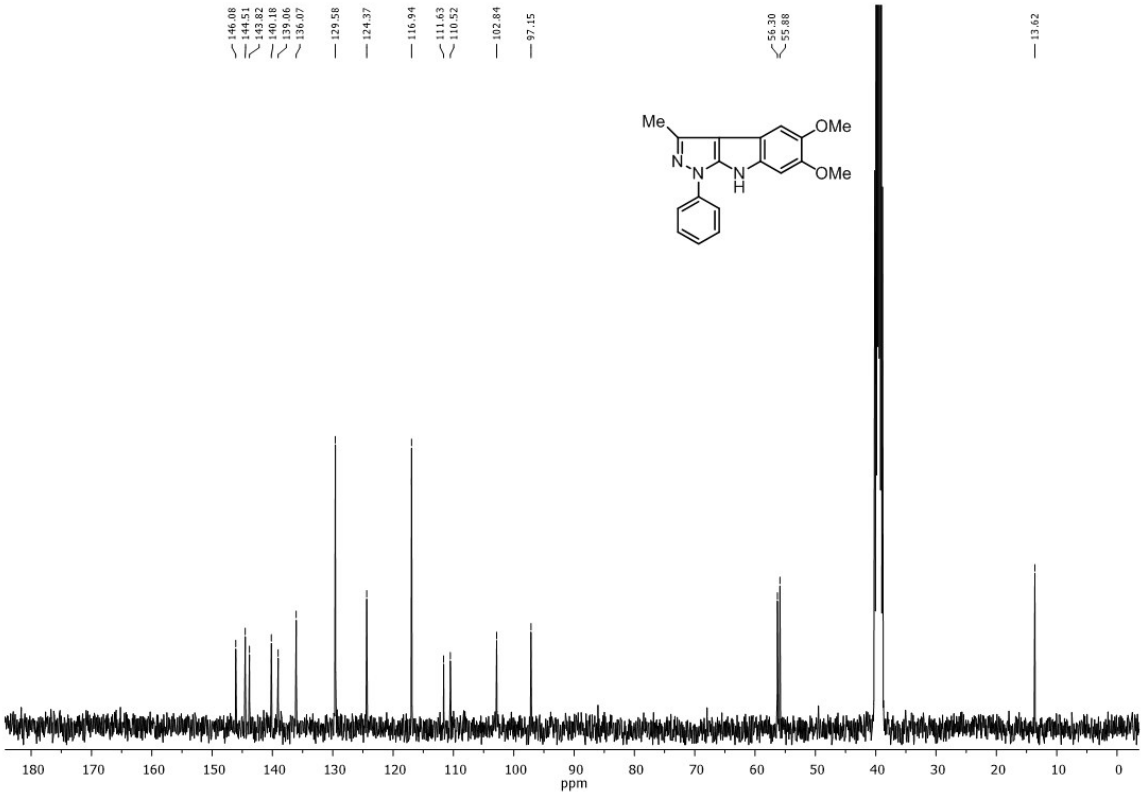
^{1}H Spectra of compound **1e** in DMSO-d_6 (700 MHz)



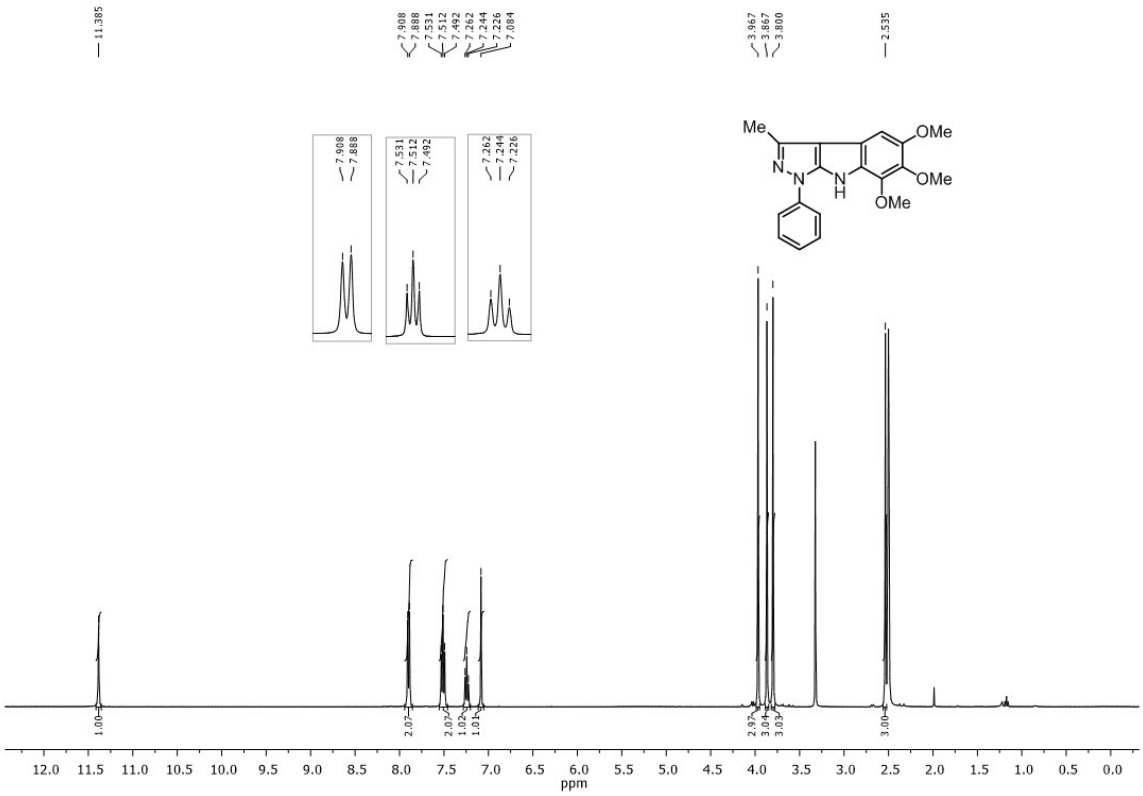
^{13}C Spectra of compound **1e** in DMSO-d_6 (175 MHz)



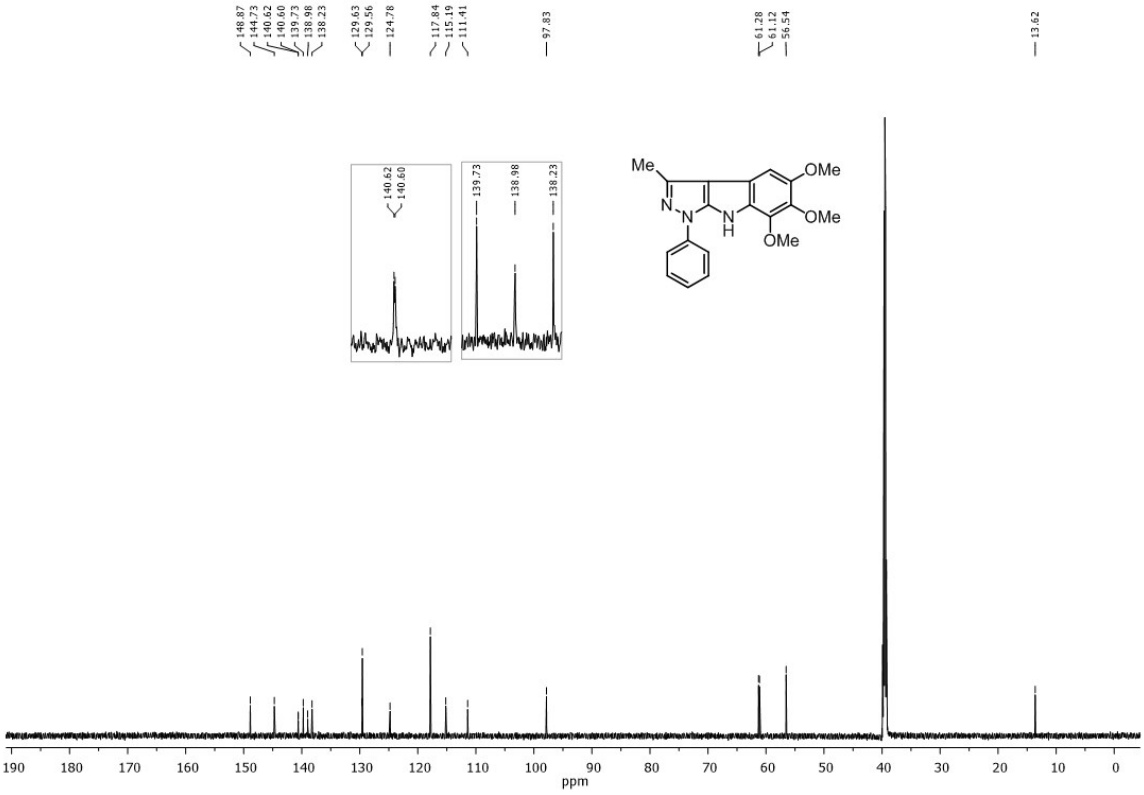
^{1}H Spectra of compound **1f** in DMSO-d_6 (400 MHz)



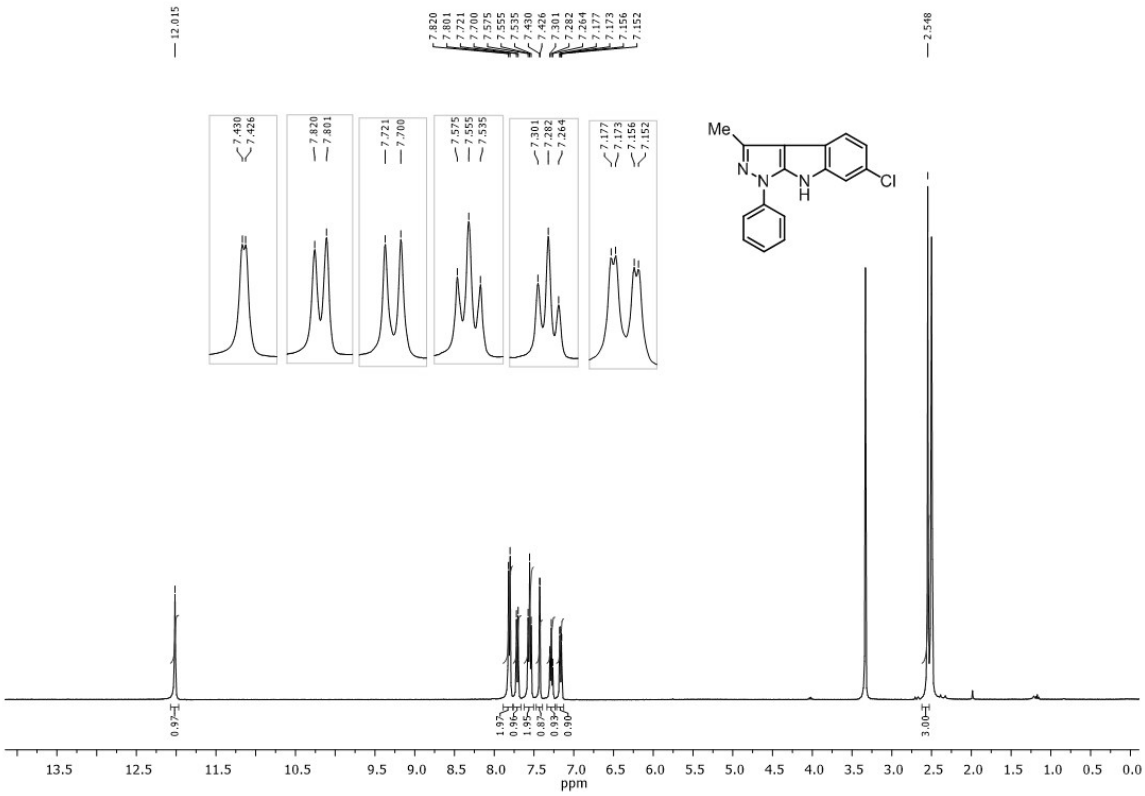
^{13}C Spectra of compound **1f** in DMSO-d_6 (100 MHz)



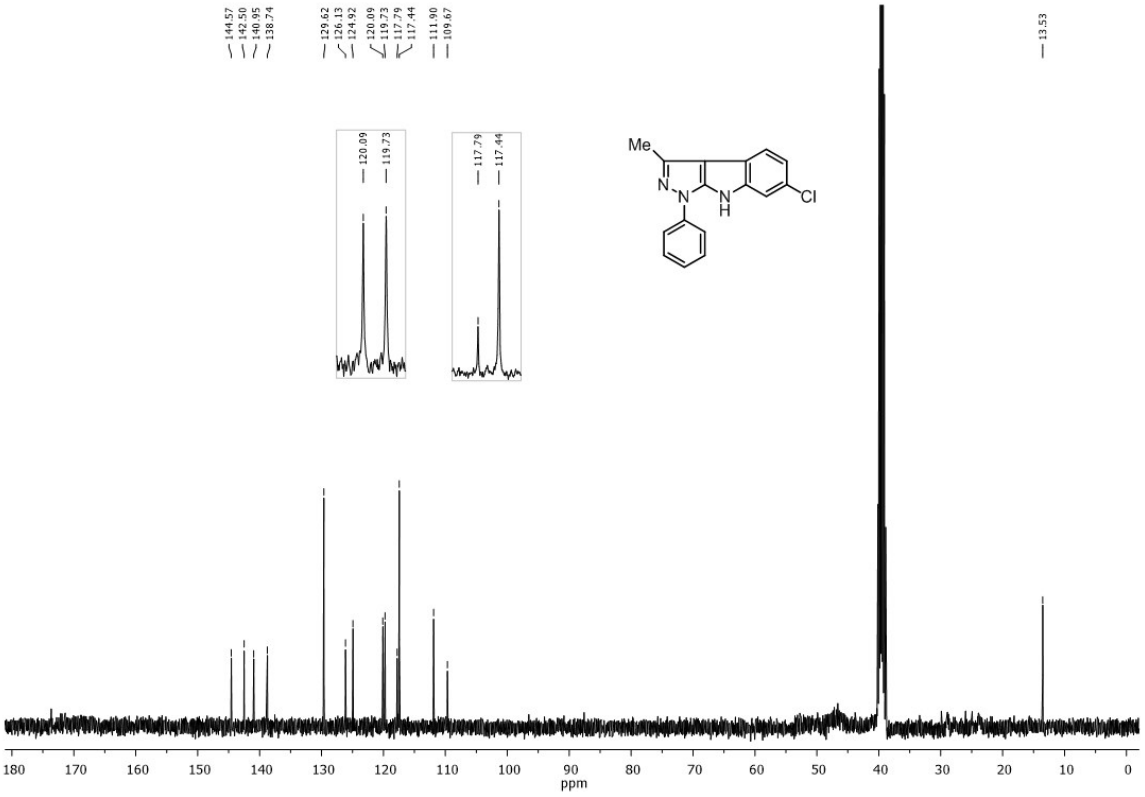
^{1}H Spectra of compound **1g** in DMSO-d_6 (400 MHz)



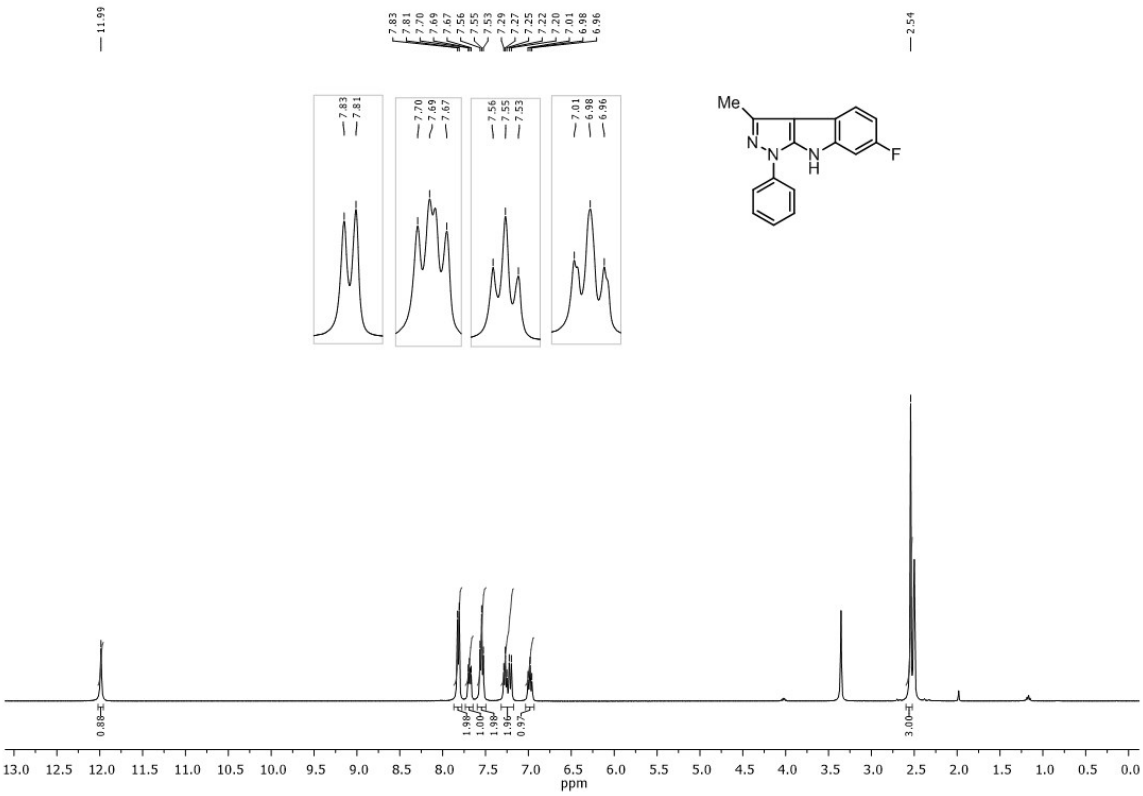
^{13}C Spectra of compound **1g** in DMSO-d_6 (175 MHz)



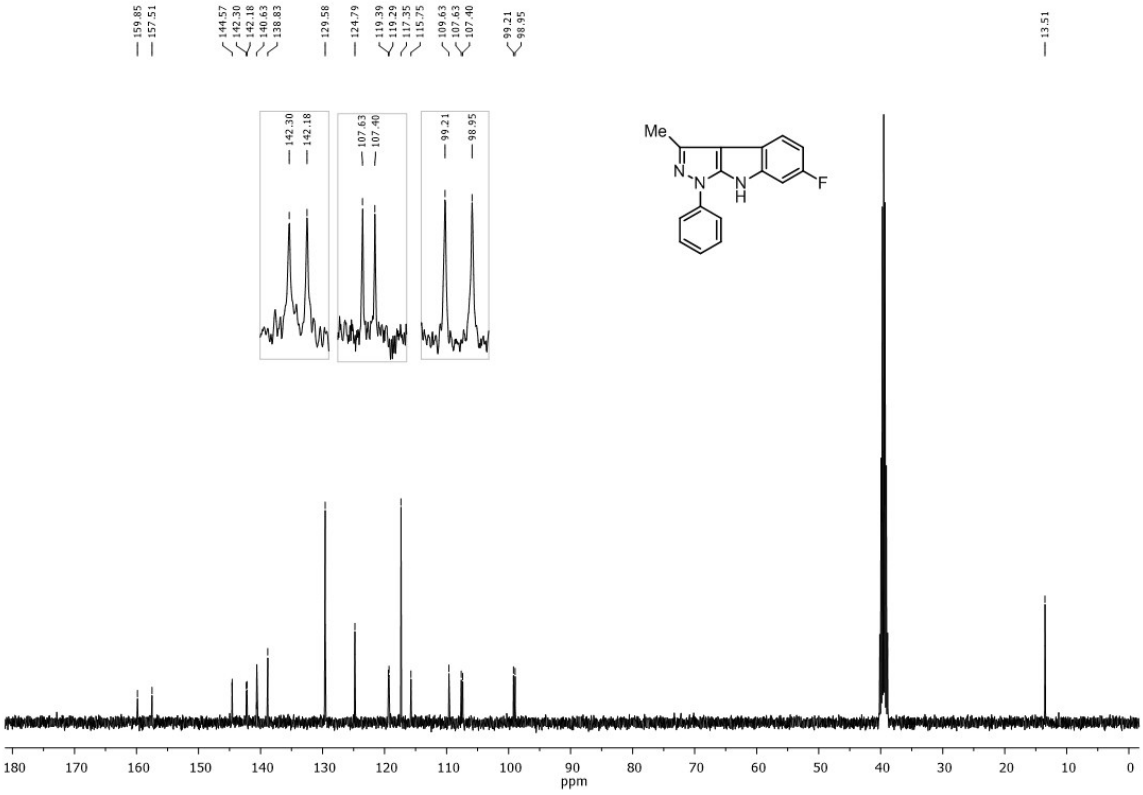
^{1}H Spectra of compound **1h** in DMSO-d_6 (400 MHz)



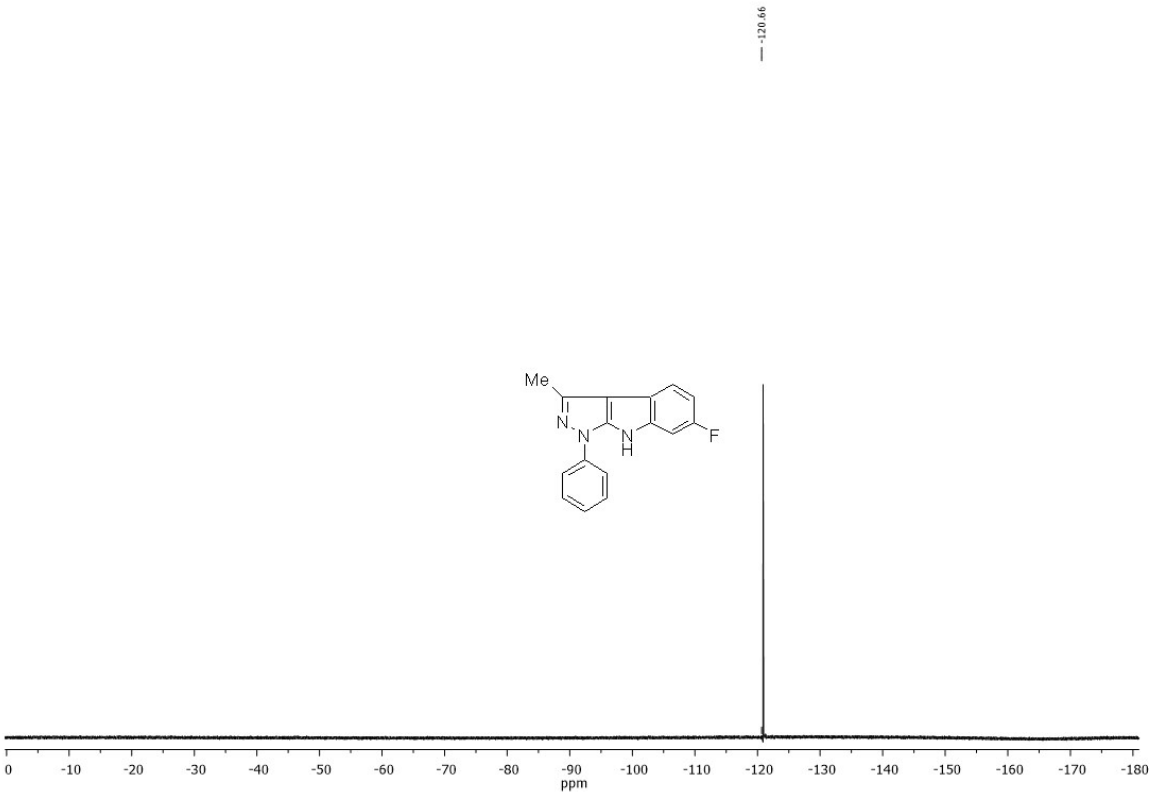
^{13}C Spectra of compound **1h** in DMSO-d_6 (100 MHz)



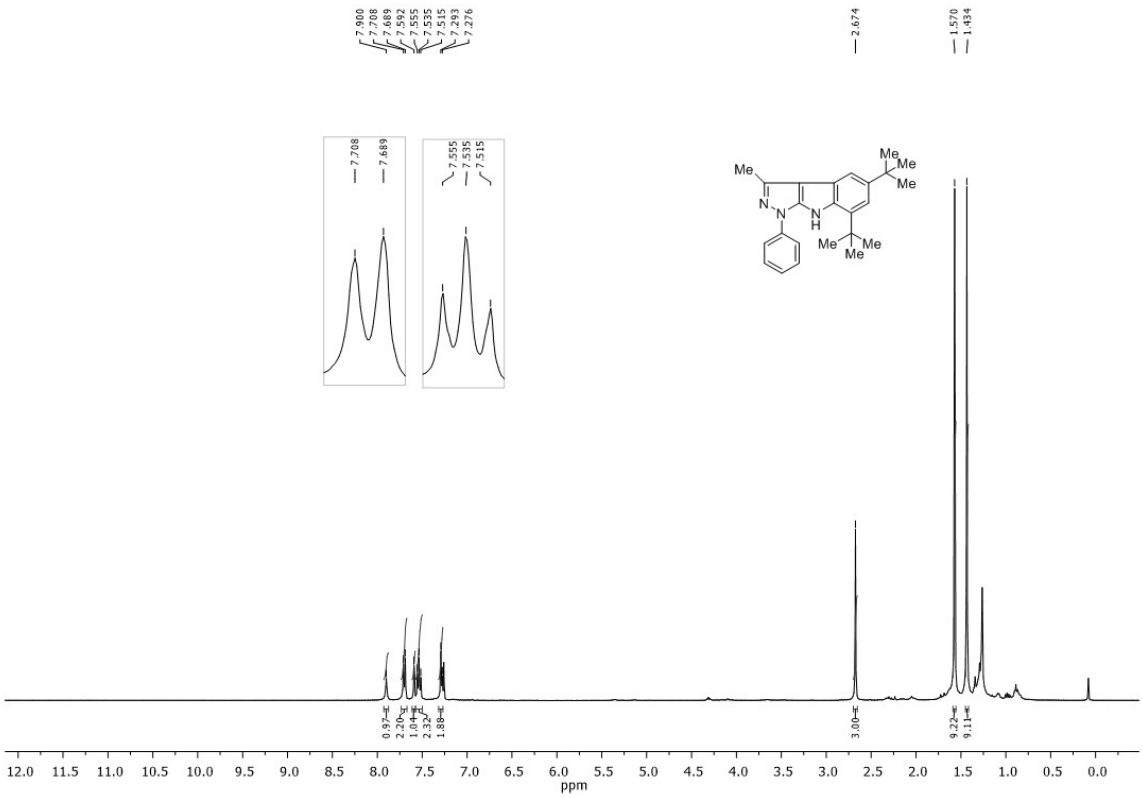
^{1}H Spectra of compound **1i** in DMSO-d_6 (400 MHz)



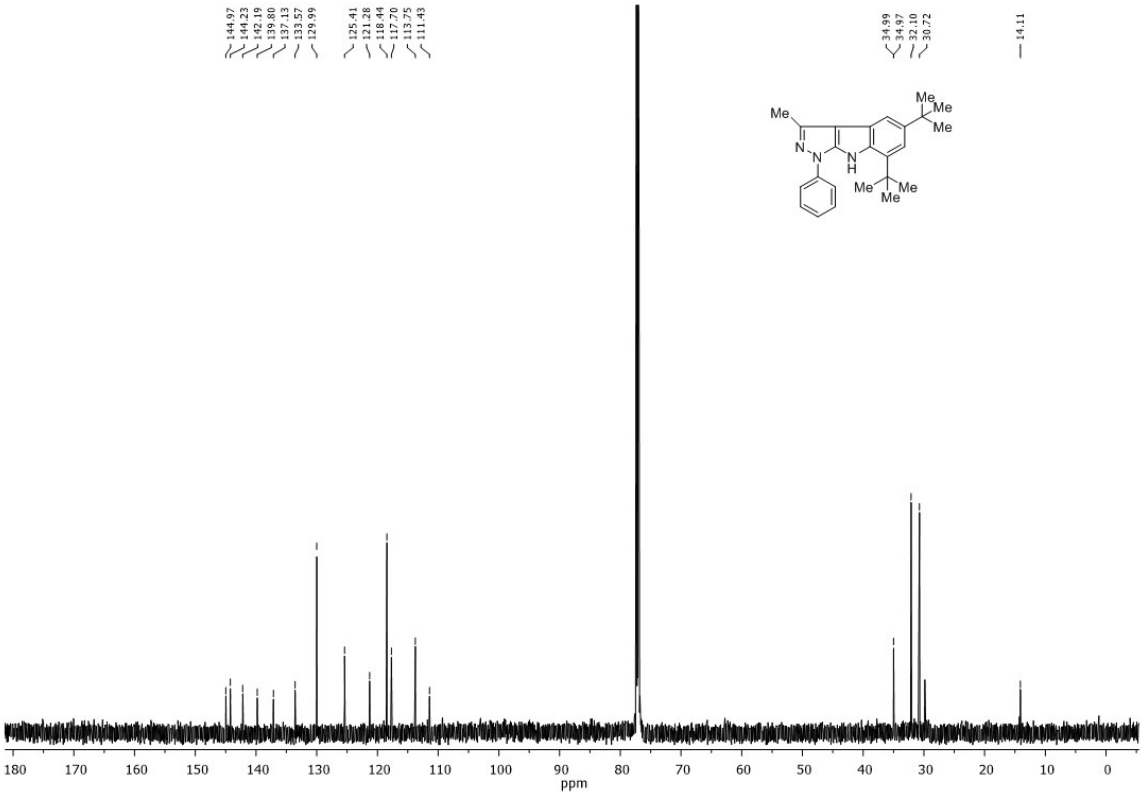
^{13}C Spectra of compound **1i** in DMSO-d_6 (100 MHz)



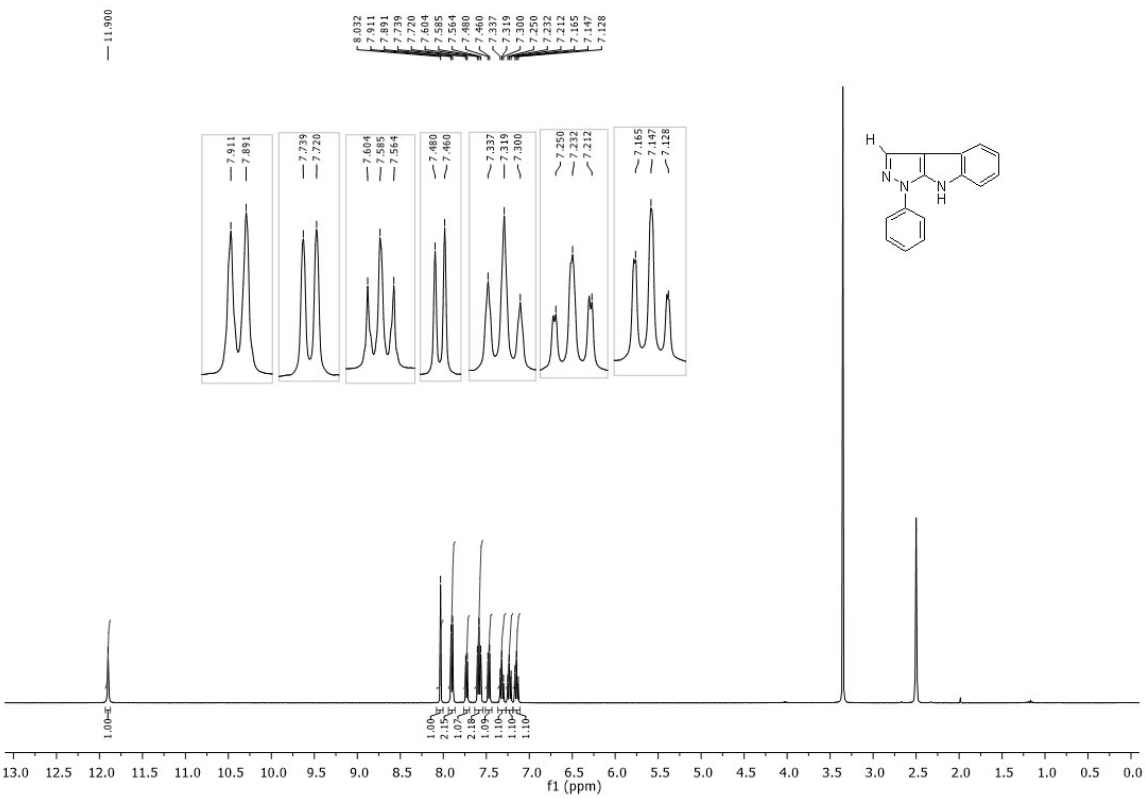
^{19}F Spectra of Compound in DMSO-d_6 (376 MHz)



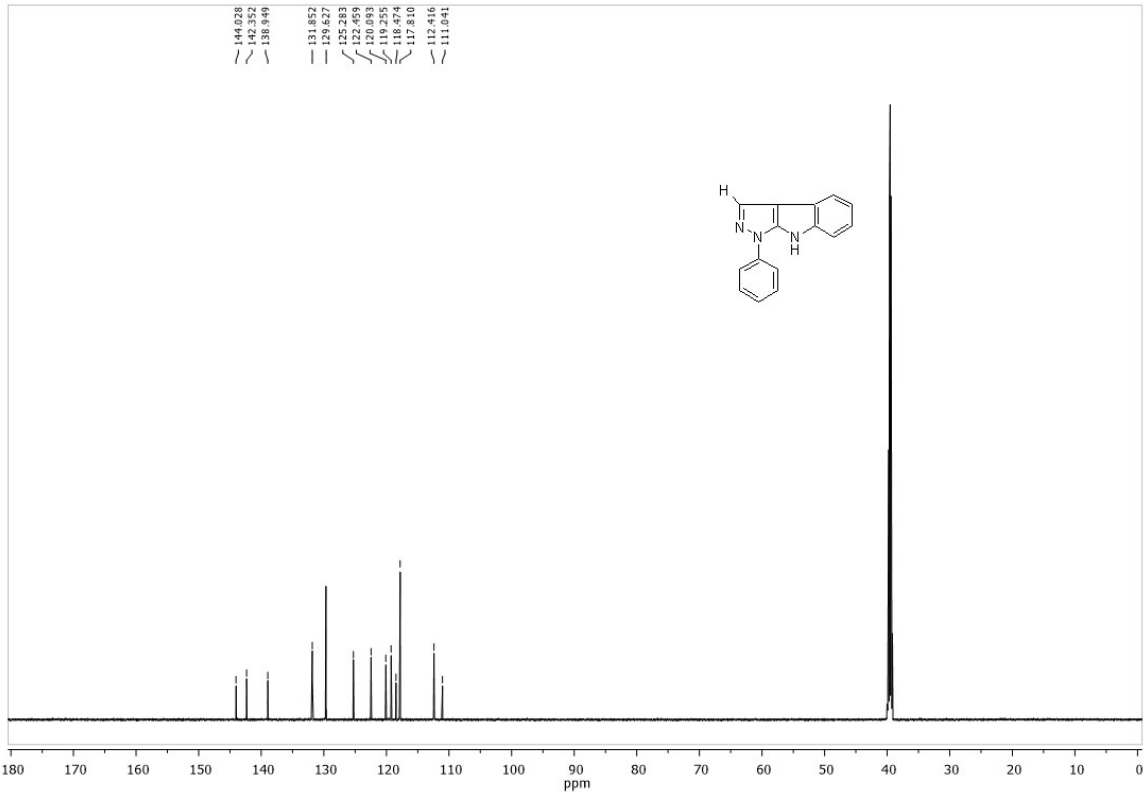
^{1}H Spectra of compound **1j** in $CDCl_3$ (400 MHz)



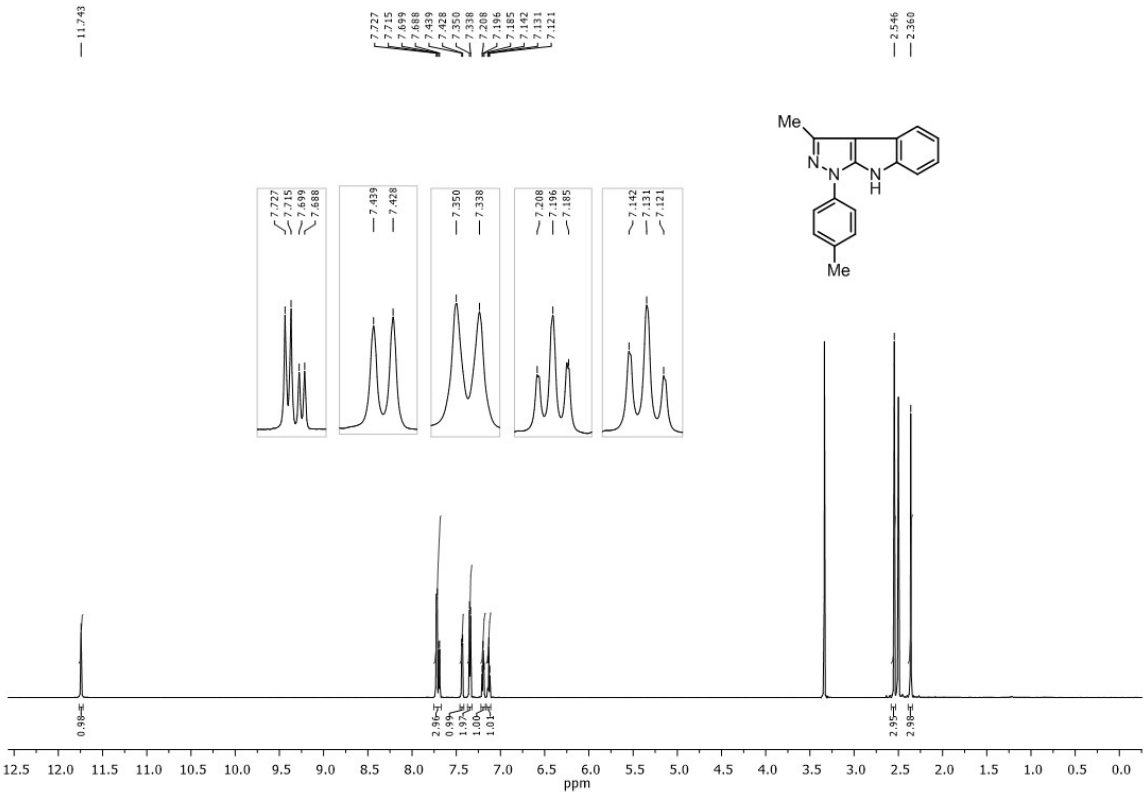
^{13}C Spectra of compound **1j** in $CDCl_3$ (175 MHz)



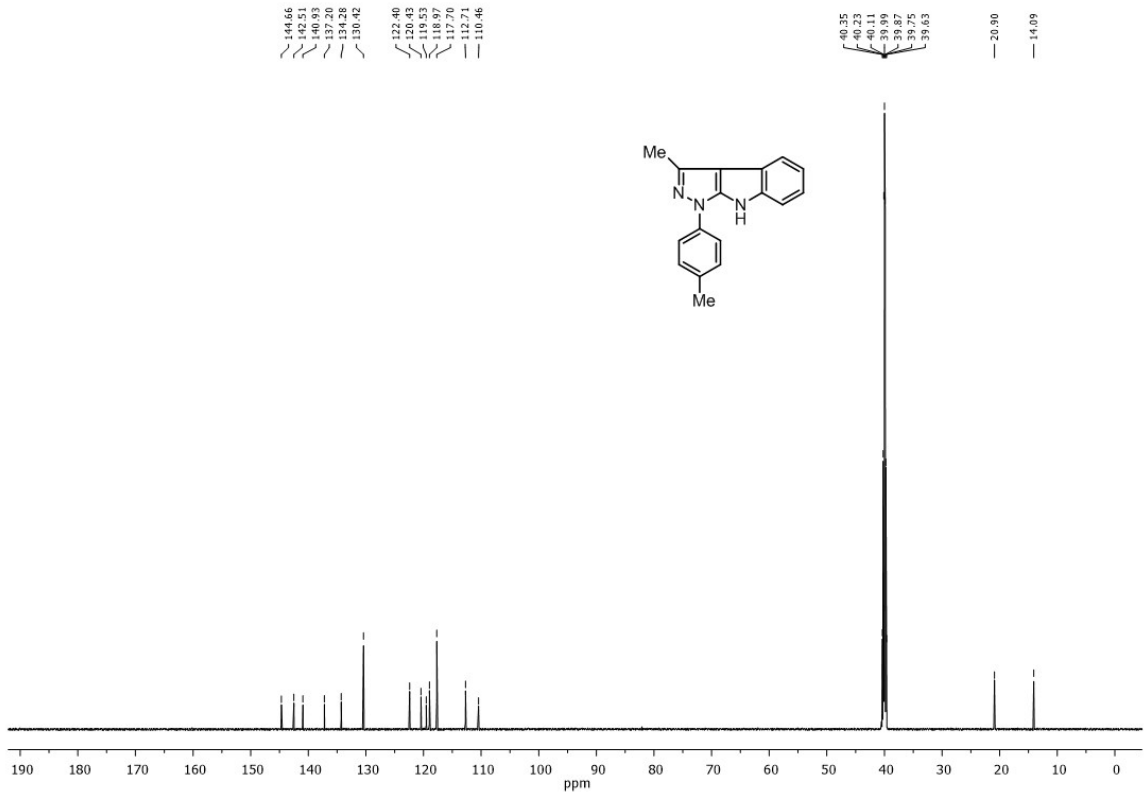
^{1}H Spectra of compound **1k** in DMSO-d_6 (400 MHz)



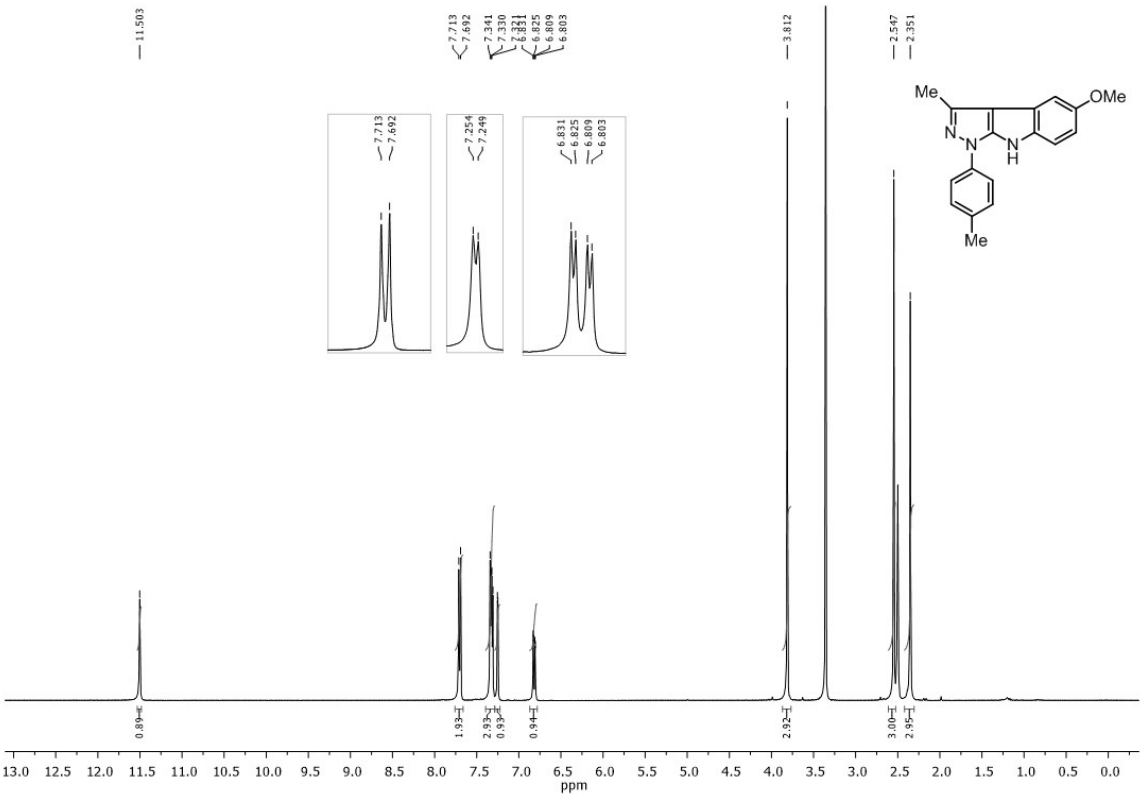
^{13}C Spectra of compound **1k** in DMSO-d_6 (175 MHz)



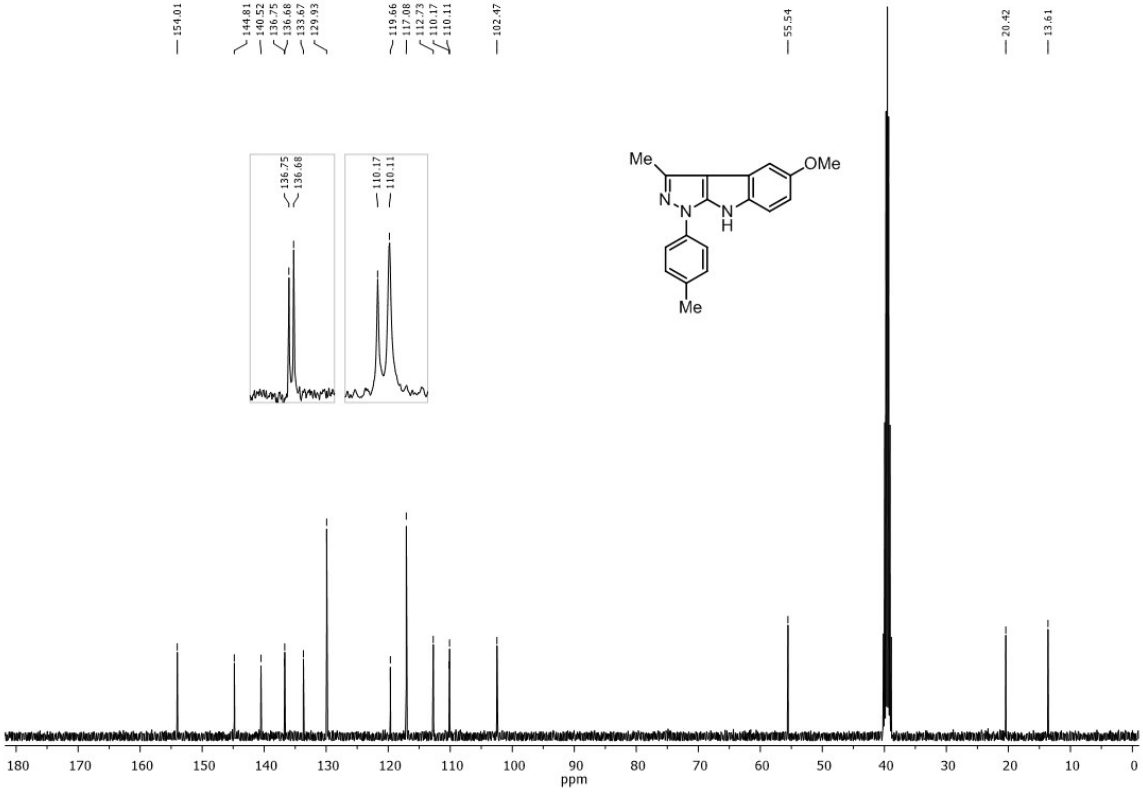
^{1}H Spectra of compound **1l** in DMSO-d_6 (700 MHz)



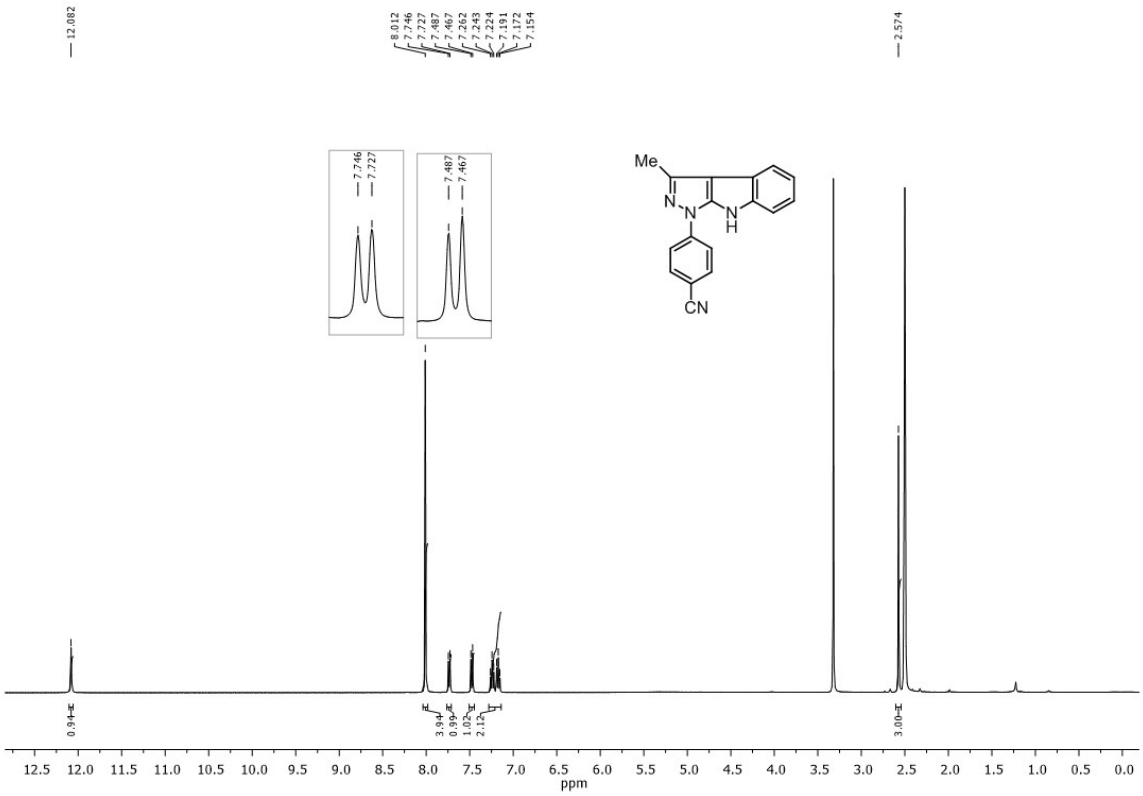
^{13}C Spectra of compound **1l** in DMSO-d_6 (175 MHz)



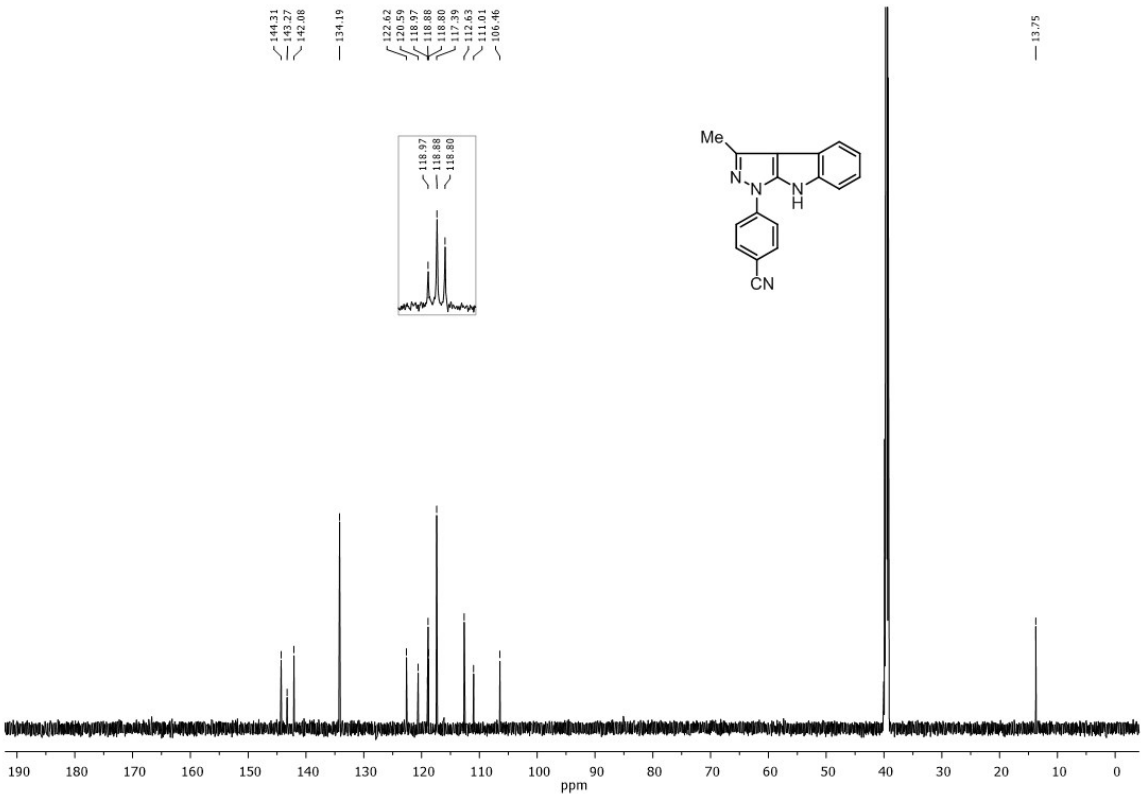
^{1}H Spectra of compound **1m** in DMSO-d_6 (400 MHz)



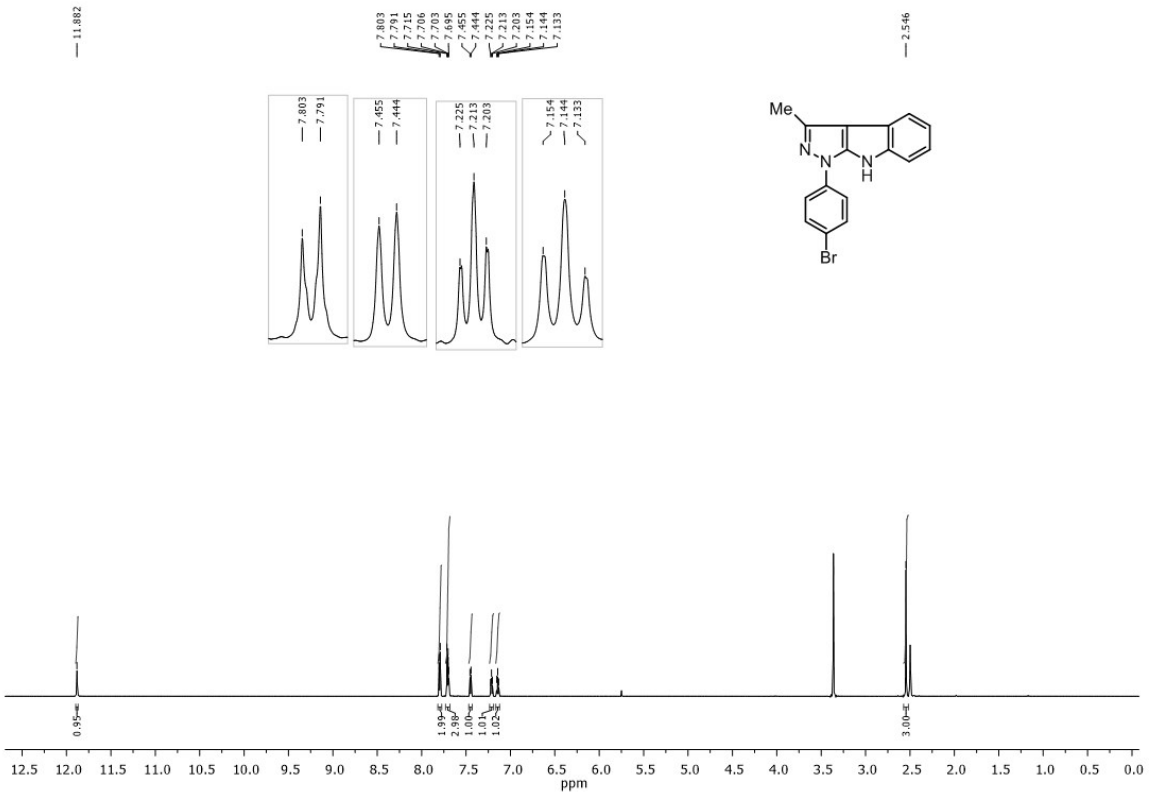
^{13}C Spectra of compound **1m** in DMSO-d_6 (100 MHz)



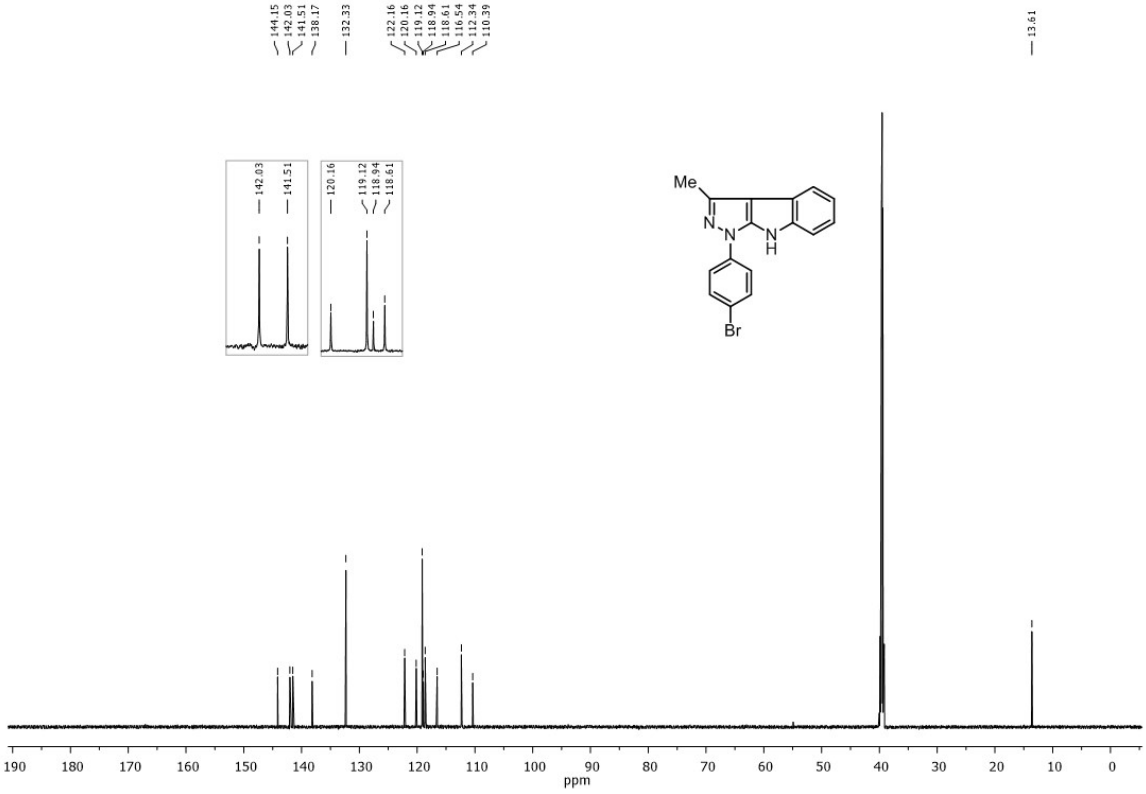
^{1}H Spectra of compound **1n** in DMSO-d_6 (400 MHz)



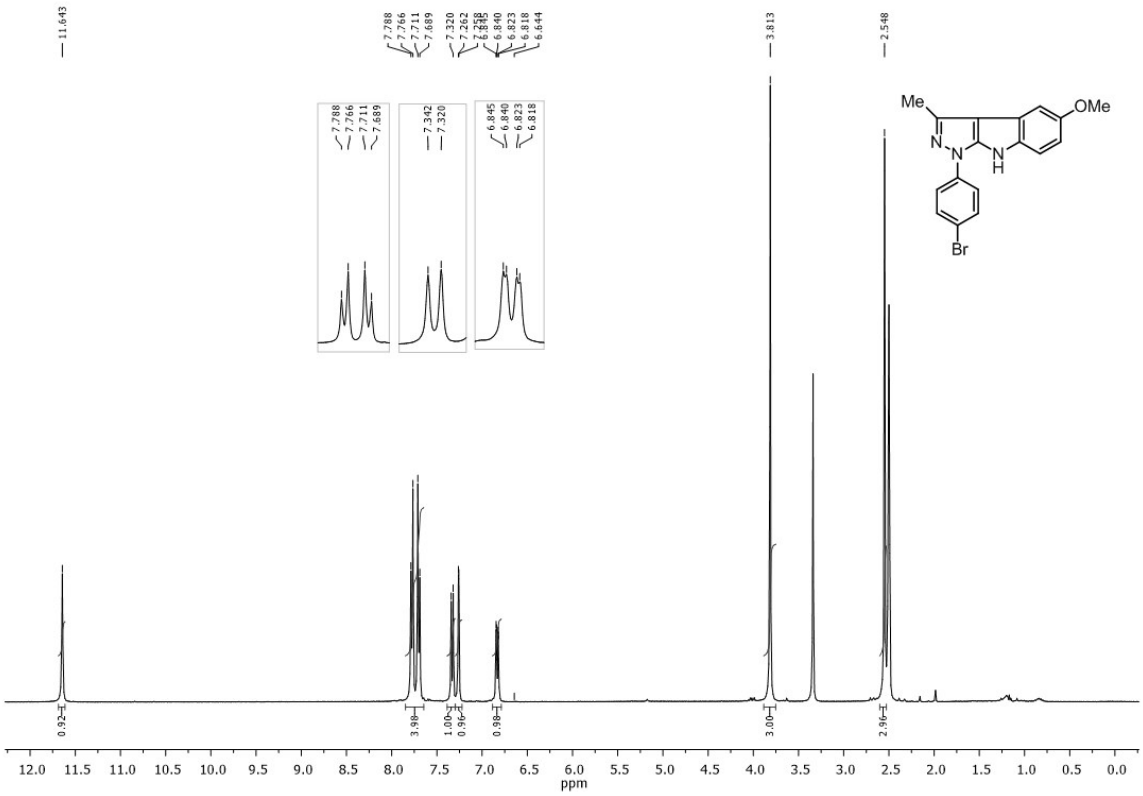
^{13}C Spectra of compound **1n** in DMSO-d_6 (175 MHz)



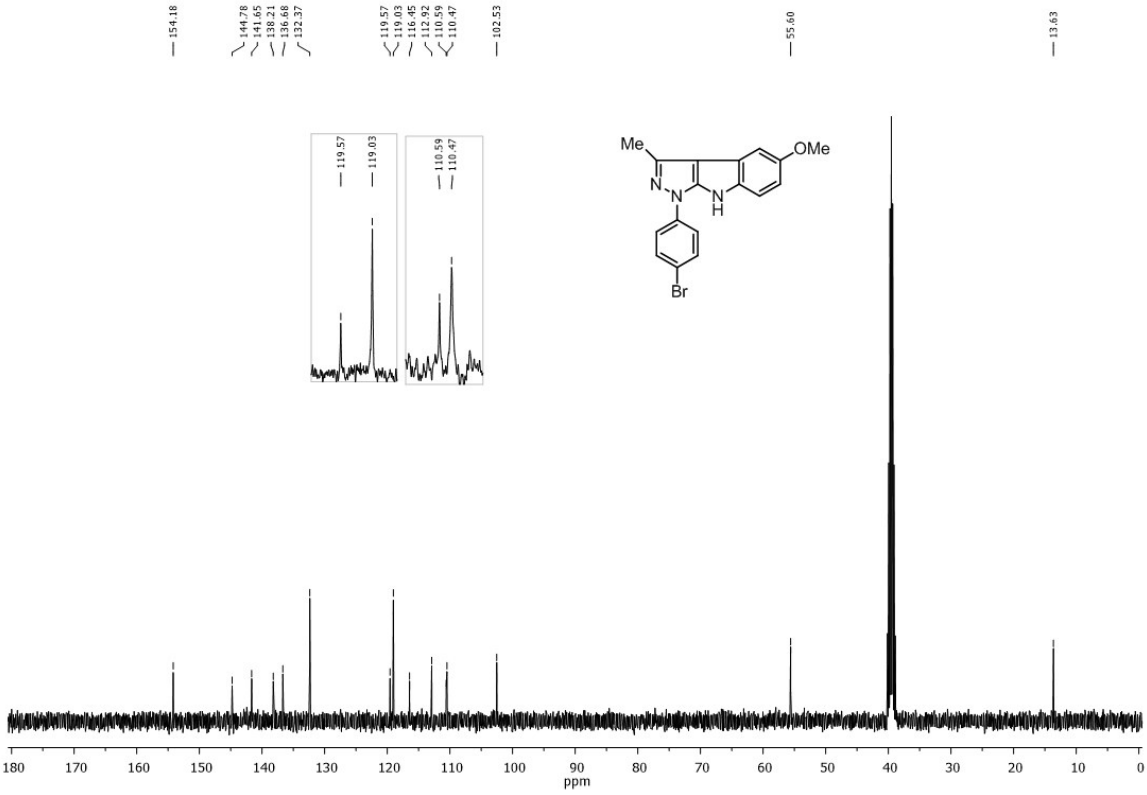
^{1}H Spectra of compound **1o** in DMSO-d_6 (700 MHz)



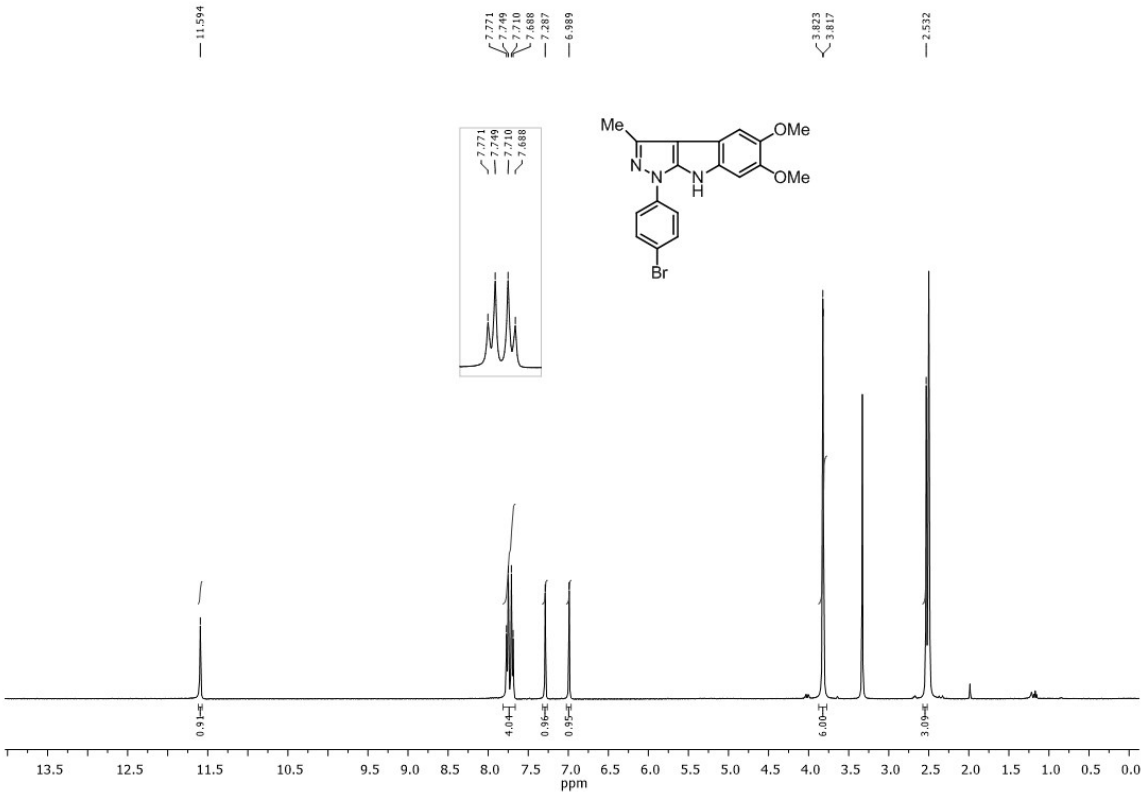
^{13}C Spectra of compound **1o** in DMSO-d_6 (175 MHz)



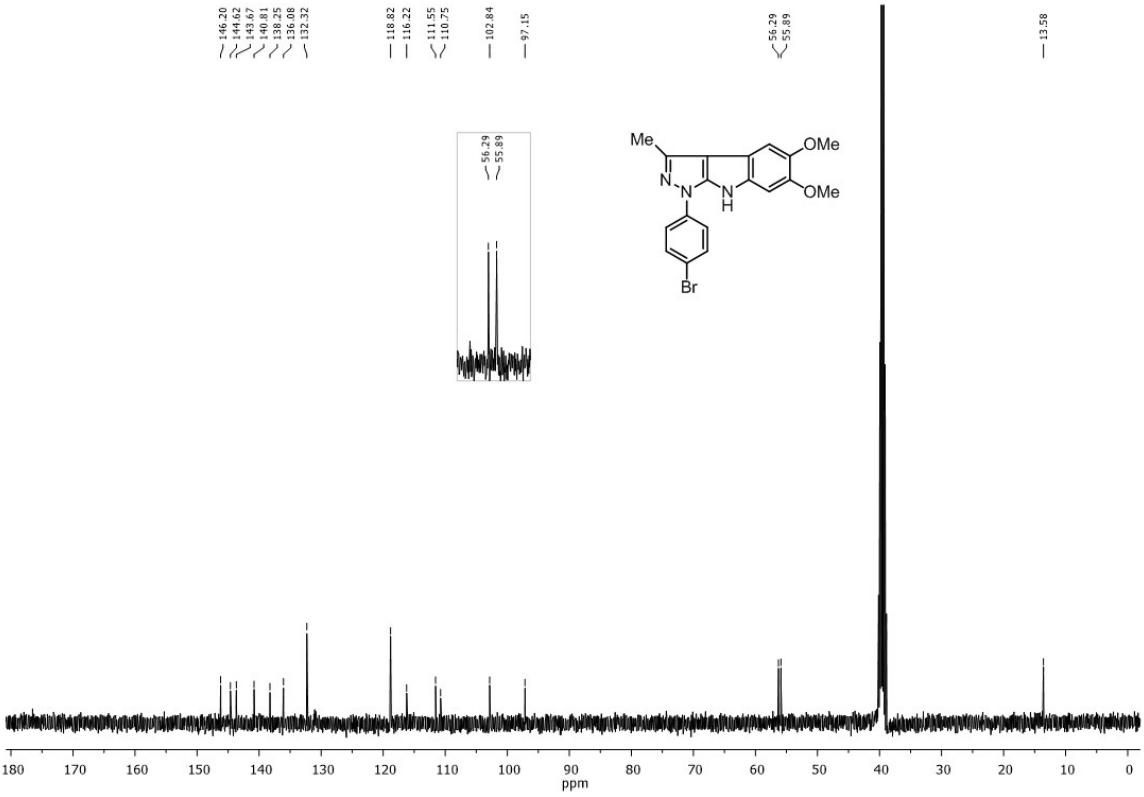
^{1}H Spectra of compound **1p** in DMSO-d_6 (400 MHz)



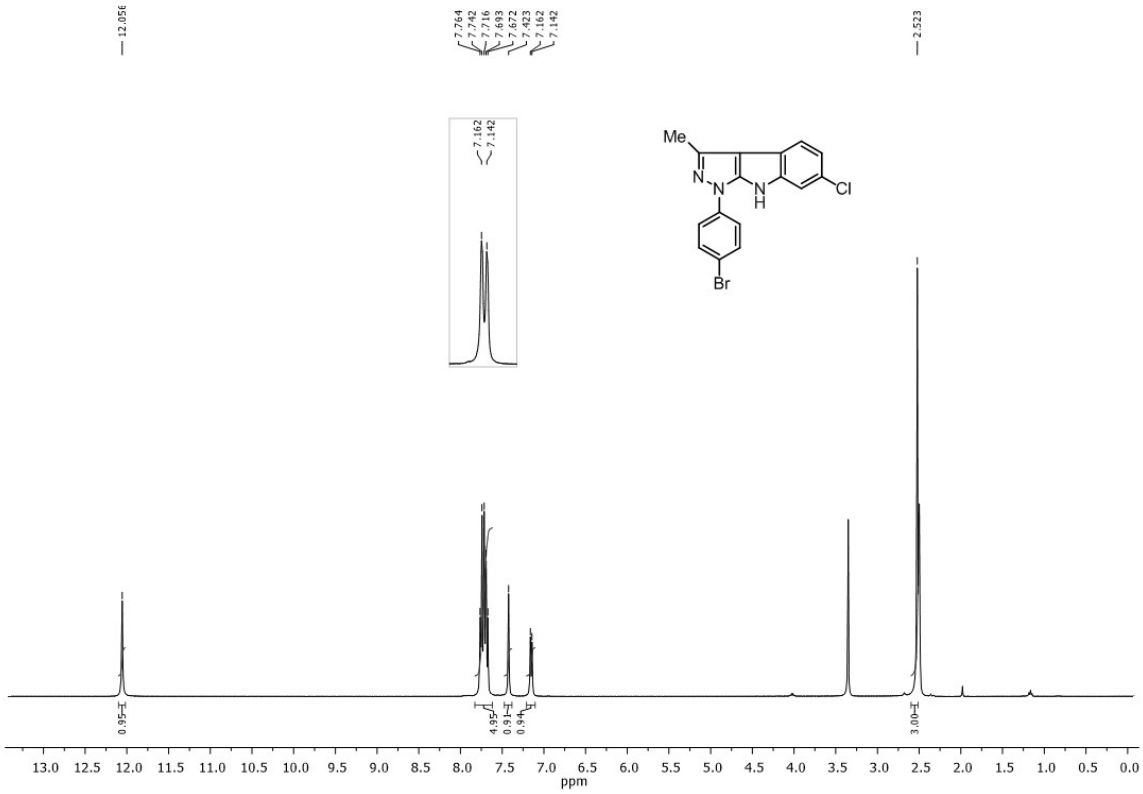
^{13}C Spectra of compound **1p** in DMSO-d_6 (100 MHz)



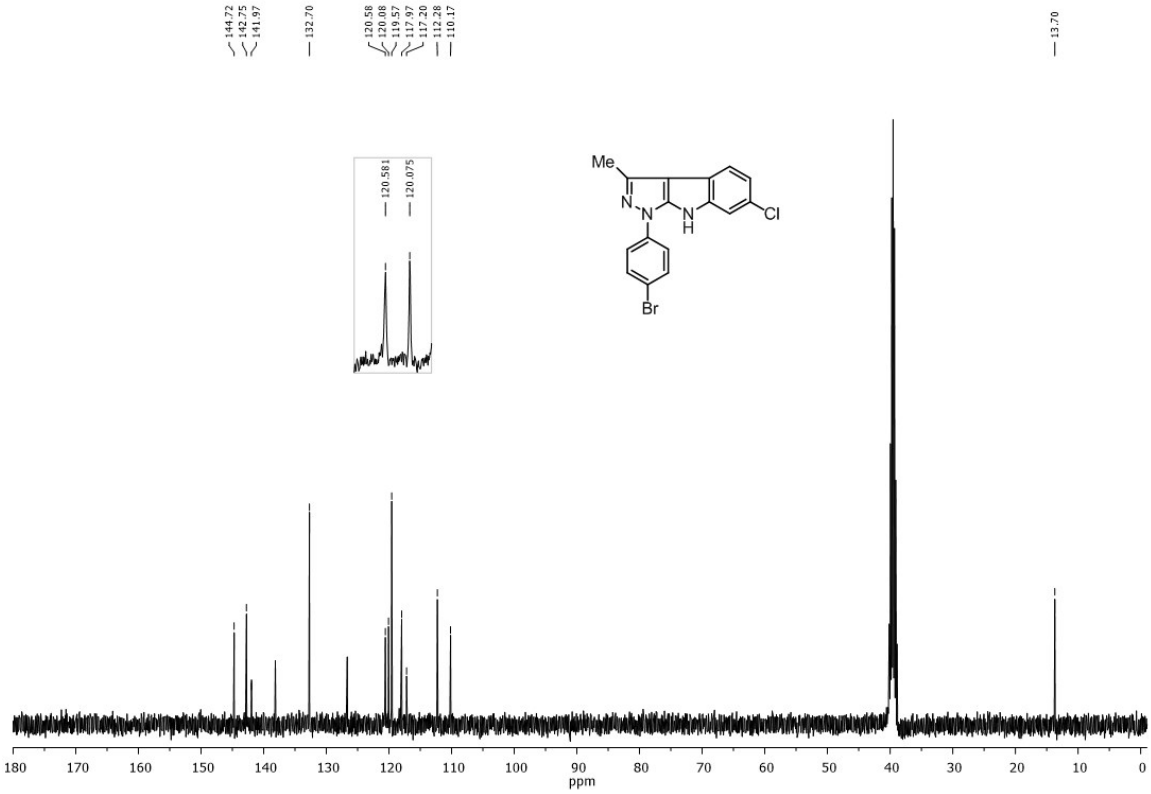
^{1}H Spectra of compound **1q** in DMSO-d_6 (400 MHz)



^{13}C Spectra of compound **1q** in DMSO-d_6 (100 MHz)

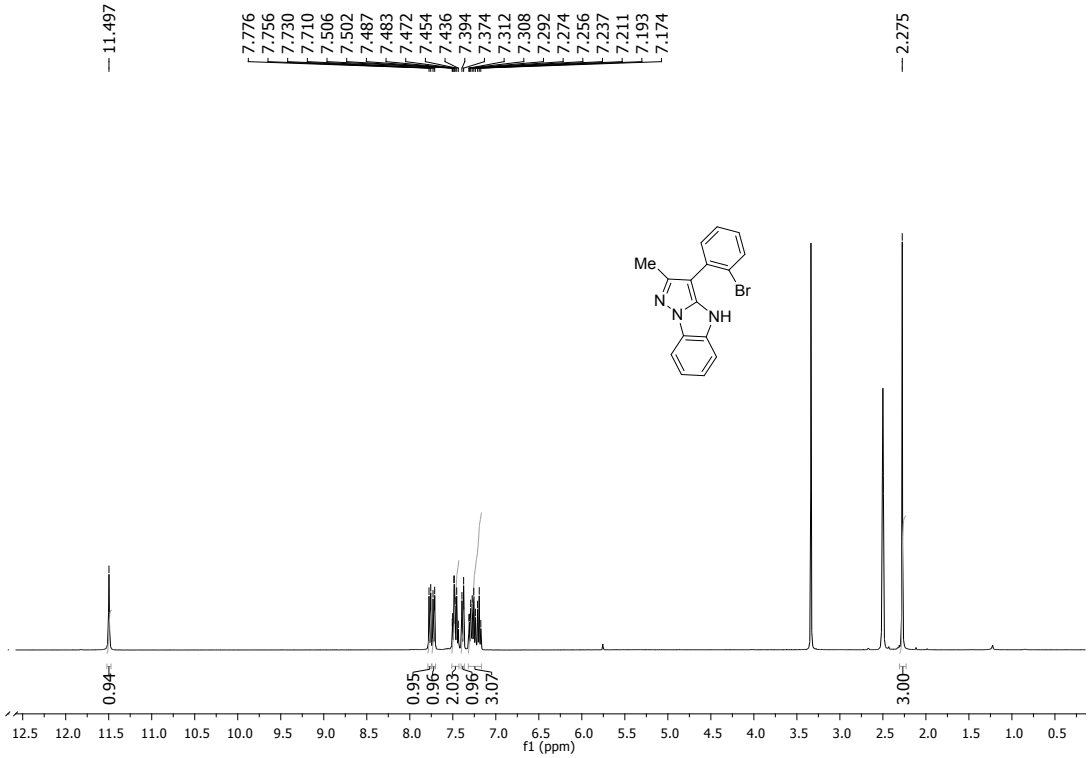


^{1}H Spectra of compound **1r** in DMSO-d_6 (400 MHz)

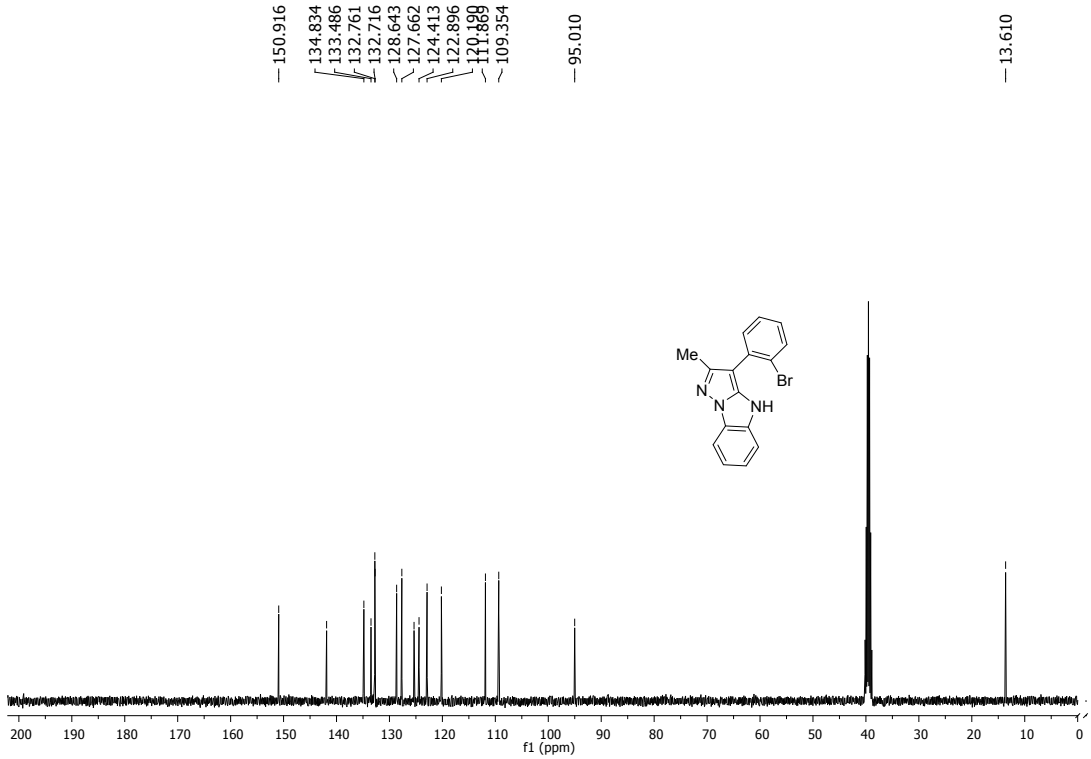


^{13}C Spectra of compound **1r** in DMSO-d_6 (100 MHz)

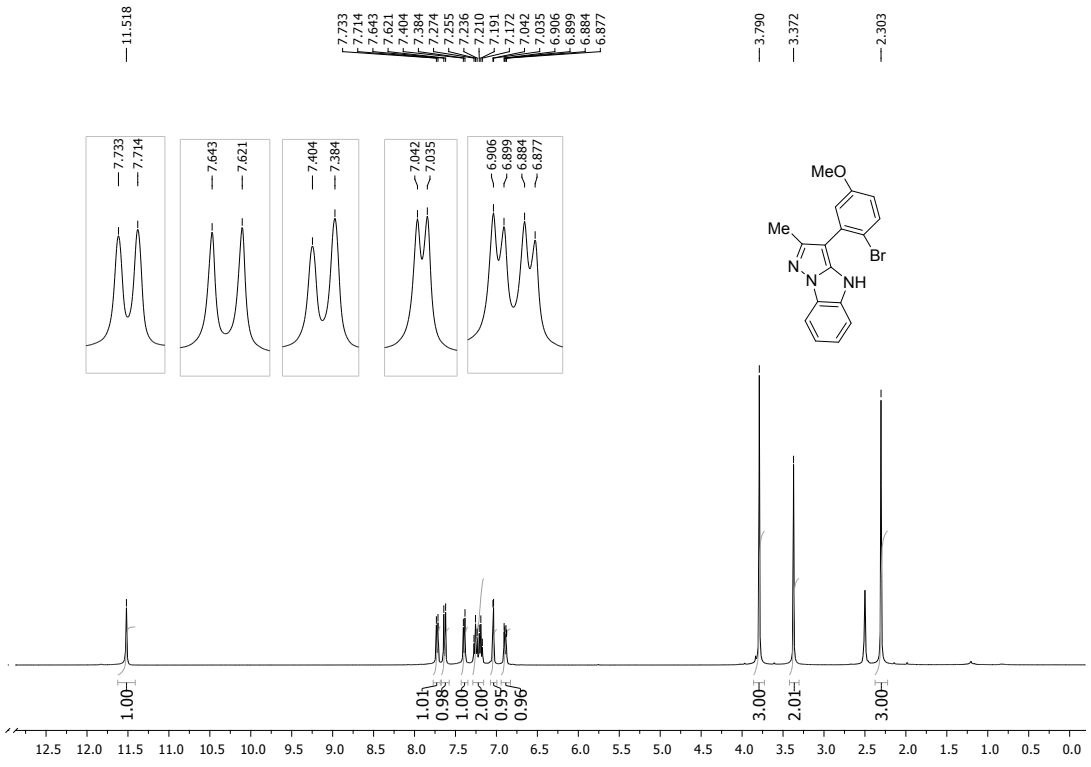
^{1}H & ^{13}C NMR of pyrazolo[1,5-*a*]benzimidazole (5s-z):



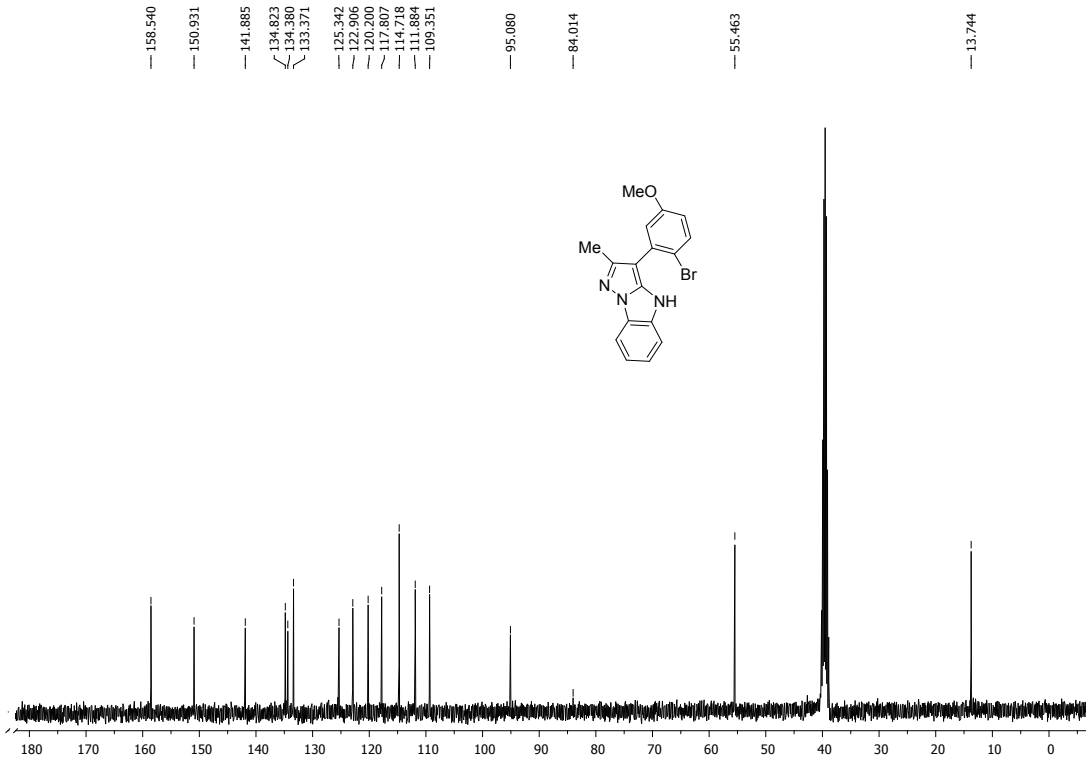
^{1}H Spectra of compound **5s** in DMSO-d_6 (400 MHz)



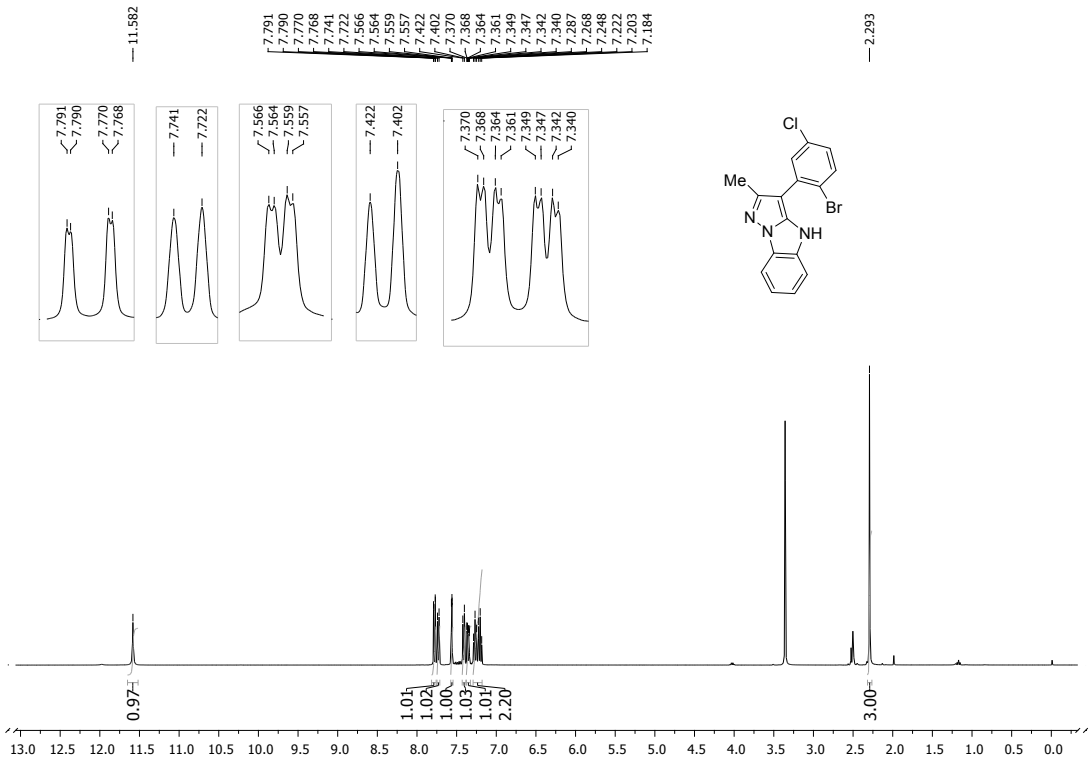
^{13}C Spectra of compound **5s** in DMSO-d_6 (100 MHz)



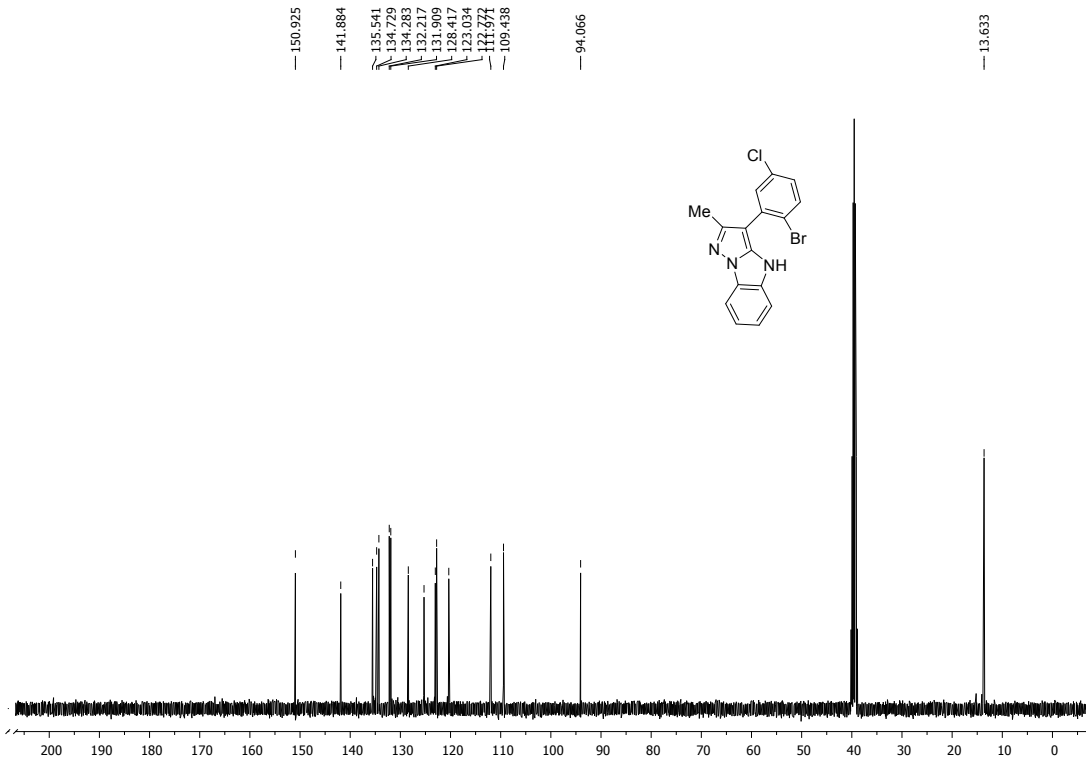
^{1}H Spectra of compound **5t** in DMSO-d_6 (400 MHz)



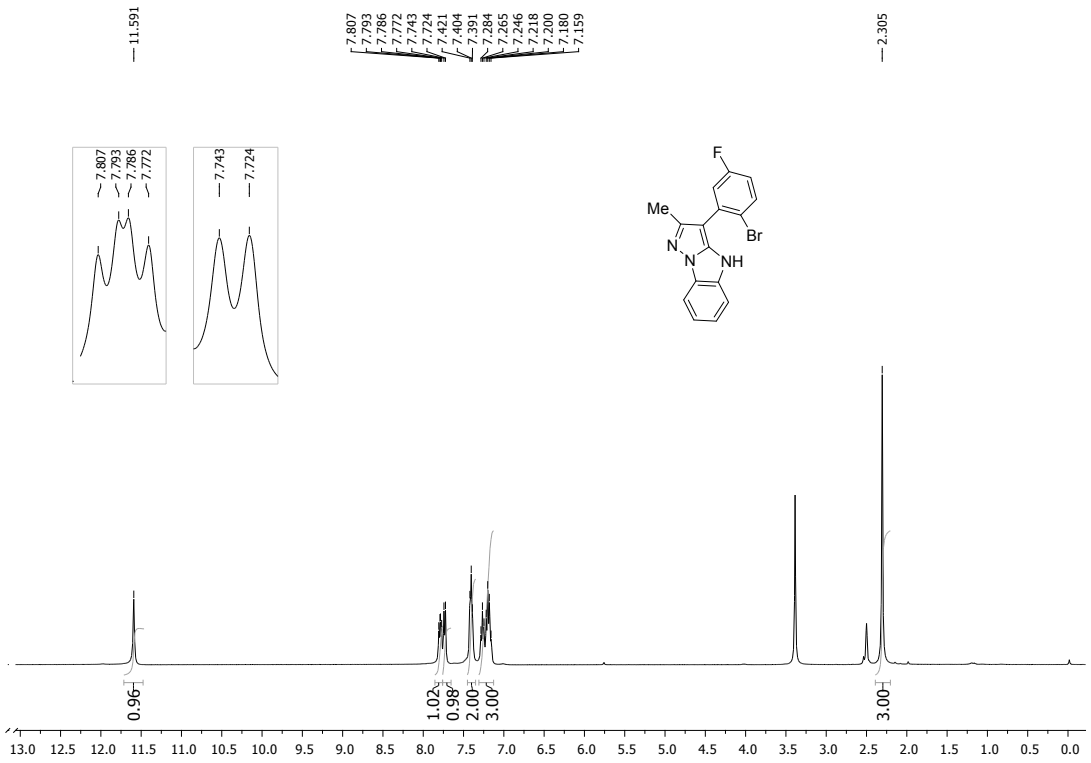
^{13}C Spectra of compound **5t** in DMSO-d_6 (100 MHz)



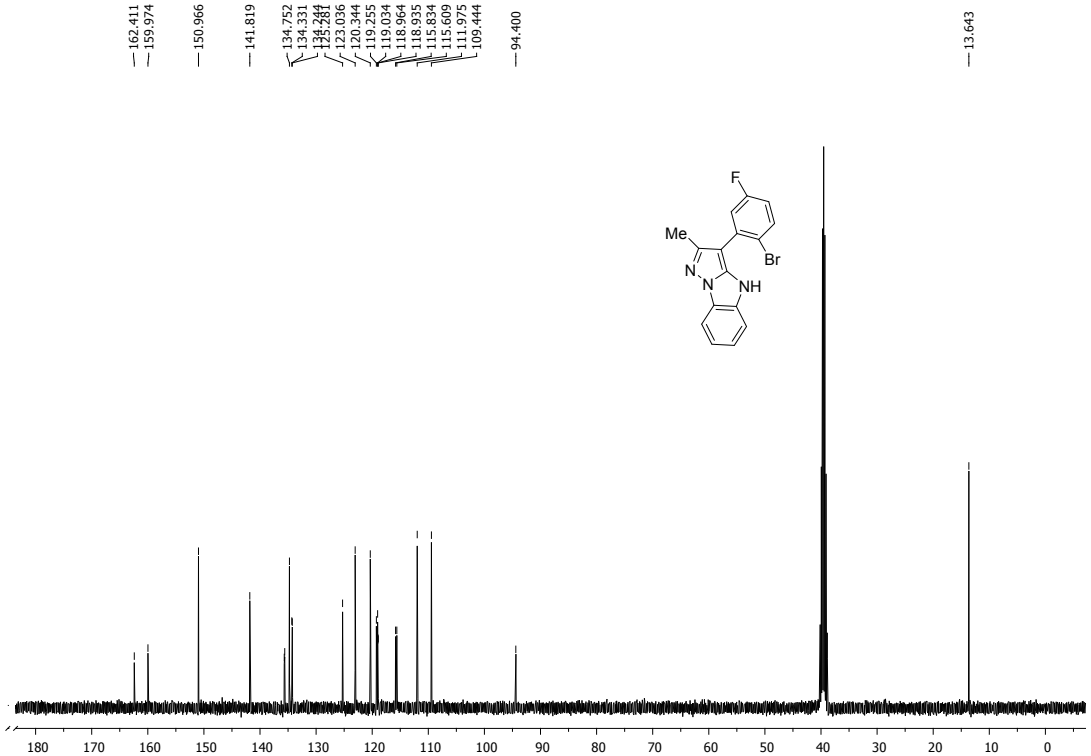
^{1}H Spectra of compound **5u** in DMSO-d_6 (400 MHz)



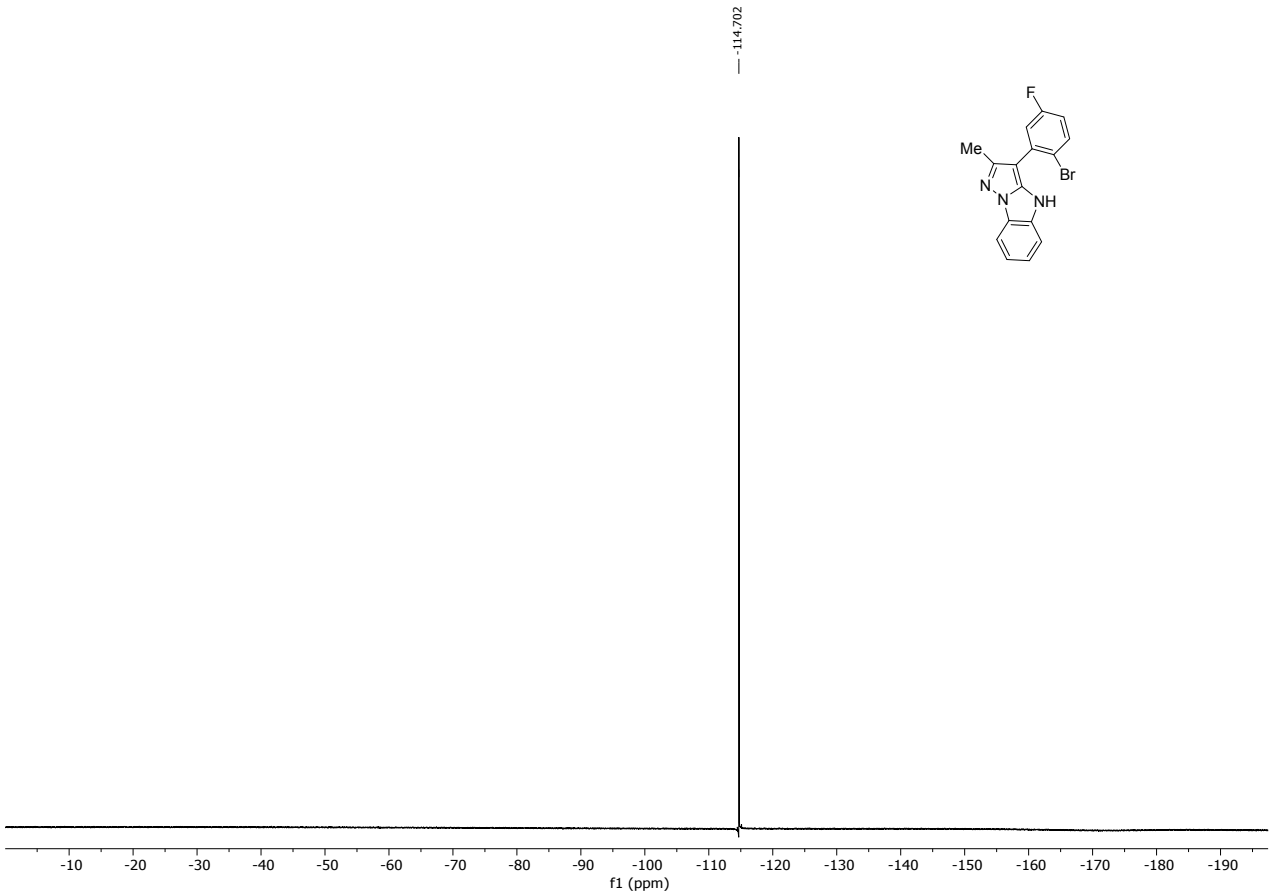
^{13}C Spectra of compound **5u** in DMSO-d_6 (100 MHz)



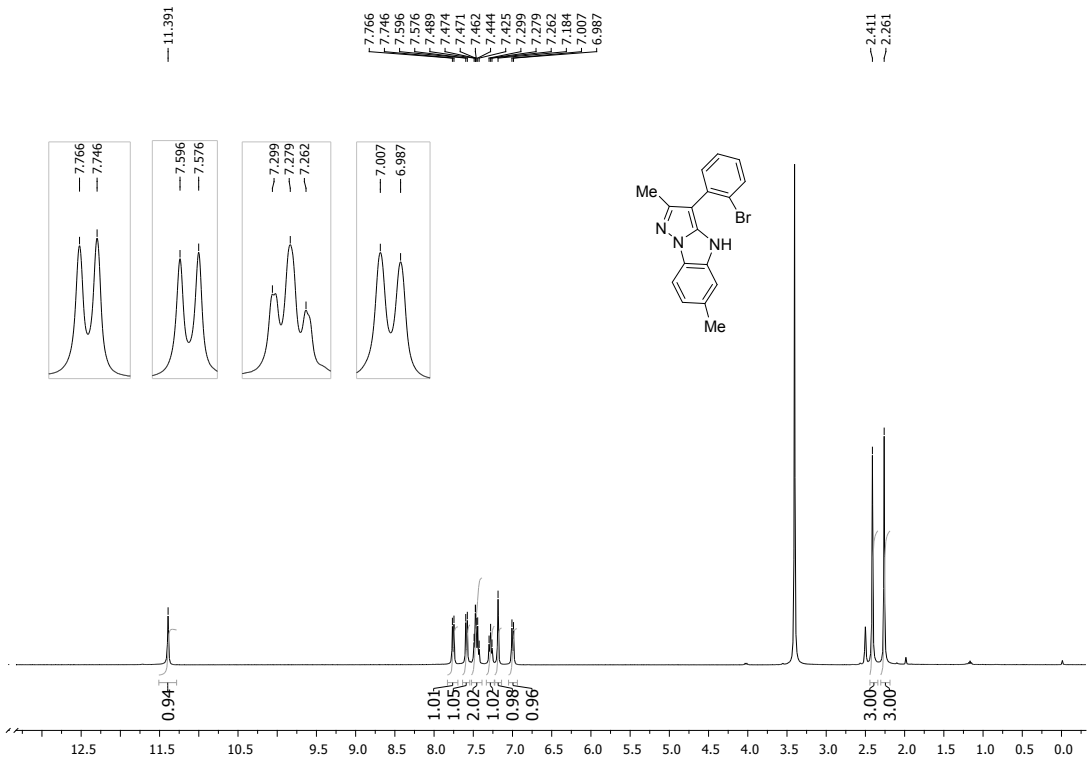
^{1}H Spectra of compound **5v** in DMSO-d_6 (400 MHz)



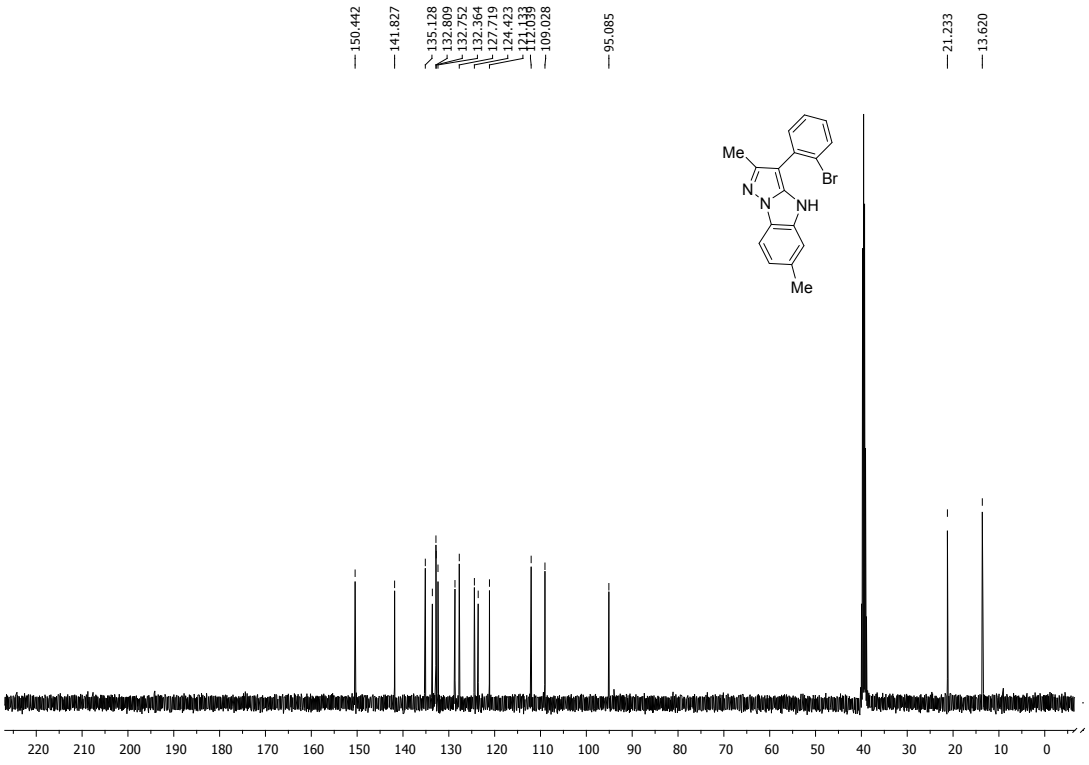
^{13}C Spectra of compound **5v** in DMSO-d_6 (100 MHz)



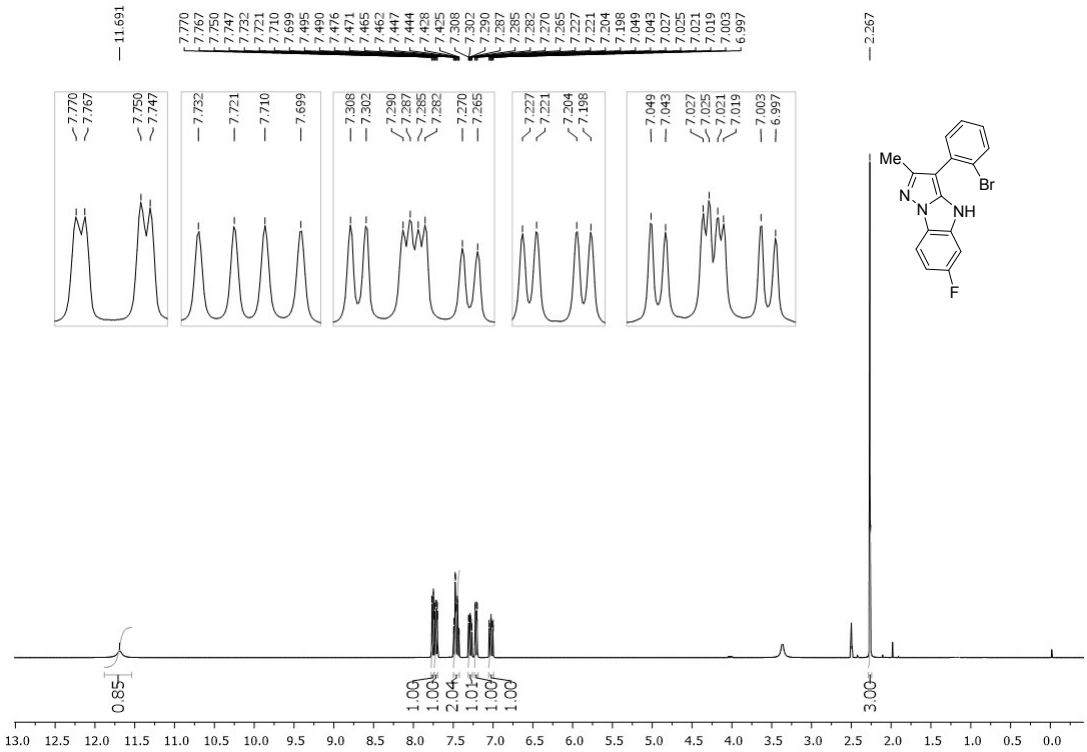
^{19}F Spectra of compound **5v** in DMSO-d_6 (376 MHz)



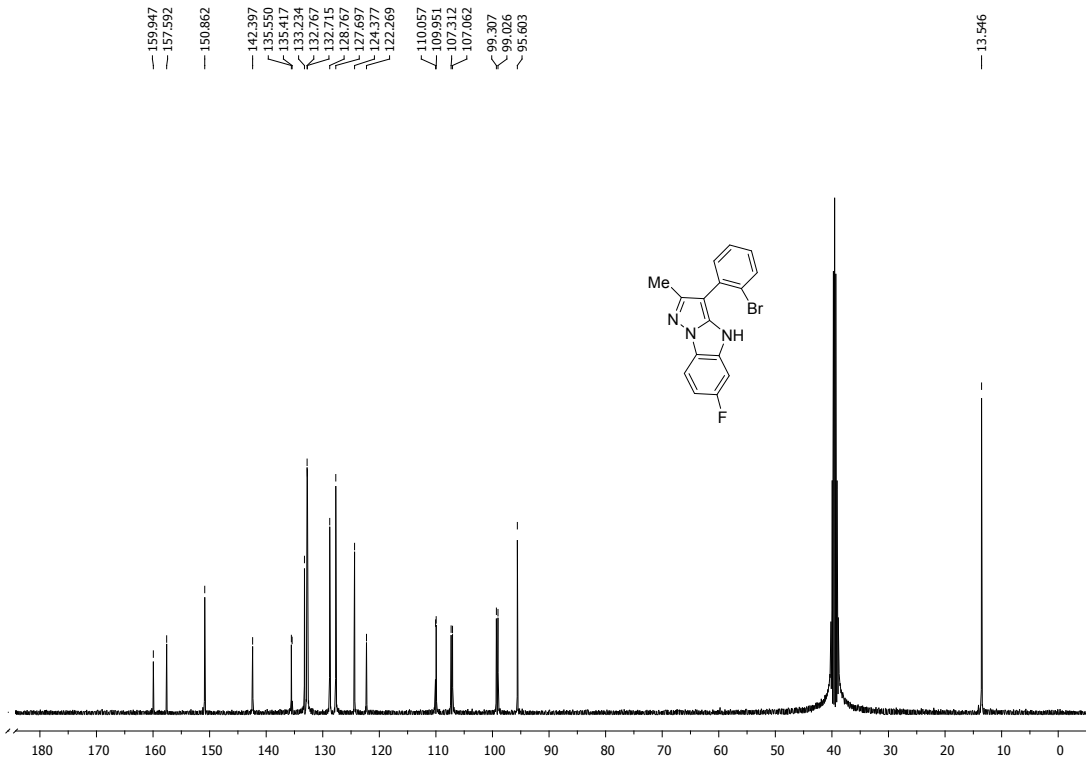
^{1}H Spectra of compound **5w** in DMSO-d_6 (400 MHz)



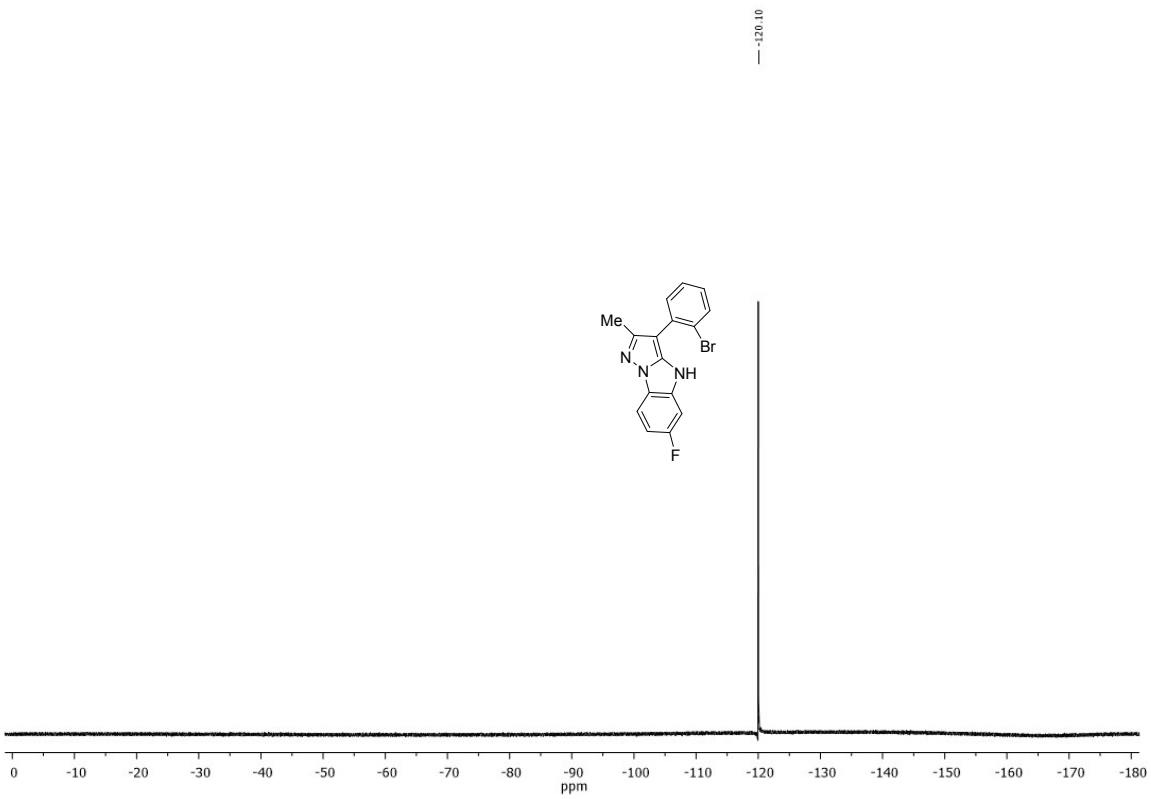
^{13}C Spectra of compound **5w** in DMSO-d_6 (100 MHz)



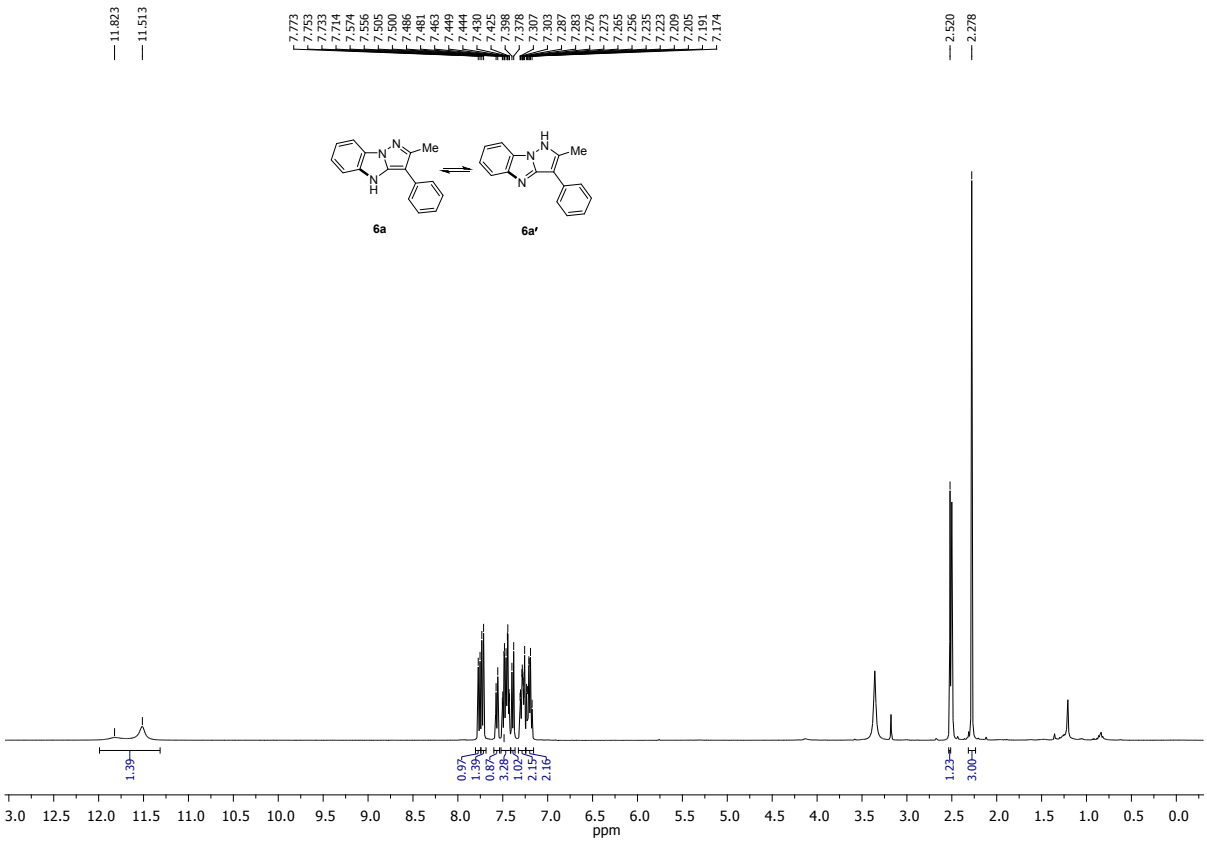
^{1}H Spectra of compound **5x** in DMSO-d_6 (400 MHz)



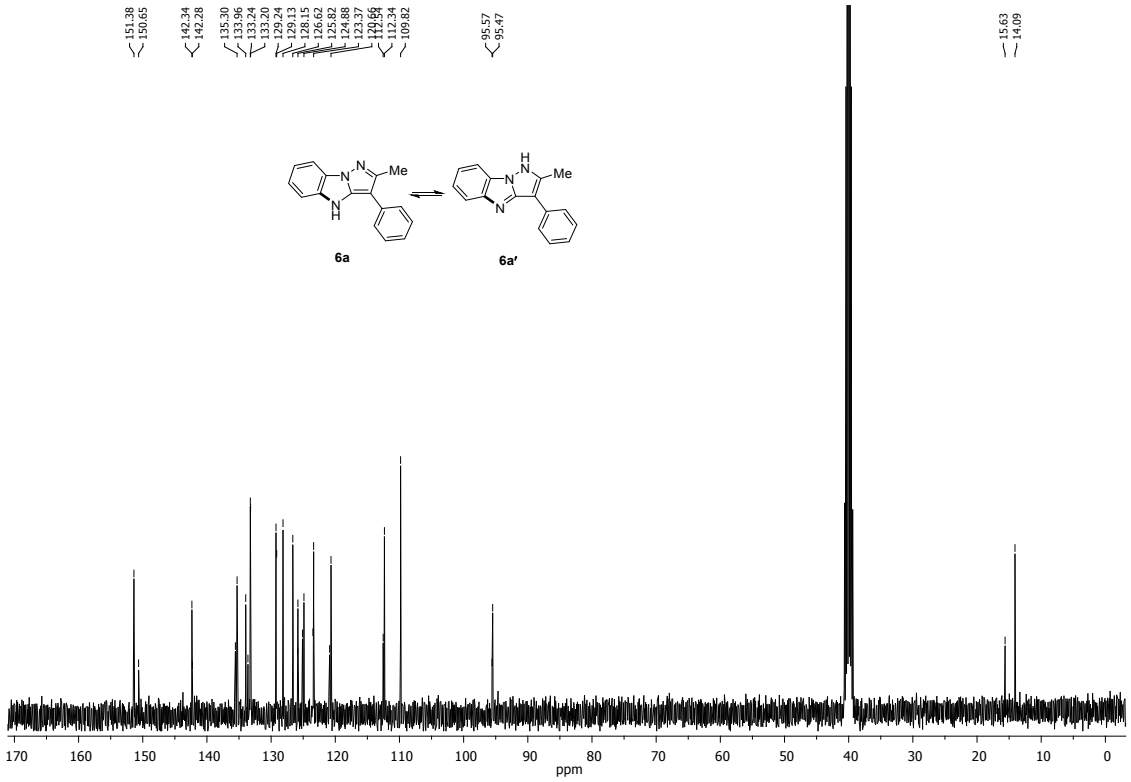
^{13}C Spectra of compound **5x** in DMSO-d_6 (100 MHz)



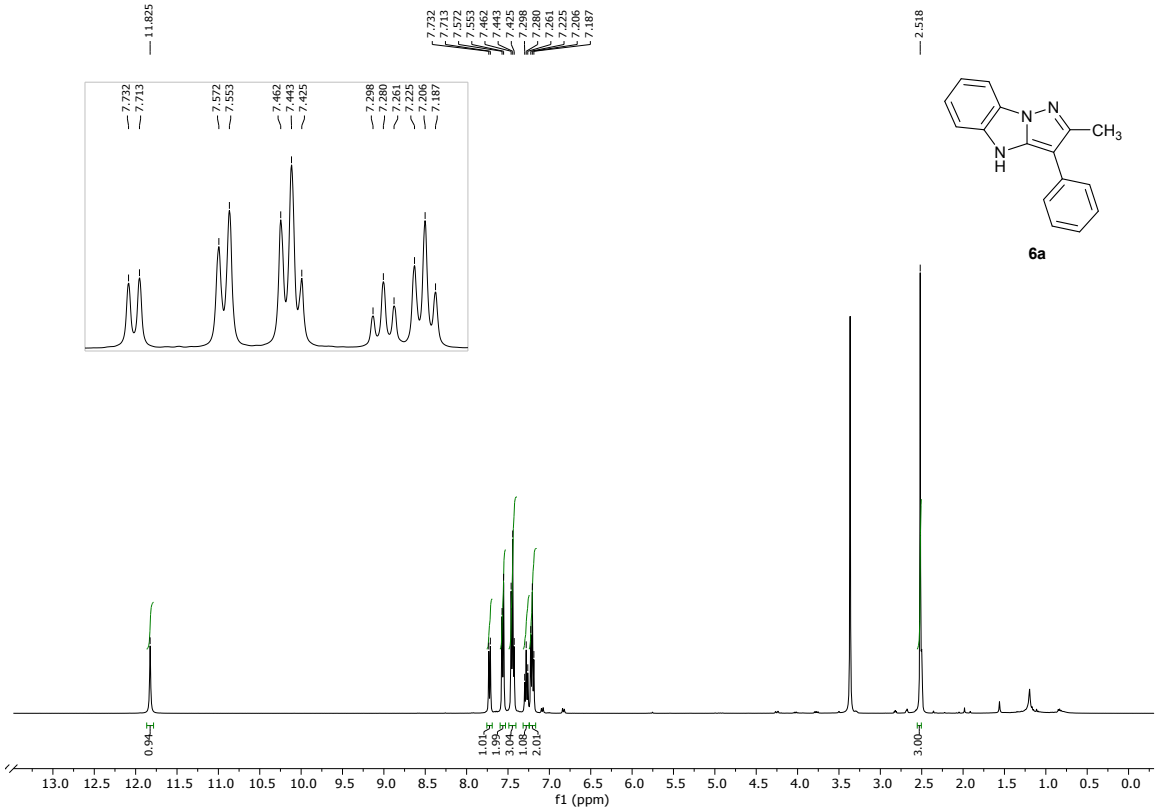
^{19}F Spectra of Compound **5x** in DMSO-d_6 (376 MHz)



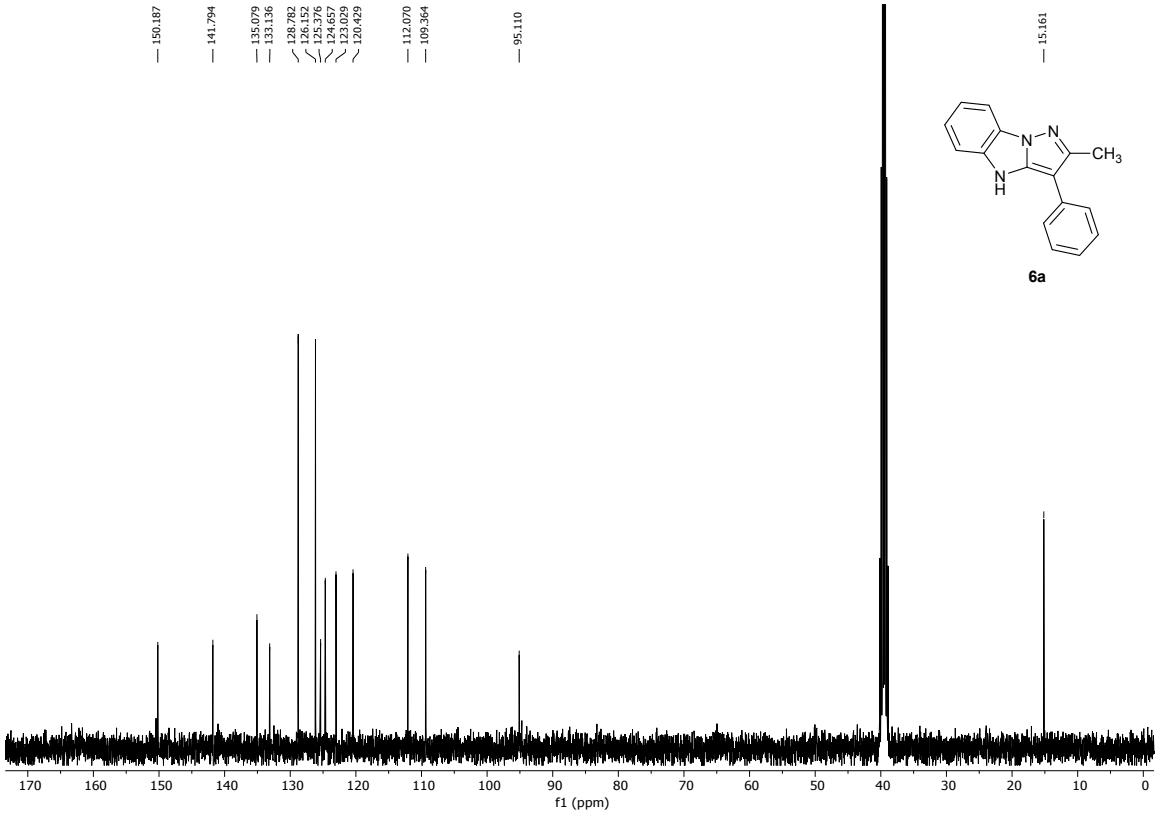
^{1}H Spectra of compound **6a** in DMSO-d_6 (400 MHz)



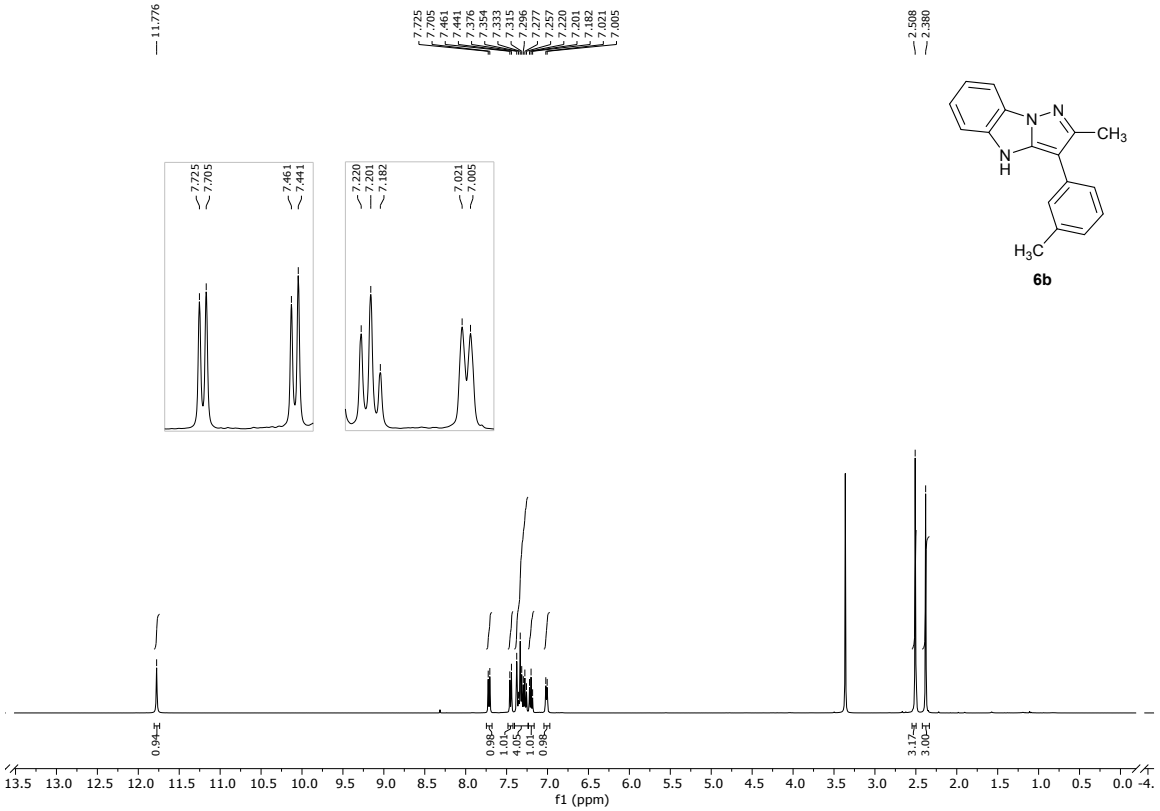
^{13}C Spectra of compound **6a** in DMSO-d_6 (100 MHz)



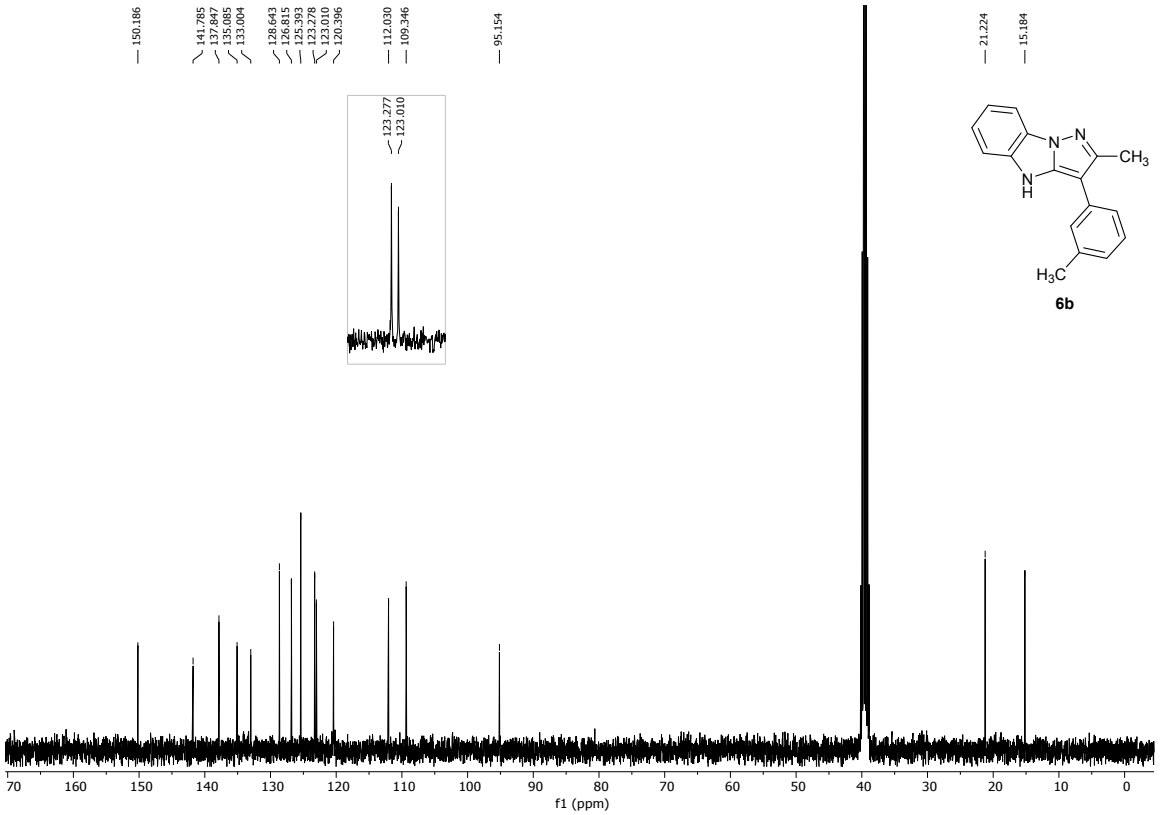
^{1}H Spectra of compound **6a** in DMSO-d_6 (400 MHz)



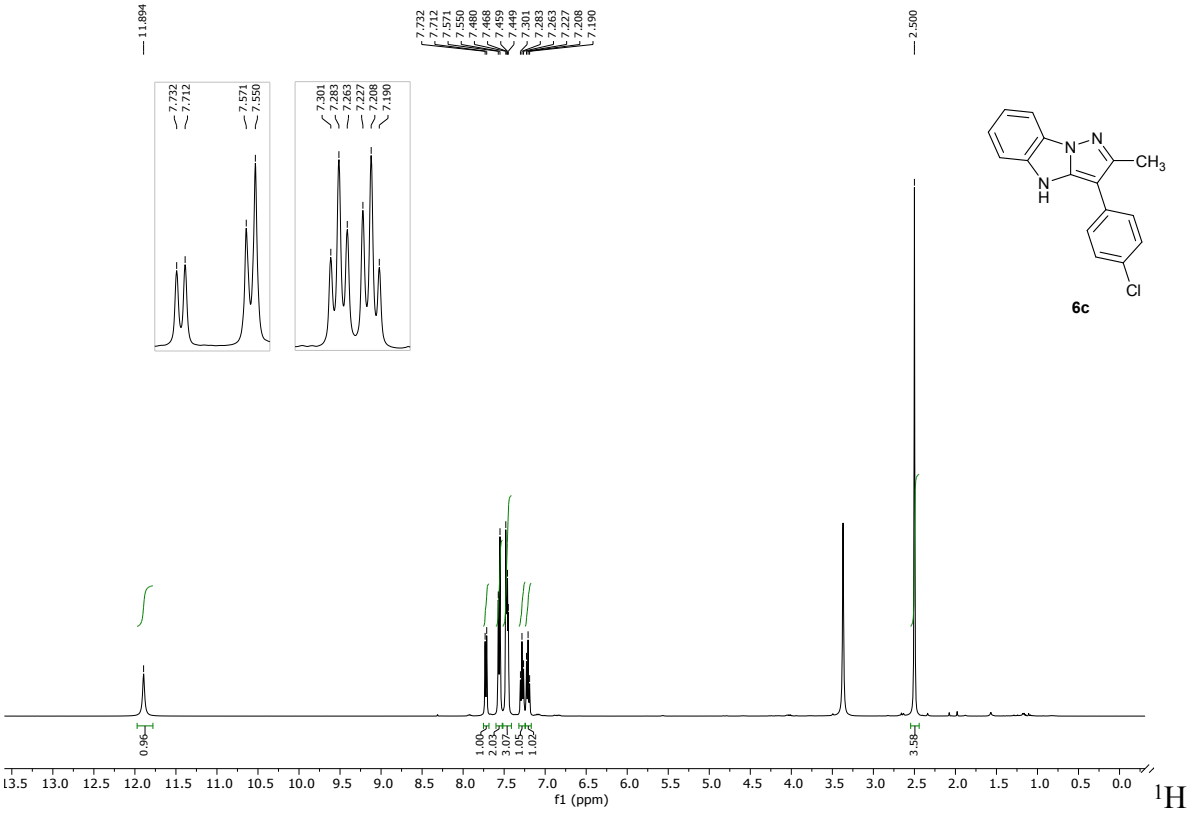
^{13}C Spectra of compound **6a** in DMSO-d_6 (100 MHz)



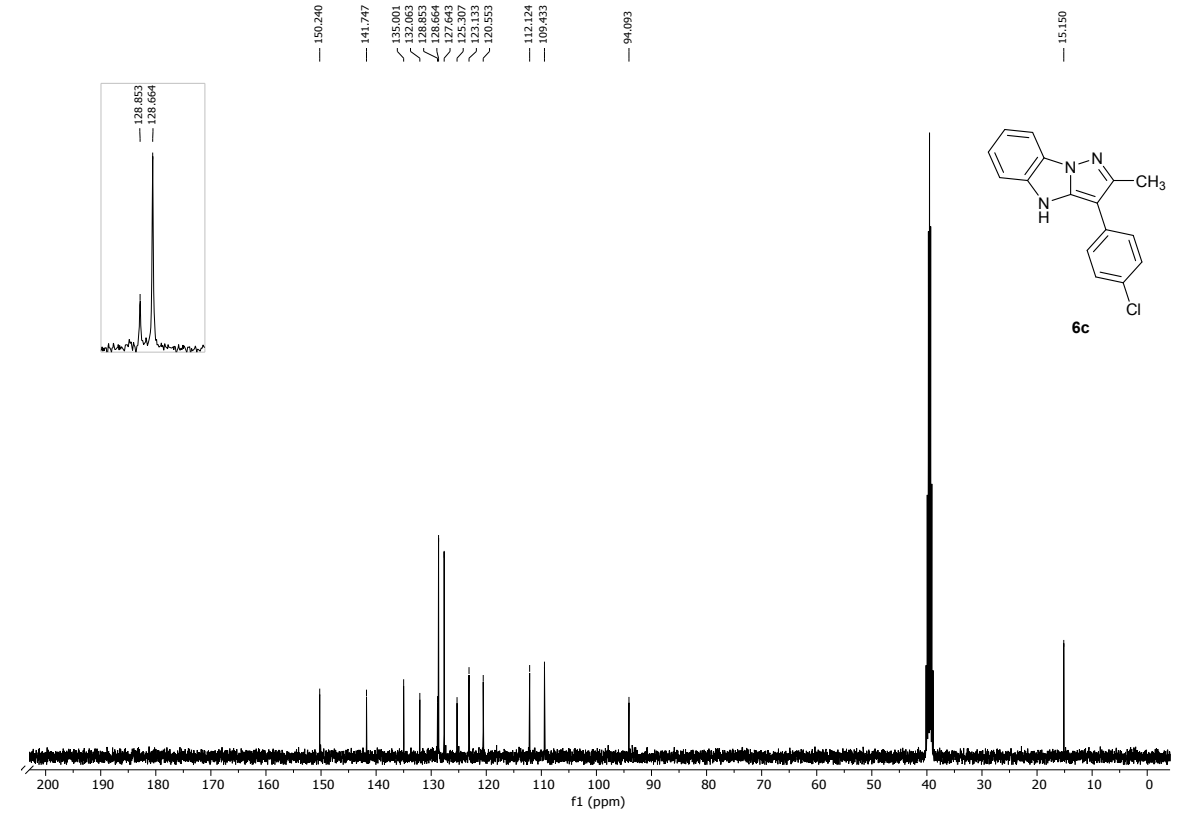
^{1}H Spectra of compound **6b** in DMSO-d_6 (400 MHz)



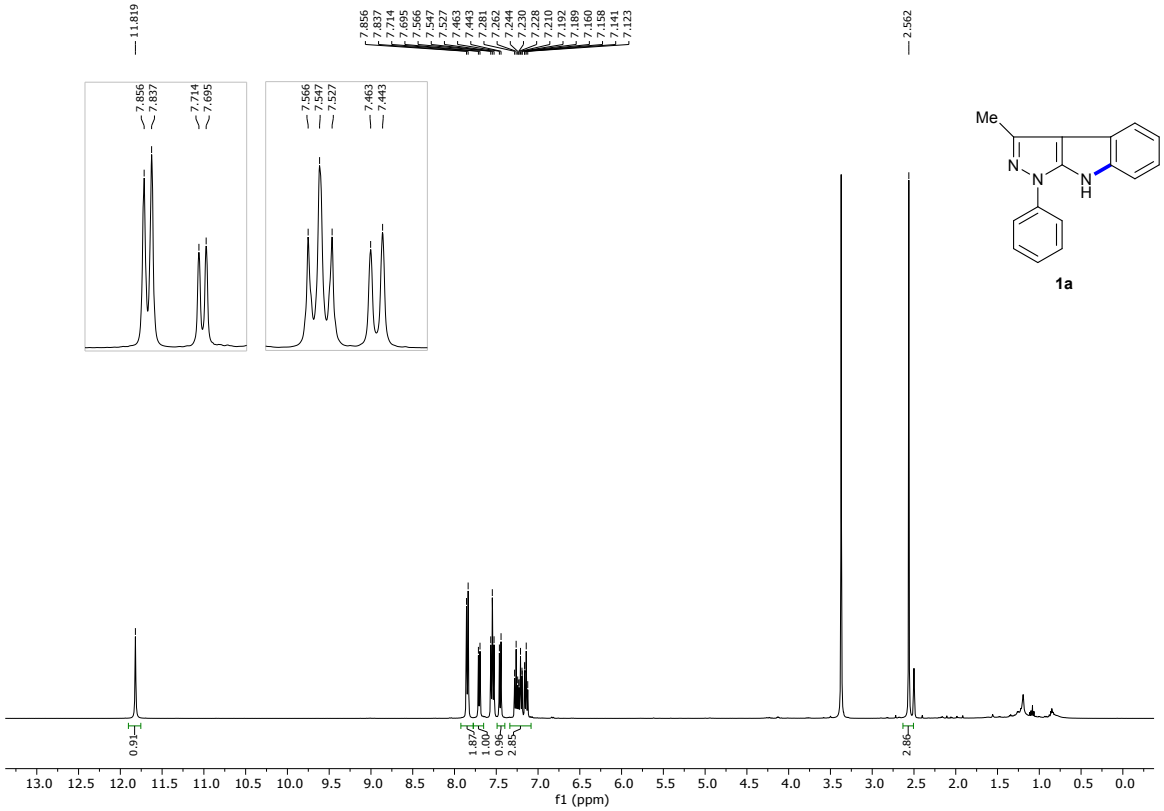
^{13}C Spectra of compound **6b** in DMSO-d_6 (100 MHz)



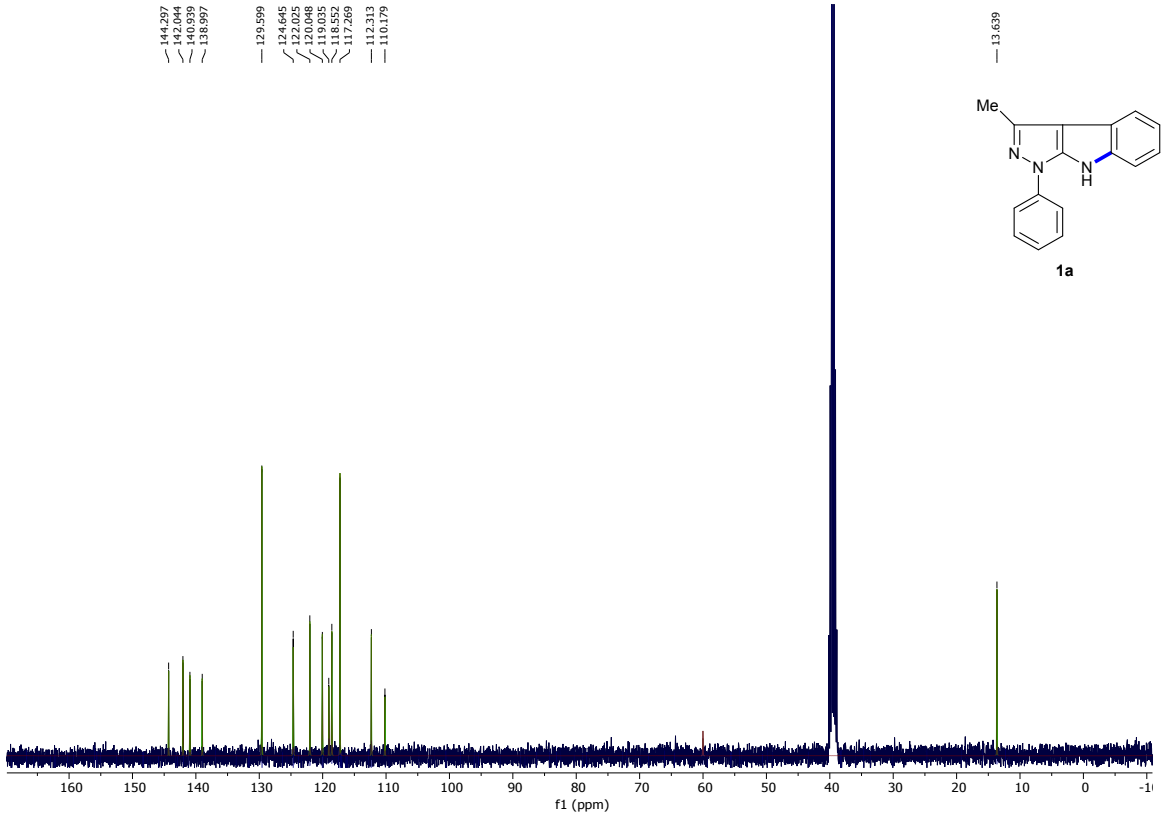
Spectra of compound **6c** in DMSO-d_6 (400 MHz)



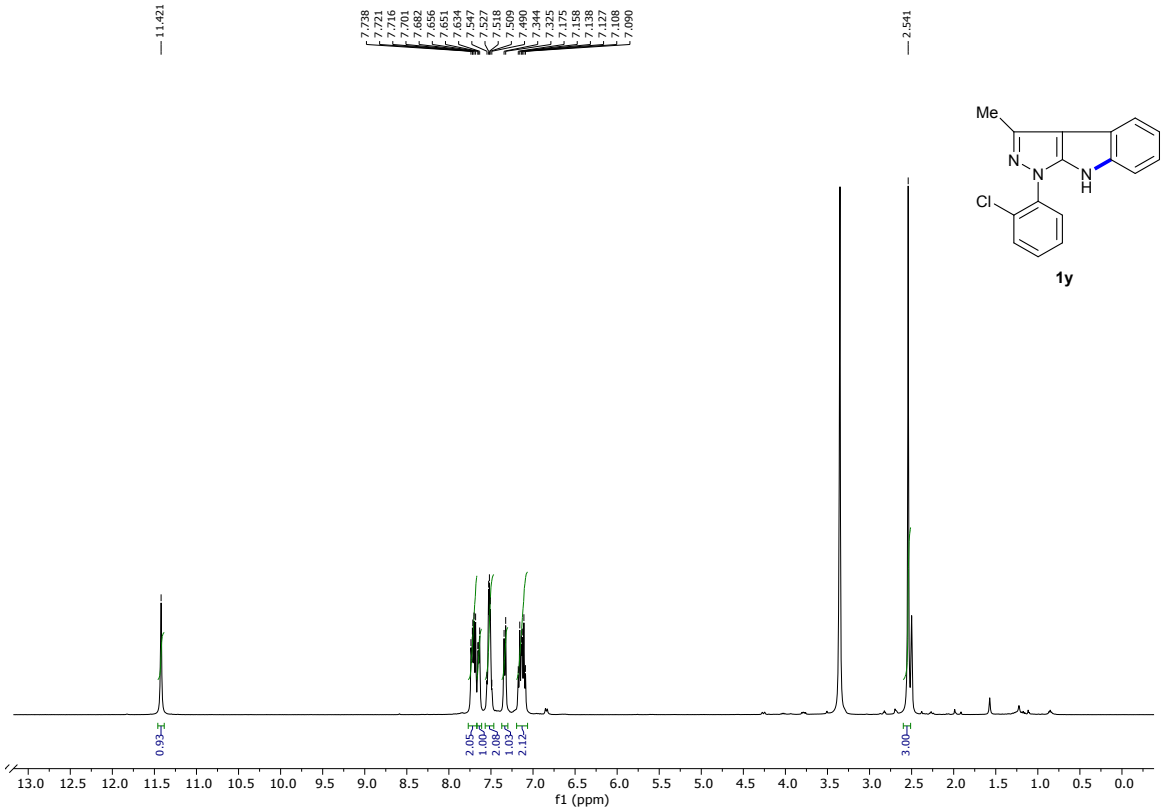
^{13}C Spectra of compound **6c** in DMSO-d_6 (100 MHz)



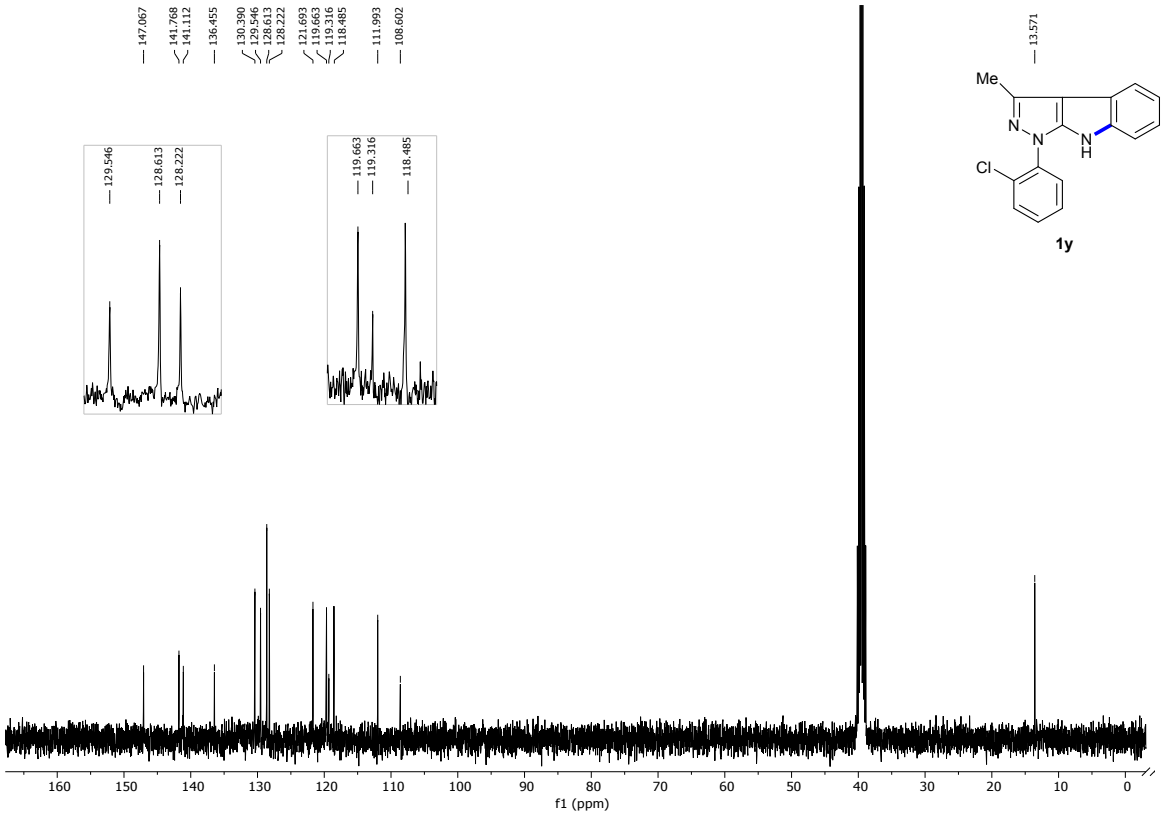
Spectra of compound **1a** from **2y** in DMSO-d_6 (400 MHz)



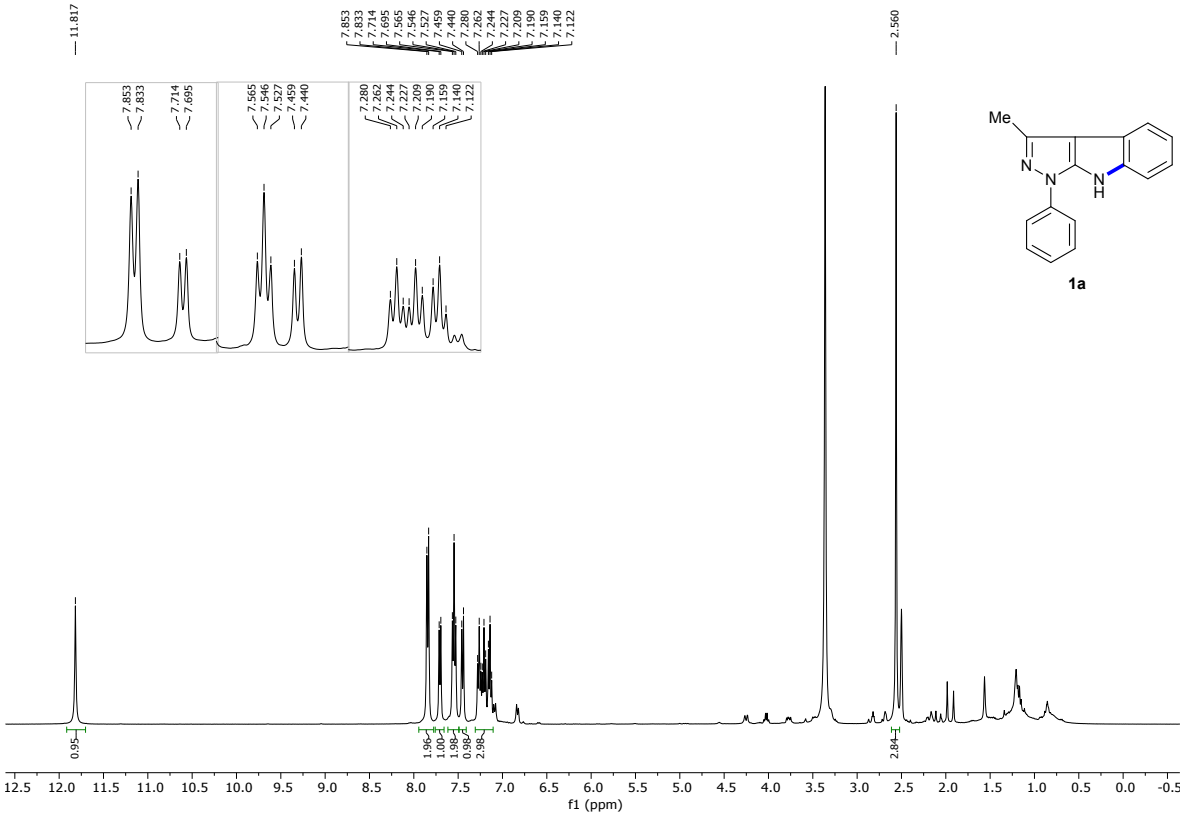
^{13}C Spectra of compound **1a** from **2y** in DMSO-d_6 (100 MHz)



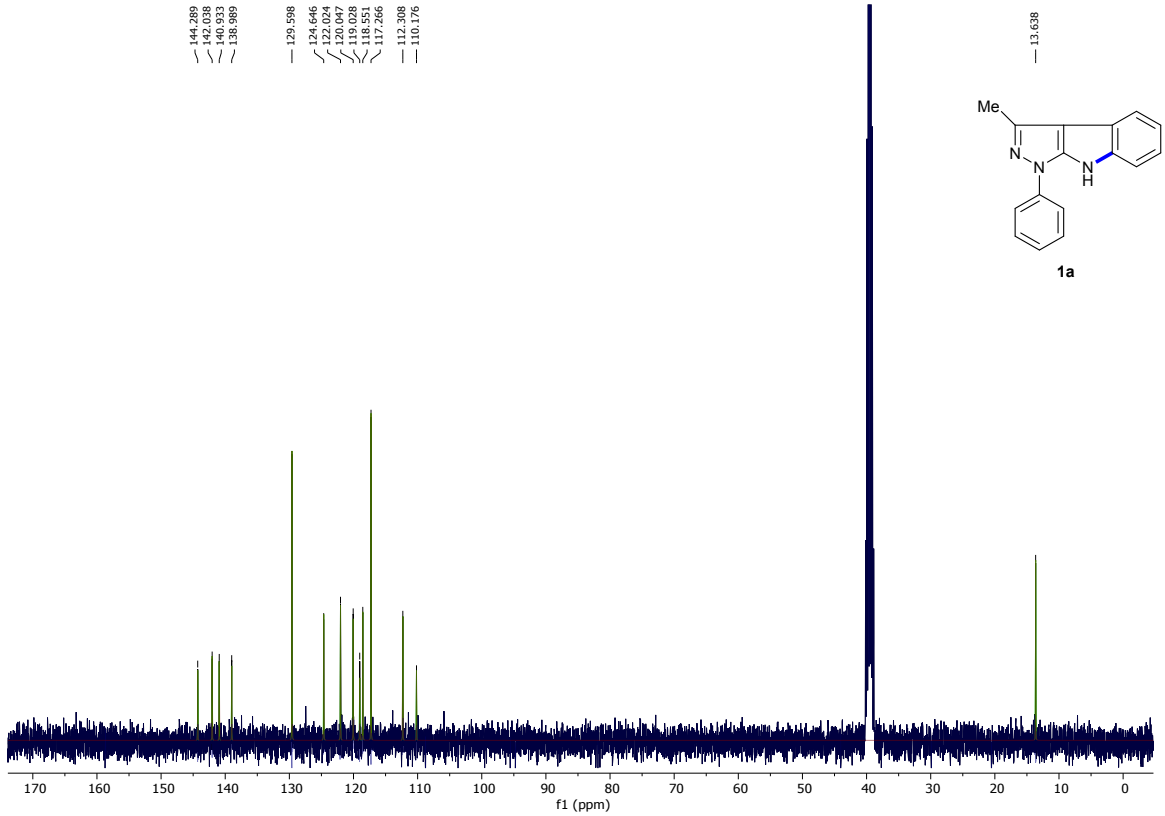
^{1}H Spectra of compound **1y** in DMSO-d_6 (400 MHz)



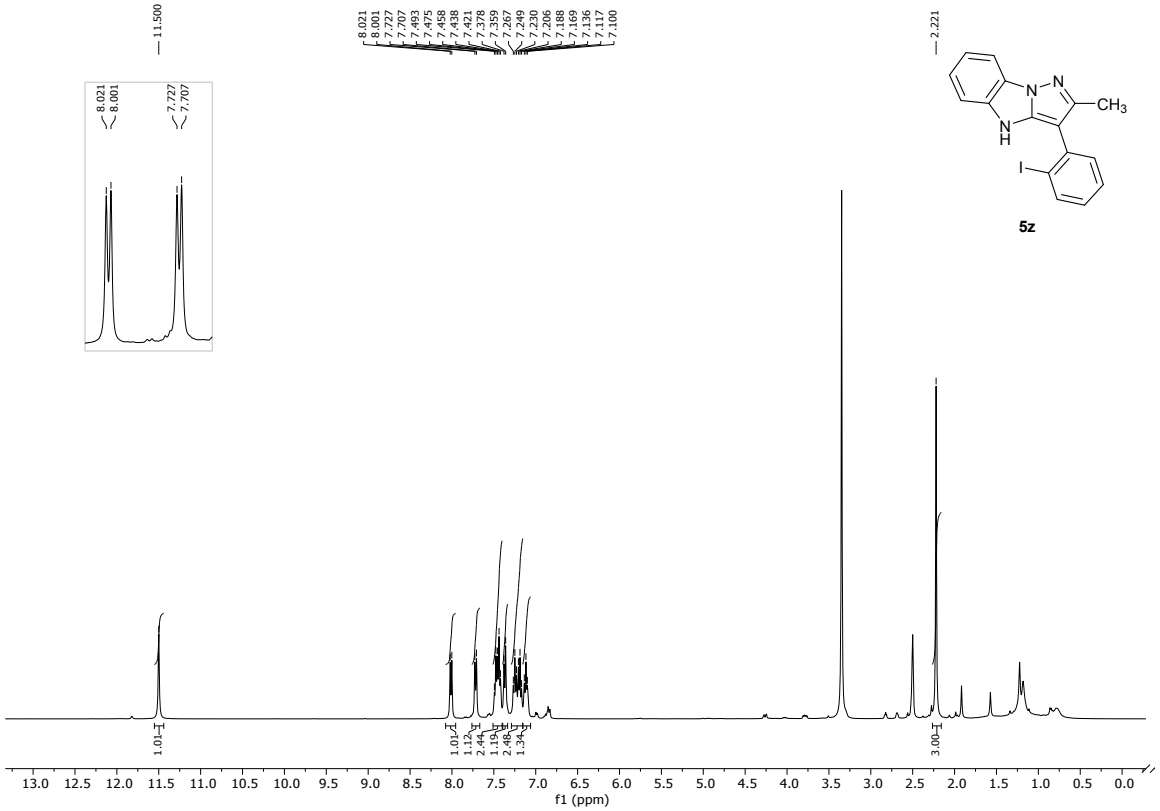
^{13}C Spectra of compound **1y** in DMSO-d_6 (100 MHz)



^{1}H Spectra of compound **1a** from **2z** in DMSO-d_6 (400 MHz)

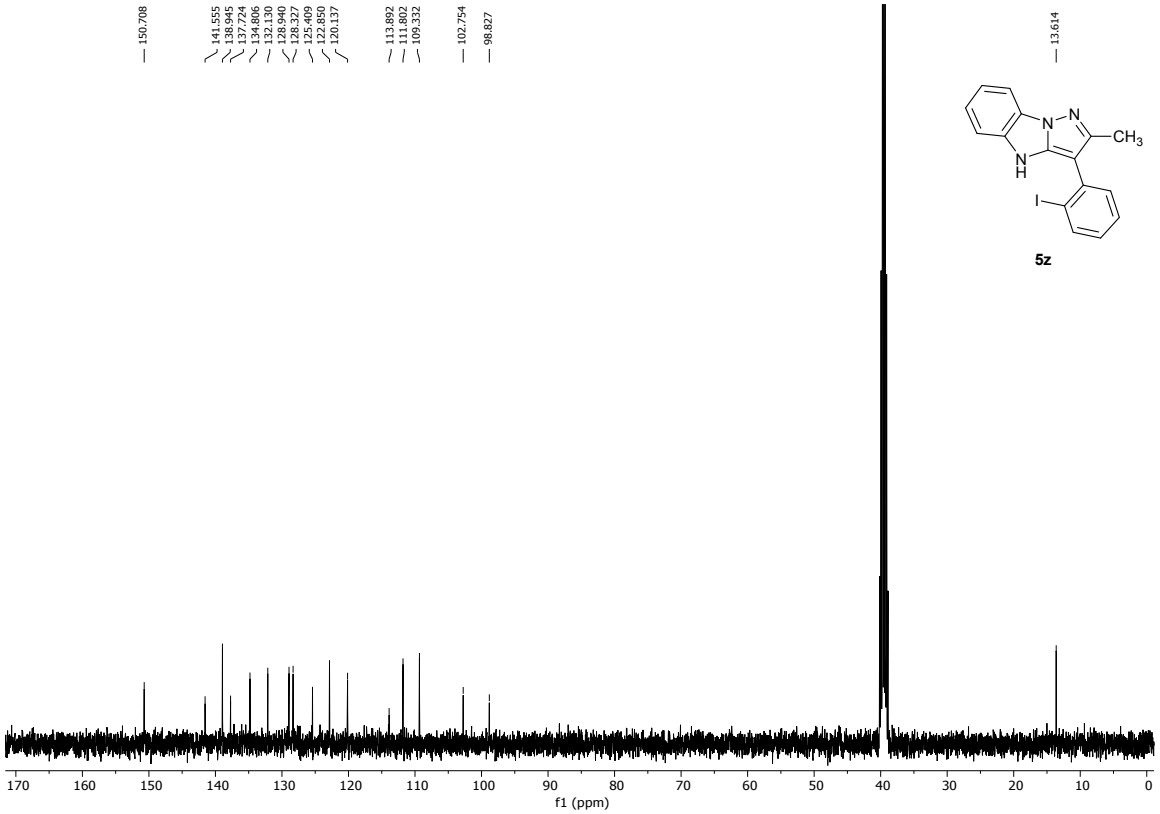


^{13}C Spectra of compound **1a** from **2z** in DMSO-d_6 (100 MHz)



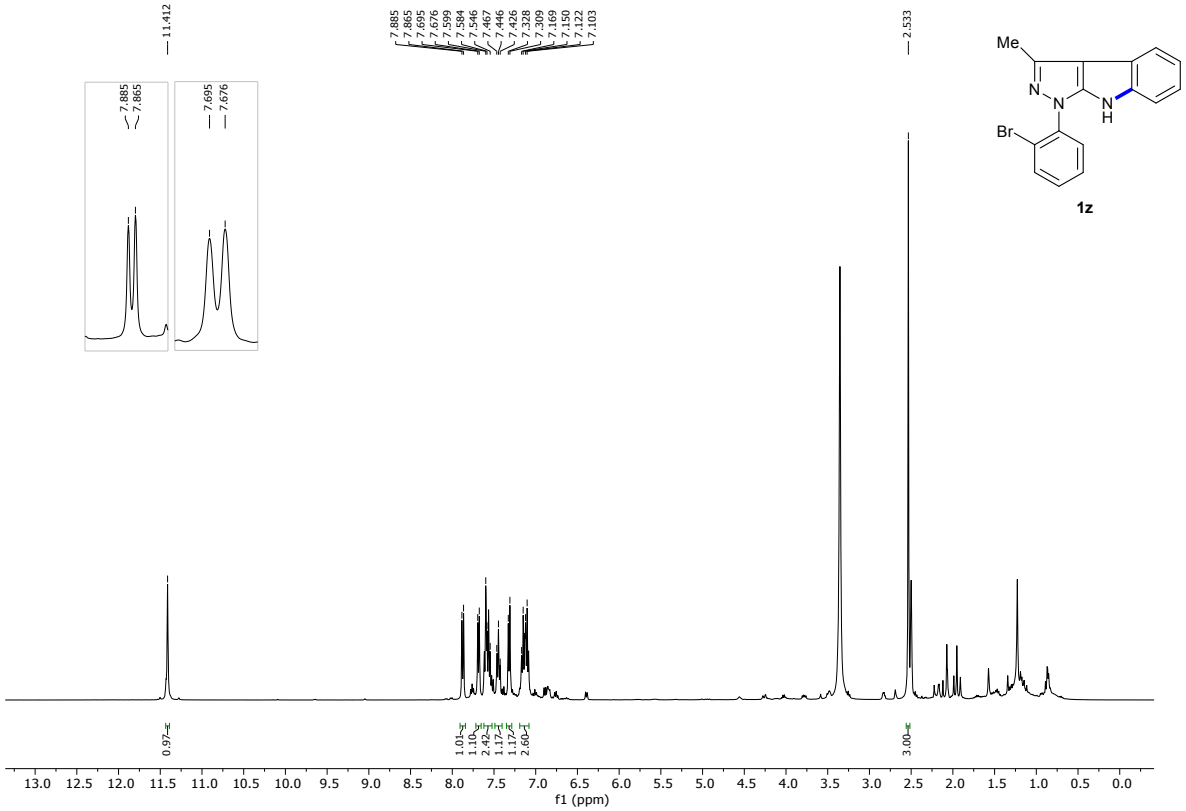
5z

^{1}H Spectra of compound **5z** in DMSO-d_6 (100 MHz)

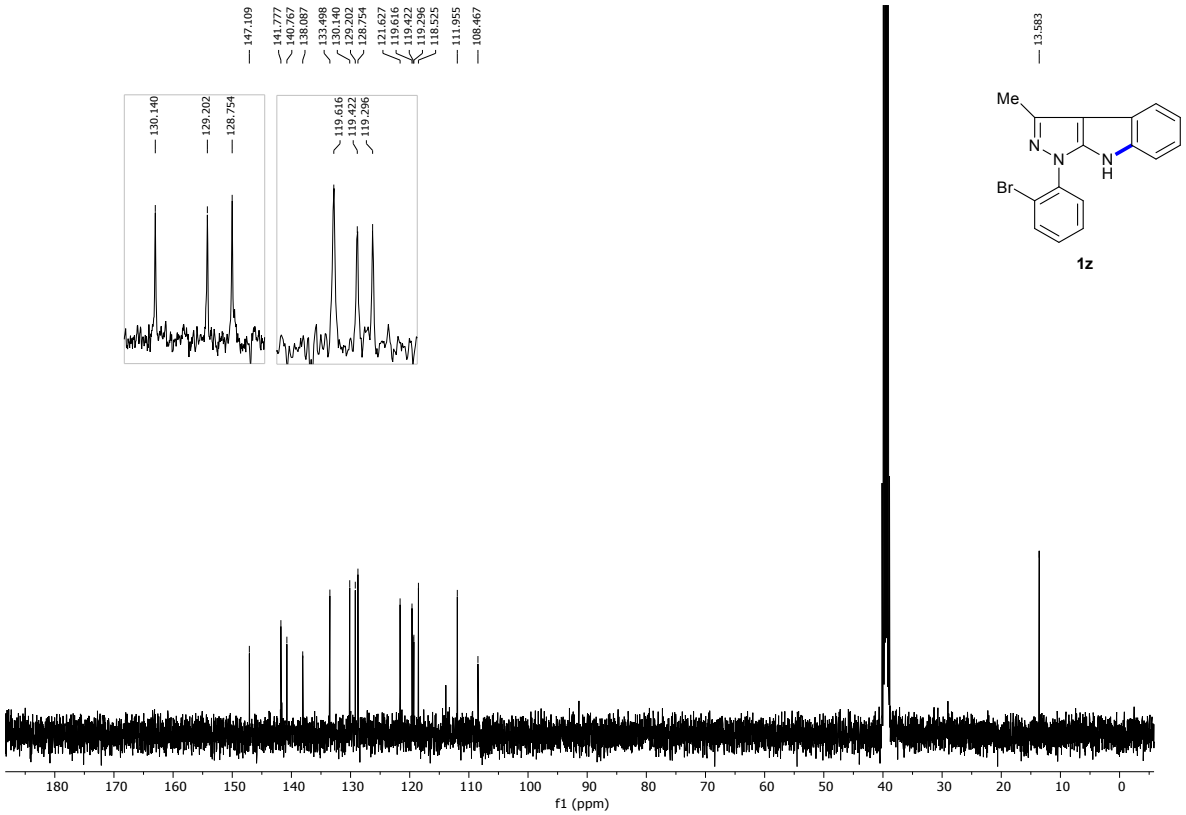


5z

^{13}C Spectra of compound **5z** in DMSO-d_6 (100 MHz)



^{1}H Spectra of compound **1z** in DMSO-d_6 (400 MHz)



^{13}C Spectra of compound **1z** in DMSO-d_6 (100 MHz)