Electronic Supplementary Information

Unexpected Dearomatization of *N*-Protected 5-Aminopyrazoles at Ambient Temperature: A Simple Route to Highly Functionalized Pyrazolines

Pradeep Natarajan, Arpita Chatterjee, Siddharth Jaya Sajeevan J, and Saravanan Peruncheralathan*

School of Chemical Sciences, National Institute of Science Education and Research (NISER) Bhubaneswar, an OCC of Homi Bhabha National Institute, Khurda – 752050, Odisha, India

Email: peru@niser.ac.in

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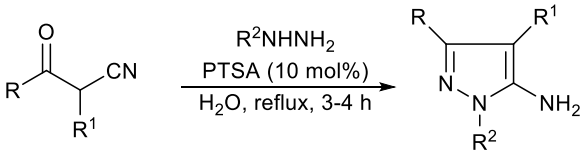
Table S1: Synthesis of 5-aminopyrazoles **2**



3 **2**

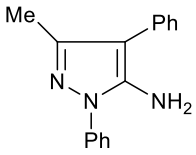
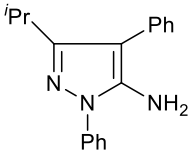
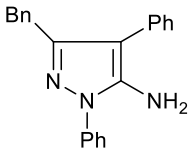
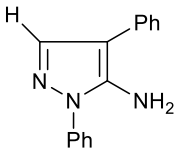
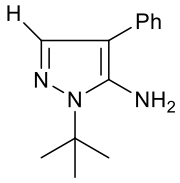
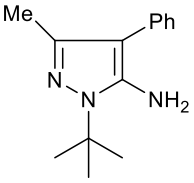
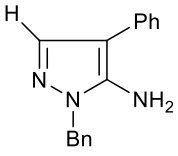
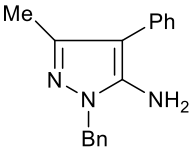
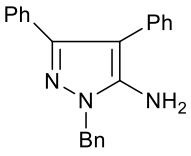
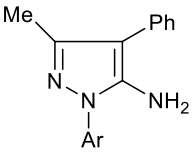
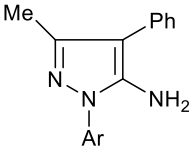
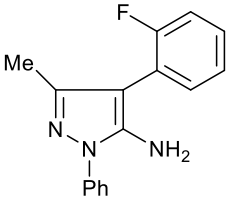
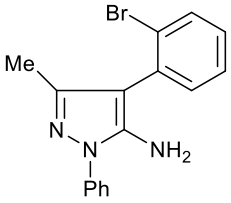
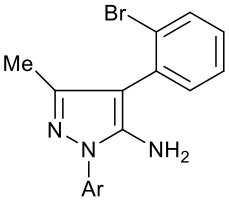
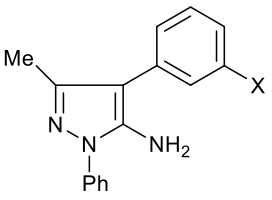
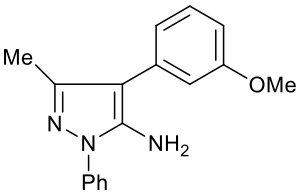
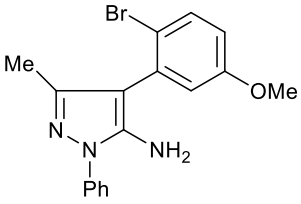
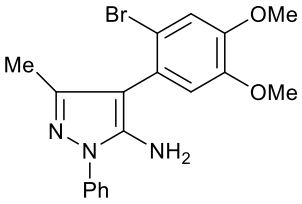
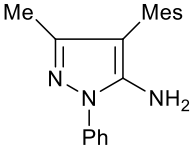
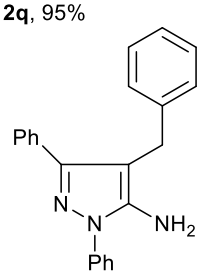
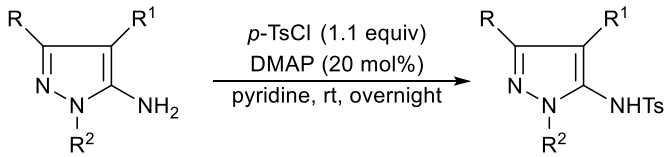
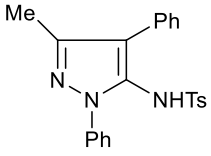
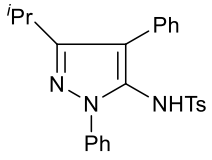
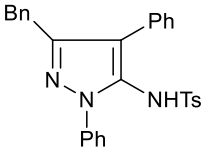
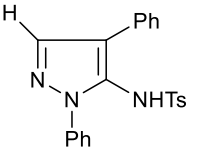
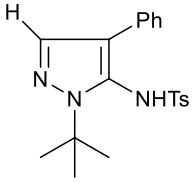
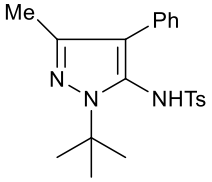
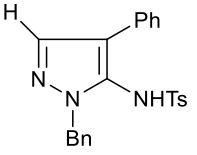
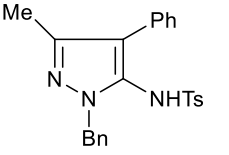
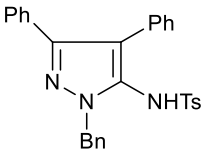
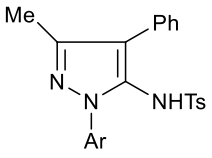
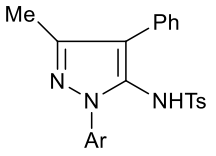
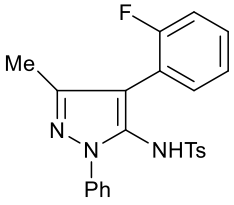
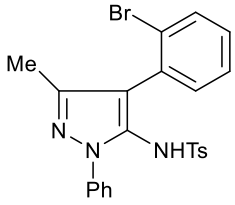
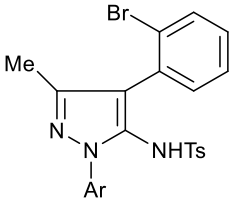
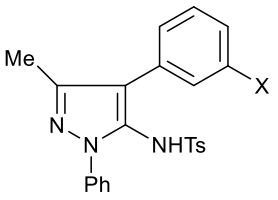
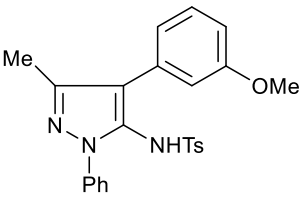
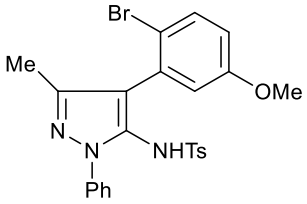
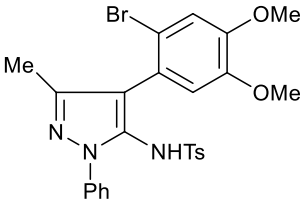
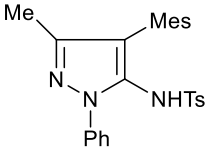
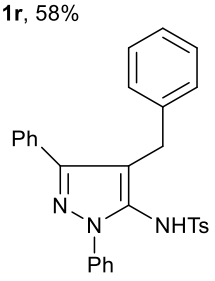
 **2a**, 99%	 **2b**, 64%	 **2c**, 65%	 **2d**, 98%
 **2e**, 68%	 **2f**, 65%	 **2g**, 71%	 **2h**, 64%
 **2i**, 62%	 **2j**, Ar = 4-MePh, 98%	 **2k**, Ar = 4-BrPh, 80%	 **2l**, 78%
 **2m**, 98%	 **2n**, Ar = 4-MePh, 93%	 **2o**, X = F, 98% **2p**, X = Cl, 88%	 **2q**, 95%
 **2r**, 95%	 **2s**, 98%	 **2t**, 94%	 **2u**, 62%

Table S2: Synthesis of 5-*N*-tosylaminopyrazoles **1**



2 **1**

 **1a**, 64%	 **1b**, 60%	 **1c**, 44%	 **1d**, 30%
 **1e**, 83%	 **1f**, 67%	 **1g**, 77%	 **1h**, 81%
 **1i**, 60%	 **1j**, Ar = 4-MePh, 53%	 **1k**, Ar = 4-BrPh, 50%	 **1l**, 57%
 **1m**, 60%	 **1n**, Ar = 4-MePh, 66%	 **1o**, X = F, 58% **1p**, X = Cl, 54% **1q**, X = CF3, 36%	 **1r**, 58%
 **1s**, 68%	 **1t**, 60%	 **1u**, 48%	 **1v**, 30%

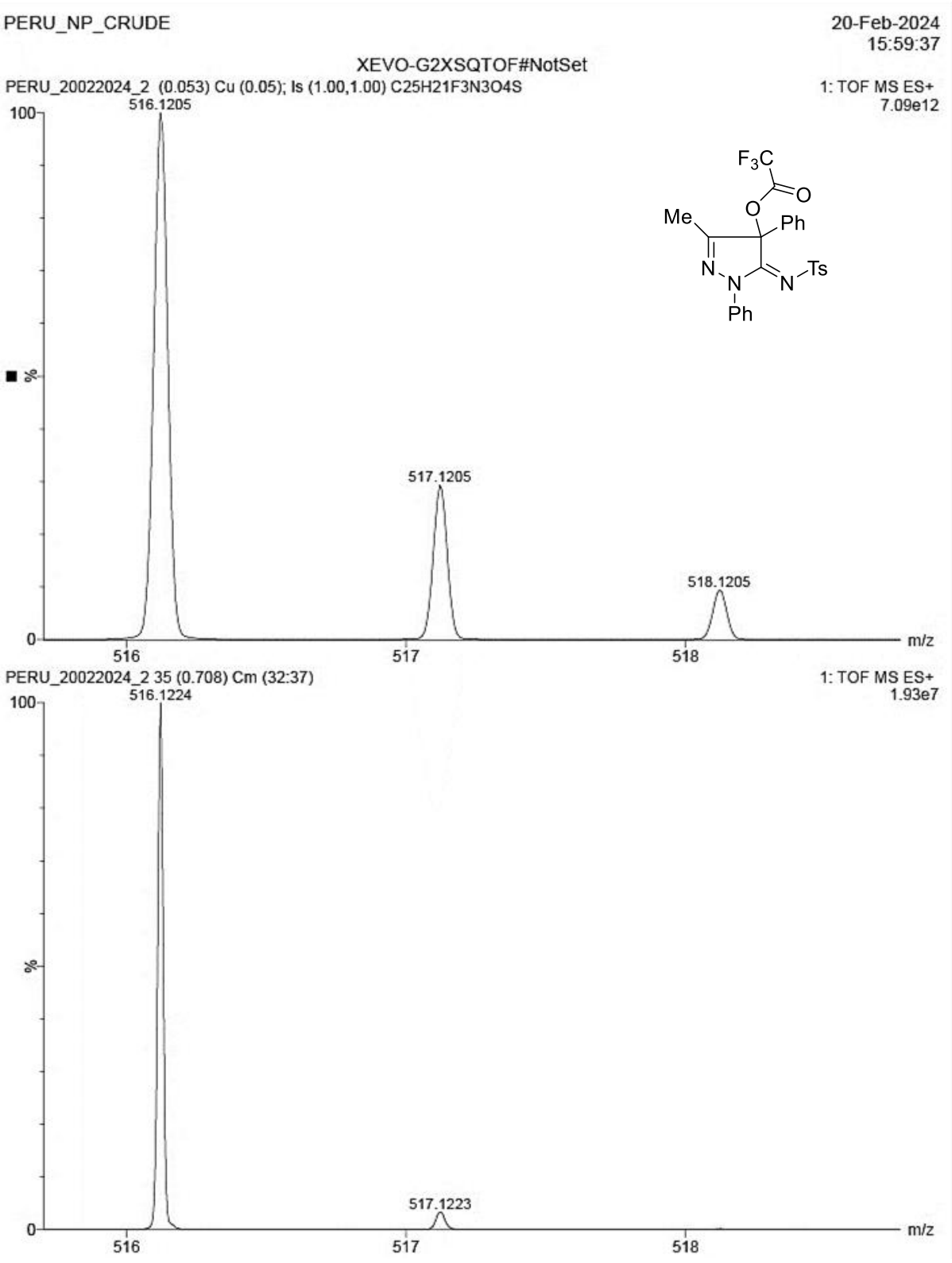


Figure S1: ESI HRMS of Compound **6a**

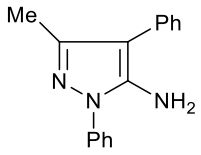
Experimental section:

General Information. All reactions were performed using the standard vial technique with a rubber septum. All solids were weighed in the air. PIFA, PIDA, TEMPO, BHT, TsCl, DMAP, BBr_3, NaH, triethyl amine, benzoyl chloride, acetyl chloride, methyl formate, substituted benzyl nitrile, aryl/alkyl ester, aryl/alkyl hydrazine and sodium were purchased from Aldrich, Merck, TCI, Spectrochem or Alfa Aesar and used as received. TFE, HFIP, pyridine and dried DMF, THF, DCM, DCE, EtOAc and 1,4-Dioxane were used. All other reagents were purchased from common suppliers and used without further purification. Flash chromatography was performed using a Merck silica gel (230−400 mesh). Fractions were monitored by thin-layer chromatography (TLC) on precoated silica gel $^{60}F_{254}$ plates (Merck & Co.) and were visualized by a UV light. Nuclear magnetic resonance (NMR) spectroscopy data were recorded using Bruker ARX 400 and 700 spectrometers. ^{13}C and ^{1}H NMR spectra were recorded in $CDCl_3$ and DMSO-d_6 referenced according to signals of deutero solvents. Electrospray ionization high-resolution mass spectrometry (ESI HR-MS) measurements were performed using a Bruker micrOTOF-Q II mass-spectrometer and Waters Xevo-G2-XS QTof. The *β*-ketonitriles **3** required for preparing 5-aminopyrazoles **2** were prepared according to the known literature procedure.[1] The unprotected 5-aminopyrazole required for preparing acetyl protected 5-aminopyrazoles **8d** was prepared according to the known literature procedure.[2]

General procedure for the synthesis of 5-aminopyrazoles 2a-v and 11a-b[1]

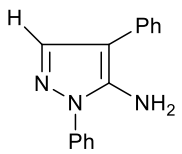
A round bottom flask was charged with *β*-ketonitrile **3** (1 equiv, 2.5 mmol), substituted hydrazine (1.1 equiv, 2.75 mmol) and PTSA (0.25 mmol) in water (10 mL), was refluxed for 3-4 h. The reaction was monitored by TLC. After disappearance of the starting material, the reaction mixture was then cooled to room temperature, water (25 mL) was added and extracted with ethyl acetate (3 × 25 mL). The combined organic layer was dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The crude products were purified through flash column chromatography using n-hexane and EtOAc as the eluents.

5-Amino-3-methyl-1,4-diphenyl-1*H*-pyrazole (2a):[3]



Reaction time: 3 h; Yield: 99% (0.616 g); Brown colour solid; R_f = 0.24 in 20% EtOAc in n-hexane; m.p = 165-167 °C; IR (KBr, ν cm^{-1}): 3421, 1627, 1559, 1506, 1454,1390, 1023, 758; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (d, *J* = 8.0 Hz, 2H), 7.50 – 7.43 (m, 4H), 7.38 – 7.27 (m, 4H), 3.95 (s, 2H), 2.32 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 147.3, 142.2, 138.6, 133.4, 129.6, 129.0, 128.6, 127.2, 126.1, 123.8, 104.9, 13.1; HR-MS (ESI) m/z: $[M + H]^+$ Calcd for $C_{16}H_{16}N_3$: 250.1339; Found: 250.1332.

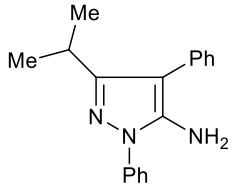
5-Amino-1,4-diphenyl-1*H*-pyrazole (2b):[4]



Reaction time: 3 h; Yield: 98% (0.576 g); Brown colour solid; R_f = 0.4 in 30% EtOAc in n-hexane; m.p = 140-144 °C; IR (KBr, ν cm^{-1}): 3095, 1688, 1599, 1572, 1513, 1314, 1070, 870; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (s, 1H), 7.64 (d, *J* = 7.6 Hz, 2H), 7.55 – 7.39 (m, 7H), 7.29

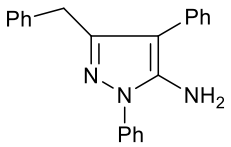
– 7.27 (m, 1H), 3.88 (s, 2H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 141.5, 139.1, 138.4, 133.2, 129.7, 129.2, 127.8, 126.5, 125.9, 124.1, 106.1; HR-MS (ESI) m/z: $[M + H]^+$ Calcd for $C_{15}H_{14}N_3$: 236.1182; Found: 236.1190.

5-Amino-3-isopropyl-1,4-diphenyl-1*H*-pyrazole (2c):



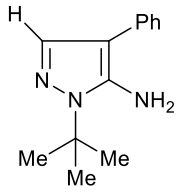
Reaction time: 4 h; Yield: 64% (0.443 g); White colour solid; R_f = 0.3 in 30% EtOAc in n-hexane; m.p = 126-130 °C; IR (KBr, ν cm^{-1}): 3075, 1679, 1607, 1602, 1553, 1304, 1067, 910; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (d, *J* = 8.0 Hz, 2H), 7.49 – 7.42 (m, 4H), 7.38 – 7.28 (m, 4H), 3.76 (s, 2H), 3.15 – 3.05 (m, 1H), 1.27 (d, *J* = 6.8 Hz, 6H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 156.5, 142.0, 139.1, 133.7, 129.5, 129.5, 129.0, 127.0, 126.4, 123.9, 104.2, 26.7, 22.4; HR-MS (ESI) m/z: $[M + H]^+$ Calcd for $C_{18}H_{20}N_3$: 278.1652; Found: 278.1665.

5-Amino-3-benzyl-1,4-diphenyl-1*H*-pyrazole (2d):



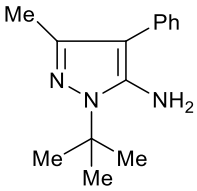
Reaction time: 3 h; Yield: 65% (0.563 g); White colour solid; R_f = 0.4 in 35% EtOAc in n-hexane; m.p = 136-139 °C; IR (KBr, ν cm^{-1}): 3061, 1669, 1632, 1592, 1503, 1331, 1069, 886; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, *J* = 8.0 Hz, 2H), 7.40 (t, *J* = 7.6 Hz, 2H), 7.29 – 7.24 (m, 3H), 7.18 – 7.12 (m, 7H), 7.07 – 7.04 (m, 1H), 3.92 (s, 2H), 3.76 (s, 2H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 149.6, 142.4, 139.9, 138.6, 133.0, 129.6, 129.2, 129.0, 128.7, 128.3, 127.4, 126.5, 126.0, 123.9, 105.2, 33.2; HR-MS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{22}H_{19}N_3Na$: 348.1471; Found: 348.1459.

5-Amino-1-(*tert*-butyl)-4-phenyl-1*H*-pyrazole (2e):



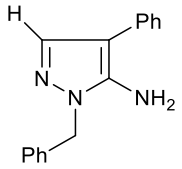
Reaction time: 3 h; Yield: 68% (0.366 g); White colour solid; R_f = 0.26 in 25% EtOAc in n-hexane; m.p = 158-160 °C; IR (KBr, ν cm^{-1}): 3330, 2367, 1609, 1517, 1368, 1230, 947, 764; ^{1}H NMR (700 MHz, $CDCl_3$) δ 7.41 (s, 1H), 7.41 – 7.31 (m, 4H), 7.22 (t, *J* = 7.2 Hz, 1H), 3.79 (s, 2H), 1.69 (s, 9H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 141.3, 135.7, 133.8, 129.1, 127.1, 125.8, 108.8, 58.9, 29.4; HR-MS (ESI) m/z: $[M + H]^+$ Calcd for $C_{13}H_{18}N_3$: 216.1501; Found: 216.1483.

5-Amino-1-(*tert*-butyl)-3-methyl-4-phenyl-1*H*-pyrazole (2f):



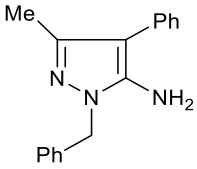
Reaction time: 3 h; Yield: 65% (0.372 g); White colour solid; R_f = 0.3 in 30% EtOAc in n-hexane; m.p = 145-148 °C; IR (KBr, ν cm^{-1}): 3023, 1619, 1528, 1572, 1478, 1366, 1082, 887; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (t, *J* = 7.6 Hz, 2H), 7.29 – 7.23 (m, 3H), 3.66 (s, 2H), 2.22 (s, 3H), 1.67 (s, 9H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 143.3, 142.0, 133.9, 129.1, 128.9, 126.0, 107.3, 58.5, 29.5, 13.0; HR-MS (ESI) m/z: $[M + H]^+$ Calcd for $C_{14}H_{20}N_3$: 230.1652; Found: 230.1669.

5-Amino-1-benzyl-4-phenyl-1*H*-pyrazole (2g):[5]



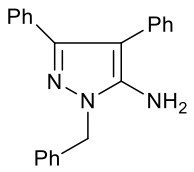
Reaction time: 3 h; Yield: 71% (0.442 g); Pale yellow colour solid; R_f = 0.4 in 50% EtOAc in n-hexane; m.p = 165-168 °C; IR (KBr, ν cm^{-1}): 3215, 1611, 1549, 1488, 1257, 1081, 872, 755; ^{1}H NMR (700 MHz, $CDCl_3$) δ 7.56 (s, 1H), 7.42 – 7.33 (m, 6H), 7.30 (t, *J* = 7.3 Hz, 1H), 7.24 – 7.18 (m, 3H), 5.26 (s, 2H), 3.66 (s, 2H); ^{13}C{^{1}H} NMR (175 MHz, $CDCl_3$) δ 141.4, 137.5, 136.4, 133.6, 129.14, 129.11, 128.0, 126.9, 126.4, 125.8, 107.1, 52.1; HR-MS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{16}H_{15}N_3Na$: 272.1158; Found: 272.1149.

5-Amino-1-benzyl-3-methyl-4-phenyl-1*H*-pyrazole (2h):



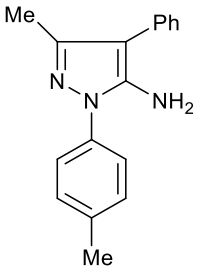
Reaction time: 3 h; Yield: 64% (0.421 g); Brown colour viscous liquid; R_f = 0.22 in 30% EtOAc in n-hexane; IR (KBr, ν cm^{-1}): 3338, 1709, 1650, 1530, 1496, 1265, 1016, 764; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (t, *J* = 7.6 Hz, 2H), 7.39 – 7.22 (m, 8H), 5.24 (s, 2H), 3.56 (s, 2H), 2.30 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 145.3, 142.3, 136.6, 133.6, 129.0, 129.0, 128.6, 127.9, 127.0, 126.1, 105.7, 51.7, 13.1; HR-MS (ESI) m/z: $[M + H]^+$ Calcd for $C_{17}H_{18}N_3$: 264.1495; Found: 264.1493.

5-Amino-1-benzyl-3,4-diphenyl-1*H*-pyrazole (2i):



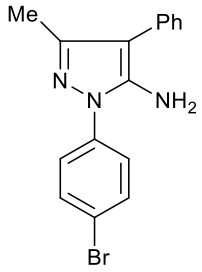
Reaction time: 3 h; Yield: 62% (0.512 g); Brown colour solid; R_f = 0.25 in 30% EtOAc in n-hexane; m.p = 155-158 °C; IR (KBr, ν cm-^{1}): 3153, 2304, 1710, 1604, 1421, 1362, 1264, 895; ^{1}H NMR (700 MHz, DMSO-d_6) δ 7.35 (t, *J* = 7.5 Hz, 2H), 7.33 – 7.29 (m, 6H), 7.27 (t, *J* = 7.3 Hz, 1H), 7.25 – 7.19 (m, 4H), 7.16 (d, *J* = 7.3 Hz, 2H), 5.28 (s, 4H; CH_2 & NH_2); ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6) δ 146.7, 144.9, 137.8, 134.2, 133.8, 129.4, 128.5, 128.4, 128.0, 127.5, 127.4, 127.2, 127.1, 125.6, 101.3, 50.1; HR-MS (ESI) m/z: $[M + H]^+$ Calcd for $C_{22}H_{20}N_3$: 326.1652; Found: 326.1675.

5-Amino-3-methyl-4-phenyl-1-(*p*-tolyl)-1*H*-pyrazole (2j):



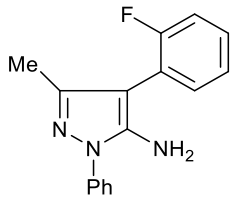
Reaction time: 3 h; Yield: 98% (0.644 g); White colour solid; R_f = 0.38 in 30% EtOAc in n-hexane; m.p = 140-143 °C; IR (KBr, ν cm^{-1}): 3417, 2055, 1650, 1521, 1395, 1265, 1010, 821; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (d, *J* = 8.0 Hz, 2H), 7.44 (d, *J* = 7.6 Hz, 2H), 7.39 – 7.37 (m, 2H), 7.29 – 7.27 (m, 3H), 3.87 (s, 2H), 2.40 (s, 3H), 2.31 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 147.0, 142.2, 137.3, 136.0, 133.5, 130.1, 129.0, 128.6, 126.1, 123.9, 104.7, 21.2, 13.1; HR-MS (ESI) m/z: $[M + H]^+$ Calcd for $C_{17}H_{18}N_3$: 264.1501; Found: 264.1508.

5-Amino-1-(4-bromophenyl)-3-methyl-4-phenyl-1*H*-pyrazole (2k):



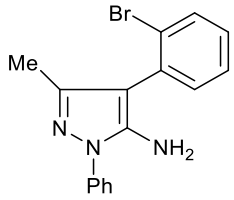
Reaction time: 3 h; Yield: 80% (0.656 g); White colour solid; R_f = 0.24 in 20% EtOAc in n-hexane; m.p = 165-168 °C; IR (KBr, ν cm^{-1}): 3437, 1634, 1506, 1485, 1402, 1070, 1011, 828; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, *J* = 8.5 Hz, 2H), 7.53 (d, *J* = 8.6 Hz, 2H), 7.45 (t, *J* = 7.5 Hz, 2H), 7.35 (d, *J* = 7.6 Hz, 2H), 7.29 (t, *J* = 7.3 Hz, 1H), 3.88 (s, 2H), 2.30 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 147.8, 142.3, 137.7, 133.1, 132.7, 129.2, 128.7, 126.5, 125.1, 120.7, 105.6, 13.1; HR-MS (ESI) m/z: $[M + H]^+$ Calcd for $C_{16}H_{15}BrN_3$: 328.0444 & 330.0424; Found: 328.0435 & 330.0416.

5-Amino-4-(2-fluorophenyl)-3-methyl-1-phenyl-1*H* -pyrazole (2l):[3]



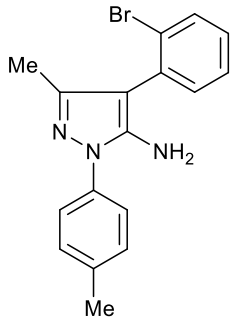
Reaction time: 3 h; Yield: 78% (0.521 g); White colour solid; R_f = 0.24 in 20% EtOAc in n-hexane; m.p = 165-168 °C; IR (KBr, ν cm^{-1}): 3437, 2423, 1597, 1575, 1516, 1504, 1447, 1394, 1253, 758; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (d, *J* = 8.4 Hz, 2H), 7.49 (t, *J* = 7.7 Hz, 2H), 7.40 – 7.26 (m, 3H), 7.25 – 7.13 (m, 2H), 3.88 (s, 2H), 2.26 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 159.9 (d, *J* = 244 Hz), 147.9, 142.8, 138.5, 131.5 (d, *J* = 3 Hz), 129.5, 128.4 (d, *J* = 8 Hz), 127.4, 124.50 (d, *J* = 3 Hz), 124.0, 120.5 (d, *J* = 15 Hz), 116.1 (d, *J* = 23 Hz), 99.1, 12.9; HR-MS (ESI) m/z: $[M + H]^+$ Calcd for $C_{16}H_{15}FN_3$: 268.1245; Found: 268.1239.

5-Amino-4-(2-bromophenyl)-3-methyl-1-phenyl-*1H*-pyrazole (2m):[1]



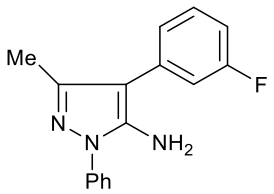
Reaction time: 3 h; Yield: 98% (0.804 g); Brown colour solid; R_f = 0.2 in 20% EtOAc in n-hexane; m.p = 100-103 °C; IR (KBr, ν cm^{-1}): 3339, 1652, 1569, 1512, 1498, 1322, 1023, 1006, 755; ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.72 (d, *J* = 8 Hz, 1H), 7.64 (d, *J* = 7.6 Hz, 2H), 7.49 – 7.40 (m, 3H), 7.35 – 7.25 (m, 3H), 4.93 (s, 2H), 1.98 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6) 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; HR-MS (ESI) m/z: $[M + H]^+$ Calcd for $C_{16}H_{15}BrN_3$: 328.0444 & 330.0424; Found: 328.0438 & 330.0417.

5-Amino-4-(2-bromophenyl)-3-methyl-1-(*p*-tolyl)-*1H*-pyrazole (2n):[3]



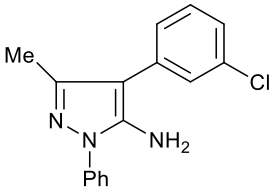
Reaction time: 3 h; Yield: 93% (0.795 g); Pale pink colour solid; R_f = 0.28 in 20% EtOAc in n-hexane; m.p = 119-123 °C; IR (KBr, ν cm^{-1}): 3438, 1655, 1619, 1571, 1519, 1393, 1059, 1019, 821,755; ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.72 (d, *J* = 7.2 Hz, 1H), 7.51 (d, *J* = 8.4 Hz, 2H), 7.42 (t, *J* = 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{^{1}H} NMR (100 MHz, DMSO-d_6) 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; HR-MS (ESI) m/z: $[M + H]^+$ Calcd for $C_{17}H_{17}BrN_3$: 342.0600 & 344.0580; Found: 342.0580 & 344.0557.

5-Amino-4-(3-fluorophenyl)-3-methyl-1-phenyl-1*H*-pyrazole (2o):[3]



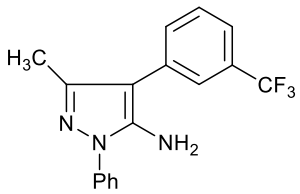
Reaction time: 3 h; Yield: 98% (0.654 g); Pale yellow colour solid; R_f = 0.24 in 20% EtOAc in n-hexane; m.p = 165-168 °C; IR (KBr, ν cm^{-1}): 3437, 1615, 1516, 1429, 1395, 1324, 1187, 762, 693; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 – 7.57 (m, 2H), 7.48 (t, *J* = 7.6 Hz, 2H), 7.42 – 7.33 (m, 2H), 7.15 (dt, *J* = 7.6 Hz, 1Hz, 1H), 7.11 – 7.05 (m, 1H), 6.98 – 6.93 (m, 1H), 3.94 (s, 2H), 2.31 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 163.4 (d, *J* = 244 Hz), 147.2, 142.3, 138.4, 135.8 (d, *J* = 8 Hz), 130.6 (d, *J* = 8 Hz), 129.7, 127.5, 124.1 (d, *J* = 2 Hz), 124.0, 115.2 (d, *J* = 21 Hz), 113.0 (d, *J* = 21 Hz), 103.9, 13.2; HR-MS (ESI) m/z: $[M + H]^+$ Calcd for $C_{16}H_{15}FN_3$: 268.1245; Found: 268.1235.

5-Amino-4-(3-chlorophenyl)-3-methyl-1-phenyl-1*H*-pyrazole (2p):



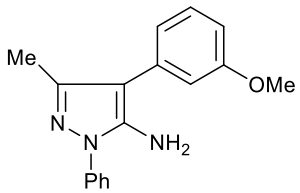
Reaction time: 3 h; Yield: 88% (0.623 g); Pale brown colour solid; R_f = 0.24 in 20% EtOAc in n-hexane; m.p = 100-103 °C; IR (KBr, ν cm^{-1}): 3437, 1622, 1596, 1568, 1515, 1322, 1079, 1035, 776; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (d, *J* = 7.5 Hz, 2H), 7.48 (t, *J* = 7.8 Hz, 2H), 7.41 – 7.30 (m, 3H), 7.27 – 7.21 (m, 2H), 3.93 (s, 2H), 2.29 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 147.1, 142.2, 138.3, 135.35, 135.34, 134.7, 130.2, 129.6, 128.3, 127.4, 126.6, 126.1, 103.6, 13.1; HR-MS (ESI) m/z: $[M + H]^+$ Calcd for $C_{16}H_{15}ClN_3$: 284.0949; Found: 284.0951.

5-Amino-3-methyl-1-phenyl-4-(3-(trifluoromethyl)phenyl)-1*H*-pyrazole (2q):



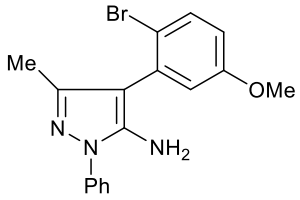
Reaction time: 3 h; Yield: 84% (0.666 g); White colour solid; R_f = 0.24 in 20% EtOAc in Hexane; m.p = 165-168 °C; IR (KBr, ν cm^{-1}): 3437, 1621, 1571, 1518, 1337, 1303, 1164, 1122, 1073, 806; ^{1}H NMR (700 MHz, $CDCl_3$) δ 7.64 (s, 1H), 7.60 (d, *J* = 7.7 Hz, 2H), 7.57 – 7.52 (m, 3H), 7.50 (t, *J* = 7.8 Hz, 2H), 7.37 (t, *J* = 7.4 Hz, 1H), 3.91 (s, 2H), 2.31 (s, 3H); ^{13}C{^{1}H} NMR (175 MHz, $CDCl_3$) δ 147.3, 142.4, 138.5, 134.6, 131.9, 131.8 (q, *J* = 32.1 Hz), 129.7, 129.6, 127.6, 125.22 (q, *J* = 3.5 Hz), 124.3 (q, *J* = 270.7 Hz), 124.1, 121.9, 103.7, 13.12; HR-MS (ESI) m/z: $[M + H]^+$ Calcd for $C_{17}H_{15}F_3N_3$: 318.1213; Found: 318.1193.

5-Amino-4-(3-methoxyphenyl)-3-methyl-1-phenyl-1*H*-pyrazole (2r):



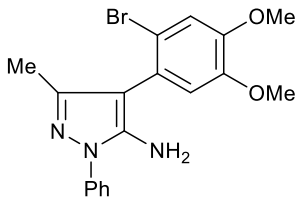
Reaction time: 3 h; Yield: 95% (0.663 g); Pale orange gel; R_f = 0.20 in 20% EtOAc in n-hexane; IR (KBr, ν cm^{-1}): 3440, 2624, 1608, 1543, 1344, 1278, 1182, 1074, 994; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (d, *J* = 7.6 Hz, 2H), 7.57 (d, *J* = 8.8 Hz, 1H), 7.50 (t, *J* = 7.6 Hz, 2H), 7.37 (t, *J* = 7.6 Hz, 1H), 7.26 (s, 1H), 6.88 (d, *J* = 3.2 Hz, 1H), 6.80 (dd, *J* = 8.8, 3.2 Hz, 1H), 3.82 (s, 5H; Ar-OCH_3 & NH_2), 2.22 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 159.2, 147.6, 143.9, 142.7, 133.9, 129.8, 127.8, 127.0, 124.1, 118.2, 115.8, 115.5, 105.5, 55.7, 12.8; HR-MS (ESI) m/z: $[M + H]^+$ Calcd for $C_{17}H_{18}N_3O$: 280.1332; Found: 280.1309.

5-Amino-4-(2-bromo-4-methoxyphenyl)-3-methyl-1-phenyl-1*H*-pyrazol (2s):[3]



Reaction time: 3 h; Yield: 95% (0.848 g); White colour solid; R_f = 0.26 in 20% EtOAc in n-hexane; m.p = 148-151 °C; IR (KBr, ν cm^{-1}): 3422, 1618, 1570, 1513, 1434, 1323, 1282, 1221, 1178, 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, 5H; Ar-OCH_3 & NH_2), 2.17 (s, 3H); ^{13}C{^{1}H} 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; HR-MS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{17}H_{16}BrN_3ONa$: 380.0369 & 382.0349; Found: 380.0340 & 382.0326.

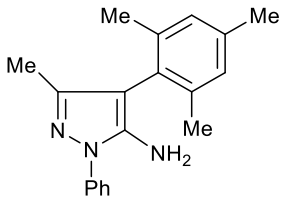
5-Amino-4-(2-bromo-4,5-dimethoxyphenyl)-3-methyl-1-phenyl-1*H*-pyrazole (2t):[3]



Reaction time: 3 h; Yield: 98% (0.951 g); Pale brown colour solid; R_f = 0.16 in 20% EtOAc in n-hexane; m.p = 162-164 °C; IR (KBr, ν cm^{-1}): 3430, 2304, 1618, 1507, 1463, 1264, 1208, 1174, 1064, 896; ^{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{^{1}H} NMR (175 MHz, $CDCl_3$) δ 149.1, 148.5, 147.9, 142.3, 138.9, 129.6,

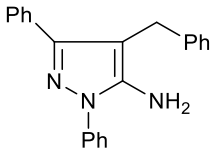
127.1, 125.7, 123.8, 115.7, 115.6, 115.1, 105.3, 56.3, 56.2, 13.0; HR-MS (ESI) m/z: $[M + H]^+$ Calcd for $C_{18}H_{19}BrN_3O_2$: 388.0655 & 390.0635; Found: 388.0677 & 390.0656.

5-Amino-4-mesityl-3-methyl-1-phenyl-1*H*-pyrazole (2u):[3]



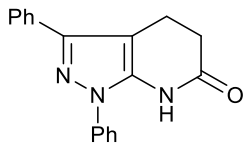
Reaction time: 3 h; Yield: 94% (0.684 g); White colour solid; R_f = 0.24 in 20% EtOAc in n-hexane; m.p = 165-168 °C; IR (KBr, ν cm^{-1}): 3437, 1634, 1506, 1576, 1456, 1387, 1288, 868; ^1H NMR (400 MHz, $CDCl_3$) δ 7.65 (d, *J* = 7.6 Hz, 2H), 7.47 (t, *J* = 7.6 Hz, 2H), 7.31 (t, *J* = 7.4 Hz, 1H), 6.97 (s, 2H), 3.56 (s, 2H), 2.32 (s, 3H), 2.13 (s, 6H), 2.03 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 148.0, 141.8, 139.1, 139.0, 137.4, 129.5, 128.4, 127.7, 126.9, 123.3, 103.3, 21.2, 20.4, 12.7; HR-MS (ESI) m/z: $[M + H]^+$ Calcd for $C_{19}H_{22}N_3$: 292.1808; Found: 292.1793.

5-Amino-4-benzyl-1,3-diphenyl-1*H*-pyrazole (2v):[3]



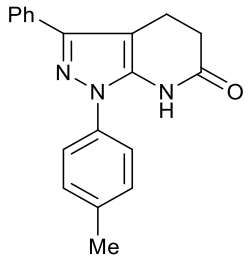
Reaction time: 4 h; Yield: 62% (0.504 g); White colour solid; R_f = 0.27 in 20% EtOAc in n-hexane; m.p = 148-151 °C; IR (KBr, ν cm^{-1}): 3421, 1627, 1559, 1506, 1454, 1390, 1023, 758; ^1H NMR (400 MHz, $CDCl_3$) δ 7.49 (t, *J* = 7.2 Hz, 4H), 7.31 (t, *J* = 7.5 Hz, 2H), 7.26 – 7.05 (m, 9H), 3.77 (s, 2H), 3.39 (brs, 2H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 151.3, 143.6, 139.9, 138.7, 133.8, 129.4, 128.7, 128.4, 128.1, 127.9, 127.7, 127.2, 126.3, 123.8, 99.6, 29.3; HR-MS (ESI) m/z: $[M + H]^+$ Calcd for $C_{22}H_{20}N_3$: 326.1652; Found: 326.1675.

1,3-Diphenyl-1,4,5,7-tetrahydro-6*H*-pyrazolo[3,4-*b*]pyridin-6-one (12a):



Reaction time: 3 h; yield: 67% (0.484 g); Brown colour solid; Rf = 0.15 in 30% EtOAc in Hexane; m.p = 210-213 °C; IR (KBr, ν cm-1): 3013, 2925, 2810, 1601, 1566, 1419, 1377, 1123, 933; ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.40 (s, 1H), 7.72 (d, *J* = 7.2 Hz, 2H), 7.59 (d, *J* = 7.5 Hz, 2H), 7.53 (t, *J* = 7.8 Hz, 2H), 7.46 (t, *J* = 7.5 Hz, 2H), 7.43 – 7.34 (m, 2H), 2.97 (t, *J* = 7.5 Hz, 2H), 2.63 (t, *J* = 7.5 Hz, 2H); ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6) δ 170.6, 146.9, 139.8, 137.9, 133.1, 129.3, 128.7, 127.8, 127.3, 126.4, 123.2, 99.6, 31.6, 17.5; HR-MS (ESI) m/z: $[M + H]^+$ Calcd for $C_{18}H_{16}N_3O$: 290.1293; Found: 290.1288.

3-Phenyl-1-(*p*-tolyl)-1,4,5,7-tetrahydro-6*H*-pyrazolo[3,4-*b*]pyridin-6-one (12b):

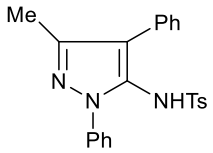


Reaction time: 3 h; yield: 65% (0.492 g); Brown colour solid; Rf = 0.18 in 30% EtOAc in Hexane; m.p = 182-185 °C; IR (KBr, ν cm-1): 3169, 3044, 2850, 1695, 1545, 1359, 1199, 938, 776; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (s, 1H), 7.74 (d, *J* = 7.2 Hz, 2H), 7.45 – 7.29 (m, 7H), 3.06 (t, *J* = 7.6 Hz, 2H), 2.75 (t, *J* = 7.6 Hz, 2H), 2.41 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 170.6, 148.18, 138.34, 138.31, 135.0, 133.2, 130.5, 128.8, 128.2, 126.9, 123.4, 98.8, 31.8, 21.2, 18.2; HR-MS (ESI) m/z: [M + H]+ Calcd for $C_{19}H_{18}N_3O$: 304.1450; Found: 304.1434.

General procedure for the synthesis of 5-*N*-tosylaminopyrazoles 1a-v

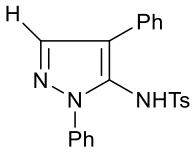
A round bottom flask was charged with 5-aminopyrazoles **2** (1.5 mmol, 1 equiv) in pyridine, *p*-TsCl (1.65 mmol, 1.1 equiv) and DMAP (0.3 mmol) were added and the reaction mixture was stirred for overnight at room temperature. The reaction mixture was monitored by TLC. After the completion of reaction, pyridine was evaporated under reduced pressure. After which water (20 mL) was added to the reaction mixture and extracted with ethyl acetate (3 × 20 mL). The combined organic layer was dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The crude products were purified through flash column chromatography using n-hexane and EtOAc as the eluents.

4-Methyl-*N*-(3-methyl-1,4-diphenyl-1*H*-pyrazol-5-yl)benzenesulfonamide (1a):



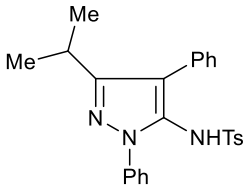
Reaction time: 12 h; Yield: 64% (0.387 g); Pale yellow colour solid; R_f = 0.24 in 20% EtOAc in n-hexane; m.p = 198-200 °C; IR (KBr, ν cm^{-1}): 3429, 1631, 1500, 1432, 1333, 1164, 1091,753; ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.40 (s, 1H), 7.54 (d, *J* = 7.6 Hz, 2H), 7.41 (t, *J* = 7.6 Hz, 2H), 7.34 – 7.31 (m, 1H), 7.19 (s, 5H), 7.13 (d, *J* = 8.0 Hz, 2H), 6.85 (d, *J* = 8.0 Hz, 2H), 2.21 (s, 3H), 2.20 (s, 3H); ^{13}C{^{1}H} NMR (175 MHz, $CDCl_3$) δ 147.4, 143.7, 138.8, 136.1, 131.4, 130.2, 129.3, 129.1, 129.0, 128.5, 127.7, 127.1, 126.8, 124.9, 119.4, 21.6, 13.2; HR-MS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{23}H_{21}N_3O_2SNa$: 426.1247; Found: 426.1252.

***N*-(1,4-Diphenyl-1*H*-pyrazol-5-yl)-4-methylbenzenesulfonamide (1b):**



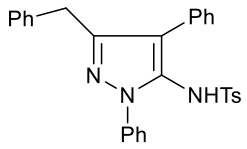
Reaction time: 12 h; Yield: 30% (0.175 g); White colour solid; R_f = 0.33 in 25% EtOAc in n-hexane; m.p = 218-221 °C; IR (KBr, ν cm^{-1}): 3077, 1693, 1327, 1236, 1072, 876; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (s, 1H), 7.34 (d, *J* = 7.6 Hz, 2H), 7.27 – 7.24 (m, 2H), 7.15 – 7.08 (m, 8H), 6.73 (d, *J* = 8.0 Hz, 2H), 2.17 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 143.8, 139.3, 138.6, 135.9, 131.0, 129.5, 129.3, 129.1, 128.6, 128.0, 127.3, 127.1, 126.8, 125.0, 120.8, 21.5; HR-MS (ESI) m/z: $[M + H]^+$ Calcd for $C_{22}H_{20}N_3O_2S$: 390.1276; Found: 390.1271.

***N*-(3-Isopropyl-1,4-diphenyl-1*H*-pyrazol-5-yl)-4-methylbenzenesulfonamide (1c):**



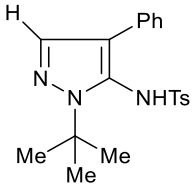
Reaction time: 12 h; Yield: 60% (0.388 g); White colour solid; R_f = 0.25 in 20% EtOAc in n-hexane; m.p = 201-204 °C; IR (KBr, ν cm^{-1}): 3077, 1698, 1337, 1235, 1079, 881; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, *J* = 8.0 Hz, 2H), 7.37 (t, *J* = 7.2 Hz, 2H), 7.31 – 7.28 (m, 1H), 7.22 – 7.18 (m, 5H), 7.03 – 7.01 (m, 2H), 6.88 (d, *J* = 8.0 Hz, 2H), 6.59 (s, 1H), 3.05 – 2.95, (m, 1H), 2.32 (s, 3H), 1.21 (d, *J* = 6.9 Hz, 6H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 156.4, 143.6, 139.3, 136.3, 131.7, 130.2, 129.6, 129.3, 129.0, 128.4, 127.4, 127.1, 126.9, 124.9, 118.6, 26.7, 22.3, 21.5; HR-MS (ESI) m/z: $[M + H]^+$ Calcd for $C_{25}H_{26}N_3O_2S$: 432.1733; Found: 432.1740.

***N*-(3-Benzyl-1,4-diphenyl-1*H*-pyrazol-5-yl)-4-methylbenzenesulfonamide (1d):**



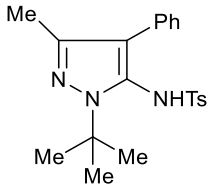
Reaction time: 12 h; Yield: 44% (0.316 g); Pale brown colour solid; R_f = 0.28 in 25% EtOAc in n-hexane; m.p = 168-170 °C; IR (KBr, ν cm^{-1}): 3077, 1693, 1327, 1236, 1072, 876; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, 2H), 7.43 (t, *J* = 7.5 Hz, 2H), 7.39 – 7.32 (m, 1H), 7.25 – 7.10 (m, 10H), 6.88 – 6.82 (m, 4H), 3.99 (s, 2H), 2.30 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 149.6, 143.7, 139.4, 138.7, 135.7, 130.8, 130.7, 129.37, 129.31, 129.1, 128.8, 128.6, 128.3, 127.8, 127.07, 127.03, 126.2, 124.9, 119.7, 33.2, 21.5; HR-MS (ESI) m/z: $[M + H]^+$ Calcd for $C_{29}H_{26}N_3O_2S$: 480.1740; Found: 480.1731.

***N*-(1-(*Tert*-butyl)-4-phenyl-1*H*-pyrazol-5-yl)-4-methylbenzenesulfonamide (1e):**



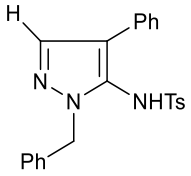
Reaction time: 12 h; Yield: 83% (0.459 g); Pale yellow colour solid; R_f = 0.326 in 20% EtOAc in n-hexane; m.p = 205-208 °C; IR (KBr, ν cm^{-1}): 3236, 2985, 1494, 1442, 1357, 1261, 1159, 896; ^{1}H NMR (700 MHz, $CDCl_3$) δ 7.49 (s, 1H), 7.27 (d, *J* = 8.2 Hz, 2H), 7.03 – 6.90 (m, 5H), 6.78 (d, *J* = 7.9 Hz, 2H), 2.25 (s, 3H), 1.83 (s, 9H); ^{13}C{^{1}H} NMR (175 MHz, $CDCl_3$) δ 143.7, 136.9, 136.4, 131.8, 129.2, 128.8, 128.2, 127.4, 127.3, 125.9, 120.6, 62.6, 30.9, 21.5; HR-MS (ESI) m/z: $[M + H]^+$ Calcd for $C_{20}H_{24}N_3O_2S$: 370.1589; Found: 370.1581.

***N*-(1-(*Tert*-butyl)-3-methyl-4-phenyl-1*H*-pyrazol-5-yl)-4-methylbenzenesulfonamide (1f):**



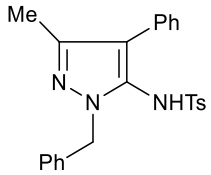
Reaction time: 12 h; Yield: 67% (0.385 g); White colour solid; R_f = 0.34 in 25% EtOAc in n-hexane; m.p = 157-159 °C; IR (KBr, ν cm^{-1}): 3071, 1689, 1325, 1236, 1079, 886; ^{1}H NMR (700 MHz, $CDCl_3$) δ 7.22 – 7.21 (m, 2H), 7.04 – 6.99 (m, 3H), 6.80 – 6.79 (m, 4H), 2.28 (s, 3H), 2.12 (s, 3H), 1.81 (s, 9H); ^{13}C{^{1}H} NMR (175 MHz, $CDCl_3$) δ 144.1, 143.3, 136.5, 132.2, 129.2, 129.1, 129.0, 128.1, 127.1, 125.8, 118.7, 61.9, 30.9, 21.5, 13.2; HR-MS (ESI) m/z: $[M + H]^+$ Calcd for $C_{21}H_{26}N_3O_2S$: 384.1740; Found:384.1762.

***N*-(1-Benzyl-4-phenyl-1*H*-pyrazol-5-yl)-4-methylbenzenesulfonamide (1g):**



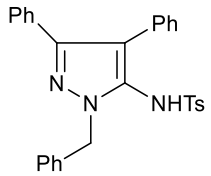
Reaction time: 12 h; Yield: 77% (0.465 g); Pale yellow colour solid; R_f = 0.4 in 50% EtOAc in n-hexane; m.p = 215-217 °C; IR (KBr, ν cm^{-1}): 3077, 1698, 1341, 1239, 1092, 867; ^{1}H NMR (700 MHz, $CDCl_3$) δ 7.83 (s, 1H), 7.63 – 7.54 (m, 7H), 7.40 – 7.31 (m, 3H), 7.19 (d, J = 6.8 Hz, 2H), 7.12 (d, J = 8.0 Hz, 2H), 5.81 (s, 2H), 2.53 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 144.2, 138.0, 136.6, 135.1, 131.1, 129.5, 129.3, 128.9, 128.3, 127.99, 127.96, 127.4, 126.9, 126.4, 119.6, 53.1, 21.6; HR-MS (ESI) m/z: $[M + H]^+$ Calcd for $C_{23}H_{22}N_3O_2S$: 404.1433; Found: 404.1455.

***N*-(1-Benzyl-3-methyl-4-phenyl-1*H*-pyrazol-5-yl)-4-methylbenzenesulfonamide (1h):**



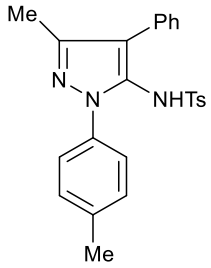
Reaction time: 12 h; Yield: 81% (0.507 g); White colour solid; R_f = 0.25 in 20% EtOAc in n-hexane; m.p = 187-190 °C; IR (KBr, ν cm^{-1}): 3443, 3053, 2985, 1711, 1497, 1362, 1265, 896; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 – 7.27 (m, 5H), 7.24 (d, *J* = 8.3 Hz, 2H), 7.09 – 7.08 (m, 3H), 6.92 (s, 1H), 6.83 (d, *J* = 8.0 Hz, 2H), 6.76 – 6.74 (m, 2H), 5.51 (s, 2H), 2.29 (s, 3H), 2.14 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 145.8, 143.9, 137.0, 135.0, 131.3, 130.2, 129.3, 128.7, 128.6, 128.1, 127.8, 127.7, 127.2, 126.3, 117.8, 52.6, 21.6, 13.0; HR-MS (ESI) m/z: $[M + H]^+$ Calcd for $C_{24}H_{24}N_3O_2S$: 418.1584; Found: 418.1572.

***N*-(1-Benzyl-3,4-diphenyl-1*H*-pyrazol-5-yl)-4-methylbenzenesulfonamide (1i):**



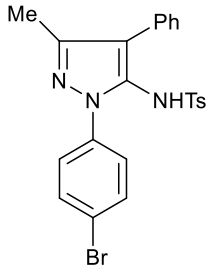
Reaction time: 12 h; Yield: 60% (0.431 g); White colour solid; R_f = 0.25 in 20% EtOAc in n-hexane; m.p = 213-215 °C; IR (KBr, ν cm^{-1}): 3433, 2985, 1503, 1274, 1260, 1164, 1164, 749; ^{1}H NMR (700 MHz, $CDCl_3$) δ 7.36 – 7.33 (m, 6H), 7.30 – 7.28 (m, 1H), 7.24 (d, *J* = 8.4 Hz, 2H), 7.21 – 7.20 (m, 3H), 7.10 (t, *J* = 7.0 Hz, 1H), 7.01 (t, *J* = 7.0 Hz, 2H), 6.85 (d, *J* = 7.7 Hz, 2H), 6.65 (t, *J* = 7.7 Hz, 2H), 6.62 (brs, 1H), 5.66 (s, 2H), 2.28 (s, 3H); ^{13}C{^{1}H} NMR (175 MHz, $CDCl_3$) δ 148.1, 144.0, 136.8, 135.0, 133.0, 131.3, 131.1, 129.5, 129.3, 128.7 (2C), 128.2 (2C), 128.0, 127.8, 127.6, 127.2, 126.6, 117.3, 53.4, 21.6; HR-MS (ESI) m/z: $[M + H]^+$ Calcd for $C_{29}H_{26}N_3O_2S$: 480.1736; Found: 480.1721.

4-Methyl-*N*-(3-methyl-4-phenyl-1-(*p*-tolyl)-1*H*-pyrazol-5-yl)benzenesulfonamide (1j):



Reaction time: 12 h; Yield: 53% (0.332 g); White colour solid; R_f = 0.3 in 25% EtOAc in n-hexane; m.p = 215-217 °C; IR (KBr, ν cm^{-1}): 3066, 1701, 1517, 1372, 1334, 1233, 1164, 1019, 888; ^{1}H NMR (700 MHz, $CDCl_3$) δ 7.33 (d, *J* = 7.7 Hz, 2H), 7.20 – 7.17 (m, 5H), 7.13 (d, *J* = 7.7 Hz, 2H), 7.06 – 7.03 (m, 3H), 6.83 (d, *J* = 7.7 Hz, 2H), 2.36 (s, 3H), 2.30 (s, 3H), 2.26 (s, 3H); ^{13}C{^{1}H} NMR (175 MHz, $CDCl_3$) δ 147.0, 143.5, 137.5, 136.2, 136.2, 131.4, 130.2, 129.5, 129.2, 129.0, 128.4, 127.0, 126.6, 124.8, 119.2, 21.6, 21.2, 13.2; HR-MS (ESI) m/z: [M + H]$^+$ Calcd for $C_{24}H_{24}N_3O_2S$: 418.1584; Found: 418.1598.

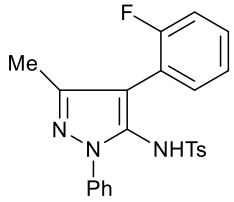
***N*-(1-(4-Bromophenyl)-3-methyl-4-phenyl-1*H*-pyrazol-5-yl)-4-methyl benzenesulfonamide (1k):**



Reaction time: 12 h; Yield: 50% (0.362 g); White colour solid; R_f = 0.25 in 20% EtOAc in n-hexane; m.p = 192-195 °C; IR (KBr, ν cm^{-1}): 3440, 1631, 1492, 1438, 1333, 1163, 1091, 1011, 811; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (d, *J* = 8.7 Hz, 2H), 7.39 (d, *J* = 8.8 Hz, 2H), 7.26 – 7.22 (m, 3H), 7.19 (d, *J* = 8.3 Hz, 2H), 7.09 – 7.04 (m, 2H), 6.97 (s, 1H), 6.89 (d, *J* = 8.1 Hz, 2H), 2.35 (s, 3H), 2.26 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 147.8, 144.0, 137.8, 136.0, 132.1, 131.0, 130.4, 129.4, 129.1, 128.6, 127.1, 127.0, 126.2, 121.4, 120.0, 21.7, 13.2; HR-MS

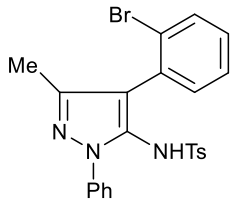
(ESI) m/z: $[M + H]^+$ Calcd for $C_{23}H_{21}BrN_3O_2S$: 482.0532 & 484.0513; Found: 482.0514 & 484.0492.

***N*-(4-(2-Fluorophenyl)-3-methyl-1-phenyl-1*H*-pyrazol-5-yl)-4-methyl benzenesulfonamide (1l):**



Reaction time: 12 h; Yield: 57% (0.360 g); White colour solid; R_f = 0.22 in 20% EtOAc in n-hexane; m.p = 184-186 °C; IR (KBr, ν cm^{-1}): 3440, 1637, 1502, 1333, 1288, 1164, 1091, 668; ^1H NMR (700 MHz, $CDCl_3$) δ 7.58 (d, *J* = 8.4 Hz, 2H), 7.41 (t, *J* = 7.7 Hz, 2H), 7.33 (t, *J* = 7.7 Hz, 1H), 7.22 (d, *J* = 8.4 Hz, 2H), 7.20 – 7.16 (m, 1H), 6.99 (t, *J* = 7.7 Hz, 1H), 6.93 (t, *J* = 7.7 Hz, 2H), 6.83 (d, *J* = 7.7 Hz, 2H), 6.70 (s, 1H), 2.26 (s, 3H), 2.24 (s, 3H); $^{13}C\{^1H\}$ NMR (175 MHz, $CDCl_3$) δ 159.9 (d, *J* = 243.25 Hz), 147.5, 143.7, 138.7, 135.7, 131.3 (d, *J* = 3.5 Hz), 131.1, 129.3, 129.0, 128.8 (d, *J* = 8.75 Hz) 127.7, 126.9, 124.9, 124.1 (d, *J* = 3.5 Hz), 118.9 (d, *J* = 15.75 Hz), 115.7 (d, *J* = 22.75 Hz), 112.9, 21.5, 13.1; HR-MS (ESI) m/z: $[M + H]^+$ Calcd for $C_{23}H_{21}FN_3O_2S$: 422.1333; Found: 422.1354.

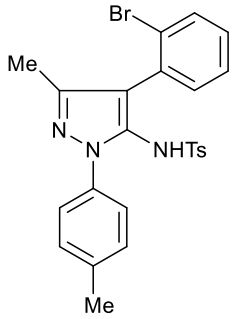
***N*-(4-(2-Bromophenyl)-3-methyl-1-phenyl-1*H*-pyrazol-5-yl)-4-methyl benzenesulfonamide (1m):**



Reaction time: 12 h; Yield: 60% (0.434 g); White colour solid; R_f = 0.25 in 20% EtOAc in n-hexane; m.p = 192-195 °C; IR (KBr, ν cm^{-1}): 3440, 1632, 1501, 1426, 1369, 1333, 1164, 1092,

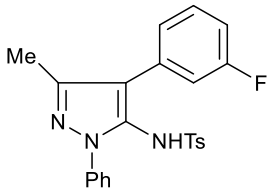
811; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (d, *J* = 8.0 Hz, 2H), 7.52 (d, *J* = 7.5 Hz, 1H), 7.44 (t, *J* = 7.4 Hz, 2H), 7.37 (t, *J* = 7.0 Hz, 1H), 7.27 (d, *J* = 8.3 Hz, 2H), 7.19 – 7.09 (m, 2H), 6.95 – 6.87 (m, 3H), 6.58 (s, 1H), 2.33 (s, 3H), 2.18 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 147.5, 143.7, 138.7, 135.9, 132.7, 132.4, 132.1, 130.5, 129.5, 129.1, 128.9, 127.8, 127.3, 126.9, 125.0, 123.6, 118.4, 21.6, 13.0; HR-MS (ESI) m/z: $[M + H]^+$ Calcd for $C_{23}H_{21}BrN_3O_2S$: 482.0532 & 484.0513; Found: 482.0510 & 484.0482.

***N*-(4-(2-Bromophenyl)-3-methyl-1-(*p*-tolyl)-1*H*-pyrazol-5-yl)-4-methyl benzenesulfonamide (1n):**



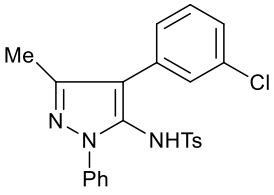
Reaction time: 12 h; Yield: 66% (0.491 g); White colour solid; R_f = 0.24 in 20% EtOAc in n-hexane; m.p = 190-193 °C; IR (KBr, ν cm^{-1}): 3441,1638, 1554, 1517, 1501, 1492, 1162, 1092, 565; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (dd, *J* = 7.6, 1.4 Hz, 1H), 7.40 (d, *J* = 8.4 Hz, 2H), 7.25 (d, *J* = 8.8 Hz, 2H), 7.19 (d, *J* = 8.0 Hz, 2H), 7.16 – 7.05 (m, 2H), 6.95 – 6.83 (m, 3H), 6.71 (s, 1H), 2.39 (s, 3H), 2.31 (s, 3H), 2.15 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 147.3, 143.5, 137.7, 136.3, 136.2, 132.7, 132.5, 132.4, 130.7, 129.6, 129.3, 128.8, 127.3, 126.9, 124.9, 123.8, 118.3, 21.6, 21.3, 13.0; HR-MS (ESI) m/z: $[M + H]^+$ Calcd for $C_{24}H_{23}BrN_3O_2S$: 496.0689 & 498.0669; Found: 496.0702 & 498.0684.

***N*-(4-(3-Fluorophenyl)-3-methyl-1-phenyl-1*H*-pyrazol-5-yl)-4-methylbenzenesulfonamide (1o):**



Reaction time: 12 h; Yield: 58% (0.366 g); White colour solid; R_f = 0.22 in 20% EtOAc in n-hexane; m.p = 185-187 °C; IR (KBr, ν cm^{-1}): 3248, 1618, 1584, 1501, 1432, 1333, 1163, 1091, 692; ^{1}H NMR (700 MHz, $CDCl_3$) δ 7.48 (d, *J* = 8.4 Hz, 2H), 7.39 (t, *J* = 7.7 Hz, 2H), 7.34 (t, *J* = 7.0 Hz, 1H), 7.22 – 7.18 (m, 3H), 6.91 – 6.88 (m, 4H), 6.81 (s, 1H), 6.65 (d, *J* = 9.8 Hz, 1H), 2.32 (s, 3H), 2.26 (s, 3H); ^{13}C{^{1}H} NMR (175 MHz, $CDCl_3$) δ 162.7 (d, *J* = 243.25 Hz), 147.2, 144.0, 138.59, 135.9, 133.6 (d, *J* = 8.75 Hz), 130.4, 129.9 (d, *J* = 8.75 Hz), 129.4, 129.1, 127.9, 127.1, 125.0, 124.7 (d, *J* = 1.75 Hz), 118.2, 115.9 (d, *J* = 22.75 Hz), 113.7 (d, *J* = 21.0 Hz), 21.5, 13.2; HR-MS (ESI) m/z: $[M + H]^+$ Calcd for $C_{23}H_{21}FN_3O_2S$: 422.1333; Found: 422.1337.

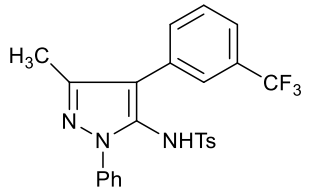
***N*-(4-(3-Chlorophenyl)-3-methyl-1-phenyl-1*H*-pyrazol-5-yl)-4-methyl benzenesulfonamide (1p):**



Reaction time: 12 h; Yield: 54% (0.354 g); Brown colour solid; R_f = 0.23 in 20% EtOAc in n-hexane; m.p = 169-171 °C; IR (KBr, ν cm^{-1}): 3440, 1632, 1502, 1432, 1369, 1334, 1163, 1091, 882; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (d, *J* = 7.2 Hz, 2H), 7.38 (t, *J* = 7.4 Hz, 2H), 7.36 – 7.30 (m, 1H), 7.21 (d, *J* = 8.0 Hz, 2H), 7.14 – 7.13 (m, 3H), 6.98 – 6.98 (m, 1H), 6.92 (s, 1H), 6.90 (d, *J* = 8.1 Hz, 2H), 2.32 (s, 3H), 2.25 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 147.2, 144.0, 138.5, 135.9, 134.2, 133.2, 130.3, 129.6, 129.4, 129.1, 128.9, 127.9, 127.1, 127.0, 126.8,

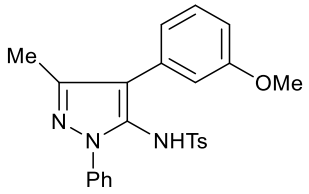
125.0, 118.1, 21.6, 13.2; HR-MS (ESI) m/z: $[M + H]^+$ Calcd for $C_{23}H_{21}ClN_3O_2S$: 438.1038; Found: 438.1013.

4-Methyl-*N*-(3-methyl-1-phenyl-4-(3-(trifluoromethyl)phenyl)-1*H*-pyrazol-5-yl)benzenesulfonamide (1q):



Reaction time: 12 h; Yield: 36% (0.255 g); White colour solid; R_f = in 20% EtOAc in Hexane; m.p = 167-170 °C; IR (KBr, ν cm^{-1}): 3448, 1647, 1513, 1342, 1261, 1182, 1119, 698; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (d, *J* = 7.3 Hz, 2H), 7.47 – 7.29 (m, 7H), 7.21 (d, *J* = 8.2 Hz, 2H), 6.86 (d, *J* = 8.0 Hz, 2H), 6.74 (s, 1H), 2.29 (s, 3H), 2.28 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 147.3, 144.0, 138.4, 136.2, 132.5, 132.4, 130.5, 130.8 (q, *J* = 32.0), 129.5, 129.3, 129.0, 128.2, 127.1, 125.7 (q, *J* = 4.0), 125.2, 124.1 (q, *J* = 271), 123.5 (q, *J* = 4.0), 118.0, 21.5, 13.3; HR-MS (ESI) m/z: $[M + H]^+$ Calcd for $C_{29}H_{26}N_3O_2S$: 472.1301; Found: 472.1273.

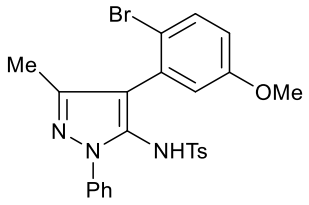
***N*-(4-(3-Methoxyphenyl)-3-methyl-1-phenyl-1*H*-pyrazol-5-yl)-4-methylbenzenesulfonamide (1r):**



Reaction time: 12 h; Yield: 58% (0.376 g); White colour solid; R_f = 0.22 in 20% EtOAc in n-hexane; m.p = 170-173 °C; IR (KBr, ν cm^{-1}): 3445, 1738, 1600, 1539, 1428, 1349, 1262, 1191, 990; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (d, *J* = 7.6 Hz, 2H), 7.35 (t, *J* = 7.2 Hz, 2H), 7.29 (d, *J* = 8.7 Hz, 2H), 7.20 – 7.18 (m, 2H), 6.81 (d, *J* = 8.0 Hz, 2H), 6.61 – 6.57 (m, 2H), 6.24 (d, *J* = 2.8 Hz, 1H), 3.65 (s, 3H), 2.22 (s, 3H), 2.09 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ

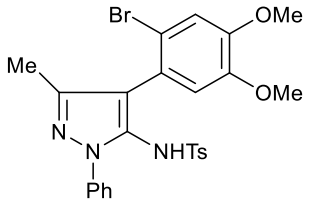
158.6, 147.3, 143.8, 138.7, 136.1, 133.2, 132.8, 130.5, 129.3, 129.0, 127.8, 127.0, 125.0, 118.3, 117.4, 115.0, 113.8, 55.3, 21.4, 13.0; HR-MS (ESI) m/z: $[M + H]^+$ Calcd for $C_{24}H_{24}N_3O_3S$: 434.1538; Found: 434.1577.

***N*-(4-(2-Bromo-4-methoxyphenyl)-3-methyl-1-phenyl-1*H*-pyrazol-5-yl)-4-methylbenzenesulfonamide (1s):**



Reaction time: 12 h; Yield: 68% (0.522 g); Pale yellow solid; R_f = 0.24 in 20% EtOAc in n-hexane; m.p = 133-135 °C; IR (KBr, ν cm^{-1}): 3445, 1642, 1509, 1462, 1329, 1314, 1193, 1041, 752; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (d, *J* = 8.0 Hz, 2H), 7.43 (t, *J* = 7.6 Hz, 2H), 7.38 – 7.34 (m, 2H), 7.27 (d, *J* = 8.1 Hz, 2H), 6.90 (d, *J* = 8.0 Hz, 2H), 6.66 (dd, *J* = 8.0, 2.8 Hz, 1H), 6.58 (s, 1H), 6.32 (d, *J* = 2.8 Hz, 1H), 3.73 (s, 3H), 2.30 (s, 3H), 2.18 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 158.6, 147.2, 143.8, 138.7, 136.0, 133.2, 132.9, 130.5, 129.3, 129.0, 127.8, 127.0, 125.0, 118.3, 117.3, 115.0, 113.7, 55.3, 21.5, 13.0; HR-MS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{24}H_{22}BrN_3O_3SNa$: 534.0457 & 536.0438; Found: 534.0411 & 536.0393.

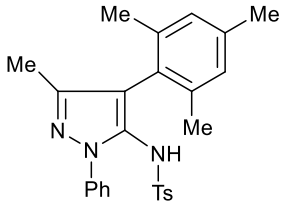
***N*-(4-(2-Bromo-4,5-dimethoxyphenyl)-3-methyl-1-phenyl-1*H*-pyrazol-5-yl)-4-methylbenzenesulfonamide (1t):**



Reaction time: 12 h; Yield: 60% (0.488 g); Pale yellow colour solid; R_f = 0.23 in 20% EtOAc in n-hexane; m.p = 142-145 °C; IR (KBr, ν cm^{-1}): 3440, 1638, 1500, 1439, 1328, 1249, 1162,

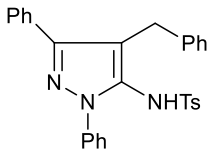
1091, 667; ^{1}H NMR (700 MHz, $CDCl_3$) δ 7.57 (d, *J* = 7.7 Hz, 2H), 7.41 (t, *J* = 7.7 Hz, 2H), 7.34 (t, *J* = 7.7 Hz, 1H), 7.29 (d, *J* = 7.7 Hz, 2H), 6.93 (s, 1H), 6.89 (d, *J* = 7.7 Hz, 2H), 6.60 (s, 1H), 6.35 (s, 1H), 3.90 (s, 3H), 3.76 (s, 3H), 2.31 (s, 3H), 2.17 (s, 3H); ^{13}C{^{1}H} NMR (175 MHz, $CDCl_3$) δ 149.3, 148.2, 147.4, 143.8, 138.7, 136.7, 130.6, 129.2, 129.0, 127.8, 127.0, 125.0, 124.2, 118.5, 115.0, 114.3, 113.5, 56.3, 55.8, 21.4, 13.1; HR-MS (ESI) m/z: $[M + H]^+$ Calcd for $C_{25}H_{25}BrN_3O_4S$: 542.0744 & 544.0724; Found: 542.0733 & 544.0718.

***N*-(4-Mesityl-3-methyl-1-phenyl-1*H*-pyrazol-5-yl)-4-methylbenzenesulfonamide (1u):**



Reaction time: 12 h; Yield: 48% (0.320 g); White colour solid; R_f = 0.13 in 20% EtOAc in n-hexane; m.p = 174-176 °C; IR (KBr, ν cm^{-1}): 3440, 2923, 1639, 1502, 1451, 1365, 1331, 1160, 565; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (d, *J* = 7.2 Hz, 2H), 7.38 – 7.31 (m, 3H), 7.17 (d, *J* = 8.4 Hz, 2H), 6.89 (d, *J* = 8.0 Hz, 2H), 6.73 (s, 2H), 2.34 (s, 3H), 2.28 (s, 3H), 2.01 (s, 3H), 1.97 (s, 6H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 148.2, 143.2, 138.5, 137.7, 137.2, 137.0, 130.7, 129.1 (2C), 128.1, 127.7, 127.0, 126.4, 125.1, 117.3, 21.6, 21.2, 20.4, 12.9; HR-MS (ESI) m/z: $[M + H]^+$ Calcd for $C_{26}H_{28}N_3O_2S$: 446.1897; Found: 446.1908.

***N*-(4-Benzyl-1,3-diphenyl-1*H*-pyrazol-5-yl)-4-methylbenzenesulfonamide (1v):**



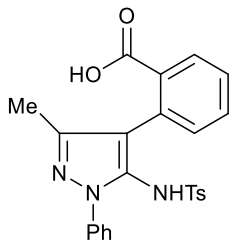
Reaction time: 12 h; Yield: 30% (0.216 g); Pale yellow solid; R_f = 0.30 in 25% EtOAc in n-hexane; m.p = 172-174 °C; IR (KBr, ν cm^{-1}): 3054, 1621, 1554, 1348, 1331, 1267, 1012, 847; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (d, *J* = 7.3 Hz, 2H), 7.45 – 7.18 (m, 13H), 7.14 – 7.00 (m,

4H), 6.27 (s, 1H), 3.92 (s, 2H), 2.39 (s, 3H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 151.0, 144.2, 139.7, 138.6, 136.2, 133.2, 132.0, 129.7, 128.9, 128.7, 128.6, 128.3, 128.1, 128.0, 127.5, 127.3, 126.4, 124.6, 116.8, 29.0, 21.7; HR-MS (ESI) m/z: $[M + H]^+$ Calcd for $C_{29}H_{26}N_3O_2S$: 480.1736; Found: 480.1715.

Procedure for the synthesis of 2-(3-methyl-5-((4-methylphenyl)sulfonamido)-1-phenyl-1*H*-pyrazol-4-yl)benzoic acid (1w).

To an oven dried 25 mL round bottom flask containing 5-*N*-tosylaminopyrazoles **1m** (0.4 mmol, 1 equiv) in dried THF (5 mL), 2M n-BuLi in cyclohexane (0.84 mmol, 2.1 equiv) was added dropwise at -78 °C under N_2 atmosphere. Then the resulting suspension was stirred at -78 °C for 30 min. After which the reaction mixture was allowed to reach 0 °C followed by CO_2 gas was purged into the reaction mixture for 10 min. The reaction was monitored by TLC. After the starting material was completely consumed, the reaction mixture was quenched with aq.1M HCl (15 mL) and extracted with ethyl acetate (3 × 20 mL). The combined organic layer was dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The crude products were purified through flash column chromatography using n-hexane and EtOAc as the eluents.

2-(3-Methyl-5-((4-methylphenyl)sulfonamido)-1-phenyl-1*H*-pyrazol-4-yl)benzoic acid (1w):



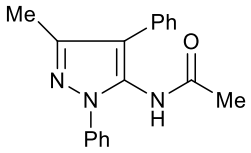
Reaction time: 40 min; Yield: 88% (0.179 g); Pale yellow colour solid; R_f = 0.30 in 80% EtOAc in n-hexane; m.p = 173-176 °C; IR (KBr, ν cm^{-1}): 3221, 1792, 1515, 1498, 1331, 1257, 1001,

978, 860, 774; ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.59 (s, 1H), 10.25 (s, 1H), 7.82 – 7.72 (m, 1H), 7.55 (d, *J* = 7.7 Hz, 2H), 7.41 (t, *J* = 7.7 Hz, 2H), 7.37 – 7.27 (m, 3H), 7.16 (d, *J* = 8.1 Hz, 2H), 7.13 – 7.06 (m, 1H), 6.84 (d, *J* = 8.0 Hz, 2H), 2.23 (s, 3H), 1.93 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 167.9, 146.9, 142.4, 138.8, 137.4, 132.0, 131.9, 131.3, 131.2, 130.2, 130.1, 128.9, 128.6 (2C), 126.9, 126.8, 126.1, 123.9, 119.9, 20.9, 12.8; HR-MS (ESI) m/z: $[M + H]^+$ Calcd for $C_{24}H_{21}N_3O_4S$: 448.1326; Found: 448.1342.

Procedure for the synthesis of acetyl and benzoyl protected 5-aminopyrazoles 8a-d

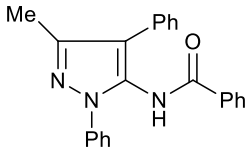
To the stirred solution 5-aminopyrazole **2** (1.0 mmol, 1 equiv) in THF was added Et_3N (1 mmol, 1 equiv) at room temperature. Then acetyl chloride/benzoyl chloride (1.1 mmol, 1.1 equiv) in THF was added dropwise to the reaction mixture at 0° C. Then the resulting solution was allowed to warm at room temperature and stirred for overnight. The reaction was monitored by TLC. After completion of reaction, the reaction mixture was quenched with 1M aq.HCl (20 mL) and extracted with ethyl acetate (3 × 25 mL). The combined organic layer was dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The crude products were purified through flash column chromatography using n-hexane and EtOAc as the eluents.

***N*-(3-Methyl-1,4-diphenyl-1*H*-pyrazol-5-yl)acetamide (8a):**



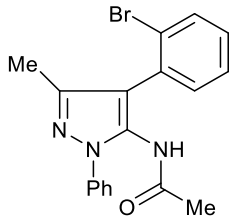
Reaction time: 12 h; Yield: 71% (0.206 g); White colour solid; R_f = 0.38 in 40% EtOAc in n-hexane; m.p = 187-190 °C; IR (KBr, ν cm^{-1}): 3143, 2952, 2796, 1687, 1502, 1378, 1275, 1159; ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.85 (s, 1H), 7.72 – 7.22 (m, 10H), 2.30 (s, 3H), 1.89 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6) δ 170.7, 146.0, 138.6, 132.7, 131.9, 129.05, 128.5, 128.3, 127.2, 126.7, 123.1, 117.7, 22.4, 13.2; HR-MS (ESI) m/z: $[M + H]^+$ Calcd for $C_{18}H_{18}N_3O$: 291.1450; Found: 291.1444.

***N*-(3-Methyl-1,4-diphenyl-1*H*-pyrazol-5-yl)benzamide (8b):**



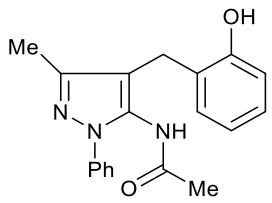
Reaction time: 12 h; Yield: 61% (0.215 g); White colour solid; R_f = 0.38 in 40% EtOAc in n-hexane; m.p = 165-168 °C; IR (KBr, ν cm^{-1}): 3245, 2911, 2561, 1685, 1510, 1371, 1268, 1053; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 – 7.26 (m, 16H), 2.38 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 168.1, 147.4, 138.8, 133.2, 132.5, 132.1, 131.6, 131.6, 129.2, 129.0, 128.9, 128.8, 127.9, 127.4, 127.1, 124.2, 13.4; HR-MS (ESI) m/z: $[M + H]^+$ Calcd for $C_{23}H_{20}N_3O$: 354.1606; Found: 354.1631.

***N*-(3-Methyl-1,4-diphenyl-1*H*-pyrazol-5-yl)benzamide (8c):**



Reaction time: 12 h; Yield: 78% (0.289 g); White colour solid; R_f = 0.35 in 50% EtOAc in n-hexane; m.p = 192-195 °C; IR (KBr, ν cm^{-1}): 3103, 2934, 2568, 1671, 1502, 1376, 1286, 1066; ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.77 (s, 1H), 7.71 (d, *J* = 7.7 Hz, 1H), 7.54 – 7.44 (m, 4H), 7.40 (t, *J* = 7.4 Hz, 1H), 7.38 – 7.23 (m, 3H), 2.11 (s, 3H), 1.78 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, DMSO-d_6) δ 170.2, 146.6, 138.6, 133.4, 132.8, 132.6, 132.4, 129.7, 129.1, 127.6, 127.1, 124.2, 122.8, 118.0, 22.4, 13.3; HR-MS (ESI) m/z: $[M + H]^+$ Calcd for $C_{18}H_{17}BrN_3O$: 370.0555 & 372.0555; Found: 370.0576 & 372.0558.

***N*-(4-(2-Hydroxybenzyl)-3-methyl-1-phenyl-1*H*-pyrazol-5-yl)acetamide (8d):**

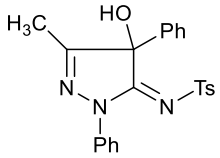


Reaction time: 12 h; Yield: 60% (0.222 g); White colour solid; R_f = 0.20 in 20% EtOAc in n-hexane; m.p = 221-224 °C; IR (KBr, ν cm^{-1}): 3112, 2938, 2567, 1685, 1500, 1366, 1291, 1122; ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.68 (s, 1H), 9.40 (s, 1H), 7.51 – 7.41 (m, 4H), 7.31 (t, *J* = 6.8 Hz, 1H), 6.98 (t, *J* = 7.0 Hz, 1H), 6.88 (d, *J* = 7.4 Hz, 1H), 6.79 (d, *J* = 7.7 Hz, 1H), 6.67 (t, *J* = 7.3 Hz, 1H), 3.54 (s, 2H), 2.04 (s, 3H), 1.93 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6) δ 169.8, 154.8, 147.3, 139.0, 133.8, 129.3, 128.9, 126.8, 126.5, 125.9, 122.6, 118.8, 114.7, 114.6, 22.5, 22.1, 12.4; HR-MS (ESI) m/z: $[M + H]^+$ Calcd for $C_{19}H_{20}N_3O_2$: 322.1555; Found: 322.1555.

General procedure for the synthesis of 4-hydroxypyrazolines 7a-v, 5a and 16

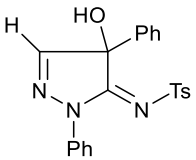
To an oven dried 8 mL vial containing 5-*N*-tosylaminopyrazoles **1** (0.3 mmol, 1 equiv) in DCM (2 mL), PIFA (0.3 mmol, 1 equiv) was added. Then the reaction mixture was stirred at room temperature. The reaction was monitored by TLC. After the starting material was completely consumed, the reaction mixture was directly loaded on a silica gel column without work-up and purified by using n-hexane and EtOAc as the eluents.

(*E*)-*N*-(4-Hydroxy-5-methyl-2,4-diphenyl-2,4-dihydro-3*H*-pyrazol-3-ylidene)-4-methylbenzenesulfonamide (7a):



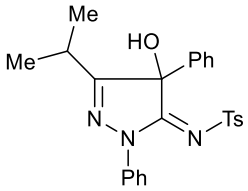
Reaction time: 15 min; Yield: 98% (0.123 g); White colour solid; R_f = 0.41 in 20% EtOAc in n-hexane; m.p = 198-200 °C; IR (KBr, ν cm^{-1}): 3437, 1644, 1568, 1495, 1298, 1287, 1138, 1092, 1079, 860; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, *J* = 7.7 Hz, 2H), 7.49 – 7.35 (m, 7H), 7.31 (t, *J* = 7.5 Hz, 1H), 7.27 (d, *J* = 8.5 Hz, 2H), 7.10 (d, *J* = 8.1 Hz, 2H), 6.32 (s, 1H), 2.37 (s, 3H), 1.97 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 165.5, 165.2, 143.1, 138.3, 137.5, 135.5, 129.4, 129.29, 129.27, 128.9, 127.1, 126.6, 124.5, 122.1, 87.5, 21.6, 11.8; HR-MS (ESI) m/z: $[M + H]^+$ Calcd for $C_{23}H_{22}N_3O_3S$: 420.1376; Found: 420.1387.

(*E*)-*N*-(4-Hydroxy-2,4-diphenyl-2,4-dihydro-3*H*-pyrazol-3-ylidene)-4-methylbenzenesulfonamide (7b):



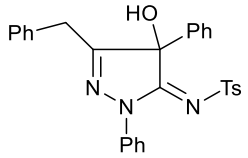
Reaction time: 30 min; Yield: 78% (0.095 g); White colour solid; R_f = 0.45 in 30% EtOAc in n-hexane; m.p = 148-150 °C; IR (KBr, ν cm^{-1}): 3053, 1711, 1571, 1496, 1222, 1145, 1085, 965; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, *J* = 8.0 Hz, 2H), 7.44 – 7.39 (m, 8H), 7.34 (d, *J* = 8.1 Hz, 2H), 7.30 (t, *J* = 7.8 Hz, 1H), 7.12 (d, *J* = 8.0 Hz, 2H), 6.26 (d, *J* = 1.2 Hz, 1H), 2.36 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 164.6, 154.8, 143.4, 138.0, 137.4, 134.5, 129.5, 129.4, 129.4, 128.9, 127.3, 126.8, 124.9, 122.1, 87.3, 21.6; HR-MS (ESI) m/z: $[M + H]^+$ Calcd for $C_{22}H_{20}N_3O_3S$: 406.1225; Found: 406.1248.

(*E*)-*N*-(4-Hydroxy-5-isopropyl-2,4-diphenyl-2,4-dihydro-3*H*-pyrazol-3-ylidene)-4-methylbenzenesulfonamide (7c):



Reaction time: 20 min; Yield: 92% (0.123 g); White colour solid; R_f = 0.39 in 20% EtOAc in n-hexane; m.p = 167-170 °C; IR (KBr, ν cm^{-1}): 3053, 1721, 1579, 1489, 1232, 1141, 1089, 973; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, *J* = 8.0 Hz, 2H), 7.43 (t, *J* = 7.6 Hz, 2H), 7.44 – 7.36 (m, 5H), 7.29 – 7.28 (m, 1H), 7.22 (d, *J* = 8.4 Hz, 2H), 7.06 (d, *J* = 8.0 Hz, 2H), 6.35 (s, 1H), 2.66 – 2.56 (m, 1H), 2.34 (s, 3H), 1.27 (d, *J* = 6.8 Hz, 3H), 0.87 (d, *J* = 7.2 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 172.1, 165.4, 143.0, 138.4, 137.6, 135.4, 129.3, 129.2, 128.9, 127.0, 126.6, 124.6, 122.1, 88.1, 27.2, 21.6, 21.09, 21.00; HR-MS (ESI) m/z: $[M + H]^+$ Calcd for $C_{25}H_{26}N_3O_3S$: 448.1695; Found: 448.1701.

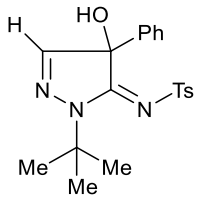
(*E*)-*N*-(5-Benzyl-4-hydroxy-2,4-diphenyl-2,4-dihydro-3*H*-pyrazol-3-ylidene)-4-methylbenzenesulfonamide (7d):



Reaction time: 50 min; Yield: 80% (0.124 g); White colour solid; R_f = 0.47 in 30% EtOAc in n-hexane; m.p = 140-143 °C; IR (KBr, ν cm^{-1}): 3056, 1725, 1571, 1491, 1233, 1167, 1077, 912; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, *J* = 8.0 Hz, 2H), 7.43 – 7.27 (m, 8H), 7.23 – 7.18 (m, 5H), 7.11 – 7.06 (m, 4H), 6.35 (s, 1H), 3.73 (d, *J* = 16.4 Hz, 1H), 3.52 (d, *J* = 16.4 Hz, 1H), 2.35 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 166.4, 165.4, 143.1, 138.2, 137.5, 135.1,

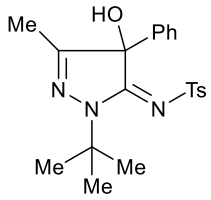
134.7, 129.36, 129.30, 129.2, 128.8, 128.4, 127.0, 126.9, 126.6, 124.6, 122.1, 87.6, 51.0, 32.5, 21.5; HR-MS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{29}H_{25}N_3O_3SNa$: 518.1509; Found: 518.1538.

(*E*)-*N*-(2-(*Tert*-butyl)-4-hydroxy-4-phenyl-2,4-dihydro-3*H*-pyrazol-3-ylidene)-4-methylbenzenesulfonamide (7e):



Reaction time: 20 min; Yield: 95% (0.110 g); White colour solid; R_f = 0.35 in 30% EtOAc in n-hexane; m.p = 155-158 °C; IR (KBr, ν cm^{-1}): 3382, 1731, 1552, 1398, 1282, 1150, 1083, 846; ^1H NMR (700 MHz, $CDCl_3$) δ 7.40 – 7.34 (m, 5H), 7.29 (d, *J* = 7.2 Hz, 2H), 7.19 (s, 1H), 7.13 (d, *J* = 8.1 Hz, 2H), 6.25 (s, 1H), 2.38 (s, 3H), 1.61 (s, 9H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 166.2, 152.9, 142.8, 138.9, 134.7, 129.26, 129.24, 129.21, 126.4, 124.8, 87.2, 61.0, 28.0, 21.6; HR-MS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{20}H_{23}N_3O_3SNa$: 408.1358; Found: 408.1380.

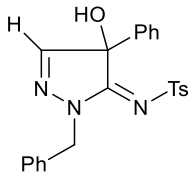
(*E*)-*N*-(2-(*Tert*-butyl)-4-hydroxy-5-methyl-4-phenyl-2,4-dihydro-3*H*-pyrazol-3-ylidene)-4-methylbenzenesulfonamide (7f):



Reaction time: 30 min; Yield: 98% (0.117 g); White colour solid; R_f = 0.36 in 20% EtOAc in n-hexane; m.p = 155-158 °C; IR (KBr, ν cm^{-1}): 3011, 1737, 1571, 1489, 1322, 1152, 1095, 977; ^1H NMR (700 MHz, $CDCl_3$) δ 7.34 – 7.29 (m, 3H), 7.24 – 7.23 (m, 4H), 7.04 (d, *J* = 7.7 Hz, 2H), 6.26 (s, 1H), 2.33 (s, 3H), 1.79 (s, 3H), 1.58 (s, 9H); $^{13}C\{^1H\}$ NMR (175 MHz, $CDCl_3$) δ

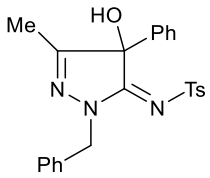
167.0, 163.0, 142.4, 139.2, 135.5, 129.18, 129.12, 128.9, 126.2, 124.3, 87.2, 60.7, 28.1, 21.5, 11.6; HR-MS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{21}H_{25}N_3O_3SNa$: 422.1509; Found: 422.1517.

(*E*)-*N*-(2-Benzyl-4-hydroxy-4-phenyl-2,4-dihydro-3*H*-pyrazol-3-ylidene)-4-methylbenzenesulfonamide (7g):



Reaction time: 30 min; Yield: 90% (0.117 g); White colour solid; R_f = 0.35 in 30% EtOAc in n-hexane; m.p = 167-170 °C; IR (KBr, ν cm^{-1}): 3061, 1701, 1581, 1487, 1225, 1149, 1095, 978; ^{1}H NMR (700 MHz, $CDCl_3$) δ 7.42 – 7.29 (m, 10H), 7.26 (s, 1H), 7.20 (d, *J* = 7.6 Hz, 2H), 7.12 (d, *J* = 8.0 Hz, 2H), 6.14 (s, 1H), 5.08 (d, *J* = 14.5 Hz, 1H), 5.00 (d, *J* = 14.5 Hz, 1H), 2.40 (s, 3H); ^{13}C{^{1}H} NMR (175 MHz, $CDCl_3$) δ 166.5, 154.8, 143.1, 138.3, 134.8, 134.1, 129.3, 129.3, 129.2, 128.9, 128.7, 128.4, 126.6, 124.7, 86.5, 50.8, 21.6; HR-MS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{23}H_{21}N_3O_3SNa$: 442.1201; Found: 442.1225.

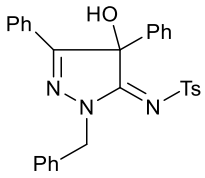
(*E*)-*N*-(2-Benzyl-4-hydroxy-5-methyl-4-phenyl-2,4-dihydro-3*H*-pyrazol-3-ylidene)-4-methylbenzenesulfonamide (7h):



Reaction time: 1 h; Yield: 95% (0.124 g); White colour solid; R_f = 0.39 in 30% EtOAc in n-hexane; m.p = 188-190 °C; IR (KBr, ν cm^{-1}): 3053, 1711, 1569, 1420, 1362, 1272, 1258, 1222, 1082, 895; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 – 7.20 (m, 6H), 7.17 (t, *J* = 7.2 Hz, 2H), 7.10 (d, *J* = 8.0 Hz, 2H), 7.04 (d, *J* = 7.6 Hz, 2H), 6.95 (d, *J* = 8.0 Hz, 2H), 6.05 (s, 1H), 4.90 (dd, *J* = 52.4, 14.4 Hz, 2H), 2.27 (s, 3H), 1.73 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 167.4,

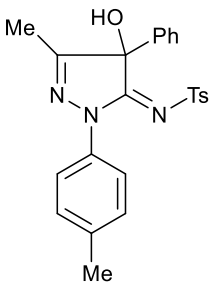
165.2, 142.7, 138.66, 138.64, 135.0, 129.2, 129.1, 129.0, 128.8, 128.7, 128.3, 126.4, 124.3, 86.5, 50.6, 21.5, 11.6; HR-MS (ESI) m/z: $[M + H]^+$ Calcd for $C_{24}H_{24}N_3O_3S$: 434.1533; Found: 434.1573.

(*E*)-*N*-(2-Benzyl-4-hydroxy-4,5-diphenyl-2,4-dihydro-3*H*-pyrazol-3-ylidene)-4-methylbenzenesulfonamide (7i):



Reaction time: 45 min; Yield: 95% (0.141 g); Pale brown colour solid; R_f = 0.29 in 40% EtOAc in n-hexane; m.p = 188-190 °C; IR (KBr, ν cm^{-1}): 3453, 1591, 1557, 1446, 1287, 1144, 1080, 881; ^1H NMR (400 MHz, $CDCl_3$) δ 7.68 (d, *J* = 7.6 Hz, 2H), 7.28 – 7.22 (m, 2H), 7.17 – 7.09 (m, 11H), 7.02 (d, *J* = 8.0 Hz, 2H), 6.89 (d, *J* = 7.6 Hz, 2H), 6.51 (s, 1H), 5.03 (d, *J* = 14.5 Hz, 1H), 4.87 (d, *J* = 14.5 Hz, 1H), 2.21 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 167.5, 162.1, 142.8, 138.4, 135.0, 134.9, 131.0, 129.1 (2C), 128.9, 128.89, 128.87, 128.5, 128.3, 128.0, 127.6, 126.3, 124.6, 86.8, 50.9, 21.5; HR-MS (ESI) m/z: $[M + H]^+$ Calcd for $C_{29}H_{26}N_3O_3S$: 496.1689; Found: 496.1712.

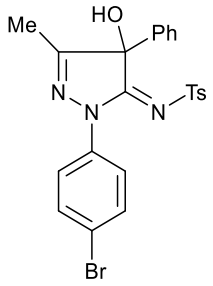
(*E*)-*N*-(4-Hydroxy-5-methyl-4-phenyl-2-(*p*-tolyl)-2,4-dihydro-3*H*-pyrazol-3-ylidene)-4-methylbenzenesulfonamide (7j):



Reaction time: 30 min; Yield: 84% (0.110 g); White colour solid; R_f = 0.35 in 30% EtOAc in n-hexane; m.p = 159-162 °C; IR (KBr, ν cm^{-1}): 3346, 1641, 1577, 1508, 1448, 1134, 1073, 861;

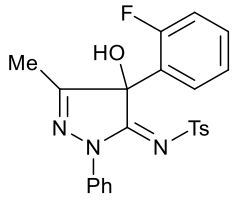
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, *J* = 8.5 Hz, 2H), 7.42 – 7.31 (m, 5H), 7.23 (d, *J* = 8.1 Hz, 4H), 7.06 (d, *J* = 8.1 Hz, 2H), 6.30 (s, 1H), 2.37 (s, 3H), 2.34 (s, 3H), 1.94 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 165.2, 165.1, 143.0, 138.4, 137.1, 135.5, 134.9, 129.4, 129.3, 129.2, 129.2, 126.6, 124.5, 122.1, 87.4, 21.6, 21.2, 11.7; HR-MS (ESI) m/z: $[M + H]^+$ Calcd for $C_{24}H_{24}N_3O_3S$: 434.1533; Found: 434.1534.

(*E*)-*N*-(2-(4-Bromophenyl)-4-hydroxy-5-methyl-4-phenyl-2,4-dihydro-3*H*-pyrazol-3-ylidene)-4-methylbenzenesulfonamide (7k):



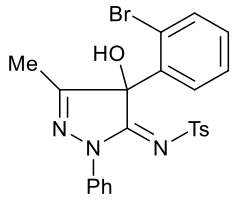
Reaction time: 30 min; Yield: 90% (0.133 g); White colour solid; R_f = 0.33 in 20% EtOAc in n-hexane; m.p = 167-170 °C; IR (KBr, ν cm^{-1}): 3421, 1640, 1600, 1566, 1489, 1373, 1301, 1091, 1074, 859; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, *J* = 9.0 Hz, 2H), 7.54 (d, *J* = 9.0 Hz, 2H), 7.42 – 7.29 (m, 5H), 7.23 (d, *J* = 8.3 Hz, 2H), 7.08 (d, *J* = 8.1 Hz, 2H), 6.25 (s, 1H), 2.35 (s, 3H), 1.94 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6) δ 166.2, 165.3, 142.6, 139.5, 136.6, 135.3, 131.9, 129.3, 128.7, 128.4, 126.2, 124.1, 123.7, 119.1, 86.4, 20.9, 11.3; HR-MS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{23}H_{20}BrN_3O_3SNa$: 520.0301 & 522.0281; Found: 520.0276 & 522.0266.

(*E*)-*N*-(4-(2-Fluorophenyl)-4-hydroxy-5-methyl-2-phenyl-2,4-dihydro-3*H*-pyrazol-3-ylidene)-4-methylbenzenesulfonamide (7l):



Reaction time: 1 h; Yield: 80% (0.105 g); White colour solid; R_f = 0.27 in 20% EtOAc in n-hexane; m.p = 185-187 °C; IR (KBr, ν cm^{-1}): 3437, 1634, 1559, 1456, 1394, 1284, 1227,1137, 1081, 976, 862; ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.87 (td, *J* = 7.9, 1.6 Hz, 1H), 7.69 (d, *J* = 7.7 Hz, 2H), 7.58 (s, 1H), 7.52 – 7.35 (m, 6H), 7.32 (t, *J* = 7.4 Hz, 1H), 7.27 (d, *J* = 8.1 Hz, 2H), 7.14 – 7.04 (m, 1H), 2.34 (s, 3H), 1.79 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 164.8, 161.2, 158.9 (d, *J* = 245 Hz), 143.0, 138.5, 137.6, 131 (d, *J* = 8), 129.3, 128.9, 128.1 (d, *J* = 3), 127.2, 126.3, 125.2 (d, *J* = 3), 122.8 (d, *J* = 13), 122.5, 115.9 (d, *J* = 22), 83.7, 21.6, 11.8; HR-MS (ESI) m/z: $[M + H]^+$ Calcd for $C_{23}H_{21}FN_3O_3S$: 438.1282; Found: 438.1273.

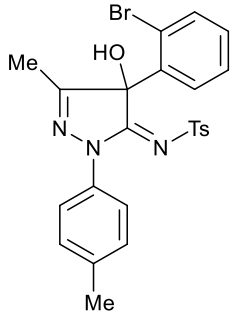
(*E*)-*N*-(4-(2-Bromophenyl)-4-hydroxy-5-methyl-2-phenyl-2,4-dihydro-3*H*-pyrazol-3-ylidene)-4-methylbenzenesulfonamide (7m):



Reaction time: 15 min; Yield: 99% (0.148 g); White colour solid; R_f = 0.24 in 20% EtOAc in n-hexane; m.p = 165-168 °C; IR (KBr, ν cm^{-1}): 3437, 1635, 1586, 1496, 1327, 1138, 1083, 677; ^{1}H NMR (700 MHz, $CDCl_3$) δ 8.08 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.92 (d, *J* = 7.7 Hz, 2H), 7.59 (t, *J* = 7.7 Hz, 1H), 7.45 (t, *J* = 8.0 Hz, 2H), 7.41 – 7.35 (m, 3H), 7.33 – 7.27 (m, 2H), 7.11 (d, *J* = 8.1 Hz, 2H), 6.30 (s, 1H), 2.39 (s, 3H), 1.90 (s, 3H); ^{13}C{^{1}H} NMR (175 MHz, $CDCl_3$) δ 164.4, 160.3, 142.9, 138.4, 137.9, 134.5, 134.0, 130.8, 129.5, 129.2, 128.9, 128.1, 127.0,

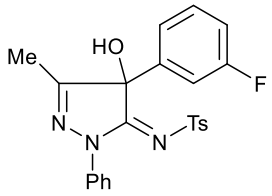
126.4, 122.1, 120, 86.1, 21.6, 12.2; HR-MS (ESI) m/z: $[M + H]^+$ Calcd for $C_{23}H_{21}BrN_3O_3S$: 498.0482 & 500.0462; Found: 498.0474 & 500.0456.

(*E*)-*N*-(4-(2-Bromophenyl)-4-hydroxy-5-methyl-2-(p-tolyl)-2,4-dihydro-*3H*-pyrazol-3-ylidene)-4-methylbenzenesulfonamide (7n):



Reaction time: 15 min; Yield: 84% (0.129 g); White colour solid; R_f = 0.4 in 20% EtOAc in n-hexane; m.p = 188-190 °C; IR (KBr, ν cm^{-1}): 3437, 1635, 1512, 1436, 1557, 1137, 1082, 564; ^1H NMR (400 MHz, $CDCl_3$) δ 8.04 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.74 (d, *J* = 8.8 Hz, 2H), 7.54 (td, *J* = 7.6, 1.2, 1H), 7.34 – 7.30 (m, 3H), 7.24 – 7.20 (m, 3H), 7.06 (d, *J* = 8.0 Hz, 2H), 6.26 (s, 1H), 2.35 (s, 3H) 2.34 (s, 3H), 1.84 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 164.1, 160.2, 142.7, 138.4, 136.9, 135.4, 134.4, 133.9, 130.7, 129.4, 129.4, 129.1, 128.0, 126.3, 121.9, 120.1, 85.9, 21.5, 21.1, 12.0; HR-MS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{24}H_{22}BrN_3O_3SNa$: 534.0457 & 536.0438; Found: 534.0476 & 536.0453.

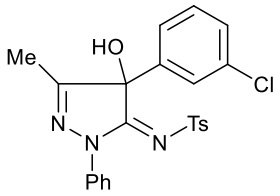
(*E*)-*N*-(4-(3-Fluorophenyl)-4-hydroxy-5-methyl-2-phenyl-2,4-dihydro-3*H*-pyrazol-3-ylidene)-4-methylbenzenesulfonamide (7o):



Reaction time: 1 h; Yield: 72% (0.095 g); White colour solid; R_f = 0.28 in 20% EtOAc in n-hexane; m.p = 150-153 °C; IR (KBr, ν cm^{-1}): 3437, 1613, 1568, 1497, 1301, 1271, 1147, 1094,

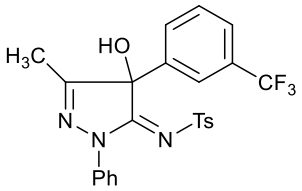
860; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, *J* = 7.7 Hz, 2H), 7.44 (t, *J* = 8.0 Hz, 2H), 7.38 – 7.27 (m, 4H), 7.17 – 7.03 (m, 5H), 6.34 (s, 1H), 2.36 (s, 3H), 1.96 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 164.8, 163.3 (d, *J* = 248 Hz), 164.5, 143.3, 138.2, 138.1 (d, *J* = 7 Hz), 137.3, 131.0 (d, *J* = 9 Hz), 129.3, 128.9, 127.2, 126.5, 122.07, 120.2 (d, *J* = 4 Hz), 116.4 (d, *J* = 21 Hz), 112.2 (d, *J* = 23 Hz), 86.9 (d, *J* = 3 Hz), 21.6, 11.7; HR-MS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{23}H_{20}FN_3O_3SNa$: 460.1102; Found: 460.1100.

(*E*)-*N*-(4-(3-Chlorophenyl)-4-hydroxy-5-methyl-2-phenyl-2,4-dihydro-3*H*-pyrazol-3-ylidene)-4-methylbenzenesulfonamide (7p):



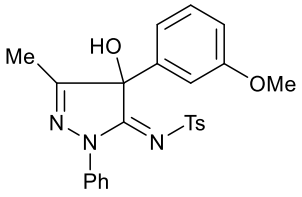
Reaction time: 1 h; Yield: 99% (0.134 g); White colour solid; R_f = 0.27 in 20% EtOAc in n-hexane; m.p = 178-180 °C; IR (KBr, ν cm^{-1}): 3433, 1639, 1561, 1489, 1311, 1145, 1080, 866; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, *J* = 7.6 Hz, 2H), 7.44 (t, *J* = 8.0 Hz, 2H), 7.36 – 7.26 (m, 6H), 7.24 (s, 1H), 7.10 (d, *J* = 8.4 Hz, 2H), 6.31 (s, 1H), 2.36 (s, 3H), 1.95 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 164.6, 164.4, 143.3, 138.1, 137.5, 137.3, 135.4, 130.6, 129.4, 129.3, 128.9, 127.2, 126.4, 124.7, 122.7, 122.0, 86.8, 21.5, 11.7; HR-MS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{23}H_{20}ClN_3O_3SNa$: 476.0806; Found: 476.0809.

(*E*)-*N*-(4-Hydroxy-5-methyl-2-phenyl-4-(3-(trifluoromethyl)phenyl)-2,4-dihydro-3*H*-pyrazol-3-ylidene)-4-methylbenzenesulfonamide (7q):



Reaction time: 1 h; Yield: 80% (0.117 g); White colour solid; R_f = 0.27 in 20% EtOAc in Hexane; m.p = 185-187 °C; IR (KBr, ν cm-1): 3420, 1634, 1575, 1498, 1328, 1277, 1132, 1076, 860; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, *J* = 7.9 Hz, 2H), 7.64 (d, *J* = 7.5 Hz, 1H), 7.59 – 7.41 (m, 5H), 7.32 (t, *J* = 7.4 Hz, 1H), 7.27 (d, *J* = 8.0 Hz, 2H), 7.08 (d, *J* = 8.2 Hz, 2H), 6.40 (s, 1H), 2.34 (s, 3H), 1.95 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 164.7, 164.4, 143.5, 138.1, 137.3, 136.8, 131.8 (q, *J* = 32.7), 129.9, 129.4, 129.1, 128.1, 127.7, 127.4, 126.3, 126.2 (q, *J* = 3.7), 123.7 (q, *J* = 271), 122.2, 121.4 (q, *J* = 4), 87.0, 21.6, 11.8; HR-MS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{24}H_{20}F_3N_3O_3SNa$: 510.1070; Found: 510.1077.

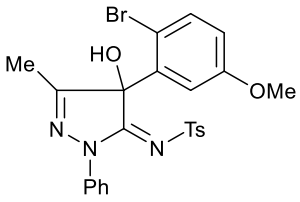
(*E*)-*N*-(4-Hydroxy-4-(3-methoxyphenyl)-5-methyl-2-phenyl-2,4-dihydro-3H-pyrazol-3-ylidene)-4-methylbenzenesulfonamide (7r):



Reaction time: 15 min; Yield: 80% (0.108 g); White colour solid; R_f = 0.55 in 20% EtOAc in n-hexane; m.p = 121-123 °C; IR (KBr, ν cm^{-1}): 3447, 1639, 1524, 1516, 1500, 1285, 1245, 1160, 987; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, *J* = 8.1 Hz, 2H), 7.58 (d, *J* = 2.7 Hz, 1H), 7.42 (t, *J* = 8.0 Hz, 2H), 7.38 (d, *J* = 8.3 Hz, 2H), 7.31 – 7.25 (m, 2H), 7.19 (d, *J* = 8.7 Hz, 1H), 7.10 (d, *J* = 8.1 Hz, 2H), 6.81 (dd, *J* = 8.8, 2.8 Hz, 1H), 6.29 (s, 1H), 3.91 (s, 3H), 2.36 (s, 3H), 1.88 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 163.1, 158.9, 158.5, 141.8, 137.1, 136.7,

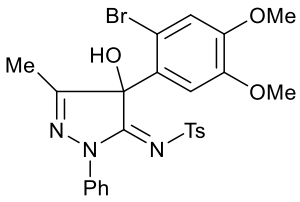
134.2, 133.6, 128.0, 127.7, 125.8, 125.2, 120.9, 115.7, 113.6, 109.1, 84.7, 54.6, 20.4, 11.0; HR-MS (ESI) m/z: $[M + H]^+$ Calcd for $C_{24}H_{24}N_3O_4S$: 450.1456; Found: 450.1487.

(*E*)-*N*-(4-(2-Hromo-4-methoxyphenyl)-4-hydroxy-5-methyl-2-phenyl-2,4-dihydro-3*H*-pyrazol-3-ylidene)-4-methylbenzenesulfonamide (7s):



Reaction time: 15 min; Yield: 75% (0.119 g); White colour solid; R_f = 0.53 in 20% EtOAc in n-hexane; m.p = 180-183 °C; IR (KBr, ν cm^{-1}): 3433, 1654, 1528, 1437, 1321, 1149, 1060, 870; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, *J* = 8.4 Hz, 2H), 7.59 (d, *J* = 3.2 Hz, 1H), 7.44 – 7.38 (m, 4H), 7.28 (t, *J* = 7.6 Hz, 1H), 7.19 (d, *J* = 8.8 Hz, 1H), 7.09 (d, *J* = 8.4 Hz, 2H), 6.80 (dd, *J* = 8.7, 2.8 Hz, 1H), 6.30 (s, 1H), 3.91 (s, 3H), 2.36 (s, 3H), 1.88 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 164.2, 160.0, 159.7, 142.9, 138.3, 137.9, 135.4, 134.7, 129.1, 128.9, 127.0, 126.4, 122.1, 116.9, 114.8, 110.3, 85.9, 55.8, 21.6, 12.1; HR-MS (ESI) m/z: $[M + H]^+$ Calcd for $C_{24}H_{23}BrN_3O_4S$: 528.0593 & 530. 0593; Found: 528.0570 & 528.0583.

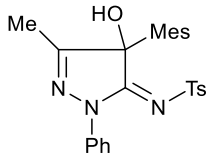
(*E*)-*N*-(4-(2-Bromo-4,5-dimethoxyphenyl)-4-hydroxy-5-methyl-2-phenyl-2,4-dihydro-3*H*-pyrazol-3-ylidene)-4-methylbenzenesulfonamide (7t):



Reaction time: 15 min; Yield: 65% (0.109 g); Pale orange colour solid; R_f = 0.55 in 20% EtOAc in n-hexane; m.p = 185-187 °C; IR (KBr, ν cm^{-1}): 3437, 1633, 1574, 1556, 1500, 1260, 1215, 1164, 1135, 683; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, *J* = 8.4 Hz, 2H), 7.50 (s, 1H), 7.46 –

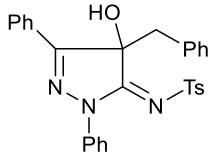
7.36 (m, 4H), 7.29 (t, *J* = 7.6 Hz, 1H), 7.09 (d, *J* = 8.0 Hz, 2H), 6.66 (s, 1H), 6.38 (s, 1H), 4.01 (s, 3H), 3.83 (s, 3H), 2.35 (s, 3H), 1.88 (s, 3H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 164.6, 160.5, 150.2, 149.1, 142.6, 138.6, 137.9, 129.0, 128.9, 127.0, 126.2, 126.0, 122.1, 116.2, 111.7, 110.3, 85.8, 56.4, 56.2, 21.6, 12.0; HR-MS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{25}H_{24}BrN_3O_5SNa$: 580.0512 & 582.0493; Found: 580.0493 & 582.0475.

(*E*)-*N*-(4-Hydroxy-4-mesityl-5-methyl-2-phenyl-2,4-dihydro-3*H*-pyrazol-3-ylidene)-4-methylbenzenesulfonamide (7u):



Reaction time: 15 min; Yield: 64% (0.089 g); Pale Orange colour solid; R_f = 0.5 in 20% EtOAc in n-hexane; m.p = 185-187 °C; IR (KBr, ν cm^{-1}): 3372, 1559, 1495, 1456, 1298, 1267, 1135, 863; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, *J* = 8.0 Hz, 2H), 7.42 (t, *J* = 7.6 Hz, 2H), 7.35 (d, *J* = 8.0 Hz, 2H), 7.28 (t, *J* = 7.6 Hz, 1H), 7.07 (d, *J* = 8.4 Hz, 2H), 6.99 (s, 1H), 6.50 (s, 1H), 6.13 (s, 1H), 2.78 (s, 3H), 2.36 (s, 3H), 2.26 (s, 3H), 2.01 (s, 3H), 1.77 (s, 3H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 166.4, 162.3, 142.7, 138.6, 138.5, 138.2, 137.6, 134.9, 133.6, 131.4, 129.0, 128.9, 127.4, 126.9, 126.4, 121.9, 89.4, 24.4, 21.6, 20.7, 20.1, 12.5; HR-MS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{26}H_{27}N_3O_3SNa$: 484.1665; Found: 484.1685.

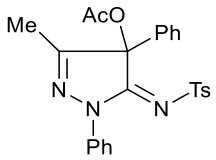
(*E*)-*N*-(4-Benzyl-4-hydroxy-2,5-diphenyl-2,4-dihydro-3*H*-pyrazol-3-ylidene)-4-methylbenzenesulfonamide (7v):



Reaction time: 30 min; Yield: 90% (0.134 g); White colour solid; R_f = 0.55 in 20% EtOAc in n-hexane; m.p = 185-187 °C; IR (KBr, ν cm^{-1}): 3437, 1633, 1574, 1556, 1500, 1260, 1215,

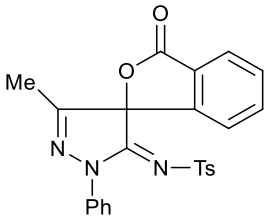
1164, 1135, 683; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 (d, *J* = 6.7 Hz, 2H), 7.93 (d, *J* = 8.0 Hz, 2H), 7.62 – 7.50 (m, 3H), 7.34 (d, *J* = 8.0 Hz, 2H), 7.32 – 7.20 (m, 5H), 7.19 – 7.09 (m, 3H), 7.04 (d, *J* = 6.6 Hz, 2H), 6.74 (s, 1H), 4.26 (d, *J* = 12.9 Hz, 1H), 3.61 (d, *J* = 12.8 Hz, 1H), 2.46 (s, 3H); ^{13}C{^{1}H} NMR (175 MHz, $CDCl_3$) δ 165.3, 159.7, 143.5, 139.1, 136.8, 132.0, 131.5, 129.9, 129.7, 129.2, 129.1, 128.6, 128.3, 127.8, 127.7, 127.4, 126.7, 123.0, 88.7, 45.9, 21.7; HR-MS (ESI) m/z: $[M + H]^+$ Calcd for $C_{29}H_{26}N_3O_3S$: 496.1695; Found: 496.1687.

(*E*)-3-Methyl-1,4-diphenyl-5-(tosylimino)-4,5-dihydro-1*H*-pyrazol-4-yl acetate (5a) (Synthesized from PIDA):



Reaction time: 30 min; Yield: 85% (0.118 g); White colour solid; R_f = 0.26 in 25% EtOAc in n-hexane; m.p = 140-143 °C; IR (KBr, ν cm^{-1}): 3041, 2972, 1715, 1561, 1501, 1224, 1135, 1099, 972; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, *J* = 7.9 Hz, 2H), 7.58 (d, *J* = 8.2 Hz, 2H), 7.51 – 7.38 (m, 6H), 7.32 – 7.23 (m, 2H), 7.16 (d, *J* = 8.1 Hz, 2H), 2.44 (s, 3H), 2.38 (s, 3H), 1.92 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 169.7, 162.1, 161.3, 142.5, 139.9, 138.0, 131.3, 129.5, 129.3, 129.1, 128.8, 126.9, 126.4, 124.5, 122.2, 87.8, 21.6, 21.0, 11.7; HR-MS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{25}H_{23}N_3O_4SNa$: 484.1301; Found: 484.1324.

(*E*)-4-Methyl-*N*-(3'-methyl-3-oxo-1'-phenyl-3*H*-spiro[isobenzofuran-1,4'-pyrazol]-5'(1'*H*)-ylidene)benzenesulfonamide (16):

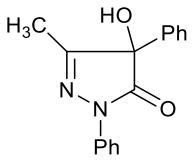


Reaction time: 2 h; Yield: 86% (0.127 g); Off white colour solid; R_f = 0.50 in 40% EtOAc in n-hexane; m.p = 170-173 °C; IR (KBr, ν cm^{-1}): 1796, 1593, 1495, 1311, 1279, 1153, 1050, 838, 789, 679; $^{1}H\{^{1}H\}$ NMR (400 MHz, DMSO-d_6) δ 8.13 (d, *J* = 7.3 Hz, 1H), 7.93 – 7.80 (m, 2H), 7.78 – 7.68 (m, 3H), 7.51 (t, *J* = 7.8 Hz, 2H), 7.44 – 7.35 (m, 3H), 7.30 (d, *J* = 8.1 Hz, 2H), 2.34 (s, 3H), 1.80 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 168.4, 159.9, 157.4, 143.2, 141.6, 138.6, 136.9, 135.8, 131.6, 129.6, 128.9, 127.6, 126.3, 125.9, 125.7, 122.7, 121.9, 89.1, 21.0, 11.0; HR-MS (ESI) m/z: $[M + H]^+$ Calcd for $C_{24}H_{20}N_3O_4S$: 446.1169; Found: 446.1163.

Procedure for the synthesis of compounds 10a, 10c and 11d

To an oven dried 8 mL vial containing compound **8** (0.5 mmol, 1 equiv) in DCM (2 mL), PIFA (0.75 mmol, 1.5 equiv) was added. Then the reaction mixture was stirred at room temperature. The reaction was monitored by TLC. After the starting material was completely consumed, the reaction mixture was directly loaded on a silica gel column without work-up and purified by using n-hexane and EtOAc as the eluents.

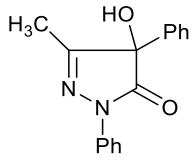
4-Hydroxy-5-methyl-2,4-diphenyl-2,4-dihydro-3*H*-pyrazol-3-one (10a) (from 8a):



Reaction time: 1 h; Yield: 56% (0.075 g); White colour solid; R_f = 0.35 in 40% EtOAc in n-hexane; m.p = 168-170 °C; IR (KBr, ν cm^{-1}): 3325, 2917, 1673, 1578, 1464, 1252, 1195, 968;

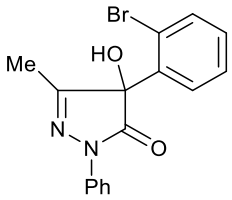
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, *J* = 8.1 Hz, 2H), 7.31 (t, *J* = 7.8 Hz, 2H), 7.27 (s, 5H), 7.12 (t, *J* = 7.4 Hz, 1H), 4.66 (s, 1H), 1.93 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 173.7, 163.1, 137.5, 135.7, 129.1, 129.0, 128.9, 125.5, 124.7, 119.0, 81.8, 12.9; HR-MS (ESI) m/z: $[M + H]^+$ Calcd for $C_{16}H_{15}N_2O_2$: 267.1133; Found: 267.1106.

4-Hydroxy-5-methyl-2,4-diphenyl-2,4-dihydro-3*H*-pyrazol-3-one (10a) (from 8b):



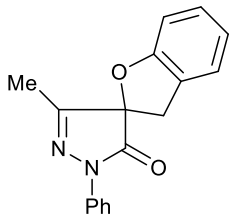
Reaction time: 1 h; Yield: 74% (0.098 g).

4-(2-Bromophenyl)-4-hydroxy-5-methyl-2-phenyl-2,4-dihydro-3*H*-pyrazol-3-one (10c):



Reaction time: 2 h; Yield: 52% (0.090 g); White colour solid; R_f = 0.4 in 30% EtOAc in n-hexane; m.p = 177-180 °C; IR (KBr, ν cm^{-1}): 3251, 2917, 1680, 1500, 1403, 1284, 1197, 967; ^{1}H NMR (700 MHz, $CDCl_3$) δ 7.92 (d, *J* = 8.1 Hz, 2H), 7.90 (d, *J* = 7.8 Hz, 1H), 7.56 (d, *J* = 7.9 Hz, 1H), 7.45 (t, *J* = 7.9 Hz, 2H), 7.40 (t, *J* = 7.6 Hz, 1H), 7.28 – 7.23 (m, 2H), 4.31 (s, 1H), 1.96 (s, 3H); ^{13}C{^{1}H} NMR (175 MHz, $CDCl_3$) δ 171.8, 158.8, 137.9, 135.2, 133.9, 130.8, 129.1, 129.0, 127.9, 125.6, 120.1, 119.2, 80.8, 13.4; HR-MS (ESI) m/z: $[M + H]^+$ Calcd for $C_{16}H_{14}BrN_2O_2$: 345.0239 & 347.0239; Found: 345.0255 & 347.0261.

3'-Methyl-1'-phenyl-3*H*-spiro[benzofuran-2,4'-pyrazol]-5'(1'*H*)-one (11d):

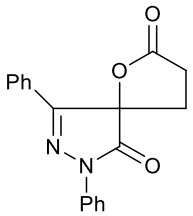


Reaction time: 2 h; yield: 48% (0.067 g); White colour solid; R_f = 0.65 in 20% EtOAc in n-hexane; m.p = 164-1167 °C; IR (KBr, ν cm^{-1}): 1708, 1477, 1365, 1229, 1050, 946, 838, 755, 601; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, *J* = 7.8 Hz, 2H), 7.38 (t, *J* = 8.0 Hz, 2H), 7.24 – 7.14 (m, 3H), 6.95 (t, *J* = 7.3 Hz, 1H), 6.90 (d, *J* = 8.1 Hz, 1H), 3.61 (d, *J* = 16.0 Hz, 1H), 3.36 (d, *J* = 16.0 Hz, 1H), 2.09 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 170.7, 159.4, 158.8, 137.8, 129.10, 129.08, 125.5, 125.1, 124.1, 122.2, 118.8, 110.3, 86.9, 36.8, 12.8; HR-MS (ESI) m/z: $[M + H]^+$ Calcd for $C_{17}H_{15}N_2O_2$: 279.1133; Found: 279.1161.

Procedure for the synthesis of spirolactone 13a-b

To an oven dried 8 mL vial containing compound **11** (0.3 mmol, 1 equiv) in DCM (2 mL), PIFA (0.39 mmol, 1.3 equiv) was added. Then the reaction mixture was stirred at room temperature. The reaction was monitored by TLC. After the starting material was completely consumed, the reaction mixture was directly loaded on a silica gel column without work-up and purified by using n-hexane and EtOAc as the eluents.

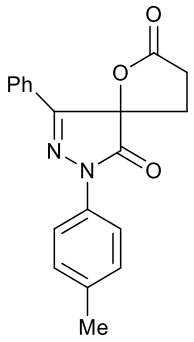
7,9-Diphenyl-1-oxa-7,8-diazaspiro[4.4]non-8-ene-2,6-dione (13a):



Reaction time: 12 h; yield: 87% (0.080 g); Brown colour solid; R_f = 0.18 in 20% EtOAc in n-hexane; m.p = 161-163 °C; IR (KBr, ν cm^{-1}) = 3121, 2369, 1795, 1757, 1501, 1388, 1146, 988,

812; ^{1}H NMR (700 MHz, $CDCl_3$) δ 7.98 (d, *J* = 8.0 Hz, 2H), 7.87 (d, *J* = 7.7 Hz, 2H), 7.56 – 7.47 (m, 5H), 7.30 – 7.28 (m, 1H), 3.29 – 3.23 (m, 1H), 2.81 – 2.78 (m, 1H), 2.66 – 2.58 (m, 2H); ^{13}C{^{1}H} NMR (175 MHz, $CDCl_3$) δ 175.0, 170.3, 155.0, 137.5, 131.9, 129.4, 129.2, 128.6, 126.8, 126.1, 119.0, 83.6, 29.7, 26.6; HR-MS (ESI) m/z: $[M + H]^+$ Calcd for $C_{18}H_{15}N_2O_3$: 307.1077; Found: 307.1100.

9-Phenyl-7-(*p*-tolyl)-1-oxa-7,8-diazaspiro[4.4]non-8-ene-2,6-dione (13b):

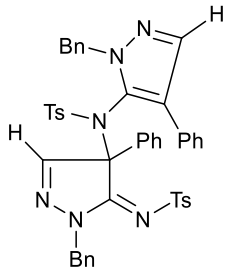


Reaction time: 12 h; yield: 78% (0.072 g); White colour solid; R_f = 0.11 in 20% EtOAc in n-hexane; m.p = 128-131 °C; IR (KBr, ν cm^{-1}): 3023, 2369, 1797, 1715, 1515, 1398, 1155, 994, 811; ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.84 (d, *J* = 6.2 Hz, 2H), 7.73 (d, *J* = 8.3 Hz, 2H), 7.59 – 7.46 (m, 3H), 7.28 (d, *J* = 8.2 Hz, 2H), 3.08 – 2.85 (m, 2H), 2.82 – 2.70 (m, 1H), 2.66 – 2.53 (m, 1H), 2.29 (s, 3H); ^{13}C{^{1}H} NMR (175 MHz, $CDCl_3$) δ 175.0, 170.2, 154.9, 135.9, 135.0, 131.5, 129.7, 129.3, 128.6, 126.7, 119.0, 83.6, 29.6, 26.6, 21.1; HR-MS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{19}H_{16}N_2O_3Na$: 343.1059; Found: 343.1031.

Procedure for the synthesis of 4-aminopyrazolines 14g-h

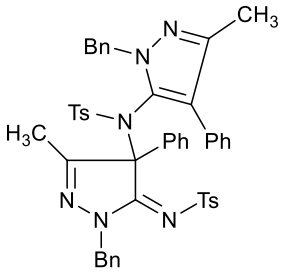
To an oven dried 8 mL vial 5-*N*-tosylaminopyrazoles **2** (0.3 mmol, 1 equiv) and PhIO (0.33 mmol, 1.1 equiv) was taken in DCM (2 mL). Then the reaction mixture was stirred at room temperature. The reaction was monitored by TLC. After the starting material was completely consumed, the reaction mixture was directly loaded on a silica gel column without work-up and purified by using n-hexane and EtOAc as the eluents.

(*E*)-*N*-(1-Benzyl-4-phenyl-1*H*-pyrazol-5-yl)-*N*-(1-benzyl-4-phenyl-5-(tosylimino)-4,5-dihydro-1*H*-pyrazol-4-yl)-4-methylbenzenesulfonamide (14g):



Reaction time: 30 min; Yield: 91% (0.110 g); White colour solid; R_f = 0.38 in 40% EtOAc in n-hexane; m.p = 132-134 °C; IR (KBr, ν cm^{-1}): 3436, 2359, 1652, 1601, 1549, 1457, 1240, 666; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, *J* = 8.0 Hz, 2H), 7.76 (s, 1H), 7.67 (d, *J* = 8.1 Hz, 2H), 7.37 – 7.15 (m, 15H), 7.11 (d, *J* = 8.0 Hz, 2H), 7.00 – 6.92 (m, 4H), 6.83 – 6.69 (m, 4H), 5.75 (d, *J* = 15.4 Hz, 1H), 5.52 (d, *J* = 15.4 Hz, 1H), 4.75 (s, 2H), 2.43 (s, 3H), 2.30 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 160.7, 154.4, 145.6, 142.9, 139.9, 138.6, 135.7, 135.2, 135.0, 131.5, 131.0, 130.4, 130.3, 130.1, 129.3, 129.1, 128.7, 128.65, 128.60, 128.4, 128.34, 128.30, 128.1, 127.9, 127.8, 127.6, 127.3, 126.5, 121.6, 79.8, 55.3, 52.2, 21.7, 21.5; HR-MS (ESI) m/z: $[M + H]^+$ Calcd for $C_{46}H_{41}N_6O_4S_2$: 805.2631; Found: 805.2606.

(*E*)-*N*-(1-Benzyl-3-methyl-4-phenyl-1*H*-pyrazol-5-yl)-*N*-(1-benzyl-3-methyl-4-phenyl-5-(tosylimino)-4,5-dihydro-1*H*-pyrazol-4-yl)-4-methylbenzenesulfonamide (14h):



Reaction time: 20 min; Yield: 75% (0.094 g); White colour solid; R_f = 0.32 in 30% EtOAc in n-hexane; m.p = 120-124 °C; IR (KBr, ν cm^{-1}): 3031, 2367, 1584, 1457, 1353, 1150, 1088, 764; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, *J* = 8.0 Hz, 4H), 7.42 – 7.17 (m, 16H), 7.13 (t, *J* = 7.2

Hz, 2H), 7.0 (d, *J* = 8.0 Hz, 2H), 6.80 (d, *J* = 6.8 Hz, 2H), 6.37 (d, *J* = 7.2 Hz, 2H), 5.83 (d, *J* = 15.6 Hz, 1H), 5.37 (d, *J* = 16.0 Hz, 1H), 4.79 (d, *J* = 15.6 Hz, 1H), 4.08 (d, *J* = 15.6 Hz, 1H), 2.42 (s, 3H), 2.29 (s, 3H), 1.79 (s, 3H), 1.51 (s, 3H); $^{13}C\{^{1}H\}$ NMR (175 MHz, DMSO-d_6) δ 164.2, 162.5, 146.2, 143.4, 139.5, 136.1, 135.8, 134.8, 131.7, 131.6, 131.1, 130.6, 130.5, 130.4, 129.9, 129.2, 129.1, 129.0, 128.8, 128.7, 128.6, 128.5, 128.4, 128.1, 127.97, 127.90, 127.1, 126.4, 121.6, 82.7, 54.4, 51.5, 21.6, 21.5, 14.6, 12.9; HR-MS (ESI) m/z: $[M + H]^+$ Calcd for $C_{48}H_{45}N_6O_4S_2$: 833.2994; Found: 833.2963.

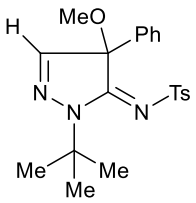
Procedure for the synthesis of 4-methoxypyrazolines 15

To an oven dried 8 mL vial containing 5-*N*-tosylaminopyrazoles **1** (0.3 mmol, 1 equiv) in MeOH (2 mL), PIFA (0.3 mmol, 1 equiv) was added. Then the reaction mixture was stirred at room temperature. The reaction was monitored by TLC. After the starting material was completely consumed, the reaction mixture was directly loaded on a silica gel column without work-up and purified by using n-hexane and EtOAc as the eluents.

(*E*)-*N*-(2-(*Tert*-butyl)-4-hydroxy-4-phenyl-2,4-dihydro-3*H*-pyrazol-3-ylidene)-4-methylbenzenesulfonamide (7e):

Reaction time: 1 h; Yield: 38% (0.044 g).

(*E*)-*N*-(2-(*Tert*-butyl)-4-methoxy-4-phenyl-2,4-dihydro-3*H*-pyrazol-3-ylidene)-4-methylbenzenesulfonamide (15e):



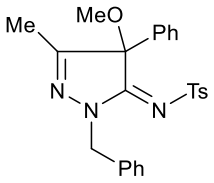
Reaction time: 1 h; Yield: 58% (0.070 g); White colour solid; R_f = 0.25 in 20% EtOAc in n-hexane; m.p = 140-143 °C; IR (KBr, ν cm^{-1}): 1597, 1588, 1452, 1308, 1149, 1087, 1028, 847; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (d, *J* = 8.2 Hz, 2H), 7.42 – 7.28 (m, 5H), 7.17 (d, *J* = 8.1

Hz, 2H), 7.14 (s, 1H), 3.46 (s, 3H), 2.36 (s, 3H), 1.58 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.0, 152.4, 142.3, 140.4, 133.3, 129.1, 128.8, 126.6 (2C), 124.7, 92.7, 60.9, 54.8, 27.9, 21.6; HR-MS (ESI) m/z: $[M + H]^+$ Calcd for $C_{21}H_{26}N_3O_3S$: 400.1695; Found: 400.1677.

(*E*)-*N*-(2-Benzyl-4-hydroxy-5-methyl-4-phenyl-2,4-dihydro-3*H*-pyrazol-3-ylidene)-4-methylbenzenesulfonamide (7h):

Reaction time: 1 h; Yield: 40% (0.052 g).

***E*)-*N*-(2-Benzyl-4-methoxy-5-methyl-4-phenyl-2,4-dihydro-3*H*-pyrazol-3-ylidene)-4-methylbenzenesulfonamide (15h):**



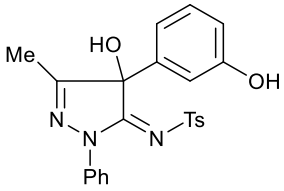
Reaction time: 1 h; Yield: 55% (0.074 g); Colourless viscous liquid; R_f = 0.25 in 30% EtOAc in n-hexane; IR (KBr, ν cm^{-1}): 1630, 1575, 1497, 1453, 1420, 1316, 1303, 1159, 1088, 998; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (d, *J* = 8.2 Hz, 2H), 7.40 – 7.26 (m, 8H), 7.19 (d, *J* = 6.8 Hz, 2H), 7.14 (d, *J* = 8.1 Hz, 2H), 5.07 (d, *J* = 14.5 Hz, 1H), 5.00 (d, *J* = 14.5 Hz, 1H), 3.34 (s, 3H), 2.39 (s, 3H), 1.78 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.6, 163.5, 142.3, 140.0, 135.5, 133.8, 129.0, 128.85, 128.82, 128.7, 128.3, 126.7, 124.5, 92.3, 54.5, 50.9, 21.6, 11.9; HR-MS (ESI) m/z: $[M + H]^+$ Calcd for $C_{25}H_{26}N_3O_3S$: 448.1695; Found: 448.1703.

Procedure for the synthesis of compounds 16

In an oven dried round-bottom flask, 4-hydroxypyrazoline **7** (0.3 mmol, 1 equivalent) was dissolved in 5 mL of DCM. The solution was cooled to 0 °C and BBr_3 (2.5/5 equivalent, 0.75/1.5 mmol) in DCM was added dropwise under N_2 atmosphere. Then the reaction mixture was stirred for 2 h at 0 °C. The reaction was monitored by TLC. After the starting material was completely consumed, the reaction mixture was quenched with crushed ice and extracted with

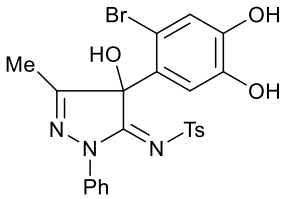
EtOAc (3 × 10 mL). The combined organic layer was dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The crude products were purified through flash column chromatography using n-hexane and EtOAc as the eluents.

(*E*)-*N*-(4-hydroxy-4-(3-hydroxyphenyl)-5-methyl-2-phenyl-2,4-dihydro-3*H*-pyrazol-3-ylidene)-4-methylbenzenesulfonamide (16r):



Reaction time: 3 h; Yield: 78% (0.102 g); Pale yellow colour solid; R_f = 0.33 in 20% EtOAc in n-hexane; m.p = 200-203 °C; IR (KBr, ν cm^{-1}) = 3444, 3211, 2870, 2349, 1554, 1647, 1417, 543; NMR (400 MHz, $CDCl_3$) δ 7.85 (d, *J* = 7.6 Hz, 2H), 7.53 (d, *J* = 3.0 Hz, 1H), 7.46 – 7.37 (m, 4H), 7.31 – 7.23 (m, 2H), 7.17 – 7.06 (m, 3H), 6.72 (dd, *J* = 8.6, 3.0 Hz, 1H), 6.18 (s, 1H), 6.01 (brs, 1H), 2.36 (s, 3H), 1.85 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 164.5, 160.5, 156.5, 143.2, 138.1, 137.7, 135.1, 134.9, 129.3, 128.9, 127.1, 126.4, 122.1, 118.6, 116.5, 109.4, 86.0, 21.6, 12.1; HR-MS (ESI) m/z: $[M + H]^+$ Calcd for $C_{23}H_{21}N_3O_4S$: 435.1253; Found: 435.1256.

(*E*)-*N*-(4-(2-bromo-4,5-dihydroxyphenyl)-4-hydroxy-5-methyl-2-phenyl-2,4-dihydro-3*H*-pyrazol-3-ylidene)-4-methylbenzenesulfonamide (16t):



Reaction time: 1 h; Yield: 81% (0.129 g); White colour solid; R_f = 0.28 in 50% EtOAc in n-hexane; m.p = 205-208 °C; IR (KBr, ν cm^{-1}): 3426, 3271, 3010, 2573, 2146, 1599, 1473, 1255, 765; ^1H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, *J* = 8.0 Hz, 2H), 7.59 (d, *J* = 8.0 Hz, 2H), 7.54 (s,

1H), 7.42 (t, *J* = 8.0 Hz, 2H), 7.28 (t, *J* = 8.2 Hz, 1H), 7.19 (d, *J* = 8.0 Hz, 2H), 6.85 (s, 1H), 6.58 (brs, 2H), 6.20 (s, 1H), 2.38 (s, 3H), 1.86 (s, 3H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 165.3, 161.4, 146.3, 144.2, 143.5, 138.4, 137.8, 129.4, 128.9, 127.2, 126.3, 125.6, 122.2, 120.3, 115.7, 109.6, 86.1, 21.7, 12.1; HR-MS (ESI) m/z: $[M + H]^+$ Calcd for $C_{23}H_{21}BrN_3O_5S$: 530.0385 & 532.0385; Found: 530.0373 & 532.0365.

X-Ray structure and crystal data of compounds 5a, 7a, 13b & 14h

Table S3. Crystal data and structure refinement for compound **5a**

CCDC 2357783

Identification code	**5a**
Empirical formula	$C_{25}H_{23}N_3O_4S$
Formula weight	461.52
Temperature/K	259(8)
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	13.6412(4)
b/Å	10.7301(2)
c/Å	16.2702(4)
α/°	90
β/°	101.061(3)
γ/°	90
Volume/Å^3	2337.25(10)
Z	4
ρ_{calc}g/cm^3	1.312
μ/mm^{-1}	1.535
F(000)	968.0
Crystal size/mm^3	0.9 × 0.18 × 0.11
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	7.762 to 156.548
Index ranges	-17 ≤ h ≤ 17, -13 ≤ k ≤ 13, -18 ≤ l ≤ 20
Reflections collected	19304
Independent reflections	4886 [R_{int} = 0.0317, R_{sigma} = 0.0211]
Data/restraints/parameters	4886/0/302
Goodness-of-fit on F^2	1.105
Final R indexes [I>=2σ (I)]	R_1 = 0.0479, wR_2 = 0.1310
Final R indexes [all data]	R_1 = 0.0505, wR_2 = 0.1336
Largest diff. peak/hole / e Å^{-3}	0.28/-0.28

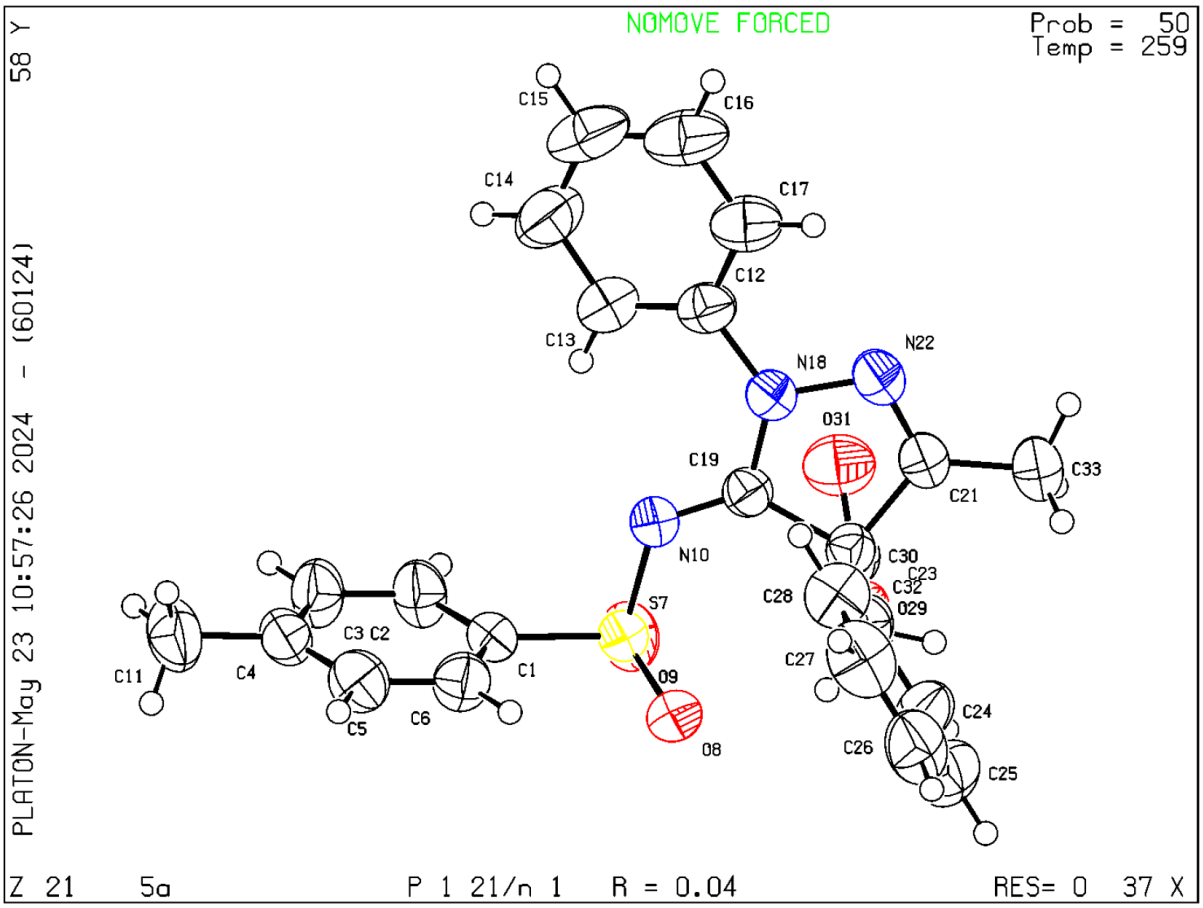


Figure S2: ORTEP Views of the Molecular Structure of **5a** with Thermal Ellipsoids Set at 50% Probability

Table S4. Crystal data and structure refinement for compound **7a**

CCDC 2357781

Identification code	**7a**
Empirical formula	$C_{23}H_{21}N_3O_3S$
Formula weight	419.508
Temperature/K	295.77(13)
Crystal system	triclinic
Space group	P-1
a/Å	8.4579(1)
b/Å	11.1076(2)
c/Å	11.4172(2)
α/°	86.767(1)
β/°	79.589(1)
γ/°	76.363(1)
Volume/Å^3	1025.11(3)
Z	2
ρ_{calc}g/cm^3	1.359
μ/mm^{-1}	1.655
F(000)	442.1
Crystal size/mm^3	0.17 × 0.12 × 0.09
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	7.88 to 150.86
Index ranges	$-7 \leq h \leq 10$, $-13 \leq k \leq 13$, $-14 \leq l \leq 14$
Reflections collected	14687
Independent reflections	4139 [R_{int} = 0.0519, R_{sigma} = 0.0380]
Data/restraints/parameters	4139/72/311
Goodness-of-fit on F^2	1.033
Final R indexes [I>=2σ (I)]	R_1 = 0.0557, wR_2 = 0.1624
Final R indexes [all data]	R_1 = 0.0612, wR_2 = 0.1736
Largest diff. peak/hole / e Å^{-3}	0.29/-0.47

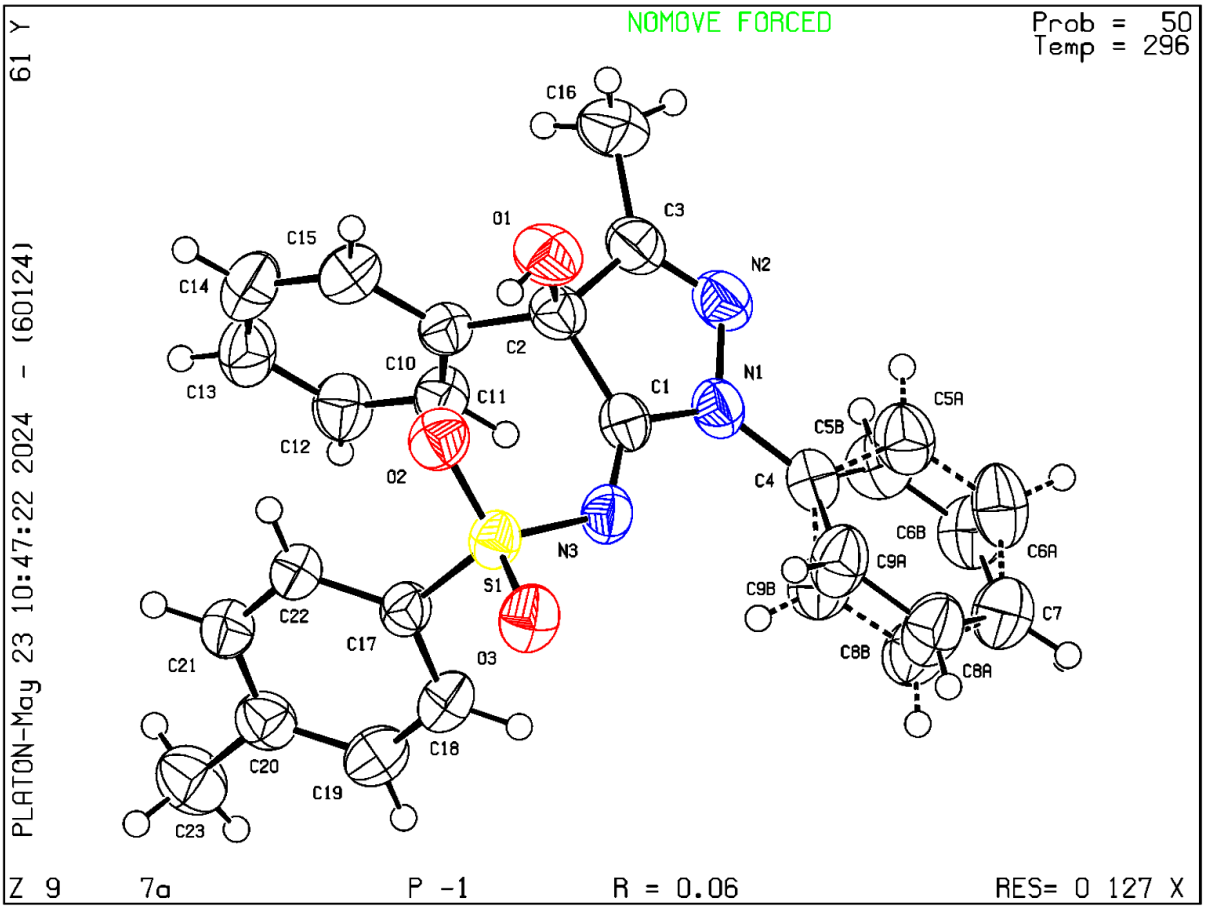


Figure S3: ORTEP Views of the Molecular Structure of **7a** with Thermal Ellipsoids Set at 50% Probability

Table S5. Crystal data and structure refinement for compound **13b.**

CCDC 2357782

Identification code	**13b**
Empirical formula	$C_{19}H_{16}N_2O_3$
Formula weight	320.350
Temperature/K	101(2)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	12.3207(4)
b/Å	5.5406(2)
c/Å	22.9882(8)
α/°	90
β/°	105.284(4)
γ/°	90
Volume/Å^3	1513.76(10)
Z	4
ρ_{calc}g/cm^3	1.406
μ/mm^{-1}	0.096
F(000)	672.5
Crystal size/mm^3	0.17 × 0.11 × 0.09
Radiation	Mo Kα (λ = 0.71073)
2Θ range for data collection/°	6.86 to 60.68
Index ranges	$-16 \leq h \leq 16$, $-6 \leq k \leq 7$, $-32 \leq l \leq 32$
Reflections collected	25833
Independent reflections	3916 [R_{int} = 0.0342, R_{sigma} = 0.0217]
Data/restraints/parameters	3916/0/218
Goodness-of-fit on F^2	1.028
Final R indexes [I>=2σ (I)]	R_1 = 0.0359, wR_2 = 0.0923
Final R indexes [all data]	R_1 = 0.0411, wR_2 = 0.0957
Largest diff. peak/hole / e Å^{-3}	0.40/-0.21

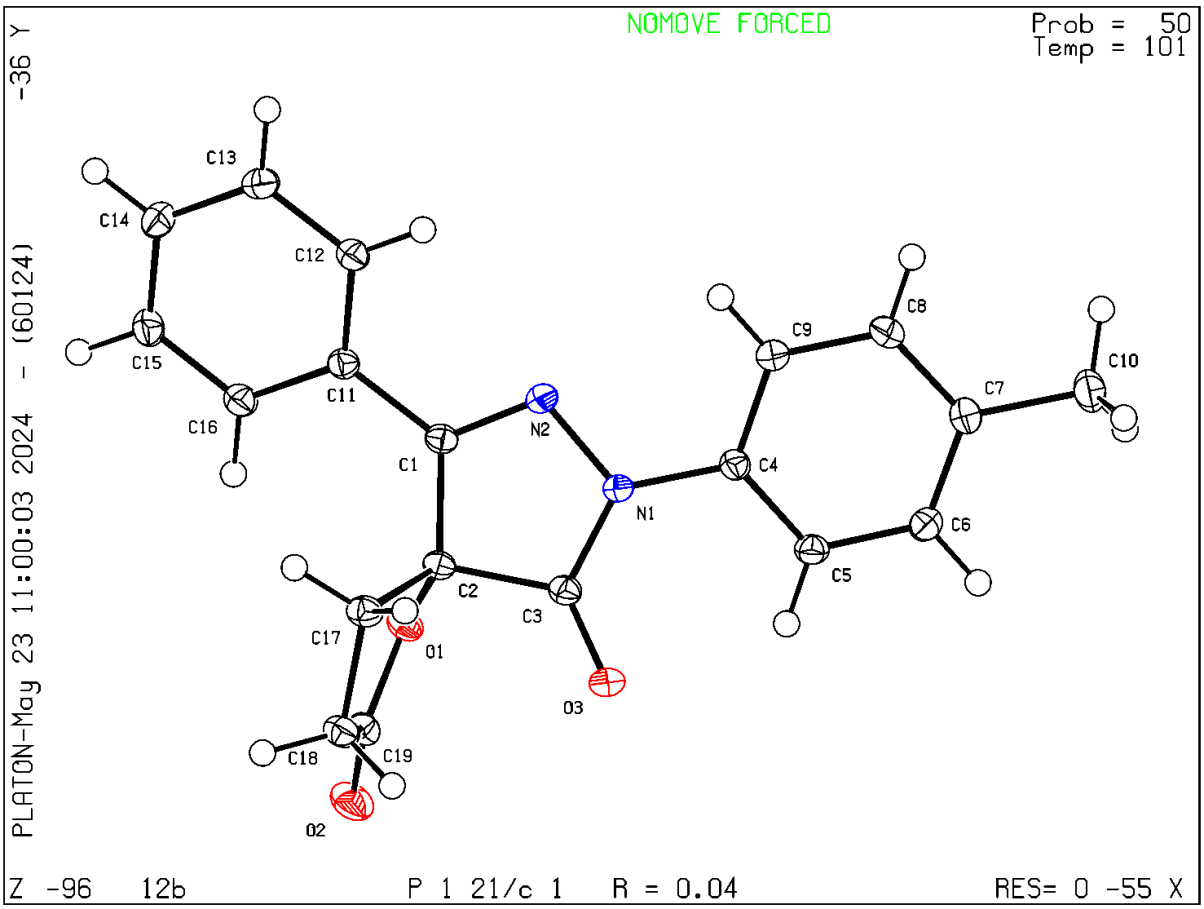


Figure S4: ORTEP Views of the Molecular Structure of **12b** with Thermal Ellipsoids Set at 50% Probability

Table S6. Crystal data and structure refinement for compound **14h**

CCDC 2357784

Identification code	**14h**
Empirical formula	$C_{48}H_{44}N_6O_4S_2$
Formula weight	833.054
Temperature/K	297.9(2)
Crystal system	triclinic
Space group	P-1
a/Å	9.4999(1)
b/Å	13.2071(3)
c/Å	17.4714(3)
α/°	96.635(1)
β/°	100.372(1)
γ/°	91.122(1)
Volume/Å^3	2139.98(7)
Z	2
ρ_{calc}g/cm^3	1.293
μ/mm^{-1}	1.546
F(000)	880.0
Crystal size/mm^3	0.19 × 0.09 × 0.08
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	8 to 157.68
Index ranges	$-9 \le h \le 12$, $-16 \le k \le 16$, $-21 \le l \le 22$
Reflections collected	34700
Independent reflections	8982 [R_{int} = 0.0302, R_{sigma} = 0.0219]
Data/restraints/parameters	8982/479/693
Goodness-of-fit on F^2	1.037
Final R indexes [I>=2σ (I)]	R_1 = 0.0417, wR_2 = 0.1169
Final R indexes [all data]	R_1 = 0.0439, wR_2 = 0.1187
Largest diff. peak/hole / e Å^{-3}	0.31/-0.32

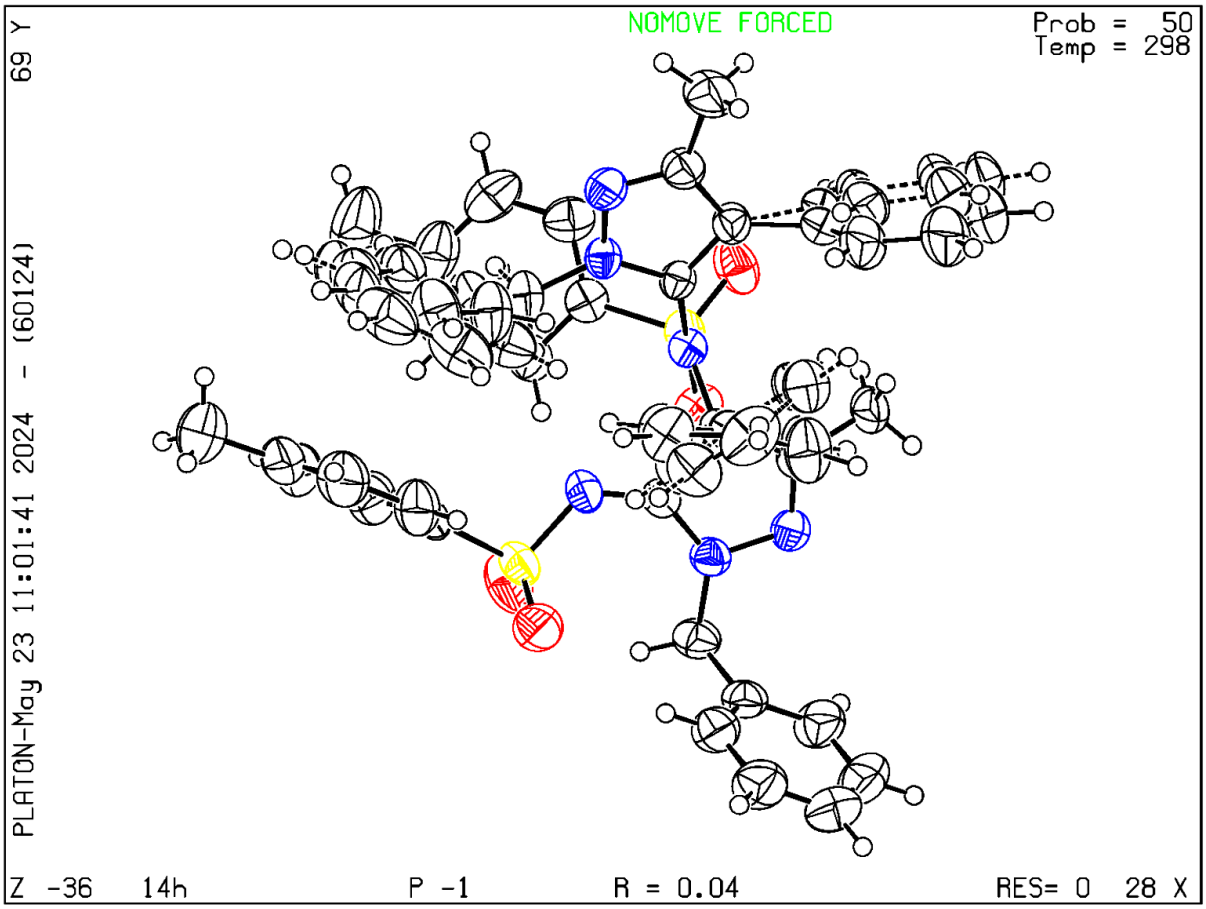


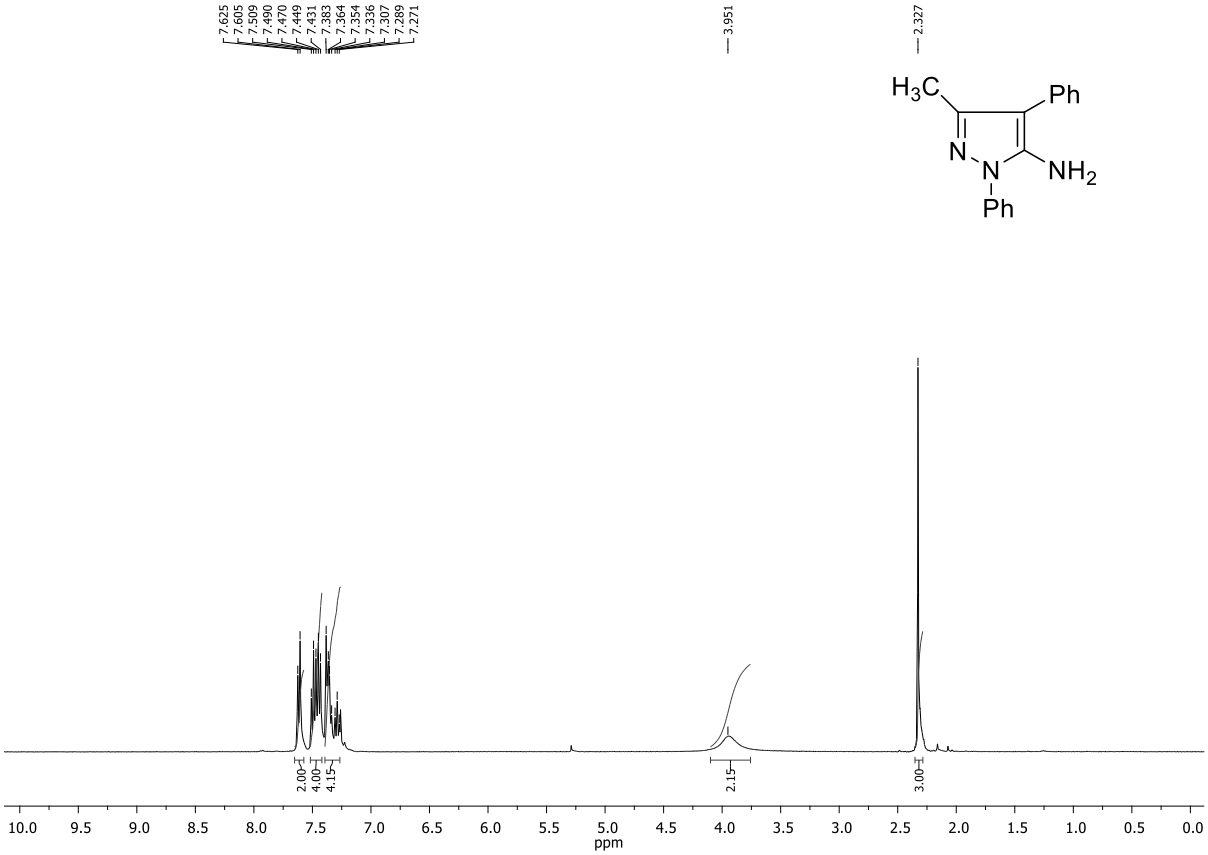
Figure S5: ORTEP Views of the Molecular Structure of **14h** with Thermal Ellipsoids Set at 50% Probability

References

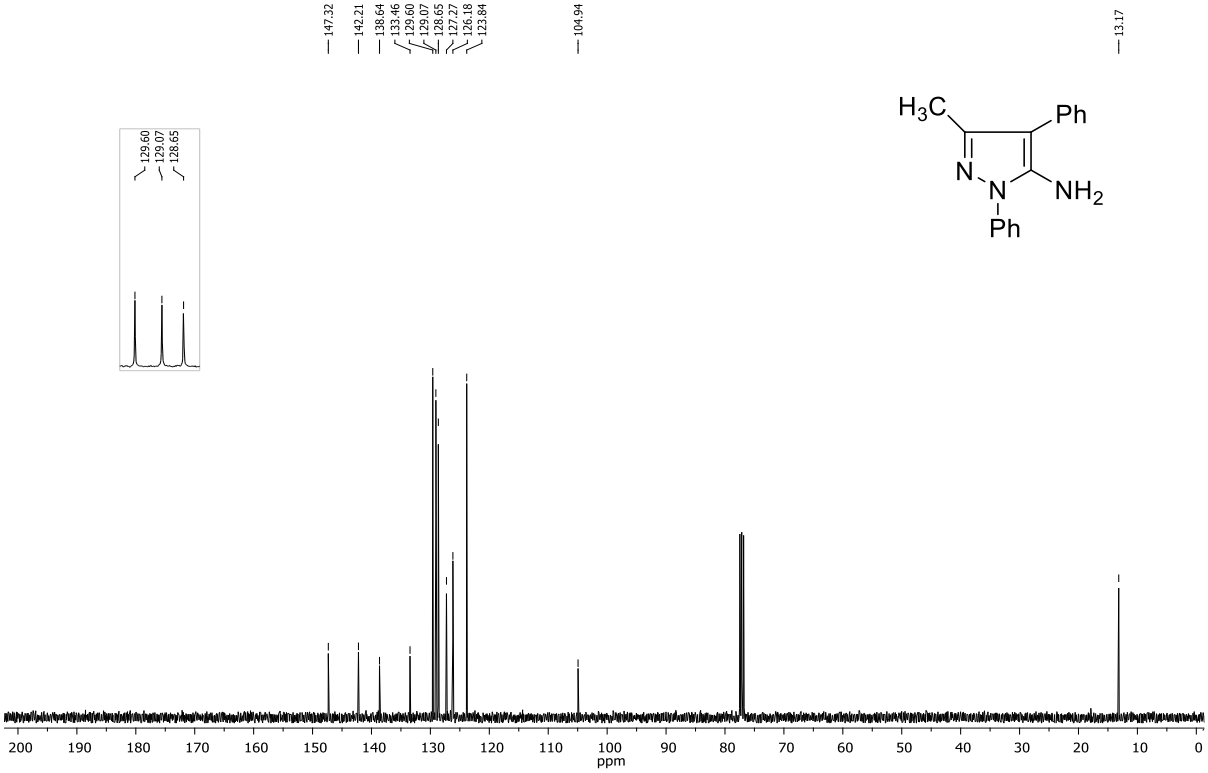
1. A. Chatterjee, C. Murmu and S. Peruncheralathan, *Org. Biomol. Chem.*, 2020, **18**, 6571-6581.
2. P. Natarajan, S. Kanchithalaivan, A. Chatterjee and S. Peruncheralathan, *Asian J. Org. Chem.*, 2024, **13**, e202300628.
3. A. Chatterjee, D. Radhakrishnan, D. Bandyopadhyay, S. Kanchithalaivan and S. Peruncheralathan, *J. Heterocycl. Chem.*, 2022, **59**, 1016-1024.
4. S. B. Annes, R. Saritha, K. Chandru, P. K. Mandali and S. Ramesh, *J. Org. Chem.*, 2021, **86**, 16473-16484.
5. G. Ege and H. Franz, *J. Heterocycl. Chem.*, 2009, **19**, 1267-1273.

NMR Spectra

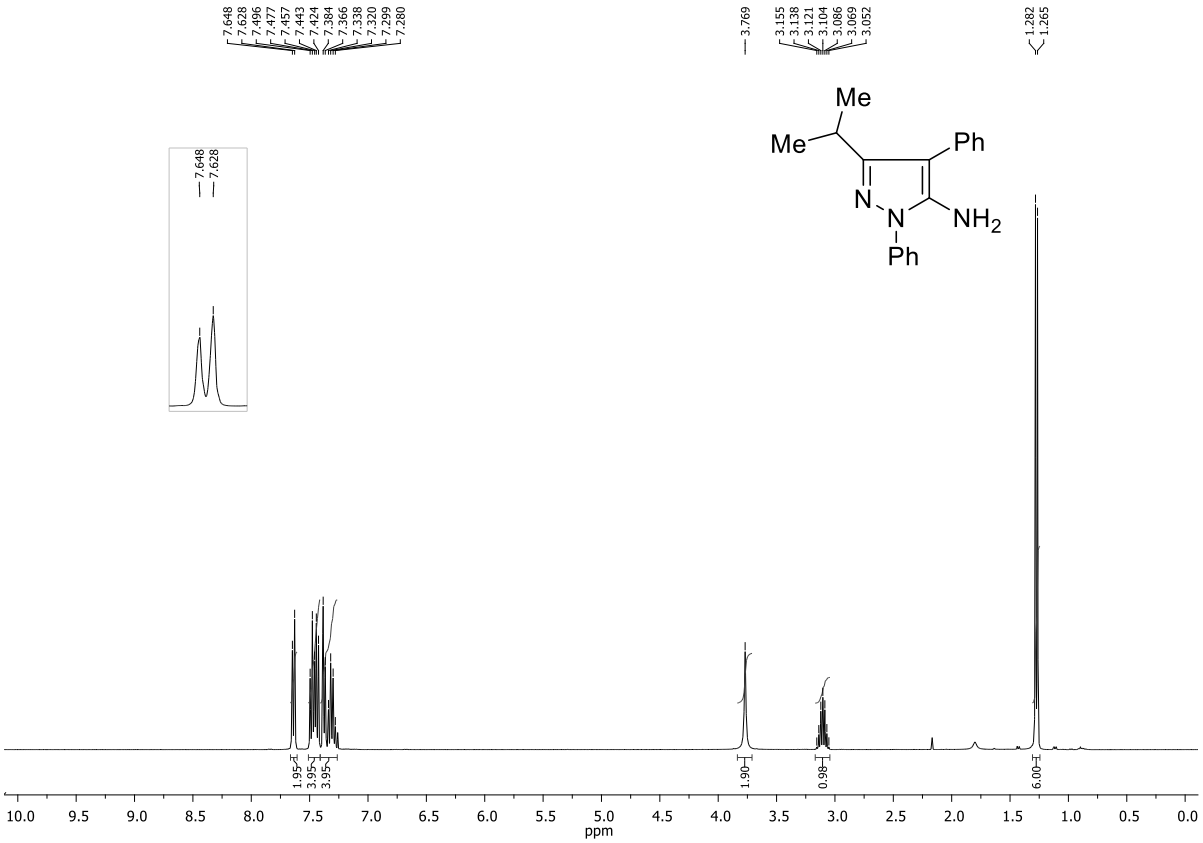
^{1}H NMR of **2a** in $CDCl_3$ (400 MHz):



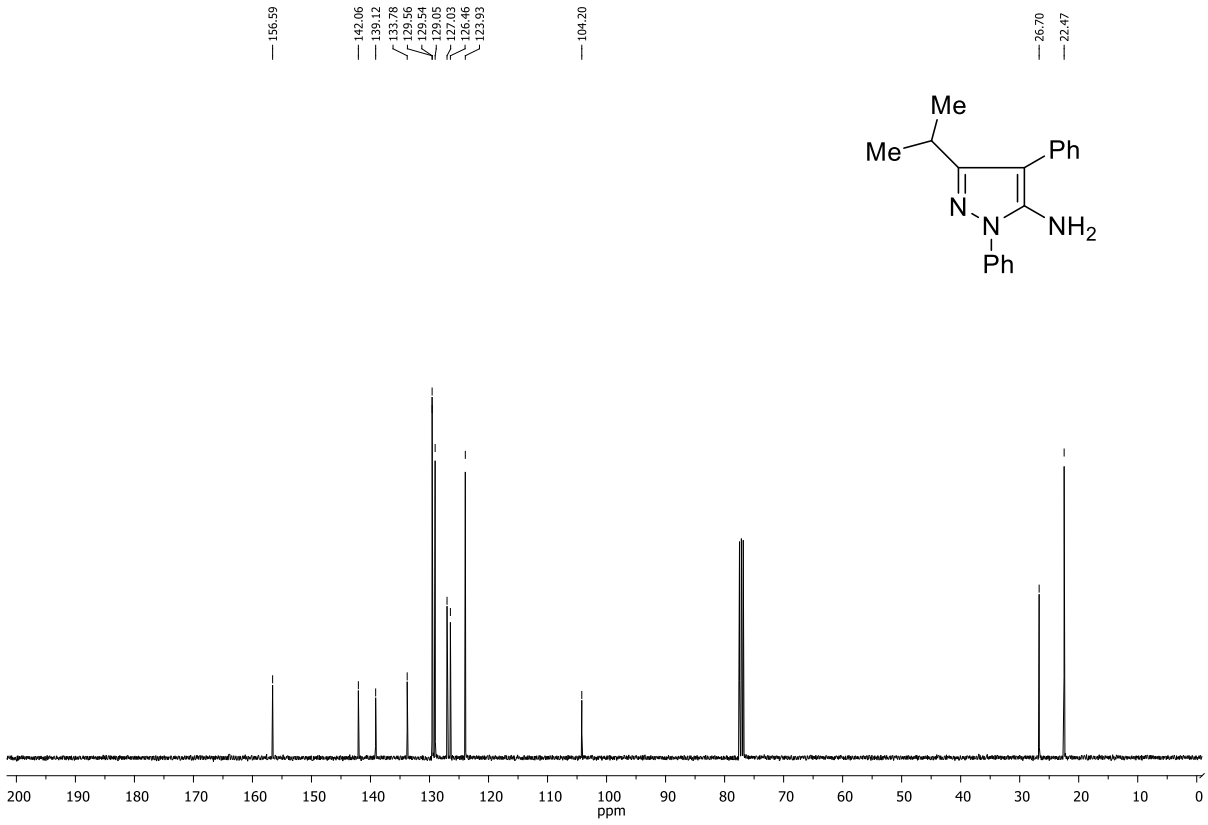
^{13}C{^{1}H} NMR of **2a** in $CDCl_3$ (100 MHz):



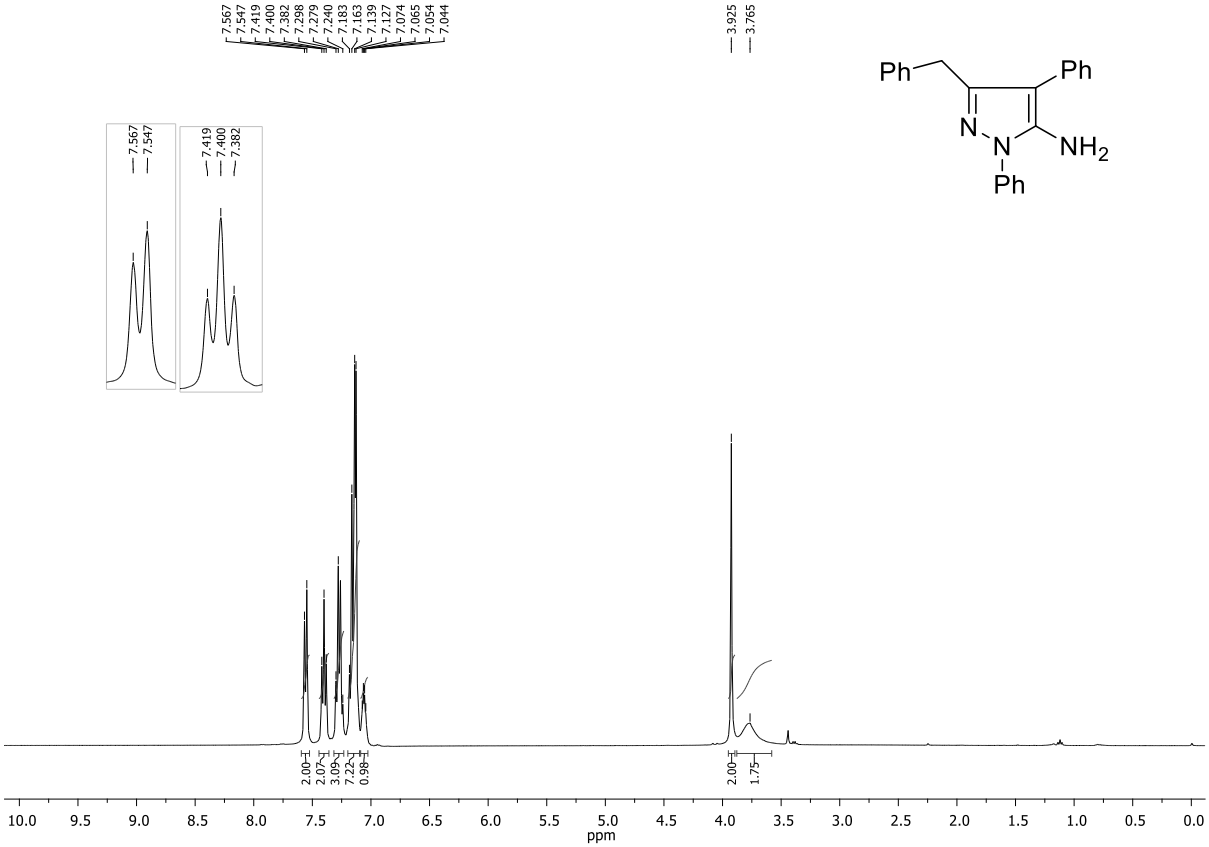
^{1}H NMR of **2b** in $CDCl_3$ (400 MHz):



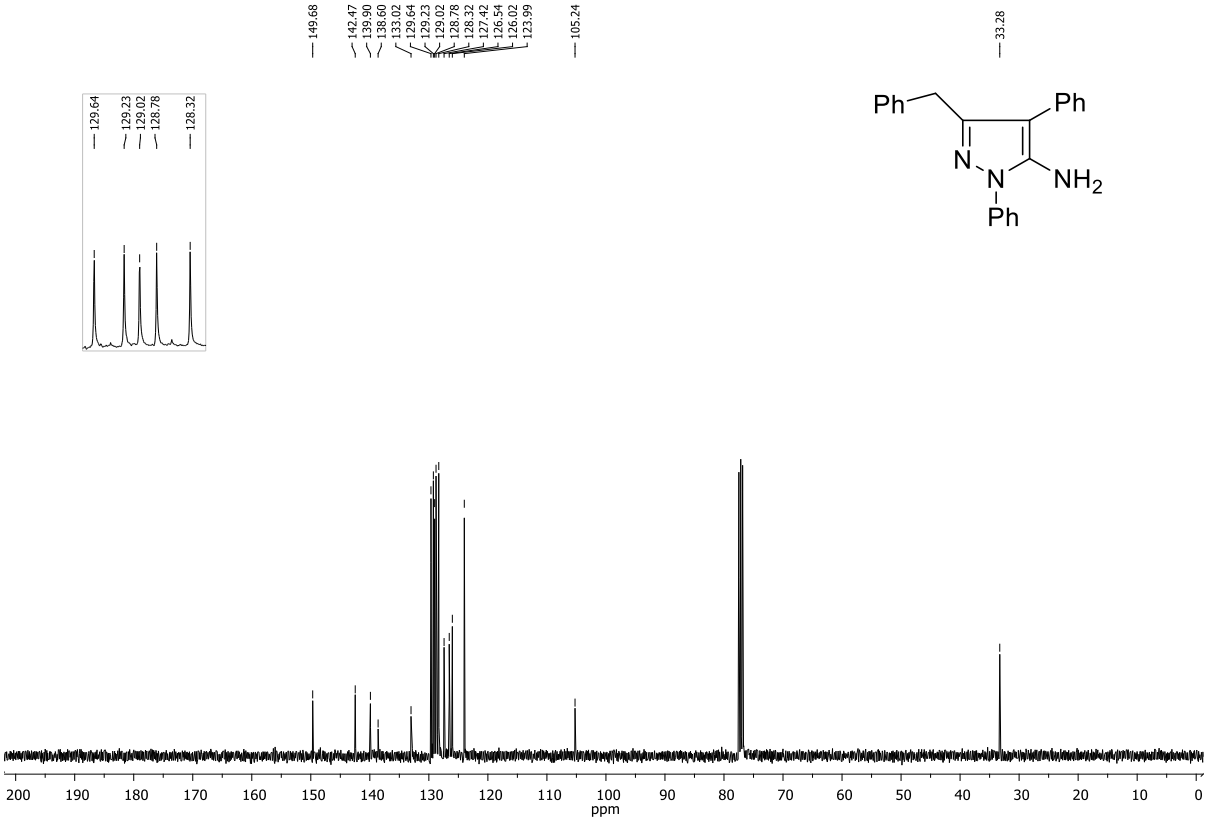
^{13}C{^{1}H} NMR of **2b** in $CDCl_3$ (100 MHz):



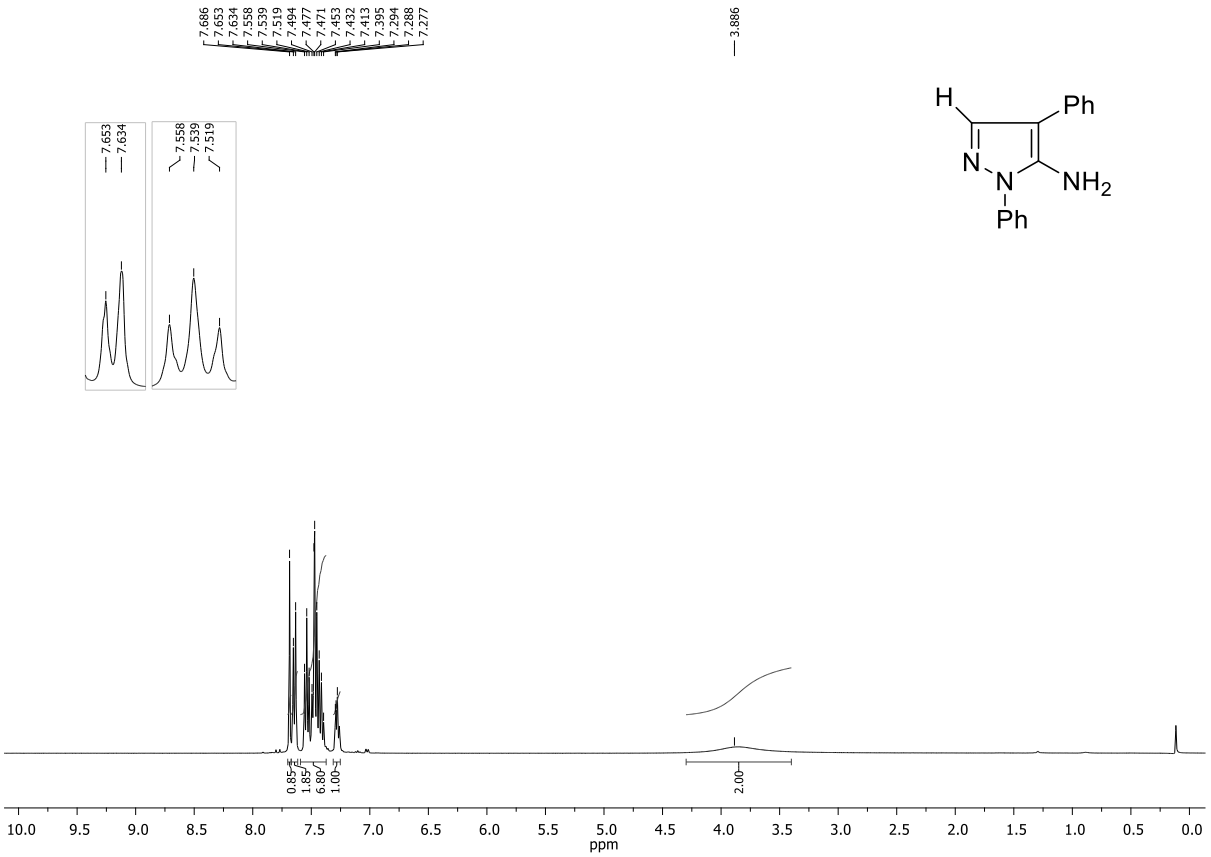
^{1}H NMR of **2c** in $CDCl_3$ (400 MHz):



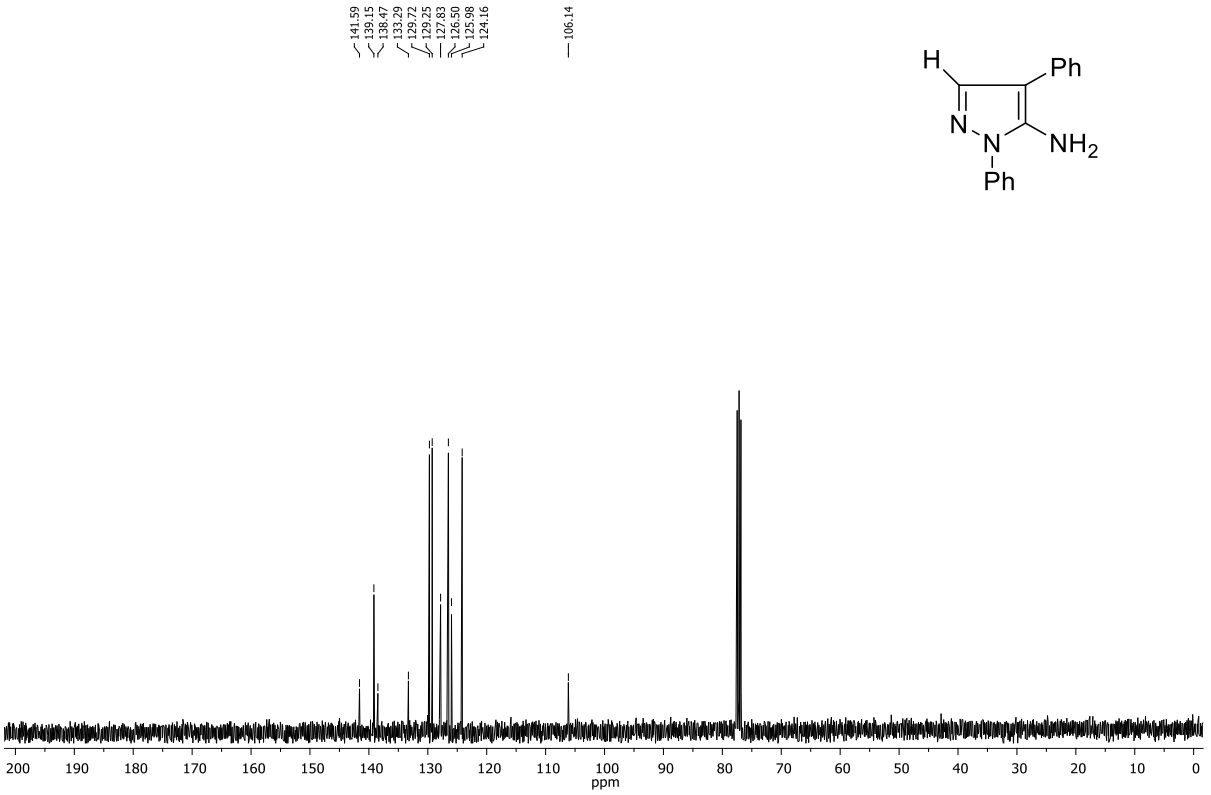
^{13}C{^{1}H} NMR of **2c** in $CDCl_3$ (100 MHz):



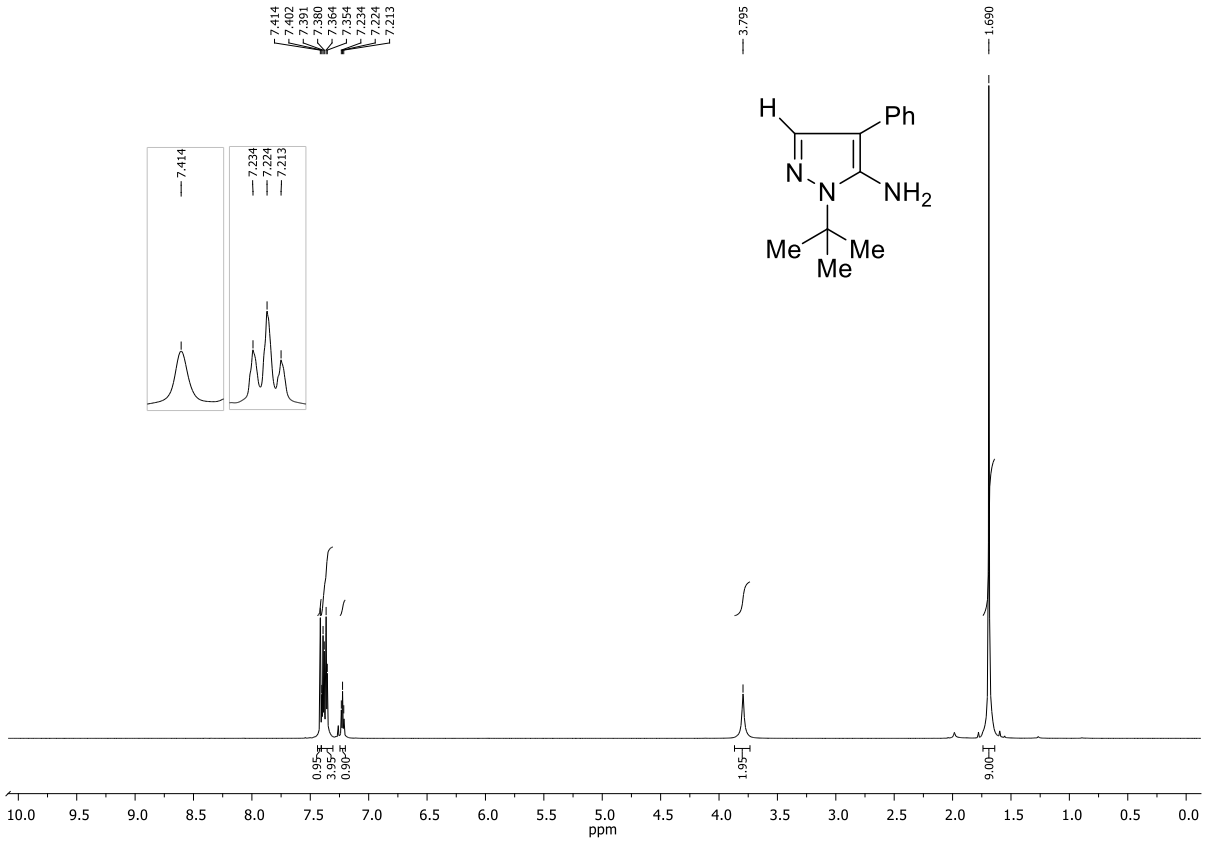
^{1}H NMR of **2d** in $CDCl_3$ (400 MHz):



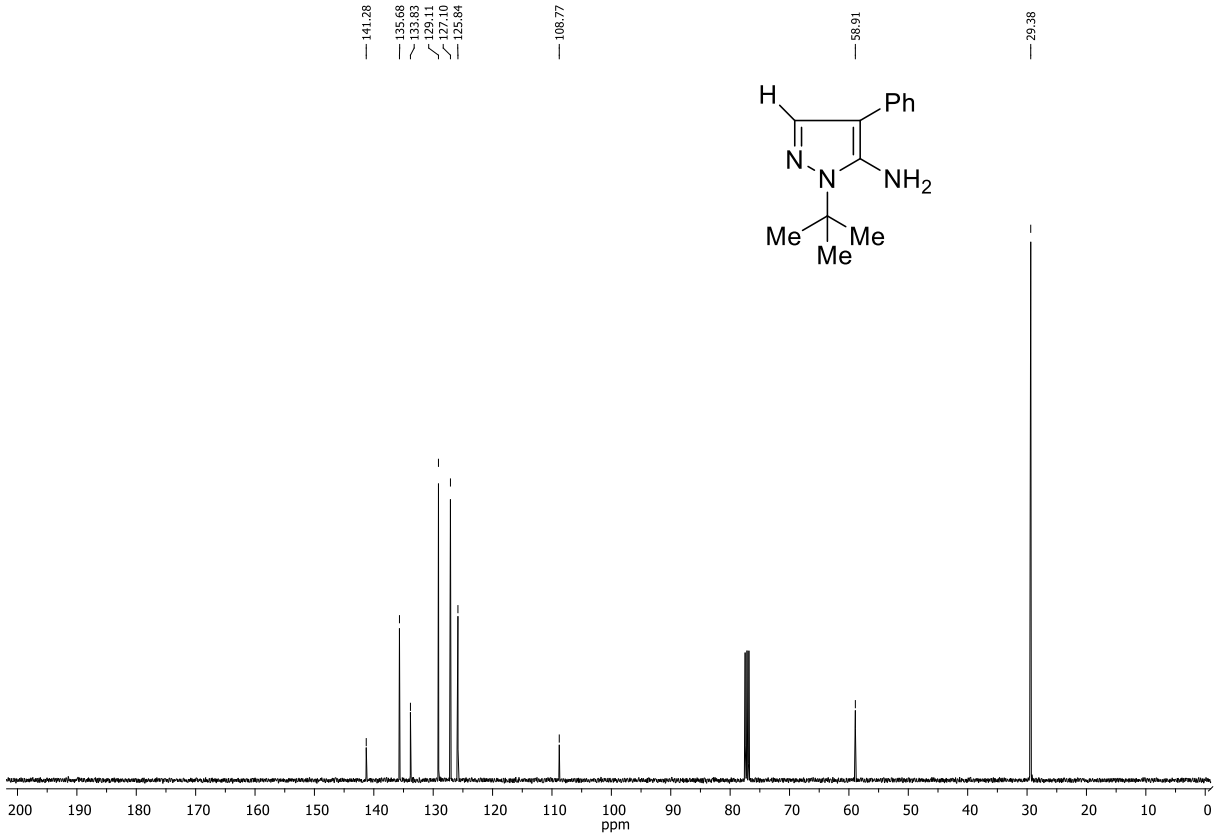
^{13}C{^{1}H} NMR of **2d** in $CDCl_3$ (100 MHz):



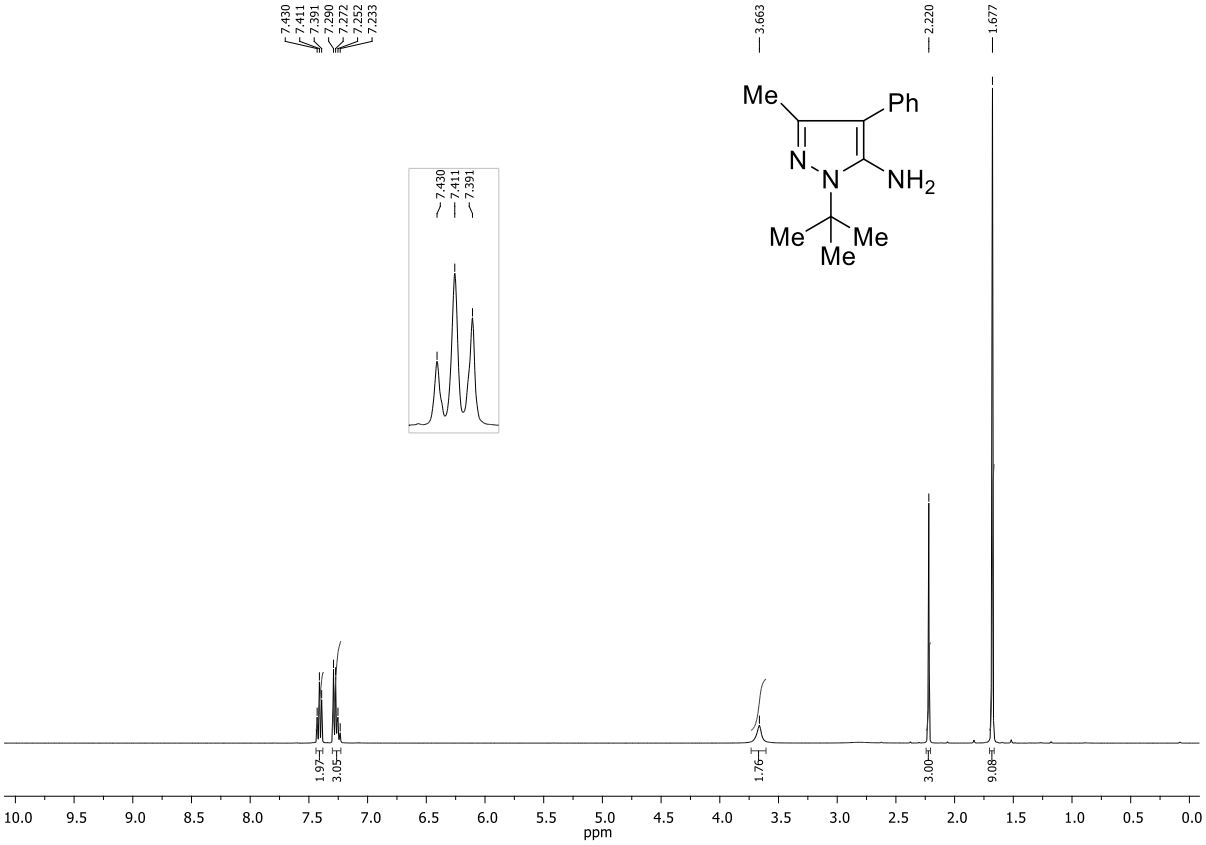
^{1}H NMR of **2e** in $CDCl_3$ (700 MHz):



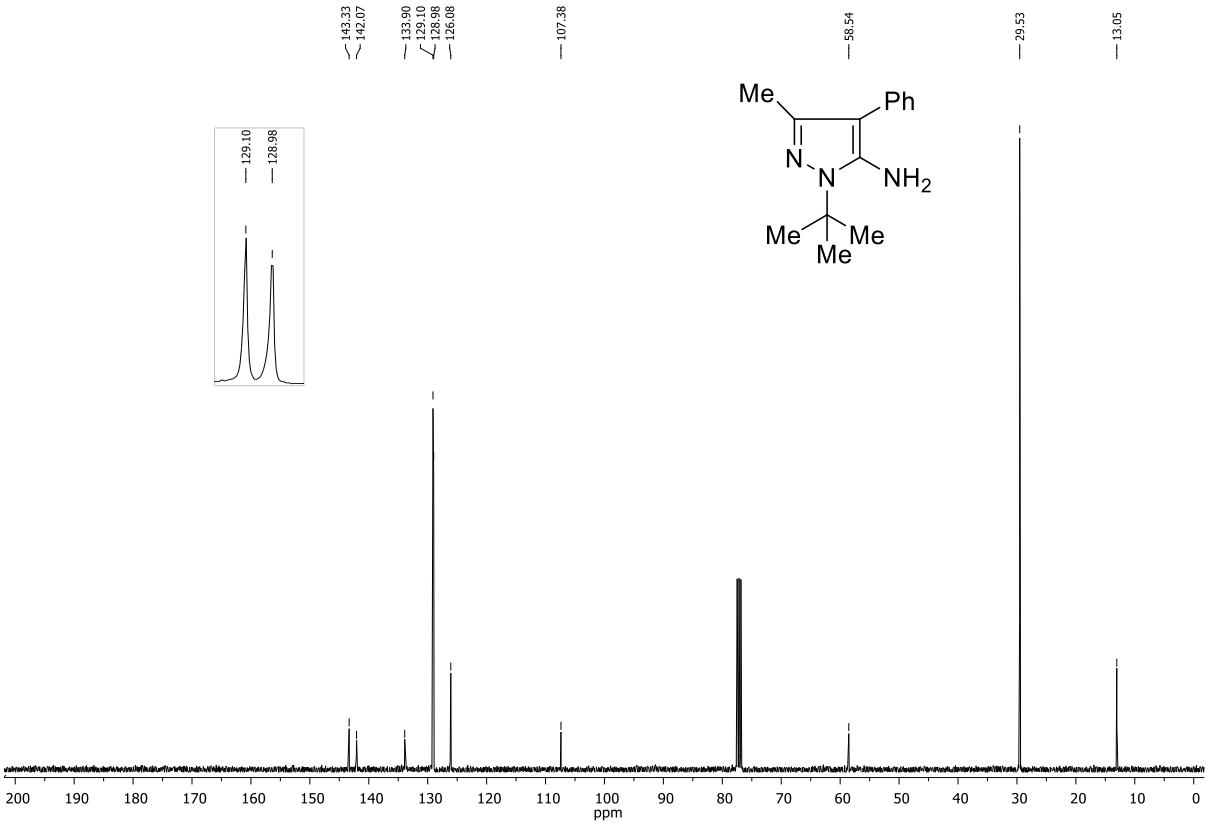
^{13}C{^{1}H} NMR of **2e** in $CDCl_3$ (100 MHz):



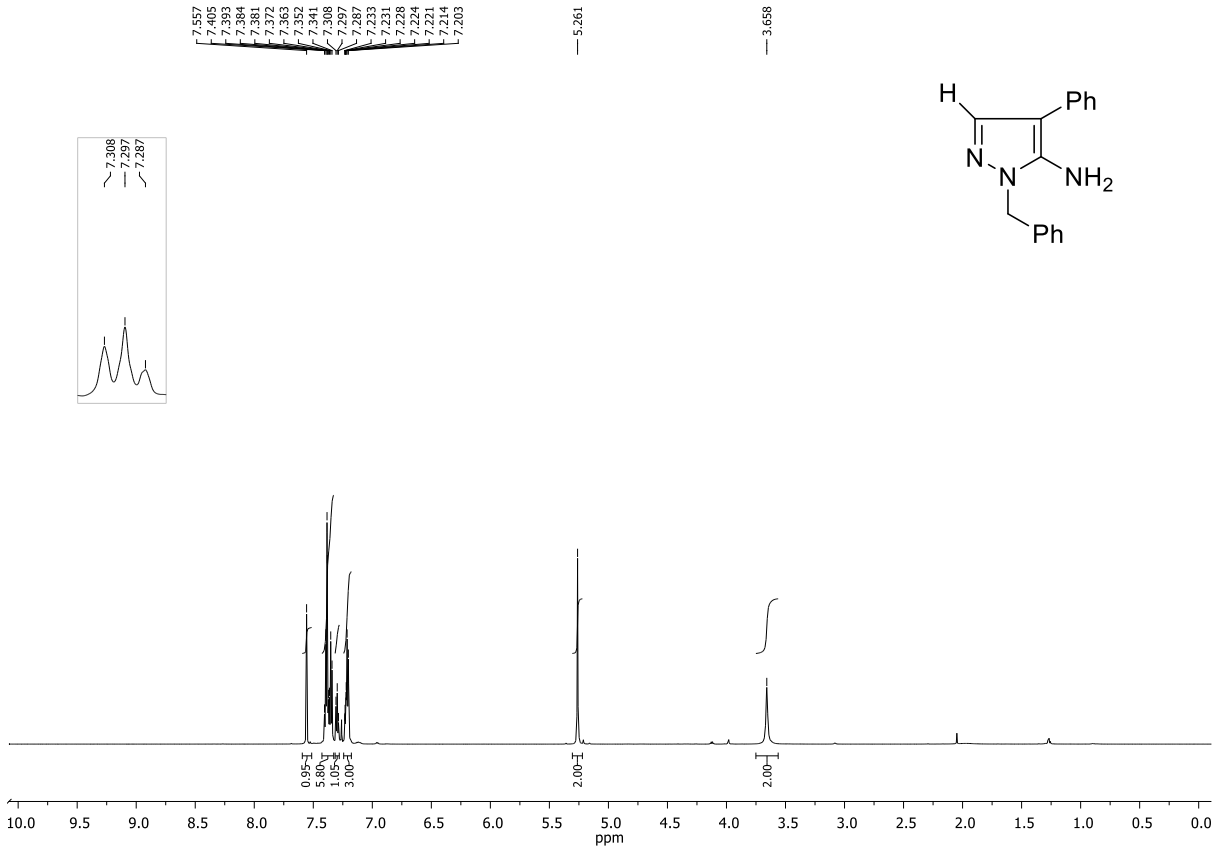
^{1}H NMR of **2f** in $CDCl_3$ (400 MHz):



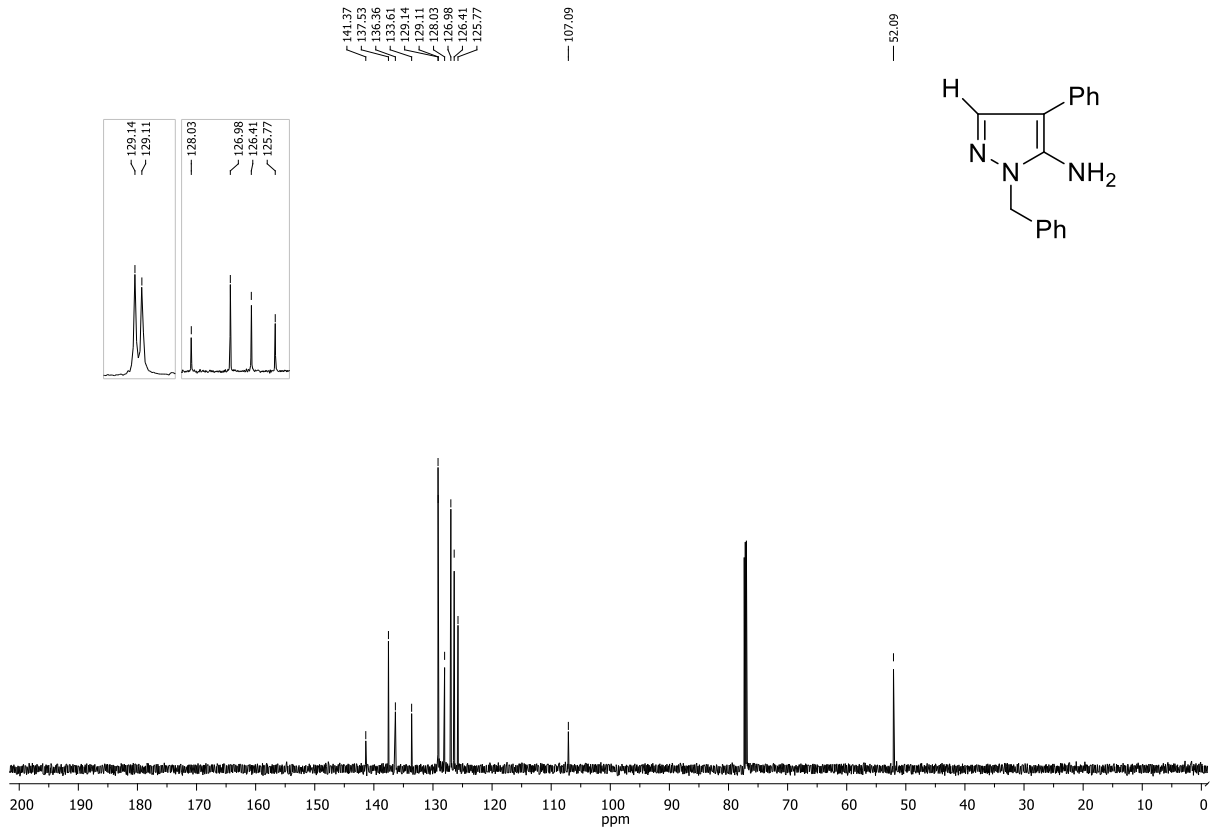
^{13}C{^{1}H} NMR of **2f** in $CDCl_3$ (100 MHz):



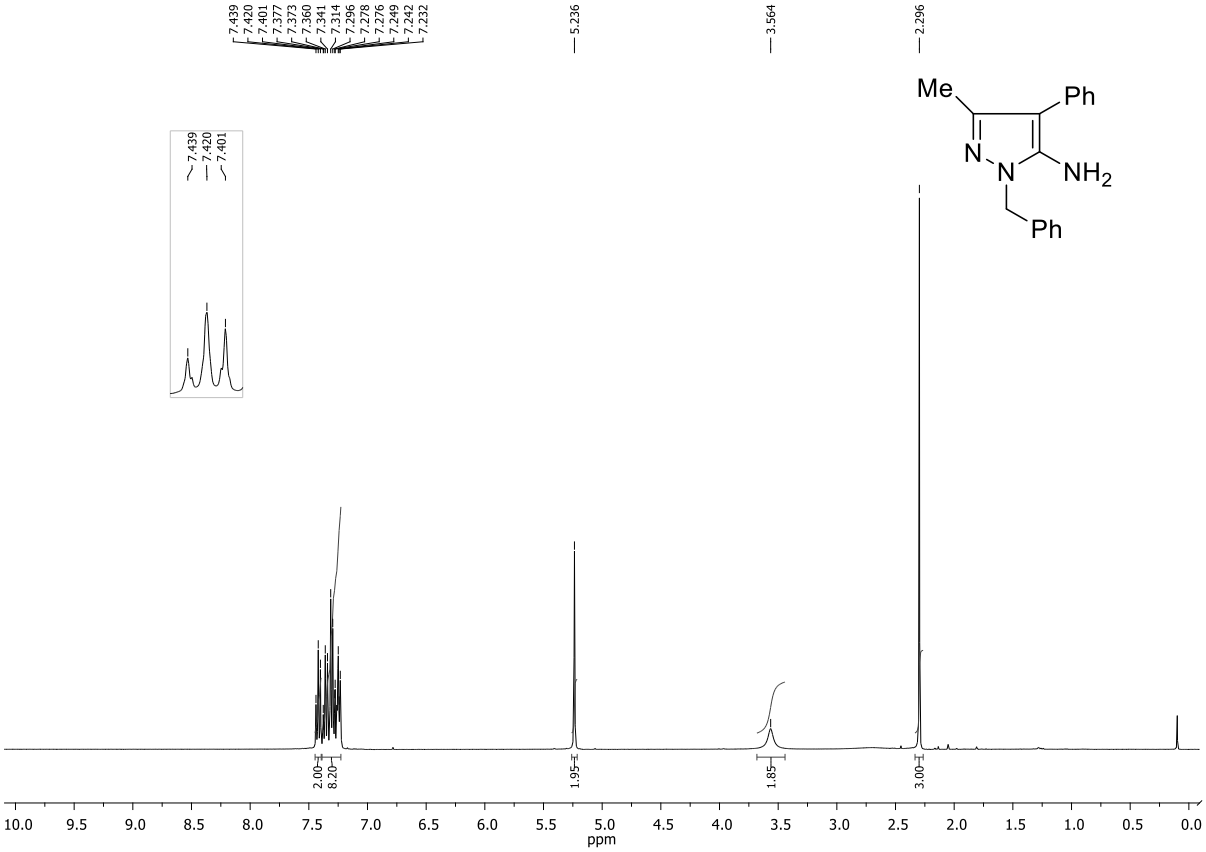
^{1}H NMR of **2g** in $CDCl_3$ (700 MHz):



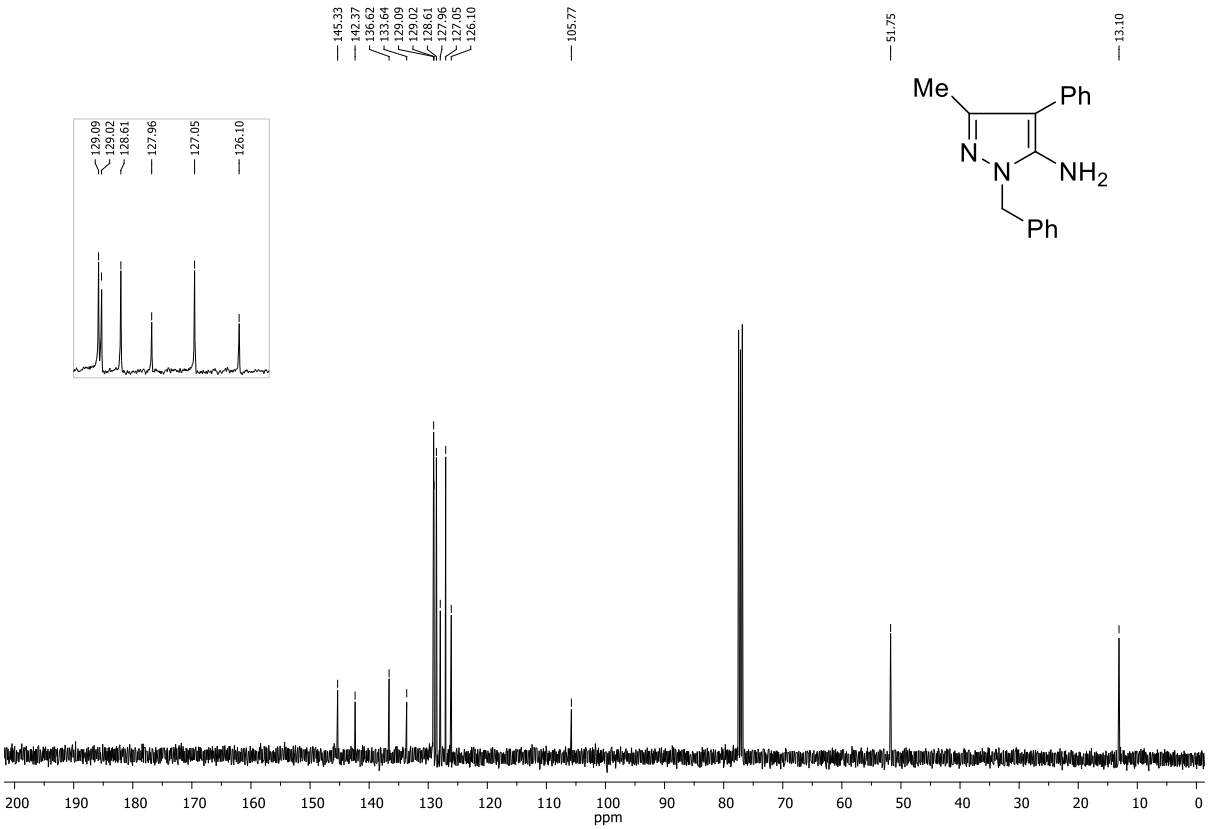
^{13}C{^{1}H} NMR of **2g** in $CDCl_3$ (175 MHz):



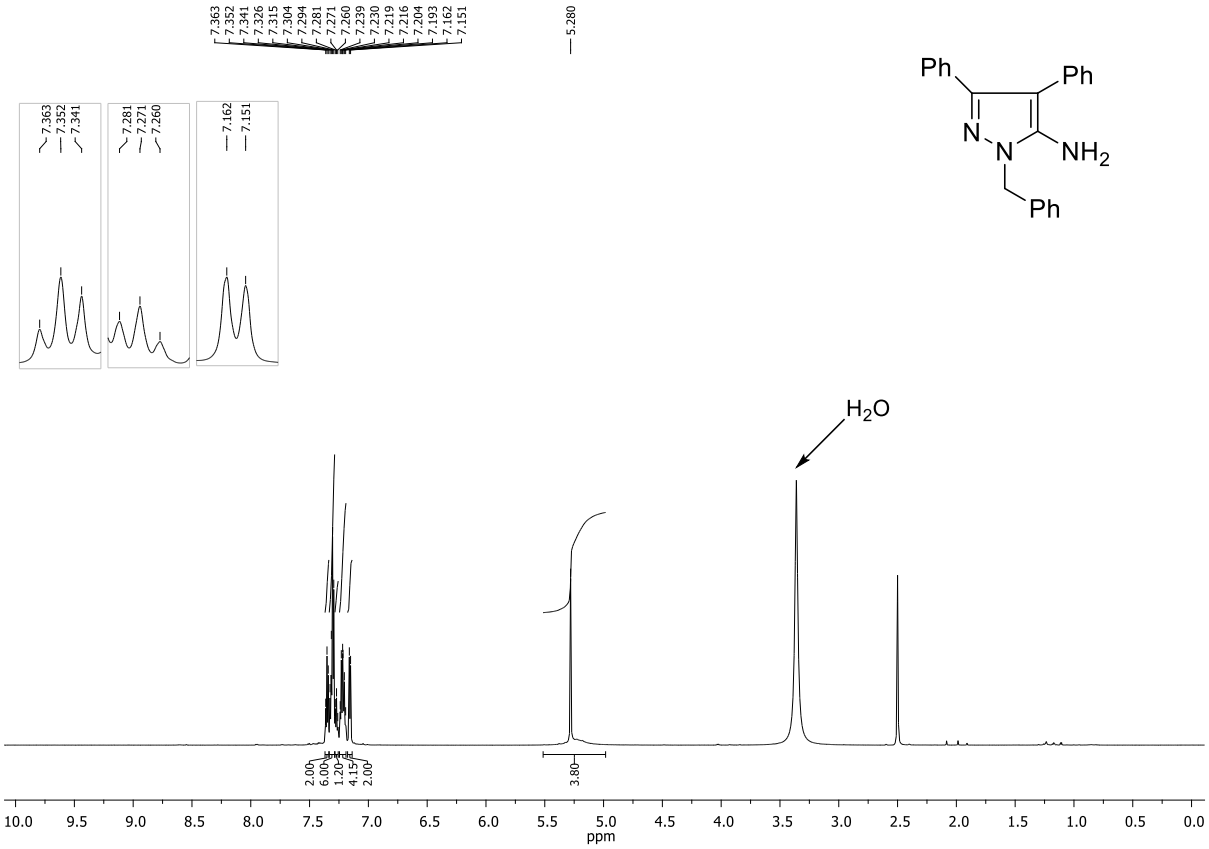
^{1}H NMR of **2h** in $CDCl_3$ (400 MHz):



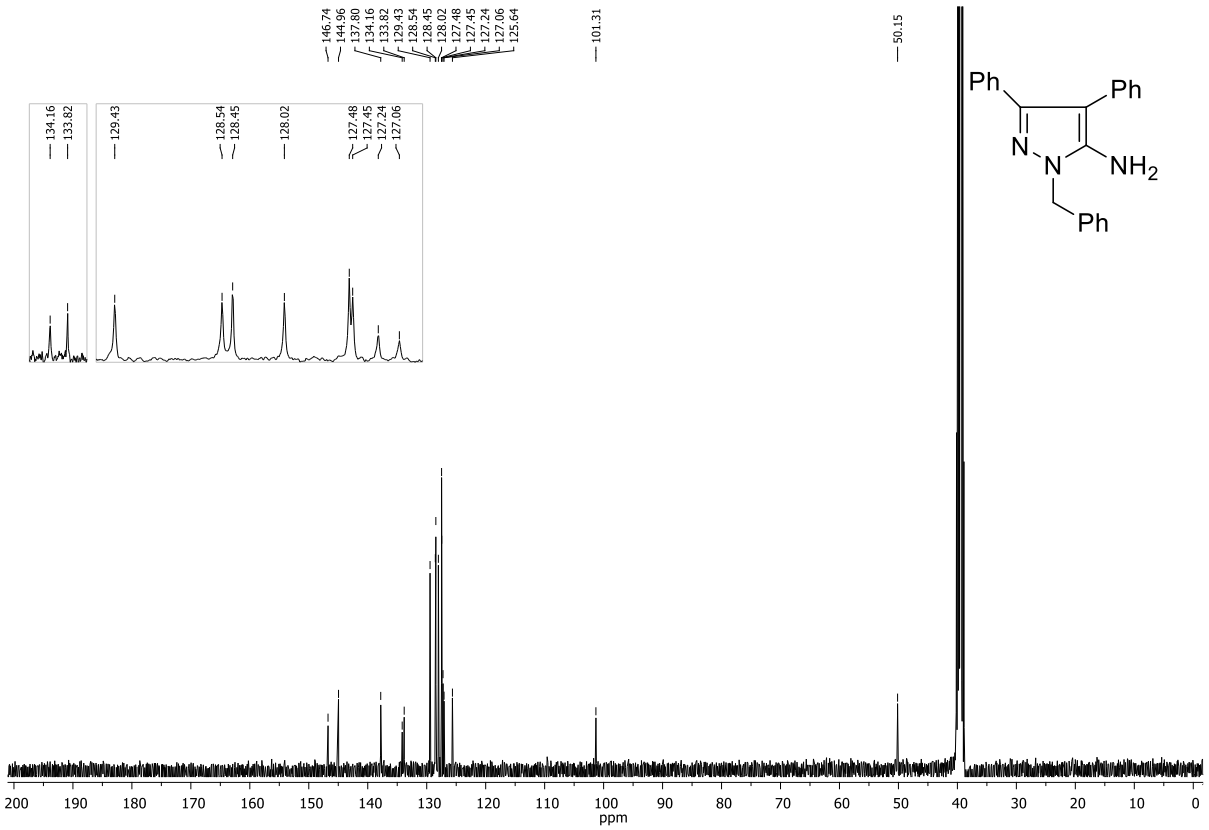
^{13}C{^{1}H} NMR of **2h** in $CDCl_3$ (100 MHz):



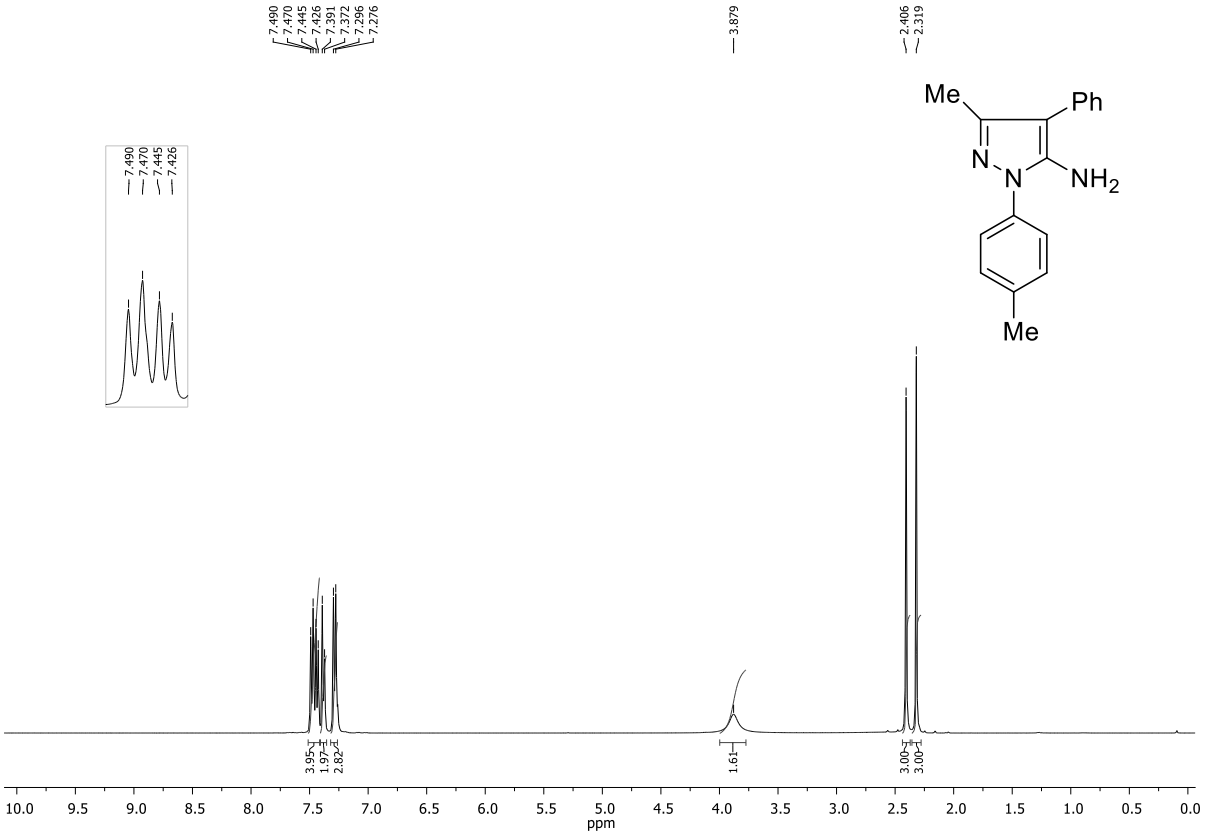
^{1}H NMR of **2i** in DMSO-d_6 (700 MHz):



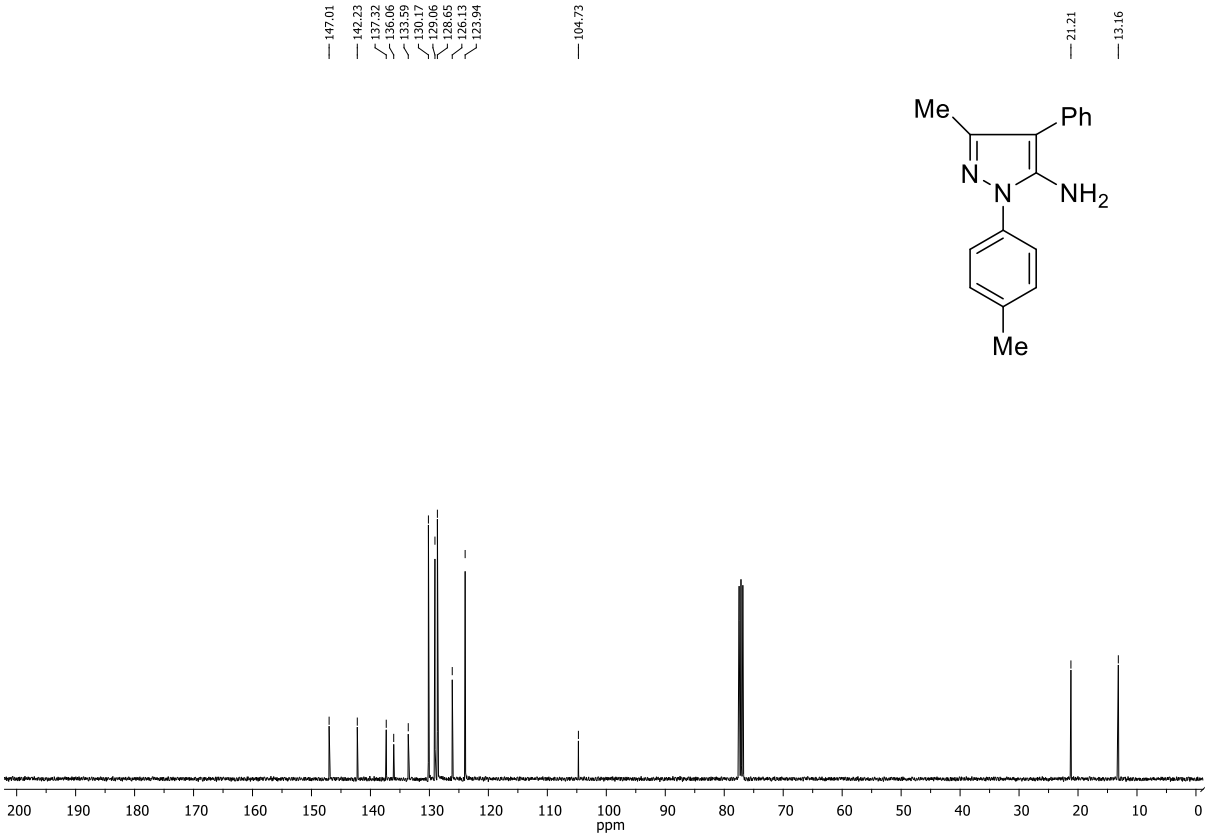
^{13}C{^{1}H} NMR of **2i** in DMSO-d_6 (100 MHz):



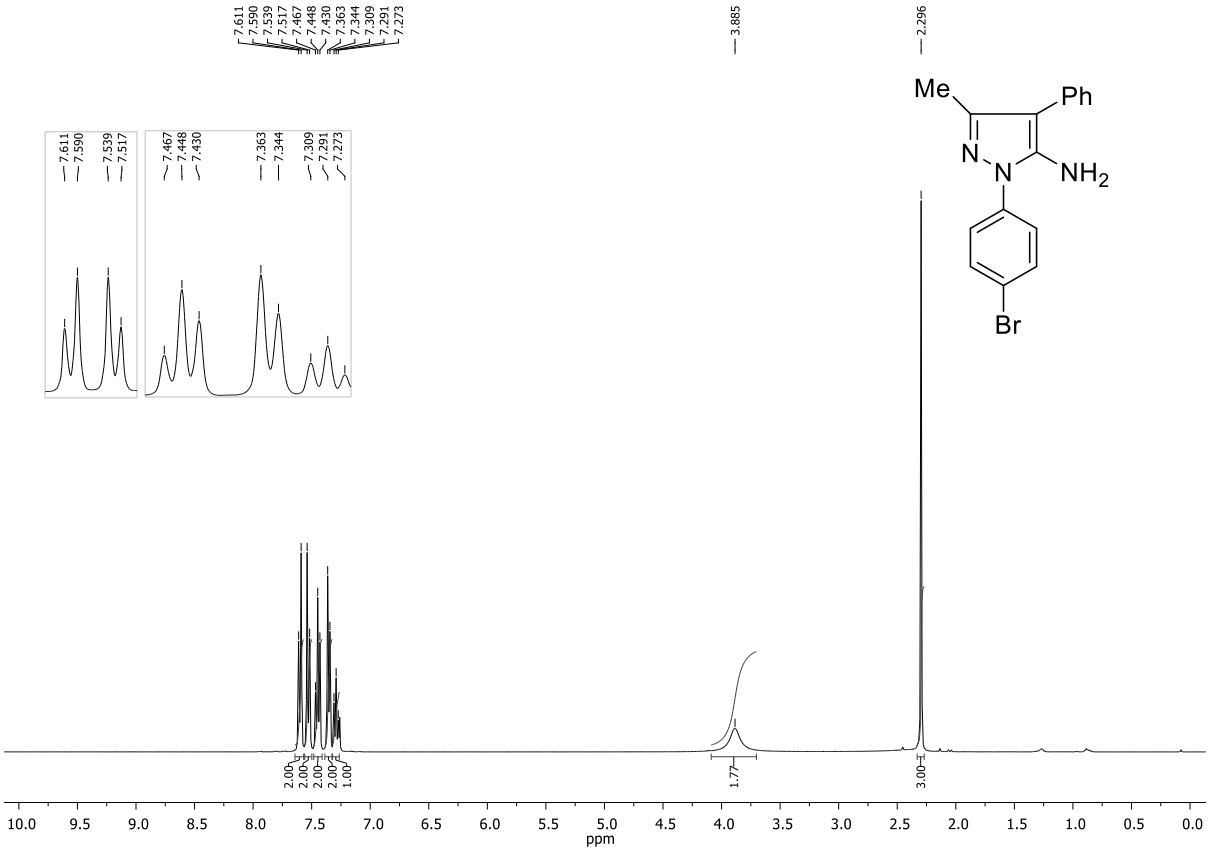
^{1}H NMR of **2j** in $CDCl_3$ (400 MHz):



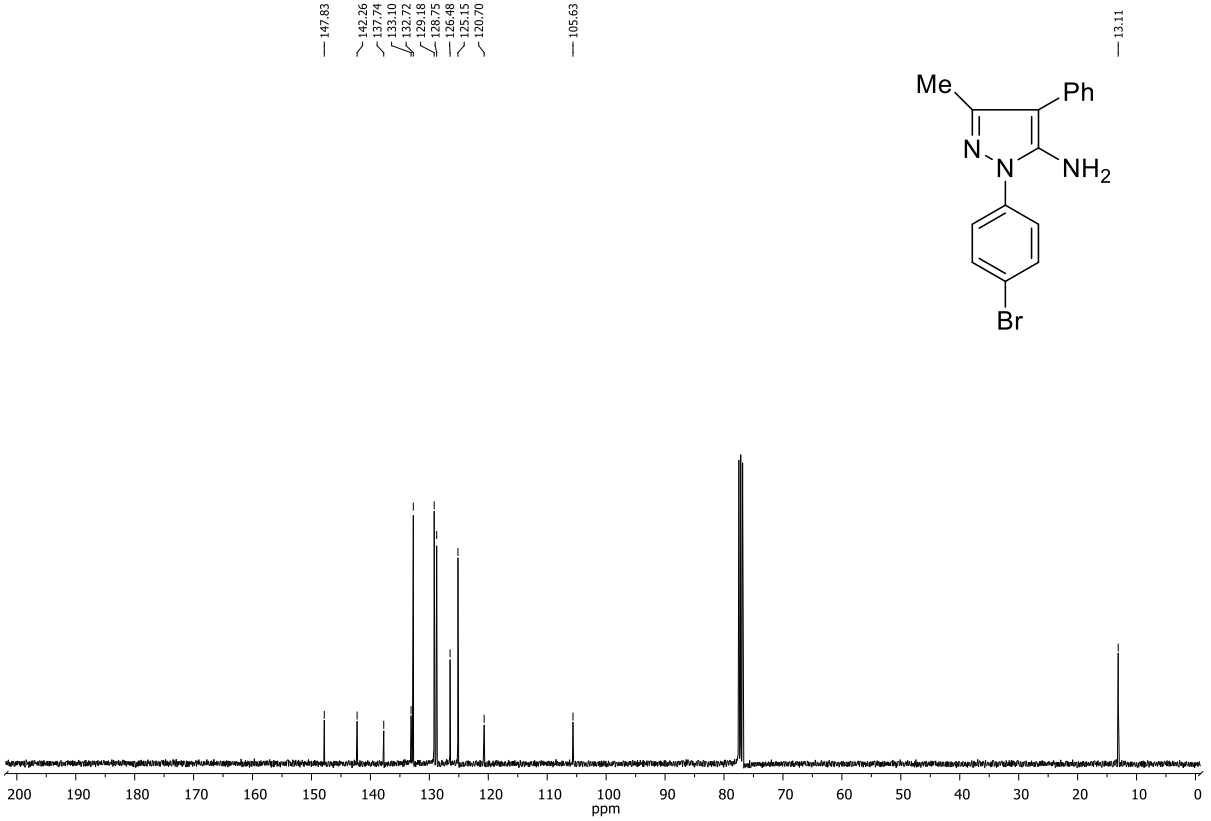
^{13}C{^{1}H} NMR of **2j** in $CDCl_3$ (100 MHz):



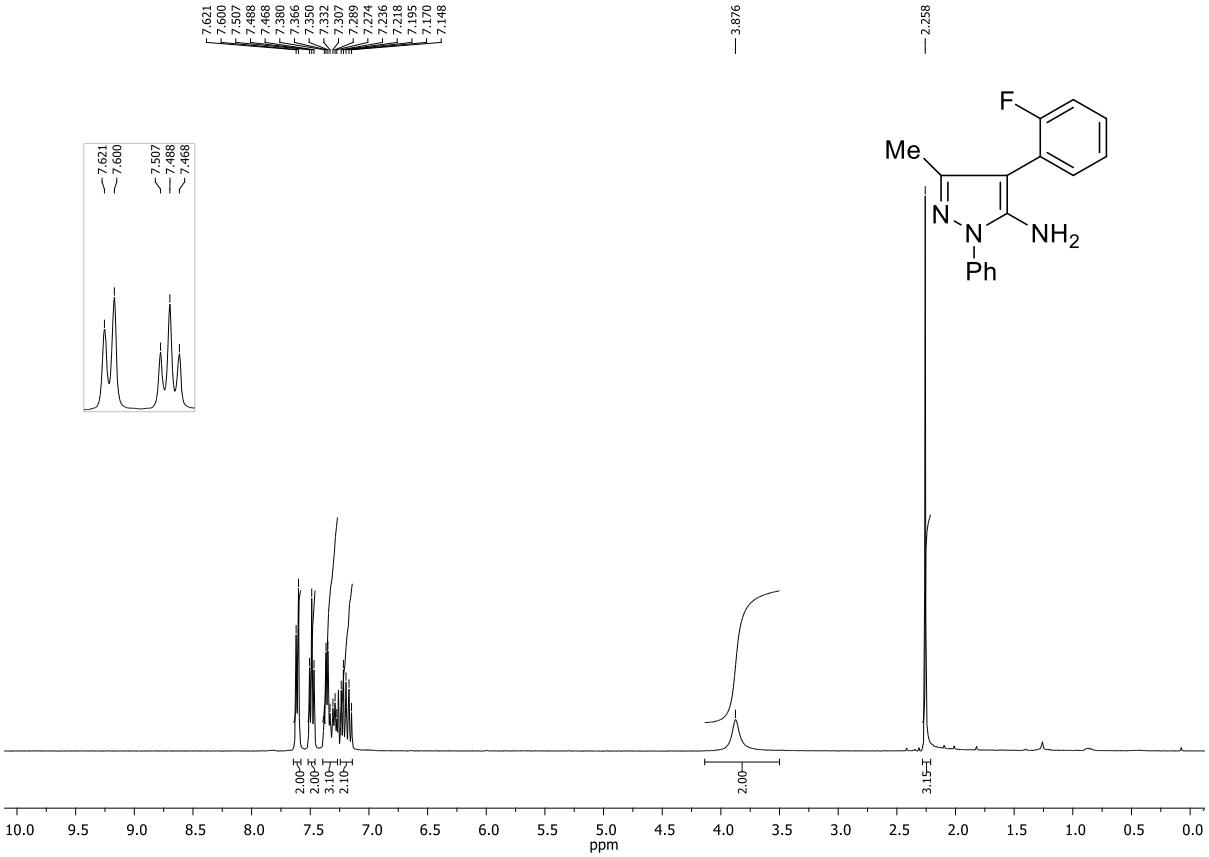
^{1}H NMR of **2k** in $CDCl_3$ (400 MHz):



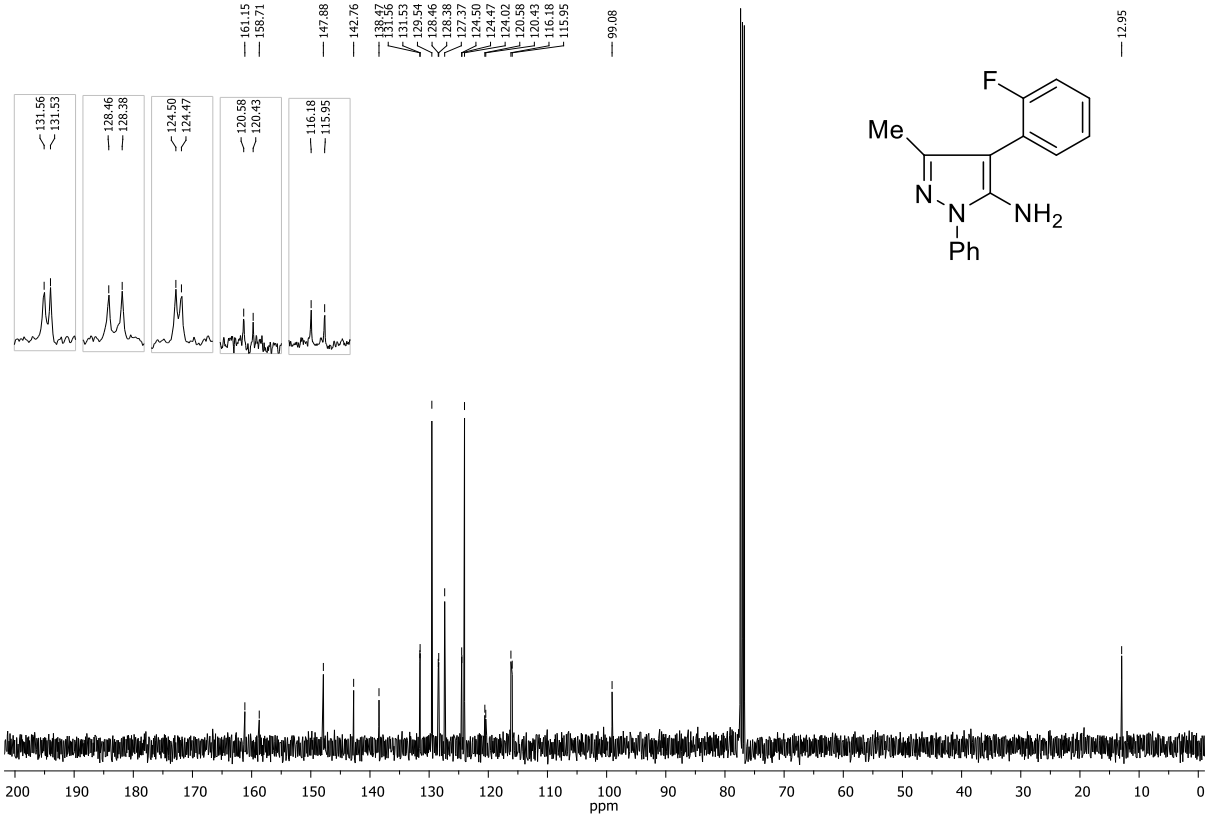
^{13}C{^{1}H} NMR of **2k** in $CDCl_3$ (100 MHz):



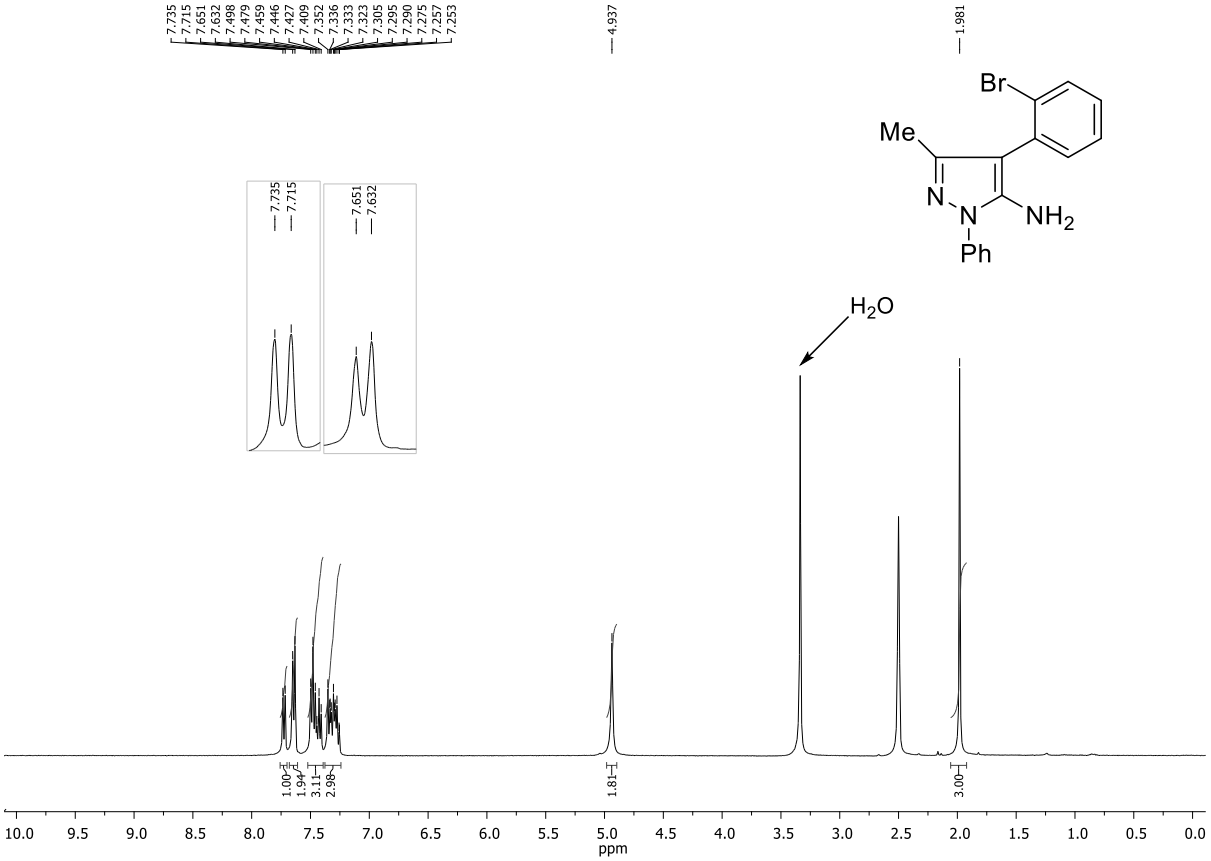
^{1}H NMR of **2l** in $CDCl_3$ (400 MHz):



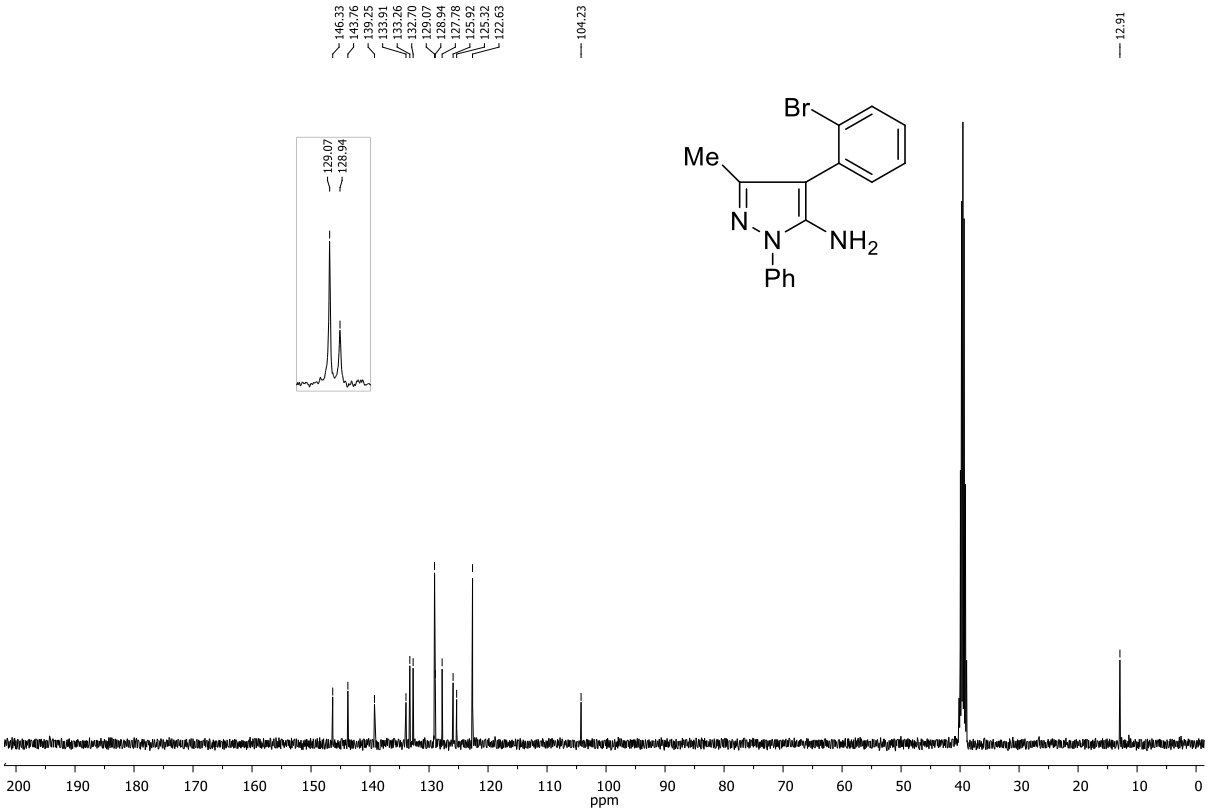
^{13}C{^{1}H} NMR of **2l** in $CDCl_3$ (100 MHz):



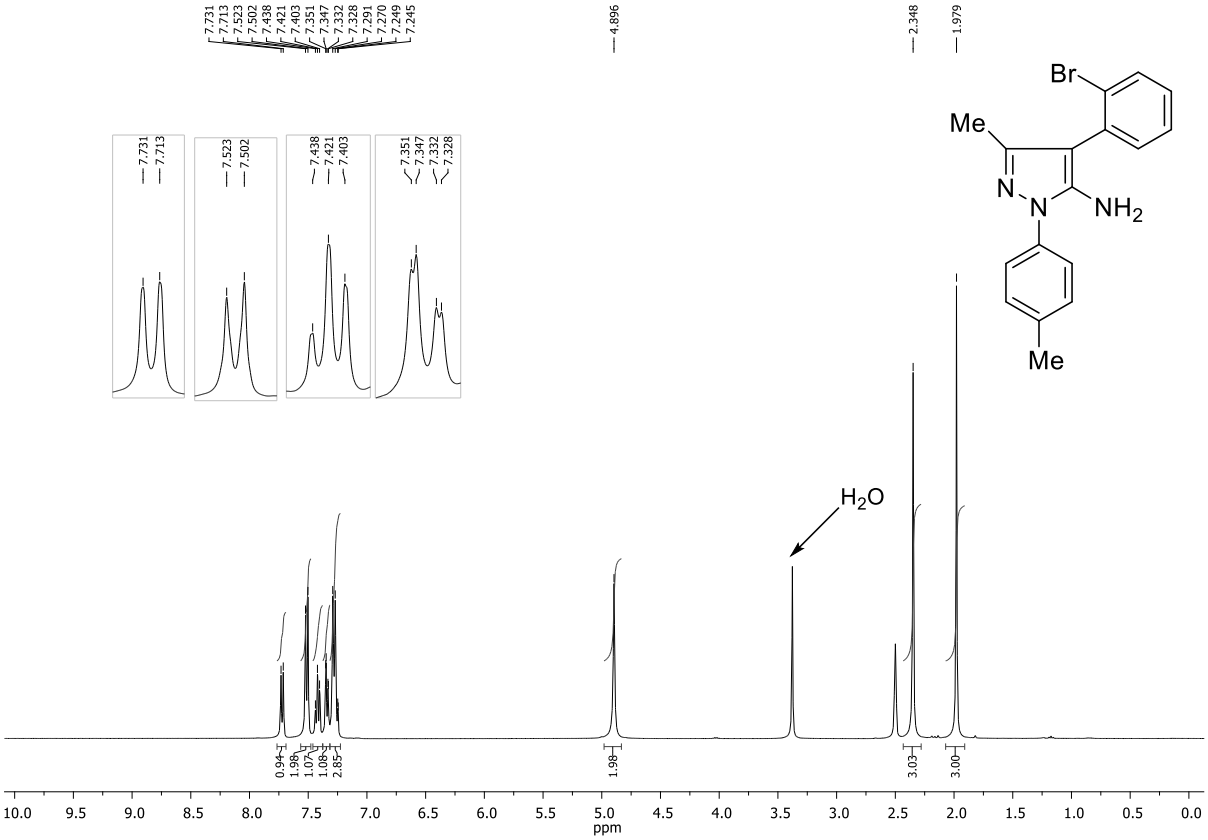
^{1}H NMR of **2m** in DMSO-d_6 (400 MHz):



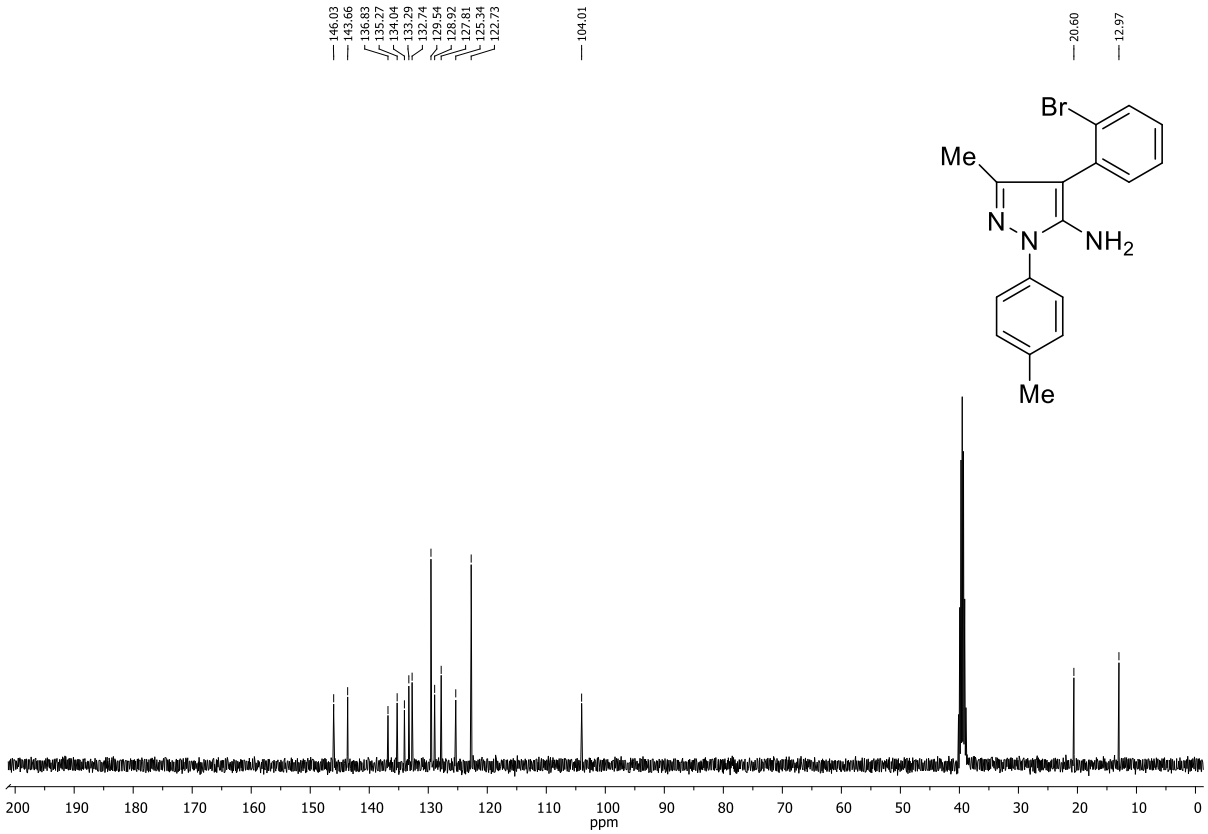
^{13}C{^{1}H} NMR of **2m** in DMSO-d_6 (100 MHz):



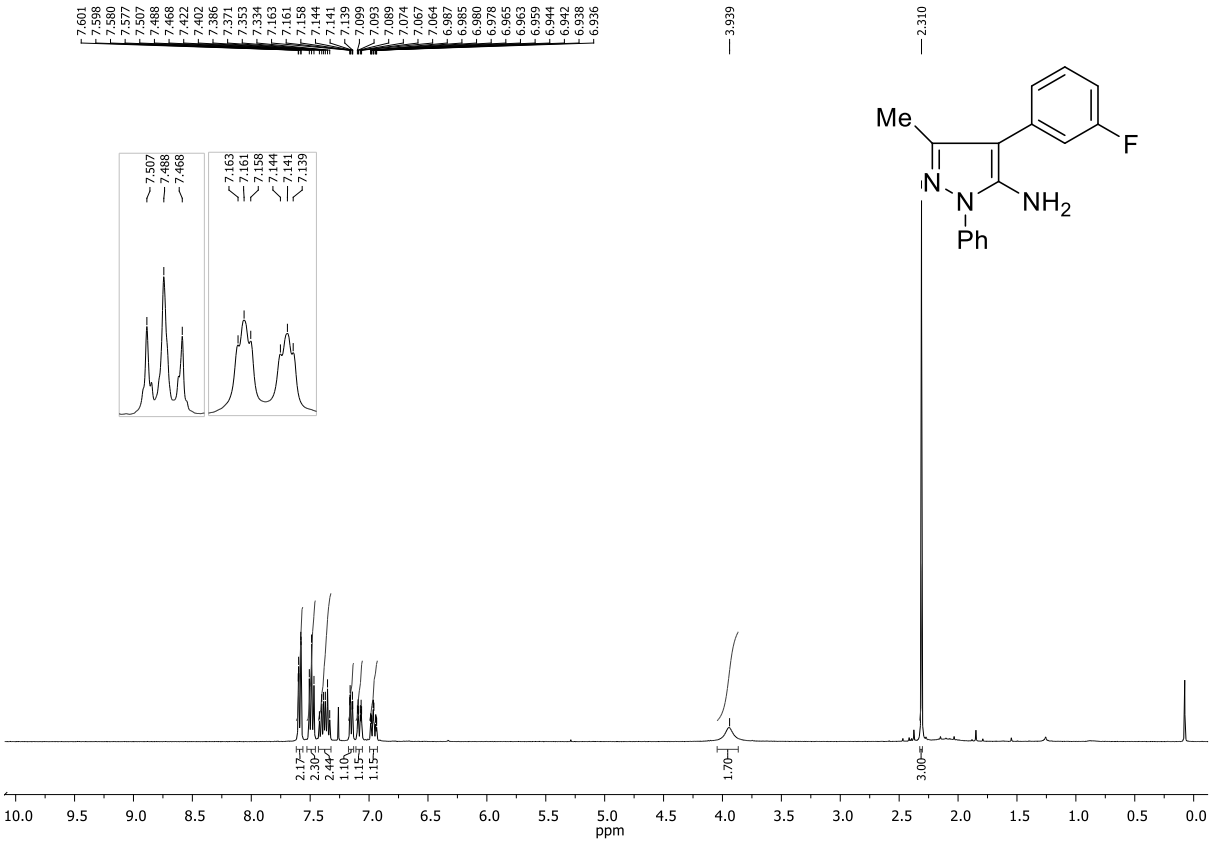
^{1}H NMR of **2n** in DMSO-d_6 (400 MHz):



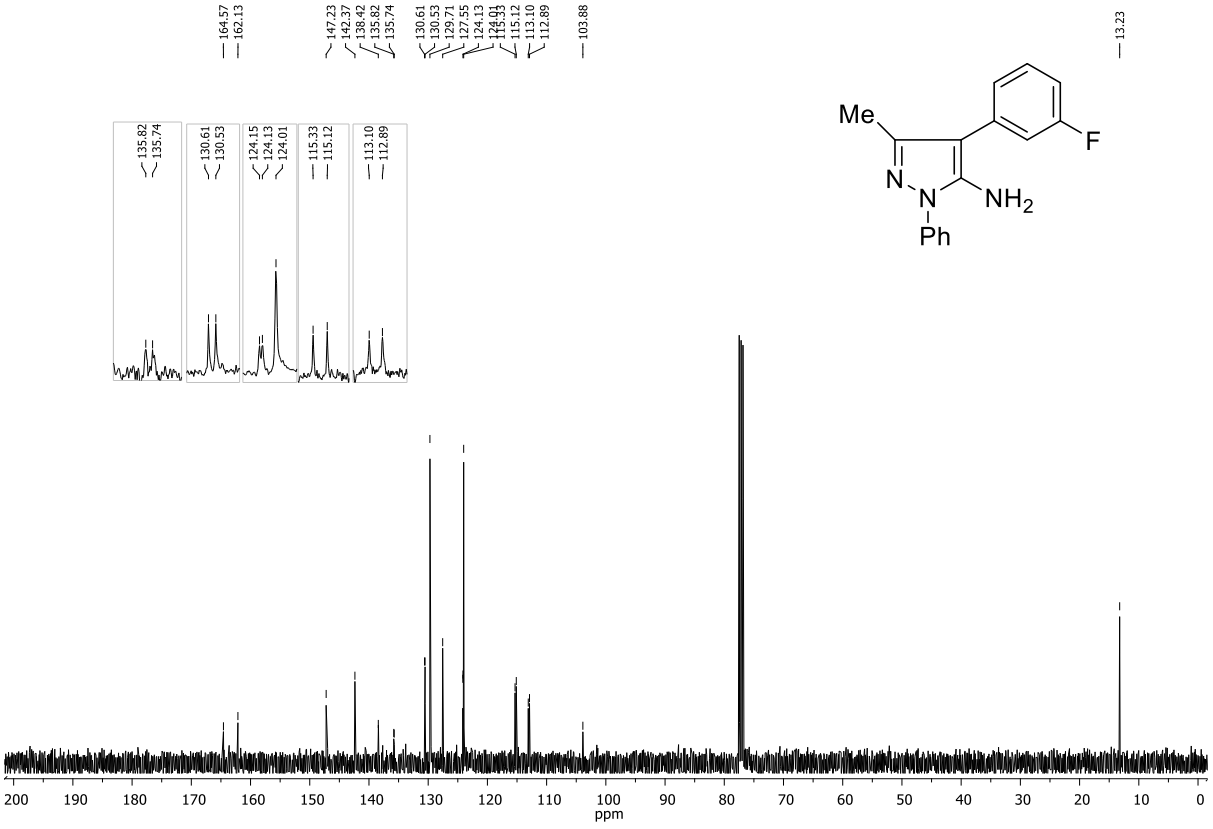
^{13}C{^{1}H} NMR of **2n** in DMSO-d_6 (100 MHz):



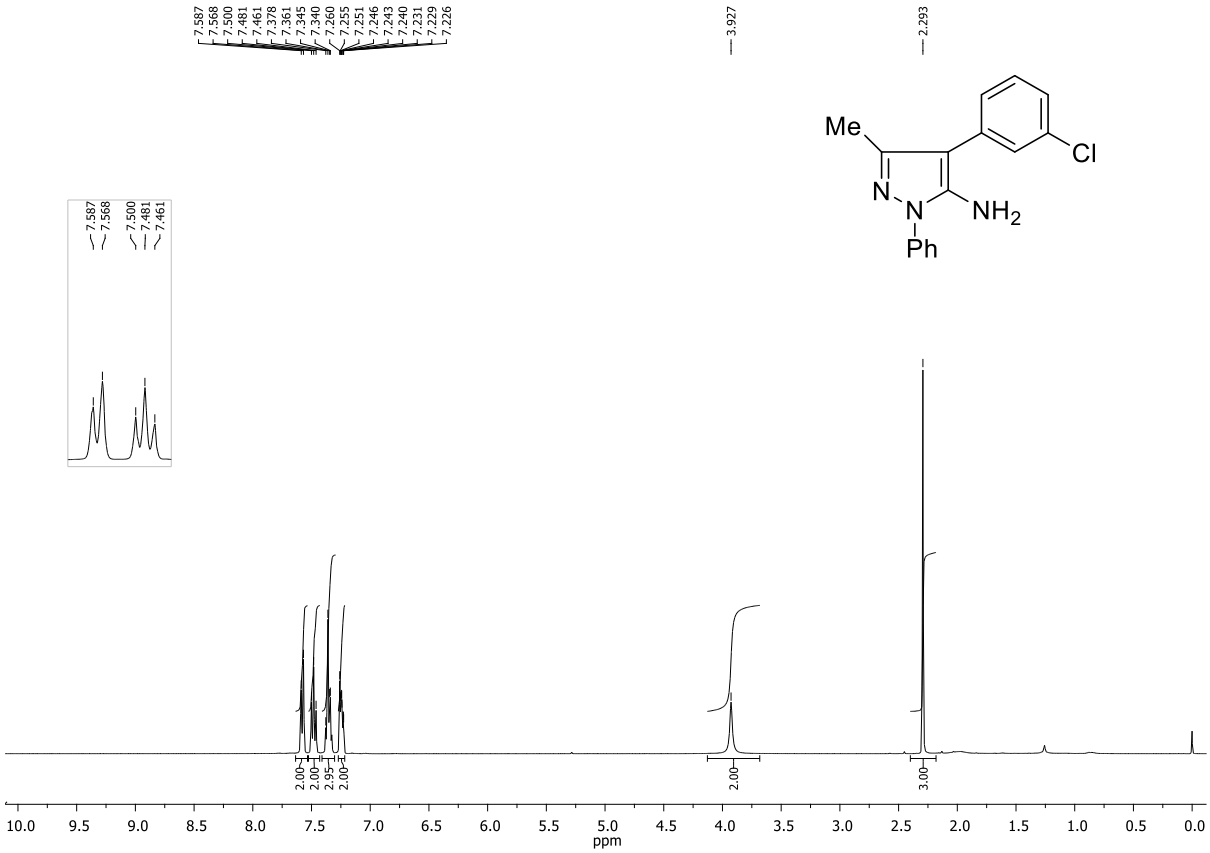
^{1}H NMR of **2o** in $CDCl_3$ (400 MHz):



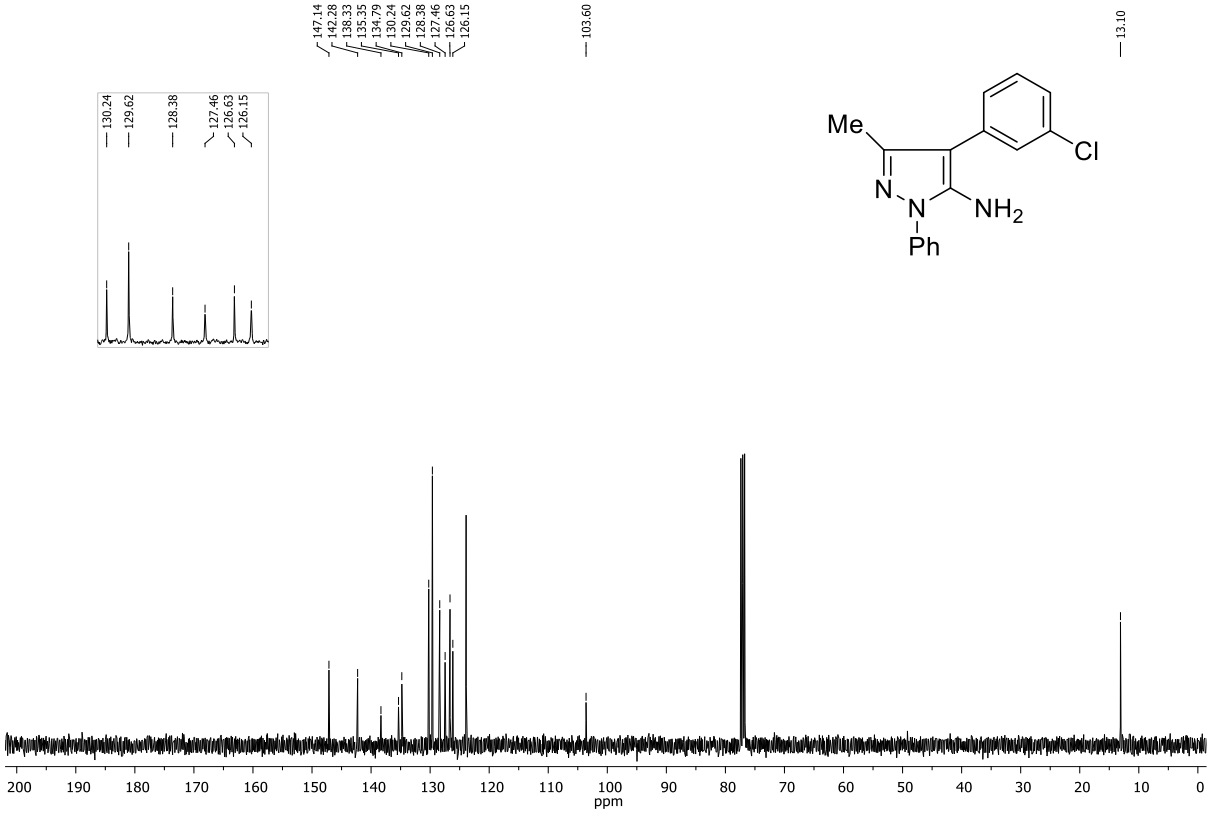
^{13}C{^{1}H} NMR of **2o** in $CDCl_3$ (100 MHz):



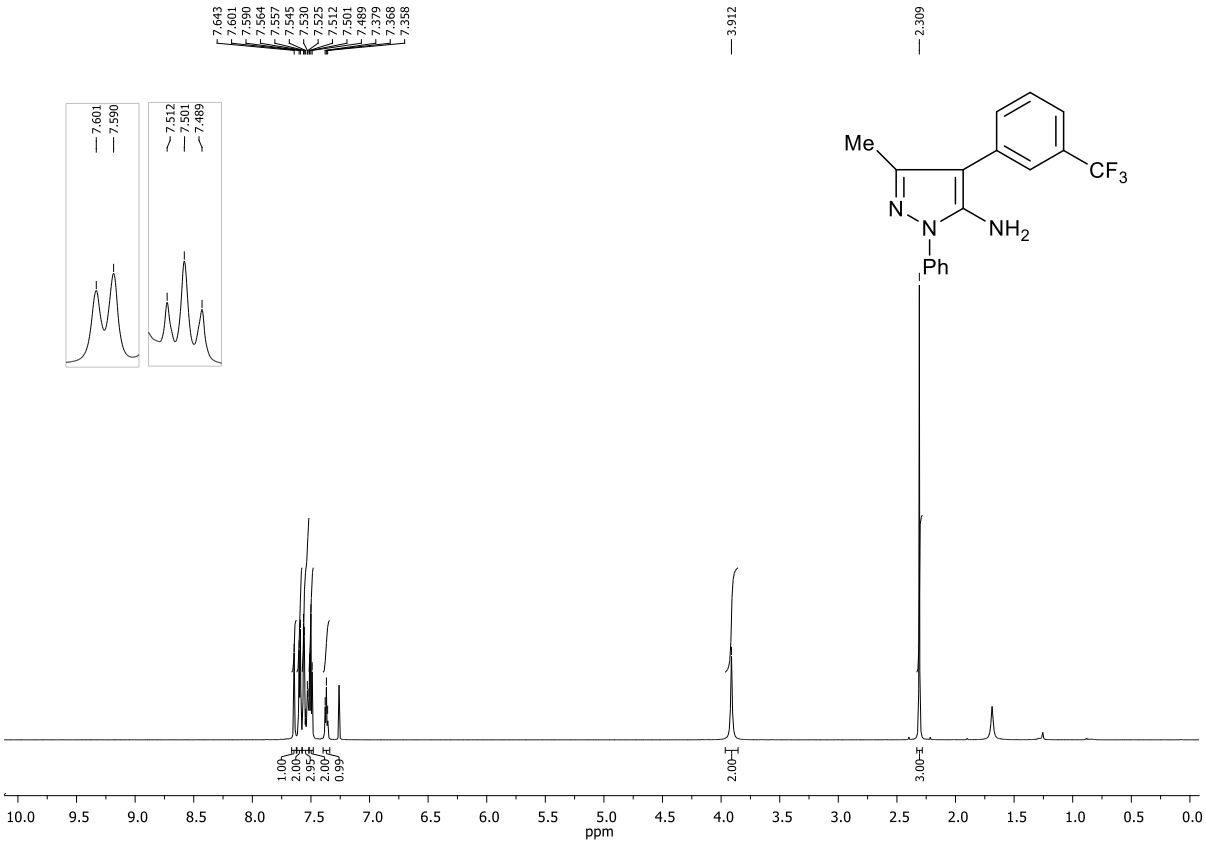
^{1}H NMR of **2p** in $CDCl_3$ (400 MHz):



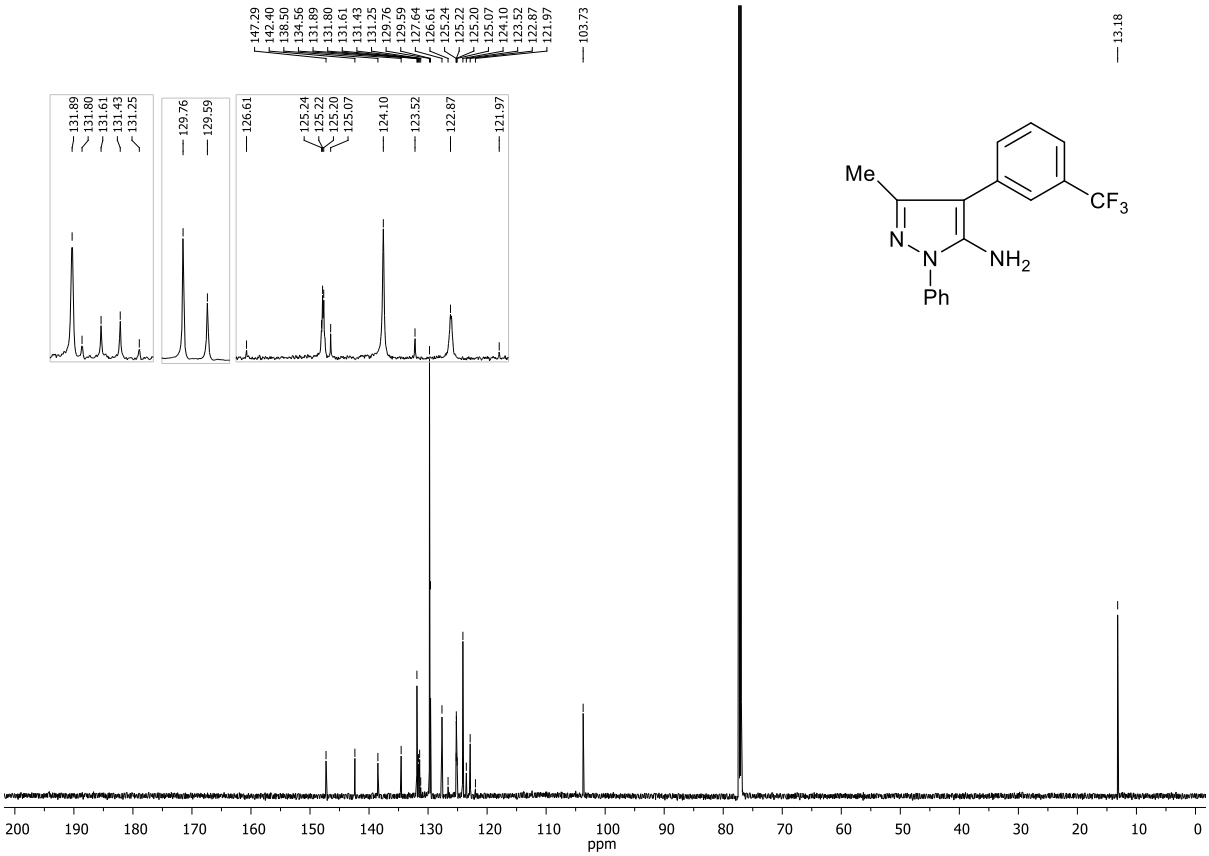
^{13}C{^{1}H} NMR of **2p** in $CDCl_3$ (100 MHz):



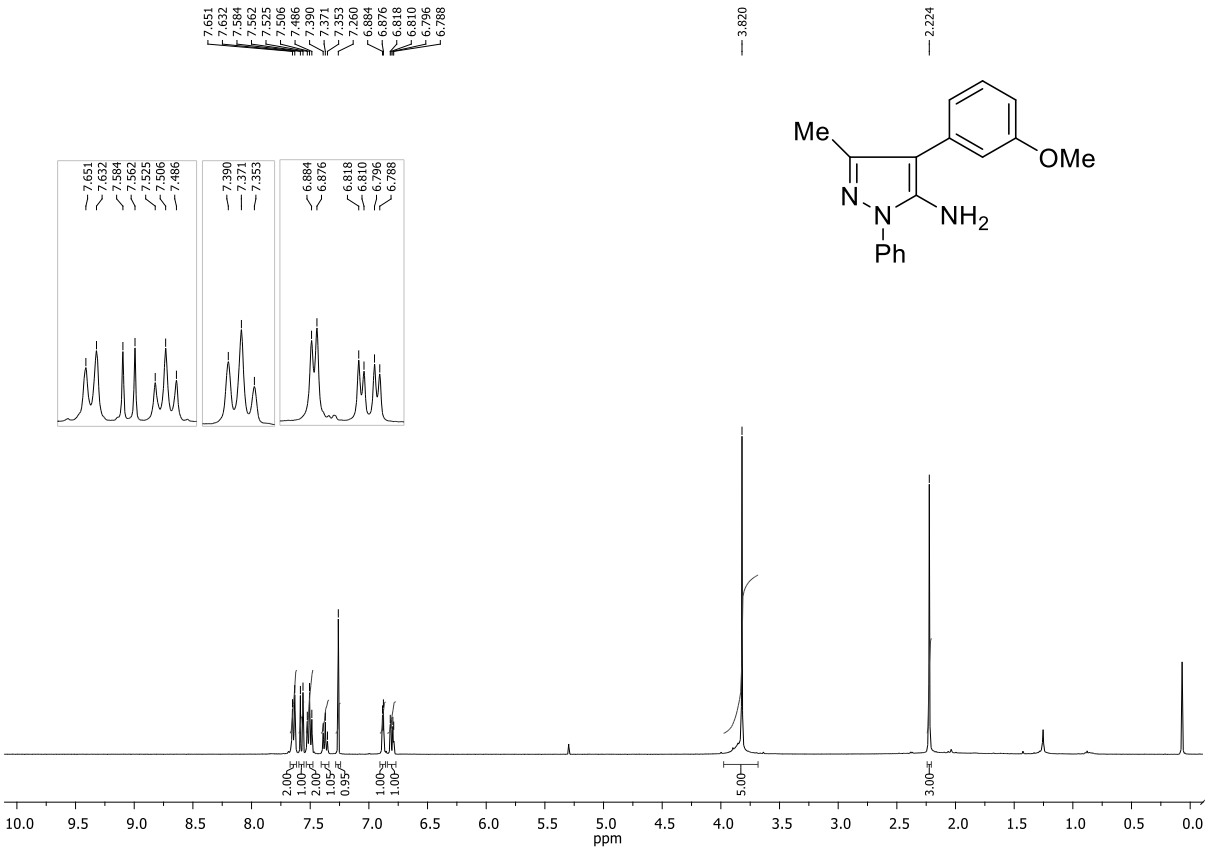
^{1}H NMR of **2q** in $CDCl_3$ (700 MHz):



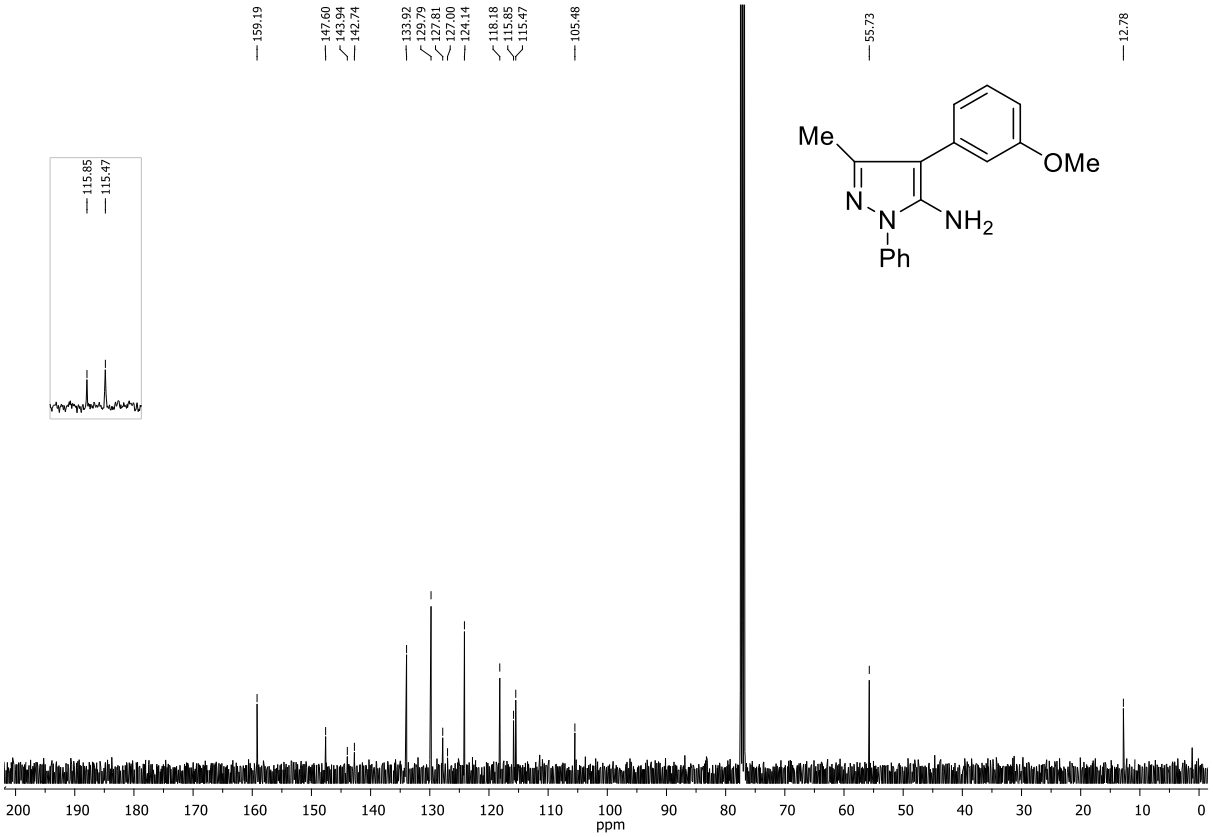
^{13}C{^{1}H} NMR of **2q** in $CDCl_3$ (175 MHz):



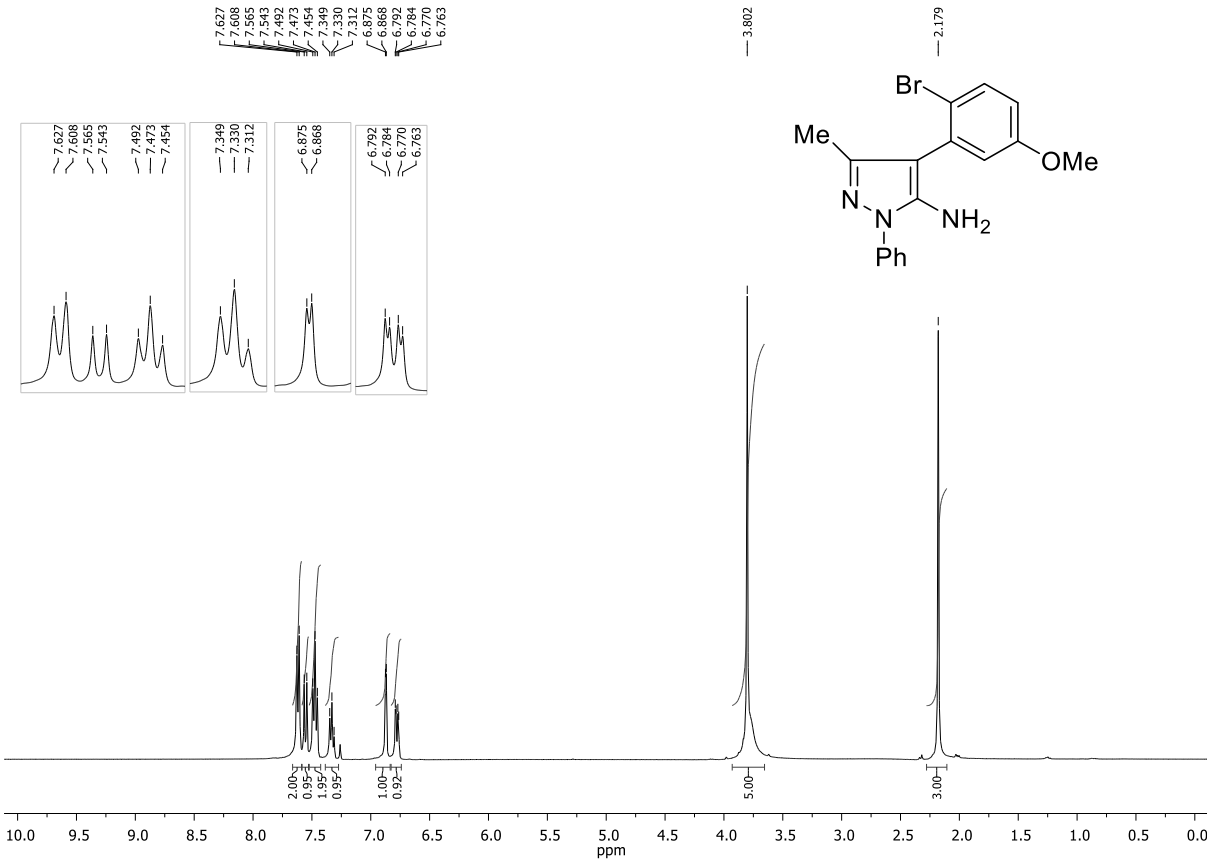
^{1}H NMR of **2r** in $CDCl_3$ (400 MHz):



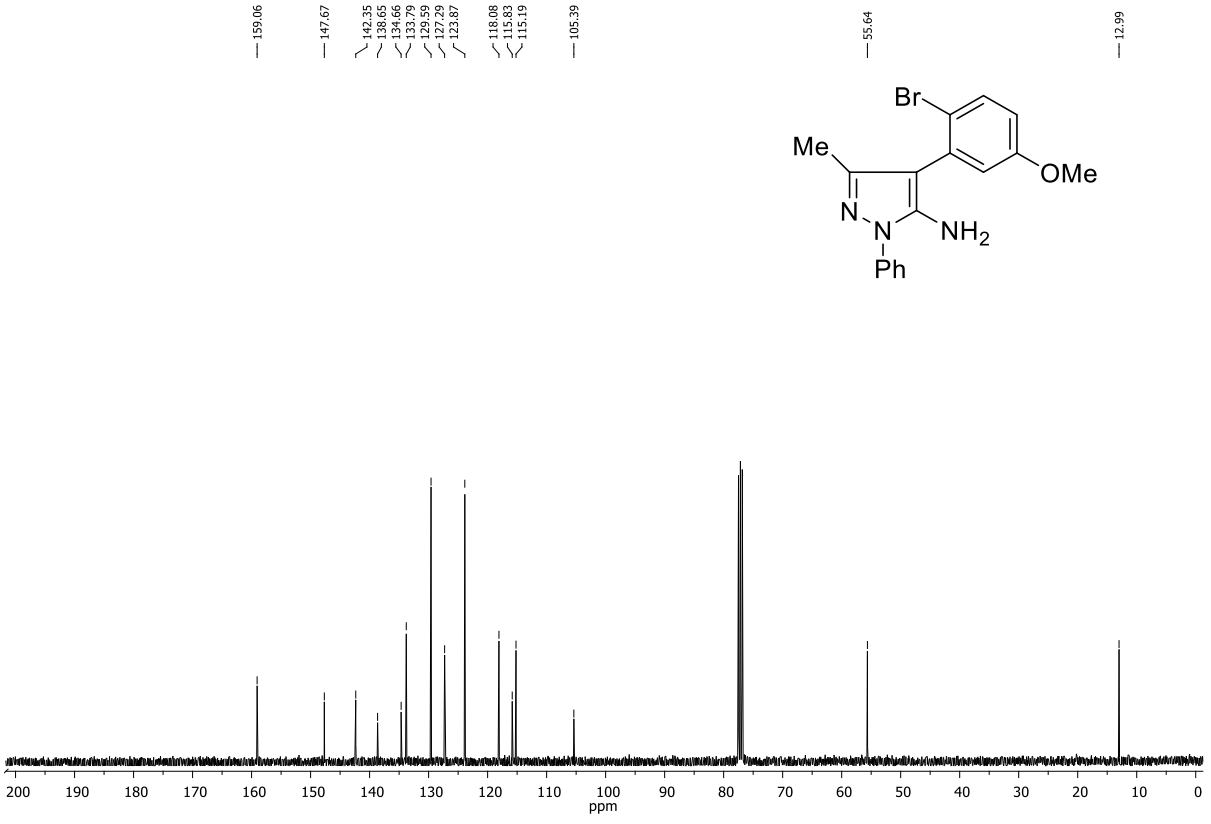
^{13}C{^{1}H} NMR of **2r** in $CDCl_3$ (100 MHz):



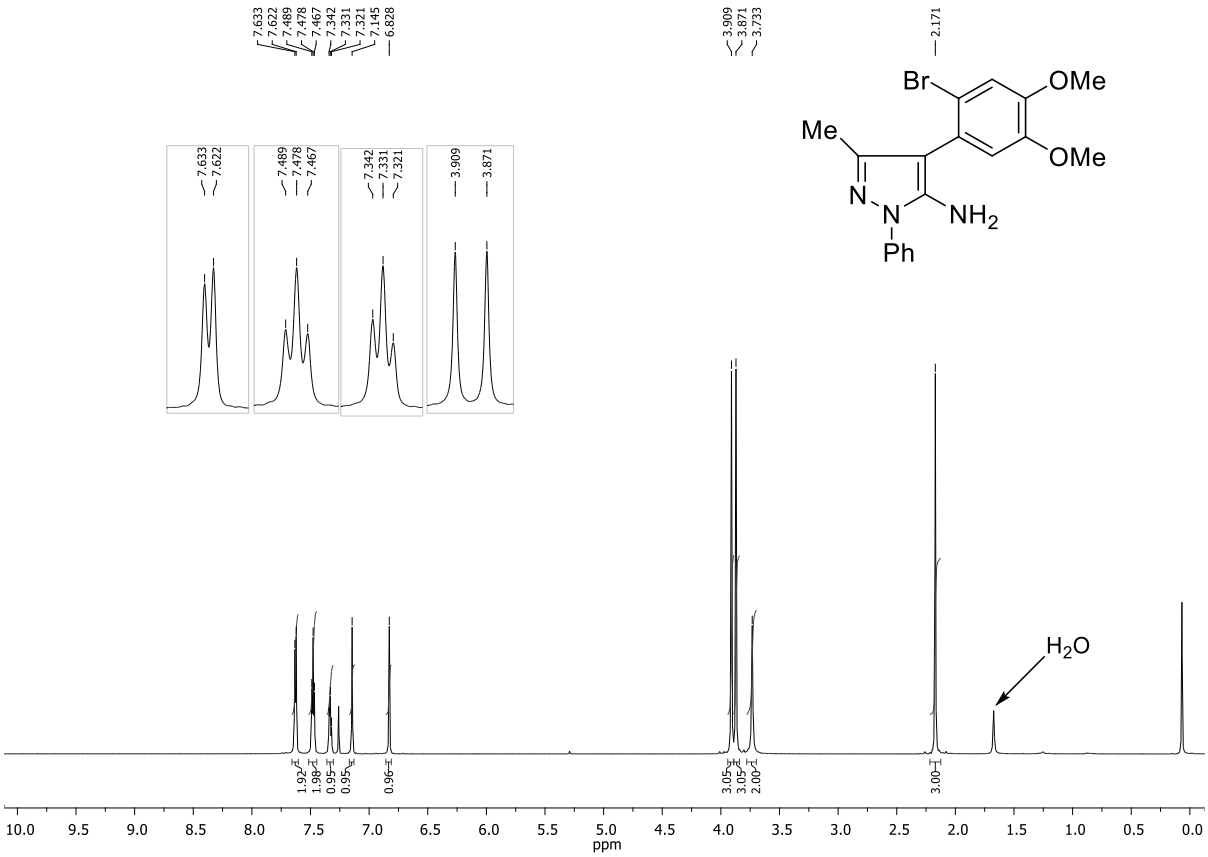
^{1}H NMR of **2s** in $CDCl_3$ (400 MHz):



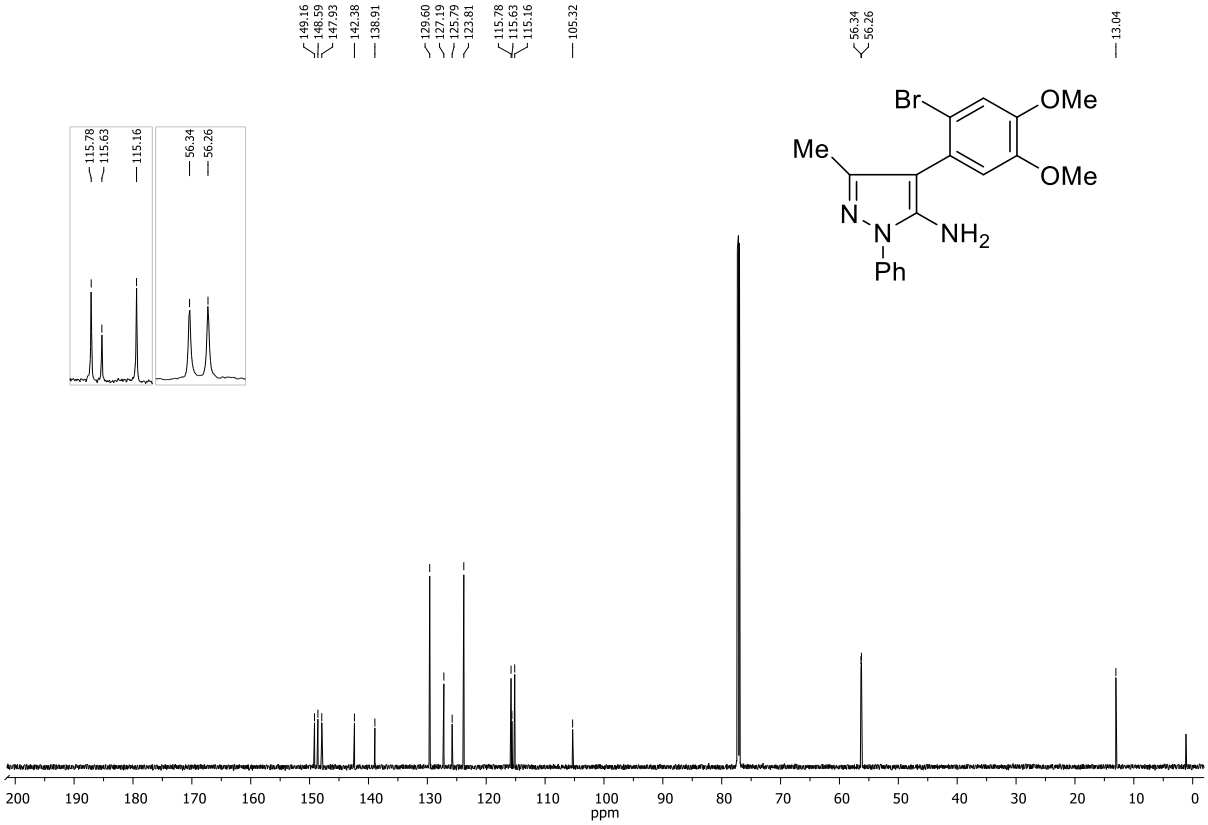
^{13}C{^{1}H} NMR of **2s** in $CDCl_3$ (100 MHz):



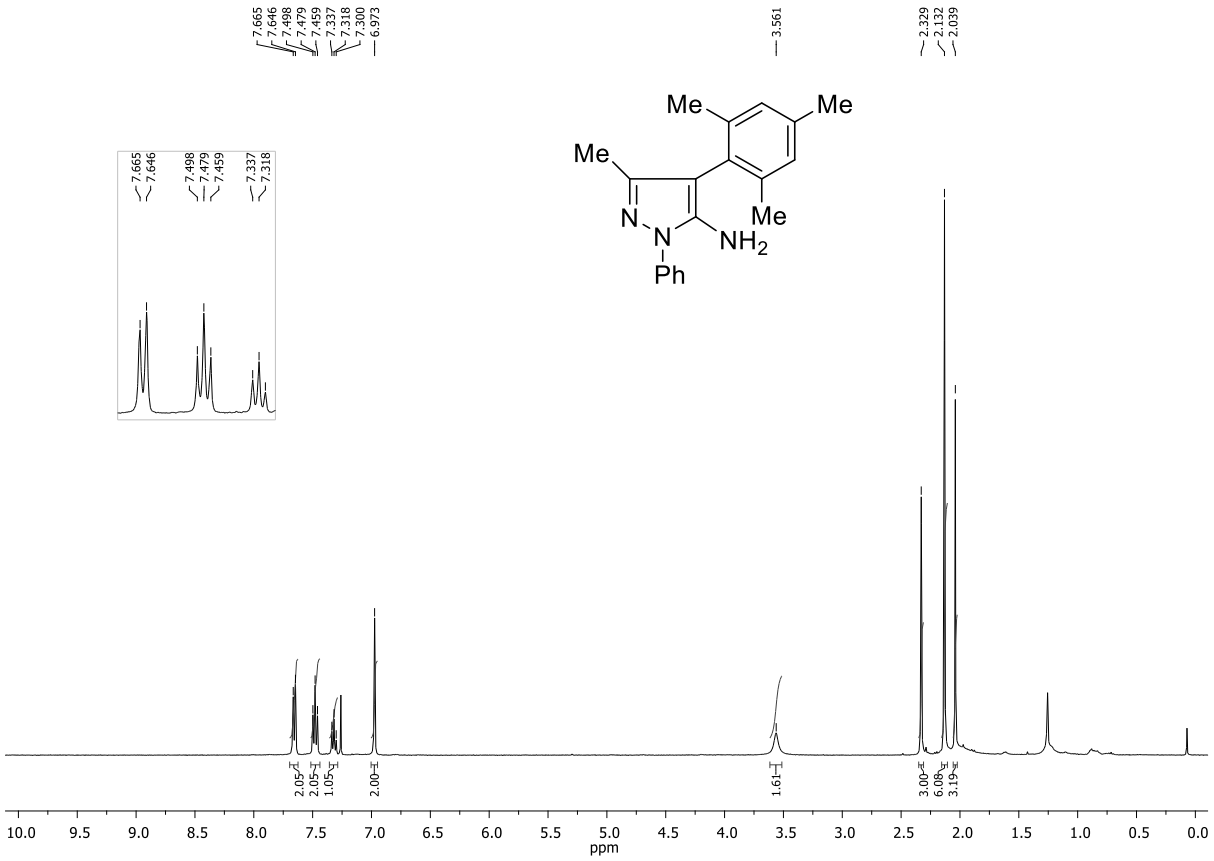
^{1}H NMR of **2t** in $CDCl_3$ (700 MHz):



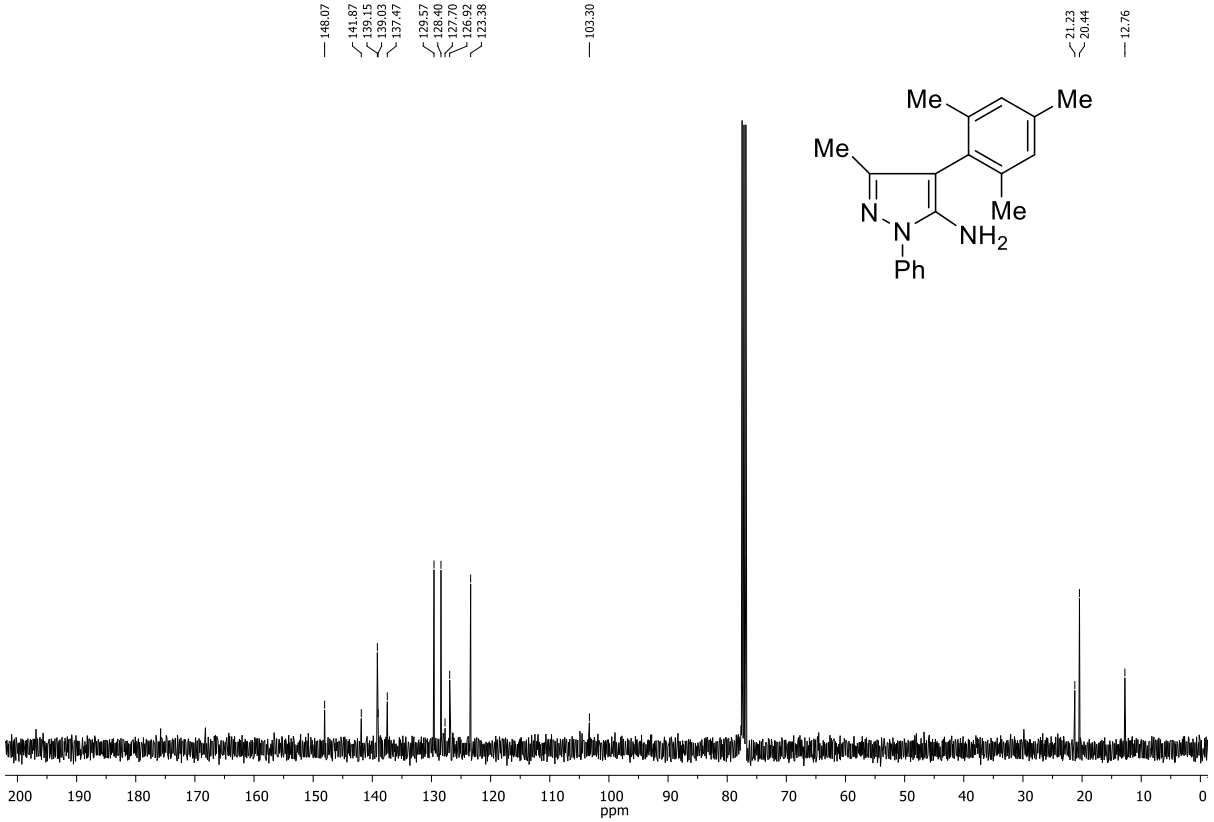
^{13}C{^{1}H} NMR of **2t** in $CDCl_3$ (175 MHz):



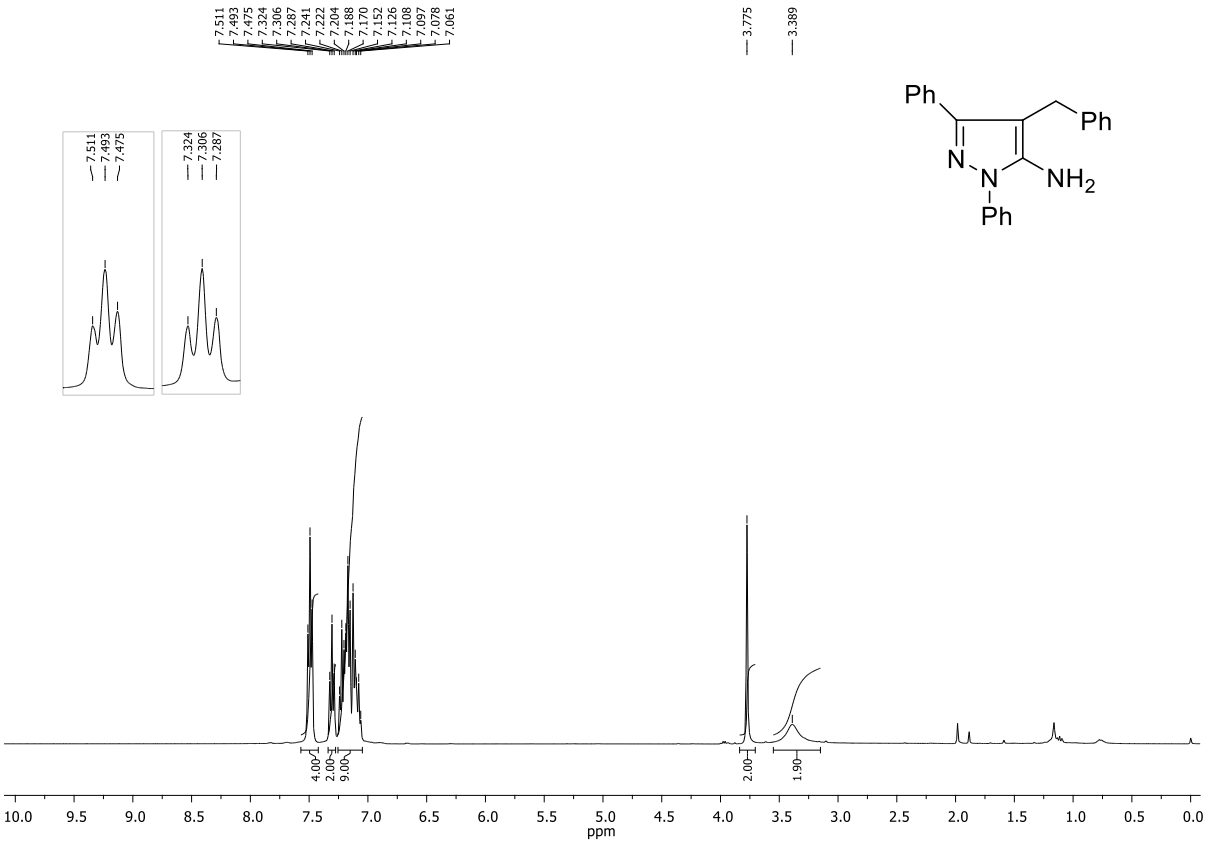
^{1}H NMR of **2u** in $CDCl_3$ (400 MHz):



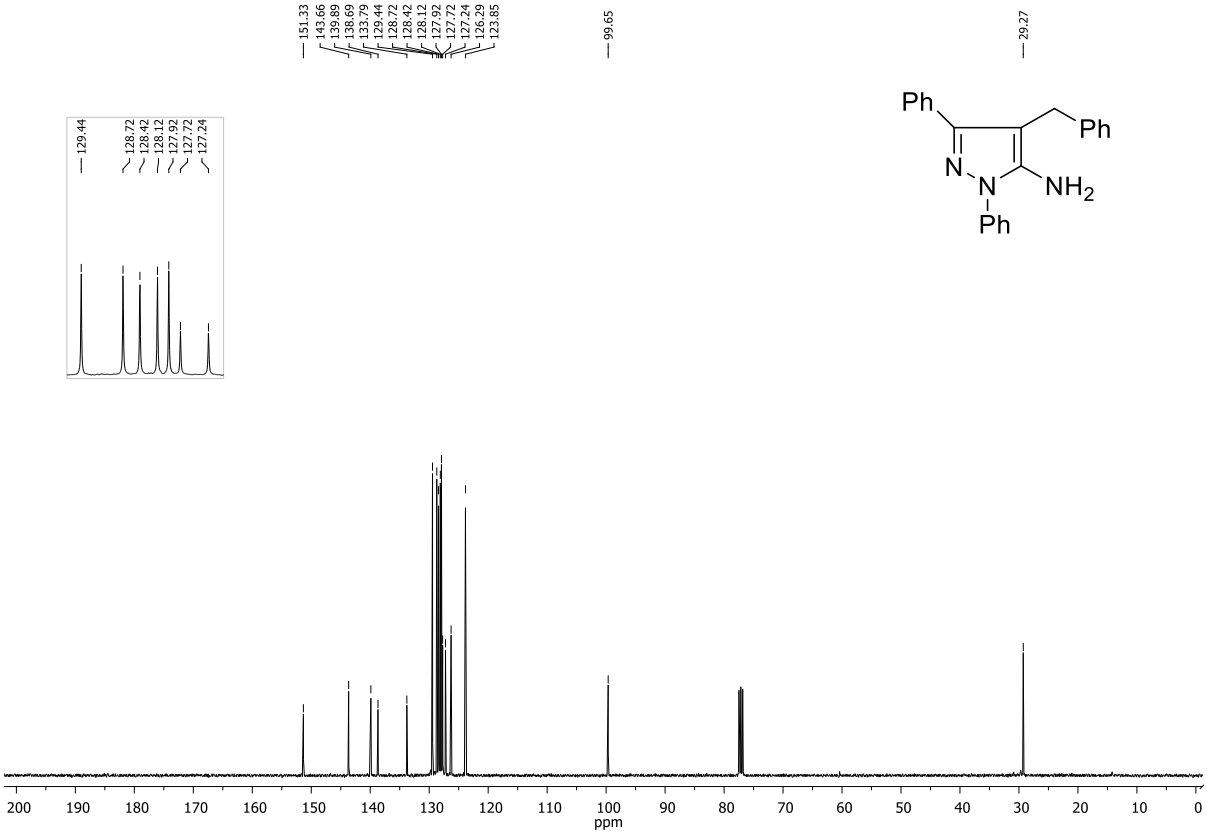
^{13}C{^{1}H} NMR of **2u** in $CDCl_3$ (100 MHz):



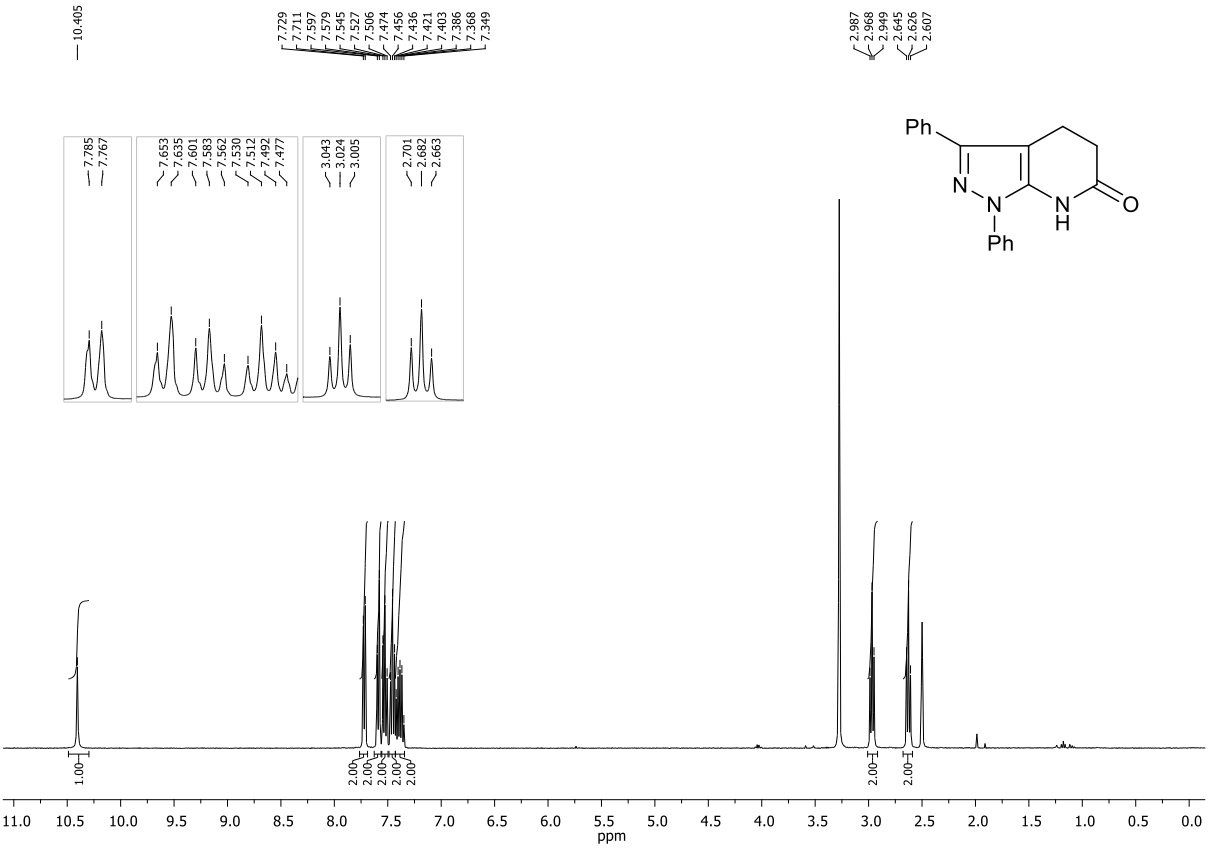
^{1}H NMR of **2v** in $CDCl_3$ (400 MHz):



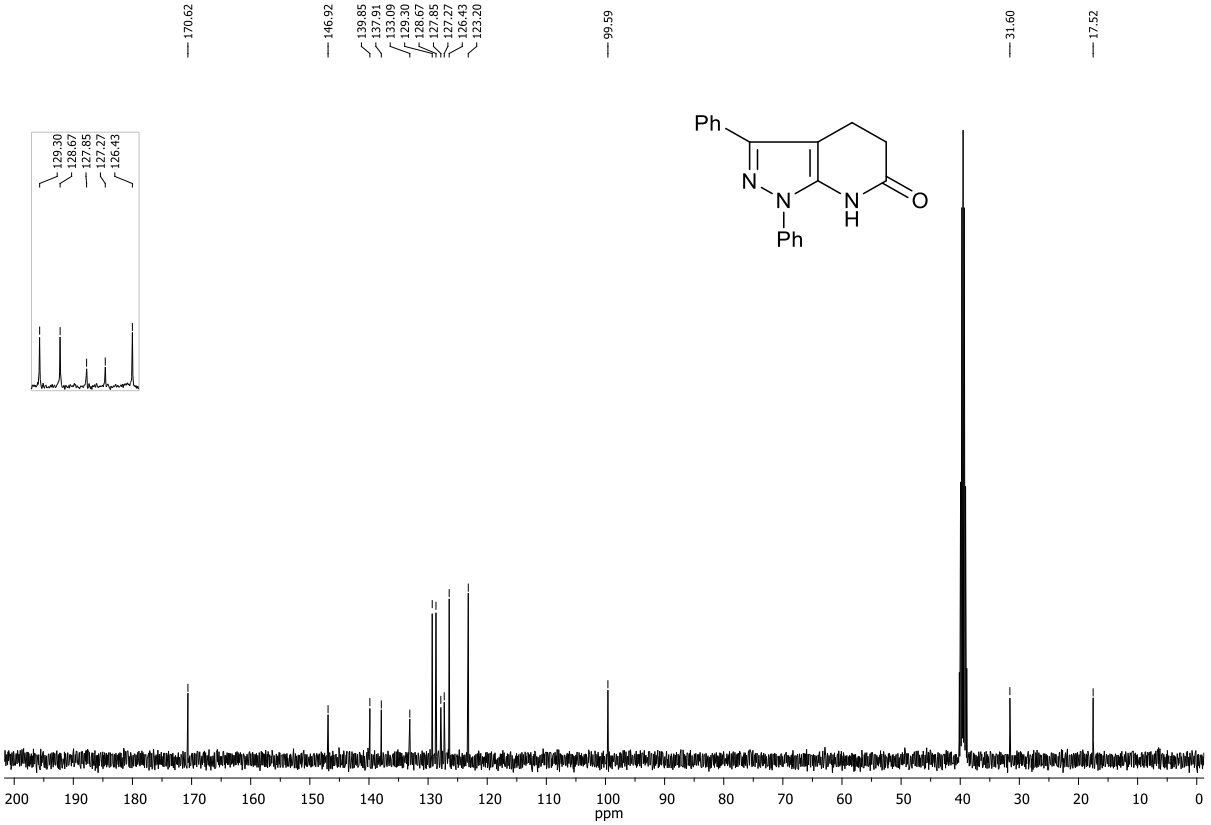
^{13}C{^{1}H} NMR of **2v** in $CDCl_3$ (100 MHz):



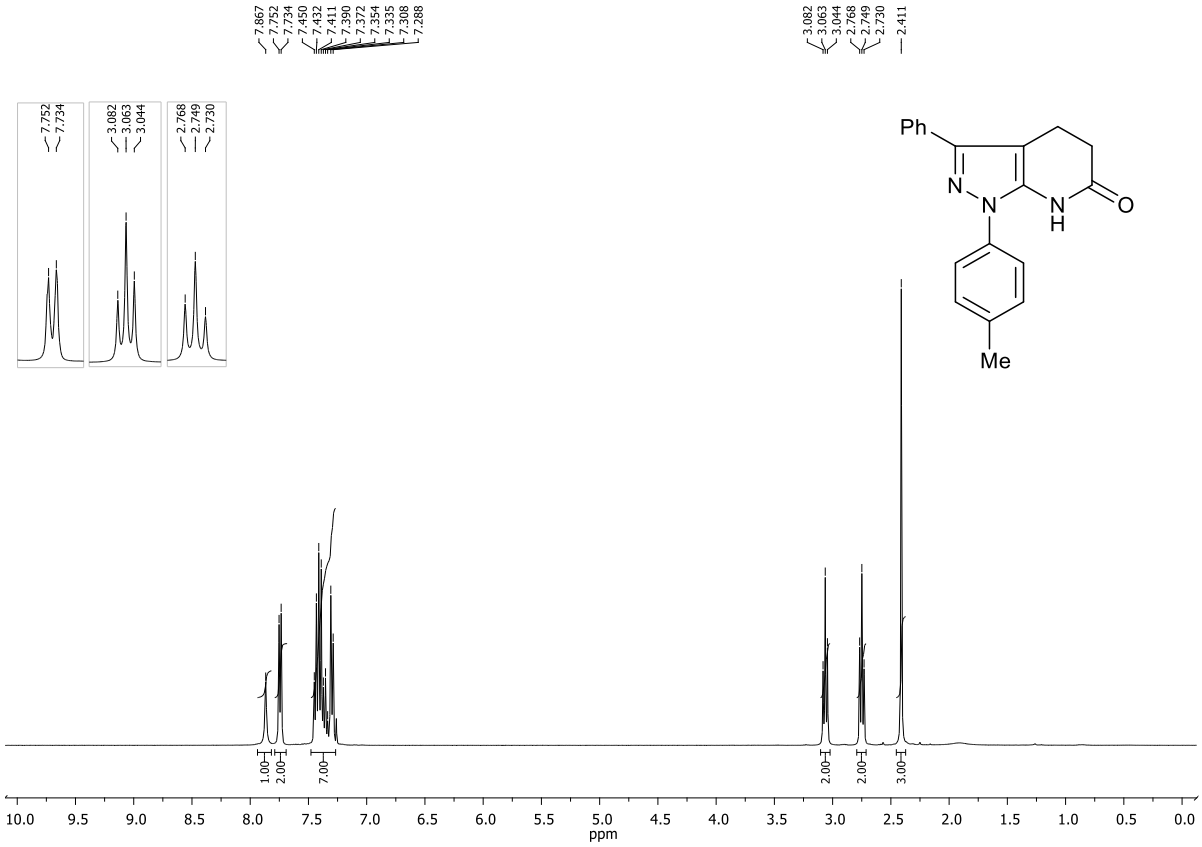
^{1}H NMR of **12a** in DMSO-d_6 (400 MHz):



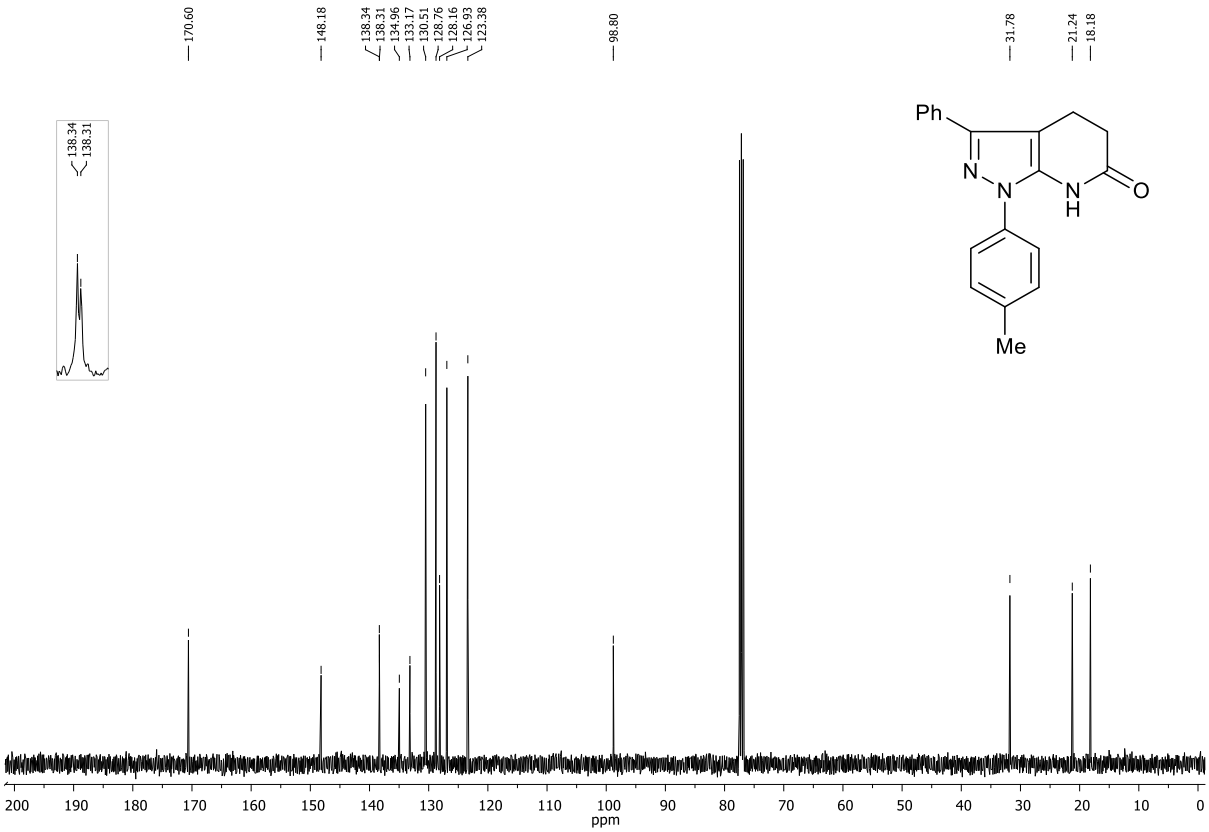
^{13}C{^{1}H} NMR of **12a** in DMSO-d_6 (100 MHz):



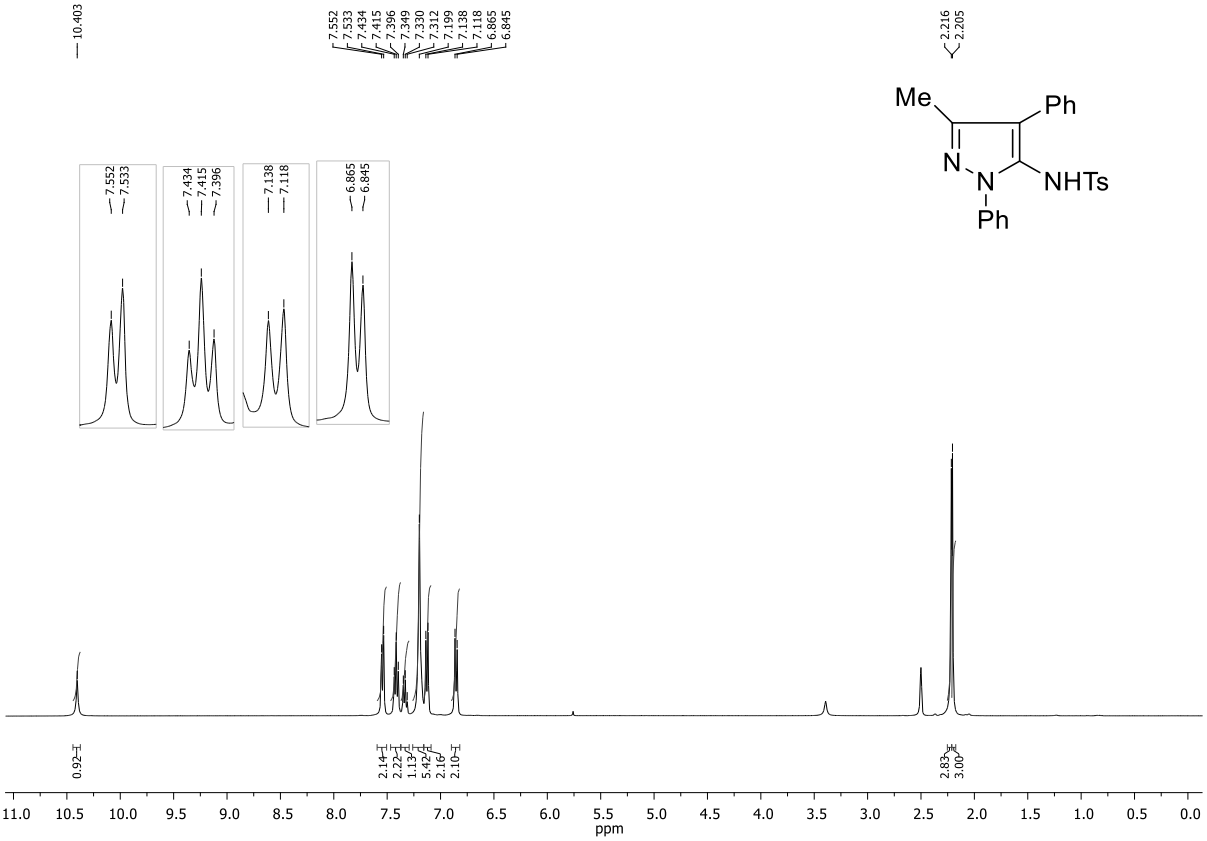
^{1}H NMR of **12b** in $CDCl_3$ (400 MHz):



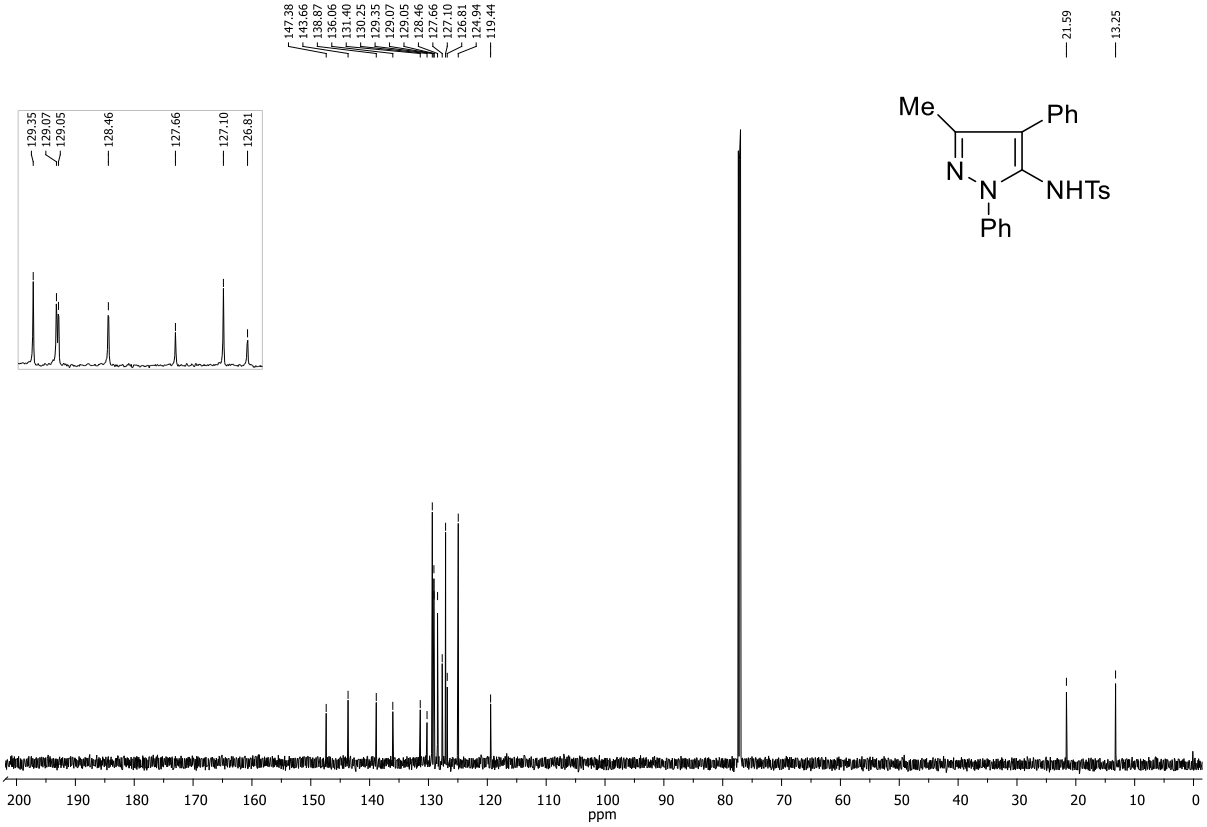
^{13}C{^{1}H} NMR of **12b** in $CDCl_3$ (100 MHz):



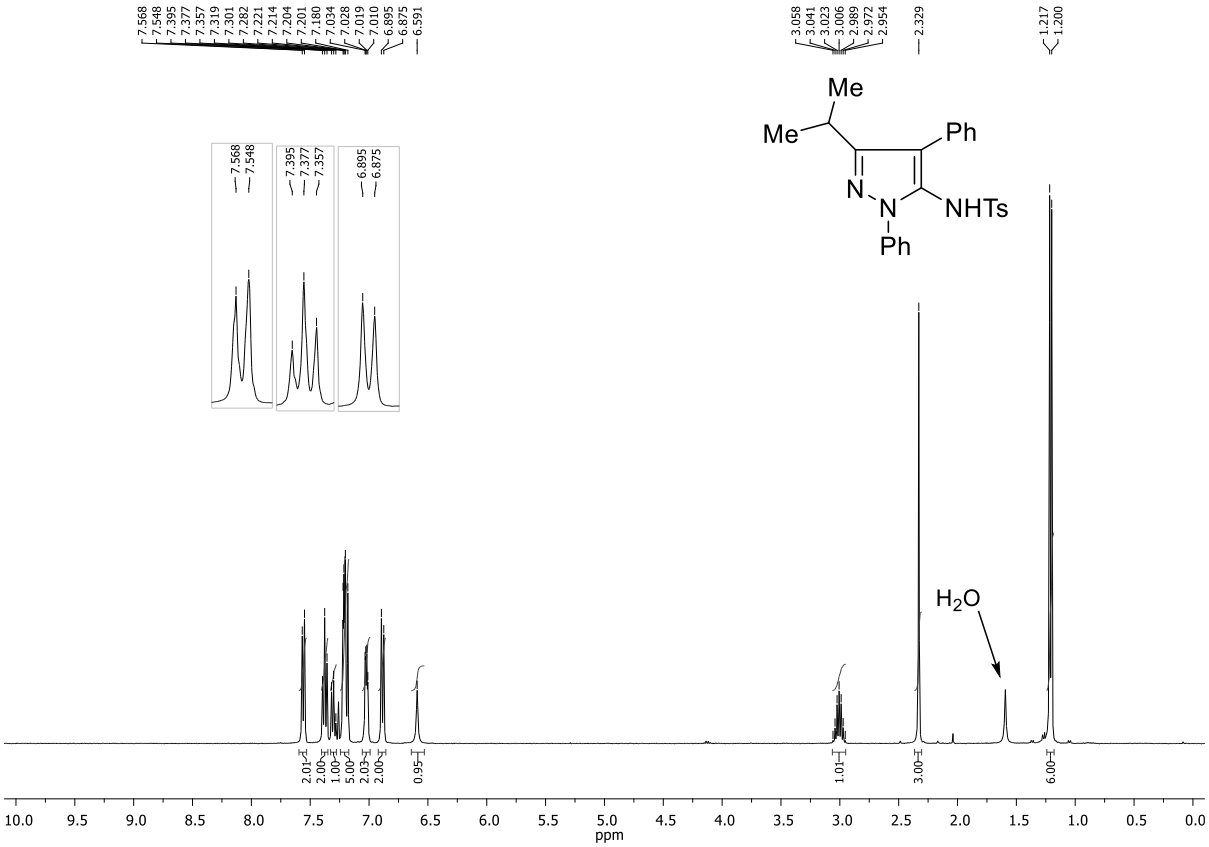
^{1}H NMR of **1a** in DMSO-d_6 (400 MHz):



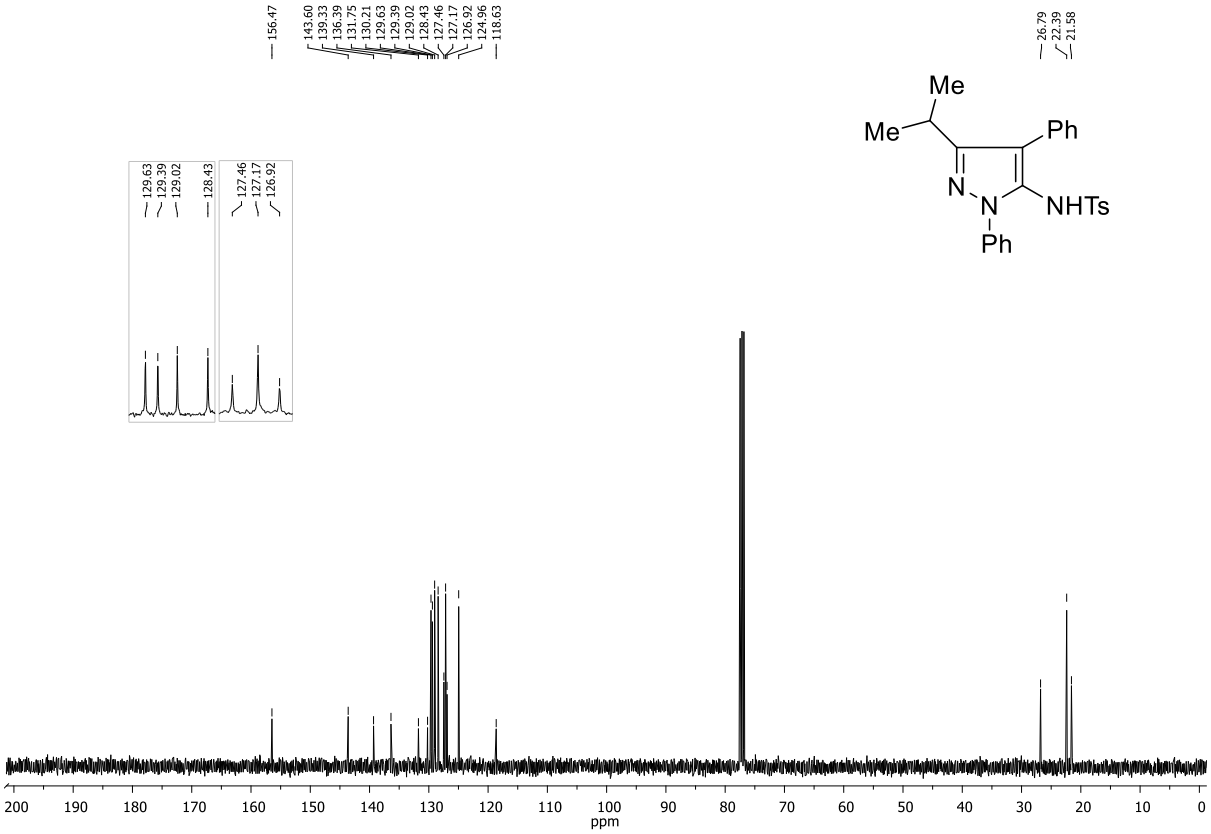
^{13}C{^{1}H} NMR of **1a** in DMSO-d_6 (100 MHz):



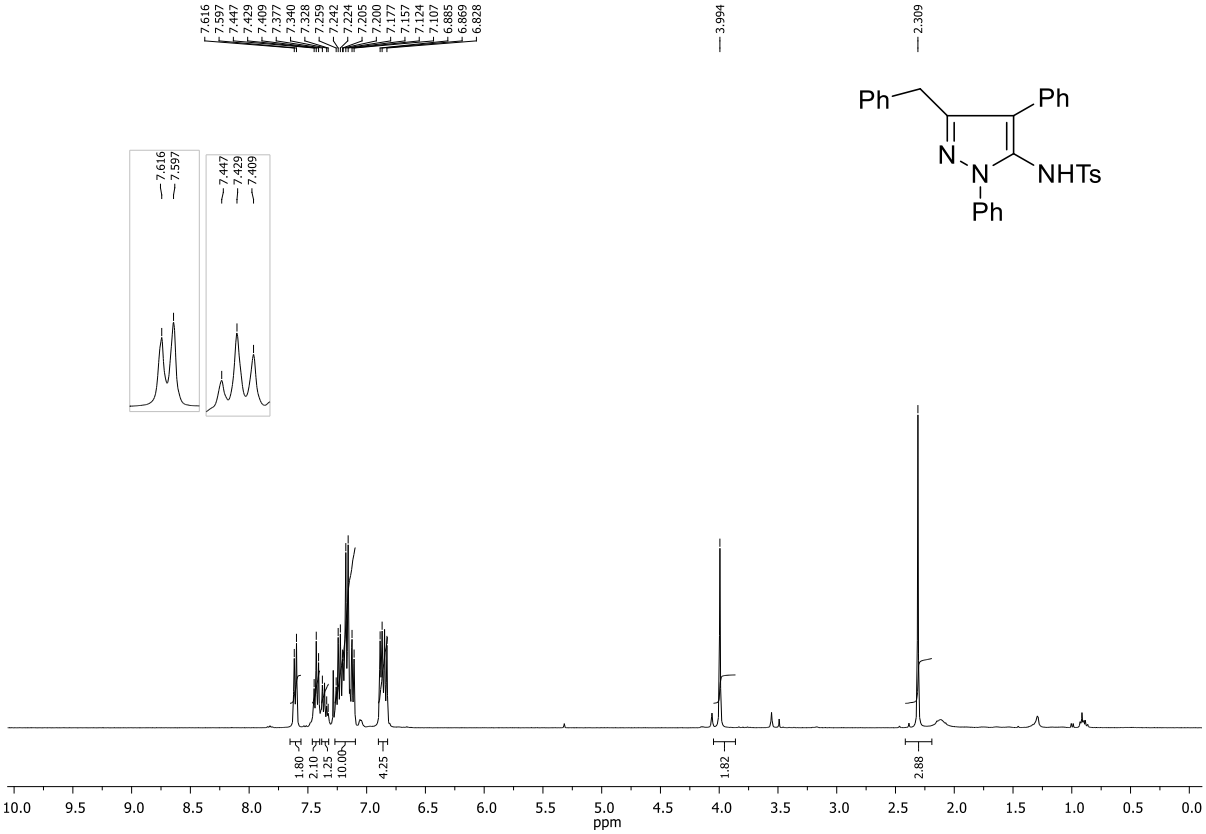
^{1}H NMR of **1b** in $CDCl_3$ (400 MHz):



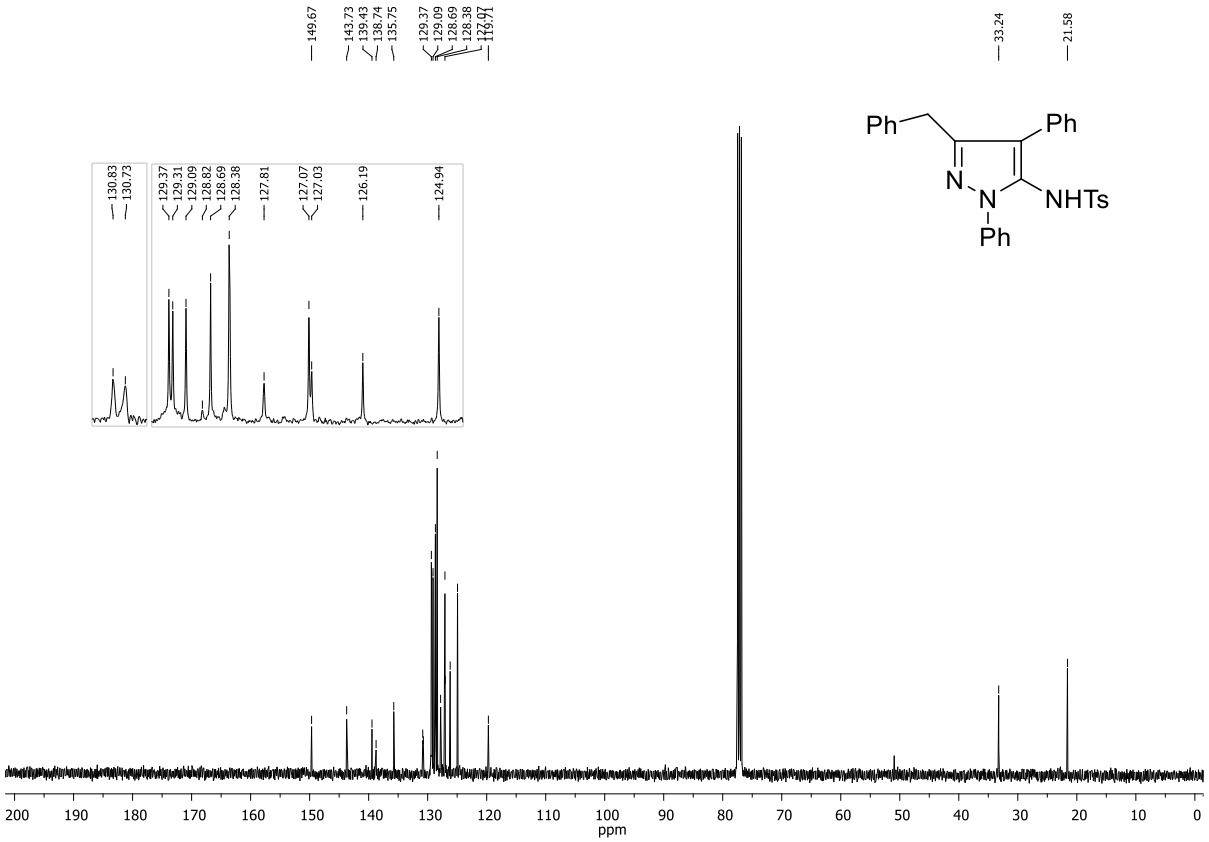
^{13}C{^{1}H} NMR of **1b** in $CDCl_3$ (100 MHz):



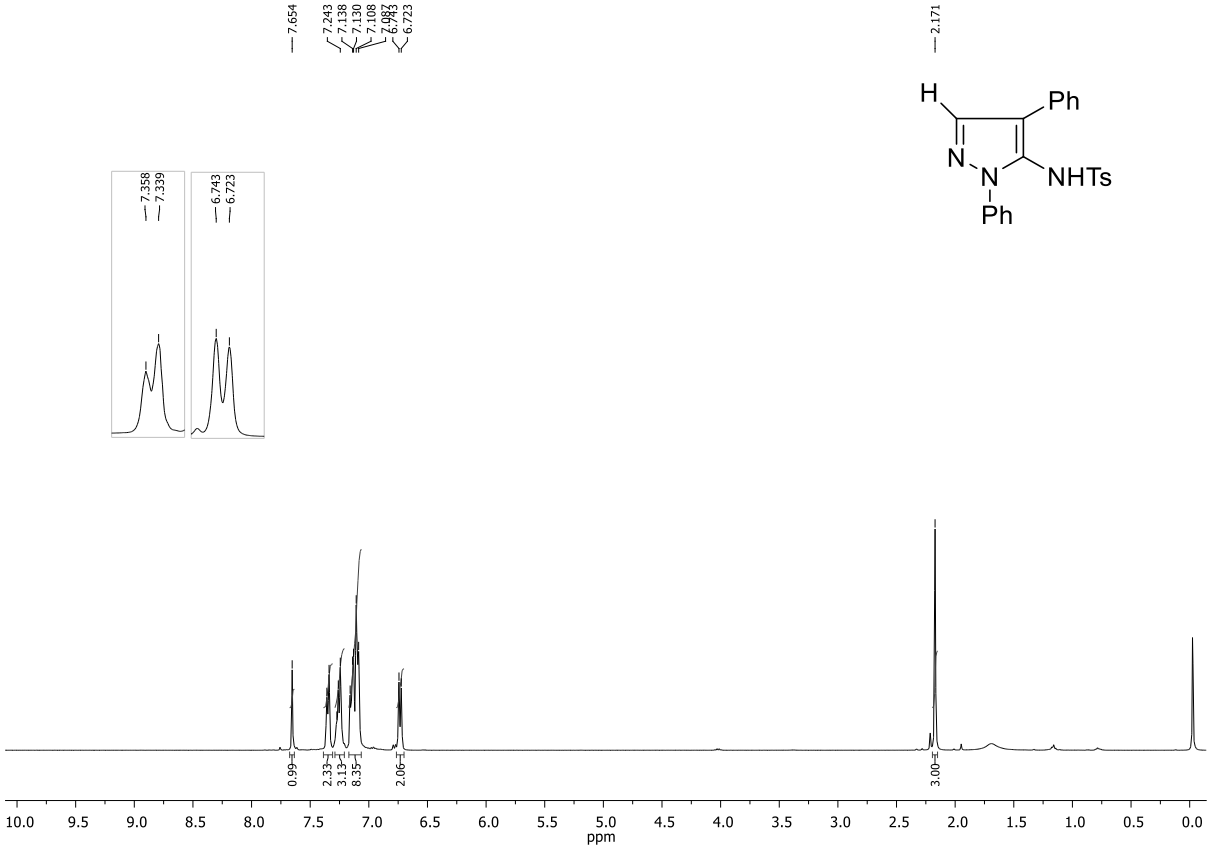
^{1}H NMR of **1c** in $CDCl_3$ (400 MHz):



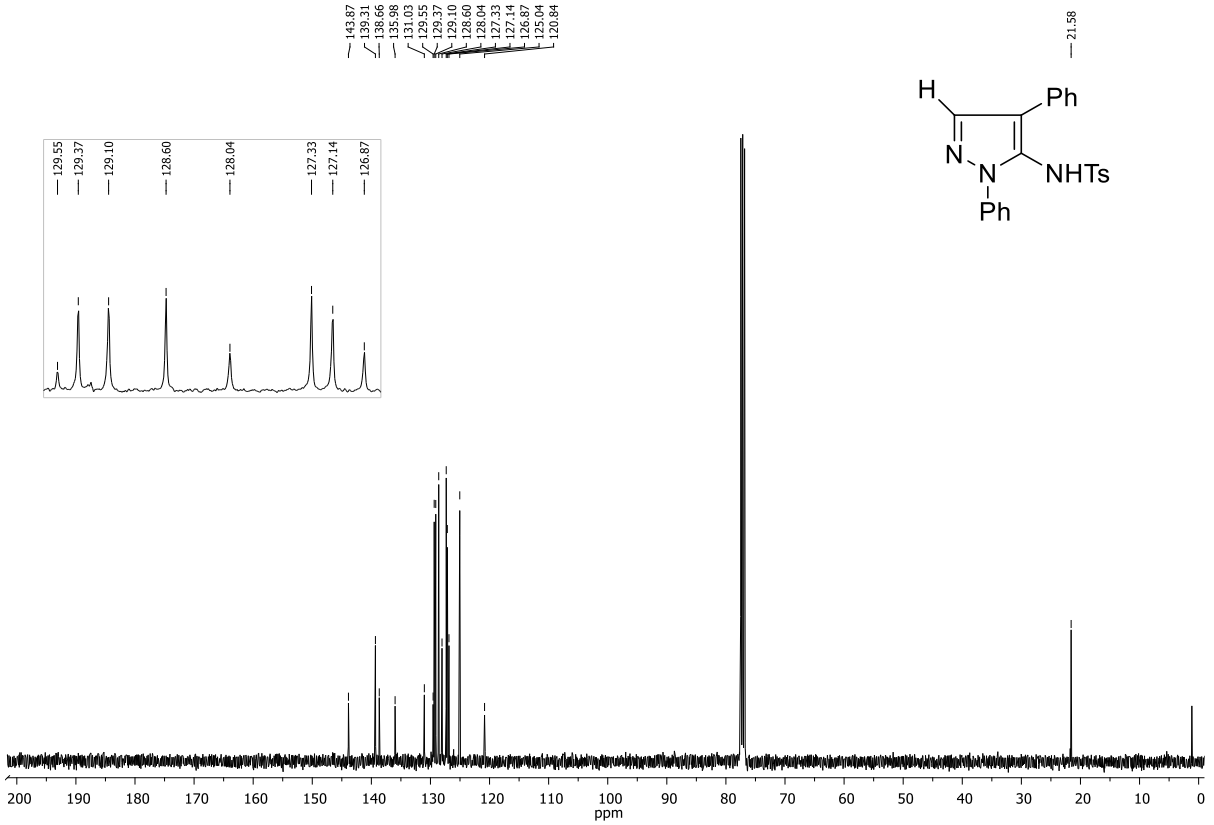
^{13}C{^{1}H} NMR of **1c** in $CDCl_3$ (100 MHz):



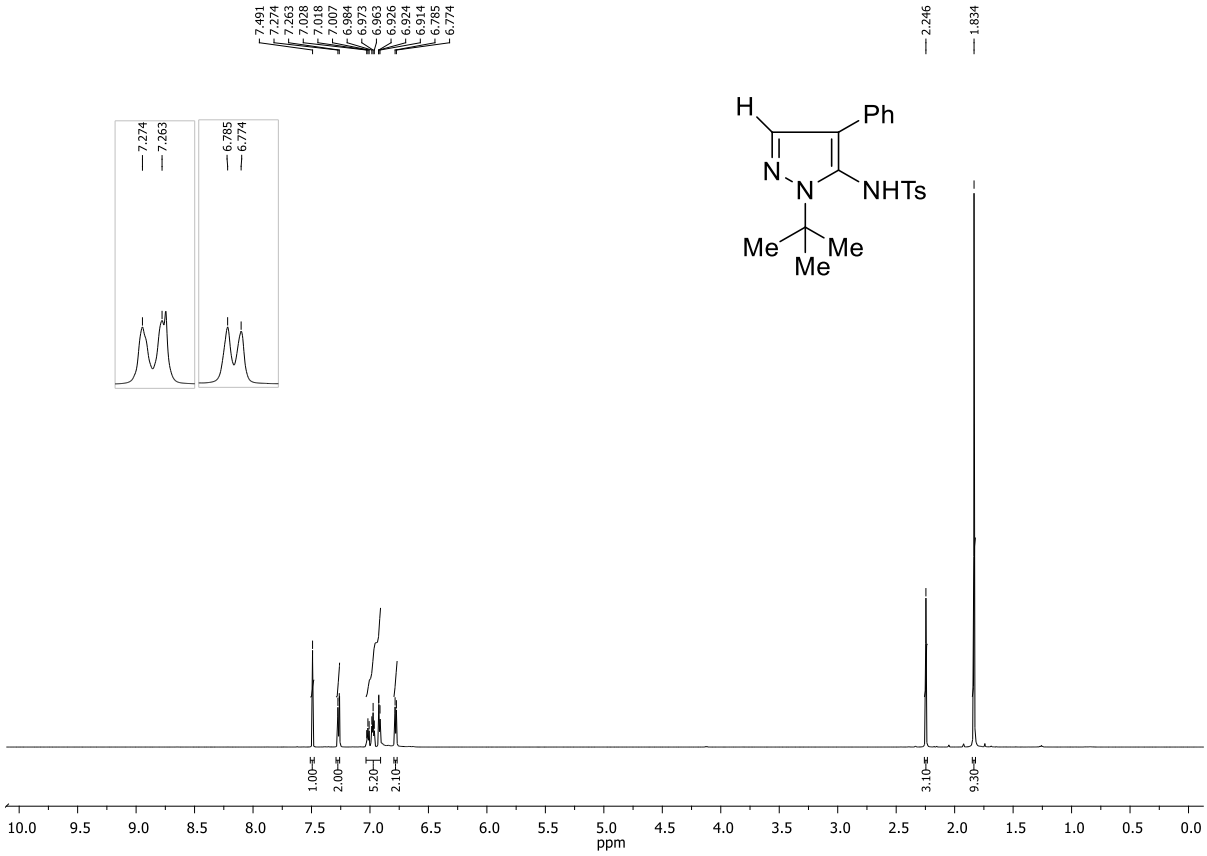
^{1}H NMR of **1d** in $CDCl_3$ (400 MHz):



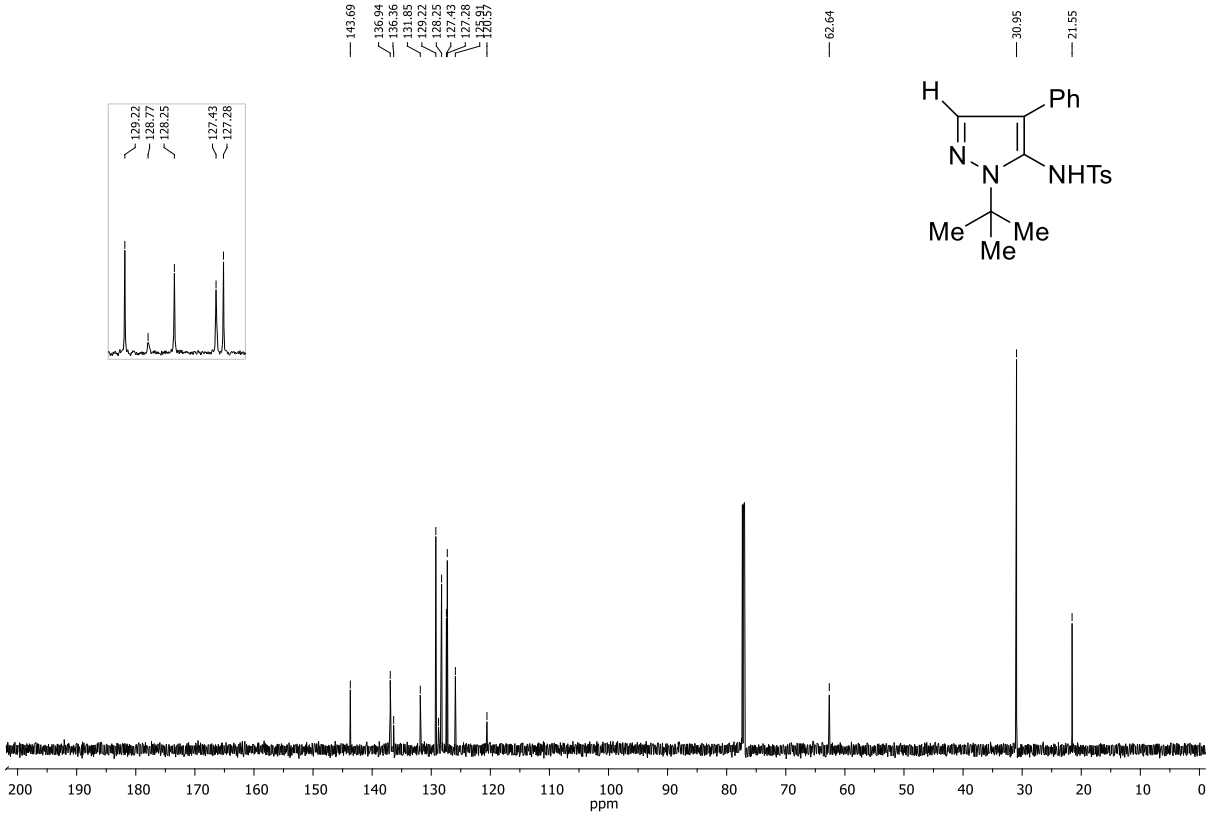
^{13}C{^{1}H} NMR of **1d** in $CDCl_3$ (100 MHz):



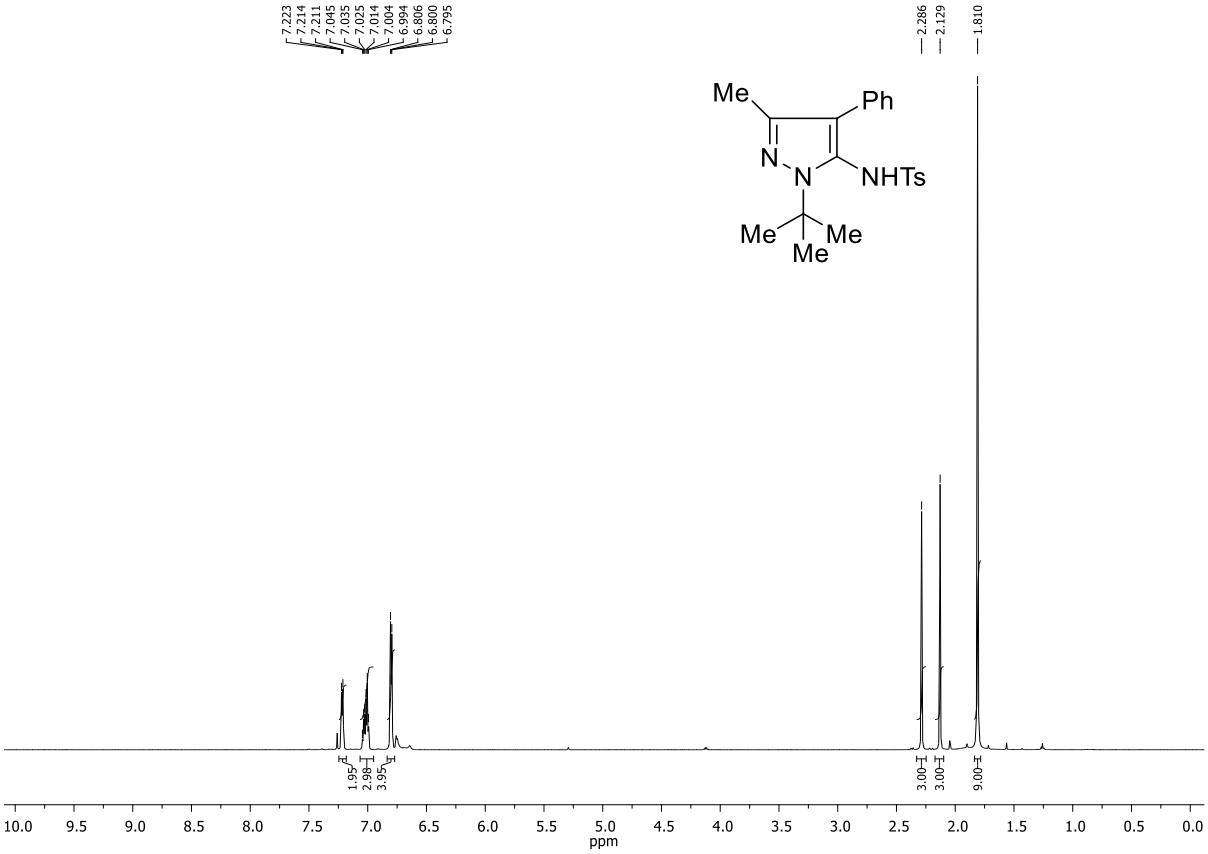
^{1}H NMR of **1e** in $CDCl_3$ (700 MHz):



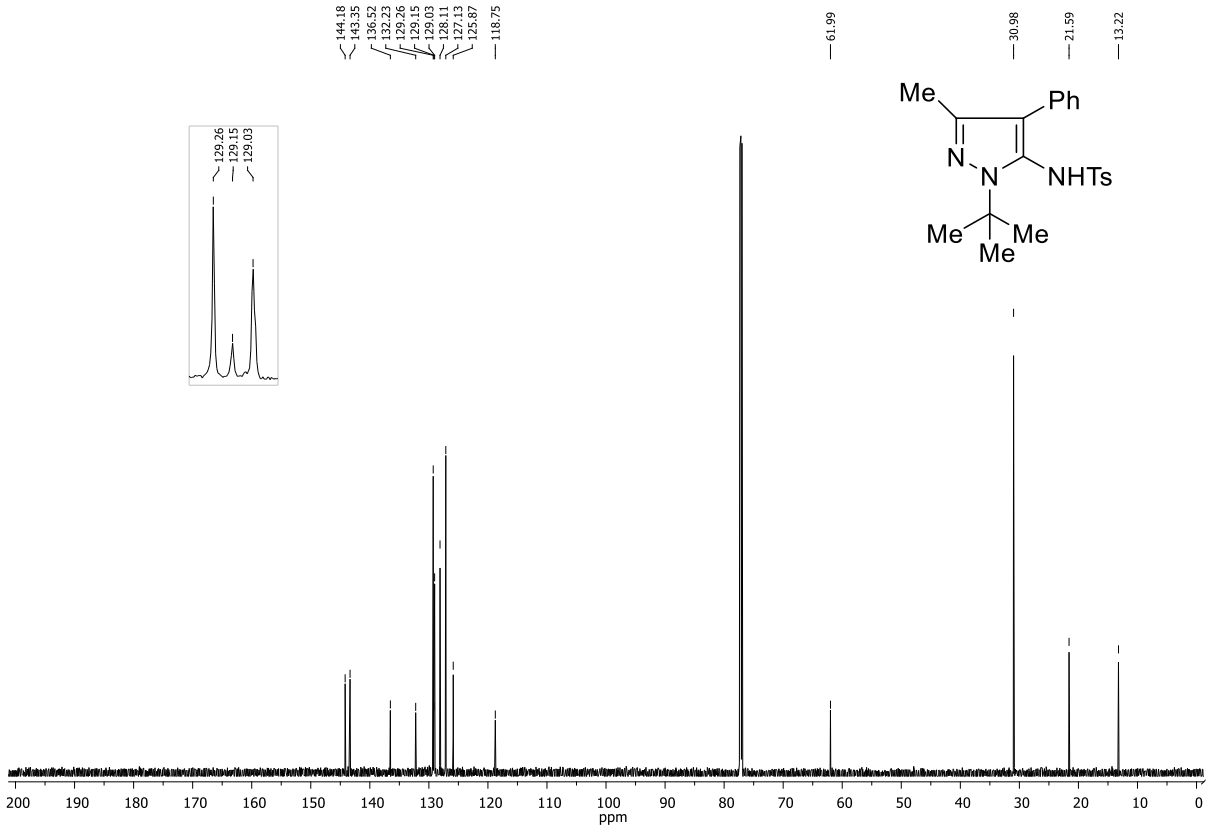
^{13}C{^{1}H} NMR of **1e** in $CDCl_3$ (175 MHz):



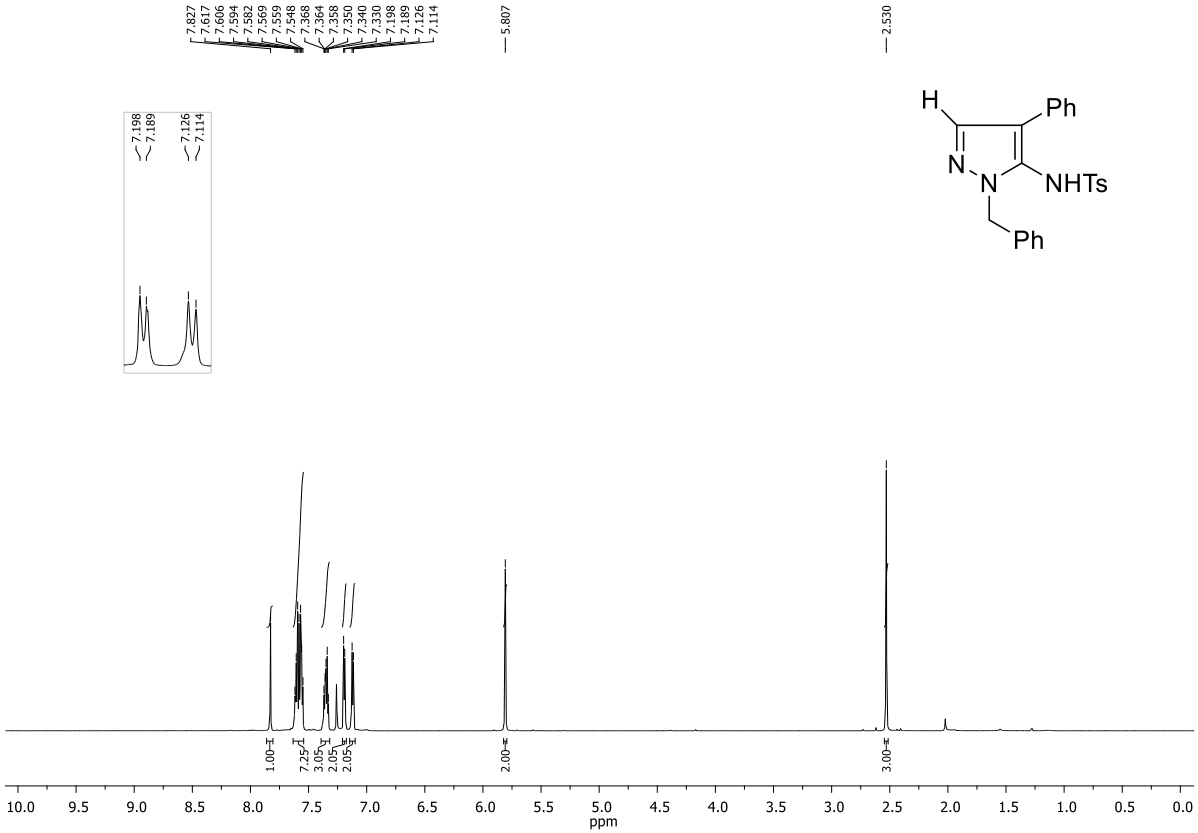
^{1}H NMR of **1f** in $CDCl_3$ (700 MHz):



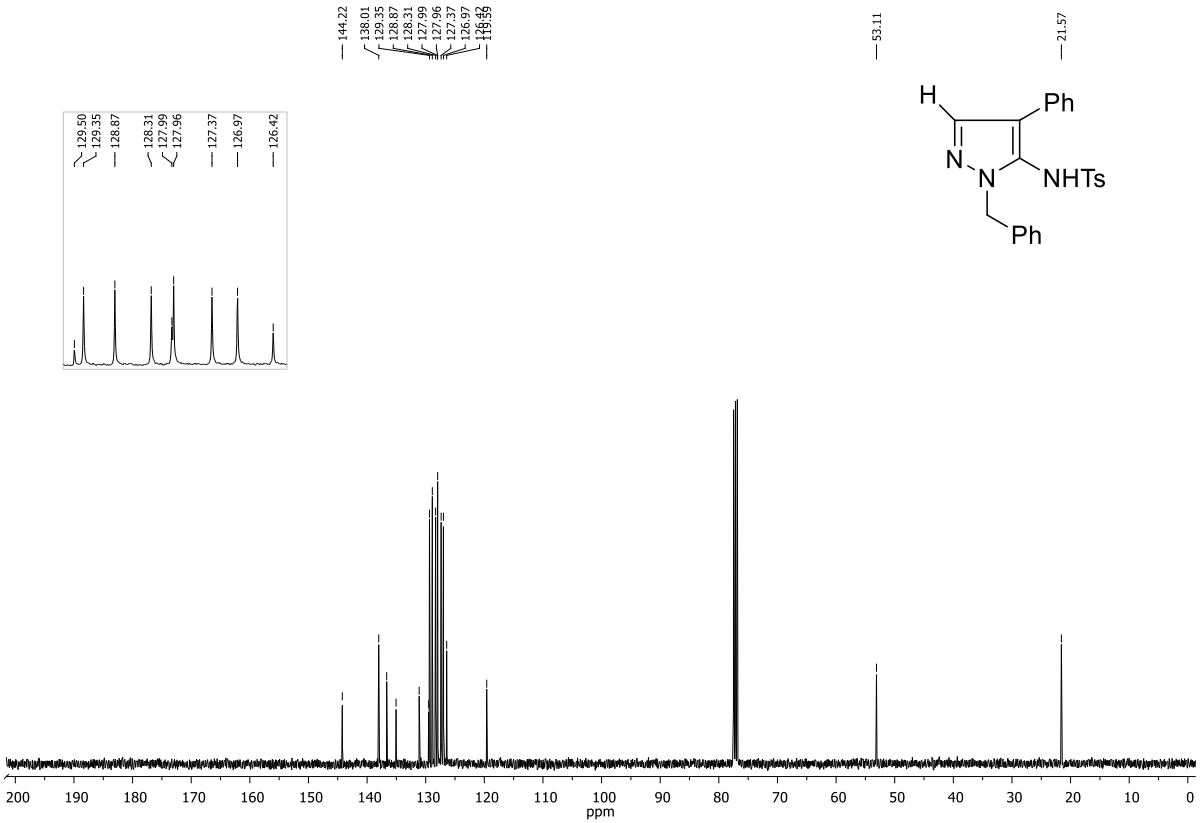
^{13}C{^{1}H} NMR of **1f** in $CDCl_3$ (700 MHz):



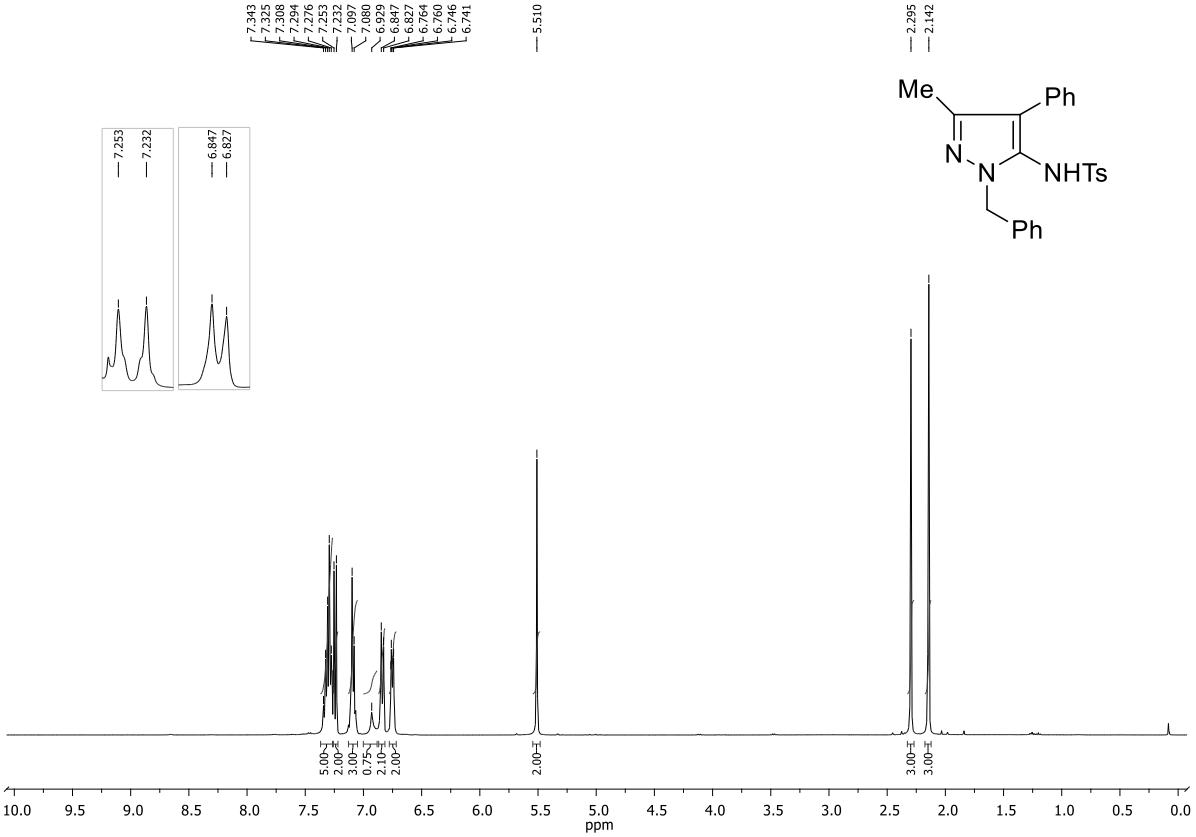
^{1}H NMR of **1g** in $CDCl_3$ (700 MHz):



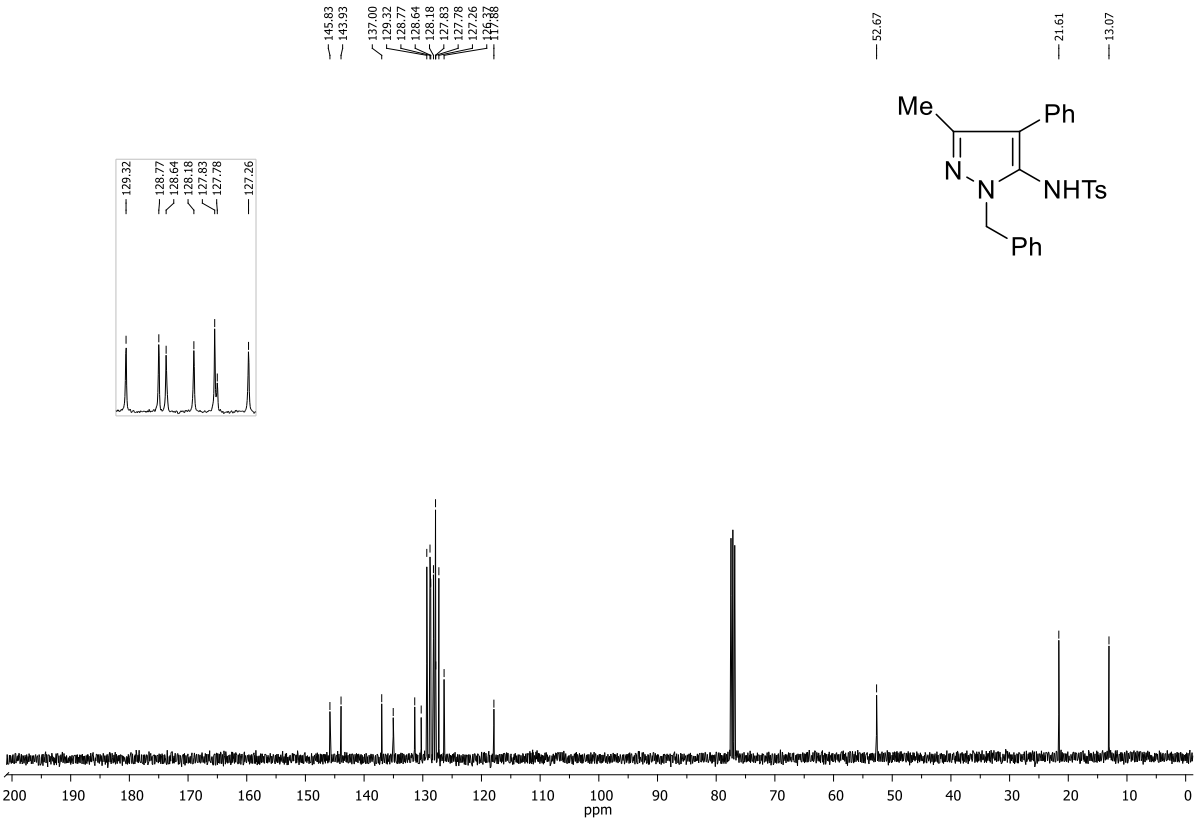
^{13}C{^{1}H} NMR of **1g** in $CDCl_3$ (100 MHz):



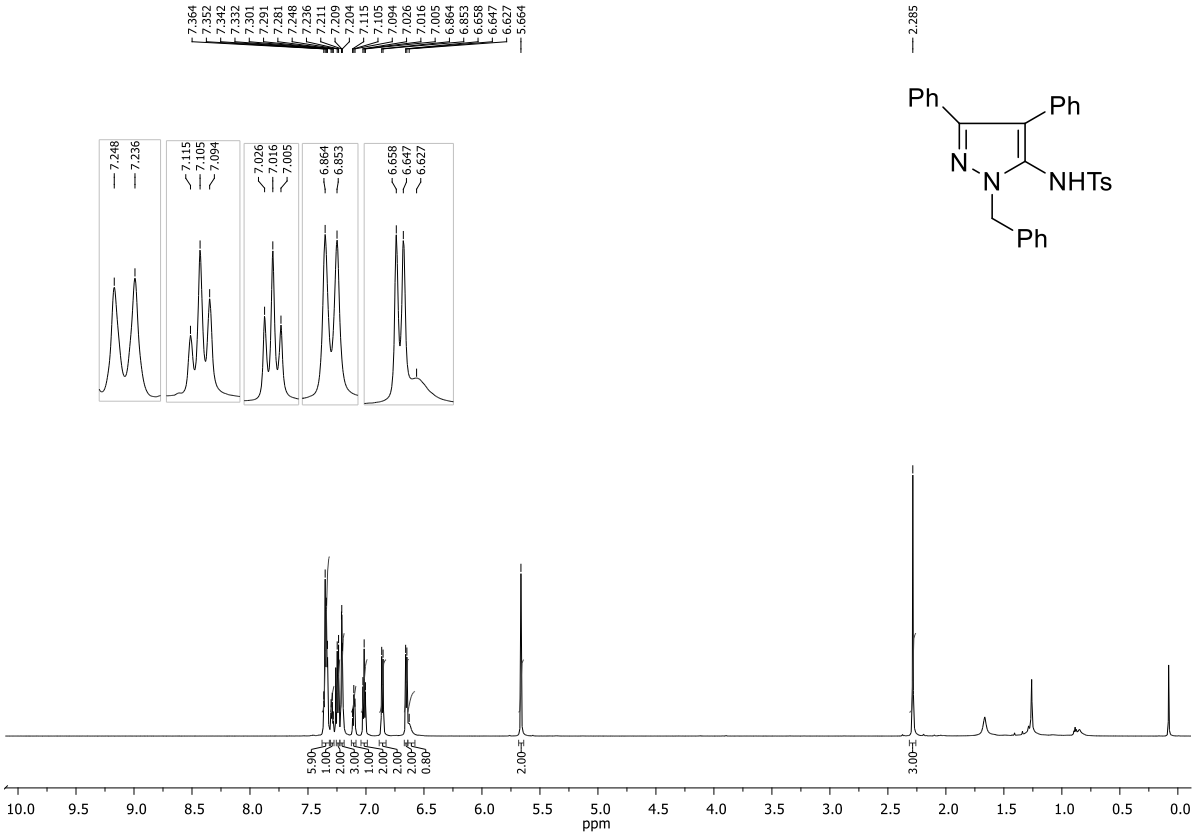
^{1}H NMR of **1h** in $CDCl_3$ (400 MHz):



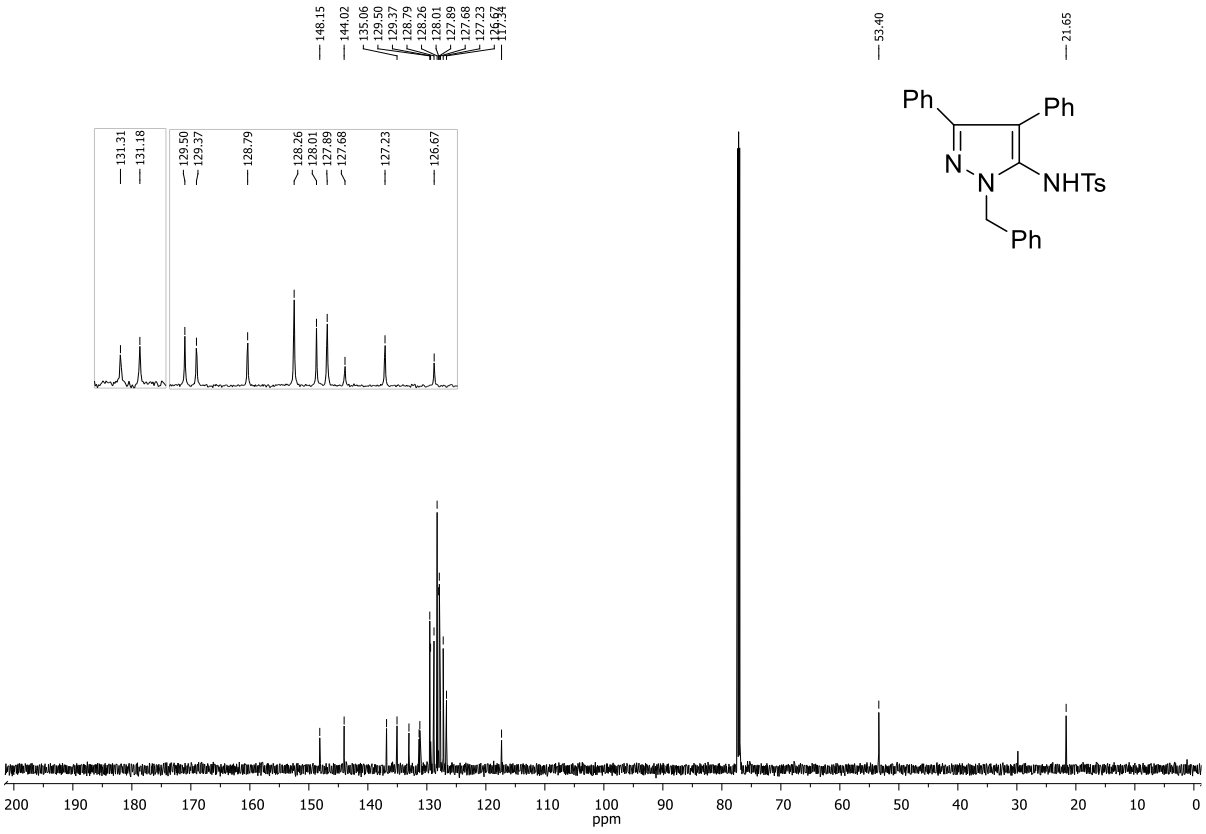
^{13}C{^{1}H} NMR of **1h** in $CDCl_3$ (100 MHz):



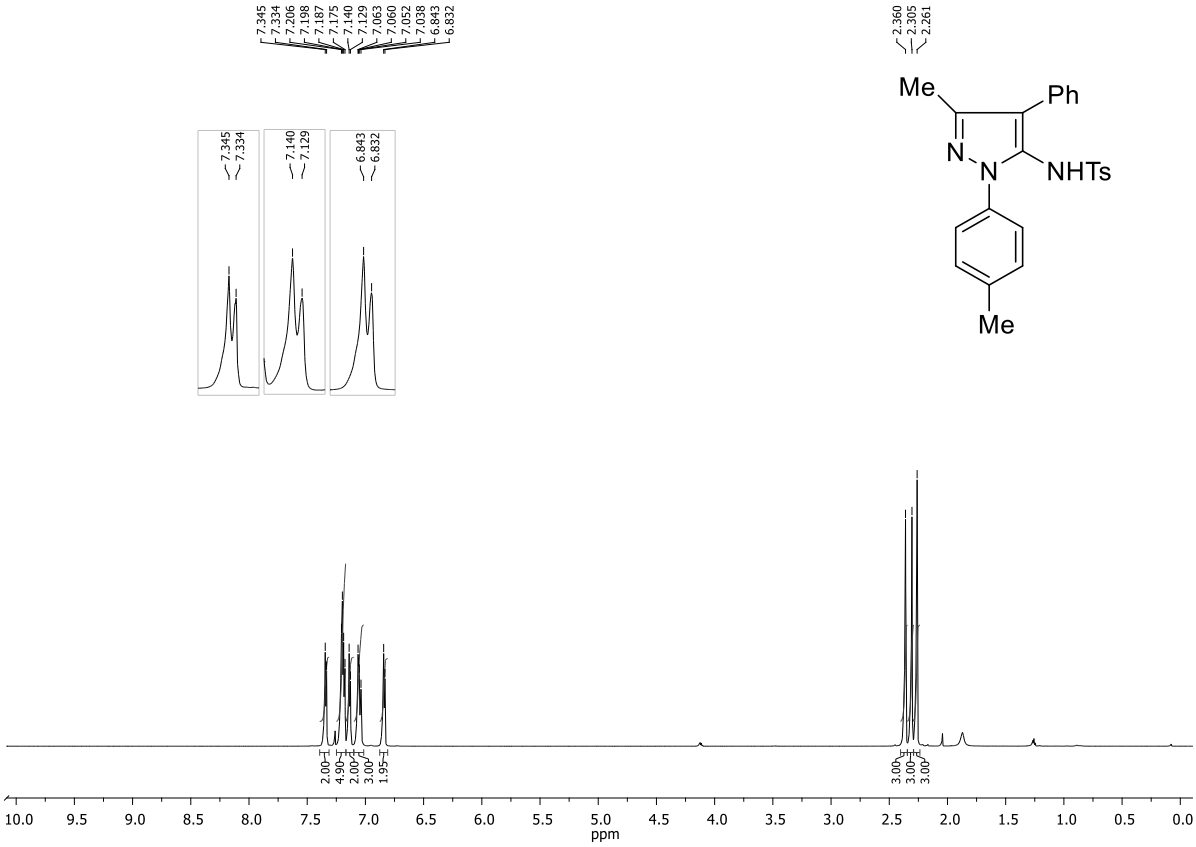
^{1}H NMR of **1i** in $CDCl_3$ (700 MHz):



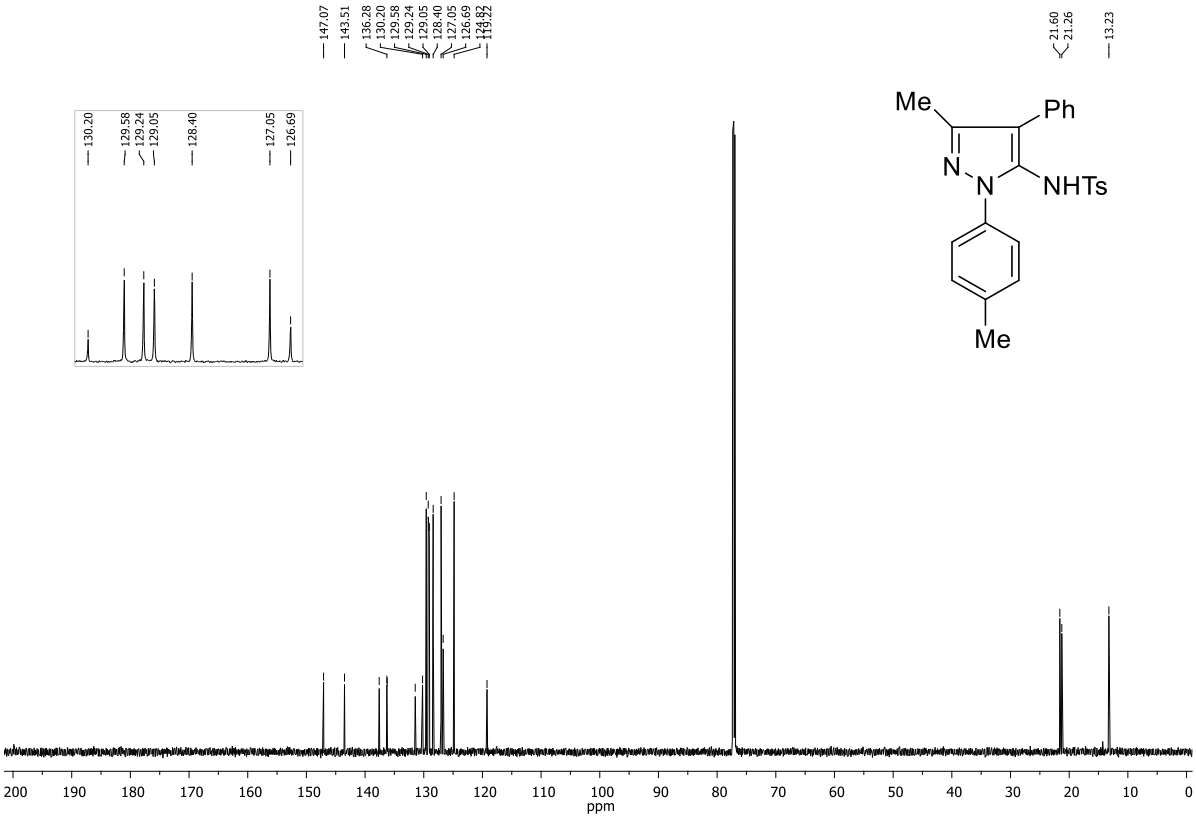
^{13}C{^{1}H} NMR of **1i** in $CDCl_3$ (175 MHz):



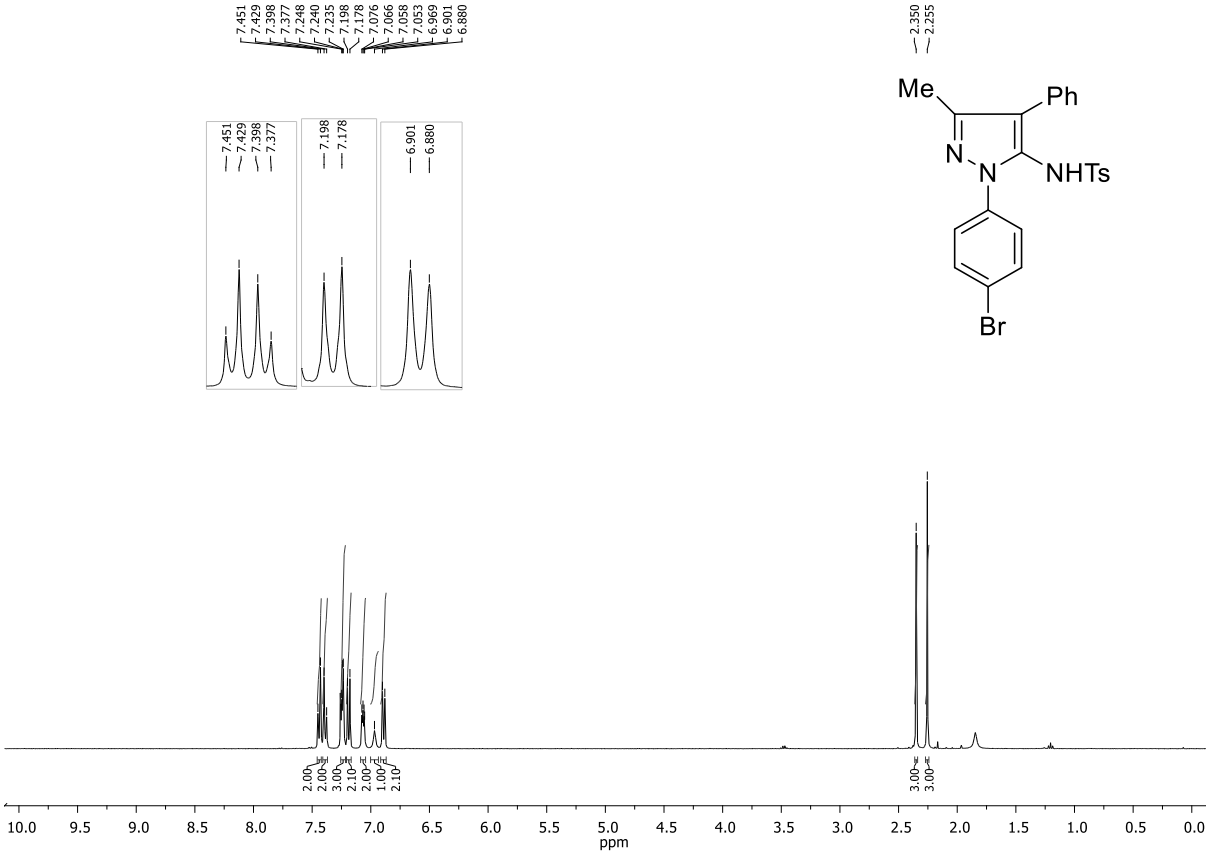
^{1}H NMR of **1j** in $CDCl_3$ (700 MHz):



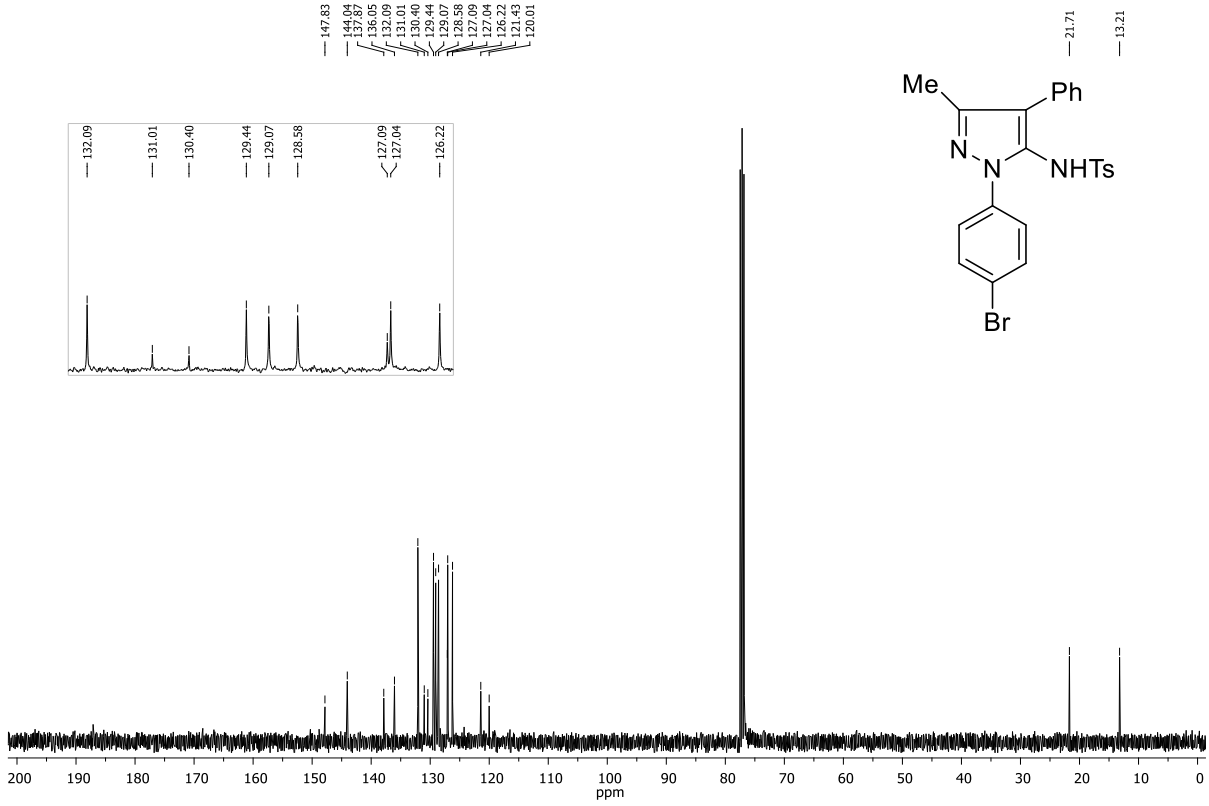
^{13}C{^{1}H} NMR of **1j** in $CDCl_3$ (175 MHz):



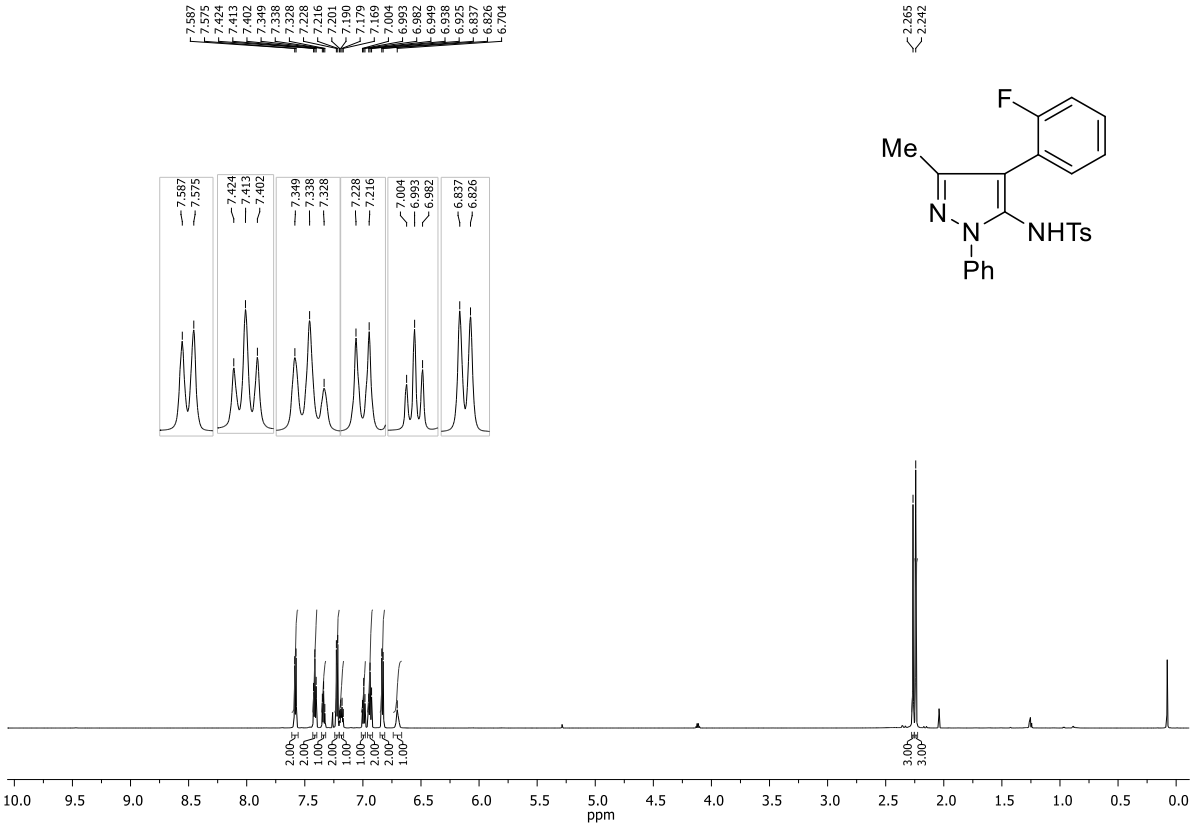
^{1}H NMR of **1k** in $CDCl_3$ (400 MHz):



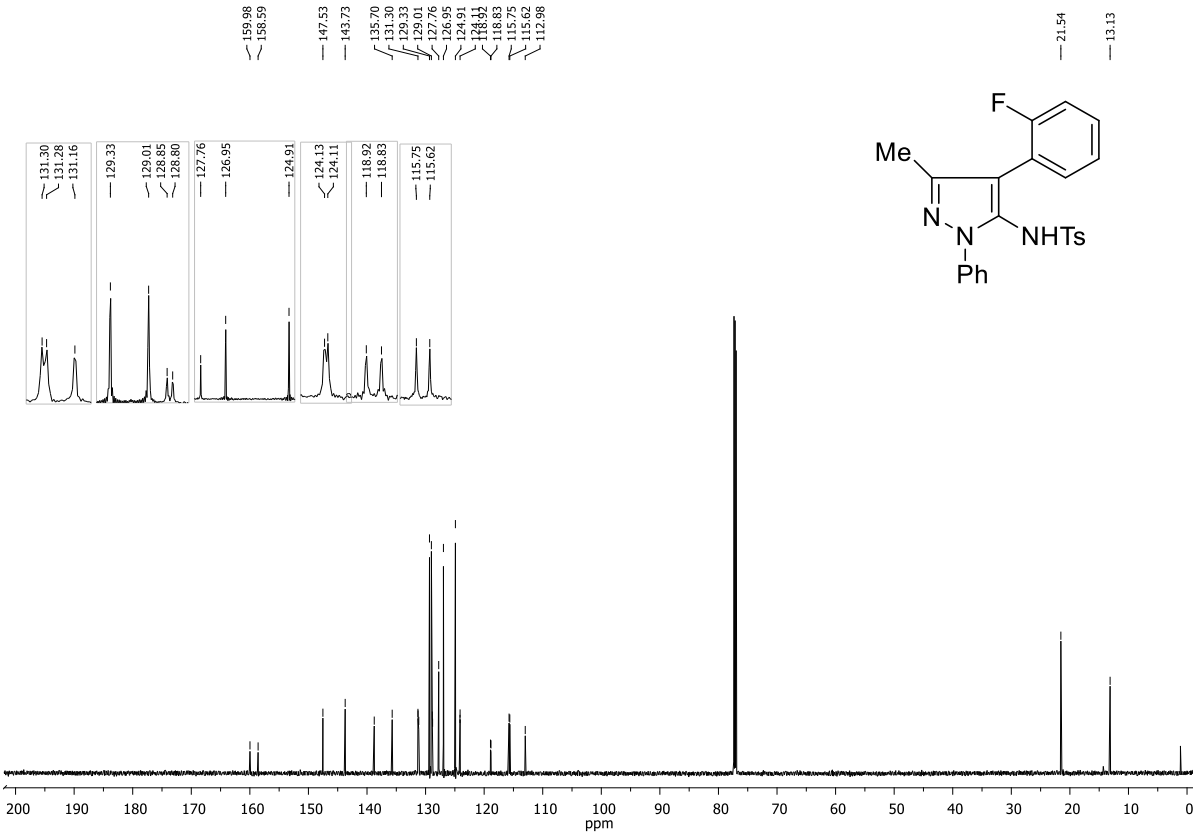
^{13}C{^{1}H} NMR of **1k** in $CDCl_3$ (100 MHz):



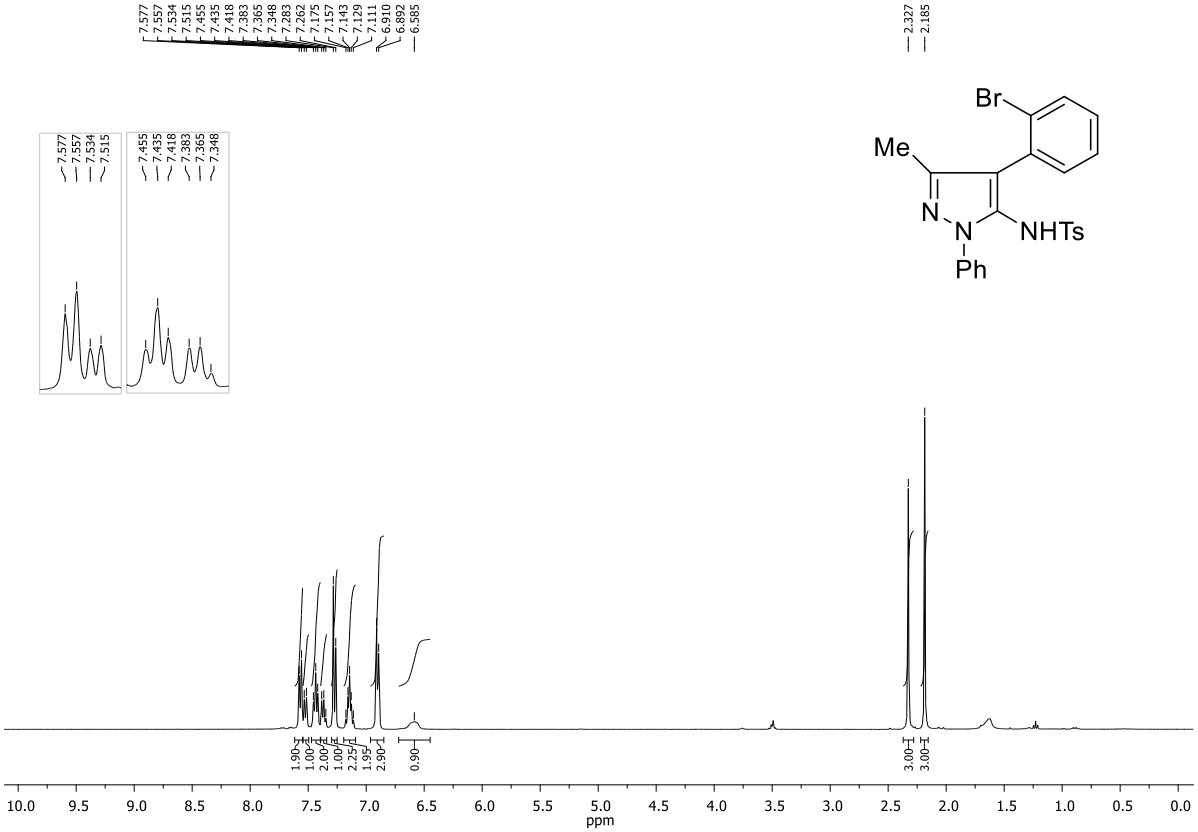
^{1}H NMR of **1l** in $CDCl_3$ (700 MHz):



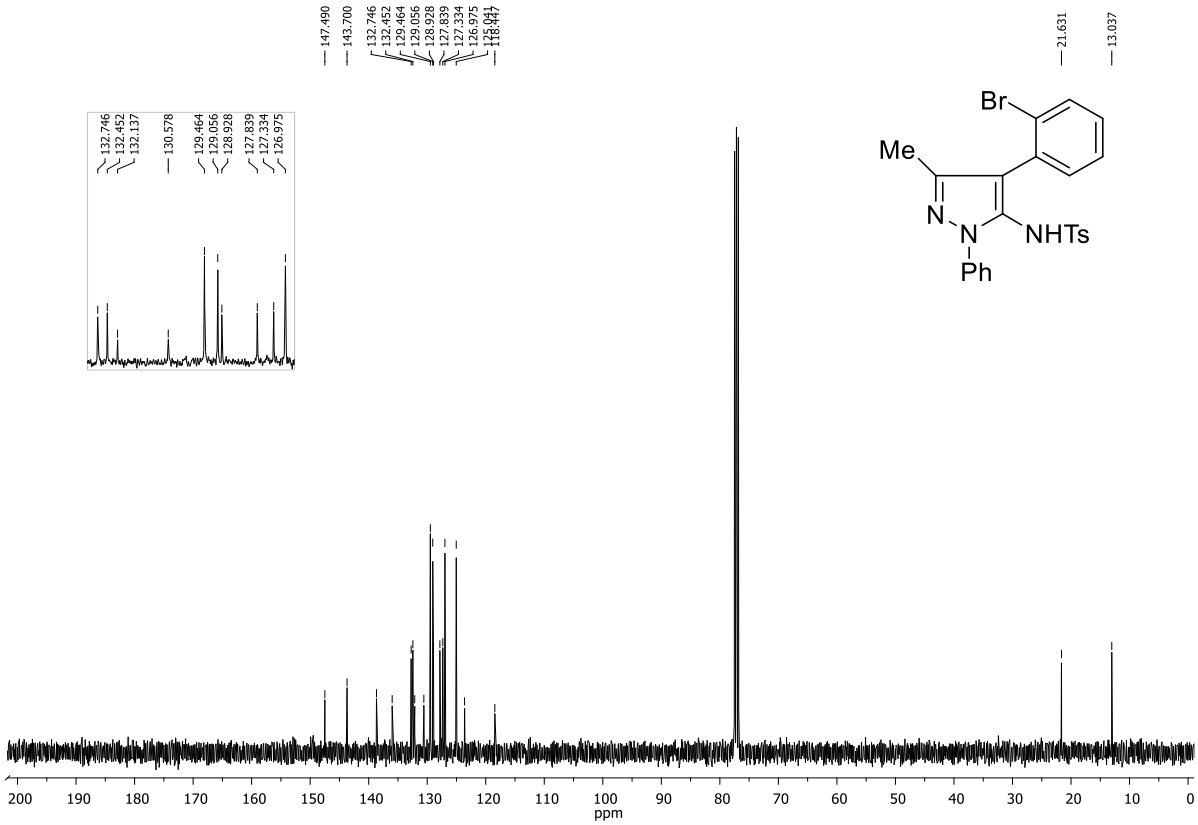
^{13}C{^{1}H} NMR of **1l** in $CDCl_3$ (175 MHz):



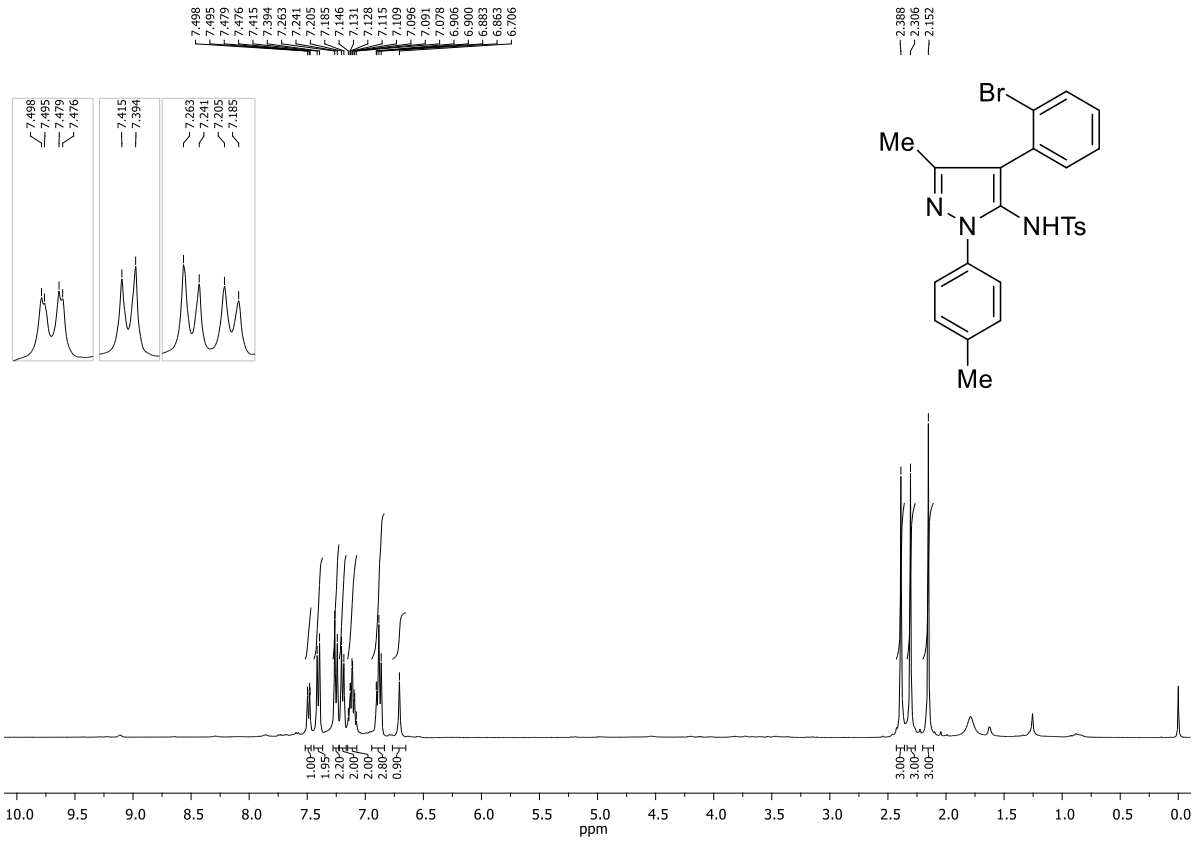
^{1}H NMR of **1m** in $CDCl_3$ (400 MHz):



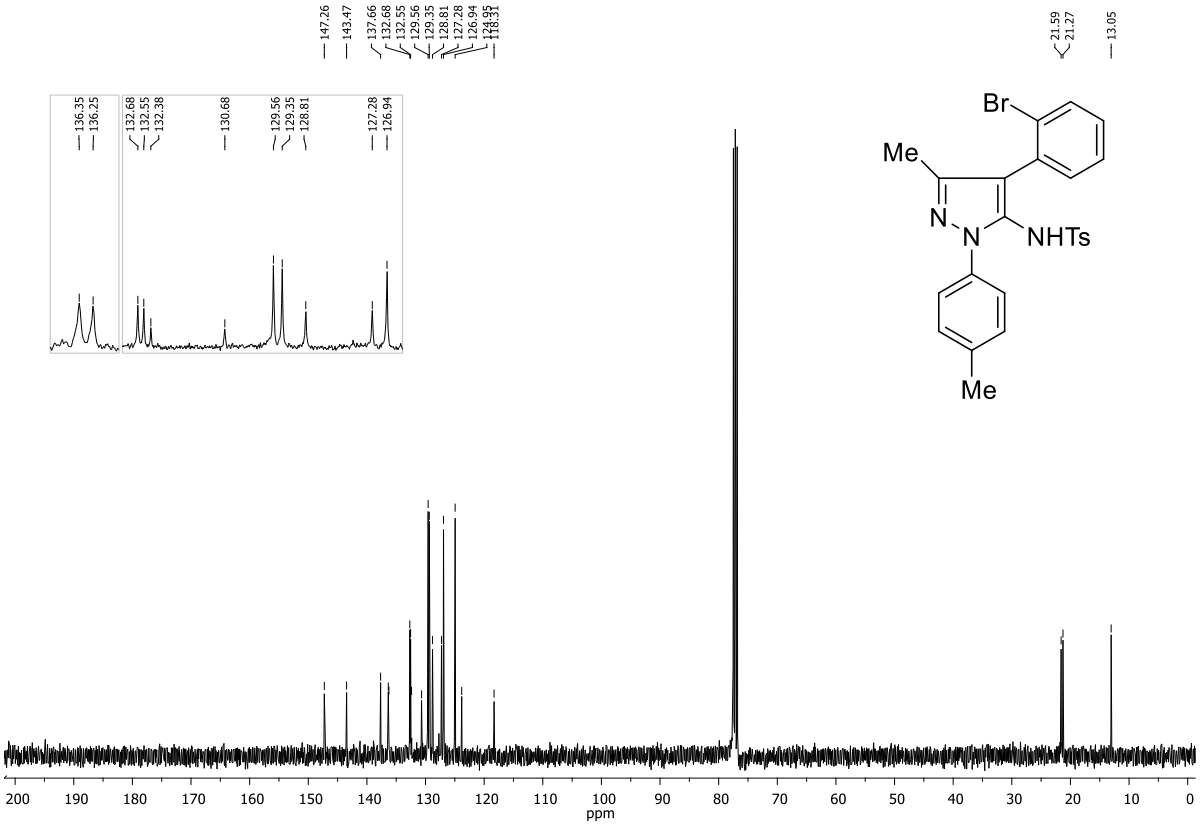
^{13}C{^{1}H} NMR of **1m** in $CDCl_3$ (100 MHz):



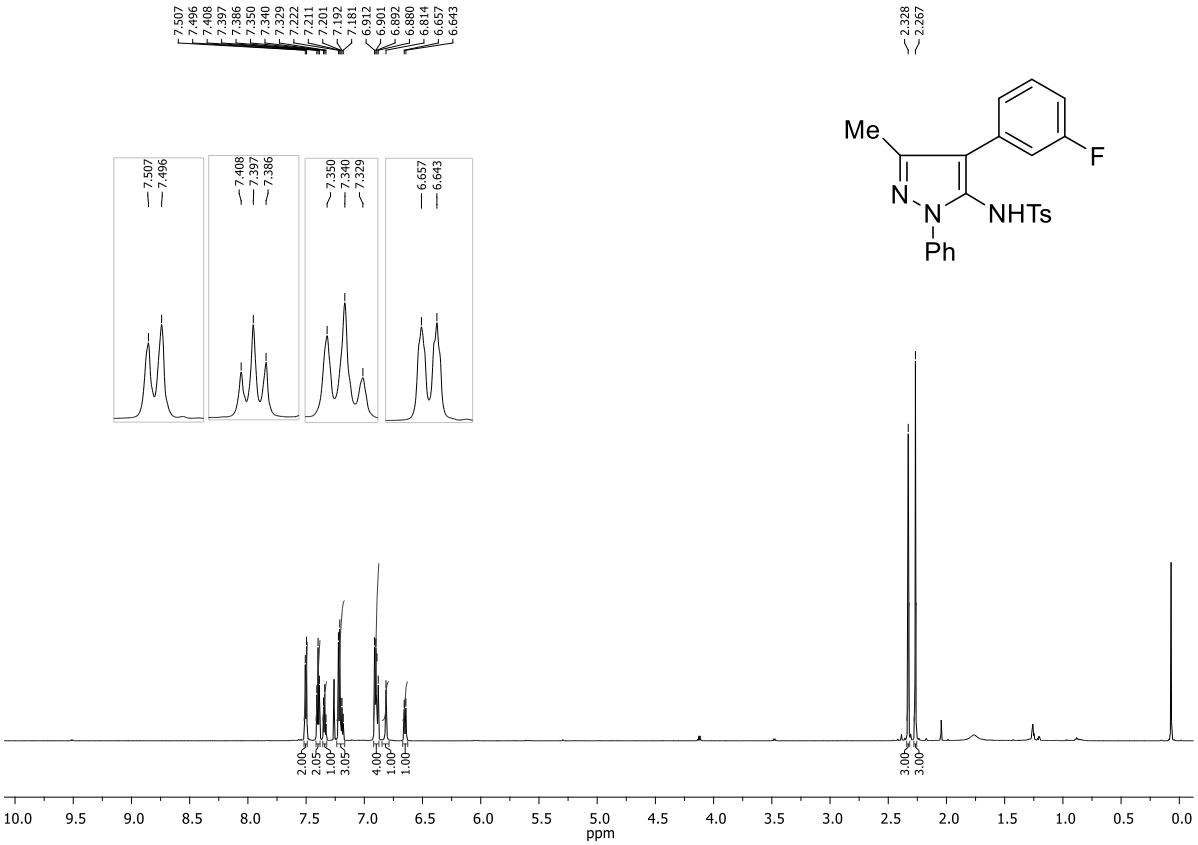
^{1}H NMR of **1n** in $CDCl_3$ (400 MHz):



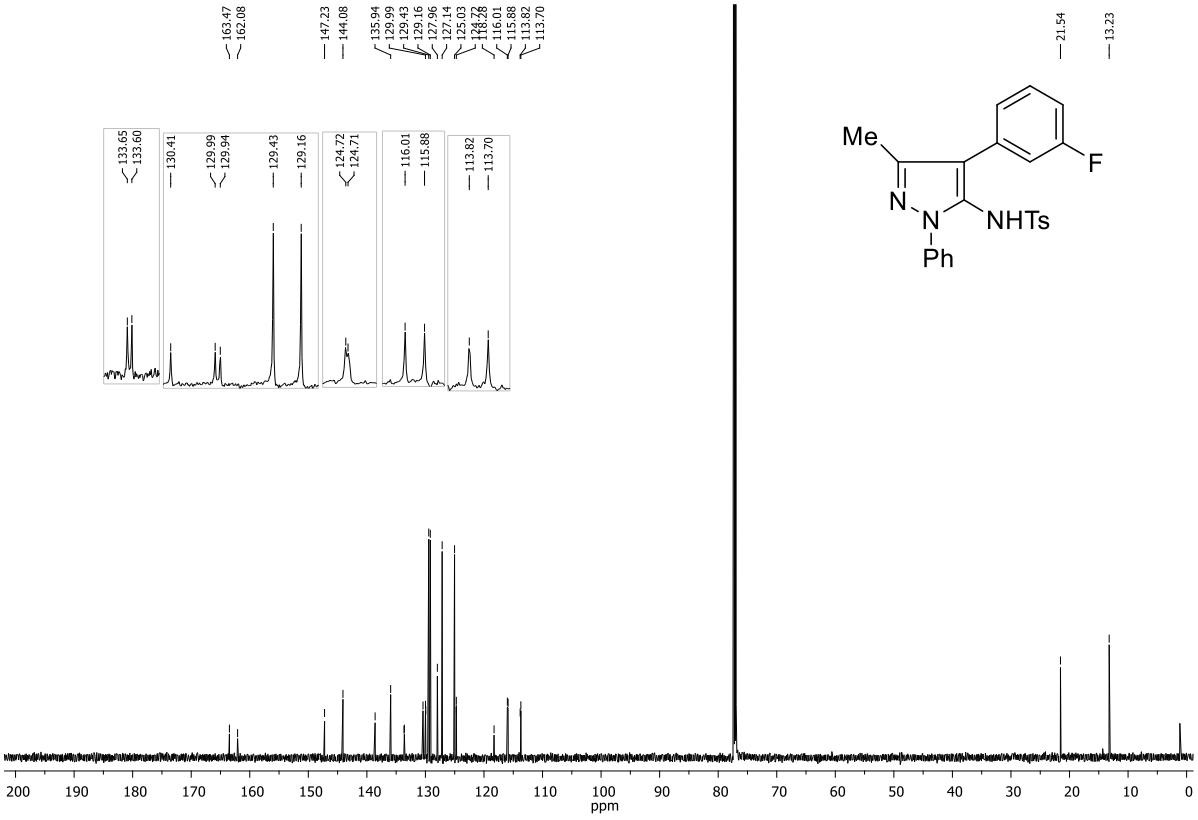
^{13}C{^{1}H} NMR of **1n** in $CDCl_3$ (100 MHz):



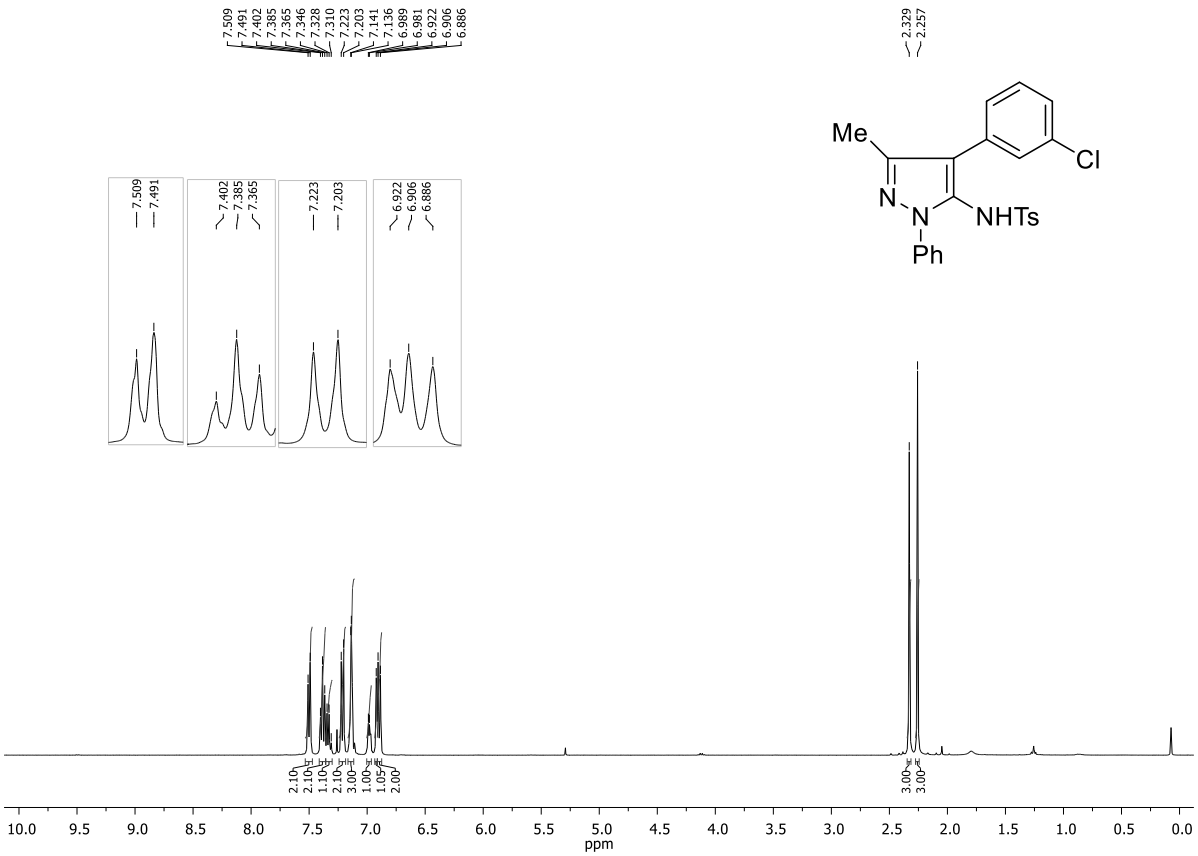
^{1}H NMR of **1o** in $CDCl_3$ (700 MHz):



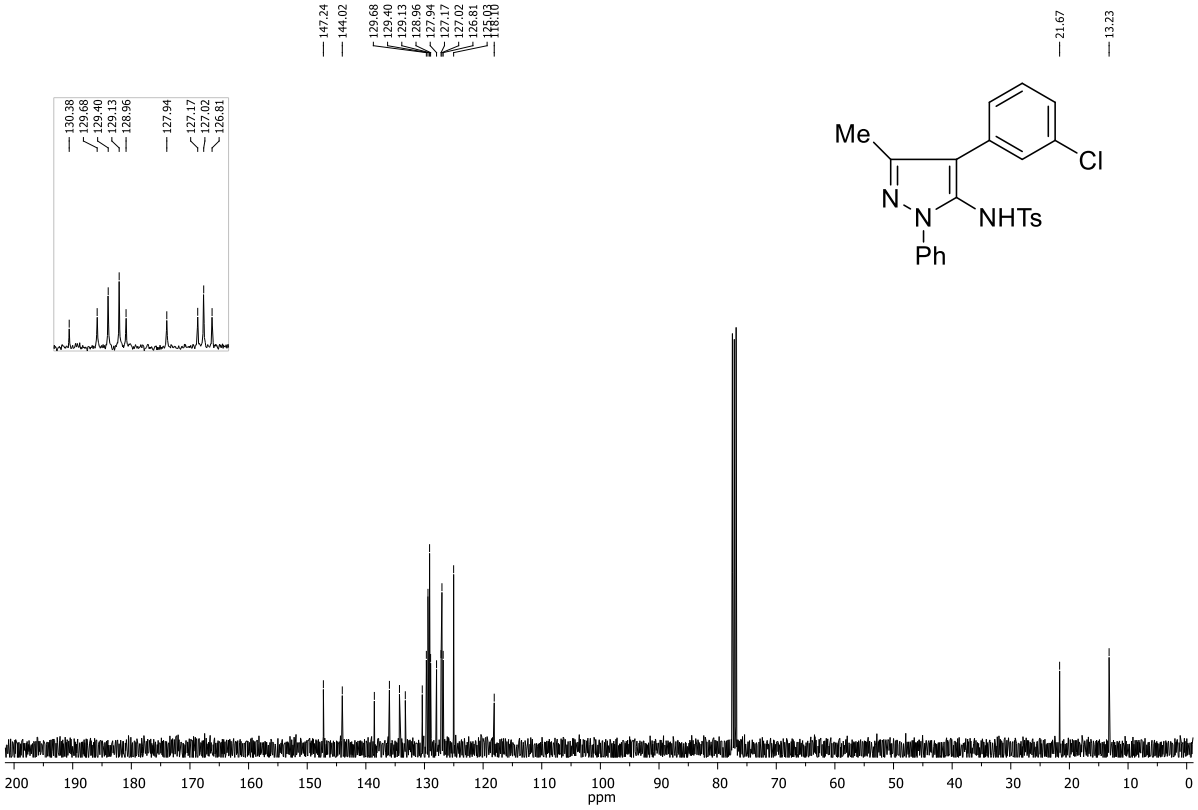
^{13}C{^{1}H} NMR of **1o** in $CDCl_3$ (175 MHz):



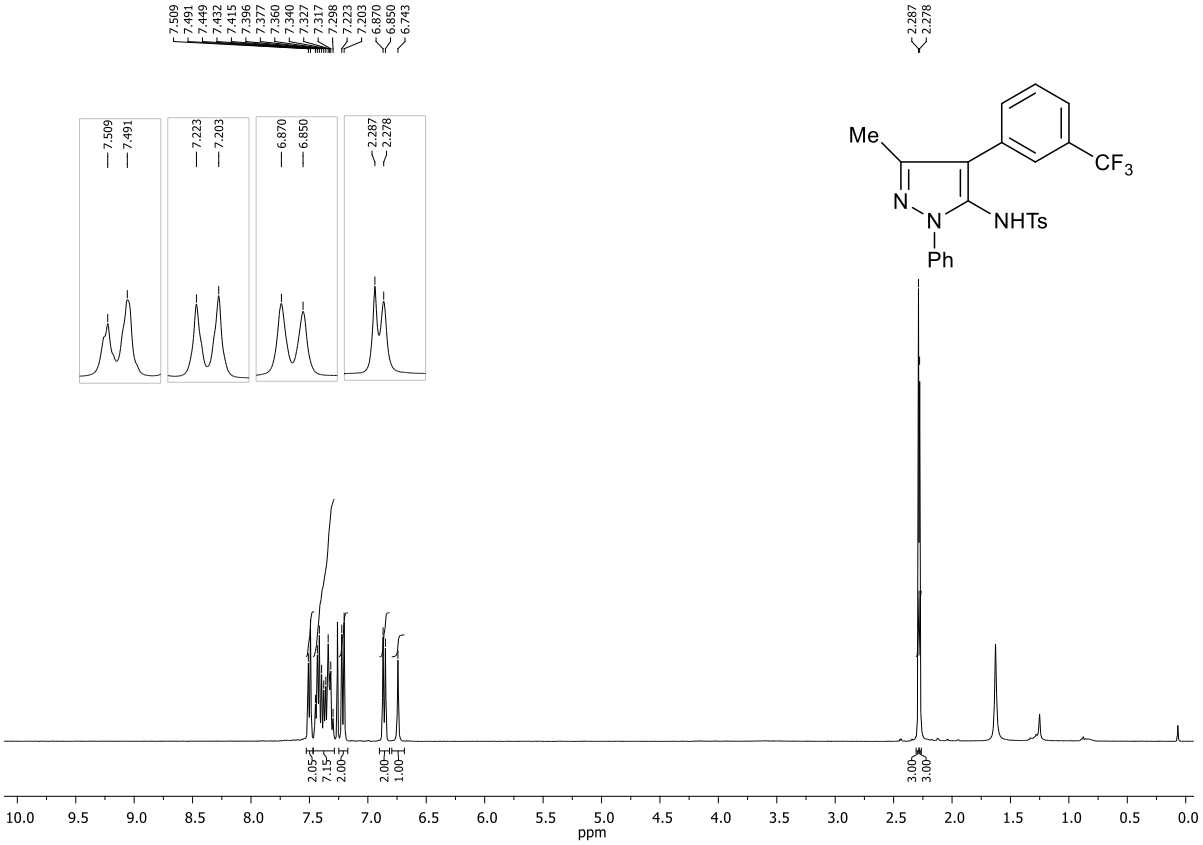
^{1}H NMR of **1p** in $CDCl_3$ (400 MHz):



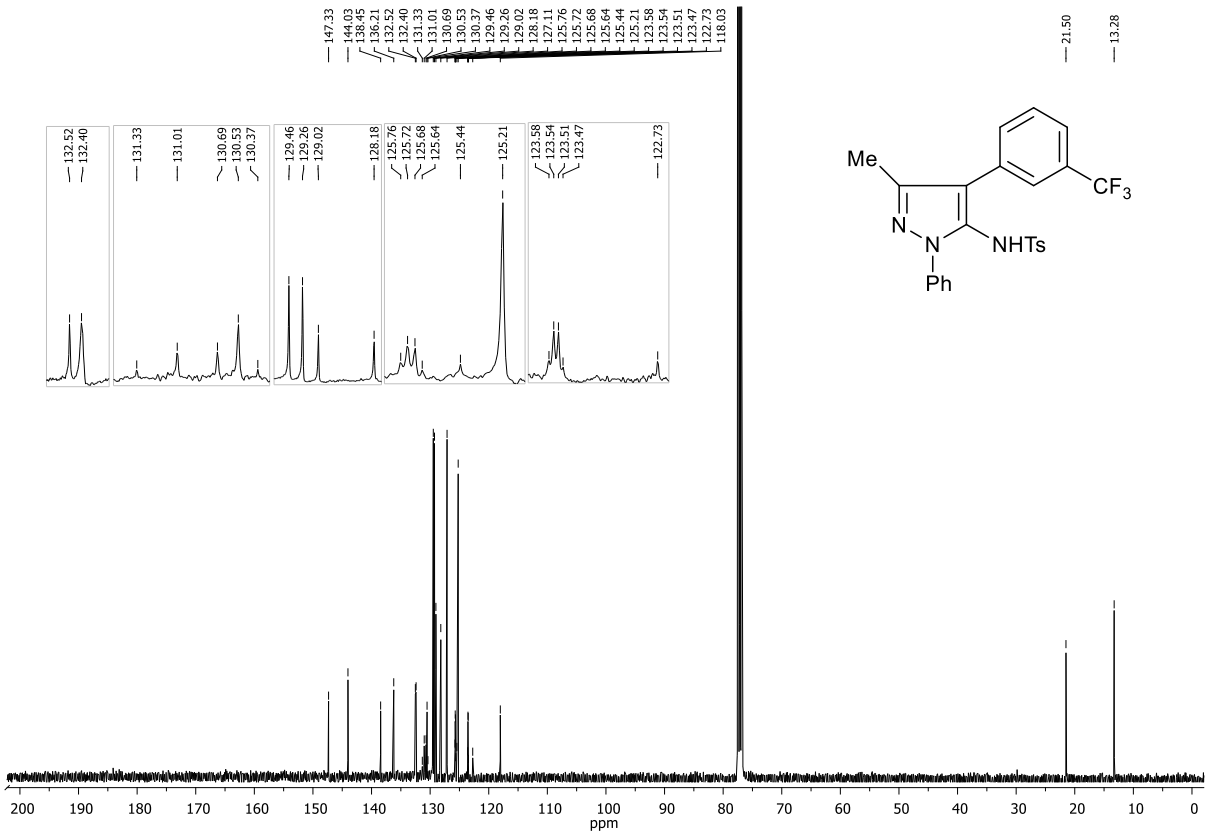
^{13}C{^{1}H} NMR of **1p** in $CDCl_3$ (100 MHz):



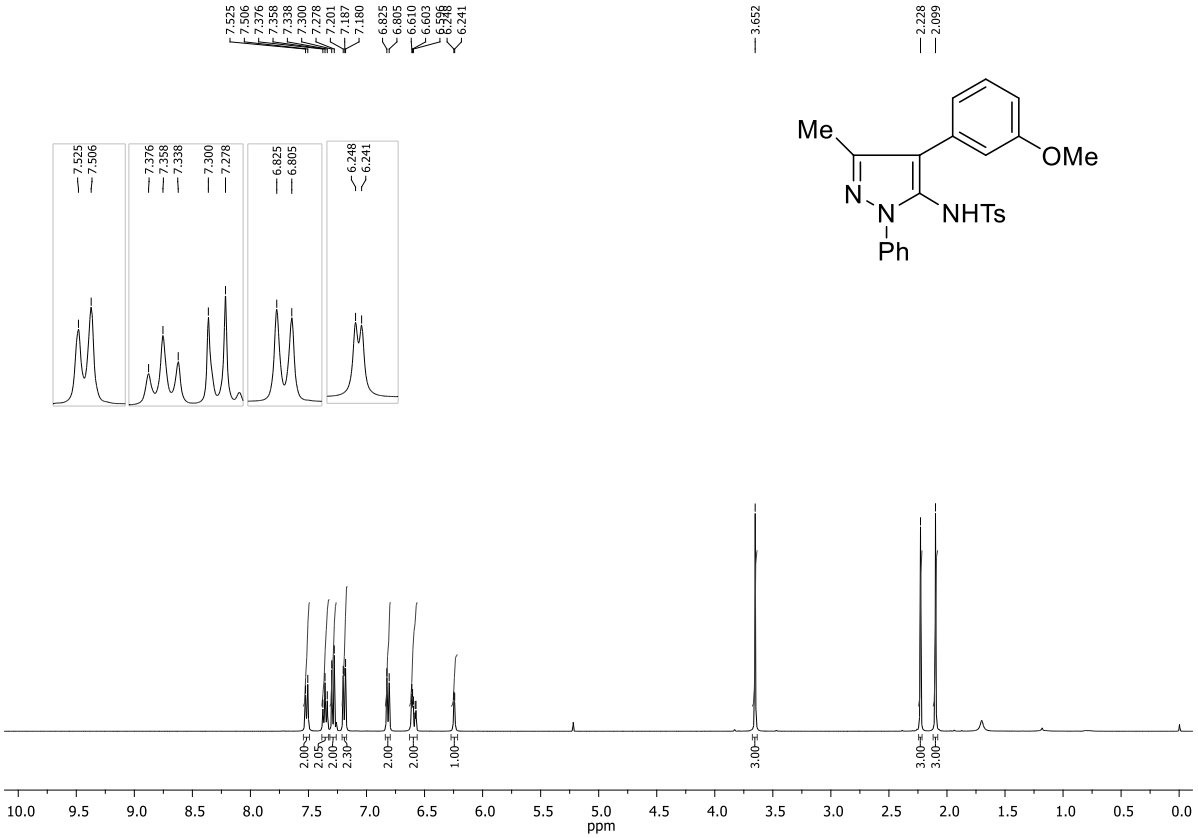
^{1}H NMR of **1q** in $CDCl_3$ (400 MHz):



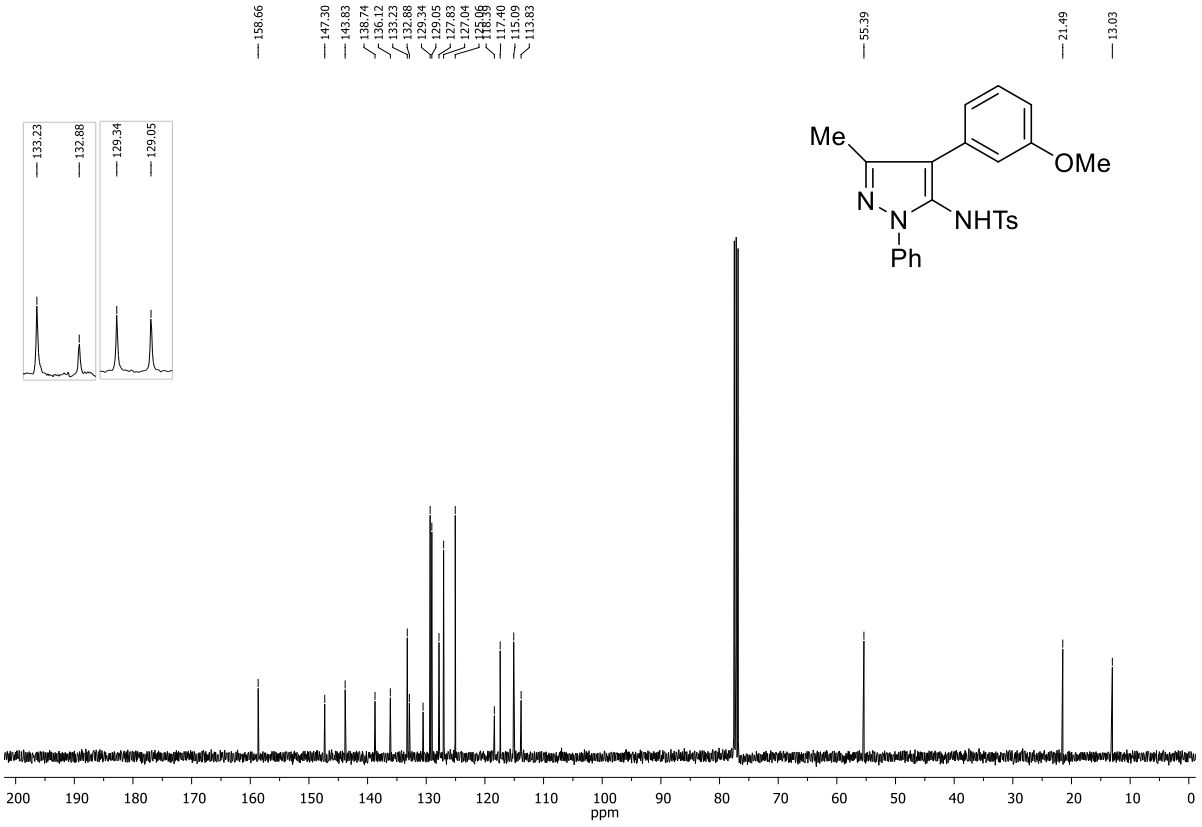
^{13}C{^{1}H} NMR of **1q** in $CDCl_3$ (100 MHz):



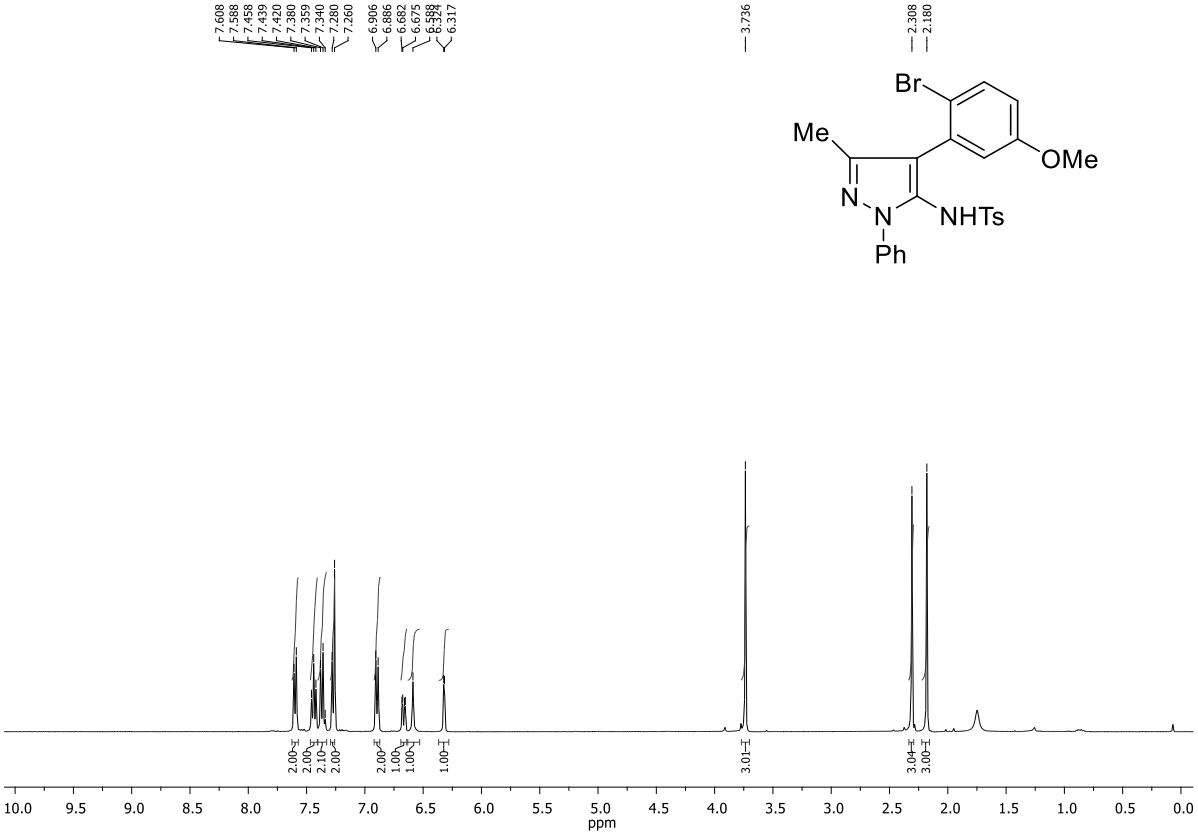
^{1}H NMR of **1r** in $CDCl_3$ (400 MHz):



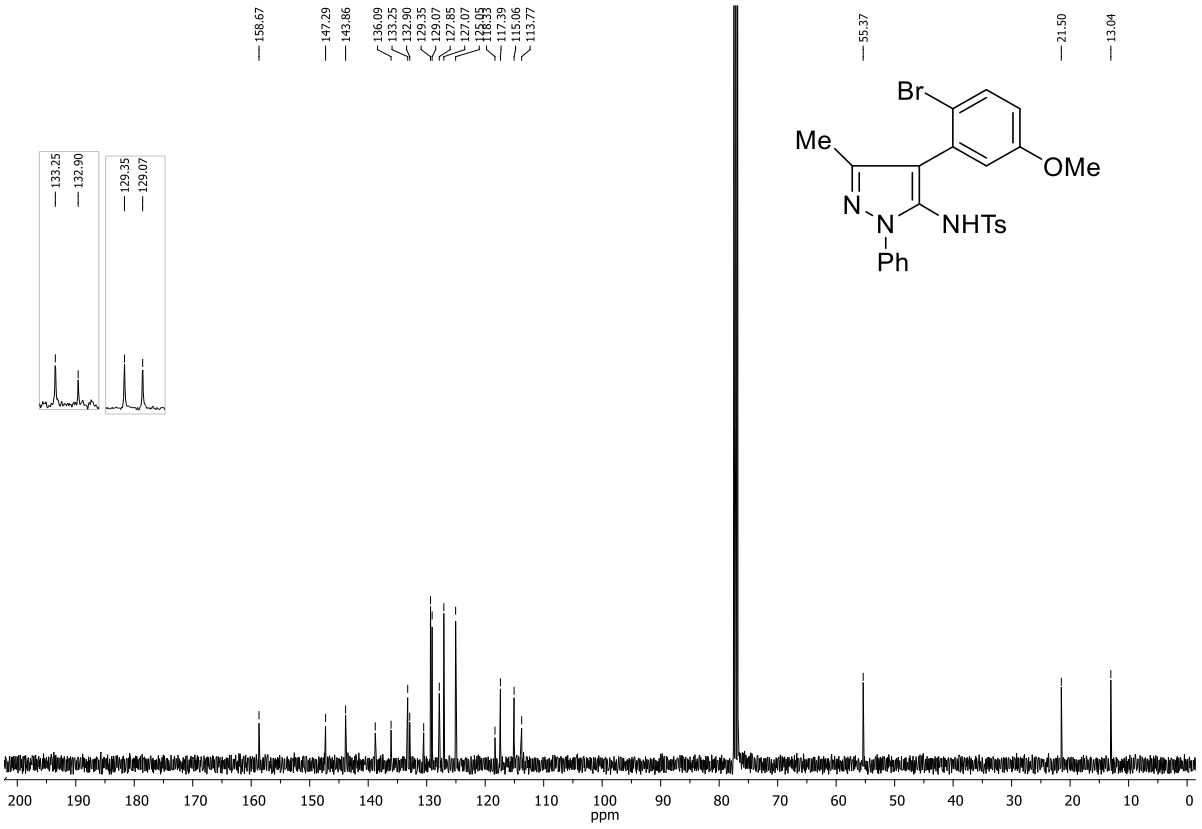
^{13}C{^{1}H} NMR of **1r** in $CDCl_3$ (100 MHz):



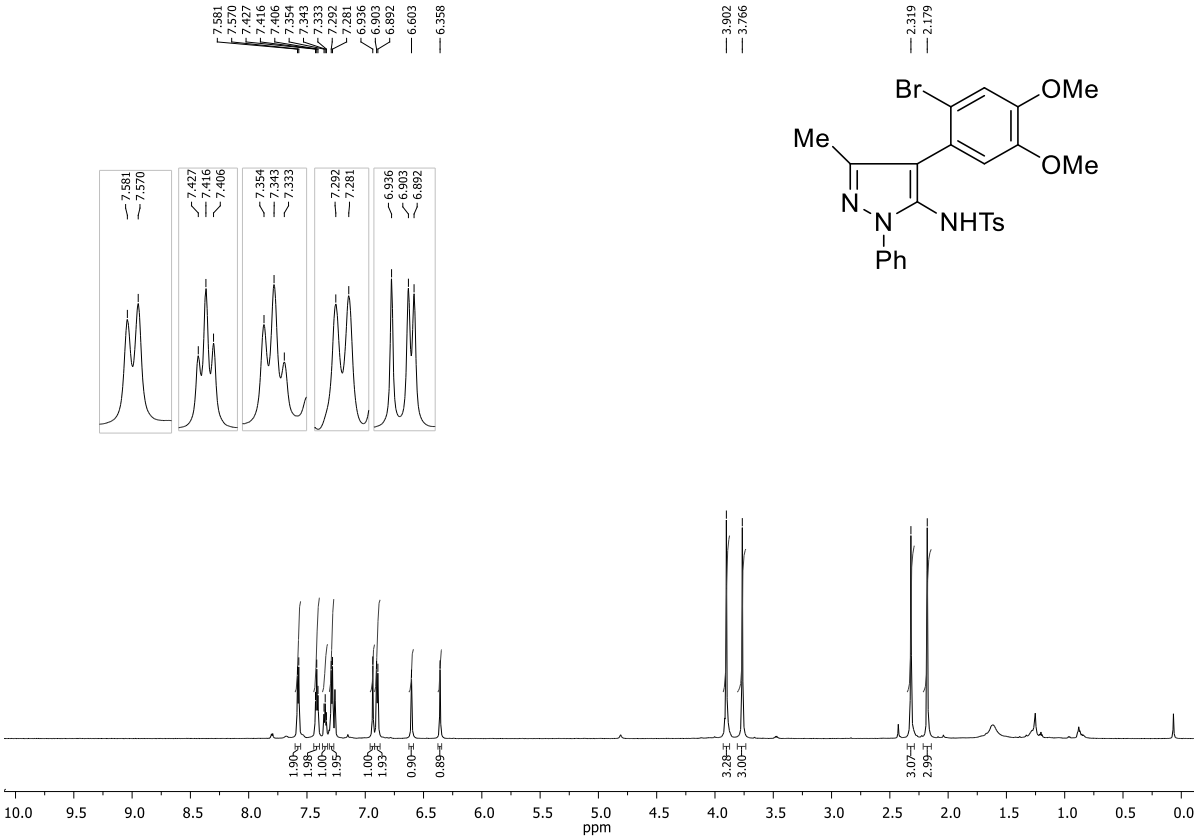
^{1}H NMR of **1s** in $CDCl_3$ (400 MHz):



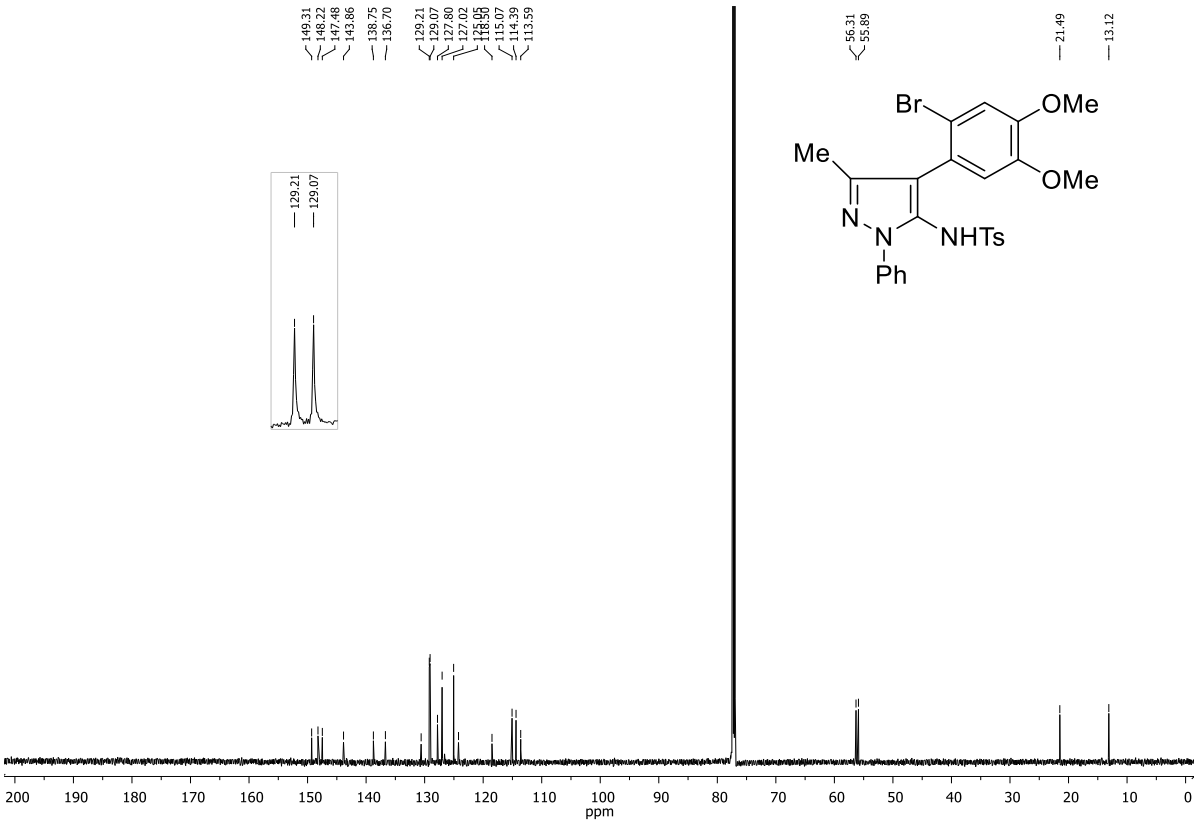
^{13}C{^{1}H} NMR of **1s** in $CDCl_3$ (100 MHz):



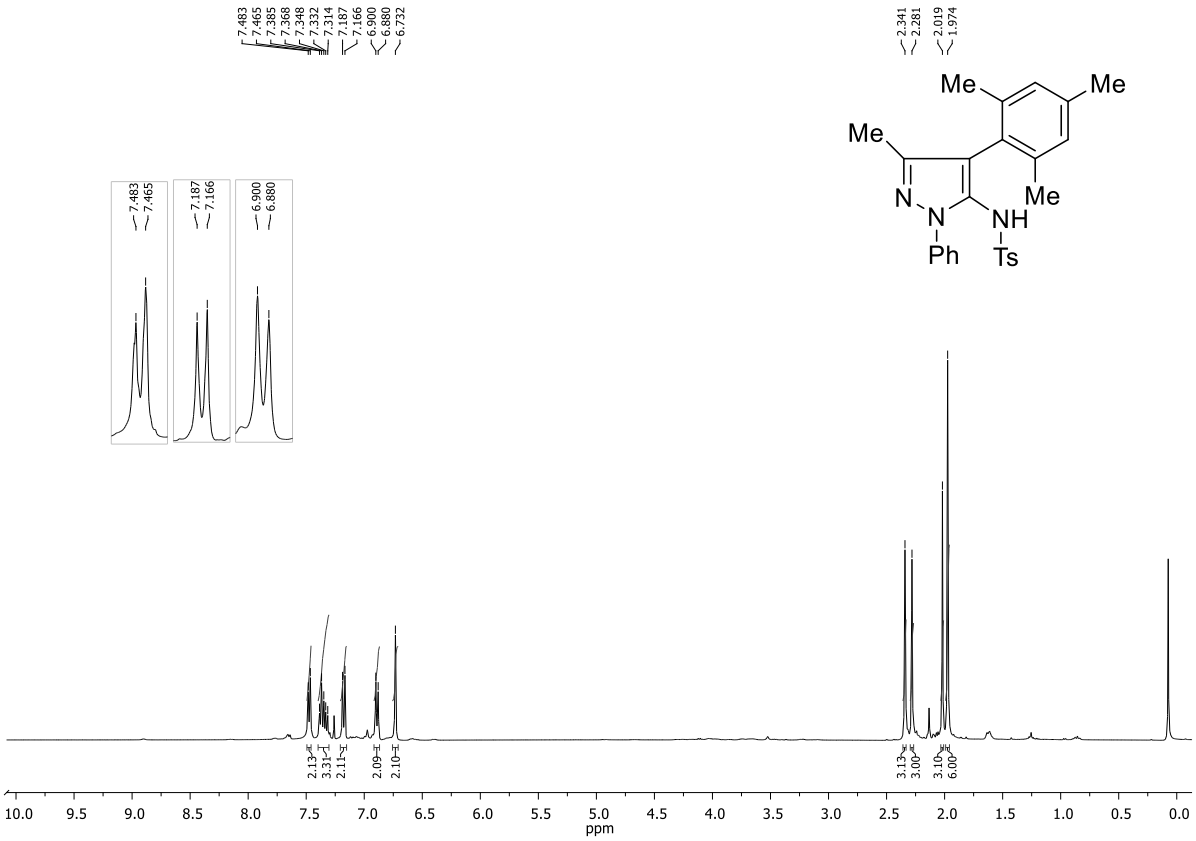
^{1}H NMR of **1t** in $CDCl_3$ (700 MHz):



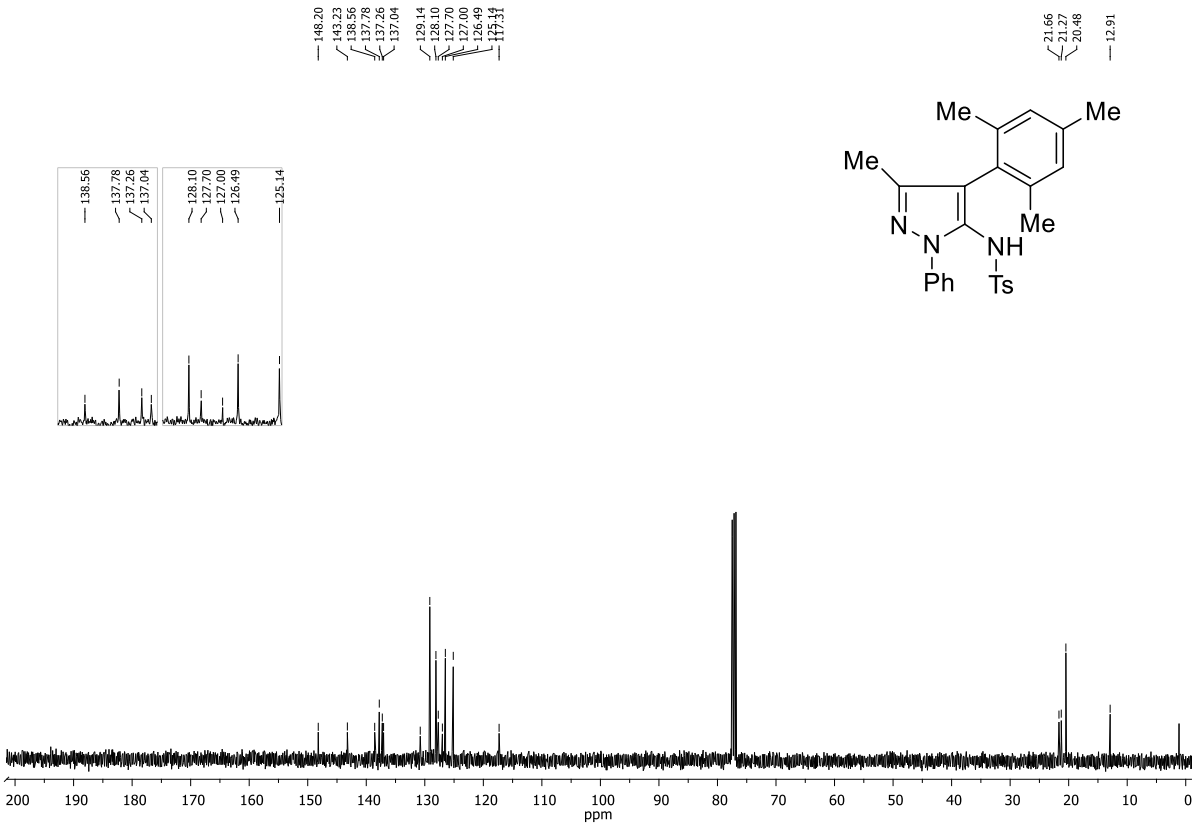
^{13}C{^{1}H} NMR of **1t** in $CDCl_3$ (175 MHz):



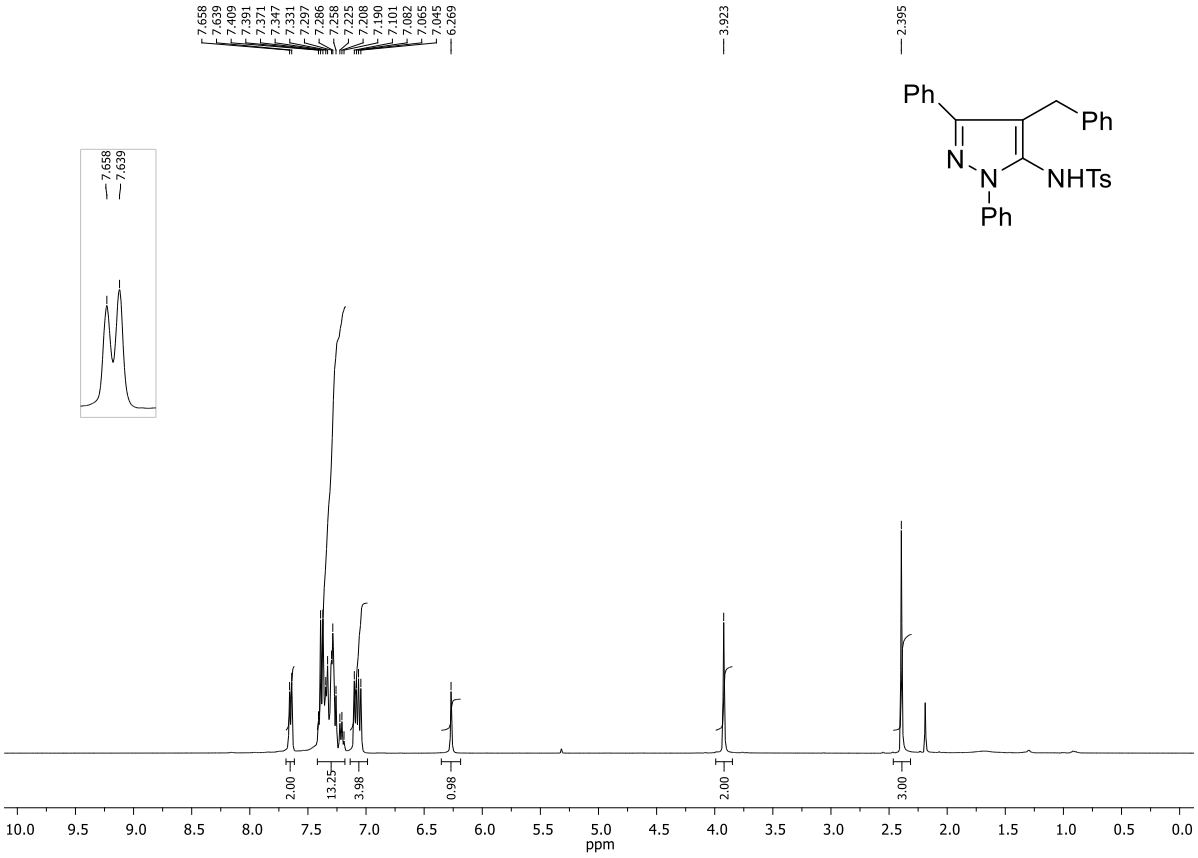
^{1}H NMR of **1u** in $CDCl_3$ (400 MHz):



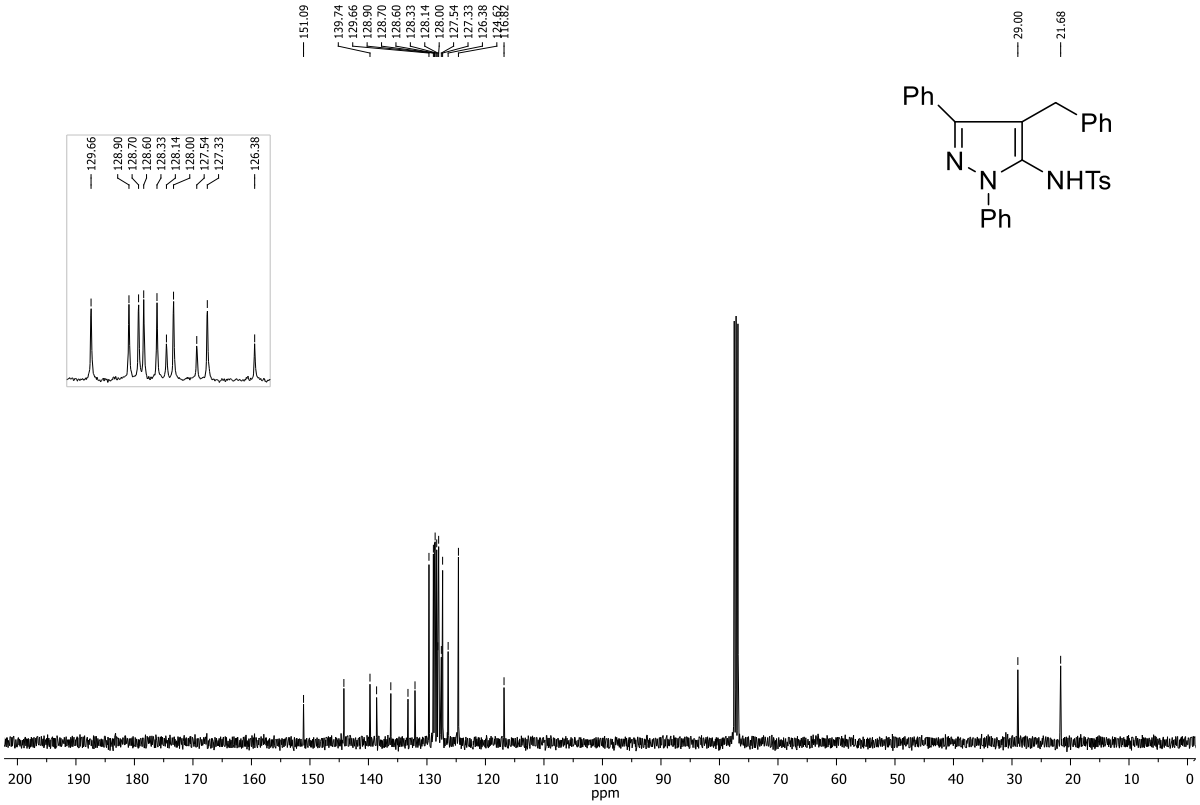
^{13}C{^{1}H} NMR of **1u** in $CDCl_3$ (100 MHz):



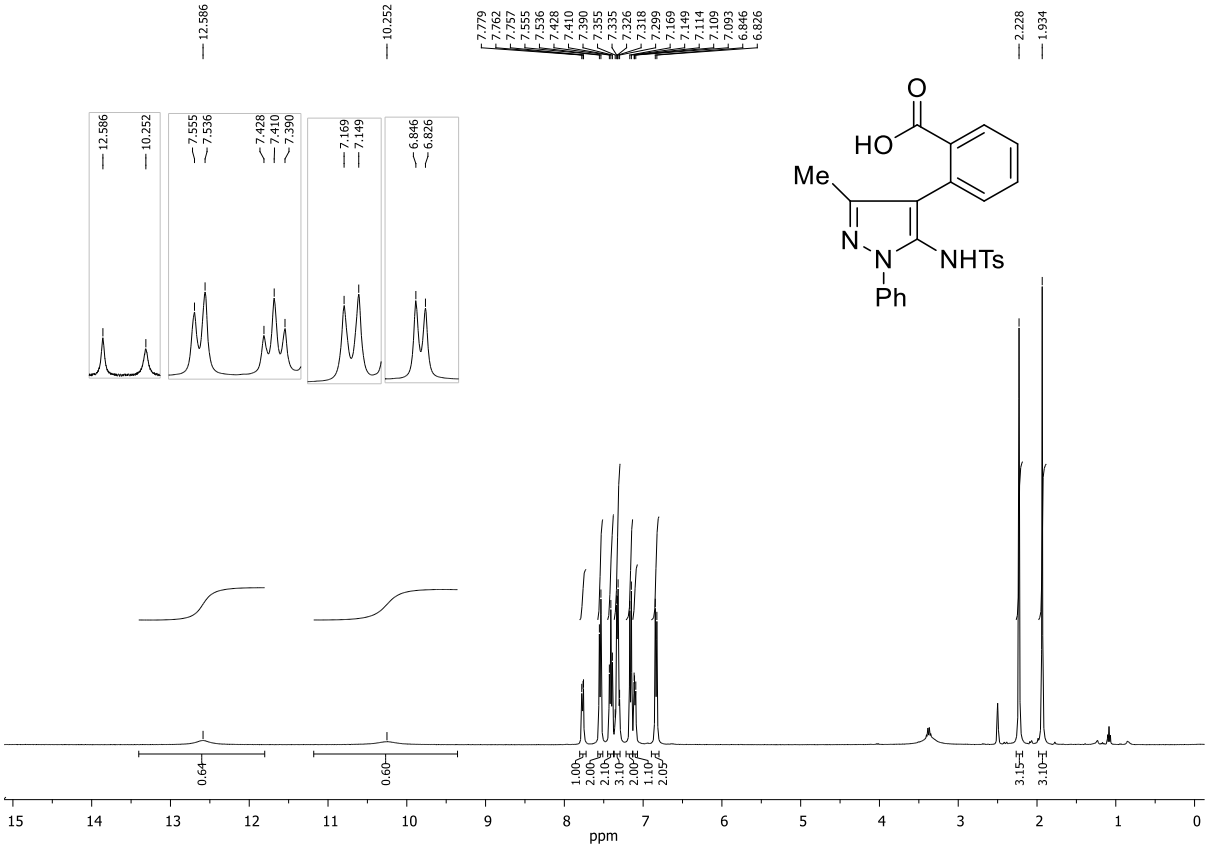
^{1}H NMR of **1v** in $CDCl_3$ (400 MHz):



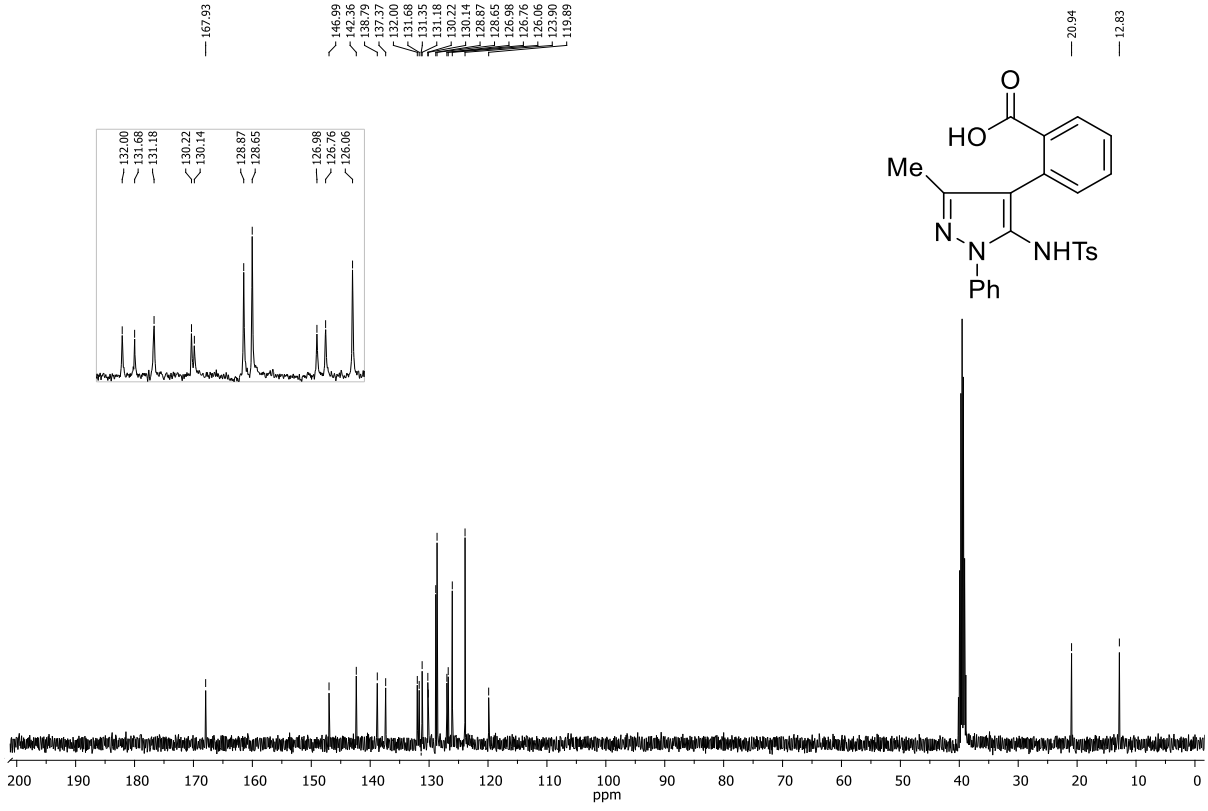
^{13}C{^{1}H} NMR of **1v** in $CDCl_3$ (100 MHz):



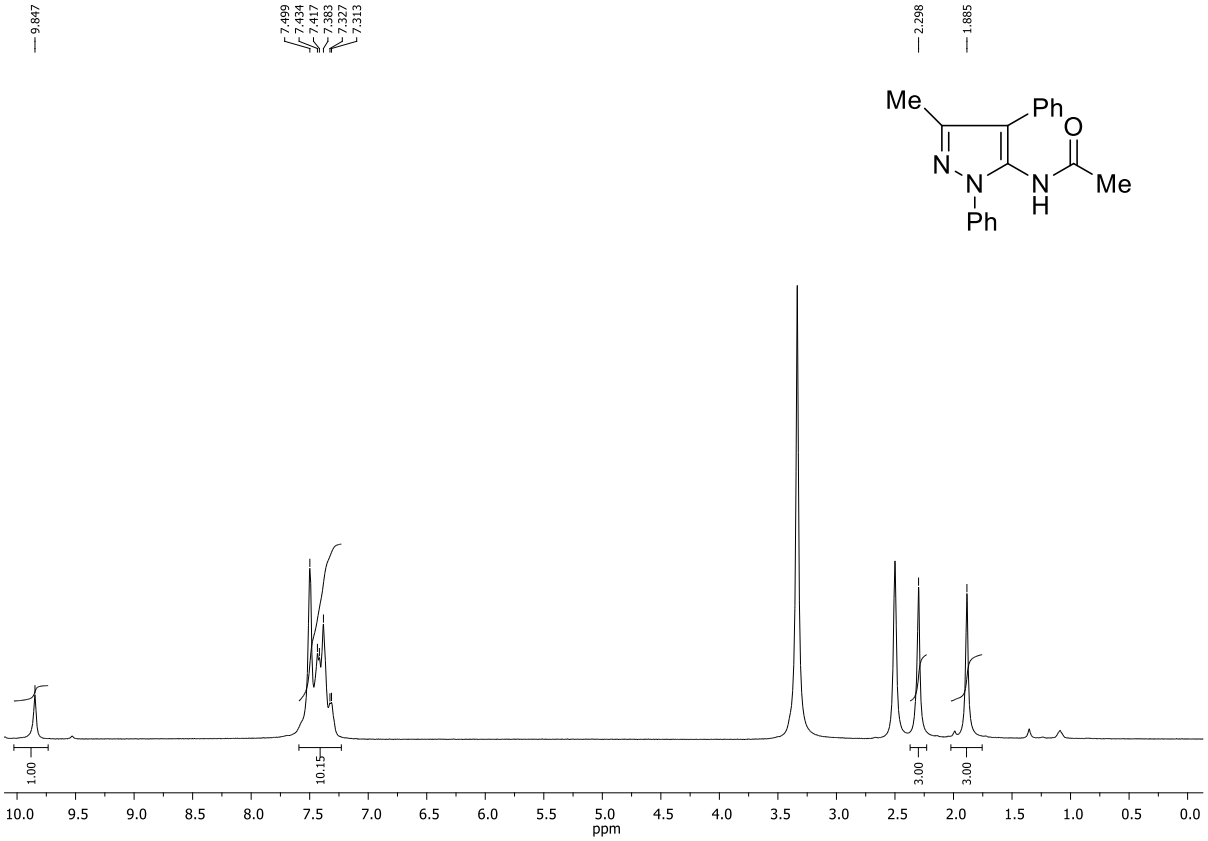
^{1}H NMR of **1w** in DMSO-d_6 (400 MHz):



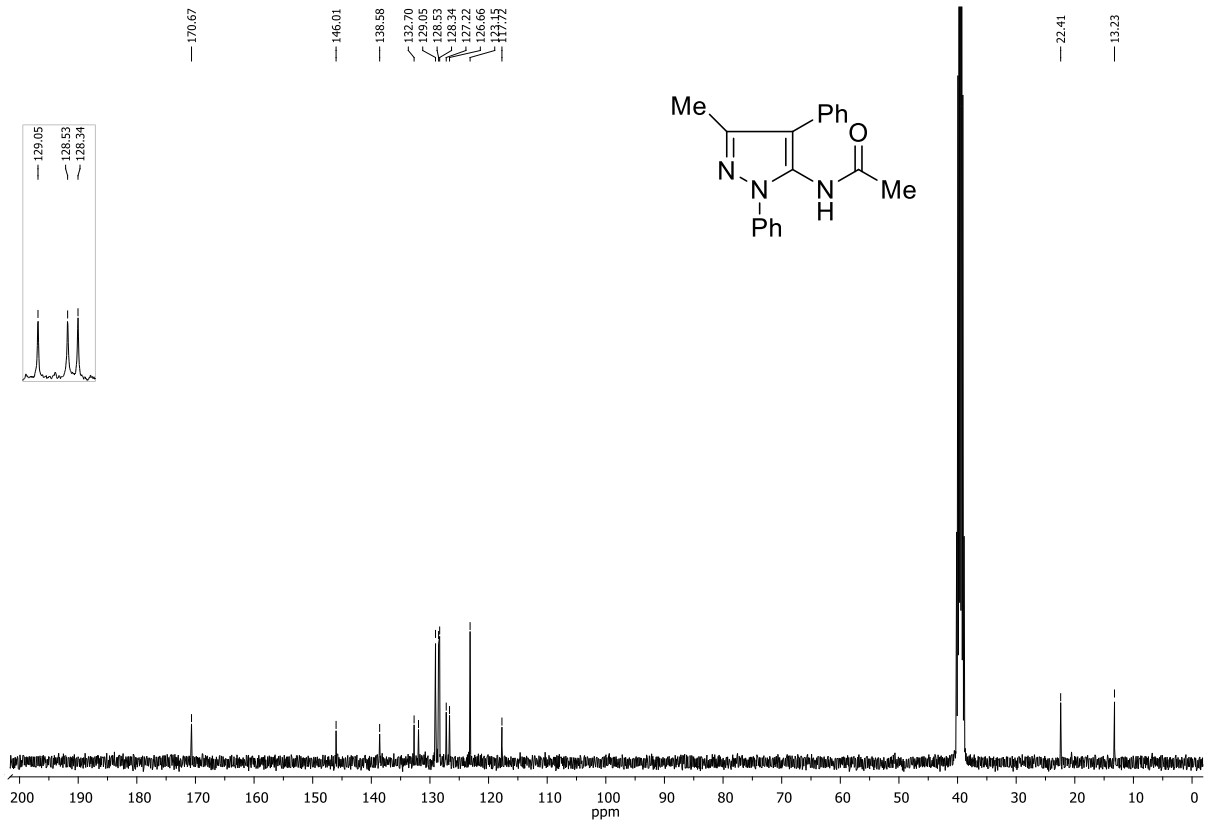
^{13}C{^{1}H} NMR of **1w** in DMSO-d_6 (100 MHz):



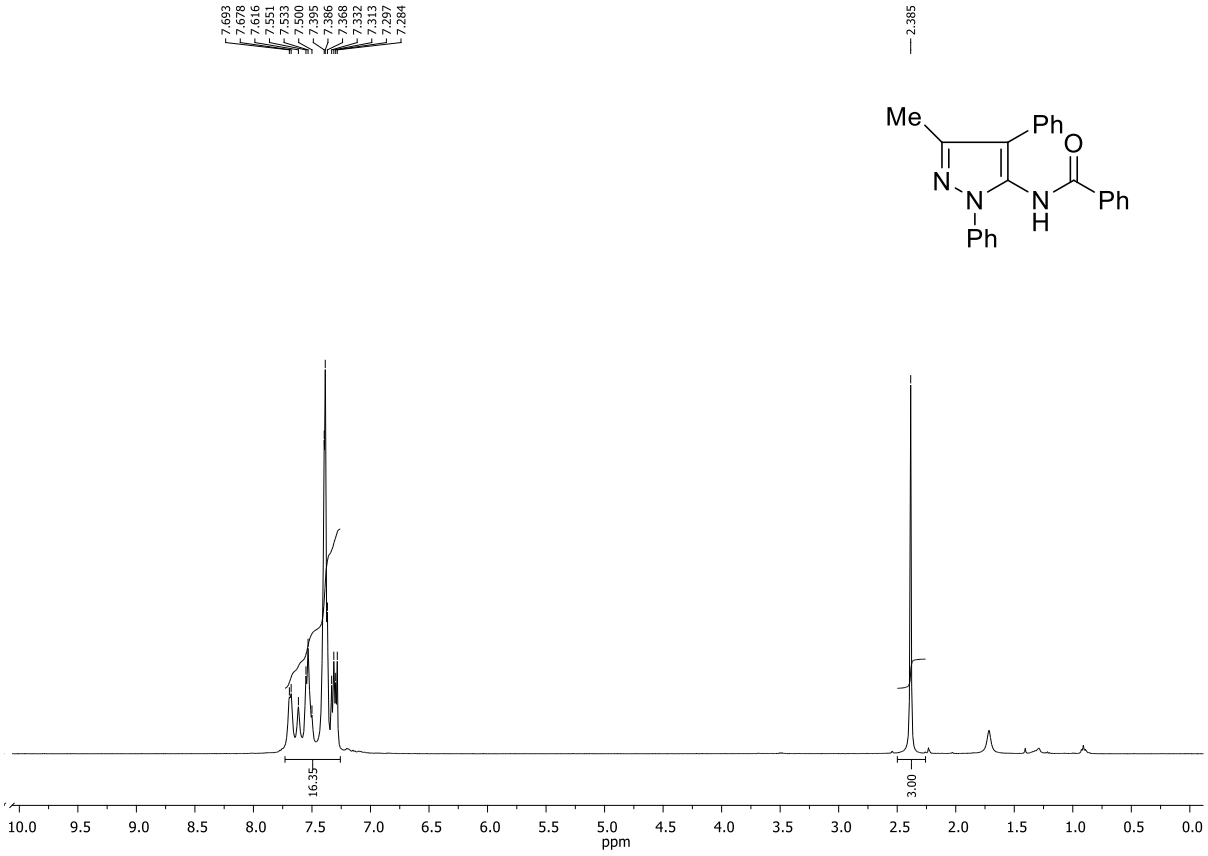
^{1}H NMR of **8a** in DMSO-d_6 (400 MHz):



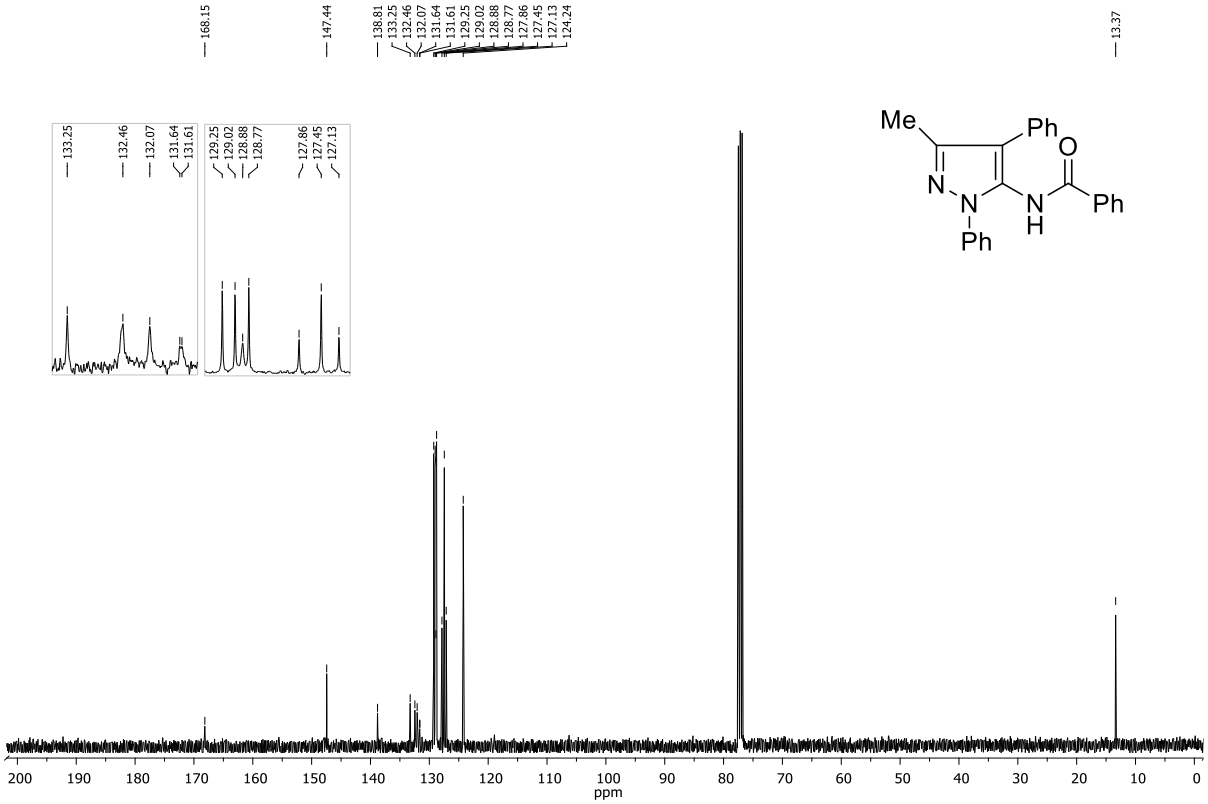
^{13}C{^{1}H} NMR of **8a** in DMSO-d_6 (100 MHz):



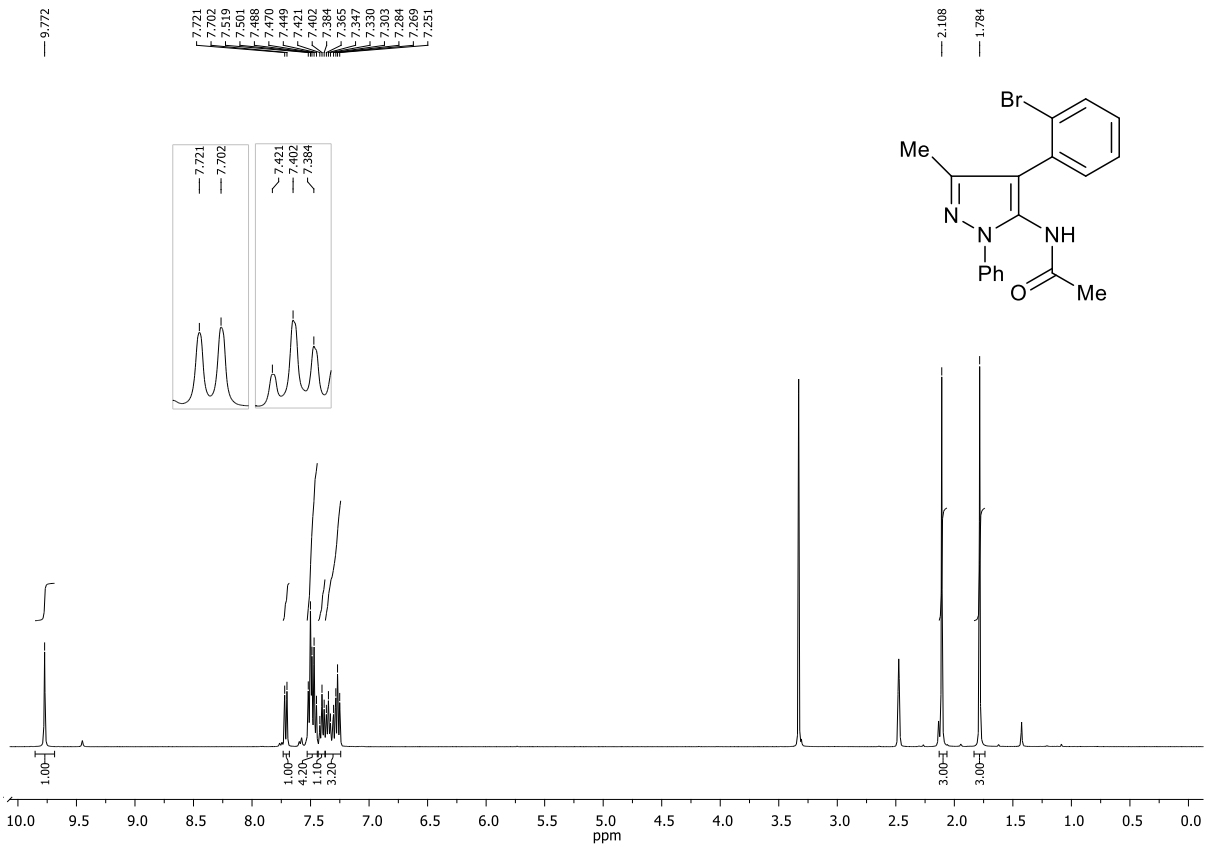
^{1}H NMR of **8b** in $CDCl_3$ (400 MHz):



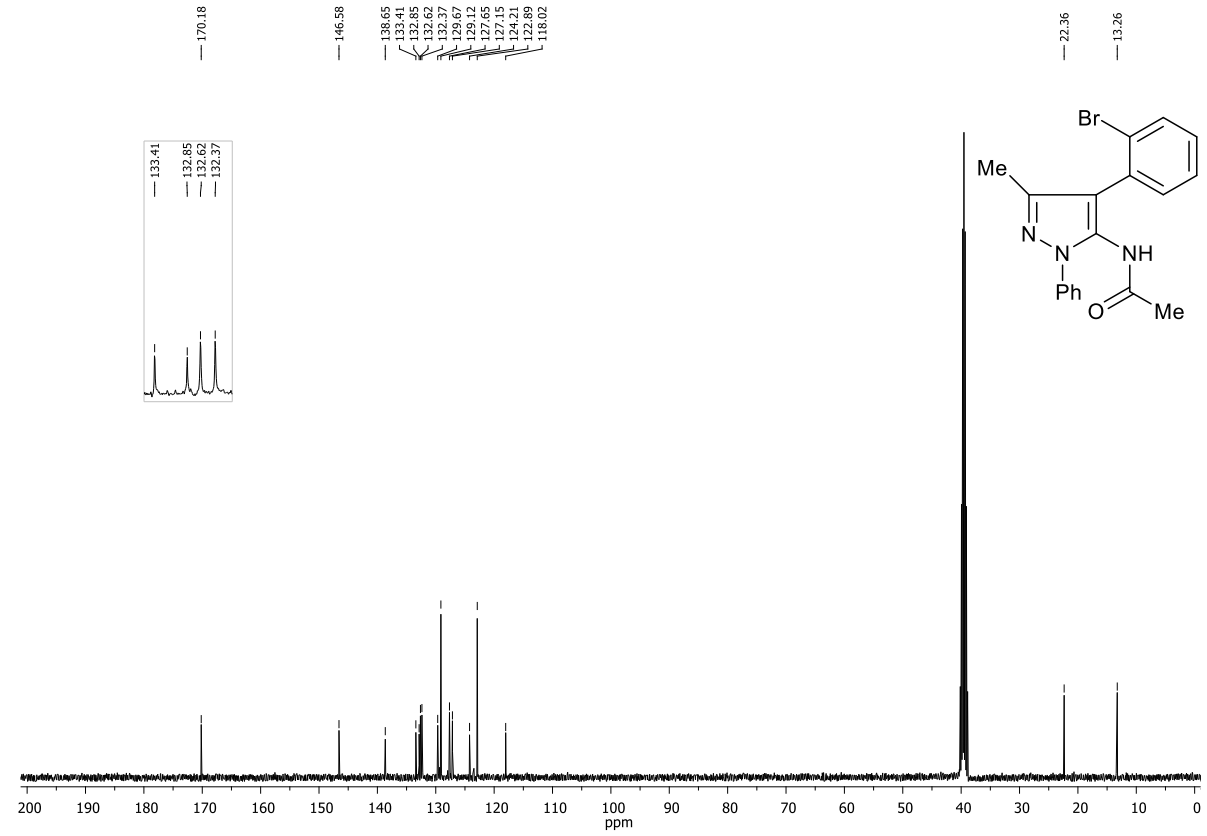
^{13}C{^{1}H} NMR of **8b** in $CDCl_3$ (100 MHz):



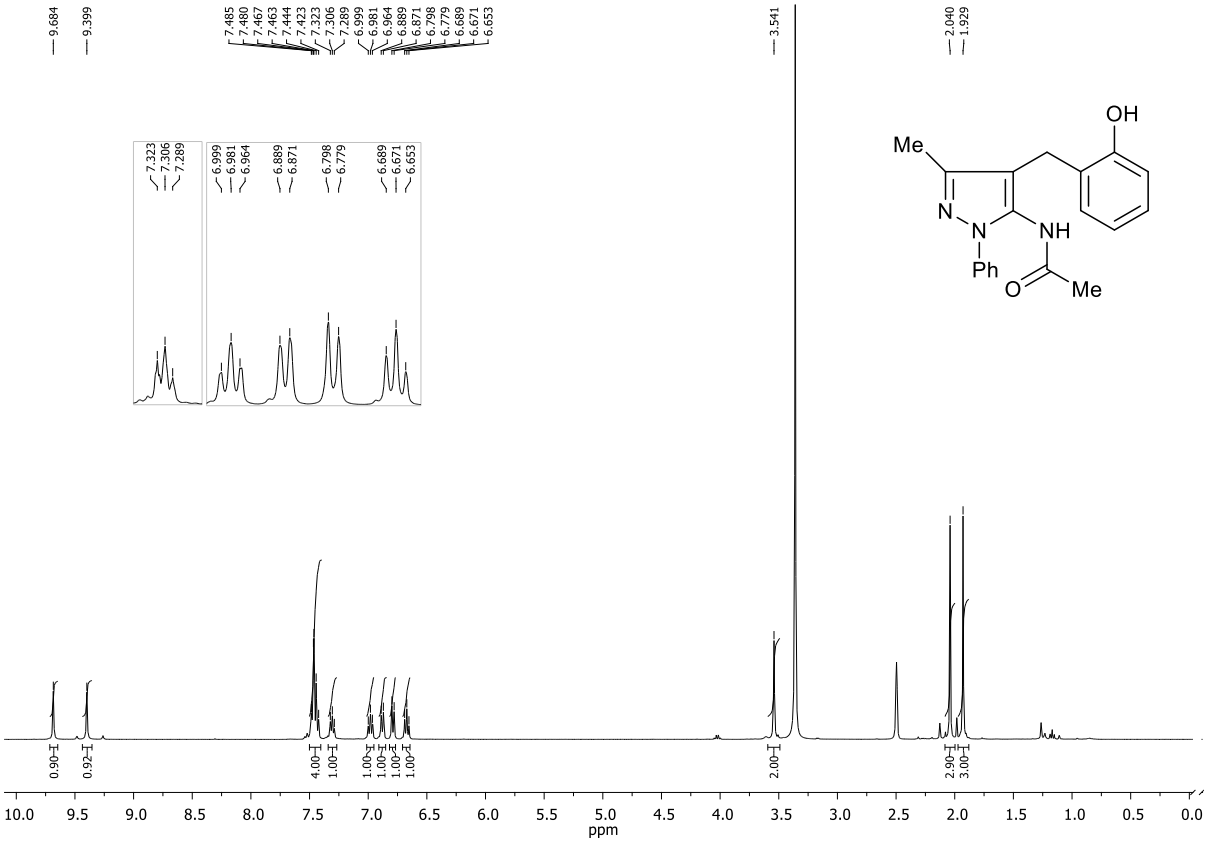
^{1}H NMR of **8c** in DMSO-d_6 (400 MHz):



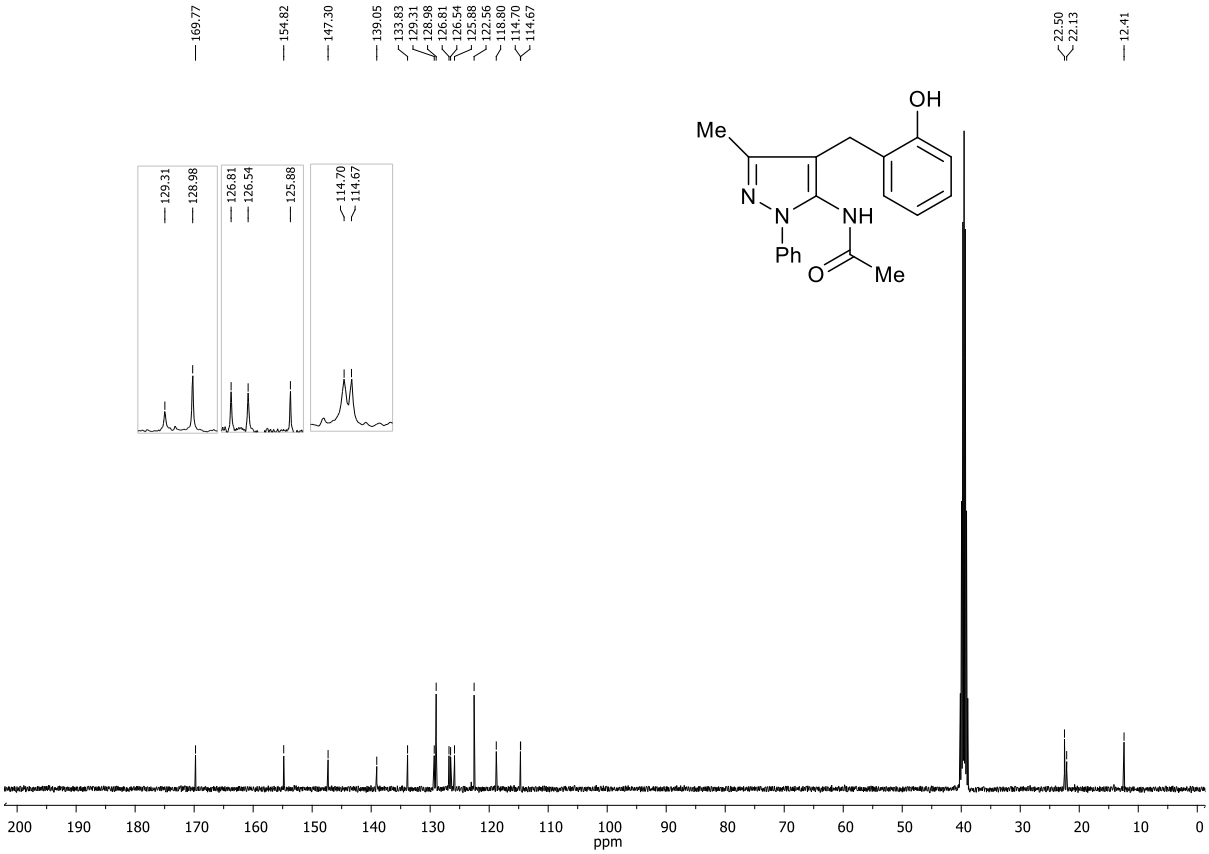
^{13}C{^{1}H} NMR of **8c** in DMSO-d_6 (100 MHz):



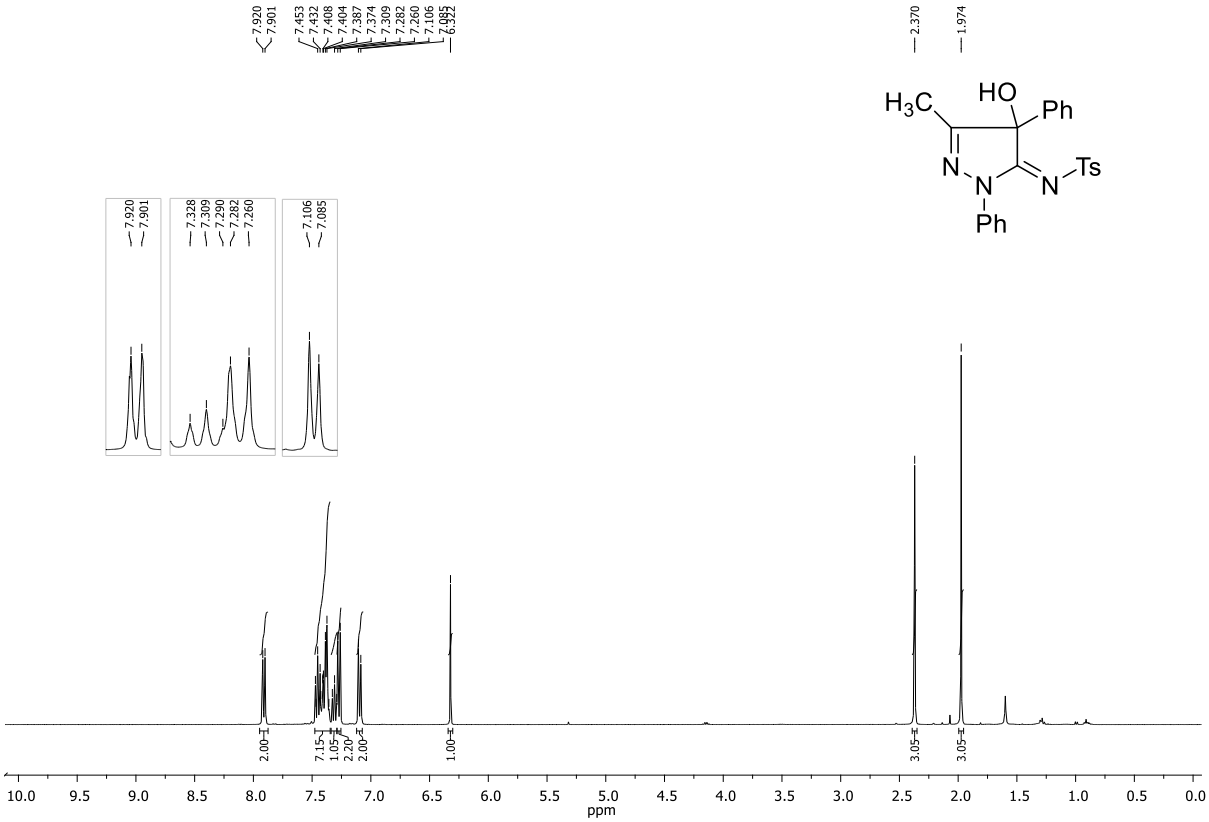
^{1}H NMR of **8d** in DMSO-d_6 (400 MHz):



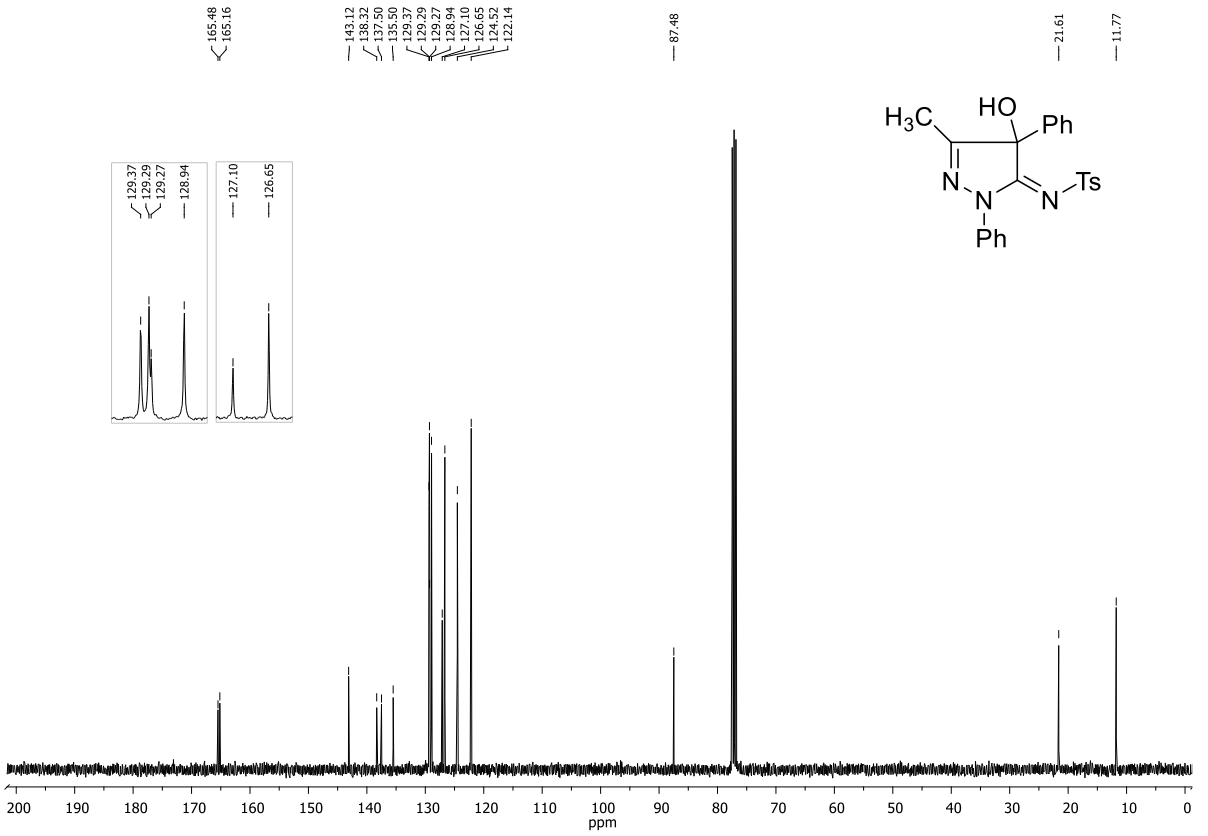
^{13}C{^{1}H} NMR of **8d** in DMSO-d_6 (100 MHz):



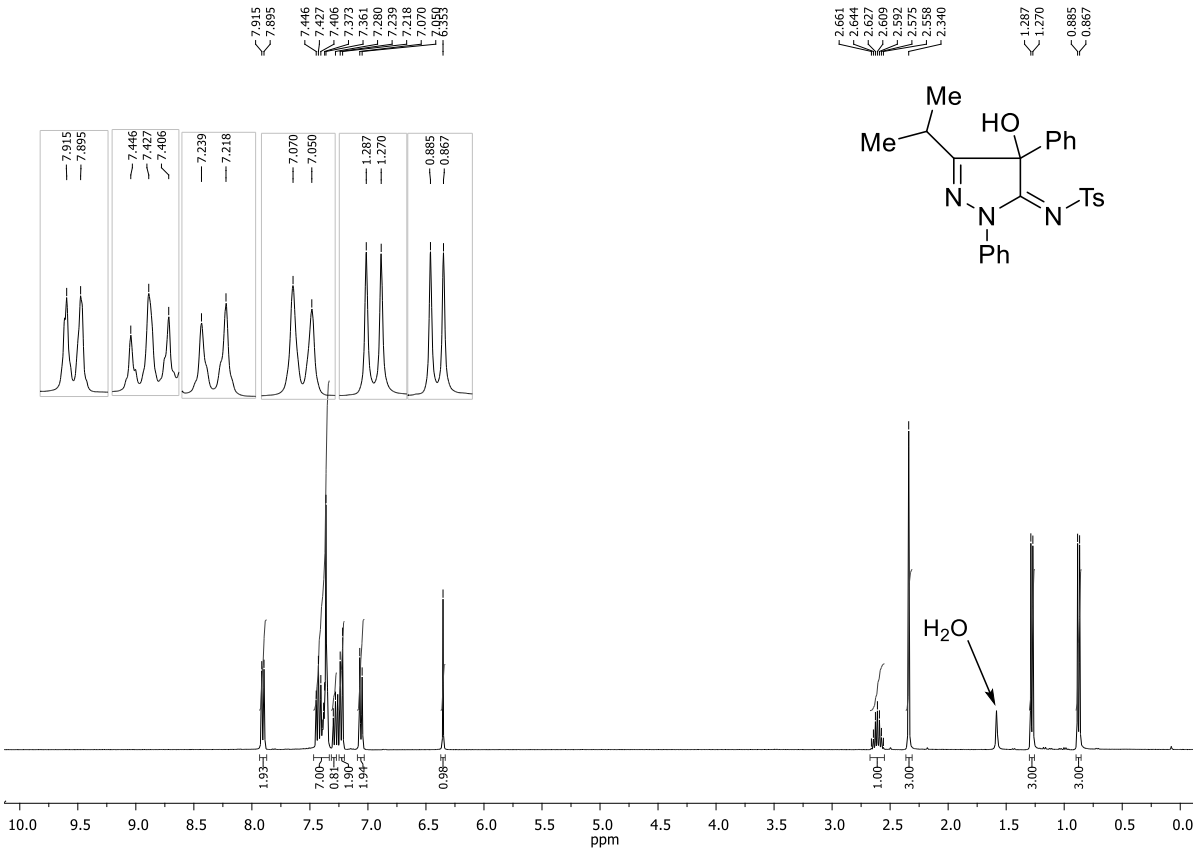
^{1}H NMR of **7a** in $CDCl_3$ (400 MHz):



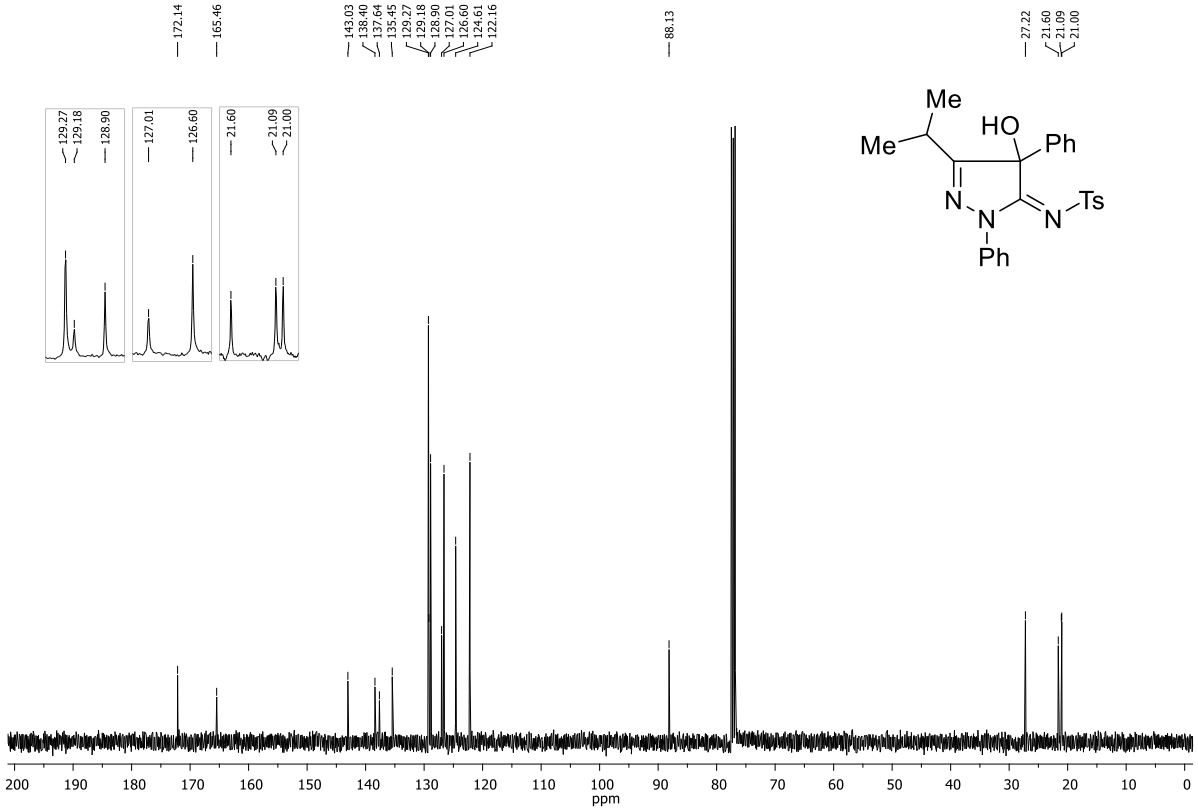
^{13}C{^{1}H} NMR of **7a** in $CDCl_3$ (100 MHz):



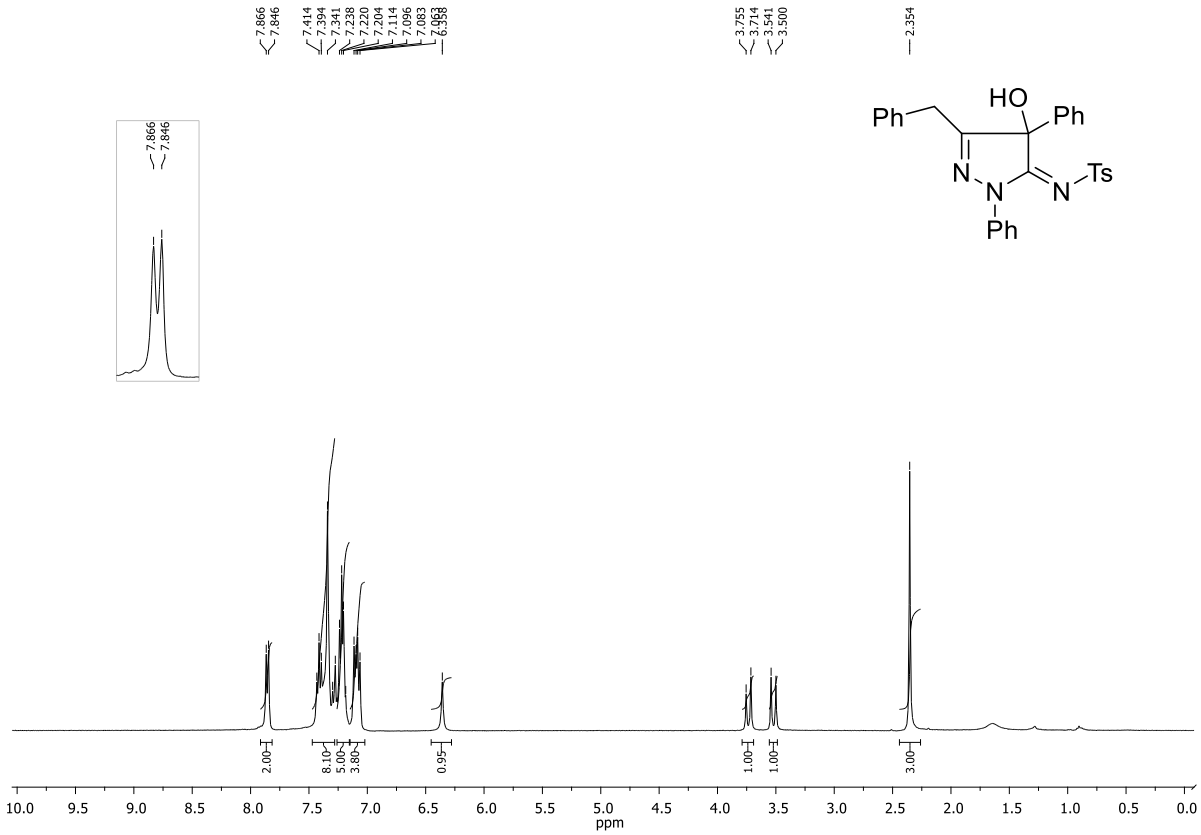
^{1}H NMR of **7b** in $CDCl_3$ (700 MHz):



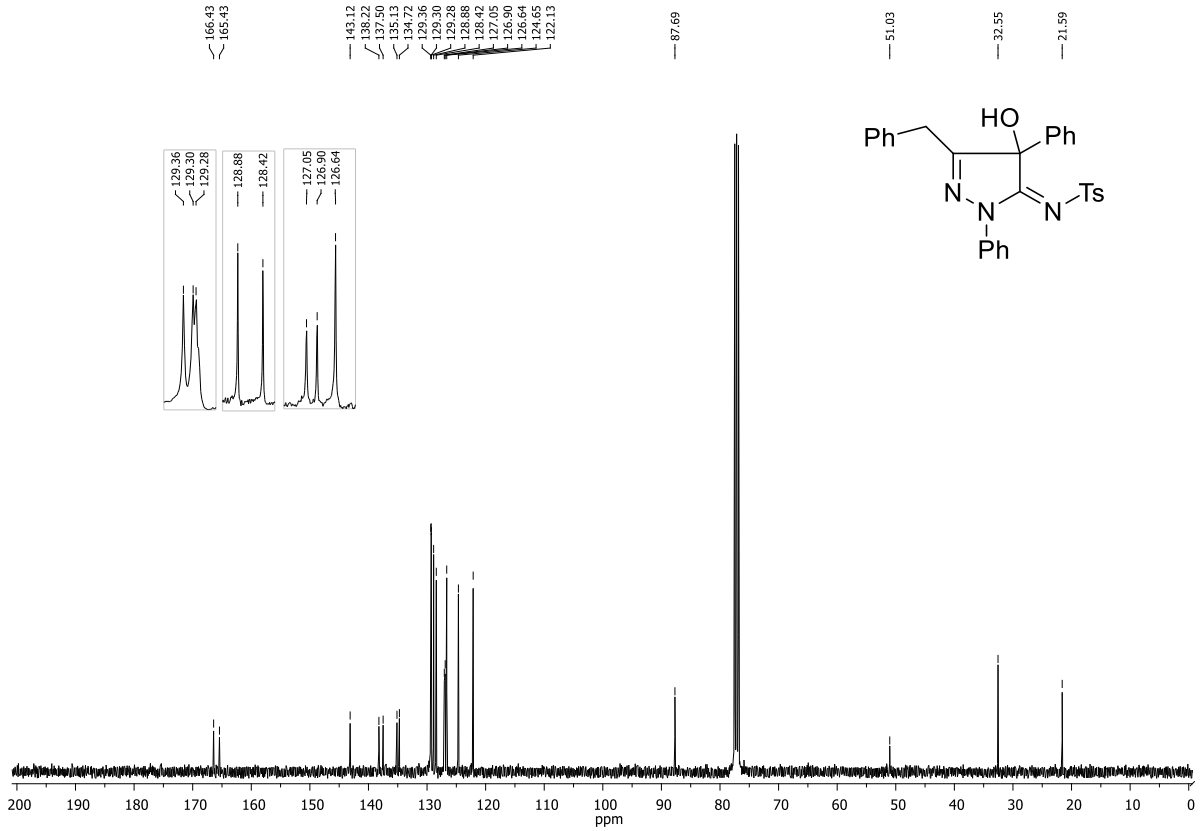
^{13}C{^{1}H} NMR of **7b** in $CDCl_3$ (100 MHz):



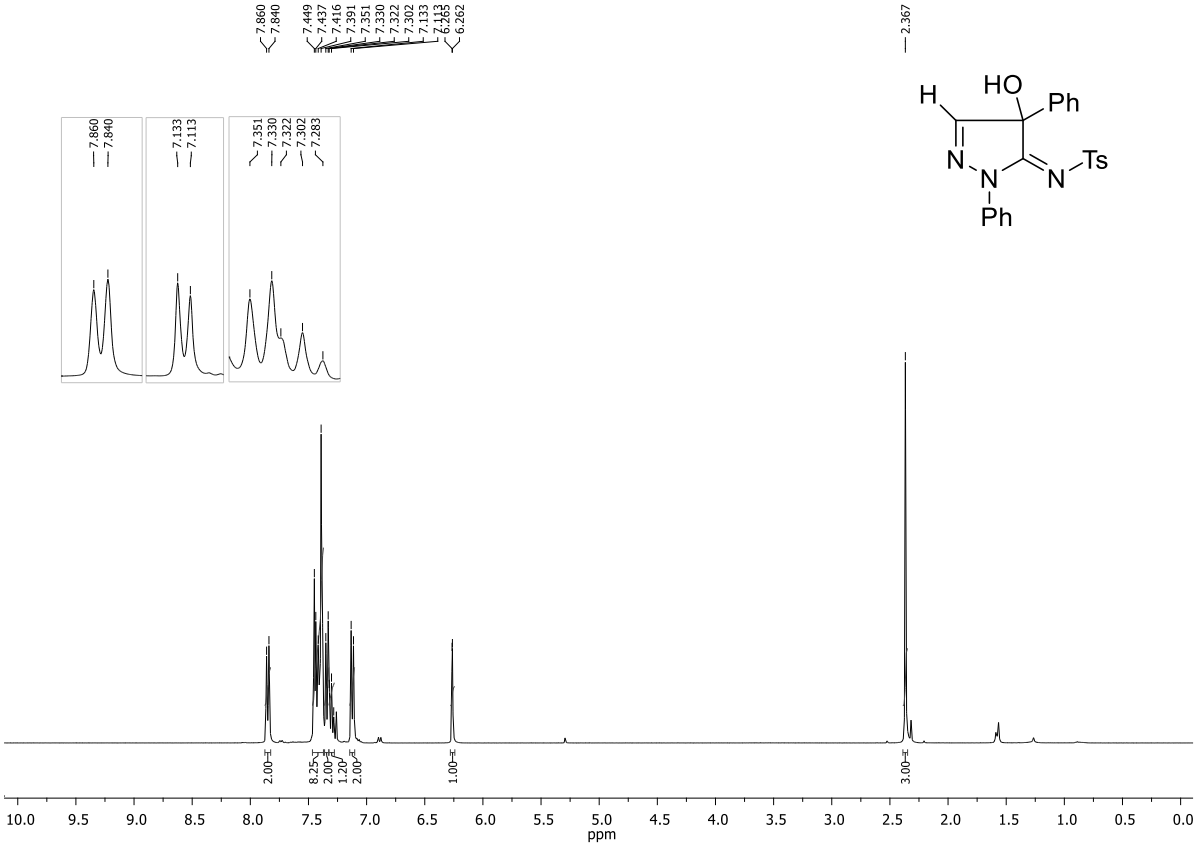
^{1}H NMR of **7c** in $CDCl_3$ (400 MHz):



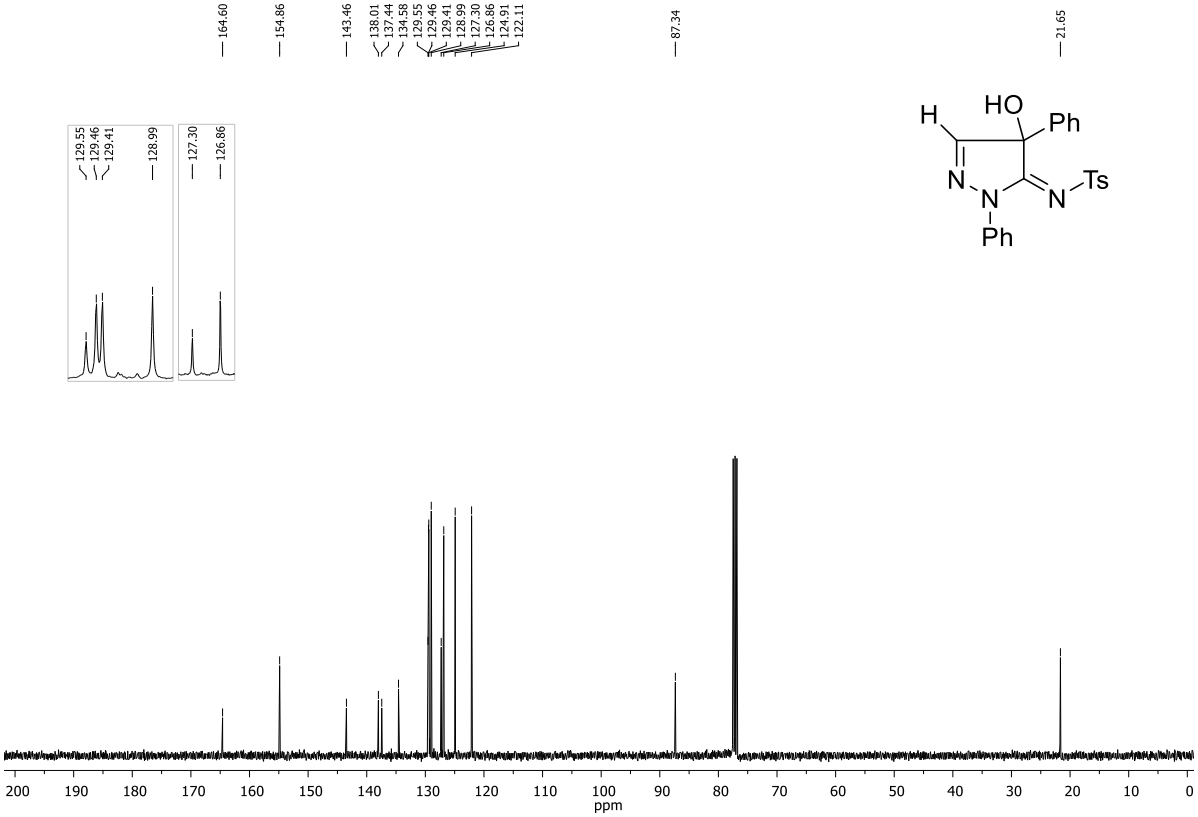
^{13}C{^{1}H} NMR of **7c** in $CDCl_3$ (100 MHz):



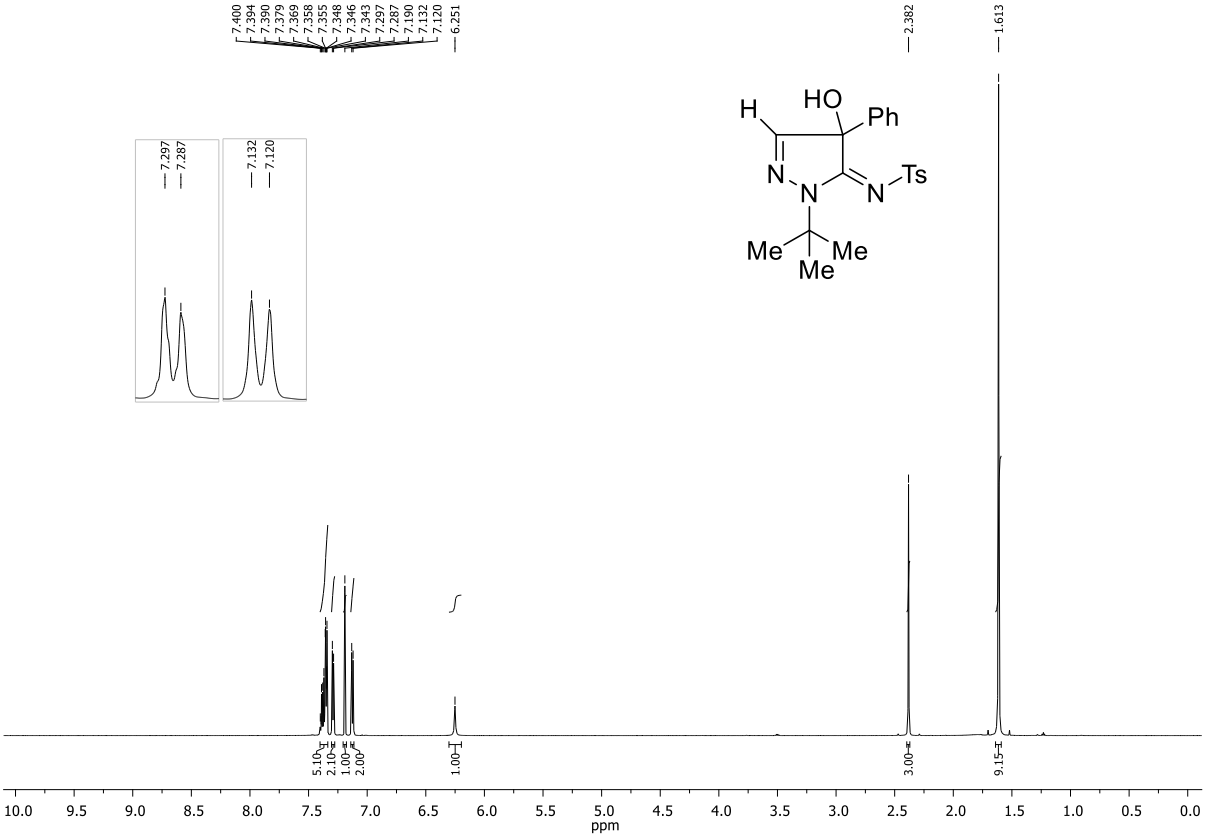
^{1}H NMR of **7d** in $CDCl_3$ (400 MHz):



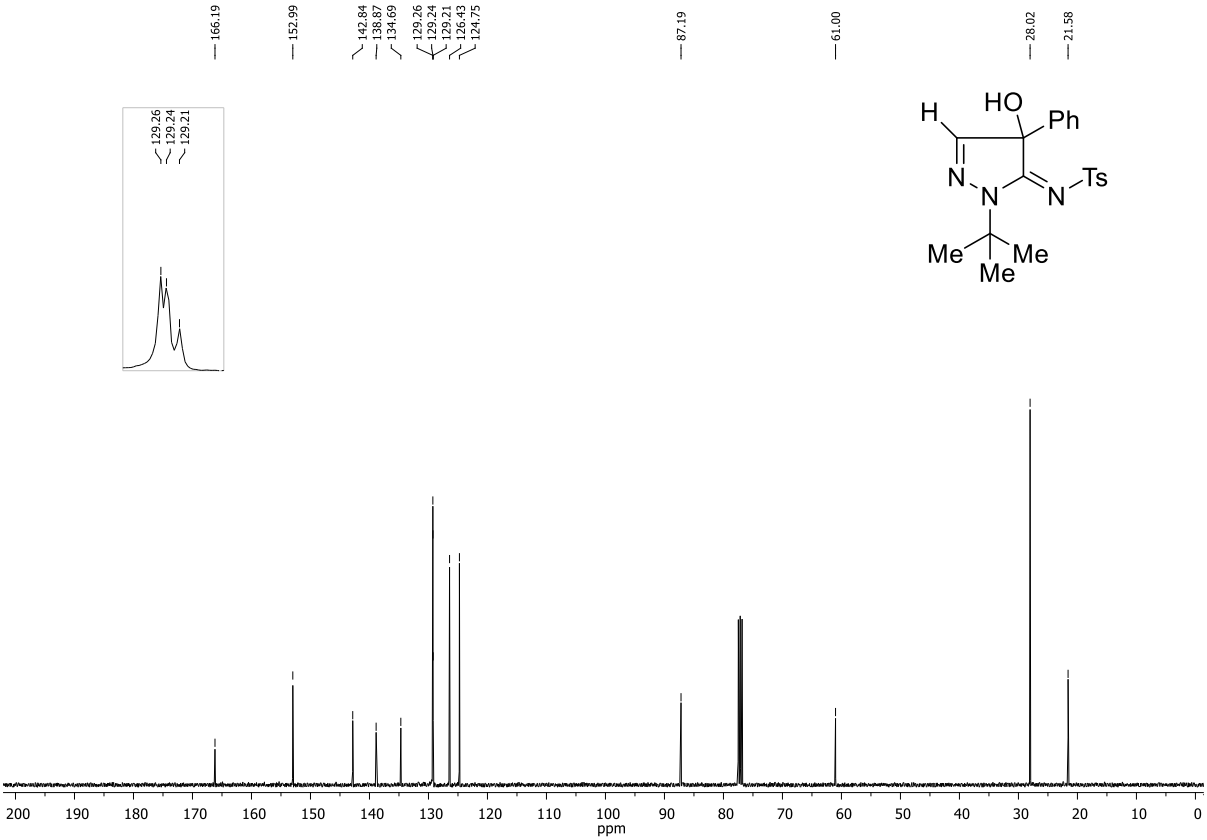
^{13}C{^{1}H} NMR of **7d** in $CDCl_3$ (100 MHz):



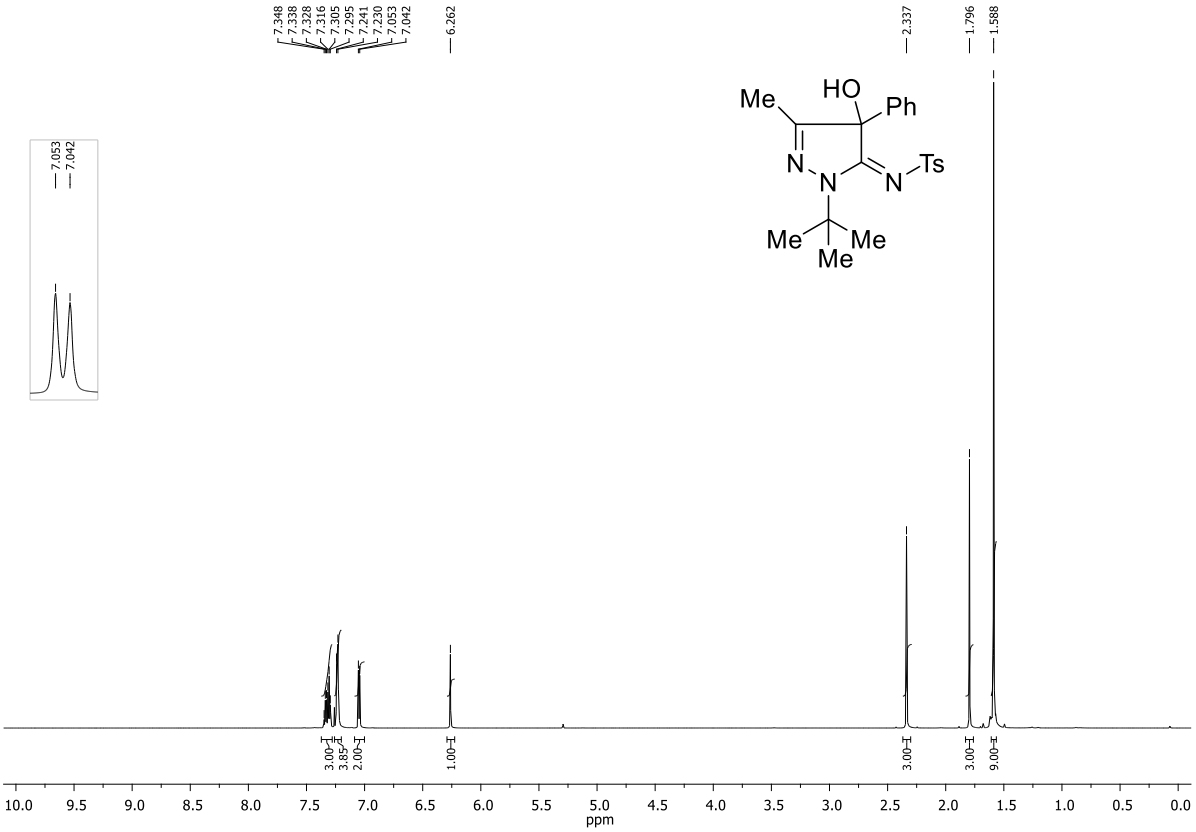
^{1}H NMR of **7e** in $CDCl_3$ (700 MHz):



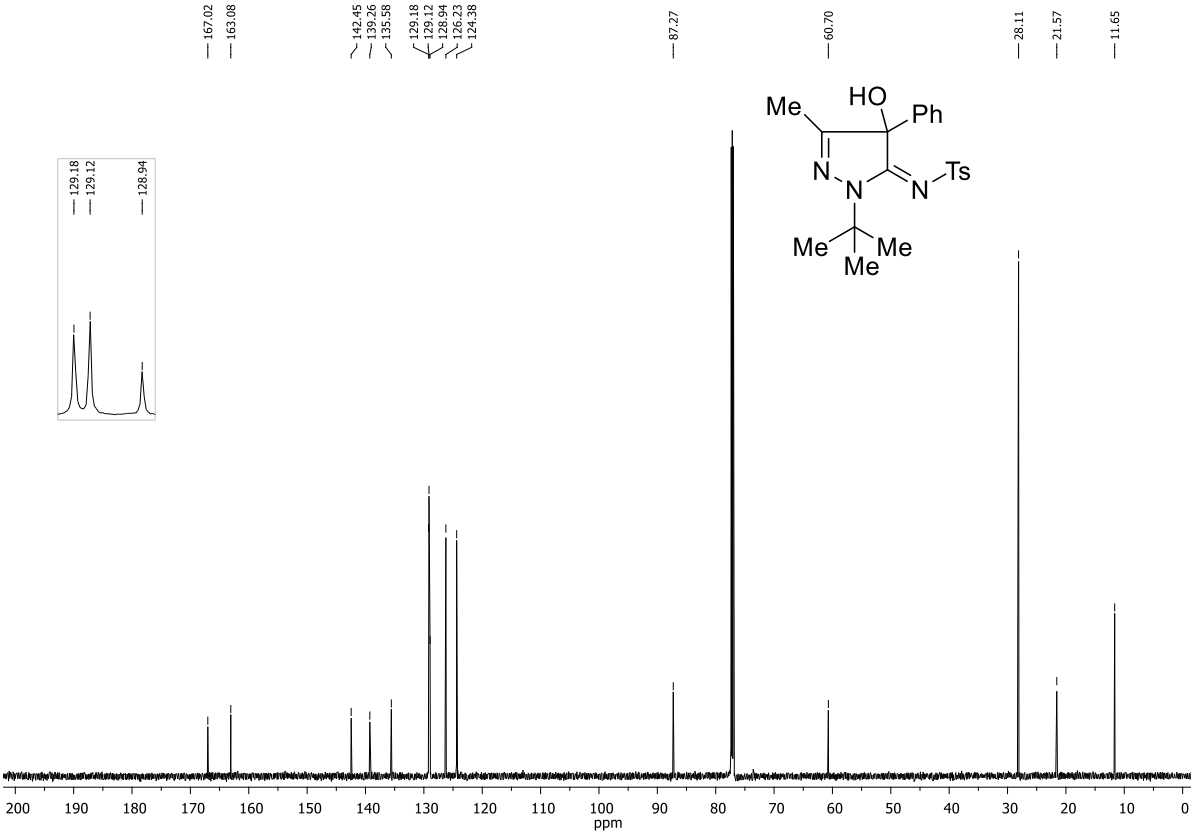
^{13}C{^{1}H} NMR of **7e** in $CDCl_3$ (100 MHz):



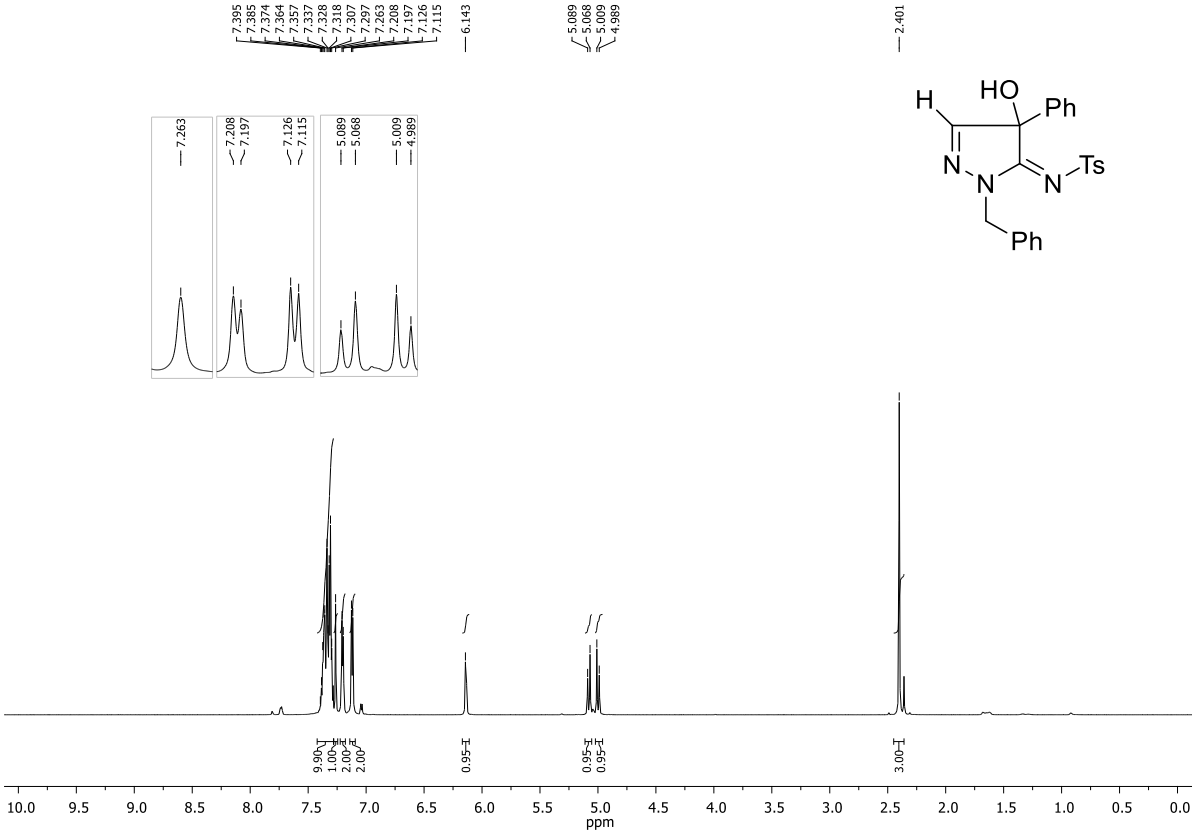
^{1}H NMR of **7f** in $CDCl_3$ (700 MHz):



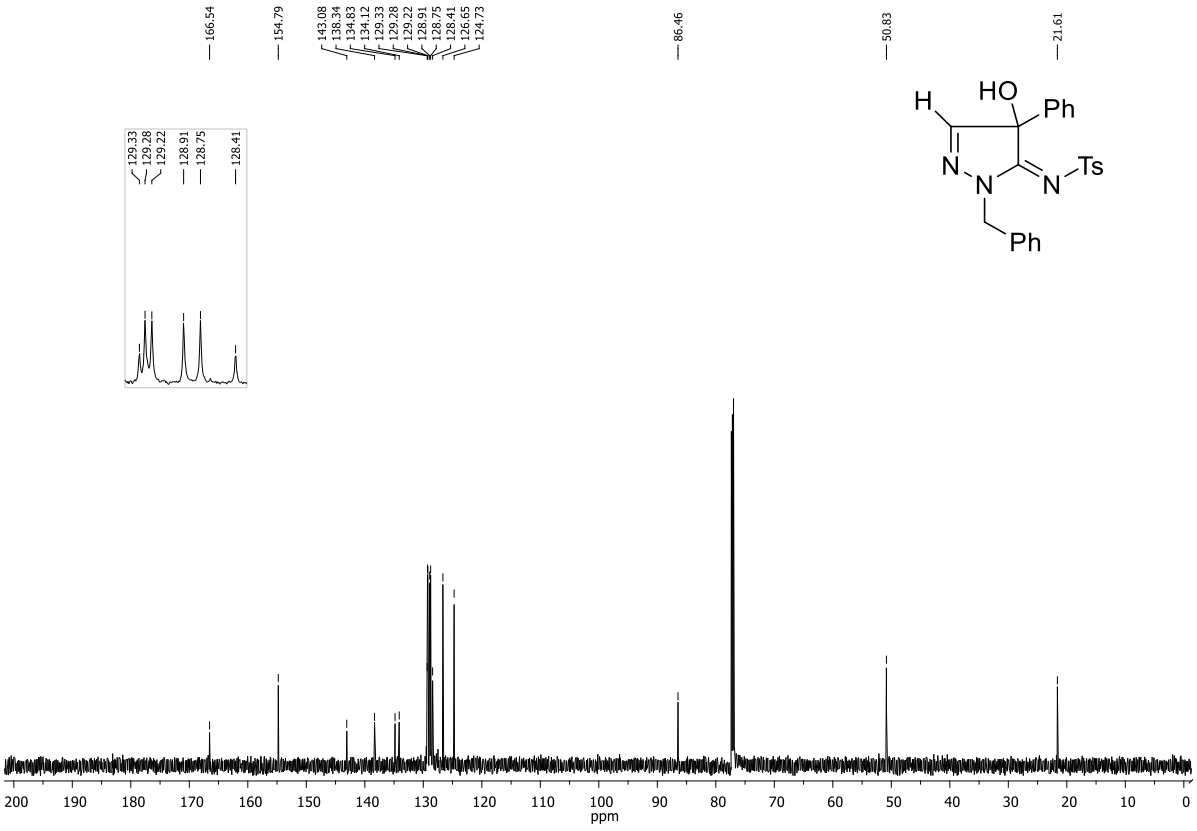
^{13}C{^{1}H} NMR of **7f** in $CDCl_3$ (175 MHz):



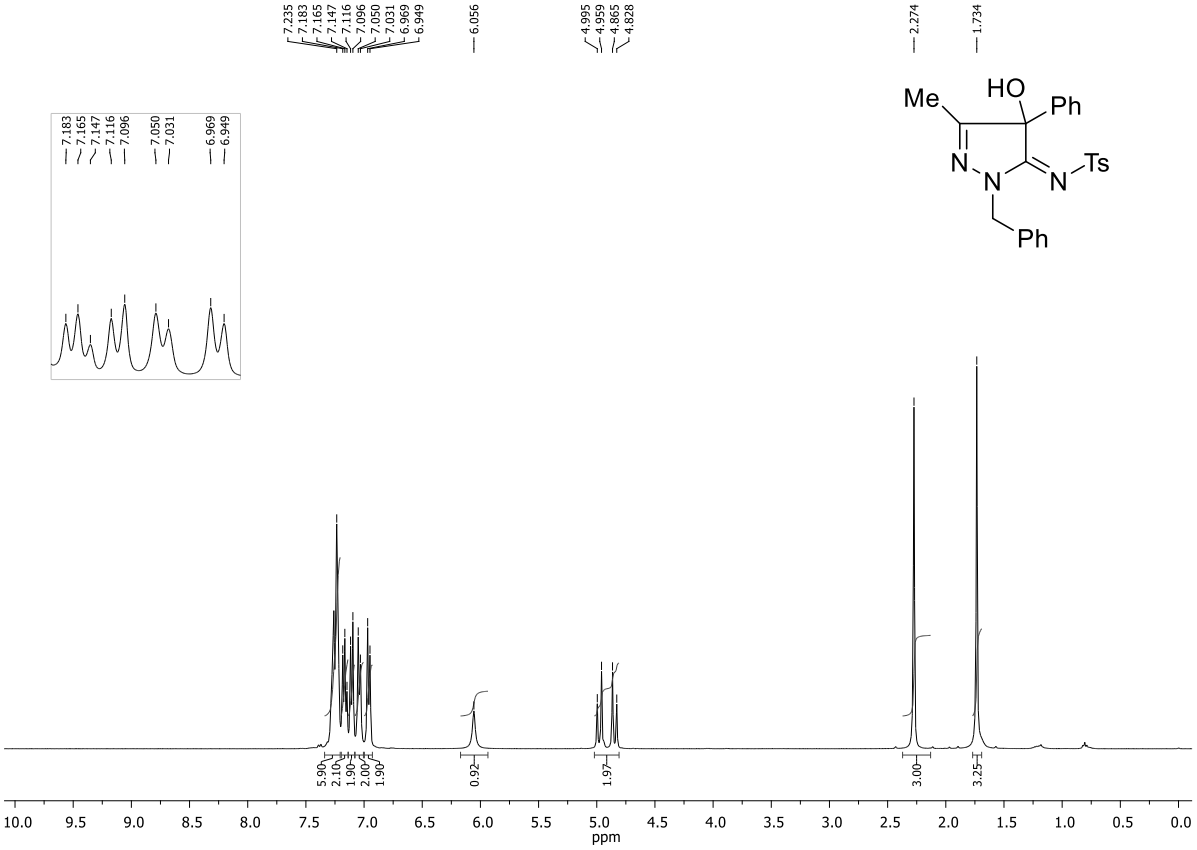
^{1}H NMR of **7g** in $CDCl_3$ (700 MHz):



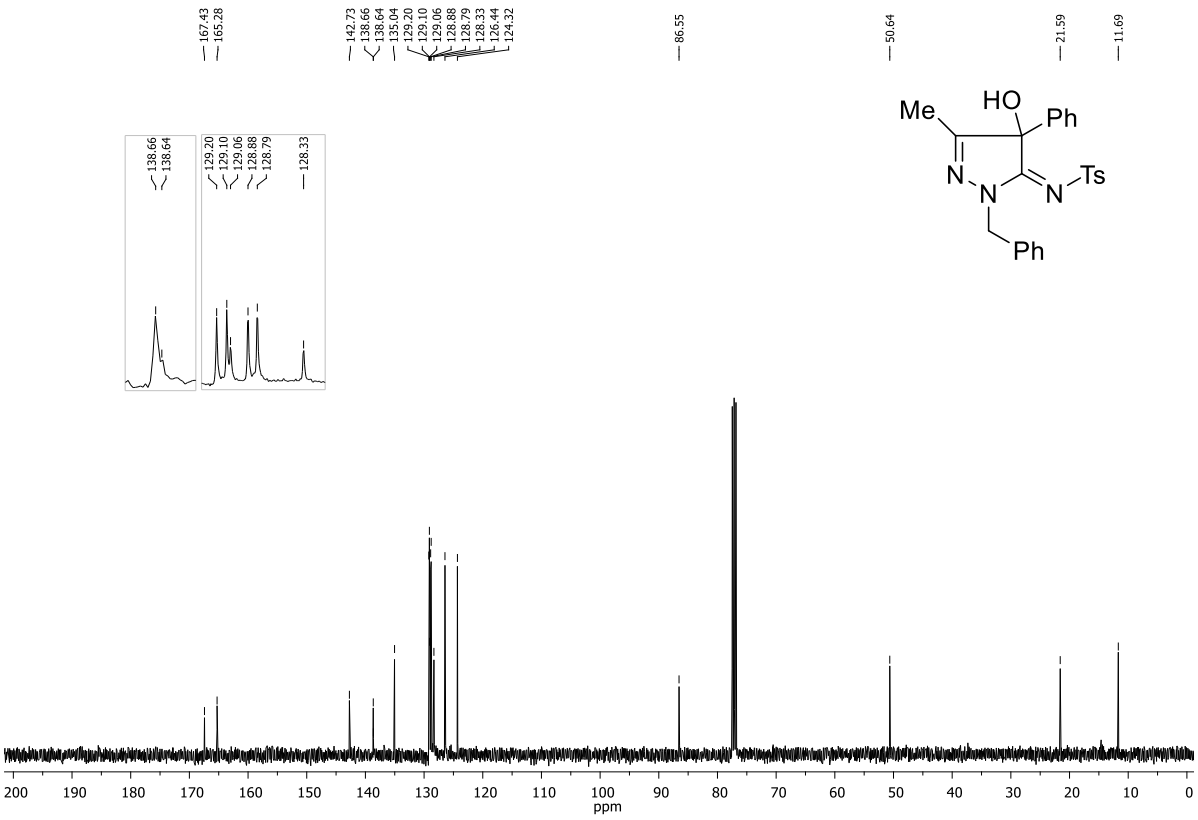
^{13}C{^{1}H} NMR of **7g** in $CDCl_3$ (175 MHz):



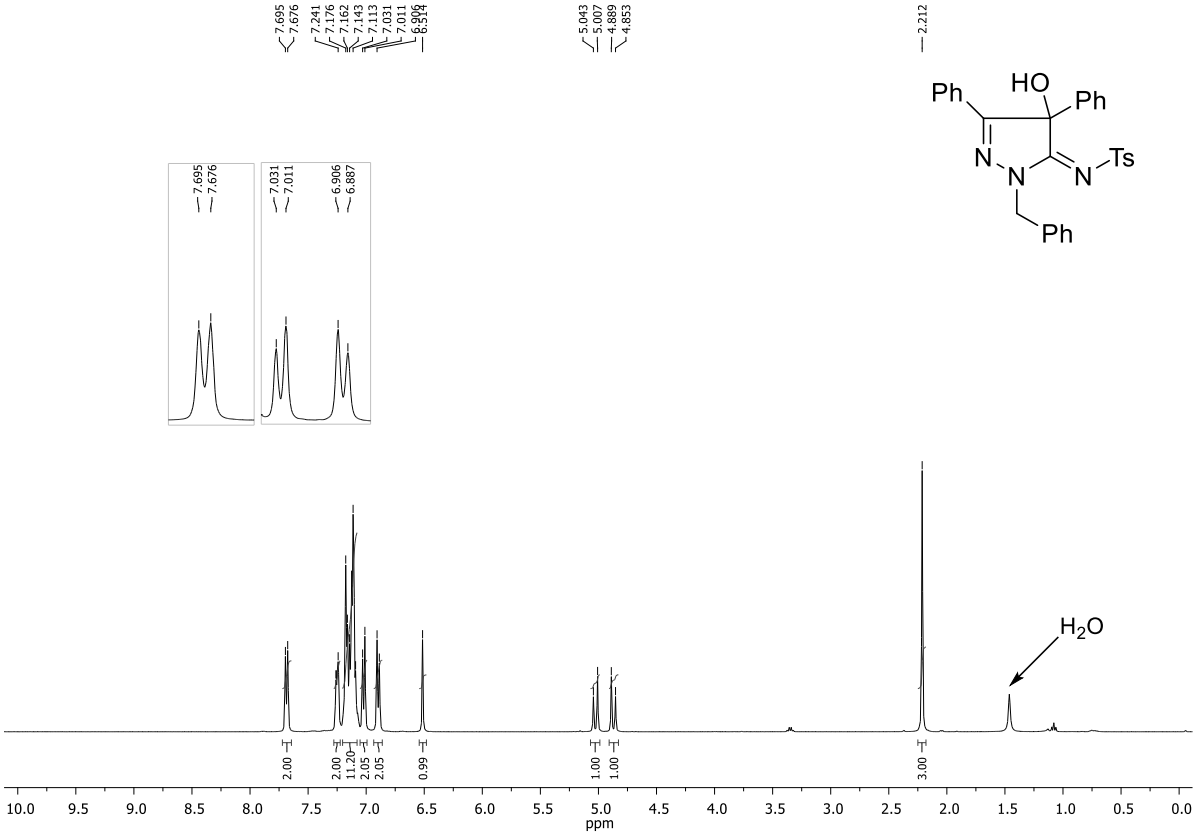
^{1}H NMR of **7h** in $CDCl_3$ (400 MHz):



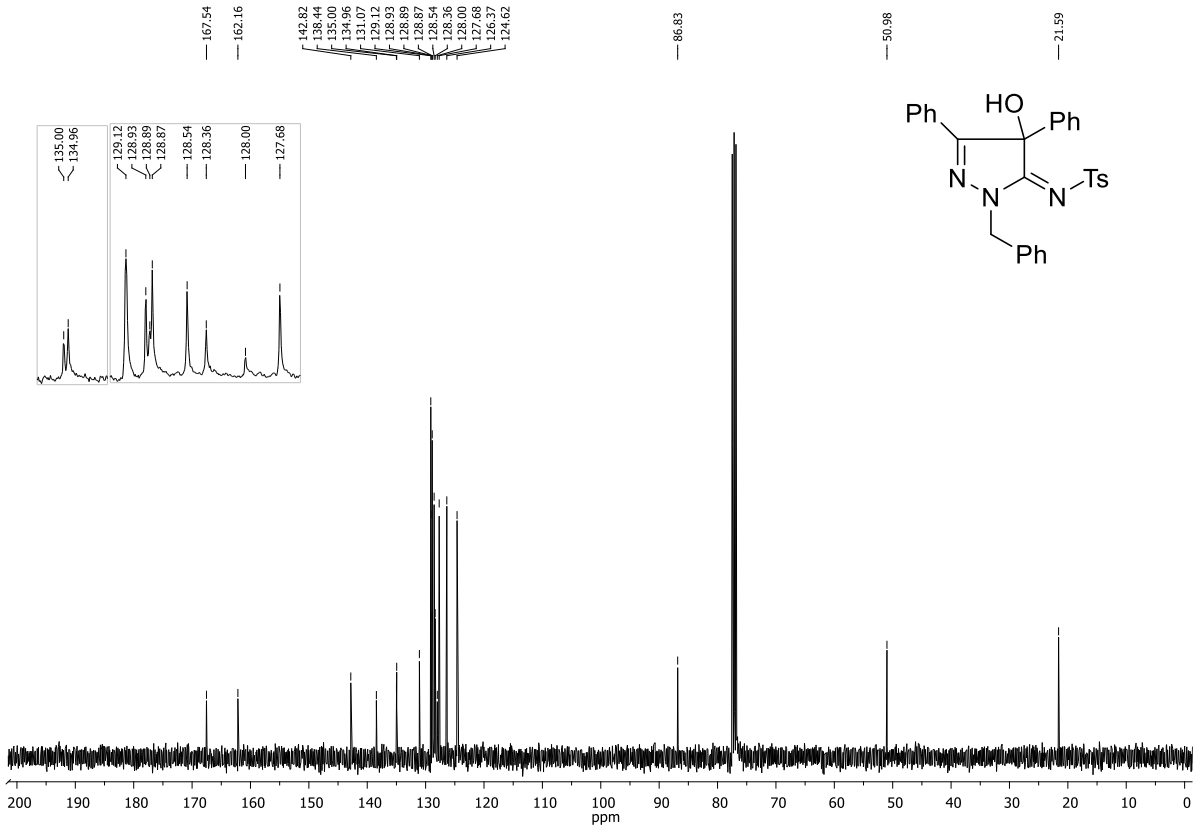
^{13}C{^{1}H} NMR of **7h** in $CDCl_3$ (100 MHz):



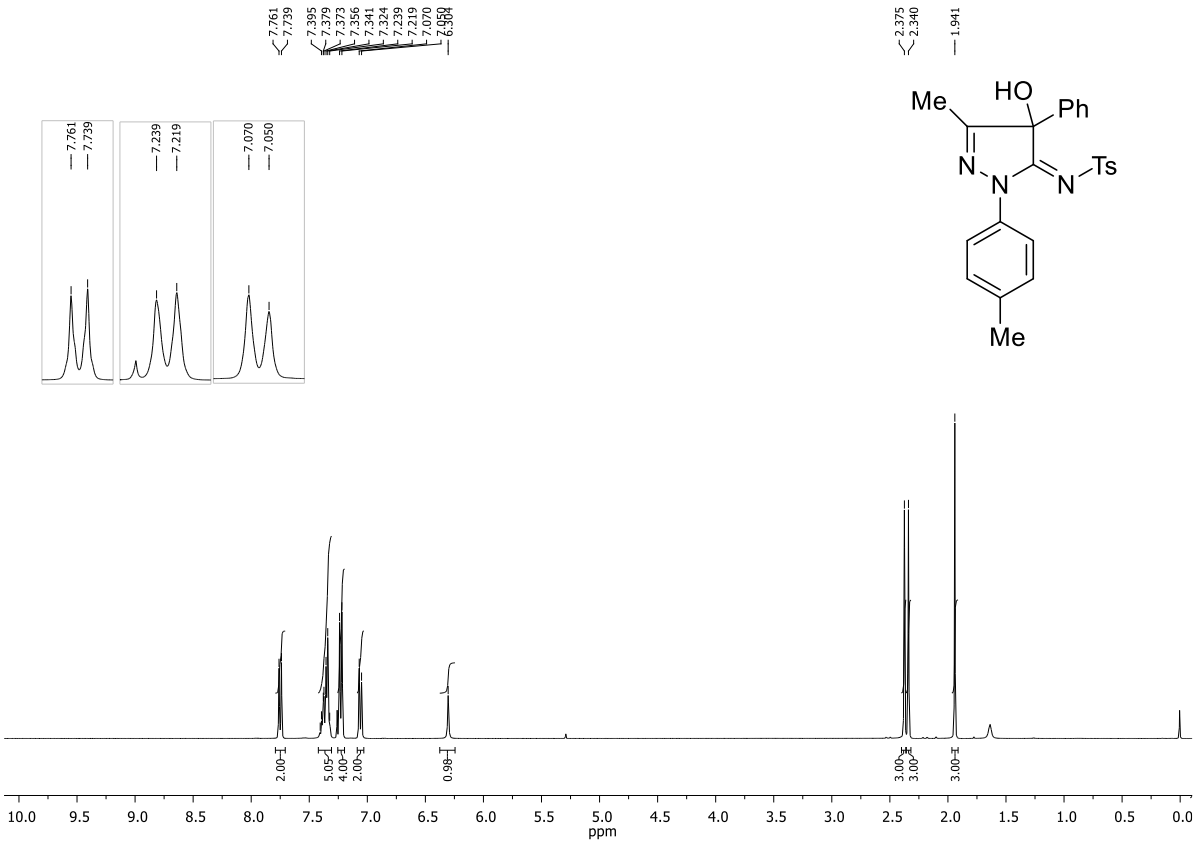
^{1}H NMR of **7i** in $CDCl_3$ (400 MHz):



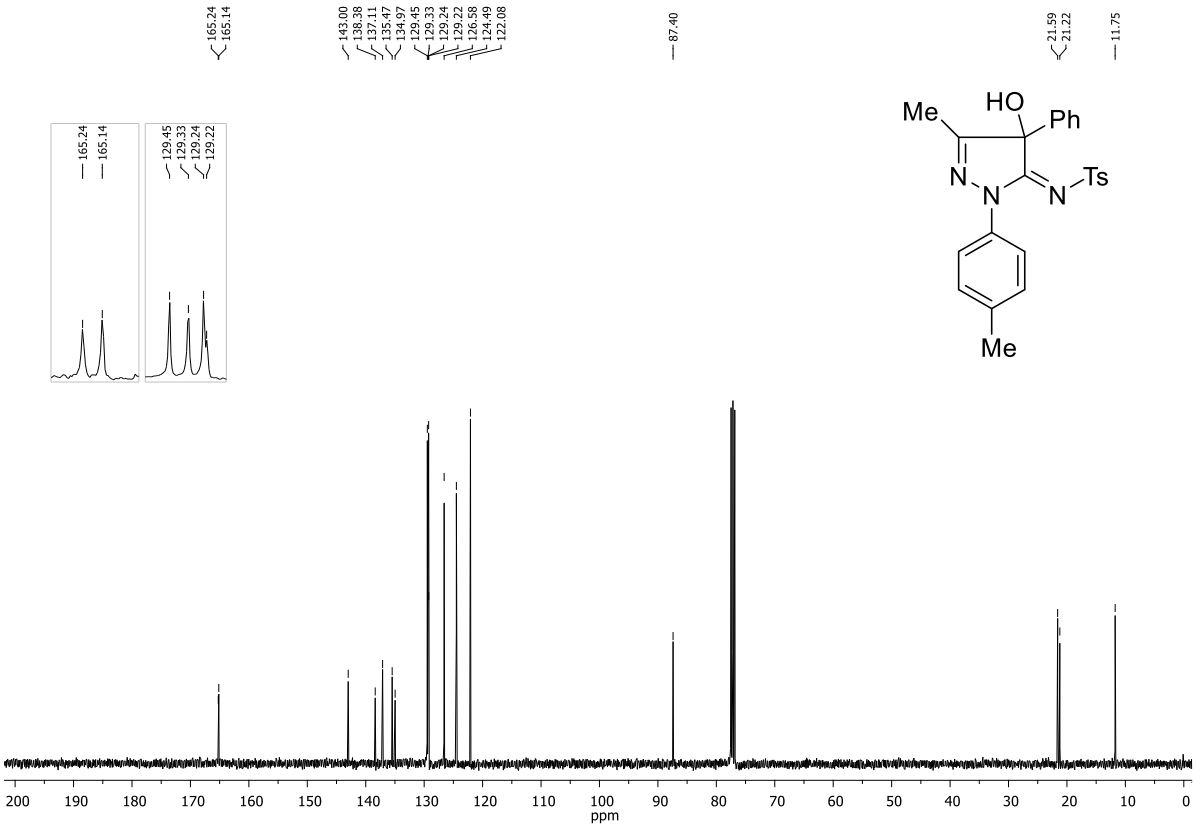
^{13}C{^{1}H} NMR of **7i** in $CDCl_3$ (100 MHz):



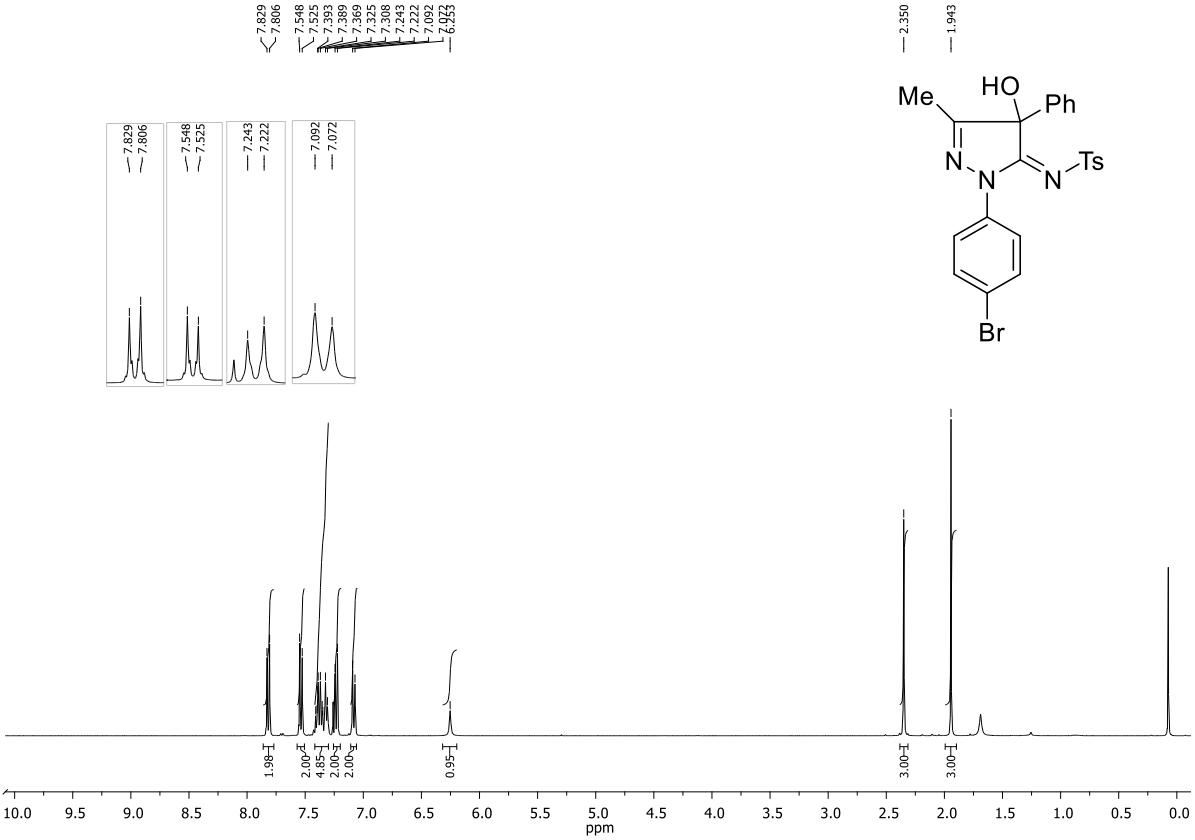
^{1}H NMR of **7j** in $CDCl_3$ (400 MHz):



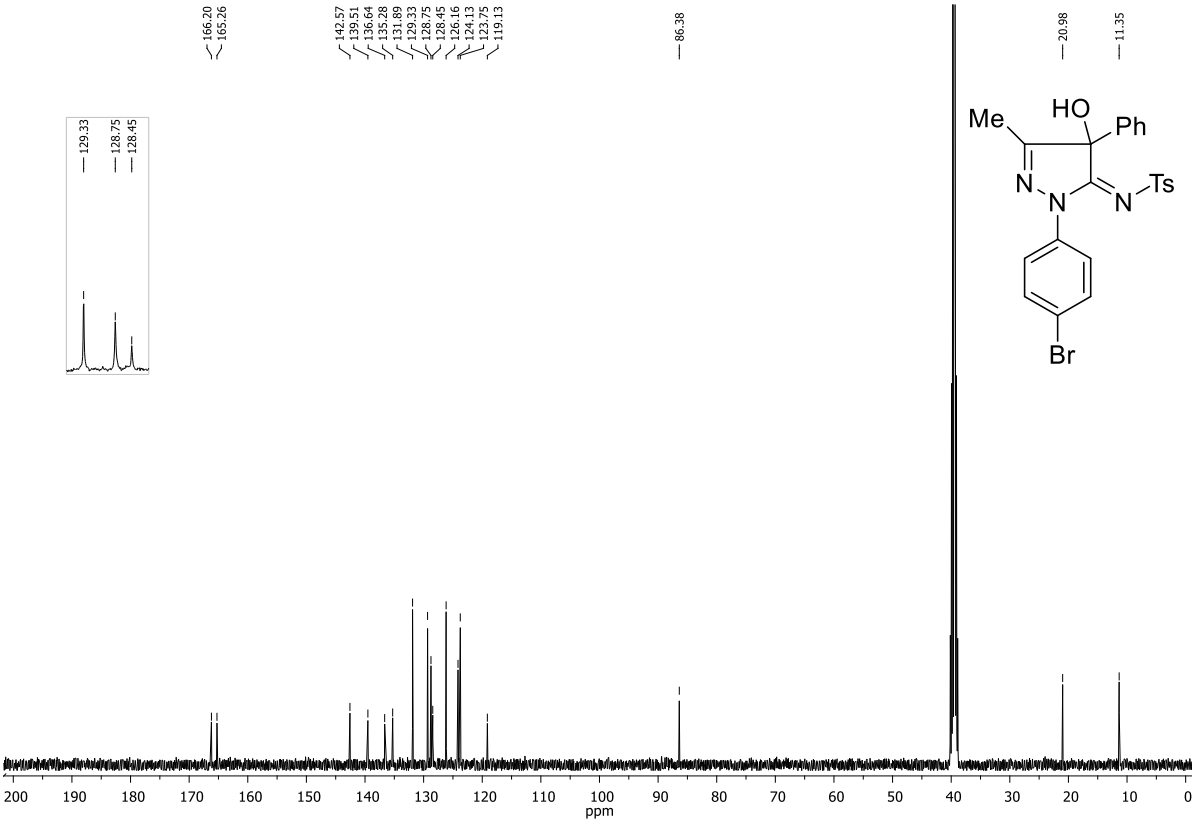
^{13}C{^{1}H} NMR of **7j** in $CDCl_3$ (100 MHz):



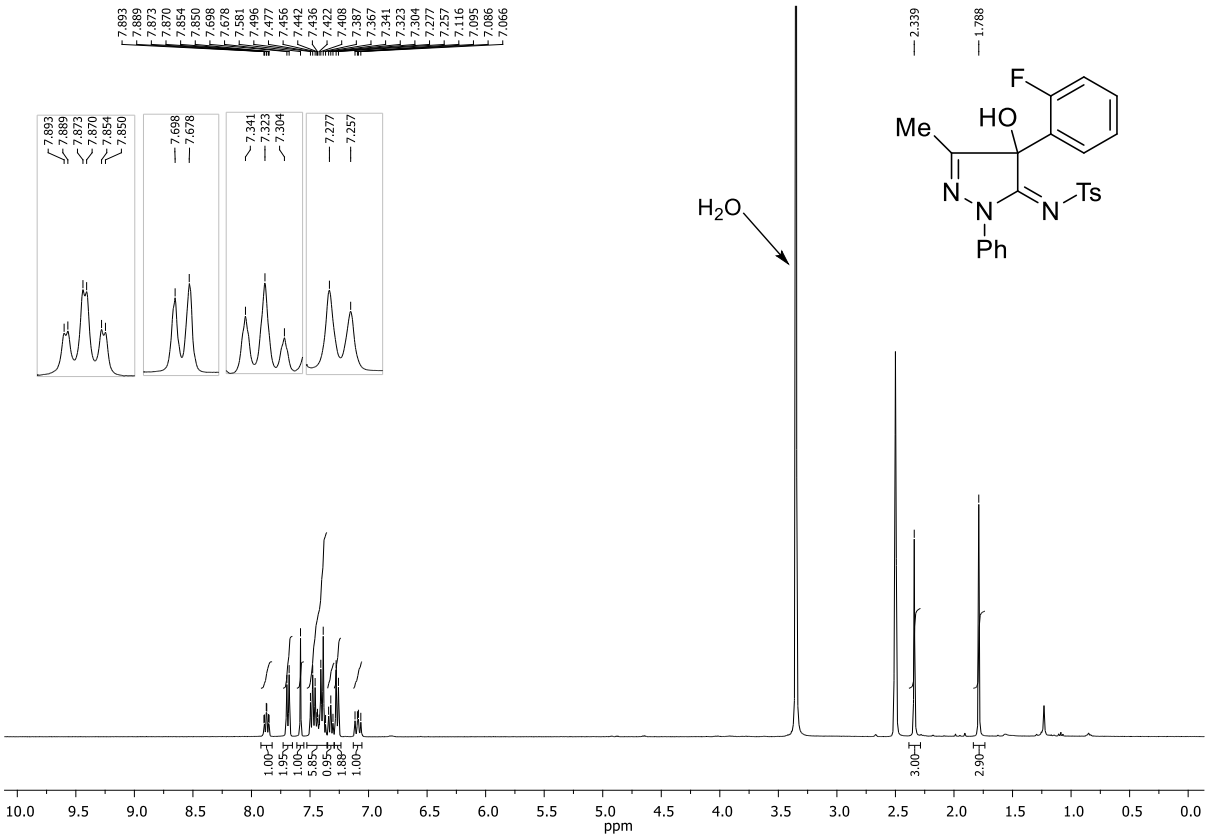
^{1}H NMR of **7k** in $CDCl_3$ (400 MHz):



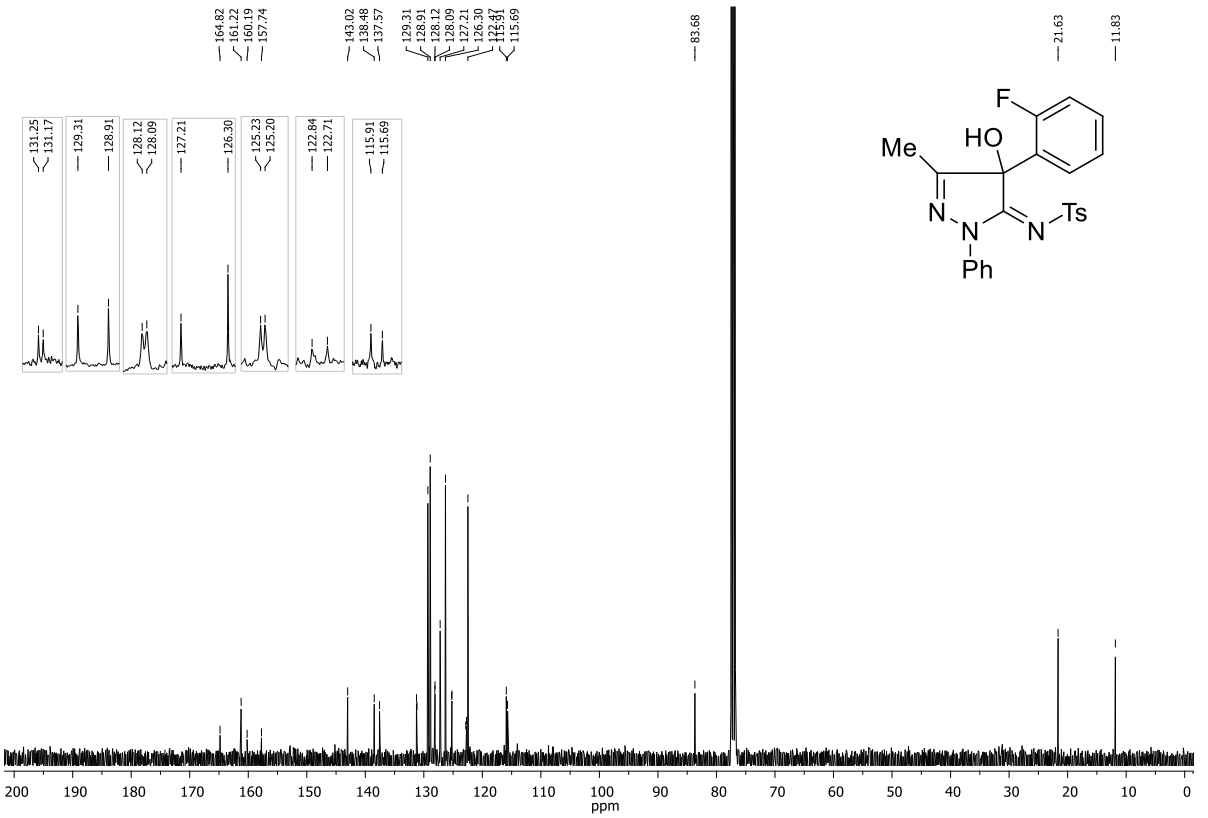
^{13}C{^{1}H} NMR of **7k** in DMSO-d_6 (100 MHz):



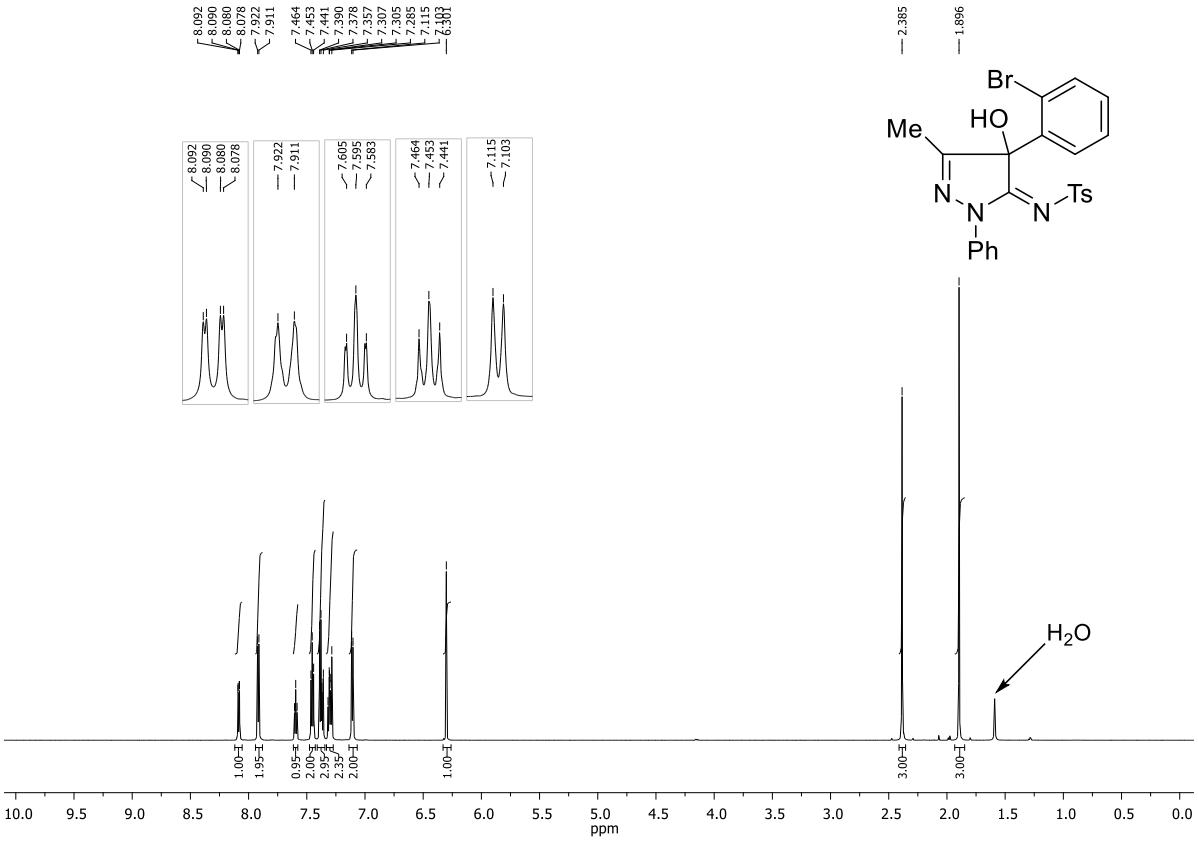
^{1}H NMR of **7l** in DMSO-d_6 (400 MHz):



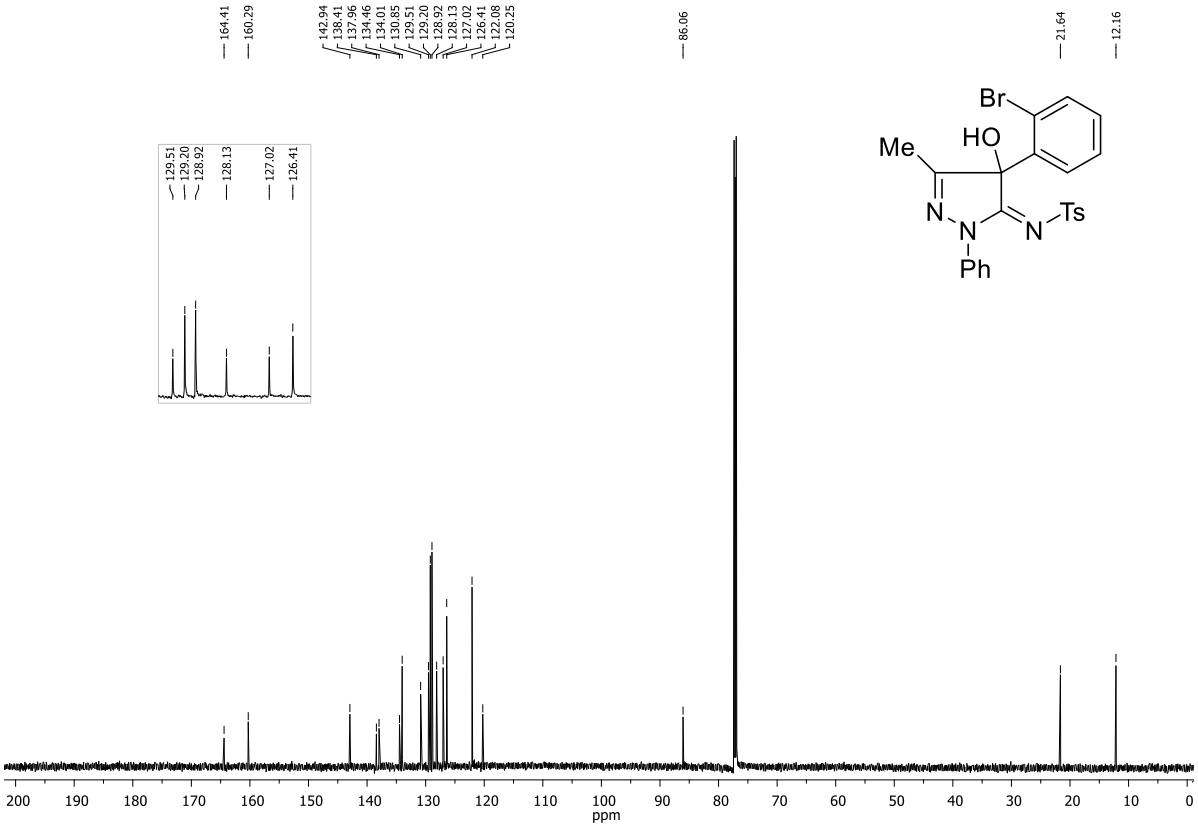
^{13}C{^{1}H} NMR of **7l** in $CDCl_3$ (100 MHz):



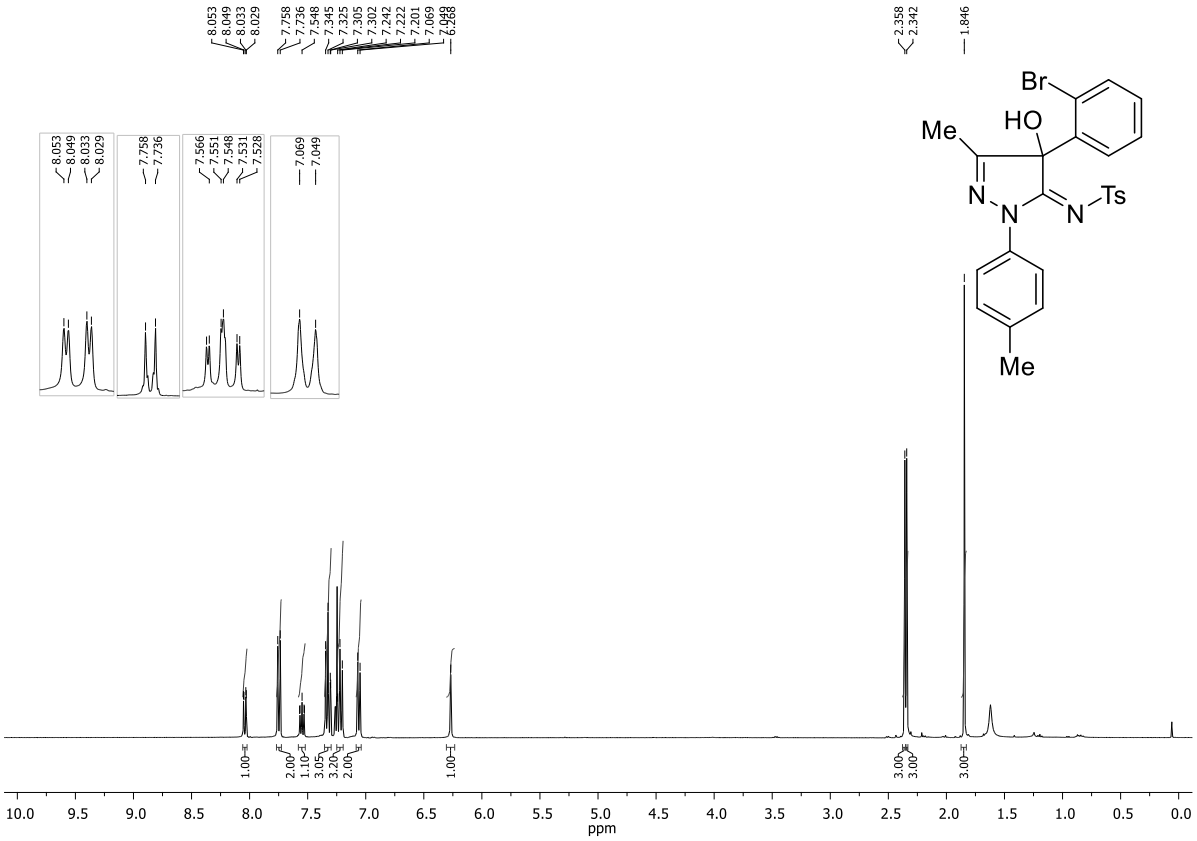
^{1}H NMR of **7m** in $CDCl_3$ (700 MHz):



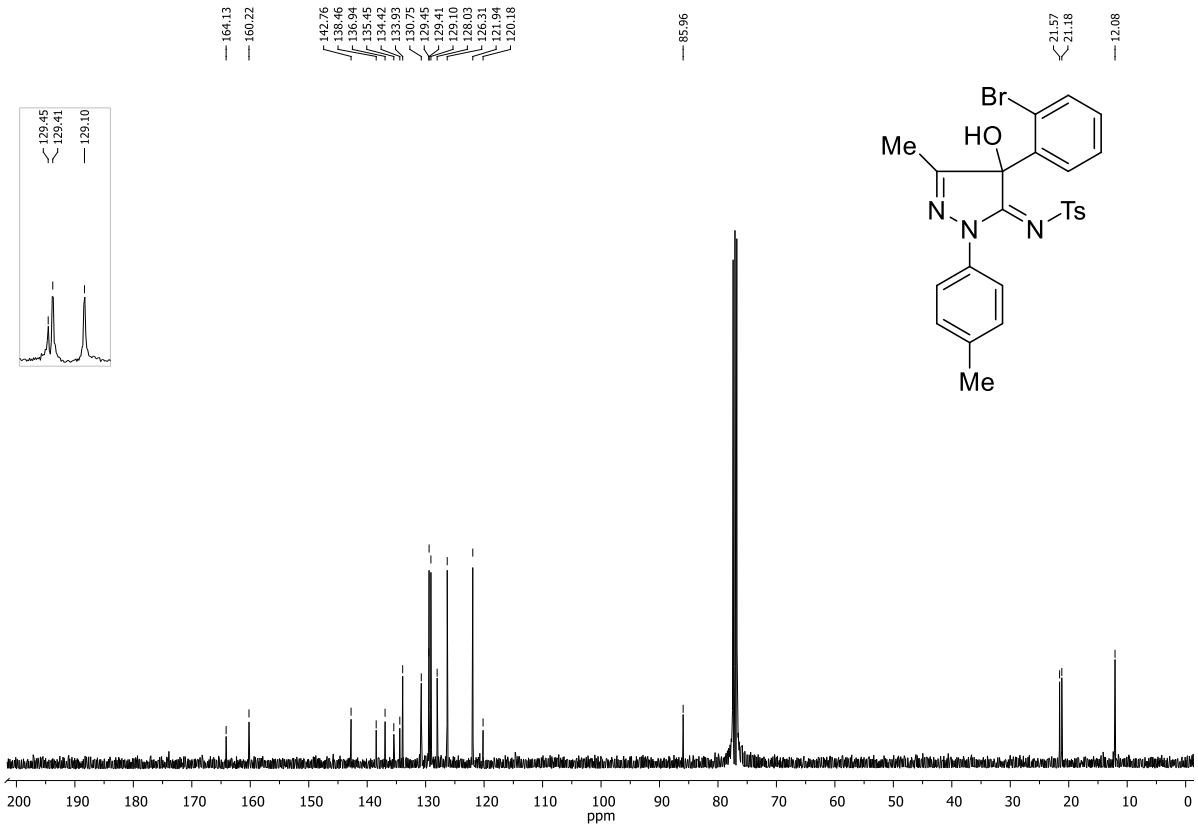
^{13}C{^{1}H} NMR of **7m** in $CDCl_3$ (175 MHz):



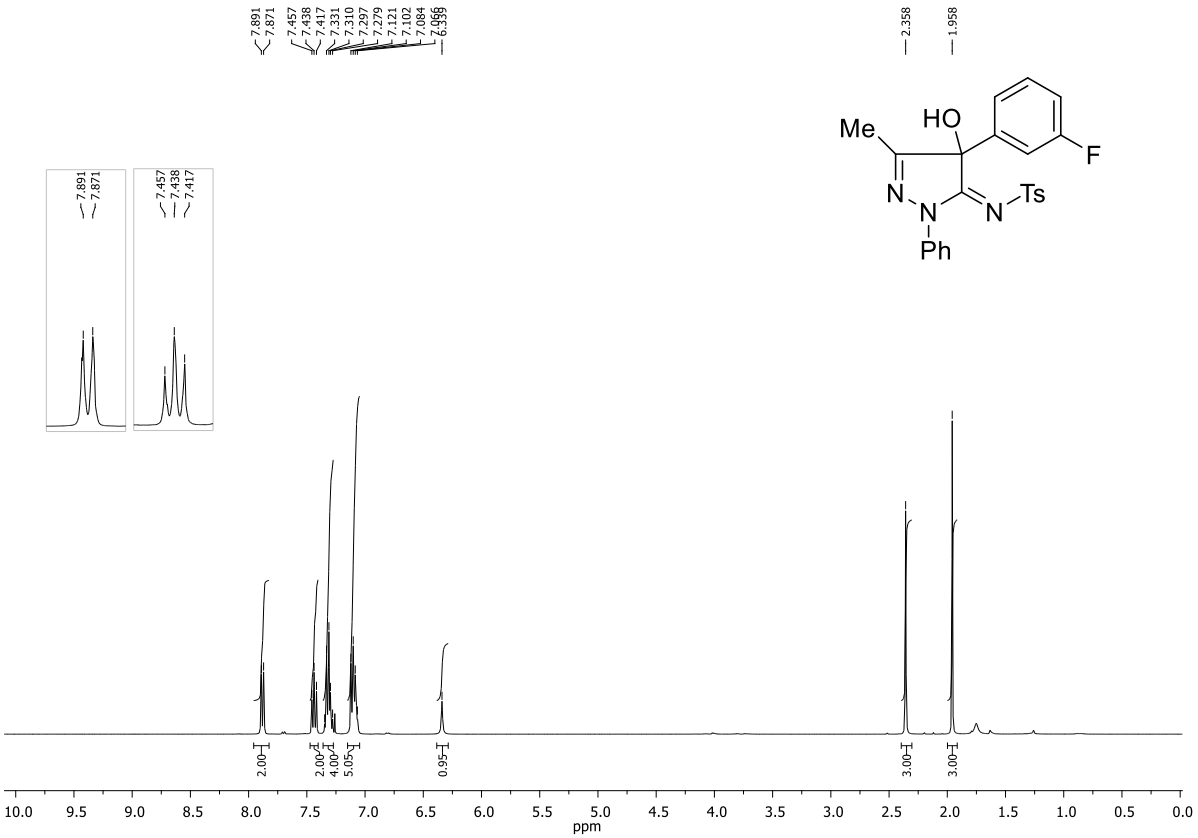
^{1}H NMR of **7n** in $CDCl_3$ (400 MHz):



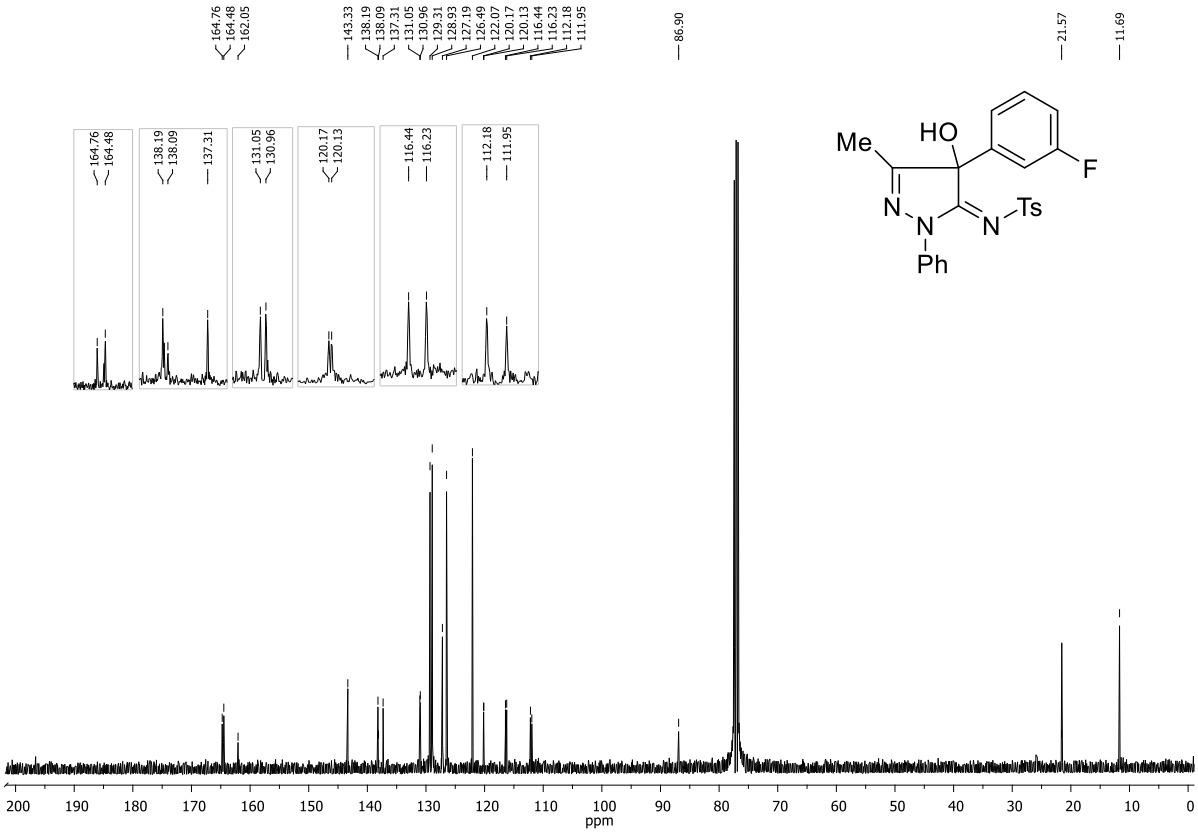
^{13}C{^{1}H} NMR of **7n** in $CDCl_3$ (100 MHz):



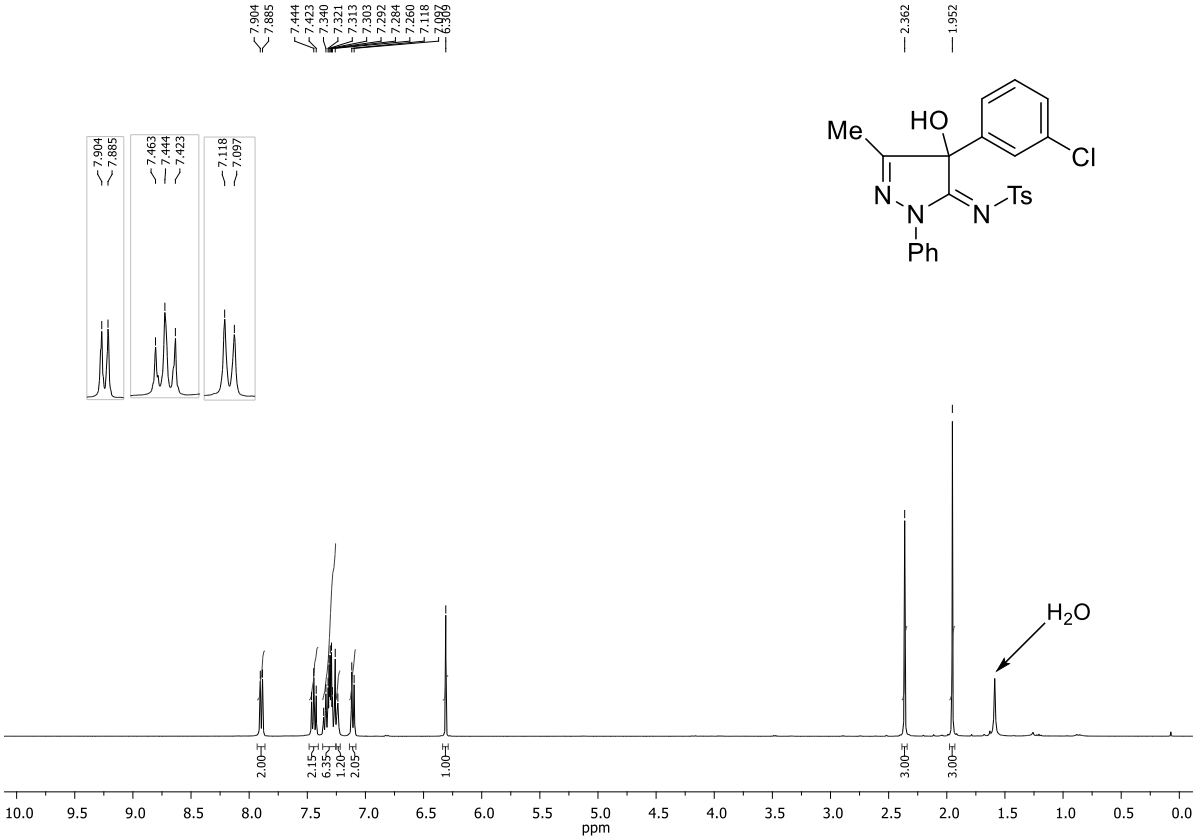
^{1}H NMR of **7o** in $CDCl_3$ (400 MHz):



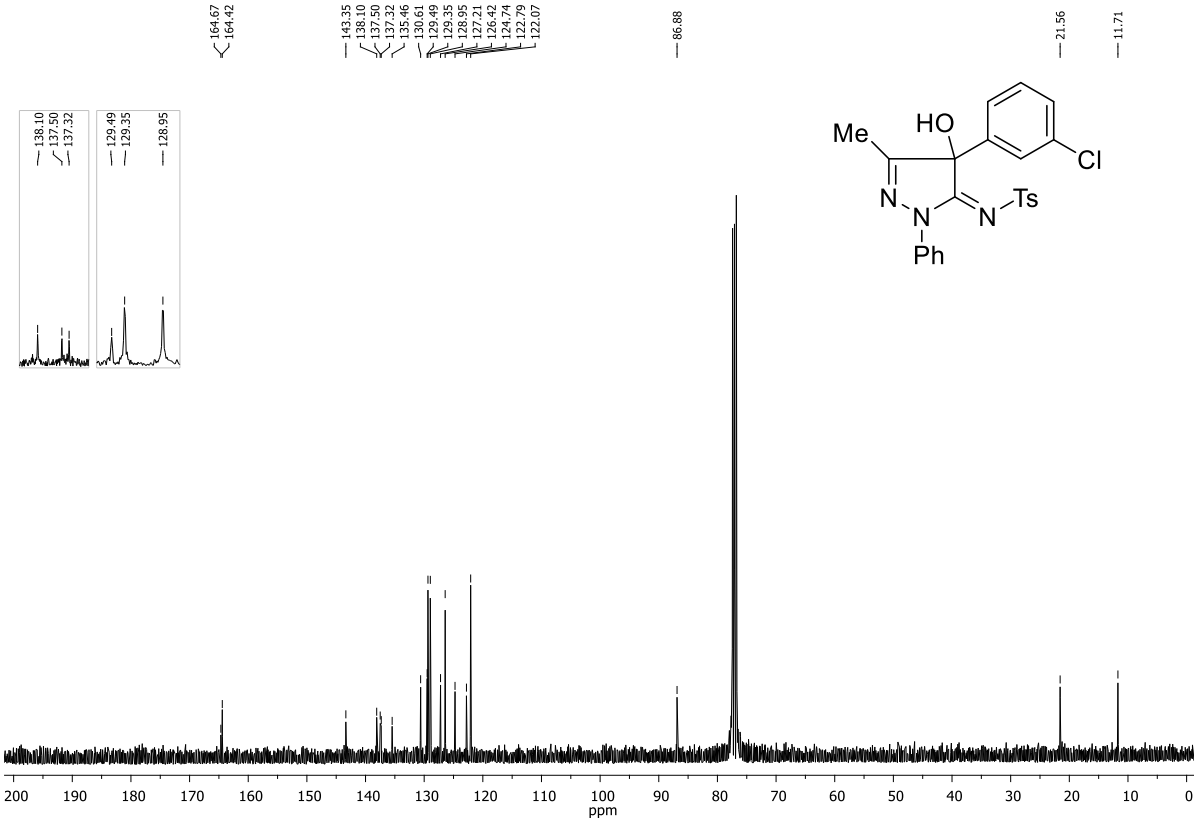
^{13}C{^{1}H} NMR of **7o** in $CDCl_3$ (100 MHz):



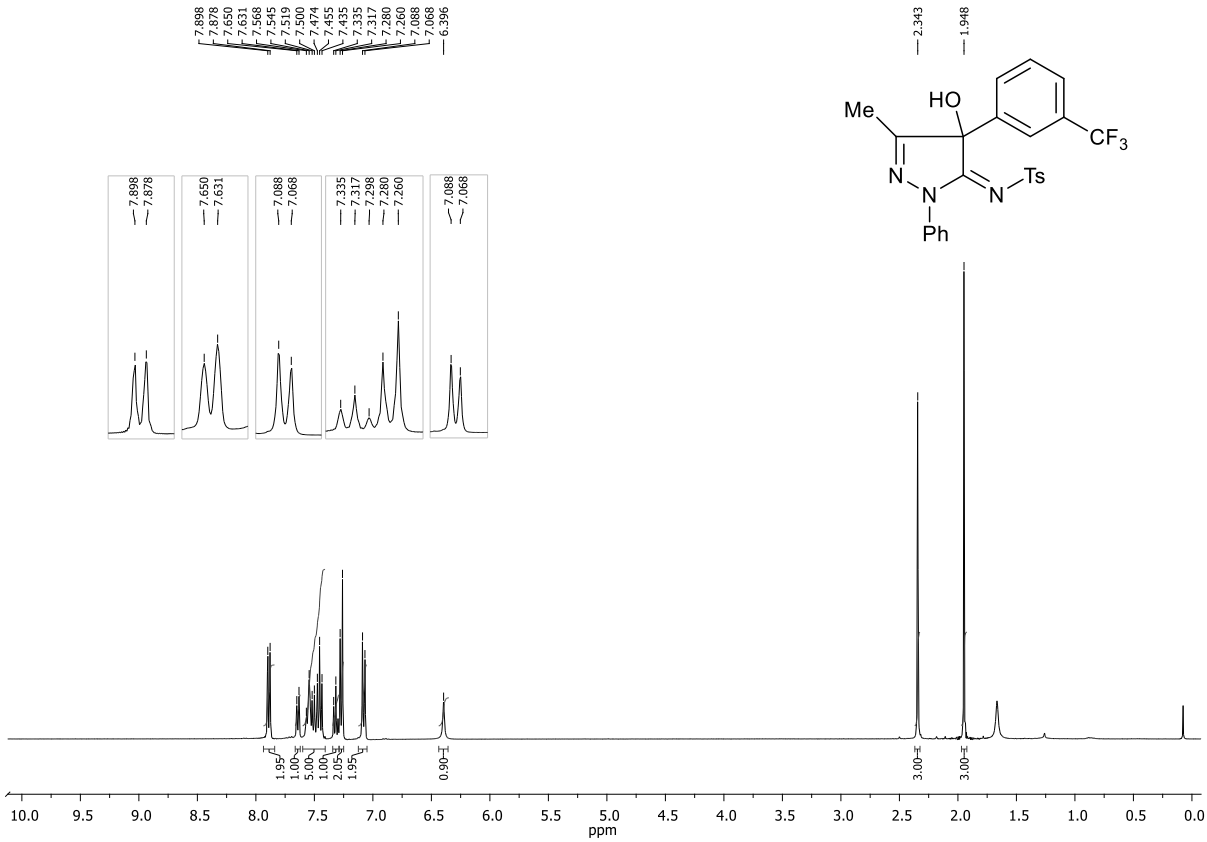
^{1}H NMR of **7p** in $CDCl_3$ (400 MHz):



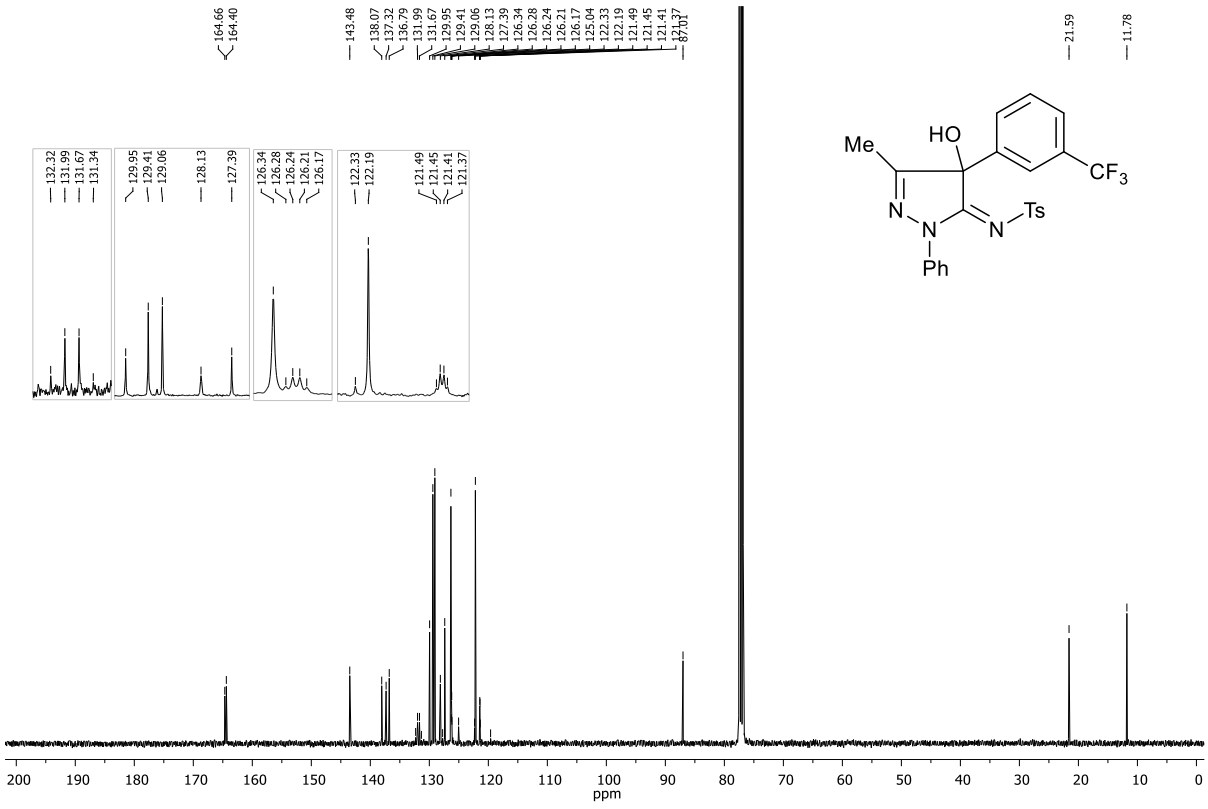
^{13}C{^{1}H} NMR of **7p** in $CDCl_3$ (100 MHz):



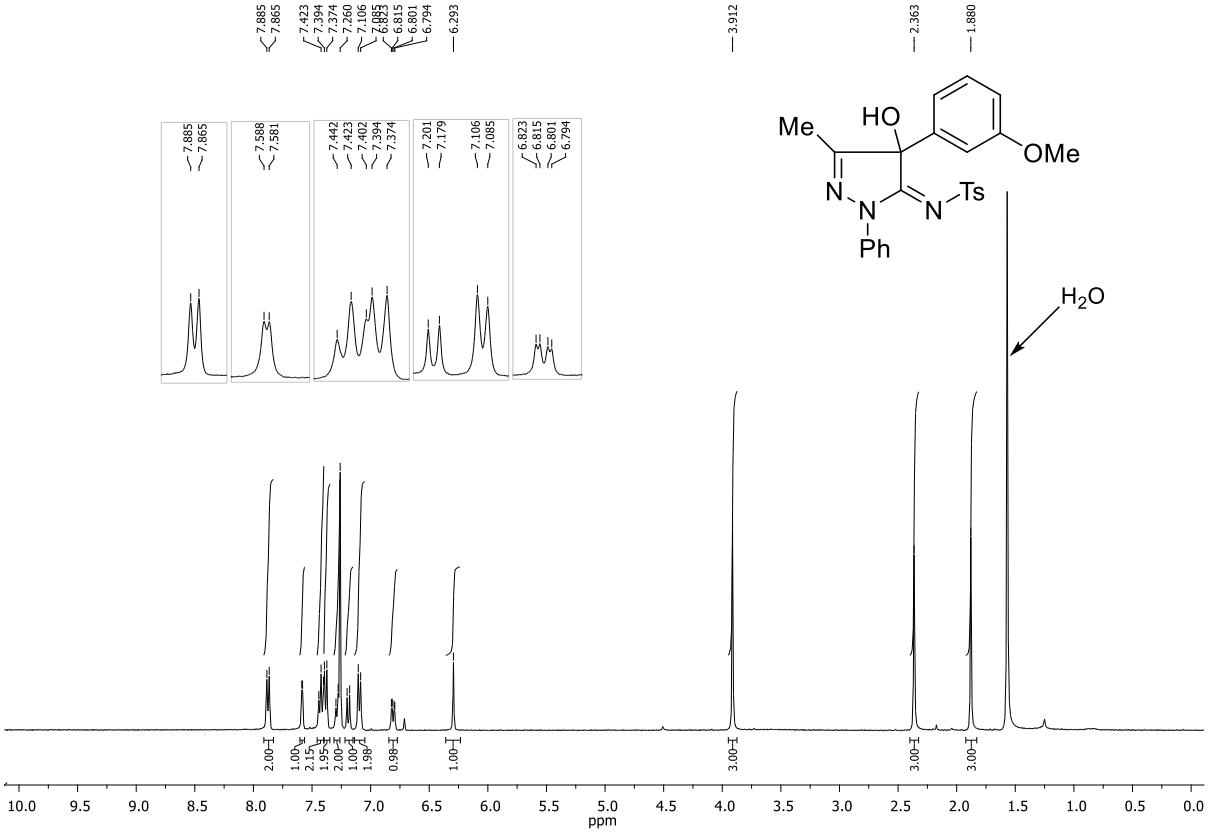
^{1}H NMR of **7q** in $CDCl_3$ (400 MHz):



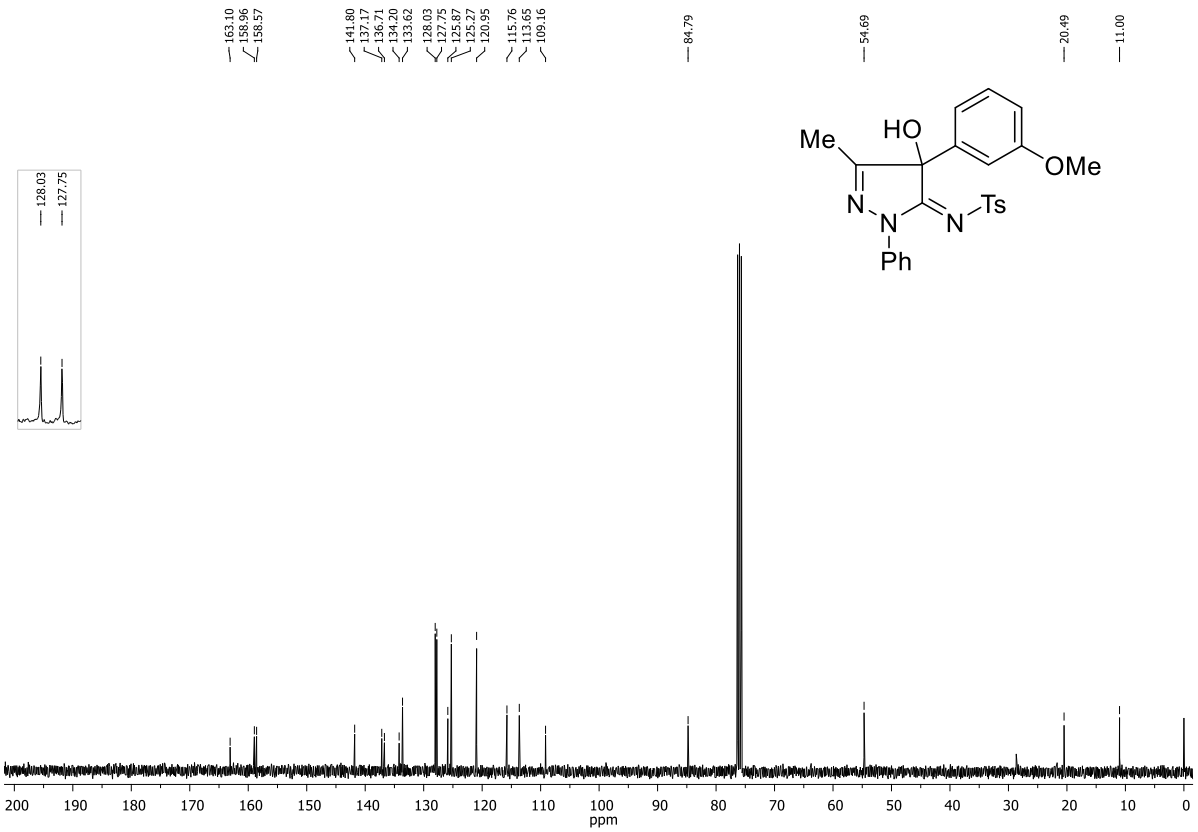
^{13}C{^{1}H} NMR of **7q** in $CDCl_3$ (100 MHz):



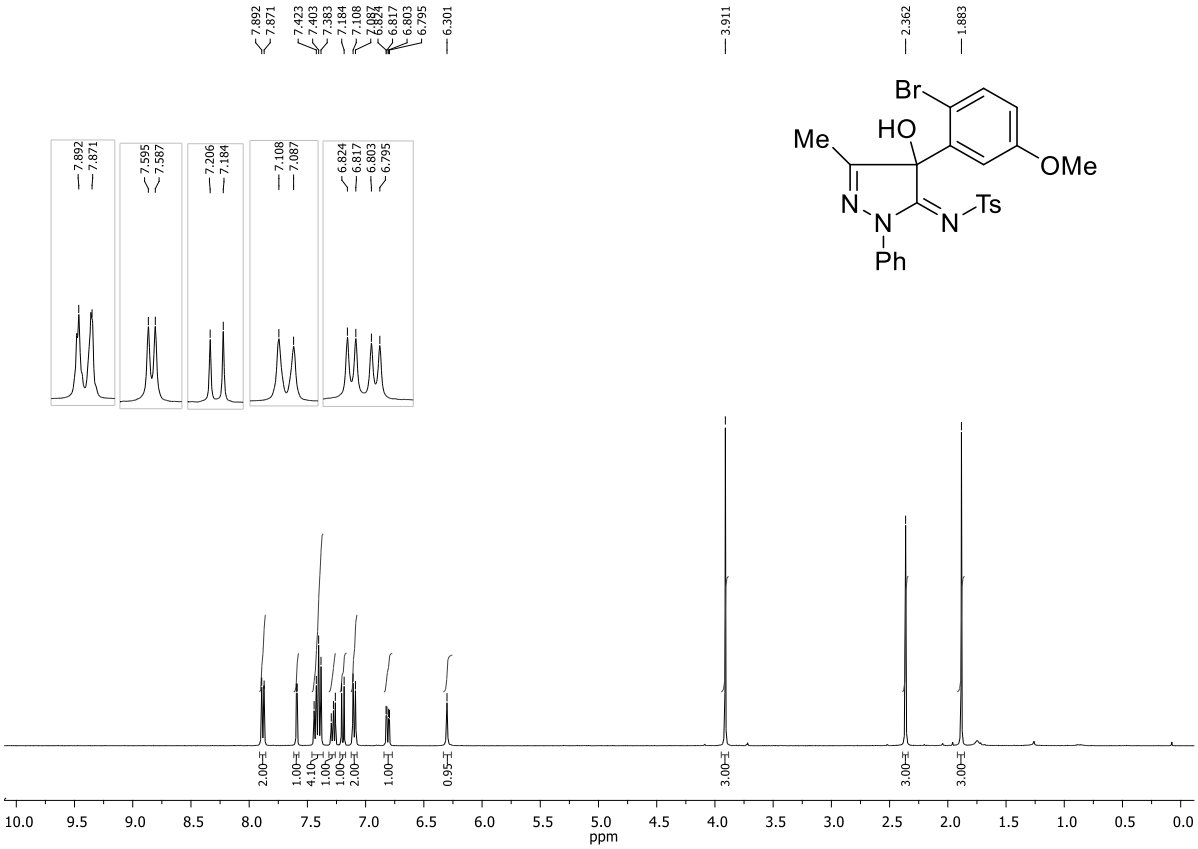
^{1}H NMR of **7r** in $CDCl_3$ (400 MHz):



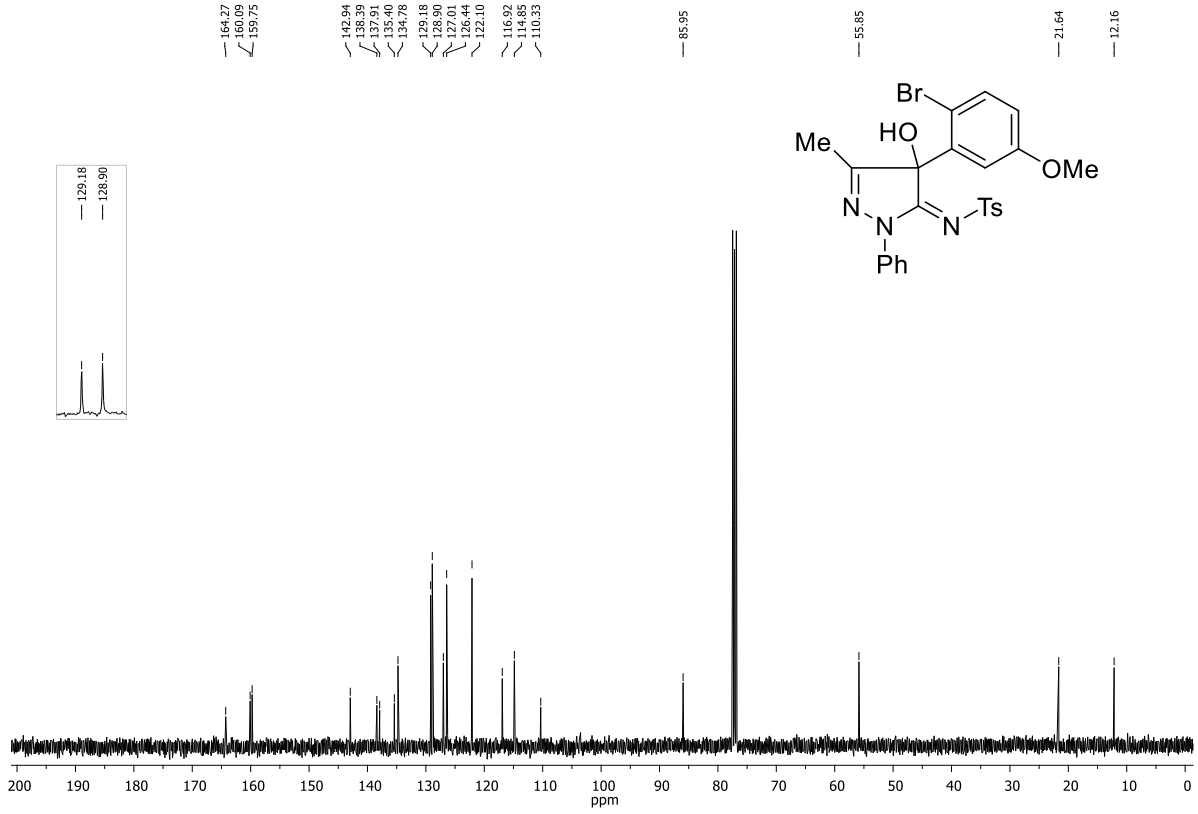
^{13}C{^{1}H} NMR of **7r** in $CDCl_3$ (100 MHz):



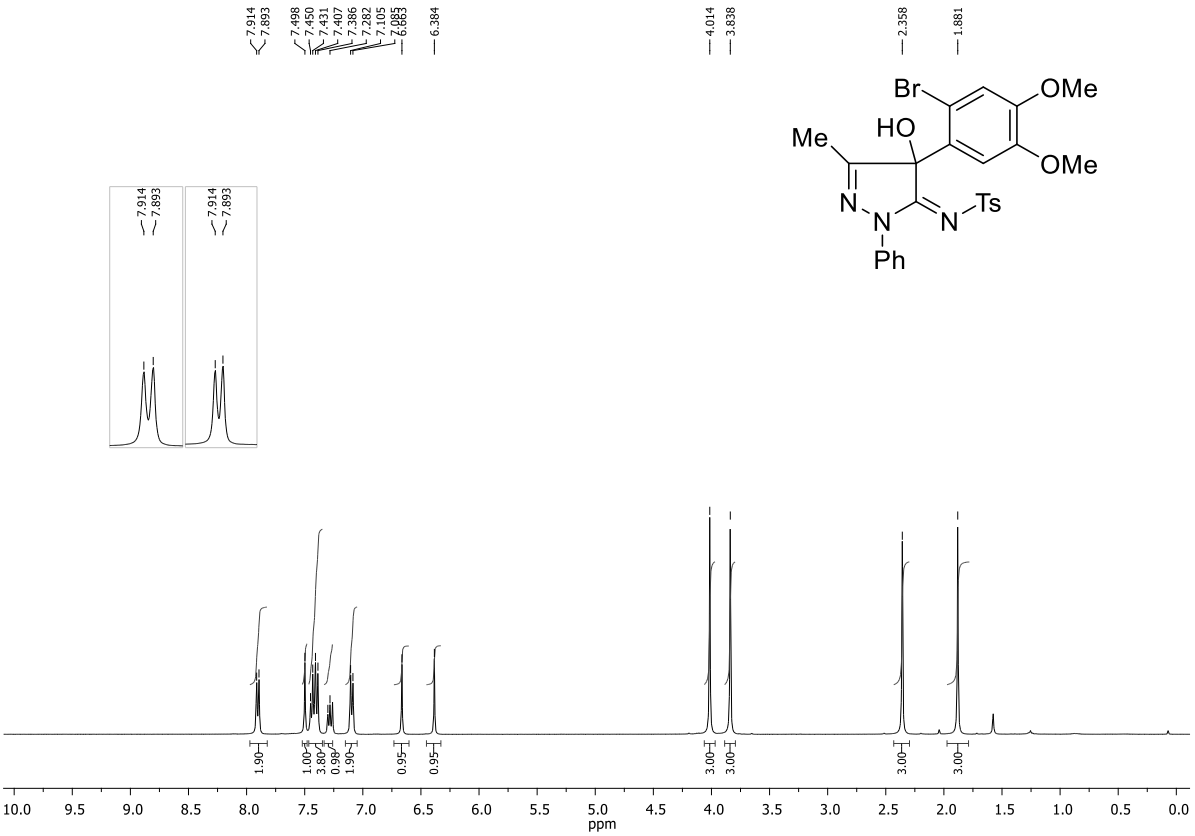
^{1}H NMR of **7s** in $CDCl_3$ (400 MHz):



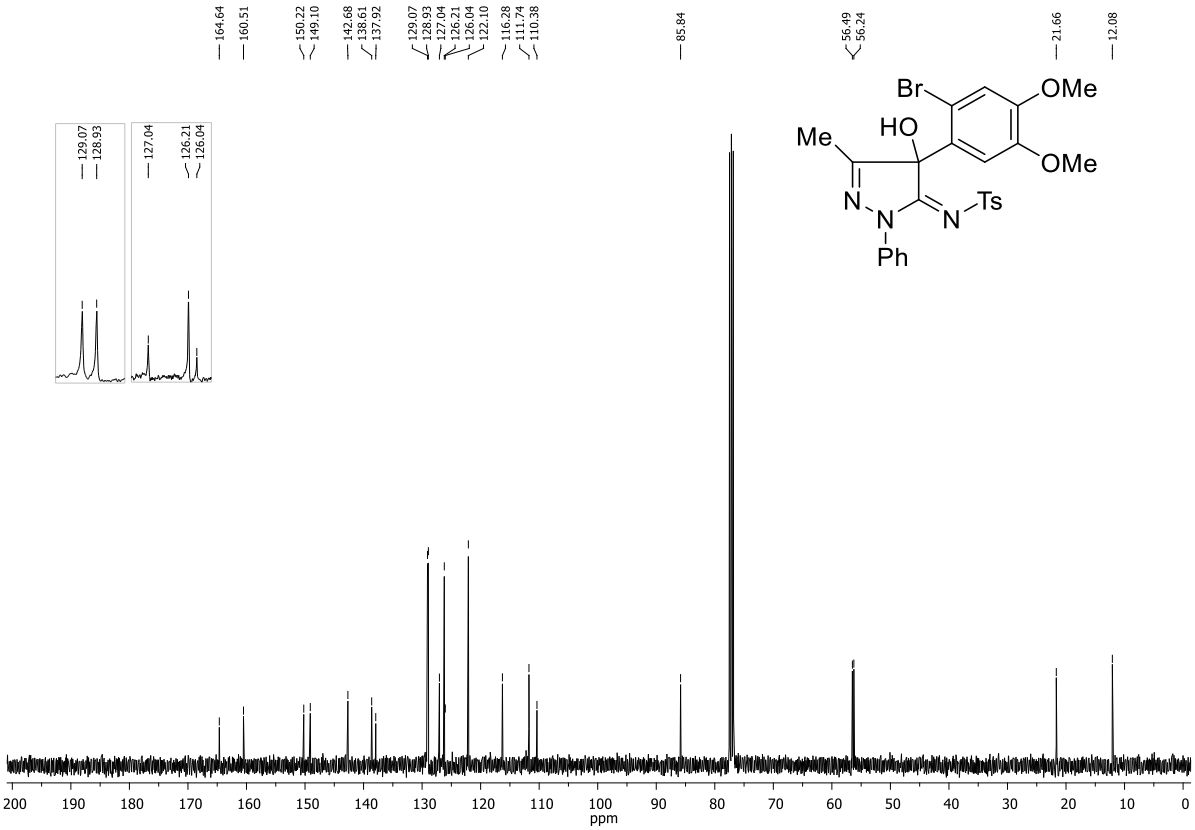
^{13}C{^{1}H} NMR of **7s** in $CDCl_3$ (100 MHz):



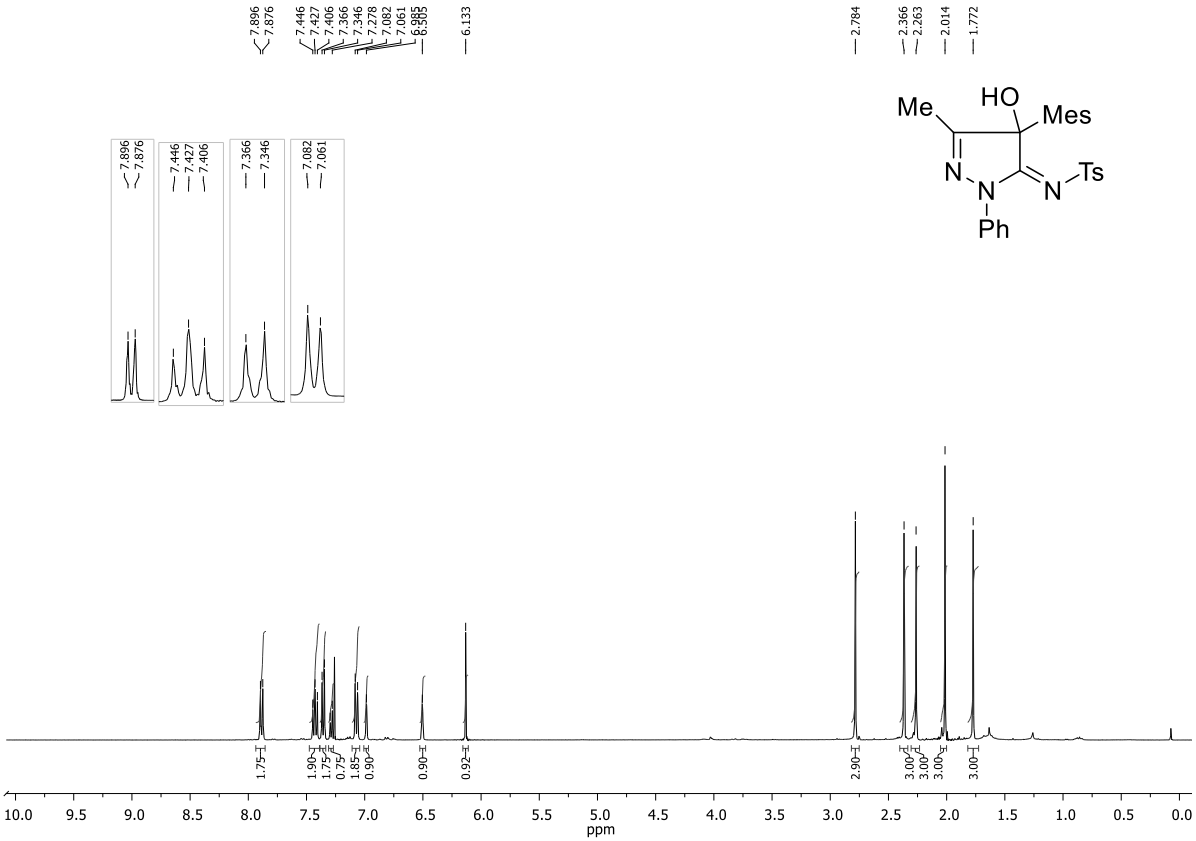
^{1}H NMR of **7t** in $CDCl_3$ (400 MHz):



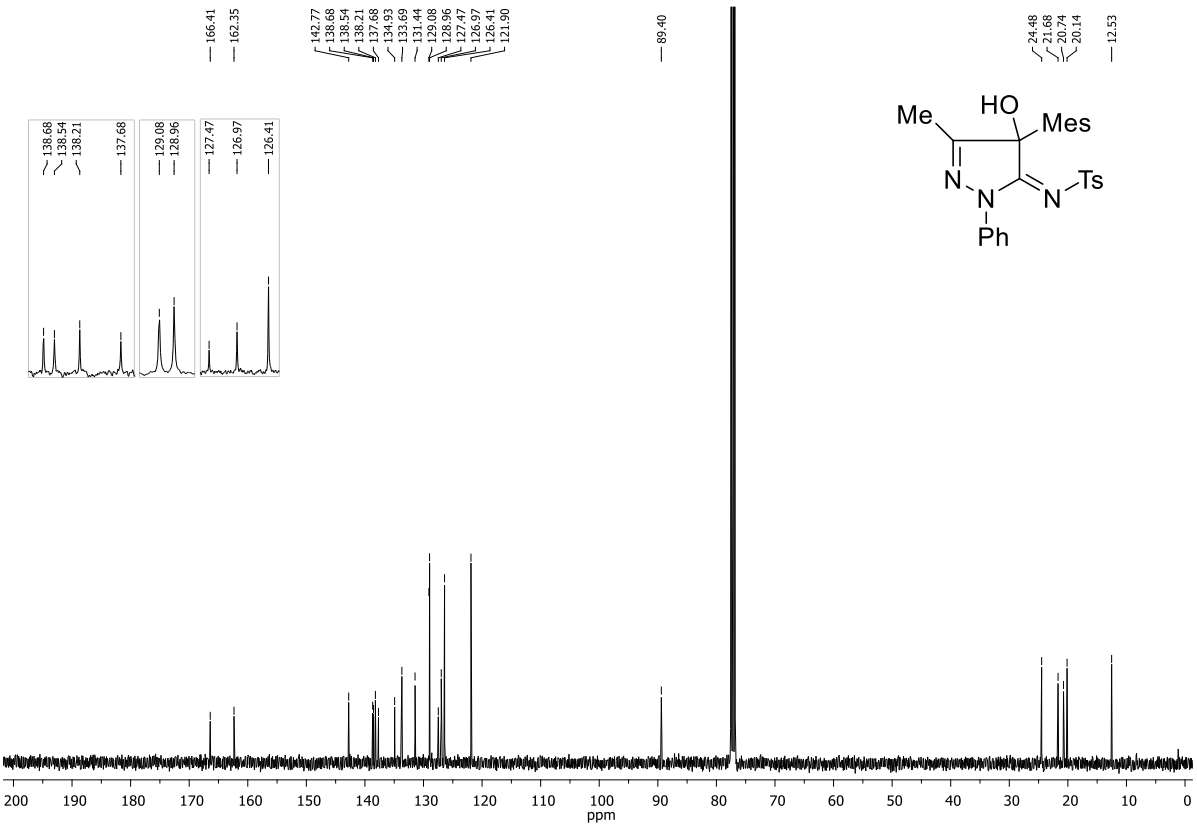
^{13}C{^{1}H} NMR of **7t** in $CDCl_3$ (100 MHz):



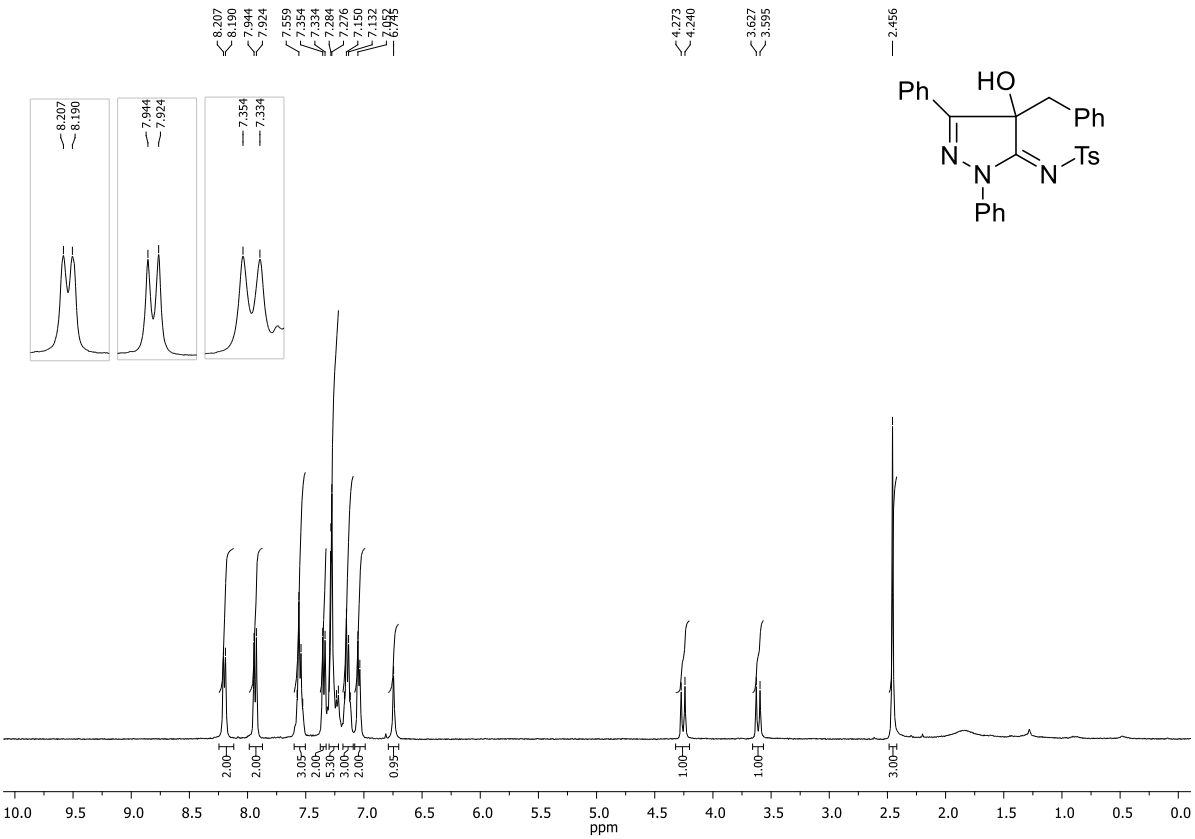
^{1}H NMR of **7u** in $CDCl_3$ (400 MHz):



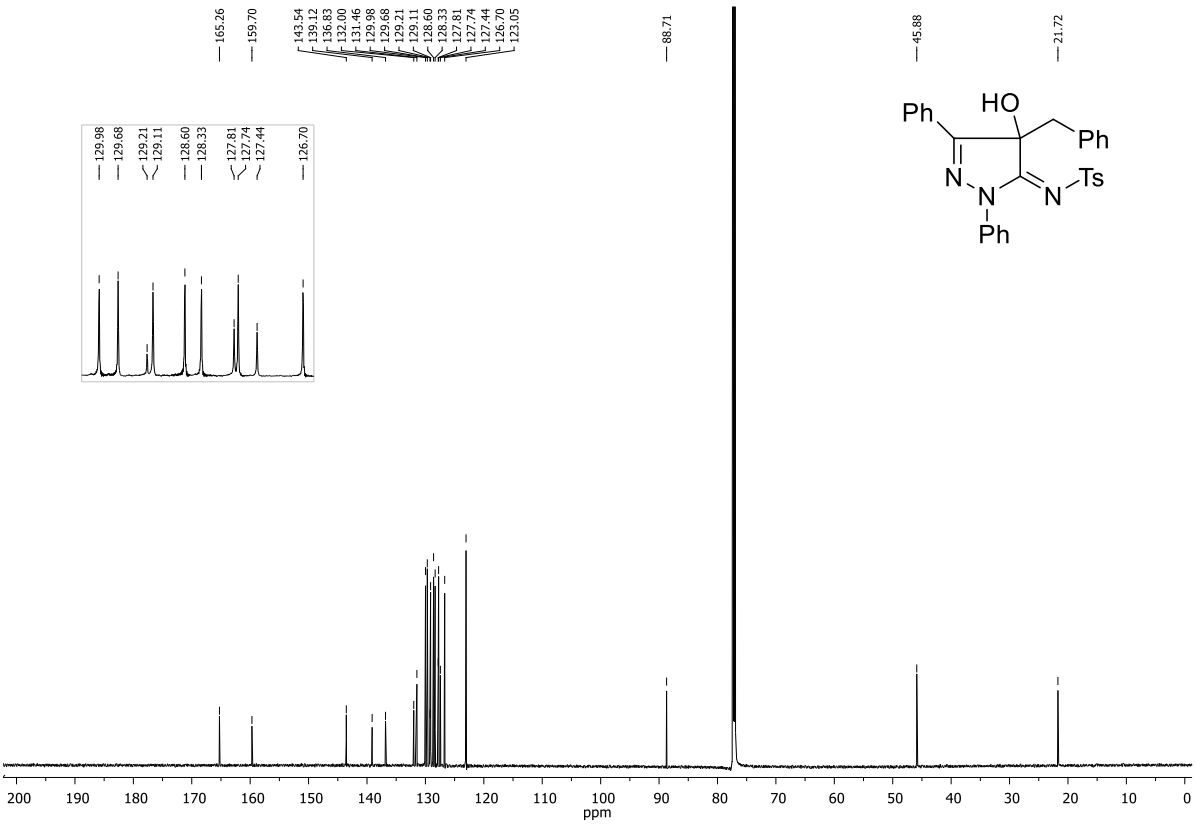
^{13}C{^{1}H} NMR of **7u** in $CDCl_3$ (100 MHz):



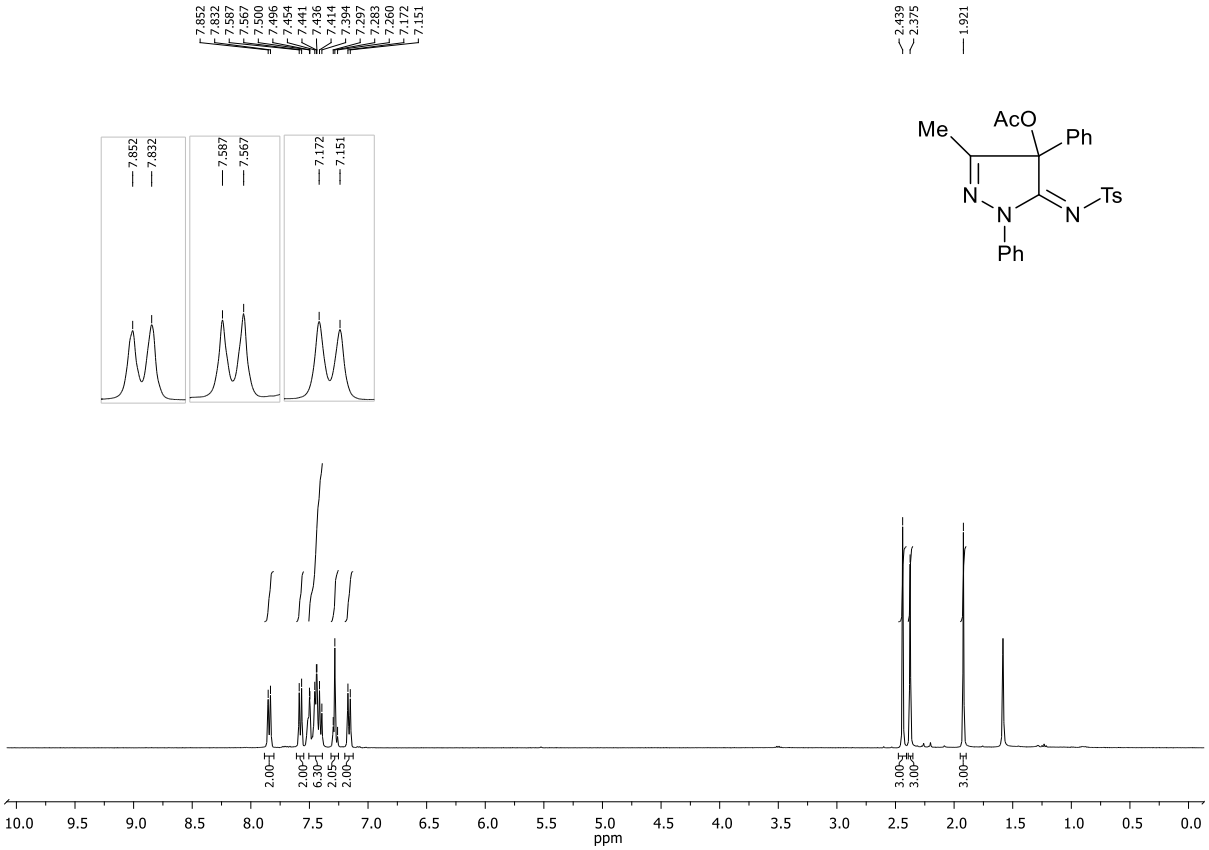
^{1}H NMR of **7v** in $CDCl_3$ (400 MHz):



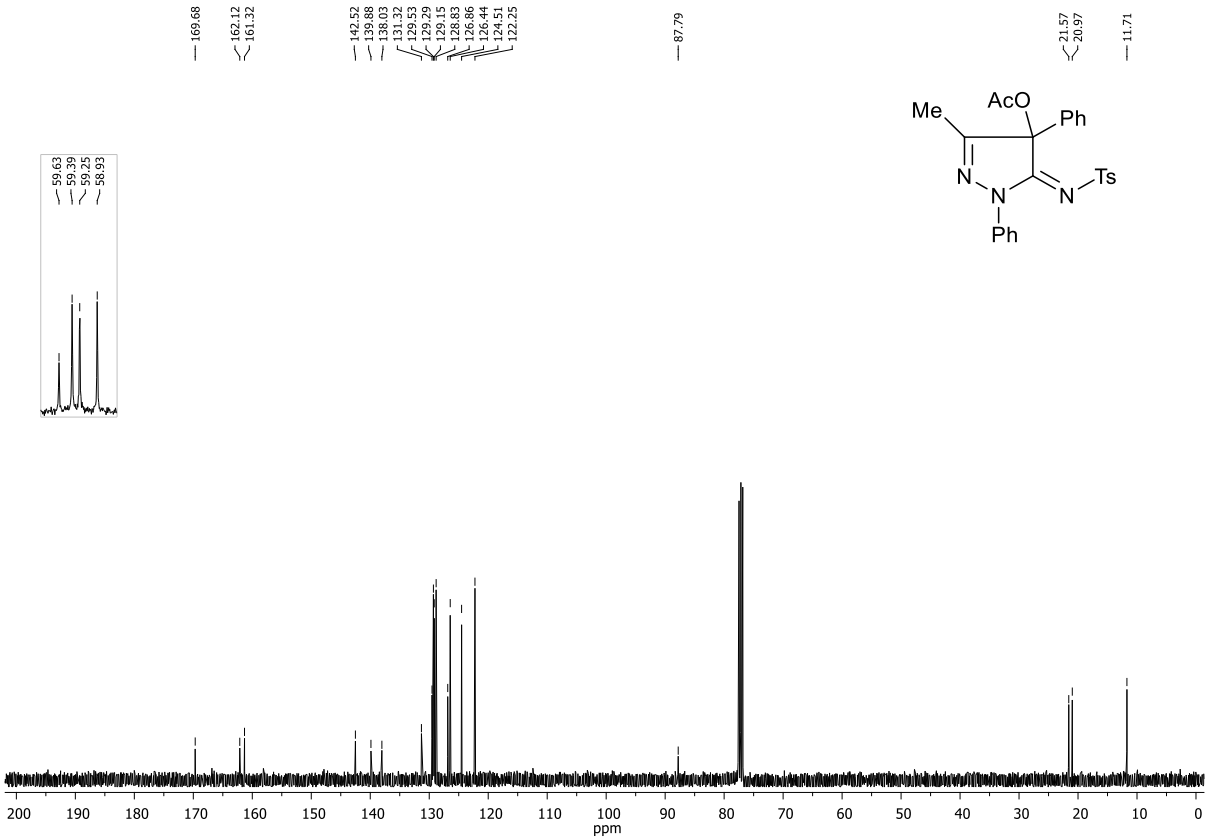
^{13}C{^{1}H} NMR of **7v** in $CDCl_3$ (175 MHz):



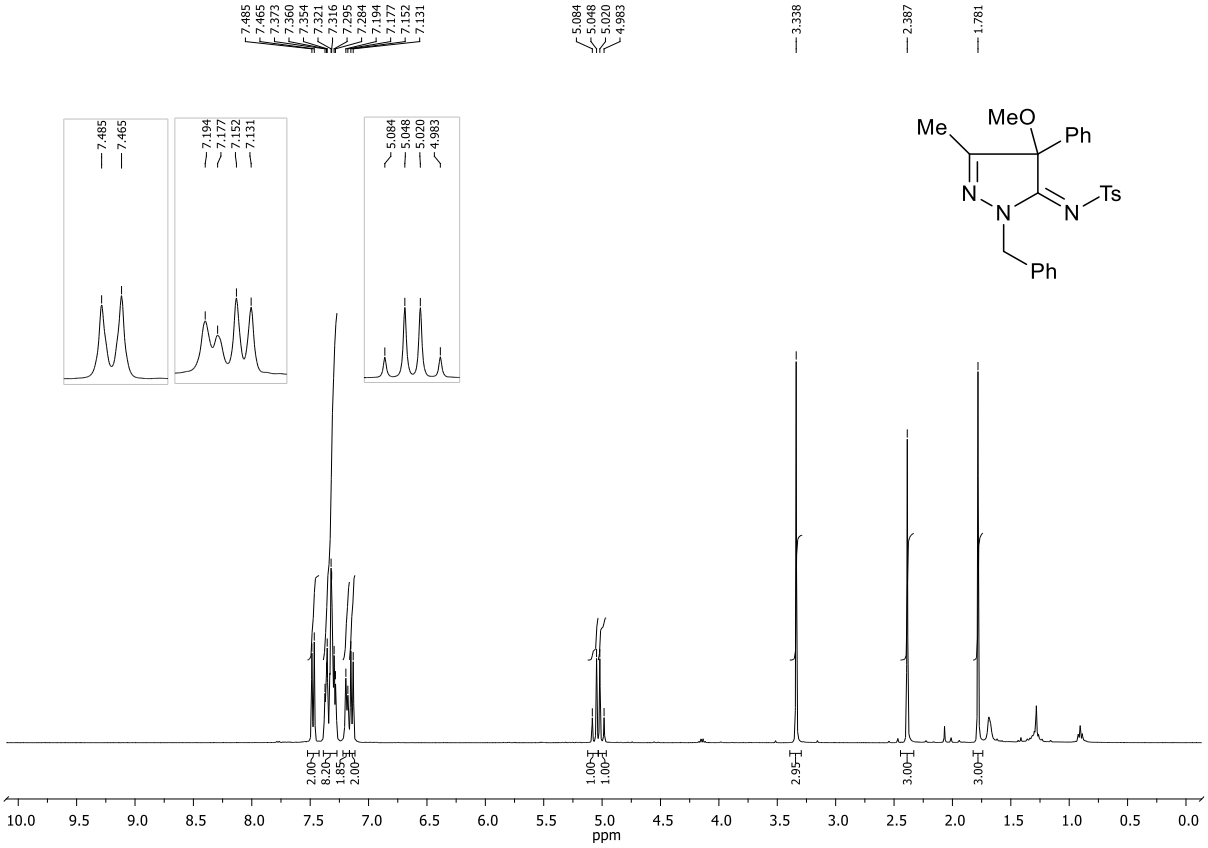
^{1}H NMR of **5a** in $CDCl_3$ (400 MHz):



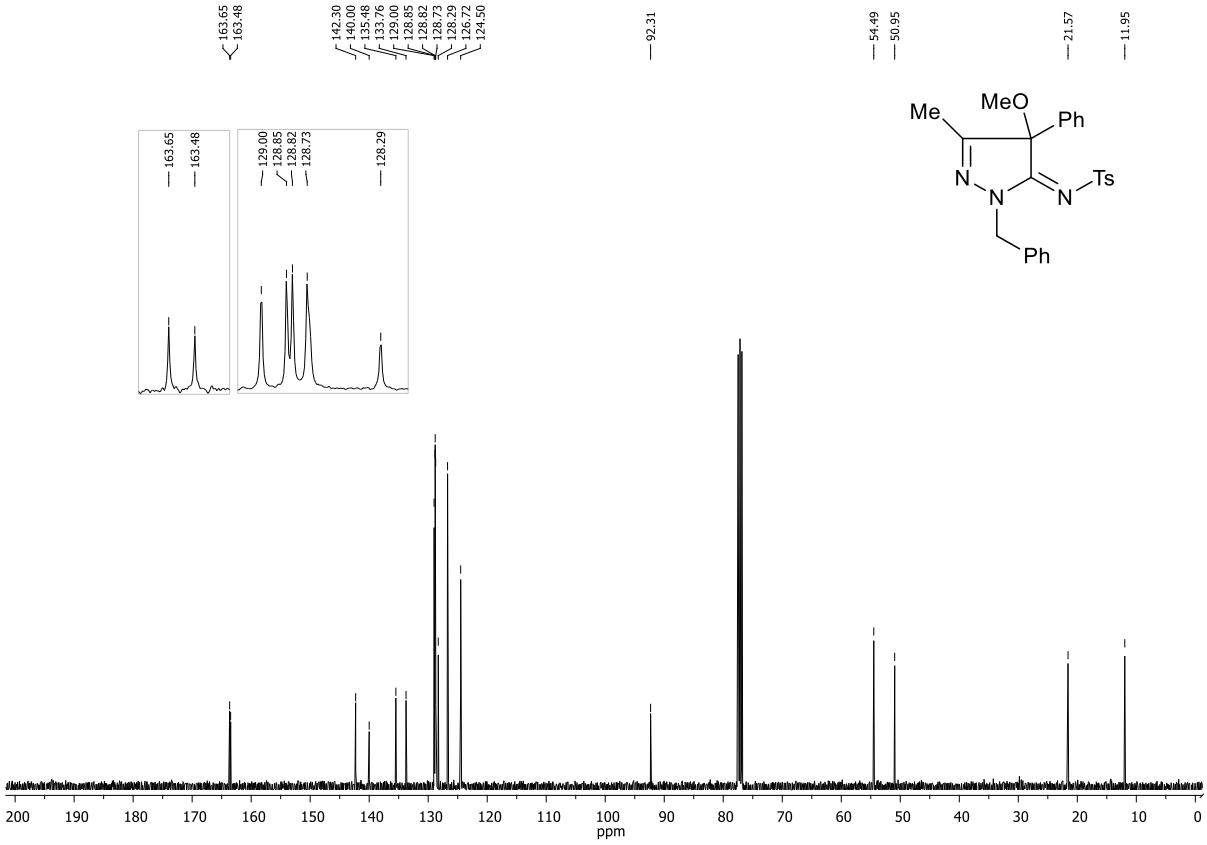
^{13}C{^{1}H} NMR of **5a** in $CDCl_3$ (100 MHz):



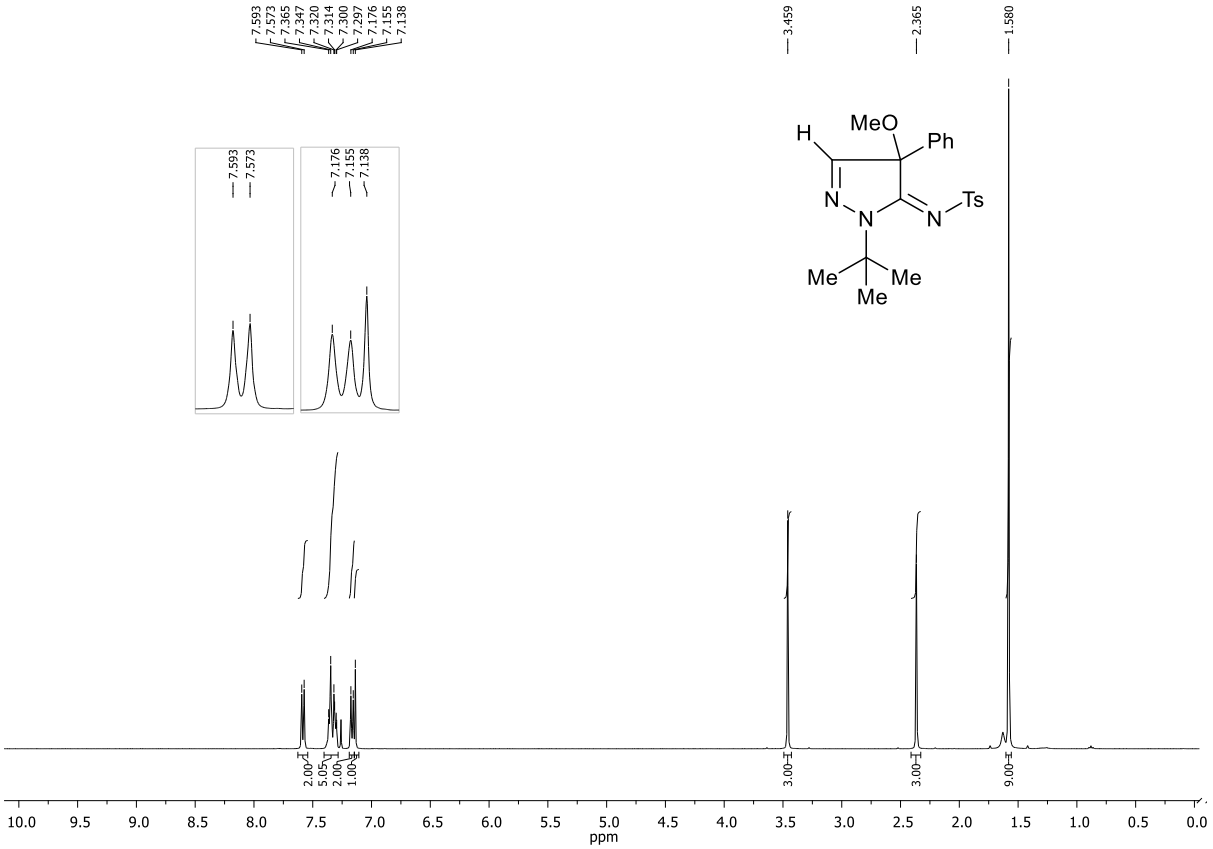
^{1}H NMR of **15h** in $CDCl_3$ (400 MHz):



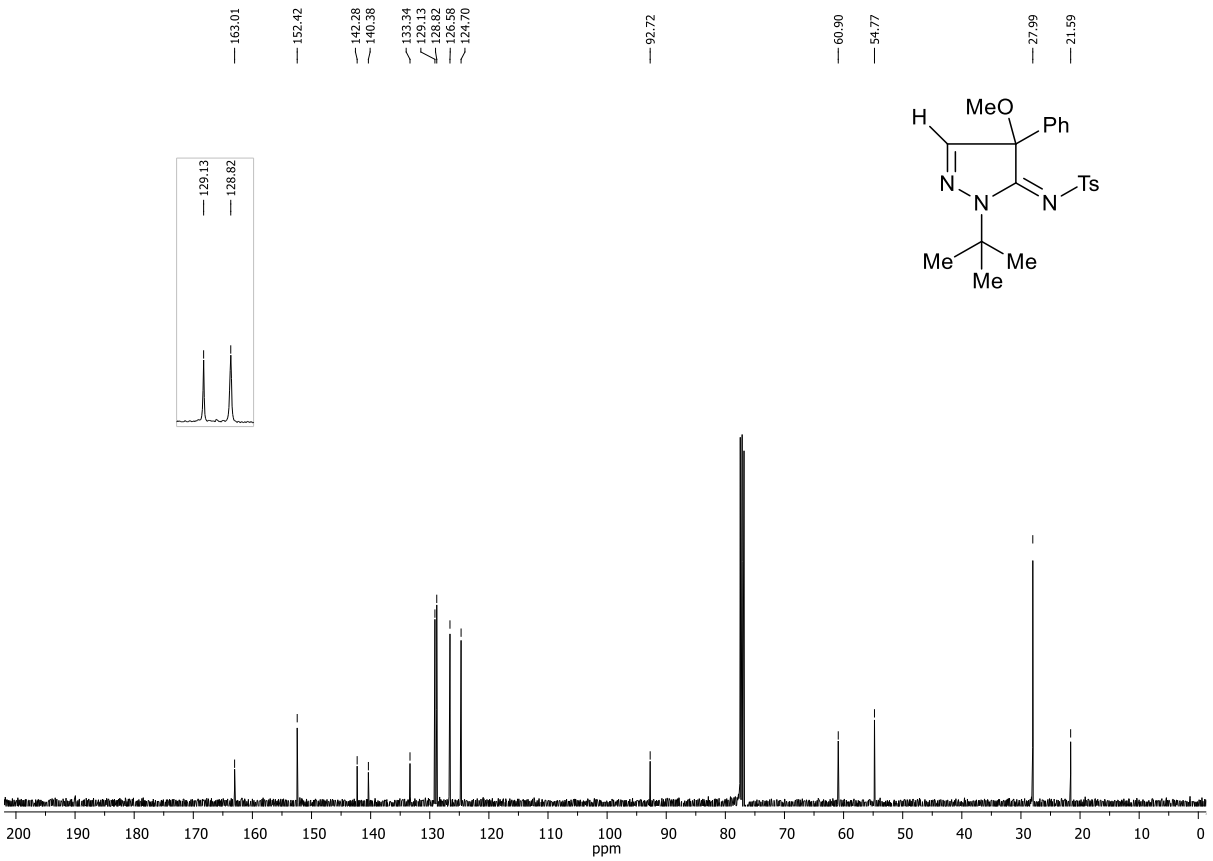
^{13}C{^{1}H} NMR of **15h** in $CDCl_3$ (100 MHz):



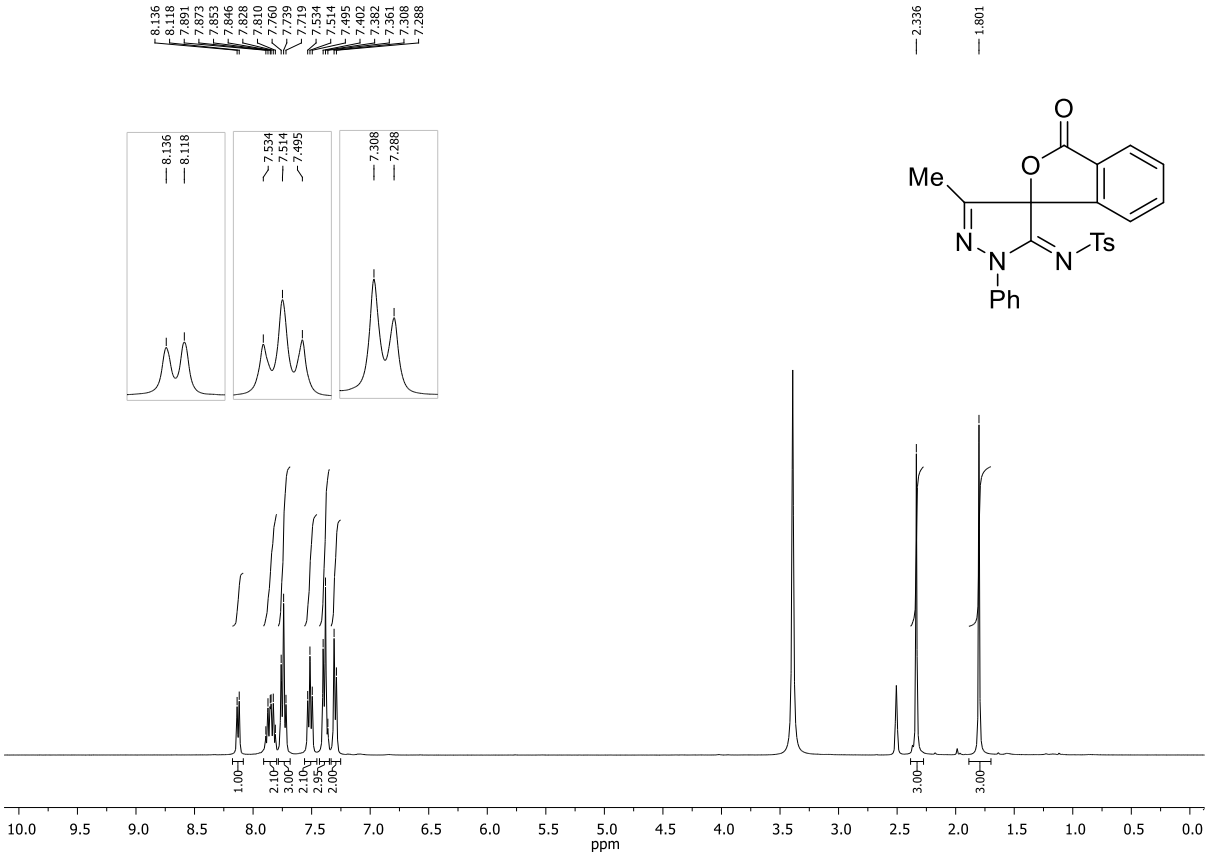
^{1}H NMR of **15e** in $CDCl_3$ (400 MHz):



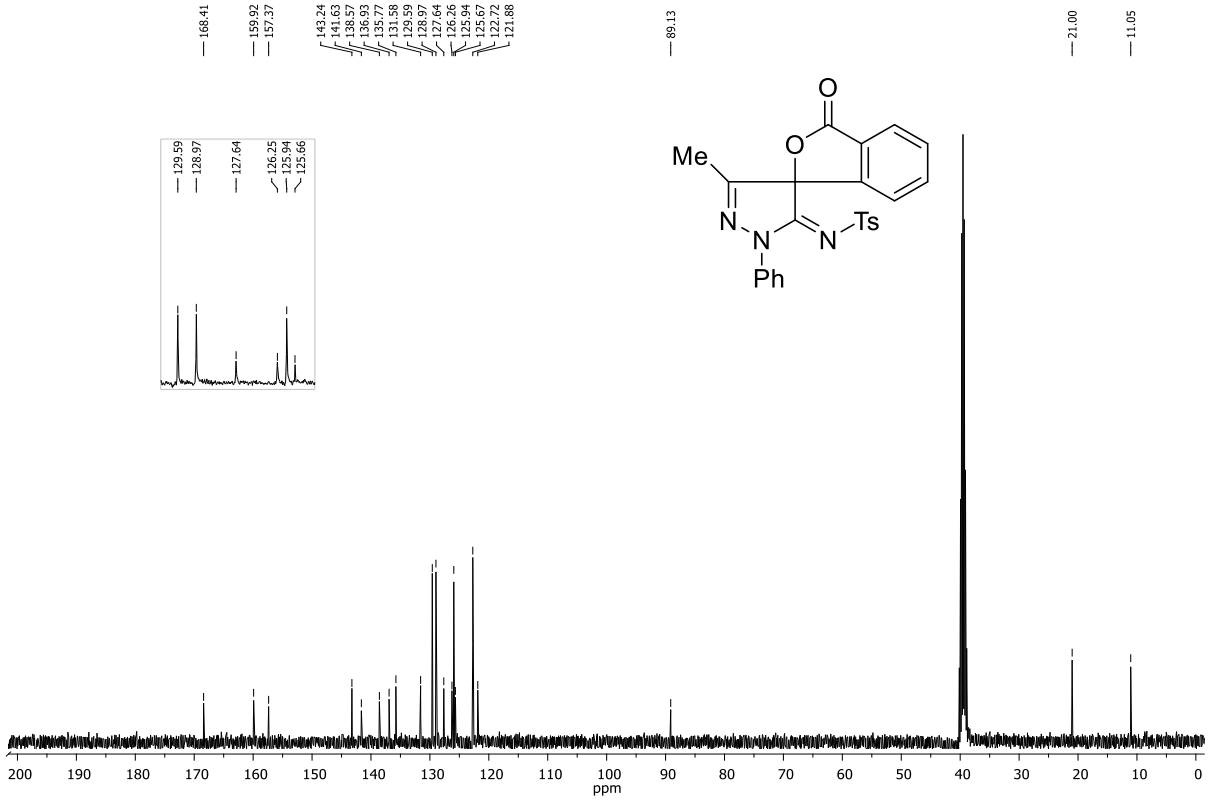
^{13}C{^{1}H} NMR of **15e** in $CDCl_3$ (100 MHz):



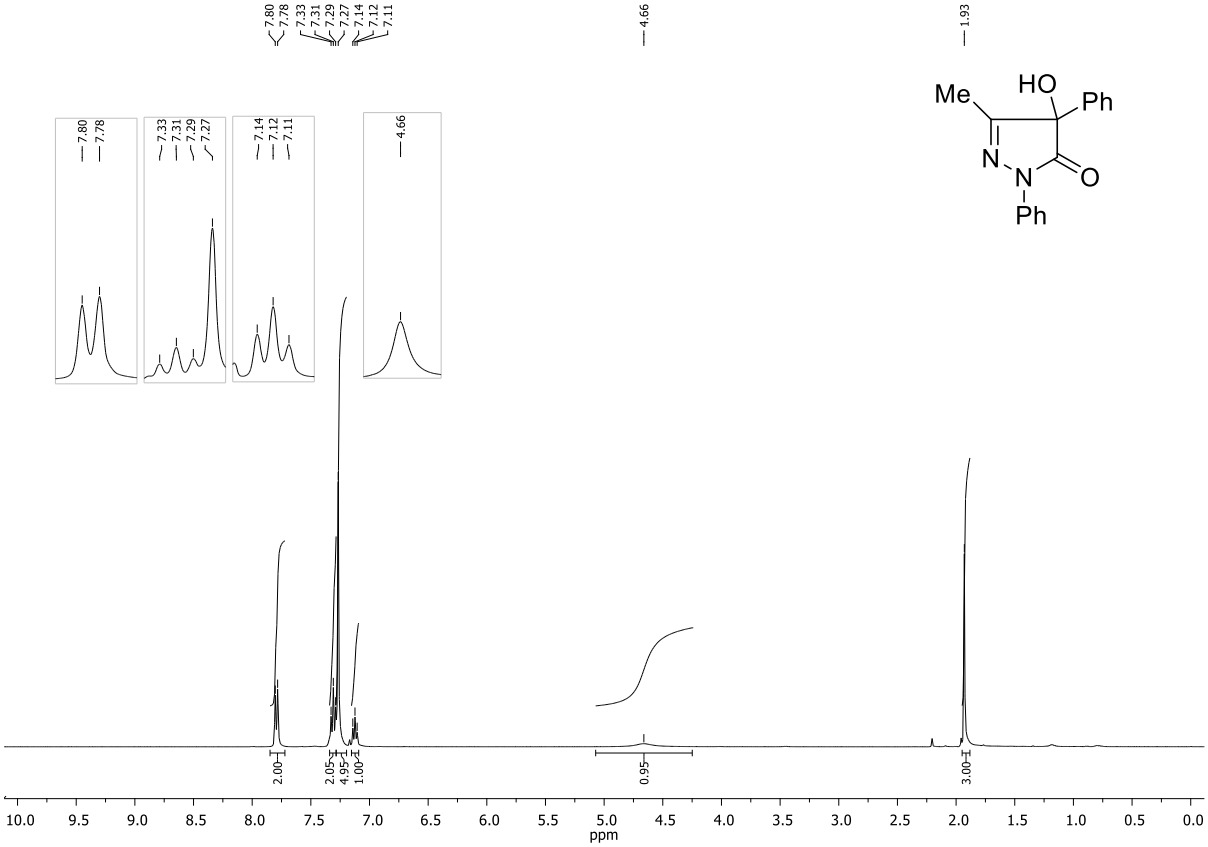
^{1}H NMR of **17w** in DMSO-d_6 (400 MHz):



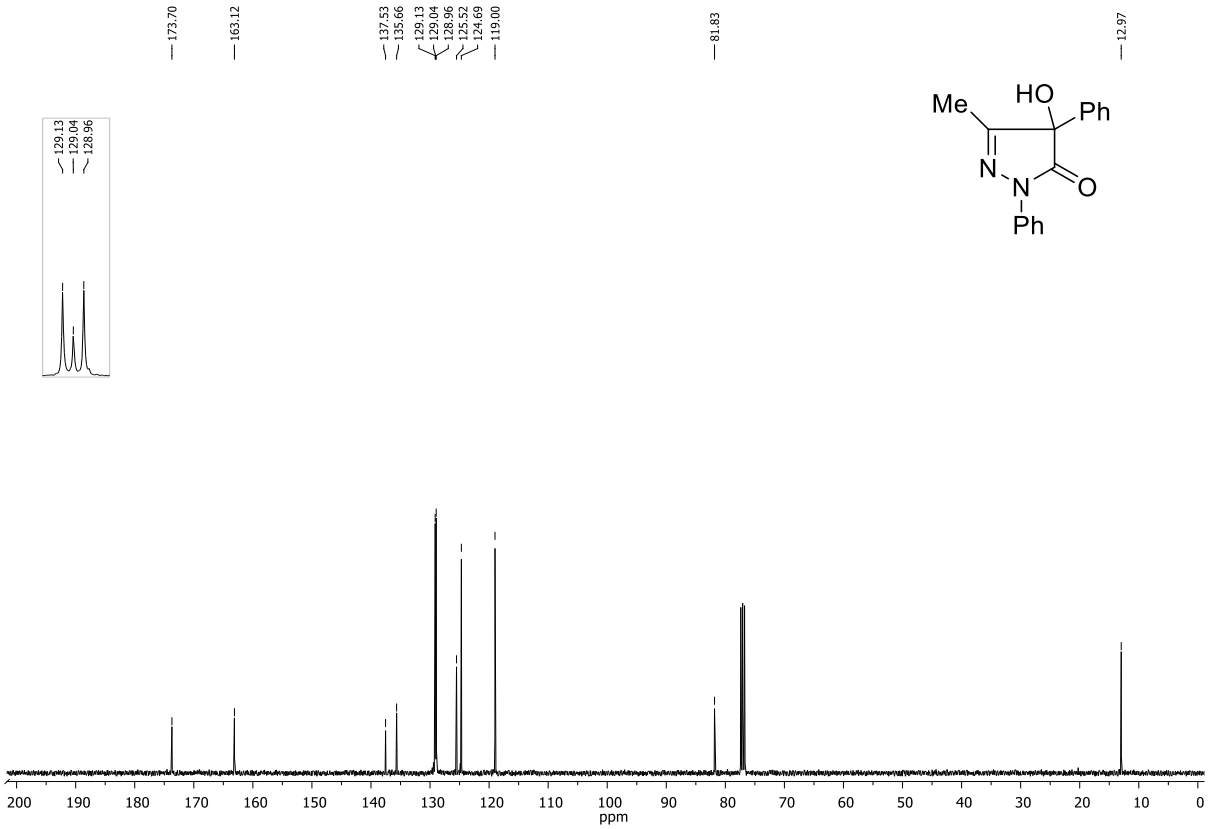
^{13}C{^{1}H} NMR of **17w** in DMSO-d_6 (100 MHz):



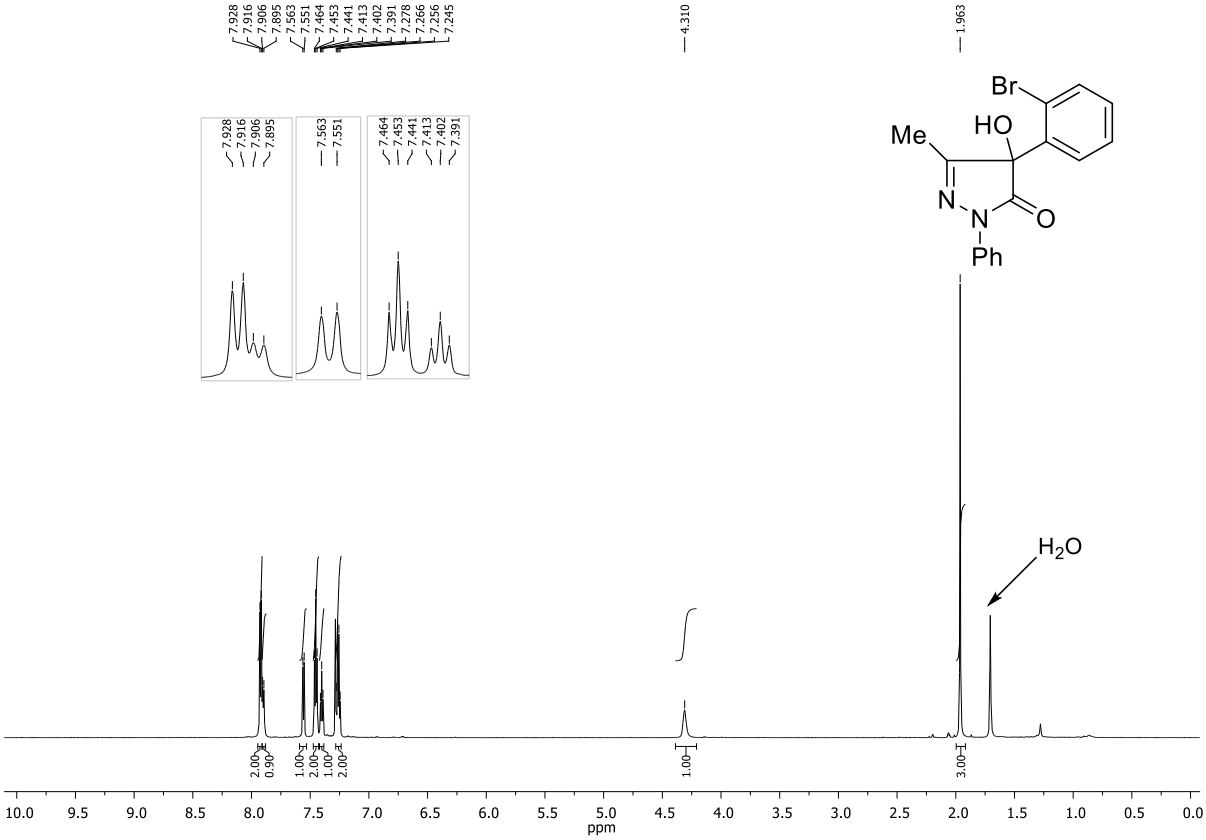
^{1}H NMR of **10a** in $CDCl_3$ (400 MHz):



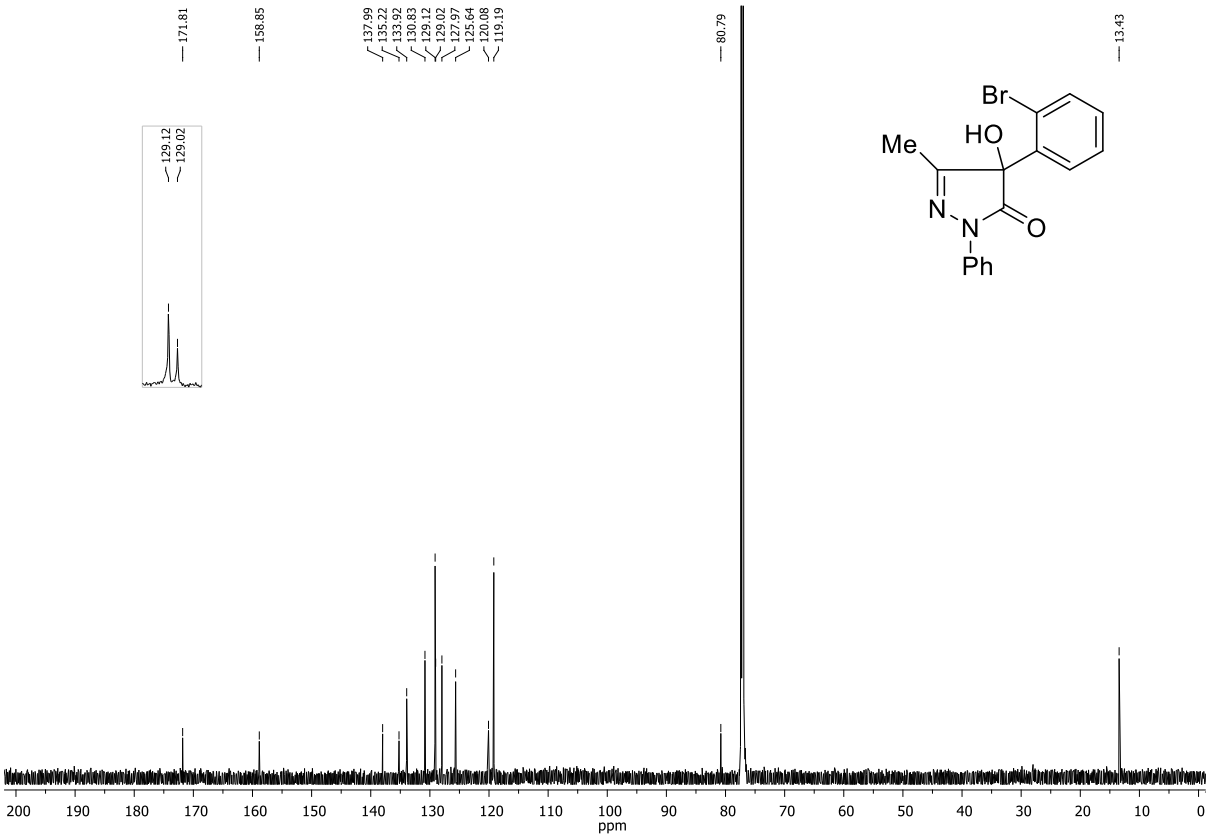
^{13}C{^{1}H} NMR of **10a** in $CDCl_3$ (100 MHz):



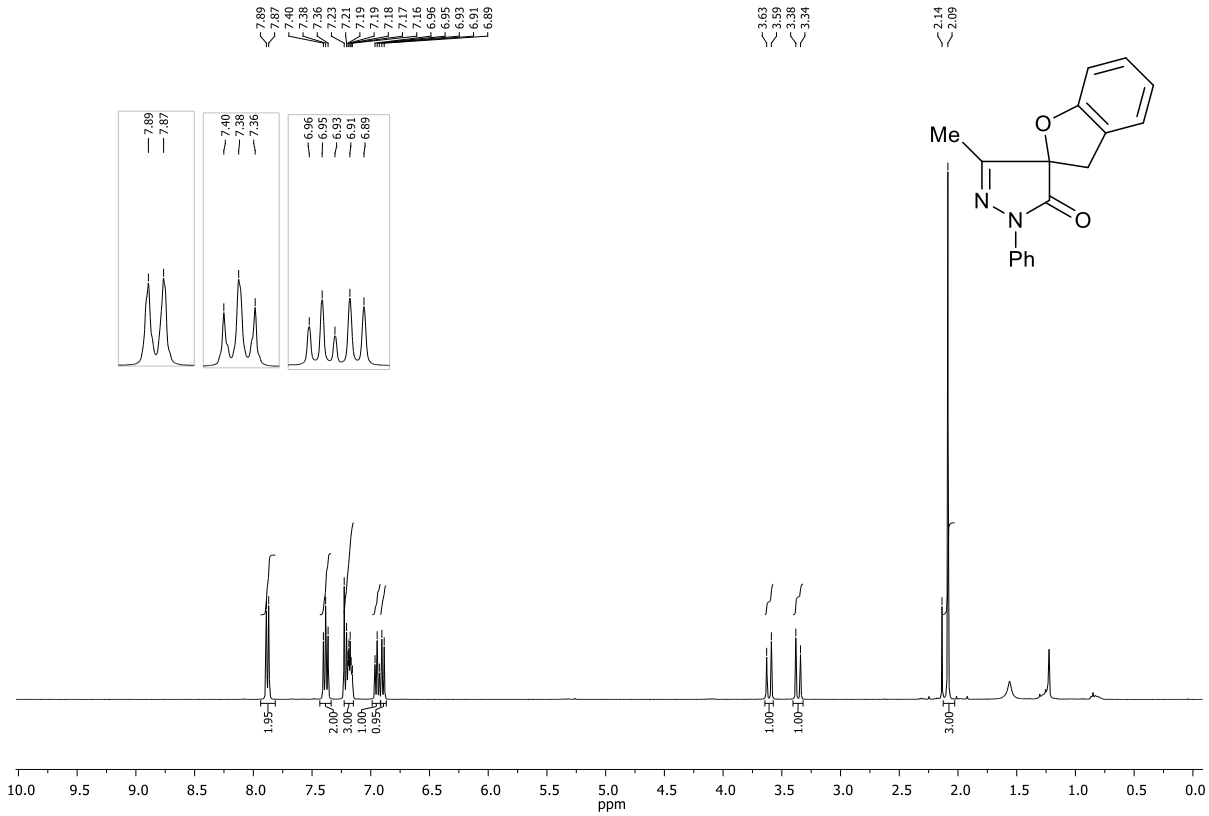
^{1}H NMR of **10c** in $CDCl_3$ (700 MHz):



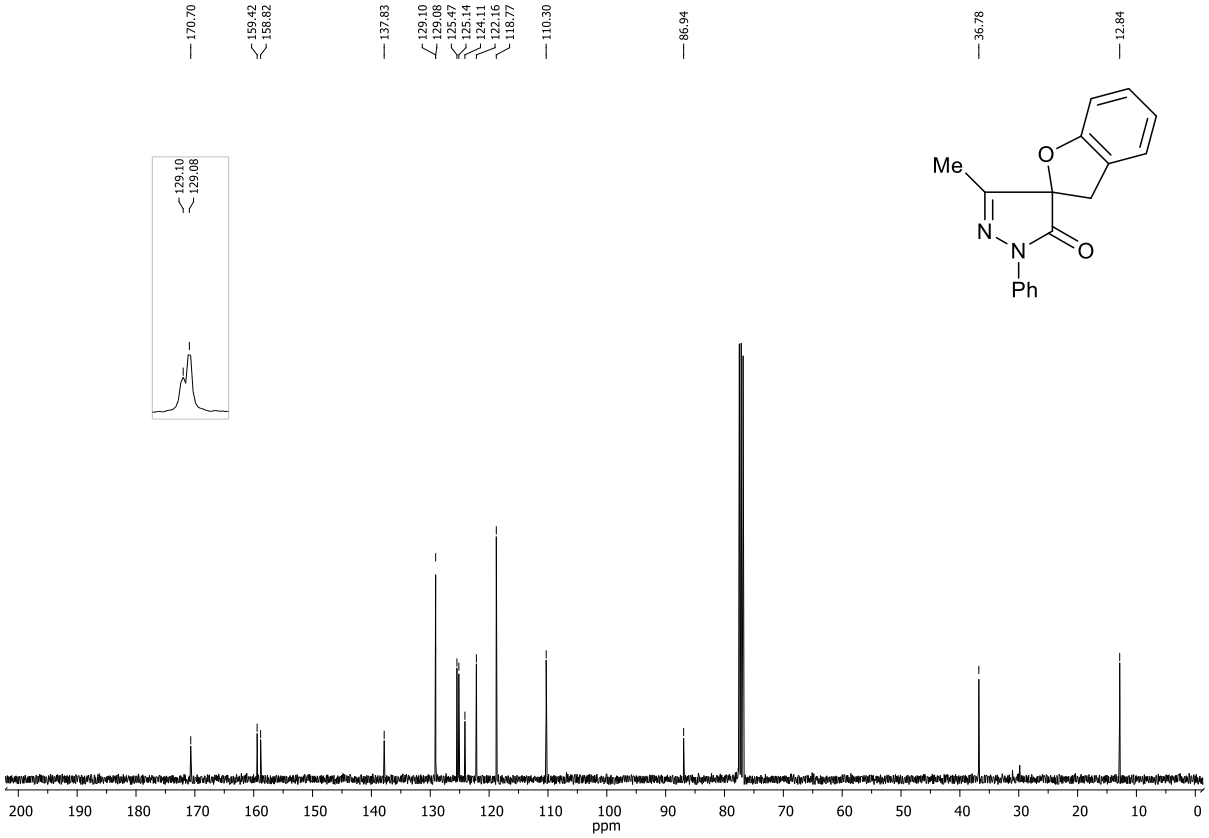
^{13}C{^{1}H} NMR of **10c** in $CDCl_3$ (175 MHz):



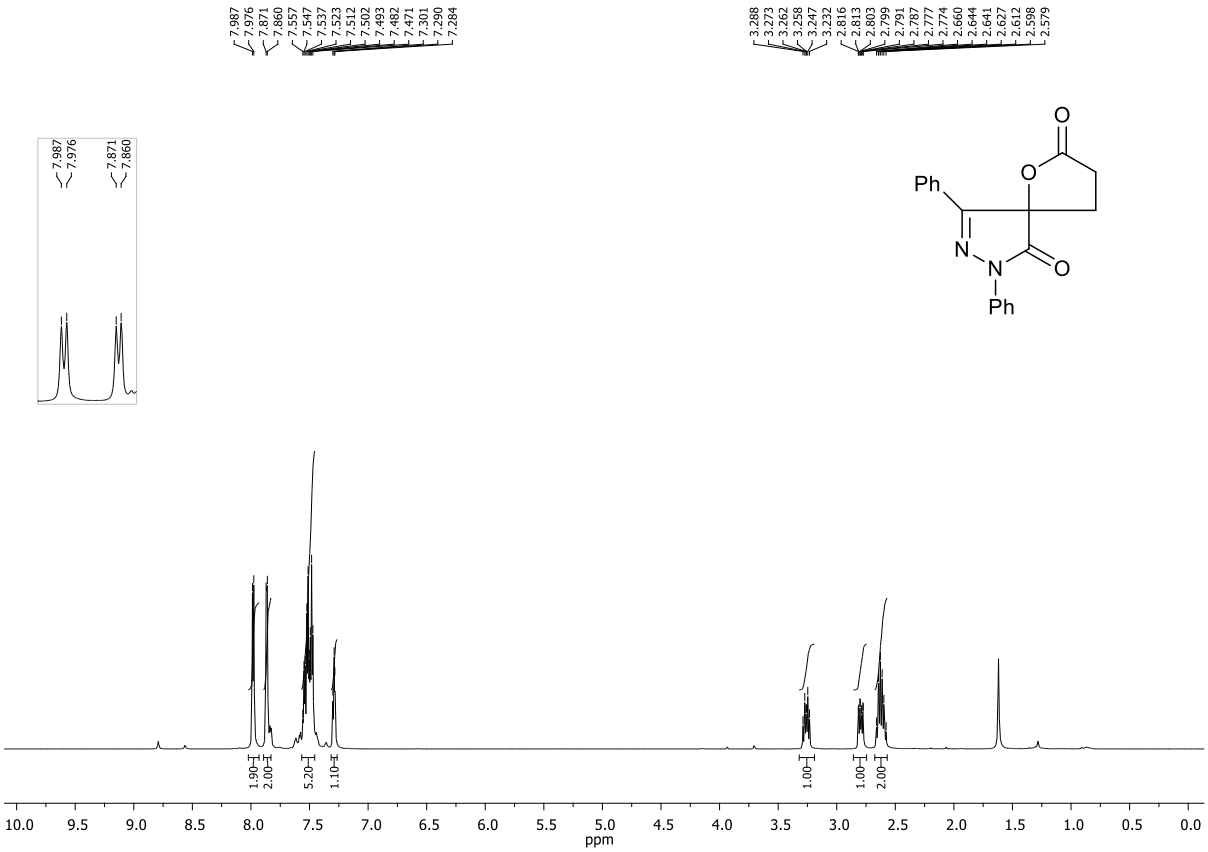
^{1}H NMR of **11d** in $CDCl_3$ (400 MHz):



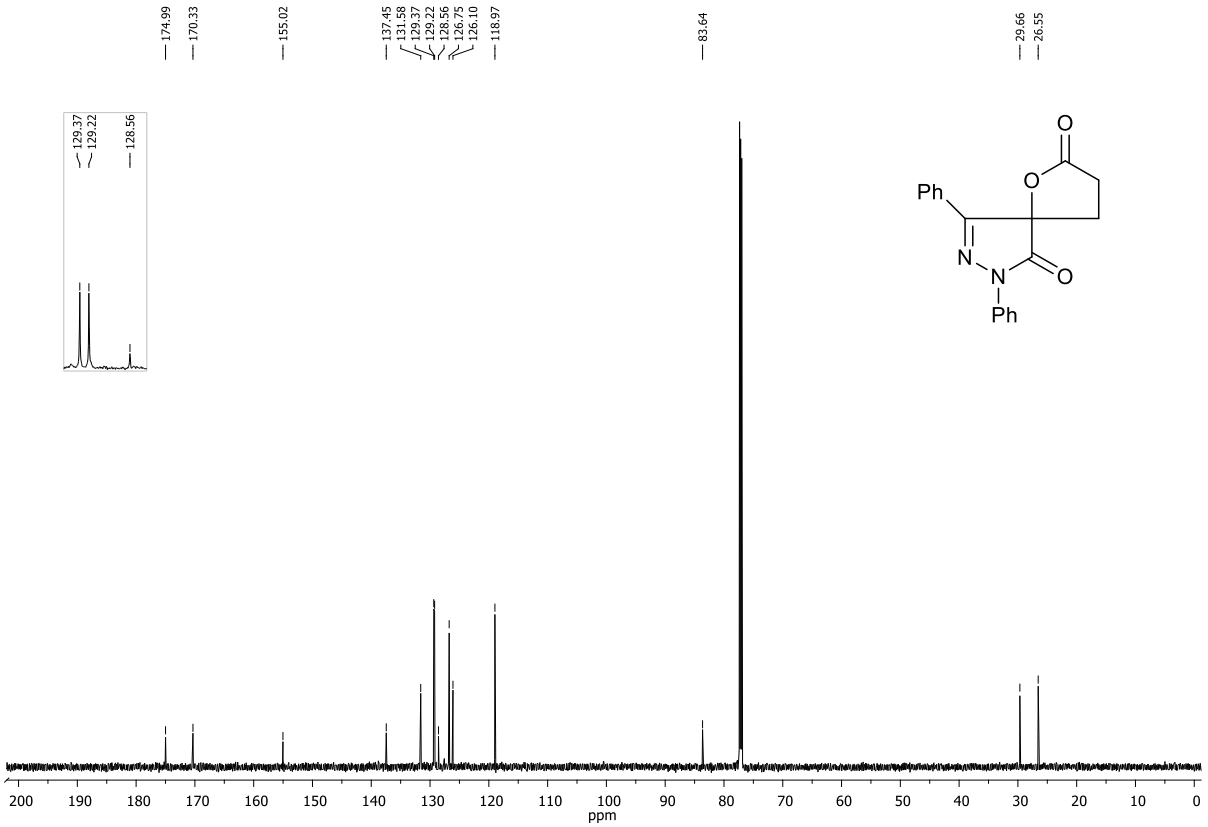
^{13}C{^{1}H} NMR of **11d** in $CDCl_3$ (100 MHz):



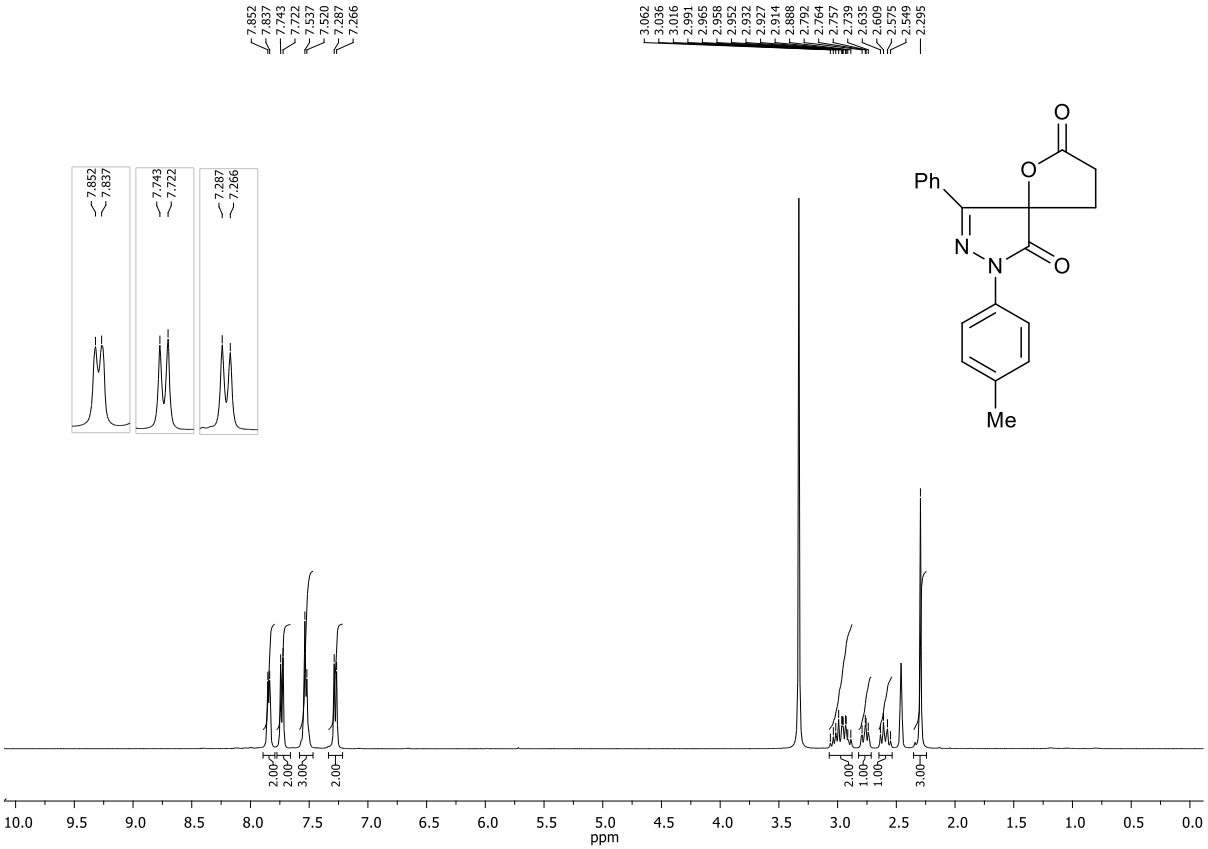
^{1}H NMR of **13a** in $CDCl_3$ (700 MHz):



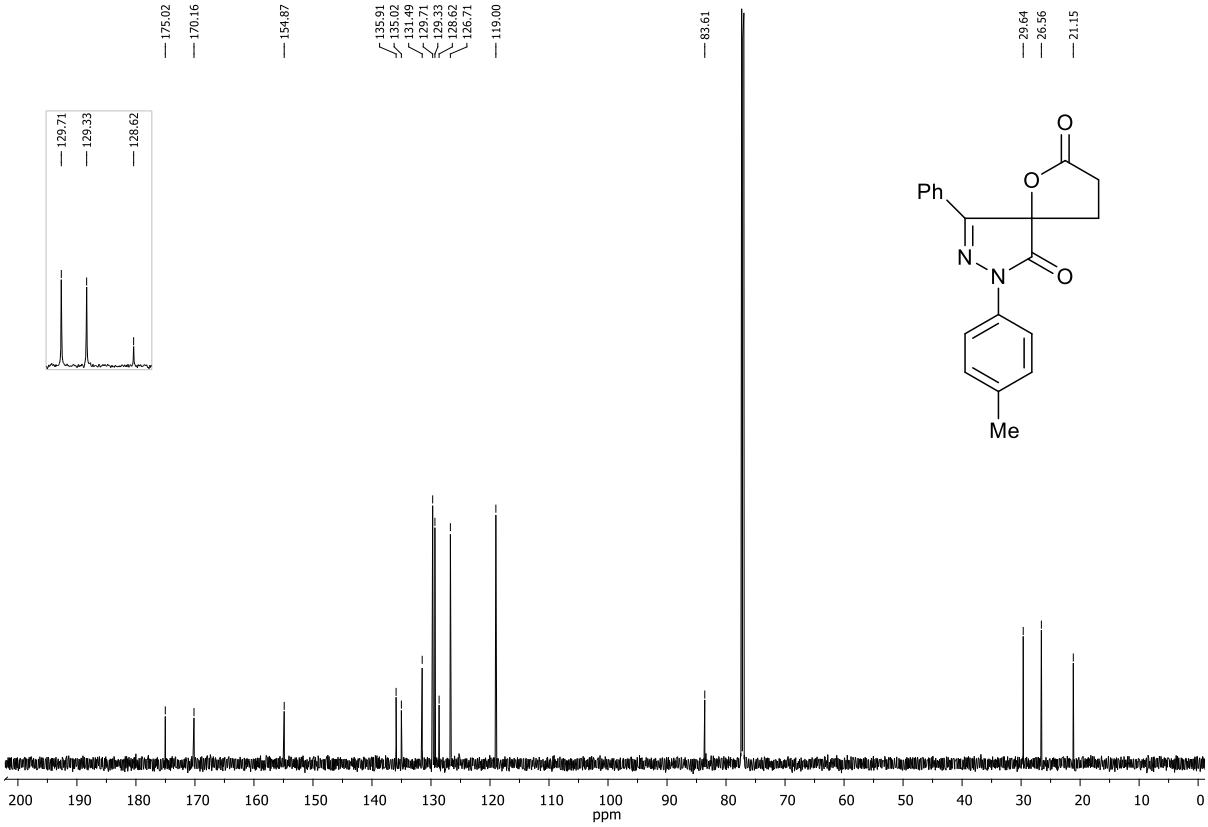
^{13}C{^{1}H} NMR of **13a** in $CDCl_3$ (175 MHz):



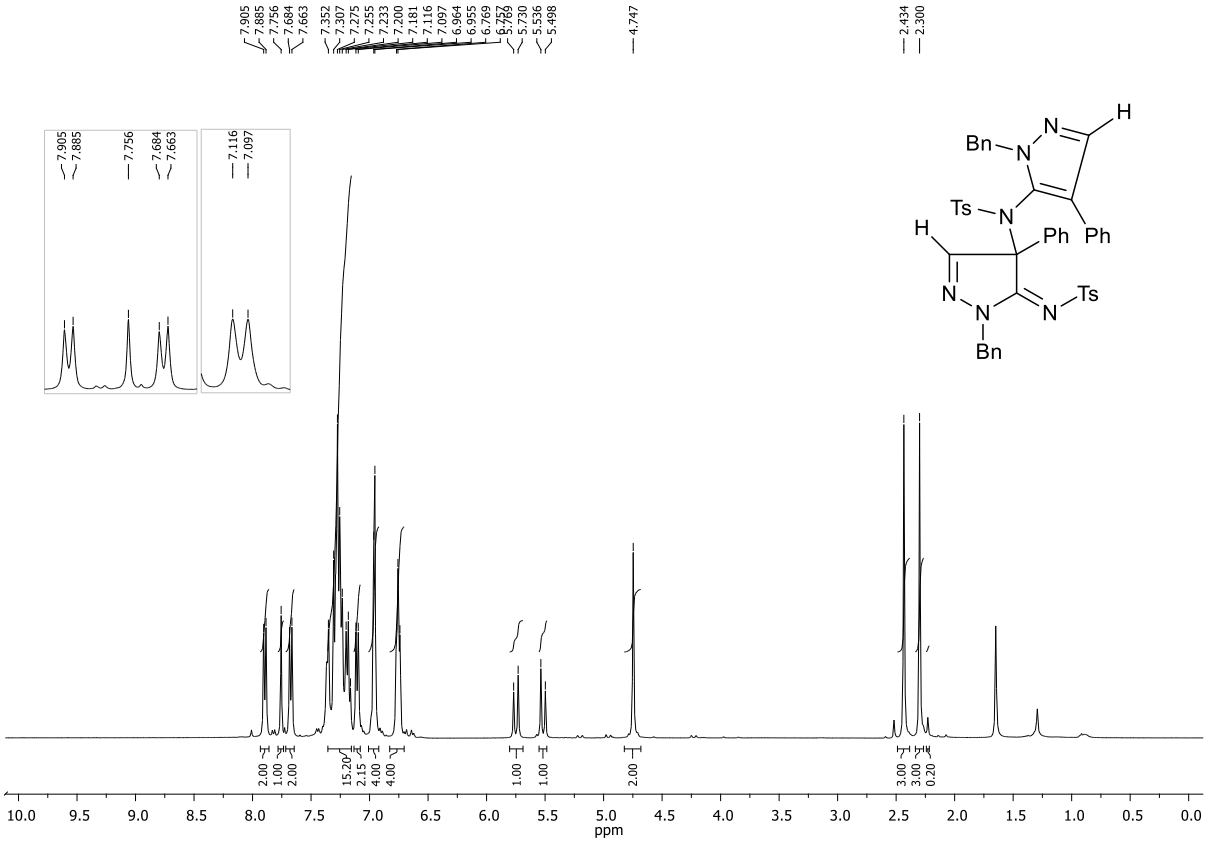
^{1}H NMR of **13b** in DMSO-d_6 (400 MHz):



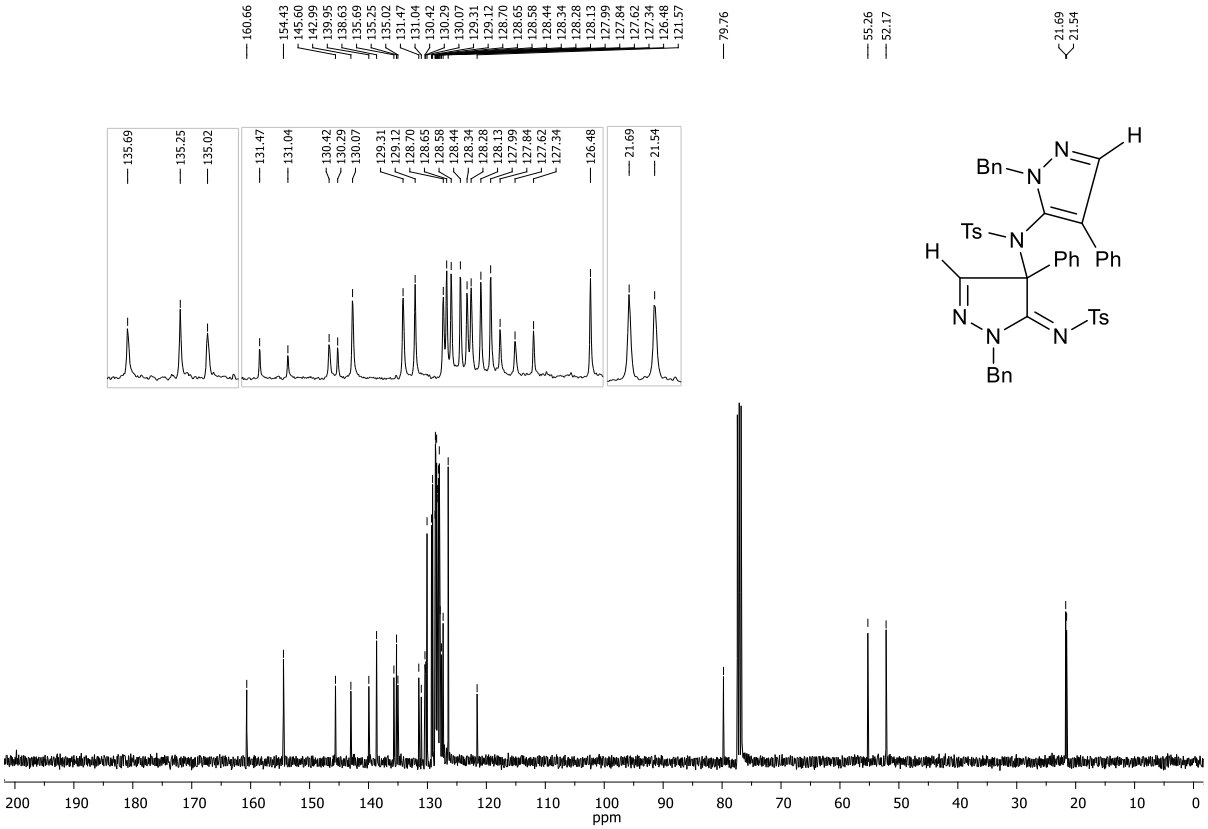
^{13}C{^{1}H} NMR of **13b** in $CDCl_3$ (175 MHz):



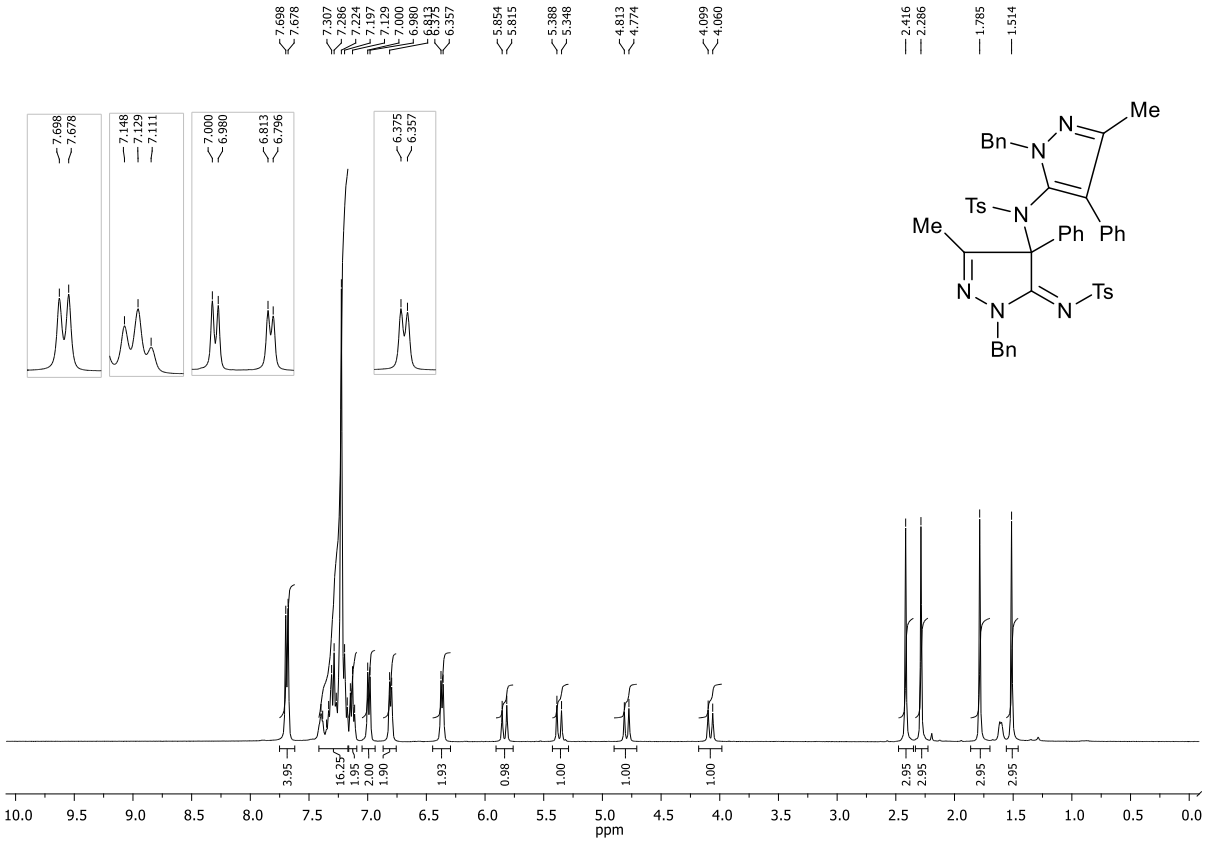
^{1}H NMR of **14g** in $CDCl_3$ (400 MHz):



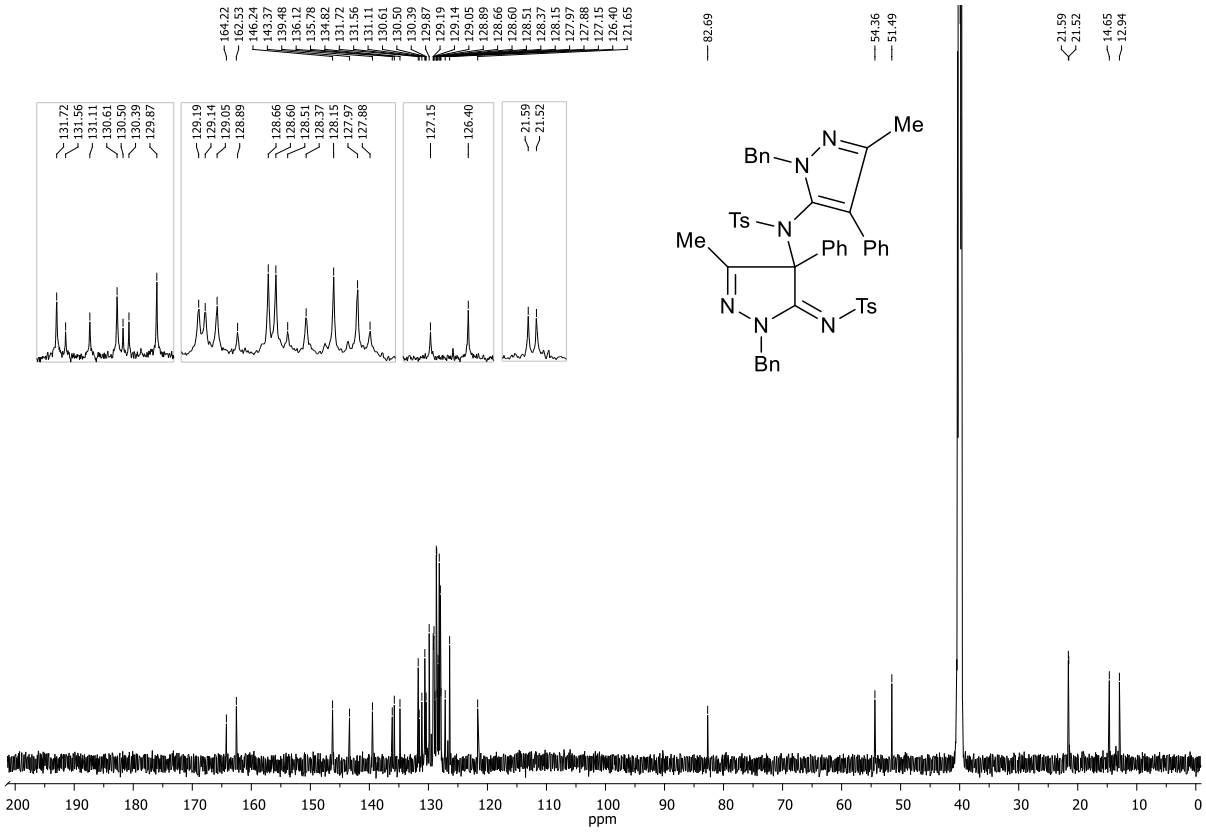
^{13}C{^{1}H} NMR of **14g** in $CDCl_3$ (100 MHz):



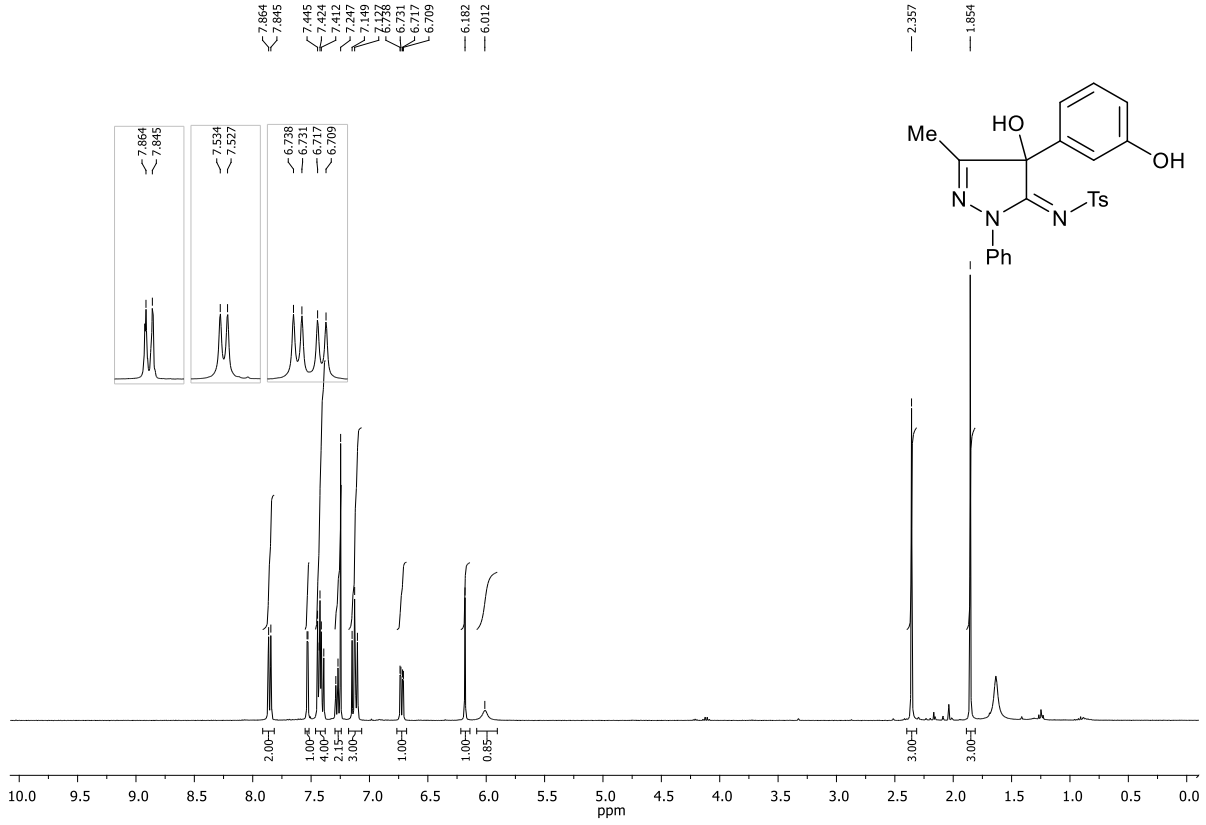
^{1}H NMR of **14h** in $CDCl_3$ (400 MHz):



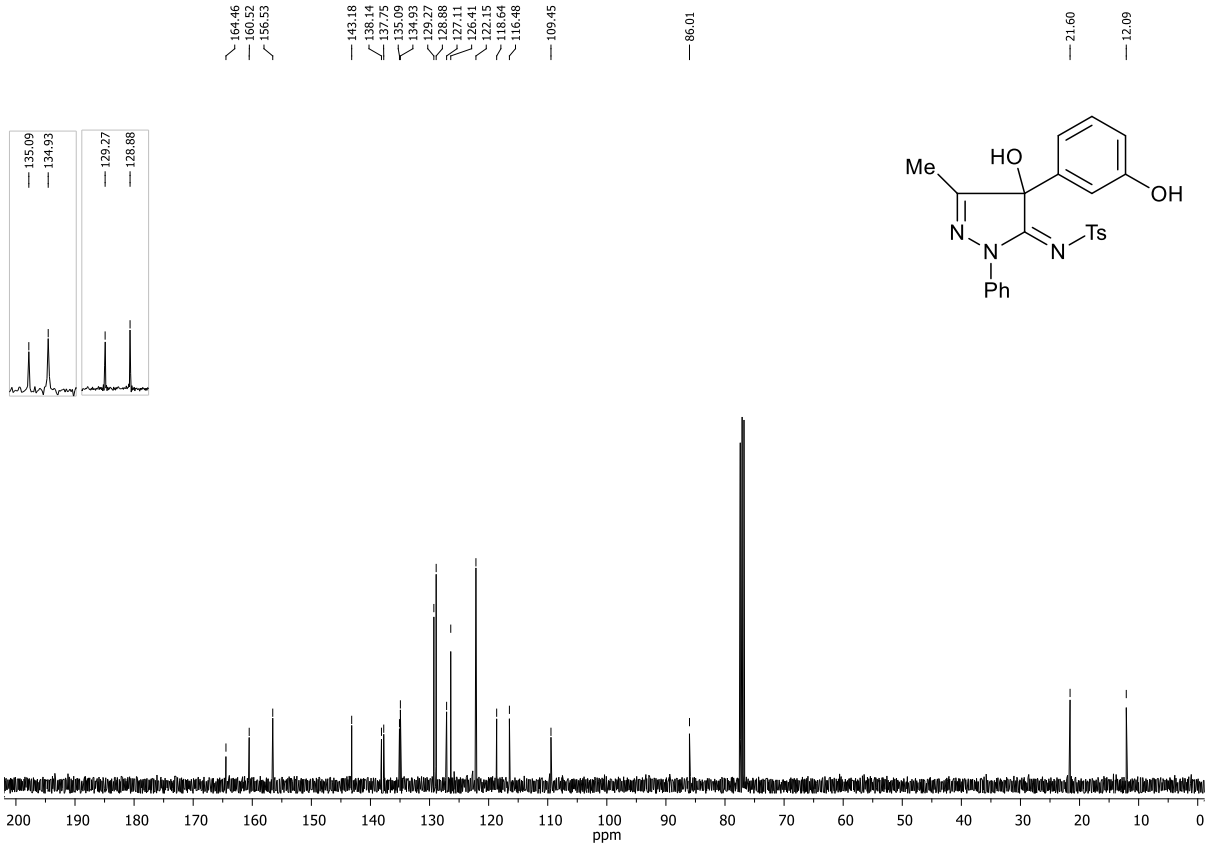
^{13}C{^{1}H} NMR of **14h** in $CDCl_3$ (100 MHz):



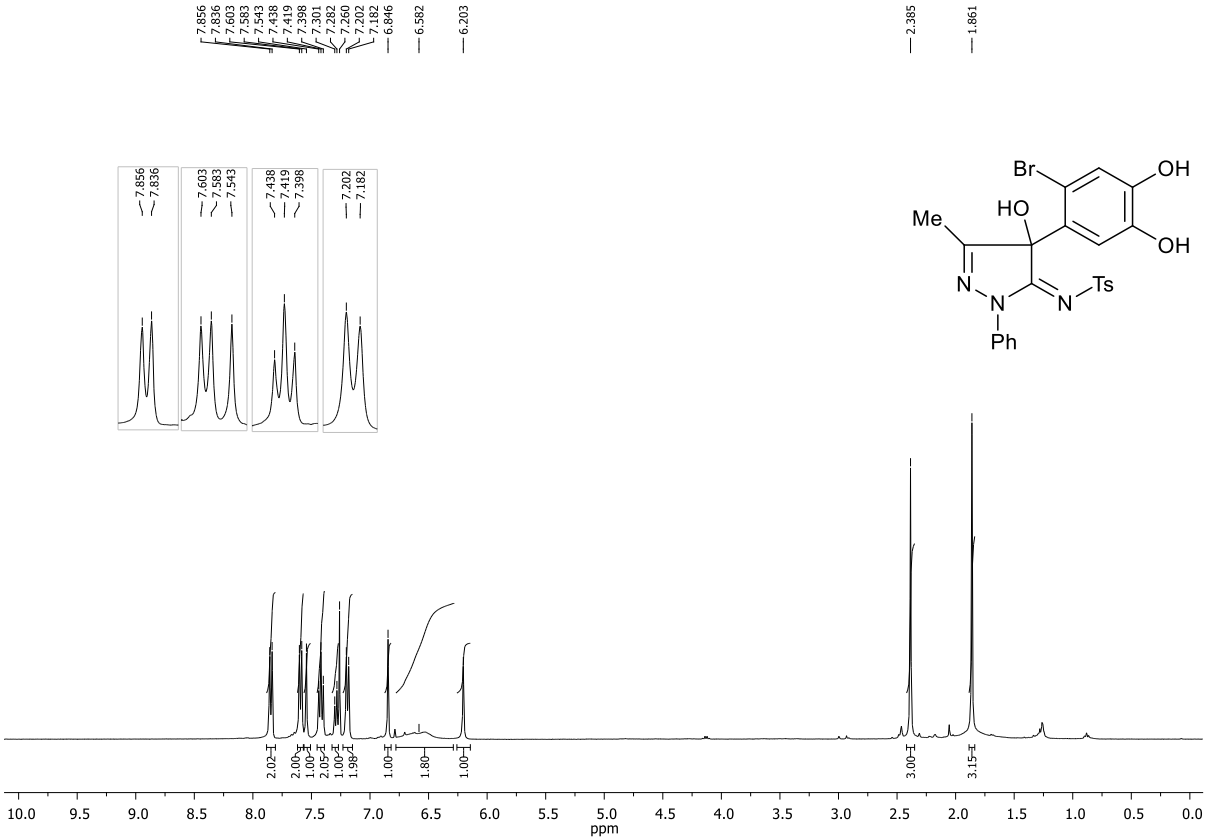
^{1}H NMR of **16r** in $CDCl_3$ (400 MHz):



^{13}C{^{1}H} NMR of **16r** in $CDCl_3$ (100 MHz):



^{1}H NMR of **16t** in $CDCl_3$ (400 MHz):



^{13}C{^{1}H} NMR of **16t** in $CDCl_3$ (100 MHz):