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The reaction of acetylenes with aldazines in the NaOBu^t/DMSO system: a contribution to the pyrazole chemistry

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Contents

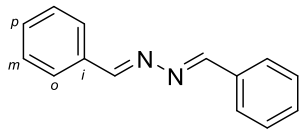
1. General information

The NMR spectra were recorded on a Bruker DPX-400 and AV-400 spectrometers (400.1 MHz for ^{1}H, 100.6 MHz for ^{13}C, and 40.5 MHz for ^{15}N) in $CDCl_3$. The values of the δ ^{15}N were measured through the 2D ^{1}H-^{15}N HMBC experiment and were referenced to CH_3NO_2 (0.0 ppm). Coupling constants (*J*) in hertz (Hz) were measured from one-dimensional spectra and multiplicities were abbreviated as following: s (singlet), br. s (broad singlet), d (doublet), dd (doublet of doublets), m (multiplet). IR spectra were taken with FT-IR. Mass spectra of positive electron ionization ions (70 eV) were registered on a Shimadzu GCMS-QP5050A with a DI-50 direct sample injection system (quadrupole mass analyzer, range of detected masses 34 - 650 Da). Melting points (uncorrected) were measured on a SMP50 Stuart apparatus. The microanalyses were performed on a Flash EA 1112 Series elemental analyzer. Thin layer chromatography was carried out on Merck silica gel 60 F_{254} pre-coated aluminium foil sheets (eluent: hexane – diethyl ether = 3:1 or hexane/ethyl acetate= 1:1) and were visualized using UV light (254 nm). Column chromatography was carried out using slurry packed Sigma Aldrich silica gel, 70-230 mesh, pore size 60 Å (eluent: hexane/ethyl acetate).

2. Starting materials

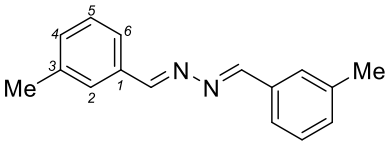
Azines **1** were synthesized from aldehydes and hydrazine hydrate by published procedures.[S1] Acetylenes **2**, aldehydes, and all other chemicals and solvents are commercially available and were used without further purification.

1,2-Di((E)-benzylidene)hydrazine (1a).[S2] Following the procedure,[S1] **1a** was prepared from



benzaldehyde (10 mmol, 1.061 g). Pure **1a** was isolated as a yellow solid (0.875 g, 84% yield). M. p. = 86-89 °C (lit.[S2] 91-93 °C). Elemental analysis calcd (%) for $C_{14}H_{12}N_2$ (208.26): C, 80.74; H, 5.81; N, 13.45; found: C, 80.63; H, 5.98; N, 13.39. R_f = 0.48 (hexane – diethyl ether = 3:1). ^{1}H NMR: *δ* 8.70 (s, 2H, HC=N), 7.94 – 7.76 (m, 4H, H*o*), 7.57 – 7.40 (m, 6H, H*m,p*) ppm. $^{13}C\{^{1}H\}$ NMR: *δ* 162.1 (C=N), 134.2 (C*i*), 131.3 (C*p*), 128.9, 128.7 (C*m,o*) ppm. IR (film): ν_{max} 3057, 3026, 3000, 2936, 2852, 1685, 1624, 1575, 1559, 1541, 1508, 1473, 1448, 1420, 1398, 1310, 1292, 1213, 1103, 1073, 1025, 967 cm^{-1}. MS (EI), m/z (%): 208.15 $[M]^{+\cdot}$. Calc. for $C_{14}H_{12}N_2$, m/z: 208.10.

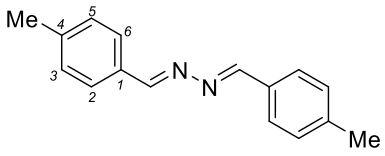
1,2-Bis((E)-3-methylbenzylidene)hydrazine (1b).[S3] Following



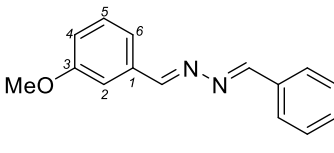
the procedure,[S1] **1b** was prepared from 3-methylbenzaldehyde (10 mmol, 1.202 g). Pure **1b** was isolated as a yellow solid (0.792 g, 67% yield). M. p. = 73-74 °C (lit.[S4] 74 °C). Elemental analysis calcd (%) for $C_{16}H_{16}N_2$ (236.32): C, 81.32; H, 6.82; N, 11.85; found: C, 81.26; H, 6.98;

N, 11.76. R_f = 0.62 (hexane – diethyl ether = 3:1). ^{1}H NMR: δ 8.65 (s, 2H, HC=N), 7.70 (s, 2H, H*2*), 7.63 (d, ^3J = 7.5 Hz, 2H, H*4*), 7.35 (dd, ^3J = 7.5 Hz, ^3J = 7.5 Hz, 2H, H*5*), 7.29 (d, ^3J = 7.5 Hz, 2H, H*6*), 2.42 (s, 6H, *3*-Me) ppm. ^{13}C{^{1}H} NMR: δ 162.3 (C=N), 138.6, 134.2, 132.2, 128.9, 128.8, 126.2 (12C, *Ar*), 21.4 (*3*-Me) ppm. IR (film): ν_{max} 3051, 3033, 3017, 2998, 2934, 2922, 2863, 1626, 1603, 1583, 1483, 1453, 1379, 1320, 1284, 1249, 1167, 1155, 1091, 1041, 997, 960 cm^{-1}. MS (EI), m/z (%): 236.05 $[M]^{+\cdot}$. Calc. for $C_{16}H_{16}N_2$, m/z: 236.13.

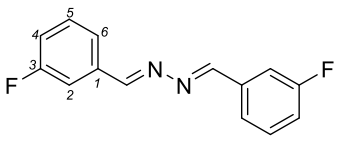
1,2-Bis((E)-4-methylbenzylidene)hydrazine (1c).[S5] Following the procedure,[S1] **1c** was prepared from 4-methylbenzaldehyde (10 mmol, 1.202 g). Pure **1c** was isolated as a light yellow solid (0.969 g, 82% yield). M. p. = 156-158 °C (lit.[5] 154-155 °C). Elemental analysis calcd (%) for $C_{16}H_{16}N_2$ (236.32): C, 81.32; H, 6.82; N, 11.85; found: C, 81.44; H, 6.71; N, 11.85. R_f = 0.46 (hexane – diethyl ether = 3:1). ^{1}H NMR: δ 8.64 (s, 2H, HC=N), 7.93 – 7.71 (m, 4H), 7.31 – 7.12 (m, 4H) [*Ar*], 2.41 (s, 6H, *4*-Me) ppm. ^{13}C{^{1}H} NMR: δ 161.9 (C=N), 141.6, 131.6 (4C, C*1*,*4*), 129.6, 128.6 (8C, *Ar*), 21.7 (*4*-Me) ppm. IR (film): ν_{max} 2921, 2852, 1735, 1685, 1654, 1623, 1560, 1543, 1509, 1458, 1437, 1420, 1387, 1321, 1302, 1210, 1175, 1142, 1108, 1073, 1044, 968, 943 cm^{-1}. MS (EI), m/z (%): 236.20 $[M]^{+\cdot}$. Calc. for $C_{16}H_{16}N_2$, m/z: 236.13.



1,2-Bis((E)-3-methoxybenzylidene)hydrazine (1d).[S6] Following the procedure,[S1] **1d** was prepared from 3-methoxybenzaldehyde (10 mmol, 1.362 g). Pure **1d** was isolated as a yellow solid (1.248 g, 93% yield). M. p. = 75-76 °C (lit.[S7] 77-78 °C). Elemental analysis calcd (%) for $C_{16}H_{16}N_2O_2$ (268.32): C, 71.62; H, 6.01; N, 10.44; found: C, 71.83; H, 5.96; N, 10.37. R_f = 0.22 (hexane – diethyl ether = 3:1). ^{1}H NMR: δ 8.63 (s, 2H, HC=N), 7.46 (s, 2H, H*2*), 7.40 – 7.32 (m, 4H), 7.12 – 6.95 (m, 2H) [*Ar*], 3.88 (s, 6H, *3*-OMe) ppm. ^{13}C{^{1}H} NMR: δ 162.0, 160.0 (C*3*, C=N), 135.6 (C*1*), 129.9, 122.1, 118.0, 112.1 (8C, *Ar*), 55.5 (*3*-OMe) ppm. IR (film): ν_{max} 3067, 3001, 2954, 2939, 2835, 1627, 1601, 1571, 1485, 1464, 1431, 1324, 1284, 1265, 1195, 1168, 1155, 1044, 994, 958 cm^{-1}. MS (EI), m/z (%): 268.15 $[M]^{+\cdot}$. Calc. for $C_{16}H_{16}N_2O_2$, m/z: 268.12.

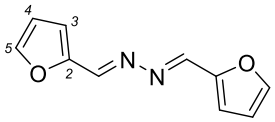


1,2-Bis((E)-3-fluorobenzylidene)hydrazine (1e).[S8] Following the procedure,[S1] **1e** was prepared from 3-fluorobenzaldehyde (10 mmol, 1.241 g). Pure **1e** was isolated as a yellow solid (1.038 g, 85% yield). M. p. = 132-133 °C (lit.[S9] 132 °C). Elemental analysis calcd (%) for $C_{14}H_{10}F_2N_2$ (244.24): C, 68.85; H, 4.13; F, 15.56; N, 11.47; found: C, 68.97; H, 4.02; F, 15.55; N, 11.46. R_f = 0.48 (hexane – diethyl ether = 3:1). ^{1}H NMR: δ 8.60 (s, 2H, HC=N), 7.65 – 7.52 (m, 4H), 7.46 – 7.37 (m, 2H), 7.21 – 7.09 (m, 2H) [*Ar*] ppm. ^{13}C{^{1}H} NMR: δ 162.5 (d, ^1J = 246.8 Hz, C*3*), 160.7 (d, ^4J = 3.0



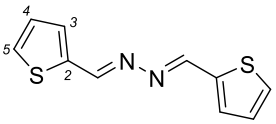
Hz, C=N), 135.8 (d, ^3J = 7.7 Hz, C*1*), 129.9 (d, ^3J = 8.1 Hz, C*5*), 124.4 (d, ^4J = 2.9 Hz, C*6*), 117.8 (d, ^2J = 21.5 Hz), 114.1 (d, ^2J = 22.5 Hz) [C*2,4*] ppm. IR (film): ν_{max} 3065, 3034, 2953, 2923, 2853, 1747, 1717, 1700, 1684, 1653, 1626, 1581, 1559, 1541, 1508, 1485, 1453, 1271, 1247, 1162, 1135, 1103, 957, 876, 779, 675 cm^{-1}. MS (EI), m/z (%): 244.10 $[M]^{+\cdot}$. Calc. for $C_{14}H_{10}F_2N_2$, m/z: 244.08.

(1E,2E)-1,2-Bis(furan-2-ylmethylene)hydrazine (1f).[S10] Following the procedure,[S1] **1f** was



prepared from furfural (10 mmol, 0.961 g). Pure **1f** was isolated as a yellow solid (0.621 g, 66% yield). M. p. = 105-110 °C (lit.[S11] 111-112 °C). Elemental analysis calcd (%) for $C_{10}H_8N_2O_2$ (188.19): C, 63.83; H, 4.29; N, 14.89; found: C, 63.95; H, 4.21; N, 14.76. R_f = 0.13 (hexane – diethyl ether = 3:1). ^{1}H NMR: δ 8.53 (s, 2H, HC=N), 7.60 (d, ^3J = 1.7 Hz, 2H, H*5*), 6.90 (d, ^3J = 3.5 Hz, 2H, H*3*), 6.55 (dd, ^3J = 3.5 Hz, ^3J = 1.7 Hz, 2H, H*4*) ppm. ^{13}C{^{1}H} NMR: δ 150.9 (C=N), 149.5 (C*2*), 145.8 (C*5*), 116.7, 112.3 (C*3*,*4*) ppm. IR (film): ν_{max} 3145, 3135, 3102, 3078, 3003, 2956, 2923, 2855, 1639, 1574, 1544, 1521, 1470, 1421, 1393, 1290, 1271, 1218, 1151, 1078, 1021, 950, 929 cm^{-1}. MS (EI), m/z (%): 188.10 $[M]^{+\cdot}$. Calc. for $C_{10}H_8N_2O_2$, m/z: 188.06.

(1E,2E)-1,2-Bis(thiophen-2-ylmethylene)hydrazine (1g).[S12] Following the procedure,[S1] **1g** was



prepared from thiophene-2-carbaldehyde (10 mmol, 1.122 g). Pure **1g** was isolated as a yellow solid (0.793 g, 72% yield). M. p. = 144-145 °C (lit.[S12] 143-146 °C). Elemental analysis calcd (%) for $C_{10}H_8N_2S_2$ (220.31): C, 54.52; H, 3.66; N, 12.72; S, 29.10; found: C, 54.66; H, 3.68; N, 12.65; S, 29.01. R_f = 0.45 (hexane – diethyl ether = 3:1). ^{1}H NMR: δ 8.78 (s, 2H, HC=N), 7.48 (dd, ^3J = 5.0 Hz, ^4J = 1.1 Hz, 2H, H*5*), 7.42 (dd, ^3J = 3.7 Hz, ^4J = 1.1 Hz, 2H, H*3*), 7.12 (dd, ^3J = 5.0 Hz, ^3J = 3.7 Hz, 2H, H*4*) ppm. ^{13}C{^{1}H} NMR: δ 155.9 (C=N), 139.0 (C*2*), 132.6, 130.2, 127.9 (*Thioph*) ppm. IR (film): ν_{max} 3100, 3084, 3066, 2955, 2918, 2851, 1611, 1560, 1543, 1522, 1455, 1421, 1356, 1284, 1234, 1212, 1090, 1041, 948, 856, 833, 764, 722 cm^{-1}. MS (EI), m/z (%): 220.00 $[M]^{+\cdot}$. Calc. for $C_{10}H_8N_2S_2$, m/z: 220.01.

3. Synthesis of pyrazoles 3 (*general procedure*)

Azine **1** (2 mmol) in DMSO (2 mL) was added dropwise to a mixture of acetylene **2** (2 mmol), $NaOBu^t$ (2 mmol, 0.192 g), and ethanol (60 μl) in DMSO (4 mL) at 20 °C for 20 min. Then, the reaction mixture was stirred at 20 °C for 2 h, diluted with solution of K_2CO_3 (0.2 g) in H_2O (15 mL), and extracted with Et_2O (5 mL × 7). The organic extract was washed with H_2O (5 mL × 3) and dried over K_2CO_3 for 1 h. Et_2O was evaporated under reduced pressure, and pure pyrazole **3** was obtained by column chromatography [SiO_2, eluent: hexane/ethyl acetate = 5:1].

4-Benzyl-3,5-diphenyl-1H-pyrazole (3aa).[S13] Following the general procedure, **3aa** was prepared from **1a** (2 mmol, 0.417 g) and **2a** (2 mmol, 0.204 g). Pure **3aa** was isolated as a colorless solid (0.292 g, 47% yield). M. p. = 181-182 °C (lit.[S13] 156-158 °C). Elemental analysis calcd (%) for $C_{22}H_{18}N_2$ (310.40): C, 85.13; H, 5.85; N, 9.03; found: C, 85.27; H, 5.61; N, 9.12. R_f = 0.28 (hexane/ethyl acetate = 1:1). ^{1}H NMR: δ 11.13 (br. s, 1H, NH), 7.45 – 7.37 (m, 4H, H*o1*,*o2*), 7.28 – 7.21 (m, 8H, *Ph*), 7.19 – 7.15 (m, 1H, H*p3*), 7.14 – 7.07 (m, 2H, H*m3*), 4.08 (s, 2H, *4*-CH_2) ppm. ^{13}C{^{1}H} NMR: δ 147.5 (br. s, C*3*,*5*), 141.4 (C*i3*), 131.9 (br. s, C*i1*,*i2*), 128.8, 128.7, 128.2, 128.1, 127.7 (14C, *Ph*), 126.1 (C*p3*), 112.9 (C*4*), 29.7 (*4*-CH_2) ppm. IR (film): ν_{max} 3397, 3183, 3101, 3061, 3028, 2922, 2854, 1734, 1652, 1603, 1560, 1542, 1493, 1451, 1401, 1320, 1252, 1174, 1099, 1075, 1030, 976, 917 cm^{-1}. MS (EI), m/z (%): 310.15 $[M]^{+\cdot}$. Calc. for $C_{22}H_{18}N_2$, m/z: 310.20.

4-Benzyl-3,5-di-m-tolyl-1H-pyrazole (3ba). Following the general procedure, **3ba** was prepared from **1b** (2 mmol, 0.473 g) and **2a** (2 mmol, 0.204 g). Pure **3ba** was isolated as a colorless oil (0.156 g, 23% yield). Elemental analysis calcd (%) for $C_{24}H_{22}N_2$ (338.45): C, 85.17; H, 6.55; N, 8.28; found: C, 85.07; H, 6.65; N, 8.28. R_f = 0.58 (hexane/ethyl acetate = 1:1). ^{1}H NMR: δ 9.61 (br. s, 1H, NH), 7.33 – 7.21 (m, 6H), 7.21 – 7.05 (m, 7H) [*Ar*], 4.07 (s, 2H, *4*-CH_2), 2.23 (s, 6H, *3′*,*3″*-Me) ppm. ^{13}C{^{1}H} NMR: δ 147.7 (br. s, C*3*,*5*), 141.6 (C*i3*), 138.3 (br. s, C*1′*,*1″*), 131.8, 128.89, 128.86, 128.63, 128.59, 128.5, 128.3 (12C, *Ar*), 126.0 (C*p3*), 124.8 (2C, *Ar*), 113.0 (C*4*), 29.8 (*4*-CH_2), 21.5 (*3′*,*3″*-Me) ppm. IR (film): ν_{max} 3397, 3148, 3101, 3026, 2919, 2855, 2735, 1607, 1589, 1493, 1452, 1381, 1297, 1235, 1169, 1129, 1094, 1030, 1012, 933, 909, 855, 789, 732, 697 cm^{-1}. MS (EI), m/z (%): 338.18 $[M]^{+\cdot}$. Calc. for $C_{24}H_{22}N_2$, m/z: 338.05.

4-Benzyl-3,5-di-p-tolyl-1H-pyrazole (3ca). Following the general procedure, **3ca** was prepared from **1c** (2 mmol, 0.473 g) and **2a** (2 mmol, 0.204 g). Pure **3ca** was isolated as a colorless oil (0.291 g, 43% yield). Elemental analysis calcd (%) for $C_{24}H_{22}N_2$ (338.45): C, 85.17; H, 6.55; N, 8.28; found: C, 85.03; H, 6.68; N, 8.19. R_f = 0.37 (hexane/ethyl acetate = 1:1). ^{1}H NMR: δ 8.72 (br. s, 1H, NH), 7.39 – 7.34 (m, 4H, H*o1*,*o2*), 7.30 – 7.25 (m, 2H, H*m3*), 7.22 – 7.11 (m, 7H) [*Ar*], 4.09 (s, 2H, *4*-CH_2), 2.35 (s, 6H, *p1*,*p2*-Me) ppm. ^{13}C{^{1}H} NMR: δ 147.6 (br. s, C*3*,*5*), 141.6 (C*i3*), 137.8, 129.4, 129.1, 128.6, 128.2, 127.6 (16C, *Ar*), 126.0 (C*p3*), 112.4 (C*4*), 29.8 (*4*-CH_2), 21.3 (*p1*,*p2*-Me) ppm. IR (film): ν_{max} 3390, 3158, 3111, 3057, 3025, 2958, 2920, 2892, 2853, 1510, 1493, 1450, 1291, 1254, 1225, 1184, 1167, 1121, 1080, 1046, 1031,

978, 910, 887, 873, 825, 732 cm^{-1}. MS (EI), m/z (%): 338.18 $[M]^{+\cdot}$. Calc. for $C_{24}H_{22}N_2$, m/z: 338.35.

4-Benzyl-3,5-bis(3-methoxyphenyl)-1H-pyrazole (3da). Following the general procedure, **3da** was prepared from **1d** (2 mmol, 0.537 g) and **2a** (2 mmol, 0.204 g). Pure **3da** was isolated as a light yellow oil (0.133 g, 18% yield). Elemental analysis calcd (%) for $C_{24}H_{22}N_2O_2$ (370.45): C, 77.81; H, 5.99; N, 7.56; found: C, 77.64; H, 6.07; N, 7.49. R_f = 0.29 (hexane/ethyl acetate = 1:1). ^{1}H NMR: δ 11.87 (br. s, 1H, NH), 7.27 – 7.19 (m, 2H), 7.19 – 7.06 (m, 5H), 7.04 – 6.96 (m, 2H), 6.94 – 6.87 (m, 2H), 6.80 – 6.71 (m, 2H) [*Ar*], 4.07 (s, 2H, *4*-C<u>H</u>$_2$), 3.42 (s, 6H, *3′,3″*-OMe) ppm. ^{13}C{^{1}H} NMR: δ 159.8 (C*3′,3″*), 147.7 (br. s, C*3,5*), 141.4 (C*i3*), 132.9 (br. s, C*1′,1″*), 129.8, 128.8, 128.2, 126.2, 119.9, 115.0 (11C, *Ar*), 112.6 (C*4*), 112.3 (C*2′,2″*), 55.0 (*3′,3″*-OMe), 29.8 (*4*-CH_2) ppm. IR (film): ν_{max} 3147, 3086, 3025, 3003, 2957, 2935, 2915, 2857, 2834, 1603, 1494, 1466, 1436, 1320, 1286, 1246, 1223, 1181, 1169, 1130, 1081, 1043, 997, 933, 909, 859, 789, 781, 732 cm^{-1}. MS (EI), m/z (%): 370.10 $[M]^{+\cdot}$. Calc. for $C_{24}H_{22}N_2O_2$, m/z: 370.17.

4-Benzyl-3,5-bis(3-fluorophenyl)-1H-pyrazole (3ea). 14% Analytical yield (from ^{1}H NMR spectrum). ^{1}H NMR: δ 9.60 (br. s, 1H, NH), 4.08 (s, 2H, *4*-C<u>H</u>$_2$) ppm. ^{13}C{^{1}H} NMR: δ 162.9 (d, ^1J = 246.8 Hz, C*3′,3″*), 140.2 (C*i3*), 130.6 (d, ^3J = 8.3 Hz, C*5′,5″*), 128.9, 128.0 (C*o3,m3*), 126.6 (C*p3*), 123.6 (d, ^4J = 2.6 Hz, C*6′,6″*), 115.8 (d, ^2J = 21.1 Hz), 114.9 (d, ^2J = 22.7 Hz) [C*2′,2″,4′,4″*], 113.6 (C*4*), 29.8 (*4*-CH_2) ppm.

4-Benzyl-3,5-di(furan-2-yl)-1H-pyrazole (3fa). Following the general procedure, **3fa** was prepared from **1f** (2 mmol, 0.376 g) and **2a** (2 mmol, 0.204 g). Pure **3fa** was isolated as a brown solid (0.197 g, 34% yield). M. p. = 129-130 °C. Elemental analysis calcd (%) for $C_{18}H_{14}N_2O_2$ (290.11): C, 74.47; H, 4.86; N, 9.65; found: C, 74.58; H, 4.72; N, 9.34. R_f = 0.44 (hexane/ethyl acetate = 1:1). ^{1}H NMR: δ 9.53 (br. s, 1H, NH), 7.37 (d, ^3J = 1.8 Hz, 2H, *Fur5′,5″*), 7.27 – 7.19 (m, 2H), 7.20 – 7.12 (m, 3H) [*Ph*], 6.43 (d, ^3J = 3.4 Hz, 2H, *Fur3′,3″*), 6.36 (dd, ^3J = 3.4 Hz, ^3J = 1.8 Hz, 2H, *Fur4′,4″*), 4.22 (s, 2H, *4*-CH_2) ppm. ^{13}C{^{1}H} NMR: δ 146.3 (br. s, C*3,5*), 142.2 (*Fur2′,5′,2″,5″*), 139.9 (C*i3*), 128.6, 128.1 (C*o3,m3*), 126.2 (C*p3*), 112.3 (C*4*), 111.5, 107.6 (*Fur3′,4′,3″,4″*), 29.6 (*4*-CH_2) ppm. IR (film): ν_{max} 3385, 3179, 3148, 3121, 3086, 3063, 3027, 2977, 2953, 2924, 2903, 2875, 1669, 1623, 1602, 1566, 1550, 1512, 1493, 1466, 1455, 1436, 1395, 1293, 1226, 1169, 1127, 1076, 1014, 988, 907, 886, 809 cm^{-1}. MS (EI), m/z (%): 290.11 $[M]^{+\cdot}$. Calc. for $C_{18}H_{14}N_2O_2$, m/z: 290.30.

4-Benzyl-3,5-di(thiophen-2-yl)-1H-pyrazole (3ga). Following the general procedure, **3ga** was prepared from **1g** (2 mmol, 0.441 g) and **2a** (2 mmol, 0.204 g). Pure **3ga** was isolated as a light yellow oil (0.097 g, 15% yield). Elemental analysis calcd (%) for $C_{18}H_{14}N_2S_2$ (322.44): C, 67.05; H, 4.38; N, 8.69; S, 19.89; found: C, 67.32; H, 4.23; N, 8.58; S, 19.87. R_f = 0.12 (hexane/diethyl ether = 1:1). ^{1}H NMR: δ 9.50 (br. s, 1H, NH), 7.36 – 7.26 (m, 4H), 7.25 – 7.19 (m, 1H), 7.21 – 7.15 (m, 4H) [*Ph*, *Thioph*], 7.00 (dd, ^3J = 5.1 Hz, ^3J = 3.7 Hz, 2H, *Thioph4',4''*), 4.22 (s, 2H, *4*-CH_2) ppm. ^{13}C{^{1}H} NMR: δ 142.2 (br. s, C*3*,*5*), 139.5 (C*i3*), 131.4, 128.8, 128.0, 127.9, 126.8, 126.7 (10C, *Ph*, *Thioph*), 126.4 (C*p3*), 113.4 (C*4*), 29.8 (*4*-CH_2) ppm. IR (film): ν_{max} 3445, 3112, 3083, 3065, 3030, 2956, 2923, 2852, 1739, 1661, 1602, 1586, 1493, 1465, 1452, 1434, 1410, 1357, 1321, 1241, 1211, 1159, 1108, 1048, 944, 908, 732, 704 cm^{-1}. MS (EI), m/z (%): 322.05 $[M]^{+\cdot}$. Calc. for $C_{18}H_{14}N_2S_2$, m/z: 322.06.

4-(4-Methylbenzyl)-3,5-diphenyl-1H-pyrazole (3ab). Following the general procedure, **3ab** was prepared from **1a** (2 mmol, 0.417 g) and **2b** (2 mmol, 0.232 g). Pure **3ab** was isolated as a colorless solid (0.285 g, 44% yield). M. p. = 199-201 °C. Elemental analysis calcd (%) for $C_{23}H_{20}N_2$ (324.43): C, 85.15; H, 6.21; N, 8.63; found: C, 85.29; H, 6.12; N, 8.59. R_f = 0.27 (hexane/ethyl acetate = 1:1). ^{1}H NMR: δ 7.53 – 7.45 (m, 4H, H*o1*,*o2*), 7.38 – 7.30 (m, 6H, H*m1*,*p1*,*m2*,*p2*), 7.16 – 6.99 (m, 4H, H*2'*,*3'*,*5'*,*6'*), 4.07 (s, 2H, *4*-CH_2), 2.33 (s, 3H, *4'*-Me) ppm. ^{13}C{^{1}H} NMR: δ 161.2 (br. s, C*3*,*5*), 138.2, 135.6 (C*1'*,*4'*), 131.8 (C*i1*,*i2*), 129.4, 128.9, 128.3, 128.1, 127.7 (14C, *Ar*), 112.8 (C*4*), 29.3 (*4*-CH_2), 21.1 (*4'*-Me) ppm. IR (film): ν_{max} 3397, 3157, 3141, 3097, 3025, 2956, 2920, 2879, 1605, 1583, 1567, 1511, 1497, 1450, 1297, 1267, 1226, 1181, 1168, 1134, 1074, 1030, 1019, 978, 909 cm^{-1}. MS (EI), m/z (%): 324.30 $[M]^{+\cdot}$. Calc. for $C_{23}H_{20}N_2$, m/z: 324.16.

4-(3-Fluorobenzyl)-3,5-diphenyl-1H-pyrazole (3ac). Following the general procedure, **3ac** was prepared from **1a** (2 mmol, 0.417 g) and **2c** (2 mmol, 0.240 g). Pure **3ac** was isolated as a colorless solid (0.250 g, 38% yield). M. p. = 149-150 °C. Elemental analysis calcd (%) for $C_{22}H_{17}FN_2$ (328.39): C, 80.47; H, 5.22; F, 5.79; N, 8.53; found: C, 80.49; H, 5.31; F, 5.72; N, 8.48. R_f = 0.27 (hexane/ethyl acetate = 1:1). ^{1}H NMR: δ 10.75 (br. s, 1H, N<u>H</u>), 7.44 – 7.35 (m, 4H), 7.32 – 7.27 (m, 6H) [*Ph*], 7.24 – 7.15 (m, 1H), 6.92 – 6.78 (m, 3H) [*Ar*], 4.07 (s, 2H, *4*-C<u>H</u>$_2$) ppm. ^{13}C{^{1}H} NMR: δ 163.3 (d, ^1J = 245.7 Hz, C*3'*), 147.6 (C*3*,*5*), 144.1 (d, ^3J = 6.9 Hz, C*1'*), 131.7 (C*i1*,*i2*), 130.1 (d, ^3J = 8.2 Hz, C*5'*), 128.8, 128.2, 127.7 (10C, *Ph*), 123.8 (d, ^4J = 2.8 Hz, C*6'*), 115.1 (d, ^2J = 21.6 Hz), 113.1 (d, ^2J = 21.2 Hz) [C*2'*,*4'*], 112.2 (C*4*), 29.5 (*4*-<u>C</u>H$_2$) ppm. IR (film): ν_{max} 3157, 3142, 3098, 3060, 3028, 2957, 2922, 2876, 2857, 1614, 1587, 1486, 1448, 1267, 1246,

12221, 1178, 1130, 1074, 1030, 977, 940, 927, 890, 850, 765, 744, 697 cm^{-1}. MS (EI), m/z (%): 328.25 $[M]^{+\cdot}$. Calc. for $C_{22}H_{17}FN_2$, m/z: 328.14.

3-[(3,5-Diphenyl-1H-pyrazol-4-yl)methyl]pyridine (3ad). Following the general procedure, **3ad** was prepared from **1a** (2 mmol, 0.417 g) and **2d** (2 mmol, 0.206 g). Pure **3ad** was isolated as a colorless solid (0.131 g, 21% yield). M. p. = 208-209 °C. Elemental analysis calcd (%) for $C_{21}H_{17}N_3$ (311.39): C, 81.00; H, 5.50; N, 13.49; found: C, 81.23; H, 5.42; N, 13.35. R_f = 0.06 (hexane/ethyl acetate = 1:1). ^{1}H NMR: δ 10.20 (br. s, 1H, NH), 8.44 – 8.39 (m, 2H, H*2′*,*6′*), 7.47 – 7.38 (m, 4H, H*o1*,*o2*), 7.35 (d, ^3J = 7.8 Hz, 1H, H*4′*), 7.33 – 7.26 (m, 6H, H*m1*,*p1*,*m2*,*p2*), 7.13 (dd, ^3J = 7.8 Hz, ^3J = 5.1 Hz, 1H, H*5′*), 4.11 (s, 2H, *4*-CH_2) ppm. ^{13}C{^{1}H} NMR: δ 149.5, 147.2 (*Pyr2′*,*6′*), 147.6 (C*3*,*5*), 136.9 (*Pyr3′*), 136.0 (*Pyr4′*), 131.7 (C*i1*,*i2*), 128.9, 128.4, 127.8 (10C, *Ph*), 123.6 (*Pyr5′*), 111.8 (C*4*), 27.2 (*4*-CH_2) ppm. IR (film): ν_{max} 3397, 3178, 3159, 3142, 3102, 3058, 3029, 2956, 2920, 2875, 2852, 1604, 1576, 1495, 1479, 1449, 1424, 1348, 1296, 1269, 1219, 1176, 1134, 1101, 1074, 1028, 975, 910 cm^{-1}. MS (EI), m/z (%): 311.10 $[M]^{+\cdot}$. Calc. for $C_{21}H_{17}N_3$, m/z: 311.14.

4-Methyl-3,5-diphenyl-1H-pyrazole (3ae).[S14] A mixture of imine **1a** (10 mmol, 2.083 g) and $NaOBu^t$ (10 mmol, 0.961 g) in DMSO (50 mL) was placed into a steel stirred reactor (*V* = 250 mL). The latter was fed with acetylene under pressure (initial pressure at ambient temperature was ~ 3 atm) and then decompressed to atmospheric pressure to remove air. The reactor was fed with acetylene again and stirred at 20-22 °C for 2 h. Acetylene pressure in reaction course was ~2 atm. The reaction mixture was diluted with solution of K_2CO_3 (~2 g) in H_2O (100 mL) and extracted with Et_2O (20 mL × 7). The combined organic extract was washed with H_2O (20 mL × 3) and dried over K_2CO_3 for 1 h. Et_2O was evaporated under reduced pressure, and the residue was purified by column chromatography (hexane : ethyl acetate = 10:1). Pure **3ae** was isolated as a light yellow solid (0.352 g, 15% yield). M. p. = 215-216 °C (lit.[S14] 171-172 °C). Elemental analysis calcd (%) for $C_{16}H_{14}N_2$ (234.30): C, 82.02; H, 6.02; N, 11.96; found: C, 82.14; H, 5.97; N, 11.89. R_f = 0.32 (hexane – ethyl acetate = 1:1). ^{1}H NMR: δ 10.49 (br. s, 1H, NH), 7.67 – 7.59 (m, 4H, H*o1*,*o2*), 7.52 – 7.42 (m, 4H, H*m1*,*m2*), 7.43 – 7.34 (m, 2H, H*p1*,*p2*), 2.33 (s, 3H, *4*-Me) ppm. ^{13}C{^{1}H} NMR: δ 146.9 (C*3*,*5*), 132.0 (C*i1*,*i2*), 128.8, 128.2, 127.9 (10C, *Ph*), 110.9 (C*4*), 10.2 (*4*-Me) ppm. IR (film): ν_{max} 3320, 3056, 3032, 2951, 2920, 2851, 1732, 1720, 1678, 1656, 1447, 1435, 1386, 1263, 1098, 1067, 1003, 938, 902, 763, 690, 644 cm^{-1}. MS (EI), m/z (%): 234.05 $[M]^{+\cdot}$. Calc. for $C_{16}H_{14}N_2$, m/z: 234.12.

1-Benzyl-3,5-diphenyl-1H-pyrazole (4aa).[S13] Following the general procedure, **4aa** was prepared from **1a** (2 mmol, 0.417 g) and **2a** (2 mmol, 0.204 g). Pure **4aa** was isolated as a light yellow solid (0.051 g, 8% yield). M. p. = 120-122 °C (lit.[S13] 119-121 °C). Elemental analysis calcd (%) for $C_{22}H_{18}N_2$ (310.40): C, 85.13; H, 5.85; N, 9.03; found: C, 85.34; H, 5.67; N, 8.99. R_f = 0.43 (hexane/ethyl acetate = 1:1). ^{1}H NMR: δ 7.92 – 7.78 (m, 2H), 7.41 – 7.17 (m, 9H), 7.18 – 7.10 (m, 2H), 7.11 – 7.02 (m, 2H) [*Ph*], 6.63 (s, 1H, H*4*), 5.36 (s, 2H, N-CH_2) ppm. ^{13}C{^{1}H} NMR: δ 151.1, 145.6 (C*3*,*5*), 137.9, 133.6, 130.8 (C*i1*,*i2*,*i3*), 129.0, 128.8, 128.73, 128.71, 127.8, 127.5 (15C, *Ph*), 126.9, 103.9 (C*4*), 53.4 (N-CH_2) ppm. IR (film): ν_{max} 3119, 3062, 3032, 2930, 1605, 1549, 1485, 1459, 1438, 1365, 1306, 1277, 1203, 1188, 1157, 1075, 1028, 1006, 998, 957, 910 cm^{-1}. MS (EI), m/z (%): 310.05 $[M]^{+\cdot}$. Calc. for $C_{22}H_{18}N_2$, m/z: 310.15.

1-(3-Fluorobenzyl)-3-(3-fluorophenyl)-5-phenyl-1H-pyrazole (4ea). Following the general procedure, **4ea** was prepared from **1e** (2 mmol, 0.488 g) and **2a** (2 mmol, 0.204 g). Pure **4ea** was isolated as a light yellow solid (0.263 g, 38% yield). M. p. = 99-100 °C. Elemental analysis calcd (%) for $C_{22}H_{16}F_2N_2$ (346.38): C, 76.29; H, 4.66; F, 10.97; N, 8.09; found: C, 76.43; H, 4.57; N, 8.07. R_f = 0.30 (hexane/ethyl acetate = 1:1). ^{1}H NMR: δ 7.67 – 7.61 (m, 1H), 7.64 – 7.55 (m, 1H), 7.45 – 7.31 (m, 6H), 7.31 – 7.21 (m, 1H), 7.06 – 6.97 (m, 1H), 7.00 – 6.90 (m, 1H), 6.92 – 6.85 (m, 1H), 6.86 – 6.78 (m, 1H) [*Ar*], 6.66 (s, 1H, H*4*), 5.37 (s, 2H, N-CH_2) ppm. ^{13}C{^{1}H} NMR: δ 163.4 (d, ^1J = 244.9 Hz), 163.2 (d, ^1J = 246.5 Hz) [H*3′*,*3″*], 150.3 (d, ^4J = 2.3 Hz, H*3*), 145.9 (H*5*), 140.2 (d, ^3J = 7.2 Hz), 135.8 (d, ^3J = 8.4 Hz) [H*1′*,*1″*], 130.4 (d, ^3J = 9.1 Hz, H*5′*,*5″*), 130.2 (C*i3*), 129.1 (C*p3*), 129.0, 128.9 (C*o3*,*m3*), 122.5 (d, ^4J = 2.9 Hz), 121.5 (d, ^4J = 2.8 Hz) [H*6′*,*6″*], 114.7 (d, 2C, ^2J = 21.4 Hz), 114.0 (d, ^2J = 22.3 Hz), 112.7 (d, ^2J = 22.6 Hz) [H*2′*,*4′*,*2″*,*4″*], 104.2 (C*4*), 53.0 (d, ^4J = 1.1 Hz, N-CH_2) ppm. IR (film): ν_{max} 3120, 3065, 3032, 2929, 2852, 1616, 1590, 1558, 1509, 1487, 1470, 1455, 1432, 1360, 1307, 1267, 1252, 1222, 1176, 1142, 1075, 1007, 986, 861 cm^{-1}. MS (EI), m/z (%): 346.15 $[M]^{+\cdot}$. Calc. for $C_{22}H_{16}F_2N_2$, m/z: 346.13.

1,2-Bis(3,5-diphenyl-1H-pyrazol-1-yl)-1,2-diphenylethane (5aa). Following the general procedure, **5aa** was prepared from **1a** (2 mmol, 0.417 g) and **2a** (2 mmol, 0.204 g). Pure **5aa** was isolated as a colorless solid (0.031 g, 5% yield). M. p. = 249-250 °C. Elemental analysis calcd (%) for $C_{44}H_{34}N_4$ (618.78): C, 85.41; H, 5.54; N, 9.05; found: C, 85.65; H, 5.38; N, 8.97. R_f = 0.49 (hexane/diethyl ether = 3:1). ^{1}H NMR: δ 7.78 – 7.62 (m, 4H, H*o1*), 7.45 –

7.20 (m, 20H, *Ph*), 7.13 – 6.99 (m, 6H, H*m3*,*p3*), 6.56 (s, 2H, N-CH), 6.36 (s, 2H, H*4*) ppm. $^{13}C\{^1H\}$ NMR: δ 149.9 (C*3*), 146.2 (C*5*), 137.8 (C*i3*), 133.7 (C*i1*), 130.9 (C*i2*), 129.7, 128.6, 128.5, 128.4 (18C, *Ph*), 128.2 (C*m3*), 127.8 (C*p2*), 127.5 (C*p1*), 125.7 (C*o1*), 103.0 (C*4*), 66.5 (N-CH) ppm. IR (film): ν_{max} 3062, 2923, 2852, 1604, 1550, 1484, 1459, 1437, 1413, 1386, 1346, 1303, 1276, 1211, 1195, 1182, 1156, 1104, 1075, 1029, 1007, 998, 958, 916, 787, 760, 697 cm^{-1}. MS (EI), m/z (%): 617.80 $[M]^{+\cdot}$. Calc. for $C_{44}H_{34}N_4$, m/z: 618.28.

1,2-Bis(3-methoxyphenyl)-1,2-bis(3-(3-methoxyphenyl)-5-phenyl-1H-pyrazol-1-yl)ethane (5da). Following the general procedure, **5da** was prepared from **1d** (2 mmol, 0.537 g) and **2a** (2 mmol, 0.204 g). Pure **5da** was isolated as a light yellow oil (0.096 g, 13% yield). Elemental analysis calcd (%) for $C_{48}H_{42}N_4O_4$ (738.89): C, 78.03; H, 5.73; N, 8.66; found: C, 78.24; H, 5.62; N, 8.54. R_f = 0.62 (hexane/ethyl acetate = 1:1). ^1H NMR: δ 7.45 – 7.38 (m, 2H), 7.38 – 7.24 (m, 14H), 7.06 – 6.96 (m, 2H), 6.91 – 6.81 (m, 6H), 6.68 – 6.63 (m, 2H) [*Ar*], 6.50 (s, 2H, N-C<u>H</u>), 6.36 (s, 2H, H*4*), 3.87 (s, 6H), 3.60 (s, 6H) [*3′*-OMe, *3″*-OMe] ppm. $^{13}C\{^1H\}$ NMR: δ 159.9, 159.3 (C*3′*,*3″*), 149.8 (C*3*), 146.3 (C*5*), 139.3, 135.2 (C*1′*,*1″*), 130.8 (C*i2*), 129.7, 129.4, 129.2, 128.5, 121.1, 118.4, 114.1, 113.5, 113.0, 111.3 (26C, *Ar*), 103.2 (C*4*), 66.4 (N-<u>C</u>H), 55.4, 55.2 (*3′*-OMe, *3″*-OMe) ppm. IR (film): ν_{max} 3058, 3001, 2956, 2937, 2834, 1604, 1586, 1551, 1509, 1476, 1437, 1337, 1316, 1282, 1260, 1216, 1196, 1161, 1152, 1089, 1046, 1008, 995, 976, 910, 855, 822, 782, 765, 733, 700 cm^{-1}. MS (EI), m/z (%): 738.30 $[M]^{+\cdot}$. Calc. for $C_{48}H_{42}N_4O_4$, m/z: 738.32.

1,2-Diphenyl-1,2-bis[3-phenyl-5-(p-tolyl)-1H-pyrazol-1-yl]ethane (5ab). Following the general procedure, **5ab** was prepared from **1a** (2 mmol, 0.417 g) and **2b** (2 mmol, 0.232 g). Pure **5ab** was isolated as a colorless solid (0.136 g, 21% yield). M. p. = 253-256 °C. Elemental analysis calcd (%) for $C_{46}H_{38}N_4$ (646.84): C, 85.42; H, 5.92; N, 8.66; found: C, 85.37; H, 6.12; N, 8.51. R_f = 0.42 (hexane/diethyl ether = 3:1). ^1H NMR: δ 7.72 – 7.66 (m, 4H, H*o1*), 7.38 – 7.33 (m, 4H, H*m1*), 7.30 – 7.25 (m, 2H, H*p1*), 7.25 – 7.22 (m, 4H, H*o3*), 7.16 – 7.12 (m, 4H, H*o2*), 7.13 – 7.09 (m, 4H, H*m2*), 7.08 – 6.99 (m, 6H, H*m3*,*p3*), 6.54 (s, 2H, N-CH), 6.31 (s, 2H, H*4*), 2.41 (s, 6H, *p2*-Me) ppm. $^{13}C\{^1H\}$ NMR: δ 149.9 (C*3*), 146.3 (C*5*), 138.2 (C*p2*), 138.0 (C*i3*), 134.0 (C*i1*), 129.6 (C*o2*), 129.2 (C*m2*), 128.7 (C*o3*), 128.4 (C*m1*), 128.1 (C*m3*), 128.0 (C*i2*), 127.7 (C*p2*), 127.4 (C*p1*), 125.8 (C*o1*), 102.8 (C*4*), 66.5 (N-CH), 21.6 (*p2*-Me) ppm. ^{15}N NMR: δ -86.87 (N*1*), -170.30 (N*2*) ppm. IR (film): ν_{max} 3126, 3061, 3030, 2920, 2861, 1604, 1492, 1458, 1438, 1344, 1304, 1276, 1211, 1194, 1183, 1078, 1028, 1004, 958, 909, 825, 766, 734, 696 cm^{-1}. MS (EI), m/z (%): 646.30 $[M]^{+\cdot}$. Calc. for $C_{46}H_{38}N_4$, m/z: 646.31.

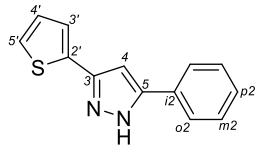
1-[Ethoxy(phenyl)methyl]-3,5-diphenyl-1H-pyrazole (6aa). Following the general procedure, **6aa** was prepared from **1a** (2 mmol, 0.417 g) and **2a** (2 mmol, 0.204 g). Pure **6aa** was isolated as a light yellow oil (0.043 g, 6% yield). R_f = 0.51 (hexane/diethyl ether = 3:1). ^{1}H NMR: δ 7.92 – 7.84 (m, 2H), 7.48 – 7.09 (m, 13H) [*Ph*], 6.63 (s, 1H), 6.51 (s, 1H) [C*4*,N-CH], 3.62 – 3.43 (m, 2H, CH_2-Me), 1.18 (t, ^3J = 6.9 Hz, 3H, CH_2-Me) ppm. ^{13}C{^{1}H} NMR: δ 151.4 (C*3*), 146.4 (C*5*), 138.4 (C*i3*), 133.5 (C*i1*), 130.8 (C*i2*), 129.6, 128.7, 128.4, 128.3, 128.1, 127.9, 126.7, 126.0 (15C, *Ph*), 104.8 (C*4*), 89.0 (N-CH), 64.2 (CH_2-Me), 14.9 (CH_2-Me) ppm.

3,5-Diphenyl-1H-pyrazole (7aa).[S15] Following the general procedure, **7aa** was prepared from **1a** (2 mmol, 0.417 g) and **2a** (2 mmol, 0.204 g). Pure **7aa** was isolated as a colorless solid (0.013 g, 3% yield). M. p. = 196-199 °C (lit.[S15] 168-174 °C). Elemental analysis calcd (%) for $C_{15}H_{12}N_2$ (220.28): C, 81.79; H, 5.49; N, 12.72; found: C, 81.91; H, 5.38; N, 12.71. R_f = 0.36 (hexane/ethyl acetate = 1:1). ^{1}H NMR: δ 12.06 (br. s, 1H, NH), 7.81 – 7.62 (m, 4H, H*o1*,*o2*), 7.46 – 7.21 (m, 6H, H*m1*,*p1*,*m2*,*p2*), 6.79 (s, 1H, H*4*) ppm. ^{13}C{^{1}H} NMR: δ 148.7 (br. s, C*3*,*5*), 131.5 (br. s, C*i1*,*i2*), 129.0, 128.4, 125.8 (10C, *Ph*), 100.2 (C*4*) ppm. IR (film): ν_{max} 3406, 3182, 3133, 3098, 3064, 3005, 2925, 2872, 2856, 1682, 1604, 1573, 1494, 1461, 1407, 1316, 1272, 1219, 1181, 1102, 1075, 1057, 1028, 973 cm^{-1}. MS (EI), m/z (%): 220.10 $[M]^{+\cdot}$. Calc. for $C_{15}H_{12}N_2$, m/z: 220.10.

3-(3-Methoxyphenyl)-5-phenyl-1H-pyrazole (7da).[S15] Following the general procedure, **7da** was prepared from **1d** (2 mmol, 0.537 g) and **2a** (2 mmol, 0.204 g). Pure **7da** was isolated as a light yellow solid (0.035 g, 7% yield). M. p. = 137-139 °C (lit.[S15] 134-138 °C). Elemental analysis calcd (%) for $C_{16}H_{14}N_2O$ (250.30): C, 76.78; H, 5.64; N, 11.19; found: C, 76.86; H, 5.54; N, 11.03. R_f = 0.35 (hexane/ethyl acetate = 1:1). ^{1}H NMR: δ 11.58 (br. s, 1H, NH), 7.62 (d, ^3J = 7.1 Hz, 2H, H*o2*), 7.29 – 7.19 (m, 7H, *Ar*), 6.79 (s, 1H, H*2'*), 6.71 (s, 1H, H*4*), 3.62 (s, 3H, OMe) ppm. ^{13}C{^{1}H} NMR: δ 160.1 (C*3'*), 149.0, 148.6 (C*3*,*5*), 132.7, 131.2 (C*1'*,*i2*), 129.9, 128.9, 128.3, 125.7, 118.2, 114.4, 110.7 (9C, Ar), 100.2 (C*4*), 55.2 (OMe) ppm. IR (film): ν_{max} 3397, 3183, 3135, 3103, 3066, 3021, 3002, 2955, 2932, 2854, 2833, 1604, 1594, 1481, 1479, 1464, 1437, 1318, 1286, 1253, 1209, 1177, 1075, 1043, 985, 909, 844, 784, 763, 732, 692 cm^{-1}. MS (EI), m/z (%): 250.10 $[M]^{+\cdot}$. Calc. for $C_{16}H_{14}N_2O$, m/z: 250.11.

3-(3-Fluorophenyl)-5-phenyl-1H-pyrazole (7ea).[S15] Following the general procedure, **7ea** was prepared from **1e** (2 mmol, 0.488 g) and **2a** (2 mmol, 0.204 g). Pure **7ea** was isolated as a colorless solid (0.091 g, 19% yield). M. p. = 177-181

°C (lit.[S15] 171-173 °C). Elemental analysis calcd (%) for $C_{15}H_{11}FN_2$ (238.27): C, 75.62; H, 4.65; F, 7.97; N, 11.76; found: C, 75.78; H, 4.61; F, 7.92; N, 11.69. R_f = 0.35 (hexane/ethyl acetate = 1:1). ^{1}H NMR (400.1 MHz, DMSO-d6): δ 13.48 (br. s, 1H, NH), 7.87 – 7.80 (m, 2H, H*o2*), 7.74 – 7.63 (m, 2H, H*2′*,*6′*), 7.54 – 7.42 (m, 3H, H*m2*,*5′*), 7.40 – 7.31 (m, 1H H*p2*), 7.27 (s, 1H, H*4*), 7.22 – 7.10 (m, 1H, H*4′*) ppm. ^{13}C{^{1}H} NMR (100.6 MHz, DMSO-d6): δ 162.6 (d, ^1J = 242.7 Hz, C*3′*), 152.7 – 133.3 (C3,5,*1′*,*i2*) 130.8 (d, ^3J = 7.9 Hz, C*5′*), 128.8, 127.9, 125.1 (5C, *Ph*), 121.1 (d, ^4J = 2.0 Hz, C*6′*), 114.3 (d, ^2J = 19.9 Hz), 111.6 (d, ^2J = 22.6 Hz) [C*2′*,*4′*], 100.2 (C*4*) ppm. IR (film): ν_{max} 3151, 3104, 3087, 3028, 2918, 2859, 2791, 2736, 1616, 1589, 1492, 1456, 1268, 1236, 1194, 1160, 1119, 1076, 1002, 909, 873, 787, 733 cm^{-1}. MS (EI), m/z (%): 238.05 $[M]^{+\cdot}$. Calc. for $C_{15}H_{11}FN_2$, m/z: 238.09.



5-Phenyl-3-(thiophen-2-yl)-1H-pyrazole (7ga).[S16] Following the general procedure, **7ga** was prepared from **1g** (2 mmol, 0.441 g) and **2a** (2 mmol, 0.204 g). Pure **7ga** was isolated as a light yellow solid (0.009 g, 2% yield). M. p. = 184-185 °C (lit.[S16] 184-185 °C). R_f = 0.33 (hexane/ethyl acetate = 1:1). ^{1}H NMR: δ 10.40 (br. s, 1H, NH), 7.66 – 7.45 (m, 2H, H*o2*), 7.29 – 7.19 (m, 4H), 7.19 – 7.12 (m, 1H) [*Ph*, H*4*,*5′*], 6.93 (dd, ^3J = 5.1 Hz, ^3J = 3.8 Hz, 1H, H*4′*), 6.62 (d, ^3J = 5.1 Hz, 1H, H*3′*) ppm. ^{13}C{^{1}H} NMR: δ 147.1, 145.3 (C*3*,*5*), 135.0, 130.2 (C*2′*,*i2*), 129.0, 128.5, 127.7, 125.7, 124.9, 124.3 (8C, *Ph*, *Thioph*), 100.2 (C*4*) ppm.

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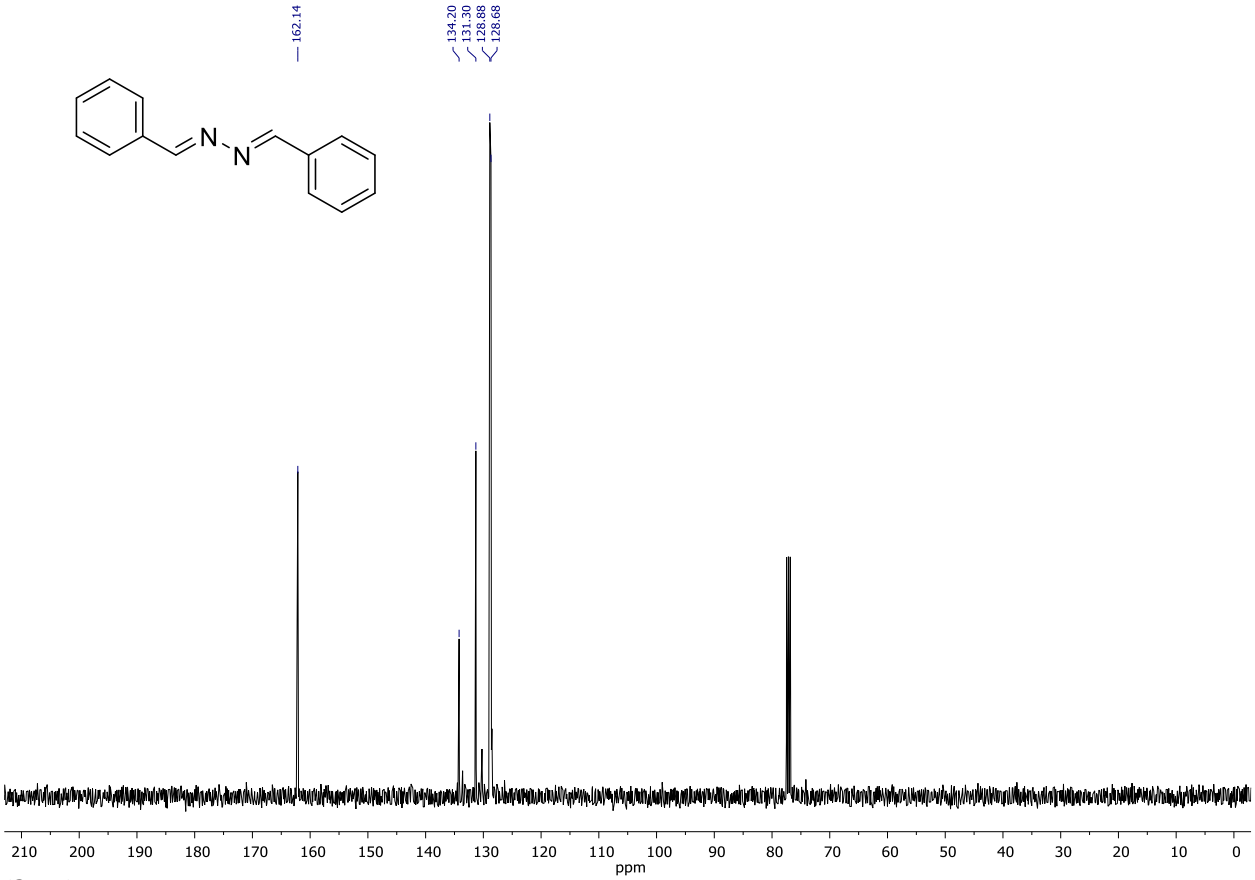
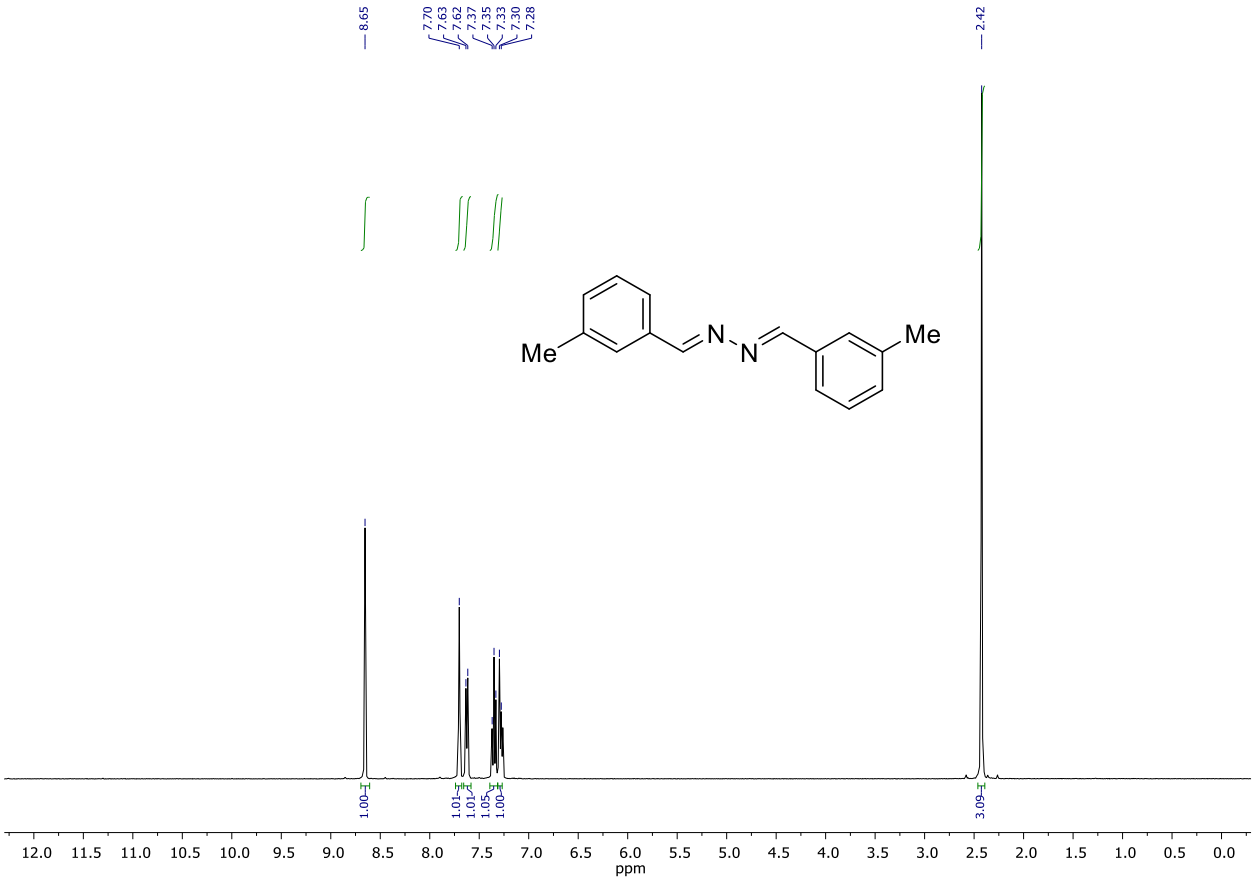
5. NMR Spectra

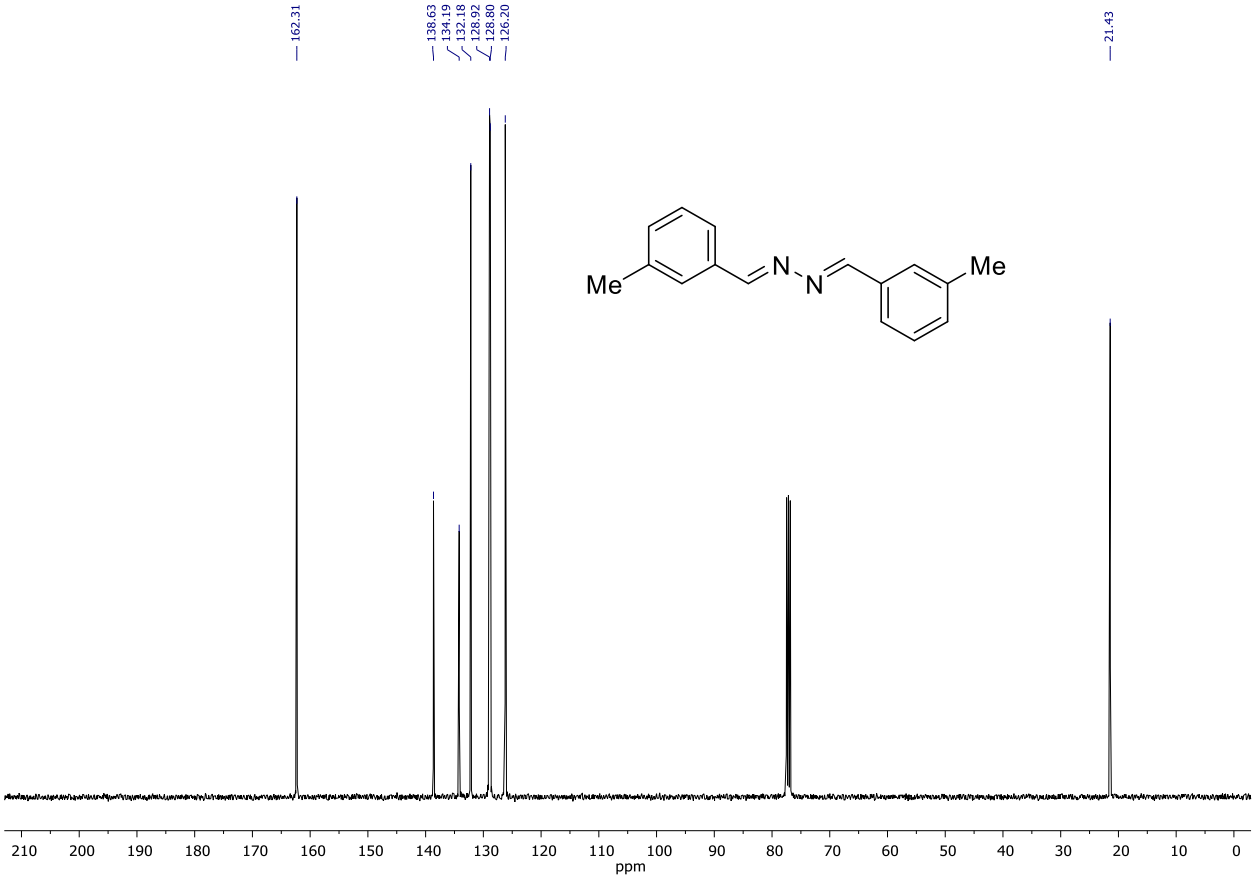
^{1}H NMR Spectrum of **1a** (400.1 MHz, $CDCl_3$)



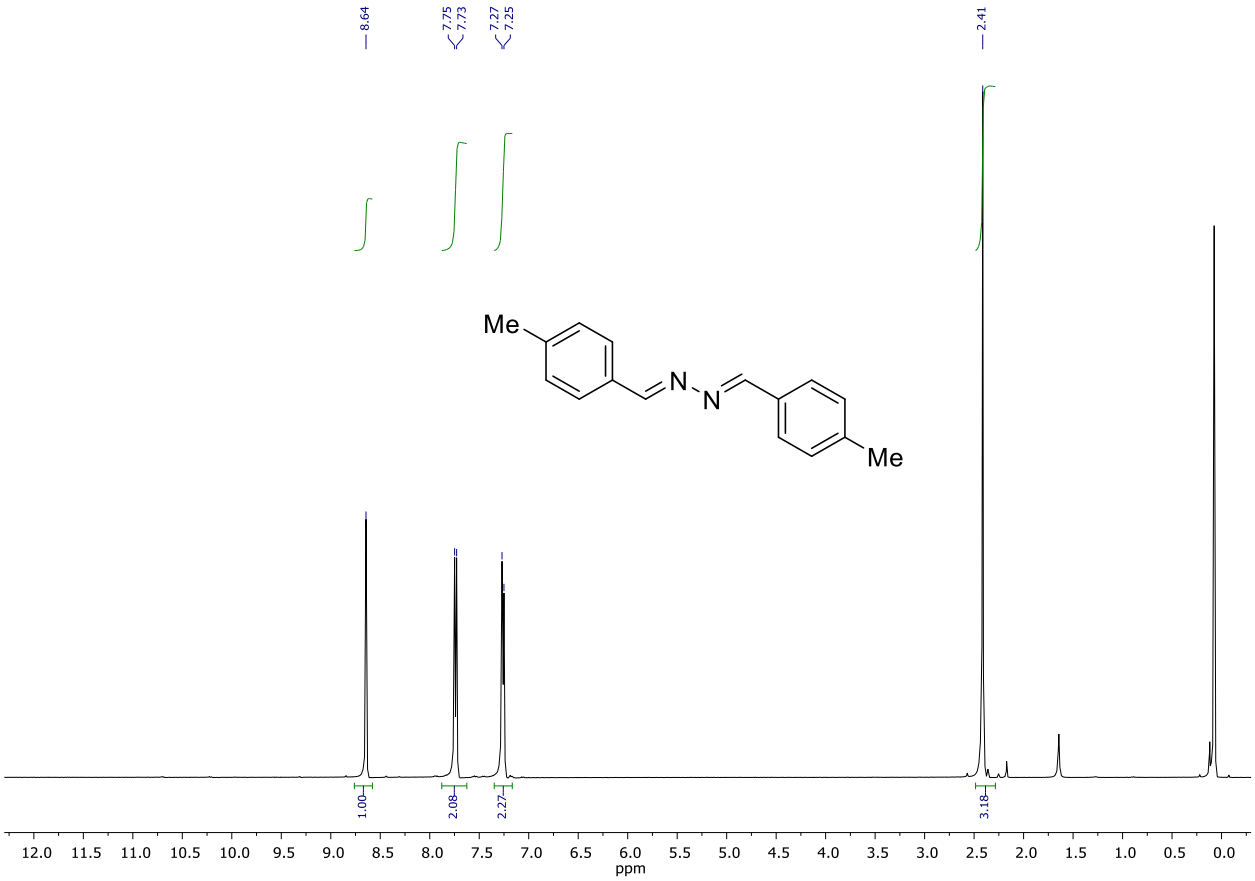
^{13}C{^{1}H} NMR Spectrum of **1a** (100.6 MHz, $CDCl_3$)



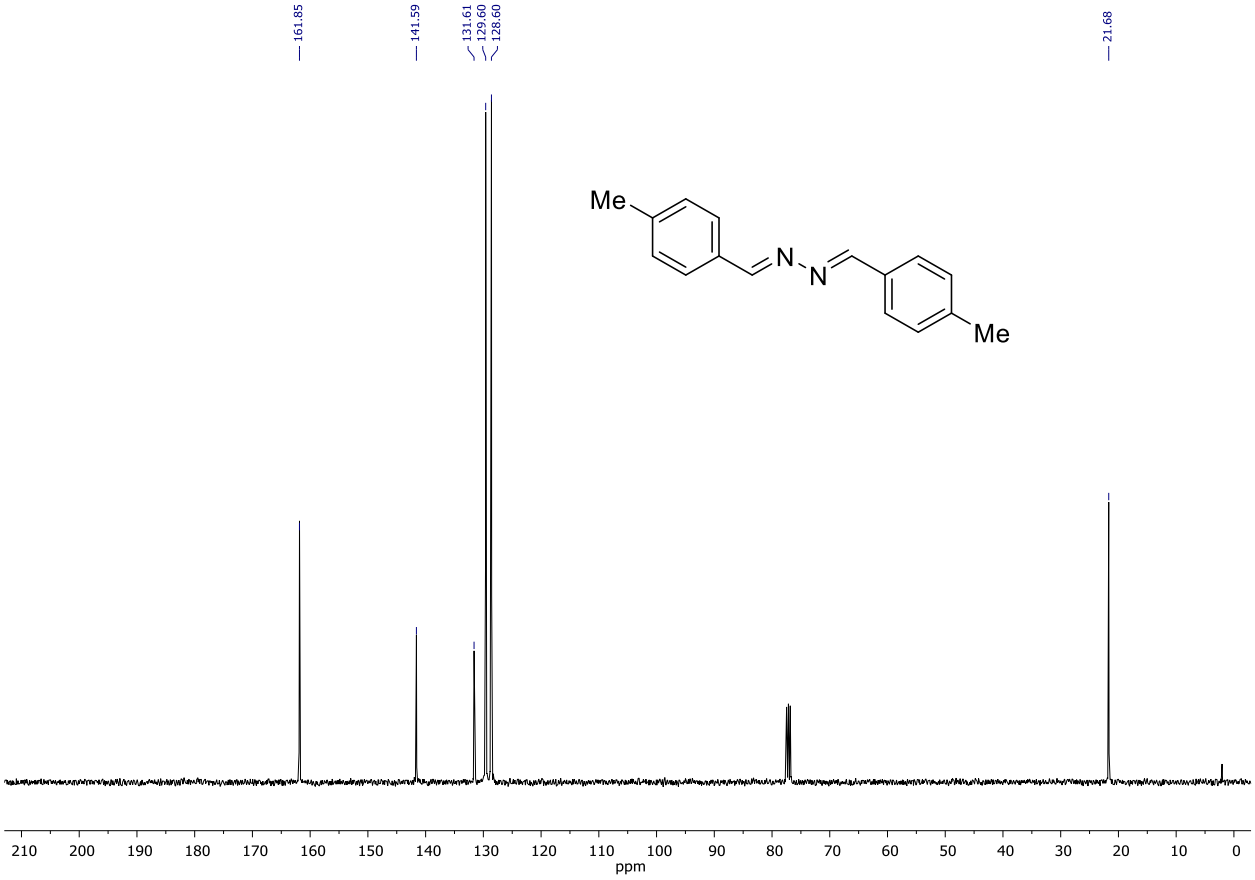
^{1}H NMR Spectrum of **1b** (400.1 MHz, $CDCl_3$)



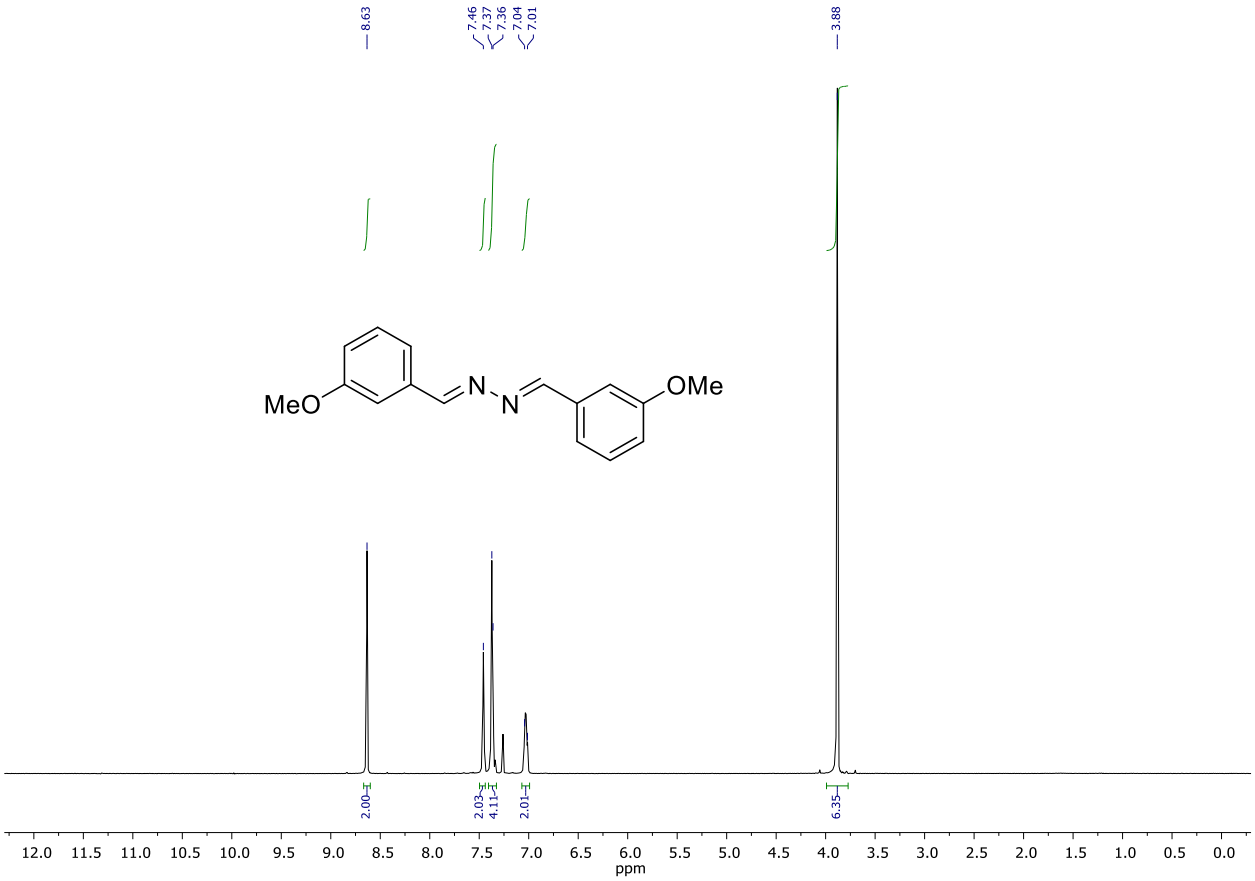
^{13}C{^{1}H} NMR Spectrum of **1b** (100.6 MHz, $CDCl_3$)



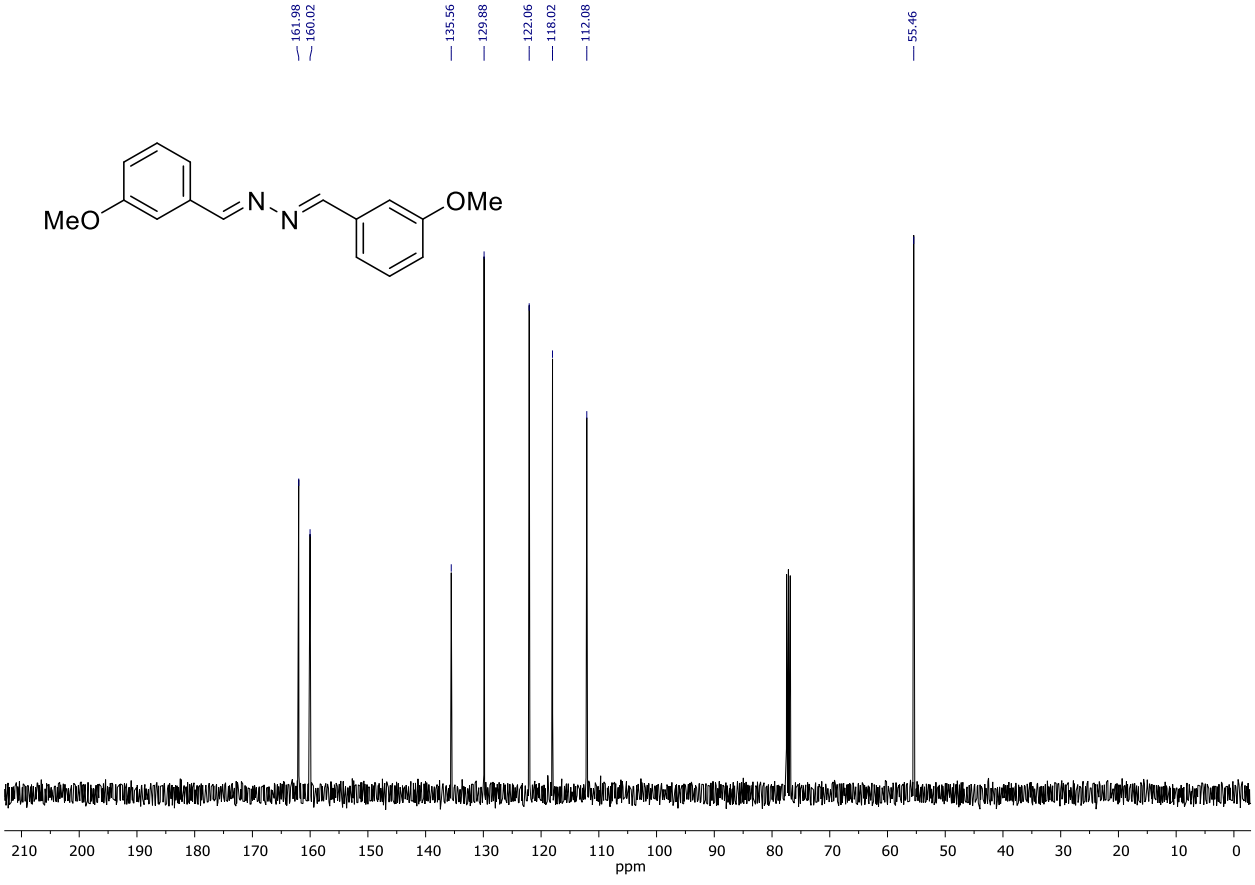
^{1}H NMR Spectrum of **1c** (400.1 MHz, $CDCl_3$)



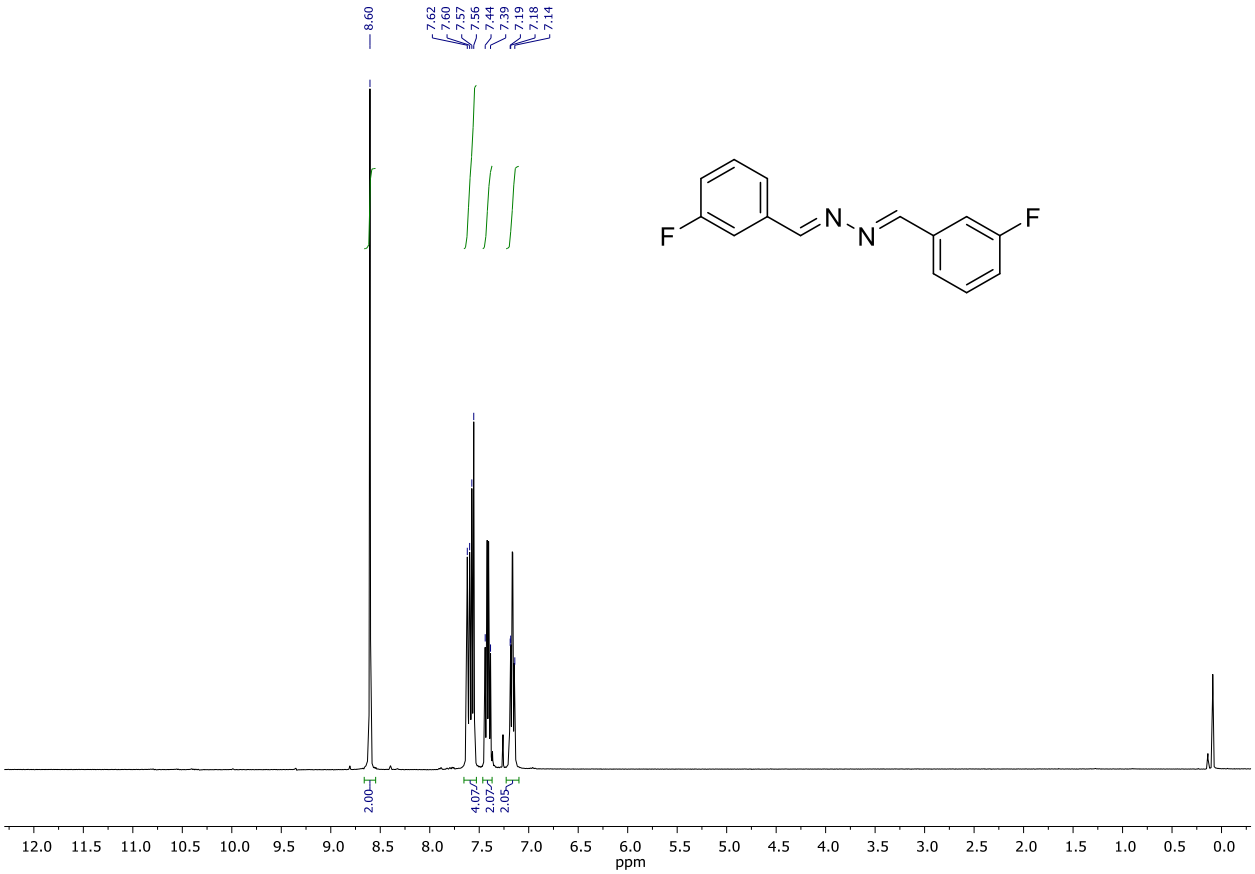
^{13}C{^{1}H} NMR Spectrum of **1c** (100.6 MHz, $CDCl_3$)



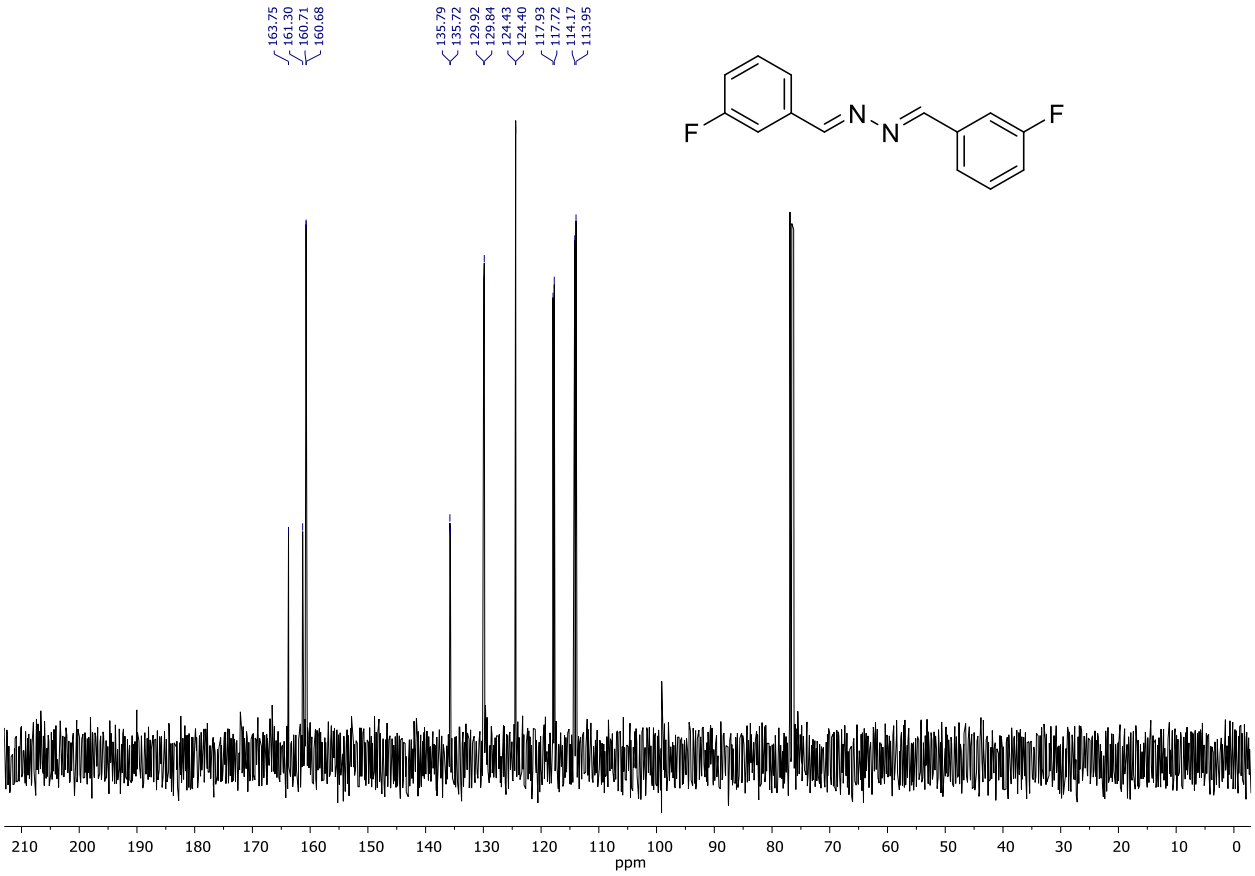
^{1}H NMR Spectrum of **1d** (400.1 MHz, $CDCl_3$)



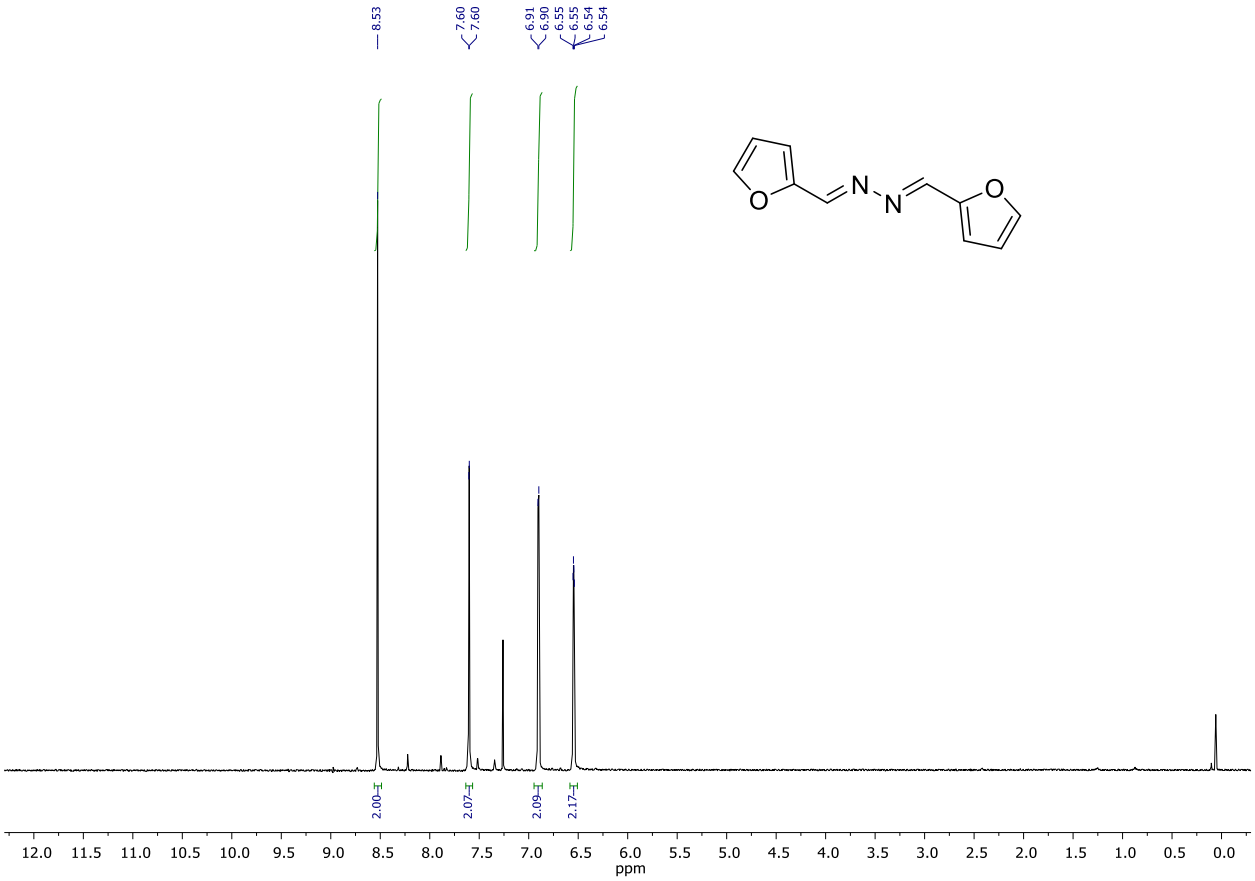
^{13}C{^{1}H} NMR Spectrum of **1d** (100.6 MHz, $CDCl_3$)



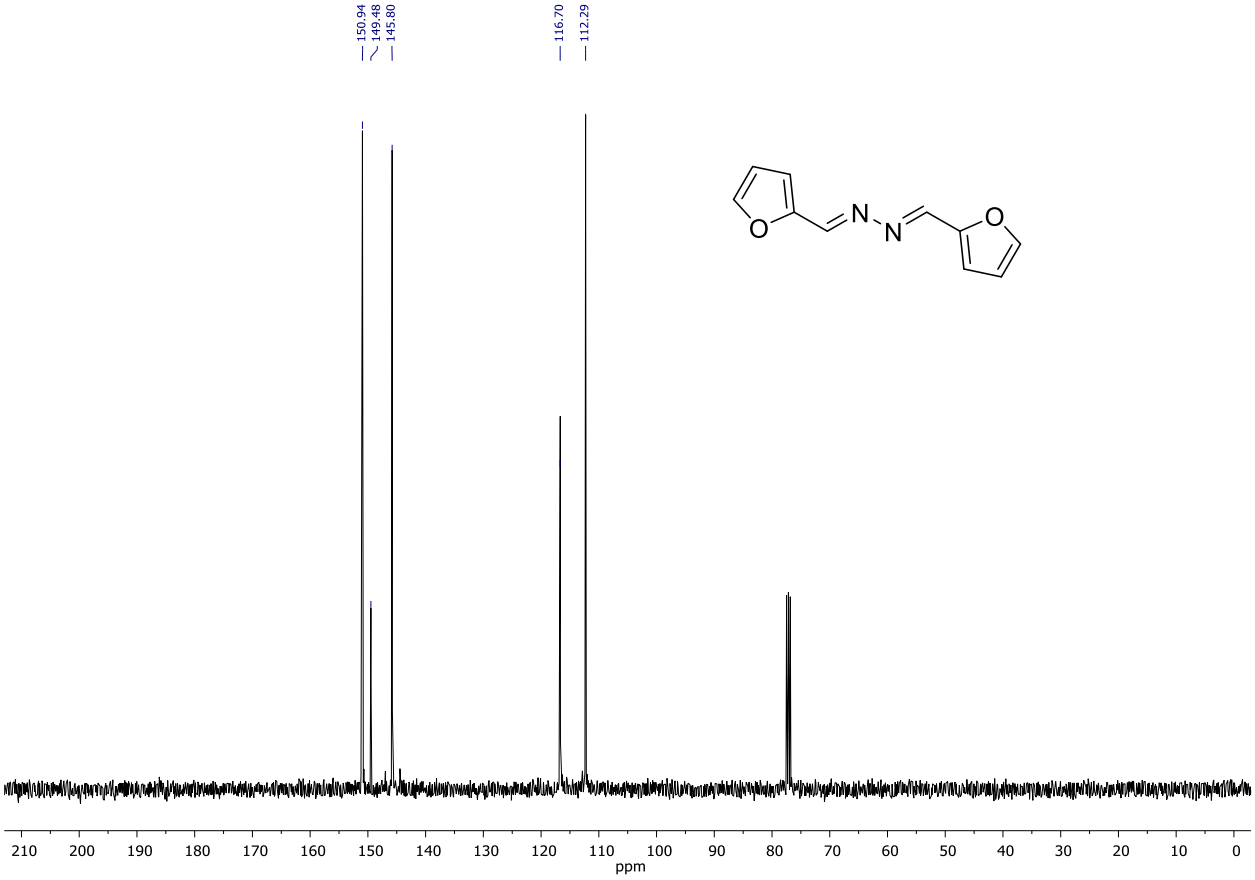
^{1}H NMR Spectrum of **1e** (400.1 MHz, $CDCl_3$)



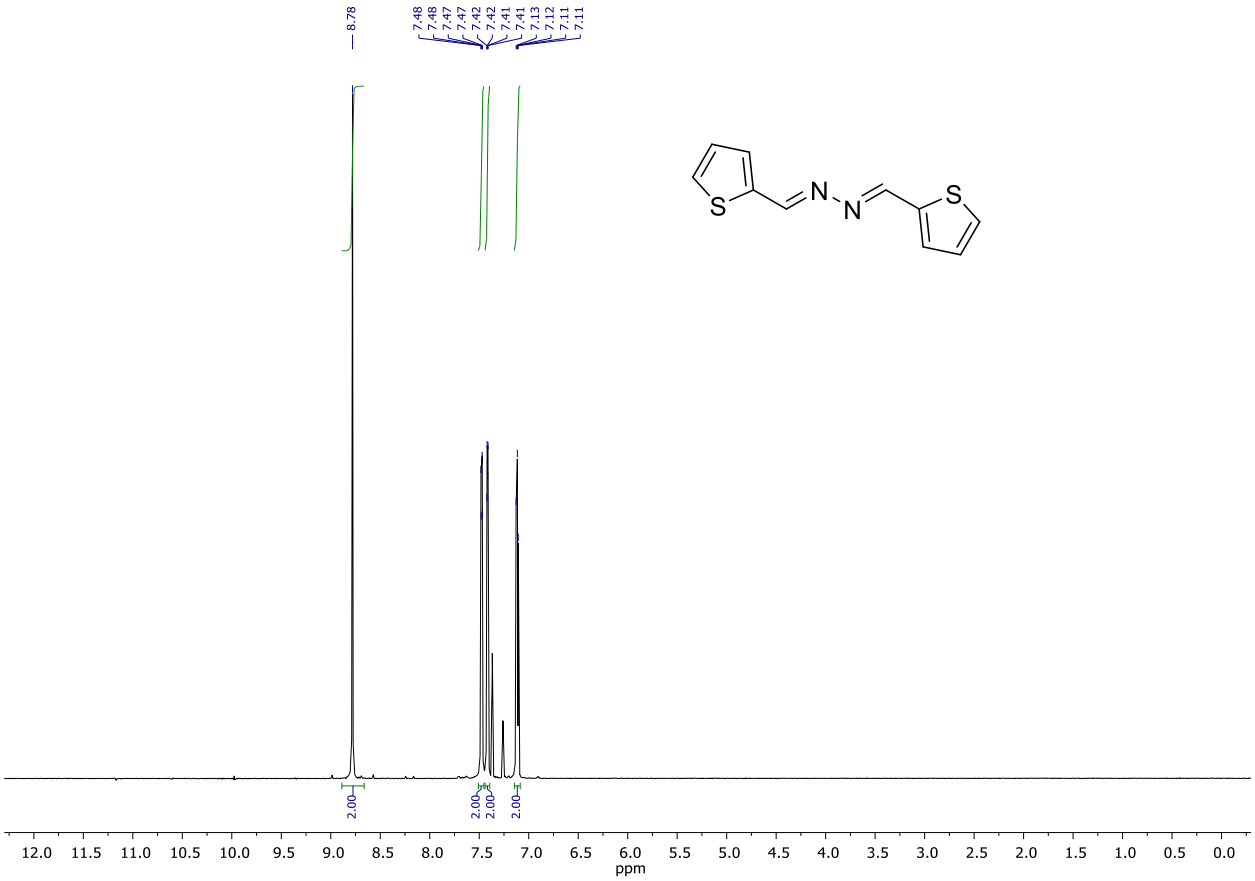
^{13}C{^{1}H} NMR Spectrum of **1e** (100.6 MHz, $CDCl_3$)



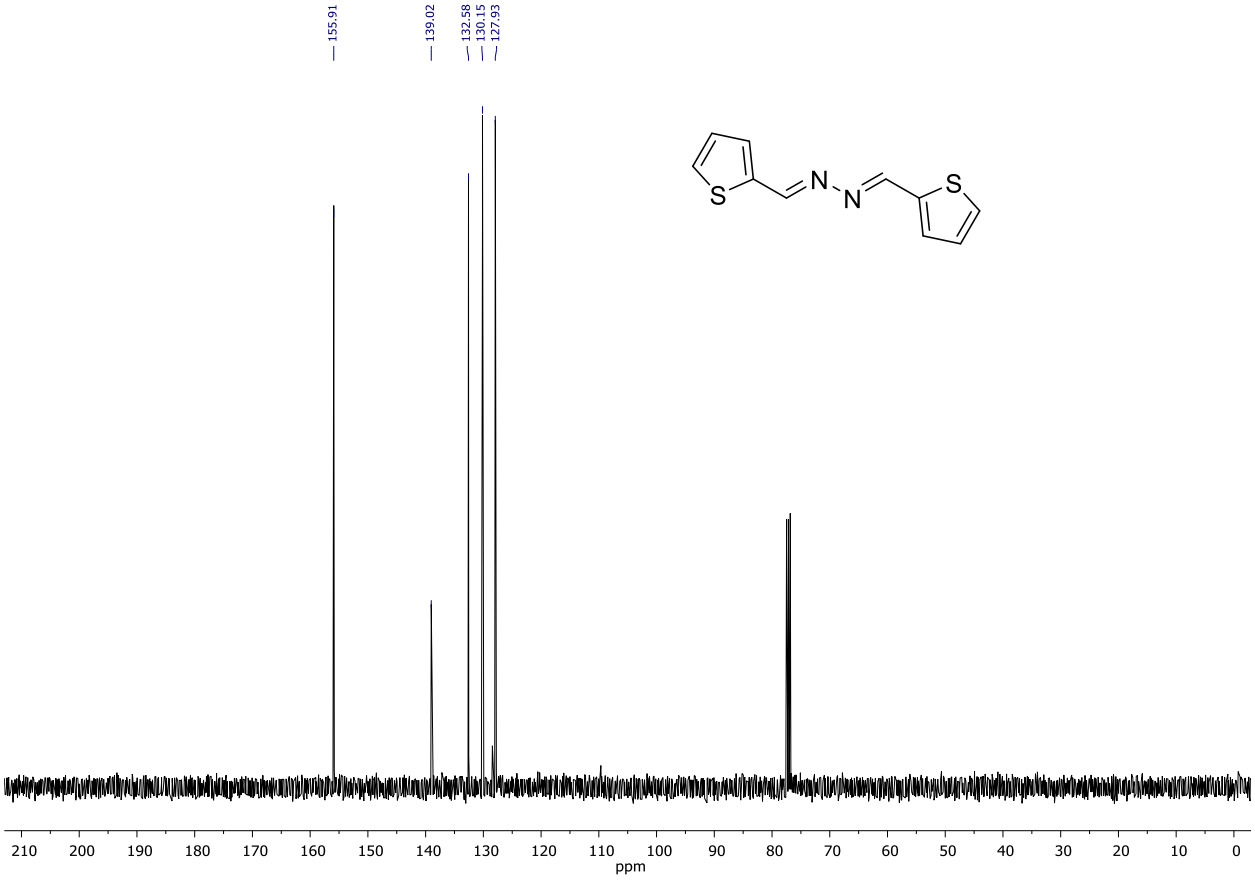
^{1}H NMR Spectrum of **1f** (400.1 MHz, $CDCl_3$)



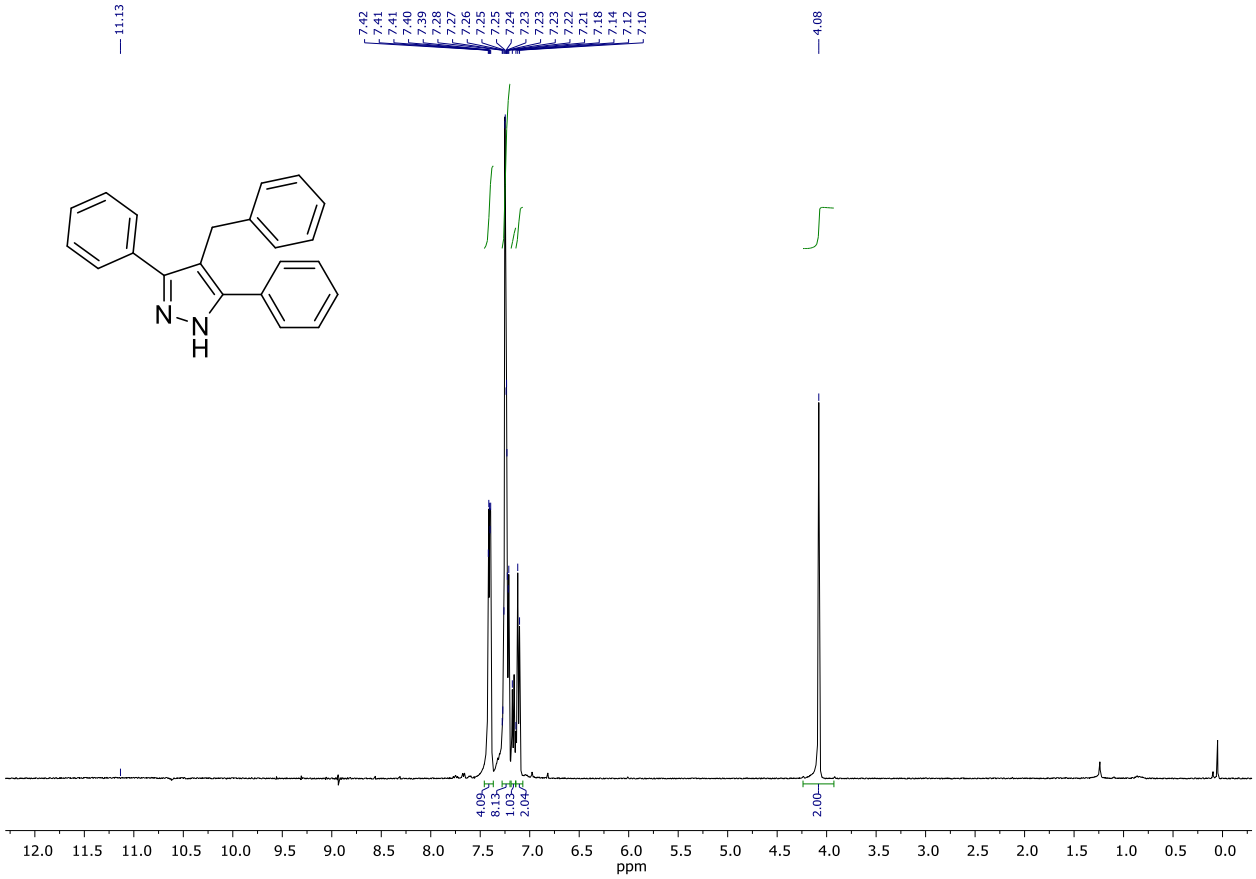
^{13}C{^{1}H} NMR Spectrum of **1f** (100.6 MHz, $CDCl_3$)



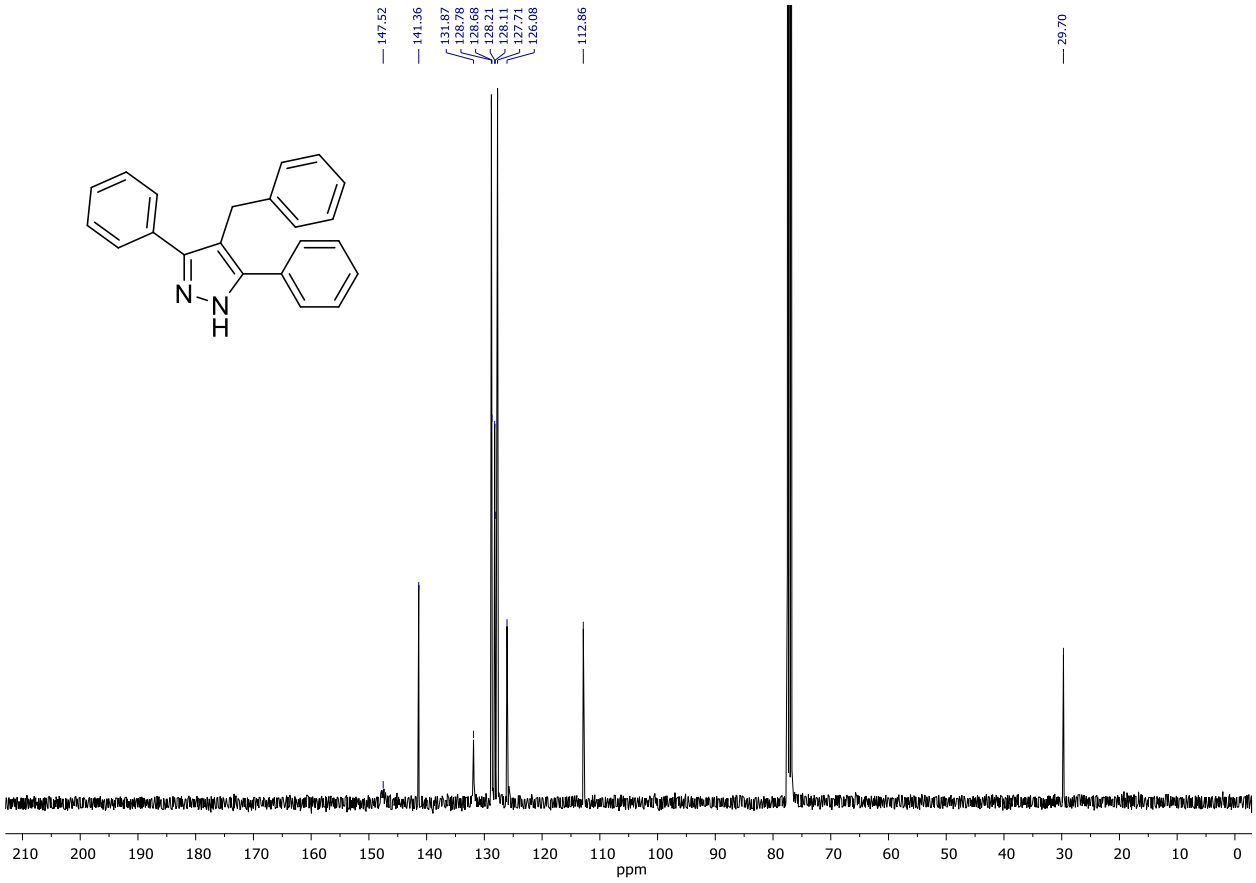
^{1}H NMR Spectrum of **1g** (400.1 MHz, $CDCl_3$)



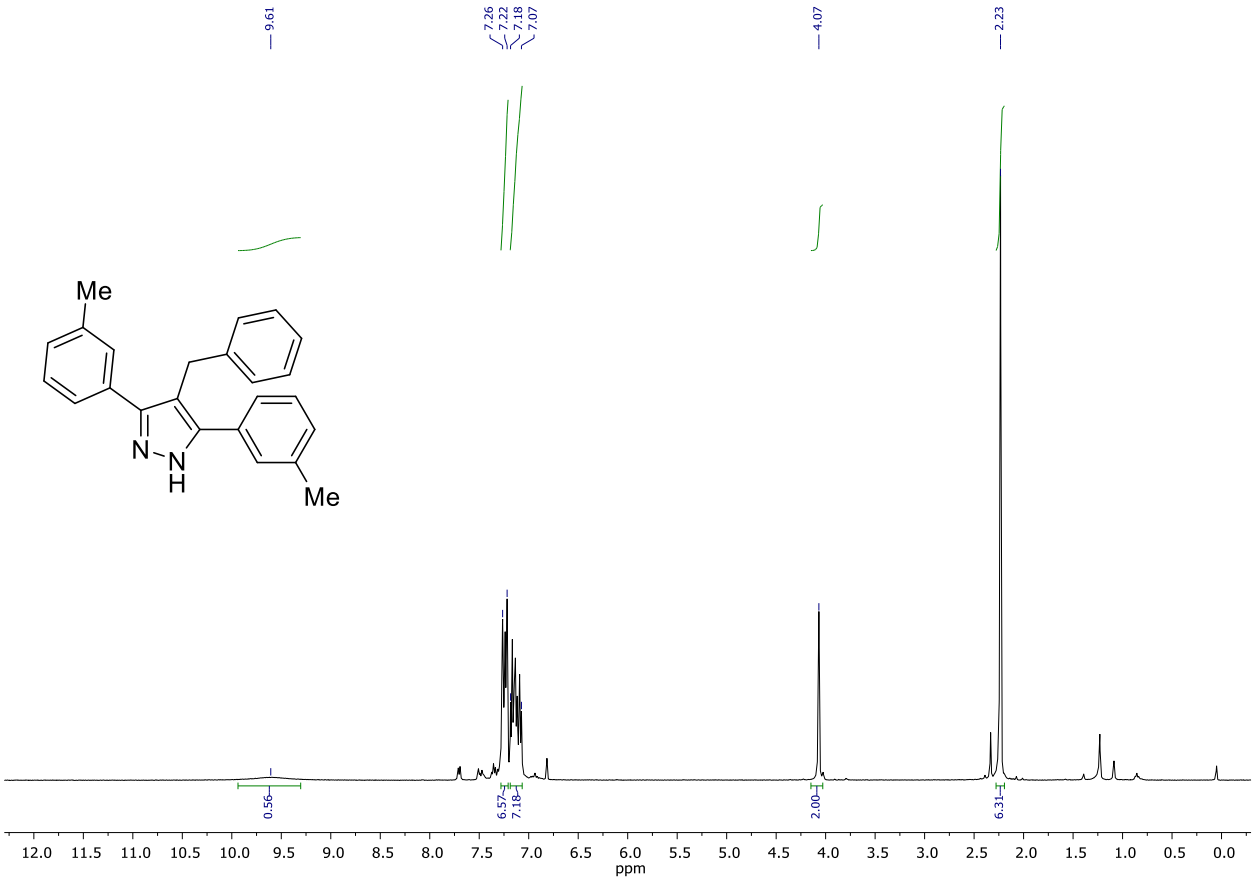
^{13}C{^{1}H} NMR Spectrum of **1g** (100.6 MHz, $CDCl_3$)



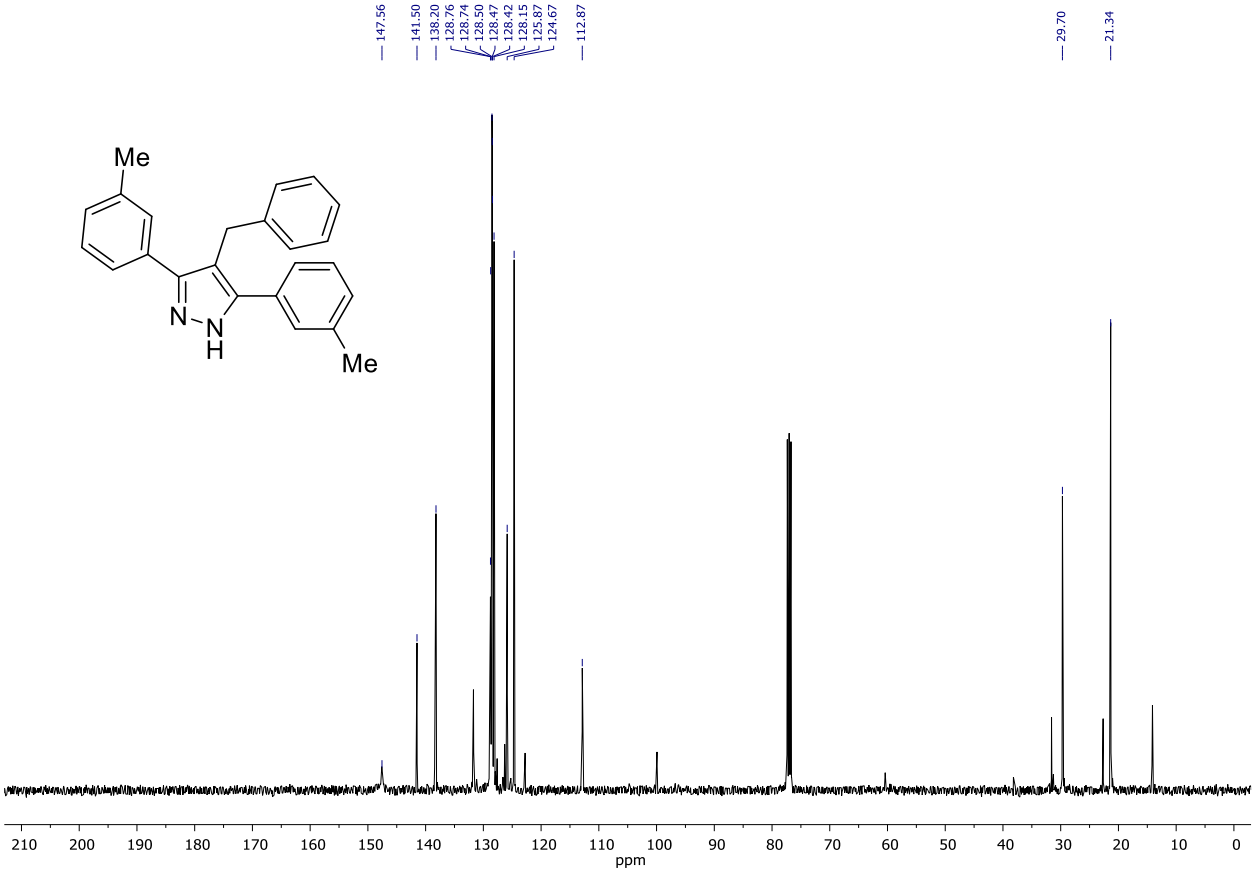
^{1}H NMR Spectrum of **3aa** (400.1 MHz, $CDCl_3$)



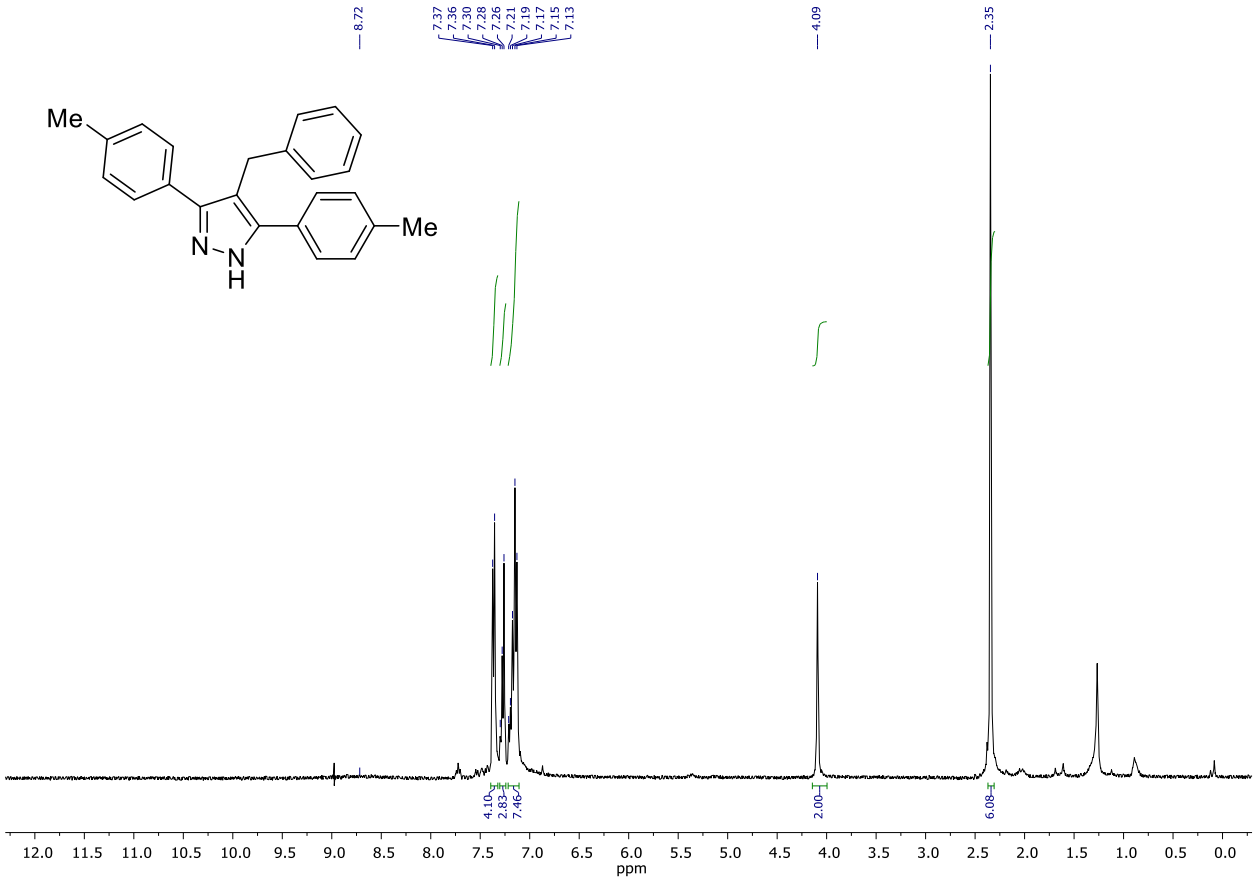
^{13}C{^{1}H} NMR Spectrum of **3aa** (100.6 MHz, $CDCl_3$)



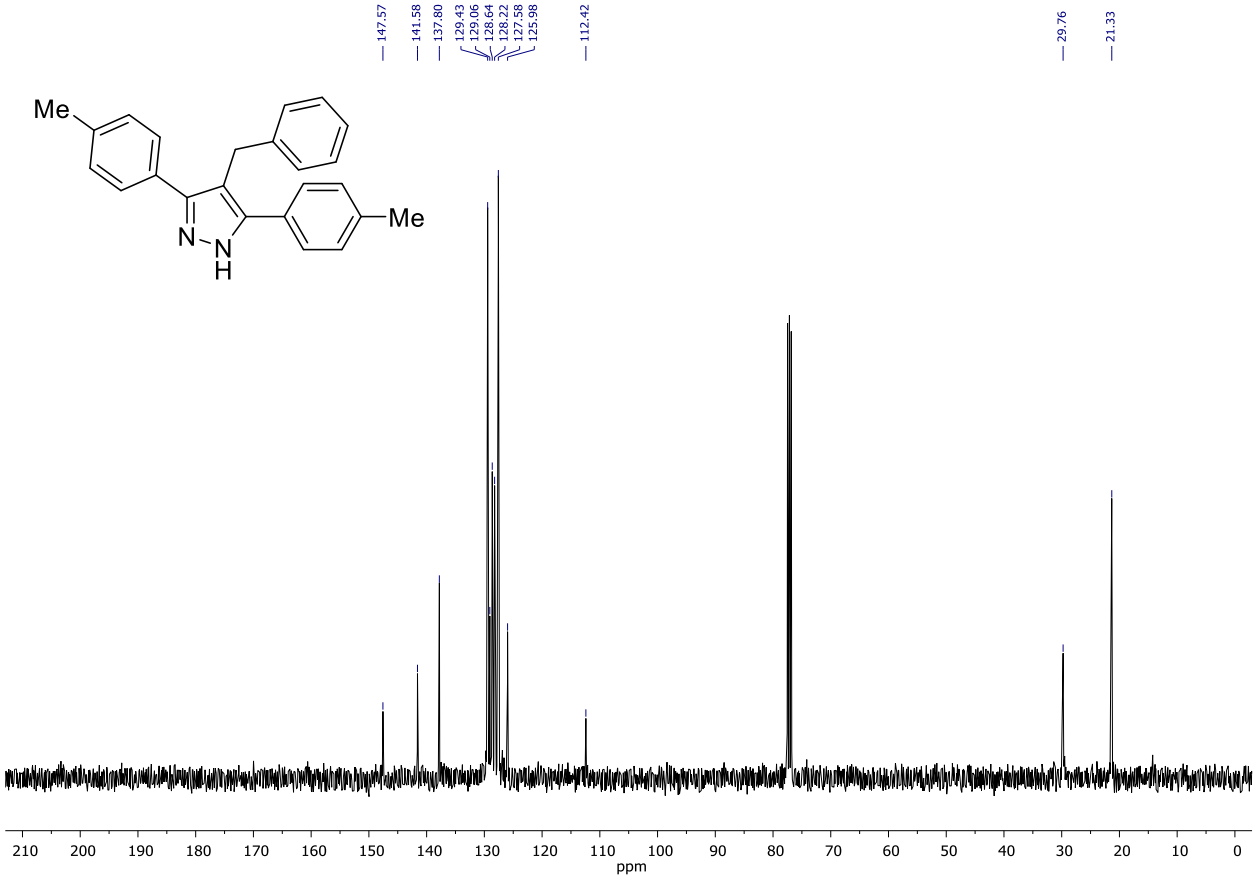
^{1}H NMR Spectrum of **3ba** (400.1 MHz, $CDCl_3$)



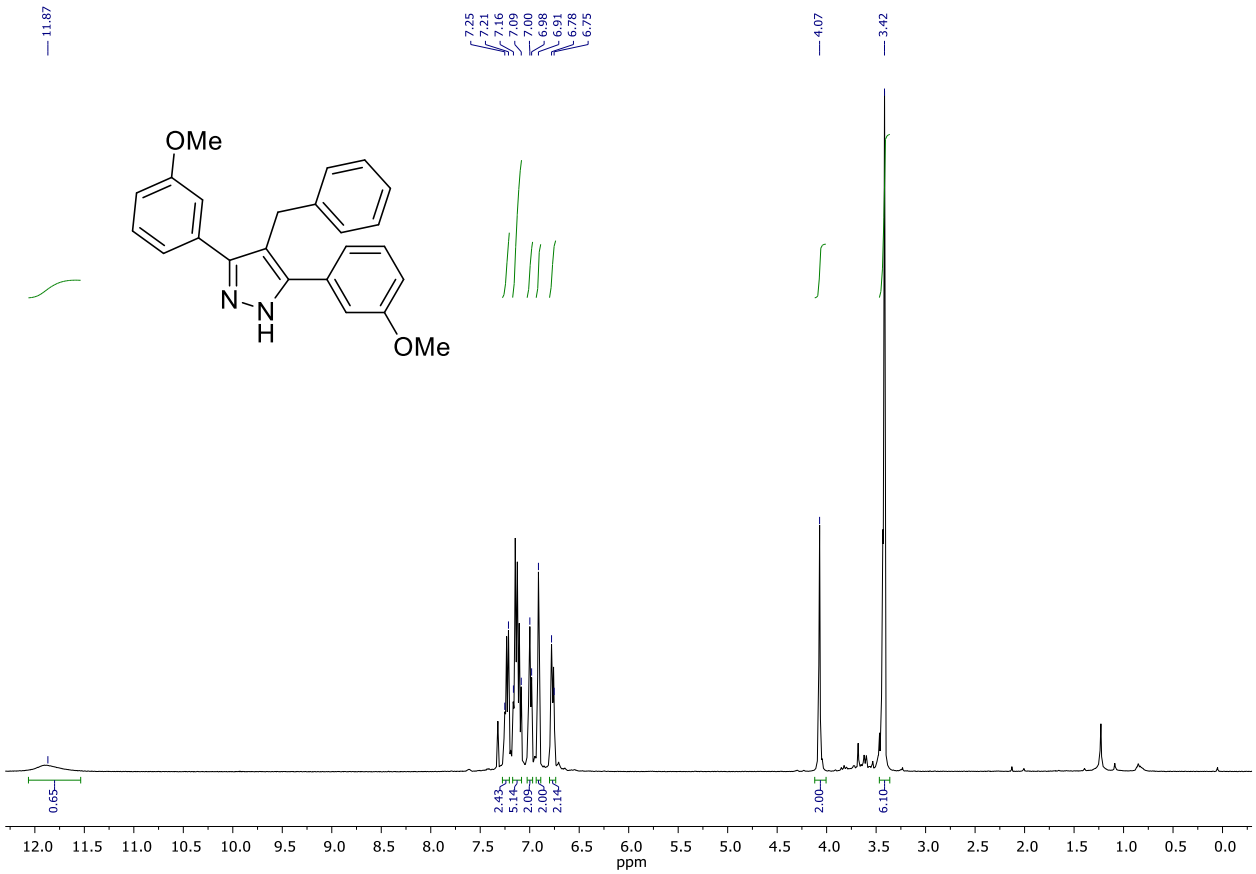
^{13}C{^{1}H} NMR Spectrum of **3ba** (100.6 MHz, $CDCl_3$)



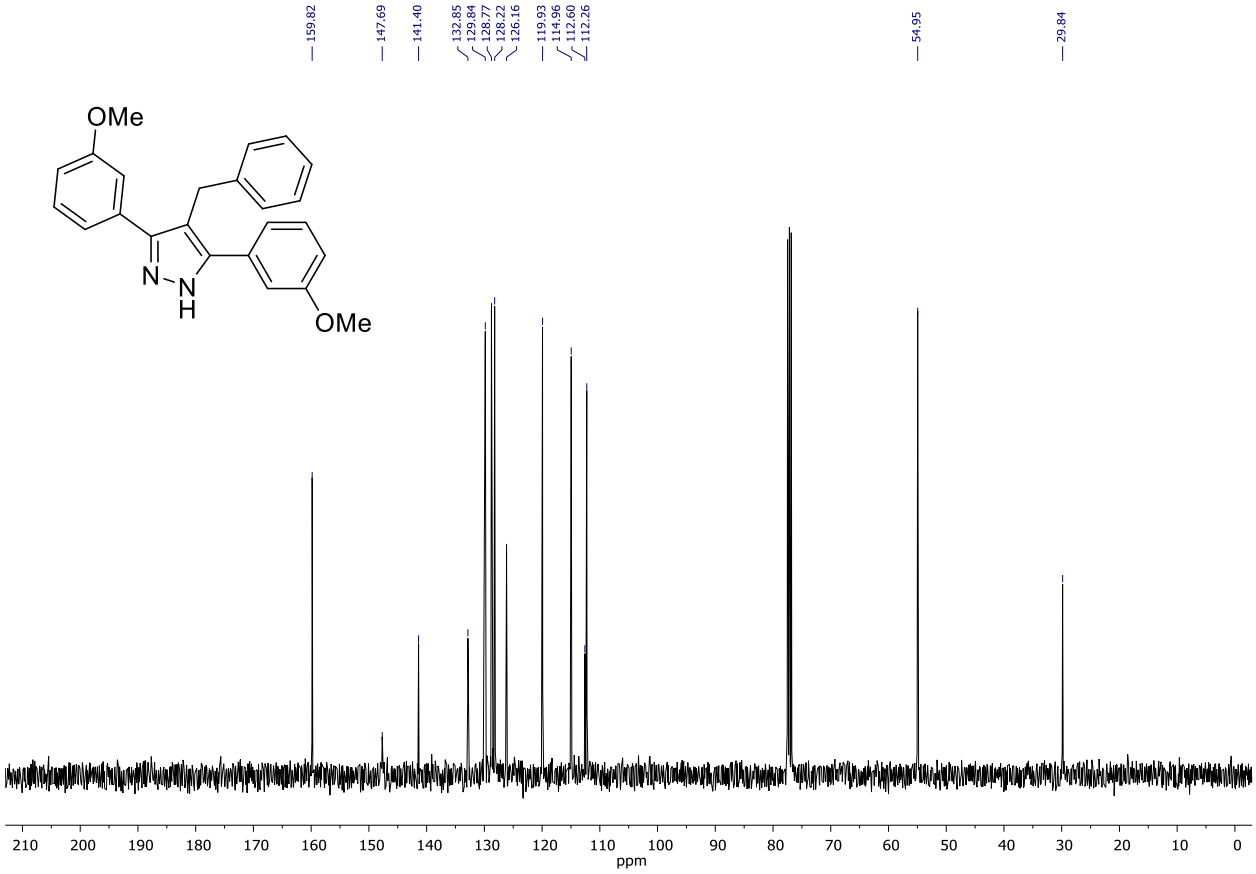
^{1}H NMR Spectrum of **3ca** (400.1 MHz, $CDCl_3$)



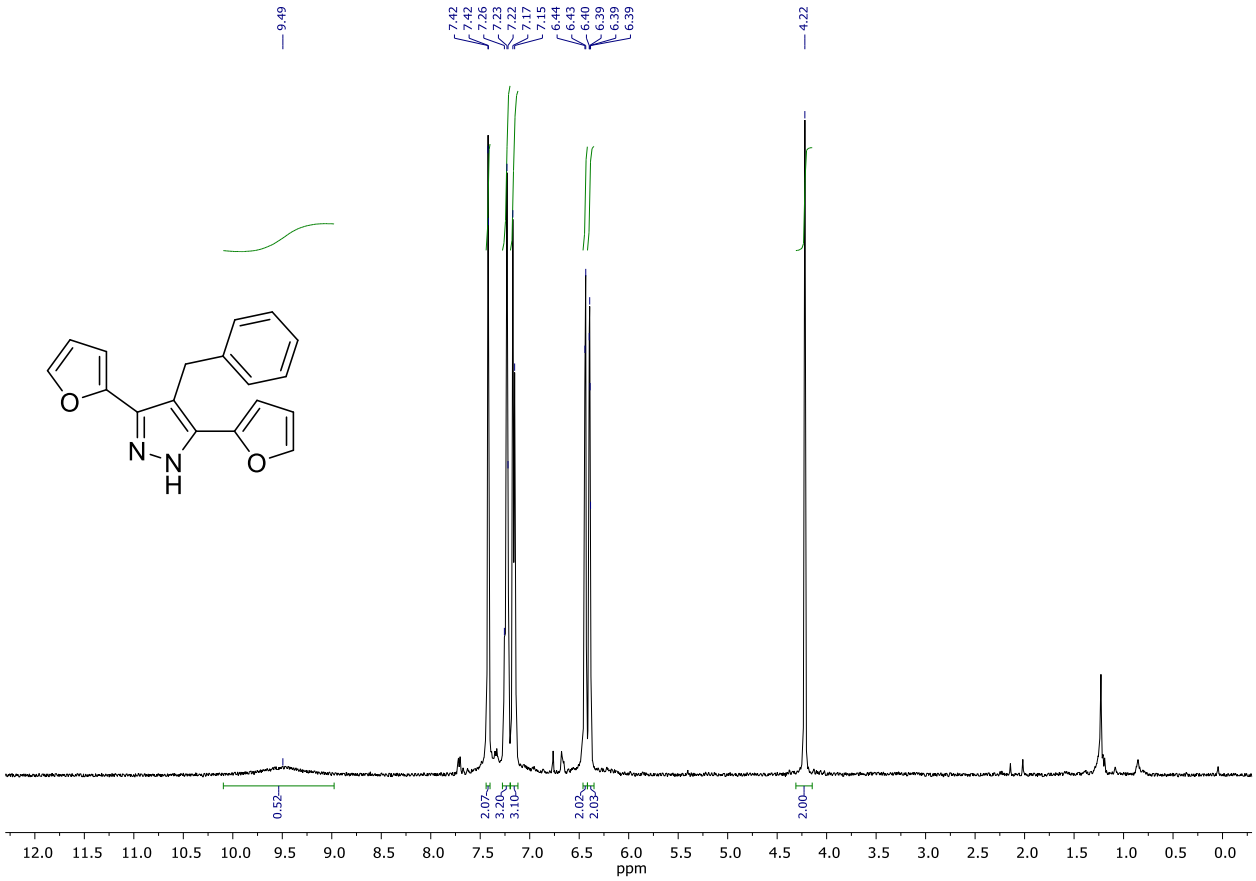
^{13}C{^{1}H} NMR Spectrum of **3ca** (100.6 MHz, $CDCl_3$)



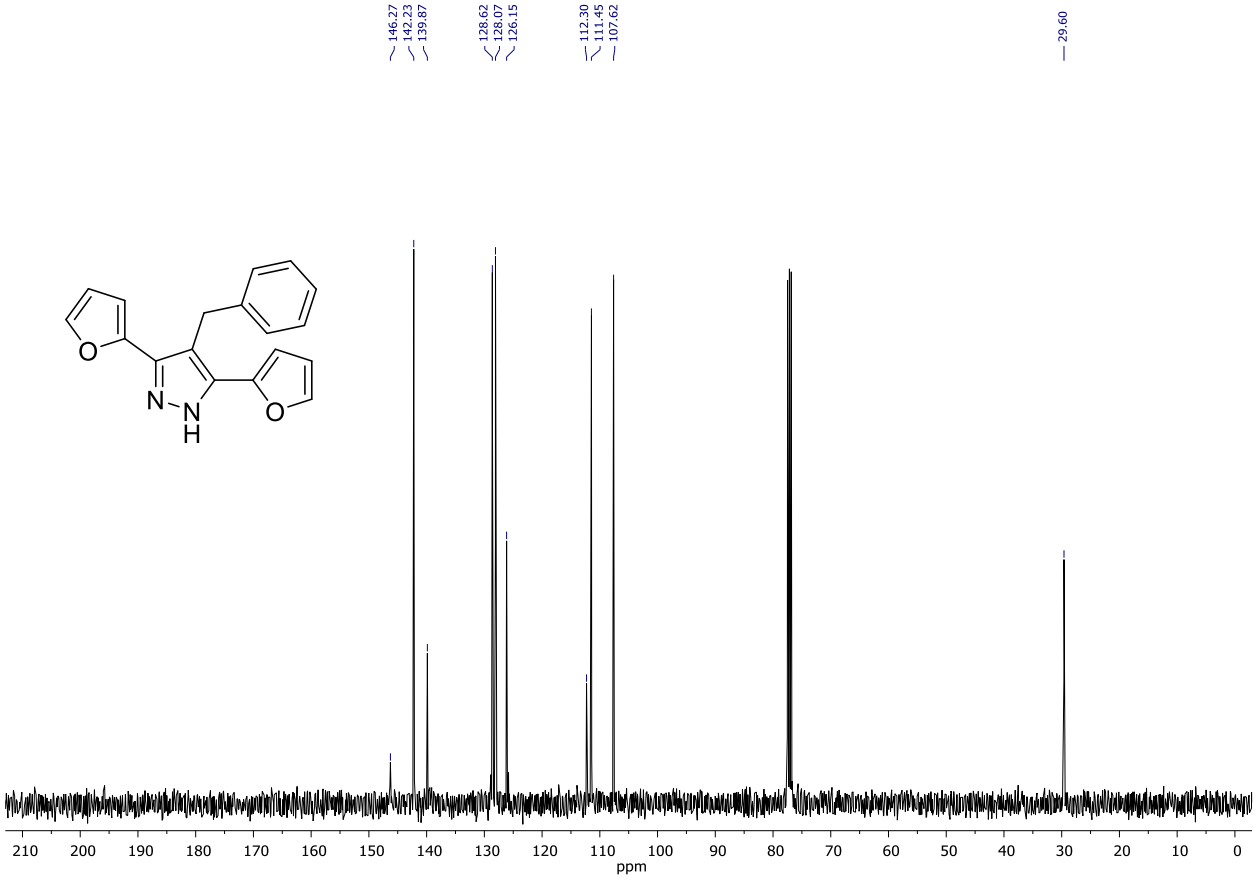
^{1}H NMR Spectrum of **3da** (400.1 MHz, $CDCl_3$)



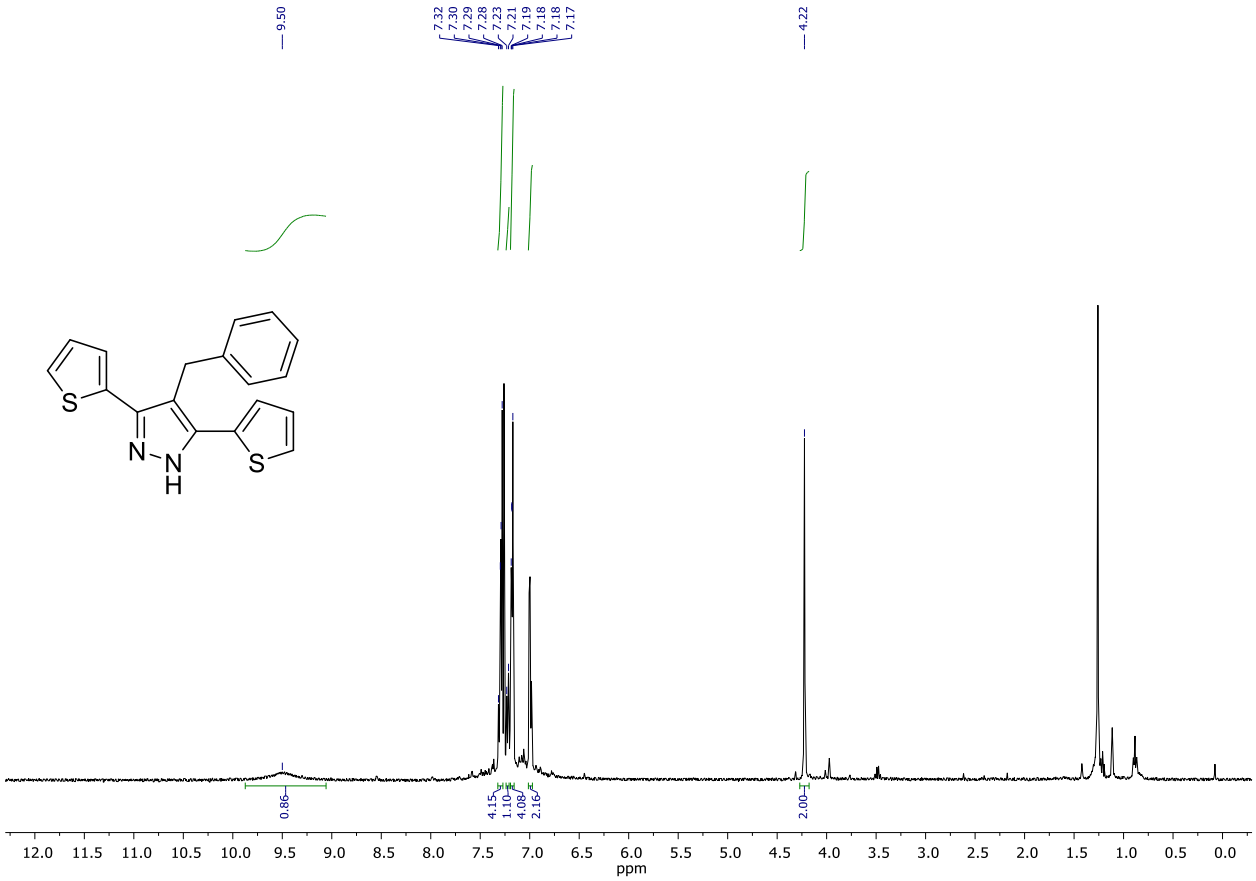
^{13}C{^{1}H} NMR Spectrum of **3da** (100.6 MHz, $CDCl_3$)



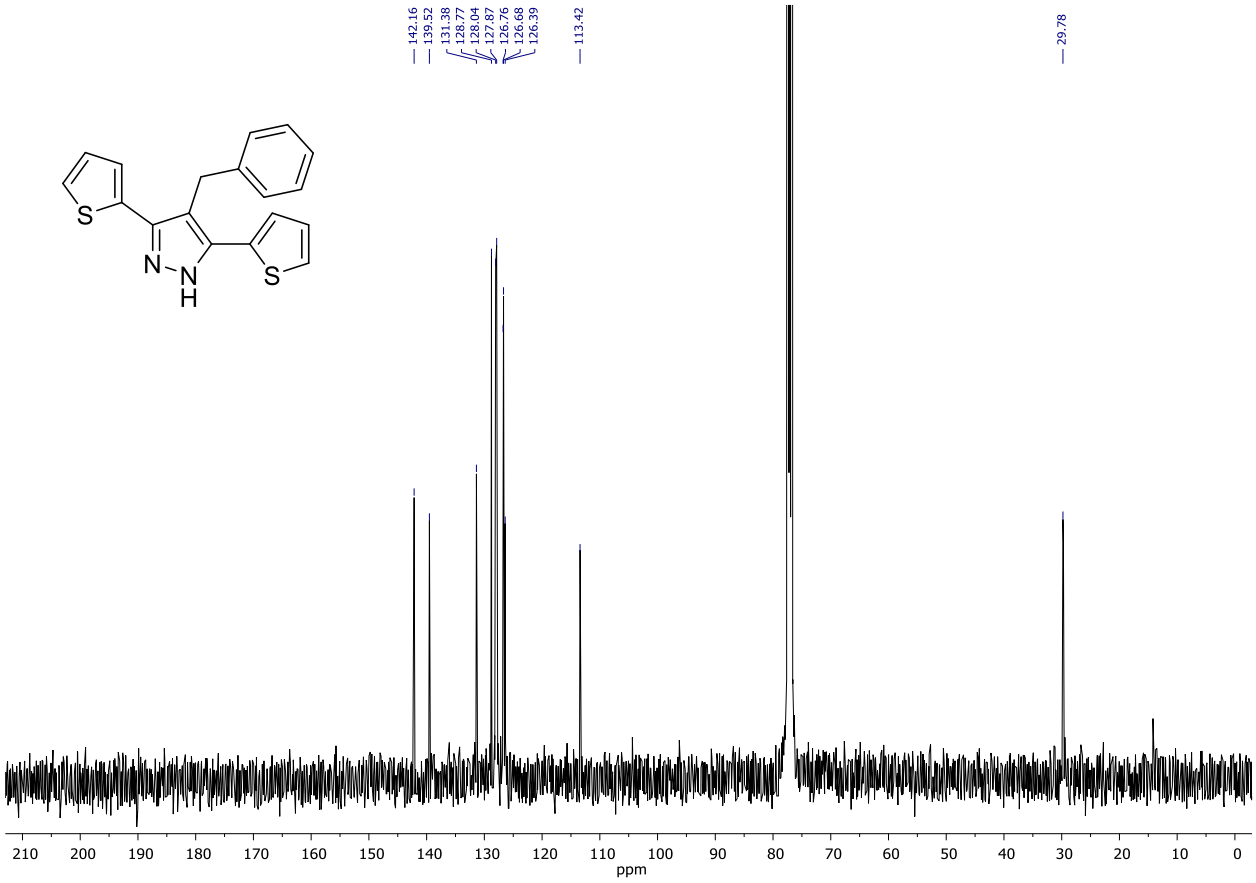
^{1}H NMR Spectrum of **3fa** (400.1 MHz, $CDCl_3$)



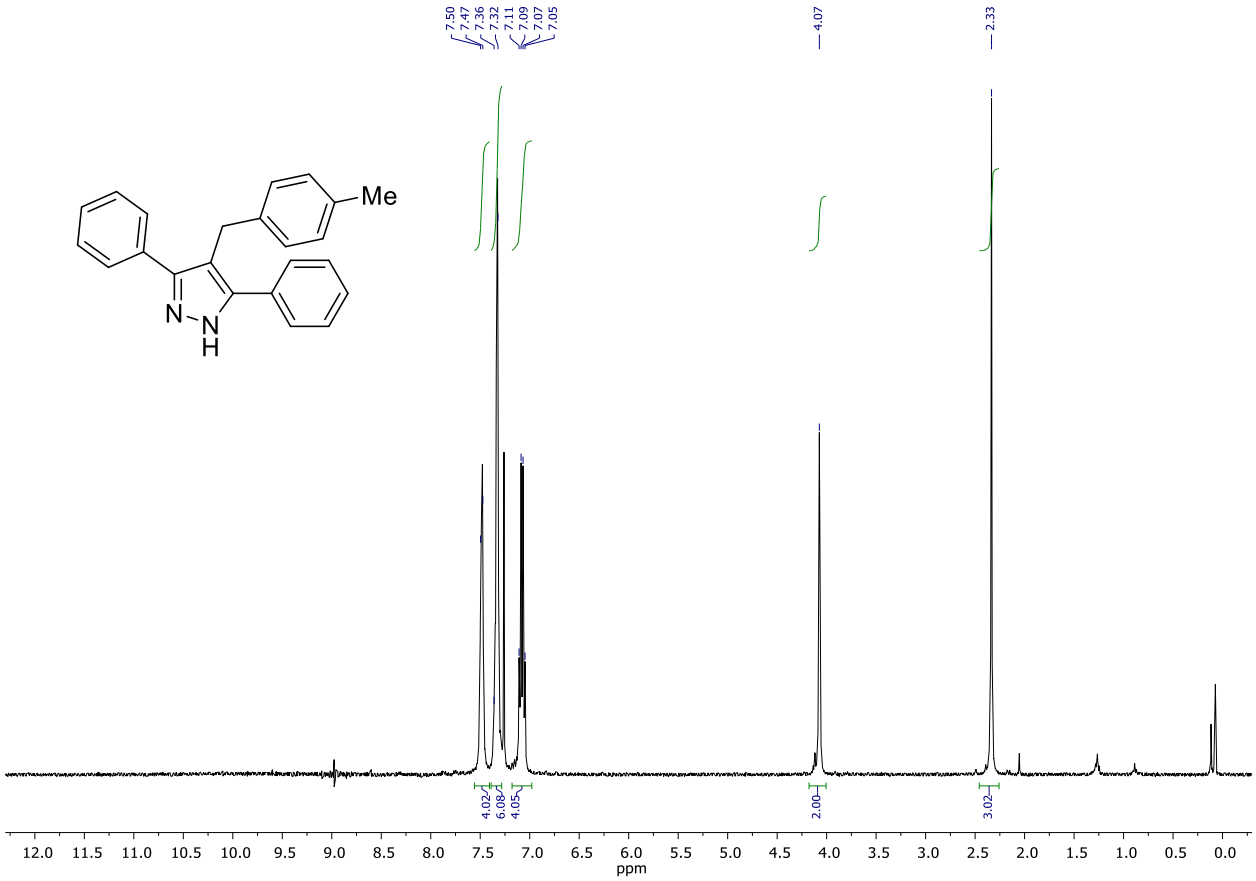
^{13}C{^{1}H} NMR Spectrum of **3fa** (100.6 MHz, $CDCl_3$)



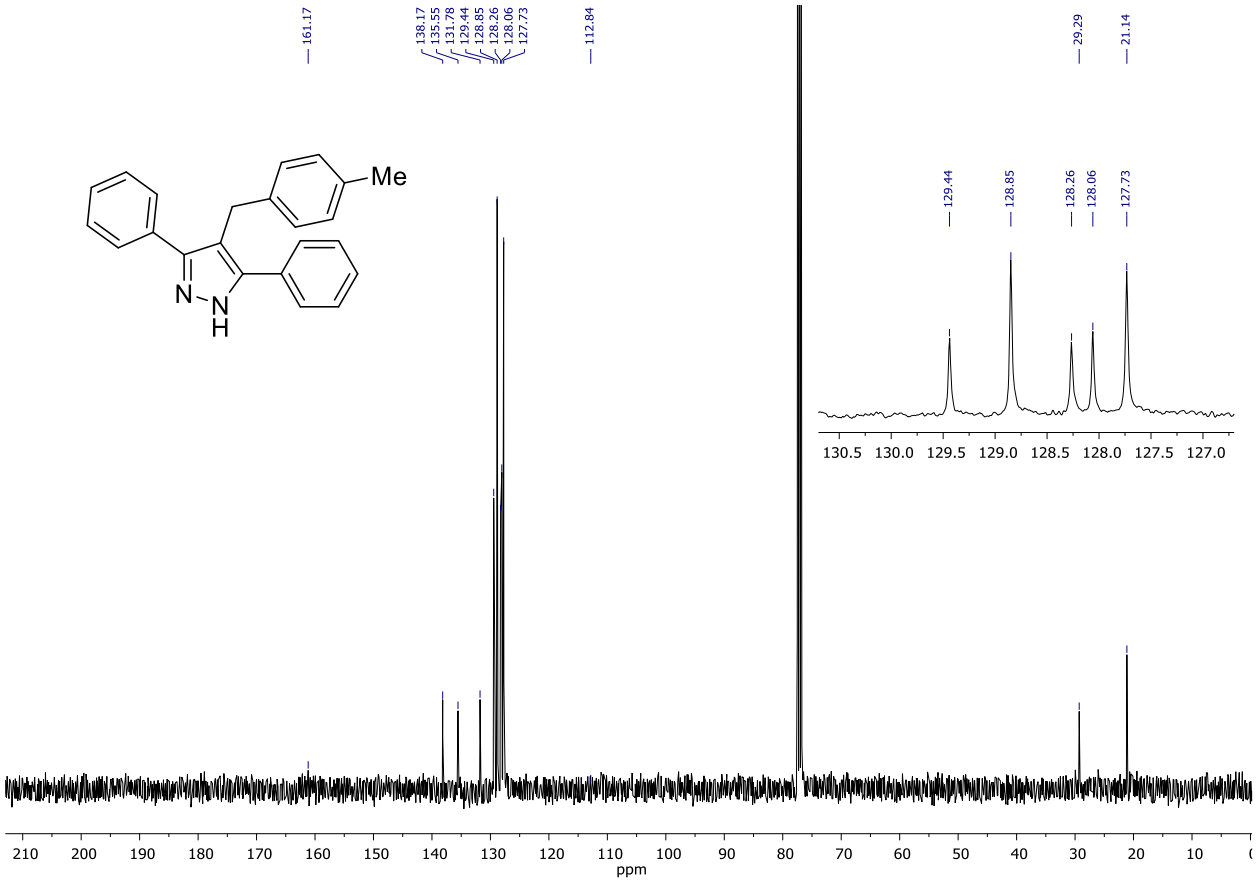
^{1}H NMR Spectrum of **3ga** (400.1 MHz, $CDCl_3$)



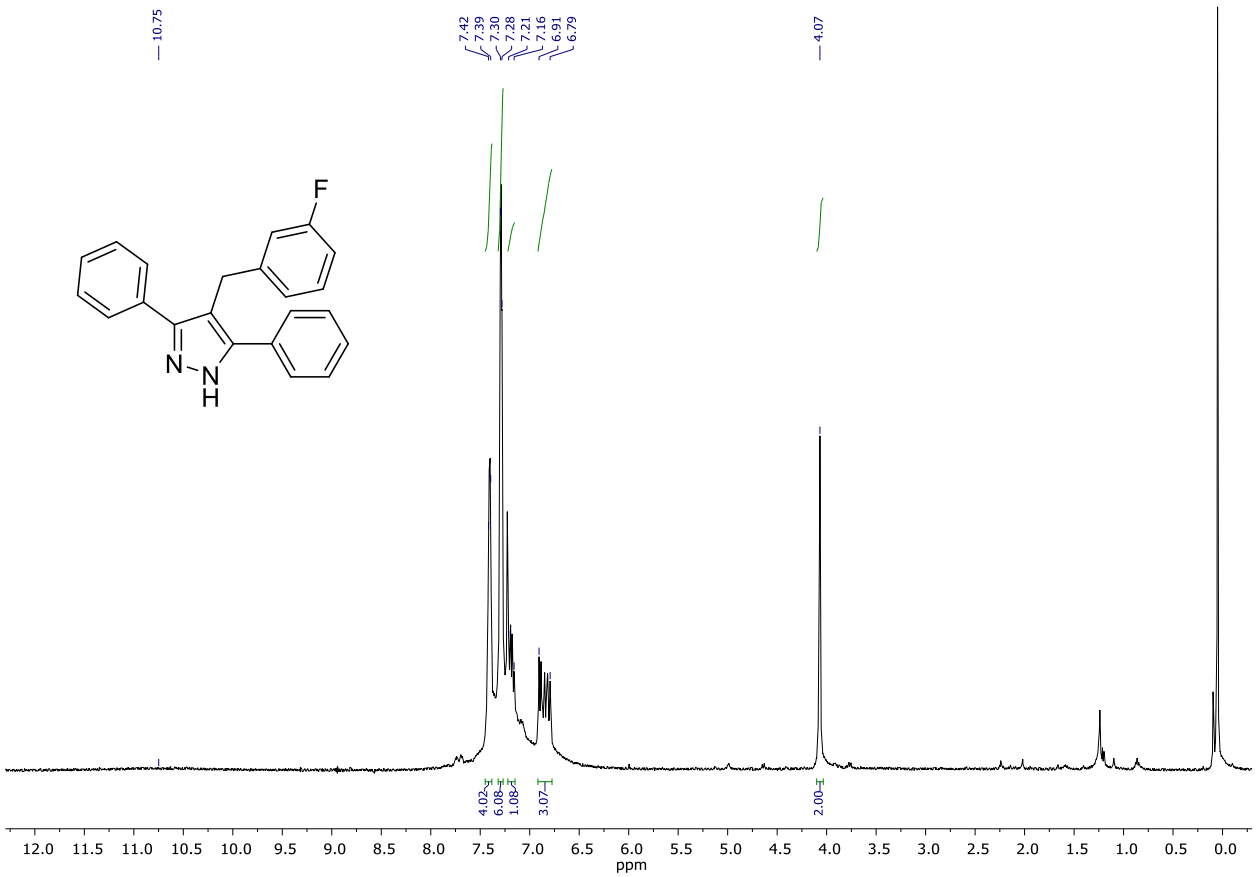
^{13}C{^{1}H} NMR Spectrum of **3ga** (100.6 MHz, $CDCl_3$)



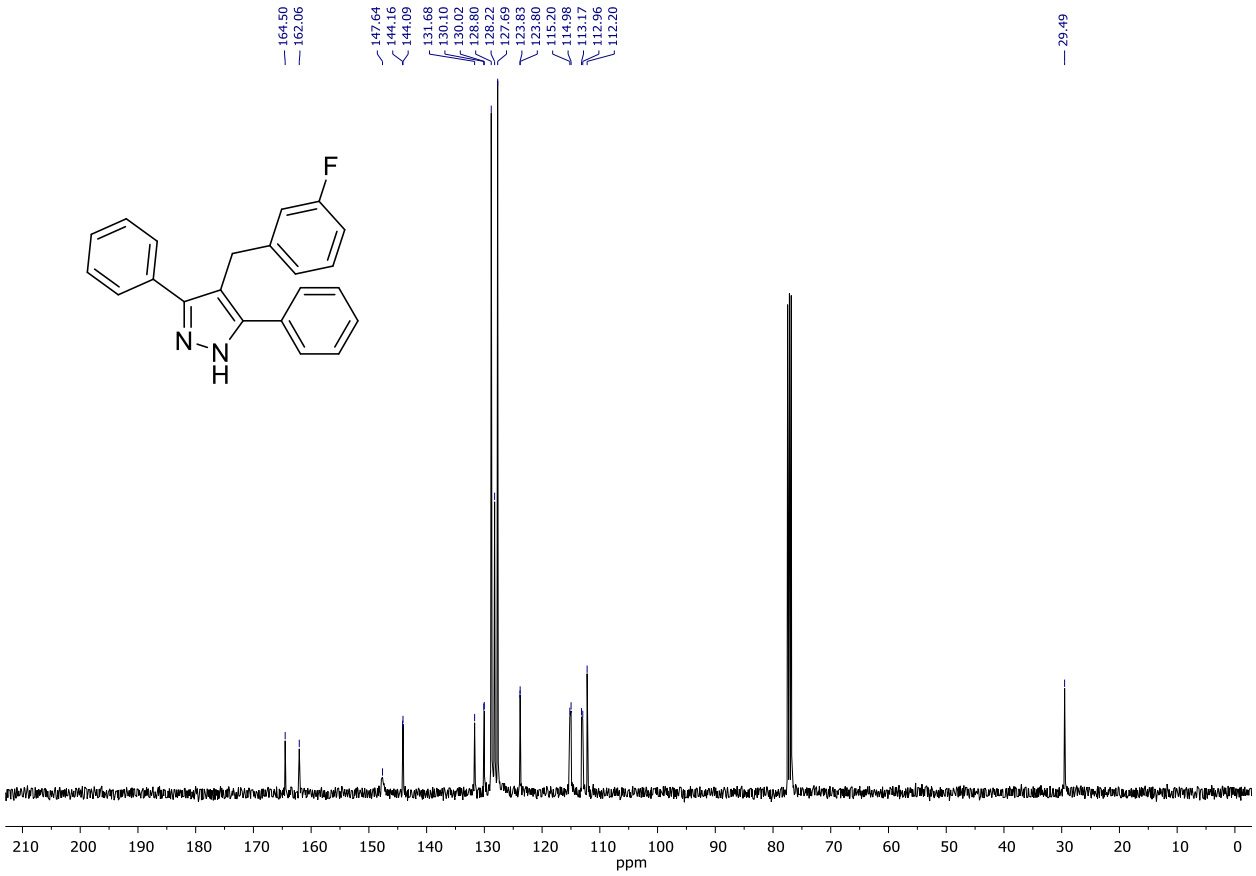
^{1}H NMR Spectrum of **3ab** (400.1 MHz, $CDCl_3$)



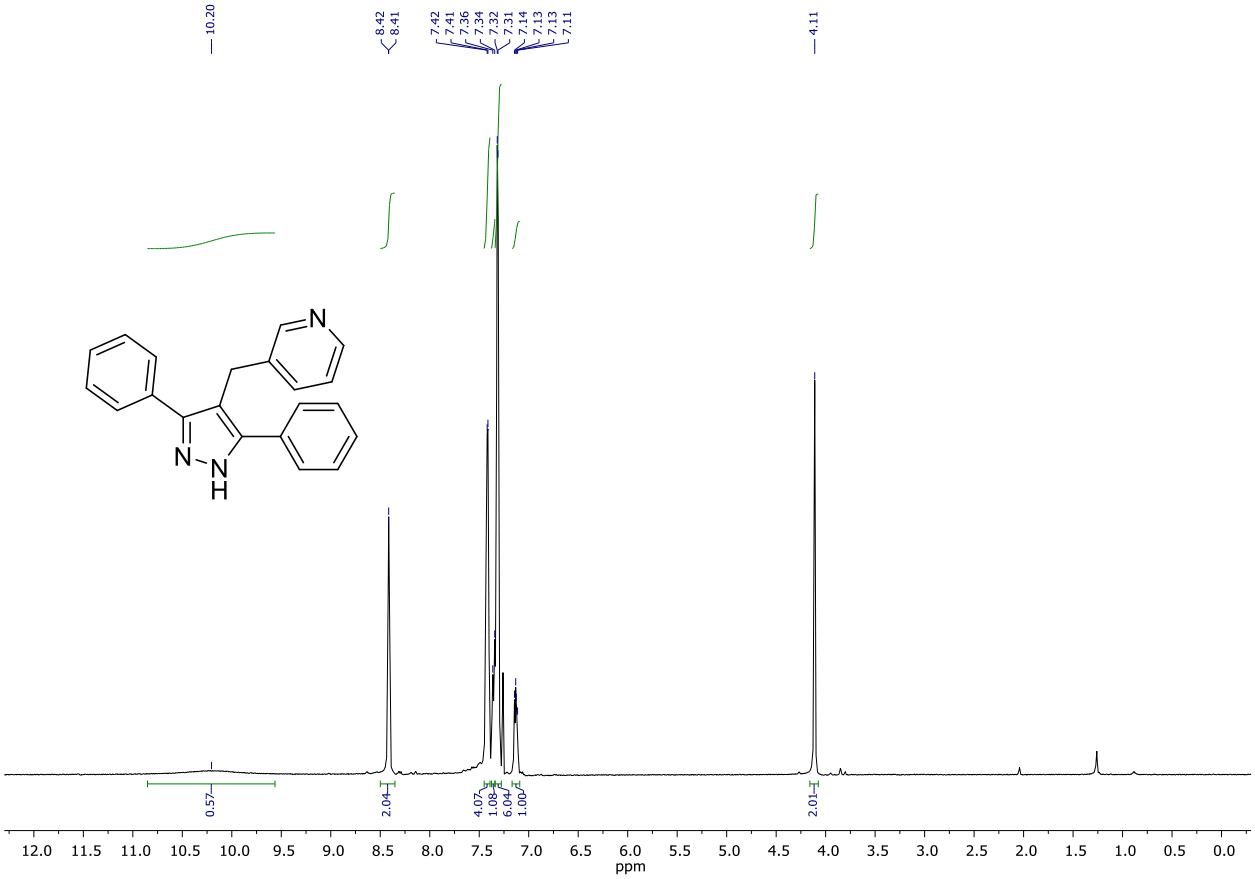
^{13}C{^{1}H} NMR Spectrum of **3ab** (100.6 MHz, $CDCl_3$)



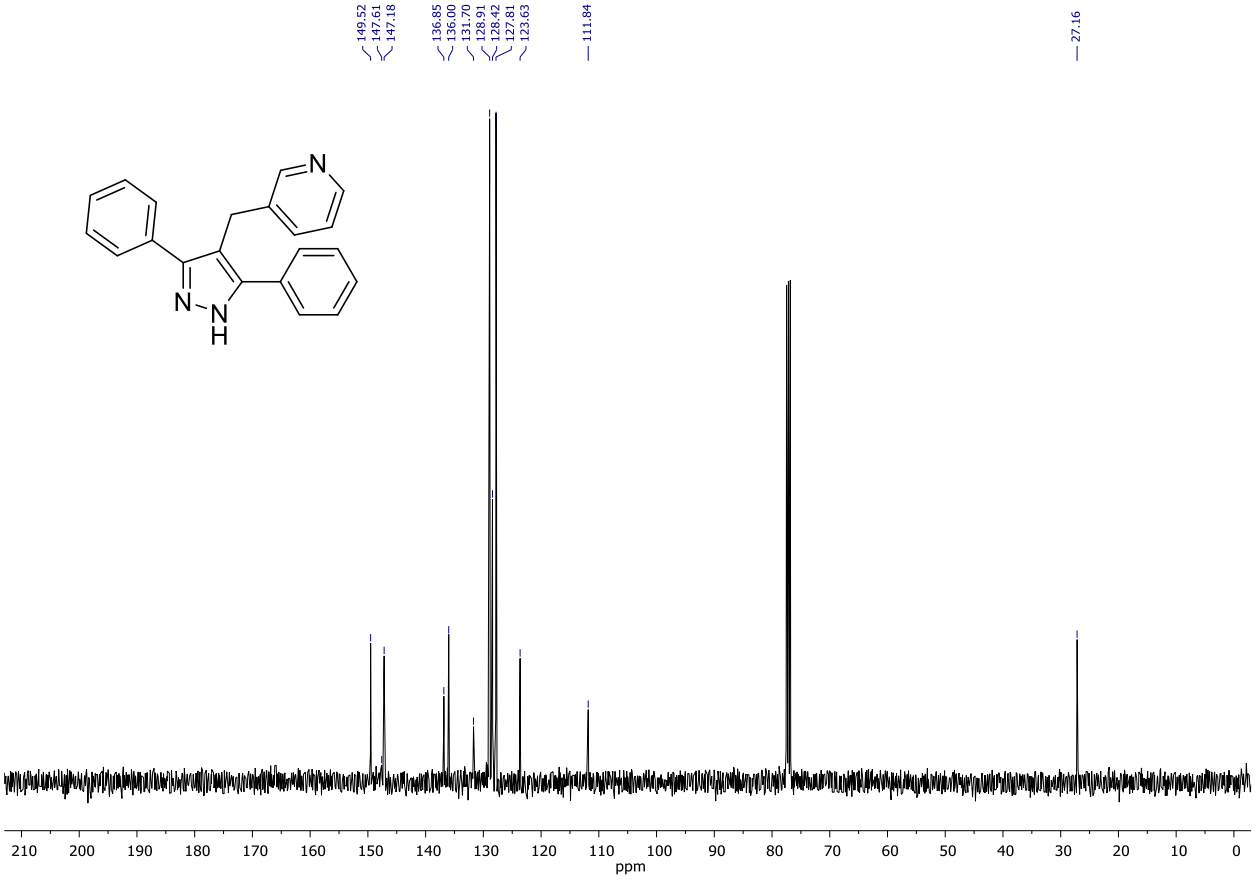
^{1}H NMR Spectrum of **3ac** (400.1 MHz, $CDCl_3$)



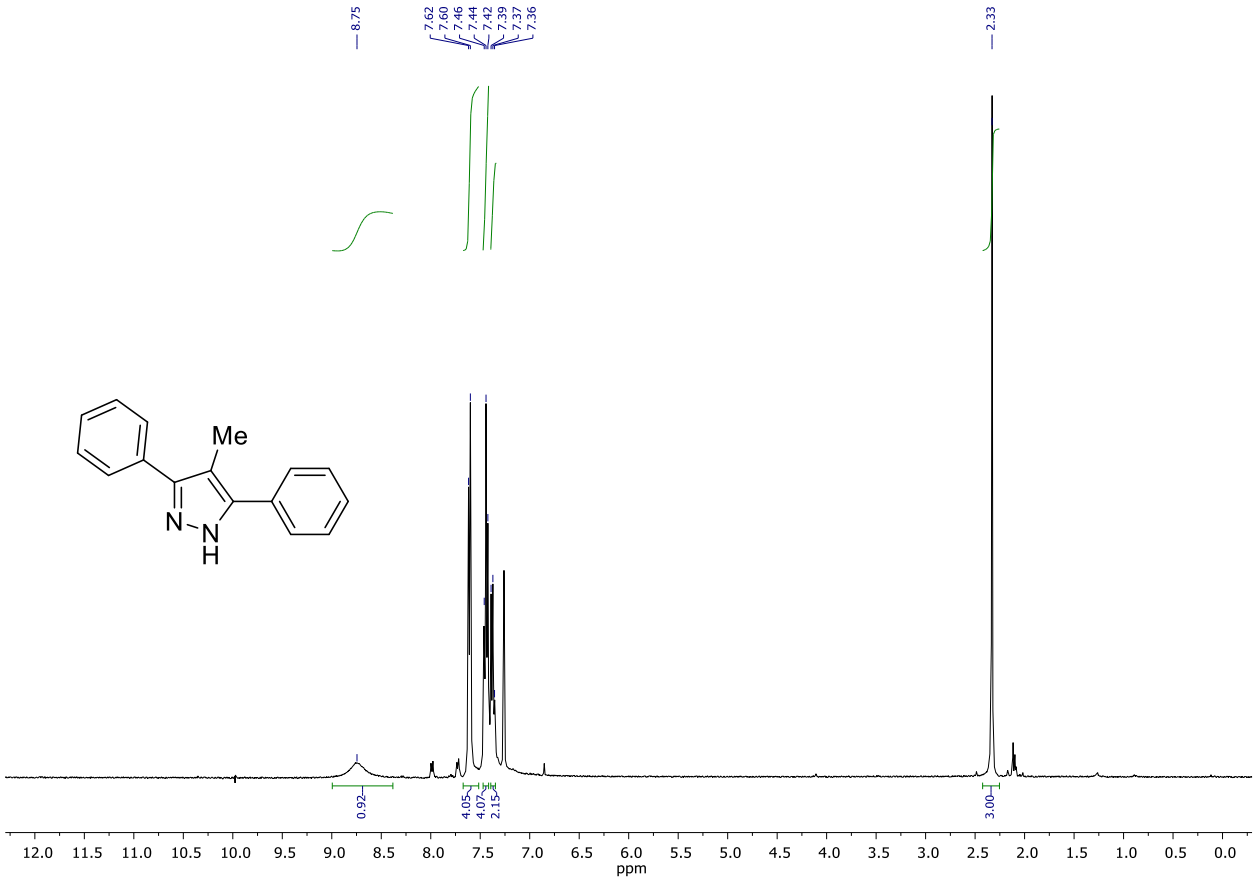
^{13}C{^{1}H} NMR Spectrum of **3ac** (100.6 MHz, $CDCl_3$)



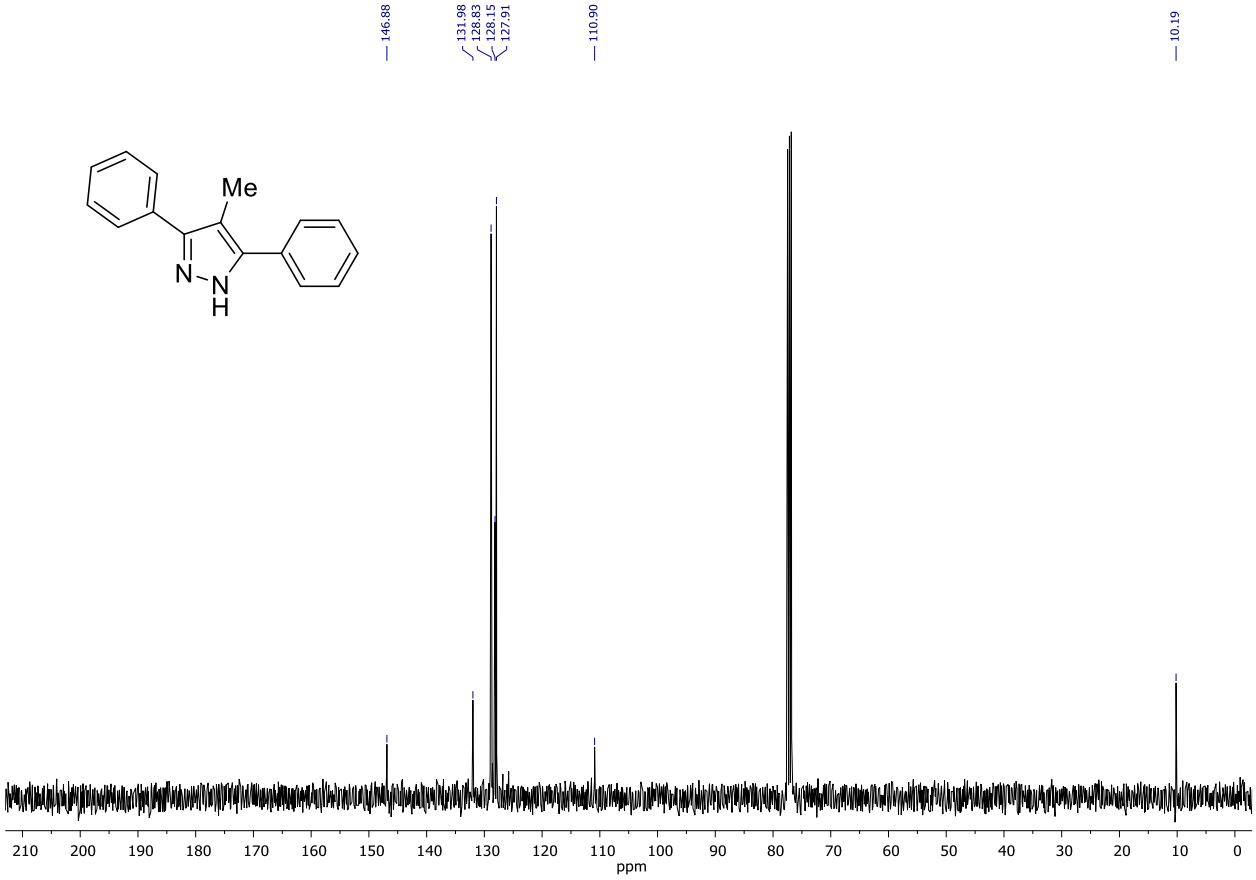
^{1}H NMR Spectrum of **3ad** (400.1 MHz, $CDCl_3$)



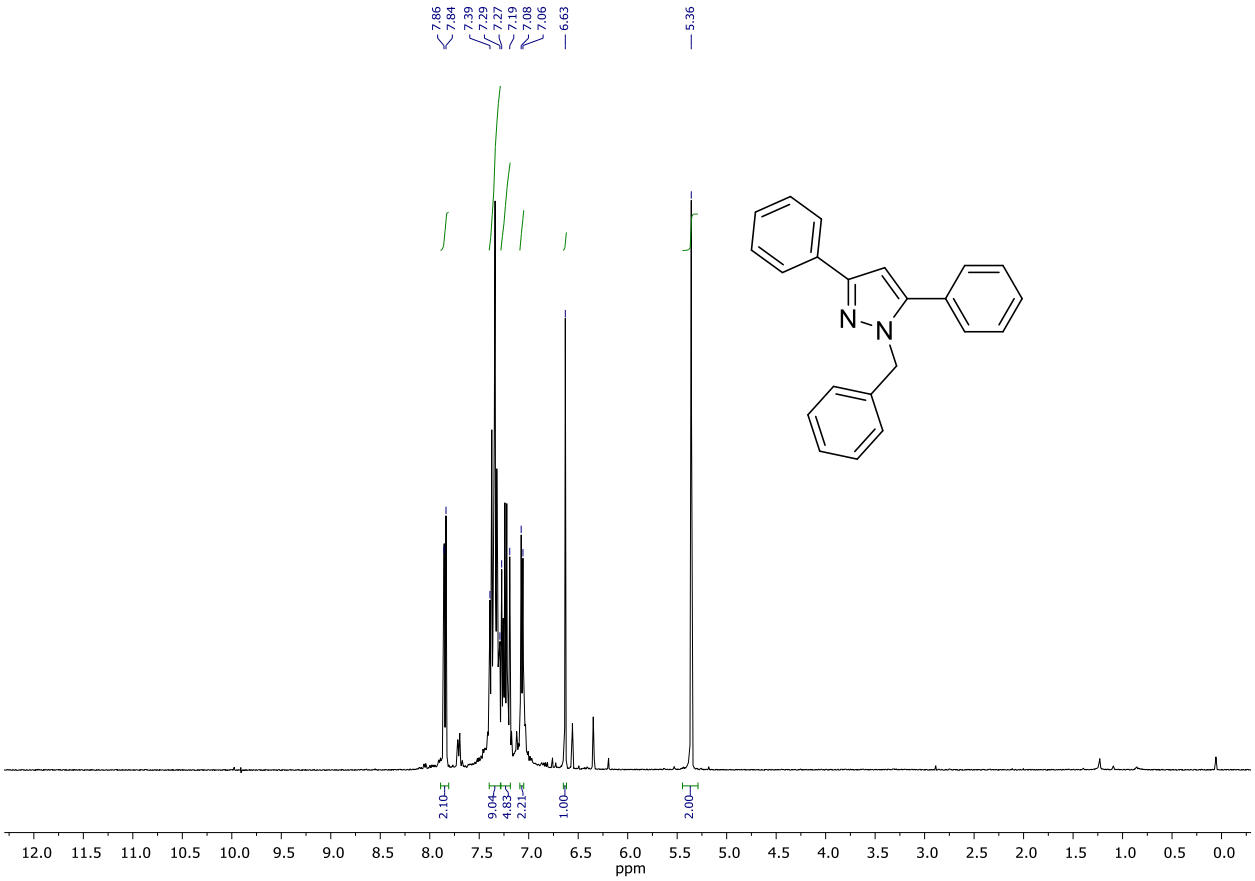
^{13}C{^{1}H} NMR Spectrum of **3ad** (100.6 MHz, $CDCl_3$)



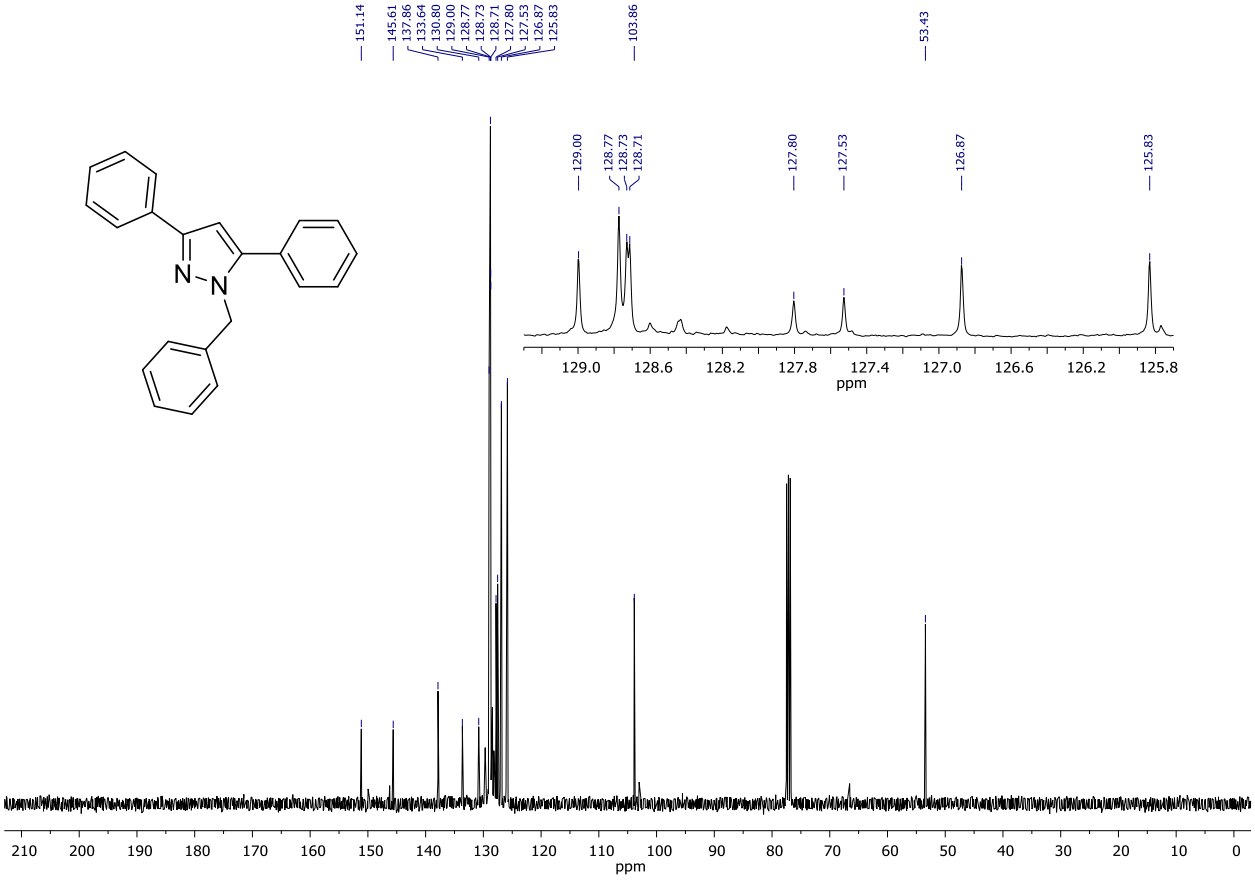
^{1}H NMR Spectrum of **3ae** (400.1 MHz, $CDCl_3$)



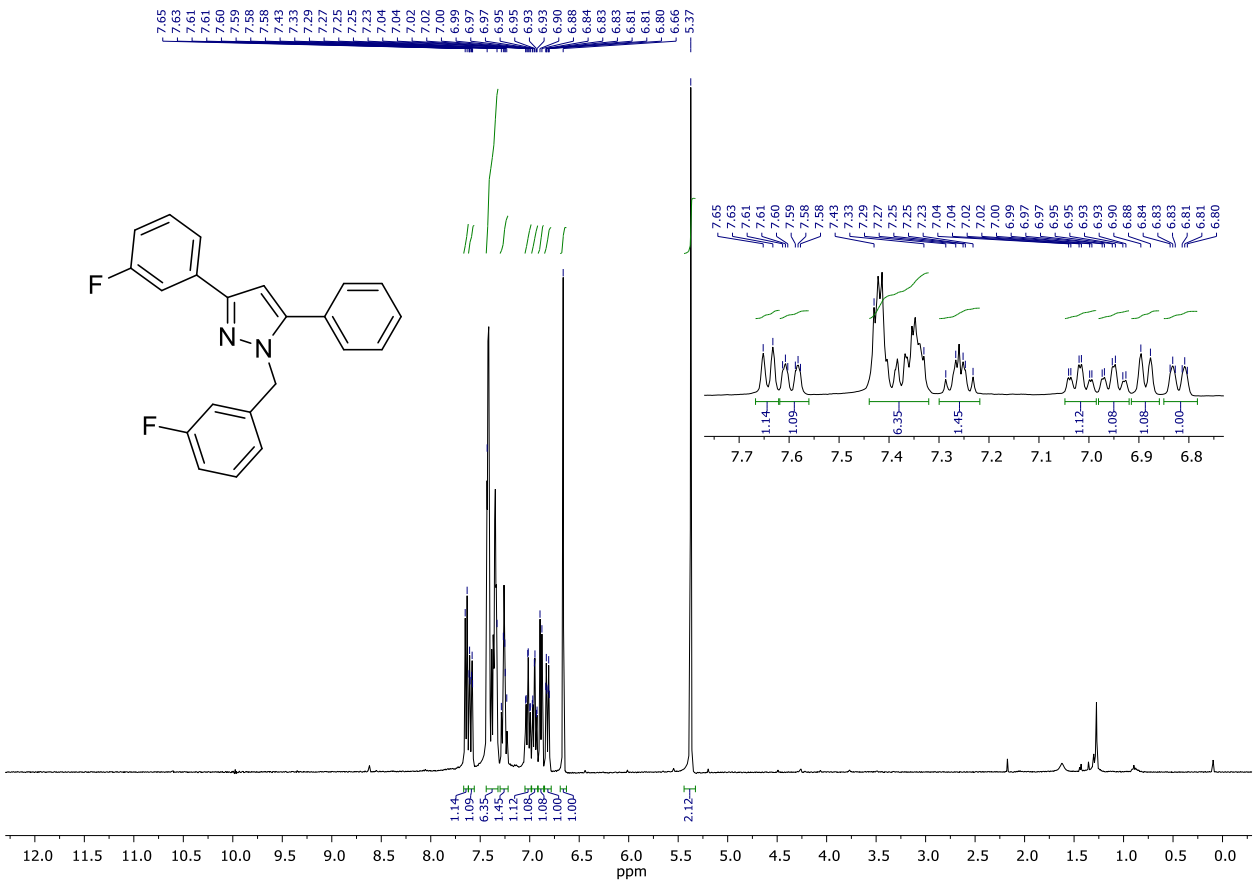
^{13}C{^{1}H} NMR Spectrum of **3ae** (100.6 MHz, $CDCl_3$)



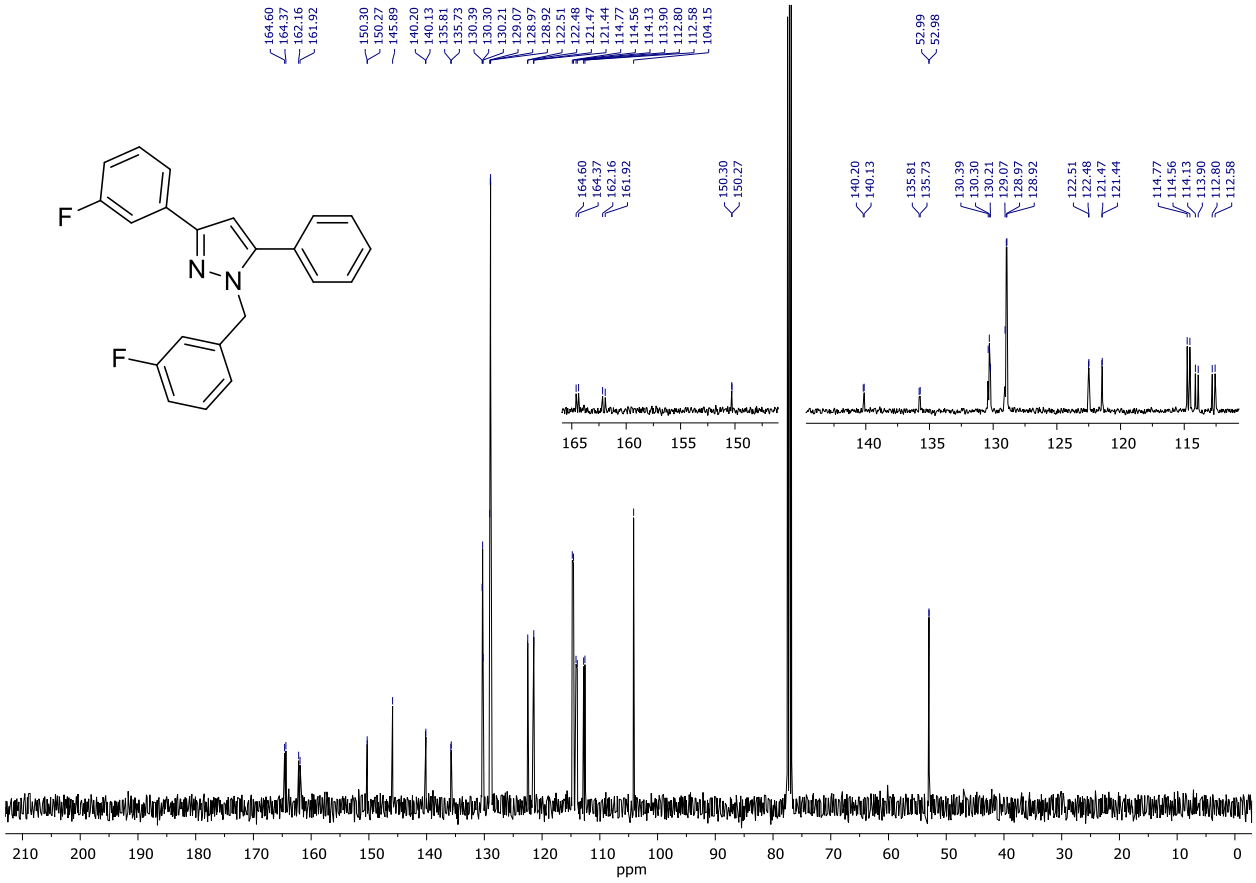
^{1}H NMR Spectrum of **4aa** (400.1 MHz, $CDCl_3$)



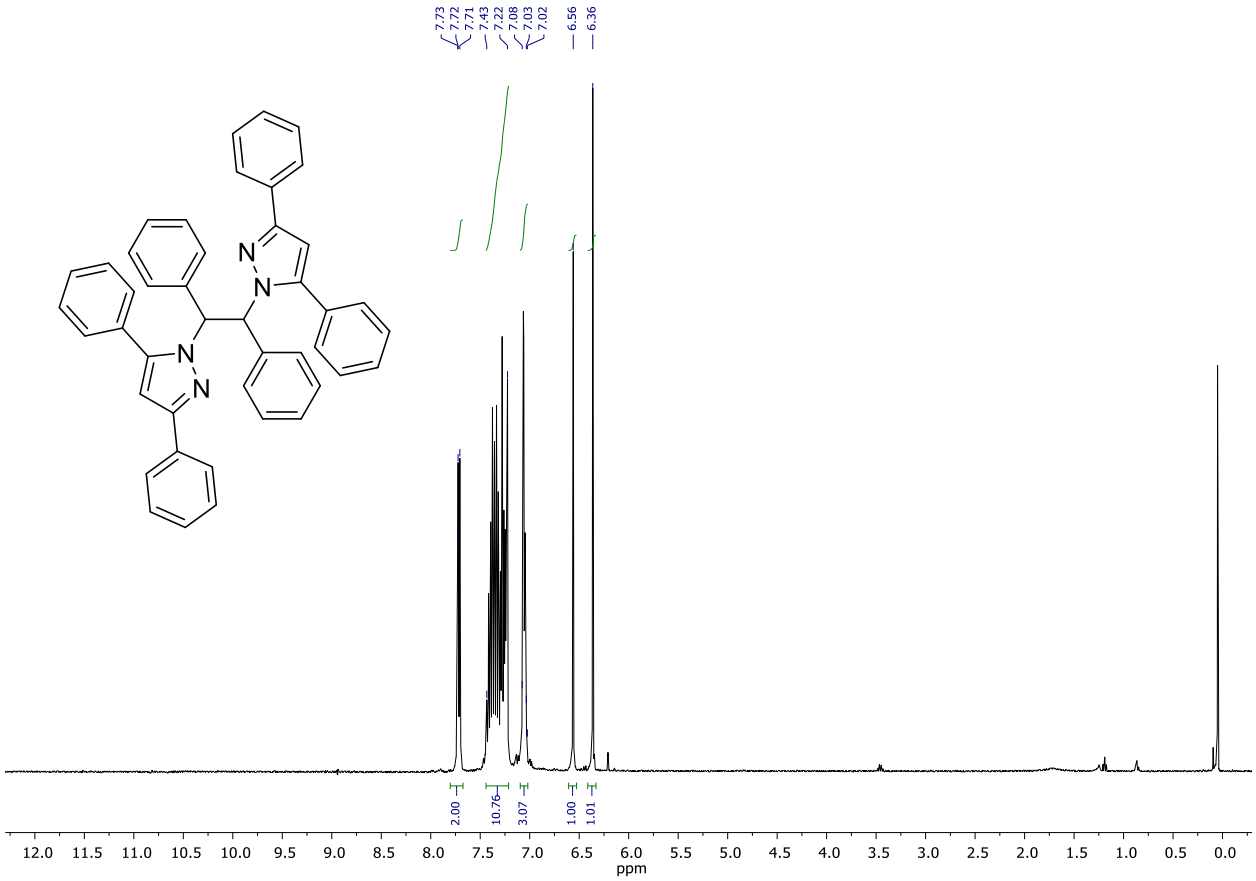
^{13}C{^{1}H} NMR Spectrum of **4aa** (100.6 MHz, $CDCl_3$)



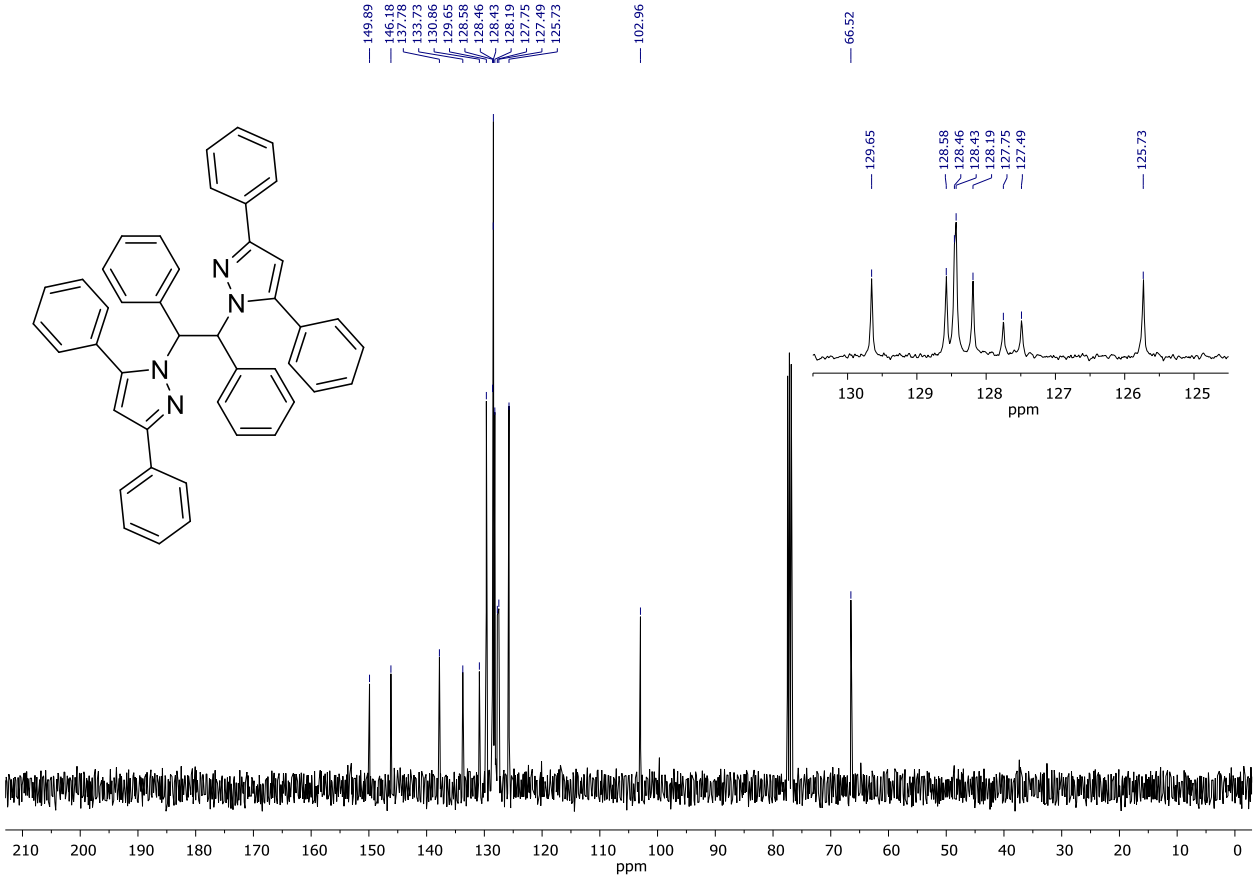
^{1}H NMR Spectrum of **4ea** (400.1 MHz, $CDCl_3$)



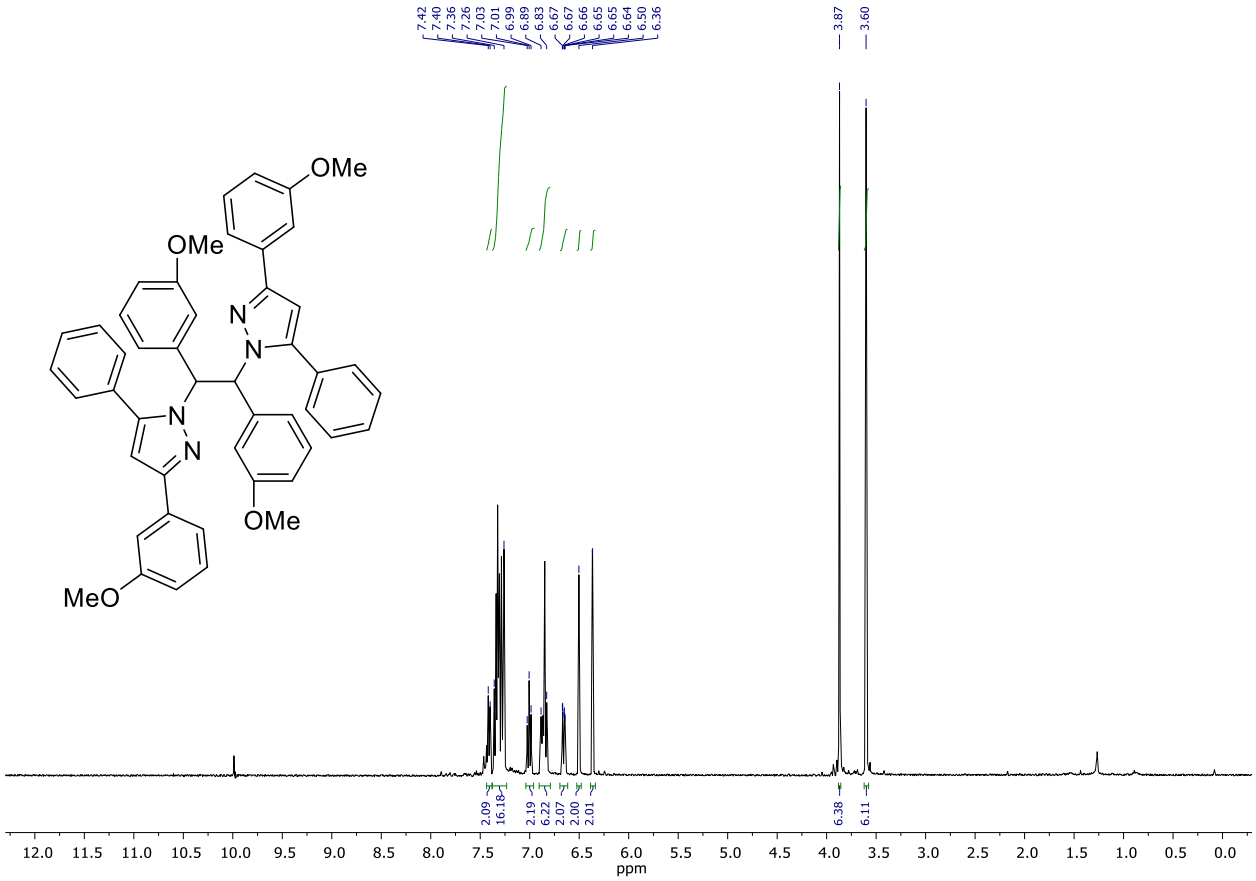
^{13}C{^{1}H} NMR Spectrum of **4ea** (100.6 MHz, $CDCl_3$)



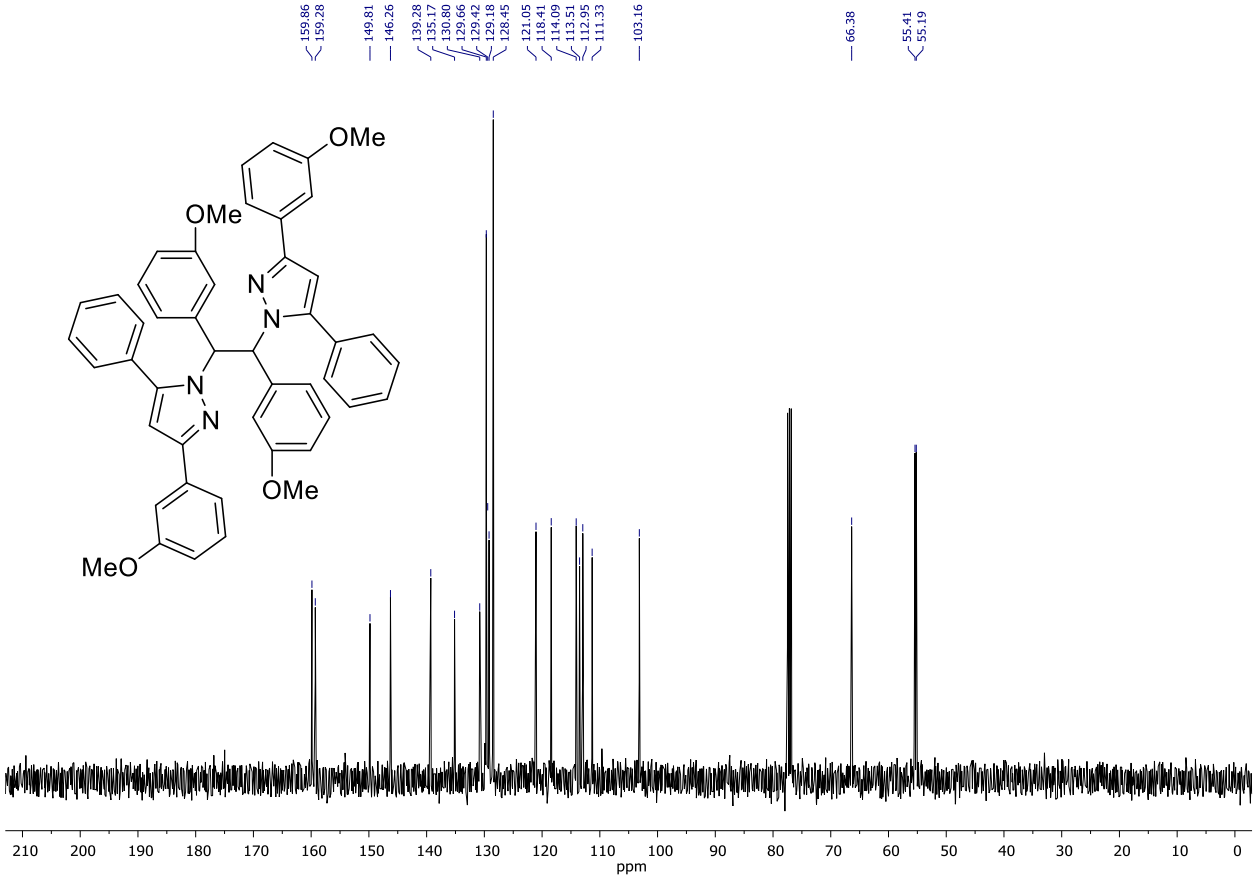
^{1}H NMR Spectrum of **5aa** (400.1 MHz, $CDCl_3$)



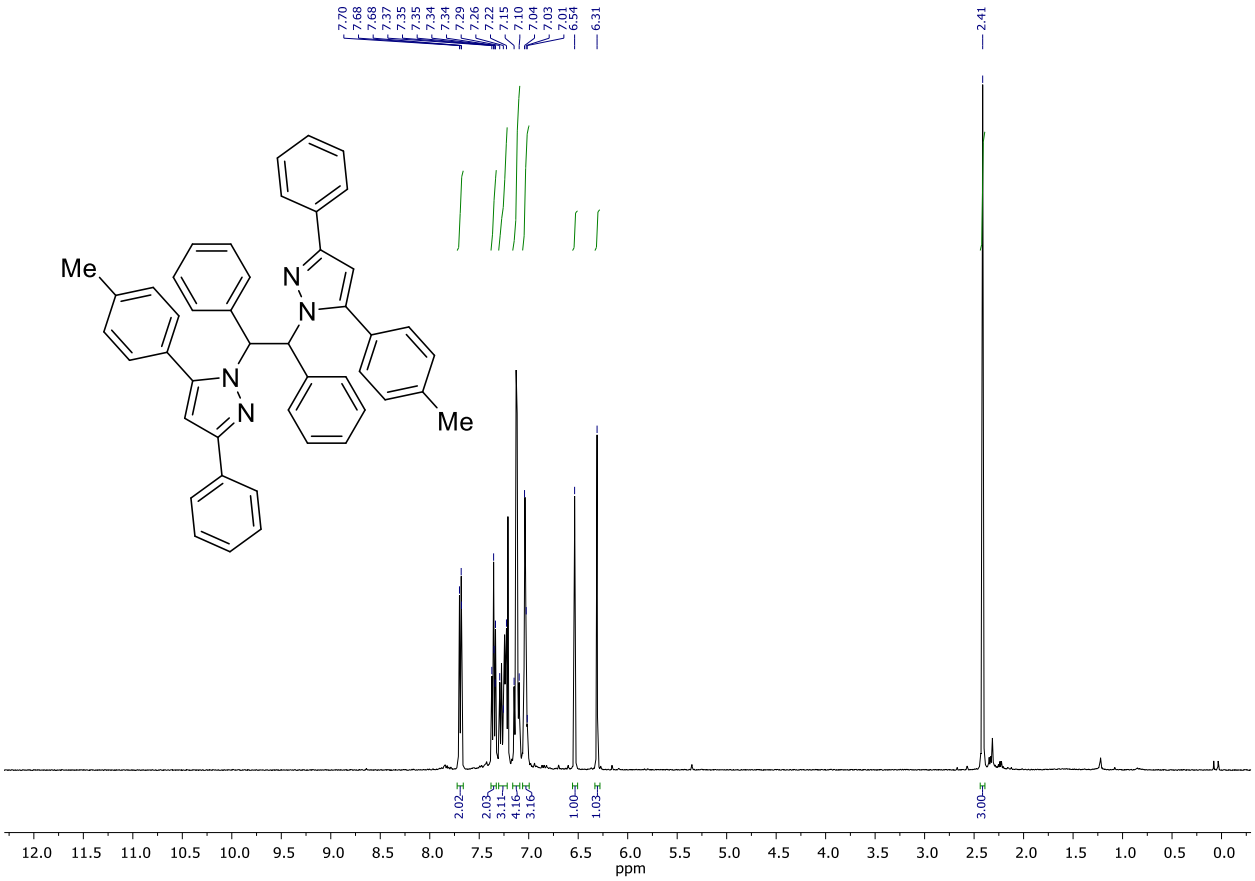
^{13}C{^{1}H} NMR Spectrum of **5aa** (100.6 MHz, $CDCl_3$)



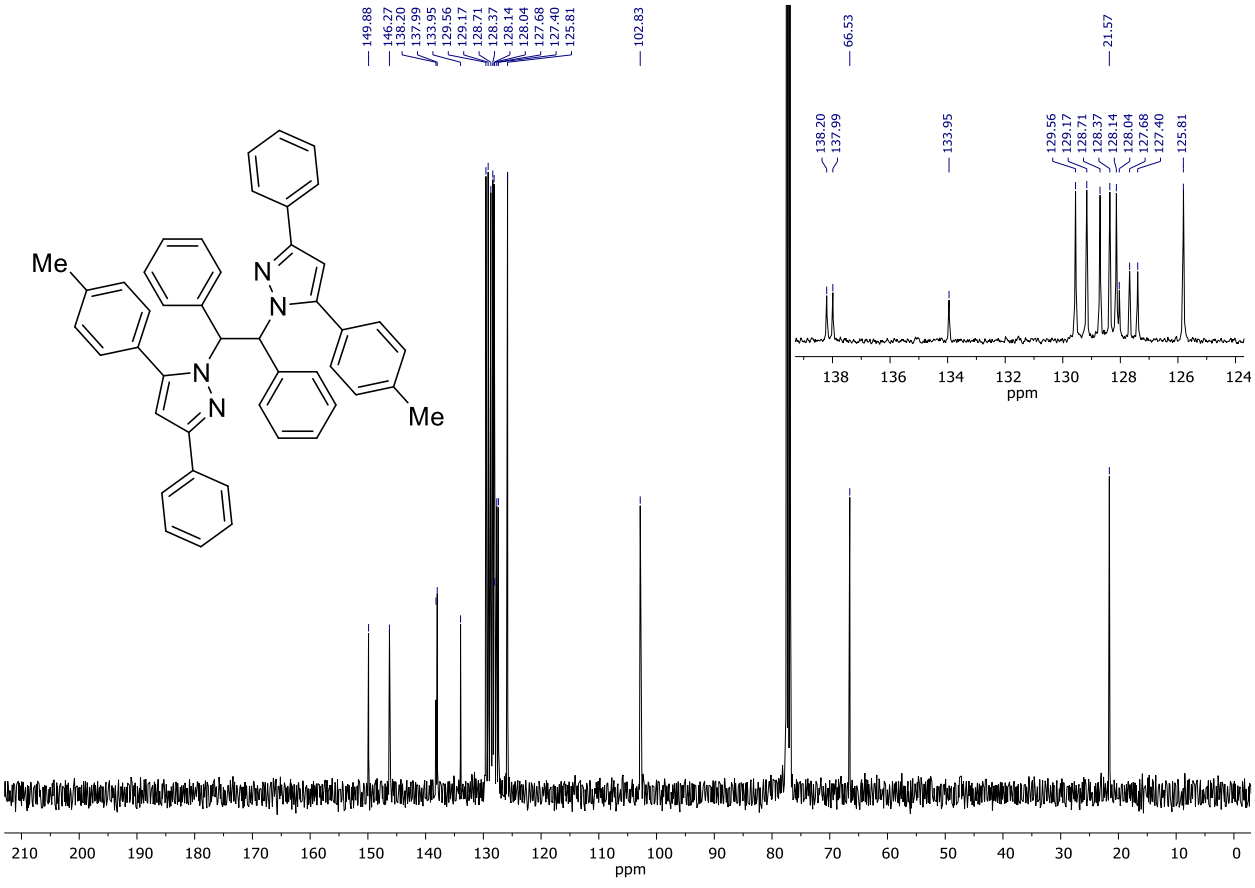
^{1}H NMR Spectrum of **5da** (400.1 MHz, $CDCl_3$)



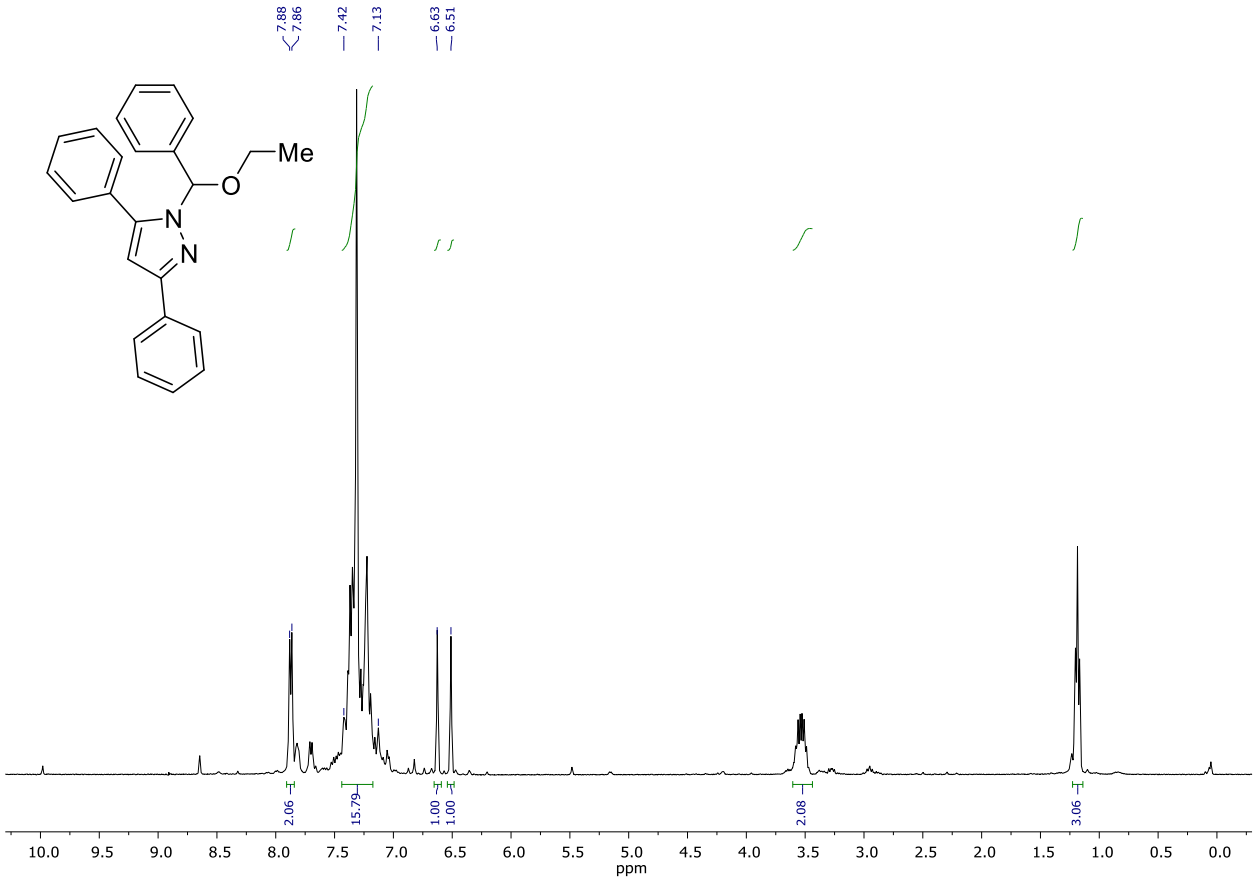
^{13}C{^{1}H} NMR Spectrum of **5da** (100.6 MHz, $CDCl_3$)



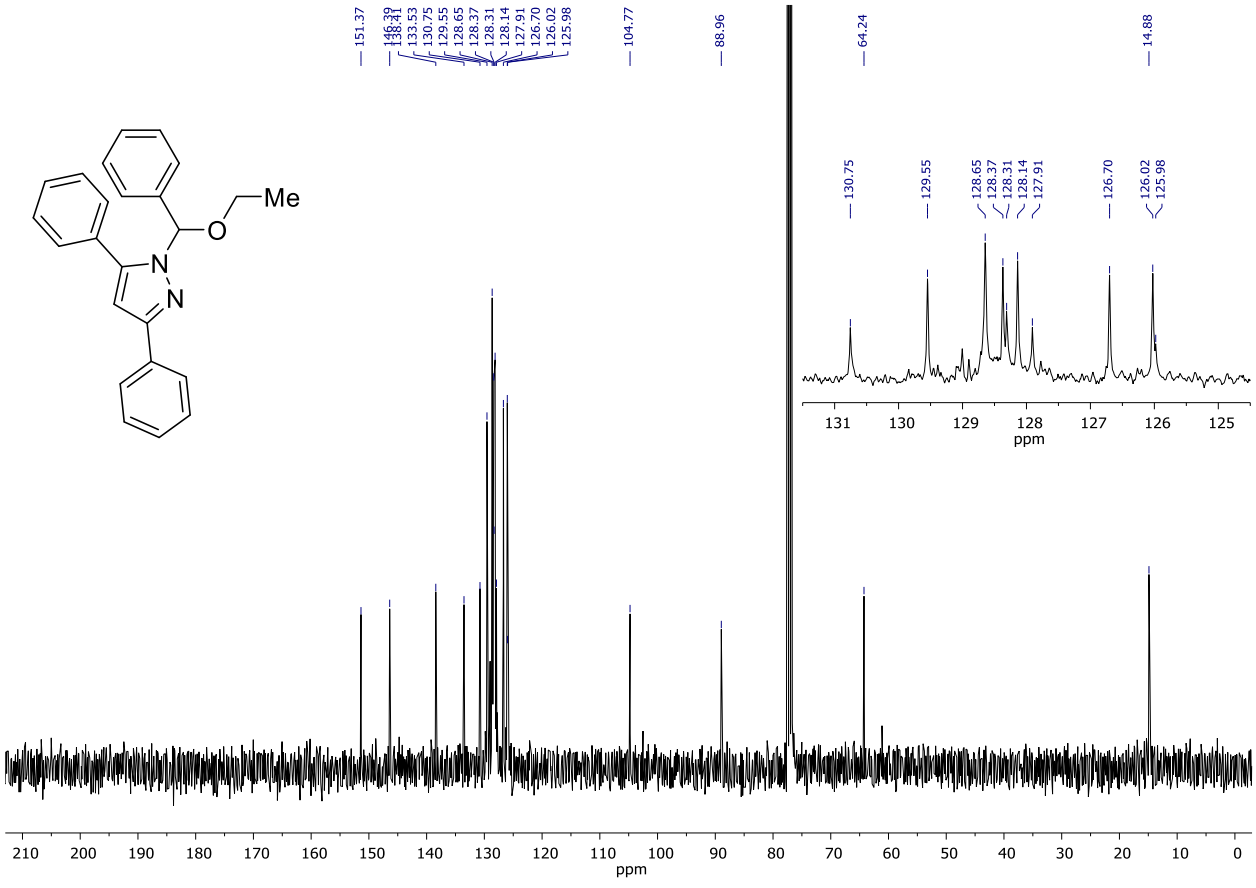
^{1}H NMR Spectrum of **5ab** (400.1 MHz, $CDCl_3$)



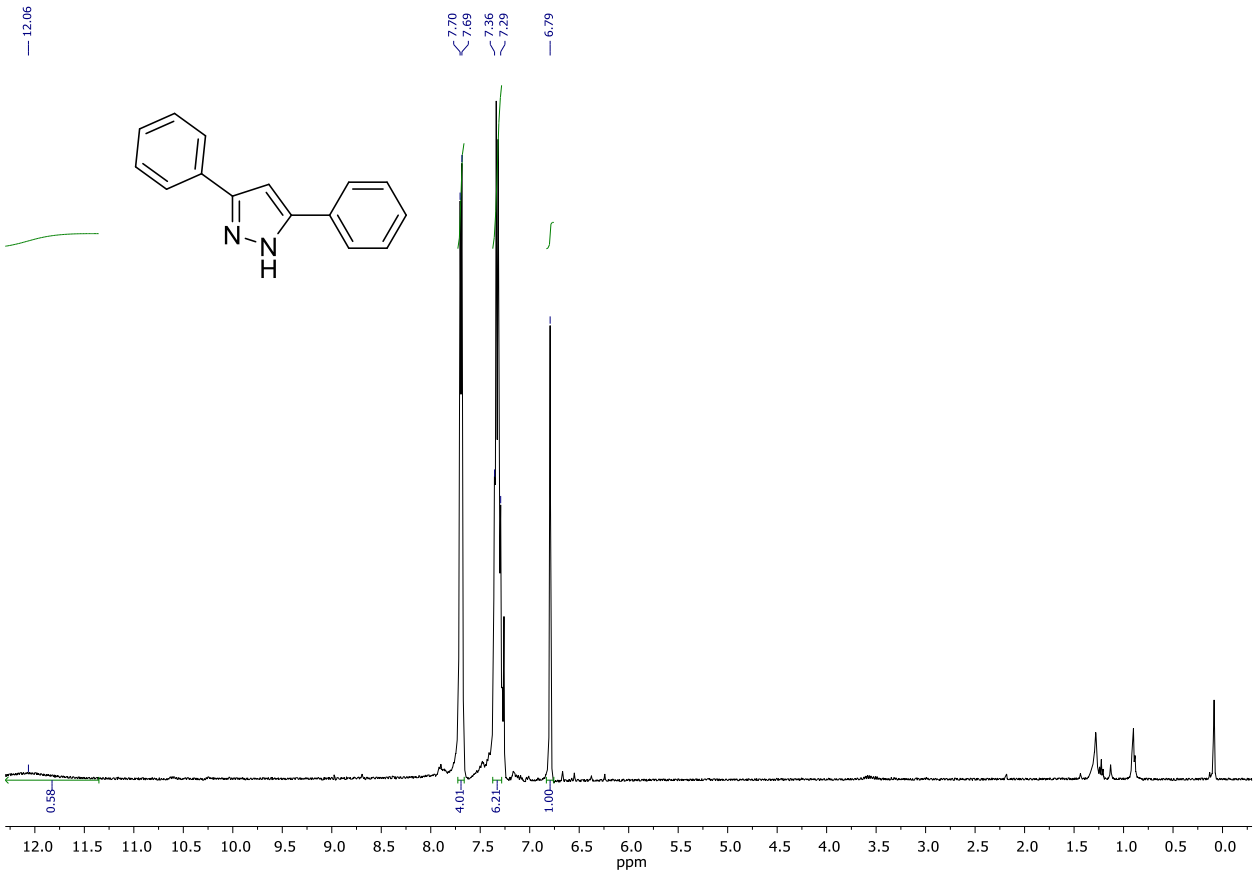
^{13}C{^{1}H} NMR Spectrum of **5ab** (100.6 MHz, $CDCl_3$)



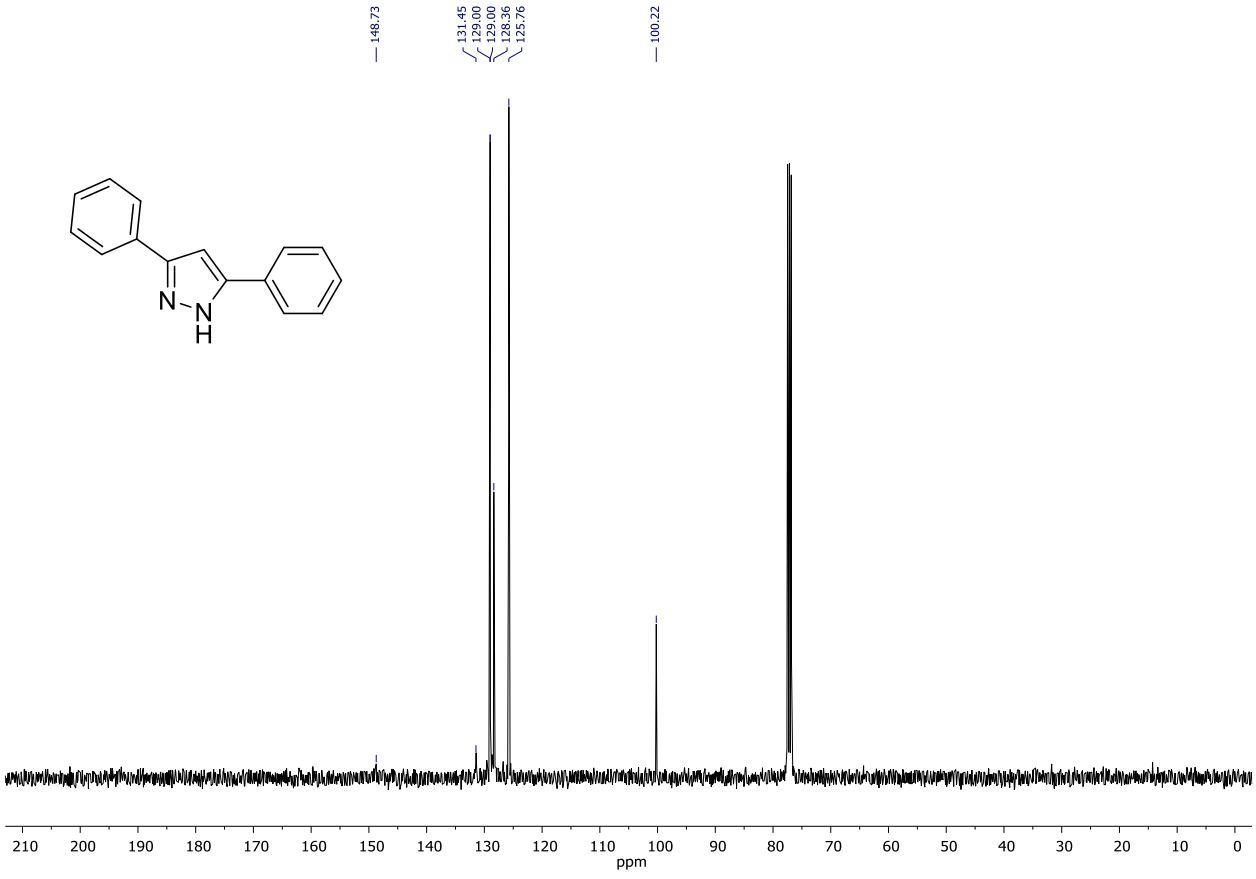
^{1}H NMR Spectrum of **6aa** (400.1 MHz, $CDCl_3$)



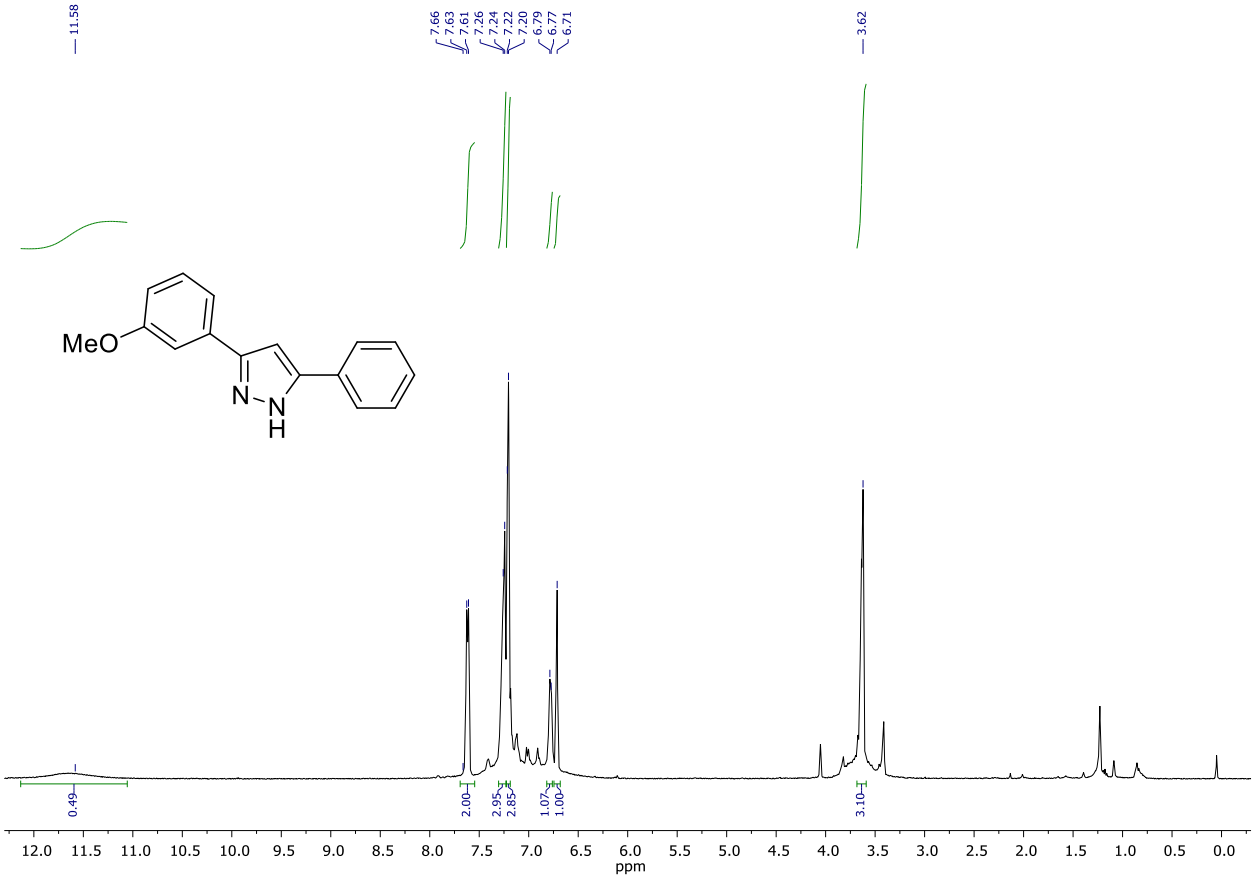
^{13}C{^{1}H} NMR Spectrum of **6aa** (100.6 MHz, $CDCl_3$)



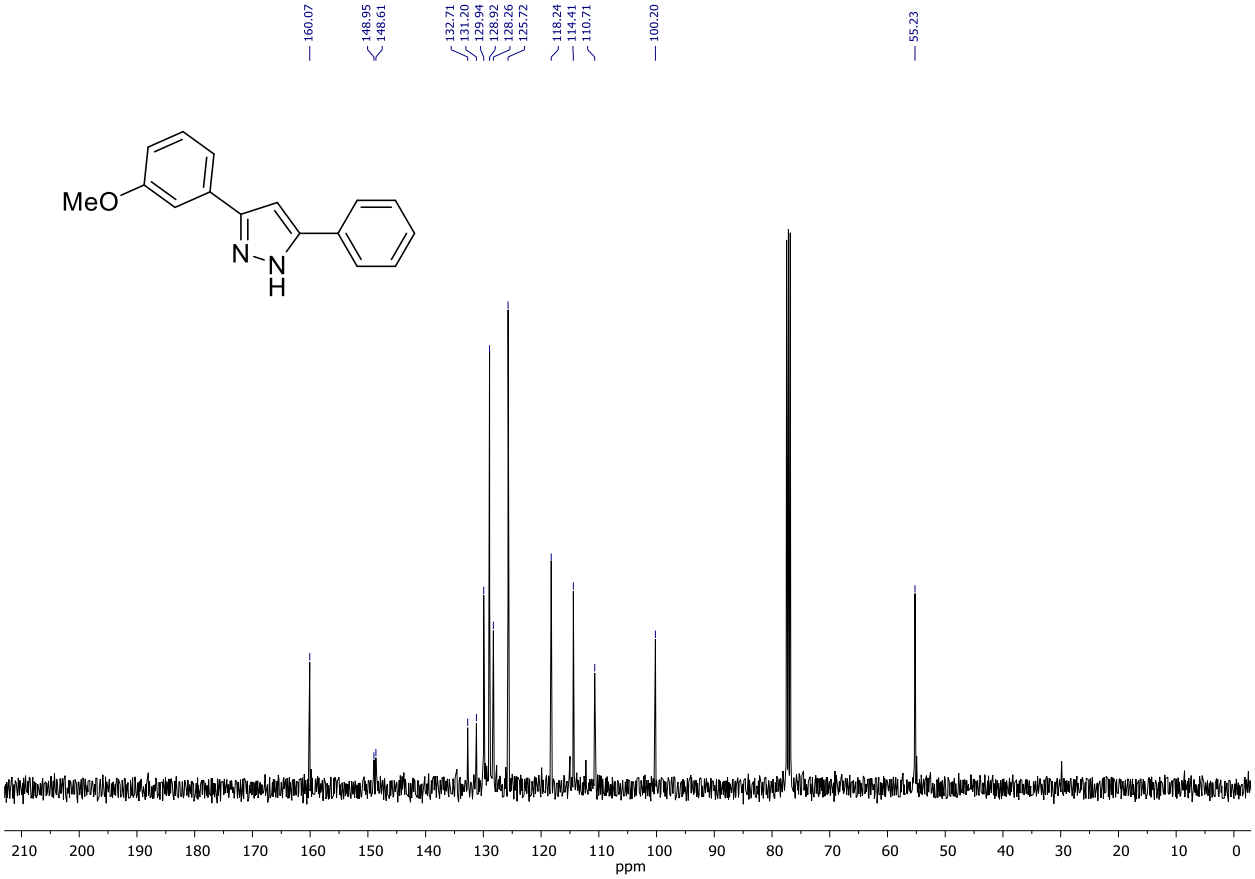
^{1}H NMR Spectrum of **7aa** (400.1 MHz, $CDCl_3$)



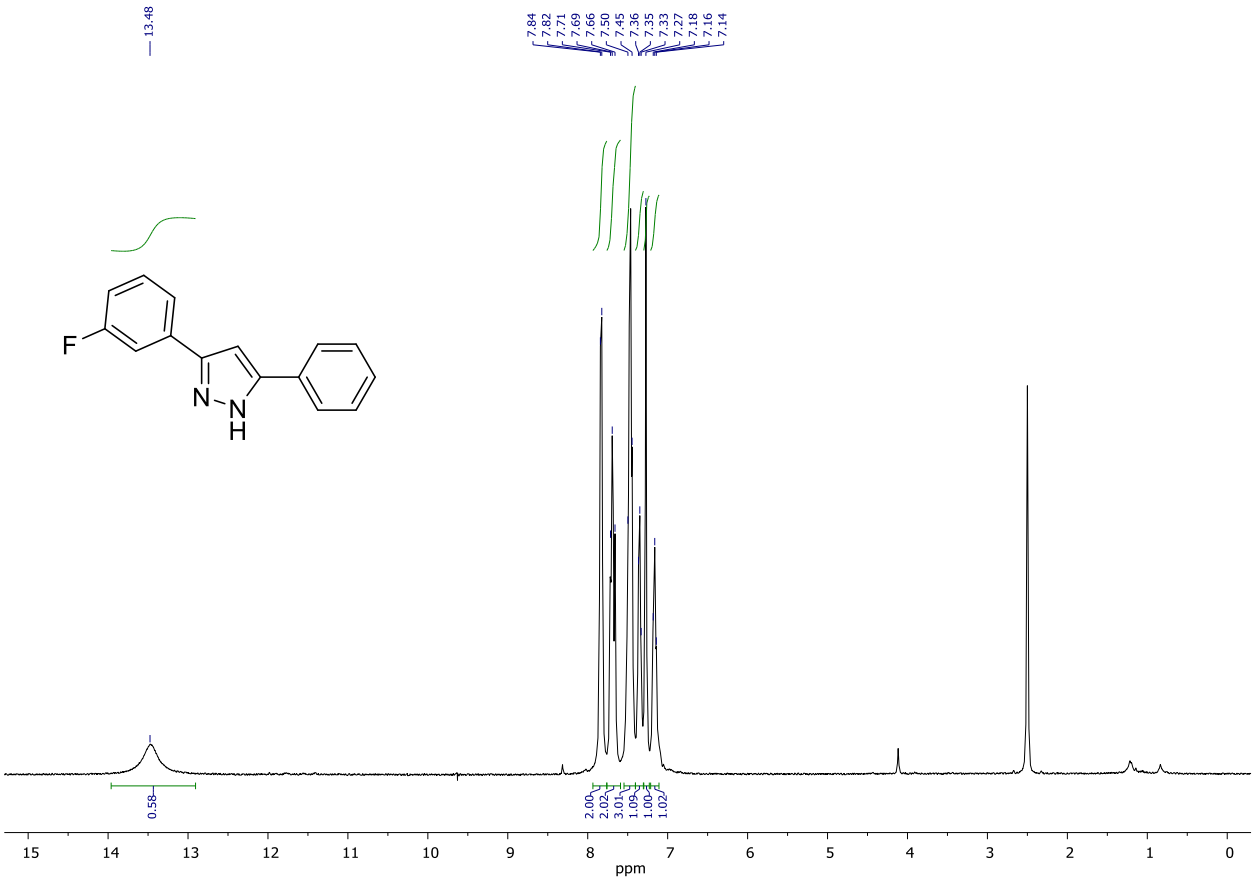
^{13}C{^{1}H} NMR Spectrum of **7aa** (100.6 MHz, $CDCl_3$)



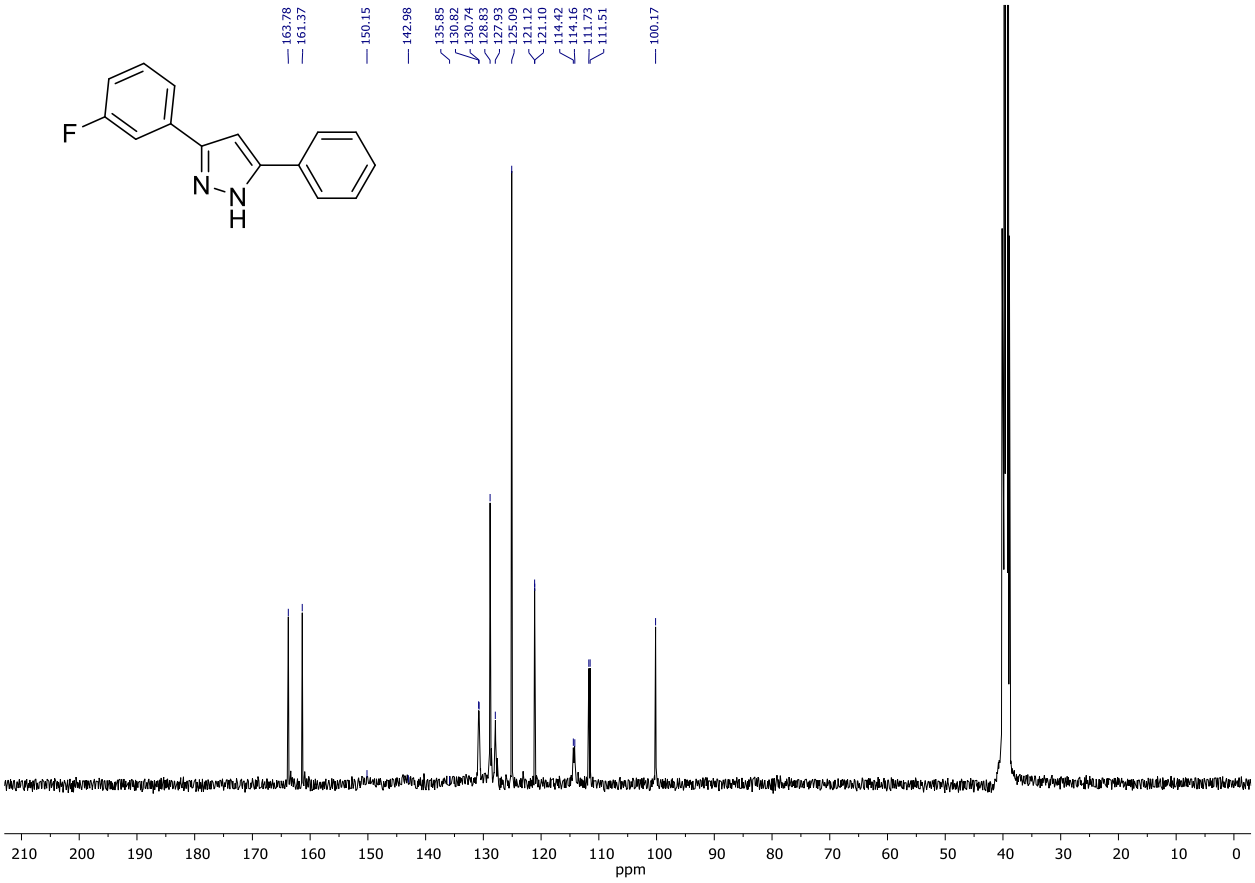
^{1}H NMR Spectrum of **7da** (400.1 MHz, $CDCl_3$)



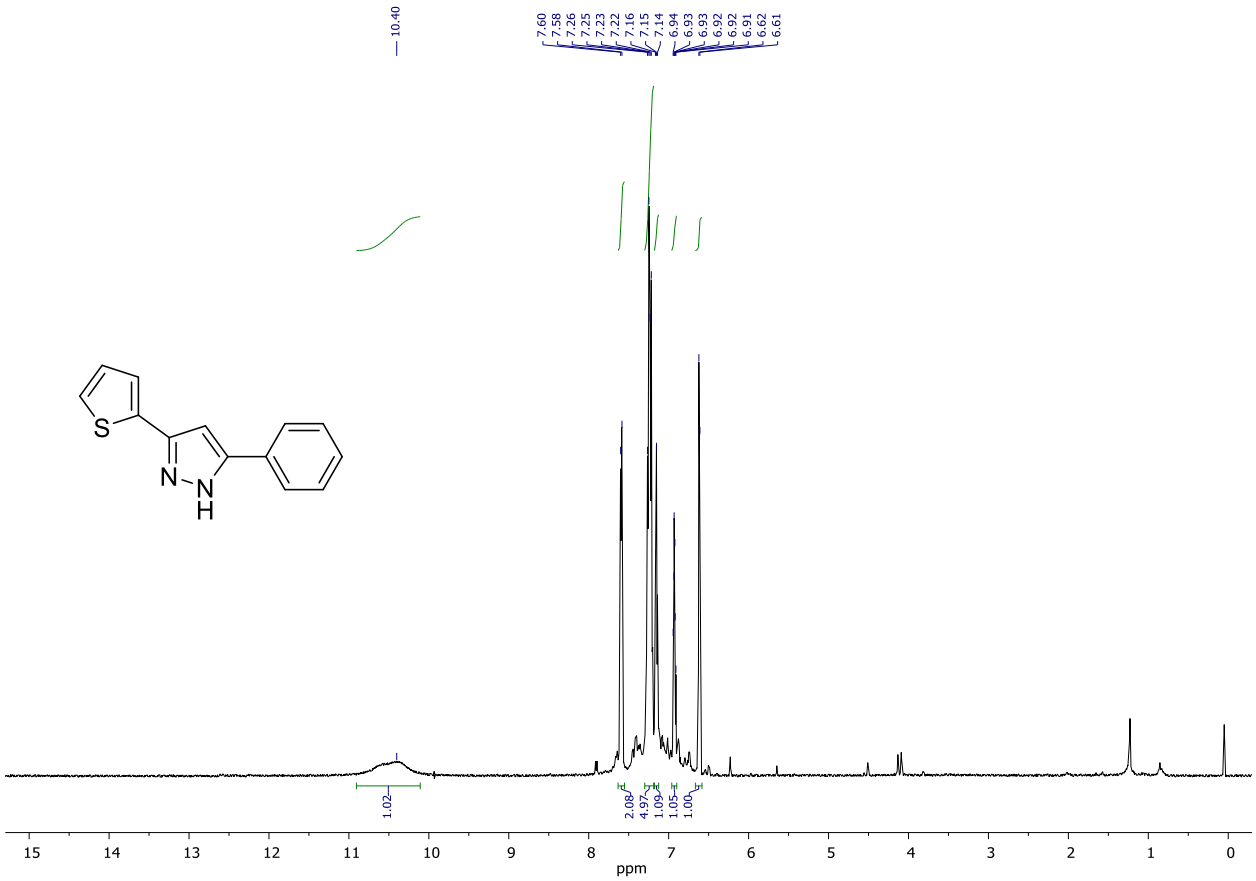
^{13}C{^{1}H} NMR Spectrum of **7da** (100.6 MHz, $CDCl_3$)



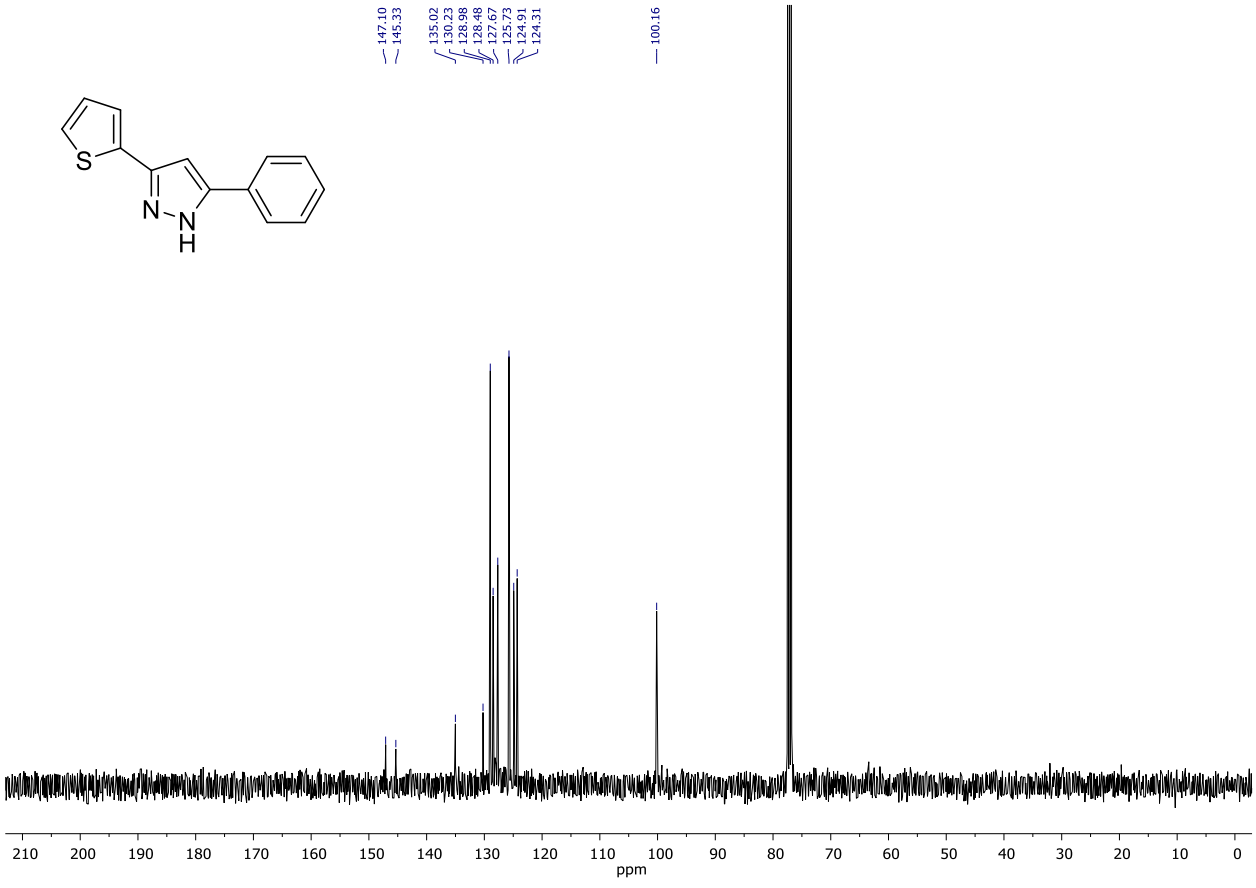
^{1}H NMR Spectrum of **7ea** (400.1 MHz, DMSO-d6)



^{13}C{^{1}H} NMR Spectrum of **7ea** (100.6 MHz, DMSO-d6)



^{1}H NMR Spectrum of **7ga** (400.1 MHz, $CDCl_3$)



^{13}C{^{1}H} NMR Spectrum of **7ga** (100.6 MHz, $CDCl_3$)