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Supplementary Information

Direct *N*-heterocyclization of hydrazines to access styrylated pyrazoles: Synthesis of 1,3,5-trisubstituted pyrazoles and dihydropyrazoles

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General Information. All reactions were carried out under microwave irradiation conditions. All solvents were purified and dried as per standard protocols. All reagents were obtained from commercial sources and used without purification. ^{1}H NMR spectra were obtained at 400 MHz or 500 MHz and recorded relative to tetramethylsilane signal (0 ppm). ^{13}C NMR spectra were obtained at 100 MHz or 125 MHz and chemical shifts were recorded relative to the $CDCl_3$ (77.0 ppm). Data for ^{1}H NMR are recorded as follows, chemical shift (δ, ppm). Multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet, br = broad singlet, coupling constant(s) in Hz, integration). Data for ^{13}C NMR were reported in terms of chemical shift (δ, ppm). The HRMS spectra were recorded on Agilent 6540 Ultra-High-Definition (UHD) Accurate-Mass Quadrupole Time-of-Flight (Q-TOF) liquid chromatography/mass spectrometry (LC/MS) system.

General Procedure for Synthesis of (E)-1-(4-Methoxyphenyl)-5-phenyl-3-styryl-1*H*-pyrazole. In a typical procedure, (4-methoxyphenyl) hydrazine hydrochloride (1 mmol), $Pd_2(dba)_3$ (0.5 equiv.) or $Pd(dba)_2$ (0.5 equiv.) in 1 mL of DMSO were placed in a 10 mL crimp-sealed thick-walled glass tube equipped with a pressure sensor and a magnetic stirrer. The reaction tube was placed in a microwave system and operated at 100 °C using 50 W for 5 min. After completion of the reaction (as monitored by TLC), the organic portion was extracted into ethyl acetate. Removal of the solvent under reduced pressure and flash column chromatography (*n*-hexane:ethyl acetate (95:5)) afforded the product as (*E*)1-(4-methoxyphenyl)-5-phenyl-3-styryl-1*H*-pyrazole.

General Procedure for Synthesis of (E)-1-(4-Methoxyphenyl)-5-phenyl-3-styryl-4,5,-dihydro-1*H*-pyrazole. In a typical procedure, (4-methoxyphenyl) hydrazine (1 mmol), $Pd_2(dba)_3$ (0.5 equiv.) or $Pd(dba)_2$ (0.5 equiv.) in 1 mL of H_2O were placed in a 10 mL crimp-sealed thick-walled glass tube equipped with a pressure sensor and a magnetic stirrer. The reaction tube was placed in a microwave system and operated at 100 °C using 50 W for 5 min. After completion of the reaction (as monitored by TLC), the organic portion was extracted into ethyl acetate. Removal of the solvent under reduced pressure and flash column chromatography (*n*-hexane:ethyl acetate (95:5)) afforded the product as 1-(4-methoxyphenyl)-5-phenyl-3-styryl-4,5-dihydro-1*H*-pyrazole.

General Procedure for Synthesis of 3,5-Dimethyl-1-phenyl-1*H*-pyrazole. In a typical procedure, phenyl hydrazine (1 mmol), $Cu(acac)_2$ (0.5 equiv.) in 1 mL of water were placed in a 10 mL crimp-sealed thick-walled glass tube equipped with a pressure sensor and a magnetic stirrer. The reaction tube was placed in a microwave system and operated at 100 °C

using 50 W for 5 min. After completion of the reaction (as monitored by TLC), the organic portion was extracted into ethyl acetate. Removal of the solvent under reduced pressure and flash column chromatography (*n*-hexane:ethyl acetate (95:5)) afforded the product as 3,5-dimethyl-1-phenyl-1*H*-pyrazole.

General Procedure for Synthesis of 3,5-Dimethyl-1-(phenylsulfonyl)-1*H*-pyrazole. In a typical procedure benzenesulfonohydrazide (1 mmol), $Cu(acac)_2$ (0.5 equiv.) in H_2O (1 mL) were placed in a 10 mL crimp-sealed thick-walled glass tube equipped with a pressure sensor and a magnetic stirrer. The reaction tube was placed in a microwave system and operated at 100 °C using 50 W for 5 min. After completion of the reaction (as monitored by TLC), the organic portion was extracted into ethyl acetate. Removal of the solvent under reduced pressure and flash column chromatography (*n*-hexane:ethyl acetate (95:5)) afforded the product as 3,5-dimethyl-1-(phenylsulfonyl)-1*H*-pyrazole.

^{1}H NMR, ^{13}C NMR, HRMS characterization data of compounds:

*(E)-5-Phenyl-3-styryl-1-(4-(trifluoromethoxy)phenyl)-1H-pyrazole (**2a**)*. Yellow solid, 292 mg, 71% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.46 (d, J = 7.3 Hz, 2H), 7.33-7.25 (m, 7H), 7.21 (m, 3H), 7.16-7.08 (m, 4H), 6.67 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 151.5, 147.6, 144.34, 138.4, 136.8, 131.1, 130.1, 128.74 (d, J = 2.4 Hz), 128.6, 127.9, 126.5, 126.2, 121.3, 120.1, 105.5; HRMS (ESI) calcd for $C_{24}H_{18}F_3N_2O$ [M+H$^+$] 407.1371, found 407.1367.

*(E)-4-(5-Phenyl-3-styryl-1H-pyrazol-1-yl)benzonitrile (**2b**)*. Yellow solid, 245 mg, 70% yield; ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 7.64 (d, J = 8.6 Hz, 2H), 7.57 (d, J = 7.7 Hz, 2H), 7.47 (d, J = 8.6 Hz, 2H), 7.42 (dd, J = 15.1, 6.9 Hz, 5H), 7.33 (d, J = 7.4 Hz, 1H), 7.32–7.29 (m, 3H), 7.24 (d, J = 3.8 Hz, 1H), 6.79 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ ppm 152.4, 144.5, 143.2, 136.7, 132.9, 131.9, 129.9, 129.0, 128.9, 128.8, 128.1, 126.6, 124.7; HRMS (ESI) calcd for $C_{24}H_{18}N_3$ [M+H$^+$] 348.1501, found 348.1505.

*(E)-1-(4-Methoxyphenyl)-5-phenyl-3-styryl-1H-pyrazole (**2c**)*. Yellow solid, 245 mg, 69% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.53 (d, J = 7.3 Hz, 2H), 7.36 (t, J = 7.5 Hz, 3H), 7.31 (dd, J = 6.5, 3.4 Hz, 3H), 7.28-7.24 (m, 3H), 7.23 (d, J = 2.1 Hz, 1H), 7.21 (d, J = 1.5 Hz, 2H), 6.86 (d, J = 2.1 Hz, 1H), 6.85 (d, J = 2.1 Hz, 1H), 6.72 (s, 1H), 3.81 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 158.8, 150.8, 144.1, 137.2, 133.3, 130.4, 128.7, 128.4, 128.2, 127.7, 126.6, 126.5, 120.5, 114.1, 104.5, 55.4; HRMS (ESI) calcd for $C_{24}H_{21}N_2O$ [M+H$^+$] 353.1654, found 353.1649.

*(E)-5-Phenyl-3-styryl-1-(2-(trifluoromethyl)phenyl)-1H-pyrazole (**2d**)*. Yellow solid, 310 mg, 76% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.75 (d, J = 8.3 Hz, 1H), 7.50 (d, J = 7.1 Hz, 2H), 7.45–7.37 (m, 2H), 7.37–7.32 (m, 2H), 7.29 (d, J = 7.2 Hz, 2H), 7.23–7.19 (m, 2H), 7.18 (s, 1H), 7.00 (dd, J = 16.7, 12.2 Hz, 2H), 6.87–6.81 (m, 2H), 6.70 (d, J = 17.1 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 145.7, 141.8, 139.1, 136.8, 135.5, 133.2, 132.6, 129.2, 129.0, 128.7, 128.0, 127.9, 126.9, 126.7, 126.1 (q, J = 5.3 Hz), 119.2, 116.8, 114.5; HRMS (ESI) calcd for $C_{24}H_{18}F_3N_2$ [M+H$^+$] 391.1422, found 391.1422.

*(E)-1-(3-Bromophenyl)-5-phenyl-3-styryl-1H-pyrazole (**2e**)*. Yellow solid, 278 mg, 72% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.44 (d, J = 7.8 Hz, 2H), 7.34 (dd, J = 13.1, 5.5 Hz, 5H), 7.30–7.23 (m, 5H), 7.21 (d, J = 4.7 Hz, 1H), 6.97 (t, J = 8.0 Hz, 1H), 6.87 (d, J = 7.2 Hz, 1H), 6.75 (d, J = 8.2 Hz, 1H), 6.57 (d, J = 16.3 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ ppm 162.6, 160.6, 151.2, 144.3, 137.0, 136.1, 130.9, 130.1, 128.7, 128.6, 128.5, 127.8, 126.9, 126.5, 120.1, 115.9, 115.8, 105.0; HRMS (ESI) calcd for $C_{23}H_{18}N_2$ Br [M+H$^+$] 401.0653, found 401.0662.

*(E)-1-(3-Chlorophenyl)-5-phenyl-3-styryl-1H-pyrazole (**2f**)*. Yellow solid, 280 mg, 78% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.36 (d, J = 7.4 Hz, 2H), 7.31–7.22 (m, 5H), 7.23–7.10 (m, 5H), 7.05 (t, J = 1.9 Hz, 1H), 6.96 (t, J = 8.1 Hz, 1H), 6.70–6.61 (m, 2H), 6.49 (d, J = 16.3 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ ppm 151.64, 144.37, 140.90, 136.93, 134.64, 131.27, 130.05, 129.78, 128.76, 128.73, 128.68, 127.95, 127.95, 127.49, 127.49, 126.60, 125.17, 123.09, 120.07, 105.54; HRMS (ESI) calcd for $C_{23}H_{18}ClN_2$ [M+H$^+$] 357.1159, found 357.1162.

*(E)-1-(3-Fluorophenyl)-5-phenyl-3-styryl-1H-pyrazole (**2g**)*. Yellow solid, 248 mg, 73% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.47 (d, J = 7.4 Hz, 2H), 7.37 (t, J = 7.3 Hz, 5H), 7.27 (dd, J = 18.8, 6.3 Hz, 5H), 7.10 (dd, J = 14.9, 8.1 Hz, 1H), 6.82 (d, J = 11.8 Hz, 1H), 6.71 (d, J = 8.1 Hz, 1H), 6.60 (d, J = 16.3 Hz, 1H), 6.53–6.46 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ ppm 151.5, 149.1, 144.3, 141.9, 136.9, 133.4, 131.2, 130.1, 129.2, 128.7, 126.6, 125.7, 121.3, 120.6, 120.0, 114.2, 112.5, 112.3, 105.2; HRMS (ESI) calcd for $C_{23}H_{18}N_2F$ [M+H$^+$] 341.1454, found 341.1458.

*(E)-1-(4-Bromophenyl)-5-phenyl-3-styryl-1H-pyrazole (**2h**)*. Yellow solid, 262 mg, 70% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.47 (d, J = 7.4 Hz, 2H), 7.37 (t, J = 7.6 Hz, 5H), 7.32–7.27 (m, 5H), 7.25 (d, J = 4.8 Hz, 2H), 6.90 (d, J = 8.9 Hz, 2H), 6.59 (d, J = 16.3 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 151.5, 144.2, 138.9, 136.9, 132.0, 131.1, 128.7, 128.6, 126.5, 126.4, 120.0, 114.9, 105.5; HRMS (ESI) calcd for $C_{23}H_{18}N_2$ Br [M+H$^+$] 401.0653, found 401.0685.

*(E)-1-(4-Fluorophenyl)-5-phenyl-3-styryl-1H-pyrazole (**2i**)*. Yellow solid, 220 mg, 64% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.43 (d, J = 7.5 Hz, 1H), 7.33 (t, J = 6.2 Hz, 2H), 7.29–7.22 (m, 2H), 7.21 (d, J = 3.5 Hz, 1H), 6.93 (dd, J = 9.1, 4.6 Hz, 1H), 6.86 (t, J = 8.7 Hz, 1H), 6.53 (d, J = 16.3 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ ppm 144.3, 141.7, 136.4, 133.2, 131.2, 129.3, 128.8, 128.6, 128.3, 126.7, 126.6, 125.7, 121.9, 120.0, 116.5, 111.5, 105.5; HRMS (ESI) calcd for $C_{23}H_{18}N_2F$ [M+H$^+$] 341.1454, found 341.1460.

*(E)-1-(4-Chlorophenyl)-5-phenyl-3-styryl-1H-pyrazole (**2j**).*[1] Yellow solid, 244 mg, 67% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.37 (d, J = 7.4 Hz, 1H), 7.27 (t, J = 7.4 Hz, 2H), 7.23–7.17 (m, 2H), 7.14 (d, J = 3.9 Hz, 1H), 7.03 (d, J = 9.0 Hz, 1H), 6.85 (d, J = 9.0 Hz, 1H), 6.48 (d, J = 16.3 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ ppm 149.3, 145.1, 136.4, 133.5, 131.2, 129.3, 128.8, 128.7, 128.3, 128.0, 126.6, 125.7, 123.5, 121.9, 121.3, 120.0, 116.3, 111.5, 105.5; HRMS (ESI) calcd for $C_{23}H_{18}ClN_2$ [M+H$^+$] 357.1159, found 357.1164.

*(E)-1,5-Diphenyl-3-styryl-1H-pyrazole (**2k**)*. Yellow solid, 239 mg, 74% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.37 (d, J = 7.5 Hz, 2H), 7.27 (dd, J = 13.5, 6.0 Hz, 5H), 7.20 (dd, J = 13.8, 5.9 Hz, 5H), 7.16–7.12 (m, 1H), 7.09 (d, J = 7.6 Hz, 1H), 6.94 (d, J = 8.0 Hz, 1H), 6.70 (dd, J = 14.0, 6.7 Hz, 2H), 6.46 (d, J = 16.3 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ ppm 151.1, 144.2, 139.9, 137.0, 130.4, 128.9, 128.8, 128.7, 128.4, 128.3, 127.7, 127.4, 126.5, 125.1, 120.4, 105.0; HRMS (ESI) calcd for $C_{23}H_{19}N_2$ [M+H$^+$] 323.1548, found 323.1559.

*(E)-5-Phenyl-3-styryl-1-(4-(trifluoromethoxy)phenyl)-4,5-dihydro-1H-pyrazole (**2l**)*. Yellow solid, 322 mg, 79% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.37 (d, J = 7.4 Hz, 2H), 7.31–7.23 (m, 4H), 7.23–7.17 (m, 4H), 7.12 (d, J = 16.4 Hz, 1H), 6.97–6.86 (m, 4H), 6.49 (d, J = 16.3 Hz, 1H), 5.22–5.05 (m, 1H), 3.65 (dd, J = 16.8, 12.3 Hz, 1H), 2.95(dd, J = 16.3, 8.2 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ ppm 152.4, 144.5, 134.9, 133.3, 132.9, 131.9, 129.4, 128.9, 128.8, 128.1, 126.8, 126.6, 125.5, 124.7, 120.8, 113.0, 106.6, 50.9, 42.4. HRMS (ESI) calcd for $C_{24}H_{20}F_3N_2O$ [M+H$^+$] 409.1528, found 409.1583.

*(E)-4-(5-Phenyl-3-styryl-4,5-dihydro-1H-pyrazol-1-yl)benzonitrile (**2m**)*. Yellow solid, 285 mg, 81% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.59–7.52 (m, 1H), 7.47 (d, J = 7.2 Hz, 1H), 7.42–7.36 (m, 2H), 7.36–7.30 (m, 3H), 7.31–7.25 (m, 3H), 7.25–7.20 (m, 2H), 7.15 (dd, J = 8.6, 2.3 Hz, 2H), 6.92 (d, J = 8.9 Hz, 1H), 6.57 (d, J = 16.4 Hz, 1H), 5.24 (dd, J = 12.2, 5.6 Hz, 1H), 3.70 (dd, J = 16.9, 12.2 Hz, 1H), 3.02 (dd, J = 17.0, 5.5 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ ppm 151.5, 147.9, 144.3, 138.3, 136.9, 131.2, 128.7, 127.9, 126.6, 126.2, 121.4, 120.0, 105.4, 63.9, 42.3; HRMS (ESI) calcd for $C_{24}H_{20}N_3$ [M+H$^+$] 350.1657, found 350.1453.

*(E)-1-(3-Bromophenyl)-5-phenyl-3-styryl-4,5-dihydro-1H-pyrazole (**2n**)*. Yellow solid, 336 mg, 83% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.44 (d, J = 7.8 Hz, 2H), 7.36–7.32 (m, 5H), 7.28–7.21 (m, 5H), 6.97 (t, J = 8.0 Hz, 1H), 6.87 (d, J = 7.2 Hz, 1H), 6.75 (d, J = 8.9 Hz, 1H), 6.57 (d, J = 16.3 Hz, 1H), 5.22 (dd, J = 12.2, 6.4 Hz, 1H), 3.72 (dd, J = 16.8, 12.4 Hz, 1H), 3.03 (dd, J = 16.8, 6.4 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ ppm 162.6, 160.6, 151.2, 144.3, 130.9, 128.7, 128.6, 128.5, 127.8, 127.0, 126.9, 126.5, 120.1, 115.9, 115.8, 105.0, 64.8, 42.4; HRMS (ESI) calcd for $C_{23}H_{20}BrN_2$ [M+H$^+$] 403.0810, found 403.0760.

*(E)-1-(3-Chlorophenyl)-5-phenyl-3-styryl-4,5-dihydro-1H-pyrazole (**2o**)*. Yellow solid, 318 mg, 88% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.36 (d, J = 7.4 Hz, 2H), 7.27 (t, J = 7.4 Hz, 4H), 7.22–7.13 (m, 6H), 7.05 (t, J = 1.9 Hz, 1H), 6.96 (t, J = 8.1 Hz, 1H), 6.65–6.67 (m, 1H), 6.49 (d, J = 16.3 Hz, 1H), 5.15 (dd, J = 12.2, 6.4 Hz, 1H), 3.64 (dd, J = 16.8, 12.3 Hz, 1H), 2.95 (dd, J = 16.9, 6.4 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ ppm 151.6, 144.3, 140.9, 136.9, 134.6, 131.2, 130.0, 129.7, 128.7, 128.7, 128.6, 127.9, 127.9, 127.4, 127.4, 126.6, 125.1, 123.0, 120.0, 59.5, 39.9; HRMS (ESI) calcd for $C_{23}H_{20}ClN_2$ [M+H$^+$] 359.1315, found 359.1218.

*(E)-1-(3-Fluorophenyl)-5-phenyl-3-styryl-4,5-dihydro-1H-pyrazole (**2p**)*. Yellow solid, 261 mg, 76% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.47 (d, J = 7.4 Hz, 1H), 7.37 (t, J = 7.3 Hz, 4H), 7.30–7.24 (m, 6H), 7.10 (dd, J = 14.9, 8.1 Hz, 1H), 6.82 (d, J = 11.8 Hz, 1H), 6.72–6.70 (m, 1H), 6.60 (d, J = 16.3 Hz, 1H), 6.49 (m, 1H), 5.26 (dd, J = 12.2, 6.5 Hz, 1H), 3.76 (dd, J = 16.8, 12.3 Hz, 1H), 3.06 (dd, J = 16.8, 6.4 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ ppm 151.5, 149.1, 144.3, 141.9, 136.9, 133.4, 131.2, 129.2, 128.7, 126.6, 125.7, 121.3, 120.6, 120.0, 114.2, 105.2, 64.0, 42.4; HRMS (ESI) calcd for $C_{23}H_{20}FN_2$ [M+H$^+$] 343.1611, found 343.1625.

*(E)-1-(4-Bromophenyl)-5-phenyl-3-styryl-4,5-dihydro-1H-pyrazole (**2q**)*. Yellow solid, 345 mg, 85% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.47 (d, J = 7.4 Hz, 2H), 7.37 (t, J = 7.6 Hz, 3H), 7.32-7.24 (m, 8H), 6.90 (d, J = 8.9 Hz, 2H), 6.59 (d, J = 16.3 Hz, 1H), 5.25 (dd, J = 12.3, 6.6 Hz, 1H), 3.75 (dd, J = 16.8, 12.3 Hz, 1H), 3.06 (dd, J = 16.9, 6.6 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ ppm 151.5, 144.2, 138.9, 136.9, 132.0, 131.1, 128.7, 128.6, 126.5, 126.4, 120.0, 114.9, 105.5, 64.0, 42.3; HRMS (ESI) calcd for $C_{23}H_{20}BrN_2$ [M+H$^+$] 403.0810, found 403.0735.

*(E)-1-(4-Fluorophenyl)-5-phenyl-3-styryl-4,5-dihydro-1H-pyrazole (**2r**)*. Yellow solid, 276 mg, 80% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.43 (d, J = 7.5 Hz, 1H), 7.33 (t, J = 6.2 Hz, 4H), 7.28–7.17 (m, 6H), 6.93 (m, 2H), 6.86 (t, J = 8.7 Hz, 2H), 6.53 (d, J = 16.3 Hz, 1H), 5.17 (dd, J = 12.2, 7.4 Hz, 1H), 3.70 (dd, J = 16.7, 12.3 Hz, 1H), 3.01 (dd, J = 16.8, 7.3 Hz,

1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ ppm 144.3, 141.7, 136.4, 133.5, 129.3, 126.7, 126.6, 125.7, 121.9, 121.3, 120.0, 116.3, 111.5, 105.5, 63.9, 42.3. HRMS (ESI) calcd for $C_{23}H_{20}FN_2$ [M+H$^+$] 343.1611, found 343.1318.

*(E)-1-(4-Chlorophenyl)-5-phenyl-3-styryl-4,5-dihydro-1H-pyrazole (**2s**).* Yellow solid, 299 mg, 83% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.37 (d, J = 7.4 Hz, 2H), 7.29–7.25 (m, 4H), 7.23–7.16 (m, 5H), 7.15–7.11 (m, 1H), 7.03 (d, J = 9.0 Hz, 1H), 6.85 (d, J = 9.0 Hz, 2H), 6.48 (d, J = 16.3 Hz, 1H), 5.15 (dd, J = 12.3, 6.7 Hz, 1H), 3.65 (dd, J = 16.8, 12.4 Hz, 1H), 2.96 (dd, J = 16.8, 6.7 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ ppm 151.5, 144.2, 131.1, 129.1, 128.8, 128.7, 128.6, 128.6, 127.9, 126.6, 120.1, 105.4, 31.6, 29.7; HRMS (ESI) calcd for $C_{23}H_{20}ClN_2$ [M+H$^+$] 359.1315, found 359.1108.

*(E)-1,5-Diphenyl-3-styryl-4,5-dihydro-1H-pyrazole (**2t**).*[2] Yellow solid, 289 mg, 89% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.46 (d, J = 7.4 Hz, 1H), 7.37 (d, J = 7.5 Hz, 2H), 7.29–7.25 (m, 5H), 7.23–7.15 (m, 5H), 6.94 (d, J = 8.0 Hz, 2H), 6.70 (dd, J = 14.0, 6.7 Hz, 1H), 6.46 (d, J = 16.3 Hz, 1H), 5.19 (dd, J = 12.3, 6.8 Hz, 1H), 3.65 (dd, J = 16.6, 12.4 Hz, 1H), 2.95 (dd, J = 16.7, 6.8 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ ppm 151.1, 144.2, 139.9, 137.0, 130.4, 128.9, 128.8, 128.7, 128.4, 128.3, 127.7, 127.4, 126.5, 125.1, 120.4, 105.0, 64.0, 42.3 HRMS (ESI) calcd for $C_{23}H_{21}N_2$ [M+H$^+$] 343.1705, found 325.1538.

*3, 5-Dimethyl-1-phenyl-1H-pyrazole (**3a**).*[3] Light yellow oil, 166 mg, 96% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.38–7.32 (m, 4H), 7.27–7.23 (m, 1H), 5.91 (s, 1H), 2.22 (s, 3H), 2.21 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 148.9, 139.9, 139.3, 129.0, 127.2, 124.7, 106.9, 13.5, 12.4; HRMS (ESI) calcd for $C_{11}H_{13}N_2$ [M+H$^+$] 173.1079, found 173.1081

*1-(2-Chlorophenyl)-3,5-dimethyl-1H-pyrazole (**3b**).* Light yellow oil, 176 mg, 85% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.46–7.40 (m, 1H), 7.34–7.26 (m, 3H), 5.92 (s, 1H), 2.23 (s, 3H), 2.04 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 149.4, 141.2, 137.5, 132.5, 130.1, 129.9, 127.5, 105.5, 13.6, 11.2; HRMS (ESI) calcd for $C_{11}H_{12}ClN_2$ [M+H$^+$] 207.0689, found 207.0682.

*1-(3-Chlorophenyl)-3,5-dimethyl-1H-pyrazole (**3c**).* Light yellow oil, 179 mg, 86% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.48 (s, 1H), 7.39–7.23 (m, 3H), 5.99 (s, 1H), 2.31 (s, 3H), 2.28 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 149.4, 140.9, 139.4, 134.6, 129.9, 127.1, 124.7, 122.3, 107.6, 13.5, 12.5; HRMS (ESI) calcd for $C_{11}H_{12}ClN_2$ [M+H$^+$] 207.0689, found 207.0694.

*1-(4-Chlorophenyl)-3,5-dimethyl-1H-pyrazole (**3d**).*[4] Light yellow oil, 180 mg, 87% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.26 (q, J = 9.0 Hz, 4H), 5.87 (s, 1H), 2.17 (s, 3H), 2.16 (s,

3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 149.3, 139.3, 138.46, 132.7, 129.1, 125.7, 107.3, 13.5, 12.4; HRMS (ESI) calcd for $C_{11}H_{12}ClN_2$ [M+H$^+$] 207.0689, found 207.0694.

*1-(3-Fluorophenyl)-3,5-dimethyl-1H-pyrazole (**3e**).* Light yellow oil, 169 mg, 89% yield; ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 7.33 (td, J = 8.2, 6.3 Hz, 1H), 7.19–7.09 (m, 2H), 6.99–6.92 (m, 1H), 5.94 (s, 1H), 2.26 (s, 3H), 2.22 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ ppm 162.3 (d, J = 277.3 Hz), 149.4, 141.1, 130.1 (d, J = 9.1 Hz), 119.9 (d, J = 3.1 Hz), 114.0 (d, J = 21.1 Hz), 112.0 (d, J = 24.4 Hz), 107.5, 13.5, 12.5; HRMS (ESI) calcd for $C_{11}H_{12}FN_2$ [M+H$^+$] 191.0985, found 191.1006.

*4-(3,5-Dimethyl-1H-pyrazol-1-yl)-6-hydrazinylquinoline (**3f**).* Light yellow oil, 257 mg, 85% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 9.13 (s, 1H), 8.10 (s, 1H), 7.93–7.79 (m, 2H), 7.52 (d, J = 33.9 Hz, 1H), 7.39 (s, 1H), 2.37 (s, 3H), 2.19 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 142.9, 142.5, 133.7, 133.6, 132.0, 131.4, 127.5, 126.3, 122.1, 121.8, 114.0, 13.6, 11.8. HRMS (ESI) calcd for $C_{14}H_{13}BrN_3$ [M+H$^+$] 302.0293, found 302.0297.

*1-(4-Bromophenyl)-3,5-dimethyl-1H-pyrazole(**3g**).*[3,5] Colourless liquid, 238 mg, 95% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.49 (d, J = 8.5 Hz, 2H), 7.24 (d, J = 8.5 Hz, 2H), 5.93 (s, 1H), 2.23 (s, 3H), 2.21 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 149.4, 139.4, 138.9, 132.1, 132.0, 126.0, 120.7, 119.4, 107.4, 13.5, 12.4; HRMS (ESI) calcd for $C_{11}H_{12}BrN_2$ [M+H$^+$] 251.0182, found 251.0183.

*3,5-Dimethyl-1-(2-(trifluoromethyl)phenyl)-1H-pyrazole (**3h**).* Light yellow oil, 210 mg, 87% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.80 (d, J = 7.7 Hz, 1H), 7.65 (t, J = 7.5 Hz, 1H), 7.58 (t, J = 7.6 Hz, 1H), 7.35 (d, J = 7.6 Hz, 1H), 5.97 (s, 1H), 2.28 (s, 3H), 2.05 (s, 3H); ^{19}F NMR (376 MHz, $CDCl_3$) δ ppm -60.56 (s, 3F); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 149.0, 141.3, 137.6, 132.5, 130.6, 129.4, 128.5 (d, J = 36 Hz), 127.2 (q, J = 5 Hz), 122.9 (q, J = 272 Hz), 105.4, 13.5, 11.2; HRMS (ESI) calcd for $C_{12}H_{12}F_3N_2$ [M+H$^+$] 241.0953, found 241.0949.

*3,5-Dimethyl-1-(4-(trifluoromethyl)phenyl)-1H-pyrazole(**3i**).*[6] Light yellow oil, 215 mg, 89% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.63 (d, J = 8.4 Hz, 2H), 7.51 (d, J = 8.3 Hz, 2H), 5.96 (s, 1H), 2.29 (s, 3H), 2.23 (s, 3H); ^{19}F NMR (376 MHz, $CDCl_3$) δ ppm -62.37; ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 149.9, 142.7, 139.5, 128.8 (d, J = 32.8 Hz), 126.2 (q, J = 3.7 Hz), 124.1, 123.9 (d, J = 271 Hz), 108.1, 13.4, 12.6; HRMS (ESI) calcd for $C_{12}H_{12}F_3N_2$ [M+H$^+$] 241.0953, found 241.0951.

*3,5-Dimethyl-1-(4-(trifluoromethoxy)phenyl)-1H-pyrazole (**3j**).* Light yellow oil, 226 mg, 85% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.48 (d, J = 8.7 Hz, 2H), 7.30 (d, J = 8.4 Hz, 2H), 6.02 (s, 1H), 2.32 (s, 3H), 2.30 (s, 3H); ^{19}F NMR (376 MHz, $CDCl_3$) δ ppm -58.06 (s,

3F); ^{13}C NMR (125 MHz, $CDCl_3$) δ ppm 149.4, 147.8, 139.4, 138.4, 125.8, 121.5, 120.4 (q, J = 256.2 Hz), 107.4, 13.4, 12.3; HRMS (ESI) calcd for $C_{11}H_{12}N_3O_2$ [M+H$^+$] 218.0930, found 218.0922.

*4-(3,5-Dimethyl-1H-pyrazol-1-yl)benzonitrile (**3k**).*[7] Colourless solid, 180 mg, 91% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.71 (d, J = 8.5 Hz, 2H), 7.59 (d, J = 8.5 Hz, 2H), 6.04 (s, 1H), 2.37 (s, 3H), 2.27 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 150.4, 143.4, 139.6, 133.0, 123.8, 118.3, 109.9, 108.9, 13.4, 12.9; HRMS (ESI) calcd for $C_{12}H_{12}N_3$ [M+H$^+$] 198.1031, found 198.1037.

*3,5-Dimethyl-1-(3-nitrophenyl)-1H-pyrazole (**3l**).* Yellow oil, 192 mg, 88% yield; ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 8.27 (t, J = 2.1 Hz, 1H), 8.15–8.10 (m, 1H), 7.81–7.76 (m, 1H), 7.57 (t, J = 8.1 Hz, 1H), 5.99 (s, 1H), 2.33 (s, 3H), 2.23 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 150.4, 148.5, 141.0, 139.7, 129.9, 129.7, 121.4, 118.8, 108.4, 13.5, 12.7; HRMS (ESI) calcd for $C_{11}H_{12}N_3O_2$ [M+H$^+$] 218.0930, found 218.0922.

*1-(4-Methoxyphenyl)-3,5-dimethyl-1H-pyrazole (**3m**).*[8,9] Light yellow oil, 195 mg, 96% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.32 (d, J = 8.6 Hz, 2H), 6.95 (d, J = 8.7 Hz, 2H), 5.96 (s, 1H), 3.83 (s, 3H), 2.29 (s, 3H), 2.24 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 158.7, 148.5, 139.4, 133.0, 126.3, 114.1, 106.2, 55.5, 13.5, 12.1; HRMS (ESI) calcd for $C_{12}H_{15}N_2O$ [M+H$^+$] 203.1184, found 203.1166.

*3,5-Dimethyl-1-(p-tolyl)-1H-pyrazole (**3n**).*[3,8] Light yellow oil, 174 mg, 93% yield; ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 7.30 (d, J = 8.3 Hz, 2H), 7.23 (d, J = 8.1 Hz, 2H), 5.98 (s, 1H), 2.39 (s, 3H), 2.29 (s, 3H), 2.27 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 148.7, 139.3, 137.4, 137.1, 129.4, 124.7, 106.6, 21.1, 13.4, 12.2; HRMS (ESI) calcd for $C_{12}H_{15}N_2$ [M+H$^+$] 187.1235, found 187.1248.

*1-(3,4-Dimethylphenyl)-3,5-dimethyl-1H-pyrazole (**3o**).*[10] Light yellow oil, 185 mg, 93% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.24 (s, 1H), 7.20 (d, J = 7.9 Hz, 1H), 7.13 (d, J = 7.9 Hz, 1H), 5.99 (s, 1H), 2.32 (s, 9H), 2.29 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 148.5, 139.3, 137.6, 137.5, 135.8, 129.8, 126.0, 122.0, 106.4, 19.8, 19.4, 13.5, 12.3; HRMS (ESI) calcd for $C_{13}H_{17}N_2$ [M+H$^+$] 201.1392, found 201.1396.

*1-(Benzo[d][1,3]dioxol-5-yl)-3,5-dimethyl-1H-pyrazole (**3p**).*[9] Colourless liquid, 176 mg, 81% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 6.83 (s, 1H), 6.77 (s, 2H), 5.95 (s, 2H), 5.88 (s, 1H), 2.21 (s, 3H), 2.18 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 148.6, 147.8, 146.9, 139.6, 134.1, 118.6, 107.9, 106.7, 106.4, 101.7, 13.5, 12.1; HRMS (ESI) calcd for $C_{12}H_{13}N_2O_2$ [M+H$^+$] 217.0977, found 217.0983.

*Butyl 4-(3,5-dimethyl-1H-pyrazol-1-yl)benzoate (**3q**)*. Light yellow oil, 245 mg, 90% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 8.12 (d, J = 8.5 Hz, 2H), 7.54 (d, J = 8.4 Hz, 2H), 6.03 (s, 1H), 4.34 (t, J = 6.6 Hz, 2H), 2.36 (s, 3H), 2.30 (s, 3H), 1.76 (dd, J = 14.5, 6.9 Hz, 2H), 1.49 (dq, J = 14.6, 7.4 Hz, 2H), 0.99 (t, J = 7.4 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ ppm 166.0, 149.8, 143.5, 139.5, 130.5, 128.6, 123.5, 108.1, 65.0, 30.7, 19.2, 13.7, 13.5, 12.8; HRMS (ESI) calcd for $C_{16}H_{21}N_2O_2$ [M+H$^+$] 273.1603, found 273.1598.

*1-(Anthracen-2-yl)-3,5-dimethyl-1H-pyrazole (**3r**)*. Light yellow oil, 226 mg, 83% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 8.38 (d, J = 7.7 Hz, 2H), 8.01 (d, J = 9.0 Hz, 1H), 7.96-7.87 (m, 3H), 7.55 (d, J = 9.0 Hz, 1H), 7.46-7.38 (m, 2H), 5.99 (s, 1H), 2.35 (s, 3H), 2.28 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ ppm149.3, 139.7, 136.8, 132.1, 131.9, 131.1, 130.2, 129.5, 128.2, 128.0, 126.5, 126.4, 125.8, 125.6, 123.4, 121.9, 107.2, 13.6, 12.7; HRMS (ESI) calcd for $C_{19}H_{17}N_2$ [M+H$^+$] 273.1392, found 273.1408.

*3,5-Dimethyl-1-tosyl-1H-pyrazole (**5a**).*[11] White solid, 232 mg, 92% yield; ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 7.84 (d, J = 8.1 Hz, 2H), 7.31 (d, J = 8.1 Hz, 2H), 5.90 (s, 1H), 2.50 (s, 3H), 2.42 (s, 3H), 2.20 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ ppm 151.9, 143.6, 142.5, 133.8, 128.4, 126.0, 109.2, 20.2, 12.3, 11.6. MS (ESI) calcd for $C_{12}H_{15}N_2SO_2$[M+H$^+$] 251.0, found 251.1.

*3,5-Dimethyl-1-((2,3,4,5,6-pentamethylphenyl)sulfonyl)-1H-pyrazole (**5b**)*. White solid, 285 mg, 93% yield; ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 5.90 (s, 1H), 2.49 (s, 6H), 2.40 (s, 3H), 2.29 (s, 3H), 2.24 (s, 6H), 2.18 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ ppm 151.5, 143.4, 141.5, 136.1, 134.9, 109.4, 18.5, 18.0, 17.0, 13.8, 12.8; HRMS (ESI) calcd for $C_{16}H_{23}N_2SO_2$[M+H$^+$] 307.1480, found 307.1479.

*1-((4-Methoxyphenyl)sulfonyl)-3,5-dimethyl-1H-pyrazole (**5c**)*. White solid, 239 mg, 89% yield; ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 7.89 (d, J = 8.2 Hz, 2H), 6.97 (d, J = 8.3 Hz, 2H), 5.90 (s, 1H), 3.86 (s, 3H), 2.49 (s, 3H), 2.20 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ ppm 163.9, 154.2, 144.5, 129.8, 114.4, 111.6, 55.7, 13.8, 13.1; HRMS (ESI) calcd for $C_{12}H_{15}N_2SO_3$[M+H$^+$] 267.0803, found 267.0824.

*1-((3,4-Dimethoxyphenyl)sulfonyl)-3,5-dimethyl-1H-pyrazole (**5d**).*[12] White solid, 268 mg, 90% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.58 (d, J = 8.4 Hz, 1H), 7.42 (s, 1H), 6.93 (d, J = 8.5 Hz, 1H), 5.91 (s, 1H), 3.93 (s, 3H), 3.92 (s, 3H), 2.49 (s, 3H), 2.21 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 153.6, 149.1, 129.7, 121.7, 110.5, 110.0, 56.2, 29.6, 13.8; MS (ESI) calcd for $C_{13}H_{17}N_2SO_4$[M+H$^+$] 297.0, found 297.1.

*1-((2-Bromo-6-methoxyphenyl)sulfonyl)-3,5-dimethyl-1H-pyrazole (**5e**)*. White solid, 335 mg, 97% yield; ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 8.23 (d, J = 2.4 Hz, 1H), 7.66 (dd, J = 8.8, 2.5

Hz, 1H), 6.84 (d, *J* = 8.8 Hz, 1H), 5.90 (s, 1H), 3.78 (s, 3H), 2.59 (s, 3H), 2.17 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ ppm 156.1, 138.6, 133.5, 127.7, 114.0, 112.6, 109.3, 56.3, 29.7, 13.8; HRMS (ESI) calcd for $C_{12}H_{14}BrN_2SO_3$[M+H$^+$] 344.9909, found 344.9913.

*1-((4-Fluorophenyl)sulfonyl)-3,5-dimethyl-1H-pyrazole (**5f**).* White solid, 215 mg, 95% yield; ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 8.06–7.92 (m, 2H), 7.24–7.14 (m, 2H), 5.92 (s, 1H), 2.50 (s, 3H), 2.21 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ ppm 165.3, 163.3, 152.4, 142.8, 132.7, 129.1, 129.0, 115.3, 115.1, 109.5, 12.3, 11.7; HRMS (ESI) calcd for $C_{11}H_{12}BrN_2SO_3$[M+H$^+$] 255.0604, found 255.0601.

*3,5-Dimethyl-1-((3-(trifluoromethyl)phenyl)sulfonyl)-1H-pyrazole (**5g**).* Colorless Liquid, 257 mg, 83% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 8.23 (s, 1H), 8.16 (d, *J* = 7.7 Hz, 1H), 7.88 (d, *J* = 7.7 Hz, 1H), 7.69 (t, *J* = 7.6 Hz, 1H), 5.98 (s, 1H), 2.52 (s, 3H), 2.20 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 136.9, 129.6, 129.3, 128.4, 128.2, 128.2 (d, *J* = 3.4 Hz), 127.7, 122.2, 122.2 121.5, 119.3, 11.3, 10.7; HRMS (ESI) calcd for $C_{12}H_{12}FN_2SO_2$[M+H$^+$] 305.0572, found 305.0578.

*3,5-Dimethyl-1-((4-(trifluoromethoxy)phenyl)sulfonyl)-1H-pyrazole (**5h**).* Colorless liquid, 285 mg, 89% yield; ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 8.03 (d, *J* = 9.0 Hz, 2H), 7.35 (d, *J* = 8.1 Hz, 2H), 5.94 (s, 1H), 2.52 (s, 3H), 2.22 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ ppm 153.8, 152.7, 144.0, 135.9, 129.6, 120.5, 110.7, 13.5, 12.8; HRMS (ESI) calcd for $C_{12}H_{12}F_3N_2SO_3$[M+H$^+$] 321.0521, found 321.0501.

*3,5-Dimethyl-1-((2-(trifluoromethoxy)phenyl)sulfonyl)-1H-pyrazole (**5i**).* Colorless liquid, 263 mg, 82% yield; NMR (500 MHz, $CDCl_3$) δ ppm 8.23-8.22 (m, 1H), 7.72-7.61 (m, 1H), 7.53-7.43 (m, 1H), 7.41-7.31 (m, 1H), 5.94 (s, 1H), 2.57 (s, 3H), 2.15 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ ppm 153.8, 146.4, 145.8, 135.9, 131.9, 130.0, 126.5, 119.7 (d, *J* = 2.2 Hz), 109.9, 13.7, 13.0; HRMS (ESI) calcd for $C_{12}H_{12}F_3N_2SO_3$[M+H$^+$] 321.0501, found 321.0508.

*1-((3,5-Bis(trifluoromethoxy)phenyl)sulfonyl)-3,5-dimethyl-1H-pyrazole (**5j**).* Colorless liquid, 356 mg, 88% yield; ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 8.42 (s, 2H), 8.11 (s, 1H), 5.98 (s, 1H), 2.54 (s, 3H), 2.22 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ ppm 155.3, 144.9, 140.7, 133.1 (q, *J* = 34.8 Hz), 128.0 (d, *J* = 3.3 Hz), 127.5 (m, Hz), 125.4, 123.3, 121.1, 111.7, 13.8, 13.2; HRMS (ESI) calcd for $C_{13}H_{11}F_6N_2SO_4$[M+H$^+$] 405.0344, found 405.0341.

*4-((3,5-Dimethyl-1H-pyrazol-1-yl)sulfonyl)benzonitrile (**5k**).* White solid, 240 mg, 91% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 8.07 (d, *J* = 8.4 Hz, 2H), 7.82 (d, *J* = 8.4 Hz, 2H), 7.27 (s, 1H), 2.51 (s, 3H), 2.20 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ ppm 166.8, 164.8, 153.9, 144.2, 133.0, 130.5, 128.3, 116.7, 116.6, 111.5, 13.8, 13.1; HRMS (ESI) calcd for $C_{12}H_{12}N_3SO_2$[M+H$^+$] 262.0650, found 262.0652.

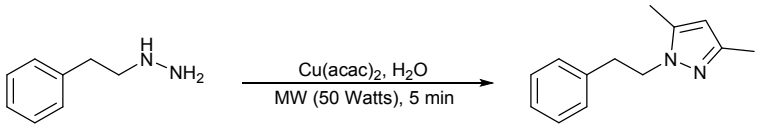
*3,5-Dimethyl-1-(naphthalen-2-ylsulfonyl)-1H-pyrazole (**5l**).* White solid, 253 mg, 88% yield; ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 8.59 (s, 1H), 8.00 (d, J = 8.1 Hz, 1H), 7.95 (d, J = 8.8 Hz, 1H), 7.91-7.86 (m, 2H), 7.66 (m, 2H), 5.90 (s, 1H), 2.55 (s, 3H), 2.20 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ ppm 153.4, 144.0, 135.1, 134.9, 131.7, 129.4, 129.4, 129.3, 129.2, 127.7, 127.6, 121.9, 110.6, 13.6, 13.0; HRMS (ESI) calcd for $C_{15}H_{15}N_2SO_2$[M+H$^+$] 287.0854, found 287.0856.

*3,5-Dimethyl-1-(phenylsulfonyl)-1H-pyrazole (**5m**).*[13] White solid, 215 mg, 91% yield; ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 7.96 (d, J = 7.7 Hz, 2H), 7.62 (t, J = 7.2 Hz, 1H), 7.54-7.51 (m, 2H), 5.91 (s, 1H), 2.50 (s, 3H), 2.21 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ ppm 153.6, 144.2, 138.2, 134.0, 129.3, 127.5, 110.9, 13.8, 13.2; MS (ESI) calcd for $C_{11}H_{13}N_2SO_2$[M+H$^+$] 237.0, found 237.1.

*Sildenafil-pyrazole analogue: 5-(5-((3,5-dimethyl-1H-pyrazol-1-yl)sulfonyl)-2-ethoxyphenyl)-1-methyl-3-propyl-1,6-dihydro-7H-pyrazolo[4,3-d]pyrimidin-7-one (**Figure 1**).* Off-white solid, 165 mg, 70% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 10.73 (s, 1H), 8.98 (s, 1H), 8.10 (dd, J = 7.7, 3.2 Hz, 1H), 7.15 (d, J = 7.7 Hz, 1H), 5.96 (s, 1H), 4.37 (q, 6.8 Hz, 2H), 4.27 (s, 3H), 2.93 (t, J = 7.2 Hz, 2H), 2.58 (s, 3H), 2.21 (s, 3H), 1.89–1.83 (m, 2H), 1.62 (t, J = 6.8 Hz, 3H), 1.04 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 161.5, 155.0, 147.5, 133.8, 133.2, 132.9, 132.4, 132.4, 123.2, 122.7, 114.7, 67.6, 39.7, 29.2, 23.7, 15.9, 15.4, 15.3, 14.6. HRMS (ESI) calcd for $C_{22}H_{27}N_6SO_4$[M+H$^+$] 471.1814, found 471.1829.

Reaction with Alkyl hydrazine (Phenethylhydrazine hydrochloride)

3,5-dimethyl-1-phenethyl-1*H*-pyrazole



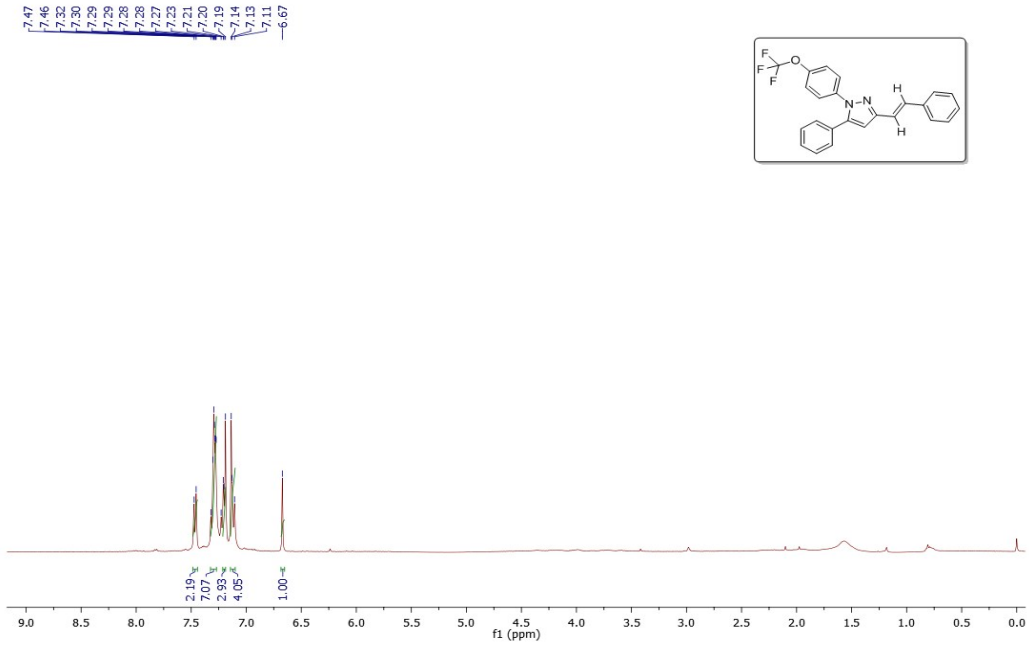
traces

In a typical procedure phenethylhydrazine hydrochloride[14] (1 mmol), $Cu(acac)_2$ (0.5 equiv.) in H_2O (1 mL) were placed in a 10 mL crimp-sealed thick-walled glass tube equipped with a pressure sensor and a magnetic stirrer. The reaction tube was placed in a microwave system and operated at 100 °C using 50 W for 5 min. After completion of the reaction (as monitored by TLC), the organic portion was extracted into ethyl acetate. Removal of the solvent under reduced pressure and flash column chromatography (*n*-hexane:ethyl acetate (95:5)) afforded the product as 3,5-dimethyl-1-phenethyl-1*H*-pyrazole. Off-white semisolid, traces. ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.20-7.33 (m, 5H), 4.93 (s, 1H), 3.45-3.90 (m, 2H), 2.86-2.89 (m, 2H), 2.00 (s, 3H), 1.90 (s, 3H). MS (ESI) calcd for $C_{13}H_{17}N_2$ [M+H$^+$] 201.13, found 204.0.

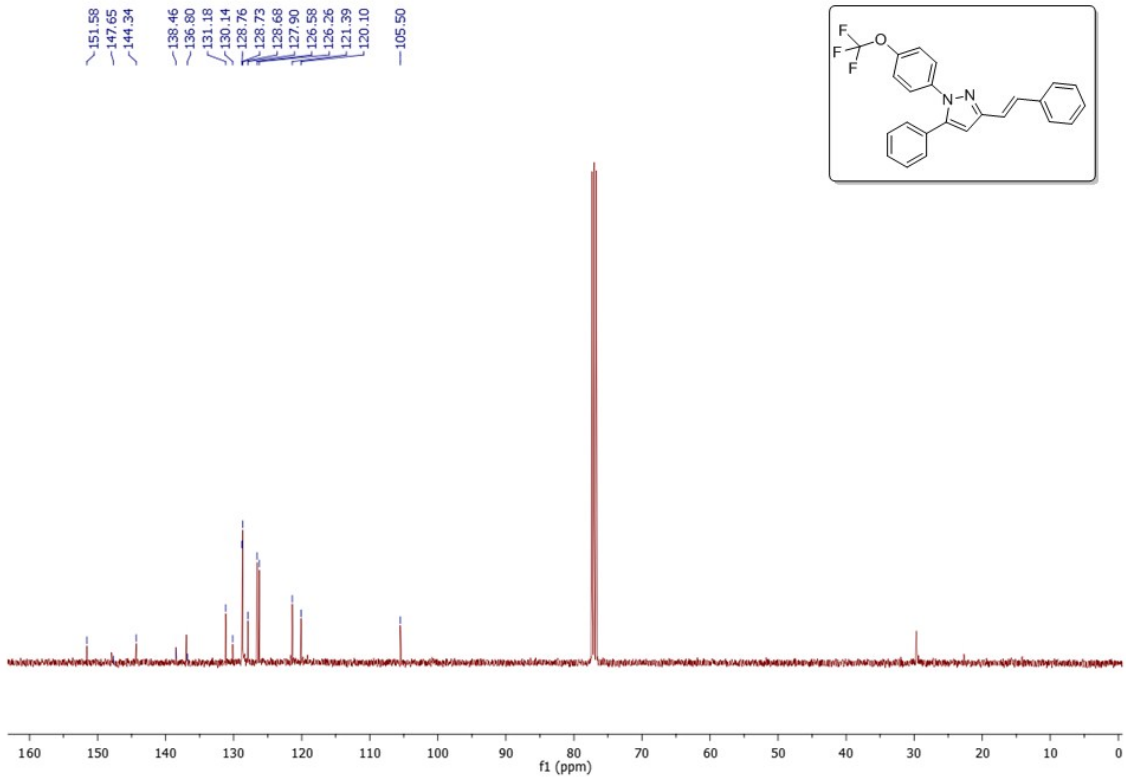
^{1}H and ^{13}C NMR spectra

*(E)-5-Phenyl-3-styryl-1-(4-(trifluoromethoxy)phenyl)-1H-pyrazole (**2a**)*

^{1}H NMR

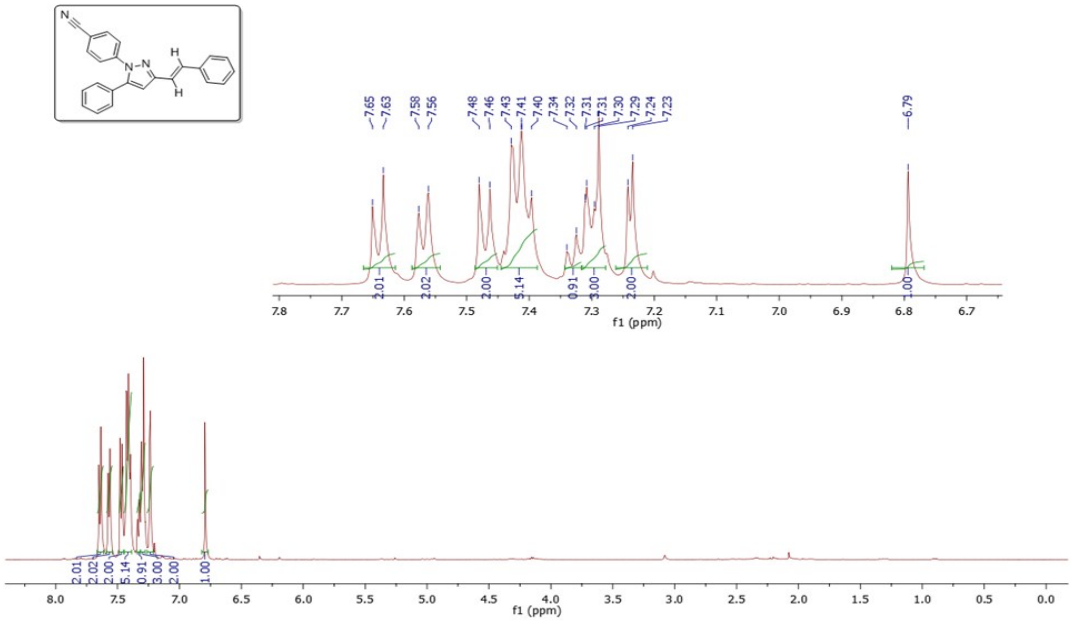


^{13}C NMR

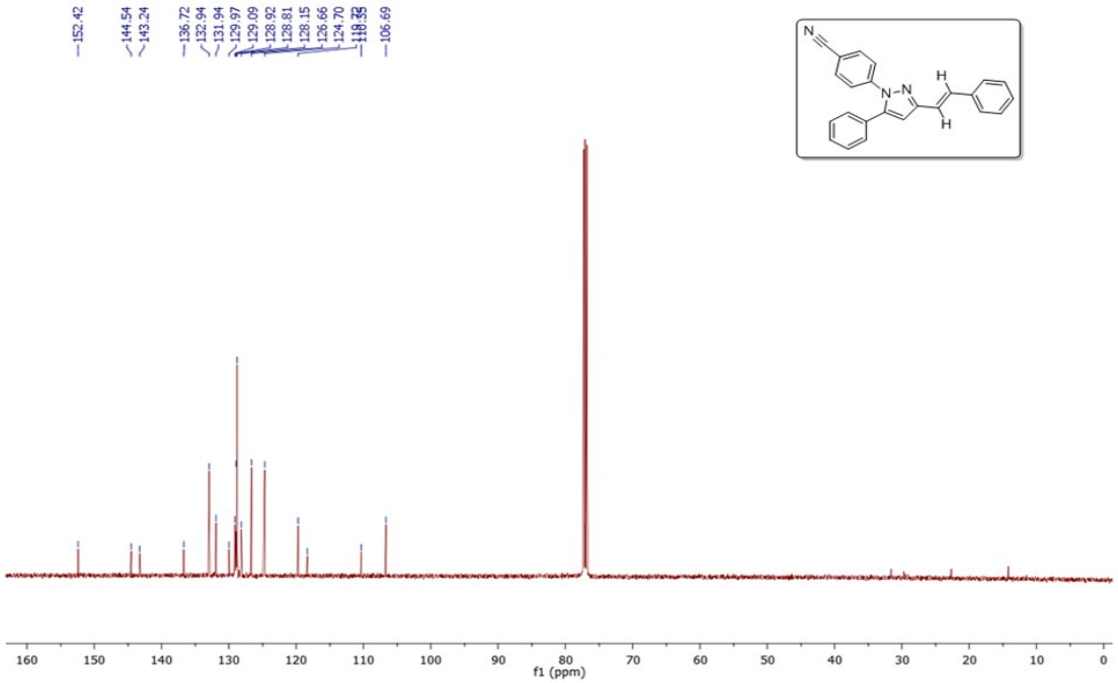


*(E)-4-(5-Phenyl-3-styryl-1H-pyrazol-1-yl)benzonitrile (**2b**)*

^{1}H NMR

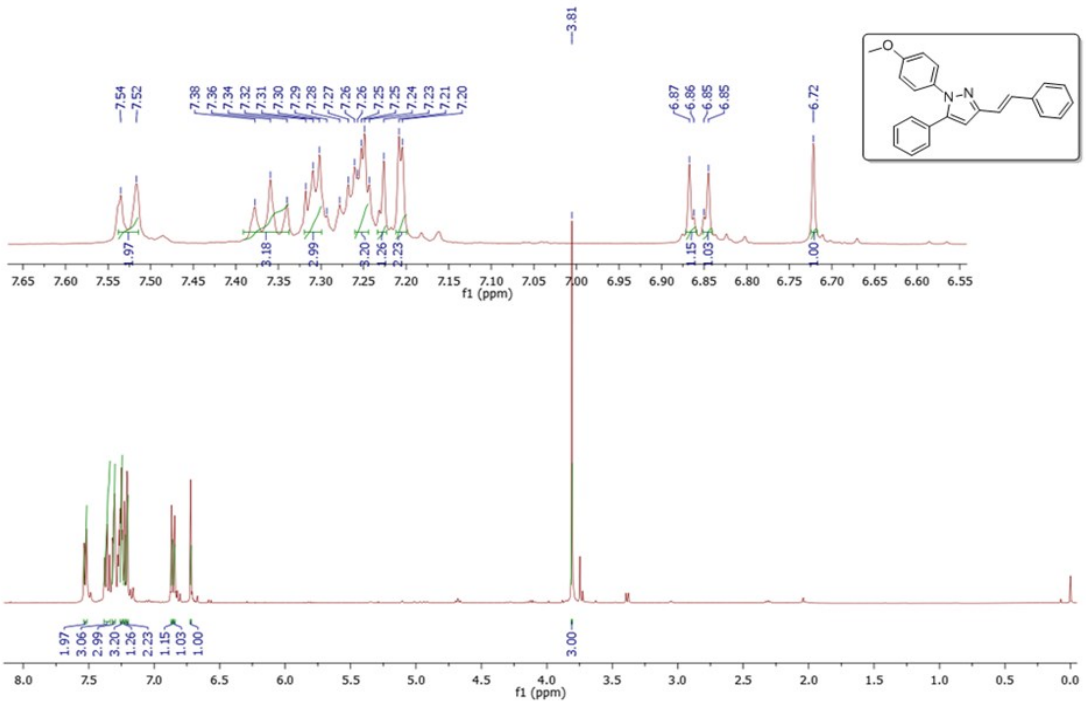


^{13}C NMR

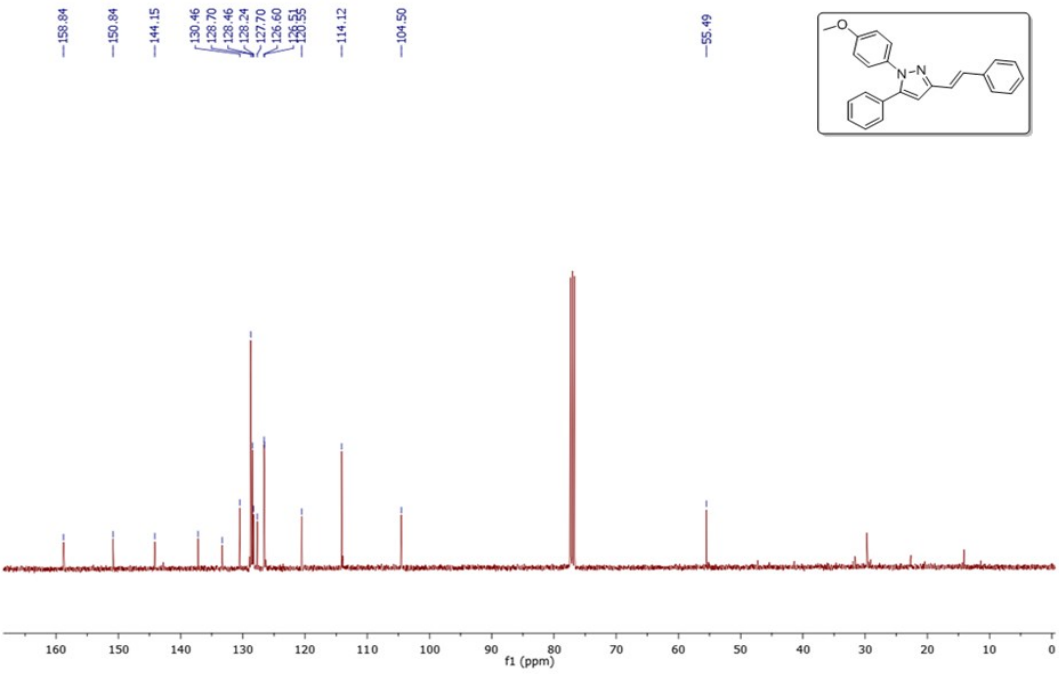


*(E)-1-(4-Methoxyphenyl)-5-phenyl-3-styryl-1H-pyrazole (**2c**)*

^{1}H NMR

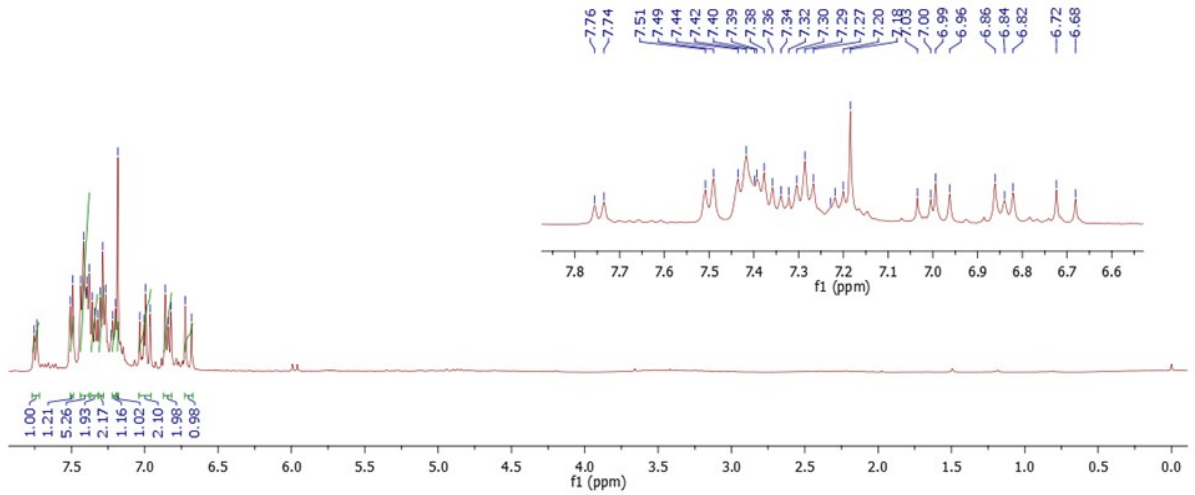


^{13}C NMR

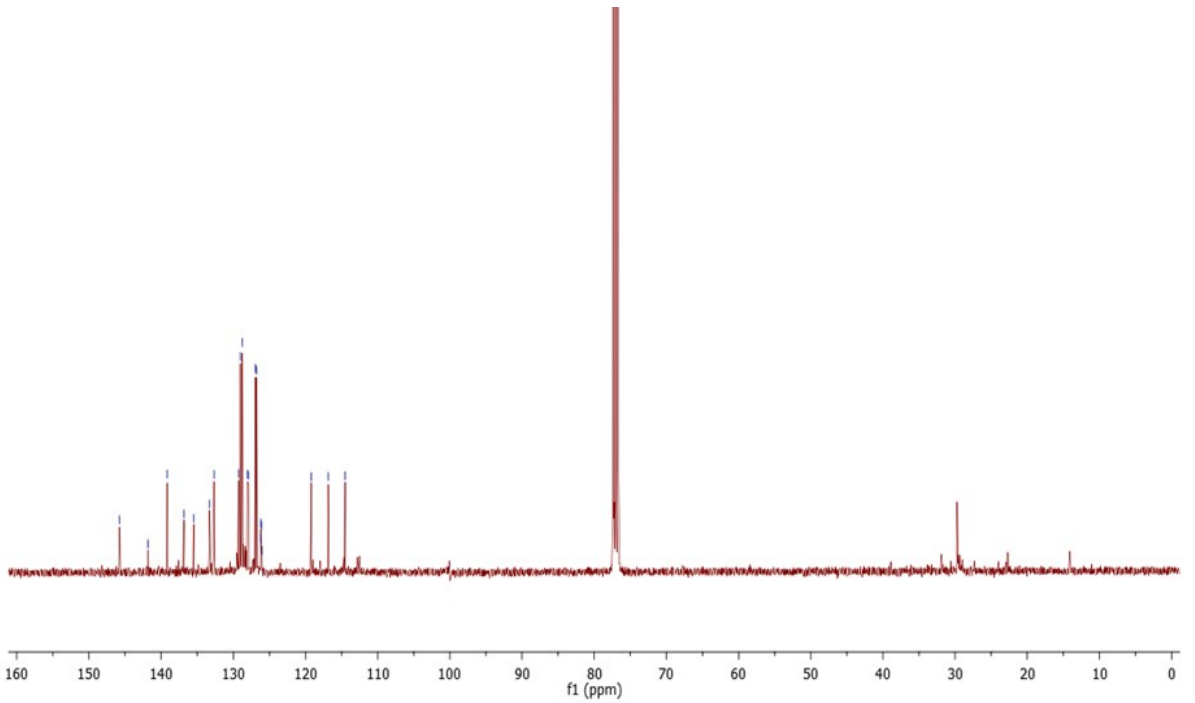


*(E)-5-Phenyl-3-styryl-1-(2-(trifluoromethyl)phenyl)-1H-pyrazole (**2d**)*

^{1}H NMR

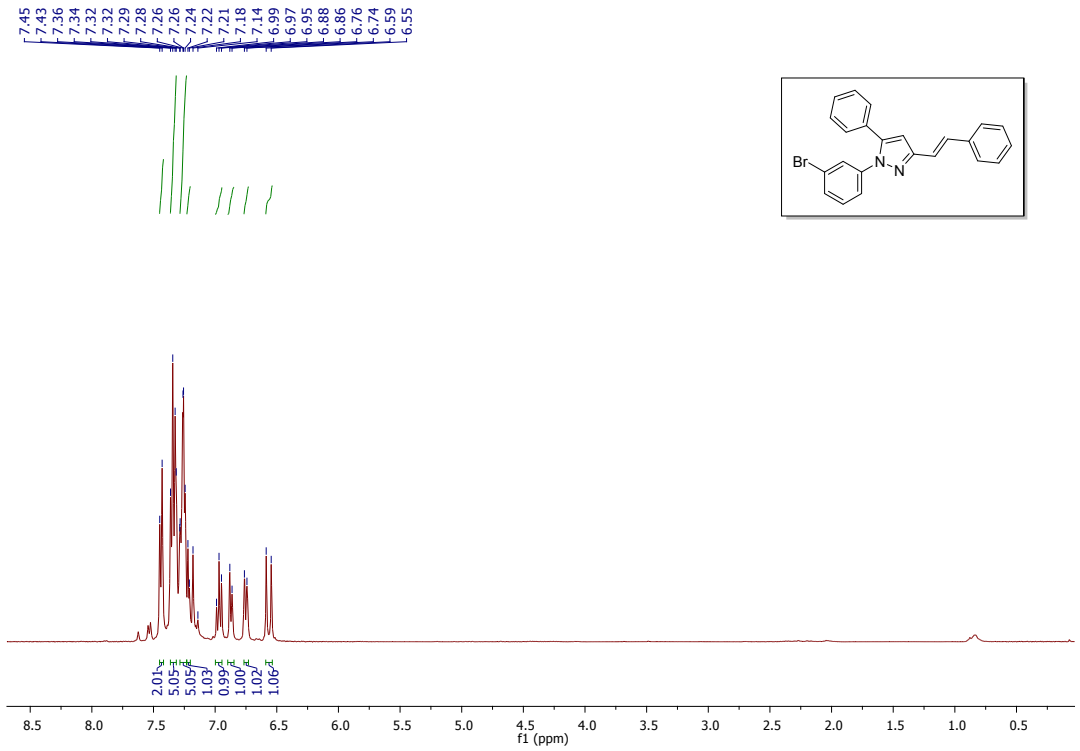


^{13}C NMR

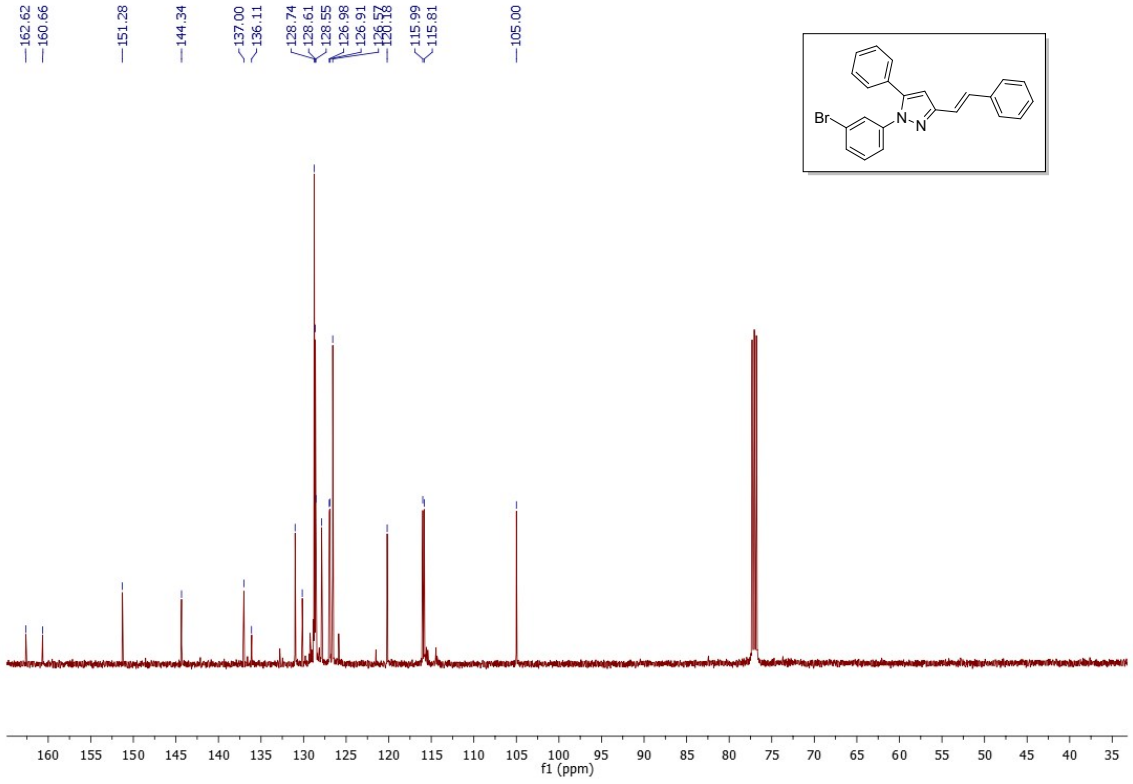


*(E)-1-(3-Bromophenyl)-5-phenyl-3-styryl-1H-pyrazole (**2e**)*

^{1}H NMR

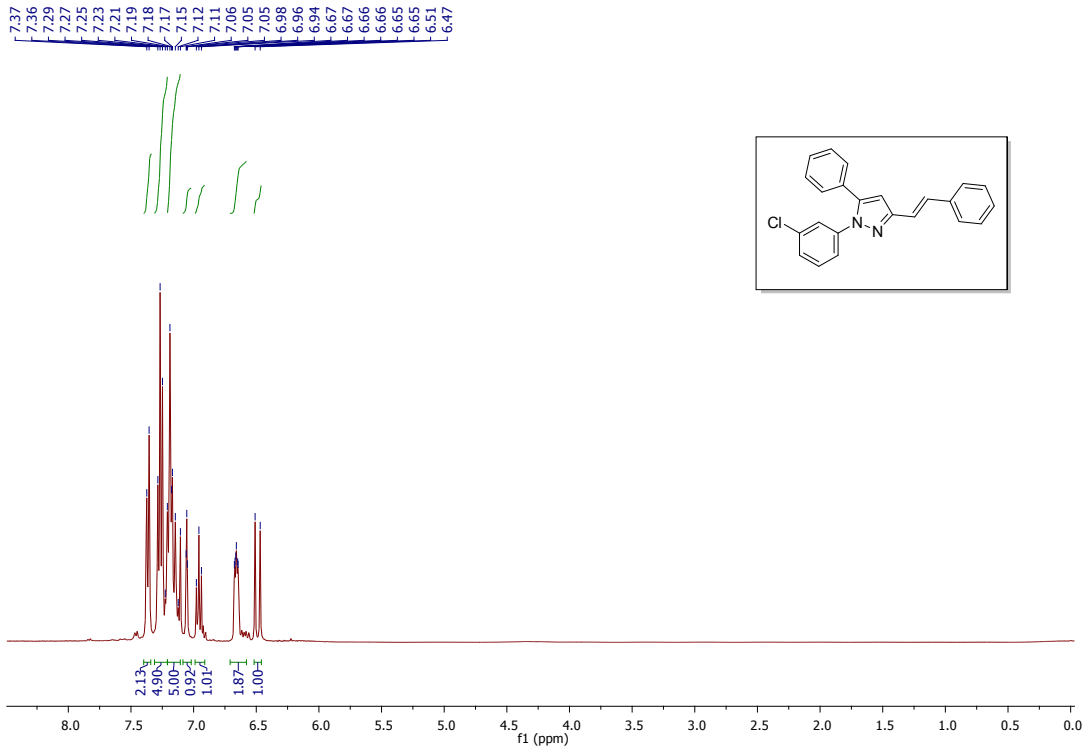


^{13}C NMR

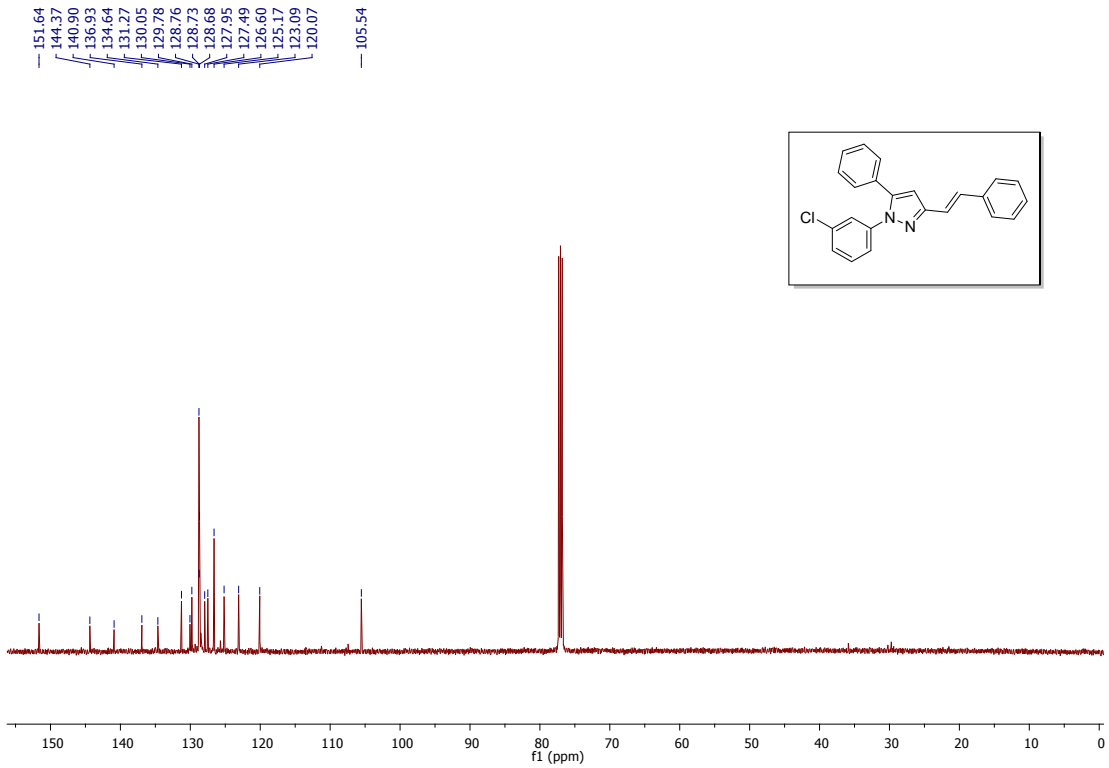


*(E)-1-(3-Chlorophenyl)-5-phenyl-3-styryl-1H-pyrazole (**2f**)*

^{1}H NMR

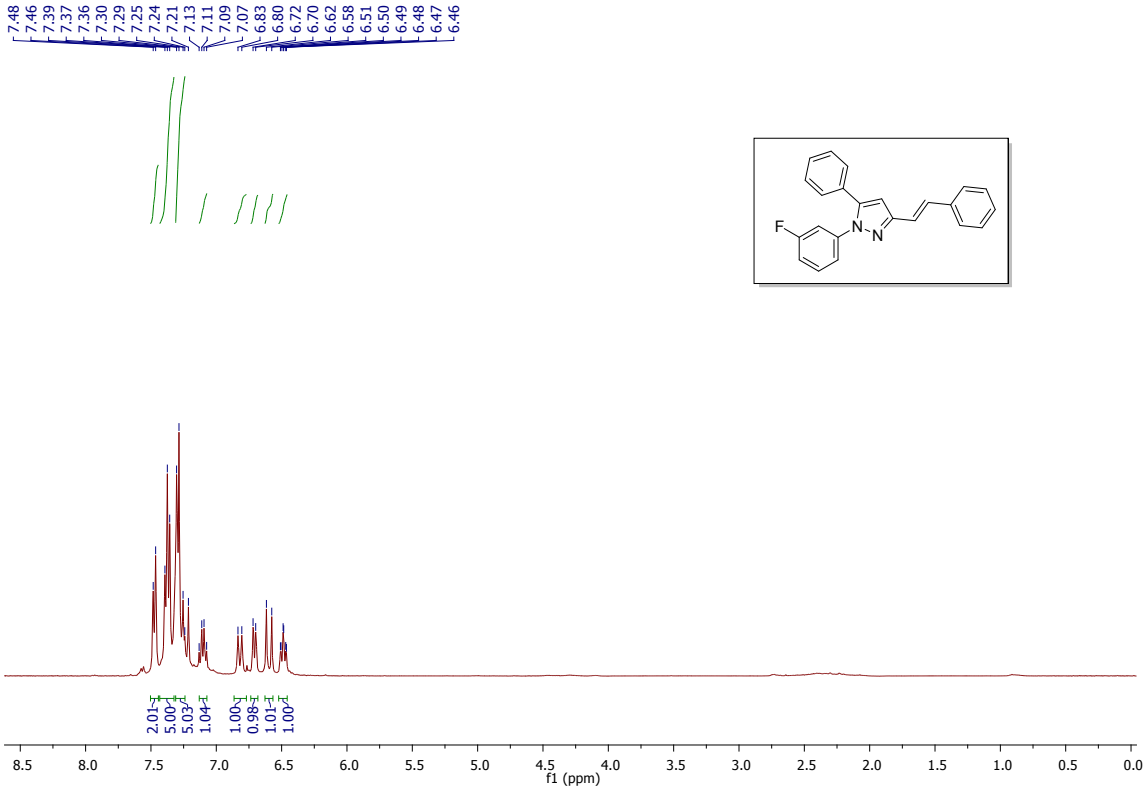


^{13}C NMR

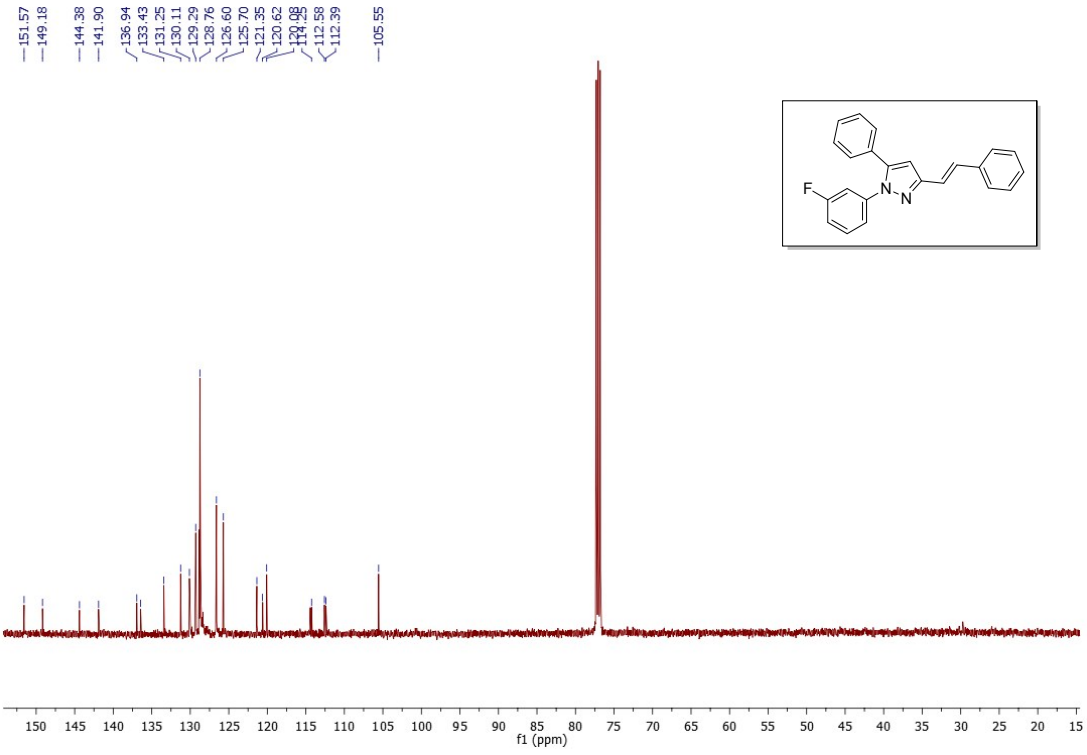


*(E)-1-(3-Fluorophenyl)-5-phenyl-3-styryl-1H-pyrazole (**2g**)*

^{1}H NMR

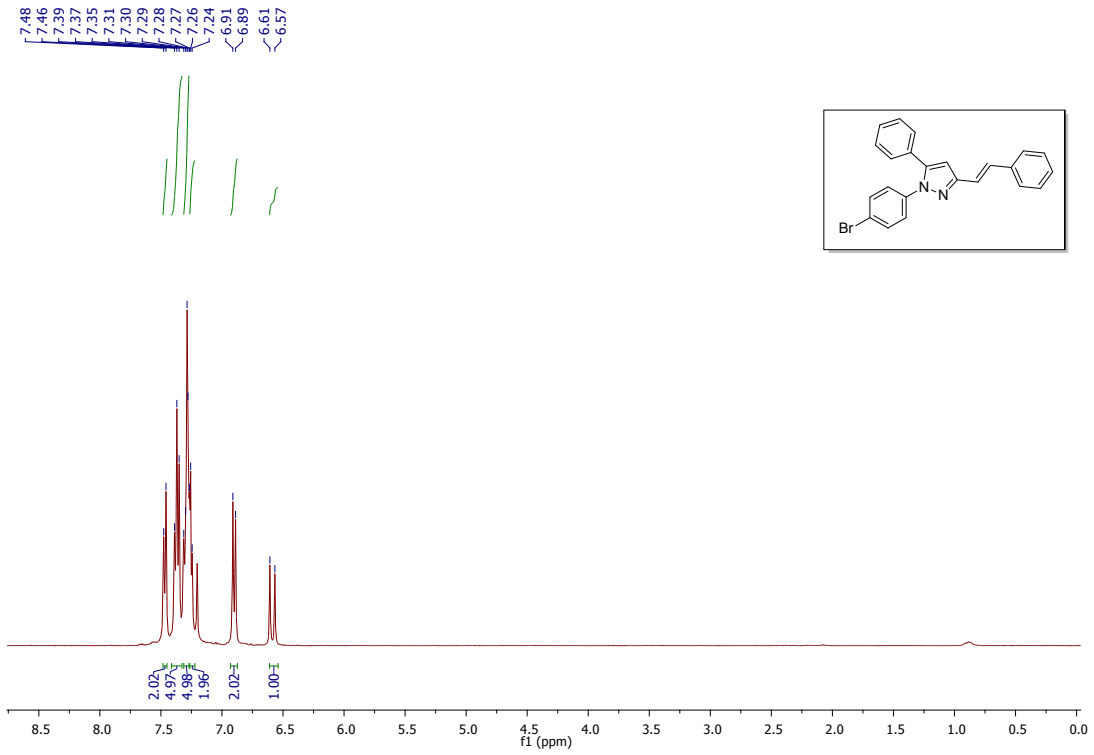


^{13}C NMR

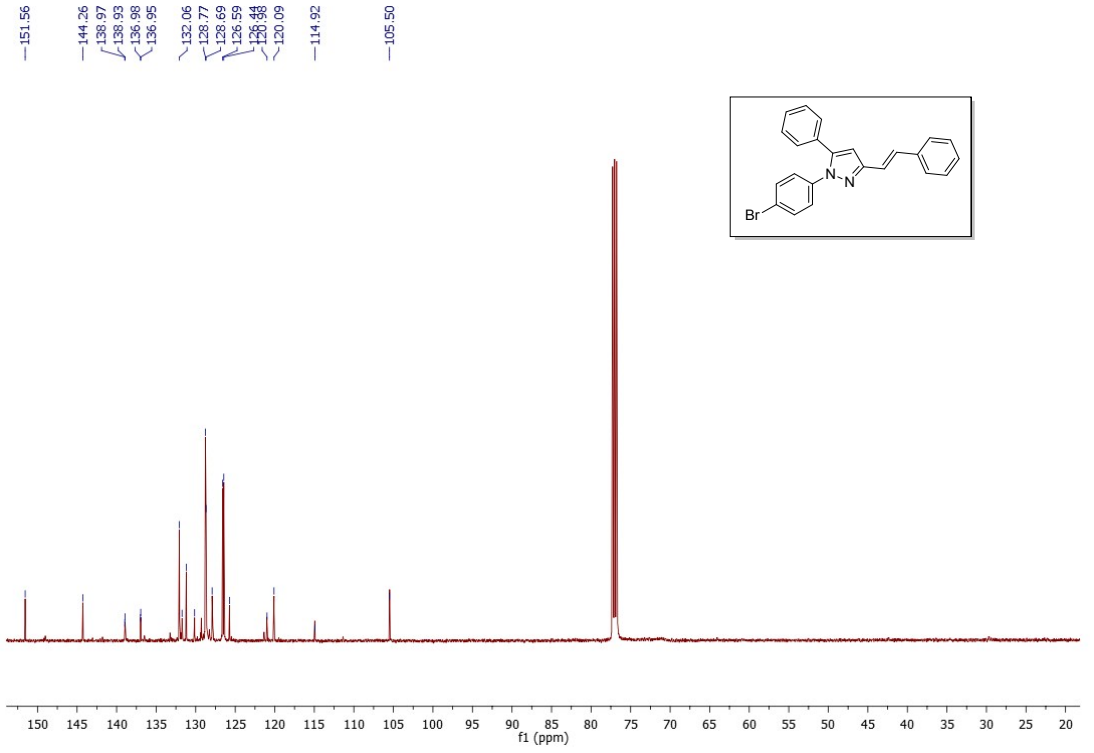


*(E)-1-(4-Bromophenyl)-5-phenyl-3-styryl-1H-pyrazole (**2h**)*

^{1}H NMR

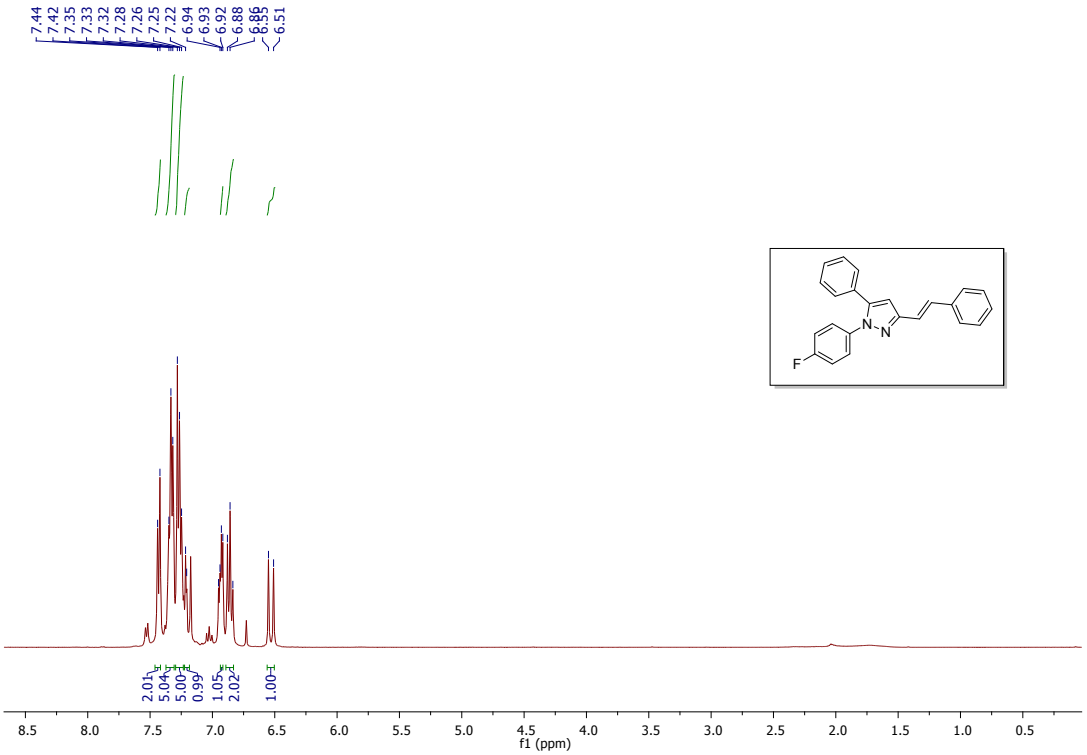


^{13}C NMR

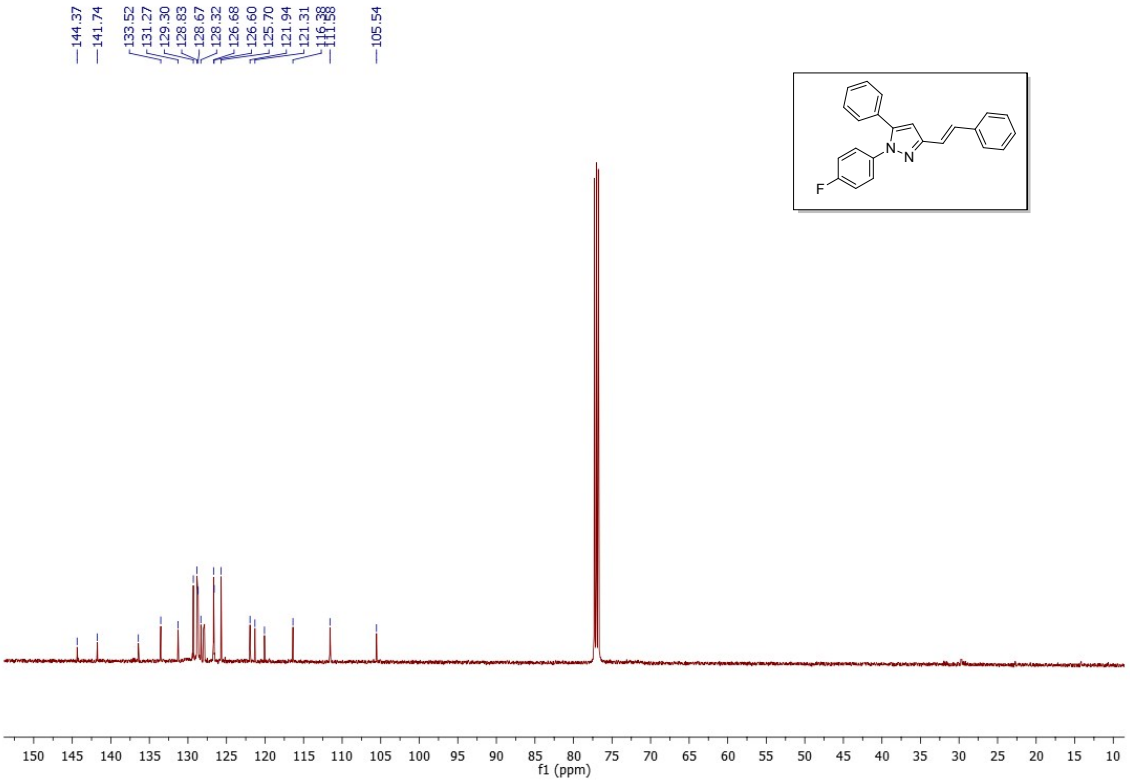


*(E)-1-(4-Fluorophenyl)-5-phenyl-3-styryl-1H-pyrazole (**2i**)*

^{1}H NMR

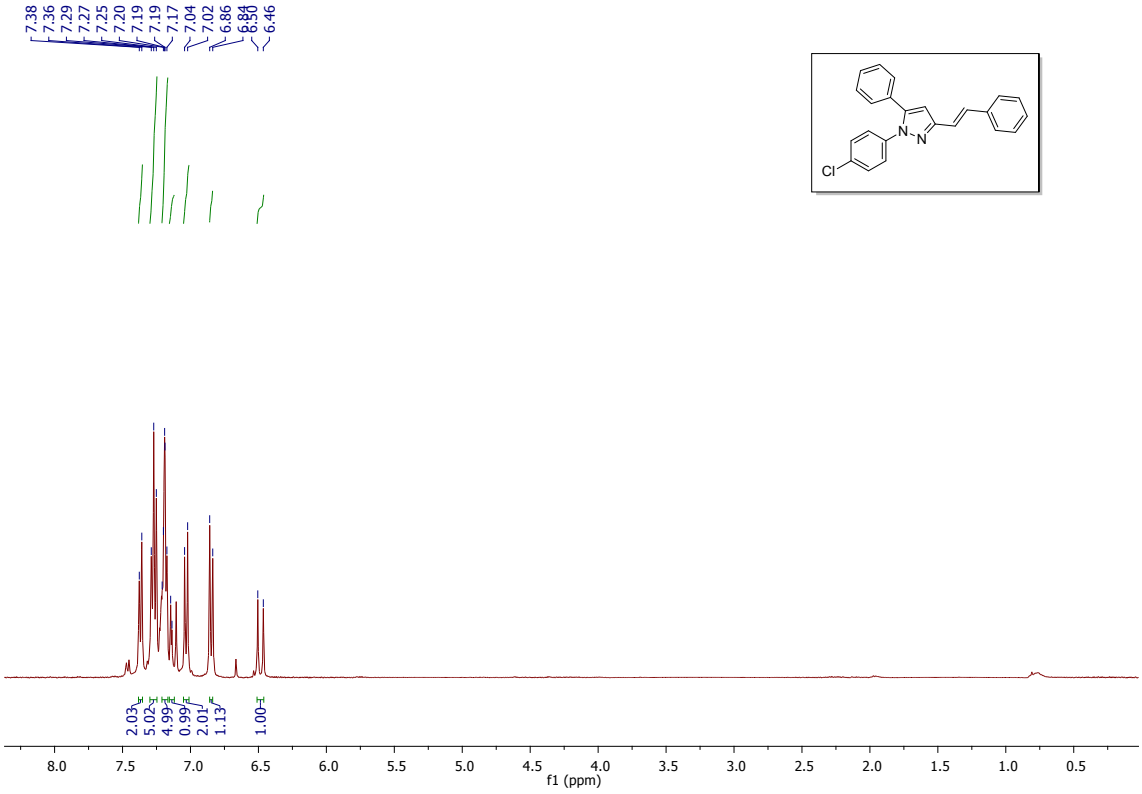


^{13}C NMR

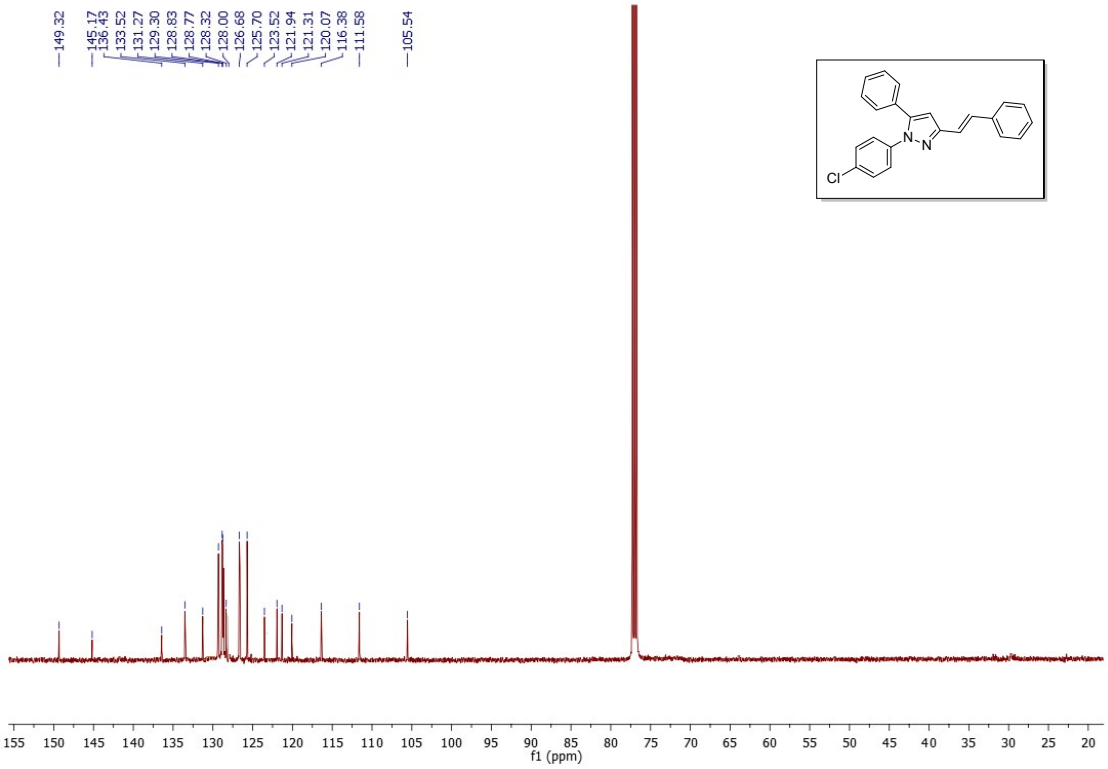


*(E)-1-(4-Chlorophenyl)-5-phenyl-3-styryl-1H-pyrazole (**2j**)*

^{1}H NMR

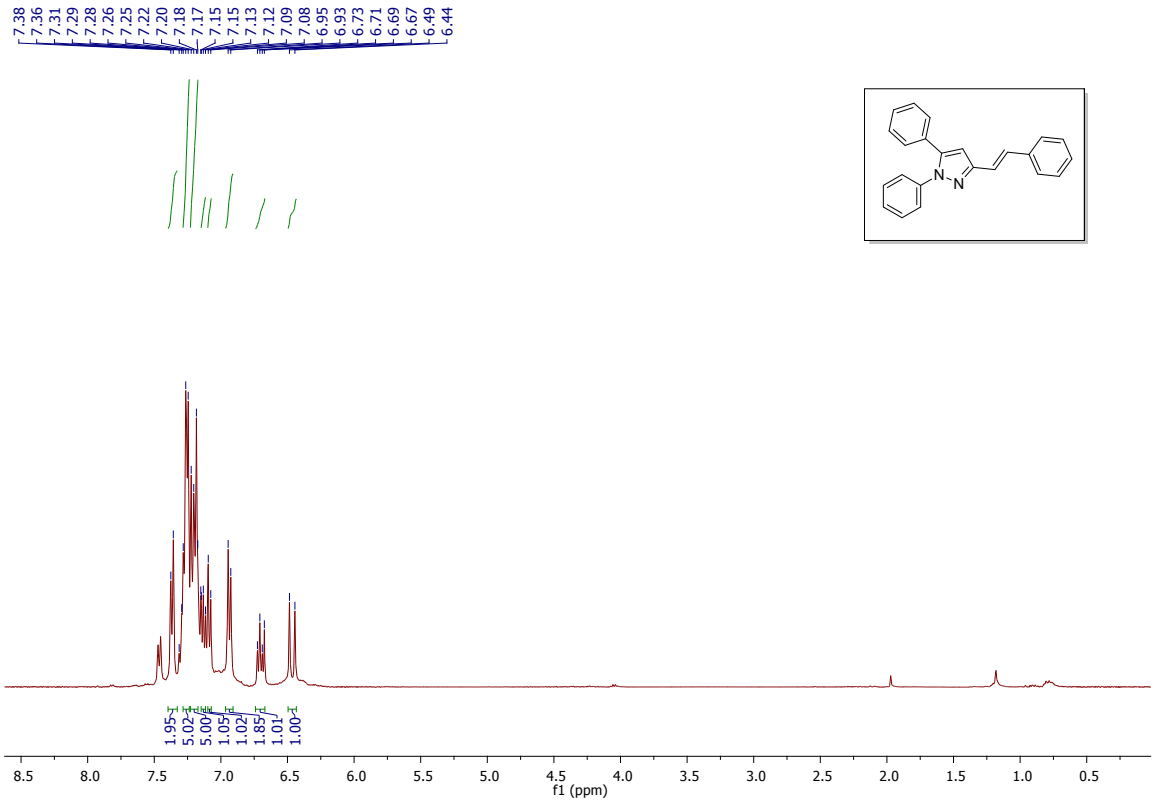


^{13}C NMR

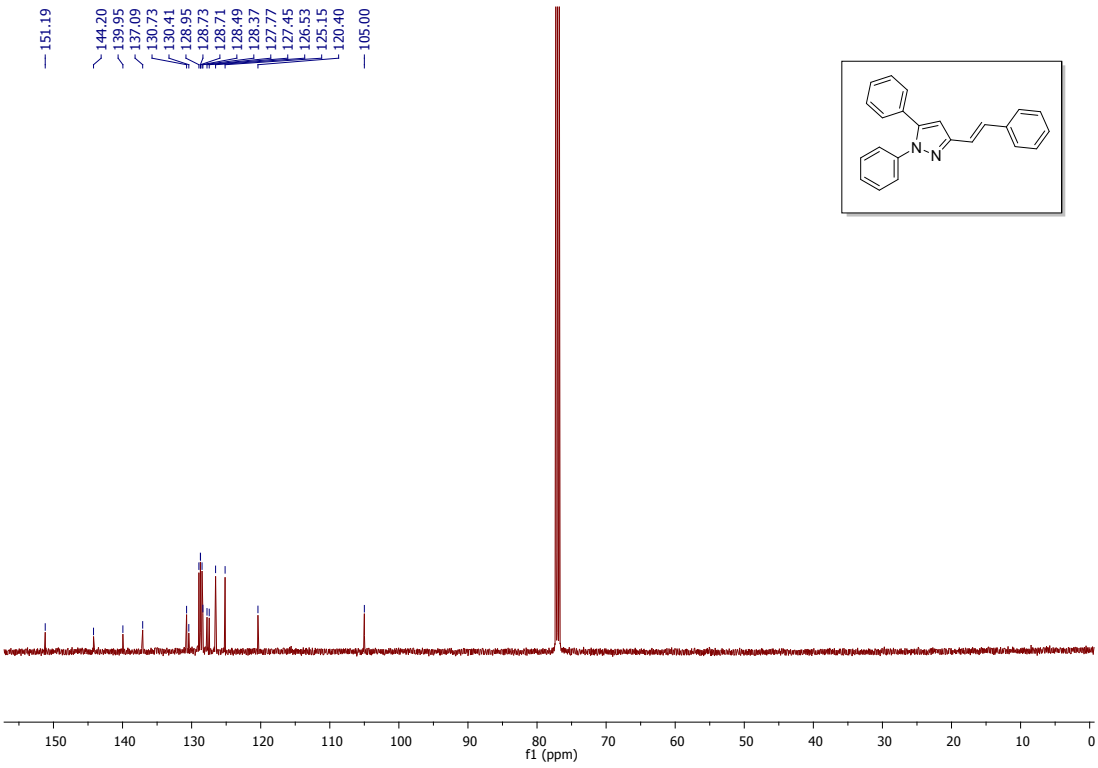


*(E)-1,5-Diphenyl-3-styryl-1H-pyrazole (**2k**)*

^{1}H NMR

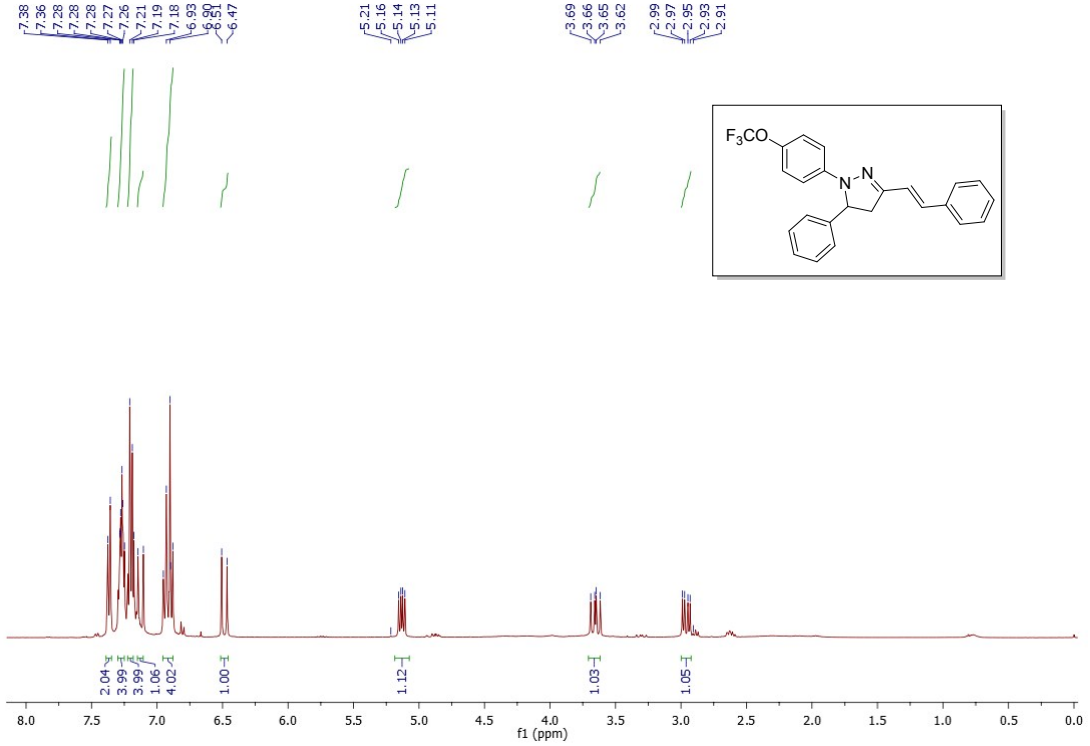


^{13}C NMR

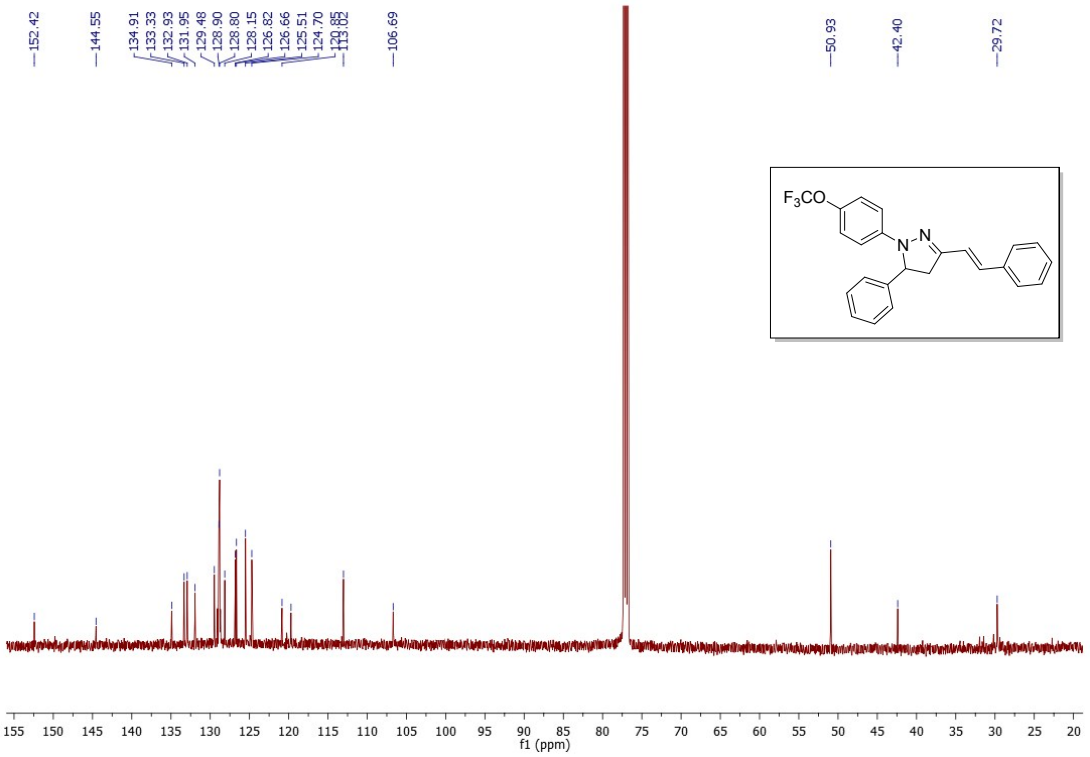


*(E)-5-Phenyl-3-styryl-1-(4-(trifluoromethoxy)phenyl)-4,5-dihydro-1H-pyrazole (**2l**)*

^{1}H NMR

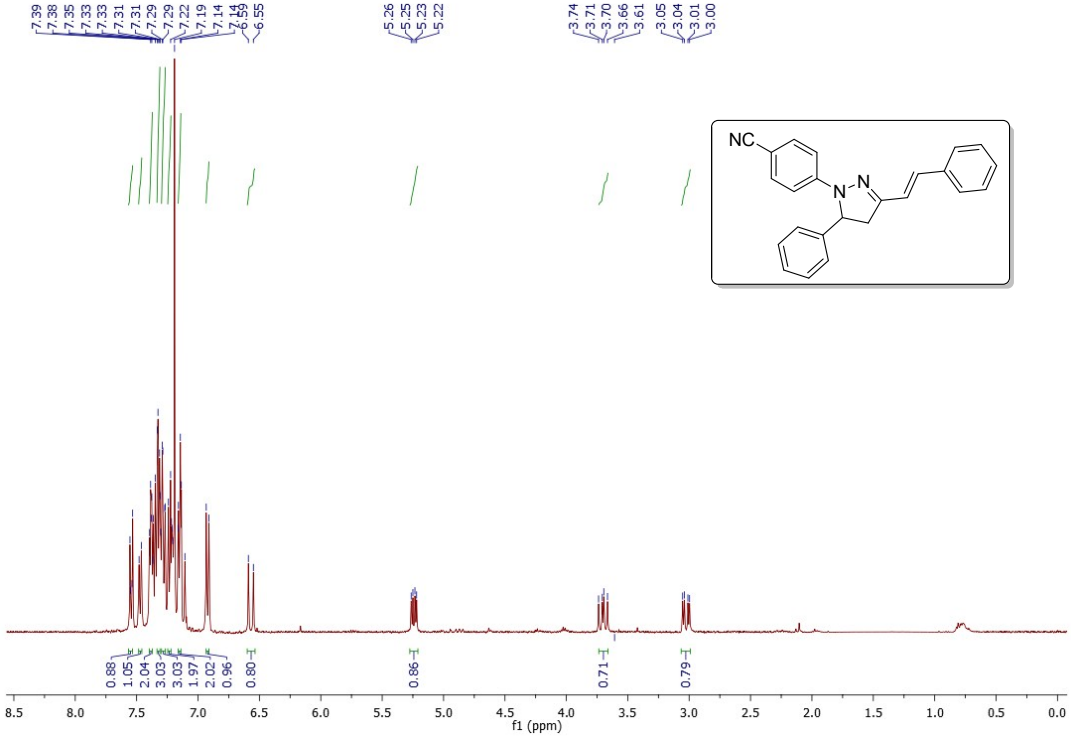


^{13}C NMR

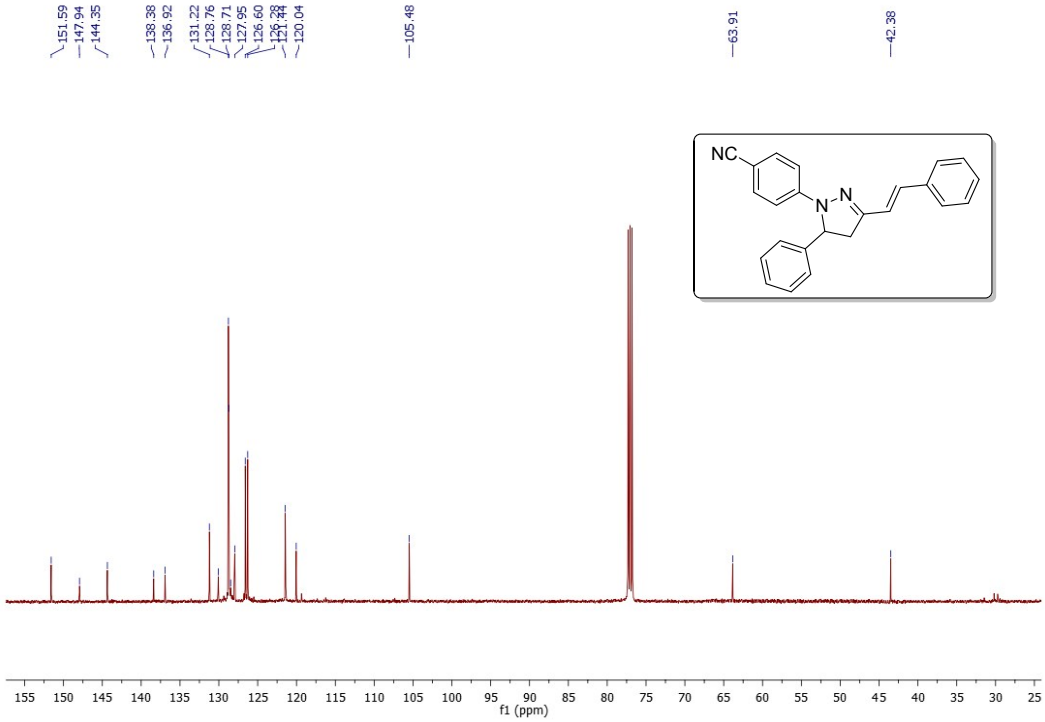


*(E)-4-(5-Phenyl-3-styryl-4,5-dihydro-1H-pyrazol-1-yl)benzonitrile (**2m**)*

^{1}H NMR

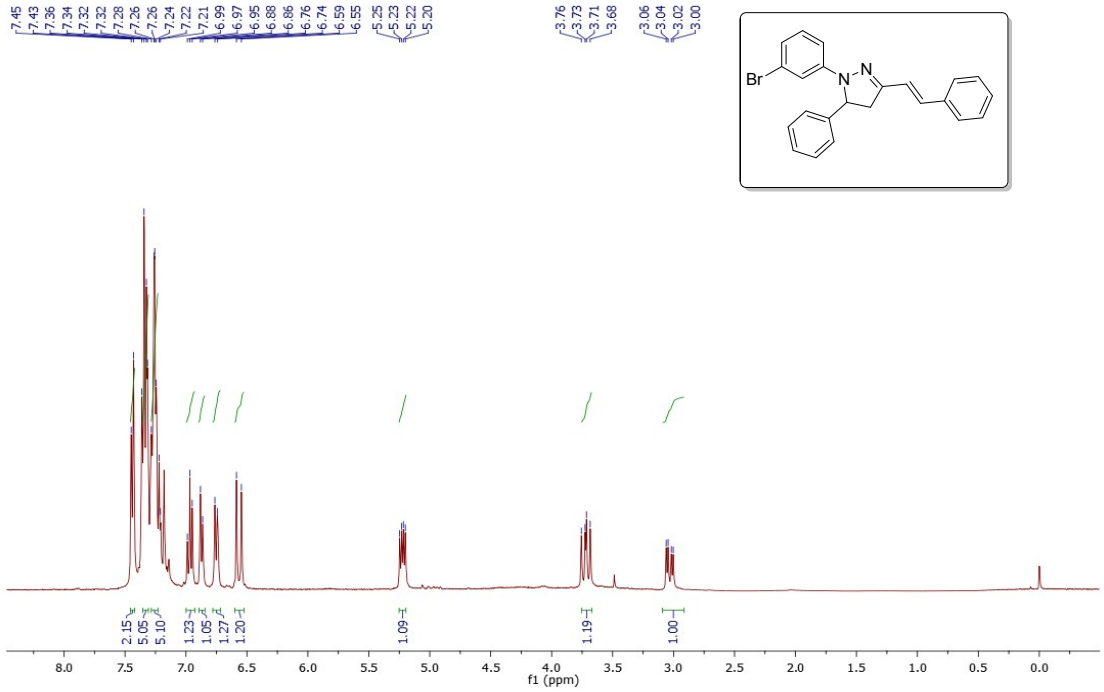


^{13}C NMR

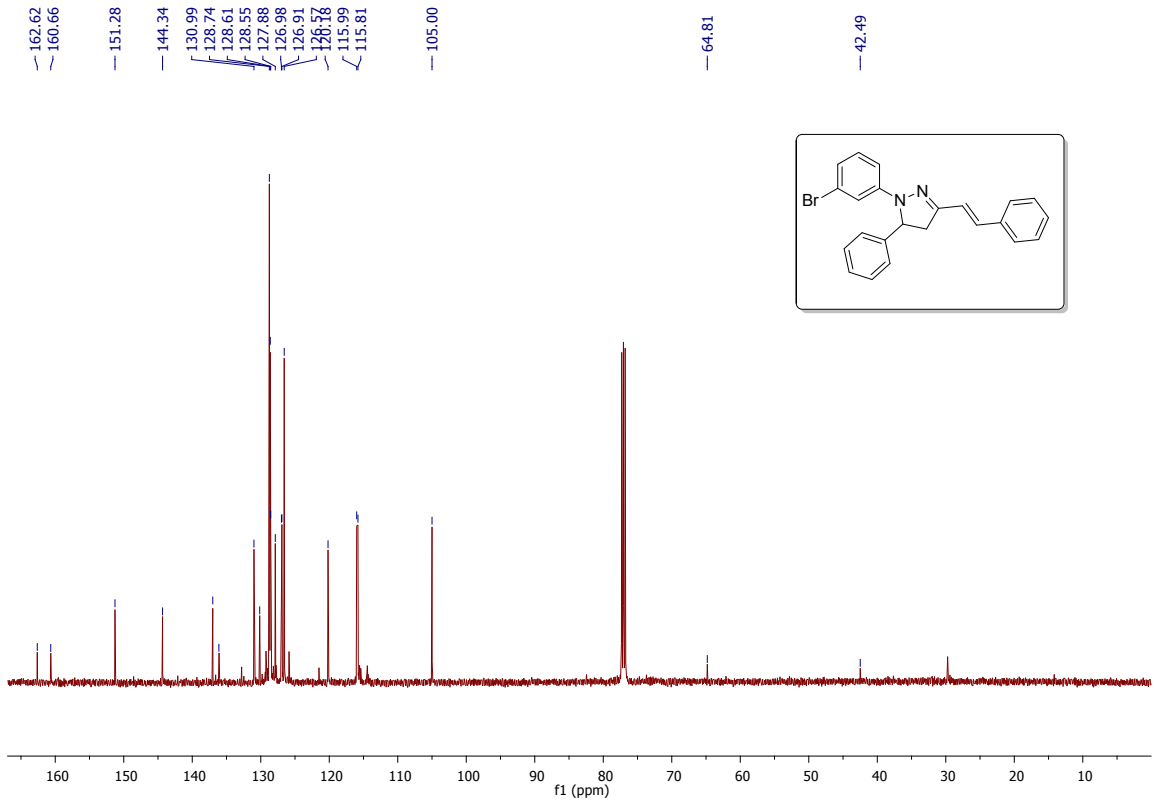


*(E)-1-(3-Bromophenyl)-5-phenyl-3-styryl-4,5-dihydro-1H-pyrazole (**2n**)*

^{1}H NMR

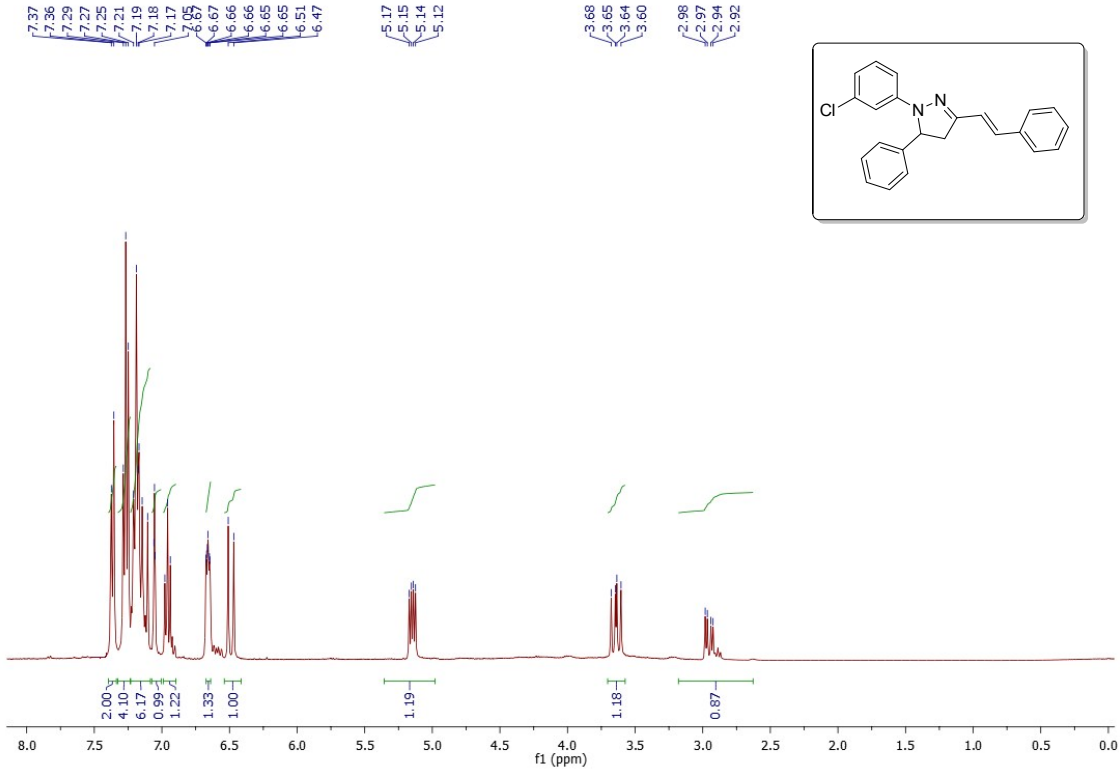


^{13}C NMR

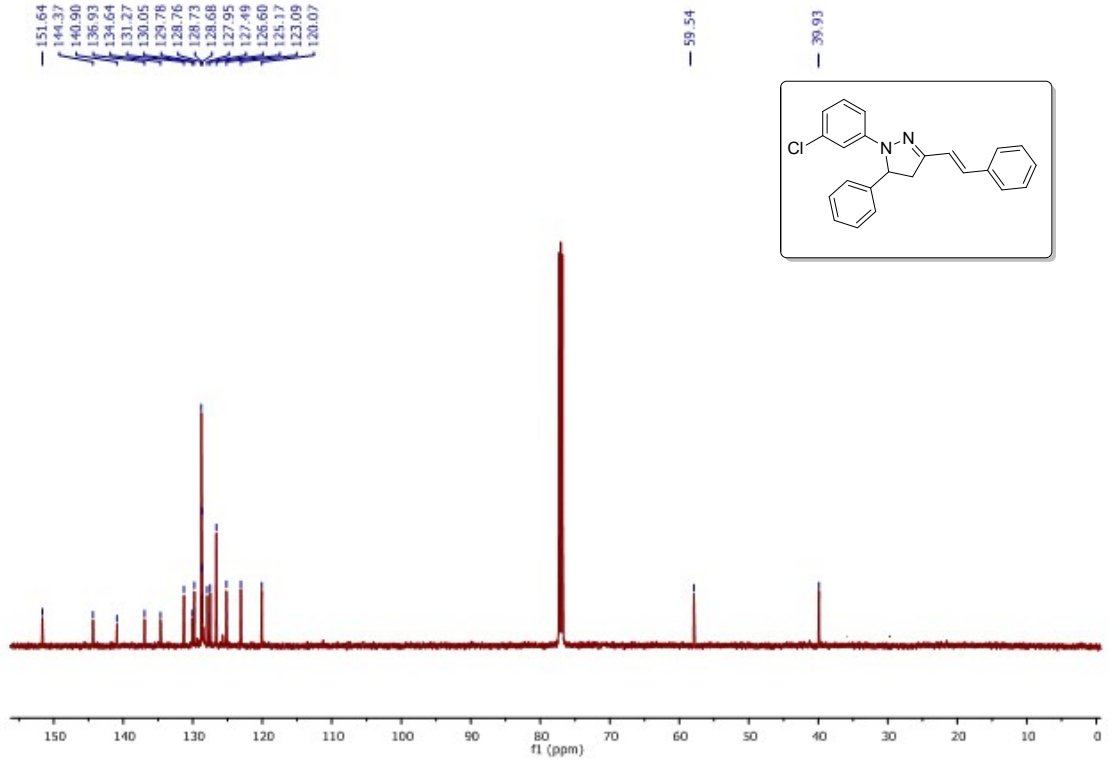


*(E)-1-(3-Chlorophenyl)-5-phenyl-3-styryl-4,5-dihydro-1H-pyrazole (**2o**)*

^{1}H NMR

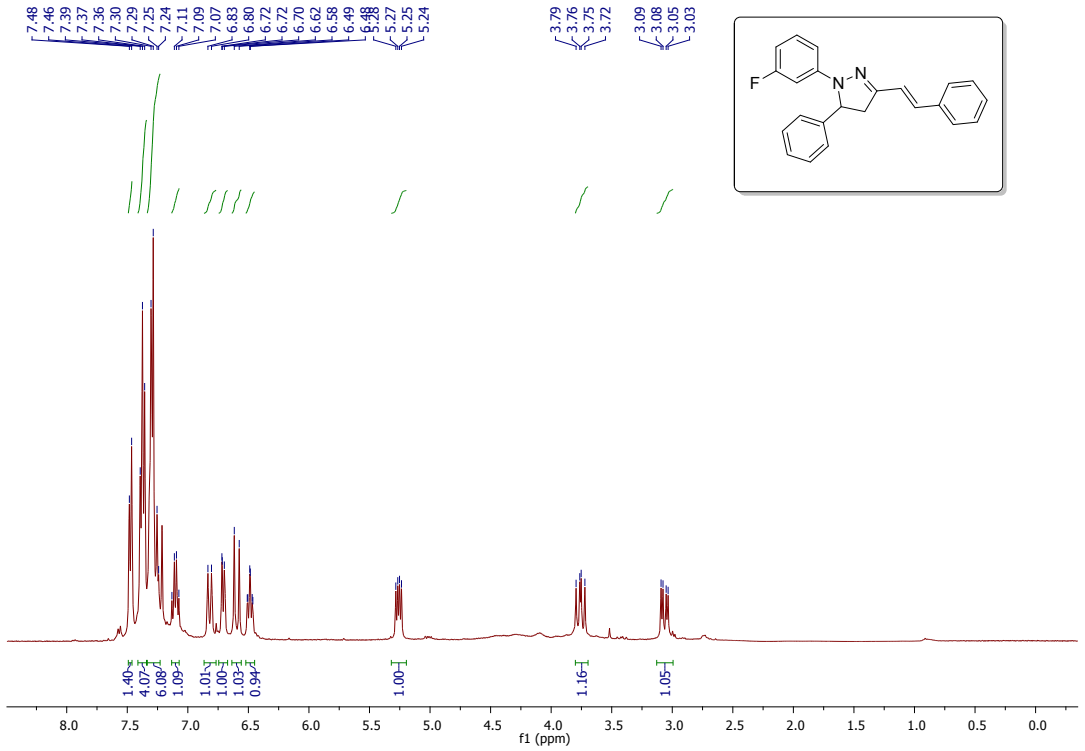


^{13}C NMR

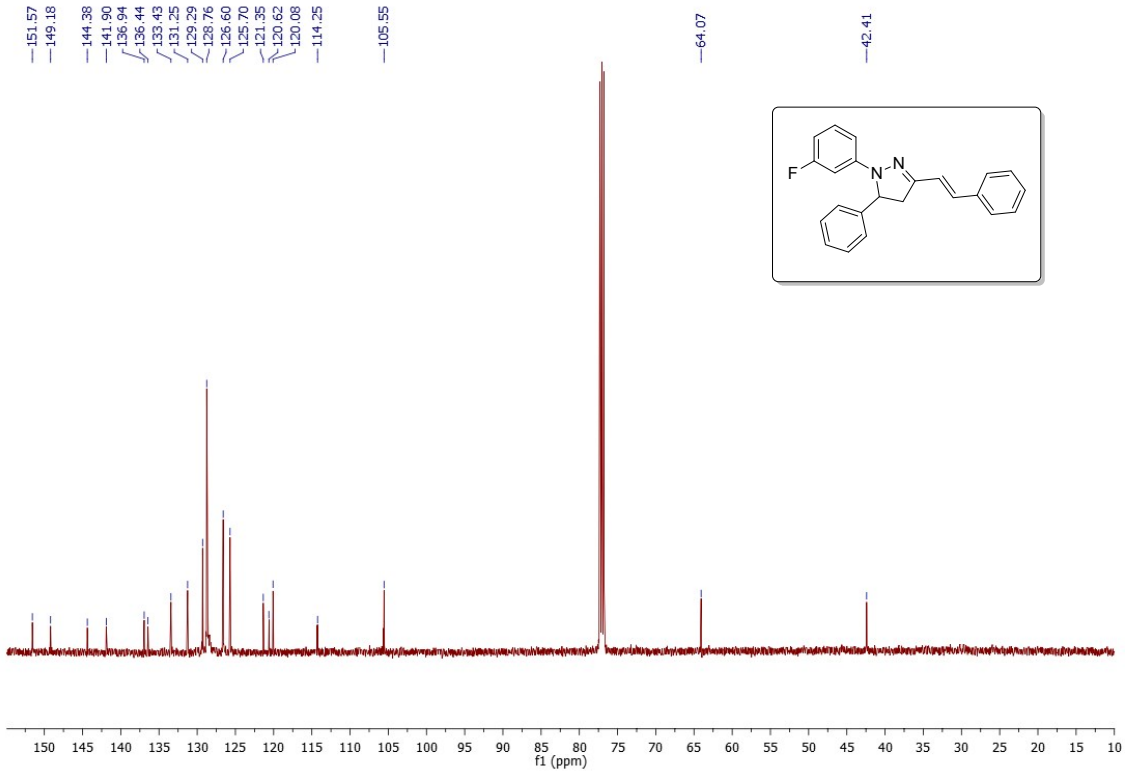


*(E)-1-(3-Fluorophenyl)-5-phenyl-3-styryl-4,5-dihydro-1H-pyrazole (**2p**)*

^{1}H NMR

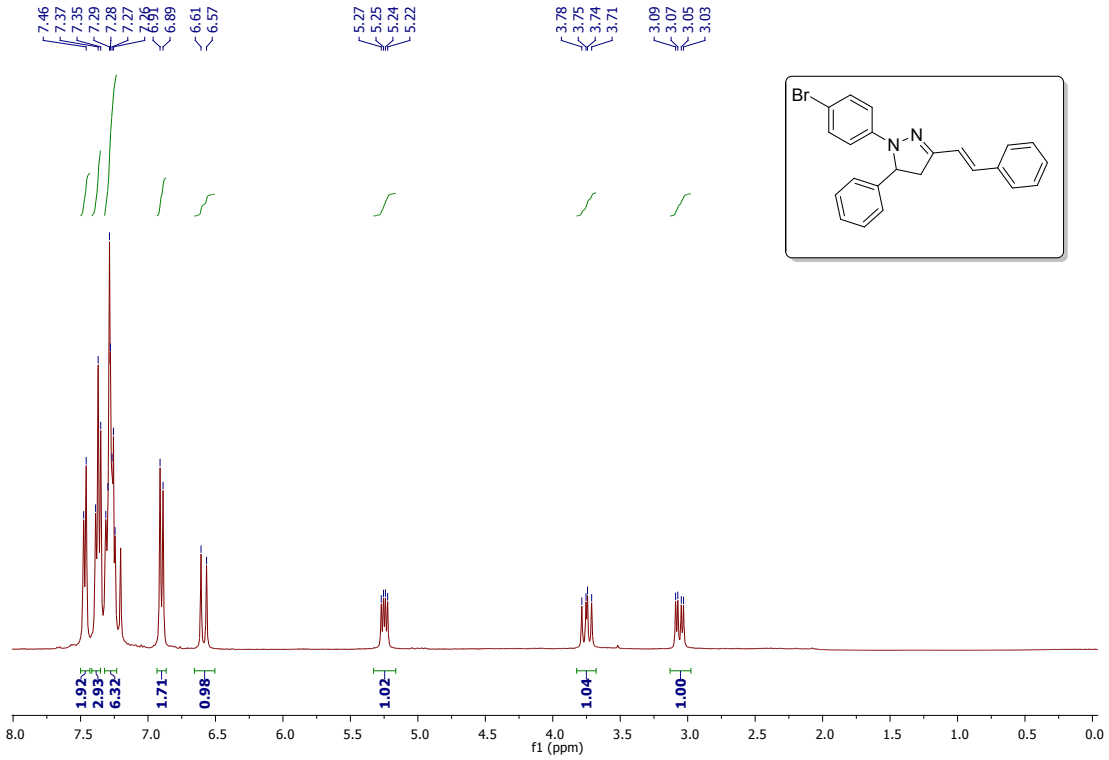


^{13}C NMR

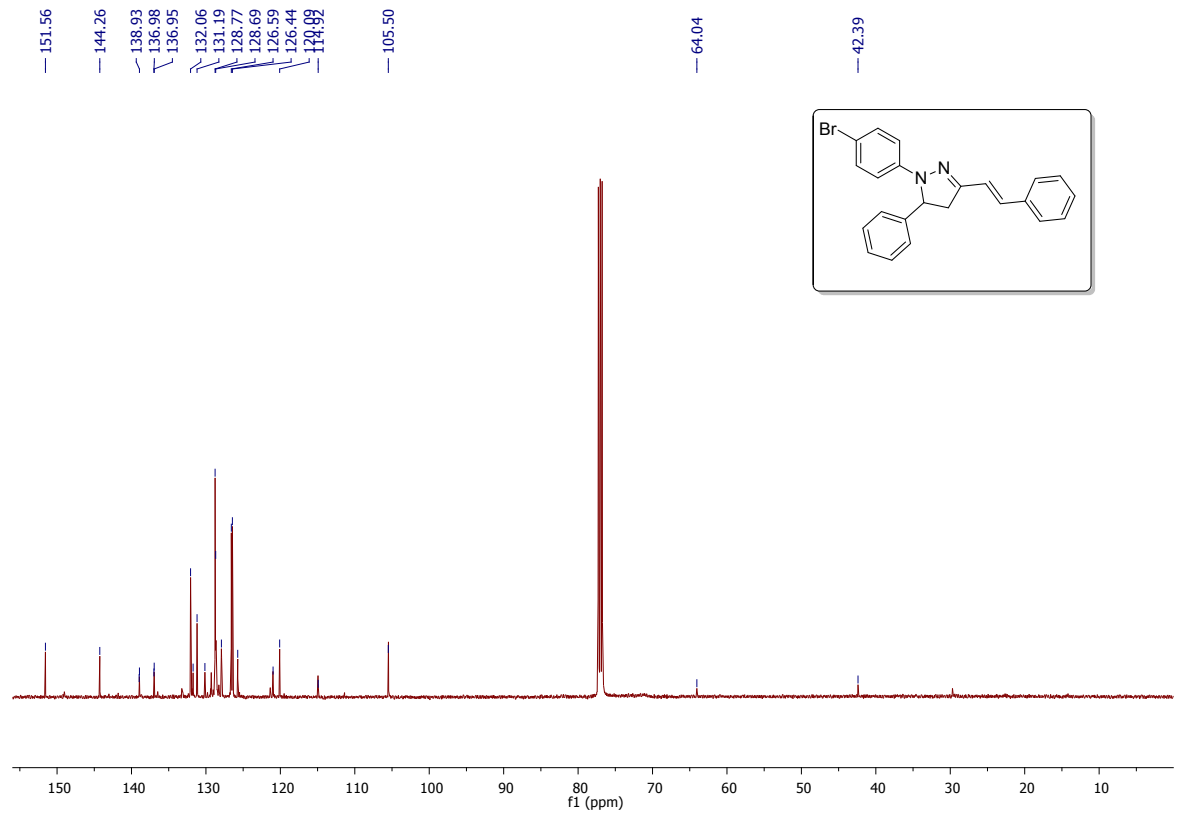


*(E)-1-(4-Bromophenyl)-5-phenyl-3-styryl-4,5-dihydro-1H-pyrazole (**2q**)*

^{1}H NMR

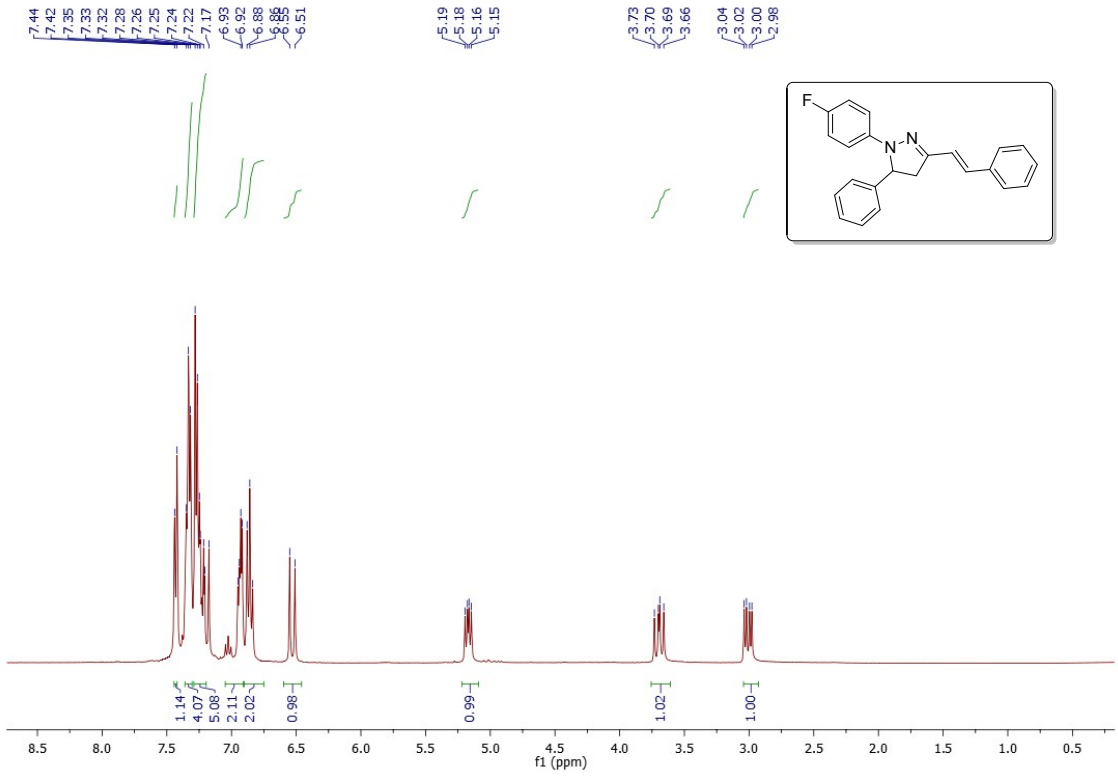


^{13}C NMR

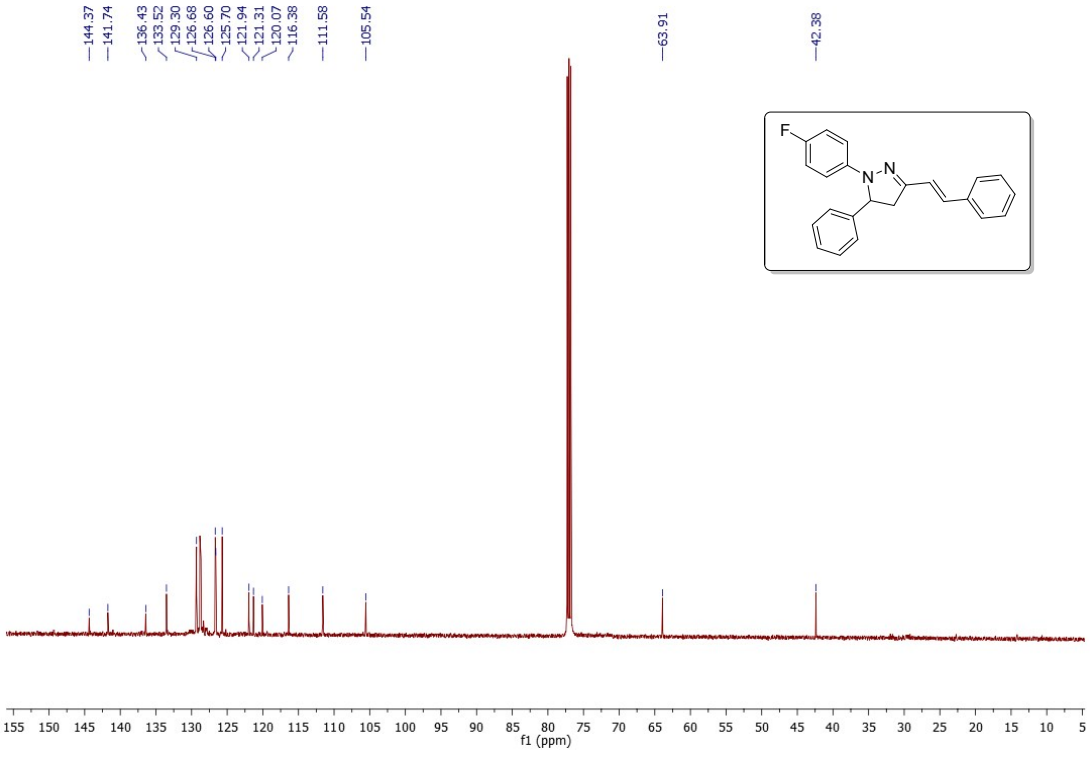


*(E)-1-(4-Fluorophenyl)-5-phenyl-3-styryl-4,5-dihydro-1H-pyrazole (**2r**)*

^{1}H NMR

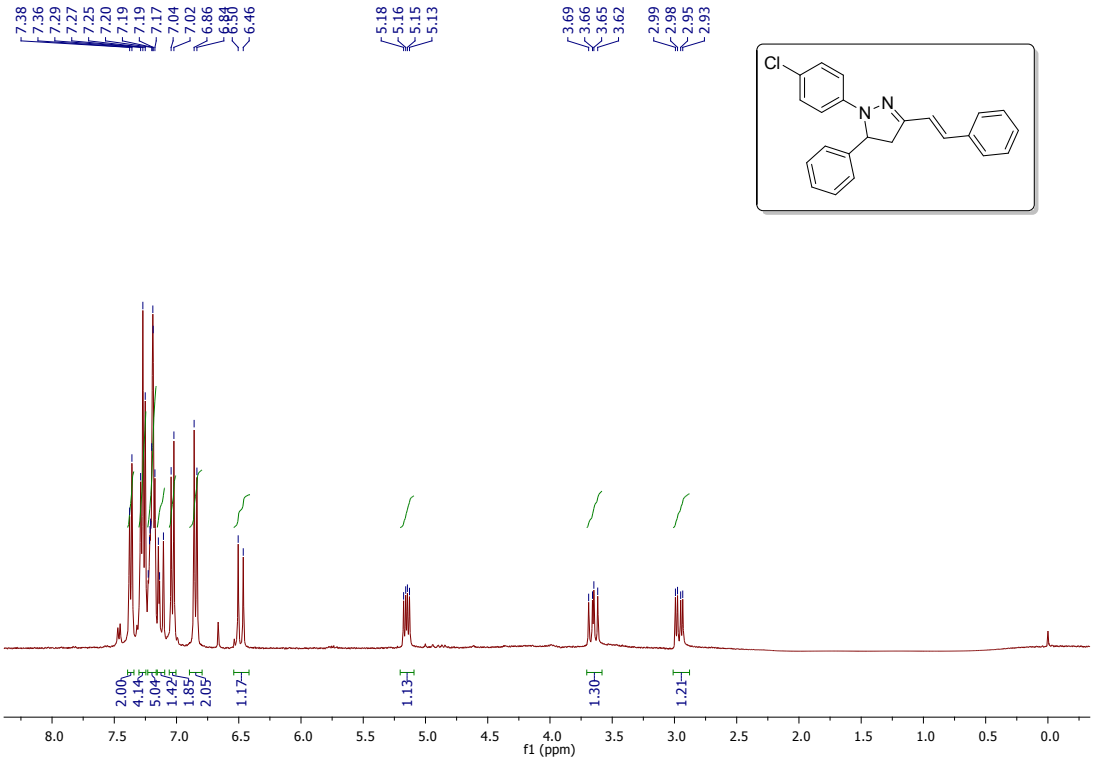


^{13}C NMR

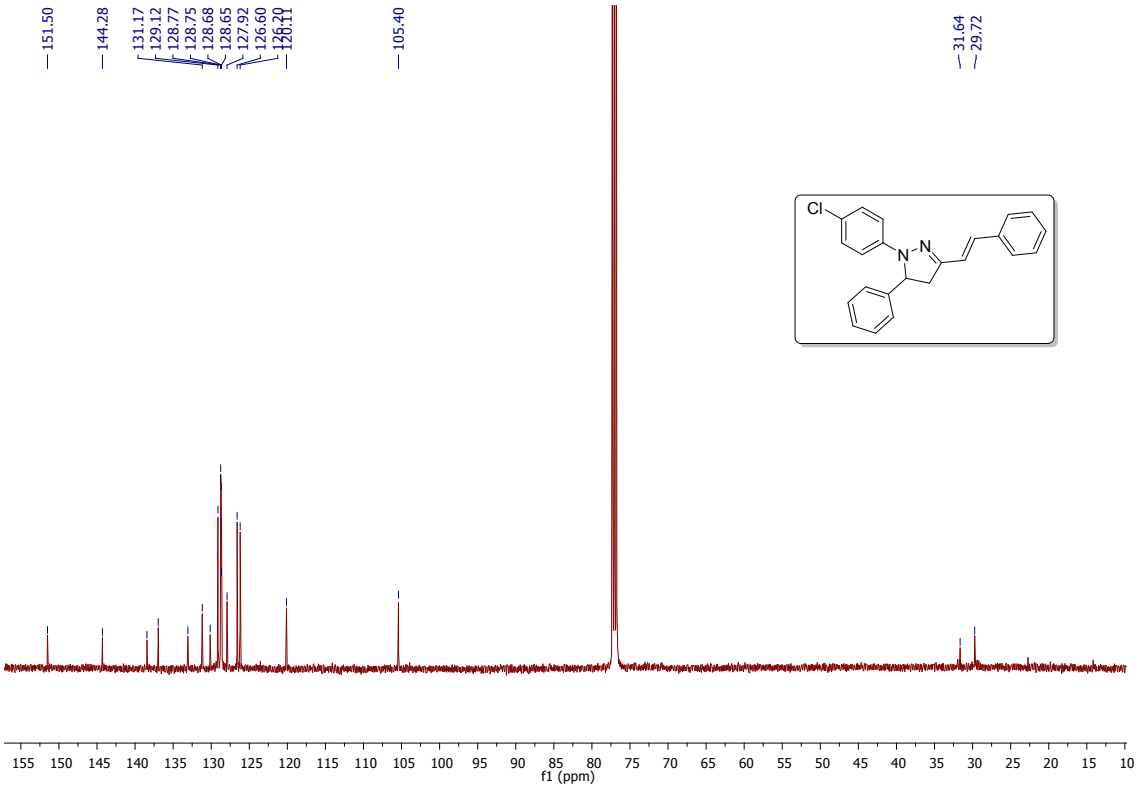


*(E)-1-(4-Chlorophenyl)-5-phenyl-3-styryl-4,5-dihydro-1H-pyrazole (**2s**)*

^{1}H NMR

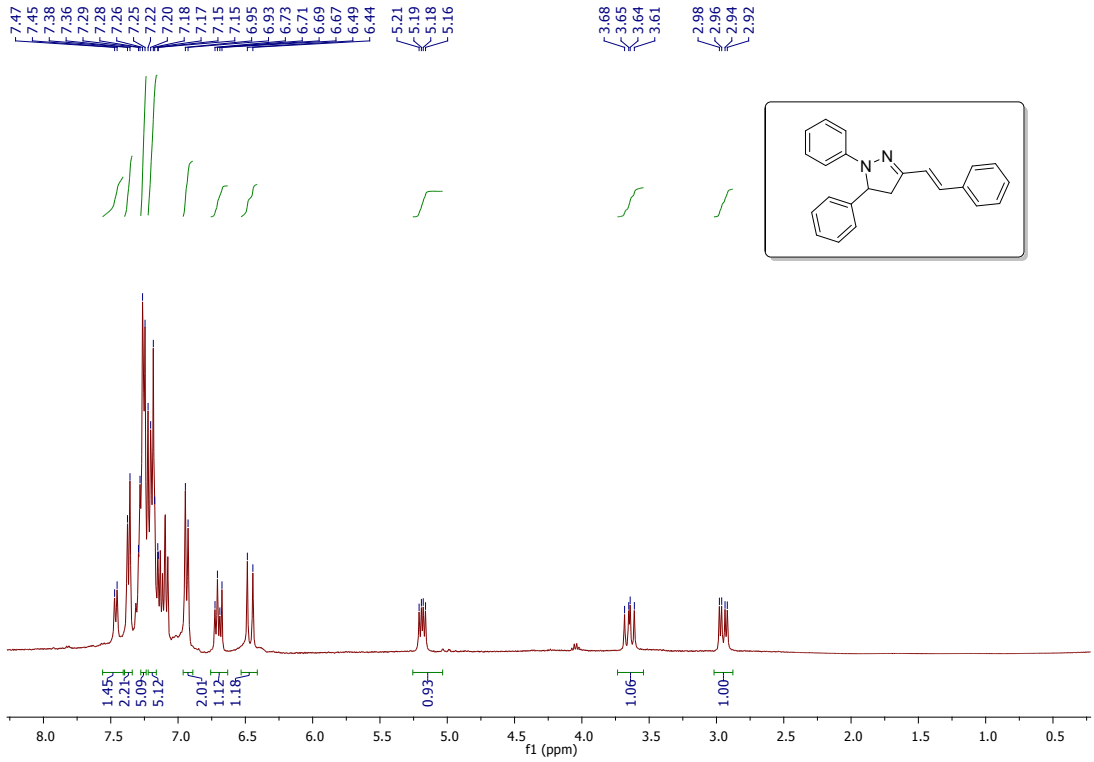


^{13}C NMR

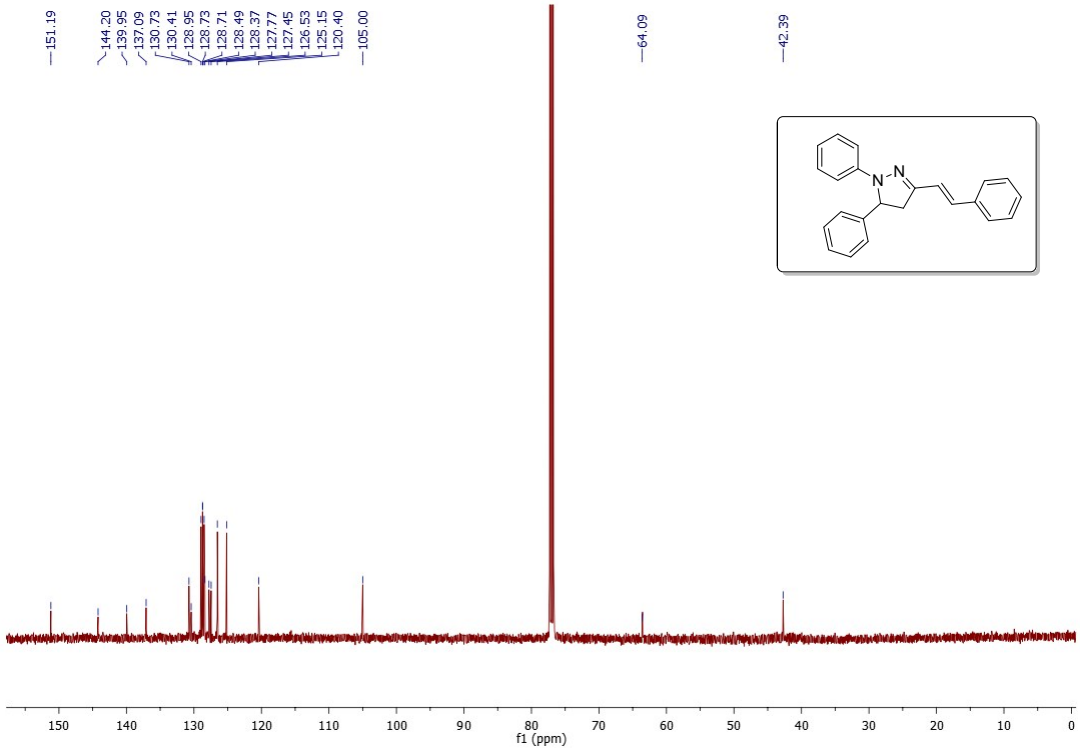


*(E)-1,5-Diphenyl-3-styryl-4,5-dihydro-1H-pyrazole (**2t**)*

^{1}H NMR

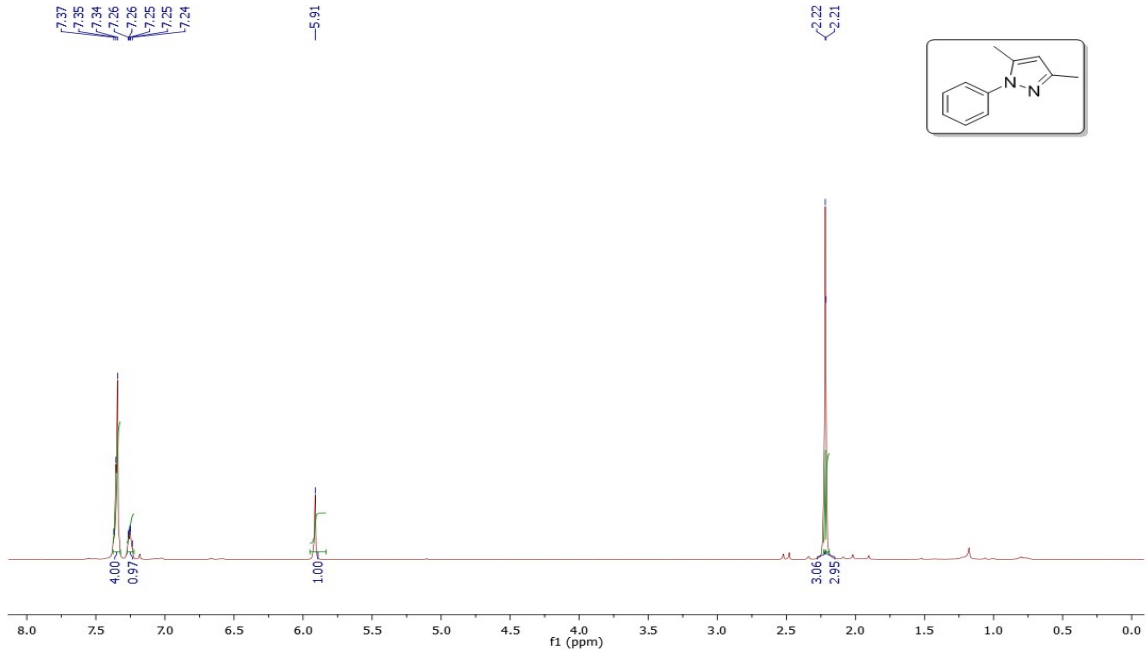


^{13}C NMR

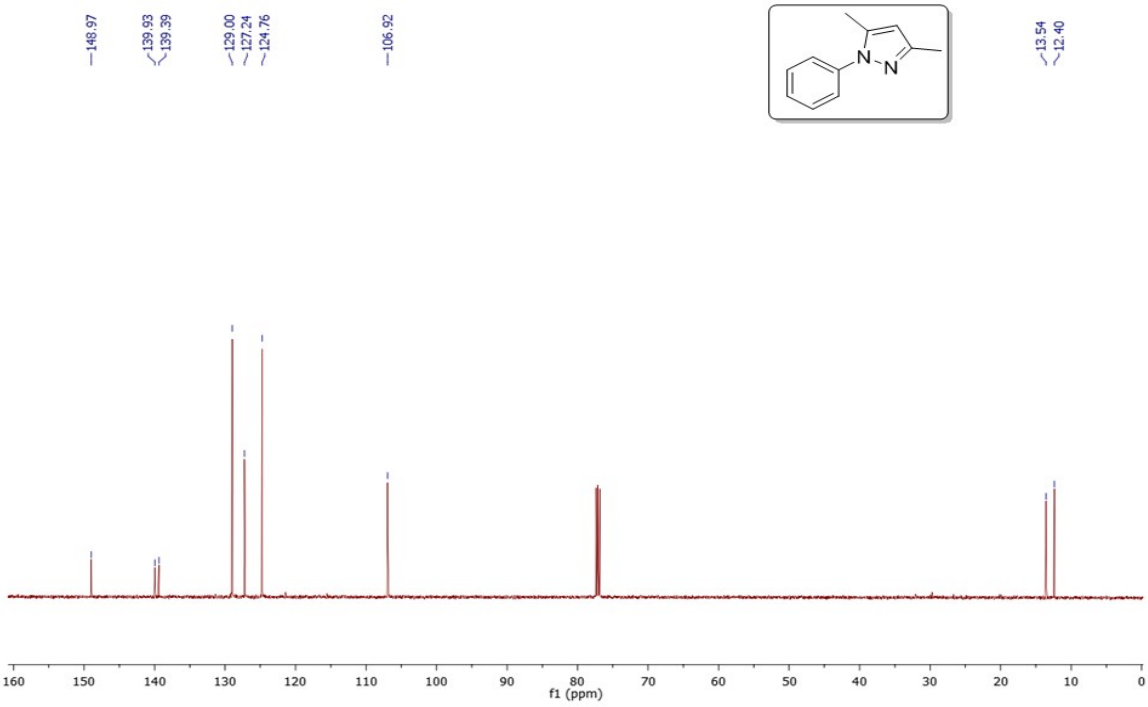


*3,5-Dimethyl-1-phenyl-1H-pyrazole (**3a**)*

^{1}H NMR

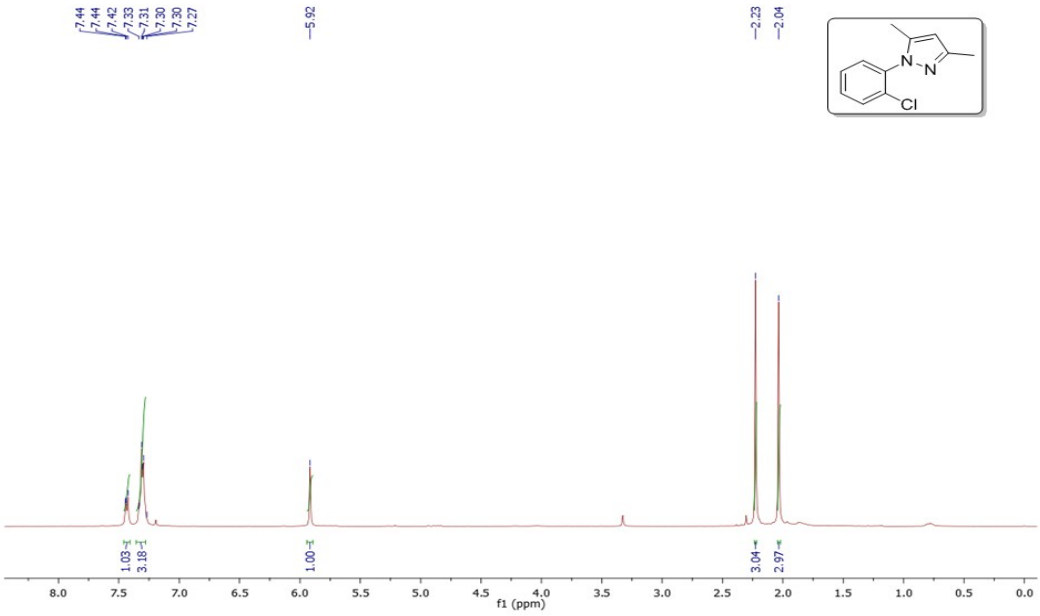


^{13}C NMR

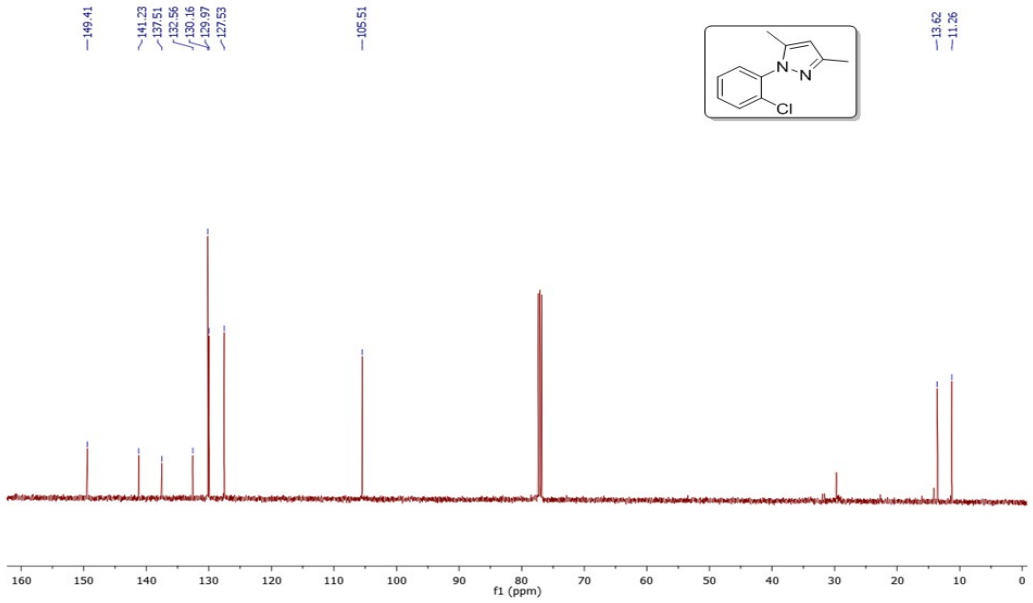


*1-(2-Chlorophenyl)-3,5-dimethyl-1H-pyrazole (**3b**)*

^{1}H NMR

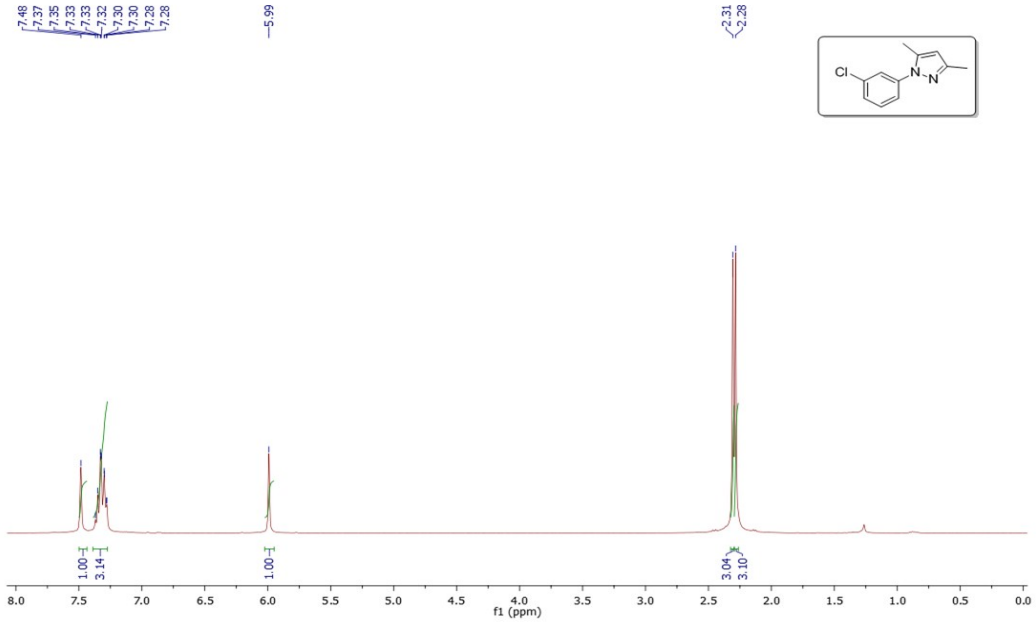


^{13}C NMR

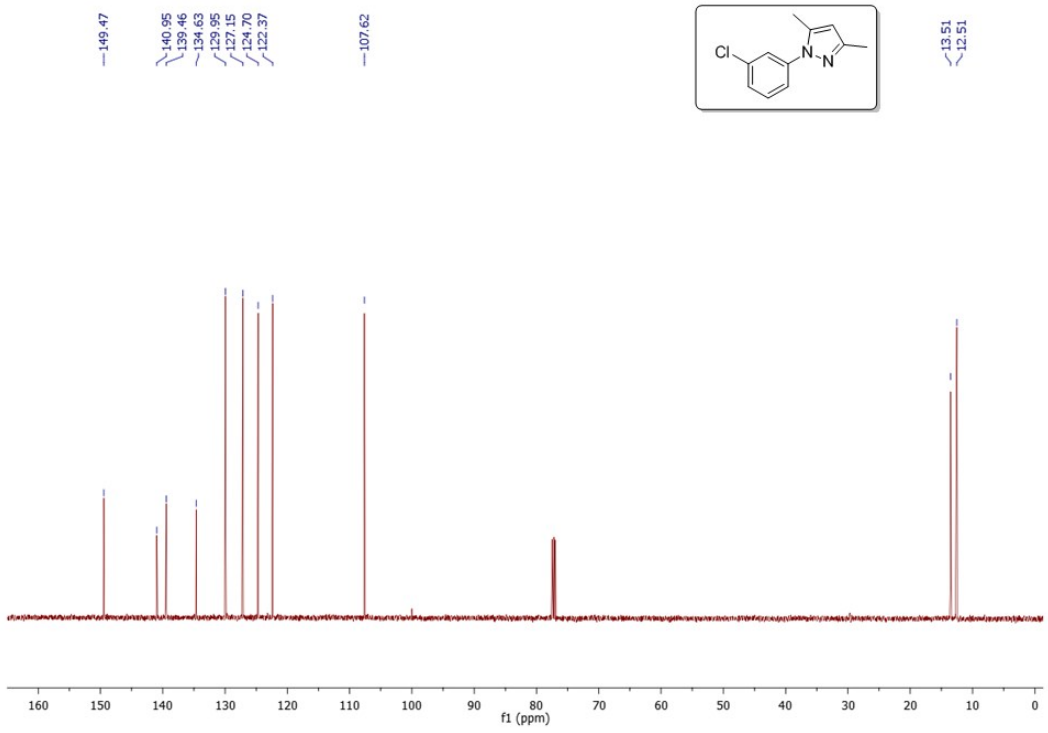


*1-(3-Chlorophenyl)-3,5-dimethyl-1H-pyrazole (**3c**)*

^{1}H NMR

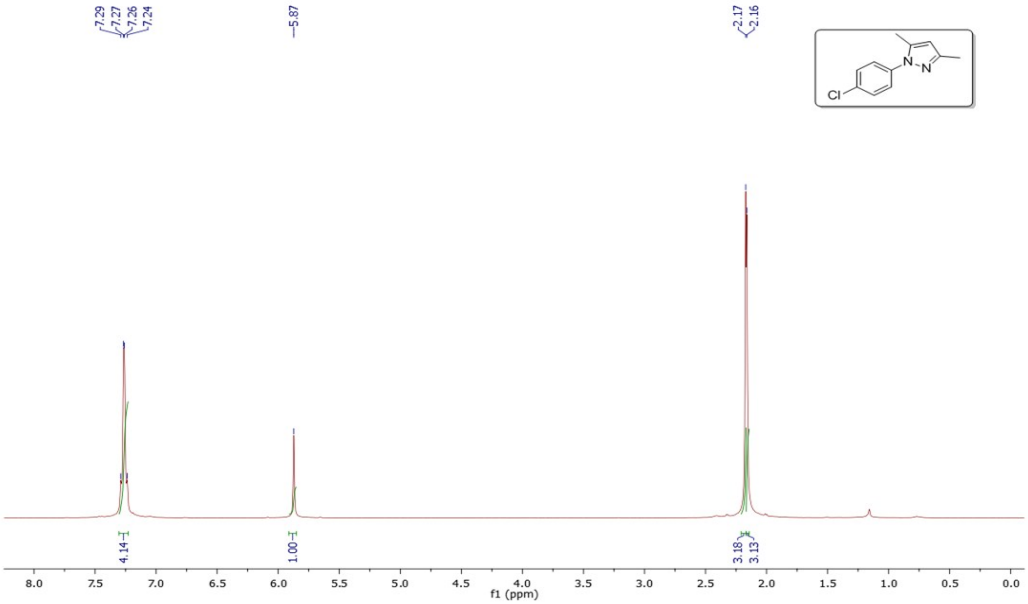


^{13}C NMR

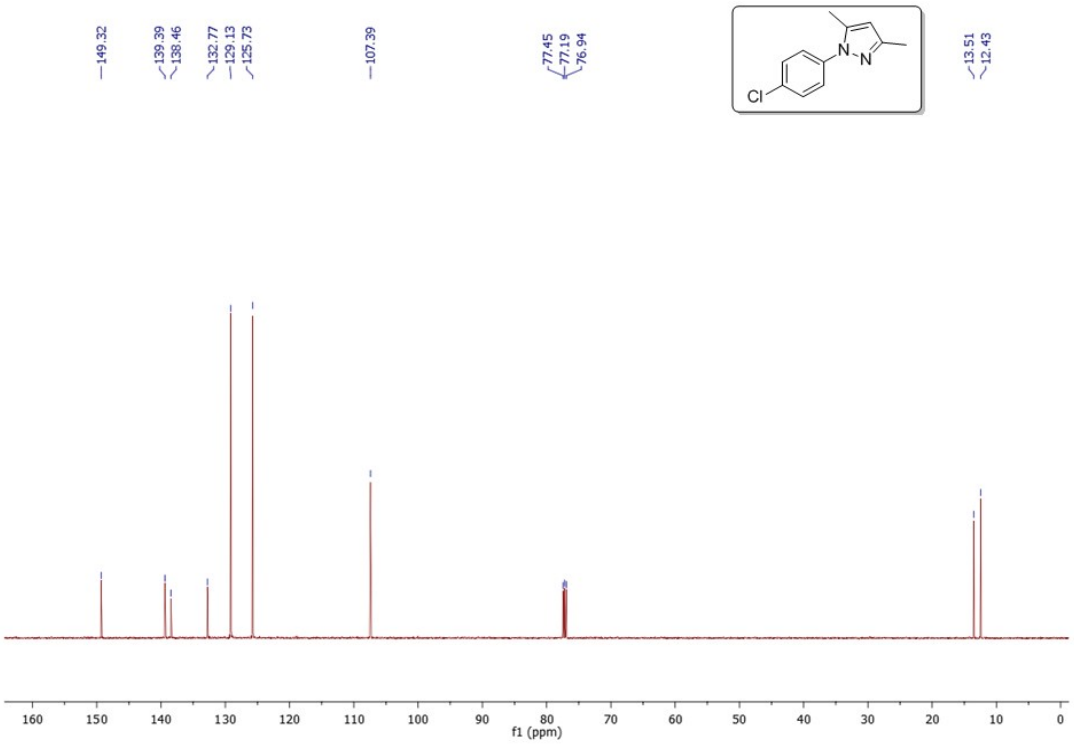


*1-(4-Chlorophenyl)-3,5-dimethyl-1H-pyrazole (**3d**)*

^{1}H NMR

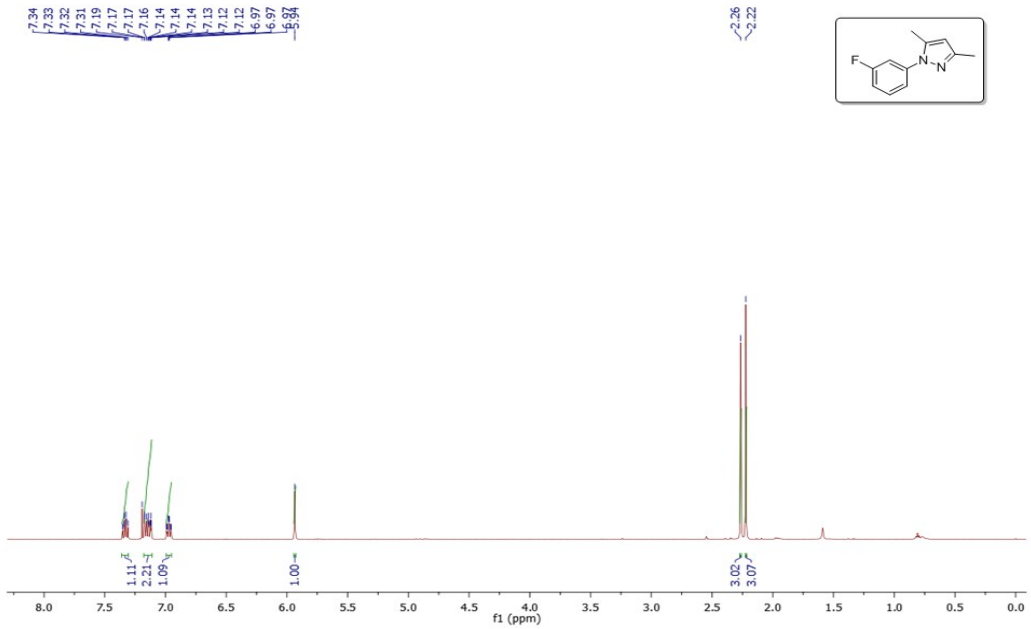


^{13}C NMR

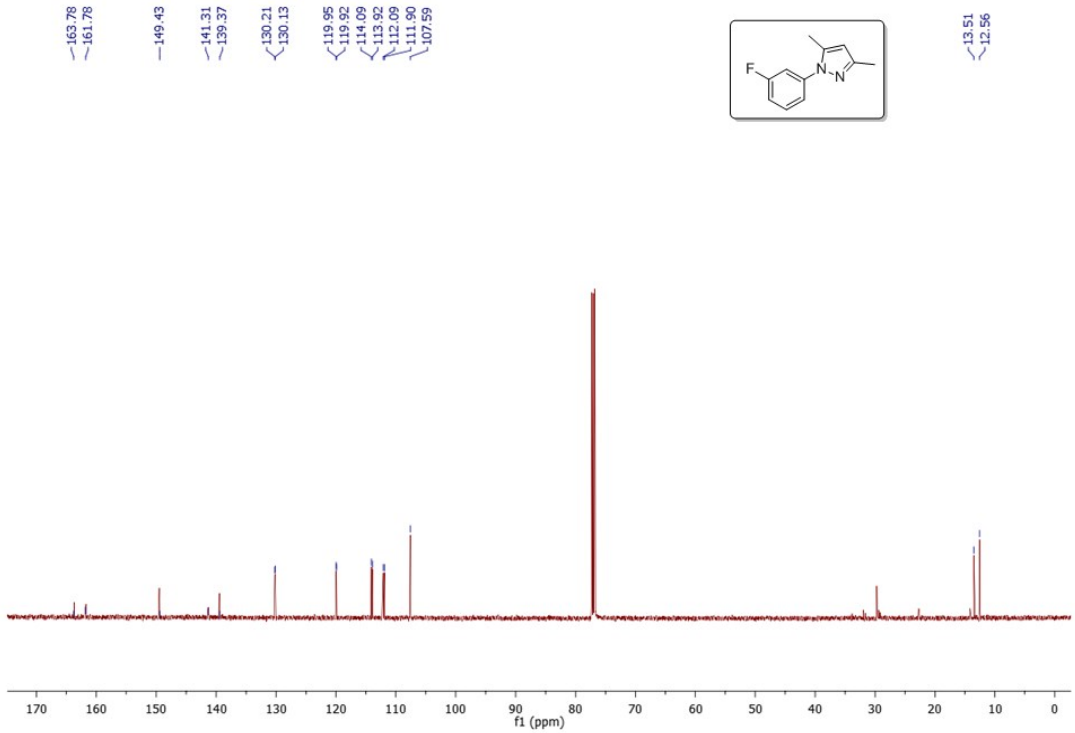


*1-(3-Fluorophenyl)-3,5-dimethyl-1H-pyrazole (**3e**)*

^{1}H NMR

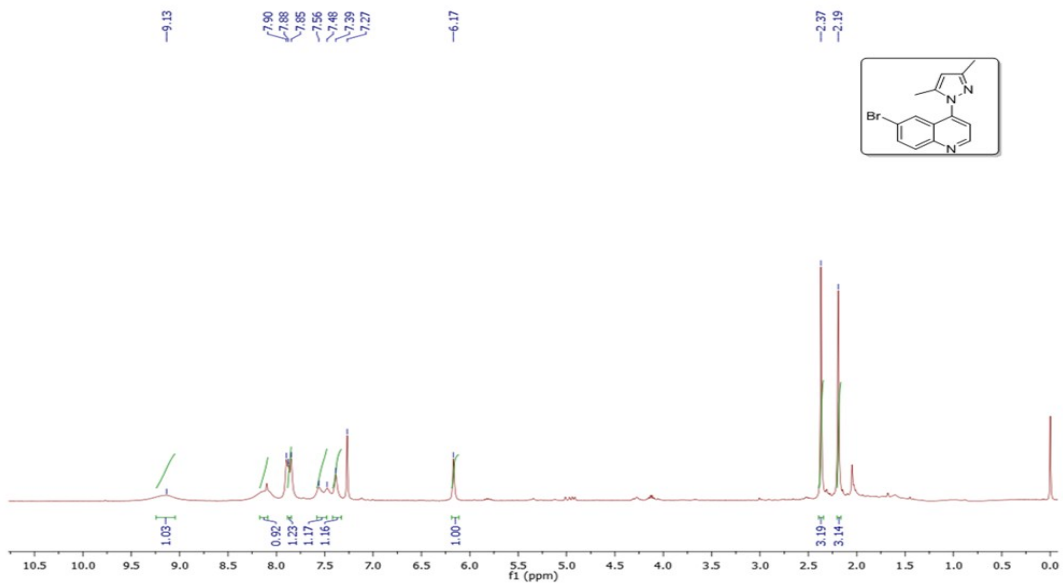


^{13}C NMR

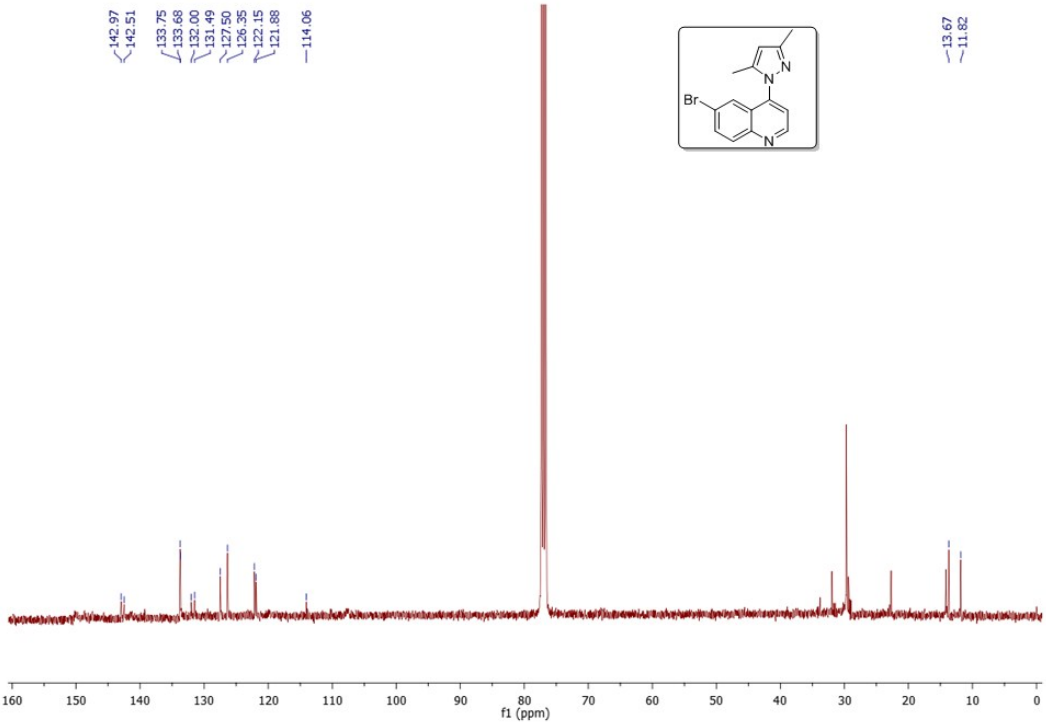


*4-(3,5-Dimethyl-1H-pyrazol-1-yl)-6-bromoquinoline (**3f**)*

^{1}H NMR

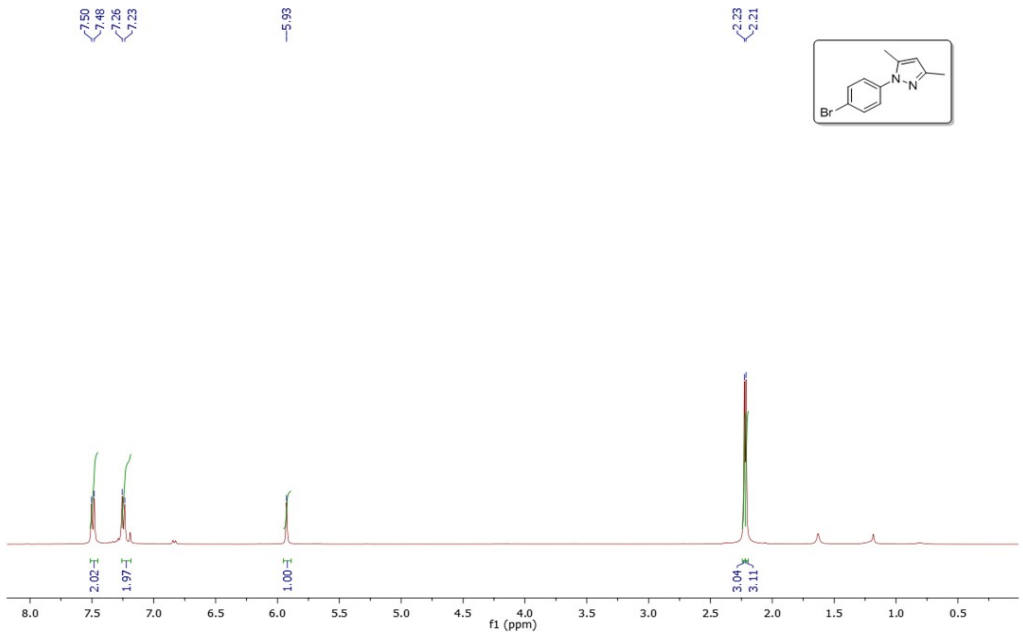


^{13}C NMR

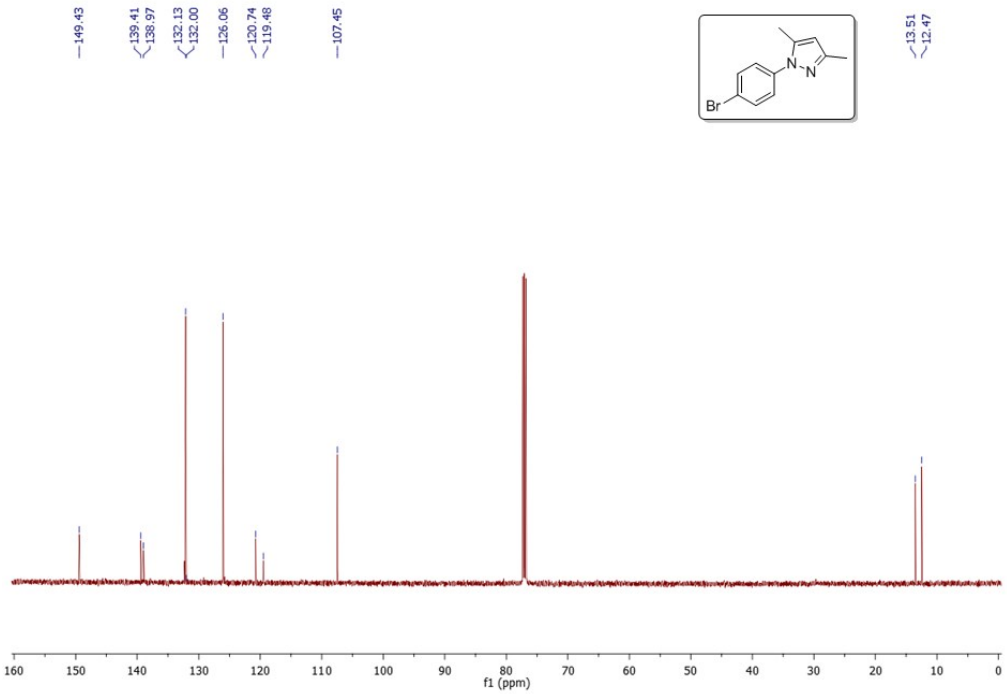


*1-(4-Bromophenyl)-3,5-dimethyl-1H-pyrazole (**3g**)*

^{1}H NMR

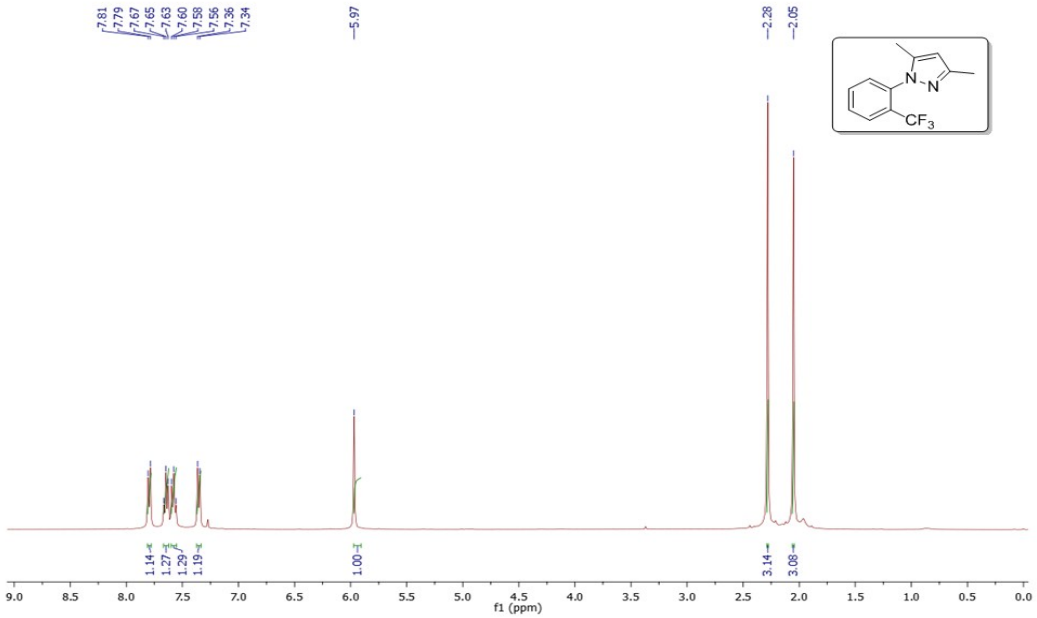


^{13}C NMR

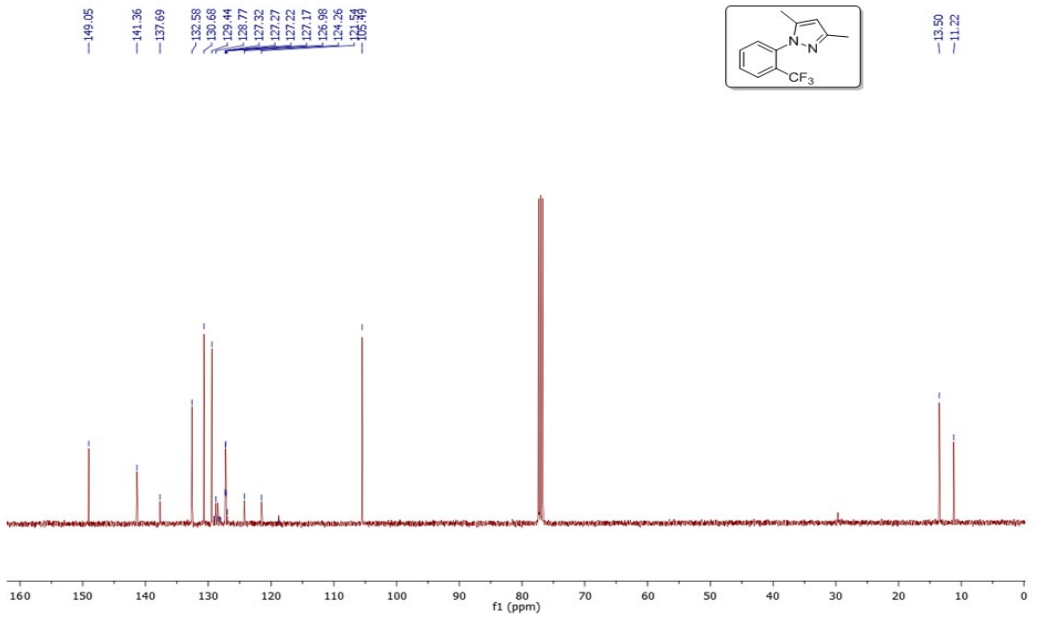


*3,5-Dimethyl-1-(2-(trifluoromethyl)phenyl)-1H-pyrazole (**3h**)*

^{1}H NMR

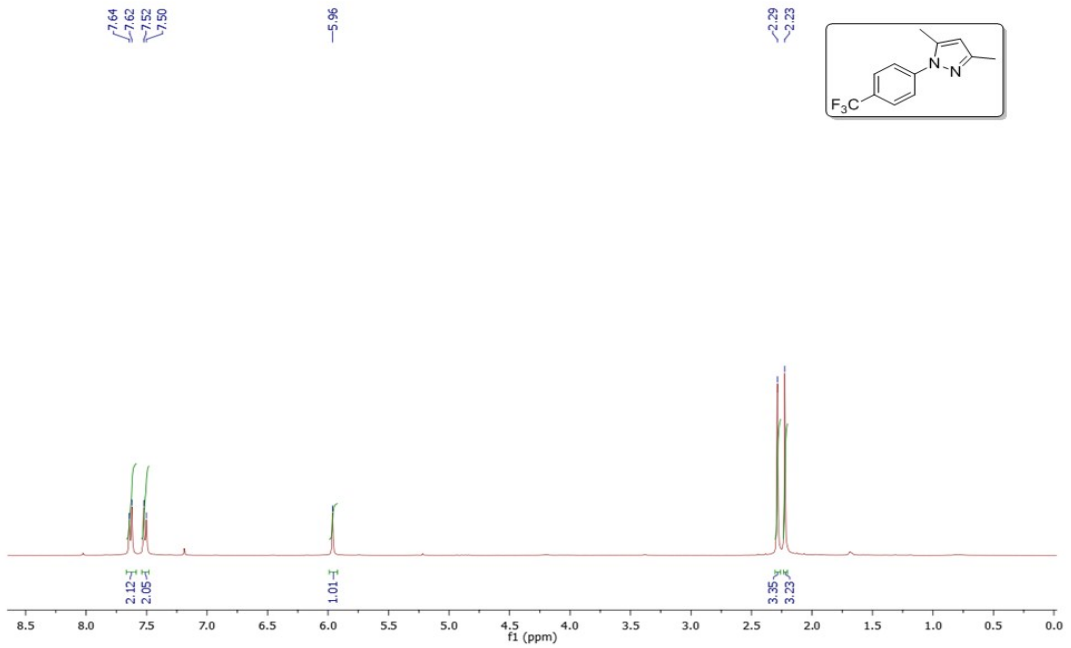


^{13}C NMR

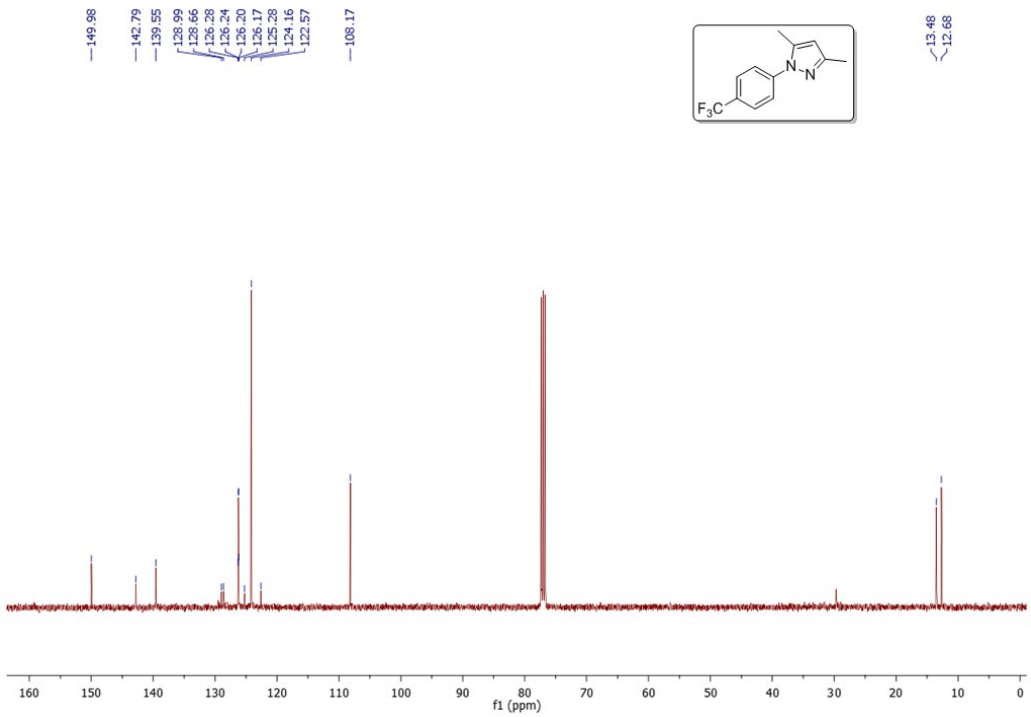


*3,5-Dimethyl-1-(4-(trifluoromethyl)phenyl)-1H-pyrazole (**3i**)*

^{1}H NMR

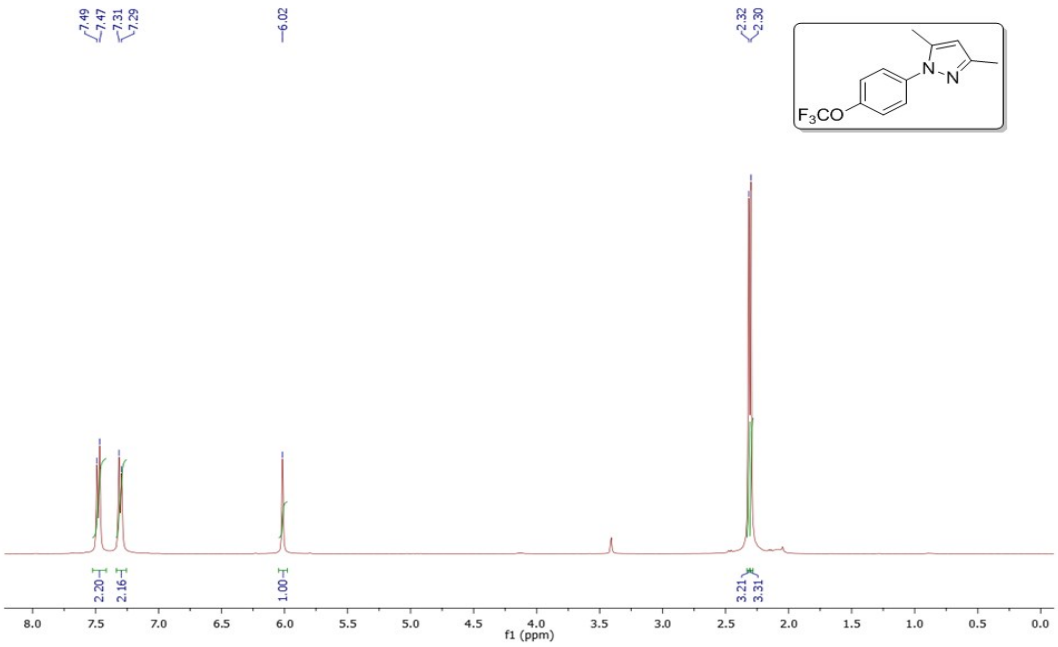


^{13}C NMR

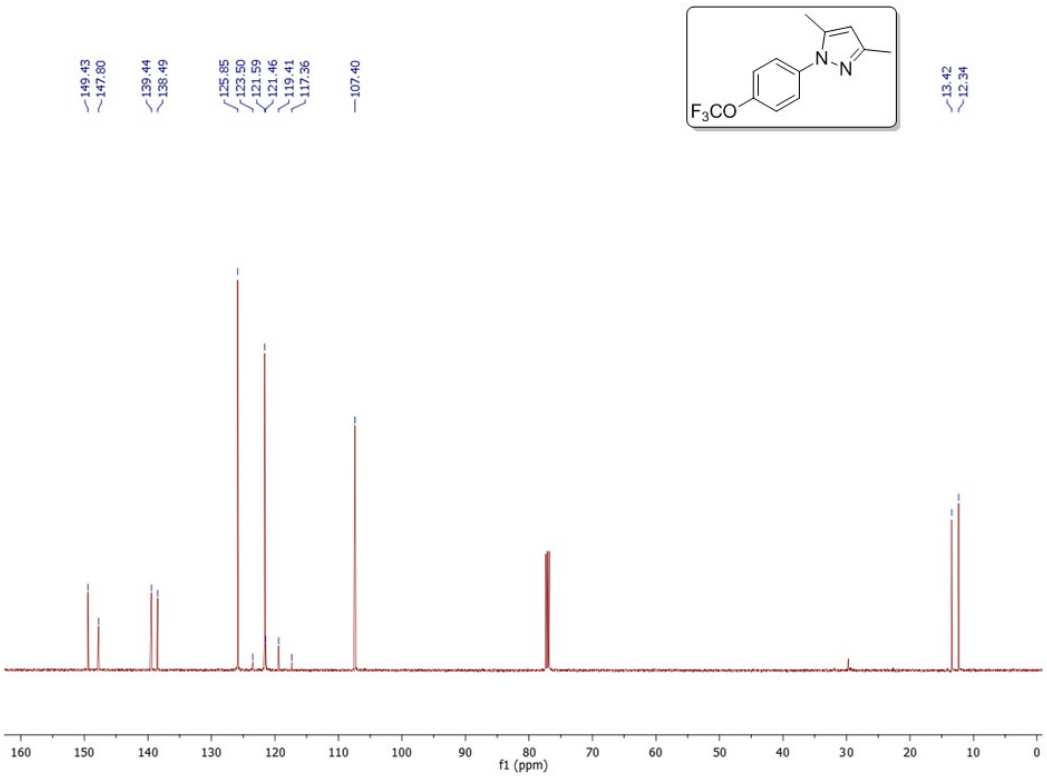


*3,5-Dimethyl-1-(4-(trifluoromethoxy)phenyl)-1H-pyrazole (**3j**)*

^{1}H NMR

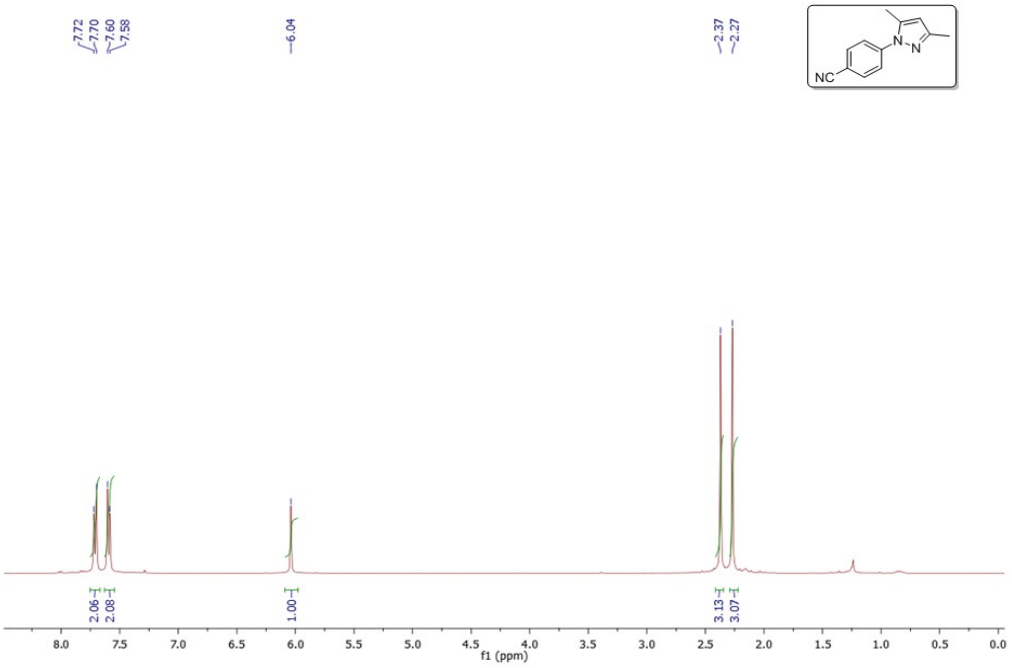


^{13}C NMR

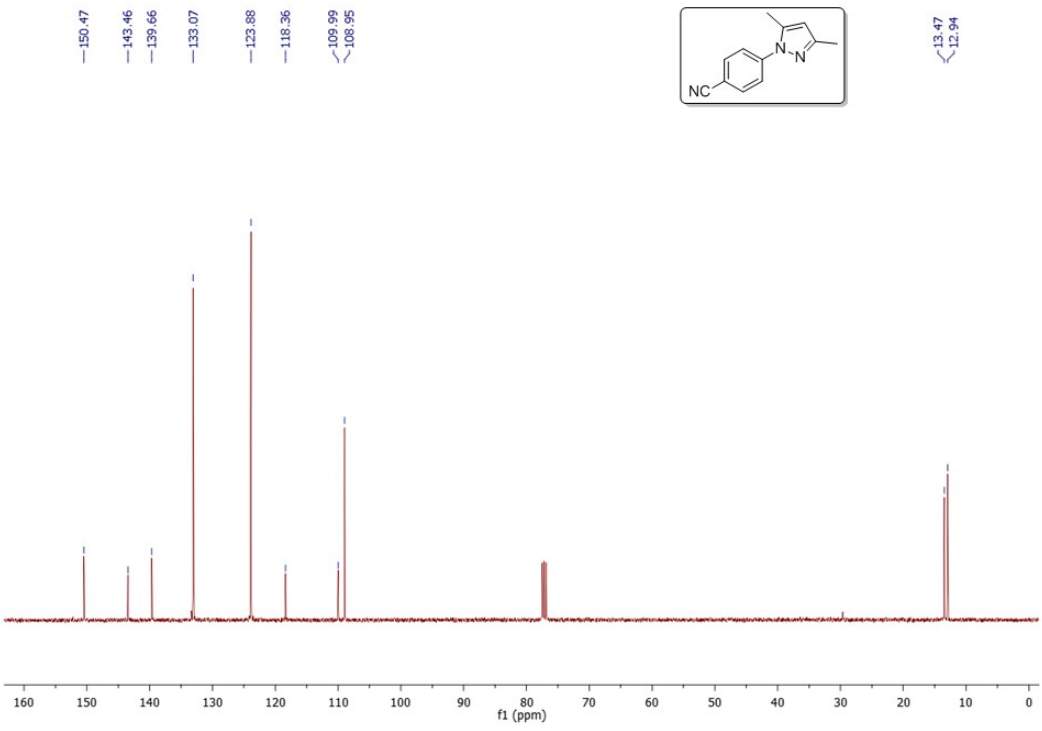


*4-(3,5-Dimethyl-1H-pyrazol-1-yl)benzonitrile (**3k**)*

^{1}H NMR

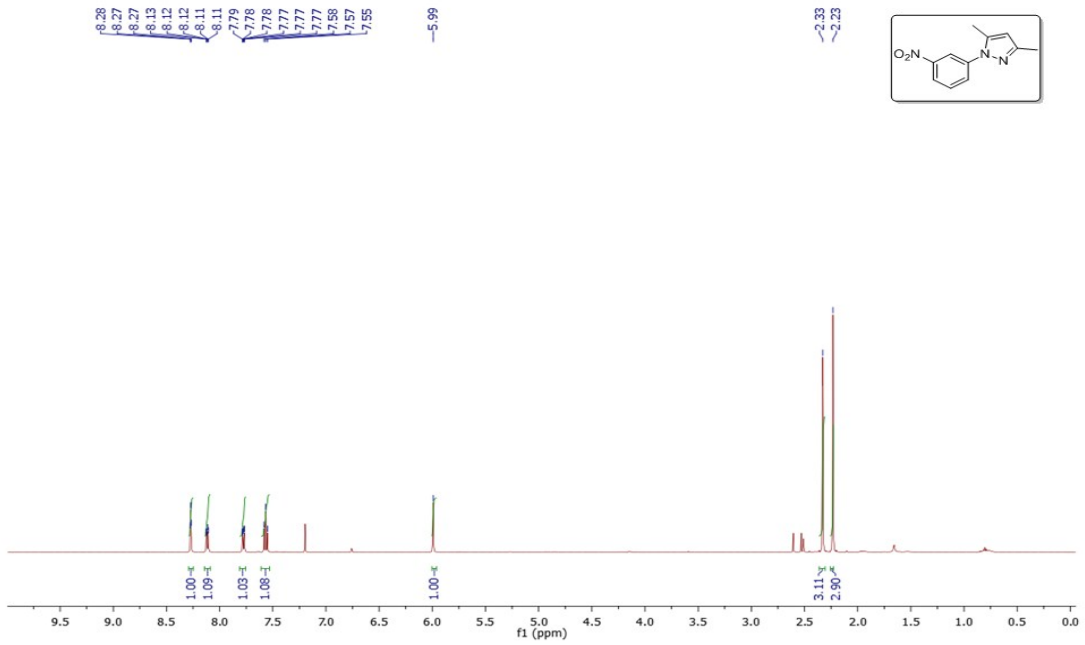


^{13}C NMR

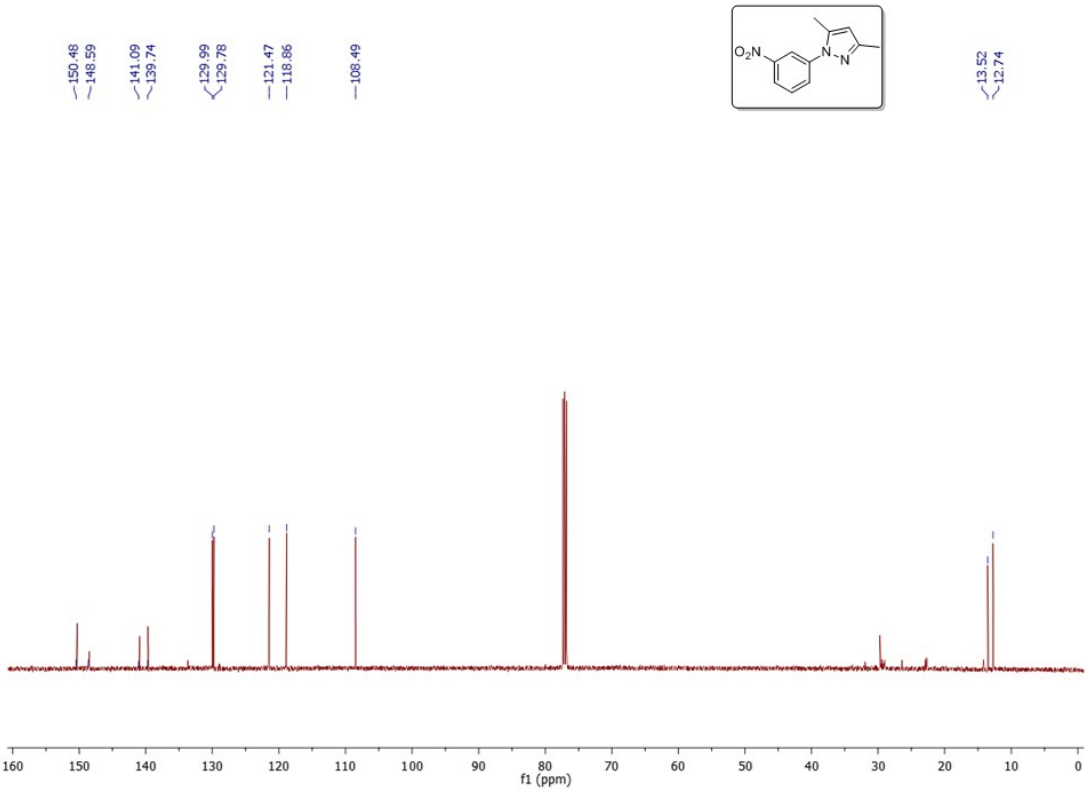


*3,5-Dimethyl-1-(3-nitrophenyl)-1H-pyrazole (**3l**)*

^{1}H NMR

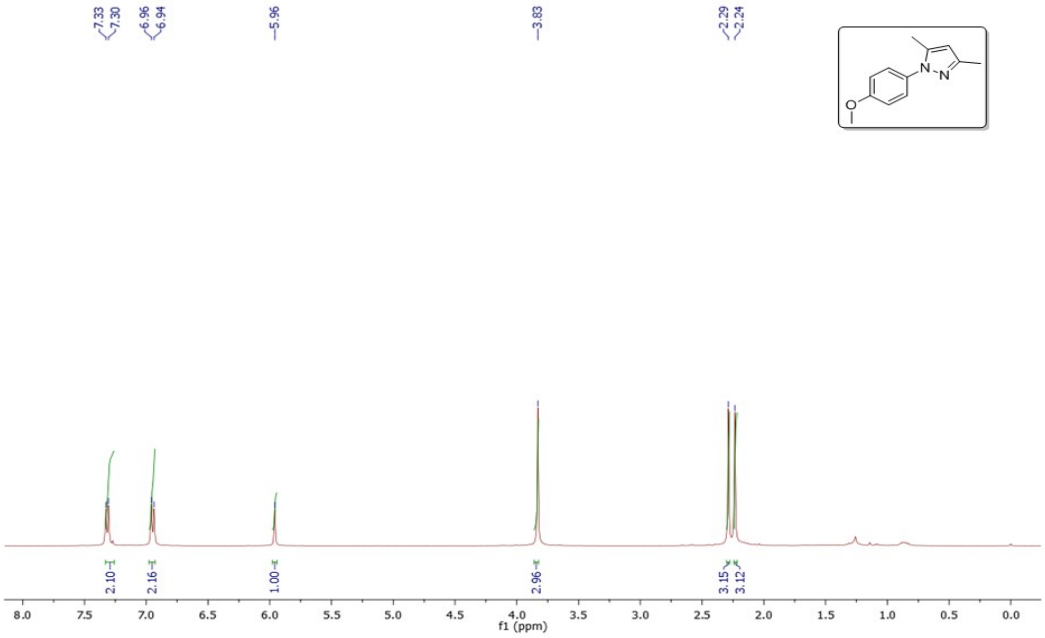


^{13}C NMR

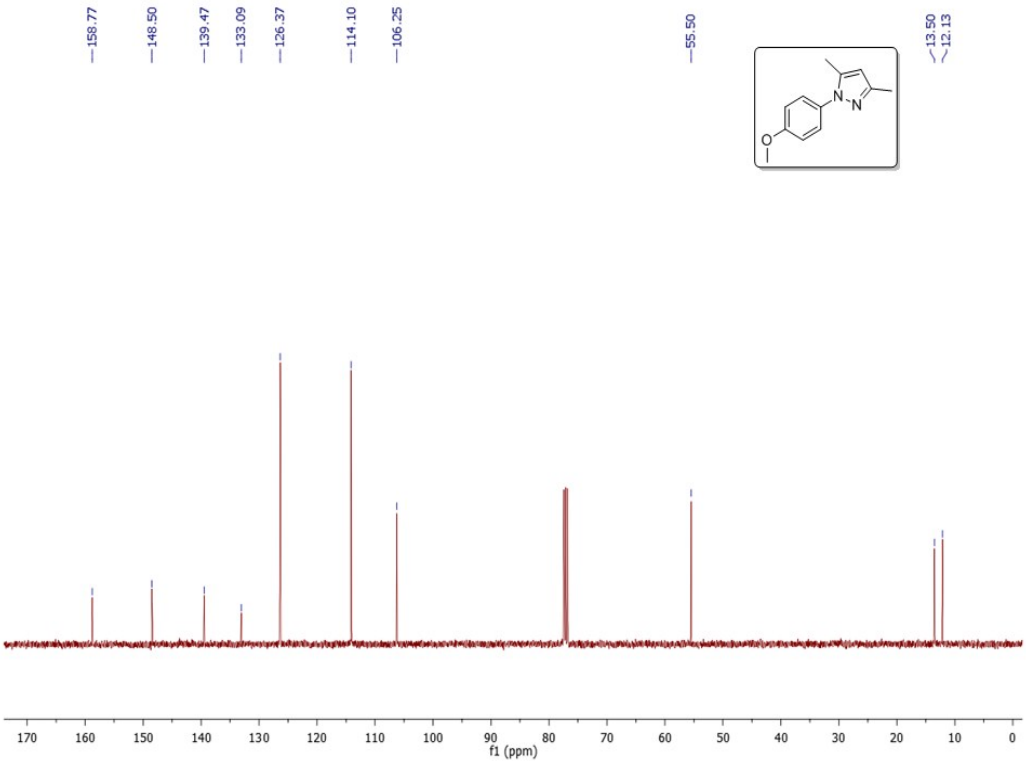


*1-(4-Methoxyphenyl)-3,5-dimethyl-1H-pyrazole (**3m**)*

^{1}H NMR

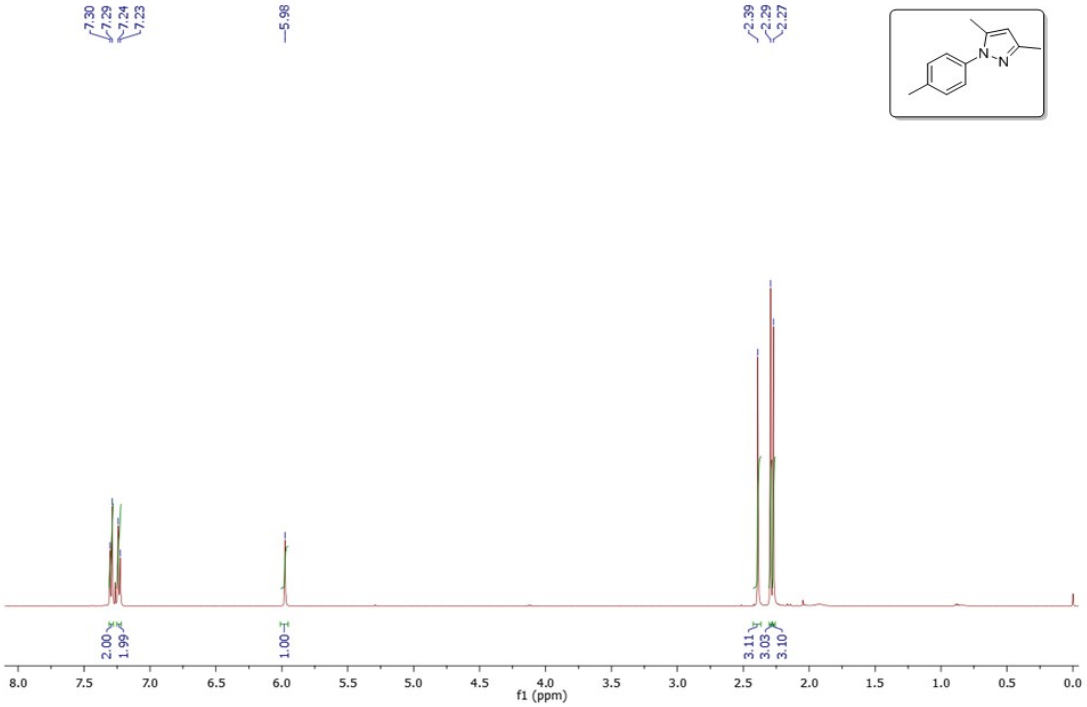


^{13}C NMR

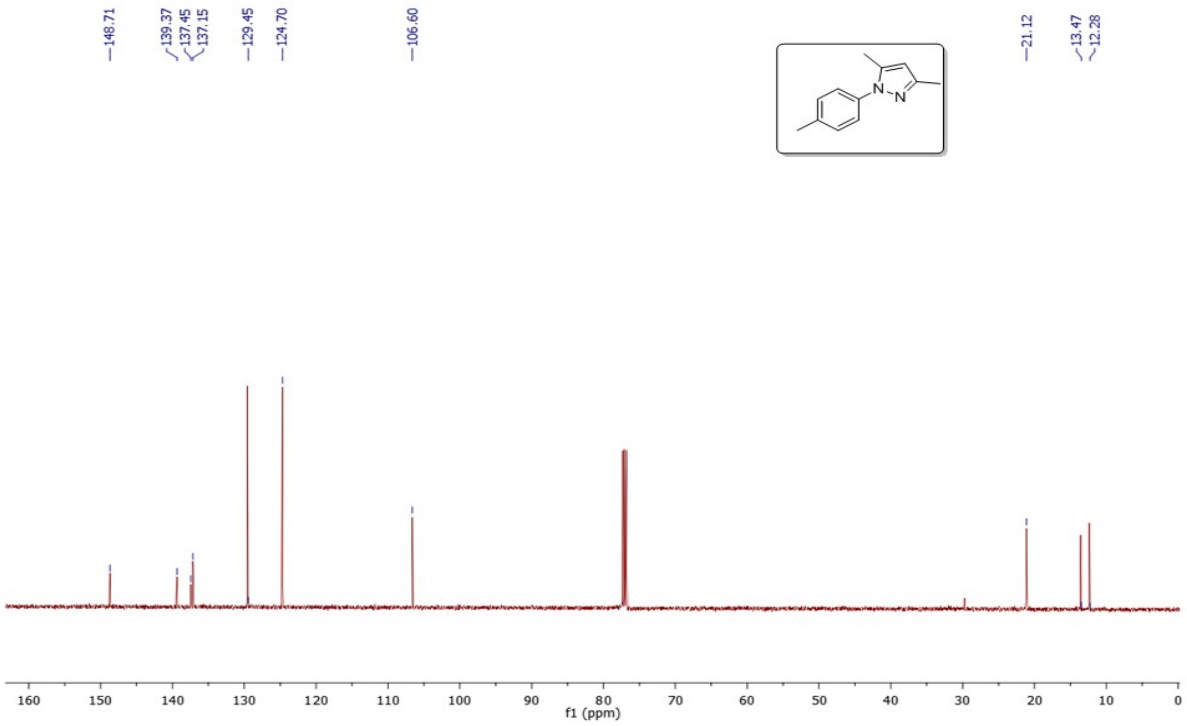


*3,5-Dimethyl-1-(p-tolyl)-1H-pyrazole (**3n**)*

^{1}H NMR

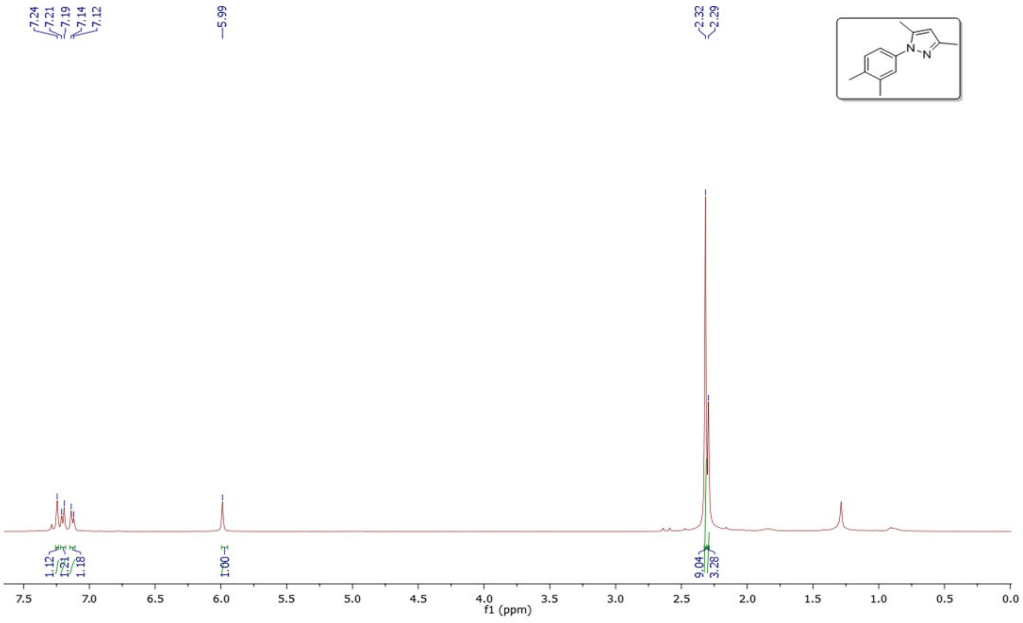


^{13}C NMR

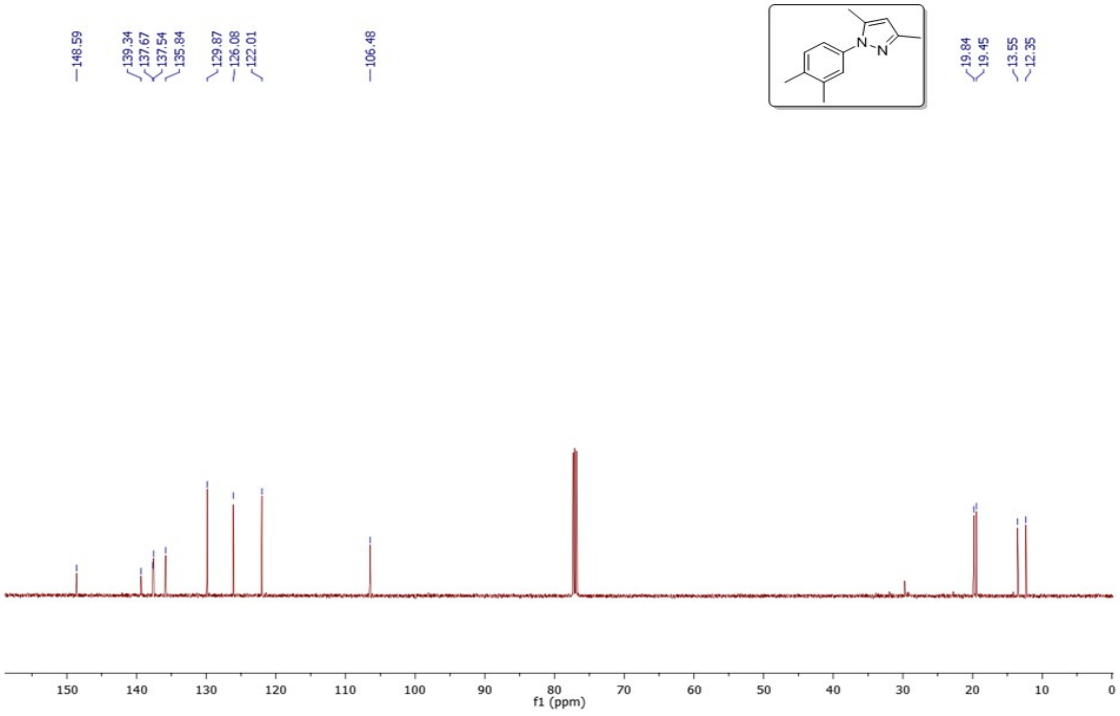


*1-(3,4-Dimethylphenyl)-3,5-dimethyl-1H-pyrazole (**3o**)*

^{1}H NMR

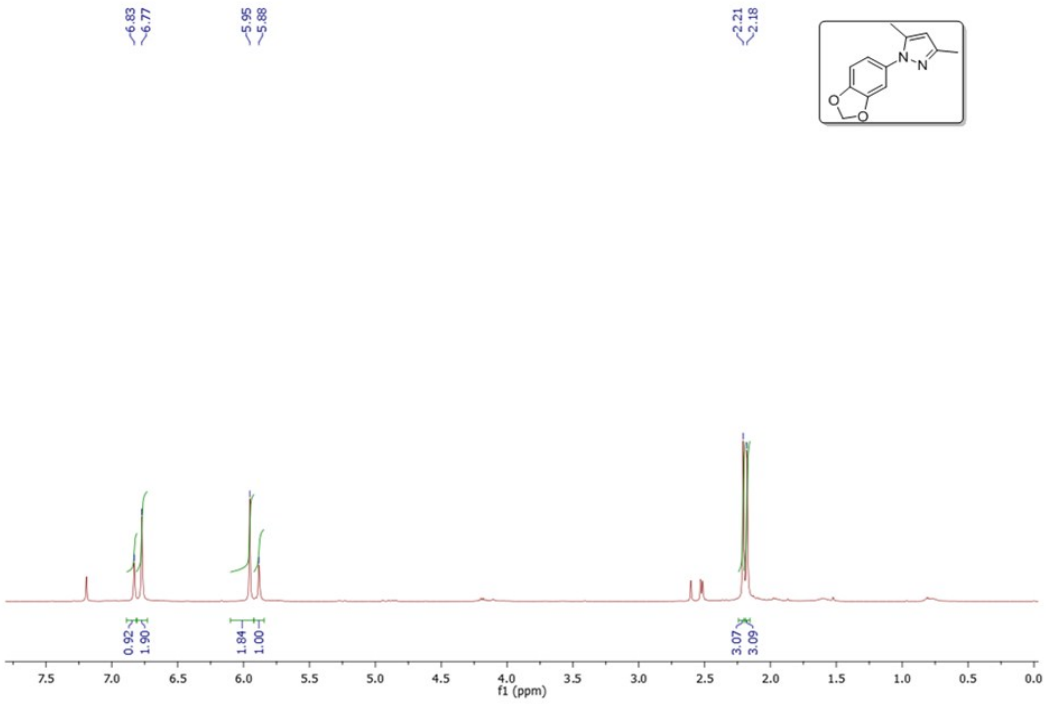


^{13}C NMR

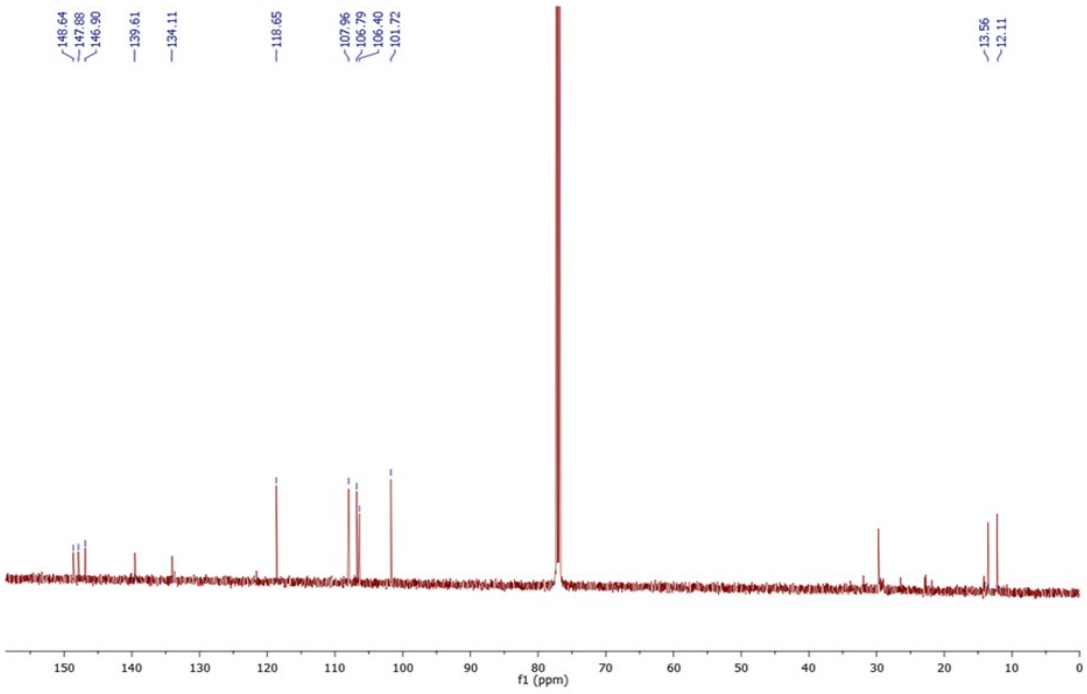


*1-(Benzo[d][1,3]dioxol-5-yl)-3,5-dimethyl-1H-pyrazole (**3p**)*

^{1}H NMR

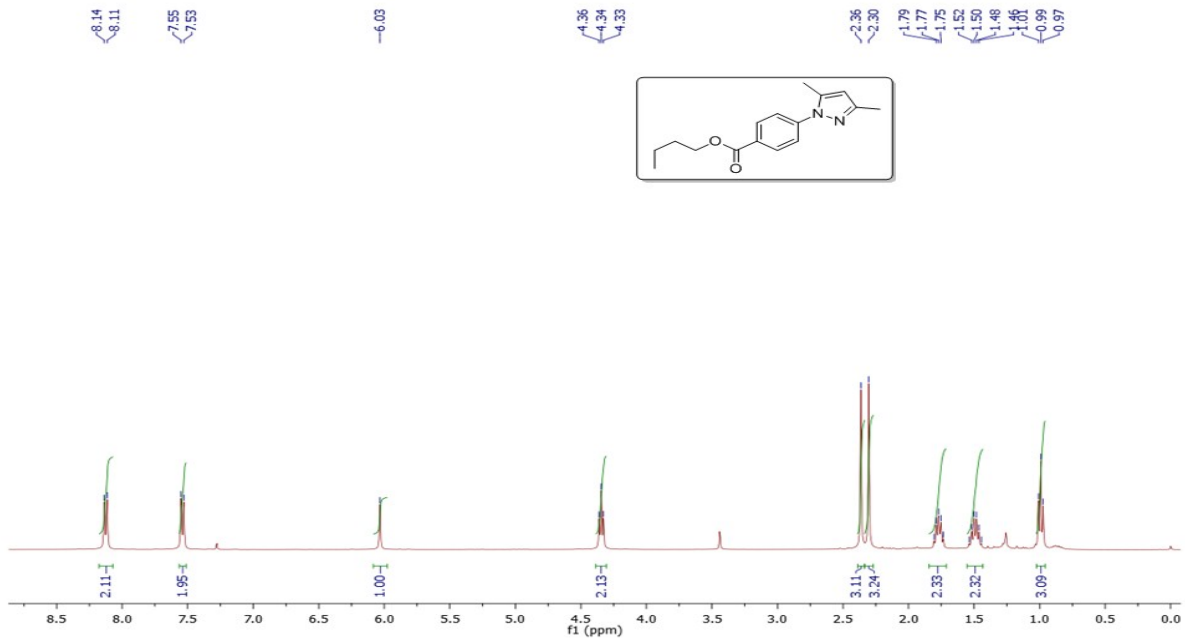


^{13}C NMR

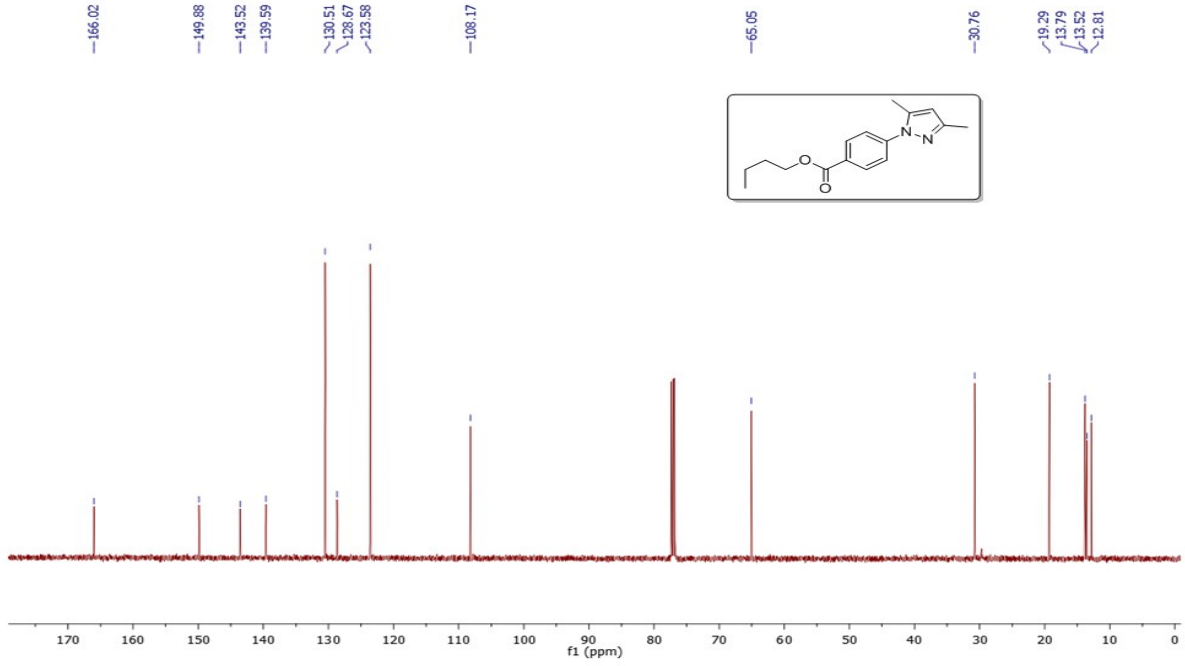


*Butyl 4-(3,5-dimethyl-1H-pyrazol-1-yl)benzoate (**3q**)*

^{1}H NMR

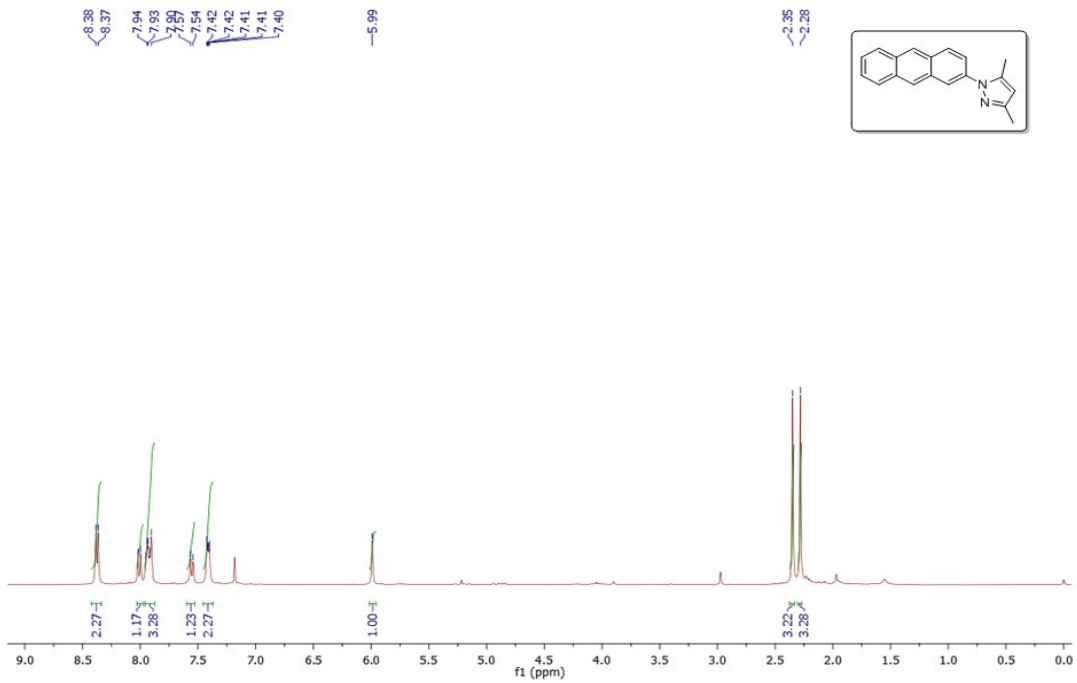


^{13}C NMR

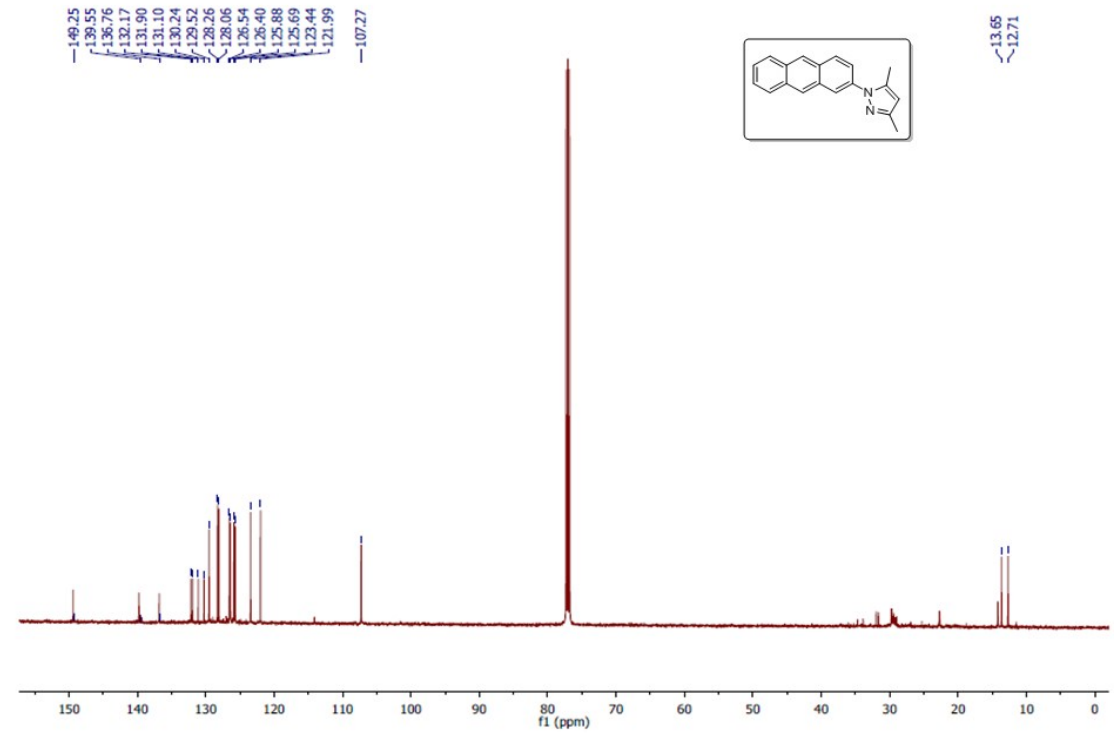


*1-(Anthracen-2-yl)-3,5-dimethyl-1H-pyrazole (**3r**)*

^{1}H NMR

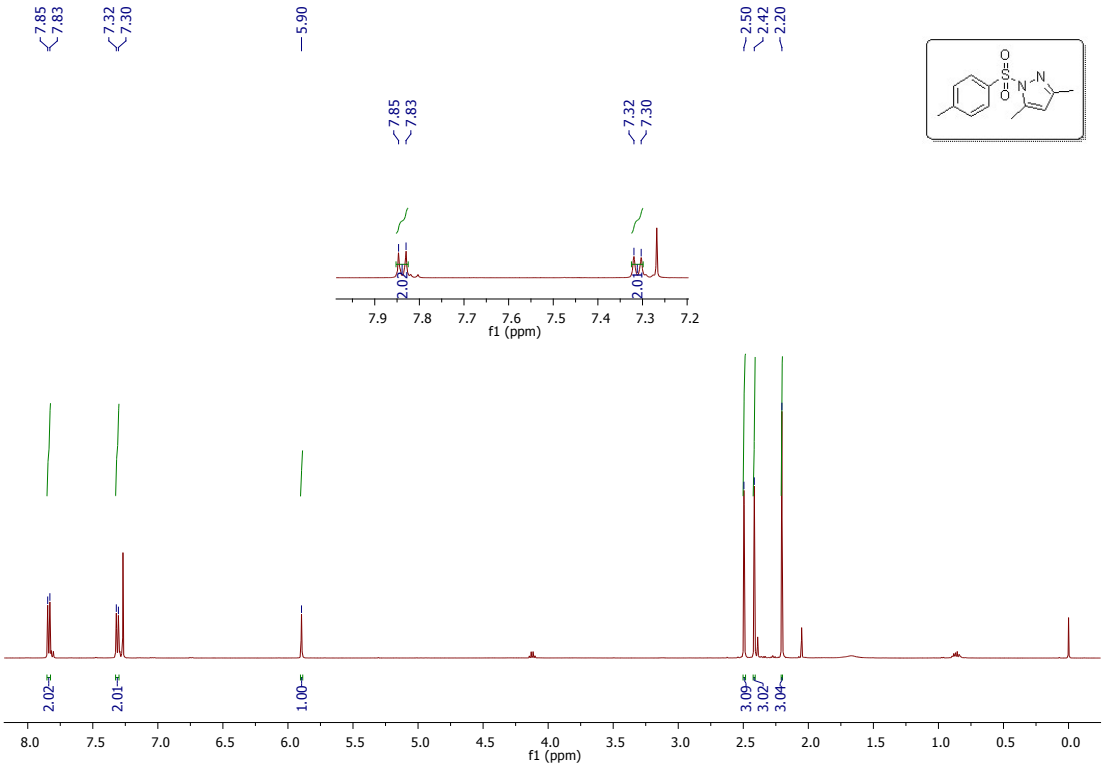


^{13}C NMR

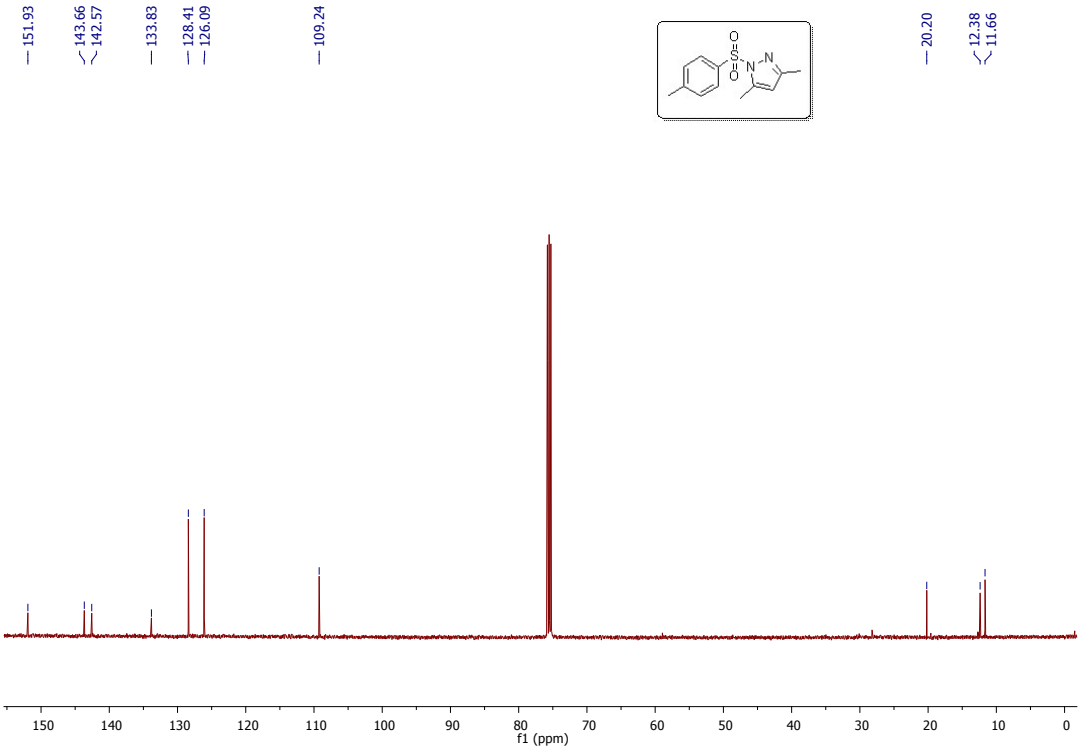


*3,5-Dimethyl-1-tosyl-1H-pyrazole (**5a**)*

^{1}H NMR

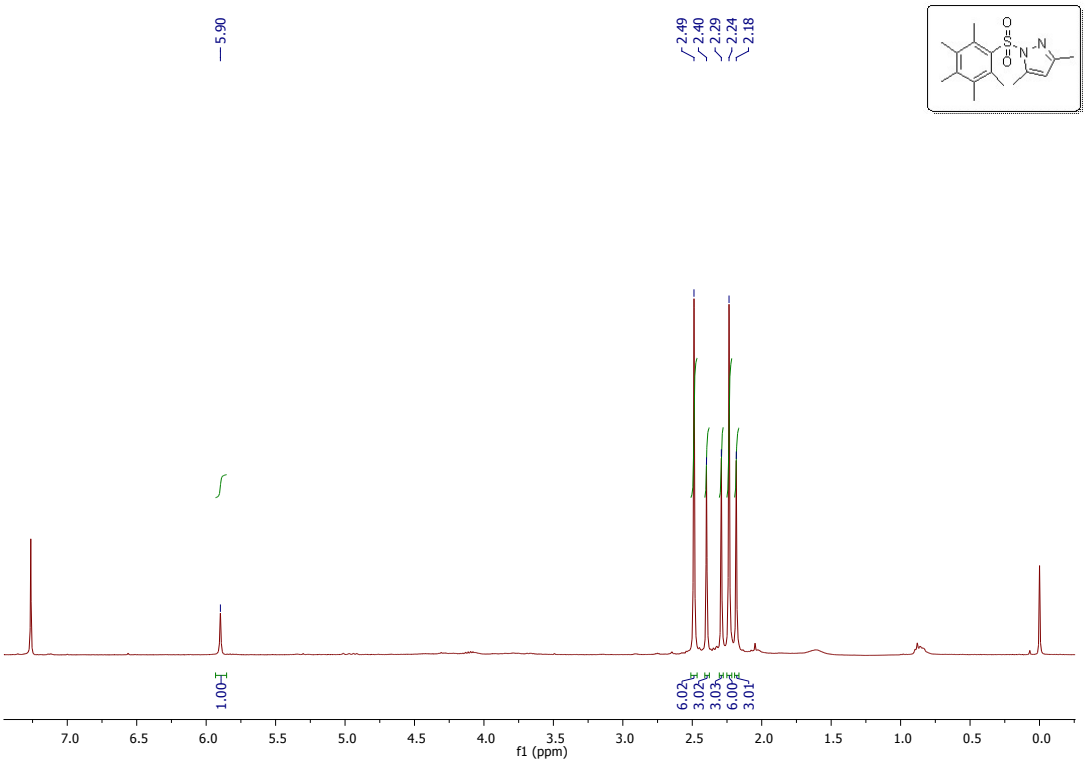


^{13}C NMR

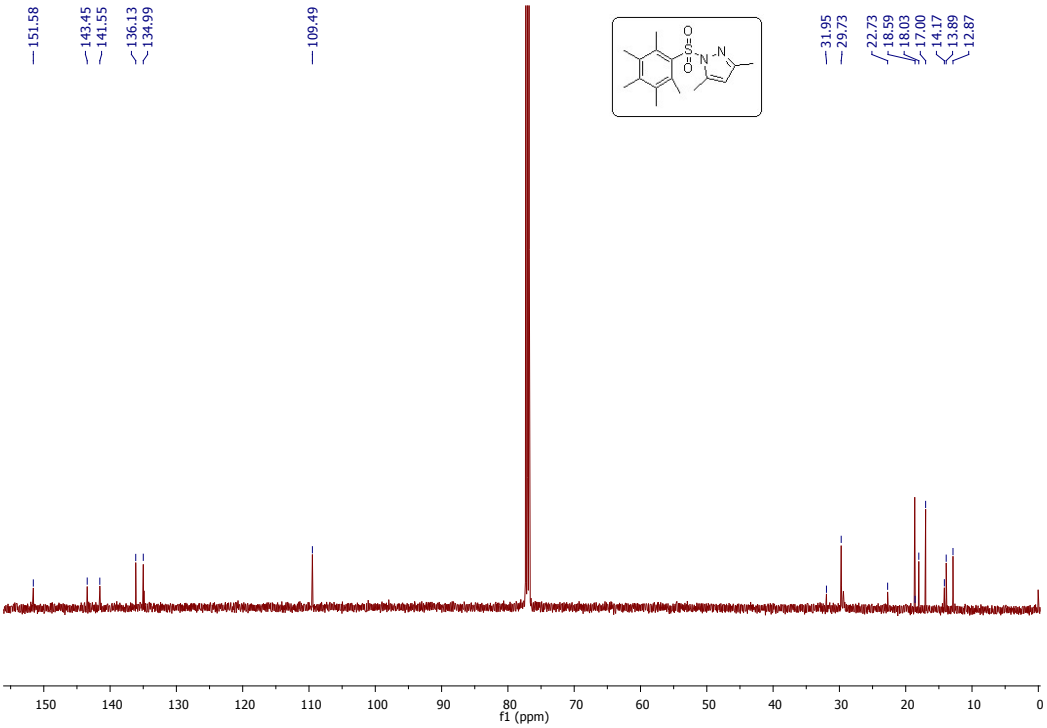


*3,5-Dimethyl-1-((2,3,4,5,6-pentamethylphenyl)sulfonyl)-1H-pyrazole (**5b**)*

^{1}H NMR

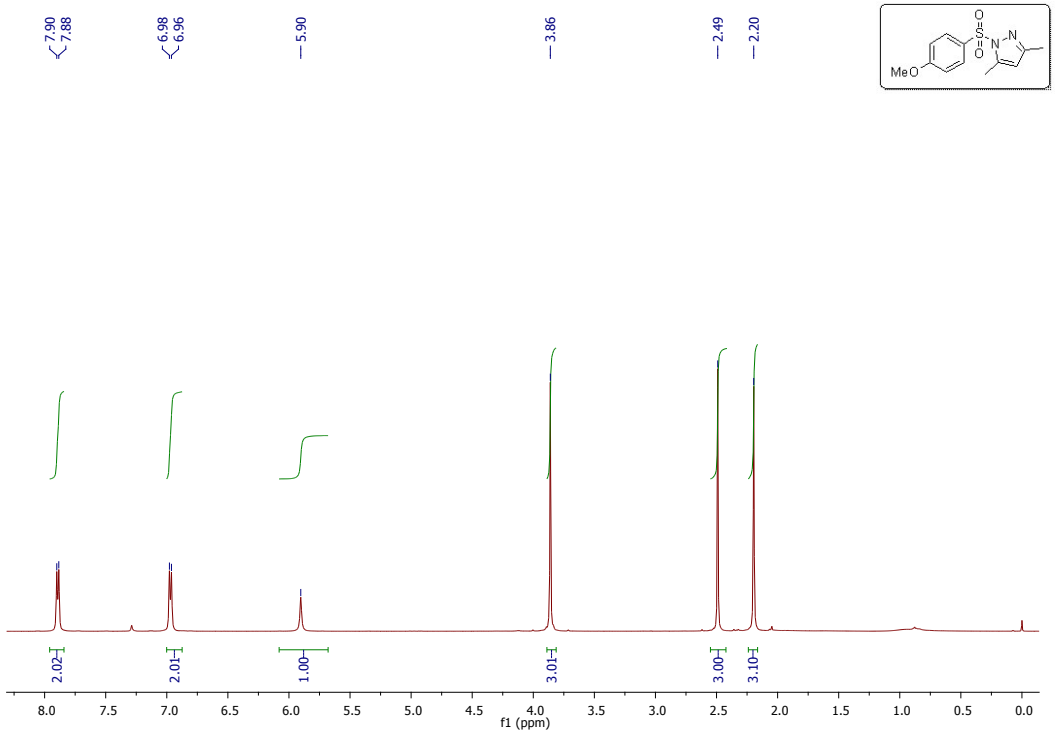


^{13}C NMR

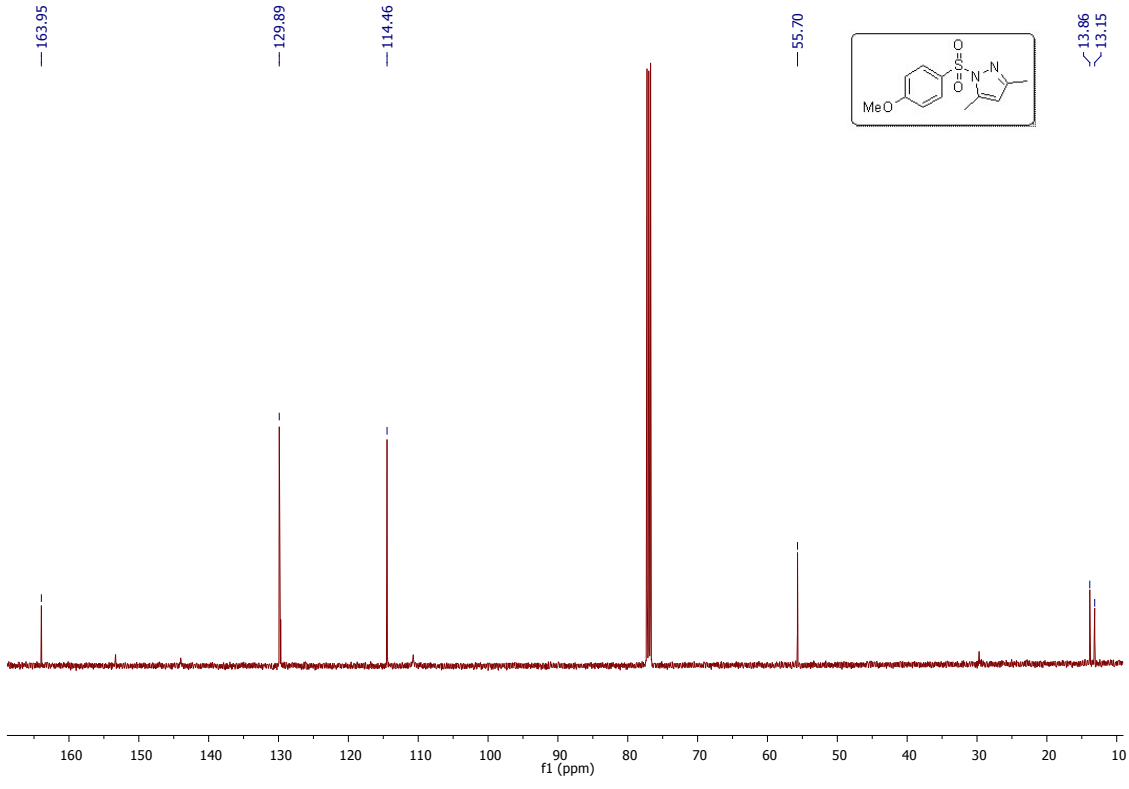


*1-((4-Methoxyphenyl)sulfonyl)-3,5-dimethyl-1H-pyrazole (**5c**)*

^{1}H NMR

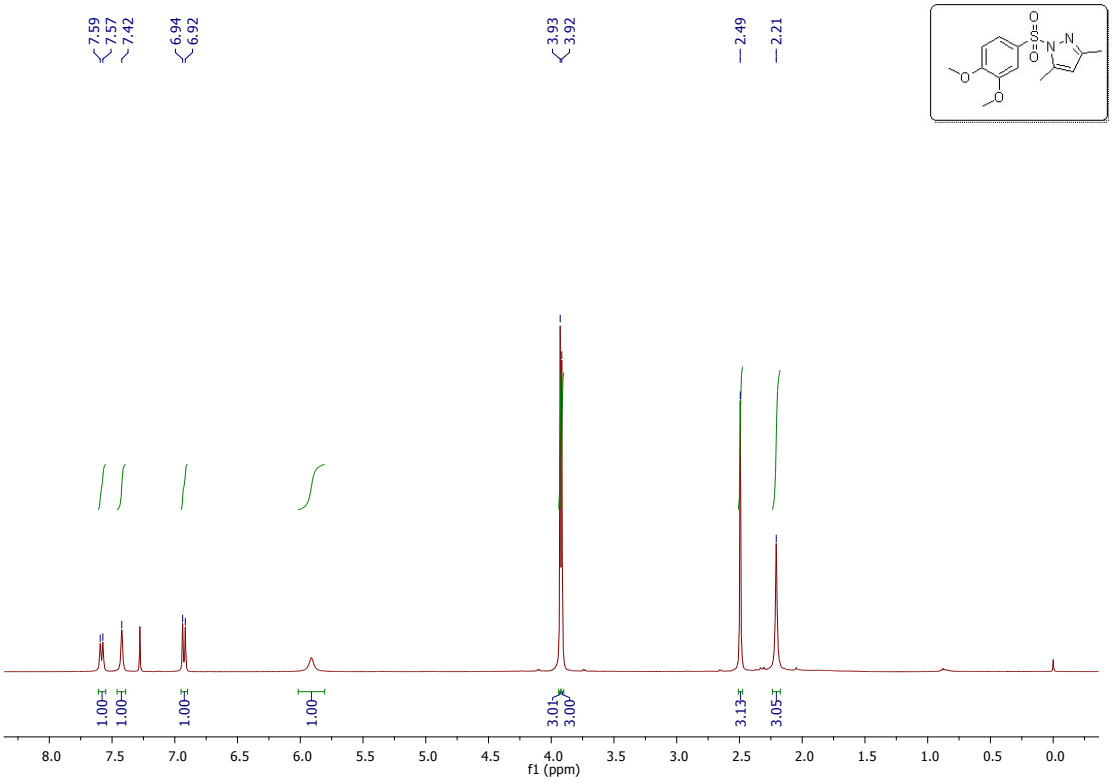


^{13}C NMR

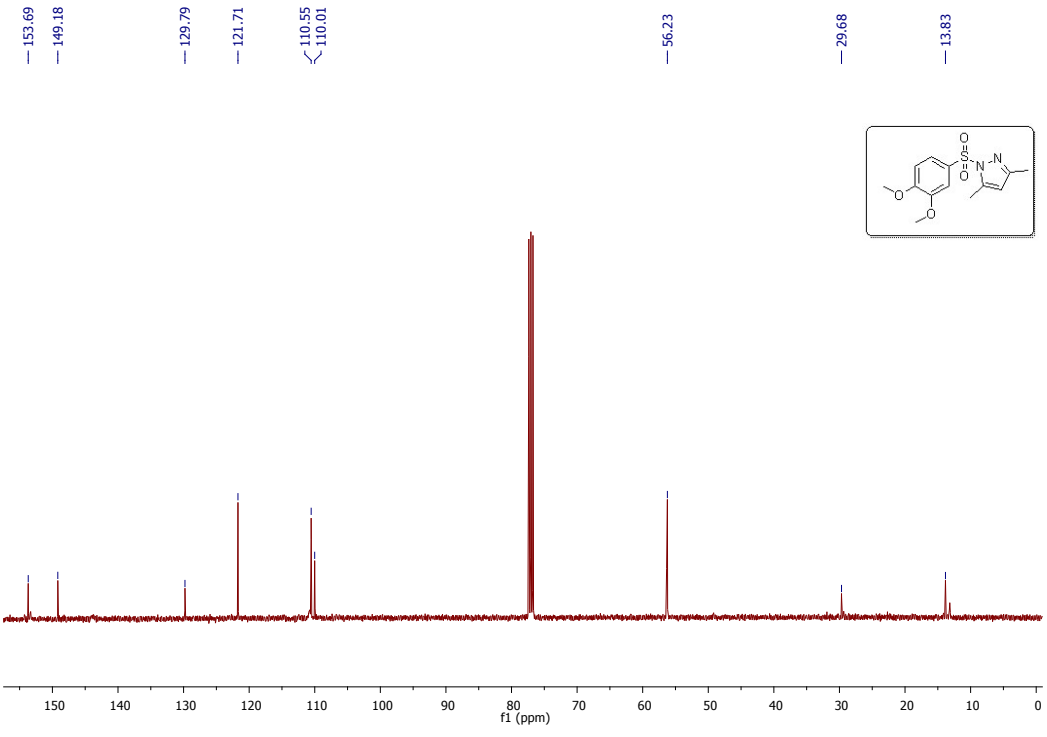


*1-((3,4-Dimethoxyphenyl)sulfonyl)-3,5-dimethyl-1H-pyrazole (**5d**)*

^{1}H NMR

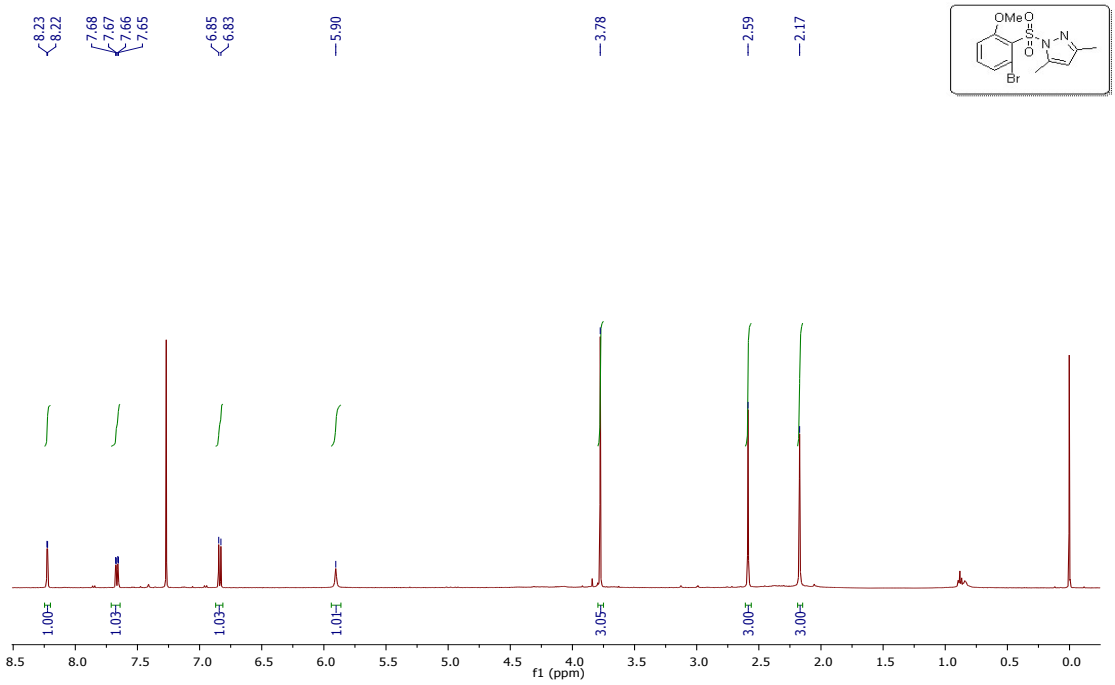


^{13}C NMR

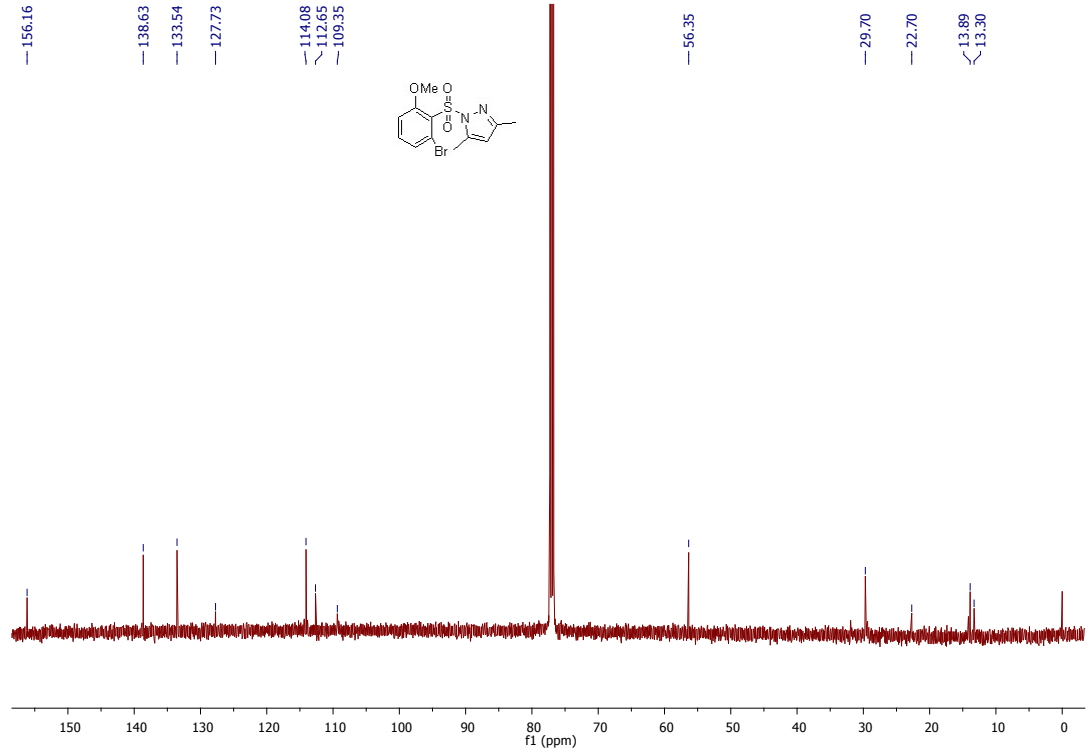


*1-((2-Bromo-6-methoxyphenyl)sulfonyl)-3,5-dimethyl-1H-pyrazole (**5e**)*

^{1}H NMR

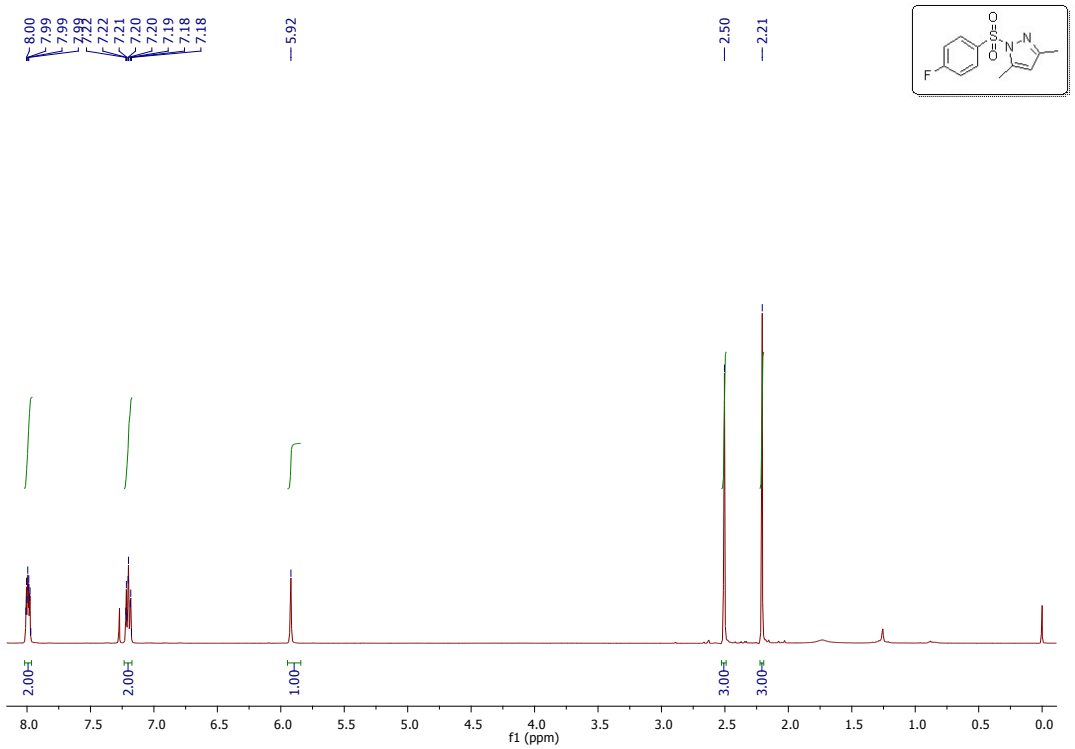


^{13}C NMR

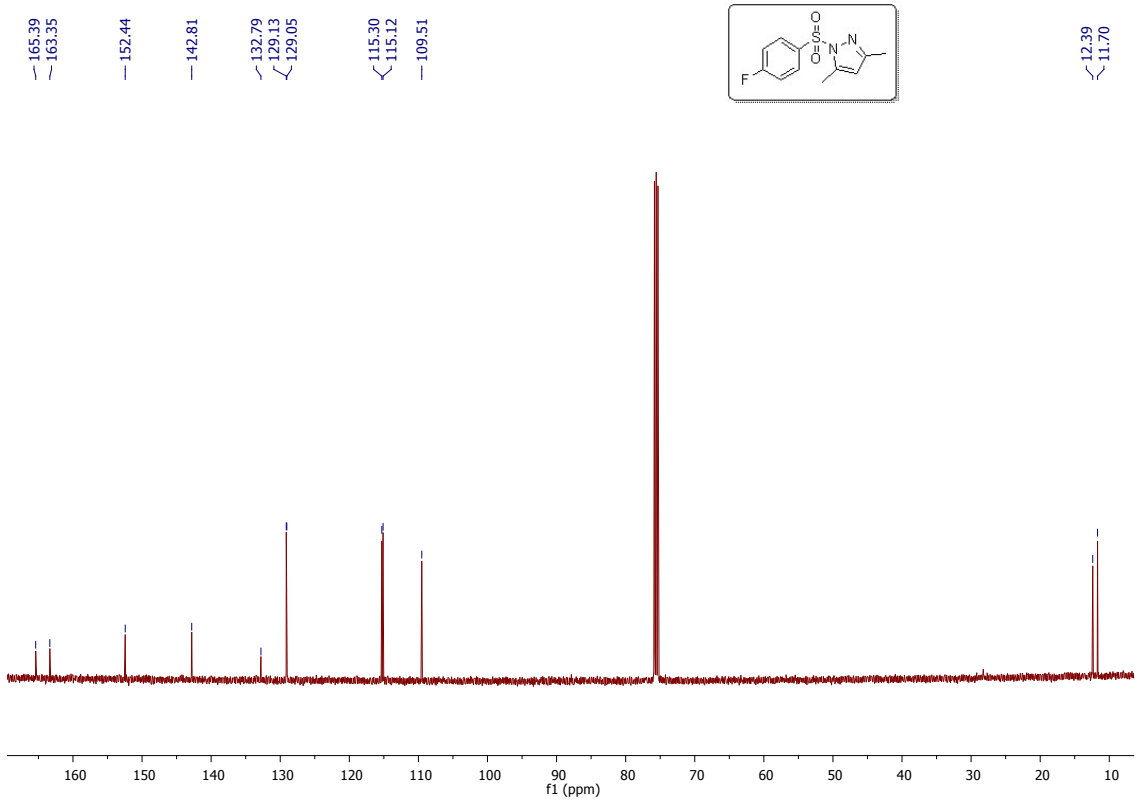


*1-((4-Fluorophenyl)sulfonyl)-3,5-dimethyl-1H-pyrazole (**5f**)*

^{1}H NMR

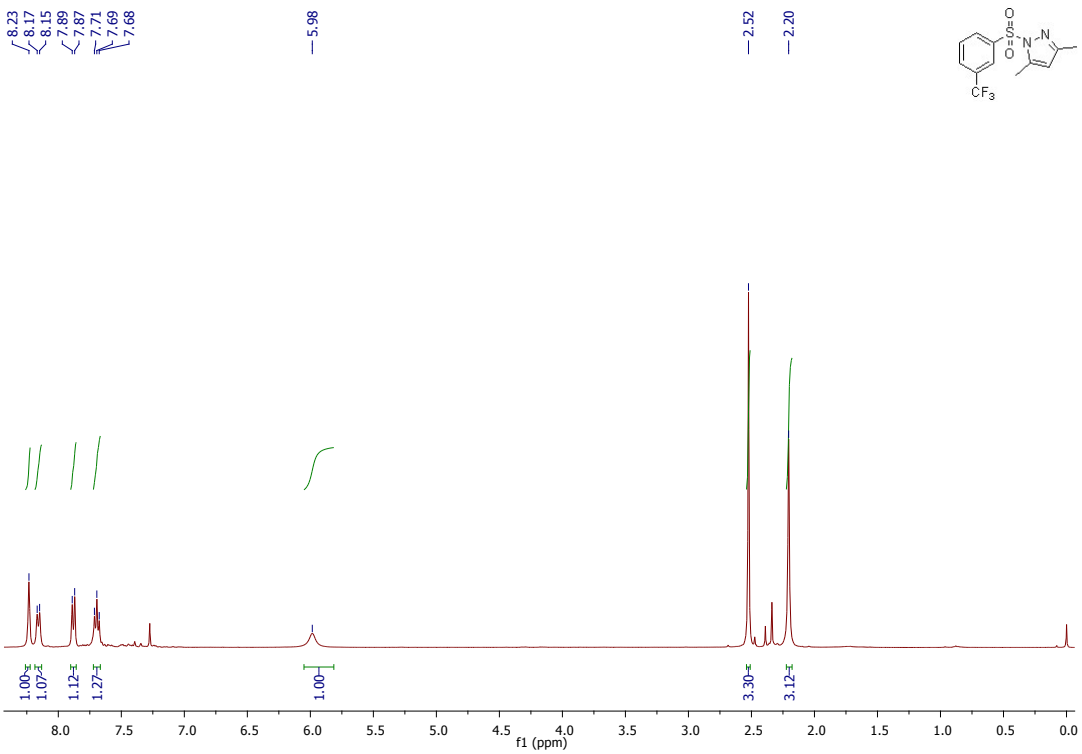


^{13}C NMR

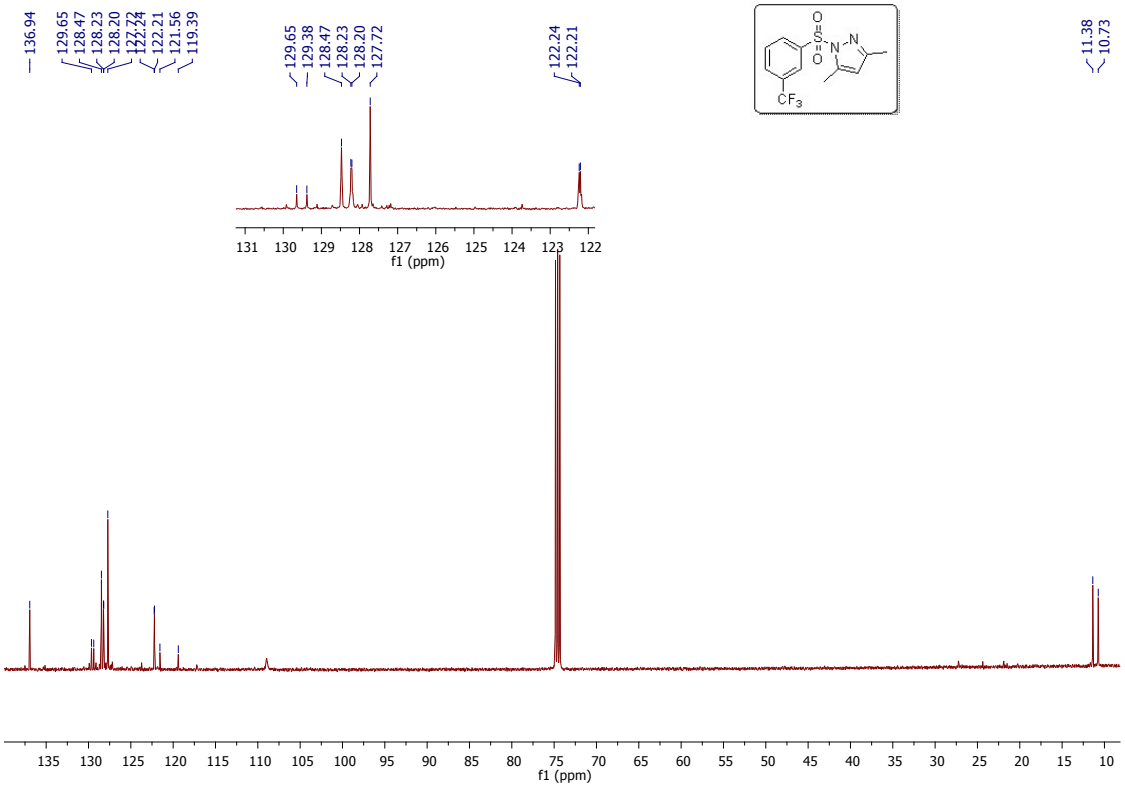


*3,5-Dimethyl-1-((3-(trifluoromethyl)phenyl)sulfonyl)-1H-pyrazole (**5g**)*

^{1}H NMR

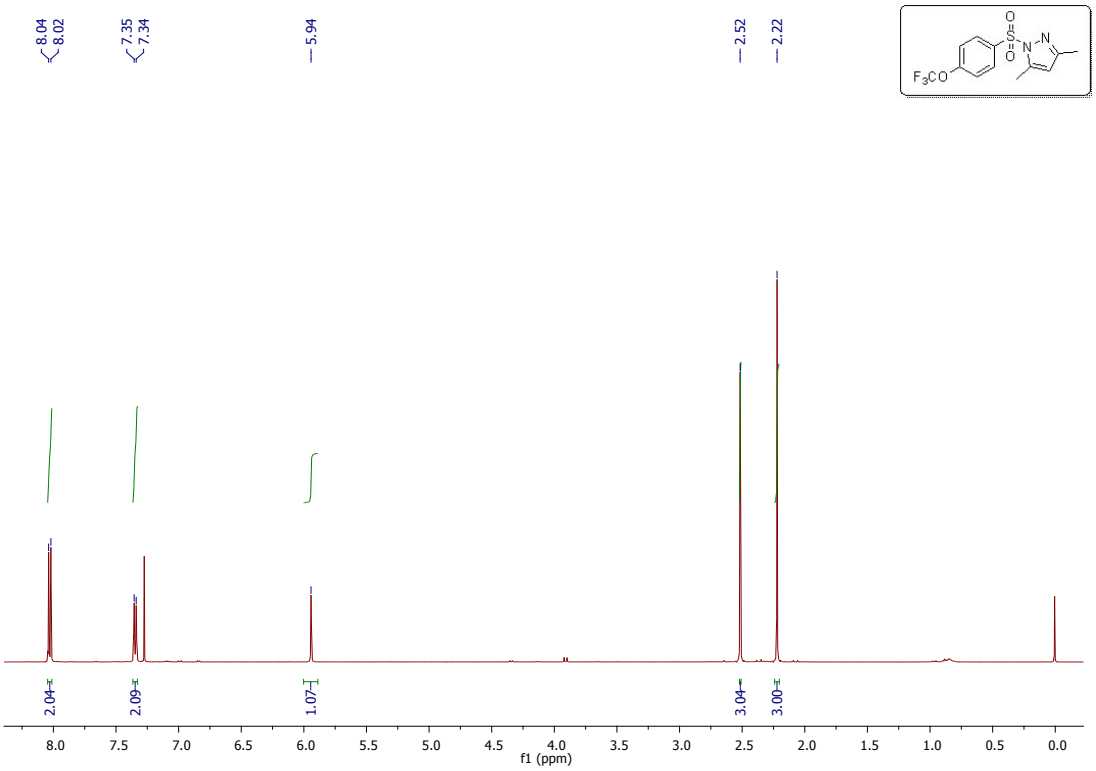


^{13}C NMR

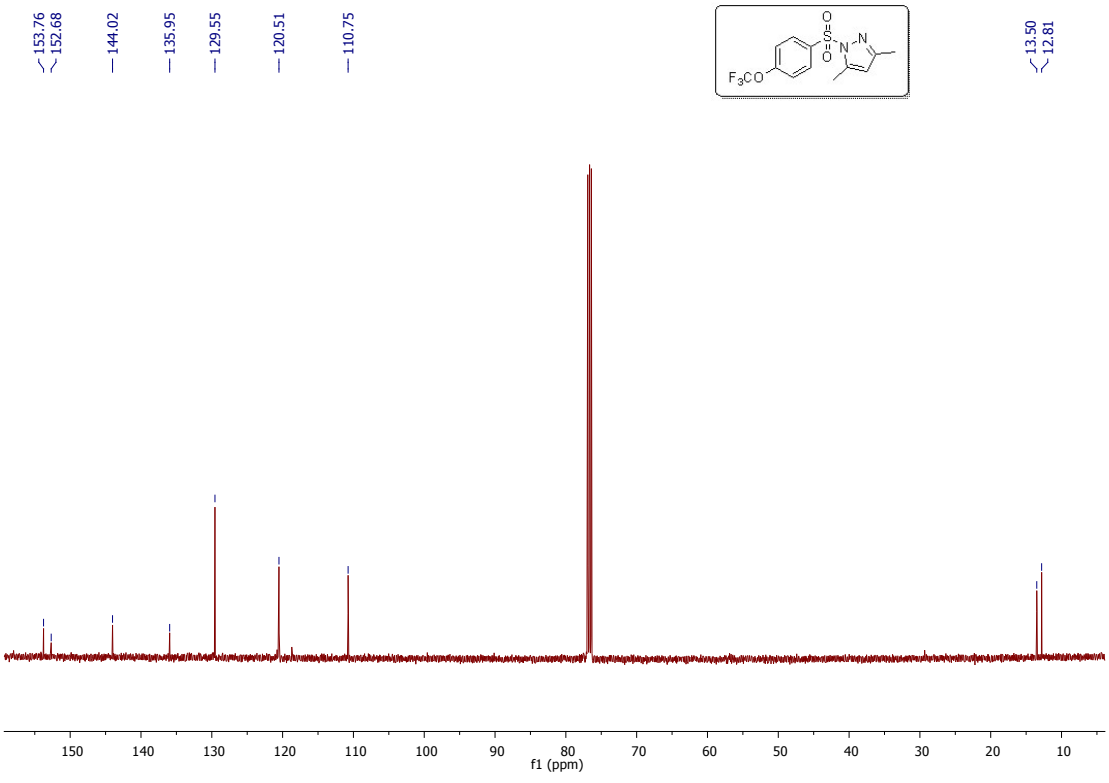


*3,5-Dimethyl-1-((4-(trifluoromethoxy)phenyl)sulfonyl)-1H-pyrazole (**5h**)*

^{1}H NMR

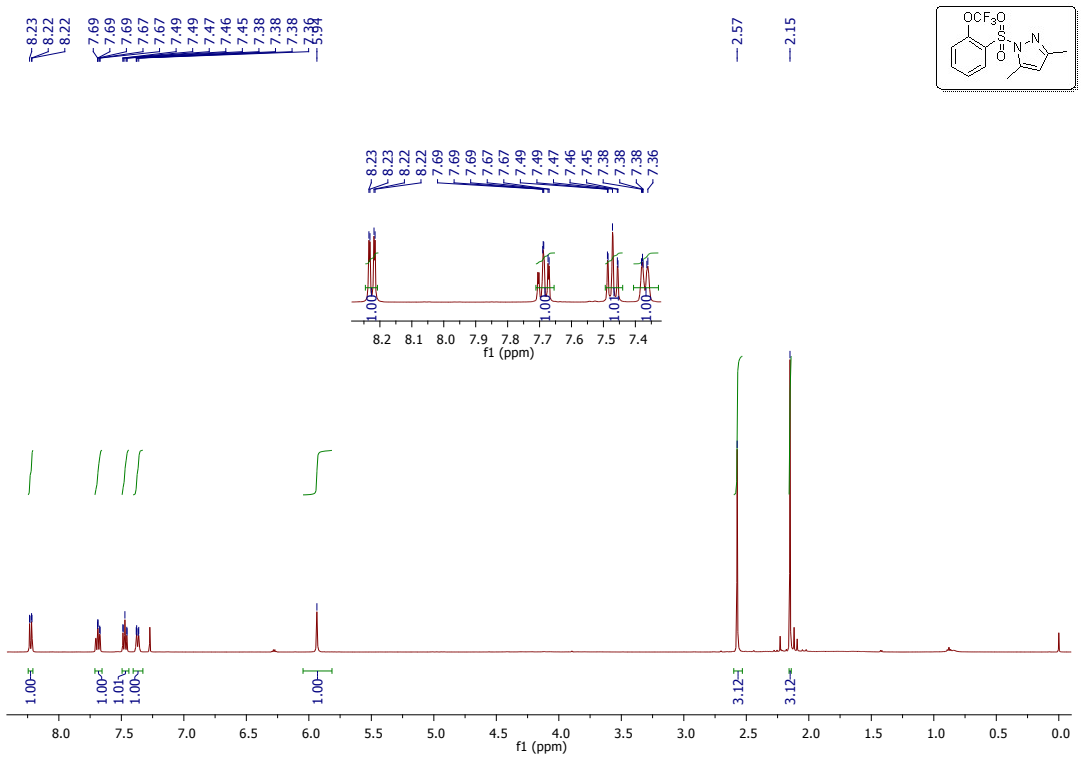


^{13}C NMR

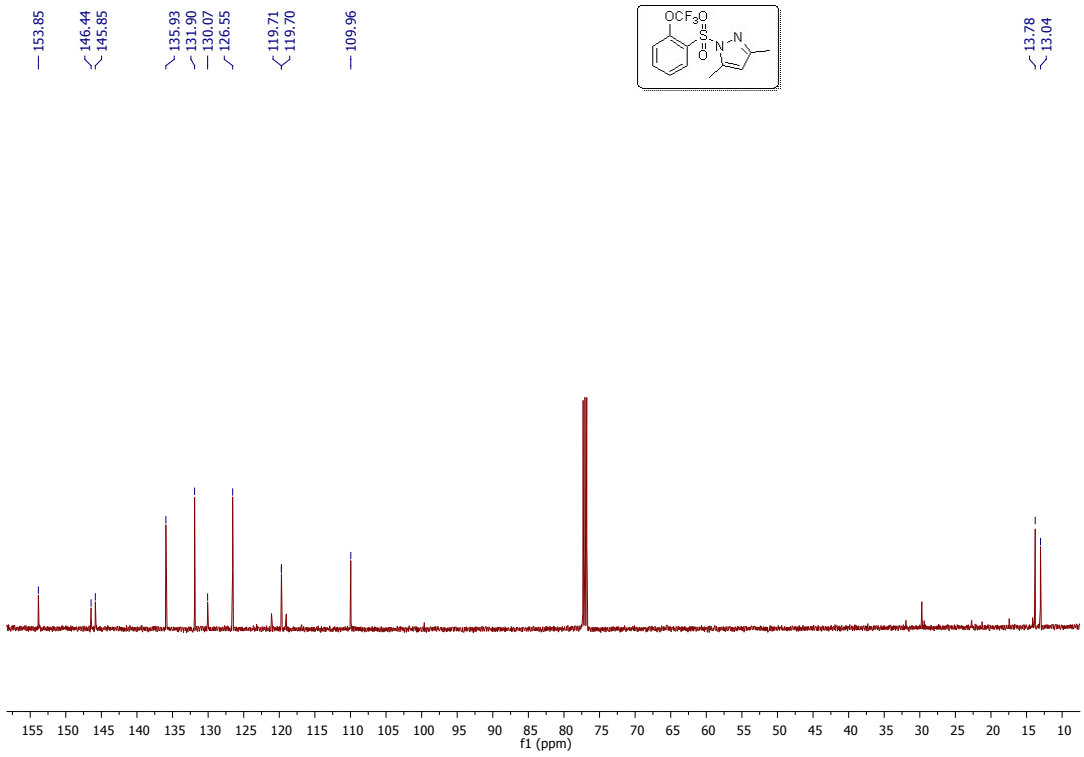


*3,5-Dimethyl-1-((2-(trifluoromethoxy)phenyl)sulfonyl)-1H-pyrazole (**5i**)*

^{1}H NMR

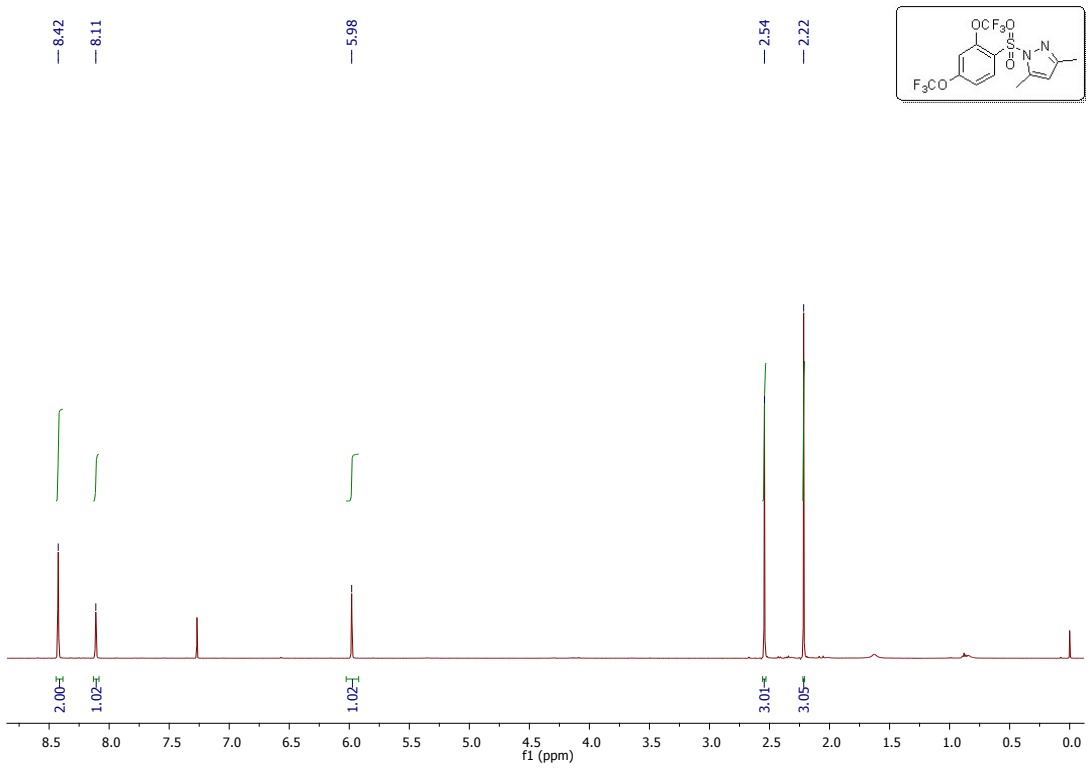


^{13}C NMR

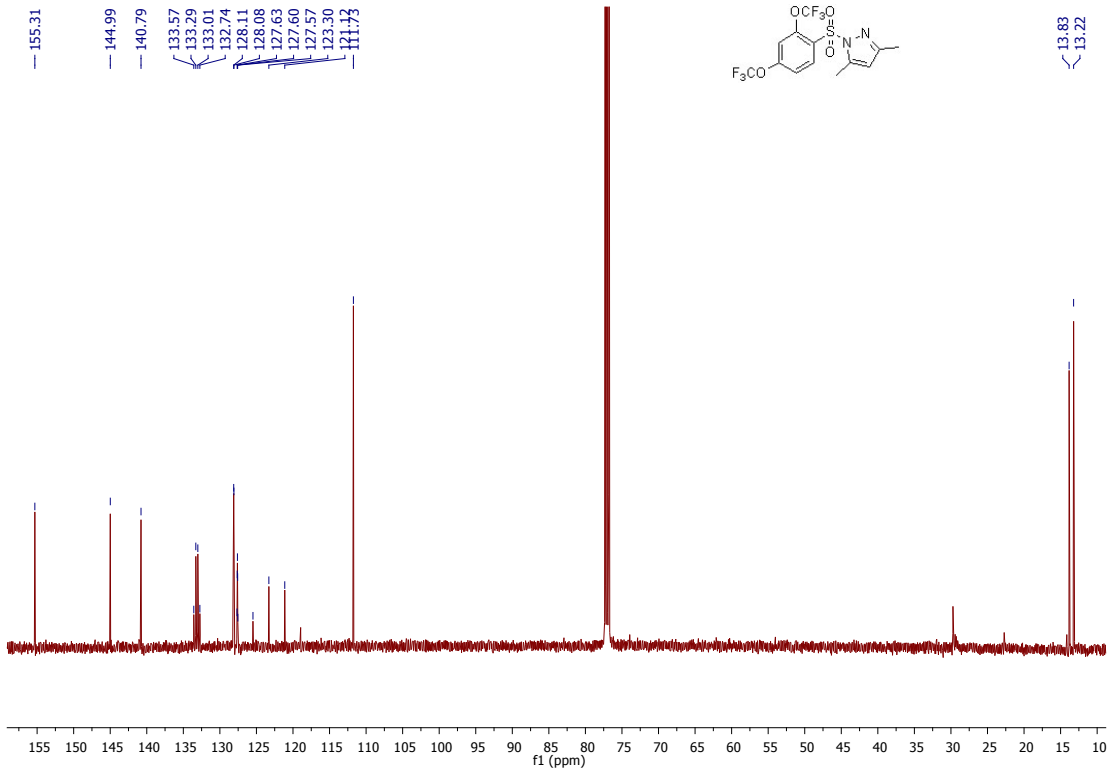


*1-((3,5-Bis(trifluoromethoxy)phenyl)sulfonyl)-3,5-dimethyl-1H-pyrazole (**5j**)*

^{1}H NMR

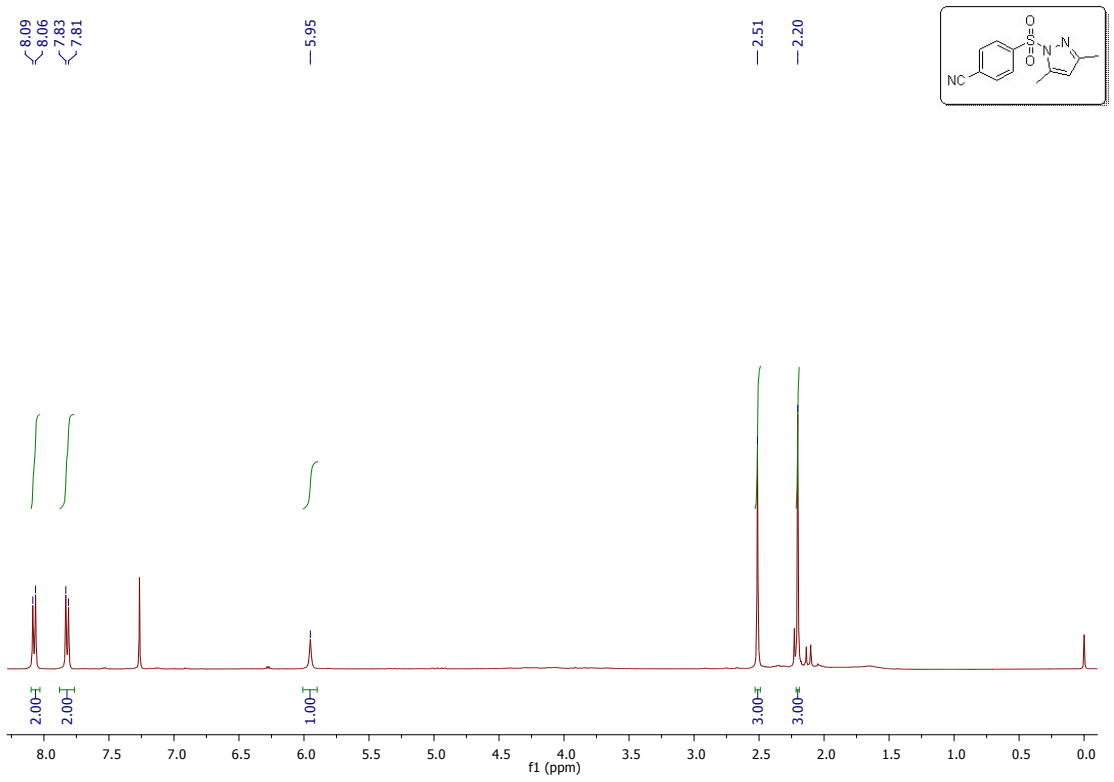


^{13}C NMR

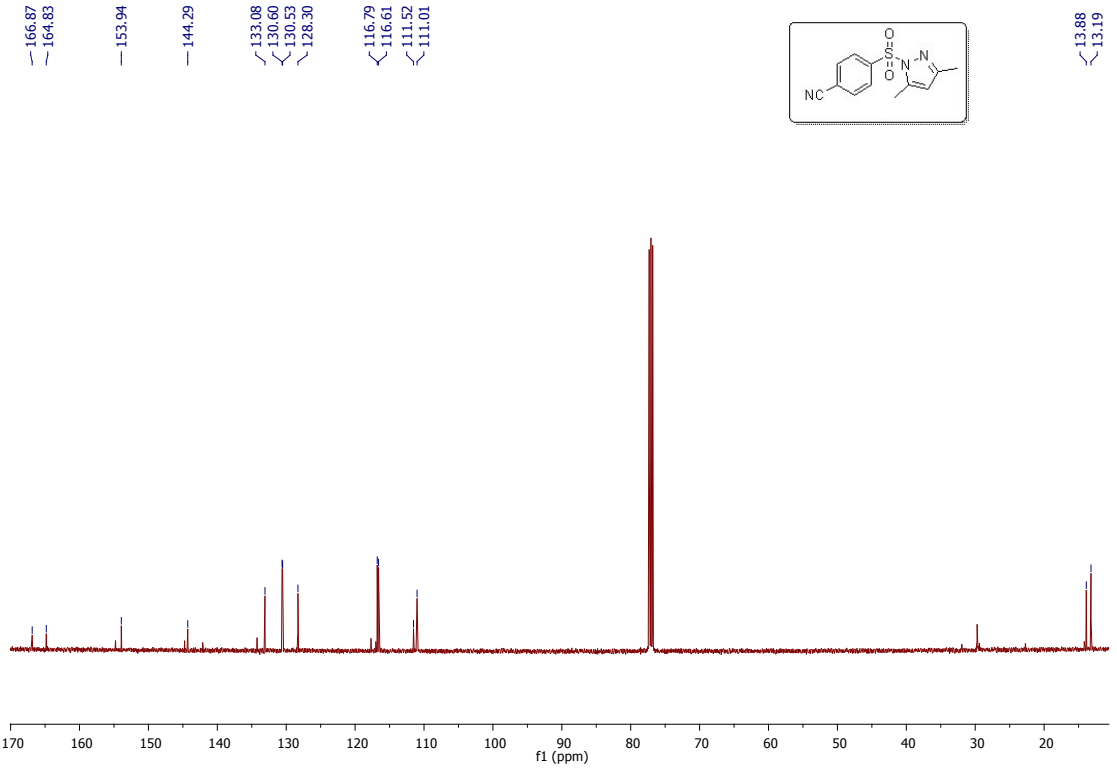


*4-((3,5-Dimethyl-1H-pyrazol-1-yl)sulfonyl)benzonitrile (**5k**)*

^{1}H NMR

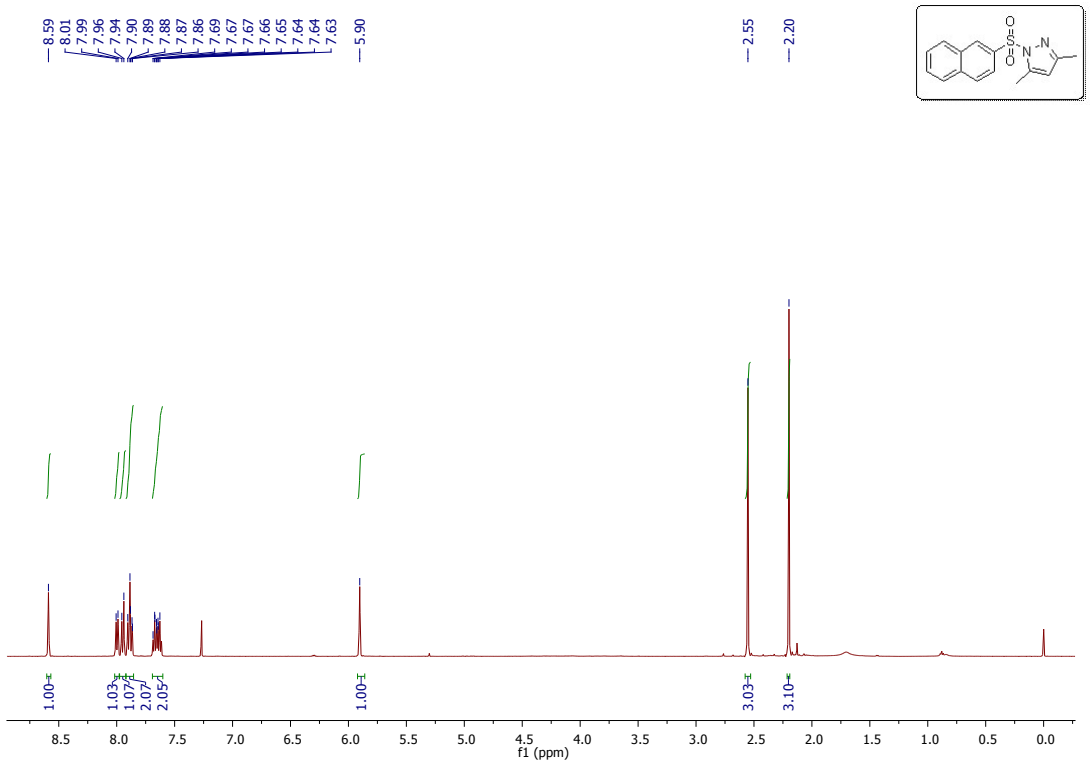


^{13}C NMR

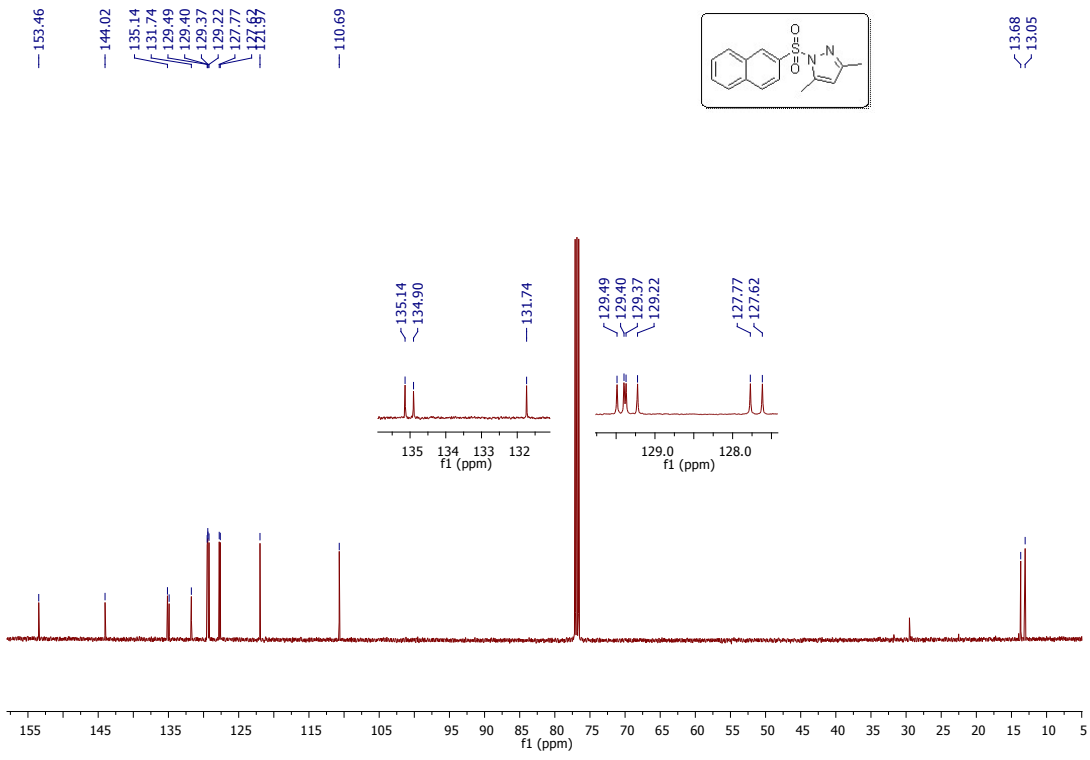


*3,5-Dimethyl-1-(naphthalen-2-ylsulfonyl)-1H-pyrazole (**5l**)*

^{1}H NMR

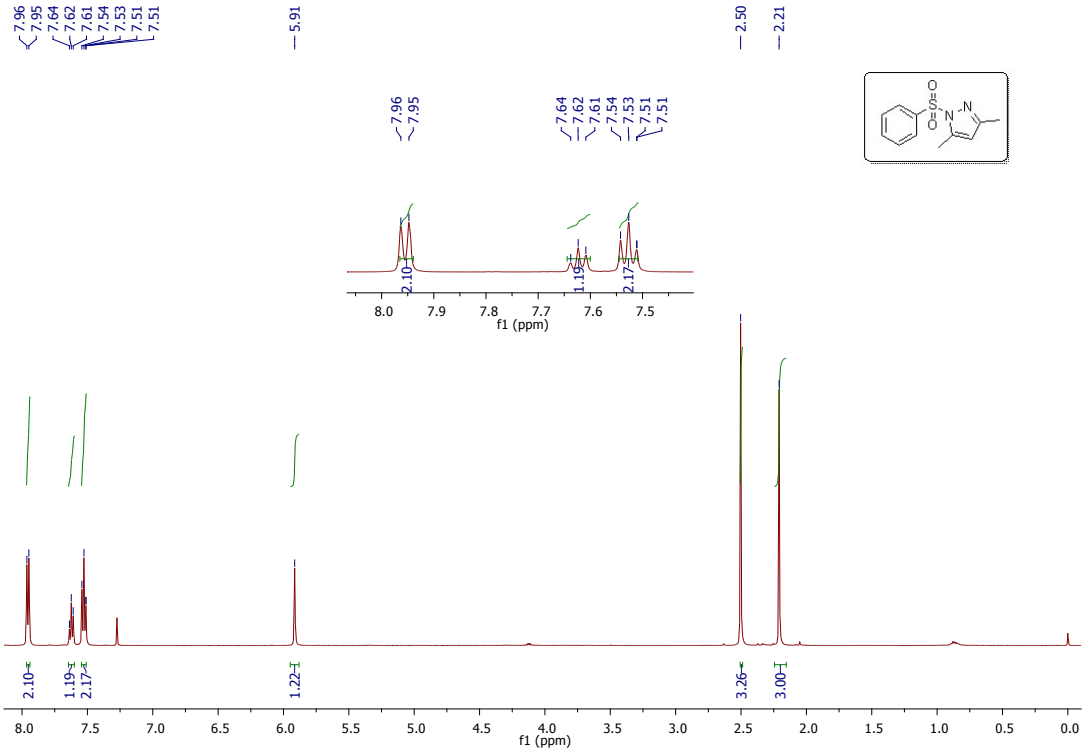


^{13}C NMR

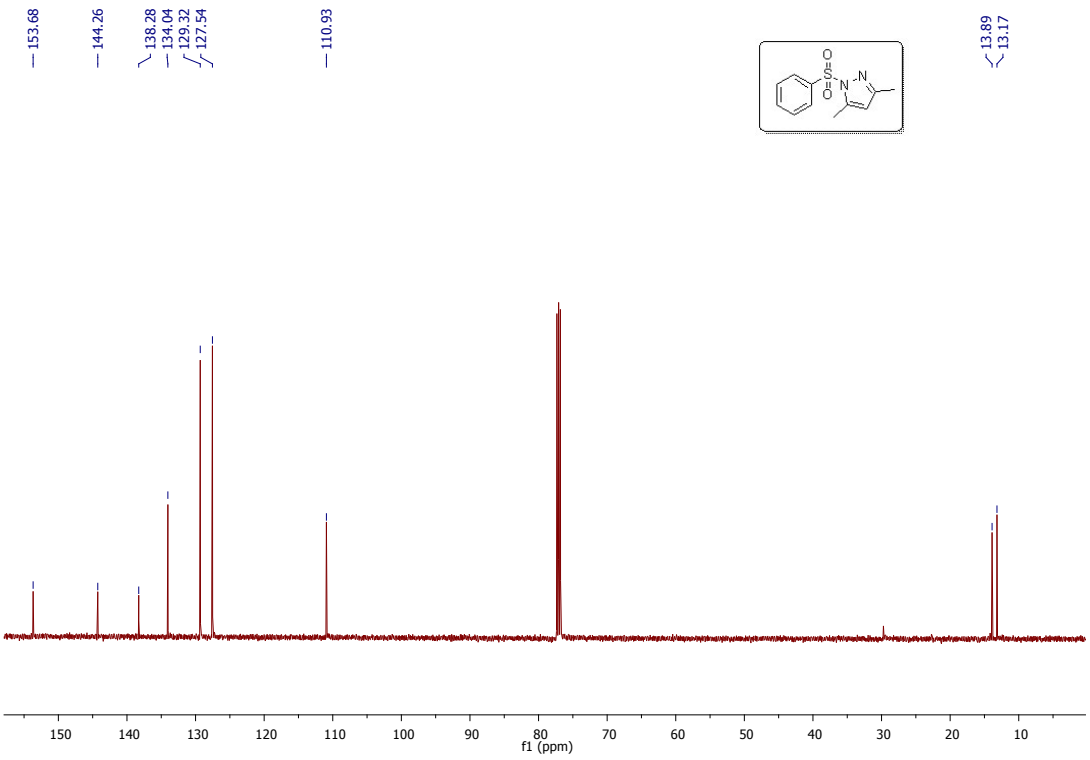


*3,5-Dimethyl-1-(phenylsulfonyl)-1H-pyrazole (**5m**)*

^{1}H NMR

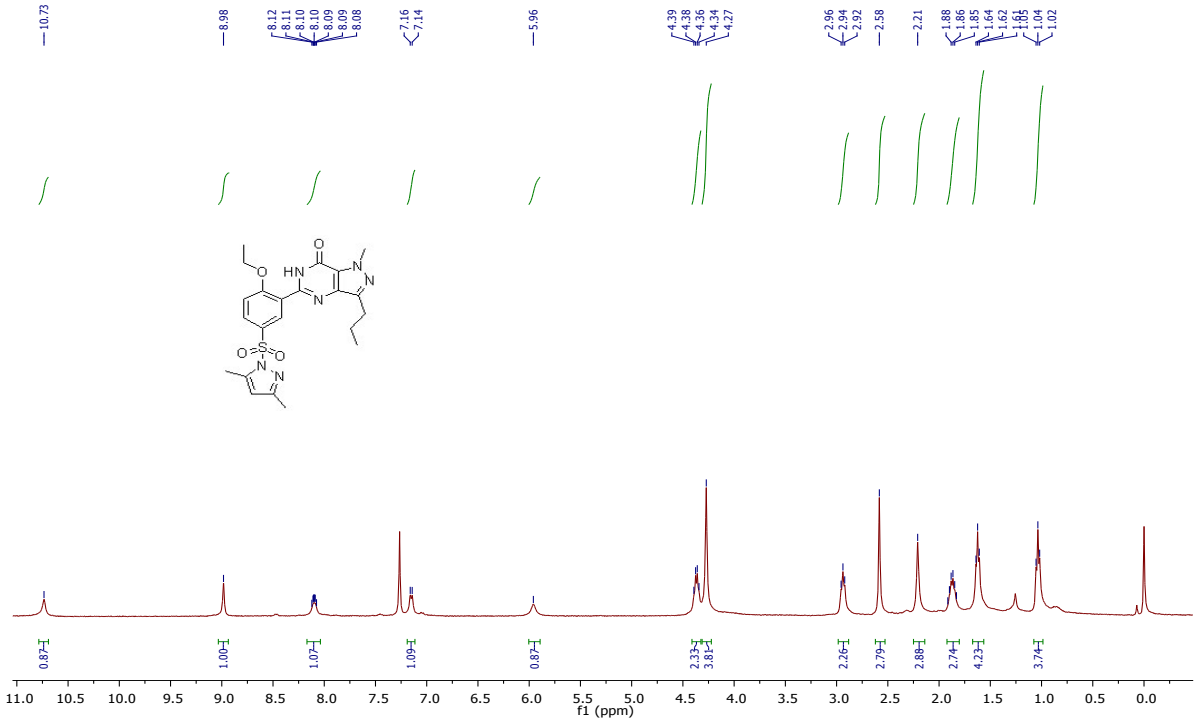


^{13}C NMR

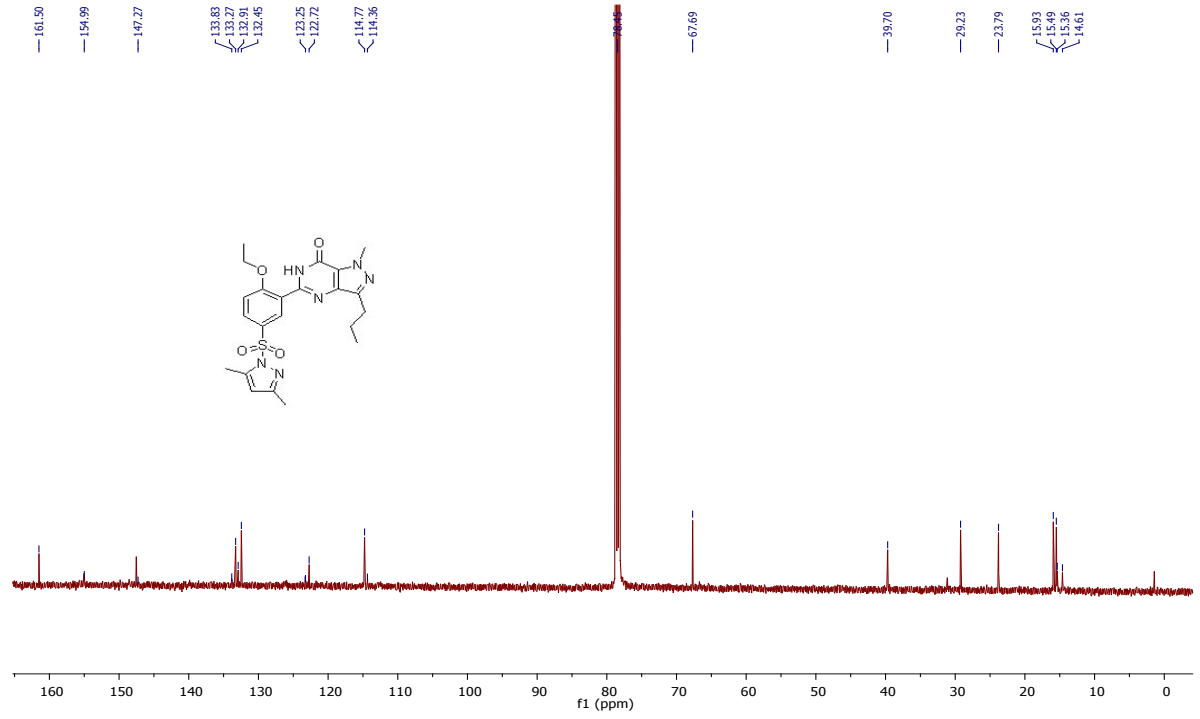


*Sildenafil-pyrazole analogue (**Figure 1**)*

^{1}H NMR

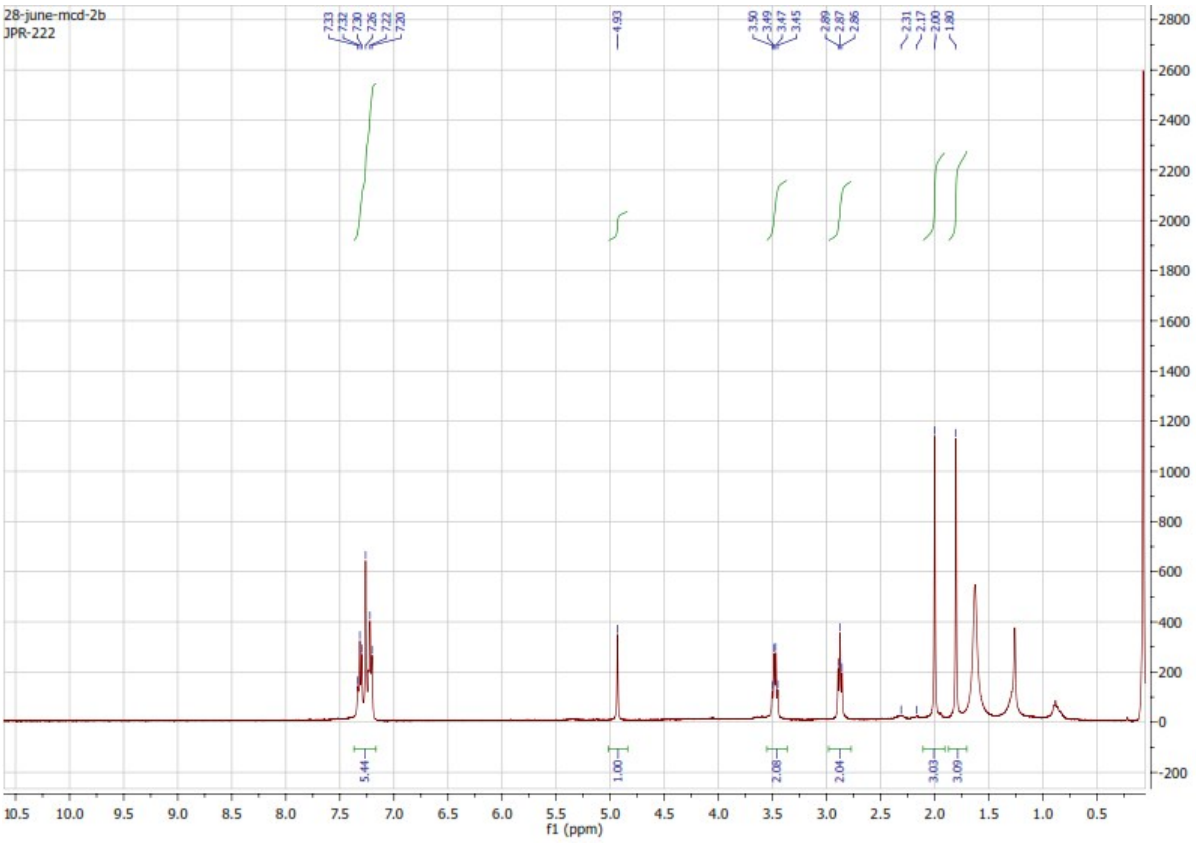


^{13}C NMR



3,5-dimethyl-1-phenethyl-1*H*-pyrazole

^{1}H NMR



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