Electronic Supplementary Material (ESI) for RSC Advances.

Brönsted acid-mediated Annulations of 1-Cyanocyclopropane-1-carboxylates with Arylhydrazines: Efficient Strategy for Synthesis of 1,3,5-Trisubstituted Pyrazoles

Shuwen Xue, Jiaming Liu, Xushun Qing and Cunde Wang*[a]

School of Chemistry and Chemical Engineering, Yangzhou University,180 Siwangting Street, Yangzhou 225002, P. R. China. Fax: +86-514-8797-5244; Tel: +86-514-8797-5568; E-mail: wangcd@yzu.edu.cn

CONTENTS

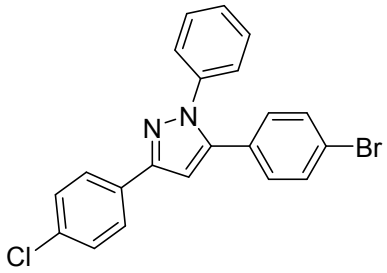
Experimental section

All melting points were determined in a Yanaco melting point apparatus and are uncorrected. IR spectra were recorded in a Nicolet FT-IR 5DX spectrometer. The ^{1}H NMR (400 or 600 MHz) and ^{13}C NMR (100 or 150 MHz) spectra were recorded in a Bruker AV-400 spectrometer with TMS as internal reference in $CDCl_3$ solutions. The *J* values are given in hertz. Only discrete or characteristic signals for the ^{1}H NMR are reported. The MS spectra were obtained on a ZAB-HS mass spectrometer with 70 eV. High-resolution ESI mass spectra were obtained on a UHR-TOF maXis (ESI) mass spectrometer. X-ray crystallographic analysis was performed with a SMART APEX-Ⅱ diffractometer. Flash chromatography was performed on silica gel (230-400 mesh) eluting with ethyl acetate-hexanes mixture. All reactions were monitored by thin layer chromatography (TLC). All reagents and solvents were purchased from commercial sources and purified commonly before used.

General procedure for preparation of 1*H*-pyrazole 3a-t

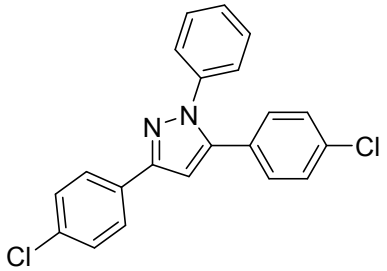
The standard procedure for the synthesis of 1*H*-pyrazoles via annulation reactions between substituted ethyl 2-aroyl-3-aryl-1-cyanocyclopropane-1-carboxylates **1a-p** and arylhydrazines **2a-c** as follows. To the mixture of 2-aroyl-3-aryl-1-cyanocyclopropane-1-carboxylates **1a-s** (1 mmol) and arylhydrazines **2a-c** (2 mmol) in toluene (5 mL) was added H_2SO_4 (40 mg, 0.4 mmol, 0.8 equiv.). The resulting mixture was stirred at 110 ^{o}C for 12 h, and the completion of reaction was confirmed by TLC (Hexanes/EtOAc, 6:1). Subsequently, the solvent was removed by reduced pressure, the residues was added with ice-water (10 mL) and was extracted with dichloromethane (10 mL X 2). The organic phase was washed with water (10 mL) and brine (5 mL), and dried over anhydrate sodium sulfate. After removal of dichloromethane, the crude product was purified by flash chromatography (silica gel, EtOAc/hexanes, 1/15) to give the desirable products **3a-t**,

5-(4-Bromophenyl)-3-(4-chlorophenyl)-1-phenyl-1*H*-pyrazole (**3a**)



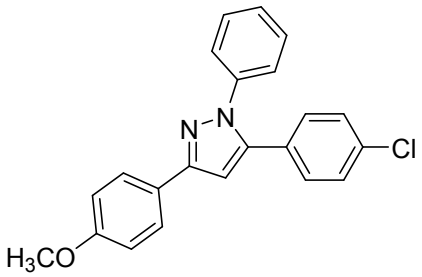
White solid; m.p. 147.5-147.6°C (PE/EA); ^{1}H-NMR ($CDCl_3$, 400 MHz) δ (*ppm*): 7.78 (d, *J* = 7.6 Hz, 2H), 7.39 (d, *J* = 8.4 Hz, 2H), 7.33 (d, *J* = 8.8 Hz, 2H), 7.31 (d, *J* = 8.0 Hz, 2H), 7.27 (d, *J* = 7.6 Hz, 3H), 7.06 (d, *J* = 7.6 Hz, 2H), 6.72 (s, 1H); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ (*ppm*): 150.0, 142.5, 138.7, 133.0, 130.9, 130.3, 129.2, 128.2, 127.9, 127.0, 126.1, 124.4, 121.8, 104.2; IR (KBr, cm^{-1}) ν: 3064, 2923, 2855, 1593, 1476, 1437, 1262, 1205, 1070, 1013, 969, 790, 746, 692; HRMS (EI) calcd for $C_{21}H_{14}BrClN_2$ $[M+H]^+$ 432.9900, Found 432.9903.

3,5-Bis(4-chlorophenyl)-1-phenyl-1H-pyrazole (**3b**)



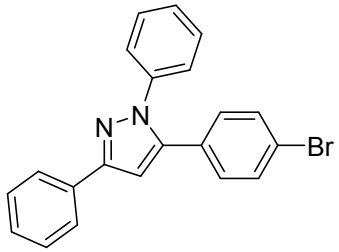
White solid; m.p. 137.4-137.5°C (PE/EA); ^{1}H-NMR ($CDCl_3$, 400 MHz) δ (*ppm*): 7.83 (d, *J* = 8.4 Hz, 2H), 7.38 (d, *J* = 8.4 Hz, 2H), 7.36 (d, *J* = 6.0 Hz, 2H), 7.34 -7.32 (m, 3H), 7.29 (d, *J* = 8.4 Hz, 2H), 7.18 (d, *J* = 8.4 Hz, 2H), 6.77 (s, 1H); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ (*ppm*): 150.0, 142.4, 138.8, 133.5, 132.9, 130.4, 129.0, 128.1, 127.8, 126.8, 126.0, 124.3, 104.2; IR (KBr, cm^{-1}) ν: 2935, 2853, 1592, 1467, 1438, 1258, 1206, 1072, 1015, 972, 785, 746, 693; HRMS (EI) calcd for $C_{21}H_{14}Cl_2N_2$ $[M+Na]^+$ 387.0400; Found 387.0426.

5-(4-Chlorophenyl)-3-(4-methoxyphenyl)-1-phenyl-1*H*-pyrazole (**3c**)



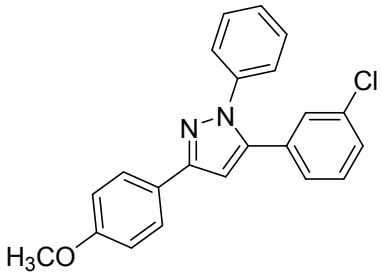
White solid; m.p. 144.3-144.4°C (PE/EA); ^{1}H-NMR ($CDCl_3$, 400 MHz) δ (*ppm*): 7.77 (d, *J* = 8.4 Hz, 2H), 7.33-7.27 (m, 5H), 7.22 (d, *J* = 8.0 Hz, 2H), 7.13 (d, *J* = 8.0 Hz, 2H), 6.89 (d, *J* = 8.4 Hz, 2H), 6.67 (s, 1H), 3.78 (s, 3H); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ (*ppm*): 158.7, 150.9, 142.1, 138.9, 133.3, 129.9, 129.2, 128.9, 128.0, 127.7, 126.5, 126.1, 124.3, 113.1, 103.9, 54.3; IR (KBr, cm^{-1}) ν: 2925, 1659, 1608, 1456, 1382, 1253, 1183, 1074, 967, 836, 801, 763, 696; HRMS (EI) calcd for $C_{22}H_{17}ClN_2O$ $[M+Na]^+$ 383.0900; Found 383.0922.

5-(4-Bromophenyl)-1,3-diphenyl-1*H*-pyrazole (**3d**)



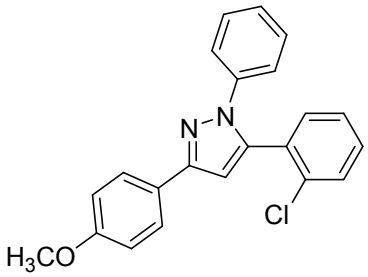
White solid; m.p. 129.2-129.3°C (PE/EA); ^{1}H-NMR ($CDCl_3$, 600 MHz) δ (*ppm*): 7.84 (d, *J* = 7.8 Hz, 2H), 7.38 (d, *J* = 9.0 Hz, 2H), 7.35 (d, *J* = 7.8 Hz, 2H), 7.31 (d, *J* = 8.4 Hz, 1H), 7.32-7.29 (m, 3H), 7.27 (d, *J* = 8.4 Hz, 2H), 7.07 (d, *J* = 8.4 Hz, 2H), 6.75 (s, 1H); ^{13}C-NMR ($CDCl_3$, 150 MHz) δ (*ppm*): 151.1, 142.2, 138.8, 131.7, 130.7, 129.2, 128.4, 128.1, 127.7, 127.2, 126.7, 124.8, 124.4, 121.6, 104.3; IR (KBr, cm^{-1}) ν: 3050, 2950, 1630, 1578, 1440, 1270, 1206, 1072, 1015, 982, 792, 784, 693; HRMS (EI) calcd for $C_{21}H_{15}BrN_2$ $[M+Na]^+$ 397.0300; Found 397.0311.

5-(3-Chlorophenyl)-3-(4-methoxyphenyl)-1-phenyl-1*H*-pyrazole (**3e**)



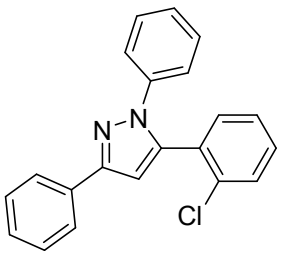
White solid; m.p. 142.2-142.3°C (PE/EA); ^{1}H-NMR ($CDCl_3$, 600 MHz) δ (*ppm*): 7.77 (d, *J* = 8.4 Hz, 2H), 7.32-7.28 (m, 4H), 7.26-7.25 (m, 2H), 7.22 (d, *J* = 7.8 Hz, 1H), 7.14 (dd, *J* = 7.8 and 8.4 Hz, 1H), 7.01 (d, *J* = 7.8 Hz, 1H), 6.89 (d, *J* = 7.8 Hz, 2H), 6.69 (s, 1H), 3.78 (s, 3H); ^{13}C-NMR ($CDCl_3$, 150 MHz) δ (*ppm*): 159.7, 151.9, 142.8, 139.9, 134.4, 132.4, 129.7, 129.1, 128.7, 128.3, 127.7, 127.1, 126.9, 125.6, 125.3, 114.1, 105.1, 55.3; IR (KBr, cm^{-1}) ν: 3484, 3066, 1597, 1525, 1497, 1470, 1438, 1353, 1293, 1255, 1179, 1080, 1023, 981, 953, 884, 839, 813, 771, 694; HRMS (EI) calcd for $C_{22}H_{17}ClN_2O$ $[M+Na]^+$ 383.0900; Found 383.0920.

5-(2-Chlorophenyl)-3-(4-methoxyphenyl)-1-phenyl-1*H*-pyrazole (**3f**)



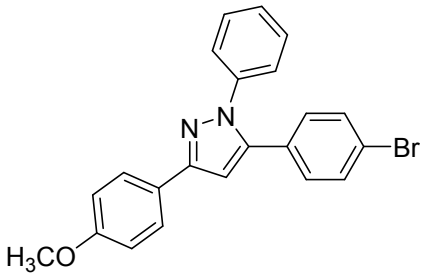
White solid; m.p. 115.6-115.7°C (PE/EA); ^{1}H-NMR ($CDCl_3$, 600 MHz) δ (*ppm*): 7.79 (d, *J* = 8.4 Hz, 2H), 7.32 (d, *J* = 7.8 Hz, 1H), 7.23 (d, *J* = 7.8 Hz, 2H), 7.22 (d, *J* = 9.6 Hz, 3H), 7.20-7.19 (m, 1H), 7.17 (d, *J* = 6.6 Hz, 1H), 7.14 (dd, *J* = 7.2 and 7.2 Hz, 1H), 6.89 (d, *J* = 9.0 Hz, 2H), 6.68 (s, 1H), 3.76 (s, 3H); ^{13}C-NMR ($CDCl_3$, 150 MHz) δ (*ppm*): 158.6, 150.5, 139.4, 139.1, 133.0, 131.1, 129.4, 129.2, 129.0, 127.8, 126.1, 126.0, 125.7, 124.7, 123.0, 113.0, 105.4, 54.3; IR (KBr, cm^{-1}) ν: 3480, 2977, 1602, 1526, 1497, 1466, 1436, 1354, 1293, 1179, 1109, 1074, 1023, 968, 837, 810, 759, 692; HRMS (EI) calcd for $C_{22}H_{17}ClN_2O$ $[M+Na]^+$ 383.0900; Found 383.0916.

5-(2-Chlorophenyl)-1,3-diphenyl-1*H*-pyrazole (**3g**)



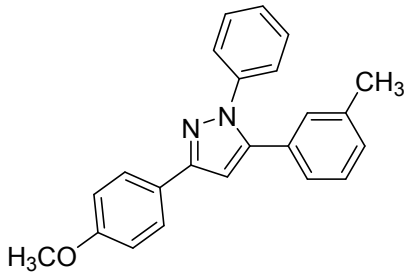
White solid; m.p. 145.2-145.3°C (PE/EA); ^{1}H-NMR ($CDCl_3$, 600 MHz) δ (*ppm*): 7.86 (d, *J* = 7.8Hz, 2H), 7.35 (dd, *J* = 7.8 and 7.8 Hz, 2H), 7.33 (d, *J* = 7.8 Hz, 1H), 7.27 (d, *J* = 7.2 Hz, 1H), 7.24 (dd, *J* = 7.8 and 7.8 Hz, 3H), 7.21 (d, *J* = 9.0 Hz, 2H), 7.20 (d, *J* = 7.8 Hz, 1H), 7.19-7.17 (m, 1H), 7.15 (d, *J* = 7.2 Hz, 1H), 6.76 (s, 1H); ^{13}C-NMR ($CDCl_3$, 150 MHz) δ (*ppm*): 150.7, 140.0, 139.1, 133.0, 131.9, 131.1, 129.3, 129.2, 129.0, 127.8, 127.6, 127.0, 126.1, 125.7, 124.8, 123.1, 105.8; IR (KBr, cm^{-1}) ν: 3466, 3060, 1628, 1596, 1494, 1453, 1362, 1181, 1073, 971, 915, 811, 761, 695; HRMS (EI) calcd for $C_{21}H_{15}ClN_2$ $[M+Na]^+$ 353.0800; Found 353.0810.

5-(4-Bromophenyl)-3-(4-methoxyphenyl)-1-phenyl-1*H*-pyrazole (**3h**)



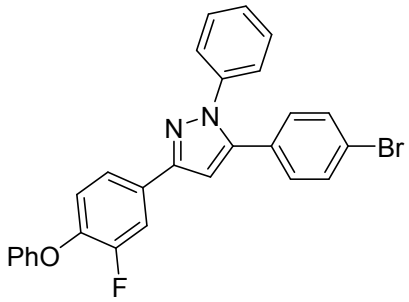
White solid; m.p. 144.6-144.7°C (PE/EA); ^{1}H-NMR ($CDCl_3$, 400 MHz) δ (*ppm*): 7.84 (d, *J* = 8.8 Hz, 2H), 7.44 (d, *J* = 8.4 Hz, 2H), 7.30 (d, *J* = 5.6 Hz, 2H), 7.28 (d, *J* = 6.8 Hz, 2H), 7.20-7.17 (m, 1H), 7.07 (d, *J* = 8.4 Hz, 2H), 6.90 (d, *J* = 8.4 Hz, 2H), 6.68 (s, 1H), 3.78 (s, 3H); ^{13}C-NMR ($CDCl_3$, 150 MHz) δ (*ppm*): 158.7, 150.9, 142.1, 138.8, 130.7, 129.2, 128.5, 128.0, 126.6, 126.1, 124.5, 124.3, 121.6, 113.1, 103.9, 54.3; IR (KBr, cm^{-1}) ν: 3455, 2932, 1598, 1498, 1438, 1356, 1293, 1254, 1177, 1109, 1069, 1023, 967, 836, 801, 762, 693,618, 593, 506; HRMS (EI) calcd for $C_{22}H_{17}BrN_2O$ $[M+H]^+$ 405.0600, Found 405.0597.

3-(4-Methoxyphenyl)-1-phenyl-5-(m-tolyl)-1H-pyrazole (**3i**)



White solid; m.p. 101.1-101.2°C (PE/EA); ^{1}H-NMR ($CDCl_3$, 400 MHz) δ (*ppm*): 7.86 (d, *J* = 8.4 Hz, 2H), 7.35 (dd, *J* = 6.0 and 8.0 Hz, 3H), 7.30 (dd, *J* = 6.0 and 7.2 Hz, 2H), 7.17 (dd, *J* = 7.2 and 7.6 Hz, 1H), 7.14 (d, *J* = 7.6 Hz, 2H), 7.01 (d, *J* = 7.2 Hz, 1H), 6.95 (d, *J* = 8.4 Hz, 2H), 6.73 (s, 1H), 3.84 (s, 3H), 2.29 (s, 3H); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ (*ppm*): 158.6, 151.7, 143.5, 139.2, 137.2, 129.6, 128.4, 128.0, 127.8, 127.3, 126.3, 126.1, 124.9, 124.3, 113.1, 103.8, 54.3, 20.4; IR (KBr, cm^{-1}) ν: 3468, 2921, 1609, 1525, 1497, 1434, 1387, 1356, 1294, 1254, 1182, 1026, 953, 883, 839, 811, 782, 760, 697; HRMS (EI) calcd for $C_{23}H_{20}N_2O$ $[M+H]^+$ 341.1700; Found 341.1661.

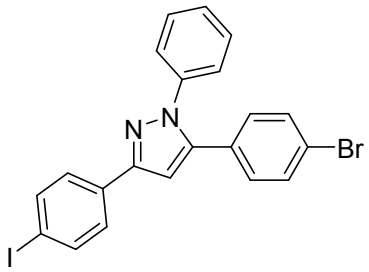
5-(4-Bromophenyl)-3-(3-fluoro-4-phenoxyphenyl)-1-phenyl-1*H*-pyrazole (**3j**)



White solid; m.p. 104.6-104.7°C (PE/EA); ^{1}H-NMR ($CDCl_3$, 600 MHz) δ (*ppm*): 7.66 (d, *J* = 8.4 Hz, 2H), 7.45 (d, *J* = 8.4 Hz, 2H), 7.29 (d, *J* = 6.6 Hz, 1H), 7.27 (s, 1H), 7.26 (d, *J* = 6.6 Hz, 1H), 7.21 (d, *J* = 6.6 Hz, 2H), 7.17 (dd, *J* = 7.8 and 7.8 Hz, 2H), 7.07 (dd, *J* = 8.4 and 9.0 Hz, 1H), 7.01 (dd, *J* = 7.8 and 8.4 Hz, 1H), 6.98-6.95 (m, 1H), 6.75 (d, *J* = 8.4 Hz, 3H), 6.64 (s, 1H); ^{13}C-NMR ($CDCl_3$, 150 MHz) δ (*ppm*): 155.3, 152.9 (d, *J* = 250 Hz), 149.9, 143.2 (d, *J* = 12 Hz), 142.2, 138.6, 130.8 (d, *J* = 6 Hz), 130.7, 128.8, 128.1, 126.8, 126.3, 126.1 (d, *J* = 3.9 Hz), 124.3, 123.6 (d, *J* = 7.1 Hz), 122.7, 121.0, 120.3, 116.9, 116.3 (d, *J* = 19 Hz), 104.1; IR (KBr, cm^{-1}) ν: 3055, 2924, 1589, 1490, 1440, 1349, 1297, 1264, 1210, 1159, 1112, 1070, 1003, 955, 905,

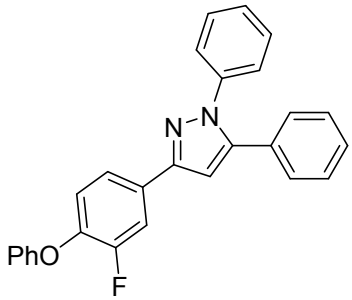
871, 800, 761, 688, 502; HRMS (EI) calcd for $C_{27}H_{18}BrFN_2$ O$[M+H]^+$ 507.0500, Found 507.0480.

5-(4-Bromophenyl)-3-(4-iodophenyl)-1-phenyl-1*H*-pyrazole (**3k**)



White solid; m.p. 141.5-142.6°C (PE/EA); ^{1}H-NMR ($CDCl_3$, 600 MHz) δ (*ppm*): 7.70 (d, *J* = 8.4 Hz, 2H), 7.58 (d, *J* = 7.8 Hz, 2H), 7.48 (d, *J* = 8.4 Hz, 2H), 7.31 (dd, *J* = 7.8 and 8.4 Hz, 2H), 7.27 (d, *J* = 6.0 Hz, 3H), 6.92 (d, *J* = 7.8 Hz, 2H), 6.71 (s, 1H); ^{13}C-NMR ($CDCl_3$, 150 MHz) δ (*ppm*): 150.0, 142.5, 138.8, 136.7, 130.9, 130.8, 129.3, 128.8, 128.1, 126.8, 126.3, 124.3, 121.0, 104.1, 93.4; IR (KBr, cm^{-1}) ν: 2935, 1594, 1477, 1439, 1272, 1234, 1178, 1072, 1015, 967, 792, 693; HRMS (EI) calcd for $C_{21}H_{14}BrIN_2$ $[M+H]^+$ 522.9300, Found 522.9269.

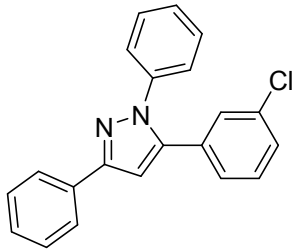
3-(3-Fluoro-4-phenoxyphenyl)-1,5-diphenyl-1*H*-pyrazole (**3l**)



White solid; m.p. 102.2-102.3°C (PE/EA); ^{1}H-NMR ($CDCl_3$, 600 MHz) δ (*ppm*): 7.81 (d, *J* = 7.8 Hz, 2H), 7.34 (dd, *J* = 7.2 and 7.2 Hz, 2H), 7.29 (d, *J* = 7.2 Hz, 2H), 7.26 (d, *J* = 6.6 Hz, 2H), 7.24 (d, *J* = 7.8 Hz,2H), 7.18 (d, *J* = 7.8 Hz, 2H), 7.08 (dd, *J* = 7.8 and 9.0 Hz, 1H), 7.01 (dd, *J* = 7.2 and 7.2 Hz, 2H), 6.77 (dd, *J* = 7.2 and 7.2 Hz, 3H), 6.69 (s, 1H); ^{13}C-NMR ($CDCl_3$, 150 MHz) δ (*ppm*): 155.3, 152.8 (d, *J* = 250 Hz), 151.0, 143.2 (d, *J* = 12 Hz), 141.9, 138.8, 131.8, 128.8, 128.1, 127.6, 127.1, 126.7, 126.3 (d, *J* = 3.9 Hz), 124.8, 124.4, 123.6 (d, *J* = 7.1 Hz), 122.6, 120.4, 116.9, 116.3

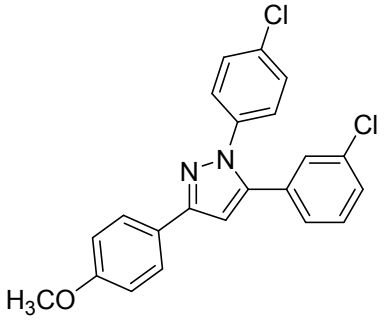
(d, *J* = 19 Hz), 104.1; IR (KBr, cm^{-1}) ν: 3052, 2954, 1587, 1492, 1440, 1352, 1298, 1272, 1212, 1157, 1120, 1072, 1002, 958, 902, 871, 801, 762, 683, 502; HRMS (EI) calcd for $C_{27}H_{19}FN_2O$ $[M+Na]^+$ 429.1400, Found 429.1391.

5-(3-Chlorophenyl)-1,3-diphenyl-1*H*-pyrazole (**3m**)



White solid; m.p. 96.2-96.3°C (PE/EA); ^{1}H-NMR ($CDCl_3$, 600 MHz) δ (*ppm*): 7.84 (d, *J* = 7.8 Hz, 2H), 7.36 (dd, *J* = 7.8 and 7.8 Hz, 2H), 7.31 (d, *J* = 8.4 Hz, 1H), 7.29 (d, *J* = 5.4 Hz, 3H), 7.28 (d, *J* = 7.2 Hz, 1H), 7.27 (dd, *J* = 6.6 and 7.2 Hz, 2H), 7.23 (d, *J* = 8.4 Hz, 1H), 7.15 (dd, *J* = 7.8 Hz, 1H), 7.02 (d, *J* = 7.8 Hz, 1H), 6.77 (s, 1H); ^{13}C-NMR ($CDCl_3$, 150 MHz) δ (*ppm*): 152.1, 142.9, 139.8, 134.5, 132.8, 132.3, 129.7, 129.1, 128.70, 128.69, 128.4, 128.2, 127.8, 126.9, 125.9, 125.4, 105.5; IR (KBr, cm^{-1}) ν: 3052, 1632, 1595, 1492, 1450, 1370, 1182, 1075, 980, 912, 811, 782, 694; HRMS (EI) calcd for $C_{21}H_{15}ClN_2$ $[M+H]^+$ 331.0900, Found 331.0989.

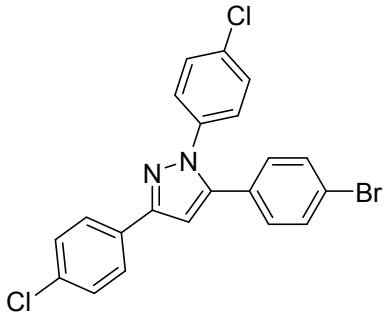
5-(3-Chlorophenyl)-1-(4-chlorophenyl)-3-(4-methoxyphenyl)-1*H*-pyrazole (**3n**)



Yellow solid; m.p. 139.6-139.7°C (PE/EA); ^{1}H-NMR ($CDCl_3$, 600 MHz) δ (*ppm*): 7.76 (d, *J* = 8.4 Hz, 2H), 7.29 (d, *J* = 8.4 Hz, 1H), 7.28-7.27 (m, 3H), 7.25 (s, 1H), 7.20 (d, *J* = 7.8 Hz, 1H), 7.13 (dd, *J* = 7.8 and 7.8 Hz, 1H), 6.99 (d, *J* = 7.8 Hz, 1H), 6.88 (d, *J* = 8.4 Hz, 2H), 6.68 (s, 1H); ^{13}C-NMR ($CDCl_3$, 150 MHz) δ (*ppm*): 158.7, 150.9, 141.8, 138.8, 133.4, 131.4, 128.7, 128.0, 127.6, 127.3, 126.6, 126.1, 125.9,

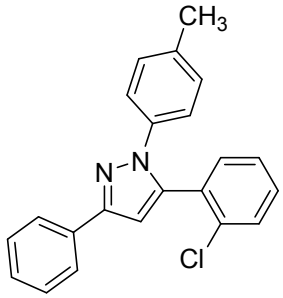
124.5, 124.3, 113.1, 104.1, 54.3; IR (KBr, cm^{-1}) ν: 2925, 1606, 1495, 1437, 1356, 1293, 1243, 1172, 1088, 1030, 984, 877, 828, 790, 688, 617, 543, 502; HRMS (EI) calcd for $C_{22}H_{16}Cl_2N_2O$ $[M+Na]^+$ 417.0500, Found 417.0526.

5-(4-Bromophenyl)-1,3-bis(4-chlorophenyl)-1*H*-pyrazole (**3o**)



Yellow solid; m.p. 131.2-131.3°C (PE/EA); ^{1}H-NMR ($CDCl_3$, 600 MHz) δ (*ppm*): 7.74 (d, *J* = 9.0 Hz, 2H), 7.40 (d, *J* = 8.4 Hz, 2H), 7.32 (d, *J* = 8.4 Hz, 2H), 7.26 (d, *J* = 9.0 Hz, 2H), 7.20 (d, *J* = 8.4 Hz, 2H), 7.05 (d, *J* = 8.4 Hz, 2H), 6.69 (s, 1H); ^{13}C-NMR ($CDCl_3$, 150 MHz) δ (*ppm*): 150.3, 142.4, 137.2, 133.0, 132.5, 131.0, 130.2, 129.2, 128.3, 128.0, 127.9, 126.0, 125.3, 122.0, 104.5; IR (KBr, cm^{-1}) ν: 3469, 1594, 1491, 1437, 1407, 1346, 1214, 1175, 1092, 1070, 1009, 968, 828, 791, 593, 570, 496; HRMS (EI) calcd for $C_{21}H_{13}BrCl_2N_2$ $[M+Na]^+$ 464.9500, Found 464.9514.

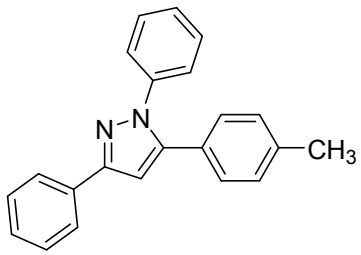
5-(2-Chlorophenyl)-3-phenyl-1-(p-tolyl)-1*H*-pyrazole (**3p**)



White solid; m.p. 137.2-137.3°C (PE/EA); ^{1}H-NMR ($CDCl_3$, 400 MHz) δ (*ppm*): 7.85 (d, *J* = 7.6 Hz, 2H), 7.34 (dd, *J* = 7.6 Hz, 3H), 7.25 (d, *J* = 7.6 Hz, 1H), 7.23 (d, *J* = 9.6 Hz, 1H), 7.21 (d, *J* = 7.2 Hz, 1H), 7.16 (d, *J* = 6.4 Hz, 1H), 7.12 (d, *J* = 8.0 Hz, 2H), 6.99 (d, *J* = 7.6 Hz, 2H), 6.73 (s, 1H), 2.23 (s, 3H); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ (*ppm*): 150.5, 140.0, 136.7, 136.0, 133.0, 132.0, 131.1, 130.4, 129.2, 129.0, 128.4,

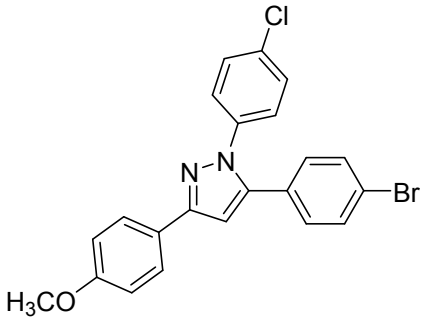
127.7, 127.0, 125.7, 124.8, 123.0, 105.6, 20.1; IR (KBr, cm^{-1}) ν: 3250, 1620, 1502, 1420, 1346, 1211, 1092, 972, 915, 816, 792, 695; HRMS (EI) calcd for $C_{22}H_{17}ClN_2$ $[M+H]^+$ 345.1200, Found 345.1146.

1,3-Diphenyl-5-(p-tolyl)-1H-pyrazole (**3q**)



White solid; m.p. 115.5-115.6°C (PE/EA); ^{1}H-NMR ($CDCl_3$, 600 MHz) δ (*ppm*): 7.74 (d, *J* = 7.8 Hz, 2H), 7.44-7.40 (m, 1H), 7.37 (dd, *J* = 7.8 and 8.4 Hz, 2H), 7.36 (d, *J* = 7.2 Hz, 1H), 7.32 (d, *J* = 8.4 Hz, 1H), 7.29 (d, *J* = 6.0 Hz, 3H), 7.28 (dd, *J* = 7.2 and 7.2 Hz, 2H), 7.09 (dd, *J* = 7.2 and 7.2 Hz,1H), 7.06 (d, *J* = 7.8 Hz, 1H), 6.77 (s, 1H), 1.19 (s, 3H); ^{13}C-NMR ($CDCl_3$, 150 MHz) δ (*ppm*): 151.1, 141.8, 138.8, 131.8, 131.6, 130.5, 130.3, 128.9, 128.1, 127.7, 127.1, 126.8, 126.3, 124.8, 124.3, 121.5, 104.5, 28.7; IR (KBr, cm^{-1}) ν: 3020, 2925, 1592, 1438, 1305, 1282, 1232, 1075, 1072, 965, 792, 693; MS(EI) (m/z) for $C_{22}H_{18}N_2$: 311.15 $[(M+H)^+]$ (100%).

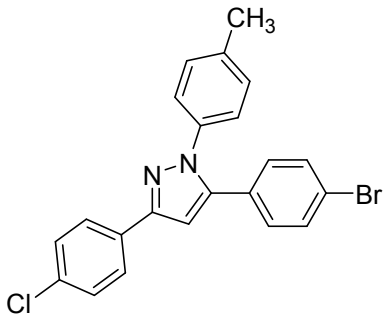
5-(4-Bromophenyl)-1-(4-chlorophenyl)-3-(4-methoxyphenyl)-1*H*-pyrazole (**3r**)



Yellow solid; m.p. 145.4-145.5°C (PE/EA); ^{1}H-NMR ($CDCl_3$, 600 MHz) δ (*ppm*): 7.76 (d, *J* = 8.4 Hz, 2H), 7.28 -7.24 (m, 6 H), 7.19 (d, *J* = 5.4 Hz, 1H), 7.00 (d, *J* = 7.8 Hz, 1H), 6.90 (d, *J* = 7.8 Hz, 2H), 6.69 (s, 1H), 3.79 (s, 3H); ^{13}C-NMR ($CDCl_3$, 150 MHz) δ (ppm): 158.8, 151.2, 141.9, 137.3, 133.6, 132.3, 131.1, 128.9, 128.2, 127.7,

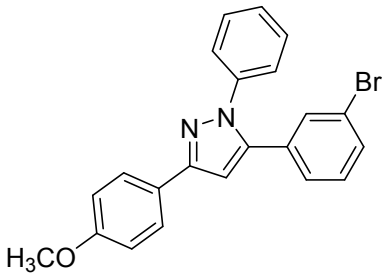
127.6, 126.1, 125.9, 125.3, 124.2, 113.1, 104.6, 54.3; IR (KBr, cm^{-1}) ν: 3305, 1635, 1525, 1432, 1402, 1352, 1215, 1176, 1093, 1006, 982, 913, 816, 793, 692,618, 593, 506; MS(EI) (m/z) for $C_{22}H_{16}BrClN_2O$: 440.01 $[(M+H)^+]$ (100%).

5-(4-Bromophenyl)-3-(4-chlorophenyl)-1-(p-tolyl)-1*H*-pyrazole (**3s**)



Yellow solid; m.p. 147.6-147.8°C (PE/EA); ^{1}H-NMR ($CDCl_3$, 600 MHz) δ (*ppm*): 7.76 (d, *J* = 8.4 Hz, 2H), 7.37 (d, *J* = 8.4 Hz, 2H), 7.31 (d, *J* = 8.4 Hz, 2H), 7.14 (d, *J* = 8.4 Hz, 2H), 7.09 (d, *J* = 8.4 Hz, 2H), 7.05 (d, *J* = 8.4 Hz, 2H), 6.69 (s, 1H), 2.30 (s, 3H); ^{13}C-NMR ($CDCl_3$, 150 MHz) δ (*ppm*): 149.7, 142.4, 136.9, 136.3, 132.8, 130.7, 130.4, 129.2, 128.7, 128.3, 127.8, 126.0, 124.2, 121.7, 103.9, 20.1; IR (KBr, cm^{-1}) ν: 3425, 1595, 1492, 1435, 1402, 1352, 1218, 1185, 1082, 1072, 1007, 965, 835, 795, 592, 571; HRMS (EI) calcd for $C_{22}H_{16}BrClN_2$ $[M+Na]^+$ 445.0100, Found 445.0077.

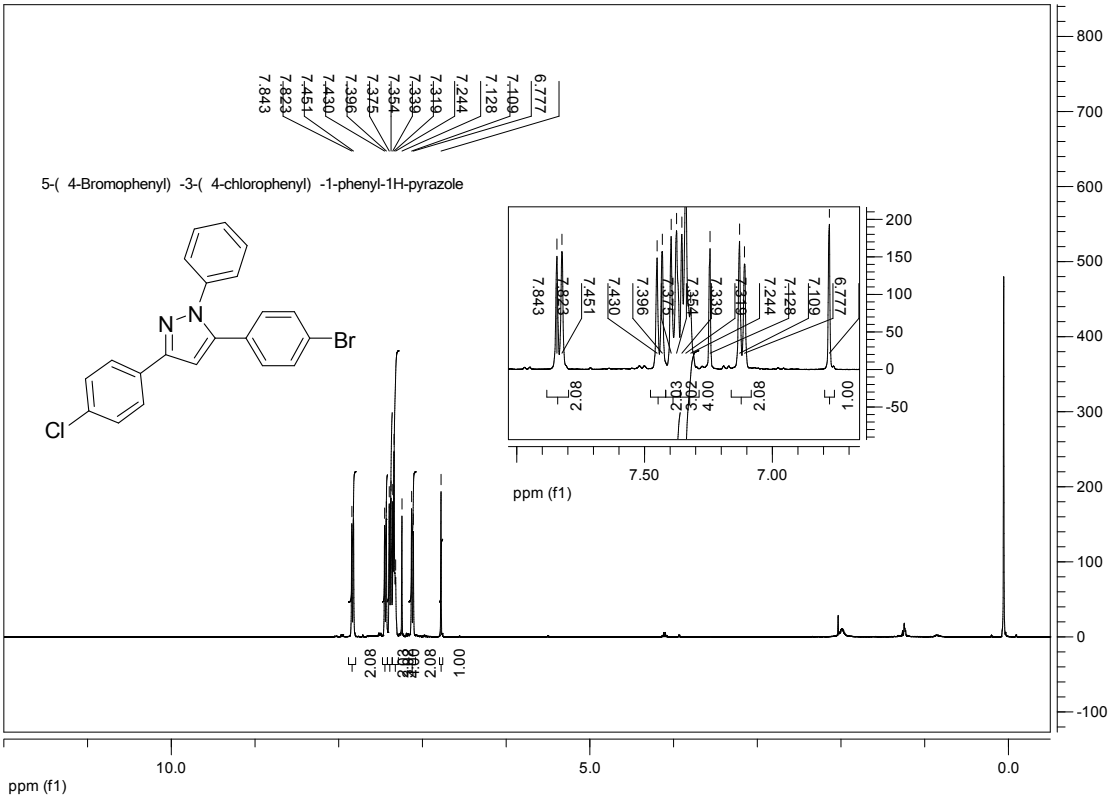
5-(3-Bromophenyl)-3-(4-methoxyphenyl)-1-phenyl-1*H*-pyrazole (**3t**)

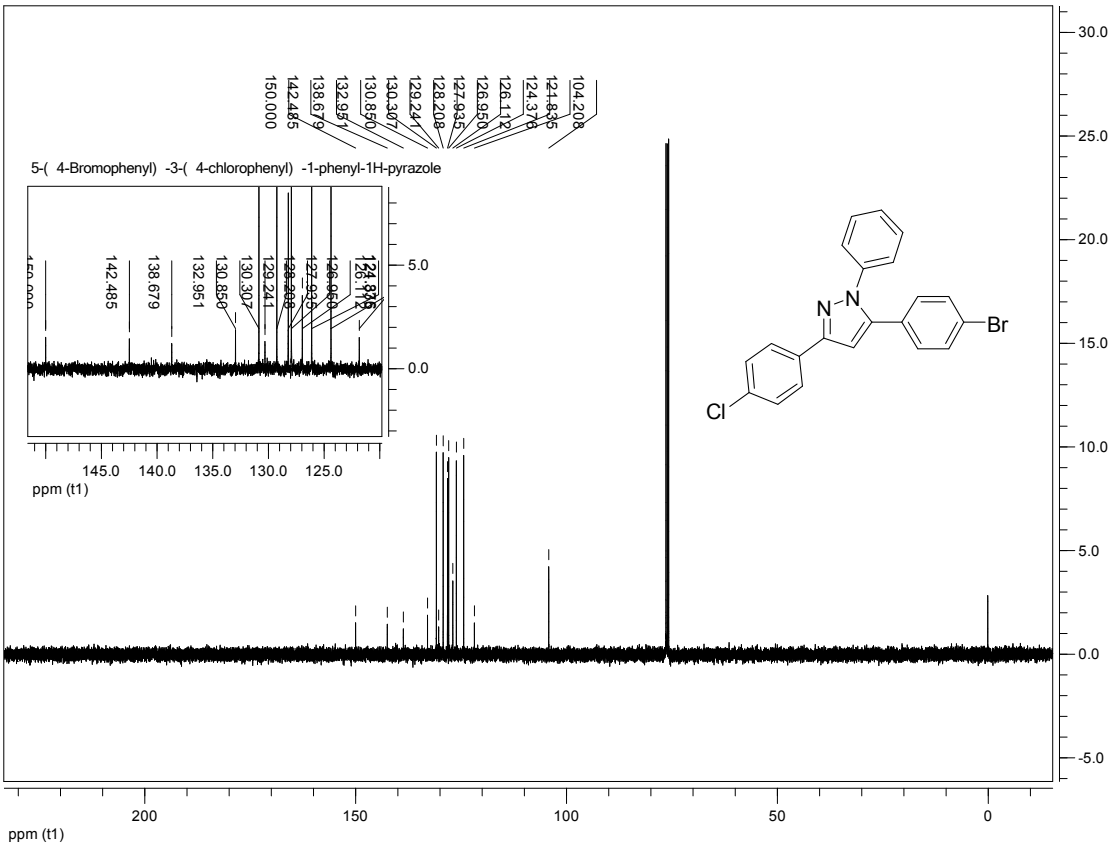


White solid; m.p. 115.5-115.6°C (PE/EA); ^{1}H-NMR ($CDCl_3$, 400 MHz) δ (*ppm*): 7.86 (d, *J* = 8.4 Hz, 2H), 7.37 (s, 1H), 7.36 (dd, *J* = 7.2 and 7.2 Hz, 4H), 7.31 (dd, *J* = 5.2 and 7.2 Hz, 1H), 7.29 (d, *J* = 8.4 Hz, 1H), 7.20 (dd, *J* = 7.2 and 7.2 Hz, 1H), 7.08 (d, *J* = 7.6 Hz, 1H), 6.97 (d, *J* = 8.4 Hz, 2H), 6.76 (s, 1H), 3.83 (s, 3H); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ (*ppm*): 158.7, 150.9, 141.7, 138.9, 133.4, 131.4, 128.7, 128.0, 127.6, 127.3, 126.6, 126.1, 125.9, 124.6, 124.3, 113.1, 104.1, 54.3; IR (KBr, cm^{-1}) ν:

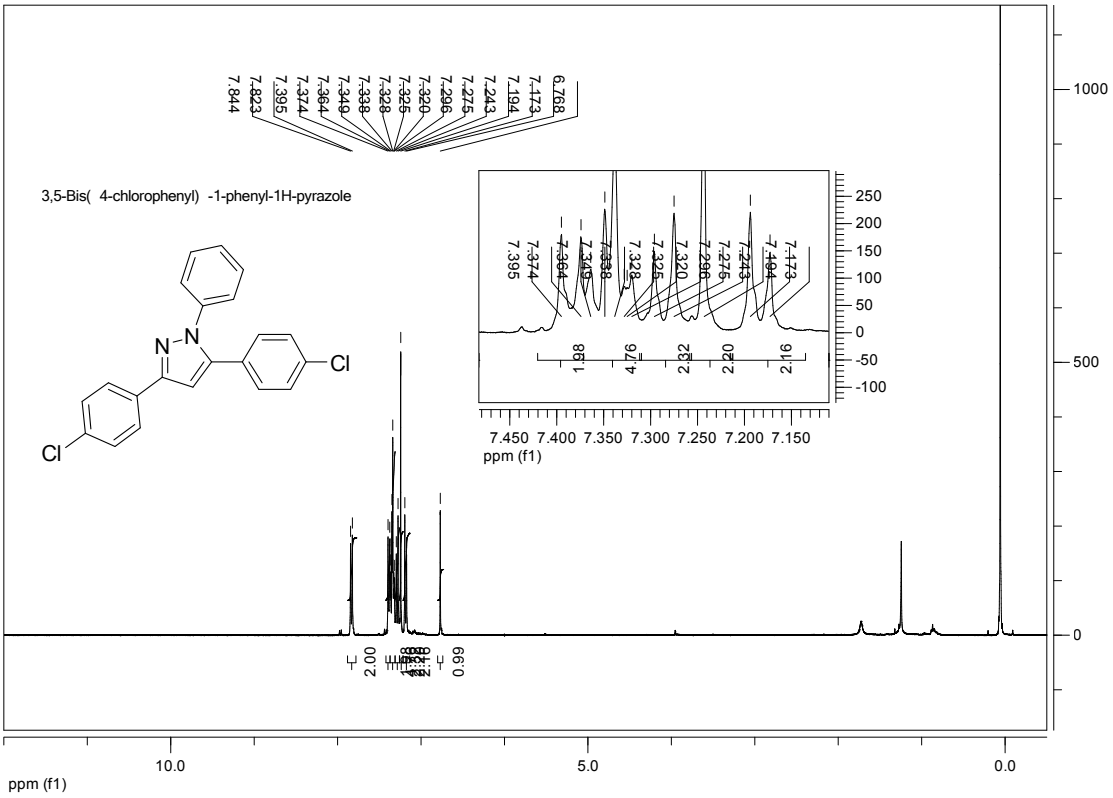
3450, 2930, 1595, 1482, 1431, 1354, 1294, 1272, 1181, 1121, 1072, 1015, 962, 832, 801, 762, 693; HRMS (EI) calcd for $C_{22}H_{17}BrN_2$ O$[M+H]^+$405.0500, Found 405.0599.

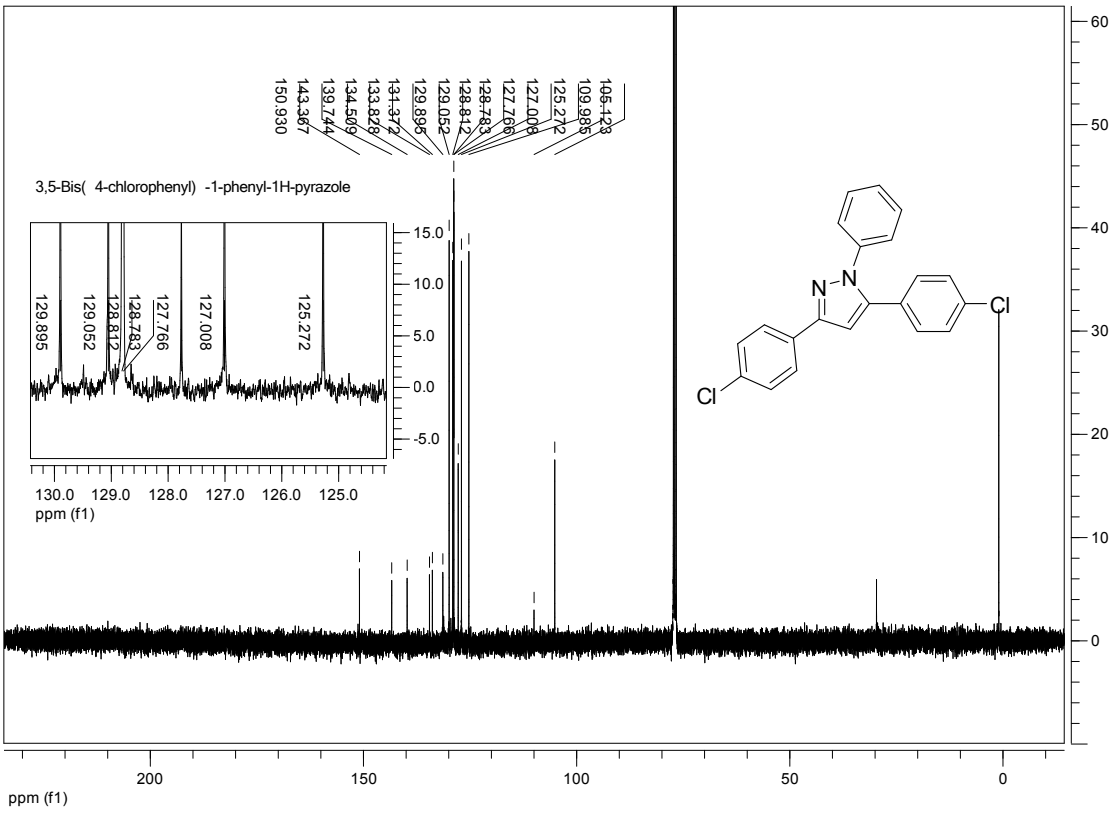
5-(4-Bromophenyl)-3-(4-chlorophenyl)-1-phenyl-1*H*-pyrazole (**3a**)



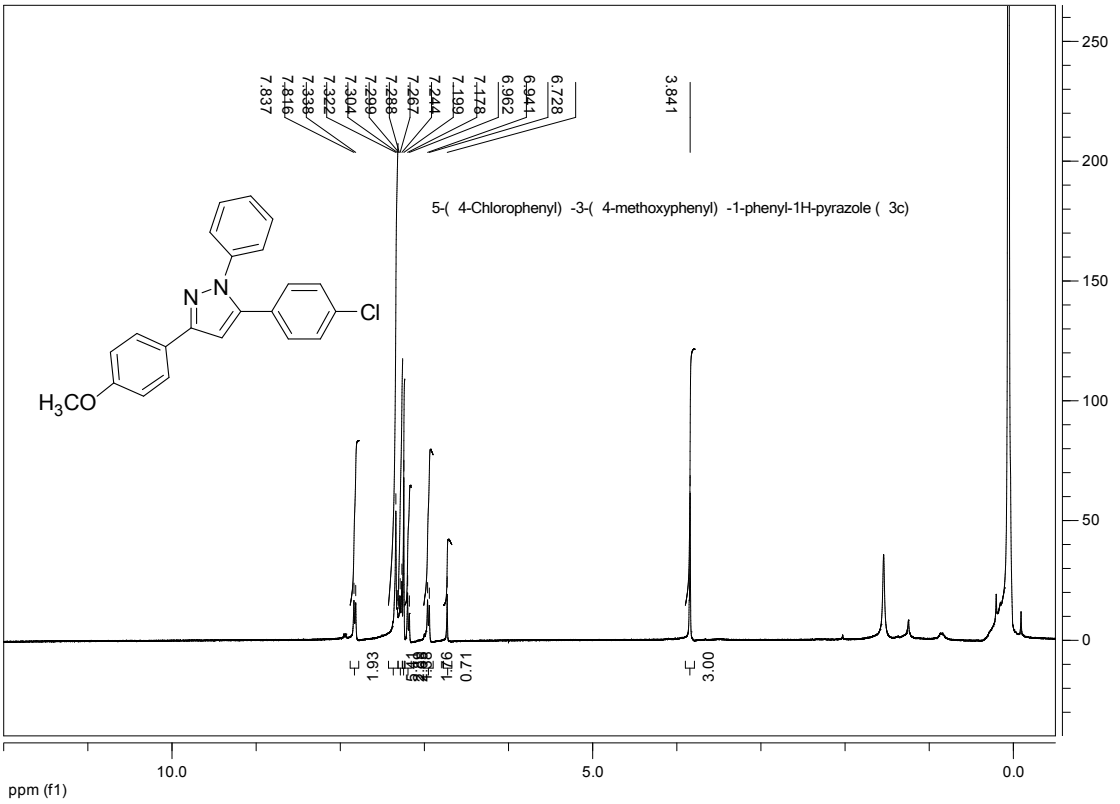


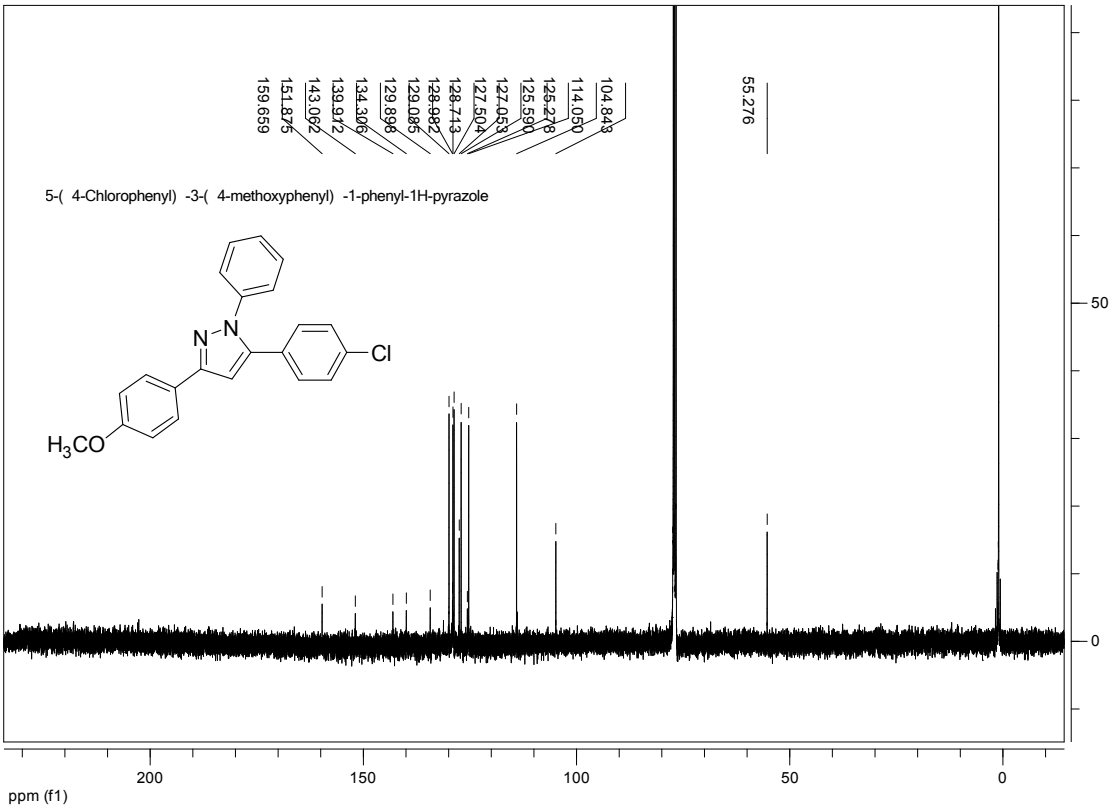
3,5-Bis(4-chlorophenyl)-1-phenyl-1H-pyrazole (**3b**)



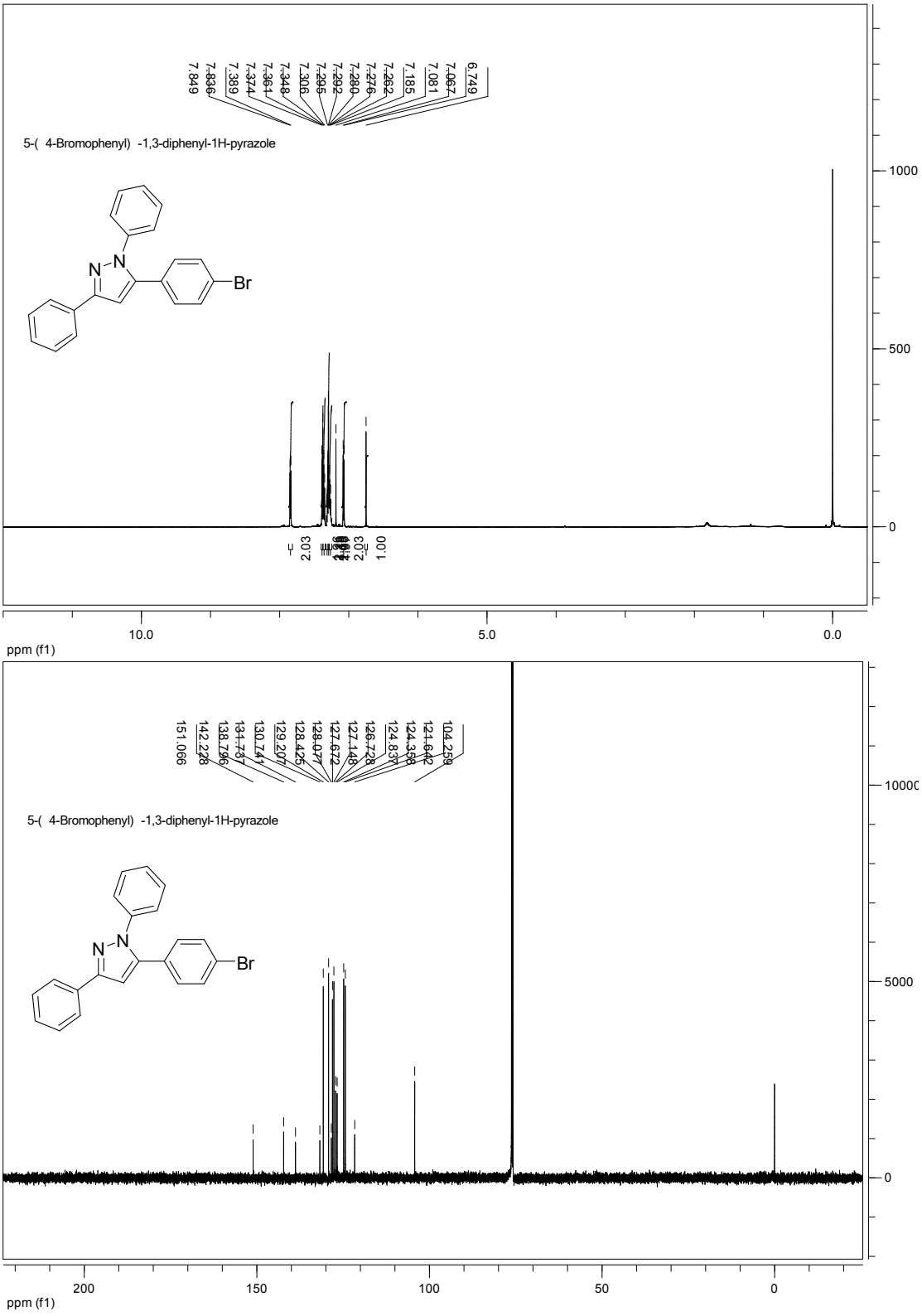


5-(4-Chlorophenyl)-3-(4-methoxyphenyl)-1-phenyl-1*H*-pyrazole (**3c**)

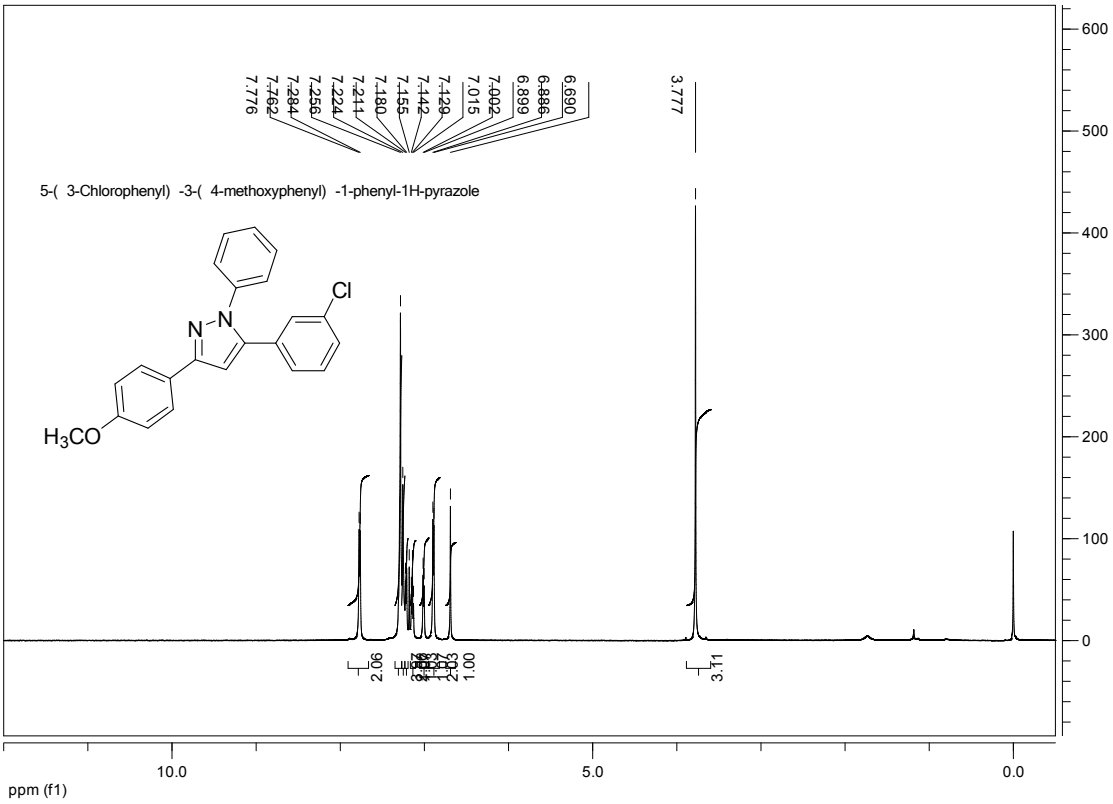


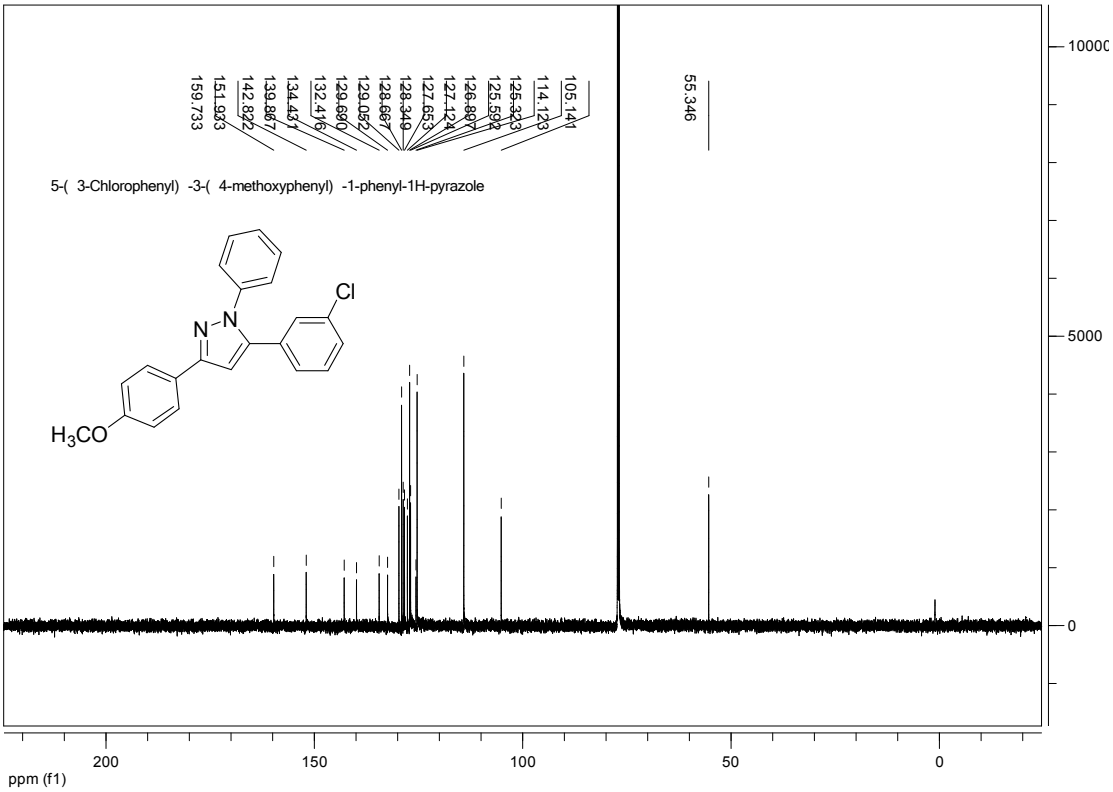


5-(4-Bromophenyl)-1,3-diphenyl-1*H*-pyrazole (**3d**)

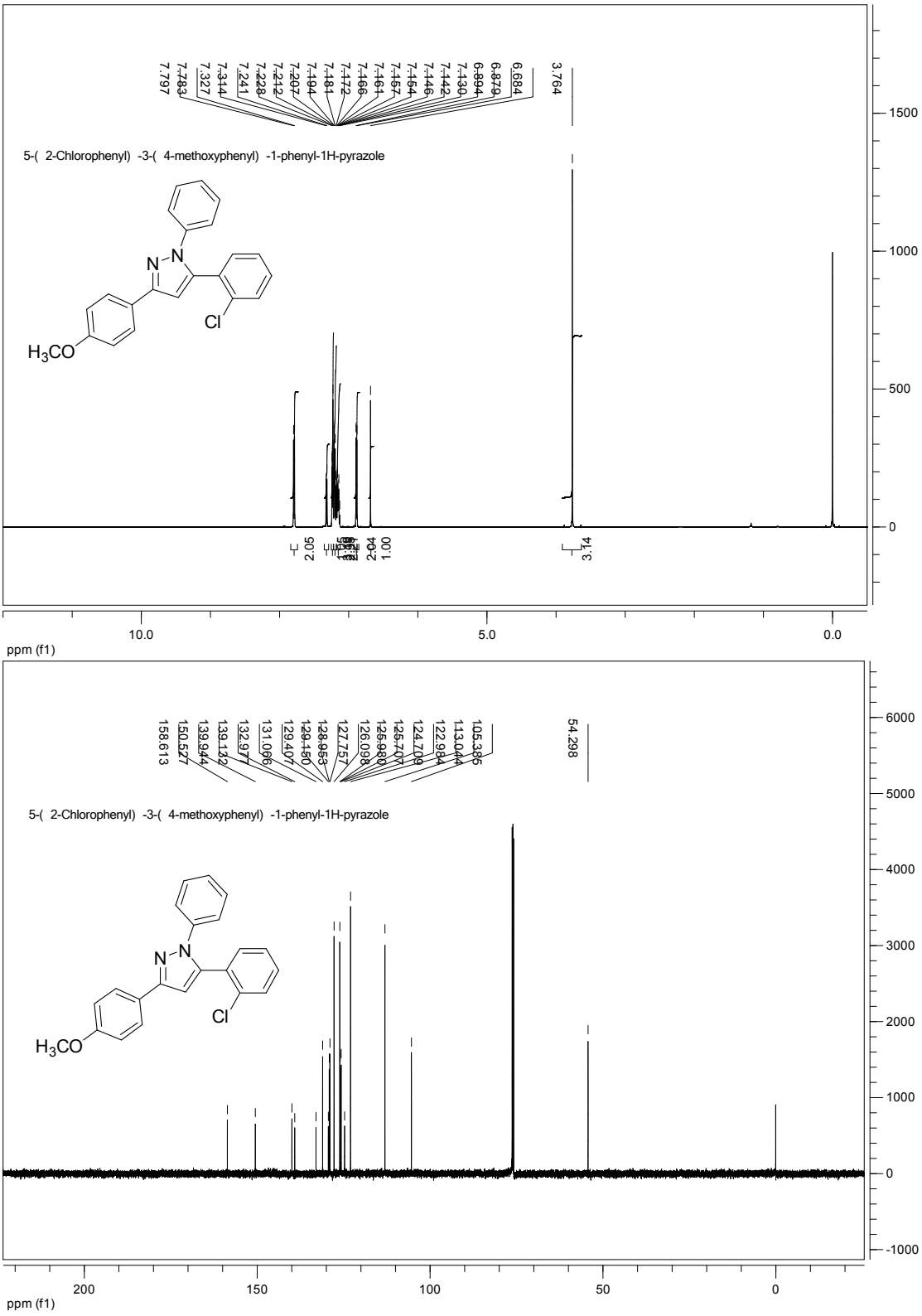


5-(3-Chlorophenyl)-3-(4-methoxyphenyl)-1-phenyl-1*H*-pyrazole (**3e**)

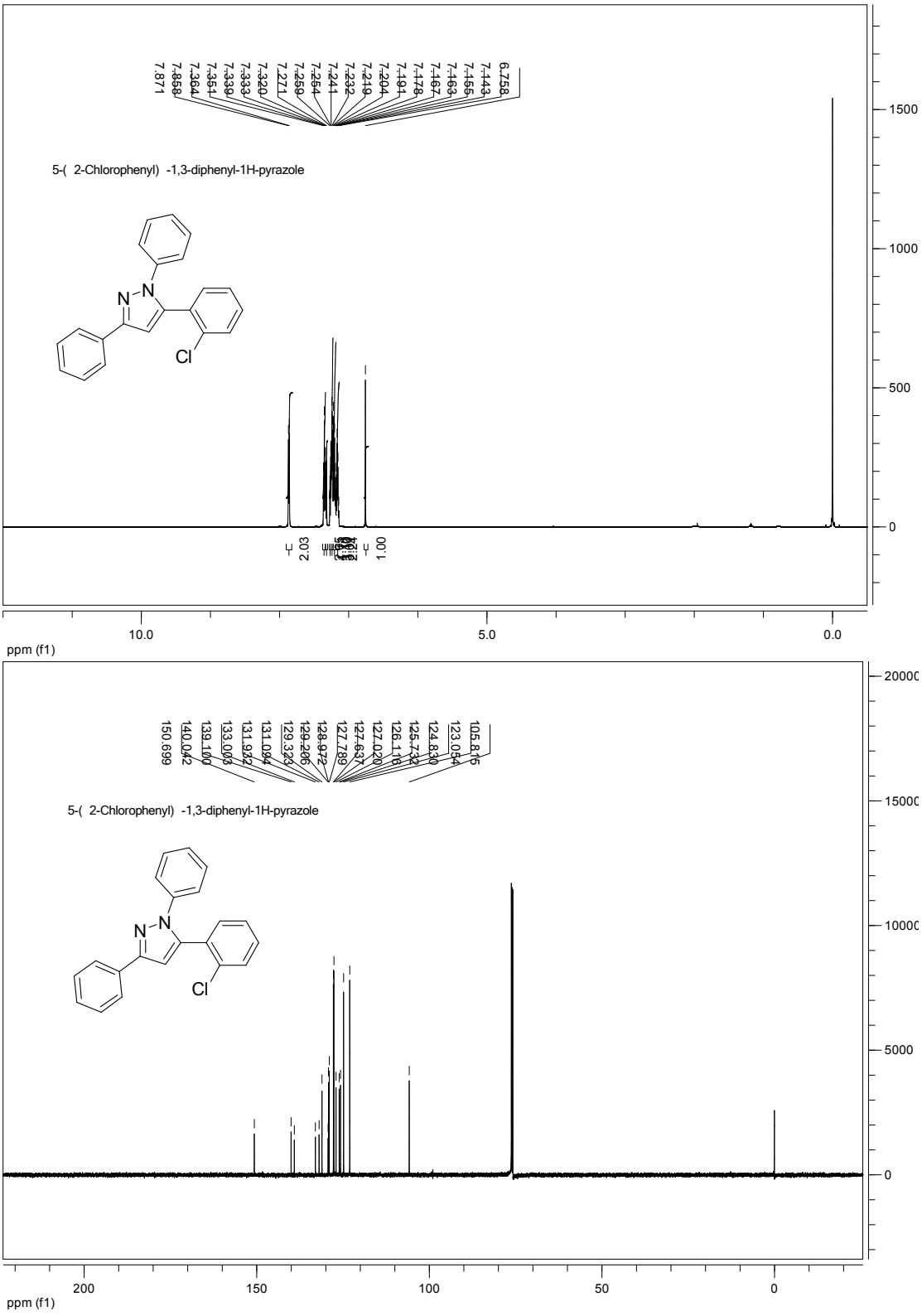




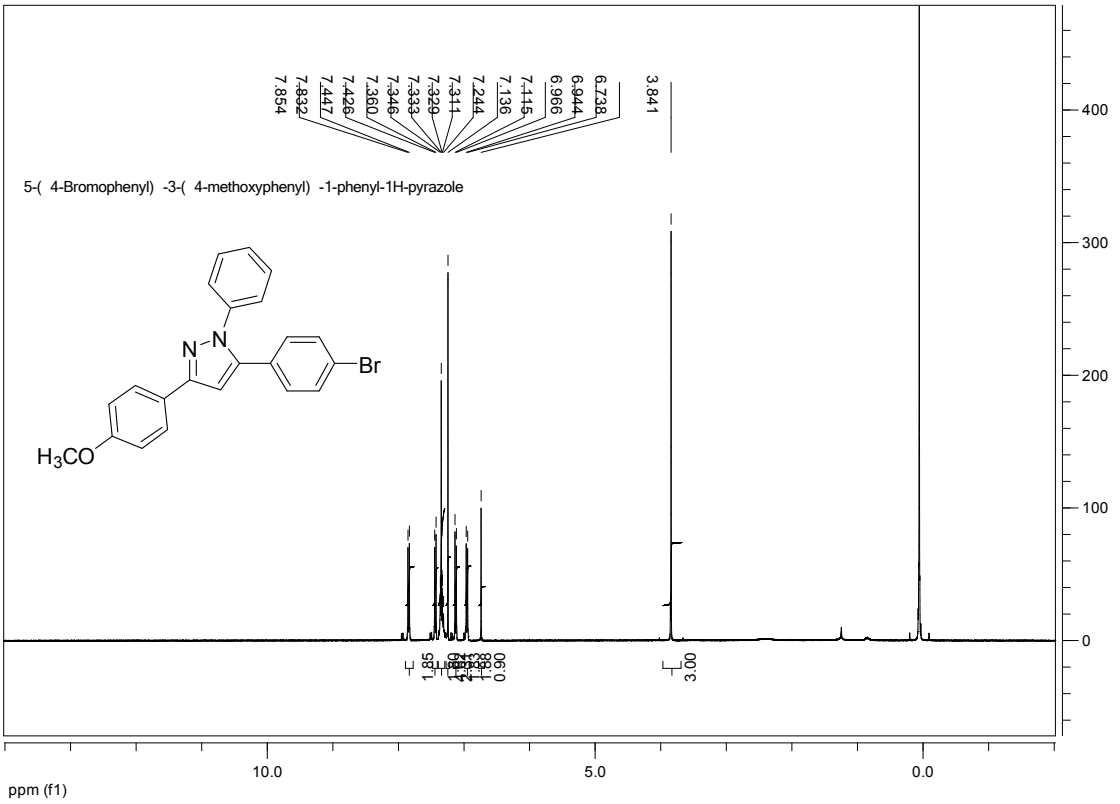
5-(2-Chlorophenyl)-3-(4-methoxyphenyl)-1-phenyl-1*H*-pyrazole (**3f**)

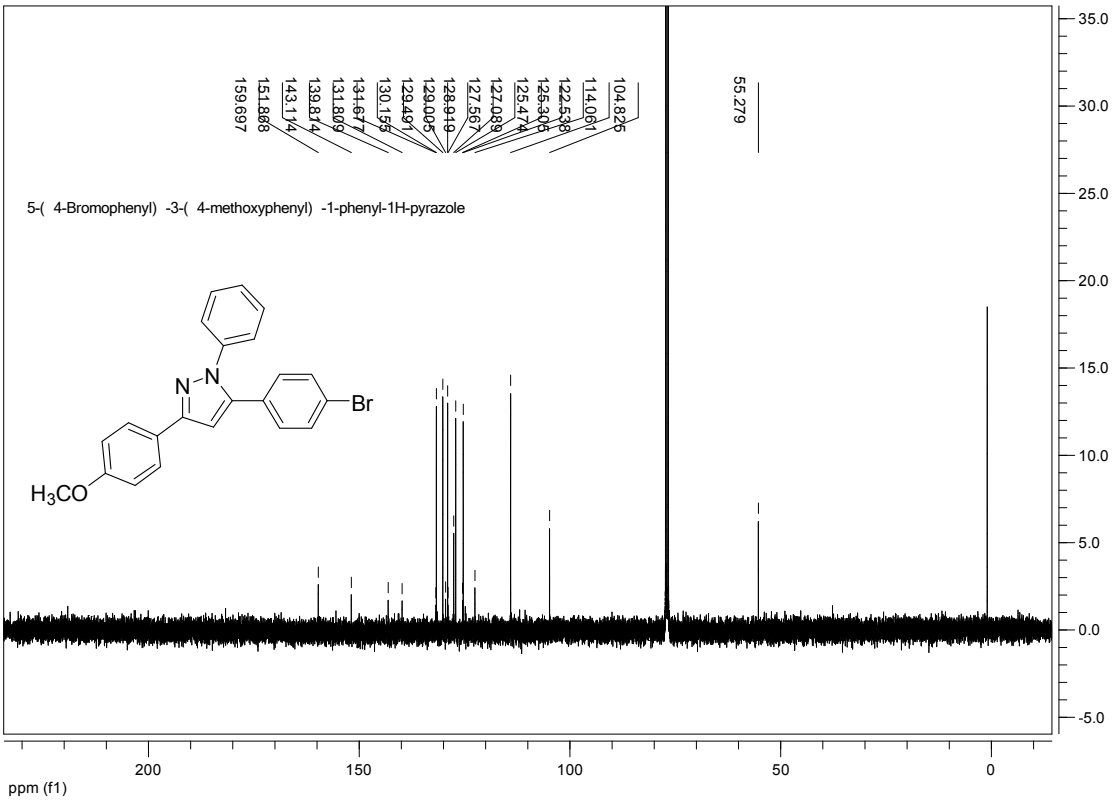


5-(2-Chlorophenyl)-1,3-diphenyl-1*H*-pyrazole (**3g**)

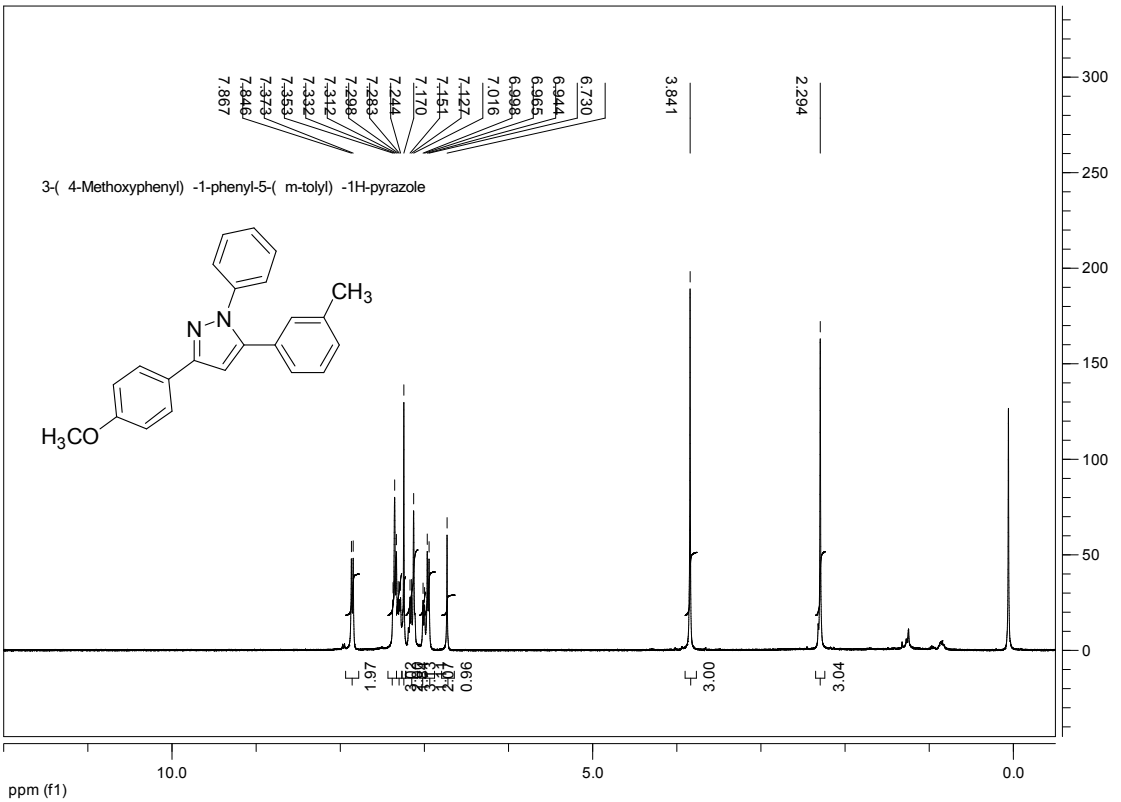


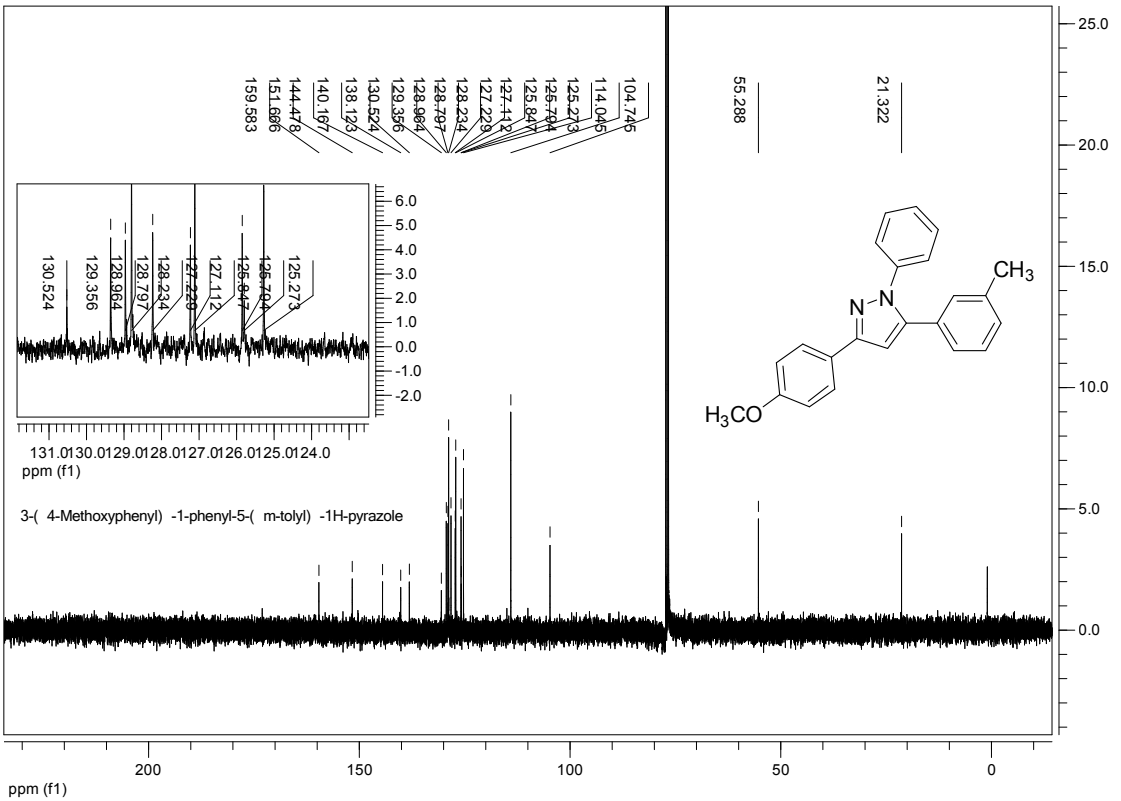
5-(4-Bromophenyl)-3-(4-methoxyphenyl)-1-phenyl-1*H*-pyrazole (**3h**)



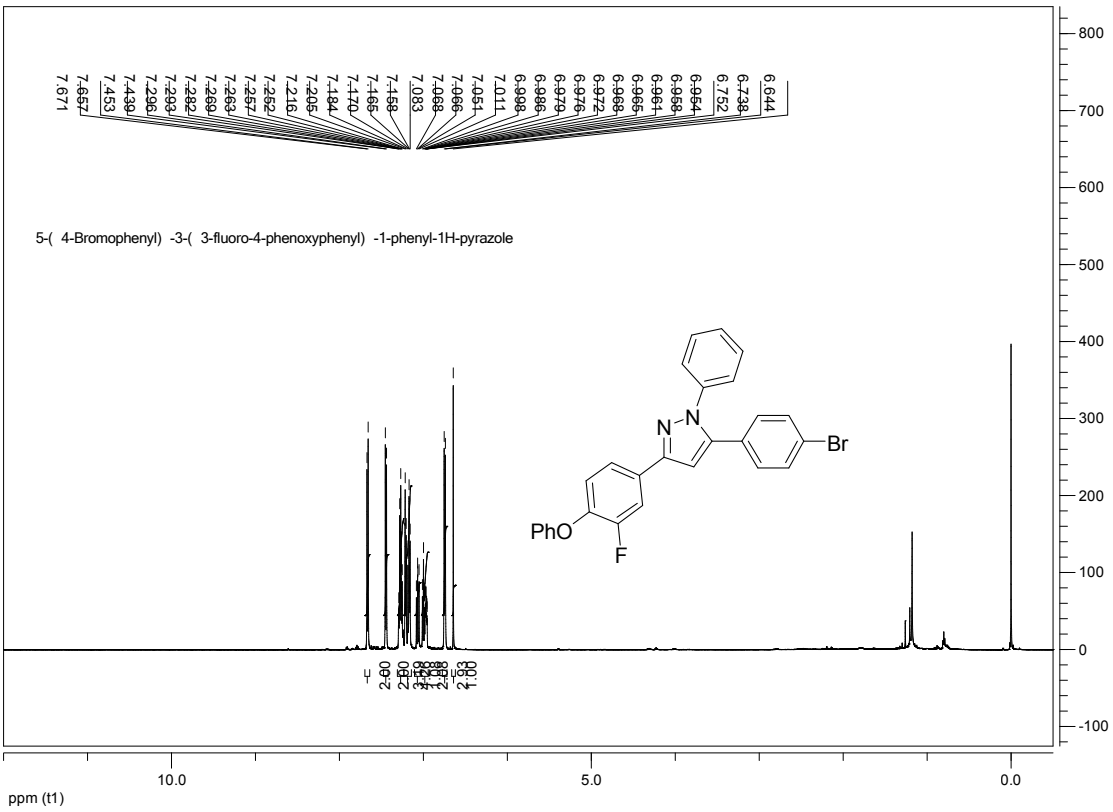


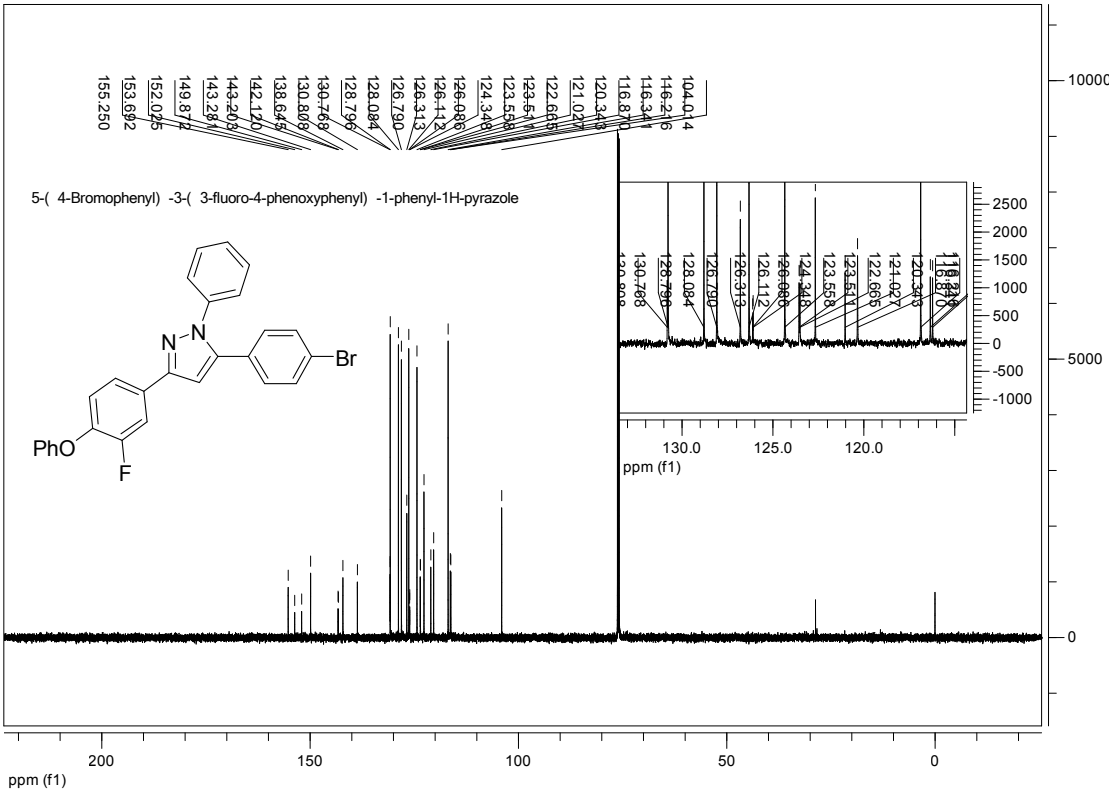
3-(4-Methoxyphenyl)-1-phenyl-5-(m-tolyl)-1H-pyrazole (**3i**)



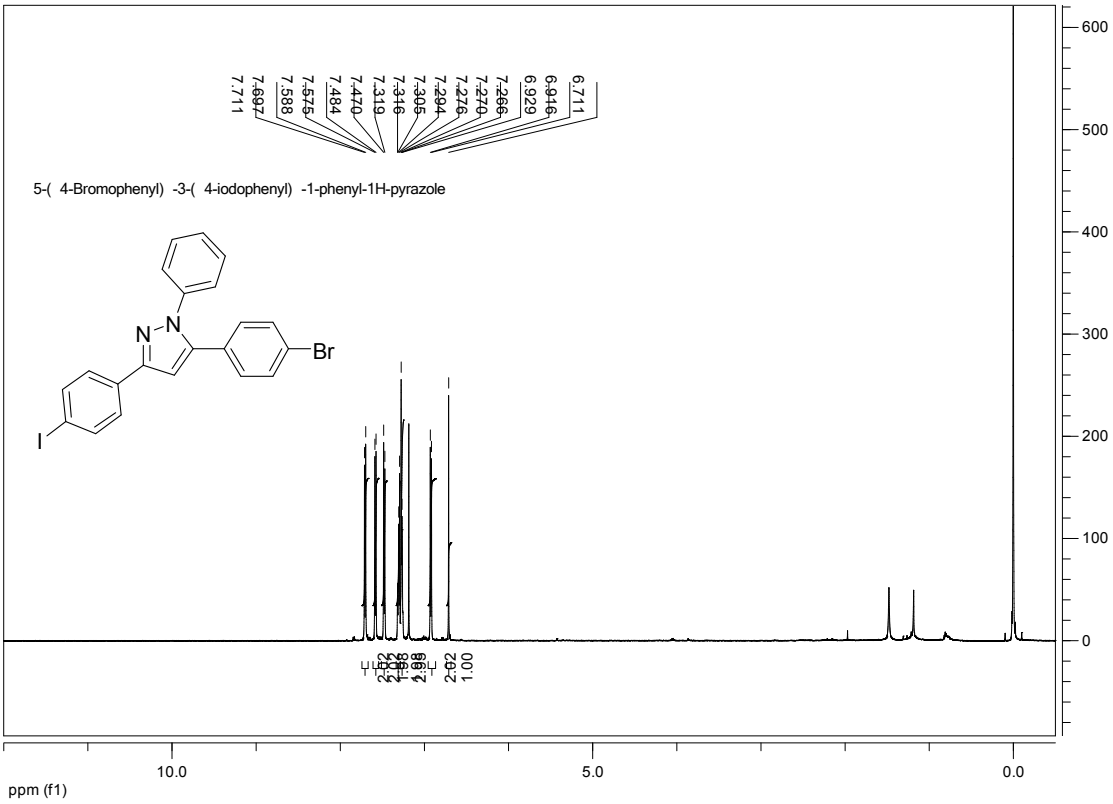


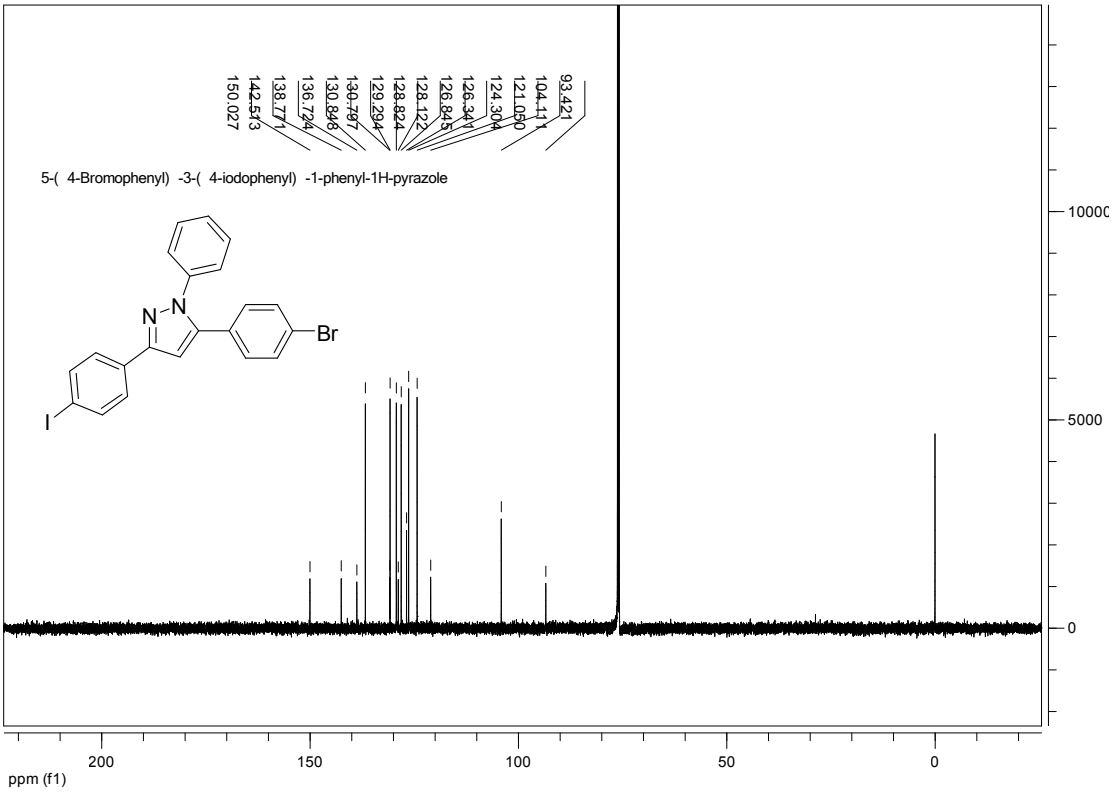
5-(4-Bromophenyl)-3-(3-fluoro-4-phenoxyphenyl)-1-phenyl-1*H*-pyrazole (**3j**)



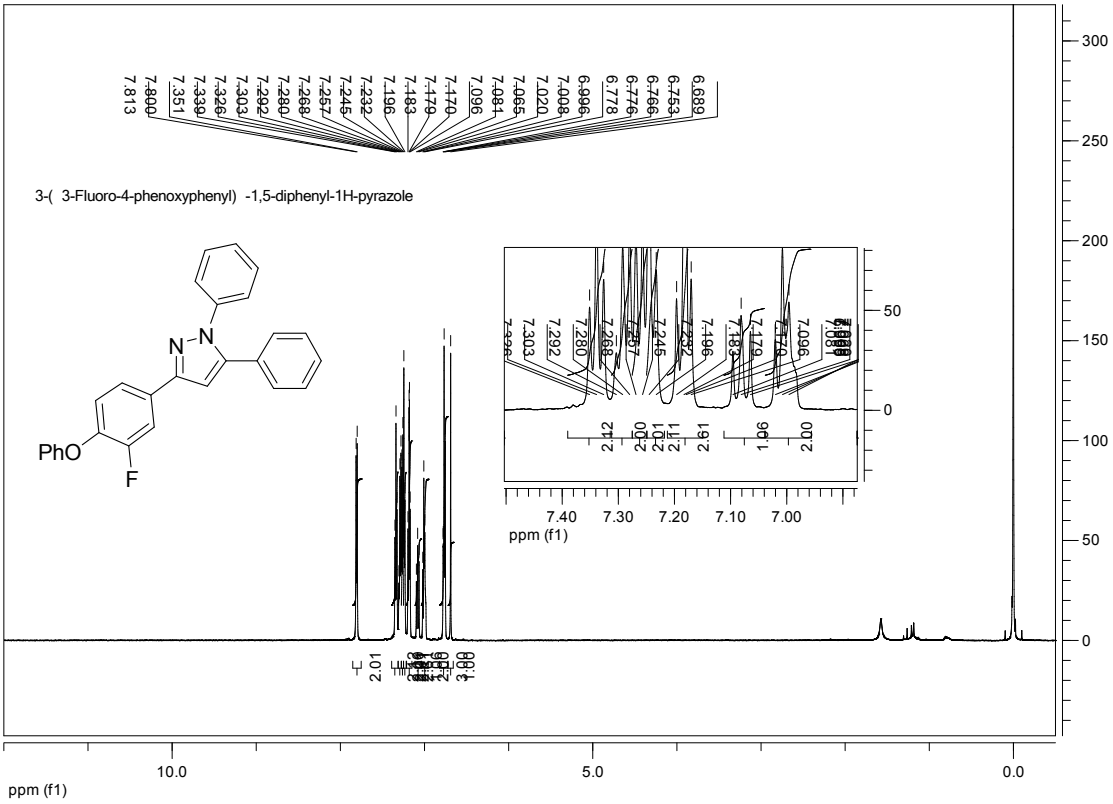


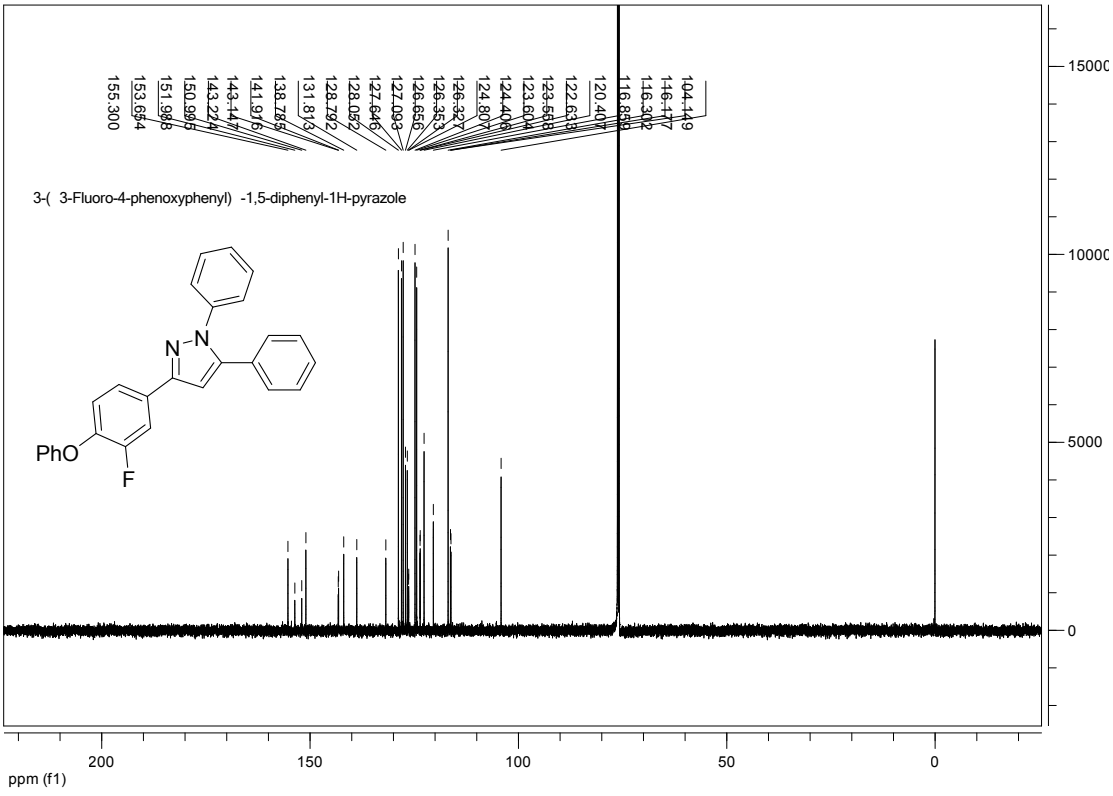
5-(4-Bromophenyl)-3-(4-iodophenyl)-1-phenyl-1*H*-pyrazole (**3k**)



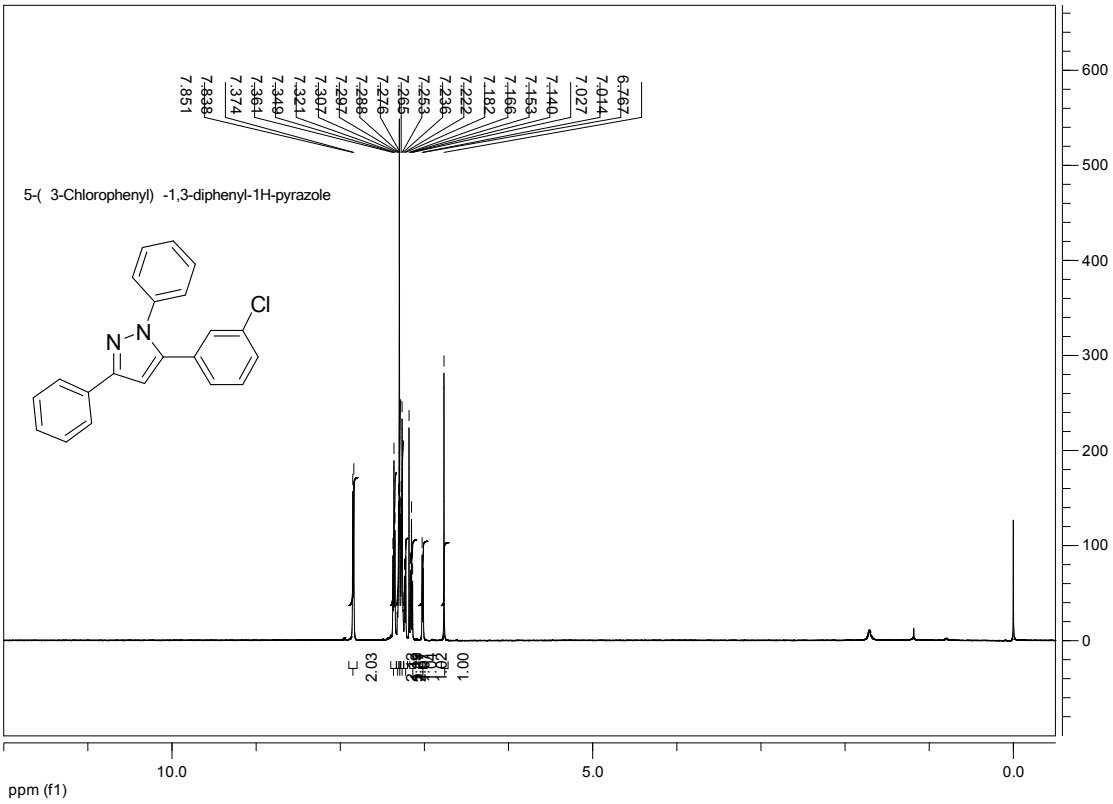


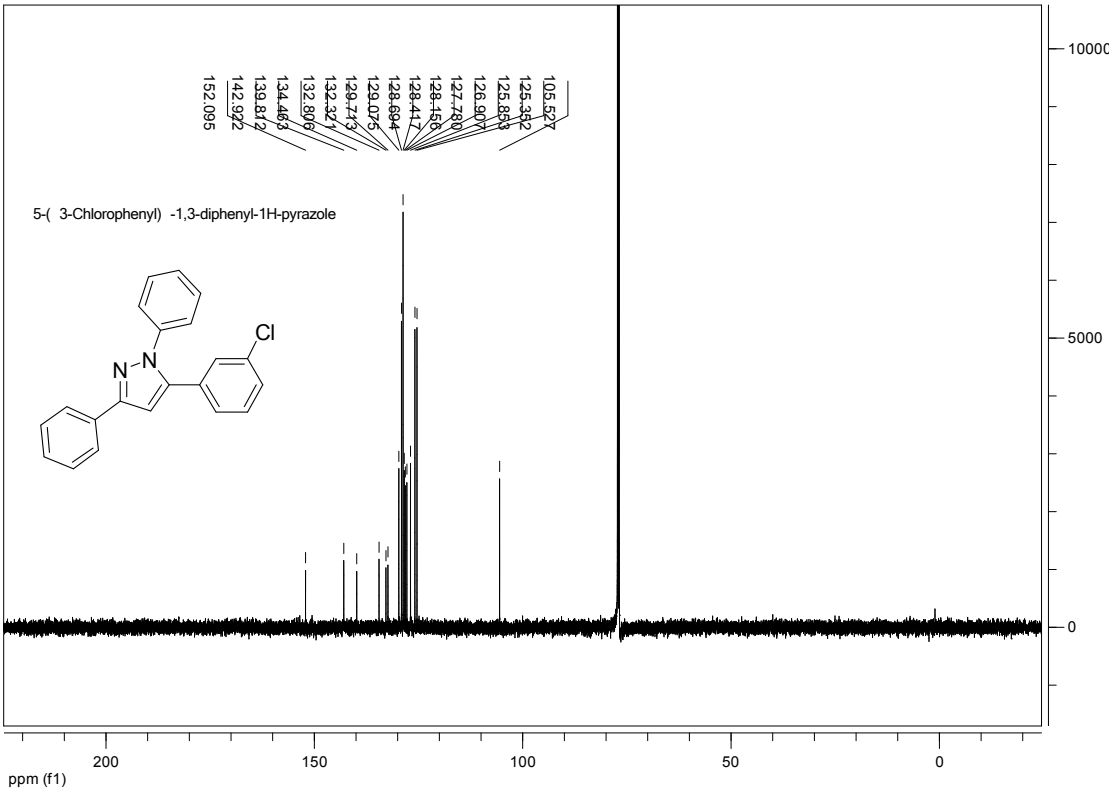
3-(3-Fluoro-4-phenoxyphenyl)-1,5-diphenyl-1*H*-pyrazole (**3l**)



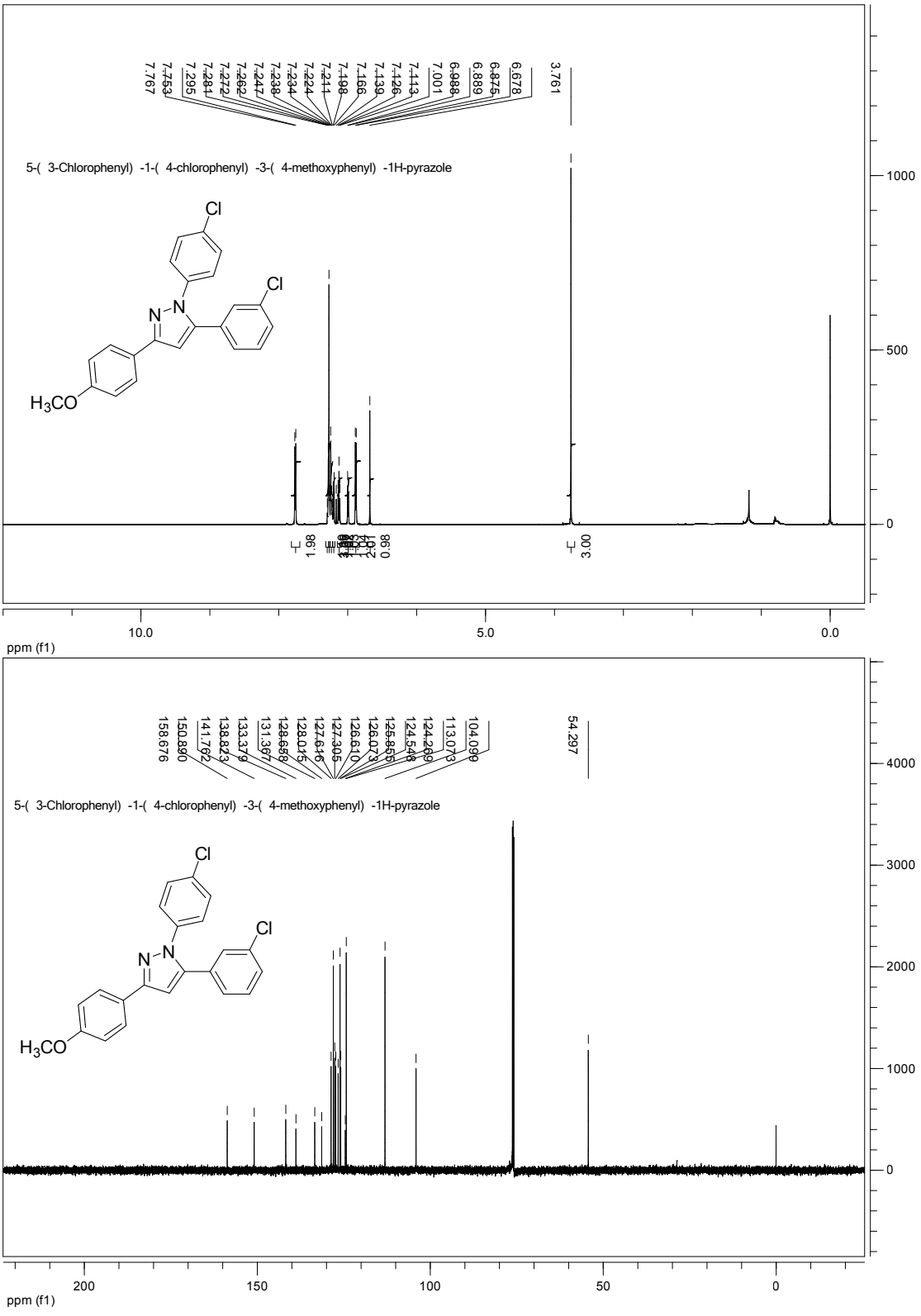


5-(3-Chlorophenyl)-1,3-diphenyl-1*H*-pyrazole (**3m**)

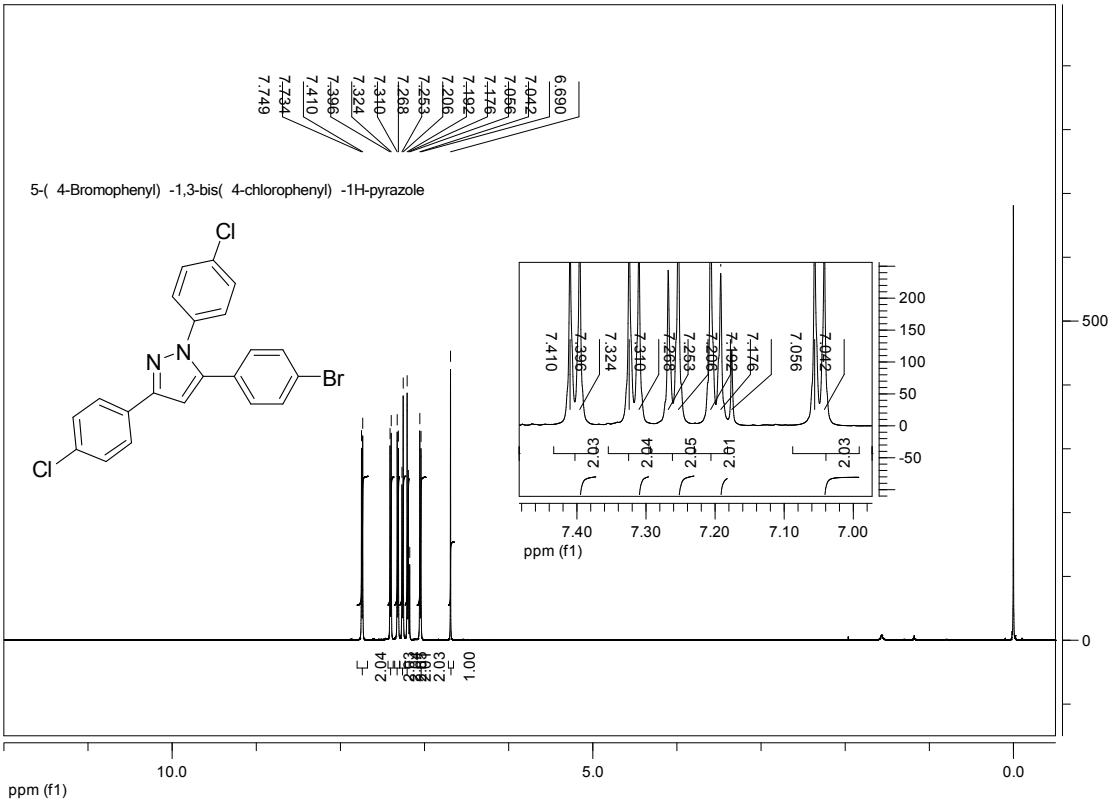


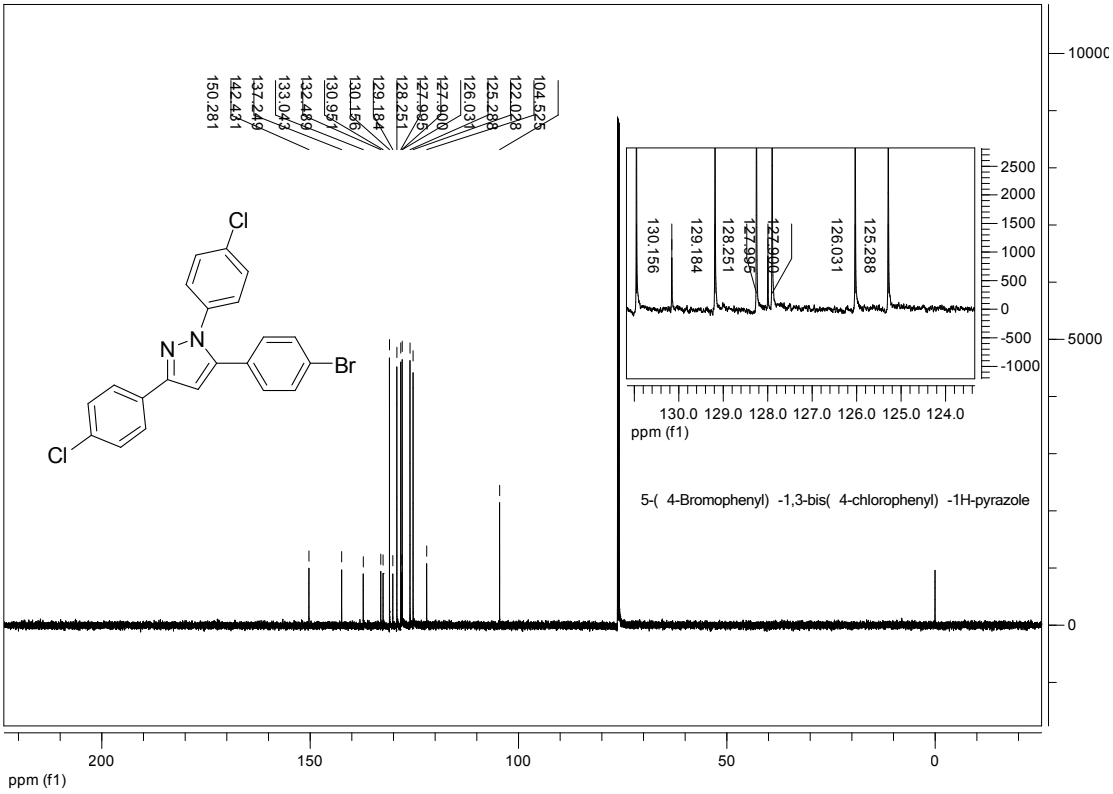


5-(3-Chlorophenyl)-1-(4-chlorophenyl)-3-(4-methoxyphenyl)-1*H*-pyrazole (**3n**)

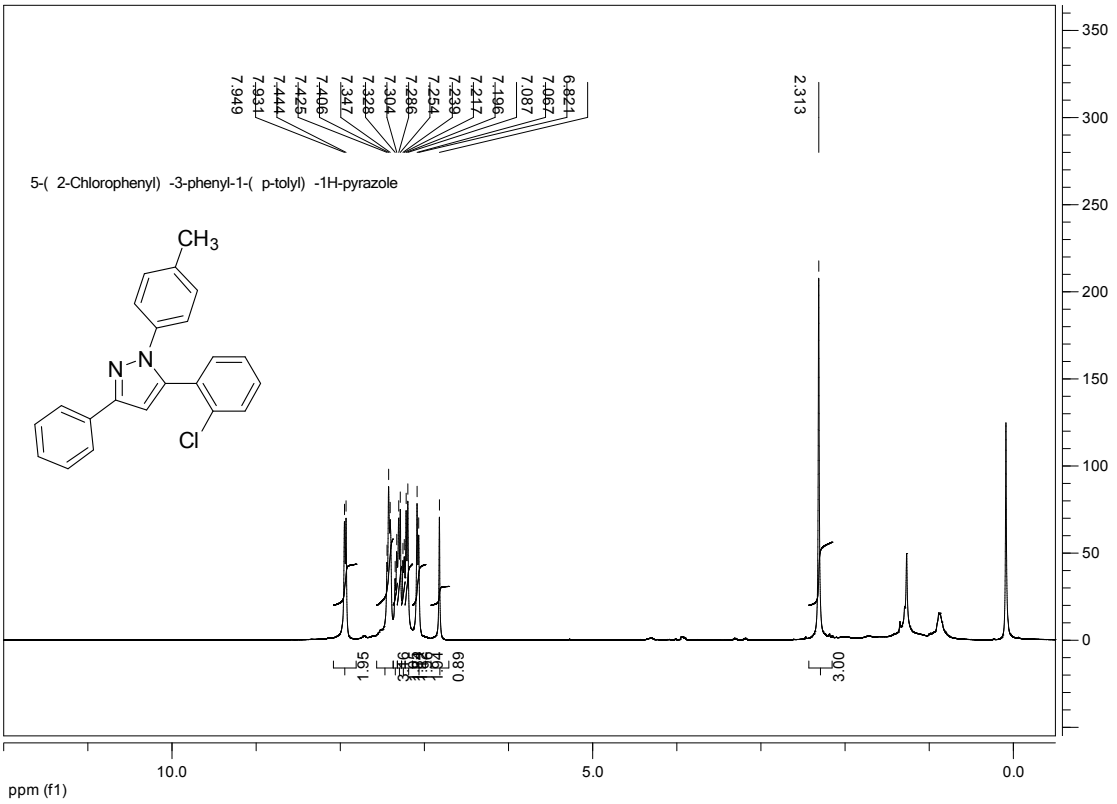


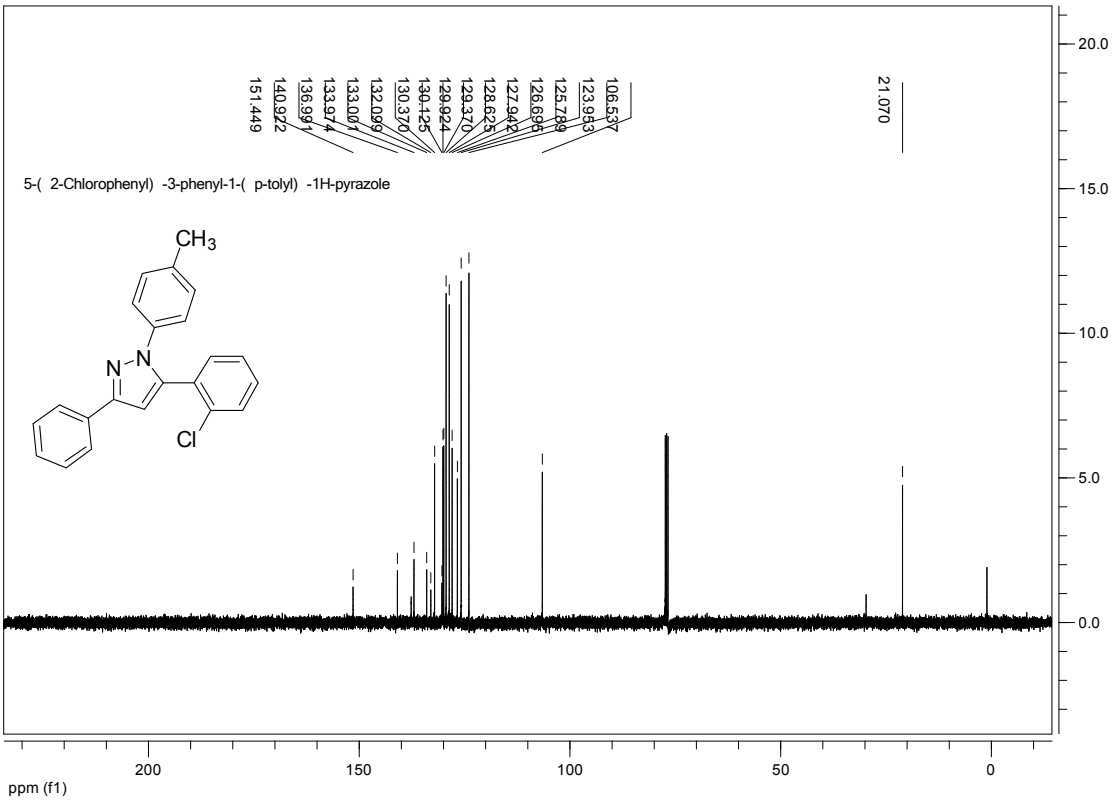
5-(4-Bromophenyl)-1,3-bis(4-chlorophenyl)-1*H*-pyrazole (**3o**)



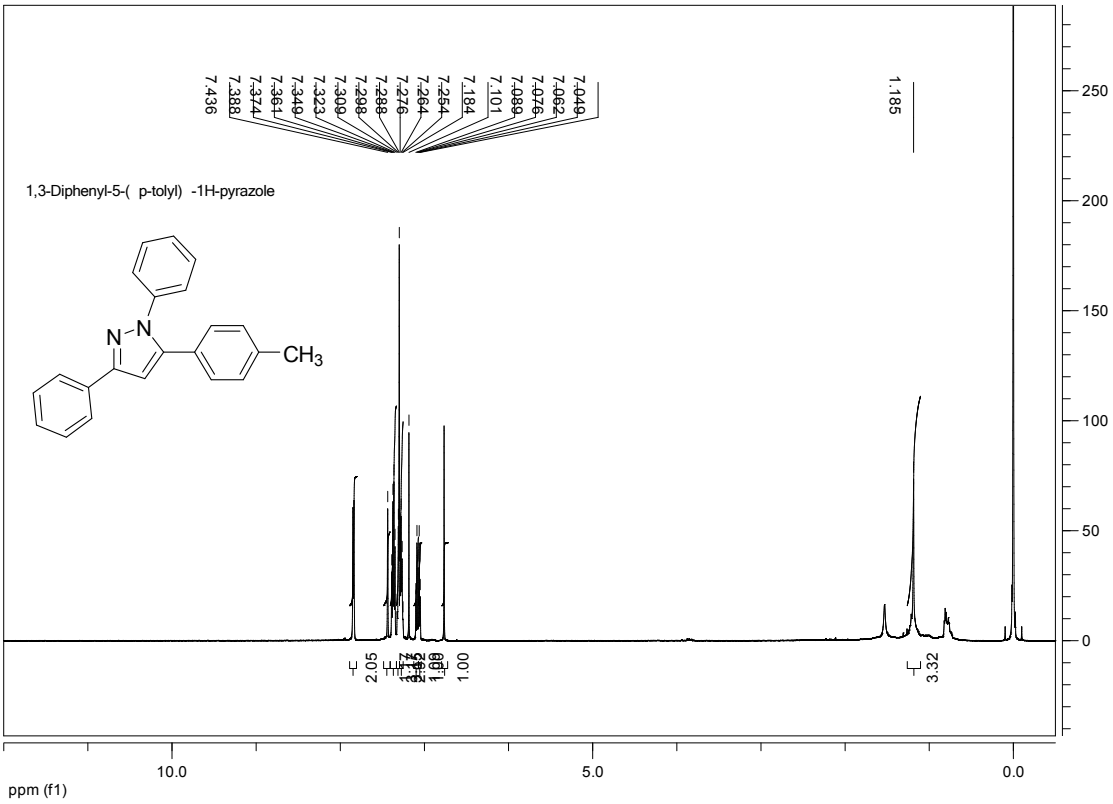


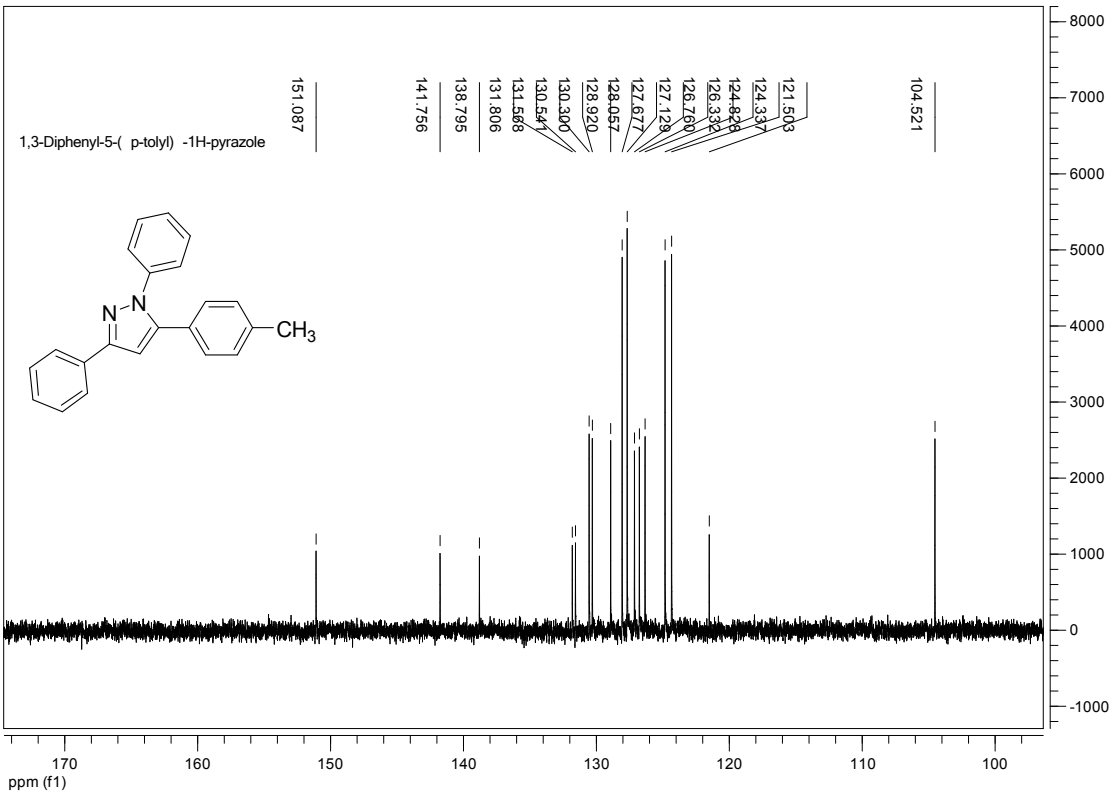
5-(2-Chlorophenyl)-3-phenyl-1-(p-tolyl)-1*H*-pyrazole (**3p**)



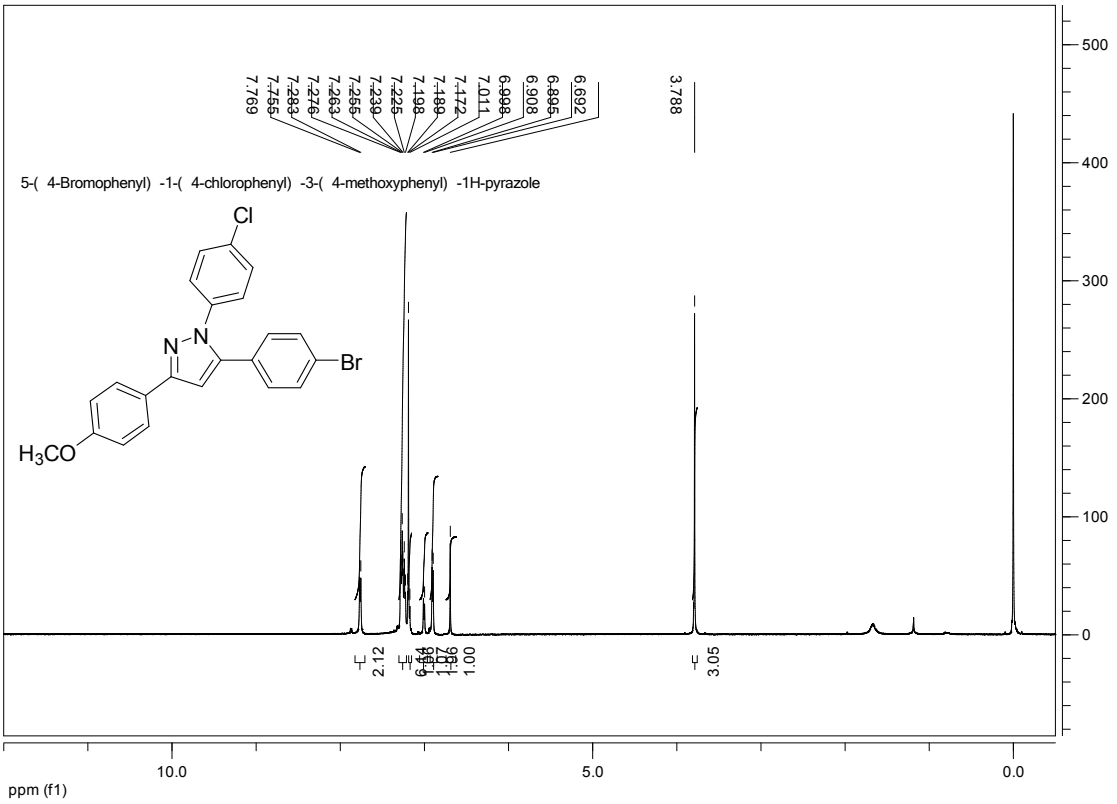


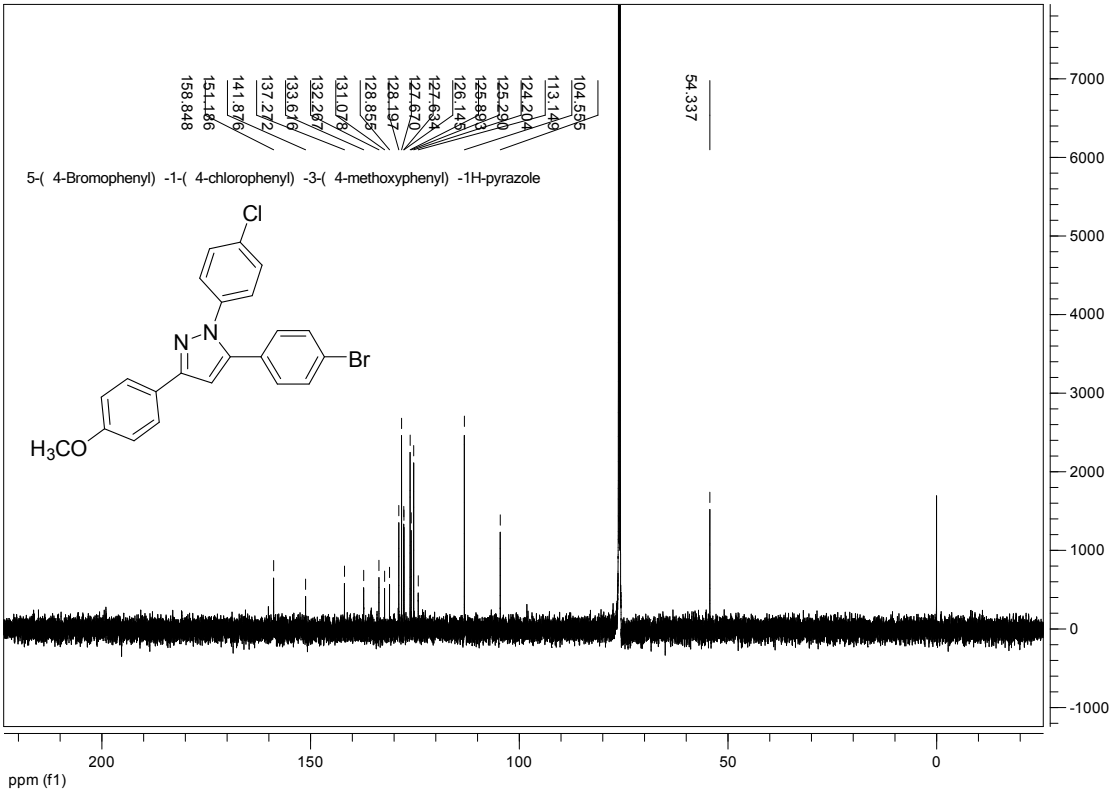
1,3-Diphenyl-5-(p-tolyl)-1H-pyrazole (**3q**)



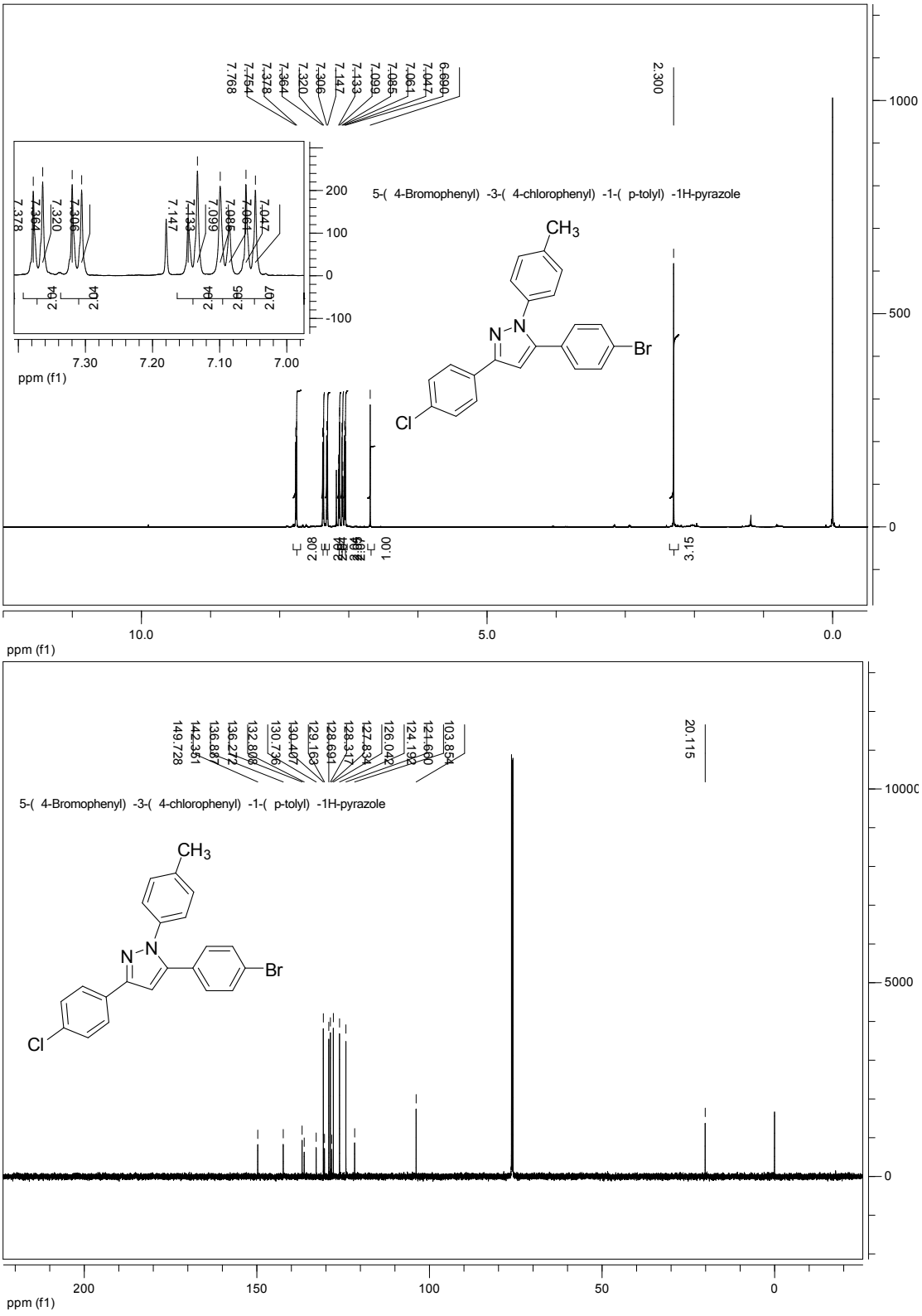


5-(4-Bromophenyl)-1-(4-chlorophenyl)-3-(4-methoxyphenyl)-1*H*-pyrazole (**3r**)

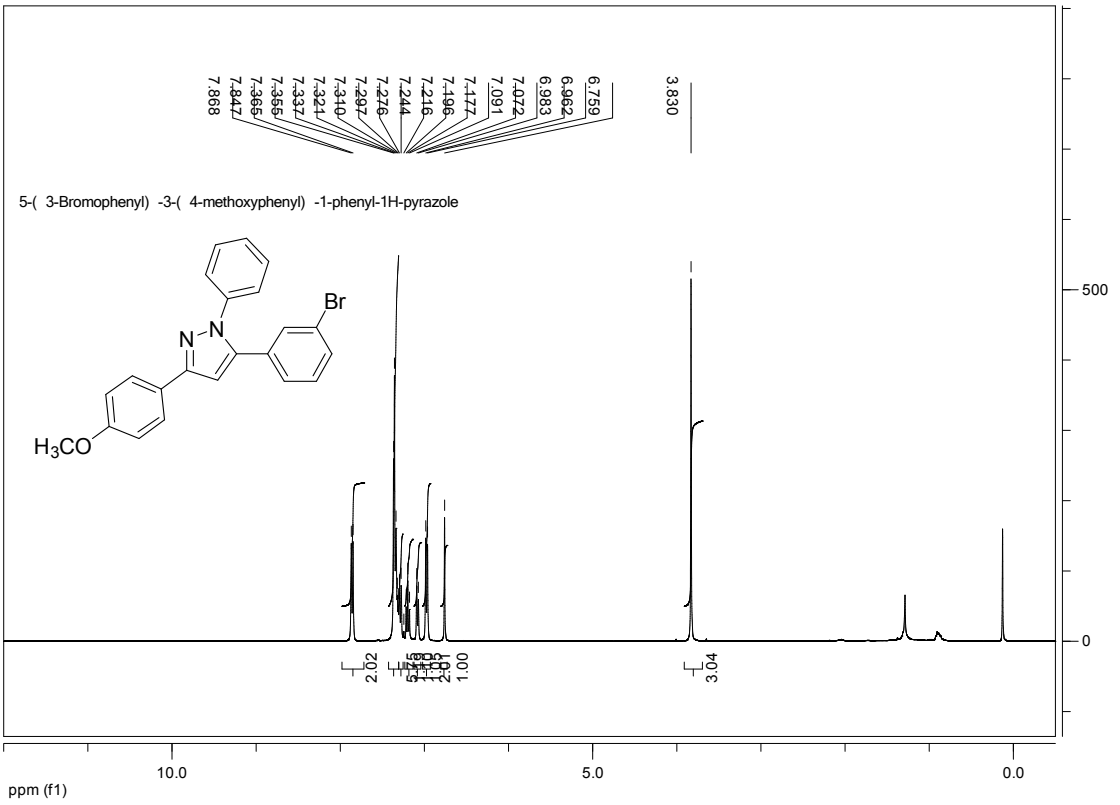


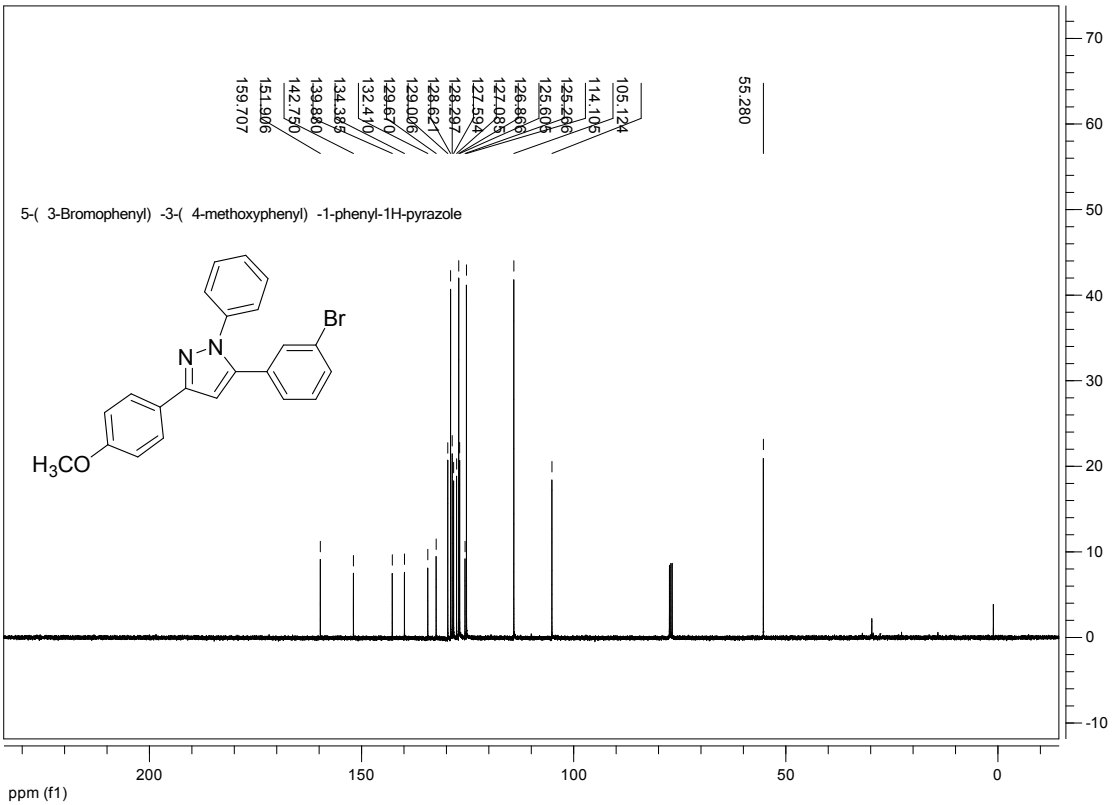


5-(4-Bromophenyl)-3-(4-chlorophenyl)-1-(p-tolyl)-1*H*-pyrazole (**3s**)



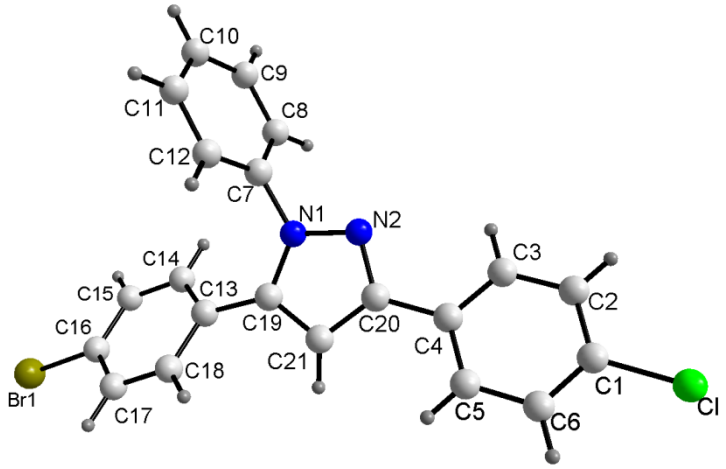
5-(3-Bromophenyl)-3-(4-methoxyphenyl)-1-phenyl-1*H*-pyrazole (**3t**)





Content

S1 Crystal data and structure refinement for pyrazole **3a**



CCDC 1427486

Table S1-1. Crystal data and structure refinement for **3a**.

Identification code	**3a**
Empirical formula	$C_{21}H_{14}BrClN_2$
Formula weight	409.69
Temperature	296 K
Wavelength	0.71073 A
Crystal system, space group	Triclinic, P-1
Unit cell dimensions	a = 5.9188(9) A alpha = 83.228(5) deg. b = 9.0339(15) A beta = 87.565(5) deg. c = 16.647(3) A gamma = 87.189(5) deg.
Volume	882.2(2) A^3
Z, Calculated density	2, 1.542 Mg/m^3
Absorption coefficient	2.486 mm^-1
F(000)	412
Crystal size	0.35 x 0.33 x 0.3 mm
Theta range for data collection	1.23 to 27.53 deg.
Limiting indices	-7<=h<=7, -11<=k<=11, -20<=l<=21
Reflections collected / unique	13553 / 4070 [R(int) = 0.0351]
Completeness to theta = 27.53	99.0 %
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4029 / 0 / 226
Goodness-of-fit on F^2	1.001
Final R indices [I>2sigma(I)]	R1 = 0.0397, wR2 = 0.0948
R indices (all data)	R1 = 0.0758, wR2 = 0.1060
Largest diff. peak and hole	0.369 and -0.309 e.A^-3

Table S1-2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for **3a**.
U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
Br(1)	-6979(1)	7241(1)	79(1)	67(1)
Cl	7161(1)	6086(1)	6564(1)	72(1)
N(2)	1974(3)	9739(2)	3333(1)	52(1)
N(1)	522(3)	9874(2)	2713(1)	47(1)
C(16)	-5092(4)	7740(3)	892(2)	49(1)
C(7)	179(4)	11311(3)	2264(1)	45(1)
C(4)	3033(4)	7813(3)	4414(2)	47(1)
C(1)	5548(5)	6766(3)	5737(2)	52(1)
C(19)	-666(4)	8622(3)	2699(1)	44(1)
C(3)	5085(4)	8428(3)	4536(2)	53(1)
C(20)	1691(4)	8375(3)	3708(1)	45(1)
C(12)	-1836(5)	12094(3)	2373(2)	57(1)
C(2)	6342(5)	7916(3)	5204(2)	55(1)
C(18)	-4132(4)	7548(3)	2273(2)	48(1)
C(8)	1874(5)	11919(3)	1758(2)	57(1)
C(14)	-1841(4)	8925(3)	1261(2)	52(1)
C(11)	-2133(5)	13519(3)	1970(2)	66(1)
C(21)	53(4)	7647(3)	3336(2)	48(1)
C(13)	-2246(4)	8397(3)	2073(2)	44(1)
C(10)	-462(5)	14123(3)	1473(2)	62(1)
C(17)	-5555(4)	7222(3)	1693(2)	51(1)
C(6)	3553(5)	6144(4)	5630(2)	67(1)
C(15)	-3254(5)	8590(3)	676(2)	57(1)
C(5)	2296(5)	6676(3)	4965(2)	61(1)
C(9)	1545(6)	13328(3)	1358(2)	66(1)

Table S1-3. Bond lengths [A] and angles [deg] for **3a**.

Br(1)-C(16)	1.898(3)
Cl-C(1)	1.744(3)
N(2)-C(20)	1.329(3)
N(2)-N(1)	1.361(3)
N(1)-C(19)	1.365(3)
N(1)-C(7)	1.430(3)
C(16)-C(15)	1.374(4)
C(16)-C(17)	1.381(4)
C(7)-C(12)	1.373(4)
C(7)-C(8)	1.374(4)
C(4)-C(5)	1.369(4)
C(4)-C(3)	1.393(4)
C(4)-C(20)	1.473(3)
C(1)-C(6)	1.360(4)
C(1)-C(2)	1.373(4)
C(19)-C(21)	1.365(3)
C(19)-C(13)	1.466(3)
C(3)-C(2)	1.385(3)
C(20)-C(21)	1.402(3)
C(12)-C(11)	1.387(4)
C(18)-C(17)	1.375(4)
C(18)-C(13)	1.392(3)
C(8)-C(9)	1.374(4)
C(14)-C(15)	1.380(4)
C(14)-C(13)	1.395(3)
C(11)-C(10)	1.355(4)
C(10)-C(9)	1.376(4)
C(6)-C(5)	1.385(4)
C(20)-N(2)-N(1)	104.6(2)
N(2)-N(1)-C(19)	112.24(19)
N(2)-N(1)-C(7)	118.1(2)
C(19)-N(1)-C(7)	128.83(19)
C(15)-C(16)-C(17)	120.7(2)
C(15)-C(16)-Br(1)	119.6(2)
C(17)-C(16)-Br(1)	119.7(2)
C(12)-C(7)-C(8)	120.8(2)
C(12)-C(7)-N(1)	118.7(2)
C(8)-C(7)-N(1)	120.4(2)
C(5)-C(4)-C(3)	118.4(2)

C(5)-C(4)-C(20)	120.9(2)
C(3)-C(4)-C(20)	120.7(2)
C(6)-C(1)-C(2)	121.5(2)
C(6)-C(1)-Cl	119.7(2)
C(2)-C(1)-Cl	118.8(2)
N(1)-C(19)-C(21)	105.8(2)
N(1)-C(19)-C(13)	124.8(2)
C(21)-C(19)-C(13)	129.2(2)
C(2)-C(3)-C(4)	121.0(3)
N(2)-C(20)-C(21)	111.1(2)
N(2)-C(20)-C(4)	120.3(2)
C(21)-C(20)-C(4)	128.6(2)
C(7)-C(12)-C(11)	118.9(3)
C(1)-C(2)-C(3)	118.6(3)
C(17)-C(18)-C(13)	121.6(2)
C(9)-C(8)-C(7)	119.5(3)
C(15)-C(14)-C(13)	120.7(2)
C(10)-C(11)-C(12)	120.4(3)
C(19)-C(21)-C(20)	106.2(2)
C(18)-C(13)-C(14)	117.9(2)
C(18)-C(13)-C(19)	120.0(2)
C(14)-C(13)-C(19)	121.9(2)
C(11)-C(10)-C(9)	120.5(3)
C(18)-C(17)-C(16)	119.2(2)
C(1)-C(6)-C(5)	119.4(3)
C(16)-C(15)-C(14)	119.9(2)
C(4)-C(5)-C(6)	121.1(3)
C(8)-C(9)-C(10)	119.8(3)

Symmetry transformations used to generate equivalent atoms:

Table S1-4. Anisotropic displacement parameters (A^2 x 10^3) for **3a**.
The anisotropic displacement factor exponent takes the form:
-2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

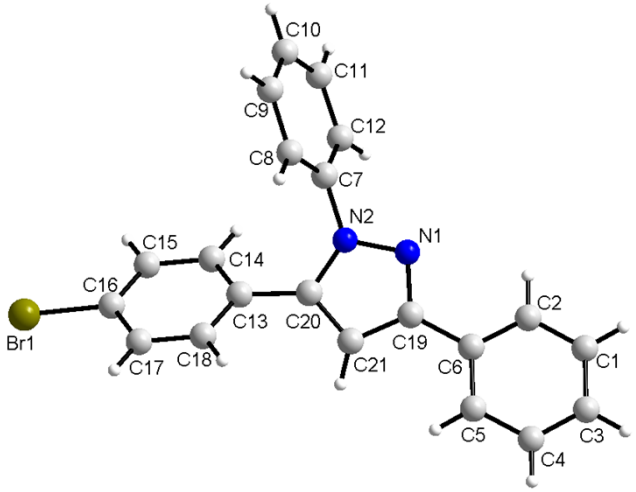
	U11	U22	U33	U23	U13	U12
Br(1)	71(1)	76(1)	58(1)	-5(1)	-22(1)	-17(1)
Cl	83(1)	76(1)	54(1)	1(1)	-27(1)	12(1)
N(2)	59(1)	46(1)	51(1)	-3(1)	-18(1)	2(1)
N(1)	54(1)	40(1)	47(1)	0(1)	-18(1)	0(1)
C(16)	53(1)	45(2)	49(1)	-5(1)	-13(1)	-1(1)
C(7)	55(2)	39(1)	42(1)	-5(1)	-15(1)	-4(1)
C(4)	54(2)	46(2)	42(1)	-4(1)	-7(1)	6(1)
C(1)	60(2)	53(2)	42(1)	-6(1)	-13(1)	10(1)
C(19)	47(1)	41(1)	44(1)	-4(1)	-4(1)	2(1)
C(3)	61(2)	46(2)	51(2)	1(1)	-9(1)	1(1)
C(20)	48(1)	45(2)	43(1)	-4(1)	-6(1)	6(1)
C(12)	57(2)	52(2)	60(2)	-1(1)	-5(1)	-1(1)
C(2)	56(2)	52(2)	59(2)	-10(1)	-17(1)	2(1)
C(18)	52(1)	47(2)	44(1)	2(1)	-4(1)	-3(1)
C(8)	56(2)	59(2)	56(2)	-4(1)	-7(1)	-5(1)
C(14)	54(1)	55(2)	47(1)	2(1)	-6(1)	-16(1)
C(11)	69(2)	49(2)	77(2)	1(2)	-16(2)	7(2)
C(21)	56(1)	41(2)	47(1)	1(1)	-7(1)	-4(1)
C(13)	48(1)	39(1)	45(1)	-3(1)	-8(1)	2(1)
C(10)	82(2)	41(2)	64(2)	7(1)	-26(2)	-8(2)
C(17)	48(1)	55(2)	51(2)	0(1)	-2(1)	-10(1)
C(6)	71(2)	70(2)	55(2)	15(2)	-12(1)	-5(2)
C(15)	67(2)	62(2)	41(1)	2(1)	-8(1)	-13(1)
C(5)	57(2)	66(2)	59(2)	6(2)	-15(1)	-9(1)
C(9)	80(2)	60(2)	58(2)	8(2)	-7(2)	-24(2)

—

Table S1-5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for **3a**.

	x	y	z	U(eq)
H(3)	5630	9210	4157	64
H(12)	-3007	11666	2720	68
H(2)	7727	8352	5291	66
H(18)	-4443	7184	2824	58
H(8)	3263	11370	1686	68
H(14)	-579	9520	1109	62
H(11)	-3517	14075	2042	79
H(21)	-455	6670	3496	58
H(10)	-677	15103	1203	75
H(17)	-6842	6647	1842	62
H(6)	3027	5351	6006	80
H(15)	-2955	8947	123	68
H(5)	899	6246	4890	73
H(9)	2699	13751	1002	79

S2 Crystal data and structure refinement for pyrazole **3d**



CCDC 1433734

Table S2-1. Crystal data and structure refinement for **3d**.

Identification code	**3d**
Empirical formula	$C_{21}H_{15}BrN_2$
Formula weight	375.25
Temperature	296 K
Wavelength	0.71073 A
Crystal system, space group	Orthorhombic, P2(1)2(1)2(1)
Unit cell dimensions	a = 5.8446(7) A alpha = 90 deg. b = 10.7346(16) A beta = 90 deg. c = 27.540(4) A gamma = 90 deg.
Volume	1727.8(4) A^3
Z, Calculated density	4, 1.443 Mg/m^3
Absorption coefficient	2.382 mm^-1
F(000)	760
Crystal size	0.35 x 0.33 x 0.3 mm
Theta range for data collection	1.48 to 27.50 deg.
Limiting indices	-7<=h<=7, -13<=k<=13, -35<=l<=34
Reflections collected / unique	15441 / 3917 [R(int) = 0.0410]
Completeness to theta = 27.50	99.4 %
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3917 / 0 / 217
Goodness-of-fit on F^2	1.046
Final R indices [I>2sigma(I)]	R1 = 0.0696, wR2 = 0.1993
R indices (all data)	R1 = 0.1064, wR2 = 0.2228
Absolute structure parameter	1.00(2)
Largest diff. peak and hole	0.440 and -0.610 e.A^-3

Table S2-2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for **3d**.
U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
Br(1)	-1942(2)	-840(1)	10095(1)	73(1)
N(2)	6217(10)	1823(5)	8524(2)	47(1)
C(13)	3208(12)	1459(6)	9162(2)	45(1)
C(6)	8882(12)	4775(6)	8640(2)	48(2)
C(7)	5852(12)	737(6)	8229(2)	47(1)
N(1)	7767(10)	2682(5)	8375(2)	48(1)
C(18)	1278(12)	2018(6)	9354(2)	47(2)
C(21)	5715(12)	3409(6)	9003(2)	48(2)
C(17)	-271(12)	1341(7)	9627(2)	53(2)
C(19)	7463(12)	3653(6)	8676(2)	46(2)
C(14)	3610(13)	204(6)	9251(3)	51(2)
C(5)	8273(13)	5851(6)	8885(3)	59(2)
C(8)	3787(13)	617(7)	7987(3)	56(2)
C(2)	10891(15)	4794(7)	8368(3)	63(2)
C(15)	2035(14)	-475(6)	9524(3)	56(2)
C(20)	4948(12)	2230(6)	8905(2)	45(1)
C(3)	11618(16)	6902(8)	8588(3)	71(2)
C(12)	7548(15)	-142(7)	8189(3)	64(2)
C(1)	12224(15)	5847(7)	8339(3)	71(2)
C(9)	3439(16)	-434(8)	7696(3)	66(2)
C(4)	9651(15)	6908(7)	8855(3)	65(2)
C(16)	143(13)	81(7)	9710(2)	54(2)
C(11)	7125(18)	-1193(7)	7901(3)	72(2)
C(10)	5118(19)	-1326(8)	7659(3)	73(2)

Table S2-3. Bond lengths [A] and angles [deg] for **3d**.

Br(1)-C(16)	1.894(7)
N(2)-N(1)	1.356(7)
N(2)-C(20)	1.358(8)
N(2)-C(7)	1.437(8)
C(13)-C(18)	1.382(10)
C(13)-C(14)	1.390(9)
C(13)-C(20)	1.490(9)
C(6)-C(5)	1.385(10)
C(6)-C(2)	1.392(11)
C(6)-C(19)	1.466(9)
C(7)-C(12)	1.373(10)
C(7)-C(8)	1.385(10)
N(1)-C(19)	1.342(8)
C(18)-C(17)	1.384(9)
C(21)-C(20)	1.369(9)
C(21)-C(19)	1.388(10)
C(17)-C(16)	1.393(10)
C(14)-C(15)	1.395(10)
C(5)-C(4)	1.394(10)
C(8)-C(9)	1.399(10)
C(2)-C(1)	1.374(10)
C(15)-C(16)	1.356(11)
C(3)-C(4)	1.365(13)
C(3)-C(1)	1.370(12)
C(12)-C(11)	1.401(11)
C(9)-C(10)	1.375(13)
C(11)-C(10)	1.356(14)
N(1)-N(2)-C(20)	112.3(5)
N(1)-N(2)-C(7)	118.7(5)
C(20)-N(2)-C(7)	128.1(6)
C(18)-C(13)-C(14)	119.5(6)
C(18)-C(13)-C(20)	119.8(6)
C(14)-C(13)-C(20)	120.5(7)
C(5)-C(6)-C(2)	117.8(6)
C(5)-C(6)-C(19)	120.5(6)
C(2)-C(6)-C(19)	121.7(6)
C(12)-C(7)-C(8)	121.8(6)
C(12)-C(7)-N(2)	119.8(6)
C(8)-C(7)-N(2)	118.5(6)

C(19)-N(1)-N(2)	104.7(5)
C(13)-C(18)-C(17)	120.9(6)
C(20)-C(21)-C(19)	106.7(6)
C(18)-C(17)-C(16)	119.1(7)
N(1)-C(19)-C(21)	110.6(5)
N(1)-C(19)-C(6)	121.4(6)
C(21)-C(19)-C(6)	128.0(6)
C(13)-C(14)-C(15)	119.3(7)
C(6)-C(5)-C(4)	120.2(7)
C(7)-C(8)-C(9)	118.5(7)
C(1)-C(2)-C(6)	121.4(8)
C(16)-C(15)-C(14)	120.8(6)
N(2)-C(20)-C(21)	105.7(6)
N(2)-C(20)-C(13)	124.2(6)
C(21)-C(20)-C(13)	130.0(6)
C(4)-C(3)-C(1)	119.4(7)
C(7)-C(12)-C(11)	118.2(8)
C(3)-C(1)-C(2)	120.3(8)
C(10)-C(9)-C(8)	120.0(7)
C(3)-C(4)-C(5)	120.9(8)
C(15)-C(16)-C(17)	120.4(7)
C(15)-C(16)-Br(1)	120.4(5)
C(17)-C(16)-Br(1)	119.1(6)
C(10)-C(11)-C(12)	121.0(9)
C(11)-C(10)-C(9)	120.5(7)

Symmetry transformations used to generate equivalent atoms:

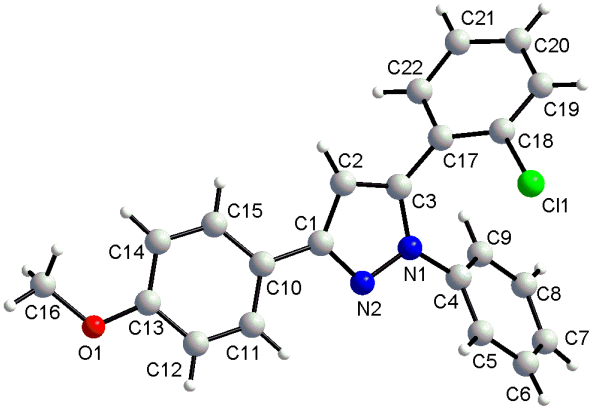
Table S2-4. Anisotropic displacement parameters (A^2 x 10^3) for **3d**.
The anisotropic displacement factor exponent takes the form:
-2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
Br(1)	71(1)	81(1)	69(1)	20(1)	2(1)	-31(1)
N(2)	53(3)	42(3)	47(3)	-1(2)	0(3)	-9(2)
C(13)	50(3)	43(3)	44(3)	5(3)	-1(3)	-11(3)
C(6)	53(4)	46(3)	45(3)	5(3)	-9(3)	-10(3)
C(7)	54(3)	41(3)	45(3)	2(3)	0(3)	-9(3)
N(1)	48(3)	47(3)	49(3)	3(2)	4(2)	-12(2)
C(18)	51(4)	43(3)	48(3)	7(3)	-3(3)	1(3)
C(21)	55(4)	41(3)	48(4)	0(3)	-1(3)	-1(3)
C(17)	47(4)	62(4)	49(4)	6(3)	1(3)	-4(3)
C(19)	56(4)	42(3)	41(3)	7(3)	-7(3)	-7(3)
C(14)	52(4)	44(4)	58(4)	7(3)	-2(3)	-7(3)
C(5)	61(4)	44(4)	72(4)	-3(3)	1(4)	-8(4)
C(8)	54(4)	55(4)	57(4)	0(3)	-1(3)	-9(3)
C(2)	61(4)	57(4)	69(5)	0(4)	8(4)	-6(4)
C(15)	67(4)	39(3)	64(4)	9(3)	-4(4)	-8(3)
C(20)	51(3)	39(3)	44(3)	2(3)	1(3)	-4(3)
C(3)	77(6)	58(4)	78(5)	11(4)	-6(5)	-28(4)
C(12)	65(5)	64(5)	63(4)	-13(3)	1(4)	7(4)
C(1)	64(4)	73(5)	74(5)	11(4)	9(4)	-19(5)
C(9)	70(5)	70(5)	59(4)	-5(4)	-10(4)	-20(4)
C(4)	75(5)	48(4)	71(5)	-1(3)	2(4)	-14(4)
C(16)	53(4)	58(4)	49(4)	5(3)	-6(3)	-18(3)
C(11)	86(6)	58(4)	71(5)	-15(4)	5(5)	8(4)
C(10)	94(6)	66(5)	58(4)	-13(4)	7(5)	-21(5)

Table S2-5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for **3d**.

	x	y	z	U(eq)
H(18)	1012	2879	9297	57
H(21)	5159	3954	9248	57
H(17)	-1599	1730	9756	63
H(14)	4945	-188	9127	61
H(5)	6912	5869	9073	71
H(8)	2632	1234	8018	67
H(2)	11351	4064	8199	75
H(15)	2290	-1336	9581	68
H(3)	12558	7623	8574	85
H(12)	8968	-40	8352	77
H(1)	13571	5842	8146	85
H(9)	2042	-531	7524	80
H(4)	9215	7643	9024	78
H(11)	8261	-1823	7875	86
H(10)	4871	-2041	7463	87

S3 Crystal data and structure refinement for pyrazole **3f**



CCDC 1465079

Table S3-1. Crystal data and structure refinement for **3f**.

Identification code	**3f**
Empirical formula	$C_{22}H_{17}ClN_2O$
Formula weight	360.83
Temperature	296 K
Wavelength	0.71073 A
Crystal system, space group	Triclinic, P-1
Unit cell dimensions	a = 9.490(3) A alpha = 100.826(8) deg. b = 12.047(4) A beta = 99.318(8) deg. c = 16.469(5) A gamma = 90.148(8) deg.
Volume	1823.9(10) A^3
Z, Calculated density	4, 1.314 Mg/m^3
Absorption coefficient	0.222 mm^-1
F(000)	752
Crystal size	0.35 x 0.33 x 0.3 mm
Theta range for data collection	1.28 to 25.00 deg.
Limiting indices	-11<=h<=11, -14<=k<=14, -19<=l<=17
Reflections collected / unique	15240 / 6439 [R(int) = 0.0670]
Completeness to theta = 25.00	89.3 %
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	5747 / 0 / 471
Goodness-of-fit on F^2	1.048
Final R indices [I>2sigma(I)]	R1 = 0.1081, wR2 = 0.2915
R indices (all data)	R1 = 0.1998, wR2 = 0.3159
Largest diff. peak and hole	0.602 and -0.295 e.A^-3

Table S3-2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for **3f**.
U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
Cl(1)	-923(2)	4511(2)	684(1)	78(1)
Cl(2)	4288(2)	-433(2)	899(1)	86(1)
O(2)	3352(4)	5419(4)	5969(3)	63(1)
O(1)	1937(4)	10244(4)	6057(3)	65(1)
C(23)	3344(6)	1455(5)	3539(3)	42(2)
N(4)	2172(5)	1071(4)	2993(3)	47(1)
N(2)	1862(5)	6072(4)	2994(3)	48(1)
N(1)	1305(5)	5102(4)	2471(3)	47(1)
C(32)	3368(6)	2487(5)	4171(3)	46(2)
N(3)	2571(5)	88(4)	2522(3)	42(1)
C(10)	1108(6)	7433(5)	4136(3)	43(2)
C(13)	1586(6)	9313(5)	5440(4)	49(2)
C(1)	878(6)	6406(5)	3480(3)	46(2)
C(35)	3428(6)	4450(5)	5390(3)	48(2)
C(34)	2331(6)	4244(5)	4721(4)	47(2)
C(36)	4531(6)	3705(5)	5454(4)	50(2)
C(26)	1492(6)	-575(5)	1904(3)	46(2)
C(37)	4452(7)	2750(5)	4832(4)	59(2)
C(25)	3962(6)	-130(5)	2770(4)	48(2)
C(33)	2276(6)	3260(5)	4118(4)	48(2)
C(3)	-7(6)	4812(5)	2623(4)	47(2)
C(15)	296(7)	7614(5)	4757(4)	57(2)
C(17)	-866(6)	3806(5)	2173(4)	49(2)
C(4)	2179(6)	4489(5)	1937(4)	51(2)
C(18)	-1349(6)	3566(5)	1294(4)	61(2)
C(14)	488(7)	8536(5)	5398(4)	60(2)
C(39)	4740(6)	-1104(5)	2403(4)	46(2)
C(9)	2291(7)	3333(6)	1879(4)	59(2)
C(24)	4473(6)	731(5)	3415(3)	48(2)
C(2)	-301(6)	5639(5)	3249(4)	50(2)
C(12)	2416(6)	9154(5)	4812(4)	53(2)
C(31)	1432(6)	-1738(5)	1847(4)	53(2)

C(11)	2186(6)	8228(5)	4174(4)	51(2)
C(27)	528(7)	-43(6)	1406(4)	64(2)
C(16)	1060(7)	10455(6)	6708(4)	69(2)
C(22)	-1355(7)	3065(6)	2623(5)	64(2)
C(29)	-532(7)	-1871(7)	728(4)	75(2)
C(30)	400(7)	-2363(6)	1234(4)	66(2)
C(38)	4494(7)	5701(6)	6657(4)	70(2)
C(19)	-2121(7)	2593(6)	892(5)	68(2)
C(28)	-510(8)	-691(6)	815(4)	71(2)
C(40)	4961(7)	-1316(6)	1583(4)	64(2)
C(8)	3216(7)	2752(7)	1407(4)	77(2)
C(5)	3026(7)	5073(6)	1531(4)	66(2)
C(44)	5376(6)	-1809(6)	2929(4)	62(2)
C(41)	5779(9)	-2223(7)	1293(5)	90(3)
C(20)	-2562(7)	1873(6)	1358(5)	79(2)
C(21)	-2222(7)	2111(6)	2217(6)	81(2)
C(6)	3925(7)	4500(7)	1040(5)	86(3)
C(7)	4072(7)	3361(8)	1019(4)	86(3)
C(43)	6199(7)	-2702(6)	2642(5)	75(2)
C(42)	6403(9)	-2890(7)	1837(6)	95(3)

Table S3-3. Bond lengths [A] and angles [deg] for **3f**.

Cl(1)-C(18)	1.740(7)
Cl(2)-C(40)	1.740(7)
O(2)-C(35)	1.372(7)
O(2)-C(38)	1.425(7)
O(1)-C(13)	1.365(7)
O(1)-C(16)	1.447(8)
C(23)-N(4)	1.334(6)
C(23)-C(24)	1.399(8)
C(23)-C(32)	1.461(8)
N(4)-N(3)	1.378(6)
N(2)-C(1)	1.340(7)
N(2)-N(1)	1.363(6)
N(1)-C(3)	1.366(7)
N(1)-C(4)	1.415(7)
C(32)-C(37)	1.360(8)
C(32)-C(33)	1.399(8)
N(3)-C(25)	1.359(7)
N(3)-C(26)	1.440(7)
C(10)-C(15)	1.363(8)
C(10)-C(11)	1.386(8)
C(10)-C(1)	1.473(8)
C(13)-C(12)	1.384(8)
C(13)-C(14)	1.383(8)
C(1)-C(2)	1.406(8)
C(35)-C(34)	1.372(8)
C(35)-C(36)	1.384(8)
C(34)-C(33)	1.392(8)
C(36)-C(37)	1.383(8)
C(26)-C(27)	1.371(8)
C(26)-C(31)	1.386(8)
C(25)-C(24)	1.363(7)
C(25)-C(39)	1.473(8)
C(3)-C(2)	1.357(8)
C(3)-C(17)	1.464(8)
C(15)-C(14)	1.371(8)
C(17)-C(22)	1.386(9)
C(17)-C(18)	1.419(9)
C(4)-C(9)	1.383(9)
C(4)-C(5)	1.392(9)
C(18)-C(19)	1.378(9)

C(39)-C(40)	1.377(8)
C(39)-C(44)	1.396(9)
C(9)-C(8)	1.373(9)
C(12)-C(11)	1.371(8)
C(31)-C(30)	1.391(8)
C(27)-C(28)	1.388(9)
C(22)-C(21)	1.404(9)
C(29)-C(30)	1.334(10)
C(29)-C(28)	1.402(10)
C(19)-C(20)	1.366(10)
C(40)-C(41)	1.397(10)
C(8)-C(7)	1.396(11)
C(5)-C(6)	1.369(9)
C(44)-C(43)	1.387(9)
C(41)-C(42)	1.378(12)
C(20)-C(21)	1.374(11)
C(6)-C(7)	1.374(11)
C(43)-C(42)	1.348(11)
C(35)-O(2)-C(38)	118.5(5)
C(13)-O(1)-C(16)	117.3(5)
N(4)-C(23)-C(24)	110.4(5)
N(4)-C(23)-C(32)	122.3(5)
C(24)-C(23)-C(32)	127.3(5)
C(23)-N(4)-N(3)	104.8(4)
C(1)-N(2)-N(1)	105.5(4)
N(2)-N(1)-C(3)	111.8(4)
N(2)-N(1)-C(4)	118.2(4)
C(3)-N(1)-C(4)	129.5(5)
C(37)-C(32)-C(33)	116.7(5)
C(37)-C(32)-C(23)	122.0(5)
C(33)-C(32)-C(23)	121.3(5)
C(25)-N(3)-N(4)	111.7(4)
C(25)-N(3)-C(26)	130.0(5)
N(4)-N(3)-C(26)	118.2(4)
C(15)-C(10)-C(11)	117.2(5)
C(15)-C(10)-C(1)	120.8(5)
C(11)-C(10)-C(1)	122.0(5)
O(1)-C(13)-C(12)	115.9(5)
O(1)-C(13)-C(14)	125.4(5)
C(12)-C(13)-C(14)	118.7(5)
N(2)-C(1)-C(2)	109.3(5)
N(2)-C(1)-C(10)	121.5(5)
C(2)-C(1)-C(10)	129.2(5)
C(34)-C(35)-O(2)	116.1(5)

C(34)-C(35)-C(36)	120.4(5)
O(2)-C(35)-C(36)	123.5(5)
C(35)-C(34)-C(33)	120.6(5)
C(37)-C(36)-C(35)	117.2(5)
C(27)-C(26)-C(31)	121.6(5)
C(27)-C(26)-N(3)	119.4(5)
C(31)-C(26)-N(3)	118.9(5)
C(32)-C(37)-C(36)	124.8(6)
N(3)-C(25)-C(24)	106.0(5)
N(3)-C(25)-C(39)	126.2(5)
C(24)-C(25)-C(39)	127.8(5)
C(34)-C(33)-C(32)	120.2(5)
C(2)-C(3)-N(1)	105.7(5)
C(2)-C(3)-C(17)	129.6(5)
N(1)-C(3)-C(17)	124.7(5)
C(10)-C(15)-C(14)	123.4(6)
C(22)-C(17)-C(18)	115.9(6)
C(22)-C(17)-C(3)	119.4(6)
C(18)-C(17)-C(3)	124.6(6)
C(9)-C(4)-C(5)	120.1(6)
C(9)-C(4)-N(1)	120.3(6)
C(5)-C(4)-N(1)	119.3(6)
C(19)-C(18)-C(17)	122.7(7)
C(19)-C(18)-Cl(1)	117.8(6)
C(17)-C(18)-Cl(1)	119.5(5)
C(15)-C(14)-C(13)	119.0(6)
C(40)-C(39)-C(44)	117.9(6)
C(40)-C(39)-C(25)	123.8(6)
C(44)-C(39)-C(25)	118.2(5)
C(8)-C(9)-C(4)	120.2(7)
C(25)-C(24)-C(23)	107.1(5)
C(3)-C(2)-C(1)	107.6(5)
C(11)-C(12)-C(13)	120.9(5)
C(26)-C(31)-C(30)	117.8(6)
C(12)-C(11)-C(10)	120.9(5)
C(26)-C(27)-C(28)	118.9(6)
C(17)-C(22)-C(21)	121.1(7)
C(30)-C(29)-C(28)	120.1(6)
C(29)-C(30)-C(31)	121.8(7)
C(20)-C(19)-C(18)	119.2(7)
C(27)-C(28)-C(29)	119.5(6)
C(39)-C(40)-C(41)	120.3(7)
C(39)-C(40)-Cl(2)	120.9(5)
C(41)-C(40)-Cl(2)	118.8(6)

C(9)-C(8)-C(7)	118.5(7)
C(6)-C(5)-C(4)	120.2(7)
C(43)-C(44)-C(39)	121.6(6)
C(42)-C(41)-C(40)	119.9(7)
C(19)-C(20)-C(21)	120.3(7)
C(20)-C(21)-C(22)	120.3(7)
C(5)-C(6)-C(7)	118.8(7)
C(6)-C(7)-C(8)	121.8(7)
C(42)-C(43)-C(44)	119.4(7)
C(43)-C(42)-C(41)	120.8(7)

Symmetry transformations used to generate equivalent atoms:

Table S3-4. Anisotropic displacement parameters (A^2 x 10^3) for **3f**.
The anisotropic displacement factor exponent takes the form:
-2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

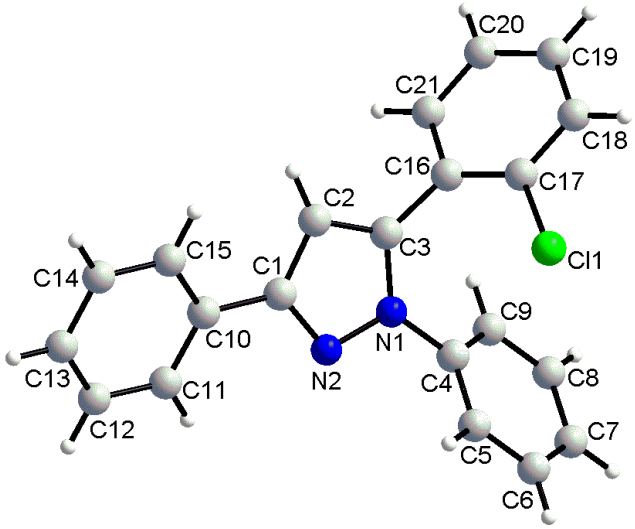
	U11	U22	U33	U23	U13	U12
Cl(1)	90(1)	80(1)	61(1)	14(1)	1(1)	-7(1)
Cl(2)	106(1)	100(2)	57(1)	17(1)	23(1)	-9(1)
O(2)	55(2)	61(3)	65(3)	-4(2)	3(2)	-1(2)
O(1)	52(2)	72(3)	64(3)	-6(2)	8(2)	-8(2)
C(23)	39(3)	37(3)	47(3)	7(3)	3(3)	-3(3)
N(4)	40(3)	41(3)	56(3)	7(2)	2(2)	-4(2)
N(2)	49(3)	45(3)	51(3)	10(2)	14(2)	4(2)
N(1)	37(2)	50(3)	53(3)	2(2)	9(2)	5(2)
C(32)	42(3)	49(4)	45(3)	12(3)	0(3)	-6(3)
N(3)	37(2)	38(3)	49(3)	2(2)	4(2)	0(2)
C(10)	38(3)	40(3)	55(3)	16(3)	9(3)	9(3)
C(13)	44(3)	50(4)	50(4)	8(3)	4(3)	11(3)
C(1)	43(3)	46(4)	51(3)	16(3)	11(3)	11(3)
C(35)	55(3)	50(4)	39(3)	3(3)	12(3)	-14(3)
C(34)	35(3)	46(4)	62(4)	16(3)	6(3)	7(3)
C(36)	41(3)	52(4)	48(4)	-5(3)	-4(3)	4(3)
C(26)	35(3)	48(4)	50(4)	-2(3)	4(3)	4(3)
C(37)	53(4)	58(4)	61(4)	7(3)	1(3)	15(3)
C(25)	40(3)	52(4)	50(3)	9(3)	5(3)	6(3)
C(33)	38(3)	56(4)	51(4)	10(3)	9(3)	12(3)
C(3)	39(3)	50(4)	56(4)	18(3)	10(3)	10(3)
C(15)	60(4)	46(4)	71(4)	12(3)	29(3)	0(3)
C(17)	32(3)	48(4)	64(4)	6(3)	6(3)	5(3)
C(4)	41(3)	59(4)	54(4)	10(3)	9(3)	10(3)
C(18)	39(3)	49(4)	89(5)	-1(3)	9(3)	1(3)
C(14)	61(4)	53(4)	70(4)	1(3)	34(3)	8(3)
C(39)	31(3)	49(4)	56(4)	0(3)	13(3)	-1(3)
C(9)	50(4)	58(4)	65(4)	4(3)	5(3)	12(3)
C(24)	47(3)	42(3)	49(4)	1(3)	5(3)	-7(3)
C(2)	40(3)	47(4)	64(4)	8(3)	15(3)	2(3)
C(12)	45(3)	51(4)	59(4)	2(3)	6(3)	-19(3)
C(31)	53(4)	45(4)	56(4)	4(3)	5(3)	7(3)
C(11)	33(3)	68(4)	53(4)	13(3)	11(3)	13(3)
C(27)	53(4)	58(4)	74(4)	11(3)	-6(4)	13(3)
C(16)	75(4)	58(4)	74(4)	1(3)	26(4)	24(4)

C(22)	47(4)	62(4)	86(5)	21(4)	8(3)	9(3)
C(29)	48(4)	87(6)	74(5)	-7(4)	-10(4)	-13(4)
C(30)	60(4)	53(4)	73(5)	-10(4)	2(4)	-12(4)
C(38)	68(4)	65(5)	67(4)	-8(4)	6(4)	-18(4)
C(19)	49(4)	61(5)	89(5)	8(4)	0(4)	0(4)
C(28)	66(4)	80(5)	59(4)	12(4)	-13(4)	-2(4)
C(40)	61(4)	67(4)	64(4)	4(3)	23(3)	-10(4)
C(8)	67(4)	77(5)	75(5)	-6(4)	0(4)	40(4)
C(5)	62(4)	64(5)	74(4)	12(4)	18(4)	3(4)
C(44)	50(3)	68(4)	75(4)	22(3)	27(3)	11(3)
C(41)	95(5)	90(6)	80(5)	-18(4)	40(4)	-11(5)
C(20)	50(4)	54(5)	123(6)	-2(4)	5(4)	-5(4)
C(21)	58(4)	56(4)	141(7)	33(4)	35(4)	14(4)
C(6)	64(4)	110(6)	88(5)	-2(5)	46(4)	0(5)
C(7)	46(4)	139(7)	62(5)	-11(5)	9(3)	41(5)
C(43)	57(4)	60(5)	116(6)	23(4)	32(4)	21(4)
C(42)	80(5)	62(5)	141(8)	-10(5)	42(5)	20(4)

Table S3-5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for **3f**.

	x	y	z	U(eq)
H(34)	1603	4778	4670	57
H(36)	5308	3845	5907	60
H(37)	5211	2239	4869	71
H(33)	1495	3113	3668	58
H(15)	-440	7072	4745	68
H(14)	-123	8640	5808	72
H(9)	1726	2940	2167	71
H(24)	5416	822	3723	57
H(2)	-1150	5690	3489	60
H(12)	3155	9693	4824	63
H(31)	2075	-2096	2213	63
H(11)	2773	8131	3752	61
H(27)	570	756	1464	76
H(16A)	50	10403	6452	103
H(16B)	1291	11214	7045	103
H(16C)	1245	9892	7068	103
H(22)	-1099	3204	3216	77
H(29)	-1213	-2322	308	90
H(30)	359	-3163	1175	79
H(38A)	4523	5134	7014	105
H(38B)	4344	6447	6984	105
H(38C)	5400	5718	6446	105
H(19)	-2345	2424	298	82
H(28)	-1200	-337	472	85
H(8)	3271	1954	1345	93
H(5)	2981	5872	1594	80
H(44)	5241	-1674	3498	74
H(41)	5904	-2380	723	108
H(20)	-3106	1205	1086	95
H(21)	-2575	1628	2538	97
H(6)	4438	4884	720	104
H(7)	4776	2978	733	103
H(43)	6615	-3176	3009	90
H(42)	6985	-3489	1642	114

S4 Crystal data and structure refinement for **3g**.



CCDC1457746

Table S4-1. Crystal data and structure refinement for **3g**.

Identification code	**3g**
Empirical formula	$C_{21}H_{15}ClN_2$
Formula weight	330.80
Temperature	296 K
Wavelength	0.71073 A
Crystal system, space group	Tetragonal, I4(1)/a
Unit cell dimensions	a = 20.6551(5) A alpha = 90 deg.
	b = 20.6551(5) A beta = 90 deg.
	c = 15.9903(8) A gamma = 90 deg.
Volume	6822.0(4) A^3
Z, Calculated density	16, 1.288 Mg/m^3
Absorption coefficient	0.227 mm^-1
F(000)	2752
Crystal size	0.35 x 0.33 x 0.3 mm
Theta range for data collection	1.61 to 25.00 deg.
Limiting indices	-21<=h<=24,-21<=k<=24,-19<=l<=18
Reflections collected / unique	14912 / 3004 [R(int) = 0.0211]
Completeness to theta = 25.00	99.3 %
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2984 / 0 / 217
Goodness-of-fit on F^2	1.073
Final R indices [I>2sigma(I)]	R1 = 0.0383, wR2 = 0.1039
R indices (all data)	R1 = 0.0477, wR2 = 0.1139
Largest diff. peak and hole	0.158 and -0.245 e.A^-3

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for **3g**.
U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
Cl(1)	9598(1)	6691(1)	311(1)	60(1)
N(1)	8579(1)	6113(1)	1708(1)	40(1)
N(2)	8658(1)	5925(1)	2520(1)	43(1)
C(4)	8582(1)	5633(1)	1067(1)	42(1)
C(16)	8430(1)	7135(1)	853(1)	39(1)
C(1)	8626(1)	6468(1)	2962(1)	41(1)
C(3)	8502(1)	6766(1)	1640(1)	39(1)
C(10)	8709(1)	6465(1)	3880(1)	43(1)
C(17)	8898(1)	7152(1)	226(1)	41(1)
C(9)	8134(1)	5662(1)	429(1)	52(1)
C(18)	8831(1)	7545(1)	-467(1)	53(1)
C(11)	8614(1)	5908(1)	4352(1)	51(1)
C(21)	7895(1)	7532(1)	753(1)	50(1)
C(2)	8525(1)	7003(1)	2440(1)	46(1)
C(12)	8709(1)	5923(1)	5215(1)	58(1)
C(13)	8899(1)	6480(1)	5604(1)	59(1)
C(15)	8895(1)	7025(1)	4290(1)	56(1)
C(5)	9031(1)	5144(1)	1107(1)	64(1)
C(20)	7829(1)	7931(1)	65(1)	59(1)
C(14)	8991(1)	7033(1)	5146(1)	62(1)
C(19)	8297(1)	7936(1)	-545(1)	60(1)
C(8)	8147(2)	5195(1)	-185(2)	81(1)
C(6)	9030(2)	4678(1)	490(2)	95(1)
C(7)	8592(2)	4710(1)	-154(2)	107(1)

Table S4-3. Bond lengths [A] and angles [deg] for **3g**.

Cl(1)-C(17)	1.7361(18)
N(1)-C(3)	1.364(2)
N(1)-N(2)	1.3651(18)
N(1)-C(4)	1.426(2)
N(2)-C(1)	1.327(2)
C(4)-C(5)	1.373(3)
C(4)-C(9)	1.379(2)
C(16)-C(21)	1.387(2)
C(16)-C(17)	1.392(2)
C(16)-C(3)	1.478(2)
C(1)-C(2)	1.402(2)
C(1)-C(10)	1.477(2)
C(3)-C(2)	1.370(2)
C(10)-C(15)	1.384(3)
C(10)-C(11)	1.389(3)
C(17)-C(18)	1.381(2)
C(9)-C(8)	1.376(3)
C(18)-C(19)	1.372(3)
C(11)-C(12)	1.393(3)
C(21)-C(20)	1.381(3)
C(12)-C(13)	1.365(3)
C(13)-C(14)	1.370(3)
C(15)-C(14)	1.384(3)
C(5)-C(6)	1.377(3)
C(20)-C(19)	1.373(3)
C(8)-C(7)	1.361(4)
C(6)-C(7)	1.372(4)
C(3)-N(1)-N(2)	111.74(13)
C(3)-N(1)-C(4)	129.23(13)
N(2)-N(1)-C(4)	119.04(13)
C(1)-N(2)-N(1)	105.17(13)
C(5)-C(4)-C(9)	121.32(17)
C(5)-C(4)-N(1)	118.74(16)
C(9)-C(4)-N(1)	119.93(15)
C(21)-C(16)-C(17)	117.12(15)
C(21)-C(16)-C(3)	118.85(15)
C(17)-C(16)-C(3)	123.79(15)
N(2)-C(1)-C(2)	110.84(15)
N(2)-C(1)-C(10)	121.36(15)

C(2)-C(1)-C(10)	127.77(15)
N(1)-C(3)-C(2)	106.02(14)
N(1)-C(3)-C(16)	126.05(14)
C(2)-C(3)-C(16)	127.91(15)
C(15)-C(10)-C(11)	118.30(16)
C(15)-C(10)-C(1)	119.89(16)
C(11)-C(10)-C(1)	121.80(16)
C(18)-C(17)-C(16)	121.54(17)
C(18)-C(17)-Cl(1)	117.94(14)
C(16)-C(17)-Cl(1)	120.50(13)
C(8)-C(9)-C(4)	118.97(19)
C(19)-C(18)-C(17)	119.92(18)
C(10)-C(11)-C(12)	119.99(19)
C(20)-C(21)-C(16)	121.53(18)
C(3)-C(2)-C(1)	106.22(15)
C(13)-C(12)-C(11)	120.70(19)
C(12)-C(13)-C(14)	119.86(18)
C(14)-C(15)-C(10)	121.15(19)
C(4)-C(5)-C(6)	118.6(2)
C(19)-C(20)-C(21)	120.02(19)
C(13)-C(14)-C(15)	120.0(2)
C(18)-C(19)-C(20)	119.86(17)
C(7)-C(8)-C(9)	120.2(2)
C(7)-C(6)-C(5)	120.4(2)
C(8)-C(7)-C(6)	120.5(2)

Symmetry transformations used to generate equivalent atoms:

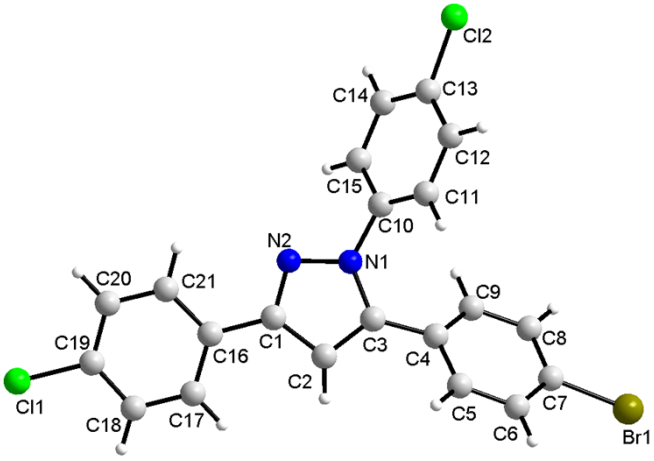
Table S4-4. Anisotropic displacement parameters (A^2 x 10^3) for **3g**.
The anisotropic displacement factor exponent takes the form:
-2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
Cl(1)	49(1)	77(1)	55(1)	12(1)	11(1)	11(1)
N(1)	53(1)	37(1)	29(1)	1(1)	2(1)	3(1)
N(2)	58(1)	41(1)	30(1)	3(1)	1(1)	2(1)
C(4)	54(1)	38(1)	34(1)	-1(1)	3(1)	2(1)
C(16)	48(1)	36(1)	32(1)	-1(1)	0(1)	-1(1)
C(1)	49(1)	42(1)	32(1)	0(1)	6(1)	1(1)
C(3)	46(1)	39(1)	33(1)	2(1)	4(1)	3(1)
C(10)	50(1)	49(1)	31(1)	1(1)	6(1)	4(1)
C(17)	46(1)	43(1)	36(1)	0(1)	-1(1)	-3(1)
C(9)	59(1)	48(1)	47(1)	-1(1)	-8(1)	-1(1)
C(18)	61(1)	59(1)	37(1)	10(1)	2(1)	-9(1)
C(11)	62(1)	54(1)	38(1)	3(1)	5(1)	1(1)
C(21)	54(1)	49(1)	47(1)	2(1)	3(1)	8(1)
C(2)	64(1)	38(1)	35(1)	-1(1)	7(1)	5(1)
C(12)	63(1)	71(1)	40(1)	16(1)	8(1)	5(1)
C(13)	56(1)	91(2)	32(1)	-3(1)	3(1)	7(1)
C(15)	74(1)	53(1)	40(1)	-2(1)	5(1)	-2(1)
C(5)	87(2)	57(1)	48(1)	-7(1)	-9(1)	26(1)
C(20)	65(1)	53(1)	60(1)	8(1)	-10(1)	11(1)
C(14)	75(1)	70(1)	41(1)	-12(1)	2(1)	-2(1)
C(19)	75(1)	57(1)	47(1)	18(1)	-12(1)	-3(1)
C(8)	119(2)	64(1)	59(1)	-15(1)	-34(1)	3(1)
C(6)	148(3)	68(2)	69(2)	-22(1)	-17(2)	53(2)
C(7)	187(3)	72(2)	63(2)	-33(1)	-32(2)	39(2)

Table S4-5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for **3g**.

	x	y	z	U(eq)
H(9)	7821	5999	413	62
H(18)	9154	7545	-890	63
H(11)	8483	5518	4087	61
H(21)	7565	7530	1168	60
H(2)	8480	7442	2607	55
H(12)	8642	5541	5535	70
H(13)	8966	6484	6192	71
H(15)	8958	7411	3977	67
H(5)	9337	5127	1550	76
H(20)	7459	8202	13	71
H(14)	9121	7421	5416	74
H(19)	8251	8209	-1019	72
H(8)	7845	5211	-632	97
H(6)	9334	4333	511	114
H(7)	8600	4391	-581	129

S5 Crystal data and structure refinement for **3o**.



CCDC 1473251

Table S5-1. Crystal data and structure refinement for **3o**.

Identification code	**3o**
Empirical formula	$C_{21}H_{13}BrCl_2N_2$
Formula weight	444.13
Temperature	296 K
Wavelength	0.71073 A
Crystal system, space group	Orthorhombic, Pca2(1)
Unit cell dimensions	a = 9.1743(6) A alpha = 90 deg.
	b = 12.4421(9) A beta = 90 deg.
	c = 16.5980(12) A gamma = 90 deg.
Volume	1894.6(2) A^3
Z, Calculated density	4, 1.557 Mg/m^3
Absorption coefficient	2.459 mm^-1
F(000)	888
Crystal size	0.35 x 0.33 x 0.3 mm
Theta range for data collection	1.64 to 25.00 deg.
Limiting indices	-10<=h<=10, -13<=k<=14, -17<=l<=19
Reflections collected / unique	14820 / 3117 [R(int) = 0.0376]
Completeness to theta = 25.00	99.9 %
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3117 / 1 / 235
Goodness-of-fit on F^2	1.042
Final R indices [I>2sigma(I)]	R1 = 0.0665, wR2 = 0.1928
R indices (all data)	R1 = 0.0833, wR2 = 0.2118
Absolute structure parameter	0.95(2)
Largest diff. peak and hole	0.419 and -0.422 e.A^-3

Table S5-2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for **3o**.
U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
Br(1)	3175(1)	7786(1)	11731(1)	76(1)
C(2)	8117(7)	10538(6)	9278(5)	44(2)
N(1)	9055(7)	8919(5)	9134(4)	45(1)
C(1)	9235(8)	10528(6)	8693(5)	46(2)
C(10)	9624(8)	7866(6)	9274(5)	45(2)
C(4)	6966(8)	9026(7)	10104(5)	47(2)
N(2)	9795(7)	9556(5)	8600(4)	47(2)
C(8)	5281(10)	7628(7)	10485(5)	52(2)
C(16)	9813(8)	11452(6)	8237(5)	42(2)
C(6)	5311(11)	9284(9)	11220(6)	64(2)
C(7)	4753(9)	8278(8)	11091(5)	53(2)
C(17)	9184(11)	12459(7)	8293(6)	55(2)
C(11)	9949(11)	7546(7)	10038(6)	59(2)
C(9)	6391(9)	8017(6)	9999(5)	49(2)
C(3)	8033(7)	9496(6)	9551(5)	42(2)
C(5)	6421(9)	9655(7)	10731(5)	55(2)
C(15)	9956(10)	7235(6)	8616(6)	56(2)
C(13)	11009(10)	5950(7)	9501(7)	62(2)
C(14)	10662(10)	6265(7)	8732(7)	63(2)
C(20)	11628(11)	12189(8)	7348(7)	66(3)
C(21)	11053(10)	11340(7)	7755(5)	54(2)
C(18)	9766(12)	13329(8)	7878(6)	67(3)
Cl(1)	11736(4)	14281(3)	6910(2)	104(1)
Cl(2)	12019(4)	4774(2)	9636(3)	111(1)
C(19)	10989(12)	13180(8)	7419(6)	66(3)
C(12)	10654(10)	6572(8)	10157(7)	67(3)

Table S5-3. Bond lengths [A] and angles [deg] for **3o**.

Br(1)-C(7)	1.897(8)
C(2)-C(3)	1.375(12)
C(2)-C(1)	1.413(11)
N(1)-C(3)	1.369(10)
N(1)-N(2)	1.369(9)
N(1)-C(10)	1.429(10)
C(1)-N(2)	1.323(11)
C(1)-C(16)	1.475(12)
C(10)-C(11)	1.362(13)
C(10)-C(15)	1.379(12)
C(4)-C(9)	1.374(12)
C(4)-C(5)	1.395(12)
C(4)-C(3)	1.463(11)
C(8)-C(7)	1.377(13)
C(8)-C(9)	1.386(13)
C(16)-C(17)	1.383(12)
C(16)-C(21)	1.398(12)
C(6)-C(7)	1.370(14)
C(6)-C(5)	1.382(13)
C(17)-C(18)	1.390(15)
C(11)-C(12)	1.388(13)
C(15)-C(14)	1.383(13)
C(13)-C(14)	1.373(15)
C(13)-C(12)	1.375(15)
C(13)-Cl(2)	1.746(9)
C(20)-C(21)	1.360(14)
C(20)-C(19)	1.371(15)
C(18)-C(19)	1.369(15)
Cl(1)-C(19)	1.749(10)
C(3)-C(2)-C(1)	105.0(7)
C(3)-N(1)-N(2)	111.3(6)
C(3)-N(1)-C(10)	130.4(7)
N(2)-N(1)-C(10)	117.0(6)
N(2)-C(1)-C(2)	111.7(7)
N(2)-C(1)-C(16)	120.9(7)
C(2)-C(1)-C(16)	127.4(7)
C(11)-C(10)-C(15)	121.5(7)
C(11)-C(10)-N(1)	120.0(7)
C(15)-C(10)-N(1)	118.3(7)

C(9)-C(4)-C(5)	118.0(8)
C(9)-C(4)-C(3)	122.9(8)
C(5)-C(4)-C(3)	118.9(7)
C(1)-N(2)-N(1)	105.1(6)
C(7)-C(8)-C(9)	118.6(8)
C(17)-C(16)-C(21)	118.0(8)
C(17)-C(16)-C(1)	121.4(8)
C(21)-C(16)-C(1)	120.6(7)
C(7)-C(6)-C(5)	119.3(8)
C(6)-C(7)-C(8)	121.3(8)
C(6)-C(7)-Br(1)	119.5(7)
C(8)-C(7)-Br(1)	119.2(7)
C(16)-C(17)-C(18)	120.8(10)
C(10)-C(11)-C(12)	119.4(9)
C(4)-C(9)-C(8)	121.9(8)
N(1)-C(3)-C(2)	106.8(7)
N(1)-C(3)-C(4)	124.5(7)
C(2)-C(3)-C(4)	128.3(7)
C(6)-C(5)-C(4)	121.0(8)
C(10)-C(15)-C(14)	119.4(9)
C(14)-C(13)-C(12)	121.4(8)
C(14)-C(13)-Cl(2)	118.8(8)
C(12)-C(13)-Cl(2)	119.7(8)
C(13)-C(14)-C(15)	119.1(9)
C(21)-C(20)-C(19)	119.4(10)
C(20)-C(21)-C(16)	121.5(8)
C(19)-C(18)-C(17)	119.1(9)
C(18)-C(19)-C(20)	121.3(9)
C(18)-C(19)-Cl(1)	118.9(8)
C(20)-C(19)-Cl(1)	119.7(8)
C(13)-C(12)-C(11)	119.3(10)

Symmetry transformations used to generate equivalent atoms:

Table S5-4. Anisotropic displacement parameters (A^2 x 10^3) for **3o**.
The anisotropic displacement factor exponent takes the form:
-2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
Br(1)	56(1)	114(1)	58(1)	25(1)	6(1)	-2(1)
C(2)	32(3)	43(4)	57(5)	-8(4)	-3(3)	-4(3)
N(1)	38(3)	45(3)	51(4)	2(3)	4(3)	2(3)
C(1)	39(4)	45(4)	53(4)	-6(4)	-14(3)	1(3)
C(10)	38(4)	45(4)	51(5)	1(3)	0(4)	3(3)
C(4)	36(4)	56(5)	48(4)	-4(4)	-2(3)	5(3)
N(2)	38(3)	48(4)	55(4)	3(3)	-1(3)	1(3)
C(8)	53(5)	51(4)	52(5)	7(4)	-1(4)	-7(4)
C(16)	38(4)	42(4)	46(4)	1(3)	-9(3)	-3(3)
C(6)	55(5)	81(7)	55(6)	-15(5)	7(4)	6(5)
C(7)	43(4)	74(6)	42(4)	13(4)	-3(3)	1(4)
C(17)	56(5)	49(5)	60(6)	1(4)	-4(4)	1(4)
C(11)	59(5)	60(5)	57(5)	-7(4)	-7(5)	5(4)
C(9)	49(4)	46(4)	50(5)	-3(4)	-2(4)	5(4)
C(3)	30(3)	40(4)	56(5)	-3(4)	-3(3)	3(3)
C(5)	47(4)	59(5)	61(5)	-18(4)	5(4)	1(4)
C(15)	53(5)	52(5)	63(6)	3(4)	11(4)	1(4)
C(13)	49(5)	44(4)	93(7)	9(5)	7(5)	2(4)
C(14)	60(5)	42(5)	88(7)	-10(5)	18(5)	-6(4)
C(20)	65(6)	77(7)	57(6)	-7(5)	10(5)	-17(5)
C(21)	52(5)	55(5)	55(5)	-4(4)	-6(4)	-3(4)
C(18)	80(7)	50(5)	72(7)	6(5)	-11(6)	-2(5)
Cl(1)	142(3)	76(2)	93(3)	12(2)	18(2)	-35(2)
Cl(2)	108(2)	55(1)	169(4)	22(2)	7(2)	29(2)
C(19)	88(7)	60(6)	50(5)	0(4)	-8(5)	-20(5)
C(12)	58(5)	62(6)	81(7)	22(5)	-8(5)	5(5)

Table S5-5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for **3o**.

	x	y	z	U(eq)
H(2)	7547	11134	9446	53
H(8)	4892	6929	10402	63
H(6)	4938	9723	11640	77
H(17)	8344	12558	8619	66
H(11)	9694	7985	10485	70
H(9)	6765	7572	9582	58
H(5)	6819	10349	10823	67
H(15)	9701	7464	8089	67
H(14)	10904	5822	8285	76
H(20)	12465	12095	7018	79
H(21)	11505	10655	7710	65
H(18)	9322	14017	7912	80
H(12)	10889	6338	10686	81