Supporting Information

Ruthenium-Catalyzed C-H/CO/Olefin Coupling Reaction of *N*-Arylpyrazoles. Extraordinary Reactivity of *N*-Arylpyrazoles toward Carbonylation at C-H Bonds

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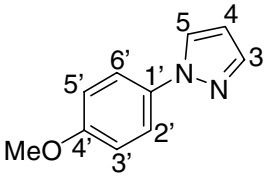
Materials. *N,N*-dimethylacetamide (DMA) was distilled over BaO. Toluene, and 1,3-dimethyl-2-imidazolidinone (DMI) were distilled over CaH_2. $Ru_3(CO)_{12}$ was prepared from $RuCl_3 \cdot nH_2O$ and carbon monoxide according to the literature procedure[1], and used after recrystallization from hexane. 1-Phenyl-1*H*-pyrazole (**1a**) was commercially available, and used after distillation over CaH_2. Substituted 1-arylpyrazoles were obtained from the corresponding substituted phenylboronic acids or phenylbromides and pyrazoles according to the literature procedure.[2,3] 1-Methyl-3-phenyl-1*H*-pyrazole

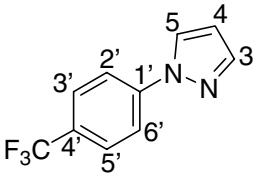
(**3**) was prepared from 3-phenyl-1*H*-pyrazole[4], with modifying the literature procedure.[5]

1-(4-Methoxyphenyl)-1*H*-pyrazole (1c). Colorless oil; bp 120 °C (1 mmHg); *Rf* 0.46 (hexane/EtOAc = 2/1); ^{1}H NMR ($CDCl_3$) δ 3.81 (s, 3H), 6.41 (dd, *J* = 2.3, 1.6 Hz, 1H), 6.94 (dt, *J* = 9.9 Hz, 3.0 Hz, 2H), 7.57 (dt, *J* = 9.9 Hz, 3.0 Hz, 2H), 7.68 (d, *J* = 1.6 Hz, 1H), 7.80 (dd, *J* = 2.3, 0.66 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 55.5, 107.0, 114.4, 120.7, 126.6, 133.8, 140.4, 158.0; IR (neat) 3472 w, 3132 w, 3008 w, 2956 w, 2840 w, 2048 w, 1882 w, 1598 w, 1528 s, 1489 m, 1400 m, 1302 m, 1248 s, 1174 m, 1122 w, 1040 m, 940 m, 916 m, 884 w, 832 m, 800 w; MS, *m*/*z* (relative intensity, %) 175 (M^++1, 16), 174 (M^+, 100), 159 (71), 132 (11), 131 (23), 77 (12); Anal. Calcd for $C_{10}H_{10}N_2O$: C, 68.95. H, 5.79; N, 16.08; Found: C, 68.82; H, 5.71; N, 15.97.



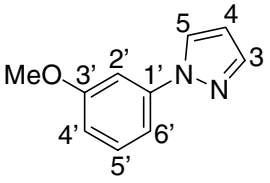
1c

1-(4-Trifluoromethyl)-1*H*-pyrazole (1d). Colorless solid; mp 92-94 °C; *Rf* 0.40 (hexane/EtOAc = 2/1); ^{1}H NMR ($CDCl_3$) δ 6.51 (dd, *J* = 2.3, 1.6 Hz, 1H), 7.71 (d, *J* = 8.7 Hz, 2H), 7.76 (d, *J* = 1.6 Hz, 1H), 7.82 (d, *J* = 8.7 Hz, 2H), 7.98 (d, *J* = 2.3 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 108.3, 118.6, 123.7 (q, *J* = 271.3 Hz), 126.5, 126.6, 128.1 (q, *J* = 33.0 Hz), 141.7, 142.3; IR (KBr) 3880 w, 3700 w, 3608 w, 3144 m, 3096 m, 2644 w, 2444 w, 2304 w, 1942 w, 1922 w, 1900 w, 1818 w, 1780 w, 1734 w, 1694 w, 1668 w, 1622 s, 1602 s, 1538 s, 1444 s, 1416 s, 1396 s, 1332 s, 1254 s, 1126 s, 1070 s, 1028 s, 1012 s, 938 s, 914 m, 890 m, 852 s, 824 s; MS, *m*/*z* (relative intensity, %) 213 (M^++1, 11), 212 (M^+, 100), 185 (22), 158 (14), 145 (32); Anal. Calcd for $C_{10}H_7F_3N_2$: C, 56.61; H, 3.33; N, 13.20. Found: C, 56.34; H, 3.30; N, 13.10.



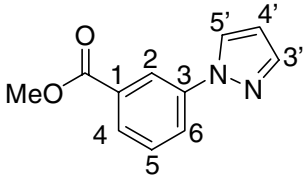
1d

1-(3-Methoxyphenyl)-1*H*-pyrazole (1e). Colorless oil; bp 125 °C (1 mmHg); *Rf* 0.40 (hexane/EtOAc = 2/1); ^{1}H NMR ($CDCl_3$) δ 3.80 (s, 3H), 6.39 (dd, *J* = 2.3, 2.0 Hz, 1H), 6.76 (ddd, *J* = 8.2, 2.3, 0.99 Hz, 1H), 7.14-7.19 (m, 1H), 7.24-7.30 (c, 2H), 7.65 (dd, *J* = 2.3, 0.66 Hz, 1H), 7.84 (dd, *J* = 2.0, 0.66 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 55.5, 105.0, 107.5, 110.1, 112.3, 126.8, 130.0, 140.9, 141.2, 160.4; IR (neat) 3476 w, 3128 m, 3008 m, 2944 m, 2840 m, 2648 w, 2448 w, 2324 w, 2172 w, 2072 w, 1934 w, 1714 w, 1612 s, 1522 s, 1502 s, 1444 s, 1396 s, 1338 s, 1314 m, 1296 s, 1268 s, 1228 s, 1198 s, 1166 s, 1080 m, 1046 s, 996 w, 950 s, 916 m, 846 s; MS, *m*/*z* (relative intensity, %) 174 (M^+, 100), 173 (54), 145 (14), 144 (28), 77 (13); Anal. Calcd for $C_{10}H_{10}N_2O$: C, 68.95; H, 5.79; N, 16.08. Found: C, 69.00; H, 5.91; N, 16.07.



1e

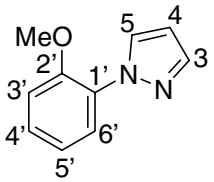
3-(1*H*-Pyrazolyl)benzoic acid methyl ester (1f). Colorless solid; mp 54-56 °C; *Rf* 0.34 (hexane/EtOAc = 2/1); ^{1}H NMR ($CDCl_3$) δ 3.91 (s, 3H), 6.45 (dd, *J* = 2.3, 1.6 Hz, 1H), 7.47 (td, *J* = 7.9, 2.0 Hz, 1H), 7.72 (d, *J* = 1.6 Hz, 1H), 7.78-7.93 (c, 2H), 7.97 (d, *J* = 2.3 Hz, 1H), 8.30 (dd, *J* = 2.0, 1.6 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 52.1, 107.8, 119.4, 123.0, 126.5, 127.0, 129.3, 131.2, 140.0, 141.2, 166.0; IR (KBr) 3592 w, 3404 w, 3312 w, 3076 m, 2956 w, 1962 w, 1896 w, 1710 s, 1612 m, 1590 s, 1498 m, 1450 s, 1418 m, 1392 s, 1262 s, 1196 m, 1158 m, 1108 s, 1078 m, 1038 m, 970 m, 932 m, 908 m, 836 w; MS, *m*/*z* (relative intensity, %) 203 (M^++1, 16), 202 (M^+, 100), 172 (10), 171 (79), 144 (28), 143



1f

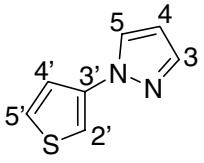
(43), 116 (15); Anal. Calcd for $C_{11}H_{10}N_2O_2$: C, 65.43; H, 5.16; N, 13.83. Found: C, 65.43; H, 5.16; N, 13.83.

1-(2-Methoxyphenyl)-1*H*-pyrazole (1g). Colorless oil; bp 130 °C (1 mmHg); *Rf* 0.60 (hexane/EtOAc = 1/1); ^{1}H NMR ($CDCl_3$) δ 3.86 (s, 3H), 6.44 (dd, *J* = 2.3, 1.7 Hz, 1H), 6.82 (dd, *J* = 8.2 Hz, 1.3 Hz, 1H), 7.23 (dd, *J* = 8.9, 4.9 Hz, 1H), 7.30-7.33 (c, 2H), 7.71 (d, *J* = 1.7 Hz, 1H), 7.90 (d, *J* = 2.3 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 55.5, 105.0, 107.5, 111.1, 112.3, 126.8, 130.0, 140.1, 141.2, 160.4; IR (neat) 3964 w, 3752 w, 3640 w, 3396 w, 3064 w, 3012 w, 2944 w, 2844 w, 2562 w, 2260 w, 2036 w, 1726 m, 1604 s, 1526 s, 1502 s, 1472 s, 1420 m, 1400 s, 1332 m, 1308 m, 1284 s, 1243 s, 1182 s, 1162 m, 1076 s, 1048 s, 1022 m, 938 s, 916 m, 882 m; MS, *m*/*z* (relative intensity, %) 175 (M^++1, 16), 174 (M^+, 100), 173 (55), 145 (17), 144 (32), 143 (10), 77 (16); Anal. Calcd for $C_{10}H_{10}N_2O$: C, 68.95; H, 5.79; N, 16.08. Found: C, 68.87; H, 5.77; N, 16.09.



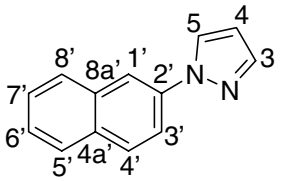
1g

1-(3-Thiophenyl)-1*H*-pyrazole (1h). Colorless oil; bp 90 °C (1 mmHg); *Rf* 0.49 (hexane/EtOAc = 2/1); ^{1}H NMR ($CDCl_3$) δ 6.37-6.38 (m, 1H), 7.31-7.37 (c, 3H), 7.64-7.65 (m, 1H), 7.76 (d, *J* = 2.6 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 106.8, 110.3, 120.1, 126.2, 127.2, 139.6, 140.3; IR (neat) 3720 w, 3432 w, 3112 s, 2716 w, 2560 w, 2440 w, 2296 w, 2152 w, 2080 w, 1922 w, 1832 w, 1760 m, 1722 w, 1668 w, 1618 m, 1568 s, 1522 s, 1468 s, 1442 s, 1404 s, 1310 m, 1274 m, 1252 m, 1182 s, 1114 s, 1086 m, 1038 s, 956 s, 916 s, 884 s, 856 s; MS, *m*/*z* (relative intensity, %) 151 (M^++1, 13), 150 (M^+, 100), 149 (25), 96 (17), 39 (13); Anal. Calcd for $C_7H_6N_2S$: C, 55.97; H, 4.03; N, 18.65; S, 21.35. Found: C, 55.95; H, 4.01; N, 18.82; S, 21.10.



1h

1-(2-Naphthalenyl)-1*H*-pyrazole (1i). Colorless solid; mp 88-90 °C; *Rf* 0.49 (hexane/EtOAc = 2/1); ^{1}H NMR ($CDCl_3$) δ 6.47-6.52 (m, 1H), 7.44-7.54 (td, *J* = 6.6, 1.3 Hz, 2H), 7.76-7.80 (m, 1H), 7.84-7.94 (c, 4H), 8.05 (d, *J* = 2.3 Hz, 1H), 8.10 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 107.7, 116.3, 118.5, 125.8, 126.9, 127.7, 127.8, 129.4, 131.7, 133.5, 137.5, 141.1; IR (KBr) 3824 w, 3140 w, 3052 w, 2656 w, 2440 w, 1920 w, 1854 w, 1820 w, 1774 w, 1728 w, 1688 w, 1632 m, 1602 m, 1522 s, 1482 m, 1420 w, 1396 s, 1370 w, 1320 m, 1266 w, 1200 w, 1188 w, 1146 m, 1134 m, 1030 m, 1016 m, 958 w, 928 w, 860 s; MS, *m*/*z* (relative intensity, %) 194 (M^+, 100), 193 (18), 167 (15), 166 (10), 140 (10), 127 (20); Anal. Calcd for $C_{13}H_{10}N_2$: C, 80.39; H, 5.19; N, 14.42. Found: C, 80.44; H, 5.33; N, 14.47.

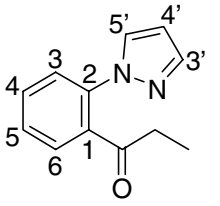


1i

General Procedure for Ru-Catalyzed Carbonylation Reactions. In a 50-mL stainless autoclave were placed $Ru_3(CO)_{12}$ (32 mg, 0.05 mmol) , 1-phenylpyrazole (288 mg, 2 mmol), and DMA (6 mL). After the system was flushed with 10 atm of ethylene three times, it was pressurized with ethylene to 7 atm and then with carbon monoxide to an additional 20 atm. The autoclave was then immersed in an oil bath at 160 °C. After 20 hours had elapsed, it was removed from the oil bath, allowed to cool for ca. 1 h and the gases were then released. The contents were transferred to a separatory funnel with EtOAc. EtOAc (50 mL) and water (50 mL) were added, and the organic layer was separated, washed with water (50 mL×2) and saturated brine (50 mL), and dried over anhydrous $MgSO_4$. After filteration and evaporation, the resulting residue was subjected to column chromatography on silica-gel with hexane/EtOAc as the eluent to give 1-[2-(*1H*-pyrazolyl)phenyl]-1-

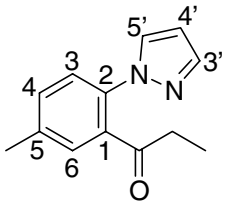
propanone (**2a**) (377 mg, 94 % yield) as a colorless oil. An analytical sample was obtained by bulb-to-bulb distillation.

1-[2-(1*H*-Pyrazolyl)phenyl]-1-propanone (2a). Colorless oil; bp 130 °C (1 mmHg); *Rf* 0.49 (hexane/EtOAc = 2/1); ^{1}H NMR ($CDCl_3$) δ 1.03 (t, *J* = 7.3 Hz, 3H), 2.21 (q, *J* = 7.3 Hz, 2H), 6.48 (dd, *J* = 2.6, 1.3 Hz, 1H), 7.38-7.54 (c, 4H), 7.71 (d, *J* = 1.3 Hz, 1H), 7.74 (d, *J* = 2.6 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 8.4, 35.4, 107.9, 123.4, 127.6, 128.3, 129.4, 130.8, 136.1, 137.6, 141.3, 205.0; IR (neat) 2982 w, 2942 w, 1699 s, 1604 m, 1582 w, 1522 m, 1499 m, 1454 m, 1395 m, 1350 m, 1333 m, 1213 m, 1106 w, 1045 m, 1020 m, 939 m; MS, *m/z* (relative intensity, %) 200 (M^+, 0), 172 (16), 171 (100); Anal. Calcd for $C_{12}H_{12}N_2O$: C, 71.98; H, 6.04; N, 13.99. Found: C, 72.05; H, 6.03; N, 13.07.



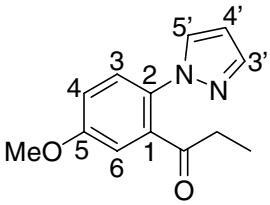
2a

1-[2-(1*H*-Pyrazolyl)-5-methylphenyl]-1-propanone (2b). Colorless oil; bp 130 °C (1 mmHg); *Rf* 0.43 (hexane/EtOAc = 2/1) ^{1}H NMR ($CDCl_3$) δ 1.02 (t, *J* = 7.3 Hz, 3H), 2.17 (q, *J* = 7.3 Hz, 2H), 2.42 (s, 3H), 6.45 (m, 1H), 7.28 (s, 1H), 7.32-7.35 (c, 2H), 7.69 (c, 2H); ^{13}C NMR ($CDCl_3$) δ 8.5, 21.0, 35.4, 107.6, 123.6, 128.7, 129.5, 131.4, 135.4, 136.0, 137.9, 141.1, 205.2; IR (neat) 3120 w, 2982 w, 2942 w, 1695 s, 1611 s, 1522 s, 1461 w, 1395 m, 1331 m, 1300 m, 1261 w, 1228 w, 1170 w, 1111 w, 1080 m, 1043 m, 1020 m, 971 w, 939 m, 915 m, 853 w, 824 m; MS, *m/z* (relative intensity, %) 214 (M^+, 0), 186 (13), 185 (100), 77 (16); Anal. Calcd for $C_{13}H_{14}N_2O$: C, 72.87. H, 6.59; N, 13.07. Found: C, 73.15; H, 6.67; N, 12.97.



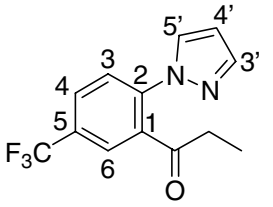
2b

1-[2-(1*H*-Pyrazolyl)-5-methoxyphenyl]-1-propanone (2c). Colorless solid; mp 88 °C; *Rf* 0.34 (hexane/EtOAc = 2/1) ^{1}H NMR ($CDCl_3$) δ 1.00 (t, *J* = 7.3 Hz, 3H), 2.13 (q, *J* = 7.3 Hz, 2H), 3.86 (s, 3H), 6.45 (dd, *J* = 2.3, 1.3 Hz, 1H), 6.99-7.06 (c, 2H), 7.36 (d, *J* = 8.6 Hz, 1H), 7.65 (d, *J* = 2.3 Hz, 1H), 7.67 (d, *J* = 1.3 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 8.4, 35.0, 55.7, 107.4, 112.7, 116.7, 125.6, 129.8, 131.1, 137.4, 140.9, 158.8, 204.5; IR (neat); 3124 w, 2944 m, 1690 s, 1606 m, 1512 s, 1467 m, 1418 s, 1395 s, 1346 s, 1309 s, 1266 s, 1227 s, 1197 s, 1173 s, 1107 w, 1077 m, 1040 s, 981 m, 940 m, 914 w, 893 w, 871 m, 850 s, 835 s, 802 m; MS, *m/z* (relative intensity, %) 230 (M^+, 7), 202 (15), 201 (100), 186 (13). Anal. Calcd for $C_{13}H_{14}N_2O_2$: C, 67.81; H, 6.13; N, 12.17. Found: C, 67.89; H, 6.31; N, 12.11.



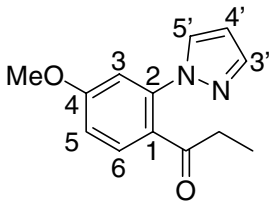
2c

1-[2-(1*H*-Pyrazolyl)-5-trifluoromethyl]-1-propanone (2d). Colorless oil; mp 94-96 °C; *Rf* 0.45 (hexane/EtOAc = 2/1) ^{1}H NMR ($CDCl_3$) δ 1.08 (t, *J* = 7.3 Hz, 3H), 2.30 (q, *J* = 7.3 Hz, 2H), 6.53 (dd, *J* = 2.6, 2.0 Hz, 1H), 7.59 (d, *J* = 8.2 Hz, 1H), 7.71-7.79 (c, 3H), 7.82 (d, *J* = 2.3 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 8.2, 35.7, 108.7, 122.7, 123.2 (q, *J* = 271.9 Hz), 125.6 (q, *J* = 3.9 Hz), 127.5 (d, *J* = 3.4 Hz), 128.9, 129.4 (q, *J* = 33.5 Hz), 136.0, 139.8, 142.0, 203.6; IR (KBr) 3932 w, 3384 w, 3132 m, 3056 m, 3000 m. 2958 w, 2920 w, 2892 w, 1926 w, 1858 w, 1702 s, 1622 m, 1594 m, 1528 m, 1470 m, 1422 m, 1400 s, 1330 s, 1310 s, 1288 s, 1254 m, 1208 s, 1164 s, 1128 s, 1082 m, 1048 m, 1032 m, 972 m, 940 s, 890 m, 842 s, 828 m, 800 m; MS, *m/z* (relative intensity, %) 268 (M^+, 0), 240 (16), 239 (100); Anal. Calcd for $C_{13}H_{11}F_3N_2O$: C, 58.21; H, 4.13; N, 10.44. Found: C, 58.02; H, 4.12; N, 10.44.



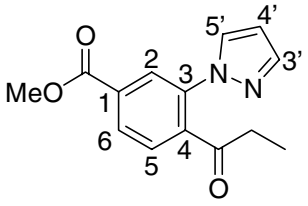
2d

1-[2-(1*H*-Pyrazolyl)-4-methoxyphenyl]-1-propanone (2e). Colorless oil; bp 140 °C (1 mmHg); R_f 0.11 (hexane/EtOAc = 5/1) ^{1}H NMR (C_6D_6) δ 0.49 (t, J = 7.3 Hz, 3H), 1.50 (q, J = 7.3 Hz, 2H), 2.64 (s, 3H), 5.54 (dd, J = 2.3, 1.7 Hz, 1H), 6.04 (dd, J = 8.6, 2.3 Hz, 1H), 6.23 (d, J = 2.6 Hz, 1H), 6.67 (d, J = 2.3 Hz, 1H), 6.87 (d, J = 8.6 Hz, 1H), 7.01 (d, J = 1.7 Hz, 1H); ^{13}C NMR (C_6D_6) δ 8.9, 35.0, 55.1, 107.8, 110.0, 113.5, 129.3, 129.9, 130.8, 140.3, 141.4, 161.8, 202.4; IR (neat) 3124 w, 2970 m, 2942 m, 2842 w, 1692 s, 1610 s, 1577 s, 1517 s, 1458 s, 1414 s, 1396 s, 1349 s, 1302 s, 1232 s, 1180 s, 1139 w, 1103 s, 1044 s, 1029 s, 950 s, 916 w, 857 m, 800 m; MS, *m*/*z* (relative intensity, %) 230 (M^+, 1), 202 (18), 201 (100), 186 (16); Anal. Calcd for $C_{13}H_{14}N_2O_2$: C, 67.81; H, 6.13; N, 12.17. Found: C, 67.88; H, 6.31; N, 12.11.



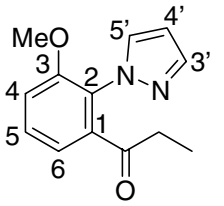
2e

4-Propionyl-3-(1*H*-pyrazolyl)benzoic acid methyl ester (2f). Colorless oil; bp 150 °C (1 mmHg); R_f 0.34 (hexane/EtOAc = 2/1) ^{1}H NMR ($CDCl_3$) δ 1.06 (t, J = 7.3 Hz, 3H), 2.28 (q, J = 7.3 Hz, 2H), 3.96 (s, 3H), 6.51 (dd, J = 2.6, 1.7 Hz, 1H), 7.50 (d, J = 8.0 Hz, 1H), 7.71 (d, J = 1.7 Hz, 1H), 7.85 (d, J = 2.6 Hz, 1H), 8.04 (dd, J = 7.9, 1.3 Hz, 1H), 8.12 (d, J = 1.3 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 8.3, 35.7, 52.6, 108.3, 123.7, 128.3, 128.3, 129.0, 132.3, 137.5, 139.6, 141.6, 165.3, 204.3; IR (neat) 3448 w, 3376 w, 3116 m, 2948 m, 2584 w, 2324 w, 2248 w, 2100 w, 1956 w, 1722 s, 1616 m, 1570 s, 1506 s, 1446 s, 1332 s, 1292 s, 1260 s, 1206 s, 1110 s, 1040 s, 1016 s, 970 s, 940 s, 900 m, 842 s; MS, *m*/*z* (relative intensity, %) 256 (M^+, 0), 230 (18), 229 (100); Anal. Calcd for $C_{14}H_{14}N_2O_3$: C, 65.11; H, 5.46; N, 10.85. Found: C, 65.21; H, 5.61; N, 10.77.



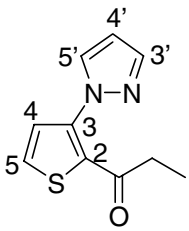
2f

1-[2-(1*H*-Pyrazolyl)-3-methoxyphenyl]-1-propanone (2g). Colorless solid; mp 87 °C; R_f 0.46 (hexane/EtOAc = 1/1); ^{1}H NMR ($CDCl_3$) δ 0.95 (t, J = 7.3 Hz, 3H), 2.04 (q, J = 7.3 Hz, 2H), 3.82 (s, 3H), 6.44 (dd, J = 2.6, 0.66 Hz, 1H), 7.06 (d, J = 7.7 Hz, 1H), 7.09 (d, J = 8.1 Hz, 1H), 7.37 (dd, J = 8.1, 7.7 Hz, 1H), 7.65 (d, J = 0.66 Hz, 1H), 7.77 (d, J = 2.6 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 8.3, 34.8, 56.3, 106.8, 113.7, 119.7, 126.8, 129.0, 132.3, 139.3, 140.4, 152.9, 204.1; IR (neat) 3124 w, 2970 w, 2942 w, 2842 w, 1688 s, 1581 s, 1516 m, 1488 m, 1474 m, 1456 m, 1442 m, 1393 s, 1375 m, 1347 m, 1301 s, 1277 s, 1254 s, 1189 m, 1121 m, 1084 m, 1047 s, 1018 s, 938 s, 885 w, 858 m; MS, *m*/*z* (relative intensity, %) 230 (M^+, 0), 202 (16), 201 (100), 186 (32); Calcd for $C_{13}H_{14}N_2O_2$: C, 67.81; H, 6.13; N, 12.17. Found: C, 67.87; H, 6.06; N, 11.92.



2g

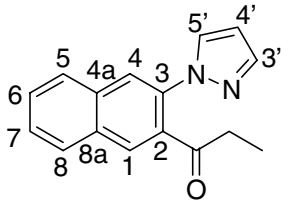
1-[3-(1*H*-Pyrazolyl)-2-thiophenyl]-1-propanone (2h). Colorless oil; bp 120 °C (1 mmHg); R_f 0.34 (hexane/EtOAc = 2/1); ^{1}H NMR ($CDCl_3$) δ 1.10 (t, J = 7.3 Hz, 3H), 2.61 (q, J = 7.3 Hz, 2H), 6.46 (dd, J = 2.3, 1.7 Hz, 1H), 7.30 (d, J = 7.3 Hz, 1H), 7.55 (d, J = 7.3 Hz, 1H), 7.73 (d, J = 1.7 Hz, 1H), 8.01 (d, J = 2.3 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 8.1, 34.2, 106.9, 127.5, 129.9, 132.0, 132.5, 140.4, 141.2, 193.1; IR (neat) 3432 w, 3100 m, 2972 m, 2940 m, 2624 w, 2440 w, 1986 w, 1884 w, 1662 s, 1540 s, 1456 s, 1412 s, 1376 m, 1346 m, 1306 m, 1238 m, 1070 m, 1040 m, 960 m, 940 m, 906



2h

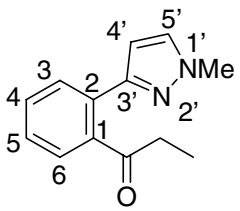
m, 866 s; MS, *m*/*z* (relative intensity, %) 206 (M^+, 20), 191 (17), 178 (12), 177 (100), 122 (12), 52 (12); Calcd for $C_{10}H_{10}N_2OS$: C, 58.23; H, 4.89; N, 13.58. Found: C, 58.19; H, 4.89; N, 13.51.

1-[3-(1*H*-Pyrazolyl)-2-naphthalenyl]-1-propanone (2i). Colorless solid; mp 112-115 °C; *Rf* 0.54 (hexane/EtOAc = 2/1); ^{1}H NMR ($CDCl_3$) δ 1.08 (t, *J* = 7.3 Hz, 3H), 2.33 (q, *J* = 7.3 Hz, 2H), 6.52 (dd, *J* = 2.5, 1.8 Hz, 1H), 7.54-7.64 (c, 2H), 7.75 (d, *J* = 1.8 Hz, 1H), 7.88 (d, *J* = 2.5 Hz, 1H), 7.90-7.96 (c, 3H), 8.10 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 8.5, 35.3, 107.9, 121.9, 127.2, 127.7, 128.3, 128.7, 128.9, 129.7, 131.7, 133.7, 135.0, 135.3, 141.5, 204.8; IR (neat) 3372 w, 3124 w, 3060 m, 2984 w, 2884 w, 2312 w, 1698 s, 1634 s, 1602 m, 1514 s, 1478 m, 1454 s, 1396 s, 1350 s, 1276 m, 1236 m, 1194 s, 1178 s, 1136 m, 1106 s, 1078 m, 1044 s, 998 m, 958 s, 932 s, 888 s, 864 s; MS, *m*/*z* (relative intensity, %) 250 (M^+, 0.89), 222 (14), 221 (100), 166 (13), 140 (11), 139 (12), 111 (13), 69 (11); Anal. Calcd for $C_{16}H_{14}N_2O$: C, 76.78; H, 5.64; N, 11.19. Found: C, 76.56; H, 5.56; N, 11.19.



2i

1-[2-(1-Methyl-3-(1*H*-pyrazolyl))phenyl]-1-propanone (4). Colorless oil; bp 115 °C (1 mmHg); *Rf* 0.11 (hexane/Et_2O = 2/1); ^{1}H NMR ($CDCl_3$) δ 1.09 (t, *J* = 7.3 Hz, 3H), 2.50 (q, *J* = 7.3 Hz, 2H), 3.92 (s, 3H), 6.39 (d, *J* = 2.3 Hz, 1H), 7.31-7.36 (c, 2H), 7.38 (d, *J* = 2.3 Hz, 1H), 7.45 (ddd, *J* = 8.9, 6.6, 0.99 Hz, 1H), 7.62 (dd, *J* = 7.9, 0.99 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 8.7, 36.3, 39.0, 104.7, 126.7, 127.6, 128.4, 129.7, 130.8, 131.2, 140.9, 150.0, 209.2; IR (neat) 3340 w, 3120 w, 2938 m, 2660 w, 1934 w, 1690 s, 1600 m, 1502 m, 1440 s, 1398 s, 1348 s, 1306 m, 1264 m, 1210 s, 1068 m, 1006 m, 944 m, 874 w; MS, *m*/*z* (relative intensity, %) 214 (M^+, 19), 199 (12), 186 (21), 185 (100), 142 (11), 116 (14); Calcd for $C_{13}H_{14}N_2O$: C, 72.87; H, 6.59; N, 13.07. Found: C, 72.68; H, 6.49; N, 13.21.



4

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