Supporting Information
for the Article entitled

Regioselective Synthesis of 1-Aryl-3,4-substituted/annulated-5-(methylthio)pyrazoles and 1-Aryl-3-(methylthio)-4,5-substituted/ annulated Pyrazoles

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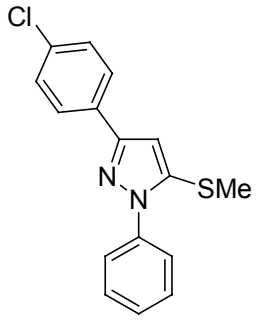
Experimental Section

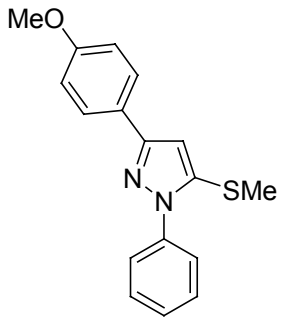
General. ^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were recorded in $CDCl_3$ and TMS was used as an internal reference. Melting points were uncorrected. Chromatographic purification was conducted by column chromatography using 100-200 mesh silica gel obtained. CH_2Cl_2 was distilled over P_2O_5 and stored over 4Å molecular sieves. THF, ether and benzene were distilled over sodium/benzophenone prior to use. NaH (as 60% suspension in oil) and potassium *t*-butoxide were purchased from the standard firms whereas $NiCl_2(PPh_3)_2$ and $NiCl_2$(dppp) catalysts were prepared[1] according to the literature procedure. *m*-CPBA (50-55% suspension in water) was diluted with CH_2Cl_2 and dried over anhydrous Na_2SO_4.



2b

3-(4′-Chlorophenyl)-5-(methylthio)-1-phenyl-1*H*-pyrazole (2b)

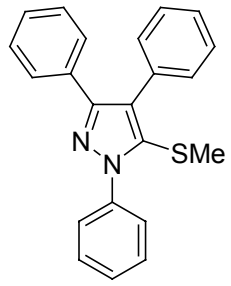
Yield 70% (1.05 g); Light yellow solid; m.p. 61-62 ºC; R_f 0.6 (9.2:0.8 hexanes-EtOAc); IR (KBr): 2924, 1595, 1502, 1479, 1431, 1361 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.79 (d, J = 8.3 Hz, 2H), 7.64 (dd, J = 8.5, 1.2 Hz, 2H), 7.49 (t, J = 8.0 Hz, 2H), 7.38-7.42 (m, 1H), 7.37 (d, J = 8.5 Hz, 2H), 6.63 (s, 1H), 2.42 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 151.0, 139.5, 139.3, 133.8, 131.4, 129.0, 128.8, 128.0, 126.9, 124.8, 105.4, 18.1; MS (*m/z*, %): 301 (M^+, 100), 300 (50); Anal. Calcd. for $C_{16}H_{13}ClN_2S$ (300.81): C, 63.89; H, 4.36; N, 9.31 %. Found C, 63.97; H, 4.49; N, 9.21 %.



2c

3-(4′-Methoxyphenyl)-5-(methylthio)-1-phenyl-1*H*-pyrazole (2c)

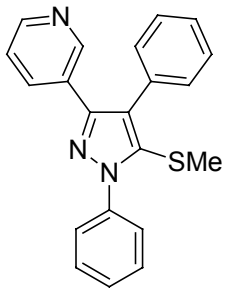
Yield 94% (1.39 g); Colourless solid; m.p. 86-87 ºC; R_f 0.46 (9.2:0.8 hexanes-EtOAc); IR (KBr): 3050, 1610, 1594, 1535, 1499, 1455, 1393, 1358, 1294, 1245, 1175 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.78 (d, J = 8.8 Hz, 2H), 7.64 (d, J = 8.5 Hz, 2H), 7.47 (t, J = 8.1 Hz, 2H), 7.33 (dt, J = 7.8, 1.2 Hz, 1H), 6.94 (d, J = 8.8 Hz, 2H), 6.59 (s, 1H), 3.83 (s, 3H), 2.40 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.6, 151.9, 139.6, 138.8, 128.9, 127.8, 126.9, 125.6, 124.8, 114.0, 105.1, 55.3, 18.1; MS (*m/z*, %): 297 (M+1, 100), 296 (M^+, 90); Anal. Calcd. for $C_{17}H_{16}N_2OS$ (296.40): C, 68.89; H, 5.44; N, 9.45 %. Found C, 68.75; H, 5.52; N, 9.34 %.



2d

5-(Methylthio)-1,3,4-triphenyl-1*H*-pyrazole (2d)

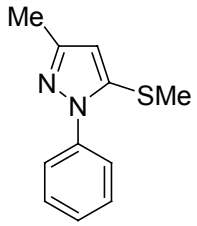
Yield 80% (1.37 g); Colourless solid; m.p. 97-98 ºC; R_f 0.47 (9.2:0.8 hexanes-EtOAc); IR (KBr): 3058, 2921, 1678, 1594, 1494, 1436, 1373 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.73 (d, J = 7.3 Hz, 2H), 7.48-7.52 (m, 4H), 7.42-7.44 (m, 1H), 7.37-7.39 (m, 4H), 7.34-7.36 (m, 1H), 7.23-7.26 (m, 3H), 1.93 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.0, 139.7, 134.4, 132.9, 132.8, 130.4, 128.8, 128.3, 128.2, 128.06, 128.08, 127.7, 127.3, 125.8, 125.7, 18.7; MS (*m/z*, %): 343 (M+1, 100), 342 (M^+, 50); Anal. Calcd. for $C_{22}H_{18}N_2S$ (342.46): C, 77.16; H, 5.30; N, 8.18 %. Found C, 77.25; H, 5.38; N, 8.11 %.



2e

1,4-Diphenyl-3-(3′-pyridyl)-5-(methylthio)-1*H*-pyrazole (2e)

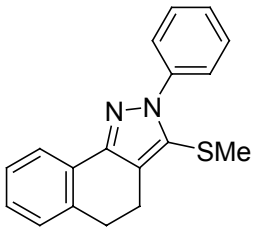
Yield 85% (1.46 g); White solid; m.p. 200-202 °C; R_f 0.36 (4:1 hexanes-EtOAc); IR (KBr): 3057, 2924, 1694, 1596, 1497, 1441, 1410 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 8.80 (s, 1H), 8.50 (d, J = 3.6 Hz, 1H), 7.79 (d, J = 8.0 Hz, 1H), 7.73 (d, J = 7.8 Hz, 2H), 7.50-7.54 (m, 2H), 7.26-7.46 (m, 6H), 7.19 (dd, J = 7.7, 4.6 Hz, 1H), 1.94 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.0, 147.7, 146.6, 139.4, 135.7, 135.1, 131.9, 130.1, 129.2, 128.9, 128.6, 128.3, 127.7, 126.1, 125.5, 123.3, 18.6; MS (*m/z*, %): 344 (M+1, 100); Anal. Calcd. for $C_{21}H_{17}N_3S$ (343.44): C, 73.44; H, 4.99; N, 12.23 %. Found C, 73.33; H, 4.89; N, 12.31%.



2f

3-Methyl-5-(methylthio)-1-phenyl-1*H*-pyrazole (2f)

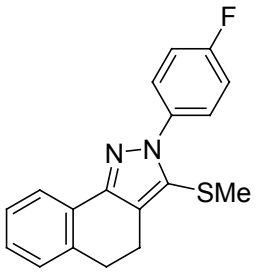
Yield 96% (0.98 g); Pale yellow liquid; R_f 0.44 (9.2:0.8 hexanes-EtOAc); IR (CH_2Cl_2): 3046, 2925, 1597, 1518, 1500, 1457, 1421 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.55 (dt, J = 6.8, 1.7 Hz, 2H), 7.42 (dt, J = 7.1, 1.7 Hz, 2H), 7.32 (tt, J = 7.1, 1.2 Hz, 1H), 6.13 (s, 1H), 2.32 (s, 3H), 2.31 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 149.3, 139.3, 137.7, 128.6, 127.2, 124.2, 107.6, 17.6, 13.4; MS (*m/z*, %): 205 (M+1, 100), 204 (M^+, 70); Anal. Calcd. for $C_{11}H_{12}N_2S$ (204.29): C, 64.67; H, 5.92; N, 13.71 %. Found C, 64.76; H, 5.81; N, 13.65 %.



2i

3-(Methylthio)-2-phenyl-4,5-dihydro-2*H*-benzo[*g*]indazole (2i)

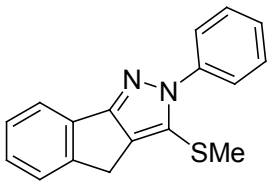
Yield 90% (1.31 g); Colourless solid; m.p. 91-92 ºC; R_f 0.55 (9.2:0.8 hexanes-EtOAc); IR (KBr): 2943, 2892, 2831, 1592, 1494, 1471, 1401, 1355 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.92 (d, J = 7.1 Hz, 1H), 7.67 (d, J = 8.2 Hz, 2H), 7.48 (dt, J = 7.2, 1.7 Hz, 2H), 7.37-7.41 (m, 1H), 7.21-7.29 (m, 3H), 3.01 (t, J = 6.8 Hz, 2H), 2.86 (t, J = 6.8 Hz, 2H), 2.13 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.7, 139.9, 136.7, 131.3, 129.3, 128.8, 128.4, 127.8, 127.7, 126.9, 125.4, 122.9, 122.3, 29.3, 19.5, 18.9; MS (*m/z*, %): 293 (M+1, 100), 292 (M^+, 50); Anal. Calcd. for $C_{18}H_{16}N_2S$ (292.40): C, 73.94; H, 5.52; N, 9.58 %. Found C, 74.02; H, 5.41; N, 9.65 %.



7i

2-(4'-Fluorophenyl)-3-(methylthio)-4,5-dihydro-2*H*-benzo[*g*]indazole (7i)

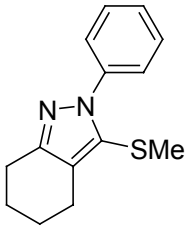
Yield 88% (1.36 g); Pale yellow liquid; R_f 0.64 (9.2:0.8 hexanes-EtOAc); IR (CH_2Cl_2): 3059, 2927, 1508, 1472, 1438, 1399, 1222 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.90 (d, J = 7.6 Hz, 1H), 7.62 (ddd, J = 6.9, 5.0, 2.0 Hz, 2H), 7.20-7.27 (m, 3H), 7.12-7.17 (m. 2H), 2.98 (t, J = 6.8 Hz, 2H), 2.83 (t, J = 6.8 Hz, 2H), 2.09 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.7 (d, J = 246.8 Hz), 148.7, 136.6, 135.9, 131.4, 129.1, 128.3, 127.9, 127.1 (d, J = 8.2 Hz), 126.8, 122.9, 122.2, 115.5 (d, J = 23.0 Hz), 29.2, 19.4, 18.7; MS (*m/z*, %): 311 (M+1, 100), 310 (M^+, 50); Anal. Calcd. for $C_{18}H_{15}FN_2S$ (310.39): C, 69.65; H, 4.87; N, 9.03 %. Found C, 69.56; H, 4.91; N, 9.15 %.



2j

3-(Methylthio)-2-phenyl-2,4-dihydro-indeno[1,2-*c*]pyrazole (2j)

Yield 51% (0.71 g); Colourless solid; m.p. 120-121 ºC; R_f 0.57 (9.2:0.8 hexanes-EtOAc); IR (KBr): 3052, 2921, 1595, 1528, 1491, 1427, 1348 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.67 (d, J = 7.6 Hz, 2H), 7.50 (d, J = 7.8 Hz, 1H), 7.46-7.47 (m, 2H), 7.44-7.45 (m, 1H), 7.36 (t, J = 7.1 Hz, 1H), 7.22-7.25 (m, 2H), 3.59 (s, 2H), 2.61 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.9 (× 2C), 142.4, 139.9, 131.8, 129.3, 127.5, 127.4, 126.59, 126.56, 126.2, 122.9, 119.5, 28.7, 15.4; MS (*m/z*, %): 279 (M+1, 100), 278 (M^+, 70); Anal. Calcd. for $C_{17}H_{14}N_2S$ (278.37): C, 73.35; H, 5.07; N, 10.06 %. Found C, 73.27; H, 5.17; N, 9.95 %.



2k

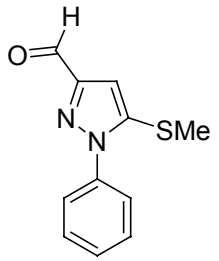
3-(Methylthio)-2-phenyl-4,5,6,7-tetrahydro-2*H*-indazole (2k)

Yield 79% (0.96 g); Pale yellow liquid; R_f 0.50 (9.2:0.8 hexanes-EtOAc); IR (CH_2Cl_2): 2943, 2892, 2831, 1592, 1494, 1471, 1401, 1355 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.58 (d, J = 7.6 Hz, 2H), 7.44 (t, J = 7.6 Hz, 2H), 7.35 (t, J = 7.6 Hz, 1H), 2.73 (t, J = 6.4 Hz, 2H), 2.61 (t, J = 6.4 Hz, 2H), 2.11 (s, 3H), 1.79-1.87 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.1, 139.9, 130.8, 128.6, 127.3, 125.1, 122.5, 23.4, 23.2, 23.1, 21.1, 18.3; MS (*m/z*, %): 245 (M+1, 100), 244 (M^+, 40); Anal. Calcd. for $C_{14}H_{16}N_2S$ (244.36): C, 68.81; H, 6.60; N, 11.46 %. Found C, 68.70; H, 6.51; N, 11.59 %.

Procedure for Hydrolysis of 2h

The crude **2h** (~ 5 mmol) was treated with 50% aqueous AcOH (20 mL) and heated at 60 °C for 4 h (monitored by TLC). The reaction mixture was neutralized

with saturated $NaHCO_3$ solution (100 mL) and extracted with CH_2Cl_2 (3 × 20 mL). The combined extracts were washed with H_2O (3 × 100 mL), brine (100 mL), dried (Na_2SO_4) and the solvent evaporated at reduced pressure to give aldehyde **8** which was purified by column chromatography using EtOAc/hexane (1:9) as eluent.



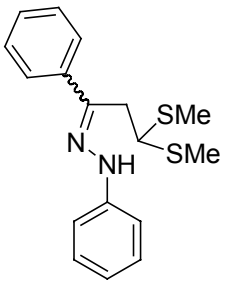
8

5-(Methylthio)-1-phenyl-1*H*-pyrazole-3-carbaldehyde (8)

Yield 77% (0.84 g) (Yield was calculated from **1h**); Colourless solid; m.p. 79-80 °C; R_f 0.41 (9.2:0.8 hexanes-EtOAc); IR (KBr): 3132, 2922, 2821, 1691, 1592, 1455, 1404, 1370, 1340 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 9.98 (s, 1H), 7.58-7.62 (m, 2H), 7.50-7.54 (m, 2H), 7.45-7.48 (m, 1H), 6.82 (s, 1H), 2.44 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 186.3, 151.7, 141.6, 138.7, 129.2, 129.0, 124.8, 105.9, 17.5; MS (*m/z*, %): 219 (M+1, 100), 218 (M^+, 20); Anal. Calcd. for $C_{11}H_{10}N_2OS$ (218.27): C, 60.53; H, 4.62; N, 12.83 %. Found C, 60.61; H, 4.68; N, 12.75 %.

Preparation of Phenylhydrazone 6a

A solution of 3,3-bis(methylthio)-1-phenyl-propan-1-one **5a** (1.13 g, 5 mmol) and phenylhydrazine (0.65 g, 6 mmol) in 50 mL EtOH and AcOH (0.2 mL) was stirred at room temperature for 3 h (monitored by TLC). The solvent was removed under reduced pressure to give phenylhydrazone **6a**, which was found to be unstable upon purification. Therefore the **6a** was characterized only by its ^1H and ^{13}C NMR spectra and used as such for the next step. [**6a** exists as a isomeric mixture of *cis/trans*, minor isomer δ value is given inside bracket and (2:1) ratio was determined by crude ^1H NMR]



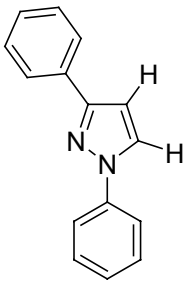
6a

***N*-[3,3-Bis(methylthio)-1-phenyl-propylidene]-*N*'-phenylhydrazine (6a)**

Yield 93% (1.46 g); Colourless solid; R_f 0.61 (9.2:0.8 hexanes-EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$): δ [7.95-7.97 (m, 2H)]7.86-7.88 (m, 2H), 7.24-7.53 (m, 2 × 7H), 6.93-7.00 (m, 2H)[6.81-6.86 (m, 2H)], 3.96 (t, J = 6.8 Hz, 1H)[3.82 (t, J = 6.8 Hz, 1H)], 3.28 (d, J = 6.8 Hz, 2H)[3.10 (t, J = 6.8 Hz, 2H)], 2.20 (s, 6H)[2.15 (s, 6H)]; ^{13}C NMR (100 MHz, $CDCl_3$): δ 145.2[144.8], [143.5]142.4, 137.6[133.4], 129.44[129.38], 129.2[129.1], 128.5[128.1], 127.8[125.6], 120.4[119.7], 113.4[112.6], [51.44]51.38, [42.8]33.6, 13.8[12.3].

BF_3·Et_2O Induced Cyclization of Phenylhydrazone 6a

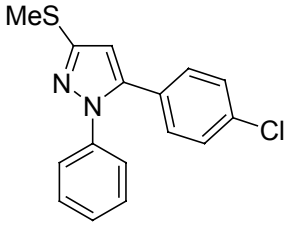
To a solution of phenylhydrazone **6a** (5 mmol) in dry benzene (25 mL), BF_3·Et_2O (1.08 g, 7.5 mmol) was added and the reaction mixture was refluxed with stirring for 4 h (monitored by TLC). It was neutralized with saturated $NaHCO_3$ solution (100 mL) and extracted with benzene (3 × 20 mL). The combined extracts were washed with H_2O (3 × 100 mL), brine (100 mL), dried (Na_2SO_4) and the solvent was evaporated at reduced pressure. The crude product was purified by column chromatography using EtOAc/hexane (1:9) as eluent to give pure pyrazole **4a**.



4a

1,3-Diphenyl-1*H*-pyrazole (4a)

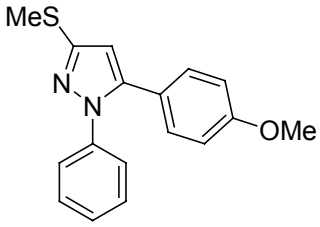
Yield 70% (0.77 g); White solid; m.p. 84-85 ºC (Lit. 84-85 °C)[2]; R_f 0.65 (9.2:0.8 hexanes-EtOAc); IR (KBr): 3033, 1595, 1526, 1502, 1453, 1385, 1360 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.95 (d, J = 2.4 Hz, 1H), 7.92 (d, J = 7.7 Hz, 2H), 7.77 (d, J = 8.1 Hz, 2H), 7.41-7.49 (m, 4H), 7.25-7.35 (m, 2H), 6.77 (d, J = 2.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.9, 140.2, 133.1, 129.4, 128.6, 128.0, 127.9, 126.3, 125.8, 118.9, 105.0.



3b

5-(4′-Chlorophenyl)-3-(methylthio)-1-phenyl-1*H*-pyrazole (3b)

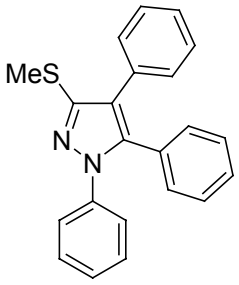
Yield 68% (1.02 g); Light yellow solid; m.p. 65-66 °C; R_f 0.6 (9.2:0.8 hexanes-EtOAc); IR (KBr): 3054, 2924, 1597, 1499, 1480, 1455, 1428, 1355 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.26-7.30 (m, 3H), 7.20-7.25 (m, 4H), 7.10 (d, J = 7.3 Hz, 2H), 6.39 (s, 1H), 2.55 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.4, 143.1, 139.5, 134.5, 129.8, 128.9, 128.7, 128.5, 127.5, 125.0, 107.6, 15.6; MS (*m/z*, %): 301 (M^+, 100), 300 (40); Anal. Calcd. for $C_{16}H_{13}ClN_2S$ (300.81): C, 63.89; H, 4.36; N, 9.31 %. Found C, 63.99; H, 4.47; N, 9.23 %.



3c

5-(4′-Methoxyphenyl)-3-(methylthio)-1-phenyl-1*H*-pyrazole (3c)

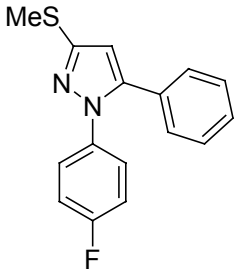
Yield 80% (1.18 g); Orange liquid; R_f 0.46 (9.2:0.8 hexanes-EtOAc); IR (CH_2Cl_2): 3002, 2929, 2837, 1612, 1546, 1500, 1458, 1357, 1292, 1251 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.20-7.25 (m, 5H), 7.07 (dd, J = 6.7, 2.0 Hz, 2H), 6.78 (dd, J = 6.7, 2.0 Hz, 2H), 6.32 (s, 1H), 3.73 (s, 3H), 2.53 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.6, 148.1, 144.2, 139.9, 129.9, 128.8, 127.2, 125.0, 122.5, 113.9, 107.1, 55.2, 15.7; MS (*m/z*, %): 297 (M+1, 100), 296 (M^+, 50); Anal. Calcd. for $C_{17}H_{16}N_2OS$ (296.40): C, 68.89; H, 5.44; N, 9.45 %. Found C, 68.91; H, 5.53; N, 9.56 %.



3d

3-(Methylthio)-1,4,5-triphenyl-1*H*-pyrazole (3d)

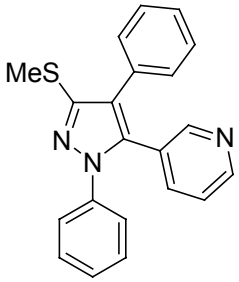
Yield 75% (1.28 g); Colourless solid; m.p. 205-206 ºC; R_f 0.65 (9.2:0.8 hexanes-EtOAc); IR (KBr): 3055, 2923, 1595, 1547, 1499, 1445, 1385 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.16-7.27 (m, 13H), 7.03-7.05 (m, 2H), 2.56 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 146.8, 140.9, 139.8, 131.9, 130.3, 129.8, 129.7, 128.7, 128.4, 128.3, 128.1, 126.9, 126.7, 124.9, 121.4, 15.1; MS (*m/z*, %): 343 (M+1, 100), 342 (M^+, 60); Anal. Calcd. for $C_{22}H_{18}N_2S$ (342.46): C, 77.16; H, 5.30; N, 8.18 %. Found C, 77.05; H, 5.40; N, 8.12 %.



11a

1-(4′-Fluorophenyl)-3-(methylthio)-5-phenyl-1*H*-pyrazole (11a)

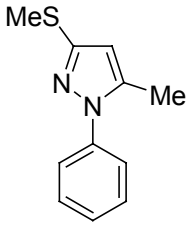
Yield 69% (0.98 g); Orange liquid; R_f 0.64 (9.2:0.8 hexanes-EtOAc); IR (CH_2Cl_2): 3060, 2925, 1510, 1482, 1422, 1365, 1316, 1222 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.18-7.23 (m, 3H), 7.16 (ddd, J = 6.7, 4.6, 2.2 Hz, 2H), 7.09-7.12 (m, 2H), 6.88-6.94 (m, 2H), 6.34 (s, 1H), 2.49 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 162.5 (d, J = 246.8 Hz), 148.4, 144.5, 135.8, 129.8, 128.6, 128.53, 128. 51, 126.8 (d, J = 9.0 Hz), 115.7 (d, J = 23.0 Hz), 107.5, 15.6; MS (*m/z*, %): 285 (M+1, 100), 284 (M^+, 40); Anal. Calcd. for $C_{16}H_{13}FN_2S$ (284.36): C, 67.58; H, 4.61; N, 9.85 %. Found C, 67.46; H, 4.72; N, 9.74 %.



3e

1,4-Diphenyl-5-(3′-pyridyl)-3-(methylthio)-1*H*-pyrazole (3e)

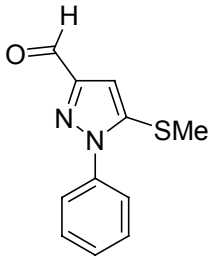
Yield 69% (1.18 g); White solid; m.p. 200-202 ºC: R_f 0.36 (4:1 hexanes-EtOAc); IR (KBr): 3046, 2924, 1595, 1566, 1497, 1385, 1356 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 8.49 (d, J = 3.6 Hz, 1H), 8.31 (s, 1H), 7.19-7.38 (m, 11H), 7.16 (dd, J = 7.7, 4.9 Hz, 1H), 2.58 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.5, 149.0, 147.3, 139.2, 137.6, 137.5, 131.2, 129.7, 129.0, 128.5, 127.6, 127.2, 126.2, 125.2, 123.2, 122.2, 15.0; MS (*m/z*, %): 344 (M+1, 100), 343 (M^+, 50); Anal. Calcd. for $C_{21}H_{17}N_3S$ (343.44): C, 73.44; H, 4.99; N, 12.23 %. Found C, 73.53; H, 5.07; N, 12.12 %.



3f

5-Methyl-3-(methylthio)-1-phenyl-1*H*-pyrazole (3f)

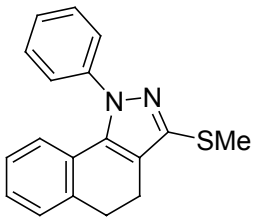
Yield 45% (0.46 g); Pale yellow liquid; R_f 0.44 (9.2:0.8 hexanes-EtOAc); IR (CH_2Cl_2): 2925, 1596, 1538, 1500, 1419, 1359, 1315 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.42-7.48 (m, 4H), 7.32-7.40 (m, 1H), 6.14 (s, 1H), 2.53 (s, 3H), 2.31 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.6, 140.2, 139.5, 128.9, 127.5, 124.7, 106.9, 15.7, 12.4; MS (*m/z*, %): 205 (M+1, 100), 204 (M^+, 50); Anal. Calcd. for $C_{11}H_{12}N_2S$ (204.29): C, 64.67; H, 5.92; N, 13.71 %. Found C, 64.78; H, 5.80; N, 13.64 %.



8

5-(Methylthio)-1-phenyl-1*H*-pyrazole-3-carbaldehyde (8)

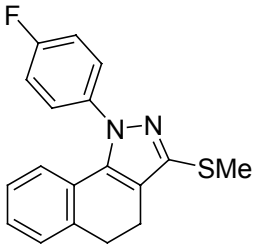
Yield 51% (0.56 g) (Yield was calculated from **9h**); Colourless solid; m.p. 78-79 °C; R_f 0.41 (9.2:0.8 hexanes-EtOAc); IR (KBr): 3131, 2922, 2821, 1693, 1592, 1454, 1404, 1372, 1339 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 9.98 (s, 1H), 7.58-7.62 (m, 2H), 7.50-7.54 (m, 2H), 7.45-7.48 (m, 1H), 6.82 (s, 1H), 2.44 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 186.3, 151.7, 141.6, 138.7, 129.2, 129.0, 124.8, 105.9, 17.5; MS (*m/z*, %): 219 (M+1, 100), 218 (M^+, 20); Anal. Calcd. for $C_{11}H_{10}N_2OS$ (218.27): C, 60.53; H, 4.62; N, 12.83 %. Found C, 60.61; H, 4.68; N, 12.75 %.



3i

3-(Methylthio)-1-phenyl-4,5-dihydro-1*H*-benzo[*g*]indazole (3i)

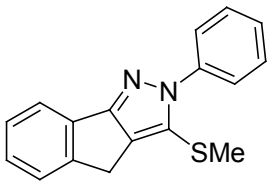
Yield 70% (1.02 g); Pale yellow viscous liquid; R_f 0.45 (9.2:0.8 hexanes-EtOAc); IR (CH_2Cl_2): 3050, 2937, 1597, 1505, 1448, 1411, 1307, 1265 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.39-7.51 (m, 5H), 7.27 (d, J = 7.6 Hz, 1H), 7.14 (t, J = 7.6 Hz, 1H), 6.98 (t, J = 7.6 Hz, 1H), 6.80 (d, J = 7.6 Hz, 1H), 2.99 (t, J = 6.8 Hz, 2H), 2.70 (t, J = 6.8 Hz, 2H), 2.56 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.3, 140.6, 138.8, 137.2, 129.2, 128.6, 128.1, 127.6, 126.6, 126.2, 125.6, 123.1, 119.9, 30.3, 19.3, 15.8; MS (*m/z*, %): 293 (M+1, 100), 292 (M^+, 50); Anal. Calcd. for $C_{18}H_{16}N_2S$ (292.40): C, 73.94; H, 5.52; N, 9.58 %. Found C, 73.83; H, 5.61; N, 9.46 %.



11i

1-(4′-Fluorophenyl)-3-(methylthio)-4,5-dihydro-1*H*-benzo[*g*]indazole (11i)

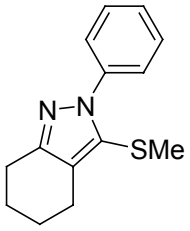
Yield 72% (1.12 g); Light yellow solid; m.p. 108-109 °C; R_f 0.64 (9.2:0.8 hexanes-EtOAc); IR (KBr): 3071, 2937, 1578, 1515, 1454, 1414, 1337, 1287, 1220 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.44 (ddd, J = 6.8, 4.8, 2.2 Hz, 2H), 7.25 (d, J = 7.6 Hz, 1H), 7.09-7.14 (m, 3H), 6.97 (dt, J = 7.7, 1.7 Hz, 1H), 6.74 (d, J = 7.7 Hz, 1H), 2.95 (t, J = 7.8 Hz, 2H), 2.66 (t, J = 7.8 Hz, 2H), 2.52 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 162.1 (d, J = 246.8 Hz), 144.5, 138.9, 137.3, 136.6, 128.7, 127.8, 127.5 (d, J = 8.2 Hz), 127.4, 126.3, 122.9, 119.8, 116.1 (d, J = 23.1 Hz), 30.3, 19.2, 15.7; MS (*m/z*, %): 311 (M+1, 100), 310 (M^+, 100); Anal. Calcd. for $C_{18}H_{15}FN_2S$ (310.39): C, 69.65; H, 4.87; N, 9.03 %. Found C, 69.76; H, 4.78; N, 9.12 %.



2j

3-(Methylthio)-2-phenyl-2,4-dihydro-indeno[1,2-*c*]pyrazole (2j)

Yield 51% (0.71 g); Colourless solid; m.p. 120-121 ºC; R_f 0.57 (9.2:0.8 hexanes-EtOAc); IR (KBr): 3052, 2921, 1595, 1528, 1491, 1427, 1348 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.67 (d, J = 7.6 Hz, 2H), 7.50 (d, J = 7.8 Hz, 1H), 7.46-7.47 (m, 2H), 7.44-7.45 (m, 1H), 7.36 (t, J = 7.1 Hz, 1H), 7.22-7.25 (m, 2H), 3.59 (s, 2H), 2.61 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.9 (× 2C), 142.4, 139.9, 131.8, 129.3, 127.5, 127.4, 126.59, 126.56, 126.2, 122.9, 119.5, 28.7, 15.4; MS (*m/z*, %): 279 (M+1, 100), 278 (M^+, 70); Anal. Calcd. for $C_{17}H_{14}N_2S$ (278.37): C, 73.35; H, 5.07; N, 10.06 %. Found C, 73.27; H, 5.17; N, 9.95 %.



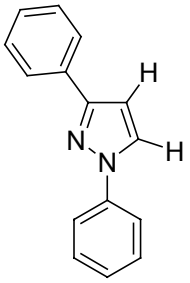
2k

3-(Methylthio)-2-phenyl-4,5,6,7-tetrahydro-2*H*-indazole (2k)

Yield 61% (0.74 g); Pale yellow liquid; R_f 0.50 (9.2:0.8 hexanes-EtOAc); IR (CH_2Cl_2): 2943, 2892, 2831, 1592, 1494, 1471, 1401, 1355 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.58 (d, J = 7.6 Hz, 2H), 7.44 (t, J = 7.6 Hz, 2H), 7.35 (t, J = 7.6 Hz, 1H), 2.73 (t, J = 6.4 Hz, 2H), 2.61 (t, J = 6.4 Hz, 2H), 2.11 (s, 3H), 1.79-1.87 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.1, 139.9, 130.8, 128.6, 127.3, 125.1, 122.5, 23.4, 23.2, 23.1, 21.1, 18.3; MS (*m/z*, %): 245 (M+1, 100), 244 (M^+, 40); Anal. Calcd. for $C_{14}H_{16}N_2S$ (244.36): C, 68.81; H, 6.60; N, 11.46 %. Found C, 68.70; H, 6.51; N, 11.59 %.

General Procedure for Dethiomethylation of Pyrazoles 2 and 3 with Raney Nickel

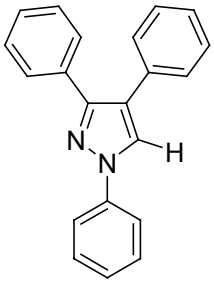
To a solution of appropriate pyrazole (1 mmol) in ethanol (30 mL), Raney Nickel (W_4, 4 times by weight) was added and the suspension was refluxed with stirring for 2-6 h (monitored by TLC). The reaction mixture was filtered through sintered funnel and the residue was washed with ethanol. The filtrate was concentrated *in vacuo* and passed through small silica gel column using EtOAc/hexane as eluent.



4a

1,3-Diphenyl-1*H*-pyrazole (4a)

Yield 98% (0.22 g); White solid; m.p. 84-85 ºC (Lit. 84-85 °C)[2]; R_f 0.65 (9.2:0.8 hexanes-EtOAc); IR (KBr): 3033, 1595, 1526, 1502, 1453, 1385, 1360 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.95 (d, J = 2.4 Hz, 1H), 7.92 (d, J = 7.7 Hz, 2H), 7.77 (d, J = 8.1 Hz, 2H), 7.41-7.49 (m, 4H), 7.25-7.35 (m, 2H), 6.77 (d, J = 2.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.9, 140.2, 133.1, 129.4, 128.6, 128.0, 127.9, 126.3, 125.8, 118.9, 105.0.

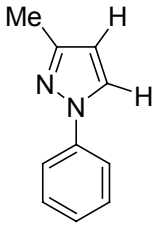


4d

1,3,4-Triphenyl-1*H*-pyrazole (4d)

Yield 93% (0.28 g); Colourless solid; m.p. 92-93 ºC (Lit. 93-94 °C)[3]; R_f 0.50 (9.2:0.8 hexanes-EtOAc); IR (KBr): 3060, 1599, 1555, 1503, 1436, 1402, 1352, 1217 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.93 (s, 1H), 7.71 (d, J = 7.8 Hz, 2H), 7.51-7.53 (m,

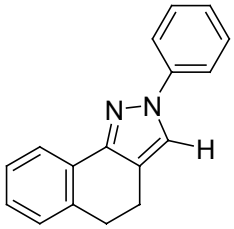
2H), 7.39 (t, J = 7.6 Hz, 2H), 7.19-7.27 (m, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.4, 139.9, 133.1, 132.8, 129.4, 128.7, 128.5, 128.4, 128.3, 127.9, 126.9, 126.6, 126.4, 122.9, 118.9.



4f

3-Methyl-1-phenyl-1*H*-pyrazole (4f)

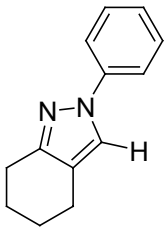
Yield 91% (0.14 g); Colourless viscous liquid (Lit. 35-36 °C)[4]; R_f 0.5 (9.2:0.8 hexanes-EtOAc); IR (CH_2Cl_2): 3047, 2928, 1598, 1534, 1504, 1458, 1396, 1364, 1329, 1255 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.71 (d, J = 2.4 Hz, 1H), 7.55 (d, J = 7.1 Hz, 2H), 7.33 (dt, J = 7.0, 2.0 Hz, 2H), 7.15 (t, J = 7.3 Hz, 1H), 6.15 (d, J = 2.4 Hz, 1H), 2.29 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.5, 140.1, 129.3, 127.3, 125.8, 118.7, 107.4, 13.7.



4i

2-Phenyl-4,5-dihydro-2*H*-benzo[*g*]indazole (4i)[5]

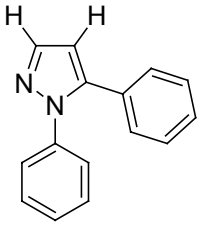
Yield 95% (0.23 g); Colourless solid; m.p. 102-103 ºC; R_f 0.34 (9.2:0.8 hexanes-EtOAc); IR (KBr): 3048, 2928, 1596, 1561, 1501, 1468, 1440, 1376, 1327, 1275 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.99 (d, J = 7.4 Hz, 1H), 7.73 (d, J = 8.3 Hz, 2H), 7.68 (s, 1H), 7.43 (t, J = 7.6 Hz, 2H), 7.28-7.32 (m, 1H), 7.21-7.26 (m, 3H), 2.97 (t, J = 7.1 Hz, 2H), 2.83 (d, J = 7.1 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 149.8, 140.4, 136.9, 129.5, 129.3, 128.3, 127.7, 126.9, 125.8, 123.4, 122.6, 118.79, 118.76, 29.5, 19.3.



4k

2-Phenyl-4,5,6,7-tetrahydro-2*H*-indazole (4k)

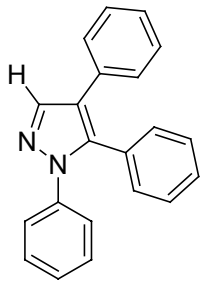
Yield 91% (0.18 g); Pale yellow viscous liquid (Lit. 48-49 °C)[6]; R_f 0.57 (9.2:0.8 hexanes-EtOAc); IR (KBr): 2943, 2892, 2831, 1592, 1494, 1471, 1401, 1355 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.54 (dd, J = 7.7, 1.0 Hz, 2H), 7.52 (s, 1H), 7.31 (t, J = 7.8 Hz, 2H), 7.12 (t, J = 7.3 Hz, 1H), 2.69 (t, J = 6.6 Hz, 2H), 2.52 (t, J = 6.1 Hz, 2H), 1.75-1.80 (m, 2H), 1.66-1.70 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 151.2, 140.3, 129.2, 125.5, 123.7, 118.5, 118.2, 23.43, 23.37, 23.35, 20.6.



10a

1,5-Diphenyl-1*H*-pyrazole (10a)

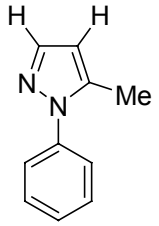
Yield 88% (0.19 g); Colourless viscous liquid (Lit. 53 °C)[2]; R_f 0.48 (9.2:0.8 hexanes-EtOAc); IR (KBr): 3050, 2921, 1597, 1501, 1449, 1385, 1265 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.66 (d, J = 2.0 Hz, 1H), 7.19-7.25 (m, 8H) 7.15-7.18 (m, 2H), 6.44 (d, J = 2.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 142.8, 140.2, 139.9, 130.5, 128.8, 128.6, 128.3, 128.1, 127.3, 125.1, 107.7.



10d

1,4,5-Triphenyl-1*H*-pyrazole (10d)

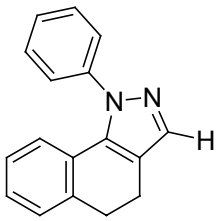
Yield 95% (0.28 g); Colourless solid; m.p. 207-208 ºC (Lit. 212 °C)[3]; R_f 0.35 (9.2:0.8 hexanes-EtOAc); IR (KBr): 3060, 1595, 1510, 1496, 1432, 1383 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.84 (s, 1H), 7.11-7.38 (m, 13H), 7.06 (dd, J = 8.0, 1.7 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 139.8, 139.7, 139.2, 132.7, 130.4, 130.1, 128.7, 128.6, 128.44, 128.39, 127.9, 127.2, 126.4, 125.1, 122.4.



10f

5-Methyl-1-phenyl-1*H*-pyrazole (10f)[4]

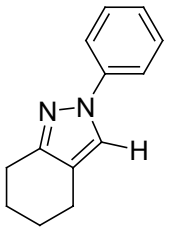
Yield 85% (0.13 g); Pale yellow liquid; R_f 0.34 (9.2:0.8 hexanes-EtOAc); IR (CH_2Cl_2): 2922, 1748, 1560, 1455, 1261, 1144 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.51 (brs, 1H) 7.37-7.41 (m, 4H), 7.28-7.32 (m, 1H), 6.13 (brs, 1H), 2.28 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ 139.8, 138.7, 129.1, 127.6, 124.8, 118.8, 106.8, 12.4.



10i

1-Phenyl-4,5-dihydro-1*H*-benzo[*g*]indazole (10i)

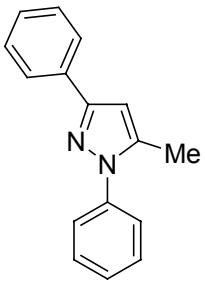
Yield 84% (0.21 g); Colourless solid; m.p. 125-126 °C (Lit. 127-129 °C)[7]; R_f 0.34 (9.2:0.8 hexanes-EtOAc); IR (KBr): 3049, 2928, 1595, 1510, 1446, 1405, 1292, 1224 1162 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.48 (s, 1H), 7.32-7.44 (m, 5H), 7.20 (d, J = 7.6 Hz, 1H), 7.06 (dt, J = 7.6, 1.2 Hz, 1H), 6.90 (t, J = 7.6 Hz, 1H), 6.75 (d, J = 7.8 Hz, 1H), 2.90 (t, J = 6.8 Hz, 2H), 2.68 (t, J = 6.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 140.9, 137.6 (× 2C), 137.4, 129.2, 128.6, 128.1, 127.3, 126.8, 126.2, 125.5, 122.9, 120.1, 30.6, 19.9.



4k

2-Phenyl-4,5,6,7-tetrahydro-2*H*-indazole (4k)[6]

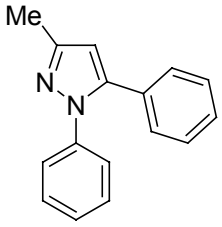
Yield 90% (0.18 g); Pale yellow liquid; R_f 0.57 (9.2:0.8 hexanes-EtOAc); IR (CH_2Cl_2): 2943, 2892, 2831, 1592, 1494, 1471, 1401, 1355 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.54 (dd, J = 7.7, 1.0 Hz, 2H), 7.52 (s, 1H), 7.31 (t, J = 7.8 Hz, 2H), 7.12 (t, J = 7.3 Hz, 1H), 2.69 (t, J = 6.6 Hz, 2H), 2.52 (t, J = 6.1 Hz, 2H), 1.75-1.80 (m, 2H), 1.66-1.70 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 151.2, 140.3, 129.2, 125.5, 123.7, 118.5, 118.2, 23.43, 23.37, 23.35, 20.6.



13a

1,3-Diphenyl-5-methyl-1*H*-pyrazole (13a)[8]

Yield 80% (0.19 g); Pale yellow viscous liquid; R_f 0.46 (9.2:0.8 hexanes-EtOAc); IR (CH_2Cl_2): 3062, 1598, 1551, 1501, 1457, 1436, 1413, 1368, 1139 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.87 (d, J = 7.6 Hz, 2H), 7.46-7.53 (m, 4H), 7.36-7.42 (m, 3H), 7.31 (t, J = 7.3 Hz, 1H), 6.53 (s, 1H), 2.37 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 151.4, 140.1, 139.8, 133.2, 129.0, 128.5, 127.7, 127.5, 125.6, 124.9, 104.3, 12.5; MS (*m/z*, %): 235 (M+1, 100), 234 (M^+, 40); Anal. Calcd. for $C_{16}H_{14}N_2$ (234.30): C, 82.02; H, 6.02; N, 11.96 %. Found C, 82.11; H, 6.13; N, 11.84 %.



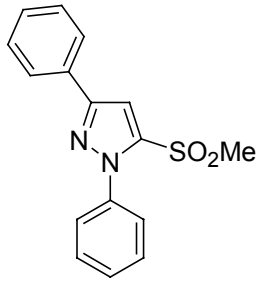
15a

1,5-Diphenyl-3-methyl-1*H*-pyrazole (15a)[8]

Yield 74% (0.17 g); Colourless liquid; R_f 0.47 (9.2:0.8 hexanes-EtOAc); IR (CH_2Cl_2): 3060, 2924, 1596, 1553, 1503, 1455, 1416, 1363, 1072 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.21-7.29 (m, 8H), 7.15-7.19 (m, 2H), 6.28 (s, 1H), 2.36 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 149.3, 143.8, 139.8, 130.5, 128.9, 128.6, 128.4, 128.2, 127.2, 125.1, 107.7, 13.5; MS (*m/z*, %): 235 (M+1, 100), 234 (M^+, 40); Anal. Calcd. for $C_{16}H_{14}N_2$ (234.30): C, 82.02; H, 6.02; N, 11.96 %. Found C, 82.13; H, 6.11; N, 11.83 %.

Procedure for the Preparation of 5- or 3-(Methylsulfonyl)pyrazoles 16 and 18

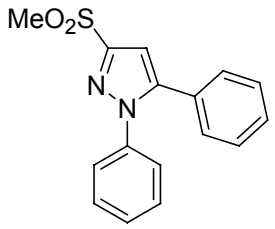
A solution of *m*-CPBA (1.58 g, 9.15 mmol) in CH_2Cl_2 (25 mL) was added dropwise to a stirred solution of pyrazoles **2a** or **3a** (1.1 g, 4.15 mmol) in CH_2Cl_2 (25 mL) at 0 °C over a period of 0.5 h. The reaction mixture was further stirred at room temperature for 5-6 h (monitored by TLC). It was then poured into ice-cold water, washed with 10% $NaHCO_3$ solution (2 × 50 mL), water (50 mL), followed by brine (50 mL) and then dried over anhydrous Na_2SO_4. The solvent was evaporated under vacuum to give crude products which were purified by either crystallization using ether or by column chromatography over silica gel using hexane:EtOAc (10:2) as eluent to give **16** and **18** as colourless crystals.



16

1,3-Diphenyl-5-(methylsulfonyl)-1*H*-pyrazole (16)

Yield 85% (1.05 g); Colourless crystals; m.p. 146-148 °C; R_f 0.23 (4:1 hexanes-EtOAc); IR (KBr): 3071, 2925, 1592, 1527, 1497, 1453, 1402, 1323, 1152, 1106 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.78 (dd, J = 8.3, 1.7 Hz, 2H), 7.59-7.62 (m, 2H), 7.46-7.48 (m, 3H), 7.35-7.38 (m, 2H), 7.32 (s, 1H), 7.31-7.33 (m, 1H), 2.80 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 151.2, 142.8, 138.5, 131.3, 129.9, 129.2, 128.89. 128.86, 126.8, 125.8, 109.9, 43.8; MS (*m/z*, %): 299 (M+1, 100), 298 (M^+, 40); Anal. Calcd. for $C_{16}H_{14}N_2O_2S$ (298.36): C, 64.41; H, 4.73; N, 9.39 %. Found C, 64.52; H, 4.64; N, 9.48 %.



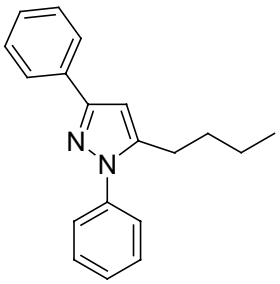
18

1,5-Diphenyl-3-(methylsulfonyl)-1*H*-pyrazole (18)

Yield 82% (1.01 g); Colourless crystals; m.p. 122-123 °C; R_f 0.25 (4:1 hexanes-EtOAc); IR (KBr): 3061, 2926, 1595, 1497, 1480, 1451, 1423, 1364, 1315, 1154, 1120 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.33-7.40 (m, 8H), 7.23 (d, J = 7.3 Hz, 2H), 7.03 (s, 1H), 3.32 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.1, 145.2, 138.7, 129.2, 129.1, 128.75, 128.72, 128.69, 128.63, 125.4, 107.2, 43.2; MS (*m/z*, %): 299 (M+1, 100), 298 (M^+, 40); Anal. Calcd. for $C_{16}H_{14}N_2O_2S$ (298.36): C, 64.41; H, 4.73; N, 9.39 %. Found C, 64.52; H, 4.64; N, 9.48 %.

Procedure for Nickel-Catalyzed Cross-Coupling Reactions of 16 and 18 with *n*-Butyl Grignard Reagent: Synthesis of 17 and 19

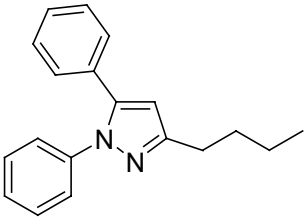
A solution of *n*-butyl Grignard reagent (0.10 mmol) in Et_2O was added dropwise to a stirring suspension of $NiCl_2$(dppp) (0.16 g, 30 mol %) in 25 mL dry benzene under nitrogen atmosphere and the mixture was refluxed for 15 minutes. After the catalyst reduction, 1.90 mmol of the *n*-butyl Grignard reagent and a solution of pyrazoles **16** or **18** (0.3 g, 1.0 mmol) in dry benzene (20 mL) were added to the reaction mixture and refluxed for 12 h. It was then cooled, poured into 50 mL of saturated NH_4Cl solution and extracted with CH_2Cl_2 (3 × 50 mL). The organic layer was dried (anhydrous Na_2SO_4) and evaporated to give crude products **17** or **19**, which were purified by column chromatography using hexane:EtOAc as eluent.



17

5-Butyl-1,3-diphenyl-1*H*-pyrazole (17)

Yield 63% (0.17 g); Colourless solid; m.p. 49-50 °C; R_f 0.47 (9.2:0.8 hexanes-EtOAc); IR (KBr): 3062, 2956, 1598, 1546, 1500, 1457, 1368, 1072, 1027 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.79 (d, J = 7.7 Hz, 2H), 7.37-7.40 (m, 4H), 7.29-7.35 (m, 3H), 7.22 (t, J = 7.3 Hz, 1H), 6.46 (s, 1H), 2.59 (t, J = 7.6 Hz, 2H), 1.50-1.57 (m, 2H), 1.24-1.29 (m, 2H), 0.81 (t, J = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 151.3, 145.7, 139.8, 133.2, 129.1, 128.5, 127.9, 127.7, 125.7, 125.5, 102.7, 30.8, 25.9, 22.3, 13.7; MS (*m/z*, %): 277 (M+1, 100), 276 (M^+, 30); Anal. Calcd. for $C_{19}H_{20}N_2$ (276.38): C, 82.57; H, 7.29; N, 10.14 %. Found C, 82.65; H, 7.35; N, 10.06 %.



19

3-Butyl-1,5-diphenyl-1*H*-pyrazole (19)

Yield 60% (0.16 g); Colourless liquid; R_f 0.47 (9.2:0.8 hexanes-EtOAc); IR (CH_2Cl_2): 3059, 2955, 2927, 1596, 1552, 1503, 1455, 1375 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.13-7.29 (m, 10H), 6.30 (s, 1H), 2.73 (t, J = 7.8 Hz, 2H), 1.61-1.69 (m, 2H), 1.34-1.42 (m, 2H), 0.90 (t, J = 7.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 154.3, 143.4, 140.2, 130.9, 128.8, 128.6, 128.3, 127.9, 126.9, 125.1, 106.7, 31.8, 28.0, 22.6, 13.9; MS (*m/z*, %): 277 (M+1, 100), 276 (M^+, 20); Anal. Calcd. for $C_{19}H_{20}N_2$ (276.38): C, 82.57; H, 7.29; N, 10.14 %. Found C, 82.65; H, 7.35; N, 10.06 %.

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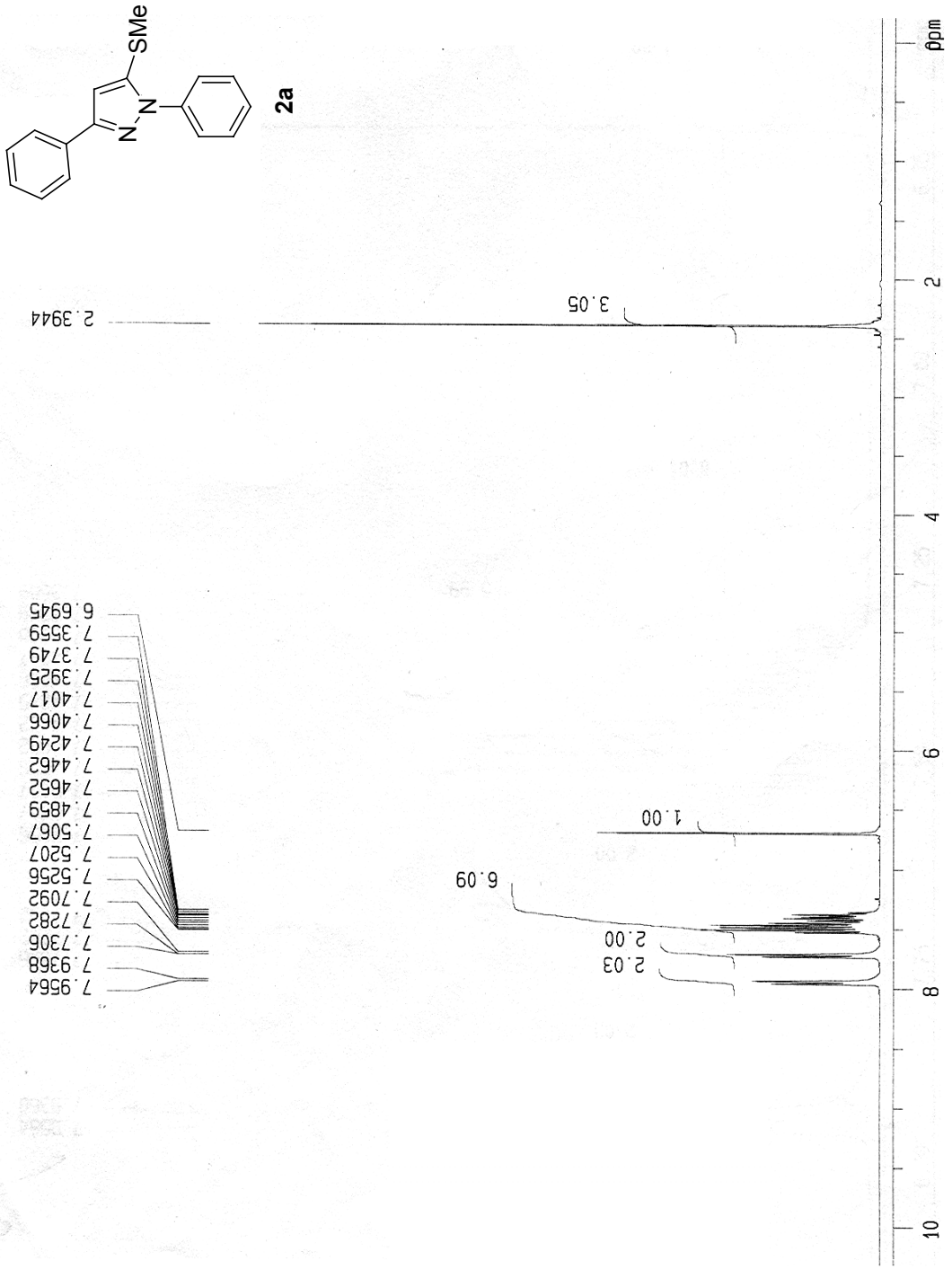
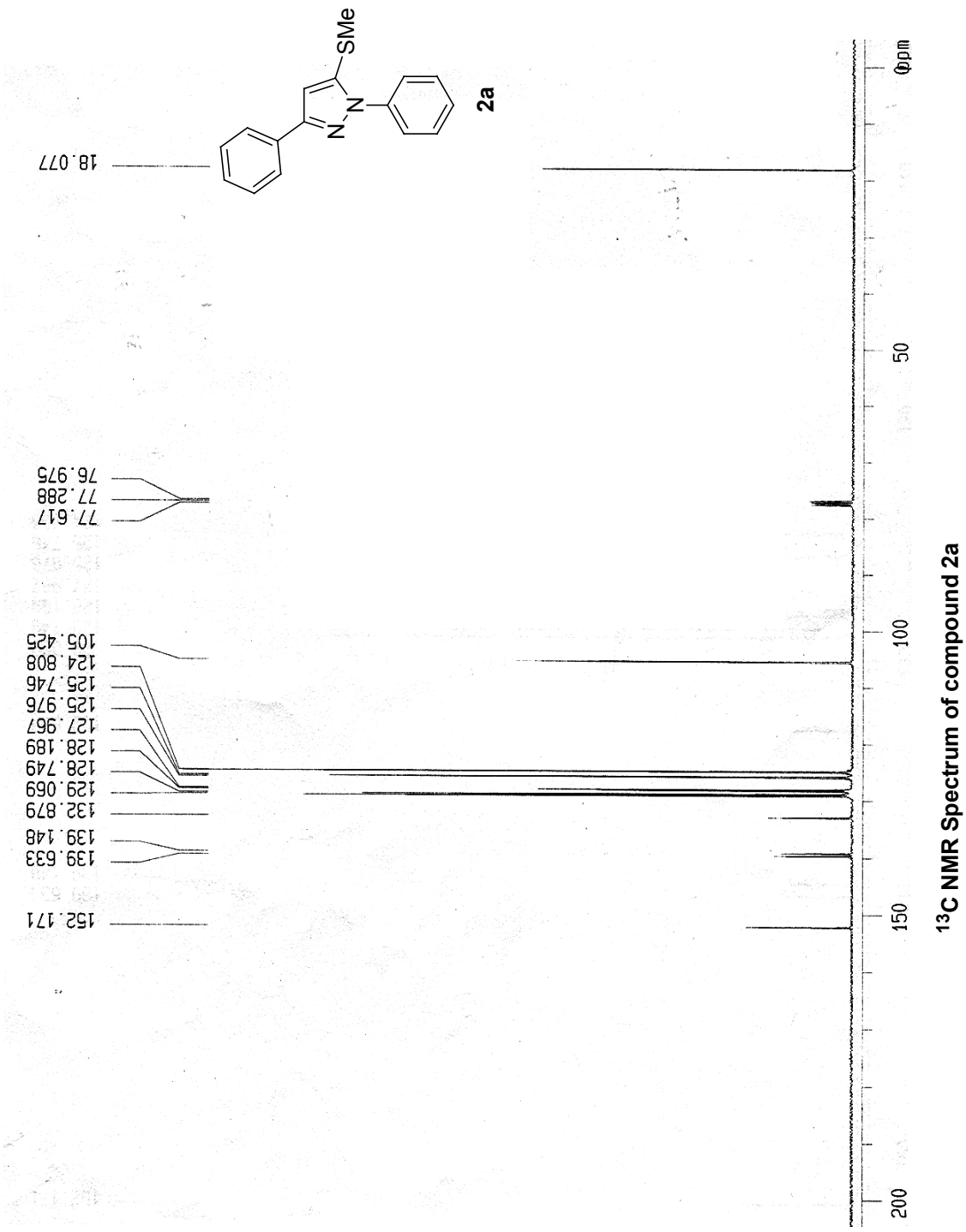
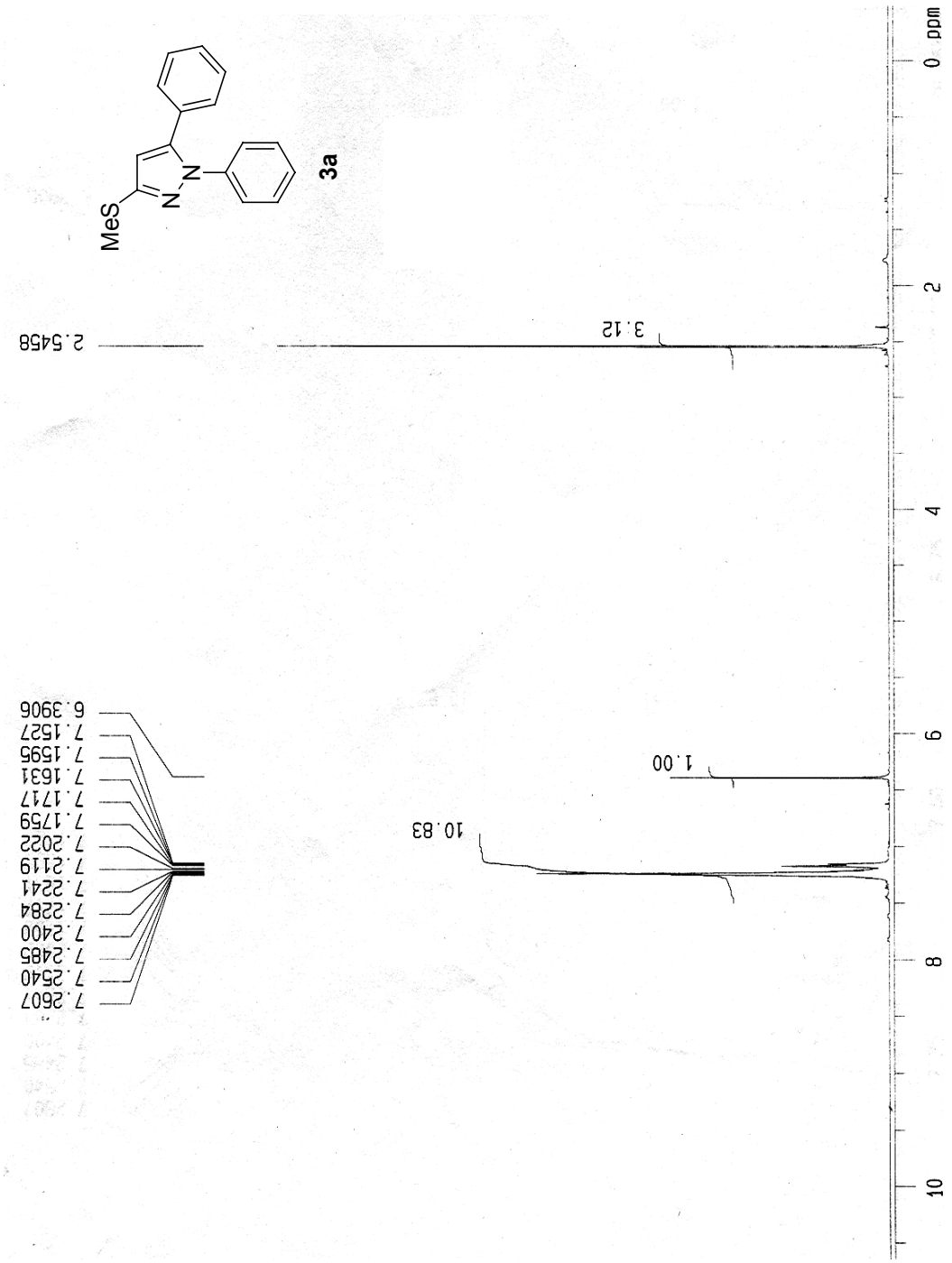


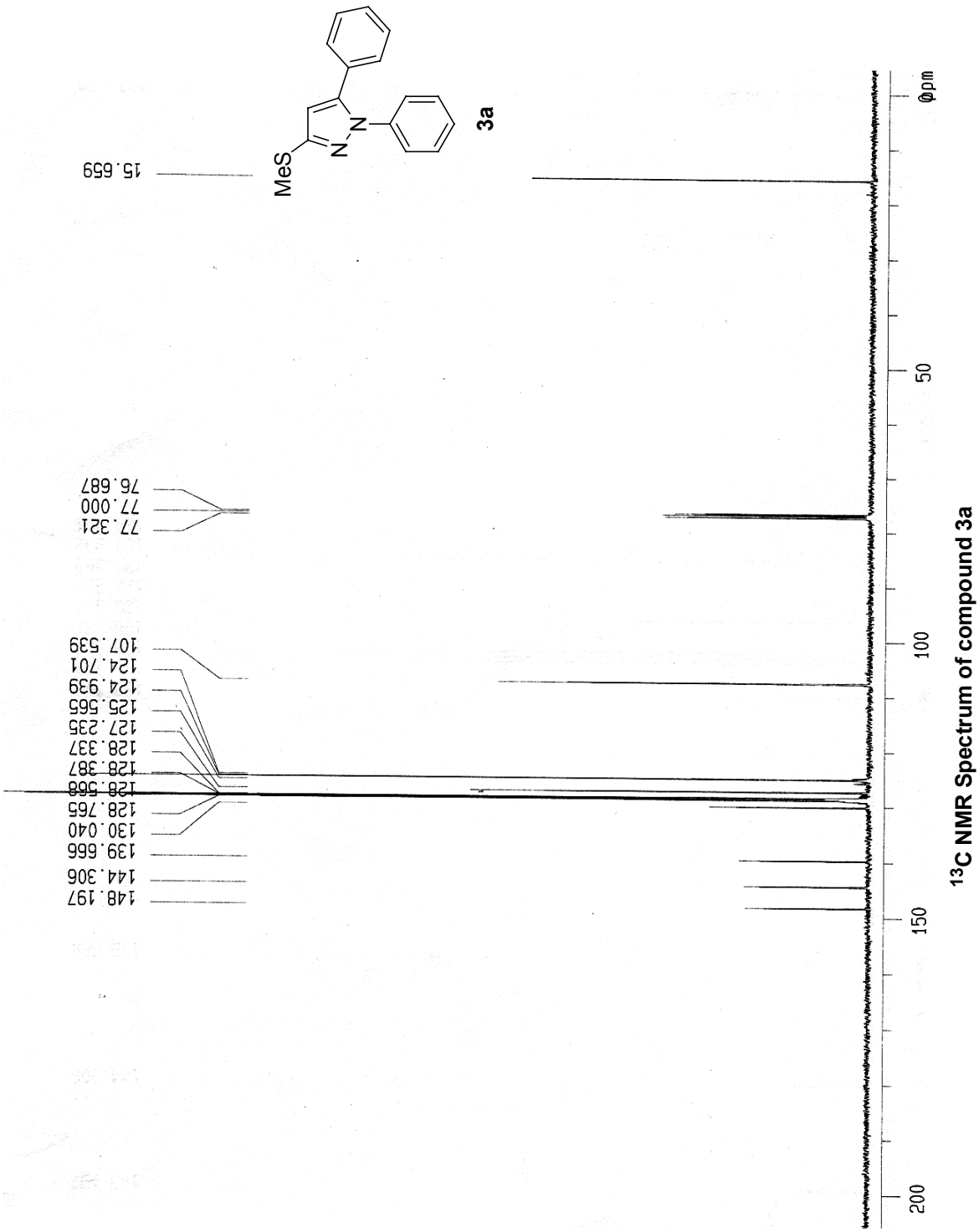
^{1}H NMR Spectrum of compound 2a



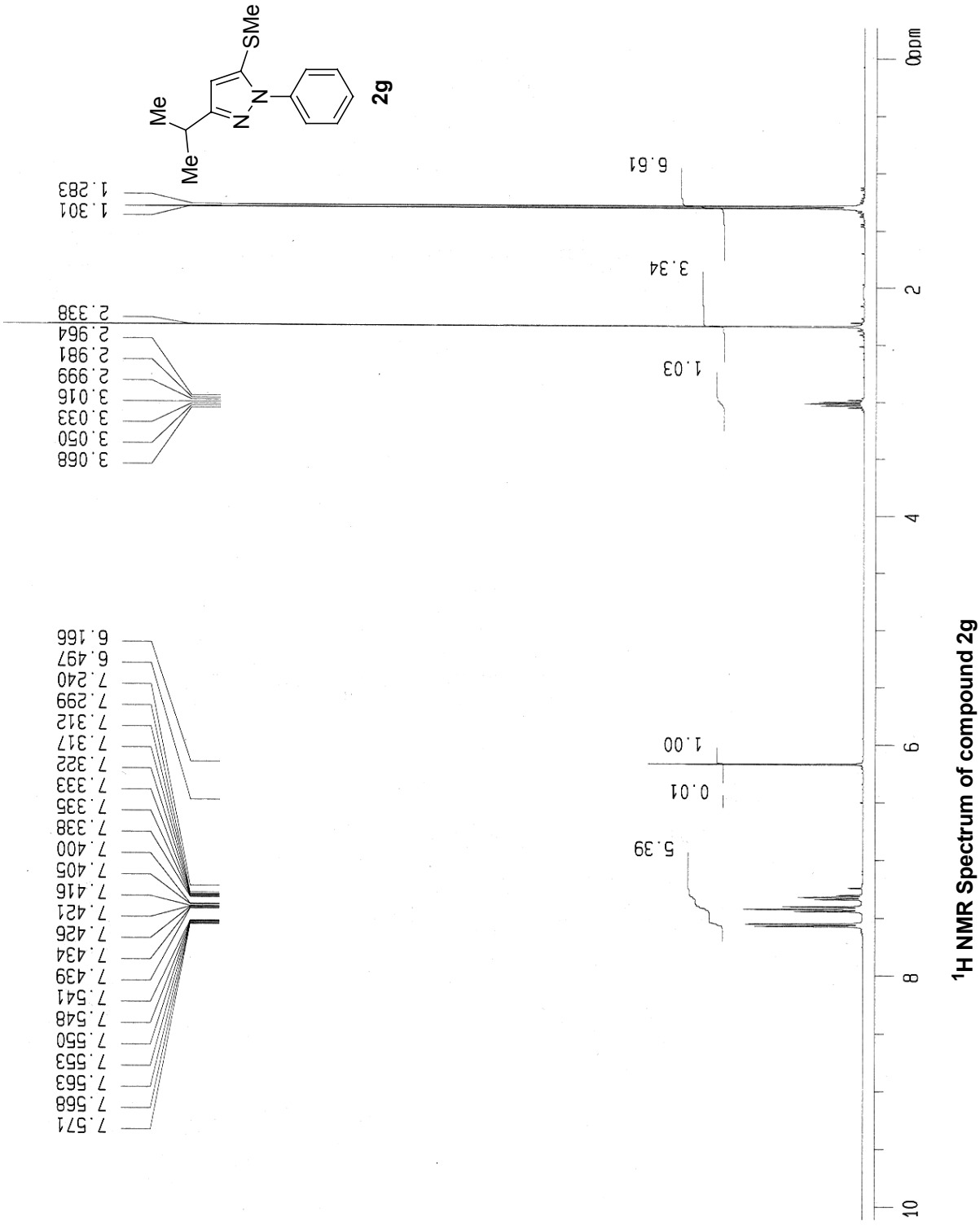
^{13}C NMR Spectrum of compound 2a



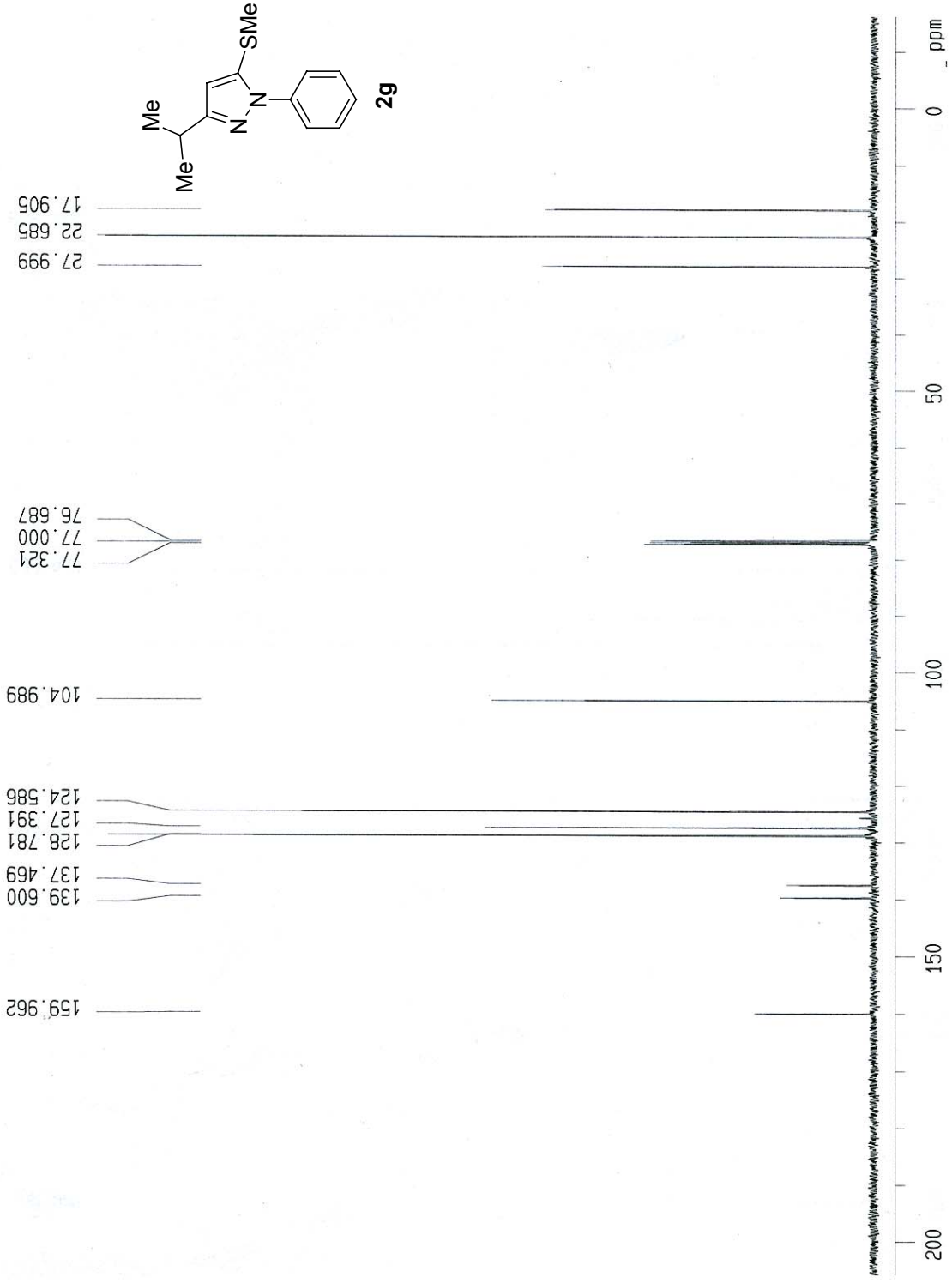
^{1}H NMR Spectrum of compound 3a



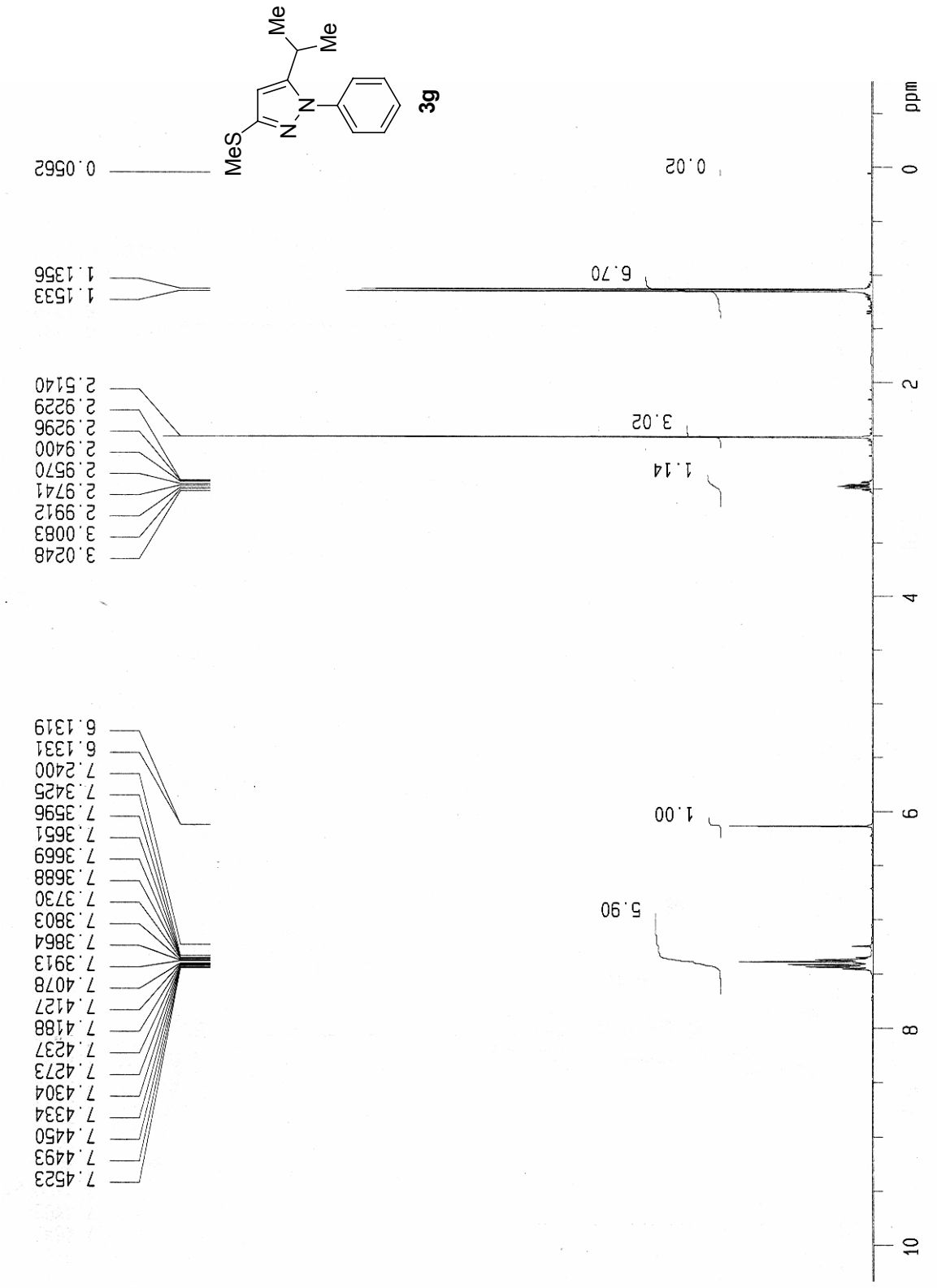
^{13}C NMR Spectrum of compound 3a



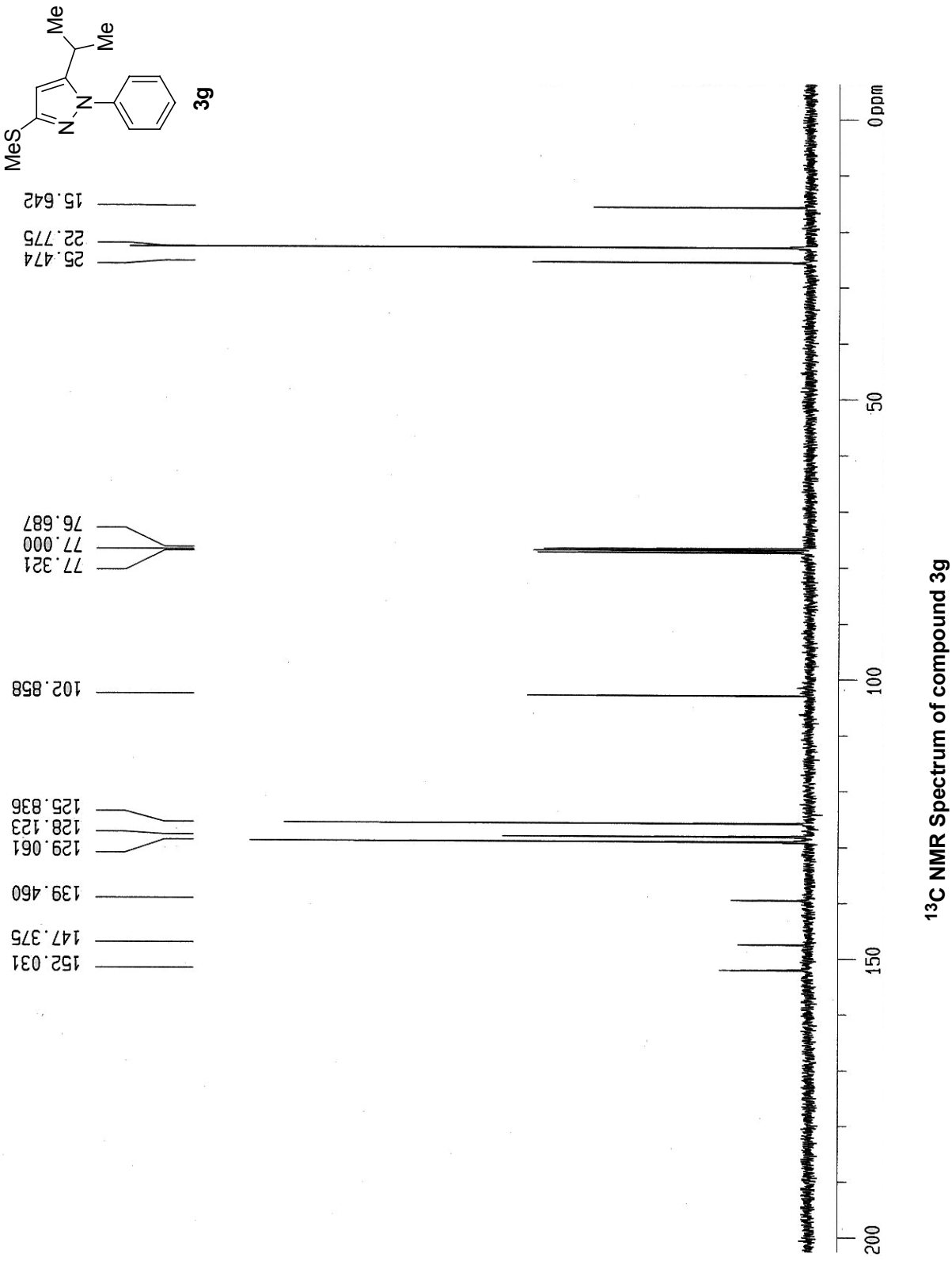
^{1}H NMR Spectrum of compound 2g



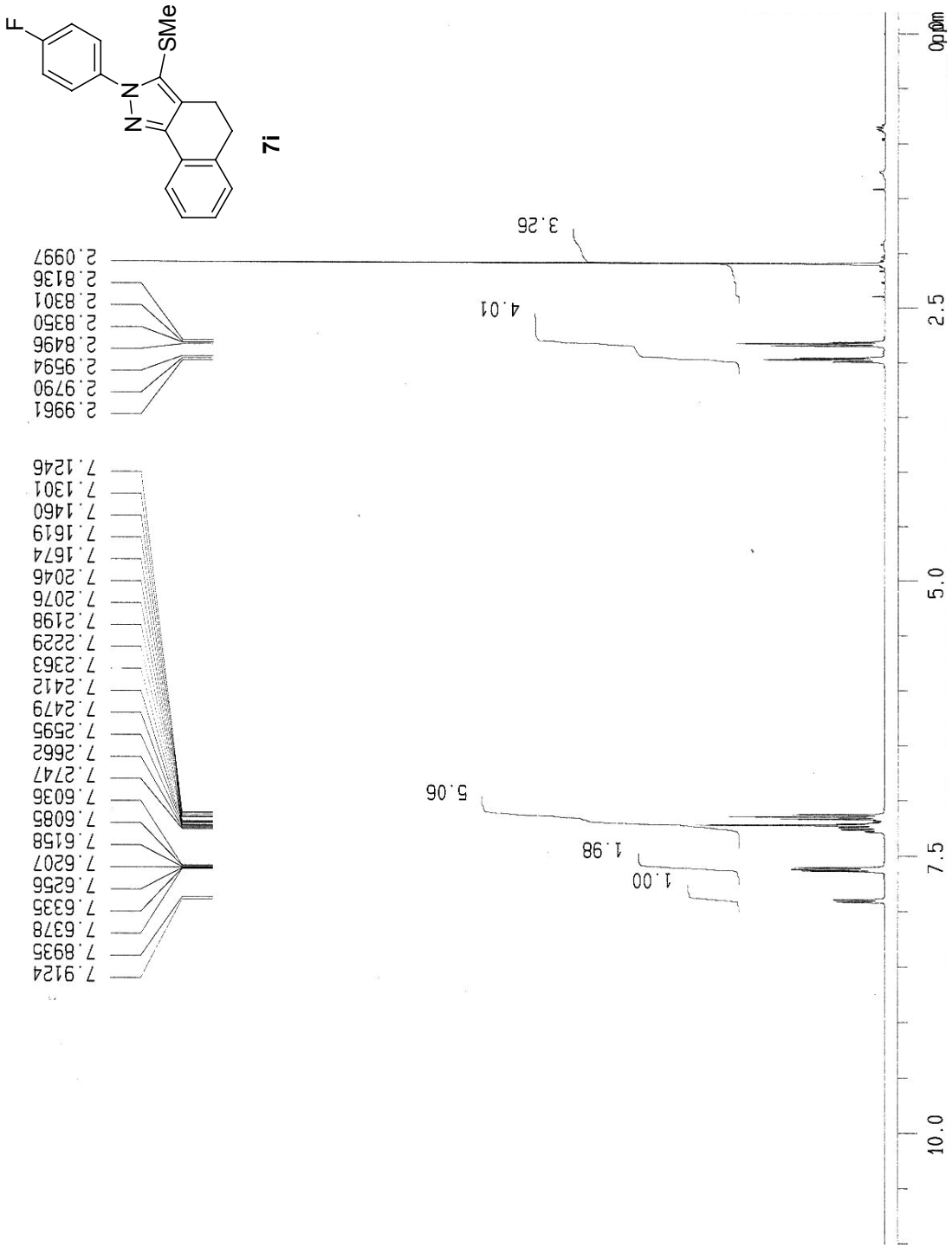
^{13}C NMR Spectrum of compound 2g



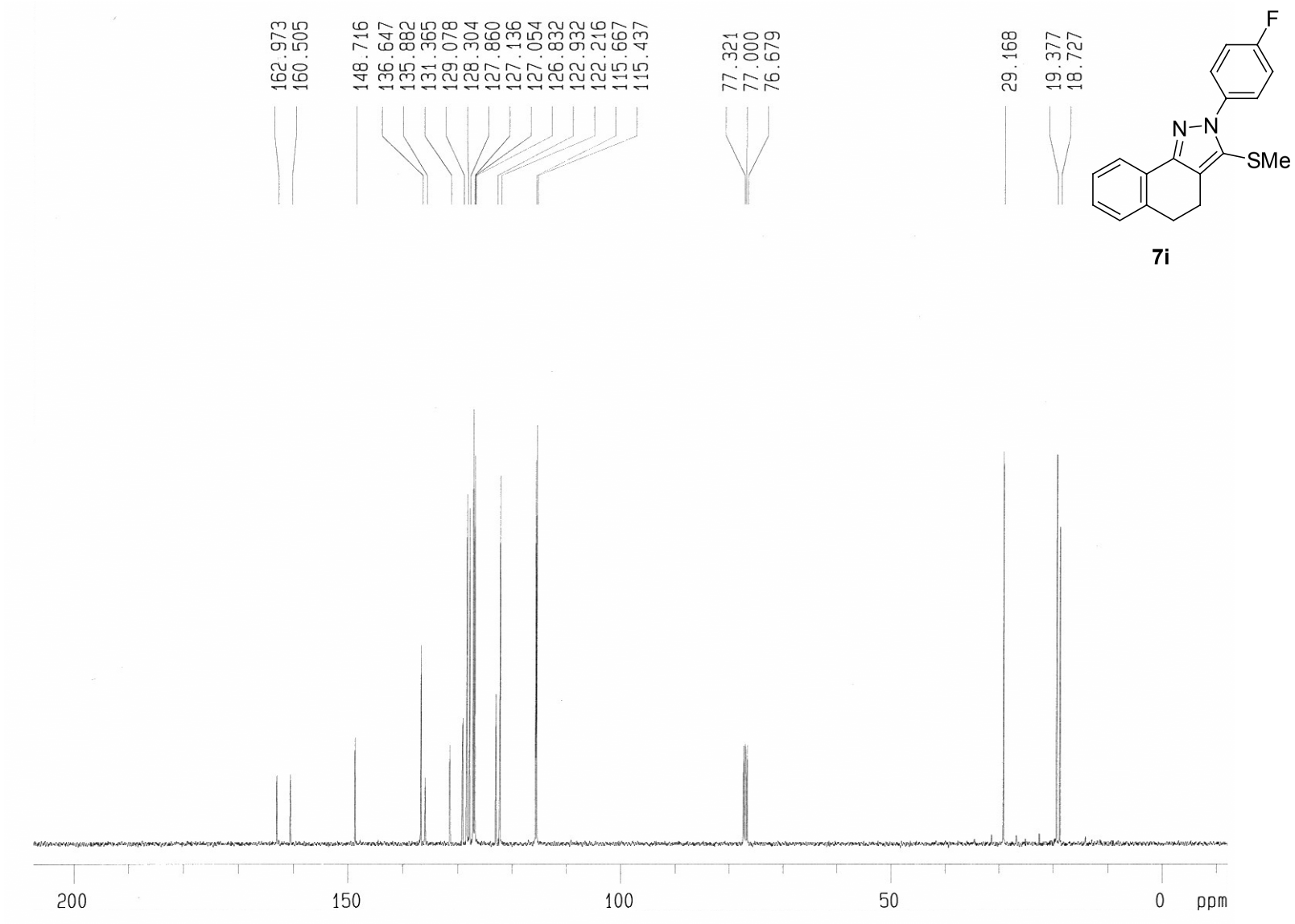
^{1}H NMR Spectrum of compound 3g



^{13}C NMR Spectrum of compound 3g

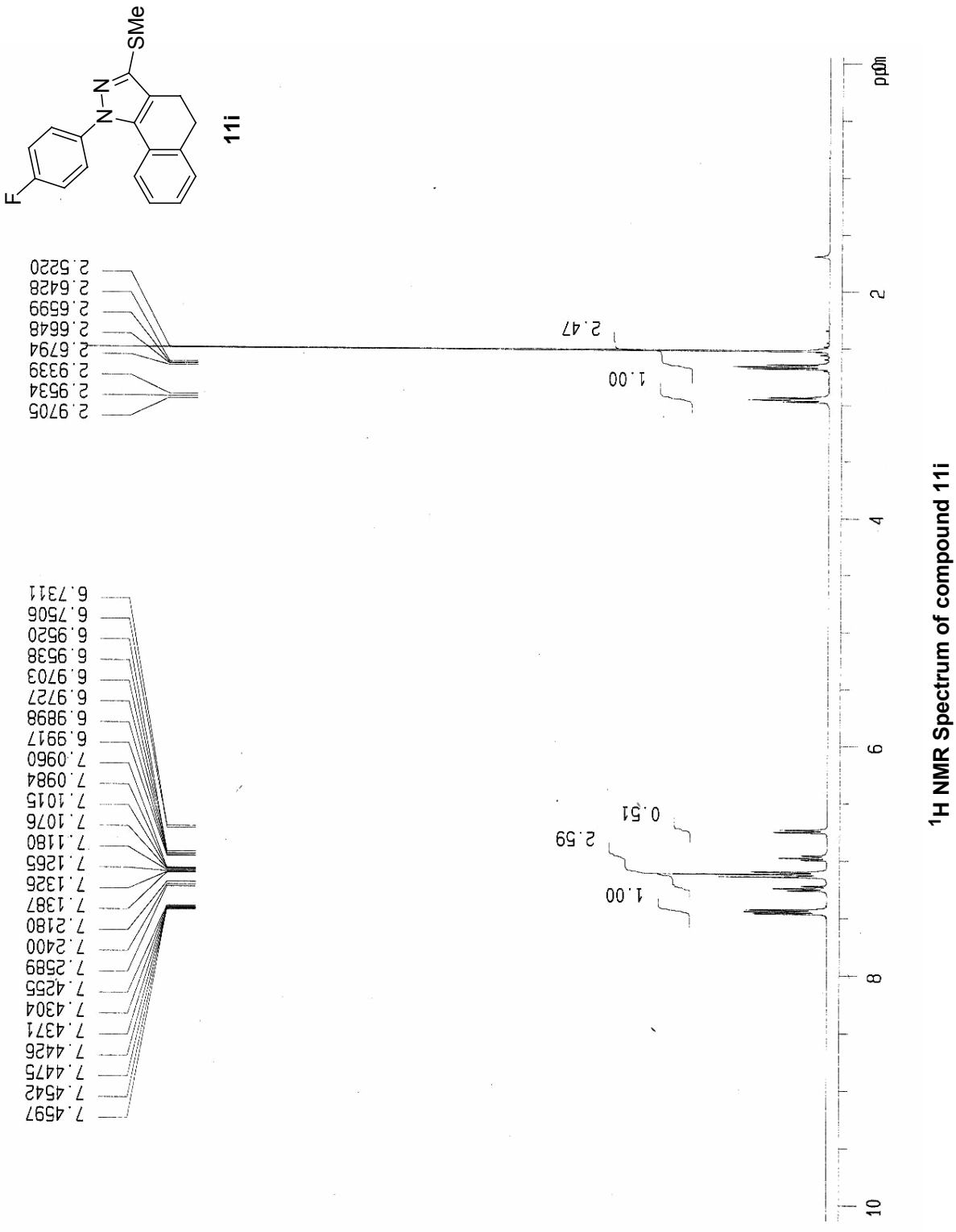


^{1}H NMR Spectrum of compound 7i

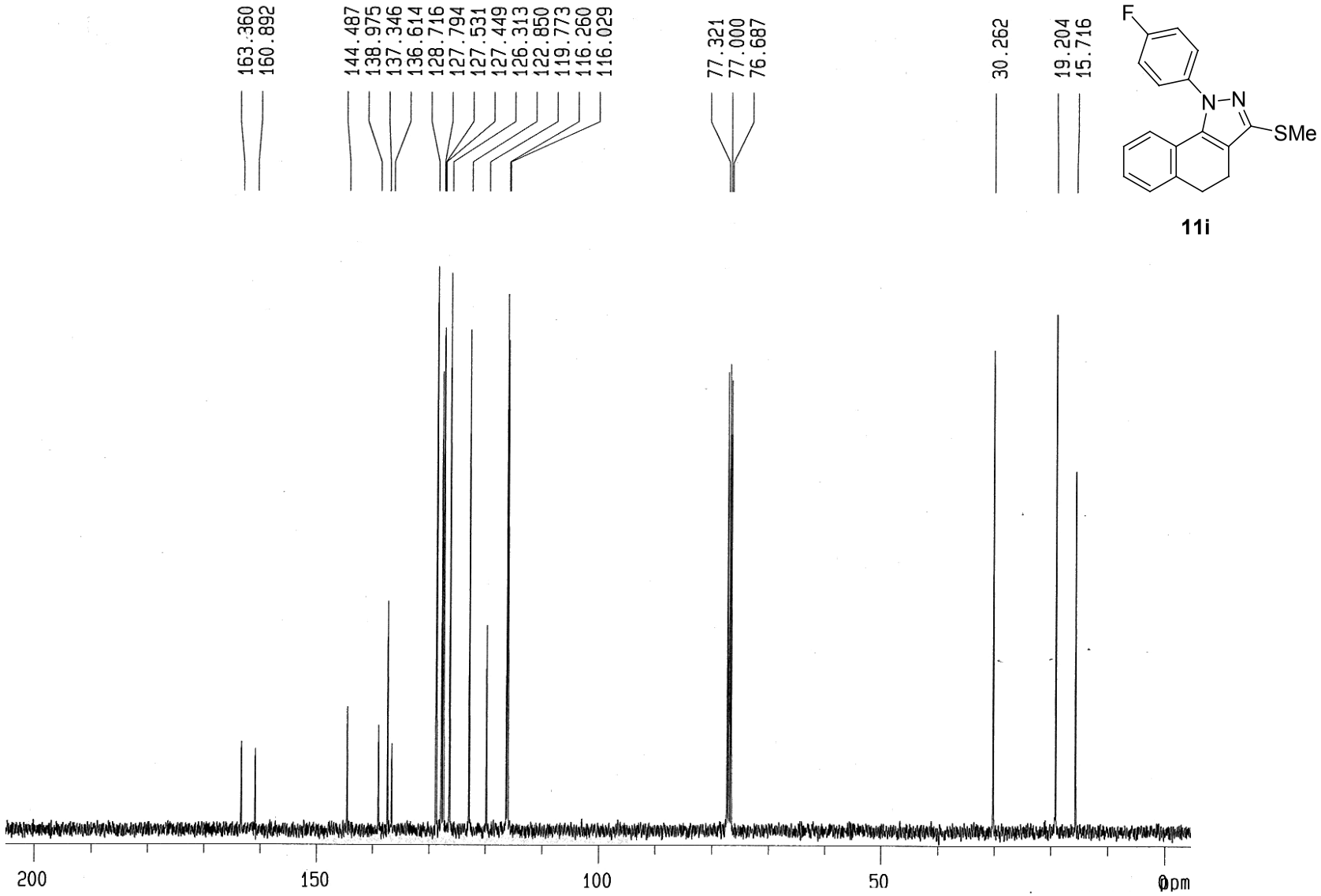


7i

^{13}C NMR Spectrum of compound 7i

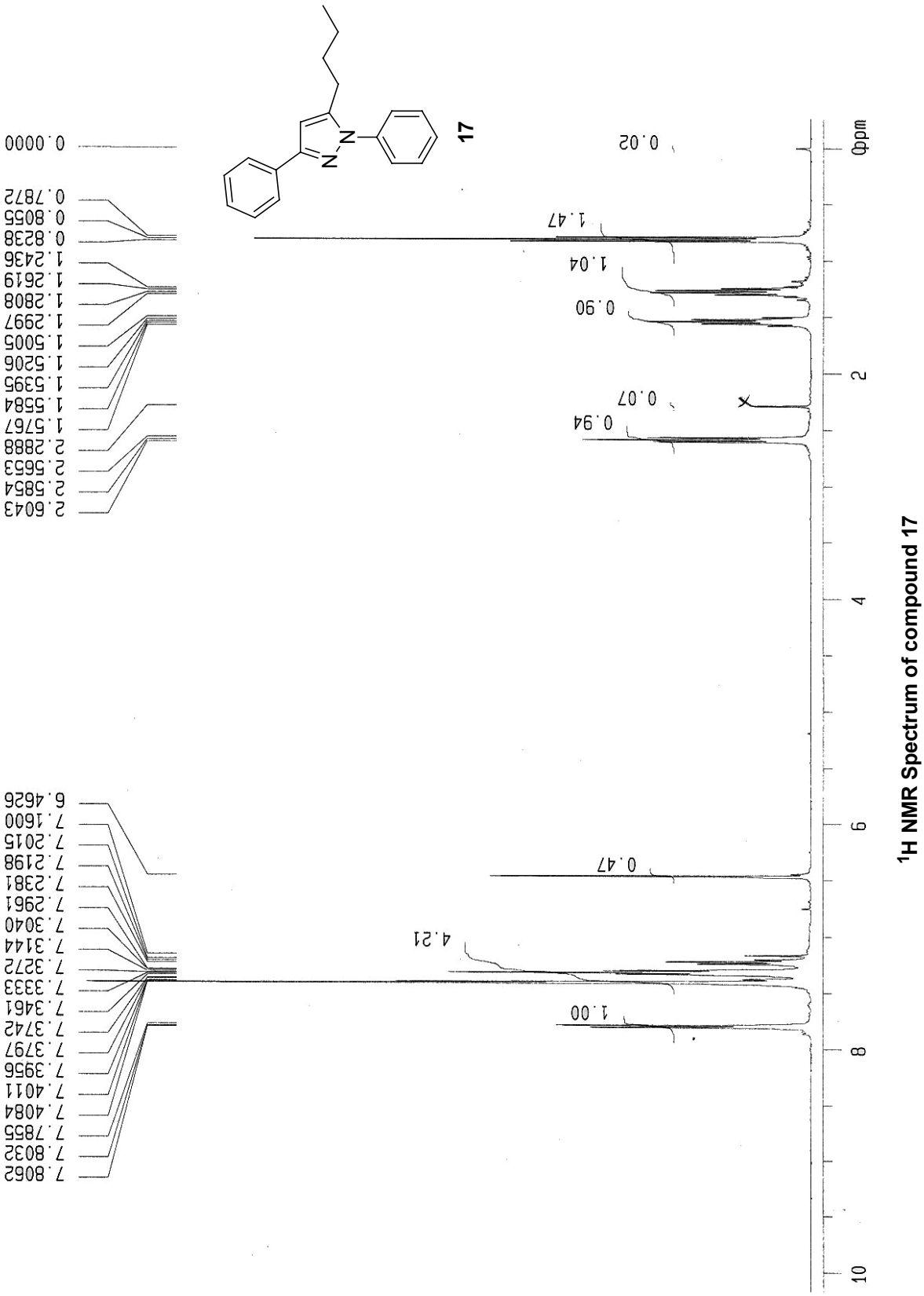


^{1}H NMR Spectrum of compound 11i

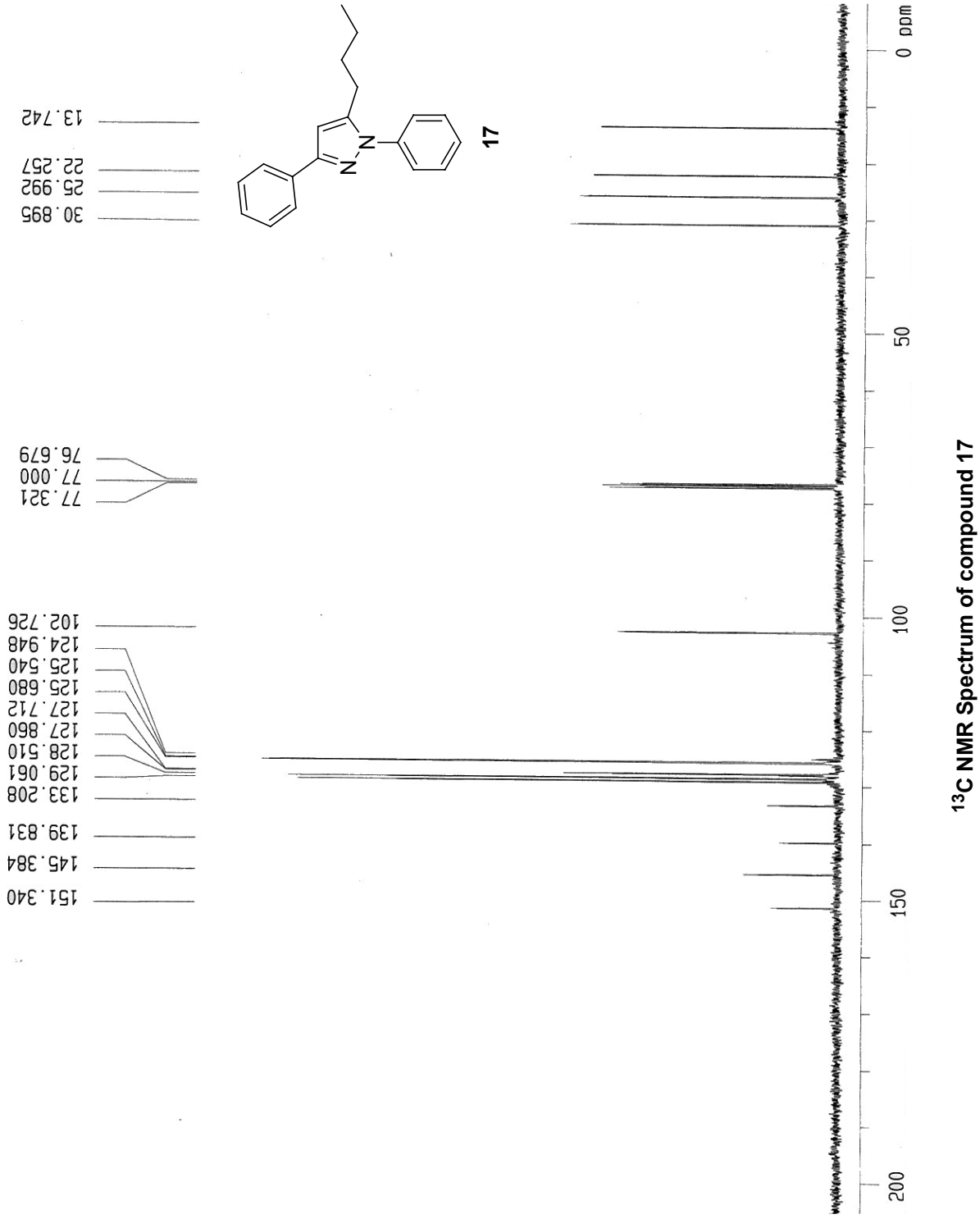


11i

^{13}C NMR Spectrum of compound 11i

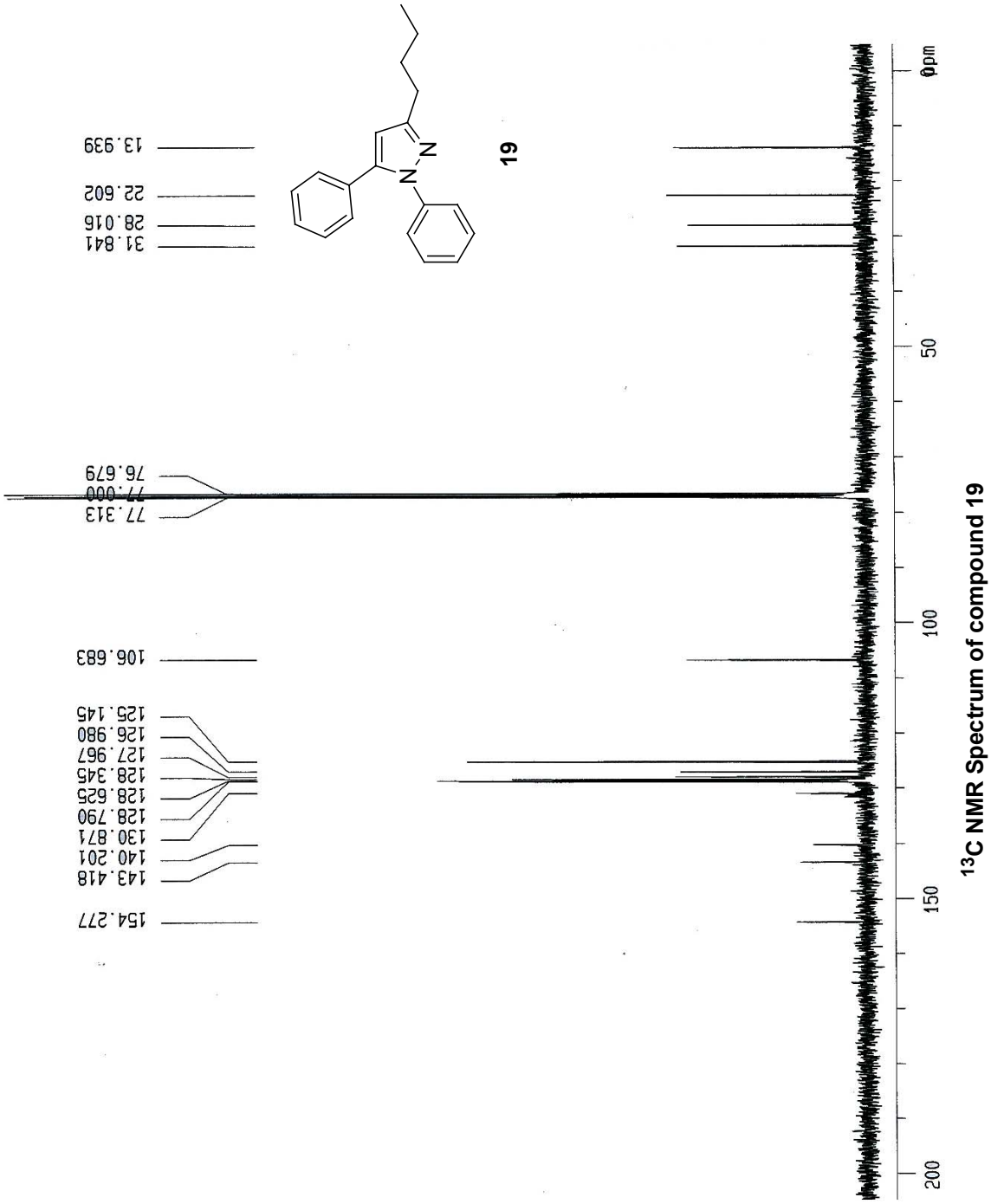


^{1}H NMR Spectrum of compound 17

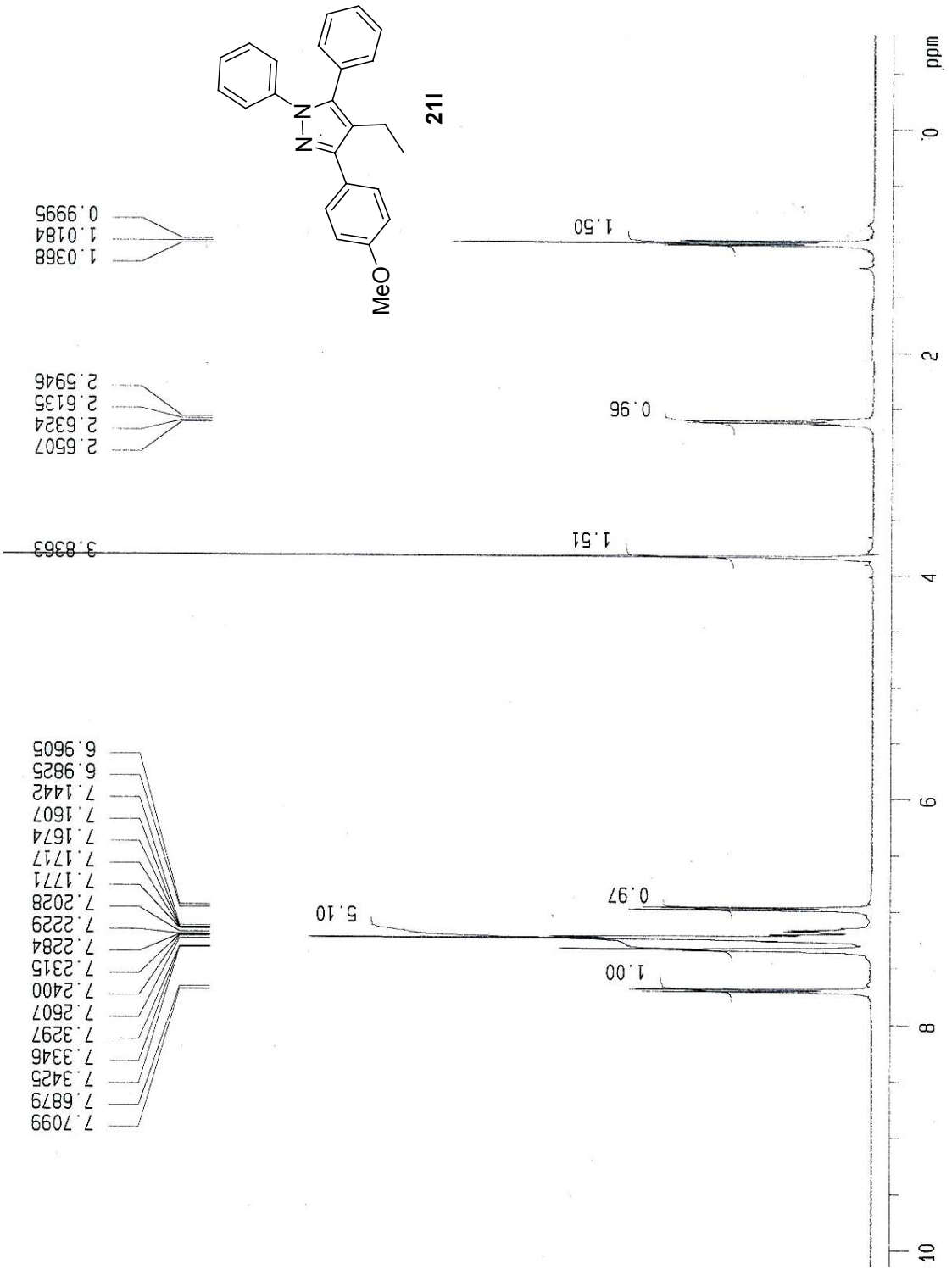


^{13}C NMR Spectrum of compound 17

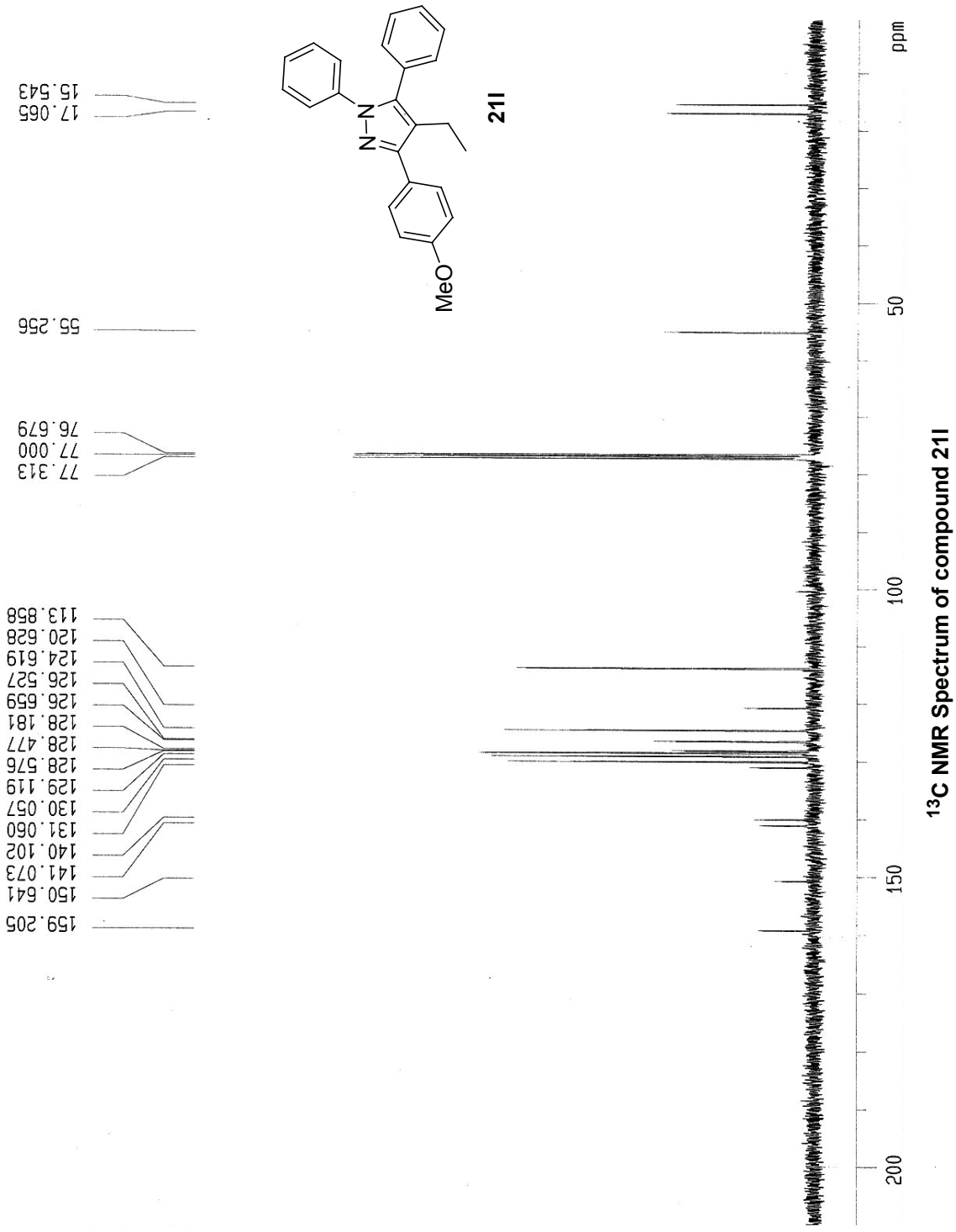
^{1}H NMR Spectrum of compound 19



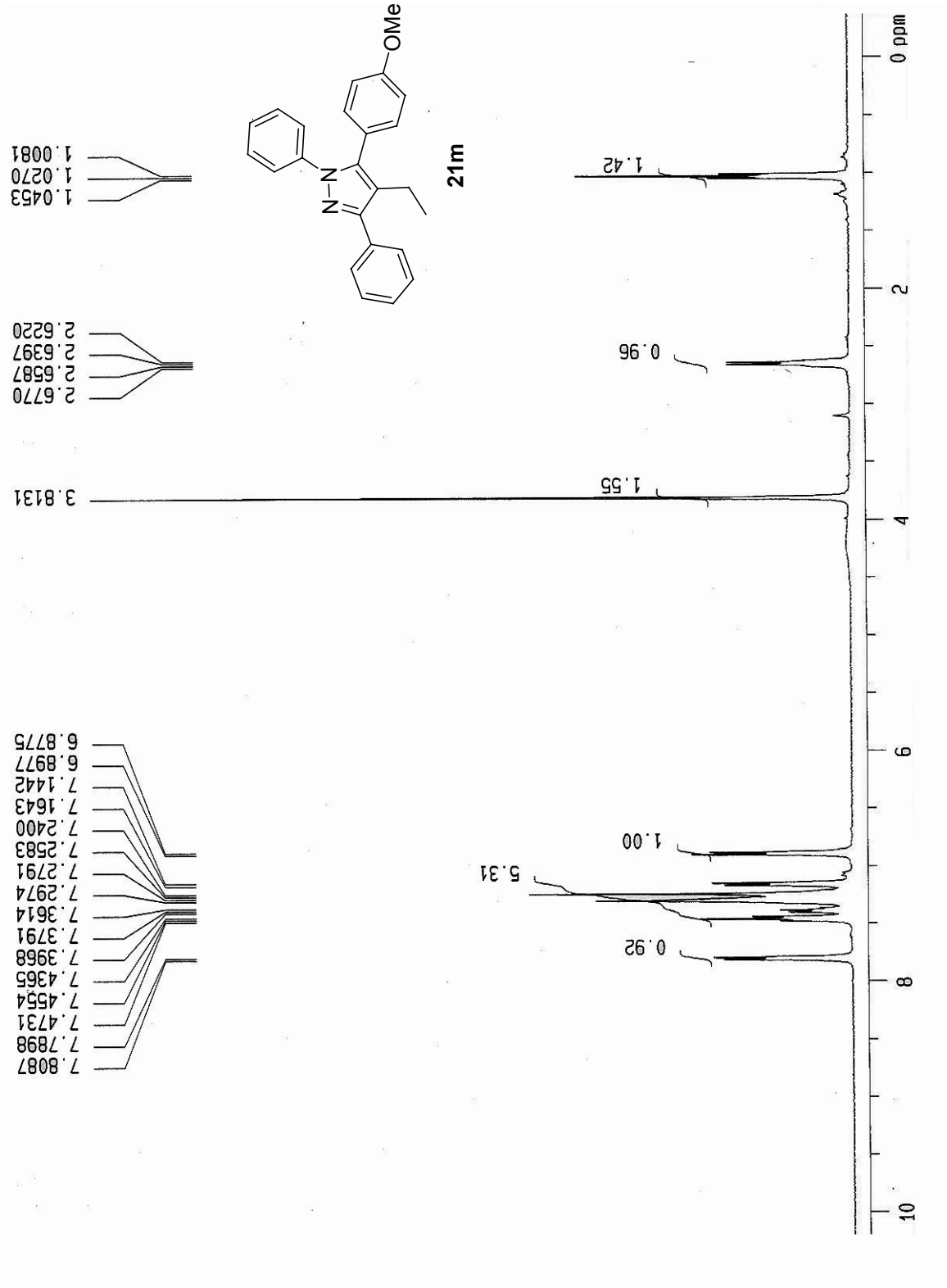
^{13}C NMR Spectrum of compound 19



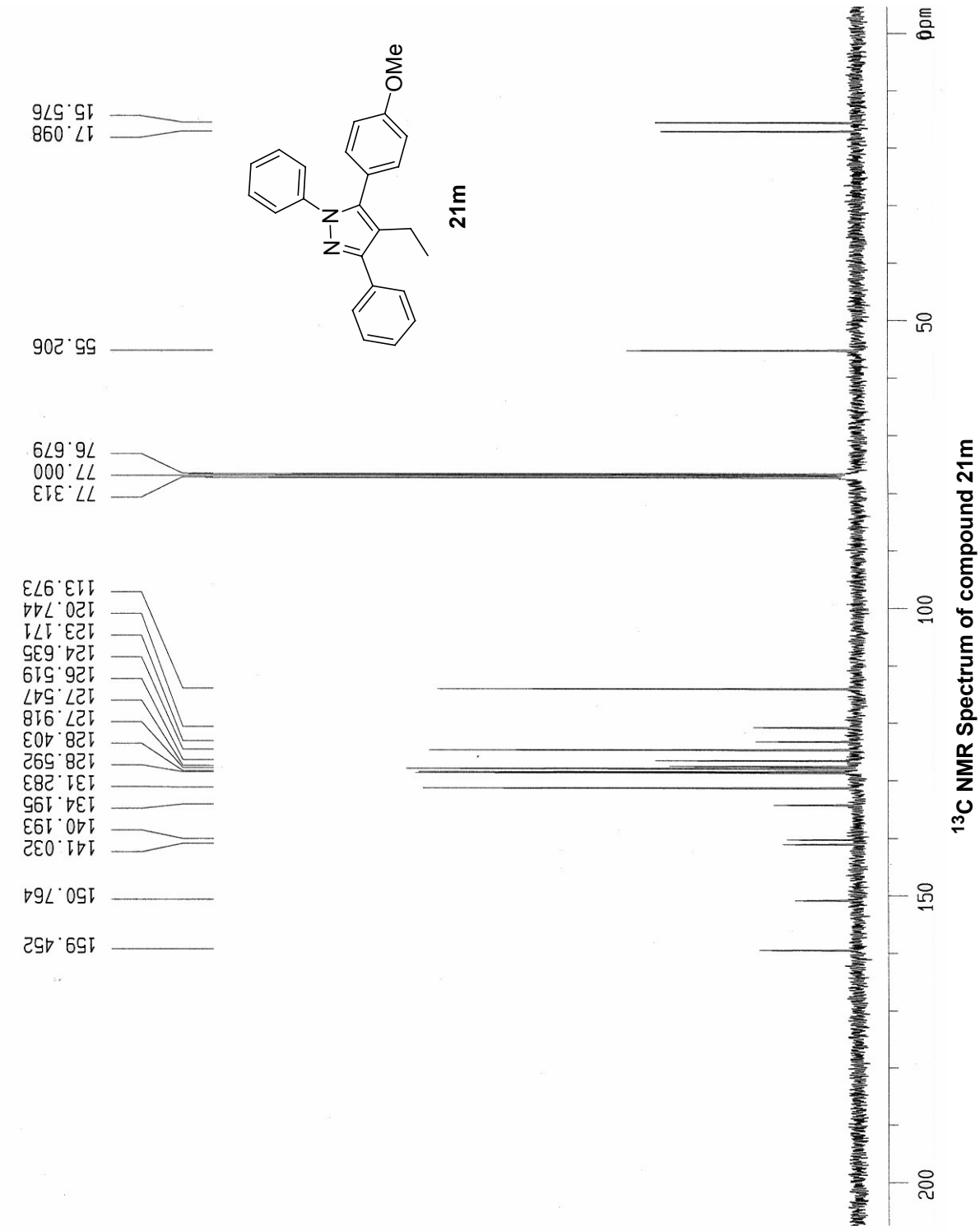
^{1}H NMR Spectrum of compound 21l



^{13}C NMR Spectrum of compound 21l



^{1}H NMR Spectrum of compound 21m



^{13}C NMR Spectrum of compound 21m