SUPPORTING INFORMATION FOR:

Synthesis of Quinolines, 2-Quinolones, Phenanthridines and 6(5*H*)-Phenanthridinones via Palladium[0]-Mediated Ullmann Cross-Coupling of 1-Bromo-2-nitroarenes with β-Halo-enals, -enones or –esters*

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Experimental Procedures and Product Characterization

General Experimental:

Melting points were measured on a Reichert hot-stage microscope apparatus and are uncorrected. Proton (^{1}H) and carbon (^{13}C) NMR spectra were recorded on a Varian Inova 500 spectrometer operating at 500 MHz for proton and 126 MHz for carbon. In certain cases a Gemini 300 NMR spectrometer, operating at 300 MHz (for proton) and 75 MHz (for carbon), was employed. Spectra were acquired at 20°C in deuterochloroform ($CDCl_3$) which had been filtered through basic alumina prior to use, or deuteromethanol (CD_3OD), deuterium oxide (D_2O) or deuterodimethyl sulfoxide [$(CD_3)_2SO$]. Signals arising from the residual protio-forms of the solvent were used as the internal standard. Chemical shifts were recorded as δ values in parts per million (ppm). The assignments of signals observed in the various NMR spectra were often assisted by conducting DEPT, APT, homonuclear (^{1}H/^{1}H) correlation spectroscopy (gDQFCOSY), and/or heteronuclear (^{1}H/^{13}C) correlation spectroscopy (gHMQC or gHMBC) experiments. Infrared spectra (ν_{max}) were recorded on a Perkin–Elmer 1800 Series FTIR Spectrometer. Samples were analysed as KBr disks (for solids) or as thin films on NaCl plates (for oils). Low resolution mass spectra were recorded on a Micromass–Waters LC-ZMD single quadrupole liquid chromatograph-MS or VG Quattro II triple quadrupole MS instrument using electrospray techniques in positive and/or negative ionization mode. Low resolution EI and FAB mass spectra were recorded on an AUTOSPEC spectrometer or a Kratos Analytical Concept ISQ instrument, the latter being located at the University of Tasmania. High resolution mass spectra were acquired by FAB methods on a Thermoquest Mat95XL instrument (located at CSIRO Molecular Science, Melbourne) or by EI methods on an AUTOSPEC instrument. Optical rotations were measured with a Perkin–Elmer 241 polarimeter at the sodium-D line (589 nm) and the concentrations (*c*) (g/100 mL) indicated using spectroscopic grade $CHCl_3$ unless otherwise specified. The measurements were carried out in a cell with a path length (l) of 1 dm. Specific rotations $[\alpha]_D$ were calculated using the equation $[\alpha]_D = 100.\alpha/(c.l)$ and are given in 10^{-1}.deg.cm^2.g^{-1}. Elemental analyses were performed by the Australian National University's Microanalytical Services Unit based at the Research School of Chemistry, Canberra, Australia. The unit cell parameters were recorded on a Nonius Kappa CCD instrument. Dichloromethane and chloroform were distilled from calcium hydride and THF and benzene were distilled, under nitrogen, from sodium benzophenone ketyl. Where necessary, reactions were performed under a nitrogen atmosphere.

(*Z*)–β-(2'-Nitrophenyl)cinnamaldehyde (7). A solution of 1-bromo-2-nitrobenzene (**1**, R=H) (396 mg, 2 mmol) and (*Z*)-β-bromocinnamaldehyde (**6**)[1] (420 mg, 2 mmol) in DMSO (6 mL) was treated with $Pd_2(dba)_3$ (60 mg, 3 mol%) and copper powder (630 mg, 0.01 g.-atom). The ensuing mixture was heated at 80 °C (oil bath) with vigorous stirring for 2 h then cooled and diluted with diethyl ether (50 mL). The resulting mixture was filtered through a pad of Celite™ and the solids thus retained were washed with diethyl ether (5 × 10 mL). The combined filtrates were washed with water (3 × 20 mL) and brine (1 × 30 mL) then dried ($MgSO_4$), filtered and concentrated under reduced pressure to give a yellow oil. Subjection of this material to flash chromatography (4:1 v/v hexane-ethyl acetate elution) and concentration of the appropriate fractions (R_f = 0.2) afforded compound **7** (310 mg, 68%) as a yellow crystalline solid, mp = 114–121 °C. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 9.42 (d, *J* = 8.1 Hz,1H), 8.22 (dd, *J* = 1.5 and 8.1 Hz, 1H), 7.78 (dt, *J* = 1.2 and 7.2 Hz, 1H), 7.68 (dt, *J* = 1.5 and 8.1 Hz, 1H), 7.48 (dd, *J* = 1.5 and 7.5 Hz, 1H), 7.26–7.39 (m, 5H), 6.70 (d, *J* = 8.1 Hz, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 191.5, 158.4, 148.1, 137.1, 133.5, 133.1, 131.9, 130.8, 130.3, 128.8, 127.2, 126.8, 125.3; IR ν_{max} (KBr) 3063, 2847, 2753, 1670, 1595, 1572, 1526, 1447, 1346, 1234, 1132, 1077, 855 cm^{-1}; MS, *m/z* (EI, 70eV) 253 ($M^{+\bullet}$, 13%), 233 (4), 224 (100), 196 (92), 180 (55), 178 (53), 167 (50), 165 (47), 152 (42), 77 (52); HRMS, Found: $M^{+\bullet}$, 253.0741 $C_{15}H_{11}NO_3$ requires $M^{+\bullet}$, 253.0739.

4-Phenylquinoline (8). Commercially available titanium(III) chloride tetrahydrofuran complex (1.68 g, 4 mmol) was dissolved in water (3 mL) then ammonium acetate (6 mL of a 2.5 M aqueous solution) and acetone (3 mL) were added. The resulting dark-blue and biphasic mixture was stirred at 18 °C for 10 minutes then a solution of compound **7** (127 mg, 0.5 mmol) in acetone (6 mL) was added dropwise. After 0.25 h the now pale-blue reaction mixture was diluted with water (100 mL) and extracted with ethyl acetate (3 × 75 mL). The combined extracts were washed with sodium bicarbonate (3 × 75 mL of a saturated aqueous solution) then brine (3 × 75 mL) before being dried ($MgSO_4$), filtered and concentrated under reduced pressure to give a light-yellow oil. Subjection of this material to flash chromatography (80:20:1 v/v/v hexane-ethyl acetate-triethylamine elution) and concentration of the appropriate fractions (R_f = 0.2) afforded compound **8**[2] (51%) as an opaque oil (lit.[2] mp = 61–62 °C). ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.94 (d, *J* = 4.5 Hz, 1H), 8.18 (dd, *J* = 1.2 and 8.7 Hz, 1H), 7.92 (d, *J* = 7.8 Hz, 1H), 7.72 (ddd, *J* = 1.2, 6.9 and 9.9 Hz, 1H), 7.54–7.46 (m, 6H), 7.34 (d, *J* = 4.5 Hz, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 149.9, 148.6, 148.5, 137.9, 129.8, 129.5, 129.3, 128.5, 128.4, 126.6, 125.8, 121.3, 125.3; IR ν_{max} (KBr) 3058, 1584, 1508, 1490, 1444, 1418, 1389, 850, 768, 698, 611 cm^{-1}; MS, *m/z* (EI, 70eV) 205 ($M^{+\bullet}$, 100%), 204 (93), 176 (28), 102 (23), 88 (15).

2-(2'-Nitrophenyl)cyclopent-1-enecarbaldehyde (10). Cross-coupling of 1-bromo-2-nitrobenzene (**1**, R=H) with 2-bromocyclopent-1-enecarboxaldehyde (**9**)[1] in the same manner as described above for the preparation of compound **7** gave an oily solid on work-up. Subjection of this material to flash

chromatography (4:1 v/v hexane-ethyl acetate elution) and concentration of the appropriate fractions (R_f = 0.3) afforded compound **10** (82%) as a yellow crystalline solid, mp = 105–115 °C. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 9.45 (s, 1H), 8.13 (dd, *J* = 1.2 and 8.1 Hz, 1H), 7.67 (dt, *J* = 1.5 and 7.5 Hz, 1H), 7.56 (dt, *J* = 1.2 and 7.5 Hz, 1H), 7.32 (dd, *J* = 1.5 and 7.5 Hz, 1H), 2.85 (broad t, *J* = 7.5 Hz, 2H), 2.71 (tt, *J* = 2.1 and 7.5 Hz, 2H), 2.07 (p, *J* = 7.5 Hz, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 188.5, 160.1, 147.5, 141.0, 133.4, 131.2(0), 131.1(8), 129.5, 125.0, 40.2, 30.1, 22.4; IR ν_{max} (neat) 2949, 2855, 1671, 1602, 1570, 1526, 1346, 1302, 1237, 847, 789, 746 cm^{-1}; MS, *m/z* (EI, 70eV) 218 ($M^{+\bullet}$, 37%), 188 (10), 131 (20), 89 (100), 88 (57), 73 (46), 70 (69), 61 (86); HRMS, Found: $(M+H)^+$, 218.0814. $C_{12}H_{11}NO_3$ requires $(M+H)^+$, 218.0817.

2,3-Dihydro-1*H*-cyclopenta[*c*]quinoline (11). A magnetically stirred solution of compound **10** (100 mg, 0.46 mmol) in methanol (20 mL) maintained at 18 °C was treated with 10% palladium on carbon (23 mg) and the resulting mixture exposed to an atmosphere of dihydrogen (1 atm.) while being protected from light. After 10 h the reaction mixture was filtered through a pad of Celite™ and the solids thus retained washed with methanol (20 mL). The combined filtrates were concentrated under reduced pressure to give a light-yellow oil. Subjection of this material to flash chromatography (80:20:1 v/v hexane-ethyl acetate-triethylamine elution) and concentration of the appropriate fractions (R_f = 0.3) afforded compound **11**[3] (92%) as a pale-yellow crystalline solid, mp = 45–52 °C (lit.[3] mp = 58–59 °C). ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.80 (s, 1H), 8.10 (d, *J* = 8.4 Hz, 1H), 7.76 (broad d, *J* = 7.8 Hz, 1H), 7.63 (broad t, *J* = 8.4 Hz, 1H), 7.50 (broad t, *J* = 7.8 Hz, 1H), 3.23 (t, *J* = 7.5 Hz, 2H), 3.10 (t, *J* = 7.5 Hz, 2H), 2.50 (p, *J* = 7.5 Hz, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 149.9, 147.6, 146.7, 136.6, 129.5, 128.2, 126.3, 126.0, 124.1, 31.2, 30.8, 24.3; IR ν_{max} (KBr) 3298, 2937, 2856, 1646, 1587, 1568, 1508, 1461, 1435, 1402, 1310, 1295, 1152, 1141, 756 cm^{-1}; MS, *m/z* (EI, 70eV) 169 ($M^{+\bullet}$, 40%), 168 (35), 167 (10), 115 (12), 65 (30), 63 (100), 62 (42), 58 (50); HRMS, Found: $M^{+\bullet}$, 169.0888. $C_{12}H_{11}N$ requires $M^{+\bullet}$, 169.0891.

2-(2'-Nitrophenyl)cyclohex-1-enecarbaldehyde (13). Cross-coupling of 1-bromo-2-nitrobenzene (**1**, R=H) with 2-bromocyclohex-1-enecarboxaldehyde (**12**)[1] in the same manner as described above for the preparation of compound **7** gave an oily solid on work-up. Subjection of this material to flash chromatography (9:1 v/v hexane-ethyl acetate elution) and concentration of the appropriate fractions (R_f = 0.2) afforded compound **13** (82%) as a yellow crystalline solid, mp = 55–58 °C. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 9.22 (s, 1H), 8.08 (dd, *J* = 1.2 and 8.1 Hz, 1H), 7.62 (dt, *J* = 1.2 and 7.5 Hz, 1H), 7.50 (dt, *J* = 1.2 and 8.1 Hz, 1H), 7.28 (dd, *J* = 1.2 and 7.5 Hz, 1H), 2.50 (m, 1H), 2.42–2.16 (complex m, 3H), 1.84–1.70 (complex m, 3H), 1.60 (m, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 191.3, 156.3, 147.2, 135.4, 135.1, 133.3, 131.0, 129.0, 124.8, 33.6, 22.1, 21.7, 21.0; IR ν_{max} (neat) 2931, 2867, 1670, 1630, 1606, 1570, 1522, 1345, 1273, 1212, 980, 855, 787, 747 cm^{-1}; MS, *m/z* (EI, 70eV) 232 [$(M+H)^+$, 1%), 202 (40), 186 (32), 174 (35), 158 (100), 146 (55), 144 (39), 132 (97), 130 (95), 128 (65), 115 (80), 91 (58), 77 (75); HRMS, Found: $(M+H)^+$, 232.0972 $C_{13}H_{13}NO_3$ requires $(M+H)^+$, 232.0974.

7,8,9,10-Tetrahydrophenanthridine (14). Reductive cyclization of compound **13** in the same manner as described above for the preparation of compound **11** afforded a light-yellow oil on work-up. Subjection of this material to flash chromatography (80:20:1 v/v/v hexane-ethyl acetate-triethylamine elution) and concentration of the appropriate fractions (R_f = 0.15) afforded compound **14**[2] (82%) as a pale-yellow crystalline solid, mp = 52–58 °C (lit.[2] mp = 61–62 °C). ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.62 (s, 1H), 8.06 (d, *J* = 8.4 Hz, 1H), 7.92 (d, *J* = 8.4 Hz, 1H), 7.63 (t, *J* = 8.4 Hz, 1H), 7.53 (t, *J* = 8.4 Hz, 1H), 3.11 (t, *J* = 6.3 Hz, 2H), 2.90 (t, *J* = 6.3 Hz, 2H), 1.93 (m, 4H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 152.3, 146.2, 141.4, 129.7, 129.6, 128.0, 127.6, 126.3, 122.6, 27.1, 24.9, 22.4, 22.3; IR ν_{max} (KBr) 2932, 1714, 1591, 1573, 1505, 1434, 1387, 1337, 1216, 1162, 1127, 909, 755 cm^{-1}; MS, *m/z* (EI, 70eV) 183 ($M^{+\bullet}$, 100%), 182 (75), 168 (39), 167 (42), 155 (75), 154 (50), 115 (35).

2-(2'-Nitrophenyl)cyclohept-1-enecarbaldehyde (16). Cross-coupling of 1-bromo-2-nitrobenzene (**1**, R=H) with 2-bromocyclohept-1-enecarboxaldehyde (**15**)[1] in the same manner as described above for the preparation of compound **7** gave yellow solid on work-up. Subjection of this material to flash chromatography (4:1 v/v hexane-ethyl acetate elution) and concentration of the appropriate fractions (R_f = 0.35) afforded compound **16** (75%) as a yellow crystalline solid, mp = 98–102 °C. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 9.21 (s, 1H), 8.15 (dd, *J* = 1.5 and 8.1 Hz, 1H), 7.63 (dt, *J* = 1.5 and 7.5 Hz, 1H), 7.53 (dt, *J* = 1.5 and 7.5 Hz, 1H), 7.24 (dd, *J* = 1.5 and 7.5 Hz, 1H), 2.93–2.77 (m, 2H), 2.40 (m, 2H), 1.99–1.68 (complex m, 4H), 1.58–1.30 (complex m, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 191.0, 162.4, 146.5, 141.3, 136.6, 133.4, 131.4, 129.1, 125.1, 38.4, 31.9, 25.7, 25.4, 24.0; IR ν_{max} (KBr) 2924, 2852, 1671, 1623, 1605, 1570, 1526, 1449, 1344, 749 cm^{-1}; MS, *m/z* (EI, 70eV) 245 ($M^{+\bullet}$, 10%), 216 (40), 197 (38), 172 (100), 146 (90), 132 (95), 130 (91), 115 (81), 77 (84); HRMS, Found: $M^{+\bullet}$, 245.1046 $C_{14}H_{15}NO_3$ requires $M^{+\bullet}$, 245.1052.

8,9,10,11-Tetrahydro-7*H*-cyclohepta[*c*]quinoline (17). Reductive cyclization of compound **16** in the same manner as described above for the preparation of compound **11** afforded a light-yellow oil on work-up. Subjection of this material to flash chromatography (70:30:1 v/v hexane-ethyl acetate-triethylamine elution) and concentration of the appropriate fractions (R_f = 0.35) afforded compound **17**[4] (84%) as an orange crystalline solid, mp = 65–67 °C (lit.[4] mp = 67 °C). ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.78 (d, *J* = 9.3 Hz, 1H), 8.40 (s, 1H), 8.07 (d, *J* = 9.3 Hz, 1H), 7.62–7.56 (complex m, 2H), 3.18 (m, 2H), 2.87 (m, 2H), 1.02 (m, 2H), 1.69 (m, 4H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 139.5, 136.3(4), 136.2(6), 128.9, 128.7, 128.2, 123.8, 120.1, 33.2, 31.9, 27.7, 27.0, 26.3; IR ν_{max} (KBr) 2923, 2852, 1627, 1387, 1307, 1187, 1146, 1083, 960, 761 cm^{-1}; MS, *m/z* (EI, 70eV) 197 ($M^{+\bullet}$, 100%), 168 (55), 155 (40), 86 (72), 84 (90), 75 (45).

2-(4'-Methoxy-2'-nitrophenyl)cyclohex-1-enecarbaldehyde (18). Cross-coupling of 1-bromo-4-methoxy-2-nitrobenzene (**1**, R=OMe) with 2-bromocyclohex-1-enecarbox-aldehyde (**12**)[1] in the same manner as described above for the preparation of compound **7** gave a yellow oil on work-up. Subjection of

this material to flash chromatography (7:3 v/v hexane-ethyl acetate elution) and concentration of the appropriate fractions (R_f 0.35) afforded compound **18** (88%) as a yellow oil. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 9.26 (s, 1H), 7.59 (m, 1H), 7.15 (m, 2H), 3.86 (s, 3H), 2.50–2.21 (complex m, 4H), 1.81–1.57 (complex m, 4H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 191.6, 159.6, 156.4, 147.9, 135.8, 131.9, 127.1, 119.8, 109.5, 55.8, 33.8, 22.2, 21.9, 21.1; IR ν_{max} (KBr) 2937, 2841, 1673, 1631, 1563, 1531, 1460, 1349, 1302, 1035, 1275, 1255, 1224, 799 cm^{-1}; MS, *m/z* (EI, 70eV) 261 ($M^{+\bullet}$, 1%), 232 (40), 216 (45), 215 (60), 204 (45), 188 (100), 176 (57), 162 (85), 160 (75), 115 (60), 77 (47); HRMS, Found: $M^{+\bullet}$, 261.0997 $C_{14}H_{15}NO_4$ requires $M^{+\bullet}$, 261.1001.

3-Methoxy-7,8,9,10-tetrahydrophenanthridine (19). Reductive cyclization of compound **18** in the same manner as described above for the preparation of compound **11** afforded a light-yellow oil on work-up. Subjection of this material to flash chromatography (75:25:1 v/v hexane-ethyl acetate-triethylamine elution) and concentration of the appropriate fractions (R_f = 0.2) afforded compound **19**[5] (68%) as an orange crystalline solid, mp = 75–78 °C (lit.[5] mp = 53–54.7 °C). ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.26 (s, 1H), 8.04 (s, 1H), 7.79 (d, *J* = 8.7 Hz, 1H), 7.22 (d, *J* = 8.7 Hz, 1H), 3.95 (s, 3H), 2.98 (t, *J* = 6.3 Hz, 2H), 2.73 (t, *J* = 6.3 Hz, 2H), 1.92–1.80 (complex m, 4H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 160.7, 140.5, 136.9, 133.6, 127.9, 124.6, 124.4, 121.1, 98.6, 55.8, 26.7, 24.7, 22.1, 22.0; IR ν_{max} (KBr) 2936, 1625, 1589, 1573, 1512, 1421, 1392, 1281, 1232, 1178, 1029, 733 cm^{-1}; MS, *m/z* (EI, 70eV) 213 ($M^{+\bullet}$, 60%), 200 (25), 199 (25), 185 (35), 115 (25), 86 (77), 84 (100); HRMS, Found: $M^{+\bullet}$, 213.1154. $C_{14}H_{15}NO$ requires $M^{+\bullet}$, 213.1154.

(*E*)-2-(2'-Nitrobenzylidene)cyclohexanone (21). A magnetically stirred mixture of (*E*)-2-(bromomethylene)cyclohexanone (**20**)[6] (234 mg, 1.24 mmol) and copper(I) iodide (283 mg, 1.49 mmol) in DMSO (8 mL) maintained at 70 °C was treated with 1-bromo-2-nitrobenzene (**1**, R=H) (500 mg, 2.48 mmol), copper powder (315 mg, 4.96 mmol) and $PdCl_2(dppf)_2{\cdot}CH_2Cl_2$ (25 mg). The resulting mixture was heated at 90 °C (oil bath) for 2 h, cooled to 18 °C and diluted with CH_2Cl_2 (60 mL) then ammonium chloride (120 mL of a saturated aqueous solution). The separated organic phase was washed with ammonium chloride (2 × 100 mL of a saturated aqueous solution) then dried ($MgSO_4$), filtered and concentrated under reduced pressure to give a yellow oil. Subjection of this material to flash chromatography (100:3 → 100:10 v/v hexane-ethyl acetate gradient elution) and concentration of the appropriate fractions (R_f = 0.4 in 55:25:10 v/v/v hexane-CH_2Cl_2-ethyl acetate) afforded compound **21** (204 mg, 71%) as a light-yellow solid, mp = 102–104 °C. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.11 (dd, *J* = 1.2 and 8.2 Hz, 1H), 7.63 (dt, *J* = 1.2 and 7.7 Hz, 1H), 7.59 (broad s, 1 H), 7.49 (dt, *J* = 1.2 and 8.2 Hz, 1H), 7.32 (d, *J* = 7.7 Hz, 1H), 2.60–2.44 (complex m, 4H), 1.93 (m, 2H), 1.73 (m, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 201.4 (C), 148.3 (C), 138.9 (C), 133.2 (CH), 131.8 (C), 131.3 (CH), 131.2 (CH), 129.0 (CH), 125.0 (CH), 40.7 (CH_2), 28.8 (CH_2), 24.0 (CH_2), 23.8 (CH_2); IR ν_{max} (KBr) 2937, 2864, 1690, 1602, 1524,

1344, 1142, 717 cm^{-1}; MS, *m/z* (EI, 70eV) 231 ($M^{+\bullet}$, 2%), 215 (8), 199 (44), 185 (25), 120 (65), 119 (100), 92 (50), 77 (27), 55 (35); HRMS, Found: $M^{+\bullet}$, 231.0892. $C_{13}H_{13}NO_3$ requires $M^{+\bullet}$, 231.0895.

1,2,3,4-Tetrahydroacridine (22). Reductive cyclization of compound **21** in the same manner as described above for the preparation of compound **11**, save for running the reaction for only 2 h, afforded a light-yellow oil on work-up. Subjection of this material to flash chromatography (100:5 → 100:25 v/v hexane-ethyl acetate gradient elution) and concentration of the appropriate fractions (R_f = 0.3 in 55:25:20 v/v/v hexane-CH_2Cl_2-ethyl acetate) afforded compound **22**[7] (46%) as a light-yellow solid, mp = 53–55 °C (lit.[7] mp = 55–57 °C). ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.98 (d, *J* = 8.4 Hz, 1H), 7.77 (s, 1H), 7.67 (d, *J* = 8.1 Hz, 1H), 7.59 (dt, *J* = 1.4 and 8.4 Hz, 1H), 7.41 (t, *J* = 8.1 Hz, 1H), 3.12 (t, *J* = 6.5 Hz, 2H), 2.94 (t, *J* = 6.5 Hz, 2H, 2H), 1.96 (m, 2H), 1.88 (m, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 159.3 (C), 146.6 (C), 135.2 (CH), 131.1 (C), 128.6 (CH), 128.3 (CH), 127.3 (C), 127.0 (CH), 125.7 (CH), 33.6 (CH_2), 29.3 (CH_2), 23.3 (CH_2), 23.0 (CH_2); IR ν_{max} (KBr) 2935, 2858, 1623, 1491, 1437, 1414, 1243, 750 cm^{-1}; MS, *m/z* (EI, 70eV) 183 ($M^{+\bullet}$, 100%), 182 (79), 168 (41), 154 (37), 115 (19), 77 (14); HRMS, Found: $M^{+\bullet}$, 183.1045. $C_{13}H_{13}N$ requires $M^{+\bullet}$, 183.1048.

(*E*)-2-(2'-Nitrobenzylidene)cycloheptanone (24). Cross-coupling of 1-bromo-2-nitrobenzene (**1**, R=H) with (*E*)-2-(bromomethylene)cycloheptanone (**23**)[6] in the same manner as described above for the preparation of compound **21** gave a yellow oil on work-up. Subjection of this material to flash chromatography (100:3 → 100:6 v/v hexane-ethyl acetate gradient elution) and concentration of the appropriate fractions (R_f = 0.4 in 55:25:10 v/v/v hexane-CH_2Cl_2-ethyl acetate) afforded compound **24**[8] (73%) as a yellow crystalline solid, mp = 105–107 °C (lit.[8] mp = 95–97 °C). ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.12 (dd, *J* = 1.2 and 8.2 Hz, 1 H), 7.71 (s, 1H), 7.63 (dt, *J* = 1.2 and 7.7 Hz, 1H), 7.49 (dt, *J* = 1.2 and 8.2 Hz, 1H), 7.27 (d, *J* = 7.7 Hz, 1H), 2.71 (m, 2H), 2.40 (m, 2H), 1.76 (m, 4H), 1.62 (m, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 203.6 (C), 148.2 (C), 141.6 (C), 133.4 (CH), 133.0 (CH), 132.8 (C), 131.1 (CH), 128.9 (CH), 125.0 (CH), 43.5 (CH_2), 31.3 (CH_2), 29.9 (CH_2), 28.1 (CH_2), 25.5 (CH_2); IR ν_{max} (KBr) 2933, 2917, 2858, 1682, 1614, 1599, 1523, 1349, 1173, 752 cm^{-1}; MS, *m/z* (EI, 70eV) 245 ($M^{+\bullet}$, <1%), 213 (6), 199 (27), 120 (96), 119 (100), 92 (57), 77 (30) HRMS, Found: $M^{+\bullet}$, 245.1050. $C_{14}H_{15}NO_3$ requires: $M^{+\bullet}$, 245.1052.

7,8,9,10-Tetrahydro-6*H*-cyclohepta[*b*]quinoline (25). A magnetically stirred mixture of compound **24** (310 mg, 1.26 mmol) and 10% Pd on carbon (78 mg) in methanol (2 mL) was exposed to dihydrogen (1 atm.). After stirring at 18 °C for 1 h, the reaction mixture was treated with triethylamine (1 mL) and after a further 5 h filtered through a short pad of Celite™ and the filtrate concentrated under reduced pressure. The ensuing light-yellow was subjected to flash chromatography (100:5 → 100:20 v/v hexane-ethyl acetate gradient elution) thus affording, after concentration of the appropriate fractions (R_f = 0.5 in 55:25:20 v/v/v hexane-CH_2Cl_2-ethyl acetate), compound **25**[9] (152 mg, 61%) as a white crystalline solid,

mp = 90–91.5 °C (lit.[9] mp = 91–92 °C). ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.00 (d, *J* = 8.4 Hz, 1H), 7.79 (s, 1H), 7.70 (dd, *J* = 1.3 and 8.2 Hz, 1H), 7.61 (m, 1H), 7.44 (m, 1H), 3.21 (m, 2H), 2.93 (m, 2H), 1.88 (m, 2H), 1.75 (m, 4H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 164.8 (C), 146.2 (C), 136.6 (C), 134.8 (CH), 128.6 (CH), 128.5 (CH), 127.5 (C), 126.9 (CH), 125.9 (CH), 40.1 (CH_2), 35.6 (CH_2), 32.3 (CH_2), 29.0 (CH_2), 27.1 (CH_2); IR ν_{max} (KBr) 2924, 2850, 1491, 1448, 1420, 1340, 750 cm^{-1}; MS, *m/z* (EI, 70eV) 197 ($M^{+\bullet}$, 100%), 196 (56), 182 (41), 168 (59), 115 (17); HRMS, Found: $M^{+\bullet}$, 197.1202. $C_{14}H_{15}N$ requires: $M^{+\bullet}$, 197.1205.

2-(4'-Methoxy-2'-nitrobenzylidene)cyclohexanone (26). Cross-coupling of 1-bromo-4-methoxy-2-nitrobenzene (**1**, R=OMe) with (*E*)-2-(bromomethylene)cyclohexanone (**20**)[6] in the same manner as described above for the preparation of compound **21** gave a yellow oil on work-up. Subjection of this material to flash chromatography (100:3 → 100:5 v/v hexane-ethyl acetate gradient elution) and concentration of the appropriate fractions (R_f = 0.3 in 55:25:10 v/v/v hexane-CH_2Cl_2-ethyl acetate) afforded compound **26** (75%) as a light-yellow solid, mp = 90–92 °C. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.61 (d, *J* = 2.6 Hz, 1H), 7.52 (m, 1H), 7.24 (d, *J* = 9.6 Hz, 1H), 7.15 (dd, *J* = 2.6 and 9.6 Hz, 1H), 3.89 (s, 3H), 2.55 (m, 4H), 1.92 (m, 2H), 1.73 (m, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 201.6 (C), 159.8 (C), 149.3 (C), 138.3 (C), 132.4 (CH), 131.2 (CH), 123.8 (C), 119.7 (CH), 109.6 (CH), 56.1 (CH_3), 40.7 (CH_2), 28.9 (CH_2), 24.1 (CH_2), 23.9 (CH_2); IR ν_{max} (KBr) 2942, 2867, 1686, 1619, 1529, 1345, 1250, 1141, 1033 cm^{-1}; MS, *m/z* (EI, 70eV) 261 ($M^{+\bullet}$, <1%), 229 (7), 215 (37), 150 (59), 149 (100), 122 (22), 77 (14), 55 (21); HRMS, Found: $M^{+\bullet}$, 261.1010. $C_{14}H_{15}NO_4$ requires: $M^{+\bullet}$, 261.1001.

1,2,3,4-Tetrahydro-6-methoxyacridine (27). Reductive cyclization of compound **26** in the same manner as described above for the preparation of compound **25** afforded a light-solid on work-up. Subjection of this material to flash chromatography (100:30 v/v hexane-ethyl acetate elution) and concentration of the appropriate fractions (R_f = 0.5 in 40:25:55 v/v/v ethyl acetate-CH_2Cl_2-hexane) afforded compound **27**[10] (51%) as a light-yellow crystalline solid, mp = 51–52 °C (lit.[10] mp = 58–59 °C). ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.70 (s, 1H), 7.55 (d, *J* = 8.9 Hz, 1H), 7.31 (d, *J* = 2.5 Hz, 1H), 7.08 (dd, *J* = 2.5 and 8.9 Hz, 1H), 3.91 (s, 3H), 3.08 (t, *J* = 6.5 Hz, 2H), 2.91 (t, *J* = 6.3 Hz, 2H), 1.96 (m, 2H), 1.86 (m, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 160.2 (C), 159.3 (C), 148.1 (C), 135.1 (CH), 128.7 (C), 128.0 (CH), 122.5 (C), 118.9 (CH), 106.3 (CH), 55.5 (CH_3), 33.5 (CH_2), 29.8 (CH_2), 23.3 (CH_2), 23.1 (CH_2); IR ν_{max} (KBr) 2933, 2858, 1626, 1498, 1454, 1239, 1031, 732 cm^{-1}; MS, *m/z* (EI, 70eV) 213 ($M^{+\bullet}$, 100%), 212 (44), 198 (39), 185 (24), 170 (18), 115 (12); HRMS, Found: $M^{+\bullet}$, 213.1151. $C_{14}H_{15}NO$ requires: $M^{+\bullet}$, 213.1154.

1-(2'-Nitrophenyl)-3,4-dihydronaphthalene-2-carbaldehyde (29). Cross-coupling of 1-bromo-2-nitrobenzene (**1**, R=H) with aldehyde **28**[11] in the same manner as described above for the preparation of compound **7** gave an oily solid on work-up. Subjection of this material to flash chromatography (3:1 v/v

hexane-ethyl acetate elution) and concentration of the appropriate fractions (R_f = 0.4) afforded compound **29** (93%) as a yellow powder, mp = 118 °C. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 9.49 (s, 1H), 8.26 (ddd, *J* = 0.6, 1.2 and 8.1 Hz, 1H), 7.77 (dt, *J* = 1.5 and 7.5 Hz, 1H), 7.68 (m, 1H), 7.44 (dd, *J* = 1.5 and 7.5 Hz, 1H), 7.29 (complex m, 1H), 7.28 (d, *J* = 0.9 Hz, 1H), 7.08 (m, 1H), 6.59 (d, *J* = 7.5 Hz, 1H), 3.10–2.83 (complex m, 3H), 2.61–2.49 (complex m, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 191.3, 151.1, 148.7, 138.4, 134.2, 133.8, 133.4, 133.1, 131.2, 130.5, 129.9, 128.1, 126.8, 126.3, 125.2, 27.2, 20.0; IR ν_{max} (NaCl) 2848, 1665, 1525, 1345, 855, 777, 721 cm^{-1}; MS, *m/z* (EI, 70eV) 279 ($M^{+\bullet}$, 9%), 250 (76), 231 (36), 217 (25), 206 (100), 202 (89), 189 (22), 180 (36), 165 (22), 101 (24); HRMS, Found: $M^{+\bullet}$, 279.0895. $C_{17}H_{13}NO_3$ requires $M^{+\bullet}$, 279.0895.

7,8-Dihydrobenzo[*k*]phenanthridine (30). Reductive cyclization of compound **29** in the same manner as described above for the preparation of compound **11** afforded a light-yellow oil on work-up. Subjection of this material to flash chromatography (47:47:6 v/v/v hexane-ethyl acetate-triethylamine elution) and concentration of the appropriate fractions (R_f = 0.4) afforded compound **30**[11] (87%) as a light-yellow oil. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.83 (s, 1H), 8.51 (d, *J* = 8.4 Hz, 1H), 8.15 (dd, *J* = 0.9 and 8.4 Hz, 1H), 8.01–7.98 (complex m, 1H), 7.69 (two overlapping dd, *J* = 1.2 and 6.9 Hz, 1H), 7.57 (two overlapping dd, *J* = 1.4 and 6.9 Hz, 1H), 7.45–7.38 (complex m, 3H), 2.96–2.85 (complex m, 4H); IR ν_{max} (CH_2Cl_2) 1651, 1607, 1569, 1558, 1505, 1487 cm^{-1}; MS, *m/z* (EI, 70eV) 231 ($M^{+\bullet}$, 100%), 230 (78), 202 (37), 101 (24).

1-(4'-Methoxy-2'-nitrophenyl)-3,4-dihydronaphthalene-2-carbaldehyde (31). Cross-coupling of 1-bromo-4-methoxy-2-nitrobenzene (**1**, R=OMe) with aldehyde **28**[11] in the same manner as described above for the preparation of compound **7** gave a yellow crystalline solid on work-up. Subjection of this material to flash chromatography (4:1 v/v hexane-ethyl acetate elution) and concentration of the appropriate fractions (R_f = 0.7) afforded compound **31** (89%) as a yellow crystalline solid, mp = 204 °C. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 9.52 (s, 1H), 7.75 (d, *J* = 2.1 Hz, 1H), 7.33–7.24 (complex m, 4H), 7.10–7.05 (complex m, 1H), 6.63 (d, *J* = 7.5 Hz, 1H), 3.96 (s, 3H), 3.07–2.81 (complex m, 3H), 2.58–2.47 (complex m, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 191.6, 160.3, 151.1, 149.4, 138.5, 134.4, 134.2, 133.9, 130.4, 128.0, 126.7, 126.2, 122.9, 119.8, 109.9, 56.0, 27.2, 20.1; IR ν_{max} (NaCl) 2840, 1663, 1531, 1347, 1300, 1031, 775, 736 cm^{-1}; MS, *m/z* (EI, 70eV) 309 ($M^{+\bullet}$, 14%), 280 (60), 263 (42), 236 (100), 189 (61), 165 (30), 152 (17), 115 (16), 63 (11); HRMS, Found: $M^{+\bullet}$, 309.0999. $C_{18}H_{15}NO_4$ requires $M^{+\bullet}$, 309.1001.

3-Methoxy-7,8-dihydrobenzo[*k*]phenanthridine (32). Reductive cyclization of compound **31** in the same manner as described above for the preparation of compound **11** afforded a light-yellow oil on work-up. Subjection of this material to flash chromatography (47:47:6 v/v/v hexane-ethyl acetate-triethylamine elution) and concentration of the appropriate fractions (R_f = 0.2) afforded compound **32** (91%) as a yellow oil. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.34 (d, *J* = 9.6 Hz, 1H), 8.33 (s, 1H), 8.12 (d, *J* = 2.7 Hz, 1H), 7.79

(d, J = 6.6 Hz, 1H), 7.42–7.34 (complex m, 3H), 7.27 (dd, J = 2.7 and 9.6 Hz, 1H), 4.00 (s, 3H), 2.84–2.69 (complex m, 4H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 160.9, 142.4, 139.6, 135.4, 132.0, 131.2, 129.3, 128.7, 128.6, 128.4, 127.5, 126.7, 121.8, 121.6, 98.4, 55.9, 28.7, 26.5; IR ν_{max} (NaCl) 2927, 1645, 1624, 1481, 1384, 1275, 1225, 1199, 1164, 1026 cm^{-1}; MS, *m/z* (EI, 70eV) 277 ([M+O]$^{+\bullet}$, 100%), 261 (M$^{+\bullet}$, 99%), 247 (14), 230 (20), 217 (28), 189 (25); HRMS, Found: M$^{+\bullet}$, 261.1156. $C_{18}H_{15}NO$ requires M$^{+\bullet}$, 261.1154.

4,5-Methylenedioxy-2'-nitro-2-biphenylcarbaldehyde (34). Cross-coupling of 1-bromo-2-nitrobenzene (**1**, R=H) with aldehyde **33** in the same manner as described above for the preparation of compound **7** gave a yellow solid on work-up. Subjection of this material to flash chromatography (4:1 v/v hexane-ethyl acetate elution) and concentration of the appropriate fractions (R_f = 0.45 in 7:3 v/v hexane-ethyl acetate) afforded compound **34**[12] (57%) as a yellow solid, mp = 135–138 °C (lit.[12] mp = 227–228 °C). ^{1}H NMR ($CDCl_3$, 300 MHz) δ 9.57 (s, 1H), 8.07 (dd, J = 1.8 and 7.5 Hz, 1H), 7.67 (dt, J = 1.5 and 7.5 Hz, 1H), 7.60 (dt, J = 1.8 and 7.5 Hz, 1H), 7.45 (s, 1H), 7.37 (dd, J = 1.5 and 7.5 Hz, 1H), 6.67 (s, 1H), 6.12 (m, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 188.8, 152.1, 149.1, 148.4, 137.7, 132.8, 132.6, 129.4, 128.8, 124.4, 109.5, 107.2, 102.4 (one signal obscured or overlapping); IR ν_{max} (KBr) 1678, 1609, 1523, 1476, 1407, 1360, 1349, 1270, 1255, 1230, 1035 cm^{-1}; MS, *m/z* (EI, 70eV) 271 (M$^{+\bullet}$, 30%), 242 (20), 225 (100), 198 (24), 139 (65); HRMS, Found: M$^{+\bullet}$, 271.0471 $C_{14}H_9NO_5$ requires M$^{+\bullet}$, 271.0481.

Trispheridine {[1,3]Dioxolo[4,5-*j*]phenanthridine} (35). Reductive cyclization of compound **34** in the same manner as described above for the preparation of compound **11** afforded compound **35**[13] (68%) as a pale-yellow solid, mp = 111–125 °C, [lit.[13] mp = 144.5–145 °C (sublimation from 119 °C onwards)]. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 9.09 (s, 1H), 8.38 (d, J = 7.2 Hz, 1H), 8.14 (d, J = 8.7 Hz, 1H), 7.91 (s, 1H), 7.69 (t, J = 8.7 Hz, 1H), 7.63 (d, J = 7.2 Hz, 1H), 7.34 (s, 1H), 6.17 (s, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 151.7, 151.5, 148.2, 144.0, 130.2, 130.0, 128.0, 126.7, 124.2, 123.0, 122.0, 105.5, 101.9, 99.9; IR ν_{max} (KBr) 2916, 1620, 1583, 1499, 1484, 1464, 1393, 1256, 1226, 1197, 1038, 942, 830, 760 cm^{-1}; MS, *m/z* (EI, 70eV) 223 (M$^{+\bullet}$, 100%), 164 (12), 138 (20), 111 (10), 86 (42), 84 (57); HRMS, Found: M$^{+\bullet}$, 223.0631 $C_{14}H_9NO_2$ requires M$^{+\bullet}$, 223.0633.

7-Methoxy-8-(2'-nitrophenyl)-3,4,-dihydro-2*H*-naphthalen-1-one (37). A magnetically stirred mixture of 1-bromo-2-nitrobenzene (**1**, R=H) (300 mg, 1.5 mmol), $Pd_2(dba)_3$ (25 mg, 5 mol%) and copper powder (160 mg, 2.5 mmol) in DMSO (3 mL) was heated to 80 °C whilst being maintained under a nitrogen atmosphere then a solution of tetralone **36**[14] (125 mg, 0.5 mmol) in DMSO (1 mL) was added *via* syringe pump over a period of 1 h. After addition was complete the reaction mixture was maintained at 80 °C for 4 h. Work-up of the cooled reaction mixture in the same manner as described for the preparation of compound **7** gave a yellow powder. Subjection of this material to flash chromatography (3:2 v/v hexane-ethyl acetate elution) afforded two major fractions, A and B.

Concentration of fraction A (R_f = 0.6) afforded a mixture of the desired cross-coupling product and 2,2'-dinitrobiphenyl [product from reductive dimerization of compound (**1** R=H)].

Concentration of fraction B (R_f = 0.3) afforded **2,2'-dimethoxy-6,6'7',7'-5H,5'H-[1,1]binaphthalenyl-8,8'-dione** (product from reductive dimerization of compound **36**) (34%) as a white crystalline solid, mp = 178–180 °C. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.21 (d, *J* = 8.4 Hz, 2H), 7.07 (d, *J* = 8.4 Hz, 2H), 3.63 (s, 6H), 2.96 (complex m, 4H), 2.47 (t, *J* = 6.6 Hz, 4H), 2.16–1.98 (complex m, 4H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 198.6, 155.0, 136.9, 131.4, 128.8, 128.1, 115.8, 56.4, 40.0, 30.0, 23.2; IR ν_{max} (NaCl) 2923, 2857, 1681, 1483, 1268, 1219, 1189, 1027, 988, 921, 824 cm^{-1}; MS, *m/z* (EI, 70eV) 350 ($M^{+\bullet}$, 100%), 319 (56), 294 (53), 279 (44), 251 (21), 189 (48), 147 (18); HRMS, Found: $M^{+\bullet}$, 350.1520. $C_{22}H_{22}O_4$ requires $M^{+\bullet}$, 350.1518.

Subjection of fraction A, obtained as described above, to flash chromatography (4:1 v/v dichloromethane-pentane elution) and concentration of the appropriate fractions (R_f = 0.6) afforded compound **37** (53%) as a yellow solid, mp = 204 °C. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.16 (dd, *J* = 1.2 and 8.4 Hz, 1H), 7.59 (dt, *J* = 1.5 and 7.5 Hz, 1H), 7.47 (dt, *J* = 1.5 and 7.5 Hz, 1H), 7.30 (d, *J* = 8.4 Hz, 1H), 7.12 (dd, *J* = 1.5 and 7.5 Hz, 1H), 7.10 (d, *J* = 8.4 Hz, 1H), 3.65 (s, 3H), 2.98 (t, *J* = 6.3 Hz, 2H), 2.53 (t, *J* = 6.1 Hz, 2H), 2.18–2.00 (complex m, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 198.4, 154.9, 148.0, 137.4, 134.8, 132.8, 131.2, 130.8, 129.6, 128.0, 127.3, 124.2, 115.8, 56.1, 40.0, 29.8, 23.1; IR ν_{max} (NaCl) 2937, 1678, 1520, 1347, 1270, 1028, 936, 854, 788, 754 cm^{-1}; MS, *m/z* (EI, 70eV) 297 ($M^{+\bullet}$, 1%), 251 (100), 236 (12), 198 (11), 149 (7); HRMS, Found: $M^{+\bullet}$, 297.1012. $C_{17}H_{15}NO_4$ requires $M^{+\bullet}$, 297.1001.

5,6-Dihydro-11-Methoxy-4*H*-benz[*kl*]acridine (38). Reductive cyclization of compound **37** in the same manner as described above for the preparation of compound **11** afforded a clear colorless oil on work-up. Subjection of this material to flash chromatography (63:31:6 v/v/v hexane-ethyl acetate-triethylamine elution) and concentration of the appropriate fractions (R_f = 0.4) afforded compound **38** (92%) as a clear, yellow oil. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 9.45 (d, *J* = 8.4 Hz, 1H), 8.17 (d, *J* = 8.4 Hz, 1H), 7.69 (t, *J* = 8.4 Hz, 1H), 7.58 (t, *J* = 8.4 Hz, 1H), 7.40 (d, *J* = 8.4 Hz, 1H), 7.23 (d, *J* = 8.1 Hz, 1H), 4.09 (s, 3H), 3.36 (t, *J* = 6.0 Hz, 2H), 3.12 (t, *J* = 6.0 Hz, 2H), 2.22–2.14 (complex m, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 159.7, 156.3, 143.9, 131.1, 128.7, 127.9, 126.7, 125.8, 124.8, 123.7, 123.0, 111.7, 55.7, 35.7, 30.8, 23.2 (one signal obscured or overlapping); IR ν_{max} (NaCl) 2926, 2855, 1574, 1455, 1435, 1361, 1248, 1122, 1046, 1027, 814, 765 cm^{-1}; MS, *m/z* (EI, 70eV) 249 ($M^{+\bullet}$, 100%), 234 (45), 206 (19), 204 (22); HRMS, Found: $M^{+\bullet}$, 249.1148. $C_{17}H_{15}NO$ requires $M^{+\bullet}$, 249.1154.

3-(2'-Nitrophenyl)-1*H*-indole-2-carbaldehyde (40). Cross-coupling of 1-bromo-2-nitrobenzene (**1**, R=H) with aldehyde **39**[15] in the same manner as described above for the preparation of compound **7** gave a yellow powder on work-up. Subjection of this material to flash chromatography (1:1 v/v hexane-ethyl acetate elution) and concentration of the appropriate fractions (R_f = 0.7) afforded a mixture of the desired cross-coupling product and 2,2'-dinitrobiphenyl [product from reductive dimerization of compound (**1**

R=H)]. Subjection of this material to flash chromatography (1:1 v/v hexane-diethyl ether elution) and concentration of the appropriate fractions (R_f = 0.4) then afforded compound **40** (63%) as a powder solid, mp = 158 °C. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 9.72 (s, 1H), 9.33 (broad s, 1H), 8.11 (dd, *J* = 1.5 and 7.5 Hz, 1H), 7.74 (dt, *J* = 1.5 and 7.5 Hz, 1H), 7.65 (dt, *J* = 1.8 and 8.1 Hz, 1H), 7.58 (dd, *J* = 1.8 and 7.5 Hz, 1H), 7.48 (t, *J* = 8.4 Hz, 1H), 7.45–7.38 (complex m, 2H), 7.19–7.13 (complex m, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 181.4, 136.7, 134.2, 132.6, 132.0, 129.4, 127.9, 126.9, 126.5, 124.8(4), 124.8(0), 123.8, 121.9, 121.1, 112.7; IR ν_{max} (NaCl) 1652, 1525, 1349, 1333, 1231, 1231, 1016, 867, 851, 785, 740, 702 cm^{-1}; MS, *m/z* (EI, 70eV) 266 ($M^{+\bullet}$, 100%), 221 (64), 219 (60), 210 (83), 209 (93), 190 (49), 181 (67), 165 (68), 152 (44), 139 (24), 77 (28), 63 (24); HRMS, Found: $M^{+\bullet}$, 266.0689. $C_{15}H_{10}N_2O_3$ requires $M^{+\bullet}$, 266.0691.

7*H*-Indolo[2,3-*c*]quinoline (41). Reductive cyclization of compound **40** in the same manner as described above for the preparation of compound **11** afforded a clear colorless oil on work-up. Subjection of this material to flash chromatography (42:42:8 v/v/v hexane-ethyl acetate-triethylamine elution) and concentration of the appropriate fractions (R_f = 0.1) afforded compound **41**[16] (66%) as a yellow powder, mp = 251 °C (lit.[16] mp = 249 °C). ^{1}H NMR [$(CD_3)_2CO$, 300 MHz] δ 11.24 (broad s, 1H), 9.31 (s, 1H), 8.81 (dd, *J* = 1.2 and 8.4 Hz, 1H), 8.68 (d, *J* = 8.1 Hz, 1H), 8.22 (dd, *J* = 1.2 and 8.1 Hz, 1H), 7.81–7.73 (complex m, 2H), 7.65 (ddd, J = 1.5, 6.9 and 8.1 Hz, 1H), 7.59 (ddd, *J* = 1.2, 7.2 and 8.1 Hz, 1H), 7.42 (ddd, *J* = 1.2, 7.2 and 8.1 Hz, 1H); ^{13}C NMR [$(CD_3)_2CO$, 75 MHz] δ 143.9, 140.6, 139.5, 133.9, 131.3, 127.8, 127.5, 126.0, 125.6, 124.1, 123.8, 122.9, 121.3, 121.0, 113.4; IR ν_{max} (KBr disc) 2924, 2853, 1622, 1341, 1137, 1110, 762, 745 cm^{-1}; MS, *m/z* (EI, 70eV) 218 ($M^{+\bullet}$, 100%), 190 (12), 164 (6), 163 (6), 109 (7); HRMS, Found: $M^{+\bullet}$, 218.0837. $C_{15}H_{10}N_2$ requires $M^{+\bullet}$, 218.0844.

2-(2'-Nitrophenyl)cyclohex-1-ene Carboxylic Acid Methyl Ester (43). Cross-coupling of 1-bromo-2-nitrobenzene (**1**, R=H) with bromo-ester **42**[17] was carried out in the same manner as described above for the preparation of compound **7** save for the use of a reaction temperature of 90 °C and a reaction time of 6 h. The yellow oil obtained on work-up was subjected to flash chromatography (9:1 v/v hexane-ethyl acetate elution) and three fractions, A–C, were obtained.

Concentration of fraction A (R_f = 0.4) afforded the starting ester **42** (8% recovery) which was identical, in all respects, with an authentic sample.

Concentration of fraction B (R_f = 0.2) afforded 2,2'-dinitrobiphenyl (18% at 92% conversion) which was identical, in all respects, with an authentic sample.

Concentration of fraction C (R_f = 0.1) afforded compound **43** (39% at 92% conversion) as a yellow oil. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.04 (dd, *J* = 1.2 and 8.2 Hz, 1H), 7.55 (dt, *J* = 1.2 and 7.4 Hz, 1H), 7.39 (ddd, *J* = 1.5, 7.4 and 8.2 Hz, 1H), 7.10 (dd, *J* = 1.5 and 7.4 Hz, 1H), 3.38 (s, 3H), 2.60–2.18 (complex m, 4H), 1.86–1.54 (complex m, 4H); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 167.6 (CO), 147.0 (C), 146.9 (C), 139.8 (C), 133.2 (CH), 129.0 (CH), 127.5 (CH), 125.8 (C), 124.2 (CH), 51.3 (CH_3), 33.6

(CH_2), 25.8 (CH_2), 22.2 (CH_2), 21.9 (CH_2); IR ν_{max} (KBr) 2935, 1716, 1524, 1348, 1241, 1052 cm^{-1}; MS, *m/z* (EI, 70eV) 261 ($M^{+\bullet}$, 2%), 243 (40), 215 (78), 202 (70), 146 (100%), 132 (93), 130 (70), 115 (64), 77 (60); HRMS, Found: $M^{+\bullet}$, 261.0999. $C_{14}H_{15}NO_4$ requires $M^{+\bullet}$, 261.1001

7,8,9,10-Tetrahydro-6(5*H*)-phenanthridinone (44). Reductive cyclization of compound **43** was achieved in the same manner as described above for the preparation of compound **11** save for the use of a 1 h reaction time. In this manner a clear, colorless oil was obtained on work-up. Subjection of this material to flash chromatography (95:4.25:0.75 v/v/v dichloromethane-methanol-15% aq. ammonia elution) and concentration of the appropriate fractions (R_f = 0.15) afforded an orange solid. Recrystallization (from ethyl acetate–hexane) of this material yielded compound **44**[18] (78%) as a white crystalline masses, mp = 263–265 °C (lit.[18] mp = 268–270 °C). ^{1}H NMR (CD_3OD, 300 MHz) δ 7.76 (dd, *J* = 0.9 and 8.1 Hz, 1H), 7.46 (m, 1H), 7.33–7.22 (complex m, 2H), 2.93 (m, 2H), 2.58 (m, 2H), 1.95–1.78 (complex m, 4H); ^{13}C NMR (CD_3OD, 126 MHz) δ 164.6 (CO), 146.3 (C), 137.7 (C), 130.4 (CH), 128.8 (C), 124.4 (CH), 123.7 (CH), 121.8 (C), 116.7 (CH), 26.6 (CH_2), 24.9 (CH_2), 23.0 (CH_2), 22.9 (CH_2); IR ν_{max} (KBr) 2935, 2854, 1648, 1566, 1505, 1437, 746 cm^{-1}; MS, *m/z* (EI, 70eV) 199 ($M^{+\bullet}$, 100%), 198 (73), 184 (67); HRMS, Found: $M^{+\bullet}$, 199.0995. $C_{13}H_{13}NO$ requires $M^{+\bullet}$, 199.0997

2'Nitro-[1,1'-biphenyl]-2-carboxylic Acid Methyl Ester (46). Cross-coupling of 1-iodo-2-nitrobenzene with commercially available iodo-ester **45** was carried out in the same manner as described above for the preparation of compound **7** save for the use of a reaction temperature of 90 °C and a reaction time of 2.5 h. The yellow solid obtained on work-up was subjected to flash chromatography (9:1 v/v hexane-ethyl acetate elution) and two fractions, A and B, thereby obtained.

Concentration of fraction A (R_f = 0.3) afforded 2,2'-dinitrobiphenyl (78%) which was identical, in all respects, with an authentic sample.

Concentration of fraction B (R_f = 0.2) afforded a *ca*. 1:1 mixture of compound **46** and **[1,1'-biphenyl]-2,2'-dicarboxylic acid dimethyl ester** (product from reductive dimerization of compound **45**) as a yellow oil. This mixture was immediately subject to a reductive cyclization reaction as detailed below.

6(5*H*)-phenanthridinone (47). A *ca*. 1:1 mixture of compound **46** and **[1,1'-biphenyl]-2,2'-dicarboxylic acid dimethyl ester**, obtained as detailed immediately above, was subjected to reductive cyclization in the same manner as described earlier for the preparation of compound **11** save for use of a reaction time of 0.75 h. In this way a clear colorless oil was obtained on work-up. Subjection of this material to flash chromatography (70:27:3 v/v hexane-ethyl acetate-triethylamine elution) afforded two fractions, A and B.

Concentration of fraction A (R_f = 0.5 in 7:3 v/v hexane-ethyl acetate) afforded pure **[1,1'-biphenyl]-2,2'-dicarboxylic acid dimethyl ester**[19] (40%) as light-pink crystalline masses, mp = 72–73

°C (lit.[19] mp = 73–74 °C). ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.99 (dd, *J* = 1.4 and 7.7 Hz, 2H), 7.52 (dt, *J* = 1.4 and 7.5 Hz, 2H), 7.41 (dt, *J* = 1.4 and 7.7 Hz, 2H), 7.18 (dd, *J* = 1.4 and 7.5 Hz, 2H), 3.59 (s, 6H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 167.4 (CO), 143.2 (C), 131.4 (CH), 130.1 (CH), 129.8 (CH), 129.3 (C), 127.1 (CH), 51.8 (CH_3); IR ν_{max} (thin film) 2924, 1727, 1598, 1574, 1431, 1259, 1189, 1081, 1049, 962, 799, 752, 706 cm^{-1}; MS, *m/z* (EI, 70eV) 270 ($M^{+\bullet}$, 23%), 239 (13), 211 (100), 197 (27), 180 (30), 152 (27), 139 (20), 76 (23); HRMS, Found: $M^{+\bullet}$, 270.0892. $C_{16}H_{14}O_4$ requires $M^{+\bullet}$, 270.0892.

Concentration of fraction B (R_f = 0.15 in 7:3 v/v hexane-ethyl acetate) afforded compound **47**[20] (28% from **45**) as a white crystalline solid, mp = 291–293 °C (lit.[20] mp = 291–292 °C). ^{1}H NMR [$(CD_3)_2SO$, 300 MHz] δ 11.69 (br. s, 1H), 8.50 (d, *J* = 7.7 Hz, 1H), 8.38 (d, *J* = 7.4 Hz, 1H), 8.31 (dd, *J* = 1.1 and 7.8 Hz, 1H), 7.84 (dt, *J* = 1.1 and 7.8 Hz, 1H), 7.63 (dt, *J* = 1.1 and 7.4 Hz, 1H), 7.48 (dt, *J* = 1.1 and 7.8 Hz, 1H), 7.35 (dd, *J* = 1.1 and 7.8 Hz, 1H), 7.25 (dt, *J* = 1.1 and 7.8, 1H); ^{13}C NMR [$(CD_3)_2SO$, 125 MHz] δ 160.8 (CO), 136.6 (C), 134.3 (C), 132.8 (CH), 129.6 (CH), 128.0 (CH), 127.5 (CH), 125.7 (C), 123.3 (CH), 122.6 (CH), 122.3 (CH), 117.6 (C), 116.1 (CH); IR ν_{max} (KBr) 2923, 1660, 1632, 1607, 1557, 1511, 1469, 1424, 1369, 1361, 1154, 1037, 749, 726 cm^{-1}; MS, *m/z* (EI, 70eV) 195 ($M^{+\bullet}$, 100%), 167 (23), 166 (13), 140 (10), 139 (14); HRMS, Found: $M^{+\bullet}$, 195.0684. $C_{13}H_9NO$ requires $M^{+\bullet}$, 195.0684.

4,2'-Dinitro-biphenyl-2-carboxylic Acid Methyl Ester (49). Cross-coupling of 1-bromo-2-nitrobenzene (**1**, R=H) with commercially available compound **48** in the same manner as described above for the preparation of compound **21** gave a yellow oil on work-up. Subjection of this material to flash chromatography flash chromatography (100:3 → 100:8 v/v hexane-ethyl acetate gradient elution) afforded, after concentration of the appropriate fractions (R_f = 0.4 in 55:25:10 v/v/v hexane-CH_2Cl_2-ethyl acetate), compound **49** (83%) as a light-yellow solid, mp = 141–142 °C. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.94 (d, *J* = 2.5 Hz, 1H), 8.45 (dd, *J* = 1.5 and 8.4 Hz, 1H), 8.24 (dd, *J* = 1.4 and 8.4 Hz, 1H), 7.72 (dt, *J* = 1.5 and 7.6 Hz, 1H), 7.63 (dt, *J* = 1.5 and 7.8 Hz, 1H), 7.46 (d, *J* = 8.4 Hz, 1H), 7.26 (dd, *J* = 1.5 and 7.6 Hz, 1H), 3.75 (s, 3 H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 164.6 (C), 147.4 (C), 147.3 (C), 146.9 (C), 135.3 (C), 133.4 (CH), 131.3 (CH), 130.7 (CH), 129.9 (C), 129.4 (CH), 126.7 (CH), 125.7 (CH), 124.5 (CH), 52.8 (CH_3); IR ν_{max} (KBr) 3098, 2957, 2853, 1731, 1607, 1524, 1439, 1350, 1255, 1124, 794 cm^{-1}; MS, *m/z* (EI, 70eV) 302 ($M^{+\bullet}$, 2%), 301 (17), 271 (2), 256 (100), 201 (56), 139 (30); HRMS, Found: $M^{+\bullet}$, 302.0542. $C_{14}H_{10}N_2O_6$ requires $M^{+\bullet}$, 302.0539.

8-Amino-6(5*H*)-phenanthridinone (50). A magnetically stirred mixture of compound **49** (655 mg, 2.17 mmol) and 10% Pd on carbon C (328 mg) in methanol (5 mL) was exposed to dihydrogen (1 atm.). After stirring at 18 °C for 2 h, the reaction mixture was filtered through a short pad of Celite™ and the filtrate was concentrated under reduced pressure. The ensuing light-yellow oil was subjected to flash chromatography (100:5 v/v methanol/triethylamine elution) and thus affording, after concentration of the appropriate fractions ($R_{f=}$ 0.5 in 8:3:1 v/v/v ethyl acetate/hexane/methanol), compound **50** (283 mg, 62%)

as a light-yellow solid, mp could not be determined, sublimation: >217 °C. ^{1}H NMR [$(CD_3)_2SO$, 300 MHz] δ 11.40 (s, 1H), 8.14 (m, 2H), 7.43 (m, 1H), 7.28 (m, 2H), 7.15 (m, 1H), 7.08 (dd, *J* = 1.5 and 8.7 Hz, 1H), 5.73 (s, 2H); ^{13}C NMR [$(CD_3)_2SO$, 75 MHz] δ 160.9 (C), 148.9 (C), 134.6 (C), 127.0 (C), 126.8 (CH), 123.6 (CH), 122.9 (C), 121.9 (CH), 121.5 (CH), 120.1 (CH), 118.7 (C), 115.7 (CH), 109.2 (CH); IR ν_{max} (KBr) 3442, 3384, 2923, 2852, 1729, 1663, 1558, 1516, 1485, 1372, 1305, 1082, 896, 826, 744 cm^{-1}; MS, *m/z* (EI, 70eV) 210 ($M^{+\bullet}$, 100%), 181 (21), 154 (9), 85 (16), 71 (21), 57 (29); HRMS, Found: $M^{+\bullet}$, 210.0790. $C_{13}H_{10}N_2O$ requires $M^{+\bullet}$, 210.0793.

4-Methoxy-2'-nitro-biphenyl-2-carboxylic Acid Methyl Ester (52). Cross-coupling of 1-bromo-2-nitrobenzene (**1**, R=H) with commercially available compound **51** in the same manner as described above for the preparation of compound **21** gave a yellow oil on work-up. Subjection of this material to flash chromatography (100:2 → 100:6 v/v hexane-ethyl acetate gradient elution) afforded, after concentration of the appropriate fractions (R_f = 0.4 in 55:25:5 v/v/v hexane-CH_2Cl_2-ethyl acetate), compound **52** (36%) as a light-yellow solid, mp = 102–103.5. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.06 (dd, *J* = 1.4 and 8.1 Hz, 1H), 7.60 (m, 2H), 7.50 (dt, *J* = 2.0 and 7.6 Hz, 1H), 7.27 (dd, *J* = 1.5 and 7.1 Hz, 1H), 7.14 (m, 2H), 3.90 (s, 3H), 3.66 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 166.6 (C), 159.2 (C), 148.8 (C), 137.1 (C), 132.6 (CH), 132.0 (C), 131.9 (CH), 131.3 (CH), 129.7 (C), 128.1 (CH), 124.0 (CH), 118.3 (CH), 115.4 (CH), 55.6 (CH_3), 52.2 (CH_3); IR ν_{max} (KBr) 2952, 2852, 1723, 1609, 1573, 1522, 1468, 1434, 1349, 1222, 1077, 1048, 855, 787, 755 cm^{-1}; MS, *m/z* (EI, 70eV) 287 ($M^{+\bullet}$, 23%), 242 (38), 241 (100), 226 (52), 211 (28), 139 (26), 127 (20); HRMS, Found: $M^{+\bullet}$, 287.0793. $C_{15}H_{13}NO_5$ requires $M^{+\bullet}$, 287.0794.

8-Methoxy-6(5*H*)-phenanthridinone (53). A magnetically stirred mixture of compound **52** (155 mg, 0.54 mmol) and 10% Pd on carbon C (39 mg) in methanol (4 mL) was exposed to dihydrogen (1 atm.). After stirring at 18 °C for 1 h, the reaction mixture was filtered through a short pad of Celite™ and the filtrate was concentrated under reduced pressure. The ensuing light-yellow oil was subjected to flash chromatography 100:5 v/v methanol/triethylamine elution) thus affording, after concentration of the appropriate fractions (R_f 0.4 in 80:55:25 v/v/v ethyl acetate/hexane/ CH_2Cl_2), compound **53** (104 mg, 85%) as a light-yellow solid, mp could not be determined, sublimation: >163 °C. ^{1}H NMR [$(CD_3)_2SO$, 300 MHz] δ 11.39 (s, 1H), 8.50 (d, *J* = 8.9 Hz, 1H), 8.41 (d, *J* = 7.8 Hz, 1H), 7.77 (m, 2H), 7.57 (t, *J* = 7.8 Hz, 1H), 7.46 (m, 1H), 7.34 (t, *J* = 7.8 Hz, 1H), 3.93 (s, 3H); ^{13}C NMR [$(CD_3)_2SO$, 75 MHz] δ 159.1 (C), 156.4 (C), 135.9 (C), 128.8 (CH), 126.8 (C), 125.7 (C), 124.7 (CH), 122.7 (CH), 121.4 (CH), 117.4 (C), 113.0 (CH), 108.5 (CH), 55.5 (CH_3) (one signal obscured or overlapping); IR ν_{max} (KBr) 2921, 2847, 1658, 1609, 1453, 1363, 1290, 1217, 1024, 867, 845, 818, 739 cm^{-1}; MS, *m/z* (EI, 70eV) 225 ($M^{+\bullet}$, 100%), 210 (30), 196 (32), 182 (18), 154 (30), 153 (22), 57 (16); HRMS, Found: $M^{+\bullet}$, 225.0790. $C_{14}H_{11}NO_2$ requires $M^{+\bullet}$, 225.0790.

2'-Nitro-biphenyl-2,5-dicarboxylic Acid Dimethyl Ester (55). Cross-coupling of 1-bromo-2-nitrobenzene (**1**, R=H) with commercially available compound **54** in the same manner as described above for the preparation of compound **21** gave a yellow oil on work-up. Subjection of this material to flash chromatography (100:3 → 100:10 v/v hexane-ethyl acetate gradient elution) afforded, after concentration of the appropriate fractions (R_f = 0.4 in 55:25:10 v/v/v hexane/CH_2Cl_2/ethyl acetate), compound **55** (48%) as a light-yellow solid, mp = 122.5–124 °C. ^{1}H NMR [$(CD_3)_2SO$, 300 MHz] δ 8.17 (dd, J = 1.2 and 8.1 Hz, 1H), 8.12 (s, 2H), 7.83–7.60 (complex m, 2H), 7.69 (m, 1H), 7.42 (dd, J = 1.4 and 7.6 Hz, 1H), 3.88 (s, 3H), 3.61 (s, 3H); ^{13}C NMR [$(CD_3)_2SO$, 75 MHz] δ 166.0 (C), 165.8 (C), 147.9 (C), 140.4 (C), 136.4 (C), 133.3 (C), 133.0 (CH), 132.3 (C), 131.4 (CH), 131.0 (CH), 130.6 (CH), 129.0 (CH), 128.7 (CH), 124.2 (CH), 52.6 (CH_3), 52.4 (CH_3); IR ν_{max} (KBr) 2954, 2850, 1725, 1613, 1573, 1525, 1435, 1349, 1289, 1241, 1117, 749 cm^{-1}; MS, *m/z* (EI, 70eV) 284 [$(M–CH_3O\cdot)^+$, 19%], 269 (100), 223 (23), 195 (170, 167 (13), 151 (16), 139 (25), 119 (9); HRMS, Found: $(M–CH_3O\cdot)^+$, 284.0561. $C_{16}H_{13}NO_6$ requires $(M–CH_3O\cdot)^+$, 284.0559.

6-Oxo-5,6-dihydrophenanthridine-9-carboxylic Acid Methyl Ester (56). A magnetically stirred mixture of compound **55** (253 mg, 0.80 mmol) and 10% Pd on carbon (63 mg) in methanol (4 mL) was exposed to dihydrogen (1 atm.). After stirring at 18 °C for 1 h, the reaction mixture was filtered through a short pad of Celite™ and the filtrate was concentrated under reduced pressure. The ensuing residue was subjected to flash chromatography (100:5 v/v methanol/ triethylamine elution) thus affording, after concentration of the appropriate fractions (R_f = 0.4 in 80:55:25 v/v/v ethyl acetate/hexane/CH_2Cl_2), compound **56** (108 mg, 53%) as a white solid, mp could not be determined, sublimation: > 185 °C. ^{1}H NMR [$(CD_3)_2SO$, 300 MHz] δ 11.89 (s, 1H), 8.96 (s, 1 H), 8.44 (d, J = 8.4 Hz, 2H), 8.13 (d, J = 8.4 Hz, 1H), 7.54 (t, J = 7.6 Hz, 1H), 7.39 (d, J = 8.4 Hz, 1H), 7.30 (t, J = 7.6 Hz, 1H), 3.96 (s, 3H); ^{13}C NMR [$(CD_3)_2SO$, 75 MHz] δ 165.8 (C), 160.1 (C), 136.8 (C), 134.3 (C), 133.3 (C), 130.2 (CH), 128.7 (C), 128.3 (CH), 127.6 (CH), 123.6 (CH), 123.4 (CH), 122.6 (CH), 117.0 (C), 116.3 (CH), 52.7 (CH_3); IR ν_{max} (KBr) 2918, 2849, 1728, 1657, 1611, 1503, 1434, 1419, 1287, 1256, 1026, 856, 748, 724 cm^{-1}; MS, *m/z* (EI, 70eV) 253 ($M^{+\bullet}$, 48%), 222 (17), 194 (12), 149 (23), 71 (54), 57 (100); HRMS, Found: $M^{+\bullet}$, 253.0739. $C_{15}H_{11}NO_3$ requires $M^{+\bullet}$, 253.0739.

6-(2-Nitrophenyl)benzo[1,3]dioxole-5-carboxylic Acid Methyl Ester (58). Cross-coupling of 1-bromo-2-nitrobenzene (**1**, R=H) with bromo-ester **57**[21] was carried out in the same manner as described above for the preparation of compound **21** save for the use of a reaction temperature of 90 °C and a reaction time of 6 h. Subjection of the yellow oil obtained on work-up to flash chromatography (4:1 v/v hexane-ethyl acetate elution) afforded two fractions, A and B.

Concentration of fraction A (R_f = 0.2) afforded a *ca*. 2:1 mixture of compound **58** (40% as determined by ^{1}H NMR analysis) and **2,2'-dinitrobiphenyl** [product from reductive dimerization of compound **1** (R=H)] as a yellow oil. Trituration (diethyl ether) of a small portion of this mixture afforded

an analytically pure sample of compound **58** as a yellow crystalline solid, mp = 133–134 °C. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.06 (dd, *J* = 1.3 and 8.1 Hz, 1H), 7.59 (dt, *J* = 1.3 and 8.1 Hz, 1H), 7.50 (s, 1H), 7.48 (dt, *J* = 1.3 and 8.1 Hz, 1H), 7.23 (dd, *J* = 1.3 and 8.1 Hz, 1H), 6.64 (s, 1H), 6.08 (m, 2H), 3.60 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 165.8 (CO), 150.8 (C), 148.3 (C), 147.4 (C), 137.1 (C), 135.8 (C), 132.6 (CH), 131.3 (CH), 128.2 (CH), 124.0 (CH), 121.9 (C), 110.3 (CH), 110.1 (CH), 102.2 (CH_2), 52.0 (CH_3); IR ν_{max} (KBr) 1721, 1525, 1505, 1479, 1374, 1349, 1255, 1037 cm^{-1}; MS, *m/z* (EI, 70eV) 301 ($M^{+\bullet}$, 28%), 255 (100), 240 (58); HRMS, Found: $M^{+\bullet}$, 301.0588. $C_{15}H_{11}NO_6$ requires $M^{+\bullet}$, 301.0586. Anal.: Found C 59.85; H 3.65; N 4.70. Calculated for $C_{15}H_{11}NO_6$; C 59.80; H 3.68; N 4.65%.

Concentration of fraction B (R_f = 0.1) afforded **[5,5']bi{benzo[1,3]dioxolyl}-6,6'-dicarboxylic acid dimethyl ester**[21] (product from reductive dimerization of compound **57**) (27% as determined by ^{1}H NMR analysis) as a white crystalline solid, mp = 159–160 °C (lit.[21] mp = 160–160.5 °C). ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.44 (s, 2H), 6.58 (s, 2H), 6.04 (m, 4H), 3.61 (s, 6H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 166.3 (CO), 150.2 (C), 146.6 (C), 139.5 (C), 122.4 (C), 110.3 (CH), 109.8 (CH), 101.9 (CH_2), 51.8 (CH_3); IR ν_{max} (KBr) 2953, 2923, 1727, 1615, 1504, 1481, 1435, 1374, 1353, 1248, 1123, 1037, 933 cm^{-1}; MS, *m/z* (EI, 70eV) 358 ($M^{+\bullet}$, 62%), 299 (100), 284 (59), 268 (45); HRMS, Found: $M^{+\bullet}$, 358.0691. $C_{18}H_{14}O_8$ requires $M^{+\bullet}$, 358.0689.

Crinasidine {[1,3]-Dioxolo[4,5-*j*]-6(5*H*)-phenanthridinone} (59). A solution of compound **58** (11.0 mg, 0.037 mmol) in ethanol (10 mL) was treated with 10% Pd on carbon (3 mg) and the resulting mixture stirred at 18 °C under an atmosphere of dihydrogen for 16 h. The dihydrogen atmosphere was then replaced by nitrogen and the reaction mixture treated with sodium ethoxide (2.0 mL of a 0.4 M solution in ethanol). After 5 h at 18 °C the reaction mixture was concentrated under reduced pressure and the residue subjected to flash chromatography (90:9.5:0.5 v/v/v chloroform-methanol-5% aq. ammonia elution). In this manner two fractions, A and B, were obtained.

Concentration of fraction A (R_f = 0.8) afforded compound **58** (3.2 mg, 29% recovery) as yellow crystalline solid and identical, in all respects, with an authentic sample.

Concentration of fraction B (R_f = 0.4) afforded compound **59**[13] (5.8 mg, 92% at 71% conversion) as white crystalline masses, mp = > 350 °C (lit.[13] mp = > 350 °C with partial sublimation at 340 °C). ^{1}H NMR [$(CD_3)_2SO$, 500 MHz] δ 11.62 (broad s, 1H), 8.29 (d, *J* = 8.0 Hz, 1H), 8.03 (s, 1H), 7.63 (s, 1H), 7.42 (t, *J* = 8.0 Hz, 1H), 7.32 (d, *J* = 8.0 Hz, 1H), 7.20 (t, *J* = 8.0 Hz, 1H), 6.22 (s, 2H); ^{13}C NMR [$(CD_3)_2SO$, 125 MHz] δ 160.2, 152.2, 148.1, 135.9, 131.2, 128.8, 123.2, 122.1, 121.1, 117.7, 115.9, 105.1, 102.3, 101.6; IR ν_{max} (KBr) 1663, 1584, 1472, 1430, 1240, 1040 cm^{-1}; MS, *m/z* (EI, 70eV) 239 ($M^{+\bullet}$, 100%), 162 (26), 91 (25); HRMS, Found: $M^{+\bullet}$, 239.0581. $C_{14}H_9NO_3$ requires $M^{+\bullet}$, 239.0582.

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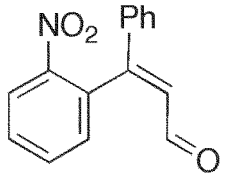
300 MHz ^{1}H NMR Spectrum in $CDCl_3$



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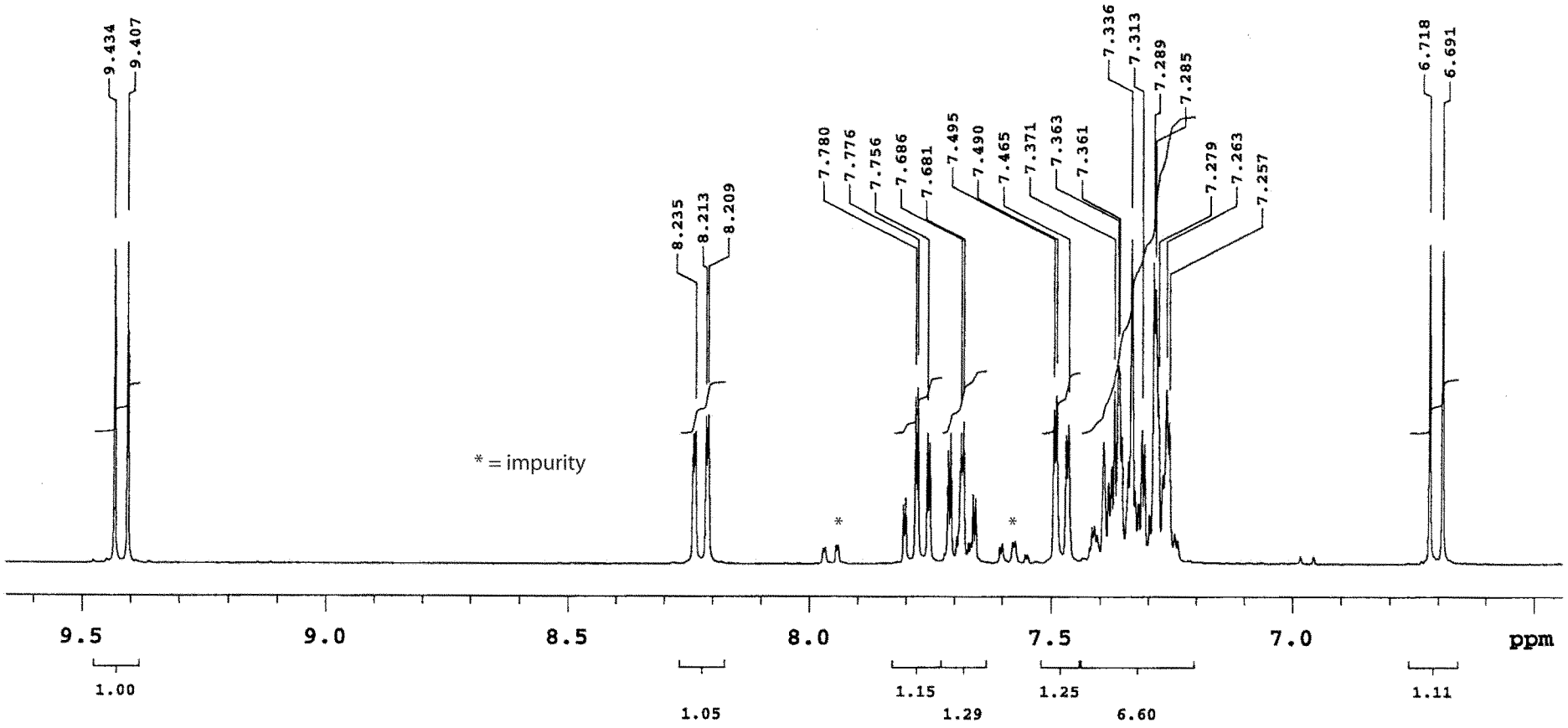
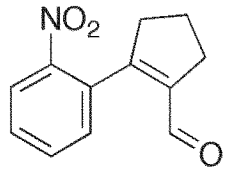


75 MHz ^{13}C NMR Spectrum in $CDCl_3$



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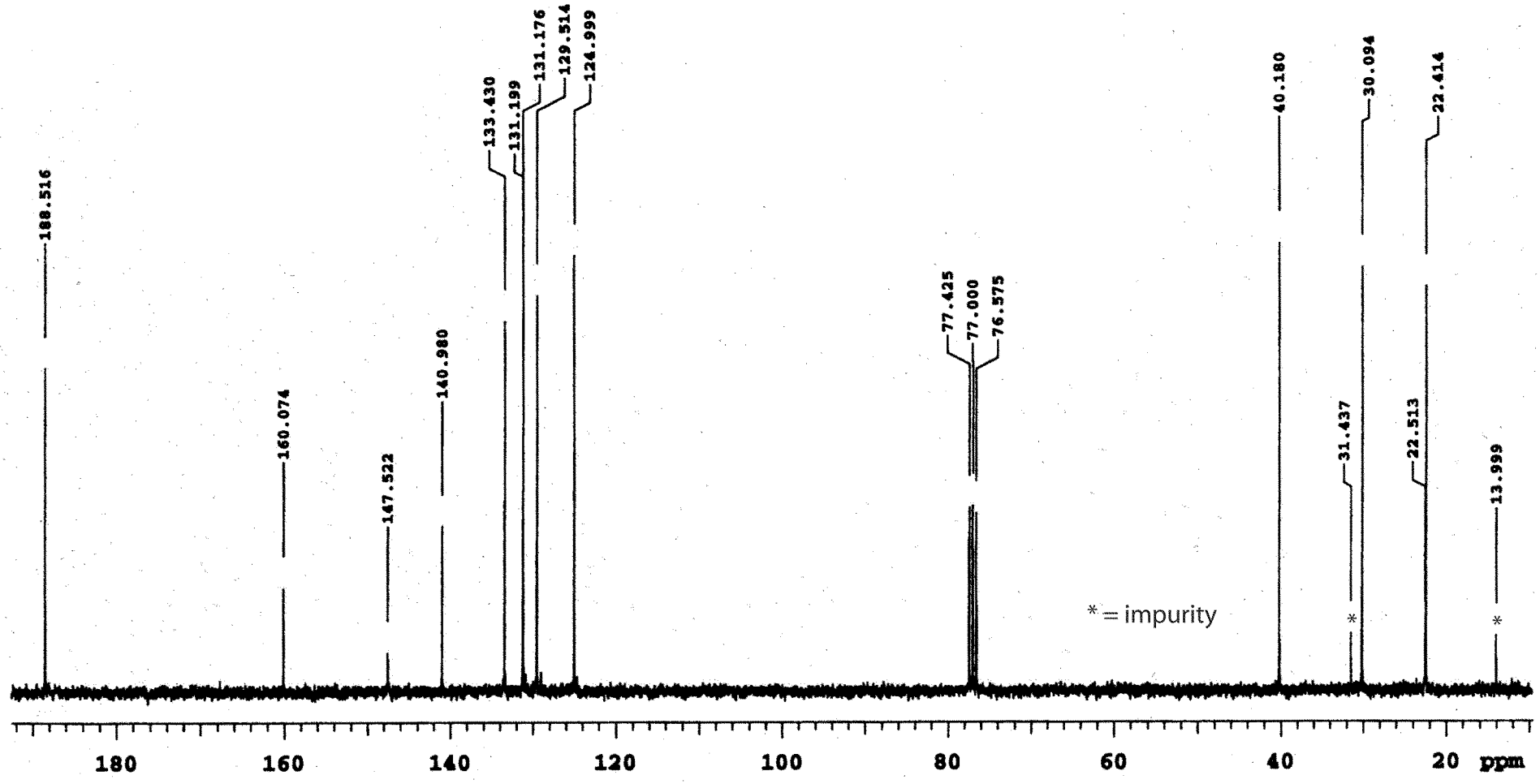
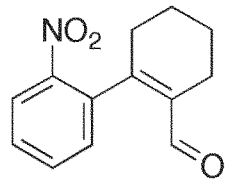


75 MHz ^{13}C NMR Spectrum in $CDCl_3$



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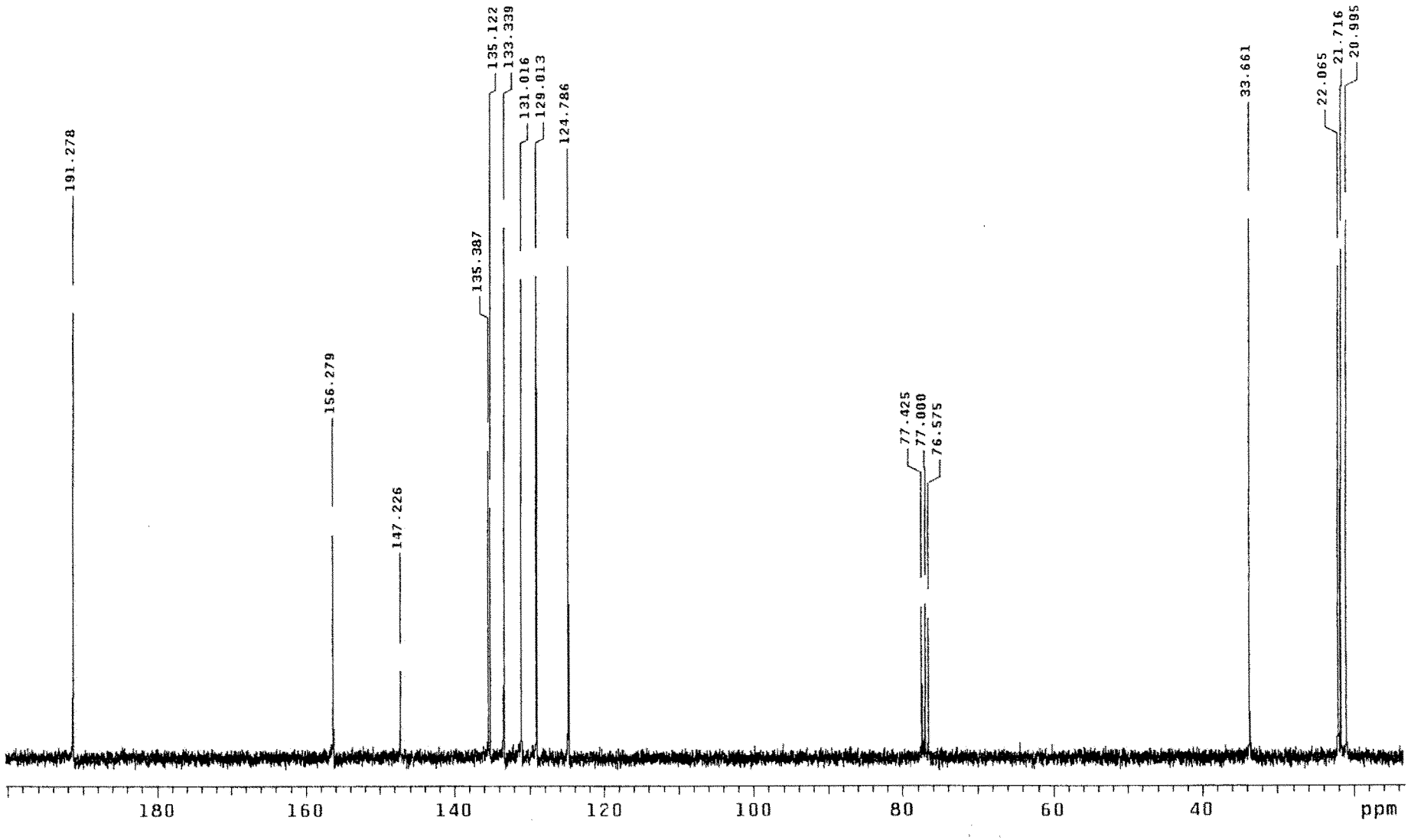
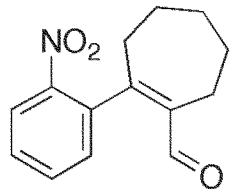


75 MHz ^{13}C NMR Spectrum in $CDCl_3$



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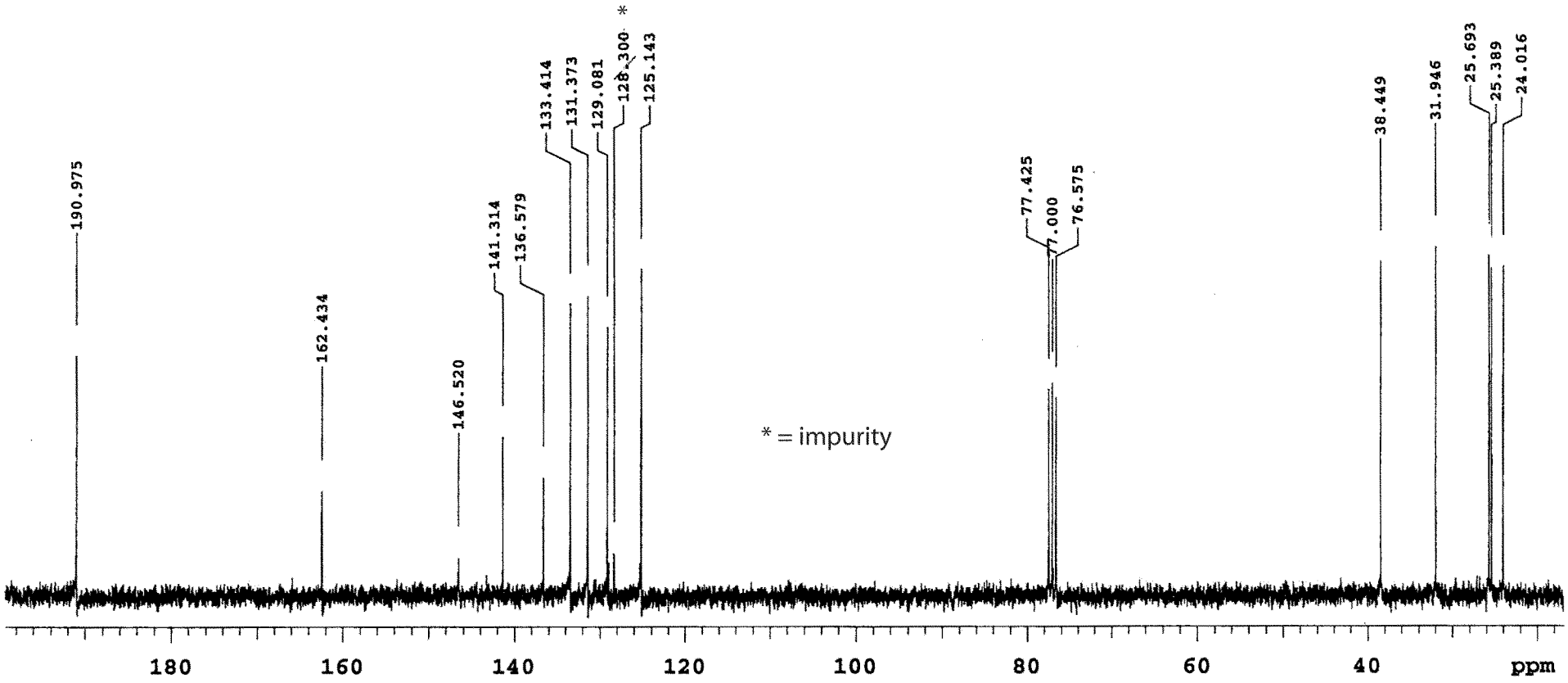
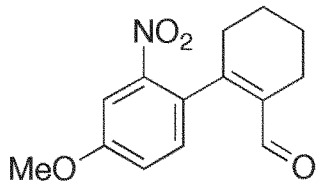


75 MHz ^{13}C NMR Spectrum in $CDCl_3$



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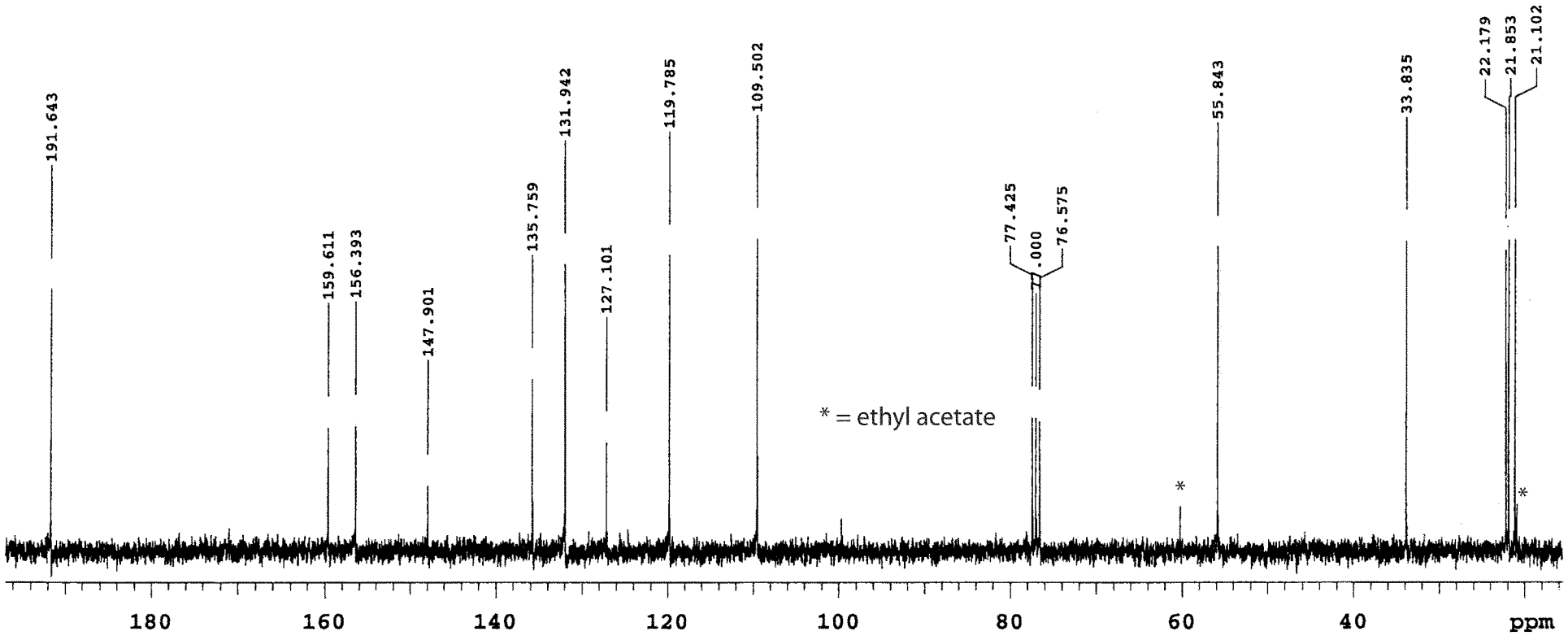
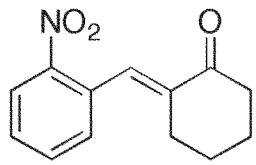


300 MHz ^{1}H NMR Spectrum in $CDCl_3$



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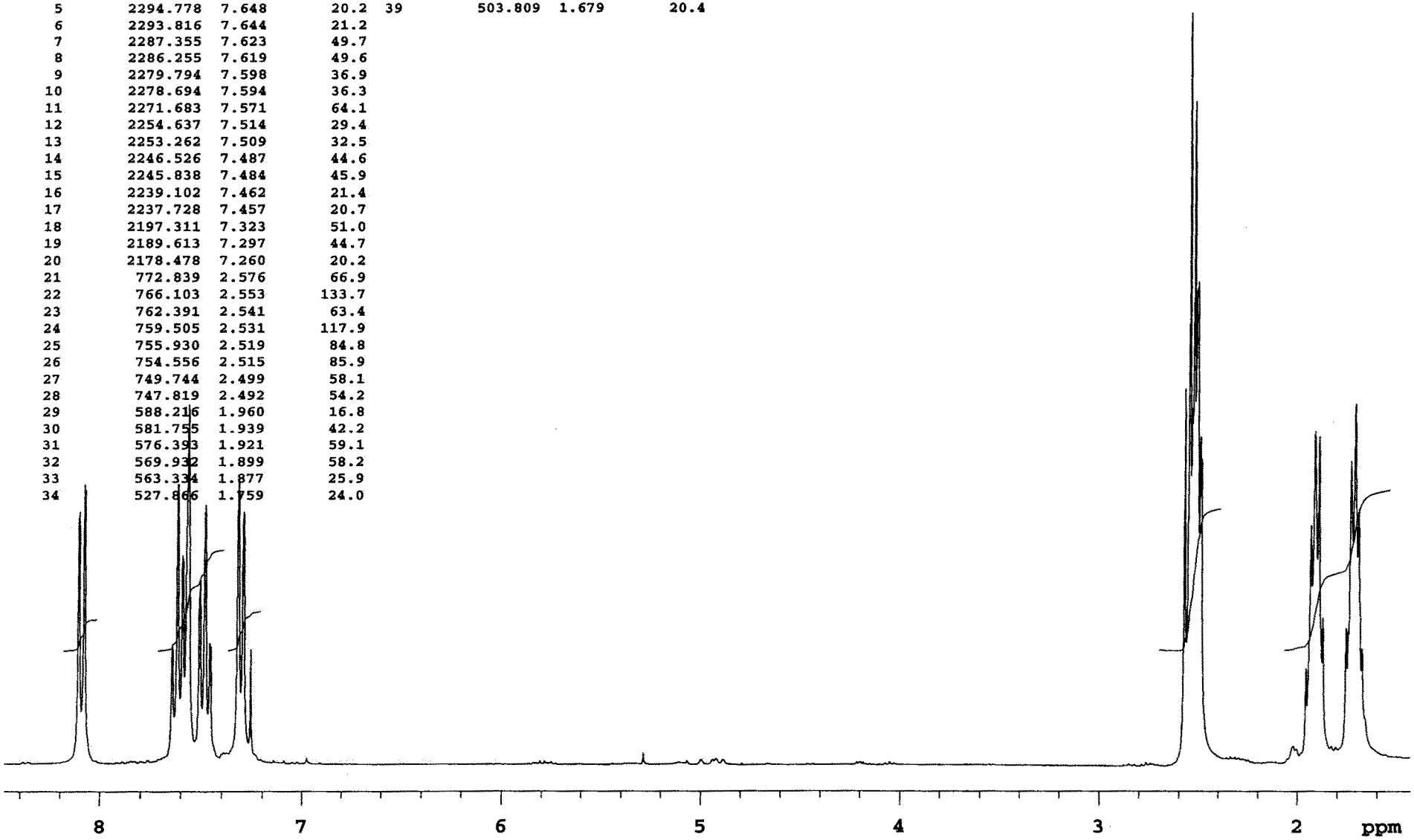
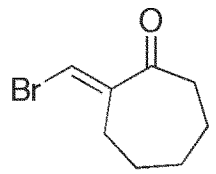
INDEX	FREQUENCY	PPM	HEIGHT	INDEX	FREQUENCY	PPM	HEIGHT
1	2433.623	8.110	44.0	35	524.842	1.749	23.5
2	2432.524	8.107	44.7	36	521.543	1.738	53.8
3	2425.513	8.083	49.5	37	515.356	1.717	64.0
4	2424.413	8.080	48.7	38	509.720	1.699	45.2
5	2294.778	7.648	20.2	39	503.809	1.679	20.4
6	2293.816	7.644	21.2				
7	2287.355	7.623	49.7				
8	2286.255	7.619	49.6				
9	2279.794	7.598	36.9				
10	2278.694	7.594	36.3				
11	2271.683	7.571	64.1				
12	2254.637	7.514	29.4				
13	2253.262	7.509	32.5				
14	2246.526	7.487	44.6				
15	2245.838	7.484	45.9				
16	2239.102	7.462	21.4				
17	2237.728	7.457	20.7				
18	2197.311	7.323	51.0				
19	2189.613	7.297	44.7				
20	2178.478	7.260	20.2				
21	772.839	2.576	66.9				
22	766.103	2.553	133.7				
23	762.391	2.541	63.4				
24	759.505	2.531	117.9				
25	755.930	2.519	84.8				
26	754.556	2.515	85.9				
27	749.744	2.499	58.1				
28	747.819	2.492	54.2				
29	588.216	1.960	16.8				
30	581.755	1.939	42.2				
31	576.393	1.921	59.1				
32	569.932	1.899	58.2				
33	563.334	1.877	25.9				
34	527.866	1.759	24.0				



INDEX	FREQUENCY	PPM	HEIGHT
1	2159.507	7.197	87.7
2	2158.957	7.195	86.3
3	768.578	2.561	74.8
4	761.842	2.539	123.9
5	757.992	2.526	110.7
6	751.806	2.505	67.1
7	496.660	1.655	141.5
8	492.124	1.640	110.4
9	487.037	1.623	106.5

300 MHz ^{1}H NMR Spectrum in $CDCl_3$



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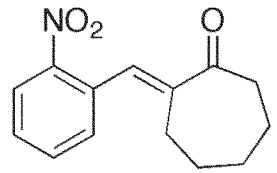
INDEX	FREQUENCY	PPM	HEIGHT	INDEX	FREQUENCY	PPM	HEIGHT
1	2440.909	8.135	49.5	35	815.455	2.718	51.4
2	2439.672	8.130	50.0	36	808.857	2.696	52.9
3	2432.661	8.107	54.8	37	727.474	2.424	66.0
4	2431.424	8.103	54.8	38	726.786	2.422	71.3
5	2314.711	7.714	87.0	39	721.563	2.405	47.9
6	2298.902	7.661	23.4	40	716.339	2.387	70.3
7	2297.940	7.658	22.5	41	537.764	1.792	20.1
8	2297.527	7.657	23.6	42	531.715	1.772	74.5
9	2291.341	7.636	55.6	43	528.829	1.762	104.4
10	2290.104	7.632	53.8	44	525.804	1.752	107.7
11	2283.780	7.611	38.8	45	517.006	1.723	15.8
12	2282.818	7.608	33.3	46	504.909	1.683	32.9
13	2282.406	7.606	35.9	47	495.011	1.650	23.1
14	2256.699	7.521	26.1	48	489.924	1.633	34.4
15	2256.149	7.519	29.8	49	486.075	1.620	40.6
16	2255.324	7.516	31.6	50	481.401	1.604	27.2
17	2254.637	7.514	30.7	51	479.339	1.597	23.9
18	2248.588	7.494	43.1				
19	2247.900	7.491	46.3				
20	2247.076	7.489	46.2				
21	2246.388	7.486	30.1				
22	2241.164	7.469	18.6				
23	2240.477	7.467	20.7				
24	2239.652	7.464	20.1				
25	2238.965	7.462	19.0				
26	2187.001	7.288	40.3				
27	2186.451	7.287	43.4				
28	2185.901	7.285	52.6				
29	2185.076	7.282	40.6				
30	2184.664	7.281	37.3				
31	2178.478	7.260	104.7				
32	2177.378	7.256	36.9				
33	2176.966	7.255	32.4				
34	819.717	2.732	45.7				

300 MHz ^{1}H NMR Spectrum in $CDCl_3$



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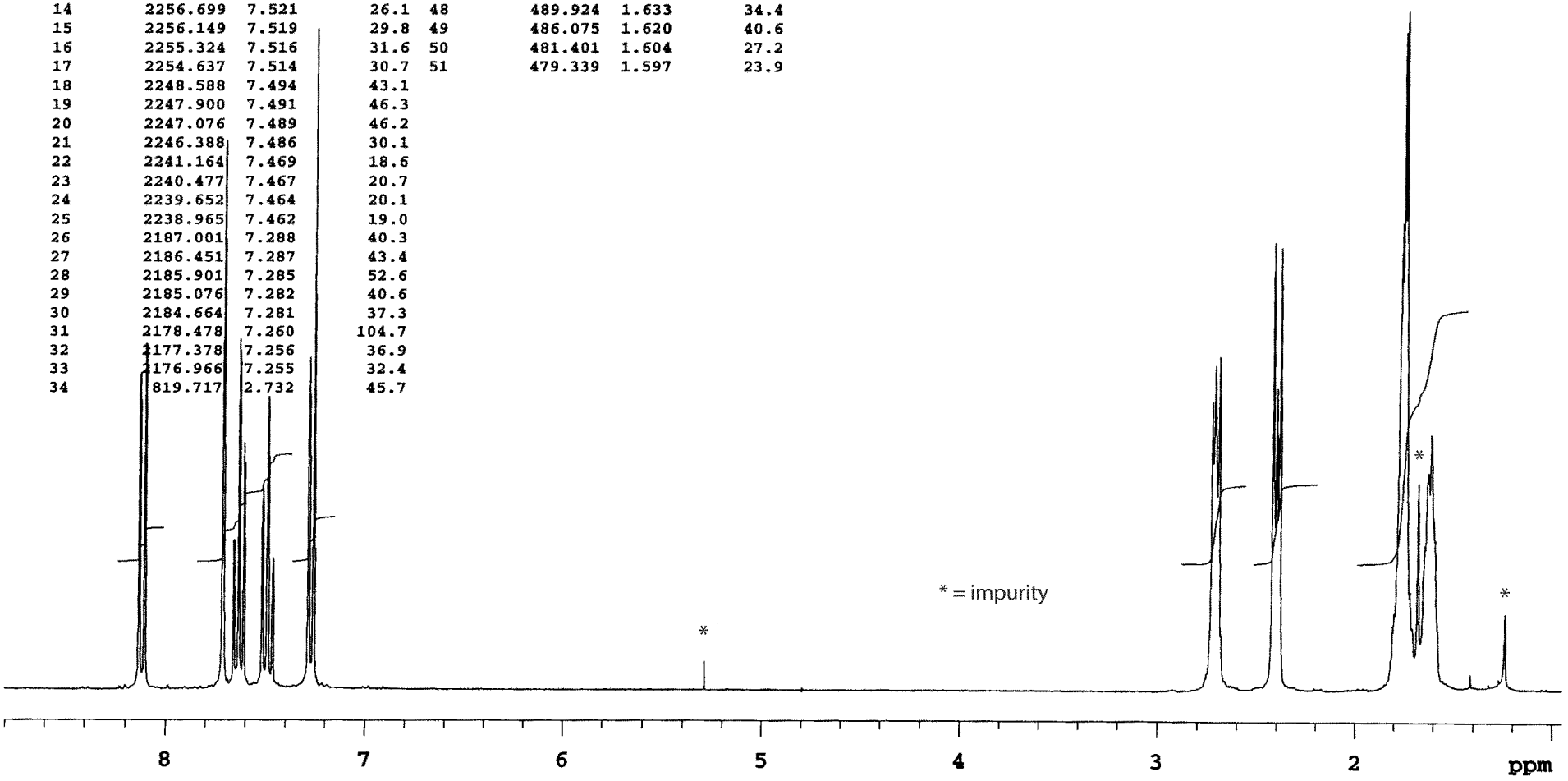
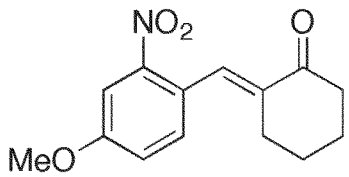


INDEX	FREQUENCY	PPM	HEIGHT
1	2283.368	7.610	16.3
2	2280.756	7.601	16.6
3	2259.448	7.530	6.2
4	2257.523	7.523	11.2
5	2255.599	7.517	5.7
6	2178.478	7.260	16.5
7	2175.591	7.250	9.5
8	2166.793	7.221	18.2
9	2150.021	7.165	12.5
10	2147.409	7.156	11.5
11	2141.498	7.137	6.3
12	2138.749	7.128	6.1
13	1177.141	3.923	1.6
14	1168.343	3.894	139.7
15	772.702	2.575	16.0
16	769.815	2.565	8.8
17	766.103	2.553	33.7
18	759.367	2.531	23.2
19	757.168	2.523	8.4
20	589.591	1.965	3.0
21	582.992	1.943	6.5
22	577.768	1.925	8.5
23	575.156	1.917	5.1
24	571.170	1.903	8.6
25	568.145	1.893	2.2
26	564.571	1.881	3.6
27	530.203	1.767	3.9
28	527.179	1.757	3.0
29	524.017	1.746	8.0
30	517.693	1.725	9.0
31	511.920	1.706	5.9
32	509.720	1.699	2.8
33	505.871	1.686	3.1
34	503.259	1.677	3.3

300 MHz ^{1}H NMR Spectrum in $CDCl_3$



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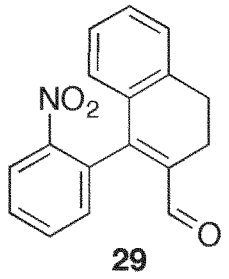
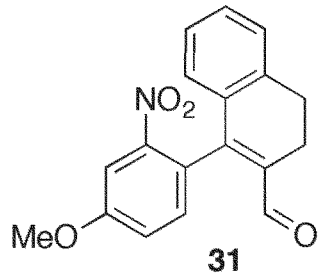
300 MHz ^{1}H NMR Spectrum in $CDCl_3$



29

300 MHz ^{1}H NMR Spectrum in $CDCl_3$



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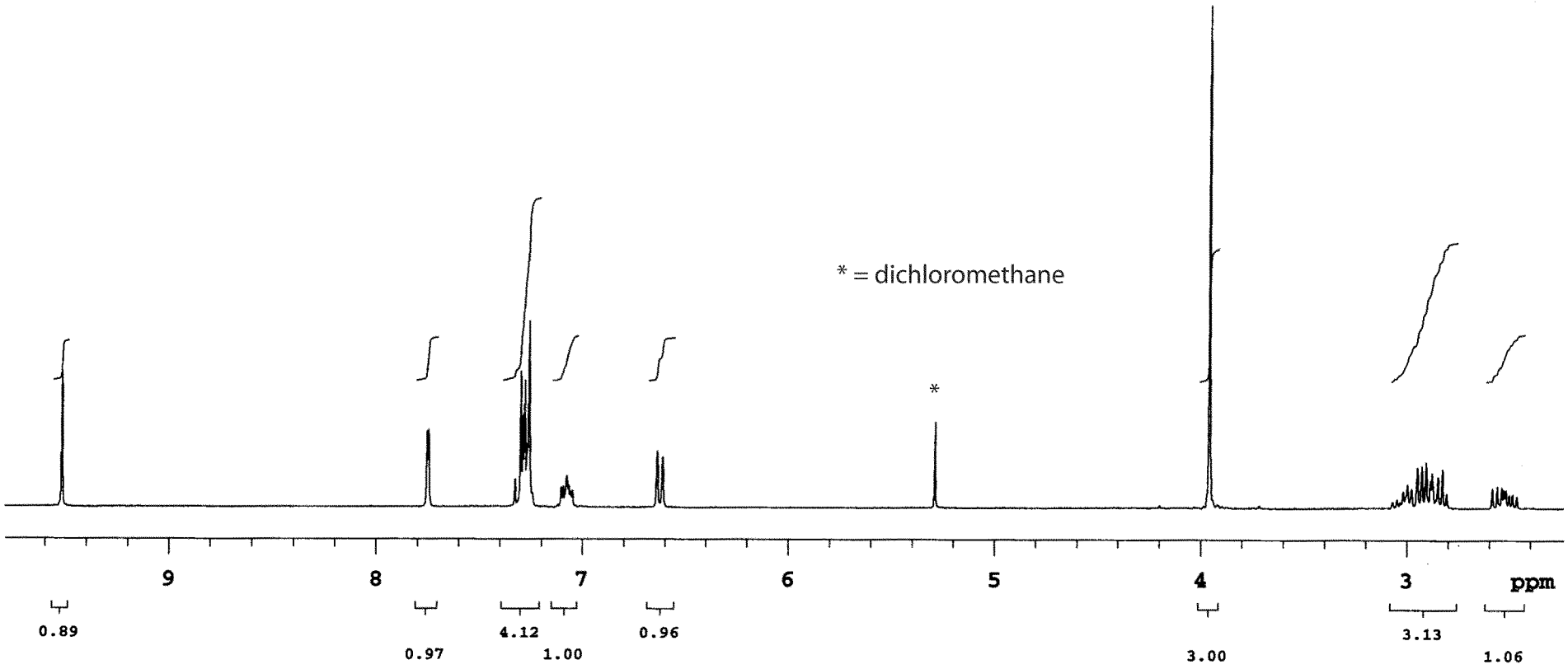
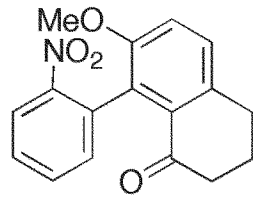


300 MHz ^{1}H NMR Spectrum in $CDCl_3$



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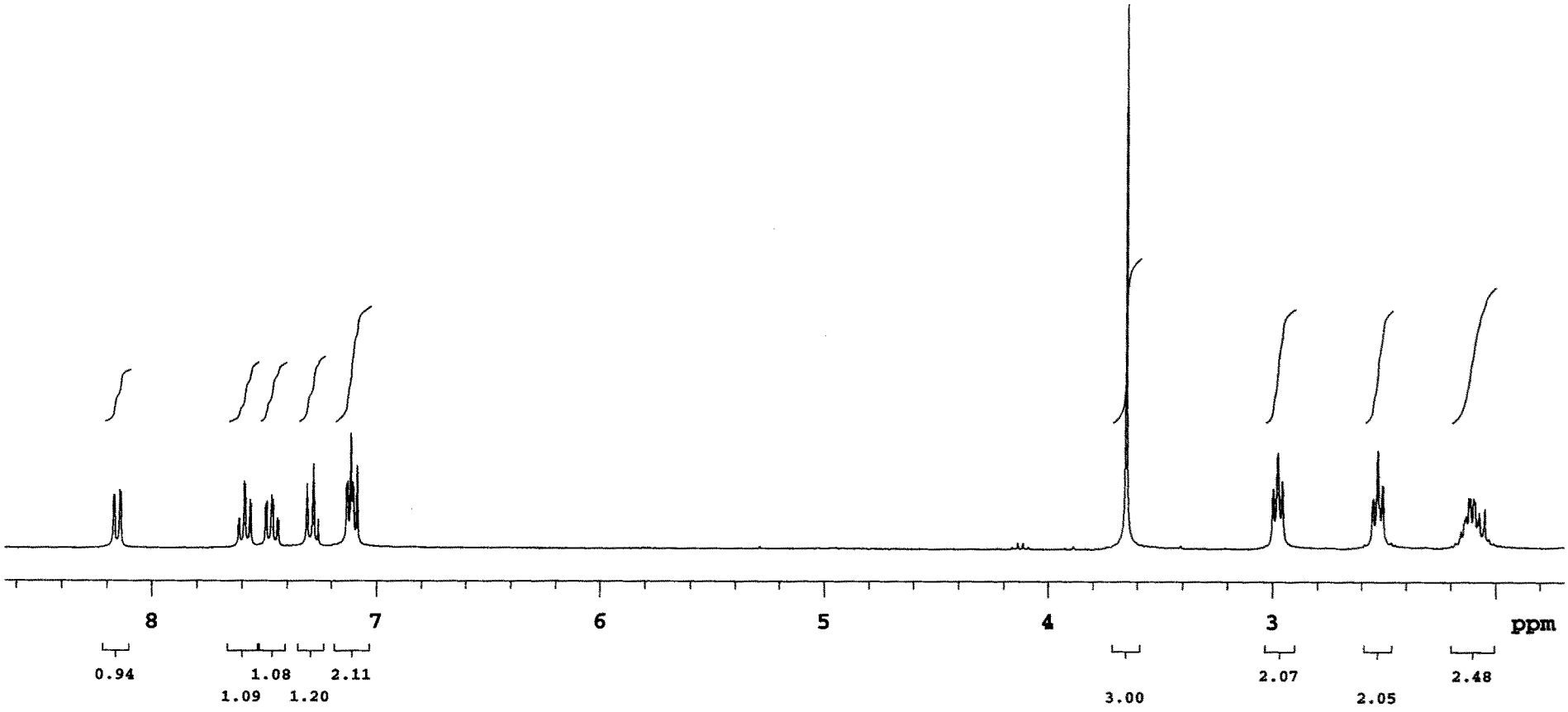
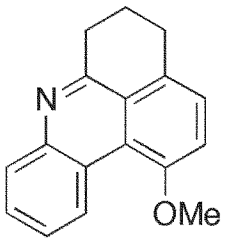


300 MHz ^{1}H NMR Spectrum in $CDCl_3$



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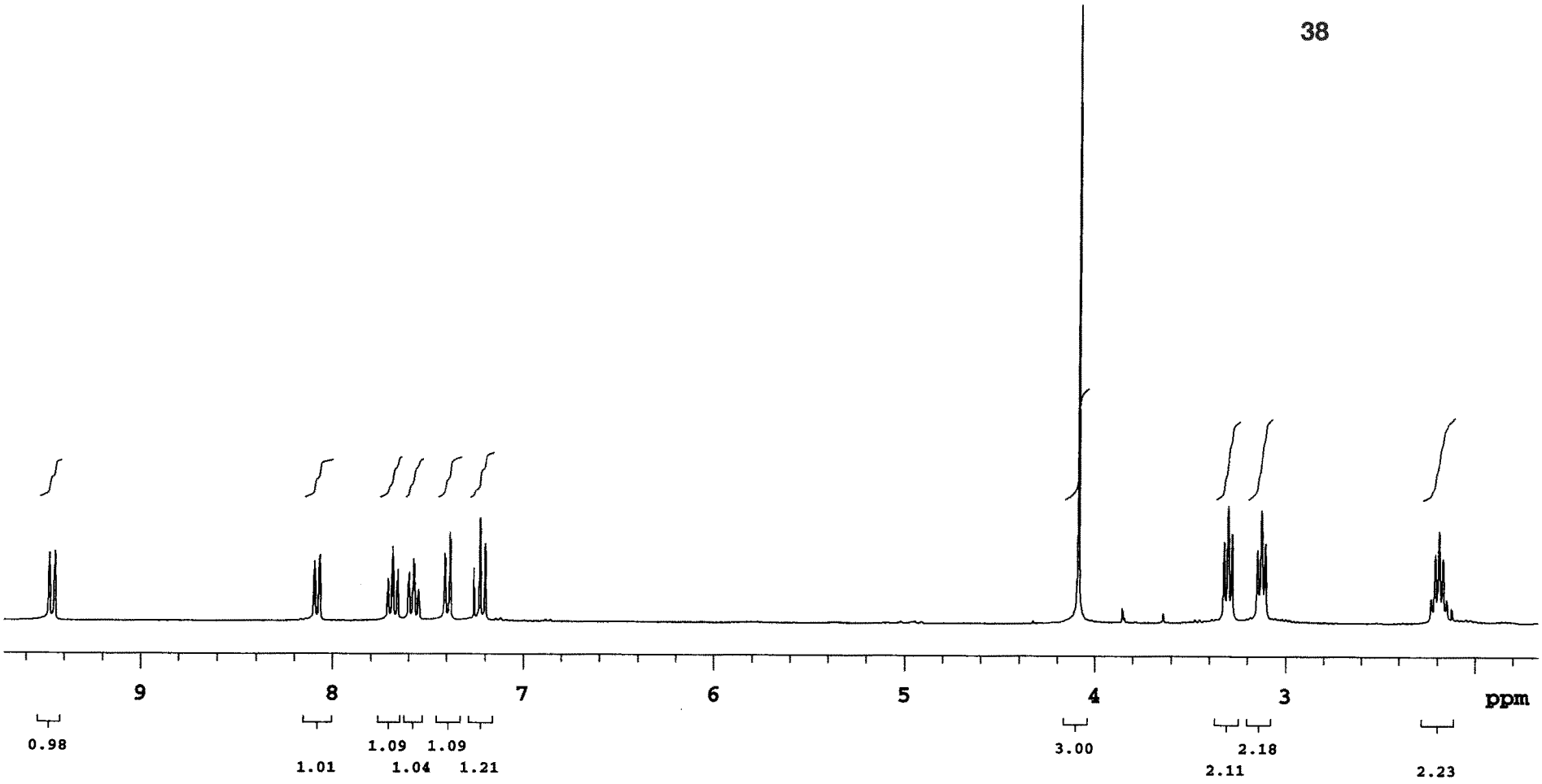
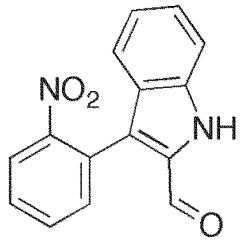


300 MHz ^{1}H NMR Spectrum in $CDCl_3$



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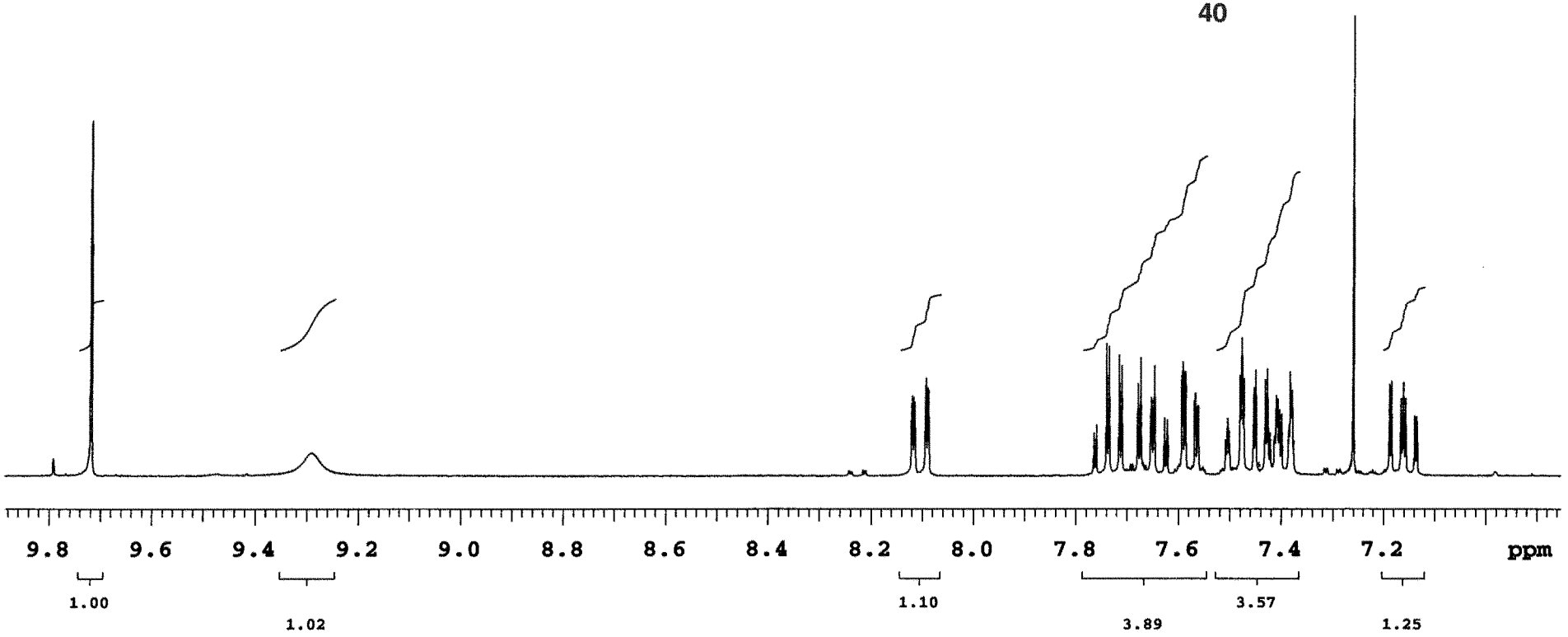
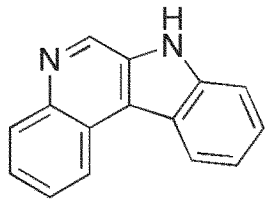


300 MHz ^{1}H NMR Spectrum in $(CD_3)_2CO$



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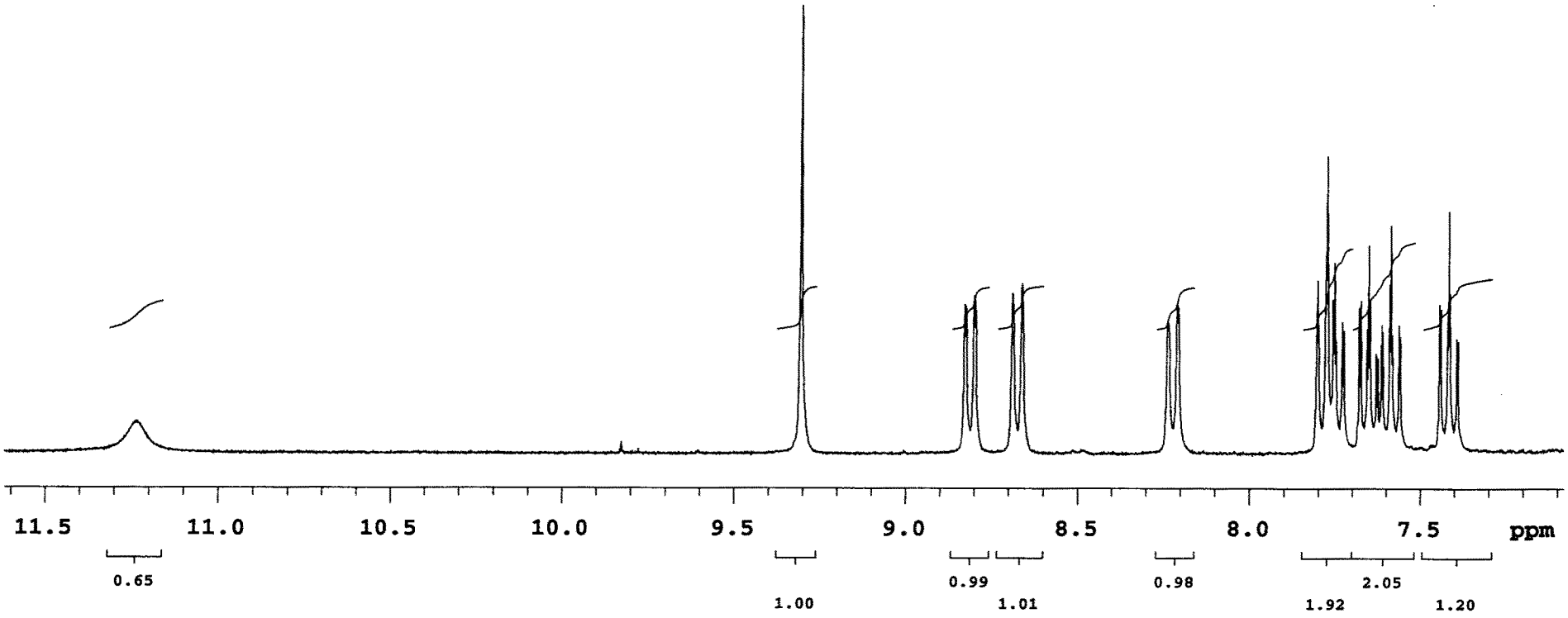
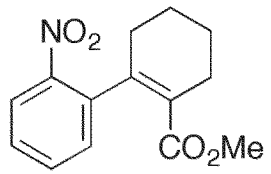


75 MHz ^{1}H NMR Spectrum in $CDCl_3$



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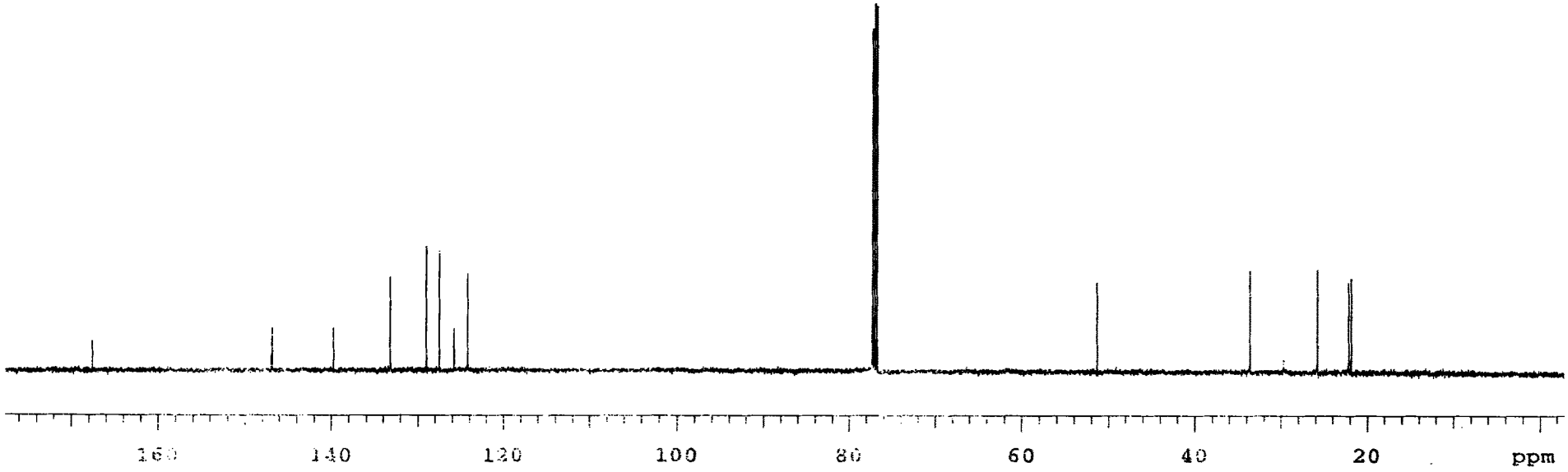
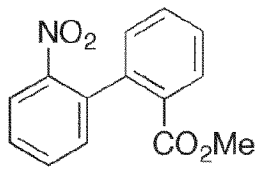


300 MHz ^{1}H NMR Spectrum in $CDCl_3$



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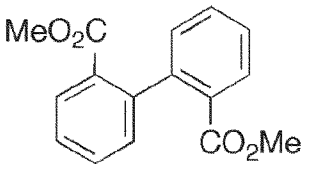

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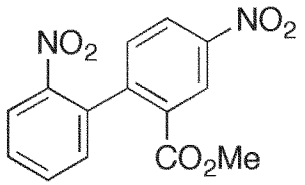
[1,1'-Biphenyl]-2,2'-dicaboxyli
Acid Dimethyl Ester

ca 1:1 mixture

INDEX	FREQUENCY	PPM	HEIGHT
1	2684.804	8.947	26.5
2	2682.330	8.939	27.8
3	2540.872	8.468	16.7
4	2538.398	8.459	16.6
5	2532.349	8.439	17.5
6	2530.012	8.432	16.9
7	2477.636	8.257	14.4
8	2476.261	8.252	14.2
9	2469.525	8.230	16.1
10	2468.150	8.225	15.5
11	2326.280	7.753	6.5
12	2324.906	7.748	7.2
13	2318.719	7.727	16.6
14	2317.345	7.723	17.2
15	2311.296	7.703	12.8
16	2309.921	7.698	12.0
17	2298.649	7.660	11.4
18	2296.999	7.655	12.6
19	2290.538	7.633	12.9
20	2289.576	7.630	10.7
21	2289.026	7.628	13.8
22	2282.977	7.608	7.0
23	2281.465	7.603	6.8
24	2243.798	7.478	31.1
25	2235.412	7.450	29.6
26	2183.998	7.278	17.1
27	2182.486	7.273	17.8
28	2180.836	7.268	15.7
29	2176.437	7.253	15.1
30	2174.925	7.248	15.0
31	1124.648	3.748	200.0

300 MHz ^{1}H NMR Spectrum in $CDCl_3$



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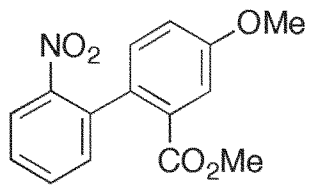
INDEX	FREQUENCY	PPM	HEIGHT	INDEX	FREQUENCY	PPM	HEIGHT
1	2425.122	8.082	7.0	35	2152.242	7.173	2.6
2	2424.297	8.079	5.9	36	2151.555	7.170	4.3
3	2423.747	8.077	7.4	37	2151.005	7.168	3.2
4	2417.011	8.055	7.8	38	2143.719	7.144	16.5
5	2415.636	8.050	7.9	39	2143.032	7.142	23.6
6	2293.012	7.642	3.2	40	2142.482	7.140	15.5
7	2292.462	7.640	3.2	41	2141.107	7.135	15.3
8	2291.638	7.637	3.6	42	2140.695	7.134	14.6
9	2291.088	7.635	3.3	43	2138.633	7.127	13.3
10	2285.451	7.617	8.2	44	2138.220	7.126	12.6
11	2285.039	7.615	8.5	45	2132.584	7.107	2.5
12	2284.077	7.612	8.7	46	2132.172	7.106	2.5
13	2283.664	7.611	8.0	47	2130.109	7.099	3.0
14	2279.265	7.596	13.3	48	2129.697	7.097	2.9
15	2277.478	7.590	14.5	49	1169.464	3.897	90.6
16	2276.653	7.587	16.4	50	1169.189	3.896	87.3
17	2259.744	7.531	5.2	51	1097.567	3.658	101.0
18	2259.195	7.529	5.4	52	1097.017	3.656	92.8
19	2258.095	7.525	6.0				
20	2257.682	7.524	5.5				
21	2252.184	7.506	4.5				
22	2251.634	7.504	7.4				
23	2250.946	7.502	6.1				
24	2250.121	7.499	7.6				
25	2244.073	7.479	3.5				
26	2243.523	7.477	3.4				
27	2242.561	7.474	3.5				
28	2242.011	7.472	3.1				
29	2186.198	7.286	9.0				
30	2184.685	7.281	8.7				
31	2179.049	7.262	23.8				
32	2178.499	7.260	23.7				
33	2177.537	7.257	6.6				
34	2177.124	7.255	8.0				

300 MHz ^{1}H NMR Spectrum in $CDCl_3$



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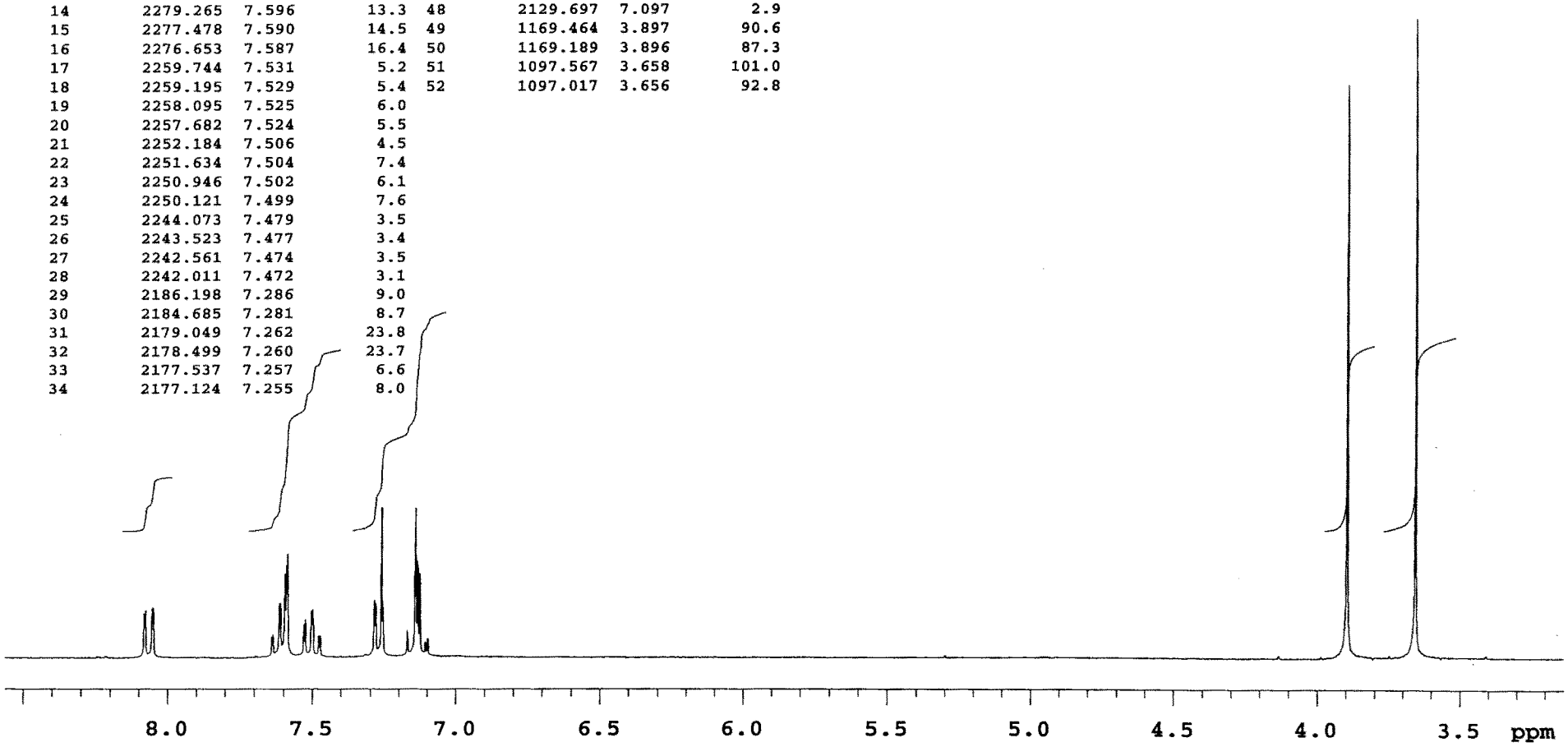
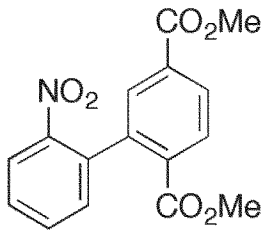


INDEX	FREQUENCY	PPM	HEIGHT
1	2452.319	8.173	11.1
2	2451.082	8.168	11.8
3	2448.608	8.160	4.5
4	2444.209	8.146	15.0
5	2442.834	8.141	18.9
6	2441.322	8.136	48.9
7	2440.360	8.133	41.1
8	2375.748	7.917	14.4
9	2374.786	7.914	21.4
10	2373.686	7.911	13.8
11	2307.700	7.691	5.2
12	2306.326	7.686	5.5
13	2300.139	7.665	12.4
14	2298.765	7.661	12.2
15	2292.716	7.641	9.3
16	2291.341	7.636	8.6
17	2276.219	7.586	8.4
18	2274.707	7.581	9.1
19	2268.109	7.559	9.6
20	2267.009	7.555	9.9
21	2260.685	7.534	5.6
22	2259.173	7.529	5.2
23	2189.888	7.298	12.1
24	2188.376	7.293	12.3
25	2182.464	7.273	10.9
26	2180.815	7.268	10.8
27	2178.478	7.260	7.1
28	1178.928	3.929	122.8
29	1104.281	3.680	123.4

300 MHz ^{1}H NMR Spectrum in $(CD_3)_2SO$



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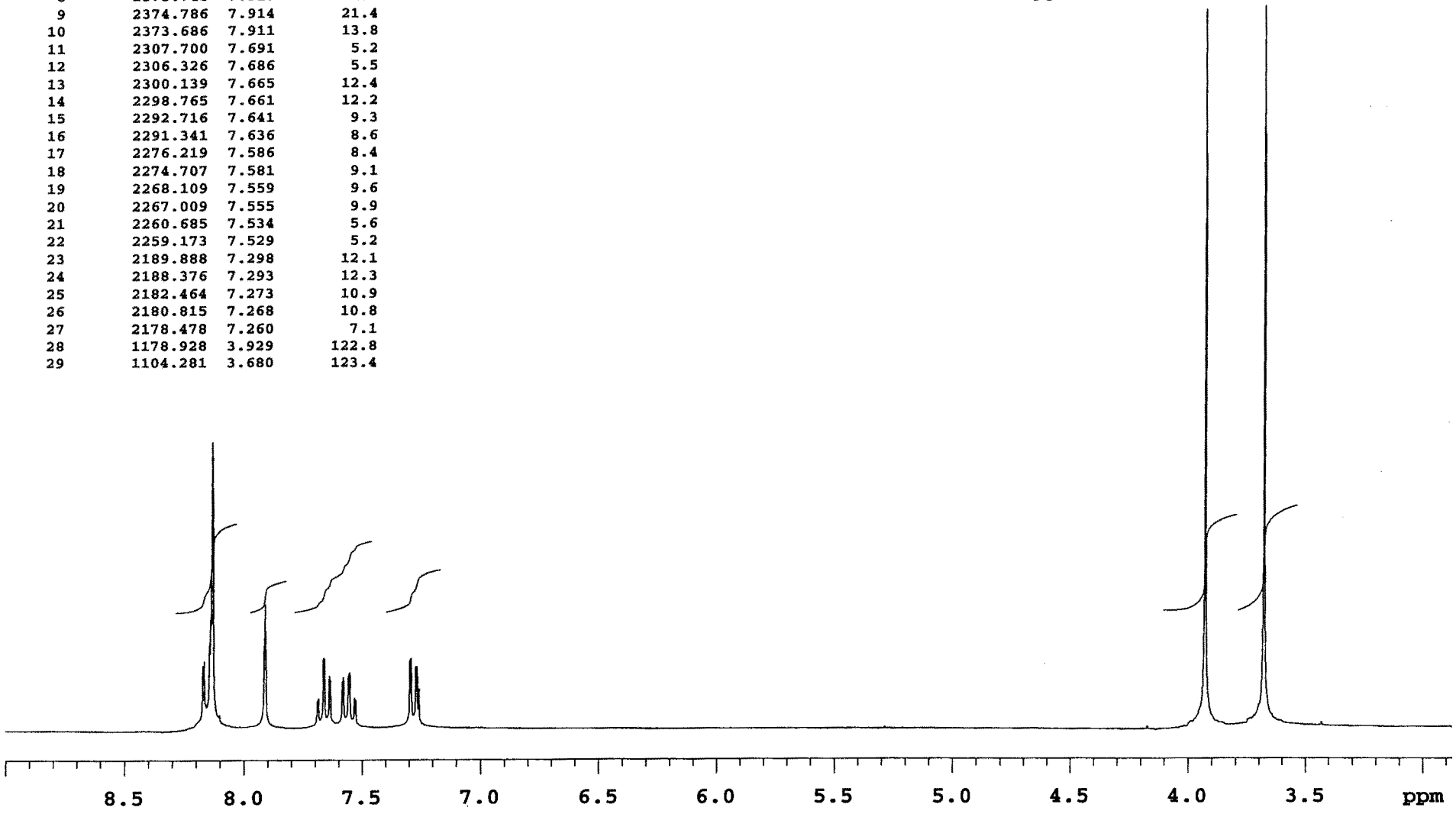
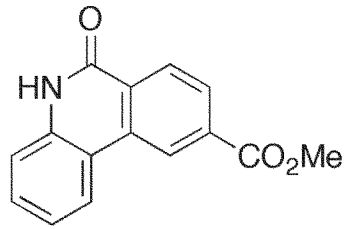


INDEX	FREQUENCY	PPM	HEIGHT
1	3567.219	11.888	16.1
2	2690.155	8.965	38.3
3	2534.676	8.447	44.0
4	2526.428	8.420	49.7
5	2495.359	8.316	51.1
6	2494.260	8.312	50.6
7	2444.495	8.146	24.9
8	2436.110	8.119	21.2
9	2270.045	7.565	9.4
10	2261.934	7.538	19.5
11	2254.648	7.514	15.7
12	2221.518	7.403	27.2
13	2213.269	7.376	19.5
14	2198.697	7.327	14.3
15	2191.686	7.304	20.6
16	2183.576	7.277	11.4
17	1188.287	3.960	142.4

300 MHz ^{1}H NMR Spectrum in $(CD_3)_2SO$



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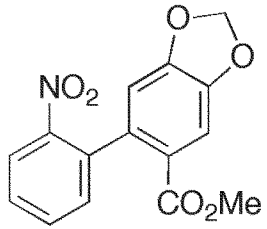
300 MHz ^{1}H NMR Spectrum in $CDCl_3$



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