SUPPORTING INFORMATION

The Synthesis of Indoles via Palladium[0]-Mediated Ullmann Cross-Coupling of *o*-Halonitroarenes with α -Halo-enones or -enals*

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Preparation and Characterization of Compounds

3, 4, 7, 8, 10, 11, 13, 14, 16, 17, 19, 20, 22, 23, 25–28 and 30–34.

(i) (Z)-2-Iodocrotonaldehyde (**32**)

Following the protocol developed by Johnson *et al.*¹, a solution of iodine (4.06 g, 16 mmol) in 1:1 v/v CCl₄/pyridine (10 mL) was added, dropwise, to a magnetically stirred solution of crotonaldehyde (280 mg, 4 mmol) in 1:1 v/v CCl₄/pyridine (10 mL) maintained at 0 °C (ice-water bath) under a nitrogen atmosphere. The resulting solution was stirred for a further 24 h during which time temperature was allowed to rise to 18 °C. After dilution with diethyl ether (250 mL) the reaction mixture was washed with water (3 × 75 mL), HCl (2 × 50 mL of a 1 M aq. solution), water (1 × 40 mL) and Na₂S₂O₃ (20 w/v% aq. solution) then dried (MgSO₄) filtered and concentrated under reduced pressure to give the title aldehyde (463 mg, 62%) as an unstable light-yellow oil that was used immediately in the Ullmann cross-coupling reaction with *o*-iodonitrobenzene.

(ii) General Procedure for Pd[0]-Catalysed Ullmann Coupling Reactions Used in Preparing Compounds **3, 7, 10, 13, 16, 19, 22, 25, 26, 30 and 33**

A magnetically stirred mixture of the appropriate 2-halonitroarene (10 mmol), the appropriate α -halo-enone or -enal (5 mmol), copper powder (1.59 g of 99% material, 25 g.atom, CAS No. 7440-50-8) and Pd₂(dba)₃ (260 mg, 0.25 mmol) in DMSO (15 mL) was heated at 70 °C for 1 h under a nitrogen atmosphere then cooled and diluted with diethyl ether (150 mL). The resulting mixture was then filtered through a pad of Celite and the solids thus retained washed with ether (50 mL). The combined filtrates were washed with water (2 × 150 mL) and brine (1 × 150 mL) then dried (MgSO₄), filtered and concentrated under reduced pressure to give a brown oil which often solidified. Subjection of this material to flash chromatography (silica, ethyl acetate/hexane elution) and concentration of the appropriate fractions then afforded the title coupling products.

(iii) Preparation of Compound **26**

The title compound was prepared by Suzuki-Miyaura cross-coupling of bromo-arene **25** with 1,3-benzodioxol-5-ylboronic acid.² Thus, a magnetically stirred mixture of compound **25** (225 mg, 0.76 mmol), the above-mentioned acid, Pd(PPh₃)₄ (27 mg, 0.02 mmol), K₂CO₃ (1.8 mL of a 2 M aqueous solution), benzene (10 mL) and ethanol (3.75 mL) was heated at reflux for 16 h. The cooled reaction mixture was partitioned between ethyl

acetate (100 mL) and water (150 mL) and the separated organic phase dried (MgSO₄), filtered and concentrated at reduced pressure. The resulting brown residue was subject to flash chromatography (silica, 1:2 v/v ethyl acetate/hexane elution) and concentration of the appropriate fractions (*R_f* 0.2) then gave the title compound **26** (196 mg, 77%) as a yellow crystalline solid, mp 188–189 °C.

(iv) General Procedure for Reductive Cyclisation Reactions Used in Preparing Compounds 4, 8, 11, 14, 17, 20, 23, 27, 28, 31 and 34

A mixture of the relevant substrate (0.11 mmol) and 10% Pd on C (20 weight% wrt substrate) in methanol (5 mL) was stirred under an atmosphere of dihydrogen for 0.75 h then filtered through a pad of Celite. The solids thus retained were washed with methanol (*ca.* 5 mL) and the combined filtrates concentrated under reduced pressure. Subjection of the residue thus obtained to flash chromatography (silica, ethyl acetate/hexane elution) and concentration of the appropriate fractions then afforded the title coupling products.

When compound **26** was subject to the hydrogenation conditions defined above two products were obtained. Subjection of the crude reaction mixture to preparative TLC (silica, 1:4 v/v ethyl acetate/hexane elution) afforded two bands, A and B. Extraction of band A (*R_f* 0.3) afforded compound **27** (43%) as white crystalline solid whilst extraction of band B (*R_f* 0.5) compound **28** (38%), also obtained as white crystalline solid. Subjection of compound **26** to the reductive cyclisation conditions defined above for 16 h resulted in its complete conversion into indole **28**.

(v) Characterization Data for Compounds 3, 4, 7, 8, 10, 11, 13, 14, 16, 17, 19, 20, 22, 23, 25–28 and 30–34.

2-(2-Nitrophenyl)-2-cyclohexen-1-one (3)³

R_f 0.35 (silica, 3:7 v/v ethyl acetate/hexane), mp = 92–95 °C (Lit.^{3a} mp = 96–98 °C). ¹H NMR (CDCl₃, 300 MHz) δ 7.99 (dd, *J* = 8.1 and 1.5 Hz, 1H), 7.58 (td, *J* = 7.5 and 1.5 Hz, 1H), 7.45 (td, *J* = 8.1 and 1.5 Hz, 1H), 7.24 (dd, *J* = 7.5 and 1.5 Hz, 1H), 7.01 (t, *J* = 4.2 Hz, 1H), 2.62–2.52 (complex m, 4H), 2.13 (p, *J* = 6.9 Hz, 2H); ¹³C NMR (CDCl₃, 75 MHz) δ 196.4, 148.4, 146.8, 139.2, 133.2, 131.9, 131.5, 128.6, 123.9, 38.1, 26.1, 22.4; IR, ν_{max} (NaCl) 2942, 1674, 1519, 1345, 789, 749, 710, 562 cm⁻¹; MS, *m/z* (EI, 70 eV) 217 (M⁺, 11%), 172 (46), 145 (47), 115 (69), 77 (75), 55 (100); HRMS, Found: M⁺, 217.0737. C₁₂H₁₁NO₃ requires M⁺, 217.0739.

2,3,4,9-Tetrahydro-1H-carbazole (4)³

R_f 0.65 (silica, 1:4 v/v ethyl acetate/hexane), mp = 110–115 °C (Lit.⁴ mp = 117 °C). ¹H NMR (CDCl₃, 300 MHz) δ 7.63 (broad s, 1H), 7.48 (m, 1H), 7.28 (m, 1H), 7.16–7.06 (complex m, 2H), 2.73 (m, 4H), 1.92 (m, 4H); ¹³C NMR (CDCl₃, 75 MHz) δ 135.5, 134.0, 127.7, 120.9, 119.0, 117.6, 110.2, 110.1, 23.4, 23.3(1), 23.2(8), 21.0.

2-(2-Nitrophenyl)-2-cyclopenten-1-one (7)³

R_f 0.3 (silica, 3:7 v/v ethyl acetate/hexane), mp = 90–94 °C. ¹H NMR (CDCl₃, 300 MHz) δ 7.97 (dd, J = 8.1 and 1.2 Hz, 1H), 7.68 (t, J = 2.7 Hz, 1H), 7.58 (dt, J = 8.1 and 1.5 Hz, 1H), 7.46 (dt, J = 7.3 and 1.2 Hz, 1H), 7.31 (dd, J = 7.3 and 1.5 Hz, 1H), 2.80–2.76 (complex m, 2H), 2.56–2.52 (complex m, 2H); ¹³C NMR (CDCl₃, 75 MHz) δ 205.1, 158.8, 148.2, 143.7, 133.0, 131.1, 129.0, 127.1, 124.3, 34.6, 27.1; IR, $\nu_{\max}$ (KBr) 3072, 2927, 1700, 1631, 1576, 1519, 1472, 1438, 1400, 1343, 1318, 1140 cm⁻¹; MS, m/z (EI, 70 eV) 203 (M⁺, 75%), 157 (60), 148 (90), 120 (82), 104 (98), 91 (62), 77 (87), 63 (61), 55 (100); HRMS, Found: M⁺, 203.0581. C₁₁H₉NO₃ requires M⁺, 203.0582.

1,2,3,4-Tetrahydrocyclopent[b]indole (8)⁵

R_f 0.6 (silica, 1:4 v/v ethyl acetate/hexane), mp = 97–102 °C (Lit.⁴⁵ mp = 103–106 °C). ¹H NMR (CDCl₃, 300 MHz) δ 7.73 (broad s, 1H), 7.52 (m, 1H), 7.30 (m, 1H), 7.17 (m, 2H), 2.94–2.84 (complex m, 4H), 2.61 (m, 2H); ¹³C NMR (CDCl₃, 75 MHz) δ 143.5, 140.8, 124.5, 120.3, 119.5, 119.3, 118.3, 111.2, 28.7, 25.8, 24.4; MS, m/z (EI, 70 eV) 157 (M⁺, 100%), 156 (52), 130 (32), 128 (29).

2-(2-Nitrophenyl)-2-cyclohepten-1-one (10)³

R_f 0.5 (silica, 2:3 v/v ethyl acetate/hexane), mp = 76–78 °C. ¹H NMR (CDCl₃, 300 MHz) δ 8.05 (dd, J = 8.1 and 1.3 Hz, 1H), 7.60 (td, J = 7.5 and 1.3 Hz, 1H), 7.46 (td, J = 8.1 and 1.5 Hz, 1H), 7.29 (dd, J = 7.5 and 1.5 Hz, 1H), 6.72 (t, J = 6.3 Hz, 1H), 2.79 (m, 2H), 2.59 (m, 2H), 1.92 (m, 4H); ¹³C NMR (CDCl₃, 75 MHz) δ 202.7, 143.1, 143.0, 135.2, 133.5, 132.7, 128.6, 124.4, 42.5, 27.9, 25.1, 21.1 (one signal overlapping or obscured); IR, $\nu_{\max}$ (KBr) 2940, 1670, 1523, 1349, 788, 747 cm⁻¹; MS, m/z (EI, 70 eV) 231 (M⁺, 3%), 185 (70), 158 (60), 115 (61), 104 (64), 91 (56), 77 (79); HRMS, Found: M⁺, 231.0894. C₁₃H₁₃NO₃ requires M⁺, 231.0895.

5,6,7,8,9,10-Hexahydrocyclohept[b]indole (11)⁶

R_f 0.5 (silica, 1:4 v/v ethyl acetate/hexane), mp = 135–138 °C (Lit.⁶ mp = 140–141 °C). ¹H NMR (CDCl₃, 300 MHz) δ 7.70 (broad s, 1H), 7.47 (m, 1H), 7.25 (m, 1H), 7.08 (m, 2H), 2.81 (m, 4H), 2.00–1.50 (complex m, 6H); ¹³C NMR (CDCl₃, 75 MHz)

δ 137.4, 134.2, 129.2, 120.6, 119.0, 117.6, 113.7, 110.1, 31.8, 29.6, 28.7, 27.5, 24.6; IR, $\nu_{\max}$ (KBr) 3392, 2913, 1466, 1437, 740 cm^{-1} ; MS, m/z (EI, 70 eV) 185 (M^+ , 100%), 184 (62), 156 (76); HRMS, Found: M^+ , 185.1201. $\text{C}_{13}\text{H}_{15}\text{N}$ requires M^+ , 185.1204.

3-(2-Nitrophenyl)-4-oxo-2-cyclopentene-1-acetic acid Ethyl Ester (13)

R_f 0.3 (silica, 2:3 v/v ethyl acetate/hexane), mp = 85–87 °C, $[\alpha]_D + 9.2$ (c 2.7, CHCl_3); ^1H NMR (CDCl_3 , 300 MHz) δ 8.03 (dd, J = 8.1 and 1.2 Hz, 1H), 7.62 (d, J = 2.7 Hz, 1H), 7.61 (td, J = 7.5 and 1.2 Hz, 1H), 7.51 (dt, J = 8.1 and 1.5 Hz, 1H), 7.33 (dd, J = 7.5 and 1.5 Hz, 1H), 4.18 (q, J = 7.0 Hz, 2H), 3.47 (m, 1H), 2.86 (dd, J = 19.0 and 6.6 Hz, 1H), 2.62 (m, 2H), 2.30 (dd, J = 19.0 and 2.7 Hz, 1H), 1.28 (t, J = 7.0 Hz, 3H); ^{13}C NMR (CDCl_3 , 75 MHz) δ 203.8, 171.2, 160.0, 148.4, 144.2, 133.2, 131.3, 129.4, 126.9, 124.6, 60.9, 41.2, 38.7, 35.6, 14.2; IR, $\nu_{\max}$ (KBr) 2983, 1728 (sh), 1714, 1528, 1354, 1183, 1026, 788 cm^{-1} .

1,2,3,4-Tetrahydrocyclopent[b]indole-2-acetic acid Ethyl Ester (14)

R_f 0.25 (silica, 1:4 v/v ethyl acetate/hexane), mp = 77–79 °C, $[\alpha]_D -25.1$ (c 0.8, CHCl_3); ^1H NMR (CDCl_3 , 300 MHz) δ 7.84 (broad s, 1H), 7.41 (m, 1H), 7.30 (m, 1H), 7.08 (m, 2H), 4.17 (q, J = 6.9 Hz, 2H), 3.38 (m, 1H), 3.12 (m, 2H), 2.68–2.48 (complex m, 4H), 1.28 (t, J = 6.9 Hz, 3H); ^{13}C NMR (CDCl_3 , 75 MHz) δ 172.9, 141.6, 140.7, 124.7, 120.7, 119.6, 118.4, 118.0, 111.3, 60.3, 41.2, 39.9, 32.4, 31.3, 14.3; IR, $\nu_{\max}$ (KBr) 3401, 2931, 2349, 1731, 1719 (sh), 1454, 1371, 1262, 1192, 1027, 741 cm^{-1} ; MS, m/z (EI, 70 eV) 243 (M^+ , 76%), 156 (38), 155 (100); HRMS, Found: M^+ , 243.1260. $\text{C}_{15}\text{H}_{17}\text{NO}_2$ requires M^+ , 243.1259.

(Z)-2-(2-Nitrophenyl)-3-phenyl-2-propenal (16)

R_f 0.45 (silica, 1:2 v/v ethyl acetate/hexane), mp = 73–75 °C. ^1H NMR (CDCl_3 , 300 MHz) δ 9.72 (s, 1H), 8.23 (m, 1H), 7.59 (m, 2H), 7.54 (s, 1H), 7.36–7.22 (complex m, 3H), 7.22–7.12 (complex m, 3H); ^{13}C NMR (CDCl_3 , 75 MHz) δ 191.8, 148.9, 148.7, 139.4, 133.9, 133.2, 131.9, 130.4, 130.4, 129.5, 129.4, 128.6, 124.8; IR, $\nu_{\max}$ (KBr) 3068, 1684, 1628, 1607, 1573, 1522, 1347, 1110, 1063, 857, 788, 746, 716, 694 cm^{-1} ; MS, m/z (EI, 70 eV) 253 (M^+ , <1%), 224 (76), 208 (40), 180 (43), 178 (46), 165 (48), 152 (72), 119 (74), 91 (100), 77 (52); HRMS, Found: M^+ , 253.0733. $\text{C}_{15}\text{H}_{11}\text{NO}_3$ requires M^+ , 253.0739.

3-(Phenylmethyl)-1H-indole (17)⁷

R_f 0.4 (silica, 1:4 v/v ethyl acetate/hexane), mp = 104–106 °C (Lit.⁷ mp = 102–105 °C). ^1H NMR (CDCl_3 , 300 MHz) δ 7.94 (s, 1H), 7.54 (d, J = 8.0 Hz, 1H), 7.36

(dm, $J = 8.0$ Hz, 1H), 7.34–7.16 (complex m, 6H), 7.10 (tm, $J = 7.2$ Hz, 1H), 6.92 (broad s, 1H), 4.14 (s, 2H); ^{13}C NMR (CDCl_3 , 75 MHz) δ 141.2, 136.4, 128.7, 128.3, 127.4, 125.8, 122.3, 122.0, 119.3, 119.1, 115.8, 111.0, 31.6; IR, ν_{max} (KBr) 3402, 1457, 1339, 1088, 1075, 1009, 743, 711 cm^{-1} ; MS, m/z (EI, 70 eV) 207 (M^+ , 100%), 206 (80), 130 (85); HRMS, Found: M^+ , 207.1043. $\text{C}_{15}\text{H}_{13}\text{N}$ requires M^+ , 207.1048.

2-(2,4-Dinitrophenyl)-2-cyclohexen-1-one (19)

R_f 0.25 (silica, 2:3 v/v ethyl acetate/hexane), mp = 142–143 °C. ^1H NMR (CDCl_3 , 300 MHz) δ 8.86 (d, $J = 2.4$ Hz, 1H), 8.44 (dd, $J = 8.4$ and 2.1 Hz, 1H), 7.49 (d, $J = 8.4$ Hz, 1H), 7.15 (t, $J = 3.9$ Hz, 1H), 2.63 (m, 4H), 2.18 (p, $J = 6.9$ Hz, 2H); ^{13}C NMR (CDCl_3 , 75 MHz) δ 195.7, 148.8, 148.6, 147.3, 138.0, 137.9, 132.9, 127.4, 119.6, 38.0, 26.3, 22.3; IR, ν_{max} (KBr) 3109, 1684, 1600, 1528, 1348, 1158, 1120, 907, 833, 734 cm^{-1} ; MS, m/z (EI, 70 eV) 262 (M^+ , 2%), 217 (24), 216 (32), 55 (100); HRMS, Found: M^+ , 262.0583. $\text{C}_{12}\text{H}_{10}\text{N}_2\text{O}_5$ requires M^+ , 262.0590.

2,2',4,4',-Tetranitrobiphenyl (by-product associated with the formation of compound 19)

R_f 0.25 (silica, 3:7 v/v ethyl acetate/hexane), mp = 148–152 °C. ^1H NMR (CDCl_3 , 300 MHz) δ 9.16 (d, $J = 2.4$ Hz, 2H), 8.62 (dd, $J = 8.4$ and 2.4 Hz, 2H), 7.56 (d, $J = 8.4$ Hz, 2H); ^{13}C NMR (CDCl_3 , 75 MHz) δ 148.3, 146.8, 138.7, 131.7, 128.2, 120.8; IR, ν_{max} (KBr) 3109, 2925, 2854, 1600, 1348, 1525, 1343, 1080, 1008, 908, 833 cm^{-1} ; MS, m/z (EI, 70 eV) 318 (3%), 288 (95), 214 (100); HRMS, Found: $(\text{M}-\text{NO}_2)^+$, 288.0255. $\text{C}_{12}\text{H}_6\text{N}_4\text{O}_8$ requires $(\text{M}-\text{NO}_2)^+$, 288.0257.

2,3,4,9-Tetrahydro-1H-carbazol-7-amine (20)⁸

R_f 0.1 (silica, 2:3 v/v ethyl acetate/hexane), mp = 103–108 °C (Lit.⁸ mp = 103–104 °C). ^1H NMR (CDCl_3 , 300 MHz) δ 7.43 (broad s, 1H), 7.23 (d, $J = 7.8$ Hz, 1H), 6.59 (broad s, 1H), 6.53 (d $J = 7.8$ Hz, 1H), 3.45 (broad s, 2H), 2.65 (broad s, 4H), 1.86 (broad s, 4H); ^{13}C NMR (CD_3OD , 75 MHz) δ 151.6, 138.6, 133.4, 123.4, 118.5, 110.7, 109.6, 99.0, 24.7, 24.5, 24.0, 22.0; IR, ν_{max} (KBr) 3392, 2928, 1631, 1504, 1470, 1328, 1151, 801 cm^{-1} ; MS, m/z (EI, 70 eV) 186 (M^+ , 100%), 185 (30), 158 (100); HRMS, Found: M^+ , 186.1157. $\text{C}_{12}\text{H}_{14}\text{N}_2$ requires M^+ , 186.1157.

2-(4-Methoxy-2-nitrophenyl)-2-cyclohexen-1-one (22)

R_f 0.3 (silica, 3:7 v/v ethyl acetate/hexane), mp = 64–66 °C. ^1H NMR (CDCl_3 , 300 MHz) δ 7.54 (d, $J = 2.4$ Hz, 1H), 7.14–7.13 (complex m, 2H), 6.96 (t, $J = 4.2$ Hz, 1H), 3.87 (s, 3H), 2.59–2.53 (complex m, 4H), 2.15–2.11 (complex m, 2H); ^{13}C NMR (CDCl_3 , 75 MHz) δ 196.9, 159.5, 149.1, 146.1, 139.1, 132.5, 124.3, 119.6, 109.1, 55.9, 38.3,

26.3, 22.6; IR, ν_{max} (KBr) 2913, 2847, 1678, 1613, 1523, 1494, 1454, 1346, 1230, 1035 cm^{-1} ; MS, m/z (EI, 70 eV) 247 (M^+ , 15%), 201 (100), 134 (20), 121 (17), 77 (17); HRMS, Found: M^+ , 247.0843. $\text{C}_{13}\text{H}_{13}\text{NO}_4$ requires M^+ , 247.0845.

2,3,4,9-Tetrahydro-7-methoxy-1H-carbazole (23)⁹

R_f 0.2 (silica, 1:9 v/v ethyl acetate/hexane), mp = 136–142 °C [Lit.⁹ mp = 145.5–147 °C (vac)]. ^1H NMR (CDCl_3 , 300 MHz) δ 7.54 (broad s, 1H), 7.33 (d, J = 8.4 Hz, 1H), 6.80 (d, J = 2.1 Hz, 1H), 6.76 (dd, J = 8.7 and 2.1 Hz, 1H), 3.84 (s, 3H), 2.71–2.67 (complex m, 4H), 1.92–1.85 (complex m, 4H); ^{13}C NMR (CDCl_3 , 75 MHz) δ 155.8, 136.3, 132.8, 122.4, 118.2, 109.9, 108.2, 94.8, 55.8, 23.3, 23.2, 20.9 (one signal obscured or overlapping); IR, ν_{max} (KBr) 3405, 2913, 2833, 1627, 1566, 1450, 1154, 1028 cm^{-1} ; MS, m/z (EI, 70 eV) 201 (M^+ , 100%), 186 (55), 173 (75); HRMS, Found: M^+ , 201.1156. $\text{C}_{13}\text{H}_{15}\text{NO}$ requires M^+ , 201.1154.

2-(4-Bromo-2-nitrophenyl)-2-cyclohexen-1-one (25)

R_f 0.3 (silica, 1:2 v/v ethyl acetate/hexane), oil. ^1H NMR (CDCl_3 , 300 MHz) δ 8.16 (d, J = 2.1 Hz, 1H), 7.72 (dd, J = 8.1 and 2.1 Hz, 1H), 7.13 (d, J = 8.1 Hz, 1H), 7.02 (t, J = 4.2 Hz, 1H), 2.58 (m, 4H), 2.15 (m, 2H); ^{13}C NMR (CDCl_3 , 75 MHz) δ 196.2, 148.9, 147.1, 138.5, 136.2, 132.9, 130.9, 127.2, 121.9, 38.2, 26.3, 22.5; IR, ν_{max} (KBr) 2984, 1681, 1529, 1351, 1095 876, 830, 741 cm^{-1} ; MS, m/z (EI, 70 eV) 297 and 295 (M^+ , 12 and 12%), 251 and 249 (68 and 68), 55 (100); HRMS, Found: M^+ , 294.9847. $\text{C}_{12}\text{H}_{10}^{79}\text{BrNO}_3$ requires M^+ , 294.9844.

2-{{4-Benzo[1,3]dioxol-5-yl}-2-nitrophenyl}-2-cyclohexen-1-one (26)

R_f 0.2 (silica, 1:2 v/v ethyl acetate/hexane), mp = 188–189 °C. ^1H NMR (CDCl_3 , 300 MHz) δ 8.15 (d, J = 2.1 Hz, 1H), 7.72 (dd, J = 8.1 and 2.1 Hz, 1H), 7.28 (d, J = 8.1 Hz, 1H), 7.08 (dd, J = 8.1 and 1.8 Hz, 1H), 7.07 (s, 1H), 7.04 (t, J = 4.2 Hz, 1H), 6.90 (dm, J = 8.1 Hz, 1H), 6.03 (s, 2H), 2.59 (m, 4H), 2.16 (p, J = 7.2 Hz, 2H); ^{13}C NMR (CDCl_3 , 75 MHz) δ 196.6, 148.8, 148.4, 148.0, 146.6, 141.8, 139.1, 132.5, 132.0, 131.1, 130.2, 122.3, 120.8, 108.8, 107.3, 101.4, 38.3, 26.3, 22.6; IR, ν_{max} (KBr) 2953, 1680, 1531, 1509, 1480, 1356, 1250, 1229, 1109, 1038, 862, 812 cm^{-1} ; MS, m/z (EI, 70 eV) 337 (M^+ , 43%), 291 (38), 177 (100), 149 (71); HRMS, Found: M^+ , 337.0951. $\text{C}_{19}\text{H}_{15}\text{NO}_5$ requires M^+ , 337.0950.

2-{{4-Benzo[1,3]dioxol-5-yl}-2-nitrophenyl}cyclohexanone (27)

R_f 0.3 (silica, 1:4 v/v ethyl acetate/hexane), mp = 153–155 °C. ^1H NMR (CDCl_3 , 300 MHz) δ 8.13 (d, J = 2.1 Hz, 1H), 7.72 (dd, J = 8.1 and 1.8 Hz, 1H), 7.37 (d, J = 8.1 Hz,

1H), 7.07 (dd, $J = 7.2$ and 2.1 Hz, 1H), 6.90 (d, $J = 6.9$ Hz, 1H), 6.03 (s, 2H), 4.31 (dd, $J = 14.0$ and 6.0 Hz, 1H), 2.51 (m, 2H), 2.40 (m, 1H), 2.20 (m, 1H), 2.10 (m, 2H), 1.85 (m, 2H), 1.65 (broad s, 1H); ^{13}C NMR (CDCl_3 , 75 MHz) δ 208.3, 149.6, 148.5, 148.0, 140.9, 132.6, 132.2, 131.1, 130.7, 123.0, 120.9, 108.8, 107.4, 101.4, 53.2, 42.2, 33.8, 27.3, 25.4; IR, ν_{max} (KBr) 2933, 1712, 1532, 1509, 1481, 1351, 1229, 1039, 811 cm^{-1} ; MS, m/z (EI, 70 eV) 399 (M^+ , 100%), 322 (915), 266 (45), 250 (30); HRMS, Found: M^+ , 339.1100. $\text{C}_{19}\text{H}_{17}\text{NO}_5$ requires M^+ , 339.1107.

7-{4-Benzo[1,3]dioxol-5-yl}-2,3,4,9-tetrahydro-1H-carbazole (28)

R_f 0.5 (silica, 1:4 v/v ethyl acetate/hexane), mp = 169–171 °C. ^1H NMR (CDCl_3 , 300 MHz) δ 7.71 (s, 1H), 7.47 (d, $J = 8.1$ Hz, 1H), 7.39 (m, 1H), 7.26 (m, 1H), 7.14–7.06 (complex m, 2H), 6.88 (d, $J = 8.1$ Hz, 1H), 5.99 (s, 2H), 2.73 (m, 4H), 1.90 (m, 4H); ^{13}C NMR (CDCl_3 , 75 MHz) δ 147.9, 146.3, 137.1, 136.1, 134.8, 134.2, 126.9, 120.5, 118.7, 117.8, 110.1, 108.7, 108.4, 107.9, 100.9, 23.3, 23.2, 23.1, 20.9; IR, ν_{max} (KBr) 3393, 2929, 1508, 1472, 1241, 1042, 927, 801 cm^{-1} ; MS, m/z (EI, 70 eV) 291 (M^+ , 100%), 263 (73); HRMS, Found: M^+ , 291.1262. $\text{C}_{19}\text{H}_{17}\text{NO}_2$ requires M^+ , 291.1259.

(3Z)-3-(2-Nitrophenyl)-4-phenyl-3-buten-2-one (30)

R_f 0.2 (silica, 1:4 v/v ethyl acetate/hexane), yellow oil. ^1H NMR (CDCl_3 , 300 MHz) δ 8.22 (m, 1H), 7.69 (s, 1H), 7.55 (m, 2H), 7.25–7.10 (complex m, 4H), 7.01 (m, 1H), 6.98 (m, 1H), 2.52 (s, 3H); ^{13}C NMR (CDCl_3 , 75 MHz) δ 197.3, 139.3, 139.0, 133.9(2), 133.9(0), 132.4, 130.2, 129.5, 129.1, 128.5, 124.8, 26.5 (two signals obscured or overlapping); IR, ν_{max} (KBr) 3065, 1667, 1624, 1606, 1519, 1346, 1234, 1168, 851, 789 cm^{-1} ; MS, m/z (EI, 70 eV) 267 (M^+ , <1%), 266 (<1), 251 (<1), 208 (54), 198 (100), 180 (48), 168 (40), 152 (32), 119 (36), 105 (50); HRMS, Found: M^+ , 267.0903. $\text{C}_{16}\text{H}_{13}\text{NO}_3$ requires M^+ , 267.0895.

2-Methyl-3-(phenylmethyl)-1H-indole (31)¹⁰

R_f 0.35 (silica, 1:4 v/v ethyl acetate/hexane), oil (Lit.^{10a} mp = 117–119 °C, Lit.^{10b} mp = 89–90 °C). ^1H NMR (CDCl_3 , 300 MHz) δ 7.76 (broad s, 1H), 7.42 (d, $J = 7.8$ Hz, 1H), 7.30–7.14 (complex m, 6H), 7.13 (t, $J = 7.2$ Hz, 1H), 7.05 (t, $J = 6.9$ Hz, 1H), 4.10 (s, 2H), 2.38 (s, 3H); ^{13}C NMR (CDCl_3 , 75 MHz) δ 141.6, 135.2, 131.6, 128.8, 128.2(3), 128.2(2), 128.1(7), 125.6, 120.9, 119.2, 118.3, 110.5, 110.1, 30.0, 11.7 (one signal due to unidentified impurity); IR, ν_{max} (KBr) 3405, 3057, 1458, 1302, 1241, 1075, 739, 695, 590 cm^{-1} ; MS, m/z (EI, 70 eV) 221 (M^+ , 93%), 220 (56), 206 (58), 144 (100); Found: M^+ , 221.1206. $\text{C}_{16}\text{H}_{15}\text{N}$ requires M^+ , 221.1204.

(Z)-2-Iodocrotonaldehyde (32)

R_f 0.5 (silica, 3:7 v/v ethyl acetate/hexane), unstable oil. ^1H NMR (CDCl_3 , 300 MHz) δ 8.68 (s, 1H), 7.28 (q, $J = 6.9$ Hz, 1H), 2.20 (d, $J = 6.9$ Hz, 3H); ^{13}C NMR (CDCl_3 , 75 MHz) δ 187.7, 158.0, 113.3, 22.6.

(Z)-2-(2-Nitrophenyl)crotonaldehyde (33)

R_f 0.4 (silica, 3:7 v/v ethyl acetate/hexane), oil. ^1H NMR (CDCl_3 , 300 MHz) δ 9.56 (s, 1H), 8.13 (dd, $J = 7.8$ and 1.5 Hz, 1H), 7.64 (td, $J = 7.8$ and 1.5 Hz, 1H), 7.55 (td, $J = 7.8$ and 1.5 Hz, 1H), 7.19 (dd, $J = 7.8$ and 1.5 Hz, 1H), 6.96 (q, $J = 7.1$ Hz, 1H), 1.94 (d, $J = 7.1$ Hz, 3H); ^{13}C NMR (CDCl_3 , 75 MHz) δ 191.6, 149.7, 143.3, 133.3, 132.1, 129.3, 129.1, 128.3, 124.8, 15.9; IR, ν_{max} (KBr) 2827, 1687, 1644, 1522, 1347, 1225, 1133, 788, 743, 708 cm^{-1} ; MS, m/z (EI, 70 eV) 191 (M^+ , 6%), 198 (43), 162 (55), 135 (100), 115 (67), 104 (52), 91 (53), 77 (55); HRMS, Found: M^+ , 191.0576. $\text{C}_{10}\text{H}_9\text{NO}_3$ requires M^+ , 191.0582.

3-Ethyl-1H-indole (34)¹¹

R_f 0.7 (silica, 1:4 v/v ethyl acetate/hexane), oil (Lit.^{11a} mp = 43–45 °C). ^1H NMR (CDCl_3 , 300 MHz) δ 7.91 (broad s, 1H), 7.62 (d, $J = 7.3$ Hz, 1H), 7.36 (d, $J = 7.8$ Hz, 1H), 7.19 (t, $J = 7.8$ Hz, 1H), 7.12 (t, $J = 7.3$ Hz, 1H), 6.98 (broad s, 1H), 2.80 (q, $J = 7.5$ Hz, 2H), 1.34 (t, $J = 7.5$ Hz, 3H); ^{13}C NMR (CDCl_3 , 75 MHz) δ 136.4, 121.8, 120.4, 119.0, 118.9, 118.8, 111.0, 18.3, 14.4 (one signal overlapping or obscured); IR, ν_{max} (KBr) 3405, 2963, 1617, 1454, 1338, 1089, 739 cm^{-1} ; MS, m/z (EI, 70 eV) 145 (M^+ , 63%), 144 (30), 131 (30), 130 (100), 77 (25).

References

1. Johnson, C. R.; Adams, J. P.; Braun, M. P.; Senanayake, C. B. W.; Wovkulich, P. M.; Uskokovic, M. R. *Tetrahedron Lett.* **1992**, *33*, 917.
2. Banwell, M. G.; Cowden, C. J. *Aust. J. Chem.* **1994**, *47*, 2235.
3. (a) Scott, T. L.; Söderberg, B. C. G. *Tetrahedron Lett.* **2002**, *43*, 1621. (b) Solé, D.; Bosch, J.; Bonjoch, J. *Tetrahedron* **1996**, *52*, 4013.
4. Adam, G.; Andrieux, J.; Plat, M. *Tetrahedron* **1985**, *41*, 399.
5. (a) Miyata, O.; Kimura, Y.; Naito, T. *Synthesis* **2001**, 1635. (b) Wender, P. A.; Cooper, C. B. *Tetrahedron* **1986**, *42*, 2985.
6. Anderson, A. G., Jr.; Richards, H. F.; Haddock, R. D. *Org. Prep. Proced. Int.* **1989**, *21*, 649.
7. Stuetz, P.; Stadler, P. A. *Org. Synth.* **1977**, *56*, 8.
8. Kuehne, M. E. *J. Am. Chem. Soc.* **1962**, *84*, 837.
9. Wender, P. A.; White, A. W. *Tetrahedron* **1983**, *39*, 3767.
10. (a) Dave, V.; Warnhoff, E. W. *Can. J. Chem.* **1976**, *54*, 1015. (b) Satoh, T.; Kaneko, Y.; Sakata, K.; Yamakawa, K. *Bull. Chem. Soc. Jpn.* **1986**, *59*, 457.
11. (a) Kubo, A.; Nakai, T. *Synthesis* **1980**, 365. (b) Amat, M.; Hadida, S.; Sathyanarayana, S.; Bosch, J. *Org. Synth.* **1996**, *74*, 248.

300 MHz ^1H NMR Spectrum of
Compound **4** (solvent CDCl_3)

300 MHz ^1H NMR Spectrum of
Compound 7 (solvent CDCl_3)

300 MHz ^1H NMR Spectrum of
Compound **8** (solvent CDCl_3)

300 MHz ^1H NMR Spectrum of
Compound **10** (solvent CDCl_3)

300 MHz ^1H NMR Spectrum of
Compound **11** (solvent CDCl_3)

300 MHz ^1H NMR Spectrum of
Compound **13** (solvent CDCl_3)

300 MHz ^1H NMR Spectrum of
Compound **14** (solvent CDCl_3)

300 MHz ^1H NMR Spectrum of
Compound **16** (solvent CDCl_3)

300 MHz ^1H NMR Spectrum of
Compound **19** (solvent CDCl_3)

300 MHz ^1H NMR Spectrum of
Compound **20** (solvent CDCl_3)

300 MHz ^1H NMR Spectrum of
Compound **22** (solvent CDCl_3)

300 MHz ^1H NMR Spectrum of
Compound **23** (solvent CDCl_3)

300 MHz ^1H NMR Spectrum of
Compound **26** (solvent CDCl_3)

300 MHz ^1H NMR Spectrum of
Compound **27** (solvent CDCl_3)

300 MHz ^1H NMR Spectrum of
Compound **28** (solvent CDCl_3)

300 MHz ^1H NMR Spectrum of
Compound **30** (solvent CDCl_3)

300 MHz ^1H NMR Spectrum of
Compound **31** (solvent CDCl_3)

300 MHz ^1H NMR Spectrum of
Compound **32** (solvent CDCl_3)

300 MHz ^1H NMR Spectrum of
Compound **33** (solvent CDCl_3)

300 MHz ^1H NMR Spectrum of
Compound **34** (solvent CDCl_3)