Oxindole Synthesis by Direct C-H, Ar-H Coupling

Alexis Perry and Richard J. K. Taylor*

Department of Chemistry, University of York, Heslington, York YO10 5DD, UK.
rjkt1@york.ac.uk

Supporting Information

Known compounds:

The following compounds referred to in this communication have previously been reported in the literature: **1b**,[1] **1f**,[2] **1g**,[3] **4a**,[4] **4c**,[4] **4d**,[5] **5**.[6]

Data for novel compounds:

Ethyl 2-methyl-3-(methyl(phenyl)amino)-3-oxopropanoate 1a

Colourless oil, R_f = 0.4 (1:1 petrol:EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.47-7.35 (m, 3H; Ph 3-, 4- and 5-H), 7.25 (d, *J* = 7.5 Hz, 2H; Ph 2- and 6-H), 4.17-4.04 (m, 2H; OCH_2), 3.39 (q, *J* = 7.0 Hz, 1H; 2-H), 3.29 (s, 3H; NMe), 1.31 (d, *J* = 7.0 Hz, 3H; 1-Me), 1.23 ppm (t, *J* = 7.0, 3H; CH_2CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.8, 170.1, 143.6, 129.9, 128.2, 127.5, 61.1, 43.5, 37.6, 14.1, 14.0 ppm; IR (Neat): ν̃ = 2983, 1741, 1661, 1595, 1496, 1385, 1197 cm^{-1}; HRMS (ESI) calculated for $C_{13}H_{18}NO_3$ $[MH]^+$ requires 236.1281, found 236.1283 (0.8 ppm error).

Ethyl 3-(methyl(phenyl)amino)-3-oxo-2-phenylpropanoate 1c

Colourless oil, R_f = 0.3 (7:3 petrol:EtOAc); ^{1}H NMR (270 MHz, $CDCl_3$): δ = 7.44-7.37 (m, 3H; Ph 3-, 4- and 5-H), 7.30-7.24 (m, 3H; Ph 3-, 4- and 5-H), 7.19-7.07 (m, 4H; Ph 2- and 6-H), 4.58 (s, 1H; 2-H), 4.15 (q, *J* = 7.0 Hz, 2H; OCH_2), 3.27 (s, 3H; NMe), 1.22 ppm (t, *J* = 7.0, 3H; CH_2CH_3); ^{13}C NMR (68 MHz, $CDCl_3$): δ = 168.7, 167.6, 143.1, 133.4, 129.6, 129.3, 128.2, 128.1, 127.7, 127.6, 61.4, 55.6, 37.6, 13.9 ppm; IR (Neat): ν̃ = 2982, 1749, 1661, 1596, 1496, 1380, 1302, 1194 cm^{-1}; HRMS (ESI) calculated for $C_{18}H_{20}NO_3$ $[MH]^+$ requires 298.1438, found 298.1437 (0.3 ppm error).

2-Cyano-*N*-methyl-*N*-phenylpropanamide 1d

Colourless oil, R_f = 0.4 (1:1 petrol:EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.51-7.39 (m, 3H; Ph 3-, 4- and 5-H), 7.26 (d, *J* = 7.5 Hz, 2H; Ph 2- and 6-H), 3.43 (q, *J* = 7.0 Hz, 1H; 2-H), 3.30 (s, 3H; NMe), 1.44 ppm (d, *J* = 7.0, 3H; 3-H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 165.5, 142.2, 130.4, 128.9, 127.2, 118.3, 38.2, 29.4, 15.8 ppm; IR (Neat): ν̃ = 2921, 2201, 1667, 1596, 1496, 1388, 1122 cm^{-1}; HRMS (ESI) calculated for $C_{11}H_{13}N_2O$ $[MH]^+$ requires 189.1022, found 189.1022 (0.0 ppm error).

Diethyl (1-(methyl(phenyl)amino)-1-oxopropan-2-yl)phosphonate 1e

Colourless oil, R_f = 0.2 (EtOAc); ^{1}H NMR (270 MHz, $CDCl_3$): δ = 7.46-7.24 (m, 5H; Ph 2-, 3-, 4-, 5- and 6-H), 4.25-3.90 (m, 2H; OCH_2), 3.27 (d, *J*(H,P) = 1.0 Hz, 3H; NMe), 3.03 (dq, *J*(H,P) = 20.5 Hz, *J* = 7.0 Hz, 1H; 2-H), 1.33 (dd, *J*(H,P) = 18.5 Hz, *J* = 7.0 Hz, 3H; 3-H), 1.32 (t, *J* = 7.0 Hz, 3H; $CH_2C\mathit{H_3}$), 1.25 ppm (t, *J* = 7.0 Hz, 3H; $CH_2C\mathit{H_3}$); ^{13}C NMR (68 MHz, $CDCl_3$): δ = 169.1 (d, *J*(C,P) = 4.0 Hz), 143.3, 129.3, 127.6, 126.9, 62.3 (d, *J*(C,P) = 7.5 Hz), 61.5 (d, *J*(C,P) = 7.5 Hz), 37.1, 36.2 (d, *J*(C,P) = 139 Hz), 15.9 (d, *J*(C,P) = 6.0 Hz), 15.8 (d, *J*(C,P) = 6.0 Hz), 12.6 ppm (d, *J*(C,P) = 7.5 Hz); IR (Neat): ν̃ = 2980, 1658, 1595, 1496, 1385, 1249, 1027 cm^{-1}; HRMS (ESI) calculated for $C_{14}H_{23}NO_4P$ $[MH]^+$ requires 300.1359, found 300.1358 (0.3 ppm error).

Diethyl (1,3-dimethyl-2-oxo-2,3-dihydro-1*H*-indol-3-yl)phosphonate 4e

Colourless oil, R_f = 0.3 (EtOAc); ^{1}H NMR (270 MHz, $CDCl_3$): δ = 7.50 (d, *J* = 8.0 Hz, 1H; 4-H), 7.33 (tt, *J* = 8.0 Hz, *J* = 1.5 Hz, 1H; 6-H), 7.11 (t, *J* = 8.0 Hz, 1H; 5-H), 6.86 (d, *J* = 8.0 Hz, 1H; 7-H), 4.21 (dq, *J*(H,P) = 8.0 Hz, *J* = 7.0 Hz, 2H; OCH_2), 4.05-3.79 (m, 2H; OCH_2), 3.22 (s, 3H; NMe), 1.73 (d, *J*(H,P) = 17.0 Hz, 3H; 3-Me), 1.38 (t, *J* = 7.0 Hz, 3H; $CH_2C\mathit{H_3}$), 1.08 ppm (t, *J* = 7.0 Hz, 3H; $CH_2C\mathit{H_3}$); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 206.8, 128.7, 127.9, 125.2, 122.7, 122.6, 108.0, 63.9 (d, *J*(C,P) = 7.0 Hz), 63.1 (d, *J*(C,P) = 7.5 Hz), 50.1 (d, *J*(C,P) = 136 Hz), 29.7, 18.5 (d, *J*(C,P) = 6.0 Hz), 16.4 (d, *J*(C,P) = 6.0 Hz), 16.2 ppm (d, *J*(C,P) = 6.0 Hz); IR (Neat): ν̃ = 2927, 1715, 1611, 1471, 1373, 1250, 1024 cm^{-1}; HRMS (ESI) calculated for $C_{14}H_{21}NO_4P$ $[MH]^+$ requires 298.1203, found 298.1191 (4.1 ppm error).

Ethyl 3-benzyl-1-methyl-2-oxo-2,3-dihydro-1*H*-indole-3-carboxylate 4f

Colourless needles, m.p. 117-118 °C; R_f = 0.2 (6:4 petrol:EtOAc); ^{1}H NMR (270 MHz, $CDCl_3$): δ = 7.34 (dd, *J* = 7.5 Hz, *J* = 1.0 Hz, 1H; 4-H), 7.23 (td, *J* = 7.5 Hz, *J* = 1.0 Hz, 1H; 6-H), 7.07 (td, *J* = 7.5 Hz, *J* = 1.0 Hz, 1H; 5-H), 7.06-6.97 (m, 3H; Ph 3-, 4- and 5-H), 6.85 (dd, *J* = 8.0 Hz, *J* = 2.0 Hz, 2H; Ph 2- and 6-H), 6.58 (d, *J* = 7.5 Hz, 1H; 7-H), 4.20 (qd, *J* = 7.0 Hz, *J* = 2.0 Hz, 2H; OCH_2), 3.52 (s, 2H; CH_2Ph), 2.93 (s, 3H; NMe), 1.19 ppm (t, *J* = 7.0 Hz, 3H; CH_2CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 173.5, 169.2, 144.0, 134.3, 129.9, 128.9, 127.5, 127.4, 126.7, 123.8, 122.4, 108.1, 62.0, 60.9, 40.0, 26.1, 13.9 ppm; IR (Neat): ν̃ = 2930, 1739, 1715, 1611, 1470, 1352, 1234 cm^{-1}; HRMS (ESI) calculated for $C_{19}H_{19}NO_3Na$ $[MNa]^+$ requires 332.1257, found 332.1251 (1.0 ppm error).

Ethyl 1-methyl-2-oxo-3-(prop-2-en-1-yl)-2,3-dihydro-1*H*-indole-3-carboxylate 4g

Colourless oil, R_f = 0.5 (6:4 petrol:EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.33 (td, *J* = 7.5 Hz, *J* = 1.0 Hz, 1H; 6-H), 7.28 (dd, *J* = 7.5 Hz, *J* = 1.0 Hz, 1H; 4-H), 7.08 (td, *J* = 7.5 Hz, *J* = 1.0 Hz, 1H; 5-H), 6.85 (d, *J* = 7.5 Hz, 1H; 7-H), 5.37 (dddd, *J* = 17.0 Hz, *J* = 10.0 Hz, *J* = 8.0 Hz, *J* = 7.0 Hz, 1H; allyl 2-H), 5.05 (dd, *J* = 17.0 Hz, *J* = 1.5 Hz, 1H; allyl 3-H), 4.93 (dd, *J* = 10.0 Hz, *J* = 1.5 Hz, 1H; allyl 3-H), 4.15 (qd, *J* = 7.0 Hz, *J* = 6.0 Hz, 2H; OCH_2), 3.18 (s, 3H; NMe), 3.01 (dd, *J* = 14.0 Hz, *J* = 7.0 Hz, 1H; allyl 1-H), 2.95 (dd, *J* = 14.0 Hz, *J* = 8.0 Hz, 1H; allyl 1-H), 1.10 ppm (t, *J* = 7.0 Hz, 3H; CH_2CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 173.7, 169.0, 144.1, 131.0, 129.0, 127.6, 123.6, 122.7, 119.7, 108.2, 62.0, 59.2, 38.4, 26.4, 13.9 ppm; IR (Neat): ν̃ = 2981, 1740, 1611, 1471, 1350, 1231 cm^{-1}; HRMS (ESI) calculated for $C_{15}H_{17}NO_3Na$ $[MNa]^+$ requires 282.1101, found 282.1098 (0.3 ppm error).

Ethyl 2-cyclopropyl-3-(methyl(phenyl)amino)-3-oxopropanoate 1h

Colourless oil, R_f = 0.2 (6:4 petrol:EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.45-7.33 (m, 3H; Ph 3-, 4- and 5-H), 7.22 (d, *J* = 7.5 Hz, 2H; Ph 2- and 6-H), 4.14 (qd, *J* = 7.0 Hz, *J* = 5.0 Hz, 2H; OCH_2), 3.37 (s, 3H; NMe), 2.61 (d, *J* = 9.5 Hz, 1H; 2-H), 1.57-1.42 (m, 1H; CHCH), 1.25 (t, *J* = 7.0, 3H; CH_2CH_3), 0.65-0.50 (m, 2H; $CHCH_2$), 0.06-0.03 (m, 1H; CHCHH), 0.01-−0.05 ppm (m, 1H; CHCHH); ^{13}C NMR (100 MHz, $CDCl_3$): δ =

169.9, 169.0, 143.5, 129.8, 128.2, 127.8, 61.1, 54.2, 37.7, 14.1, 11.0, 4.2, 3.8 ppm; IR (Neat): $\tilde{\nu}$ = 2919, 1746, 1660, 1595, 1496, 1384, 1147 cm^{-1}; HRMS (ESI) calculated for $C_{15}H_{20}NO_3$ $[MH]^+$ requires 262.1438, found 262.1437 (0.2 ppm error).

Ethyl (2*Z*)-2-(methyl(phenyl)carbamoyl)penta-2,4-dienoate 1i

Colourless oil, R_f = 0.6 (2:8 petrol:EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.32-7.22 (m, 3H; Ph 3-, 4- and 5-H), 7.14-7.09 (m, 2H; Ph 2- and 6-H), 6.97 (d, *J* = 11.5 Hz, 1H; 3-H), 6.61 (ddd, *J* = 16.5 Hz, *J* = 11.5 Hz, *J* = 10.0 Hz, 1H; 4-H), 5.62 (d, *J* = 16.5 Hz, 1H; 5-H), 5.60 (d, *J* = 10.0 Hz, 1H; 5-H), 4.14 (q, *J* = 7.0 Hz, 2H; OCH_2), 3.45 (s, 3H; NMe), 1.25 ppm (t, *J* = 7.0, 3H; $CH_2C\mathit{H}_3$); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 165.8, 164.2, 142.9, 141.3, 132.1, 130.8, 129.2, 127.9, 127.7, 126.8, 61.1, 36.9, 14.2 ppm; IR (Neat): $\tilde{\nu}$ = 2928, 1714, 1650, 1595, 1496, 1384, 1241 cm^{-1}; HRMS (ESI) calculated for $C_{15}H_{17}NO_3Na$ $[MNa]^+$ requires 282.1101, found 282.1099 (0.3 ppm error).

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