Supporting Information

Oxidative rearrangement of indoles to oxindoles

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General. $^1$H NMR spectra were recorded at 400 MHz. Chemical shifts are reported in ppm from tetramethylsilane with the solvent resonance as the internal standard (CDCl$_3$: 7.26 ppm). Data are reported as follows: chemical shift, integration, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, br = broad, m = multiplet), and coupling constants (Hz). $^{13}$C NMR were recorded at 100 MHz with complete proton decoupling. Chemical shifts are reported in ppm from tetramethylsilane with the solvent as the internal standard (CDCl$_3$: 77.4 ppm). Mass spectrometry (m/z) was performed in ESI mode, with only molecular ions being reported. Infrared (IR) spectra $\nu_{\text{max}}$ are reported in cm$^{-1}$. Bands are characterized as broad (br), strong (s), medium (m) and weak (w). All purchased reagents were used as received without further purification. THF was pre-dried with 3Å molecular sieves then distilled from sodium benzophenone ketyl. All reactions were performed in oven dried glassware.

Synthesis of diethyl 2-hydroxy-2-(1-methyl-1H-indol-3-yl)malonate, 1a.$^1$

![Structural diagram](image)

1-Methyl-1H-indole 3a (1.07 g, 8.2 mmol) and diethyl ketomalonate (1.26 mL, 8.2 mmol) were refluxed in toluene (67 mL) for 16 hours open to air. The solvent was removed in vacuo to furnish the desired product 1a as a red solid (2.36 g, 95%).

IR (neat): 1754 (w), 1722 (s), 1276 (m), 1217 (s), 1063 (m), 1017 (m), 732 (s) cm$^{-1}$

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.74 (1H, d, $J = 8.5$ Hz), 7.40 (1H, s), 7.34 (1H, d, $J = 8.5$ Hz), 7.26 (1H, t, $J = 7.6$ Hz), 7.14 (1H, t, $J = 7.6$ Hz), 4.27-4.40 (5H, m), 3.80 (3H, s), 1.32 (6H, t, $J = 7.6$ Hz).

$^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 170.4 (2C), 137.3, 128.5, 125.9, 121.9, 121.0, 119.6, 110.3, 109.4, 77.6, 62.8 (2C), 33.0, 14.0 (2C).

MS: m/z (M+23) 328.1

HRMS: m/z calc’d for C$_{16}$H$_{19}$NaNO$_5$ 328.1155, found 328.1146

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Melting point: 77-79 °C (lit. 78 °C)\(^1\)

**Synthesis of diethyl 2-(1-ethyl-1H-indol-3-yl)-2-hydroxymalonate, 1b.**

![Diagram](image)

1-Ethyl-1H-indole 3b (100 mg, 0.69 mmol) and diethyl ketomalonate (0.11 mL, 0.69 mmol) were refluxed in toluene (5.5 mL) for 16 hours. The solvent was removed *in vacuo* and the mixture was purified by flash chromatography on silica gel (20:1 petroleum ether 40-60 °C/ethyl acetate). The product 1b was isolated as a brown/red oil (195 mg, 89%).

IR (neat): 1749 (m), 1723 (s), 1463 (m), 1273 (s), 1213 (s), 1189 (s), 1139 (m), 1093 (m), 1055 (m), 1008 (s), 745 (s) cm\(^{-1}\)

\(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 7.74 (1H, d, \(J = 8.2\) Hz), 7.46 (1H, s), 7.35 (1H, d, \(J = 8.2\) Hz), 7.23 (1H, t, \(J = 8.0\) Hz), 7.12 (1H, t, \(J = 7.5\)), 4.26-4.42 (5H, m), 4.15 (2H, q, \(J = 7.0\)), 1.48 (3H, t, \(J = 7.0\)), 1.30 (6H, t, \(J = 7.0\) Hz).

\(^1\)C NMR (100 MHz, CDCl\(_3\)): \(\delta\) 170.6 (2C), 136.7, 127.1, 126.3, 122.0, 121.5, 119.8, 110.6, 109.8, 78.0, 63.1 (2C), 41.4, 15.6, 14.3 (2C).

MS: m/z (M+23) 342.1

HRMS: m/z calc’d for C\(_{17}\)H\(_{21}\)NaNO\(_5\) 342.1312, found 342.1312

**Synthesis of diethyl 2-(1-benzyl-1H-indol-3-yl)-2-hydroxymalonate, 1c.**

![Diagram](image)

1-Benzyl-1H-indole 3c (2.53 g, 12 mmol) and diethyl ketomalonate (1.89 mL, 12 mmol) were refluxed in toluene (100 mL) for 16 hours. The solvent was removed *in vacuo* and the
mixture was purified by flash chromatography on silica gel (5:1 petroleum ether 40-60 °C/ethyl acetate). The product 1c was isolated as a red solid (2.37 g, 51%).

IR (neat): 1722 (s), 1469 (w), 1238 (s), 1215 (m), 1090 (m), 1028 (m), 749 (m), 734 (s) cm⁻¹

¹H NMR (400 MHz, CDCl₃): δ 7.79 (1H, dd, J = 7.2, 1.1 Hz), 7.48 (1H, s), 7.22-7.33 (4H, m), 7.11-7.22 (4H, m), 5.27 (2H, s), 4.43 (1H, s), 4.23-4.41 (4H, m), 1.29 (6H, t, J = 7.1 Hz).

¹³C NMR (100 MHz, CDCl₃): δ 170.4 (2C), 137.2, 137.1, 129.0 (2C), 128.3, 127.9, 127.2 (2C), 126.50, 122.3, 121.5, 120.1, 111.2, 110.2, 78.0, 63.1 (2C), 50.5, 14.3 (2C).

MS: m/z (M+23) 404.1

HRMS: m/z calc’d for C₂₂H₂₃NaNO₅ 404.1468, found 404.1534

Melting point: 68-71 °C

Synthesis of diethyl 2-hydroxy-2-(1-phenyl-1H-indol-3-yl)malonate, 1d.

1-Phenyl-1H-indole 3d (319 mg, 1.7 mmol) and diethyl ketomalonate (0.26 mL, 1.7 mmol) were refluxed in toluene (14 mL) for 16 hours. The solvent was removed in vacuo and the mixture was purified by flash chromatography on silica gel (20:1 petroleum ether 40-60 °C/ethyl acetate). The product 1d was isolated as a yellow oil (258 mg, 43%).

IR (neat): 1731 (s), 1596 (w), 1500 (s), 1457 (m), 1205 (s), 1019 (m), 741 (s), 697 (s) cm⁻¹

¹H NMR (400 MHz, CDCl₃): δ 7.76-7.81 (1H, d, J = 7.5 Hz), 7.65 (1H, s), 7.48-7.55 (5H, m), 7.34-7.40 (1H, m), 7.14-7.25 (2H, m), 4.24-4.44 (5H, m), 1.31 (6H, t, J = 7.1 Hz).

¹³C NMR (100 MHz, CDCl₃): δ 170.4 (2C), 139.6, 136.9, 129.9 (2C), 128.0, 127.1, 127.0, 124.9 (2C), 123.0, 121.7, 120.9, 113.2, 111.0, 77.9, 63.3 (2C), 14.4 (2C).

MS: m/z (M+23) 390.1
HRMS: m/z calc’d for C_{21}H_{21}NaNO_{5} 390.1303, found 390.1312

**Synthesis of diethyl 2-(5-bromo-1-methyl-1H-indol-3-yl)-2-hydroxymalonate, 1e.**

5-Bromo-1-methyl-1H-indole 3e (200 mg, 0.95 mmol) and diethyl ketomalonate (0.15 mL, 0.95 mmol) were refluxed in toluene (7.8 mL) for 16 hours. The solvent was removed *in vacuo* and the mixture was purified by flash chromatography on silica gel (3:1 petroleum ether 40-60 °C/ethyl acetate). The product 1e was isolated as an orange/brown solid (174 mg, 53%).

IR (neat): 1749 (m), 1720 (s), 1474 (m), 1274 (m), 1216 (m), 1196 (s), 1136 (s), 1107 (s), 1048 (s), 1016 (s), 781 (s) cm⁻¹

{\textsuperscript{1}}H NMR (400 MHz, CDCl₃): δ 7.88 (1H, d, J = 1.8 Hz), 7.36 (1H, s), 7.26-7.31 (1H, m), 7.14 (1H, d, J = 8.7 Hz), 4.22-4.40 (5H, m), 3.71 (3H, s), 1.30 (6H, t, J = 7.2 Hz).

{\textsuperscript{13}}C NMR (100 MHz, CDCl₃): δ 170.3 (2C), 136.3, 129.9, 127.7, 125.0, 124.2, 113.4, 111.2, 110.2, 77.8, 63.3 (2C), 33.4, 14.3 (2C).

MS: m/z (M+23) 406.0

HRMS: m/z calc’d for C_{16}H_{18}BrNaNO_{5} 406.0261, found 406.0262

Melting point: 109-111 °C

**Synthesis of diethyl 2-(6-chloro-1-methyl-1H-indol-3-yl)-2-hydroxymalonate, 1f.**
6-Chloro-1-methyl-1H-indole 3f (200 mg, 1.2 mmol) and diethyl ketomalonate (0.19 mL, 1.2 mmol) were refluxed in toluene (9.7 mL) for 16 hours. The solvent was removed in vacuo and the mixture was purified by flash chromatography on silica gel (20:1 petroleum ether 40-60 °C/ethyl acetate). The product 1f was isolated as a brown solid (321 mg, 78%).

IR (neat): 1723 (s), 1217 (m), 1190 (s), 1063 (s), 1019 (s), 928 (s), 802 (s) cm⁻¹

¹H NMR (400 MHz, CDCl₃): δ 7.63 (1H, d, J = 8.6 Hz), 7.35 (1H, s), 7.26-7.29 (1H, m), 7.07 (1H, dd, J = 8.6, 1.8 Hz), 4.39 (1H, br), 4.21-4.36 (4H, m), 3.69 (3H, s), 1.27 (6H, t, J = 7.1 Hz).

¹³C NMR (100 MHz, CDCl₃): δ 170.4 (2C), 138.1, 129.5, 128.3, 124.8, 122.5, 120.7, 111.0, 109.8, 77.8, 63.3 (2C), 33.4, 14.4 (2C).

MS: m/z (M+23) 362.1

HRMS: m/z calc’d for C₁₆H₁₈ClNaNO₅ 362.0733, found 362.0766

Melting point: 86-89 °C

Synthesis of diethyl 2-(7-chloro-1-methyl-1H-indol-3-yl)-2-hydroxymalonate, 1g.

7-Chloro-1-methyl-1H-indole 3g (100 mg, 0.60 mmol) and diethyl ketomalonate (0.09 mL, 0.60 mmol) were refluxed in toluene (4.8 mL) for 16 hours. The solvent was removed in vacuo, to furnish the desired product 1g as a yellow oil (201 mg, 98%).

IR (neat): 1726 (s), 1246 (m), 1211 (s), 1193 (s), 1072 (s), 1037 (m), 854 (w), 782 (m), 734 (m) cm⁻¹

¹H NMR (400 MHz, CDCl₃): δ 7.55-7.60 (1H, m), 7.31 (1H, s), 7.14 (1H, d, J = 7.6 Hz), 6.97 (1H, t, J = 7.8 Hz), 4.21-4.39 (5H, m), 4.12 (3H, s), 1.27 (6H, t, J = 7.1 Hz).
Synthesis of diethyl 2-hydroxy-2-(5-methoxy-1-methyl-1H-indol-3-yl)malonate, 1h.

5-Methoxy-1-methyl-1H-indole 3h (400 mg, 2.5 mmol), cerium(III) chloride heptahydrate (475 mg, 2.7 mmol) and diethyl ketomalonate (0.42 mL, 2.7 mmol) were dissolved in CH₂Cl₂ (8 mL) and stirred at room temperature for 6 hours. The reaction mixture was quenched by addition of saturated aqueous ammonium chloride solution and extracted with CH₂Cl₂. The organic layer was dried over MgSO₄, filtered and concentrated in vacuo. The mixture was purified by flash chromatography on silica gel (5:1 petroleum ether 40-60 °C/ethyl acetate). The product 1h was isolated as a pale yellow oil (0.79 g, 95%).

IR (neat): 1732 (s), 1490 (m), 1219 (s) cm⁻¹

¹H NMR (400 MHz, CDCl₃): δ 7.32 (1H, s), 7.17 (1H, d, J = 9.2 Hz), 7.16 (1H, d, J = 2.0 Hz), 6.88 (1H, dd, J = 8.8, 2.5 Hz), 4.22-4.39 (5H, m), 3.83 (3H, s), 3.72 (3H, s), 1.29 (6H, t, J = 7.1 Hz).

¹³C NMR (100 MHz, CDCl₃): δ 170.6 (2C), 154.3, 133.0, 129.2, 126.5, 112.6, 110.5, 110.0, 103.0, 78.0, 63.1 (2C), 56.0, 33.4, 14.4 (2C).

MS: m/z (M+23) 358.1

HRMS: m/z calc'd for C₁₇H₂₁NaNO₆ 358.1261, found 358.1261
Synthesis of diethyl 2-(7-ethyl-1-methyl-1H-indol-3-yl)-2-hydroxymalonate 1i

7-Ethyl-1-methyl-1H-indole 3i (100 mg, 0.63 mmol), cerium(III) chloride heptahydrate (234 mg, 0.63 mmol) and diethyl ketomalonate (0.11 mL, 0.69 mmol) were dissolved in CH$_2$Cl$_2$ (2 mL) and stirred at room temperature for 6 hours. The reaction mixture was quenched by addition of saturated aqueous ammonium chloride solution and extracted with CH$_2$Cl$_2$. The organic layer was dried over MgSO$_4$, filtered and concentrated in vacuo. The mixture was purified by flash chromatography on silica gel (5:1 petroleum ether 40-60 °C/ethyl acetate). The product 1i was isolated as a dark red solid (0.16 g, 74%).

IR (neat): 3485 (br), 1754 (s), 1728 (s) cm$^{-1}$

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.52 (1H, dd, $J$ = 7.7, 1.2 Hz), 7.26 (1H, s), 7.06-6.95 (2H, m), 4.42-4.20 (5H, m), 4.01 (3H, s), 3.10 (2H, q, $J$ = 7.5 Hz), 1.40-1.23 (9H, m).

$^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 170.6 (2C), 135.6, 130.7, 128.2, 127.6, 123.2, 120.3, 119.2, 110.4, 77.9, 63.1 (2C), 37.4, 25.7, 17.0, 14.4 (2C).

MS: m/z (M+23) 356.1

HRMS: m/z calc’d for C$_{18}$H$_{23}$NaNO$_5$ 356.1468, found 356.1452

Melting point: 65-68 °C

Synthesis of diethyl 2-(1,5-dimethyl-1H-indol-3-yl)-2-hydroxymalonate 1j

5-Methyl-1-methyl-1H-indole 3j (400 mg, 2.75 mmol), cerium(III) chloride heptahydrate (1.0 g, 2.75 mmol) and diethyl ketomalonate (0.46 mL, 3.0 mmol) were dissolved in CH$_2$Cl$_2$
(6 mL) and stirred at room temperature for 6 hours. The reaction mixture was quenched by addition of saturated aqueous ammonium chloride solution and extracted with CH₂Cl₂. The organic layer was dried over MgSO₄, filtered and concentrated in vacuo. The mixture was purified by flash chromatography on silica gel (5:1 petroleum ether 40-60 °C/ethyl acetate). The product 1j was isolated as a red solid (0.60 g, 69%).

IR (neat): 3467 (br), 1753 (s), 1720 (s), 1190 (s) cm⁻¹

¹H NMR (400 MHz, CDCl₃): δ 7.48 (1H, br), 7.31 (1 H, s), 7.18 (1H, d, J = 8.4 Hz), 7.05 (1H, dd, J = 8.4, 1.3 Hz), 4.41-4.22 (5H, m), 3.74 (3H, s), 2.44 (3H, s), 1.30 (6H, t, J = 7.1 Hz).

¹³C NMR (100 MHz, CDCl₃): δ 170.6 (2C), 136.1, 129.2, 128.8, 126.4, 123.9, 120.9, 110.0, 109.4, 78.0, 63.1 (2C), 33.3, 21.9, 14.3 (2C).

MS: m/z (M+23) 342.1

HRMS: m/z calc’d for C₁₇H₂₁NaNO₅ 342.1312, found 342.1311

Melting point: 83-85 °C

**Representative procedure for the oxidative rearrangement: Preparation of diethyl 2-(1-methyl-2-oxoindolin-3-ylidene)malonate, 2a.**

Iodine (83 mg, 0.33 mmol) in dry THF (0.9 mL) was added via cannula to a mixture of silver trifluoroacetate (87 mg, 0.39 mmol) and diethyl 2-hydroxy-2-(1-methyl-1H-indol-3-yl)malonate 1a (100 mg, 0.33 mmol) in dry THF (1.8 mL) at room temperature under nitrogen. The reaction mixture was stirred for 16 hours, then quenched with saturated sodium thiosulfate solution and extracted with EtOAc. The combined organic fractions were dried over magnesium sulfate, filtered and concentrated. The resulting mixture was purified by flash chromatography on silica gel (9:1 petroleum ether 40-60 °C/ethyl acetate). The product 2a was isolated as a red solid (60 mg, 61%).
IR (neat): 1730 (s), 1709 (s), 1599 (m), 1469 (m), 1375 (m), 1238 (s), 1079 (s), 1013 (s) cm⁻¹

¹H NMR (400 MHz, CDCl₃): ð 8.40 (1H, d, J = 7.8 Hz), 7.38 (1H, t, J = 7.8 Hz), 7.04 (1H, t, J = 7.8 Hz), 6.80 (1H, d, J = 7.8 Hz), 4.44 (2H, q, J = 7.1 Hz), 4.37 (2H, q, J = 7.1 Hz), 3.19 (3H, s), 1.38 (3H, t, J = 7.1 Hz), 1.36 (3H, t, J = 7.1 Hz).

¹³C NMR (100 MHz, CDCl₃): ð 166.5, 165.9, 163.3, 146.4, 134.8, 133.5, 129.9, 129.3, 123.3, 119.5, 108.7, 62.7, 62.6, 26.5, 14.3, 14.2.

MS: m/z (M+23) 326.1
HRMS: m/z calc’d for C₁₆H₁₇NaNO₅ 326.0999, found 326.0996

Melting point: 112-115 °C

Diethyl 2-(1-ethyl-2-oxoindolin-3-ylidene)malonate, 2b.

Prepared according to the representative procedure using iodine (40 mg, 0.16 mmol), THF (0.42 mL), silver trifluoroacetate (42 mg, 0.19 mmol) and diethyl 2-(1-ethyl-1H-indol-3-ylidene)malonate 1b (50 mg, 0.16 mmol) in THF (0.84 mL). Purified by flash chromatography on silica gel (5:1 petroleum ether 40-60 °C/ethyl acetate). The product 2b was isolated as an orange solid (21 mg, 42%).

IR (neat): 1707 (s), 1602 (m), 1470 (m), 1362 (m), 1242 (s), 1224 (s), 1183 (s), 1091 (m), 1077 (s), 753 (s) cm⁻¹

¹H NMR (400 MHz, CDCl₃): ð 8.37 (1H, d, J = 7.8 Hz), 7.36 (1H, td, J = 7.8, 1.2 Hz), 7.01 (1H, td, J = 7.8, 1.0 Hz), 6.78 (1H, d, J = 7.8 Hz), 4.43 (2H, q, J = 7.2 Hz), 4.36 (2H, q, J = 7.1 Hz), 3.73 (2H, q, J = 7.2 Hz), 1.37 (3H, t, J = 7.1 Hz), 1.35 (3H, t, J = 7.2 Hz), 1.24 (3H, t, J = 7.2 Hz).

¹³C NMR (100 MHz, CDCl₃): ð 166.0, 165.9, 163.3, 145.5, 134.8, 133.3, 129.7, 129.3, 123.0, 119.7, 108.8, 62.6, 26.5, 35.0, 14.3, 14.2, 12.9.
MS: m/z (M+23) 340.1

HRMS: m/z calc’d for C$_{17}$H$_{19}$NaNO$_5$ 340.1155, found 340.1154

Melting point: 78-80 °C

Diethyl 2-(1-benzyl-2-oxoindolin-3-ylidene)malonate, 2c.

Prepared according to the representative procedure using iodine (33 mg, 0.13 mmol), THF (0.38 mL), silver trifluoroacetate (35 mg, 0.16 mmol) and diethyl 2-(1-benzyl-1H-indol-3-yl)-2-hydroxymalonate 1c (50 mg, 0.13 mmol) in THF (0.76 mL). Purified by flash chromatography on silica gel (9:1 petroleum ether 40-60 °C/ethyl acetate). The product 2c was isolated as an orange solid (31 mg, 62%).

IR (neat): 1716 (s), 1604 (m), 1469 (m), 1245 (s), 1182 (m), 1093 (m) cm$^{-1}$

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.41 (1H, d, $J = 7.6$ Hz), 7.25-7.38 (6H, m), 7.03 (1H, td, $J = 7.8$, 0.8 Hz), 6.69 (1H, d, $J = 7.8$ Hz), 4.92 (2H, s), 4.49 (2H, q, $J = 7.2$ Hz), 4.41 (2H, q, $J = 7.1$ Hz), 1.42 (3H, t, $J = 7.2$ Hz), 1.40 (3H, t, $J = 7.1$ Hz).

$^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 166.4, 165.8, 163.3, 145.5, 135.5, 134.6, 133.3, 130.1, 129.2 (2C), 129.1, 128.1, 127.6 (2C), 123.3, 119.6, 109.7, 62.7, 62.6, 44.1, 14.4, 14.3.

MS: m/z (M+23) 402.1

HRMS: m/z calc’d for C$_{22}$H$_{21}$NO$_5$Na 402.1312 , found 402.1322

Melting point: 93-96 °C

Diethyl 2-(2-oxo-1-phenylindolin-3-ylidene)malonate, 2d.
Prepared according to the representative procedure using iodine (35 mg, 0.14 mmol), THF (0.37 mL), silver trifluoroacetate (36 mg, 0.16 mmol) and diethyl 2-hydroxy-2-(1-phenyl-1H-indol-3-yl)malonate 1d (50 mg, 0.14 mmol) in THF (0.74 mL). Purified by flash chromatography on silica gel (9:1 petroleum ether 40-60 °C/ethyl acetate). The product 2d was isolated as a yellow solid (17 mg, 34%).

IR (neat): 1731 (m), 1710 (s), 1601 (m), 1462 (m), 1375 (m), 1243 (s), 1188 (m), 1084 (s), 759 (s), 751 (s) cm⁻¹

¹H NMR (400 MHz, CDCl₃): δ 8.45 (1H, dd, J = 7.9, 0.7 Hz), 7.51 (2H, t, J = 7.9 Hz), 7.36-7.44 (3H, m), 7.30 (1H, td, J = 7.7, 1.2 Hz), 7.08 (1H, td, J = 7.9, 1.0 Hz), 6.75 (1H, d, J = 7.9 Hz), 4.36-4.44 (4H, m), 1.38 (3H, t, J = 7.1), 1.35 (3H, t, J = 7.1).

¹³C NMR (100 MHz, CDCl₃): δ 165.8, 165.7, 163.3, 146.4, 134.5, 133.8, 133.3, 130.3, 130.1 (2C), 129.3, 128.8, 127.0 (2C), 123.7, 119.5, 110.0, 62.7, 62.6, 14.4, 14.3.

MS: m/z (M+23) 388.1

HRMS: m/z calc’d for C₂₁H₁₉NaNO₅ 388.1155, found 388.1145

Melting point: 98-101 °C

Diethyl 2-(5-bromo-1-methyl-2-oxoindolin-3-ylidene)malonate, 2e.

Prepared according to the representative procedure using iodine (31 mg, 0.12 mmol), THF (0.30 mL), silver trifluoroacetate (32 mg, 0.15 mmol) and diethyl 2-(5-bromo-1-methyl-1H-indol-3-yl)-2-hydroxymalonate 1e (47 mg, 0.12 mmol) in THF (0.60 mL). Purified by flash chromatography on silica gel (3:1 petroleum ether 40-60 °C/ethyl acetate). The product 2e was isolated as a red solid (24 mg, 51%).

IR (neat): 1738 (m), 1723 (m), 1706 (s), 1598 (m), 1472 (m), 1364 (m), 1240 (s), 1175 (s), 1080 (s), 1020 (s), 838 (s) cm⁻¹
Diethyl 2-(6-chloro-1-methyl-2-oxindolin-3-ylidene)malonate, 2f.

Prepared according to the representative procedure using iodine (37 mg, 0.15 mmol), THF (0.39 mL), silver trifluoroacetate (39 mg, 0.18 mmol) and diethyl 2-(6-chloro-1-methyl-1H-indol-3-yl)-2-hydroxymalonate 1f (50 mg, 0.15 mmol) in THF (0.78 mL). Purified by flash chromatography on silica gel (5:1 petroleum ether 40-60 °C/ethyl acetate). The product 2f was isolated as a yellow solid (23 mg, 45%).

IR (neat): 1728 (s), 1709 (s), 1597 (s), 1375 (w), 1254 (s), 1233 (s), 1179 (s), 1065 (s), 1019 (m) cm⁻¹

¹H NMR (400 MHz, CDCl₃): δ 8.39 (1H, d, J = 8.4 Hz), 7.00 (1H, dd, J = 8.4, 2.0 Hz), 6.78 (1H, d, J = 1.9 Hz), 4.43 (2H, q, J = 7.1 Hz), 4.35 (2H, q, J = 7.1 Hz), 3.18 (3H, s), 1.38 (3H, t, J = 7.2 Hz), 1.35 (3H, t, J = 7.2 Hz).

¹³C NMR (100 MHz, CDCl₃): δ 166.4, 165.6, 163.2, 147.4, 139.4, 133.8, 130.5, 130.1, 123.2, 117.9, 109.4, 62.8, 62.6, 26.6, 14.3, 14.2.

MS: m/z (M+23) 360.1
HRMS: m/z calc’d for C₁₆H₁₈ClNaNO₅ 360.0609, found 360.0590

Melting point: 138-140 °C
Diethyl 2-(7-chloro-1-methyl-2-oxoindolin-3-ylidene)malonate, 2g.

Prepared according to the representative procedure using iodine (37 mg, 0.15 mmol), THF (0.39 mL), silver trifluoroacetate (39 mg, 0.18 mmol) and diethyl 2-(7-chloro-1-methyl-1H-indol-3-yl)-2-hydroxymalonate 1g (50 mg, 0.15 mmol) in THF (0.78 mL). Purified by flash chromatography on silica gel (9:1 petroleum ether 40-60 °C/ethyl acetate). The product 2g was isolated as an orange solid (17 mg, 34%).

IR (neat): 1734 (m), 1712 (s), 1596 (m), 1454 (m), 1368 (m), 1247 (s), 1209 (s), 1181 (s), 1135 (s), 1077 (s), 1054 (s), 1018 (m), 724 (s) cm⁻¹

¹H NMR (400 MHz, CDCl₃): δ 8.31 (1H, dd, J = 7.8, 1.1 Hz), 7.30 (1H, dd, J = 8.2, 1.1 Hz), 6.95 (1H, t, J = 8.0 Hz), 4.44 (2H, q, J = 7.1 Hz), 4.37 (2H, q, J = 7.1 Hz), 3.58 (3H, s), 1.38 (3H, t, J = 7.2 Hz), 1.36 (3H, t, J = 7.2 Hz).

¹³C NMR (100 MHz, CDCl₃): δ 166.7, 165.5, 163.1, 142.0, 135.4, 133.1, 131.0, 127.5, 123.8, 122.2, 116.2, 62.9, 62.7, 30.2, 14.3, 14.2.

MS: m/z (M+23) 360.1

HRMS: m/z calc’d for C₁₆H₁₅ClNaNO₅ 360.0609, found 360.0625

Melting point: 93-95 °C

Diethyl 2-(5-methoxy-1-methyl-2-oxoindolin-3-ylidene)malonate, 2h

Iodine (76 mg, 0.30 mmol) in dry THF (0.9 mL) was added via cannula to a mixture of silver trifluoroacetate (87 mg, 0.39 mmol) and diethyl 2-hydroxy-2-(5-methoxy-1-methyl-
1H-indol-3-yl)malonate 1h (100 mg, 0.30 mmol) in dry THF (1.8 mL) at 0 °C under nitrogen. The reaction mixture was stirred for 16 hours, then quenched with saturated sodium thiosulfate solution and extracted with EtOAc. The combined organic fractions were dried over magnesium sulfate, filtered and concentrated. The resulting mixture was purified by flash chromatography on silica gel (5:1 petroleum ether 40-60 °C/ethyl acetate).

The product 2h was isolated as a dark red solid (66 mg, 68%).

IR (neat): 1728 (s), 1707 (s), 1481 (m), 1215 (s) cm⁻¹

¹H NMR (400 MHz, CDCl₃): δ 8.11 (1H, d, J = 2.7 Hz), 6.93 (1H, dd, J = 8.5, 2.5 Hz), 6.67 (1H, d, J = 8.7 Hz), 4.43 (2H, q, J = 7.2 Hz), 4.36 (2H, q, J = 7.0 Hz), 3.81 (3H, s), 3.15 (3H, s), 1.38 (3H, t, J = 7.0 Hz), 1.35 (3H, t, J = 7.2 Hz).

¹³C NMR (100 MHz, CDCl₃): δ 166.3, 165.8, 163.2, 156.1, 140.3, 135.3, 130.1, 120.2, 118.9, 115.5, 109.0, 62.7, 62.5, 56.3, 26.5, 14.3 (2C).

MS: m/z (M+23) 356.1

HRMS: m/z calc’d for C₁₇H₁₉NaNO₆ 356.1105, found 356.1105

Melting point: 85-88 °C

Diethyl 2-(7-ethyl-1-methyl-2-oxoindolin-3-ylidene)malonate, 2i

Iodine (76 mg, 0.30 mmol) in dry THF (0.9 mL) was added via cannula to a mixture of silver trifluoroacetate (87 mg, 0.39 mmol) and diethyl 2-(7-ethyl-1-methyl-1H-indol-3-yl)-2-hydroxymalonate 1i (100 mg, 0.30 mmol) in dry THF (1.8 mL) at 0 °C under nitrogen. The reaction mixture was stirred for 16 hours, then quenched with saturated sodium thiosulfate solution and extracted with EtOAc. The combined organic fractions were dried over magnesium sulfate, filtered and concentrated. The resulting mixture was purified by flash chromatography on silica gel (5:1 petroleum ether 40-60 °C/ethyl acetate). The product 2i was isolated as a red solid (58 mg, 58%).
IR (neat): 1732 (s), 1709 (s), 1446 (m), 1252 (s) cm⁻¹

¹H NMR (400 MHz, CDCl₃): δ 8.20 (1H, dd, J = 7.8, 1.0 Hz), 7.16 (1H, d, J = 7.7 Hz), 6.95 (1H, t, J = 7.8 Hz), 4.44 (2H, q, J = 7.2 Hz), 4.36 (2H, q, J = 7.1 Hz), 3.47 (3H, s), 2.86 (2H, q, J = 7.5 Hz), 1.38 (3H, t, J = 7.1 Hz), 1.35 (3H, t, J = 7.2 Hz), 1.25 (3H, t, J = 7.6 Hz).

¹³C NMR (100 MHz, CDCl₃): δ 167.4, 165.9, 163.4, 143.4, 135.9, 134.1, 129.4, 126.9, 126.6, 123.2, 120.4, 62.6, 62.5, 29.9, 25.2, 17.0, 14.3 (2C).

MS: m/z (M+23) 354.1

HRMS: m/z calc’d for C₁₈H₂₁NaNO₅ 354.1312, found 354.1304

Melting point: 61-63 °C

**Diethyl 2-(1,5-dimethyl-2-oxoindolin-3-ylidene)malonate, 2j**

Iodine (76 mg, 0.30 mmol) in dry THF (0.9 mL) was added via cannula to a mixture of silver trifluoroacetate (87 mg, 0.39 mmol) and diethyl 2-(1,5-dimethyl-1H-indol-3-yl)-2-hydroxymalonate 1j (96 mg, 0.30 mmol) in dry THF (1.8 mL) at 0 °C under nitrogen. The reaction mixture was stirred for 16 hours, then quenched with saturated sodium thiosulfate solution and extracted with EtOAc. The combined organic fractions were dried over magnesium sulfate, filtered and concentrated. The resulting mixture was purified by flash chromatography on silica gel (5:1 petroleum ether 40-60 °C/ethyl acetate). The product 2j was isolated as a red solid (50 mg, 53%).

IR (neat): 1738 (m), 1716 (s), 1245 (s), 1066 (s) cm⁻¹

¹H NMR (400 MHz, CDCl₃): δ 8.20 (1H, s), 7.17 (1H, d, J = 7.9 Hz), 6.65 (1H, t, J = 8.0 Hz), 4.43 (2H, q, J = 7.2 Hz), 4.36 (2H, q, J = 7.1 Hz), 3.15 (3H, s), 2.32 (3H, s), 1.38 (3H, t, J = 7.1 Hz), 1.36 (3H, t, J = 7.2 Hz).
$^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 166.4, 165.9, 163.4, 144.2, 135.1, 133.8, 132.6, 129.8, 129.5, 119.4, 108.4, 62.6, 62.4, 26.4, 21.5, 14.3 (2C).

MS: m/z (M+23) 340.1

HRMS: m/z calc’d for C$_{17}$H$_{19}$NaNO$_5$ 340.1155, found 340.1143

Melting point: 142-144 °C

**Synthesis of diethyl 2-(1-methyl-2-oxoindolin-3-yl)malonate, 4**

![Diagram](image)

Sodium borohydride (7.2 mg, 0.19 mmol) was added to ethyl 3-(2-ethoxy-2-oxoacetyl) 1-methyl-1H-pyrrolo[2,3-b]pyridine-2-carboxylate 2a (29 mg, 0.096 mmol) in MeOH (2 mL) and stirred at room temperature. The reaction was stirred until completion was indicated by TLC analysis. Then it was quenched with saturated ammonium chloride solution and extracted with ethyl acetate. After drying over MgSO$_4$, filtration and concentration, the product 4 was isolated as a red liquid (21 mg, 71%).

IR (neat): 1720 (s), 1612 (s), 1353 (s), 752 (s) cm$^{-1}$

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.39 (1H, d, $J = 7.4$ Hz), 7.25-7.32 (1H, m), 7.02 (1H, td, $J = 7.6$, 0.76 Hz), 6.82 (1H, $J = 7.8$ Hz), 4.22-4.32 (2H, m), 4.21 (1H, d, $J = 3.6$ Hz), 3.92-4.03 (3H, m), 3.23 (3H, s), 1.28 (3H, t, $J = 7.1$ Hz), 0.98 (3H, t, $J = 7.2$ Hz).

$^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 175.7, 168.5, 167.3, 145.1, 129.0, 125.9, 125.3, 122.9, 108.3, 62.3, 62.0, 52.7, 45.0, 26.8, 14.4, 14.1.

MS: m/z (M+23) 328.1

HRMS: m/z calc’d for C$_{16}$H$_{15}$NaNO$_5$ 328.3155, found 328.1156
NMR spectra for diethyl 2-(1-ethyl-1H-indol-3-yl)-2-hydroxymalonate 1b
NMR spectra for diethyl 2-(1-benzyl-1\textit{H}-indol-3-yl)-2-hydroxymalonate 1c
NMR spectra for diethyl 2-hydroxy-2-(1-phenyl-1H-indol-3-yl)malonate 1d

Current Data Parameters
NAME: KM-242_3
EXPNO: 5
PROCNO: 1
F2 - Acquisition Parameters
Date: 20100701
Time: 10.15
INSTRUM: dpx400
PROBHD: 5 mm QNP 1H/1
PULPROG: zg30
TD: 65536
SOLVENT: CDCl3
NS: 16
DS: 2
SWH: 8278.146 Hz
FIDRES: 0.126314 Hz
AQ: 3.9584243 sec
RG: 406.4
DW: 60.400 usec
DE: 6.00 usec
TE: 293.3 K
D1: 1.00000000 sec
TD0: 1
======== CHANNEL f1 ========
NUC1: 1H
P1: 8.40 usec
PL1: -3.00 dB
SFO1: 400.1324710 MHz

Current Data Parameters
NAME: KM-242_4
EXPNO: 2
PROCNO: 1
F2 - Acquisition Parameters
Date: 20100825
Time: 14.59
INSTRUM: dpx400
PROBHD: 5 mm QNP 1H/1
PULPROG: zgpg30
TD: 65536
SOLVENT: CDCl3
NS: 256
DS: 4
SWH: 23980.814 Hz
FIDRES: 0.365918 Hz
AQ: 1.3664756 sec
RG: 16384
DW: 20.850 usec
DE: 6.00 usec
TE: 293.7 K
D1: 2.00000000 sec
d11: 0.03000000 sec
DELTA: 1.89999998 sec
TD0: 8
======== CHANNEL f1 ========
NUC1: 13C
P1: 9.70 usec
PL1: -3.00 dB
SFO1: 100.6228298 MHz

F2 - Processing parameters
SI: 32768
SF: 100.6127407 MHz
WDW: EM
SSB: 0
LB: 1.00 Hz
GB: 0
PC: 1.40

F2 - Processing parameters
SI: 32768
SF: 100.6127407 MHz
WDW: EM
SSB: 0
LB: 1.00 Hz
GB: 0
PC: 1.40
NMR spectra for diethyl 2-(5-bromo-1-methyl-1H-indol-3-yl)-2-hydroxymalonate 1e
NMR spectra for diethyl 2-(6-chloro-1-methyl-1H-indol-3-yl)-2-hydroxymalonate

1f
NMR spectra for diethyl 2-(7-chloro-1-methyl-1H-indol-3-yl)-2-hydroxymalonate 1g
NMR spectra for diethyl 2-hydroxy-2-(5-methoxy-1-methyl-1H-indol-3-yl)malonate 1h
NMR spectra for diethyl 2-(7-ethyl-1-methyl-1H-indol-3-yl)-2-hydroxymalonate 1i

Current Data Parameters
NAME           WM JM-10
EXPNO                 3
PROCNO                1
F2 - Acquisition Parameters
Date_          20111020
Time              11.49
INSTRUM          dpx400
PROBHD   5 mm QNP  1H/1
PULPROG            zg30
TD                65536
SOLVENT           CDCl3
NS                   16
DS                    2
SWH            8278.146 Hz
FIDRES         0.126314 Hz
AQ            3.9584243 sec
RG                143.7
DW               60.400 usec
DE                 6.00 usec
TE                293.0 K
D1           1.00000000 sec
TD0                   1
======== CHANNEL f1 ========
NUC1                 1H
P1                 8.40 usec
PL1               -3.00 dB
SFO1        400.1324710 MHz
F2 - Processing parameters
SI                32768
SF          400.1300089 MHz
WDW                  EM
SSB                   0
LB                 0.30 Hz
GB                    0
PC                 1.00

Current Data Parameters
NAME           WM JM-10
EXPNO                 4
PROCNO                1
F2 - Acquisition Parameters
Date_          20111020
Time              11.52
INSTRUM          dpx400
PROBHD   5 mm QNP  1H/1
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                  256
DS                    4
SWH           23980.814 Hz
FIDRES         0.365918 Hz
AQ            1.3664756 sec
RG              10321.3
DW               20.850 usec
DE                 6.00 usec
TE                293.3 K
D1           2.00000000 sec
d11          0.03000000 sec
DELTA        1.89999998 sec
TD0                   8
======== CHANNEL f1 ========
NUC1                13C
P1                 9.70 usec
PL1               -3.00 dB
SFO1        100.6228298 MHz
======== CHANNEL f2 ========
CPDPRG2         waltz16
NUC2                 1H
PCPD2             84.00 usec
PL2               -3.00 dB
PL12              16.08 dB
PL13              18.00 dB
SFO2        400.1316005 MHz

FT - Processing parameters
SI                32768
SF          100.6127365 MHz
WDW                  EM
SSB                   0
LB                 1.00 Hz
GB                    0
PC                 1.40

HO
CO2Et
CO2Et

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NMR spectra for diethyl 2-(1,5-dimethyl-1H-indol-3-yl)-2-hydroxymalonate 1j
NMR spectra for diethyl 2-(1-methyl-2-oxoindolin-3-ylidene)malonate 2a

Electronic Supplementary Material (ESI) for RSC Advances
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NMR spectra for diethyl 2-(1-ethyl-2-oxoindolin-3-ylidene)malonate 2b
NMR spectra for diethyl 2-(1-benzyl-2-oxoindolin-3-ylidene)malonate 2c

Electronic Supplementary Material (ESI) for RSC Advances
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NMR spectra for diethyl 2-(2-oxo-1-phenylindolin-3-ylidene)malonate 2d
NMR spectra for diethyl 2-(5-bromo-1-methyl-2-oxindolin-3-ylidene)malonate 2e

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Electronic Supplementary Material (ESI) for RSC Advances
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NMR spectra for diethyl 2-(6-chloro-1-methyl-2-oxoindolin-3-ylidene)malonate 2f

Current Data Parameters
NAME              KM-267
EXPNO              7
PROCNO             1
F2 - Acquisition Parameters
Date_               20100729
Time               12.11
INSTRUM           dpx400
PROBHD    5 mm QNP 1H/1
PULPROG           zg30
TD                65536
SOLVENT           CDCl3
NS                  16
DS                    2
SWH           8278.146 Hz
FIDRES         0.126314 Hz
AQ            3.9584243 sec
RG                 228.1
DW               60.400 usec
DE                 6.00 usec
TE                293.4 K
D1           1.00000000 sec
td0                   1
======== CHANNEL f1 ========
NUC1                1H
P1                 8.40 usec
PL1               -3.00 dB
SFO1        400.1324710 MHz

Current Data Parameters
NAME              KM-267
EXPNO              8
PROCNO             1
F2 - Acquisition Parameters
Date_               20100729
Time               12.14
INSTRUM           dpx400
PROBHD   5 mm QNP 1H/1
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                  256
DS                    4
SWH           23980.814 Hz
FIDRES         0.365918 Hz
AQ            1.3664756 sec
RG                 6502
DW               20.850 usec
DE                 6.00 usec
TE                293.6 K
D1           2.00000000 sec
d11          0.03000000 sec
DELTA        1.89999998 sec
td0                   8
======== CHANNEL f1 ========
NUC1                13C
P1                 9.70 usec
PL1               -3.00 dB
SFO1        100.6228298 MHz

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NMR spectra for diethyl 2-(7-chloro-1-methyl-2-oxoindolin-3-ylidene)malonate 2g
NMR spectra for diethyl 2-(5-methoxy-1-methyl-2-oxoindolin-3-ylidene)malonate 2h
NMR spectra for diethyl 2-(7-ethyl-1-methyl-2-oxoindolin-3-ylidene)malonate 2i

Current Data Parameters
NAME             WM-465
EXPNO                 2
PROCNO                1
F2 - Acquisition Parameters
Date_          20111004
Time              13.51
INSTRUM          dpx400
PROBHD   5 mm QNP  1H/1
PULPROG            zg30
TD                65536
SOLVENT           CDCl3
NS                   16
DS                    2
SWH            8278.146 Hz
FIDRES         0.126314 Hz
AQ            3.9584243 sec
RG                  256
DW               60.400 usec
DE                 6.00 usec
TE                293.3 K
D1           1.00000000 sec
TD0                   1
======== CHANNEL f1 ========
NUC1                 1H
P1                 8.40 usec
PL1               -3.00 dB
SFO1        400.1324710 MHz
F2 - Processing parameters
SI                32768
SF          400.1300098 MHz
WDW                  EM
SSB                   0
LB                 0.30 Hz
GB                    0
PC                 1.00

Current Data Parameters
NAME             WM-468
EXPNO                 5
PROCNO                1
F2 - Acquisition Parameters
Date_          20111018
Time              11.00
INSTRUM          dpx400
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PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                  256
DS                    4
SWH           23980.814 Hz
FIDRES         0.365918 Hz
AQ            1.3664756 sec
RG                 6502
DW               20.850 usec
DE                 6.00 usec
TE                293.6 K
D1           2.00000000 sec
d11          0.03000000 sec
DELTA        1.89999998 sec
TD0                   8
======== CHANNEL f1 ========
NUC1                13C
P1                 9.70 usec
PL1               -3.00 dB
SFO1        100.6228298 MHz
======== CHANNEL f2 ========
CPDPRG2         waltz16
NUC2                 1H
PCPD2             84.00 usec
PL2               -3.00 dB
PL12              16.08 dB
PL13              18.00 dB
SFO2        400.1316005 MHz
F2 - Processing parameters
SI                32768
SF          100.6127366 MHz
WDW                  EM
SSB                   0
LB                 1.00 Hz
GB                    0
PC                 1.40

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NMR spectra for diethyl 2-(1,5-dimethyl-2-oxoindolin-3-ylidene)malonate 2j
NMR spectra for diethyl 2-(1-methyl-2-oxoindolin-3-yl)malonate 4