

## Supporting Information

### **Active Methylene Compounds (AMCs) Controlled Facile Synthesis of Acridine and Phenanthridine from Morita Baylis-Hillman Acetate**

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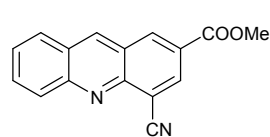
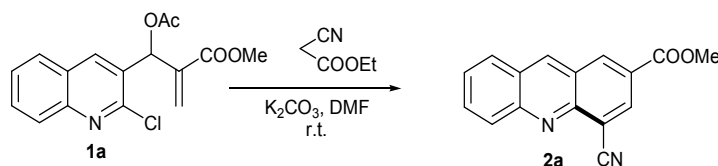
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## General remarks

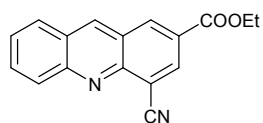
All reactions were carried out under inert atmosphere using dry solvent.  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra were recorded at ambient temperature using JEOL at 500 & 300 MHz and 125 & 75 MHz spectrometer respectively. IR spectra were recorded on VARIAN 3300 FTIR spectrophotometers in  $\text{cm}^{-1}$  units. Melting points were measured using Buchi melting-point apparatus in an open capillary tube and are uncorrected (**3a-3i**, **4a-4c**) and compounds **2a-2l** are not melted upto  $240\text{ }^\circ\text{C}$ . High resolution mass spectra (HRMS) were obtained on Bruker Daltonics MicroTOF-Q-II. Thin-layer chromatography (TLC) was performed on glass plates (7.5 x 2.5 and 7.5 x 5.0 cm) coated with silica gel GF 254 and visualized by UV light.

## Representative procedure for the synthesis of acridine derivatives:

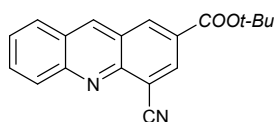
To a solution of MBH acetate **1a** (0.16 g, 0.5 mmol), was added ethylcyanoacetate (0.80 mL, 0.75 mmol) and potassium carbonate (0.103 g, 0.75 mmol), in DMF (2.0 mL) and reaction was stirred at room temperature. After completion of the reaction, Ethyl acetate was added to reaction mixture. Organic phase was then washed with water (3 times), concentrated and dried. Residue obtained was purified by column chromatography (hexane/ethyl acetate, 90:10) to obtain **2a** (0.102 g) as yellow solid in 78% yield.



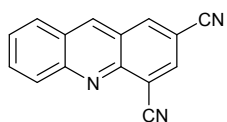
**4-Cyano-acridine-2-carboxylic acid methyl ester (2a):** Reaction time: 30 min; yield: 78%; yellow solid; IR (KBr):  $\nu$  3066, 2227, 1723  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  4.05 (s, 3H), 7.69 (t,  $J = 7.5$  Hz, 1H), 7.95 (t,  $J = 7.5$  Hz, 1H), 8.09 (d,  $J = 8.5$  Hz, 1H), 8.42 (d,  $J = 9.0$  Hz, 1H), 8.78 (s, 1H), 9.00 (d,  $J = 9.0$  Hz, 2H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  52.93, 113.84, 116.81, 124.85, 126.37, 127.41, 127.62, 128.39, 130.24, 132.88, 136.12, 136.62, 139.02, 147.69, 151.15, 164.99; HRMS (ESI) exact mass calcd for  $\text{C}_{16}\text{H}_{10}\text{N}_2\text{O}_2$ : 263.0821 ( $\text{M} + \text{H}$ ) $^+$  found: 263.0815 ( $\text{M} + \text{H}$ ) $^+$ .



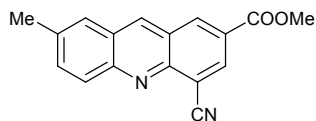
**4-Cyano-acridine-2-carboxylic acid ethyl ester (2b):** Reaction time: 60 min; yield: 72%; yellow solid; IR (KBr):  $\nu$  2926, 2228, 1722  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  1.49 (t,  $J = 7.0$  Hz, 3H), 4.51 (q,  $J = 7.0$  Hz, 2H), 7.68 (t,  $J = 7.5$  Hz, 1H), 7.95 (t,  $J = 7.5$  Hz, 1H), 8.09 (d,  $J = 8.5$  Hz, 1H), 8.41 (d,  $J = 8.5$  Hz, 1H), 8.79 (s, 1H), 9.00 (s, 2H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  14.33, 62.07, 113.71, 116.88, 124.85, 126.70, 127.39, 127.58, 128.39, 130.21, 132.83, 136.22, 136.52, 139.00, 147.69, 151.10, 164.49; HRMS (ESI) exact mass calcd for  $\text{C}_{17}\text{H}_{12}\text{N}_2\text{O}_2$ : 277.0977 ( $\text{M} + \text{H}$ ) $^+$  found: 277.0974 ( $\text{M} + \text{H}$ ) $^+$ .



**4-Cyano-acridine-2-carboxylic acid tert-butyl ester (2c):** Reaction time: 90 min; yield: 72%; yellow solid; IR (KBr):  $\nu$  2975, 2224, 1713  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  1.68 (s, 9H), 7.67 (t,  $J = 7.5$  Hz, 1H), 7.94 (t,  $J = 9.0$  Hz, 1H), 8.08 (d,  $J = 8.5$  Hz, 1H), 8.40 (d,  $J = 9.0$  Hz, 1H), 8.73 (s, 1H), 8.93 (s, 1H), 8.99 (s, 1H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  28.18, 82.80, 113.42, 117.03, 124.86, 127.36, 127.48, 128.20, 128.36, 130.19, 132.68, 136.16, 136.50, 138.88, 147.65, 150.98, 163.49; HRMS (ESI) exact mass calcd for  $\text{C}_{19}\text{H}_{16}\text{N}_2\text{O}_2$ : 305.1290 ( $\text{M} + \text{H}$ ) $^+$  found: 305.1279 ( $\text{M} + \text{H}$ ) $^+$ .

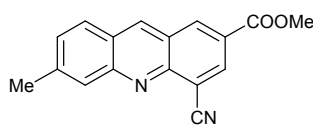


**acridine-2,4-dicarbonitrile (2d):** Reaction time: 30 min; yield: 68%; yellow solid; IR (KBr):  $\nu$  2903, 2255, 2216,  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.74 (t,  $J = 7.5$  Hz, 1H), 8.01 (t,  $J = 7.5$  Hz, 1H), 8.12 (d,  $J = 8.5$  Hz, 1H), 8.30 (s, 1H), 8.44 (d,  $J = 9.0$  Hz, 1H), 8.66 (s, 1H), 8.97 (s, 1H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  108.71, 115.53, 115.61, 116.91, 124.78, 127.65, 128.38, 128.46, 130.32, 133.63, 135.99, 138.23, 139.69, 146.46, 151.53; HRMS (ESI) exact mass calcd for  $\text{C}_{15}\text{H}_7\text{N}_3$ : 230.0718 ( $\text{M} + \text{H}$ ) $^+$  found: 230.0712 ( $\text{M} + \text{H}$ ) $^+$ .



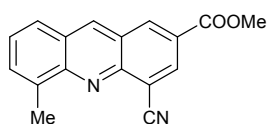
**4-Cyano-7-methyl-acridine-2-carboxylic acid methyl ester (2e):** Reaction time: 45 min; yield: 75%; yellow solid; IR (KBr):  $\nu$  2923, 2229, 1721  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  2.62 (s, 3H), 4.04 (s, 3H), 7.76-7.81 (m, 2H), 8.29 (d,  $J = 9.0$  Hz, 1H), 8.73 (s, 1H), 8.84 (s, 1H), 8.96 (s, 1H);  $^{13}\text{C}$  NMR (125 MHz,

CDCl<sub>3</sub>):  $\delta$  21.88, 52.87, 113.72, 116.89, 124.97, 126.20, 126.34, 127.56, 129.81, 135.58, 135.85, 136.51, 137.71, 137.81, 147.19, 150.16, 165.06; HRMS (ESI) exact mass calcd for C<sub>17</sub>H<sub>12</sub>N<sub>2</sub>O<sub>2</sub>: 277.0977 (M + H)<sup>+</sup> found: 277.0972 (M + H)<sup>+</sup>.



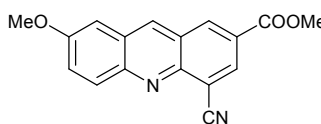
**4-Cyano-6-methyl-acridine-2-carboxylic acid methyl ester (2f):**

Reaction time: 30 min; yield: 80%; yellow solid; IR (KBr):  $\nu$  2924, 2226, 1723 cm<sup>-1</sup>; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  2.65 (s, 3H), 4.04 (s, 3H), 7.50 (d, J = 8.1 Hz, 1H), 7.96 (d, J = 8.1 Hz, 1H), 8.17 (s, 1H), 8.74 (s, 1H), 8.90 (s, 1H), 8.96 (s, 1H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  22.38, 52.82, 113.58, 116.96, 124.56, 125.92, 128.05, 128.56, 130.22, 130.57, 136.03, 136.70, 138.59, 144.19, 147.95, 151.55, 165.20; HRMS (ESI) exact mass calcd for C<sub>17</sub>H<sub>12</sub>N<sub>2</sub>O<sub>2</sub>: 277.0977 (M + H)<sup>+</sup> found: 277.0972 (M + H)<sup>+</sup>.



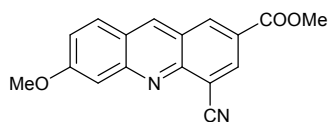
**4-Cyano-5-methyl-acridine-2-carboxylic acid methyl ester (2g):**

Reaction time: 30 min; yield: 82%; yellow solid; IR (KBr):  $\nu$  2924, 2229, 1722 cm<sup>-1</sup>; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  3.00 (s, 3H), 4.05 (s, 3H), 7.57 (t, J = 8.0 Hz, 1H), 7.78 (d, J = 7.0 Hz, 1H), 7.92 (d, J = 8.5 Hz, 1H), 8.75 (s, 1H), 8.93 (s, 1H), 8.98 (s, 1H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  18.04, 52.89, 114.15, 116.74, 124.60, 126.25, 127.44, 127.56, 132.15, 135.62, 136.38, 138.36, 138.85, 146.81, 150.41, 165.10; HRMS (ESI) exact mass calcd for C<sub>17</sub>H<sub>12</sub>N<sub>2</sub>O<sub>2</sub>: 277.0977 (M + H)<sup>+</sup> found: 277.0972 (M + H)<sup>+</sup>.



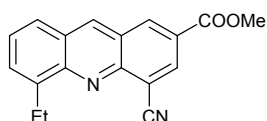
**4-Cyano-7-methoxy-acridine-2-carboxylic acid methyl ester (2h):**

Reaction time: 50 min; yield: 74%; yellow solid; IR (KBr):  $\nu$  2926, 2232, 1723 cm<sup>-1</sup>; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  4.01 (s, 3H), 4.04 (s, 3H), 7.20 (s, 1H), 7.62 (d, J = 7.0 Hz, 1H), 8.29 (d, J = 9.5 Hz, 1H), 8.70 (s, 1H), 8.79 (s, 1H), 8.94 (s, 1H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  52.81, 56.06, 105.91, 112.75, 117.12, 123.33, 123.79, 123.87, 125.26, 129.61, 136.06, 136.61, 138.29, 148.29, 153.35, 163.67, 165.15; HRMS (ESI) exact mass calcd for C<sub>17</sub>H<sub>12</sub>N<sub>2</sub>O<sub>3</sub>: 293.0926 (M + H)<sup>+</sup> found: 293.0921 (M + H)<sup>+</sup>.



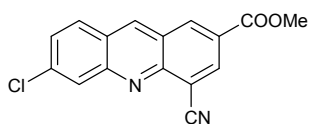
**4-Cyano-6-methoxy-acridine-2-carboxylic acid methyl ester (2i):**

Reaction time: 30 min; yield: 75%; yellow solid; IR (KBr):  $\nu$  2920, 2227, 1717  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  4.04 (s, 3H), 4.06 (s, 3H), 7.33 (d,  $J = 7.0$  Hz, 1H), 7.62 (s, 1H), 7.94 (d,  $J = 9.5$  Hz, 1H), 8.75 (s, 1H), 8.83 (s, 1H), 8.95 (s, 1H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  52.82, 56.06, 105.89, 112.72, 117.12, 123.31, 123.76, 123.85, 125.23, 129.60, 136.05, 136.60, 138.28, 148.27, 153.33, 163.65, 165.14; HRMS (ESI) exact mass calcd for  $\text{C}_{17}\text{H}_{12}\text{N}_2\text{O}_3$ : 293.0926 (M + H) $^+$  found: 293.0921 (M + H) $^+$ .



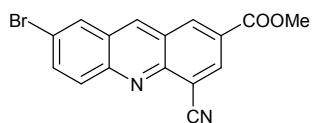
**4-Cyano-5-ethyl-acridine-2-carboxylic acid methyl ester (2j):**

Reaction time: 30 min; yield: 82%; yellow solid; IR (KBr):  $\nu$  2924, 2229, 1722  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  1.50 (t,  $J = 7.5$  Hz, 3H), 3.52 (q,  $J = 7.5$  Hz, 2H), 4.05 (s, 3H), 7.60 (t,  $J = 7.5$  Hz, 1H), 7.78 (d,  $J = 7.0$  Hz, 1H), 7.92 (d,  $J = 8.5$  Hz, 1H), 8.75 (s, 1H), 8.93 (s, 1H), 8.98 (s, 1H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  14.54, 24.74, 52.88, 114.20, 116.73, 124.57, 126.20, 126.23, 127.56, 127.70, 130.54, 135.55, 136.34, 138.87, 143.98, 146.79, 149.85, 165.12; HRMS (ESI) exact mass calcd for  $\text{C}_{18}\text{H}_{14}\text{N}_2\text{O}_2$ : 291.1130 (M + H) $^+$  found: 291.1128 (M + H) $^+$ .



**6-Chloro-4-cyano-acridine-2-carboxylic acid methyl ester (2k):**

Reaction time: 90 min; yield: 70%; yellow solid; IR (KBr):  $\nu$  2924, 2233, 1729  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  4.06 (s, 3H), 7.76 (d,  $J = 7.0$  Hz, 1H), 7.86 (t,  $J = 7.5$  Hz, 1H), 8.35 (d,  $J = 9.0$  Hz, 1H), 8.83 (s, 1H), 9.09 (s, 1H), 9.41 (s, 1H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  53.02, 113.78, 116.51, 125.07, 125.78, 127.06, 127.20, 129.47, 131.74, 132.21, 136.78, 136.87, 147.95, 151.26, 164.77; HRMS (ESI) exact mass calcd for  $\text{C}_{16}\text{H}_9\text{ClN}_2\text{O}_2$ : 297.0430 (M + H) $^+$  found: 297.0425 (M + H) $^+$ .

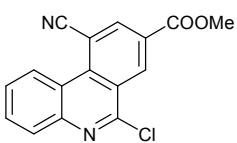
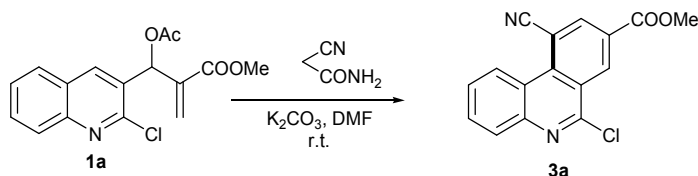


**7-Bromo-4-cyano-acridine-2-carboxylic acid methyl ester (2I):**

Reaction time: 120 min; yield: 64%; yellow solid; IR (KBr):  $\nu$  2924, 2215, 1729  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  4.06 (s, 3H), 7.76-7.77 (m, 1H), 7.86 (t,  $J = 7.5$  Hz, 1H), 8.35 (d,  $J = 8.5$  Hz, 1H), 8.83 (s, 1H), 9.09 (s, 1H), 9.42 (s, 1H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  52.92, 113.84, 116.80, 124.85, 126.38, 127.41, 127.62, 128.39, 130.24, 132.88, 136.12, 136.61, 139.01, 147.69, 151.16, 164.99; HRMS (ESI) exact mass calcd for  $\text{C}_{16}\text{H}_9\text{BrN}_2\text{O}_2$ : 340.9925 (M + H)<sup>+</sup> found: 340.9920 (M + H)<sup>+</sup>.

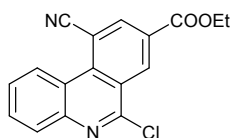
**Representative procedure for the synthesis of phenanthridine derivatives:**

To a solution of MBH acetate **1a** (0.16 g, 0.5 mmol), was added cyanoacetamide (0.63 g, 0.75 mmol) and potassium carbonate (0.103 g, 0.75 mmol), in DMF (2.0 mL) and reaction was stirred at room temperature. After completion of the reaction, Ethyl acetate was added to reaction mixture. Organic phase was then washed with water (3 times), concentrated and dried. Residue obtained was purified by column chromatography (hexane/ethyl acetate, 93:7) to obtain **3a** (0.91 g) as white solid in 62% yield.



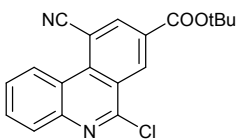
**6-Chloro-10-cyano-phenanthridine-8-carboxylic acid methyl ester (3a):**

Reaction time: 2.5 h; yield: 62%; white solid; mp: 174-176°C; IR (KBr):  $\nu$  2924, 2226, 1732  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  4.08 (s, 3H), 7.84 (t,  $J = 7.0$  Hz, 1H), 7.94 (t,  $J = 7.5$  Hz, 1H), 8.18 (d,  $J = 7.5$  Hz, 1H), 8.92 (s, 1H), 9.44 (s, 1H), 9.71 (d,  $J = 8.5$  Hz, 1H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  53.20, 108.35, 119.17, 121.74, 124.65, 125.49, 128.73, 129.33, 130.09, 132.23, 134.38, 136.56, 140.14, 144.93, 151.22, 164.14; HRMS (ESI) exact mass calcd for  $\text{C}_{16}\text{H}_9\text{ClN}_2\text{O}_2$ : 297.0431 (M + H)<sup>+</sup> found: 297.0430 (M + H)<sup>+</sup>.



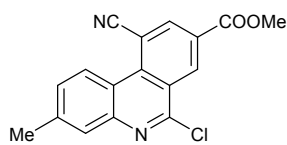
**6-Chloro-10-cyano-phenanthridine-8-carboxylic acid ethyl ester (3b):**

Reaction time: 3 h; yield: 60%; white solid; mp: 180-182°C; IR (KBr):  $\nu$  2985, 2224, 1730  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  1.50 (t,  $J = 7.0$  Hz, 3H) 4.54 (q,  $J = 7.5$  Hz, 2H), 7.82 (t,  $J = 8.0$  Hz, 1H), 7.92 (t,  $J = 7.0$  Hz, 1H), 8.15 (d,  $J = 8.5$  Hz, 1H), 8.89 (s, 1H), 9.40 (s, 1H), 9.67 (d,  $J = 8.5$  Hz, 1H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  14.30, 62.45, 108.19, 119.19, 121.68, 124.58, 125.39, 128.67, 129.66, 130.03, 132.16, 134.30, 136.39, 140.12, 144.82, 151.20, 163.60; HRMS (ESI) exact mass calcd for  $\text{C}_{17}\text{H}_{11}\text{ClN}_2\text{O}_2$ : 311.0587 (M + H)<sup>+</sup> found: 311.0561 (M + H)<sup>+</sup>.



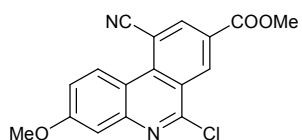
**6-Chloro-10-cyano-phenanthridine-8-carboxylic acid tert-butyl ester (3c):**

Reaction time: 3 h; yield: 60%; white solid; mp: 208-210°C; IR (KBr):  $\nu$  2987, 2225, 1713  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  1.69 (s, 9H), 7.81 (t,  $J = 8.5$  Hz, 1H), 7.91 (t,  $J = 8.0$  Hz, 1H), 8.15 (d,  $J = 8.0$  Hz, 1H), 8.83 (s, 1H), 9.36 (s, 1H), 9.67 (d,  $J = 8.5$  Hz, 1H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  28.13, 83.46, 107.96, 119.36, 121.76, 124.56, 125.35, 128.61, 130.02, 131.17, 132.02, 134.22, 136.14, 140.18, 144.77, 151.28, 162.58; HRMS (ESI) exact mass calcd for  $\text{C}_{19}\text{H}_{15}\text{ClN}_2\text{O}_2$ : 339.0900 (M + H)<sup>+</sup> found: 339.0876 (M + H)<sup>+</sup>.



**6-Chloro-10-cyano-3-methyl-phenanthridine-8-carboxylic acid methyl ester (3d):**

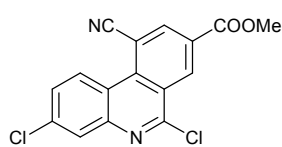
Reaction time: 1.5 h; yield: 70%; white solid; mp: 244-246°C; IR (KBr):  $\nu$  2922, 2226, 1726  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  2.63 (s, 3H), 4.07 (s, 3H), 7.65 (d,  $J = 8.5$  Hz, 1H), 7.96 (s, 1H), 8.87 (s, 1H), 9.40 (s, 1H), 9.56 (d,  $J = 8.5$  Hz, 1H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  21.66, 53.14, 107.99, 119.26, 119.42, 124.37, 125.08, 128.79, 129.67, 130.36, 134.40, 136.59, 140.05, 143.29, 145.13, 151.22, 164.23; HRMS (ESI) exact mass calcd for  $\text{C}_{17}\text{H}_{11}\text{ClN}_2\text{O}_2$ : 311.0587 (M + H)<sup>+</sup> found: 311.0570 (M + H)<sup>+</sup>.



**6-Chloro-10-cyano-3-methoxy-phenanthridine-8-carboxylic acid methyl ester (3e):**

Reaction time: 2h; yield: 67%; white solid; mp: 250-

252°C; IR (KBr):  $\nu$  2924, 2223, 1727  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  4.01 (s, 3H), 4.07 (s, 3H), 7.42 (d,  $J = 11.5$  Hz, 1H), 7.56 (s, 1H), 8.86 (s, 1H), 9.38 (s, 1H), 9.59 (d,  $J = 9.5$  Hz, 1H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  53.09, 55.84, 107.44, 110.25, 115.68, 119.31, 119.38, 124.23, 125.93, 128.05, 134.58, 136.54, 140.24, 147.18, 151.93, 162.51, 164.27; HRMS (ESI) exact mass calcd for  $\text{C}_{17}\text{H}_{11}\text{ClN}_2\text{O}_3$ : 327.0536 (M + H)<sup>+</sup> found: 327.0528 (M + H)<sup>+</sup>.

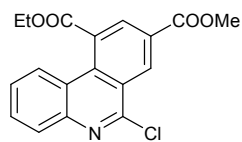


**3,6-Dichloro-10-cyano-phenanthridine-8-carboxylic acid methyl ester**

**(3f):** Reaction time: 3.5 h; yield: 54%; white solid; mp: 230-232°C; IR

(KBr):  $\nu$  2922, 2225, 1727  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  4.09 (s, 3H),

7.78 (d,  $J = 7.0$  Hz, 1H), 8.16 (s, 1H), 8.91 (s, 1H), 9.42 (s, 1H), 9.63 (d,  $J = 9.0$  Hz, 1H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  53.27, 108.28, 118.95, 120.17, 125.40, 125.86, 129.24, 129.33, 129.59, 134.51, 136.04, 138.28, 140.38, 145.60, 152.59, 163.97; HRMS (ESI) exact mass calcd for  $\text{C}_{16}\text{H}_8\text{Cl}_2\text{N}_2\text{O}_2$ : 331.0041 (M + H)<sup>+</sup> found: 331.0040 (M + H)<sup>+</sup>.

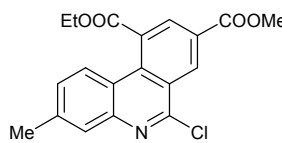


**6-Chloro-phenanthridine-8,10-dicarboxylic acid 10-ethyl ester 8-methyl**

**ester (3g):** Reaction time: 5 h; yield: 59%, white solid; mp: 238-240°C; IR

(KBr):  $\nu$  2927, 1732, 1606  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  1.41 (t,  $J = 7.5$

Hz, 3H), 4.05 (s, 3H), 4.55 (q,  $J = 7.0$  Hz, 2H), 7.63 (t,  $J = 8.0$  Hz, 1H), 7.81 (t,  $J = 8.0$  Hz, 1H), 8.13 (d,  $J = 8.5$  Hz, 1H), 8.20 (d,  $J = 8.5$  Hz, 1H), 8.57 (s, 1H), 9.27 (s, 1H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  13.93, 52.86, 62.66, 121.98, 125.54, 125.84, 127.28, 129.00, 129.72, 130.91, 131.41, 131.62, 132.27, 134.50, 144.83, 151.58, 165.18, 169.88; HRMS (ESI) exact mass calcd for  $\text{C}_{18}\text{H}_{14}\text{ClNO}_4$ : 344.0689 (M + H)<sup>+</sup> found: 344.0688 (M + H)<sup>+</sup>.



**6-Chloro-3-methyl-phenanthridine-8,10-dicarboxylic acid 10-ethyl**

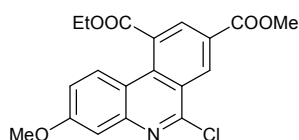
**ester 8-methyl ester (3h):** Reaction time: 3.5 h; yield: 65%; white solid;

mp: 128-130°C; IR (KBr):  $\nu$  2984, 1730, 1607  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (500 MHz,

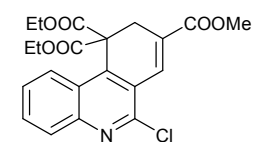
$\text{CDCl}_3$ ):  $\delta$  1.41 (t,  $J = 7.0$  Hz, 3H), 2.58 (s, 3H), 4.04 (s, 3H), 4.54 (q,  $J = 7.5$  Hz, 2H), 7.45 (d,  $J = 7.0$



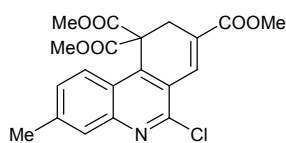
Hz, 1H), 7.91 (s, 1H), 8.06 (d, J = 8.5 Hz, 1H), 8.54 (s, 1H), 9.25 (s, 1H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  13.96, 21.52, 52.81, 62.58, 119.64, 125.17, 125.54, 128.47, 129.01, 129.28, 131.10, 131.66, 132.16, 134.53, 141.69, 145.02, 151.57, 165.26, 169.98; HRMS (ESI) exact mass calcd for  $\text{C}_{19}\text{H}_{16}\text{ClNO}_4$ : 358.0846 (M + H) $^+$  found: 358.0841 (M + H) $^+$ .



**6-Chloro-3-methoxy-phenanthridine-8,10-dicarboxylic acid 10-ethyl ester 8-methyl ester (3i):** Reaction time: 4 h; yield: 62%; white solid; mp: 140-142 $^\circ\text{C}$ ; IR (KBr):  $\nu$  2955, 1724, 1605  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  1.40 (t, J = 7.0 Hz, 3H), 3.98 (s, 3H), 4.04 (s, 3H), 4.53 (q, J = 7.5 Hz, 2H), 7.22-7.24 (m, 1H), 7.52 (s, 1H), 8.07 (d, J = 9.5 Hz, 1H), 8.53 (s, 1H), 9.23 (s, 1H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  13.97, 52.77, 55.73, 62.56, 109.66, 115.91, 118.22, 124.38, 126.98, 127.78, 130.58, 131.86, 132.36, 134.61, 146.88, 152.20, 161.56, 165.30, 169.96; HRMS (ESI) exact mass calcd for  $\text{C}_{19}\text{H}_{16}\text{ClNO}_5$ : 374.0795 (M + H) $^+$  found: 374.0790 (M + H) $^+$ .

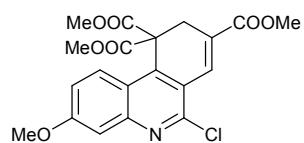


**6-Chloro-9H-phenanthridine-8,10,10-tricarboxylic acid diethyl ester methyl ester (4a):** Reaction time: 2.5 h; yield: 67%; white solid; mp: 114-116 $^\circ\text{C}$ ; IR (KBr):  $\nu$  2984, 1757, 1734, 1690, 1632  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  1.15 (t, J = 7.5 Hz, 6H), 3.45 (s, 2H), 3.88 (s, 3H) 4.16-4.25 (m, 4H), 7.50 (t, J = 8.5 Hz, 1H), 7.69 (t, J = 8.0 Hz, 1H), 7.89 (d, J = 8.5 Hz, 1H), 7.93 (s, 1H), 7.99 (d, J = 8.5 Hz, 1H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  13.73, 31.17, 52.37, 59.66, 62.81, 124.95, 125.82, 125.86, 126.96, 128.90, 129.49, 130.61, 130.81, 141.96, 148.28, 149.41, 165.62, 169.57; HRMS (ESI) exact mass calcd for  $\text{C}_{21}\text{H}_{20}\text{ClNO}_6$ : 418.1057 (M + H) $^+$  found: 418.1052 (M + H) $^+$ .



**6-Chloro-3-methyl-9H-phenanthridine-8,10,10-tricarboxylic acid trimethyl ester (4b):** Reaction time: 2 h; yield: 74%; white solid; mp: 154-156 $^\circ\text{C}$ ; IR (KBr):  $\nu$  2953, 1739, 1731, 1705, 1620  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  2.54 (s, 3H), 3.56 (s, 2H), 3.80 (s, 6H), 3.85 (s, 3H), 7.37 (d, J = 8.0 Hz, 1H), 7.66-

7.70 (m, 1H), 7.86 (s, 1H), 7.94 (s, 1H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  21.48, 30.50, 52.21, 53.28, 62.21, 124.16, 125.70, 127.52, 127.79, 129.10, 129.56, 134.61, 134.68, 140.94, 147.81, 153.91, 166.38, 170.14; HRMS (ESI) exact mass calcd for  $\text{C}_{20}\text{H}_{18}\text{ClNO}_6$ : 404.0901 ( $\text{M} + \text{H}$ ) $^+$  found: 404.0907 ( $\text{M} + \text{H}$ ) $^+$ .



**6-Chloro-3-methoxy-9H-phenanthridine-8,10,10-tricarboxylic acid trimethyl ester (4c)** : Reaction time: 2 h; yield: 70%; white solid; mp:

120-122°C; IR (KBr):  $\nu$  2961, 1735, 1738, 1703, 1618  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  3.55 (s, 2H), 3.81 (s, 3H), 3.84 (s, 6H), 3.94 (s, 3H), 7.18 (d,  $J = 11.5$  Hz, 1H), 7.40 (s, 1H), 7.64-7.69 (m, 1H), 7.90 (s, 1H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  30.52, 52.17, 53.34, 55.62, 62.27, 108.24, 120.55, 122.83, 122.95, 127.00, 128.92, 134.64, 134.73, 149.55, 154.25, 161.54, 166.43, 170.19; HRMS (ESI) exact mass calcd for  $\text{C}_{20}\text{H}_{18}\text{ClNO}_7$ : 420.0850 ( $\text{M} + \text{H}$ ) $^+$  found: 420.0845 ( $\text{M} + \text{H}$ ) $^+$ .

