Electronic Supplementary Information

Metal-free, visible-light-promoted oxidative radical cyclization of N-biaryl glycine esters: one-pot construction of phenanthridine-6-carboxylates in water

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General Aspects

Unless otherwise noted, all reactions were performed in a 10 mL vial in the open air atmosphere. Photoirradiation was performed with a 34 W blue LED. All commercial chemicals, reagents and precursors were purchased from commercial suppliers and used without further purification. All organic solvents were dried over 4Å molecular sieves and distilled prior to use. Water was double-distilled prior to use. Reactions were monitored by analytical thin layer chromatography on silica gel and visualization was accomplished by irradiation with short wave UV light at 254 nm and near UV 366 nm lights. $^1$H NMR and $^{13}$C NMR spectra were measured in deuterated DMSO (DMSO-d$_6$) and recorded on Brucker spectrometer. Chemical shifts are expressed in parts per million (ppm) and were calibrated using the residual protonated solvent peak. High resolution mass spectra (HRMS) were recorded on an ESI-Q-TOF-Premier instrument. IR spectra were recorded on a Perkin Elmer Spectrum 1000 FT-IR spectrometer. Melting points were determined by a PERFIT-melting point apparatus and are uncorrected. Compounds described in the literature were characterized by comparing their physical and spectroscopic data to the reported values.

General procedure to prepare phenanthridine-6-carboxylates

To a vial (10 mL) equipped with a magnetic stir bar was charged with N-biaryl glycine esters (0.3 mmol), rose bengal (5 mol%) and 3-4 mL of water. The mixture was stirred few minutes to mix well at room temperature and then vial was irradiated through the plane bottom side of the vial using a 34 W blue LED at a distance of 2 cm for 24 h. Subsequently, the reaction mixture was removed from irradiation and the organic matters were completely precipitated by cooling to 0 °C. Precipitates were isolated by filtration and purified further by recrystallization using ethanol or ethyl acetate solution. The purity of the compound was confirmed by melting point, IR, NMR and mass spectral analyses, vide infra.
Synthesis of methyl 5,6-dihydrophenanthridine-6-carboxylate (1-IV)

To a screw-topped Pyrex reaction tube was added methyl phenanthridine-6-carboxylate (2a, 1.0 mmol), isopropanol (2.0 mL) and then concentrated hydrochloric acid (5.0 mmol, 400 μL). The solution was degassed by freeze-pump-thaw method, sealed and irradiated with a LED (λ = 410 nm) at a distance of 1.0 mm for 12 hours. Afterwards, the reaction mixture was neutralized with 1.0 M aqueous sodium hydroxide solution and extracted with ethyl acetate (3 × 20 mL). The combined organic extracts were dried over MgSO₄, filtered and concentrated. The crude residue was purified by a column chromatography on neutral alumina using solution mixture of methanol-dichloromethane as eluents.
Experimental characterization data for products

Methyl phenanthridine-6-carboxylate (2a).\(^{1-3}\) Pale yellow solid (67 mg, 93%): \(R_f\) 0.6 in ethyl acetate–hexane (25:75); mp = 98–100 °C (lit.\(^3\) mp 98–100 °C); IR (neat, cm\(^{-1}\)): \(\nu\) 3056, 3017, 1743, 1724, 1620, 1609, 1566, 1483, 1446, 1390, 1327, 1248, 1136, 713, 612. \(^1\)H NMR (300 MHz, DMSO-d\(_6\)) \(\delta\) 8.69-8.55 (m, 3H), 8.31 (m, 1H), 7.89 (m, 1H), 7.79-7.73 (m, 3H), 4.15 (s, 3H). \(^{13}\)C NMR (75 MHz, DMSO-d\(_6\)) \(\delta\) 166.4, 150.4, 142.6, 133.4, 131.2, 131.0, 129.1, 128.7, 127.8, 127.4, 124.9, 123.6, 122.2, 122.0, 53.2. HRMS (ESI) m/z [M + Na]\(^+\) calcd for C\(_{15}\)H\(_{11}\)NNaO\(_2\) 260.0687, found 260.0685.

Methyl 2-methylphenanthridine-6-carboxylate (2b).\(^{1-3}\) Colorless solid (76 mg, 92%): \(R_f\) 0.58 in ethyl acetate–hexane (25:75); mp = 135–137 °C (lit.\(^3\) mp 136–137 °C); IR (neat, cm\(^{-1}\)): \(\nu\) IR (neat, cm\(^{-1}\)): \(\nu\) 3058, 3023, 1742, 1723, 1620, 1611, 1567, 1483, 1447, 1392, 1327, 1248, 1131. \(^1\)H NMR (300 MHz, DMSO-d\(_6\)) \(\delta\) 8.63 (m, 2H), 8.35 (s, 1H), 8.18 (d, \(J = 8.4\) Hz, 1H), 7.89-7.81 (m, 1H), 7.73-7.68 (m, 1H), 7.60 (m, 1H), 4.14 (s, 3H), 2.64 (s, 3H). \(^{13}\)C NMR (75 MHz, DMSO-d\(_6\)) \(\delta\) 166.7, 149.1, 140.9, 139.0, 133.2, 130.9, 130.8, 130.7, 127.8, 127.4, 124.8, 123.8, 122.2, 121.6, 53.1, 22.1. HRMS (ESI) m/z [M + Na]\(^+\) calcd for C\(_{16}\)H\(_{13}\)NNaO\(_2\) 274.0844, found 274.0839.
**Methyl 3-methylphenanthridine-6-carboxylate (2c).** White solid (72 mg, 88%): \( R_f 0.58 \) in ethyl acetate–hexane (25:75); mp = 82–83 °C (lit.1 mp 81–83 °C); IR (neat, \( \text{cm}^{-1} \)): v 3061, 3056, 3014, 2921, 1741, 1723, 1622, 1614, 1571, 1473, 1456, 1306, 774, 752. \(^1\)H NMR (300 MHz, DMSO-\( \text{d}_6 \)) \( \delta \) 8.61-8.55 (m, 2H), 8.41 (d, \( J = 8.6 \) Hz, 1H), 8.07 (s, 1H), 7.83 (t, \( J = 8.4 \) Hz, 1H), 7.66 (t, \( J = 8.4 \) Hz, 1H), 7.54 (d, \( J = 8.4 \) Hz, 1H), 4.14 (s, 3H), 2.56 (s, 3H). \(^{13}\)C NMR (75 MHz, DMSO-\( \text{d}_6 \)) \( \delta \) 166.6, 150.3, 142.7, 139.4, 133.5, 131.1, 130.5, 130.4, 127.6, 127.3, 123.2, 122.5, 121.9, 121.8, 53.2, 21.4. HRMS (ESI) m/z [M + Na]^+ calcd for C_{16}H_{13}NNaO_2 274.0844, found 274.0839.

**Methyl 2-methoxyphenanthridine-6-carboxylate (2d).** White solid (82 mg, 94%): \( R_f 0.52 \) in ethyl acetate–hexane (25:75); mp = 159–162 °C; IR (neat, \( \text{cm}^{-1} \)): v 3076, 3017, 1743, 1723, 1616, 1564, 1365, 1306, 1150, 771. \(^1\)H NMR (300 MHz, DMSO-\( \text{d}_6 \)) \( \delta \) 8.67 (d, \( J = 8.6 \) Hz, 1H), 8.59-8.55 (m, 2H), 8.24 (d, \( J = 8.6 \) Hz, 1H), 7.93 (t, \( J = 8.2 \) Hz, 1H), 7.79 (t, \( J = 8.4 \) Hz, 1H), 7.75-7.71 (m, 1H), 4.17 (s, 3H), 3.94 (s, 1H). \(^{13}\)C NMR (75 MHz, DMSO-\( \text{d}_6 \)) \( \delta \) 165.9, 150.2, 140.6, 134.6, 132.1, 131.1, 129.5, 128.3, 127.2, 125.7, 123.5, 122.1, 121.6, 55.5, 53.2. HRMS (ESI) m/z [M + Na]^+ calcd for C_{16}H_{13}NNaO_3 290.0793, found 290.0791.
Methyl 3-methoxyphenanthridine-6-carboxylate (2e).\textsuperscript{1,2} White solid (78 mg, 90\%): $R_f$ 0.51 in ethyl acetate–hexane (25:75); mp = 111–113 °C (lit.\textsuperscript{1} mp 110–112 °C); IR (neat, cm\textsuperscript{-1}): $\nu$ 3057, 3014, 1742, 1723, 1614, 1487, 1461, 1363, 1141, 773. $^1$H NMR (300 MHz, DMSO-d$_6$) $\delta$ 8.61 (d, $J = 8.6$ Hz, 1H), 8.57 (d, $J = 8.6$ Hz, 1H), 8.50 (d, $J = 8.4$ Hz, 1H), 7.85 (t, $J = 7.2$ Hz, 1H), 7.69-7.66 (m, 2H), 7.42-7.36 (m, 1H), 4.16 (s, 3H), 3.98 (s, 3H). $^{13}$C NMR (75 MHz, DMSO-d$_6$) $\delta$ 166.6, 160.3, 150.4, 144.3, 133.6, 131.2, 127.4, 127.0, 123.3, 122.7, 121.5, 120.3, 119.3, 110.2, 55.7, 53.2. HRMS (ESI) m/z [M + Na]$^+$ calcd for C$_{16}$H$_{13}$NNaO$_3$ 290.0793, found 290.0789.

Methyl 3-nitrophenanthridine-6-carboxylate (2f).\textsuperscript{2} Pale yellow solid (52 mg, 56\%): $R_f$ 0.42 in ethyl acetate–hexane (25:75); mp = 176–178 °C; IR (neat, cm\textsuperscript{-1}): $\nu$ 3064, 3019, 1744, 1722, 1620, 1607, 1561, 1521, 1479, 1476, 1362, 1347, 791, 704. $^1$H NMR (300 MHz, DMSO-d$_6$) $\delta$ 9.18-9.14 (m, 1H), 8.74-8.71 (m, 2H), 8.66 (d, $J = 8.4$ Hz, 1H), 8.54-8.50 (m, 1H), 8.03 (t, $J = 7.4$ Hz, 1H), 7.89 (t, $J = 7.4$ Hz, 1H), 4.19 (s, 3H). $^{13}$C NMR (75 MHz, DMSO-d$_6$) $\delta$ 165.8, 152.7, 147.8, 142.1, 132.3, 132.2, 129.9, 129.2, 127.9, 126.6, 124.4, 123.6, 123.0, 122.2, 53.5. HRMS (ESI) m/z [M + Na]$^+$ calcd for C$_{15}$H$_{10}$N$_2$NaO$_4$ 305.0538, found 305.0532.
Methyl 2-chlorophenanthridine-6-carboxylate (2g).\(^{1-3}\) White solid (69 mg, 78\%): \(R_f\) 0.59 in ethyl acetate–hexane (25:75); mp = 145–147 °C (lit.\(^3\) mp 146–147 °C); IR (neat, cm\(^{-1}\)): \(v\) 3094, 3059, 3018, 1743, 1723, 1617, 1489, 1366, 1143, 729. \(^1\)H NMR (300 MHz, DMSO-\(d_6\)) \(\delta\) 8.66 (d, \(J = 8.5\) Hz, 1H), 8.59–8.54 (m, 2H), 8.23 (d, \(J = 8.8\) Hz, 1H), 7.92 (t, \(J = 8.2\) Hz, 1H), 7.78 (t, \(J = 7.4\) Hz, 1H), 7.74–7.71 (m, 1H), 4.16 (s, 3H). \(^{13}\)C NMR (75 MHz, DMSO-\(d_6\)) \(\delta\) 166.1, 150.4, 150.1, 134.9, 132.5, 132.4, 131.4, 129.8, 128.6, 127.4, 126.0, 123.8, 122.3, 121.9, 53.4. HRMS (ESI) m/z [M + Na]\(^+\) calcd for \(C_{15}H_{10}ClNaO_2\) 294.0298, found 294.0291.

Methyl 2-fluorophenanthridine-6-carboxylate (2h).\(^{1,2}\) White solid (58 mg, 69\%): \(R_f\) 0.60 in ethyl acetate–hexane (25:75); mp = 145–146 °C (lit.\(^1\) mp 144–146 °C); IR (neat, cm\(^{-1}\)): \(v\) 3057, 3021, 1741, 1724, 1618, 1560, 1491, 1363, 1143, 728. \(^1\)H NMR (300 MHz, DMSO-\(d_6\)) \(\delta\) 8.67 (d, \(J =8.6\) Hz, 1H), 8.53 (d, \(J =8.6\) Hz, 1H), 8.32–8.27 (m, 1H), 8.21–8.18 (m, 1H), 7.91 (t, \(J =7.7\) Hz, 1H), 7.77 (t, \(J =7.7\) Hz, 1H), 7.55–7.52 (m, 1H), 4.15 (s, 3H). \(^{13}\)C NMR (75 MHz, DMSO-\(d_6\)) \(\delta\) 166.4, 163.5, 149.3, 139.4, 133.5, 132.9, 131.3, 128.7, 127.5, 126.6, 123.4, 122.3, 118.5, 107.2, 53.2. \(^{19}\)F NMR (282 MHz, DMSO-\(d_6\)): \(\delta\) –109.3. HRMS (ESI) m/z [M + Na]\(^+\) calcd for \(C_{15}H_{10}FNNaO_2\) 278.0593, found 278.0587.
Methyl 3-fluorophenanthridine-6-carboxylate (2i).\(^1,2\) Pale yellow solid (64 mg, 77%): \(R_f\) 0.60 in ethyl acetate–hexane (25:75); mp = 129–131 °C (lit.\(^1\) mp 128–130 °C); IR (neat, cm\(^{-1}\)): \(\nu\) 3072, 3058, 3019, 1744, 1722, 1623, 1608, 1567, 1484, 1269, 1144, 707. \(^1\)H NMR (300 MHz, DMSO-d\(_6\)) \(\delta\) 8.62-8.58 (m, 3H), 7.94-7.89 (m, 2H), 7.76-7.73 (m, 1H), 7.53-7.49 (m, 1H), 4.16 (s, 3H). \(^{13}\)C NMR (75 MHz, DMSO-d\(_6\)) \(\delta\) 166.3, 164.0, 151.6, 143.9, 133.4, 131.7, 130.9, 127.9, 127.6, 124.2, 123.1, 121.9, 121.7, 118.0, 115.5, 53.3. \(^{19}\)F NMR (282 MHz, DMSO-d\(_6\)): \(\delta\) −110.7. HRMS (ESI) m/z [M + Na]\(^+\) calcd for C\(_{15}\)H\(_{10}\)FNNaO\(_2\) 278.0593, found 278.0590.

\[\text{Methyl 8-methylphenanthridine-6-carboxylate (2k).}\(^1,3\) Yellow solid (72 mg, 88%): \(R_f\) 0.57 in ethyl acetate–hexane (25:75); mp = 79–81 °C (lit.\(^1\) mp 80–81 °C); IR (neat, cm\(^{-1}\)): \(\nu\) 3068, 3054, 3015, 1743, 1723, 1619, 1610, 1566, 1492, 1343, 1232, 1029, 712, 601. \(^1\)H NMR (300 MHz, DMSO-d\(_6\)) \(\delta\) 8.57-8.51 (m, 2H), 8.39-8.36 (m, 1H), 8.28-8.23 (m, 1H), 7.76-7.68 (m, 3H), 4.16 (s, 3H), 2.61 (s, 3H). \(^{13}\)C NMR (75 MHz, DMSO-d\(_6\)) \(\delta\) 166.8, 150.1, 142.4, 138.2, 133.0, 131.5, 131.0, 128.5, 126.6, 125.2, 123.7, 122.0, 121.9, 53.2, 21.7. HRMS (ESI) m/z [M + Na]\(^+\) calcd for C\(_{16}\)H\(_{13}\)NNaO\(_2\) 274.0844, found 274.0839.
Methyl 8-methoxyphenanthridine-6-carboxylate (2l). Yellow solid (79 mg, 90%): $R_f$ 0.52 in ethyl acetate–hexane (25:75); mp = 101–103 °C (lit.3 mp 102–103 °C); IR (neat, cm$^{-1}$): $\nu$ 3055, 3016, 1742, 1724, 1620, 1613, 1563, 1491, 1345, 1233, 1029, 713. $^1$H NMR (300 MHz, DMSO-d$_6$) $\delta$ 8.56 (d, $J$ = 8.8 Hz, 1H), 8.52-8.48 (m, 1H), 8.33-8.22 (m, 1H), 8.17 (d, $J$ = 2.8 Hz, 1H), 7.79-7.67 (m, 2H), 7.54-7.50 (m, 1H), 4.16 (s, 3H), 3.98 (s, 3H). $^{13}$C NMR (75 MHz, DMSO-d$_6$) $\delta$ 166.7, 159.3, 148.6, 141.9, 131.0, 128.8, 128.2, 128.1, 125.4, 125.2, 123.9, 122.5, 121.6, 106.9, 55.6, 53.3. HRMS (ESI) m/z [M + Na]$^+$ calcd for C$_{16}$H$_{13}$NNaO$_3$ 290.0793, found 290.0786.

Methyl 8-(tert-butyl)phenanthridine-6-carboxylate (2m). Light brown liquid (88 mg, 92%): $R_f$ 0.64 in ethyl acetate–hexane (25:75); IR (neat, cm$^{-1}$): $\nu$ 3066, 3055, 3017, 1743, 1721, 1621, 1610, 1567, 1494, 1343, 1231, 1029, 714, 603. $^1$H NMR (300 MHz, DMSO-d$_6$) $\delta$ 8.66-8.64 (m, 1H), 8.59-8.52 (m, 2H), 8.30-8.24 (m, 1H), 7.96-7.94 (m, 1H), 7.77-7.70 (m, 2H), 4.17 (s, 3H), 1.47 (s, 9H). $^{13}$C NMR (75 MHz, DMSO-d$_6$) $\delta$ 166.6, 151.2, 150.2, 142.5, 131.4, 131.0, 129.7, 128.8, 125.0, 123.7, 122.8, 122.0, 121.9, 53.3, 35.2, 31.1. HRMS (ESI) m/z [M + Na]$^+$ calcd for C$_{19}$H$_{19}$NNaO$_2$ 316.1313, found 316.1309.
Methyl 8-(trifluoromethyl)phenanthridine-6-carboxylate (2n).\textsuperscript{1,3} White solid (88 mg, 89%): $R_f$ 0.57 in ethyl acetate–hexane (25:75); mp = 110–112 °C (lit.\textsuperscript{3} mp 110–112 °C); IR (neat, cm$^{-1}$): ν 3061, 3056, 3014, 1742, 1720, 1619, 1612, 1567, 1331, 1232, 1163, 1132, 1081, 710. $^1$H NMR (300 MHz, DMSO-d$_6$) δ 9.08 (s, 1H), 8.77 (d, J = 8.8 Hz, 1H), 8.63-8.58 (m, 1H), 8.36-8.31 (m, 1H), 8.11-8.05 (m, 1H), 7.85-7.81 (m, 2H), 4.18 (s, 3H). $^{13}$C NMR (75 MHz, DMSO-d$_6$) δ 165.8, 149.4, 143.3, 135.6, 131.4, 130.3, 129.8 (q, J = 33.2 Hz), 129.6, 127.0 (q, J = 3.2 Hz), 125.2 (q, J = 4.4 Hz), 124.2, 124.0 (q, J = 271.2 Hz), 123.4, 123.0, 122.4, 53.5. $^{19}$F NMR (282 MHz, DMSO-d$_6$): δ −62.5. HRMS (ESI) m/z [M + Na$^+$] calcd for C$_{16}$H$_{10}$F$_3$NNaO$_2$ 328.0561, found 328.0556.

Methyl 8-fluorophenanthridine-6-carboxylate (2o).\textsuperscript{3} White solid (70 mg, 84%): $R_f$ 0.59 in ethyl acetate–hexane (25:75); mp = 159–162 °C (lit.\textsuperscript{3} mp 159–161 °C); IR (neat, cm$^{-1}$): ν 3069, 3056, 3017, 1745, 1724, 1621, 1612, 1567, 1344, 1232, 714, 607. $^1$H NMR (300 MHz, DMSO-d$_6$) δ 8.65-8.61 (m, 1H), 8.53-8.48 (m, 1H), 8.45-8.41 (m, 1H), 8.34-8.28 (m, 1H), 7.82-7.71 (m, 2H), 7.66-7.59 (m, 1H), 4.16 (s, 3H). $^{13}$C NMR (75 MHz, DMSO-d$_6$) δ 166.2, 161.5 (d, J = 247.8 Hz), 148.6 (d, J = 4.4 Hz), 142.4, 131.3, 130.2 (d, J = 1.8 Hz), 129.4, 129.0, 124.9 (d, J = 9.0 Hz), 124.8 (d, J = 8.8 Hz), 121.8, 120.6 (d, J = 24.2 Hz), 112.3 (d, J = 23.3 Hz), 53.4. $^{19}$F NMR (282 MHz, DMSO-d$_6$): δ −110.5. HRMS (ESI) m/z [M + Na$^+$] calcd for C$_{15}$H$_{10}$FNNaO$_2$ 278.0593, found 278.0591.
Methyl 8-chlorophenanthridine-6-carboxylate (2p).\textsuperscript{1,3} Yellow solid (77 mg, 87\%): \(R_f\) 0.59 in ethyl acetate–hexane (25:75); mp = 140–142 °C (lit.\textsuperscript{3} mp 141–143 °C); IR (neat, cm\(^{-1}\)): \(\nu\) 3061, 3055, 3016, 2931, 1744, 1723, 1613, 1532, 1496, 1464, 1363, 1257, 1173, 773, 739. \(^1\)H NMR (300 MHz, DMSO-d\(_6\)) \(\delta\) 8.74 (d, \(J = 2.4\) Hz, 1H), 8.57 (d, \(J = 8.8\) Hz, 1H), 8.56-8.49 (m, 1H), 8.31-8.26 (m, 1H), 7.86-7.73 (m, 3H), 4.16 (s, 3H). \(^13\)C NMR (75 MHz, DMSO-d\(_6\)) \(\delta\) 166.1, 148.8, 142.5, 134.3, 131.8, 131.2, 129.5, 129.3, 126.6, 124.5, 123.8, 121.9, 53.3. HRMS (ESI) m/z [M + Na]\(^+\) calcd for C\(_{15}\)H\(_{10}\)ClNNaO\(_2\) 294.0298, found 294.0293.

Ethyl 2-methylphenanthridine-6-carboxylate (2q).\textsuperscript{2} White solid (80 mg, 92\%): \(R_f\) 0.58 in ethyl acetate–hexane (25:75); mp = 83–85 °C; IR (neat, cm\(^{-1}\)): \(\nu\) 3072, 3057, 3018, 1744, 1722, 1621, 1614, 1568, 1346, 1232, 714, 609. \(^1\)H NMR (300 MHz, DMSO-d\(_6\)) \(\delta\) 8.65 (d, \(J = 8.6\) Hz, 1H), 8.56 (d, \(J = 8.6\) Hz, 1H), 8.37 (s, 1H), 8.17 (d, \(J = 8.4\) Hz, 1H), 7.88-7.85 (m, 1H), 7.72-7.69 (m, 1H), 7.62-7.59 (m, 1H), 4.65 (q, \(J = 7.4\) Hz, 2H), 2.65 (s, 3H), 1.54 (t, \(J = 8.0\) Hz, 3H). \(^13\)C NMR (75 MHz, DMSO-d\(_6\)) \(\delta\) 166.5, 150.1, 141.0, 138.9, 133.2, 130.9, 130.8, 130.6, 127.8, 127.2, 124.7, 123.6, 122.1, 121.6, 62.4, 22.2, 14.4. HRMS (ESI) m/z [M + Na]\(^+\) calcd for C\(_{17}\)H\(_{15}\)NNaO\(_2\) 288.1000, found 288.996.
Propyl 2-methylphenanthridine-6-carboxylate (2r). Light yellow liquid (84 mg, 93%): $R_f$ 0.57 in ethyl acetate–hexane (25:75); IR (neat, cm$^{-1}$): $\nu$ 3074, 3057, 3021, 1743, 1722, 1622, 1614, 1569, 1234, 715, 608. $^1$H NMR (300 MHz, DMSO-d$_6$) $\delta$ 8.66 (d, $J = 8.6$ Hz, 1H), 8.54 (d, $J = 8.6$ Hz, 1H), 8.39 (s, 1H), 8.17 (d, $J = 8.4$ Hz, 1H), 7.89-7.86 (m, 1H), 7.74-7.71 (m, 1H), 7.64-7.60 (m, 1H), 4.54 (t, $J = 7.0$ Hz, 2H), 2.65 (s, 3H), 1.94-1.89 (m, 2H), 1.09 (t, $J = 7.2$ Hz, 3H). $^{13}$C NMR (75 MHz, DMSO-d$_6$) $\delta$ 166.7, 152.3, 141.2, 138.9, 133.1, 130.9, 130.8, 130.6, 127.8, 127.2, 124.6, 123.5, 122.2, 121.6, 67.8, 22.1, 22.0, 10.6. HRMS (ESI) m/z [M + Na]$^+$ calcd for C$_{18}$H$_{17}$NaO$_2$ 302.1157, found 302.1151.

Phenyl 2-methylphenanthridine-6-carboxylate (2s). White solid (84 mg, 83%): $R_f$ 0.55 in ethyl acetate–hexane (25:75); mp = 59–61 °C; IR (neat, cm$^{-1}$): $\nu$ 3068, 3057, 3019, 1744, 1723, 1621, 1614, 1568, 1346, 1234, 717, 607. $^1$H NMR (300 MHz, DMSO-d$_6$) $\delta$ 8.78 (d, $J = 8.4$ Hz, 1H), 8.72 (d, $J = 8.4$ Hz, 1H), 8.43 (s, 1H), 8.28 (d, $J = 8.4$ Hz, 1H), 7.94-7.90 (m, 1H), 7.78-7.75 (m, 1H), 7.67-7.63 (m, 1H), 7.53-7.49 (m, 2H), 7.44-7.39 (m, 2H), 7.35-7.31 (m, 1H), 2.69 (s, 3H). $^{13}$C NMR (75 MHz, DMSO-d$_6$) $\delta$ 164.7, 150.9, 148.5, 141.2, 139.4, 133.3, 131.0, 130.9, 129.6, 128.0, 127.3, 126.2, 125.0, 123.9, 122.3, 121.9, 121.7, 22.2. HRMS (ESI) m/z [M + Na]$^+$ calcd for C$_{21}$H$_{15}$NaO$_2$ 336.1000, found 336.997.
Methyl 5,6-dihydrophenanthridine-6-carboxylate (1-IV).\textsuperscript{4,5} This compound was synthesized following the literature procedure.\textsuperscript{5} Pale yellow solid: $R_f$ 0.12 in ethyl acetate–hexane (25:75). IR (neat, cm\textsuperscript{-1}): $\nu$ 3354, 3214, 3198, 3021, 1717, 1620, 1609, 1564, 1134, 721. $^1$H NMR (300 MHz, DMSO-d$_6$) $\delta$ 7.67-7.64 (m, 1H), 7.53-7.51 (m, 1H), 7.31-7.27 (m, 2H), 7.08-7.01 (m, 2H), 6.88 (d, J = 2.2 Hz, 1H), 6.77-6.74 (m, 1H), 6.67-6.63 (m, 1H), 5.12 (d, J = 2.2 Hz, 1H), 4.01 (s, 3H). HRMS (ESI) m/z [M + H]$^+$ calcd for C$_{15}$H$_{14}$NO$_2$ 240.1019, found 240.1011.

References


Copies of $^1\text{H}$, $^{13}\text{C}$ and $^{19}\text{F}$-NMR Spectra

**Figure S1.** $^1\text{H}$ (top) and $^{13}\text{C}$ (bottom) NMR spectra of 2a in DMSO-d$_6$. 
Figure S2. $^1$H (top) and $^{13}$C (bottom) NMR spectra of 2b in DMSO-d$_6$. 

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Figure S3. $^1$H (top) and $^{13}$C (bottom) NMR spectra of 2c in DMSO-d$_6$. 
Figure S4. $^1$H (top) and $^{13}$C (bottom) NMR spectra of 2d in DMSO-d$_6$
Figure S5. $^1$H (top) and $^{13}$C NMR (bottom) spectra of 2e in DMSO-d$_6$.
Figure S6. $^1$H (top) and $^{13}$C NMR (bottom) spectra of 2f in DMSO-d$_6$
Figure S7. $^1$H (top) and $^{13}$C NMR (bottom) spectra of 2g in DMSO-$d_6$. 

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Figure S8. $^1$H (top) and $^{13}$C NMR (bottom) spectra of 2h in DMSO-d$_6$. 

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Figure S9. $^1$H (top) and $^{13}$C NMR (bottom) spectra of 2i in DMSO-d$_6$
Figure S10. $^1$H (top) and $^{13}$C NMR (bottom) spectra of 2k in DMSO-d$_6$
Figure S11. $^1$H (top) and $^{13}$C NMR (bottom) spectra of 2I in DMSO-d$_6$
Figure S12. $^1$H (top) and $^{13}$C NMR (bottom) spectra of 2m in DMSO-$d_6$
Figure S13. $^1$H (top) and $^{13}$C NMR (bottom) spectra of 2n in DMSO-d$_6$
Figure S14. $^1$H (top) and $^{13}$C NMR (bottom) spectra of 2o in DMSO-d$_6$.  

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Figure S15. $^1$H (top) and $^{13}$C NMR (bottom) spectra of 2p in DMSO-$d_6$
Figure S16. $^1$H (top) and $^{13}$C NMR (bottom) spectra of 2q in DMSO-d$_6$
**Figure S17.** $^1$H (top) and $^{13}$C NMR (bottom) spectra of 2r in DMSO-d$_6$
Figure S18. $^1$H (top) and $^{13}$C NMR (bottom) spectra of 2s in DMSO-d$_6$
Figure S19. $^{1}$H NMR spectra of 1-IV in DMSO-$d_6$
Figure S20. $^{19}$F NMR spectra of 2h (top) and 2i (bottom) in DMSO-d$_6$. 
Figure S21. $^{19}$F NMR spectra of 2n (top) and 2o (bottom) in DMSO-d$_6$. 

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