Supporting Information for

Cascade Approach to Substituted 6-Aryl-phenanthridines from Aromatic Aldehydes, Anilines and Benzenediazonium-2-carboxylate

*Wang-Ge Shou, Yun-Yun Yang, Yan-Guang Wang **

Department of Chemistry, Zhejiang University, Hangzhou 310027, P. R. China

Fax: +86-571-87951512; E-mail: orgwyg@zju.edu.cn

Table of Contents

General Considerations	SI 2
General Procedure for the Synthesis of Phenanthridines 6~8	SI 2
Characterization Data of Compounds 6~8	SI 3~18
Copies of ^1H and ^{13}C NMR Spectra for Compounds 6~8	SI 19~47
X-ray Crystallography Structure of Compound 6d	SI 48

General Considerations

IR spectra were recorded on a FT-IR spectrometer (KBr) and reported in reciprocal centimeters (cm^{-1}). NMR spectra were recorded for ^1H NMR at 500 MHz, for ^{13}C NMR at 125 MHz. For ^1H NMR, tetramethylsilane (TMS) served as internal standard ($\delta = 0$) and data are reported as follows: chemical shift, integration, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), and coupling constant in Hz. For ^{13}C NMR, CDCl_3 ($\delta = 77.25$ ppm) or $\text{DMSO}-d_6$ ($\delta = 40.00$ ppm) was used as internal standard and spectra were obtained with complete proton decoupling. Low-resolution MS and HRMS data were obtained using ESI ionization.

General procedure for the synthesis of 6-arylphenanthridines 6~8.

To a solution of aromatic aldehyde **2** (1 mmol) and aniline **3** (1 mmol) in DCE (5 ml) was added a suspension of benzenediazonium-2-carboxylate (2 mmol) in DCE (30 ml) at 80°C over a period of 1 h. The color of the reaction mixture changed from light yellow to deep brown. After completion of the reaction as indicated by TLC, the solvent was evaporated in vacuum and residue was purified by silica gel column chromatography using hexane-EtOAc (15:1) as the eluant to afford pure **6**, which could be recrystallized from hexane-EtOAc.

Characterization Data of Compounds 6~8

2-Ethoxy-6-(4-nitrophenyl)phenanthridine (**6a**): a yellow solid, m.p. 176-177 °C; IR (KBr) 1620, 1602, 1595, 1561, 1519, 1497, 1258, 1204 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3): δ 8.62 (d, J = 8.2 Hz, 1 H), 8.39 (d, J = 8.2 Hz, 2 H), 8.12 (d, J = 8.9 Hz, 1 H), 7.96-7.93 (m, 2 H), 7.90 (d, J = 8.2 Hz, 2 H), 7.85 (t, J = 7.5 Hz, 1 H), 7.62 (d, J = 7.5 Hz, 1 H), 7.40 (t, J = 7.2 Hz, 1 H), 4.28 (q, J = 6.8 Hz, 2 H), 1.54 (t, J = 6.8 Hz, 3 H) ppm; ^{13}C NMR (125 MHz, CDCl_3): δ 158.6, 156.1, 148.1, 146.5, 139.1, 133.2, 133.1, 131.1, 130.7, 128.0, 127.8, 125.3, 124.8, 123.8, 122.8, 119.6, 103.9, 64.2, 15.1 ppm; MS: m/z 345 ($[\text{M}+\text{H}]^+$); HRMS: m/z calcd for ($\text{C}_{21}\text{H}_{16}\text{N}_2\text{O}_3+\text{H}$) 345.1234, found 345.1235.

2-Methyl-6-(4-nitrophenyl)phenanthridine (**6b**): a yellow solid, m.p. 168-169 °C; IR (KBr) 1597, 1520, 1347, 1323 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3): δ 8.73 (d, J = 8.3 Hz, 1 H), 8.43-8.41 (m, 3 H), 8.12 (d, J = 8.3 Hz, 1 H), 7.96 (d, J = 8.2 Hz, 1 H), 7.93-7.90 (m, 2 H), 7.87-7.86 (m, 1 H), 7.63-7.61 (m, 2 H), 2.67 (s, 3 H) ppm; ^{13}C NMR (125 MHz, CDCl_3): δ 157.9, 148.2, 146.5, 142.1, 138.0, 133.5, 131.2, 131.1, 131.0, 130.4, 128.6, 127.6, 124.8, 124.0, 123.9, 122.8, 121.9, 22.3 ppm; MS: m/z 315 ($[\text{M}+\text{H}]^+$); HRMS: m/z calcd for ($\text{C}_{20}\text{H}_{14}\text{N}_2\text{O}_2+\text{H}$) 315.1128, found 315.1127.

6-(4-Nitrophenyl)phenanthridine (**6c**): a yellow solid, m.p. 85-86 °C; IR (KBr) 1602, 1517, 1484, 1350, 1328 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3): δ 8.74 (d, J = 8.3 Hz, 1 H), 8.64 (d, J = 8.1 Hz, 1 H), 8.42 (d, J = 8.5 Hz, 2 H), 8.23 (d, J = 8.1 Hz, 1 H), 8.00 (d, J = 8.2 Hz, 1 H), 7.93-7.89 (m, 3 H), 7.80 (t, J = 7.2 Hz, 1 H), 7.74 (t, J = 7.8 Hz, 1 H), 7.65 (t, J = 7.8 Hz, 1 H) ppm; ^{13}C NMR (125 MHz, CDCl_3): δ 158.9, 148.2, 146.3, 143.7, 133.7, 131.2, 131.1, 130.6, 129.4, 128.1, 127.9, 127.8, 124.7, 124.1, 123.9, 122.8, 122.3 ppm; MS: m/z 301 ($[\text{M}+\text{H}]^+$); HRMS: m/z calcd for ($\text{C}_{19}\text{H}_{12}\text{N}_2\text{O}_2+\text{H}$) 301.0972, found 301.0975.

2-Ethoxy-6-phenylphenanthridine (**6d**): a white solid, m.p. 161-162 °C; IR (KBr) 1614, 1566, 1520, 1495, 1476, 1630, 1244 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3): δ 8.58 (d, J = 8.3 Hz, 1 H), 8.15 (d, J = 9.0 Hz, 1 H), 8.10 (d, J = 8.2 Hz, 1 H), 7.92-7.80 (m, 1 H), 7.80-7.77 (m, 1 H), 7.58-7.39 (m, 4 H), 7.72-7.70 (m, 2 H), 7.36-7.35 (m, 1 H), 4.25 (q, J = 6.9 Hz, 2 H), 1.53 (t, J = 6.9 Hz, 3 H) ppm; ^{13}C NMR (125 MHz, CDCl_3): δ 158.9, 158.0, 140.1, 139.3, 133.1, 131.9, 130.3, 130.0, 129.0, 128.7, 128.6, 127.3, 125.5, 125.0, 122.4, 119.1, 103.9, 64.1, 15.1 ppm; MS: m/z 300 ($[\text{M}+\text{H}]^+$); HRMS: m/z calcd for ($\text{C}_{21}\text{H}_{17}\text{NO}+\text{H}$) 300.1383, found 300.1380.

6-(3,4-Dimethylphenyl)-2-ethoxyphenanthridine (**6e**): a white solid, m.p. 133-134 °C; IR (KBr) 1615, 1562, 1494, 1445, 1360, 1320 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3): δ 8.56 (d, J = 8.2 Hz, 1 H), 8.14 (t, J = 9.2 Hz, 2 H), 7.92 (d, J = 2.3 Hz, 1 H), 7.79 (t, J = 7.8 Hz, 1 H), 7.57 (t, J = 7.8 Hz, 1 H), 7.51 (s, 1 H), 7.43 (d, J = 7.4 Hz, 1 H), 7.37-7.35 (m, 1 H), 7.29 (d, J = 7.6 Hz, 1 H), 4.26 (q, J = 6.9 Hz, 2 H), 2.36 (s, 6 H), 1.53 (t, J = 6.9 Hz, 3 H) ppm; ^{13}C NMR (125 MHz, CDCl_3): δ 158.8, 157.5, 138.9, 137.3, 136.8, 136.6, 132.7, 131.5, 130.7, 129.8, 129.3, 128.8, 127.1, 126.9, 125.3, 124.5, 122.0, 118.7, 103.5, 63.7, 19.8, 19.6, 14.8 ppm; MS: m/z 328 ($[\text{M}+\text{H}]^+$); HRMS: m/z calcd for ($\text{C}_{23}\text{H}_{21}\text{NO}+\text{H}$) 328.1696, found 328.1694.

6-(3,4-Dimethylphenyl)-2-methoxyphenanthridine (**6f**): an oil; IR (neat) 1723, 1615, 1562, 1580, 1438, 1413, 1247 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3): δ 8.60 (d, J = 8.3 Hz, 1 H), 8.18-8.14 (m, 2 H), 7.93 (d, J = 2.6 Hz, 1 H), 7.82-7.79 (m, 1 H), 7.59 (t, J = 7.3 Hz, 1 H), 7.53 (s, 1 H), 7.46-7.44 (m, 1 H), 7.40-7.39 (m, 1 H), 7.31 (d, J = 7.6 Hz, 1 H), 4.03 (s, 3 H), 2.39 (s, 6 H) ppm; ^{13}C NMR (125 MHz, CDCl_3): δ 159.2, 158.5, 139.4, 137.6, 137.2, 136.9, 133.1, 131.9, 131.0, 130.2, 129.7, 129.2, 127.5, 127.2, 125.7, 124.9, 122.3, 118.8, 103.0, 55.8, 20.1, 19.9 ppm; MS: m/z 314 ($[\text{M}+\text{H}]^+$); HRMS: m/z calcd for ($\text{C}_{22}\text{H}_{19}\text{NO}+\text{H}$) 314.1539, found 314.1536.

6-(4-Bromophenyl)-2-methylphenanthridine (**6g**): a white solid, m.p. 51-52 °C; IR (KBr) 1611, 1590, 1489, 1390, 1362 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3): δ 8.69 (d, $J = 8.2$ Hz, 1 H), 8.39 (s, 1 H), 8.11 (d, $J = 8.3$ Hz, 1 H), 8.03 (d, $J = 8.2$ Hz, 1 H), 7.84 (t, $J = 7.5$ Hz, 1 H), 7.69 (d, $J = 8.2$ Hz, 2 H), 7.62-7.57 (m, 4 H), 2.65 (s, 3 H) ppm; ^{13}C NMR (125 MHz, CDCl_3): δ 159.3, 142.3, 139.1, 137.3, 133.5, 131.8, 131.7, 130.9, 130.7, 130.3, 128.6, 127.4, 125.3, 123.8, 123.5, 122.5, 121.8, 22.3 ppm; MS: m/z 348 ($[\text{M}+\text{H}]^+$); HRMS: m/z calcd for ($\text{C}_{20}\text{H}_{14}\text{NBr}+\text{H}$) 348.0382, found 348.0385.

6-(4-Chlorophenyl)-2-methylphenanthridine (**6h**): a white solid, m.p. 45-46 °C; IR (KBr) 1603, 1569, 1506, 1494, 1363, 1281 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3): δ 8.65 (d, $J = 8.3$ Hz, 1 H), 8.35 (s, 1 H), 8.10 (d, $J = 8.3$ Hz, 1 H), 8.02 (d, $J = 8.3$ Hz, 1 H), 7.80-7.69 (m, 1 H), 7.67 (d, $J = 8.3$ Hz, 2 H), 7.57-7.55 (m, 2 H), 7.51 (d, $J = 8.3$ Hz, 2 H), 2.63 (s, 3 H) ppm; ^{13}C NMR (125 MHz, CDCl_3): δ 159.2, 142.2, 138.5, 137.3, 134.9, 133.4, 131.4, 130.9, 130.6, 130.2, 128.8, 128.6, 127.3, 125.2, 123.8, 122.5, 121.8, 22.2 ppm; MS: m/z 304 ($[\text{M}+\text{H}]^+$); HRMS: m/z calcd for ($\text{C}_{20}\text{H}_{14}\text{NCl}+\text{H}$) 304.0888, found 304.0881.

6-(4-Fluorophenyl)-2-methylphenanthridine (**6i**): a white solid, m.p. 40-41 °C; IR (KBr) 1610, 1594, 1560, 1490, 1363, 1321 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3): δ 8.67 (d, $J = 8.3$ Hz, 1 H), 8.38 (s, 1 H), 8.11 (d, $J = 8.3$ Hz, 1 H), 8.04 (d, $J = 8.3$ Hz, 1 H), 7.83-7.62 (m, 1 H), 7.73-7.71 (m, 2 H), 7.59-7.56 (m, 2 H), 7.24 (d, $J = 8.6$ Hz, 2 H), 2.64 (s, 3 H) ppm; ^{13}C NMR (125 MHz, CDCl_3): δ 164.0 (d, $J_{\text{C-F}} = 246.3$ Hz), 159.4, 142.2, 137.2, 136.0 (d, $J_{\text{C-F}} = 3.0$ Hz), 133.4, 131.8 (d, $J_{\text{C-F}} = 8.1$ Hz), 130.8, 130.6, 130.2, 128.7, 127.3, 125.4, 123.8, 122.5, 121.8, 115.7 (d, $J_{\text{C-F}} = 21.5$ Hz), 22.3 ppm; MS: m/z 288 ($[\text{M}+\text{H}]^+$); HRMS: m/z calcd for ($\text{C}_{20}\text{H}_{14}\text{NF}+\text{H}$) 288.1183, found 288.1177.

Ethyl 4-(2-ethoxyphenanthridin-6-yl)benzoate (**6j**): a white solid, m.p. 136-137 °C; IR (KBr) 1710, 1609, 1496, 1447, 1363, 1209 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3): δ 8.60 (d, $J = 8.3$ Hz, 1 H), 8.24 (d, $J = 8.2$ Hz, 2 H), 8.15 (d, $J = 9.0$ Hz, 1 H), 8.01 (d, $J = 8.2$ Hz, 1 H), 7.93 (d, $J = 2.5$ Hz, 1 H), 7.82-7.79 (m, 3 H), 7.39-7.36 (m, 1 H), 7.29-7.25 (m, 1 H), 4.45 (q, $J = 7.1$ Hz, 2 H), 4.26 (q, $J = 7.0$ Hz, 2 H), 1.54 (t, $J = 7.0$ Hz, 3 H), 1.44 (t, $J = 7.1$ Hz, 3 H) ppm; ^{13}C NMR (125 MHz, CDCl_3): δ 166.7, 158.3, 157.7, 144.5, 139.2, 133.1, 132.0, 130.6, 130.4, 130.1, 129.9, 128.5, 127.5, 125.2, 125.1, 122.6, 119.3, 103.9, 64.2, 61.3, 15.1, 14.6 ppm; MS: m/z 372 ($[\text{M}+\text{H}]^+$); HRMS: m/z calcd for ($\text{C}_{24}\text{H}_{21}\text{NO}_3+\text{H}$) 372.1594, found 372.1597.

Ethyl 4-(2-methoxyphenanthridin-6-yl)benzoate (**6k**): a white solid, m.p. 174-175 °C; IR (KBr) 1719, 1609, 1497, 1281 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3): δ 8.61 (d, $J = 8.3$ Hz, 1 H), 8.24 (d, $J = 8.2$ Hz, 2 H), 8.15 (d, $J = 9.0$ Hz, 1 H), 8.01 (d, $J = 8.2$ Hz, 1 H), 7.93 (d, $J = 2.4$ Hz, 1 H), 7.83-7.80 (m, 3 H), 7.58 (t, $J = 7.5$ Hz, 1 H), 7.39-7.37 (m, 1 H), 4.45 (q, $J = 7.1$ Hz, 2 H), 4.03 (s, 3 H), 1.44 (t, $J = 7.1$ Hz, 3 H), ppm; ^{13}C NMR (125 MHz, CDCl_3): δ 166.5, 158.8, 157.7, 144.4, 139.1, 133.0, 131.9, 130.5, 130.4, 130.0, 129.8, 128.4, 127.4, 125.1, 125.0, 122.4, 119.0, 103.0, 61.2, 55.8, 14.5 ppm; MS: m/z 358 ($[\text{M}+\text{H}]^+$); HRMS: m/z calcd for ($\text{C}_{23}\text{H}_{19}\text{NO}_3+\text{H}$) 358.1438, found 358.1439.

6-(4-Fluorophenyl)-2-methoxyphenanthridine (**6l**): a white solid, m.p. 123-124 °C; IR (KBr) 1719, 1609, 1497, 1281 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3): δ 8.59 (d, $J = 8.6$ Hz, 1 H), 8.13 (d, $J = 8.9$ Hz, 1 H), 8.03 (d, $J = 8.2$ Hz, 1 H), 7.91 (d, $J = 2.7$ Hz, 1 H), 7.82-7.71 (m, 1 H), 7.71-7.69 (m, 2 H), 7.61-7.58 (m, 1 H), 7.38-7.25 (m, 1 H), 7.25-7.21 (m, 2 H), 4.01 (s, 3 H) ppm; ^{13}C NMR (125 MHz, CDCl_3): δ 164.3 (d, $J_{\text{C-F}} = 246.1$ Hz), 158.7, 157.8, 139.3, 136.2 (d, $J_{\text{C-F}} = 3.3$ Hz), 133.2, 131.9 (d, $J_{\text{C-F}} = 7.9$ Hz), 131.8, 130.4, 128.7, 127.5, 125.4, 125.0, 122.5, 119.0, 115.7 (d, $J_{\text{C-F}} = 21.2$ Hz), 103.1 55.9 ppm; MS: m/z 304 ($[\text{M}+\text{H}]^+$); HRMS: m/z calcd for ($\text{C}_{20}\text{H}_{14}\text{NFO}+\text{H}$) 304.1132, found 304.1130.

6-(4-Chlorophenyl)-2-methoxyphenanthridine (**6m**): a white solid, m.p. 91-92 °C; IR (KBr) 1719, 1609, 1497, 1281 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3): δ 8.59 (d, J = 8.3 Hz, 1 H), 8.13 (d, J = 8.9 Hz, 1 H), 8.03 (d, J = 8.2 Hz, 1 H), 7.90 (d, J = 2.3 Hz, 1 H), 7.80 (t, J = 7.4 Hz, 1 H), 7.66 (d, J = 8.2 Hz, 2 H), 7.60 (t, J = 7.5 Hz, 1 H), 7.52 (d, J = 8.2 Hz, 2 H), 7.38-7.36 (m, 1 H), 4.01 (s, 3 H) ppm; ^{13}C NMR (125 MHz, CDCl_3): δ 158.8, 157.6, 139.2, 138.5, 134.9, 133.1, 132.0, 131.4, 130.4, 128.8, 128.6, 127.5, 125.3, 125.0, 122.5, 119.0, 103.1, 55.9 ppm; MS: m/z 320 ($[\text{M}+\text{H}]^+$); HRMS: m/z calcd for ($\text{C}_{20}\text{H}_{14}\text{NClO}+\text{H}$) 320.0837, found 320.0838.

2-Ethoxy-6-(4-fluorophenyl)phenanthridine (**6n**): a white solid, m.p. 134-135 °C; IR (KBr) 1611, 1505, 1497, 1477, 1357, 1245 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3): δ 8.58 (d, J = 8.3 Hz, 1 H), 8.13 (d, J = 8.9 Hz, 1 H), 8.03 (d, J = 8.2 Hz, 1 H), 7.91 (d, J = 2.5 Hz, 1 H), 7.80 (t, J = 7.3 Hz, 1 H), 7.71-7.68 (m, 2 H), 7.58 (t, J = 7.5 Hz, 1 H), 7.37-7.35 (m, 1 H), 7.23 (t, J = 8.5 Hz, 2 H), 4.25 (q, J = 6.9 Hz, 2 H), 1.52 (t, J = 6.9 Hz, 3 H) ppm; ^{13}C NMR (125 MHz, CDCl_3): δ 164.2 (d, $J_{\text{C-F}}$ = 246.3 Hz), 158.1, 157.7, 139.1, 136.2 (d, $J_{\text{C-F}}$ = 3.1 Hz), 133.1, 131.9 (d, $J_{\text{C-F}}$ = 8.4 Hz), 131.8, 130.3, 128.7, 127.4, 125.4, 125.0, 122.5, 119.3, 115.1 (d, $J_{\text{C-F}}$ = 21.6 Hz), 103.9, 64.2, 15.1 ppm; MS: m/z 318 ($[\text{M}+\text{H}]^+$); HRMS: m/z calcd for ($\text{C}_{21}\text{H}_{16}\text{NFO}+\text{H}$) 318.1289, found 318.1277.

6-(4-Chlorophenyl)-2-ethoxyphenanthridine (**6o**): a white solid, m.p. 174-175 °C; IR (KBr) 1619, 1559, 1489, 1392, 1255 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3): δ 8.59 (d, $J = 8.3$ Hz, 1 H), 8.14 (d, $J = 8.9$ Hz, 1 H), 8.03 (d, $J = 8.2$ Hz, 1 H), 7.92 (d, $J = 2.4$ Hz, 1 H), 7.83-7.80 (m, 1 H), 7.67 (d, $J = 8.3$ Hz, 2 H), 7.60 (t, $J = 7.4$ Hz, 1 H), 7.51 (d, $J = 8.3$ Hz, 2 H), 7.38-7.36 (m, 1 H), 4.27 (q, $J = 6.9$ Hz, 2 H), 1.53 (t, $J = 6.9$ Hz, 3 H) ppm; ^{13}C NMR (125 MHz, CDCl_3): δ 158.2, 157.6, 139.2, 138.6, 134.9, 133.2, 131.9, 131.4, 130.4, 128.9, 128.6, 127.5, 125.3, 125.1, 122.6, 119.3, 103.9, 64.2, 15.1 ppm; MS: m/z 334 ($[\text{M}+\text{H}]^+$); HRMS: m/z calcd for ($\text{C}_{21}\text{H}_{16}\text{NClO}+\text{H}$) 334.0993, found 334.0990.

6-(4-Bromophenyl)-2-methoxyphenanthridine (**6p**): a white solid, m.p. 90-91 °C; IR (KBr) 1619, 1559, 1489, 1392, 1255 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3): δ 8.59 (d, $J = 8.2$ Hz, 1 H), 8.13 (d, $J = 8.9$ Hz, 1 H), 8.02 (d, $J = 8.2$ Hz, 1 H), 7.90 (d, $J = 1.9$ Hz, 1 H), 7.80 (t, $J = 7.4$ Hz, 1 H), 7.68 (d, $J = 8.1$ Hz, 2 H), 7.60-7.57 (m, 3 H), 7.38-7.36 (m, 1 H), 4.01 (s, 3 H) ppm; ^{13}C NMR (125 MHz, CDCl_3): δ 158.8, 157.6, 139.2, 139.0, 133.1, 132.0, 131.8, 131.6, 130.4, 128.6, 127.5, 125.2, 125.0, 123.1, 122.5, 119.0, 103.1, 55.9 ppm; MS: m/z 366 ($[\text{M}+\text{H}]^+$); HRMS: m/z calcd for ($\text{C}_{20}\text{H}_{14}\text{NBrO}-1$) 364.0332, found 364.0328.

6-(4-Bromophenyl)-2-ethoxyphenanthridine (**6q**): a white solid, m.p. 182-183 °C; IR (KBr) 1620, 1558, 1496, 1390, 1256, 1202 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3): δ 8.58 (d, J = 8.3 Hz, 1 H), 8.12 (d, J = 8.9 Hz, 1 H), 8.01 (d, J = 8.2 Hz, 1 H), 7.91 (d, J = 2.1 Hz, 1 H), 7.82-7.79 (m, 1 H), 7.68 (d, J = 8.0 Hz, 2 H), 7.60-7.57 (m, 3 H), 7.38-7.36 (m, 1 H), 4.26 (q, J = 6.9 Hz, 2 H), 1.53 (t, J = 6.9 Hz, 3 H) ppm; ^{13}C NMR (125 MHz, CDCl_3): δ 158.2, 157.5, 139.2, 139.0, 133.2, 131.9, 131.8, 131.7, 130.4, 128.6, 127.5, 125.2, 125.1, 123.1, 122.5, 119.3, 103.9, 64.2, 15.1 ppm; MS: m/z 382 ($[\text{M}+\text{H}]^+$); HRMS: m/z calcd for ($\text{C}_{21}\text{H}_{16}\text{NBrO-H}$) 380.0488, found 380.0487.

2-Methoxy-6-phenylphenanthridine (**6r**): a white solid, m.p. 178-179 °C; IR (KBr) 1615, 1495, 1461, 1439, 1362, 1291 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3): δ 8.60 (d, J = 8.4 Hz, 1 H), 8.16 (d, J = 8.9 Hz, 1 H), 8.08 (d, J = 8.2 Hz, 1 H), 7.93 (d, J = 2.5 Hz, 1 H), 7.82 (t, J = 7.6 Hz, 1 H), 7.72 (d, J = 7.0 Hz, 2 H), 7.60 (d, J = 7.7 Hz, 1 H), 7.53 (t, J = 6.9 Hz, 2 H), 7.51 (d, J = 7.1 Hz, 1 H), 7.39-7.37 (m, 1 H), 4.03 (s, 3 H) ppm; ^{13}C NMR (125 MHz, CDCl_3): δ 159.0, 158.7, 140.1, 139.4, 133.1, 132.0, 130.3, 130.0, 129.0, 128.7, 128.6, 127.4, 125.6, 125.0, 122.4, 118.9, 103.1, 55.9 ppm; MS: m/z 286 ($[\text{M}+\text{H}]^+$); HRMS: m/z calcd for ($\text{C}_{20}\text{H}_{15}\text{NO}+\text{H}$) 286.1226, found 286.1217.

2-Methoxy-6-(4-nitrophenyl)phenanthridine (**6s**): a yellow solid, m.p. 144-145 °C; IR (KBr) 1615, 1595, 1513, 1495, 1438, 1345 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3): δ 8.64 (d, J = 8.3 Hz, 1 H), 8.38 (d, J = 8.3 Hz, 2 H), 8.12 (d, J = 9.0 Hz, 1 H), 7.97-7.84 (m, 5 H), 7.63 (t, J = 7.5 Hz, 1 H), 7.41-7.39 (m, 1 H), 4.04 (s, 3 H) ppm; ^{13}C NMR (125 MHz, CDCl_3): δ 159.3, 156.3, 148.1, 146.6, 139.2, 133.2, 132.2, 131.2, 130.8, 128.0, 127.9, 125.3, 124.9, 123.9, 122.8, 119.4, 103.1, 56.0 ppm; MS: m/z 331 ($[\text{M}+\text{H}]^+$); HRMS: m/z calcd for ($\text{C}_{20}\text{H}_{14}\text{N}_2\text{O}_3+\text{H}$) 331.1077, found 331.1082.

2-methoxy-6-(naphthalen-2-yl)phenanthridine (**6t**): a yellow solid, m.p. 184-185 °C; IR (KBr) 1620, 1590, 1523, 1495, 1438, 1347 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3): δ 8.62 (d, J = 8.3 Hz, 1 H), 8.20 (s, 1 H), 8.18 (d, J = 8.2 Hz, 1 H), 8.13 (d, J = 8.2 Hz, 1 H), 8.01 (d, J = 8.3 Hz, 1 H), 7.95-7.92 (m, 3 H), 7.85-7.80 (m, 2 H), 7.59-7.52 (m, 3 H), 7.40-7.38 (m, 1 H), 4.02 (s, 3 H) ppm; ^{13}C NMR (125 MHz, CDCl_3): δ 158.9, 158.8, 139.5, 137.5, 133.6, 133.5, 133.2, 132.0, 130.4, 129.5, 129.1, 128.7, 128.3, 128.0, 127.8, 127.5, 126.7, 126.6, 125.7, 125.1, 122.5, 119.0, 103.2, 55.9 ppm; MS: m/z 336 ($[\text{M}+\text{H}]^+$); Anal. Calcd. for $\text{C}_{24}\text{H}_{17}\text{NO}$: C, 85.94, H, 5.11, N, 4.18. Found: C, 85.93, H, 5.11, N, 4.17.

2-Ethoxy-6-(naphthalen-2-yl)phenanthridine (**6u**): a light yellow solid, m.p. 138-139 °C; IR (KBr) 1623, 1593, 1533, 1495, 1438, 1332 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3): δ 8.60 (d, J = 8.3 Hz, 1 H), 8.19 (s, 1 H), 8.17 (d, J = 8.2 Hz, 1 H), 8.12 (d, J = 8.2 Hz, 1 H), 8.01 (d, J = 8.3 Hz, 1 H), 7.94-7.91 (m, 3 H), 7.85-7.83 (m, 1 H), 7.91 (t, J = 7.5 Hz, 1 H), 7.57-7.51 (m, 3 H), 7.39-7.37 (m, 1 H), 4.26 (q, J = 6.9 Hz, 2 H), 1.54 (t, J = 6.9 Hz, 3 H) ppm; ^{13}C NMR (125 MHz, CDCl_3): δ 158.8, 158.2, 139.3, 137.6, 133.5, 133.48, 133.2, 131.9, 130.3, 129.5, 129.1, 128.7, 128.2, 128.0, 127.8, 127.4, 126.7, 126.6, 125.7, 125.1, 122.5, 119.2, 104.0, 64.2, 15.1 ppm; MS: m/z 350 ($[\text{M}+\text{H}]^+$); Anal. Calcd. for $\text{C}_{25}\text{H}_{19}\text{NO}$: C, 85.93, H, 5.48, N, 4.01. Found: C, 85.93, H, 5.44, N, 3.99.

2-(2-Methoxyphenanthridin-6-yl)phenol (**6v**): a light yellow solid, m.p. 160-161 °C; IR (KBr) 3614, 1627, 1590, 1533, 1485, 1438, 1225 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3): δ 11.8 (br, 1H), 8.52 (d, J = 8.2 Hz, 1 H), 8.42 (d, J = 8.2 Hz, 1 H), 7.93 (d, J = 8.9 Hz, 1 H), 7.81-7.78 (m, 2 H), 7.69 (d, J = 7.5 Hz, 1 H), 7.61 (t, J = 7.6 Hz, 1 H), 7.37 (t, J = 7.5 Hz, 1 H), 7.30 (m, 1 H), 7.18 (d, J = 8.1 Hz, 1 H), 7.00 (t, J = 7.3 Hz, 1 H), 3.98 (s, 3 H) ppm; ^{13}C NMR (125 MHz, CDCl_3): δ

159.0, 158.0, 156.8, 136.9, 134.0, 131.8, 131.0, 130.8, 130.5, 129.2, 127.5, 124.9, 124.8, 122.7, 121.8, 119.3, 119.0, 118.3, 103.2, 55.9 ppm; MS: m/z 302 ($[M+H]^+$); Anal. Calcd. for $C_{20}H_{15}NO_2$: C, 79.72, H, 5.02, N, 4.65. Found: C, 79.70, H, 5.05, N, 4.66.

2-(2-Ethoxyphenanthridin-6-yl)phenol (**6w**): a yellow solid, m.p. 198-199 °C; IR (KBr) 3612, 1624, 1595, 1543, 1485, 1235 cm^{-1} ; 1H NMR (500 MHz, $CDCl_3$): δ 11.8 (br, 1H), 8.53 (d, J = 8.2 Hz, 1 H), 8.44 (d, J = 8.2 Hz, 1 H), 7.96 (d, J = 8.9 Hz, 1 H), 7.84-7.70 (m, 2 H), 7.69 (d, J = 7.5 Hz, 1 H), 7.62 (t, J = 7.6 Hz, 1 H), 7.35 (t, J = 7.6 Hz, 1 H), 7.33 (m, 1 H), 7.18 (d, J = 8.1 Hz, 1 H), 7.02 (t, J = 7.3 Hz, 1 H), 4.24 (q, J = 7.0 Hz, 2 H), 1.52 (t, J = 7.0 Hz, 3 H), ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ 158.4, 158.0, 156.7, 136.8, 134.1, 131.8, 131.0, 130.8, 130.5, 129.2, 127.5, 125.0, 124.8, 122.7, 121.8, 119.6, 119.0, 118.3, 104.0, 64.2, 15.1 ppm; MS: m/z 316 ($[M+H]^+$); Anal. Calcd. for $C_{21}H_{17}NO_2$: C, 79.98, H, 5.43, N, 4.44. Found: C, 79.99, H, 5.44, N, 4.43.

4-Bromo-2-(2-methoxyphenanthridin-6-yl)phenol (**6x**): a light yellow solid, m.p. 178-179 °C; IR (KBr) 3613, 1625, 1596, 1540, 1485, 1230 cm^{-1} ; 1H NMR (500 MHz, $CDCl_3$): δ 11.8 (br, 1H),

8.61 (d, $J = 8.3$ Hz, 1 H), 8.44 (d, $J = 8.2$ Hz, 1 H), 7.99 (d, $J = 8.9$ Hz, 1 H), 7.89-7.83 (m, 3 H), 7.72 (d, $J = 7.7$ Hz, 1 H), 7.47-7.45 (m, 1 H), 7.37-7.35 (t, $J = 7.6$ Hz, 1 H), 7.08 (t, $J = 8.8$ Hz, 1 H), 4.04 (s, 3 H), ppm; ^{13}C NMR (125 MHz, CDCl_3): δ 159.4, 157.1, 155.3, 136.7, 134.1, 133.9, 133.7, 131.2, 130.5, 128.7, 128.0, 125.2, 124.5, 123.4, 122.9, 120.3, 119.6, 110.9, 103.2, 56.0 ppm; MS: m/z 381 ($[\text{M}+\text{H}]^+$); Anal. Calcd. for $\text{C}_{20}\text{H}_{14}\text{BrNO}_2$: C, 63.18, H, 3.71, N, 3.68. Found: C, 63.17, H, 3.70, N, 3.67.

4-Bromo-2-(2-ethoxyphenanthridin-6-yl)phenol (**6y**): a light yellow solid, m.p. 156-157 °C; IR (KBr) 3610, 1620, 1596, 1547, 1485, 1225 cm^{-1} ; ^1H NMR (500 MHz, DMSO): δ 9.93 (s, 1 H), 8.91 (d, $J = 8.3$ Hz, 1 H), 8.20 (d, $J = 1.7$ Hz, 1 H), 8.02 (d, $J = 8.9$ Hz, 1 H), 7.89 (t, $J = 7.1$ Hz, 1 H), 7.74-7.68 (m, 2 H), 7.55-7.52 (m, 1 H), 7.49-7.41 (m, 2 H), 7.02 (d, $J = 8.7$ Hz, 1 H), 4.34 (q, $J = 6.9$ Hz, 2 H), 1.46 (t, $J = 6.9$ Hz, 3 H) ppm; ^{13}C NMR (125 MHz, DMSO): δ 158.4, 156.1, 155.3, 139.2, 133.7, 133.0, 132.5, 131.8, 131.1, 129.9, 129.0, 128.3, 125.8, 125.6, 123.6, 119.9, 118.6, 110.8, 104.8, 64.5, 15.4 ppm; MS: m/z 395 ($[\text{M}+\text{H}]^+$); Anal. Calcd. for $\text{C}_{21}\text{H}_{16}\text{BrNO}_2$: C, 63.97, H, 4.09, N, 3.55. Found: C, 63.97, H, 4.08, N, 3.54.

4-Bromo-2-(2-methylphenanthridin-6-yl)phenol (**6z**): a light yellow solid, m.p. 135-136 °C; IR (KBr) 3611, 1622, 1592, 1534, 1485, 1438, 1227 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3): δ 11.8 (br, 1H), 8.68 (d, $J = 8.2$ Hz, 1 H), 8.43 (d, $J = 8.2$ Hz, 1 H), 8.34 (s, 1 H), 7.95 (d, $J = 8.2$ Hz, 1 H), 7.90-7.85 (m, 2 H), 7.70 (d, $J = 7.6$ Hz, 1 H), 7.56-7.52 (m, 1 H), 7.48-7.46 (m, 1 H), 7.09 (d, $J = 8.7$ Hz, 1 H), 2.64 (s, 3 H) ppm; ^{13}C NMR (125 MHz, CDCl_3): δ 157.3, 157.0, 139.7, 138.1, 134.4, 134.0, 133.8, 131.4, 131.3, 128.8, 128.7, 127.8, 124.4, 123.8, 123.3, 122.9, 122.0, 120.3, 110.8, 22.3 ppm; MS: m/z 365 ($[\text{M}+\text{H}]^+$); Anal. Calcd. for $\text{C}_{20}\text{H}_{14}\text{BrNO}$: C, 65.95, H, 3.87, N, 3.85. Found: C, 65.94, H, 3.88, N, 3.84.

2-(2,3-Dimethylphenanthridin-6-yl)phenol (**7a**): a yellow solid, m.p. 121-122 °C; IR (KBr) 3611, 1625, 1590, 1534, 1485, 1230 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3): δ 11.8 (br, 1H), 8.55 (d, $J = 8.2$ Hz, 1 H), 8.41 (d, $J = 8.2$ Hz, 1 H), 8.21 (s, 1 H), 7.78 (t, $J = 7.4$ Hz, 1 H), 7.75 (s, 1 H), 7.70 (d, $J = 7.5$ Hz, 1 H), 7.57 (t, $J = 7.6$ Hz, 1 H), 7.37 (t, $J = 7.6$ Hz, 1 H), 7.18 (d, $J = 8.1$ Hz, 1 H), 7.00 (t, $J = 7.4$ Hz, 1 H), 2.49 (s, 3 H), 2.43 (s, 3 H) ppm; ^{13}C NMR (125 MHz, CDCl_3): δ 158.4, 158.2, 140.3, 139.1, 137.1, 134.3, 131.9, 131.1, 131.0, 129.2, 128.8, 126.8, 124.3, 122.4, 122.2, 121.8,

118.9, 118.4, 20.7, 20.3 ppm; MS: m/z 300 ($[M+H]^+$); Anal. Calcd. for $C_{21}H_{17}NO$: C, 84.25, H, 5.72, N, 4.68. Found: C, 84.27, H, 5.73, N, 4.68.

4-Bromo-2-(2,3-dimethylphenanthridin-6-yl)phenol (**7b**): a yellow solid, m.p. 141-142 °C; IR (KBr) 3610, 1620, 1590, 1545, 1485, 1225 cm^{-1} ; 1H NMR (500 MHz, DMSO): δ 9.95 (s, 1H), 8.83 (d, J = 8.2 Hz, 1 H), 8.59 (s, 1 H), 7.88 (m, 2 H), 7.74 (d, J = 8.1 Hz, 1 H), 7.64 (t, J = 7.3 Hz, 1 H), 7.54 (d, J = 8.4 Hz, 1 H), 7.48 (s, 1 H), 7.01 (d, J = 8.6 Hz, 1 H), 2.53 (s, 3 H), 2.47 (s, 3 H) ppm; ^{13}C NMR (125 MHz, DMSO): δ 157.5, 155.0, 142.7, 138.6, 137.0, 133.4, 132.8, 132.4, 131.1, 129.9, 129.7, 128.8, 127.4, 125.2, 122.9, 122.6, 122.0, 118.4, 110.5, 20.3, 20.1 ppm; MS: m/z 379 ($[M+H]^+$); Anal. Calcd. for $C_{21}H_{16}BrNO$: C, 66.68, H, 4.26, N, 3.70. Found: C, 66.69, H, 4.25, N, 3.72.

4-Bromo-2-(1,2-dimethylphenanthridin-6-yl)phenol (**8b**): a light yellow solid, m.p. 137-138 °C; IR (KBr) 3610, 1621, 1590, 1545, 1485, 1226 cm^{-1} ; 1H NMR (500 MHz, $CDCl_3$): δ 12.4 (br, 1H), 8.65 (d, J = 8.2 Hz, 1 H), 8.38 (d, J = 8.2 Hz, 1 H), 7.78-7.74 (m, 3 H), 7.64 (t, J = 7.3 Hz, 1 H), 7.49-7.43 (m, 2 H), 7.07 (d, J = 8.7 Hz, 1 H), 2.88 (s, 3 H), 2.53 (s, 3 H) ppm; ^{13}C NMR (125

MHz, CDCl₃): δ 157.9, 156.8, 140.4, 137.9, 135.1, 134.0, 133.8, 132.6, 131.4, 130.0, 128.4, 127.7, 127.2, 126.1, 125.3, 124.3, 122.4, 120.3, 110.6, 21.7, 21.3 ppm; MS: m/z 379 ($[M+H]^+$); Anal. Calcd. for C₂₁H₁₆BrNO: C, 66.68, H, 4.26, N, 3.70. Found: C, 66.67, H, 4.26, N, 3.75.

Copies of ^1H and ^{13}C NMR Spectra for Compounds 6~8

Compound 6a:

Compound **6b**:

Compound **6c**:

Zhejiang University Avance DMX 500
QNP 5mm Sample: swg-I-23 in CDCL3

Zhejiang University Avance DMX 500
 QNP 5mm Sample: swg-I-23 in CDCL3

Zhejiang University Avance DMX 500
 GNP 5mm Sample: swg-I-17 in CDCl3

Zhejiang University Avance DMX 500
QNP 5mm Sample: swg-I-21 in CDCl₃

Compound **6g**:

Compound **6h**:

Zhejiang University Avance DMX 500
QNP 5mm Sample: swg-I-22 in CDCl₃

Zhejiang University Avance DMX 500
QNP 5mm Sample: swg-I-22 in CDCl₃

Compound **6i**:

Compound **6j**:

Compound **6l**:

Compound **6m**:

Compound **6n**:

Compound **60**:

Compound **6p**:

Compound **6q**:

Compound **6r**:

Compound **6s**:

Zhejiang University Avance DMX 500
QNP 5mm Sample: swg-Na-1 in CDCl₃

Compound **6u**:

Zhejiang University Avance DMX 500
QNP 5mm Sample: swg-Na-2 in CDCL3

Zhejiang University Avance DMX 500
QNP 5mm Sample: swg-Na-2 in CDCL3

Compound **6v**:

Compound **6w**:

Zhejiang University Avance DMX 500
QNP 5mm Sample: swg-Na-4 in CDCL₃

Zhejiang University Avance DMX 500
QNP 5mm Sample: swg-Na-4 in CDCL₃

Zhejiang University Avance DMX 500
QNP 5mm Sample: swg-Na-5 in CDCl₃

Compound **6y**:

Compound **6z**:

Compound **7a**:

Compound **7b**:

Compound **8b**:

X-ray Crystallography Structure of Compound 6d