**Supporting Information for**

Mn(III)-mediated Reactions of 2-Isocyanobiaryl with 1, 3-Dicarbonyl Compounds: Efficient Synthesis of 6-Alkylated and 6-Monofluoro-alkylated Phenanthridines

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Electronic Supplementary Material (ESI) for *Chemical Communication*
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Experimental Section

General
Melting points were recorded on an Electrothermal digital melting point apparatus and were uncorrected. IR spectra were recorded on a Varian FT-1000 spectrophotometer. $^1$H NMR, $^{13}$C NMR and $^{19}$F NMR spectra were recorded on a Varian INOVA 400 MHz ($^1$H NMR), 101 ($^{13}$C NMR) and 376 ($^{19}$F NMR) spectrometer using CDCl$_3$ as solvent and TMS as internal standard. High resolution mass spectra were obtained using GCT-TOF instrument with CI source.

Table 1. Screening of reaction conditions$^a$

<table>
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<tr>
<th>Entry</th>
<th>Oxidant (equiv.)</th>
<th>Solvent</th>
<th>Temp. ($^\circ$C)</th>
<th>Time (h)</th>
<th>Yield (%)</th>
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<tr>
<td>1</td>
<td>Mn(OAc)$_3$.2H$_2$O (3)</td>
<td>MeCN</td>
<td>110</td>
<td>4</td>
<td>92 (68$^c$)</td>
</tr>
<tr>
<td>2</td>
<td>Mn(OAc)$_3$.2H$_2$O (1.5)</td>
<td>MeCN</td>
<td>110</td>
<td>4</td>
<td>21</td>
</tr>
<tr>
<td>3$^d$</td>
<td>Mn(OAc)$_3$.2H$_2$O (3)</td>
<td>MeCN</td>
<td>110</td>
<td>4</td>
<td>32</td>
</tr>
<tr>
<td>4$^e$</td>
<td>Mn(OAc)$_3$.2H$_2$O (3)</td>
<td>MeCN</td>
<td>110</td>
<td>4</td>
<td>62</td>
</tr>
<tr>
<td>5$^f$</td>
<td>Mn(OAc)$_3$.2H$_2$O (3)</td>
<td>MeCN</td>
<td>110</td>
<td>4</td>
<td>68</td>
</tr>
<tr>
<td>6</td>
<td>Mn(OAc)$_3$.2H$_2$O (3)</td>
<td>MeCN</td>
<td>110</td>
<td>3</td>
<td>44</td>
</tr>
<tr>
<td>7</td>
<td>Mn(OAc)$_3$.2H$_2$O (3)</td>
<td>MeCN</td>
<td>110</td>
<td>2</td>
<td>32</td>
</tr>
<tr>
<td>8$^g$</td>
<td>Mn(OAc)$_3$.2H$_2$O (3)</td>
<td>MeCN</td>
<td>110</td>
<td>4</td>
<td>19</td>
</tr>
<tr>
<td>9$^h$</td>
<td>Mn(OAc)$_3$.2H$_2$O (3)</td>
<td>MeCN</td>
<td>110</td>
<td>4</td>
<td>32</td>
</tr>
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$^a$Reaction conditions: 1a (0.5 mmol), 2a (10 equiv.) in 2 mL solvent. $^b$Yields were determined by LC with an internal standard (biphenyl) as the ratio between the formed products and the initial amount of limiting reactant. $^c$Isolated yields. $^d$2a (1 equiv.). $^e$2a (2 equiv.). $^f$2a (5 equiv.). $^g$Under argon. $^h$Under O$_2$.

Typical procedure for products 3:

A mixture of isocyanide 1 (1 equiv.), acetylacetone 2a (10 equiv.), Mn(OAc)$_3$.2H$_2$O (3 equiv) and 2mL MeCN were added into a flask. Then the mixture was vigorously stirred under at 110 $^\circ$C for 4 h (monitored by TLC). After removing the solvents in vacuo, the residue was directly purified by flash column chromatography by using ethyl acetate and petroleum ether as eluents to afford pure product 3.

Scheme 1 The reaction of 1m with 2a.

When 2-isocyano-3',4'-dimethoxy-1,1'-biphenyl (1m) was subjected to the reaction, the desired products 3m
and 3m’ can be detected by LC-MS analysis. Unfortunately, it’s difficult to purify them.

**Typical procedure for products 4:**

A mixture of isocyanide 1a (1 equiv.), 1, 3-dicarbonyl derivatives 2 (10 equiv.), Mn(OAc)$_2$.2H$_2$O (3 equiv) and 2mL MeCN were added into a flask. Then the mixture was vigorously stirred under at 110 °C for 4 h (monitored by TLC). After removing the solvents in vacuo, the residue was directly purified by flash column chromatography by using ethyl acetate and petroleum ether as eluents to afford pure product 4.

**Typical procedure for products 5:**

A mixture of isocyanide 1 (1 equiv.), 2-fluoro-3-oxobutanoate 2f (10 equiv.), Mn(OAc)$_2$.2H$_2$O (3 equiv) and 2mL MeCN were added into a flask. Then the mixture was vigorously stirred under at 110 °C for 4 h (monitored by TLC). After removing the solvents in vacuo, the residue was directly purified by flash column chromatography by using ethyl acetate and petroleum ether as eluents to afford pure product 5/5b’.

**Typical procedure for products 6:**

To a methanol (1mL) solution of 5a and 5a’ (0.1 mmol) was added 1 M K$_2$CO$_3$ (1mL) at room temperature. After the reaction was complete (monitored by TLC), the pH value was adjusted to 2-4. Then the mixture was poured into a separatory funnel containing 10 mL H$_2$O and 10 mL EtOAc. The layers were separated and the aqueous layer was extracted with EtOAc (2 × 0 mL). The combined organic layers were dried with Na$_2$SO$_4$ and concentrated under reduced pressure after filtration. The crude product was purified by flash chromatography on silica gel to afford the desired product phenanthridine 6.
Preparation of isonitriles:

All isonitriles were prepared according to a reported method.[1]

References
Compound characterizations:

(Z)-1-(phenanthridin-6(5H)-ylidene)propan-2-one (3a)
Yield=68%. Yellow solid. M.p. 138-140 °C. IR (neat) 3058, 3031, 2909, 1620, 1603, 1552, 1356, 1203, 748, 730 cm⁻¹. ¹H NMR (400 MHz, CDCl₃) δ = 15.18 (s, 1H), 8.30 (d, J = 8.2 Hz, 1H), 8.16 (d, J = 8.1 Hz, 1H), 8.09 (d, J = 8.2 Hz, 1H), 7.72 (t, J = 7.7 Hz, 1H), 7.53 (dd, J = 8.2, 7.2 Hz, 1H), 7.46 (dd, J = 8.0, 7.3 Hz, 1H), 7.34 (d, J = 8.1 Hz, 1H), 2.27 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ = 194.41, 151.45, 134.86, 132.21, 131.83, 129.78, 127.98, 125.05, 124.09, 123.16, 122.55, 122.46, 119.91, 117.75, 88.14, 29.50. HRMS (+) m/z calculated for C₁₆H₁₃NO, [M+H]⁺ 236.1075; found 236.1082.

(Z)-1-(8-methoxyphenanthridin-6(5H)-ylidene)propan-2-one (3b)
Yield=65%. Yellow solid. M.p. 146-148 °C. IR (neat) 3060, 3008, 2964, 2838, 1601, 1550, 1486, 1363, 1252, 746, 732 cm⁻¹. ¹H NMR (400 MHz, CDCl₃) δ = 8.18 (d, J = 9.0 Hz, 1H), 8.05 (d, J = 8.0 Hz, 1H), 7.44 – 7.36 (m, 2H), 7.35 – 7.27 (m, 2H), 7.27 – 7.20 (m, 1H), 5.96 (s, 1H), 3.94 (s, 3H), 2.27 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ = 194.10, 159.27, 151.08, 133.80, 128.68, 125.85, 125.21, 124.16, 123.21, 121.82, 120.79, 120.00, 117.64, 106.72, 87.91, 55.55, 29.44. HRMS (+) m/z calculated for C₁₆H₁₃NO₂, [M+H]⁺ 266.1181; found 266.1183.

(Z)-1-(8-fluorophenanthridin-6(5H)-ylidene)propan-2-one (3c)
Yield=30%. Yellow solid. M.p. 164-167 °C. IR (neat) 3049, 2906, 1604, 1557, 1484, 1316, 1192, 751 cm⁻¹. ¹H NMR (400 MHz, CDCl₃) δ = 15.11 (s, 1H), 8.29 (dd, J = 9.0, 5.4 Hz, 1H), 8.10 (d, J = 8.1 Hz, 1H), 7.73 (dd, J = 10.0, 2.6 Hz, 1H), 7.45 (ddd, J = 7.8, 6.2, 3.8 Hz, 2H), 7.35 (d, J = 7.5 Hz, 1H), 7.30 – 7.24 (m, 2H), 5.97 (s, 1H), 2.28 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ = 194.80, 162.14 (d, J = 248.5 Hz), 150.36, 134.50, 129.67,
128.74 (d, $J = 2.5$ Hz), 125.98 (d, $J = 8.2$ Hz), 124.98 (d, $J = 8.4$ Hz), 123.36, 122.27, 120.16 (d, $J = 22.9$ Hz), 119.36, 117.79, 110.65 (d, $J = 23.1$ Hz), 88.49, 29.51. $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta = -111.92$ (s, 1F). HRMS (CI$^+$) m/z calculated for C$_{18}$H$_{12}$FNO, [M+H]$^+$ 254.0981; found 254.0989.

(Z)-1-(8-acetylphenanthridin-6(5H)-ylidene)propan-2-one (3d)
Yield=51%. Yellow solid. M.p. 169-171 °C. IR (neat) 3044, 3000, 2961, 1726, 1605, 1552, 1493, 1300, 745 cm$^{-1}$. $^1$H NMR (400 MHz, CDCl$_3$) $\delta = 15.03$ (s, 1H), 8.60 (s, 1H), 8.29 (d, $J = 8.5$ Hz, 1H), 8.19 (dd, $J = 8.5$, 1.4 Hz, 1H), 7.49 (t, $J = 7.6$ Hz, 1H), 7.33 – 7.22 (m, 2H), 6.13 (s, 1H), 2.72 (s, 3H), 2.29 (s, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta = 196.73$, 195.05, 150.84, 135.87, 135.76, 131.06, 130.70, 125.41, 124.11, 123.34, 123.19, 122.89, 118.99, 117.82, 88.75, 29.58, 26.70. HRMS (CI$^+$) m/z calculated for C$_{18}$H$_{15}$NO$_2$, [M+H]$^+$ 278.1181; found 278.1180.

(Z)-1-(8-methylphenanthridin-6(5H)-ylidene)propan-2-one (3e)
Yield=70%. Yellow solid. M.p. 159-160 °C. IR (neat) 3032, 2913, 1598, 1482, 1316, 750 cm$^{-1}$. $^1$H NMR (400 MHz, CDCl$_3$) $\delta = 15.19$ (s, 1H), 8.19 (d, $J = 8.3$ Hz, 1H), 8.13 (d, $J = 8.0$ Hz, 1H), 7.88 (s, 1H), 7.54 (dd, $J = 8.3$, 1.2 Hz, 1H), 7.46 – 7.40 (m, 1H), 7.34 (dd, $J = 8.1$, 0.8 Hz, 1H), 7.29 – 7.23 (m,1H), 6.07 (s, 1H), 2.52 (s, 3H), 2.27 (s, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta = 194.22$, 151.45, 138.03, 134.47, 133.30, 129.81, 129.29, 124.92, 123.98, 123.13, 122.49, 122.21, 120.05, 117.69, 87.96, 29.46, 21.59. HRMS (CI$^+$) m/z calculated for C$_{17}$H$_{15}$NO, [M+H]$^+$ 250.1232; found 250.1238.

(Z)-1-(10-methylphenanthridin-6(5H)-ylidene)propan-2-one (3f)
Yield=20%. Yellow solid. M.p. 83-85 °C. IR (neat) 3019, 2959, 2922, 2853, 1699, 1663, 1610, 1593, 1555,
1437, 1362, 751 cm$^{-1}$. $^1$H NMR (400 MHz, CDCl$_3$) $\delta = 15.40$ (s, 1H), 8.39 (d, $J = 8.4$ Hz, 1H), 8.06 (d, $J = 8.0$ Hz, 1H), 7.59 (d, $J = 7.3$ Hz, 1H), 7.44 (dt, $J = 16.4, 7.9$ Hz, 3H), 7.27 (s, 1H), 6.09 (s, 1H), 2.97 (s, 3H), 2.27 (s, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta = 194.08$, 136.41, 135.78, 129.14, 129.01, 129.01, 127.42, 127.20, 125.65, 123.34, 122.39, 122.39, 121.21, 117.95, 88.15, 29.48, 26.56. HRMS (CI$^+$) m/z calculated for C$_{17}$H$_{15}$NO, [M+H]$^+$ 250.1232; found 250.1239.

(Z)-1-(dibenzo[i,k]phenanthridin-5(6H)-ylidene)propan-2-one (3g)
Yield=56%. Orange solid. M.p. 217-219 °C. IR (neat) 3063, 3030, 2912, 1712, 1609, 1560, 1447, 749 cm$^{-1}$. $^1$H NMR (400 MHz, CDCl$_3$) $\delta = 15.97$ (s, 1H), 8.91 (d, $J = 8.2$ Hz, 1H), 8.64 (t, $J = 7.5$ Hz, 2H), 8.59 (d, $J = 7.9$ Hz, 1H), 8.23 (d, $J = 8.2$ Hz, 1H), 7.78 – 7.71 (m, 1H), 7.63 (ddddd, $J = 19.1, 15.3, 7.1, 1.2$ Hz, 3H), 7.54 – 7.44 (m, 2H), 7.28 – 7.21 (m, 1H), 6.23 (s, 1H), 2.21 (s, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta = 192.46$, 150.54, 136.28, 134.54, 132.44, 130.73, 129.75, 128.86, 128.81, 128.31, 128.24, 127.83, 127.51, 126.96, 126.86, 125.90, 123.75, 123.53, 122.85, 121.42, 120.46, 117.93, 93.87, 29.25. HRMS (Cl$^+$) m/z calculated for C$_{24}$H$_{17}$NO, [M+H]$^+$ 336.1388; found 336.1393.

(Z)-1-(2-methylphenanthridin-6(5H)-ylidene)propan-2-one (3h)
Yield=68%. Yellow solid. M.p. 121-124 °C. IR (neat) 3029, 2987, 2917, 2855, 1718, 1618, 1552, 1499, 1326, 727 cm$^{-1}$. $^1$H NMR (400 MHz, CDCl$_3$) $\delta = 15.18$ (s, 1H), 8.22 (d, $J = 8.2$ Hz, 1H), 8.02 (d, $J = 8.1$ Hz, 1H), 7.88 (s, 1H), 7.64 (t, $J = 7.6$ Hz, 1H), 7.45 (t, $J = 7.6$ Hz, 1H), 7.26 – 7.06 (m, 2H), 5.99 (s, 1H), 2.39 (s, 3H), 2.19 (s, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta = 193.80$, 151.42, 132.82, 132.70, 132.16, 131.73, 130.98, 127.82, 125.10, 124.06, 122.49, 122.41, 119.81, 117.68, 87.71, 29.36, 21.41. HRMS (Cl$^+$) m/z calculated for C$_{17}$H$_{15}$NO, [M+H]$^+$ 250.1232; found 250.1232.
(Z)-1-(2-fluorophenanthridin-6(5H)-ylidene)propan-2-one (3i)
Yield=35%. Yellow solid. M.p. 149-152 °C. IR (neat) 3061, 3029, 2914, 2862, 1617, 1601, 1554, 1499, 1359, 762 cm\(^{-1}\). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta = 15.28\) (s, 1H), 8.12 (d, \(J = 8.1\) Hz, 1H), 8.04 (d, \(J = 7.9\) Hz, 1H), 7.75 (dd, \(J = 9.9, 2.6\) Hz, 1H), 7.72 – 7.63 (m, 1H), 7.56 – 7.48 (m, 1H), 7.26 (dd, \(J = 8.9, 4.9\) Hz, 1H), 7.13 (td, \(J = 8.4, 2.7\) Hz, 1H), 6.01 (s, 1H), 2.20 (s, 3H). \(^13\)C NMR (101 MHz, CDCl\(_3\)) \(\delta = 194.09, 158.97\) (d, \(J = 242.1\) Hz), 151.33, 131.97, 131.46 (d, \(J = 3.1\) Hz), 128.65, 125.17, 124.28, 122.79, 121.14 (d, \(J = 8.3\) Hz), 119.33 (d, \(J = 8.5\) Hz), 117.68 (d, \(J = 24.2\) Hz), 108.38 (d, \(J = 24.0\) Hz), 88.08, 29.31. \(^19\)F NMR (376 MHz, CDCl\(_3\)) \(\delta = -118.36\) (s, 1F). HRMS (CI\(^+\)) m/z calculated for C\(_{16}\)H\(_{12}\)FNO, [M+H]\(^+\) 254.0981; found 254.0988.

(Z)-1-(2-chlorophenanthridin-6(5H)-ylidene)propan-2-one (3j)
Yield=55%. Yellow solid. M.p. 187-189 °C. IR (neat) 3067, 3032, 2912, 1616, 1597, 1567, 1486, 1203, 728 cm\(^{-1}\). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta = 15.14\) (s, 1H), 8.15 (d, \(J = 8.1\) Hz, 1H), 8.05 (dd, \(J = 4.9, 2.6\) Hz, 2H), 7.70 (dd, \(J = 11.2, 4.2\) Hz, 1H), 7.55 (t, \(J = 7.7\) Hz, 1H), 7.38 (dd, \(J = 8.6, 2.1\) Hz, 1H), 7.23 (d, \(J = 8.6\) Hz, 1H), 6.06 (s, 1H), 2.28 (s, 3H). \(^13\)C NMR (101 MHz, CDCl\(_3\)) \(\delta = 194.09, 151.06, 133.38, 131.95, 130.95, 129.78, 128.58, 128.49, 125.00, 124.18, 122.55, 122.24, 121.04, 118.92, 88.55, 29.31. \(^19\)F NMR (376 MHz, CDCl\(_3\)) \(\delta = -118.36\) (s, 1F). HRMS (CI\(^+\)) m/z calculated for C\(_{16}\)H\(_{12}\)ClNO, [M+H]\(^+\) 270.0686; found 270.0691.

(Z)-1-(2-nitrophenanthridin-6(5H)-ylidene)propan-2-one (3k)
Yield=32%. Orange solid. M.p. 255-257 °C. IR (neat) 3102, 2919, 2851, 1603, 1577, 1556, 1519, 1493, 1360, 1314, 1300, 853, 745 cm\(^{-1}\). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta = 14.97\) (s, 1H), 9.00 (s, 1H), 8.29 (dd, \(J = 13.5, 8.8\) Hz, 2H), 8.07 (d, \(J = 8.0\) Hz, 1H), 7.79 (t, \(J = 7.3\) Hz, 1H), 7.62 (t, \(J = 7.4\) Hz, 1H), 7.31 (d, \(J = 8.9\) Hz, 1H), 6.18 (s, 1H), 2.32 (s, 3H). \(^13\)C NMR (101 MHz, CDCl\(_3\)) \(\delta = 196.96, 150.28, 142.77, 139.71, 132.50, 130.78, 129.45, 127.86, 124.97, 124.88, 124.45, 122.99, 119.64, 119.06, 117.69, 90.92, 29.97. HRMS (CI\(^+\)) m/z
calculated for C_{16}H_{12}N_{2}O_{3}, [M+H]^+ 281.0926; found 281.0925.

(Z)-1-(benzo[c][1,5]naphthyridin-6(5H)-ylidene)propan-2-one (3l)
Yield=50%. Yellow solid. M.p. 140-143 °C. IR (neat) 3001, 2961, 2928, 2872, 1726, 1604, 1587, 1551, 1425, 803, 744 cm\(^{-1}\). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta = 15.11\) (s, 1H), 8.29 (dd, \(J = 9.0, 5.4\) Hz, 1H), 8.10 (d, \(J = 8.1\) Hz, 1H), 7.73 (dd, \(J = 10.0, 2.6\) Hz, 1H), 7.45 (ddd, \(J = 7.8, 6.2, 3.2\) Hz, 2H), 7.35 (d, \(J = 7.5\) Hz, 1H), 7.30 – 7.26 (m, 1H), 5.97 (s, 1H), 2.28 (s, 3H).

\(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta = 195.07, 151.12, 144.69, 137.96, 133.09, 132.09, 130.94, 129.63, 125.81, 124.30, 124.27, 124.23, 124.21, 89.33, 29.50. HRMS (CI\(^+\)) m/z calculated for C\(_{15}\)H\(_{12}\)N\(_2\)O, [M+H]\(^+\) 237.1028; found 237.1028.

(Z)-1,1,1-trifluoro-3-(phenanthridin-6(5H)-ylidene)propan-2-one (4a)
Yield=24%. Yellow solid. M.p. 178-181 °C. IR (neat) 1625, 1598, 1574, 1489, 1456, 882, 727 cm\(^{-1}\). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta = 15.38\) (s, 1H), 8.43 (d, \(J = 8.2\) Hz, 1H), 8.13 (d, \(J = 8.1\) Hz, 1H), 8.22 (d, \(J = 8.2\) Hz, 1H), 7.93 – 7.84 (m, 1H), 7.72 – 7.64 (m, 1H), 7.63 – 7.57 (m, 1H), 7.54 – 7.43 (m, 2H), 6.45 (s, 1H). \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta = 174.71\) (q, \(J = 32.9\) Hz), 155.17, 133.36, 133.24, 132.54, 130.33, 128.63, 125.86, 125.40, 123.08, 122.76 (q, \(J = 7.7\) Hz), 121.08, 118.77, 118.20(q, \(J = 287.9\) Hz), 82.53 (q, \(J = 1.9\) Hz). \(^{19}\)F NMR (376 MHz, CDCl\(_3\)) \(\delta = -76.01\). \(^{19}\)F NMR (376 MHz, CDCl\(_3\)) \(\delta = -76.01\) (s, 3F). HRMS (CI\(^+\)) m/z calculated for C\(_{16}\)H\(_{10}\)F\(_3\)NO, [M+H]\(^+\) 290.0793; found 290.0800.

ethyl 2-(phenanthridin-6-yl)acetate (4b)
(Z)-ethyl 2-(phenanthridin-6(5H)-ylidene)acetate (4b’)
Yield=46% (4b:4b’=1:4:1). Yellow solid. M.p. 90-92 ºC. IR (neat) 3048, 3004, 2971, 2966, 1627, 1603, 1592, 1506, 1458, 738 cm⁻¹. ¹H NMR (400 MHz, CDCl₃) δ = 12.39 (s, 0.7H), 8.65 (d, J = 8.3 Hz, 1H), 8.56 (d, J = 8.1 Hz, 1H), 8.19 (d, J = 8.2 Hz, 0.7H), 8.15 (d, J = 7.9 Hz, 0.7H), 7.97 (d, J = 8.2 Hz, 0.7H), 7.87 – 7.82 (m, 1H), 7.74 – 7.61 (m, 3.7H), 7.45 (t, J = 7.7 Hz, 0.7H), 7.40 – 7.35 (m, 0.7H), 7.14 (t, J = 7.7 Hz, 1.4H), 5.53 (s, 0.7H), 4.42 (s, 2H), 4.27 – 4.17 (m, 3.44H), 1.35 (q, J = 7.1 Hz, 2.1H), 1.22 (q, J = 7.1 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ = 171.40, 170.40, 154.98, 150.98, 143.64, 135.59, 133.06, 131.55, 131.40, 130.64, 129.96, 128.71, 127.95, 127.55, 127.00, 126.17, 125.51, 124.95, 124.82, 124.05, 122.55, 122.50, 122.09, 118.78, 116.40, 61.23, 59.04, 43.25, 14.69, 14.18. HRMS (CI⁺) m/z calculated for C₁₇H₁₅NO₂, [M+H]⁺ 266.1181; found 266.1188.

dimethyl 2-(phenanthridin-6-yl)malonate (4c)
Yield=25%. Light yellow solid. M.p. 124-126 ºC. IR (neat) 2945, 2931, 1731, 1578, 1431, 766 cm⁻¹. ¹H NMR (400 MHz, CDCl₃) δ = 8.59 (d, J = 8.3 Hz, 1H), 8.50 – 8.46 (m, 1H), 8.08 (dd, J = 8.0, 1.1 Hz, 1H), 7.92 (d, J = 8.2 Hz, 1H), 7.80 – 7.75 (m, 1H), 7.67 – 7.58 (m, 3H), 5.62 (s, 1H), 3.75 (d, J = 9.3 Hz, 6H). ¹³C NMR (101 MHz, CDCl₃) δ = 167.94, 153.35, 143.29, 133.31, 130.76, 130.64, 128.74, 127.77, 127.53, 125.13, 124.95, 124.07, 122.76, 121.90, 59.35, 53.10. HRMS (CI⁺) m/z calculated for C₁₈H₁₅NO₄, [M+H]⁺ 310.1079; found 310.1081.

dimethyl 2-fluoro-2-(phenanthridin-6-yl)malonate (4d)
Yield=37%. Yellow solid. M.p. 140-141 ºC. IR (neat) 2961,1773, 1749, 1612, 1578, 1444, 1293, 760 cm⁻¹. ¹H NMR (400 MHz, CDCl₃) δ = 8.67 (d, J = 8.4 Hz, 1H), 8.59 – 8.46 (m, 1H), 8.11 (dd, J = 7.1, 2.1 Hz, 2H), 7.86 (t, J = 7.7 Hz, 1H), 7.76 – 7.65 (m, 3H), 3.95 (s, 6H). ¹³C NMR (101 MHz, CDCl₃) δ = 166.03 (d, J = 26.5 Hz), 152.54 (d, J = 23.6 Hz), 142.13, 133.73, 130.99 (d, J = 4.2 Hz), 128.89, 128.53, 127.90 (d, J = 1.4 Hz), 125.48
(d, J = 6.9 Hz), 124.55, 123.46 (d, J = 1.9 Hz), 122.77, 121.97, 97.67 (d, J = 199.8 Hz), 53.71. $\text{F NMR (376 MHz, CDCl}_3\delta = -150.76$ (d, J = 1.3 Hz, 1F). HRMS (CI$^+$) m/z calculated for C$_{18}$H$_{14}$FNO$_4$, [M+H]$^+$ 328.0985; found 328.0989.

**ethyl 2-fluoro-2-(phenanthridin-6-yl)acetate (5a)**

![Image](image)

**ethyl 2-fluoro-2-(8-methoxyphenanthridin-6-yl)acetate (5b)**

![Image](image)
(E)-ethyl 2-fluoro-2-(8-methoxyphenanthridin-6(5H)-ylidene)acetate (5b’)

Yield=52% (5b:5b’ =1:3.3). Yellow solid. M.p. 142-144 °C. IR (neat) 2981, 2968, 2937, 1733, 1700, 1613, 1574, 1459, 1212, 759, 713 cm⁻¹. ¹H NMR (400 MHz, CDCl₃) δ = 8.68 (d, J = 2.5 Hz, 1H), 8.54 (dd, J = 18.2, 11.0 Hz, 2.9H), 8.27 – 8.12 (m, 1.3H), 7.92 – 7.57 (m, 3.9H), 7.58 – 7.41 (m, 1.3H), 7.26 (s, 0.3H), 6.45 (d, J = 47.9 Hz, 0.3H), 4.57 (q, J = 7.1 Hz, 2H), 4.40 – 4.24 (m, 0.6H), 4.01 (d, J = 1.9 Hz, 3H), 3.98 (s, 0.9H), 1.50 (t, J = 7.1 Hz, 3H), 1.23 (t, J = 7.1 Hz, 0.9H). ¹³C NMR (101 MHz, CDCl₃) δ = 189.71, 168.11 (d, J = 25.9 Hz), 166.14, 159.88, 158.97, 151.93 (d, J = 20.9 Hz), 146.81, 142.21, 141.84, 131.60, 130.58, 130.35, 128.22, 128.14, 127.91, 125.96, 125.53, 124.10, 123.70, 122.19, 121.71, 121.55, 105.79, 105.55 (d, J = 5.3 Hz), 91.93 (d, J = 187.1 Hz), 62.12, 61.92, 55.67, 55.61, 14.24, 14.14. ¹⁹F NMR (376 MHz, CDCl₃) δ = -181.70 (d, J = 2.6 Hz, 1F). HRMS (Cl⁺) m/z calculated for C₁₉H₁₄FNO₃, [M+H]⁺ 314.1192; found 314.1194.

![Diagram of ethyl 2-(8-acetylphenanthridin-6-yl)-2-fluoroacetate (5c)](image)

ethyl 2-(8-acetylphenanthridin-6-yl)-2-fluoroacetate (5c)

(E)-ethyl 2-(8-acetylphenanthridin-6(5H)-ylidene)-2-fluoroacetate (5c’)

Yield=71% (5c:5c’=5.9:1). White solid. M.p. 124-126 °C. IR (neat) 2991, 1758, 1683, 1612, 1353, 1224. 767 cm⁻¹. ¹H NMR (400 MHz, CDCl₃) δ = 9.83 (d, J = 1.6 Hz, 0.17H), 9.05 (t, J = 1.7 Hz, 1H), 8.72 (d, J = 8.7 Hz, 1H), 8.61 (d, J = 8.2 Hz, 1H), 8.44 (dd, J = 8.7, 1.6 Hz, 1H), 8.23 (d, J = 8.0 Hz, 1H), 8.06 (d, J = 8.4 Hz, 0.51H), 7.88 – 7.74 (m, 2.17H), 7.74 – 7.69 (m, 0.51H), 6.53 (d, J = 47.9 Hz, 1H), 4.58 (q, J = 7.1 Hz, 0.34H), 4.47 – 4.20 (m, 2H), 2.82 (s, 0.51H), 2.79 (s, 3H), 1.51 (t, J = 7.1 Hz, 0.51H), 1.26 (t, J = 7.1 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ = 197.61, 197.45, 197.20, 188.99, 167.85 (d, J = 25.7 Hz), 165.50, 153.25 (d, J = 20.7 Hz), 144.32, 143.84, 143.34, 136.57, 136.36, 135.79, 131.78, 130.84, 130.74, 130.39, 130.20, 129.48, 129.30, 129.01, 128.67, 128.36, 127.56 (d, J = 5.4 Hz), 127.44, 125.01, 123.88, 123.51, 123.14, 122.82 (d, J = 3.8 Hz), 122.68, 91.54 (d, J = 187.9 Hz), 62.34, 62.18, 26.71, 26.65, 14.22. ¹⁹F NMR (376 MHz, CDCl₃) δ = -180.05 (s, 1F). HRMS (Cl⁺) m/z calculated for C₁₉H₁₄FNO₃, [M+H]⁺ 326.1192; found 326.1193.
ethyl 2-fluoro-2-(8-methylphenanthridin-6-yl)acetate (5d)

(E)-ethyl 2-fluoro-2-(8-methylphenanthridin-6(5H)-ylidene)acetate (5d')

Yield=70% (5d:5d'=12.5:1). Light yellow solid. M.p. 126-128 °C. IR (neat) 2981, 2905, 1761, 1624, 1577, 1461, 1221, 757 cm⁻¹. ¹H NMR (400 MHz, CDCl₃) δ = 8.98 (s, 0.08 H), 8.53 (dd, J = 7.8, 3.0 Hz, 2.16H), 8.26 – 8.08 (m, 2H), 7.83 – 7.59 (m, 3.24H), 7.25 (s, 0.16H), 6.50 (d, J = 48.1 Hz, 1H), 4.56 (q, J = 7.1 Hz, 0.16H), 4.45 – 4.23 (m, 2H), 2.60 (d, J = 5.6 Hz, 3.24H), 1.49 (t, J = 7.1 Hz, 0.24H), 1.26 (t, J = 7.1 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ = 168.11 (d, J = 25.6 Hz), 166.01, 152.56 (d, J = 20.2 Hz), 148.05, 142.66, 139.06, 137.96, 133.11, 132.82 , 131.53, 131.44, 130.61, 130.11, 128.67, 128.45, 128.08, 126.08, 125.24 (d, J = 4.1 Hz), 124.65, 124.30, 122.41, 122.00 (d, J = 2.9 Hz), 121.85, 91.20 (d, J = 187.3 Hz), 62.03, 61.95, 21.94, 21.86, 14.23, 14.13. ¹⁹F NMR (376 MHz, CDCl₃) δ = -180.67 (dd, J = 3.2, 1.9 Hz, 1F). HRMS (Cl⁺) m/z calculated for C₁₈H₁₆FNO₂, [M+H⁺]⁺ 298.1243; found 298.1245.

ethyl 2-fluoro-2-(2-methylphenanthridin-6-yl)acetate (5e)

(E)-ethyl 2-fluoro-2-(2-methylphenanthridin-6(5H)-ylidene)acetate (5e')

Yield=60% (5e:5e'=1.4:1). White solid. M.p. 94-97 °C. IR (neat) 3071, 2989, 2926, 1741, 1698, 1613, 1441, 816, 725 cm⁻¹. ¹H NMR (400 MHz, CDCl₃) δ = 9.21 (d, J = 8.3 Hz, 0.7H), 8.63 (d, J = 7.7 Hz, 1.7H), 8.35 (dd,
**ethyl 2-fluoro-2-(2-methoxyphenanthridin-6-yl)acetate (5f)**

Yield=72%. White solid. M.p. 101-103 °C. IR (neat) 2988, 2940, 2903, 1753, 1614, 1499, 1437, 842, 757 cm⁻¹. ¹H NMR (400 MHz, CDCl₃) δ = 8.59 (d, J = 8.3 Hz, 1H), 8.36 (dd, J = 8.2, 1.5 Hz, 1H), 8.10 (d, J = 9.0 Hz, 1H), 7.90 (d, J = 2.3 Hz, 1H), 7.85 (t, J = 7.7 Hz, 1H), 7.72 (t, J = 7.6 Hz, 1H), 7.38 (dd, J = 9.0, 2.7 Hz, 1H), 6.48 (d, J = 48.1 Hz, 1H), 4.48 – 4.20 (m, 2H), 4.03 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ = 168.21 (d, J = 25.8 Hz), 159.41, 150.28 (d, J = 20.4 Hz), 138.28, 132.98, 132.15, 130.53, 127.91, 125.89 (d, J = 4.3 Hz), 124.28, 122.53, 118.94, 102.80, 91.28 (d, J = 187.0 Hz), 62.03, 55.70, 14.12. ¹⁹F NMR (376 MHz, CDCl₃) δ = -179.99 (d, J = 3.2 Hz, 1F). HRMS (CI⁺) m/z calculated for C₁₉H₁₅FNO₂, [M+H]⁺ 314.1192; found 314.1192.

![ethyl 2-fluoro-2-(2-methoxyphenanthridin-6-yl)acetate (5f)](image)

**ethyl 2-fluoro-2-(2-fluorophenanthridin-6-yl)acetate (5g)**

![ethyl 2-fluoro-2-(2-fluorophenanthridin-6-yl)acetate (5g)](image)

**(E)-ethyl 2-fluoro-2-(2-fluorophenanthridin-6(5H)-ylidene)acetate (5g')**

Yield=34% (5g:5g' = 5:6:1). White solid. M.p. 120-123 °C. IR (neat) 2992, 2924, 2852, 1754, 1619, 1495, 1444, 1080, 825, 761 cm⁻¹. ¹H NMR (400 MHz, CDCl₃) δ = 9.23 (d, J = 8.3 Hz, 1H), 8.53 (d, J = 8.3 Hz, 0.18H), 8.39 (dd, J = 8.3, 2.0 Hz, 1H), 8.29 – 8.10 (m, 2.36H), 7.97 – 7.79 (m, 1.36H), 7.79 – 7.73 (m, 1H), 7.56 – 7.43 (m, 1.18H), 7.26 (s, 0.18H), 6.49 (d, J = 48.0 Hz, 1H), 4.56 (q, J = 7.1 Hz, 0.36H), 4.44 – 4.27 (m, 2H), 1.49 (t,
$J = 7.1$ Hz, 0.54H), 1.25 (t, $J = 7.1$ Hz, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta = 188.90, 167.91$ (d, $J = 25.6$ Hz), 165.76, 164.62, 163.29, 162.11, 160.82, 152.19 (dd, $J = 20.5, 3.0$ Hz), 139.78 (d, $J = 1.4$ Hz), 139.40, 134.15 (d, $J = 9.8$ Hz), 133.05, 132.99, 132.95, 131.39, 131.09, 129.46, 128.52, 127.49 (d, $J = 9.8$ Hz), 127.00, 126.12 (d, $J = 1.0$ Hz), 126.03 (d, $J = 4.3$ Hz), 124.10, 123.85, 122.70, 122.30, 118.51 (d, $J = 24.8$ Hz), 117.95 (d, $J = 24.4$ Hz), 107.47, 107.08 (d, $J = 23.6$ Hz), 91.11 (d, $J = 187.5$ Hz).62.14, 62.04, 14.21, 14.12.

$^{19}$F NMR (376 MHz, CDCl$_3$) $\delta = -180.65$ (d, $J = 1.8$ Hz, 1F).

HRMS (Cl$^+$/m/z calculated for C$_{17}$H$_{13}$F$_2$NO$_2$, [M+H]$^+$ 302.0993; found 302.0993.

**ethyl 2-((2-chlorophenantridin-6-yl)-2-fluoroacetate (5h)**

![Image](image1.png)

(E)-ethyl 2-((2-chlorophenantridin-6(5H)-ylidene)-2-fluoroacetate (5h$'$)

Yield=52% (5h:5h$'$=2.4:1). Light yellow solid. M.p. 108-109°C. IR (neat) 2989, 2938, 1739, 1709, 1601, 1568, 1439, 825, 758 cm$^{-1}$. $^1$H NMR (400 MHz, CDCl$_3$) $\delta = 9.21$ (d, $J = 8.4$ Hz, 0.41H), 8.66 – 8.49 (m, 2.82H), 8.39 (d, $J = 7.6$ Hz, 1H), 8.13 (dd, $J = 14.7, 8.7$ Hz, 1.41H), 7.92 (dt, $J = 20.9, 7.6$ Hz, 1.41H), 7.83 (t, $J = 7.7$ Hz, 0.41H), 7.79 – 7.66 (m, 2.41H), 7.26 (s, 0.41H), 6.48 (d, $J = 48.0$ Hz, 1H), 4.55 (q, $J = 7.1$ Hz, 0.82H), 4.43 – 4.26 (m, 2H), 1.49 (t, $J = 7.1$ Hz, 1.23H), 1.25 (t, $J = 7.1$ Hz, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta = 188.75, 167.82$ (d, $J = 25.6$ Hz), 165.63, 153.15 (d, $J = 20.4$ Hz), 148.49, 141.33, 140.86, 136.54, 134.27, 132.96, 132.53, 132.12, 131.64, 131.34, 129.89, 129.53, 129.45, 128.55, 127.02, 126.71, 126.07 (d, $J = 4.6$ Hz), 125.64, 124.23, 124.01, 122.57, 122.07 (d, $J = 21.6$ Hz), 121.75, 91.09 (d, $J = 187.7$ Hz), 62.17, 62.10, 14.21, 14.12. $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta = -106.78$ (s, 1F). HRMS (Cl$^+$/m/z calculated for C$_{17}$H$_{13}$CIFNO$_2$, [M+H]$^+$ 318.0697; found 318.0702.

![Image](image2.png)

ethyl 2-((benzo[c][1,5]naphthyridin-6-yl)-2-fluoroacetate (5i)

S15
(E)-ethyl 2-(benzo[c][1,5]naphthyridin-6(5H)-ylidene)-2-fluoroacetate (5i′)
Yield=80% (5i:5i′=20:1). White solid. M.p. 93-95 °C. IR (neat) 3046, 2986, 1749, 1592, 1485, 1266, 778, 724 cm⁻¹. ¹H NMR (400 MHz, CDCl₃) δ = 9.29 (t, J = 7.5 Hz, 1H), 9.20 – 9.11 (m, 0.1H), 9.05 (dd, J = 4.3, 1.5 Hz, 1H), 8.49 (ddd, J = 15.1, 8.3, 1.6 Hz, 1H), 8.41 (dd, J = 8.3, 2.1 Hz, 1H), 8.00 (dt, J = 15.2, 7.2 Hz, 1.05H), 7.95 – 7.77 (m, 1.1H), 7.72 (ddd, J = 12.6, 8.3, 4.3 Hz, 1.05H), 6.52 (d, J = 47.9 Hz, 1H), 4.56 (q, J = 7.1 Hz, 0.1H), 4.49 – 4.18 (m, 2H), 1.48 (t, J = 7.1 Hz, 0.15H), 1.25 (t, J = 7.1 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ = 167.70 (d, J = 25.5 Hz), 153.88 (d, J = 20.4 Hz), 152.39, 150.52, 141.40, 138.45, 137.81, 137.72, 134.43, 131.86, 131.56, 130.40, 129.51, 126.24, 126.07 (d, J = 0.8 Hz), 125.33 (d, J = 4.6 Hz), 124.38, 124.12 (d, J = 4.7 Hz), 123.83, 90.86 (d, J = 187.9 Hz), 62.22, 62.17, 14.19, 14.10. ¹⁹F NMR (376 MHz, CDCl₃) δ = -181.09 (s, 1F). HRMS (CI⁺) m/z calculated for C₁₁₇H₃₅FNO₂, [M+H]⁺ 285.1039; found 285.1040.

6-(fluoromethyl)phenanthridine (6)
Yield=80%. White solid. M.p. 118-120 °C. IR (neat) 3059, 2958, 2923, 2853, 1613, 1527, 1460, 722 cm⁻¹. ¹H NMR (400 MHz, CDCl₃) δ = 8.68 (d, J = 8.3 Hz, 1H), 8.59 (d, J = 7.9 Hz, 1H), 8.36 (d, J = 8.2 Hz, 1H), 8.26 – 8.13 (m, 1H), 7.95 – 7.85 (m, 1H), 7.82 – 7.67 (m, 3H), 6.02 (d, J = 47.3 Hz, 2H). ¹³C NMR (101 MHz, CDCl₃) δ = 154.81 (d, J = 16.9 Hz), 143.18, 133.21, 130.94, 130.36, 128.91, 127.74 (d, J = 5.6 Hz), 126.21 (d, J = 4.2 Hz), 124.69, 124.57 (d, J = 1.4s Hz), 122.44, 122.08, 85.49 (d, J = 169.4 Hz). ¹⁹F NMR (376 MHz, CDCl₃) δ = -212.88 (s, 1F). HRMS (CI⁺) m/z calculated for C₁₀H₁₀FN, [M+H]⁺ 212.0876; found 212.0882.
NMR Spectra

\((Z)-1-(\text{phenanthridin-6(5H)-ylidene})\text{propan-2-one (3a)}:\)

\[\text{Chemical Structure} \]

\[\text{NMR Spectra} \]

\[\text{Chemical Structure} \]

\[\text{NMR Spectra} \]
(Z)-1-(8-methoxyphenanthridin-6(5H)-ylidene)propan-2-one (3b):
(Z)-1-(8-fluorophenanthridin-6(5H)-ylidene)propan-2-one (3c):
(Z)-1-(8-acetylphenanthridin-6(5H)-ylidene)propan-2-one (3d):
(Z)-1-(8-methylphenanthridin-6(5H)-ylidene)propan-2-one (3e):
(Z)-1-(10-methylphenanthridin-6(5H)-ylidene)propan-2-one (3f):
(Z)-1-(dibenzo[i,k]phenanthridin-5(6H)-ylidene)propan-2-one (3g):
(Z)-1-(2-methylphenanthridin-6(5H)-ylidene)propan-2-one (3h):
(Z)-1-(2-fluorophenanthridin-6(5H)-ylidene)propan-2-one (3i):
(Z)-1-(2-chlorophenanthridin-6(5H)-ylidene)propan-2-one (3j):
(Z)-1-(2-nitrophenanthridin-6(5H)-ylidene)propan-2-one (3k):
(Z)-1-(benzo[c][1,5]naphthyridin-6(5H)-ylidene)propan-2-one (3l):
(Z)-1,1,1-trifluoro-3-(phenanthridin-6(5H)-ylidene)propan-2-one (4a):
ethyl 2-(phenanthridin-6-yl)acetate (4b) and (Z)-ethyl 2-(phenanthridin-6(5H)-ylidene)acetate (4b'): 

![Chemical structures](image)

![NMR spectrum](image)
dimethyl 2-(phenanthridin-6-yl)malonate (4c):
dimethyl 2-fluoro-2-(phenanthridin-6-yl)malonate (4d):
ethyl 2-fluoro-2-(phenanthridin-6-yl)acetate (5a) and (E)-ethyl
2-fluoro-2-(phenanthridin-6(5H)-ylidene)acetate (5a'):
ethyl 2-fluoro-2-(8-methoxyphenanthridin-6-yl)acetate (5b) and (E)-ethyl 
2-fluoro-2-(8-methoxyphenanthridin-6(5H)-ylidene)acetate (5b’):
2-fluoro-2-(8-methoxyphenanthridin-6(5H)-ylidene)acetate (5b’): (after recrystallization)
ethyl 2-(8-acetylphenanthridin-6-yl)-2-fluoroacetate (5c) and (E)-ethyl 2-(8-acetylphenanthridin-6(5H)-ylidene)-2-fluoroacetate (5c'):
ethyl 2-fluoro-2-(8-methylphenanthridin-6-yl)acetate (5d) and (E)-ethyl
2-fluoro-2-(8-methylphenanthridin-6(5H)-ylidene)acetate (5d ):
ethyl 2-fluoro-2-(2-methylphenanthridin-6-yl)acetate (5e) and (E)-ethyl 2-fluoro-2-(2-methylphenanthridin-6(5H)-ylidene)acetate (5e’):
ethyl 2-fluoro-2-(2-methoxyphenanthridin-6-yl)acetate (5f):
ethyl 2-fluoro-2-(2-fluorophenanthridin-6-yl)acetate (5g) and (E)-ethyl 2-fluoro-2-(2-fluorophenanthridin-6(5H)-ylidene)acetate (5g'):
ethyl 2-(2-chlorophenanthridin-6-yl)-2-fluoroacetate (5h) and (E)-ethyl
2-(2-chlorophenanthridin-6(5H)-ylidene)-2-fluoroacetate (5g'):
ethyl 2-(benzo[c][1,5]naphthyridin-6-yl)-2-fluoroacetate (5i) and (E)-ethyl 2-(benzo[c][1,5]naphthyridin-6(5H)-ylidene)-2-fluoroacetate (5i'):
6-(fluoromethyl)phenanthridine (6):
Electronic Supplementary Material (ESI) for Chemical Communication
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