

Supporting Information

Visible-light-promoted iminyl radical formation from vinyl azides:

Synthesis of 6-(fluoro)alkylated phenanthridines

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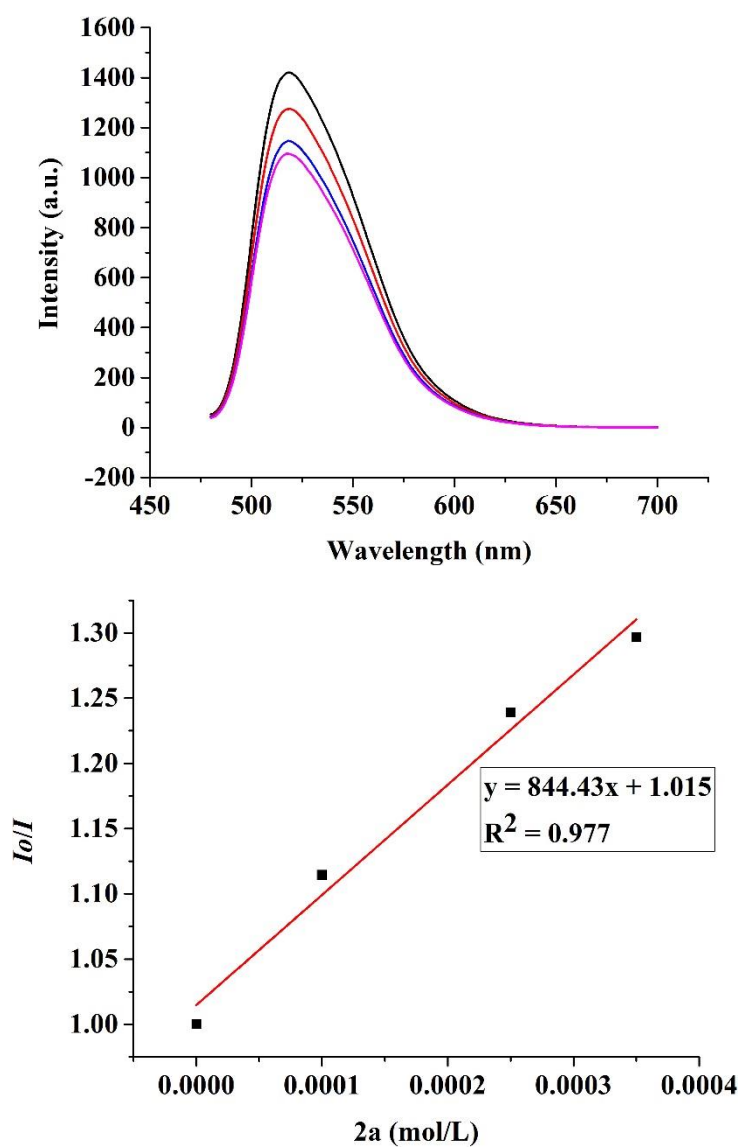
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1. General Methods.

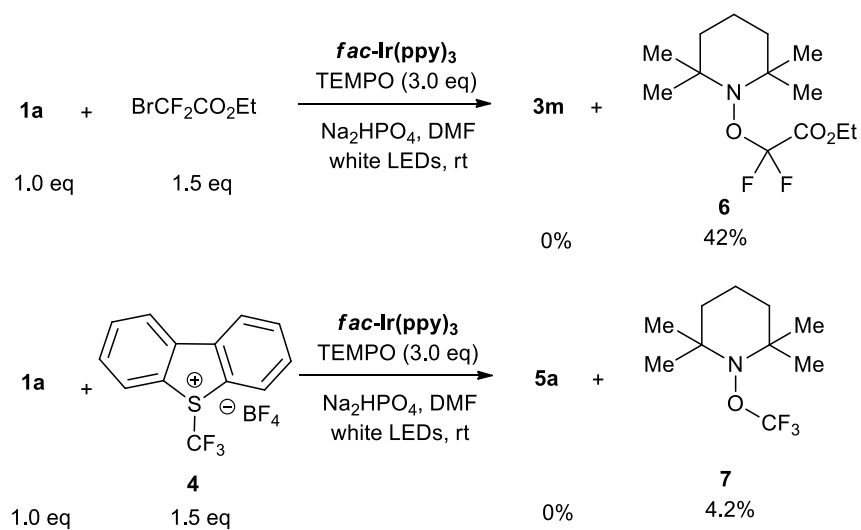
DMF was dried according to *Purification of Common Laboratory Chemicals*. Other reagents were used without further purification. Thin layer chromatography (TLC) was performed on EMD precoated plates (silica gel 60 F254, Art 5715) and visualized by fluorescence quenching under UV light and by staining with phosphomolybdic acid or potassium permanganate, respectively. Column chromatography was performed on EMD Silica Gel 60 (300–400 Mesh) using a forced flow of 0.5–1.0 bar. ^1H NMR (400 MHz), ^{13}C NMR (100 MHz) and ^{19}F (376 MHz) were measured on a Bruker AVANCE III-400 spectrometer. Chemical shifts are expressed in parts per million (ppm) with respect to the residual solvent peak. Coupling constants are reported as Hertz (Hz), signal shapes and splitting patterns are indicated as follows: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet. Infrared (IR) spectra were recorded on a Nicolet 6700 spectrophotometer and are reported as wavenumber (cm^{-1}). Vinyl azides were prepared according to published literature procedures.¹

2. Stern-Volmer Studies.

A Hitachi F-7000 fluorescence spectrometer was used to record the emission intensities. All the solutions were excited at 463 nm and the emission intensity at 518 nm was observed. DMF was degassed with a stream of Ar for 15 min. In a typical experiment, the emission spectrum of a 5×10^{-4} M solution of *fac*-Ir(ppy)₃ in DMF was collected. Then, appropriate amount of quencher **2a** was added to the measured solution in a quartz cuvette and the emission spectrum of the sample was collected. I_0 and I represent the intensities of the emission in the absence and presence of the quencher at 518 nm.



3. TEMPO Trapping Experiments.

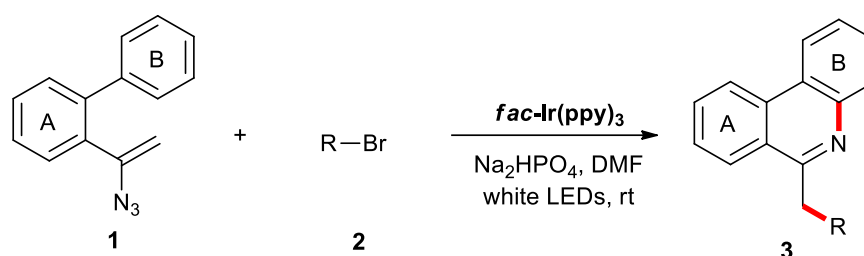


Reaction conditions: A solution of **1a** (0.2 mmol), $\text{BrCF}_2\text{CO}_2\text{Et}$ or **4** (0.3 mmol),

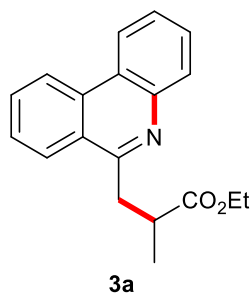
Na₂HPO₄ (0.3 mmol), TEMPO (0.6 mmol) and *fac*-Ir(ppy)₃ (0.002 mmol, 1.0 mol%) in DMF (2.0 mL) was irradiated by white LED strips at rt for 24h or 12 h. Yields of TEMPO trapping products **6** and **7** were determined based on ¹⁹F NMR using benzotrifluoride as the internal standard.

4. General Procedures.

4.1 General procedure for alkyl radical onto vinyl azides.



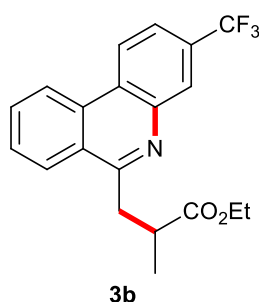
A 10 mL round bottom flask equipped with a rubber septum and magnetic stir bar was charged with vinyl azides **1** (0.2 mmol, 1.0 equiv), *fac*-Ir(ppy)₃ (0.002 mmol, 0.01 equiv), Na₂HPO₄ (0.3 mmol, 1.5 equiv). The flask was evacuated and backfilled with N₂ for 3 times. Bromides **2** (0.3 mmol, 1.5 equiv) and DMF (2.0 mL, 0.1 M) were added with syringe under N₂. The mixture was then irradiated by white LED strips at room temperature for 24 h. Then the mixture was poured into a separatory funnel containing 20 mL H₂O and 20 mL Et₂O. The layers were separated and the aqueous layer was extracted with Et₂O (2 × 20 mL). The combined organic layers were dried with Na₂SO₄ and concentrated under reduced pressure after filtration. The crude product was purified by flash chromatography on silica gel to afford the desired product phenanthridine derivatives **3**.



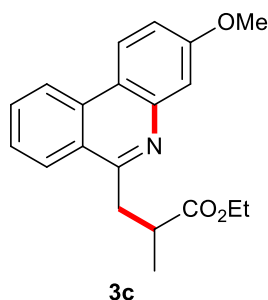
Ethyl 2-methyl-3-(phenanthridin-6-yl)propanoate (3a): yellow solid, yield: 70%.

¹H NMR (400 MHz, CDCl₃): δ 8.60 (d, *J* = 8.2 Hz, 1H), 8.51 (d, *J* = 8.1 Hz, 1H), 8.25

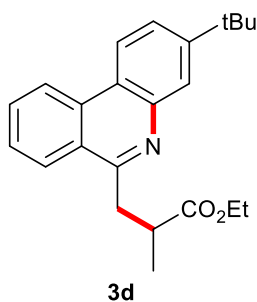
(d, $J = 8.1$ Hz, 1H), 8.07 (dd, $J = 8.1, 0.9$ Hz, 1H), 7.84 – 7.76 (m, 1H), 7.68 (tdd, $J = 8.1, 3.4, 1.2$ Hz, 2H), 7.64 – 7.55 (m, 1H), 4.13 (q, $J = 7.1$ Hz, 2H), 3.82 (dq, $J = 6.9, 3.9$ Hz, 1H), 3.49 – 3.30 (m, 2H), 1.36 (d, $J = 6.9$ Hz, 3H), 1.19 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 176.72, 158.83, 143.55, 132.71, 130.28, 129.76, 128.48, 127.28, 126.40, 125.75, 125.50, 123.60, 122.43, 121.89, 60.30, 38.45, 38.12, 17.54, 14.25. FTIR (film) ν_{max} 2978.63, 2898.13, 1721.04, 1605.61, 1585.86, 1527.10, 1486.49, 1415.35, 1379.30, 1299.03, 954.46 cm^{-1} . HRMS (ESI): m/z calcd for $\text{C}_{19}\text{H}_{20}\text{NO}_2$ $[\text{M}+\text{H}]^+$ 294.1494, found 294.1495.



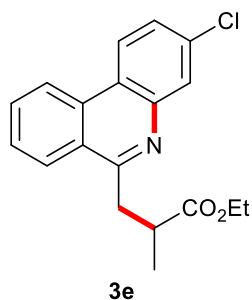
Ethyl 2-methyl-3-(3-(trifluoromethyl)phenanthridin-6-yl)propanoate (3b): yellow solid, yield: 65%. ^1H NMR (400 MHz, CDCl_3): δ 8.58 (t, $J = 8.4$ Hz, 2H), 8.33 (s, 1H), 8.28 (d, $J = 7.7$ Hz, 1H), 7.90 – 7.81 (m, 1H), 7.81 – 7.72 (m, 2H), 4.25 – 4.07 (m, 2H), 3.83 (dd, $J = 15.5, 7.6$ Hz, 1H), 3.51 – 3.33 (m, 2H), 1.39 (d, $J = 6.9$ Hz, 3H), 1.22 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 176.66, 160.46, 142.79, 131.78, 130.82, 130.25 (q, $J = 32.6$ Hz), 128.46, 127.24 (q, $J = 4.1$ Hz), 126.69, 126.05, 125.87, 124.20 (q, $J = 270.7$ Hz), 122.92, 122.76, 122.21 (q, $J = 3.3$ Hz), 60.38, 38.37, 37.73, 17.64, 14.23; ^{19}F NMR (376 MHz, CDCl_3) δ -62.22. FTIR (film) ν_{max} 1720.68, 1591.59, 1529.91, 1414.95, 1375.70, 1331.50, 1286.80, 1273.52, 1225.55, 1168.36, 1111.86, 1067.31, 934.70, 903.38, 758.65 cm^{-1} . HRMS (ESI): m/z calcd for $\text{C}_{20}\text{H}_{19}\text{F}_3\text{NO}_2$ $[\text{M}+\text{H}]^+$ 362.1368, found 362.1373.



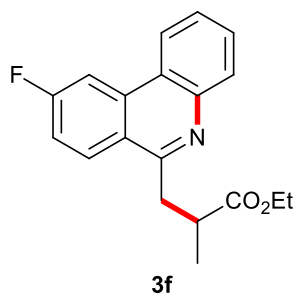
Ethyl 3-(3-methoxyphenanthridin-6-yl)-2-methylpropanoate (3c): yellow solid, yield: 59%. ^1H NMR (400 MHz, CDCl_3): δ 8.50 (d, J = 8.3 Hz, 1H), 8.40 (d, J = 9.0 Hz, 1H), 8.23 (d, J = 8.2 Hz, 1H), 7.77 (t, J = 7.6 Hz, 1H), 7.60 (t, J = 7.6 Hz, 1H), 7.48 (d, J = 2.6 Hz, 1H), 7.24 (dd, J = 9.0, 2.6 Hz, 1H), 4.19 – 4.04 (m, 2H), 3.97 (s, 3H), 3.88 – 3.76 (m, 1H), 3.44 – 3.21 (m, 2H), 1.35 (d, J = 6.7 Hz, 3H), 1.18 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 176.64, 160.01, 159.50, 145.14, 132.95, 130.38, 126.21, 125.85, 124.57, 123.14, 121.96, 117.63, 117.41, 109.60, 60.31, 55.56, 38.54, 38.39, 17.50, 14.26. FTIR (film) ν_{max} 2973.83, 2920.56, 2842.06, 1726.17, 1611.21, 1583.18, 1485.05, 1442.99, 1154.21, 1030.84, 851.40, 826.17 cm^{-1} . HRMS (ESI): m/z calcd for $\text{C}_{20}\text{H}_{22}\text{NO}_3$ $[\text{M}+\text{H}]^+$ 324.1600, found 323.1594.



Ethyl 3-(3-(tert-butyl)phenanthridin-6-yl)-2-methylpropanoate (3d): white solid, yield: 80%. ^1H NMR (400 MHz, CDCl_3): δ 8.58 (d, J = 8.2 Hz, 1H), 8.45 (d, J = 8.6 Hz, 1H), 8.25 (d, J = 8.2 Hz, 1H), 8.06 (d, J = 1.8 Hz, 1H), 7.79 (t, J = 7.6 Hz, 1H), 7.73 – 7.60 (m, 2H), 4.14 (qq, J = 10.8, 7.1 Hz, 2H), 3.83 (q, J = 2.5 Hz, 1H), 3.47 – 3.32 (m, 2H), 1.46 (s, 9H), 1.35 (d, J = 6.7 Hz, 3H), 1.20 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 176.76, 158.88, 151.84, 143.53, 132.72, 130.25, 126.87, 125.82, 125.63, 125.29, 124.69, 122.32, 121.60, 121.22, 60.33, 38.57, 38.43, 34.96, 31.39, 17.52, 14.27. FTIR (film) ν_{max} 2960.83, 1721.91, 1612.35, 1586.55, 1486.24, 1457.75, 1443.62, 1378.39, 1298.44, 1232.83, 1033.93, 854.29, 825.98 cm^{-1} . HRMS (ESI): m/z calcd for $\text{C}_{23}\text{H}_{28}\text{NO}_2$ $[\text{M}+\text{H}]^+$ 350.2120, found 350.2124.

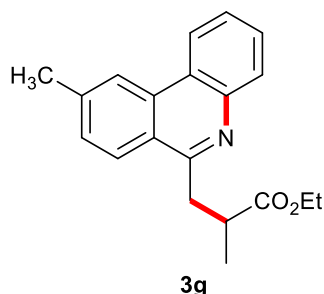


Ethyl 3-(3-chlorophenanthridin-6-yl)-2-methylpropanoate (3e): yellow solid, yield: 75%. ^1H NMR (400 MHz, CDCl_3): δ 8.52 (d, J = 8.3 Hz, 1H), 8.39 (d, J = 8.8 Hz, 1H), 8.24 (d, J = 8.2 Hz, 1H), 8.03 (d, J = 2.1 Hz, 1H), 7.81 (t, J = 7.3 Hz, 1H), 7.69 (t, J = 7.6 Hz, 1H), 7.53 (dd, J = 8.7, 2.2 Hz, 1H), 4.14 (q, J = 7.1 Hz, 2H), 3.80 (dd, J = 15.2, 7.3 Hz, 1H), 3.46 – 3.32 (m, 2H), 1.37 (d, J = 6.9 Hz, 3H), 1.21 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 176.69, 160.20, 144.19, 134.04, 132.20, 130.68, 128.95, 127.59, 126.89, 125.84, 125.40, 123.29, 122.35, 122.07, 60.37, 38.36, 37.80, 17.63, 14.29. FTIR (film) ν_{max} 2978.57, 1719.48, 1601.98, 1587.46, 1570.32, 1477.85, 1443.88, 1369.41, 1352.08, 1275.40, 1259.49, 1230.81, 1170.16, 1079.56, 1028.60, 879.12 cm^{-1} . HRMS (ESI): m/z calcd for $\text{C}_{19}\text{H}_{19}\text{ClNO}_2$ $[\text{M}+\text{H}]^+$ 328.1104, found 328.1099.

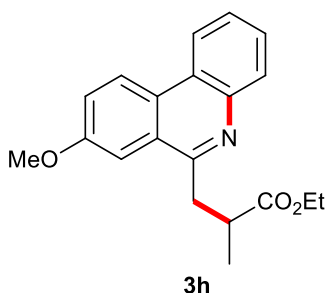


Ethyl 3-(9-fluorophenanthridin-6-yl)-2-methylpropanoate (3f): yellow solid, yield: 67%. ^1H NMR (400 MHz, CDCl_3): δ 8.36 (d, J = 8.1 Hz, 1H), 8.26 (dd, J = 9.0, 5.7 Hz, 1H), 8.17 (dd, J = 10.4, 2.5 Hz, 1H), 8.05 (d, J = 8.1 Hz, 1H), 7.70 (t, J = 7.6 Hz, 1H), 7.59 (t, J = 7.6 Hz, 1H), 7.39 (td, J = 8.6, 2.5 Hz, 1H), 4.13 (q, J = 7.1 Hz, 2H), 3.79 (dd, J = 15.3, 7.6 Hz, 1H), 3.46 – 3.30 (m, 2H), 1.37 (d, J = 6.9 Hz, 3H), 1.20 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 176.68, 163.63 (d, J = 249.7 Hz), 158.24, 143.83, 135.14 (d, J = 9.2 Hz), 129.82, 129.17, 128.64 (d, J = 9.3 Hz), 126.47, 123.16 (d, J = 4.0 Hz), 122.49 (d, J = 1.7 Hz), 122.09, 116.25 (d, J = 23.5 Hz), 107.56

(d, $J = 21.9$ Hz), 60.36, 38.49, 38.03, 17.61, 14.28; ^{19}F NMR (376 MHz, CDCl_3) δ -107.45. FTIR (film) ν_{max} 2981.26, 1712.38, 1620.37, 1588.23, 1532.86, 1497.64, 1457.79, 1443.56, 1378.86, 1260.17, 1228.82, 1029.53, 868.29 cm^{-1} . HRMS (ESI): m/z calcd for $\text{C}_{19}\text{H}_{19}\text{FNO}_2$ $[\text{M}+\text{H}]^+$ 312.1400, found 312.1404.

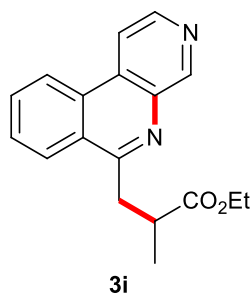


Ethyl 2-methyl-3-(9-methylphenanthridin-6-yl)propanoate (3g): yellow solid, yield: 74%. ^1H NMR (400 MHz, CDCl_3): δ 8.49 (d, $J = 7.8$ Hz, 1H), 8.37 (s, 1H), 8.13 (d, $J = 8.4$ Hz, 1H), 8.04 (dd, $J = 8.1, 0.8$ Hz, 1H), 7.69 – 7.61 (m, 1H), 7.61 – 7.53 (m, 1H), 7.48 (dd, $J = 8.4, 1.1$ Hz, 1H), 4.12 (q, $J = 7.1$ Hz, 2H), 3.78 (dd, $J = 14.7, 6.9$ Hz, 1H), 3.48 – 3.22 (m, 2H), 2.61 (s, 3H), 1.34 (d, $J = 6.9$ Hz, 3H), 1.18 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 176.74, 158.70, 143.74, 140.57, 132.85, 129.69, 128.95, 128.33, 126.15, 125.68, 123.64, 123.50, 122.09, 121.87, 60.28, 38.44, 38.21, 22.20, 17.51, 14.26. FTIR (film) ν_{max} 3130.46, 3056.43, 2973.93, 2931.34, 2801.76, 1721.07, 1617.76, 1587.37, 1520.40, 1455.68, 1409.53, 1233.29, 1032.62, 818.76 cm^{-1} . HRMS (ESI): m/z calcd for $\text{C}_{20}\text{H}_{22}\text{NO}_2$ $[\text{M}+\text{H}]^+$ 308.1651, found 308.1656.

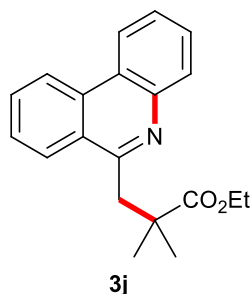


Ethyl 3-(8-methoxyphenanthridin-6-yl)-2-methylpropanoate (3h): yellow solid, yield: 75%. ^1H NMR (400 MHz, CDCl_3): δ 8.53 (d, $J = 9.1$ Hz, 1H), 8.44 (dd, $J = 8.1, 1.2$ Hz, 1H), 8.04 (dd, $J = 8.0, 1.2$ Hz, 1H), 7.68 – 7.54 (m, 3H), 7.45 (dd, $J = 9.0, 2.6$ Hz, 1H), 4.14 (q, $J = 7.1$ Hz, 2H), 4.00 (s, 3H), 3.78 (dd, $J = 15.5, 7.6$ Hz, 1H), 3.38

(ddd, $J = 21.8, 14.6, 6.6$ Hz, 2H), 1.38 (d, $J = 7.0$ Hz, 3H), 1.20 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 176.85, 158.67, 157.91, 142.71, 129.70, 127.48, 127.03, 126.77, 126.46, 124.14, 123.70, 121.40, 120.71, 105.99, 60.33, 55.59, 38.66, 37.98, 17.56, 14.27. FTIR (film) ν_{max} 2978.43, 1718.91, 1617.70, 1574.47, 1533.33, 1484.09, 1464.78, 1388.59, 1218.74, 1129.03, 1038.61, 830.73 cm^{-1} . HRMS (ESI): m/z calcd for $\text{C}_{20}\text{H}_{22}\text{NO}_3$ $[\text{M}+\text{H}]^+$ 324.1600, found 323.1604.

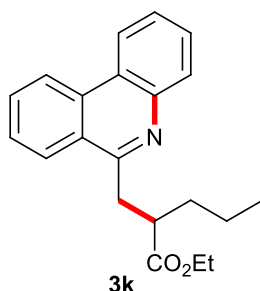


Ethyl 3-(benzo[c][1,7]naphthyridin-6-yl)-2-methylpropanoate (3i): yellow solid, yield: 78%. ^1H NMR (400 MHz, CDCl_3): δ 9.38 (s, 1H), 8.72 (d, $J = 5.5$ Hz, 1H), 8.60 (d, $J = 7.9$ Hz, 1H), 8.32 (d, $J = 7.6$ Hz, 1H), 8.26 (d, $J = 5.6$ Hz, 1H), 7.94 – 7.87 (m, 1H), 7.86 – 7.75 (m, 1H), 4.25 – 4.06 (m, 2H), 3.85 (dd, $J = 15.7, 8.0$ Hz, 1H), 3.55 – 3.33 (m, 2H), 1.41 (d, $J = 6.9$ Hz, 3H), 1.24 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 176.69, 160.84, 152.99, 149.46, 145.07, 130.93, 130.63, 129.60, 128.59, 127.01, 125.90, 123.04, 115.15, 60.44, 38.40, 37.61, 17.71, 14.31. FTIR (film) ν_{max} 2974.84, 1725.89, 1589.31, 1574.77, 1518.69, 1454.21, 1406.54, 1377.60, 1260.58, 1232.43, 1162.68, 824.26 cm^{-1} . HRMS (ESI): m/z calcd for $\text{C}_{18}\text{H}_{19}\text{N}_2\text{O}_2$ $[\text{M}+\text{H}]^+$ 295.1447, found 295.1450.

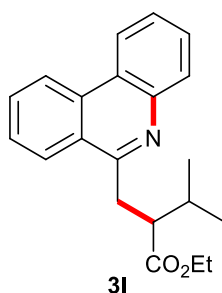


Ethyl 2,2-dimethyl-3-(phenanthridin-6-yl)propanoate (3j): yellow solid, yield: 73%. ^1H NMR (400 MHz, CDCl_3): δ 8.62 (d, $J = 8.2$ Hz, 1H), 8.51 (d, $J = 7.2$ Hz, 1H), 8.22 (d, $J = 8.2$ Hz, 1H), 8.03 (d, $J = 8.0$ Hz, 1H), 7.86 – 7.74 (m, 1H), 7.72 –

7.55 (m, 3H), 4.11 (q, $J = 7.1$ Hz, 2H), 3.64 (s, 2H), 1.44 (s, 6H), 1.10 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 178.14, 157.76, 143.30, 132.63, 130.12, 129.74, 128.42, 127.11, 126.36, 125.89, 125.72, 123.36, 122.43, 121.82, 60.20, 44.33, 41.70, 26.19, 14.16. FTIR (film) ν_{max} 2966.23, 1717.53, 1588.25, 1470.42, 1361.27, 1309.22, 1276.61, 1256.63, 1197.32, 1144.28, 1033.19, 751.19 cm^{-1} . HRMS (ESI): m/z calcd for $\text{C}_{20}\text{H}_{22}\text{NO}_2$ $[\text{M}+\text{H}]^+$ 308.1651, found 308.1654.

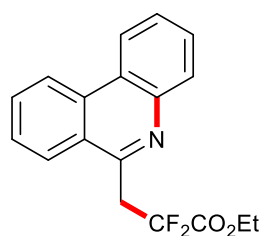


Ethyl 2-(phenanthridin-6-ylmethyl)pentanoate (3k): yellow solid, yield: 62%. ^1H NMR (400 MHz, CDCl_3): δ 8.60 (d, $J = 8.3$ Hz, 1H), 8.50 (d, $J = 8.1$ Hz, 1H), 8.25 (d, $J = 8.2$ Hz, 1H), 8.06 (d, $J = 8.1$ Hz, 1H), 7.80 (t, $J = 7.6$ Hz, 1H), 7.67 (td, $J = 7.4$, 3.3 Hz, 2H), 7.59 (t, $J = 7.5$ Hz, 1H), 4.11 (q, $J = 7.1$ Hz, 2H), 3.76 (dd, $J = 15.8$, 9.2 Hz, 1H), 3.45 (dd, $J = 15.8$, 5.2 Hz, 1H), 3.35 (ddd, $J = 10.7$, 8.8, 5.5 Hz, 1H), 1.84 (ddd, $J = 14.2$, 12.0, 7.4 Hz, 1H), 1.69 (ddd, $J = 19.5$, 11.4, 6.3 Hz, 1H), 1.53 – 1.39 (m, 2H), 1.16 (t, $J = 7.1$ Hz, 3H), 0.95 (t, $J = 7.3$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 176.40, 158.98, 143.52, 132.68, 130.29, 129.75, 128.47, 127.29, 126.39, 125.75, 125.48, 123.60, 122.43, 121.90, 60.14, 43.55, 37.20, 34.89, 20.67, 14.32, 14.14. FTIR (film) ν_{max} 2957.88, 2932.13, 1712.01, 1587.14, 1486.04, 1447.30, 1413.61, 1372.93, 1276.30, 1236.56, 1204.43, 1176.78, 1152.32, 1035.25, 921.25 cm^{-1} . HRMS (ESI): m/z calcd for $\text{C}_{21}\text{H}_{24}\text{NO}_2$ $[\text{M}+\text{H}]^+$ 322.1807, found 322.1802.



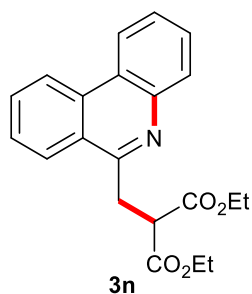
Ethyl 3-methyl-2-(phenanthridin-6-ylmethyl)butanoate (3l): yellow solid, yield:

49%. ^1H NMR (400 MHz, CDCl_3): δ 8.61 (d, $J = 8.3$ Hz, 1H), 8.51 (d, $J = 8.1$ Hz, 1H), 8.27 (d, $J = 8.2$ Hz, 1H), 8.05 (d, $J = 8.1$ Hz, 1H), 7.81 (t, $J = 7.6$ Hz, 1H), 7.73 – 7.63 (m, 2H), 7.59 (t, $J = 7.5$ Hz, 1H), 4.08 (q, $J = 7.1$ Hz, 2H), 3.78 (dd, $J = 16.2$, 10.8 Hz, 1H), 3.50 (dd, $J = 16.2$, 3.8 Hz, 1H), 3.36 – 3.19 (m, 1H), 2.25 – 2.02 (m, 1H), 1.15 (dt, $J = 7.1$, 3.7 Hz, 6H), 1.10 (d, $J = 6.8$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 175.50, 159.27, 143.51, 132.63, 130.25, 129.73, 128.42, 127.24, 126.32, 125.70, 125.53, 123.58, 122.42, 121.88, 49.72, 34.26, 30.84, 20.62, 20.43, 14.37. FTIR (film) ν_{max} 2961.93, 1711.53, 1611.21, 1587.02, 1472.21, 1407.55, 1373.84, 1348.60, 1275.65, 1257.69, 1115.61, 1037.67 cm^{-1} . HRMS (ESI): m/z calcd for $\text{C}_{21}\text{H}_{24}\text{NO}_2$ $[\text{M}+\text{H}]^+$ 322.1807, found 322.1802.

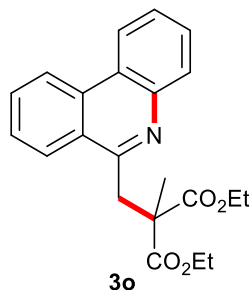


3m

Ethyl 2,2-difluoro-3-(phenanthridin-6-yl)propanoate (3m): yellow oil, yield: 55%. ^1H NMR (400 MHz, CDCl_3): δ 8.62 (d, $J = 8.3$ Hz, 1H), 8.52 (d, $J = 7.9$ Hz, 1H), 8.12 (d, $J = 8.2$ Hz, 1H), 8.02 (d, $J = 7.8$ Hz, 1H), 7.84 (t, $J = 7.6$ Hz, 1H), 7.74 – 7.66 (m, 2H), 7.63 (t, $J = 7.0$ Hz, 1H), 4.36 (q, $J = 7.1$ Hz, 2H), 4.23 (t, $J = 14.0$ Hz, 2H), 1.27 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 163.96 (t, $J = 31.5$ Hz), 152.92 (t, $J = 6.0$ Hz), 142.84, 132.86, 130.86, 129.59, 128.78, 127.64, 127.17, 125.45, 125.09, 123.70, 122.58, 121.97, 115.88 (t, $J = 248.0$ Hz), 62.62, 40.13 (t, $J = 24.9$ Hz), 13.97; ^{19}F NMR (376 MHz, CDCl_3) δ -103.33. FTIR (film) ν_{max} 2993.46, 1765.42, 1726.17, 1681.31, 1614.02, 1591.59, 1524.30, 1490.65, 1462.62, 1370.09, 1339.25, 1305.61, 1255.14, 1221.50, 1193.46, 751.76 cm^{-1} . HRMS (ESI): m/z calcd for $\text{C}_{18}\text{H}_{16}\text{F}_2\text{I}_2\text{NO}_2$ $[\text{M}+\text{H}]^+$ 316.1149, found 316.1144.

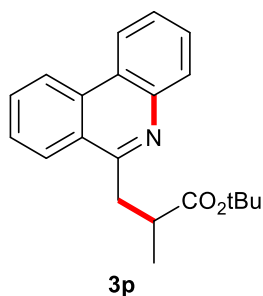


Diethyl 2-(phenanthridin-6-ylmethyl)malonate (3n): yellow solid, yield: 65%. ^1H NMR (400 MHz, CDCl_3): δ 8.59 (d, $J = 8.3$ Hz, 1H), 8.50 (d, $J = 8.0$ Hz, 1H), 8.26 (d, $J = 8.1$ Hz, 1H), 8.01 (d, $J = 8.0$ Hz, 1H), 7.81 (t, $J = 7.6$ Hz, 1H), 7.68 (dd, $J = 14.0$, 7.1 Hz, 2H), 7.60 (t, $J = 7.5$ Hz, 1H), 4.57 (t, $J = 7.4$ Hz, 1H), 4.26 (q, $J = 7.1$ Hz, 4H), 4.00 (d, $J = 7.4$ Hz, 2H), 1.29 (t, $J = 7.1$ Hz, 6H); ^{13}C NMR (100 MHz, CDCl_3): δ 170.00, 156.96, 143.27, 132.57, 130.45, 129.70, 128.47, 127.41, 126.53, 125.43, 125.26, 123.70, 122.42, 121.94, 61.47, 49.47, 33.64, 14.20. FTIR (film) ν_{max} 2990.31, 2939.19, 1744.53, 1720.74, 1612.90, 1587.17, 1487.47, 1465.75, 1448.70, 1422.88, 1387.44, 1365.38, 1339.87, 1256.95, 1155.62, 1100.24, 1007.04, 949.98, 860.87 cm^{-1} . HRMS (ESI): m/z calcd for $\text{C}_{21}\text{H}_{22}\text{NO}_4$ $[\text{M}+\text{H}]^+$ 352.1549, found 352.1553.



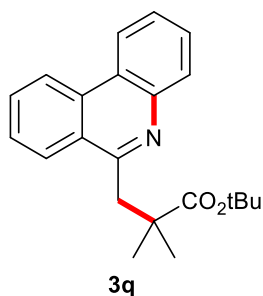
Diethyl 2-methyl-2-(phenanthridin-6-ylmethyl)malonate (3o): yellow solid, yield: 90%. ^1H NMR (400 MHz, CDCl_3): δ 8.60 (d, $J = 8.2$ Hz, 1H), 8.50 (d, $J = 8.0$ Hz, 1H), 8.28 (d, $J = 8.2$ Hz, 1H), 8.01 (d, $J = 8.0$ Hz, 1H), 7.81 (t, $J = 7.6$ Hz, 1H), 7.67 (dd, $J = 12.4$, 7.4 Hz, 2H), 7.59 (t, $J = 7.1$ Hz, 1H), 4.25 (q, $J = 7.1$ Hz, 4H), 4.05 (s, 2H), 1.72 (s, 3H), 1.23 (t, $J = 7.1$ Hz, 6H); ^{13}C NMR (100 MHz, CDCl_3): δ 172.56, 156.40, 143.07, 132.63, 130.32, 129.59, 128.48, 127.32, 126.54, 125.72, 125.54, 123.40, 122.47, 121.86, 61.29, 53.04, 39.39, 20.70, 14.10. FTIR (film) ν_{max} 2979.44, 2931.78, 1757.16, 1723.48, 1622.43, 1591.59, 1580.37, 1440.19, 1378.50, 1361.68, 1275.22, 1249.03, 1184.26, 1099.15, 1022.43, 859.81 cm^{-1} . HRMS (ESI): m/z calcd

for C₂₂H₂₄NO₄ [M+H]⁺ 366.1705, found 366.1700.



Tert-butyl 2-methyl-3-(phenanthridin-6-yl)propanoate (3p): yellow oil, yield: 59%.

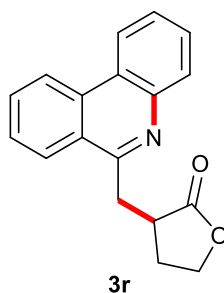
¹H NMR (400 MHz, CDCl₃): δ 8.61 (d, *J* = 8.2 Hz, 1H), 8.52 (d, *J* = 7.9 Hz, 1H), 8.27 (d, *J* = 8.2 Hz, 1H), 8.09 (d, *J* = 7.9 Hz, 1H), 7.81 (t, *J* = 7.2 Hz, 1H), 7.68 (q, *J* = 6.0 Hz, 2H), 7.59 (dd, *J* = 11.1, 4.0 Hz, 1H), 3.78 (td, *J* = 9.7, 4.1 Hz, 1H), 3.33 (tt, *J* = 18.8, 6.6 Hz, 2H), 1.39 (s, 9H), 1.33 (d, *J* = 6.8 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 175.95, 159.16, 143.56, 132.70, 130.26, 129.75, 128.47, 127.28, 126.35, 125.88, 125.54, 123.61, 122.42, 121.91, 79.85, 38.98, 38.55, 28.08, 17.61. FTIR (film) ν_{max} 2979.44, 2934.58, 1728.97, 1608.41, 1585.98, 1485.05, 1459.81, 1361.68, 1277.57, 1255.14, 1232.71, 1145.79, 753.27 cm⁻¹. HRMS (ESI): *m/z* calcd for C₂₁H₂₄NO₂ [M+H]⁺ 322.1807, found 322.1802.



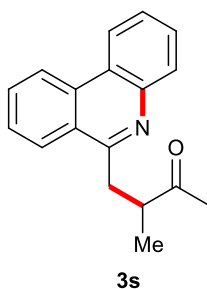
Tert-butyl 2,2-dimethyl-3-(phenanthridin-6-yl)propanoate (3q): yellow solid, yield:

75%. ¹H NMR (400 MHz, CDCl₃): δ 8.63 (d, *J* = 8.3 Hz, 1H), 8.52 (d, *J* = 8.0 Hz, 1H), 8.25 (d, *J* = 8.2 Hz, 1H), 8.08 (d, *J* = 8.0 Hz, 1H), 7.81 (t, *J* = 7.6 Hz, 1H), 7.67 (t, *J* = 7.5 Hz, 2H), 7.59 (t, *J* = 7.5 Hz, 1H), 3.60 (s, 2H), 1.41 (s, 6H), 1.35 (s, 9H); ¹³C NMR (100 MHz, CDCl₃): δ 177.20, 157.96, 143.33, 132.60, 130.04, 129.87, 128.36, 127.10, 126.25, 125.92, 125.81, 123.34, 122.40, 121.80, 79.24, 44.05, 42.03, 28.00, 26.34. FTIR (film) ν_{max} 2973.04, 2920.56, 2864.49, 1717.57, 1619.63, 1586.82, 1474.32, 1447.39, 1362.96, 1313.91, 1172.13, 899.28, 853.87 cm⁻¹. HRMS (ESI): *m/z*

calcd for C₂₂H₂₆NO₂ [M+H]⁺ 336.1964, found 336.1967.



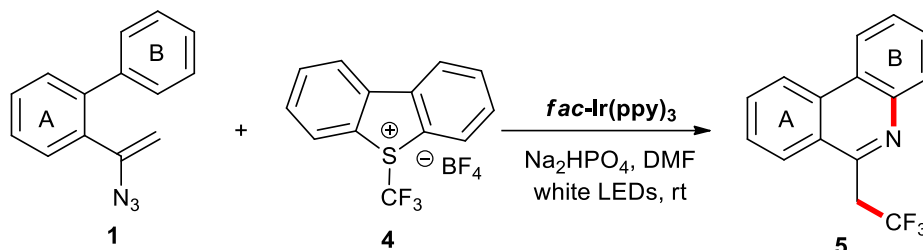
3-(Phenanthridin-6-ylmethyl)dihydrofuran-2(3H)-one (3r): yellow solid, yield: 75%. ¹H NMR (400 MHz, CDCl₃): δ 8.64 (d, *J* = 8.3 Hz, 1H), 8.55 (d, *J* = 7.8 Hz, 1H), 8.24 (d, *J* = 8.2 Hz, 1H), 8.09 (d, *J* = 7.7 Hz, 1H), 7.85 (t, *J* = 7.6 Hz, 1H), 7.71 (t, *J* = 7.5 Hz, 2H), 7.64 (t, *J* = 7.6 Hz, 1H), 4.52 (td, *J* = 8.9, 2.7 Hz, 1H), 4.36 (td, *J* = 9.3, 7.1 Hz, 1H), 4.07 (d, *J* = 13.9 Hz, 1H), 3.59 – 3.37 (m, 2H), 2.79 – 2.62 (m, 1H), 2.19 (tt, *J* = 12.7, 7.2 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃): δ 180.14, 157.30, 143.36, 132.73, 130.58, 129.73, 128.63, 127.59, 126.72, 125.42, 125.33, 123.72, 122.57, 122.01, 67.03, 37.53, 35.57, 29.11. FTIR (film) ν_{max} 2907.72, 1755.88, 1585.98, 1485.18, 1412.54, 1382.45, 1276.12, 1260.56, 1169.18, 1153.29, 1030.39, 960.90 cm⁻¹. HRMS (ESI): *m/z* calcd for C₁₈H₁₆NO₂ [M+H]⁺ 278.1181, found 278.1176.



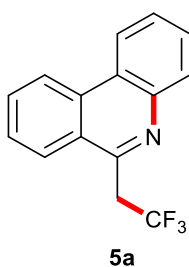
3-Methyl-4-(phenanthridin-6-yl)butan-2-one (3s): yellow solid, yield: 62%. ¹H NMR (400 MHz, CDCl₃): δ 8.61 (d, *J* = 8.2 Hz, 1H), 8.52 (d, *J* = 8.2 Hz, 1H), 8.26 (d, *J* = 8.2 Hz, 1H), 8.06 (d, *J* = 8.1 Hz, 1H), 7.82 (t, *J* = 7.7 Hz, 1H), 7.75 – 7.65 (m, 2H), 7.62 (t, *J* = 7.5 Hz, 1H), 3.88 (dd, *J* = 16.5, 9.0 Hz, 1H), 3.66 (tt, *J* = 14.4, 7.2 Hz, 1H), 3.37 (dd, *J* = 16.5, 4.8 Hz, 1H), 2.48 (s, 3H), 1.33 (d, *J* = 7.1 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 212.77, 158.78, 143.44, 132.57, 130.28, 129.44, 128.40, 127.27, 126.34, 125.69, 125.48, 123.60, 122.36, 121.93, 43.93, 38.20, 29.31, 17.13. FTIR

(film) $\nu_{\max}$ 2970.96, 1701.94, 1614.02, 1585.95, 1524.30, 1486.34, 1409.63, 1377.81, 1364.05, 1344.99, 1297.20, 1224.30, 1168.35, 1036.45, 952.34, 919.38 cm^{-1} . HRMS (ESI): m/z calcd for $\text{C}_{18}\text{H}_{18}\text{NO}$ $[\text{M}+\text{H}]^+$ 264.1388, found 264.1384.

4.2 General procedure for trifluoromethyl radical onto vinyl azides.

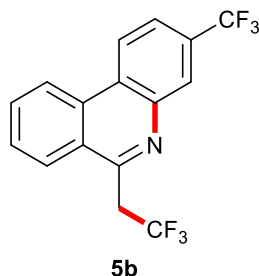


A 10 mL round bottom flask equipped with a rubber septum and magnetic stir bar was charged with vinyl azides **1** (0.2 mmol, 1.0 equiv), Umemoto's reagent **4** (0.3 mmol, 1.5 equiv), *fac*-Ir(ppy)₃ (0.002 mmol, 0.01 equiv), Na₂HPO₄ (0.3 mmol, 1.5 equiv). The flask was evacuated and backfilled with N₂ for 3 times. DMF (2.0 mL, 0.1 M) were added with syringe under N₂. The mixture was then irradiated by white LED strips at room temperature for 12 h. Then the mixture was poured into a separatory funnel containing 20 mL H₂O and 20 mL Et₂O. The layers were separated and the aqueous layer was extracted with Et₂O (2 × 20 mL). The combined organic layers were dried with Na₂SO₄ and concentrated under reduced pressure after filtration. The crude product was purified by flash chromatography on silica gel to afford the desired product phenanthridine derivatives **5**.

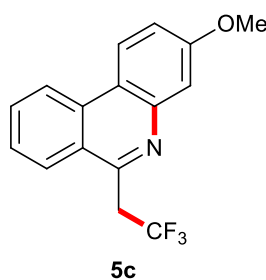


6-(2,2,2-Trifluoroethyl)phenanthridine (5a): yellow solid, yield: 79%. ¹H NMR (400 MHz, CDCl₃): δ 8.63 (d, J = 8.3 Hz, 1H), 8.53 (d, J = 7.5 Hz, 1H), 8.17 (d, J = 8.1 Hz, 2H), 7.89 – 7.79 (m, 1H), 7.79 – 7.62 (m, 3H), 4.19 (q, J = 10.4 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃): δ 151.14 (q, J = 3.2 Hz), 143.45, 133.20, 130.79, 130.18, 128.91, 127.62, 127.53, 126.21, 125.65 (q, J = 276.5 Hz), 125.51, 124.05, 122.53,

121.98, 40.52 (q, $J = 29.0$ Hz); ^{19}F NMR (376 MHz, CDCl_3) δ -62.46. FTIR (film) ν_{max} 3068.92, 2953.79, 1969.29, 1930.84, 1613.51, 1575.20, 1526.88, 1488.67, 1460.78, 1445.82, 1434.06, 1368.08, 1347.92, 1307.06, 959.59 cm^{-1} . HRMS (ESI): m/z calcd for $\text{C}_{15}\text{H}_{11}\text{F}_3\text{N}$ $[\text{M}+\text{H}]^+$ 262.0844, found 262.0838.

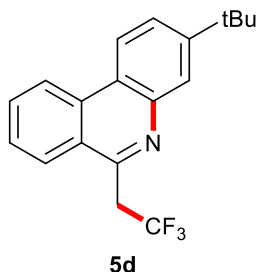


6-(2,2,2-Trifluoroethyl)-3-(trifluoromethyl)phenanthridine (5b): white solid, yield: 83%. ^1H NMR (400 MHz, CDCl_3): δ 8.70 – 8.57 (m, 2H), 8.46 (s, 1H), 8.23 (d, $J = 8.3$ Hz, 1H), 7.97 – 7.88 (m, 1H), 7.88 – 7.75 (m, 2H), 4.21 (q, $J = 10.3$ Hz, 2H); ^{13}C NMR (100 MHz, CDCl_3): δ 152.80 (q, $J = 3.3$ Hz), 142.67, 132.37, 131.40, 130.74 (q, $J = 32.6$ Hz), 128.84, 127.76 (q, $J = 4.1$ Hz), 126.39, 126.27, 126.05, 125.44 (q, $J = 276.4$ Hz), 124.01 (q, $J = 270.6$ Hz), 123.34 (q, $J = 3.3$ Hz), 123.06, 122.90, 40.47 (q, $J = 29.2$ Hz); ^{19}F NMR (376 MHz, CDCl_3) δ -62.33, -62.43. FTIR (film) ν_{max} 2921.75, 2851.37, 1625.23, 1614.02, 1583.18, 1532.71, 1487.85, 1465.42, 1440.26, 1362.08, 1331.44, 1250.21, 1167.45, 951.08 cm^{-1} . HRMS (ESI): m/z calcd for $\text{C}_{16}\text{H}_{10}\text{F}_6\text{N}$ $[\text{M}+\text{H}]^+$ 330.0717, found 330.0714.

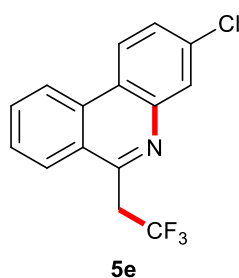


3-Methoxy-6-(2,2,2-trifluoroethyl)phenanthridine (5c): white solid, yield: 66%. ^1H NMR (400 MHz, CDCl_3): δ 8.52 (d, $J = 8.3$ Hz, 1H), 8.41 (d, $J = 9.1$ Hz, 1H), 8.14 (d, $J = 8.3$ Hz, 1H), 7.80 (ddd, $J = 8.3, 7.1, 1.1$ Hz, 1H), 7.63 (ddd, $J = 8.2, 7.1, 1.0$ Hz, 1H), 7.56 (d, $J = 2.7$ Hz, 1H), 7.30 (dd, $J = 9.0, 2.7$ Hz, 1H), 4.18 (q, $J = 10.4$ Hz, 2H), 3.98 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 160.29, 151.56 (q, $J = 3.4$ Hz), 145.07, 133.43, 130.85, 126.53, 126.23, 125.82 (q, $J = 276.5$ Hz), 124.61, 123.20, 122.04,

118.85, 118.13, 109.66, 55.63, 40.49 (q, $J = 29.0$ Hz); ^{19}F NMR (376 MHz, CDCl_3) δ -62.52. FTIR (film) ν_{max} 2836.45, 1615.38, 1580.37, 1532.71, 1486.27, 1466.48, 1377.18, 1363.33, 1331.22, 1034.08, 966.83, 952.31 cm^{-1} . HRMS (ESI): m/z calcd for $\text{C}_{16}\text{H}_{13}\text{F}_3\text{N}$ $[\text{M}+\text{H}]^+$ 292.0949, found 292.0944.

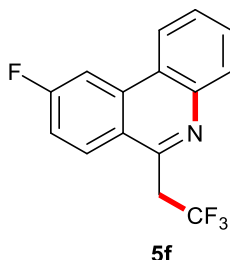


3-(Tert-butyl)-6-(2,2,2-trifluoroethyl)phenanthridine (5d): yellow solid, yield: 90%. ^1H NMR (400 MHz, CDCl_3): δ 8.62 (d, $J = 8.3$ Hz, 1H), 8.49 (d, $J = 8.7$ Hz, 1H), 8.22 – 8.13 (m, 2H), 7.84 (ddd, $J = 8.3, 7.1, 1.2$ Hz, 1H), 7.77 (dd, $J = 8.7, 2.1$ Hz, 1H), 7.69 (ddd, $J = 8.2, 7.1, 1.1$ Hz, 1H), 4.20 (q, $J = 10.4$ Hz, 2H), 1.47 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3): δ 152.43, 151.03 (q, $J = 3.4$ Hz), 143.49, 133.19, 130.75, 127.21, 126.23, 126.00, 125.93, 125.67 (q, $J = 276.5$ Hz), 125.34, 122.41, 121.71, 121.52, 40.57 (q, $J = 29.0$ Hz), 35.07, 31.34; ^{19}F NMR (376 MHz, CDCl_3) δ -62.50. FTIR (film) ν_{max} 2959.94, 1614.82, 1436.44, 1366.89, 1343.51, 1247.82, 1126.55, 1100.73, 1045.74, 958.18 cm^{-1} . HRMS (ESI): m/z calcd for $\text{C}_{19}\text{H}_{19}\text{F}_3\text{N}$ $[\text{M}+\text{H}]^+$ 318.1470, found 318.1475.

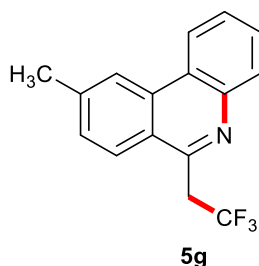


3-Chloro-6-(2,2,2-trifluoroethyl)phenanthridine (5e): yellow solid, yield: 86%. ^1H NMR (400 MHz, CDCl_3): δ 8.52 (d, $J = 8.3$ Hz, 1H), 8.38 (d, $J = 8.8$ Hz, 1H), 8.16 (d, $J = 8.3$ Hz, 1H), 8.13 (d, $J = 2.1$ Hz, 1H), 7.84 (t, $J = 7.7$ Hz, 1H), 7.72 (t, $J = 7.7$ Hz, 1H), 7.57 (dd, $J = 8.8, 2.1$ Hz, 1H), 4.16 (q, $J = 10.3$ Hz, 2H); ^{13}C NMR (100 MHz, CDCl_3): δ 152.47 (q, $J = 3.3$ Hz), 143.98, 134.55, 132.71, 131.21, 129.35, 128.03, 127.93, 126.32, 125.51 (q, $J = 276.5$ Hz), 125.36, 123.31, 122.46, 122.43, 40.42 (q, J

= 29.1 Hz); ^{19}F NMR (376 MHz, CDCl_3) δ -62.43. FTIR (film) ν_{max} 2920.56, 1605.61, 1563.55, 1478.25, 1442.99, 1368.99, 1341.82, 1266.39, 1238.68, 1135.97, 1079.75, 1044.16, 946.90, 874.61 cm^{-1} . HRMS (ESI): m/z calcd for $\text{C}_{15}\text{H}_{10}\text{ClF}_3\text{N}$ $[\text{M}+\text{H}]^+$ 296.0454, found 296.0455.

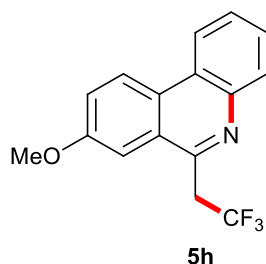


9-Fluoro-6-(2,2,2-trifluoroethyl)phenanthridine (5f): yellow solid, yield: 82%. ^1H NMR (400 MHz, CDCl_3): δ 8.39 (d, J = 8.2 Hz, 1H), 8.24 – 8.11 (m, 3H), 7.77 (t, J = 7.6 Hz, 1H), 7.67 (t, J = 7.6 Hz, 1H), 7.44 (td, J = 8.7, 2.5 Hz, 1H), 4.16 (q, J = 10.3 Hz, 2H); ^{13}C NMR (100 MHz, CDCl_3): δ 163.81 (d, J = 251.3 Hz), 150.38 (q, J = 3.9 Hz), 143.70, 135.69 (d, J = 9.5 Hz), 130.25, 129.62, 129.19 (d, J = 47.1 Hz), 127.61, 125.52 (q, J = 276.6 Hz), 123.61 (d, J = 4.2 Hz), 122.52, 122.15, 116.79 (d, J = 23.8 Hz), 107.69 (d, J = 22.1 Hz), 40.71 (q, J = 29.1 Hz); ^{19}F NMR (376 MHz, CDCl_3) δ -62.53 (3F), -106.09 (1F). FTIR (film) ν_{max} 2988.10, 1623.69, 1586.51, 1529.74, 1499.73, 1464.77, 1426.02, 1372.05, 1349.09, 1242.14, 1134.70, 1094.24, 1044.67, 935.09 cm^{-1} . HRMS (ESI): m/z calcd for $\text{C}_{15}\text{H}_{10}\text{F}_4\text{N}$ $[\text{M}+\text{H}]^+$ 280.0749, found 280.0744.

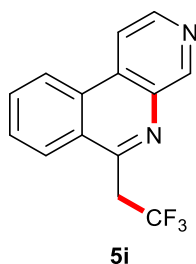


9-Methyl-6-(2,2,2-trifluoroethyl)phenanthridine (5g): yellow solid, yield: 85%. ^1H NMR (400 MHz, CDCl_3): δ 8.51 (d, J = 8.1 Hz, 1H), 8.39 (s, 1H), 8.15 (dd, J = 8.1, 0.9 Hz, 1H), 8.05 (d, J = 8.4 Hz, 1H), 7.77 – 7.68 (m, 1H), 7.68 – 7.59 (m, 1H), 7.51 (dd, J = 8.4, 1.1 Hz, 1H), 4.15 (q, J = 10.4 Hz, 2H), 2.62 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 150.95 (q, J = 3.3 Hz), 143.61, 141.32, 133.35, 130.08, 129.34, 128.77,

127.27, 126.11, 125.68 (q, $J = 276.5$ Hz), 123.93, 123.68, 122.14, 121.97, 40.51 (q, $J = 28.9$ Hz), 22.21; ^{19}F NMR (376 MHz, CDCl_3) δ -62.51. FTIR (film) ν_{max} 2952.38, 2257.23, 2219.10, 2177.70, 2141.68, 2069.50, 2030.65, 1914.09, 1621.97, 1577.60, 1499.35, 1462.42, 1432.81, 1349.65, 1261.60, 1095.52, 935.41 cm^{-1} . HRMS (ESI): m/z calcd for $\text{C}_{16}\text{H}_{13}\text{F}_3\text{N}$ $[\text{M}+\text{H}]^+$ 276.1000, found 276.0995.

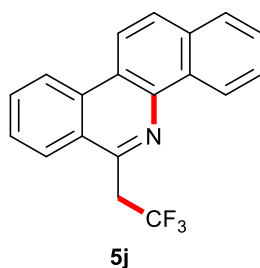


8-Methoxy-6-(2,2,2-trifluoroethyl)phenanthridine (5h): yellow solid, yield: 85%. ^1H NMR (400 MHz, CDCl_3): δ 8.51 (d, $J = 8.9$ Hz, 1H), 8.43 (d, $J = 8.8$ Hz, 1H), 8.14 (d, $J = 7.7$ Hz, 1H), 7.72 – 7.57 (m, 2H), 7.51 – 7.39 (m, 2H), 4.15 (q, $J = 10.4$ Hz, 2H), 3.97 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 158.80, 150.22 (q, $J = 3.3$ Hz), 142.62, 130.09, 127.91, 127.58, 127.55, 126.81, 125.65 (q, $J = 276.6$ Hz), 124.17, 124.14, 121.49, 121.28, 106.44, 55.55, 40.78 (q, $J = 29.0$ Hz); ^{19}F NMR (376 MHz, CDCl_3) δ -62.61. FTIR (film) ν_{max} 1618.51, 1573.02, 1533.53, 1485.94, 1467.46, 1419.83, 1382.84, 1350.34, 1257.08, 1222.58, 1129.35, 1090.45, 1041.83, 937.70, 848.46 cm^{-1} . HRMS (ESI): m/z calcd for $\text{C}_{16}\text{H}_{13}\text{F}_3\text{N}$ $[\text{M}+\text{H}]^+$ 292.0949, found 292.0944.

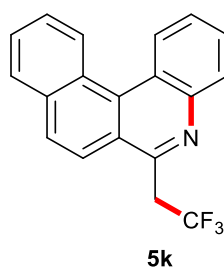


6-(2,2,2-Trifluoroethyl)benzo[c][1,7]naphthyridine (5i): yellow solid, yield: 98%. ^1H NMR (400 MHz, CDCl_3): δ 9.51 (s, 1H), 8.79 (d, $J = 5.5$ Hz, 1H), 8.65 (d, $J = 8.1$ Hz, 1H), 8.28 (dd, $J = 13.7, 6.9$ Hz, 2H), 7.96 (t, $J = 7.2$ Hz, 1H), 7.89 (t, $J = 7.2$ Hz, 1H), 4.24 (q, $J = 10.2$ Hz, 2H); ^{13}C NMR (100 MHz, CDCl_3): δ 153.47, 153.08 (q, $J = 3.3$ Hz), 145.96, 131.52, 131.23, 129.97, 128.95, 127.00, 126.45, 125.37 (q, $J = 276.6$

Hz), 123.17, 115.11, 40.47 (q, $J = 29.3$ Hz); ^{19}F NMR (376 MHz, CDCl_3) δ -62.40. FTIR (film) ν_{max} 1589.42, 1569.34, 1528.16, 1482.66, 1449.83, 1429.78, 1409.48, 1394.27, 1259.90, 1103.16, 1044.29, 1029.21, 928.15 cm^{-1} . HRMS (ESI): m/z calcd for $\text{C}_{14}\text{H}_{10}\text{F}_3\text{N}_2$ $[\text{M}+\text{H}]^+$ 263.0796, found 263.0791.



6-(2,2,2-Trifluoroethyl)benzo[c]phenanthridine (5j): yellow solid, yield: 98%. ^1H NMR (400 MHz, CDCl_3): δ 9.42 (d, $J = 8.2$ Hz, 1H), 8.65 (d, $J = 8.4$ Hz, 1H), 8.44 (d, $J = 9.0$ Hz, 1H), 8.19 (d, $J = 8.3$ Hz, 1H), 7.96 (d, $J = 9.0$ Hz, 1H), 7.93 (d, $J = 7.9$ Hz, 1H), 7.87 – 7.80 (m, 1H), 7.77 – 7.63 (m, 3H), 4.28 (q, $J = 10.4$ Hz, 2H); ^{13}C NMR (100 MHz, CDCl_3): δ 149.53 (q, $J = 3.2$ Hz), 140.30, 133.39, 133.26, 131.91, 130.48, 128.23, 127.55, 127.54, 127.28, 127.11, 125.84, 125.49 (q, $J = 276.2$ Hz), 124.99, 122.93, 120.91, 119.56, 40.33 (q, $J = 28.8$ Hz); ^{19}F NMR (376 MHz, CDCl_3) δ -62.45. FTIR (film) ν_{max} 1615.30, 1507.18, 1372.55, 1338.06, 1274.56, 1267.62, 1234.15, 1139.01, 1099.02, 1038.74, 927.15 cm^{-1} . HRMS (ESI): m/z calcd for $\text{C}_{19}\text{H}_{13}\text{F}_3\text{N}$ $[\text{M}+\text{H}]^+$ 312.1000, found 312.0995.



6-(2,2,2-Trifluoroethyl)benzo[k]phenanthridine (5k): yellow solid, yield: 56%. ^1H NMR (400 MHz, CDCl_3): δ 9.10 – 9.02 (m, 1H), 8.96 (d, $J = 8.4$ Hz, 1H), 8.29 (dd, $J = 8.2, 1.0$ Hz, 1H), 8.08 – 7.93 (m, 3H), 7.83 – 7.61 (m, 4H), 4.26 (q, $J = 10.3$ Hz, 2H); ^{13}C NMR (100 MHz, CDCl_3): δ 150.12 (q, $J = 3.1$ Hz), 145.41, 134.59, 132.57, 130.00, 128.97, 128.67, 128.63, 128.57, 128.15, 127.13, 127.08, 127.05, 125.51 (q, $J = 274.4$ Hz), 124.25, 122.24, 122.23, 40.74 (q, $J = 29.1$ Hz); ^{19}F NMR (376 MHz,

CDCl₃) δ -62.55. FTIR (film) $\nu_{\max}$ 1600.00, 1563.55, 1476.64, 1389.72, 1356.41, 1274.77, 1254.86, 1140.88, 1106.82, 1070.00, 934.78, 842.31 cm⁻¹. HRMS (ESI): m/z calcd for C₁₉H₁₃F₃N [M+H]⁺ 312.1000, found 312.0995.

1. Wang, Y.-F.; Lonca, G. H.; Le Runigo, M.; Chiba, S. *Org. Lett.* **2014**, *16*, 4272.

5. NMR Spectra for All Compounds.

