

Synthesis of 6-(sulfonylmethyl)phenanthridines through a reaction of aryldiazonium tetrafluoroborates, sulfur dioxide, and vinyl azides

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Supporting Information

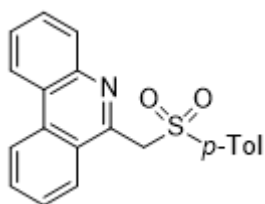
1. General experimental methods (S2).
2. General experimental procedure and characterization data (S2-S10).
3. ¹H and ¹³C NMR spectra of compounds **3** (S11–S46).

General experimental methods:

Unless otherwise stated, all commercial reagents were used as received. All solvents were dried and distilled according to standard procedures. Flash column chromatography was performed using silica gel (60-Å pore size, 32–63µm, standard grade). Analytical thin-layer chromatography was performed using glass plates pre-coated with 0.25 mm 230–400 mesh silica gel impregnated with a fluorescent indicator (254 nm). Thin layer chromatography plates were visualized by exposure to ultraviolet light. Organic solutions were concentrated on rotary evaporators at ~20 Torr at 30–35°C. Nuclear magnetic resonance (NMR) spectra are recorded in parts per million(ppm) from internal tetramethylsilane on the δ scale. ^1H and ^{13}C NMR spectra were recorded in CDCl_3 or $\text{DMSO}-d_6$ on a Bruker DRX-400 spectrometer operating at 400 MHz and 100 MHz, respectively. All chemical shift values are quoted in ppm and coupling constants quoted in Hz. High resolution mass spectrometry (HRMS) spectra were obtained on a micrOTOF II Instrument.

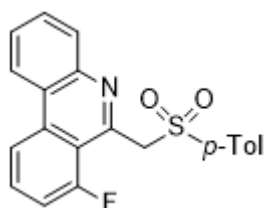
*General experimental procedure for the reaction of 2-(1-azidovinyl)-1,1'-biphenyls **1**, aryldiazonium tetrafluoroborates **2** and $\text{DABCO}\cdot(\text{SO}_2)_2$*

2-(1-Azidovinyl)-1,1'-biphenyl **1** (0.20 mmol) was added to a mixture of aryldiazonium tetrafluoroborate **2** (0.30 mmol) and $\text{DABCO}\cdot(\text{SO}_2)_2$ (0.30 mmol) in MeCN (2.0 mL) under N_2 atmosphere. The suspension is stirred at 20 °C for 16 hours. After the conversion was completed as indicated by TLC, the solvent was evaporated under reduced pressure. The residue was purified directly by flash column chromatography to afford the corresponding product **3**.



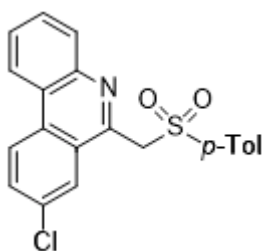
6-(Tosylmethyl)phenanthridine (**3a**)^[1]

¹H NMR (400 MHz, Chloroform-*d*) δ 8.63 (d, *J* = 8.3 Hz, 1H), 8.57 – 8.47 (m, 1H), 8.34 (d, *J* = 8.3 Hz, 1H), 7.85 (d, *J* = 6.7 Hz, 2H), 7.77 – 7.63 (m, 3H), 7.58 (d, *J* = 7.9 Hz, 2H), 7.19 (d, *J* = 7.9 Hz, 2H), 5.16 (s, 2H), 2.38 (s, 3H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 149.8, 144.7, 143.2, 135.5, 133.1, 130.9, 129.9, 129.4, 128.7, 127.6, 127.0, 125.6, 124.0, 122.2, 122.0, 62.6, 21.6.



7-Fluoro-6-(tosylmethyl)phenanthridine (**3b**)

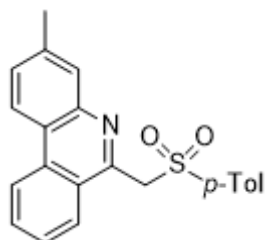
¹H NMR (400 MHz, Chloroform-*d*) δ 8.55 – 8.51 (m, 1H), 8.46 (d, *J* = 8.2 Hz, 1H), 7.91 – 7.87 (m, 1H), 7.81 (td, *J* = 8.1, 5.3 Hz, 1H), 7.76 – 7.68 (m, 2H), 7.57 (d, *J* = 8.3 Hz, 2H), 7.40 – 7.38 (m, 1H), 7.20 (d, *J* = 8.0 Hz, 2H), 5.33 (s, 2H), 2.41 (s, 3H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 159.8 (d, ¹*J*_{CF} = 255.5 Hz), 146.2 (d, ⁴*J*_{CF} = 5.5 Hz), 144.4, 143.2, 136.3, 135.6, 131.5 (d, ³*J*_{CF} = 10.2 Hz), 130.0, 129.4, 128.6, 128.2, 122.8 (d, ⁴*J*_{CF} = 3.2 Hz), 122.4, 118.5 (d, ⁴*J*_{CF} = 4.0 Hz), 115.8 (d, ³*J*_{CF} = 11.6 Hz), 114.0 (d, ²*J*_{CF} = 24.7 Hz), 65.7 (d, ³*J*_{CF} = 13.2 Hz), 21.6. HRMS (ESI) calcd for C₂₁H₁₇FNO₂S⁺: 366.0959 (M + H⁺), found: 366.0951.



8-Chloro-6-(tosylmethyl)phenanthridine (**3c**)^[1]

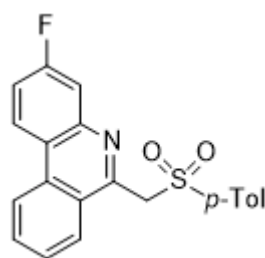
¹H NMR (400 MHz, Chloroform-*d*) δ 8.54 (d, *J* = 8.9 Hz, 1H), 8.51 – 8.46 (m, 1H), 8.15 (d, *J* = 2.0 Hz, 1H), 7.93 – 7.87 (m, 1H), 7.77 (dd, *J* = 8.8, 2.1 Hz, 1H), 7.74 – 7.66 (m, 2H), 7.57 (d, *J* = 8.3 Hz, 2H), 7.20 (d, *J* = 8.0 Hz, 2H), 5.09 (s, 2H), 2.40 (s, 3H). ¹³C NMR

(101 MHz, Chloroform-*d*) δ 148.7, 145.0, 143.2, 135.4, 133.6, 131.5, 131.4, 130.1, 129.6, 129.1, 128.7, 128.1, 126.4, 126.1, 124.0, 123.4, 121.8, 62.5, 21.6.



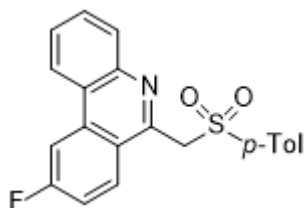
3-Methyl-6-(tosylmethyl)phenanthridine (**3d**)^[1]

¹H NMR (400 MHz, Chloroform-*d*) δ 8.58 (d, J = 8.3 Hz, 1H), 8.42 (d, J = 8.4 Hz, 1H), 8.30 (d, J = 8.2 Hz, 1H), 7.83 (t, J = 8.2 Hz, 1H), 7.71 – 7.65 (m, 2H), 7.58 (d, J = 8.2 Hz, 2H), 7.49 (d, J = 8.4 Hz, 1H), 7.19 (d, J = 8.0 Hz, 2H), 5.14 (s, 2H), 2.55 (s, 3H), 2.38 (s, 3H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 149.6, 144.7, 143.3, 139.0, 135.6, 133.2, 130.9, 129.5, 129.3, 128.7, 127.2, 127.0, 125.3, 122.1, 121.7, 121.7, 62.6, 21.6, 21.5.



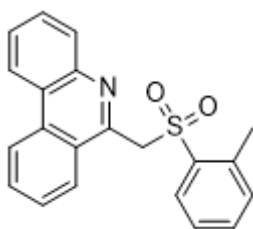
3-Fluoro-6-(tosylmethyl)phenanthridine (**3e**)^[1]

¹H NMR (400 MHz, Chloroform-*d*) δ 8.55 (d, J = 8.3 Hz, 1H), 8.53 – 8.49 (m, 1H), 8.35 (d, J = 8.2 Hz, 1H), 7.91 – 7.83 (m, 1H), 7.72 (t, J = 8.2 Hz, 1H), 7.57 (d, J = 8.3 Hz, 2H), 7.50 – 7.37 (m, 2H), 7.20 (d, J = 8.0 Hz, 2H), 5.13 (s, 2H), 2.40 (s, 3H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 162.5 (d, ¹ J_{CF} = 249.6 Hz), 151.2, 144.8, 144.4 (d, ³ J_{CF} = 11.9 Hz), 135.4, 133.0, 131.3, 129.5, 128.6, 127.5, 127.2, 125.2, 124.0 (d, ³ J_{CF} = 9.6 Hz), 123.9, 122.1, 120.7, 116.8 (d, ² J_{CF} = 23.9 Hz), 114.2 (d, ² J_{CF} = 20.6 Hz), 62.6, 21.6.



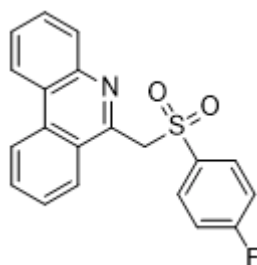
9-Fluoro-6-(tosylmethyl)phenanthridine (**3f**)^[1].

¹H NMR (400 MHz, Chloroform-*d*) δ 8.47 – 8.39 (m, 2H), 8.24 (dd, *J* = 10.2, 2.5 Hz, 1H), 7.88 – 7.81 (m, 1H), 7.74 - 7.67 (m, 2H), 7.57 (d, *J* = 8.3 Hz, 2H), 7.51 – 7.46 (m, 1H), 7.21 (d, *J* = 7.9 Hz, 2H), 5.13 (s, 2H), 2.40 (s, 3H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 163.9 (d, ¹*J*_{CF} = 254.1 Hz), 149.2, 144.8, 143.5, 135.7(d, ³*J*_{CF} = 9.5 Hz), 135.4, 130.2(d, ³*J*_{CF} = 9.7 Hz), 130.0, 129.5, 129.4, 128.6, 127.7, 123.6(d, ⁴*J*_{CF} = 4.5 Hz), 122.7, 122.2, 116.9(d, ²*J*_{CF} = 24.0 Hz), 107.4(d, ²*J*_{CF} = 22.4 Hz), 62.8, 21.6.



6-((*o*-Tolylsulfonyl)methyl)phenanthridine (**3g**).

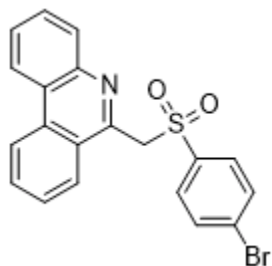
¹H NMR (400 MHz, Chloroform-*d*) δ 8.60 (d, *J* = 8.3 Hz, 1H), 8.54 – 8.48 (m, 1H), 8.37 (d, *J* = 8.0 Hz, 1H), 7.85 (t, *J* = 7.1 Hz, 1H), 7.82 – 7.78 (m, 1H), 7.73 (t, *J* = 7.7 Hz, 1H), 7.69 – 7.61 (m, 3H), 7.41 (t, *J* = 6.9 Hz, 1H), 7.26 (d, *J* = 7.6 Hz, 1H), 7.11 (t, *J* = 7.6 Hz, 1H), 5.20 (s, 2H), 2.62 (s, 3H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 149.6, 143.2, 138.9, 136.6, 133.6, 133.1, 132.4, 130.9, 130.4, 129.9, 128.7, 127.7, 127.6, 127.0, 126.3, 125.6, 123.9, 122.3, 121.9, 62.1, 20.6. HRMS (ESI) calcd for C₂₁H₁₈NO₂S⁺: 348.1053 (M + H⁺), found: 348.1050.



6-(((4-Fluorophenyl)sulfonyl)methyl)phenanthridine (**3h**).

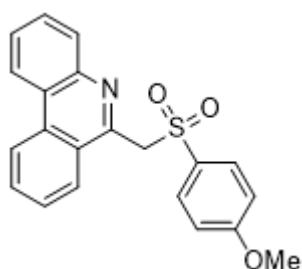
¹H NMR (400 MHz, Chloroform-*d*) δ 8.62 (d, *J* = 8.3 Hz, 1H), 8.55 – 8.50 (m, 1H), 8.33 (d, *J* = 8.3 Hz, 1H), 7.86 (t, *J* = 7.7 Hz, 1H), 7.82 – 7.76 (m, 1H), 7.73 (t, *J* = 7.7 Hz, 1H), 7.69 – 7.62 (m, 4H), 7.04 (t, *J* = 8.6 Hz, 2H), 5.16 (s, 2H). ¹³C NMR (101 MHz,

Chloroform-*d*) δ 165.8 (d, $^1J_{\text{CF}} = 257.2$ Hz), 149.5, 143.1, 134.2, 133.2, 131.7 (d, $^3J_{\text{CF}} = 9.8$ Hz), 129.8, 128.9, 127.8 (d, $^4J_{\text{CF}} = 6.1$ Hz), 126.9, 125.4, 124.0, 122.4, 122.0, 116.1 (d, $^2J_{\text{CF}} = 22.8$ Hz), 62.5. HRMS (ESI) calcd for $\text{C}_{20}\text{H}_{15}\text{FNO}_2\text{S}^+$: 352.0802 ($\text{M} + \text{H}^+$), found: 352.0802.



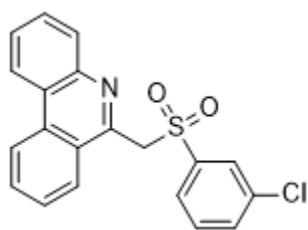
6-(((4-Bromophenyl)sulfonyl)methyl)phenanthridine (**3i**)

^1H NMR (400 MHz, Chloroform-*d*) δ 8.65 (d, $J = 8.3$ Hz, 1H), 8.59 – 8.50 (m, 1H), 8.33 (d, $J = 8.2$ Hz, 1H), 7.89 (t, $J = 7.7$ Hz, 1H), 7.82 – 7.78 (m, 1H), 7.75 (t, $J = 7.7$ Hz, 1H), 7.72 – 7.65 (m, 2H), 7.51 (s, 4H), 5.16 (s, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 149.3, 143.1, 137.2, 133.2, 132.1, 131.1, 130.3, 129.8, 129.1, 128.9, 127.9, 127.8, 126.8, 125.5, 124.0, 122.4, 122.0, 62.4. HRMS (ESI) calcd for $\text{C}_{20}\text{H}_{15}\text{BrNO}_2\text{S}^+$: 412.0002 ($\text{M} + \text{H}^+$), found: 412.0002.



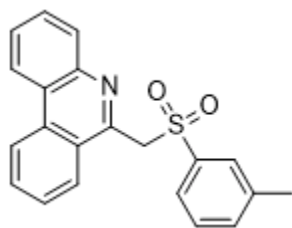
6-(((4-Methoxyphenyl)sulfonyl)methyl)phenanthridine (**3j**).

^1H NMR (400 MHz, DMSO-*d*₆) δ 8.87 (d, $J = 8.3$ Hz, 1H), 8.80 (d, $J = 7.3$ Hz, 1H), 8.45 (d, $J = 8.2$ Hz, 1H), 7.95 (t, $J = 7.6$ Hz, 1H), 7.89 – 7.82 (m, 1H), 7.79 – 7.72 (m, 3H), 7.64 (d, $J = 8.9$ Hz, 2H), 7.04 (d, $J = 8.9$ Hz, 2H), 5.42 (s, 2H), 3.82 (s, 3H). ^{13}C NMR (101 MHz, DMSO-*d*₆) δ 163.8, 150.9, 143.2, 132.9, 131.6, 130.9, 130.9, 129.8, 129.4, 128.2, 128.0, 125.7, 125.6, 123.9, 123.1, 122.9, 114.7, 61.8, 56.2. HRMS (ESI) calcd for $\text{C}_{21}\text{H}_{18}\text{NO}_3\text{S}^+$: 364.1002 ($\text{M} + \text{H}^+$), found: 364.1007.



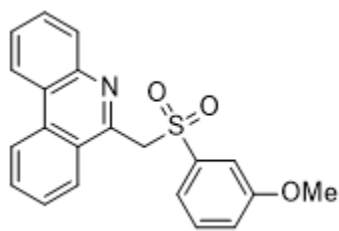
6-(((3-Chlorophenyl)sulfonyl)methyl)phenanthridine (**3k**).

^1H NMR (400 MHz, Chloroform-*d*) δ 8.68 (d, J = 8.3 Hz, 1H), 8.61 – 8.54 (m, 1H), 8.36 (d, J = 8.6 Hz, 1H), 7.91 (t, J = 7.3 Hz, 1H), 7.84 – 7.75 (m, 2H), 7.71 – 7.69 (m, 3H), 7.55 – 7.51 (m, 2H), 7.32 (t, J = 8.0 Hz, 1H), 5.20 (s, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 149.2, 143.1, 139.9, 135.1, 133.8, 133.2, 131.1, 130.0, 129.8, 128.9, 128.9, 127.9, 127.8, 126.9, 126.8, 125.4, 124.0, 122.4, 122.0, 62.3. HRMS (ESI) calcd for $\text{C}_{20}\text{H}_{14}\text{ClNO}_2\text{S}^+$: 368.0507 ($\text{M} + \text{H}^+$), found: 368.0511.



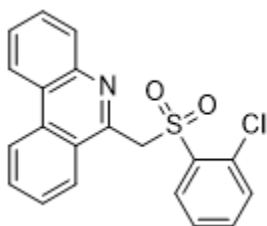
6-((*m*-Tolylsulfonyl)methyl)phenanthridine (**3l**).

^1H NMR (400 MHz, Chloroform-*d*) δ 8.62 (d, J = 8.3 Hz, 1H), 8.57 – 8.49 (m, 1H), 8.34 (d, J = 8.1 Hz, 1H), 7.89 – 7.83 (m, 2H), 7.75 – 7.69 (m, 1H), 7.69 – 7.62 (m, 2H), 7.51 (d, J = 7.7 Hz, 1H), 7.45 (s, 1H), 7.35 (d, J = 7.6 Hz, 1H), 7.29 (d, J = 7.7 Hz, 1H), 5.17 (s, 2H), 2.23 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 149.7, 143.2, 139.1, 138.1, 134.4, 133.1, 131.0, 129.8, 129.1, 128.7, 128.7, 127.7, 127.7, 127.0, 125.7, 125.6, 124.0, 122.3, 122.0, 62.5, 21.0. HRMS (ESI) calcd for $\text{C}_{21}\text{H}_{18}\text{NO}_2\text{S}^+$: 348.1053 ($\text{M} + \text{H}^+$), found: 348.1052.



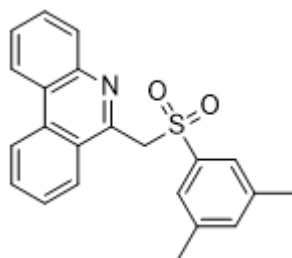
6-(((3-Methoxyphenyl)sulfonyl)methyl)phenanthridine (**3m**).

^1H NMR (400 MHz, Chloroform-*d*) δ 8.66 (d, J = 8.3 Hz, 1H), 8.59 – 8.54 (m, 1H), 8.35 (d, J = 8.2 Hz, 1H), 7.93 – 7.84 (m, 2H), 7.75 (t, J = 7.7 Hz, 1H), 7.72 – 7.66 (m, 1H), 7.32 (dd, J = 4.7, 2.1 Hz, 2H), 7.09 (dd, J = 7.9, 2.5 Hz, 2H), 5.19 (s, 2H), 3.57 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 159.7, 149.7, 143.2, 139.4, 133.1, 131.0, 129.9, 129.9, 128.8, 127.7, 127.7, 126.9, 125.6, 124.0, 122.3, 122.0, 120.9, 120.9, 112.6, 62.6, 55.4. HRMS (ESI) calcd for $\text{C}_{21}\text{H}_{18}\text{NO}_3\text{S}^+$: 364.1002 ($\text{M} + \text{H}^+$), found: 364.0999.



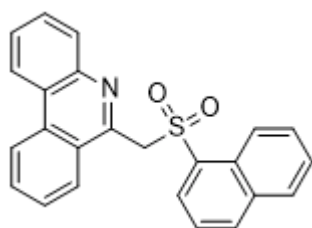
6-(((2-Chlorophenyl)sulfonyl)methyl)phenanthridine (**3n**).

^1H NMR (400 MHz, Chloroform-*d*) δ 8.63 (d, J = 8.2 Hz, 1H), 8.57 – 8.49 (m, 1H), 8.41 (d, J = 8.2 Hz, 1H), 7.87 (t, J = 8.0 Hz, 1H), 7.78 – 7.72 (m, 3H), 7.68 – 7.59 (m, 3H), 7.51 (td, J = 7.7, 1.5 Hz, 1H), 7.21 (t, J = 8.0 Hz, 1H), 5.45 (s, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 149.3, 143.2, 136.2, 134.6, 133.5, 133.1, 131.9, 131.7, 130.9, 130.0, 128.6, 127.8, 127.7, 127.0, 126.8, 125.7, 123.9, 122.3, 121.9, 59.9. HRMS (ESI) calcd for $\text{C}_{20}\text{H}_{14}\text{ClNO}_2\text{S}^+$: 368.0507 ($\text{M} + \text{H}^+$), found: 368.0504.



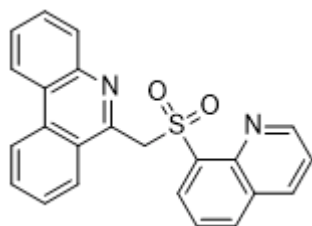
6-(((3,5-Dimethylphenyl)sulfonyl)methyl)phenanthridine (**3o**).

^1H NMR (400 MHz, Chloroform-*d*) δ 8.60 (d, $J = 8.3$ Hz, 1H), 8.56 – 8.49 (m, 1H), 8.31 (d, $J = 8.2$ Hz, 1H), 7.90 – 7.81 (m, 2H), 7.74 – 7.62 (m, 3H), 7.26 (s, 2H), 7.14 (s, 1H), 5.14 (s, 2H), 2.18 (s, 6H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 149.8, 143.2, 138.9, 138.0, 135.3, 133.1, 130.9, 129.8, 128.7, 127.7, 127.6, 127.0, 126.2, 125.6, 124.0, 122.2, 122.0, 62.6, 20.9. HRMS (ESI) calcd for $\text{C}_{22}\text{H}_{20}\text{NO}_2\text{S}^+$: 362.1209 ($\text{M} + \text{H}^+$), found: 362.1212.



6-((Naphthalen-1-ylsulfonyl)methyl)phenanthridine (**3p**).

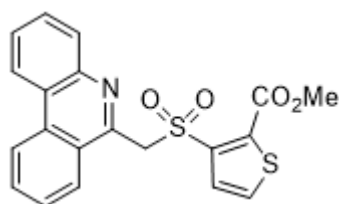
^1H NMR (400 MHz, Chloroform-*d*) δ 8.77 – 8.69 (m, 1H), 8.57 (d, $J = 8.3$ Hz, 1H), 8.51 – 8.44 (m, 1H), 8.28 (d, $J = 8.2$ Hz, 1H), 8.04 (d, $J = 7.7$ Hz, 2H), 7.92 – 7.87 (m, 1H), 7.82 (t, $J = 8.2$ Hz, 1H), 7.69 – 7.57 (m, 4H), 7.54 – 7.48 (m, 2H), 7.37 (t, $J = 7.8$ Hz, 1H), 5.34 (s, 2H). ^{13}C NMR (101 MHz, CDCl_3) δ 149.5, 143.1, 135.3, 134.0, 133.8, 133.1, 131.2, 130.9, 129.8, 129.5, 128.9, 128.6, 128.5, 127.6, 127.6, 126.7, 126.7, 125.6, 124.1, 123.9, 122.2, 121.8, 62.3. HRMS (ESI) calcd for $\text{C}_{24}\text{H}_{18}\text{NO}_2\text{S}^+$: 384.1053 ($\text{M} + \text{H}^+$), found: 384.1053.



6-((Quinolin-8-ylsulfonyl)methyl)phenanthridine (**3q**).

^1H NMR (400 MHz, Chloroform-*d*) δ 9.27 (dd, $J = 4.2, 1.7$ Hz, 1H), 8.69 (d, $J = 8.1$ Hz, 1H), 8.61 (d, $J = 8.2$ Hz, 1H), 8.54 – 8.47 (m, 1H), 8.37 – 8.30 (m, 2H), 8.10 (d, $J = 8.2$ Hz, 1H), 7.86 (t, $J = 7.6$ Hz, 1H), 7.77 (t, $J = 7.6$ Hz, 1H), 7.69 – 7.51 (m, 5H), 5.94 (s, 2H). ^{13}C NMR (101 MHz, CDCl_3) δ 151.6, 150.1, 144.6, 143.3, 136.7, 136.2, 134.4, 133.1, 132.4, 130.8, 129.9, 128.9, 128.5, 127.7, 127.5, 127.4, 126.1, 125.5, 124.0,

122.2, 122.2, 121.9, 61.2. HRMS (ESI) calcd for $C_{23}H_{17}N_2O_2S^+$: 385.1005 ($M + H^+$), found: 385.1004.



Methyl 3-((phenanthridin-6-ylmethyl)sulfonyl)thiophene-2-carboxylate (**3r**).

1H NMR (400 MHz, Chloroform-*d*) δ 8.64 (d, $J = 8.2$ Hz, 1H), 8.58 – 8.50 (m, 2H), 7.93 – 7.85 (m, 2H), 7.82 – 7.75 (m, 1H), 7.71 – 7.63 (m, 2H), 7.34 (d, $J = 5.2$ Hz, 1H), 7.26 (d, $J = 5.2$ Hz, 1H), 5.69 (s, 2H), 4.06 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.4, 149.6, 143.3, 142.8, 135.0, 133.1, 131.6, 130.9, 130.0, 129.3, 128.7, 127.8, 127.6, 127.1, 125.8, 124.0, 122.2, 121.9, 60.4, 53.2. HRMS (ESI) calcd for $C_{20}H_{16}NO_4S_2^+$: 398.0515 ($M + H^+$), found: 398.0515.

[1] X. Bi et al. *Org. Lett.* **2017**, *19*, 4026-4029.

