Supporting Information

TBPB-initiated Cascade Cyclization of 3-Arylethynyl-[1,1'-biphenyl]-2-carbonitriles with Sulfinic Acids: Access to Sulfone-Containing Cyclopenta[gh]phenantridines

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General Information:

All reactions were carried out under Ar atmosphere unless otherwise noted. All catalysts and solvents were obtained from commercial suppliers. Reactions were monitored by TLC on silica gel plates (GF254), and the analytical thin-layer chromatography (TLC) was performed on precoated, glass-backed silica gel plates. Sulfinic acids 2a–2g were synthesized according to the literature. [1] ¹H NMR and ¹³C NMR spectra were recorded on 500 MHz spectrometer at room temperature. ¹⁹F NMR spectra was recorded on 400 MHz spectrometer at room temperature. Chemical shifts (δ) are reported in ppm downfield from tetramethylsilane. High resolution mass spectra were obtained on a high–resolution mass spectrometer in the ESI mode.

General Procedure for the Synthesis of 1.[2]

![Chemical structure diagram]

Step I: Substituted phenylboronic acid (6 mmol), 2-amino-6-bromobenzonitrile (5 mmol), PdCl₂(PPh₃)₂ (35.0 mg, 0.05 mmol) and Cs₂CO₃ (4.89 g, 15.0 mmol) were added in CH₃CN (20 mL) and H₂O (1.6 mL). The reaction mixture was stirred at 80 °C under argon atmosphere for 12 h. After the reaction was finished, the mixture was cooled to room temperature and extracted with EtOAc (40 × 3 mL). The combined organic phase was washed with brine (40 mL), dried over anhydrous MgSO₄. The solvent was removed under vacuum to give the crude products C without further purification.

Step II: To a solution of C, NaNO₂ (3 equiv) and KI (3 equiv) in MeCN (30 mL) at 0 °C was added cold concd HCl (12 equiv) drop wise. The reaction mixture was stirred at 0 °C for 30 min. Then, the reaction was allowed to warm to room temperature and monitored by TLC. After the reaction was finished, the solvent was removed under vacuum to give the crude products D without further purification.

Step III: To a solution of D, PdCl₂(PPh₃)₂ (2 mol%), and Cul (2 mol%) in NEt₃ (0.25 M) was added
acetylene (1.2 equiv). The resulting mixture was heated under Ar atmosphere at 50 °C for 6-18 hours. After the reaction was finished, the crude mixture was purified by silica gel column chromatography to give the desired products 1.

3-(phenylethynyl)-[1,1'-biphenyl]-2-carbonitrile (1a). Grey solid (57% yield for three steps); mp: 96-98 °C; Rf = 0.52 (petroleum ether/ethyl acetate 10:1); 1H NMR (500 MHz, CDCl3): δ = 7.66-7.57 (m, 6H), 7.53-7.43 (m, 4H), 7.40-7.38 (m, 3H) ppm; 13C NMR (126 MHz, CDCl3): δ 146.6, 138.4, 132.5, 131.1, 129.8, 129.6, 129.3, 129.2, 129.1, 128.8, 122.5, 117.5, 114.5, 96.3, 86.5 ppm. ESI-HRMS: m/z Calcd for C21H13N [M+H+]: 279.1048, found 279.1045.

Grey solid (55% yield for three steps); mp: 95-97 °C; Rf = 0.52 (petroleum ether/ethyl acetate 10:1); 1H NMR (500 MHz, CDCl3): δ = 7.65-7.63 (m, 2H), 7.61-7.56 (m, 2H), 7.47 (d, J = 8.0 Hz, 2H), 7.44-7.42 (m, 1H), 7.40-7.37 (m, 3H), 7.31 (d, J = 8.0 Hz, 2H), 2.43 (s, 3H) ppm; 13C NMR (126 MHz, CDCl3): δ 146.7, 139.3, 135.5, 132.5, 130.9, 129.9, 129.8, 129.6, 129.0, 128.833, 128.760, 122.6, 117.7, 114.4, 96.2, 86.6, 21.7 ppm. ESI-HRMS: m/z Calcd for C22H16N [M+H+]: 294.1277, found 294.1276.

4'-methoxy-3-(phenylethynyl)-[1,1'-biphenyl]-2-carbonitrile (1c). Grey solid (49% yield for three steps); mp: 88-89 °C; Rf = 0.52 (petroleum ether/ethyl acetate 10:1); 1H NMR (500 MHz, CDCl3): δ = 7.65-7.63 (m, 2H), 7.59-7.56 (m, 2H), 7.54-7.51 (m, 2H), 7.42-7.41 (m, 1H), 7.39-7.37 (m, 3H), 7.04-7.02 (m, 2H), 3.87 (s, 3H) ppm; 13C NMR (126 MHz, CDCl3): δ 160.6, 146.3, 132.450,
132.422, 130.7, 130.6, 130.4, 129.7, 129.6, 128.825, 128.775, 122.6, 117.8, 114.6, 114.2, 96.2, 86.6, 55.8 ppm. ESI-HRMS: m/z Calcd for C_{22}H_{16}NO [M+H^{+}]: 310.1226, found 310.1228.

[Diagram]

4'-(tert-butyl)-3-(phenylethynyl)-[1,1'-biphenyl]-2-carbonitrile (1d). Grey solid (51% yield for three steps); mp: 96-98 °C; R_f = 0.52 (petroleum ether/ethyl acetate 10:1); ¹H NMR (500 MHz, CDCl₃): δ = 7.66-7.64 (m, 2H), 7.60-7.56 (m, 2H), 7.54-7.51 (m, 4H), 7.45-7.43 (m, 1H), 7.40-7.36 (m, 3H), 1.38 (s, 9H) ppm; ¹³C NMR (126 MHz, CDCl₃): δ 152.4, 146.5, 133.4, 132.523, 132.465, 130.9, 129.9, 129.6, 128.8, 126.1, 122.6, 117.7, 114.2, 96.2, 86.7, 35.1, 31.7 ppm. ESI-HRMS: m/z Calcd for C_{25}H_{22}N [M+H^{+}]: 336.1747, found 336.1744.

[Diagram]

2'-methyl-3-(phenylethynyl)-[1,1'-biphenyl]-2-carbonitrile (1e). Grey solid (49% yield for three steps); mp: 91-93 °C; R_f = 0.52 (petroleum ether/ethyl acetate 10:1); ¹H NMR (500 MHz, CDCl₃): δ = 7.64-7.62 (m, 3H), 7.59 (d, J = 7.5 Hz, 1H), 7.34-7.28 (m, 3H), 7.23-7.21 (m, 1H), 2.22 (s, 3H) ppm; ¹³C NMR (126 MHz, CDCl₃): δ 146.9, 138.2, 136.0, 132.4, 132.2, 131.1, 130.9, 130.2, 129.7, 129.6, 129.3, 128.8, 128.1, 126.3, 122.5, 117.0, 116.0, 96.3, 86.4, 21.7 ppm. ESI-HRMS: m/z Calcd for C_{22}H_{16}N [M+H^{+}]: 294.1277, found 294.1274.

[Diagram]

3'-methyl-3-(phenylethynyl)-[1,1'-biphenyl]-2-carbonitrile (1f). Grey solid (46% yield for three steps); mp: 94-96 °C; R_f = 0.52 (petroleum ether/ethyl acetate 10:1); ¹H NMR (500 MHz, CDCl₃): δ = 7.66-7.64 (m, 2H), 7.62-7.56 (m, 2H), 7.44-7.41 (m, 1H), 7.40-7.37 (m, 6H), 7.28 (d, J = 6.0 Hz, 1H), 2.45 (s, 3H) ppm; ¹³C NMR (126 MHz, CDCl₃): δ 146.8, 138.8, 138.3, 132.5, 132.4, 131.0, 129.9, 129.8, 129.6, 129.0, 128.840, 128.760, 126.3, 122.6, 117.6, 114.5, 96.3, 86.6 ppm. ESI-
HRMS: m/z Calcd for C$_{22}$H$_{16}$N [M+H$^+$]: 294.1277, found 294.1281.

3-(phenylethynyl)-[1,1′:4′,1″-terphenyl]-2-carbonitrile (Ig). Grey solid (46% yield for three steps); mp: 93-95 ºC; $R_f$ = 0.52 (petroleum ether/ethyl acetate 10:1); $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ = 7.75-7.72 (m, 2H), 7.68-7.56 (m, 8H), 7.52-7.44 (m, 4H), 7.41-7.38 (m, 3H) ppm; $^{13}$C NMR (126 MHz, CDCl$_3$): $\delta$ 146.2, 142.2, 140.7, 137.2, 132.537, 132.479, 131.1, 129.8, 129.6, 129.3, 128.9, 128.1, 127.9, 127.6, 122.5, 117.6, 114.4, 96.4, 86.5 ppm. ESI-HRMS: m/z Calcd for C$_{27}$H$_{18}$ClN [M+H$^+$]: 356.1434, found 356.1431.

4′-fluoro-3-(phenylethynyl)-[1,1′-biphenyl]-2-carbonitrile (Ih). Grey solid (48% yield for three steps); mp: 92-94 ºC; $R_f$ = 0.52 (petroleum ether/ethyl acetate 10:1); $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ = 7.65-7.58 (m, 4H), 7.56-7.50 (m, 2H), 7.42-7.36 (m, 4H), 7.22-7.17 (m, 2H) ppm; $^{13}$C NMR (126 MHz, CDCl$_3$): $\delta$ 165.9 (d, $J$ = 249 Hz), 145.6, 134.4 (d, $J$ = 4 Hz), 132.6, 132.5, 131.7, 131.0 (d, $J$ = 9 Hz), 129.7, 128.905, 128.861, 122.4, 117.4, 116.2 (d, $J$ = 42 Hz), 114.5, 96.5, 86.4 ppm. $^{19}$F NMR (376 MHz, CDCl$_3$): $\delta$ -112.5 ppm. ESI-HRMS: m/z Calcd for C$_{21}$H$_{13}$FN [M+H$^+$]: 298.1027, found 298.1031.

4′-chloro-3-(phenylethynyl)-[1,1′-biphenyl]-2-carbonitrile (II). Grey solid (53% yield for three steps); mp: 101-102 ºC; $R_f$ = 0.52 (petroleum ether/ethyl acetate 10:1); $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ = 7.64-7.58 (m, 4H), 7.52-7.47 (m, 4H), 7.41-7.38 (m, 4H) ppm; $^{13}$C NMR (126 MHz, CDCl$_3$): $\delta$ 145.3, 136.7, 135.6, 132.6, 132.5, 131.4, 130.5, 129.7, 129.6, 129.4, 129.0, 128.9, 122.4, 117.3,
114.4, 96.6, 86.3 ppm. ESI-HRMS: m/z Calcd for C_{21}H_{13}ClN [M+H^+]: 310.1226, found 310.1228.

![Image](image-url)

3',5'-dimethyl-3-(phenylethynyl)-[1,1'-biphenyl]-2-carbonitrile (Ij). Grey solid (53% yield for three steps); mp: 87-89 °C; R_f = 0.52 (petroleum ether/ethyl acetate 10:1); ^1H NMR (500 MHz, CDCl_3): δ = 7.65-7.63 (m, 4H), 7.61-7.55 (m, 1H), 7.43-7.41 (m, 1H), 7.39-7.37 (m, 3H), 7.18 (s, 2H), 7.10 (s, 1H), 2.40 (s, 6H) ppm; ^13C NMR (126 MHz, CDCl_3): δ 147.0, 138.8, 138.3, 132.4, 132.3, 130.9, 130.8, 129.8, 129.6, 128.8, 128.7, 127.0, 122.6, 117.6, 114.5, 96.2, 86.7, 21.7 ppm. ESI-HRMS: m/z Calcd for C_{23}H_{18}N [M+H^+]: 308.1434, found 308.1432.

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3',5'-dichloro-3-(phenylethynyl)-[1,1'-biphenyl]-2-carbonitrile (Ik). Grey solid (46% yield for three steps); mp: 105-106 °C; R_f = 0.52 (petroleum ether/ethyl acetate 10:1); ^1H NMR (500 MHz, CDCl_3): δ = 7.67-7.60 (m, 4H), 7.47-7.46 (m, 1H), 7.44 (d, J = 1.5 Hz, 2H), 7.41-7.38 (m, 4H) ppm; ^13C NMR (126 MHz, CDCl_3): δ 143.7, 141.1, 135.8, 132.7, 132.5, 132.0, 129.8, 129.42, 129.40, 129.2, 128.9, 127.7, 122.3, 116.8, 114.5, 97.1, 86.1 ppm. ESI-HRMS: m/z Calcd for C_{21}H_{12}Cl_2N [M+H^+] : 347.0269, found 347.0266.

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2-(naphthalen-1-yl)-6-(phenylethynyl)benzonitrile (II). Grey solid (52% yield for three steps); mp: 96-98 °C; R_f = 0.52 (petroleum ether/ethyl acetate 10:1); ^1H NMR (500 MHz, CDCl_3): δ = 7.98-7.94 (m, 2H), 7.73-7.64 (m, 4H), 7.61-7.46 (m, 7H), 7.39-7.37 (m, 2H) ppm; ^13C NMR (126 MHz, CDCl_3): δ 145.5, 136.0, 134.1, 132.5, 132.1, 131.7, 131.4, 131.2, 130.0, 129.8, 129.6, 129.0, 128.9, 128.5, 127.9, 127.1, 126.6, 125.6, 125.5, 122.5, 116.9, 116.8, 96.5, 86.4 ppm. ESI-HRMS: m/z Calcd for C_{25}H_{16}N [M+H^+] : 330.1277, found 330.1278.
2-(naphthalen-2-yl)-6-(phenylethynyl)benzonitrile (1m). Grey solid (52% yield for three steps); mp: 103-105 °C; \( R_f = 0.52 \) (petroleum ether/ethyl acetate 10:1); \(^1\)H NMR (500 MHz, CDCl\(_3\)): \( \delta = 8.06-7.97 \) (m, 2H), 7.94-7.90 (m, 2H), 7.70-7.61 (m, 5H), 7.57-7.53 (m, 3H), 7.40-7.38 (m, 3H) ppm; \(^{13}\)C NMR (126 MHz, CDCl\(_3\)): \( \delta = 146.6, 135.7, 133.6, 133.5, 132.530, 132.486, 131.1, 130.0, 129.6, 129.0, 128.926, 128.854, 128.8, 128.2, 127.3, 127.1, 126.6, 122.5, 117.6, 114.7, 96.4, 86.6 \) ppm. ESI-HRMS: m/z Calcd for C\(_{25}\)H\(_{16}\)N [M+H\(^+\)]: 330.1277, found 330.1275.

2-(phenylethynyl)-6-(thiophen-2-yl)benzonitrile (1n). Grey solid (46% yield for three steps); mp: 95-96 °C; \( R_f = 0.52 \) (petroleum ether/ethyl acetate 10:1); \(^1\)H NMR (500 MHz, CDCl\(_3\)): \( \delta = 7.69-7.68 \) (m, 1H), 7.66-7.64 (m, 2H), 7.58-7.54 (m, 3H), 7.45 (dd, \( J = 6 \) Hz, \( J = 1 \) Hz, 1H), 7.40-7.37 (m, 3H), 7.18 (dd, \( J = 5 \) Hz, \( J = 3.5 \) Hz, 1H) ppm; \(^{13}\)C NMR (126 MHz, CDCl\(_3\)): \( \delta = 139.5, 138.7, 132.6, 132.50, 131.1, 129.7, 129.5, 129.4, 128.9, 128.7, 128.5, 127.9, 122.4, 117.7, 113.2, 96.7, 86.4 \) ppm. ESI-HRMS: m/z Calcd for C\(_{19}\)H\(_{12}\)NS [M+H\(^+\)]: 286.0685, found 286.0687.

3-(p-tolylethynyl)-[1,1'-biphenyl]-2-carbonitrile (1o). Grey solid (53% yield for three steps); mp: 94-96 °C; \( R_f = 0.52 \) (petroleum ether/ethyl acetate 10:1); \(^1\)H NMR (500 MHz, CDCl\(_3\)): \( \delta = 7.61-7.56 \) (m, 4H), 7.55-7.45 (m, 5H), 7.43-7.41 (m, 1H), 7.19 (d, \( J = 8.5 \) Hz, 2H), 2.38 (s, 3H) ppm; \(^{13}\)C NMR (126 MHz, CDCl\(_3\)): \( \delta = 146.6, 139.9, 138.4, 132.443, 132.378, 131.0, 129.6, 129.3, 129.2, 129.121, 129.064, 119.5, 117.6, 114.3, 96.7, 86.0, 20.0 \) ppm. ESI-HRMS: m/z Calcd for C\(_{22}\)H\(_{16}\)N [M+H\(^+\)]: 294.1277, found 294.1279.
3-((4-ethylphenyl)ethynyl)-[1,1’-biphenyl]-2-carbonitrile (1p). Grey solid (56% yield for three steps); mp: 95-97 °C; \( R_f = 0.52 \) (petroleum ether/ethyl acetate 10:1); \(^1\)H NMR (500 MHz, CDCl\(_3\)): \( \delta = 7.61-7.55 \) (m, 6H), 7.52-7.46 (m, 3H), 7.43-7.41 (m, 1H), 7.21 (d, \( J = 8 \) Hz, 2H), 2.68 (q, \( J = 15.0 \) Hz, \( J = 7.5 \) Hz, 2H), 1.25 (t, \( J = 7.5 \) Hz, 2H) ppm; \(^{13}\)C NMR (126 MHz, CDCl\(_3\)): \( \delta \) 146.6, 146.2, 138.4, 132.5, 131.0, 129.6, 129.3, 129.2, 129.121, 129.078, 128.4, 119.7, 117.6, 114.4, 96.7, 86.0, 29.3, 15.7 ppm. ESI-HRMS: m/z Calcd for C\(_{23}\)H\(_{18}\)N [M+H\(^+\)]: 308.1434, found 308.1431.

3-((3-methoxyphenyl)ethynyl)-[1,1’-biphenyl]-2-carbonitrile (1q). Grey solid (52% yield for three steps); mp: 99-101 °C; \( R_f = 0.52 \) (petroleum ether/ethyl acetate 10:1); \(^1\)H NMR (500 MHz, CDCl\(_3\)): \( \delta = 7.63-7.56 \) (m, 4H), 7.52-7.43 (m, 4H), 7.30-7.23 (m, 2H), 7.16 (t, \( J = 8 \) Hz, 1H), 6.96-6.94 (m, 1H), 3.83 (s, 3H) ppm; \(^{13}\)C NMR (126 MHz, CDCl\(_3\)): \( \delta \) 159.8, 146.6, 138.3, 132.5, 131.1, 129.930, 129.858, 129.3, 129.2, 129.1, 128.7, 125.1, 123.5, 117.5, 117.0, 116.4, 114.5, 96.3, 55.8 ppm. ESI-HRMS: m/z Calcd for C\(_{22}\)H\(_{16}\)N [M+H\(^+\)]: 310.1226, found 310.1228.

3-((4-fluorophenyl)ethynyl)-[1,1’-biphenyl]-2-carbonitrile (1r). Grey solid (43% yield for three steps); mp: 95-96 °C; \( R_f = 0.52 \) (petroleum ether/ethyl acetate 10:1); \(^1\)H NMR (500 MHz, CDCl\(_3\)): \( \delta = 7.64-7.56 \) (m, 6H), 7.53-7.43 (m, 4H), 7.10-7.05 (m, 2H) ppm; \(^{13}\)C NMR (126 MHz, CDCl\(_3\)): \( \delta \) 163.5 (d, \( J = 251 \) Hz), 146.7, 138.3, 134.5 (d, \( J = 8 \) Hz), 132.5, 131.0, 129.9, 129.3, 129.1, 128.7, 118.6 (d, \( J = 4 \) Hz), 117.5, 116.3, 116.1, 114.4, 95.3, 86.3 ppm. \(^{19}\)F NMR (376 MHz, CDCl\(_3\)): \( \delta \) -109.2 ppm. ESI-HRMS: m/z Calcd for C\(_{23}\)H\(_{15}\)FN [M+H\(^+\)]: 298.1027, found 298.1025.
3-((4-chlorophenyl)ethynyl)-[1,1'-biphenyl]-2-carbonitrile (1s). Grey solid (46% yield for three steps); mp: 98-99 °C; Rf = 0.52 (petroleum ether/ethyl acetate 10:1); 1H NMR (500 MHz, CDCl₃): δ = 7.61-7.56 (m, 6H), 7.52-7.44 (m, 4H), 7.35 (d, J = 8.5 Hz, 2H) ppm; 13C NMR (126 MHz, CDCl₃): δ 146.7, 138.2, 135.8, 133.7, 132.6, 131.0, 130.1, 129.4, 129.244, 129.1, 128.5, 121.0, 117.5, 114.5, 95.1, 87.5 ppm. ESI-HRMS: m/z Calcd for C₂₁H₁₃ClN [M+H⁺]: 314.0731, found 314.0728.

3-((4-bromophenyl)ethynyl)-[1,1'-biphenyl]-2-carbonitrile (1t). Grey solid (48% yield for three steps); mp: 101-103 °C; Rf = 0.52 (petroleum ether/ethyl acetate 10:1); 1H NMR (500 MHz, CDCl₃): δ = 7.61-7.56 (m, 4H), 7.53-7.45 (m, 8H) ppm; 13C NMR (126 MHz, CDCl₃): δ 146.7, 138.2, 133.8, 132.5, 132.2, 131.0, 130.1, 129.4, 129.2, 129.1, 128.5, 124.1, 121.5, 117.5, 114.5, 95.1, 87.6 ppm. ESI-HRMS: m/z Calcd for C₂₁H₁₃BrN [M+H⁺]: 358.0226, found 358.0229.

3-(thiophen-3-ylethynyl)-[1,1'-biphenyl]-2-carbonitrile (1u). Grey solid (36% yield for three steps); mp: 91-93 °C; Rf = 0.52 (petroleum ether/ethyl acetate 10:1); 1H NMR (500 MHz, CDCl₃): δ = 7.68-7.67 (m, 1H), 7.61-7.56 (m, 4H), 7.52-7.46 (m, 3H), 7.44-7.42 (m, 1H), 7.34-7.32 (d, J = 7.5 Hz, 1H), 7.29-7.28 (m, 1H) ppm; 13C NMR (126 MHz, CDCl₃): δ 146.6, 138.3, 132.5, 131.0, 130.8, 130.4, 129.7, 129.3, 129.2, 129.1, 128.9, 126.0, 121.6, 117.5, 114.3, 91.5, 86.2 ppm. ESI-HRMS: m/z Calcd for C₁₉H₁₂NS [M+H⁺]: 286.0685, found 286.0687.
3-ethynyl-[1,1'-biphenyl]-2-carbonitrile (1v). Grey solid (42% yield for four steps); mp: 83-85 °C; Rf = 0.52 (petroleum ether/ethyl acetate 10:1); 1H NMR (500 MHz, CDCl3): δ = 7.61-7.57 (m, 2H), 7.55-7.53 (m, 2H), 7.51-7.44 (m, 4H), 3.50 (s, 1H) ppm; 13C NMR (126 MHz, CDCl3): δ 146.7, 138.1, 132.5, 132.0, 130.6, 129.4, 129.2, 129.1, 127.5, 117.3, 115.0, 84.1, 80.5 ppm. ESI-HRMS: m/z Calcd for C15H10N [M+H]+: 204.0808, found 204.0805.

3-(hex-1-yn-1-yl)-[1,1'-biphenyl]-2-carbonitrile (1w). Grey solid (52% yield for three steps); mp: 85-86 °C; Rf = 0.52 (petroleum ether/ethyl acetate 10:1); 1H NMR (500 MHz, CDCl3): δ = 7.55-7.56 (m, 3H), 7.50-7.43 (m, 4H), 7.36 (d, J = 7.5 Hz, 1H), 2.51 (t, J = 7.0 Hz, 2H), 1.69-1.63 (m, 2H), 1.57-1.50 (m, 2H), 0.96 (t, J = 7.5 Hz, 3H) ppm; 13C NMR (126 MHz, CDCl3): δ 146.4, 138.5, 132.4, 131.2, 129.7, 129.2, 129.150, 129.064, 117.8, 114.5, 98.4, 30.9, 22.4, 19.7, 14.0 ppm. ESI-HRMS: m/z Calcd for C19H18N [M+H]+: 260.1434, found 260.1435.

**General Procedure for Synthesis of Products 3.**

An oven-dried Schlenk tube (10 mL) was equipped with a magnetic stir bar, 1 (0.1 mmol), 2 (2 equiv, 0.2 mmol), NaOAc (2 equiv, 0.2 mmol). The flask was evacuated and backfilled with Ar for 3 times. Then 1 mL dichloromethane was added followed by TBPB (18 mg, 28 μL, 2.0 equiv). The tube was then sealed and the mixture was stirred for 24 h at 80 °C under Argon (1 atm). After the reaction was finished, the solvent was concentrated in vacuo and the residue was purified by chromatography on silica gel to afford the corresponding products 3.

**Experimental Procedure for Scale-up Reaction**
An oven-dried Schlenk tube (50 mL) was equipped with a magnetic stir bar, 1a (1 mmol), 2a (2 equiv, 2 mmol), NaOAc (2 equiv, 2 mmol). The flask was evacuated and backfilled with Ar for 3 times. Then 10 mL dichloromethane was added followed by TBPB (180 mg, 280 μL, 2.0 equiv). The tube was then sealed and the mixture was stirred for 24 h at 80 °C under Argon (1 atm). After the reaction was finished, the solvent was concentrated in vacuo and the residue was purified by chromatography on silica gel to afford the corresponding products 3aa in 58% yield.

5-phenyl-4-tosylcyclopenta[gh]phenanthridine (3aa). Yellow solid; (29.4 mg, 68%); mp: 195-197 °C; R_f = 0.36 (petroleum ether/ethyl acetate 5:1); 1H NMR (500 MHz, CDCl_3): -8.53 (dd, J = 6.0 Hz, J = 3.0 Hz, 1H), 8.38-8.34 (m, 2H), 8.30 (dd, J = 6.5 Hz, J = 3.5 Hz, 1H), 7.88-7.85 (m, 1H), 7.76-7.73 (m, 2H), 7.68-7.66 (m, 2H), 7.57 (d, J = 8.0 Hz, 2H), 7.53-7.48 (m, 3H), 7.11 (d, J = 8.0 Hz, 2H), 2.32 (s, 3H) ppm; 13C NMR (126 MHz, CDCl_3): 161.8, 148.7, 148.6, 144.7, 143.2, 138.9, 135.7, 133.3, 132.8, 131.6, 130.2, 129.9, 129.8, 129.4, 129.3, 128.1, 128.0, 125.8, 124.9, 123.6, 123.3, 120.2, 22.0 ppm. ESI-HRMS: m/z Caled for C_{28}H_{19}NO_{2}S [M+H]^+: 434.1209, found 434.1204.

8-methyl-5-phenyl-4-tosylcyclopenta[gh]phenanthridine (3ba). Yellow solid; (27.3 mg, 61%); mp: 184-186 °C; R_f = 0.32 (petroleum ether/ethyl acetate 5:1); 1H NMR (500 MHz, CDCl_3): -8.42 (d, J = 8.0 Hz, 1H), 8.35-8.31 (m, 2H), 8.11 (s, 1H), 8.74 (t, J = 8.0 Hz, 2H), 7.66-7.65 (m, 2H), 7.59-7.56 (m, 3H), 7.52-7.46 (m, 3H), 7.11 (d, J = 8.5 Hz, 2H), 2.57 (s, 3H), 2.32 (s, 3H) ppm; 13C NMR
8-methoxy-5-phenyl-4-tosylcyclopenta[gh]phenanthridine (3ca). Yellow solid; (24.5 mg, 53%);
mp: 188-190 °C; Rf = 0.35 (petroleum ether/ethyl acetate 5:1); 1H NMR (500 MHz, CDCl3): δ =
8.40 (d, J = 9.0 Hz, 1H), 8.29-8.27 (m, 2H), 7.82 (t, J = 7.5 Hz, 1H), 7.70 (d, J = 2.5 Hz, 1H), 7.67-
7.65 (m, 2H), 7.57 (d, J = 9.5 Hz, 2H), 7.52-7.48 (m, 3H), 7.39-7.36 (m, 1H), 7.11 (d, J = 8.0 Hz,
2H), 3.94 (s, 3H), 2.32 (s, 3H) ppm; 13C NMR (126 MHz, CDCl3); δ 162.1, 160.5, 150.5, 148.6,
144.6, 142.9, 139.0, 135.6, 133.3, 131.5, 130.3, 129.9, 129.8, 129.1, 128.0, 125.1, 124.2,
123.4, 120.4, 119.3, 119.1, 112.4, 56.0, 22.0 ppm. ESI-HRMS: m/z Calcd for C29H21NO3S [M+H]+:
464.1315, found 464.1317.

8-(tert-butyl)-5-phenyl-4-tosylcyclopenta[gh]phenanthridine (3da). Yellow solid; (26.9 mg, 55%);
mp: 192-194 °C; Rf = 0.32 (petroleum ether/ethyl acetate 5:1); 1H NMR (500 MHz, CDCl3): δ =
8.47 (d, J = 8.5 Hz, 1H), 8.37-8.30 (m, 3H), 7.87-7.83 (m, 2H), 7.69-7.67 (m, 2H), 7.58 (d, J = 8.5
Hz, 2H), 7.52-7.48 (m, 3H), 7.11 (d, J = 8.5 Hz, 2H), 2.32 (s, 3H), 1.44 (s, 9H) ppm; 13C NMR (126
MHz, CDCl3): δ 161.7, 152.8, 148.9, 148.7, 144.6, 142.9, 139.0, 135.6, 133.2, 131.6, 130.3, 129.9,
129.8, 129.3, 128.9, 128.1, 128.0, 127.6, 125.4, 123.6, 122.9, 122.6, 120.1, 35.6, 31.7, 22.0 ppm.
ESI-HRMS: m/z Calcd for C32H26NO3S [M+H]+: 490.1835, found 490.1837.

10-methyl-5-phenyl-4-tosylcyclopenta[gh]phenanthridine (3ea). Yellow solid; (19.2 mg, 43%);
7-methyl-5-phenyl-4-tosylcyclopenta[gh]phenanthridine (3fa) and 9-methyl-5-phenyl-4-tosylcyclopenta[gh]phenanthridine (3fa'). Yellow solid; (13.4 mg, 36%); mp: 181-183 °C; \( R_f = 0.36 \) (petroleum ether/ethyl acetate 5:1); \(^1\)H NMR (500 MHz, CDCl\(_3\)): \( \delta = 8.41-8.30 \) (m, 3H), 8.19 (d, \( J = 8.5 \) Hz, 2H), 7.69-7.67 (m, 2H), 7.58 (d, \( J = 8.0 \) Hz, 2H), 7.51-7.48 (m, 3H), 7.10 (d, \( J = 8.5 \) Hz, 2H), 2.72 (d, \( J = 72.5 \) Hz, 3H), 2.31 (d, \( J = 3.5 \) Hz, 3H) ppm; \(^{13}\)C NMR (126 MHz, CDCl\(_3\)): \( \delta \) 160.8, 148.7, 147.1, 144.6, 142.6, 139.7, 139.1, 139.0, 135.8, 135.6, 133.0, 132.5, 132.0, 131.6, 131.1, 130.4, 130.2, 129.9, 129.8, 129.1, 128.8, 128.046, 127.966, 127.9, 127.8, 125.6, 125.5, 124.9, 123.7, 123.5, 123.0, 121.1, 120.3, 22.4, 21.9, 19.0 ppm. ESI-HRMS: m/z Calcd for C\(_{29}\)H\(_{22}\)NO\(_2\)S [M+H\(^+\)]: 448.1366, found 448.1368.

5,8-diphenyl-4-tosylcyclopenta[gh]phenanthridine (3ga). Yellow solid; (23.4 mg, 46%); mp: 190-191 °C; \( R_f = 0.32 \) (petroleum ether/ethyl acetate 5:1); \(^1\)H NMR (500 MHz, CDCl\(_3\)): \( \delta = 8.60-8.56 \) (m, 2H), 8.40-8.34 (m, 2H), 8.04-8.02 (m, 1H), 7.88 (t, \( J = 7.5 \) Hz, 1H), 7.76 (d, \( J = 7.5 \) Hz, 2H), 7.69-7.67 (m, 2H), 7.58 (d, \( J = 8.0 \) Hz, 2H), 7.52-7.47 (m, 5H), 7.41-7.38 (m, 1H), 7.11 (d, \( J = 8.0 \) Hz, 2H), 2.32 (s, 3H) ppm; \(^{13}\)C NMR (126 MHz, CDCl\(_3\)): \( \delta \) 162.2, 149.1, 148.6, 144.7, 143.3, 142.1, 140.2, 138.9, 135.8, 133.4, 131.6, 130.6, 130.2, 130.0, 129.8, 129.4, 129.3, 128.327, 128.262, 128.1, 128.0, 127.8, 125.8, 123.9, 123.8, 123.7, 120.3, 22.0 ppm. ESI-HRMS: m/z Calcd for C\(_{34}\)H\(_{24}\)NO\(_2\)S [M+H\(^+\)]: 510.1522, found 510.1525.
8-fluoro-5-phenyl-4-tosylcyclopenta[gh]phenanthridine (3ha). Yellow solid; (21.6 mg, 48%); mp: 178-179 °C; $R_f = 0.34$ (petroleum ether/ethyl acetate 5:1); $^1$H NMR (500 MHz, CDCl$_3$): $\delta = 8.51$-8.48 (m, 1H), 8.34-8.30 (m, 2H), 7.97-7.95 (m, 1H), 7.86 (d, $J = 7.5$ Hz, 2H), 7.65 (d, $J = 6.5$ Hz, 2H), 7.56 (d, $J = 8.0$ Hz, 2H), 7.53-7.49 (m, 4H), 7.11 (d, $J = 8.0$ Hz, 2H), 2.32 (s, 3H) ppm; $^{13}$C NMR (126 MHz, CDCl$_3$): $\delta$ 163.0, 162.9 (d, $J = 249$ Hz), 149.9 (d, $J = 12$ Hz), 148.3, 144.8, 143.7, 138.7, 135.8, 133.7, 131.5, 130.0, 129.8, 129.3, 128.1, 128.0, 125.8, 125.0 (d, $J = 10$ Hz), 123.5, 121.6, 119.8, 118.2 (d, $J = 24$ Hz), 117.3 (d, $J = 21$ Hz), 22.0 ppm; $^{19}$F NMR (376 MHz, CDCl$_3$): $\delta$ -110.7 ppm. ESI-HRMS: m/z Calcd for C$_{28}$H$_{19}$FNO$_2$S [M+H$^+$]: 452.1115, found 452.1117.

8-chloro-5-phenyl-4-tosylcyclopenta[gh]phenanthridine (3ia). Yellow solid; (25.7 mg, 55%); mp: 193-194 °C; $R_f = 0.33$ (petroleum ether/ethyl acetate 5:1); $^1$H NMR (500 MHz, CDCl$_3$): $\delta = 8.44$ (d, $J = 9.0$ Hz, 1H), 8.34 (d, $J = 7.0$ Hz, 2H), 8.32-8.30 (m, 3H), 7.87 (t, $J = 8.0$ Hz, 1H), 7.71-7.68 (m, 1H), 7.65-7.63 (m, 2H), 7.56 (d, $J = 8.5$ Hz, 2H), 7.52-7.47 (m, 3H), 7.11 (d, $J = 8.0$ Hz, 2H), 2.32 (s, 3H) ppm; $^{13}$C NMR (126 MHz, CDCl$_3$): $\delta$ 162.9, 149.2, 148.3, 144.8, 143.8, 138.7, 135.8, 135.0, 133.8, 131.8, 131.5, 130.1, 130.0, 129.8, 129.5, 129.1, 128.1, 128.0, 126.2, 124.4, 123.5, 123.4, 120.2, 22.0 ppm. ESI-HRMS: m/z Calcd for C$_{28}$H$_{19}$ClNO$_2$S [M+H$^+$]: 468.0820, found 468.0823.

7,9-dimethyl-5-phenyl-4-tosylcyclopenta[gh]phenanthridine (3ja). Yellow solid; (23.0 mg, 50%); mp: 179-180 °C; $R_f = 0.32$ (petroleum ether/ethyl acetate 5:1); $^1$H NMR (500 MHz, CDCl$_3$): $\delta = 8.35$-8.29 (m, 2H), 8.16 (s, 1H), 7.82 (t, $J = 7.5$ Hz, 1H), 7.79-7.77 (m, 2H), 7.59 (d, $J = 8.0$ Hz, 2H), 7.49-7.46 (m, 4H), 7.10 (d, $J = 8.0$ Hz, 2H), 2.74 (s, 3H), 2.59 (s, 3H), 2.31 (s, 3H) ppm; $^{13}$C NMR (126 MHz, CDCl$_3$): $\delta$ 159.1, 148.8, 145.9, 144.5, 141.6, 140.5, 139.2, 135.7, 132.7, 132.032,
131.988, 130.6, 129.8, 129.7, 127.9, 127.8, 125.4, 124.8, 123.6, 120.8, 120.0, 22.4, 21.9, 18.9 ppm. ESI-HRMS: m/z Calcd for C_{30}H_{24}NO_{2}S [M+H^+] 462.1522, found 462.1520.

![Diagram of 7,9-dichloro-5-phenyl-4-tosylcyclopenta[gh]phenanthridine (3ka).](image)

7,9-dichloro-5-phenyl-4-tosylcyclopenta[gh]phenanthridine (3ka). Yellow solid; (17.5 mg, 35%); mp: 208-209 °C; R_f = 0.34 (petroleum ether/ethyl acetate 5:1); ¹H NMR (500 MHz, CDCl₃): δ = 8.40-8.37 (m, 2H), 8.27 (d, J = 8.5 Hz, 1H), 7.90-7.85 (m, 1H), 7.79-7.77 (m, 2H), 7.57 (d, J = 8.0 Hz, 2H), 7.51-7.46 (m, 3H), 7.10 (d, J = 8.0 Hz, 2H), 2.31 (s, 3H) ppm; ¹³C NMR (126 MHz, CDCl₃): δ 162.2, 148.3, 144.9, 143.5, 143.4, 138.6, 138.1, 136.1, 134.7, 134.0, 132.0, 130.229, 130.205, 129.8, 129.7, 128.5, 128.0, 127.1, 127.0, 123.5, 121.9, 120.9, 21.9 ppm. ESI-HRMS: m/z Calcd for C_{28}H_{17}Cl_{2}NO_{2}S [M+H^+] 501.0357, found 501.0356.

![Diagram of 5-phenyl-4-tosylbenzo[a]cyclopenta[gh]phenanthridine (3la).](image)

5-phenyl-4-tosylbenzo[a]cyclopenta[gh]phenanthridine (3la). Yellow solid; (27.0 mg, 56%); mp: 187-188 °C; R_f = 0.35 (petroleum ether/ethyl acetate 5:1); ¹H NMR (500 MHz, CDCl₃): δ = 9.15 (d, J = 8.5 Hz, 1H), 8.95 (d, J = 9.0 Hz, 1H), 8.44 (d, J = 7.0 Hz, 1H), 8.21 (d, J = 8.5 Hz, 1H), 8.04-8.01 (m, 2H), 7.93 (t, J = 7.5 Hz, 1H), 7.78 (t, J = 7.5 Hz, 1H), 7.72-7.69 (m, 3H), 7.79 (d, J = 8.5 Hz, 1H), 7.51-7.51 (m, 3H), 7.12 (d, J = 8.0 Hz, 2H), 2.32 (s, 3H) ppm; ¹³C NMR (126 MHz, CDCl₃): δ 161.1, 149.0, 148.5, 144.6, 141.8, 139.1, 136.1, 134.3, 133.5, 131.7, 131.0, 130.6, 130.313, 130.262, 129.9, 129.8, 129.4, 129.0, 128.7, 128.1, 128.0, 127.8, 127.6, 126.0, 122.6, 120.9, 22.0 ppm. ESI-HRMS: m/z Calcd for C_{32}H_{23}NO_{2}S [M+H^+] 484.1366, found 484.1368.

![Diagram of 5-phenyl-4-tosylbenzo[c]cyclopenta[gh]phenanthridine (3ma).](image)

5-phenyl-4-tosylbenzo[c]cyclopenta[gh]phenanthridine (3ma). Yellow solid; (25.1 mg, 52%); mp: 186-187 °C; R_f = 0.34 (petroleum ether/ethyl acetate 5:1); ¹H NMR (500 MHz, CDCl₃): δ = 9.27-9.25 (m, 1H), 8.46-8.38 (m, 3H), 8.05 (d, J = 8.5 Hz, 1H), 7.96-7.92 (m, 1H), 7.88-7.83 (m, 3H), 
7.69-7.65 (m, 2H), 7.62 (d, $J = 8.5$ Hz, 2H), 7.58-7.55 (m, 3H), 7.12 (d, $J = 8.5$ Hz, 2H), 2.31 (s, 3H) ppm; $^{13}$C NMR (126 MHz, CDCl$_3$): $\delta$ 159.6, 149.1, 145.8, 144.6, 141.3, 139.2, 135.8, 133.6, 133.2, 133.1, 132.0, 130.6, 130.3, 129.9, 129.8, 129.4, 128.1, 128.0, 127.9, 127.7, 126.4, 125.6, 124.3, 122.7, 120.7, 120.3, 21.9 ppm. ESI-HRMS: $m/z$ Calcd for C$_{32}$H$_{22}$NO$_2$S [M+H$^+$]: 484.1366, found 484.1368.

5-phenyl-4-tosylcyclopenta[fij]thieno[3,2-c]isoquinoline (3na). Yellow solid; (16.7 mg, 38%); mp: 177-179 $^\circ$C; $R_f = 0.35$ (petroleum ether/ethyl acetate 5:1); $^1$H NMR (500 MHz, CDCl$_3$): $\delta = 8.38$ (d, $J = 7.0$ Hz, 1H), 8.05 (d, $J = 8.5$ Hz, 1H), 7.82 (t, $J = 8.0$ Hz, 1H), 7.79-7.72 (m, 2H), 7.63 (d, $J = 7.0$ Hz, 1H), 7.54 (d, $J = 8.0$ Hz, 2H), 7.51-7.47 (m, 3H), 7.10 (d, $J = 8.0$ Hz, 2H), 2.31 (s, 3H) ppm; $^{13}$C NMR (126 MHz, CDCl$_3$): $\delta$ 159.7, 155.9, 149.8, 144.5, 140.2, 139.2, 136.0, 133.4, 131.4, 131.1, 130.4, 130.0, 129.8, 128.2, 128.1, 127.9, 127.6, 127.4, 126.7, 124.5, 119.1, 21.9 ppm. ESI-HRMS: $m/z$ Calcd for C$_{26}$H$_{16}$NO$_2$S [M+H$^+$]: 440.0773, found 440.0776.

5-(p-tolyl)-4-tosylcyclopenta[gh]phenanthridine (3oa). Yellow solid; (30.4 mg, 68%); mp: 197-199 $^\circ$C; $R_f = 0.33$ (petroleum ether/ethyl acetate 5:1); $^1$H NMR (500 MHz, CDCl$_3$): $\delta = 8.52-8.50$ (m, 1H), 8.34-8.29 (m, 3H), 7.85-7.82 (m, 1H), 7.75-7.71 (m, 2H), 7.62 (d, $J = 8.0$ Hz, 4H), 7.32 (d, $J = 8.0$ Hz, 2H), 7.13 (d, $J = 8.0$ Hz, 2H), 2.48 (s, 1H), 2.32 (s, 3H) ppm; $^{13}$C NMR (126 MHz, CDCl$_3$): $\delta$ 161.9, 148.9, 148.6, 144.6, 142.4, 140.2, 139.1, 135.8, 133.2, 132.8, 131.6, 129.8, 129.4, 129.2, 129.1, 128.9, 128.0, 127.3, 125.5, 124.9, 123.4, 123.3, 120.3, 22.047, 21.967 ppm. ESI-HRMS: $m/z$ Calcd for C$_{29}$H$_{22}$NO$_2$S [M+H$^+$]: 448.1366, found 448.1365.

5-(4-ethylphenyl)-4-tosylcyclopenta[gh]phenanthridine (3pa). Yellow solid; (30.9 mg, 67%); mp: 195-196 $^\circ$C; $R_f = 0.35$ (petroleum ether/ethyl acetate 5:1); $^1$H NMR (500 MHz, CDCl$_3$): $\delta = 8.57-$
8.55 (m, 1H), 8.39-8.33 (m, 3H), 7.90-7.86 (m, 1H), 7.80-7.75 (m, 2H), 7.66-7.60 (m, 4H), 7.35 (d, \(J = 10.5\) Hz, 2H), 7.13 (d, \(J = 10.5\) Hz, 2H), 2.80 (q, \(J = 19.5\) Hz, \(J = 9.5\) Hz, 2H), 2.34 (s, 3H), 1.37 (t, \(J = 9.5\) Hz, 3H) ppm; \(^{13}\)C NMR (126 MHz, CDCl\(_3\)): \(\delta\) 161.9, 148.8, 148.7, 146.4, 144.5, 142.6, 139.0, 135.9, 133.3, 132.8, 131.7, 129.7, 129.4, 129.2, 129.1, 128.0, 127.7, 127.5, 125.6, 125.0, 123.4, 123.3, 120.2, 29.3, 21.9, 15.9 ppm. ESI-HRMS: m/z Calcd for C\(_{30}\)H\(_{24}\)NO\(_2\)S [M+H\(^+\)]: 462.1522, found 462.1524.

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\begin{align*}
\text{5-(3-methoxyphenyl)-4-tosylcyclopenta[gh]phenanthridine (3qa). Yellow solid; (26.8 mg, 58%); mp: 192-193 °C; } R_f = 0.32 \text{ (petroleum ether/ethyl acetate 5:1); } ^1\text{H NMR (500 MHz, CDCl}_3\text{): } \delta = 8.53-8.51 \text{ (m, 1H), 8.37-8.35 \text{ (m, 2H), 8.32-8.30 \text{ (m, 1H), 7.86 (t, } J = 7.5 \text{ Hz, 1H), 7.75-7.73 \text{ (m, 2H), 7.59 (d, } J = 8.5 \text{ Hz, 2H), 7.39 (t, } J = 8.0 \text{ Hz, 1H), 7.21 (d, } J = 9.0 \text{ Hz, 2H), 7.12 (d, } J = 8.5 \text{ Hz, 2H), 7.05 (d, } J = 8.5 \text{ Hz, 1H), 3.86 (s, 3H), 2.32 (s, 3H) ppm; } ^{13}\text{C NMR (126 MHz, CDCl}_3\text{): } \delta 161.7, 159.2, 148.6, 148.3, 144.7, 143.4, 138.8, 135.7, 133.3, 132.8, 131.4, 129.8, 129.4, 129.3, 129.2, 128.0, 125.9, 125.0, 124.0, 123.7, 123.3, 120.1, 116.6, 116.2, 55.7, 22.0 ppm. ESI-HRMS: m/z Calcd for C\(_{29}\)H\(_{22}\)NO\(_3\)S [M+H\(^+\)]: 464.1315, found 464.1318.}
\end{align*}
\]

5-(4-fluorophenyl)-4-tosylcyclopenta[gh]phenanthridine (3ra). Yellow solid; (25.3 mg, 56%); mp: 195-196 °C; \(R_f = 0.36\) (petroleum ether/ethyl acetate 5:1); \(^1\)H NMR (500 MHz, CDCl\(_3\)): \(\delta = 8.55-8.53 \text{ (m, 1H), 8.39-8.33 \text{ (m, 2H), 8.32-8.30 \text{ (m, 1H), 7.87 (t, } J = 7.5 \text{ Hz, 1H), 7.78-7.76 \text{ (m, 2H), 7.73-7.70 \text{ (m, 2H), 7.58 (d, } J = 8.0 \text{ Hz, 2H), 7.20 (t, } J = 8.0 \text{ Hz, 2H), 7.14 (d, } J = 8.0 \text{ Hz, 2H), 2.33 (s, 3H) ppm; } ^{13}\text{C NMR (126 MHz, CDCl}_3\text{): } \delta 164.1 \text{ (d, } J = 250 \text{ Hz), 161.5, 148.6, 147.4, 144.9, 143.2, 138.8, 133.7, 135.6, 133.8 (d, } J = 8 \text{ Hz), 133.4, 132.7, 129.9, 129.5, 129.3 (d, } J = 17 \text{ Hz), 127.9, 126.2, 125.8, 125.0, 123.7, 123.3, 120.1, 115.3 (d, } J = 17 \text{ Hz), 22.0 ppm; } ^{19}\text{F NMR (376 MHz, CDCl}_3\text{): } \delta -111.0 \text{ ppm. ESI-HRMS: m/z Calcd for C\(_{28}\)H\(_{19}\)FNO\(_2\)S [M+H\(^+\)]: 452.1115, found 452.1117.}
5-(4-chlorophenyl)-4-tosylcyclopenta[gh]phenanthridine (3sa). Yellow solid; (24.7 mg, 53%); mp: 199-201 °C; \( R_f = 0.35 \) (petroleum ether/ethyl acetate 5:1); \(^1\)H NMR (500 MHz, CDCl\(_3\)): \( \delta = 8.55-8.52 \) (m, 1H), 8.39-8.29 (m, 3H), 7.87 (t, \( J = 8.0 \) Hz, 1H), 7.77-7.75 (m, 2H), 7.64 (d, \( J = 7.0 \) Hz, 2H), 7.60 (d, \( J = 7.5 \) Hz, 2H), 7.47 (d, \( J = 7.0 \) Hz, 2H), 7.15 (d, \( J = 7.5 \) Hz, 2H), 2.33 (s, 3H) ppm; \(^{13}\)C NMR (126 MHz, CDCl\(_3\)): \( \delta = 161.4, 148.6, 147.1, 145.0, 143.4, 138.8, 136.3, 135.5, 133.4, 133.0, 132.7, 131.9, 130.8, 130.0, 129.4, 129.3, 128.4, 128.0, 125.9, 125.0, 123.8, 123.4, 120.1, 22.0 \) ppm. ESI-HRMS: m/z Calcd for C\(_{28}\)H\(_{19}\)ClNO\(_2\)S \([M+H]^+\): 468.0820, found 468.0818.

5-(4-bromophenyl)-4-tosylcyclopenta[gh]phenanthridine (3ta). Yellow solid; (25.6 mg, 50%); mp: 206-207 °C; \( R_f = 0.32 \) (petroleum ether/ethyl acetate 5:1); \(^1\)H NMR (500 MHz, CDCl\(_3\)): \( \delta = 8.55-8.53 \) (m, 1H), 8.39-8.32 (m, 2H), 8.31-8.29 (m, 1H), 7.87 (d, \( J = 7.5 \) Hz, 1H), 7.77-7.75 (m, 2H), 7.64-7.56 (m, 6H), 7.15 (d, \( J = 7.5 \) Hz, 2H), 2.34 (s, 3H) ppm; \(^{13}\)C NMR (126 MHz, CDCl\(_3\)): \( \delta = 161.3, 148.6, 147.1, 145.0, 143.4, 138.8, 135.5, 133.4, 133.2, 132.7, 131.4, 130.0, 129.5, 129.4, 129.3, 129.1, 128.0, 125.9, 125.0, 124.7, 123.8, 123.4, 120.1, 22.0 \) ppm. ESI-HRMS: m/z Calcd for C\(_{28}\)H\(_{19}\)BrNO\(_2\)S \([M+H]^+\): 512.0314, found 512.0317.

5-(thiophen-3-yl)-4-tosylcyclopenta[gh]phenanthridine (3ua). Yellow solid; (21.1 mg, 48%); mp: 185-186 °C; \( R_f = 0.34 \) (petroleum ether/ethyl acetate 5:1); \(^1\)H NMR (500 MHz, CDCl\(_3\)): \( \delta = 8.51-8.49 \) (m, 1H), 8.35-8.29 (m, 4H), 7.85-7.80 (m, 2H), 7.77-7.72 (m, 2H), 7.65 (d, \( J = 8.5 \) Hz, 2H), 7.44-7.42 (m, 1H), 7.14 (d, \( J = 8.5 \) Hz, 2H), 2.31 (s, 3H) ppm; \(^{13}\)C NMR (126 MHz, CDCl\(_3\)): \( \delta = 161.6, 148.4, 144.7, 142.7, 140.9, 138.9, 136.2, 133.4, 132.7, 131.7, 131.2, 130.3, 129.9, 129.4, 129.3, 129.1, 127.6, 125.7, 125.0, 124.9, 123.3, 120.2, 22.0 \) ppm. ESI-HRMS: m/z Calcd for C\(_{26}\)H\(_{18}\)NO\(_2\)S\(_2\) \([M+H]^+\]: 440.0773, found 440.0776.
5-phenyl-4-(phenylsulfonyl)cyclopenta[gh]phenanthridine (3ab). Yellow solid; (26.8 mg, 64%); mp: 193-194 °C; \( R_f = 0.35 \) (petroleum ether/ethyl acetate 5:1); \(^1\)H NMR (500 MHz, CDCl\(_3\)): \( \delta = 8.55-8.51 \) (m, 1H), 8.38-8.36 (m, 2H), 8.32-8.28 (m, 1H), 7.87 (t, \( J = 8.0 \) Hz, 1H), 7.66-7.63 (m, 2H), 7.69-7.65 (m, 4H), 7.51-7.47 (m, 1H), 7.31 (t, \( J = 8.0 \) Hz, 2H) ppm; \(^{13}\)C NMR (126 MHz, CDCl\(_3\)): \( \delta = 161.7, 149.0, 148.7, 142.9, 141.7, 135.7, 133.7, 133.3, 132.8, 131.6, 130.2, 130.0, 129.5, 129.331, 129.259, 129.2, 128.1, 127.9, 125.8, 125.0, 123.7, 123.3, 120.1 ppm. ESI-HRMS: m/z Calcd for C\(_{27}\)H\(_{18}\)NO\(_2\)S [M+H\(^{+}\)]: 420.1053, found 420.1057.

4-((4-chlorophenyl)sulfonyl)-5-phenylcyclopenta[gh]phenanthridine (3ac). Yellow solid; (24.9 mg, 55%); mp: 183-185 °C; \( R_f = 0.35 \) (petroleum ether/ethyl acetate 5:1); \(^1\)H NMR (500 MHz, CDCl\(_3\)): \( \delta = 8.57-8.55 \) (m, 1H), 8.41-8.35 (m, 2H), 8.33-8.31 (m, 1H), 7.89 (t, \( J = 8.0 \) Hz, 1H), 7.78-7.76 (m, 2H), 7.65-7.63 (m, 2H), 7.56 (d, \( J = 9.0 \) Hz, 2H), 7.53-7.48 (m, 3H), 7.25 (d, \( J = 9.0 \) Hz, 2H) ppm; \(^{13}\)C NMR (126 MHz, CDCl\(_3\)): \( \delta = 161.4, 149.3, 148.7, 142.6, 140.3, 140.1, 135.4, 133.4, 132.9, 131.5, 130.2, 130.1, 129.6, 129.403, 129.367, 129.3, 128.2, 125.8, 125.0, 123.9, 123.4, 120.1 ppm. ESI-HRMS: m/z Calcd for C\(_{27}\)H\(_{17}\)ClNO\(_2\)S [M+H\(^{+}\)]: 454.0663, found 454.0661.

4-((4-bromophenyl)sulfonyl)-5-phenylcyclopenta[gh]phenanthridine (3ad). Yellow solid; (26.3 mg, 53%); mp: 185-186 °C; \( R_f = 0.35 \) (petroleum ether/ethyl acetate 5:1); \(^1\)H NMR (500 MHz, CDCl\(_3\)): \( \delta = 8.56-8.54 \) (m, 1H), 8.40-8.34 (m, 2H), 8.32-8.30 (m, 1H), 7.88 (d, \( J = 7.5 \) Hz, 1H), 7.78-7.75 (m, 2H), 7.65-7.63 (m, 2H), 7.55-7.47 (m, 5H), 7.43-7.41 (m, 2H) ppm; \(^{13}\)C NMR (126 MHz, CDCl\(_3\)): \( \delta = 161.4, 149.3, 148.7, 142.6, 140.3, 140.1, 135.4, 133.4, 132.9, 131.5, 130.2, 130.1, 129.6, 129.403, 129.367, 129.3, 128.2, 125.8, 125.0, 123.9, 123.4, 120.1 ppm. ESI-HRMS: m/z Calcd for C\(_{27}\)H\(_{17}\)BrNO\(_2\)S [M+H\(^{+}\)]: 468.0885, found 468.0884.
MHz, CDCl$_3$): $\delta$ 161.4, 149.3, 148.7, 142.5, 140.7, 135.4, 133.3, 132.8, 132.4, 131.5, 130.2, 130.0, 129.6, 129.4, 129.3, 129.0, 128.2, 125.8, 125.0, 123.9, 123.4, 120.1 ppm. ESI-HRMS: m/z Calcd for C$_{27}$H$_{17}$BrNO$_2$S [M+H$^+$]: 498.0158, found 498.0155.

4-((2-bromophenyl)sulfonyl)-5-phenylcyclopenta[gh]phenanthridine (3ae). Yellow solid; (23.7 mg, 48%); mp: 193-195 °C; $R_f = 0.36$ (petroleum ether/ethyl acetate 5:1); $^1$H NMR (500 MHz, CDCl$_3$): $\delta = 8.59-8.57$ (m, 1H), 8.41-8.36 (m, 2H), 8.33-8.31 (m, 1H), 7.89-7.86 (m, 2H), 7.78-7.76 (m, 2H), 7.55 (d, $J = 7.5$ Hz, 2H), 7.42 (d, $J = 7.5$ Hz, 1H), 7.30-7.27 (m, 3H), 7.20-7.13 (m, 2H) ppm; $^{13}$C NMR (126 MHz, CDCl$_3$): $\delta$ 161.4, 148.7, 147.9, 141.7, 139.8, 136.2, 135.0, 134.4, 133.4, 132.7, 131.8, 131.0, 129.9, 129.8, 129.5, 129.3, 129.2, 128.1, 127.4, 126.2, 125.1, 123.6, 123.4, 121.5, 120.1 ppm. ESI-HRMS: m/z Calcd for C$_{27}$H$_{17}$NO$_3$S [M+H$^+$]: 498.0158, found 498.0155.

4-((4-nitrophenyl)sulfonyl)-5-phenylcyclopenta[gh]phenanthridine (3af). Yellow solid; (16.7 mg, 36%); mp: 212-213 °C; $R_f = 0.32$ (petroleum ether/ethyl acetate 5:1); $^1$H NMR (500 MHz, CDCl$_3$): $\delta = 8.59-8.57$ (m, 1H), 8.45-8.39 (m, 2H), 8.34-8.32 (m, 1H), 8.09 (d, $J = 8.5$ Hz, 2H), 7.94-7.91 (m, 1H), 7.82-7.77 (m, 4H), 7.65-7.63 (m, 2H), 7.56-7.48 (m, 3H) ppm; $^{13}$C NMR (126 MHz, CDCl$_3$): $\delta$ 161.0, 150.6, 150.4, 148.8, 147.1, 141.5, 135.1, 133.5, 133.0, 131.5, 129.8, 129.7, 129.612, 129.584, 129.2, 128.4, 125.9, 125.0, 124.211, 124.161, 123.4, 120.1 ppm. ESI-HRMS: m/z Calcd for C$_{27}$H$_{17}$N$_2$O$_4$S [M+H$^+$]: 465.0904, found 465.0906.
4-(naphthalen-2-ylsulfonyl)-5-phenylcyclopenta[gh]phenanthridine (3ag). Yellow solid; (22.0 mg, 47%); mp: 178-179 °C; R_f = 0.32 (petroleum ether/ethyl acetate 5:1); ^1H NMR (500 MHz, CDCl_3): δ = 8.56-8.54 (m, 1H), 8.45-8.38 (m, 2H), 8.30-8.28 (m, 1H), 8.16 (s, 1H), 7.91-7.81 (m, 1H), 7.79-7.73 (m, 5H), 7.65-7.62 (m, 3H), 7.60-7.51 (m, 2H), 7.45-7.40 (m, 3H) ppm; ^13C NMR (126 MHz, CDCl_3): δ 161.7, 149.1, 148.7, 143.0, 138.3, 135.7, 135.4, 133.4, 132.8, 132.2, 131.5, 130.2, 130.0, 129.9, 129.8, 129.5, 129.3, 129.2, 128.1, 128.0, 127.7, 125.9, 125.0, 123.7, 123.3, 122.7, 120.2 ppm. ESI-HRMS: m/z Calcd for C_{31}H_{20}NO_2S_2 [M+H]^+: 470.1209, found 470.1212.

Reference


X-ray crystal structure of 3ad

X-ray Crystal Structure of 3ad, CCDC 1952616. Thermal ellipsoids are drawn at 30% probability level.

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