

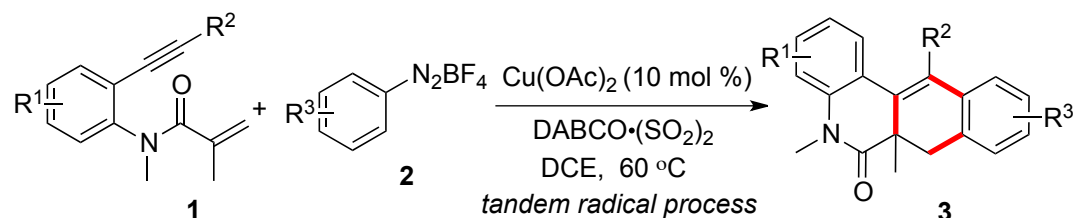
Supporting Information

1. General experimental methods (S2).
2. General experimental procedure and characterization data (S3-S13).
3. ^1H and ^{13}C NMR spectra of compound **3** (S14-S61).

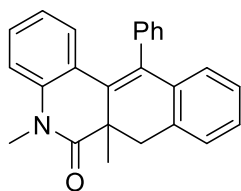
General experimental methods:

Unless otherwise stated, all commercial reagents were used as received. 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 25–35°C. Nuclear magnetic resonance (NMR) spectra are recorded in parts per million from internal tetramethylsilane on the δ scale. ^1H and ^{13}C NMR spectra were recorded in CDCl_3 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 radical cyclization of benzene-tethered 1,7-enynes **1** with aryldiazonium tetrafluoroborates **2** in the presence of $\text{DABCO}\cdot(\text{SO}_2)_2$*

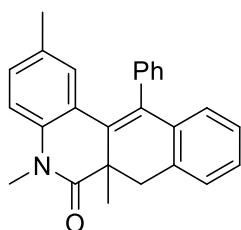


Benzene-tethered 1,7-enyne **1** (0.2 mmol) was added to a mixture of aryldiazonium tetrafluoroborate **2** (0.3 mmol), $\text{DABCO}\cdot(\text{SO}_2)_2$ (0.18 mmol), $\text{Cu}(\text{OAc})_2$ (10 mol%) in DCE (2.0 mL). The mixture was stirred at 60°C for 4 hours. After completion of reaction as indicated by TLC, the solvent was evaporated. The residue was purified directly by flash column chromatography (EtOAc/*n*-hexane, 1:4) to give the desired product **3**.



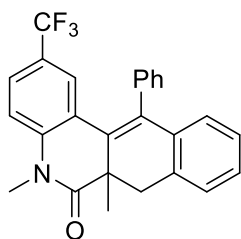
5,6a-dimethyl-12-phenyl-6a,7-dihydrobenzo[*j*]phenanthridin-6(5*H*)-one (**3a**)

Yield: 57%; ^1H NMR (400 MHz, CDCl_3) δ 1.24 (s, 3H), 3.34 (d, $J = 16.3$ Hz, 1H), 3.41 (s, 3H), 3.48 (d, $J = 16.3$ Hz, 1H), 6.59 (t, $J = 7.4$ Hz, 1H), 6.80 (d, $J = 7.1$ Hz, 1H), 6.94 (d, $J = 8.0$ Hz, 1H), 7.08-7.11 (m, 3H), 7.16-7.20 (m, 1H), 7.25-7.29 (m, 3H), 7.34-7.41 (m, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 22.6, 30.4, 37.9, 43.3, 114.2, 121.9, 123.1, 125.9, 126.4, 127.2, 127.6, 128.1, 128.5, 128.6, 130.7, 130.9, 132.2, 132.6, 134.2, 135.4, 138.8, 139.4, 174.1; HRMS (ESI) calcd for $\text{C}_{25}\text{H}_{21}\text{NO}$: ($\text{M} + \text{H}^+$) 352.1696, found: 352.1697.



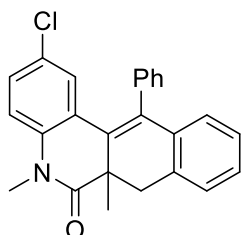
2,5,6a-trimethyl-12-phenyl-6a,7-dihydrobenzo[*j*]phenanthridin-6(5*H*)-one (**3b**)

Yield: 56%; ^1H NMR (400 MHz, CDCl_3) δ 1.24 (s, 3H), 1.87 (s, 3H), 3.34 (d, $J = 16.4$ Hz, 1H), 3.38 (s, 3H), 3.46 (d, $J = 16.3$ Hz, 1H), 6.55 (s, 1H), 6.82 (d, $J = 8.2$ Hz, 1H), 6.89 (d, $J = 8.1$ Hz, 1H), 7.12 (t, $J = 6.6$ Hz, 2H), 7.16-7.20 (m, 1H), 7.25-7.29 (m, 3H), 7.35-7.42 (m, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 20.3, 22.6, 30.3, 37.9, 43.3, 113.9, 122.7, 125.9, 126.4, 127.1, 127.5, 128.5, 128.6, 128.6, 130.9, 131.2, 131.6, 132.4, 132.7, 134.2, 135.2, 137.1, 139.1, 173.9; HRMS (ESI) calcd for $\text{C}_{26}\text{H}_{23}\text{NO}$: ($\text{M} + \text{H}^+$) 366.1852, found: 366.1850.



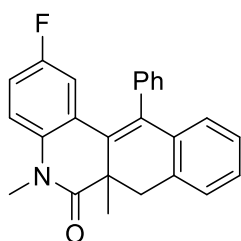
5,6a-dimethyl-12-phenyl-2-(trifluoromethyl)-6a,7-dihydrobenzo[*j*]phenanthridin-6(5*H*)-one (**3c**)

Yield: 71%; ^1H NMR (400 MHz, CDCl_3) δ 1.27 (s, 3H), 3.36 (d, $J = 16.4$ Hz, 1H), 3.43 (s, 3H), 3.49 (d, $J = 16.3$ Hz, 1H), 7.01 (d, $J = 8.5$ Hz, 1H), 7.04 (s, 1H), 7.11-7.16 (m, 2H), 7.20-7.25 (m, 2H), 7.29-7.33 (m, 3H), 7.38-7.42 (m, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 22.7, 30.5, 37.8, 43.2, 114.2, 123.2, 123.9, 124.7, 124.8, 126.3, 126.6, 127.7, 127.8, 127.9, 128.1, 128.6, 128.9, 130.5, 132.5, 133.6, 137.1, 137.8, 141.9, 174.2; HRMS (ESI) calcd for $\text{C}_{26}\text{H}_{20}\text{F}_3\text{NO}$: ($\text{M} + \text{H}^+$) 420.1570, found: 420.1561.



2-Chloro-5,6a-dimethyl-12-phenyl-6a,7-dihydrobenzo[*j*]phenanthridin-6(5*H*)-one
(**3d**)

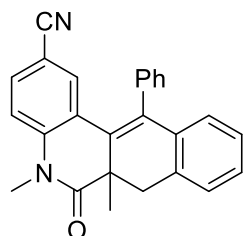
Yield: 66%; ^1H NMR (400 MHz, CDCl_3) δ 1.24 (s, 3H), 3.34 (d, $J = 16.4$ Hz, 1H), 3.38 (s, 3H), 3.47 (d, $J = 16.4$ Hz, 1H), 6.71 (d, $J = 2.2$ Hz, 1H), 6.85 (d, $J = 8.7$ Hz, 1H), 7.04 (dd, $J_1 = 8.7$ Hz, $J_2 = 2.3$ Hz, 1H), 7.11 (d, $J = 3.9$ Hz, 2H), 7.18-7.29 (m, 4H), 7.40-7.44 (m, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 22.7, 30.5, 37.8, 43.1, 115.3, 124.6, 126.2, 126.6, 127.4, 127.7, 127.8, 128.0, 128.5, 128.9, 130.5, 130.6, 130.8, 132.6, 133.7, 136.7, 138.0, 138.1, 173.8; HRMS (ESI) calcd for $\text{C}_{25}\text{H}_{20}\text{NOCl}$: ($\text{M} + \text{H}^+$) 386.1306, found: 386.1298.



2-Fluoro-5,6a-dimethyl-12-phenyl-6a,7-dihydrobenzo[*j*]phenanthridin-6(5*H*)-one
(**3e**)

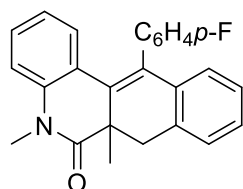
Yield: 58%; ^1H NMR (400 MHz, CDCl_3) δ 1.24 (s, 3H), 3.34 (d, $J = 16.4$ Hz, 1H), 3.39 (s, 3H), 3.47 (d, $J = 16.4$ Hz, 1H), 6.47 (dd, $J_1 = 11.0$ Hz, $J_2 = 2.7$ Hz, 1H), 6.77-6.82 (m, 1H), 6.87 (dd, $J_1 = 8.9$ Hz, $J_2 = 5.0$ Hz, 1H), 7.08-7.13 (m, 2H), 7.18-7.40 (m, 4H), 7.37-7.43 (m, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 22.7, 30.6, 37.8, 43.0, 114.6 (d, $^2J_{\text{CF}} = 22.9$ Hz), 115.2 (d, $^3J_{\text{CF}} = 8.2$ Hz), 117.2 (d, $^2J_{\text{CF}} = 25.4$ Hz), 124.9 (d, $^3J_{\text{CF}} = 8.1$ Hz), 126.2, 126.5,

127.7, 128.0, 128.5, 128.9, 130.5, 131.1, 132.7, 133.8, 135.8, 136.7, 138.2, 157.8 (d, $^1J_{\text{CF}} = 240.4$ Hz), 173.6; HRMS (ESI) calcd for $\text{C}_{25}\text{H}_{20}\text{NOF}$: ($\text{M} + \text{H}^+$) 370.1602, found: 370.1608.



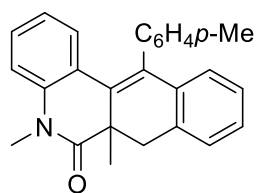
5,6a-dimethyl-6-oxo-12-phenyl-5,6,6a,7-tetrahydrobenzo[*j*]phenanthridine-2-carbonitrile (**3f**)

Yield: 50%; ^1H NMR (400 MHz, CDCl_3) δ 1.25 (s, 3H), 3.34 (d, $J = 16.4$ Hz, 1H), 3.43 (s, 3H), 3.50 (d, $J = 16.3$ Hz, 1H), 6.99-7.01 (m, 2H), 7.13 (d, $J = 3.7$ Hz, 2H), 7.21-7.26 (m, 3H), 7.29 (d, $J = 7.2$ Hz, 1H), 7.36 (dd, $J_1 = 8.5$ Hz, $J_2 = 1.5$ Hz, 1H), 7.44 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 22.8, 30.5, 37.7, 43.1, 105.5, 114.7, 118.4, 123.9, 126.4, 126.7, 128.1, 128.4, 128.6, 129.1, 129.6, 130.4, 131.6, 132.4, 133.4, 134.4, 137.5, 137.8, 142.8, 174.1; HRMS (ESI) calcd for $\text{C}_{26}\text{H}_{20}\text{N}_2\text{O}$: ($\text{M} + \text{H}^+$) 377.1648, found: 377.1651.



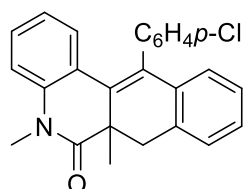
12-(4-Fluorophenyl)-5,6a-dimethyl-6a,7-dihydrobenzo[*j*]phenanthridin-6(5*H*)-one (**3g**)

Yield: 58%; ^1H NMR (400 MHz, CDCl_3) δ 1.23 (s, 3H), 3.33 (d, $J = 16.3$ Hz, 1H), 3.41 (s, 3H), 3.48 (d, $J = 16.3$ Hz, 1H), 6.64 (t, $J = 7.6$ Hz, 1H), 6.76 (d, $J = 7.2$ Hz, 1H), 6.96 (d, $J = 8.1$ Hz, 1H), 7.03-7.14 (m, 5H), 7.17-7.30 (m, 4H); ^{13}C NMR (100 MHz, CDCl_3) δ 22.7, 30.4, 37.8, 43.3, 114.3, 115.7 (d, $^2J_{\text{CF}} = 21.3$ Hz), 122.1, 123.0, 125.7, 126.5, 127.8, 128.2, 128.6, 130.6, 132.4, 132.5, 132.6, 132.8, 134.0, 134.5 (d, $^2J_{\text{CF}} = 23.3$ Hz), 139.5, 162.1 (d, $^1J_{\text{CF}} = 246.5$ Hz), 173.9; HRMS (ESI) calcd for $\text{C}_{25}\text{H}_{20}\text{NOF}$: ($\text{M} + \text{H}^+$) 370.1602, found: 370.1610.



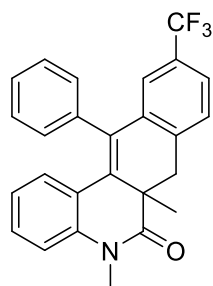
5,6a-dimethyl-12-(*p*-tolyl)-6a,7-dihydrobenzo[*j*]phenanthridin-6(5*H*)-one (**3h**)

Yield: 48%; ^1H NMR (400 MHz, CDCl_3) δ 1.23 (s, 3H), 2.40 (s, 3H), 3.33 (d, J = 16.3 Hz, 1H), 3.41 (s, 3H), 3.46 (d, J = 16.3 Hz, 1H), 6.61 (t, J = 7.6 Hz, 1H), 6.65 (d, J = 7.9 Hz, 1H), 6.94 (d, J = 8.1 Hz, 1H), 7.11-7.21 (m, 8H), 7.26-7.28 (m, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 21.3, 22.6, 30.3, 37.9, 43.3, 114.1, 122.0, 123.3, 125.9, 126.4, 127.5, 127.9, 128.4, 129.3, 130.6, 130.7, 132.0, 132.6, 134.4, 135.4, 135.7, 136.8, 139.4, 174.1; HRMS (ESI) calcd for $\text{C}_{26}\text{H}_{23}\text{NO}$: ($\text{M} + \text{H}^+$) 366.1852, found: 366.1848.



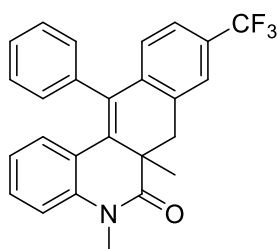
12-(4-Chlorophenyl)-5,6a-dimethyl-6a,7-dihydrobenzo[*j*]phenanthridin-6(5*H*)-one (**3i**)

Yield: 62%; ^1H NMR (400 MHz, CDCl_3) δ 1.23 (s, 3H), 3.33 (d, J = 16.3 Hz, 1H), 3.40 (s, 3H), 3.48 (d, J = 16.3 Hz, 1H), 6.66 (t, J = 7.6 Hz, 1H), 6.79 (d, J = 7.9 Hz, 1H), 6.96 (d, J = 8.1 Hz, 1H), 7.01 (d, J = 7.8 Hz, 1H), 7.09-7.21 (m, 5H), 7.29 (d, J = 7.1 Hz, 1H), 7.37 (d, J = 7.8 Hz, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 22.7, 30.4, 37.8, 43.3, 114.3, 122.2, 122.9, 125.6, 126.5, 127.8, 128.3, 128.6, 128.9, 130.6, 132.3, 132.6, 132.8, 133.2, 133.8, 134.2, 137.3, 139.5, 173.9; HRMS (ESI) calcd for $\text{C}_{25}\text{H}_{20}\text{NOCl}$: ($\text{M} + \text{H}^+$) 386.1306, found: 386.1296.



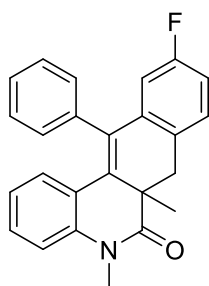
5,6a-dimethyl-12-phenyl-10-(trifluoromethyl)-6a,7-dihydrobenzo[*j*]phenanthridin-6(5*H*)-one (**3j**)

Yield: 24%; ^1H NMR (400 MHz, CDCl_3) δ 1.26 (s, 3H), 3.39 (d, $J = 19.8$ Hz, 4H), 3.51 (d, $J = 16.5$ Hz, 1H), 6.61 (t, $J = 7.5$ Hz, 1H), 6.81 (d, $J = 7.2$ Hz, 1H), 6.97 (t, $J = 8.1$ Hz, 1H), 7.13 (t, $J = 7.3$ Hz, 1H), 7.18 (d, $J = 8.2$ Hz, 1H), 7.23-7.26 (m, 2H), 7.33 (d, $J = 8.2$ Hz, 1H), 7.37-7.43 (m, 3H), 7.52 (s, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 22.9, 30.4, 37.6, 43.4, 114.3, 122.1, 122.6, 123.4, 125.0, 125.1, 125.9, 127.6, 128.7, 128.8, 128.9, 130.7, 130.8, 133.3, 134.3, 134.9, 137.4, 138.1, 139.5, 173.4; HRMS (ESI) calcd for $\text{C}_{26}\text{H}_{20}\text{NOF}_3$: ($\text{M} + \text{H}^+$) 420.1570, found: 420.1573.



5,6a-dimethyl-12-phenyl-9-(trifluoromethyl)-6a,7-dihydrobenzo[*j*]phenanthridin-6(5*H*)-one (**3j'**)

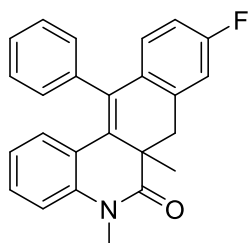
Yield: 26%; ^1H NMR (400 MHz, CDCl_3) δ 1.24 (s, 3H), 3.40 (d, $J = 15.1$ Hz, 4H), 3.50 (d, $J = 16.7$ Hz, 1H), 6.61 (t, $J = 7.5$ Hz, 1H), 6.78 (d, $J = 7.9$ Hz, 1H), 6.96 (d, $J = 8.1$ Hz, 1H), 7.13 (t, $J = 7.2$ Hz, 1H), 7.26 (s, 2H), 7.35-7.44 (m, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 22.8, 30.4, 37.8, 43.3, 114.3, 122.2, 122.3, 122.3, 122.7, 124.1, 124.2, 127.7, 128.6, 128.8, 128.9, 130.7, 130.7, 134.0, 134.3, 134.8, 136.5, 137.8, 139.5, 173.5; HRMS (ESI) calcd for $\text{C}_{26}\text{H}_{20}\text{NOF}_3$: ($\text{M} + \text{H}^+$) 420.1570, found: 420.1573.



10-fluoro-5,6a-dimethyl-12-phenyl-6a,7-dihydrobenzo[*j*]phenanthridin-6(5*H*)-one (**3k**)

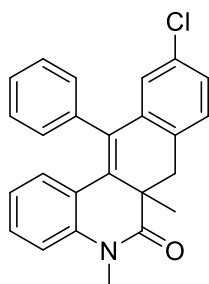
Yield: 28%; ^1H NMR (400 MHz, CDCl_3) δ 1.23 (s, 3H), 3.32 (d, $J = 16.2$ Hz, 1H), 3.40 (d, $J = 9.6$ Hz, 4H), 6.60 (t, $J = 7.6$ Hz, 1H), 6.79-6.89 (m, 3H), 6.95 (d, $J = 8.1$ Hz, 1H), 7.11 (t, $J = 7.2$ Hz, 1H), 7.23 (dd, $J_1 = 12.6$ Hz, $J_2 = 6.2$ Hz, 3H), 7.36-7.42 (m, 3H); ^{13}C NMR

(100 MHz, CDCl₃) δ 22.6, 30.4, 37.1, 43.5, 112.9 (d, $^2J_{CF}$ = 23.9 Hz), 113.9 (d, $^2J_{CF}$ = 21.5 Hz), 114.2, 122.1, 122.7, 127.5, 128.0, 128.4, 128.8, 129.3, 129.5, 129.6, 130.7, 133.6, 134.6, 138.3, 139.5, 161.8 (d, $^1J_{CF}$ = 242.0 Hz), 173.8; HRMS (ESI) calcd for C₂₅H₂₀NOF: (M + H⁺) 370.1602, found: 370.1608.



9-fluoro-5,6a-dimethyl-12-phenyl-6a,7-dihydrobenzo[j]phenanthridin-6(5H)-one
(**3k'**)

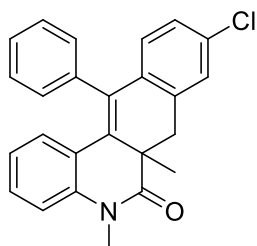
Yield: 42%; ¹H NMR (400 MHz, CDCl₃) δ 1.24 (s, 3H), 3.31 (d, J = 16.5 Hz, 1H), 3.41 (s, 3H), 3.48 (d, J = 16.4 Hz, 1H), 6.59 (t, J = 7.6 Hz, 1H), 6.77 (d, J = 8.7 Hz, 2H), 6.95 (d, J = 8.0 Hz, 1H), 6.98-7.05 (m, 2H), 7.10 (t, J = 7.2 Hz, 1H), 7.23-7.26 (m, 2H), 7.35-7.41 (m, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 22.8, 30.4, 37.9, 43.1, 112.9 (d, $^2J_{CF}$ = 21.0 Hz), 114.2, 115.4 (d, $^2J_{CF}$ = 21.8 Hz), 122.1, 123.0, 127.4, 127.8 (d, $^3J_{CF}$ = 8.1 Hz), 128.1, 128.7, 130.4, 130.6, 130.8, 131.3, 134.6, 135.2, 138.7, 139.3, 162.1 (d, $^1J_{CF}$ = 248.5 Hz), 173.8; HRMS (ESI) calcd for C₂₅H₂₀NOF: (M + H⁺) 370.1602, found: 370.1611.



10-chloro-5,6a-dimethyl-12-phenyl-6a,7-dihydrobenzo[j]phenanthridin-6(5H)-one
(**3l**)

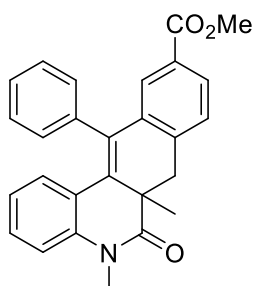
Yield: 38%; ¹H NMR (400 MHz, CDCl₃) δ 1.23 (s, 3H), 3.31 (d, J = 16.4 Hz, 1H), 3.40 (s, 3H), 3.41 (d, J = 16.0 Hz, 1H), 6.60 (t, J = 7.6 Hz, 1H), 6.78 (d, J = 7.1 Hz, 1H), 6.95 (d, J = 8.1 Hz, 1H), 7.07-7.16 (m, 3H), 7.20-7.25 (m, 3H), 7.37-7.43 (m, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 22.7, 30.4, 37.3, 43.4, 114.3, 122.1, 122.7, 125.8, 127.4, 127.6, 128.5, 128.9, 129.7, 130.7, 130.9, 132.3, 133.8, 134.4, 135.9, 138.1, 139.5, 173.7; HRMS (ESI)

calcd for $C_{25}H_{20}NOCl$: ($M + H^+$) 386.1306, found: 386.1309.



9-chloro-5,6a-dimethyl-12-phenyl-6a,7-dihydrobenzo[*j*]phenanthridin-6(5*H*)-one (**3l'**)

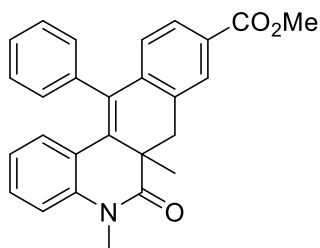
Yield: 30%; 1H NMR (400 MHz, $CDCl_3$) δ 1.23 (s, 3H), 3.30 (d, $J = 16.5$ Hz, 1H), 3.41 (s, 3H), 3.46 (d, $J = 16.5$ Hz, 1H), 6.59 (t, $J = 7.6$ Hz, 1H), 6.77 (d, $J = 7.3$ Hz, 1H), 6.95 (d, $J = 8.1$ Hz, 1H), 7.00 (d, $J = 8.5$ Hz, 1H), 7.05 (d, $J = 9.9$ Hz, 1H), 7.11 (t, $J = 7.3$ Hz, 1H), 7.23-7.26 (m, 3H), 7.34-7.41 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 22.7, 30.4, 37.7, 43.3, 114.3, 122.1, 122.9, 126.5, 127.2, 127.4, 128.3, 128.8, 130.6, 130.7, 132.5, 132.8, 133.1, 134.5, 138.4, 139.4, 173.7; HRMS (ESI) calcd for $C_{25}H_{20}NOCl$: ($M + H^+$) 386.1306, found: 386.1304.



Methyl

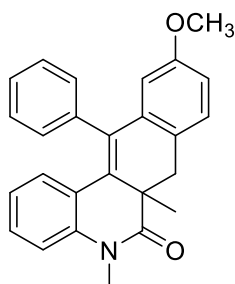
5,6a-dimethyl-6-oxo-12-phenyl-5,6,6a,7-tetrahydrobenzo[*j*]phenanthridine-10-carboxylate (**3m**)

Yield: 33%; 1H NMR (400 MHz, $CDCl_3$) δ 1.24 (s, 3H), 3.41 (s, 3H), 3.51 (d, $J = 17.3$ Hz, 1H), 3.99 (d, $J = 19.2$ Hz, 4H), 6.60 (t, $J = 7.5$ Hz, 1H), 6.79 (d, $J = 7.6$ Hz, 1H), 6.95 (d, $J = 8.1$ Hz, 1H), 7.12 (td, $J_1 = 7.6$ Hz, $J_2 = 2.6$ Hz, 2H), 7.23 (d, $J = 7.5$ Hz, 3H), 7.36-7.42 (m, 3H), 7.65 (d, $J = 7.5$ Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 23.1, 30.4, 34.6, 43.0, 52.2, 114.2, 121.9, 122.8, 125.8, 127.4, 128.3, 128.7, 129.1, 129.2, 130.4, 130.9, 133.3, 133.4, 134.7, 135.3, 138.6, 139.5, 168.5, 173.6; HRMS (ESI) calcd for $C_{27}H_{23}NO_3$: ($M + H^+$) 410.1751, found: 410.1769.



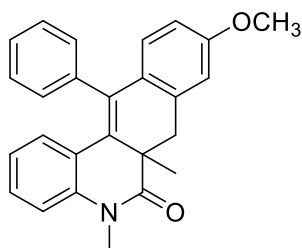
Methyl 5,6a-dimethyl-6-oxo-12-phenyl-5,6,6a,7-tetrahydrobenzo[j]phenanthridine-9-carboxylate
(**3m'**)

Yield: 38%; ^1H NMR (400 MHz, CDCl_3) δ 1.23 (s, 3H), 3.41 (d, $J = 16.5$ Hz, 1H), 3.43 (s, 3H), 3.50 (d, $J = 16.6$ Hz, 1H), 3.82 (s, 3H), 6.60 (t, $J = 7.6$ Hz, 1H), 6.79 (d, $J = 7.1$ Hz, 1H), 6.96 (d, $J = 8.1$ Hz, 1H), 7.11 (t, $J = 7.1$ Hz, 1H), 7.26 (s, 1H), 7.34-7.44 (m, 5H), 7.83-7.87 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 22.7, 30.4, 38.1, 43.3, 51.9, 114.3, 122.1, 122.8, 125.7, 126.8, 127.6, 127.9, 128.4, 128.6, 128.7, 128.9, 129.4, 130.8, 133.3, 134.4, 134.7, 138.1, 139.4, 167.0, 173.7; HRMS (ESI) calcd for $\text{C}_{27}\text{H}_{23}\text{NO}_3$: ($\text{M} + \text{H}^+$) 410.1751, found: 410.1760.



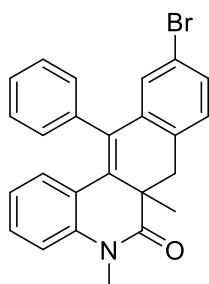
10-methoxy-5,6a-dimethyl-12-phenyl-6a,7-dihydrobenzo[j]phenanthridin-6(5H)-one
(**3n**)

Yield: 28%; ^1H NMR (400 MHz, CDCl_3) δ 1.23 (s, 3H), 3.28 (d, $J = 16.1$ Hz, 1H), 3.39 (d, $J = 11.8$ Hz, 4H), 3.68 (s, 3H), 6.59 (t, $J = 7.6$ Hz, 1H), 6.69 (d, $J = 2.4$ Hz, 1H), 6.74 (dd, $J_1 = 8.1$ Hz, $J_2 = 2.5$ Hz, 1H), 6.80 (d, $J = 7.9$ Hz, 1H), 6.94 (d, $J = 8.1$ Hz, 1H), 7.09 (t, $J = 7.7$ Hz, 1H), 7.19-7.25 (m, 3H), 7.33-7.40 (m, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 22.5, 30.3, 37.1, 43.5, 55.2, 111.9, 112.9, 114.2, 121.9, 123.1, 124.8, 127.3, 128.1, 128.7, 129.2, 130.8, 131.1, 132.9, 135.2, 135.3, 138.7, 139.5, 158.3, 174.1; HRMS (ESI) calcd for $\text{C}_{26}\text{H}_{23}\text{NO}_2$: ($\text{M} + \text{H}^+$) 382.1802, found: 382.1811.



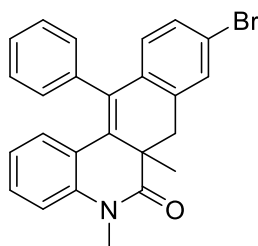
9-methoxy-5,6a-dimethyl-12-phenyl-6a,7-dihydrobenzo[*j*]phenanthridin-6(5*H*)-one
(**3n'**)

Yield: 43%; ^1H NMR (400 MHz, CDCl_3) δ 1.23 (s, 3H), 3.30 (d, $J = 16.4$ Hz, 1H), 3.40 (s, 3H), 3.47 (d, $J = 16.3$ Hz, 1H), 3.80 (s, 3H), 6.58 (t, $J = 7.2$ Hz, 1H), 6.62 (dd, $J_1 = 8.7$ Hz, $J_1 = 2.5$ Hz, 1H), 6.76 (d, $J = 8.0$ Hz, 1H), 6.85 (d, $J = 2.1$ Hz, 1H), 6.93 (d, $J = 7.7$ Hz, 1H), 6.99 (d, $J = 8.7$ Hz, 1H), 7.07 (t, $J = 7.7$ Hz, 1H), 7.19-7.25 (m, 2H), 7.33-7.40 (m, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 22.8, 30.4, 38.4, 43.2, 55.3, 111.4, 114.2, 114.3, 122.0, 123.5, 127.2, 127.4, 127.5, 127.7, 128.7, 129.4, 130.5, 130.8, 134.6, 135.3, 139.1, 139.3, 159.2, 174.2; HRMS (ESI) calcd for $\text{C}_{26}\text{H}_{23}\text{NO}_2$: ($\text{M} + \text{H}^+$) 382.1802, found: 382.1810.



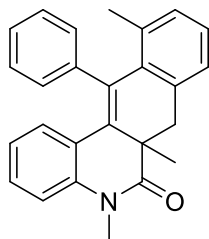
10-bromo-5,6a-dimethyl-12-phenyl-6a,7-dihydrobenzo[*j*]phenanthridin-6(5*H*)-one
(**3o**)

Yield: 32%; ^1H NMR (400 MHz, CDCl_3) δ 1.22 (s, 3H), 3.30 (d, $J = 16.4$ Hz, 1H), 3.39 (d, $J = 13.7$ Hz, 4H), 6.59 (t, $J = 7.6$ Hz, 1H), 6.77 (d, $J = 7.8$ Hz, 1H), 6.95 (d, $J = 8.1$ Hz, 1H), 7.11 (t, $J = 7.7$ Hz, 1H), 7.15 (d, $J = 7.9$ Hz, 1H), 7.21-7.25 (m, 3H), 7.30 (d, $J = 7.9$ Hz, 1H), 7.35-7.43 (m, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 22.7, 30.4, 37.4, 43.4, 114.3, 120.4, 122.1, 122.7, 127.6, 128.5, 128.6, 128.9, 130.0, 130.3, 130.7, 131.4, 133.8, 134.3, 136.3, 138.0, 139.5, 173.7; HRMS (ESI) calcd for $\text{C}_{25}\text{H}_{20}\text{NOBr}$: ($\text{M} + \text{H}^+$) 430.0801, found: 430.0791.



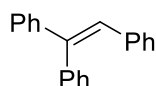
9-bromo-5,6a-dimethyl-12-phenyl-6a,7-dihydrobenzo[*j*]phenanthridin-6(5*H*)-one
(**3o'**)

Yield: 20%; ^1H NMR (400 MHz, CDCl_3) δ 1.23 (s, 3H), 3.30 (d, $J = 16.5$ Hz, 1H), 3.41 (s, 3H), 3.46 (d, $J = 16.4$ Hz, 1H), 6.59 (t, $J = 7.6$ Hz, 1H), 6.77 (d, $J = 8.0$ Hz, 1H), 6.94 (t, $J = 7.6$ Hz, 2H), 7.11 (t, $J = 7.7$ Hz, 1H), 7.20-7.22 (m, 3H), 7.36-7.42 (m, 4H); ^{13}C NMR (100 MHz, CDCl_3) δ 22.7, 30.4, 37.6, 43.3, 114.3, 121.4, 122.1, 122.9, 127.4, 127.5, 128.3, 128.8, 129.5, 130.6, 130.7, 131.2, 132.7, 133.2, 134.5, 134.8, 138.3, 139.4, 173.6; HRMS (ESI) calcd for $\text{C}_{25}\text{H}_{20}\text{NOBr}$: ($\text{M} + \text{H}^+$) 430.0801, found: 430.0792.



5,6a,11-trimethyl-12-phenyl-6a,7-dihydrobenzo[*j*]phenanthridin-6(5*H*)-one (**3p**)

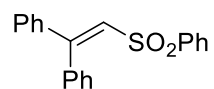
Yield: 43%; ^1H NMR (400 MHz, CDCl_3) δ 1.24 (s, 3H), 2.42 (s, 3H), 3.32 (d, $J = 16.8$ Hz, 1H), 3.41 (s, 3H), 3.45 (d, $J = 16.8$ Hz, 1H), 6.59 (t, $J = 7.6$ Hz, 1H), 6.78 (d, $J = 7.9$ Hz, 1H), 6.93 (d, $J = 6.7$ Hz, 2H), 6.99 (d, $J = 7.6$ Hz, 1H), 7.06-7.11 (m, 2H), 7.24 (s, 2H), 7.31-7.39 (m, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 19.8, 23.4, 30.4, 34.1, 43.1, 114.1, 121.9, 123.4, 124.3, 125.7, 127.1, 127.9, 128.6, 129.7, 130.5, 130.8, 130.9, 131.5, 133.9, 135.8, 135.9, 139.1, 139.3, 174.3; HRMS (ESI) calcd for $\text{C}_{26}\text{H}_{23}\text{NO}$: ($\text{M} + \text{H}^+$) 366.1852, found: 366.1866.



Ethene-1,1,2-triyltribenzene ¹

^1H NMR (400 MHz, CDCl_3) δ 6.97 (s, 1H), 7.03 (d, $J = 6.9$ Hz, 2H), 7.11-7.13 (m, 3H), 7.20-7.21 (m, 2H), 7.29-7.32 (m, 8H); ^{13}C NMR (100 MHz, CDCl_3) δ 126.7, 127.4, 127.5,

127.6, 127.9, 128.1, 128.2, 128.6, 129.5, 130.4, 137.3, 140.4, 142.5, 143.4.



(2-(phenylsulfonyl)ethene-1,1-diyl)dibenzene ²

¹H NMR (400 MHz, CDCl₃) δ 7.03 (s, 1H), 7.08 (d, *J* = 7.3 Hz, 2H), 7.21 (d, *J* = 7.5 Hz, 2H), 7.26-7.36 (m, 8H), 7.48 (t, *J* = 7.4 Hz, 1H), 7.58 (t, *J* = 7.6 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 127.6, 127.8, 128.2, 128.5, 128.6, 128.7, 128.8, 129.7, 130.3, 132.8, 135.4, 139.1, 141.4, 155.2.

References:

- 1) B. J. Li, Y. Z. Li, X. Y. Lu, J. Lu, B. T. Guan, Z. J. Shi, *Angew. Chem., Int. Ed.* 2008, **120**, 10278.
- 2) G. A. Russell, P. Ngoviwatthai, H. Tashtoush, J. Hershberger, *Organometallics* 1987, **6**, 1414.

