Supplementary Information

Copper-Catalyzed Cascade Cyclization of 1,7-Enynes with Aromatic Sulfonyl Chlorides toward Benzo[j]phenanthridin-6(5H)-ones

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(A) Typical Experimental Procedure

(a) Typical Experimental Procedure for the Copper-Catalyzed Synthesis of Benzo[j]phenanthridin-6(5H)-ones (3):

To a Schlenk tube were added N-Arylacrylamides 1 (0.3 mmol), aromatic sulfonyl chlorides 2 (2 equiv), CuCl (20 mol%), Na$_2$CO$_3$ (2 equiv) and m-xylene (2 mL). Then the tube was charged with argon, and was stirred at 130 °C (oil bath temperature) for the indicated times until complete consumption of starting material as monitored by TLC and/or GC-MS analysis. After the reaction was finished, the reaction mixture was washed with brine. The aqueous phase was re-extracted with ethyl acetate. The combined organic extracts were dried over Na$_2$SO$_4$, concentrated in vacuum, and the resulting residue was purified by silica gel column chromatography (hexane/ethyl acetate = 12:1) to afford the desired benzo[j]phenanthridin-6(5H)-ones 3.

(b) Mechanism Discussion

Three radical inhibitors, including TEMPO, hydroquinone and BHT, were examined. While 2 equiv TEMPO completely suppressed the current cyclization reaction, the other radical inhibitors, hydroquinone and BHT, slightly decreased the yield of 3ab from 84% to 68 and 70%, respectively. Thus, we can not rule a radical process.

The possible mechanisms consistent with the present results are outlined in
Scheme S1. Oxidative addition of the active Cu$^+$ species to benzenesulfonyl chloride (2b) produces Ph-Cu$^{2+}$ intermediate A. Addition of Ph-Cu$^{2+}$ intermediate A to the C-C triple bond yields alkenyl-Cu$^{2+}$ intermediate B, followed by cyclization with the C-C double bond affords alkyl-Cu$^{2+}$ intermediate C. Finally, alkyl-Cu$^{2+}$ intermediate C undergoes the cyclization with an aryl sp$^2$ C-H bond results in the formation of the desired product 3ab and regeneration of the active Cu$^+$ species.

On the other hand, benzenesulfonyl chloride (2b) may be converted into a phenyl radical, followed by addition and cascade cyclization with substrate 1a form radical intermediate D. Single electron transfer of intermediate D takes place to give cation intermediate E and regenerate the active Cu$^+$ species. Finally, deprotonation of intermediate E de

**(B) Analytical data**
9-Chloro-5,6a-dimethyl-12-phenyl-6a,7-dihydrobenzo[j]phenanthridin-6(5H)-one (3aa):

White solid, mp 183.3-184.2 °C (uncorrected); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ (ppm): 7.42-7.34 (m, 3H), 7.26-7.23 (m, 3H), 7.11 (t, $J = 8.0$ Hz, 1H), 7.05 (d, $J = 8.8$ Hz, 1H), 7.00 (d, $J = 8.4$ Hz, 1H), 6.95 (d, $J = 8.0$ Hz, 1H), 6.77 (d, $J = 8.0$ Hz, 1H), 6.60 (t, $J = 7.6$ Hz, 1H), 3.46 (d, $J = 16.4$ Hz, 1H), 3.41 (s, 3H), 3.30 (d, $J = 16.4$ Hz, 1H), 1.23 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ (ppm): 173.7, 139.4, 138.4, 134.5 (2C), 133.1, 132.8, 132.5, 130.7, 130.6, 128.8, 128.3 (2C), 127.4, 127.2, 126.5, 122.9, 122.1, 114.3, 43.3, 37.7, 30.4, 22.7; IR (KBr, cm$^{-1}$): 1681, 1477; LRMS (EI 70 ev) m/z (%): 387 (M$^+$+2, 6), 385 (M$^+$, 19), 371 (30), 370 (100); HRMS (ESI) for C$_{25}$H$_{21}$Cl$_3$NO [(M+H)$^+$]: calcd 386.1306, found 386.1299.

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

White solid, mp 173.5-174.8 °C (uncorrected); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ (ppm): 7.40-7.32 (m, 3H), 7.29-7.24 (m, 3H), 7.20-7.16 (m, 1H), 7.11-7.07 (m, 3H), 6.94 (d, $J = 8.0$ Hz, 1H), 6.80 (d, $J = 8.0$ Hz, 1H), 6.59 (t, $J = 8.4$ Hz, 1H), 3.48 (d, $J = 16.4$ Hz, 1H), 3.40 (s, 3H), 3.34 (d, $J = 16.4$ Hz, 1H), 1.24 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ (ppm): 174.1, 139.4, 138.7, 135.4, 134.1, 132.6, 132.1, 130.8, 130.7,
128.6, 128.5, 128.1, 127.6, 127.2, 126.4, 125.9, 123.1, 122.0, 114.2, 43.3, 37.9, 30.3, 22.6; IR (KBr, cm⁻¹): 1676, 1474; LRMS (EI 70 ev) m/z (%): 351 (M⁺, 21), 337 (31), 336 (100); HRMS (ESI) for C₂₅H₂₂NO [(M+H)⁺]: calcd 352.1696, found 352.1698.

![Chemical structure of 9-Methoxy-5,6a-dimethyl-12-phenyl-6a,7-dihydrobenzo[j]phenanthridin-6(5H)-one (3ac)](image)

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

White solid, mp 203.4-205.6 °C (uncorrected); ¹H NMR (400 MHz, CDCl₃) δ (ppm): 7.44-7.33 (m, 3H), 7.26-7.24 (m, 2H), 7.08 (t, J = 8.4 Hz, 1H), 7.00 (d, J = 8.8 Hz, 1H), 6.94 (d, J = 8.0 Hz, 1H), 6.86 (s, 1H), 6.76 (d, J = 8.0 Hz, 1H), 6.64-6.57 (m, 2H), 3.81 (s, 3H), 3.47 (d, J = 16.0 Hz, 1H), 3.41 (s, 3H), 3.30 (d, J = 16.4 Hz, 1H), 1.24 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ (ppm): 174.2, 159.2, 139.2, 139.1, 135.2, 134.6, 130.7, 130.5, 129.4, 128.6, 127.7, 127.5, 127.3, 127.1, 123.4, 122.0, 114.2 (2C), 111.3, 55.2, 43.1, 38.3, 30.4, 22.7; IR (KBr, cm⁻¹): 1655, 1473; LRMS (EI 70 ev) m/z (%): 381 (M⁺, 39), 367 (27), 366 (100); HRMS (ESI) for C₂₆H₂₄NO₂ [(M+H)⁺]: calcd 382.1802, found 382.1792.

![C-H Cosy (HSQC)](image)
C-H Cosy (HMBC)

H-H Cosy
9-Fluoro-5,6a-dimethyl-12-phenyl-6a,7-dihydrobenzo[j]phenanthridin-6(5H)-one (3ad)

White solid, mp 190.3-192.5 °C (uncorrected); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ (ppm): 7.34-7.26 (m, 3H), 7.18-7.16 (m, 2H), 7.03 (t, $J = 7.6$ Hz, 1H), 6.98-6.92 (m, 2H), 6.87 (d, $J = 7.6$ Hz, 1H), 6.69 (t, $J = 8.0$ Hz, 2H), 6.52 (t, $J = 7.6$ Hz, 1H), 3.40 (d, $J = 16.4$ Hz, 1H), 3.34 (s, 3H), 3.23 (d, $J = 16.4$ Hz, 1H), 1.16 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ (ppm): 173.8, 162.1 (d, $J = 247.1$ Hz, 1C), 139.3, 138.6, 135.3 (d, $J = 7.8$ Hz, 1C), 134.6, 131.3, 130.7, 130.5 (d, $J = 17.1$ Hz, 1C), 128.7, 128.1, 127.8, 127.7, 127.4, 123.0, 122.1, 115.4 (d, $J = 21.8$ Hz, 1C), 114.3, 112.9 (d, $J = 21.0$ Hz, 1C), 43.1, 37.9, 30.4, 22.7; IR (KBr, cm$^{-1}$): 1663, 1470; LRMS (EI 70 ev) m/z
9-Iodo-5,6a-dimethyl-12-phenyl-6a,7-dihydrobenzo[j]phenanthridin-6(5H)-one (3ae)

White solid, mp 242.5-243.8 °C (uncorrected); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ (ppm): 7.50 (d, $J = 8.0$ Hz, 1H), 7.43-7.37 (m, 4H), 7.26-7.21 (m, 2H), 7.10 (t, $J = 8.4$ Hz, 1H), 7.02 (d, $J = 8.0$ Hz, 1H), 6.95 (d, $J = 8.4$ Hz, 1H), 6.75 (t, $J = 8.0$ Hz, 1H), 6.59 (t, $J = 8.4$ Hz, 1H), 3.40-3.38 (m, 4H), 3.28 (d, $J = 8.4$ Hz, 1H), 1.22 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ (ppm): 173.7, 139.5, 138.0, 136.5, 136.4, 134.5, 134.1, 133.7, 132.2, 130.7, 130.3, 128.9, 128.5, 127.6, 122.7, 122.1, 114.3, 100.0, 91.7, 43.3, 37.5, 30.4, 22.6; IR (KBr, cm$^{-1}$): 1663, 1475; LRMS (EI 70 ev) $m/z$ (%): 497 (M$^+$, 11), 483 (26), 482 (83), 371 (36), 370 (100); HRMS (ESI) for C$_{25}$H$_{21}$INO [(M+H)$^+$]: calcd 498.9022, found 498.9016.

9-Acetyl-5,6a-dimethyl-12-phenyl-6a,7-dihydrobenzo[j]phenanthridin-6(5H)-one (3af)
White solid, mp 195.2-197.1 °C (uncorrected); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ (ppm): 7.79-7.70 (m, 1H), 7.66-7.60 (m, 1H), 7.35-7.30 (m, 4H), 7.19-7.16 (m, 2H), 7.04 (t, $J = 7.6$ Hz, 1H), 6.88 (d, $J = 8.0$ Hz, 1H), 6.72 (d, $J = 8.0$ Hz, 1H), 6.53 (t, $J = 7.6$ Hz, 1H), 3.44-3.31 (m, 5H), 2.36 (s, 3H), 1.16 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ (ppm): 197.7, 173.5, 139.4, 138.3, 138.0, 135.8, 134.6, 134.4, 133.4, 130.7 (2C), 128.9, 128.7, 128.4, 127.6, 127.5, 125.6, 122.1, 114.3, 43.3, 38.0, 30.4, 26.4; IR (KBr, cm$^{-1}$): 1671, 1624, 1589, 1457; LRMS (EI 70 ev) $m/z$ (%): 393 (M$^+$, 32), 379 (28), 378 (100); HRMS (ESI) for C$_{27}$H$_{24}$NO$_2$ [(M+H)$^+$]: calcd 394.1802, found 394.1795.

![5,6a-Dimethyl-9-nitro-12-phenyl-6a,7-dihydrobenzo[j]phenanthridin-6(5H)-one](image)

5,6a-Dimethyl-9-nitro-12-phenyl-6a,7-dihydrobenzo[j]phenanthridin-6(5H)-one (3ag)

Yellow solid, mp 185.8-186.7 °C (uncorrected); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ (ppm): 8.04 (d, $J = 8.0$ Hz, 1H), 7.99 (s, 1H), 7.48-7.44 (m, 4H), 7.27-7.25 (m, 2H), 7.15 (t, $J = 8.0$ Hz, 1H), 6.99 (d, $J = 8.0$ Hz, 1H), 6.80 (d, $J = 8.0$ Hz, 1H), 6.32 (d, $J = 8.4$ Hz, 1H), 3.56-3.44 (m, 2H), 3.43 (s, 3H), 1.26 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ (ppm): 173.1, 147.3, 140.1, 137.3, 130.8, 130.6, 129.2 (2C), 128.9, 128.0, 122.3 (2C), 120.4, 114.4, 43.4, 37.9, 30.4, 23.0; IR (KBr, cm$^{-1}$): 1679, 1489; LRMS (EI 70 ev) $m/z$ (%): 396 (M$^+$, 23), 382 (27), 381 (100); HRMS (ESI) for C$_{25}$H$_{21}$N$_2$O$_3$ [(M+H)$^+$]: calcd 397.1547, found 397.1549.
5,6a-Dimethyl-10-nitro-12-phenyl-6a,7-dihydrobenzo[j]phenanthridin-6(5H)-one (3ah)

Yellow solid, mp 189.2-192.0 °C (uncorrected); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ (ppm): 7.65 (d, $J = 8.0$ Hz, 1H), 7.44-7.39 (m, 3H), 7.31 (d, $J = 7.6$ Hz, 1H), 7.24-7.13 (m, 4H), 6.97 (d, $J = 8.4$ Hz, 1H), 6.79 (d, $J = 7.6$ Hz, 1H), 6.62 (t, $J = 7.6$ Hz, 1H), 3.73 (d, $J = 17.6$ Hz, 1H), 3.55 (d, $J = 18.0$ Hz, 1H), 3.41 (s, 3H), 1.25 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ (ppm): 172.8, 150.1, 139.4, 137.9, 130.8, 130.4, 129.7, 129.0, 128.8, 127.7, 126.9, 126.6, 122.8, 122.3, 114.3, 42.8, 32.9, 30.4, 23.5; IR (KBr, cm$^{-1}$): 1677, 1490; LRMS (EI 70 ev) m/z (%): 396 (M$^+$, 38), 382 (33), 381 (100); HRMS (ESI) for C$_{25}$H$_{21}$N$_2$O$_3$ [(M+H)$^+$]: calcd 397.1547, found 397.1548.

5,6a,9-Trimethyl-10-nitro-12-phenyl-6a,7-dihydrobenzo[j]phenanthridin-6(5H)-one (3ai)

White solid, mp 202.9-203.6 °C (uncorrected); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ (ppm): 7.43-7.36 (m, 3H), 7.24-7.20 (m, 2H), 7.15-7.08 (m, 2H), 7.00 (d, $J = 8.0$ Hz, 1H), 6.95 (d, $J = 7.6$ Hz, 1H), 6.77 (d, $J = 8.0$ Hz, 1H), 6.61 (t, $J = 8.0$ Hz, 1H), 3.40-3.36 (m, 4H), 3.27 (d, $J = 16.8$ Hz, 1H), 2.30 (s, 3H), 1.24 (s, 3H); $^{13}$C NMR (100
5-Benzyl-6a-methyl-12-phenyl-6a,7-dihydrobenzo[j]phenanthridin-6(5H)-one (3bb)

White solid, mp 201.5-203.3 °C (uncorrected); $^1$H NMR (400 MHz, CDCl$_3$) δ (ppm): 7.39-7.30 (m, 6H), 7.25-7.20 (m, 6H), 7.13-7.07 (m, 2H), 6.92 (t, $J = 8.0$ Hz, 1H), 6.83-6.78 (m, 2H), 6.54 (t, $J = 7.6$ Hz, 1H), 5.50 (d, $J = 16.4$ Hz, 1H), 4.93 (d, $J = 16.4$ Hz, 1H), 3.62 (d, $J = 16.8$ Hz, 1H), 3.35 (d, $J = 16.8$ Hz, 1H), 1.38 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ (ppm): 174.1, 138.8, 138.6, 137.0, 135.8, 134.1, 132.6, 131.9, 130.9, 128.8, 128.5, 128.0, 127.7, 127.3, 127.1, 126.5, 126.2, 126.0, 123.7, 122.1, 115.2, 46.8, 43.4, 37.6, 23.4; IR (KBr, cm$^{-1}$): 1735, 1497; LRMS (EI 70 ev) m/z (%): 427 (M$^+$, 16), 413 (24), 412 (100); HRMS (ESI) for C$_{31}$H$_{26}$NO [(M+H)$^+$]: calcd 428.2009, found 428.2016.

5-Allyl-6a-methyl-12-phenyl-6a,7-dihydrobenzo[j]phenanthridin-6(5H)-one (3cb)
White solid, mp 142.1-144.6 °C (uncorrected); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ (ppm): 7.40-7.33 (m, 4H), 7.28-7.24 (m, 2H), 7.19-7.15 (m, 1H), 7.09-7.02 (m, 3H), 6.92 (d, $J = 8.0$ Hz, 1H), 6.79 (d, $J = 8.0$ Hz, 1H), 6.57 (t, $J = 7.2$ Hz, 1H), 5.96-5.89 (m, 1H), 5.22-5.13 (m, 2H), 4.89-4.85 (m, 1H), 4.34-4.28 (m, 1H), 3.55 (d, $J = 16.4$ Hz, 1H), 3.30 (d, $J = 16.4$ Hz, 1H), 1.29 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ (ppm): 173.5, 138.8, 138.6, 135.6, 134.1, 132.6, 132.4, 132.0, 130.9, 130.7, 128.6, 128.4, 127.9, 127.7, 127.2, 126.4, 125.9, 123.4, 122.0, 116.1, 114.9, 45.6, 43.3, 37.5, 23.2; IR (KBr, cm$^{-1}$): 1667, 1457; LRMS (EI 70 ev) $m/z$ (%): 377 (M$^+$, 33), 363 (28), 362 (100); HRMS (ESI) for C$_{27}$H$_{24}$NO [(M+H)$^+$]: calcd 378.1852, found 378.1822.

5,6a-Dimethyl-12-$p$-tolyl-6a,7-dihydrobenzo[j]phenanthridin-6(5H)-one (3eb)

White solid, mp 200.3-201.8 °C (uncorrected); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ (ppm): 7.28-7.25 (m, 2H), 7.20-7.16 (m, 3H), 7.15-7.08 (m, 4H), 6.94 (d, $J = 8.0$ Hz, 1H), 6.85 (d, $J = 8.0$ Hz, 1H), 6.61 (t, $J = 7.6$ Hz, 1H), 3.46 (d, $J = 16.4$ Hz, 1H), 3.41 (s, 3H), 3.32 (d, $J = 16.0$ Hz, 1H), 2.40 (s, 3H), 1.23 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ (ppm): 173.9, 139.1, 137.1, 135.2, 134.2, 132.7, 132.4, 131.6, 131.2, 130.9, 128.6 (2C), 128.5, 127.5, 127.1, 126.4, 125.9, 122.7, 113.9, 43.3, 38.0, 30.3, 22.7, 20.3; IR (KBr, cm$^{-1}$): 1666, 1455; LRMS (EI 70 ev) $m/z$ (%): 365 (M$^+$, 23), 351 (41), 350 (100); HRMS (ESI) for C$_{26}$H$_{24}$NO [(M+H)$^+$]: calcd 366.1852, found 366.1853.
12-(4-Methoxyphenyl)-5,6a-dimethyl-6a,7-dihydrobenzo[j]phenanthridin-6(5H)-one (3fb)

White solid, mp 143.3-144.6 °C (uncorrected); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ (ppm): 7.27 (t, $J = 6.8$ Hz, 1H), 7.20-7.08 (m, 6H), 6.95-6.92 (m, 3H), 6.83 (d, $J = 8.0$ Hz, 1H), 6.64 (t, $J = 8.0$ Hz, 1H), 3.84 (s, 3H), 3.46 (d, $J = 16.0$ Hz, 1H), 3.41 (s, 3H), 3.32 (d, $J = 16.0$ Hz, 1H), 1.22 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ (ppm): 174.1, 158.7, 139.4, 135.0, 134.5, 132.6, 132.2, 131.9, 130.8, 130.7, 128.4, 127.9, 127.5, 126.4, 125.8, 122.1, 114.1, 55.2, 43.3, 37.9, 50.4, 51.2; IR (KBr, cm$^{-1}$): 1660, 1481; LRMS (EI 70 ev) $m/z$ (%): 381 (M$^+$, 62), 367 (27), 366 (100); HRMS (ESI) for C$_{26}$H$_{24}$NO$_2$ [(M+H)$^+$]: calcd 382.1802, found 382.1794.

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

White solid, mp 163.5-164.6 °C (uncorrected); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ (ppm): 7.30-7.25 (m, 1H), 7.21-7.17 (m, 3H), 7.14-7.07 (m, 4H), 7.04 (d, $J = 8.0$ Hz, 1H), 6.95 (d, $J = 8.0$ Hz, 1H), 6.76 (d, $J = 6.8$ Hz, 1H), 6.64 (t, $J = 7.6$ Hz, 1H), 3.48 (d, $J = 16.4$ Hz, 1H), 3.41 (s, 3H), 3.32 (d, $J = 16.4$ Hz, 1H), 1.23 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ (ppm): 174.0, 162.0 (d, $J = 245.1$ Hz, 1C), 139.5 (d, $J = 3.6$ Hz,
12-(4-Chlorophenyl)-5,6a-dimethyl-6a,7-dihydrobenzo[j]phenanthridin-6(5H)-one (3hb)

White solid, mp 213.0-214.8 °C (uncorrected); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) (ppm): 7.38 (t, \(J = 8.4\) Hz, 2H), 7.29 (d, \(J = 7.2\) Hz, 1H), 7.22-7.18 (m, 3H), 7.16-7.12 (m, 2H), 7.02 (d, \(J = 8.0\) Hz, 1H), 6.96 (d, \(J = 8.4\) Hz, 1H), 6.79 (d, \(J = 8.0\) Hz, 1H), 6.67 (t, \(J = 7.6\) Hz, 1H), 3.48 (d, \(J = 16.4\) Hz, 1H), 3.41 (s, 3H), 3.33 (d, \(J = 16.4\) Hz, 1H), 1.24 (s, 3H); \(^1^3\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) (ppm): 173.9, 139.5, 137.2, 134.2, 133.7, 133.2, 132.8, 132.6, 132.3, 130.6, 128.9, 128.6, 128.3, 127.8, 126.5, 122.9, 122.2, 114.3, 43.3, 37.8, 30.4, 22.7; IR (KBr, cm\(^{-1}\)) : 1669, 1473; LRMS (EI 70 ev) \(m/z\) (%): 387 (M\(^+\)+2, 6), 385 (M\(^+\), 18), 371 (30), 370 (100); HRMS (ESI) for C\(_{25}\)H\(_{21}\)ClNO [(M+H)+]: calcd 386.1306, found 386.1304.

12-(4-Bromophenyl)-5,6a-dimethyl-6a,7-dihydrobenzo[j]phenanthridin-6(5H)-one (3ib)
White solid, mp 207.9-209.3 °C (uncorrected); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ (ppm): 7.53 (d, $J = 8.4$ Hz, 1H), 7.29 (d, $J = 6.8$ Hz, 1H), 7.20 (t, $J = 7.2$ Hz, 1H), 7.16-7.09 (m, 4H), 7.01 (d, $J = 8.0$ Hz, 1H), 6.96 (d, $J = 7.2$ Hz, 1H), 6.80 (d, $J = 7.2$ Hz, 1H), 6.67 (d, $J = 8.0$ Hz, 1H), 3.48 (d, $J = 16.4$ Hz, 1H), 3.41 (s, 3H), 3.33 (d, $J = 16.0$ Hz, 1H), 1.24 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ (ppm): 173.9, 139.5, 137.7, 134.1, 133.6, 132.8, 132.6 (2C), 131.8, 130.6, 128.6, 128.3, 127.8, 126.5, 125.6, 122.8, 122.2, 121.3, 114.3, 43.3, 37.8, 30.3, 22.7; IR (KBr, cm$^{-1}$): 1634, 1466; LRMS (EI 70 ev) $m/z$ (%): 431 ($M^++2$, 69), 429 ($M^+$, 70), 415 (19), 414 (64), 450 (100); HRMS (ESI) for C$_{25}$H$_{21}$BrNO [(M+H)$^+$]: calcd 430.0801, found 430.0795.

5,6a-Dimethyl-12-(pyridin-2-yl)-6a,7-dihydrobenzo[j]phenanthridin-6(5H)-one (3jb)

White solid, mp 145.2-146.3 °C (uncorrected); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ (ppm): 8.84 (d, $J = 4.8$ Hz, 1H), 7.61 (t, $J = 7.6$ Hz, 1H), 7.30-7.28 (m, 2H), 7.27-7.17 (m, 2H), 7.14-7.08 (m, 3H), 6.95 (d, $J = 8.0$ Hz, 1H), 6.67 (d, $J = 7.6$ Hz, 1H), 6.60 (t, $J = 7.6$ Hz, 1H), 3.46-3.43 (m, 5H), 1.24 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ (ppm): 173.9, 158.7, 149.3, 139.5, 137.3, 132.4, 130.8, 128.6, 128.5, 127.7, 126.6, 125.8, 125.5, 122.3, 122.2 (2C), 114.2, 43.8, 38.0, 30.3, 21.7; IR (KBr, cm$^{-1}$): 1659, 1484; LRMS (EI 70 ev) $m/z$ (%): 352 ($M^+$, 51), 351 (35), 338 (26), 337 (100); HRMS (ESI) for C$_{24}$H$_{21}$N$_2$O [(M+H)$^+$]: calcd 353.1648, found 353.1655.
5,6a-Dimethyl-12-(thiophen-2-yl)-6a,7-dihydrobenzo[j]phenanthridin-6(5H)-one (3kb)

White solid, mp 158.4-159.7 °C (uncorrected); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) (ppm): 7.45 (d, \(J = 7.2\) Hz, 1H), 7.34-7.32 (m, 1H), 7.30-7.25 (m, 1H), 7.21-7.16 (m, 3H), 7.13-7.06 (m, 3H), 6.98-6.96 (m, 1H), 6.72 (t, \(J = 8.0\) Hz, 1H), 3.41-3.40 (m, 4H), 3.32 (d, \(J = 16.4\) Hz, 1H), 1.21 (s, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) (ppm): 173.6, 139.5, 139.2, 135.9, 133.9, 132.3, 129.7, 129.4, 129.6, 128.6, 128.5, 127.8, 127.4, 127.2, 126.7, 126.1, 125.4, 122.8, 122.3, 114.3, 43.9, 37.3, 30.4, 22.1; IR (KBr, cm\(^{-1}\)): 1651, 1443; LRMS (EI 70 ev) \(m/z\) (%): 357 (M\(^{+}\), 22), 343 (39), 342 (100); HRMS (ESI) for C\(_{23}\)H\(_{20}\)NOS \([\text{M}+\text{H}]^{+}\): calcd 358.1260, found 358.1256.

5,6a-Dimethyl-12-(thiophen-3-yl)-6a,7-dihydrobenzo[j]phenanthridin-6(5H)-one (3lb)

White solid, mp 141.1-142.6 °C (uncorrected); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) (ppm): 7.35-7.33 (m, 1H), 7.21-7.01 (m, 6H), 6.95 (d, \(J = 2.4\) Hz, 1H), 6.87 (d, \(J = 8.0\) Hz, 1H), 6.72 (d, \(J = 8.0\) Hz, 1H), 6.60 (t, \(J = 7.6\) Hz, 1H), 3.38-3.33 (m, 4H), 3.24 (d, \(J = 16.0\) Hz, 1H), 1.13 (s, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) (ppm): 173.9, 139.4, 138.5, 134.2, 133.6, 132.5, 130.5, 130.1, 128.5, 128.3, 127.7, 126.6, 125.8,
5,6a-Dimethyl-12-octyl-6a,7-dihydrobenzo[j]phenanthridin-6(5H)-one (3mb)

Colourless oil; \(^{1}\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) (ppm): 7.42-7.39 (m, 1H), 7.33-7.30 (m, 2H), 7.28-7.22 (m, 2H), 7.15 (t, \(J = 7.2\) Hz, 1H), 7.06 (t, \(J = 7.2\) Hz, 1H), 7.06 (d, \(J = 4.0\) Hz, 1H), 3.36 (s, 3H), 3.15-3.04 (m, 3H), 2.84-2.77 (m, 1H), 1.55-1.51 (m, 1H), 1.34-1.31 (m, 1H), 1.23-1.18 (m, 10H), 0.95 (s, 3H), 0.81 (t, \(J = 6.8\) Hz, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) (ppm): 174.5, 139.9, 136.6, 134.7, 134.4 (2C), 132.0, 130.4, 128.5 (2C), 127.0, 126.5, 124.2, 122.4, 114.4, 44.0, 37.9, 31.8, 30.2, 29.3 (2C), 29.2, 29.1 (2C), 22.6, 20.5, 14.1; IR (KBr, cm\(^{-1}\)): 1653, 1481; LRMS (EI 70 ev) \(m/z\) (%): 387 (M\(^{+}\), 9), 386 (7), 372 (38), 371 (100); HRMS (ESI) for C\(_{27}\)H\(_{34}\)NO \([(\text{M}+\text{H})^{+}]\): calcd 388.2635, found 388.2639.

2,5,6a-Trimethyl-12-phenyl-6a,7-dihydrobenzo[j]phenanthridin-6(5H)-one (3nb)

White solid, mp 231.3-232.8 \(^{\circ}\)C (uncorrected); \(^{1}\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) (ppm): 7.42-7.35 (m, 3H), 7.33-7.25 (m, 3H), 7.20-7.16 (m, 1H), 7.15-7.10 (m, 2H), 6.89 (d, \(J = 8.4\) Hz, 1H), 6.81 (d, \(J = 8.8\) Hz, 1H), 6.56 (s, 1H), 3.46 (d, \(J = 16.4\) Hz,
1H), 3.39 (s, 3H), 3.34 (d, J = 16.0 Hz, 1H), 1.87 (s, 3H), 1.24 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ (ppm): 173.9, 139.1, 137.1, 135.2, 134.2, 132.7, 132.4, 131.6, 131.2, 130.9, 128.6 (2C), 128.5, 127.5, 127.1, 126.4, 125.9, 122.7, 113.9, 43.3, 38.0, 30.3, 22.7, 20.3; IR (KBr, cm$^{-1}$): 1662, 1471; LRMS (EI 70 ev) m/z (%): 365 (M+, 38), 351 (41), 350 (100); HRMS (ESI) for C$_{26}$H$_{24}$NO [(M+H)$^+$]: calcd 366.1852, found 366.1855.

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

White solid, mp 192.8-193.6 °C (uncorrected); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ (ppm): 7.44-7.37 (m, 3H), 7.30-7.18 (m, 4H), 7.13-7.08 (m, 2H), 6.90-6.86 (m, 1H), 6.83-6.77 (m, 1H), 6.46 (d, J = 11.2 Hz, 1H), 3.50 (d, J = 16.0 Hz, 1H), 4.00 (s, 3H), 3.33 (d, J = 16.4 Hz, 1H), 1.24 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ (ppm): 173.7, 157.8 (d, J = 238.9 Hz, 1C), 138.2, 136.7, 135.8, 133.8, 132.7, 131.1, 130.6, 128.9, 128.6, 128.0, 127.7, 126.5, 126.2, 125.0, 117.2 (d, J = 25.3 Hz, 1C), 115.2 (d, J = 8.2 Hz, 1C), 114.6 (d, J = 22.7 Hz, 1C), 43.0, 37.8, 30.6, 22.7; IR (KBr, cm$^{-1}$): 1690, 1462; LRMS (EI 70 ev) m/z (%): 369 (M+, 24), 355 (28), 354 (100); HRMS (ESI) for C$_{25}$H$_{21}$FNO [(M+H)$^+$]: calcd 370.1602, found 370.1598.
2-Chloro-5,6a-dimethyl-12-phenyl-6a,7-dihydrobenzo[j]phenanthridin-6(5H)-one (3pb)

White solid, mp 209.6-211.3 °C (uncorrected); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ (ppm): 7.37-7.30 (m, 3H), 7.21-7.10 (m, 4H), 7.02 (d, $J = 4.0$ Hz, 2H), 6.96 (d, $J = 8.8$ Hz, 1H), 6.76 (d, $J = 7.6$ Hz, 1H), 6.63 (s, 1H), 3.39 (d, $J = 16.4$ Hz, 1H), 3.30 (s, 3H), 3.25 (d, $J = 16.4$ Hz, 1H), 1.16 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ (ppm): 173.8, 138.1, 138.0, 136.7, 133.7, 132.6, 130.8, 130.5, 130.4, 128.9, 128.5, 128.0, 127.8, 127.6, 127.4, 126.5, 126.2, 124.6, 115.4, 43.1, 37.8, 30.4, 22.7; IR (KBr, cm$^{-1}$): 1668, 1477; LRMS (EI 70 ev) m/z (%): 387 (M$^+2$, 3), 385 (M$^+$, 10), 371 (30), 370 (100); HRMS (ESI) for C$_{25}$H$_{21}$Cl$_2$NO [(M+H)$^+$]: 386.1306, found 386.1296.

6a-Benzyl-5-methyl-12-phenyl-6a,7-dihydrobenzo[j]phenanthridin-6(5H)-one (3qb)

White solid, mp 221.5-222.8 °C (uncorrected); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ (ppm): 7.56-7.51 (m, 3H), 7.43-7.39 (m, 5H), 7.26-7.12 (m, 6H), 7.05 (d, $J = 7.6$ Hz, 1H), 6.86 (d, $J = 8.4$ Hz, 1H), 6.76 (d, $J = 8.0$ Hz, 1H), 6.63 (t, $J = 7.6$ Hz, 1H), 3.60 (d, $J = 14.4$ Hz, 1H), 3.50-3.46 (m, 3H), 3.24 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ (ppm): 170.2, 139.7, 139.4, 138.4, 137.8, 134.3, 133.3, 131.2, 131.1, 130.3 (2C), 128.9, 128.8, 128.6, 128.4, 128.2, 127.9, 127.4, 127.2, 126.7, 122.4, 122.3, 114.2, 58.8, 44.8, 38.5, 30.7; IR (KBr, cm$^{-1}$): 1700, 1484; LRMS (EI 70 ev) m/z (%): 427 (M$^+$, 20), 413
5-Methyl-6a,12-diphenyl-6a,7-dihydrobenzo[j]phenanthridin-6(5H)-one (3rb)

White solid, mp 173.2-175.6 °C (uncorrected); $^1$H NMR (400 MHz, CDCl$_3$) δ (ppm): 7.44-7.41 (m, 3H), 7.40-7.34 (m, 4H), 7.15-7.05 (m, 7H), 6.98-6.93 (m, 1H), 6.83-6.78 (m, 2H), 6.54 (t, $J = 8.0$ Hz, 1H), 3.96 (d, $J = 16.4$ Hz, 1H), 3.55 (d, $J = 16.8$ Hz, 1H), 3.45 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ (ppm): 171.3, 141.0, 138.9, 138.8, 138.4, 133.9, 132.5, 130.9, 130.3, 129.8, 128.6, 128.3, 128.0 (2C), 127.7, 127.4, 126.9, 126.6, 126.4, 126.1, 125.2, 122.0, 114.4, 52.0, 40.2, 39.7; IR (KBr, cm$^{-1}$): 1653, 1488; LRMS (EI 70 ev) $m/z$ (%): 413 (M$^+$, 21), 399 (21), 398 (100); HRMS (ESI) for C$_{31}$H$_{26}$NO [(M+H)$^+$]: calcd 428.2009, found 428.2016.

5-methyl-12-phenylbenzo[j]phenanthridin-6(5H)-one (3sb)

White solid, mp 183.2-185.6 °C (uncorrected); $^1$H NMR (400 MHz, CDCl$_3$) δ (ppm): 9.26 (s, 1H), 8.10 (d, $J = 8.0$ Hz, 1H), 7.61-7.52 (m, 5H), 7.49-7.45 (m, 1H), 7.37-7.33 (m, 4H), 7.22 (d, $J = 8.4$ Hz, 1H), 6.77-6.73 (m, 1H), 3.80 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ (ppm): 162.2, 140.8, 138.5, 135.4, 131.8, 130.4 (2C), 129.8, 128.6, 128.3, 128.0 (2C), 127.7, 127.4, 126.9, 126.6, 126.4, 126.1, 125.2, 122.0, 114.4, 52.0, 40.2, 39.7; IR (KBr, cm$^{-1}$): 1653, 1488; LRMS (EI 70 ev) $m/z$ (%): 413 (M$^+$, 21), 399 (21), 398 (100); HRMS (ESI) for C$_{30}$H$_{24}$NO [(M+H)$^+$]: calcd 414.1852, found 414.1850.
129.6, 129.3, 129.0, 128.5, 128.1, 127.9, 127.5, 126.8, 126.3, 124.5, 121.4, 120.5, 114.8, 30.5; IR (KBr, cm⁻¹): 1659, 1478; LRMS (EI 70 ev) m/z (%): 335 (M⁺, 100), 334 (53), 320 (19), 319 (31); HRMS (ESI) for C₂₄H₁₈NO [(M+H)⁺]: calcd 336.1383, found 336.1389.
9-Chloro-5,6a-dimethyl-12-phenyl-6a,7-dihydrobenzo[j]phenanthridin-6(5H)-one (3aa)
9-Chloro-5,6a-dimethyl-12-phenyl-6a,7-dihydrobenzo[j]phenanthridin-6\((5H)\)-one (3aa)
5,6a-Dimethyl-12-phenyl-6a,7-dihydrobenzo[j]phenanthridin-6(5H)-one (3ab)
5,6a-Dimethyl-12-phenyl-6a,7-dihydrobenzo[j]phenanthridin-6(5H)-one (3ab)
9-Methoxy-5,6a-dimethyl-12-phenyl-6a,7-dihydrobenzo[j]phenanthridin-6(5H)-one (3ac)
9-Methoxy-5,6a-dimethyl-12-phenyl-6a,7-dihydrobenz[j]phenanthridin-6(5H)-one (3ac)
9-Fluoro-5,6a-dimethyl-12-phenyl-6a,7-dihydrobenzo[j]phenanthridin-6(5H)-one (3ad)
9-Fluoro-5,6a-dimethyl-12-phenyl-6a,7-dihydrobenzo[j]phenanthridin-6(5H)-one (3ad)
9-Iodo-5,6a-dimethyl-12-phenyl-6a,7-dihydrobenzo[j]phenanthridin-6(5H)-one (3ae)
9-Iodo-5,6a-dimethyl-12-phenyl-6a,7-dihydrobenzo[j]phenanthridin-6(5H)-one 

(3ae)
9-Acetyl-5,6a-dimethyl-12-phenyl-6a,7-dihydropbenzol[j]phenanthridin-6(5H)-one (3af)
9-Acetyl-5,6a-dimethyl-12-phenyl-6a,7-dihydrobenzo[j]phenanthridin-6(5H)-one (3af)
5,6a-Dimethyl-9-nitro-12-phenyl-6a,7-dihydrobenzo[j]phenanthridin-6(5H)-one (3ag)
5,6a-Dimethyl-9-nitro-12-phenyl-6a,7-dihydrobenzo[j]phenanthridin-6(5H)-one (3ag)
5,6a-Dimethyl-10-nitro-12-phenyl-6a,7-dihydrobenzo[j]phenanthridin-6(5H)-one (3ah)
5,6a-Dimethyl-10-nitro-12-phenyl-6a,7-dihydrobenzo[j]phenanthridin-6(5H)-one (3ah)
5,6a,9-Trimethyl-10-nitro-12-phenyl-6a,7-dihydrobenzo[j]phenanthridin-6(5H)-one (3ai)
5,6a,9-Trimethyl-10-nitro-12-phenyl-6a,7-dihydrobenzo[j]phenanthridin-6(5H)-one (3ai)
5-Benzyl-6a-methyl-12-phenyl-6a,7-dihydrobenzo[j]phenanthridin-6(5H)-one (3bb)
5-Benzyl-6a-methyl-12-phenyl-6a,7-dihydrobenzo[j]phenanthridin-6(5H)-one

(3bb)
5-Allyl-6a-methyl-12-phenyl-6a,7-dihydrobenzo[j]phenanthridin-6(5H)-one (3cb)
5-Allyl-6a-methyl-12-phenyl-6a,7-dihydrobenzo[j]phenanthridin-6(5H)-one

(3cb)
5,6a-Dimethyl-12-p-tolyl-6a,7-dihydrobenzo[j]phenanthridin-6(5H)-one (3eb)
5,6a-Dimethyl-12-<i>p</i>-tolyl-6a,7-dihydrobenzo[j]phenanthridin-6(5H)-one (3eb)
12-(4-Methoxyphenyl)-5,6a-dimethyl-6a,7-dihydrobenzo[j]phenanthridin-6(5H)-one (3fb)
12-(4-Methoxyphenyl)-5,6a-dimethyl-6a,7-dihydrobenzo[j]phenanthridin-6(5H)-one (3fb)
12-(4-Fluorophenyl)-5,6a-dimethyl-6a,7-dihydrobenzo[j]phenanthridin-6(5H)-one (3gb)
12-(4-Fluorophenyl)-5,6a-dimethyl-6a,7-dihydrobenzo[j]phenanthridin-6(5H)-one (3gb)
12-(4-Chlorophenyl)-5,6a-dimethyl-6a,7-dihydrobenzo[j]phenanthridin-6(5H)-one (3hb)
12-(4-Chlorophenyl)-5,6a-dimethyl-6a,7-dihydrobenzo[j]phenanthridin-6(5H)-one (3hb)
12-(4-Bromophenyl)-5,6a-dimethyl-6a,7-dihydrobenzo[j]phenanthridin-6(5H)-one (3ib)
12-(4-Bromophenyl)-5,6a-dimethyl-6a,7-dihydrobenzo[j]phenanthridin-6(5H)-one (3ib)
5,6a-Dimethyl-12-(pyridin-2-yl)-6a,7-dihydrobenzo[j]phenanthridin-6(5H)-one

(3jb)
5,6a-Dimethyl-12-(pyridin-2-yl)-6a,7-dihydropyrazolo[3,4-d]pyridin-6(5H)-one

(3jb)
5,6a-Dimethyl-12-(thiophen-2-yl)-6a,7-dihydrobenzo[j]phenanthridin-6(5H)-one (3kb)
5,6a-Dimethyl-12-(thiophen-2-yl)-6a,7-dihydrobenzo[j]phenanthridin-6(5H)-one (3kb)
5,6a-Dimethyl-12-(thiophen-3-yl)-6a,7-dihydrobenzo[j]phenanthridin-6(5H)one (3lb)
5,6a-Dimethyl-12-(thiophen-3-yl)-6a,7-dihydrobenzo[j]phenanthridin-6(5H)-one (3lb)
5,6a-Dimethyl-12-octyl-6a,7-dihydrobenzo[j]phenanthridin-6(5H)-one (3mb)
5,6a-Dimethyl-12-octyl-6a,7-dihydrobenzo[j]phenanthridin-6(5H)-one (3mb)
2,5,6a-Trimethyl-12-phenyl-6a,7-dihydrobenzo[j]phenanthridin-6(5H)-one

(3nb)
2,5,6a-Trimethyl-12-phenyl-6a,7-dihydrobenzo[j]phenanthridin-6(5H)-one

(3nb)
2-Fluoro-5,6a-dimethyl-12-phenyl-6a,7-dihydrobenzo[j]phenanthridin-6(5H)-one (3ob)
2-Fluoro-5,6a-dimethyl-12-phenyl-6a,7-dihydrobenzo[j]phenanthridin-6(5H)-one (3ob)
2-Chloro-5,6a-dimethyl-12-phenyl-6a,7-dihydrobenzo[j]phenanthridin-6(5H)-one (3pb)
2-Chloro-5,6a-dimethyl-12-phenyl-6a,7-dihydrobenzo[j]phenanthridin-6(5H)-one (3pb)
6a-Benzyl-5-methyl-12-phenyl-6a,7-dihydrobenzo[j]phenanthridin-6(5H)-one

(3qb)
6a-Benzyl-5-methyl-12-phenyl-6a,7-dihydrobenzo[j]phenanthridin-6(5H)-one

(3qb)
5-Methyl-6a,12-diphenyl-6a,7-dihydrobenzo[j]phenanthridin-6(5H)-one (3rb)
5-Methyl-6a,12-diphenyl-6a,7-dihydrobenzo[j]phenanthridin-6(5H)-one (3rb)
5-methyl-12-phenylbenzo[j]phenanthridin-6(5H)-one (3sb)
5-methyl-12-phenylbenzo[j]phenanthridin-6(5H)-one (3sb)