Palladium-Catalyzed Annulation of Benznes with N-
Substituted-N-(2-halophenyl)formamides: Synthesis of
Phenanthridinones

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1) General Information

$^1$H and $^{13}$C NMR spectra were recorded on a Bruker ARX500 spectrometer (FT, 500 MHz for $^1$H; 125 MHz for $^{13}$C) at room temperature, respectively. The $^1$HNMR spectra were taken in CDCl$_3$ and the chemical shifts are given in ppm with respect to tetramethylsilane (TMS) used as an internal standard. The $^{13}$C NMR spectra were taken in CDCl$_3$ and the central peak of the solvent was adjusted to 77.00 ppm and used as a reference. High-resolution mass spectra (HRMS) were recorded on a Bruker Apex IV FTMS mass spectrometer using ESI (electrospray ionization). Melting points were measured uncorrected. Reactions were monitored by thin-layer chromatography or GC-MS analysis. Column chromatography (petroleum ether/ethyl acetate) was performed on silica gel (200-300 mesh). Unless otherwise noted, all reactions were run under nitrogen atmosphere.

2) Synthesis of Starting Materials

Preparation of 1:

To a schlenk tube were added o-iodoaniline (1 mmol), HCOONa (0.5 mmol), and HCOOH (2 mL). The resulting mixture was stirred at 70°C for appropriate time. After completion of the reaction, water was added to the reaction mixture. The resulting solution was extracted with ethyl acetate. The organic layers were combined and dried over anhydrous Na$_2$SO$_4$. The solvent was removed under vacuum and the residue was purified by flash column chromatography on silica gel using petroleum ether/ethyl acetate as the eluent.

Preparation of 2:

Compounds 2b-2e were prepared according the literature method.\(^2\)
3) Typical Procedures

To a schlenk tube were added $N$-substituted-$N$-(2-iodophenyl)form-amide (0.3 mmol), aryne (0.36 mmol), Pd(OAc)$_2$ (5 mol%), P(o-tolyl)$_3$ (10 mol%), CsF (0.9 mmol), and MeCN/toluene (1:1, 2 mL). Then under the protection of nitrogen, the mixture was stirred at 110 °C (oil bath temperature) for the indicated time until complete consumption of starting material as monitored by TLC and GC-MS analysis. After the reaction was finished, the reaction mixture was filtered by a crude column with ethyl acetate as eluent, and evaporated under vacuum. The resulting residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 6:1) to afford the desired product.

4) Characterization Data

5-benzylphenanthridin-6(5H)-one (3a): $^3$ Pale yellow solid, isolated yield 93% (79.5 mg); mp: 115.6-115.9 °C; $^1$H NMR (500 MHz, CDCl$_3$) δ: 8.61 (d, $J = 8.0$ Hz, 1H), 8.24 (t, $J = 8.8$ Hz, 2H), 7.74 (t, $J = 7.8$ Hz, 1H), 7.58 (t, $J = 7.5$ Hz, 1H), 7.35 (t, $J = 7.8$ Hz, 1H), 7.28-7.20 (m, 7H), 5.63 (s, 2H); $^{13}$C NMR (125 MHz, CDCl$_3$) δ: 161.81, 137.23, 136.51, 133.75, 132.60, 129.45, 129.07, 128.71, 127.94, 127.10, 126.45, 125.32, 123.19, 122.48, 121.61, 119.41, 115.92, 46.39; IR (KBr): 1635 (C=O) cm$^{-1}$.

5-(4-methylbenzyl)phenanthridin-6(5H)-one (3b): $^3$ Pale yellow solid, isolated yield 88% (79.1 mg); mp: 108.4-109.5 °C; $^1$H NMR (500 MHz, CDCl$_3$) δ: 8.60 (dd, $J = 7.5$ Hz, 1.0 Hz, 1H), 8.22-8.18 (m, 2H), 7.71 (td, $J = 7.8$ Hz, 1.0 Hz, 1H), 7.49 (br s, 1H), 7.32 (s, 2H), 7.10-7.00 (m, 7H), 7.00 (d, $J = 8.0$ Hz, 2H), 6.94 (d, $J = 8.0$ Hz, 2H); $^{13}$C NMR (125 MHz, CDCl$_3$) δ: 162.35, 138.23, 136.91, 133.71, 132.69, 129.40, 129.07, 128.78, 127.94, 127.10, 126.40, 125.37, 123.19, 122.48, 121.54, 119.42, 115.93, 46.40; IR (KBr): 1635 (C=O) cm$^{-1}$.
1H), 7.56 (td, \( J = 7.5 \) Hz, 1.0 Hz, 1H), 7.33 (td, \( J = 7.8 \) Hz, 1.0 Hz, 1H), 7.28 (d, \( J = 7.5 \) Hz, 1H), 7.19 (td, \( J = 7.5 \) Hz, 1.0 Hz, 1H), 7.14 (d, \( J = 8.5 \) Hz, 2H), 7.06 (d, \( J = 8.0 \) Hz, 2H), 5.58 (s, 2H), 2.25 (s, 3H); \(^{13}\)C NMR (125 MHz, CDCl\(_3\)) \( \delta \): 161.72, 137.23, 136.69, 133.47, 132.48, 129.38, 129.33, 129.00, 127.84, 126.43, 125.33, 123.10, 122.35, 121.54, 119.33, 115.88, 46.11, 20.94; IR (KBr): 1652 (C=O) cm\(^{-1}\).

**methyl 4-((6-oxophenanthridin-5(6H)-yl)methyl)benzoate (3c):** Yellow solid, isolated yield 91% (93.6 mg); mp: 176.5-177.7 °C; \(^1\)H NMR (500 MHz, CDCl\(_3\)) \( \delta \): 8.59 (d, \( J = 8.0 \) Hz, 1H), 8.23 (t, \( J = 8.3 \) Hz, 2H), 7.94 (d, \( J = 8.0 \) Hz, 2H), 7.74 (t, \( J = 7.5 \) Hz, 1H), 7.58 (t, \( J = 7.5 \) Hz, 1H), 7.34-7.29 (m, 3H), 7.21 (t, \( J = 7.5 \) Hz, 1H), 7.16 (d, \( J = 8.5 \) Hz, 1H), 5.66 (s, 2H), 3.84 (s, 3H); \(^{13}\)C NMR (125 MHz, CDCl\(_3\)) \( \delta \): 166.52, 161.64, 141.83, 136.88, 133.63, 132.66, 129.96, 129.41, 129.03, 128.94, 127.94, 126.34, 125.07, 123.25, 122.57, 121.60, 119.34, 115.56, 51.88, 46.13; IR (KBr): 1708, 1649 (C=O) cm\(^{-1}\); HRMS (ESI, m/z) calcd for [C\(_{22}\)H\(_{17}\)NO\(_3\)]H\(^+\): 344.1281; found 344.1284.

**5-(3-nitrobenzyl)phenanthridin-6(5H)-one (3d):** Pale yellow solid, isolated yield 85% (84.2 mg); mp: 155.2-156.1 °C; \(^1\)H NMR (500 MHz, CDCl\(_3\)) \( \delta \): 8.58 (dd, \( J = 8.0 \) Hz, 1.0 Hz, 1H), 8.26 (d, \( J = 8.0 \) Hz, 2H), 8.14 (s, 1H), 8.05 (dd, \( J = 8.0 \) Hz, 1.0 Hz, 1H), 7.77 (td, \( J = 7.5 \) Hz, 1.0 Hz, 1H), 7.60 (t, \( J = 7.5 \) Hz, 0.5 Hz, 1H), 7.55 (d, \( J = 8.0 \) Hz, 1H), 7.42 (t, \( J = 8.0 \) Hz, 1H), 7.38 (td, \( J = 8.0 \) Hz, 1.0 Hz, 1H), 7.26 (t, \( J = 7.3 \) Hz, 1H), 7.17 (d, \( J = 8.5 \) Hz, 1H), 5.69 (s, 2H); \(^{13}\)C NMR (125 MHz, CDCl\(_3\)) \( \delta \): 161.70, 148.44, 138.88, 136.68, 133.65, 132.87, 132.58, 129.73, 129.60, 128.96, 128.09, 124.95, 123.50, 122.84, 122.28, 121.69, 121.51, 119.47, 115.20, 45.71; IR (KBr): 1645 (C=O) cm\(^{-1}\); HRMS (ESI, m/z) calcd for [C\(_{20}\)H\(_{14}\)N\(_2\)O\(_3\)]H\(^+\): 331.1077;
5-(naphthalen-2-ylmethyl)phenanthridin-6(5H)-one (3e): Pale yellow solid, isolated yield 89% (89.7 mg); mp: 149.2-150.5 °C; $^1$H NMR (500 MHz, CDCl$_3$) δ: 8.64 (dd, $J = 8.0$ Hz, 1.0 Hz, 1H), 8.20 (d, $J = 8.0$ Hz, 1H), 8.17 (dd, $J = 8.0$ Hz, 1.0 Hz, 1H), 7.74-7.69 (m, 3H), 7.63 (t, $J = 4.8$ Hz, 1H), 7.61 (s, 1H), 7.57 (td, $J = 7.5$ Hz, 1.0 Hz, 1H), 7.39 (dd, $J = 8.5$ Hz, 1.5 Hz, 1H), 7.36-7.34 (m, 2H), 7.29-7.24 (m, 2H), 7.19-7.13 (m, 1H), 5.75 (s, 2H); $^{13}$C NMR (125 MHz, CDCl$_3$) δ: 161.80, 137.16, 134.03, 133.74, 133.30, 132.57, 132.52, 129.40, 129.03, 128.56, 127.90, 127.55, 127.52, 126.03, 125.61, 125.28, 124.96, 124.61, 123.13, 122.43, 121.59, 119.34, 115.90, 46.55; IR (KBr): 1649 (C=O) cm$^{-1}$; HRMS (ESI, m/z) calcd for [C$_{24}$H$_{17}$NO]H$^+$: 336.1383; found 336.1386.

5-methylphenanthridin-6(5H)-one (3f): Red brown solid, isolated yield 93% (58.3 mg); mp: 113.4-114.5 °C; $^1$H NMR (500 MHz, CDCl$_3$) δ: 8.49 (dd, $J = 8.0$ Hz, 1.5 Hz, 1H), 8.13 (d, $J = 8.5$ Hz, 2H), 7.67 (td, $J = 7.5$ Hz, 1.0 Hz, 1H), 7.52 (td, $J = 7.5$ Hz, 1.0 Hz, 1H), 7.45 (td, $J = 8.0$ Hz, 1.0 Hz, 1H), 7.29 (d, $J = 8.0$ Hz, 1H), 7.22 (td, $J = 7.5$ Hz, 1.0 Hz, 1H), 3.72 (s, 2H); $^{13}$C NMR (125 MHz, CDCl$_3$) δ: 161.35, 137.74, 133.28, 132.14, 129.31, 128.63, 127.69, 125.33, 122.96, 122.22, 121.39, 118.98, 114.79, 29.74; IR (KBr): 1645 (C=O) cm$^{-1}$.

5-propylphenanthridin-6(5H)-one (3g): Yellow solid, isolated yield 85% (60.4 mg); mp: 53.5-54.5 °C; $^1$H NMR (500 MHz, CDCl$_3$) δ: 8.54 (dd, $J = 8.0$ Hz, 1.0 Hz, 1H), 8.23 (t, $J = 9.5$ Hz, 2H), 7.71 (td, $J = 7.8$ Hz, 1.0 Hz, 1H), 7.55 (t, $J = 7.5$ Hz, 1H), 7.50 (td, $J = 7.8$ Hz, 1.0 Hz, 1H), 7.36 (d, $J = 8.5$ Hz, 1H), 7.27 (t, $J = 7.5$ Hz, 1H), 4.33 (t, $J = 7.8$ Hz, 2H), 1.86-1.79 (m, 2H), 1.07 (t, $J = 7.5$ Hz, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$) δ: 161.22,
136.96, 133.40, 132.22, 129.37, 128.68, 127.76, 125.39, 123.30, 122.11, 121.42, 119.30, 114.98, 44.10, 20.63, 11.34; IR (KBr): 1645 (C=O) cm⁻¹; HRMS (ESI, m/z) calcd for [C₁₆H₁₅NO]⁺: 238.1226; found 238.1230.

5-phenethylphenanthridin-6(5H)-one (3h): Pale yellow solid, isolated yield 88% (78.9 mg); mp: 81.2-82.2 °C; ¹H NMR (500 MHz, CDCl₃) δ: 8.54 (d, J = 8.0 Hz, 1H), 8.23 (d, J = 8.0 Hz, 1H), 8.20 (d, J = 8.5 Hz, 1H), 7.71 (td, J = 7.5 Hz, 1.0 Hz, 1H), 7.55 (t, J = 7.8 Hz, 1H), 7.52 (t, J = 7.3 Hz, 1H), 7.42 (d, J = 8.5 Hz, 1H), 7.39 (d, J = 7.0 Hz, 2H), 7.34 (t, J = 7.5 Hz, 2H), 7.29-7.24 (m, 2H), 4.54 (t, J = 8.3 Hz, 2H), 3.06 (t, J = 8.5 Hz, 2H); ¹³C NMR (125 MHz, CDCl₃) δ: 161.09, 138.38, 136.77, 133.39, 132.33, 129.51, 128.71, 128.60, 128.56, 127.84, 126.56, 125.32, 123.43, 122.26, 121.48, 119.33, 114.64, 44.18, 33.48; IR (KBr): 1649 (C=O) cm⁻¹; HRMS (ESI, m/z) calcd for [C₂₁H₁₇NO]⁺: 300.1383; found 300.1387.

5-phenylphenanthridin-6(5H)-one (3i): Yellow solid, isolated yield 60% (48.8 mg); mp: 207.4-208.8 °C; ¹H NMR (500 MHz, CDCl₃) δ: 8.55 (dd, J = 8.0 Hz, 1.0 Hz, 1H), 8.29 (d, J = 8.0 Hz, 1H), 8.26 (dd, J = 7.5 Hz, 1.5 Hz, 1H), 7.77 (t, J = 7.5 Hz, 1.0 Hz, 1H), 7.61-7.56 (m, 3H), 7.51 (t, J = 7.3 Hz, 1H), 7.32-7.31 (m, 2H), 7.25 (td, J = 7.5 Hz, 1.5 Hz, 2H), 6.67 (dd, J = 7.5 Hz, 1.0 Hz, 1H); ¹³C NMR (125 MHz, CDCl₃) δ: 161.51, 139.01, 138.15, 133.85, 132.68, 130.04, 128.96 (2C), 128.83, 128.62, 127.96, 125.70, 122.86, 122.51, 121.66, 118.85, 116.85; IR (KBr): 1655 (C=O) cm⁻¹.

5-(p-tolyl)phenanthridin-6(5H)-one (3j): Pale yellow solid, isolated yield 54% (46.2 mg); mp: 173.5-174.7 °C; ¹H NMR (500 MHz, CDCl₃) δ: 8.56 (d, J = 8.0 Hz, 1H), 8.31 (d, J = 8.0 Hz, 1H), 8.28 (d, J = 7.5 Hz, 1H), 7.78 (td, J = 7.5 Hz, 1.0 Hz, 1H), 7.59 (t, J =
7.5 Hz, 1H), 7.40 (d, J = 8.5 Hz, 2H), 7.30-7.24 (m, 2H), 7.20 (d, J = 8.0 Hz, 2H), 6.73 (d, J = 8.0 Hz, 1H); $^{13}$C NMR (125 MHz, CDCl$_3$) δ: 161.70, 139.19, 138.58, 135.46, 133.87, 132.67, 130.79, 128.96, 128.93, 128.62, 127.98, 125.78, 122.86, 122.47, 121.67, 118.89, 116.99, 21.25; IR (KBr): 1659 (C=O) cm$^{-1}$.

5-benzyl-2-fluorophenanthridin-6(5H)-one (3k): Red brown solid, isolated yield 93% (84.6 mg); mp: 163.6-164.9 °C; $^1$H NMR (500 MHz, CDCl$_3$) δ: 8.59 (d, J = 8.0 Hz, 1H), 8.08 (d, J = 8.0 Hz, 1H), 7.82 (dd, J = 9.5 Hz, 3.0 Hz, 1H), 7.73 (t, J = 7.8 Hz, 1H), 7.60 (t, J = 8.0 Hz, 1H), 7.27 (d, J = 7.5 Hz, 2H), 7.22-7.18 (m, 4H), 7.03 (td, J = 8.5 Hz, 2.5 Hz, 1H), 5.59 (s, 2H); $^{13}$C NMR (125 MHz, CDCl$_3$) δ: 161.31, 158.26 (d, J = 240.63 Hz), 136.22, 133.54, 132.74 (d, J = 2.6 Hz), 132.65, 129.14, 128.75, 128.56, 127.20, 126.37, 125.48, 121.74, 120.74 (d, J = 7.8 Hz), 117.38 (d, J = 8.0 Hz), 116.64 (d, J = 23.0 Hz), 109.09 (d, J = 23.5 Hz), 46.51; IR (KBr): 1635 (C=O) cm$^{-1}$; HRMS (ESI, m/z) caled for [C$_{20}$H$_{14}$FNO]H$^+$: 304.1132; found 304.1138.

5-benzyl-2-chlorophenanthridin-6(5H)-one (3l): Yellow brown solid, isolated yield 88% (84.2 mg); mp: 167.1-168.3 °C; $^1$H NMR (500 MHz, CDCl$_3$) δ: 8.57 (dd, J = 8.0 Hz, 1.5 Hz, 1H), 8.09-8.07 (m, 2H), 7.72 (td, J = 7.5 Hz, 1.0 Hz, 1H), 7.59 (td, J = 7.5 Hz, 0.5 Hz, 1H), 7.28-7.20 (m, 6H), 7.15 (d, J = 9.0 Hz, 1H), 5.57 (s, 2H); $^{13}$C NMR (125 MHz, CDCl$_3$) δ: 161.33, 136.08, 135.64, 132.73, 132.44, 129.18, 129.10, 128.76, 128.57, 128.09, 127.24, 126.37, 125.40, 122.85, 121.61, 120.68, 117.22, 46.39; IR (KBr): 1635 (C=O) cm$^{-1}$.

5-benzyl-6-oxo-5,6-dihydrophenanthridine-2-carbonitrile (3m): Pale yellow solid, isolated yield 90% (83.7 mg); mp: 189.7-190.8 °C; $^1$H NMR (500 MHz, CDCl$_3$) δ: 8.57 (d, J =
8.0 Hz, 1H), 8.47 (d, J = 1.5 Hz, 1H), 8.18 (d, J = 8.0 Hz, 1H), 7.81 (td, J = 7.8 Hz, 1.0 Hz, 1H), 7.66 (t, J = 7.5 Hz, 1H), 7.56 (dd, J = 8.5 Hz, 1.5 Hz, 1H), 7.33 (d, J = 8.5 Hz, 1H), 7.29 (t, J = 7.3 Hz, 2H), 7.25-7.21 (m, 3H), 5.62 (s, 2H); 13C NMR (125 MHz, CDCl3) δ: 161.43, 139.99, 135.46, 133.23, 132.04, 131.93, 129.17 (2C), 128.85, 127.69, 127.45, 126.29, 125.31, 121.63, 119.88, 118.50, 116.64, 105.87, 46.46; IR (KBr): 1655 (C=O) cm⁻¹; HRMS (ESI, m/z) calcd for [C21H14N2O]H⁺: 311.1179; found 311.1183.

5-benzyl-2-(trifluoromethyl)phenanthridin-6(5H)-one (3n): Pale yellow solid, isolated yield 84% (88.9 mg); mp: 142.8-143.8 °C; 1H NMR (500 MHz, CDCl3) δ: 8.58 (dd, J = 8.0 Hz, 1.0 Hz, 1H), 8.44 (d, J = 1.0 Hz, 1H), 8.23 (d, J = 8.5 Hz, 1H), 7.78 (td, J = 7.5 Hz, 1.5 Hz, 1H), 7.63 (td, J = 7.5 Hz, 0.5 Hz, 1H), 7.56 (dd, J = 9.0 Hz, 1.5 Hz, 1H), 7.34 (d, J = 9.0 Hz, 1H), 7.30-7.27 (m, 2H), 7.22 (d, J = 7.0 Hz, 3H), 5.62 (s, 2H); 13C NMR (125 MHz, CDCl3) δ: 161.64, 139.43, 135.87, 133.03, 132.72, 129.20, 128.86 (2C), 127.39, 126.39, 125.85 (q, J = 3.5 Hz), 125.43, 124.51 (q, J = 32.6 Hz), 124.08 (q, J = 270.0 Hz), 121.69, 120.55 (q, J = 3.6 Hz), 119.40, 116.32, 46.52; IR (KBr): 1652 (C=O) cm⁻¹; HRMS (ESI, m/z) calcd for [C21H14F3NO]H⁺: 354.1100; found 354.1108.

5-benzyl-2-methylphenanthridin-6(5H)-one (3o): Yellow brown solid, isolated yield 86% (77.1 mg); mp: 162.5-163.7 °C; 1H NMR (500 MHz, CDCl3) δ: 8.59 (dd, J = 8.0 Hz, 1.5 Hz, 1H), 8.21 (d, J = 8.5 Hz, 1H), 7.98 (s, 1H), 7.70 (td, J = 7.8 Hz, 1.5 Hz, 1H), 7.55 (td, J = 7.5 Hz, 1.0 Hz, 1H), 7.26-7.20 (m, 4H), 7.18 (t, J = 7.0 Hz, 1H), 7.13 (s, 2H), 5.59 (s, 2H), 2.37 (s, 3H); 13C NMR (125 MHz, CDCl3) δ: 161.57, 136.62, 135.03, 133.62, 132.38, 131.79, 130.41, 128.99, 128.62, 127.71, 127.00, 126.42, 125.34, 123.24, 121.50, 119.16, 115.74, 46.24, 20.78; IR (KBr): 1632
(C=O) cm\(^{-1}\); HRMS (ESI, m/z) calcd for [C\(_{21}\)H\(_{17}\)NO]H\(^+\): 300.1383; found 300.1385.

**5-benzyl-3-chlorophenanthridin-6(5H)-one (3p):** Red brown solid, isolated yield 95% (91.1 mg); mp: 191.6-192.8 °C; \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\): 8.56 (d, \(J = 7.5\) Hz, 1H), 8.12 (d, \(J = 8.0\) Hz, 1H), 8.07 (d, \(J = 8.5\) Hz, 1H), 7.72 (t, \(J = 7.5\) Hz, 1H), 7.58 (t, \(J = 7.5\) Hz, 1H), 7.31-7.21 (m, 6H), 7.15 (d, \(J = 8.5\) Hz, 1H), 5.56 (s, 2H); \(^{13}\)C NMR (125 MHz, CDCl\(_3\)) \(\delta\): 161.63, 138.14, 135.91, 135.23, 132.98, 132.80, 129.13, 128.83, 128.20, 127.34, 126.50, 125.05, 124.36, 122.66, 121.53, 117.91, 115.78, 46.45; IR (KBr): 1645 (C=O) cm\(^{-1}\); HRMS (ESI, m/z) calcd for [C\(_{20}\)H\(_{14}\)ClNO]H\(^+\): 320.0837; found 320.0844.

**5-benzyl-8,9-dimethylphenanthridin-6(5H)-one (3q):** Pale yellow solid, isolated yield 83% (77.9 mg); mp: 186.8-187.9 °C; \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\): 8.33 (s, 1H), 8.17 (d, \(J = 7.5\) Hz, 1H), 7.96 (s, 1H), 7.30-7.21 (m, 6H), 7.20-7.16 (m, 2H), 5.60 (s, 2H), 2.42 (s, 3H), 2.39 (s, 3H); \(^{13}\)C NMR (125 MHz, CDCl\(_3\)) \(\delta\): 161.78, 142.28, 137.30, 136.90, 136.66, 131.56, 129.16, 128.75, 128.61, 126.96, 126.40, 123.17, 122.80, 122.22 (2C), 119.41, 115.75, 46.15, 20.49, 19.65; IR (KBr): 1635 (C=O) cm\(^{-1}\); HRMS (ESI, m/z) calcd for [C\(_{22}\)H\(_{19}\)NO]H\(^+\): 314.1539; found 314.1546.

**5-benzyl-9-methylphenanthridin-6(5H)-one (3r) and 5-benzyl-8-methylphenanthridin-6(5H)-one (3r'):**

3r:3r' = 1.1:1; Pale yellow solid, isolated yield 91% (81.6 mg); mp: 172.1-173.1 °C; \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\): 8.48 (d, \(J = 8.0\) Hz, 1H), 8.39 (s, 0.94H), 8.19 (d, \(J = 7.5\) Hz, 1H), 8.15 (t, \(J = 7.5\) Hz, 0.94H), 8.10 (d, \(J = 8.5\) Hz, 0.94H), 8.01 (s, 1H), 7.53 (dd, \(J = 8.0\) Hz, 1.0 Hz, 0.94H), 7.39 (d, \(J = 8.0\) Hz, 1H), 7.32-7.17 (m, 15.5H), 5.61 (s,
3.7H), 2.52 (s, 3H), 2.49 (s, 2.8H); $^{13}$C NMR (125 MHz, CDCl$_3$) δ: 161.77, 163.73, 143.04, 138.00, 137.22, 136.70, 136.54, 136.51, 133.85, 133.61, 131.17, 129.29, 129.23, 128.94, 128.87, 128.67, 128.62, 126.99, 126.36, 125.01, 123.03, 122.91, 122.84, 122.33, 122.26, 121.58, 121.56, 119.42, 119.26, 115.80, 115.76, 46.25, 46.17, 22.05, 21.25; IR (KBr): 1642 (C=O) cm$^{-1}$.

5-benzyl-8,9-difluorophenanthridin-6(5H)-one (3s): Red brown solid, isolated yield 24% (23.1 mg); mp: 170.2-171.2 °C; $^1$H NMR (500 MHz, CDCl$_3$) δ: 8.41-8.37 (m, 1H), 8.09 (d, $J = 7.5$ Hz, 1H), 8.05-8.01 (m, 1H), 7.43 (t, $J = 7.5$ Hz, 1H), 7.33-7.29 (m, 4H), 7.26-7.24 (m, 3H), 5.64 (s, 2H); $^{13}$C NMR (125 MHz, CDCl$_3$) δ: 160.34, 154.09 (dd, $J = 254.5$ Hz, 14.4 Hz), 150.49 (dd, $J = 250.6$ Hz, 13.1 Hz), 137.42, 136.15, 131.81 (dd, $J = 8.0$ Hz, 2.8 Hz), 130.12, 128.85, 127.33, 126.46, 123.41, 122.89, 122.75 (dd, $J = 5.4$ Hz, 1.9 Hz), 118.19, 117.53 (d, $J = 18.5$ Hz), 116.26, 110.29 (d, $J = 19.0$ Hz), 46.64; IR (KBr): 1648 (C=O) cm$^{-1}$; HRMS (ESI, m/z) calcd for [C$_{20}$H$_{13}$F$_2$NO]H$: 322.1038$; found 322.1046.

5-benzyl-8-chlorophenanthridin-6(5H)-one (3t) and 5-benzyl-9-chlorophenanthridin-6(5H)-one (3t'): $^3$

3t:3t' = 1.6:1; Red brown solid, isolated yield 32% (30.6 mg); mp: 153.2-154.7 °C; $^1$H NMR (500 MHz, CDCl$_3$) δ: 8.57 (d, $J = 2.0$ Hz, 1H), 8.52 (d, $J = 8.5$ Hz, 0.6H), 8.22-8.17 (m, 3.2H), 7.70 (dd, $J = 8.5$ Hz, 2.0 Hz, 1H), 7.53 (dd, $J = 9.0$ Hz, 2.0 Hz, 0.6H), 7.42-7.37 (m, 1.6H), 7.30-7.25 (m, 4.8H), 7.24-7.22 (m, 6.4H), 5.63 (s, 3.2H); $^{13}$C NMR (125 MHz, CDCl$_3$) δ: 161.19, 160.77, 139.44, 137.72, 137.17, 136.30, 136.26, 135.26, 134.21, 132.95, 132.22, 130.93, 130.23, 129.82, 128.79, 128.64, 128.37, 127.26, 126.63, 126.48, 123.44, 123.38, 123.24, 122.77, 122.72, 121.61,
118.74, 118.35, 116.09, 46.57, 46.47; IR (KBr): 1638 (C=O) cm⁻¹; HRMS (ESI, m/z) calcd for [C₂₀H₁₄ClNO]⁺: 320.0837; found 320.0837.

5) References

6) Scanned $^1$H NMR and $^{13}$C NMR Spectra of All New Compounds
and

3r and 3r'

and

3r and 3r'