Synthesis of Phenanthridinones via Palladium-Catalyzed Cyclization of N-Aryl-2-aminopyridines with 2-Iodobenzoic Acids in Water

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Supporting Information

Contents

Experimental section S2

General S2

General procedure for the synthesis of phenanthridinones S2

Compounds characterization S3

Procedure for the synthesis of product 6-phenanthridone 5 S9

Procedure for the synthesis of 6 S9

References S9

NMR Spectra of compounds S10

Experimental section
General

Unless otherwise noted, all reactions were carried out without exclusion of air or moisture. Commercial solvents and reagents were used without further purification. Flash chromatography was conducted on silica gel (300-400 mesh). NMR (400 MHz for $^1$H NMR, 100 MHz for $^{13}$C NMR) spectra were recorded in CDCl$_3$ or d$_2$-DMSO with TMS as the internal standard. Chemical shifts are reported in ppm and coupling constants are given in Hz. Data for $^1$H NMR are recorded as follows: chemical shift (ppm), multiplicity (s, singlet; d, doublet; t, triplet; q, quarter; m, multiplet), coupling constant (Hz), integration. Data for $^{13}$C NMR are reported in terms of chemical shift ($\delta$, ppm). High-resolution mass spectra (HRMS) were obtained on an Agilent mass spectrometer using ESI-TOF (electrospray ionization-time of flight).

The N-aryl-2-aminopyridines, N-(2-pyrimidyl)anilines and palladacycle dimer II were prepared using general procedures reported in the literatures.$^1$

General procedure for the synthesis of phenanthridinones

![Chemical Structure]

Procedure A: Pd(OAc)$_2$ (4.5 mg, 0.02 mmol) was dissolved in dichloromethane (1 mL) and 10 μL of the solution was then added to the Schlenk tube equipped with a Teflon-coated magnetic stir bar. The solvent was then evaporated under high vacuum. Then N-aryl-2-aminopyridines 1 (0.20 mmol), 2-iodobenzoic acids 2 (0.26 mmol) and Ag$_2$O (32 mg, 0.14 mmol) were loaded into a Schlenk tube. Then water (1.0 mL) was added and placed into a preheated oil bath (120 °C) and stirred for 3 h. After completion of reaction as judged by GC analysis, the reaction tube was allowed to cool to room temperature and ethyl acetate then added for dilution. The organic layer was separated, and the aqueous layer was washed with ethyl acetate. The filtrate was concentrated under reduced pressure. The crude products were purified by flash column chromatography on silica gel to afford the desired products.

Procedure B: Pd(OAc)$_2$ (4.5 mg, 0.02 mmol), N-(2-pyrimidyl)anilines 1 (0.20 mmol), 2-iodobenzoic acid 2a (64.5 mg, 0.26 mmol) and Ag$_2$O (32 mg, 0.14 mmol) were loaded into a Schlenk tube. Then water (1.0 mL) was added and placed into a preheated oil bath (120 °C) and stirred for 3 h. Then the reaction tube was allowed to cool to room temperature and ethyl acetate then added for dilution. The organic layer was separated, and the aqueous layer was washed with ethyl acetate. The filtrate was concentrated under reduced pressure. The crude products were purified by flash column chromatography on silica gel to afford the desired products.
Compounds characterization

5-(Pyridin-2-yl)phenanthridin-6(5H)-one (3a)
Prepared according to general procedure to afford 3a (50 mg, 93% yield) as a white solid; \(^1\)H NMR (400 MHz, CDCl\(_3\)): δ 8.77 (d, \(J = 4.1\) Hz, 1H), 8.53 (d, \(J = 7.9\) Hz, 1H), 8.27-8.22 (m, 2H), 7.97-7.93 (m, 1H), 7.76-7.73 (m, 1H), 7.57-7.53 (m, 1H), 7.46-7.42 (m, 2H), 7.28-7.21 (m, 2H), 6.51 (d, \(J = 8.4\) Hz, 1H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): δ 161.7, 151.9, 150.6, 139.3, 138.2, 134.2, 133.0, 129.1, 128.8, 128.1, 125.7, 124.8, 124.1, 123.1, 122.9, 121.9, 118.9, 116.4; HRMS (ESI-TOF): m/z calcd for C\(_{18}\)H\(_{13}\)N\(_2\)O \([M+H]\) 273.1028, Found 273.1036.

4-Methoxy-5-(pyridin-2-yl)phenanthridin-6(5H)-one (3b)
Prepared according to general procedure to afford 3b (47 mg, 78% yield) as a white solid; \(^1\)H NMR (400 MHz, CDCl\(_3\)): δ 8.55-8.50 (m, 2H), 8.28 (d, \(J = 8.2\) Hz, 1H), 7.92-7.85 (m, 2H), 7.78-7.74 (m, 1H), 7.59-7.55 (m, 2H), 7.33-7.22 (m, 2H), 6.92 (d, \(J = 8.1\) Hz, 1H), 3.30 (s, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): δ 162.7, 155.6, 154.3, 148.2, 148.1, 136.9, 134.4, 133.1, 128.9, 128.2, 127.9, 125.7, 124.1, 123.7, 122.4, 121.3, 115.9, 113.4, 56.6; HRMS (ESI-TOF): m/z calcd for C\(_{19}\)H\(_{15}\)N\(_2\)O\(_2\) \([M+H]\) 303.1134, Found 303.1149.

4-Phenoxy-5-(pyridin-2-yl)phenanthridin-6(5H)-one (3c)
Prepared according to general procedure to afford 3c (47 mg, 65% yield) as a white solid; \(^1\)H NMR (400 MHz, CDCl\(_3\)): 8.55-8.53 (m, 1H), 8.36 (d, \(J = 7.4\) Hz, 2H), 8.17-8.15 (m, 1H), 7.86-7.82 (m, 1H), 7.70-7.61 (m, 2H), 7.42 (d, \(J = 7.9\) Hz, 1H), 7.31-7.27 (m, 1H), 7.17-7.11 (m, 3H), 7.05-6.96 (m, 2H), 6.52 (d, \(J = 7.9\) Hz, 2H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): δ 162.5, 157.0, 154.3, 148.7, 143.8, 137.1, 134.3, 133.2, 130.6, 129.2, 129.0, 128.5, 125.9, 123.9, 123.6, 122.6, 122.3, 119.1, 116.9; HRMS (ESI-TOF): m/z calcd for C\(_{24}\)H\(_{17}\)N\(_2\)O\(_2\) \([M+H]\) 365.1290, Found 365.1298.

3-Bromo-5-(pyridin-2-yl)phenanthridin-6(5H)-one (3d)
Prepared according to general procedure to afford 3d (52 mg, 75% yield) as a white solid; \(^1\)H NMR (400 MHz, d-DMSO): δ 8.79-8.78 (m, 1H), 8.61-8.59 (m, 1H), 8.52 (d, \(J = 8.7\) Hz, 1H), 8.35-8.33 (m, 1H), 8.21-8.17 (m, 1H), 7.97-7.93 (m, 1H), 7.76-7.67 (m, 3H), 7.53-7.51 (m, 1H), 6.46 (d, \(J = 1.8\) Hz, 1H); \(^{13}\)C NMR (100 MHz, d-DMSO): δ 160.9, 151.2, 150.9, 140.5, 139.4, 134.2, 133.5, 129.4, 128.5, 126.4, 126.2, 125.4, 123.4, 122.8, 118.6, 117.9; HRMS (ESI-TOF): m/z calcd for C\(_{18}\)H\(_{12}\)BrN\(_2\)O \([M+H]\) 351.0133, Found 351.0112.

3-Methoxy-5-(pyridin-2-yl)phenanthridin-6(5H)-one (3e)
Prepared according to general procedure to afford 3e (50 mg, 83% yield) as a white solid; \(^1\)H NMR (400 MHz, CDCl\(_3\)): δ 8.78 (d, \(J = 3.6\) Hz, 1H), 8.49 (d, \(J = 7.7\) Hz, 1H), 8.14-8.11 (m, 2H), 7.99-7.95 (m, 1H), 7.72-7.69 (m, 1H), 7.49-7.43 (m, 3H), 6.82-6.79 (m, 1H), 5.96 (d, \(J = 2.3\) Hz, 1H), 3.64 (s, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): δ 162.1, 160.3, 151.9, 150.6, 139.5, 139.4.
5-(Pyridin-2-yl)-3-(trifluoromethyl)phenanthridin-6(5H)-one (3f)

Prepared according to general procedure to afford 3f (39 mg, 58% yield) as a white solid; 1H NMR (400 MHz, CDCl3): \(\delta\) 8.84-8.82 (m, 1H), 8.58-8.56 (m, 1H), 8.42-8.34 (m, 2H), 8.09-8.05 (m, 1H), 7.71-7.67 (m, 1H), 7.58-7.50 (m, 3H), 6.78 (s, 1H); 13C NMR (100 MHz, CDCl3): \(\delta\) 161.6, 151.1, 150.8, 139.6, 138.1, 133.4, 132.9, 130.9 (q, \(J = 32.7\) Hz), 129.3, 129.1, 126.2, 124.9 (q, \(J = 30.8\) Hz), 124.7, 124.6, 123.9, 122.4, 121.8, 119.4 (q, \(J = 3.5\) Hz), 113.4 (q, \(J = 4.1\) Hz); HRMS (ESI-TOF): m/z calcd for C19H15N2O2 [M+H]^+ 303.1134, Found 303.1149.

2-Fluoro-5-(pyridin-2-yl)phenanthridin-6(5H)-one (3g)

Prepared according to general procedure to afford 3g (38 mg, 65% yield) as a white solid; 1H NMR (400 MHz, CDCl3): \(\delta\) 8.82-8.81 (m, 1H), 8.58 (d, \(J = 7.9\) Hz, 1H), 8.26 (d, \(J = 8.2\) Hz, 1H), 8.0-7.96 (m, 2H), 7.88-7.84 (m, 1H), 7.69-7.66 (m, 1H), 7.55-7.49 (m, 2H), 7.08-7.03 (m, 1H), 6.55-6.52 (m, 1H); 13C NMR (100 MHz, CDCl3): \(\delta\) 161.4, 159.9 (d, \(J = 240.5\) Hz), 151.7, 150.7, 139.4, 136.7, 133.3, 133.0, 129.1, 129.0, 128.8, 128.6, 125.9, 124.7, 124.3, 122.9, 122.0, 120.4, 117.8; HRMS (ESI-TOF): m/z calcd for C18H12FN2O [M+H]^+ 291.0934, Found 291.0947.

2-Chloro-5-(pyridin-2-yl)phenanthridin-6(5H)-one (3h)

Prepared according to general procedure to afford 3h (44 mg, 72% yield) as a white solid; 1H NMR (400 MHz, CDCl3): \(\delta\) 8.81 (d, \(J = 3.9\) Hz, 1H), 8.55 (d, \(J = 7.8\) Hz, 1H), 8.26 (d, \(J = 8.2\) Hz, 1H), 8.04-8.01 (m, 1H), 7.85-7.81 (m, 1H), 7.66-7.62 (m, 1H), 7.53-7.47 (m, 2H), 7.28-7.24 (m, 1H), 6.49 (d, \(J = 8.9\) Hz, 1H); 13C NMR (100 MHz, CDCl3): \(\delta\) 161.4, 151.5, 150.7, 139.4, 136.7, 133.3, 133.0, 129.1, 129.0, 128.8, 128.6, 125.9, 124.7, 124.3, 122.9, 122.0, 120.4, 117.8; HRMS (ESI-TOF): m/z calcd for C18H11ClN2NaO [M+Na]^+ 329.0458, Found 329.0469.

6-Oxo-5-(pyridin-2-yl)-5,6-dihydrophenanthridine-2-carbonitrile (3i)

Prepared according to general procedure to afford 3i (36 mg, 61% yield) as a white solid; 1H NMR (400 MHz, CDCl3): \(\delta\) 8.81 (d, \(J = 3.7\) Hz, 1H), 8.59-8.53 (m, 2H), 8.31 (d, \(J = 8.1\) Hz, 1H), 8.07-8.04 (m, 1H), 7.91-7.88 (m, 1H), 7.72-7.68 (m, 1H), 7.57-7.47 (m, 3H), 6.64 (d, \(J = 8.7\) Hz, 1H); 13C NMR (100 MHz, CDCl3): \(\delta\) 161.5, 150.9, 150.8, 140.9, 139.6, 133.8, 132.5, 131.8, 129.5, 129.2, 127.9, 125.8, 124.7, 121.9, 119.7, 118.7, 117.2, 106.5; HRMS (ESI-TOF): m/z calcd for C19H12N3O [M+H]^+ 298.0980, Found 298.0988.

1,3-Dimethyl-5-(pyridin-2-yl)phenanthridin-6(5H)-one (3j)

Prepared according to general procedure to afford 3j (39 mg, 65% yield) as a white solid; 1H NMR
(400 MHz, CDCl₃): δ 8.82-8.81 (m, 1H), 8.64-8.62 (m, 1H), 8.51 (d, J = 8.4 Hz, 1H), 8.04-7.99 (m, 1H), 7.81-7.65 (m, 1H), 7.60-7.45 (m, 3H), 6.98 (s, 1H), 6.19 (s, 1H), 2.94 (s, 3H), 2.24 (s, 3H); 13C NMR (100 MHz, CDCl₃): δ 161.9, 152.6, 150.7, 139.4, 139.3, 138.1, 136.1, 135.6, 132.2, 129.0, 128.9, 126.9, 126.5, 126.3, 124.8, 124.0, 116.5, 115.2, 26.4, 21.4; HRMS (ESI-TOF): m/z calcd for C₂₀H₁₆N₂NaO [M+Na] 323.1160, Found 323.1170.

2,4-Dimethoxy-5-(pyridin-2-yl)phenanthridin-6(5H)-one (3k)
Prepared according to general procedure to afford 3k (46 mg, 70% yield) as a white solid; ¹H NMR (400 MHz, CDCl₃): δ 8.53-8.51 (m, 2H), 8.23 (d, J = 8.2 Hz, 1H), 7.89-7.84 (m, 1H), 7.79-7.75 (m, 1H), 7.60-7.56 (m, 2H), 7.35-7.28 (m, 2H), 6.54 (d, J = 2.6 Hz, 1H), 3.90 (s, 3H), 3.30 (s, 3H); 13C NMR (100 MHz, CDCl₃): δ 162.3, 156.1, 155.5, 149.3, 148.2, 136.9, 134.3, 132.9, 128.9, 128.3, 126.1, 124.1, 122.5, 122.3, 122.2, 121.7, 102.1, 98.2, 56.5, 55.7; HRMS (ESI-TOF): m/z calcd for C₂₀H₁₇N₂O₃ [M+H] 333.1239, Found 333.1247.

4-Bromo-2-methyl-5-(pyridin-2-yl)phenanthridin-6(5H)-one (3l)
Prepared according to general procedure to afford 3l (47 mg, 65% yield) as a white solid; ¹H NMR (400 MHz, CDCl₃): δ 8.52 (d, J = 4.4 Hz, 1H), 8.47 (d, J = 7.7 Hz, 1H), 8.23 (d, J = 8.2 Hz, 1H), 8.02 (s, 1H), 7.90-7.74 (m, 3H), 7.58-7.54 (m, 1H), 7.45 (s, 1H), 7.32-7.29 (m, 1H), 2.39 (s, 3H); 13C NMR (100 MHz, CDCl₃): δ 162.6, 153.1, 148.6, 137.1, 136.9, 134.3, 134.1, 133.8, 133.4, 129.1, 128.6, 127.4, 125.6, 123.2, 123.0, 122.9, 122.1, 111.6, 20.6; HRMS (ESI-TOF): m/z calcd for C₁₉H₁₄BrN₂O [M+H] 365.0290, Found 365.0300.

3,4-Dichloro-5-(pyridin-2-yl)phenanthridin-6(5H)-one (3m)
Prepared according to general procedure to afford 3m (46 mg, 68% yield) as a white solid; ¹H NMR (400 MHz, CDCl₃): δ 8.47-8.45 (m, 2H), 8.20-8.10 (m, 2H), 7.92-7.77 (m, 3H), 7.62-7.58 (m, 1H), 7.44 (d, J = 8.6 Hz, 1H), 7.34-7.31 (m, 1H); ¹³C NMR (100 MHz, CDCl₃): δ 162.7, 153.5, 148.5, 137.2, 136.6, 135.8, 133.8, 133.4, 129.2, 128.9, 126.5, 125.3, 122.9, 122.1, 122.0, 121.6; HRMS (ESI-TOF): m/z calcd for C₁₈H₁₀Cl₂N₂NaO [M+Na] 363.0068, Found 363.0078.

5-(Pyridin-2-yl)benzo[c]phenanthridin-6(5H)-one (3n)
Prepared according to general procedure to afford 3n (50 mg, 78% yield) as a white solid; ¹H NMR (400 MHz, CDCl₃): δ 8.59-8.57 (m, 1H), 8.49-8.48 (m, 1H), 8.38-8.29 (m, 2H), 7.99-7.95 (m, 1H), 7.88-7.77 (m, 4H), 7.65-7.61 (m, 1H), 7.38-7.35 (m, 2H), 7.09-7.02 (m, 2H); ¹³C NMR (100 MHz, CDCl₃): δ 163.4, 155.5, 149.2, 137.9, 134.9, 134.8, 134.2, 133.4, 129.1, 128.7, 128.2, 125.9, 125.7, 125.4, 125.3, 125.2, 124.9, 124.7, 122.9, 122.5, 120.1, 117.8; HRMS (ESI-TOF): m/z calcd for C₂₂H₁₅N₂O [M+H] 323.1184, Found 323.1198.
3-Chloro-5-(3-methyl pyridin-2-yl)phenanthridin-6(5H)-one (3o)
Prepared according to general procedure to afford 3o (39 mg, 62% yield) as a white solid; 1H NMR (400 MHz, CDCl3): δ 8.64-8.63 (m, 1H), 8.56-8.54 (m, 1H), 8.29-8.23 (m, 2H), 7.87-7.82 (m, 2H), 7.66-7.62 (m, 1H), 7.49-7.46 (m, 1H), 7.28-7.26 (m, 1H), 6.42-6.41 (m, 1H), 2.17 (s, 3H); 13C NMR (100 MHz, CDCl3): δ 160.9, 150.2, 148.4, 140.7, 138.4, 135.3, 133.6, 133.3, 132.7, 129.0, 128.4, 125.5, 124.9, 124.6, 123.3, 121.9, 117.7, 115.6, 17.0; HRMS (ESI-TOF): m/z calcd for C19H14ClN2O [M+H] 321.0795, Found 321.0811.

2-Chloro-5-(3-methyl pyridin-2-yl)phenanthridin-6(5H)-one (3p)
Prepared according to general procedure to afford 3p (35 mg, 55% yield) as a white solid; 1H NMR (400 MHz, CDCl3): δ 8.63-8.56 (m, 2H), 8.29-8.28 (m, 2H), 7.87-7.83 (m, 2H), 7.68-7.64 (m, 1H), 7.46-7.43 (m, 1H), 7.29-7.25 (m, 1H), 6.39 (d, J = 8.8 Hz, 1H), 2.15 (s, 3H); 13C NMR (100 MHz, CDCl3): δ 160.7, 150.4, 148.3, 140.5, 136.1, 133.3, 133.1, 132.7, 129.3, 129.1, 128.8, 128.6, 125.9, 124.8, 123.1, 122.0, 120.5, 117.1, 16.9; HRMS (ESI-TOF): m/z calcd for C19H14ClN2O [M+H] 321.0795, Found 321.0811.

5-(5-(Trifluoromethyl)pyridin-2-yl)phenanthridin-6(5H)-one (3q)
Prepared according to general procedure to afford 3q (43 mg, 63% yield) as a white solid; 1H NMR (400 MHz, CDCl3): δ 9.06 (d, J = 1.0 Hz, 1H), 8.52-8.50 (m, 1H), 8.33-8.24 (m, 3H), 7.84-7.79 (m, 1H), 7.65-7.59 (m, 2H), 7.33-7.27 (m, 2H), 6.51-6.48 (m, 1H); 13C NMR (100 MHz, CDCl3): δ 161.7, 154.9, 147.8 (q, J = 3.9 Hz), 137.6, 136.6 (q, J = 3.2 Hz), 134.2, 133.4, 129.3, 128.9, 128.3, 127.3 (q, J = 33.3 Hz), 125.4, 125.2, 124.5 (d, J = 27.1 Hz), 123.4, 123.3, 122.0, 119.1, 116.1; HRMS (ESI-TOF): m/z calcd for C19H12F3N2O [M+H] 341.0902, Found 341.0917.

5-(Quinolin-2-yl)phenanthridin-6(5H)-one (3r)
Prepared according to general procedure to afford 3r (36 mg, 56% yield) as a white solid; 1H NMR (400 MHz, CDCl3): δ 8.60 (d, J = 7.8 Hz, 1H), 8.49 (d, J = 8.4 Hz, 1H), 8.38-8.33 (m, 2H), 8.20 (d, J = 8.4 Hz, 1H), 8.01 (d, J = 8.1 Hz, 1H), 7.86-7.79 (m, 2H), 7.71-7.62 (m, 2H), 7.57 (d, J = 8.4 Hz, 1H), 7.33-7.27 (m, 2H), 6.62-6.59 (m, 1H); 13C NMR (100 MHz, CDCl3): δ 161.9, 151.3, 148.2, 139.7, 138.1, 134.3, 133.1, 130.2, 129.6, 129.3, 128.9, 128.2, 127.9, 127.7, 125.8, 123.2, 123.0, 122.1, 121.9, 119.2, 116.4; HRMS (ESI-TOF): m/z calcd for C22H15N2O [M+H] 323.1184, Found 323.1201.

5-(Isoquinolin-1-yl)phenanthridin-6(5H)-one (3s)
Prepared according to general procedure to afford 3s (37 mg, 57% yield) as a white solid; 1H NMR (400 MHz, CDCl3): δ 8.68 (d, J = 5.7 Hz, 1H), 8.58 (d, J = 7.8 Hz, 1H), 8.39-8.33 (m, 2H), 7.99 (d, J = 8.3 Hz, 1H), 7.89-7.83 (m, 2H), 7.74-7.70 (m, 1H), 7.66-7.61 (m, 2H), 7.51-7.47 (m, 1H), 7.29-7.19 (m, 2H), 6.34 (d, J = 8.2 Hz, 1H); 13C NMR (100 MHz, CDCl3): δ 161.9, 151.4, 142.5, 138.5, 138.3, 134.4, 133.3, 131.2, 129.4, 129.0, 128.9, 128.3, 127.4, 126.1, 125.7, 124.5, 123.3, 123.1, 122.5,
9-Chloro-5-(pyridin-2-yl)phenanthridin-6(5H)-one (3t)
Prepared according to general procedure to afford 3t (44 mg, 72% yield) as a white solid; 1H NMR (400 MHz, CDCl3): δ 8.79-8.76 (m, 1H), 8.45-8.41 (m, 1H), 8.24-8.11 (m, 2H), 8.02-7.98 (m, 1H), 7.55-7.44 (m, 3H), 7.31-7.21 (m, 2H), 6.51-6.43 (m, 1H); 13C NMR (100 MHz, CDCl3): δ major 161.1, 151.6, 150.7, 139.8, 139.4, 138.6, 135.7, 130.6, 129.9, 128.5, 124.8, 124.3, 123.3, 121.9, 117.8, 116.5; δ minor 160.7, 151.2, 150.7, 140.1, 139.5, 137.1, 134.4, 130.7, 129.8, 129.2, 128.8, 124.7, 124.4, 124.1, 123.0, 122.0, 119.2, 117.9; HRMS (ESI-TOF): m/z calcd for C18H11ClN2NaO [M+Na] 329.0458, Found 329.0469.

10-Methyl-5-(pyridin-2-yl)phenanthridin-6(5H)-one (3u)
Prepared according to general procedure to afford 3u (31 mg, 55% yield) as a white solid; 1H NMR (400 MHz, CDCl3): δ 8.78-8.76 (m, 1H), 8.51-8.42 (m, 2H), 7.99-7.95 (m, 1H), 7.62 (d, J = 7.4 Hz, 1H), 7.48-7.44 (m, 3H), 7.28-7.22 (m, 2H), 6.56-6.53 (m, 1H), 2.95 (s, 3H); 13C NMR (100 MHz, CDCl3): δ 161.9, 152.0, 150.6, 139.3, 138.4, 137.5, 134.8, 133.7, 128.3, 127.5, 127.4, 127.3, 124.8, 124.1, 122.1, 120.6, 116.3, 26.1; HRMS (ESI-TOF): m/z calcd for C19H15N2O [M+H] 287.1184, Found 287.1198.

8-Bromo-5-(pyridin-2-yl)phenanthridin-6(5H)-one (3v)
Prepared according to general procedure to afford 3v (50 mg, 71% yield) as a white solid; 1H NMR (400 MHz, CDCl3): δ 8.83-8.81 (m, 1H), 8.68 (d, J = 2.1 Hz, 1H), 8.27-8.19 (m, 2H), 8.07-8.02 (m, 1H), 7.93-7.90 (m, 1H), 7.55-7.47 (m, 2H), 7.37-7.29 (m, 2H), 6.55-6.53 (m, 1H); 13C NMR (100 MHz, CDCl3): δ 160.6, 151.5, 150.7, 139.4, 138.1, 136.2, 133.1, 131.5, 129.6, 127.2, 124.7, 124.3, 123.8, 123.2, 123.1, 122.3, 118.4, 116.5; HRMS (ESI-TOF): m/z calcd for C18H12BrN2O [M+H] 351.0133, Found 351.0112.

8-Methyl-5-(pyridin-2-yl)phenanthridin-6(5H)-one (3w)
Prepared according to general procedure to afford 3w (36 mg, 64% yield) as a white solid; 1H NMR (400 MHz, CDCl3): δ 8.82-8.81 (m, 1H), 8.34 (s, 1H), 8.28-8.22 (m, 2H), 8.06-8.02 (m, 1H), 7.65 (d, J = 8.2 Hz, 1H), 7.55-7.48 (m, 2H), 7.31-7.28 (m, 2H), 6.54-6.51 (m, 1H), 2.54 (s, 3H); 13C NMR (100 MHz, CDCl3): δ 161.9, 151.9, 150.5, 139.5, 139.4, 138.4, 134.4, 131.8, 128.7, 128.6, 125.5, 124.9, 124.2, 122.9, 121.9, 119.2, 116.3, 21.4; HRMS (ESI-TOF): m/z calcd for C19H15N2O [M+H] 287.1184, Found 287.1198.
7-Fluoro-5-(pyridin-2-yl)phenanthridin-6(5H)-one (3y)
Prepared according to general procedure to afford 3y (37 mg, 65% yield) as a white solid; 1H NMR (400 MHz, CDCl3): δ 8.78-8.76 (m, 1H), 8.21-8.18 (m, 1H), 8.01-7.97 (m, 1H), 7.72-7.67 (m, 1H), 7.49-7.43 (m, 2H), 7.26-7.19 (m, 1H), 6.95 (s, 1H), 6.11 (s, 1H), 2.88 (s, 3H), 2.21 (s, 3H); 13C NMR (100 MHz, CDCl3): δ 164.5 (d, J = 263.1 Hz), 159.2 (d, J = 5.0 Hz), 151.5, 150.6, 139.7, 139.1, 138.8, 138.2, 136.1, 132.9 (d, J = 10.3 Hz), 128.9, 125.1, 123.9, 122.5 (d, J = 4.4 Hz), 116.0 (d, J = 2.4 Hz), 115.4 (d, J = 3.7 Hz), 114.8, 114.6, 26.2, 21.4; HRMS (ESI-TOF): m/z calcd for C18H12FN2O [M+H] 291.0947, Found 291.1255.

7-Fluoro-1,3-dimethyl-5-(pyridin-2-yl)phenanthridin-6(5H)-one (3z)
Prepared according to general procedure to afford 3z (35 mg, 56% yield) as a white solid; 1H NMR (400 MHz, CDCl3): δ 9.08-9.07 (m, 2H), 8.51-8.48 (m, 1H), 8.26-8.22 (m, 1H), 8.14-8.09 (m, 1H), 7.82-7.77 (m, 1H), 7.63-7.55 (m, 2H), 7.41-7.38 (m, 1H), 6.55-6.54 (m, 1H); 13C NMR (100 MHz, CDCl3): δ 161.6, 160.4, 158.3, 138.1, 133.5, 133.4, 128.9, 128.6, 126.3, 125.4, 124.7, 123.1, 121.9, 121.4, 118.4, 117.8; HRMS (ESI-TOF): m/z calcd for C17H11BrN3O [M+H] 352.0095, Found 352.0095.
Procedure for the synthesis of product 6-phenanthridone 5

The phenanthridinone 3a (272 mg, 1 mmol) was dissolved in 7 mL of dry CH2Cl2 in a 25 mL round-bottom flask, filled with nitrogen. It was cooled to 0 °C in an ice bath. Then MeOTf (165 μL, 1.5 mmol) was added to it and allowed to warm to room temperature with stirring for 24 h. Volatile materials were evaporated off in vacuum. The residue was dissolved in 7 mL of dry CH3OH and cooled to 0 °C. Then NaBH4 (152 mg, 4.0 mmol) was added in three portions over 10 min, and the flask was filled with nitrogen again. The reaction mixture was allowed to warm to room temperature and stirred 8 h. The reaction mixture was quenched with HCl (2 N) and extracted with ethyl acetate. Organic layer was dried over anhydrous Na2SO4, filtered, and concentrated under reduced pressure. The residue was purified by flash chromatography to afford the product 4 (131 mg, 67% yield) as a white solid. 1H NMR (400 MHz, d-DMSO): δ 8.53-8.51 (m, 1H), 8.41-8.33 (m, 2H), 7.88-7.85 (m, 1H), 7.68-7.64 (m, 1H), 7.52-7.48 (m, 1H), 7.39-7.38 (m, 1H), 7.29-7.26 (m, 1H); 13C NMR (100 MHz, d-DMSO): δ 161.3, 137.0, 134.7, 133.3, 130.0, 128.4, 127.9, 126.2, 123.7, 123.1, 118.0, 116.6; HRMS (ESI-TOF): m/z calcd for C13H10NO [M+H] 196.0762, Found 196.0748.

Procedure for the synthesis of product 6

2-iodo-N-phenyl-N-(pyridin-2-yl)benzamide (6)

To the solution of N-phenyl-2-amino pyridine 1a (850 mg, 5 mmol) and 2-iodobenzoyle chloride (1.33 g, 5 mmol) in DCM (8 mL) at room temperature was added Et3N (1.1 mL, 7.5 mmol). The reaction was allowed to stir at room temperature for 5 h. Then the mixture was extracted with DCM, and the combined organic layer was dried over anhydrous Na2SO4, filtered and the solvent was evaporated under vacuum. The residue was purified by flash chromatography to afford the product I. 1H NMR (400 MHz, CDCl3): δ 8.21-8.20 (m, 1H), 7.55-7.53 (m, 2H), 7.43 (s, 1H), 7.27-7.16 (m, 5H), 7.09-7.05 (m, 2H), 6.96-6.93 (m, 1H), 6.77-6.74 (m, 1H); 13C NMR (100 MHz, CDCl3): δ 170.3, 154.9, 148.8, 142.1, 141.2, 139.2, 137.9, 130.2, 129.3, 128.2, 127.5, 127.4, 121.8, 121.7, 93.2; HRMS (ESI-TOF): m/z calcd for C18H13IN2NaO [M+Na] 422.9970, Found 422.9971.

References

NMR Spectra of compounds

5-(Pyridin-2-yl)phenanthridin-6(5H)-one (3a)
4-Methoxy-5-(pyridin-2-yl)phenanthridin-6(5H)-one (3b)
4-Phenoxy-5-(pyridin-2-yl)phenanthridin-6(5H)-one (3c)
3-Bromo-5-(pyridin-2-yl)phenanthridin-6(5H)-one (3d)
3-Methoxy-5-(pyridin-2-yl)phenanthridin-6(5H)-one (3e)
5-(Pyridin-2-yl)-3-(trifluoromethyl)phenanthridin-6(5H)-one (3f)
2-Fluoro-5-(pyridin-2-yl)phenanthridin-6(5H)-one (3g)
2-Chloro-5-(pyridin-2-yl)phenanthridin-6(5H)-one (3h)
6-Oxo-5-(pyridin-2-yl)-5,6-dihydrophenanthridine-2-carbonitrile (3i)
1,3-Dimethyl-5-(pyridin-2-yl)phenanthridin-6(5 H)-one (3j)
2,4-Dimethoxy-5-(pyridin-2-yl)phenanthridin-6(5H)-one (3k)
4-Bromo-2-methyl-5-(pyridin-2-yl)phenanthridin-6(5H)-one (3l)
3,4-Dichloro-5-(pyridin-2-yl)phenanthridin-6(5H)-one (3m)
5-(Pyridin-2-yl)benzo[c]phenanthridin-6(5H)-one (3n)
3-Chloro-5-(3-methylpyridin-2-yl)phenanthridin-6(5H)-one (3o)
2-Chloro-5-(3-methylpyridin-2-yl)phenanthridin-6(5H)-one  (3p)
5-(5-(Trifluoromethyl)pyridin-2-yl)phenanthridin-6(5H)-one (3q)
5-(Isoquinolin-1-yl)phenanthridin-6(5H)-one (3s)
9-Chloro-5-(pyridin-2-yl)phenanthridin-6(5H)-one (3t)
10-Methyl-5-(pyridin-2-yl)phenanthridin-6(5H)-one (3u)
8-Bromo-5-(pyridin-2-yl)phenanthridin-6(5H)-one (3v)
8-Methyl-5-(pyridin-2-yl)phenanthridin-6(5H)-one (3w)
8-Methyl-5-(pyridin-2-yl)benzo[cd]phenanthridin-6(5H)-one (3x)
7-Fluoro-5-(pyridin-2-yl)phenanthridin-6(5H)-one (3y)
7-Fluoro-1,3-dimethyl-5-(pyridin-2-yl)phenanthridin-6(5H)-one (3z)
5-((Pyrimidin-2-yl)phenanthridin-6(5H)-one (4a)
3-Bromo-5-(pyrimidin-2-yl)phenanthridin-6(5H)-one (4b)
Phenanthridin-6(5H)-one (5)
2-Iodo-N-phenyl-N-(pyridin-2-yl)benzamide (6)