Supporting Information

Synthesis of phenanthridin-6(5H)-ones via Cu-catalyzed cyclization of 2-phenylbenzamides

Qingwen Gui, a Zhiyong Yang, a Xiang Chen, a Jidan Liu, a Ze Tan**, a Ruqing Guo, a Wei Yu b

a State Key Laboratory of Chemo/Biosensing and Chemometrics, College of Chemistry and Chemical Engineering, Hunan University, Changsha 410082, P. R. China.
E-mail: ztanze@gmail.com

b Pharmaceutical department, Kunming General Hospital of PLA, Kunming Yunnan 60032, P. R. China.
E-mail: kmweiyu@163.com

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**General information**

All the solvents and commercially available reagents were purchased from commercial sources and used directly. $^1$H NMR and $^{13}$C NMR were recorded in CDCl$_3$ at room temperature on the Varian INOVA-400 spectrometer (400 MHz $^1$H). The chemical-shifts scale is based on internal TMS. The coupling constants, $J$, are reported in Hertz (Hz). HRMS were measured on a Finnigan MAT 95 XP Mass spectrometer (EI). Products were purified by flash column chromatography on 200-300 mesh silica gel, SiO$_2$.

**Experimental section**

![Diagram of experimental setup]

To a stirred solution of CuI (8.6 mg, 0.05 mmol) and PPh$_3$ (26.2 mg, 0.10 mmol) in 3.0 ml of anhydrous o-xylene were added 2-phenylbenzamide 1 (99 mg, 0.5 mmol) and KO-tBu (112 mg, 1.0 mmol) at room temperature. A balloon of air was attached to the system and the mixture was heated at 120 °C for 18 hours. After cooling to room temperature, the reaction mixture was diluted with diethyl ether (25 mL) and water (25 mL). The aqueous layer was extracted with diethyl ether (3x25 mL) and washed with brine. The organic layers were combined, dried with MgSO$_4$, filtered, and the solvent was removed under reduced pressure. The residue was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate) to afford 87.8 mg of the desired product in 90% yield.

**Analytical data of phenanthridin-6(5H)-one**

Phenanthridin-6(5H)-one2c

TLC (petroleum ether/ ethyl acetate, 2/1); Yield: 90%; white solid;

IR(KBr)/cm$^{-1}$: 3047, 1663 (CO), 1369, 748;

$^1$H NMR (400MHz, DMSO-d$_6$): $\delta$ 11.69 (s, 1 H), 8.52 (d, $J$ = 8.0 Hz, 1 H), 8.40 (d, $J$ = 8.0 Hz, 1 H), 8.83 (d, $J$ = 8.0 Hz, 1 H), 7.86 (t, $J$ = 7.6 Hz, 1 H), 7.65 (t, $J$ = 7.6 Hz, 1 H), 7.50 (t, $J$ = 7.6 Hz, 1 H), 7.37 (d, $J$ = 8.0 Hz, 1 H), 7.27 (d, $J$ = 8.0 Hz, 1 H);

$^{13}$C NMR (100MHz, DMSO-d$_6$): $\delta$ 161.09, 136.84, 134.53, 133.07, 129.85, 128.21, 127.77, 125.96, 123.56, 122.91, 122.54, 117.84, 116.39;

MS (m/z) 195.2 (M$^+$.)

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3,8-Dimethylphenanthridin-6(5H)-one

\[
\text{O} \quad \text{NH}
\]

TLC (petroleum ether/ethyl acetate, 2/1); Yield: 78%; white solid;
IR(KBr)/cm\(^{-1}\): 3370, 2920, 1660 (CO), 1410, 1050, 937;
\(^1\)H NMR (400MHz, DMSO-d\(_6\)):
δ 11.54 (s, 1 H), 8.33 (d, \(J = 8.0\) Hz, 1 H), 8.21 (d, \(J = 8.0\) Hz, 1 H), 8.10 (s, 1 H), 7.64 (d, \(J = 8.0\) Hz, 1 H), 7.14 (s, 1 H), 7.07 (d, \(J = 8.0\) Hz, 1 H), 2.47 (s, 3 H), 2.38 (s, 3 H);
\(^13\)C NMR (100MHz, DMSO-d\(_6\)):
δ 161.22, 139.09, 137.29, 136.50, 134.15, 132.21, 127.42, 125.48, 123.69, 123.15, 122.63, 116.15, 115.62, 21.35, 21.17;
HRMS: m/z calcld for C\(_{15}\)H\(_{13}\)NO: 223.0997, found: 223.0999.

3-Methyl-8-methoxyphenanthridin-6(5H)-one

\[
\text{O} \quad \text{NH}
\]

TLC (petroleum ether/ethyl acetate, 2/1); Yield: 85%; white solid;
IR(KBr)/cm\(^{-1}\): 3330, 2910, 1660 (CO), 1050, 879;
\(^1\)H NMR (400MHz, DMSO-d\(_6\)):
δ 11.65 (s, 1 H), 8.39 (d, \(J = 8.0\) Hz, 1 H), 8.18 (d, \(J = 8.0\) Hz, 1 H), 7.73 (s, 1 H), 7.42 (d, \(J = 8.0\) Hz, 1 H), 7.14 (s, 1 H), 7.07 (d, \(J = 8.0\) Hz, 1 H), 3.90 (s, 3 H), 2.38 (s, 3 H);
\(^13\)C NMR (100MHz, DMSO-d\(_6\)):
δ 160.98, 158.94, 138.40, 135.79, 128.10, 126.91, 124.56, 123.79, 122.83, 121.89, 116.11, 115.65, 108.87, 55.67, 21.32;
HRMS: m/z calcld for C\(_{15}\)H\(_{13}\)NO\(_2\): 239.0946, found: 239.0949.

3-Methyl-9-methoxyphenanthridin-6(5H)-one

\[
\text{O} \quad \text{NH}
\]

TLC (petroleum ether/ethyl acetate, 2/1); Yield: 78%; white solid;
IR(KBr)/cm\(^{-1}\): 3330, 2920, 1660 (CO), 1040, 883;
\(^1\)H NMR (400MHz, DMSO-d\(_6\)):
δ 11.44 (s, 1 H), 8.29 (d, \(J = 8.0\) Hz, 1 H), 8.20 (d, \(J = 8.0\) Hz, 1 H), 7.83 (s, 1 H), 7.17 (m, \(J = 1.6\) Hz, 1 H), 7.12 (s, 1 H), 7.07 (d, \(J = 8.0\) Hz, 1 H), 3.97 (s, 3 H), 2.38 (s, 3 H);
$^{13}$C NMR (100MHz, DMSO-d$_6$): $\delta$ 163.13, 161.05, 139.81, 137.34, 136.81, 129.81, 123.88, 123.51, 119.12, 116.18, 116.16, 115.46, 105.02, 56.03, 21.42;
HRMS: m/z calcd for C$_{15}$H$_{13}$NO$_2$: 239.0946, found: 239.0949.

3-Methyl-8,10-dimethoxyphenanthridin-6(5H)-one

![ Structure of 3-Methyl-8,10-dimethoxyphenanthridin-6(5H)-one ]

TLC (petroleum ether/ethyl acetate, 2/1); Yield: 88%; white solid;
IR(KBr)/cm$^{-1}$: 3300, 2910, 2840, 1650 (CO), 1390, 1070;
$^1$H NMR (400MHz, DMSO-d$_6$): $\delta$ 11.68 (s, 1 H), 8.84 (d, $J$ = 8.0 Hz, 1 H), 7.49 (s, 1 H), 7.14 (s, 1 H), 7.03 (m, $J$ = 8.8 Hz, 2 H), 4.04 (s, 3 H), 3.91 (s, 3 H), 2.36 (s, 3 H);
$^{13}$C NMR (100MHz, DMSO-d$_6$): $\delta$ 160.59, 159.17, 159.12, 137.47, 135.59, 128.62, 127.30, 123.47, 117.92, 115.87, 115.23, 104.45, 101.33, 56.48, 55.74, 21.22;
HRMS: m/z calcd for C$_{16}$H$_{15}$NO$_3$: 269.1052, found: 269.1057.

3,8,9-Trimethylphenanthridin-6(5H)-one

![ Structure of 3,8,9-Trimethylphenanthridin-6(5H)-one ]

TLC (petroleum ether/ethyl acetate, 2/1); Yield: 87%; white solid;
IR(KBr)/cm$^{-1}$: 3460, 2900, 1680 (CO), 1380, 1090, 868;
$^1$H NMR (400MHz, DMSO-d$_6$): $\delta$ 11.30 (s, 1 H), 8.19 (t, $J$ = 8.8 Hz, 2 H), 7.59 (d, $J$ = 8.2 Hz, 1 H), 7.07 (s, 1 H), 7.01 (d, $J$ = 8.2 Hz, 2 H), 2.83 (s, 3 H), 2.38 (s, 3 H), 2.36 (s, 3 H);
$^{13}$C NMR (100MHz, DMSO-d$_6$): $\delta$ 161.26, 142.54, 138.97, 136.7, 136.71, 132.60, 127.88, 123.61, 123.56, 123.15, 123.11, 116.15, 115.59, 21.38, 20.28, 19.71;
HRMS: m/z calcd for C$_{16}$H$_{15}$NO: 237.1154, found: 237.1158.

3,9-Dimethylphenanthridin-6(5H)-one

![ Structure of 3,9-Dimethylphenanthridin-6(5H)-one ]

TLC (petroleum ether/ethyl acetate, 2/1); Yield: 75%, white solid;
IR(KBr)/cm$^{-1}$: 3360, 2930, 1670 (CO), 1070, 897;
$^1$H NMR (400MHz, DMSO-d$_6$): $\delta$ 11.51 (s, 1 H), 8.24 (d, $J$ = 8.8 Hz, 2 H), 8.18 (d, $J$ = 8.0
Hz, 1 H), 7.41 (d, J = 8.0 Hz, 1 H), 7.14 (s, 1 H), 7.08 (d, J = 8.0 Hz, 1 H), 2.52 (s, 3 H), 2.38 (s, 3 H);
\(^{13}\)C NMR (100MHz, DMSO-\(d_6\)): \(\delta\) 161.24, 143.18, 139.50, 137.04, 134.64, 128.94, 127.71, 123.66, 123.36, 123.30, 122.50, 116.20, 115.46, 21.81, 21.35;
HRMS: m/z calcd for C\(_{15}\)H\(_{13}\)NO: 223.0997, found: 223.0999.

3-Methylphenanthridin-6(5H)-one\(^2\)

\[
\text{TLC (petroleum ether/ ethyl acetate, 2/1); Yield: 91%; white solid;}
\]
IR(KBr)/cm\(^{-1}\): 3390, 2930, 2860, 1670 (CO), 1100, 775;
\(^1\)H NMR (400MHz, DMSO-\(d_6\)): \(\delta\) 11.62 (s, 1 H), 8.45 (d, \(J = 8.2\) Hz, 1 H), 8.31 (d, \(J = 8.0\) Hz, 1 H), 8.26 (d, \(J = 8.0\) Hz, 1 H), 7.83 (t, \(J = 8.0\) Hz, 1 H), 7.61 (t, \(J = 8.0\) Hz, 1 H), 7.17 (s, 1 H), 7.09 (d, \(J = 8.0\) Hz, 1 H), 2.40 (s, 3 H);
\(^{13}\)C NMR (100MHz, DMSO-\(d_6\)): \(\delta\) 161.26, 139.68, 136.88, 134.66, 132.99, 127.69, 125.57, 123.78, 123.46, 123.40, 122.60, 116.26, 115.52, 21.42;
MS (m/z) 209.2 (M\(^+\)).

3-Chlorophenanthridin-6(5H)-one\(^2\)

\[
\text{TLC (petroleum ether/ ethyl acetate, 2/1); Yield: 40%; white solid;}
\]
IR(KBr)/cm\(^{-1}\): 2858, 1660 (CO), 1609, 762;
\(^1\)H NMR (400MHz, DMSO-\(d_6\)): \(\delta\) 11.75 (s, 1 H), 8.50 (d, \(J = 8.2\) Hz, 1 H), 8.42 (d, \(J = 8.2\) Hz, 1 H), 8.32 (d, \(J = 8.0\) Hz, 1 H), 7.87 (t, \(J = 8.0\) Hz, 1 H), 7.67 (t, \(J = 8.0\) Hz, 1 H), 7.40 (s, 1 H), 7.30 (m, \(J = 8.2\) Hz, 1 H);
\(^{13}\)C NMR (100MHz, DMSO-\(d_6\)): \(\delta\) 161.07, 137.92, 133.99, 133.79, 133.34, 128.61, 127.78, 125.77, 125.58, 123.10, 122.44, 116.84, 115.58;
MS (m/z) 223.2 (M\(^+\)).

2,4-Dimethylphenanthridin-6(5H)-one\(^4\)
TLC (petroleum ether/ethyl acetate, 2/1); Yield: 78%; white solid;
IR(KBr)/cm\(^{-1}\): 3012, 1657 (CO), 1608, 770;
\(^1\)H NMR (400MHz, DMSO-\(d_6\)): \(\delta\) 10.61 (s, 1 H), 8.48 (d, \(J = 8.0\) Hz, 1 H), 8.33 (d, \(J = 8.0\) Hz, 1 H), 8.06 (s, 1 H), 7.84 (m, \(J = 8.0\) Hz, 1 H), 7.67 (t, \(J = 7.8\) Hz, 1 H), 7.17 (s, 1 H), 2.50 (s, 3 H), 2.38 (s, 3 H);
\(^{13}\)C NMR (100MHz, DMSO-\(d_6\)): \(\delta\) 161.32, 134.76, 133.06, 132.92, 132.41, 131.09, 127.94, 127.73, 125.70, 124.26, 123.01, 121.22, 117.71, 20.83, 17.80;
MS (m/z) 229.1 (M\(^+\)).

3-Methoxyphenanthridin-6(5H)-one\(^2\)

TLC (petroleum ether/ethyl acetate, 2/1); Yield: 92%; white solid;
IR(KBr)/cm\(^{-1}\): 2875, 1663 (CO), 1506, 766;
\(^1\)H NMR (400MHz, DMSO-\(d_6\)): \(\delta\) 11.60 (s, 1 H), 8.38 (d, \(J = 8.2\) Hz, 1 H), 8.28 (t, \(J = 8.2\) Hz, 2H), 7.80 (t, \(J = 8.2\) Hz, 1 H), 7.55 (t, \(J = 7.8\) Hz, 1 H), 6.89 (m, \(J = 8.8\) Hz, 2 H), 3.84 (s, 3 H);
\(^{13}\)C NMR (100MHz, DMSO-\(d_6\)): \(\delta\) 161.43, 160.59, 138.36, 134.82, 133.05, 127.70, 127.01, 125.07, 124.71, 122.31, 111.40, 110.41, 99.82, 99.77, 55.55;
MS (m/z) 225.1 (M\(^+\)).

8,9-Dimethoxyphenanthridin-6(5H)-one

TLC (petroleum ether/ethyl acetate, 2/1); Yield: 88%; white solid;
IR (KBr)/cm\(^{-1}\): 3460, 2900, 1680 (CO), 1380,1090, 868;
\(^1\)H NMR (400MHz, DMSO-\(d_6\)): \(\delta\) 11.53 (s, 1 H), 8.34 (d, \(J = 8.0\) Hz, 1 H), 8.29 (s, 1 H), 8.06 (s, 1 H), 7.44 (t, \(J = 8.0\) Hz, 1 H), 7.33 (d, \(J = 8.0\) Hz, 1 H), 7.23 (t, \(J = 8.0\) Hz, 1 H), 2.45 (s, 3 H), 2.39 (s, 3 H);
\(^{13}\)C NMR (100MHz, DMSO-\(d_6\)): \(\delta\) 161.11, 142.62, 137.24, 136.68, 132.48, 129.25, 127.93,
8-Methoxyphenanthridin-6(5H)-one

\[
\text{O} \\ \\ \\ \\ \\ \\ \\ \text{NH} \\ \\ \\ \\ \text{O}
\]

TLC (petroleum ether/ethyl acetate, 2/1); Yield: 82%; white solid;
IR(KBr)/cm\(^{-1}\): 2902, 1667 (CO), 1369, 750;

\(^1\)H NMR (400MHz, DMSO-\(d_6\)): \(\delta\) 11.72 (s, 1 H), 8.45 (d, \(J = 9.2\) Hz, 1 H), 8.31 (d, \(J = 8.0\) Hz, 1 H), 7.76 (s, 1 H), 7.44 (m, \(J = 8.0\) Hz, 2 H), 7.35 (d, \(J = 8.0\) Hz, 1 H), 7.25 (t, \(J = 8.0\) Hz, 1 H), 3.91 (s, 3 H);

\(^{13}\)C NMR (100MHz, DMSO-\(d_6\)): \(\delta\) 160.84, 159.29, 135.76, 128.74, 128.74, 127.95, 124.88, 122.94, 122.57, 121.93, 118.00, 116.26, 108.94, 55.73;
HRMS: m/z calcd for C\(_{14}\)H\(_{11}\)NO: 225.0790, found: 225.0794.

3-Chloro-9-methoxyphenanthridin-6(5H)-one

TLC (petroleum ether/ethyl acetate, 2/1); Yield: 73%; white solid;
IR(KBr)/cm\(^{-1}\): 3330, 1660 (CO), 1609, 1369, 748;

\(^1\)H NMR (400MHz, DMSO-\(d_6\)): \(\delta\) 11.61 (s, 1 H), 8.47 (d, \(J = 8.8\) Hz, 1 H), 8.22 (d, \(J = 8.8\) Hz, 1 H), 7.89 (s, 1 H), 7.28 (d, \(J = 8.8\) Hz, 1 H), 7.23 (d, \(J = 8.8\) Hz, 1 H), 3.98 (s, 3 H);

\(^{13}\)C NMR (100MHz, DMSO-\(d_6\)): \(\delta\) 163.33, 160.88, 138.39, 135.98, 134.15, 129.91, 126.07, 122.15, 119.25, 117.00, 116.78, 115.49, 105.62, 56.16;
HRMS: m/z calcd for C\(_{14}\)H\(_{10}\)NO\(_2\)Cl: 259.0400, found: 259.0403.

3-Chloro-9-methylphenanthridin-6(5H)-one

TLC (petroleum ether/ethyl acetate, 2/1); Yield: 43%; white solid;
IR(KBr)/cm\(^{-1}\): 3400, 2920, 2850, 1690 (CO), 1090;

\(^1\)H NMR (400MHz, DMSO-\(d_6\)): \(\delta\) 11.59 (s, 1 H), 8.38 (d, \(J = 8.0\) Hz, 1 H), 8.33 (s, 1 H),
8.20 (d, $J = 8.4$ Hz, 1 H), 7.47 (d, $J = 8.0$ Hz, 1 H), 7.35 (d, $J = 8.0$ Hz, 1 H), 7.25 (m, $J = 8.0$ Hz, 1 H), 2.54 (s, 3 H);

$^{13}$C NMR (100MHz, DMSO-d$_6$): δ 161.10, 143.30, 137.01, 134.54, 129.73, 129.45, 127.77, 123.69, 123.50, 122.79, 122.42, 117.80, 116.36, 21.85;

HRMS: m/z calc for C$_{14}$H$_{10}$NOCl: 243.0451, found: 243.0456.

3-Chloro-8-methylphenanthridin-6(5H)-one

![Chemical Structure]

TLC (petroleum ether/ ethyl acetate, 2/1); Yield: 45%; white solid;

IR(KBr)/cm$^{-1}$: 3400, 2920, 2850, 1690 (CO), 1090;

$^1$H NMR (400MHz, DMSO-d$_6$): δ 11.73 (s, 1 H), 8.38 (m, $J = 8.4$ Hz, 2 H), 8.11 (s, 1 H), 7.69 (d, $J = 8.4$ Hz, 1 H), 7.38 (s, 1 H), 7.28 (d, $J = 8.4$ Hz, 1 H), 2.49 (s, 3 H);

$^{13}$C NMR (100MHz, DMSO-d$_6$): δ 160.98, 138.41, 137.56, 134.50, 133.47, 131.38, 127.52, 129.15, 123.15, 122.40, 116.97, 115.49, 21.23;

HRMS: m/z calc for C$_{14}$H$_{10}$NOCl: 243.0451, found: 243.0455.

3-Methyl-9-chlorophenanthridin-6(5H)-one

![Chemical Structure]

TLC (petroleum ether/ ethyl acetate, 2/1); Yield: 55%; white solid;

IR(KBr)/cm$^{-1}$: 3210, 2910, 2880, 1670 (CO), 1610,1400,1050, 881;

$^1$H NMR (400MHz, DMSO-d$_6$): δ 11.71 (s, 1 H), 8.55 (s, 1 H), 8.32 (d, $J = 8.4$ Hz, 1 H), 8.27 (d, $J = 8.4$ Hz, 1 H), 7.63 (d, $J = 8.4$ Hz, 1 H), 7.15 (s, 1 H), 7.28 (d, $J = 8.0$ Hz, 1 H), 2.39 (s, 3 H);

$^{13}$C NMR (100MHz, DMSO-d$_6$): δ 160.80, 140.80, 138.68, 137.53, 136.67, 130.16, 128.06, 127.90, 124.42, 124.20, 122.61, 116.47, 114.76, 21.61;

HRMS: m/z calc for C$_{14}$H$_{10}$NOCl: 243.0451, found: 243.0456.

References


