Supporting Information

Oxidative radical cascade cyclization involving C(sp$^3$)–C(sp$^3$), C(sp$^3$)–C(sp$^2$) and C(sp$^2$)–N bonds formation: direct construction of cyano and methyl substituted polyheterocycles

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1. General information

$^1$H NMR, $^{13}$C NMR and spectra were recorded on Bruker AVANCE DRX 500 (500 MHz for $^1$H; 126 MHz for $^{13}$C) and Bruker AVANCE III HD 600 (600 MHz for $^1$H; 151 MHz for $^{13}$C) instruments internally referenced to tetramethylsilane (TMS) signal. Chemical shifts (δ) and coupling constants (J) were expressed in ppm and Hz, respectively. CDCl$_3$ was used as the NMR solvent in all cases. Mass spectra were measured using Thermo LTQ Orbitrap XL spectrometer. IR spectra were recorded on a Bruker Tensor 27 FT-IR spectrometer and only major peaks are reported in cm$^{-1}$. Unless otherwise noted, materials were obtained from commercial suppliers and used without further purification. Column chromatography was carried out on silica gel (particle size 200-300 mesh ASTM).
2. Typical procedures for the synthesis of substrates

![Reaction Scheme]

To the solution of anthranilonitrile S-1 (15.0 mmol, 2.94 g) in 16 mL EtOH were added formaldehyde solution (37%, 2 equiv, 30.0 mmol, 2.2 mL) and succinimide (2 equiv, 2.85 g, 30 mmol). The mixture was allowed to reflux with stirring. After completion of the reaction, the solution was cooled to room temperature and further cooled in an ice bath. Succinimide derivative S-2 was collected by vacuum filtration, washed several times with cold ethanol, dried and was used without further purification.

To the solution of S-2 in 16 mL dry DMSO was slowly added NaBH₄ (1.1 equiv, 0.63 g, 16.5 mmol) at 0 ºC under argon. The mixture was allowed to stir at 80 ºC. After completion of the reaction, the solution was cooled to room temperature and poured into cold water. The mixture was extracted with diethyl ether and the extract was dried over Na₂SO₄. Concentration under reduced pressure to afford aniline S-3 without any further purification.

To a stirred solution of aniline S-3 (7.0 mmol) in 35 mL dry toluene were added anhydrous K₂CO₃ (14.0 mmol) and acyl chloride (10.5 mmol). The mixture was heated to 110 ºC under argon atmosphere for 12 h. After completion, the reaction was quenched with H₂O and extracted with EtOAc. The extract was washed with brine and dried over MgSO₄. Concentration under reduced pressure and purification by silica gel flash chromatography to afford the amide S-4.

Amide S-4 (4.0 mmol), phenylboronic acid (6.0 mmol), PdCl₂(PPh₃)₂ (0.12 mmol) and KOAc (8 mmol) were added in 30 mL toluene. The reaction mixture was stirred at 110 ºC under argon atmosphere for 12 h. After completion of the reaction, the resulting solution was cooled to room temperature and diluted with EtOAc. The solution was washed with water (three times) and saturated brine, and the organic layers were dried over Na₂SO₄, filtered. Concentration under reduced pressure and purification by silica gel flash chromatography to afford the desired substrates 1. [1o, 1u and 1v: Amide S-4 (4 mmol), phenylboronic acid (4.8 mmol), PdCl₂(PPh₃)₂ (0.12 mmol) and Cs₂CO₃ (10 mmol) were added in CH₃CN (40 mL) and H₂O (2 mL). The reaction mixture was stirred at 80 ºC under argon atmosphere for 12 h. After completion of the reaction, the resulting solution was cooled to room temperature and extracted with EtOAc. The combined organic layers were washed with brine, dried over anhydrous Na₂SO₄, filtered and concentrated under reduced pressure. The residue was purified by column chromatography to give the desired substrates 1.]

S3
### 3. Screening of the reaction conditions

**Table S1. Reaction conditions screening**

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*Reaction conditions: 1a (0.2 mmol), 2a, metal salt, and oxidant in solvent for 12 h under Ar. ©Isolated yield. 
©Determined by $^1$H NMR of the crude products. *Under air.
Table S2. Optimization of the reaction conditions

4. General procedure for synthesis of cyano substituted pyrido[4,3,2-\(gh\)]phenanthridinds

In a Schlenk tube, acrylamide 1 (0.2 mmol), Cu(OAc)\(_2\) (0.02 mmol), and TBPB (0.4 mmol) were added and charged with argon three times. Then, CH\(_2\)CN (8 mL) were added. The mixture was allowed to stir at 120 °C for 12 hours. After substrate was consumed, the reaction was cooled to room temperature and filtering through a bed of Celite. The filtered reaction mixture was concentrated by rotary evaporation and purified by flash chromatography on silica gel with petroleum ether/ethyl acetate as the eluent to afford the corresponding product 3.

5. General procedure for synthesis of methyl substituted pyrido[4,3,2-\(gh\)]phenanthridinds

In a Schlenk tube, acrylamide 1 (0.2 mmol) and TBPB (0.8 mmol) were added and charged with argon three times. Then, PhCl (2 mL) were added. The mixture was allowed to stir at 100 °C for 12 hours. After substrate was consumed, the reaction was cooled to room temperature and filtering through a bed of Celite. The filtered reaction mixture was concentrated by rotary evaporation and purified by flash chromatography on silica gel with petroleum ether/ethyl acetate as the eluent to afford the corresponding product 3.

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\(^a\)Reaction conditions: 1a (0.2 mmol), methyl source in solvent for 12 h under Ar. \(^b\)Isolated yield. \(^c\)Under air.
consumed, the reaction was cooled to room temperature and filtering through a bed of Celite. The filtered reaction mixture was concentrated by rotary evaporation and purified by flash chromatography on silica gel with petroleum ether/ethyl acetate as the eluent to afford the corresponding product 4.

6. Kinetic isotope effect (KIE) experiments

a) Intermolecular KIE experiment

In a Schlenk tube, acrylamide 1a (0.1 mmol, 27.6 mg), 1a-D$_5$ (0.1 mmol, 28.1 mg), Cu(OAc)$_2$ (0.02 mmol, 3.6 mg), and TBPB (0.4 mmol, 77.7 mg) were added and charged with argon three times. Then, CH$_3$CN (8 mL) were added. The mixture was allowed to stir at 120 °C for 0.5 hour. The reaction was cooled to room temperature and filtering through a bed of Celite. The filtered reaction mixture was concentrated by rotary evaporation and purified by flash chromatography on silica gel with petroleum ether/ethyl acetate as the eluent to afford the corresponding product 3 and 3a-D$_4$. The products were under $^1$H-NMR analysis (Figure S1).

b) Intramolecular KIE experiment

In a Schlenk tube, acrylamide 1a-D$_1$ (0.2 mmol, 55.5 mg), Cu(OAc)$_2$ (0.02 mmol, 3.6 mg), and TBPB (0.4 mmol, 77.7 mg) were added and charged with argon three times. Then, CH$_3$CN (8 mL) were added. The mixture was allowed to stir at 120 °C for 0.5 hour. The reaction was cooled to room temperature and filtering through a bed of Celite. The filtered reaction mixture was concentrated by rotary evaporation and purified by flash chromatography on silica gel with petroleum ether/ethyl acetate as the eluent to afford the corresponding product 3a-D$_4$. The products were under $^1$H-NMR analysis (Figure S1).
77.7 mg) were added and charged with argon three times. Then, CH₃CN (8 mL) were added. The mixture was allowed to stir at 120 °C for 12 hours. After substrate was consumed, the reaction was cooled to room temperature and filtering through a bed of Celite. The filtered reaction mixture was concentrated by rotary evaporation and purified by flash chromatography on silica gel with petroleum ether/ethyl acetate as the eluent to afford the corresponding product 3 and 3a-D₁. The products were under ¹H-NMR analysis (Figure S2).

c) The KIE studies on solvent

In a Schlenk tube, acrylamide 1a (0.2 mmol, 55.3 mg), Cu(OAc)₂ (0.02 mmol, 3.6 mg), and TBPB (0.4 mmol, 77.7 mg) were added and charged with argon three times. Then, CH₃CN (4 mL) and CD₃CN (4 mL) were added. The mixture was allowed to stir at 120 °C for 12 hours. After substrate was consumed, the reaction was cooled to room temperature and filtering through a bed of Celite. The filtered reaction mixture was concentrated by rotary evaporation and purified by flash chromatography on silica gel with petroleum ether/ethyl acetate as the eluent to afford the corresponding product 3 and 3a-D₁. The products were under ¹H-NMR analysis (Figure S3).
7. Characterization of compounds

*N-(2-cyano-[1,1′-biphenyl]-3-yl)-N-methylmethacrylamide.* Purified by column chromatography (petroleum ether : ethyl acetate = 4 : 1). Yellow solid, mp 118–119 °C. H NMR (600 MHz, CDCl₃) δ 7.64 (t, J = 7.9 Hz, 1H), 7.55 (d, J = 7.9 Hz, 2H), 7.52–7.42 (m, 4H), 7.27 (d, J = 7.6 Hz, 1H), 5.15 (s, 1H), 5.09 (s, 1H), 3.43 (s, 3H), 1.93 (s, 3H). 13C NMR (151 MHz, CDCl₃) δ 171.5, 148.3, 147.2, 139.9, 137.2, 133.3, 128.9, 128.7, 128.57, 128.55, 127.0, 119.3, 115.7, 110.8, 37.5, 19.9. IR (film) ν 2225, 1660, 1628, 1565, 1460, 1358, 1231, 1093, 925, 770, 707 cm⁻¹. HRMS (ESI): calc. for C₁₈H₁₆N₂O (M+H)⁺, 277.1335; found, 277.1341.
**N-benzyl-N-(2-cyano-[1,1'-biphenyl]-3-yl)methacrylamide.** Purified by column chromatography (petroleum ether : ethyl acetate = 4 : 1). White solid, mp 82–83 °C. $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 7.55–7.40 (m, 6H), 7.37 (dd, $J = 7.8$, 1.0 Hz, 1H), 7.30–7.14 (m, 5H), 6.94 (d, $J = 7.6$ Hz, 1H), 5.49 (s, 1H), 5.14 (s, 1H), 5.08 (s, 1H), 4.69 (s, 1H), 1.95 (s, 3H). $^{13}$C NMR (151 MHz, CDCl$_3$) $\delta$ 171.2, 147.2, 146.3, 140.1, 137.3, 136.2, 132.8, 129.0, 128.9, 128.68, 128.65, 128.3, 127.8, 119.8, 116.0, 111.6, 52.7, 20.2. IR (film) $\nu$ 3062, 2221, 1653, 1629, 1471, 1434, 1388, 1337, 1223, 764, 698 cm$^{-1}$. HRMS (ESI): calc. for C$_{24}$H$_{20}$N$_2$O (M+H)$^+$, 353.1648; found, 353.1654.

![N-benzyl-N-(2-cyano-[1,1'-biphenyl]-3-yl)methacrylamide](image)

**N-acetyl-N-(2-cyano-[1,1'-biphenyl]-3-yl)methacrylamide.** Purified by column chromatography (petroleum ether : ethyl acetate = 3 : 1). Yellow oil. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.67 (t, $J = 7.9$ Hz, 1H), 7.58–7.43 (m, 6H), 7.21 (dd, $J = 7.9$, 1.0 Hz, 1H), 5.64 (s, 1H), 5.41 (d, $J = 1.5$ Hz, 1H), 2.45 (s, 3H), 1.97 (s, 3H). $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 172.84, 172.82, 147.4, 142.8, 140.6, 137.2, 133.2, 129.9, 129.1, 128.8, 128.7, 128.1, 122.3, 115.6, 112.2, 25.7, 19.1. IR (film) $\nu$ 2923, 2223, 1714, 1637, 1536, 1468, 1272, 1003, 755, 698 cm$^{-1}$. HRMS (ESI): calc. for C$_{19}$H$_{16}$N$_2$O$_2$ (M+H)$^+$, 305.1285; found, 305.1290.

![N-acetyl-N-(2-cyano-[1,1'-biphenyl]-3-yl)methacrylamide](image)

**N-(2-cyano-[1,1'-biphenyl]-3-yl)methacrylamide.** Purified by column chromatography (petroleum ether : ethyl acetate = 6 : 1). White solid, mp 96–97 °C. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 8.52 (dd, $J = 8.5$, 0.7 Hz, 1H), 8.27 (s, 1H), 7.63 (t, $J = 8.1$ Hz, 1H), 7.58–7.40 (m, 5H), 7.23 (dd, $J = 7.7$, 0.9 Hz, 1H), 5.98 (d, $J = 0.5$ Hz, 1H), 5.59 (dd, $J = 2.9$, 1.4 Hz, 1H), 2.12 (s, 3H). $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 166.3, 145.8, 141.4, 139.9, 138.0, 133.7, 128.9, 128.8, 128.6, 124.9, 121.7, 119.2, 116.2, 101.1, 18.5. IR (film) $\nu$ 3058, 2926, 2208, 1694, 1522, 1465, 1293, 1162, 805, 760, 700 cm$^{-1}$. HRMS (ESI): calc. for C$_{17}$H$_{14}$N$_2$O (M+H)$^+$, 263.1179; found, 263.1163.

![N-(2-cyano-[1,1'-biphenyl]-3-yl)methacrylamide](image)

**N-(2-cyano-4'-methyl-[1,1'-biphenyl]-3-yl)-N-methylmethacrylamide.** Purified by column chromatography (petroleum ether : ethyl acetate = 4 : 1). White solid, mp 116–118 °C. $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 7.62 (t, $J = 7.9$ Hz, 1H), 7.50–7.39 (m, 3H), 7.30 (d, $J = 8.1$ Hz, 2H), 7.23 (d, $J = 7.5$ Hz, 1H), 5.14 (s, 1H), 5.09 (s, 1H), 3.43 (s, 3H).
$\delta_{13C} NMR (151 \text{ MHz, CDCl}_3) \delta 171.7, 148.4, 147.4, 139.9, 139.0, 134.4, 133.3, 129.4, 128.7, 128.5, 126.8, 119.6, 115.9, 110.7, 37.4, 21.1, 20.0$. IR (film) $\nu 2976, 2220, 1655, 1627, 1464, 1362, 1230, 1090, 1046, 946, 810 \text{ cm}^{-1}$. HRMS (ESI): calc. for C$_{19}$H$_{18}$N$_2$O (M+H)$^+$, 291.1492; found, 291.1498.

**N-(2-cyano-4'-methoxy-[1,1'-biphenyl]-3-yl)-N-methylmethacrylamide.** Purified by column chromatography (petroleum ether : ethyl acetate = 3 : 1). Yellow solid, mp 102–104 °C. $^1H$ NMR (600 MHz, CDCl$_3$) $\delta$ 7.61 (t, $J = 7.9$ Hz, 1H), 7.55–7.46 (m, 2H), 7.43 (dd, $J = 7.9$, 1.0 Hz, 1H), 7.21 (d, $J = 7.5$ Hz, 1H), 7.06–6.96 (m, 2H), 5.14 (s, 1H), 5.09 (s, 1H), 3.86 (s, 3H), 3.43 (s, 3H), 1.92 (s, 3H). $^{13C} NMR (151 \text{ MHz, CDCl}_3) \delta 171.7, 160.2, 148.5, 147.0, 140.0, 133.3, 130.0, 129.6, 128.6, 126.5, 119.6, 116.1, 114.1, 110.6, 55.3, 37.4, 20.1$. IR (film) $\nu 2919, 2222, 1668, 1612, 1518, 1464, 1258, 1191, 927, 836, 752 \text{ cm}^{-1}$. HRMS (ESI): calc. for C$_{19}$H$_{18}$N$_2$O$_2$ (M+H)$^+$, 307.1441; found, 307.1446.

**N-(2-cyano-4'-phenoxy-[1,1'-biphenyl]-3-yl)-N-methylmethacrylamide.** Purified by column chromatography (petroleum ether : ethyl acetate = 4 : 1). White solid, mp 99–100 °C. $^1H$ NMR (600 MHz, CDCl$_3$) $\delta$ 7.63 (t, $J = 7.9$ Hz, 1H), 7.55–7.48 (m, 2H), 7.44 (dd, $J = 7.9$, 1.0 Hz, 1H), 7.41–7.34 (m, 2H), 7.24 (d, $J = 7.7$ Hz, 1H), 7.19–7.13 (m, 1H), 7.12–7.02 (m, 4H), 5.15 (s, 1H), 5.09 (s, 1H), 3.43 (s, 3H), 1.93 (s, 3H). $^{13C} NMR (151 \text{ MHz, CDCl}_3) \delta 171.6, 158.4, 156.0, 148.4, 146.6, 139.9, 133.4, 131.7, 130.2, 129.8, 128.7, 126.8, 123.9, 119.7, 119.5, 118.2, 115.9, 110.6, 37.5, 20.0$. IR (film) $\nu 3068, 2224, 1653, 1589, 1472, 1361, 1249, 1153, 781, 753 \text{ cm}^{-1}$. HRMS (ESI): calc. for C$_{24}$H$_{20}$N$_2$O$_2$ (M+H)$^+$, 369.1598; found, 369.1614.

**N-(2-cyano-4'-(trifluoromethyl)-[1,1'-biphenyl]-3-yl)-N-methylmethacrylamide.** Purified by column chromatography (petroleum ether : ethyl acetate = 4 : 1). Yellow solid, mp 110–111 °C. $^1H$ NMR (600 MHz, CDCl$_3$) $\delta$ 7.77 (d, $J = 8.3$ Hz, 2H), 7.72 (t, $J = 7.9$ Hz, 1H), 7.69 (d, $J = 8.1$ Hz, 2H), 7.48 (dd, $J = 7.8$, 1.0 Hz, 1H), 7.36 (d,
$J = 7.9$ Hz, 1H), 5.19 (s, 1H), 5.10 (s, 1H), 3.45 (s, 3H), 1.95 (s, 3H). $^{13}$C NMR (151 MHz, CDCl$_3$) δ 171.6, 148.5, 145.6, 140.8, 139.8, 133.7, 130.9 (q, $J_{C-F} = 32.7$ Hz), 129.1, 128.7, 127.8, 125.6 (q, $J_{C-F} = 3.6$ Hz), 123.8 (q, $J_{C-F} = 273.3$ Hz), 115.4, 110.9, 37.6, 19.9. IR (film) $\nu$ 3063, 2223, 1655, 1624, 1324, 1178, 1121, 1065, 917, 849, 821 cm$^{-1}$. HRMS (ESI): calc. for C$_{19}$H$_{15}$F$_3$N$_2$O (M+H)$^+$, 345.1209; found, 345.1182.

$N$-(2,4'-dicyano-[1,1'-biphenyl]-3-yl)-N-methylmethacrylamide. Purified by column chromatography (petroleum ether : ethyl acetate = 2 : 1). Yellow solid, mp 166–167 °C. $^1$H NMR (500 MHz, CDCl$_3$) δ 7.72 (d, $J = 8.3$ Hz, 2H), 7.66 (t, $J = 7.9$ Hz, 1H), 7.60 (d, $J = 8.3$ Hz, 2H), 7.39 (d, $J = 7.7$ Hz, 1H), 7.31 (d, $J = 7.9$ Hz, 1H), 5.11 (s, 1H), 5.01 (s, 1H), 3.35 (s, 3H), 1.85 (s, 3H). $^{13}$C NMR (126 MHz, CDCl$_3$) δ 171.4, 148.5, 144.9, 141.6, 139.7, 133.8, 132.3, 129.4, 128.5, 128.1, 119.5, 118.0, 115.2, 112.7, 110.7, 37.7, 19.8. IR (film) $\nu$ 2976, 2225, 1655, 1626, 1586, 1468, 1377, 1362, 1090, 944, 818 cm$^{-1}$. HRMS (ESI): calc. for C$_{19}$H$_{15}$N$_3$O (M+H)$^+$, 302.1288; found, 302.1294.

$N$-(2-cyano-4'-fluoro-[1,1'-biphenyl]-3-yl)-N-methylmethacrylamide. Purified by column chromatography (petroleum ether : ethyl acetate = 5 : 1). White solid, mp 130–131 °C. $^1$H NMR (600 MHz, CDCl$_3$) δ 7.66 (t, $J = 7.9$ Hz, 1H), 7.57–7.50 (m, 2H), 7.44 (dd, $J = 7.9$, 1.1 Hz, 1H), 7.33–7.26 (m, 1H), 7.21–7.13 (m, 2H), 5.17 (s, 1H), 5.09 (s, 1H), 3.43 (s, 3H), 1.93 (s, 3H). $^{13}$C NMR (151 MHz, CDCl$_3$) δ 171.6, 148.5, 144.9, 141.6, 139.7, 133.8, 132.3, 129.4, 128.5, 128.1, 119.5, 118.0, 115.2, 112.7, 110.7, 37.7, 19.8. IR (film) $\nu$ 2976, 2225, 1655, 1626, 1569, 1511, 1467, 1378, 1223, 1091, 922, 849 cm$^{-1}$. HRMS (ESI): calc. for C$_{18}$H$_{15}$FN$_2$O (M+H)$^+$, 295.1241; found, 295.1244.

$N$-(4'-chloro-2-cyano-[1,1'-biphenyl]-3-yl)-N-methylmethacrylamide. Purified by column chromatography (petroleum ether : ethyl acetate = 4 : 1). Yellow solid, mp 118–119 °C. $^1$H NMR (600 MHz, CDCl$_3$) δ 7.68 (t, $J = 7.9$ Hz, 1H), 7.55–7.39 (m, 5H), 7.31 (d, $J = 5.8$ Hz, 2H), 5.17 (s, 1H), 5.09 (s, 1H), 3.43 (s, 3H), 1.93 (s, 3H). $^{13}$C
NMR (151 MHz, CDCl$_3$) $\delta$ 171.4, 148.4, 145.7, 139.7, 135.6, 135.1, 133.5, 129.9, 128.8, 128.5, 127.3, 119.6, 115.6, 110.6, 37.4, 19.9. IR (film) $\nu$ 2976, 2925, 2229, 1653, 1460, 1363, 1084, 1049, 917, 816 cm$^{-1}$. HRMS (ESI): calc. for C$_{18}$H$_{15}$ClN$_2$O (M+H)$^+$, 311.0946; found, 311.0955.

N-(4'-bromo-2-cyano-[1,1'-biphenyl]-3-yl)-N-methylmethacrylamide. Purified by column chromatography (petroleum ether : ethyl acetate = 4 : 1). White solid, mp 90–91 °C. $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 7.65 (dd, $J$ = 14.0, 8.1 Hz, 3H), 7.42 (d, $J$ = 8.4 Hz, 3H), 7.31–7.25 (m, 1H), 5.17 (s, 1H), 5.09 (s, 1H), 3.43 (s, 3H), 1.93 (s, 3H). $^{13}$C NMR (151 MHz, CDCl$_3$) $\delta$ 171.7, 148.7, 146.1, 139.9, 136.2, 133.6, 132.0, 130.3, 128.6, 127.4, 123.7, 119.7, 115.6, 110.9, 37.7, 20.1. IR (film) $\nu$ 2925, 2228, 1655, 1570, 1456, 1361, 1236, 1099, 914, 813 cm$^{-1}$. HRMS (ESI): calc. for C$_{19}$H$_{17}$BrN$_2$O (M+H)$^+$, 355.0441; found, 355.0438.

N-(2-cyano-3'-methyl-[1,1'-biphenyl]-3-yl)-N-methylmethacrylamide. Purified by column chromatography (petroleum ether : ethyl acetate = 4 : 1). Yellow solid, mp 71–72 °C. $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 7.62 (t, $J$ = 7.9 Hz, 1H), 7.44 (d, $J$ = 7.8 Hz, 1H), 7.41–7.36 (m, 1H), 7.34 (d, $J$ = 3.8 Hz, 2H), 7.28 (d, $J$ = 7.4 Hz, 1H), 7.24 (d, $J$ = 7.2 Hz, 1H), 5.15 (s, 1H), 5.11 (d, $J$ = 12.0 Hz, 1H), 3.43 (s, 3H), 2.44 (s, 3H), 1.92 (s, 3H). $^{13}$C NMR (151 MHz, CDCl$_3$) $\delta$ 171.7, 148.5, 147.6, 140.0, 138.5, 137.3, 133.3, 129.8, 129.4, 128.8, 128.6, 127.8, 127.0, 125.8, 119.7, 115.8, 110.9, 37.6, 21.4, 20.1. IR (film) $\nu$ 2925, 2223, 1657, 1570, 1456, 1362, 1236, 1099, 922, 791, 704 cm$^{-1}$. HRMS (ESI): calc. for C$_{19}$H$_{18}$N$_2$O (M+H)$^+$, 291.1492; found, 291.1497.

N-(2-cyano-3'-fluoro-[1,1'-biphenyl]-3-yl)-N-methylmethacrylamide. Purified by column chromatography (petroleum ether : ethyl acetate = 3 : 1). Yellow solid, mp 74–75 °C. $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 7.67 (t, $J$ = 7.9 Hz, 1H), 7.50–7.41 (m, 2H), 7.34 (dd, $J$ = 7.7, 0.5 Hz, 1H), 7.31 (d, $J$ = 7.7 Hz, 1H), 7.27–7.22 (m, 1H), 7.19–7.12 (m, 1H), 5.17 (s, 1H), 5.09 (s, 1H), 3.44 (s, 3H), 1.93 (s, 3H). $^{13}$C NMR (151 MHz, CDCl$_3$) $\delta$ 171.6, 162.6 (d, $J_{CF}$ = 247.5 Hz), 148.5, 145.8 (d, $J_{CF}$ = 1.2 Hz), 139.9, 139.3 (d, $J_{CF}$ = 7.8 Hz), 133.6, 130.4 (d, $J_{CF}$ = 8.4 Hz), 128.7,
127.6, 124.5 (d, $J_{CF} = 2.9$ Hz), 119.8, 116.0 (d, $J_{CF} = 21.0$ Hz), 115.8 (d, $J_{CF} = 22.7$ Hz), 115.5, 110.9, 37.6, 20.0.

IR (film) $\nu$ 2974, 2926, 2225, 1657, 1571, 1466, 1364, 1092, 785, 698 cm$^{-1}$. HRMS (ESI): calc. for C$_{18}$H$_{15}$FN$_{2}$O (M+H)$^+$, 295.1241; found, 295.1249.

$N$-(2-cyano-2'-fluoro-[1,1'-biphenyl]-3-yl)-N-methylmethacrylamide. Purified by column chromatography (petroleum ether : ethyl acetate = 4 : 1). Yellow solid, mp 81–83 °C. $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 7.67 (t, $J = 7.9$ Hz, 1H), 7.47–7.40 (m, 3H), 7.33–7.27 (m, 2H), 7.21 (t, $J = 9.2$ Hz, 1H), 5.16 (s, 1H), 5.07 (s, 1H), 3.43 (s, 3H), 1.92 (s, 3H). $^{13}$C NMR (151 MHz, CDCl$_3$) $\delta$ 171.5, 159.1 (d, $J_{CF} = 248.8$ Hz), 147.9, 141.1, 139.7, 133.2, 131.0 (d, $J_{CF} = 8.2$ Hz), 130.9 (d, $J_{CF} = 2.0$ Hz), 129.6 (d, $J_{CF} = 0.7$ Hz), 127.6, 125.0 (d, $J_{CF} = 14.7$ Hz), 124.3 (d, $J_{CF} = 3.7$ Hz), 119.7, 116.0 (d, $J = 21.8$ Hz), 115.2, 112.4, 37.4, 19.9. IR (film) $\nu$ 3065, 2229, 1654, 1629, 1569, 1467, 1368, 1219, 1081, 823, 756 cm$^{-1}$. HRMS (ESI): calc. for C$_{18}$H$_{15}$FN$_{2}$O (M+Na)$^+$, 317.1061; found, 317.1061.

$N$-(2-cyano-2'-methoxy-[1,1'-biphenyl]-3-yl)-N-methylmethacrylamide. Purified by column chromatography (petroleum ether : ethyl acetate = 2 : 1). White solid, mp 119–121 °C. $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 7.61 (t, $J = 7.9$ Hz, 1H), 7.47–7.40 (m, 1H), 7.38 (dd, $J = 7.8, 0.8$ Hz, 1H), 7.25 (dd, $J = 7.5, 1.6$ Hz, 1H), 7.21 (d, $J = 7.8$ Hz, 1H), 7.10–7.04 (m, 1H), 7.03 (d, $J = 8.3$ Hz, 1H), 5.12 (d, $J = 36.5$ Hz, 2H), 3.83 (s, 3H), 3.42 (s, 3H), 1.91 (s, 3H). $^{13}$C NMR (151 MHz, CDCl$_3$) $\delta$ 171.7, 156.2, 147.6, 144.4, 140.0, 133.0, 130.7, 130.6, 129.6, 126.8, 126.5, 120.8, 119.8, 115.8, 113.2, 111.3, 55.4, 37.4, 20.1. IR (film) $\nu$ 3432, 3060, 2932, 2228, 1657, 1627, 1499, 1367, 1244, 827, 755 cm$^{-1}$. HRMS (ESI): calc. for C$_{19}$H$_{18}$N$_2$O$_2$ (M+H)$^+$, 307.1441; found, 307.1443.

$N$-(2-cyano-3',5'-dimethyl-[1,1'-biphenyl]-3-yl)-N-methylmethacrylamide. Purified by column chromatography (petroleum ether : ethyl acetate = 4 : 1). Yellow solid, mp 132–133 °C. $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 7.61 (t, $J = 7.9$ Hz, 1H), 7.43 (dd, $J = 7.8, 1.0$ Hz, 1H), 7.22 (d, $J = 7.2$ Hz, 1H), 7.14 (s, 2H), 7.10 (s, 1H), 5.14 (s, 1H), 5.10 (s, 1H), 3.43 (s, 3H), 2.39 (s, 6H), 1.92 (s, 3H). $^{13}$C NMR (151 MHz, CDCl$_3$) $\delta$ 171.7, 148.4, 147.7, 140.0, 138.3, 137.3, 133.2, 130.6, 128.8, 126.8, 126.4, 119.7, 115.8, 110.8, 37.4, 21.2, 20.1. IR (film) $\nu$ 2925, 2225, 1649, 1622,
N-(3',5'-dichloro-2-cyano-[1,1'-biphenyl]-3-yl)-N-methylmethacrylamide. Purified by column chromatography (petroleum ether : ethyl acetate = 3 : 1). White solid, mp 110–111 °C. 1H NMR (600 MHz, CDCl$_3$) δ 7.70 (t, $J$ = 7.9 Hz, 1H), 7.45 (t, $J$ = 1.8 Hz, 1H), 7.44–7.40 (m, 3H), 7.35 (d, $J$ = 7.9 Hz, 1H), 5.19 (s, 1H), 5.09 (s, 1H), 3.44 (s, 3H), 1.94 (s, 3H). 13C NMR (151 MHz, CDCl$_3$) δ 171.5, 148.5, 144.1, 140.0, 139.7, 135.2, 133.7, 128.9, 128.5, 128.1, 127.1, 119.7, 115.0, 110.8, 37.7, 19.9. IR (film) ν 3059, 2972, 2225, 1662, 1560, 1415, 1353, 1098, 875, 796, 749 cm$^{-1}$. HRMS (ESI): calc. for C$_{20}$H$_{20}$N$_2$O (M+H)$^+$, 305.1648; found, 305.1651.

N-(2-cyano-3',4',5'-trifluoro-[1,1'-biphenyl]-3-yl)-N-methylmethacrylamide. Purified by column chromatography (petroleum ether : ethyl acetate = 3 : 1). Yellow solid, mp 96–98 °C. 1H NMR (600 MHz, CDCl$_3$) δ 7.69 (t, $J$ = 7.9 Hz, 1H), 7.40 (d, $J$ = 7.4 Hz, 1H), 7.34 (d, $J$ = 7.9 Hz, 1H), 7.24–7.13 (m, 2H), 5.20 (s, 1H), 5.09 (s, 1H), 3.43 (s, 3H), 1.94 (s, 3H). 13C NMR (151 MHz, CDCl$_3$) δ 171.7, 151.2 (ddd, $J$ = 252.1, 10.1, 4.1 Hz), 148.8, 144.0, 140.4 (dt, $J$ = 255.4, 15.1 Hz), 139.9, 133.8, 133.2 (dd, $J$ = 12.9, 8.2 Hz), 128.6, 128.2, 119.8, 115.1, 113.4 (dd, $J$ = 17.3, 5.0 Hz), 111.0, 37.9, 20.1. IR (film) ν 3076, 2226, 1650, 1573, 1473, 1416, 1362, 1089, 1044, 867, 822 cm$^{-1}$. HRMS (ESI): calc. for C$_{18}$H$_{14}$Cl$_2$N$_2$O (M+H)$^+$, 345.0556; found, 345.0539.

N-(2-cyano-3-(naphthalen-1-yl)phenyl)-N-methylmethacrylamide. Purified by column chromatography (petroleum ether : ethyl acetate = 3 : 1). Yellow solid, mp 96–97 °C. 1H NMR (600 MHz, CDCl$_3$) δ 7.94 (dd, $J$ = 13.3, 8.3 Hz, 2H), 7.68 (t, $J$ = 7.9 Hz, 1H), 7.60–7.40 (m, 6H), 7.35 (d, $J$ = 7.7 Hz, 1H), 5.23 (s, 1H), 5.11 (s, 1H), 3.46 (s, 3H), 1.96 (s, 3H). 13C NMR (151 MHz, CDCl$_3$) δ 171.6, 148.0, 146.2, 140.2, 135.0, 133.6, 133.0, 131.1, 130.2, 129.5, 128.6, 127.3, 126.7, 126.2, 125.1, 124.7, 119.7, 115.2, 113.3, 37.6, 20.1. IR (film) ν 2911, 2852, 2225, 2075, 1635, 1510, 1453, 1393, 1120, 732, 776 cm$^{-1}$. HRMS (ESI): calc. for C$_{22}$H$_{18}$N$_2$O (M+H)$^+$, 327.1492; found,
**N-(2-cyano-3-(phenanthren-9-yl)phenyl)-N-methylethacrylamide.** Purified by column chromatography (petroleum ether : ethyl acetate = 3 : 1). Yellow solid, mp 88–90 °C. $^1$H NMR (600 MHz, CDCl$_3$) δ 8.74 (d, $J$ = 8.5 Hz, 1H), 8.68 (d, $J$ = 8.3 Hz, 1H), 7.89 (d, $J$ = 7.7 Hz, 1H), 7.71 (s, 1H), 7.69–7.57 (m, 4H), 7.56–7.37 (m, 3H), 7.33 (d, $J$ = 7.8 Hz, 1H), 5.24 (s, 1H), 5.12 (s, 1H), 3.45 (s, 3H), 1.96 (s, 3H). $^{13}$C NMR (151 MHz, CDCl$_3$) δ 171.6, 147.9, 146.1, 140.1, 133.7, 133.2, 130.7, 130.5, 130.4, 130.11, 130.05, 128.9, 128.4, 127.4, 127.3, 127.0, 126.9, 126.8, 125.6, 123.1, 122.5, 119.5, 115.1, 113.3, 37.5, 20.1. IR (film) $\nu$ 3061, 2924, 2226, 1655, 1624, 1569, 1451, 1364, 743, 721 cm$^{-1}$. HRMS (ESI): calc. for C$_{26}$H$_{20}$N$_2$O (M+H)$^+$, 377.1648; found, 377.1656.

**N-(2-cyano-3-(thiophen-2-yl)phenyl)-N-methylethacrylamide.** Purified by column chromatography (petroleum ether : ethyl acetate = 3 : 1). Yellow solid, mp 63–64 °C. $^1$H NMR (600 MHz, CDCl$_3$) δ 7.67 (dd, $J$ = 3.6, 0.8 Hz, 1H), 7.62–7.53 (m, 2H), 7.47 (dd, $J$ = 5.1, 0.7 Hz, 1H), 7.24–7.13 (m, 2H), 5.15 (s, 1H), 5.10 (s, 2H), 3.42 (s, 3H), 1.92 (s, 3H). $^{13}$C NMR (151 MHz, CDCl$_3$) δ 171.7, 149.1, 139.9, 139.4, 138.5, 133.5, 128.5, 128.3, 128.2, 127.9, 127.1, 119.9, 116.0, 109.6, 37.5, 20.1. IR (film) $\nu$ 3076, 2923, 2225, 1659, 1629, 1093, 807, 707 cm$^{-1}$. HRMS (ESI): calc. for C$_{16}$H$_{14}$N$_2$O (M+H)$^+$, 283.0900; found, 283.0904.

**N-(2-cyano-3-(pyridin-4-yl)phenyl)-N-methylethacrylamide.** Purified by column chromatography (petroleum ether : ethyl acetate = 1 : 1). White solid, mp 103–105 °C. $^1$H NMR (600 MHz, CDCl$_3$) δ 8.77 (d, $J$ = 5.2 Hz, 2H), 7.73 (t, $J$ = 7.9 Hz, 1H), 7.48 (t, $J$ = 7.0 Hz, 3H), 7.38 (d, $J$ = 7.8 Hz, 1H), 5.20 (s, 1H), 5.10 (s, 1H), 3.45 (s, 3H), 1.95 (s, 3H). $^{13}$C NMR (151 MHz, CDCl$_3$) δ 171.6, 150.3, 148.9, 144.8, 144.2, 139.8, 133.9, 128.5, 128.4, 123.2, 119.9, 115.1, 110.8, 37.8, 20.0. IR (film) $\nu$ 3093, 2224, 1650, 1623, 1470, 1416, 1365, 1234, 1096, 931, 815 cm$^{-1}$. HRMS (ESI): calc. for C$_{18}$H$_{13}$F$_3$N$_2$O (M+H)$^+$, 278.1288; found, 278.1291.
**N-(2-cyano-[1,1′-biphenyl]-3-yl)-N-methyl-2-phenylacrylamide.** Purified by column chromatography (petroleum ether : ethyl acetate = 3 : 1). Yellow solid, mp 78–79 °C. 

1H NMR (600 MHz, CDCl₃) δ 7.42 (t, \( J = 7.4 \) Hz, 3H), 7.36 (t, \( J = 7.9 \) Hz, 1H), 7.30 (d, \( J = 6.6 \) Hz, 2H), 7.23 (d, \( J = 7.8 \) Hz, 1H), 7.18 (d, \( J = 3.5 \) Hz, 3H), 7.07 (d, \( J = 3.6 \) Hz, 2H), 6.98 (d, \( J = 7.9 \) Hz, 1H), 5.77 (s, 1H), 5.49 (s, 1H), 3.45 (s, 3H).

13C NMR (151 MHz, CDCl₃) δ 170.1, 146.81, 146.79, 146.0, 137.1, 136.3, 132.6, 128.7, 128.6, 128.45, 128.41, 128.3, 128.1, 127.9, 126.1, 119.9, 115.6, 111.0, 36.7. IR (film) \( \nu \) 3048, 2223, 1654, 1465, 1364, 1256, 1181, 1081, 927, 762, 701 cm\(^{-1}\).

HRMS (ESI): calc. for C\(_{23}\)H\(_{18}\)N\(_2\)O (M+H\(^+\)), 339.1492; found, 339.1500.

**2-benzyl-N-(2-cyano-[1,1′-biphenyl]-3-yl)-N-methylacrylamide.** Purified by column chromatography (petroleum ether : ethyl acetate = 4 : 1). White solid, mp 86–88 °C. 

1H NMR (600 MHz, CDCl₃) δ 7.54–7.44 (m, 5H), 7.38 (d, \( J = 6.3 \) Hz, 2H), 7.31 (t, \( J = 7.4 \) Hz, 2H), 7.25 (m, 1H), 7.15 (s, 2H), 6.39 (s, 1H), 5.09 (s, 1H), 5.03 (s, 1H), 3.76 (s, 1H), 3.49 (s, 1H), 3.35 (s, 3H).

13C NMR (151 MHz, CDCl₃) δ 170.99, 148.32, 147.24, 143.69, 137.55, 137.31, 133.29, 129.46, 129.00, 128.71, 128.48, 128.28, 126.70, 119.55, 115.90, 110.76, 40.08, 37.43. IR (film) \( \nu \) 3028, 2219, 1655, 1465, 1364, 1256, 1181, 1081, 927, 762, 701 cm\(^{-1}\).

HRMS (ESI): calc. for C\(_{24}\)H\(_{20}\)N\(_2\)O (M+H\(^+\)), 353.1648; found, 353.1653.

**3-(4,6-dimethyl-5-oxo-5,6-dihydro-4H-pyrido[4,3,2-gh]phenanthridin-6-yl)propanenitrile.** Purified by column chromatography (petroleum ether : ethyl acetate = 4 : 1). Yellow solid, mp 130–131 °C. 

1H NMR (500 MHz, CDCl₃) δ 8.54 (d, \( J = 8.2 \) Hz, 1H), 8.30 (d, \( J = 8.3 \) Hz, 1H), 8.15 (d, \( J = 8.2 \) Hz, 1H), 7.85 (t, \( J = 8.1 \) Hz, 1H), 7.78 (t, \( J = 7.6 \) Hz, 1H), 7.68 (t, \( J = 7.6 \) Hz, 1H), 7.24 (d, \( J = 8.0 \) Hz, 1H), 3.60 (s, 3H), 3.00–2.94 (m, 1H), 2.80–2.74 (m, 1H), 2.30 – 2.22 (m, 2H), 1.69 (s, 3H).

13C NMR (126 MHz, CDCl₃) δ 172.5, 157.3, 144.7, 138.3, 133.4, 132.1, 129.8, 129.3, 127.0, 122.7, 122.6, 119.3, 116.5, 112.0, 111.0, 50.7, 34.1, 30.4, 29.9, 13.6. IR (film) \( \nu \) 2981, 2244, 1671,1609, 1591, 1466, 1342, 1074, 761, 646, 496 cm\(^{-1}\). HRMS (ESI): calc. for C\(_{20}\)H\(_{17}\)N\(_3\)O (M+H\(^+\)), 316.1444; found, 316.1445.
3-(4-benzyl-6-methyl-5-oxo-5,6-dihydro-4H-pyrido[4,3,2-gh]phenanthridin-6-yl)propanenitrile. Purified by column chromatography (petroleum ether : ethyl acetate = 5 : 1). Yellow solid, mp 135–137 °C. 1H NMR (600 MHz, CDCl₃) δ 8.55–8.45 (m, 1H), 8.26 (d, J = 8.2 Hz, 1H), 8.17 (dd, J = 8.2, 0.8 Hz, 1H), 7.82–7.74 (m, 1H), 7.73–7.60 (m, 2H), 7.37–7.31 (m, 2H), 7.28 (dd, J = 13.5, 7.2 Hz, 3H), 7.15 (d, J = 7.9 Hz, 1H), 5.66 (d, J = 15.6 Hz, 1H), 5.20 (d, J = 15.5 Hz, 1H), 3.13–3.02 (m, 1H), 2.89–2.78 (m, 1H), 2.42–2.29 (m, 2H), 1.76 (s, 3H). 13C NMR (151 MHz, CDCl₃) δ 172.9, 157.2, 144.8, 137.5, 136.1, 133.7, 132.0, 129.9, 129.4, 129.0, 127.5, 127.1, 126.3, 122.9, 122.6, 119.4, 116.6, 112.21, 112.15, 51.0, 46.4, 33.7, 30.7, 13.7. IR (film) υ 2956, 2919, 2850, 2050, 1667, 1638, 1618, 1572, 1448, 1375, 1361, 1337, 1320, 1299, 1294, 1290, 1275, 1271, 1263, 1229, 1226, 1194, 1166, 11221, 11215, 51.0, 46.4, 33.7, 30.7, 13.7. HRMS (ESI): calc. for C₂₆H₂₁N₃O (M+H)+, 392.1757; found, 392.1765.

3-(4,6,9-trimethyl-5-oxo-5,6-dihydro-4H-pyrido[4,3,2-gh]phenanthridin-6-yl)propanenitrile. Purified by column chromatography (petroleum ether : ethyl acetate = 4 : 1). Yellow solid, mp 126–127 °C. 1H NMR (500 MHz, CDCl₃) δ 8.41 (dd, J = 8.4, 2.2 Hz, 1H), 8.25 (dd, J = 8.3, 2.0 Hz, 1H), 7.95 (s, 1H), 7.50 (d, J = 8.3 Hz, 1H), 7.20 (d, J = 7.9 Hz, 1H), 3.59 (d, J = 1.7 Hz, 3H), 3.01–2.89 (m, 1H), 2.81–2.70 (m, 1H), 2.61 (s, 3H), 2.32–2.18 (m, 2H), 1.68 (s, 3H). 13C NMR (126 MHz, CDCl₃) δ 172.6, 157.3, 144.9, 139.7, 138.3, 133.5, 131.9, 129.3, 128.8, 122.3, 120.4, 119.3, 116.3, 111.7, 110.5, 50.7, 34.3, 30.2, 29.9, 21.5, 13.6. IR (film) υ 2926, 2245, 1670, 1580, 1569, 1469, 1406, 1341, 1075, 802, 768 cm⁻¹. HRMS (ESI): calc. for C₂₁H₁₉N₃O (M+H)+, 330.1601; found, 330.1607.

3-(9-methoxy-4,6-dimethyl-5-oxo-5,6-dihydro-4H-pyrido[4,3,2-gh]phenanthridin-6-yl)propanenitrile. Purified by column chromatography (petroleum ether : ethyl acetate = 5 : 1). Yellow solid, mp 128–129 °C. 1H NMR (600 MHz, CDCl₃) δ 8.41 (d, J = 9.0 Hz, 1H), 8.18 (d, J = 8.4 Hz, 1H), 7.80 (t, J = 8.1 Hz, 1H), 7.53 (d, J = 2.5 Hz, 1H), 7.31 (dd, J = 9.0, 2.6 Hz, 1H), 7.15 (d, J = 7.8 Hz, 1H), 4.02 (s, 3H), 3.59 (s, 3H), 3.01–2.91 (m, 1H), 2.81–2.72 (m, 1H), 2.32–2.19 (m, 2H), 1.69 (s, 3H). 13C NMR (126 MHz, CDCl₃) δ 172.5, 160.6, 157.8, 146.5, 138.3, 133.6, 132.0, 123.7, 119.3, 118.4, 116.8, 116.0, 111.1, 109.8, 109.2, 55.6, 50.7, 34.3, 30.3, 29.8, 13.6. IR
3-(4,6-dimethyl-5-oxo-9-phenoxy-5,6-dihydro-4H-pyrido[4,3,2-gh]phenanthridin-6-yl)propanenitrile.

Purified by column chromatography (petroleum ether : ethyl acetate = 5 : 1). Yellow solid, mp 69–71 °C. $^1H$ NMR (600 MHz, CDCl$_3$) $\delta$ 8.50 (d, $J = 9.0$ Hz, 1H), 8.22 (d, $J = 8.3$ Hz, 1H), 7.83 (t, $J = 8.1$ Hz, 1H), 7.56 (d, $J = 2.5$ Hz, 1H), 7.50–7.40 (m, 3H), 7.24 (t, $J = 7.5$ Hz, 1H), 7.19 (t, $J = 7.3$ Hz, 3H), 3.59 (s, 3H), 2.93–2.85 (m, 1H), 2.78–2.69 (m, 1H), 2.28–2.16 (m, 2H), 1.66 (s, 3H).

$^{13}C$ NMR (151 MHz, CDCl$_3$) $\delta$ 172.6, 158.9, 158.3, 156.1, 146.3, 138.5, 133.5, 132.3, 130.1, 124.4, 124.2, 120.1, 119.5, 119.2, 118.4, 116.2, 115.7, 111.5, 110.4, 50.7, 34.3, 30.9, 29.9, 13.7. IR (film) $\nu$ 2959, 2920, 2085, 1639, 1530, 1487, 1408, 1255, 873, 747, 692 cm$^{-1}$. HRMS (ESI): calc. for C$_{21}$H$_{20}$N$_3$O$_2$ (M+H)$^+$, 346.1550; found, 346.1558.

3-(4,6-dimethyl-5-oxo-9-(trifluoromethyl)-5,6-dihydro-4H-pyrido[4,3,2-gh]phenanthridin-6-yl)propanenitrile.

Purified by column chromatography (petroleum ether : ethyl acetate = 4 : 1). White solid, mp 177–178 °C. $^1H$ NMR (600 MHz, CDCl$_3$) $\delta$ 8.66 (d, $J = 8.6$ Hz, 1H), 8.46 (s, 1H), 8.33 (d, $J = 8.2$ Hz, 1H), 7.93 (t, $J = 8.1$ Hz, 1H), 7.87 (dd, $J = 8.6$, 1.7 Hz, 1H), 7.34 (d, $J = 7.9$ Hz, 1H), 3.62 (s, 3H), 3.02–2.91 (m, 1H), 2.83–2.74 (m, 1H), 2.34–2.22 (m, 2H), 1.71 (s, 3H). $^{13}C$ NMR (151 MHz, CDCl$_3$) $\delta$ 172.3, 159.4, 144.1, 138.7, 132.8, 132.8, 127.4 (q, $J_{C,F} = 4.1$ Hz), 125.1, 124.0 (q, $J_{C,F} = 272.4$ Hz), 123.8, 122.8 (d, $J_{C,F} = 3.1$ Hz), 119.0, 116.7, 112.6, 112.2, 50.9, 34.2, 30.4, 30.0, 13.7. IR (film) $\nu$ 3090, 2247, 1659, 1591, 1359, 1333, 1314, 1185, 1118, 814, 772 cm$^{-1}$. HRMS (ESI): calc. for C$_{20}$H$_{14}$BrN$_3$O (M+H)$^+$, 384.1318; found, 384.1323.

6-(2-cyanoethyl)-4,6-dimethyl-5-oxo-5,6-dihydro-4H-pyrido[4,3,2-gh]phenanthridine-9-carbonitrile. Purified by column chromatography (petroleum ether : ethyl acetate = 3 : 1). Yellow solid, mp 295–296 °C. $^1H$ NMR (600 MHz, CDCl$_3$) $\delta$ 8.58 (d, $J = 9.0$ Hz, 1H), 8.27 (d, $J = 8.3$ Hz, 1H), 7.81 (t, $J = 8.1$ Hz, 1H), 7.58 (d, $J = 2.5$ Hz, 1H), 7.55–7.45 (m, 3H), 7.25 (t, $J = 7.5$ Hz, 1H), 7.16 (t, $J = 7.3$ Hz, 3H), 3.59 (s, 3H), 2.93–2.85 (m, 1H), 2.78–2.69 (m, 1H), 2.28–2.16 (m, 2H), 1.66 (s, 3H).

$^{13}C$ NMR (151 MHz, CDCl$_3$) $\delta$ 172.3, 159.4, 144.1, 138.7, 132.8, 132.8, 127.4 (q, $J_{C,F} = 4.1$ Hz), 125.1, 124.0 (q, $J_{C,F} = 272.4$ Hz), 123.8, 122.8 (d, $J_{C,F} = 3.1$ Hz), 119.0, 116.7, 112.6, 112.2, 50.9, 34.2, 30.4, 30.0, 13.7. IR (film) $\nu$ 3090, 2247, 1659, 1591, 1359, 1333, 1314, 1185, 1118, 814, 772 cm$^{-1}$. HRMS (ESI): calc. for C$_{20}$H$_{14}$BrN$_3$O (M+H)$^+$, 384.1318; found, 384.1323.
MHz, CDCl$_3$ $\delta$ 8.62 (d, $J = 8.5$ Hz, 1H), 8.50 (d, $J = 1.6$ Hz, 1H), 8.31 (d, $J = 8.2$ Hz, 1H), 7.96 (t, $J = 8.1$ Hz, 1H), 7.85 (dd, $J = 8.5$, 1.7 Hz, 1H), 7.37 (d, $J = 7.9$ Hz, 1H), 3.62 (s, 3H), 2.98–2.91 (m, 1H), 2.81–2.74 (m, 1H), 2.35–2.22 (m, 2H), 1.71 (s, 3H). $^{13}$C NMR (151 MHz, CDCl$_3$) $\delta$ 172.2, 160.1, 144.0, 138.8, 134.9, 133.1, 132.5, 128.4, 126.0, 124.1, 118.8, 118.3, 116.8, 112.8, 112.7, 50.9, 34.2, 30.4, 30.1, 13.7. IR (film) $\nu$ 2927, 2227, 1667, 1589, 1467, 1340, 1161, 1092, 804, 774, 630 cm$^{-1}$. HRMS (ESI): calc. for C$_{21}$H$_{16}$N$_4$O (M+Na)$^+$, 363.1216; found, 363.1218.

3-(9-fluoro-4,6-dimethyl-5-oxo-5,6-dihydro-4H-pyrido[4,3,2-gh]phenanthridin-6-yl)propanenitrile. Purified by column chromatography (petroleum ether : ethyl acetate = 4 : 1). Yellow solid, mp 146–147 °C. $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 8.52 (dd, $J = 9.1$, 5.8 Hz, 1H), 8.23 (d, $J = 8.3$ Hz, 1H), 7.86 (t, $J = 8.1$ Hz, 1H), 7.79 (dd, $J = 9.7$, 2.7 Hz, 1H), 7.46–7.41 (m, 1H), 7.24 (d, $J = 7.9$ Hz, 1H), 3.60 (s, 3H), 2.97–2.90 (m, 1H), 2.80–2.73 (m, 1H), 2.32–2.20 (m, 2H), 1.69 (s, 3H). $^{13}$C NMR (151 MHz, CDCl$_3$) $\delta$ 172.4, 163.1 (d, $J_{C-F} = 249.5$ Hz), 159.0, 146.1 (d, $J_{C-F} = 12.2$ Hz), 138.6, 133.3, 132.5, 124.6 (d, $J_{C-F} = 9.7$ Hz), 119.6, 119.1, 116.4, 116.2 (d, $J_{C-F} = 2.8$ Hz), 114.3 (d, $J_{C-F} = 20.5$ Hz), 111.7, 110.8, 50.8, 34.3, 30.3, 30.0, 13.7. IR (film) $\nu$ 2931, 2246, 1670, 1612, 1590, 1579, 1470, 1339, 1169, 794, 771 cm$^{-1}$. HRMS (ESI): calc. for C$_{20}$H$_{16}$FN$_3$O (M+H)$^+$, 334.1350; found, 334.1355.

3-(9-chloro-4,6-dimethyl-5-oxo-5,6-dihydro-4H-pyrido[4,3,2-gh]phenanthridin-6-yl)propanenitrile. Purified by column chromatography (petroleum ether : ethyl acetate = 4 : 1). White solid, mp 175–176 °C. $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 8.45 (d, $J = 8.8$ Hz, 1H), 8.24 (d, $J = 8.2$ Hz, 1H), 8.15 (d, $J = 2.2$ Hz, 1H), 7.87 (t, $J = 8.1$ Hz, 1H), 7.62 (dd, $J = 8.8$, 2.2 Hz, 1H), 7.26 (d, $J = 7.9$ Hz, 1H), 3.60 (s, 3H), 2.98–2.88 (m, 1H), 2.81–2.70 (m, 1H), 2.34–2.19 (m, 2H), 1.68 (s, 3H). $^{13}$C NMR (151 MHz, CDCl$_3$) $\delta$ 172.4, 159.0, 145.4, 138.6, 135.2, 133.1, 132.6, 129.0, 127.7, 124.0, 121.3, 119.1, 116.3, 112.0, 111.3, 50.8, 34.2, 30.3, 30.0, 13.7. IR (film) $\nu$ 2975, 2925, 2078, 1638, 1453, 1403, 1384, 1336, 1152, 1049, 879 cm$^{-1}$. HRMS (ESI): calc. for C$_{20}$H$_{16}$ClN$_3$O (M+H)$^+$, 350.1055; found, 350.1064.
3-(9-bromo-4,6-dimethyl-5-oxo-5,6-dihydro-4H-pyrido[4,3,2-gh]phenanthridin-6-yl)propanenitrile. Purified by column chromatography (petroleum ether : ethyl acetate = 4 : 1). Yellow solid, mp 189–190 °C. \( ^1H \) NMR (600 MHz, CDCl\(_3\)) \( \delta \) 8.38 (d, \( J = 8.7 \) Hz, 1H), 8.33 (d, \( J = 1.9 \) Hz, 1H), 8.24 (d, \( J = 8.3 \) Hz, 1H), 7.87 (t, \( J = 8.1 \) Hz, 1H), 7.75 (dd, \( J = 8.7, 1.9 \) Hz, 1H), 7.27 (d, \( J = 8.0 \) Hz, 1H), 3.60 (s, 3H), 2.98–2.86 (m, 1H), 2.80–2.70 (m, 1H), 2.33–2.19 (m, 2H), 1.68 (s, 3H). \( ^{13}C \) NMR (151 MHz, CDCl\(_3\)) \( \delta \) 172.4, 159.0, 145.6, 138.6, 133.2, 132.6, 132.2, 130.3, 124.1, 123.3, 121.7, 119.0, 116.3 112.0, 111.4, 50.8, 34.3, 30.3, 30.0, 13.6. IR (film) \( \nu \) 2952, 2851, 2026, 1664, 1638, 1589, 1466, 1340, 1080, 800, 746 cm\(^{-1} \). HRMS (ESI): calc. for C\(_{20}\)H\(_{16}\)BrN\(_3\)O (M+H\(^+\)), 394.0550; found, 394.0548.

3-(4,6,8-trimethyl-5-oxo-5,6-dihydro-4H-pyrido[4,3,2-gh]phenanthridin-6-yl)propanenitrile (3m); 3-(4,6,10-trimethyl-5-oxo-5,6-dihydro-4H-pyrido[4,3,2-gh]phenanthridin-6-yl)propanenitrile (3m’). Purified by column chromatography (petroleum ether : ethyl acetate = 6 : 1), products 3m and 3m’ can not be separated column chromatography on silica gel. Yellow solid, mp 132–133 °C. \( ^1H \) NMR (600 MHz, CDCl\(_3\)) \( \delta \) 8.40 (d, \( J = 8.1 \) Hz, 1H), 8.34–8.24 (m, 1.80H), 8.03 (d, \( J = 8.3 \) Hz, 0.36H), 7.86–7.78 (m, 1.36H), 7.64 (d, \( J = 7.0 \) Hz, 1H), 7.60 (dd, \( J = 8.3, 1.5 \) Hz, 0.4H), 7.59–7.55 (m, 1.1H), 7.24–7.19 (m, 1.35H), 3.60 (s, 3H), 3.59 (s, 1.10H), 3.02–2.92 (m, 1.52H), 2.86 (s, 3H), 2.82–2.72 (m, 1.43H), 2.63 (s, 1.14H), 2.34–2.20 (m, 2.89H), 1.69 (s, 3H), 1.68 (s, 1.17H). \( ^{13}C \) NMR (151 MHz, CDCl\(_3\)) \( \delta \) 172.72, 172.68, 156.2, 155.7, 143.4, 143.1, 138.32, 138.28, 137.7, 137.0, 133.8, 133.6, 133.2, 131.83, 131.76, 131.1, 130.1, 130.0, 129.5, 128.4, 126.7, 122.5, 122.1, 120.4, 119.3, 116.8, 116.5, 111.8, 110.9, 110.8, 50.9, 50.6, 34.4, 34.3, 30.61, 30.59, 30.2, 29.94, 29.92, 21.9, 18.2, 13.65, 13.60. IR (film) \( \nu \) 2951, 2922, 2245, 2050, 1668, 1612, 1589, 1464, 1339, 777, 751 cm\(^{-1} \). HRMS (ESI): calc. for C\(_{21}\)H\(_{19}\)N\(_3\)O (M+H\(^+\)), 330.1601; found, 330.1608.

3-(8-fluoro-4,6-dimethyl-5-oxo-5,6-dihydro-4H-pyrido[4,3,2-gh]phenanthridin-6-yl)propanenitrile (3n); 3-(10-fluoro-4,6-dimethyl-5-oxo-5,6-dihydro-4H-pyrido[4,3,2-gh]phenanthridin-6-yl)propanenitrile (3n’). Purified by column chromatography (petroleum ether : ethyl acetate = 5 : 1), products 3n and 3n’ can not be separated
column chromatography on silica gel. Yellow solid, mp 136–137 °C. \(^1\)H NMR (600 MHz, CDCl\(_3\)) \(\delta\) 8.32 (d, \(J = 8.3\) Hz, 1H), 8.17 (d, \(J = 8.3\) Hz, 0.84H), 8.15–8.09 (m, 1.64H), 7.90–7.86 (m, 1H), 7.63–7.60 (m, 1H), 7.54–7.46 (m, 2H), 7.31–7.27 (m, 1.81H), 3.62 (s, 3H), 3.61 (s, 2.66H), 3.05–2.90 (m, 1.89H), 2.82–2.70 (m, 1.85H), 2.35–2.19 (m, 3.76H), 1.72 (s, 3H), 1.68 (s, 2.59H). \(^{13}\)C NMR (126 MHz, CDCl\(_3\)) \(\delta\) 172.5, 172.5, 161.3 (d, \(J_{C-F} = 248.0\) Hz), 158.4 (d, \(J_{C-F} = 256.4\) Hz), 158.0, 156.7, 156.7, 141.6, 138.6 (d, \(J_{C-F} = 21.4\) Hz), 134.6 (d, \(J_{C-F} = 10.9\) Hz), 132.95, 132.91, 132.6, 132.1, 130.1, 128.4, 126.9 (d, \(J_{C-F} = 8.4\) Hz), 124.8 (d, \(J_{C-F} = 1.2\) Hz), 124.1 (d, \(J_{C-F} = 9.4\) Hz), 119.1 (d, \(J_{C-F} = 13.2\) Hz), 118.4 (d, \(J_{C-F} = 24.3\) Hz), 118.1 (d, \(J_{C-F} = 4.5\) Hz), 116.7, 116.6, 114.3 (d, \(J_{C-F} = 19.2\) Hz), 112.2, 112.0, 111.6 (d, \(J_{C-F} = 2.7\) Hz), 107.4 (d, \(J_{C-F} = 23.4\) Hz), 50.9, 50.7, 34.4, 34.3, 30.2, 30.2, 30.0, 13.6, 13.6. IR (film) \(\nu\) 2971, 2901, 2025, 1637, 1619, 1453, 1394, 1252, 1051, 880, 785 cm\(^{-1}\). HRMS (ESI): calc. for C\(_{20}\)H\(_{16}\)FN\(_3\)O (M+H)\(^{+}\), 334.1350; found, 334.1356.

3-(11-fluoro-4,6-dimethyl-5-oxo-5,6-dihydro-4\(H\)-pyrido[4,3,2-\(gh\])phenanthridin-6-yl)propanenitrile. Purified by column chromatography (petroleum ether : ethyl acetate = 5 : 1). Yellow solid, mp 168–170 °C. \(^1\)H NMR (600 MHz, CDCl\(_3\)) \(\delta\) 8.74 (dd, \(J = 8.4, 1.8\) Hz, 1H), 7.98 (d, \(J = 8.2\) Hz, 1H), 7.91–7.85 (m, 1H), 7.73–7.69 (m, 1H), 7.39 (ddd, \(J = 13.0, 7.9, 1.1\) Hz, 1H), 7.32 (d, \(J = 7.9\) Hz, 1H), 3.61 (s, 3H), 2.99–2.94 (m, 1H), 2.79–2.75 (m, 1H), 2.33–2.22 (m, 2H), 1.68 (s, 3H). \(^{13}\)C NMR (151 MHz, CDCl\(_3\)) \(\delta\) 172.3, 160.5 (d, \(J = 255.6\) Hz), 158.6, 146.5 (d, \(J = 2.5\) Hz), 138.2, 132.6 (d, \(J = 1.9\) Hz), 131.5 (d, \(J = 5.0\) Hz), 128.8 (d, \(J = 10.7\) Hz), 125.9 (d, \(J = 3.5\) Hz), 121.5 (d, \(J = 23.3\) Hz), 119.2, 113.4 (d, \(J = 24.0\) Hz), 112.9 (d, \(J = 9.0\) Hz), 112.4, 111.7, 50.7, 34.1, 30.3, 30.0, 13.7. IR (film) \(\nu\) 2942, 2248, 1670, 1607, 1463, 1340, 1286, 1201, 828, 768, 732 cm\(^{-1}\). HRMS (ESI): calc. for C\(_{20}\)H\(_{16}\)FN\(_3\)O (M+H)\(^{+}\), 334.1350; found, 334.1358.

3-(11-methoxy-4,6-dimethyl-5-oxo-5,6-dihydro-4\(H\)-pyrido[4,3,2-\(gh\])phenanthridin-6-yl)propanenitrile. Purified by column chromatography (petroleum ether : ethyl acetate = 3 : 1). Yellow solid, mp 129–132 °C. \(^1\)H NMR (600 MHz, CDCl\(_3\)) \(\delta\) 9.28 (d, \(J = 8.6\) Hz, 1H), 7.86–7.74 (m, 2H), 7.70 (t, \(J = 8.0\) Hz, 1H), 7.26 (d, \(J = 7.7\) Hz, 1H), 7.16 (d, \(J = 7.9\) Hz, 1H), 4.15 (s, 3H), 3.60 (s, 3H), 3.01–2.91 (m, 1H), 2.82–2.70 (m, 1H), 2.27 (t, \(J = 8.0\) Hz, 2H), 1.66 (s, 3H). \(^{13}\)C NMR (151 MHz, CDCl\(_3\)) \(\delta\) 172.4, 158.3, 157.6, 146.7, 137.7, 133.4, 131.7, 128.9, 122.60, 122.57, 119.4, 113.7, 112.4, 110.9, 108.0, 55.9, 50.4, 34.0, 30.3, 30.0, 13.7. IR (film) \(\nu\) 3164, 3003, 2944,
3-(4,6,8,10-tetramethyl-5-oxo-5,6-dihydro-4H-pyrido[4,3,2-gh]phenanthridin-6-yl)propanenitrile. Purified by column chromatography (petroleum ether : ethyl acetate = 6 : 1). Yellow solid, mp 104–105 °C. 1H NMR (500 MHz, CDCl$_3$) $\delta$ 8.28 (d, $J$ = 8.3 Hz, 1H), 8.18 (s, 1H), 7.80 (t, $J$ = 8.1 Hz, 1H), 7.48 (s, 1H), 7.20 (d, $J$ = 7.9 Hz, 1H), 3.59 (s, 3H), 3.01–2.90 (m, 1H), 2.82 (s, 3H), 2.79–2.71 (m, 1H), 2.59 (s, 3H), 2.35–2.19 (m, 2H), 1.68 (s, 3H). 

13C NMR (126 MHz, CDCl$_3$) $\delta$ 172.8, 154.7, 141.8, 138.3, 137.3, 136.6, 133.5, 131.8, 131.5, 122.5, 119.9, 119.4, 116.7, 111.9, 110.6, 50.8, 34.5, 30.5, 29.9, 21.9, 18.1, 13.6. IR (film) $\nu$ 2972, 2919, 2069, 1637, 1461, 1404, 1067, 1048, 787, 726 cm$^{-1}$. HRMS (ESI): calc. for C$_{21}$H$_{19}$N$_3$O (M+H)$^+$, 346.1550; found, 346.1552.

3-(8,10-dichloro-4,6-dimethyl-5-oxo-5,6-dihydro-4H-pyrido[4,3,2-gh]phenanthridin-6-yl)propanenitrile.

Purified by column chromatography (petroleum ether : ethyl acetate = 3 : 1). White solid, mp 187–189 °C. 1H NMR (600 MHz, CDCl$_3$) $\delta$ 8.41 (d, $J$ = 1.9 Hz, 1H), 8.19 (d, $J$ = 8.3 Hz, 1H), 7.90 (t, $J$ = 8.1 Hz, 1H), 7.84 (t, $J$ = 2.0 Hz, 1H), 7.32 (d, $J$ = 7.9 Hz, 1H), 3.61 (s, 1H), 3.02–2.95 (m, 1H), 2.79–2.71 (m, 1H), 2.41–2.30 (m, 1H), 1.71 (s, 1H). 13C NMR (126 MHz, CDCl$_3$) $\delta$ 172.4, 158.6, 139.7, 138.8, 135.5, 132.9, 132.4, 132.3, 129.9, 125.0, 121.1, 119.0, 116.6, 112.3, 112.2, 51.0, 34.2, 30.3, 30.0, 13.6. IR (film) $\nu$ 2976, 2901, 2086, 1638, 1394, 1251, 1077, 1048, 880, 623 cm$^{-1}$. HRMS (ESI): calc. for C$_{20}$H$_{15}$Cl$_2$N$_3$O (M+H)$^+$, 384.0665; found, 384.0666.

3-(8,9,10-trifluoro-4,6-dimethyl-5-oxo-5,6-dihydro-4H-pyrido[4,3,2-gh]phenanthridin-6-yl)propanenitrile.

Purified by column chromatography (petroleum ether : ethyl acetate = 3 : 1). Yellow solid, mp 175–176 °C. 1H NMR (500 MHz, CDCl$_3$) $\delta$ 8.09 (d, $J$ = 8.3 Hz, 1H), 8.07–8.02 (m, 1H), 7.91 (t, $J$ = 8.1 Hz, 1H), 7.32 (d, $J$ = 7.9 Hz, 1H), 3.62 (s, 3H), 3.01–2.91 (m, 1H), 2.80–2.70 (m, 1H), 2.38–2.23 (m, 2H), 1.72 (s, 3H). 13C NMR (126 MHz, CDCl$_3$) $\delta$ 172.2, 158.8, 150.3 (ddd, $J_{C,F}$ = 252.0, 12.6, 2.5 Hz), 146.5 (ddd, $J_{C,F}$ = 259.6, 7.6, 5.0 Hz), 140.5 (ddd, $J_{C,F}$ = 254.5, 17.6, 13.9 Hz), 138.9, 133.1, 132.5 (d, $J_{C,F}$ = 8.4 Hz), 132.1(d, $J_{C,F}$ = 2.5 Hz), 119.4 (d, $J_{C,F}$ = 8.5 Hz),
118.8, 116.4, 112.2, 112.0, 103.9 (dd, $J_{C-F} = 18.9, 4.7$ Hz), 50.9, 34.4, 30.2, 30.0, 13.6. IR (film) $\nu = 2974, 2901, 2026, 1637, 1621, 1394, 1296, 1078, 1050, 880, 739$ cm$^{-1}$. HRMS (ESI): calc. for $C_{20}H_{14}F_3N_3O (M+H)^+$, 370.1162; found, 370.1166.

3-(4,6-dimethyl-5-oxo-5,6-dihydro-4$H$-benzo[a]pyrido[4,3,2-gh]phenanthridin-6-yl)propanenitrile. Purified by column chromatography (petroleum ether : ethyl acetate = 4 : 1). Yellow solid, mp 116–117 °C. $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 9.05 (d, $J = 8.4$ Hz, 1H), 8.81 (d, $J = 8.6$ Hz, 1H), 8.08–8.05 (m, 3H), 7.88 (t, $J = 7.8$ Hz, 1H), 7.73 (t, $J = 7.4$ Hz, 1H), 7.68 (t, $J = 7.4$ Hz, 1H), 7.27 (d, $J = 7.8$ Hz, 1H), 3.65 (s, 3H), 3.03–2.98 (m, 1H), 2.29 (t, $J = 7.9$ Hz, 2H), 1.71 (s, 3H). $^{13}$C NMR (151 MHz, CDCl$_3$) $\delta$ 172.5, 156.6, 144.9, 138.2, 133.5, 133.3, 131.6, 130.4, 129.7, 128.9, 128.1, 127.5, 126.8, 126.5, 121.2, 119.5, 113.4, 113.2, 50.5, 34.4, 30.1, 13.7. IR (film) $\nu = 2919, 2901, 2251, 2077, 1667, 1455, 1426, 1156, 874, 755$ cm$^{-1}$. HRMS (ESI): calc. for $C_{24}H_{19}N_3O (M+H)^+$, 366.1601; found, 366.1606.

3-(4,6-dimethyl-5-oxo-5,6-dihydro-4$H$-dibenzo[a,c]pyrido[4,3,2-gh]phenanthridin-6-yl)propanenitrile. Purified by column chromatography (petroleum ether : ethyl acetate = 5 : 1). Yellow solid, mp 86–88 °C. $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 9.34–9.28 (m, 1H), 8.87 (d, $J = 8.1$ Hz, 1H), 8.75 (d, $J = 8.1$ Hz, 1H), 8.68–8.59 (m, 2H), 7.85–7.77 (m, 3H), 7.75–7.72 (m, 1H), 7.70–7.67 (m, 1H), 7.21 (d, $J = 7.8$ Hz, 1H), 3.64 (s, 3H), 3.13–3.05 (m, 1H), 2.40–2.28 (m, 2H), 1.78 (s, 3H). $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 172.5, 155.7, 142.3, 138.0, 133.4, 131.54, 131.04, 130.95, 130.5, 128.8, 128.7, 128.5, 127.7, 127.3, 126.5, 125.4, 123.7, 122.4, 121.4, 119.2, 118.4, 113.9, 109.8, 50.6, 34.7, 30.3, 30.0, 13.7. IR (film) $\nu = 2976, 2901, 2251, 2077, 1667, 1619 1455, 1426, 1156, 874, 755$ cm$^{-1}$. HRMS (ESI): calc. for $C_{28}H_{21}N_3O (M+H)^+$, 416.1757; found, 416.1758.

3-(4,6-dimethyl-5-oxo-5,6-dihydro-4$H$-benzo[de]thieno[3,2-b][1,6]naphthyridin-6-yl)propanenitrile. Purified by column chromatography (petroleum ether : ethyl acetate = 4 : 1). Yellow solid, mp 169–170 °C. $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 7.82–7.71 (m, 3H), 7.67 (d, $J = 5.4$ Hz, 1H), 7.12 (dd, $J = 6.8, 1.6$ Hz, 1H), 3.59 (s, 3H), 2.92–2.88
(m, 1H), 2.81–2.76 (m, 1H), 2.27–2.12 (m, 2H), 1.70 (s, 3H). $^1$C NMR (151 MHz, CDCl$_3$) δ 172.7, 155.9, 152.0, 138.6, 132.3, 132.2, 128.0, 127.8, 126.1, 119.1, 117.3, 111.2, 109.6, 50.5, 35.0, 30.6, 29.9, 13.7. IR (film) ν 3117, 2923, 2250, 1667, 1619, 1569, 1460, 1096, 814, 748, 649 cm$^{-1}$. HRMS (ESI): calc. for C$_{19}$H$_{15}$N$_3$OS (M+H)$^+$, 322.1009; found, 322.1013.

![3-(4,6-dimethyl-5-oxo-5,6-dihydro-4H-benzo|de|pyrido[3,4-b][1,6]naphthyridin-6-yl)propanenitrile](image)

3-(4,6-dimethyl-5-oxo-5,6-dihydro-4H-benzo|de|pyrido[3,4-b][1,6]naphthyridin-6-yl)propanenitrile. Purified by column chromatography (petroleum ether : ethyl acetate = 1 : 1). White solid, mp 128–129 °C. $^1$H NMR (600 MHz, CDCl$_3$) δ 9.50 (s, 1H), 8.80 (d, $J$ = 5.1 Hz, 1H), 8.38–8.24 (m, 2H), 7.96 (t, $J$ = 8.1 Hz, 1H), 7.40 (d, $J$ = 7.9 Hz, 1H), 3.63 (s, 3H), 3.01–2.95 (m, 1H), 2.82–2.76 (m, 1H), 2.34–2.25 (m, 2H), 1.72 (s, 3H). $^1$C NMR (151 MHz, CDCl$_3$) δ 172.3, 159.8, 153.2, 145.4, 139.7, 138.7, 133.0, 131.6, 127.8, 119.0, 116.9, 115.7, 113.4, 113.2, 51.0, 34.1, 30.5, 30.1, 13.7. IR (film) ν 2988, 2900, 1406, 1393, 1250, 1066, 1056, 891, 743 cm$^{-1}$. HRMS (ESI): calc. for C$_{19}$H$_{16}$N$_3$O (M+H)$^+$, 317.1397; found, 317.1400.

![3-(3-(4-methyl-5-oxo-6-phenyl-5,6-dihydro-4H-pyrido[4,3,2-gh]phenanthridin-6-yl)propanenitrile](image)

3-(4-methyl-5-oxo-6-phenyl-5,6-dihydro-4H-pyrido[4,3,2-gh]phenanthridin-6-yl)propanenitrile. Purified by column chromatography (petroleum ether : ethyl acetate = 4 : 1). Yellow solid, mp 151–152 °C. $^1$H NMR (600 MHz, CDCl$_3$) δ 8.60–8.50 (m, 1H), 8.29 (d, $J$ = 8.2 Hz, 1H), 8.24 (dd, $J$ = 8.2, 0.9 Hz, 1H), 7.85–7.75 (m, 2H), 7.74–7.68 (m, 1H), 7.19 (d, $J$ = 7.8 Hz, 1H), 7.16–7.06 (m, 3H), 7.05–6.98 (m, 2H), 3.61 (s, 3H), 3.45–3.35 (m, 1H), 3.26–3.16 (m, 1H), 2.61–2.44 (m, 2H). $^1$C NMR (151 MHz, CDCl$_3$) δ 170.5, 155.3, 144.6, 142.2, 138.4, 133.4, 132.1, 130.4, 129.5, 128.7, 127.6, 127.5, 126.3, 123.0, 122.6, 119.7, 116.5, 113.2, 59.3, 32.9, 30.3, 14.4. IR (film) ν 2922, 2848, 2025, 1637, 1511, 1399, 1148 1031, 875, 757, 625 cm$^{-1}$. HRMS (ESI): calc. for C$_{25}$H$_{19}$N$_3$O (M+Na)$^+$, 400.1420; found, 400.1419.

![3-(3-(6-benzyl-4-methyl-5-oxo-5,6-dihydro-4H-pyrido[4,3,2-gh]phenanthridin-6-yl)propanenitrile](image)

3-(6-benzyl-4-methyl-5-oxo-5,6-dihydro-4H-pyrido[4,3,2-gh]phenanthridin-6-yl)propanenitrile. Purified by column chromatography (petroleum ether : ethyl acetate = 5 : 1). White solid, mp 130–131 °C. $^1$H NMR (600 MHz, CDCl$_3$) δ 8.52 (d, $J$ = 8.2 Hz, 1H), 8.23 (d, $J$ = 8.2 Hz, 1H), 8.15 (d, $J$ = 8.3 Hz, 1H), 7.82 (t, $J$ = 7.5 Hz, 1H), 7.70
(t, J = 7.6 Hz, 1H), 7.61 (t, J = 8.1 Hz, 1H), 6.85 (t, J = 7.3 Hz, 1H), 6.80 (d, J = 7.9 Hz, 1H), 6.74 (t, J = 7.6 Hz, 2H), 6.39 (d, J = 7.6 Hz, 2H), 3.41 (d, J = 12.4 Hz, 1H), 3.35–3.34 (m, 4H), 3.25–3.19 (m, 1H), 3.02–2.92 (m, 1H), 2.31–2.19 (m, 2H).

13C NMR (151 MHz, CDCl3) δ 171.0, 156.1, 144.7, 137.8, 135.1, 132.4, 131.8, 129.9, 129.3, 129.2, 127.1, 126.7, 122.74, 122.69, 119.2, 116.1, 113.9, 110.4, 57.0, 51.9, 33.9, 29.4, 13.7. IR (film) ν 2926, 2249, 2023, 1661, 1613, 1589, 1495, 1418, 1155, 752, 705 cm⁻¹. HRMS (ESI): calc. for C26H21N3O (M+H)⁺, 392.1757; found, 392.1764.

3-(4,6-dimethyl-5-oxo-5,6-dihydro-4H-pyrido[4,3,2-gh]phenanthridin-6-yl)-2-methylpropanenitrile. Purified by column chromatography (petroleum ether : ethyl acetate = 5 : 1). Yellow solid, mp 124–126 °C. 1H NMR (600 MHz, CDCl3) δ 8.57–8.54 (m, 1H), 8.32–8.29 (m, 1H), 8.17–8.10 (m, 1H), 7.88–7.83 (m, 1H), 7.78–7.76 (m, 1H), 7.69–7.65 (m, 1H), 7.27–7.25 (m, 1H), 3.621–3.618 (m, 3H), 3.14–2.86 (m, 1H), 2.77–2.67 (m, 1H), 2.61–2.52 (m, 1H), 1.73–1.72 (m, 3H), 1.24–1.23 (m, 3H). 13C NMR (151 MHz, CDCl3) δ 173.1, 172.8, 158.2, 157.5, 144.8, 144.7, 138.8, 138.3, 133.5, 133.4, 132.3, 131.8, 129.9, 129.7, 129.3, 129.2, 126.9, 122.9, 122.7, 122.6, 122.2, 122.0, 116.7, 116.2, 112.2, 112.1, 111.2, 110.9, 50.4, 50.1, 43.2, 42.8, 31.7, 31.4, 29.95, 29.90, 22.22, 22.17, 19.0, 18.9. IR (film) ν 2957, 2922, 2851, 1670, 1589, 1464, 1360, 1165, 1081, 794 cm⁻¹. HRMS (ESI): calc. for C21H19N3O (M+H)⁺, 330.1601; found, 330.1599.

4-chloro-2-(((4,6-dimethyl-5-oxo-5,6-dihydro-4H-pyrido[4,3,2-gh]phenanthridin-6-yl)methyl)butanenitrile. Purified by column chromatography (petroleum ether : ethyl acetate = 4 : 1). Yellow solid, mp 208–209 °C. 1H NMR (600 MHz, CDCl3) δ 8.58–8.52 (m, 1H), 8.34–8.29 (m, 1H), 8.19–8.10 (m, 1H), 7.88–7.83 (m, 1H), 7.78–7.76 (m, 1H), 7.69–7.65 (m, 1H), 7.28–7.27 (m, J = 7.3 Hz, 1H), 3.66–3.56 (m, 4H), 3.55–3.49 (m, 1H), 3.23–2.97 (m, 1H), 2.94–2.88 (m, 1H), 2.85–2.55 (m, 1H), 2.12–2.02 (m, 1H), 2.00–1.91 (m, 1H), 1.71–1.70 (m, 3H). 13C NMR (151 MHz, CDCl3) δ 172.8, 172.7, 157.8, 157.4, 144.8, 144.6, 138.7, 138.2, 133.6, 133.5, 132.3, 131.9, 129.8, 129.7, 129.34, 129.31, 127.01, 126.98, 122.93, 122.88, 122.67, 122.65, 120.2, 116.7, 116.3, 112.2, 112.1, 111.2, 111.1, 50.5, 50.1, 41.3, 41.2, 40.3, 39.9, 35.8, 35.7, 32.0, 31.4, 30.01, 29.97, 25.7, 25.5. IR (film) ν 2994, 1770, 1758, 1463, 1454, 1373, 1245, 1056, 836, 772 cm⁻¹. HRMS (ESI): calc. for C22H20ClN3O (M+H)⁺, 378.1368; found, 378.1369.
6-ethyl-4,6-dimethyl-4H-pyrido[4,3,2-gh]phenanthridin-5(6H)-one. Purified by column chromatography (petroleum ether : ethyl acetate = 8 : 1). Yellow solid, mp 133–134 °C. 1H NMR (500 MHz, CDCl₃) δ 8.51 (d, J = 8.2 Hz, 1H), 8.25 (d, J = 8.3 Hz, 1H), 8.14 (d, J = 8.2 Hz, 1H), 7.79 (t, J = 7.9 Hz, 1H), 7.74 (t, J = 7.5 Hz, 1H), 7.63 (t, J = 7.6 Hz, 1H), 7.19 (d, J = 7.9 Hz, 1H), 3.58 (s, 3H), 2.41 (dq, J = 14.7, 7.4 Hz, 1H), 2.29 (dq, J = 14.5, 7.3 Hz, 1H), 1.81 (s, 3H), 0.65 (t, J = 7.4 Hz, 3H). 13C NMR (126 MHz, CDCl₃) δ 174.2, 159.8, 145.0, 139.0, 133.1, 131.6, 129.8, 129.0, 126.5, 122.6, 115.9, 112.6, 110.5, 52.0, 36.4, 29.6, 27.7, 9.8. IR (film) ν 2964, 2933, 1664, 1588, 1570, 1460, 1354, 1330, 757, 744, 644 cm⁻¹. HRMS (ESI): calc. for C₁₉H₁₈N₂O (M+H)+, 291.1492; found, 291.1494.

4-benzyl-6-ethyl-6-methyl-4H-pyrido[4,3,2-gh]phenanthridin-5(6H)-one. Purified by column chromatography (petroleum ether : ethyl acetate = 9 : 1). Yellow solid, mp 144–145 °C. 1H NMR (600 MHz, CDCl₃) δ 8.50 (d, J = 8.1 Hz, 1H), 8.22 (d, J = 8.2 Hz, 1H), 8.16 (d, J = 8.2 Hz, 1H), 7.75 (t, J = 7.5 Hz, 1H), 7.69–7.60 (m, 2H), 7.37–7.28 (m, 4H), 7.28–7.22 (m, 1H), 7.11 (d, J = 7.9 Hz, 1H), 5.44 (d, J = 41.9 Hz, 2H), 2.60–2.45 (m, 1H), 2.45–2.31 (m, 1H), 1.87 (s, 3H), 0.76 (t, J = 7.4 Hz, 3H). 13C NMR (151 MHz, CDCl₃) δ 174.6, 159.6, 144.9, 138.0, 136.4, 133.2, 131.6, 129.8, 129.1, 128.9, 127.2, 126.5, 126.4, 122.7, 122.5, 116.1, 111.7, 111.8, 52.2, 46.2, 35.8, 28.2, 10.0. IR (film) ν 3063, 2968, 2930, 1675, 1588, 1570, 1463, 1363, 740, 703, 650 cm⁻¹. HRMS (ESI): calc. for C₂₅H₂₂N₂O (M+H)+, 367.1805; found, 367.1808.

6-ethyl-4,6,9-trimethyl-4H-pyrido[4,3,2-gh]phenanthridin-5(6H)-one. Purified by column chromatography (petroleum ether : ethyl acetate = 8 : 1). Yellow solid, mp 120–121 °C. 1H NMR (600 MHz, CDCl₃) δ 8.41 (d, J = 8.3 Hz, 1H), 8.23 (d, J = 8.3 Hz, 1H), 7.96 (s, 1H), 7.79 (t, J = 8.1 Hz, 1H), 7.47 (dd, J = 8.3, 1.4 Hz, 1H), 7.17 (d, J = 7.9 Hz, 1H), 3.59 (s, 3H), 2.60 (s, 3H), 2.45–2.35 (m, 1H), 1.79 (s, 3H), 0.65 (t, J = 7.4 Hz, 3H). 13C NMR (151 MHz, CDCl₃) δ 174.3, 159.9, 145.2, 139.4, 139.0, 133.2, 129.3, 128.3, 122.3, 120.4, 115.8, 112.4, 110.1, 52.0, 36.5, 29.6, 27.8, 21.5, 9.8. IR (film) ν 2958, 2919, 2850, 1662, 1587, 1567, 1467, 1357, 1336, 801, 768 cm⁻¹. HRMS (ESI): calc. for C₂₀H₂₀N₂O (M+H)+, 305.1648; found, 305.1648.
6-ethyl-9-fluoro-4,6-dimethyl-4H-pyrido[4,3,2-gh]phenanthridin-5(6H)-one. Purified by column chromatography (petroleum ether : ethyl acetate = 8 : 1). White solid, mp 158–159 °C. ¹H NMR (600 MHz, CDCl₃) δ 8.50 (dd, J = 9.1, 5.9 Hz, 1H), 8.19 (d, J = 8.3 Hz, 1H), 7.82 (t, J = 8.1 Hz, 1H), 7.79 (dd, J = 9.9, 2.7 Hz, 1H), 7.40 (ddd, J = 9.0, 8.1, 2.7 Hz, 1H), 7.20 (d, J = 7.9 Hz, 1H), 3.59 (s, 3H), 2.45–2.34 (m, 1H), 2.34–2.24 (m, 1H), 1.79 (s, 3H), 0.65 (t, J = 7.4 Hz, 3H). ¹³C NMR (151 MHz, CDCl₃) δ 174.1, 163.0 (d, J_C-F = 249.0 Hz), 161.5, 146.5 (d, J_C-F = 12.1 Hz), 139.2, 133.0, 132.1, 124.5 (d, J_C-F = 9.4 Hz), 119.4, 115.71, 115.69 (d, J_C-F = 23.9 Hz), 114.2 (d, J_C-F = 20.3 Hz), 112.3, 110.4, 52.2, 36.4, 29.7, 27.7, 9.8. IR (film) ν 2961, 2928, 2850, 1671, 1589, 1578, 1466, 1338, 1180, 791, 767 cm⁻¹. HRMS (ESI): calc. for C₁⁹H₁⁷FN₂O (M+H)+, 309.1398; found, 309.1415.

6-ethyl-4,6,8-trimethyl-4H-pyrido[4,3,2-gh]phenanthridin-5(6H)-one (4m); 6-ethyl-4,6,10-trimethyl-4H-pyrido[4,3,2-gh]phenanthridin-5(6H)-one (4m'). Purified by column chromatography (petroleum ether : ethyl acetate = 9 : 1), products 4m and 4m' can not be separated column chromatography on silica gel. White solid, mp 108–110 °C. ¹H NMR (600 MHz, CDCl₃) δ 8.37 (d, J = 8.2 Hz, 1H), 8.29 (s, 0.5H), 8.26–8.21 (m, 1.5H), 8.03 (d, J = 8.3 Hz, 0.5H), 7.77 (t, J = 8.1 Hz, 1.5H), 7.60 (d, J = 7.0 Hz, 1H), 7.56 (dd, J = 8.4, 1.6 Hz, 0.5H), 7.53–7.49 (m, 1H), 7.17 (d, J = 7.9 Hz, 1.4H), 3.58 (s, 3H), 3.58 (s, 1.4H), 2.86 (s, 3H), 2.61 (s, 1.4H), 2.46–2.35 (m, 2H), 2.33–2.24 (m, 2H), 1.80 (s, 3H), 1.80 (s, 1.4H), 0.67–0.63 (m, 4.4H). ¹³C NMR (151 MHz, CDCl₃) δ 174.4, 174.3, 158.7, 158.1, 143.6, 143.4, 139.0, 138.9, 137.7, 136.3, 133.4, 132.8, 131.3, 130.8, 129.6, 129.5, 126.1, 122.3, 122.3, 122.0, 120.3, 116.2, 115.9, 112.7, 112.4, 110.4, 110.2, 52.2, 51.9, 36.7, 36.5, 29.6, 29.6, 28.0, 27.6, 21.9, 18.2, 9.8, 9.7. IR (film) ν 2961, 2925, 1672, 1610, 1589, 1577, 1463, 1339, 829, 774, 750 cm⁻¹. HRMS (ESI): calc. for C₂₀H₂₀N₂O (M+H)+, 305.1648; found, 305.1650.

6-ethyl-11-fluoro-4,6-dimethyl-4H-pyrido[4,3,2-gh]phenanthridin-5(6H)-one. Purified by column chromatography (petroleum ether : ethyl acetate = 10 : 1). Yellow solid, mp 106–107 °C. ¹H NMR (600 MHz,
CDCl$_3$ δ 8.73 (d, $J = 8.5$ Hz, 1H), 7.99 (d, $J = 8.2$ Hz, 1H), 7.87 (t, $J = 8.2$ Hz, 1H), 7.69 (dd, $J = 13.6$ Hz, 8.0 Hz, 1H), 7.37 (dd, $J = 13.1$, 7.9 Hz, 1H), 7.30 (d, $J = 8.0$ Hz, 1H), 3.63 (s, 3H), 2.44–2.38 (m, 1H), 2.34–2.28 (m, 1H), 1.82 (s, 3H), 0.68 (t, $J = 7.4$ Hz, 3H). $^{13}$C NMR (151 MHz, CDCl$_3$) δ 173.9, 161.0, 160.6 (d, $J_{C-F} = 255.3$ Hz), 146.8 (d, $J_{C-F} = 2.7$ Hz), 138.7, 132.2 (d, $J_{C-F} = 2.1$ Hz), 131.1 (d, $J_{C-F} = 4.9$ Hz), 128.5 (d, $J_{C-F} = 10.8$ Hz), 125.8 (d, $J_{C-F} = 3.5$ Hz), 121.0 (d, $J_{C-F} = 23.2$ Hz), 113.0, 112.8 (d, $J_{C-F} = 23.9$ Hz), 112.8, 111.3 (d, $J_{C-F} = 1.3$ Hz), 51.9, 36.4, 29.8, 27.7, 9.8. IR (film) $\nu$ 2922, 2851, 1667, 1618, 1586, 1463, 1343, 1164, 732, 517 cm$^{-1}$. HRMS (ESI): calc. for C$_{19}$H$_{17}$FN$_2$O (M+H)$^+$, 309.1398; found, 309.1395.

6-ethyl-4,6,8,10-tetramethyl-4$H$-pyrido[4,3,2-$gh$]phenanthridin-5(6$H$)-one. Purified by column chromatography (petroleum ether : ethyl acetate = 10 : 1). Yellow solid, mp 165–166 $^\circ$C. $^1$H NMR (600 MHz, CDCl$_3$) δ 8.25 (d, $J = 8.3$ Hz, 1H), 8.17 (s, 1H), 7.76 (t, $J = 8.1$ Hz, 1H), 7.46 (s, 1H), 7.17 (d, $J = 7.8$ Hz, 1H), 3.59 (s, 3H), 2.82 (s, 3H), 2.58 (s, 3H), 2.45–2.36 (m, 1H), 2.33–2.24 (m, 1H), 1.79 (s, 3H), 0.64 (t, $J = 7.4$ Hz, 3H). $^{13}$C NMR (151 MHz, CDCl$_3$) δ 174.6, 157.0, 142.0, 138.9, 137.3, 135.8, 133.1, 131.4, 131.1, 122.2, 119.8, 116.3, 112.5, 110.1, 52.1, 36.7, 29.6, 28.1, 21.9, 18.1, 9.8. IR (film) $\nu$ 2964, 2922, 2851, 1660, 1611, 1588, 1573, 1458, 1355, 1337, 820, 767 cm$^{-1}$. HRMS (ESI): calc. for C$_{22}$H$_{22}$N$_2$O (M+H)$^+$, 319.1805; found, 319.1821.

6-ethyl-4,6-dimethyl-4$H$-dibenzo[a,c]pyrido[4,3,2-$gh$]phenanthridin-5(6$H$)-one. Purified by column chromatography (petroleum ether : ethyl acetate = 8 : 1). Yellow solid, mp 184–185 $^\circ$C. $^1$H NMR (600 MHz, CDCl$_3$) δ 9.43–9.37 (m, 1H), 8.90 (d, $J = 7.8$ Hz, 1H), 8.17 (s, 1H), 7.69 (d, $J = 7.8$ Hz, 1H), 8.68–8.64 (m, 1H), 8.62 (d, $J = 8.6$ Hz, 1H), 7.83–7.75 (m, 3H), 7.73 (dt, $J = 7.2$, 1.2 Hz, 1H), 7.18 (d, $J = 7.7$ Hz, 1H), 3.65 (s, 3H), 2.58–2.50 (m, 1H), 2.44–2.35 (m, 1H), 1.91 (s, 3H), 0.71 (t, $J = 7.4$ Hz, 3H). $^{13}$C NMR (151 MHz, CDCl$_3$) δ 174.3, 158.2, 142.3, 138.7, 133.1, 131.0, 130.9, 130.8, 128.7, 128.4, 127.4, 126.9, 126.4, 125.7, 123.6, 122.3, 120.9, 117.8, 114.5, 109.2, 52.0, 36.5, 29.7, 28.1, 9.9. IR (film) $\nu$ 2967, 2926, 1671, 1581, 1566, 1452, 1375, 1337, 1066, 760, 729 cm$^{-1}$. HRMS (ESI): calc. for C$_{27}$H$_{22}$N$_2$O (M+H)$^+$, 391.1805; found, 391.1824.
6-ethyl-4,6-dimethyl-4H-benzo[de]pyrido[3,4-b][1,6]napthyridin-5(6H)-one. Purified by column chromatography (petroleum ether : ethyl acetate = 1 : 1). Yellow solid, mp 154–155 °C. $^1$H NMR (600 MHz, CDCl$_3$) δ 9.49 (s, 1H), 8.76 (d, $J = 5.5$ Hz, 1H), 8.29–8.27 (m, 2H), 7.92 (t, $J = 8.1$ Hz, 1H), 7.36 (d, $J = 7.9$ Hz, 1H), 3.61 (s, 3H), 2.46–2.40 (m, 1H), 2.35–2.29 (m, 1H), 1.82 (s, 3H), 0.66 (t, $J = 7.4$ Hz, 1H). $^{13}$C NMR (151 MHz, CDCl$_3$) δ 173.9, 162.1, 153.3, 144.9, 140.0, 139.2, 132.5, 131.2, 127.5, 116.3, 115.5, 113.9, 112.7, 52.3, 36.5, 29.7, 27.8, 9.8. IR (film) $\nu$ 2965, 2924, 1668, 1610, 1609, 1590, 1466, 1358, 1079, 913, 745 cm$^{-1}$. HRMS (ESI): calc. for C$_{18}$H$_{17}$N$_3$O (M+H)$^+$, 292.1444; found, 292.1447.

6-ethyl-4-methyl-6-phenyl-4H-pyrido[4,3,2-gh]phenanthridin-5(6H)-one. Purified by column chromatography (petroleum ether : ethyl acetate = 7 : 1). Yellow solid, mp 147–148 °C. $^1$H NMR (600 MHz, CDCl$_3$) δ 8.55 (d, $J = 8.2$ Hz, 1H), 8.31 (d, $J = 8.3$ Hz, 1H), 8.14 (d, $J = 8.2$ Hz, 1H), 7.83 (t, $J = 8.1$ Hz, 1H), 7.74 (t, $J = 7.6$ Hz, 1H), 7.66 (t, $J = 7.6$ Hz, 1H), 7.23 (d, $J = 7.9$ Hz, 1H), 7.21–7.09 (m, 4H), 3.63 (s, 3H), 3.16–3.05 (m, 1H), 3.02–2.92 (m, 1H), 0.87 (t, $J = 7.2$ Hz, 3H). $^{13}$C NMR (151 MHz, CDCl$_3$) δ 172.2, 158.2, 145.0, 144.7, 138.7, 133.1, 131.8, 130.2, 129.1, 128.3, 126.88, 126.81, 122.6, 122.5, 116.2, 113.4, 110.9, 60.6, 32.3, 30.0, 10.5. IR (film) $\nu$ 2961, 2924, 1667, 1588, 1569, 1463, 1344, 764, 753, 700 cm$^{-1}$. HRMS (ESI): calc. for C$_{24}$H$_{20}$N$_2$O (M+H)$^+$, 353.1648; found, 353.1653.

6-benzyl-6-ethyl-4-methyl-4H-pyrido[4,3,2-gh]phenanthridin-5(6H)-one. Purified by column chromatography (petroleum ether : ethyl acetate = 9 : 1). Yellow solid, mp 132–133 °C. $^1$H NMR (600 MHz, CDCl$_3$) δ 8.51 (d, $J = 8.1$ Hz, 1H), 8.24 (d, $J = 8.0$ Hz, 1H), 8.15 (d, $J = 8.3$ Hz, 1H), 7.80 (t, $J = 7.5$ Hz, 1H), 7.67 (t, $J = 7.6$ Hz, 1H), 7.62 (t, $J = 8.1$ Hz, 1H), 6.87 (d, $J = 7.8$ Hz, 1H), 6.83 (t, $J = 7.3$ Hz, 1H), 6.76 (t, $J = 7.5$ Hz, 2H), 6.58 (d, $J = 7.5$ Hz, 2H), 3.60 (d, $J = 12.2$ Hz, 1H), 3.52 (d, $J = 12.5$ Hz, 1H), 3.39 (s, 3H), 2.77–2.71 (m, 1H), 2.60–2.53 (m, 1H), 0.68 (t, $J = 7.4$ Hz, 3H). $^{13}$C NMR (151 MHz, CDCl$_3$) δ 172.8, 158.6, 145.0, 138.4, 137.1, 132.3, 131.4, 129.8, 129.3, 129.0 127.3, 126.5, 126.1, 122.6, 115.7, 114.1, 110.2, 58.9, 50.2, 35.2, 29.2, 9.9. IR (film) $\nu$ 3028, 2963, 2931, 1664, 1611, 1588, 1464, 1083, 755, 735, 701 cm$^{-1}$. HRMS (ESI): calc. for C$_{25}$H$_{22}$N$_2$O (M+H)$^+$, 367.1805; found, 367.1827.
8. Charts of compounds