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Supporting Information

Oxidative cascade cyclization of 2-cyano-3-arylaniline derived acrylamides with

toluenes, ethers, aliphatic alcohols or simple alkanes

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1. General information

¹H NMR, ¹³C NMR and spectra were recorded on Bruker AVANCE III HD 600 (600 MHz for ¹H; 151 MHz for ¹³C) instruments internally referenced to tetramethylsilane (TMS) signal. Chemical shifts (δ) and coupling constants (*J*) were expressed in ppm and Hz, respectively. CDCl₃ was used as the NMR solvent in all cases. Mass spectra were mearsured 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). All the starting arylacrylamides are known compounds, and were synthesized according to known procedures. ^{S1}

2. The radical trapping experiments



In a Schlenk tube, acrylamide **1a** (0.2 mmol), TBPB (0.6 mmol, 117 mg) and TEMPO (0.4 mmol, 63 mg) were added and charged with argon three times. Then, toluene (4.0 mL) were added. The mixture was allowed to stir at 100 °C for 24 hours. After the reaction was cooled to room temperature, the mixture was under HRMS (ESI) analysis.







In a Schlenk tube, acrylamide **1a** (0.2 mmol) and TBPB (0.6 mmol, 117 mg) were added and charged with argon three times. Then, ethene-1,1-diyldibenzene (0.6 mmol, 108 mg) and toluene (4.0 mL) were added. The mixture was allowed to stir at 100 °C for 24 hours. After the reaction was cooled to room temperature, the reaction mixture was concentrated by rotary evaporation and purified by flash chromatography on silica gel with petroleum ether/1,4-dioxane (30/1) as the eluent to afford **3aa** (13 mg, 18%) and **4** (14 mg, 9%).

3. General procedure for oxidative cascade cyclization

(1) General procedure for oxidative cascade cyclization

In a Schlenk tube, acrylamide 1 (0.2 mmol) and TBPB (0.6 mmol, 117 mg) were added and charged with argon three times. Then, 2 (4.0 mL) were added. The mixture was allowed to stir at 100 °C for 24 hours. After substrate was consumed, the reaction mixture was concentrated by rotary evaporation and purified by flash chromatography on silica gel with petroleum ether/1,4-dioxane as the eluent to afford the corresponding product 3.

(2) General procedure for synthesis of 3ai and 3ap.

In a Schlenk tube, acrylamide **1** (0.2 mmol) and TBPB (0.6 mmol, 117 mg) were added and charged with argon three times. Then, **2** (4.0 mL) were added. The mixture was allowed to stir at 100 °C for 36 hours. After substrate was consumed, the reaction mixture was concentrated by rotary evaporation and purified by flash chromatography on silica gel with petroleum ether/1,4-dioxane as the eluent to afford the corresponding product.

(3) The procedure for synthesis of 3al.

In a Schlenk tube, acrylamide **1** (0.2 mmol) and TBPB (0.6 mmol, 117 mg) were added and charged with argon three times. Then, **2** (4.0 mL) were added. The mixture was allowed to stir at 120 °C for 24 hours. After substrate was consumed, the reaction mixture was concentrated by rotary evaporation and purified by flash chromatography on silica gel with petroleum ether/1,4-dioxane as the eluent to afford the corresponding product.

(4) General procedure for synthesis of 3au, 3av and 3aw.

In a Schlenk tube, acrylamide **1** (0.2 mmol) and TBPB (0.6 mmol, 117 mg) were added and charged with argon three times. Then, **2** (4.0 mL) were added. The mixture was allowed to stir at 100 °C for 18 hours. After substrate was consumed, the reaction mixture was concentrated by rotary evaporation and purified by flash chromatography on silica gel with petroleum ether/1,4-dioxane as the eluent to afford the corresponding product.

CAUTION: Be careful when performing with larger scale! Peroxides may explode at high temperature.

4. Characterization of compounds



4,6-dimethyl-6-phenethyl-4*H***-pyrido[4,3,2-***gh***]phenanthridin-5**(6*H*)-one (3aa). Performed according to the general procedure, and purified by column chromatography (petroleum ether/1,4-dioxane = 30/1) to afford 60 mg (82%) of **3aa**. White solid, mp 110–112 °C. ¹H NMR (600 MHz, CDCl₃) δ 8.54 (d, *J* = 8.0 Hz, 1H), 8.27 (d, *J* = 8.2 Hz, 1H), 8.18 (dd, *J* = 8.2, 0.8 Hz, 1H), 7.82 (t, *J* = 8.1 Hz, 1H), 7.79–7.75 (m, 1H), 7.68–7.63 (m, 1H), 7.19 (d, *J* = 7.8 Hz, 1H), 7.11 (t, *J* = 7.4 Hz, 2H), 7.04 (t, *J* = 7.3 Hz, 1H), 6.99 (d, *J* = 7.1 Hz, 2H), 3.55 (s, 3H), 2.84–2.76 (m, 1H), 2.70–2.61 (m, 1H), 2.49–2.38 (m, 1H), 2.34–2.23 (m, 1H), 1.80 (s, 3H). ¹³C NMR (151 MHz, CDCl₃) δ 173.9, 159.5, 145.0, 141.5, 138.8, 133.2, 131.7, 129.8, 129.1, 128.3, 128.0, 126.6, 125.6, 122.6, 122.5, 116.0, 112.4, 110.7, 51.3, 43.7, 31.9, 29.7, 29.3. IR (KBr) υ_{max} : 3025, 2926, 1660, 1588, 1465, 1338, 1202, 1148, 1079, 819, 763, 648 cm⁻¹. HRMS (ESI): m/z: [M + H]⁺ calc. for C₂₅H₂₃N₂O, 367.1805; found, 367.1803.



4-benzyl-6-methyl-6-phenethyl-4*H***-pyrido**[**4**,**3**,**2***-gh*]**phenanthridin-5**(*6H*)**-one** (**3ba**). Performed according to the general procedure, and purified by column chromatography (petroleum ether/1,4-dioxane = 20/1) to afford 60 mg (68%) of **3ba**. White solid, mp 135–137 °C. ¹H NMR (600 MHz, CDCl₃) δ 8.52 (d, *J* = 8.2 Hz, 1H), 8.23 (d, *J* = 8.2 Hz, 1H), 8.20 (d, *J* = 8.1 Hz, 1H), 7.80–7.75 (m, 1H), 7.70–7.63 (m, 2H), 7.36–7.31 (m, 4H), 7.27 (dd, *J* = 8.4, 4.3 Hz, 1H), 7.16 (t, *J* = 7.4 Hz, 2H), 7.12 (d, *J* = 7.9 Hz, 1H), 7.11–7.04 (m, 3H), 5.42 (d, *J* = 36.5 Hz, 2H), 2.92–2.82 (m, 1H), 2.74–2.65 (m, 1H), 2.62–2.52 (m, 1H), 2.43–2.34 (m, 1H), 1.88 (s, 3H). ¹³C NMR (151 MHz, CDCl₃) δ 174.2, 159.3, 145.0, 141.8, 137.9, 136.4, 133.3, 131.7, 129.8, 129.1, 128.9, 128.4, 128.1, 127.3, 126.7, 126.4, 125.7, 122.7, 122.5, 116.2, 112.6, 111.8, 51.6, 46.2, 43.4, 32.0, 29.3. IR (KBr) ν_{max} : 3028, 2947, 1674, 1590, 1463, 1365, 1290, 1131, 817, 755, 698, 652. HRMS (ESI): m/z: [M + Na]⁺ calc. for C₃₁H₂₆N₂ONa, 465.1937; found, 465.1936.



4,6,9-trimethyl-6-phenethyl-4*H***-pyrido**[**4,3,2-***gh*]**phenanthridin-5**(*6H*)**-one** (**3fa**). Performed according to the general procedure, and purified by column chromatography (petroleum ether/1,4-dioxane = 40/1) to afford 52 mg (68%) of **3fa**. White solid, mp 126–128 °C. ¹H NMR (600 MHz, CDCl₃) δ 8.43 (d, *J* = 8.4 Hz, 1H), 8.24 (d, *J* = 8.3 Hz, 1H), 7.98 (s, 1H), 7.80 (t, *J* = 8.1 Hz, 1H), 7.50 (dd, *J* = 8.3, 1.3 Hz, 1H), 7.16 (d, *J* = 7.9 Hz, 1H), 7.12 (t, *J* = 7.4 Hz, 2H), 7.06 (t, *J* = 7.3 Hz, 1H), 7.00 (d, *J* = 7.2 Hz, 2H), 3.55 (s, 3H), 2.85–2.71 (m, 1H), 2.70–2.55 (m, 4H), 2.48–2.36 (m, 1H), 2.33–2.23 (m, 1H), 1.79 (s, 3H). ¹³C NMR (151 MHz, CDCl₃) δ 174.0, 159.5, 145.2, 141.6, 139.4, 138.8, 133.2, 131.7, 129.3, 128.4, 128.0, 125.6, 122.3, 120.3, 115.9, 112.2, 110.2, 51.3, 43.8, 31.9, 29.7, 29.3, 21.6. IR (KBr) ν_{max} : 3027, 2922, 1666, 1587, 1468, 1335, 1195, 1073, 879, 795, 753, 693 cm⁻¹. HRMS (ESI): m/z: [M + H]⁺ calc. for C₂₆H₂₅N₂O, 381.1961; found, 381.1962.



9-methoxy-4,6-dimethyl-6-phenethyl-4*H***-pyrido[4,3,2-***gh***]phenanthridin-5**(6*H*)-one (3ga). Performed according to the general procedure, and purified by column chromatography (petroleum ether/1,4-dioxane = 20/1) to afford 67 mg (84%) of **3ga**. White solid, mp 111–114 °C. ¹H NMR (600 MHz, CDCl₃) δ 8.42 (d, *J* = 9.0 Hz, 1H), 8.17 (d, *J* = 8.3 Hz, 1H), 7.78 (t, *J* = 8.1 Hz, 1H), 7.56 (d, *J* = 2.6 Hz, 1H), 7.30 (dd, *J* = 9.0, 2.7 Hz, 1H), 7.12 (t, *J* = 7.7 Hz, 3H), 7.06 (t, *J* = 7.3 Hz, 1H), 6.99 (d, *J* = 7.2 Hz, 2H), 4.03 (s, 3H), 3.54 (s, 3H), 2.81–2.73 (m, 1H), 2.69–2.62 (m, 1H), 2.47–2.38 (m, 1H), 2.32–2.23 (m, 1H), 1.80 (s, 3H). ¹³C NMR (151 MHz, CDCl₃) δ 173.9, 160.5, 160.0, 146.8, 141.5, 138.8, 133.4, 131.8, 128.3, 128.0, 125.6, 123.7, 118.0, 116.8, 115.6, 111.7, 109.5, 109.2, 55.6, 51.3, 43.8, 31.9, 29.7, 29.2. IR (KBr) ν_{max} : 3025, 2928, 1670, 1614, 1472, 1412, 1337, 1231, 1124, 1029, 801, 750 cm⁻¹. HRMS (ESI): m/z: [M + H]⁺ calc. for C₂₆H₂₅N₂O₂, 397.1911; found, 397.1909.



4,6-dimethyl-6-phenethyl-9-phenoxy-4*H***-pyrido**[**4,3,2-***gh*]**phenanthridin-5**(6*H*)**-one** (**3ha**). Performed according to the general procedure, and purified by column chromatography (petroleum ether/1,4-dioxane = 30/1) to afford 76 mg (83%) of **3ha**. White solid, mp 130–132 °C. ¹H NMR (600 MHz, CDCl₃) δ 8.50 (d, *J* = 9.0 Hz, 1H), 8.20 (d, *J* = 8.2 Hz, 1H), 7.81 (t, *J* = 8.1 Hz, 1H), 7.62 (d, *J* = 2.3 Hz, 1H), 7.47–7.39 (m, 3H), 7.22 (t, *J* = 7.4 Hz, 1H), 7.19 (dd, *J* = 8.6, 0.9 Hz, 2H), 7.15 (d, *J* = 7.8 Hz, 1H), 7.13–7.08 (m, 2H), 7.04 (t, *J* = 7.3 Hz, 1H), 6.97 (d, *J*

= 7.1 Hz, 2H), 3.54 (s, 3H), 2.77–2.68 (m, 1H), 2.66–2.58 (m, 1H), 2.46–2.37 (m, 1H), 2.30–2.22 (m, 1H), 1.76 (s, 3H). ¹³C NMR (151 MHz, CDCl₃) δ 173.9, 160.4, 158.5, 156.4, 146.5, 141.4, 138.9, 133.2, 131.9, 130.0, 128.3, 128.0, 125.6, 124.2, 124.1, 119.9, 119.1, 118.4, 115.9, 115.7, 111.9, 110.1, 51.3, 43.7, 31.8, 29.7, 29.2. IR (KBr) ν_{max} : 3025, 2927, 1672, 1589, 1467, 1335, 1227, 1187, 1074, 972, 750, 696 cm⁻¹. HRMS (ESI): m/z: [M + H]⁺ calc. for C₃₁H₂₇N₂O₂, 459.2067; found, 459.2065.



4,6-dimethyl-6-phenethyl-9-(trifluoromethyl)-4H-pyrido[**4,3,2-***gh*]**phenanthridin-5(***6H***)-one (3ia).** Performed according to the general procedure, and purified by column chromatography (petroleum ether/1,4-dioxane = 20/1) to afford 62 mg (71%) of **3ia**. White solid, mp 110–113 °C. ¹H NMR (600 MHz, CDCl₃) δ 8.63 (d, *J* = 8.6 Hz, 1H), 8.46 (s, 1H), 8.29 (d, *J* = 8.2 Hz, 1H), 7.89 (t, *J* = 8.1 Hz, 1H), 7.84 (dd, *J* = 8.6, 1.6 Hz, 1H), 7.28 (d, *J* = 7.9 Hz, 1H), 7.12–7.05 (m, 2H), 7.05–7.00 (m, 1H), 6.98–6.93 (m, 2H), 3.56 (s, 3H), 2.84–2.76 (m, 1H), 2.72–2.64 (m, 1H), 2.48–2.40 (m, 1H), 2.32–2.25 (m, 1H), 1.80 (s, 3H). ¹³C NMR (151 MHz, CDCl₃) δ 173.6, 161.4, 144.3, 141.2, 139.1, 132.4, 130.9 (q, *J*_{C-F} = 32.8 Hz), 128.3, 128.0, 127.3 (q, *J*_{C-F} = 4.0 Hz), 125.7, 124.9, 124.1 (q, *J*_{C-F} = 272.4 Hz), 123.7, 122.3 (q, *J*_{C-F} = 3.0 Hz), 116.2, 113.0, 111.8, 51.4, 43.8, 31.9, 29.8, 29.3. IR (KBr) ν_{max} : 3026, 2933, 1674, 1593, 1453, 1329, 1172, 1071, 905, 807, 750, 699 cm⁻¹. HRMS (ESI): m/z: [M + H]⁺ calc. for C₂₆H₂₂F₃N₂O, 435.1679; found, 435.1679.



4,6-dimethyl-5-oxo-6-phenethyl-5,6-dihydro-*4H***-pyrido**[**4,3,2***-gh*]**phenanthridine-9-carbonitrile** (3ja). Performed according to the general procedure, and purified by column chromatography (petroleum ether/1,4-dioxane = 8/1) to afford 49 mg (63%) of **3ja**. White solid, mp 142–147 °C. ¹H NMR (600 MHz, CDCl₃) δ 8.60 (d, *J* = 8.5 Hz, 1H), 8.50 (d, *J* = 1.5 Hz, 1H), 8.27 (d, *J* = 8.2 Hz, 1H), 7.92 (t, *J* = 8.1 Hz, 1H), 7.83 (dd, *J* = 8.5, 1.7 Hz, 1H), 7.31 (d, *J* = 7.9 Hz, 1H), 7.07 (t, *J* = 7.3 Hz, 2H), 7.02 (t, *J* = 7.3 Hz, 1H), 6.95 (d, *J* = 7.2 Hz, 2H), 3.56 (s, 3H), 2.84–2.75 (m, 1H), 2.71–2.64 (m, 1H), 2.49–2.41 (m, 1H), 2.31–2.23 (m, 1H), 1.79 (s, 3H). ¹³C NMR (151 MHz, CDCl₃) δ 173.5, 162.1, 144.2, 141.0, 139.2, 134.9, 132.7, 132.1, 128.3, 128.0, 127.9, 125.9, 125.7, 123.9, 118.6, 116.3, 113.1, 112.4, 112.3, 51.5, 43.7, 31.9, 29.8, 29.4. IR (KBr) ν_{max} : 3025, 2929, 2228, 1673, 1590, 1469,

1341, 1289, 1077, 899, 750, 699 cm⁻¹. HRMS (ESI): m/z: $[M + H]^+$ calc. for $C_{26}H_{22}N_3O$, 392.1757; found, 392.1758.



9-fluoro-4,6-dimethyl-6-phenethyl-4*H***-pyrido[4,3,2-***gh***]phenanthridin-5**(6*H*)-**one** (**3ka**). Performed according to the general procedure, and purified by column chromatography (petroleum ether/1,4-dioxane = 30/1) to afford 48 mg (62%) of **3ka**. White solid, mp 128–130 °C. ¹H NMR (600 MHz, CDCl₃) δ 8.51 (dd, *J* = 9.1, 5.9 Hz, 1H), 8.20 (d, *J* = 8.3 Hz, 1H), 7.86–7.78 (m, 2H), 7.44–7.39 (m, 1H), 7.19 (d, *J* = 7.9 Hz, 1H), 7.11 (dd, *J* = 10.2, 4.5 Hz, 2H), 7.04 (dd, *J* = 8.3, 6.3 Hz, 1H), 6.98 (d, *J* = 7.1 Hz, 2H), 3.55 (s, 3H), 2.82–2.75 (m, 1H), 2.69–2.62 (m, 1H), 2.47–2.39 (m, 1H), 2.30–2.23 (m, 1H), 1.78 (s, 3H). ¹³C NMR (151 MHz, CDCl₃) δ 173.7, 163.0 (d, *J*_{C-F} = 248.8 Hz), 161.1, 146.4 (d, *J*_{C-F} = 12.1 Hz), 141.4, 139.0, 133.0, 132.2, 128.3, 128.0, 125.6, 124.5 (d, *J*_{C-F} = 9.7 Hz), 119.4 (d, *J*_{C-F} = 1.9 Hz), 115.78, 115.77 (d, *J*_{C-F} = 24.0 Hz), 114.1 (d, *J*_{C-F} = 20.3 Hz), 112.1 (d, *J*_{C-F} = 0.8 Hz), 110.5, 51.4, 43.7, 31.9, 29.7, 29.3. IR (KBr) ν_{max} : 3027, 2929, 1666, 1590, 1470, 1331, 1223, 1189, 1074, 882, 799, 702 cm⁻¹. HRMS (ESI): m/z: [M + H]⁺ calc. for C₂₅H₂₂FN₂O, 385.1711; found, 385.1712.



9-chloro-4,6-dimethyl-6-phenethyl-4*H***-pyrido[4,3,2-***gh***]phenanthridin-5**(*6H*)-**one** (**3la**). Performed according to the general procedure, and purified by column chromatography (petroleum ether/1,4-dioxane = 30/1) to afford 72 mg (90 %) of **3la**. White solid, mp 124–126 °C. ¹H NMR (600 MHz, CDCl₃) δ 8.45 (d, *J* = 8.8 Hz, 1H), 8.21 (d, *J* = 8.2 Hz, 1H), 8.17 (d, *J* = 2.2 Hz, 1H), 7.84 (t, *J* = 8.1 Hz, 1H), 7.61 (dd, *J* = 8.8, 2.2 Hz, 1H), 7.21 (d, *J* = 7.9 Hz, 1H), 7.11 (dd, *J* = 10.2, 4.5 Hz, 2H), 7.04 (dd, *J* = 8.3, 6.3 Hz, 1H), 6.99–6.95 (m, 2H), 3.55 (s, 3H), 2.81–2.74 (m, 1H), 2.69–2.63 (m, 1H), 2.46–2.39 (m, 1H), 2.30–2.23 (m, 1H), 1.78 (s, 3H). ¹³C NMR (151 MHz, CDCl₃) δ 173.7, 161.1, 145.7, 141.3, 139.0, 134.8, 132.8, 132.2, 128.9, 128.3, 128.0, 127.1, 125.6, 123.9, 121.2, 115.9, 112.4, 110.9, 51.4, 43.7, 31.9, 29.7, 29.3. IR (KBr) υ_{max} : 3023, 2927, 1666, 1587, 1464, 1335, 1241, 1188, 1067, 803, 739, 694 cm⁻¹. HRMS (ESI): m/z: [M + H]⁺ calc. for C₂₅H₂₂ClN₂O, 401.1415; found, 401.1416.



9-bromo-4,6-dimethyl-6-phenethyl-4*H***-pyrido[4,3,2-***gh***]phenanthridin-5**(*6H*)-**one** (**3ma**). Performed according to the general procedure, and purified by column chromatography (petroleum ether/1,4-dioxane = 40/1) to afford 47 mg (53%) of **3ma**. White solid, mp 123–125 °C. ¹H NMR (600 MHz, CDCl₃) δ 8.38 (d, *J* = 8.8 Hz, 1H), 8.35 (d, *J* = 2.0 Hz, 1H), 8.22 (d, *J* = 8.2 Hz, 1H), 7.84 (t, *J* = 8.1 Hz, 1H), 7.74 (dd, *J* = 8.7, 2.1 Hz, 1H), 7.22 (d, *J* = 7.9 Hz, 1H), 7.11 (dd, *J* = 10.2, 4.5 Hz, 2H), 7.04 (t, *J* = 7.3 Hz, 1H), 6.97 (d, *J* = 7.0 Hz, 2H), 3.55 (s, 3H), 2.81–2.73 (m, 1H), 2.69–2.61 (m, 1H), 2.46–2.39 (m, 1H), 2.31–2.22 (m, 1H), 1.78 (s, 3H). ¹³C NMR (151 MHz, CDCl₃) δ 173.7, 161.0, 145.9, 141.3, 139.0, 132.8, 132.2, 132.1, 129.8, 128.3, 128.0, 125.6, 124.0, 123.0, 121.5, 115.8, 112.4, 111.0, 51.4, 43.7, 31.9, 29.7, 29.3. IR (KBr) υ_{max}: 3024, 2927, 1672, 1590, 1464, 1336, 1279, 1136, 1070, 907, 796, 698 cm⁻¹. HRMS (ESI): m/z: [M + H]⁺ calc. for C₂₅H₂₂BrN₂O, 445.0910; found, 445.0912.



4,6,8-trimethyl-6-phenethyl-4*H***-pyrido[4,3,2-***gh***]phenanthridin-5**(*6H*)-**one** (**3na**). Performed according to the general procedure, and purified by column chromatography (petroleum ether/1,4-dioxane = 20/1) to afford 30 mg (39%) of **3na**. White solid, mp 101–103 °C. ¹H NMR (600 MHz, CDCl₃) δ 8.40 (d, *J* = 8.2 Hz, 1H), 8.28 (d, *J* = 8.3 Hz, 1H), 7.80 (t, *J* = 8.1 Hz, 1H), 7.64 (d, *J* = 7.0 Hz, 1H), 7.57–7.53 (m, 1H), 7.19 (d, *J* = 7.8 Hz, 1H), 7.13 (t, *J* = 7.4 Hz, 2H), 7.06 (t, *J* = 7.3 Hz, 1H), 7.01 (d, *J* = 7.1 Hz, 2H), 3.57 (s, 3H), 2.90 (s, 3H), 2.88–2.82 (m, 1H), 2.70–2.63 (m, 1H), 2.48–2.40 (m, 1H), 2.33–2.26 (m, 1H), 1.77 (s, 3H). ¹³C NMR (151 MHz, CDCl₃) δ 174.1, 157.8, 143.6, 141.8, 138.8, 137.7, 133.5, 131.5, 129.6, 128.3, 128.0, 126.2, 125.6, 122.4, 120.3, 116.3, 112.2, 110.4, 51.6, 43.8, 32.0, 30.1, 29.7, 18.4. IR (KBr) υ_{max} : 3022, 2923, 1665, 1577, 1462, 1336, 1286, 1111, 1052, 755, 748, 699 cm⁻¹. HRMS (ESI): m/z: [M + H]⁺ calc. for C₂₆H₂₅N₂O, 381.1961; found, 381.1960.



4,6,10-trimethyl-6-phenethyl-4*H***-pyrido**[**4,3,2-***gh*]**phenanthridin-5(6***H***)-one (3na').** Performed according to the general procedure, and purified by column chromatography (petroleum ether/1,4-dioxane = 20/1) to afford 32 mg

(42%) of **3na'**. White solid, mp 153–155 °C. ¹H NMR (600 MHz, CDCl₃) δ 8.32 (s, 1H), 8.27 (d, *J* = 8.3 Hz, 1H), 8.07 (d, *J* = 8.3 Hz, 1H), 7.80 (t, *J* = 8.1 Hz, 1H), 7.60 (dd, *J* = 8.3, 1.4 Hz, 1H), 7.18 (d, *J* = 7.9 Hz, 1H), 7.12 (t, *J* = 7.5 Hz, 2H), 7.05 (t, *J* = 7.3 Hz, 1H), 6.99 (d, *J* = 7.3 Hz, 2H), 3.55 (s, 3H), 2.82–2.72 (m, 1H), 2.68–2.59 (m, 4H), 2.46–2.37 (m, 1H), 2.33–2.22 (m, 1H), 1.79 (s, 3H). ¹³C NMR (151 MHz, CDCl₃) δ 174.0, 158.4, 143.4, 141.6, 138.8, 136.5, 132.9, 131.4, 130.9, 129.6, 128.4, 128.0, 125.6, 122.5, 122.0, 116.0, 112.5, 110.5, 51.2, 43.8, 31.9, 29.7, 29.2, 22.0. IR (KBr) ν_{max} : 3022, 2968, 1660, 1568, 1460, 1342, 1296, 1149, 1072, 832, 772, 740 cm⁻¹. HRMS (ESI): m/z: [M + H]⁺ calc. for C₂₆H₂₅N₂O, 381.1961; found, 381.1962.



11-methoxy-4,6-dimethyl-6-phenethyl-4*H***-pyrido[4,3,2-***gh***]phenanthridin-5**(6*H*)-**one** (3oa). Performed according to the general procedure, and purified by column chromatography (petroleum ether/1,4-dioxane = 20/1) to afford 56 mg (71%) of **3oa**. White solid, mp 174–176 °C. ¹H NMR (600 MHz, CDCl₃) δ 9.27 (d, *J* = 8.6 Hz, 1H), 7.86–7.77 (m, 2H), 7.69 (t, *J* = 8.0 Hz, 1H), 7.22 (d, *J* = 7.9 Hz, 1H), 7.16–7.10 (m, 3H), 7.06 (t, *J* = 7.2 Hz, 1H), 7.01 (d, *J* = 7.3 Hz, 2H), 4.15 (s, 3H), 3.56 (s, 3H), 2.81–2.73 (m, 1H), 2.67–2.58 (m, 1H), 2.47–2.37 (m, 1H), 2.33–2.24 (m, 1H), 1.78 (s, 3H). ¹³C NMR (151 MHz, CDCl₃) δ 173.7, 159.8, 158.3, 147.1, 141.7, 138.2, 133.1, 131.4, 128.6, 128.4, 128.0, 125.6, 122.6, 122.1, 113.6, 112.9, 110.6, 107.5, 55.9, 51.0, 43.6, 31.8, 29.8, 29.1. IR (KBr) ν_{max} : 3026, 2929, 1666, 1581, 1459, 1341, 1257, 1068, 959, 828, 737, 697 cm⁻¹. HRMS (ESI): m/z: [M + H]⁺ calc. for C₂₆H₂₅N₂O₂, 397.1911; found, 397.1913.



4,6,8,10-tetramethyl-6-phenethyl-4*H***-pyrido**[**4,3,2***-gh*]**phenanthridin-5**(*6H*)**-one** (3pa). Performed according to the general procedure, and purified by column chromatography (petroleum ether/1,4-dioxane = 40/1) to afford 53 mg (67%) of **3pa**. White solid, mp 141–143 °C. ¹H NMR (600 MHz, CDCl₃) δ 8.25 (d, *J* = 8.3 Hz, 1H), 8.17 (s, 1H), 7.76 (t, *J* = 8.1 Hz, 1H), 7.47 (s, 1H), 7.17–7.10 (m, 3H), 7.06 (t, *J* = 7.3 Hz, 1H), 7.01 (d, *J* = 7.2 Hz, 2H), 3.55 (s, 3H), 2.89–2.79 (m, 4H), 2.69–2.62 (m, 1H), 2.59 (s, 3H), 2.48–2.36 (m, 1H), 2.32–2.25 (m, 1H), 1.76 (s, 3H). ¹³C NMR (151 MHz, CDCl₃) δ 174.1, 156.7, 142.0, 141.9, 138.7, 137.3, 135.9, 133.2, 131.5, 131.2, 128.3, 128.0, 125.5, 122.3, 119.8, 116.3, 112.3, 110.2, 51.4, 43.8, 31.9, 30.0, 29.6, 21.9, 18.2. IR (KBr) ν_{max} : 3025, 2924, 1671, 1588, 1465, 1337, 1283, 1138, 852, 821, 748, 697 cm⁻¹. HRMS (ESI): m/z: [M + H]⁺ calc. for C₂₇H₂₇N₂O, 395.2118; found, 395.2119.



8,10-dichloro-4,6-dimethyl-6-phenethyl-4*H***-pyrido[4,3,2-***gh***]phenanthridin-5**(6*H*)-one (3qa). Performed according to the general procedure, and purified by column chromatography (petroleum ether/1,4-dioxane = 20/1) to afford 62 mg (71%) of **3qa**. White solid, mp 150–152 °C. ¹H NMR (600 MHz, CDCl₃) δ 8.39 (d, *J* = 2.1 Hz, 1H), 8.15 (d, *J* = 8.3 Hz, 1H), 7.86 (dd, *J* = 11.4, 5.0 Hz, 2H), 7.26 (t, *J* = 3.9 Hz, 2H), 7.08 (t, *J* = 7.4 Hz, 2H), 7.01 (dd, *J* = 13.2, 7.2 Hz, 3H), 3.57 (s, 3H), 2.94–2.86 (m, 1H), 2.71–2.61 (m, 1H), 2.52–2.39 (m, 1H), 2.37–2.25 (m, 1H), 1.78 (s, 3H). ¹³C NMR (151 MHz, CDCl₃) δ 173.6, 160.6, 141.4, 139.9, 139.2, 135.4, 132.5, 132.1, 131.7, 129.6, 128.4, 128.0, 125.6, 124.8, 121.0, 116.1, 112.6, 111.7, 51.8, 43.4, 32.0, 29.9, 29.8. IR (KBr) ν_{max} : 3027, 2933, 1667, 1587, 1454, 1335, 1153, 1110, 1047, 819, 745, 702 cm⁻¹. HRMS (ESI): m/z: [M + H]⁺ calc. for C₂₅H₂₁Cl₂N₂O, 435.1025; found, 435.1027.



8,9,10-trifluoro-4,6-dimethyl-6-phenethyl-4*H***-pyrido[4,3,2-***gh***]phenanthridin-5(6***H***)-one (3ra). Performed according to the general procedure, and purified by column chromatography (petroleum ether/1,4-dioxane = 20/1) to afford 59 mg (70%) of 3ra**. White solid, mp 135–137 °C. ¹H NMR (600 MHz, CDCl₃) δ 8.04 (t, *J* = 9.6 Hz, 2H), 7.87 (t, *J* = 8.1 Hz, 1H), 7.25 (s, 1H), 7.07 (t, *J* = 7.5 Hz, 2H), 7.01 (t, *J* = 7.1 Hz, 1H), 6.96 (d, *J* = 7.6 Hz, 2H), 3.56 (s, 3H), 2.88–2.80 (m, 1H), 2.71–2.63 (m, 1H), 2.49–2.43 (m, 1H), 2.32–2.24 (m, 1H), 1.80 (s, 3H). ¹³C NMR (151 MHz, CDCl₃) δ 173.5, 160.8, 150.0 (ddd, *J*_{C-F} = 250.6, 11.5, 2.7 Hz), 146.5 (ddd, *J*_{C-F} = 13.2, 9.0, 4.6 Hz), 141.1, 140.3 (ddd, *J*_{C-F} = 253.7, 17.5, 13.7 Hz), 139.3, 132.74, 132.68, 131.8 (d, *J*_{C-F} = 1.9 Hz), 128.3, 127.9, 125.6, 119.2 (d, *J*_{C-F} = 8.0 Hz), 115.9, 112.6, 111.6, 103.7 (dd, *J*_{C-F} = 18.9, 4.6 Hz), 51.6, 43.6, 31.9, 29.8, 29.5. IR (KBr) ν_{max} : 3025, 2924, 1671, 1588, 1465, 1337, 1283, 1138, 852, 821, 748, 697 cm⁻¹. HRMS (ESI): m/z: [M + H]⁺ calc. for C₂₅H₂₀F₃N₂O, 421.1522; found, 421.1525.



4,6-dimethyl-6-phenethyl-4H-benzo[a]pyrido[4,3,2-gh]phenanthridin-5(6H)-one (3sa). Performed according to

the general procedure, and purified by column chromatography (petroleum ether/1,4-dioxane = 20/1) to afford 61 mg (73%) of **3sa**. White solid, mp 133–135 °C. ¹H NMR (600 MHz, CDCl₃) δ 9.06 (d, *J* = 8.4 Hz, 1H), 8.76 (d, *J* = 8.5 Hz, 1H), 8.09 (d, *J* = 8.7 Hz, 1H), 8.05 (d, *J* = 8.8 Hz, 2H), 7.84 (t, *J* = 8.2 Hz, 1H), 7.72 (t, *J* = 7.6 Hz, 1H), 7.66 (t, *J* = 7.4 Hz, 1H), 7.21 (d, *J* = 7.8 Hz, 1H), 7.08 (t, *J* = 7.5 Hz, 2H), 7.02 (t, *J* = 7.2 Hz, 1H), 6.98 (d, *J* = 7.5 Hz, 2H), 3.60 (s, 3H), 2.89–2.77 (m, 1H), 2.74–2.62 (m, 1H), 2.51–2.40 (m, 1H), 2.35–2.24 (m, 1H), 1.83 (s, 3H). ¹³C NMR (151 MHz, CDCl₃) δ 173.8, 158.7, 145.0, 141.5, 138.6, 133.12, 133.07, 131.3, 130.0, 129.8, 128.8, 128.32, 128.30, 128.0, 127.5, 126.6, 126.2, 125.5, 120.8, 119.1, 113.7, 109.8, 51.0, 43.8, 31.9, 29.8, 29.2. IR (KBr) ν_{max} : 3025, 2929, 1671, 1579, 1454, 1330, 1148, 1061, 837, 750, 669, 643 cm⁻¹. HRMS (ESI): m/z: [M + H]⁺ calc. for C₂₉H₂₅N₂O, 417.1961; found, 417.1961.



4,6-dimethyl-6-phenethyl-4*H***-dibenzo[***a,c***]pyrido[4,3,2-***gh***]phenanthridin-5(6***H***)-one (3ta). Performed according to the general procedure, and purified by column chromatography (petroleum ether/1,4-dioxane = 15/1) to afford 77 mg (83%) of 3ta**. White solid, mp 120–122 °C. ¹H NMR (600 MHz, CDCl₃) δ 9.45–9.40 (m, 1H), 8.89 (d, *J* = 8.0 Hz, 1H), 8.77 (d, *J* = 7.6 Hz, 1H), 8.67 (dd, *J* = 6.4, 3.0 Hz, 1H), 8.61 (d, *J* = 8.6 Hz, 1H), 7.81–7.76 (m, 3H), 7.75–7.71 (m, 1H), 7.71–7.67 (m, 1H), 7.15 (d, *J* = 7.7 Hz, 1H), 7.07 (t, *J* = 7.2 Hz, 2H), 7.04–6.96 (m, 3H), 3.61 (s, 3H), 3.00–2.92 (m, 1H), 2.80–2.72 (m, 1H), 2.56–2.45 (m, 1H), 2.42–2.30 (m, 1H), 1.89 (s, 3H). ¹³C NMR (151 MHz, CDCl₃) δ 173.9, 157.9, 142.3, 141.6, 138.5, 133.2, 131.2, 131.0, 130.9, 130.8, 128.8, 128.7, 128.0, 127.5, 127.0, 126.4, 125.6, 125.5, 123.7, 122.3, 121.0, 117.9, 114.3, 109.3, 51.3, 44.0, 32.1, 29.7. IR (KBr) ν_{max} : 3025, 2928, 1671, 1580, 1566, 1452, 1334, 1229, 1082, 826, 759, 699 cm⁻¹. HRMS (ESI): m/z: [M + H]⁺ calc. for C₃₃H₂₇N₂O, 467.2118; found, 467.2119.



6-benzyl-4-methyl-6-phenethyl-4*H***-pyrido**[**4**,**3**,**2**-*gh*]**phenanthridin-5**(6*H*)**-one** (**3ua**). Performed according to the general procedure, and purified by column chromatography (petroleum ether/1,4-dioxane = 30/1) to afford 53 mg (60%) of **3ua**. White solid, mp 193–195 °C. ¹H NMR (600 MHz, CDCl₃) δ 8.53 (d, *J* = 8.0 Hz, 1H), 8.28 (dd, *J* = 8.2, 0.7 Hz, 1H), 8.15 (d, *J* = 8.2 Hz, 1H), 7.85–7.80 (m, 1H), 7.72–7.67 (m, 1H), 7.62 (t, *J* = 8.1 Hz, 1H), 7.14 (t, *J* = 7.4 Hz, 2H), 7.06 (dd, *J* = 16.4, 7.2 Hz, 3H), 6.82 (d, *J* = 7.6 Hz, 2H), 6.75 (t, *J* = 7.6 Hz, 2H), 6.52 (d, *J* = 7.2

Hz, 2H), 3.52 (q, J = 12.5 Hz, 2H), 3.34 (s, 3H), 3.14–3.07 (m, 1H), 2.93–2.86 (m, 1H), 2.49–2.41 (m, 1H), 2.34–2.27 (m, 1H). ¹³C NMR (151 MHz, CDCl₃) δ 172.4, 158.3, 145.0, 141.7, 138.2, 136.5, 132.3, 131.5, 129.9, 129.2, 129.1, 128.4, 128.0, 127.3, 126.6, 126.2, 125.6, 122.62, 122.60, 115.7, 114.0, 110.2, 57.9, 51.1, 42.7, 31.9, 29.2. IR (KBr) v_{max} : 3025, 2933, 1654, 1584, 1465, 1360, 1287, 1075, 901, 741, 660, 595. HRMS (ESI): m/z: [M + Na]⁺ calc. for C₃₁H₂₆N₂ONa, 465.1937; found, 465.1936.



4-methyl-6-phenethyl-6-phenyl-4*H***-pyrido[4,3,2-***gh***]phenanthridin-5(6***H***)-one (3va).** Performed according to the general procedure, and purified by column chromatography (petroleum ether/1,4-dioxane = 30/1) to afford 56 mg (65%) of **3va**. White solid, mp 179–182 °C. ¹H NMR (600 MHz, CDCl₃) δ 8.58 (d, *J* = 7.9 Hz, 1H), 8.32 (d, *J* = 8.2 Hz, 1H), 8.23 (d, *J* = 8.1 Hz, 1H), 7.85 (t, *J* = 8.1 Hz, 1H), 7.81–7.77 (m, 1H), 7.72–7.68 (m, 1H), 7.23 (dd, *J* = 9.7, 6.2 Hz, 5H), 7.18–7.11 (m, 5H), 7.11–7.08 (m, 1H), 3.63 (s, 3H), 3.43–3.35 (m, 1H), 3.25–3.17 (m, 1H), 2.66–2.59 (m, 1H), 2.58–2.51 (m, 1H). ¹³C NMR (151 MHz, CDCl₃) δ 171.7, 157.7, 145.0, 144.2, 142.3, 138.7, 133.2, 131.9, 130.2, 129.2, 128.6, 128.4, 128.1, 127.0, 126.9, 126.7, 125.7, 122.7, 122.5, 116.3, 113.3, 111.0, 59.9, 40.9, 32.4, 30.1. IR (KBr) υ_{max}: 2938, 1664, 1638, 1580, 1461, 1355, 1282, 1081, 889, 823, 748, 613. HRMS (ESI): m/z: [M + Na]⁺ calc. for C₃₀H₂₄N₂ONa, 451.1781; found, 451.1782.



6-(2-iodophenethyl)-4,6-dimethyl-4*H***-pyrido[4,3,2-***gh***]phenanthridin-5(***6H***)-one (3ab).** Performed according to the general procedure, and purified by column chromatography (petroleum ether/1,4-dioxane = 20/1) to afford 72 mg (73%) of **3ab**. White solid, mp 115–117 °C. ¹H NMR (600 MHz, CDCl₃) δ 8.53 (d, *J* = 8.0 Hz, 1H), 8.28 (d, *J* = 8.2 Hz, 1H), 8.18 (dd, *J* = 8.1, 0.6 Hz, 1H), 7.83 (t, *J* = 8.1 Hz, 1H), 7.78–7.73 (m, 1H), 7.67–7.61 (m, 2H), 7.22 (d, *J* = 7.9 Hz, 1H), 7.11–7.06 (m, 1H), 7.04 (dd, *J* = 7.6, 1.7 Hz, 1H), 6.75–6.70 (m, 1H), 3.61 (s, 3H), 2.75–2.67 (m, 1H), 2.62–2.55 (m, 1H), 2.53–2.46 (m, 1H), 2.44–2.37 (m, 1H), 1.83 (s, 3H). ¹³C NMR (151 MHz, CDCl₃) δ 173.7, 159.1, 144.9, 144.2, 139.2, 138.8, 133.2, 131.7, 129.9, 129.5, 129.1, 128.1, 127.5, 126.5, 122.7, 122.5, 116.1, 112.4, 110.7, 100.2, 51.2, 42.7, 36.8, 29.8, 28.2. IR (KBr) υ_{max} : 2929, 1671, 1589, 1464, 1338, 1294, 1149, 1070, 1010, 751, 616, 495 cm⁻¹. HRMS (ESI): m/z: [M + Na]⁺ calc. for C₂₅H₂₁IN₂ONa, 515.0591; found, 515.0592.



6-(2-methoxyphenethyl)-4,6-dimethyl-4H-pyrido[**4,3,2**-*gh*]**phenanthridin-5(6H)-one** (3ac). Performed according to the general procedure, and purified by column chromatography (petroleum ether/1,4-dioxane = 30/1) to afford 30 mg (38%) of **3ac**. White solid, mp 124–126 °C. ¹H NMR (600 MHz, CDCl₃) δ 8.53 (d, *J* = 7.9 Hz, 1H), 8.25 (d, *J* = 8.2 Hz, 1H), 8.15 (dd, *J* = 8.2, 0.8 Hz, 1H), 7.80 (t, *J* = 8.1 Hz, 1H), 7.77–7.73 (m, 1H), 7.67–7.61 (m, 1H), 7.18 (d, *J* = 7.8 Hz, 1H), 6.96 (td, *J* = 7.9, 1.7 Hz, 1H), 6.84 (dd, *J* = 7.4, 1.5 Hz, 1H), 6.62 (td, *J* = 7.4, 0.8 Hz, 1H), 6.55 (d, *J* = 8.1 Hz, 1H), 3.54 (s, 3H), 3.51 (s, 3H), 2.79–2.71 (m, 1H), 2.63–2.55 (m, 1H), 2.50–2.42 (m, 1H), 2.36–2.28 (m, 1H), 1.81 (s, 3H). ¹³C NMR (151 MHz, CDCl₃) δ 174.0, 159.7, 157.2, 145.0, 139.0, 133.1, 131.5, 129.8, 129.62, 129.57, 128.9, 126.8, 126.4, 122.7, 122.5, 119.9, 115.8, 112.5, 110.5, 109.7, 55.0, 51.2, 42.5, 29.7, 28.7, 26.1. IR (KBr) ν_{max} : 2997, 2897, 1663, 1588, 1465, 1338, 1237, 1116, 1072, 820, 763, 649 cm⁻¹. HRMS (ESI): m/z: [M + Na]⁺ calc. for C₂₆H₂₄N₂O₂Na, 419.1730; found, 419.1732.



4,6-dimethyl-6-(2-(*o***-tolyloxy)ethyl)-4***H***-pyrido[4,3,2**-*gh*]**phenanthridin-5(***6H***)-one (3ac').** Performed according to the general procedure, and purified by column chromatography (petroleum ether/1,4-dioxane = 30/1) to afford 33 mg (42%) of **3ac'**. White solid, mp 125–127 °C. ¹H NMR (600 MHz, CDCl₃) δ 8.52 (d, *J* = 8.1 Hz, 1H), 8.26 (d, *J* = 8.3 Hz, 1H), 8.13 (d, *J* = 8.1 Hz, 1H), 7.79 (t, *J* = 8.1 Hz, 1H), 7.77–7.72 (m, 1H), 7.67–7.61 (m, 1H), 7.17 (d, *J* = 7.9 Hz, 1H), 6.93 (t, *J* = 7.8 Hz, 1H), 6.90 (d, *J* = 7.2 Hz, 1H), 6.67 (t, *J* = 7.3 Hz, 1H), 6.54 (d, *J* = 8.2 Hz, 1H), 3.96–3.84 (m, 2H), 3.57 (s, 3H), 3.14–3.06 (m, 1H), 3.02–2.94 (m, 1H), 1.80 (s, 3H), 1.71 (s, 3H). ¹³C NMR (151 MHz, CDCl₃) δ 173.6, 159.1, 156.7, 144.9, 138.8, 133.4, 131.7, 130.2, 129.7, 129.1, 126.6, 126.4, 126.3, 122.7, 122.5, 119.8, 116.0, 112.1, 110.6, 110.5, 64.6, 49.3, 39.5, 31.0, 29.8, 15.7. IR (KBr) ν_{max} : 3027, 2927, 1673, 1589, 1464, 1339, 1239, 1121, 1076, 819, 751, 646 cm⁻¹. HRMS (ESI): m/z: [M + Na]⁺ calc. for C₂₆H₂₄N₂O₂Na, 419.1730; found, 419.1728.



4,6-dimethyl-6-(3-methylphenethyl)-4H-pyrido[4,3,2-gh]phenanthridin-5(6H)-one (3ad). Performed according

to the general procedure, and purified by column chromatography (petroleum ether/1,4-dioxane = 20/1) to afford 40 mg (53%) of **3ad**. White solid, mp 121–123 °C. ¹H NMR (600 MHz, CDCl₃) δ 8.54 (d, *J* = 7.7 Hz, 1H), 8.27 (d, *J* = 8.2 Hz, 1H), 8.17 (dd, *J* = 8.2, 0.8 Hz, 1H), 7.81 (t, *J* = 8.1 Hz, 1H), 7.79–7.50 (m, 1H), 7.68–7.63 (m, 1H), 7.19 (d, *J* = 7.8 Hz, 1H), 6.97 (t, *J* = 7.5 Hz, 1H), 6.82 (d, *J* = 7.5 Hz, 1H), 6.80–6.74 (m, 2H), 3.56 (s, 3H), 2.84–2.76 (m, 1H), 2.69–2.61 (m, 1H), 2.45–2.37 (m, 1H), 2.30–2.22 (m, 1H), 2.14 (s, 3H), 1.80 (s, 3H). ¹³C NMR (151 MHz, CDCl₃) δ 174.0, 159.6, 145.0, 141.3, 138.8, 137.5, 133.1, 131.7, 129.8, 129.2, 129.1, 127.8, 126.5, 126.3, 125.4, 122.6, 122.5, 116.0, 112.4, 110.6, 51.3, 43.8, 31.8, 29.7, 29.3, 21.2. IR (KBr) ν_{max} : 2933, 1667, 1638, 1585, 1459, 1352, 1211, 1153, 1077, 860, 753, 648. HRMS (ESI): m/z: [M + H]⁺ calc. for C₂₆H₂₅N₂O, 381.1961; found, 381.1962.



6-(3-chlorophenethyl)-4,6-dimethyl-4*H***-pyrido[4,3,2-***gh***]phenanthridin-5(6***H***)-one (3ae).** Performed according to the general procedure, and purified by column chromatography (petroleum ether/1,4-dioxane = 30/1) to afford 58 mg (72%) of **3ae**. White solid, mp 104–106 °C. ¹H NMR (600 MHz, CDCl₃) δ 8.53 (d, *J* = 8.0 Hz, 1H), 8.27 (d, *J* = 8.2 Hz, 1H), 8.17 (dd, *J* = 8.2, 0.8 Hz, 1H), 7.82 (t, *J* = 8.1 Hz, 1H), 7.80–7.75 (m, 1H), 7.69–7.63 (m, 1H), 7.20 (d, *J* = 7.9 Hz, 1H), 7.02–6.96 (m, 2H), 6.94 (s, 1H), 6.90–6.85 (m, 1H), 3.56 (s, 3H), 2.87–2.78 (m, 1H), 2.70–2.60 (m, 1H), 2.47–2.38 (m, 1H), 2.34–2.25 (m, 1H), 1.78 (s, 3H). ¹³C NMR (151 MHz, CDCl₃) δ 173.7, 159.2, 145.0, 143.5, 138.7, 133.6, 133.2, 131.8, 129.8, 129.14, 129.12, 128.5, 126.63, 126.61, 125.7, 122.6, 122.5, 116.1, 112.3, 110.7, 51.2, 42.9, 31.7, 29.70, 29.69. IR (KBr) υ_{max}: 2932, 1671, 1590, 1464, 1357, 1201, 1148, 1073, 865, 759, 684, 647 cm⁻¹. HRMS (ESI): m/z: [M + H]⁺ calc. for C₂₅H₂₂ClN₂O, 401.1415; found, 401.1416.



3-(2-(4,6-dimethyl-5-oxo-5,6-dihydro-*4H***-pyrido**[4,3,2-*gh*]**phenanthridin-6-yl**)**ethyl**)**benzonitrile** (3af). Performed according to the general procedure, and purified by column chromatography (petroleum ether/1,4-dioxane = 20/1) to afford 54 mg (69%) of **3af**. White solid, mp 115–117 °C. ¹H NMR (600 MHz, CDCl₃) δ 8.54 (d, J = 8.1 Hz, 1H), 8.29 (d, J = 8.3 Hz, 1H), 8.16 (d, J = 7.8 Hz, 1H), 7.85 (t, J = 8.1 Hz, 1H), 7.82–7.76 (m, 1H), 7.71–7.65 (m, 1H), 7.27 (d, J = 7.8 Hz, 1H), 7.23 (dd, J = 7.8, 4.0 Hz, 2H), 7.20 (s, 1H), 7.14 (t, J = 7.7 Hz, 1H), 3.58 (s, 3H), 2.93–2.84 (m, 1H), 2.73–2.65 (m, 1H), 2.55–2.47 (m, 1H), 2.41–2.34 (m, 1H), 1.76 (s, 3H). ¹³C NMR (151 MHz, CDCl₃) δ 173.6, 159.0, 144.9, 142.9, 138.6, 133.2, 133.0, 131.93, 131.89, 129.7, 129.31, 129.27, 128.6,

126.8, 122.6, 122.5, 118.9, 116.2, 112.3, 111.8, 110.8, 51.2, 42.2, 31.7, 30.1, 29.8. IR (KBr) ν_{max} : 2931, 2228, 1670, 1589, 1464, 1339, 1255, 1149, 1072, 916, 761, 689 cm⁻¹. HRMS (ESI): m/z: [M + H]⁺ calc. for C₂₆H₂₂N₃O, 392.1757; found, 392.1759.



6-(3-methoxyphenethyl)-4,6-dimethyl-4*H***-pyrido[4,3,2-***gh***]phenanthridin-5(6***H***)-one (3ag). Performed according to the general procedure, and purified by column chromatography (petroleum ether/1,4-dioxane = 30/1) to afford 29 mg (37%) of 3ag**. White solid, mp 123–125 °C. ¹H NMR (600 MHz, CDCl₃) δ 8.54 (d, *J* = 8.1 Hz, 1H), 8.28 (d, *J* = 8.3 Hz, 1H), 8.17 (d, *J* = 8.1 Hz, 1H), 7.82 (t, *J* = 8.1 Hz, 1H), 7.77 (dd, *J* = 11.1, 4.0 Hz, 1H), 7.66 (dd, *J* = 11.2, 3.9 Hz, 1H), 7.20 (d, *J* = 7.9 Hz, 1H), 7.00 (t, *J* = 7.8 Hz, 1H), 6.60–6.55 (m, 2H), 6.51 (s, 1H), 3.66 (s, 3H), 3.56 (s, 3H), 2.85–2.76 (m, 2H), 2.70–2.61 (m, 1H), 2.47–2.39 (m, 1H), 2.31–2.24 (m, 2H), 1.79 (s, 3H). ¹³C NMR (151 MHz, CDCl₃) δ 173.9, 159.5, 159.2, 145.0, 143.1, 138.8, 133.2, 131.7, 129.8, 129.1, 128.9, 126.6, 122.6, 122.5, 120.8, 116.0, 113.7, 112.4, 111.3, 110.7, 55.0, 51.3, 43.5, 32.0, 29.7, 29.4. IR (KBr) υ_{max} : 2996, 2929, 1662, 1587, 1450, 1336, 1276, 1153, 1054, 858, 764, 688 cm⁻¹. HRMS (ESI): m/z: [M + Na]⁺ calc. for C₂₆H₂₄N₂O₂Na, 419.1730; found, 419.1728.



4,6-dimethyl-6-(2-(*m***-tolyloxy)ethyl)-4***H***-pyrido[4,3,2-***gh***]phenanthridin-5(6***H***)-one (3ag'). Performed according to the general procedure, and purified by column chromatography (petroleum ether/1,4-dioxane = 30/1) to afford 31 mg (39%) of 3ag'**. White solid, mp 123–125 °C. ¹H NMR (600 MHz, CDCl₃) δ 8.52 (d, *J* = 8.1 Hz, 1H), 8.25 (d, *J* = 8.3 Hz, 1H), 8.11 (d, *J* = 8.1 Hz, 1H), 7.78 (t, *J* = 8.1 Hz, 1H), 7.76–7.70 (m, 1H), 7.66–7.61 (m, 1H), 7.15 (d, *J* = 7.9 Hz, 1H), 6.90 (t, *J* = 7.9 Hz, 1H), 6.55 (d, *J* = 7.4 Hz, 1H), 6.23 (dd, *J* = 8.2, 2.2 Hz, 1H), 6.14 (s, 1H), 3.90–3.85 (m, 1H), 3.39–3.73 (m, 1H), 3.04–3.97 (m, 1H), 2.94–2.87 (m, 1H), 2.11 (s, 3H), 1.83 (s, 3H). ¹³C NMR (151 MHz, CDCl₃) δ 173.8, 159.4, 158.3, 144.8, 138.89, 138.85, 133.2, 131.7, 129.7, 129.0, 128.7, 126.5, 122.7, 122.5, 121.1, 115.9, 114.8, 112.2, 110.9, 110.6, 64.4, 49.2, 40.7, 30.1, 29.8, 21.4. IR (KBr) ν_{max} : 2946, 2889, 1665, 1587, 1467, 1338, 1268, 1170, 1080, 819, 764, 690 cm⁻¹. HRMS (ESI): m/z: [M + Na]⁺ calc. for C₂₆H₂₄N₂O₂Na, 419.1730; found, 419.1731.



6-(4-fluorophenethyl)-4,6-dimethyl-4*H***-pyrido[4,3,2-***gh***]phenanthridin-5(6***H***)-one (3ah). Performed according to the general procedure, and purified by column chromatography (petroleum ether/1,4-dioxane = 30/1) to afford 55 mg (72%) of 3ah**. White solid, mp 106–108 °C. ¹H NMR (600 MHz, CDCl₃) δ 8.54 (d, *J* = 8.0 Hz, 1H), 8.27 (d, *J* = 8.2 Hz, 1H), 8.17 (dd, *J* = 8.2, 0.7 Hz, 1H), 7.82 (t, *J* = 8.1 Hz, 1H), 7.80–7.75 (m, 1H), 7.69–7.64 (m, 1H), 7.19 (d, *J* = 7.8 Hz, 1H), 6.95–6.87 (m, 2H), 6.80–6.72 (m, 2H), 3.55 (s, 3H), 2.84–2.76 (m, 1H), 2.69–2.59 (m, 1H), 2.45–2.36 (m, 1H), 2.31–2.23 (m, 1H), 1.78 (s, 3H). ¹³C NMR (151 MHz, CDCl₃) δ 173.8, 161.0 (d, *J*_{C-F} = 243.1 Hz), 159.4, 145.0, 138.7, 137.1 (d, *J*_{C-F} = 3.1 Hz), 133.2, 131.8, 129.8, 129.7 (d, *J*_{C-F} = 7.7 Hz), 129.1, 126.6, 122.6, 122.5, 116.1, 114.6 (d, *J*_{C-F} = 21.0 Hz), 112.4, 110.7, 51.2, 43.5, 31.1, 29.7, 29.6. IR (KBr) ν_{max} : 2931, 2228, 1670, 1589, 1464, 1339, 1255, 1149, 1072, 916, 761, 689 cm⁻¹. HRMS (ESI): m/z: [M + H]⁺ calc. for C₂₅H₂₂FN₂O, 385.1711; found, 385.1710.



4-(2-(4,6-dimethyl-5-oxo-5,6-dihydro-4*H***-pyrido[4,3,2-***gh***]phenanthridin-6-yl)ethyl)phenyl acetate (3ai). Performed according to the general procedure, and purified by column chromatography (petroleum ether/1,4-dioxane = 30/1) to afford 40 mg (47%) of 3ai**. White solid, mp 113–115 °C. ¹H NMR (600 MHz, CDCl₃) δ 8.54 (d, J = 8.0 Hz, 1H), 8.28 (d, J = 8.2 Hz, 1H), 8.17 (d, J = 8.1 Hz, 1H), 7.82 (t, J = 8.1 Hz, 1H), 7.80–7.75 (m, 1H), 7.68–7.64 (m, 1H), 7.19 (d, J = 7.8 Hz, 1H), 6.99 (d, J = 8.5 Hz, 2H), 6.83 (d, J = 8.5 Hz, 2H), 3.53 (s, 3H), 2.85–2.76 (m, 1H), 2.72–2.64 (m, 1H), 2.44–2.36 (m, 1H), 2.33–2.26 (m, 1H), 2.24 (d, J = 9.1 Hz, 3H), 1.78 (s, 3H). ¹³C NMR (151 MHz, CDCl₃) δ 173.8, 169.6, 159.4, 148.5, 145.0, 139.1, 138.8, 133.1, 131.8, 129.8, 129.3, 129.1, 126.6, 122.6, 122.5, 121.0, 116.0, 112.4, 110.7, 51.2, 43.2, 31.3, 29.7, 29.5, 21.1. IR (KBr) υ_{max} : 3033, 2926, 1665, 1592, 1465, 1336, 1291, 1153, 1075, 833, 761, 645. HRMS (ESI): m/z: [M + H]⁺ calc. for C₂₇H₂₅N₂O₃, 425.1860; found, 425.1861.



6-(4-bromophenethyl)-4,6-dimethyl-4*H***-pyrido**[**4,3,2***-gh*]**phenanthridin-5(6***H***)-one (3aj).** Performed according to the general procedure, and purified by column chromatography (petroleum ether/1,4-dioxane = 30/1) to afford 63

mg (71%) of **3aj**. White solid, mp 135–137 °C. ¹H NMR (600 MHz, CDCl₃) δ 8.54 (d, *J* = 8.0 Hz, 1H), 8.27 (d, *J* = 8.2 Hz, 1H), 8.15 (dd, *J* = 8.2, 0.6 Hz, 1H), 7.82 (t, *J* = 8.1 Hz, 1H), 7.80–7.75 (m, 1H), 7.69–7.63 (m, 1H), 7.18 (d, *J* = 7.8 Hz, 1H), 7.14 (d, *J* = 8.3 Hz, 2H), 6.81 (d, *J* = 8.3 Hz, 2H), 3.54 (s, 3H), 2.85–2.76 (m, 1H), 2.70–2.60 (m, 1H), 2.45–2.35 (m, 1H), 2.30–2.22 (m, 1H), 1.78 (s, 3H). ¹³C NMR (151 MHz, CDCl₃) δ 173.8, 159.3, 144.9, 140.3, 138.7, 133.1, 131.7, 130.8, 130.1, 129.7, 129.1, 126.6, 122.6, 122.5, 119.3, 116.1, 112.4, 110.7, 51.2, 43.1, 31.4, 29.74, 29.68. IR (KBr) ν_{max} : 3030, 1671, 1589, 1463, 1338, 1293, 1149, 1071, 1010, 818, 760, 647 cm⁻¹. HRMS (ESI): m/z: [M + H]⁺ calc. for C₂₅H₂₂BrN₂O, 445.0910; found, 445.0912.



4,6-dimethyl-6-(4-(trifluoromethyl)phenethyl)-*4H*-pyrido[4,3,2-*gh*]phenanthridin-5(6*H*)-one (3ak). Performed according to the general procedure, and purified by column chromatography (petroleum ether/1,4-dioxane = 40/1) to afford 56 mg (64%) of **3ak**. White solid, mp 104–106 °C. ¹H NMR (600 MHz, CDCl₃) δ 8.53 (d, *J* = 7.9 Hz, 1H), 8.27 (d, *J* = 8.2 Hz, 1H), 8.19–8.13 (m, 1H), 7.83 (t, *J* = 8.1 Hz, 1H), 7.81–7.76 (m, 1H), 7.70–7.64 (m, 1H), 7.28 (d, *J* = 8.1 Hz, 2H), 7.20 (d, *J* = 7.9 Hz, 1H), 7.05 (d, *J* = 8.0 Hz, 2H), 3.55 (s, 3H), 2.93–2.84 (m, 1H), 2.74–2.66 (m, 1H), 2.56–2.48 (m, 1H), 2.42–2.34 (m, 1H), 1.80 (s, 3H). ¹³C NMR (151 MHz, CDCl₃) δ 173.7, 159.2, 145.5, 144.9, 138.7, 133.2, 131.8, 129.7, 129.2, 128.7, 127.8 (q, *J*_{C-F} = 32.3 Hz), 126.7, 124.7 (q, *J*_{C-F} = 3.8 Hz), 124.2 (q, *J*_{C-F} = 271.7 Hz), 122.62, 122.55, 121.5, 116.2, 112.4, 110.7, 51.2, 42.6, 32.0, 30.0, 29.7. IR (KBr) v_{max}: 2933, 1673, 1589, 1465, 1325, 1255, 1119, 1067, 1018, 822, 759, 646 cm⁻¹. HRMS (ESI): m/z: [M + H]⁺ calc. for C₂₆H₂₂F₃N₂O, 435.1679; found, 435.1680.



4,6-dimethyl-6-(2-(thiophen-2-yl)ethyl)-*4H*-**pyrido**[**4,3,2**-*gh*]**phenanthridin-5(***6H***)-one** (**3a**). Performed according to the general procedure, and purified by column chromatography (petroleum ether/1,4-dioxane = 30/1) to afford 35 mg (47%) of **3a**l. White solid, mp 149–151 °C. ¹H NMR (600 MHz, CDCl₃) δ 8.55 (d, *J* = 8.1 Hz, 1H), 8.29 (d, *J* = 8.3 Hz, 1H), 8.17 (d, *J* = 7.7 Hz, 1H), 7.84 (t, *J* = 8.1 Hz, 1H), 7.79–7.75 (m, 1H), 7.69–7.64 (m, 1H), 7.22 (d, *J* = 7.9 Hz, 1H), 6.99 (dd, *J* = 5.1, 0.9 Hz, 1H), 6.77 (dd, *J* = 5.0, 3.5 Hz, 1H), 6.60 (d, *J* = 2.7 Hz, 1H), 3.58 (s, 3H), 2.93–2.83 (m, 1H), 2.78–2.61 (m, 2H), 2.58–2.46 (m, 1H), 1.81 (s, 3H). ¹³C NMR (151 MHz, CDCl₃) δ 173.7, 159.1, 145.0, 144.4, 138.8, 133.2, 131.8, 129.9, 129.1, 126.6, 126.4, 124.0, 122.9, 122.7, 122.5, 116.1, 112.3, 110.7, 51.2, 43.4, 29.8, 29.2, 26.0. IR (KBr) ν_{max} : 2921, 1666, 1570, 1463, 1342, 1258, 1117, 1073, 850, 751, 702, 648 cm⁻¹. HRMS (ESI): m/z: [M + H]⁺ calc. for C₂₃H₂₁N₂OS, 373.1369; found, 373.1370.



4,6-dimethyl-6-(2-(naphthalen-1-yl)ethyl)-4*H*-pyrido[**4,3,2**-*gh*]phenanthridin-**5**(6*H*)-one (**3**am). Performed according to the general procedure, and purified by column chromatography (petroleum ether/1,4-dioxane = 20/1) to afford 67 mg (80%) of **3**am. White solid, mp 179–181 °C. ¹H NMR (600 MHz, CDCl₃) δ 8.58 (d, *J* = 7.7 Hz, 1H), 8.31 (d, *J* = 8.2 Hz, 1H), 8.25 (dd, *J* = 8.2, 0.9 Hz, 1H), 8.02–7.97 (m, 1H), 7.87–7.80 (m, 2H), 7.74 (dd, *J* = 6.3, 3.0 Hz, 1H), 7.69 (ddd, *J* = 8.2, 7.0, 1.2 Hz, 1H), 7.59 (d, *J* = 8.1 Hz, 1H), 7.40 (pd, *J* = 6.8, 1.8 Hz, 2H), 7.24 (dd, *J* = 7.9, 3.6 Hz, 2H), 7.18 (d, *J* = 6.9 Hz, 1H), 3.65 (s, 3H), 3.09–3.01 (m, 1H), 2.92–2.84 (m, 1H), 2.83–2.72 (m, 2H), 1.75 (s, 3H). ¹³C NMR (151 MHz, CDCl₃) δ 174.0, 159.5, 145.0, 138.9, 138.1, 133.6, 133.3, 131.81, 131.78, 129.8, 129.2, 128.4, 126.7, 126.5, 126.2, 125.6, 125.32, 125.28, 124.3, 122.8, 122.6, 116.1, 112.5, 110.7, 51.7, 42.1, 30.2, 29.8, 29.6. IR (KBr) ν_{max} : 3035, 2932, 1665, 1590, 1464, 1366, 1296, 1148, 1079, 801, 751, 660 cm⁻¹. HRMS (ESI): m/z: [M + H]⁺ calc. for C₂₉H₂₅N₂O, 417.1961; found, 417.1961.



4,6-dimethyl-6-(2-phenylpropyl)-4H-pyrido[**4,3,2-***gh*]**phenanthridin-5(***6H***)-one (3an).** Performed according to the general procedure, and purified by column chromatogrphy (petroleim ether/1,4-dioxane = 30/1) to afford 59 mg (78%) of **3an**. White solid, mp 131–134 °C. ¹H NMR (600 MHz, CDCl₃) δ 8.56 (d, *J* = 8.0 Hz, 1H), 8.36 (d, *J* = 8.0 Hz, 1H), 8.25 (d, *J* = 8.2 Hz, 1H), 8.19 (d, *J* = 8.0 Hz, 1H), 8.05 (t, *J* = 7.5 Hz, 2H), 7.81–7.74 (m, 2H), 7.73–7.69 (m, 1H), 7.67 (dd, *J* = 10.7, 4.7 Hz, 2H), 7.60–7.56 (m, 1H), 7.06 (d, *J* = 7.8 Hz, 1H), 7.01–6.94 (m, 3H), 6.87 (d, *J* = 7.9 Hz, 1H), 6.57 (dd, *J* = 7.6, 1.6 Hz, 2H), 6.54–6.50 (m, 2H), 6.38 (t, *J* = 7.2 Hz, 1H), 6.33 (t, *J* = 7.3 Hz, 2H), 3.58 (s, 3H), 3.01 (dd, *J* = 12.8, 10.0 Hz, 1H), 2.92–2.85 (m, 4H), 2.76–2.63 (m, 3H), 2.33–2.23 (m, 1H), 1.80 (s, 3H), 1.78 (s, 3H), 1.10 (d, *J* = 6.8 Hz, 3H), 1.02 (d, *J* = 6.9 Hz, 3H). ¹³C NMR (151 MHz, CDCl₃) δ 174.1, 173.4, 160.0, 159.7, 144.94, 144.90, 144.7, 144.6, 138.9, 138.6, 132.8, 131.7, 131.1, 129.7, 129.4, 129.3, 129.0, 128.7, 127.6, 127.5, 127.3, 126.74, 126.66, 126.5, 126.2, 126.0, 124.7, 122.62, 122.57, 122.5, 122.2, 115.7, 115.5, 112.6, 112.3, 110.4, 110.1, 51.5, 50.5, 50.3, 49.8, 37.9, 37.5, 31.0, 30.8, 29.5, 29.1, 24.4, 23.6. IR (KBr) ν_{max} : 2940, 1666, 1637, 1587, 1463, 1362, 1291, 1145, 1075, 812, 746, 663. HRMS (ESI): m/z: [M + Na]⁺ calc. for C₂₆H₂₄N₂ONa, 403.1781; found, 403.1782.



4,6-dimethyl-6-(2-phenoxyethyl)-4*H*-pyrido[**4,3,2**-*gh*]**phenanthridin-5**(*6H*)-one (**3ao**). Performed according to the general procedure, and purified by column chromatography (petroleum ether/1,4-dioxane = 30/1) to afford 41 mg (54%) of **3ao**. White solid, mp 106–108 °C. ¹H NMR (600 MHz, CDCl₃) δ 8.52 (d, *J* = 8.1 Hz, 1H), 8.24 (d, *J* = 8.3 Hz, 1H), 8.12 (d, *J* = 8.1 Hz, 1H), 7.79–7.72 (m, 2H), 7.66–7.61 (m, 1H), 7.15 (d, *J* = 7.9 Hz, 1H), 7.02 (dd, *J* = 8.4, 7.5 Hz, 2H), 6.74 (t, *J* = 7.3 Hz, 1H), 6.41 (d, *J* = 8.0 Hz, 2H), 3.92–3.85 (m, 1H), 3.80–3.74 (m, 1H), 3.58 (s, 3H), 3.04–2.98 (m, 1H), 2.96–2.89 (m, 1H), 1.83 (s, 3H). ¹³C NMR (151 MHz, CDCl₃) δ 173.8, 159.3, 158.3, 144.8, 138.8, 133.2, 131.7, 129.7, 129.04, 128.96, 126.5, 122.7, 122.5, 120.2, 116.0, 114.0, 112.2, 110.6, 64.5, 49.1, 40.5, 30.1, 29.8. IR (KBr) ν_{max} : 3012, 2944, 1659, 1586, 1467, 1339, 1242, 1172, 1081, 817, 755, 689 cm⁻¹. HRMS (ESI): m/z: [M + Na]⁺ calc. for C₂₅H₂₂N₂O₂Na, 405.1573; found, 405.1573.



4,6-dimethyl-6-(2-(phenylthio)ethyl)-4*H*-pyrido[**4,3,2**-*gh*]**phenanthridin-5(6***H*)-one (**3ap**). Performed according to the general procedure, and purified by column chromatography (petroleum ether/1,4-dioxane = 30/1) to afford 49 mg (61%) of **3ap**. White solid, mp 121–123 °C. ¹H NMR (600 MHz, CDCl₃) δ 8.55 (d, *J* = 8.0 Hz, 1H), 8.30 (d, *J* = 8.2 Hz, 1H), 8.15 (d, *J* = 8.1 Hz, 1H), 7.84 (t, *J* = 8.1 Hz, 1H), 7.81–7.76 (m, 1H), 7.70–7.65 (m, 1H), 7.23 (d, *J* = 7.9 Hz, 1H), 7.18–7.11 (m, 4H), 7.07 (ddd, *J* = 6.6, 4.1, 2.1 Hz, 1H), 3.61 (s, 3H), 3.00–2.87 (m, 1H), 2.77–2.71 (m, 1H), 2.71–2.63 (m, 2H), 1.73 (s, 3H). ¹³C NMR (151 MHz, CDCl₃) δ 173.4, 158.7, 138.7, 136.5, 133.3, 131.9, 130.3, 129.8, 129.2, 128.7, 127.6, 126.8, 125.2, 122.7, 122.6, 116.2, 112.2, 110.8, 51.4, 40.3, 29.9, 29.8, 28.4. IR (KBr) ν_{max} : 2928, 1665, 1579, 1463, 1335, 1251, 1143, 1072, 817, 738, 651, 595. HRMS (ESI): m/z: [M + H]⁺ calc. for C₂₅H₂₃N₂OS, 399.1526; found, 399.1525.



4,6-dimethyl-6-((tetrahydrofuran-2-yl)methyl)-4H-pyrido[4,3,2-gh]phenanthridin-5(6H)-one(3aq).Performed according to the general procedure, and purified by column chromatography (petroleum ether/1,4-dioxane = 20/1) to afford 40 mg (58%) of 3aq.

Isomer 1: White solid, mp 125–127 °C. ¹H NMR (600 MHz, CDCl₃) δ 8.53 (d, *J* = 8.2 Hz, 1H), 8.24 (d, *J* = 8.3 Hz, 1H), 8.11 (d, *J* = 8.2 Hz, 1H), 7.80 (t, *J* = 8.1 Hz, 1H), 7.76–7.71 (m, 1H), 7.66–7.61 (m, 1H), 7.19 (d, *J* = 7.9 Hz, 1H), 3.68–3.61 (m, 1H), 3.56 (s, 3H), 3.38–3.33 (m, 1H), 2.68 (dd, *J* = 13.3, 10.4 Hz, 1H), 2.59 (dd, *J* = 13.4, 3.9 Hz, 1H), 1.89–1.80 (m, 1H), 1.76 (s, 3H), 1.72–1.56 (m, 3H), 1.47–1.40 (m, 1H). ¹³C NMR (151 MHz, CDCl₃) δ 174.4, 160.0, 144.8, 139.4, 133.2, 131.8, 129.6, 128.9, 126.4, 122.8, 122.6, 115.5, 112.3, 110.5, 75.7, 67.0, 49.2, 47.7, 31.4, 30.4, 29.7, 25.2. IR (KBr) ν_{max} : 2967, 2928, 1677, 1588, 1467, 1339, 1256, 1146, 1078, 820, 762, 655 cm⁻¹. HRMS (ESI): m/z: [M + Na]⁺ calc. for C₂₂H₂₂N₂O₂Na, 369.1573; found, 369.1575.

Isomer 2: White solid, mp 122–124 °C. ¹H NMR (600 MHz, CDCl₃) δ 8.54–8.50 (m, 1H), 8.27 (d, *J* = 8.2 Hz, 1H), 8.12 (dd, *J* = 8.2, 0.9 Hz, 1H), 7.80 (t, *J* = 8.1 Hz, 1H), 7.76–7.71 (m, 1H), 7.65–7.60 (m, 1H), 7.21 (d, *J* = 7.8 Hz, 1H), 3.93–3.86 (m, 1H), 3.60 (s, 3H), 3.14–3.09 (m, 1H), 3.02–2.97 (m, 1H), 2.93 (dd, *J* = 13.4, 8.3 Hz, 1H), 2.41 (dd, *J* = 13.4, 5.7 Hz, 1H), 1.77 (s, 3H), 1.75–1.69 (m, 2H), 1.59–1.46 (m, 2H). ¹³C NMR (151 MHz, CDCl₃) δ 174.1, 160.6, 144.8, 138.8, 133.1, 131.5, 129.5, 129.0, 126.2, 122.6, 122.5, 116.0, 112.3, 110.7, 76.1, 66.7, 49.6, 47.6, 31.3, 30.1, 29.7, 25.2. IR (KBr) υ_{max} : 2969, 2930, 1675, 1586, 1468, 1335, 1258, 1143, 1074, 825, 764, 658 cm⁻¹. HRMS (ESI): m/z: [M + Na]⁺ calc. for C₂₂H₂₂N₂O₂Na, 369.1573; found, 369.1573.



6-(2-hydroxyethyl)-4,6-dimethyl-4*H***-pyrido[4,3,2-***gh***]phenanthridin-5(6***H***)-one (3ar). Performed according to the general procedure, and purified by column chromatography (petroleum ether/1,4-dioxane = 5/1) to afford 50 mg (82%) of 3ar**. White solid, mp 139–141 °C. ¹H NMR (600 MHz, CDCl₃) δ 8.54 (d, *J* = 8.1 Hz, 1H), 8.29 (d, *J* = 8.3 Hz, 1H), 8.11 (d, *J* = 8.2 Hz, 1H), 7.85 (t, *J* = 8.1 Hz, 1H), 7.78–7.73 (m, 1H), 7.69–7.64 (m, 1H), 7.24 (d, *J* = 7.9 Hz, 1H), 3.76–3.71 (m, 1H), 3.71–3.66 (m, 1H), 3.60 (s, 3H), 2.88–2.81 (m, 1H), 2.69–2.62 (m, 1H), 1.73 (s, 3H). ¹³C NMR (151 MHz, CDCl₃) δ 174.6, 159.8, 144.3, 138.8, 133.4, 132.1, 129.29, 129.27, 126.8, 122.7, 122.6, 116.2, 111.9, 110.9, 59.6, 50.3, 41.4, 30.0, 29.4. IR (KBr) ν_{max} : 3024, 2957, 1663, 1611, 1467, 1338, 1294, 1081, 900, 817, 757, 647. HRMS (ESI): m/z: [M + Na]⁺ calc. for C₁₉H₁₈N₂O₂Na, 329.1260; found, 329.1259.



6-(2-hydroxypropyl)-4,6-dimethyl-4*H***-pyrido**[**4,3,2-***gh*]**phenanthridin-5(6***H***)-one (3as).** Performed according to the general procedure, and purified by column chromatography (petroleum ether/ethyl acetate = 10/1) to afford 45 mg (70%) of **3as**.

Isomer 1: White solid, mp 150–152 °C. ¹H NMR (600 MHz, CDCl₃) δ 8.53 (d, J = 8.0 Hz, 1H), 8.28 (d, J = 8.2 Hz,

1H), 8.11 (dd, J = 8.2, 0.8 Hz, 1H), 7.84 (t, J = 8.1 Hz, 1H),7.77–7.72 (m, 1H), 7.67–7.63 (m, 1H), 7.24 (d, J = 7.9 Hz, 1H), 3.88 (d, J = 6.1 Hz, 1H), 3.60 (s, 3H), 3.18 (s, 1H), 2.65 (dd, J = 14.5, 9.0 Hz, 1H), 2.54 (dd, J = 14.5, 2.5 Hz, 1H), 1.72 (s, 3H), 1.17 (d, J = 6.3 Hz, 3H). ¹³C NMR (151 MHz, CDCl₃) δ 174.3, 160.6, 144.3, 138.7, 133.5, 132.0, 129.4, 129.3, 126.8, 122.8, 122.6, 116.2, 112.0, 110.9, 66.3, 51.0, 48.2, 30.0, 29.6, 24.4. IR (KBr) ν_{max} : 2996, 1665, 1644, 1487, 1336, 1280, 1146, 1078, 918, 803, 751, 653. HRMS (ESI): m/z: [M + Na]⁺ calc. for C₂₀H₂₀N₂O₂Na, 343.1417; found, 343.1418.

Isomer 2: ¹H NMR (600 MHz, CDCl₃) δ 8.56–8.51 (m, 1H), 8.28 (d, *J* = 8.2 Hz, 1H), 8.11 (dd, *J* = 8.2, 0.8 Hz, 1H), 7.84 (t, *J* = 8.1 Hz, 1H), 7.78–7.73 (m, 1H), 7.68–7.63 (m, 1H), 7.23 (d, *J* = 7.9 Hz, 1H), 3.84–3.77 (m, 1H), 3.59 (s, 3H), 2.81 (dd, *J* = 14.3, 2.4 Hz, 1H), 2.48 (dd, *J* = 14.3, 10.4 Hz, 1H), 1.73 (s, 3H), 1.20 (d, *J* = 6.2 Hz, 3H). ¹³C NMR (151 MHz, CDCl₃) δ 175.2, 160.1, 144.2, 139.0, 133.4, 132.1, 129.2, 126.8, 122.8, 122.6, 116.0, 112.0, 110.8, 65.0, 50.1, 47.7, 30.1, 30.0, 24.7. IR (KBr) ν_{max} : 2998, 1663, 1639, 1487, 1339, 1283, 1142, 1075, 917, 810, 748, 654. HRMS (ESI): m/z: [M + Na]⁺ calc. for C₂₀H₂₀N₂O₂Na, 343.1417; found, 343.1417.



6-(2-hydroxy-2-methylpropyl)-4,6-dimethyl-4*H*-pyrido[4,3,2-*gh*]phenanthridin-5(6*H*)-one (3at). Performed according to the general procedure, and purified by column chromatography (petroleum ether/1,4-dioxane = 30/1) to afford 42 mg (63%) of **3at**. White solid, mp 172–174 °C. ¹H NMR (600 MHz, CDCl₃) δ 8.54 (d, *J* = 8.1 Hz, 1H), 8.29 (d, *J* = 8.3 Hz, 1H), 8.09 (d, *J* = 8.1 Hz, 1H), 7.85 (t, *J* = 8.1 Hz, 1H), 7.75 (t, *J* = 7.3 Hz, 1H), 7.65 (t, *J* = 7.3 Hz, 1H), 7.25 (d, *J* = 7.9 Hz, 1H), 3.61 (s, 3H), 3.35 (s, 1H), 3.06 (d, *J* = 14.7 Hz, 1H), 2.94 (d, *J* = 14.7 Hz, 1H), 1.66 (s, 3H), 1.07 (s, 3H), 0.87 (s, 3H). ¹³C NMR (151 MHz, CDCl₃) δ 174.8, 160.4, 144.2, 138.7, 133.6, 132.1, 129.32, 129.28, 126.8, 122.8, 122.6, 116.2, 112.1, 110.9, 70.7, 51.1, 50.1, 33.3, 30.90, 30.88, 30.0. IR (KBr) ν_{max} : 2931, 1670, 1657, 1470, 1339, 1274, 1130, 1028, 911, 821, 751, 643. HRMS (ESI): m/z: [M + Na]⁺ calc. for C₂₁H₂₂N₂O₂Na, 357.1573; found, 357.1574.



7-(cyclopentylmethyl)-4,6-dimethyl-4*H***-pyrido[4,3,2-***gh***]phenanthridin-5(6***H***)-one (3au). Performed according to the general procedure, and purified by column chromatography (petroleum ether/1,4-dioxane = 30/1) to afford 41 mg (60%) of 3au**. White solid, mp 128–130 °C. 1H NMR (600 MHz, CDCl3) δ 8.54 (d, J = 8.1 Hz, 1H), 8.27 (d, *J* = 8.2 Hz, 1H), 8.14 (dd, *J* = 8.2, 0.6 Hz, 1H), 7.82 (t, *J* = 8.1 Hz, 1H), 7.77–7.73 (m, 1H), 7.67–7.62 (m, 1H), 7.21 (d, *J* = 7.9 Hz, 1H), 3.59 (s, 3H), 2.54 (dd, *J* = 13.3, 6.2 Hz, 1H), 2.41 (dd, *J* = 13.3, 6.6 Hz, 1H), 1.83 (s, 3H),

1.49–1.38 (m, 3H), 1.35–1.27 (m, 1H), 1.24–1.16 (m, 1H), 1.15–1.00 (m, 3H), 0.74–0.64 (m, 1H). ¹³C NMR (151 MHz, CDCl₃) δ 174.5, 160.2, 144.8, 138.9, 133.1, 131.7, 129.7, 129.1, 126.4, 122.6, 122.5, 116.0, 112.4, 110.6, 51.1, 49.6, 37.7, 33.4, 32.8, 29.72, 29.67, 24.9, 24.8. IR (KBr) umax: 2941, 1668, 1638, 1463, 1335, 1269, 1136, 1025, 908, 817, 746, 640. HRMS (ESI): m/z: [M + Na]⁺ calc. for C₂₃H₂₄N₂ONa, 367.1781; found, 367.1782.



6-(cyclohexylmethyl)-4,6-dimethyl-4*H***-pyrido[4,3,2-***gh***]phenanthridin-5(***6H***)-one (3av).** Performed according to the general procedure, and purified by column chromatography (petroleum ether/1,4-dioxane = 30/1) to afford 51 mg (71%) of **3av**. White solid, mp 143–145 °C. ¹H NMR (600 MHz, CDCl₃) δ 8.53 (d, *J* = 8.0 Hz, 1H), 8.27 (d, *J* = 8.2 Hz, 1H), 8.14 (dd, *J* = 8.2, 0.9 Hz, 1H), 7.81 (t, *J* = 8.1 Hz, 1H), 7.77–7.73 (m, 1H), 7.66–7.61 (m, 1H), 7.21 (d, *J* = 7.9 Hz, 1H), 3.58 (s, 3H), 2.52 (dd, *J* = 13.5, 6.3 Hz, 1H), 2.30 (dd, *J* = 13.5, 6.7 Hz, 1H), 1.73 (s, 3H), 1.47 (dd, *J* = 5.5, 3.7 Hz, 1H), 1.43–1.31 (m, 3H), 1.23–1.14 (m, 1H), 1.13–1.07 (m, 1H), 0.99–0.79 (m, 4H), 0.72–0.63 (m, 1H). ¹³C NMR (151 MHz, CDCl₃) δ 174.4, 160.1, 144.8, 138.8, 133.2, 131.6, 129.7, 129.0, 126.4, 122.6, 122.5, 116.0, 112.2, 110.6, 50.3, 49.4, 34.9, 33.9, 33.5, 31.0, 29.7, 26.10, 26.06, 26.0. IR (KBr) ν_{max} : 2938, 1661, 1638, 1462, 1333, 1271, 1139, 1029, 912, 823, 751, 650. HRMS (ESI): m/z: [M + Na]⁺ calc. for C₂₄H₂₆N₂ONa, 381.1937; found, 381.1936.



4-(cyclooctylmethyl)-4,6-dimethyl-4H-pyrido[**4,3,2-gh**]**phenanthridin-5(6H)-one (3aw).** Performed according to the general procedure, and purified by column chromatography (petroleum ether/1,4-dioxane = 30/1) to afford 48 mg (62%) of **3aw**. White solid, mp 164–166 °C. ¹H NMR (600 MHz, CDCl₃) δ 8.53 (dd, *J* = 8.4, 0.7 Hz, 1H), 8.27 (d, *J* = 8.2 Hz, 1H), 8.14 (dd, *J* = 8.2, 0.9 Hz, 1H), 7.82 (t, *J* = 8.1 Hz, 1H), 7.77–7.73 (m, 1H), 7.66–7.62 (m, 1H), 7.21 (d, *J* = 7.8 Hz, 1H), 3.59 (s, 3H), 2.42 (dd, *J* = 13.5, 6.0 Hz, 1H), 2.28 (dd, *J* = 13.5, 6.2 Hz, 1H), 1.80 (s, 3H), 1.47–1.33 (m, 4H), 1.31–1.24 (m, 3H), 1.22–1.10 (m, 5H), 1.08–1.01 (m, 1H), 0.95–0.82 (m, 2H). ¹³C NMR (151 MHz, CDCl₃) δ 174.5, 160.2, 144.8, 138.9, 133.1, 131.7, 129.7, 129.1, 126.4, 122.6, 122.5, 116.0, 112.4, 110.6, 51.1, 49.6, 37.7, 33.4, 32.8, 29.72, 29.67, 24.9, 24.8. IR (KBr) ν_{max} : 2929, 1669, 1637, 1458, 1339, 1275, 1134, 1025, 907, 825, 747, 651. HRMS (ESI): m/z: [M + Na]⁺ calc. for C₂₆H₃₀N₂ONa, 409.2250; found, 409.2252.

References

(S1) J.-Q. Shang, S.-S. Wang, H. Fu, Y. Li, T. Yang and Y.-M. Li, Org. Chem. Front., 2018, 5, 1945.

5. Charts of compounds







































-172.38 -158.29 -158.29 -1127.26 -1127.26 -1127.26 -1127.26 -1127.26 -110.16 -110.16 -110.16 -110.16 -110.16 -110.16



S41



S42









S46





























100 90 f1 (ppm)

 $\begin{smallmatrix} -1.3 \\ -1.3$ <1.19 -7.26 8.54 8.54 8.53 OH ò 1 3as isomer 2 100. 86.0 8 8 38 7.8 7.2 8.6 8.4 8.2 8.0 7.6 7.4 -2.50 -2.48 -2.47 -2.46 2.83 8 en o 2.9 2.7 2.5 1.07 ± 3.11 ± 1.03 3.10-1.03-03 3.11 5.0 4.5 f1 (ppm) 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -175.19 144 23 139 00 139 00 133 39 132 10 122 75 122 75 122 75 -160.08 1116.04 111.98 110.82 -50.10 -29.96 -24.65 -65.04 он ò 3as isomer 2 200 190 100 90 f1 (ppm) 80 30 10 0 180 170 160 150 140 130 120 110 70 60 50 40 20 S64

