

Supporting Information

Oxidative radical cascade cyclization involving C(sp³)-C(sp³), C(sp³)-C(sp²) and C(sp²)-N bonds formation: direct construction of cyano and methyl substituted polyheterocycles

Jia-Qi Shang, Shi-Sheng Wang, Hong Fu, Yi Li, Tao Yang, and Ya-Min Li*

Faculty of Life Science and Technology, Kunming University of Science and Technology, Kunming 650500, P. R. China.

E-mail: liym@kmust.edu.cn.

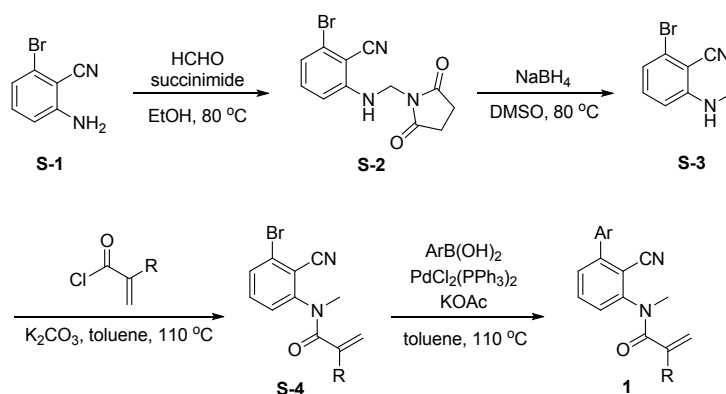
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1. General information

¹H NMR, ¹³C NMR and spectra were recorded on Bruker AVANCE DRX 500 (500 MHz for ¹H; 126 MHz for ¹³C) and 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 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



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.

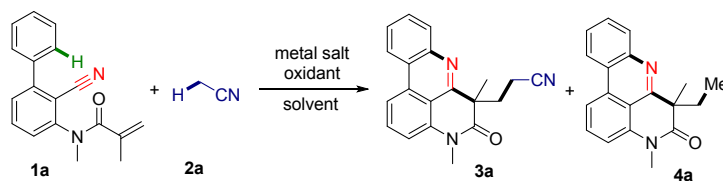
To the solution of **S-2** in 16 mL dry DMSO was slowly added NaBH₄ (1.1 equiv, 0.63 g, 16.5 mmol) at 0 °C under argon. The mixture was allowed to stir at 80 °C. After completion of the reaction, the solution was cooled to room temperature and poured into cold water. The mixture was extracted with diethyl 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 °C 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 °C 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 °C 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**.]

3. Screening of the reaction conditions

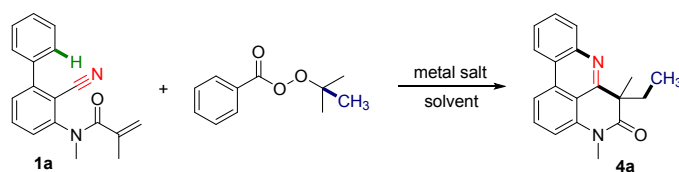
Table S1. Reaction conditions screening^a



Entry	Metal salt (mol %)	Oxidant (equiv)	Solvent (mL)	Temp (°C)	Yield of 3a ^b (%)	3a/4a ^c
1	CuCl (10)	DTBP (3.0)	CH ₃ CN (4)	120	22	2.1/1
2	CuCl (10)	TBHP (3.0)	CH ₃ CN (4)	120	0	
3	CuCl (10)	TBPB (3.0)	CH ₃ CN (4)	120	59	3.8/1
4	CuCl (10)	DCP (3.0)	CH ₃ CN (4)	120	56	1.5/1
5	CuCl (10)	BPO (3.0)	CH ₃ CN (4)	120	51	1.0/0
6	CuCl (10)	K ₂ S ₂ O ₈ (3.0)	CH ₃ CN (4)	120	0	
7	CuCl (10)	Oxone (3.0)	CH ₃ CN (4)	120	0	
8	CuBr (10)	TBPB (3.0)	CH ₃ CN (4)	120	51	4.6/1
9	CuI (10)	TBPB (3.0)	CH ₃ CN (4)	120	52	5.3/1
10	Cu ₂ O (10)	TBPB (3.0)	CH ₃ CN (4)	120	59	2.9/1
11	CuCl ₂ (10)	TBPB (3.0)	CH ₃ CN (4)	120	62	3.0/1
12	CuBr ₂ (10)	TBPB (3.0)	CH ₃ CN (4)	120	52	5.0/1
13	CuO (10)	TBPB (3.0)	CH ₃ CN (4)	120	44	5.9/1
14	Cu(OAc) ₂ (10)	TBPB (3.0)	CH ₃ CN (4)	120	63	4.7/1
15	Cu(acac) ₂ (10)	TBPB (3.0)	CH ₃ CN (4)	120	60	4.5/1
16	CuSO ₄ ·5H ₂ O (10)	TBPB (3.0)	CH ₃ CN (4)	120	33	2.8/1
17	Cu(OTf) ₂ (10)	TBPB (3.0)	CH ₃ CN (4)	120	57	6.0/1
18	FeCl ₃ (10)	TBPB (3.0)	CH ₃ CN (4)	120	37	2.9/1
19	Fe(OTf) ₂ (10)	TBPB (3.0)	CH ₃ CN (4)	120	29	3.4/1
20	IrCl ₃ (10)	TBPB (3.0)	CH ₃ CN (4)	120	40	4.5/1
21	Cu(OAc) ₂ (10)	TBPB (3.0)	CH ₃ CN (6)	120	65	6.6/1
22	Cu(OAc) ₂ (10)	TBPB (3.0)	CH ₃ CN (8)	120	71	9.0/1
23	Cu(OAc) ₂ (10)	TBPB (3.0)	CH ₃ CN (10)	120	60	9.4/1
24	Cu(OAc) ₂ (10)	TBPB (2.0)	CH ₃ CN (8)	120	75	7.8:1
25	Cu(OAc) ₂ (10)	TBPB (1.0)	CH ₃ CN (8)	120	43	3.8/1
26	Cu(OAc) ₂ (5)	TBPB (2.0)	CH ₃ CN (8)	120	70	7.4/1
27	Cu(OAc) ₂ (15)	TBPB (2.0)	CH ₃ CN (8)	120	67	6.0/1
28	Cu(OAc) ₂ (10)		CH ₃ CN (8)	120	0	
29		TBPB (2.0)	CH ₃ CN (8)	120	54	10.1/1
30	Cu(OAc) ₂ (10)	TBPB (2.0)	CH ₃ CN (8)	110	51	7.0/1
31 ^d	Cu(OAc) ₂ (10)	TBPB (2.0)	CH ₃ CN (8)	120	47	7.1/1

^aReaction conditions: **1a** (0.2 mmol), **2a**, metal salt, and oxidant in solvent for 12 h under Ar. ^bIsolated yield.

^cDetermined by ¹H NMR of the crude products. ^dUnder air.

Table S2. Optimization of the reaction conditions^a

Entry	Methyl source (equiv)	Metal salt (mol %)	Solvent (mL)	Temp (°C)	Yield ^b (%)
1	TBPB (2.0)	Cu(OAc) ₂ (10)	PhCl (2.0)	120	34
2	TBPB (2.0)		PhCl (2.0)	120	67
3	TBPB (1.0)		PhCl (2.0)	120	48
4	TBPB (3.0)		PhCl (2.0)	120	72
5	TBPB (4.0)		PhCl (2.0)	120	78
6	TBPB (5.0)		PhCl (2.0)	120	74
7	TBPB (4.0)		PhCl (1.0)	120	73
8	TBPB (4.0)		PhCl (3.0)	120	76
9	TBPB (4.0)		PhCl (2.0)	100	78
10	TBPB (4.0)		PhCl (2.0)	80	37
11	DTBP (4.0)		PhCl (2.0)	100	10
12	DCP (4.0)		PhCl (2.0)	100	47
13	TBPB (4.0)		DMSO (2.0)	100	38
14	TBPB (4.0)		DMF (2.0)	100	18
15	TBPB (4.0)		toluene (2.0)	100	15
16 ^c	TBPB (4.0)		PhCl (2.0)	100	17

^aReaction conditions: **1a** (0.2 mmol), methyl source in solvent for 12 h under Ar. ^bIsolated yield. ^cUnder air.

4. General procedure for synthesis of cyano substituted pyrido[4,3,2-*gh*]phenanthridins

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, 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**.

5. General procedure for synthesis of methyl substituted pyrido[4,3,2-*gh*]phenanthridins

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 **4**.

6. Kinetic isotope effect (KIE) experiments

a) Intermolecular KIE experiment

In a Schlenk tube, acrylamide **1a** (0.1 mmol, 27.6 mg), **1a-D₅** (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, CH₃CN (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-D₄**. The products were under ¹H-NMR analysis (Figure S1).

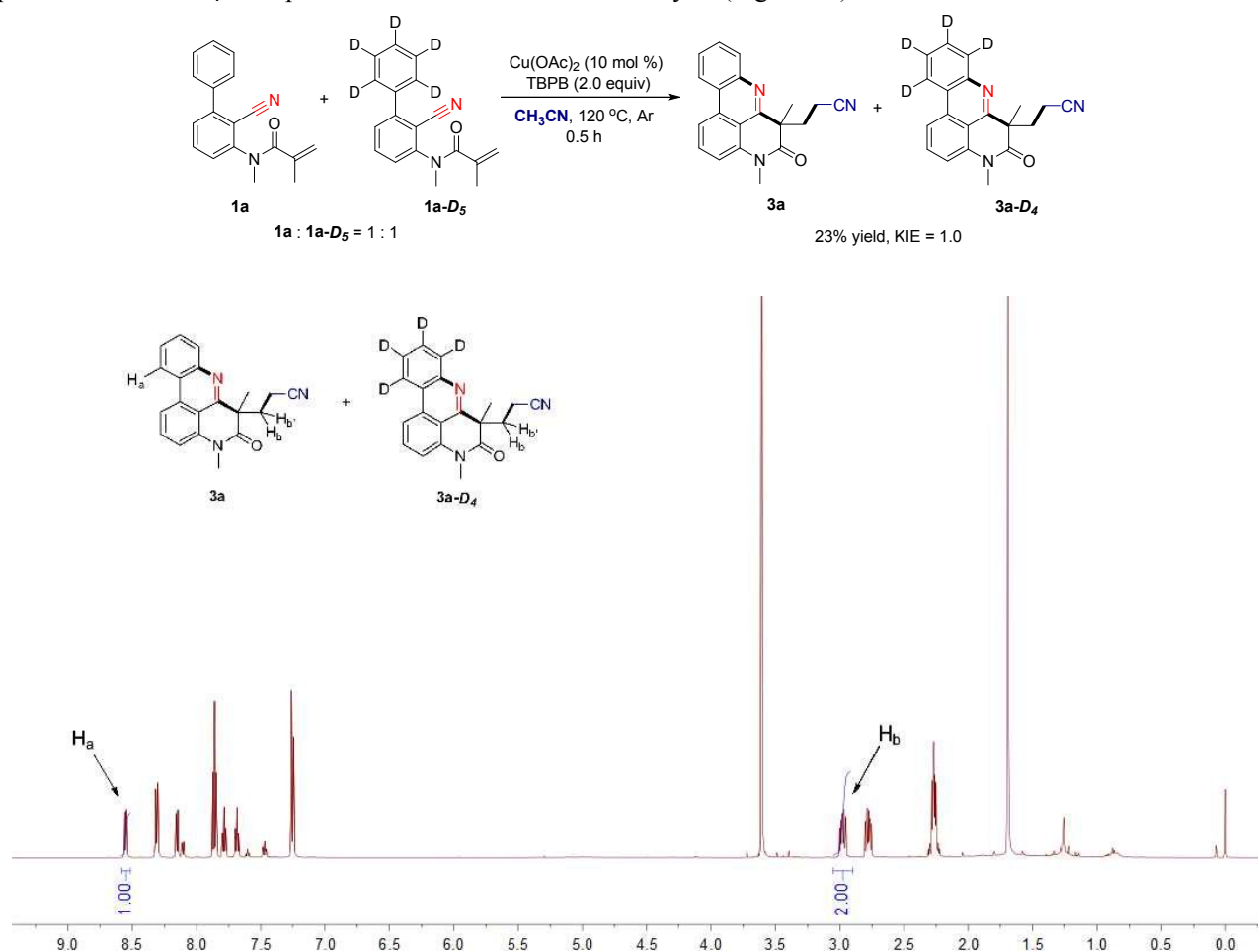


Figure S1. ¹H NMR spectra of the mixture of compound **3a** and **3a-D₄**.

b) Intramolecular KIE experiment

In a Schlenk tube, acrylamide **1a-D₁** (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, 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).

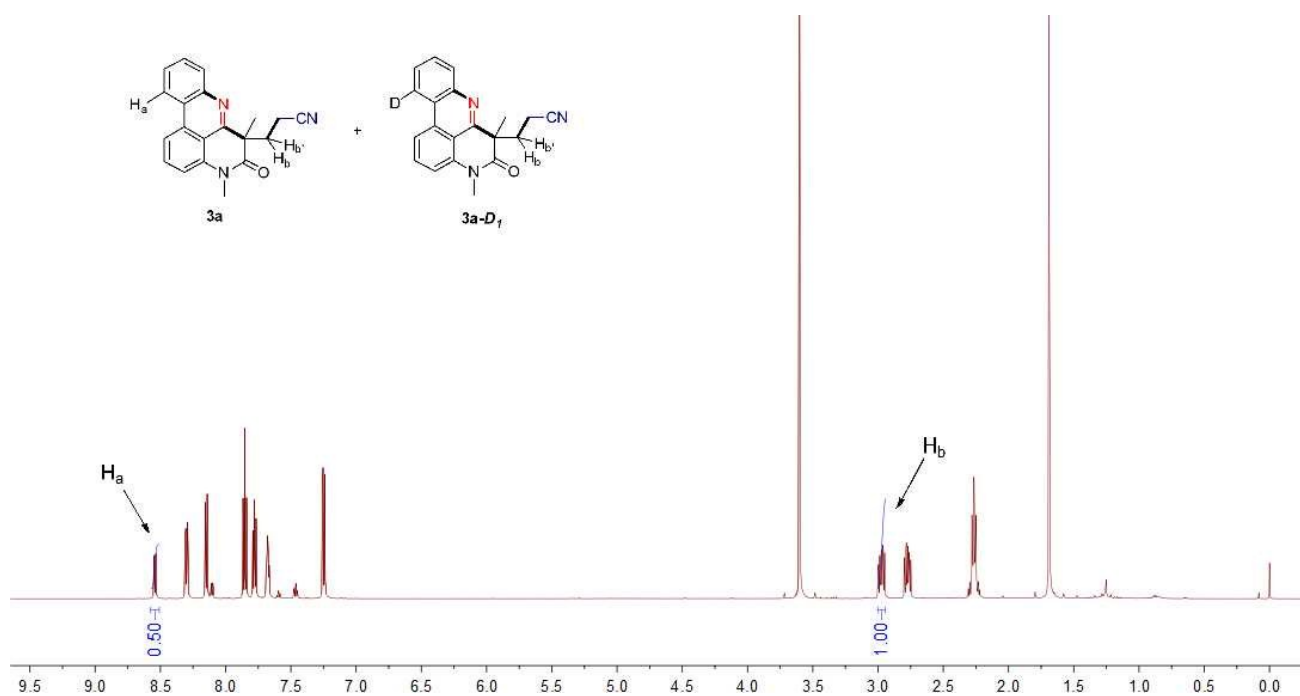
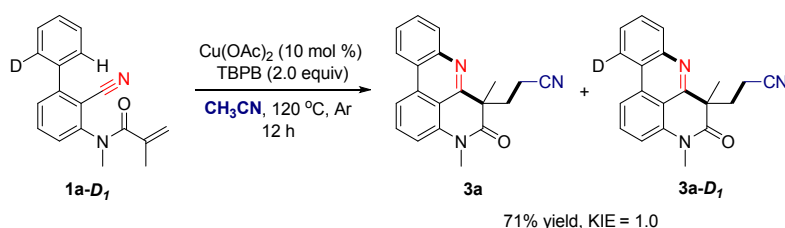


Figure S2. ¹H NMR spectra of the mixture of compound **3a** and **3a-D₁**.

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-D₂**. The products were under ¹H-NMR analysis (Figure S3).

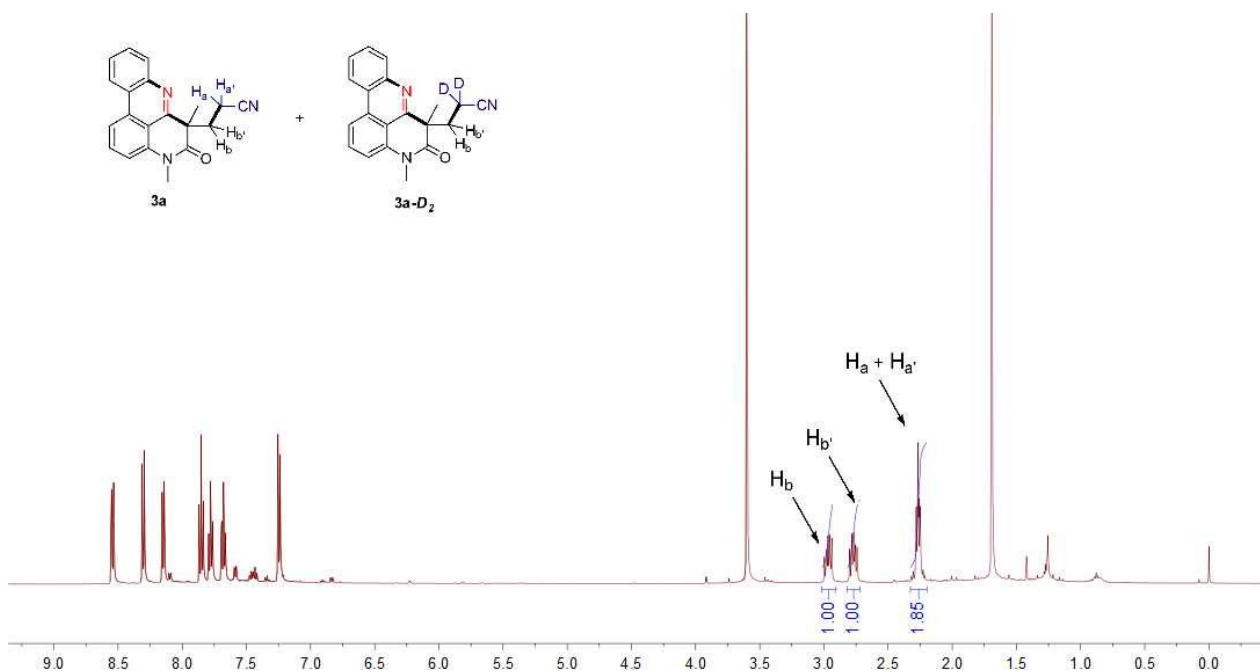
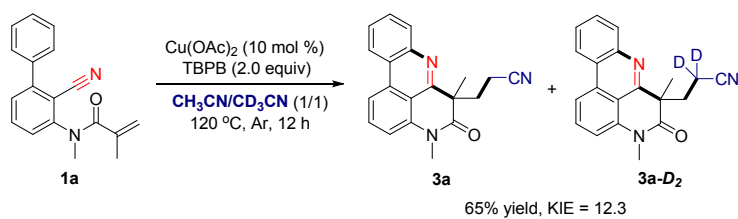
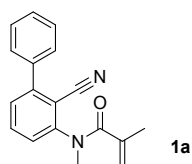
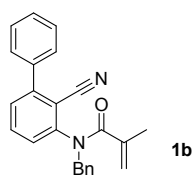


Figure S3. ^1H NMR spectra of the mixture of compound **3a** and **3a- D_2** .

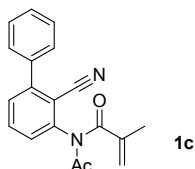
7. Characterization of compounds



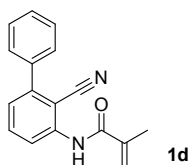
***N*-(2-cyano-[1,1'-biphenyl]-3-yl)-*N*-methylmethacrylamide.** Purified by column chromatography (petroleum ether : ethyl acetate = 4 : 1). Yellow solid, mp 118–119 °C. ^1H NMR (600 MHz, CDCl_3) δ 7.64 (t, $J = 7.9$ Hz, 1H), 7.55 (d, $J = 7.9$ Hz, 2H), 7.52–7.42 (m, 4H), 7.27 (d, $J = 7.6$ Hz, 1H), 5.15 (s, 1H), 5.09 (s, 1H), 3.43 (s, 3H), 1.93 (s, 3H). ^{13}C NMR (151 MHz, CDCl_3) 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 $\text{C}_{18}\text{H}_{16}\text{N}_2\text{O}$ ($\text{M}+\text{H}$) $^+$, 277.1335; found, 277.1341.



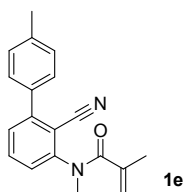
***N*-benzyl-*N*-(2-cyano-[1,1'-biphenyl]-3-yl)methacrylamide.** Purified by column chromatography (petroleum ether : ethyl acetate = 4 : 1). White solid, mp 82–83 °C. ¹H NMR (600 MHz, CDCl₃) δ 7.55–7.40 (m, 6H), 7.37 (dd, *J* = 7.8, 1.0 Hz, 1H), 7.30–7.14 (m, 5H), 6.94 (d, *J* = 7.6 Hz, 1H), 5.49 (s, 1H), 5.14 (s, 1H), 5.08 (s, 1H), 4.69 (s, 1H), 1.95 (s, 3H). ¹³C NMR (151 MHz, CDCl₃) δ 171.2, 147.2, 146.3, 140.1, 137.3, 136.2, 132.8, 129.0, 128.9, 128.68, 128.65, 128.5, 128.3, 127.8, 119.8, 116.0, 111.6, 52.7, 20.2. IR (film) ν 3062, 2221, 1653, 1629, 1471, 1434, 1388, 1337, 1223, 764, 698 cm⁻¹. HRMS (ESI): calc. for C₂₄H₂₀N₂O (M+H)⁺, 353.1648; found, 353.1654.



***N*-acetyl-*N*-(2-cyano-[1,1'-biphenyl]-3-yl)methacrylamide.** Purified by column chromatography (petroleum ether : ethyl acetate = 3 : 1). Yellow oil. ¹H NMR (500 MHz, CDCl₃) δ 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). ¹³C NMR (126 MHz, CDCl₃) δ 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) ν 2923, 2223, 1714, 1637, 1536, 1468, 1272, 1000, 803, 755, 698 cm⁻¹. HRMS (ESI): calc. for C₁₉H₁₆N₂O₂ (M+H)⁺, 305.1285; found, 305.1290.

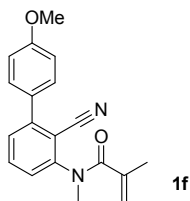


***N*-(2-cyano-[1,1'-biphenyl]-3-yl)methacrylamide.** Purified by column chromatography (petroleum ether : ethyl acetate = 6 : 1). White solid, mp 96–97 °C. ¹H NMR (500 MHz, CDCl₃) δ 8.52 (dd, *J* = 8.5, 0.7 Hz, 1H), 8.27 (s, 1H), 7.63 (t, *J* = 8.1 Hz, 1H), 7.58–7.40 (m, 5H), 7.23 (dd, *J* = 7.7, 0.9 Hz, 1H), 5.98 (d, *J* = 0.5 Hz, 1H), 5.59 (dd, *J* = 2.9, 1.4 Hz, 1H), 2.12 (s, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 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) ν 3058, 2926, 2208, 1694, 1522, 1465, 1293, 1162, 805, 760, 700 cm⁻¹. HRMS (ESI): calc. for C₁₇H₁₄N₂O (M+H)⁺, 263.1179; found, 263.1163.

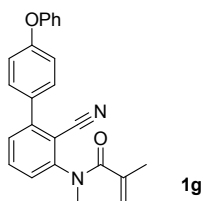


***N*-(2-cyano-4'-methyl-[1,1'-biphenyl]-3-yl)-*N*-methylmethacrylamide.** Purified by column chromatography (petroleum ether : ethyl acetate = 4 : 1). White solid, mp 116–118 °C. ¹H NMR (600 MHz, CDCl₃) δ 7.62 (t, *J* = 7.9 Hz, 1H), 7.50–7.39 (m, 3H), 7.30 (d, *J* = 8.1 Hz, 2H), 7.23 (d, *J* = 7.5 Hz, 1H), 5.14 (s, 1H), 5.09 (s, 1H), 3.43 (s,

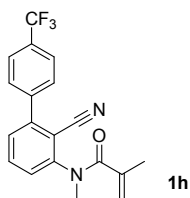
3H), 2.41 (s, 3H), 1.92 (s, 3H). ^{13}C NMR (151 MHz, CDCl_3) δ 171.7, 148.4, 147.4, 139.9, 139.0, 134.4, 133.3, 129.4, 128.7, 128.5, 126.8, 119.6, 115.9, 110.7, 37.4, 21.1, 20.0. IR (film) ν 2976, 2220, 1655, 1627, 1464, 1362, 1230, 1090, 1046, 946, 810 cm^{-1} . HRMS (ESI): calc. for $\text{C}_{19}\text{H}_{18}\text{N}_2\text{O}$ ($\text{M}+\text{H}$) $^+$, 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) δ 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). ^{13}C NMR (151 MHz, CDCl_3) δ 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) ν 2919, 2222, 1668, 1612, 1518, 1464, 1258, 1191, 927, 836, 752 cm^{-1} . HRMS (ESI): calc. for $\text{C}_{19}\text{H}_{18}\text{N}_2\text{O}_2$ ($\text{M}+\text{H}$) $^+$, 307.1441; found, 307.1446.

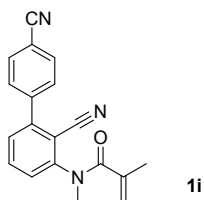


***N*-(2-cyano-4'-phenoxy-[1,1'-biphenyl]-3-yl)-*N*-methylmethacrylamide.** Purified by column chromatography (petroleum ether : ethyl acetate = 4 : 1). White solid, mp 99–100 °C. ^1H NMR (600 MHz, CDCl_3) δ 7.63 (t, J = 7.9 Hz, 1H), 7.55–7.48 (m, 2H), 7.44 (dd, J = 7.9, 1.0 Hz, 1H), 7.41–7.34 (m, 2H), 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). ^{13}C NMR (151 MHz, CDCl_3) δ 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) ν 3068, 2224, 1653, 1589, 1472, 1361, 1249, 1153, 781, 753 cm^{-1} . HRMS (ESI): calc. for $\text{C}_{24}\text{H}_{20}\text{N}_2\text{O}_2$ ($\text{M}+\text{H}$) $^+$, 369.1598; found, 369.1614.

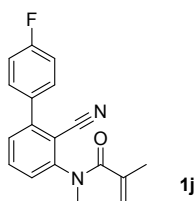


***N*-(2-cyano-4'-(trifluoromethyl)-[1,1'-biphenyl]-3-yl)-*N*-methylmethacrylamide.** Purified by column chromatography (petroleum ether : ethyl acetate = 4 : 1). Yellow solid, mp 110–111 °C. ^1H NMR (600 MHz, CDCl_3) δ 7.77 (d, J = 8.3 Hz, 2H), 7.72 (t, J = 7.9 Hz, 1H), 7.69 (d, J = 8.1 Hz, 2H), 7.48 (dd, J = 7.8, 1.0 Hz, 1H), 7.36 (d,

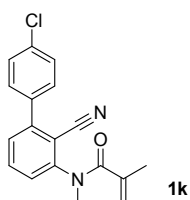
$J = 7.9$ Hz, 1H), 5.19 (s, 1H), 5.10 (s, 1H), 3.45 (s, 3H), 1.95 (s, 3H). ^{13}C NMR (151 MHz, CDCl_3) δ 171.6, 148.5, 145.6, 140.8, 139.8, 133.7, 130.9 (q, $J_{\text{C-F}} = 32.7$ Hz), 129.1, 128.7, 127.8, 125.6 (q, $J_{\text{C-F}} = 3.6$ Hz), 123.8 (q, $J_{\text{C-F}} = 273.3$ Hz), 115.4, 110.9, 37.6, 19.9. IR (film) ν 3063, 2223, 1655, 1624, 1324, 1178, 1121, 1065, 917, 849, 821 cm^{-1} . HRMS (ESI): calc. for $\text{C}_{19}\text{H}_{15}\text{F}_3\text{N}_2\text{O}$ ($\text{M}+\text{H}$) $^+$, 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. ^1H 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) ν 2976, 2225, 1655, 1626, 1586, 1468, 1377, 1362, 1090, 944, 818 cm^{-1} . HRMS (ESI): calc. for $\text{C}_{19}\text{H}_{15}\text{N}_3\text{O}$ ($\text{M}+\text{H}$) $^+$, 302.1288; found, 302.1294.

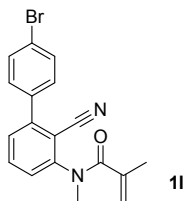


***N*-(2-cyano-4'-fluoro-[1,1'-biphenyl]-3-yl)-*N*-methylmethacrylamide.** Purified by column chromatography (petroleum ether : ethyl acetate = 5 : 1). White solid, mp 130–131 °C. ^1H NMR (600 MHz, CDCl_3) δ 7.66 (t, $J = 7.9$ Hz, 1H), 7.57–7.50 (m, 2H), 7.44 (dd, $J = 7.9, 1.1$ Hz, 1H), 7.33–7.26 (m, 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, 163.0 (d, $J_{\text{C-F}} = 249.0$ Hz), 148.3, 146.1, 139.8, 133.5, 133.3 (d, $J_{\text{C-F}} = 2.7$ Hz), 130.5 (d, $J_{\text{C-F}} = 8.4$ Hz), 128.7, 127.1, 119.7, 115.8 (d, $J_{\text{C-F}} = 16.9$ Hz), 115.6, 110.8, 37.4, 20.0. IR (film) ν 2223, 1651, 1624, 1569, 1511, 1467, 1378, 1223, 1091, 922, 849 cm^{-1} . HRMS (ESI): calc. for $\text{C}_{18}\text{H}_{15}\text{FN}_2\text{O}$ ($\text{M}+\text{H}$) $^+$, 295.1241; found, 295.1244.

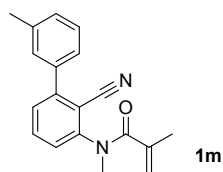


***N*-(4'-chloro-2-cyano-[1,1'-biphenyl]-3-yl)-*N*-methylmethacrylamide.** Purified by column chromatography (petroleum ether : ethyl acetate = 4 : 1). Yellow solid, mp 118–119 °C. ^1H NMR (600 MHz, CDCl_3) δ 7.68 (t, $J = 7.9$ Hz, 1H), 7.55–7.39 (m, 5H), 7.31 (d, $J = 5.8$ Hz, 2H), 5.17 (s, 1H), 5.09 (s, 1H), 3.43 (s, 3H), 1.93 (s, 3H). ^{13}C

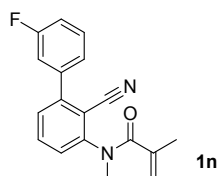
NMR (151 MHz, CDCl₃) δ 171.4, 148.4, 145.7, 139.7, 135.6, 135.1, 133.5, 129.9, 128.8, 128.5, 127.3, 119.6, 115.5, 110.6, 37.4, 19.9. IR (film) ν 2976, 2925, 2229, 1653, 1460, 1363, 1084, 1049, 917, 816 cm⁻¹. HRMS (ESI): calc. for C₁₈H₁₅ClN₂O (M+H)⁺, 311.0946; found, 311.0955.



***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. ¹H NMR (600 MHz, CDCl₃) δ 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). ¹³C NMR (151 MHz, CDCl₃) δ 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) ν 2923, 2228, 1655, 1467, 1361, 1087, 1009, 914, 813 cm⁻¹. HRMS (ESI): calc. for C₁₈H₁₅BrN₂O (M+H)⁺, 355.0441; found, 355.0438.

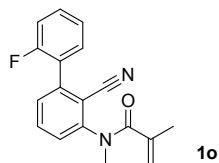


***N*-(2-cyano-3'-methyl-[1,1'-biphenyl]-3-yl)-*N*-methylmethacrylamide.** Purified by column chromatography (petroleum ether : ethyl acetate = 4 : 1). Yellow solid, mp 71–72 °C. ¹H NMR (600 MHz, CDCl₃) δ 7.62 (t, *J* = 7.9 Hz, 1H), 7.44 (d, *J* = 7.8 Hz, 1H), 7.41–7.36 (m, 1H), 7.34 (d, *J* = 3.8 Hz, 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). ¹³C NMR (151 MHz, CDCl₃) δ 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) ν 2925, 2223, 1657, 1570, 1456, 1362, 1236, 1099, 922, 791, 704 cm⁻¹. HRMS (ESI): calc. for C₁₉H₁₈N₂O (M+H)⁺, 291.1492; found, 291.1497.

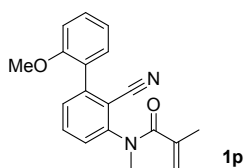


***N*-(2-cyano-3'-fluoro-[1,1'-biphenyl]-3-yl)-*N*-methylmethacrylamide.** Purified by column chromatography (petroleum ether : ethyl acetate = 3 : 1). Yellow solid, mp 74–75 °C. ¹H NMR (600 MHz, CDCl₃) δ 7.67 (t, *J* = 7.9 Hz, 1H), 7.50–7.41 (m, 2H), 7.34 (dd, *J* = 7.7, 0.5 Hz, 1H), 7.31 (d, *J* = 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). ¹³C NMR (151 MHz, CDCl₃) δ 171.6, 162.6 (d, *J*_{C-F} = 247.5 Hz), 148.5, 145.8 (d, *J*_{C-F} = 1.2 Hz), 139.9, 139.3 (d, *J*_{C-F} = 7.8 Hz), 133.6, 130.4 (d, *J*_{C-F} = 8.4 Hz), 128.7,

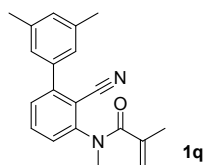
127.6, 124.5 (d, $J_{C-F} = 2.9$ Hz), 119.8, 116.0 (d, $J_{C-F} = 21.0$ Hz), 115.8 (d, $J_{C-F} = 22.7$ Hz), 115.5, 110.9, 37.6, 20.0. IR (film) ν 2974, 2926, 2225, 1657, 1571, 1466, 1364, 1092, 785, 698 cm^{-1} . HRMS (ESI): calc. for $\text{C}_{18}\text{H}_{15}\text{FN}_2\text{O}$ ($\text{M}+\text{H}$)⁺, 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. ¹H NMR (600 MHz, CDCl_3) δ 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). ¹³C NMR (151 MHz, CDCl_3) δ 171.5, 159.1 (d, $J_{C-F} = 248.8$ Hz), 147.9, 141.1, 139.7, 133.2, 131.0 (d, $J_{C-F} = 8.2$ Hz), 130.9 (d, $J_{C-F} = 2.0$ Hz), 129.6 (d, $J_{C-F} = 0.7$ Hz), 127.6, 125.0 (d, $J_{C-F} = 14.7$ Hz), 124.3 (d, $J_{C-F} = 3.7$ Hz), 119.7, 116.0 (d, $J = 21.8$ Hz), 115.2, 112.4, 37.4, 19.9. IR (film) ν 3065, 2229, 1654, 1629, 1569, 1467, 1368, 1219, 1081, 823, 756 cm^{-1} . HRMS (ESI): calc. for $\text{C}_{18}\text{H}_{15}\text{FN}_2\text{O}$ ($\text{M}+\text{Na}$)⁺, 317.1061; found, 317.1061.

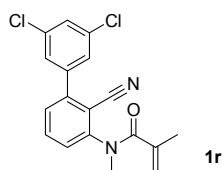


***N*-(2-cyano-2'-methoxy-[1,1'-biphenyl]-3-yl)-*N*-methylmethacrylamide.** Purified by column chromatography (petroleum ether : ethyl acetate = 2 : 1). White solid, mp 119–121 °C. ¹H NMR (600 MHz, CDCl_3) δ 7.61 (t, $J = 7.9$ Hz, 1H), 7.47–7.40 (m, 1H), 7.38 (dd, $J = 7.8, 0.8$ Hz, 1H), 7.25 (dd, $J = 7.5, 1.6$ 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). ¹³C NMR (151 MHz, CDCl_3) δ 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) ν 3432, 3060, 2923, 2228, 1657, 1627, 1499, 1367, 1244, 827, 755 cm^{-1} . HRMS (ESI): calc. for $\text{C}_{19}\text{H}_{18}\text{N}_2\text{O}_2$ ($\text{M}+\text{H}$)⁺, 307.1441; found, 307.1443.

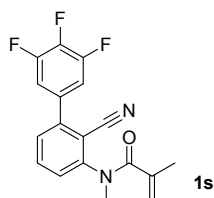


***N*-(2-cyano-3',5'-dimethyl-[1,1'-biphenyl]-3-yl)-*N*-methylmethacrylamide.** Purified by column chromatography (petroleum ether : ethyl acetate = 4 : 1). Yellow solid, mp 132–133 °C. ¹H NMR (600 MHz, CDCl_3) δ 7.61 (t, $J = 7.9$ Hz, 1H), 7.43 (dd, $J = 7.8, 1.0$ Hz, 1H), 7.22 (d, $J = 7.2$ Hz, 1H), 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). ¹³C NMR (151 MHz, CDCl_3) δ 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) ν 2925, 2225, 1649, 1622,

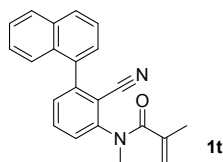
1569, 1460, 1370, 1105, 854, 820, 701 cm^{-1} . HRMS (ESI): calc. for $\text{C}_{20}\text{H}_{20}\text{N}_2\text{O}$ ($\text{M}+\text{H}$)⁺, 305.1648; found, 305.1651.



***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 $\text{C}_{18}\text{H}_{14}\text{Cl}_2\text{N}_2\text{O}$ ($\text{M}+\text{H}$)⁺, 345.0556; found, 345.0539.

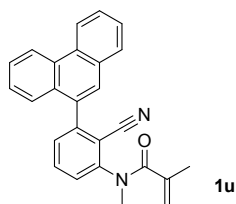


***N*-(2-cyano-3',4',5'-trifluoro-[1,1'-biphenyl]-3-yl)-*N*-methylmethacrylamide.** Purified by column chromatography (petroleum ether : ethyl acetate = 3 : 1). Yellow solid, mp 96–98 °C. ¹H NMR (600 MHz, CDCl_3) δ 7.69 (t, J = 7.9 Hz, 1H), 7.40 (d, J = 7.4 Hz, 1H), 7.34 (d, J = 7.9 Hz, 1H), 7.24–7.13 (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 $\text{C}_{18}\text{H}_{13}\text{F}_3\text{N}_2\text{O}$ ($\text{M}+\text{H}$)⁺, 331.1053; found, 331.1058.

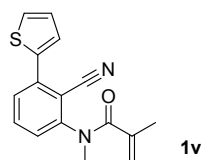


***N*-(2-cyano-3-(naphthalen-1-yl)phenyl)-*N*-methylmethacrylamide.** Purified by column chromatography (petroleum ether : ethyl acetate = 3 : 1). Yellow solid, mp 96–97 °C. ¹H NMR (600 MHz, CDCl_3) δ 7.94 (dd, J = 13.3, 8.3 Hz, 2H), 7.68 (t, J = 7.9 Hz, 1H), 7.60–7.40 (m, 6H), 7.35 (d, J = 7.7 Hz, 1H), 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 $\text{C}_{22}\text{H}_{18}\text{N}_2\text{O}$ ($\text{M}+\text{H}$)⁺, 327.1492; found,

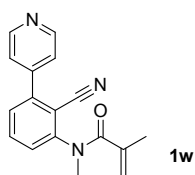
327.1495.



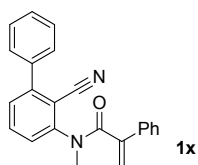
***N*-(2-cyano-3-(phenanthren-9-yl)phenyl)-*N*-methylmethacrylamide.** Purified by column chromatography (petroleum ether : ethyl acetate = 3 : 1). Yellow solid, mp 88–90 °C. ¹H NMR (600 MHz, CDCl₃) δ 8.74 (d, *J* = 8.5 Hz, 1H), 8.68 (d, *J* = 8.3 Hz, 1H), 7.89 (d, *J* = 7.7 Hz, 1H), 7.71 (s, 1H), 7.69–7.57 (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). ¹³C NMR (151 MHz, CDCl₃) 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) ν 3061, 2924, 2226, 1655, 1624, 1569, 1451, 1364, 743, 721 cm⁻¹. HRMS (ESI): calc. for C₂₆H₂₀N₂O (M+H)⁺, 377.1648; found, 377.1656.



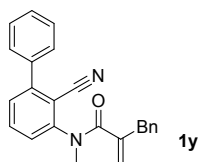
***N*-(2-cyano-3-(thiophen-2-yl)phenyl)-*N*-methylmethacrylamide.** Purified by column chromatography (petroleum ether : ethyl acetate = 3 : 1). Yellow solid, mp 63–64 °C. ¹H NMR (600 MHz, CDCl₃) δ 7.67 (dd, *J* = 3.6, 0.8 Hz, 1H), 7.62–7.53 (m, 2H), 7.47 (dd, *J* = 5.1, 0.7 Hz, 1H), 7.24–7.13 (m, 2H), 5.15 (s, 1H), 5.10 (s, 2H), 3.42 (s, 3H), 1.92 (s, 3H). ¹³C NMR (151 MHz, CDCl₃) 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) ν 3076, 2923, 2225, 1659, 1629, 1569, 1466, 1364, 1093, 807, 707 cm⁻¹. HRMS (ESI): calc. for C₁₆H₁₄N₂OS (M+H)⁺, 283.0900; found, 283.0904.



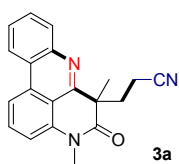
***N*-(2-cyano-3-(pyridin-4-yl)phenyl)-*N*-methylmethacrylamide.** Purified by column chromatography (petroleum ether : ethyl acetate = 1 : 1). White solid, mp 103–105 °C. ¹H NMR (600 MHz, CDCl₃) δ 8.77 (d, *J* = 5.2 Hz, 2H), 7.73 (t, *J* = 7.9 Hz, 1H), 7.48 (t, *J* = 7.0 Hz, 3H), 7.38 (d, *J* = 7.8 Hz, 1H), 5.20 (s, 1H), 5.10 (s, 1H), 3.45 (s, 3H), 1.95 (s, 3H). ¹³C NMR (151 MHz, CDCl₃) 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) ν 3093, 2224, 1650, 1623, 1470, 1416, 1365, 1234, 1096, 931, 815 cm⁻¹. HRMS (ESI): calc. for C₁₈H₁₃F₃N₂O (M+H)⁺, 278.1288; found, 278.1291.



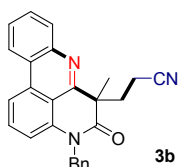
***N*-(2-cyano-[1,1'-biphenyl]-3-yl)-*N*-methyl-2-phenylacrylamide.** Purified by column chromatography (petroleum ether : ethyl acetate = 3 : 1). Yellow solid, mp 78–79 °C. ¹H NMR (600 MHz, CDCl₃) δ 7.42 (t, *J* = 7.4 Hz, 3H), 7.36 (t, *J* = 7.9 Hz, 1H), 7.30 (d, *J* = 6.6 Hz, 2H), 7.23 (d, *J* = 7.8 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) ν 3048, 2223, 1654, 1465, 1364, 1256, 1181, 1081, 927, 762, 701 cm⁻¹. HRMS (ESI): calc. for C₂₃H₁₈N₂O (M+H)⁺, 339.1492; found, 339.1500.



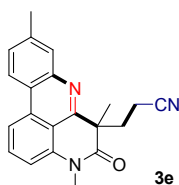
2-benzyl-*N*-(2-cyano-[1,1'-biphenyl]-3-yl)-*N*-methylacrylamide. Purified by column chromatography (petroleum ether : ethyl acetate = 4 : 1). White solid, mp 86–88 °C. ¹H NMR (600 MHz, CDCl₃) δ 7.54–7.44 (m, 5H), 7.38 (d, *J* = 6.3 Hz, 2H), 7.31 (t, *J* = 7.4 Hz, 2H), 7.25 (m, 1H), 7.15 (s, 2H), 6.39 (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, 128.66, 128.48, 127.28, 126.60, 119.55, 115.90, 110.76, 40.08, 37.43. IR (film) ν 3028, 2219, 1655, 1564, 1430, 1358, 1185, 1080, 920, 758, 700 cm⁻¹. HRMS (ESI): calc. for C₂₄H₂₀N₂O (M+H)⁺, 353.1648; found, 353.1653.



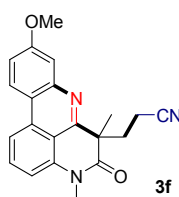
3-(4,6-dimethyl-5-oxo-5,6-dihydro-4*H*-pyrido[4,3,2-*gh*]phenanthridin-6-yl)propanenitrile. Purified by column chromatography (petroleum ether : ethyl acetate = 4 : 1). Yellow solid, mp 130–131 °C. ¹H NMR (500 MHz, CDCl₃) δ 8.54 (d, *J* = 8.2 Hz, 1H), 8.30 (d, *J* = 8.3 Hz, 1H), 8.15 (d, *J* = 8.2 Hz, 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) ν 2981, 2244, 1671, 1609, 1591, 1466, 1342, 1074, 761, 646, 496 cm⁻¹. HRMS (ESI): calc. for C₂₀H₁₇N₃O (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) ν 2956, 2919, 2850, 2050, 1667, 1638, 1618, 1455, 1187, 762, 643 cm⁻¹. HRMS (ESI): calc. for C₂₆H₂₁N₃O (M+H)⁺, 392.1757; found, 392.1765.

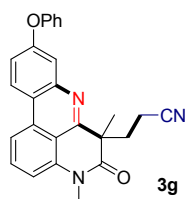


3-(4,6,9-trimethyl-5-oxo-5,6-dihydro-4H-pyrido[4,3,2-*gh*]phenanthridin-6-yl)propanenitrile. Purified by column chromatography (petroleum ether : ethyl acetate = 4 : 1). Yellow solid, mp 126–127 °C. ¹H NMR (500 MHz, CDCl₃) δ 8.41 (dd, *J* = 8.4, 2.2 Hz, 1H), 8.25 (dd, *J* = 8.3, 2.0 Hz, 1H), 7.95 (s, 1H), 7.85–7.77 (m, 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) ν 2926, 2245, 1670, 1588, 1569, 1469, 1406, 1341, 1075, 802, 768 cm⁻¹. HRMS (ESI): calc. for C₂₁H₁₉N₃O (M+H)⁺, 330.1601; found, 330.1607.



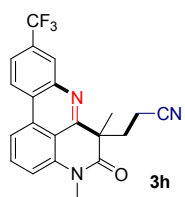
3-(9-methoxy-4,6-dimethyl-5-oxo-5,6-dihydro-4H-pyrido[4,3,2-*gh*]phenanthridin-6-yl)propanenitrile. Purified by column chromatography (petroleum ether : ethyl acetate = 5 : 1). Yellow solid, mp 128–129 °C. ¹H NMR (600 MHz, CDCl₃) δ 8.41 (d, *J* = 9.0 Hz, 1H), 8.18 (d, *J* = 8.4 Hz, 1H), 7.80 (t, *J* = 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

(film) ν 2929, 2245, 1669, 1614, 1588, 1472, 1340, 1233, 1197, 802, 767 cm^{-1} . HRMS (ESI): calc. for $\text{C}_{21}\text{H}_{19}\text{N}_3\text{O}_2$ ($\text{M}+\text{H}$)⁺, 346.1550; found, 346.1558.



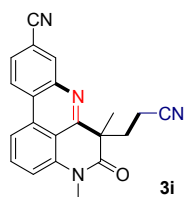
3-(4,6-dimethyl-5-oxo-9-phenoxy-5,6-dihydro-4H-pyrido[4,3,2-gh]phenanthridin-6-yl)propanenitrile.

Purified by column chromatography (petroleum ether : ethyl acetate = 5 : 1). Yellow solid, mp 69–71 °C. ¹H NMR (600 MHz, CDCl_3) δ 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). ¹³C NMR (151 MHz, CDCl_3) δ 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, 30.3, 29.9, 13.7. IR (film) ν 2959, 2920, 2085, 1639, 1530, 1487, 1408, 1255, 873, 747, 692 cm^{-1} . HRMS (ESI): calc. for $\text{C}_{26}\text{H}_{21}\text{N}_3\text{O}_2$ ($\text{M}+\text{H}$)⁺, 408.1707; found, 408.1712.



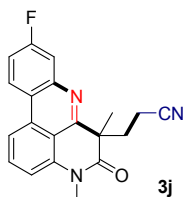
3-(4,6-dimethyl-5-oxo-9-(trifluoromethyl)-5,6-dihydro-4H-pyrido[4,3,2-gh]phenanthridin-6-yl)propanenitrile.

Purified by column chromatography (petroleum ether : ethyl acetate = 4 : 1). White solid, mp 177–178 °C. ¹H NMR (600 MHz, CDCl_3) δ 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). ¹³C NMR (151 MHz, CDCl_3) δ 172.3, 159.4, 144.1, 138.7, 132.8, 132.8, 131.2 (q, $J_{\text{C-F}}$ = 32.9 Hz), 127.4 (q, $J_{\text{C-F}}$ = 4.1 Hz), 125.1, 124.0 (q, $J_{\text{C-F}}$ = 272.4 Hz), 123.8, 122.8 (d, $J_{\text{C-F}}$ = 3.1 Hz), 119.0, 116.7, 112.6, 112.2, 50.9, 34.2, 30.4, 30.0, 13.7. IR (film) ν 3090, 2247, 1659, 1591, 1359, 1333, 1314, 1185, 1118, 814, 772 cm^{-1} . HRMS (ESI): calc. for $\text{C}_{20}\text{H}_{16}\text{BrN}_3\text{O}$ ($\text{M}+\text{H}$)⁺, 384.1318; found, 384.1323.

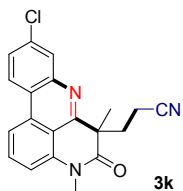


6-(2-cyanoethyl)-4,6-dimethyl-5-oxo-5,6-dihydro-4H-pyrido[4,3,2-gh]phenanthridine-9-carbonitrile. Purified by column chromatography (petroleum ether : ethyl acetate = 3 : 1). Yellow solid, mp 295–296 °C. ¹H NMR (600

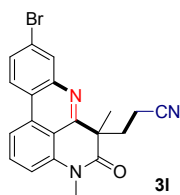
MHz, CDCl₃) δ 8.62 (d, *J* = 8.5 Hz, 1H), 8.50 (d, *J* = 1.6 Hz, 1H), 8.31 (d, *J* = 8.2 Hz, 1H), 7.96 (t, *J* = 8.1 Hz, 1H), 7.85 (dd, *J* = 8.5, 1.7 Hz, 1H), 7.37 (d, *J* = 7.9 Hz, 1H), 3.62 (s, 3H), 2.98–2.91 (m, 1H), 2.81–2.74 (m, 1H), 2.35–2.22 (m, 2H), 1.71 (s, 3H). ¹³C NMR (151 MHz, CDCl₃) δ 172.2, 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) ν 2927, 2227, 1667, 1589, 1467, 1340, 1161, 1092, 804, 774, 630 cm⁻¹. HRMS (ESI): calc. for C₂₁H₁₆N₄O (M+Na)⁺, 363.1216; found, 363.1218.



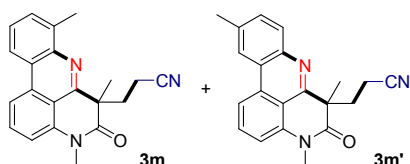
3-(9-fluoro-4,6-dimethyl-5-oxo-5,6-dihydro-4H-pyrido[4,3,2-*gh*]phenanthridin-6-yl)propanenitrile. Purified by column chromatography (petroleum ether : ethyl acetate = 4 : 1). Yellow solid, mp 146–147 °C. ¹H NMR (600 MHz, CDCl₃) δ 8.52 (dd, *J* = 9.1, 5.8 Hz, 1H), 8.23 (d, *J* = 8.3 Hz, 1H), 7.86 (t, *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). ¹³C NMR (151 MHz, CDCl₃) δ 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) ν 2931, 2246, 1670, 1612, 1590, 1579, 1470, 1339, 1169, 794, 771 cm⁻¹. HRMS (ESI): calc. for C₂₀H₁₆FN₃O (M+H)⁺, 334.1350; found, 334.1355.



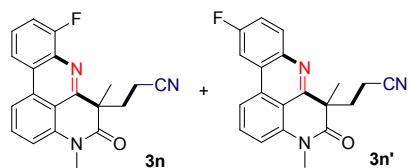
3-(9-chloro-4,6-dimethyl-5-oxo-5,6-dihydro-4H-pyrido[4,3,2-*gh*]phenanthridin-6-yl)propanenitrile. Purified by column chromatography (petroleum ether : ethyl acetate = 4 : 1). White solid, mp 175–176 °C. ¹H NMR (600 MHz, CDCl₃) δ 8.45 (d, *J* = 8.8 Hz, 1H), 8.24 (d, *J* = 8.2 Hz, 1H), 8.15 (d, *J* = 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). ¹³C NMR (151 MHz, CDCl₃) δ 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) ν 2975, 2925, 2078, 1638, 1453, 1403, 1384, 1336, 1152, 1049, 879 cm⁻¹. HRMS (ESI): calc. for C₂₀H₁₆ClN₃O (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 (3l). Purified by column chromatography (petroleum ether : ethyl acetate = 4 : 1). Yellow solid, mp 189–190 °C. ¹H NMR (600 MHz, CDCl₃) δ 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). ¹³C NMR (151 MHz, CDCl₃) δ 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) ν 2952, 2851, 2026, 1664, 1638, 1589, 1466, 1340, 1080, 800, 746 cm⁻¹. HRMS (ESI): calc. for C₂₀H₁₆BrN₃O (M+H)⁺, 394.0550; found, 394.0548.

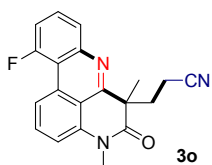


3-(4,6,8-trimethyl-5-oxo-5,6-dihydro-4H-pyrido[4,3,2-gh]phenanthridin-6-yl)propanenitrile (3m); 3-(4,6,10-trimethyl-5-oxo-5,6-dihydro-4H-pyrido[4,3,2-gh]phenanthridin-6-yl)propanenitrile (3m'). Purified by column chromatography (petroleum ether : ethyl acetate = 6 : 1), products **3m** and **3m'** can not be separated column chromatography on silica gel. Yellow solid, mp 132–133 °C. ¹H NMR (600 MHz, CDCl₃) δ 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). ¹³C NMR (151 MHz, CDCl₃) δ 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) ν 2951, 2922, 2245, 2050, 1668, 1612, 1589, 1464, 1339, 777, 751 cm⁻¹. HRMS (ESI): calc. for C₂₁H₁₉N₃O (M+H)⁺, 330.1601; found, 330.1608.

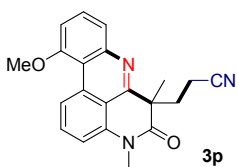


3-(8-fluoro-4,6-dimethyl-5-oxo-5,6-dihydro-4H-pyrido[4,3,2-gh]phenanthridin-6-yl)propanenitrile (3n); 3-(10-fluoro-4,6-dimethyl-5-oxo-5,6-dihydro-4H-pyrido[4,3,2-gh]phenanthridin-6-yl)propanenitrile (3n'). Purified by column chromatography (petroleum ether : ethyl acetate = 5 : 1), products **3n** and **3n'** can not be separated

column chromatography on silica gel. Yellow solid, mp 136–137 °C. ¹H NMR (600 MHz, CDCl₃) δ 8.32 (d, *J* = 8.3 Hz, 1H), 8.28 (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). ¹³C NMR (126 MHz, CDCl₃) δ 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, 132.14 (s), 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) ν 2971, 2901, 2025, 1637, 1619, 1453, 1394, 1252, 1051, 880, 785 cm⁻¹. HRMS (ESI): calc. for C₂₀H₁₆FN₃O (M+H)⁺, 334.1350; found, 334.1356.

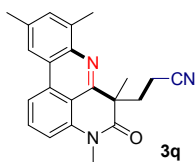


3-(11-fluoro-4,6-dimethyl-5-oxo-5,6-dihydro-4H-pyrido[4,3,2-*gh*]phenanthridin-6-yl)propanenitrile. Purified by column chromatography (petroleum ether : ethyl acetate = 5 : 1). Yellow solid, mp 168–170 °C. ¹H NMR (600 MHz, CDCl₃) δ 8.74 (dd, *J* = 8.4, 1.8 Hz, 1H), 7.98 (d, *J* = 8.2 Hz, 1H), 7.91–7.85 (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), 2.992.94 (m, 1H), 2.79–2.75 (m, 1H), 2.33–2.22 (m, 2H), 1.68 (s, 3H). ¹³C NMR (151 MHz, CDCl₃) δ 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) ν 2942, 2248, 1670, 1607, 1463, 1340, 1286, 1201, 828, 768, 732 cm⁻¹. HRMS (ESI): calc. for C₂₀H₁₆FN₃O (M+H)⁺, 334.1350; found, 334.1358.

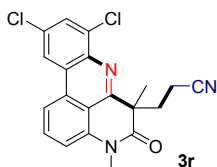


3-(11-methoxy-4,6-dimethyl-5-oxo-5,6-dihydro-4H-pyrido[4,3,2-*gh*]phenanthridin-6-yl)propanenitrile. Purified by column chromatography (petroleum ether : ethyl acetate = 3 : 1). Yellow solid, mp 129–132 °C. ¹H NMR (600 MHz, CDCl₃) δ 9.28 (d, *J* = 8.6 Hz, 1H), 7.86–7.74 (m, 2H), 7.70 (t, *J* = 8.0 Hz, 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). ¹³C NMR (151 MHz, CDCl₃) δ 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) ν 3164, 3003, 2944,

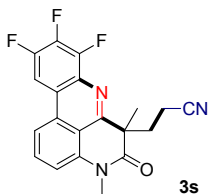
2253, 1633, 1421, 1324, 1039, 918, 750 cm^{-1} . HRMS (ESI): calc. for $\text{C}_{21}\text{H}_{19}\text{N}_3\text{O}_2$ ($\text{M}+\text{H}$) $^+$, 346.1550; found, 346.1552.



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) δ 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). ^{13}C NMR (126 MHz, CDCl_3) δ 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) ν 2972, 2919, 2069, 1637, 1461, 1404, 1067, 1048, 878, 726 cm^{-1} . HRMS (ESI): calc. for $\text{C}_{22}\text{H}_{21}\text{N}_3\text{O}$ ($\text{M}+\text{H}$) $^+$, 344.1757; found, 344.1763.

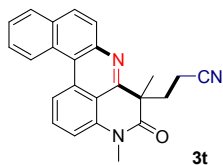


3-(8,10-dichloro-4,6-dimethyl-5-oxo-5,6-dihydro-4H-pyrido[4,3,2-gh]phenanthridin-6-yl)propanenitrile. Purified by column chromatography (petroleum ether : ethyl acetate = 3 : 1). White solid, mp 187–189 °C. ^1H NMR (600 MHz, CDCl_3) δ 8.41 (d, J = 1.9 Hz, 1H), 8.19 (d, J = 8.3 Hz, 1H), 7.90 (t, J = 8.1 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). ^{13}C NMR (126 MHz, CDCl_3) δ 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) ν 2976, 2901, 2086, 1638, 1394, 1251, 1077, 1048, 880, 623 cm^{-1} . HRMS (ESI): calc. for $\text{C}_{20}\text{H}_{15}\text{Cl}_2\text{N}_3\text{O}$ ($\text{M}+\text{H}$) $^+$, 384.0665; found, 384.0666.

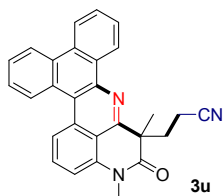


3-(8,9,10-trifluoro-4,6-dimethyl-5-oxo-5,6-dihydro-4H-pyrido[4,3,2-gh]phenanthridin-6-yl)propanenitrile. Purified by column chromatography (petroleum ether : ethyl acetate = 3 : 1). Yellow solid, mp 175–176 °C. ^1H NMR (500 MHz, CDCl_3) δ 8.09 (d, J = 8.3 Hz, 1H), 8.07–8.02 (m, 1H), 7.91 (t, J = 8.1 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). ^{13}C NMR (126 MHz, CDCl_3) δ 172.2, 158.8, 150.3 (ddd, $J_{\text{C-F}}$ = 252.0, 12.6, 2.5 Hz), 146.5 (ddd, $J_{\text{C-F}}$ = 259.6, 7.6, 5.0 Hz), 140.5 (ddd, $J_{\text{C-F}}$ = 254.5, 17.6, 13.9 Hz), 138.9, 133.1, 132.5 (d, $J_{\text{C-F}}$ = 8.4 Hz), 132.1 (d, $J_{\text{C-F}}$ = 2.5 Hz), 119.4 (d, $J_{\text{C-F}}$ = 8.5 Hz),

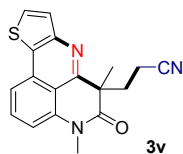
118.8, 116.4, 112.2, 112.0, 103.9 (dd, $J_{C-F} = 18.9, 4.7$ Hz), 50.9, 34.4, 30.2, 30.0, 13.6. IR (film) ν 2974, 2901, 2026, 1637, 1621, 1394, 1296, 1078, 1050, 880, 739 cm^{-1} . HRMS (ESI): calc. for $\text{C}_{20}\text{H}_{14}\text{F}_3\text{N}_3\text{O}$ ($\text{M}+\text{H}$) $^+$, 370.1162; found, 370.1166.



3-(4,6-dimethyl-5-oxo-5,6-dihydro-4H-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. ^1H NMR (600 MHz, CDCl_3) δ 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, $J = 8.2$ 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), 2.83–2.78 (m, 1H), 2.29 (t, $J = 7.9$ Hz, 2H), 1.71 (s, 3H). ^{13}C NMR (151 MHz, CDCl_3) δ 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, 119.3, 113.4, 110.2, 50.5, 34.4, 30.2, 30.1, 13.7. IR (film) ν 2919, 2901, 2251, 2077, 1667, 1619 1455, 1426, 1156, 874, 755 cm^{-1} . HRMS (ESI): calc. for $\text{C}_{24}\text{H}_{19}\text{N}_3\text{O}$ ($\text{M}+\text{H}$) $^+$, 366.1601; found, 366.1606.

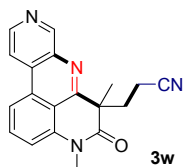


3-(4,6-dimethyl-5-oxo-5,6-dihydro-4H-dibenzo[a,c]pyrido[4,3,2-gh]phenanthridin-6-yl)propanenitrile. Purified by column chromatography (petroleum ether : ethyl acetate = 5 : 1). Yellow solid, mp 86–88 °C. ^1H NMR (600 MHz, CDCl_3) δ 9.34–9.28 (m, 1H), 8.87 (d, $J = 8.1$ Hz, 1H), 8.75 (d, $J = 8.1$ Hz, 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), 2.92–2.83 (m, 1H), 2.40–2.28 (m, 2H), 1.78 (s, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 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) ν 2976, 2910, 2026, 1625, 1402, 1255, 1055, 888, 741, 627 cm^{-1} . HRMS (ESI): calc. for $\text{C}_{28}\text{H}_{21}\text{N}_3\text{O}$ ($\text{M}+\text{H}$) $^+$, 416.1757; found, 416.1758.

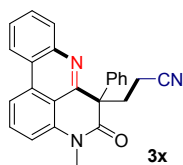


3-(4,6-dimethyl-5-oxo-5,6-dihydro-4H-benzo[de]thieno[3,2-b][1,6]naphthyridin-6-yl)propanenitrile. Purified by column chromatography (petroleum ether : ethyl acetate = 4 : 1). Yellow solid, mp 169–170 °C. ^1H NMR (600 MHz, CDCl_3) δ 7.82–7.71 (m, 3H), 7.67 (d, $J = 5.4$ Hz, 1H), 7.12 (dd, $J = 6.8, 1.6$ Hz, 1H), 3.59 (s, 3H), 2.92–2.88

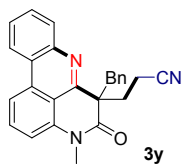
(m, 1H), 2.81–2.76 (m, 1H), 2.27–2.12 (m, 2H), 1.70 (s, 3H). ^{13}C NMR (151 MHz, CDCl_3) δ 172.7, 155.9, 152.0, 138.6, 132.3, 132.2, 128.0, 127.8, 126.1, 119.1, 117.3, 111.2, 109.6, 50.5, 35.0, 30.6, 29.9, 13.7. IR (film) ν 3117, 2923, 2250, 1667, 1619, 1569, 1460, 1096, 814, 748, 649 cm^{-1} . HRMS (ESI): calc. for $\text{C}_{18}\text{H}_{15}\text{N}_3\text{OS}$ ($\text{M}+\text{H}$) $^+$, 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. Purified by column chromatography (petroleum ether : ethyl acetate = 1 : 1). White solid, mp 128–129 °C. ^1H 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). ^{13}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 $\text{C}_{19}\text{H}_{16}\text{N}_4\text{O}$ ($\text{M}+\text{H}$) $^+$, 317.1397; found, 317.1400.

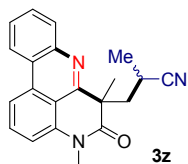


3-(4-methyl-5-oxo-6-phenyl-5,6-dihydro-4H-pyrido[4,3,2-gh]phenanthridin-6-yl)propanenitrile. Purified by column chromatography (petroleum ether : ethyl acetate = 4 : 1). Yellow solid, mp 151–152 °C. ^1H NMR (600 MHz, CDCl_3) δ 8.60–8.50 (m, 1H), 8.29 (d, J = 8.2 Hz, 1H), 8.24 (dd, J = 8.2, 0.9 Hz, 1H), 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). ^{13}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, 111.3, 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 $\text{C}_{25}\text{H}_{19}\text{N}_3\text{O}$ ($\text{M}+\text{Na}$) $^+$, 400.1420; found, 400.1419.

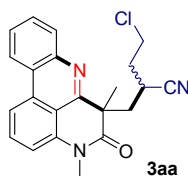


3-(6-benzyl-4-methyl-5-oxo-5,6-dihydro-4H-pyrido[4,3,2-gh]phenanthridin-6-yl)propanenitrile. Purified by column chromatography (petroleum ether : ethyl acetate = 5 : 1). White solid, mp 130–131 °C. ^1H NMR (600 MHz, CDCl_3) δ 8.52 (d, J = 8.2 Hz, 1H), 8.23 (d, J = 8.2 Hz, 1H), 8.15 (d, J = 8.3 Hz, 1H), 7.82 (t, J = 7.5 Hz, 1H), 7.70

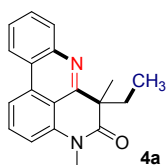
(t, $J = 7.6$ Hz, 1H), 7.61 (t, $J = 8.1$ Hz, 1H), 6.85 (t, $J = 7.3$ Hz, 1H), 6.80 (d, $J = 7.9$ Hz, 1H), 6.74 (t, $J = 7.6$ Hz, 2H), 6.39 (d, $J = 7.6$ Hz, 2H), 3.41 (d, $J = 12.4$ Hz, 1H), 3.35–3.34 (m, 4H), 3.25–3.19 (m, 1H), 3.02–2.92 (m, 1H), 2.31–2.19 (m, 2H). ^{13}C NMR (151 MHz, CDCl_3) δ 171.0, 156.1, 144.7, 137.8, 135.1, 132.4, 131.8, 129.9, 129.3, 129.2, 127.3, 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 $\text{C}_{26}\text{H}_{21}\text{N}_3\text{O}$ ($\text{M}+\text{H}$) $^+$, 392.1757; found, 392.1764.



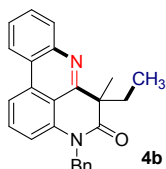
3-(4,6-dimethyl-5-oxo-5,6-dihydro-4H-pyrido[4,3,2-gh]phenanthridin-6-yl)-2-methylpropanenitrile. Purified by column chromatography (petroleum ether : ethyl acetate = 5 : 1). Yellow solid, mp 124–126 °C. ^1H NMR (600 MHz, CDCl_3) δ 8.57–8.54 (m, 1H), 8.32–8.29 (m, 1H), 8.17–8.10 (m, 1H), 7.88–7.83 (m, 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). ^{13}C NMR (151 MHz, CDCl_3) 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, 1340, 1165, 1081, 794 cm^{-1} . HRMS (ESI): calc. for $\text{C}_{21}\text{H}_{19}\text{N}_3\text{O}$ ($\text{M}+\text{H}$) $^+$, 330.1601; found, 330.1599.



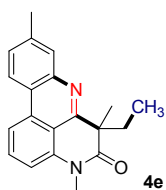
4-chloro-2-((4,6-dimethyl-5-oxo-5,6-dihydro-4H-pyrido[4,3,2-gh]phenanthridin-6-yl)methyl)butanenitrile. Purified by column chromatography (petroleum ether : ethyl acetate = 4 : 1). Yellow solid, mp 208–209 °C. ^1H NMR (600 MHz, CDCl_3) δ 8.58–8.52 (m, 1H), 8.34–8.29 (m, 1H), 8.19–8.08 (m, 1H), 7.89–7.83 (m, 1H), 7.79–7.75 (m, 1H), 7.71–7.65 (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). ^{13}C NMR (151 MHz, CDCl_3) 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 $\text{C}_{22}\text{H}_{20}\text{ClN}_3\text{O}$ ($\text{M}+\text{H}$) $^+$, 378.1368; found, 378.1369.



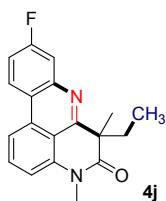
6-ethyl-4,6-dimethyl-4H-pyrido[4,3,2-*gh*]phenanthridin-5(6H)-one. Purified by column chromatography (petroleum ether : ethyl acetate = 8 : 1). Yellow solid, mp 133–134 °C. ¹H NMR (500 MHz, CDCl₃) δ 8.51 (d, *J* = 8.2 Hz, 1H), 8.25 (d, *J* = 8.3 Hz, 1H), 8.14 (d, *J* = 8.2 Hz, 1H), 7.79 (t, *J* = 7.9 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, 122.5, 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.



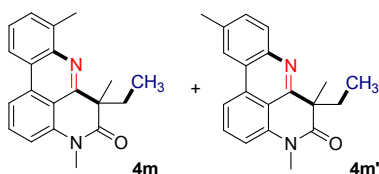
4-benzyl-6-ethyl-6-methyl-4H-pyrido[4,3,2-*gh*]phenanthridin-5(6H)-one. Purified by column chromatography (petroleum ether : ethyl acetate = 9 : 1). Yellow solid, mp 144–145 °C. ¹H NMR (600 MHz, CDCl₃) δ 8.50 (d, *J* = 8.1 Hz, 1H), 8.22 (d, *J* = 8.2 Hz, 1H), 8.16 (d, *J* = 8.2 Hz, 1H), 7.75 (t, *J* = 7.5 Hz, 1H), 7.69–7.60 (m, 2H), 7.37–7.29 (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, 112.7, 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.



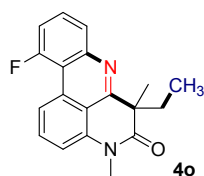
6-ethyl-4,6,9-trimethyl-4H-pyrido[4,3,2-*gh*]phenanthridin-5(6H)-one. Purified by column chromatography (petroleum ether : ethyl acetate = 8 : 1). Yellow solid, mp 120–121 °C. ¹H NMR (600 MHz, CDCl₃) δ 8.41 (d, *J* = 8.3 Hz, 1H), 8.23 (d, *J* = 8.3 Hz, 1H), 7.96 (s, 1H), 7.79 (t, *J* = 8.1 Hz, 1H), 7.47 (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), 2.35–2.24 (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, 131.6, 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.

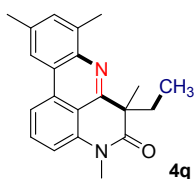


6-ethyl-4,6,8-trimethyl-4H-pyrido[4,3,2-gh]phenanthridin-5(6H)-one (4m); 6-ethyl-4,6,10-trimethyl-4H-pyrido[4,3,2-gh]phenanthridin-5(6H)-one (4m'). Purified by column chromatography (petroleum ether : ethyl acetate = 9 : 1), products **4m** and **4m'** can not be separated column chromatography on silica 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, 122.5, 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.

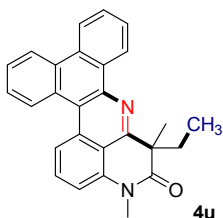


6-ethyl-11-fluoro-4,6-dimethyl-4H-pyrido[4,3,2-gh]phenanthridin-5(6H)-one. Purified by column chromatography (petroleum ether : ethyl acetate = 10 : 1). Yellow solid, mp 106–107 °C. ¹H NMR (600 MHz,

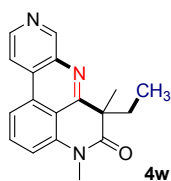
CDCl₃) δ 8.73 (d, J = 8.5 Hz, 1H), 7.99 (d, J = 8.2 Hz, 1H), 7.87 (t, J = 8.2 Hz, 1H), 7.69 (dd, J = 13.6, 8.0 Hz, 1H), 7.37 (dd, J = 13.1, 7.9 Hz, 1H), 7.30 (d, J = 8.0 Hz, 1H), 3.63 (s, 3H), 2.44–2.38 (m, 1H), 2.34–2.28 (m, 1H), 1.82 (s, 3H), 0.68 (t, J = 7.4 Hz, 3H). ¹³C NMR (151 MHz, CDCl₃) δ 173.9, 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) ν 2922, 2851, 1667, 1618, 1586 1463, 1343, 1164, 732, 517 cm⁻¹. HRMS (ESI): calc. for C₁₉H₁₇FN₂O (M+H)⁺, 309.1398; found, 309.1395.



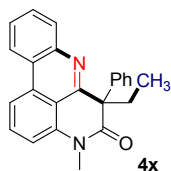
6-ethyl-4,6,8,10-tetramethyl-4H-pyrido[4,3,2-*g*]phenanthridin-5(6H)-one. Purified by column chromatography (petroleum ether : ethyl acetate = 10 : 1). Yellow solid, mp 165–166 °C. ¹H NMR (600 MHz, CDCl₃) δ 8.25 (d, J = 8.3 Hz, 1H), 8.17 (s, 1H), 7.76 (t, J = 8.1 Hz, 1H), 7.46 (s, 1H), 7.17 (d, J = 7.8 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). ¹³C NMR (151 MHz, CDCl₃) 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) ν 2964, 2922, 1660, 1611, 1588, 1573, 1458, 1355, 1337, 820, 767 cm⁻¹. HRMS (ESI): calc. for C₂₂H₂₂N₂O (M+H)⁺, 319.1805; found, 319.1821.



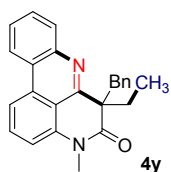
6-ethyl-4,6-dimethyl-4H-dibenzo[*a,c*]pyrido[4,3,2-*g*]phenanthridin-5(6H)-one. Purified by column chromatography (petroleum ether : ethyl acetate = 8 : 1). Yellow solid, mp 184–185 °C. ¹H NMR (600 MHz, CDCl₃) δ 9.43–9.37 (m, 1H), 8.90 (d, J = 7.8 Hz, 1H), 8.76 (d, J = 7.8 Hz, 1H), 8.68–8.64 (m, 1H), 8.62 (d, J = 8.6 Hz, 1H), 7.83–7.75 (m, 3H), 7.73 (dt, J = 7.2, 1.2 Hz, 1H), 7.69 (dt, J = 8.4, 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). ¹³C NMR (151 MHz, CDCl₃) δ 174.3, 158.2, 142.3, 138.7, 133.1, 131.1, 131.0, 130.9, 130.8, 128.8, 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) ν 2967, 2926, 1671, 1581, 1566, 1452, 1375, 1337, 1066, 760, 729 cm⁻¹. HRMS (ESI): calc. for C₂₇H₂₂N₂O (M+H)⁺, 391.1805; found, 391.1824.



6-ethyl-4,6-dimethyl-4H-benzo[de]pyrido[3,4-b][1,6]naphthyridin-5(6H)-one. Purified by column chromatography (petroleum ether : ethyl acetate = 1 : 1). Yellow solid, mp 154–155 °C. ¹H NMR (600 MHz, CDCl₃) 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). ¹³C NMR (151 MHz, CDCl₃) 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) ν 2965, 2924, 1668, 1610, 1609, 1590, 1466, 1358, 1079, 913, 745 cm⁻¹. HRMS (ESI): calc. for C₁₈H₁₇N₃O (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. ¹H NMR (600 MHz, CDCl₃) 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). ¹³C NMR (151 MHz, CDCl₃) 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) ν 2961, 2924, 1667, 1588, 1569, 1463, 1344, 764, 753, 700 cm⁻¹. HRMS (ESI): calc. for C₂₄H₂₀N₂O (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. ¹H NMR (600 MHz, CDCl₃) 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). ¹³C NMR (151 MHz, CDCl₃) 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, 35.1, 29.2, 9.9. IR (film) ν 3028, 2963, 2931, 1664, 1611, 1588, 1464, 1083, 755, 735, 701 cm⁻¹. HRMS (ESI): calc. for C₂₅H₂₂N₂O (M+H)⁺, 367.1805; found, 367.1827.

8. Charts of compounds

