

## Supporting Information

### **Synthesis of ester-containing phenanthridines via photoredox-catalyzed radical cascade cyclization of *N*-arylacrylamides with alkyloxalyl chlorides**

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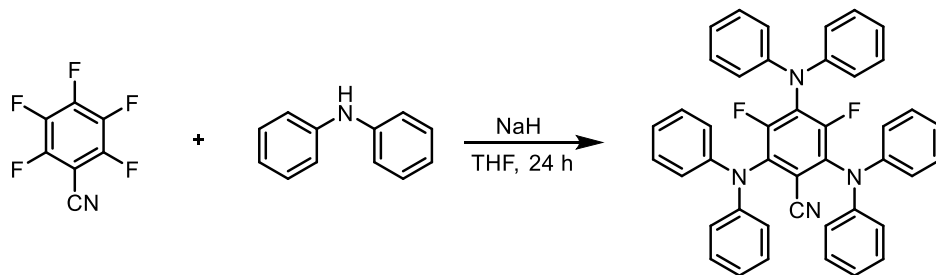
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## 1. General information

All glassware was thoroughly oven-dried. Chemicals and solvents were either purchased from commercial suppliers or purified by standard techniques. Thin-layer chromatography plates were visualized by exposure to ultraviolet light and/or staining with phosphomolybdic acid followed by heating on a hot plate. Flash chromatography was carried out using silica gel (200–300 mesh).  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra were recorded on a Bruker AM-400 (400 MHz). The spectra were recorded in deuteriochloroform ( $\text{CDCl}_3$ ) as solvent at room temperature,  $^1\text{H}$  and  $^{13}\text{C}$  NMR chemical shifts are reported in ppm relative to the residual solvent peak. The residual solvent signals were used as references and the chemical shifts were converted to the TMS scale ( $\text{CDCl}_3$ :  $\delta_{\text{H}} = 7.26$  ppm,  $\delta_{\text{C}} = 77.0$  ppm). Data for  $^1\text{H}$  NMR are reported as follows: chemical shift ( $\delta$  ppm), multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet, dd = doublet, br = broad), integration, coupling constant (Hz) and assignment. Data for  $^{13}\text{C}$  NMR are reported as chemical shift. Electrospray-ionisation HRMS data were acquired on a Q-TOF mass spectrometer (Waters SYNAPT G2-Si) LC-MS TOF.

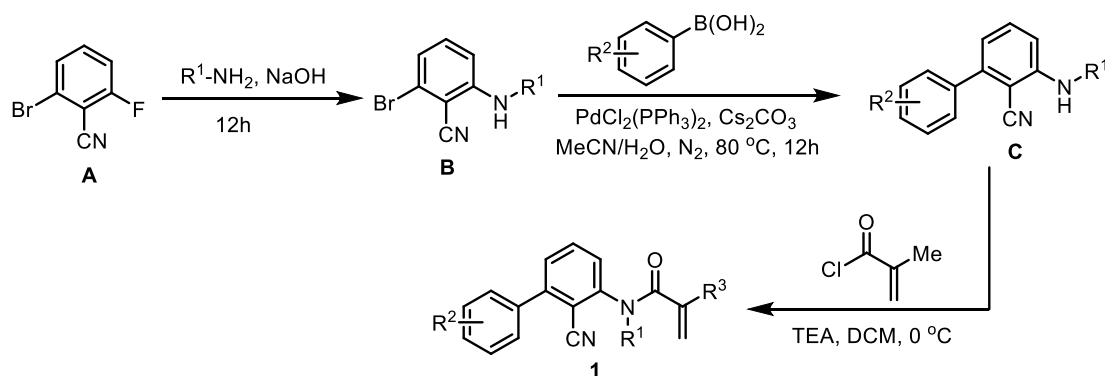
## 2. General experimental procedure

### *General procedure for the synthesis of 3PAA2FBN<sup>1</sup>*



In a flame dried Schlenk flask equipped with a magnetic stir bar diphenylamine (31.25 mmol, 6.25 equiv) were dissolved in dry THF (100 mL) under an atmosphere of N<sub>2</sub>. Then, NaH (47 mmol, 9.4 equiv, 60% in oil) were added and the suspension was stirred at 50 °C for 30 minutes. Finally, pentafluorobenzonitrile (5.0 mmol) was added and the resulting mixture was stirred at room temperature for 24 h. The reaction mixture was quenched by the addition of water. After removal of THF, the residue was dissolved in DCM and washed with water. The organic phase was dried over Na<sub>2</sub>SO<sub>4</sub> and the solvent was removed under reduced pressure. The crude product was purified by flash chromatography on silica gel.

### *General procedure for the synthesis of substrates 1<sup>2</sup>*



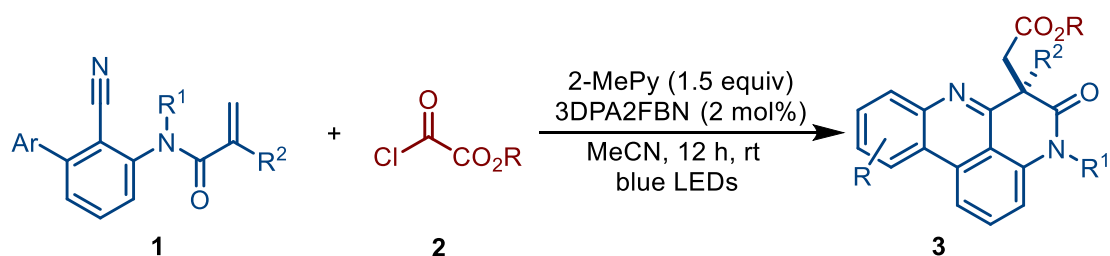
A solution of related 2-bromo-6-fluorobenzonitrile **A** (20.0 mmol, 1.0 equiv.), MeNH<sub>2</sub>•HCl (30.0 mmol, 1.5 equiv.) and NaOH (30.0 mmol, 1.5 equiv.) in CH<sub>3</sub>CN (40 mL) was stirred under air at 80 °C for 12 h. After completion of the reaction, the resulting solution was cooled to room temperature and extracted with EtOAc (100 × 3

mL), then washed with saturated brine (100 mL). The organic layer was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated in vacuo to give the intermediate products **B**.

To the above-obtained **B**, substituted phenylboronic acid (15 mmol, 1.5 equiv.), PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> (0.3 mmol, 0.02 equiv.) and Cs<sub>2</sub>CO<sub>3</sub> (42.0 mmol, 2.8 equiv.), were added MeCN (150 mL) and H<sub>2</sub>O (7.5 mL). The reaction mixture was stirred at 80 °C under nitrogen atmosphere for 12 h. After completion of the reaction, the resulting solution was cooled to room temperature and extracted with EtOAc (100 × 3 mL). The combined organic layers were washed with saturated brine (100 mL), dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated in vacuo to give the crude products **C** without further purification.

To a solution of the above-obtained **C** (10 mmol) and triethylamine (20 mmol, 2.0 equiv.) in DCM (24 mL) at 0 °C was added related methacryloyl chloride (1.5 equiv) dropwise. The reaction mixture was stirred at 0 °C overnight. After completion of the reaction, the resulting solution was extracted with DCM (30 × 3 mL) and the combined organic layers were washed with saturated brine (30 mL), dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated in vacuo. The residue was purified by column chromatography on silica gel using petroleum ether/EtOAc (20:1 to 10:1) as eluent to give the desired substrates **1**.

### 3. General procedure for ester-containing phenanthridines



All optimization reactions were set up in a glove box under N<sub>2</sub> atmosphere. Substrate **1** (0.2 mmol, 1.0 equiv), alkyloxyoxalyl chloride **2** (0.6 mmol, 3.0 equiv) and 2-MePy (0.3 mmol, 1.5 equiv) were added to a solution of photocatalyst 3DPA2FBN (2 mol %)

in dry MeCN (4 mL) at room temperature. The heterogenous mixture was placed in the irradiation apparatus equipped with blue LEDs. The resulting mixture was stirred at room temperature for 12 h. Upon completion of the reaction, the mixture was diluted with ethyl acetate (30 mL), washed with brine (10 ml x 3), dried with Na<sub>2</sub>SO<sub>4</sub> and the solvent was evaporated. The crude product was purified by column chromatography on silica gel to afford the desired product **3**.

#### **4. Devices for the photocatalytic reactions**

Irradiation of visible light was performed with a 36 W Blue LED strip. All photocatalyzed alkoxyacylation/cyclization reactions were carried out at room temperature (r.t.) with fan-assisted cooling to maintain a temperature of approximately 40-45 °C. The distance between tube and lamp was approximately 3 cm.

Manufacture of the light source: LED strip

Manufacturer: Greethink

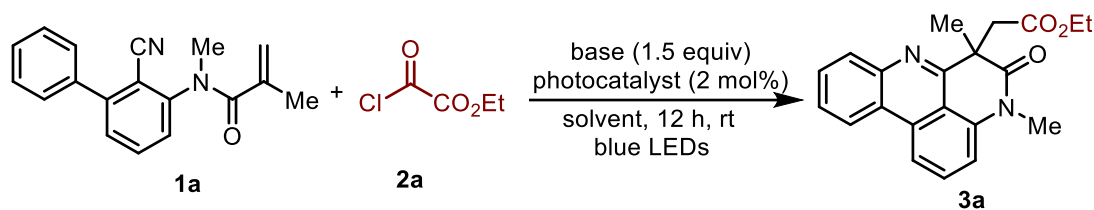
Model: GT-5050-Blue

Wavelength of peak intensity: 460-470 nm

Material of the irradiation vessel: borosilicate glass

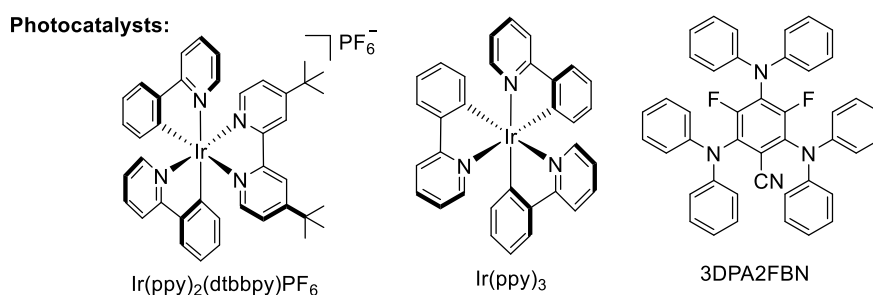
Distance of the irradiation vessel from the light source: approximately 3 cm.

## 5. Initial studies and the reaction optimization.



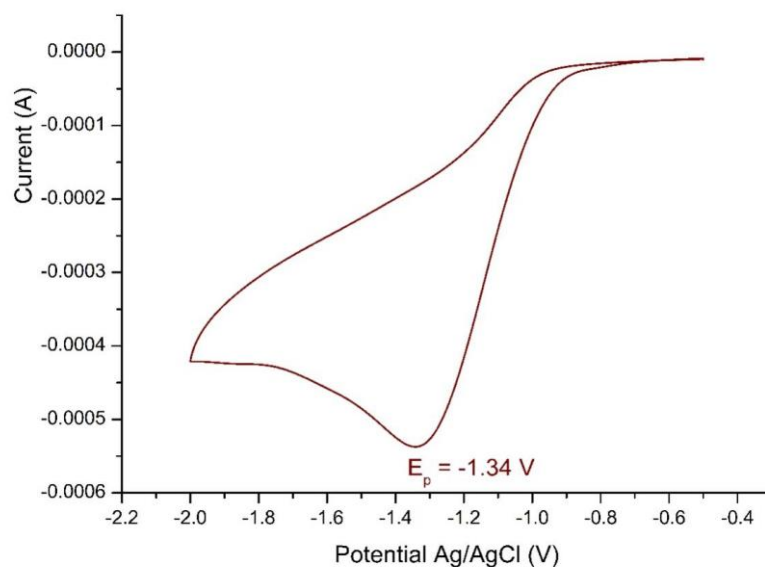
Entry <sup>a</sup>	Photocatalyst	Solvent	Base	Yield <sup>b</sup> ( <b>3a</b> , %)
1	Ir(ppy) <sub>3</sub>	MeCN	2,6-lutidine	32%
2	Ir(ppy) <sub>2</sub> (dtppy)PF <sub>6</sub>	MeCN	2,6-lutidine	62%
3	3DPA2FBN	MeCN	2,6-lutidine	63%
4	3DPA2FBN	DCM	2,6-lutidine	53%
5	3DPA2FBN	DMF	2,6-lutidine	47%
6	3DPA2FBN	PhCF <sub>3</sub>	2,6-lutidine	38%
7	3DPA2FBN	THF	2,6-lutidine	31%
8	3DPA2FBN	MeCN	2-MePy	66%
9	3DPA2FBN	MeCN	2,6-di- <sup>t</sup> Bu-4-MePy	49%
10	3DPA2FBN	MeCN	2,6-di- <sup>t</sup> BuPy	58%
11	3DPA2FBN	MeCN	2,4,6-tri-MePy	58%
12	3DPA2FBN	MeCN	4-MeOPy	13%
13	3DPA2FBN	MeCN	2-CNPy	7%
14	3DPA2FBN	MeCN	DABCO	19%
15	3DPA2FBN	MeCN	K <sub>2</sub> HPO <sub>4</sub>	25%
16	3DPA2FBN	MeCN	K <sub>2</sub> CO <sub>3</sub>	16%
17	3DPA2FBN	MeCN		11%
18		MeCN	2-MePy	NR
19 <sup>c</sup>	3DPA2FBN	MeCN	2-MePy	NR

<sup>a</sup> Unless otherwise noted, reaction conditions are as follows: **1a** (0.2 mmol), **2a** (0.6 mmol), photocatalyst (0.004 mmol), base (0.3 mmol), solvent (4 mL), blue LEDs, rt, 12 h, under a N<sub>2</sub> atmosphere. <sup>b</sup> Yield determined by <sup>1</sup>H NMR analysis using 1,3,5-trimethoxybenzene as internal standard. <sup>c</sup> In the dark.

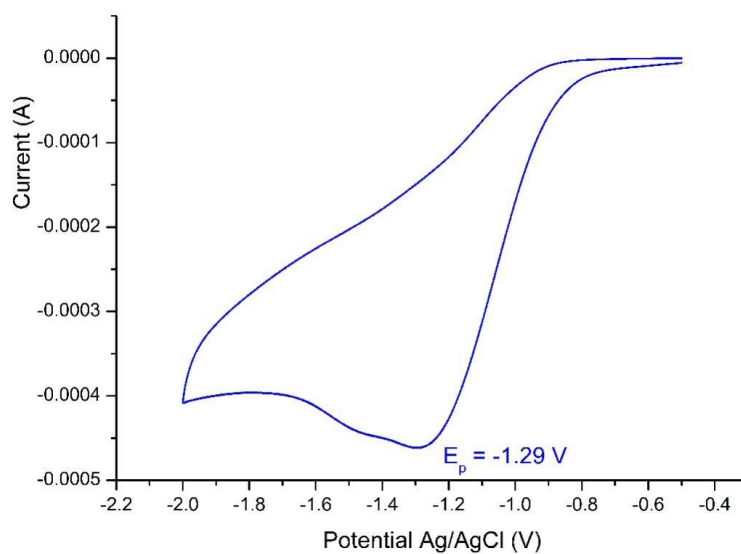


## 6. Mechanistic study

### *Cyclic Voltammetry Studies*



**Figure S1** Cyclic voltammogram of ethyl chlorooxoacetate **2b** [0.02 M] in [0.1 M] TBAPF<sub>6</sub> in CH<sub>3</sub>CN. Sweep rate: 200 mV/s. Glassy carbon working electrode, Ag/AgCl (satd. KCl) reference electrode, Pt wire auxiliary electrode. Irreversible reduction.  $E_p = -1.34$  V.

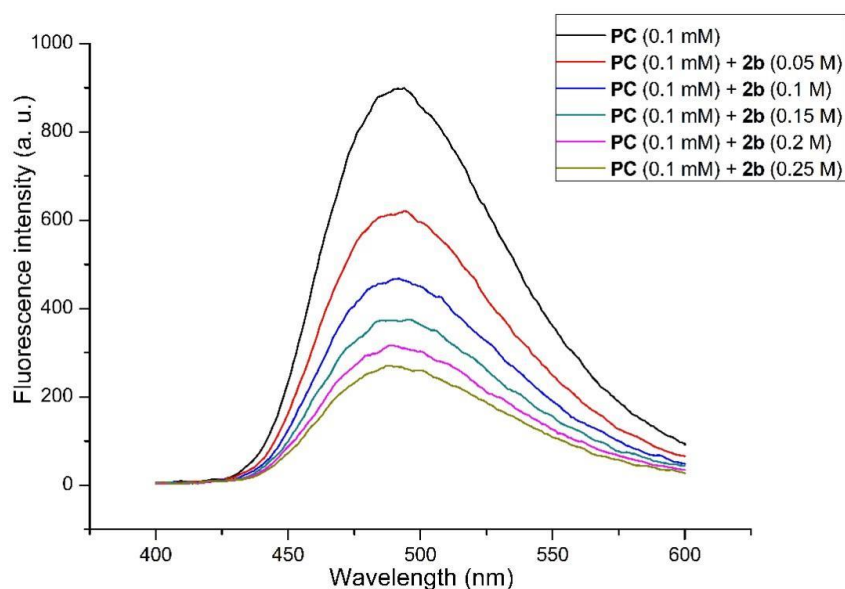


**Figure S2** Cyclic voltammogram of ethyl chlorooxoacetate **2a** [0.02 M] and 2-

methylpyridine [0.02 M] in [0.1 M] TBAPF<sub>6</sub> in CH<sub>3</sub>CN. Sweep rate: 200 mV/s. Glassy carbon working electrode, Ag/AgCl (satd. KCl) reference electrode, Pt wire auxiliary electrode. Irreversible reduction. E<sub>p</sub> = -1.29 V;

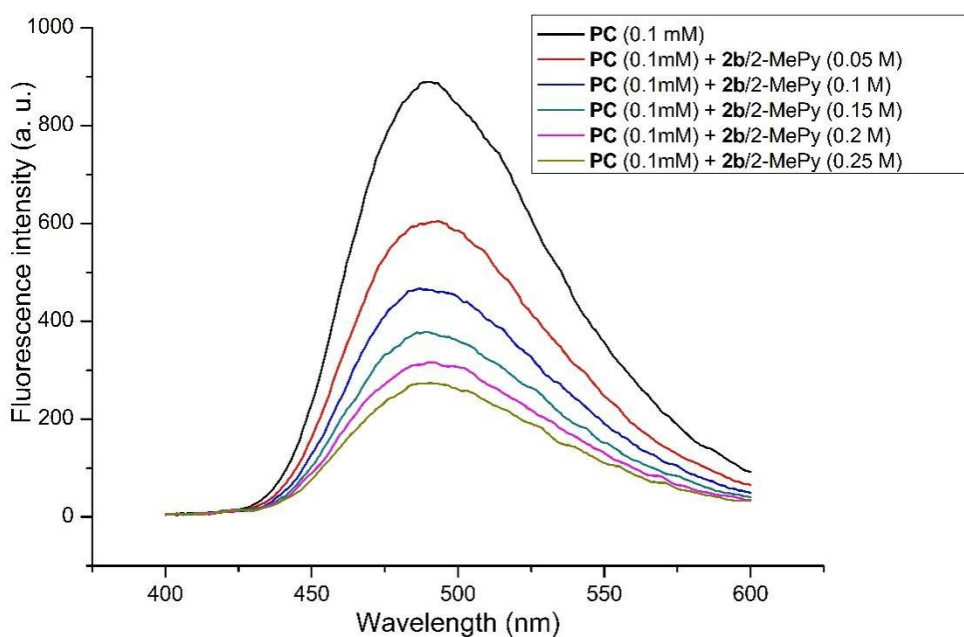
### ***Stern-Volmer fluorescence quenching experiments***

Stern-Volmer fluorescence quenching experiments were run with freshly prepared solutions of 0.1 mM 3DPA2FBN in degassed dry CH<sub>3</sub>CN added with the appropriate amount of a quencher in a screw-top quartz cuvette at room temperature. The solutions were irradiated at 370 nm and fluorescence was measured from 400 nm to 600 nm.

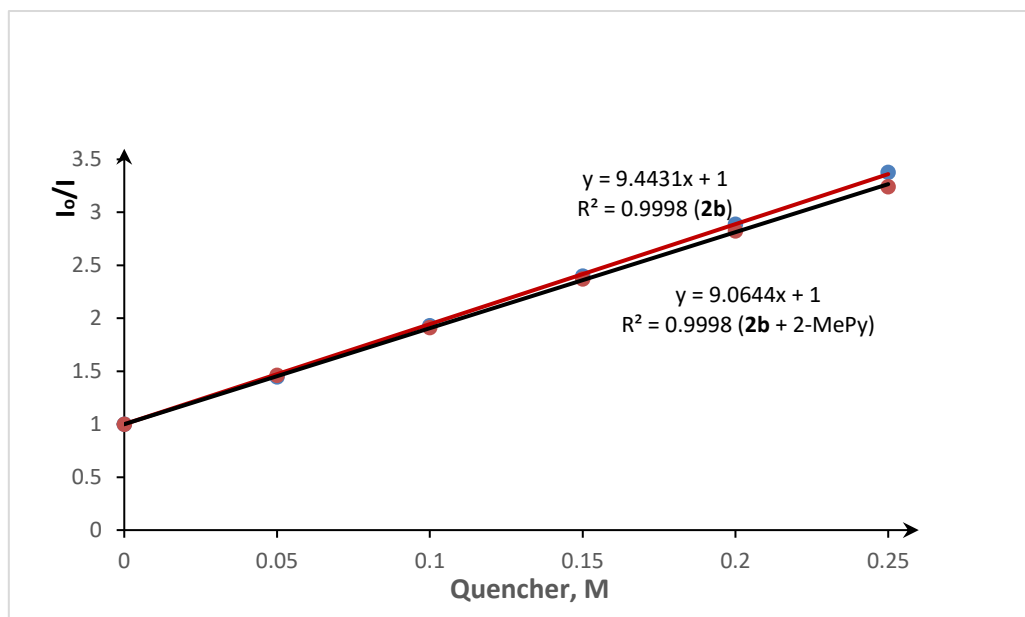


**Figure S3** Fluorescence quenching experiments of 3DPA2FBN and **2b**.





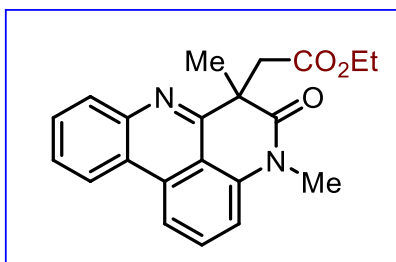
**Figure S4** Fluorescence quenching experiments of 3DPA2FBN and **2b** + 2-methylpyridine.



**Figure S5** Stern-Volmer plots of 3DPA2FBN with different quenchers.

## 7. Characterization of new substrates and all products

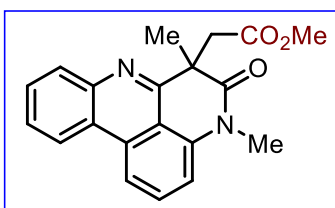
*Ethyl 2-(4,6-dimethyl-5-oxo-5,6-dihydro-4H-pyrido[4,3,2-g]phenanthridin-6-yl)acetate (3a)*



Purification by flash chromatography (PE/EA = 10/1). White solid; mp 89.1–90.3 °C; 64% yield; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ (ppm) 8.51 (d, *J* = 7.8 Hz, 1H), 8.26 (d, *J* = 8.2 Hz, 1H), 8.08 (d, *J* = 8.2, 0.6 Hz, 1H), 7.82 (t, *J* = 8.2

Hz, 1H), 7.76–7.68 (m, 1H), 7.65–7.58 (m, 1H), 7.24 (d, *J* = 8.2 Hz, 1H), 3.95 (d, *J* = 17.1 Hz, 1H), 3.91–3.81 (m, 2H), 3.63–3.54 (m, 4H), 1.58 (s, 3H), 0.99 (t, *J* = 7.1 Hz, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 174.0, 171.9, 159.7, 144.7, 138.9, 133.3, 131.7, 129.6, 128.9, 126.4, 122.9, 122.5, 116.0, 111.9, 110.8, 60.4, 48.7, 43.1, 29.9, 29.9, 13.8.; HRMS (ESI) for C<sub>21</sub>H<sub>20</sub>N<sub>2</sub>O<sub>3</sub>Na [M+Na]<sup>+</sup> calcd. 371.1366, found 371.1382.

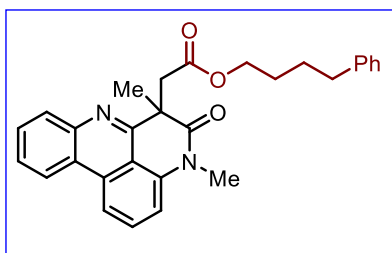
*methyl 2-(4,6-dimethyl-5-oxo-5,6-dihydro-4H-pyrido[4,3,2-gh]phenanthridin-6-yl)acetate (3b)*



Purification by flash chromatography (PE/EA = 10/1). White solid; mp 168.9–170.6 °C; 90%; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.51 (d, *J* = 8.3 Hz, 1H), 8.26 (d, *J* = 8.2 Hz, 1H), 8.08 (dd, *J* = 8.2, 1.4 Hz, 1H), 7.82 (t, *J* =

8.1 Hz, 1H), 7.71 (ddd, *J* = 8.3, 7.0, 1.4 Hz, 1H), 7.62 (ddd, *J* = 8.3, 7.0, 1.4 Hz, 1H), 7.27 – 7.23 (m, 1H), 3.99 (d, *J* = 17.2 Hz, 1H), 3.63 – 3.55 (m, 4H), 3.47 (s, 3H), 1.57 (s, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) 173.9, 172.6, 159.6, 144.7, 138.9, 133.4, 131.7, 129.6, 128.9, 126.4, 122.9, 122.6, 116.0, 111.9, 110.9, 51.6, 48.7, 42.7, 29.9, 29.9; C<sub>20</sub>H<sub>18</sub>N<sub>2</sub>O<sub>3</sub> [M+Na]<sup>+</sup> calcd 357.1210, found 357.1227.

*4-phenylbutyl 2-(4,6-dimethyl-5-oxo-5,6-dihydro-4H-pyrido[4,3,2-gh]phenanthridin-6-yl)acetate (3c)*

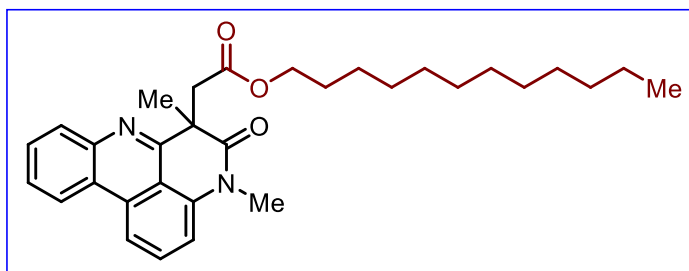


Purification by flash chromatography (PE/EA = 8/1).

Yellow oil; 54%; <sup>1</sup>H NMR (400 MHz, Chloroform-d) δ 8.49 (dd, *J* = 8.2, 1.5 Hz, 1H), 8.24 (d, *J* = 8.3 Hz, 1H), 8.06 (dd, *J* = 8.1, 1.5 Hz, 1H), 7.80 (t, *J* = 8.1 Hz, 1H), 7.69 (ddd, *J* = 8.4, 6.9, 1.5 Hz, 1H), 7.61 (ddd, *J*

= 8.3, 7.0, 1.5 Hz, 1H), 7.25 – 7.12 (m, 4H), 7.06 – 6.98 (m, 2H), 3.96 (d, *J* = 17.1 Hz, 1H), 3.82 (t, *J* = 5.9 Hz, 2H), 3.64 – 3.52 (m, 4H), 2.41 (t, *J* = 7.0 Hz, 2H), 1.56 (d, *J* = 4.0 Hz, 3H), 1.44 – 1.34 (m, 4H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 173.9, 172.0, 159.6, 144.6, 141.9, 138.9, 133.3, 131.7, 129.6, 128.9, 128.3, 128.2, 126.4, 125.7, 122.9, 122.5, 116.0, 111.9, 110.8, 77.3, 77.0, 76.7, 64.3, 48.7, 43.0, 35.2, 30.0, 29.9, 27.9, 27.3; C<sub>29</sub>H<sub>28</sub>N<sub>2</sub>O<sub>3</sub> [M+Na]<sup>+</sup> calcd 475.1992, found 475.2001.

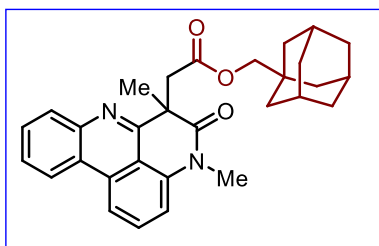
*dodecyl 2-(4,6-dimethyl-5-oxo-5,6-dihydro-4H-pyrido[4,3,2-gh]phenanthridin-6-yl)acetate (3d)*



Purification by flash chromatography (PE/EA = 8/1). Yellow oil; 47%; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.51 (dd, *J* = 8.2, 1.4 Hz, 1H),

8.26 (d, *J* = 8.3 Hz, 1H), 8.08 (dd, *J* = 8.2, 1.3 Hz, 1H), 7.82 (t, *J* = 8.1 Hz, 1H), 7.71 (ddd, *J* = 8.3, 6.9, 1.4 Hz, 1H), 7.61 (ddd, *J* = 8.3, 6.9, 1.4 Hz, 1H), 7.27 – 7.22 (m, 1H), 3.95 (d, *J* = 17.0 Hz, 1H), 3.80 (t, *J* = 6.6 Hz, 2H), 3.61 (s, 4H), 1.57 (s, 3H), 1.26 (q, *J* = 14.8, 10.8 Hz, 14H), 1.05 (d, *J* = 5.3 Hz, 6H), 0.87 (d, *J* = 7.1 Hz, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 173.9, 171.9, 159.7, 144.7, 139.0, 133.4, 131.7, 129.6, 128.9, 126.4, 122.9, 122.5, 116.0, 111.9, 110.8, 64.6, 48.7, 43.0, 31.9, 30.0, 29.9, 29.6, 29.6, 29.5, 29.3, 29.3, 29.1, 28.4, 25.6, 22.7, 14.1; C<sub>31</sub>H<sub>40</sub>N<sub>2</sub>O<sub>3</sub> [M+Na]<sup>+</sup> calcd 511.2931, found 511.2947.

*((3*r*,5*r*,7*r*)-adamantan-1-yl)methyl 2-(4,6-dimethyl-5-oxo-5,6-dihydro-4H-pyrido[4,3,2-gh]phenanthridin-6-yl)acetate (3e)*

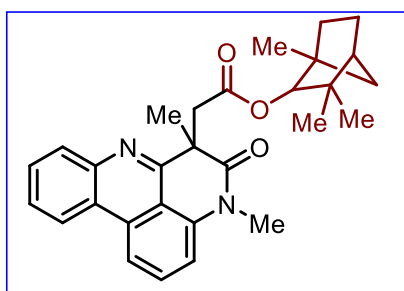


Purification by flash chromatography (PE/EA = 15/1).

Yellow oil; 82%;  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.51 (dd,  $J = 8.2, 1.4$  Hz, 1H), 8.26 (d,  $J = 8.3$  Hz, 1H), 8.08 (d,  $J = 8.2$  Hz, 1H), 7.83 (t,  $J = 8.1$  Hz, 1H), 7.71 (t,  $J = 7.5$  Hz, 1H), 7.65 – 7.58 (m, 1H), 7.29 – 7.21 (m, 1H),

3.99 (d,  $J = 17.0$  Hz, 1H), 3.67 (d,  $J = 19.6$  Hz, 1H), 3.61 (s, 3H), 3.41 (q,  $J = 10.8$  Hz, 2H), 1.70 – 1.63 (m, 4H), 1.51 (d,  $J = 12.4$  Hz, 3H), 1.37 – 1.27 (m, 4H), 1.13 – 1.01 (m, 6H), 0.90 – 0.82 (m, 1H);  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  173.8, 171.8, 159.6, 139.0, 133.5, 131.8, 129.6, 129.0, 126.5, 122.8, 122.5, 116.0, 111.9, 110.8, 74.0, 48.8, 42.5, 38.6, 36.6, 32.8, 30.2, 29.9, 27.8;  $\text{C}_{30}\text{H}_{32}\text{N}_2\text{O}_3$   $[\text{M}+\text{Na}]^+$  calcd 491.2305, found 491.2317.

*1,3,3-trimethylbicyclo[2.2.1]heptan-2-yl 2-(4,6-dimethyl-5-oxo-5,6-dihydro-4H-pyrido[4,3,2-g]phenanthridin-6-yl)acetate (3f)*

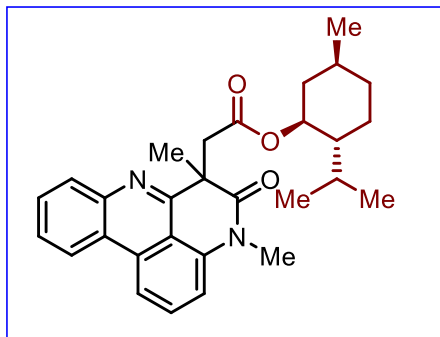


Purification by flash chromatography (PE/EA = 10/1). White solid; mp 85–84 °C; 76%;  $^1\text{H NMR}$

(400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.51 (dd,  $J = 8.3, 1.4$  Hz, 1H), 8.26 (d,  $J = 8.2$  Hz, 1H), 8.05 (ddd,  $J = 8.0, 6.4, 1.4$  Hz, 1H), 7.83 (t,  $J = 8.1$  Hz, 1H), 7.74 – 7.67 (m, 1H), 7.64 – 7.58 (m, 1H), 7.23 (dd,  $J = 7.9, 2.0$  Hz, 1H),

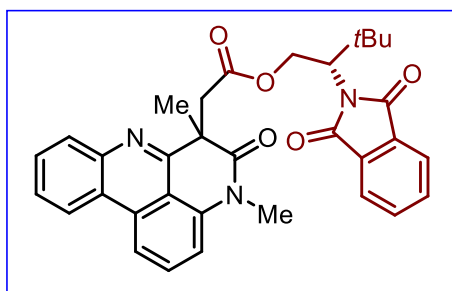
4.11 (dd,  $J = 11.6, 1.9$  Hz, 1H), 4.00 (dd,  $J = 19.7, 17.0$  Hz, 1H), 3.73 – 3.58 (m, 4H), 1.55 (d,  $J = 4.9$  Hz, 3H), 1.48 (dt,  $J = 22.3, 2.6$  Hz, 2H), 1.33 (dt,  $J = 10.3, 2.0$  Hz, 1H), 1.30 – 1.20 (m, 2H), 1.12 (dt,  $J = 6.1, 3.3$  Hz, 2H), 0.99 – 0.92 (m, 1H), 0.86 (s, 2H), 0.77 (s, 3H), 0.74 – 0.61 (m, 1H), 0.53 (d,  $J = 17.2$  Hz, 3H), 0.19 (s, 2H);  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  173.7, 173.6, 172.1, 172.0, 159.6, 159.6, 144.8, 144.7, 139.1, 139.0, 133.5, 133.5, 131.8, 131.8, 129.7, 129.6, 129.0, 129.0, 126.4, 126.4, 122.9, 122.9, 122.5, 116.0, 112.0, 111.9, 110.9, 110.8, 86.6, 86.6, 77.4, 77.3, 77.0, 76.7, 48.8, 48.8, 48.2, 48.1, 48.1, 47.9, 42.4, 42.2, 41.2, 41.1, 39.3, 39.0, 31.6, 30.6, 30.5, 29.9, 29.5, 29.5, 26.1, 26.0, 25.7, 25.5, 22.7, 20.0, 19.6, 19.0, 18.8, 14.1;  $\text{C}_{29}\text{H}_{32}\text{N}_2\text{O}_3$   $[\text{M}+\text{Na}]^+$  calcd 479.2305, found 479.2307.

*(1R,2R,5S)-2-isopropyl-5-methylcyclohexyl 2-(4,6-dimethyl-5-oxo-5,6-dihydro-4H-pyrido[4,3,2-gh]phenanthridin-6-yl)acetate (3g)*



Purification by flash chromatography (PE/EA = 10/1). White solid; mp 103–105 °C; 34%; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.51 (dt, *J* = 8.2, 2.1 Hz, 2H), 8.26 (dd, *J* = 8.3, 6.3 Hz, 2H), 8.06 (ddd, *J* = 9.6, 8.1, 1.3 Hz, 2H), 7.83 (td, *J* = 8.1, 4.1 Hz, 2H), 7.71 (ddt, *J* = 8.4, 6.9, 1.6 Hz, 2H), 7.61 (ddt, *J* = 8.4, 7.1, 1.5 Hz, 2H), 7.24 (d, *J* = 7.9 Hz, 2H), 4.34 (dtd, *J* = 18.5, 10.9, 4.4 Hz, 2H), 3.94 (d, *J* = 17.0 Hz, 1H), 3.83 (d, *J* = 16.7 Hz, 1H), 3.69 – 3.55 (m, 8H), 1.59 (d, *J* = 9.9 Hz, 7H), 1.46 (tt, *J* = 11.7, 2.5 Hz, 4H), 1.30 – 1.12 (m, 4H), 0.90 – 0.81 (m, 4H), 0.71 (d, *J* = 6.5 Hz, 4H), 0.67 (dd, *J* = 6.7, 1.4 Hz, 6H), 0.59 (td, *J* = 12.1, 11.7, 3.9 Hz, 4H), 0.32 (d, *J* = 6.9 Hz, 3H), 0.19 (d, *J* = 7.0 Hz, 3H), 0.13 (d, *J* = 6.9 Hz, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 174.0, 173.8, 171.5, 170.9, 159.9, 159.9, 144.7, 139.1, 139.0, 133.5, 133.4, 131.8, 131.7, 129.6, 129.0, 128.9, 126.5, 126.5, 122.9, 122.9, 122.5, 122.5, 116.0, 115.9, 112.1, 112.0, 110.8, 110.7, 77.4, 77.2, 77.0, 76.7, 74.1, 74.1, 48.8, 48.8, 47.0, 46.8, 43.8, 43.6, 40.6, 40.4, 34.1, 31.2, 31.1, 30.0, 30.0, 29.9, 29.7, 25.8, 25.2, 23.2, 22.7, 21.9, 21.8, 20.7, 20.3, 15.6, 15.5; C<sub>29</sub>H<sub>34</sub>N<sub>2</sub>O<sub>3</sub> [M+Na]<sup>+</sup> calcd 481.2462, found 481.2472.

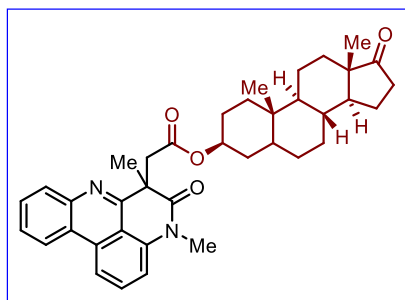
*(S)-2-(1,3-dioxo-2,3-dihydro-1H-inden-2-yl)-3,3-dimethylbutyl 2-(4,6-dimethyl-5-oxo-5,6-dihydro-4H-pyrido[4,3,2-gh]phenanthridin-6-yl)acetate (3h)*



Purification by flash chromatography (PE/EA = 2/1). Yellow oil; 86%; <sup>1</sup>H NMR (100 MHz, CDCl<sub>3</sub>) δ 8.46 (dt, *J* = 8.5, 1.8 Hz, 1H), 8.19 (d, *J* = 8.3 Hz, 1H), 7.99 (dd, *J* = 57.6, 8.1 Hz, 1H), 7.82 – 7.68 (m, 6H), 7.61 (ddd, *J* = 8.4, 6.9, 1.6 Hz, 1H), 7.22 (dd, *J* = 8.0, 4.1 Hz, 1H), 4.75 (dt, *J* = 16.4, 11.1 Hz, 1H), 4.36 (ddd, *J* = 20.7, 11.5, 4.1 Hz, 1H), 4.17 – 4.11 (m, 1H), 3.84

(dd,  $J = 17.2, 14.6$  Hz, 1H), 3.60 – 3.39 (m, 4H), 1.45 (d,  $J = 6.9$  Hz, 3H), 1.28 – 1.23 (m, 1H), 0.94 – 0.89 (m, 9H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  173.6, 173.5, 171.7, 171.7, 168.9, 168.9, 168.6, 168.6, 159.3, 159.3, 144.6, 138.8, 133.9, 133.8, 133.7, 133.7, 133.3, 131.8, 131.7, 131.3, 131.2, 129.7, 129.6, 129.0, 128.9, 128.8, 128.5, 126.4, 123.3, 123.3, 123.1, 123.0, 122.8, 122.8, 122.5, 116.0, 115.9, 111.7, 110.9, 110.8, 60.4, 60.4, 59.1, 59.0, 48.6, 48.6, 42.4, 42.2, 35.2, 35.1, 29.9, 29.9, 29.8, 27.7, 27.7;  $\text{C}_{31}\text{H}_{40}\text{N}_2\text{O}_3$   $[\text{M}+\text{Na}]^+$  calcd 511.2931, found 511.2947.

***(3S,8R,9S,10S,13S,14S)-10,13-dimethyl-17-oxohexadecahydro-1H-cyclopenta[a]phenanthren-3-yl 2-(4,6-dimethyl-5-oxo-5,6-dihydro-4H-pyrido[4,3,2-gh]phenanthridin-6-yl)acetate (3i)***



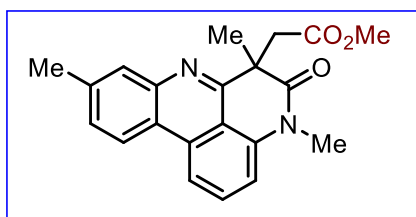
Purification by flash chromatography (PE/EA = 2/1).

Colourless oil; 91%;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.52 (d,  $J = 8.2$  Hz, 1H), 8.27 (d,  $J = 8.3$  Hz, 1H), 8.09 (s, 1H), 7.83 (t,  $J = 8.1$  Hz, 1H), 7.72 (t,  $J = 7.6$  Hz, 1H), 7.63 (t,  $J = 7.6$  Hz, 1H), 7.26 (d,  $J = 3.3$  Hz, 1H), 4.36 (m, 1H), 3.91 (d,  $J = 16.9$  Hz, 1H), 3.65 (d,

$J = 34.2$  Hz, 4H), 2.39 (dd,  $J = 19.4, 9.0$  Hz, 1H), 2.00 (dd,  $J = 19.1, 9.3$  Hz, 1H), 1.89 – 1.67 (m, 4H), 1.51 (td,  $J = 9.2, 8.5, 3.8$  Hz, 3H), 1.43 – 1.38 (m, 2H), 1.29 – 1.20 (m, 3H), 1.09 (ddd,  $J = 27.7, 14.4, 8.5$  Hz, 4H), 0.89 – 0.73 (m, 9H), 0.63 (d,  $J = 8.7$  Hz, 3H), 0.54 (d,  $J = 11.1$  Hz, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  221.2, 173.9, 171.2, 133.4, 128.9, 128.7, 128.5, 126.5, 122.8, 122.5, 122.5, 116.0, 112.0, 110.8, 73.5, 54.0, 51.2, 48.7, 47.6, 44.3, 43.8, 36.4, 35.7, 35.3, 34.8, 33.5, 31.4, 30.6, 29.9, 29.8, 27.9, 26.9, 21.6, 20.3, 13.7, 11.9;  $\text{C}_{29}\text{H}_{32}\text{N}_2\text{O}_3$   $[\text{M}+\text{Na}]^+$  calcd 615.3193, found 615.3204.

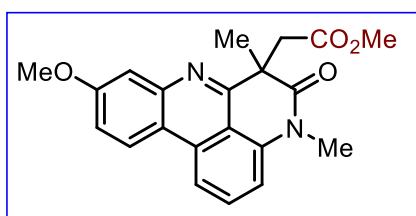
***methyl 2-(4,6,9-trimethyl-5-oxo-5,6-dihydro-4H-pyrido[4,3,2-gh]phenanthridin-6-yl)acetate (4a)***

Purification by flash chromatography (PE/EA = 6/1). White solid; mp 203–205 °C; 50%;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.39 (d,  $J = 8.3$  Hz, 1H), 8.21 (d,  $J = 8.3$  Hz, 1H), 7.88 (s, 1H), 7.79 (t,  $J = 8.1$  Hz, 1H), 7.44 (d,  $J = 8.4$  Hz, 1H), 7.21 (d,  $J = 8.0$  Hz, 1H),



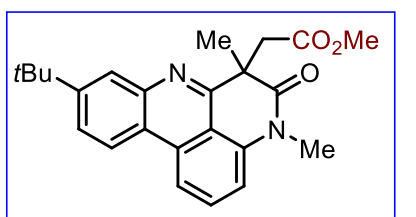
3.97 (d,  $J = 17.2$  Hz, 1H), 3.58 (d,  $J = 20.2$  Hz, 4H), 3.46 (s, 3H), 2.57 (s, 3H), 1.56 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  173.9, 172.6, 159.5, 144.8, 139.2, 138.9, 133.4, 131.7, 129.1, 128.2, 122.3, 120.6, 115.9, 111.6, 110.4, 51.6, 48.6, 42.6, 29.9, 29.9, 21.5;  $\text{C}_{21}\text{H}_{20}\text{N}_2\text{O}_3$   $[\text{M}+\text{Na}]^+$  calcd 371.1366, found 371.1380.

**Methyl**                      **2-(9-methoxy-4,6-dimethyl-5-oxo-5,6-dihydro-4H-pyrido[4,3,2-g]phenanthridin-6-yl)acetate (4b)**



Purification by flash chromatography (PE/EA = 8/1). White solid; mp 81–83 °C; 61%;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.39 (d,  $J = 9.1$  Hz, 1H), 8.15 (d,  $J = 8.3$  Hz, 1H), 7.78 (t,  $J = 8.1$  Hz, 1H), 7.47 (s, 1H), 7.29 – 7.22 (m, 1H), 7.17 (d,  $J = 7.9$  Hz, 1H), 3.99 (s, 4H), 3.61 (s, 4H), 3.48 (s, 3H), 1.57 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  173.9, 172.5, 160.3, 160.0, 146.4, 138.9, 133.6, 131.8, 123.8, 117.7, 117.0, 115.6, 111.1, 109.8, 109.2, 55.5, 51.6, 48.6, 42.7, 30.0, 29.9;  $\text{C}_{21}\text{H}_{20}\text{N}_2\text{O}_4$   $[\text{M}+\text{Na}]^+$  calcd 387.1315, found 387.1324.

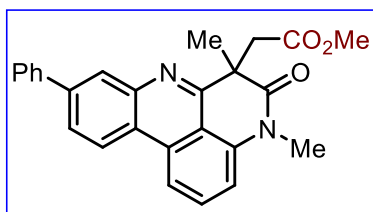
**methyl**                      **2-(9-(tert-butyl)-4,6-dimethyl-5-oxo-5,6-dihydro-4H-pyrido[4,3,2-g]phenanthridin-6-yl)acetate (4c)**



Purification by flash chromatography (PE/EA = 2/1). White solid; mp 192–193 °C; 62%;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.44 (d,  $J = 8.7$  Hz, 1H), 8.22 (d,  $J = 8.3$  Hz, 1H), 8.05 (d,  $J = 2.1$  Hz, 1H), 7.79 (t,  $J = 8.1$  Hz, 1H), 7.70 (dd,  $J = 8.7, 2.1$  Hz, 1H), 7.21 (d,  $J = 7.9$  Hz, 1H), 4.00 (d,  $J = 17.2$  Hz, 1H), 3.61 (s, 4H), 3.48 (s, 3H), 1.47 (s, 9H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  174.0, 172.6, 159.4, 152.3, 144.7, 138.8, 133.3, 131.6, 125.4, 124.8, 122.2, 120.5, 115.9, 111.7, 110.4, 51.6, 48.6, 42.7, 35.0, 31.3, 30.0, 29.8;  $\text{C}_{24}\text{H}_{27}\text{N}_2\text{O}_3$   $[\text{M}+\text{Na}]^+$  calcd 413.1836, found 413.1859.

methyl

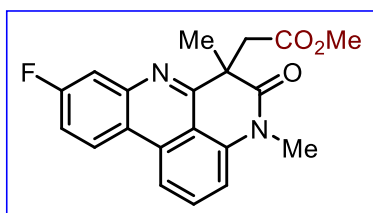
*2-(4,6-dimethyl-5-oxo-9-phenyl-5,6-dihydro-4H-pyrido[4,3,2-gh]phenanthridin-6-yl)acetate (4d)*



Purification by flash chromatography (PE/EA = 2/1). White solid; mp 226–228 °C; 52%; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.56 (d, *J* = 8.6 Hz, 1H), 8.32 (d, *J* = 1.9 Hz, 1H), 8.26 (d, *J* = 8.3 Hz, 1H), 7.91 – 7.75 (m, 4H), 7.50 (dd, *J* = 8.4, 6.9 Hz, 2H), 7.41 (d, *J* = 7.3 Hz, 1H), 7.27 – 7.23 (m, 1H), 4.00 (d, *J* = 17.2 Hz, 1H), 3.65 – 3.56 (m, 4H), 3.48 (s, 3H), 1.59 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 173.9, 172.6, 160.1, 145.0, 141.7, 140.2, 139.0, 133.2, 131.9, 128.9, 127.7, 127.5, 127.4, 125.6, 123.1, 122.0, 116.1, 111.9, 110.9, 51.7, 48.7, 42.7, 29.9, 29.9; C<sub>26</sub>H<sub>22</sub>N<sub>2</sub>O<sub>3</sub> [M+Na]<sup>+</sup> calcd 433.1523, found 433.1530.

methyl

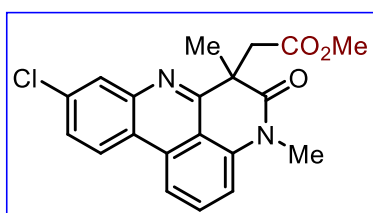
*2-(9-fluoro-4,6-dimethyl-5-oxo-5,6-dihydro-4H-pyrido[4,3,2-gh]phenanthridin-6-yl)acetate (4e)*



Purification by flash chromatography (PE/EA = 6/1). White solid; mp 173–175 °C; 33%; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.48 (dd, *J* = 9.1, 5.9 Hz, 1H), 8.18 (d, *J* = 8.3 Hz, 1H), 7.83 (t, *J* = 8.1 Hz, 1H), 7.73 (dd, *J* = 9.9, 2.7 Hz, 1H), 7.37 (td, *J* = 8.6, 2.6 Hz, 1H), 7.28 – 7.21 (m, 1H), 3.96 (d, *J* = 17.2 Hz, 1H), 3.61 (s, 4H), 3.49 (s, 3H), 1.57 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 173.7, 172.6, 163.4(d, *J* = 247 Hz), 161.1, 139.1, 133.2, 132.2, 124.6(d, *J* = 10 Hz), 119.7, 119.6, 115.8, 115.6(d, *J* = 24 Hz), 115.5, 114.0(d, *J* = 20 Hz), 111.5, 110.7, 51.7, 48.7, 42.6, 29.9, 29.9; C<sub>20</sub>H<sub>17</sub>N<sub>2</sub>O<sub>3</sub>F [M+Na]<sup>+</sup> calcd 375.1115, found 375.1131.

methyl

*2-(9-chloro-4,6-dimethyl-5-oxo-5,6-dihydro-4H-pyrido[4,3,2-gh]phenanthridin-6-yl)acetate (4f)*

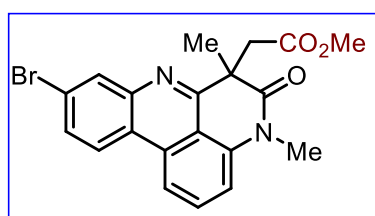


Purification by flash chromatography (PE/EA = 8/1). White solid; mp 168–170 °C; 63%; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.40 (d, *J* = 8.8 Hz, 1H), 8.18 (d, *J* = 8.3 Hz, 1H), 8.07 (d, *J* = 2.2 Hz, 1H), 7.82 (t, *J* = 8.1



Hz, 1H), 7.55 (dd,  $J = 8.8, 2.3$  Hz, 1H), 7.45 (s, 1H), 7.25 (d,  $J = 7.9$  Hz, 1H), 3.94 (d,  $J = 17.3$  Hz, 1H), 3.61 (s, 3H), 3.55 (d,  $J = 13.3$  Hz, 1H), 3.48 (s, 3H), 1.56 (s, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  180.0, 173.7, 172.6, 170.0, 161.1, 146.9, 145.3, 144.7, 139.1, 136.6, 134.9, 134.6, 133.7, 133.0, 132.2, 130.3, 128.8, 128.8, 127.0, 125.7, 123.9, 123.4, 121.4, 116.4, 115.9, 111.8, 111.1, 51.9, 51.7, 48.7, 44.1, 42.6, 41.1, 29.9, 29.8, 28.3, 24.2;  $\text{C}_{20}\text{H}_{17}\text{N}_2\text{O}_3\text{Cl}$   $[\text{M}+\text{Na}]^+$  calcd 391.0820, found 391.0827.

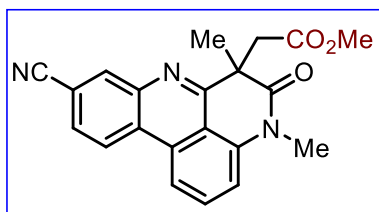
*methyl*                      **2-(9-bromo-4,6-dimethyl-5-oxo-5,6-dihydro-4H-pyrido[4,3,2-gh]phenanthridin-6-yl)acetate (4g)**



Purification by flash chromatography (PE/EA = 8/1). White solid; mp 196–198 °C; 39%;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.34 (d,  $J = 8.8$  Hz, 1H), 8.26 (d,  $J = 2.1$  Hz, 1H), 8.22 – 8.16 (m, 1H), 7.83 (t,  $J = 8.2$  Hz, 1H), 7.69 (dd,  $J = 8.7, 2.1$  Hz, 1H), 7.64 (d,  $J = 7.1$  Hz, 1H), 3.94 (d,  $J = 17.2$  Hz, 1H), 3.61 (s, 3H), 3.49 (s, 4H), 1.56 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  173.7, 172.6, 161.1, 145.5, 139.1, 133.0, 132.3, 132.0, 132.0, 129.6, 128.9, 124.1, 123.3, 122.8, 121.8, 116.1, 115.9, 111.9, 111.2, 51.7, 48.8, 42.6, 29.9, 29.9;  $\text{C}_{20}\text{H}_{17}\text{N}_2\text{O}_3\text{Br}$   $[\text{M}+\text{Na}]^+$  calcd 435.0315, found 435.0326.

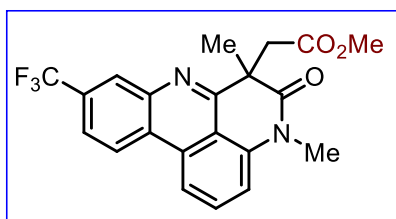
*methyl*                      **2-(9-cyano-4,6-dimethyl-5-oxo-5,6-dihydro-4H-pyrido[4,3,2-gh]phenanthridin-6-yl)acetate (4h)**

Purification by flash chromatography (PE/EA = 6/1). White solid; mp 220–221 °C; 45%;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.58 (d,  $J = 8.5$  Hz, 1H), 8.42 (d,  $J = 1.7$  Hz, 1H), 8.26 (d,  $J = 8.2$  Hz, 1H), 7.92 (t,  $J = 8.1$  Hz, 1H), 7.79 (dd,  $J = 8.5, 1.8$  Hz, 1H), 7.37 (d,  $J = 8.0$  Hz, 1H), 3.95 (d,  $J = 17.3$  Hz, 1H), 3.66 – 3.58 (m, 4H), 3.50 (s, 3H), 1.57 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  173.5, 172.6, 162.2, 143.9, 139.3, 134.7, 132.7,



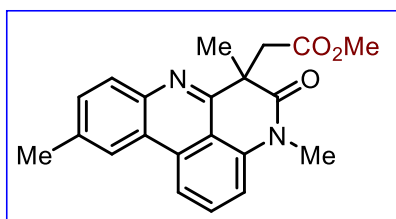
132.3, 129.8, 127.8, 126.2, 124.0, 118.6, 116.3, 112.6, 112.2, 51.7, 48.9, 42.6, 30.0, 29.8; C<sub>21</sub>H<sub>17</sub>N<sub>3</sub>O<sub>3</sub> [M+Na]<sup>+</sup> calcd 382.1162, found 382.1174.

*methyl 2-(4,6-dimethyl-5-oxo-9-(trifluoromethyl)-5,6-dihydro-4H-pyrido[4,3,2-gh]phenanthridin-6-yl)acetate (4i)*



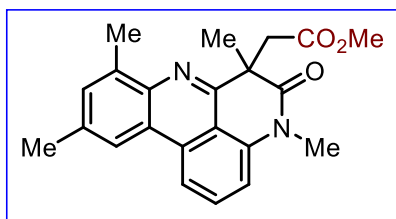
Purification by flash chromatography (PE/EA = 4/1). White solid; mp 210–211 °C; 64%; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.62 (d, *J* = 8.6 Hz, 1H), 8.38 (d, *J* = 1.9 Hz, 1H), 8.29 (d, *J* = 8.2 Hz, 1H), 7.90 (t, *J* = 8.1 Hz, 1H), 7.81 (dd, *J* = 8.6, 1.9 Hz, 1H), 7.34 (d, *J* = 8.1 Hz, 1H), 3.97 (d, *J* = 17.3 Hz, 1H), 3.65 – 3.58 (m, 4H), 3.49 (s, 3H), 1.58 (s, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 173.6, 172.6, 161.5, 144.0, 139.2, 132.5, 130.9, 130.6, 127.2 (q, *J* = 4 Hz), 125.2 (q, *J* = 271 Hz), 123.7, 122.3 (q, *J* = 3 Hz), 116.3, 112.5, 112.0, 51.7, 48.8, 42.7, 30.0, 29.9; C<sub>21</sub>H<sub>17</sub>N<sub>2</sub>O<sub>3</sub>F<sub>3</sub> [M+Na]<sup>+</sup> calcd 425.1083, found 425.1096.

*methyl 2-(4,6,10-trimethyl-5-oxo-5,6-dihydro-4H-pyrido[4,3,2-gh]phenanthridin-6-yl)acetate (4j)*



Purification by flash chromatography (PE/EA = 8/1). White solid; mp 123–124 °C; 45%; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.38 (d, *J* = 8.1 Hz, 1H), 8.26 (d, *J* = 8.3 Hz, 1H), 7.81 (t, *J* = 8.1 Hz, 1H), 7.58 (d, *J* = 7.1 Hz, 1H), 7.51 (t, *J* = 7.6 Hz, 1H), 7.28 – 7.20 (m, 1H), 3.96 (d, *J* = 17.0 Hz, 1H), 3.47 (s, 3H), 2.81 (s, 3H), 1.57 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 174.0, 172.6, 158.0, 143.3, 138.9, 137.4, 133.7, 131.5, 129.5, 126.1, 122.7, 120.4, 116.3, 111.7, 110.6, 51.6, 48.9, 42.8, 30.3, 29.9, 18.2; C<sub>21</sub>H<sub>20</sub>N<sub>2</sub>O<sub>3</sub> [M+Na]<sup>+</sup> calcd 371.1366, found 371.1382.

*methyl 2-(4,6,8,10-tetramethyl-5-oxo-5,6-dihydro-4H-pyrido[4,3,2-gh]phenanthridin-6-yl)acetate (4k)*

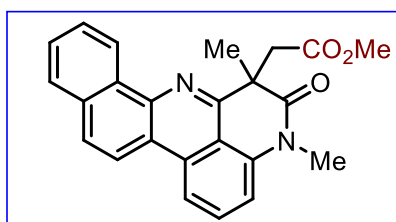


Purification by flash chromatography (PE/EA = 8/1).

White solid; mp 152–154 °C; 60%; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.23 (d, *J* = 8.3 Hz, 1H), 8.15 (s, 1H), 7.77 (t, *J* = 8.1 Hz, 1H), 7.42 (s, 1H), 7.21 (d, *J* = 7.9

Hz, 1H), 3.94 (d, *J* = 17.0 Hz, 1H), 3.61 (s, 4H), 3.46 (s, 3H), 2.77 (s, 3H), 2.56 (s, 3H), 1.56 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 174.1, 172.6, 156.9, 141.6, 138.8, 137.0, 135.8, 133.4, 131.3, 131.3, 122.5, 119.8, 116.3, 111.7, 110.5, 51.5, 48.8, 42.8, 30.3, 29.8, 21.9, 18.1; C<sub>22</sub>H<sub>22</sub>N<sub>2</sub>O<sub>3</sub> [M+Na]<sup>+</sup> calcd 385.1523, found 385.1541.

*methyl 2-(4,6-dimethyl-5-oxo-5,6-dihydro-4H-benzo[c]pyrido[4,3,2-gh]phenanthridin-6-yl)acetate (4l)*

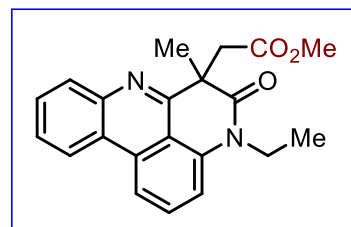


Purification by flash chromatography (PE/EA = 8/1).

Yellow oil; 78%; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 9.05 (d, *J* = 8.4 Hz, 1H), 8.77 (d, *J* = 8.6 Hz, 1H), 8.01 (s, 3H), 7.85 (t, *J* = 8.2 Hz, 1H), 7.74 – 7.60 (m,

2H), 7.30 – 7.23 (m, 1H), 4.01 (d, *J* = 17.1 Hz, 1H), 3.66 (s, 3H), 3.62 (d, *J* = 17.1 Hz, 1H), 3.48 (s, 3H), 1.60 (s, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 173.8, 172.6, 158.7, 144.6, 138.7, 133.4, 133.0, 131.4, 129.9, 129.8, 128.7, 128.2, 127.5, 126.5, 126.2, 120.9, 119.4, 113.2, 110.1, 51.6, 48.4, 42.7, 30.0, 29.9; C<sub>24</sub>H<sub>20</sub>N<sub>2</sub>O<sub>3</sub> [M+H]<sup>+</sup> calcd 385.1547, found 385.1556.

*methyl 2-(4-ethyl-6-methyl-5-oxo-5,6-dihydro-4H-pyrido[4,3,2-gh]phenanthridin-6-yl)acetate (4m)*



Purification by flash chromatography (PE/EA = 8/1).

White solid; mp 150–152 °C; 76%; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.50 (d, *J* = 8.2 Hz, 1H), 8.24 (d, *J* = 8.3 Hz, 1H), 8.07 (d, *J* = 7.9 Hz, 1H), 7.82 (t, *J* = 8.1 Hz, 1H),

7.71 (t, *J* = 7.5 Hz, 1H), 7.61 (t, *J* = 7.6 Hz, 1H), 7.27 (d, *J* = 8.3 Hz, 1H), 4.26 (q, *J* = 7.1 Hz, 2H), 3.98 (d, *J* = 17.2 Hz, 1H), 3.58 (d, *J* = 17.1 Hz, 1H), 3.46 (s, 3H), 1.56 (s, 3H), 1.36 (t, *J* = 7.1 Hz, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 173.4, 172.5, 159.7, 137.7,

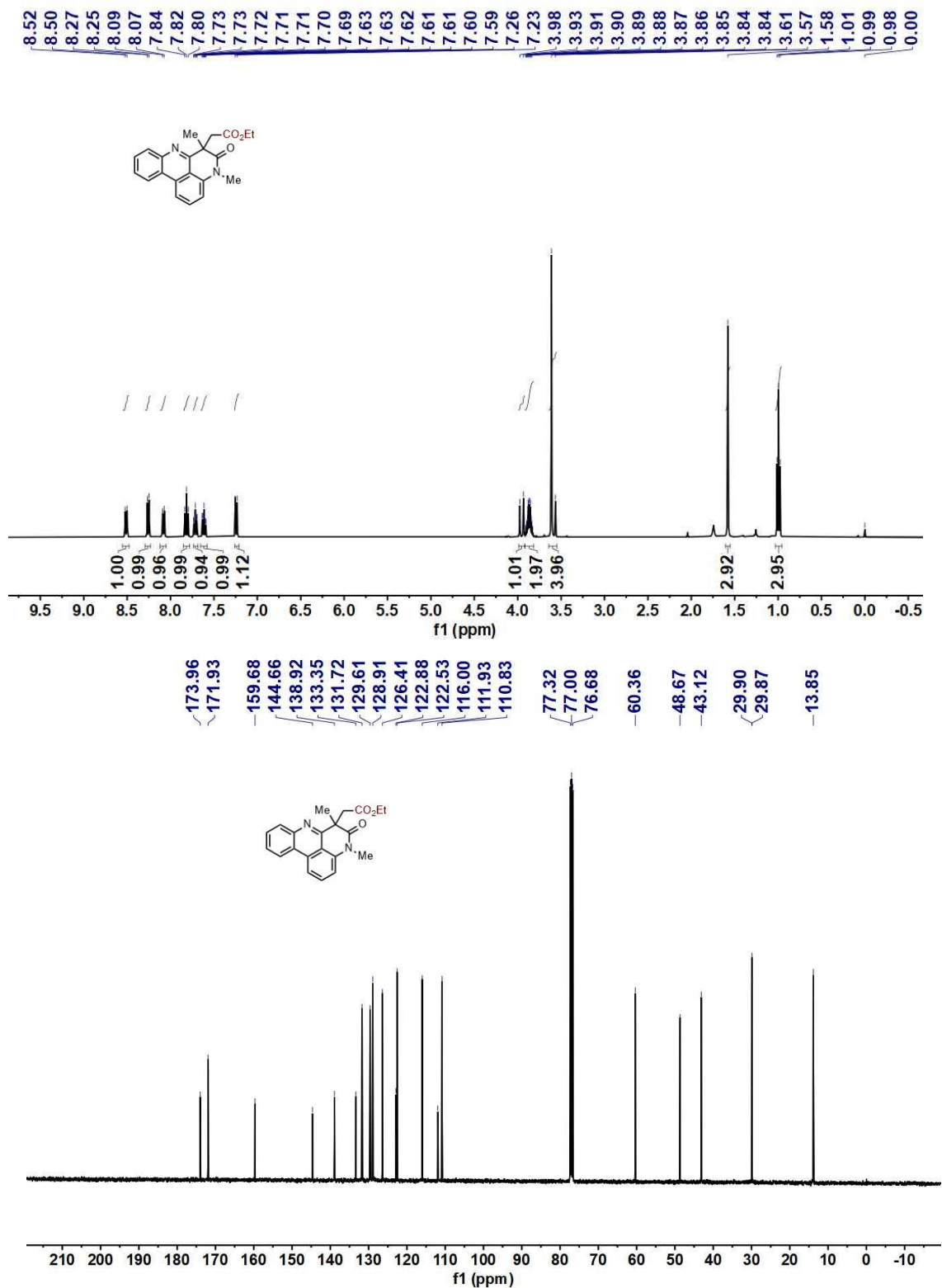
133.7, 131.8, 129.6, 128.9, 128.6, 126.4, 123.0, 122.5, 115.8, 112.2, 110.8, 51.6, 48.5, 42.6, 37.3, 29.8, 11.9; C<sub>21</sub>H<sub>20</sub>N<sub>2</sub>O<sub>3</sub> [M+Na]<sup>+</sup> calcd 371.1366, found 371.1383.

## 8. References

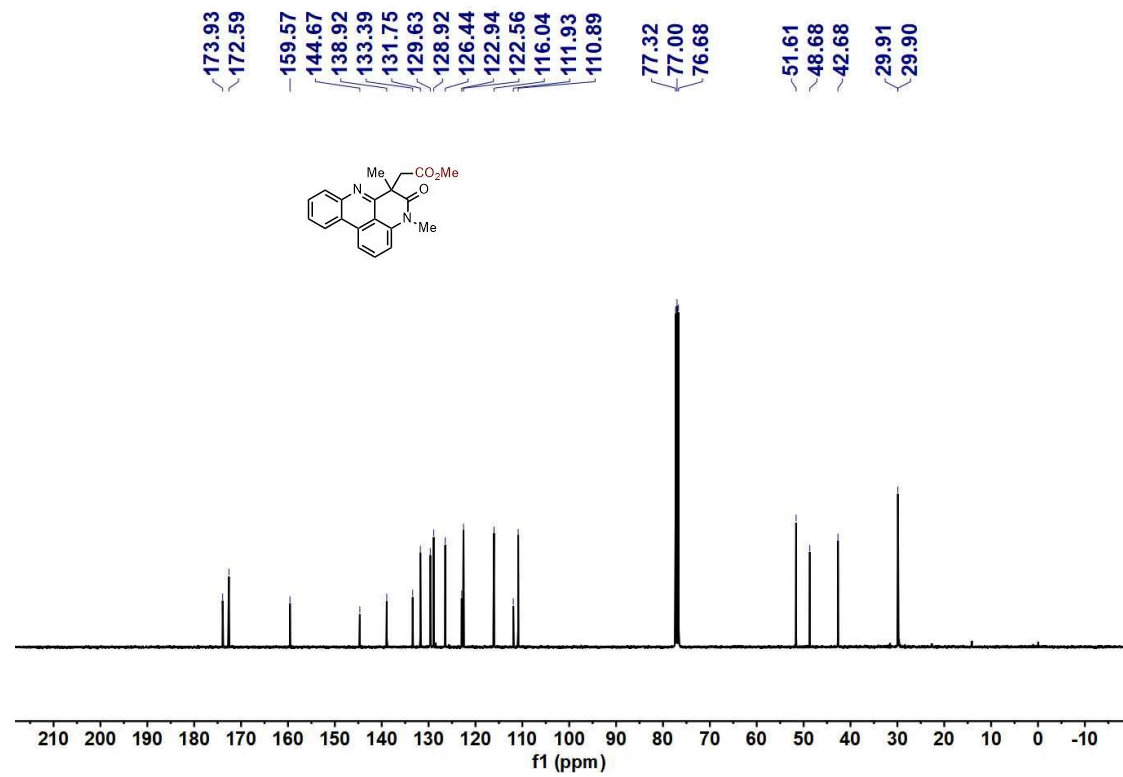
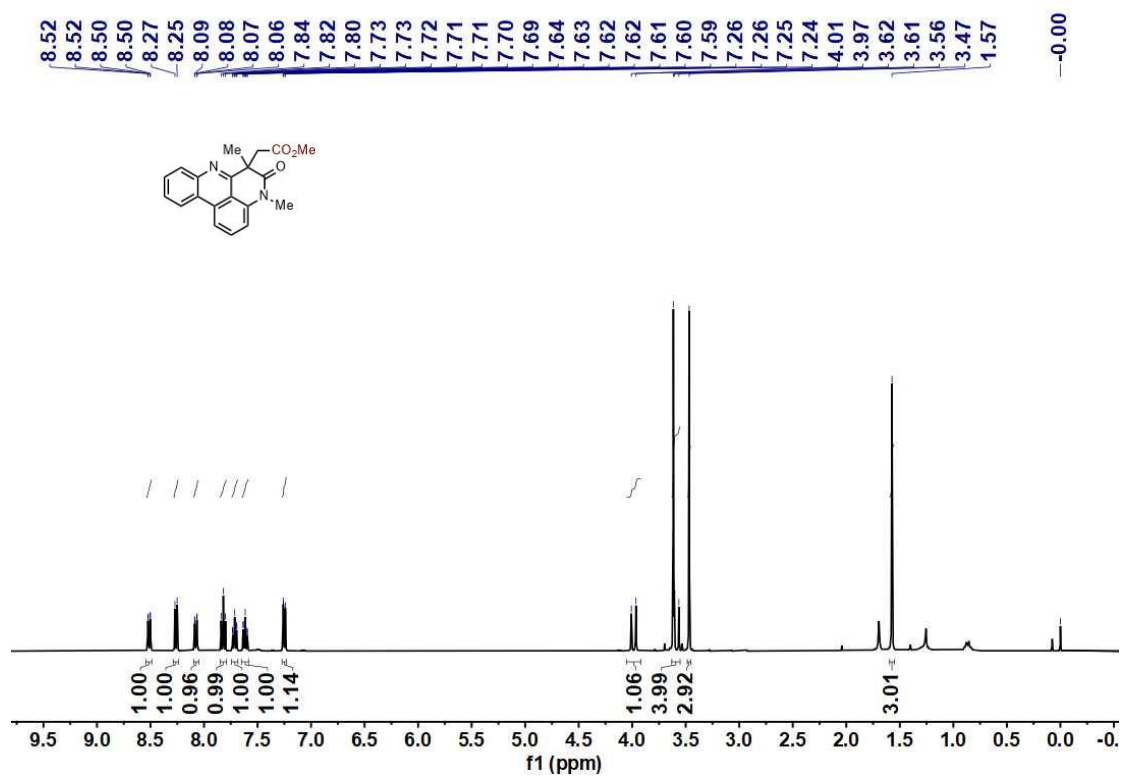
- 1 E. Speckmeier, T. G. Fischer and K. Zeitler, A toolbox approach to construct broadly applicable metal-free catalysts for photoredox chemistry: deliberate tuning of redox potentials and importance of halogens in donor–acceptor cyanoarenes, *J. Am. Chem. Soc.*, 2018, **140**, 15353–15365.
- 2 (a) X. Li, X. Fang, S. Zhuang, P. Liu and P. Sun, Photoredox catalysis: construction of polyheterocycles via alkoxyacylation/ addition/ cyclization sequence, *Org. Lett.*, 2017, **19**, 3580–3583; (b) J.-Q. Shang, S.-S. Wang, H. Fu, Y. Li, T. Yang and Y.-M. Li, Oxidative radical cascade cyclization involving C(sp<sup>3</sup>)–C(sp<sup>3</sup>), C(sp<sup>3</sup>)–C(sp<sup>2</sup>) and C(sp<sup>2</sup>)–N bonds formation: direct construction of cyano and methyl substituted polyheterocycles, *Org. Chem. Front.*, 2018, **5**, 1945–1949.

## 9. NMR spectra of compounds

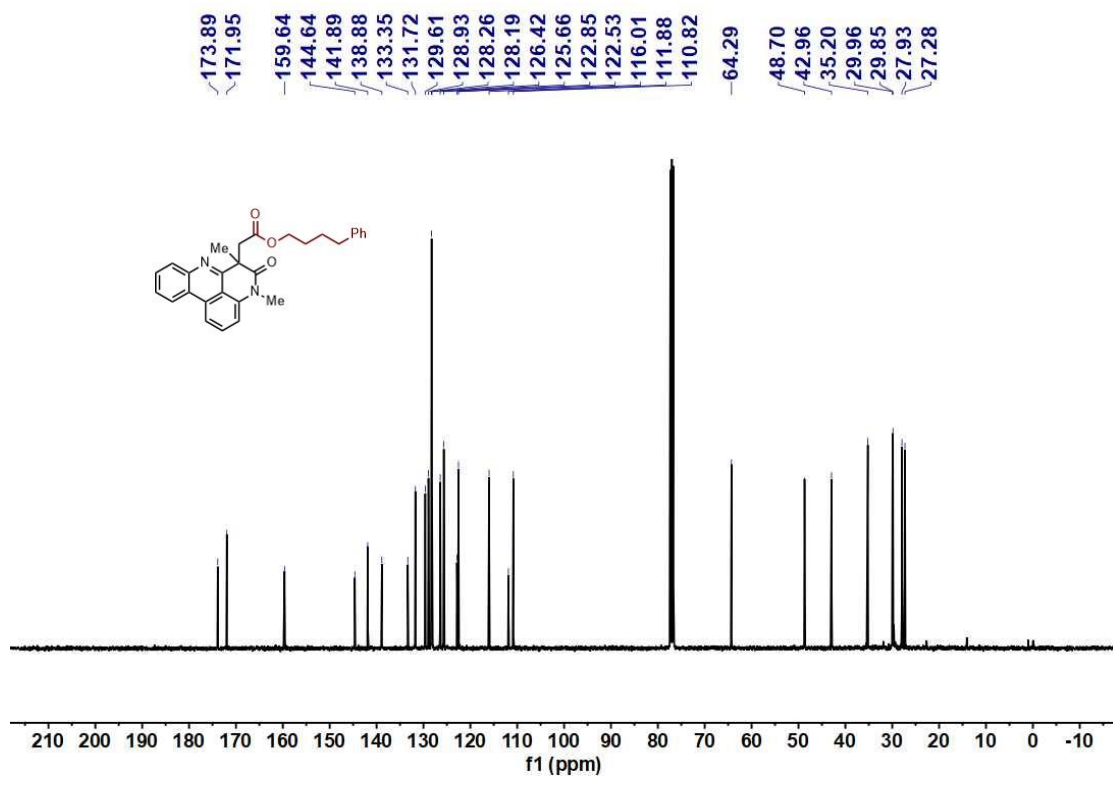
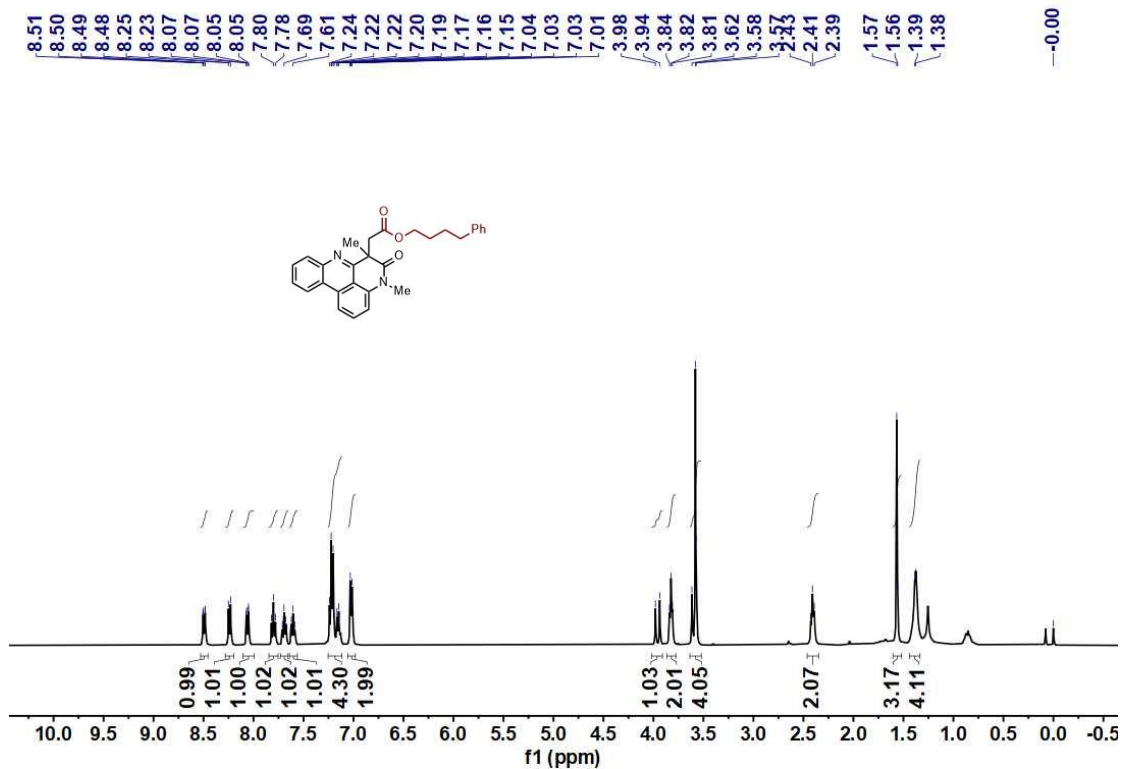
### *Ethyl 2-(4,6-dimethyl-5-oxo-5,6-dihydro-4H-pyrido[4,3,2-g]phenanthridin-6-yl)acetate (3a)*



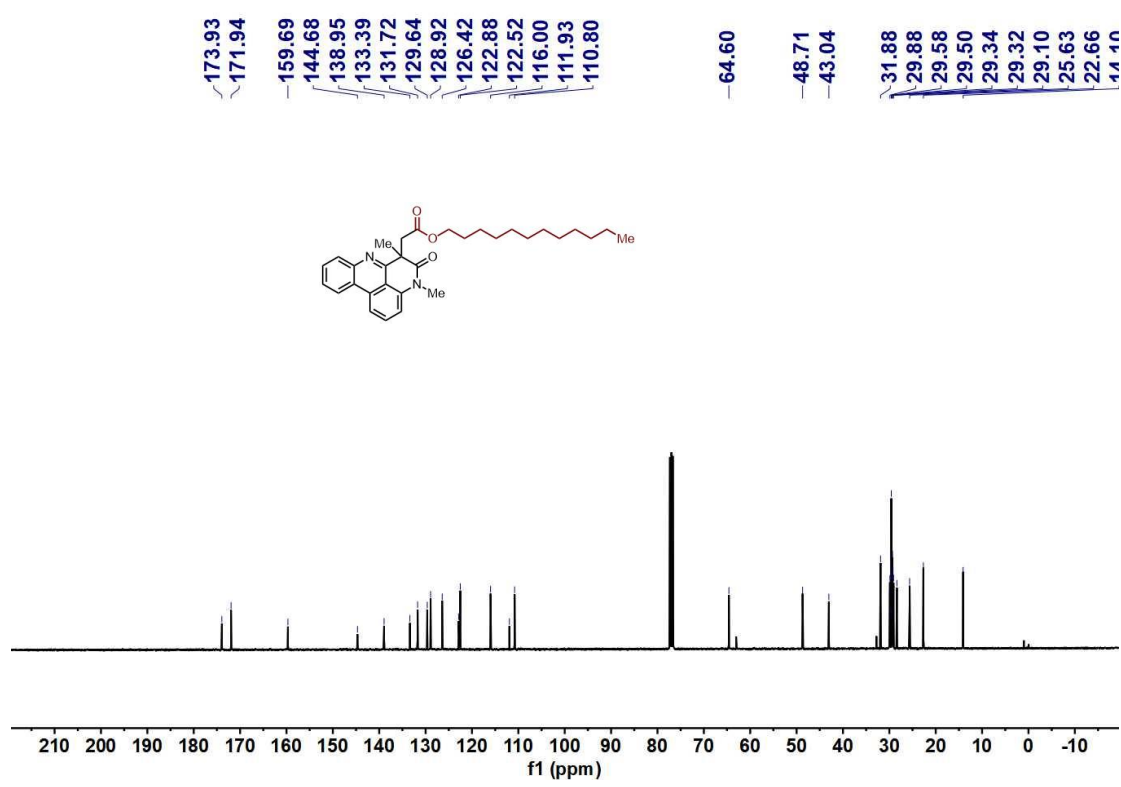
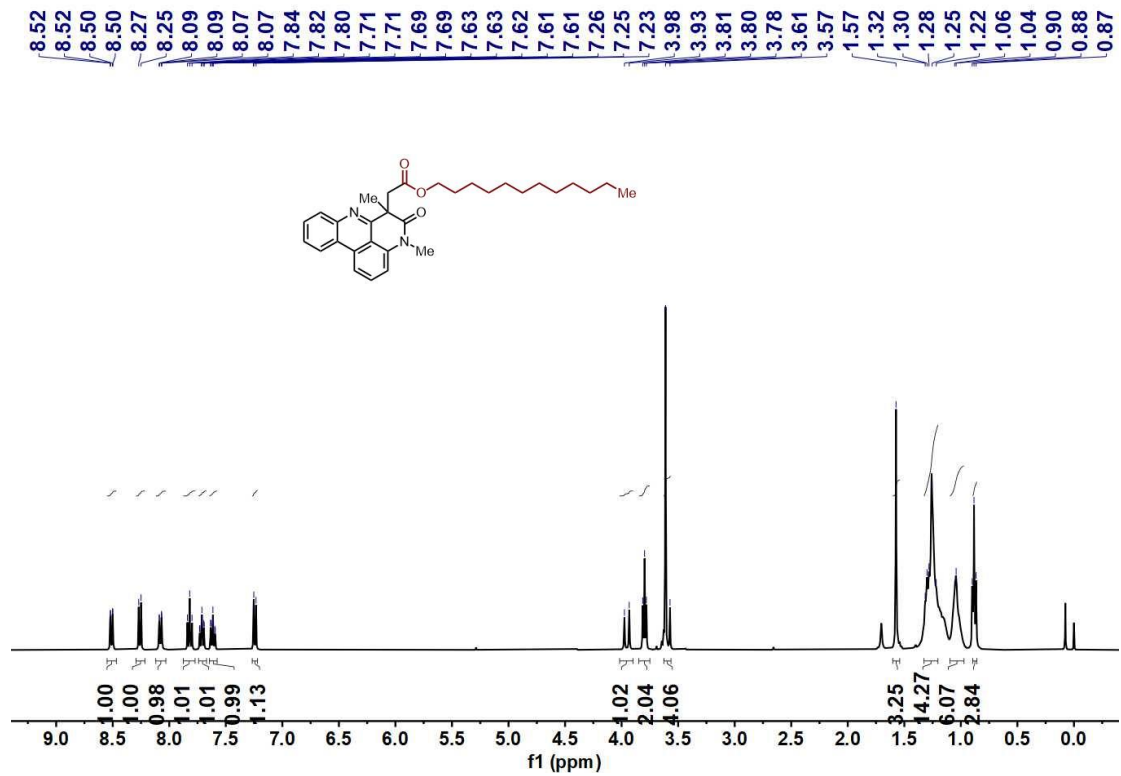
*methyl 2-(4,6-dimethyl-5-oxo-5,6-dihydro-4H-pyrido[4,3,2-gh]phenanthridin-6-yl) acetate (3b)*



4-phenylbutyl 2-(4,6-dimethyl-5-oxo-5,6-dihydro-4H-pyrido[4,3,2-gh]phenanthridi  
n-6-yl)acetate (3c)

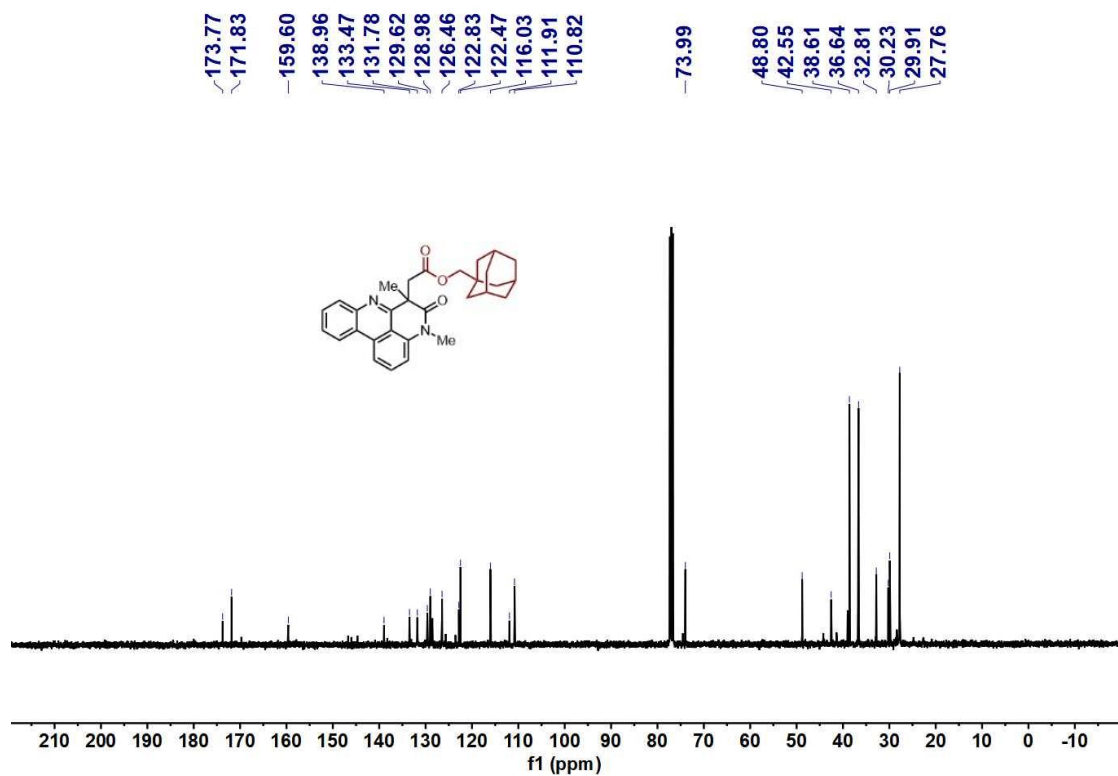
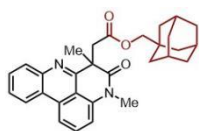
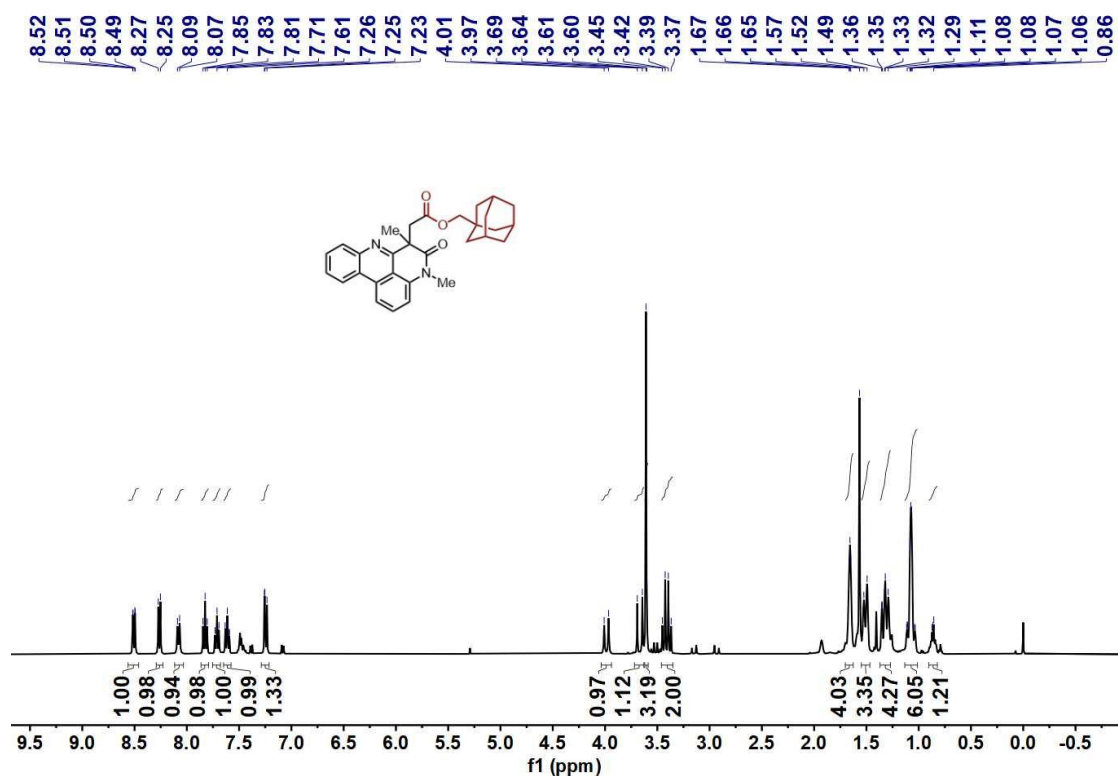


*dodecyl 2-(4,6-dimethyl-5-oxo-5,6-dihydro-4H-pyrido[4,3,2-gh]phenanthridin-6-yl) acetate (3d)*

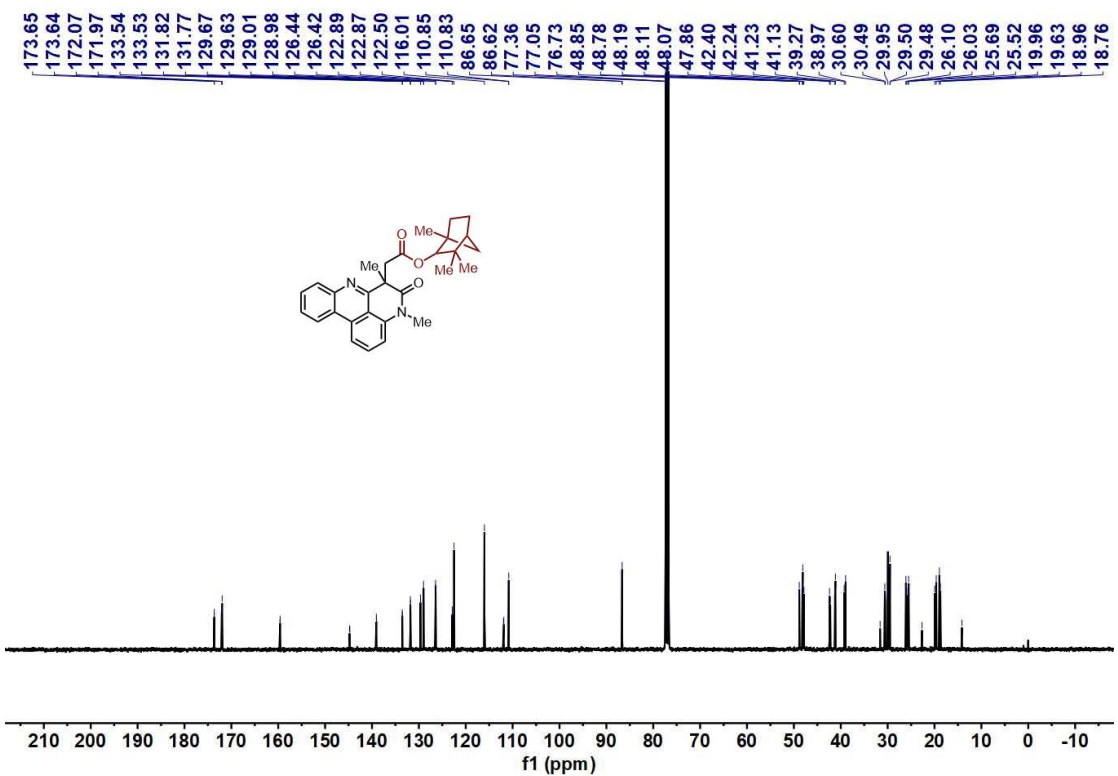
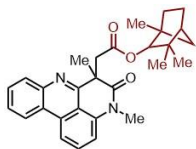
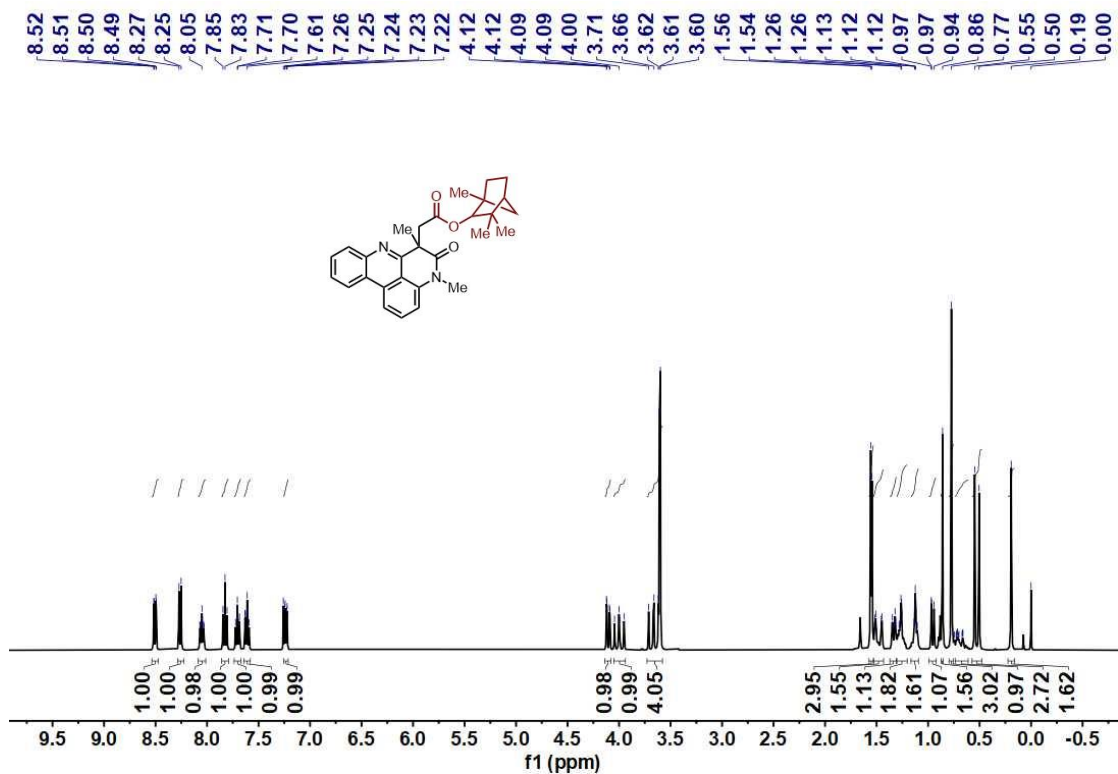




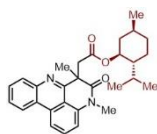
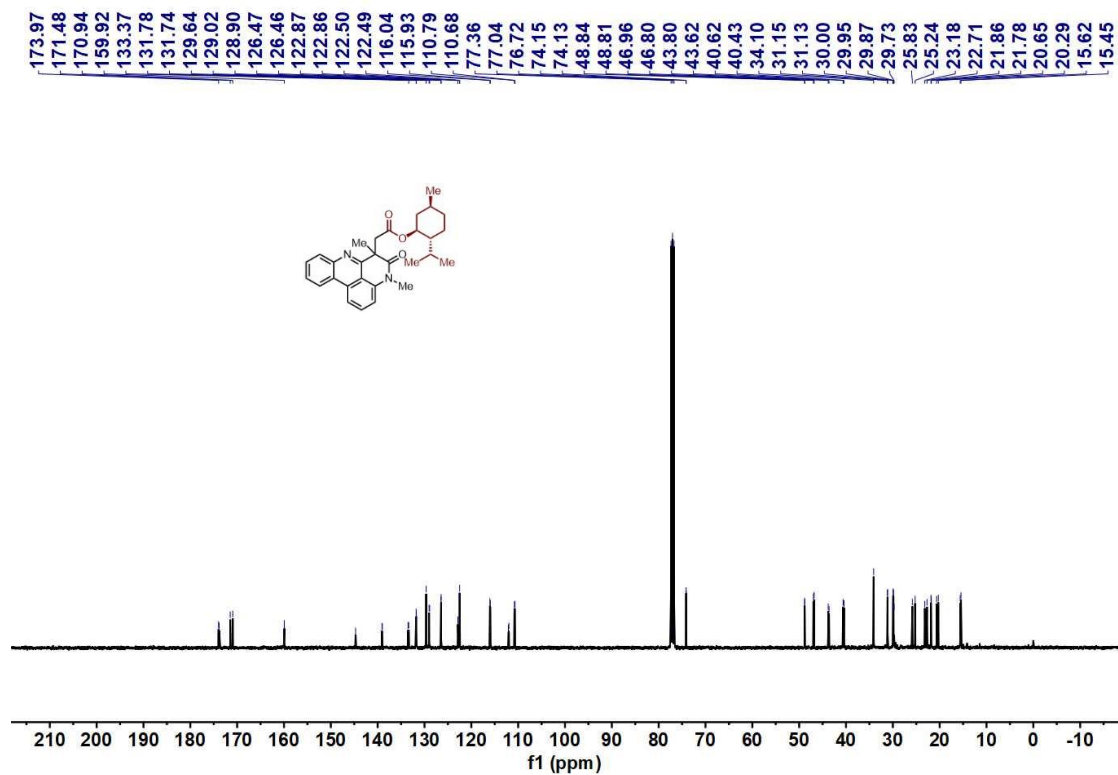
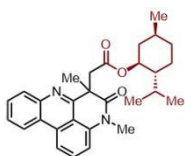
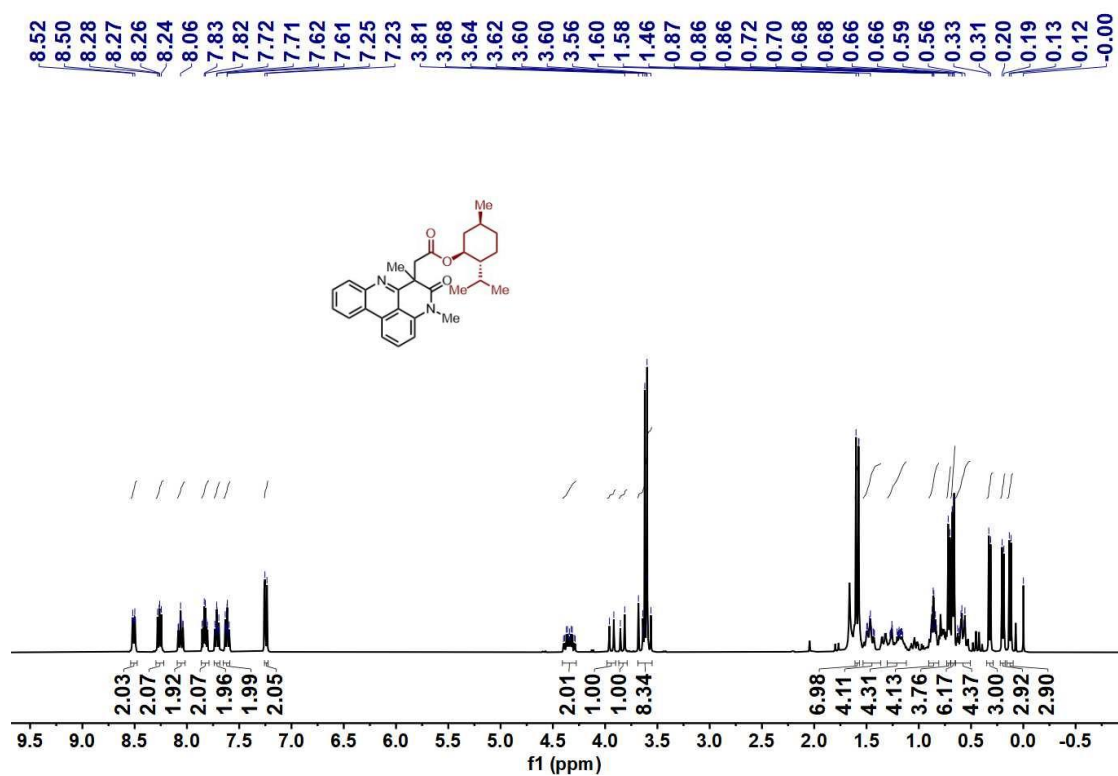
*((3r,5r,7r)-adamantan-1-yl)methyl 2-(4,6-dimethyl-5-oxo-5,6-dihydro-4H-pyrido[4,3,2-g]phenanthridin-6-yl)acetate (3e)*



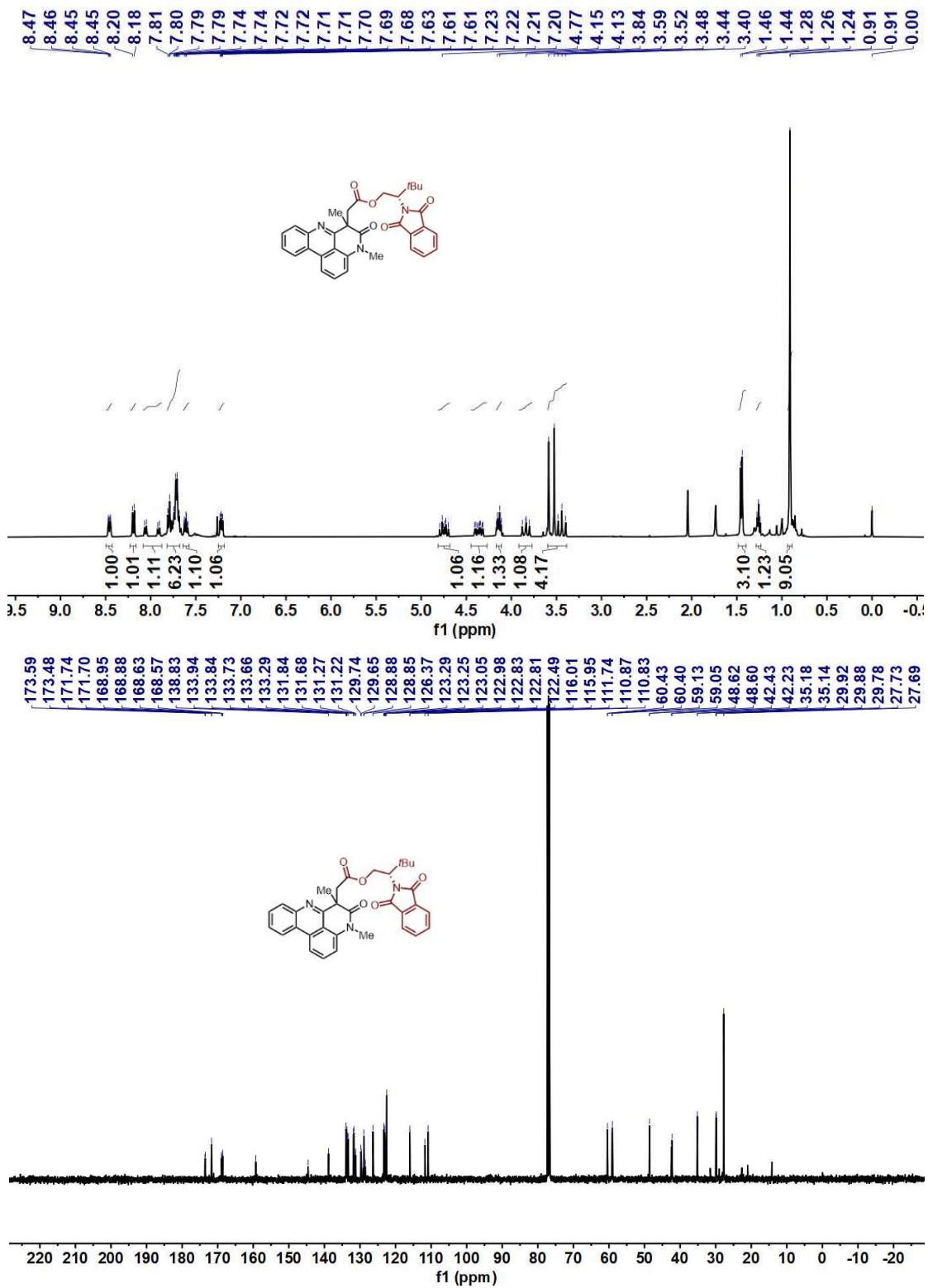
*1,3,3-trimethylbicyclo[2.2.1]heptan-2-yl 2-(4,6-dimethyl-5-oxo-5,6-dihydro-4H-pyrido[4,3,2-g]phenanthridin-6-yl)acetate (3f)*



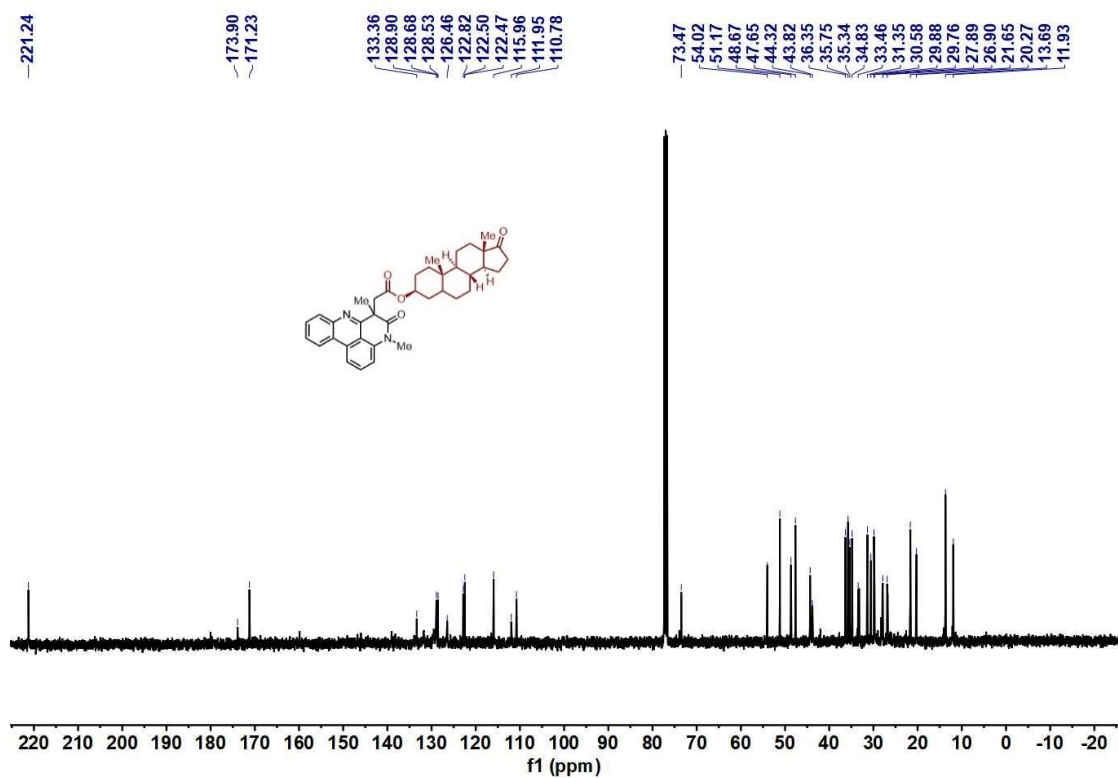
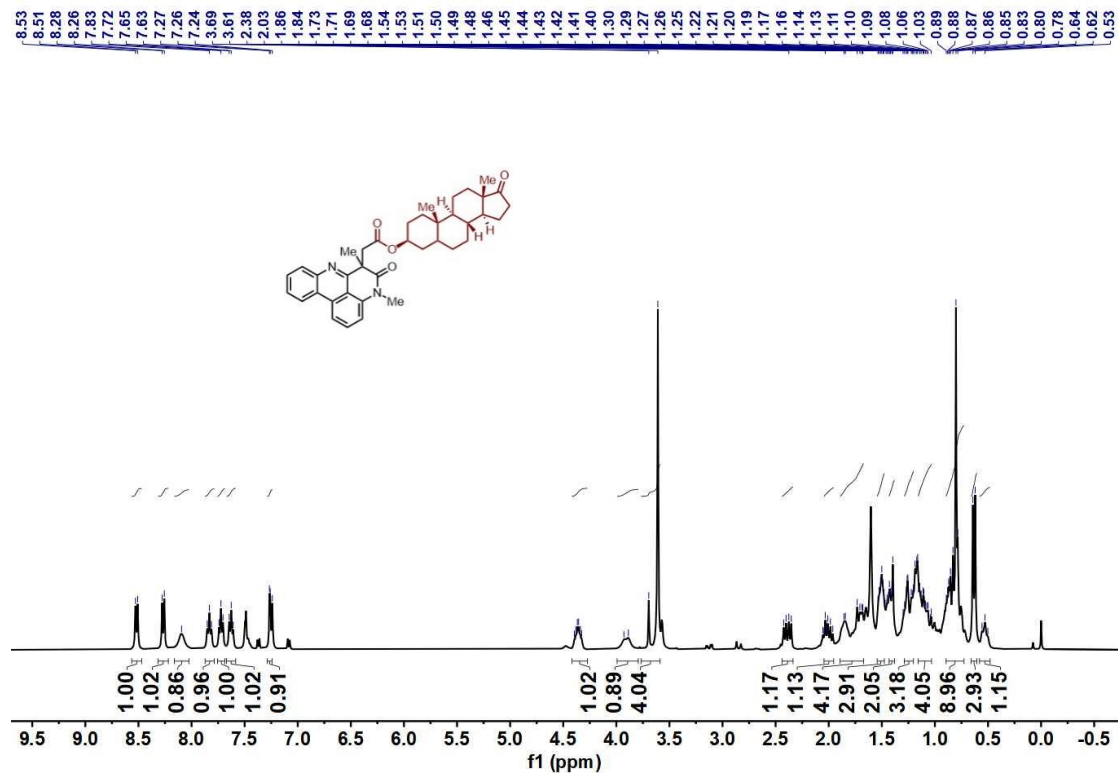
*(1R,2R,5S)-2-isopropyl-5-methylcyclohexyl 2-(4,6-dimethyl-5-oxo-5,6-dihydro-4H-pyrido[4,3,2-gh]phenanthridin-6-yl)acetate (3g)*



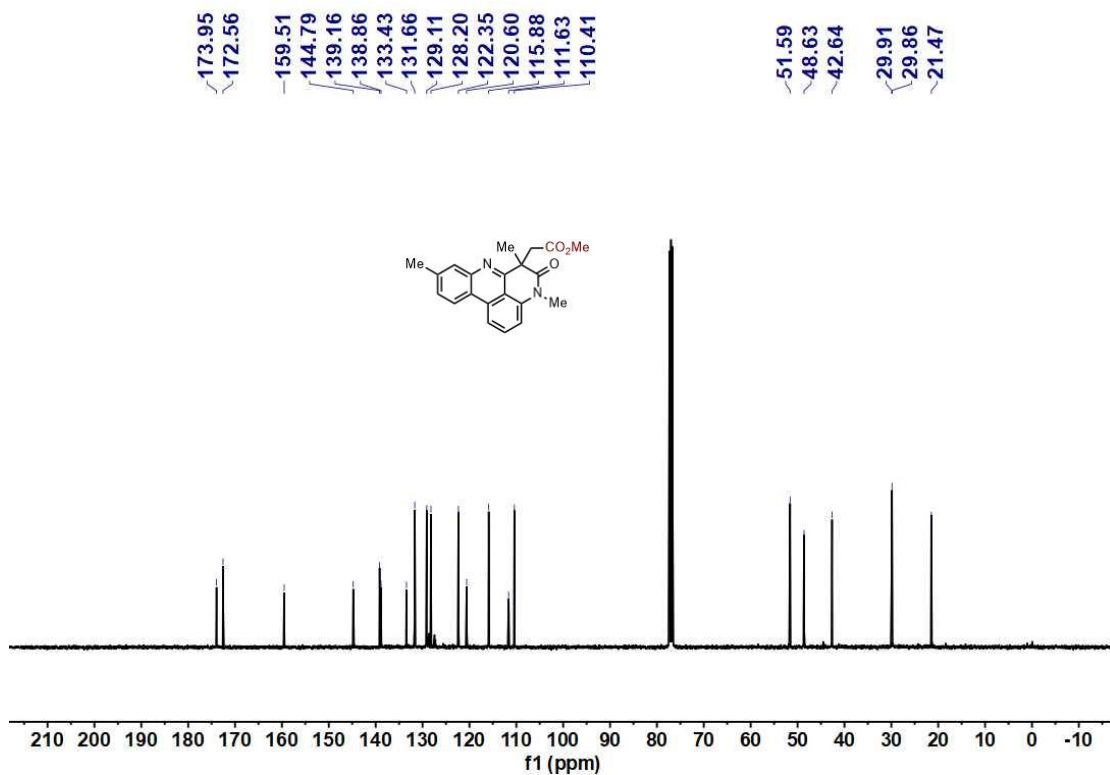
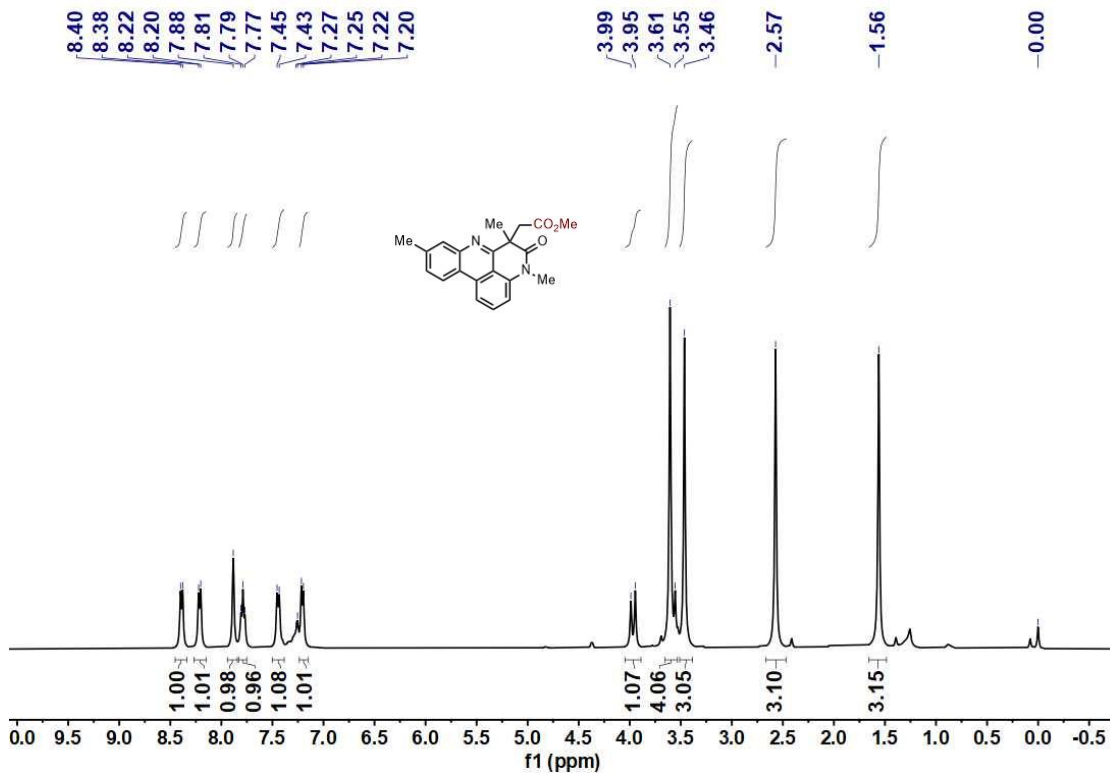
*(S)*-2-(1,3-dioxo-2,3-dihydro-1*H*-inden-2-yl)-3,3-dimethylbutyl 2-(4,6-dimethyl-5-oxo-5,6-dihydro-4*H*-pyrido[4,3,2-*gh*]phenanthridin-6-yl)acetate (**3h**)



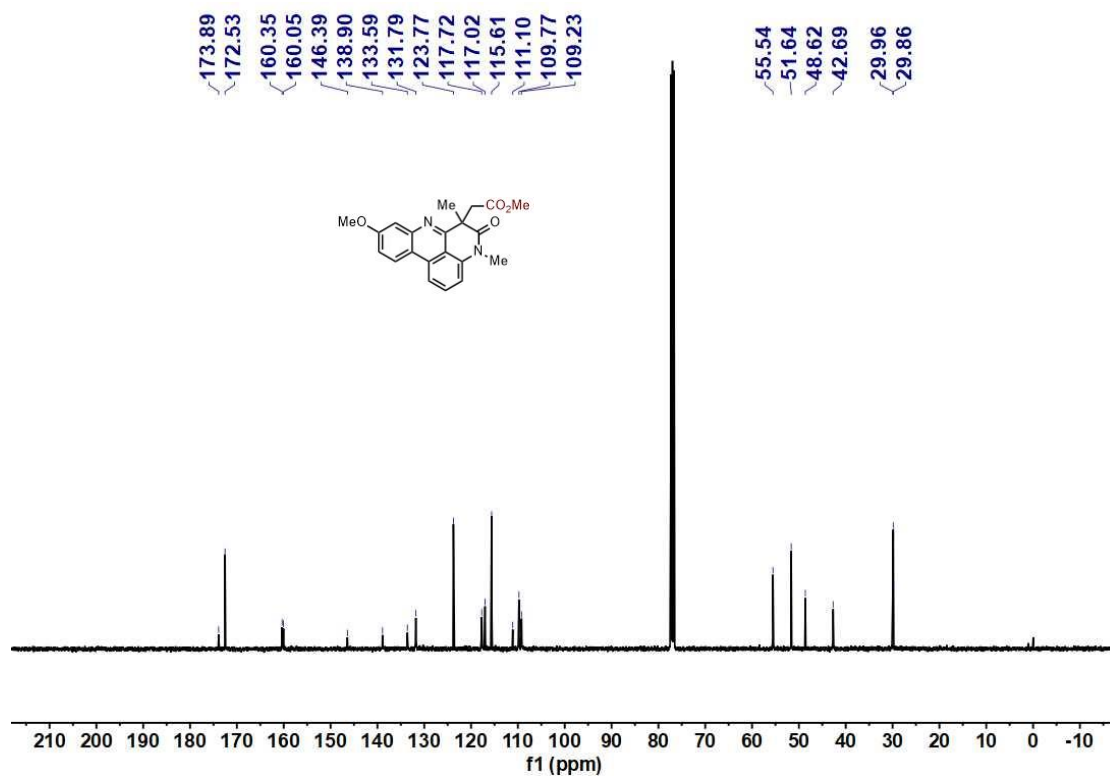
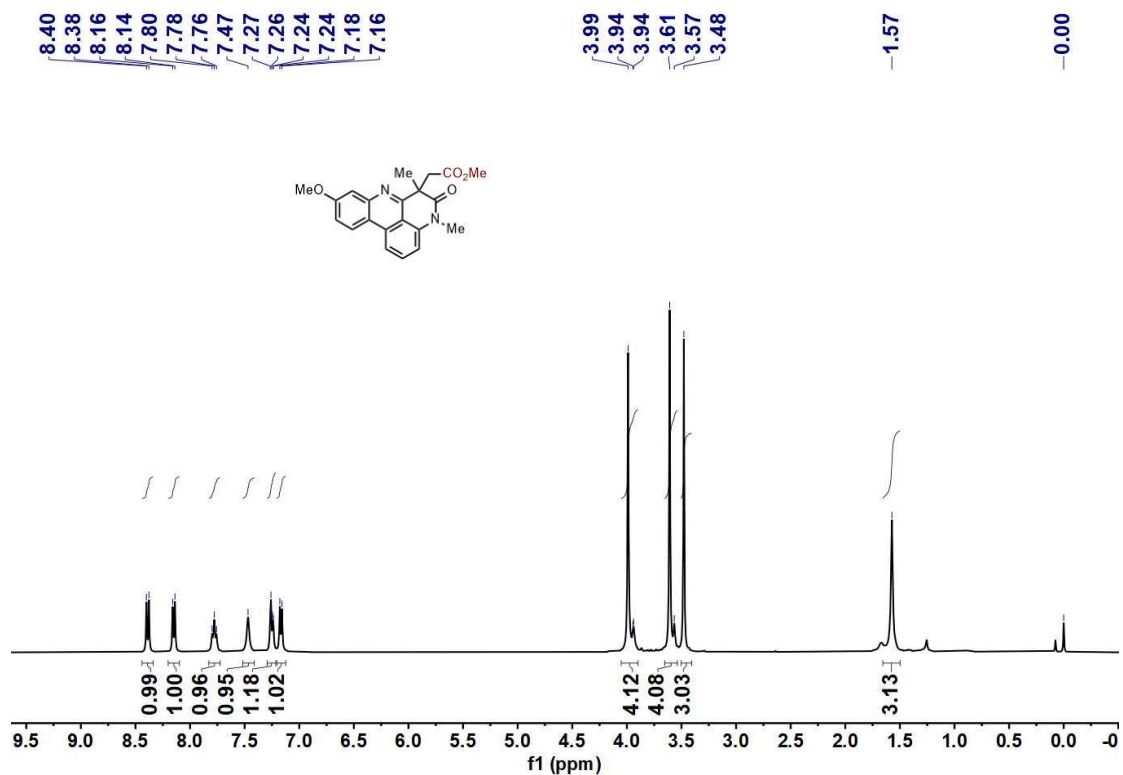
*(3S,8R,9S,10S,13S,14S)*-10,13-dimethyl-17-oxohexadecahydro-1H-cyclopenta[a]phenanthren-3-yl 2-(4,6-dimethyl-5-oxo-5,6-dihydro-4H-pyrido[4,3,2-g]phenanthridin-6-yl)acetate (**3i**)



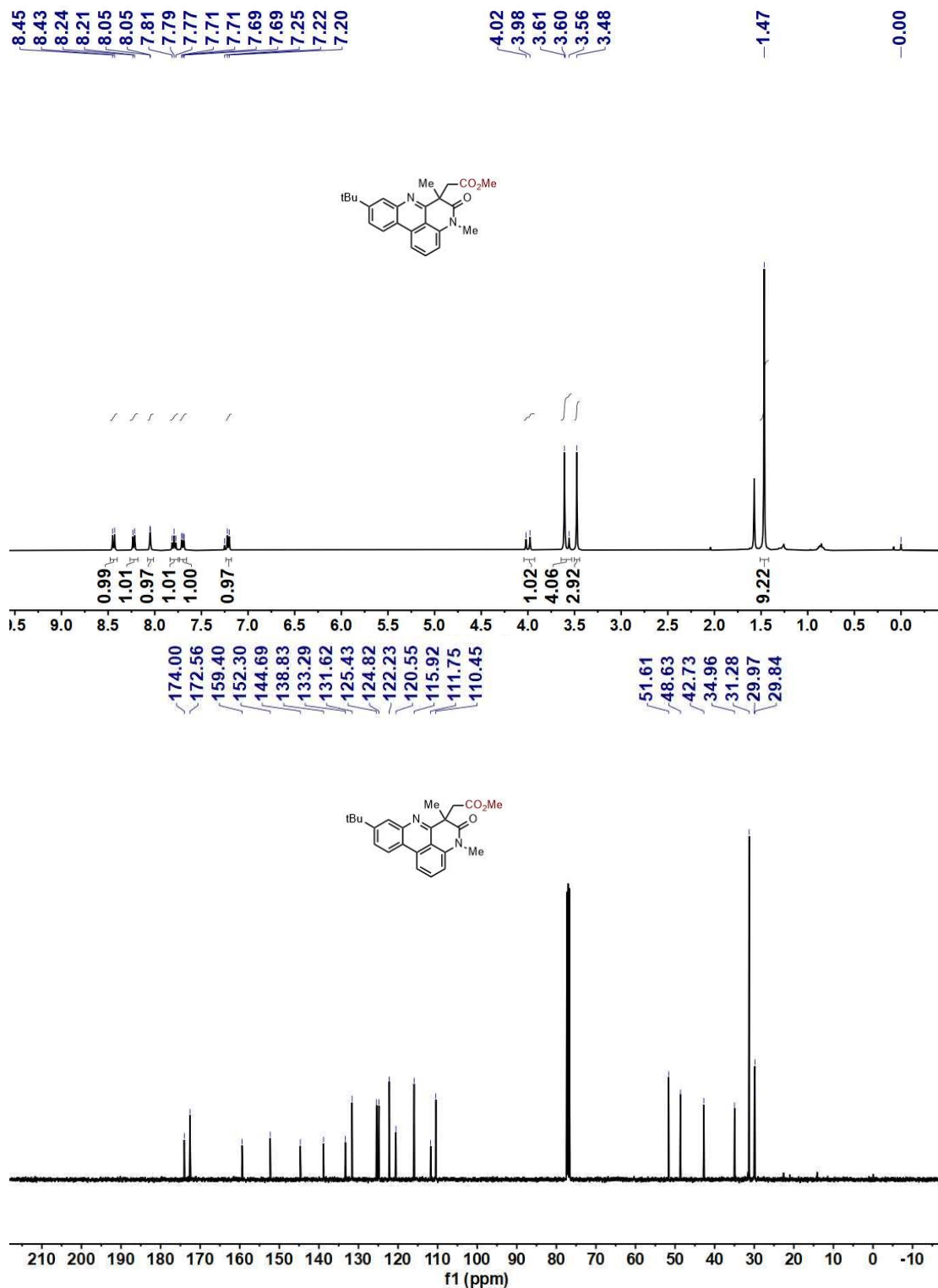
*methyl 2-(4,6,9-trimethyl-5-oxo-5,6-dihydro-4H-pyrido[4,3,2-g]phenanthridin-6-yl)acetate (4a)*



*Methyl 2-(9-methoxy-4,6-dimethyl-5-oxo-5,6-dihydro-4H-pyrido[4,3,2-g]phenanthridin-6-yl)acetate (4b)*

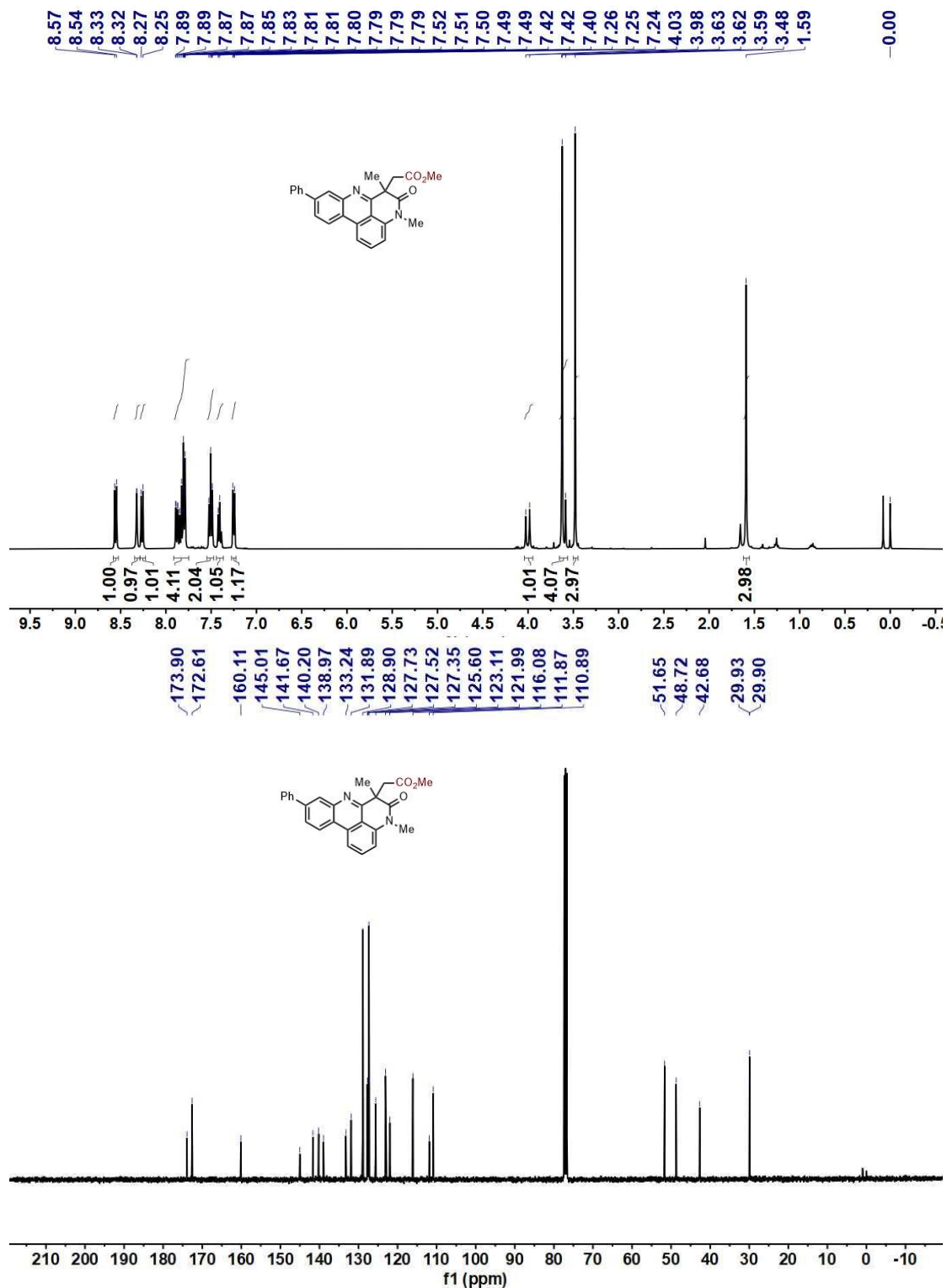


*methyl 2-(9-(tert-butyl)-4,6-dimethyl-5-oxo-5,6-dihydro-4H-pyrido[4,3,2-g]phenanthridin-6-yl)acetate (4c)*

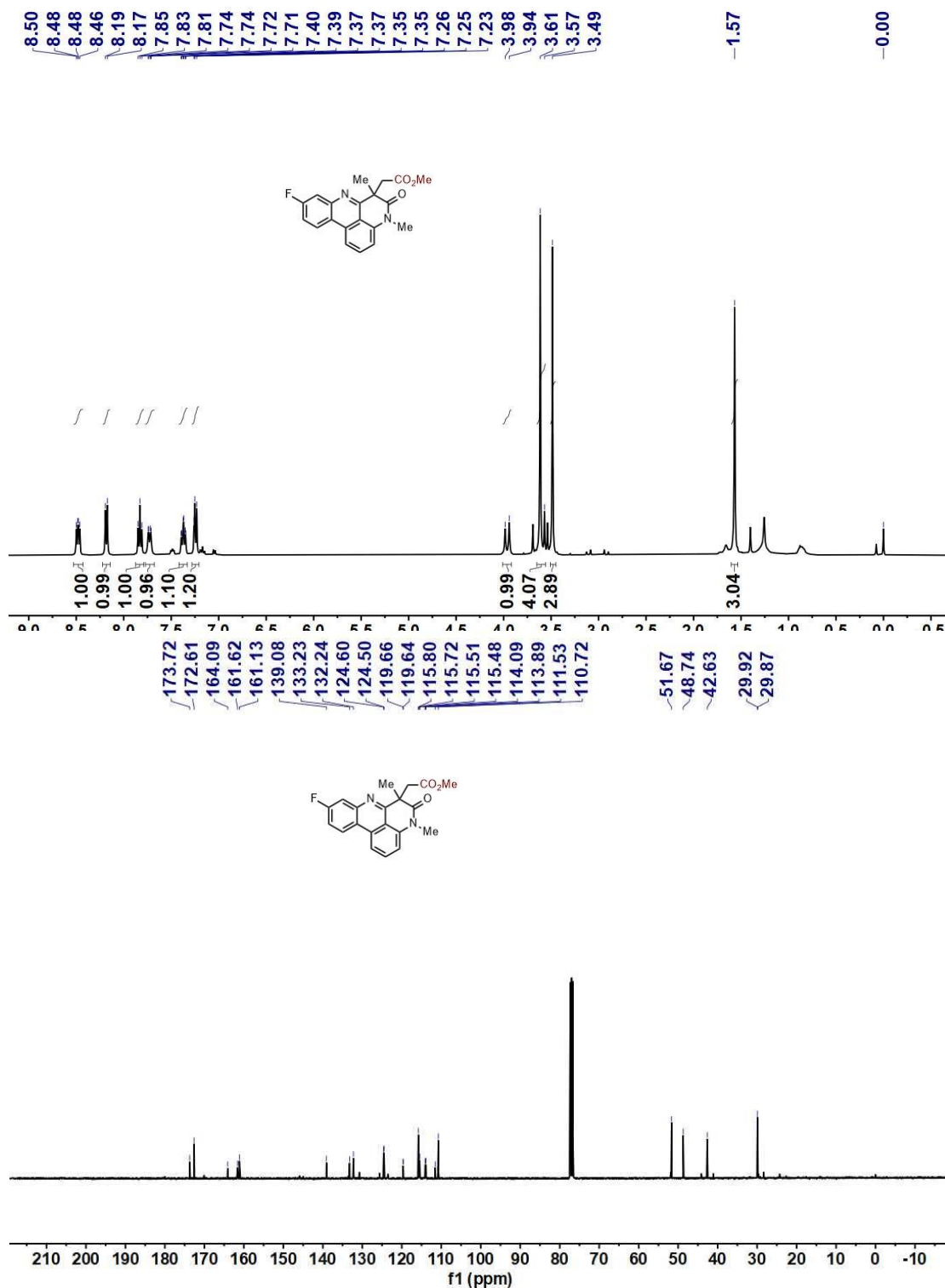




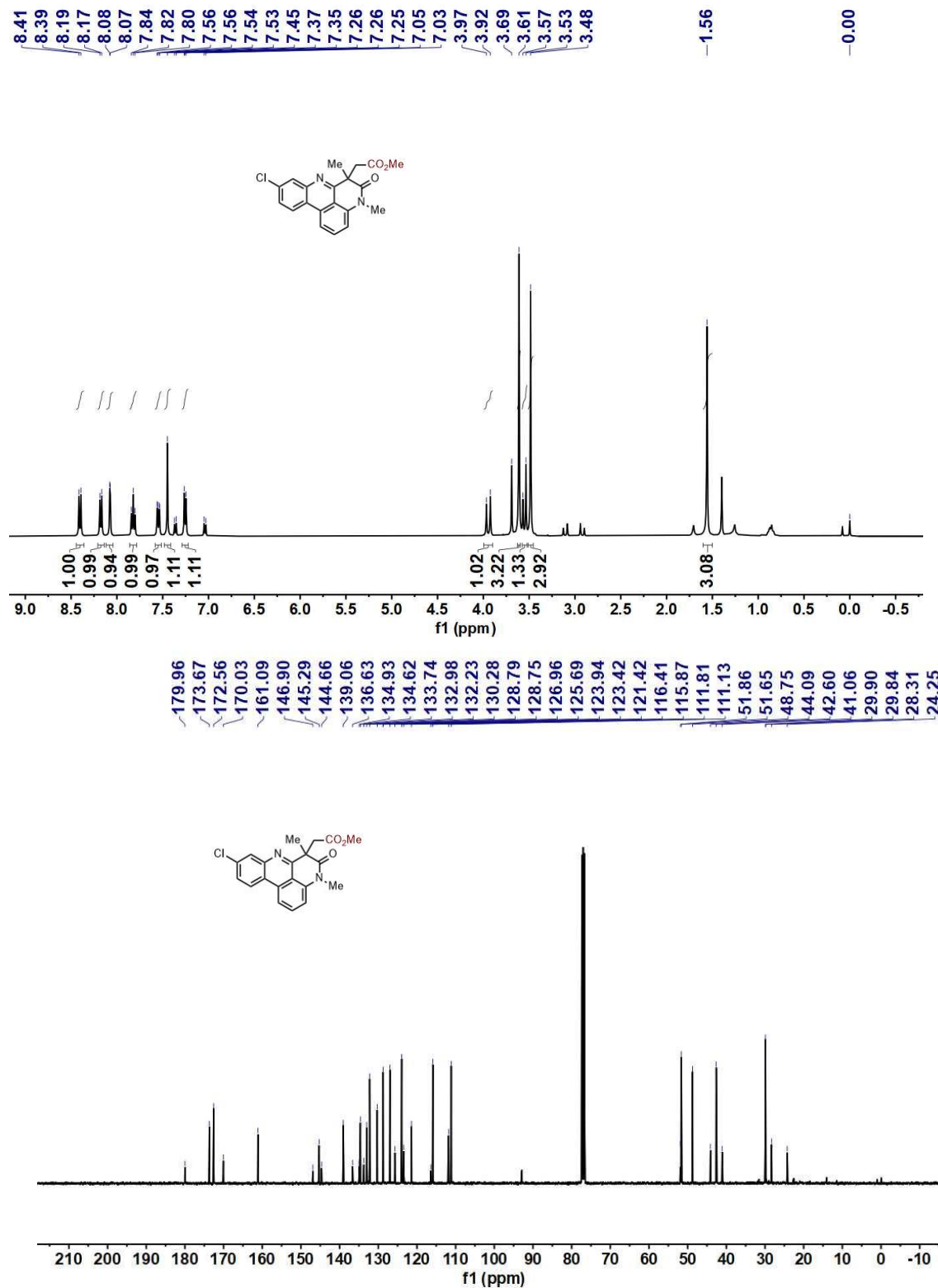
*methyl 2-(4,6-dimethyl-5-oxo-9-phenyl-5,6-dihydro-4H-pyrido[4,3,2-g]phenanthridin-6-yl)acetate (4d)*



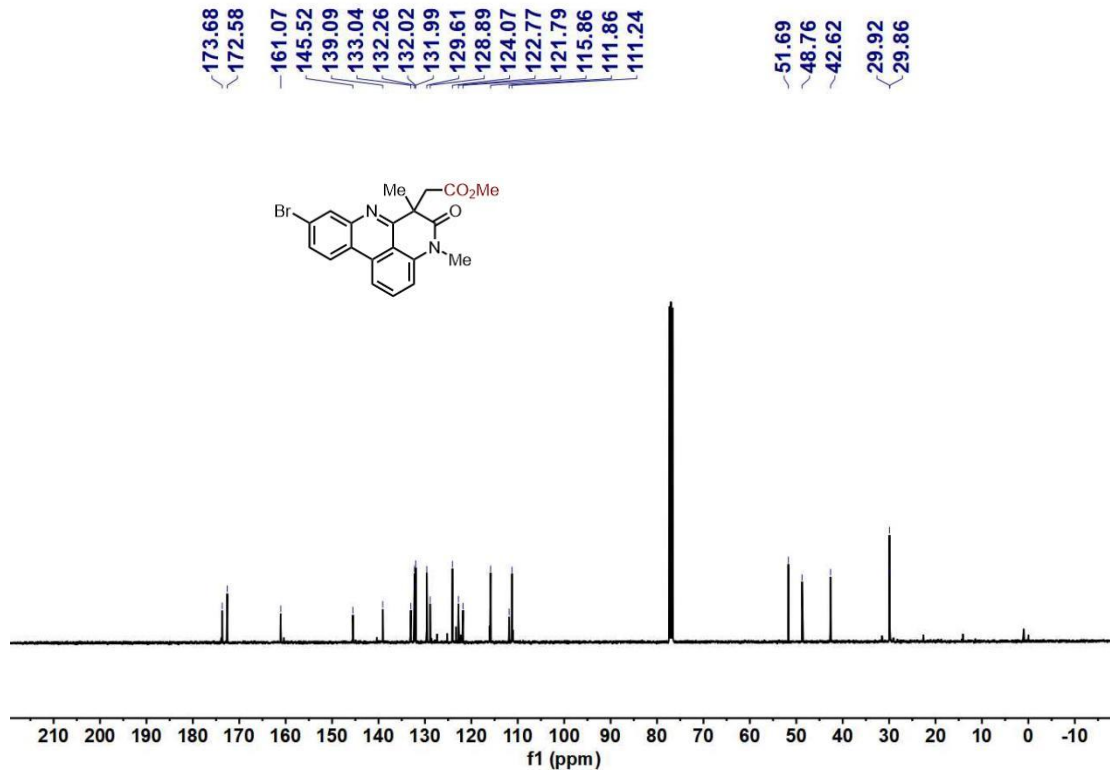
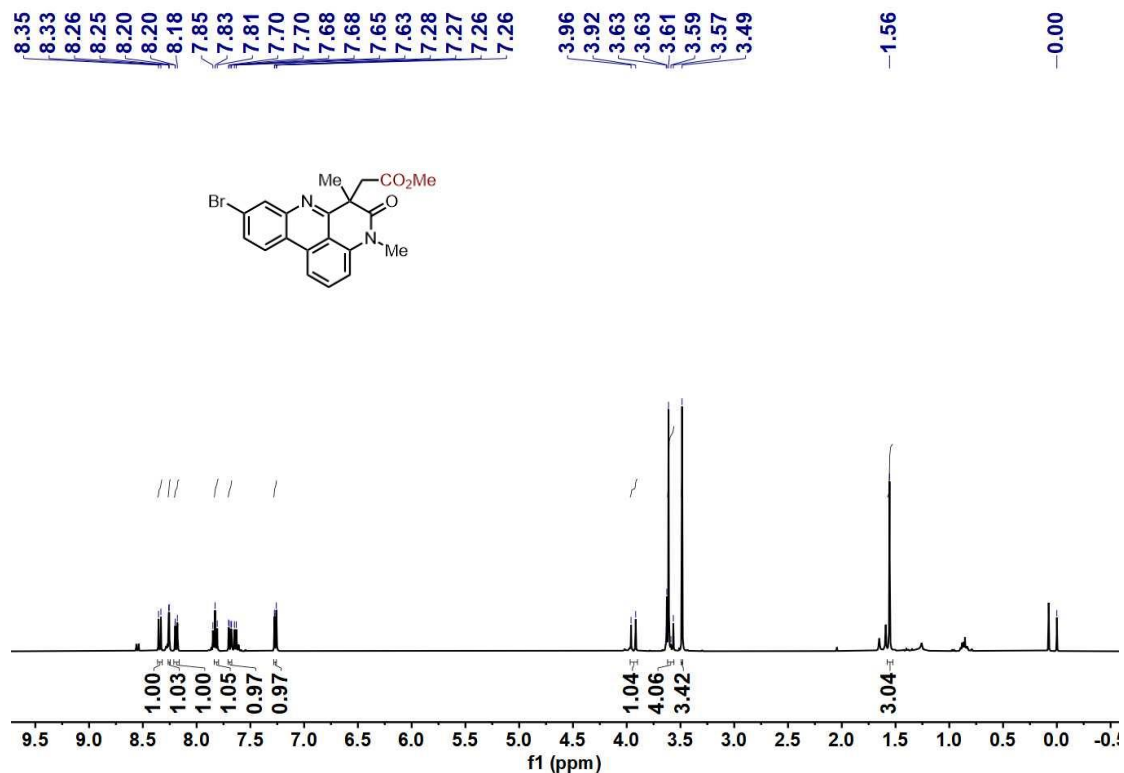
*methyl 2-(9-fluoro-4,6-dimethyl-5-oxo-5,6-dihydro-4H-pyrido[4,3,2-g]phenanthridin-6-yl)acetate (4e)*



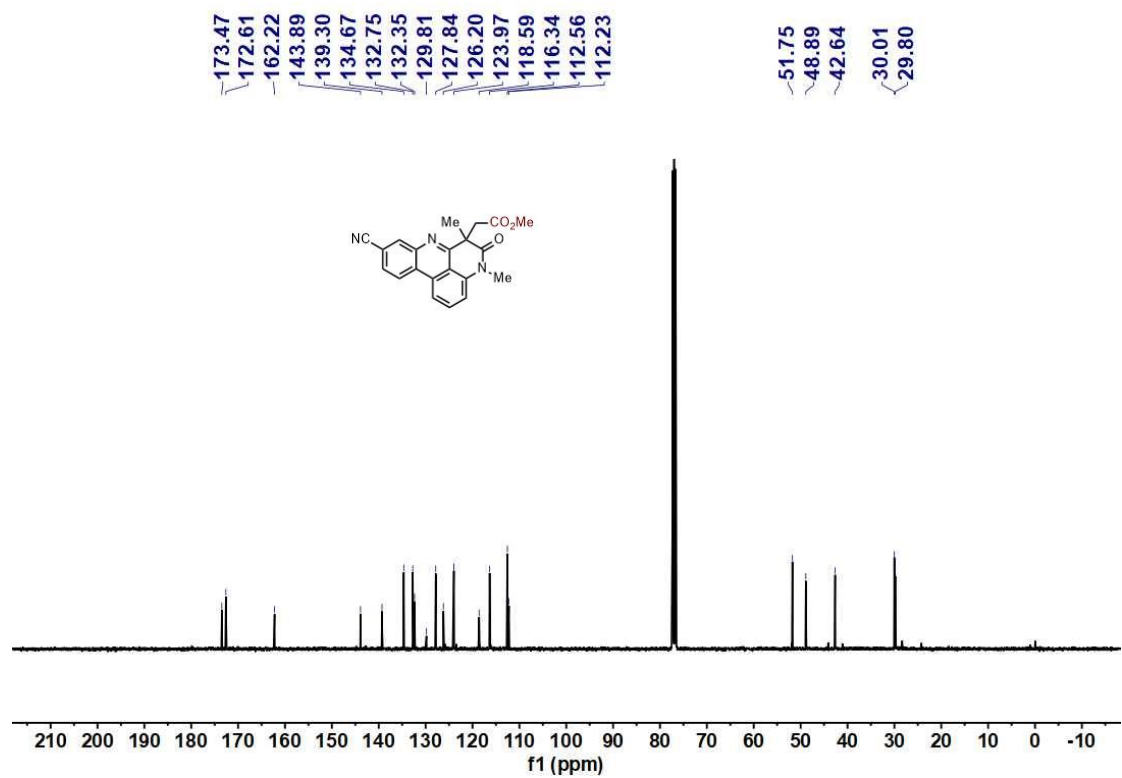
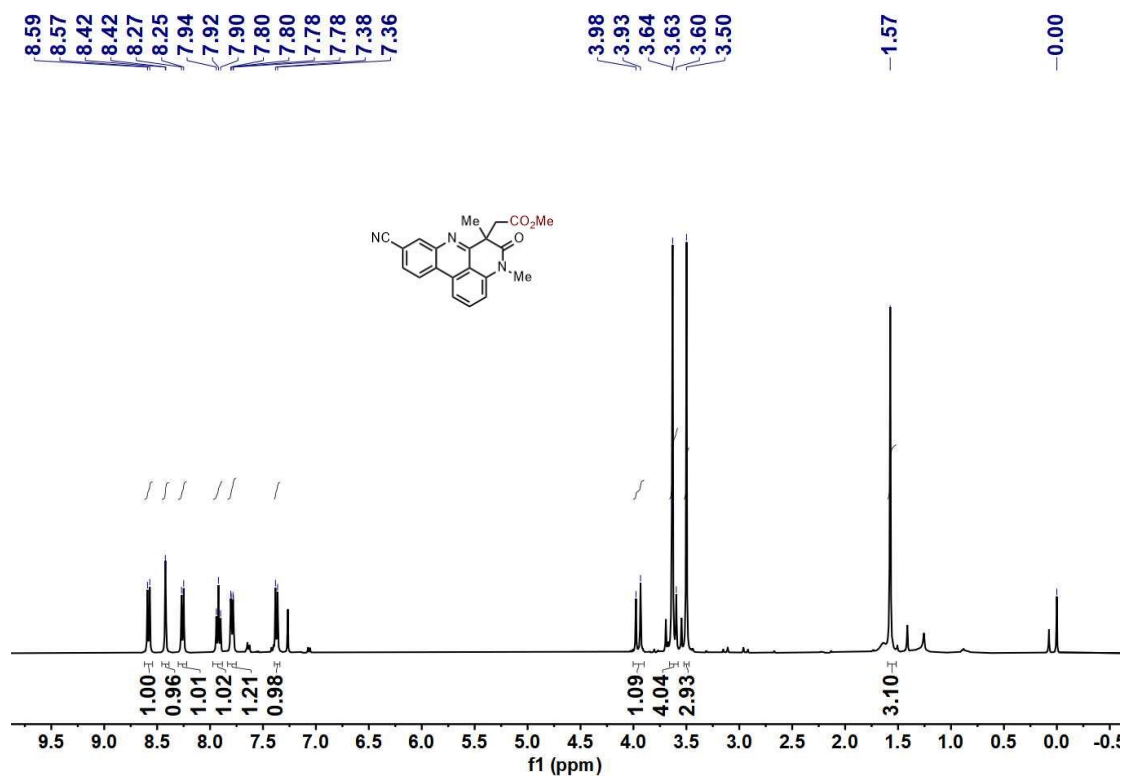
*methyl 2-(9-chloro-4,6-dimethyl-5-oxo-5,6-dihydro-4H-pyrido[4,3,2-g]phenanthridin-6-yl)acetate (4f)*



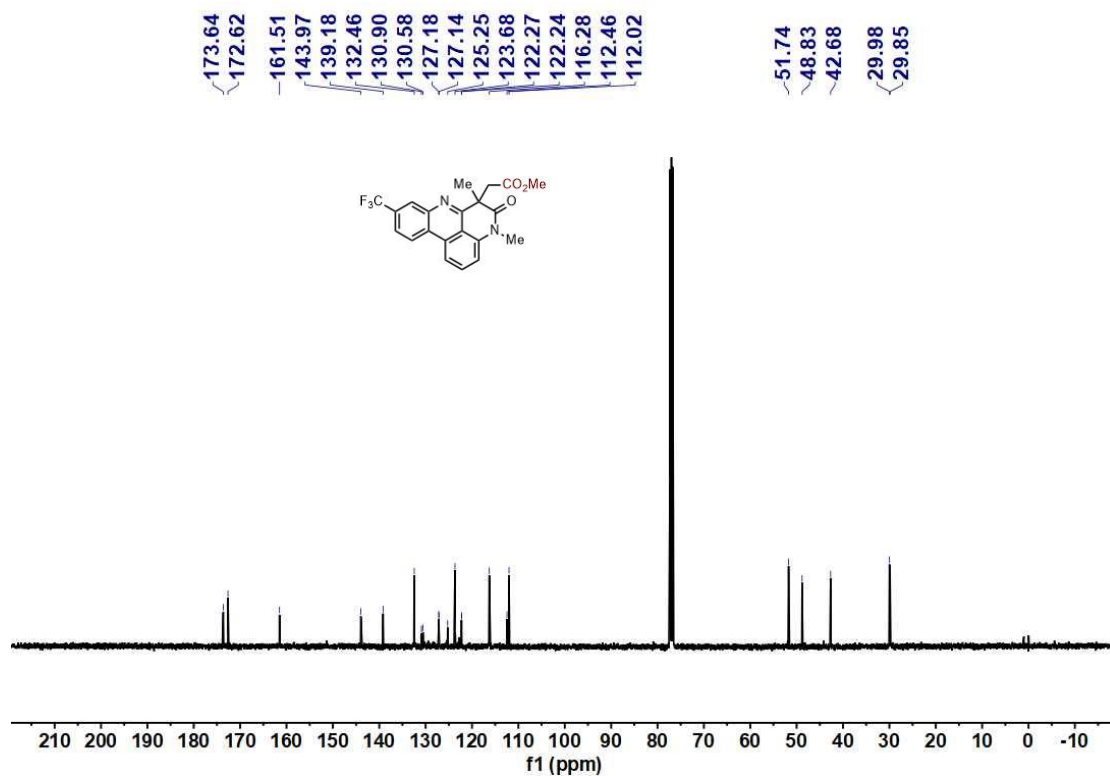
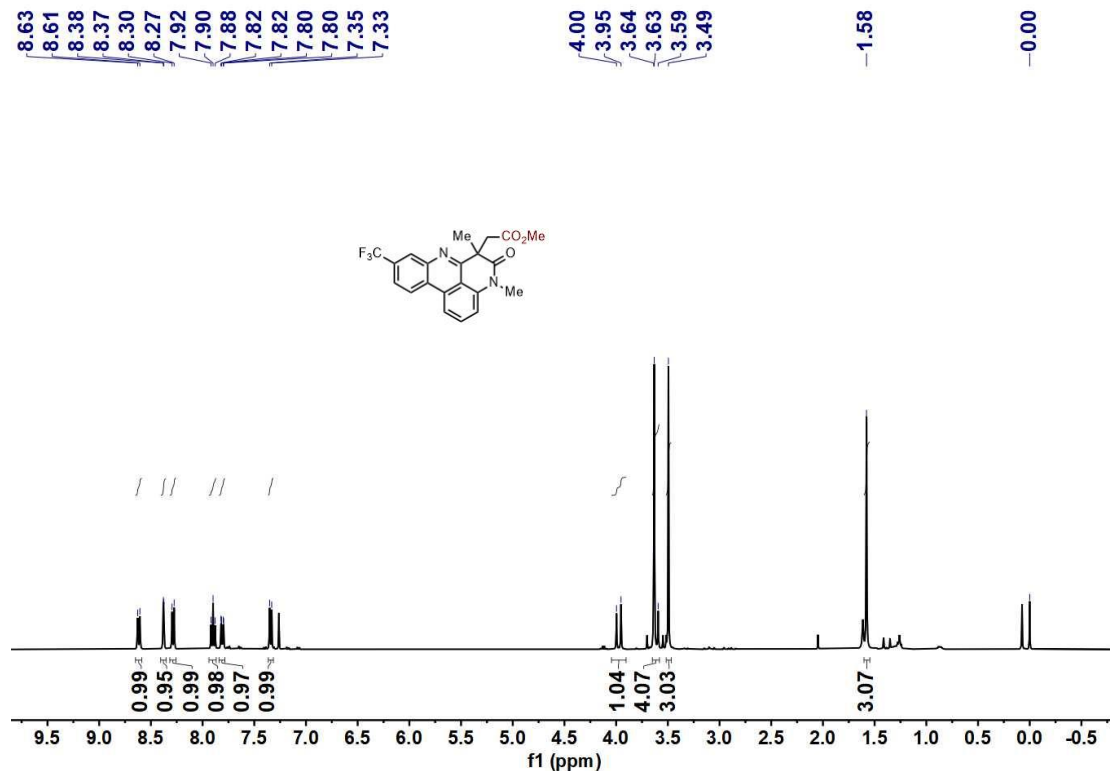
*methyl 2-(9-bromo-4,6-dimethyl-5-oxo-5,6-dihydro-4H-pyrido[4,3,2-g]phenanthridin-6-yl)acetate (4g)*



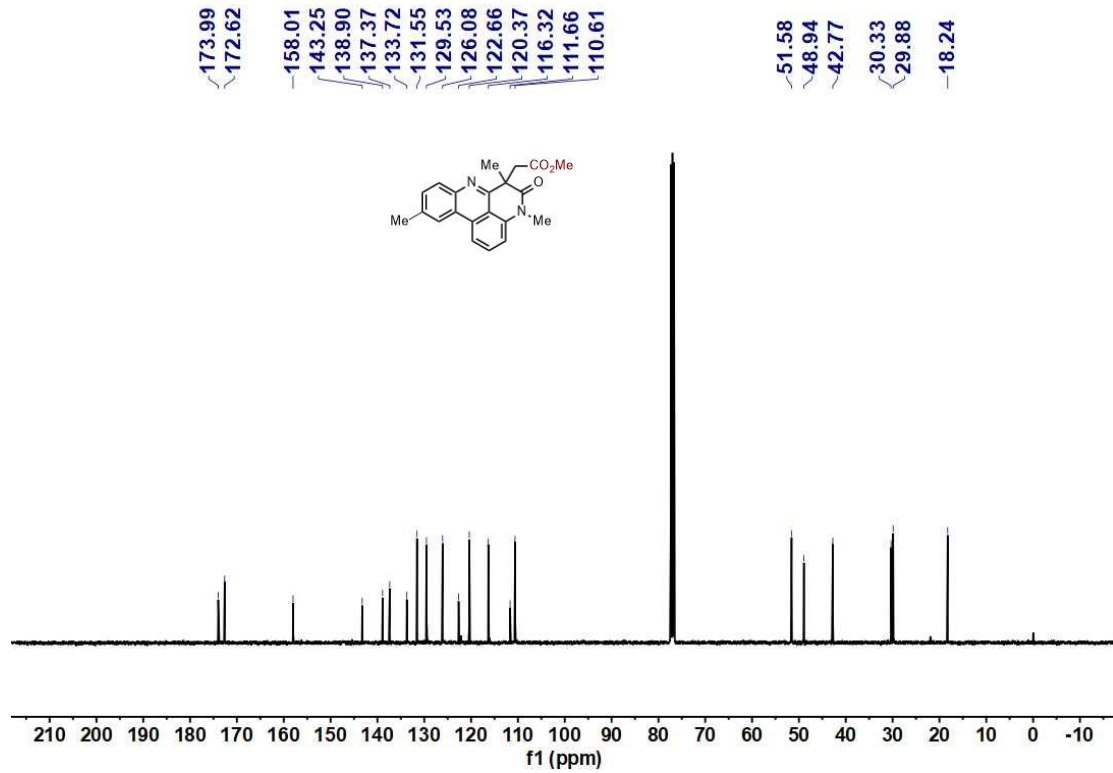
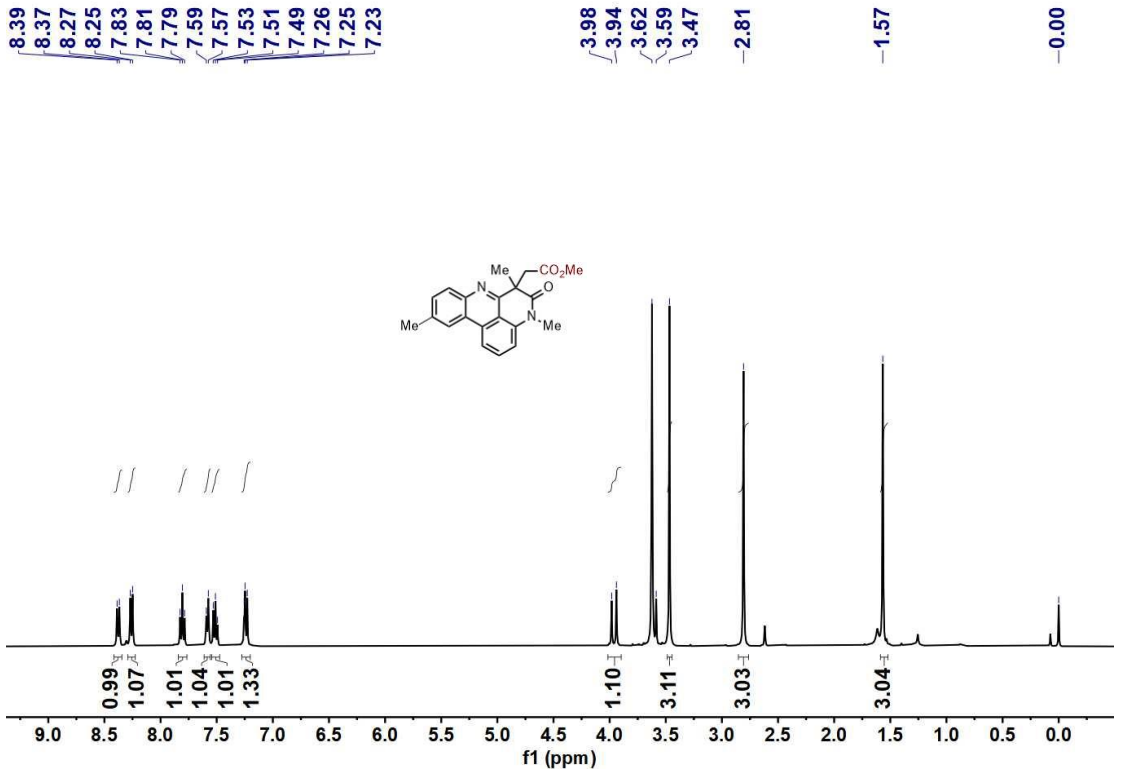
*methyl 2-(9-cyano-4,6-dimethyl-5-oxo-5,6-dihydro-4H-pyrido[4,3,2-g]phenanthri-  
din-6-yl)acetate (4h)*



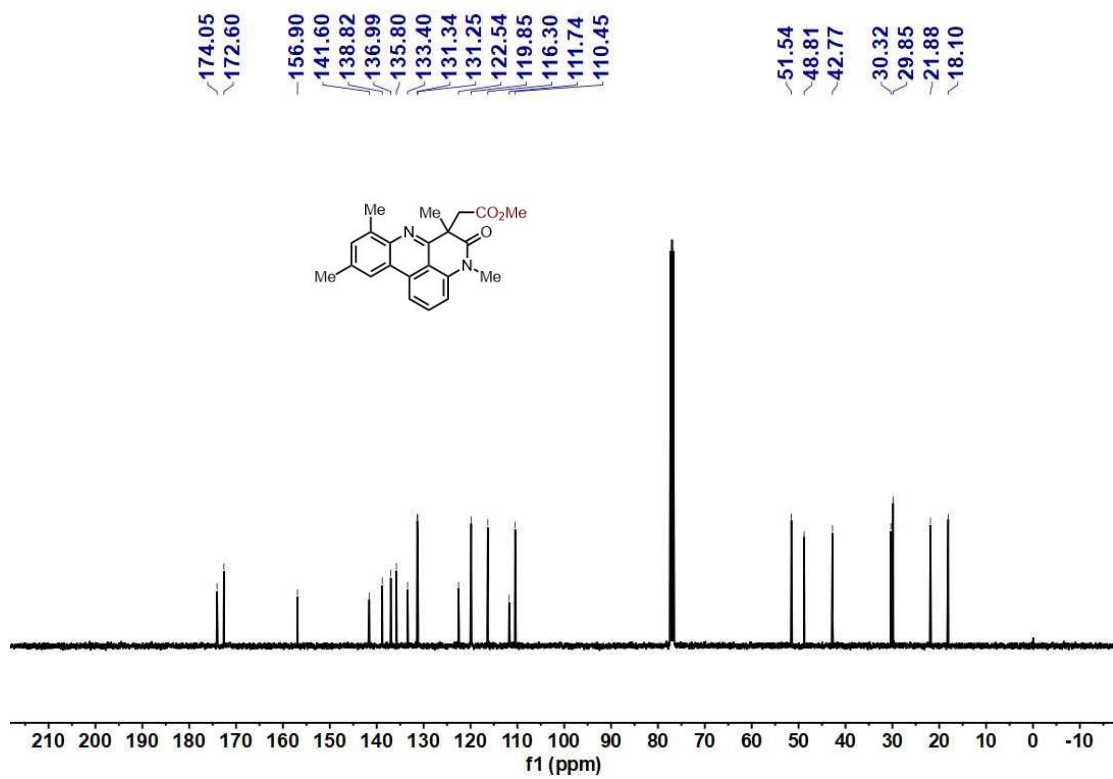
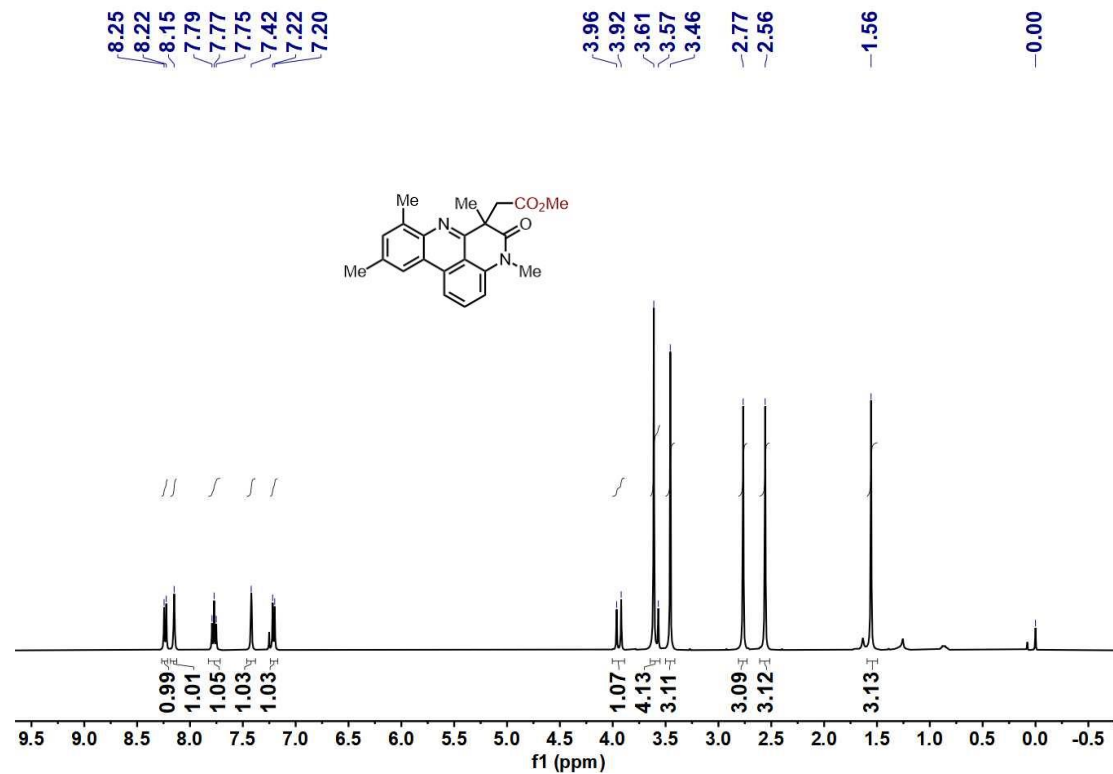
*methyl 2-(4,6-dimethyl-5-oxo-9-(trifluoromethyl)-5,6-dihydro-4H-pyrido[4,3,2-gh]p  
henanthridin-6-yl)acetate (4i)*



*methyl 2-(4,6,10-trimethyl-5-oxo-5,6-dihydro-4H-pyrido[4,3,2-g]phenanthridin-6-yl)acetate (4j)*



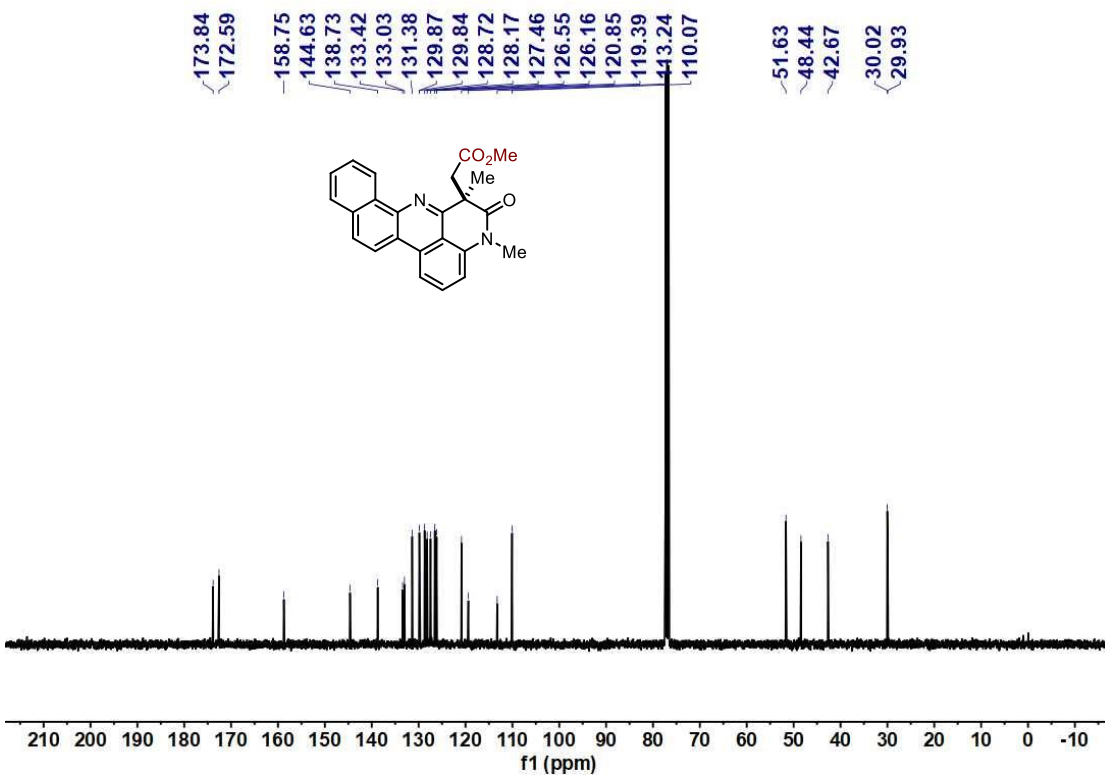
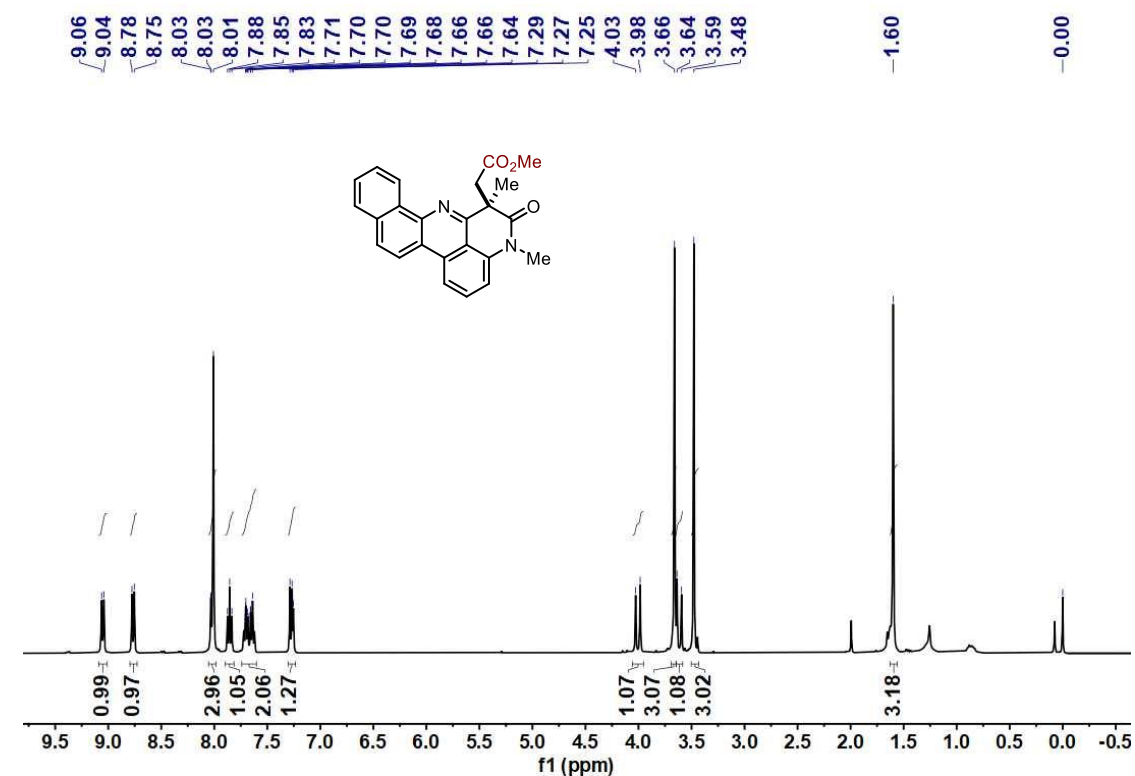
*methyl 2-(4,6,8,10-tetramethyl-5-oxo-5,6-dihydro-4H-pyrido[4,3,2-gh]phenanthridi  
n-6-yl)acetate (4k)*





methyl

2-(4,6-dimethyl-5-oxo-5,6-dihydro-4H-benzo[c]pyrido[4,3,2-gh]phenanthridin-6-yl)acetate (4l)



*methyl 2-(4-ethyl-6-methyl-5-oxo-5,6-dihydro-4H-pyrido[4,3,2-g]phenanthridin-6-yl)acetate (4m)*

