

## A switchable electrosynthesis of furoquinones in batch and continuous-flow

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## 1 General Information

Commercially available reagents and solvents are of reagent grade quality without further purification. Analytical thin-layer chromatography (TLC) is performed on 0.2 mm coated silica gel plates (HSGF 254) and visualized using a UV lamp (254 or 365 nm). Flash column chromatography is performed using silicycle silica gel (200-300 mesh).  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR are recorded on magnet system 400' 54 ascend purchased from Bruker Biospin AG. HRMS (ESI) spectra are recorded on Agilent Q-TOF 6520.

Catalyst- and oxidant-free switchable electrosynthesis of furoquinones was carried out in an undivided cell equipped with a carbon cloth anode and a platinum plate cathode under open air. The carbon cloth, graphite rod ( $\varnothing$  6 mm), platinum plate, Ni plate and Fe plate were purchased from Shanghai Jing Chong Electronic Technology Development Co., Ltd. Reticulated vitreous carbon (RVC) was purchased from Gaoss Union (Tianjin) Photoelectric Technology Co., Ltd. And, electrolysis was conducted under an AXIOMET AX3003P potentiostat in constant current mode. Cyclic voltammogram experiments were investigated using a Metrohm Autolab PGSTAT204 workstation and Nova 2.0 software.

## 2 General material information for batch setup and continuous-flow electrochemical reactor

### 2.1 General material information for batch setup

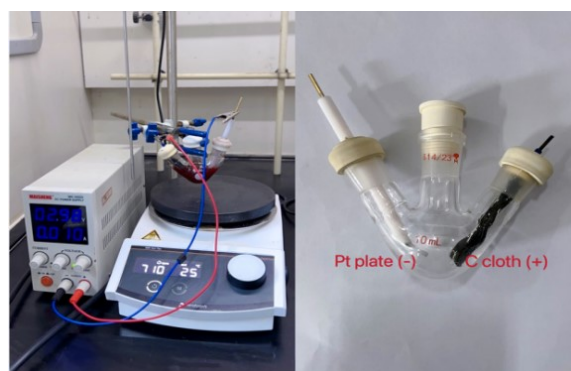


Figure S1 pictures of batch setup

The batch electrolysis setup used is shown in Figure S1.

## 2.2 General material information for continuous-flow electrochemical reactor 1

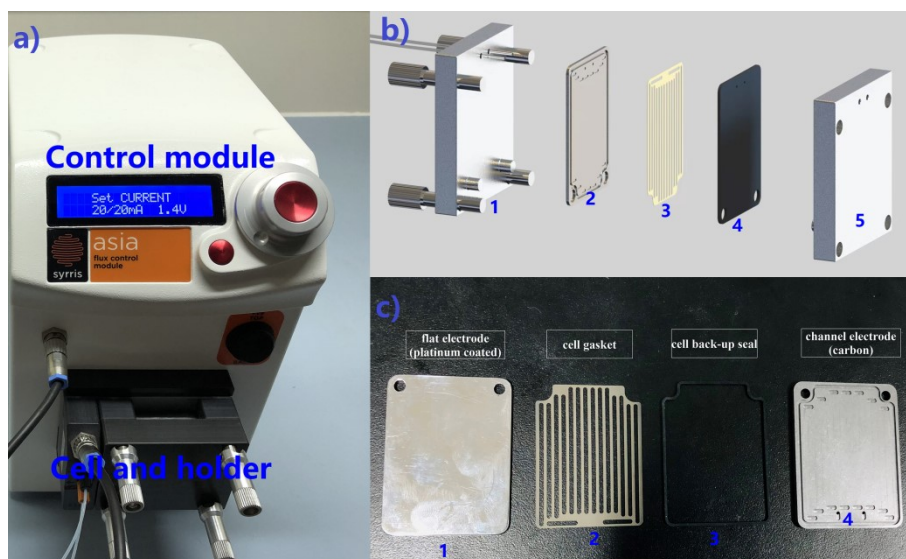


Figure S2 pictures of continuous-flow electrochemical reactor 1

(a) the outside views of control module and cell. (b) the diagram of reactor. 1 and 5: electrode holder; 2: Pt-plated flat electrode ( $5.0 \times 4.0$  cm); 3 channel reactor; 4: C gasket electrode (carbon filled PPS,  $5.0 \times 4.0$  cm). (c) the pictures of the continuous-flow electrochemical setups. 1: Pt-plated flat electrode; 2: cell gasket (channel reactor); 3: cell back-up seal; 4: C gasket electrode.

(b)

The flow electrolysis reactor **1** consists of two stainless steel holders, two flat electrodes and a channel reactor. The C gasket electrode filled with PPS is served as anode ( $5.0 \times 4.0$  cm, Fig. S2). Correspondingly, a Pt-plated flat electrode ( $5.0 \times 4.0$  cm, Fig. S2) is served as cathode. The reaction channel is 0.25 mm thickness and cut with 1.5 mm cell path width and 600 mm cell path length to give the residence volume of 0.225 mL.

## 2.3 General material information for continuous-flow electrochemical reactor 2

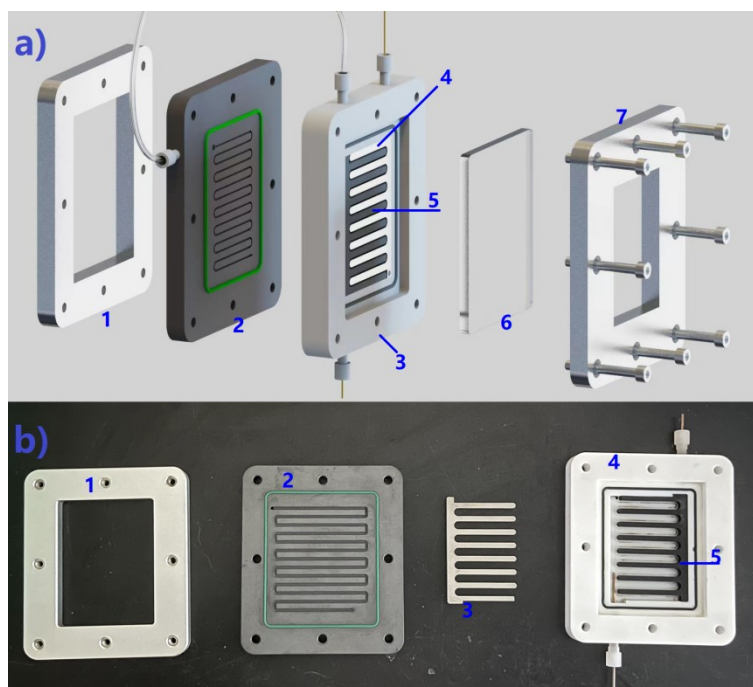


Figure S3 pictures of continuous-flow electrochemical reactor 2

(a) the diagram of reactor. 1 and 7: electrode holder; 2: preheating control module; 3: electrolytic cell; 4: comb-like Pt-plated electrode; 5: comb-like C electrode; 6: silica glass. (b) the pictures of the continuous-flow electrochemical setups. 1: electrode holder; 2: preheating control module; 3: comb-like Pt-plated electrode; 4: electrolytic cell; 5: comb-like C electrode.

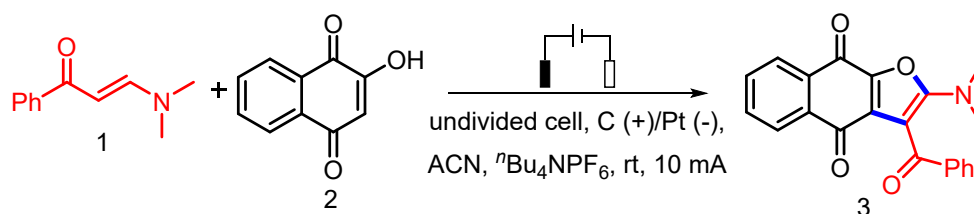
The flow electrolysis reactor 2 is also sandwich structure and consists of two aluminum holders, a preheating control module, an electrolytic cell, two comb-like electrodes and a silica glass (Fig. S3). Two comb-like electrodes interlace together in the electrolytic cell to give the reaction channel with 1 mm electrode distance, 4 mm cell path height, 600 mm cell path length and 2 mL residence volume.



### 3 Reaction optimization of electrochemical cyclization of enaminones and naphoquinones to furoquinones in batch

#### 3.1 Reaction optimization of electrosynthesis of non-deamination furoquinones in batch

Table S1: Optimization of electrosynthesis of non-deamination furoquinone **3** in batch<sup>a</sup>



Entry	Variation from “standard conditions”	Yield <sup>b</sup> (%)
1	none	80
2	<sup>t</sup> Bu <sub>4</sub> NBF <sub>4</sub> , <sup>t</sup> Bu <sub>4</sub> NOAc, <sup>t</sup> Bu <sub>4</sub> NCIO <sub>4</sub> or <sup>t</sup> Bu <sub>4</sub> NI instead of <sup>t</sup> Bu <sub>4</sub> NPF <sub>6</sub>	60, 0, 29, 21
3	DMSO, DMF, HFIP, TFE, EtOH instead of ACN	trace, 15, 30, 35, 20
4	C rod, RVC or Pt as anode	trace, 52, trace
5	Ni or Fe as cathode	69, 0
6	8 mA or 12 mA	50, 54
7	1 eq or 1.5 eq of <sup>t</sup> Bu <sub>4</sub> NPF <sub>6</sub>	40, 55
8	0.03 M, 0.04 M, 0.05 M	72, 63, 50
Control experiments		
9	Under N <sub>2</sub>	75
10	no current	0

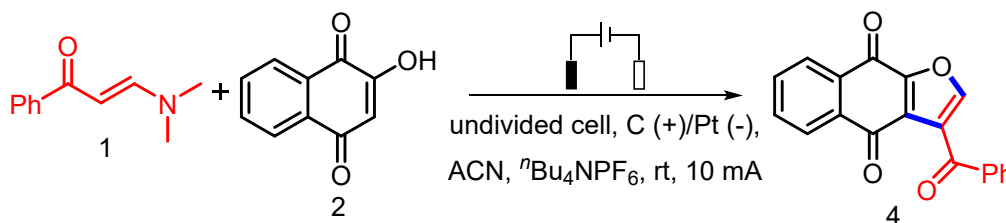
<sup>a</sup>Reaction conditions: enaminone **1** (0.3 mmol, 1.5 eq, 0.03 M, 52.5 mg), 2-hydroxynaphthalene-1,4-dione **2** (0.2 mmol, 1 eq, 0.02 M, 34.8 mg), <sup>t</sup>Bu<sub>4</sub>NPF<sub>6</sub> (0.4

mmol, 0.04 M, 155.0 mg), ACN (10 mL), 10 mA, rt, 2 h, undivided cell, carbon cloth anode (35 mm × 15 mm), platinum plate cathode (10 mm × 10 mm × 0.1 mm).

<sup>b</sup>Yields are determined by high-performance liquid chromatography analysis with **3** as the external standard.

### 3.2 Reaction optimization of electrochemical cyclization of naphoquinones and enaminones to deamination furoquinones

Table S2: Optimization of electrosynthesis of deamination furoquinone **4** in batch<sup>a</sup>

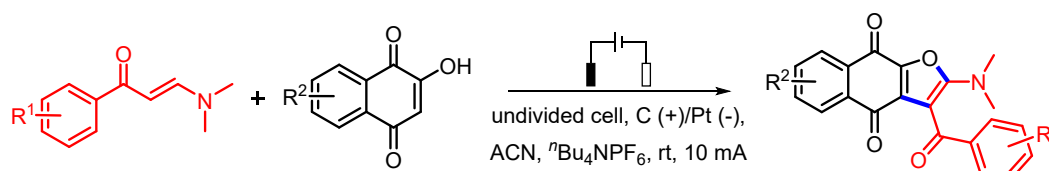


Entry	Electrolyte	Solvent	T (°C)	Additive	Yield <sup>b</sup> (%)
1	<sup>n</sup> Bu <sub>4</sub> NPF <sub>6</sub>	ACN	rt	/	trace
2	<sup>n</sup> Bu <sub>4</sub> NPF <sub>6</sub>	ACN	rt	Y(OTf) <sub>3</sub>	trace
3	<sup>n</sup> Bu <sub>4</sub> NPF <sub>6</sub>	ACN	rt	La(OTf) <sub>3</sub>	15
4	<sup>n</sup> Bu <sub>4</sub> NPF <sub>6</sub>	ACN	rt	In(OTf) <sub>3</sub>	38
5	<sup>n</sup> Bu <sub>4</sub> NPF <sub>6</sub>	ACN	rt	Bi(OTf) <sub>3</sub>	11
6	<sup>n</sup> Bu <sub>4</sub> NPF <sub>6</sub>	ACN	rt	Zn(OTf) <sub>2</sub>	45
7	<sup>n</sup> Bu <sub>4</sub> NPF <sub>6</sub>	ACN	rt	AcOH	14
8	<sup>n</sup> Bu <sub>4</sub> NPF <sub>6</sub>	ACN	rt	TFA	trace

<sup>a</sup>Reaction conditions: **1** (0.3 mmol, 1.5 eq, 0.03 M, 52.5 mg), **2** (0.2 mmol, 1 eq, 0.02 M, 34.8 mg), <sup>n</sup>Bu<sub>4</sub>NPF<sub>6</sub> (0.4 mmol, 0.04 M, 155.0 mg), additive (0.04 mmol, 0.2 eq), ACN (10 mL), 10 mA, rt, 2 h, undivided cell, carbon cloth anode (35 mm × 15 mm), platinum plate cathode (10 mm × 10 mm × 0.1 mm). <sup>b</sup>isolated yield.

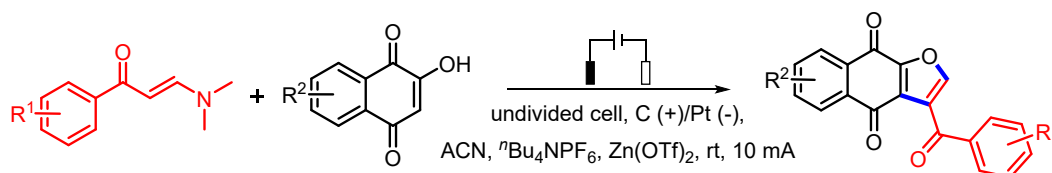
## 4 General Procedure for the electrosynthesis of furoquinones in batch

### 4.1 General Procedure for the electrosynthesis of non-deamination furoquinone in batch



In an undivided cell equipped with a carbon cloth (35 mm x 15 mm) anode and a Pt (10 mm x 10 mm x 0.1 mm) cathode, enaminone (0.3 mmol, 1.5 eq), 2-hydroxynaphthalene-1,4-dione (0.2 mmol, 1 eq), <sup>t</sup>Bu<sub>4</sub>NPF<sub>6</sub> (0.4 mmol, 2 eq, 155.0 mg) were dissolved in ACN (10 mL). The mixture above was stirred and electrolyzed at a constant current of 10 mA for 2 h under the open air. The reaction solution was diluted with ethyl acetate (100 mL) and washed with H<sub>2</sub>O (100 mL). The separated organic layer was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and filtered. The filtrate was concentrated under reduced pressure to give the crude product, which was purified by column chromatographic separation (petroleum ether/ethyl acetate: 4:1) to obtain the desired product.

### 4.2 General Procedure for the electrosynthesis of deamination furoquinone in batch



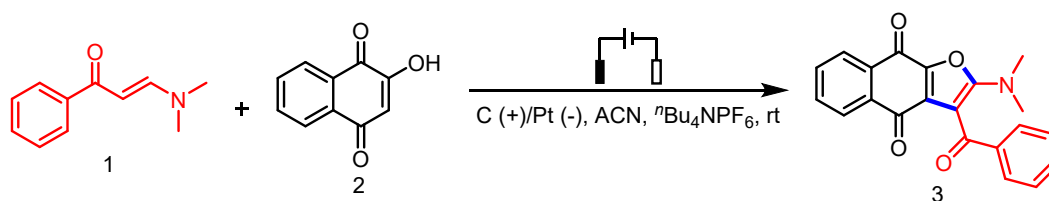
In an undivided cell equipped with a carbon cloth (35 mm x 15 mm) anode and a Pt (10 mm x 10 mm x 0.1 mm) cathode, enaminone (0.3 mmol, 1.5 eq), 2-hydroxynaphthalene-1,4-dione (0.2 mmol, 1 eq), <sup>t</sup>Bu<sub>4</sub>NPF<sub>6</sub> (0.4 mmol, 2 eq, 155.0 mg), Zn(OTf)<sub>2</sub> (0.1 mmol, 0.5 eq, 36.3 mg) were dissolved in ACN (10 mL). The

mixture above was stirred and electrolyzed at a constant current of 10 mA for 1.5-2 h under the open air. The reaction solution was diluted with ethyl acetate (100 mL) and washed with H<sub>2</sub>O (100 mL). The separated organic layer was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and filtered. The filtrate was concentrated under reduced pressure to give the crude product, which was purified by column chromatographic separation (petroleum ether/ethyl acetate: 10:1) to obtain the desired product.

## 5 Scale up investigations in batch and continuous-flow electrochemical reactor

### 5.1 Scale up investigations in batch

Table S3: Scale up investigations in batch<sup>a</sup>

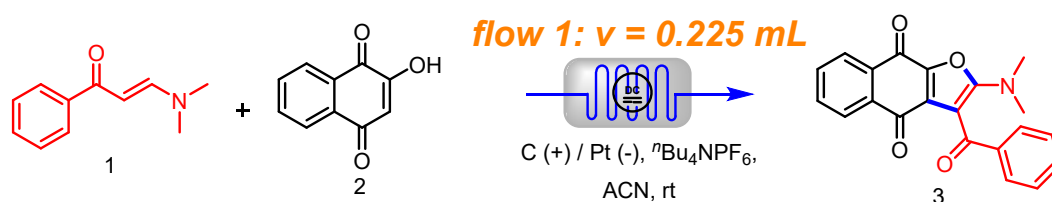


Entry	1 (mmol)	2 (mmol)	Current (mA)	ACN (mL)	T (h)	Yield (%) <sup>b</sup>
1	0.6	0.4	20	20	2.50	60
2	1.2	0.8	40	40	2.75	55
3	1.8	1.2	60	60	3.00	49
4	2.4	1.6	80	80	3.25	46
5	3.0	2.0	100	100	4.00	42
6	1.8	1.2	30	60	4.00	43
7	1.8	1.2	40	60	4.00	44
8	1.8	1.2	50	60	3.00	40

<sup>a</sup>Reaction conditions: **1** (1.5 eq), **2** (1 eq), <sup>n</sup>Bu<sub>4</sub>NPF<sub>6</sub> (2 eq), ACN, rt, undivided cell, carbon cloth anode (35 mm × 15 mm), platinum plate cathode (20 mm × 20 mm × 0.1 mm). <sup>b</sup>Yields are determined by high-performance liquid chromatography analysis with **3** as the external standard.

## 5.2 Scale up investigations continuous-flow electrochemical reactor 1

Table S4: General optimization of electrolysis conditions in continuous-flow electrochemical reactor 1<sup>a</sup>

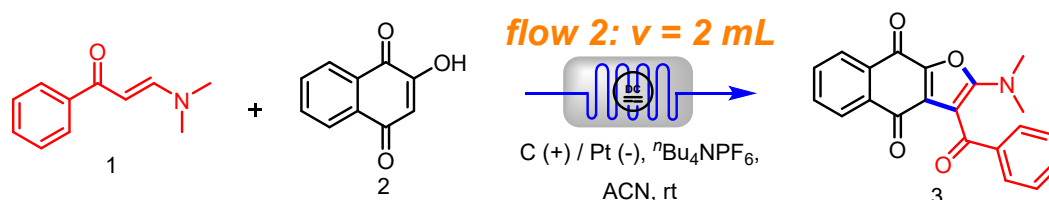


Entry	Current (mA)	Flow rate (mL/min)	Residence time (min)	Concentration (based on 2, M)	Yield <sup>b</sup> (%)
1	10	0.02	11.25	0.02	30
2	10	0.05	4.50	0.02	38
3	10	0.08	2.81	0.02	56
4	10	0.10	2.25	0.02	44
5	15	0.08	2.81	0.02	61
6	20	0.08	2.81	0.02	65
7	25	0.08	2.81	0.02	70
<b>8</b>	<b>25</b>	<b>0.08</b>	<b>2.81</b>	<b>0.03</b>	<b>78</b>

<sup>a</sup>Reaction conditions: **1** (0.3 mmol, 1.5 eq, 53.5 mg), **2** (0.2 mmol, 1 eq, 34.8 mg), <sup>n</sup>Bu<sub>4</sub>NPF<sub>6</sub> (0.4 mmol, 0.04 M, 155.0 mg), ACN (10 mL), C (carbon filled PPS, 5.0 × 4.0 cm) anode, Pt (SS 316L platinum coated, 5.0 × 4.0 cm) cathode, volume (0.225 mL), residence time, current, rt. <sup>b</sup>Yields are determined by high-performance liquid chromatography analysis with **3** as the external standard.

### 5.3 Scale up investigations and continuous-flow electrochemical reactor 2

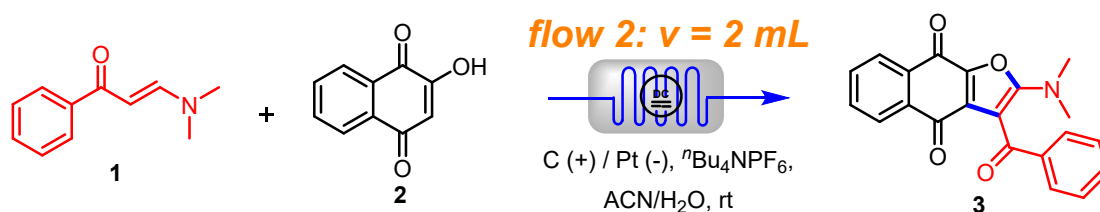
Table S5: General optimization of electrolysis conditions in continuous-flow electrochemical reactor 2<sup>a</sup>



Entry	Voltage (V)	Flow rate (mL/min)	Residence time (min)	Yield <sup>b</sup> (%)
1	1.9	0.2	10.0	19
2	2.1	0.2	10.0	30
3	2.3	0.2	10.0	34
4	2.5	0.2	10.0	36
5	2.7	0.2	10.0	38
6	2.9	0.2	10.0	37
7	2.1	0.16	12.5	50
8	2.1	0.12	16.7	52
9	2.1	0.10	20.0	43
10 <sup>c</sup>	2.1	0.16	12.5+12.5	67
<b>11<sup>c,d</sup></b>	<b>2.1</b>	<b>0.16</b>	<b>12.5+12.5</b>	<b>75</b>

<sup>a</sup>Reaction conditions: **1** (0.45 mmol, 1.5 eq, 67.5 mg), **2** (0.3 mmol, 1 eq, 52.2 mg), <sup>n</sup>Bu<sub>4</sub>NPF<sub>6</sub> (0.4 mmol, 0.04 M, 155.0 mg), ACN (10 mL), C (carbon) anode, Pt (SS 316L platinum coated) cathode, volume (2 mL), residence time, current, rt. <sup>b</sup>Yields are determined by high-performance liquid chromatography analysis with **3** as the external standard. <sup>c</sup>two continuous-flow electrochemical reactors in series. <sup>d</sup>2 eq **1** involved.

Table S6: General optimization of electrolysis conditions in continuous-flow electrochemical reactor 2 in the presence of H<sub>2</sub>O<sup>a</sup>



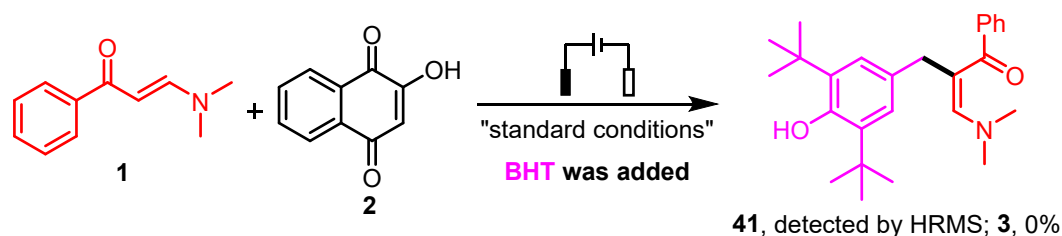
Entry	Voltage (V)	Flow rate (mL/min)	Residence time (min)	Yield <sup>b</sup> (%)
1	2.3	0.2	10	49
2	2.5	0.2	10	67
3	2.7	0.2	10	40
4	2.5	0.15	13.3	32
5	2.5	0.25	8	50
6	2.5	0.33	6	44
7	2.5	0.5	4	36
<b>8<sup>c</sup></b>	<b>2.5</b>	<b>0.2</b>	<b>10*2</b>	<b>76</b>
<b>9<sup>c</sup></b>	<b>2.5</b>	<b>0.25</b>	<b>8*2</b>	<b>75</b>
10 <sup>c</sup>	2.5	0.33	6*2	64
11 <sup>d,e</sup>	<b>2.5</b>	<b>0.2</b>	<b>10*3</b>	<b>73</b>

<sup>a</sup>Reaction conditions: **1** (0.45 mmol, 1.5 eq, 0.045 M, 67.5 mg), **2** (0.3 mmol, 0.03 M, 1 eq, 52.2 mg), <sup>t</sup>Bu<sub>4</sub>NPF<sub>6</sub> (0.4 mmol, 0.04 M, 155.0 mg), ACN/H<sub>2</sub>O (9.8 mL/0.2 mL), C anode, Pt (SS 316L platinum coated) cathode, volume (2 mL), residence time, current, rt. <sup>b</sup>Yields are determined by high-performance liquid chromatography analysis with **3** as the external standard. <sup>c</sup>Two continuous-flow electrochemical reactors in series. <sup>d</sup>Three continuous-flow electrochemical reactors in series. <sup>e</sup>**1** (0.9 mmol, 1.5 eq, 0.09 M, 135 mg), **2** (0.6 mmol, 0.06 M, 1 eq, 104.4 mg).

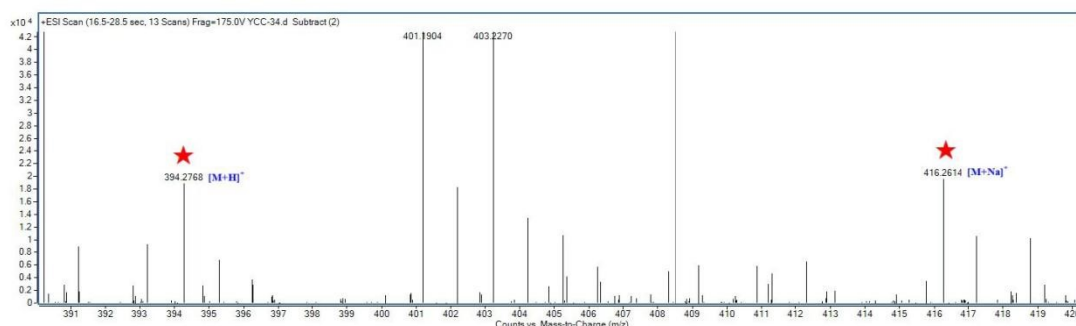
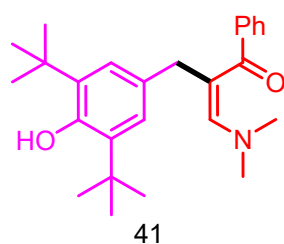
## 6 Mechanistic Studies

### 6.1 Radical-trapping experiments:

#### 6.1.1 BHT was added



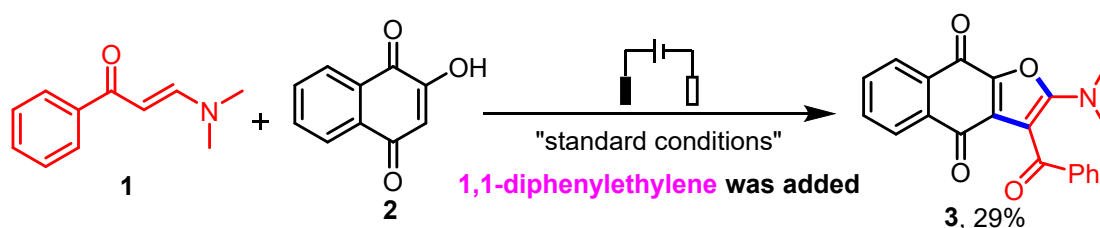
In an undivided cell equipped with a carbon cloth (35 mm x 15 mm) anode and a Pt (10 mm x 10 mm x 0.1 mm) cathode, 3-(dimethylamino)-1-phenylprop-2-en-1-one **1** (0.3 mmol, 1.5 eq, 52.5 mg), 2-hydroxynaphthalene-1,4-dione **2** (0.2 mmol, 1 eq, 34.8 mg),  $n\text{-Bu}_4\text{NPF}_6$  (0.4 mmol, 2 eq, 155.0 mg) and BHT (0.6 mmol, 3 eq, 132.2 mg) were dissolved in a solvent of ACN (10 mL). The mixture above was stirred and electrolyzed at a constant current of 10 mA for 2h under the open air. No desired product was detected. Moreover, the corresponding radical trapping product **41** was detected by HRMS.





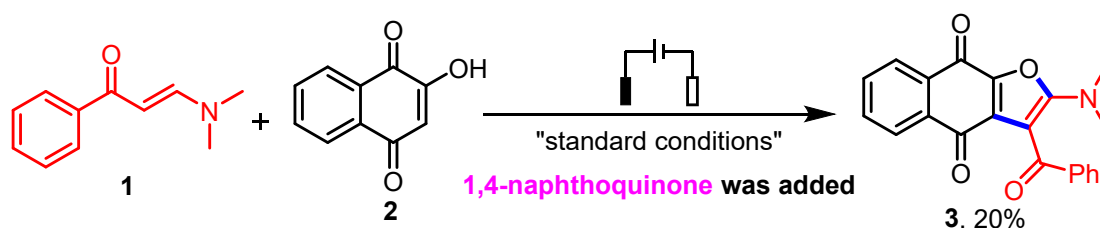
2-(3,5-di-*tert*-butyl-4-hydroxybenzyl)-3-(dimethylamino)-1-phenylprop-2-en-1-one  
(**41**): HRMS (ESI-TOF) Calcd for (C<sub>26</sub>H<sub>36</sub>O<sub>2</sub>N [M+H]<sup>+</sup>: 394.2741; found: 394.2768.  
Fig. S4; C<sub>26</sub>H<sub>35</sub>NO<sub>2</sub>Na [M+Na]<sup>+</sup>: 416.2560; found: 416.2614. Fig. S4).

### 6.1.2 1,1-diphenylethylene was added



In an undivided cell equipped with a carbon cloth (35 mm x 15 mm) anode and a Pt (10 mm x 10 mm x 0.1 mm) cathode, 3-(dimethylamino)-1-phenylprop-2-en-1-one **1** (0.3 mmol, 1.5 eq, 52.5 mg), 2-hydroxynaphthalene-1,4-dione **2** (0.2 mmol, 1 eq, 34.8 mg), <sup>n</sup>Bu<sub>4</sub>NPF<sub>6</sub> (0.4 mmol, 2 eq, 155.0 mg) and 1,1-diphenylethylene (0.6 mmol, 3 eq, 108.0 mg) were dissolved in a solvent of ACN (10 mL). The mixture above was stirred and electrolyzed at a constant current of 10 mA for 2h under the open air. The yield was determined by high-performance liquid chromatography analysis with **3** as the external standard.

### 6.1.3 1,4-naphthoquinone was added

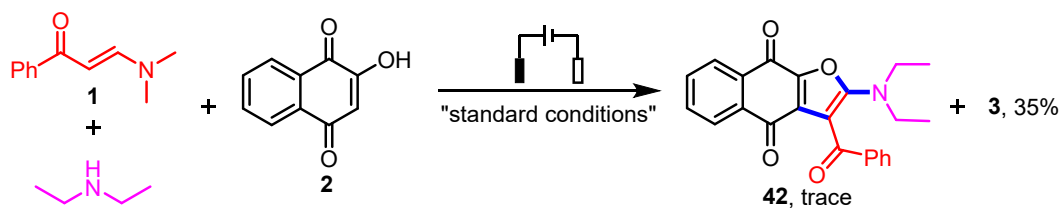


In an undivided cell equipped with a carbon cloth (35 mm x 15 mm) anode and a Pt (10 mm x 10 mm x 0.1 mm) cathode, 3-(dimethylamino)-1-phenylprop-2-en-1-one **1** (0.3 mmol, 1.5 eq, 52.5 mg), 2-hydroxynaphthalene-1,4-dione **2** (0.2 mmol, 1 eq, 34.8 mg), <sup>n</sup>Bu<sub>4</sub>NPF<sub>6</sub> (0.4 mmol, 2 eq, 155.0 mg) and 1,4-naphthoquinone (0.6 mmol, 3 eq, 94.8 mg) were dissolved in a solvent of ACN (10 mL). The mixture above was stirred and electrolyzed at a constant current of 10 mA for 2h under the open air. The

yield was determined by high-performance liquid chromatography analysis with **3** as the external standard.

## 6.2 Verification experiments of intermediates:

### 6.2.1 Diethylamine was applied



In an undivided cell equipped with a carbon cloth (35 mm x 15 mm) anode and a Pt (20 mm x 20 mm x 0.1 mm) cathode, 3-(dimethylamino)-1-phenylprop-2-en-1-one **1** (0.3 mmol, 1.5 eq, 52.5 mg), 2-hydroxynaphthalene-1,4-dione **2** (0.2 mmol, 1 eq, 34.8 mg), diethylamine (0.6 mmol, 3 eq, 43.9 mg) and  $n\text{Bu}_4\text{NPF}_6$  (0.4 mmol, 2 eq, 155.0 mg) were dissolved in ACN (10 mL). The mixture above was stirred and electrolyzed a constant current of 10 mA for 2h under the open air. 35% target product was obtained. Moreover, only a trace amount of the corresponding deamination and transamination product **42** was detected.

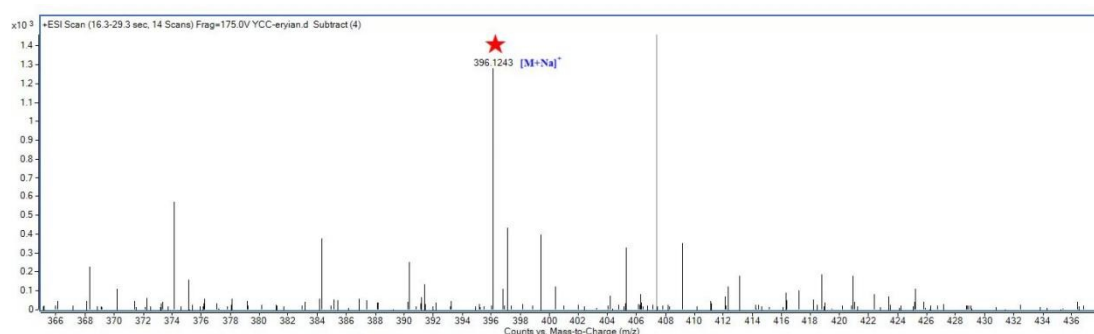
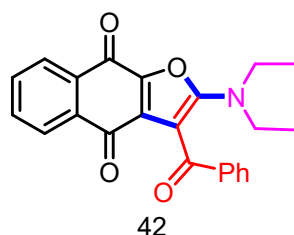
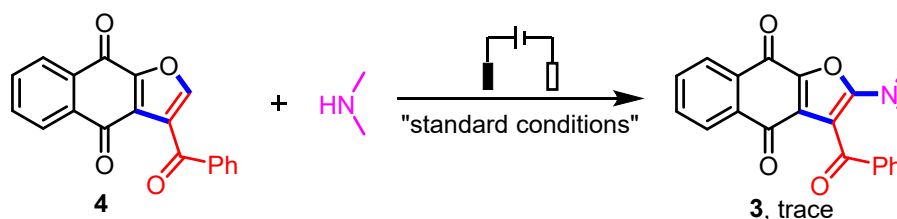


Figure S5: HRMS (ESI) analysis of radical-trapping intermediate



3-benzoyl-2-(diethylamino)naphtho[2,3-*b*]furan-4,9-dione (**42**): HRMS (ESI-TOF)  
Calcd for (C<sub>23</sub>H<sub>19</sub>NO<sub>4</sub>Na [M+Na]<sup>+</sup>: 396.1206; found: 396.1243. Fig. S5).

6.2.2 3-benzoylnaphtho[2,3-*b*]furan-4,9-dione **4** was used as starting material



In an undivided cell equipped with a carbon cloth (35 mm x 15 mm) anode and a Pt (20 mm x 20 mm x 0.1 mm) cathode, 3-benzoylnaphtho[2,3-*b*]furan-4,9-dione **4** (0.2 mmol, 1 eq, 60.4 mg), dimethylamine (0.6 mmol, 3 eq, 27.0 mg), <sup>n</sup>Bu<sub>4</sub>NPF<sub>6</sub> (0.4 mmol, 2 eq, 155.0 mg) were dissolved in ACN (10 mL). The mixture above was stirred and electrolyzed a constant current of 10 mA for 2h under the open air. Only a trace amounts of **3** was detected.

### 6.3 Cyclic voltammetry experiments

The undivided cell was equipped with glassy-carbon disk working electrode (diameter, 3.0 mm) and Pt wire auxiliary electrode. The Ag/AgCl was used as reference electrode. The scan range was 0.0 V to 2.5 V. The scan rate was 100 mVs<sup>-1</sup>. ACN (10 mL) containing <sup>n</sup>Bu<sub>4</sub>NPF<sub>6</sub> (0.4 mmol, 155.0 mg) was poured into the electrochemical cell in all experiments.

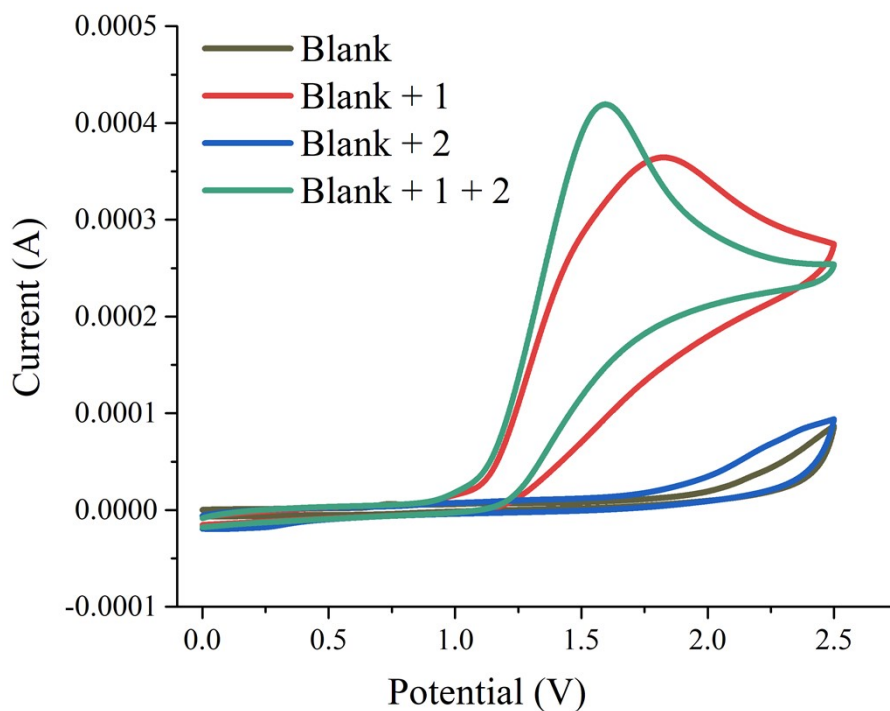


Figure S6: Cyclic voltammetry experiments of substrates

100 mVs-1: (black) blank; (red) 3-(dimethylamino)-1-phenylprop-2-en-1-one **1** (0.3 mmol, 1.5 eq, 52.5 mg); (blue) 2-hydroxynaphthalene-1,4-dione **2** (0.2 mmol, 1 eq, 34.8 mg); (green) 3-(dimethylamino)-1-phenylprop-2-en-1-one **1** (0.3 mmol, 1.5 eq, 52.5 mg) and 2-hydroxynaphthalene-1,4-dione **2** (0.2 mmol, 1 eq, 34.8 mg).

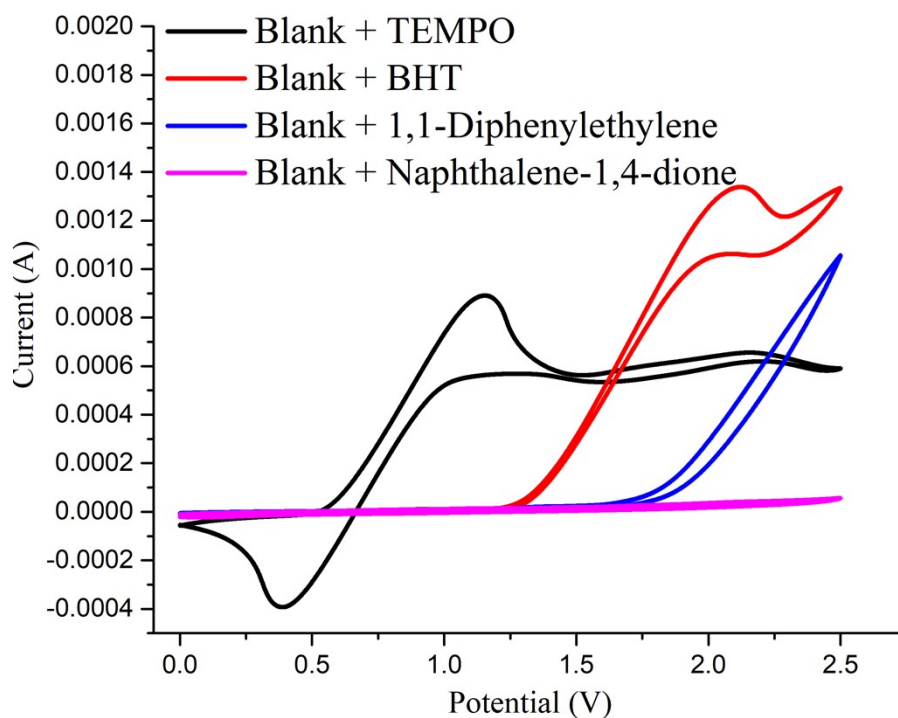
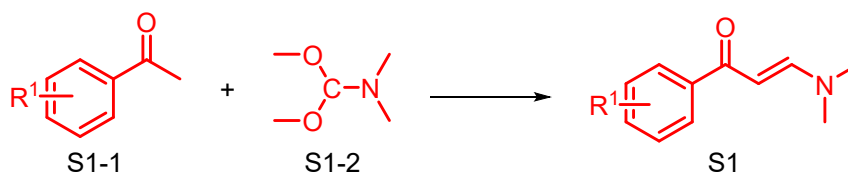


Figure S7: Cyclic voltammety experiments of radical trapping agents

100 mVs-1: (black) TEMPO (0.6 mmol, 3 eq, 93.8 mg); (red) BHT (0.6 mmol, 3 eq, 132.2 mg); (blue) 1,1-diphenylethylene (0.6 mmol, 3 eq, 108.0 mg); (pink) 1,4-naphthoquinone (0.6 mmol, 3 eq, 94.8 mg).

## 7 Synthesis of Substrates

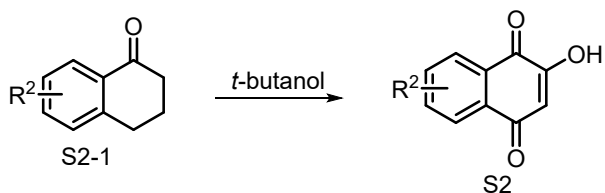
Step 1: General procedure for the synthesis of enaminone (**S1**):<sup>1</sup>



Commercial starting material acetophenone **S1-1** (1 eq, 80 mmol) and *N,N*-dimethyl formamide dimethyl acetal **S1-2** (2 eq, 160 mmol) were mixed in a 250 mL round bottom flask. The reaction mixture was stirred under reflux. Upon completion of the reaction, the mixture was cooled to room temperature. The reaction solution was diluted with ethyl acetate (300 mL) and washed with saturated  $\text{NH}_4\text{Cl}$

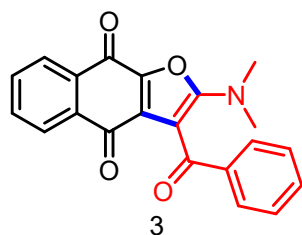
aqueous solution (300 mL) and H<sub>2</sub>O (300 mL). The separated organic layer was dried with anhydrous Na<sub>2</sub>SO<sub>4</sub> and filtered. The filtrate was concentrated under reduced pressure to give the crude product, which was purified by column chromatographic separation (petroleum ether/ethyl acetate: 3:1) to obtain the desired product.

Step 2: General procedure for the synthesis of substrates (S2):<sup>2</sup>



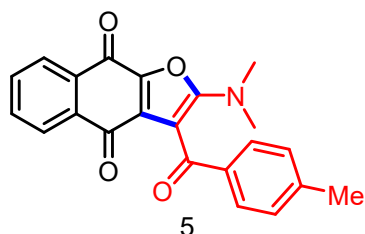
The reaction flask was first degassed and then sealed with a O<sub>2</sub> balloon. All the reactants and solvent was added under a O<sub>2</sub> atmosphere. The solution of atetralone S2-1 (10 mmol) in *t*-butanol (30 mL) was added into the solution of potassium *t*-butoxide in *t*-butanol (1 M, 50 mL). Then, the mixture was stirred under an oxygen atmosphere. After 2 h, the reaction mixture was acidified with HCl (1 M, 20 mL) and diluted extracted with CH<sub>2</sub>Cl<sub>2</sub> (200 mL). The combined organic solution was then washed with a saturated of NaHCO<sub>3</sub> aqueous solution (20 mL) and HCl aqueous solution (1 M, 40 mL). The separated organic layer was dried with anhydrous Na<sub>2</sub>SO<sub>4</sub> and filtered. The filtrate was concentrated under reduced pressure to give the crude product, which was purified by column chromatographic separation (petroleum ether/ethyl acetate: 1:3) to obtain the desired product S2.

## 8 Characterization data for electrolysis products



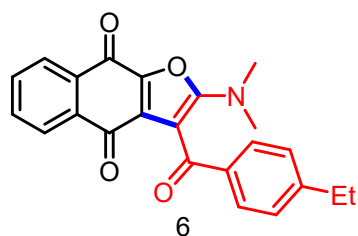
3-benzoyl-2-(dimethylamino)naphtho[2,3-*b*]furan-4,9-dione (**3**):

Purple solid; Eluent: petroluem ether/ethyl acetate 4:1; 52.4 mg, 76%; <sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 8.14 (dd, *J* = 7.6, 1 Hz, 1H), 7.95 - 7.91 (m, 2H), 7.87 (dd, *J* = 7.9, 1.3 Hz, 1H), 7.67 (td, *J* = 7.5, 1.3 Hz, 1H), 7.63 - 7.53 (m, 2H), 7.47 (t, *J* = 7.7 Hz, 2H), 3.13 (s, 6H); <sup>13</sup>C NMR (101 MHz, Chloroform-*d*) δ 190.21, 180.41, 170.44, 161.38, 142.13, 139.27, 133.77, 133.26, 133.05, 132.76, 132.68, 129.37, 128.51, 126.69, 126.17, 96.61, 40.14; HRMS (ESI-TOF) Calcd for C<sub>21</sub>H<sub>16</sub>NO<sub>4</sub> [M+H]<sup>+</sup>: 346.1096; found: 346.1094.



2-(dimethylamino)-3-(4-methylbenzoyl)naphtho[2,3-*b*]furan-4,9-dione (**5**):

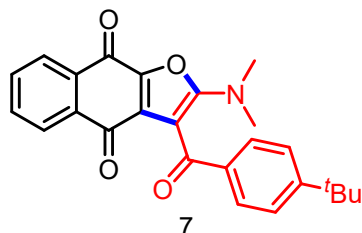
Purple solid; Eluent: petroluem ether/ethyl acetate 4:1; 56.0 mg, 78%; <sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 8.13 (d, *J* = 7.6 Hz, 1H), 7.86 (dd, *J* = 13.4, 7.8 Hz, 3H), 7.66 (t, *J* = 7.4 Hz, 1H), 7.56 (t, *J* = 7.5 Hz, 1H), 7.26 (d, *J* = 7.9 Hz, 2H), 3.11 (s, 6H), 2.43 (s, 3H); <sup>13</sup>C NMR (101 MHz, Chloroform-*d*) δ 189.88, 180.47, 170.29, 161.20, 144.21, 142.03, 136.69, 133.76, 133.13, 132.75, 132.62, 129.57, 129.30, 126.67, 126.14, 96.74, 40.03, 21.75; HRMS (ESI-TOF) Calcd for C<sub>22</sub>H<sub>18</sub>NO<sub>4</sub> [M+H]<sup>+</sup>: 360.1230; found: 360.1238.



2-(dimethylamino)-3-(4-ethylbenzoyl)naphtho[2,3-*b*]furan-4,9-dione (**6**):

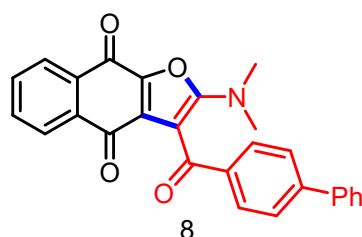
Purple solid; Eluent: petroluem ether/ethyl acetate 4:1; 56.0 mg, 75%; <sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 8.13 (d, *J* = 7.6 Hz, 1H), 7.88 - 7.85 (m, 3H), 7.68 - 7.64 (m, 1H), 7.58 - 7.54 (m, 1H), 7.28 (d, *J* = 8.4 Hz, 2H), 3.11 (s, 6H), 2.73 (q, *J* = 7.6 Hz,

2H), 1.27 (s,  $J = 7.6$  Hz, 3H);  $^{13}\text{C}$  NMR (101 MHz, Chloroform- $d$ )  $\delta$  189.94, 180.46, 170.25, 161.13, 150.29, 142.01, 136.85, 133.18, 132.76, 132.74, 132.61, 129.66, 128.08, 126.65, 126.14, 96.76, 40.01, 29.03, 15.01; HRMS (ESI-TOF) Calcd for  $\text{C}_{23}\text{H}_{20}\text{NO}_4$   $[\text{M}+\text{H}]^+$ : 374.1387; found: 374.1411.



3-(4-(*tert*-butyl)benzoyl)-2-(dimethylamino)naphtho[2,3-*b*]furan-4,9-dione (**7**):

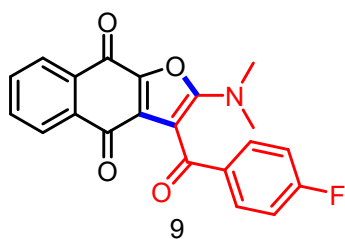
Purple solid; Eluent: petroleum ether/ethyl acetate 4:1; 60.2 mg, 75%;  $^1\text{H}$  NMR (400 MHz, Chloroform- $d$ )  $\delta$  8.15 - 8.13 (m, 1H), 7.89 - 7.85 (m, 3H), 7.69 - 7.65 (m, 1H), 7.59 - 7.55 (m, 1H), 7.47 - 7.45 (m, 2H), 3.10 (s, 6H), 1.35 (s, 9H);  $^{13}\text{C}$  NMR (101 MHz, Chloroform- $d$ )  $\delta$  190.01, 180.46, 170.25, 161.00, 157.05, 142.02, 136.48, 133.75, 133.31, 132.85, 132.77, 132.58, 129.39, 126.65, 126.18, 125.54, 96.78, 39.98, 35.21, 31.12, 29.71; HRMS (ESI-TOF) Calcd for  $\text{C}_{25}\text{H}_{24}\text{NO}_4$   $[\text{M}+\text{H}]^+$ : 402.1700; found: 402.1725.



3-([1,1'-biphenyl]-4-carbonyl)-2-(dimethylamino)naphtho[2,3-*b*]furan-4,9-dione (**8**):

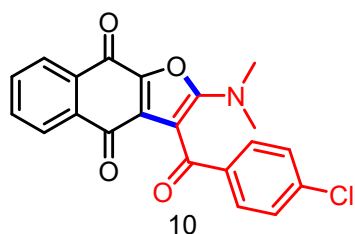
Purple solid; Eluent: petroleum ether/ethyl acetate 4:1; 61.5 mg, 73%;  $^1\text{H}$  NMR (400 MHz, Chloroform- $d$ )  $\delta$  8.15 (dd,  $J = 7.6, 1.1$  Hz, 1H), 8.03 - 7.99 (m, 2H), 7.88 (dd,  $J = 7.6, 1.1$  Hz, 1H), 7.71 - 7.63 (m, 5H), 7.57 (td,  $J = 7.6, 1.3$  Hz, 1H), 7.49 - 7.44 (m, 2H), 7.42 - 7.35 (m, 1H), 3.14 (s, 6H);  $^{13}\text{C}$  NMR (101 MHz, Chloroform- $d$ )  $\delta$  189.73, 180.51, 170.37, 161.31, 145.85, 142.10, 139.94, 137.95, 133.81, 133.12, 132.74, 132.69, 130.01, 128.93, 128.22, 127.35, 127.19, 126.68, 126.19, 96.64, 40.12; HRMS (ESI-TOF) Calcd for  $\text{C}_{27}\text{H}_{20}\text{NO}_4$   $[\text{M}+\text{H}]^+$ : 422.1387; found: 422.1419.





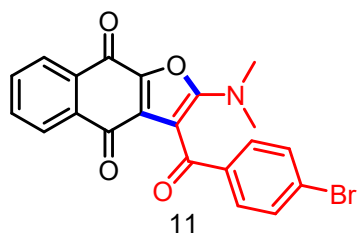
2-(dimethylamino)-3-(4-fluorobenzoyl)naphtho[2,3-*b*]furan-4,9-dione (**9**):

Purple solid; Eluent: petroluem ether/ethyl acetate 4:1; 56.6 mg, 78%; <sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 8.14 - 8.11 (m, 1H), 7.98 - 7.91 (m, 2H), 7.89 - 7.82 (m, 1H), 7.67 (td, *J* = 7.5, 1.1 Hz, 1H), 7.57 (td, *J* = 7.5, 1.1 Hz, 1H), 7.12 (t, *J* = 8.6 Hz, 2H), 3.12 (s, 6H); <sup>13</sup>C NMR (101 MHz, Chloroform-*d*) δ 188.53, 180.48, 170.46, 167.08, 164.55, 161.42, 142.17, 135.77, 135.74, 133.86, 132.77, 132.70, 132.61, 131.97, 131.88, 126.67, 126.20, 115.79, 115.57, 96.23, 40.14; <sup>19</sup>F NMR (376 MHz, Chloroform-*d*) δ -104.93; HRMS (ESI-TOF) Calcd for C<sub>21</sub>H<sub>15</sub>FNO<sub>4</sub> [M+H]<sup>+</sup>: 364.0980; found: 364.0999.



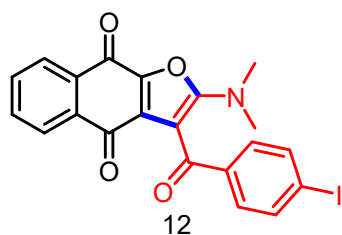
3-(4-chlorobenzoyl)-2-(dimethylamino)naphtho[2,3-*b*]furan-4,9-dione (**10**):

Purple solid; Eluent: petroluem ether/ethyl acetate 4:1; 57.6 mg, 76%; <sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 8.13 (d, *J* = 8 Hz, 1H), 7.89 - 7.83 (m, 3H), 7.63 (d, *J* = 37.8 Hz, 2H), 7.46 - 7.40 (m, 2H), 3.13 (s, 6H); <sup>13</sup>C NMR (101 MHz, Chloroform-*d*) δ 188.78, 180.45, 170.53, 161.53, 142.19, 139.57, 137.75, 133.88, 132.81, 132.69, 132.58, 130.67, 128.84, 126.71, 126.21, 96.13, 40.19; HRMS (ESI-TOF) Calcd for C<sub>21</sub>H<sub>15</sub>NCIO<sub>4</sub> [M+H]<sup>+</sup>: 380.0684; found: 380.0694.



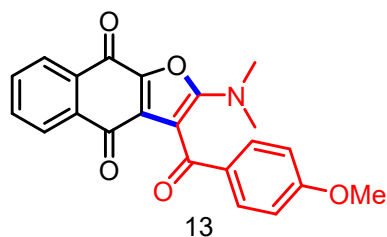
3-(4-bromobenzoyl)-2-(dimethylamino)naphtho[2,3-*b*]furan-4,9-dione (**11**):

Purple solid; Eluent: petroluem ether/ethyl acetate 4:1; 65.1 mg, 77%; <sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 8.13 (d, *J* = 7.5 Hz, 1H), 7.87 (d, *J* = 7.5 Hz, 1H), 7.78 (d, *J* = 8.2 Hz, 2H), 7.68 (t, *J* = 7.4 Hz, 1H), 7.59 (d, *J* = 8.1 Hz, 3H), 3.12 (s, 6H); <sup>13</sup>C NMR (101 MHz, Chloroform-*d*) δ 188.96, 180.45, 170.54, 161.55, 142.20, 138.17, 133.89, 132.81, 132.74, 132.68, 132.57, 131.81, 130.77, 128.38, 126.72, 126.22, 96.08, 40.20; HRMS (ESI-TOF) Calcd for C<sub>21</sub>H<sub>15</sub>NO<sub>4</sub>Br [M+H]<sup>+</sup>: 424.0179; found: 424.0210.



2-(dimethylamino)-3-(4-iodobenzoyl)naphtho[2,3-*b*]furan-4,9-dione (**12**):

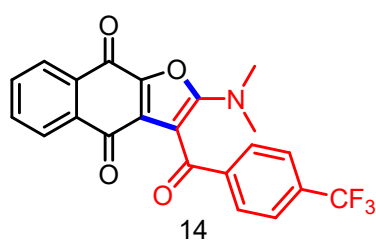
Purple solid; Eluent: petroluem ether/ethyl acetate 4:1; 68.8 mg, 73%; <sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 8.14 - 8.12 (m, 1H), 7.87 (dd, *J* = 7.8, 0.9 Hz, 1H), 7.83 - 7.81 (m, 2H), 7.70 - 7.57 (m, 4H), 3.12 (s, 6H); <sup>13</sup>C NMR (101 MHz, Chloroform-*d*) δ 189.27, 180.45, 170.54, 161.55, 142.19, 138.70, 137.80, 133.89, 132.82, 132.76, 132.68, 132.58, 130.66, 126.73, 126.22, 101.34, 96.04, 40.20; HRMS (ESI-TOF) Calcd for C<sub>21</sub>H<sub>15</sub>NIO<sub>4</sub> [M+H]<sup>+</sup>: 472.0040; found: 472.0039.



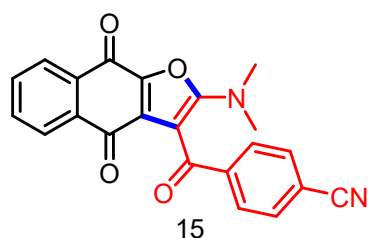
2-(dimethylamino)-3-(4-methoxybenzoyl)naphtho[2,3-*b*]furan-4,9-dione (**13**):

Purple solid; Eluent: petroluem ether/ethyl acetate 4:1; 59.3 mg, 79%; <sup>1</sup>H NMR (400

MHz, Chloroform-*d*)  $\delta$  8.14 (d,  $J = 7.5$  Hz, 1H), 7.94 - 7.89 (m, 3H), 7.65 (t,  $J = 7.5$  Hz, 1H), 7.60 - 7.54 (m, 1H), 6.94 (d,  $J = 8.8$  Hz, 2H), 3.86 (s, 3H), 3.09 (s, 6H);  $^{13}\text{C}$  NMR (101 MHz, Chloroform-*d*)  $\delta$  188.79, 180.54, 170.19, 163.78, 161.03, 142.01, 133.77, 133.10, 132.80, 132.74, 132.59, 132.17, 131.81, 126.63, 126.14, 113.80, 96.70, 55.51, 39.96; HRMS (ESI-TOF) Calcd for  $\text{C}_{22}\text{H}_{18}\text{NO}_5$   $[\text{M}+\text{H}]^+$ : 376.1179; found: 376.1201.

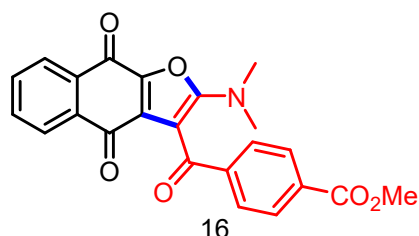


2-(dimethylamino)-3-(4-(trifluoromethyl)benzoyl)naphtho[2,3-*b*]furan-4,9-dione (**14**): Purple solid; Eluent: petroleum ether/ethyl acetate 4:1; 62.0 mg, 75%;  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  8.14 (d,  $J = 7.0$  Hz, 1H), 8.02 (d,  $J = 8.1$  Hz, 2H), 7.84 (d,  $J = 7.0$  Hz, 1H), 7.76 - 7.64 (m, 3H), 7.63 - 7.54 (m, 1H), 3.15 (s, 6H);  $^{13}\text{C}$  NMR (101 MHz, Chloroform-*d*)  $\delta$  188.83, 180.40, 170.68, 161.81, 142.27 (d,  $J = 3.5$  Hz), 133.93, 132.89, 132.63 (d,  $J = 3.1$  Hz), 132.48, 129.47, 126.73, 126.25, 125.52 (q,  $J = 3.8$  Hz), 96.03, 40.3;  $^{19}\text{F}$  NMR (376 MHz, Chloroform-*d*)  $\delta$  -62.91; HRMS (ESI-TOF) Calcd for  $\text{C}_{22}\text{H}_{15}\text{NO}_4\text{F}_3$   $[\text{M}+\text{H}]^+$ : 414.0948; found: 414.8831.



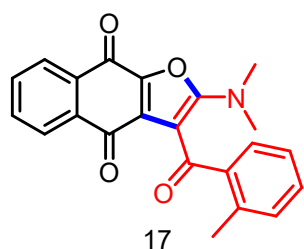
4-(2-(dimethylamino)-4,9-dioxo-4,9-dihydronaphtho[2,3-*b*]furan-3-carbonyl)benzonitrile (**15**): Purple solid; Eluent: petroleum ether/ethyl acetate 4:1; 52.5 mg, 71%;  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  8.13 (d,  $J = 7.1$  Hz, 1H), 7.98 (d,  $J = 8.0$  Hz, 2H), 7.83 (d,  $J = 7.8$  Hz, 1H), 7.75 (d,  $J = 8.0$  Hz, 2H), 7.72 - 7.65 (m, 1H), 7.63 - 7.53 (m, 1H), 3.16 (s, 6H);  $^{13}\text{C}$  NMR (101 MHz, Chloroform-*d*)  $\delta$  188.22, 180.41, 170.79, 162.08, 142.89,

142.39, 134.00, 133.00, 132.60, 132.36, 132.29, 129.46, 126.74, 126.27, 118.24, 115.97, 95.80, 40.43; HRMS (ESI-TOF) Calcd for C<sub>22</sub>H<sub>15</sub>N<sub>2</sub>O<sub>4</sub> [M+H]<sup>+</sup>: 371.1026; found: 371.1007.



Methyl 4-(2-(dimethylamino)-4,9-dioxo-4,9-dihydronaphtho[2,3-*b*]furan-3-carbonyl)benzoate (**16**):

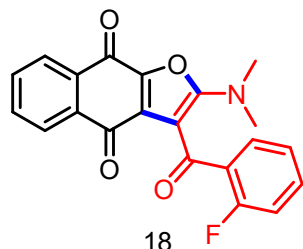
Purple solid; Eluent: petroluem ether/ethyl acetate 4:1; 59.6 mg, 74%; <sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 8.14 - 8.09 (m, 3H), 7.97 - 7.95 (m, 2H), 7.86 - 7.78 (m, 1H), 7.67 (td, *J* = 7.5, 1.2 Hz, 1H), 7.56 (td, *J* = 7.6, 1.2 Hz, 1H), 3.94 (s, 3H), 3.14 (s, 6H); <sup>13</sup>C NMR (101 MHz, Chloroform-*d*) δ 189.28, 180.34, 170.64, 166.38, 161.77, 142.86, 142.25, 133.86, 133.67, 132.83, 132.69, 132.49, 129.71, 129.08, 126.70, 126.19, 96.34, 52.44, 40.32; HRMS (ESI-TOF) Calcd for C<sub>23</sub>H<sub>18</sub>NO<sub>6</sub> [M+H]<sup>+</sup>: 404.1129; found: 404.1170.



2-(dimethylamino)-3-(2-methylbenzoyl)naphtho[2,3-*b*]furan-4,9-dione (**17**):

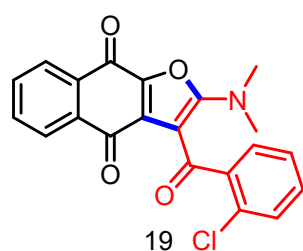
Purple solid; Eluent: petroluem ether/ethyl acetate 4:1; 56.0 mg, 78%; <sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 8.11 - 8.09 (m, 1H), 7.82 (dd, *J* = 7.8, 0.6 Hz, 1H), 7.64 (td, *J* = 7.5, 1.2 Hz, 1H), 7.59 - 7.49 (m, 2H), 7.43 - 7.33 (m, 2H), 7.14 (t, *J* = 7.8 Hz, 1H), 3.17 (s, 6H), 2.69 (s, 3H); <sup>13</sup>C NMR (101 MHz, Chloroform-*d*) δ 192.01, 180.30, 170.59, 161.51, 142.16, 139.64, 139.32, 133.63, 132.81, 132.71, 132.63, 132.53,

131.83, 131.62, 130.59, 126.69, 126.06, 125.23, 98.82, 40.22, 21.08; HRMS (ESI-TOF) Calcd for C<sub>22</sub>H<sub>18</sub>NO<sub>4</sub> [M+H]<sup>+</sup>: 360.1230; found: 360.1337.



2-(dimethylamino)-3-(2-fluorobenzoyl)naphtho[2,3-*b*]furan-4,9-dione (**18**):

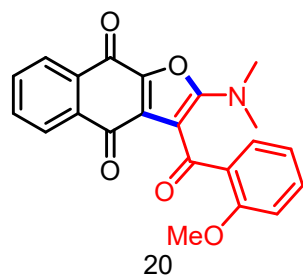
Purple solid; Eluent: petroleum ether/ethyl acetate 4:1; 55.2 mg, 76%; <sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 8.12 (d, *J* = 7.5 Hz, 1H), 7.93 - 7.84 (m, 2H), 7.66 (t, *J* = 7.4 Hz, 1H), 7.57 - 7.53 (m, 2H), 7.33 - 7.22 (m, 1H), 7.07 (dd, *J* = 10.5, 8.6 Hz, 1H), 3.19 (s, 6H); <sup>13</sup>C NMR (101 MHz, Chloroform-*d*) δ 185.08, 180.52, 170.95, 162.82, 161.99, 160.29, 142.33, 134.33 (d, *J* = 9.0 Hz), 133.68, 132.80 (d, *J* = 8.0 Hz), 132.40, 131.86 (d, *J* = 2.9 Hz), 130.91 - 130.79 (m), 128.61 (d, *J* = 10.3 Hz), 126.71, 126.06, 124.29 (d, *J* = 3.6 Hz), 116.18 (d, *J* = 22.5 Hz), 99.77 (d, *J* = 2.2 Hz), 40.59; <sup>19</sup>F NMR (376 MHz, Chloroform-*d*) δ -104.93; HRMS (ESI-TOF) Calcd for C<sub>21</sub>H<sub>15</sub>FNO<sub>4</sub> [M+H]<sup>+</sup>: 364.0980; found: 364.0991.



3-(2-chlorobenzoyl)-2-(dimethylamino)naphtho[2,3-*b*]furan-4,9-dione (**19**):

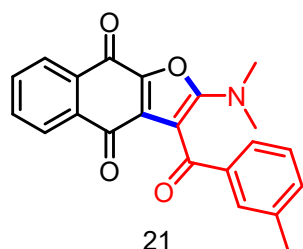
Purple solid; Eluent: petroleum ether/ethyl acetate 4:1; 56.1 mg, 74%; <sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 8.12 - 8.09 (m, 1H), 7.84 (dd, *J* = 7.7, 1.3 Hz, 1H), 7.71 (dd, *J* = 7.5, 1.7 Hz, 1H), 7.65 (td, *J* = 7.5, 1.4 Hz, 1H), 7.56 (td, *J* = 7.5, 1.4 Hz, 1H), 7.48 - 7.33 (m, 3H), 3.24 (s, 6H); <sup>13</sup>C NMR (101 MHz, Chloroform-*d*) δ 188.01, 180.15, 171.16, 162.54, 142.53, 139.95, 132.82, 132.79, 132.56, 132.22, 131.39, 130.98,

130.38, 129.37, 128.51, 126.81, 126.77, 125.99, 99.44, 40.72; HRMS (ESI-TOF)  
Calcd for C<sub>21</sub>H<sub>15</sub>ClNO<sub>4</sub> [M+H]<sup>+</sup>: 380.0684; found: 380.0694.



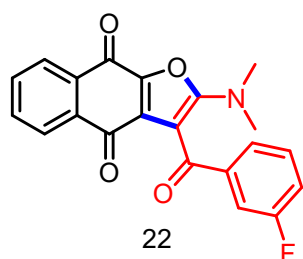
2-(dimethylamino)-3-(2-methoxybenzoyl)naphtho[2,3-*b*]furan-4,9-dione (**20**):

Purple solid; Eluent: petroleum ether/ethyl acetate 4:1; 56.3 mg, 75%; <sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 8.13 - 8.08 (m, 1H), 7.87 - 7.82 (m, 1H), 7.78 (dd, *J* = 7.7, 1.7 Hz, 1H), 7.64 (td, *J* = 7.5, 1.2 Hz, 1H), 7.56 - 7.48 (m, 2H), 7.05 (t, *J* = 7.8 Hz, 1H), 6.94 (d, *J* = 8.3 Hz, 1H), 3.72 (s, 3H), 3.16 (s, 6H); <sup>13</sup>C NMR (101 MHz, Chloroform-*d*) δ 188.06, 180.39, 170.67, 161.78, 158.97, 141.96, 133.88, 133.56, 132.90, 132.57, 132.15, 131.20, 129.79, 126.63, 125.98, 120.54, 111.61, 100.99, 55.75, 40.48; HRMS (ESI-TOF) Calcd for C<sub>22</sub>H<sub>18</sub>NO<sub>5</sub> [M+H]<sup>+</sup>: 376.1179; found: 376.1205.



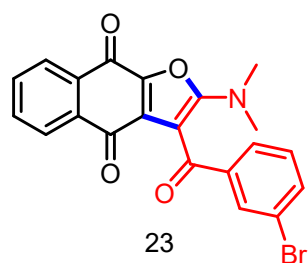
2-(dimethylamino)-3-(3-methylbenzoyl)naphtho[2,3-*b*]furan-4,9-dione (**21**):

Purple solid; Eluent: petroleum ether/ethyl acetate 4:1; 51.7 mg, 72%; <sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 8.13 (d, *J* = 7.5 Hz, 1H), 7.87 (d, *J* = 7.5 Hz, 1H), 7.78 (s, 1H), 7.72 - 7.63 (m, 2H), 7.58 - 7.55 (m, 1H), 7.41 - 7.39 (m, 1H), 7.35 - 7.31 (m, 1H), 3.11 (s, 6H), 2.41 (s, 3H); <sup>13</sup>C NMR (101 MHz, Chloroform-*d*) δ 190.45, 180.44, 170.37, 161.27, 142.07, 139.21, 138.38, 134.21, 133.76, 133.11, 132.74, 132.65, 129.52, 128.34, 127.04, 126.68, 126.16, 96.75, 40.09, 21.44; HRMS (ESI-TOF) Calcd for C<sub>22</sub>H<sub>18</sub>NO<sub>4</sub> [M+H]<sup>+</sup>: 360.1230; found: 360.1230.



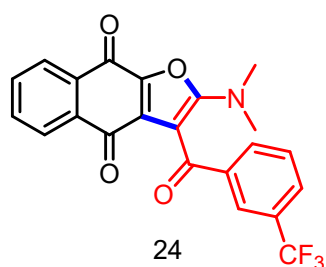
2-(dimethylamino)-3-(3-fluorobenzoyl)naphtho[2,3-*b*]furan-4,9-dione (**22**):

Purple solid; Eluent: petroluem ether/ethyl acetate 4:1; 51.5 mg, 71%; <sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 8.13 (d, *J* = 7.5 Hz, 1H), 7.86 (d, *J* = 7.5 Hz, 1H), 7.73 - 7.53 (m, 4H), 7.42 (q, *J* = 7.8 Hz, 1H), 7.30 - 7.27 (m, 1H), 3.13 (s, 6H); <sup>13</sup>C NMR (101 MHz, Chloroform-*d*) δ 188.77, 180.40, 170.57, 163.98, 161.54 (d, *J* = 4.4 Hz), 142.22, 141.55 (d, *J* = 6.0 Hz), 133.86, 132.75 (d, *J* = 10.1 Hz), 132.56, 126.71, 126.22, 125.20 (d, *J* = 2.9 Hz), 120.24, 120.02, 96.12, 40.22; <sup>19</sup>F NMR (376 MHz, Chloroform-*d*) δ -112.13; HRMS (ESI-TOF) Calcd for C<sub>21</sub>H<sub>15</sub>NO<sub>4</sub>F [M+H]<sup>+</sup>: 364.0980; found: 364.0999.

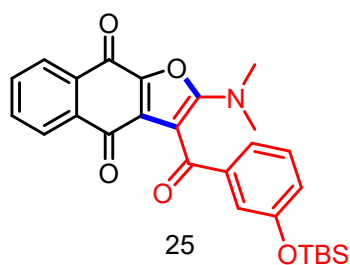


3-(3-bromobenzoyl)-2-(dimethylamino)naphtho[2,3-*b*]furan-4,9-dione (**23**):

Purple solid; Eluent: petroluem ether/ethyl acetate 4:1; 63.5 mg, 75%; <sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 8.14 (dd, *J* = 7.6, 1.1 Hz, 1H), 8.06 (t, *J* = 1.7 Hz, 1H), 7.88 (dd, *J* = 7.6, 1.1 Hz, 1H), 7.83 (dt, *J* = 7.8, 1.2 Hz, 1H), 7.73 - 7.65 (m, 2H), 7.59 (td, *J* = 7.5, 1.3 Hz, 1H), 7.34 (t, *J* = 7.8 Hz, 1H), 3.14 (s, 6H); <sup>13</sup>C NMR (101 MHz, Chloroform-*d*) δ 188.56, 180.39, 170.60, 161.66, 142.24, 141.26, 135.96, 133.88, 132.83, 132.70, 132.68, 132.56, 132.00, 130.01, 128.01, 126.73, 126.23, 122.78, 95.96, 40.25; HRMS (ESI-TOF) Calcd for C<sub>21</sub>H<sub>15</sub>NBrO<sub>4</sub> [M+H]<sup>+</sup>: 424.0179; found: 424.0160.



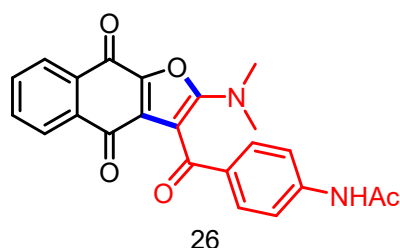
2-(dimethylamino)-3-(3-(trifluoromethyl)benzoyl)naphtho[2,3-*b*]furan-4,9-dione (**24**): Purple solid; Eluent: petroleum ether/ethyl acetate 4:1; 61.1 mg, 74%; <sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 8.18 (s, 1H), 8.14 (d, *J* = 7.5 Hz, 1H), 8.08 (d, *J* = 7.8 Hz, 1H), 7.86 - 7.81 (m, 2H), 7.70 - 7.66 (m, 1H), 7.63 - 7.55 (m, 2H), 3.15 (s, 6H); <sup>13</sup>C NMR (101 MHz, Chloroform-*d*) δ 188.39, 180.39, 170.69, 161.94, 142.33, 139.99, 133.89, 132.89, 132.68, 132.62 - 132.41 (m), 130.99 (q, *J* = 32.8 Hz), 129.38 (q, *J* = 3.6 Hz), 129.04, 126.68, 126.22, 125.93 (q, *J* = 3.7 Hz), 125.13, 122.42, 95.85, 40.33; <sup>19</sup>F NMR (376 MHz, Chloroform-*d*) δ -62.62; HRMS (ESI-TOF) Calcd for C<sub>22</sub>H<sub>15</sub>NF<sub>3</sub>O<sub>4</sub> [M+H]<sup>+</sup>: 414.0948; found: 414.0964.



3-(3-((*tert*-butyldimethylsilyloxy)benzoyl)-2-(dimethylamino)naphtho[2,3-*b*]furan-4,9-dione (**25**): Purple solid; Eluent: petroleum ether/ethyl acetate 4:1; 66.5 mg, 70%; <sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 8.13 (d, *J* = 7.0 Hz, 1H), 7.87 (d, *J* = 7.6 Hz, 1H), 7.69 - 7.65 (m, 1H), 7.59 - 7.55 (m, 1H), 7.51 (d, *J* = 7.7 Hz, 1H), 7.37 - 7.36 (m, 1H), 7.31 (t, *J* = 7.9 Hz, 1H), 7.07 - 7.04 (m, 1H), 3.12 (s, 6H), 0.94 (s, 9H), 0.16 (s, 6H); <sup>13</sup>C NMR (101 MHz, Chloroform-*d*) δ 189.90, 180.31, 170.42, 161.23, 155.84, 142.09, 140.75, 133.73, 133.15, 132.77, 132.69, 132.63, 129.51, 126.65, 126.15, 125.15, 122.60,

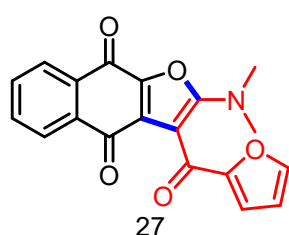


120.61, 96.69, 40.10, 25.63, 18.19, -4.41; HRMS (ESI-TOF) Calcd for  $C_{27}H_{30}NO_5Si$   $[M+H]^+$ : 476.1888; found: 476.1918.



*N*-(4-(2-(dimethylamino)-4,9-dioxo-4,9-dihydro-1H-naphtho[2,3-*b*]furan-3-carbonyl)phenyl)acetamide (**26**):

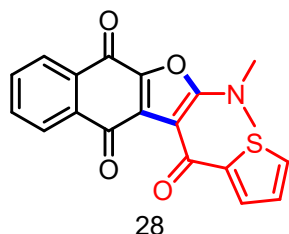
Purple solid; Eluent: petroleum ether/ethyl acetate 4:1; 60.3 mg, 75%;  $^1H$  NMR (400 MHz,  $DMSO-d_6$ )  $\delta$  10.29 (s, 1H), 8.06 (d,  $J = 7.5$  Hz, 1H), 7.88 (d,  $J = 8.7$  Hz, 2H), 7.82 (t,  $J = 7.8$  Hz, 2H), 7.74 - 7.68 (m, 3H), 3.07 (s, 6H), 2.12 (s, 3H);  $^{13}C$  NMR (101 MHz,  $DMSO-d_6$ )  $\delta$  188.48, 180.64, 169.39, 169.27, 160.82, 144.27, 141.71, 134.48, 133.75, 133.28, 133.17, 132.91, 132.71, 130.94, 126.50, 126.02, 118.58, 96.45, 24.60; HRMS (ESI-TOF) Calcd for  $C_{23}H_{19}N_2O_5$   $[M+H]^+$ : 403.1288.9923; found: 403.1310.



2-(dimethylamino)-3-(furan-2-carbonyl)naphtho[2,3-*b*]furan-4,9-dione (**27**):

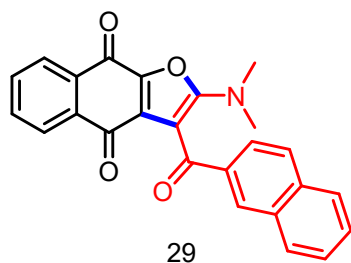
Purple solid; Eluent: petroleum ether/ethyl acetate 4:1; 48.9 mg, 73%;  $^1H$  NMR (400 MHz,  $Chloroform-d$ )  $\delta$  8.15 - 8.13 (m, 1H), 7.95 - 7.93 (m, 1H), 7.70 - 7.66 (m, 1H), 7.62 - 7.58 (m, 1H), 7.56 - 7.55 (m, 1H), 7.22 (d,  $J = 3.5$  Hz, 1H), 6.60 (dd,  $J = 3.5, 1.6$  Hz, 1H), 3.17 (s, 6H);  $^{13}C$  NMR (101 MHz,  $Chloroform-d$ )  $\delta$  180.48, 176.67, 170.56, 161.21, 154.59, 146.47, 142.31, 133.72, 133.02, 132.92, 132.72, 132.60,

126.67, 126.16, 117.98, 112.70, 95.89, 53.42, 40.13; HRMS (ESI-TOF) Calcd for  $C_{19}H_{14}NO_5$   $[M+H]^+$ : 336.0866; found: 336.0890.



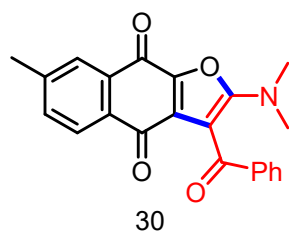
2-(dimethylamino)-3-(thiophene-2-carbonyl)naphtho[2,3-*b*]furan-4,9-dione (**28**):

Purple solid; Eluent: petroleum ether/ethyl acetate 4:1; 52.7 mg, 75%;  $^1H$  NMR (400 MHz, Chloroform-*d*)  $\delta$  8.13 (d,  $J = 7.5$  Hz, 1H), 7.92 (d,  $J = 7.5$  Hz, 1H), 7.75 - 7.64 (m, 2H), 7.51 - 7.57 (m, 2H), 7.11 (t,  $J = 4.3$  Hz, 1H), 3.14 (s, 6H);  $^{13}C$  NMR (101 MHz, Chloroform-*d*)  $\delta$  181.87, 180.48, 170.31, 160.61, 146.08, 142.08, 134.52, 134.16, 133.83, 133.02, 132.79, 132.72, 132.69, 128.21, 126.71, 126.21, 96.31, 39.93; HRMS (ESI-TOF) Calcd for  $C_{19}H_{14}NO_4S$   $[M+H]^+$ : 352.0638; found: 352.0663.



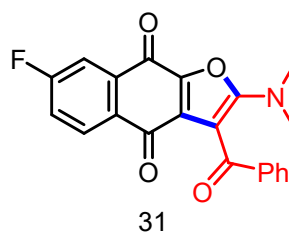
3-(2-naphthoyl)-2-(dimethylamino)naphtho[2,3-*b*]furan-4,9-dione (**29**):

Purple solid; Eluent: petroleum ether/ethyl acetate 4:1; 55.3 mg, 70%;  $^1H$  NMR (400 MHz, Chloroform-*d*)  $\delta$  8.37 (s, 1H), 8.16 - 8.13 (m, 1H), 8.07 (dd,  $J = 8.6, 1.6$  Hz, 1H), 7.93 (d,  $J = 8.6$  Hz, 1H), 7.89 (dd,  $J = 8.1, 3.1$  Hz, 2H), 7.82 - 7.78 (m, 1H), 7.66 (td,  $J = 7.6, 1.2$  Hz, 1H), 7.62 - 7.46 (m, 3H), 3.15 (s, 6H);  $^{13}C$  NMR (101 MHz, Chloroform-*d*)  $\delta$  190.26, 180.44, 170.42, 161.33, 142.15, 136.75, 135.80, 133.79, 133.25, 132.76, 132.72, 132.66, 132.51, 131.47, 129.73, 128.55, 127.94, 126.71, 126.69, 126.19, 124.73, 96.70, 40.10; HRMS (ESI-TOF) Calcd for  $C_{25}H_{18}NO_4$   $[M+H]^+$ : 396.1230; found: 396.1247.



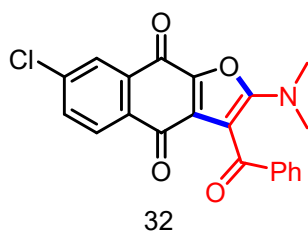
3-benzoyl-2-(dimethylamino)-7-methylnaphtho[2,3-*b*]furan-4,9-dione (**30**):

Purple solid; Eluent: petroluem ether/ethyl acetate 4:1; 53.9 mg, 75%;  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  7.93 - 7.92 (m, 3H), 7.74 (d,  $J = 7.8$  Hz, 1H), 7.60 - 7.56 (m, 1H), 7.47 - 7.44 (m, 2H), 7.34 (d,  $J = 7.8$  Hz, 1H), 3.11 (s, 6H), 2.45 (s, 3H);  $^{13}\text{C}$  NMR (101 MHz, Chloroform-*d*)  $\delta$  190.29, 180.28, 170.70, 161.32, 144.91, 142.13, 139.30, 133.19, 133.19, 133.16, 132.62, 130.47, 129.37, 128.48, 126.92, 126.72, 96.66, 40.10, 21.77; HRMS (ESI-TOF) Calcd for  $\text{C}_{22}\text{H}_{18}\text{NO}_4$   $[\text{M}+\text{H}]^+$ : 360.1230; found: 360.1235.



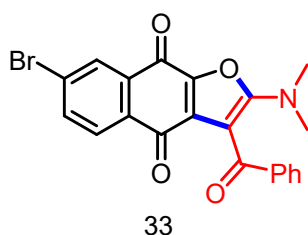
3-benzoyl-2-(dimethylamino)-7-fluoronaphtho[2,3-*b*]furan-4,9-dione (**31**):

Purple solid; Eluent: petroluem ether/ethyl acetate 4:1; 56.6 mg, 78%;  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  7.95 - 7.84 (m, 3H), 7.79 (dd,  $J = 8.8, 2.6$  Hz, 1H), 7.59 (t,  $J = 7.4$  Hz, 1H), 7.47 (t,  $J = 7.7$  Hz, 2H), 7.20 (td,  $J = 8.2, 2.6$  Hz, 1H), 3.12 (s, 6H);  $^{13}\text{C}$  NMR (101 MHz, Chloroform-*d*)  $\delta$  190.11, 179.16, 168.72, 167.58, 165.03, 161.47, 141.98, 139.12, 135.83 (d,  $J = 7.9$  Hz), 133.37, 129.67 (d,  $J = 8.8$  Hz), 129.36, 129.12 (d,  $J = 3.6$  Hz), 128.56, 119.21 (d,  $J = 22.3$  Hz), 113.40 (d,  $J = 24.0$  Hz), 96.99, 40.12;  $^{19}\text{F}$  NMR (376 MHz, Chloroform-*d*)  $\delta$  -102.32; HRMS (ESI-TOF) Calcd for  $\text{C}_{21}\text{H}_{15}\text{NFO}_4$   $[\text{M}+\text{H}]^+$ : 364.0980; found: 364.1002.



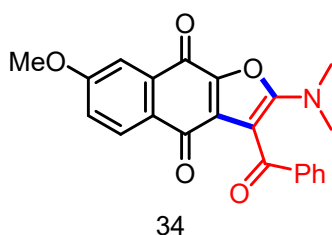
3-benzoyl-7-chloro-2-(dimethylamino)naphtho[2,3-*b*]furan-4,9-dione (**32**):

Purple solid; Eluent: petroleum ether/ethyl acetate 4:1; 57.6 mg, 76%;  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  8.09 (d,  $J = 2.1$  Hz, 1H), 7.94 - 7.90 (m, 2H), 7.80 (d,  $J = 8.3$  Hz, 1H), 7.63 - 7.56 (m, 1H), 7.54 - 7.41 (m, 3H), 3.13 (s, 6H);  $^{13}\text{C}$  NMR (101 MHz, Chloroform-*d*)  $\delta$  190.05, 179.43, 168.82, 161.49, 141.76, 140.73, 139.11, 134.17, 133.38, 133.31, 132.43, 130.91, 129.36, 128.56, 128.25, 126.31, 96.90, 40.13; HRMS (ESI-TOF) Calcd for  $\text{C}_{21}\text{H}_{15}\text{NClO}_4$   $[\text{M}+\text{H}]^+$ : 380.0684; found: 380.0643.



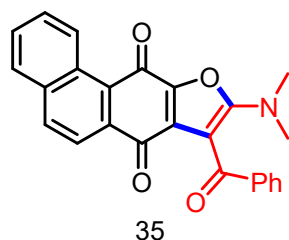
3-benzoyl-7-bromo-2-(dimethylamino)naphtho[2,3-*b*]furan-4,9-dione (**33**):

Purple solid; Eluent: petroleum ether/ethyl acetate 4:1; 59.2 mg, 70%;  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  8.26 (d,  $J = 1.6$  Hz, 1H), 7.92 (d,  $J = 8.0$  Hz, 2H), 7.76 - 7.67 (m, 2H), 7.59 (d,  $J = 7.3$  Hz, 1H), 7.47 (t,  $J = 7.7$  Hz, 2H), 3.13 (s, 6H);  $^{13}\text{C}$  NMR (101 MHz, Chloroform-*d*)  $\delta$  190.02, 179.61, 168.78, 161.49, 141.67, 139.13, 135.48, 134.02, 133.36, 133.30, 131.30, 129.35, 129.25, 128.55, 128.27, 97.01, 40.12; HRMS (ESI-TOF) Calcd for  $\text{C}_{21}\text{H}_{15}\text{O}_4\text{NBr}$   $[\text{M}+\text{H}]^+$ : 424.0179; found: 424.0221.



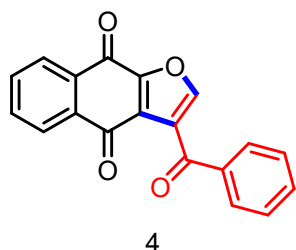
3-benzoyl-2-(dimethylamino)-7-methoxynaphtho[2,3-*b*]furan-4,9-dione (**34**):

Purple soild; Eluent: petroluem ether/ethyl acetate 4:1; 48.8 mg, 65%;  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  7.93 (d,  $J = 7.4$  Hz, 2H), 7.81 (d,  $J = 8.6$  Hz, 1H), 7.63 - 7.55 (m, 2H), 7.46 (t,  $J = 7.6$  Hz, 2H), 7.00 (dd,  $J = 8.6, 2.6$  Hz, 1H), 3.93 (s, 3H), 3.12 (s, 6H);  $^{13}\text{C}$  NMR (101 MHz, Chloroform-*d*)  $\delta$  190.37, 179.54, 170.05, 164.25, 161.31, 142.03, 139.27, 135.11, 133.55, 133.22, 129.38, 129.12, 128.48, 126.00, 118.04, 110.64, 97.01, 55.91, 40.08; HRMS (ESI-TOF) Calcd for  $\text{C}_{22}\text{H}_{18}\text{O}_5\text{N}$   $[\text{M}+\text{H}]^+$ : 376.1179; found: 376.1222.



8-benzoyl-9-(dimethylamino)phenanthro[3,2-*b*]furan-7,11-dione (**35**):

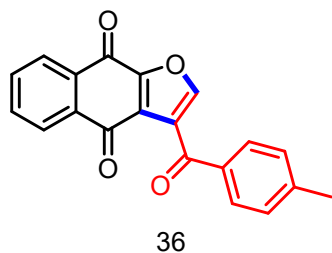
Purple soild; Eluent: petroluem ether/ethyl acetate 4:1; 39.5 mg, 50%;  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  9.77 (d,  $J = 8.9$  Hz, 1H), 8.03 - 7.98(m, 2H), 7.99 - 7.94 (m, 2H), 7.82 (d,  $J = 8.1$  Hz, 1H), 7.72 - 7.65 (m, 1H), 7.63 - 7.55 (m, 2H), 7.47 (t,  $J = 7.7$  Hz, 2H), 3.15 (s, 6H);  $^{13}\text{C}$  NMR (101 MHz, Chloroform-*d*)  $\delta$  177.36, 174.78, 139.46, 136.93, 133.99, 133.17, 133.12, 130.87, 130.28, 129.67, 129.39, 128.56, 128.47, 128.33, 128.22, 122.43, 40.22; HRMS (ESI-TOF) Calcd for  $\text{C}_{25}\text{H}_{18}\text{O}_4\text{N}$   $[\text{M}+\text{H}]^+$ : 396.1230; found: 396.1256.



3-benzoylnaphtho[2,3-*b*]furan-4,9-dione (**4**):<sup>3</sup>

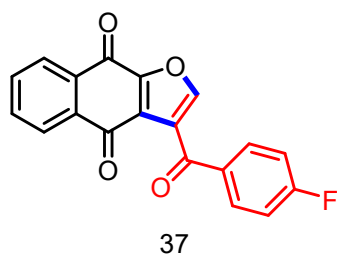
Yellow soild; Eluent: petroluem ether/ethyl acetate 10:1; 27.2 mg, 45%;  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  8.26 - 8.23 (m, 1H), 8.14 - 8.11 (m, 1H), 8.05 (s, 1H),

7.95 - 7.90 (m, 2H), 7.81 - 7.72 (m, 2H), 7.65 (t,  $J = 7.4$  Hz, 1H), 7.51 (t,  $J = 7.7$  Hz, 1H);  $^{13}\text{C}$  NMR (101 MHz, Chloroform- $d$ )  $\delta$  187.55, 179.03, 173.80, 153.10, 149.55, 137.04, 134.37, 134.07, 134.04, 133.34, 131.90, 129.62, 128.74, 128.14, 127.50, 126.93, 124.87; HRMS (ESI-TOF) Calcd for  $\text{C}_{19}\text{H}_{11}\text{O}_4$   $[\text{M}+\text{H}]^+$ : 303.0652; found: 303.0677.



3-(4-methylbenzoyl)naphtho[2,3-*b*]furan-4,9-dione (**36**):<sup>3</sup>

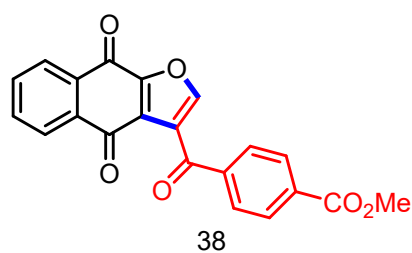
Yellow soild; Eluent: petroluem ether/ethyl acetate 10:1; 27.2 mg, 43%;  $^1\text{H}$  NMR (400 MHz, Chloroform- $d$ )  $\delta$  8.29 - 8.20 (m, 1H), 8.14 - 8.11 (m, 1H), 8.02 (s, 1H), 7.82 (d,  $J = 8.2$  Hz, 2H), 7.80 - 7.72 (m, 2H), 7.29 (d,  $J = 8.1$  Hz, 2H), 2.44 (s, 3H);  $^{13}\text{C}$  NMR (101 MHz, Chloroform- $d$ )  $\delta$  187.15, 179.08, 173.80, 153.00, 149.29, 145.14, 134.54, 134.33, 134.04, 133.35, 131.93, 129.79, 129.47, 128.18, 127.47, 126.91, 124.99, 21.85; HRMS (ESI-TOF) Calcd for  $\text{C}_{20}\text{H}_{13}\text{O}_4$   $[\text{M}+\text{H}]^+$ : 317.0808; found: 317.0786.



3-(4-fluorobenzoyl)naphtho[2,3-*b*]furan-4,9-dione (**37**):

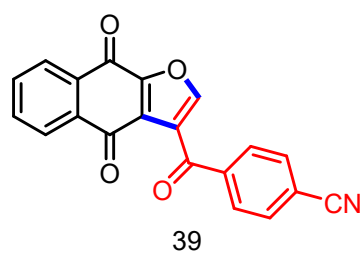
Yellow soild; Eluent: petroluem ether/ethyl acetate 10:1; 26.9 mg, 42%;  $^1\text{H}$  NMR (400 MHz, Chloroform- $d$ )  $\delta$  8.25 - 8.22 (m, 1H), 8.16 - 8.08 (m, 1H), 8.06 (s, 1H), 8.00 - 7.90 (m, 2H), 7.84 - 7.71 (m, 2H), 7.17 (t,  $J = 8.6$  Hz, 2H);  $^{13}\text{C}$  NMR (101 MHz, Chloroform- $d$ )  $\delta$  186.09, 179.10, 173.71, 167.59, 165.03, 153.06, 149.40,

134.42, 134.17, 133.46 (d,  $J = 3.2$  Hz), 133.23, 132.30 (d,  $J = 9.8$  Hz), 131.88, 127.94, 127.46, 126.98, 124.63, 116.01 (d,  $J = 22.4$  Hz);  $^{19}\text{F}$  NMR (376 MHz, Chloroform-*d*)  $\delta$  -103.12; HRMS (ESI-TOF) Calcd for  $\text{C}_{19}\text{H}_{10}\text{O}_4\text{F}$   $[\text{M}+\text{H}]^+$ : 321.2808; found: 321.2886.



Methyl 4-(4,9-dioxo-4,9-dihydronaphtho[2,3-*b*]furan-3-carbonyl)benzoate (**38**):

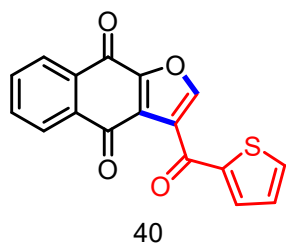
Yellow soild; Eluent: petroluem ether/ethyl acetate 10:1; 32.4 mg, 45%;  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  8.26 - 8.23 (m, 1H), 8.15 (d,  $J = 8.3$  Hz, 2H), 8.10 (s, 1H), 8.08 (d,  $J = 1.8$  Hz, 1H), 7.95 (d,  $J = 8.3$  Hz, 2H), 7.85 - 7.69 (m, 2H), 3.96 (s, 2H);  $^{13}\text{C}$  NMR (101 MHz, Chloroform-*d*)  $\delta$  187.20, 179.01, 173.70, 166.08, 153.15, 150.00, 140.31, 134.55, 134.44, 134.19, 133.21, 131.86, 129.89, 129.36, 127.85, 127.49, 126.99, 124.62, 52.57; HRMS (ESI-TOF) Calcd for  $\text{C}_{21}\text{H}_{13}\text{O}_6$   $[\text{M}+\text{H}]^+$ : 361.0707; found: 361.0668.



4-(4,9-dioxo-4,9-dihydronaphtho[2,3-*b*]furan-3-carbonyl)benzotrile (**39**):

Yellow soild; Eluent: petroluem ether/ethyl acetate 10:1; 26.2 mg, 40%;  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  8.28 - 8.23 (m, 1H), 8.14 (s, 1H), 8.11 - 8.07 (m, 1H), 7.98 (d,  $J = 8.3$  Hz, 2H), 7.85 - 7.73 (m, 4H);  $^{13}\text{C}$  NMR (101 MHz, Chloroform-*d*)  $\delta$  186.48, 178.93, 173.83, 153.18, 150.17, 140.16, 134.54, 134.38, 133.07, 132.53,

131.84, 129.75, 127.56, 127.50, 127.10, 124.16, 117.81, 117.08; HRMS (ESI-TOF)  
Calcd for C<sub>20</sub>H<sub>10</sub>O<sub>4</sub>N [M+H]<sup>+</sup>: 328.0604; found: 328.0594.



3-(thiophene-2-carbonyl)naphtho[2,3-*b*]furan-4,9-dione (**40**):

Yellow solid; Eluent: petroleum ether/ethyl acetate 10:1; 27.1 mg, 44%; <sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 8.27 - 8.22 (m, 1H), 8.20 - 8.13 (m, 1H), 8.11 (s, 1H), 7.81 - 7.76 (m, 3H), 7.67 (d, *J* = 3.7 Hz, 1H), 7.20 - 7.15 (m, 1H); <sup>13</sup>C NMR (101 MHz, Chloroform-*d*) δ 178.94, 178.73, 173.77, 153.23, 148.97, 143.86, 135.85, 134.93, 134.43, 134.08, 133.41, 131.85, 128.44, 127.87, 127.55, 126.93, 124.69; HRMS (ESI-TOF) Calcd for C<sub>17</sub>H<sub>9</sub>O<sub>4</sub>S [M+H]<sup>+</sup>: 309.0216; found: 309.0259.



## 9 X-ray crystallography studies of compound 3

### 9.1 X-ray crystallography studies of compound 3

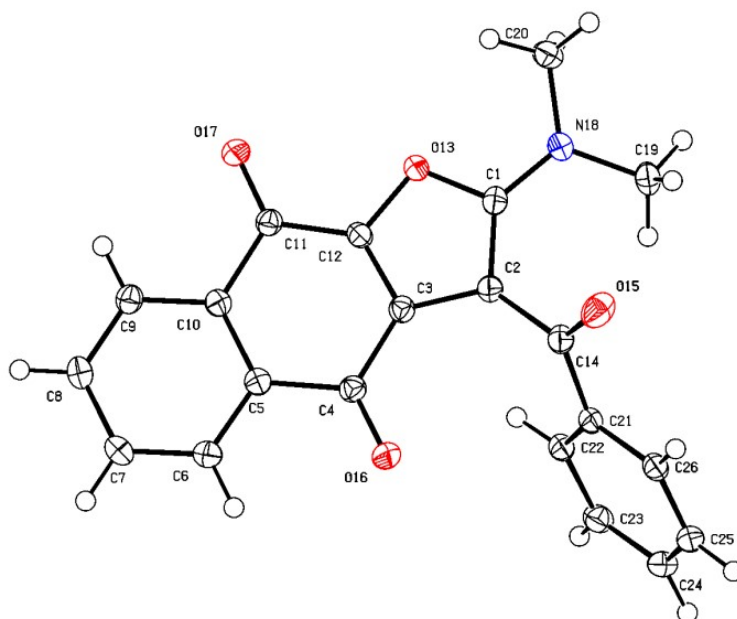


Figure S8: Structure of **3** by X-Ray crystallographic (CCDC = 2211797)

Single crystal suitable for X-ray diffraction was obtained by slow evaporation of a solution of compound **3** ( $\text{CDCl}_3$ ) in a loosely capped vial.

Table S7: Crystal data and structure refinement for **3**

Empirical formula	$\text{C}_{21}\text{H}_{15}\text{NO}_4$
Formula weight	345.34
Temperature/K	100.00(10)
Crystal system	monoclinic
Space group	$P2_1/n$
$a/\text{\AA}$	6.92640(10)
$b/\text{\AA}$	12.02970(10)
$c/\text{\AA}$	19.0496(2)
$\alpha/^\circ$	90
$\beta/^\circ$	99.2970(10)
$\gamma/^\circ$	90

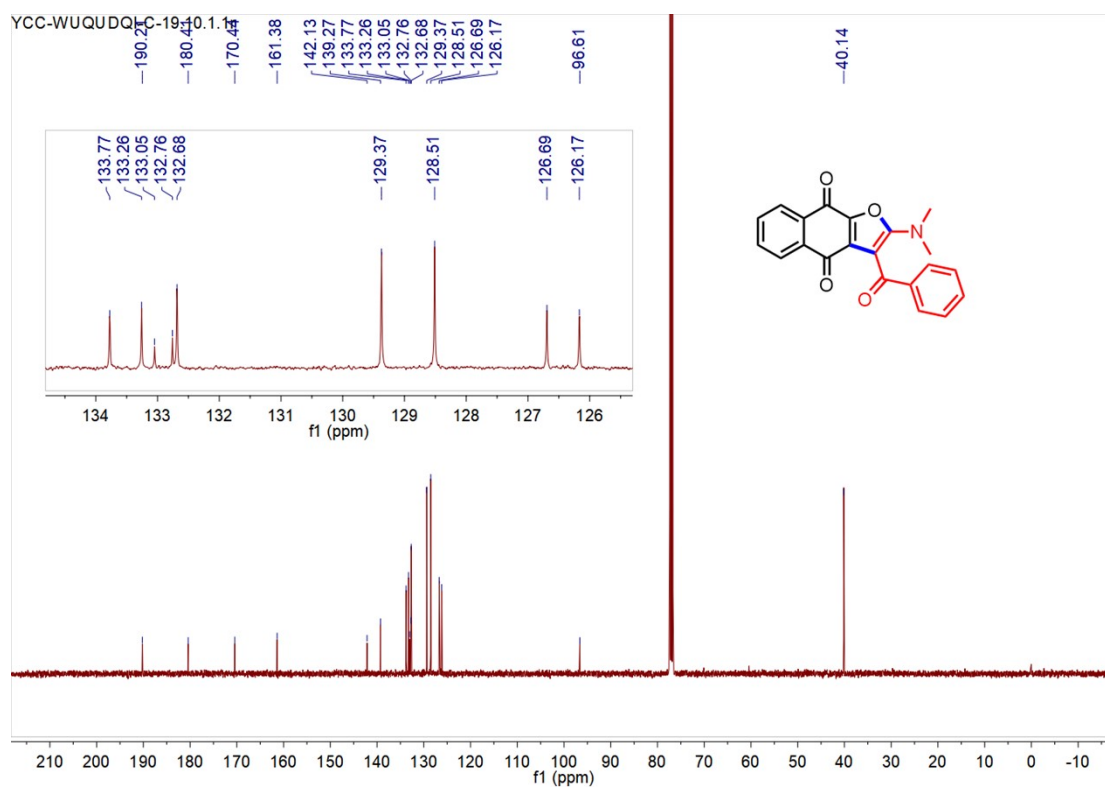
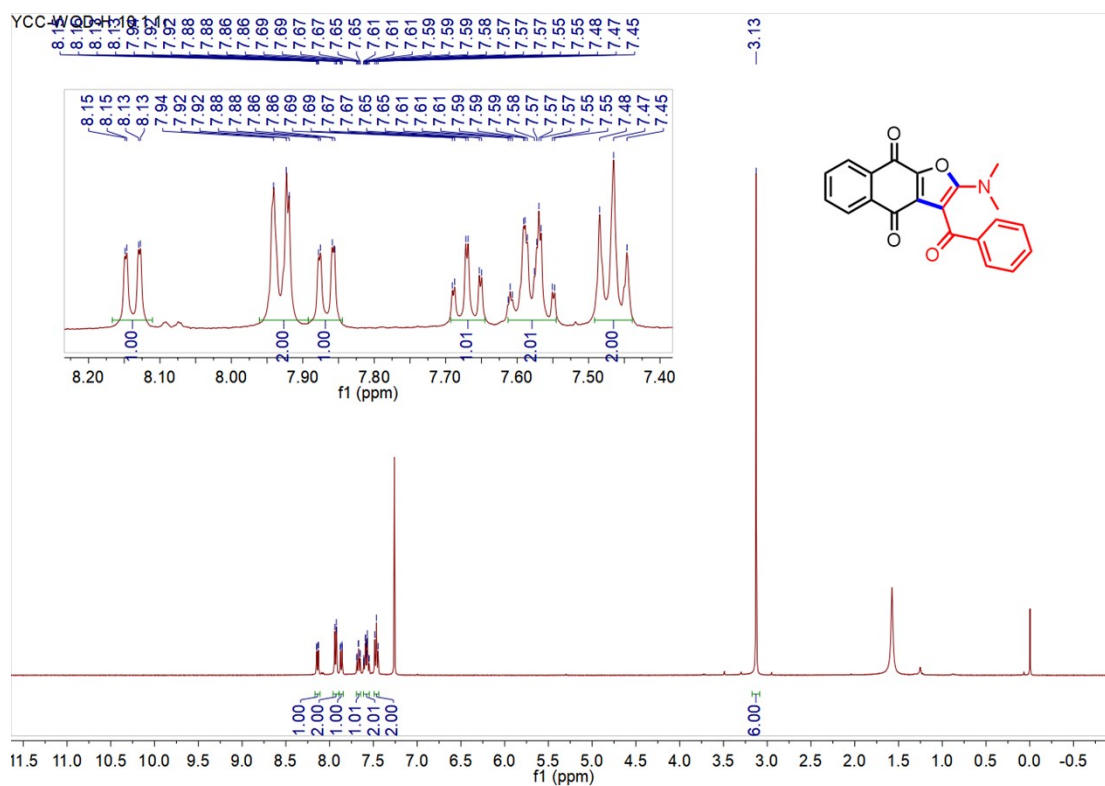
Volume/Å <sup>3</sup>	1566.41(3)
Z	4
ρ <sub>calc</sub> /cm <sup>3</sup>	1.464
μ/mm <sup>-1</sup>	0.839
F(000)	720.0
Crystal size/mm <sup>3</sup>	0.15 × 0.15 × 0.15
Radiation	CuKα (λ = 1.54184)
2θ range for data collection/°	8.726 to 153.64
Index ranges	-8 ≤ h ≤ 7, -14 ≤ k ≤ 14, -23 ≤ l ≤ 24
Reflections collected	29000
Independent reflections	3206 [R <sub>int</sub> = 0.0304, R <sub>sigma</sub> = 0.0152]
Data/restraints/parameters	3206/0/238
Largest diff. peak/hole / e Å <sup>-3</sup>	0.29/-0.19

## 10 References

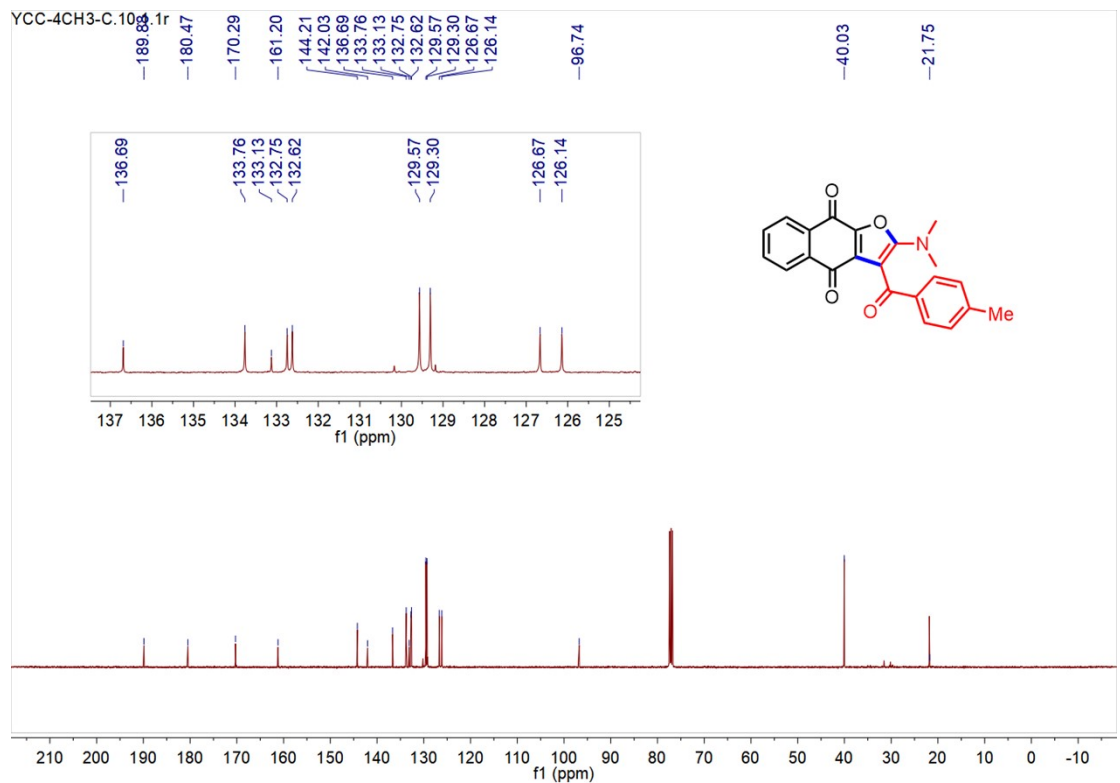
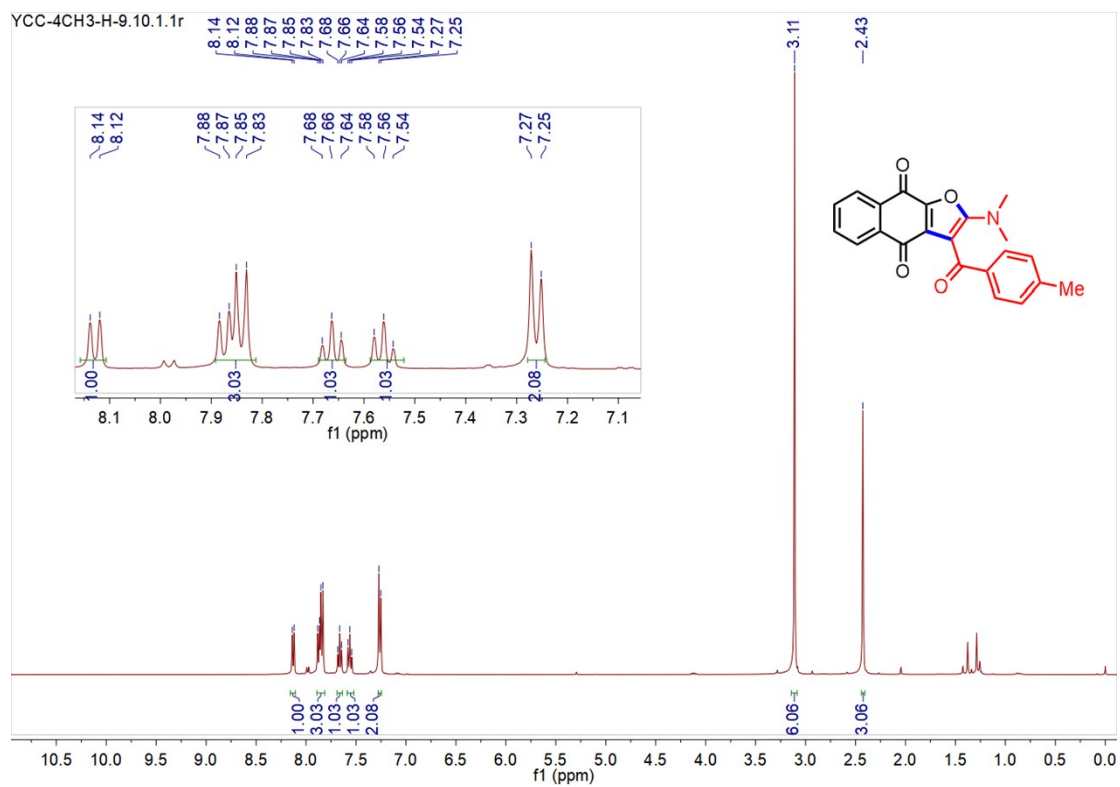
- 1 H. Jia, J. Yu, X. Du, S. Cherukupalli, P. Zhan, X. Liu, Design, diversity-oriented synthesis and biological evaluation of novel heterocycle derivatives as non-nucleoside HBV capsid protein inhibitors, *European Journal of Medicinal Chemistry*, 2020, 202, 112495.
- 2 J. Li, J. Zhang, M. Li, C. Zhang, Y. Yuan, R. Liu, Naphtho[2,3-b]furan-4,9-dione synthesis via palladium-catalyzed reverse hydrogenolysis. *Chemical Communications*, 2019, 55, 2348-2351.
- 3 L. Gomes, P. Coiffin, Synthesis and isomerization of 3-aryl-4-hydroxynaphtho [2,3-b]furans. *Comptes Rendus des Seances de l'Academie des Sciences, Serie C: Sciences Chimiques*, 1976, 282, 429-432.

# 11 NMR Spectra for Electrolysis Products

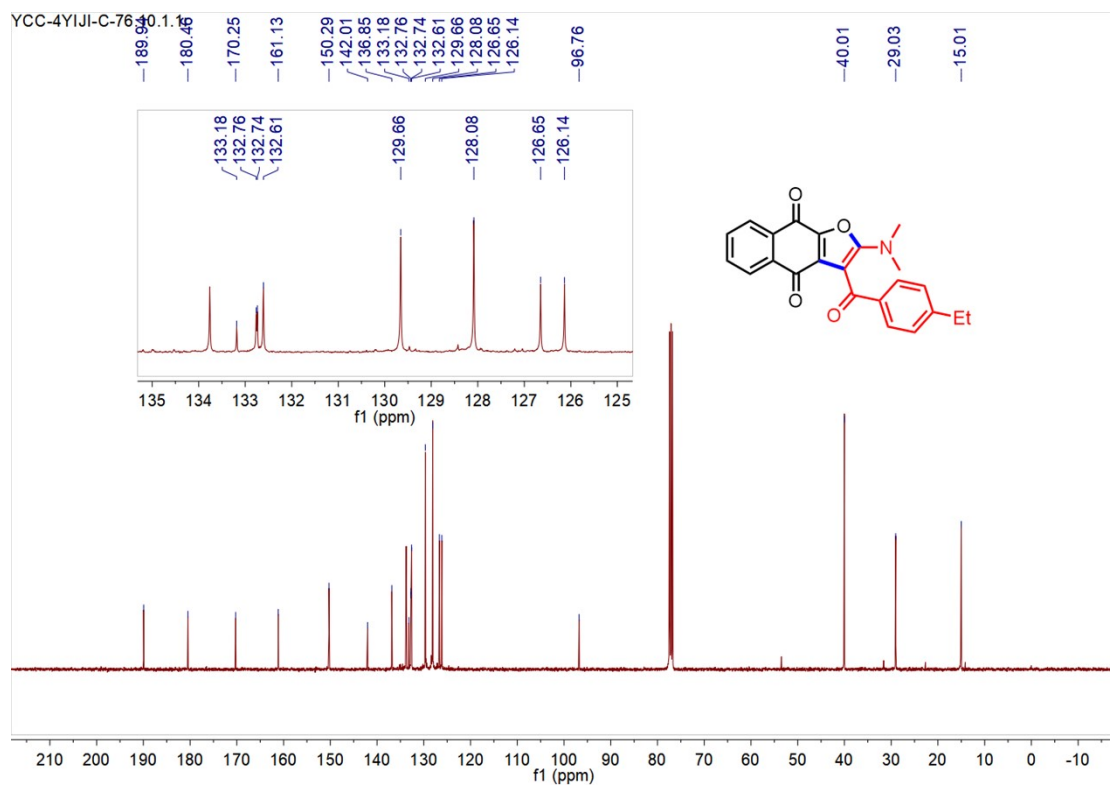
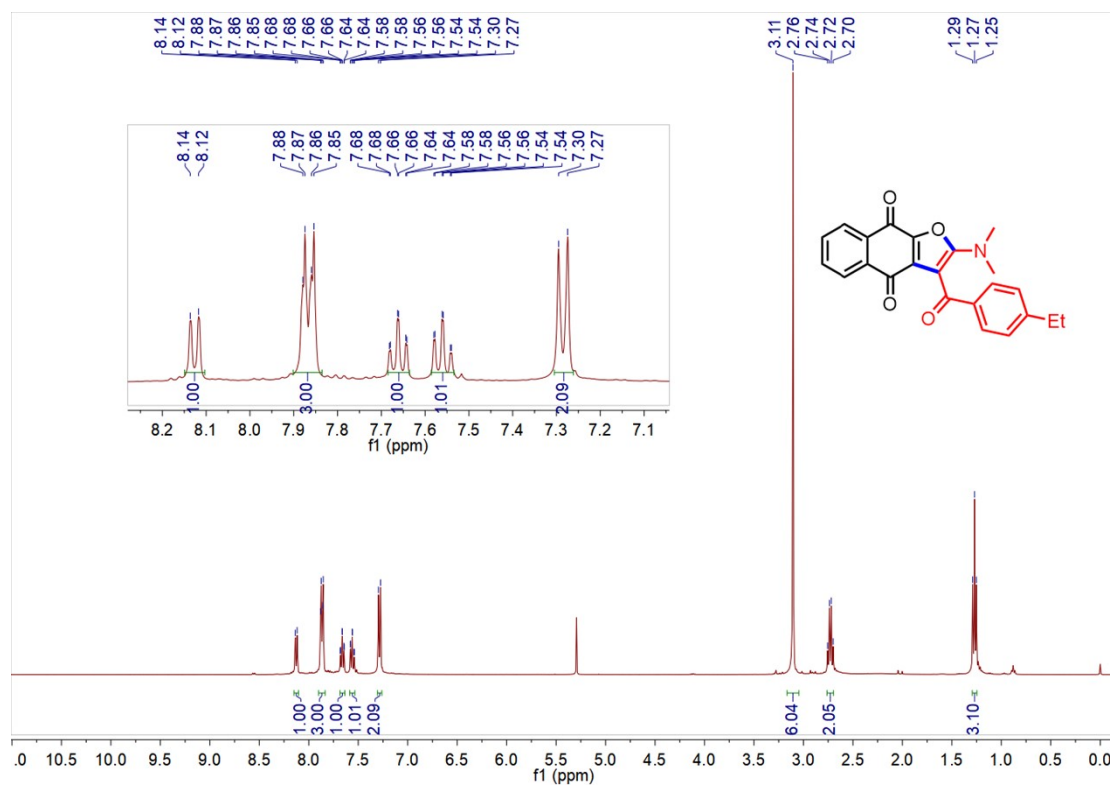
3-benzoyl-2-(dimethylamino)naphtho[1,2-*b*]furan-4,5-dione (**3**):



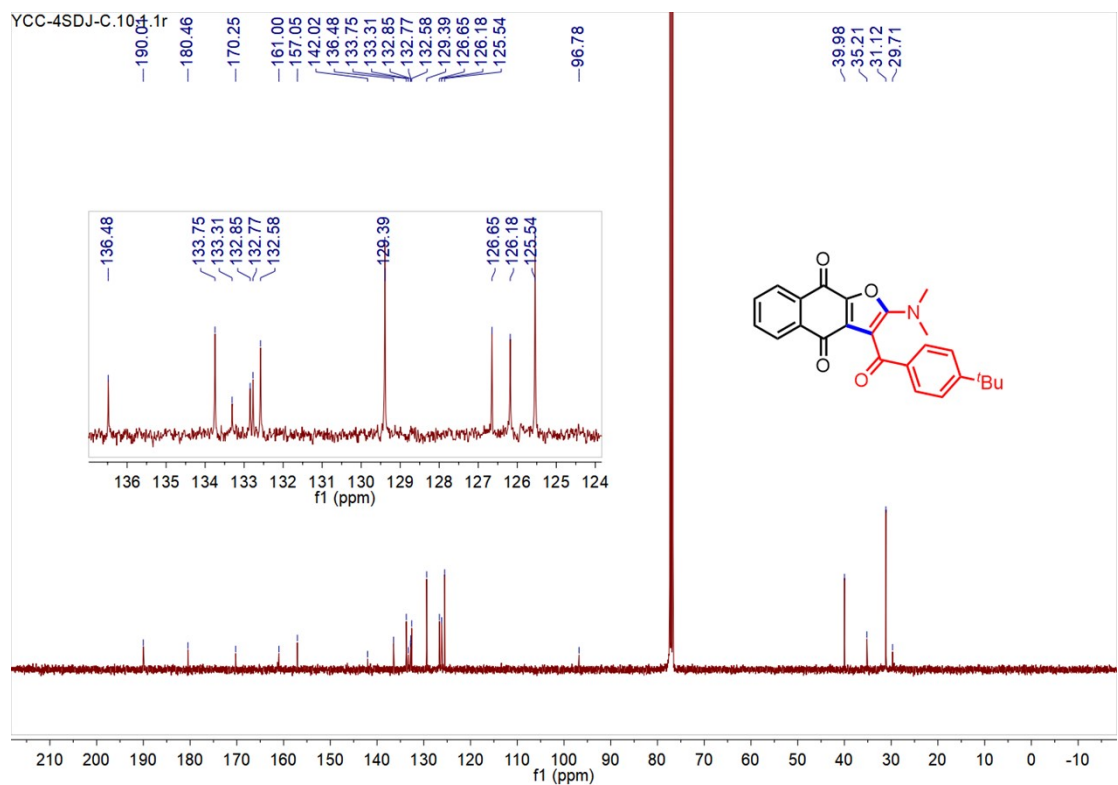
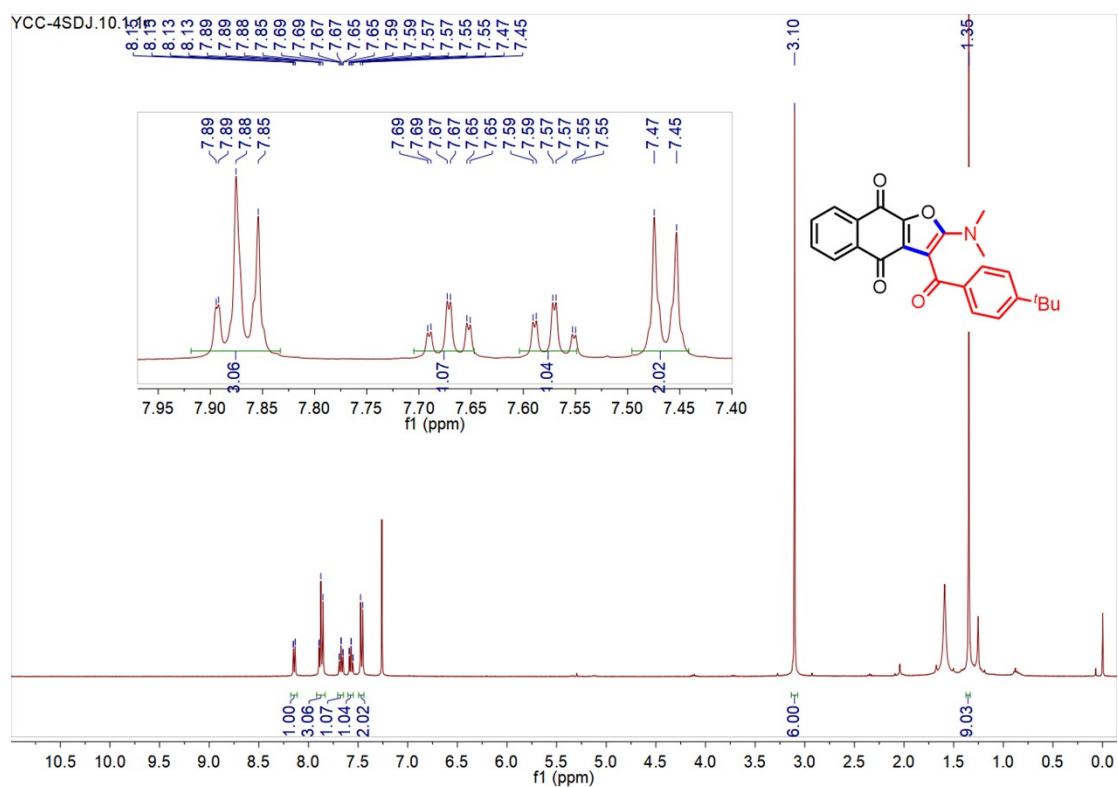
2-(dimethylamino)-3-(4-methylbenzoyl)naphtho[2,3-*b*]furan-4,9-dione (**5**):



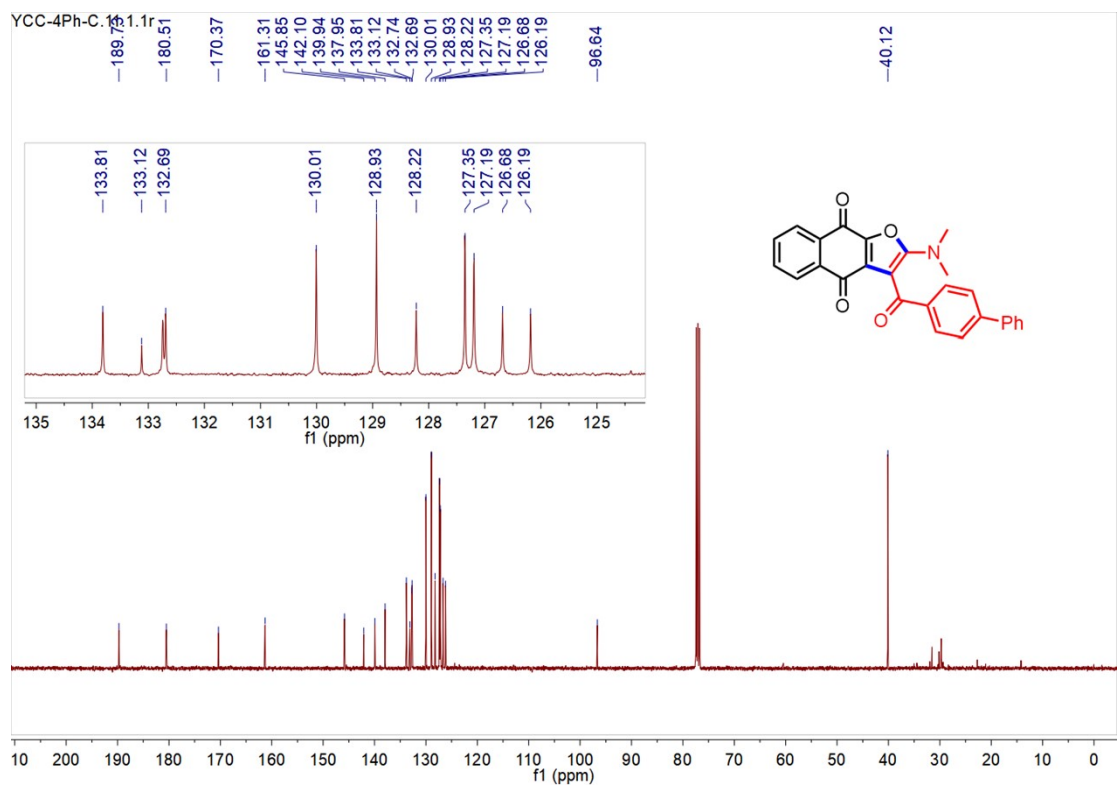
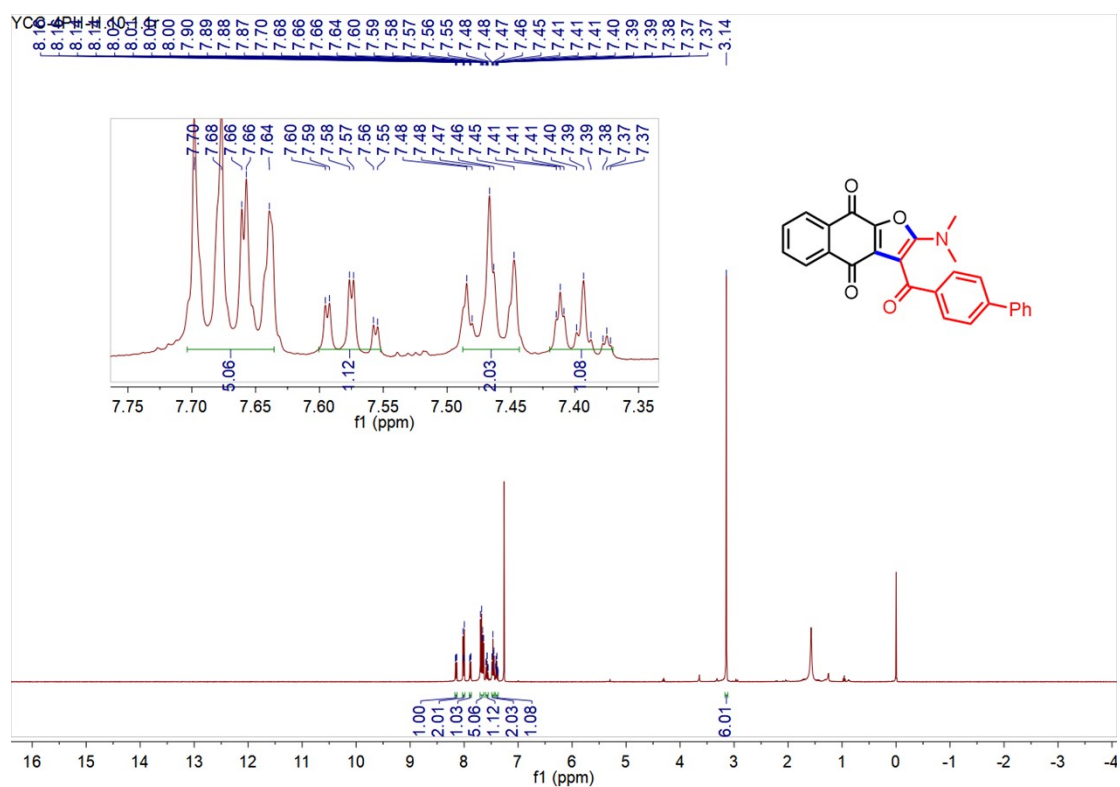
2-(dimethylamino)-3-(4-ethylbenzoyl)naphtho[2,3-*b*]furan-4,9-dione (**6**):



3-(4-(*tert*-butyl)benzoyl)-2-(dimethylamino)naphtho[2,3-*b*]furan-4,9-dione (7):

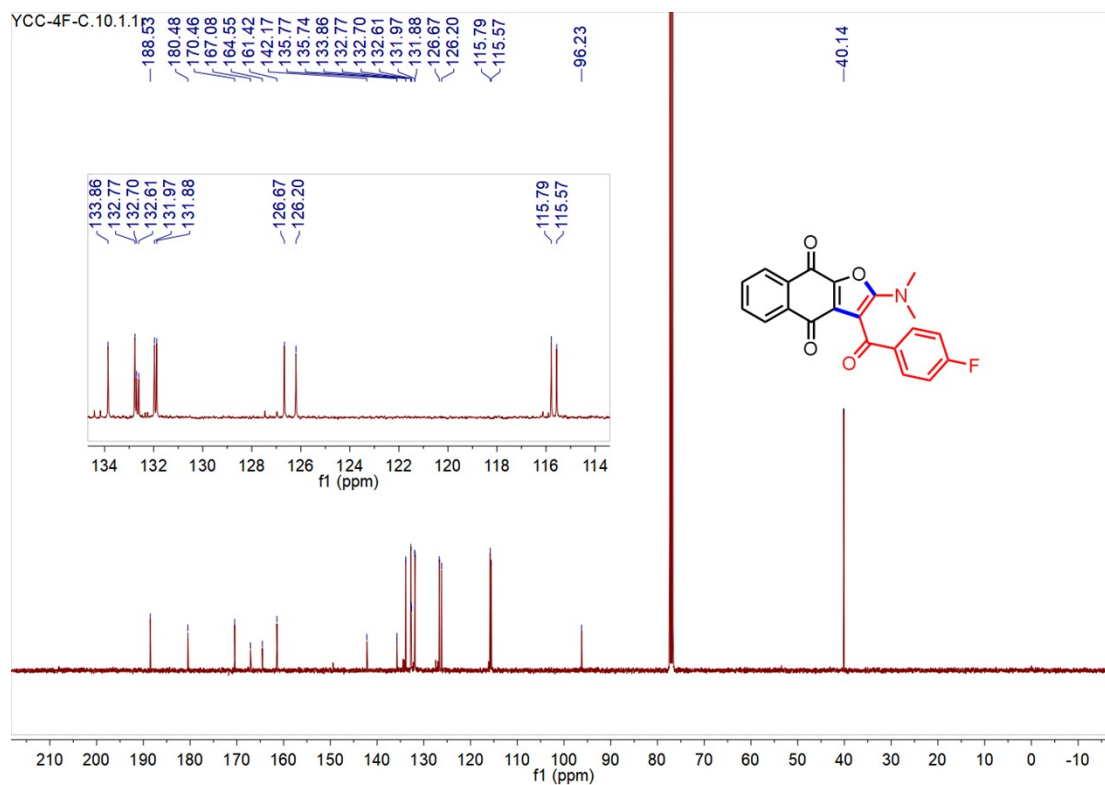
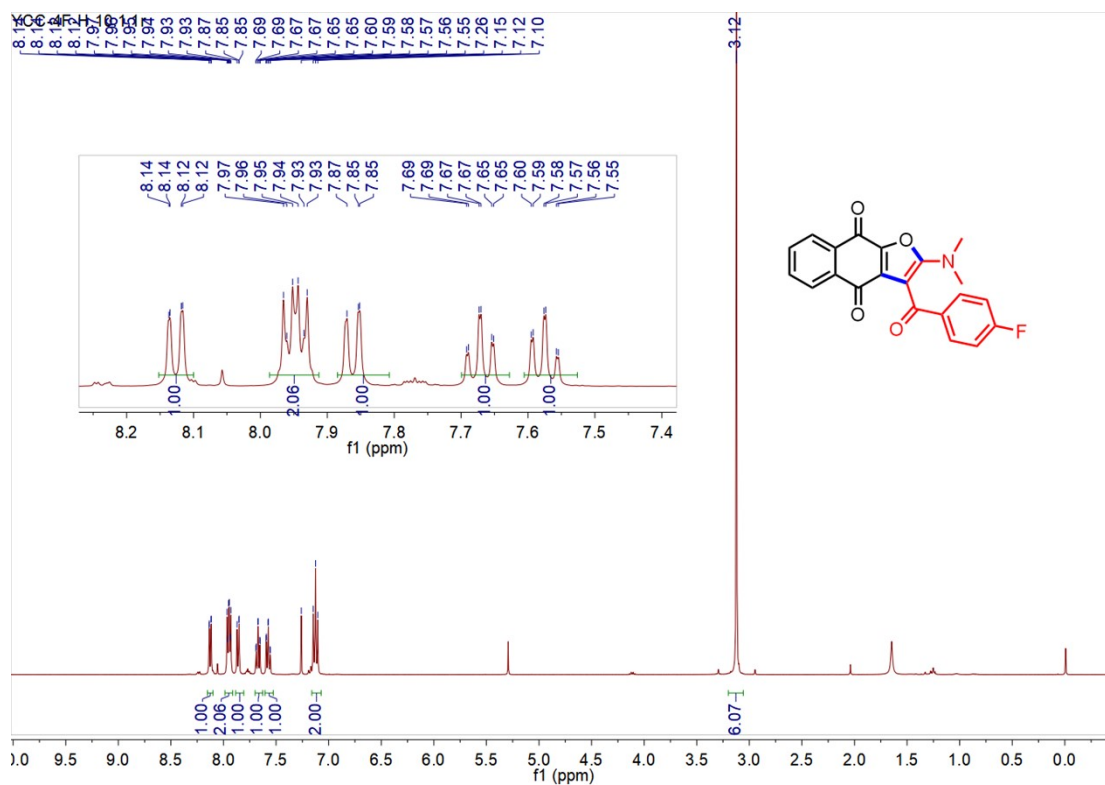


3-([1,1'-biphenyl]-4-carbonyl)-2-(dimethylamino)naphtho[2,3-*b*]furan-4,9-dione (**8**):

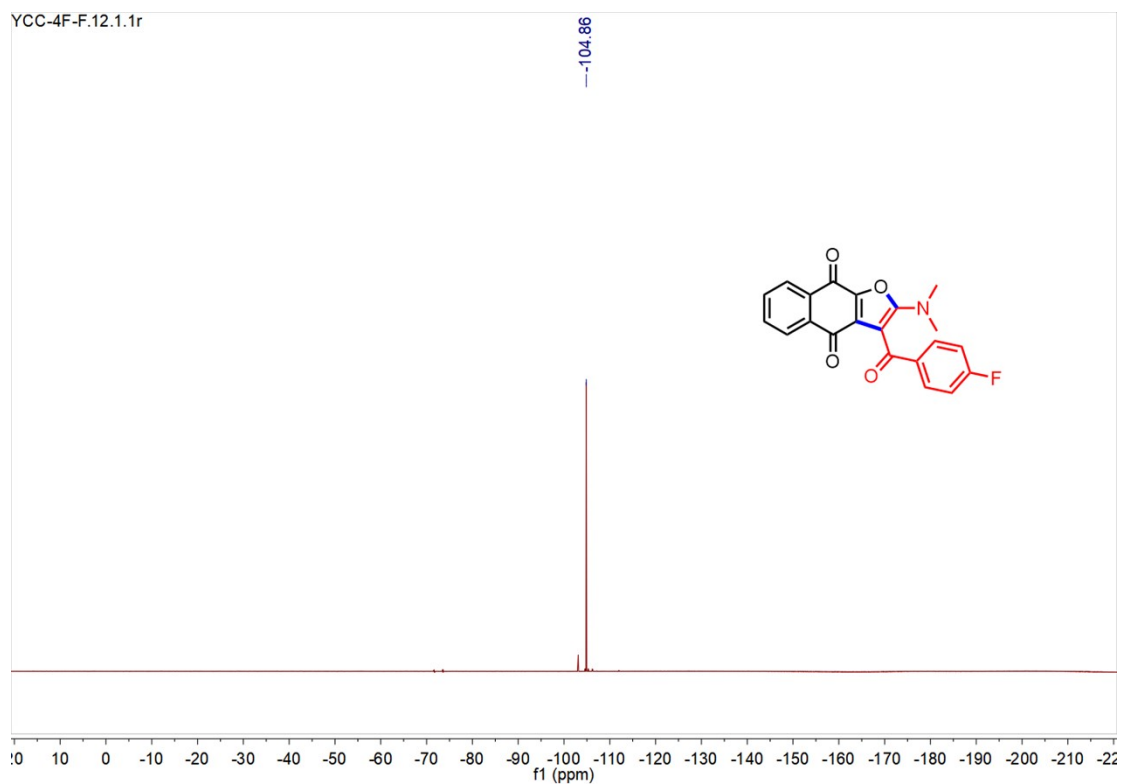




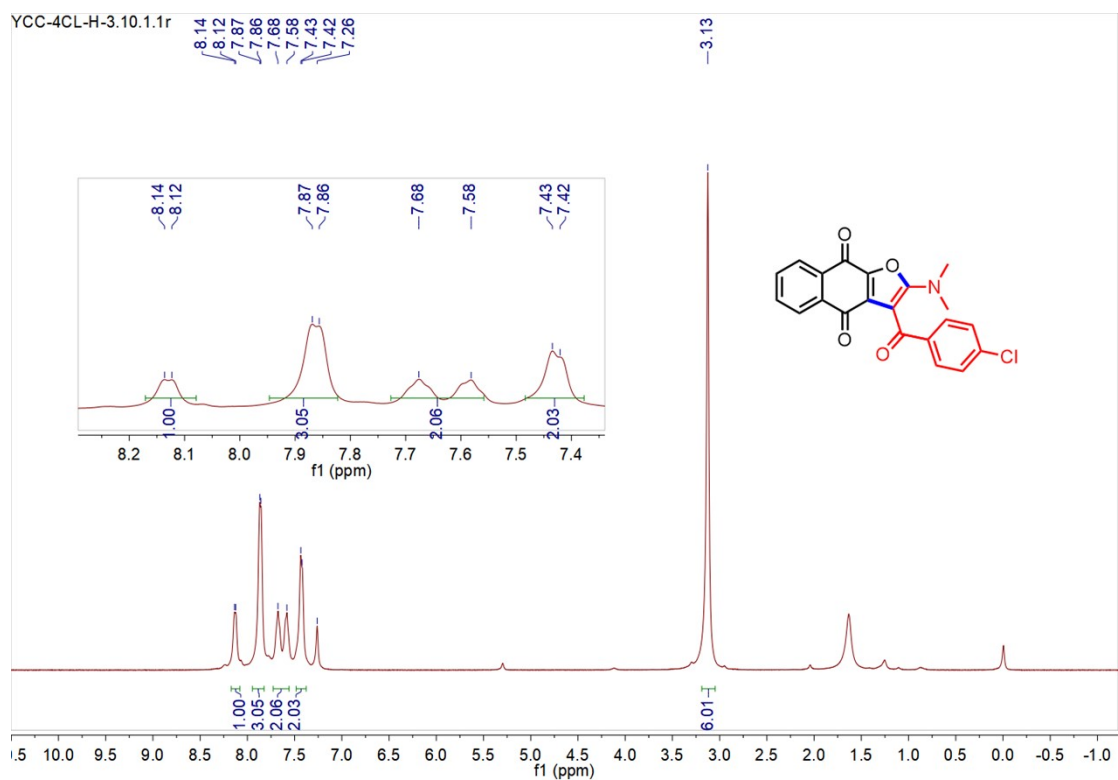
2-(dimethylamino)-3-(4-fluorobenzoyl)naphtho[2,3-*b*]furan-4,9-dione (9):

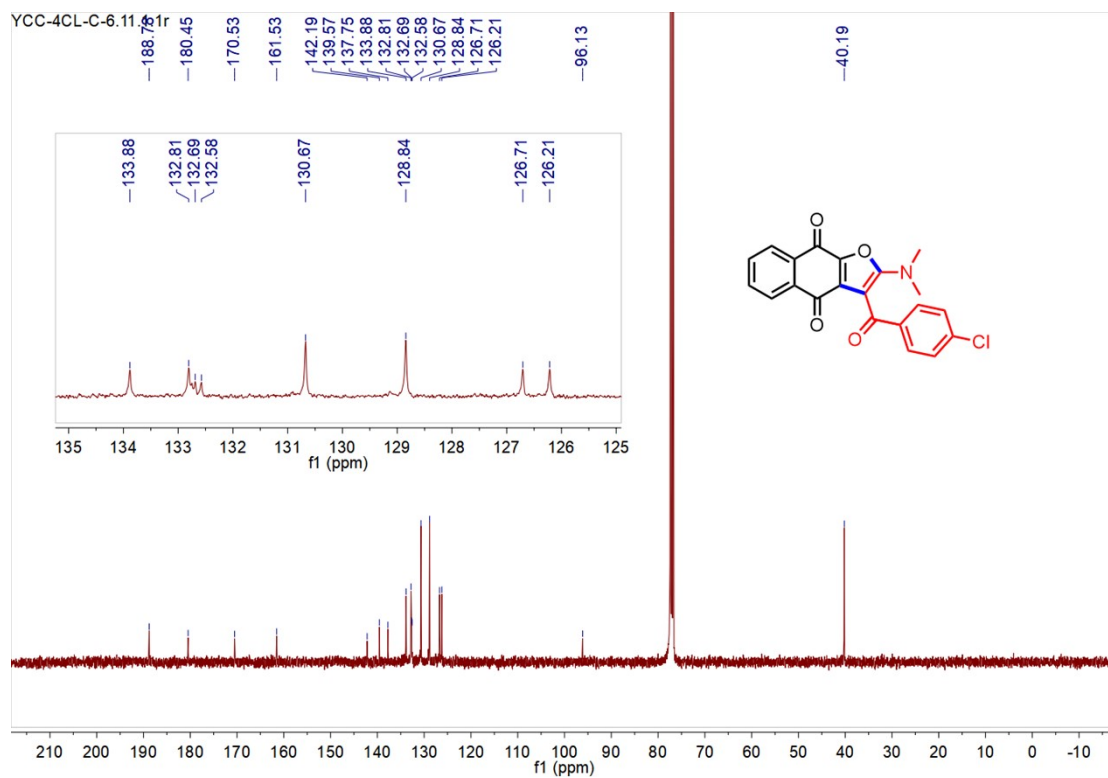




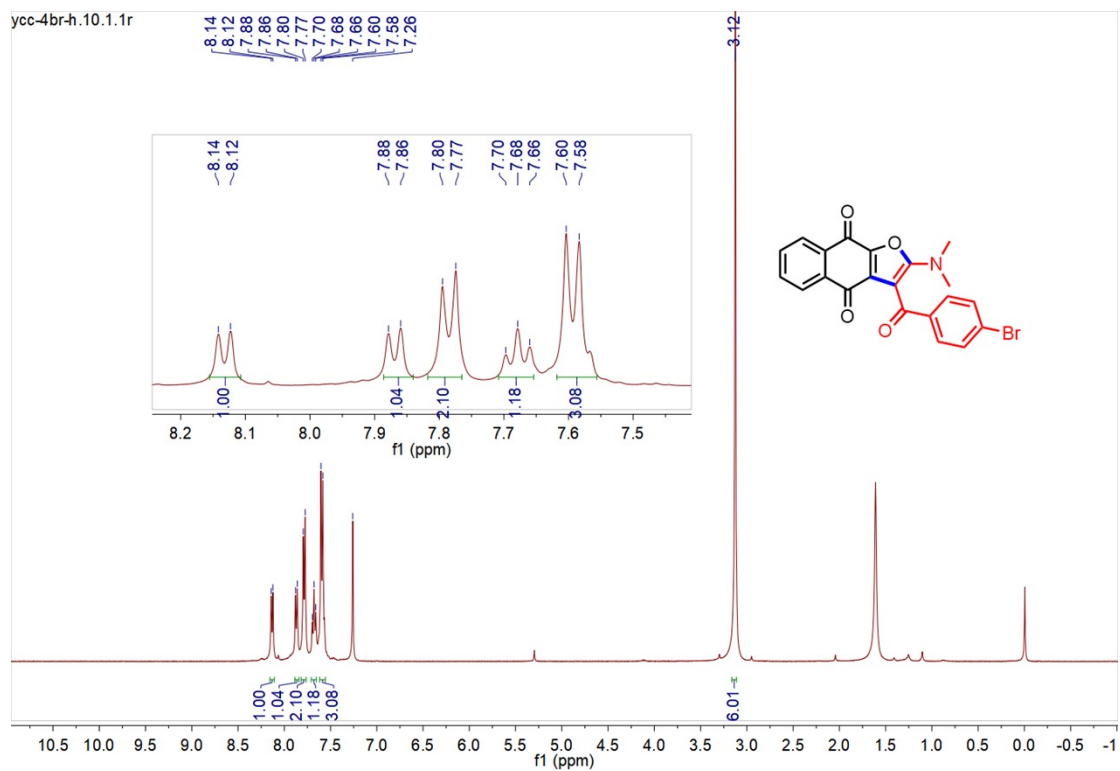


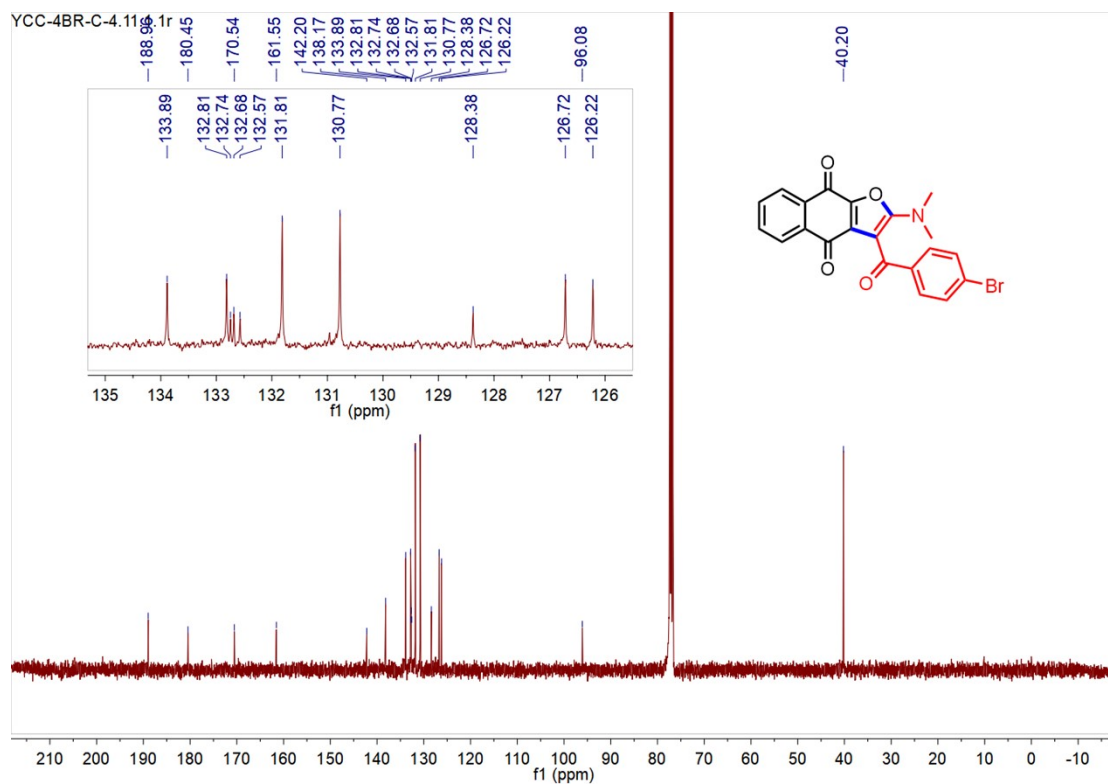
3-(4-chlorobenzoyl)-2-(dimethylamino)naphtho[2,3-b]furan-4,9-dione (**10**):



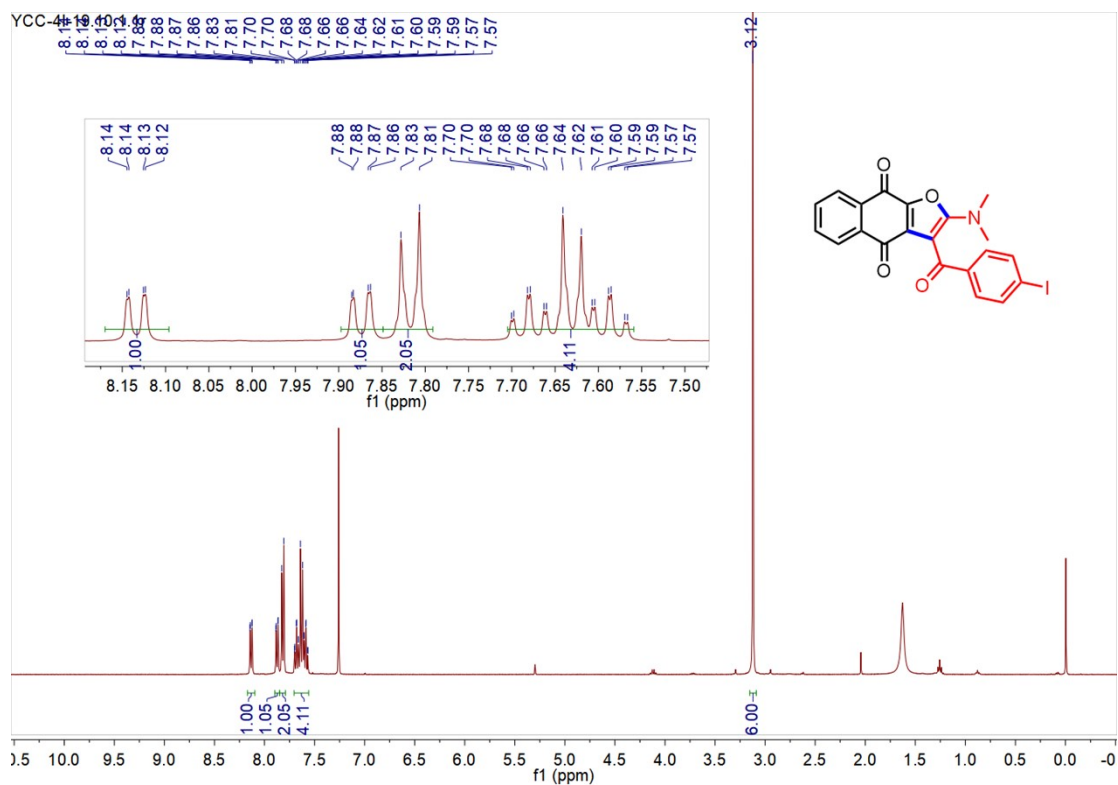


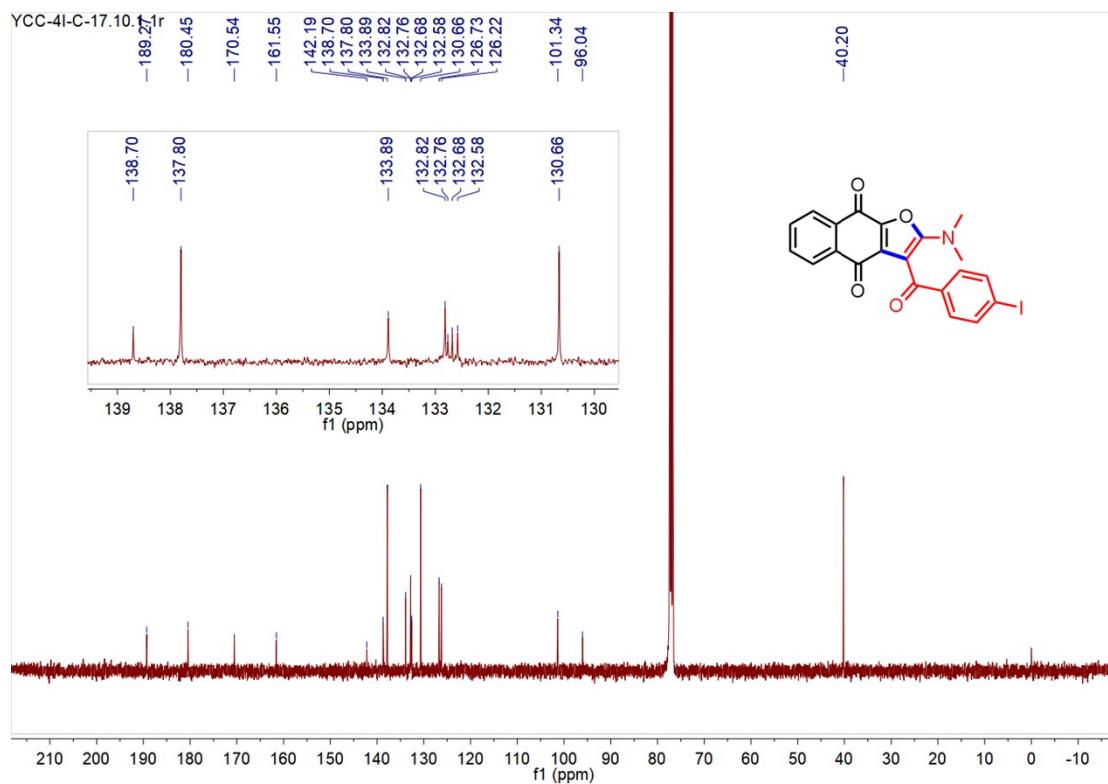
3-(4-bromobenzoyl)-2-(dimethylamino)naphtho[2,3-b]furan-4,9-dione (**11**):



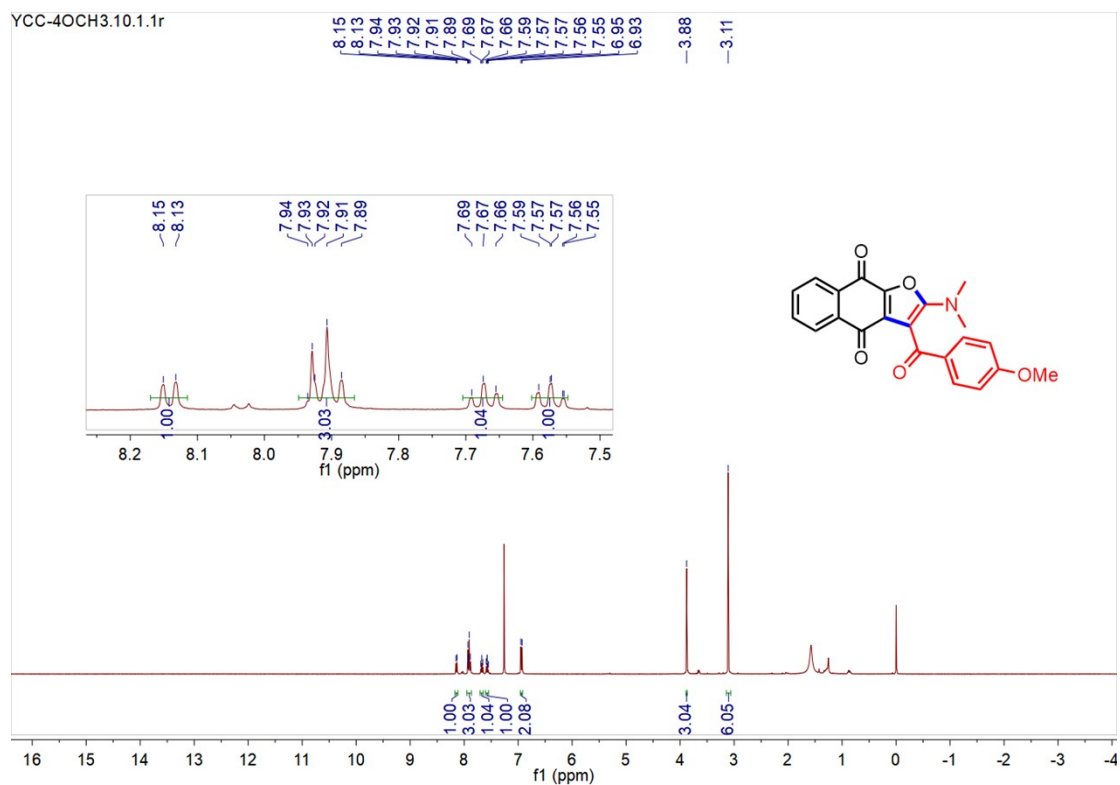


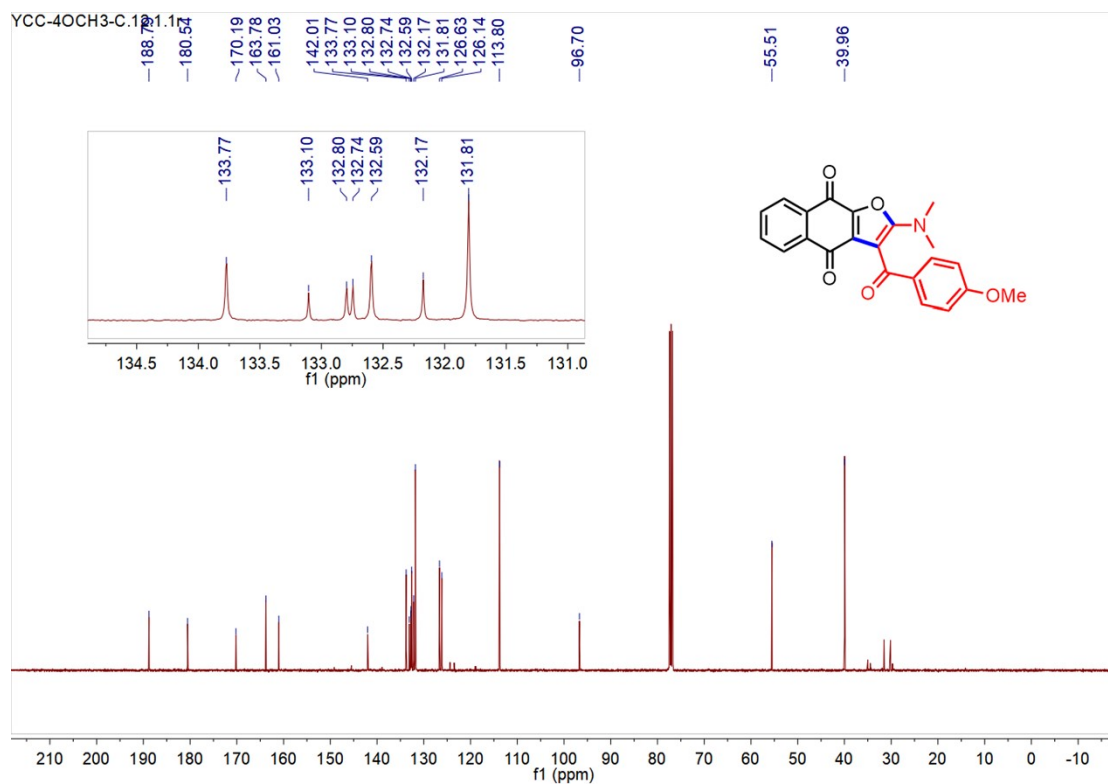
2-(dimethylamino)-3-(4-iodobenzoyl)naphtho[2,3-b]furan-4,9-dione (**12**):



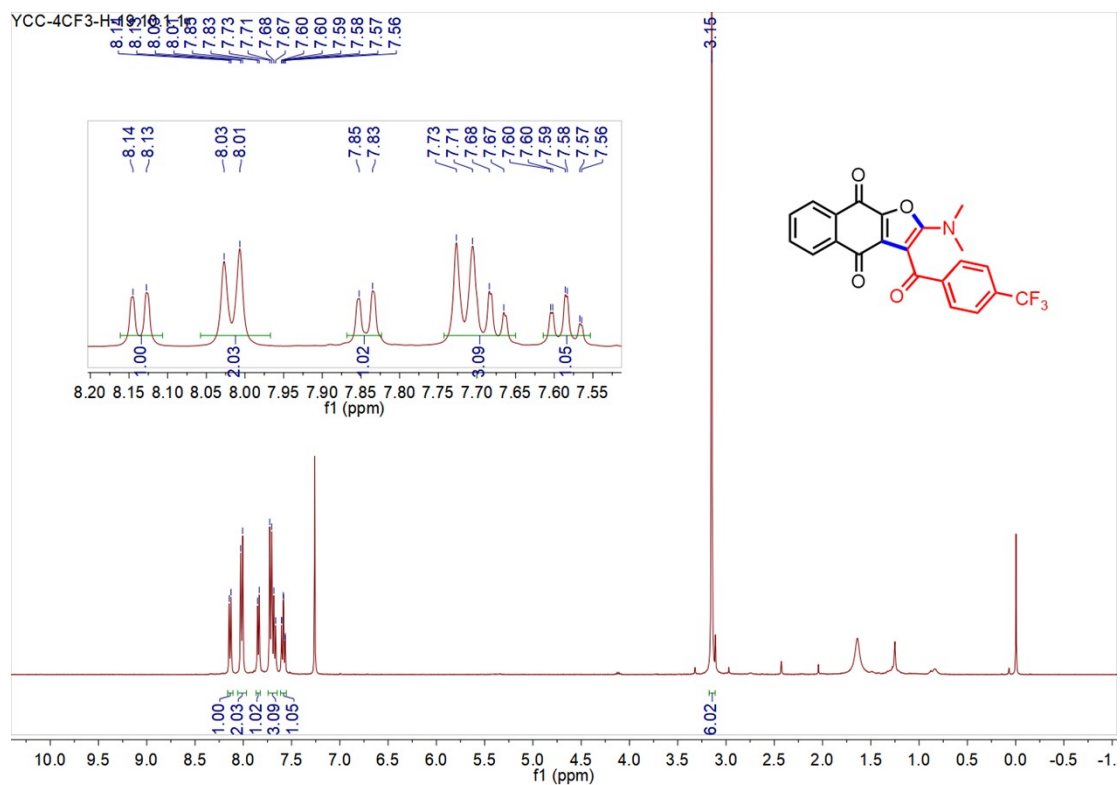


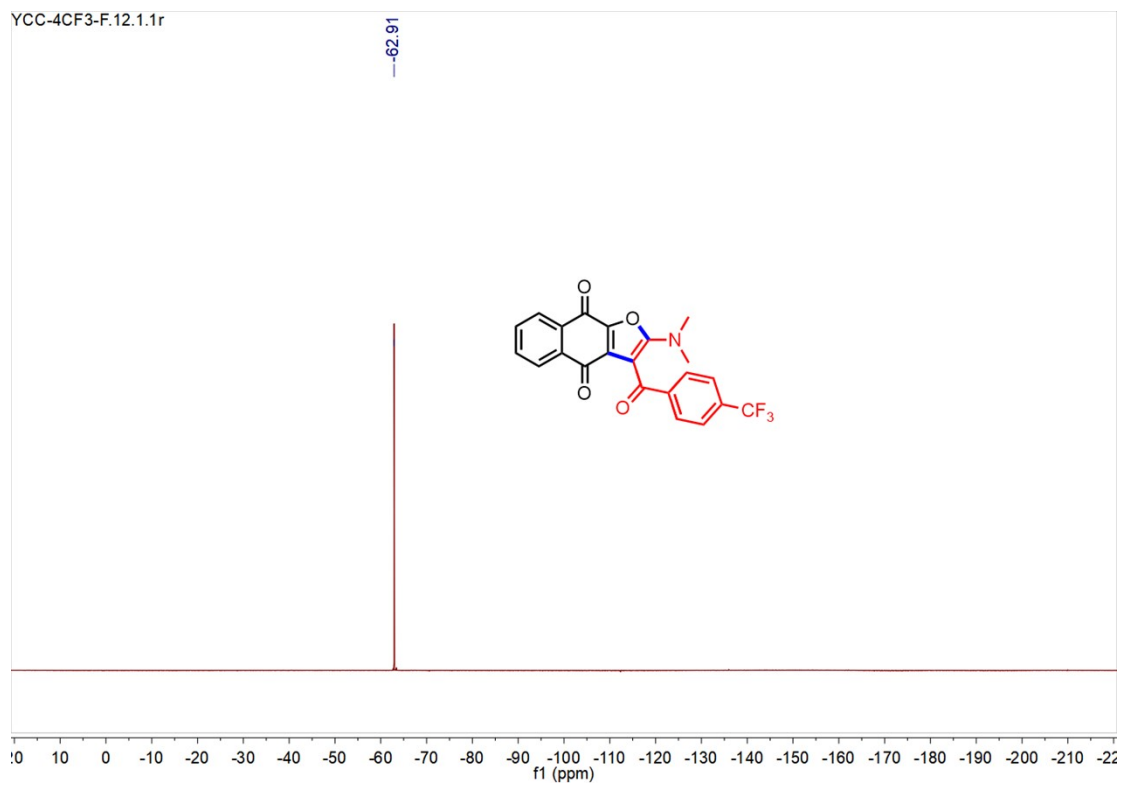
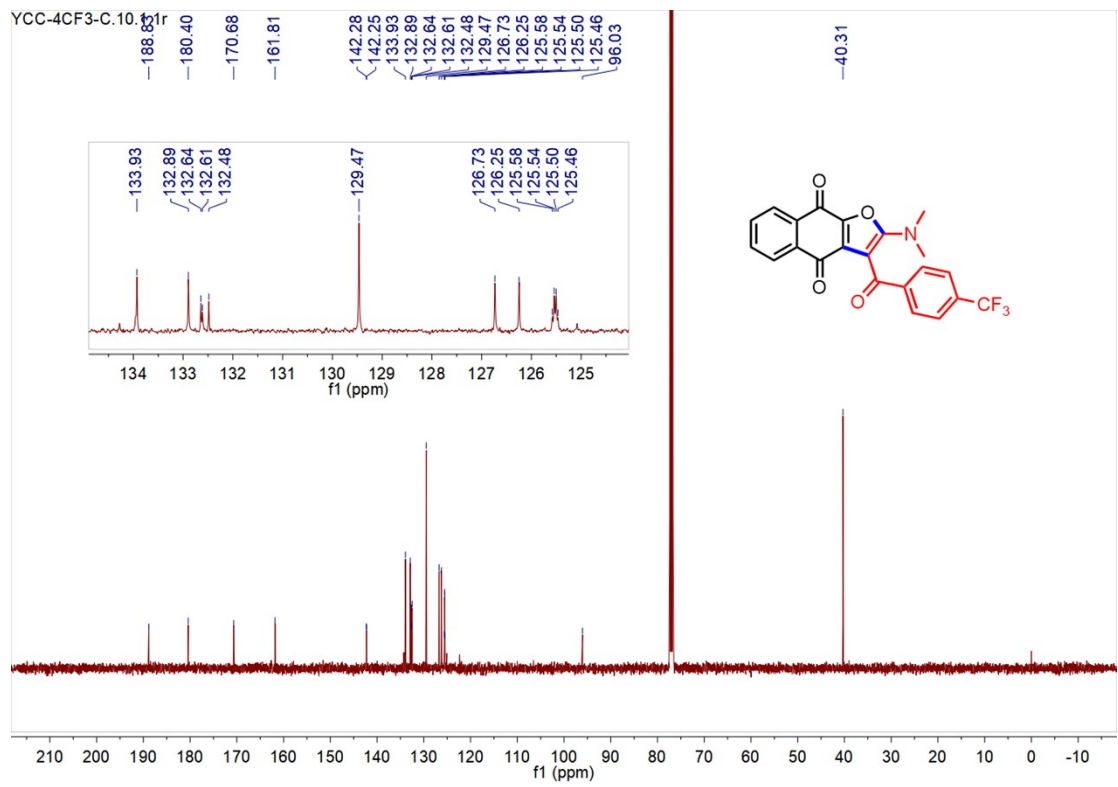
2-(dimethylamino)-3-(4-methoxybenzoyl)naphtho[2,3-b]furan-4,9-dione (**13**):



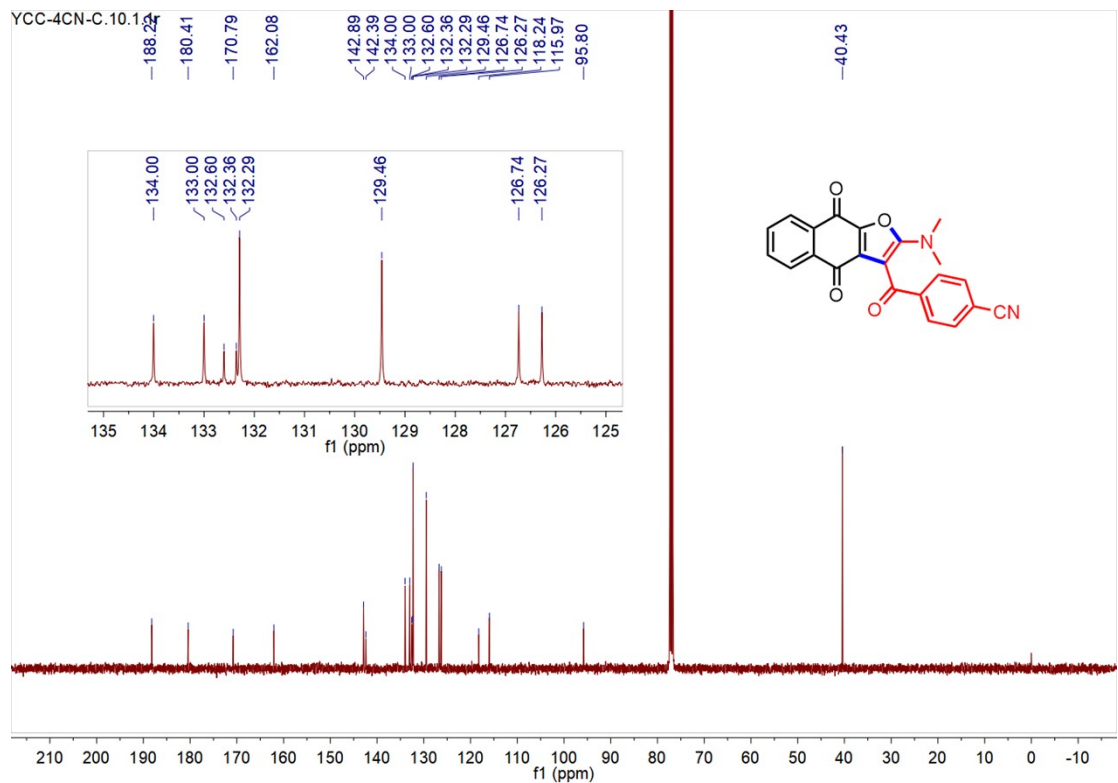
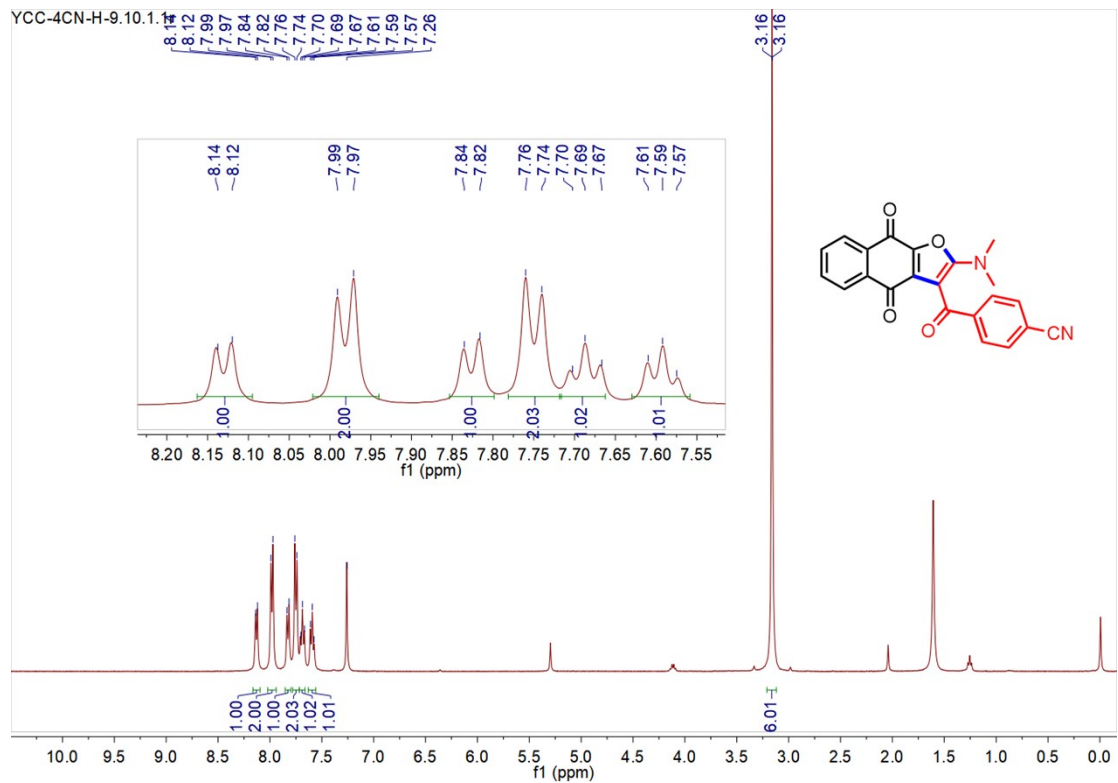


2-(dimethylamino)-3-(4-(trifluoromethyl)benzoyl)naphtho[2,3-b]furan-4,9-dione (**14**):



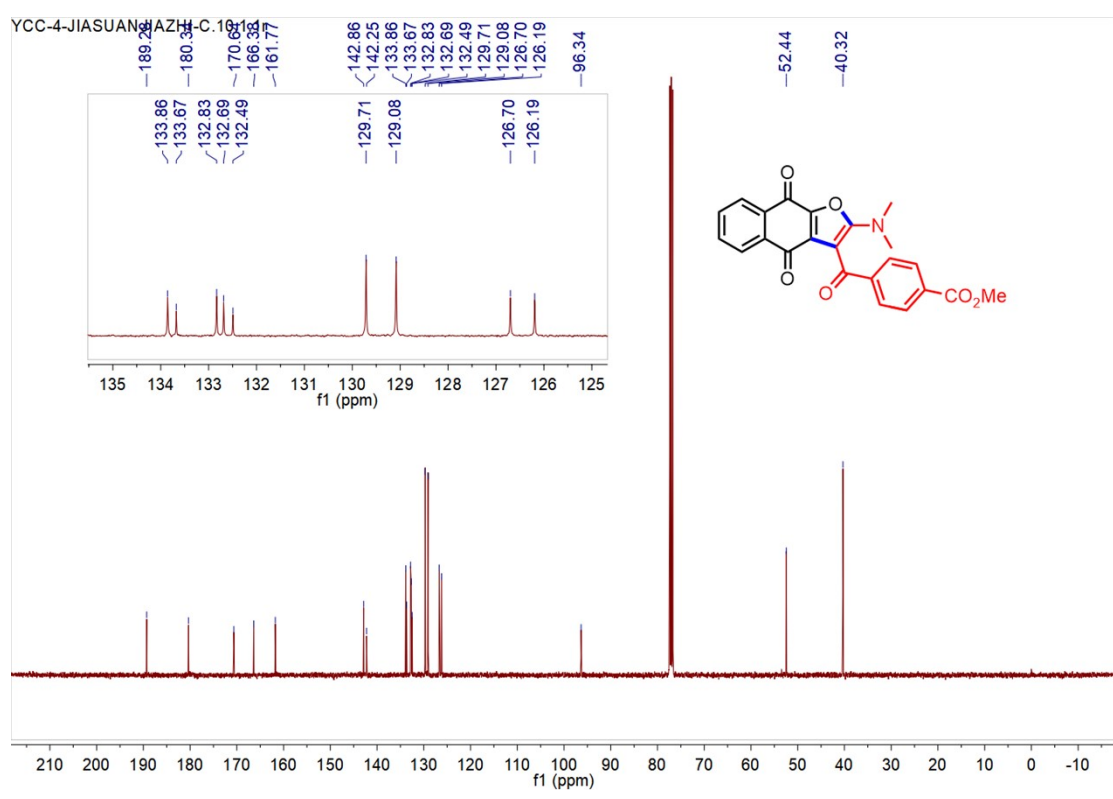
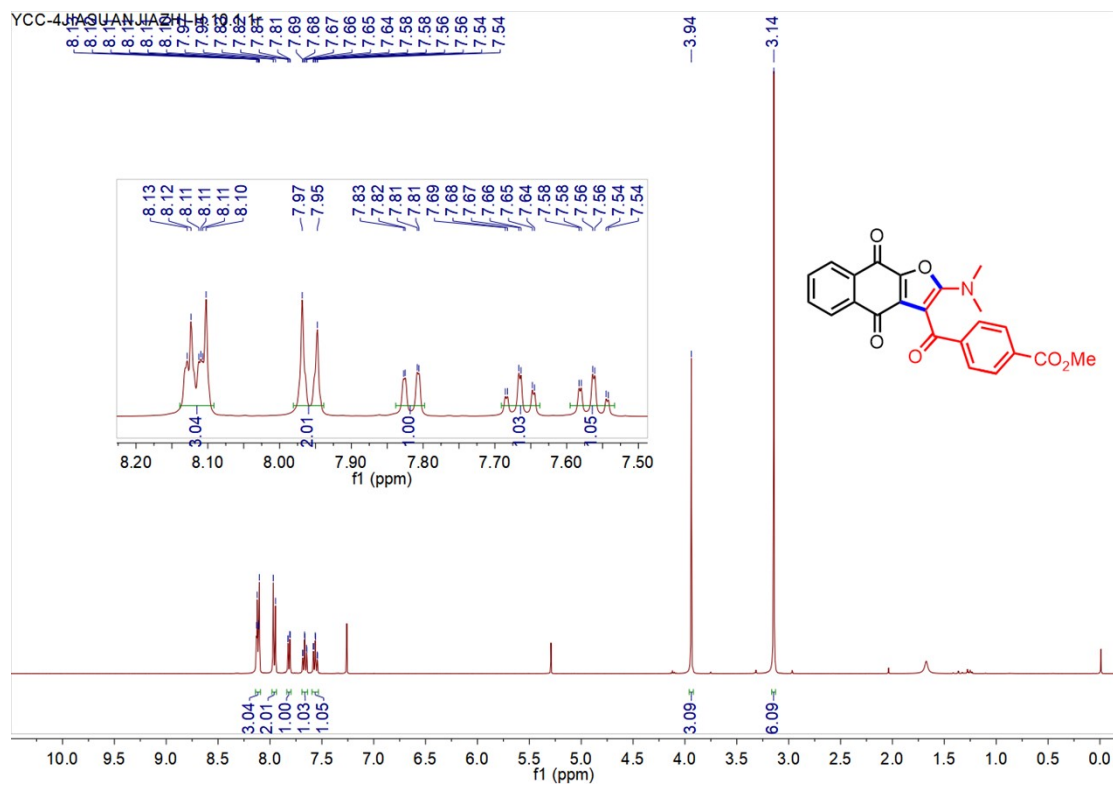


4-(2-(dimethylamino)-4,9-dioxo-4,9-dihydro-naphtho[2,3-*b*]furan-3-carbonyl)benzonitrile (**15**):



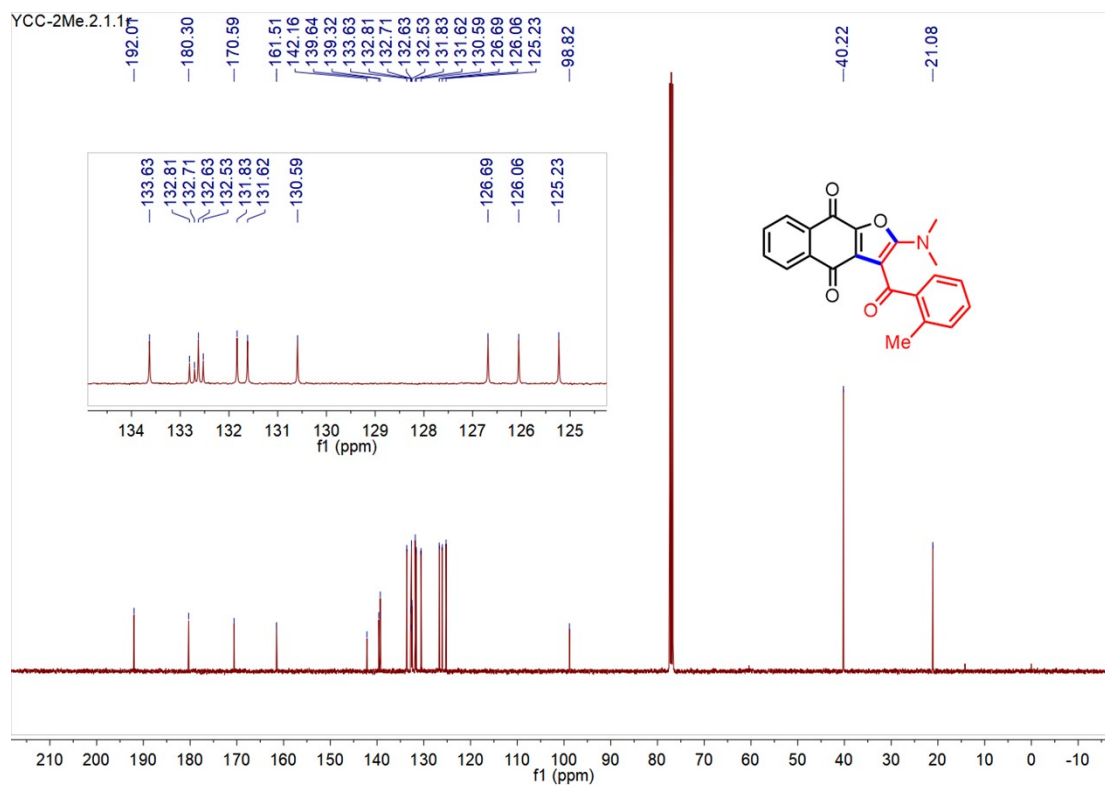
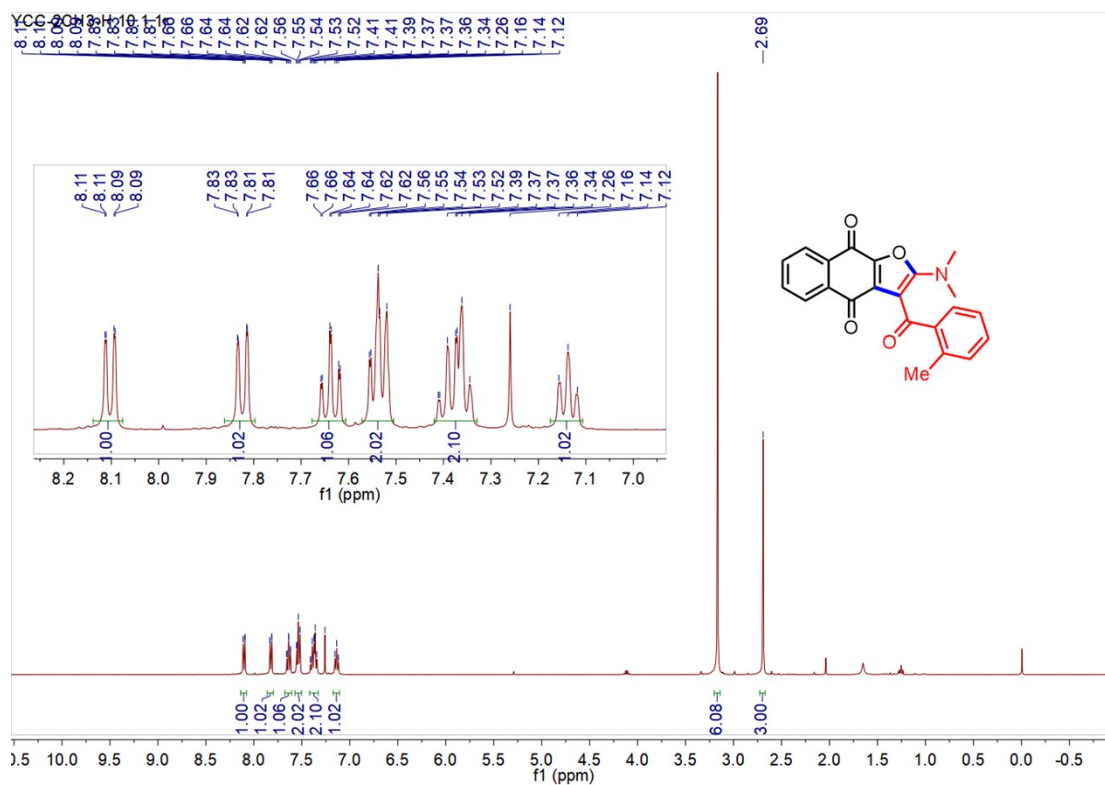


methyl 4-(2-(dimethylamino)-4,9-dioxo-4,9-dihydronaphtho[2,3-b]furan-3-carbonyl)benzoate (**16**):

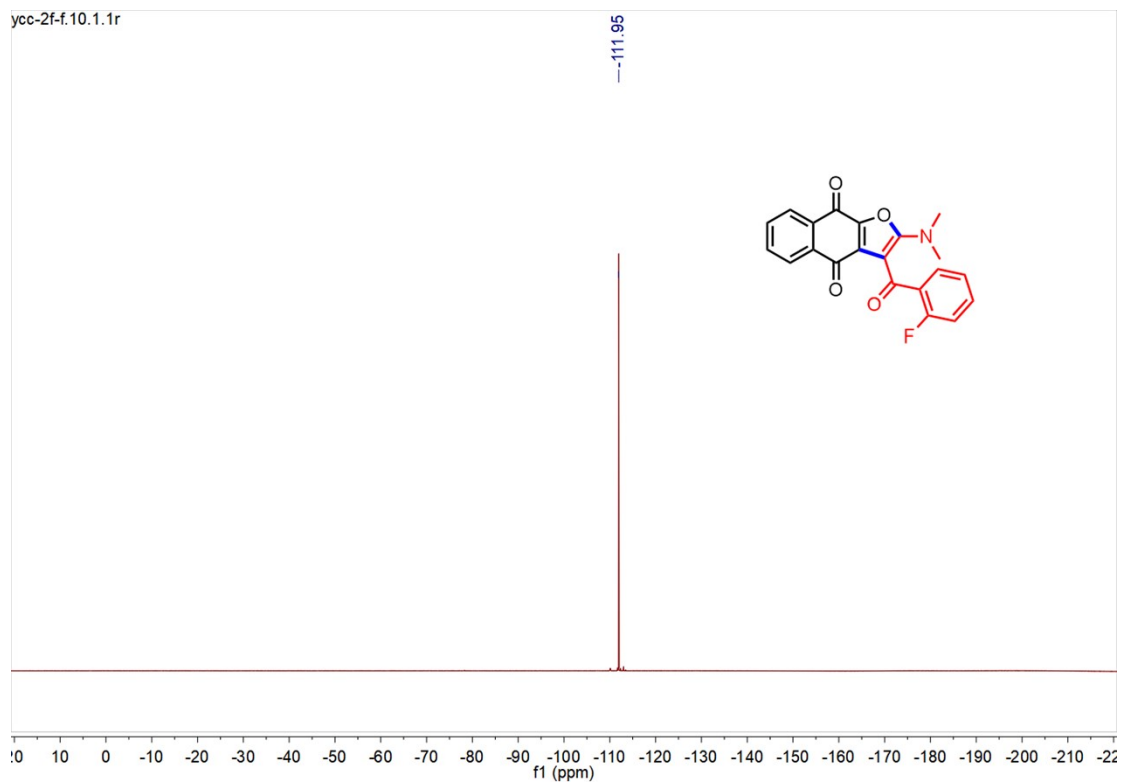




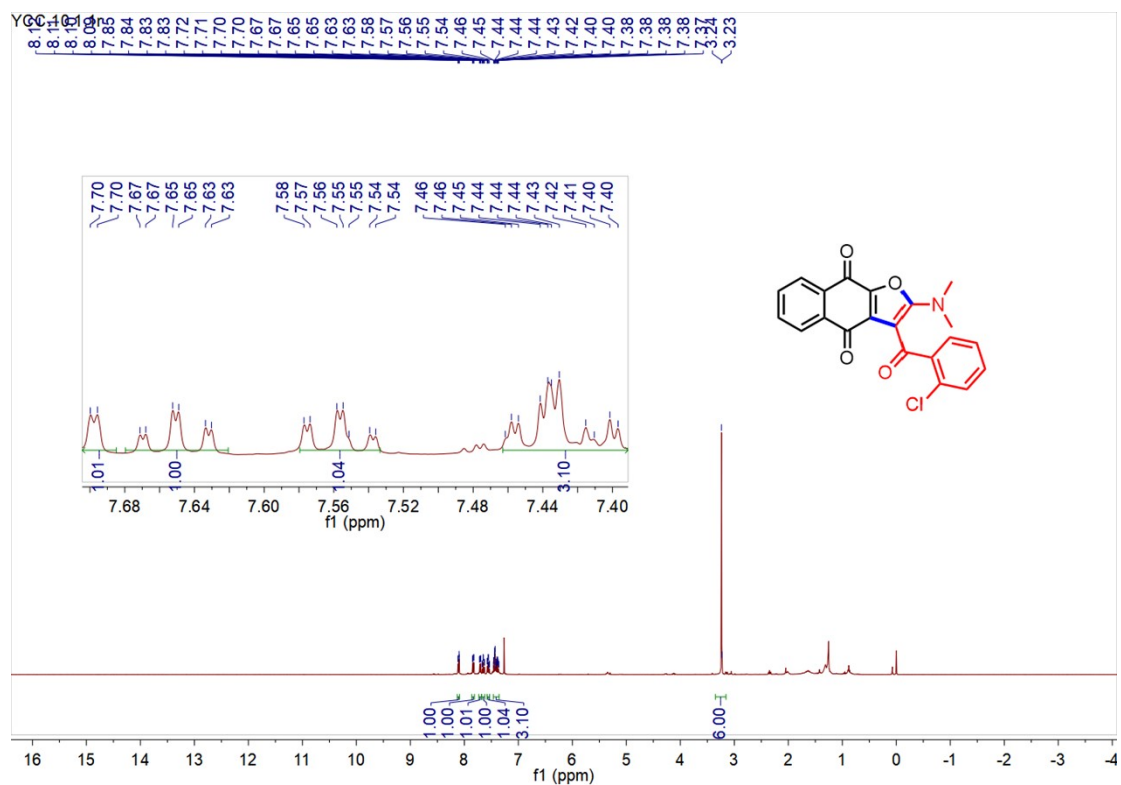
2-(dimethylamino)-3-(2-methylbenzoyl)naphtho[2,3-*b*]furan-4,9-dione (**17**):

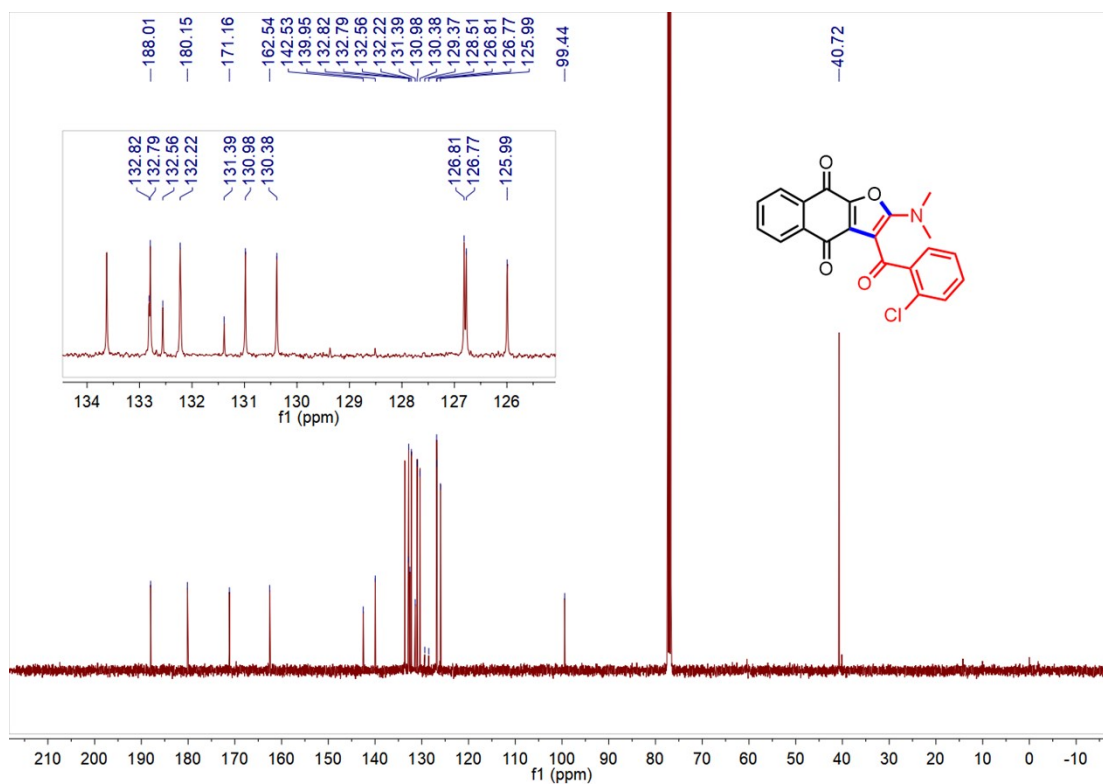




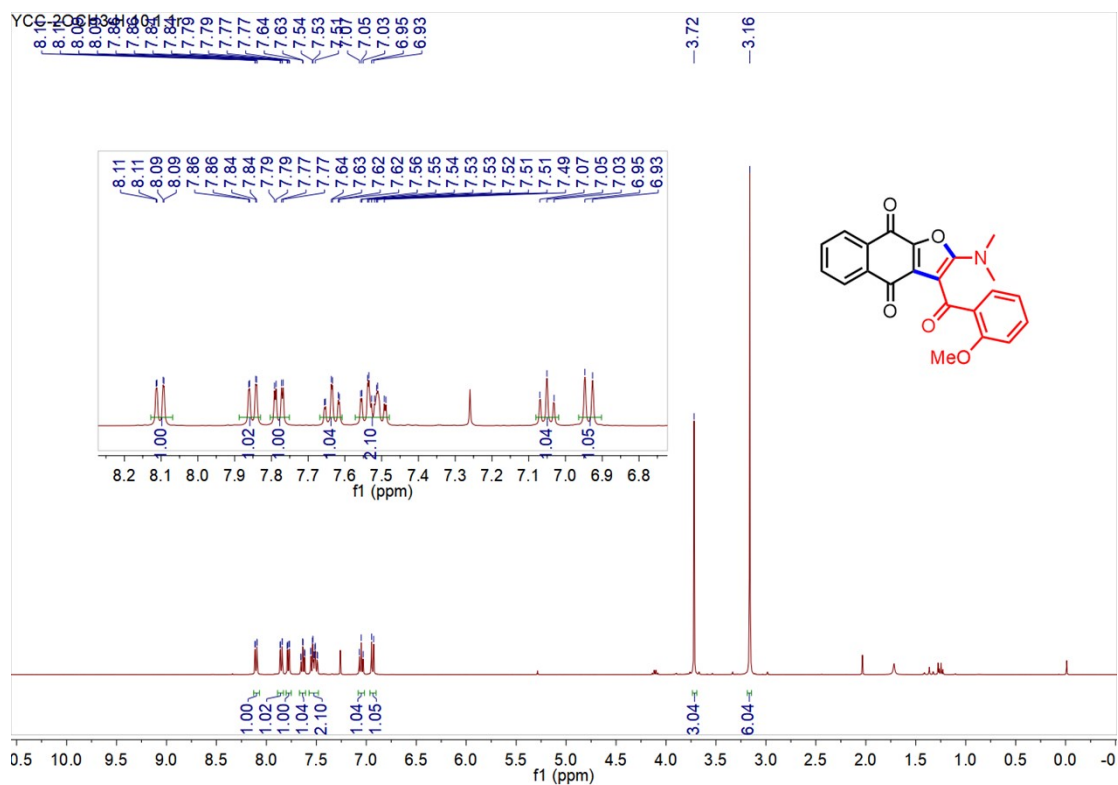


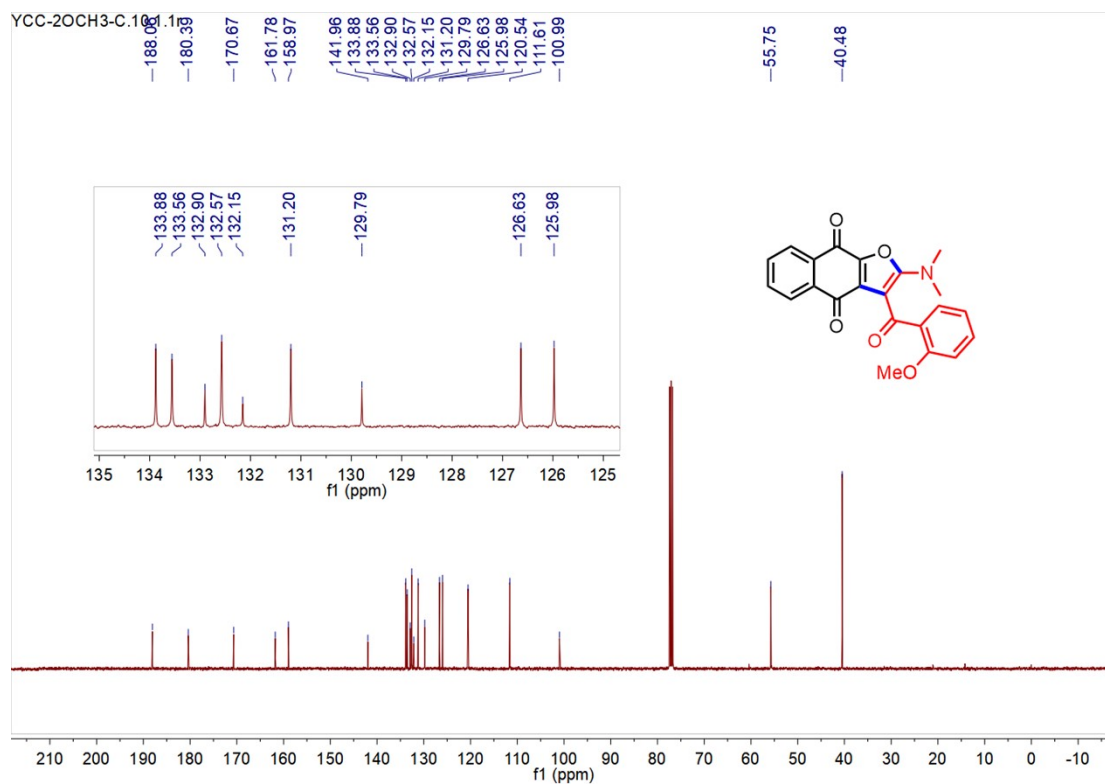
3-(2-chlorobenzoyl)-2-(dimethylamino)naphtho[2,3-b]furan-4,9-dione (19):



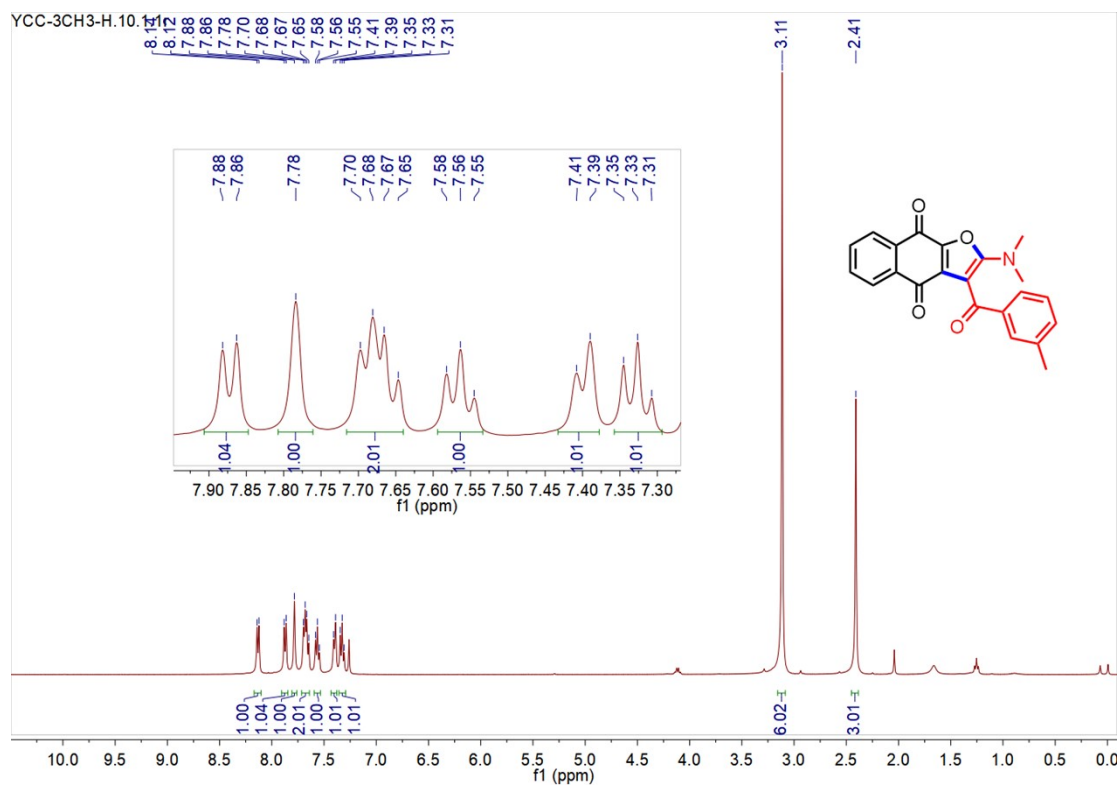


2-(dimethylamino)-3-(2-methoxybenzoyl)naphtho[2,3-*b*]furan-4,9-dione (**20**):

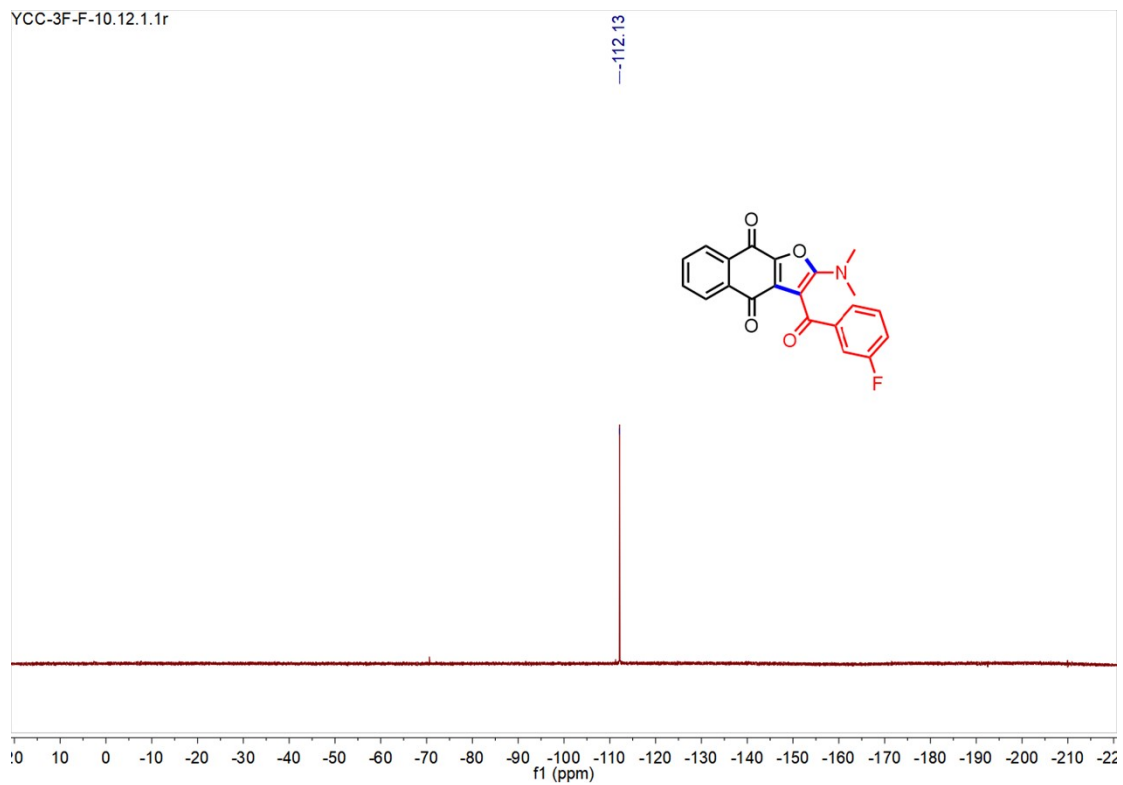
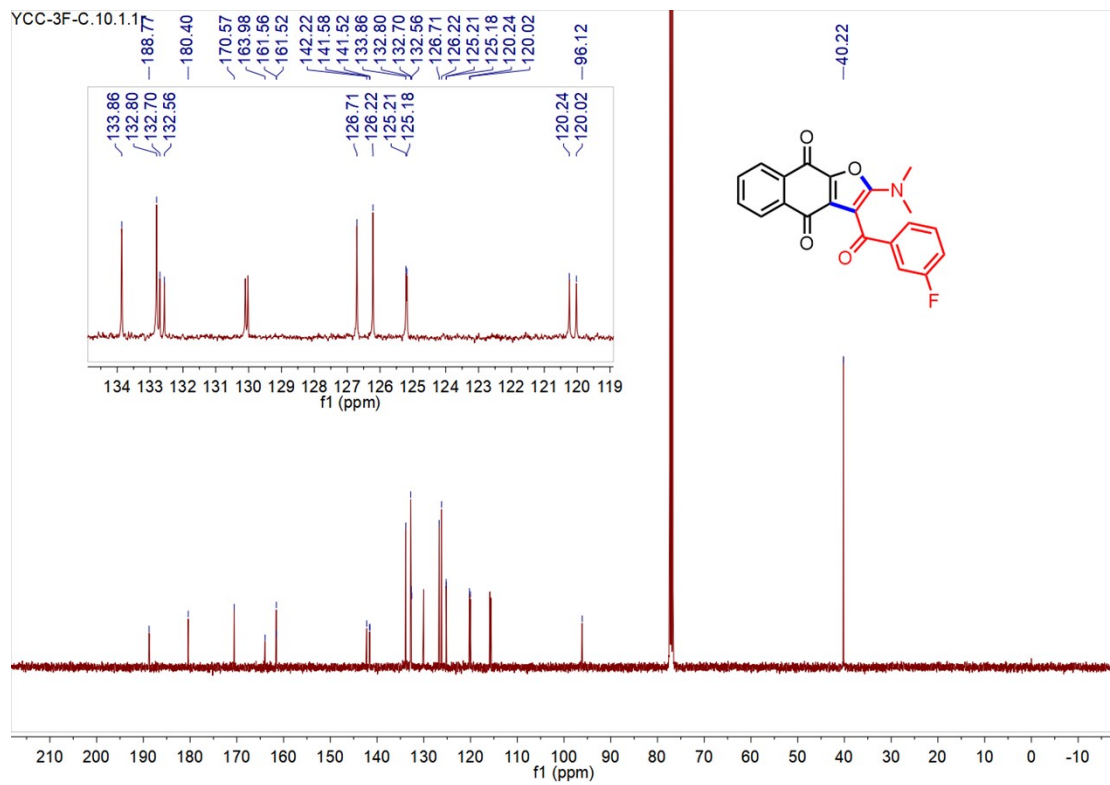




2-(dimethylamino)-3-(3-methylbenzoyl)naphtho[2,3-b]furan-4,9-dione (21):

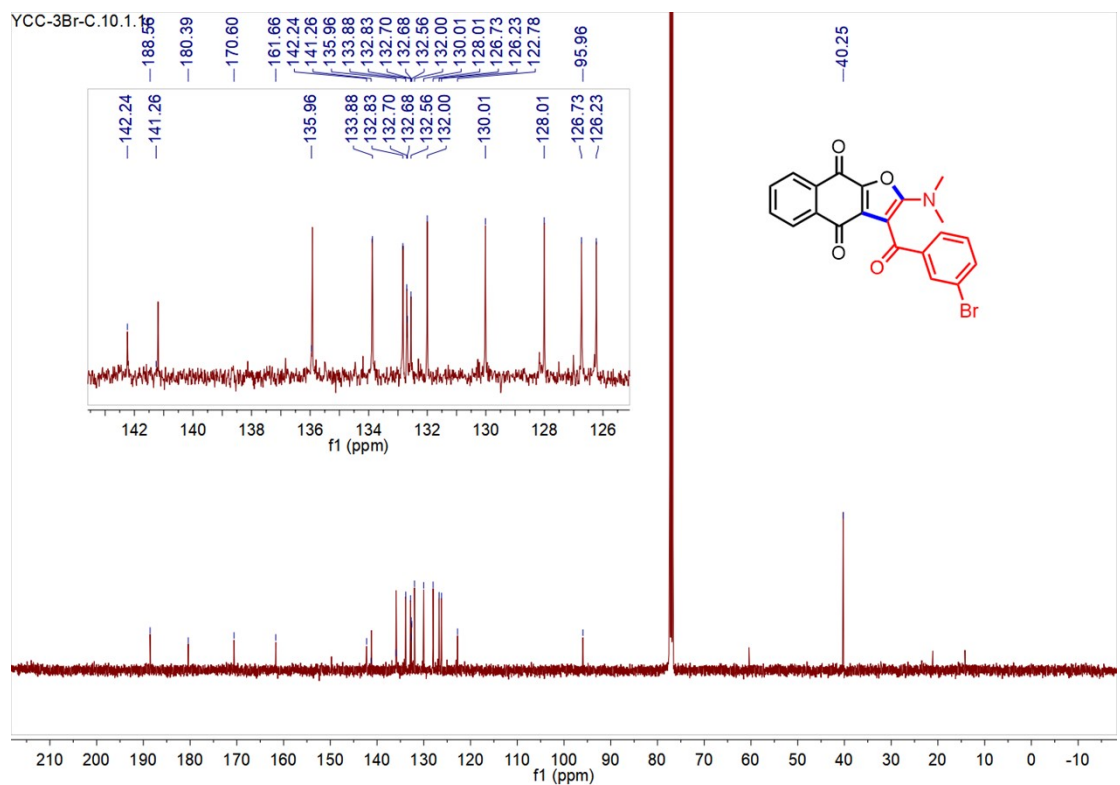
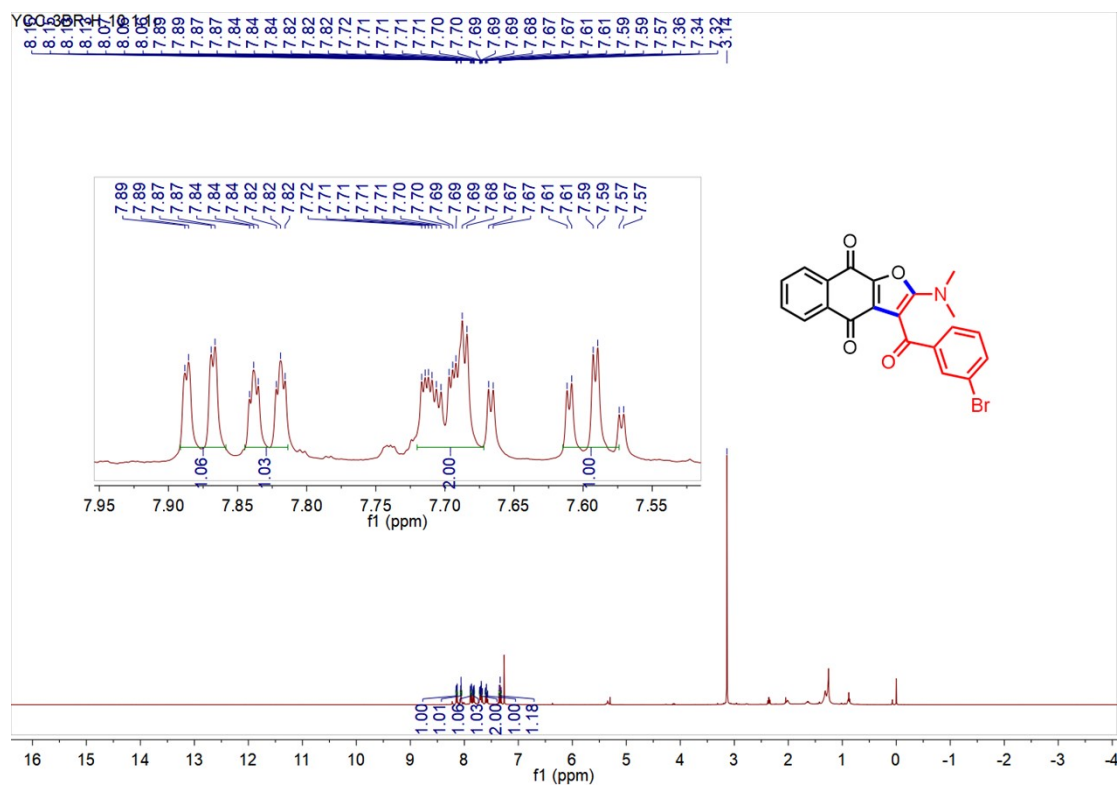






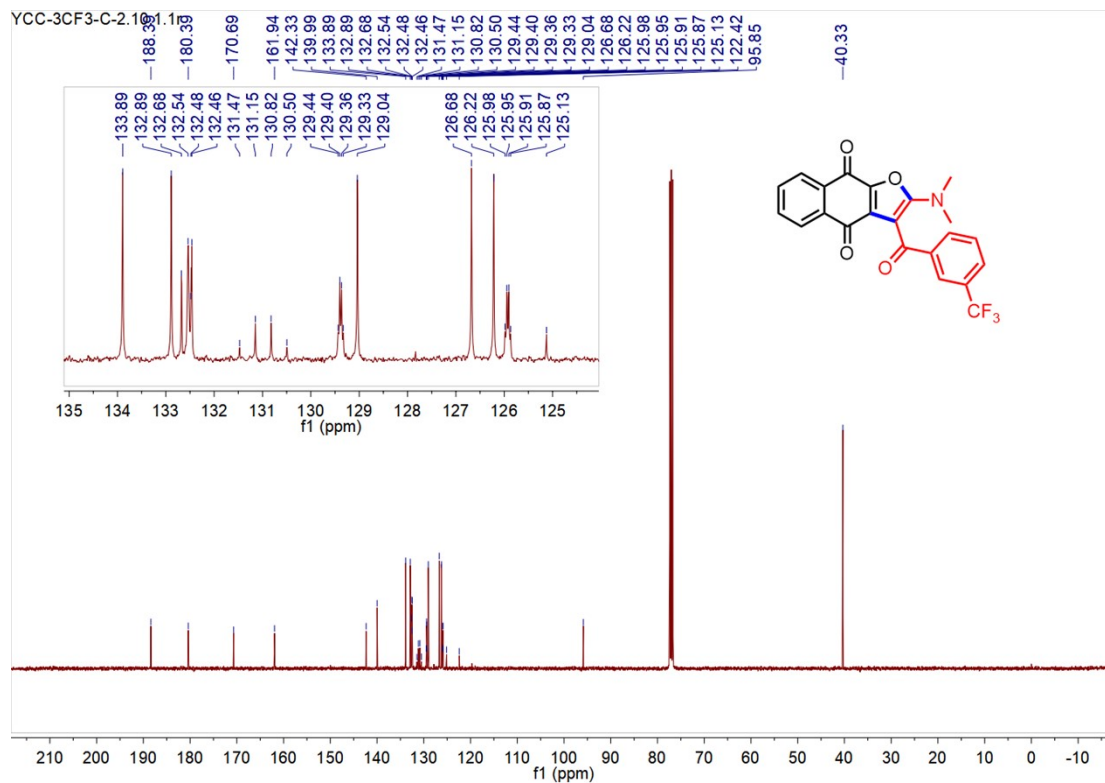
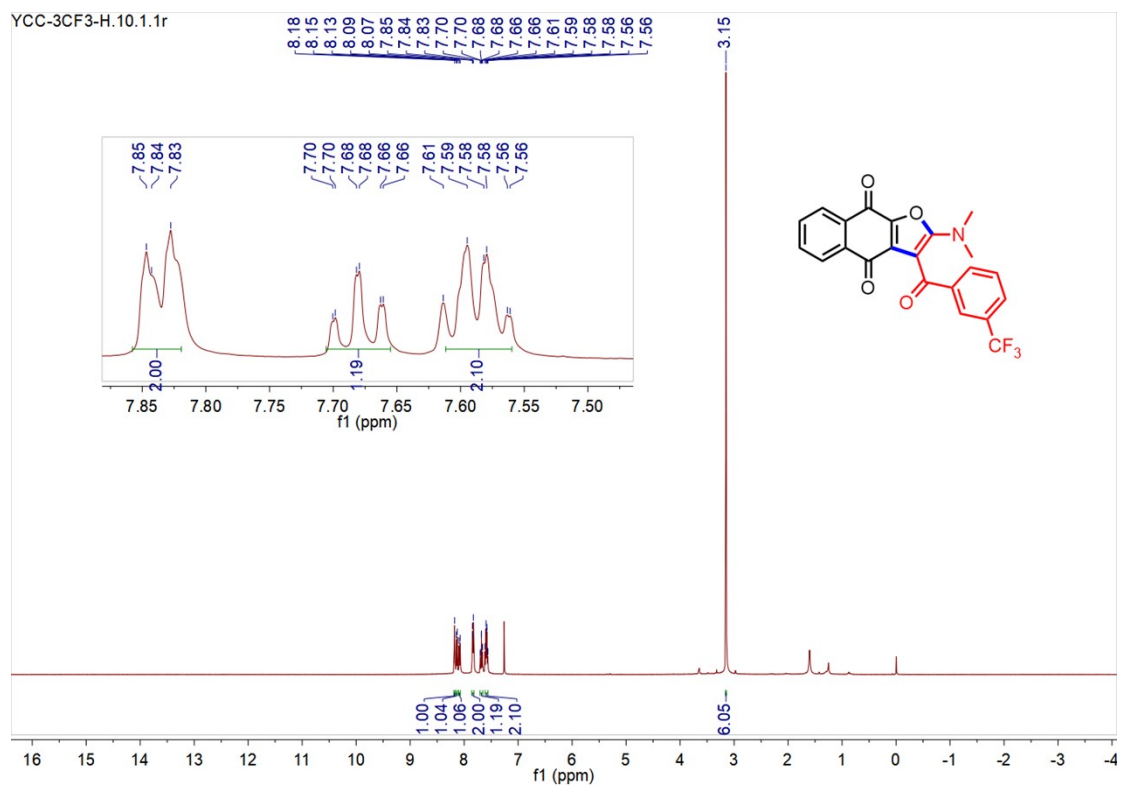


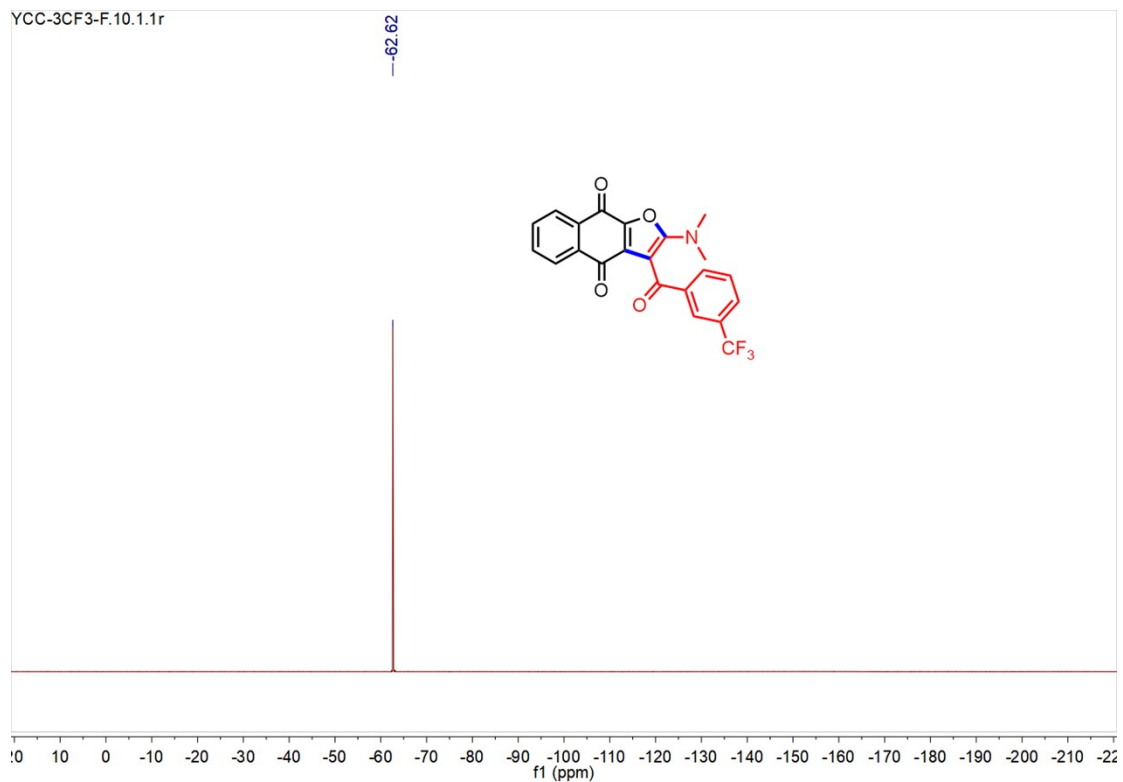
4-(3-bromobenzoyl)-2-(dimethylamino)naphtho[2,3-*b*]furan-4,9-dione (**23**):



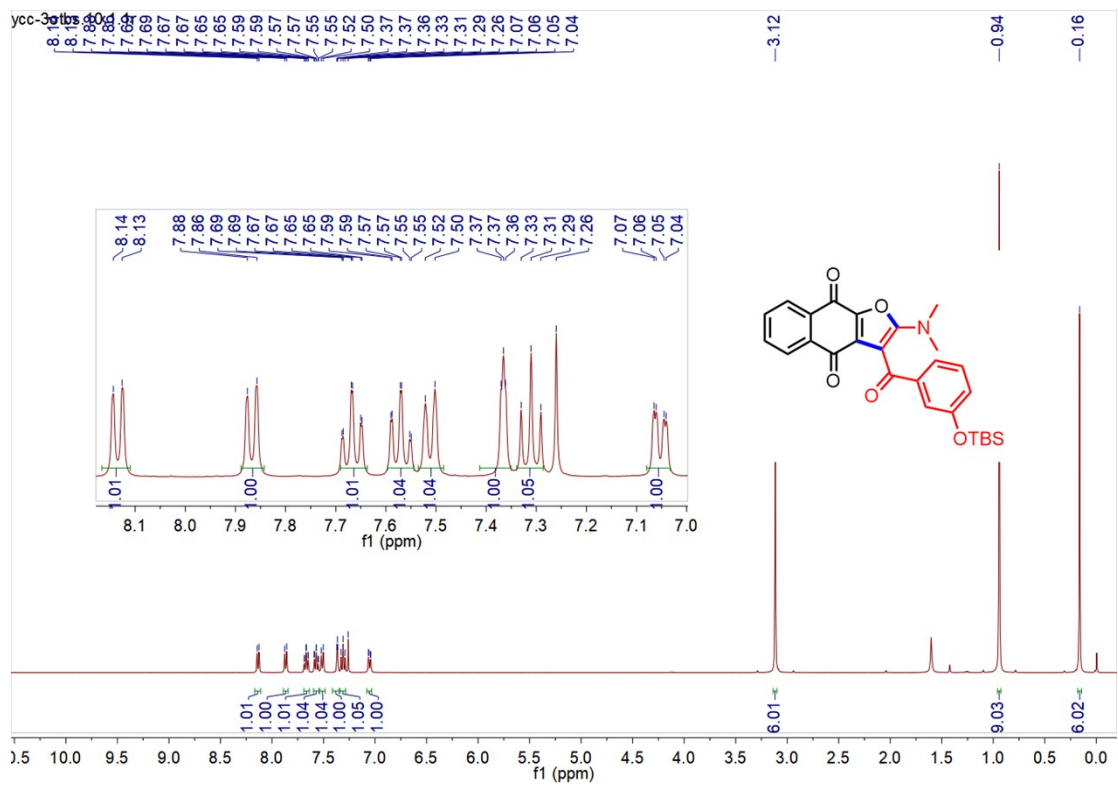


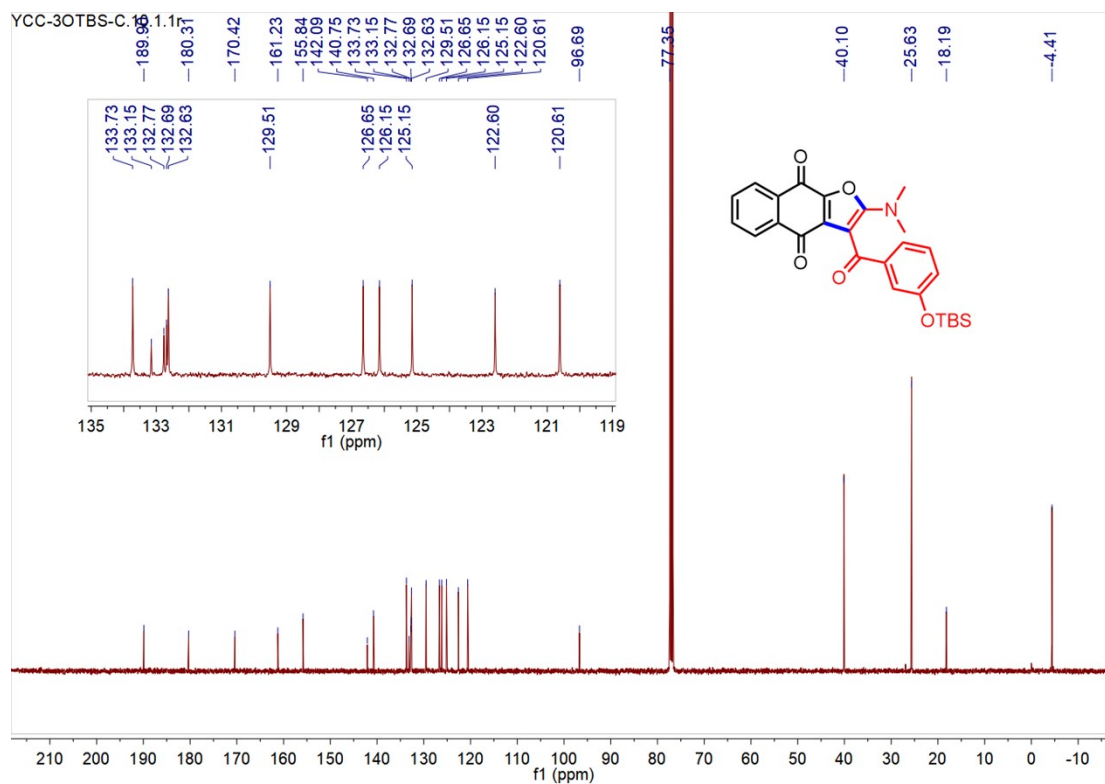
2-(dimethylamino)-3-(3-(trifluoromethyl)benzoyl)naphtho[2,3-*b*]furan-4,9-dione (**24**):



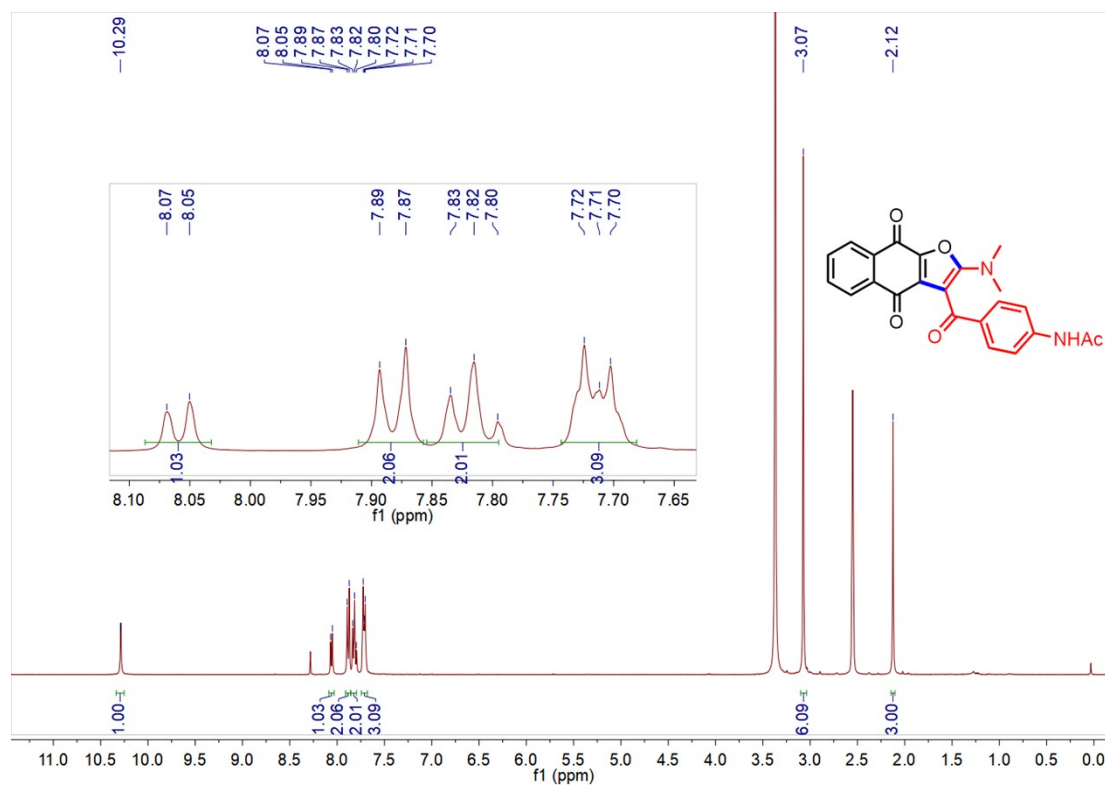


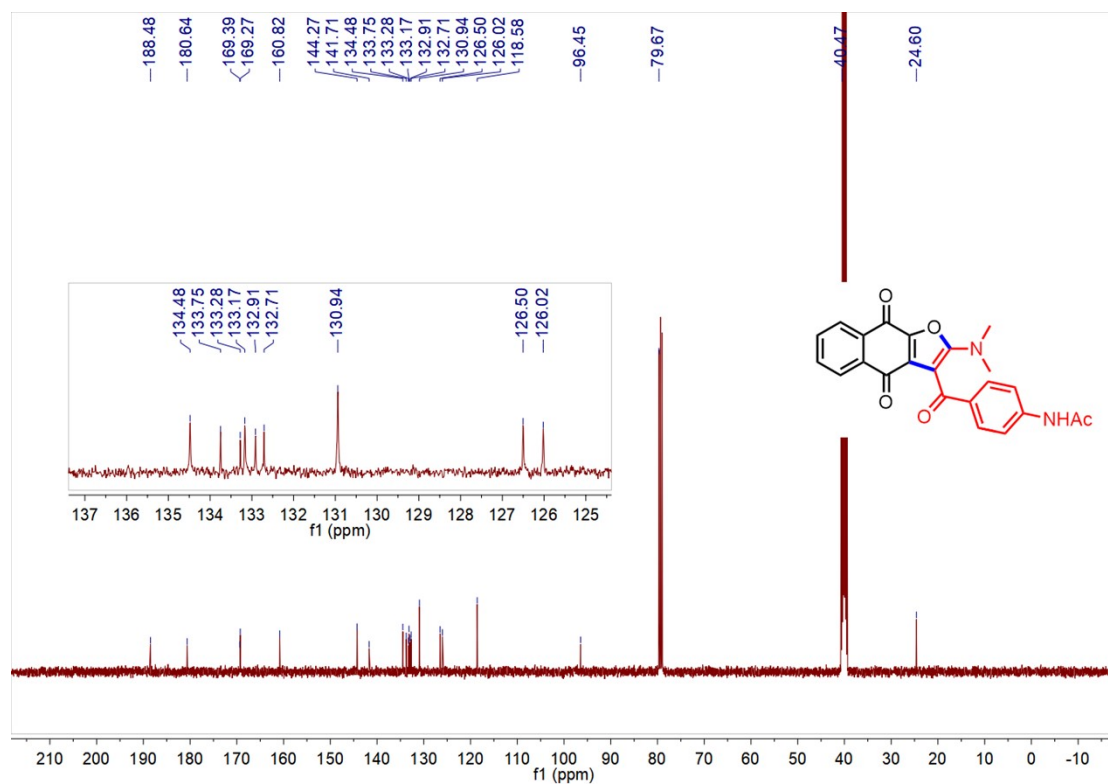
3-(3-((*tert*-butyldimethylsilyl)oxy)benzoyl)-2-(dimethylamino)naphtho[2,3-*b*]furan-4,9-dione (**25**):



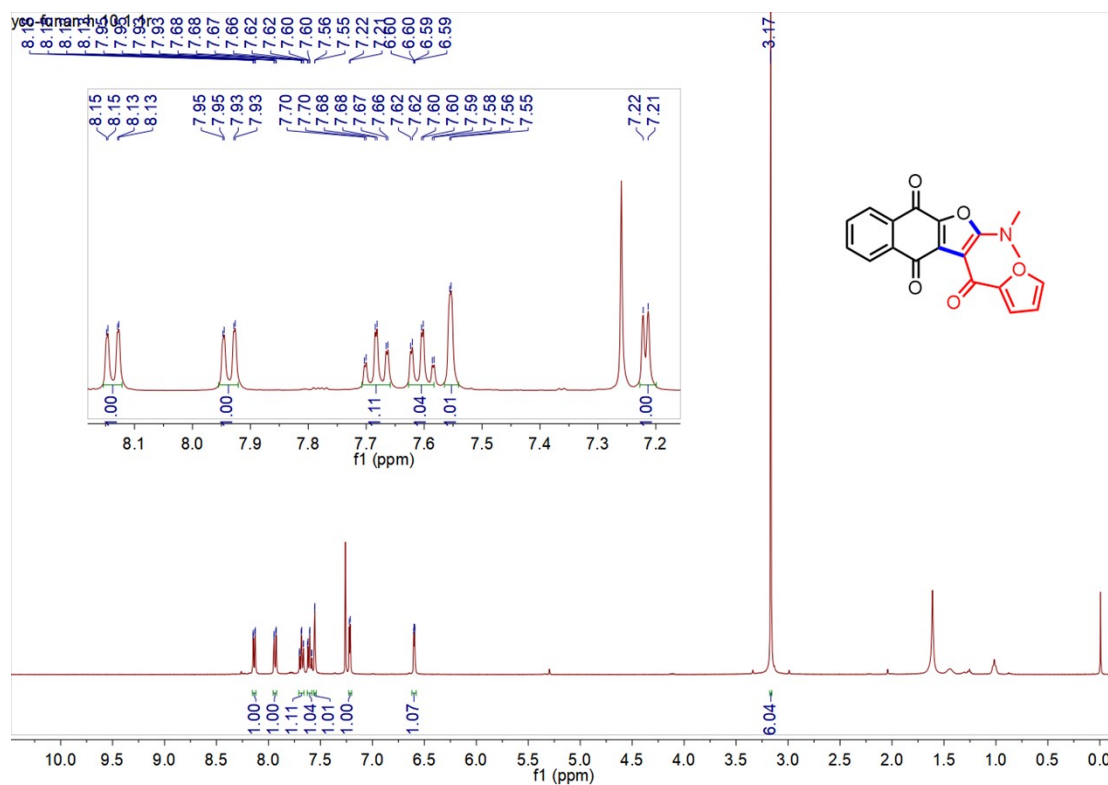


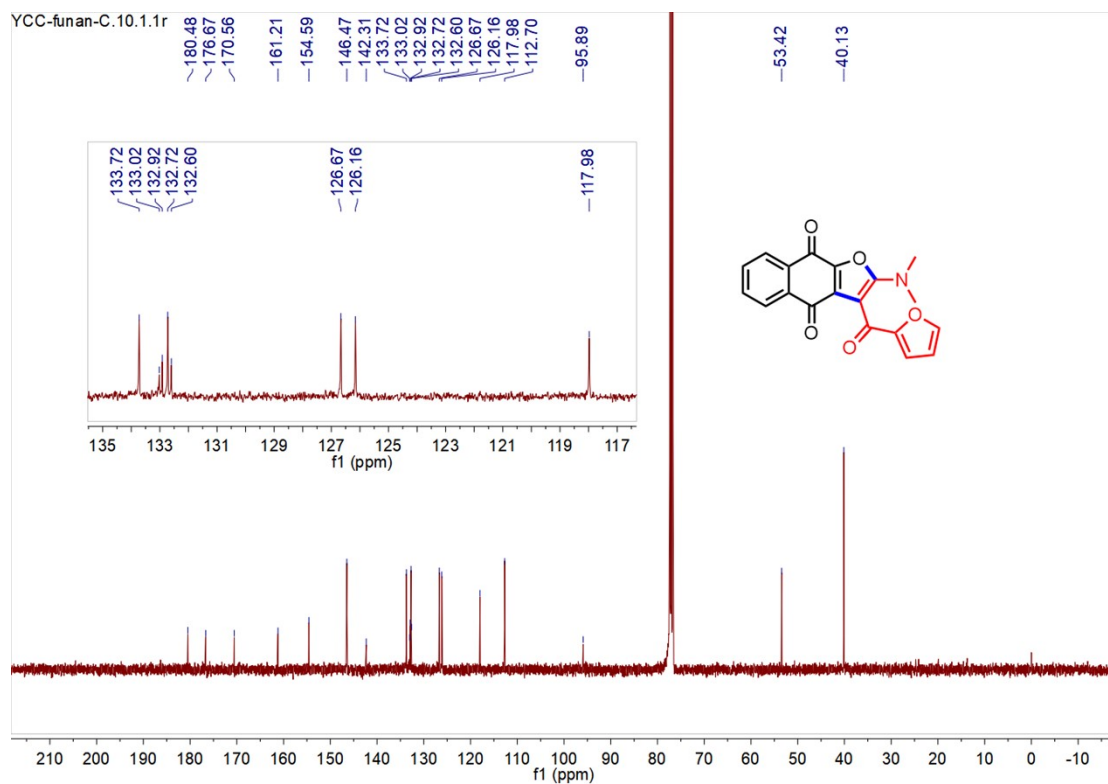
N-(4-(2-(dimethylamino)-4,9-dioxo-4,9-dihydronaphtho[2,3-*b*]furan-3-carbonyl)phenyl)acetamide (**26**):



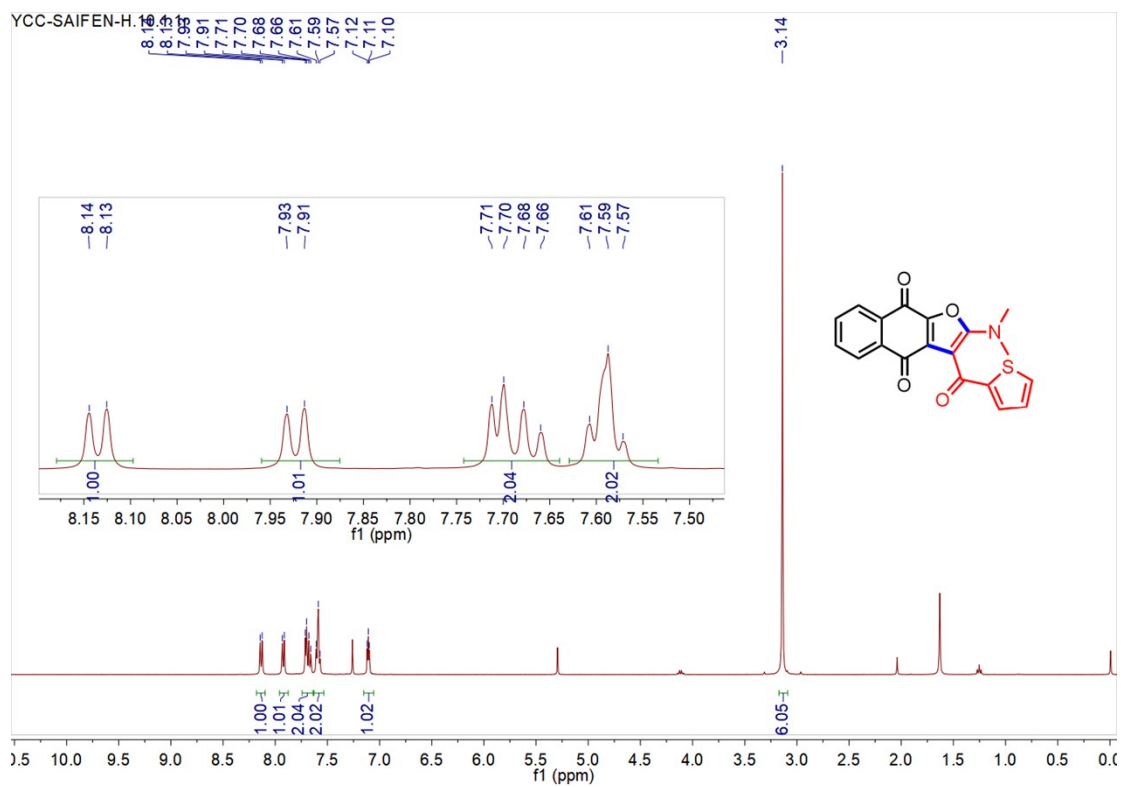


2-(dimethylamino)-3-(furan-2-carbonyl)naphtho[2,3-*b*]furan-4,9-dione (27):



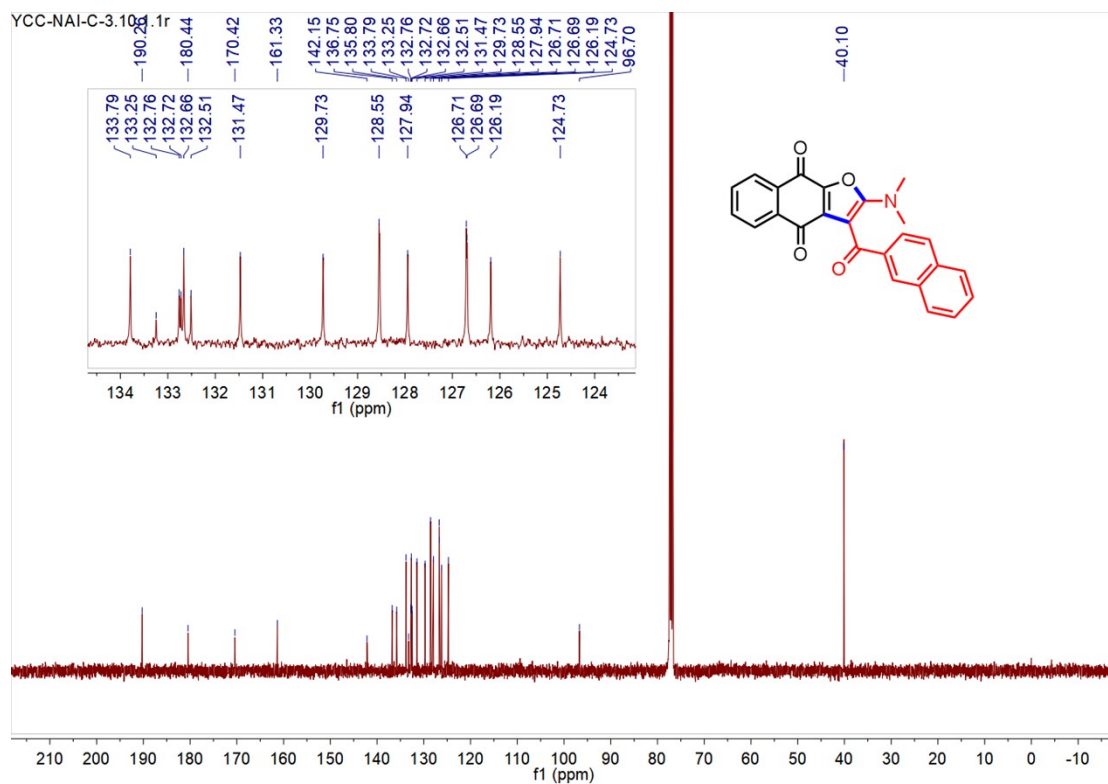


2-(dimethylamino)-3-(thiophene-2-carbonyl)naphtho[2,3-*b*]furan-4,9-dione (**28**):

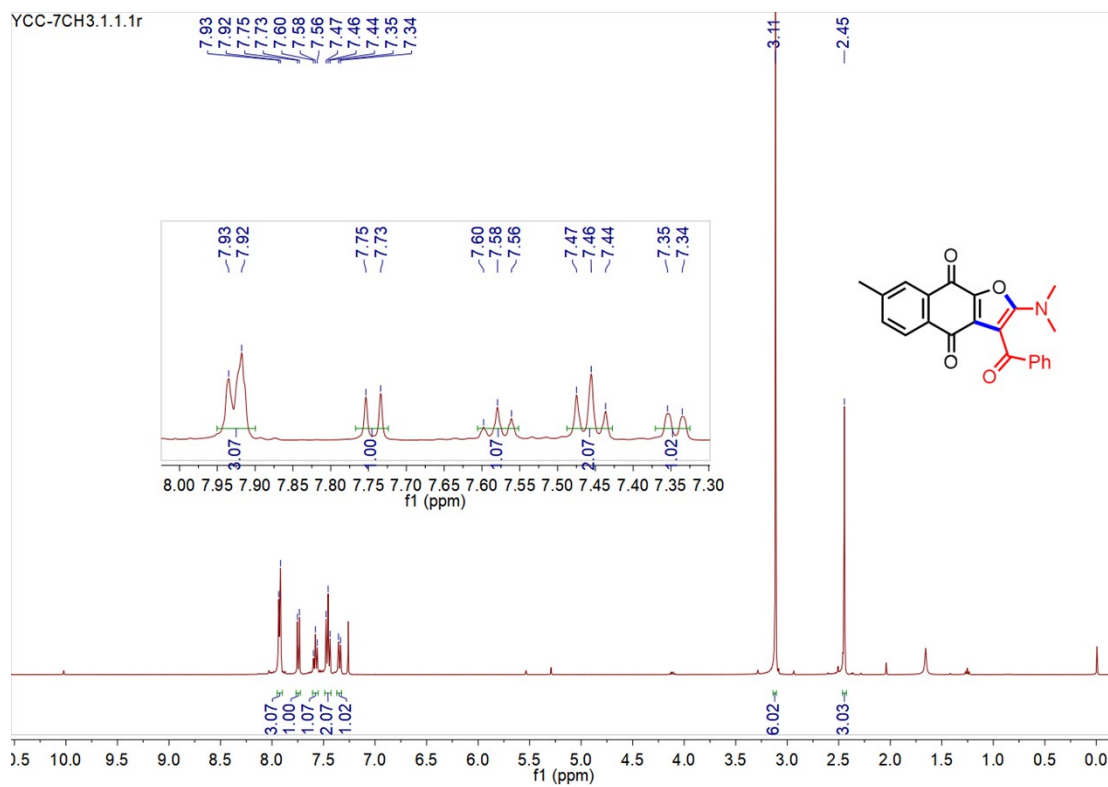


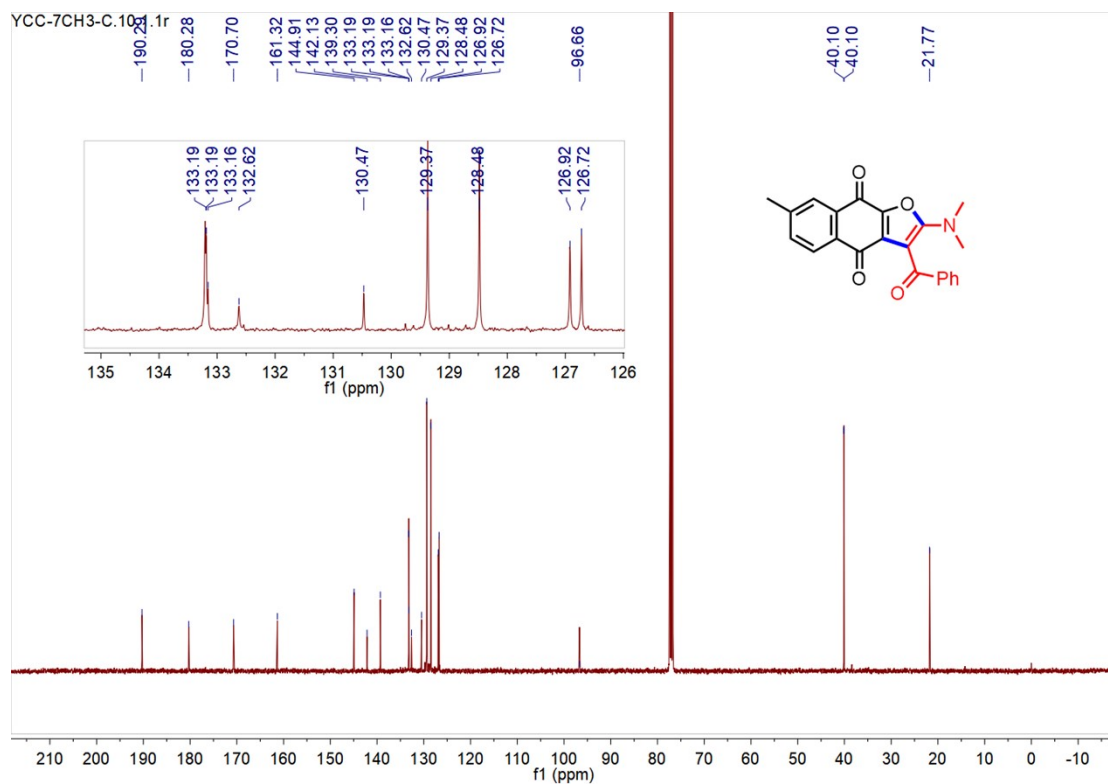




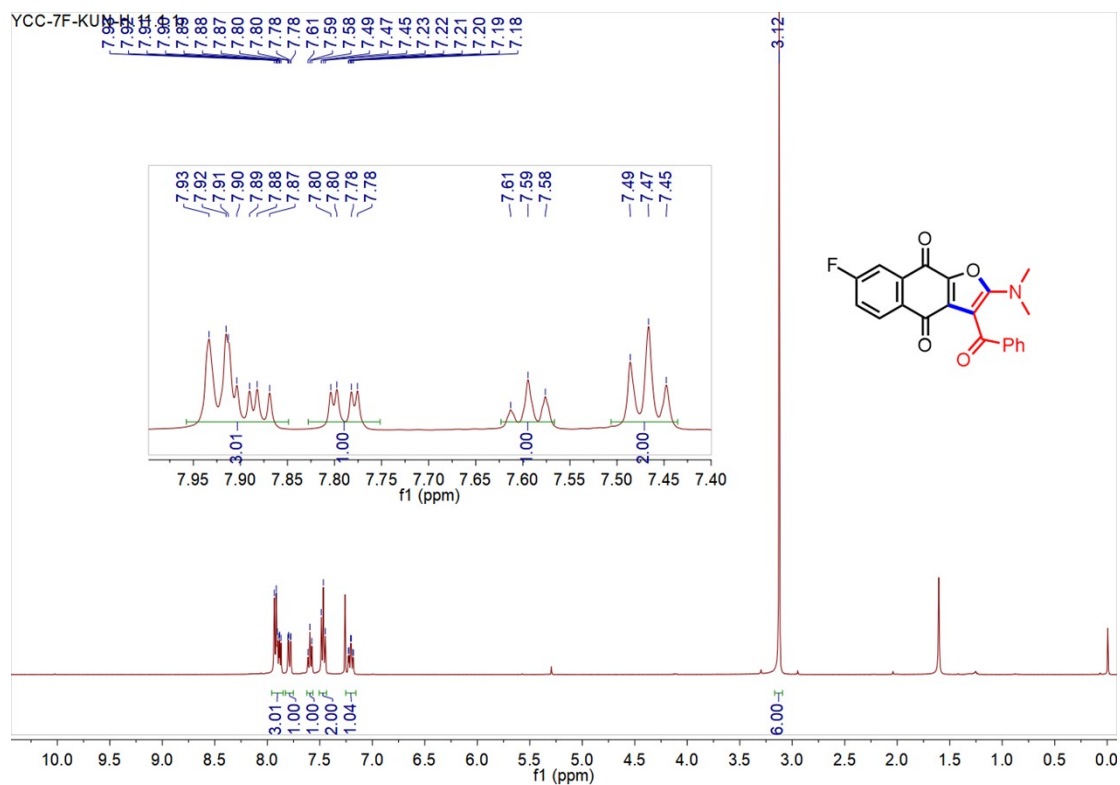


3-benzoyl-2-(dimethylamino)-7-methylnaphtho[2,3-*b*]furan-4,9-dione (**30**):

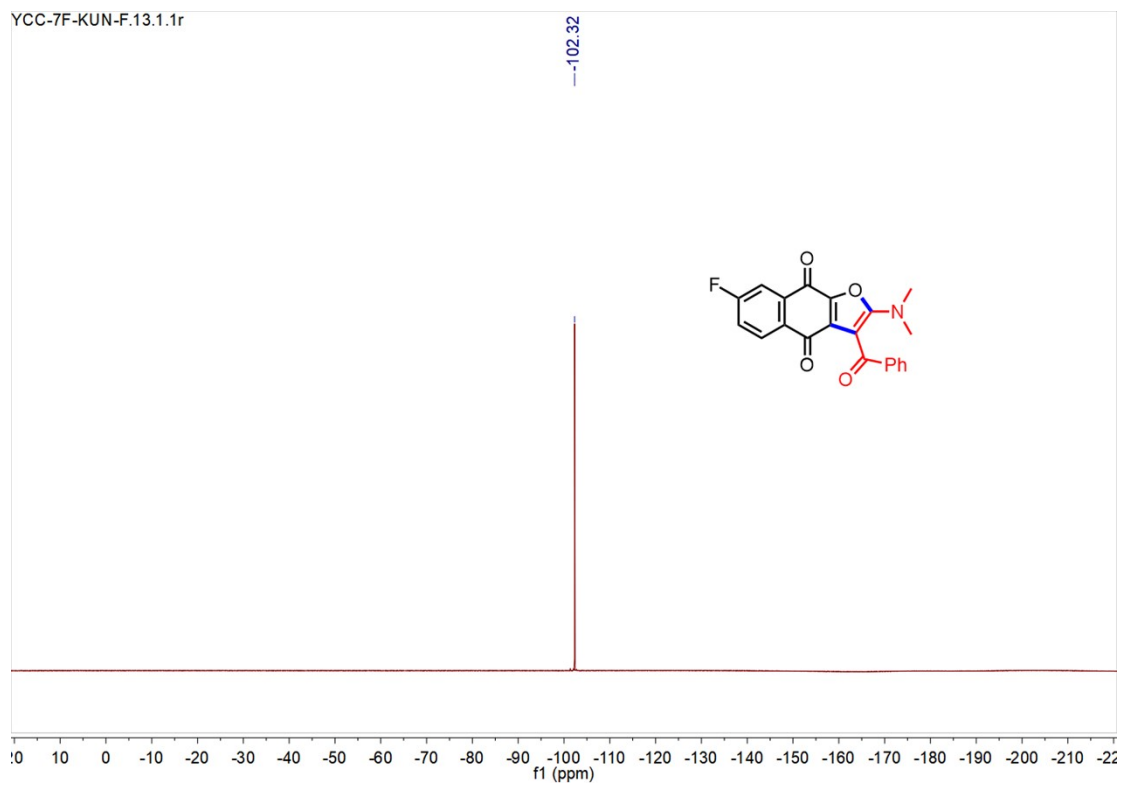
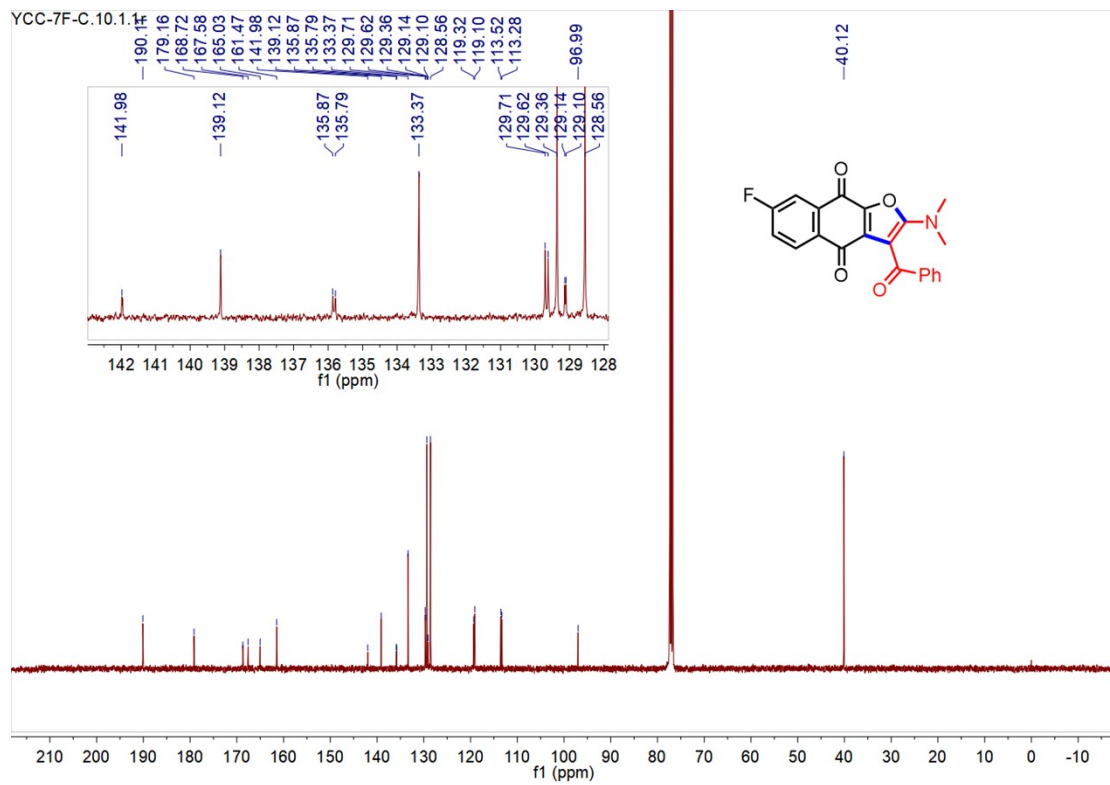




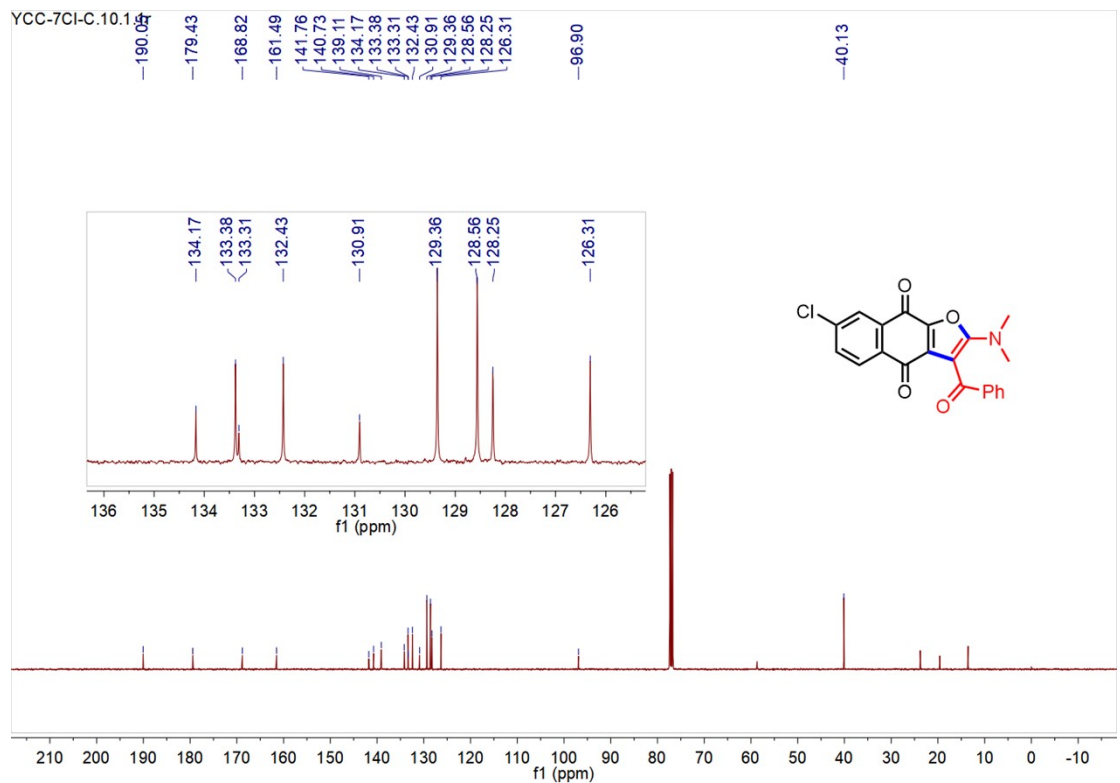
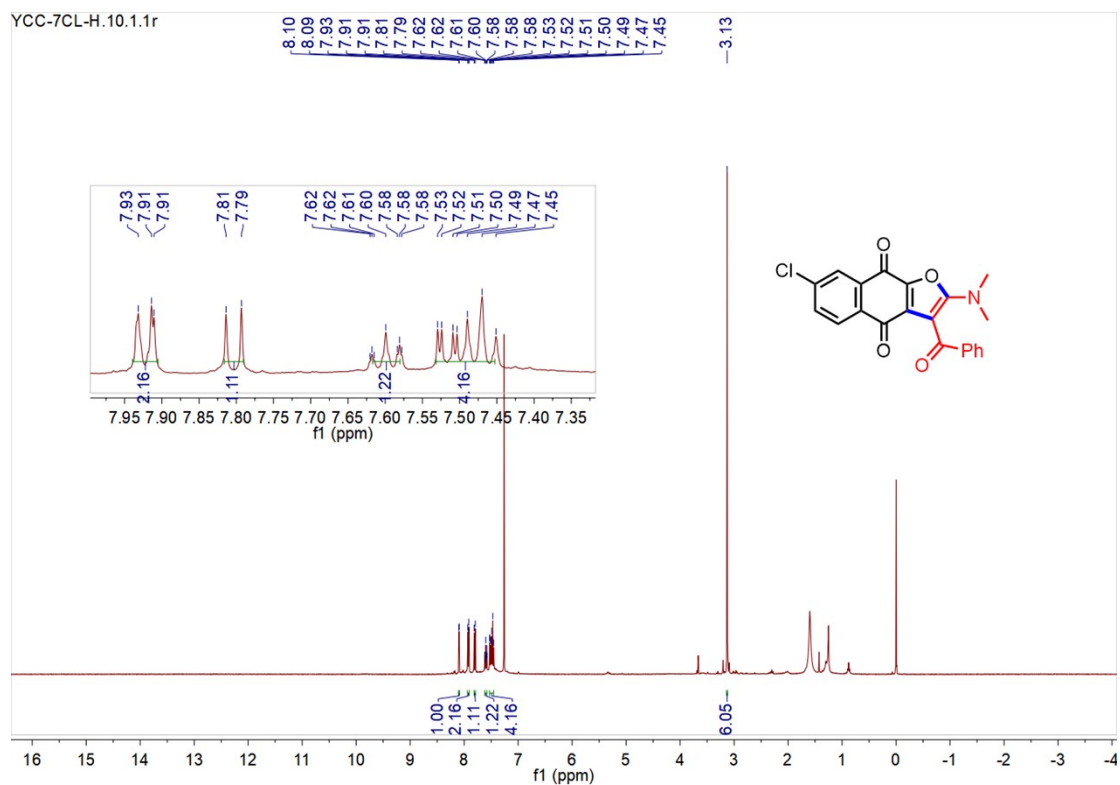
3-benzoyl-2-(dimethylamino)-7-fluoronaphtho[2,3-b]furan-4,9-dione (31):



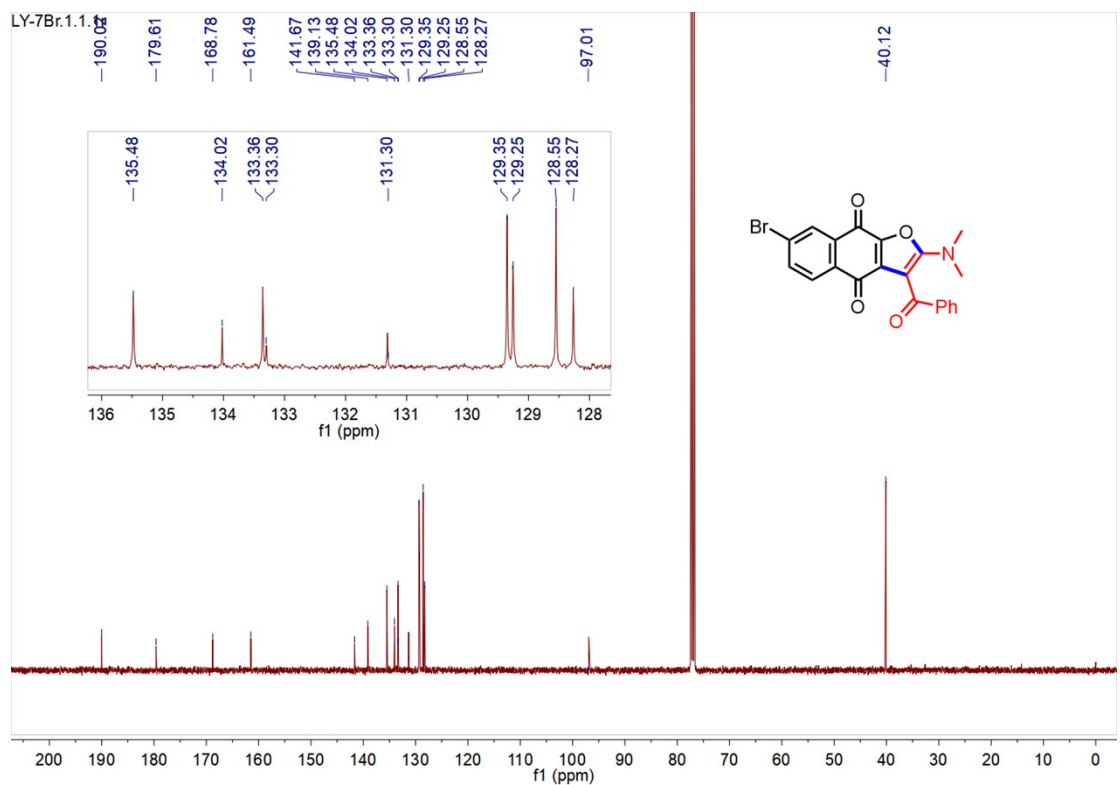
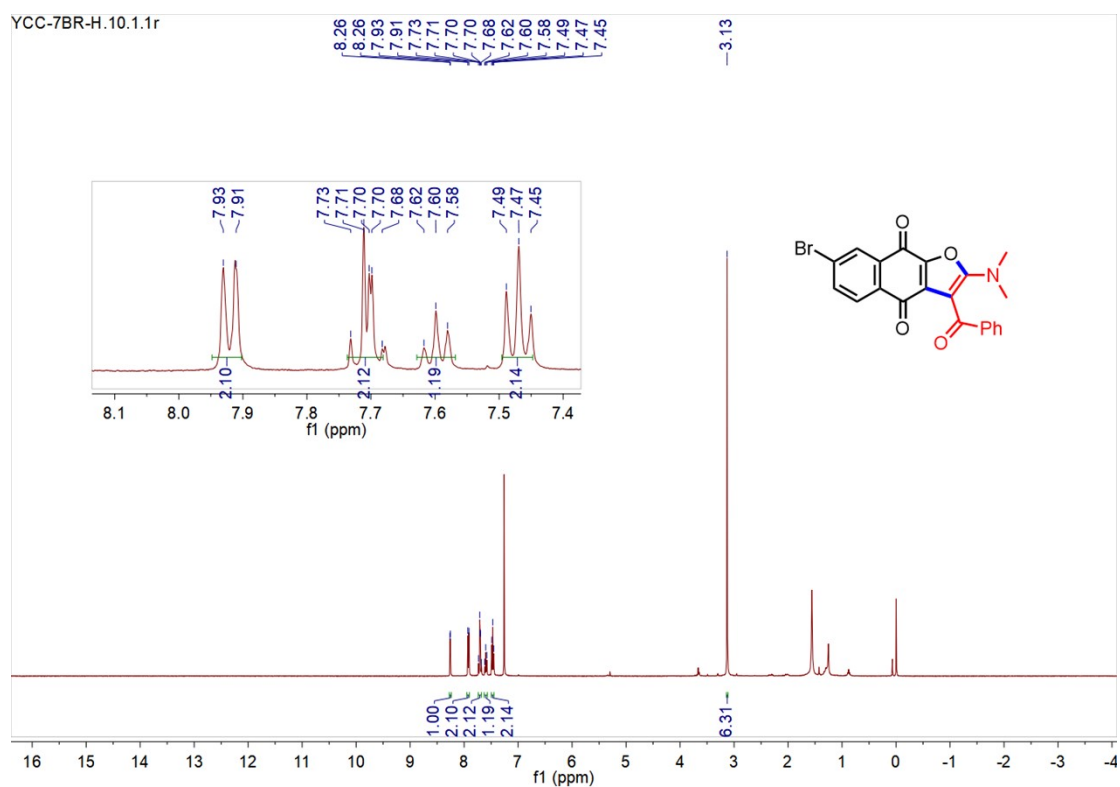




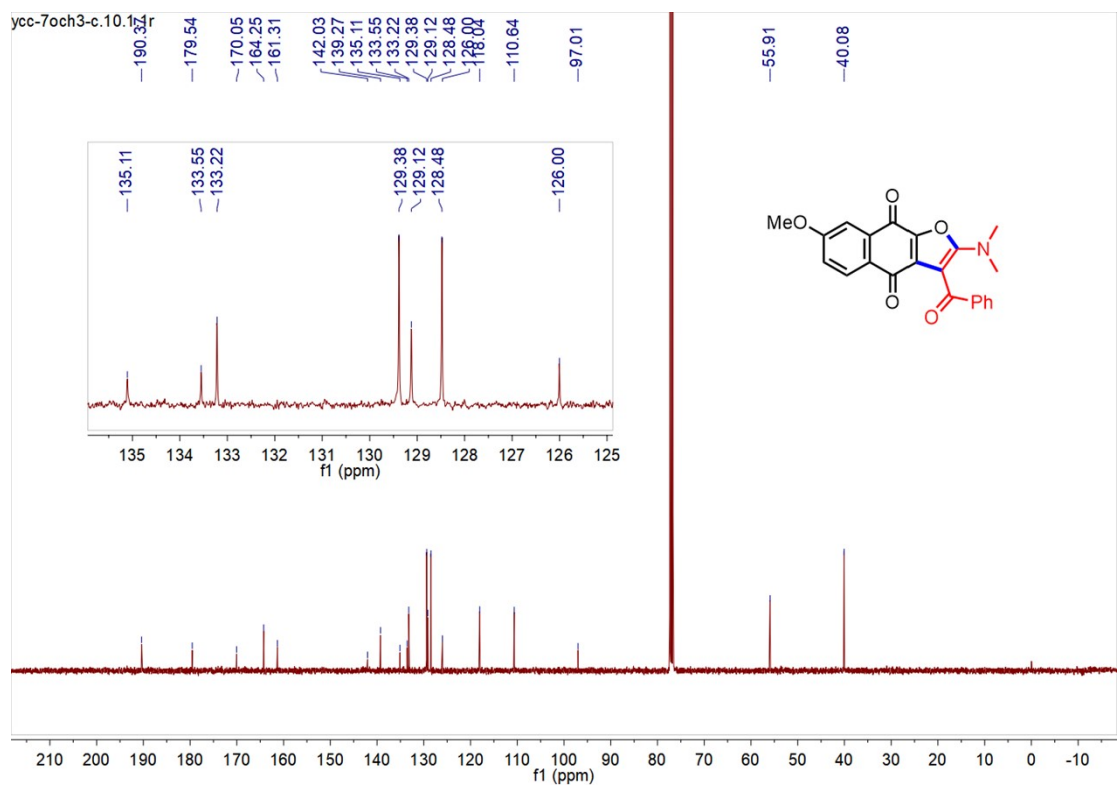
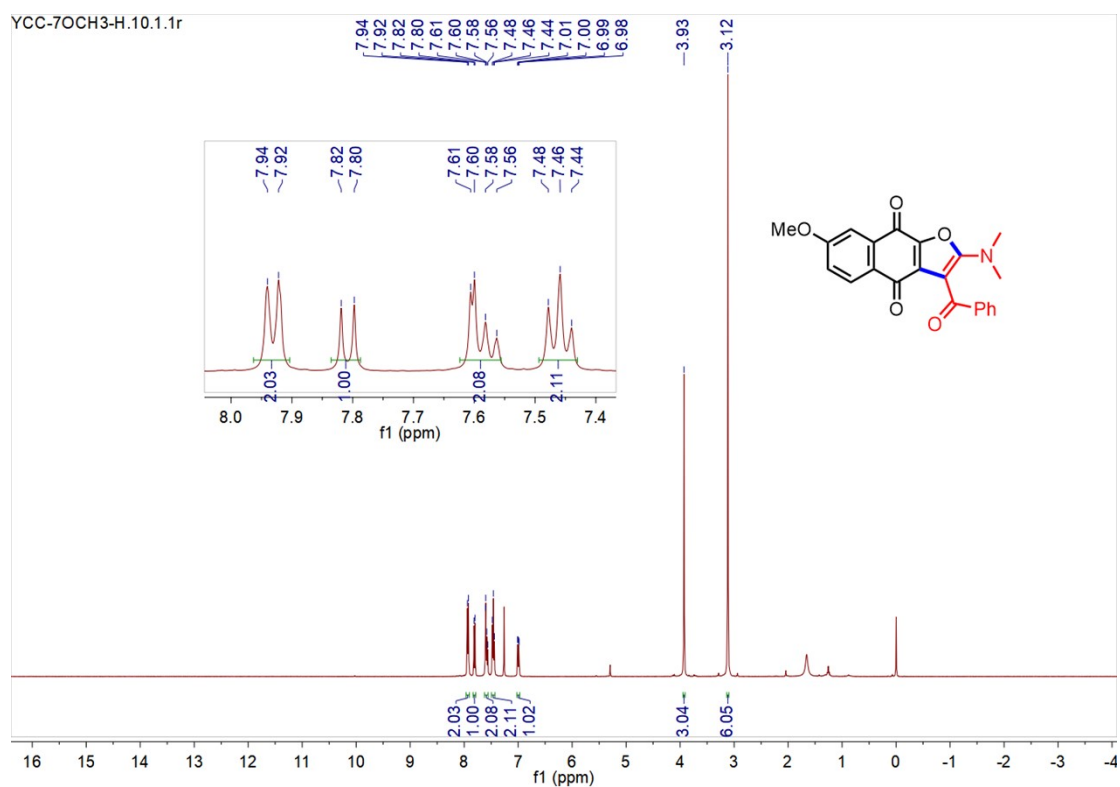
4-3-benzoyl-7-chloro-2-(dimethylamino)naphtho[2,3-*b*]furan-4,9-dione (**32**):



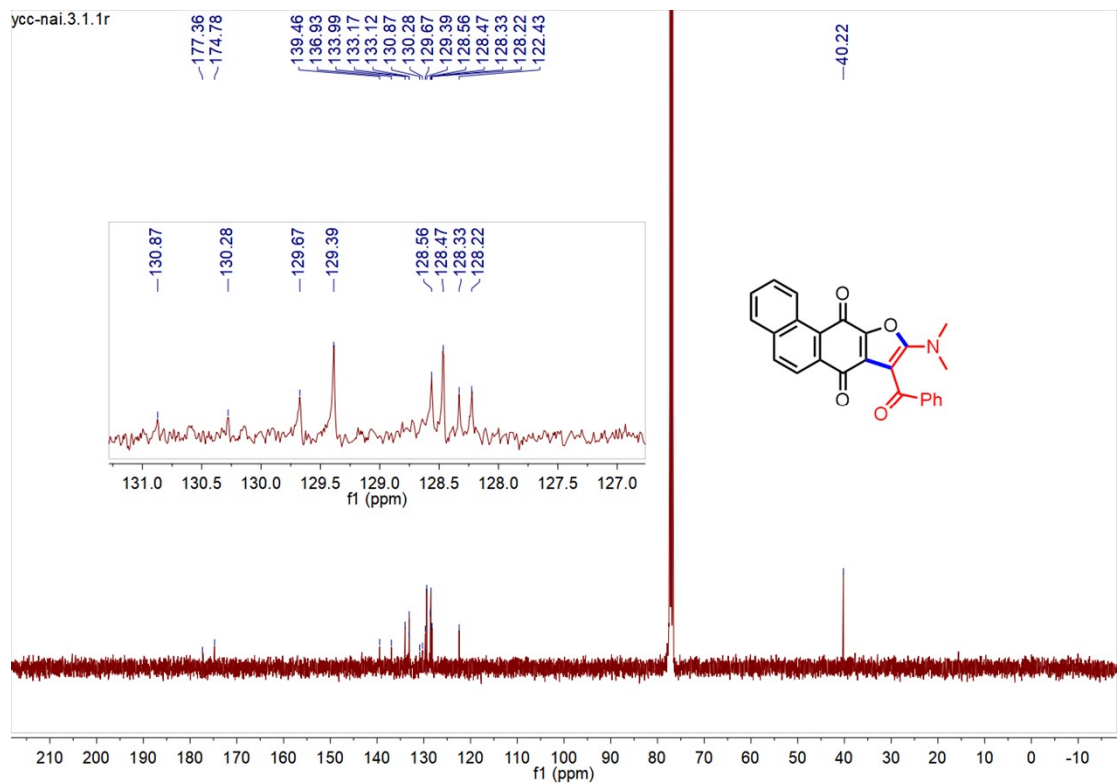
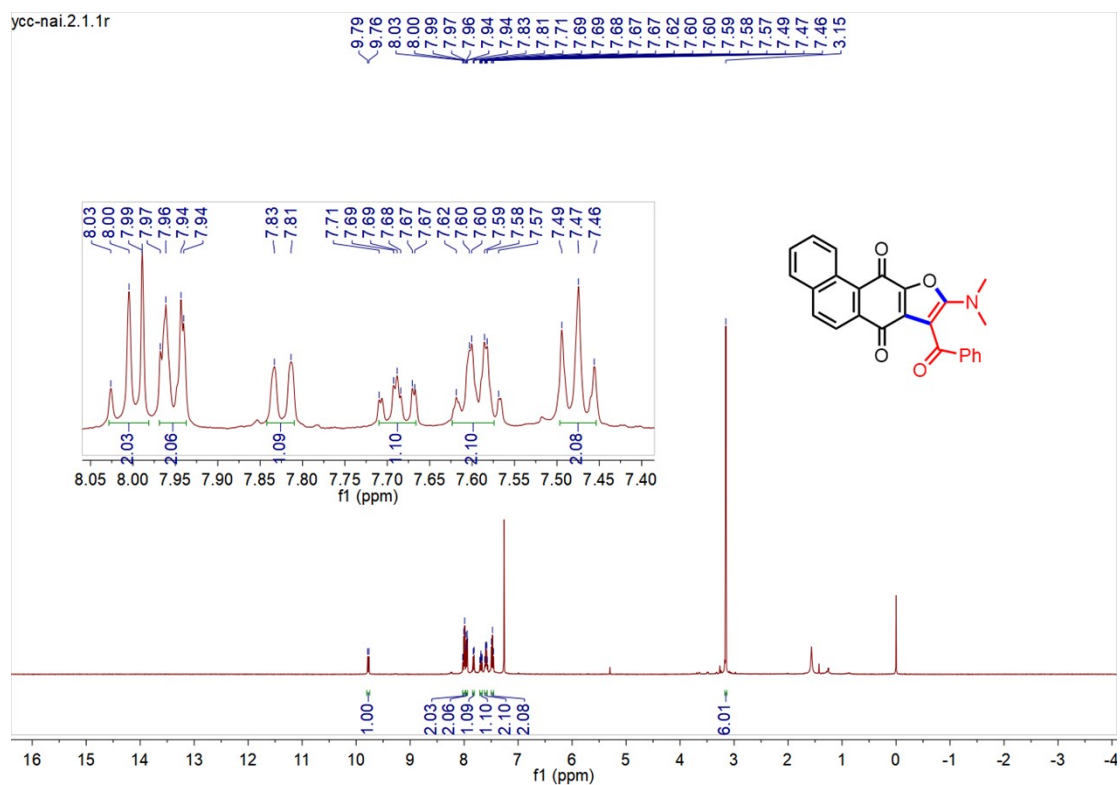
3-benzoyl-7-bromo-2-(dimethylamino)naphtho[2,3-*b*]furan-4,9-dione (**33**):



3-benzoyl-2-(dimethylamino)-7-methoxynaphtho[2,3-*b*]furan-4,9-dione (**34**):

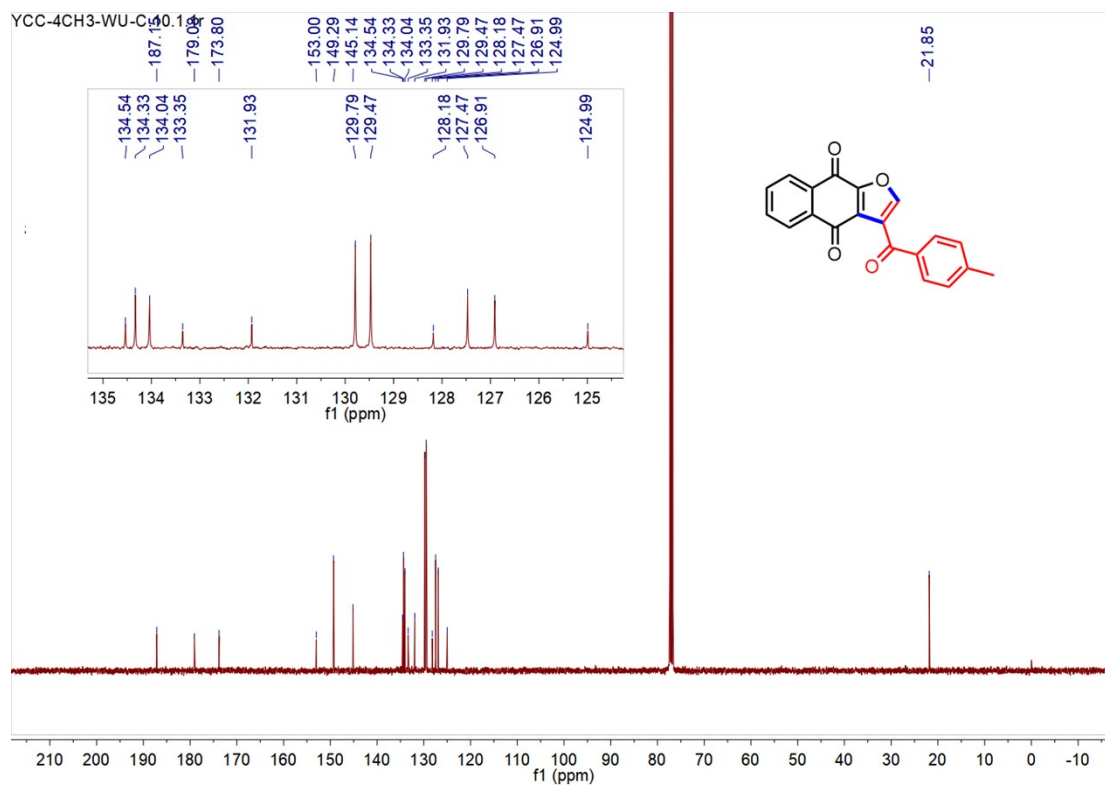
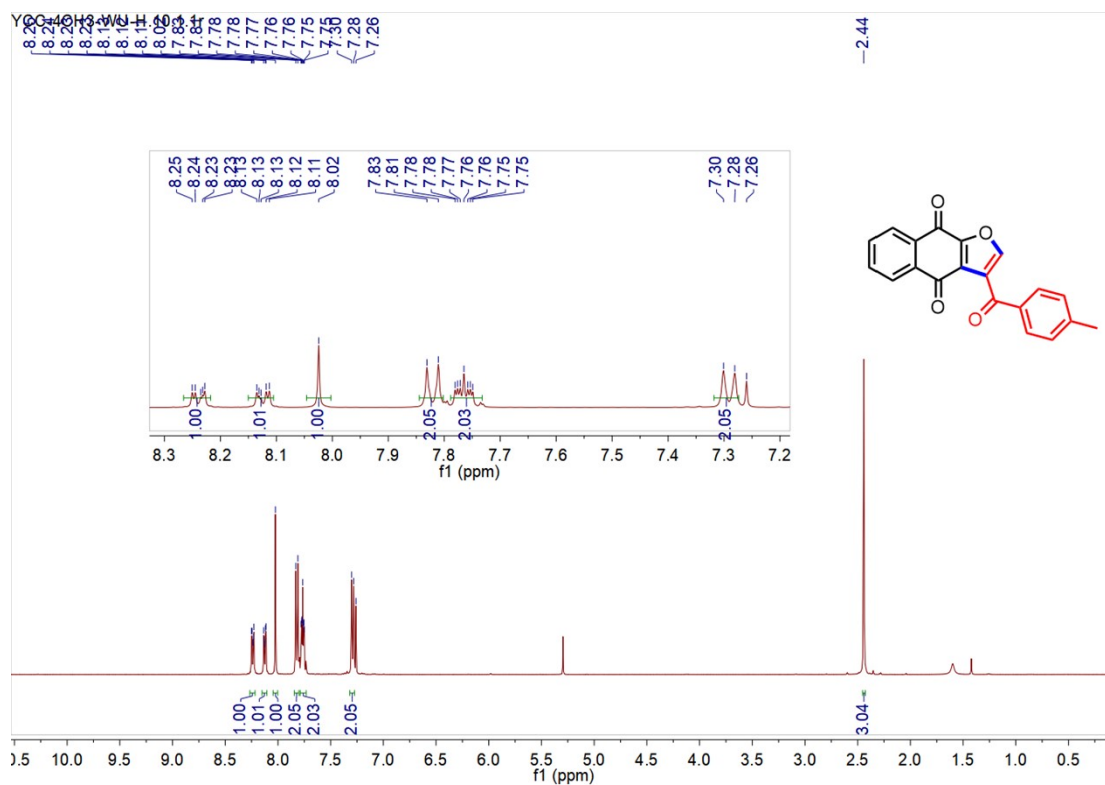


8-benzoyl-9-(dimethylamino)phenanthro[3,2-b]furan-7,11-dione (**35**):





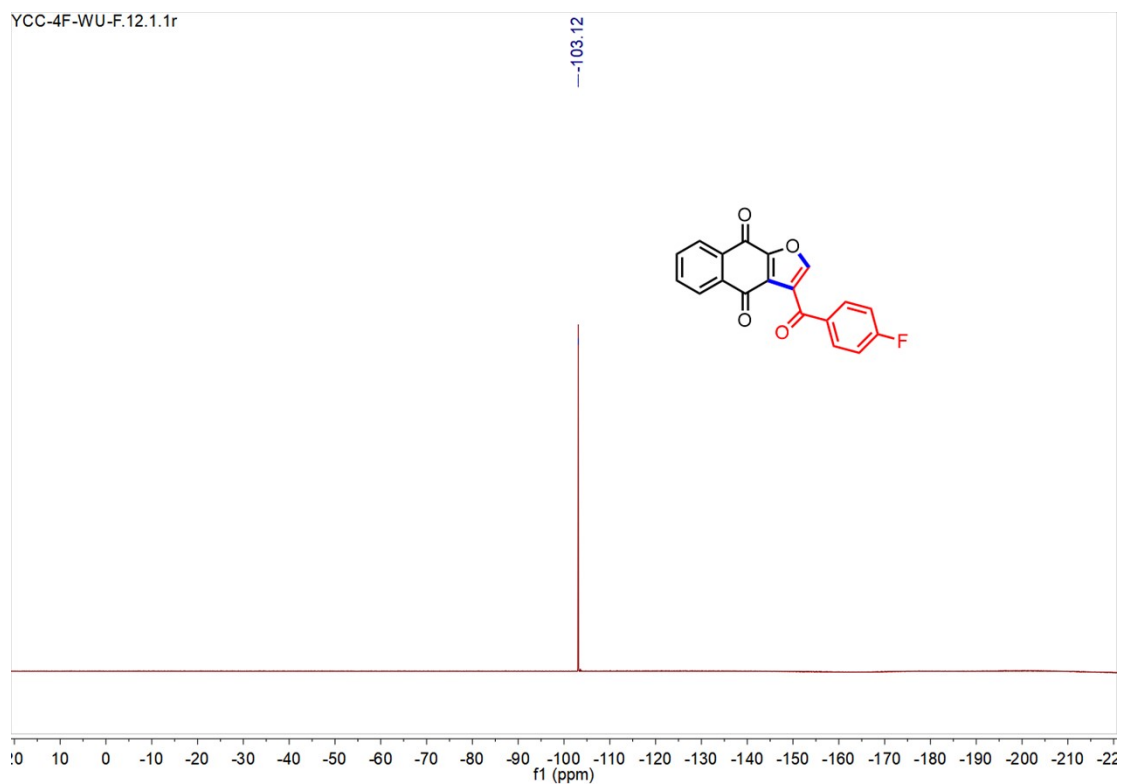
4-(4-methylbenzoyl)naphtho[2,3-b]furan-4,9-dione (**36**):



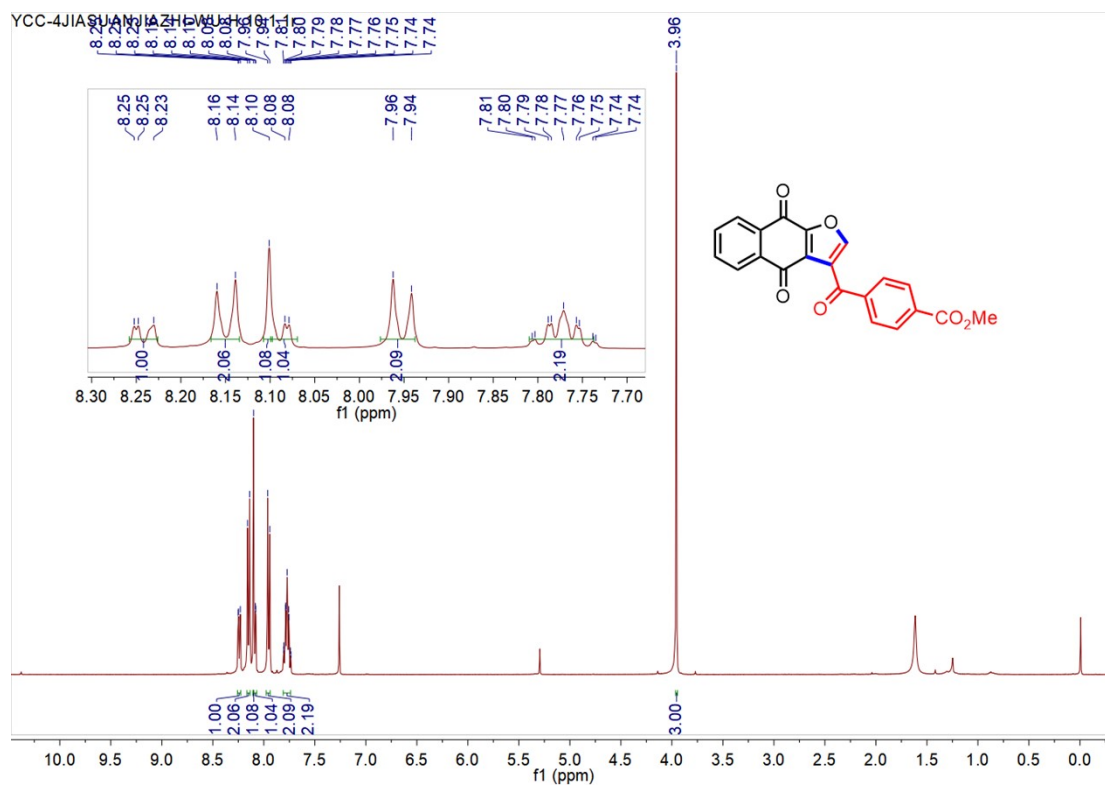


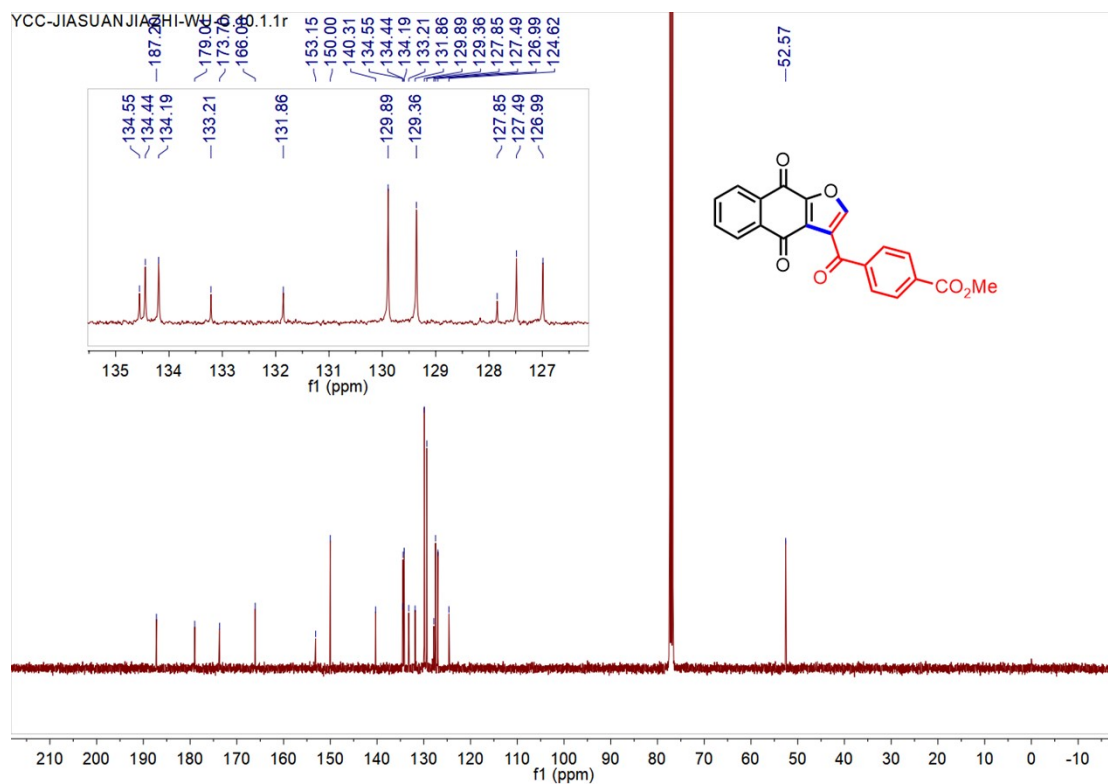




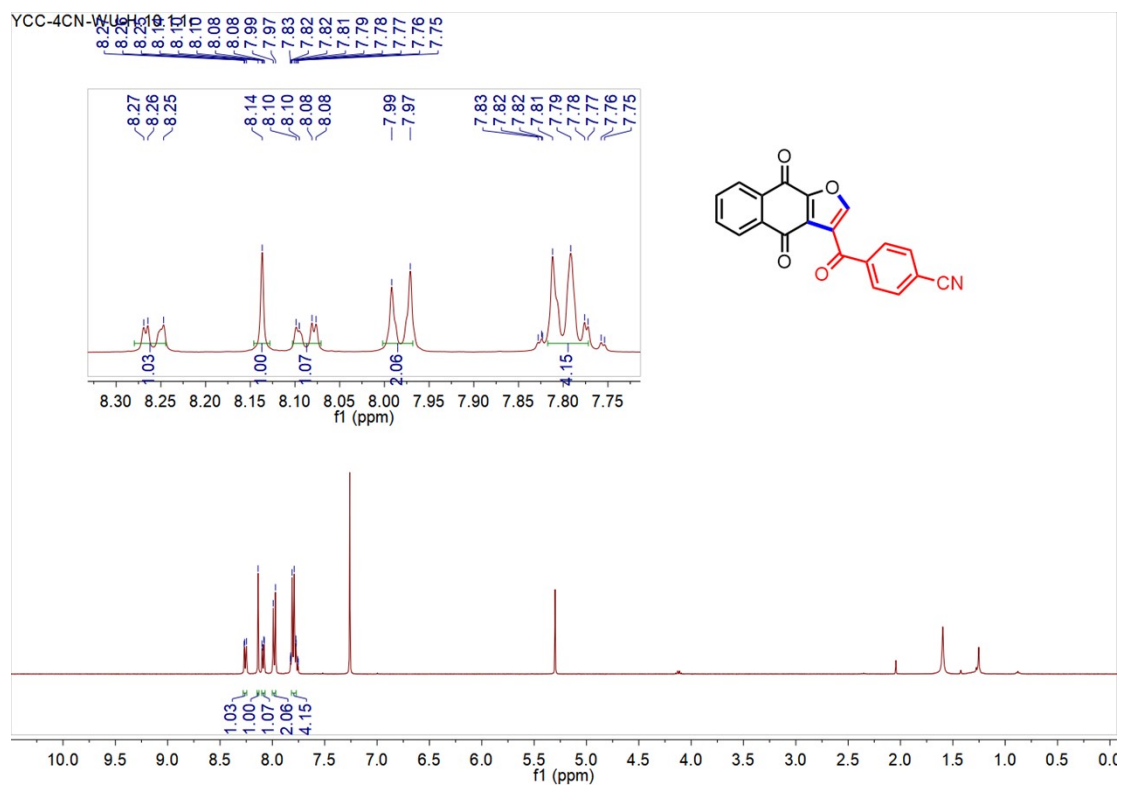


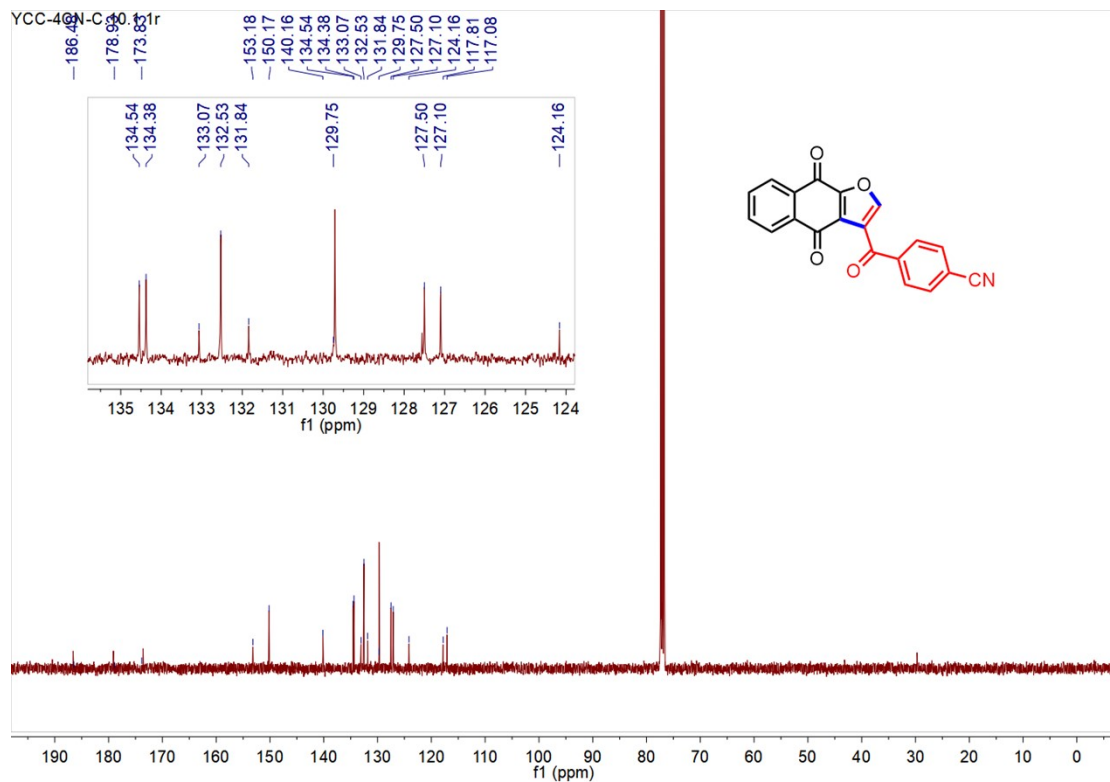
methyl 4-(4,9-dioxo-4,9-dihydronaphtho[2,3-*b*]furan-3-carbonyl)benzoate (**38**):





4-(4,9-dioxo-4,9-dihydronaphtho[2,3-*b*]furan-3-carbonyl)benzonitrile (**39**):





3-(thiophene-2-carbonyl)naphtho[2,3-*b*]furan-4,9-dione (**40**):

