

Synthesis of Antimicrobial Active 9,10-Phenanthrenequinones by Carbene Organocatalytic Tandem Reactions

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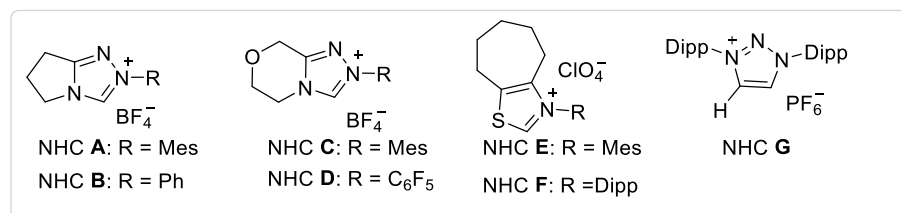
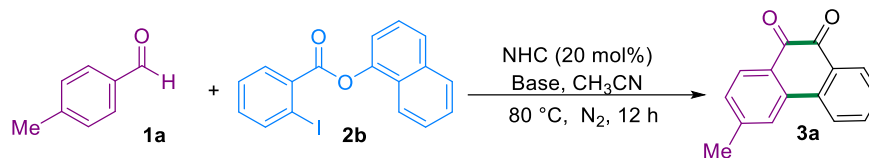
1. General information

Commercially available materials purchased from Energy Chemical and J&K were used as received. All reactions were carried out in dried glassware under an argon atmosphere. CH₃CN (99.5%, Extra Dry, over Molecular Sieves, Stabilized, AcroSeal®, Code: 364311000) and CH₂Cl₂ (99.5%, Extra Dry, over Molecular Sieves, Stabilized, AcroSeal®, Code: 348465000) and were purchased from Acros Organics. Extracts were dried over technical grade Na₂SO₄. Analytical thin layer chromatography (TLC) was performed on pre-coated Merck silica gel 60 F254 plates (0.25 mm) and visualized by UV. Concentration *in vacuo* was performed by rotary evaporation to ~ 10 mbar at 40 °C, drying at ~ 10⁻² mbar and at R.T. Visualization was performed using a UV lamp or KMnO₄ stain followed by heating. Unless otherwise specified, all reactions were prepared using 10.0 mL vial under N₂ atmosphere in glove-box from BURAN UNILAB SP. NMR spectra were measured on a Bruker ASCEND (AVANCE III HD 400 MHz) spectrometer. The chemical shift values were corrected to 7.26 ppm (¹H NMR) and 77.16 ppm (¹³C NMR) for CDCl₃, 3.30 ppm (¹H NMR), 2.50 ppm (¹H NMR) and 39.51 ppm (¹³C NMR) for DMSO-*d*₆. The multiplicities are reported in Hz as: s = singlet, br = broad singlet, d = doublet, t = triplet, q = quartet and m = multiplet. All first-order splitting patterns were assigned on the base of the appearance of the multiplet. High resolution mass spectrometer analysis (HRMS) was performed on Thermo Fisher Q Exactive mass spectrometer. Thermogravimetric Analysis (TGA) was performed on Switzerland - METTLER -TGA2.

2. Experimental Section

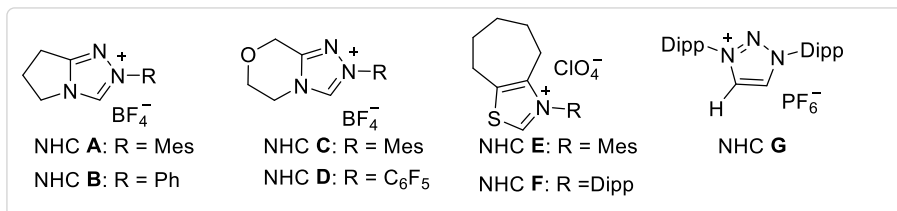
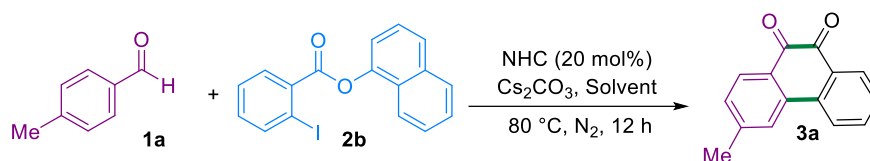
2.1 Supplemental results of condition optimization

Table S1. Additional examination of reaction conditions^{a,b}



Entry	Pre-NHC	Base	Yield (%)
1	A	Cs ₂ CO ₃	35
2	B	Cs ₂ CO ₃	43
3	C	Cs₂CO₃	52
4	D	Cs ₂ CO ₃	41
5	E	Cs ₂ CO ₃	25
6	F	Cs ₂ CO ₃	<5
7	G	Cs ₂ CO ₃	<5
8	C	K ₂ CO ₃	37
9	C	Na ₂ CO ₃	trace
10	C	Li ₂ CO ₃	trace
11	C	K ₃ PO ₄	39
12	C	<i>t</i> -BuOK	46
13	C	DABCO	trace
14	C	KOAc	trace

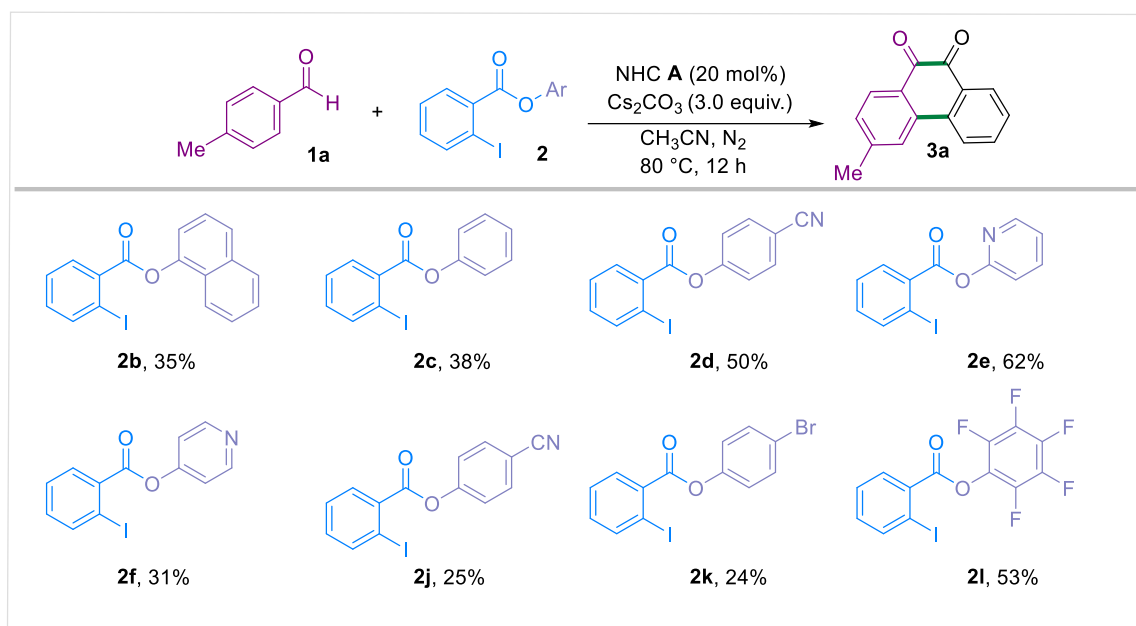
^a Unless otherwise specified, the reactions were conducted with **2b** (0.05 mmol, 1.0 equiv.), aldehyde **1a** (1.8 equiv.), NHC catalyst (20 mol%) and base (3.0 equiv.) in CH₃CN (1.0 mL) under N₂ atmosphere at 80 °C for 12 h; ^b Yields of **3a** were determined via ¹H NMR analysis with 1,3,5-trimethoxy-benzene as an internal standard; Isolated yield in the parenthesis; Mes = 2,4,6-trimethylphenyl.

Table S2. Additional examination of reaction conditions on solvents^{a,b}

Entry	Pre-NHC	Solvent	Yield (%)
1	C	DMF	27
2	C	THF	28
3	C	EA	39
4	C	1,4-dioxane	38
5	C	MTBE	26
6	C	PhCl	trace
7	C	PhCF ₃	trace

^a Unless otherwise specified, the reactions were conducted with **2b** (0.05 mmol, 1.0 equiv.), aldehyde **1a** (1.8 equiv.), NHC catalyst (20 mol%) and Cs₂CO₃ (3.0 equiv.) in solvent (1.0 mL) under N₂ atmosphere at 80 °C for 12 h; ^b Yields of **3a** were determined via ¹H NMR analysis with 1,3,5-trimethoxy-benzene as an internal standard; Isolated yield in the parenthesis; Mes = 2,4,6-trimethylphenyl.

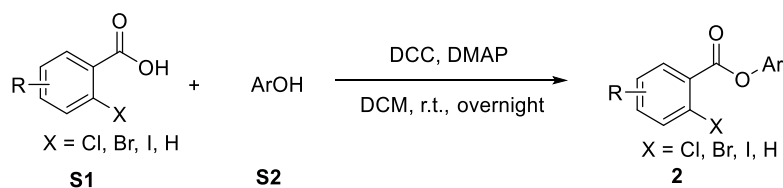
Table S3. Additional evaluation of leaving group^{a,b}



^a Unless otherwise specified, the reactions were conducted with **2** (0.05 mmol, 1.0 equiv.), aldehyde **1a** (1.8 equiv.), NHC catalyst (20 mol%) and Cs₂CO₃ (3.0 equiv.) in solvent (1.0 mL) under N₂ atmosphere at 80 °C for 12 h; ^b Yields of **3a** were determined via ¹H NMR analysis with 1,3,5-trimethoxy-benzene as an internal standard; Isolated yield in the parenthesis; Mes = 2,4,6-trimethylphenyl.

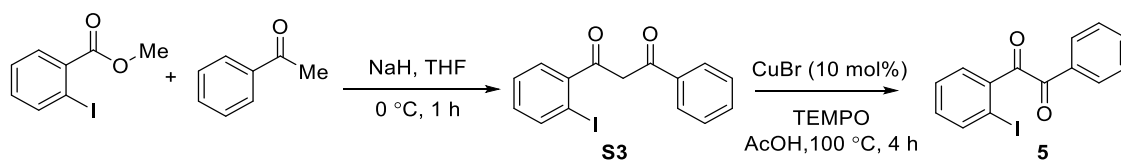
2.2 Preparation of substrates.

Scheme S1. Preparation of substrate **2** ^[1]



To a solution of the acid **S1** (5.0 mmol, 1.0 equiv.), phenol **S2** (1.1 equiv.) in DCM (20.0 mL) was added DCC (1.1 equiv.) and DMAP (0.04 equiv.). The resulting solution was kept stirring at r.t. for overnight when the substrate **S1** was consumed completely (monitored by TLC). The reaction mixture was concentrated *in vacuo* and purified by column chromatography on silica gel (Petroleum ether / Ethyl acetate = 5:1) to afford the desired product **2**, which was confirmed by ¹H NMR, ¹³C NMR spectra and HRMS.

Scheme S2. Preparation of **5** ^[2]

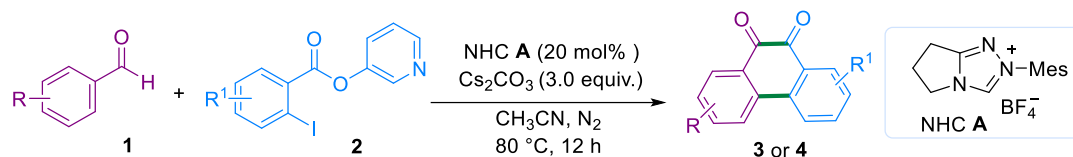


Step 1: In a 50 mL round-bottom flask, solid NaH (10.0 mmol, 2.0 equiv.) was taken in dry THF (30.0 mL) under a nitrogen atmosphere and kept the reaction mixture in an ice bath. Acetophenone (5.0 mmol, 1.0 equiv.) in dry THF (5.0 mL) was added after 5 min to the reaction mixture and allowed to stir at the same temperature for 1 h. Then, methyl 2-iodobenzoate (1.05 equiv.) in 5.0 mL dry THF was added and allowed to stir at r.t. for 5 h. Upon completion, the reaction mixture was cooled to 0 °C and quenched with aq. NH₄Cl. The mixture was extracted with ethyl acetate (3 x 15.0 mL), and the organic phase was subsequently washed with brine (1 x 10.0 mL) and dried over anhydrous Na₂SO₄. The solvent was evaporated *in vacuo*, and the crude **S3** was directly used for the next step without further purification.

Step 2: In a 50.0 mL round-bottom flask, the crude **S3** (5.0 mmol, 1.0 equiv.) was taken in 15.0 mL AcOH. Subsequently, CuBr (10 mol%) and TEMPO (2.0 equiv.) were added to the mixture and allowed to stir at 100 °C for 2 h. Upon completion, the reaction mixture was cooled to room temperature and transferred to a 250 mL of erlenmeyer flask and diluted with ethyl acetate and water. Then, the AcOH was slowly quenched with solid NaHCO₃ and the mixture was extracted with ethyl acetate (3 x 15.0 mL). The organic phase was subsequently washed with brine (1 x 10.0 mL) and dried over anhydrous Na₂SO₄. The solvent was evaporated *in vacuo*, and the crude was purified by flash column chromatography using *n*-hexane/ethyl acetate (99:1) to afford **5** as a yellow liquid.

2.3 General procedure for preparation of 9,10-phenanthrenequinones products

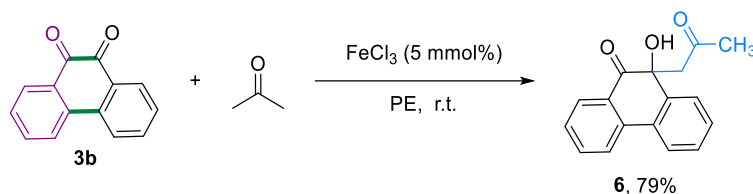
General procedure A:



In glove box under N₂ atmosphere, to an oven-dried 10.0 mL screw cap vial charged with a magnetic stirring bar was added triazolium salt NHC **A** (20 mol%), **2** (0.1 mmol, 1.0 equiv.), aldehyde **1** (1.8 equiv.) and CH₃CN (1.0 mL). The mixture was stirred for 2 min, then Cs₂CO₃ (3.0 equiv.) was added into the reaction. Then the vial was sealed and removed out from the glove box. The resulting solution was kept stirring at 80 °C for 12 h when the substrate was consumed completely (monitored by TLC). The reaction mixture was concentrated *in vacuo* and purified by column chromatography on silica gel (petroleum ether / CH₂Cl₂ = 2:1 or petroleum ether / CH₂Cl₂ = 1:1) to afford the desired product **3** or **4**. All the products were confirmed by ¹H NMR, ¹³C NMR spectra and HRMS.

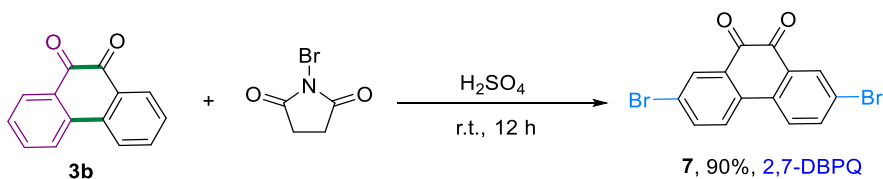
2.4 Derivatization of product 3a

Scheme S3. Preparation of **6** from 9,10-phenanthraquinone (**3b**)^[3]



To a solution of **3b** (0.1 mmol, 1.0 equiv.) in petroleum ether (PE) under N₂ at room temperature was added acetone (1.5 equiv.) and FeCl₃ (5 mmol%). The resulting mixture was stirred for 24 hours at room temperature. The resulting reaction solution was mixed with silica gel and evaporated *in vacuo*. The residue was purified by flash column chromatography using silica gel (Petroleum ether: Ethyl acetate = 5: 1) to afford the desired products **6** as a white solid (21.0 mg, 79%).

Scheme S4. Preparation of **7** from 9,10-phenanthraquinone (**3b**)^[4]



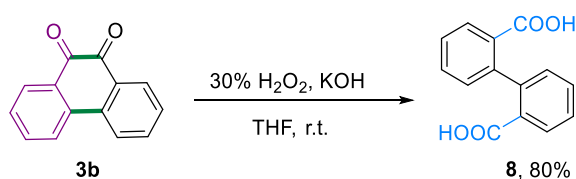
9,10-Phenanthraquinone (**3b**, 0.1 mmol, 1.0 equiv.) was added to 12 mL of 98% sulphuric acid. After gradual addition of NBS (2.1 equiv.), the system was stirred at room temperature for 12 hours. The obtained precipitate was filtered, washed with water and dried to yield the product **7** as an orange solid (32.9 mg, 90%); m.p. 272.4 – 273.6 °C.

¹H NMR (400 MHz, CDCl₃) δ 8.31 (s, 2H), 7.85 – 7.83 (d, *J* = 1.4 Hz, 4H);

HRMS (ESI, *m/z*): Calculated for C₁₄H₇Br₂O₂⁺ [M+H]⁺: 364.8807, found: 364.8807.

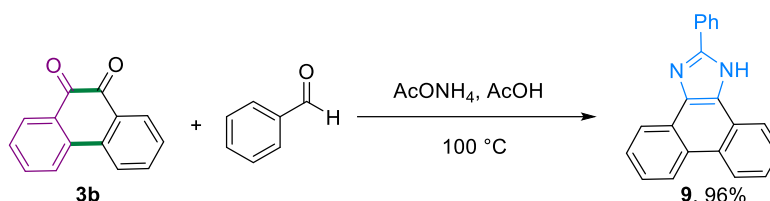
The characterization matched previous literature.^[4]

Scheme S5. Preparation of **8** from 9,10-phenanthraquinone (**3b**)^[5]



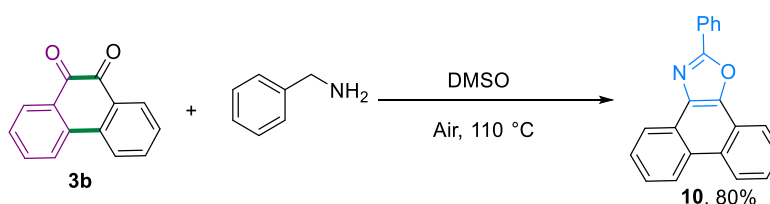
9,10-phenanthraquinone (**3b**, 0.1 mmol, 1.0 equiv.), 30% H₂O₂ (1.0 equiv.), KOH (2.0 equiv.) in H₂O₂ (1 mL) were added to THF (5 mL) and stirred at room temperature for 4 hours. The mixture was acidified (pH = 2) using concentrated HCl. Then the solution was extracted with CH₂Cl₂ (3 × 20 mL), washed with water (20 mL), brine (20 mL), dried over anhydrous Na₂SO₄ and the solvent was evaporated under reduced pressure to give the product **8** as a white solid (19.3 mg, 80%).

Scheme S6. Preparation of **9** from 9,10-phenanthraquinone (**3b**)^[6]



In a 100 mL round-bottomed flask fitted with an efficient reflux condenser were placed **3b** (0.1 mmol, 1.0 equiv.), benzaldehyde (3.0 equiv.), ammonium acetate (25.0 equiv.) and 20.0 mL acetic acid. The reactants were magnetically stirred and refluxed for 3 hours. Then the mixture was poured into ice water and solid precipitated out, which was filtered, washed with water and ether and dried under reduce pressure, obtain **9** as a white solid (28.2 mg, 96%), which was confirmed by ¹H NMR and ¹³C NMR spectra and HRMS.

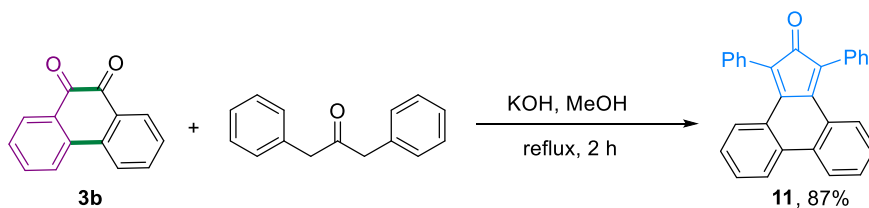
Scheme S7. Preparation of **10** from 9,10-phenanthraquinone (**3b**)^[7]



In an oven dried 9,10-phenanthraquinone (**3b**, 0.1 mmol, 1.0 equiv.), primary amine that contain benzylamine (1.0 equiv.) were taken in DMSO and stirred at 110 °C for 5 hours in an oil bath under open air. The reaction progress was monitored by TLC. Finally after the completion of the reaction the reaction mixture was cooled to 0 °C and diluted with EtOAc and washed with brine (20.0 mL). The combined organic extract were repeatedly washed with brine solution and dried over anhydrous sodium sulphate

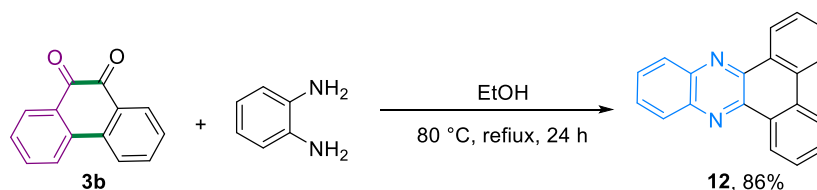
and concentrated under reduced pressure to give crude product which were purified by column chromatography [silica gel (100-200 mesh)] using Petroleum ether: Ethyl acetate (20:1) as eluent to obtained **10** as a white solid (23.6 mg). Which were confirmed by ^1H NMR and ^{13}C NMR spectra and HRMS.

Scheme S8. Preparation of **11** from 9,10-phenanthraquinone (**3b**)^[8]



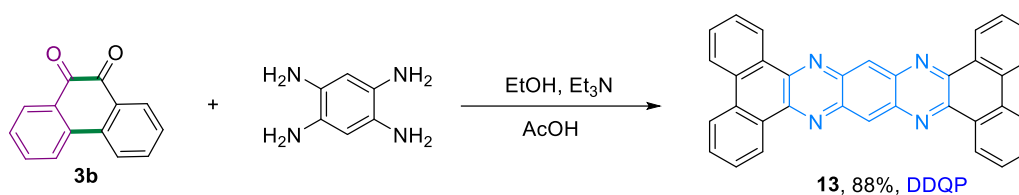
In a three-neck flask equipped with a condenser and a dropping funnel 9,10-phenanthrenequinone (**3b**, 0.1 mmol, 1.0 equiv.) and 1,3-diphenylacetone (1.0 equiv.) were suspended in MeOH (20.0 mL) and heated to reflux. Then a solution of KOH (3.5 equiv.) in MeOH (7.0 mL) was added dropwise. After complete addition of the KOH solution, the reaction mixture was refluxed for 2 h and then cooled to room temperature. The precipitated solid was collected, washed with MeOH and dried to yield the desired product **11** as a grey solid (33.2 mg, 87 %). Due to poor solubility in common NMR solvents no NMR spectra was obtained. **HRMS** (ESI, m/z): Calculated for $\text{C}_{29}\text{H}_{19}\text{O}^+$ $[\text{M}+\text{H}]^+$: 383.1430, found: 383.1420.

Scheme S9. Preparation of **12** from 9,10-phenanthraquinone (**3b**)^[9]



Add ethylenediamine (0.1 mmol, 1.0 equiv.) to a solution of **3b** (0.1 mmol, 1.0 equiv.) in EtOH (0.1 M). Heat the solution to reflux 24 h. After TLC monitoring shows the completion of the reaction, evaporate the solvent. The residue was purified by silica gel column chromatography (Petroleum ether: Ethyl acetate = 20:1), obtain **12** as a white solid (24.1 mg).

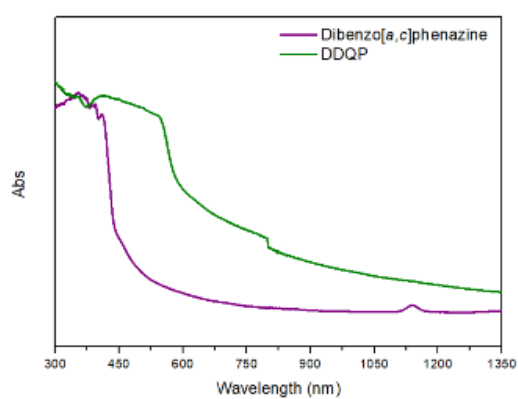
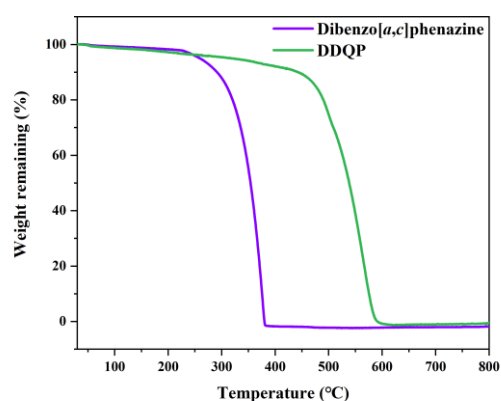
Scheme S10. Preparation of **13** from 9,10-phenanthraquinone (**3b**)^[4]



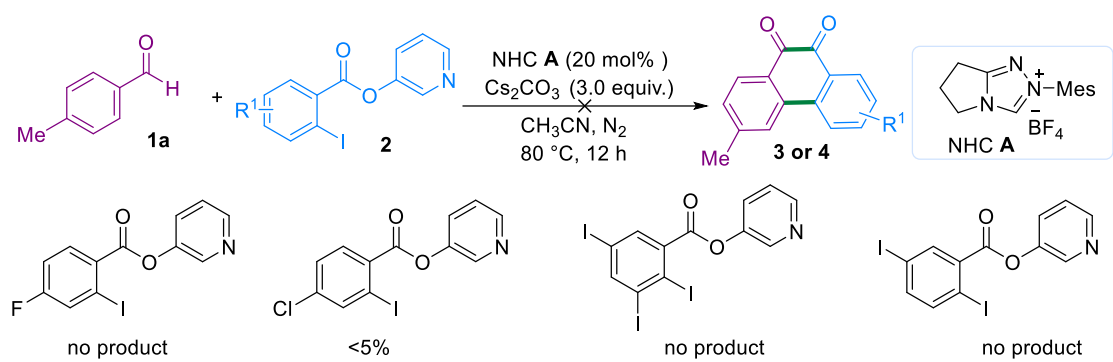
This method was adapted from the work by Kian Ping Loh *et al.* **3b** (0.1 mmol) and benzene-1,2,4,5-tetraamine tetrahydrochloride (1.0 mmol) were transferred into a round bottom flask with a magnetic spin bar, and suspended in 6 mL of ethanol and 20 mL of acetic acid to make a brown suspension in N₂ atmosphere, which was heated to 100 °C. After the addition of 1.0 mL of triethylamine, the mixture changed to red color instantly, and was further refluxed at 130 °C for 6 hours. Once cooled to room temperature, the mixture was diluted with acetic acid and poured into 200 mL of water. The red precipitate was collected and exhaustively washed by Soxhlet extraction with water, ethanol, chloroform, THF, N, N-Dimethylformamide and ethanol again, and dried at 120 °C overnight in vacuum oven to yield DDQP as copper-colored powder in quantitative yield (42.4 mg). No solution NMR data was collected due to its poor solubility.

Thermal stability study of **12** and **13**

1,4-Diazines are an important class of nitrogen-containing heterocyclic compounds with significant applications in synthetic chemistry, materials sciences, and as intermediates in fragrance and flavor synthesis.^[10] The dibenzo[a,c]phenazine (**12**) and DDQP (**13**) derivatives were thereby synthesized in good yields by simple treatment of 9,10-phenanthraquinone (**3b**) with corresponding 1,2-diamines. Notably, the DDQP product **13** showed a remarkable stability which started to decompose at approximately 460 °C from the thermal gravimetric analysis (TGA).

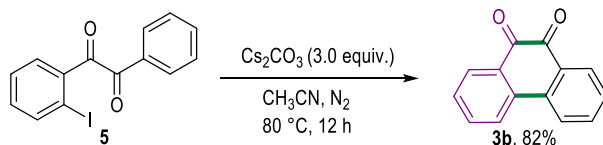


2.5 Unsuccessful substrates 2



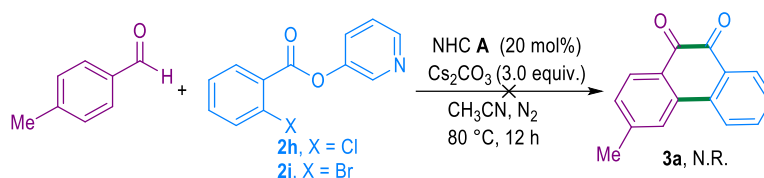
2.6 Preliminary mechanistic studies

Scheme S11. Cyclization with **5**.

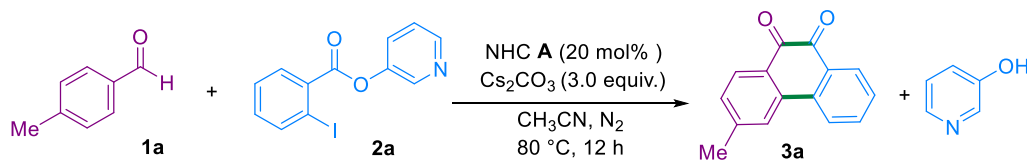


A 1,2-dione compound **5** (0.1 mmol), prepared according to a previous procedure, was first subjected to the reaction conditions with Cs_2CO_3 in CH_3CN at 80°C for 12 hours. The reaction gave the target product **3b** in 82% (17.0 mg) yield, implying that the catalytic tandem reaction most likely involves a Benzoin intermediate (Scheme S11).

Scheme S12. Control experiments.

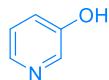


In glove box under N_2 atmosphere, to an oven-dried 10.0 mL screw cap vial charged with a magnetic stirring bar was added triazolium salt NHC **A** (20 mol%), **2** (0.1 mmol, 1.0 equiv.), aldehyde **1a** (1.8 equiv.) and CH_3CN (1.0 mL). The mixture was stirred for 2 min, then Cs_2CO_3 (3.0 equiv.) was added into the reaction. Then the vial was sealed and removed out from the glove box. The resulting solution was kept stirring at 80°C for 12 h when the substrate was consumed completely (monitored by TLC). Control experiment were carried out to shed insights into the plausible reaction process. First, experiments with ortho-Cl/Br-aryl carboxylate esters **2h** and **2i** failed to give the desired annulation product **3a** (Scheme S12).



In glove box under N_2 atmosphere, to an oven-dried 10.0 mL screw cap vial charged with a magnetic stirring bar was added triazolium salt NHC **A** (20 mol%), **2a** (0.1 mmol, 1.0 equiv.), aldehyde **1a** (1.8 equiv.) and CH_3CN (1.0 mL). The mixture was stirred for 2 min, then Cs_2CO_3 (3.0 equiv.) was added into the reaction. Then the vial was sealed and removed out from the glove box. The resulting solution was kept

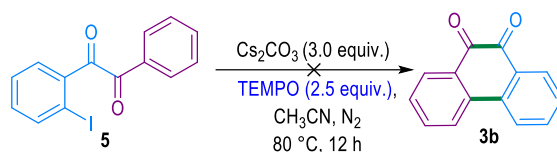
stirring at 80 °C for 12 h when the substrate was consumed completely (monitored by TLC), 3-pyridinol intermediates was isolated. The characterization matched previous literature.



¹H NMR (400 MHz, CDCl₃) δ 8.28 (d, J = 2.6 Hz, 1H), 8.09 (dd, J = 4.6, 1.6 Hz, 1H), 7.32 (dt, J = 8.6, 1.8 Hz, 1H), 7.29 – 7.27 (m, 1H).

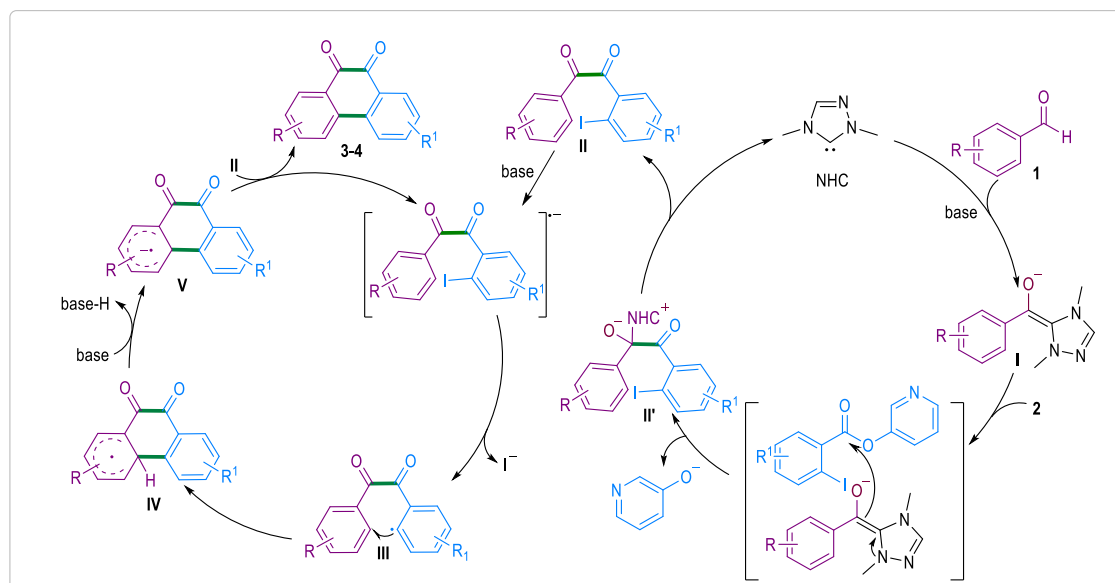
HRMS (ESI, m/z): Calculated for C₅H₆O [M + H]⁺: 96.0443, found: 96.0447.

Scheme S13. Control experiment with TEMPO in the cyclization with **5**.



In glove box under N₂ atmosphere, to an oven-dried 10.0 mL screw cap vial charged with a magnetic stirring bar was added triazolium salt NHC **A** (20 mol%), **2** (0.1 mmol, 1.0 equiv.), aldehyde **1a** (1.8 equiv.), TEMPO (2.5 equiv.) and CH₃CN (1.0 mL). The mixture was stirred for 2 min, then Cs₂CO₃ (3.0 equiv.) was added into the reaction. Then the vial was sealed and removed out from the glove box. The resulting solution was kept stirring at 80 °C for 12 h when the substrate was consumed completely (monitored by TLC). While substrate **5** was not smoothly transformed to corresponding products **3b**, which can be proved that the cyclization may be a radical process. We have endeavored to employ TEMPO as additives to the experiment in Figure 3B. The control reaction failed to give the desired annulation product **3b**, implying that the cyclization might be through a radical process.

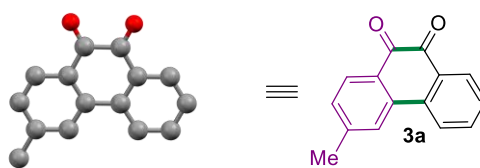
Scheme S14. Plausible mechanism



Based on these experiments and prior reports from our group and others, a plausible mechanism for the carbene-catalyzed annulation reaction is proposed in (Scheme S13). Firstly, the Breslow intermediate **I**, formed by the reaction between free carbene and aldehyde **1**, undergoes an addition reaction with ester substrate **2**, leading to the formation of intermediate **II'** after elimination of the pyridin-3-olate. Elaboration of the carbene catalyst would give the benzoin adduct **II** for further annulation process. Drawing on studies by Shi,^{11a} Hiyashi,^{11b-c} Murphy,^{11d-f} Studer,^{11g-h} and others,^{11i-k} an aryl radical intermediate **III** generated by cleavage of the C-I bond under basic conditions is proposed to initiate the annulation via intramolecular radical addition. Subsequent elimination of the H and single-electron transfer processes furnish the final 9,10-phenanthrenequinone products **3-4** in high efficiency.

2.7 X-ray crystallographic analysis of **3a**

The crystal growth procedure: Compound **3a** was dissolved into 3.0 mL of dichloromethane and *n*-Hexane. The mixture was evaporated slowly at room temperature to obtain crystal **3a**. A suitable crystal with dimensions $0.28 \times 0.25 \times 0.11$ mm³ was selected. The crystal was kept at 293(2) K during data collection. CCDC: 2381765 for **3a** contains the supplementary crystallographic data that can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.



Identification code	3a
Empirical formula	C ₁₅ H ₁₀ O ₂
Formula weight	222.23
Temperature	293(2)
Crystal system	triclinic
Space group	P-1
Unit cell dimensions	a = 7.4203(11) Å
	b = 8.0074(11) Å
	c = 10.4911(13)
Volume	538.47(13) Å ³
Z	2
Density (calculated)	1.371 Mg/m ³
Absorption coefficient	0.091 mm ⁻¹
F (000)	232
Crystal size	0.28 × 0.25 × 0.11 mm ³
Theta range for data collection	6.908 to 50.084 °.

Index ranges	$-8 \leq h \leq 8, -9 \leq k \leq 9, -10 \leq l \leq 12$
Reflections collected	3610
Independent reflections	1901 [$R_{\text{int}} = 0.0289, R_{\text{sigma}} = 0.0463$]
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	1901/0/155
Goodness-of-fit on F^2	1.054
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0550, wR_2 = 0.1201$
R indices (all data)	$R_1 = 0.1000, wR_2 = 0.1435$

2.8 Antibacterial Activity Studies *in Vitro*

Antibacterial Activity *in Vitro*: Antibacterial activities of the title compounds against *Xanthomonas oryzae* pv. *oryzae* (*Xoo*) and *Xanthomonas axonopodis* pv. *citri* (*Xac*) were evaluated by using the turbidimeter test.^[12] Thiodiazole-copper and Bismertiazol were used as the positive controls. The compound was dissolved in 150.0 μL of dimethylformamide and diluted with 0.1% (v/v) Tween-20 to prepare the solutions on a concentration of 100 $\mu\text{g}/\text{mL}$. 1.0 mL of the above solution was added to the non-toxic nutrient broth (NB: 1.5 g of beef extract, 2.5 g of peptone, 0.5 g of yeast powder, 5.0 g of glucose and 500 mL of distilled water, pH = 7.0 ~ 7.2) liquid medium in a 4.0 mL tube. Then, 40.0 μL of NB solution containing *Xoo* or *Xac* was added to 5.0 mL of the NB solution containing the test compound. The inoculated test tube was incubated at (28 ± 1) °C under continuous shaking at 180 rpm for 36 or 48 hours. The culture growth was monitored by measuring the optical density at 595 nm (OD_{595}) and expressed as corrected turbidity. The relative inhibitory rate was calculated as follows:

$$I(\%) = (C_{\text{tur}} - T_{\text{tur}}) / C_{\text{tur}} \times 100\%.$$

C_{tur} : the corrected turbidity value of bacterial growth on untreated NB;

T_{tur} : the corrected turbidity value of bacterial growth on treated NB;

I : The relative inhibitory rate.

Table S4. Antibacterial activities *in vitro* of target compounds against *Xoo*^a

Compounds	100 µg/mL	Compounds	100 µg/mL
3a	69.13 ± 1.17	3q	61.96 ± 2.52
3c	96.43 ± 0.71	3r	41.93 ± 3.06
3e	88.93 ± 1.78	3s	78.52 ± 0.98
3f	59.13 ± 2.12	3t	48.64 ± 2.82
3i	31.66 ± 0.36	3u	87.98 ± 0.46
3j	93.34 ± 1.11	3v	83.34 ± 2.46
3m	42.51 ± 0.34	4d	56.84 ± 3.80
3n	93.06 ± 0.20	4g	50.38 ± 4.22
3o	45.30 ± 2.81	8	46.97 ± 2.16
3p	71.00 ± 1.04	9	0
BT^b	47.72 ± 1.81	TC^b	45.73 ± 1.82

^aAll data were average data of three replicates; ^bCommercial bactericide was used as the positive control; BT = Bismethiazol, TC = Thiodiazole copper.

Table S5. Antibacterial activities *in vitro* of target compounds against *Xac*^a

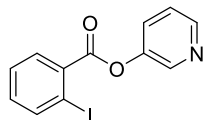
Compounds	100 µg/mL	Compounds	100 µg/mL
3a	63.70 ± 2.31	3q	53.32 ± 1.70
3c	81.20 ± 1.67	3r	61.46 ± 1.63
3e	62.37 ± 1.20	3s	100
3f	55.86 ± 0.83	3t	45.18 ± 1.74
3i	32.25 ± 3.68	3u	85.97 ± 0.45
3j	47.39 ± 1.38	3v	65.10 ± 3.08
3m	71.56 ± 2.81	4d	48.32 ± 2.28
3n	50.38 ± 1.47	4g	48.30 ± 4.21
3o	13.97 ± 1.14	8	16.65 ± 1.48
3p	58.64 ± 1.63	9	0
BT^b	42.27 ± 2.43	TC^b	31.58 ± 1.55

^aAll data were average data of three replicates; ^bCommercial bactericide was used as the positive control; BT = Bismethiazol, TC = Thiodiazole copper.

3. Characterizations of substrates and products

3.1 Characterization of substrates.

Pyridin-3-yl 2-iodobenzoate (**2a**)



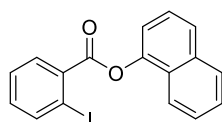
Prepared according to Scheme S1. Flash column chromatography (Petroleum ether / Ethyl acetate = 5:1) yielded the title compound **2a**, white solid; R_f 0.4 (Petroleum ether / Ethyl acetate = 5:1); m.p. 62.8 – 63.5 °C.

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.60 (d, $J = 2.6$ Hz, 1H), 8.55 (dd, $J = 4.8, 1.4$ Hz, 1H), 8.08 (ddd, $J = 9.8, 7.8, 1.4$ Hz, 2H), 7.67 (m, 1H), 7.50 (td, $J = 7.6, 1.2$ Hz, 1H), 7.40 (dd, $J = 8.4, 4.8$ Hz, 1H), 7.25 (tt, $J = 7.6, 1.4$ Hz, 1H).

$^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 164.3, 147.5, 147.3, 143.4, 141.9, 133.7, 133.3, 131.8, 129.4, 128.2, 124.0, 94.9 ppm.

HRMS (ESI, m/z): Calculated for $\text{C}_{12}\text{H}_9\text{INO}_2^+$ $[\text{M}+\text{H}]^+$: 325.9672, found: 325.9672.

Naphthalen-1-yl 2-iodobenzoate (**2b**)



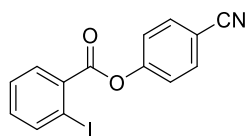
Prepared according to Scheme S1. Flash column chromatography (Petroleum ether / Ethyl acetate = 5:1) yielded the title compound **2b**, white solid; R_f 0.5 (Petroleum ether / Ethyl acetate = 5:1); m.p. 53.3 – 54.5 °C.

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.23 (dd, $J = 7.8, 1.8$ Hz, 1H), 8.11 (dd, $J = 7.8, 1.2$ Hz, 1H), 8.03 – 7.93 (m, 1H), 7.93 – 7.85 (m, 1H), 7.78 (d, $J = 8.2$ Hz, 1H), 7.51 (ddd, $J = 9.8, 5.4, 2.2$ Hz, 4H), 7.46 – 7.38 (m, 1H), 7.24 (td, $J = 7.6, 1.6$ Hz, 1H).

$^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 164.9, 146.7, 142.1, 134.8, 133.9, 133.6, 131.8, 128.3, 128.2, 126.9, 126.7, 126.6, 126.4, 125.6, 121.4, 118.3, 95.1 ppm.

HRMS (ESI, m/z): Calculated for $\text{C}_{17}\text{H}_{11}\text{IO}_2\text{Na}^+$ $[\text{M}+\text{Na}]^+$: 396.9696, found: 396.9697.

4-Cyanophenyl 2-iodobenzoate (2d)



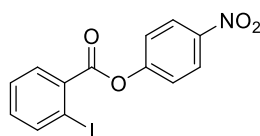
Prepared according to Scheme S1. Flash column chromatography (Petroleum ether / Ethyl acetate = 5:1) yielded the title compound **2d**, white solid; R_f 0.5 (Petroleum ether / Ethyl acetate = 5:1); m.p. 69.7 – 72.5 °C.

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.08 (m, 1H), 8.04 (m, 1H), 7.74 (m, 2H), 7.50 (m, 1H), 7.44 – 7.39 (m, 2H), 7.26 (m, 1H).

$^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 164.0, 154.0, 142.0, 133.8, 133.2, 131.8, 128.3, 122.9, 118.3, 110.1, 94.9 ppm.

HRMS (ESI, m/z): Calculated for $\text{C}_{14}\text{H}_8\text{INO}_2\text{Na}^+$ $[\text{M}+\text{Na}]^+$: 371.9491, found: 371.9491.

4-Nitrophenyl 2-iodobenzoate (2j)



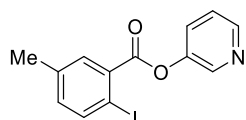
Prepared according to Scheme S1. Flash column chromatography (Petroleum ether / Ethyl acetate = 5:1) yielded the title compound **2j**, white solid; R_f 0.5 (Petroleum ether / Ethyl acetate = 5:1); m.p. 96.4 – 98.2 °C.

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.45 – 8.26 (m, 2H), 8.07 (m, 2H), 7.51 (m, 1H), 7.48 – 7.44 (m, 2H), 7.27 (m, 1H).

$^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 163.9, 155.5, 145.7, 142.1, 134.0, 133.1, 131.9, 128.4, 125.4, 122.7, 95.0 ppm.

HRMS (ESI, m/z): Calculated for $\text{C}_{13}\text{H}_8\text{INO}_4\text{Na}^+$ $[\text{M}+\text{Na}]^+$: 391.9390, found: 391.9394.

Pyridin-3-yl 2-iodo-5-methylbenzoate (2m)



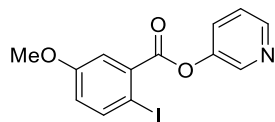
Prepared according to Scheme S1. Flash column chromatography (Petroleum ether / Ethyl acetate = 5:1) yielded the title compound **2m**, white solid; R_f 0.4 (Petroleum ether / Ethyl acetate = 5:1); m.p. 70.6 – 71.4 °C.

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.59 (d, $J = 2.6$ Hz, 1H), 8.53 (dd, $J = 4.8, 1.4$ Hz, 1H), 7.93 (d, $J = 8.2$ Hz, 1H), 7.86 (d, $J = 2.2$ Hz, 1H), 7.65 (m, 1H), 7.39 (m, 1H), 7.12 – 6.98 (m, 1H), 2.38 (s, 3H).

$^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 164.5, 147.5, 147.3, 143.5, 141.6, 138.5, 134.8, 133.1, 132.5, 129.4, 124.0, 90.8, 20.9 ppm.

HRMS (ESI, m/z): Calculated for $\text{C}_{13}\text{H}_{11}\text{INO}_2^+$ $[\text{M}+\text{H}]^+$: 339.9829, found: 339.9830.

Pyridin-3-yl 2-iodo-5-methoxybenzoate (**2n**)



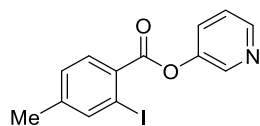
Prepared according to Scheme S1. Flash column chromatography (Petroleum ether / Ethyl acetate = 5:1) yielded the title compound **2n**, white solid; R_f 0.4 (Petroleum ether / Ethyl acetate = 5:1); m.p. 52.1 – 52.9 °C.

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.59 (d, $J = 2.6$ Hz, 1H), 8.53 (dd, $J = 4.6, 1.4$ Hz, 1H), 7.90 (d, $J = 8.7$ Hz, 1H), 7.65 (m, 1H), 7.57 (d, $J = 3.2$ Hz, 1H), 7.38 (dd, $J = 8.4, 4.8$ Hz, 1H), 6.83 (dd, $J = 8.8, 3.2$ Hz, 1H), 3.84 (s, 3H).

$^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 164.2, 159.7, 147.5, 147.4, 143.5, 142.5, 134.1, 129.4, 124.1, 120.3, 117.3, 83.2, 55.8 ppm.

HRMS (ESI, m/z): Calculated for $\text{C}_{13}\text{H}_{11}\text{INO}_3^+$ $[\text{M}+\text{H}]^+$: 355.9778, found: 355.9773.

Pyridin-3-yl 2-iodo-4-methylbenzoate (**2o**)



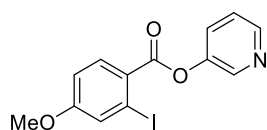
Prepared according to Scheme S1. Flash column chromatography (Petroleum ether / Ethyl acetate = 5:1) yielded the title compound **2o**, white solid; R_f 0.4 (Petroleum ether / Ethyl acetate = 5:1); m.p. 84.3 – 85.6 °C.

¹H NMR (400 MHz, CDCl₃) δ 8.56 (t, *J* = 2.0 Hz, 1H), 8.51 (m, 1H), 8.03 – 7.94 (m, 1H), 7.91 (q, *J* = 2.0 Hz, 1H), 7.62 (m Hz, 1H), 7.36 (m, 1H), 7.29 – 7.24 (m, 1H), 2.35 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 164.1, 147.5, 147.2, 145.0, 143.5, 142.7, 131.8, 129.9, 129.5, 129.1, 124.0, 95.4, 21.0 ppm.

HRMS (ESI, *m/z*): Calculated for C₁₃H₁₁INO₂⁺ [*M*+*H*]⁺:339.9829, found: 339.9832.

Pyridin-3-yl 2-iodo-4-methoxybenzoate (**2p**)



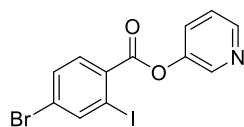
Prepared according to Scheme S1. Flash column chromatography (Petroleum ether / Ethyl acetate = 5:1) yielded the title compound **2p**, white solid; *R_f* 0.4 (Petroleum ether / Ethyl acetate = 5:1); m.p. 123.7 – 124.5 °C.

¹H NMR (400 MHz, CDCl₃) δ 8.55 (d, *J* = 2.6 Hz, 1H), 8.51 (dd, *J* = 4.8, 1.4 Hz, 1H), 8.12 (d, *J* = 8.8 Hz, 1H), 7.62 (dd, *J* = 8.6, 2.6 Hz, 2H), 7.37 (m, 1H), 6.99 (dd, *J* = 8.8, 2.6 Hz, 1H), 3.87 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 163.5, 162.9, 147.6, 147.2, 143.6, 133.6, 129.6, 127.8, 124.2, 124.0, 114.0, 96.9, 55.9 ppm.

HRMS (ESI, *m/z*): Calculated for C₁₃H₁₁INO₃⁺ [*M*+*H*]⁺: 355.9778, found: 355.9774.

Pyridin-3-yl 4-bromo-2-iodobenzoate (**2q**)



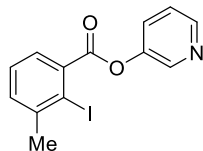
Prepared according to Scheme S1. Flash column chromatography (Petroleum ether / Ethyl acetate = 5:1) yielded the title compound **2q**, white solid; *R_f* 0.6 (Petroleum ether / Ethyl acetate = 5:1); m.p. 101.5 – 102.4 °C.

¹H NMR (400 MHz, CDCl₃) δ 8.58 (d, *J* = 2.6 Hz, 1H), 8.54 (dd, *J* = 4.8, 1.4 Hz, 1H), 8.27 (d, *J* = 1.8 Hz, 1H), 7.94 (d, *J* = 8.4 Hz, 1H), 7.75 – 7.61 (m, 2H), 7.40 (m, 1H).

^{13}C NMR (101 MHz, CDCl_3) δ 163.7, 147.5, 147.4, 144.3, 143.4, 132.8, 131.9, 131.6, 129.4, 128.1, 124.1, 95.8 ppm.

HRMS (ESI, m/z): Calculated for $\text{C}_{12}\text{H}_8\text{BrINO}_2^+$ $[\text{M}+\text{H}]^+$: 403.8777, found: 403.8770.

Pyridin-3-yl 2-iodo-3-methylbenzoate (**2r**)



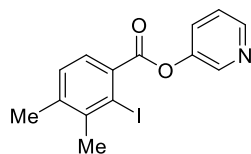
Prepared according to Scheme S1. Flash column chromatography (Petroleum ether / Ethyl acetate = 5:1) yielded the title compound **2r**, colorless oil; R_f 0.5 (Petroleum ether / Ethyl acetate = 5:1).

^1H NMR (400 MHz, CDCl_3) δ 8.53 (d, $J = 2.8$ Hz, 1H), 8.44 (dt, $J = 4.8, 1.6$ Hz, 1H), 7.59 (m, 1H), 7.52 (dt, $J = 7.6, 1.8$ Hz, 1H), 7.37 – 7.21 (m, 3H), 2.45 (s, 3H).

^{13}C NMR (101 MHz, CDCl_3) δ 165.9, 147.5, 147.2, 143.9, 143.3, 136.5, 132.8, 129.2, 128.0, 127.8, 123.9, 100.5, 29.8 ppm.

HRMS (ESI, m/z): Calculated for $\text{C}_{13}\text{H}_{11}\text{INO}_2^+$ $[\text{M}+\text{H}]^+$: 339.9829, found: 339.9836.

Pyridin-3-yl 2-iodo-3,4-dimethylbenzoate (**2s**)



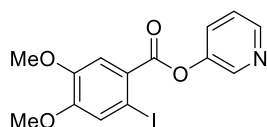
Prepared according to Scheme S1. Flash column chromatography (Petroleum ether / Ethyl acetate = 5:1) yielded the title compound **2s**, white solid; R_f 0.5 (Petroleum ether / Ethyl acetate = 5:1); m.p. 95.6 – 87.3 °C.

^1H NMR (400 MHz, CDCl_3) δ 8.60 (d, $J = 2.6$ Hz, 1H), 8.52 (dd, $J = 4.8, 1.4$ Hz, 1H), 7.68 (ddd, $J = 8.2, 2.8, 1.4$ Hz, 1H), 7.54 (d, $J = 7.8$ Hz, 1H), 7.38 (dd, $J = 8.2, 4.6$ Hz, 1H), 7.22 (d, $J = 7.8$ Hz, 1H), 2.54 (s, 3H), 2.44 (s, 3H).

^{13}C NMR (101 MHz, CDCl_3) δ 166.2, 147.7, 147.2, 143.5, 142.1, 141.6, 134.6, 129.8, 129.4, 127.9, 124.1, 26.4, 22.6 ppm.

HRMS (ESI, m/z): Calculated for $\text{C}_{14}\text{H}_{13}\text{INO}_2^+$ $[\text{M}+\text{H}]^+$: 353.9985, found: 353.9981.

Pyridin-3-yl 2-iodo-4,5-dimethoxybenzoate (2t)



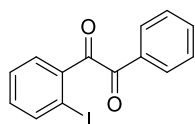
Prepared according to Scheme S1. Flash column chromatography (Petroleum ether / Ethyl acetate = 5:1) yielded the title compound **2t**, white solid; R_f 0.5 (Petroleum ether / Ethyl acetate = 5:1); m.p. 108.6 – 109.7 °C.

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.56 (d, $J = 2.6$ Hz, 1H), 8.52 (dd, $J = 4.8, 1.4$ Hz, 1H), 7.64 (s, 1H), 7.62 (m, 1H), 7.46 (s, 1H), 7.38 (dd, $J = 8.4, 4.6$ Hz, 1H), 3.94 (s, 3H), 3.93 (s, 3H).

$^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 163.5, 152.9, 149.0, 147.6, 147.3, 143.7, 129.6, 124.3, 124.2, 124.0, 114.5, 86.2, 56.5, 56.3 ppm.

HRMS (ESI, m/z): Calculated for $\text{C}_{14}\text{H}_{13}\text{INO}_4^+$ $[\text{M}+\text{H}]^+$: 385.9883, found: 385.9882.

1-(2-Iodophenyl)-2-phenylethane-1,2-dione (5)



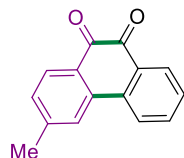
$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.11 – 8.07 (m, 2H), 7.97 (dd, $J = 7.6, 2.6$ Hz, 1H), 7.75 – 7.61 (m, 2H), 7.52 (t, $J = 7.6$ Hz, 2H), 7.49 – 7.43 (m, 1H), 7.35 – 7.19 (m, 1H).

$^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 194.7, 191.3, 141.1, 138.1, 134.7, 134.1, 133.2, 133.0, 130.4, 130.3, 128.9, 128.9, 128.4, 93.3 ppm.

HRMS (ESI, m/z): Calculated for $\text{C}_{14}\text{H}_{19}\text{IO}_2\text{Na}^+$ $[\text{M}+\text{Na}]^+$: 358.9539, found: 358.9535.

3.2 Characterization of phenanthrenequinone products 3 or 4

3-Methylphenanthrene-9,10-dione (**3a**)



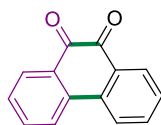
Prepared according to general procedure A. Flash column chromatography (Petroleum ether / CH₂Cl₂ = 1:1) yielded the title compound **3a**, yellow solid (15.7 mg, 71% yield); R_f 0.5 (Petroleum ether / CH₂Cl₂ = 1:1); m.p. 204.8 – 205.6 °C.

¹H NMR (400 MHz, CDCl₃) δ 8.15 (dd, *J* = 7.8, 1.6 Hz, 1H), 8.05 (d, *J* = 8.0 Hz, 1H), 7.98 (dd, *J* = 8.2, 1.2 Hz, 1H), 7.77 (s, 1H), 7.73 – 7.61 (m, 1H), 7.44 (m, 1H), 7.23 (m, 1H), 2.49 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 180.7, 180.0, 147.5, 136.0, 136.0, 135.9, 131.2, 130.9, 130.6, 130.5, 129.6, 129.0, 124.7, 124.0, 22.5 ppm.

HRMS (ESI, m/z): Calculated for C₁₅H₁₁O₂⁺ [M+H]⁺: 223.0753, found: 223.0757.

Phenanthrene-9,10-dione (**3b**)



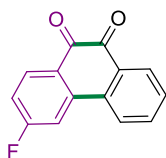
Prepared according to general procedure A. Flash column chromatography (Petroleum ether / CH₂Cl₂ = 1:1) yielded the title compound **3b**, yellow solid (15.2 mg, 73% yield); R_f 0.5 (Petroleum ether / CH₂Cl₂ = 1:1); m.p. 206.4 – 207.2 °C.

¹H NMR (400 MHz, CDCl₃) δ 8.17 (d, *J* = 7.8 Hz, 1H), 8.00 (d, *J* = 8.0 Hz, 1H), 7.71 (t, *J* = 7.6 Hz, 1H), 7.46 (t, *J* = 7.6 Hz, 1H).

¹³C NMR (101 MHz, CDCl₃) δ 180.5, 136.2, 136.0, 131.1, 130.6, 129.7, 124.1 ppm.

HRMS (ESI, m/z): Calculated for C₁₄H₉O₂⁺ [M+H]⁺: 209.0597, found: 209.0600.

3-Fluorophenanthrene-9,10-dione (**3c**)



Prepared according to general procedure A. Flash column chromatography (Petroleum ether / CH₂Cl₂ = 2:1) yielded the title compound **3c**, yellow solid (15.6 mg, 69% yield); R_f 0.3 (Petroleum ether / CH₂Cl₂ = 2:1); m.p. 207.6 – 208.9 °C.

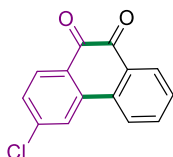
¹H NMR (400 MHz, CDCl₃) δ 8.32 – 8.15 (m, 2H), 8.01 – 7.93 (m, 1H), 7.75 (td, *J* = 7.6, 1.4 Hz, 1H), 7.68 (dd, *J* = 10.2, 2.4 Hz, 1H), 7.53 (m, 1H), 7.16 (m, 1H).

¹³C NMR (101 MHz, CDCl₃) δ 180.0, 178.9, 167.9 (d, *J* = 258.6 Hz), 139.2, 136.3, 134.7 (d, *J* = 2.6 Hz), 134.0 (d, *J* = 10.2 Hz), 131.4, 130.8, 130.5, 124.3, 117.1 (d, *J* = 22.4 Hz), 111.3 (d, *J* = 24.3 Hz) ppm.

¹⁹F NMR (377 MHz, CDCl₃) δ -99.0 ppm.

HRMS (ESI, m/z): Calculated for C₁₄H₈FO₂⁺ [M+H]⁺: 227.0502, found: 227.0501.

3-Chlorophenanthrene-9,10-dione (**3d**)



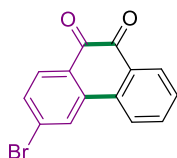
Prepared according to general procedure A. Flash column chromatography (Petroleum ether / CH₂Cl₂ = 2:1) yielded the title compound **3d**, yellow solid (15.0 mg, 62% yield); R_f 0.4 (Petroleum ether / CH₂Cl₂ = 2:1); m.p. 231.6 – 233.1 °C.

¹H NMR (400 MHz, CDCl₃) δ 8.20 (dd, *J* = 7.8, 1.6 Hz, 1H), 8.13 (d, *J* = 8.4 Hz, 1H), 8.01 – 7.95 (m, 1H), 7.96 (s, 1H), 7.74 (m, 1H), 7.52 (td, *J* = 7.6, 1.2 Hz, 1H), 7.44 (dd, *J* = 8.4, 1.8 Hz, 1H).

¹³C NMR (101 MHz, CDCl₃) δ 179.9, 179.4, 143.2, 137.6, 136.3, 134.7, 132.2, 131.4, 130.9, 130.4, 129.9, 129.5, 124.5, 124.3 ppm.

HRMS (ESI, m/z): Calculated for C₁₄H₈ClO₂⁺ [M+H]⁺: 243.0207, found: 243.0205.

3-Bromophenanthrene-9,10-dione (**3e**)



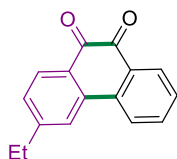
Prepared according to general procedure A. Flash column chromatography (Petroleum ether / CH₂Cl₂ = 2:1) yielded the title compound **3e**, yellow solid (16.6 mg, 58% yield); R_f 0.4 (Petroleum ether / CH₂Cl₂ = 2:1); m.p. 269.7 – 271.5 °C.

¹H NMR (400 MHz, CDCl₃) δ 8.21 (dd, *J* = 7.8, 1.6 Hz, 1H), 8.17 (d, *J* = 1.8 Hz, 1H), 8.05 (d, *J* = 8.4 Hz, 1H), 7.98 (d, *J* = 8.0 Hz, 1H), 7.74 (m, 1H), 7.61 (dd, *J* = 8.2, 1.8 Hz, 1H), 7.52 (m, 1H).

¹³C NMR (101 MHz, CDCl₃) δ 179.9, 179.7, 137.5, 136.3, 134.6, 132.9, 132.2, 132.0, 131.4, 130.9, 130.4, 129.8, 127.5, 124.3 ppm.

HRMS (ESI, *m/z*): Calculated for C₁₄H₈BrO₂⁺ [M+H]⁺: 286.9702, found: 286.9703.

3-Ethylphenanthrene-9,10-dione (**3f**)



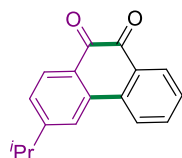
Prepared according to general procedure A. Flash column chromatography (Petroleum ether / CH₂Cl₂ = 1:1) yielded the title compound **3f**, yellow solid (16.0 mg, 68% yield); R_f 0.4 (Petroleum ether / CH₂Cl₂ = 1:1); m.p. 156.3 – 157.5 °C.

¹H NMR (400 MHz, CDCl₃) δ 8.16 (dd, *J* = 7.8, 1.6 Hz, 1H), 8.09 (d, *J* = 8.0 Hz, 1H), 8.01 (d, *J* = 8.0 Hz, 1H), 7.80 (s, 1H), 7.70 (m, *J* = 7.6, 1H), 7.45 (m, *J* = 7.4 Hz, 1H), 7.35 – 7.18 (m, 1H), 2.79 (q, *J* = 7.6 Hz, 2H), 1.33 (t, *J* = 7.6 Hz, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 180.8, 180.1, 153.6, 136.1, 136.0, 136.0, 131.2, 131.0, 130.6, 129.6, 129.5, 129.2, 124.0, 123.6, 29.8, 15.1 ppm.

HRMS (ESI, *m/z*): Calculated for C₁₆H₁₃O₂⁺ [M+H]⁺: 237.0910, found: 237.0911.

3-Isopropylphenanthrene-9,10-dione (**3g**)



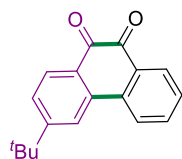
Prepared according to general procedure A. Flash column chromatography (Petroleum ether / CH₂Cl₂ = 1:1) yielded the title compound **3g**, yellow solid (16.5 mg, 66% yield); R_f 0.3 (Petroleum ether / CH₂Cl₂ = 1:1); m.p. 165.5 – 167.1 °C.

¹H NMR (400 MHz, CDCl₃) δ 8.25 – 8.13 (m, 1H), 8.11 (d, *J* = 8.0 Hz, 1H), 8.03 (d, *J* = 8.0 Hz, 1H), 7.83 (s, 1H), 7.70 (m, 1H), 7.45 (m, 1H), 7.32 (dd, *J* = 8.0, 1.6 Hz, 1H), 3.04 (m, 1H), 1.35 (s, 3H), 1.33 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 180.8, 180.0, 158.1, 136.2, 136.0, 136.0, 131.2, 131.1, 130.5, 129.5, 129.4, 128.0, 124.0, 122.3, 35.1, 23.6 ppm.

HRMS (ESI, *m/z*): Calculated for C₁₇H₁₅O₂⁺ [M+H]⁺: 251.1066, found: 251.1069.

3-(*Tert*-butyl) phenanthrene-9,10-dione (**3h**)



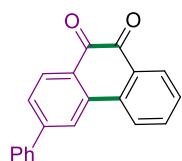
Prepared according to general procedure A. Flash column chromatography (Petroleum ether / CH₂Cl₂ = 2:1) yielded the title compound **3h**, yellow solid (16.6 mg, 63% yield); R_f 0.4 (Petroleum ether / CH₂Cl₂ = 2:1); m.p. 167.3 – 168.6 °C.

¹H NMR (400 MHz, CDCl₃) δ 8.16 (dd, *J* = 7.8, 1.6 Hz, 1H), 8.12-8.09 (d, *J* = 12.0, 1H), 8.07 – 8.00 (m, 2H), 7.71 (m, 1H), 7.56 – 7.40 (m, 2H), 1.42 (s, 9H).

¹³C NMR (101 MHz, Chloroform-*d*) δ 180.7, 179.9, 160.2, 136.3, 135.9, 135.5, 131.1, 130.6, 130.4, 129.4, 128.8, 127.0, 123.8, 120.8, 35.8, 30.9 ppm.

HRMS (ESI, *m/z*): Calculated for C₁₈H₁₇O₂⁺ [M+H]⁺: 265.1223, found: 265.1225.

3-Phenylphenanthrene-9,10-dione (**3i**)



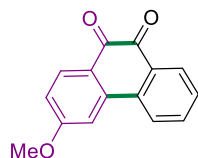
Prepared according to general procedure A. Flash column chromatography (Petroleum ether / CH₂Cl₂ = 1:1) yielded the title compound **3i**, yellow solid (20.4 mg, 72% yield); R_f 0.4 (Petroleum ether / CH₂Cl₂ = 1:1); m.p. 208.8 – 210.2 °C.

¹H NMR (400 MHz, CDCl₃) δ 8.25 (d, *J* = 8.1 Hz, 1H), 8.20 (dd, *J* = 7.9, 1.5 Hz, 2H), 8.11 (d, *J* = 8.0 Hz, 1H), 7.70 (m, 4H), 7.64 – 7.42 (m, 4H).

¹³C NMR (101 MHz, CDCl₃) δ 180.6, 180.1, 149.0, 139.6, 136.4, 136.1, 135.9, 131.4, 131.3, 130.7, 129.9, 129.8, 129.3, 129.2, 128.4, 127.5, 124.1, 122.9 ppm.

HRMS (ESI, m/z): Calculated for C₂₀H₁₃O₂⁺ [M+H]⁺: 285.0910, found: 285.0911.

3-Methoxyphenanthrene-9,10-dione (**3j**)



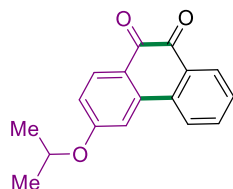
Prepared according to general procedure A. Flash column chromatography (Petroleum ether / CH₂Cl₂ = 1:1) yielded the title compound **3j**, yellow solid (18.1 mg, 76% yield); R_f 0.4 (Petroleum ether / CH₂Cl₂ = 1:1); m.p. 204.9 – 205.8 °C.

¹H NMR (400 MHz, CDCl₃) δ 8.20 – 8.14 (m, 1H), 8.15 (d, *J* = 2.6 Hz, 1H), 7.92 (d, *J* = 8.0 Hz, 1H), 7.69 (m, 1H), 7.53 – 7.42 (m, 1H), 7.41 (d, *J* = 2.4 Hz, 1H), 6.93 (dd, *J* = 8.8, 2.4 Hz, 1H), 3.97 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 180.8, 178.6, 166.0, 138.1, 135.7, 135.5, 133.6, 131.4, 130.3, 129.7, 124.9, 123.9, 114.4, 109.9, 55.9 ppm.

HRMS (ESI, m/z): Calculated for C₁₅H₁₁O₃⁺ [M+H]⁺: 239.0702, found: 239.0711.

3-Isopropoxyphenanthrene-9,10-dione (**3k**)



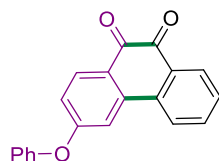
Prepared according to general procedure A. Flash column chromatography (Petroleum ether / CH₂Cl₂ = 2:1) yielded the title compound **3k**, yellow solid (21.2 mg, 80% yield); R_f 0.4 (Petroleum ether / CH₂Cl₂ = 2:1); m.p. 138.0 – 139.1 °C.

¹H NMR (400 MHz, CDCl₃) δ 8.24 – 8.11 (m, 2H), 7.92 (d, *J* = 8.0 Hz, 1H), 7.77 – 7.61 (m, 1H), 7.45 (m, *J* = 8.6, Hz, 1H), 7.40 (t, *J* = 1.8 Hz, 1H), 6.90 (m, *J* = 8.6, 1H), 4.86 – 4.65 (m, 1H), 1.44 (s, 3H), 1.42 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 181.0, 178.6, 164.7, 138.2, 135.8, 135.7, 133.8, 131.5, 130.3, 129.8, 124.6, 123.9, 115.4, 111.5, 71.0, 22.1 ppm.

HRMS (ESI, *m/z*): Calculated for C₁₇H₁₅O₃⁺ [*M*+*H*]⁺: 267.1015, found: 267.1014.

3-Phenoxyphenanthrene-9,10-dione (**3l**)



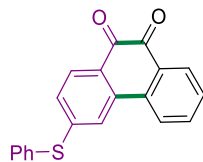
Prepared according to general procedure A. Flash column chromatography (Petroleum ether / CH₂Cl₂ = 1:1) yielded the title compound **3l**, yellow solid (22.8 mg, 76% yield); *R_f* 0.3 (Petroleum ether / CH₂Cl₂ = 1:1); m.p. 133.1 – 135.0 °C.

¹H NMR (400 MHz, CDCl₃) δ 8.17 (t, *J* = 7.8 Hz, 2H), 7.82 (d, *J* = 8.0 Hz, 1H), 7.68 (m, *J* = 7.6, 1H), 7.54 (d, *J* = 2.4 Hz, 1H), 7.52 – 7.44 (m, 3H), 7.32 – 7.22 (m, 1H), 7.19 – 7.12 (m, 2H), 6.94 (dd, *J* = 8.8, 2.2 Hz, 1H).

¹³C NMR (101 MHz, CDCl₃) δ 180.7, 178.8, 164.9, 154.7, 138.5, 136.0, 135.4, 133.6, 131.4, 130.5, 130.0, 126.1, 125.6, 124.1, 120.7, 117.9, 112.5 ppm.

HRMS (ESI, *m/z*): Calculated for C₂₀H₁₃O₃⁺ [*M*+*H*]⁺: 301.0859, found: 301.0862.

3-(Phenylthio)phenanthrene-9,10-dione (**3m**)



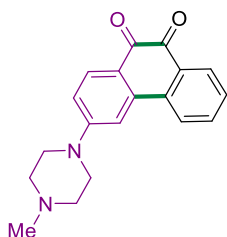
Prepared according to general procedure A. Flash column chromatography (Petroleum ether / CH₂Cl₂ = 1:1) yielded the title compound **3m**, yellow solid (23.4 mg, 74% yield); *R_f* 0.3 (Petroleum ether / CH₂Cl₂ = 1:1); m.p. 176.9 – 178.1 °C.

¹H NMR (400 MHz, CDCl₃) δ 8.16 (m, 1H), 8.01 (dd, *J* = 8.4, 1.1 Hz, 1H), 7.75 (d, *J* = 8.0 Hz, 1H), 7.70 (t, *J* = 1.5 Hz, 1H), 7.65 (m, 1H), 7.61 – 7.56 (m, 2H), 7.54 – 7.46 (m, 3H), 7.45 (dd, *J* = 7.5, 1.1 Hz, 1H), 7.08 (dd, *J* = 8.3, 1.6 Hz, 1H).

¹³C NMR (101 MHz, CDCl₃) δ 180.5, 179.3, 150.4, 136.2, 136.0, 135.4, 135.0, 131.4, 131.1, 130.6, 130.4, 130.2, 129.9, 129.9, 128.3, 127.1, 123.9, 121.5 ppm.

HRMS (ESI, *m/z*): Calculated for C₂₀H₁₃O₂S⁺ [M+H]⁺: 317.0630, found: 317.0630.

3-(4-Methylpiperazin-1-yl)phenanthrene-9,10-dione (3n)



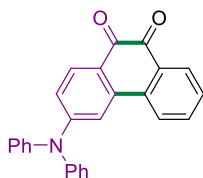
Prepared according to general procedure A. Flash column chromatography (Petroleum ether / CH₂Cl₂ = 2:1) yielded the title compound **3n**, red solid (24.2 mg, 74% yield); *R_f* 0.3 (Petroleum ether / CH₂Cl₂ = 1:1); m.p. 177.3 – 179.0 °C.

¹H NMR (400 MHz, CDCl₃) δ 8.15 (dd, *J* = 7.8, 1.4 Hz, 1H), 8.06 (d, *J* = 9.0 Hz, 1H), 7.92 (d, *J* = 8.0 Hz, 1H), 7.65 (m, 1H), 7.51 – 7.40 (m, 1H), 7.29 (d, *J* = 2.4 Hz, 1H), 6.82 (dd, *J* = 9.0, 2.6 Hz, 1H), 3.61 – 3.46 (m, 4H), 2.76 – 2.48 (m, 4H), 2.38 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 181.7, 177.6, 155.8, 137.7, 136.1, 135.3, 133.5, 131.7, 130.1, 129.5, 123.5, 121.9, 114.1, 107.5, 54.7, 46.9, 46.2 ppm.

HRMS (ESI, *m/z*): Calculated for C₁₉H₁₉N₂O₂⁺ [M+H]⁺: 307.1441, found: 307.1435.

3-(Diphenylamino)phenanthrene-9,10-dione (3o)



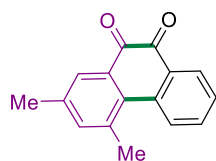
Prepared according to general procedure A. Flash column chromatography (Petroleum ether / CH₂Cl₂ = 1:1) yielded the title compound **3o**, red solid (29.2 mg, 78% yield); *R_f* 0.3 (Petroleum ether / CH₂Cl₂ = 1:1); m.p. 225.3 – 226.4 °C.

¹H NMR (400 MHz, CDCl₃) δ 8.20 – 8.13 (m, 1H), 8.03 (d, *J* = 8.8 Hz, 1H), 7.61 – 7.55 (m, 2H), 7.47 (d, *J* = 2.2 Hz, 1H), 7.42 (d, *J* = 8.0 Hz, 2H), 7.40 (d, *J* = 2.0 Hz, 3H), 7.29 – 7.23 (m, 6H), 6.89 (dd, *J* = 8.8, 2.4 Hz, 1H).

¹³C NMR (101 MHz, CDCl₃) δ 181.5, 177.8, 154.7, 145.5, 137.4, 135.8, 135.4, 132.9, 131.5, 130.1, 129.5, 126.9, 126.1, 123.7, 119.3, 113.1 ppm.

HRMS (ESI, *m/z*): Calculated for C₂₆H₁₈NO₂⁺ [M+H]⁺: 376.1332, found: 376.1328.

2,4-Dimethylphenanthrene-9,10-dione (3p)



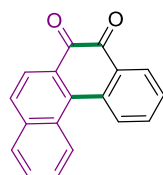
Prepared according to general procedure A. Flash column chromatography (Petroleum ether / CH₂Cl₂ = 1:1) yielded the title compound **3p**, red solid (17.2 mg, 73% yield); *R_f* 0.4 (Petroleum ether / CH₂Cl₂ = 1:1); m.p. 165.9 – 166.7 °C.

¹H NMR (400 MHz, CDCl₃) δ 8.11 (m, *J* = 7.8, 1H), 7.91 – 7.84 (m, 1H), 7.83 (s, 1H), 7.67 (m, *J* = 7.6 Hz, 1H), 7.46 – 7.33 (m, 2H), 2.70 (s, 3H), 2.37 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 183.4, 183.1, 141.4, 138.9, 137.8, 136.5, 135.3, 133.6, 131.8, 131.3, 130.3, 129.1, 129.0, 128.4, 24.4, 20.8 ppm.

HRMS (ESI, *m/z*): Calculated for C₁₆H₁₃O₂⁺ [M+H]⁺: 237.0910, found: 237.0912.

Benzo[*c*]phenanthrene-5,6-dione (3q)



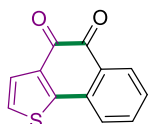
Prepared according to general procedure A. Flash column chromatography (Petroleum ether / CH₂Cl₂ = 1:1) yielded the title compound **3q**, red solid (20.1 mg, 78% yield); *R_f* 0.3 (Petroleum ether / CH₂Cl₂ = 1:1); m.p. 150.4 – 152.3 °C.

¹H NMR (400 MHz, CDCl₃) δ 8.58 (d, *J* = 8.6 Hz, 1H), 8.15 (m, *J* = 7.6, 1H), 8.10 (t, *J* = 8.4 Hz, 2H), 7.91 (d, *J* = 8.0 Hz, 1H), 7.86 (d, *J* = 8.4 Hz, 1H), 7.73 (m, 1H), 7.70 – 7.64 (m, 1H), 7.64 – 7.58 (m, 1H), 7.51 (t, *J* = 7.6 Hz, 1H).

^{13}C NMR (101 MHz, CDCl_3) δ 182.7, 182.4, 138.4, 138.0, 136.8, 134.9, 131.1, 130.8, 130.6, 130.0, 129.7, 129.6, 129.4, 129.4, 128.3, 127.8, 127.2, 123.4 ppm.

HRMS (ESI, m/z): Calculated for $\text{C}_{18}\text{H}_{11}\text{O}_2^+$ $[\text{M}+\text{H}]^+$: 259.0753, found: 259.0755.

Naphtho[1,2-*b*]thiophene-4,5-dione (**3r**)



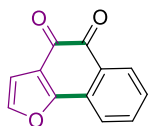
Prepared according to general procedure A. Flash column chromatography (Petroleum ether / $\text{CH}_2\text{Cl}_2 = 1:1$) yielded the title compound **3r**, red solid (17.3 mg, 81% yield); R_f 0.4 (Petroleum ether / $\text{CH}_2\text{Cl}_2 = 1:1$); m.p. 219.2 – 220.6 °C.

^1H NMR (400 MHz, CDCl_3) δ 8.08 (dd, $J = 7.8, 1.4$ Hz, 1H), 7.60 (m, 1H), 7.58 – 7.49 (m, 2H), 7.41 (m, 1H).

^{13}C NMR (101 MHz, CDCl_3) δ 180.7, 174.1, 151.4, 136.7, 136.0, 132.6, 130.5, 129.9, 129.3, 128.0, 126.2, 124.9 ppm.

HRMS (ESI, m/z): Calculated for $\text{C}_{12}\text{H}_7\text{O}_2\text{S}^+$ $[\text{M}+\text{H}]^+$: 215.0161, found: 215.0162.

Naphtho[1,2-*b*]furan-4,5-dione (**3s**)



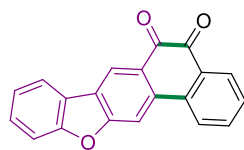
Prepared according to general procedure A. Flash column chromatography (Petroleum ether / $\text{CH}_2\text{Cl}_2 = 1:1$) yielded the title compound **3s**, red solid (16.4 mg, 83% yield); R_f 0.3 (Petroleum ether / $\text{CH}_2\text{Cl}_2 = 1:1$); m.p. 159.4 – 161.2 °C.

^1H NMR (400 MHz, CDCl_3) δ 8.09 (d, $J = 7.6$ Hz, 1H), 7.73 (d, $J = 7.8$ Hz, 1H), 7.66 (t, $J = 7.6$ Hz, 1H), 7.53 – 7.43 (m, 2H), 6.88 (d, $J = 2.0$ Hz, 1H).

^{13}C NMR (101 MHz, CDCl_3) δ 180.7, 174.7, 160.8, 145.2, 135.6, 130.8, 130.5, 128.9, 128.6, 122.5, 121.7, 109.1 ppm.

HRMS (ESI, m/z): Calculated for $\text{C}_{12}\text{H}_7\text{O}_3^+$ $[\text{M}+\text{H}]^+$: 199.0390, found: 199.0393.

Phenanthro[3,2-*b*]benzofuran-5,6-dione (**3t**)



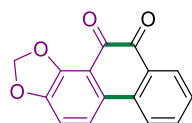
Prepared according to general procedure A. Flash column chromatography (Petroleum ether / CH₂Cl₂ = 1:1) yielded the title compound **3t**, yellow solid (20.5 mg, 69% yield); *R_f* 0.4 (Petroleum ether / CH₂Cl₂ = 1:1); m.p. 257.0 – 258.9 °C.

¹H NMR (400 MHz, CDCl₃) δ 8.77 (s, 1H), 8.18 (dd, *J* = 7.8, 1.4 Hz, 1H), 8.07 (s, 1H), 8.03 (d, *J* = 8.0 Hz, 1H), 7.97 (d, *J* = 7.6 Hz, 1H), 7.82 – 7.66 (m, 1H), 7.58 (d, *J* = 8.2 Hz, 1H), 7.56 – 7.50 (m, 1H), 7.47 (t, *J* = 7.6 Hz, 1H), 7.41 (t, *J* = 7.4 Hz, 1H).

¹³C NMR (101 MHz, CDCl₃) δ 180.7, 179.8, 161.1, 157.6, 136.3, 136.2, 135.7, 131.1, 130.6, 129.8, 129.1, 127.2, 126.0, 124.7, 124.3, 124.2, 123.2, 121.7, 112.2, 107.2 ppm.

HRMS (ESI, *m/z*): Calculated for C₂₀H₁₁O₃⁺ [*M*+*H*]⁺: 299.0702, found: 299.0702.

Phenanthro[1,2-*d*][1,3]dioxole-4,5-dione (**3u**)



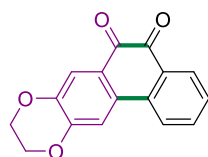
Prepared according to general procedure A. Flash column chromatography (Petroleum ether / CH₂Cl₂ = 1:1) yielded the title compound **3u**, red solid (19.4 mg, 77% yield); *R_f* 0.4 (Petroleum ether / CH₂Cl₂ = 1:1); m.p. 207.9 – 209.1 °C.

¹H NMR (400 MHz, CDCl₃) δ 8.23 – 8.11 (m, 1H), 7.97 – 7.80 (m, 1H), 7.65 (m, 1H), 7.57 – 7.47 (m, 1H), 7.48 – 7.30 (m, 1H), 7.11 – 7.03 (m, 1H), 6.43 – 6.01 (m, 2H).

¹³C NMR (101 MHz, CDCl₃) δ 179.7, 178.5, 151.5, 150.3, 136.6, 135.9, 130.6, 130.3, 128.7, 128.4, 123.9, 118.4, 115.1, 114.1, 103.8 ppm.

HRMS (ESI, *m/z*): Calculated for C₁₅H₉O₄⁺ [*M*+*H*]⁺: 253.0495, found: 253.0495.

9,10-Dihydrophenanthro[2,3-*b*][1,4]dioxine-5,6-dione (**3v**)



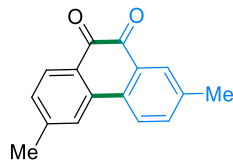
Prepared according to general procedure A. Flash column chromatography (Petroleum ether / CH₂Cl₂ = 1:1) yielded the title compound **3v**, yellow solid (21.0 mg, 79% yield); R_f 0.4 (Petroleum ether / CH₂Cl₂ = 1:1); m.p. 248.6 – 149.1 °C.

¹H NMR (400 MHz, CDCl₃) δ 8.76 (d, *J* = 8.2 Hz, 1H), 8.12 (m, 1H), 7.77 (dd, *J* = 15.8, 8.2 Hz, 1H), 7.69 – 7.56 (m, 1H), 7.47 – 7.31 (m, 1H), 6.90 (d, *J* = 8.4 Hz, 1H), 4.51 – 4.31 (m, 4H).

¹³C NMR (101 MHz, CDCl₃) δ 181.8, 180.2, 151.1, 142.5, 135.7, 135.4, 131.3, 130.4, 130.1, 128.9, 125.8, 125.5, 118.3, 64.4, 64.2 ppm.

HRMS (ESI, m/z): Calculated for C₁₆H₁₁O₄⁺ [M+H]⁺: 267.0652, found: 267.0654.

2,6-Dimethylphenanthrene-9,10-dione (**4a**)



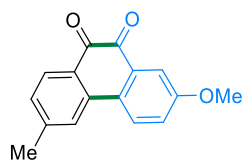
Prepared according to general procedure A. Flash column chromatography (Petroleum ether / CH₂Cl₂ = 2:1) yielded the title compound **4a**, yellow solid (15.8 mg, 67% yield); R_f 0.5 (Petroleum ether / CH₂Cl₂ = 2:1); m.p. 200.4 – 201.5 °C.

¹H NMR (400 MHz, CDCl₃) δ 8.03 (dd, *J* = 8.0, 1.4 Hz, 1H), 7.94 (s, 1H), 7.85 (dd, *J* = 8.2, 1.6 Hz, 1H), 7.71 (s, 1H), 7.47 (dd, *J* = 8.2, 2.0 Hz, 1H), 7.21 (d, *J* = 8.0 Hz, 1H), 2.47 (s, 3H), 2.40 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 181.0, 180.2, 131.1, 130.9, 130.8, 130.2, 128.7, 124.4, 124.0, 22.5, 21.1 ppm.

HRMS (ESI, m/z): Calculated for C₁₆H₁₃O₂⁺ [M+H]⁺: 237.0910, found: 237.0911.

2-Methoxy-6-methylphenanthrene-9,10-dione (**4b**)



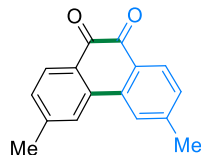
Prepared according to general procedure A. Flash column chromatography (Petroleum ether / CH₂Cl₂ = 2:1) yielded the title compound **4b**, red solid (18.6 mg, 74% yield); *R_f* 0.5 (Petroleum ether / CH₂Cl₂ = 2:1); m.p. 205.7 – 206.9 °C.

¹H NMR (400 MHz, CDCl₃) δ 8.01 (d, *J* = 8.0 Hz, 1H), 7.87 (d, *J* = 8.8 Hz, 1H), 7.64 (s, 1H), 7.60 (d, *J* = 3.0 Hz, 1H), 7.21 (dd, *J* = 8.8, 2.8 Hz, 1H), 7.17 (d, *J* = 8.0 Hz, 1H), 3.90 (s, 3H), 2.46 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 180.7, 180.1, 160.6, 147.6, 136.3, 132.5, 130.9, 129.7, 129.3, 128.1, 125.7, 124.2, 123.8, 112.7, 55.9, 22.5 ppm.

HRMS (ESI, *m/z*): Calculated for C₁₆H₁₃O₃⁺ [M+H]⁺: 253.0859, found: 253.0861.

3,6-Dimethylphenanthrene-9,10-dione (**4c**)



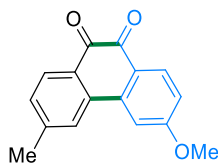
Prepared according to general procedure A. Flash column chromatography (Petroleum ether / CH₂Cl₂ = 1:1) yielded the title compound **4c**, yellow solid (16.5 mg, 70% yield); *R_f* 0.5 (Petroleum ether / CH₂Cl₂ = 1:1); m.p. 214.6 – 216.3 °C.

¹H NMR (400 MHz, CDCl₃) δ 8.04 (d, *J* = 8.0 Hz, 1H), 7.75 (s, 1H), 7.45 – 7.12 (m, 1H), 2.49 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 180.3, 147.3, 135.9, 130.8, 130.5, 129.1, 124.5, 22.5 ppm.

HRMS (ESI, *m/z*): Calculated for C₁₆H₁₃O₂⁺ [M+H]⁺: 237.0910, found: 237.0901.

3-Methoxy-6-methylphenanthrene-9,10-dione (**4d**)



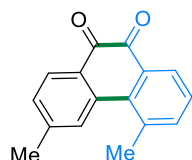
Prepared according to general procedure A. Flash column chromatography (Petroleum ether / CH₂Cl₂ = 1:1) yielded the title compound **4d**, yellow solid (18.3 mg, 73% yield); R_f 0.5 (Petroleum ether / CH₂Cl₂ = 1:1); m.p. 185.6 – 186.4 °C.

¹H NMR (400 MHz, CDCl₃) δ 8.09 (d, *J* = 8.6 Hz, 1H), 7.98 (d, *J* = 8.0 Hz, 1H), 7.60 (s, 1H), 7.30 (d, *J* = 2.4 Hz, 1H), 7.20 (dd, *J* = 8.0, 1.6 Hz, 1H), 6.87 (dd, *J* = 8.6, 2.4 Hz, 1H), 3.95 (s, 3H), 2.45 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 180.2, 178.7, 165.8, 147.0, 138.0, 135.3, 133.4, 130.6, 130.4, 129.2, 124.9, 124.4, 114.3, 109.6, 55.9, 22.3 ppm.

HRMS (ESI, m/z): Calculated for C₁₆H₁₃O₃⁺ [M+H]⁺: 253.0859, found: 253.0869.

3,5-Dimethylphenanthrene-9,10-dione (**4e**)



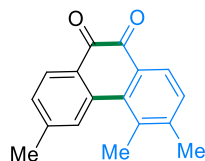
Prepared according to general procedure A. Flash column chromatography (Petroleum ether / CH₂Cl₂ = 2:1) yielded the title compound **4e**, yellow solid (15.3 mg, 65% yield); R_f 0.5 (Petroleum ether / CH₂Cl₂ = 2:1); m.p. 111.4. – 113.1 °C.

¹H NMR (400 MHz, CDCl₃) δ 8.10 – 7.80 (m, 2H), 7.62 (s, 1H), 7.48 (dd, *J* = 7.6, 1.4 Hz, 1H), 7.26 (t, *J* = 7.6 Hz, 1H), 7.20 – 7.14 (m, 1H), 2.67 (s, 3H), 2.41 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 183.3, 182.4, 146.6, 140.3, 137.6, 136.4, 136.2, 131.9, 130.5, 130.1, 129.6, 129.2, 128.6, 128.5, 24.5, 22.6 ppm.

HRMS (ESI, m/z): Calculated for C₁₆H₁₃O₂⁺ [M+H]⁺: 237.0910, found: 237.0910.

3,4,6-Trimethylphenanthrene-9,10-dione (**4f**)



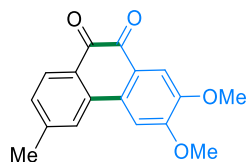
Prepared according to general procedure A. Flash column chromatography (Petroleum ether / CH₂Cl₂ = 2:1) yielded the title compound **4f**, yellow solid (15.0 mg, 60% yield); R_f 0.5 (Petroleum ether / CH₂Cl₂ = 2:1); m.p. 235.3 – 237.1 °C.

¹H NMR (400 MHz, CDCl₃) δ 7.96 (dd, *J* = 7.9, 1.6 Hz, 1H), 7.87 (dd, *J* = 7.8, 2.0 Hz, 1H), 7.54 (s, 1H), 7.24 – 7.17 (m, 2H), 2.56 (s, 3H), 2.46 (s, 3H), 2.41 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 182.9, 182.8, 147.7, 146.0, 137.9, 137.1, 135.2, 130.8, 130.5, 129.7, 129.4, 129.2, 127.6, 22.5, 22.2, 20.1 ppm.

HRMS (ESI, *m/z*): Calculated for C₁₇H₁₅O₂⁺ [M+H]⁺: 251.1066, found: 251.1063.

2,3-Dimethoxy-6-methylphenanthrene-9,10-dione (**4g**)



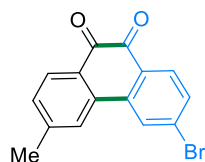
Prepared according to general procedure A. Flash column chromatography (Petroleum ether / CH₂Cl₂ = 1:1) yielded the title compound **4g**, red solid (21.9 mg, 78% yield); R_f 0.4 (Petroleum ether / CH₂Cl₂ = 1:1); m.p. 243.5 – 244.7 °C.

¹H NMR (400 MHz, CDCl₃) δ 8.0 (d, *J* = 7.8 Hz, 1H), 7.5 (s, 2H), 7.3 (s, 1H), 7.2 (d, *J* = 7.6 Hz, 1H), 4.1 (s, 3H), 4.0 (s, 3H), 2.5 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 180.0, 178.8, 155.6, 150.0, 147.1, 135.6, 131.3, 130.6, 129.8, 128.5, 125.2, 123.9, 111.3, 105.5, 56.4, 56.2, 22.3 ppm.

HRMS (ESI, *m/z*): Calculated for C₁₇H₁₅O₄⁺ [M+H]⁺: 283.0965, found: 283.0967.

3-Bromo-6-methylphenanthrene-9,10-dione (**4h**)



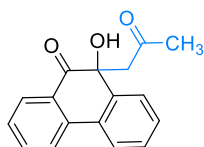
Prepared according to general procedure A. Flash column chromatography (Petroleum ether / CH₂Cl₂ = 1:1) yielded the title compound **4h**, yellow solid (17.0 mg, 57% yield); R_f 0.5 (Petroleum ether / CH₂Cl₂ = 1:1); m.p. 227.4 – 228.9 °C.

¹H NMR (400 MHz, CDCl₃) δ 8.13 (d, *J* = 1.6 Hz, 1H), 8.09 (d, *J* = 8.0 Hz, 1H), 8.02 (d, *J* = 8.4 Hz, 1H), 7.73 (s, 1H), 7.59 (dd, *J* = 8.2, 1.8 Hz, 1H), 7.31 (d, *J* = 7.7 Hz, 1H), 2.51 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 179.9, 179.3, 147.8, 137.6, 134.5, 132.7, 132.0, 131.3, 131.1, 129.9, 129.2, 127.3, 124.8, 22.5 ppm.

HRMS (ESI, *m/z*): Calculated for C₁₅H₁₀BrO₂⁺ [*M*+*H*]⁺: 300.9858, found: 300.9853.

10-Hydroxy-10-(2-oxopropyl)phenanthren-9(10*H*)-one (6)



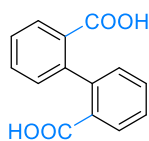
Prepared according to Scheme S3. Flash column chromatography (EA / *n*-hexane = 5:1) yielded the title compound **6**, white solid (79%, 21.0 mg); m.p. 83.6 – 84.8 °C.

¹H NMR (400 MHz, CDCl₃) δ 7.97 – 7.86 (m, 2H), 7.85 – 7.78 (m, 1H), 7.78 – 7.72 (m, 1H), 7.68 (m, 1H), 7.53 – 7.41 (m, 1H), 7.44 – 7.36 (m, 2H), 4.48 (s, 1H), 2.99 (d, *J* = 14.4 Hz, 1H), 2.81 (d, *J* = 14.6 Hz, 1H), 2.08 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 205.6, 202.5, 139.5, 136.9, 135.0, 129.4, 129.1, 128.9, 128.8, 127.8, 126.1, 124.5, 123.3, 78.4, 55.7, 32.2 ppm.

HRMS (ESI, *m/z*): Calculated for C₁₇H₁₄O₃Na⁺ [*M*+*H*]⁺: 289.0835, found: 289.0835.

[1,1'-Biphenyl]-2,2'-dicarboxylic acid (8)



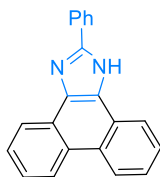
Prepared according to Scheme S5, white solid (80%, 19.3 mg); m.p. 230.5 – 231.7 °C.

¹H NMR (400 MHz, DMSO-*d*₆) δ 12.42 (s, 2H), 7.89 (m, 2H), 7.54 (td, *J* = 7.6, 1.4 Hz, 2H), 7.43 (m, 2H), 7.16 (m, 2H).

¹³C NMR (101 MHz, DMSO-*d*₆) δ 167.9, 143.1, 131.1, 130.4, 130.4, 129.5, 126.9 ppm.

HRMS (ESI, *m/z*): Calculated for C₁₄H₁₁O₄⁺ [*M*+*H*]⁺: 265.0471, found: 265.0469.

2-Phenyl-1*H*-phenanthro[9,10-*d*] imidazole (9)



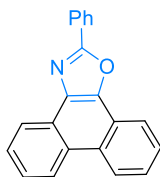
Prepared according to Scheme S6, white solid (96%, 28.2 mg); m.p. >300 °C.

¹H NMR (400 MHz, CDCl₃) δ 13.45 (s, 1H), 8.84 (t, *J* = 9.8 Hz, 2H), 8.68 – 8.55 (m, 2H), 8.34 (d, *J* = 7.8 Hz, 2H), 7.73 (t, *J* = 7.6 Hz, 2H), 7.62 (q, *J* = 8.0 Hz, 4H), 7.50 (t, *J* = 7.4 Hz, 1H).

¹³C NMR (101 MHz, CDCl₃) δ 149.2, 137.0, 130.4, 129.3, 129.0, 127.7, 127.6, 127.2, 127.1, 126.2, 125.4, 125.2, 124.1, 123.8, 122.5, 122.0, 122.0 ppm.

HRMS (ESI, *m/z*): Calculated for C₂₁H₁₅N₂⁺ [M+H]⁺: 295.1230, found: 295.1231.

2-Phenylphenanthro[9,10-*d*] oxazole (10)



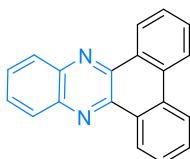
Prepared according to Scheme S7, white solid (80%, 23.6 mg); m.p. 199.8 – 200.4 °C.

¹H NMR (400 MHz, CDCl₃) δ 8.75 (t, *J* = 8.4 Hz, 2H), 8.65 (dd, *J* = 7.8, 1.6 Hz, 1H), 8.46 – 8.37 (m, 2H), 8.36 (dd, *J* = 7.6, 1.8 Hz, 1H), 7.78 – 7.65 (m, 4H), 7.63 – 7.48 (m, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 162.3, 144.9, 135.6, 131.0, 129.3, 129.0, 127.6, 127.5, 127.3, 127.2, 126.4, 126.2, 126.2, 123.8, 123.5, 123.0, 121.1, 120.9 ppm.

HRMS (ESI, *m/z*): Calculated for C₂₁H₁₄NO⁺ [M+H]⁺: 296.1069, found: 296.1064.

Dibenzo[*a, c*]phenazine (12)



Prepared according to Scheme S9. Flash column chromatography (Petroleum ether / EA = 20:1) yielded the title compound **12**, white solid (86%, 24.1 mg); m.p. 222.6 – 223.8 °C.

¹H NMR (400 MHz, CDCl₃) δ 9.37 (dd, *J* = 7.8, 1.6 Hz, 2H), 8.53 (d, *J* = 8.0 Hz, 2H), 8.31 (dd, *J* = 6.6, 3.6 Hz, 2H), 7.84 (dd, *J* = 6.4, 3.4 Hz, 2H), 7.81 – 7.70 (m, 4H).

¹³C NMR (101 MHz, CDCl₃) δ 142.6, 142.3, 132.2, 130.4, 129.9, 129.6, 128.0, 126.4, 123.0 ppm.

HRMS (ESI, *m/z*): Calculated for C₂₀H₁₃N₂⁺ [M+H]⁺: 281.1073, found: 281.1077.

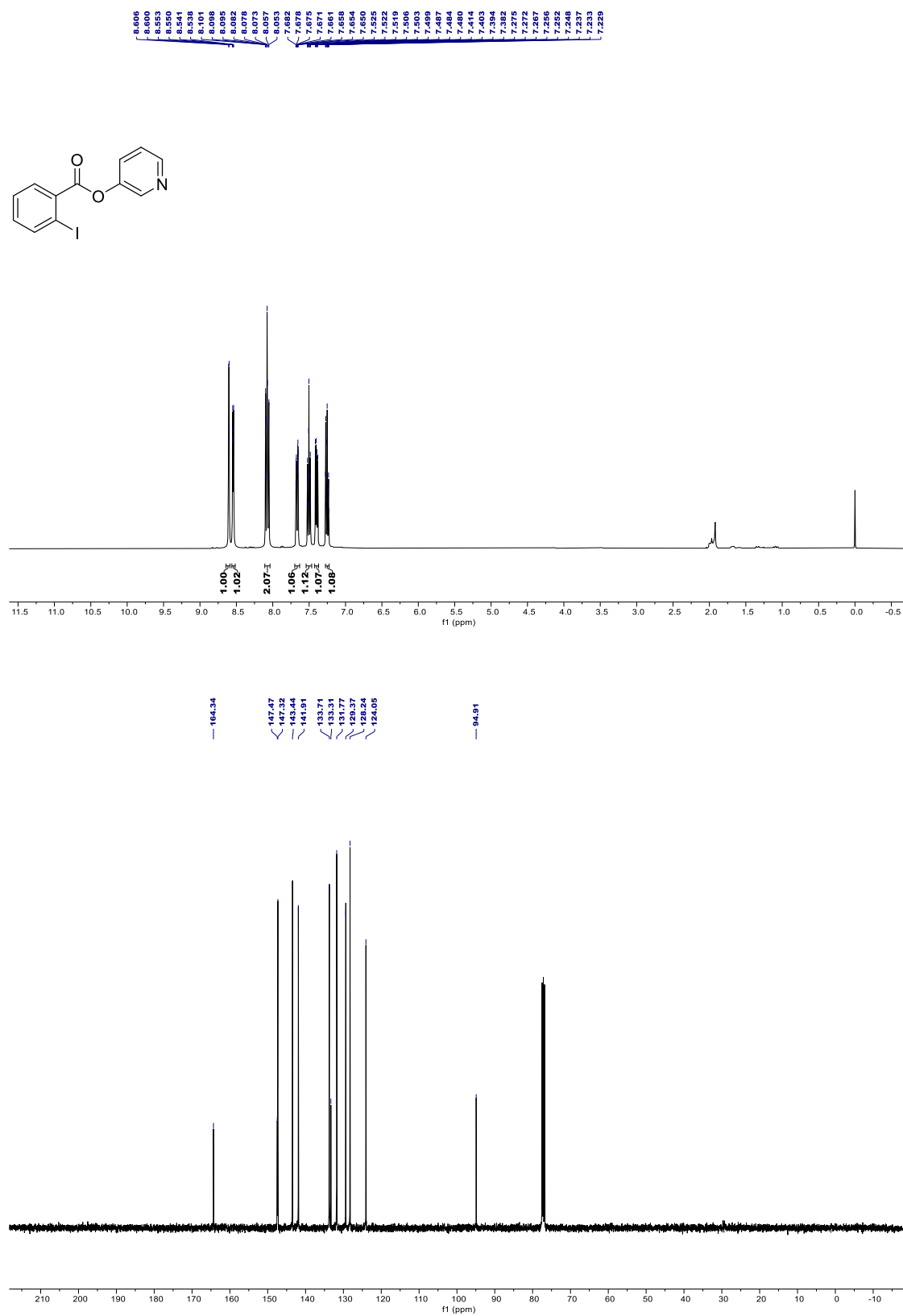
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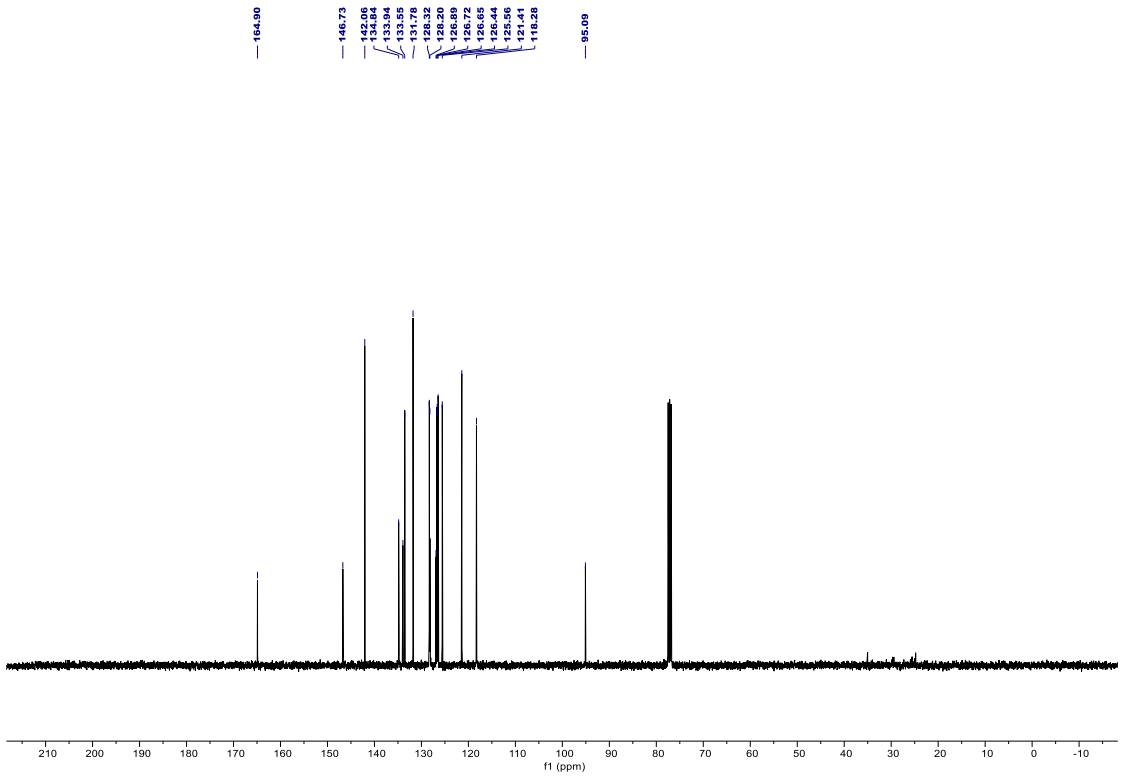
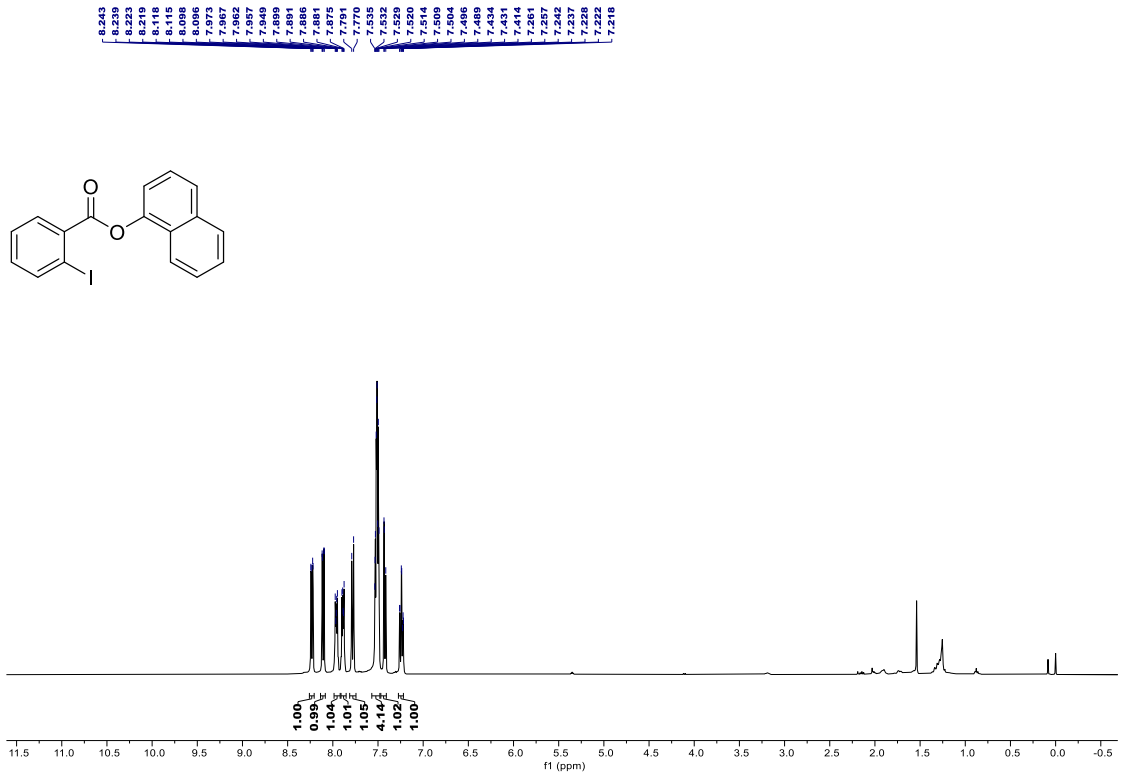
- [11] (a) C. -L. Sun, H. Li, D. -G. Yu, M. Yu, X. Zhou, X. -Y. Lu, K. Huang, S. -F. Zheng, B. -J. Li and Z. -J. Shi, An Efficient Organocatalytic Method for Constructing Biaryls through Aromatic C–H activation, *Nat. Chem.*, 2010, **2**, 1044–1049; (b) E. Shirakawa, K.-i. Itoh, T. Higashino and T. Hayashi, *tert*-Butoxide-Mediated Arylation of Benzene with Aryl Halides in the Presence of a Catalytic 1,10-Phenanthroline Derivative, *J. Am. Chem. Soc.*, 2010, **132**, 15537–15539; (c) E. Shirakawa and T. Hayashi, Transition-metal-free Coupling Reactions of Aryl Halides, *Chem. Lett.*, 2012, **41**, 130–134; (d) J. P. Barham, G. Coulthard, K. J. Emery, E. Doni, F. Cumine, G. Nocera, M. P. John, L. E. A. Berlouis, T. McGuire, T. Tuttle and J. A. Murphy, KO*t*Bu: A Privileged Reagent for Electron Transfer Reactions?, *J. Am. Chem. Soc.*, 2016, **138**, 7402–7410; (e) J. P. Barham, G. Coulthard, R. G. Kane, N. Delgado, M. P. John and J. A. Murphy, Double Deprotonation of Pyridinols Generates Potent Organic Electron-Donor Initiators for Haloarene–Arene Coupling, *Angew. Chem. Int. Ed.*, 2016, **55**, 4492–4496; (f) A. J. Smith, A. Young, S. Rohrbach, E. F. O’Connor, M. Allison, H.-S. Wang, D. L. Poole, T. Tuttle and J. A. Murphy, Electron-Transfer and Hydride-Transfer Pathways in the Stoltz–Grubbs Reducing System (KO*t*Bu/Et₃SiH), *Angew. Chem. Int. Ed.*, 2017, **56**, 13747–13751; (g) A. Studer, and D. P. Curran, Organocatalysis and C–H Activation Meet Radical and Electron-transfer Reactions. *Angew. Chem. Int. Ed.*, 2011, **50**, 5018–5022; (h) A. Studer, and D. P. Curran, The Electron is a Catalyst, *Nat. Chem.*, 2014, **6**, 765–773. (i) L. Wu, V. T. Annibale, H. Jiao, A. Brookfield, D. Collison and I. Manners, Homo- and Heterodehydro Coupling of Phosphines Mediated by Alkali Metal Catalysts , *Nat. Commun.*, 2019, **10**, 2786; (j) D. I. Bugaenko, A. A. Dubrovina, M. A. Yurovskaya and A. V. Karchava, Synthesis of Indoles via Electron-Catalyzed Intramolecular C–N Bond Formation, *Org. Lett.*, 2018, **20**, 7358–7362; (k) A. A. Toutov, W.-B. Liu, K. N. Betz, A. Fedorov, B. M. Stoltz and R. H. Grubbs, Silylation of C–H bonds in Aromatic Heterocycles by an Earth-abundant Metal Catalyst, *Nature*, 2015, **518**, 80–84.
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3.4 Copies of ^1H , ^{19}F and ^{13}C NMR spectra

Pyridin-3-yl 2-iodobenzoate (2a)

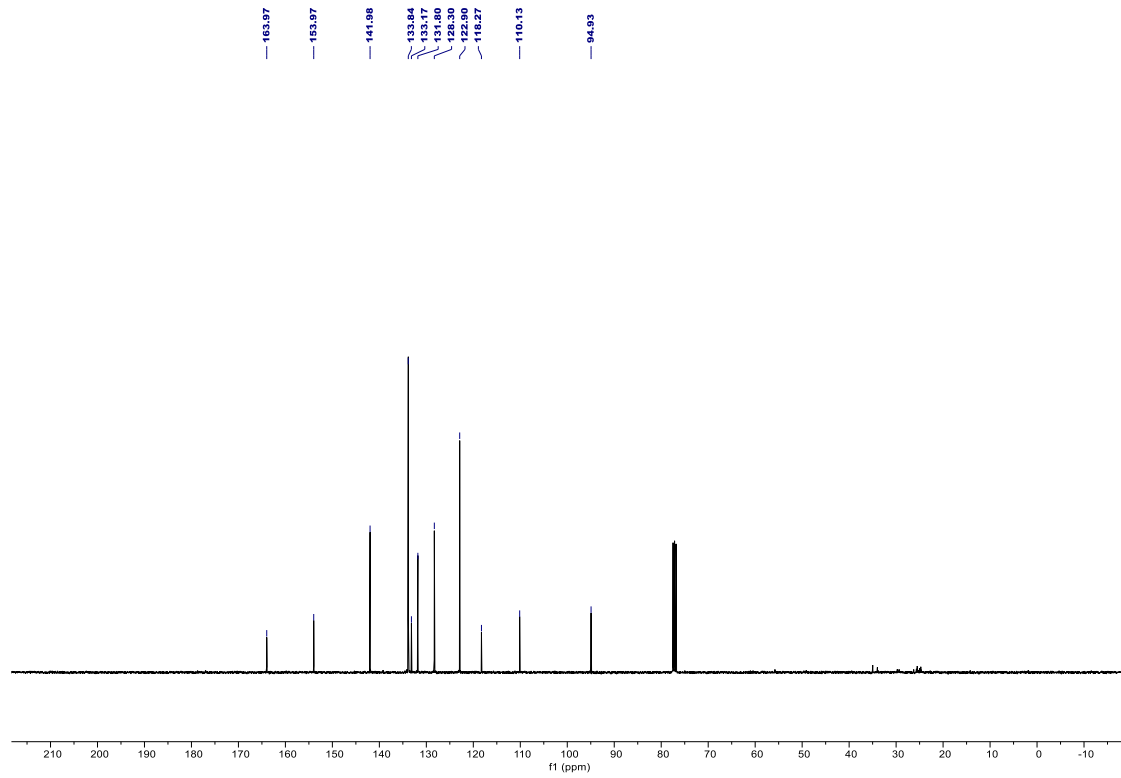
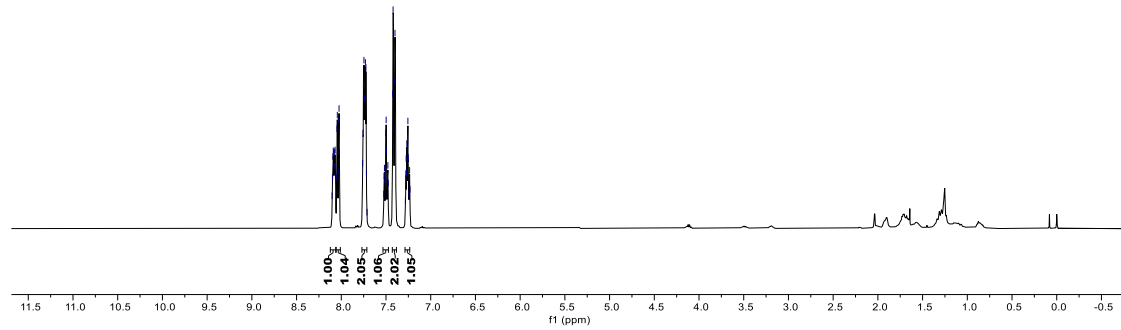
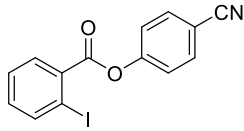


Naphthalen-1-yl 2-iodobenzoate (2b)

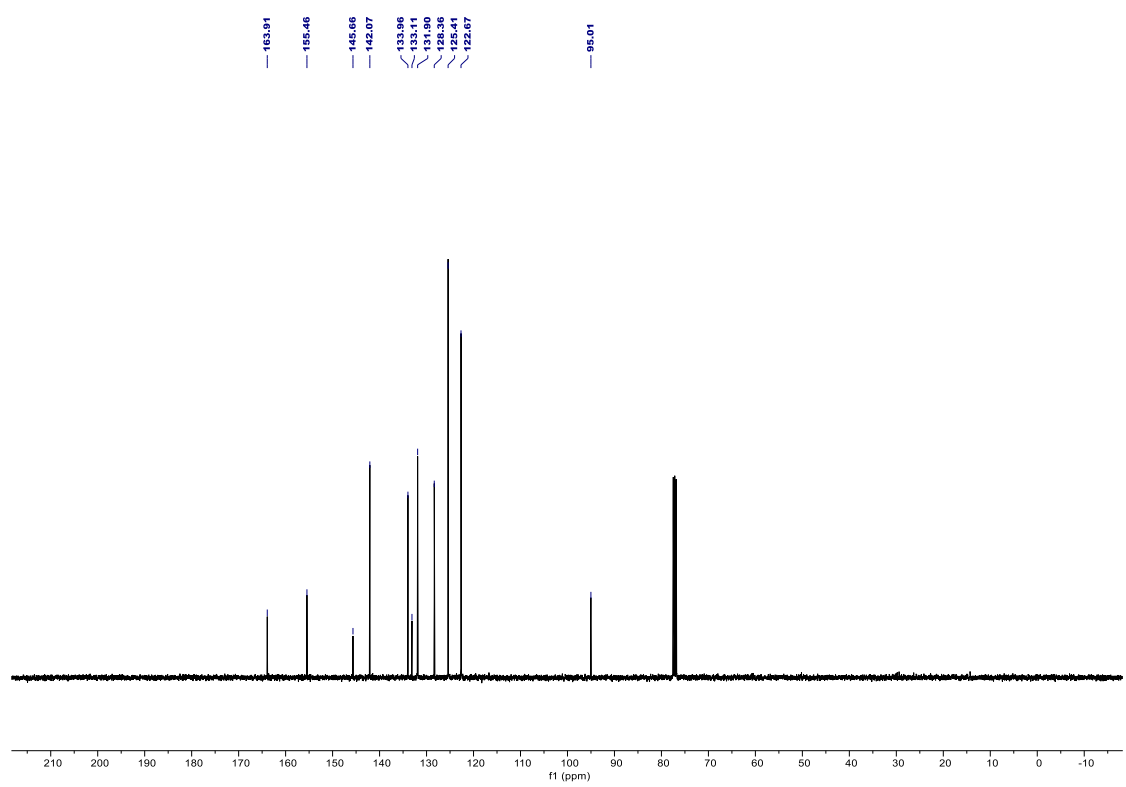
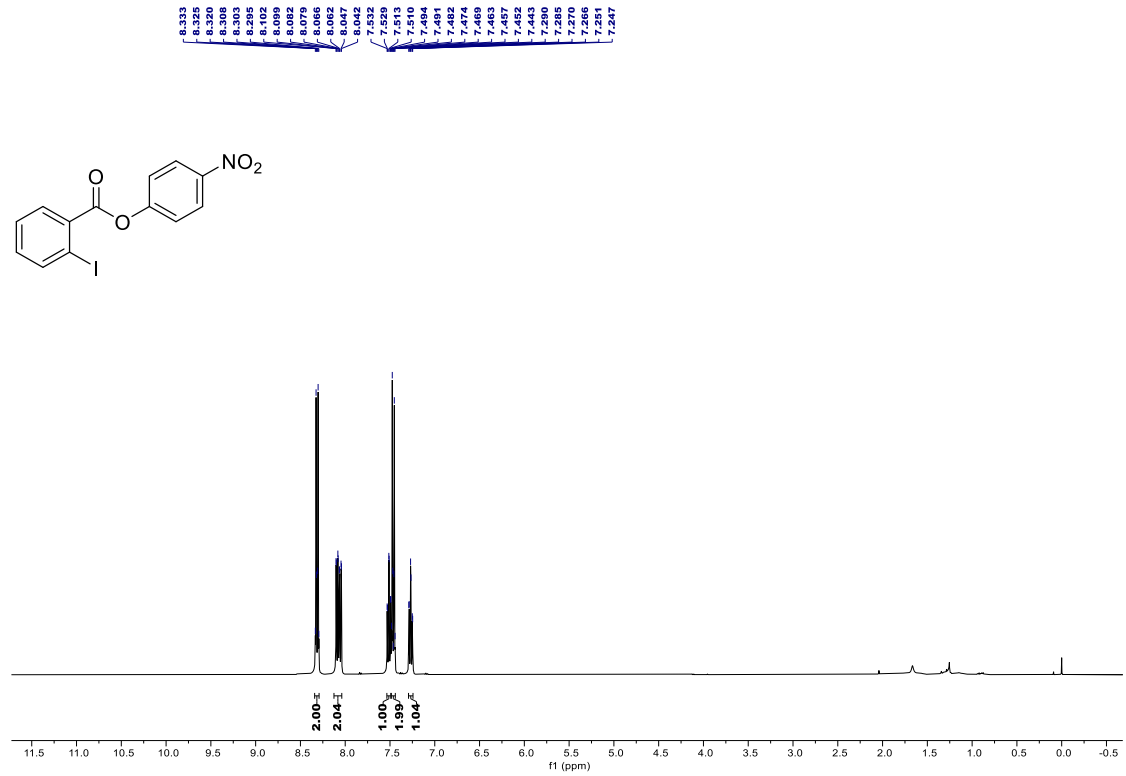


4-Cyanophenyl 2-iodobenzoate (2d)

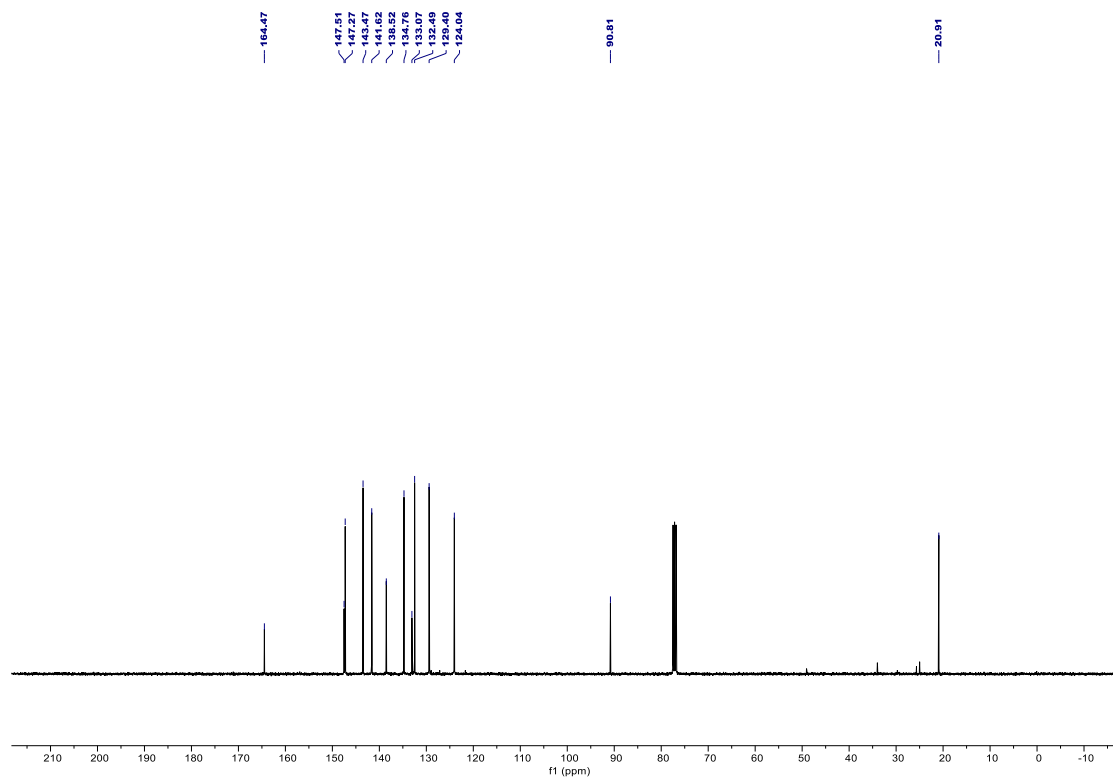
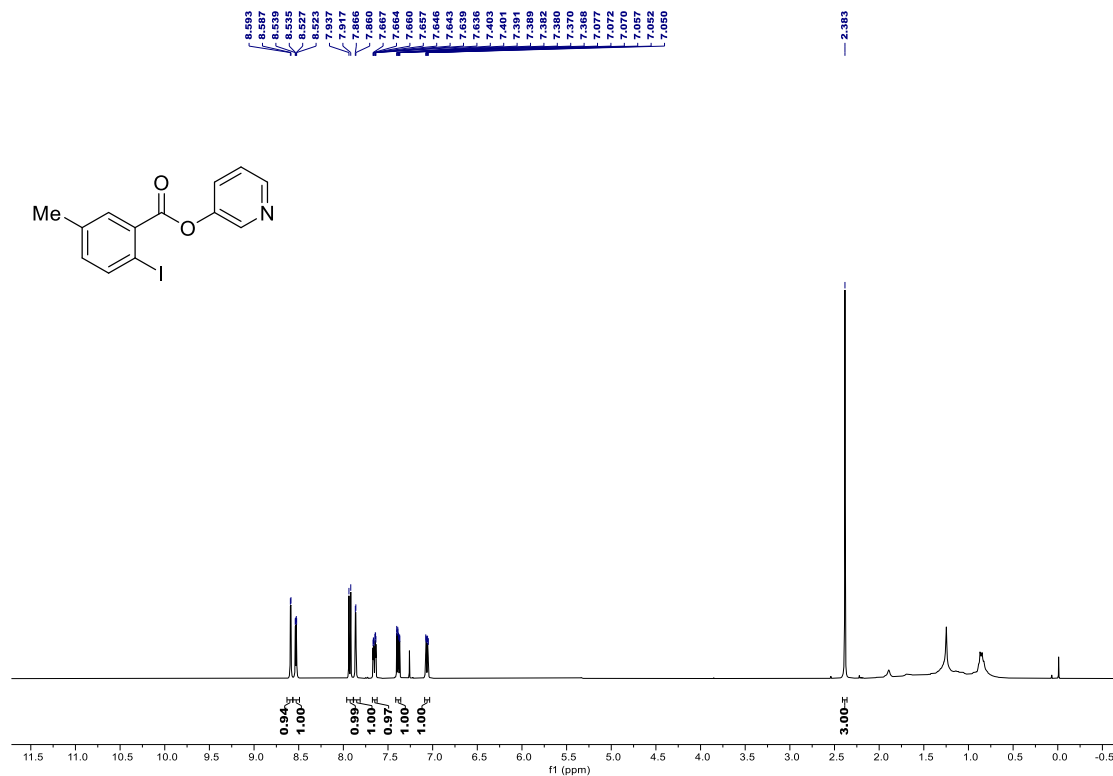
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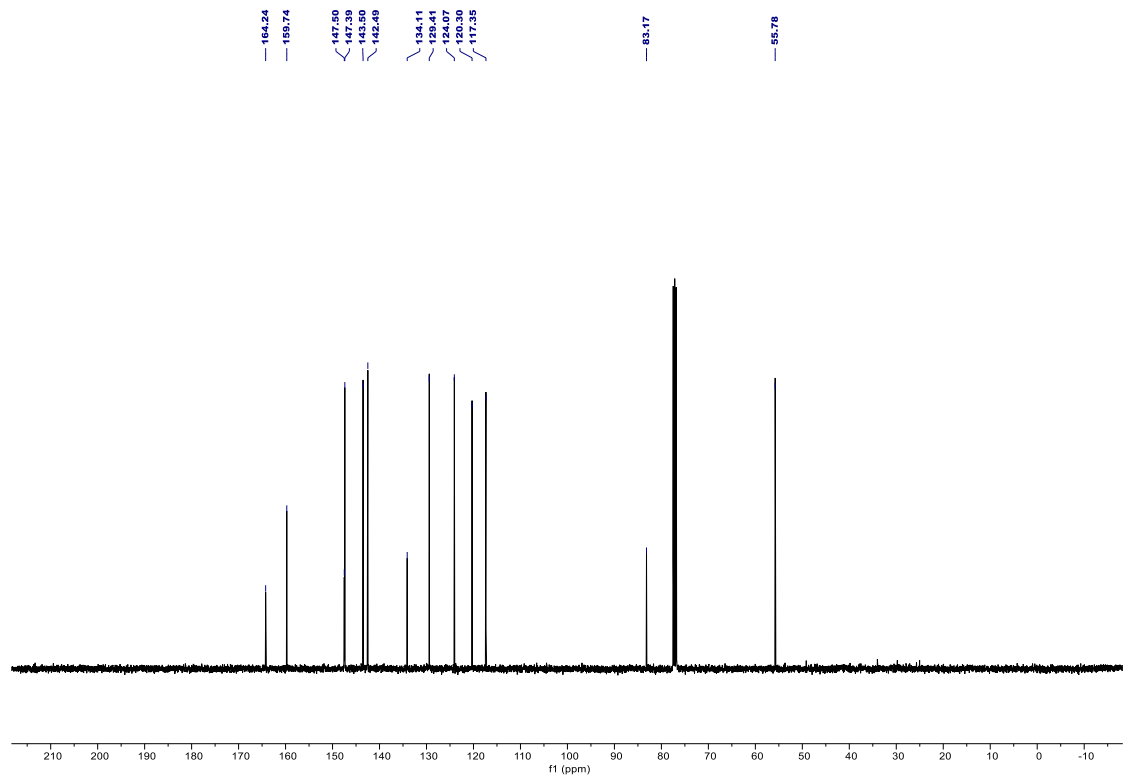
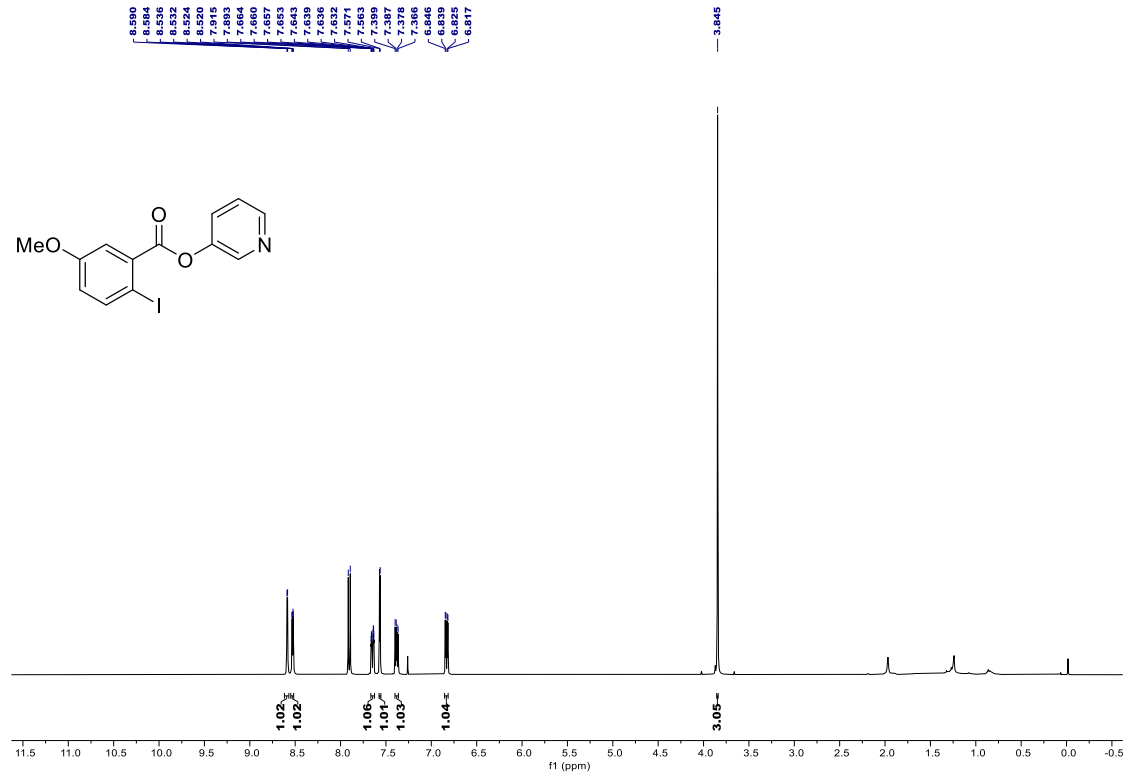
4-Nitrophenyl 2-iodobenzoate (2j)



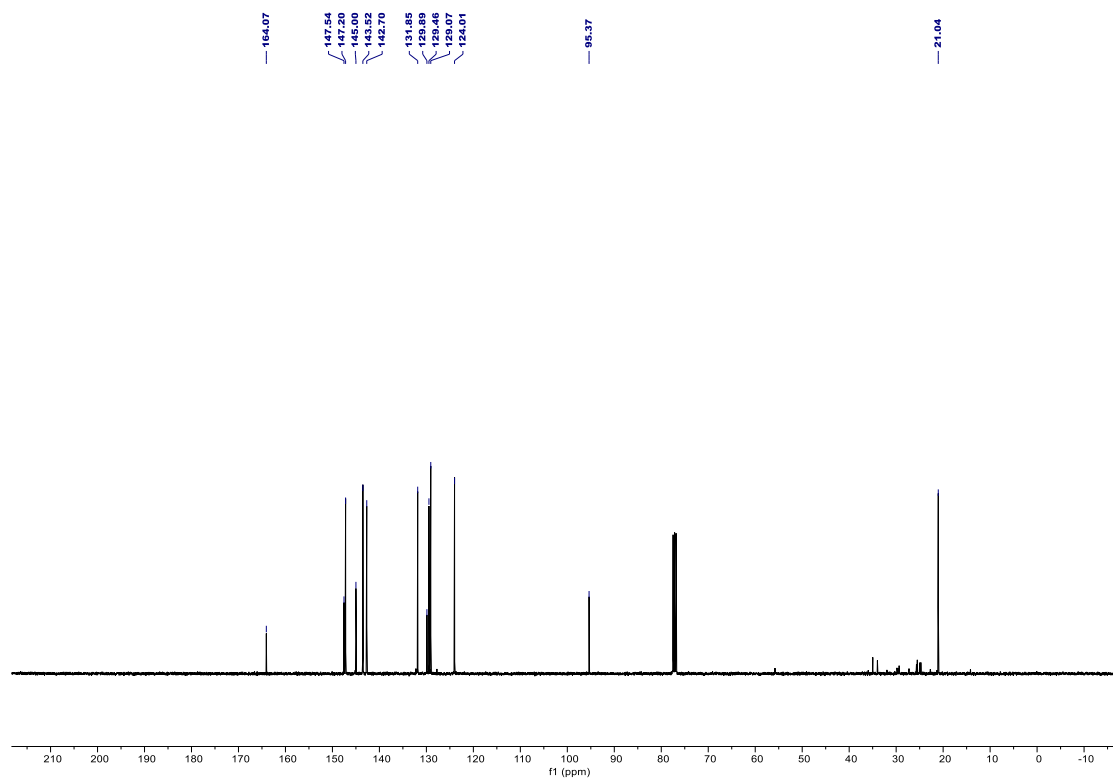
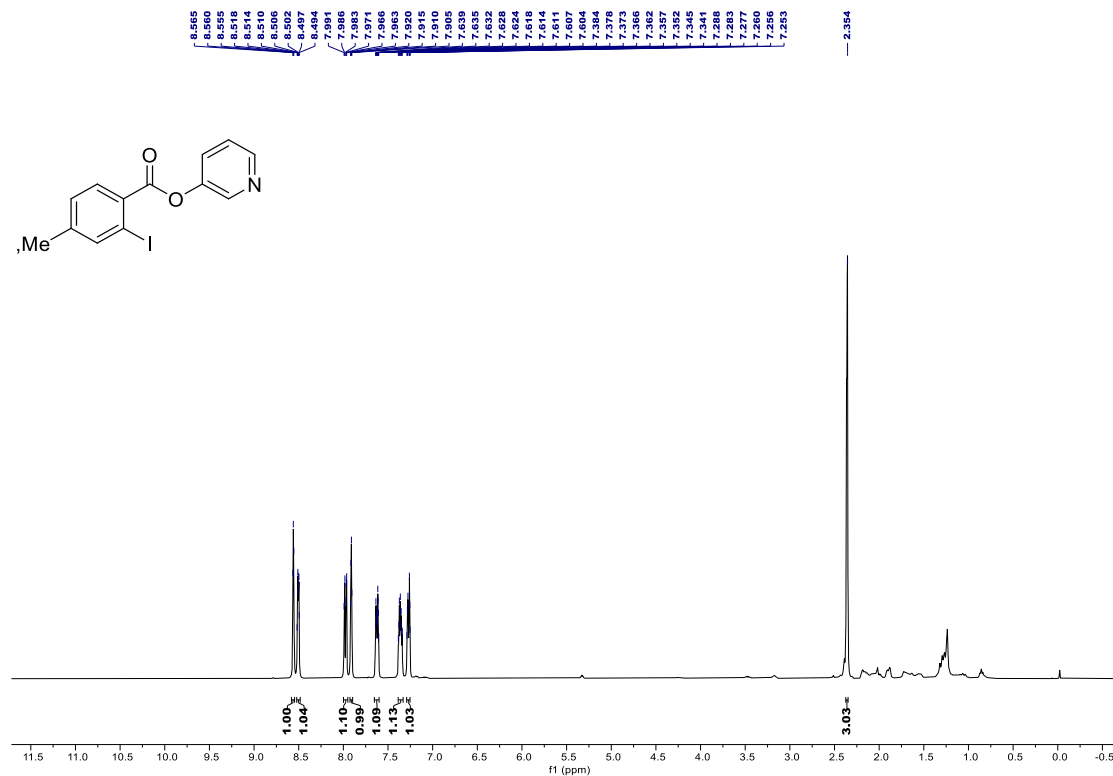
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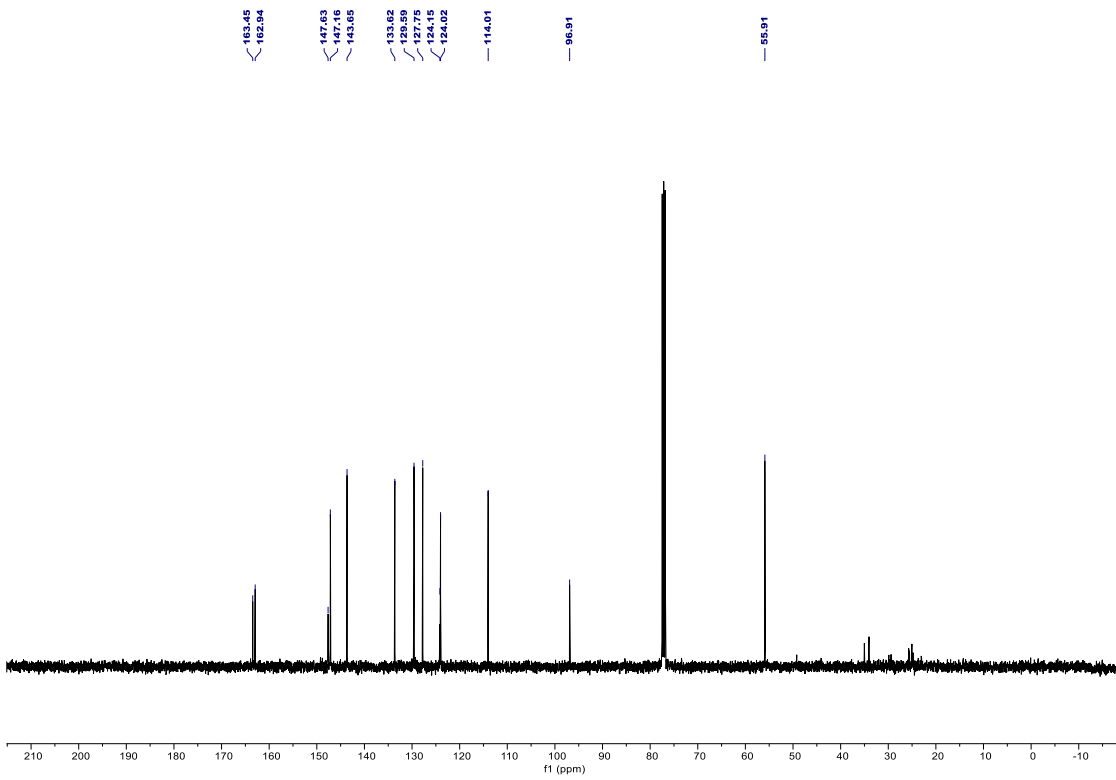
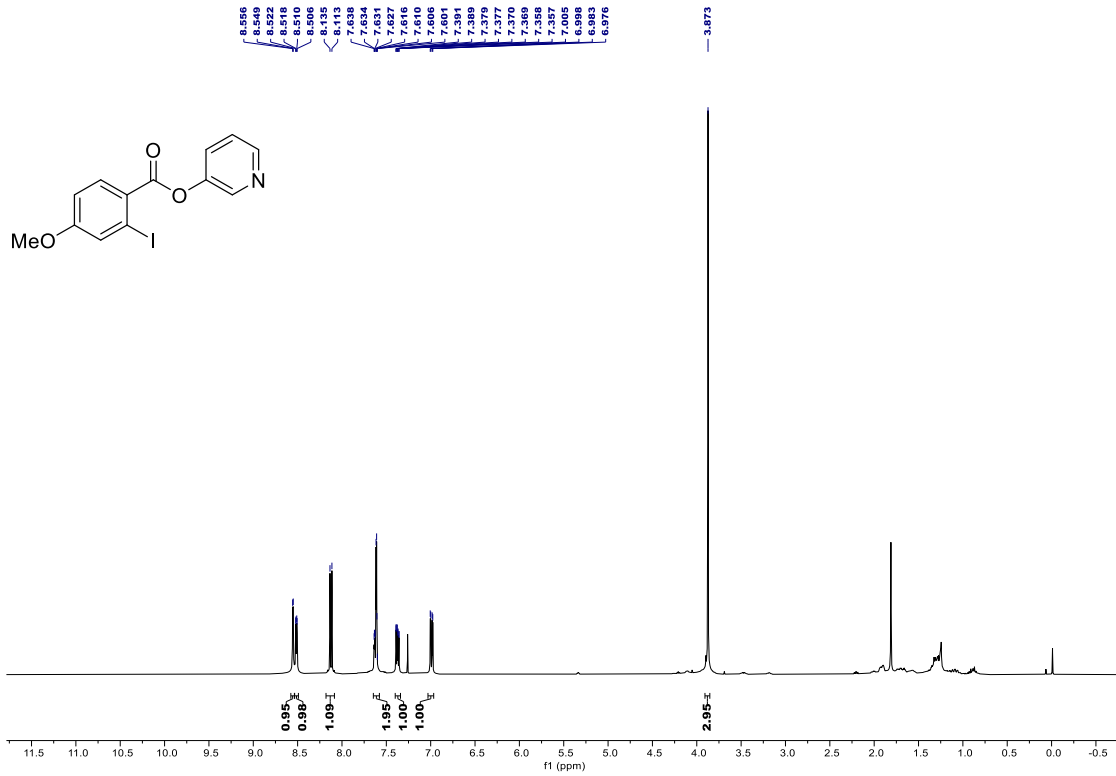
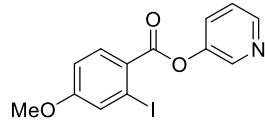
Pyridin-3-yl 2-iodo-5-methoxybenzoate (2n)



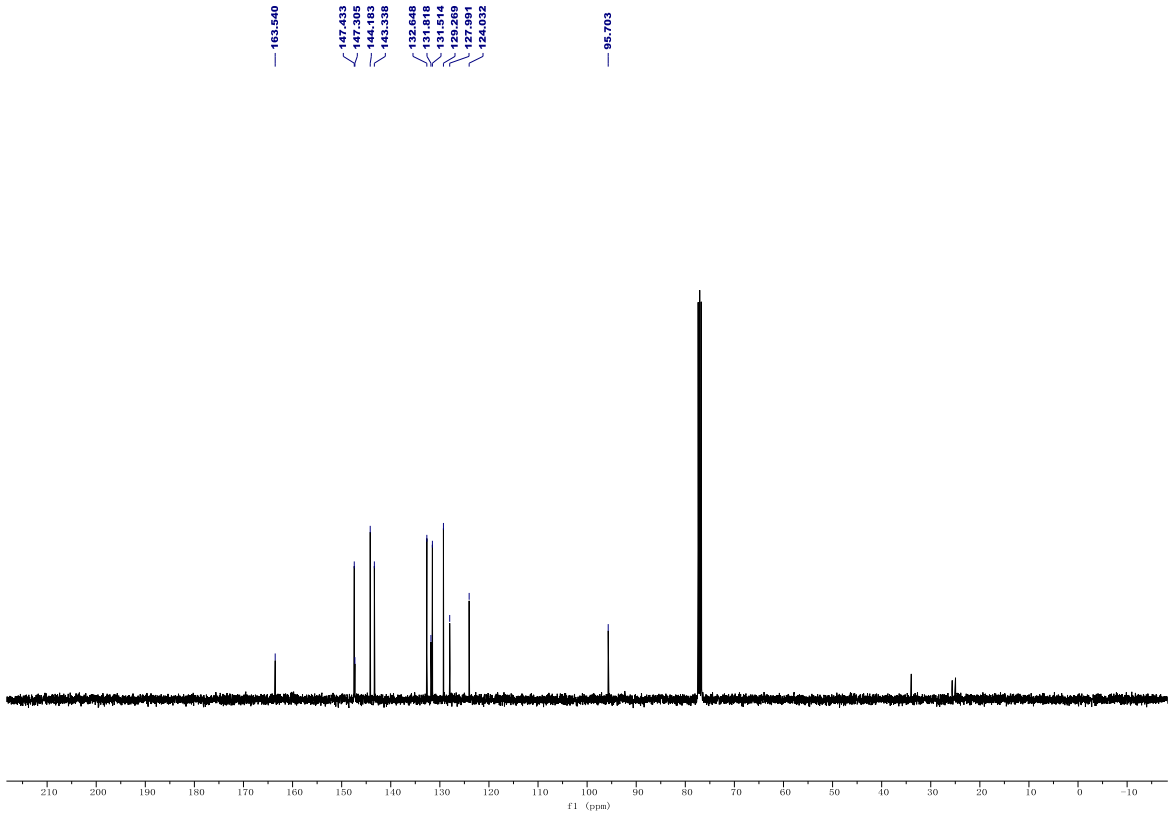
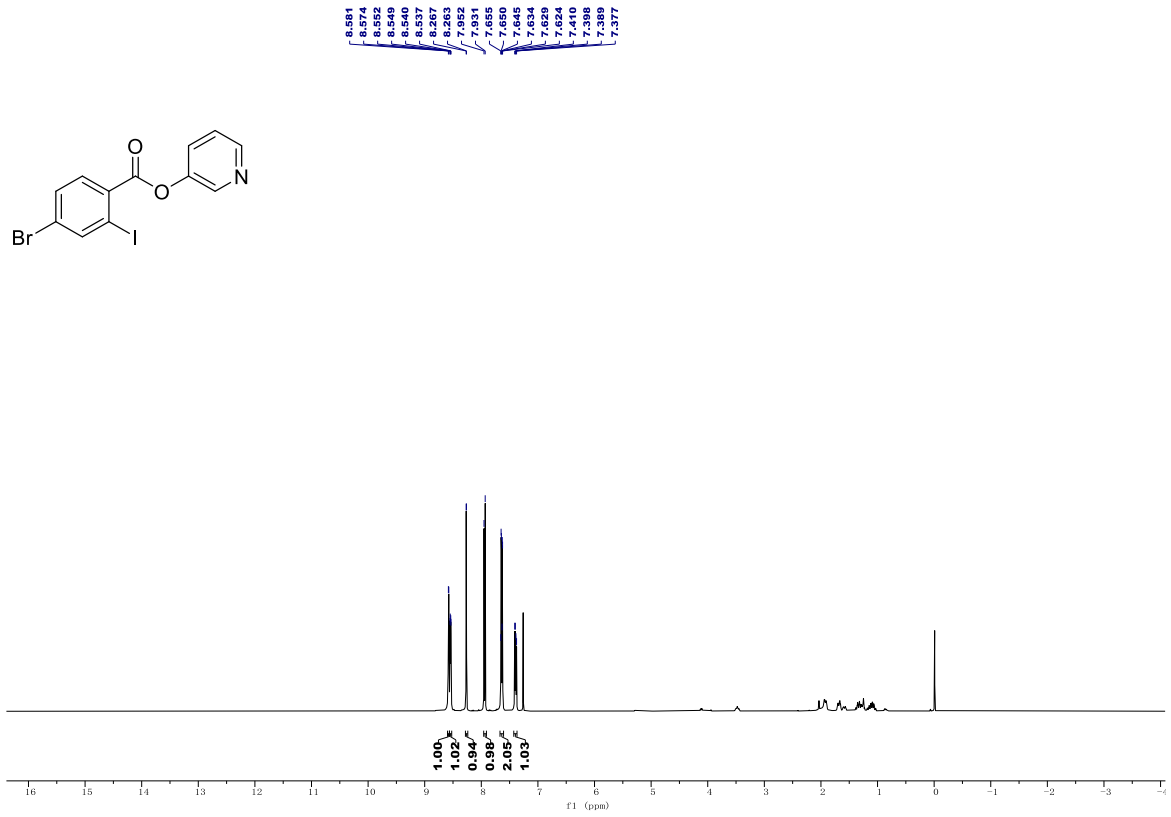
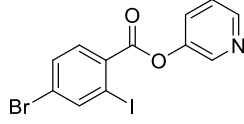
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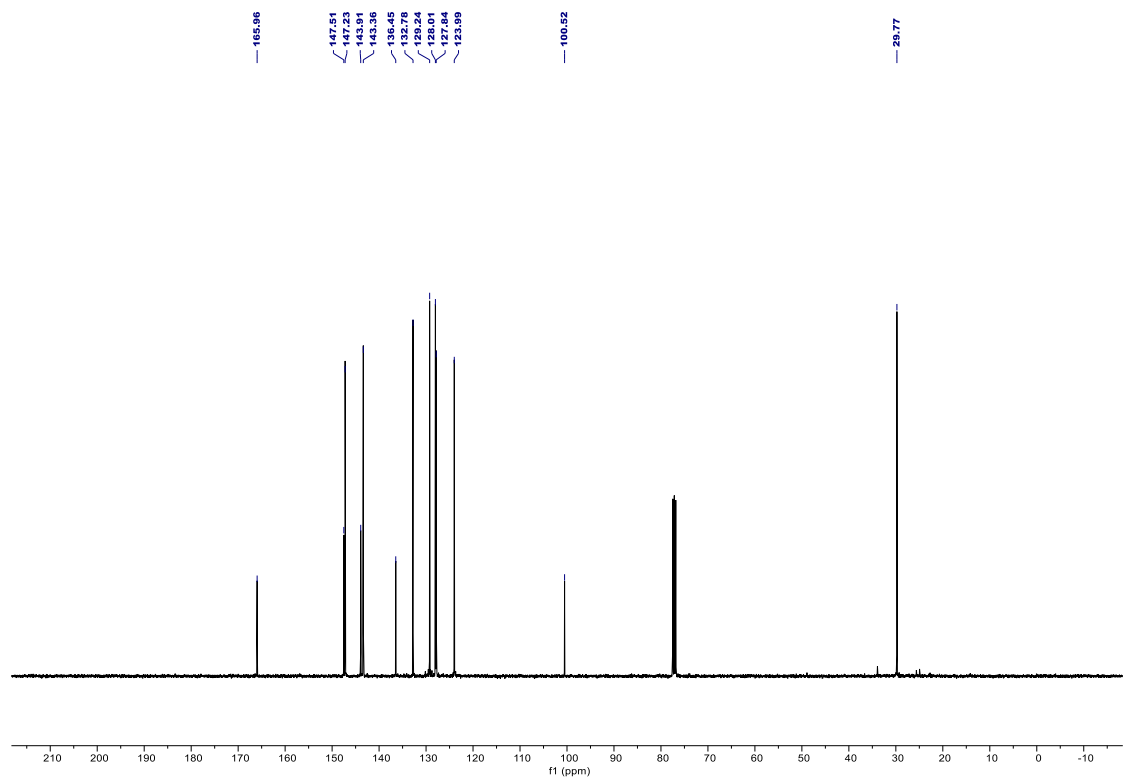
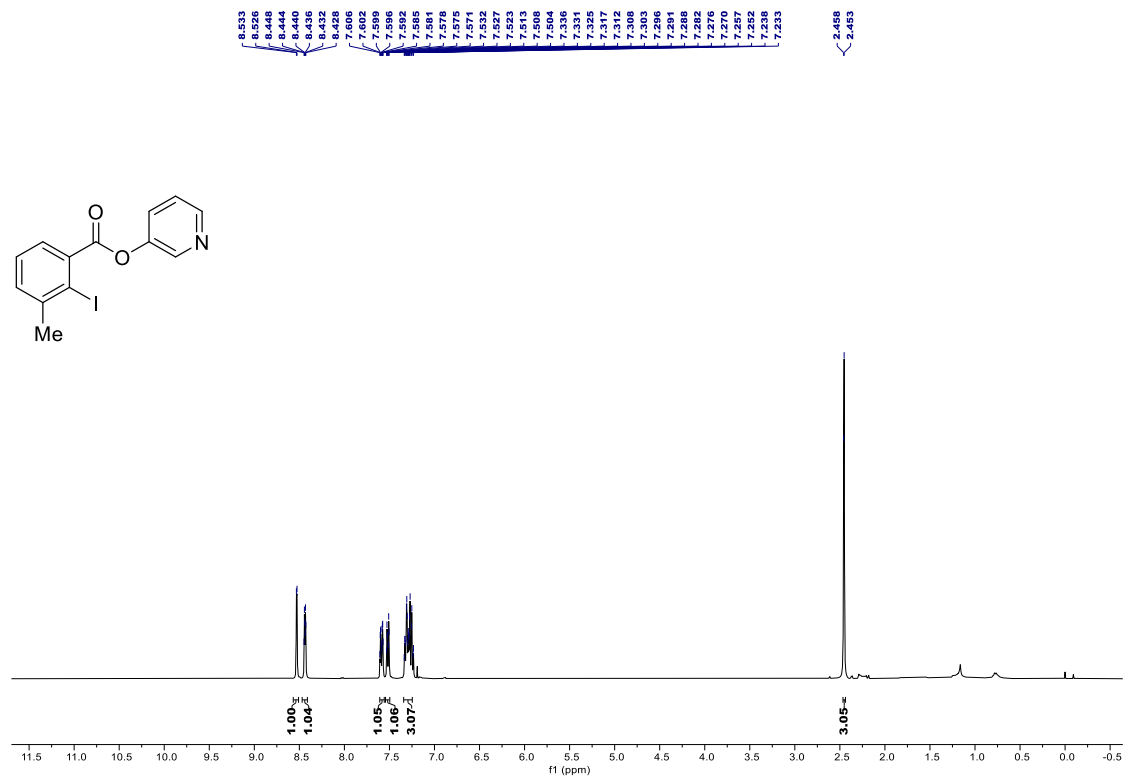
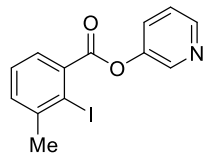
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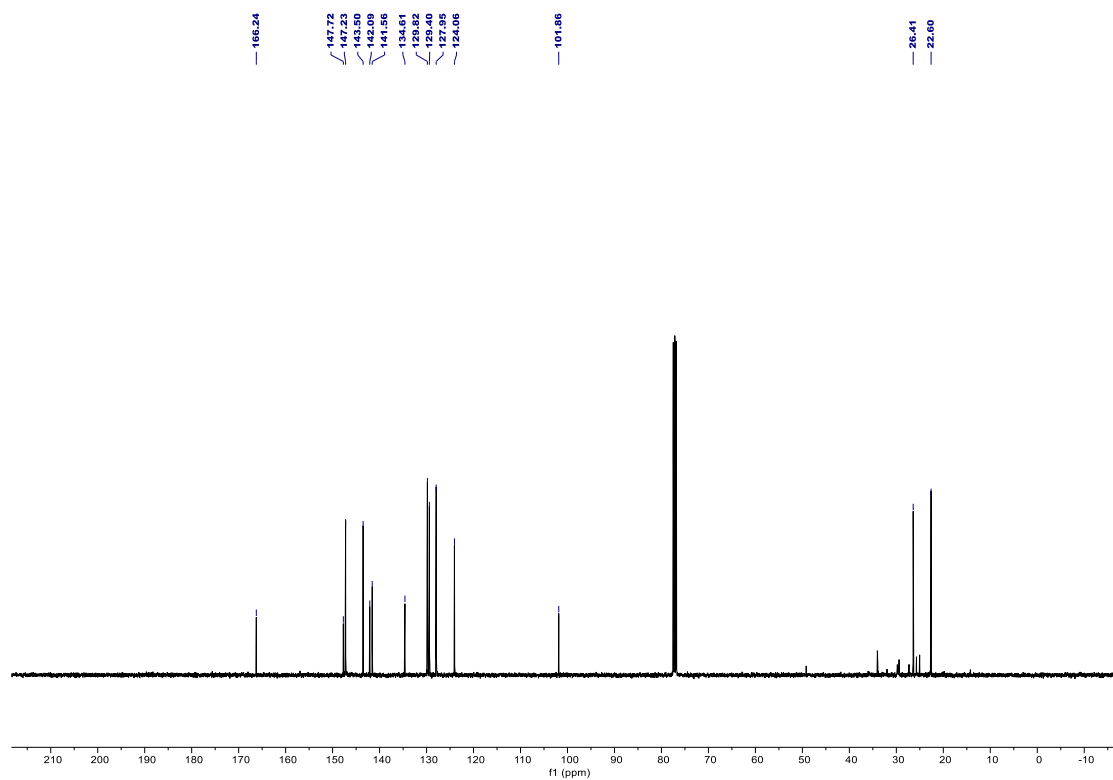
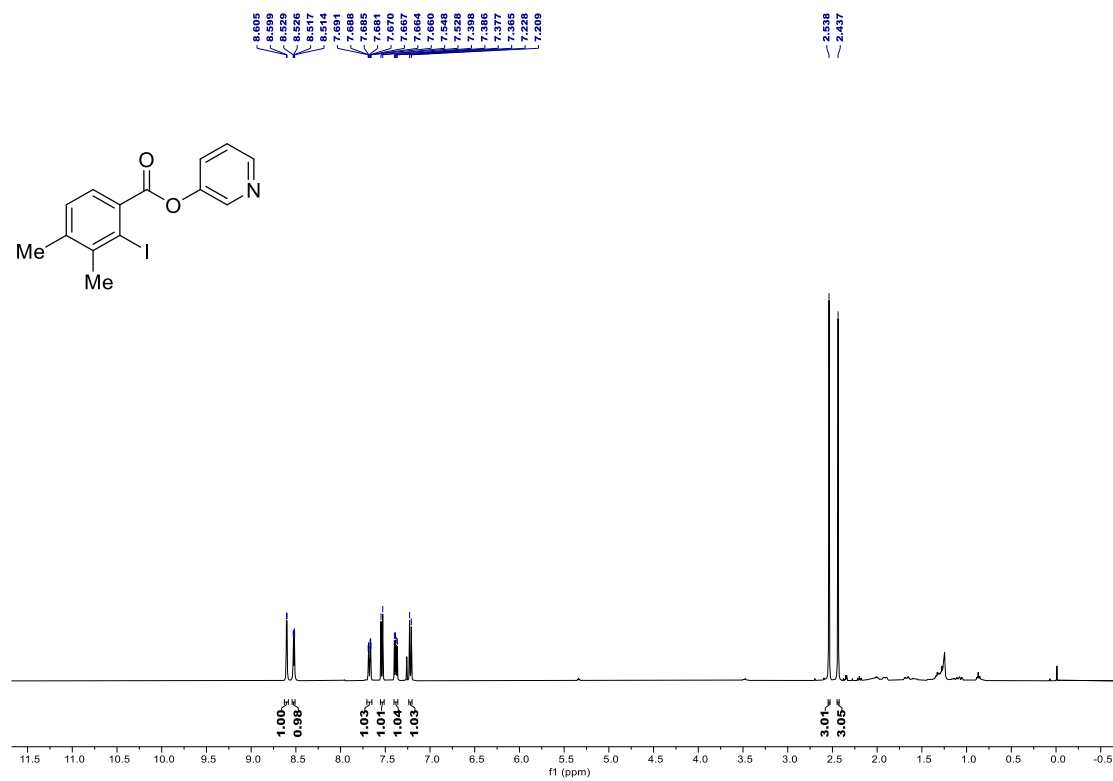
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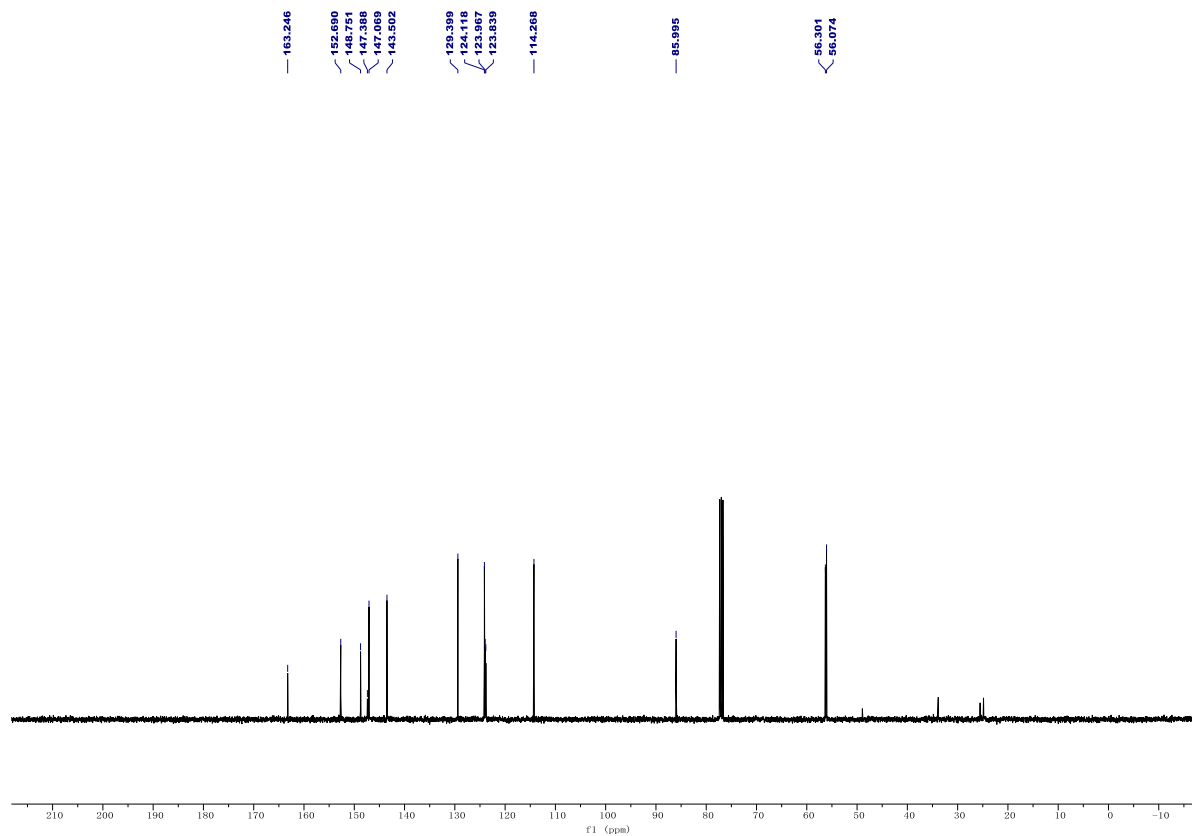
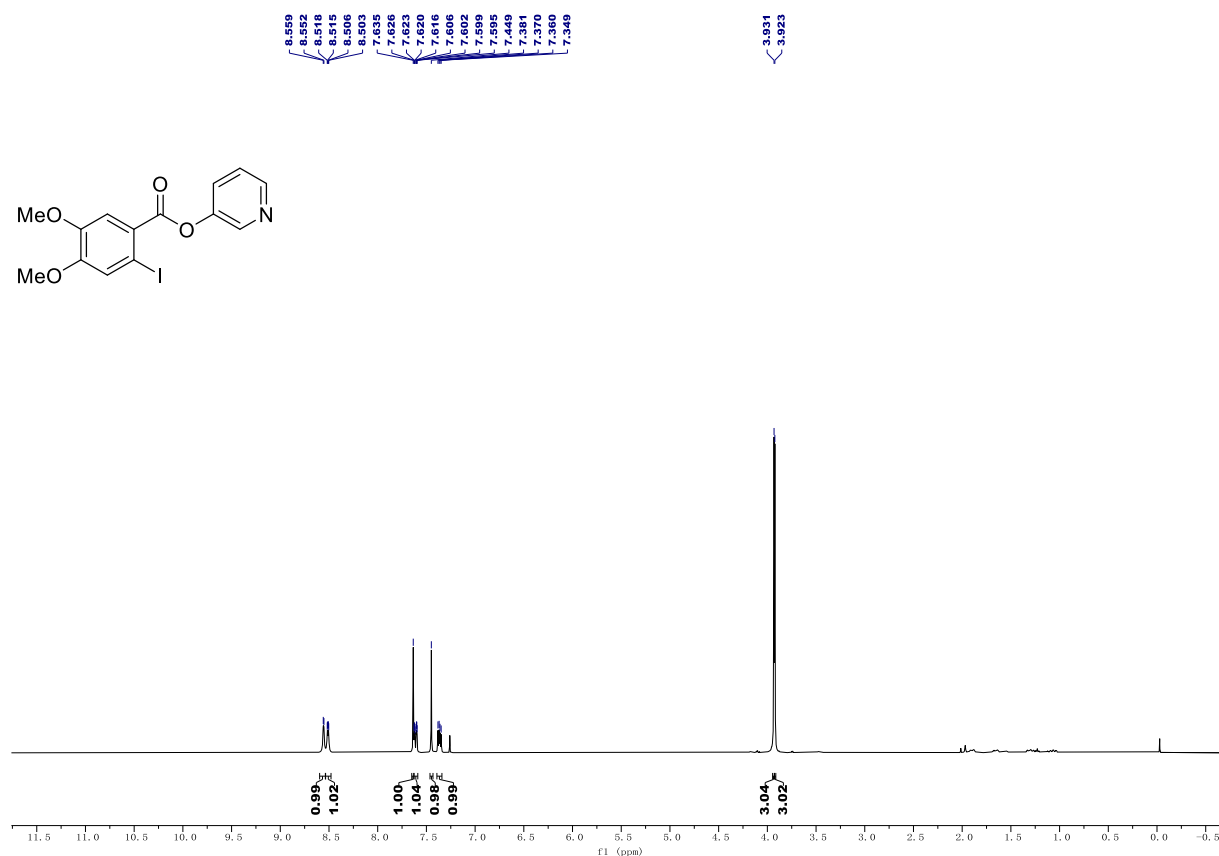
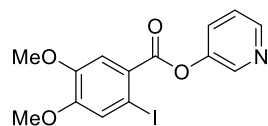
Pyridin-3-yl 2-iodo-3-methylbenzoate (2r)



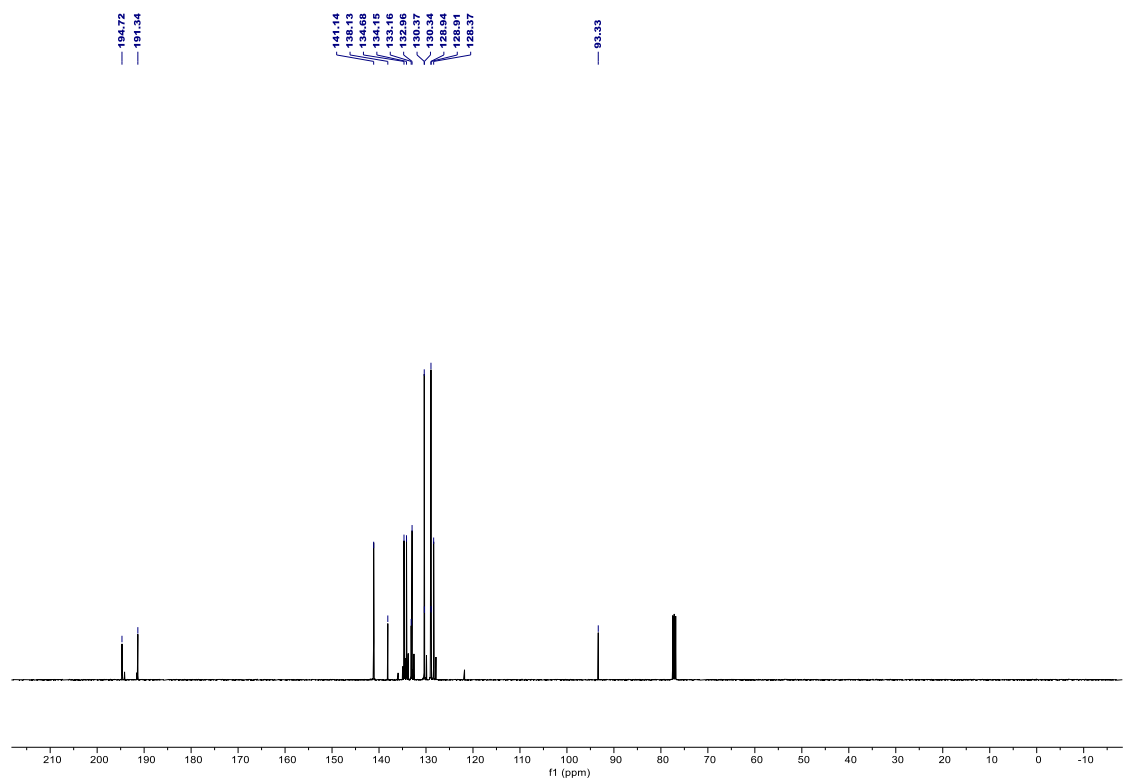
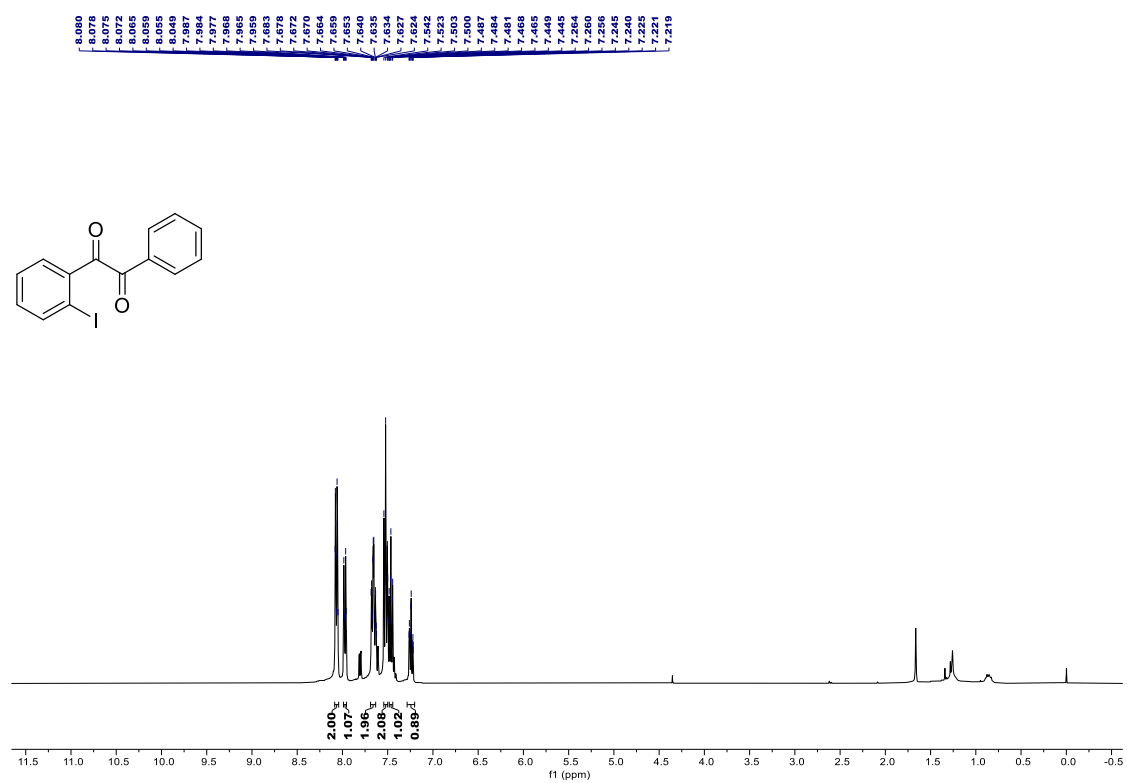
Pyridin-3-yl 2-iodo-3,4-dimethylbenzoate (2s)



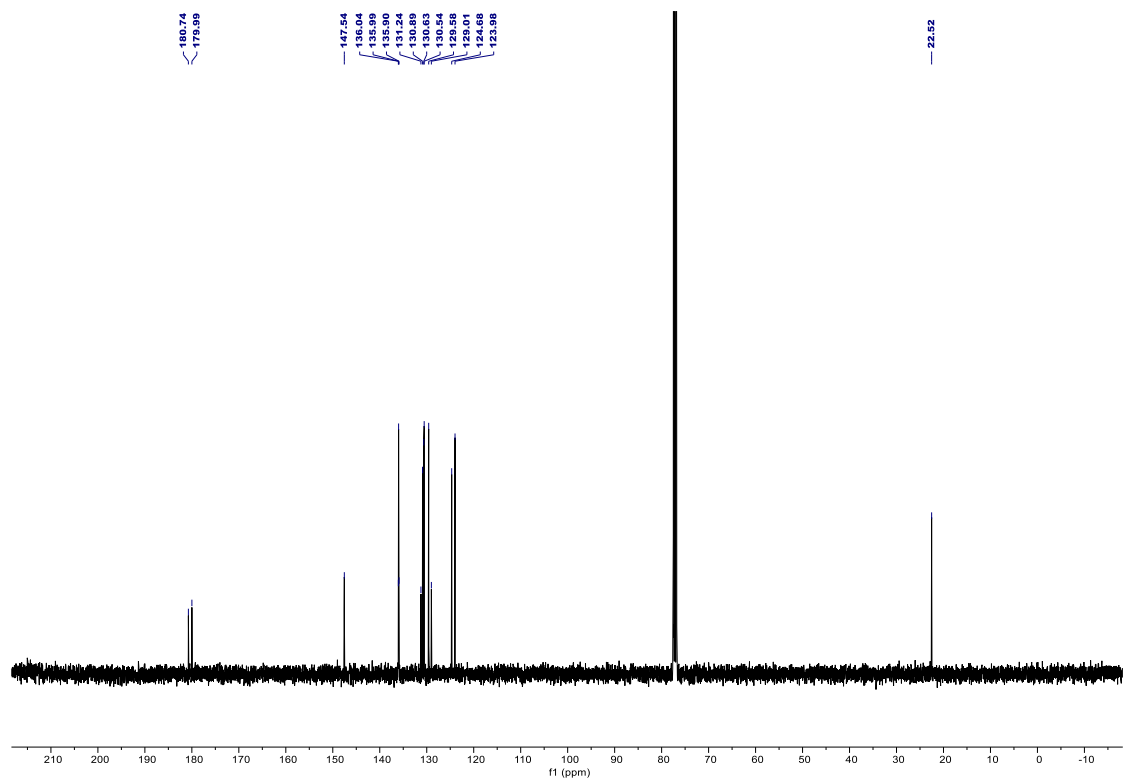
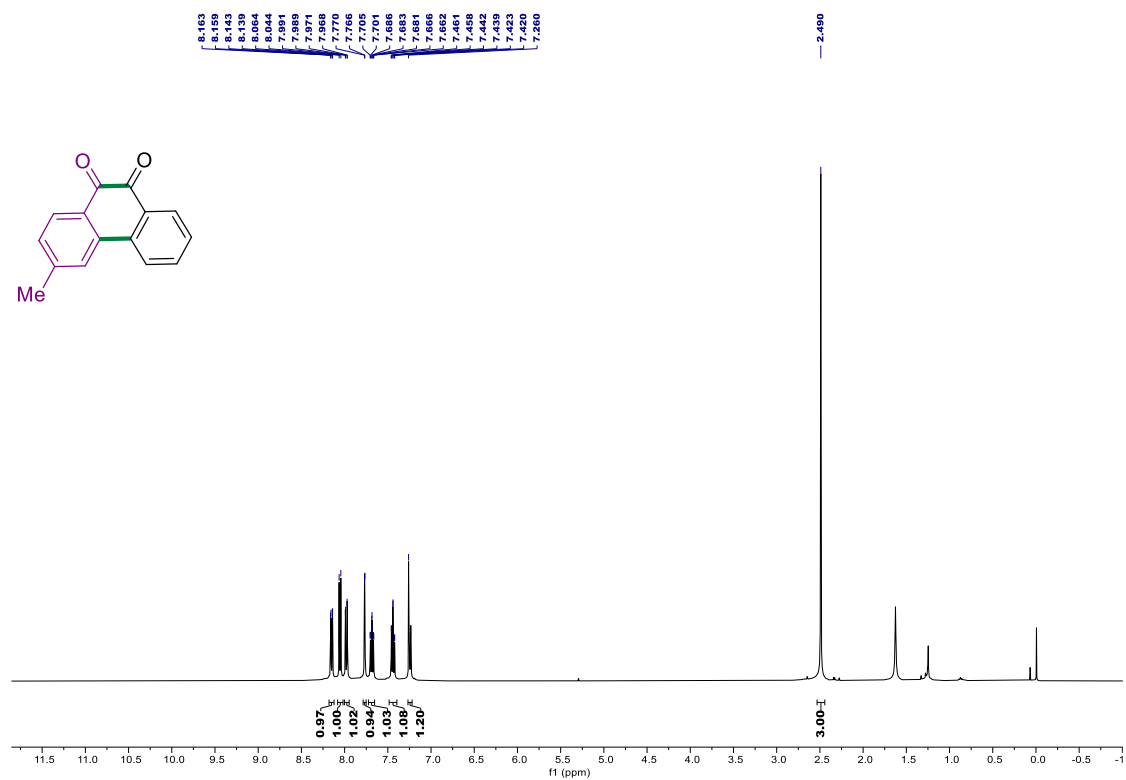
Pyridin-3-yl 2-iodo-4,5-dimethoxybenzoate (2t)



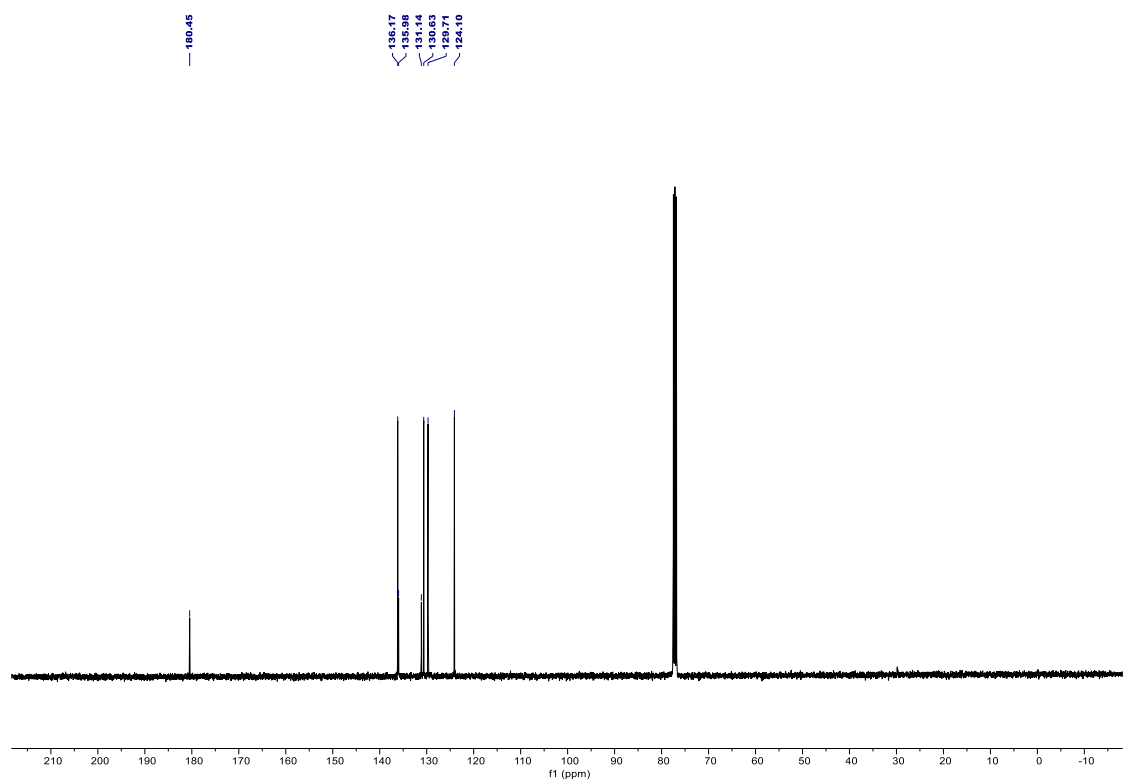
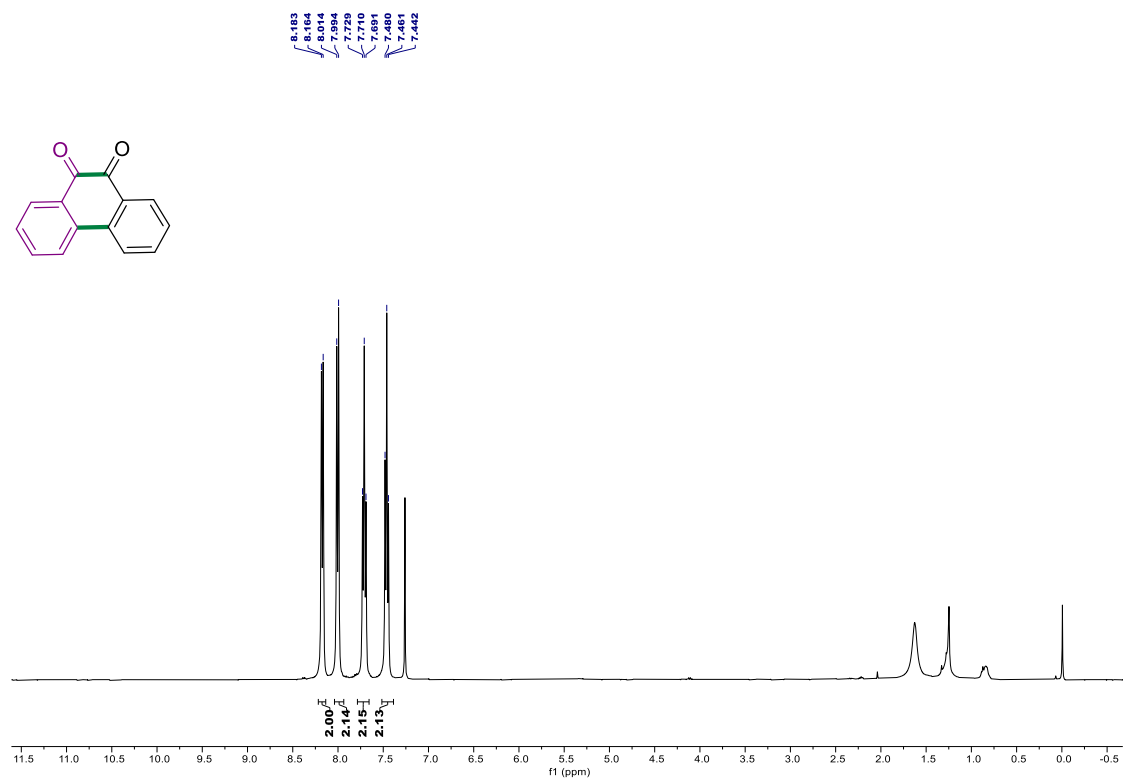
1-(2-Iodophenyl)-2-phenylethane-1,2-dione (5)



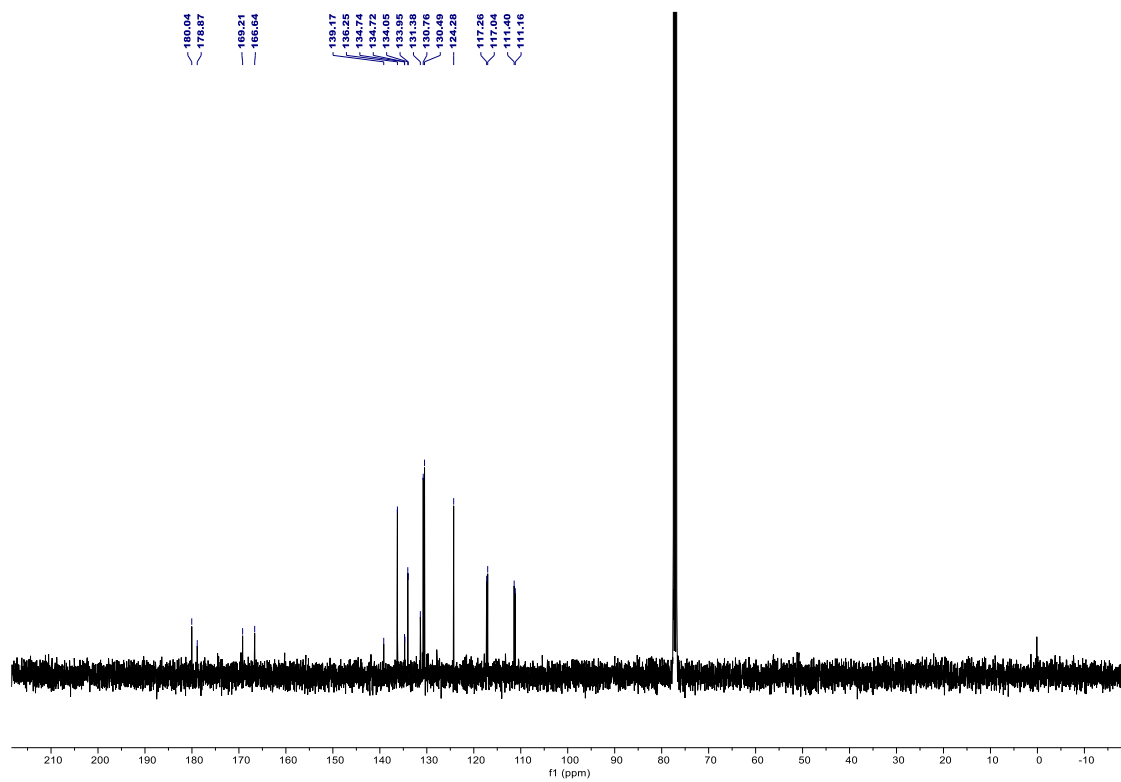
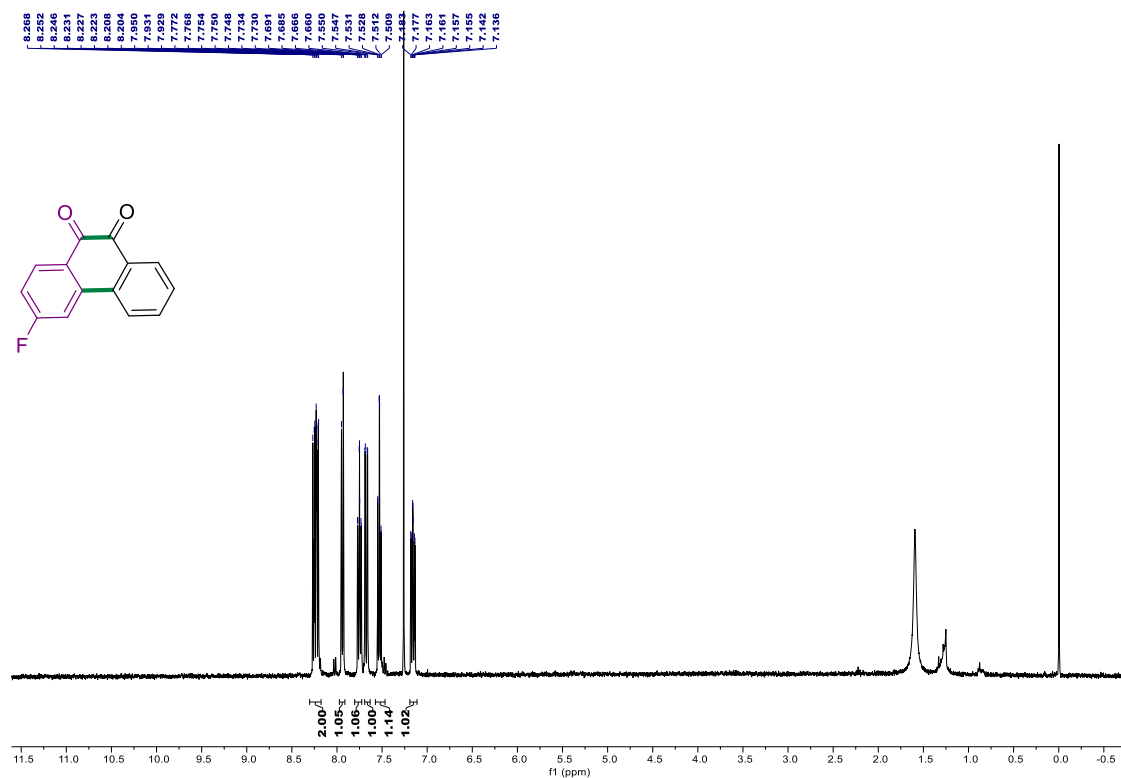
3-Methylphenanthrene-9,10-dione (3a)

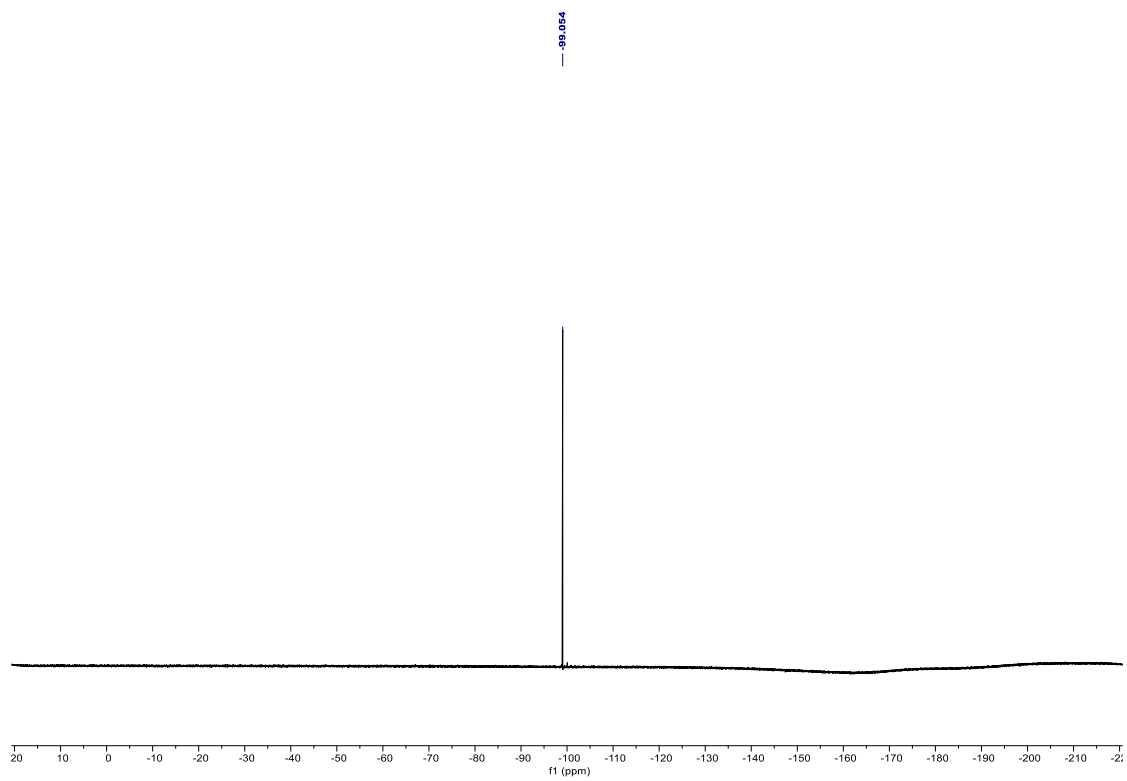


Phenanthrene-9,10-dione (3b)

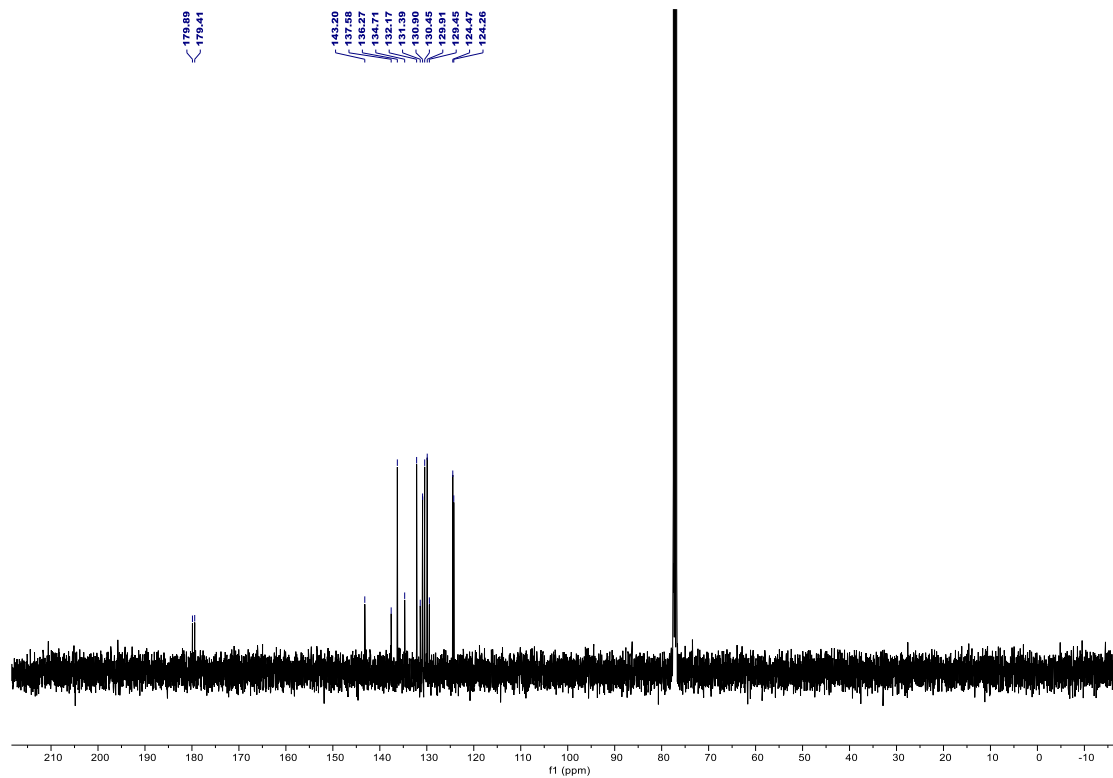
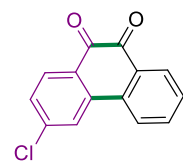
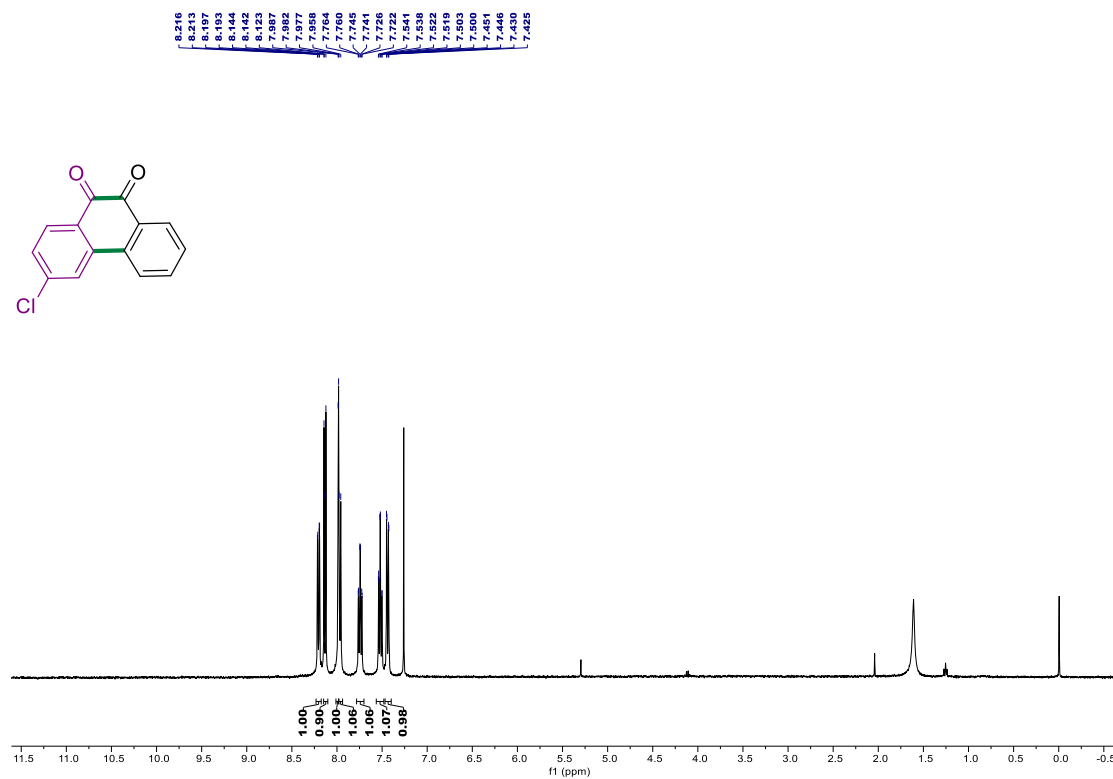


3-Fluorophenanthrene-9,10-dione (3c)

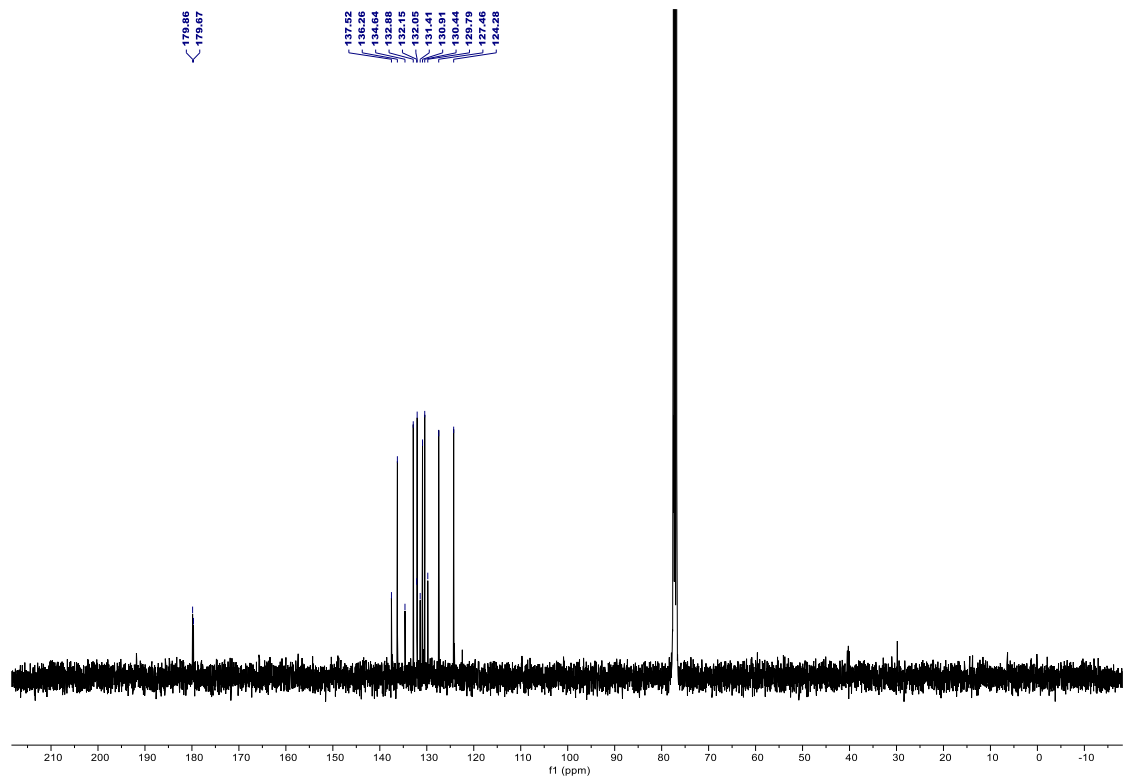
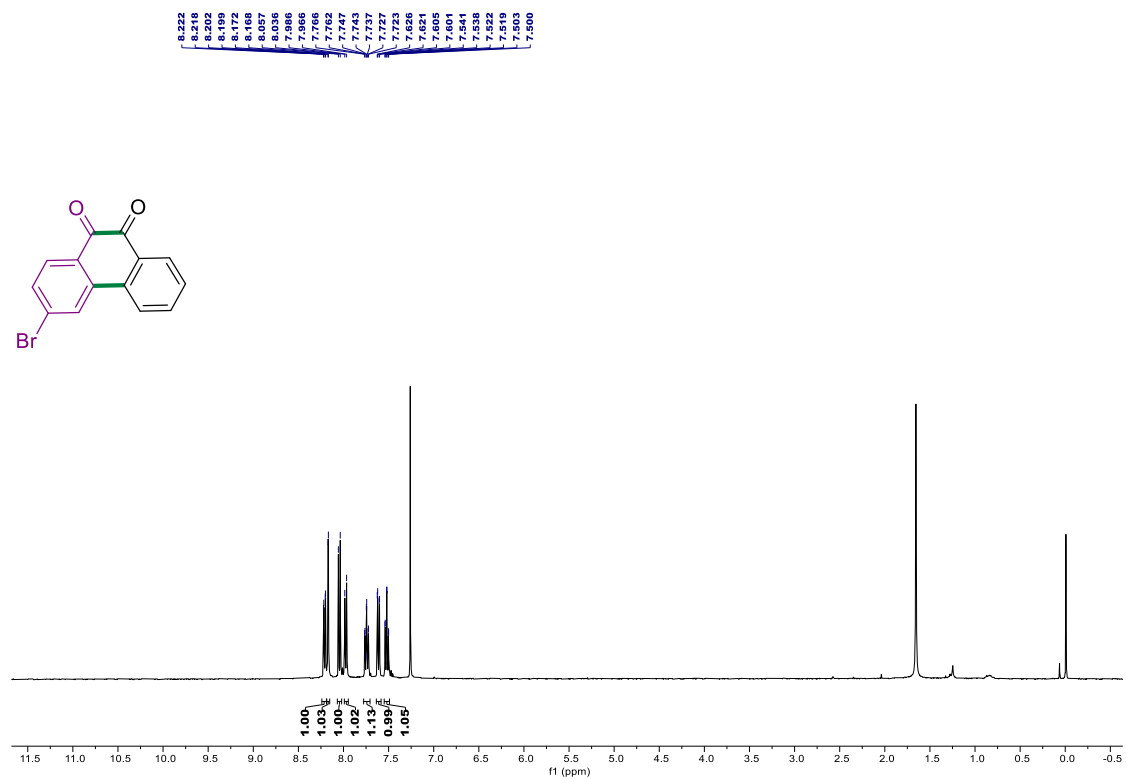




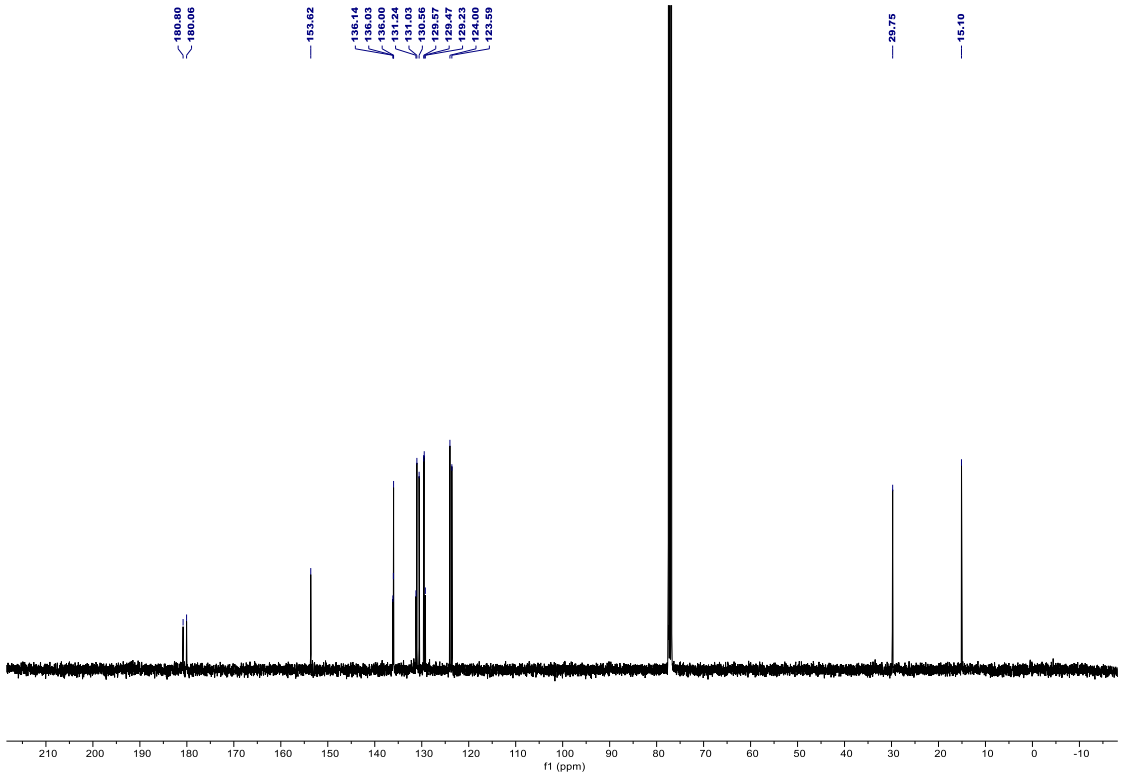
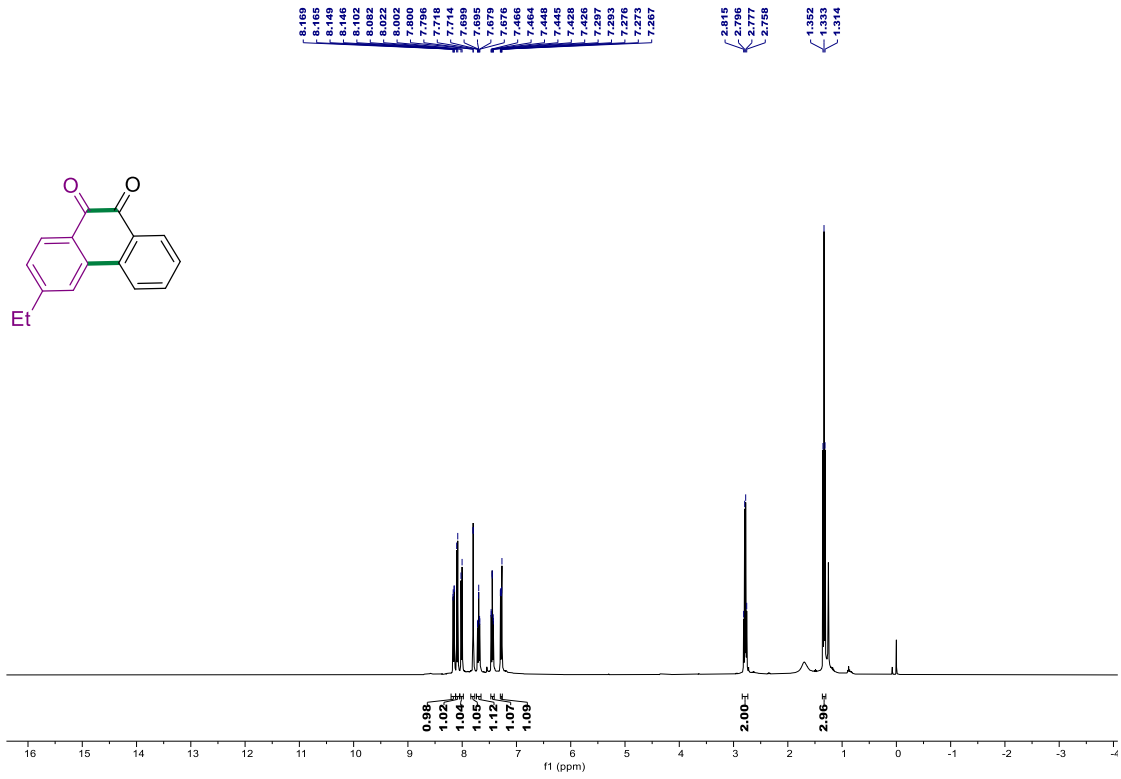
3-Chlorophenanthrene-9,10-dione (3d)



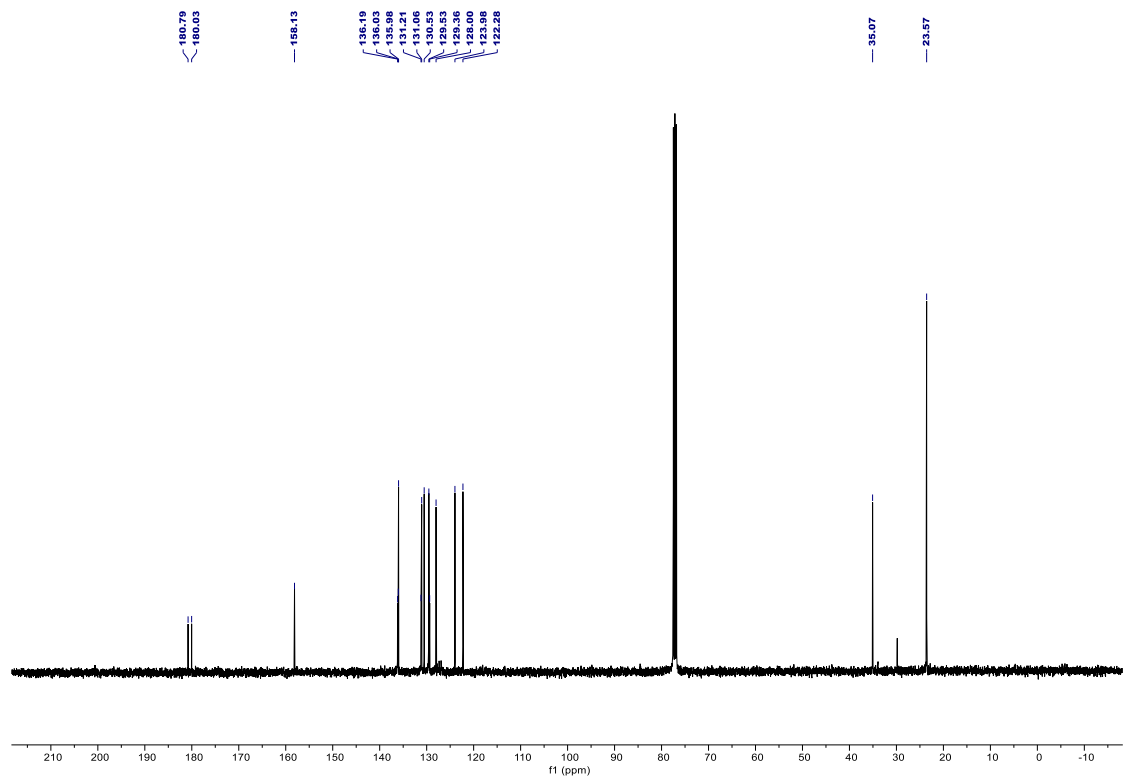
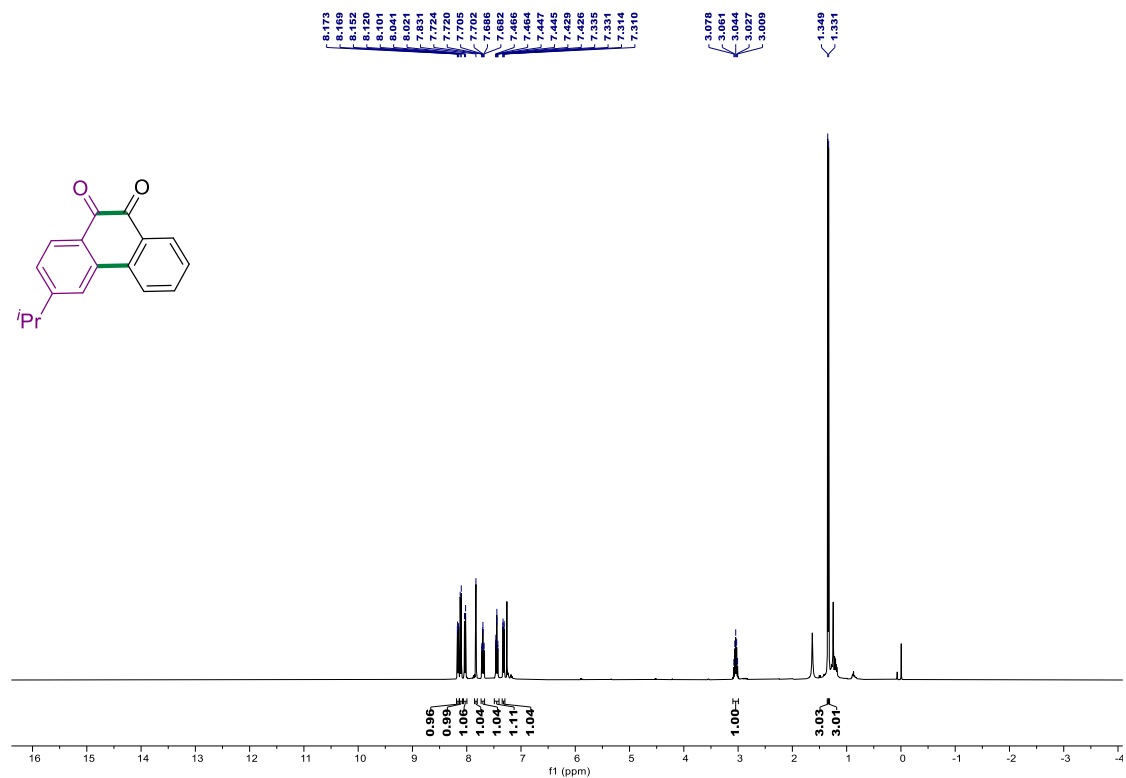
3-Bromophenanthrene-9,10-dione (3e)



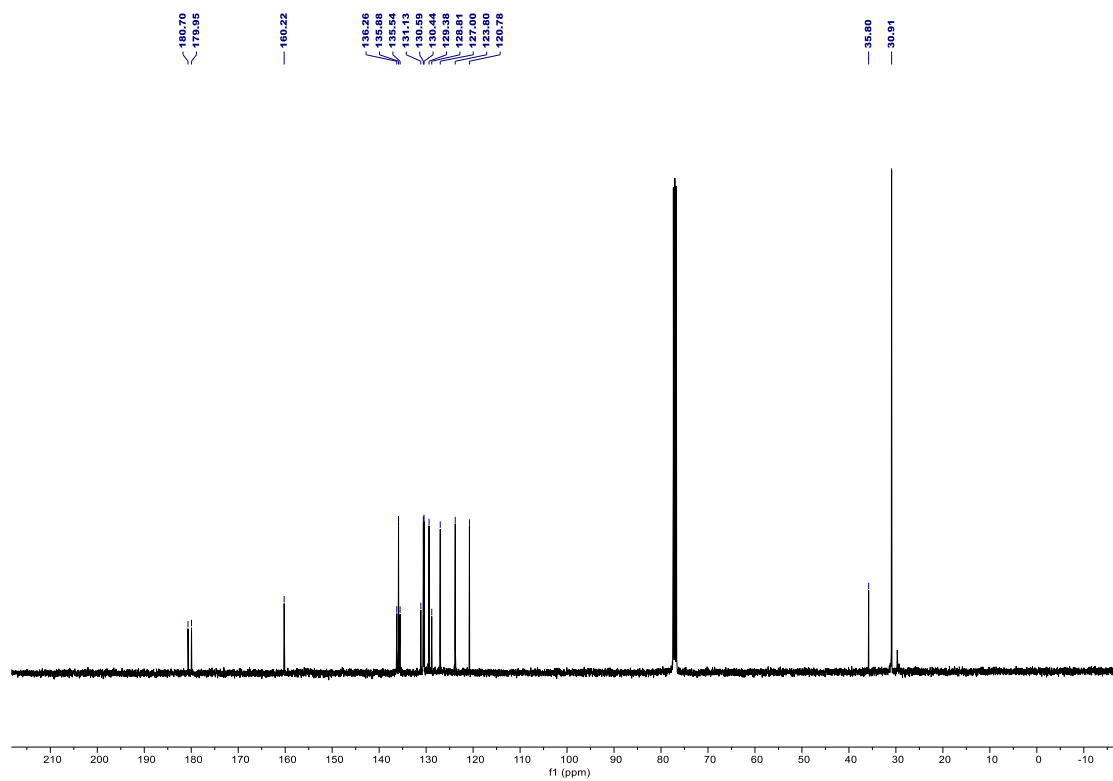
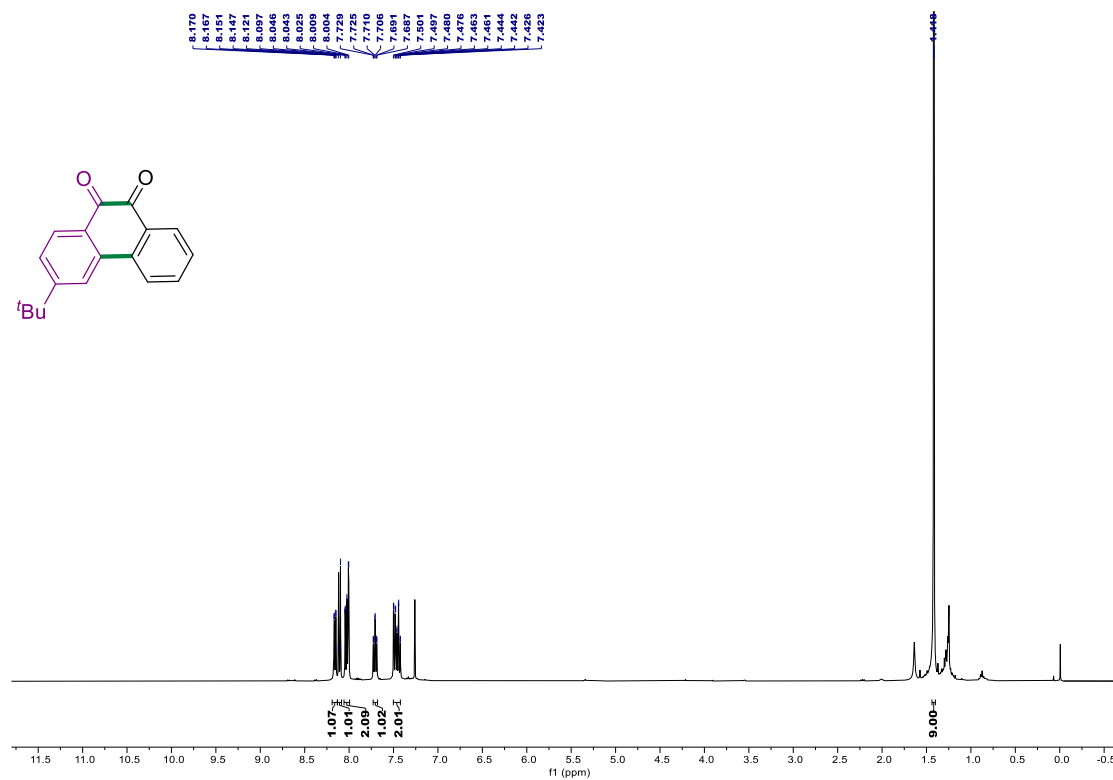
3-Ethylphenanthrene-9,10-dione (3f)



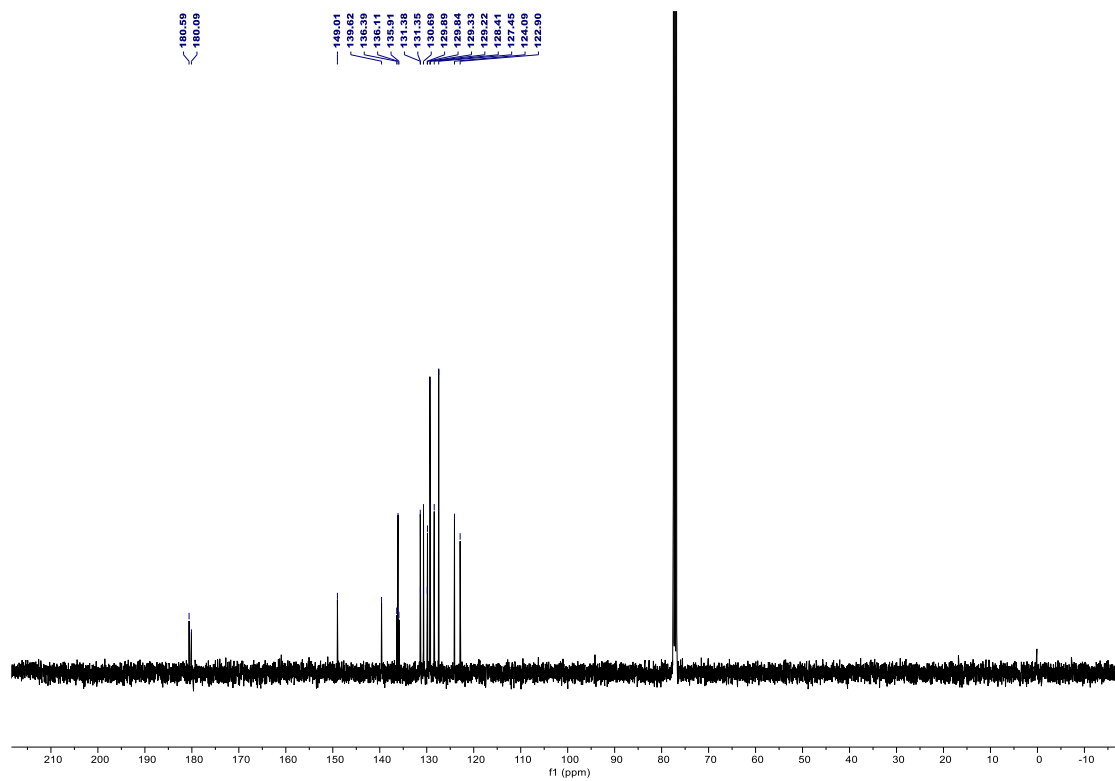
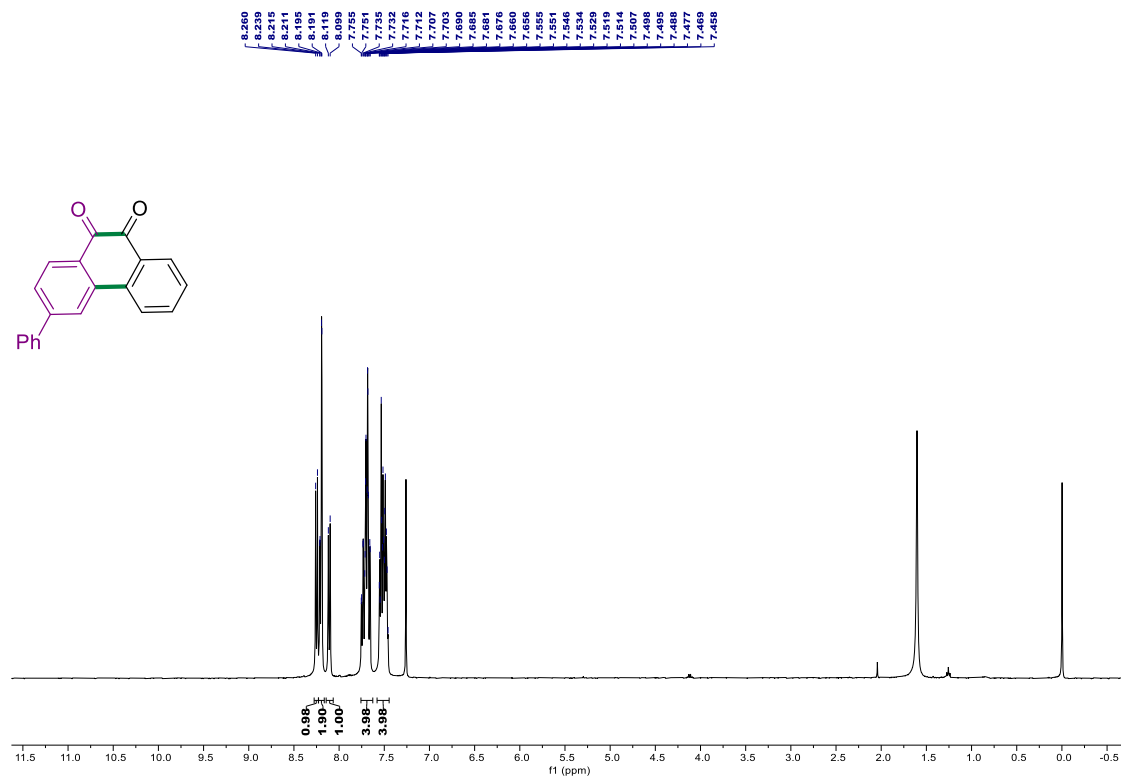
3-Isopropylphenanthrene-9,10-dione (3g)



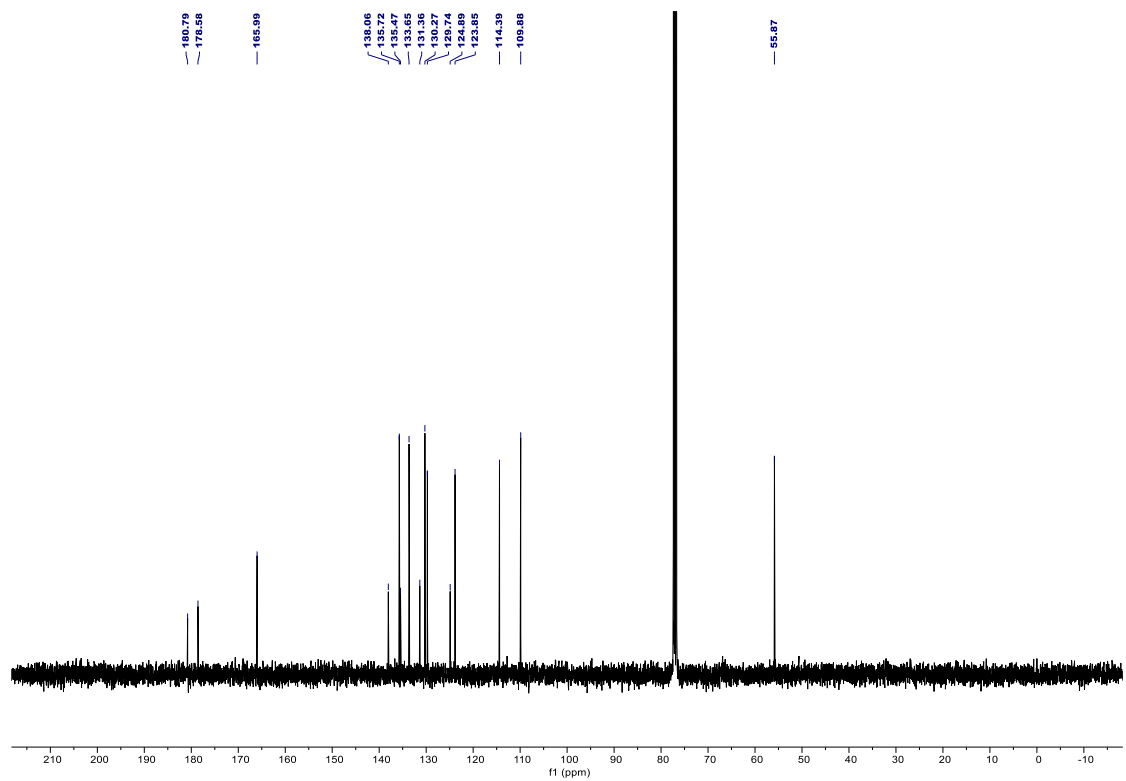
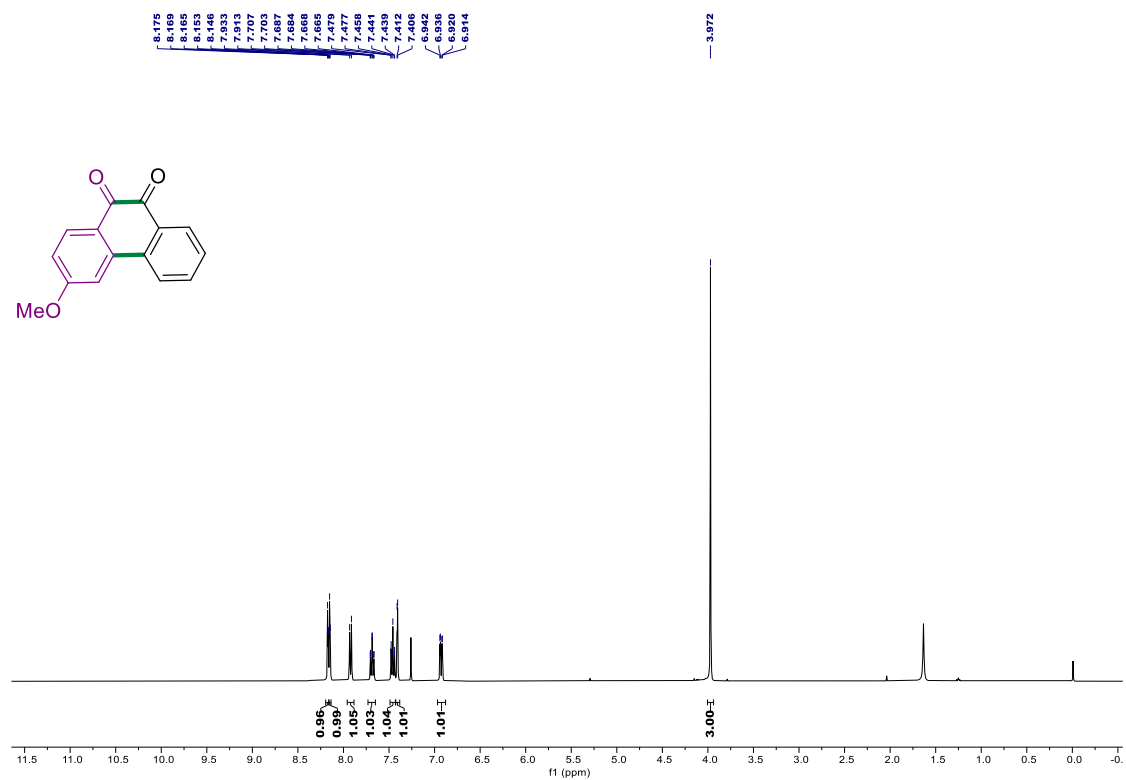
3-(*Tert-butyl*)phenanthrene-9,10-dione (3h)



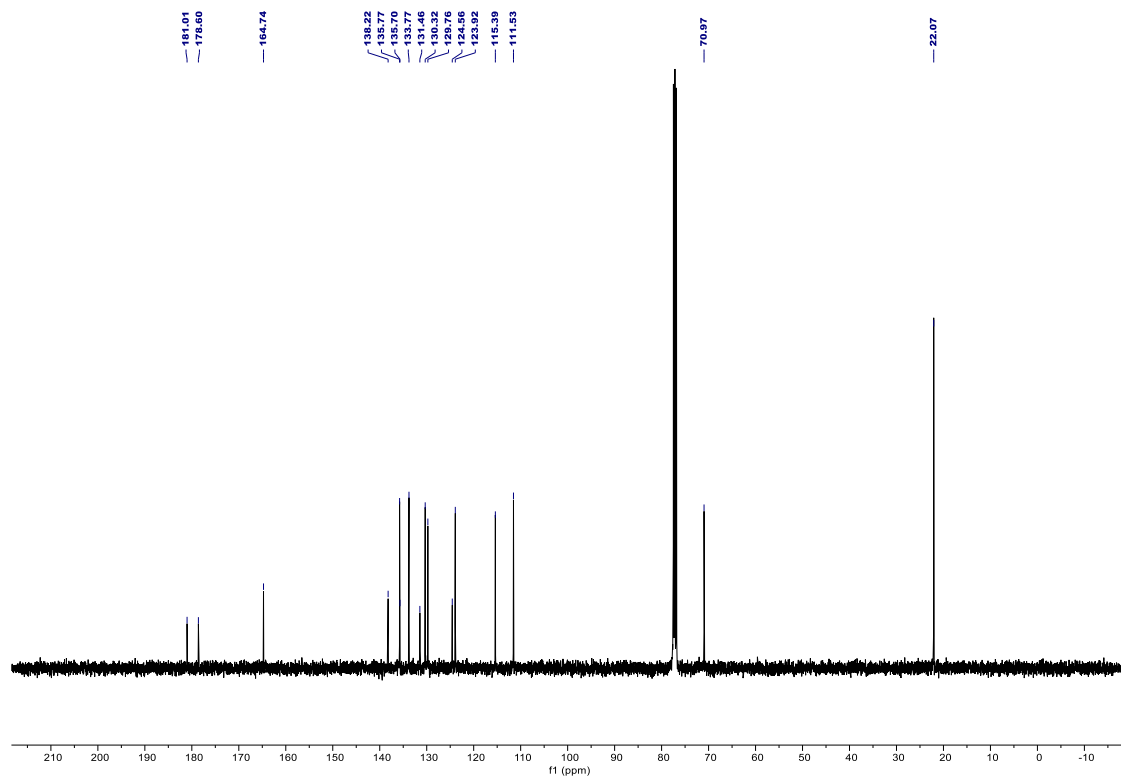
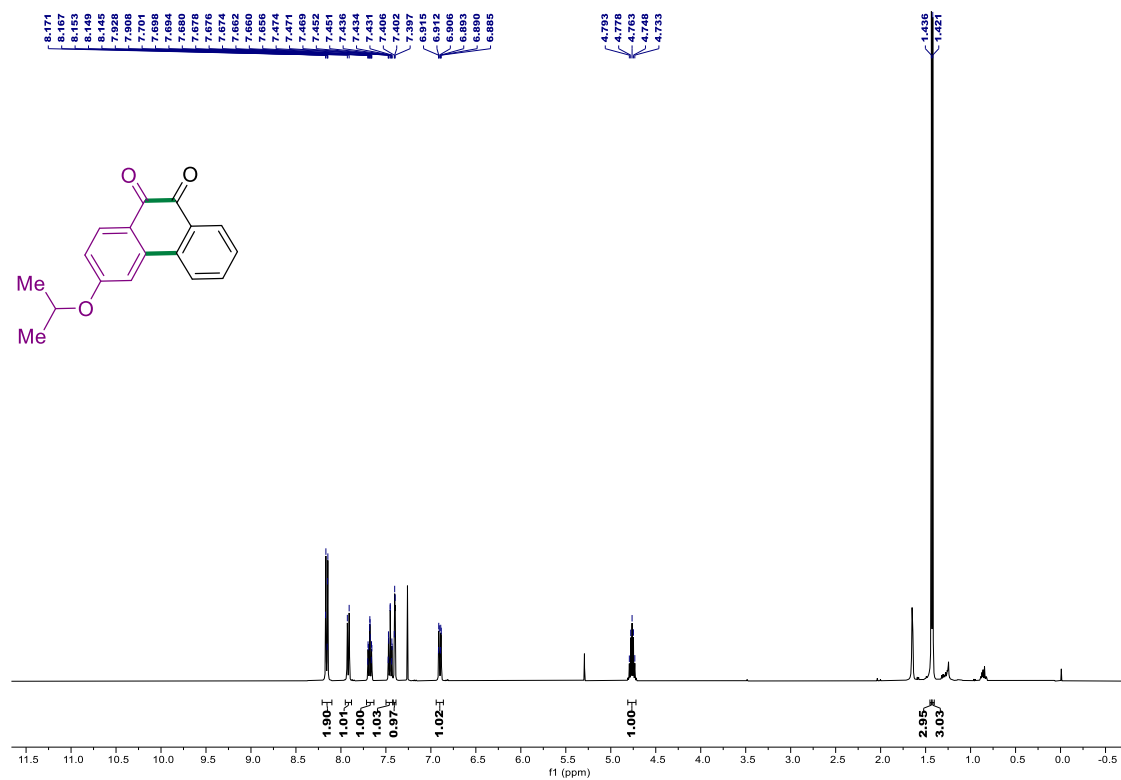
3-Phenylphenanthrene-9,10-dione (3i)



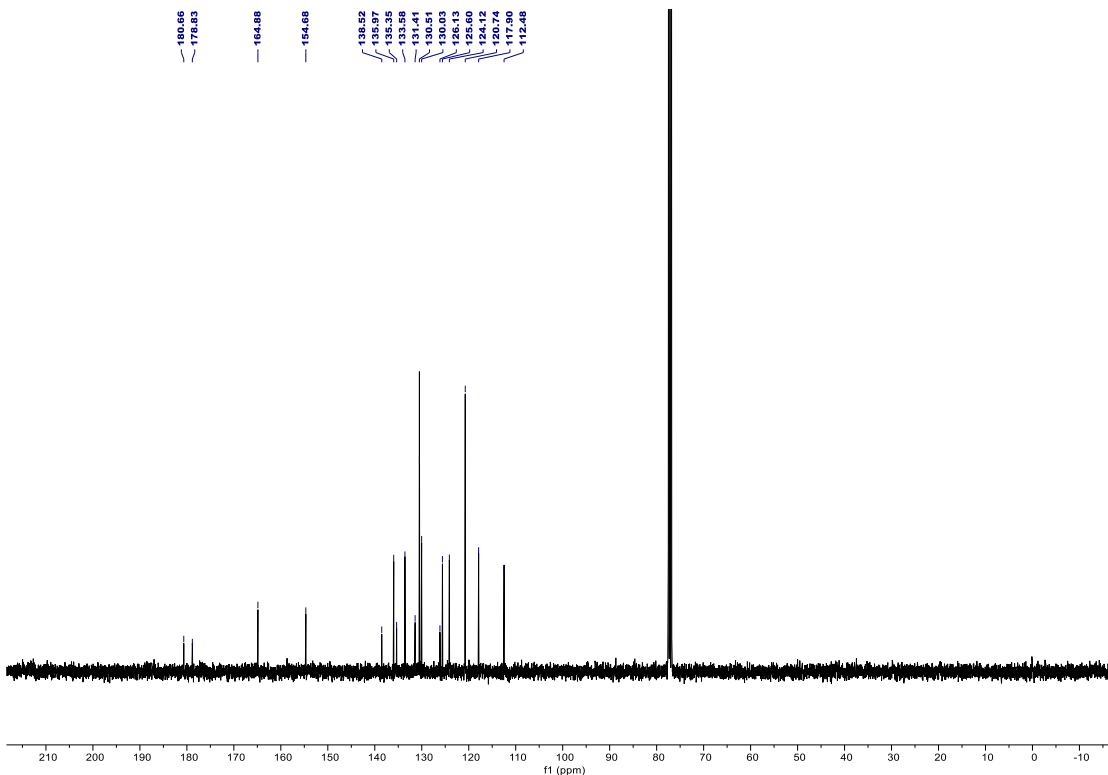
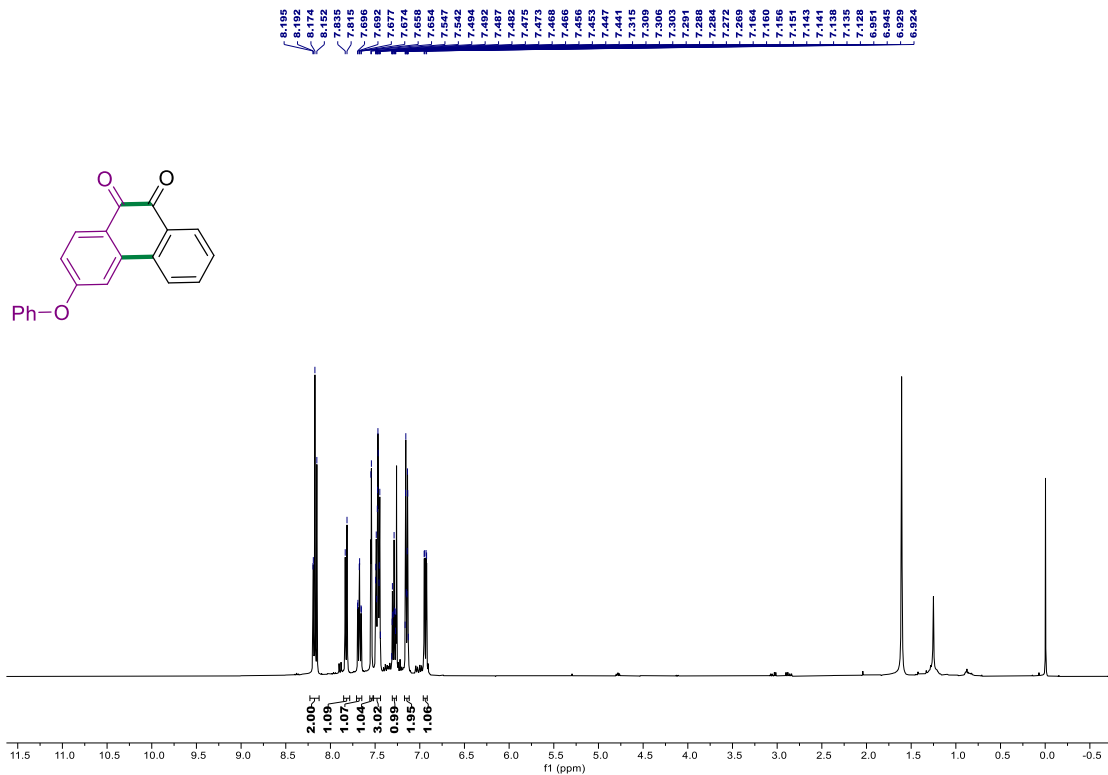
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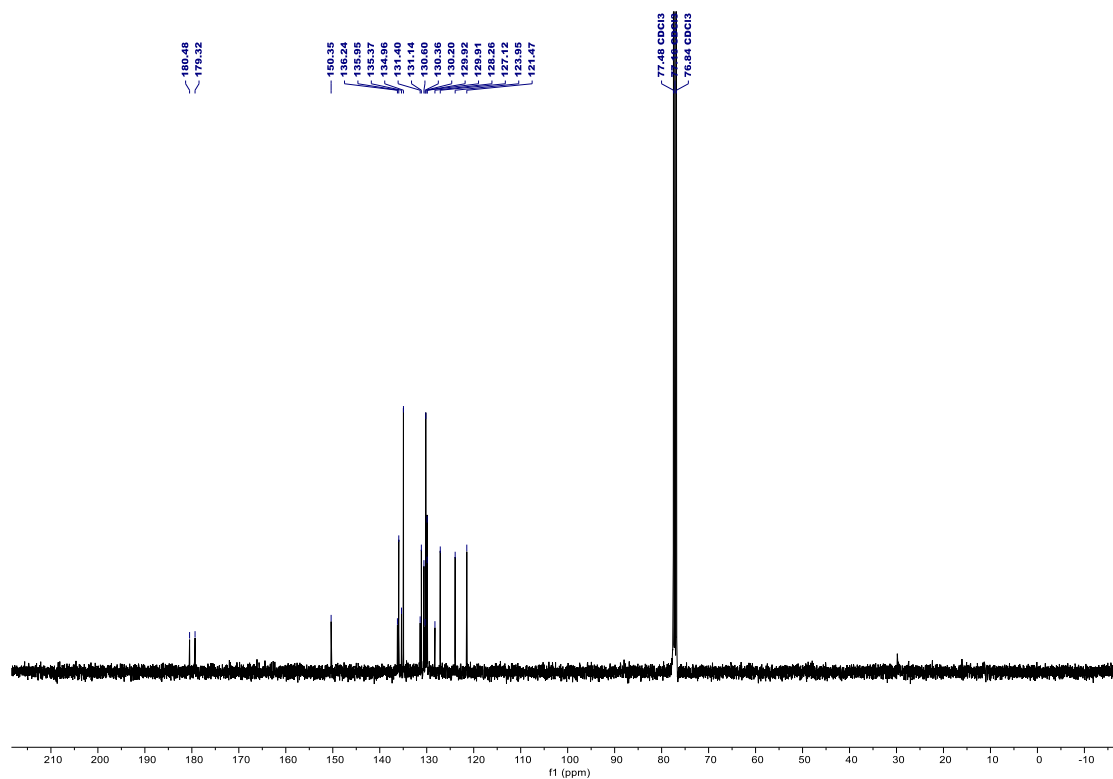
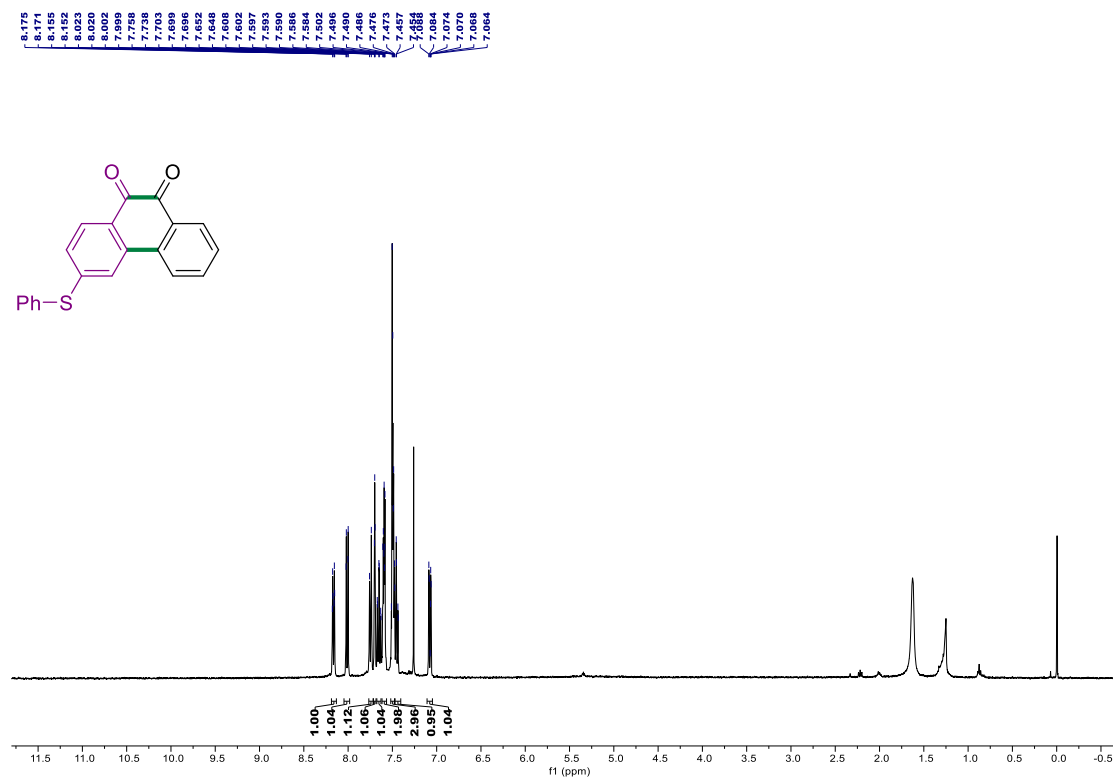
3-Isopropoxyphenanthrene-9,10-dione (3k)



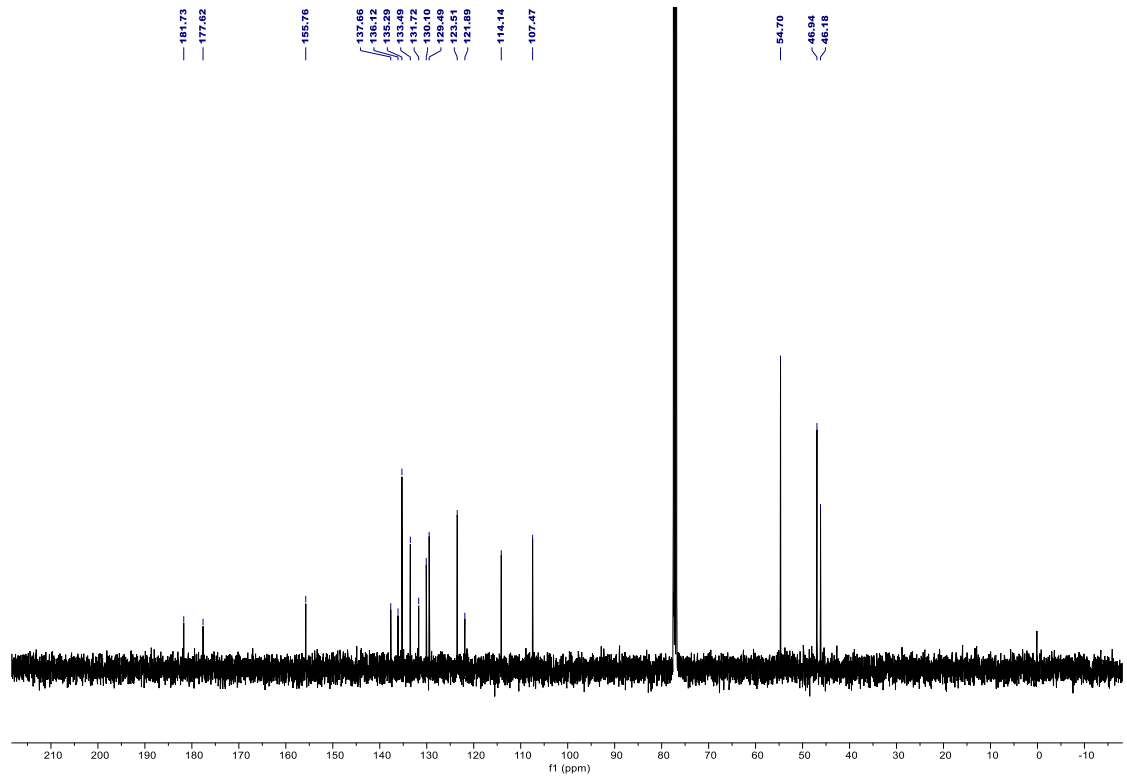
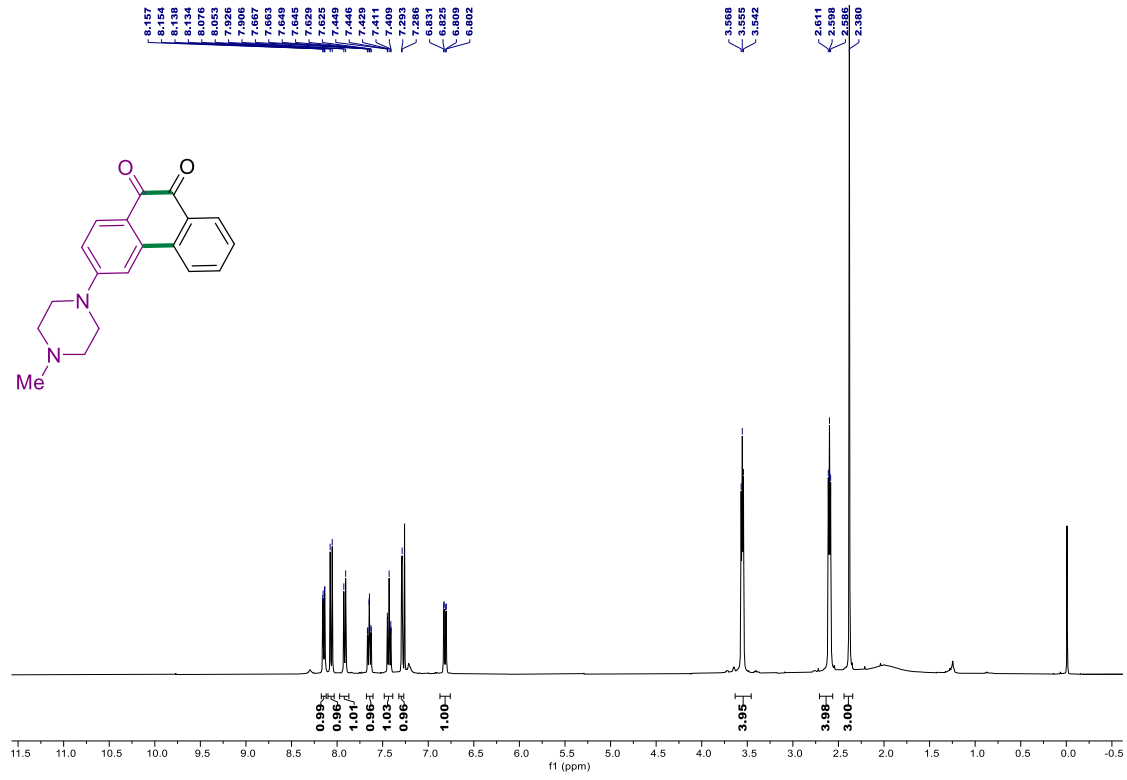
3-Phenoxyphenanthrene-9,10-dione (31)



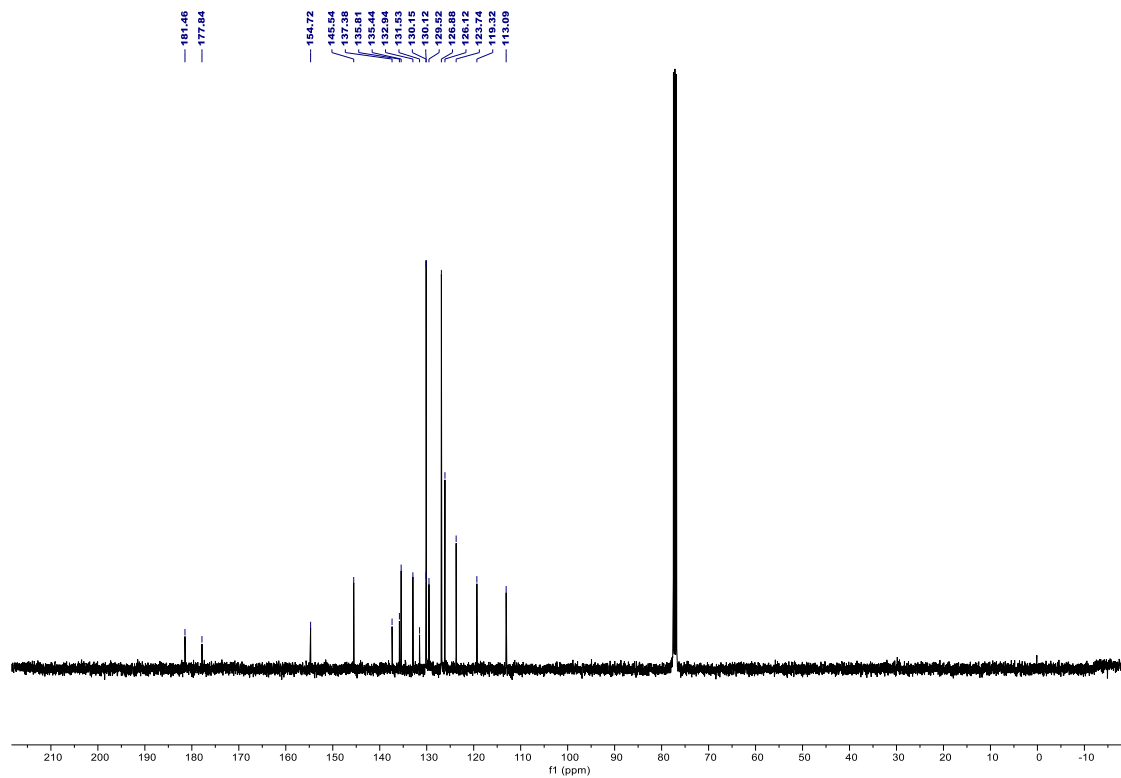
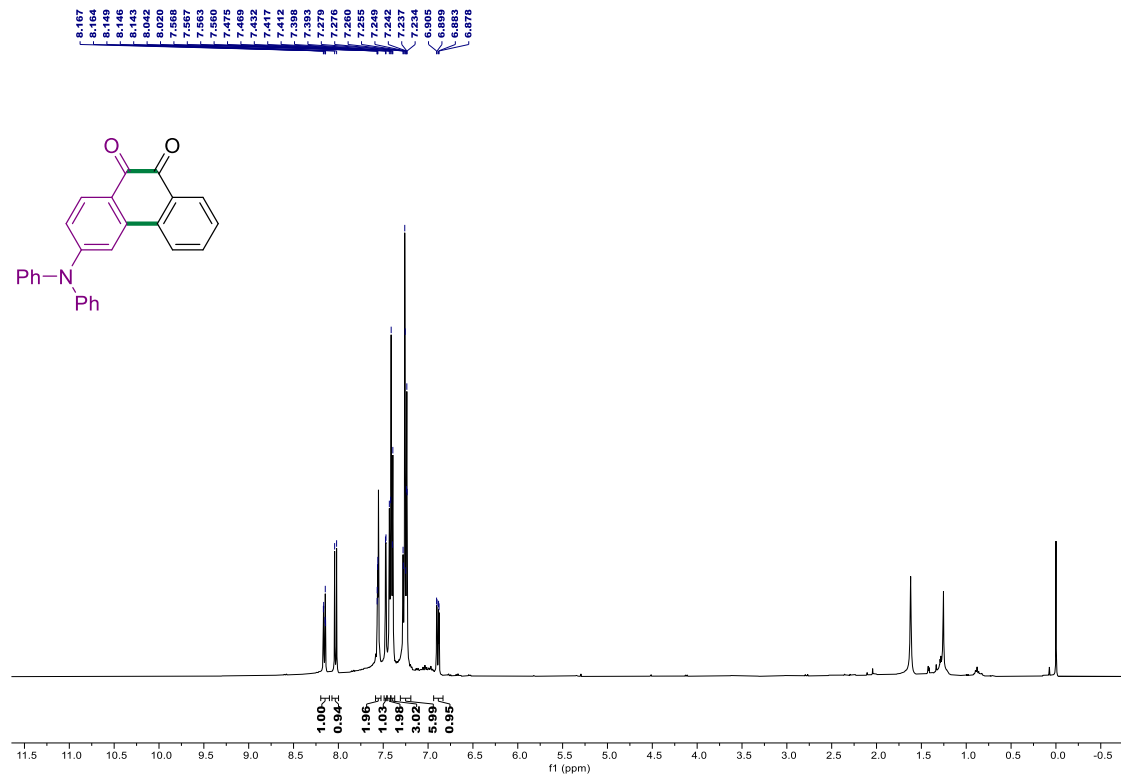
3-(Phenylthio)phenanthrene-9,10-dione (3m)



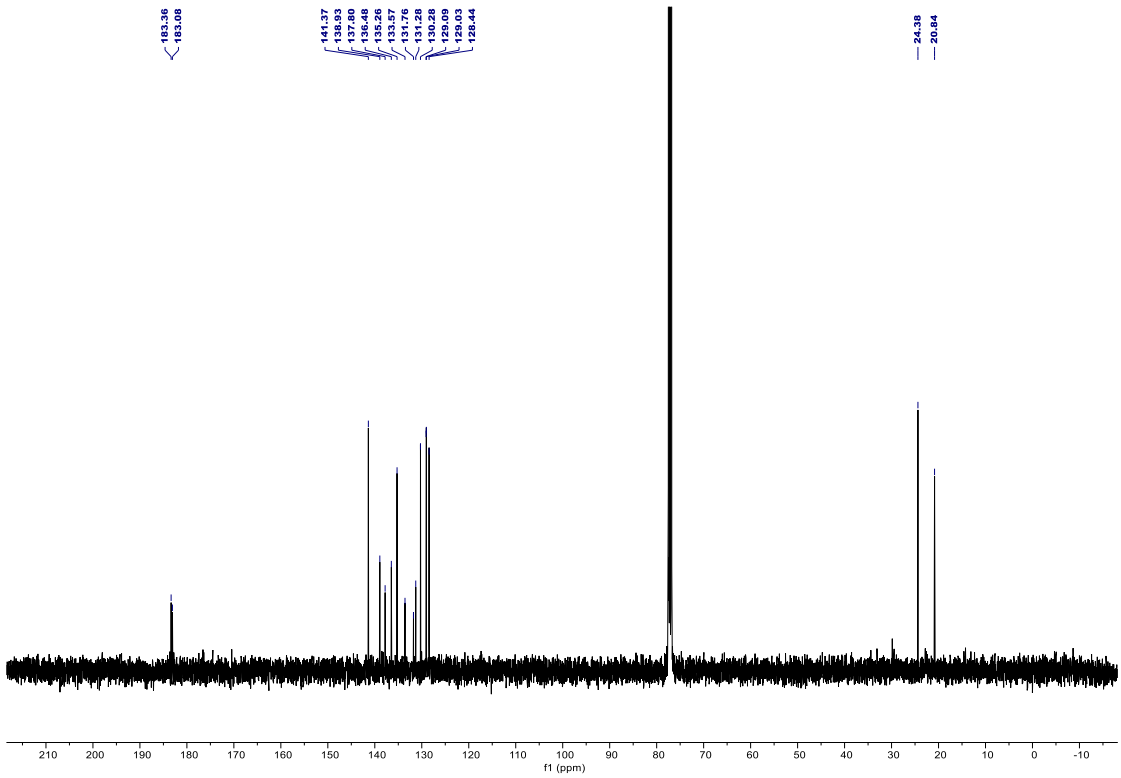
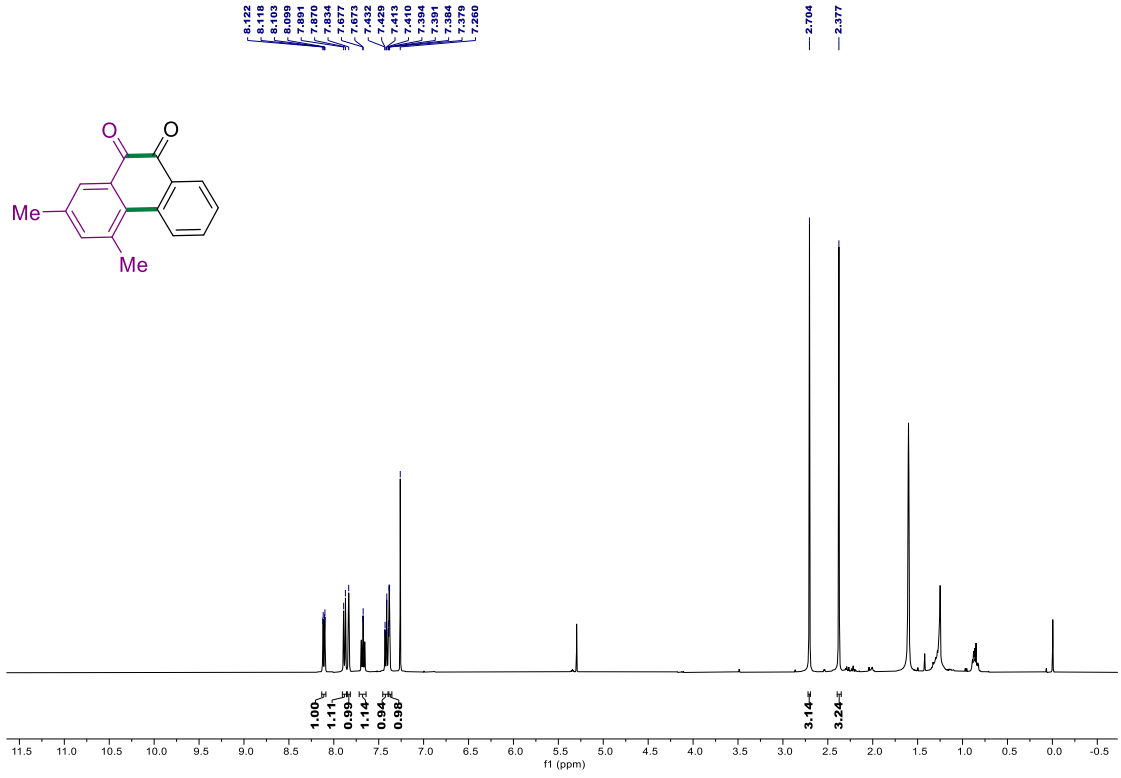
3-(4-Methylpiperazin-1-yl)phenanthrene-9,10-dione (3n)



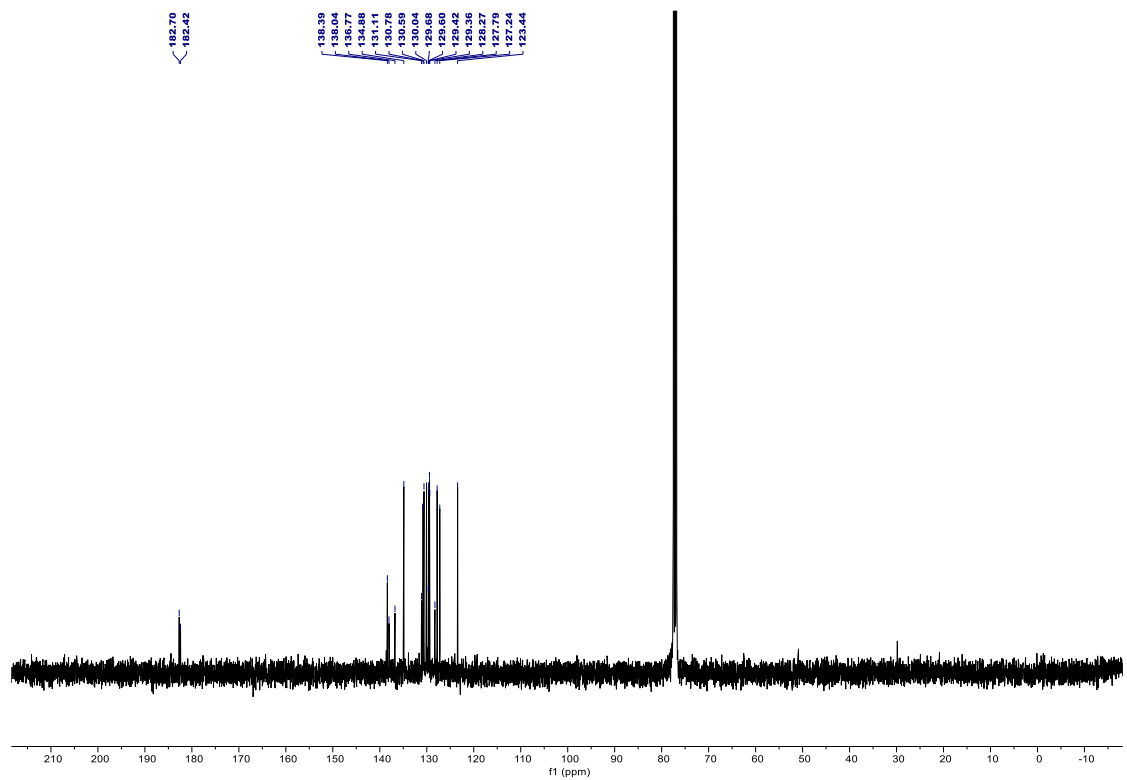
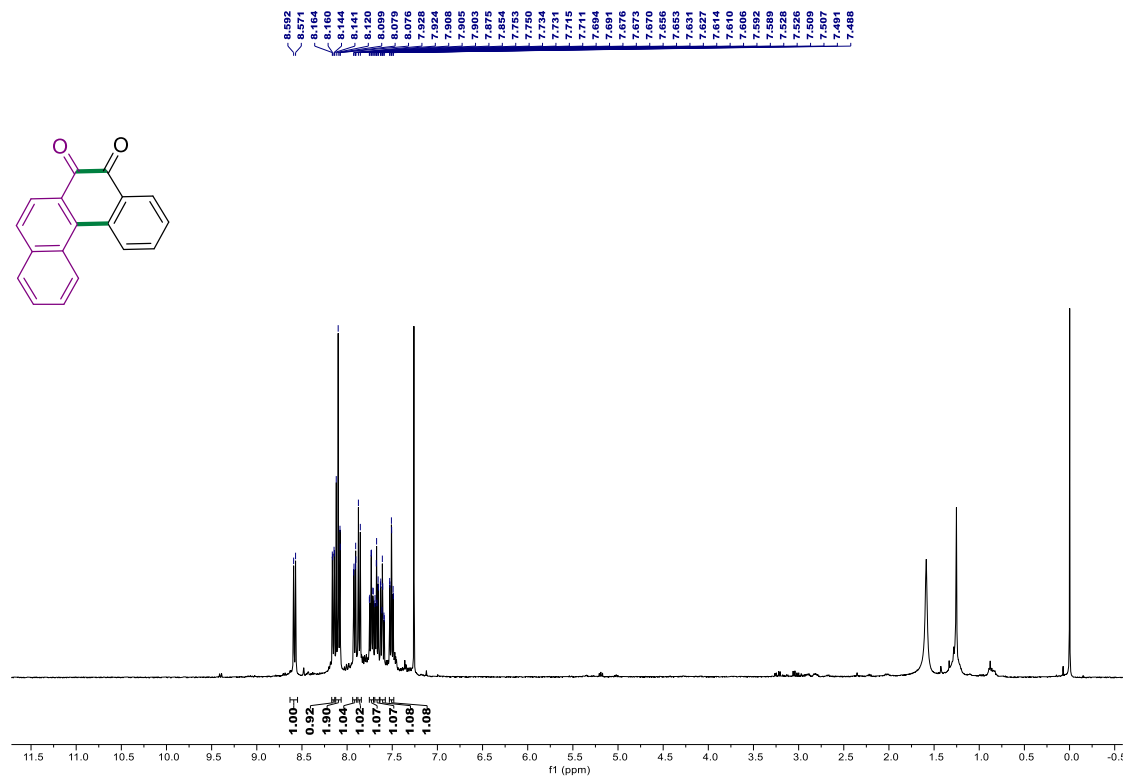
3-(Diphenylamino)phenanthrene-9,10-dione (3o)



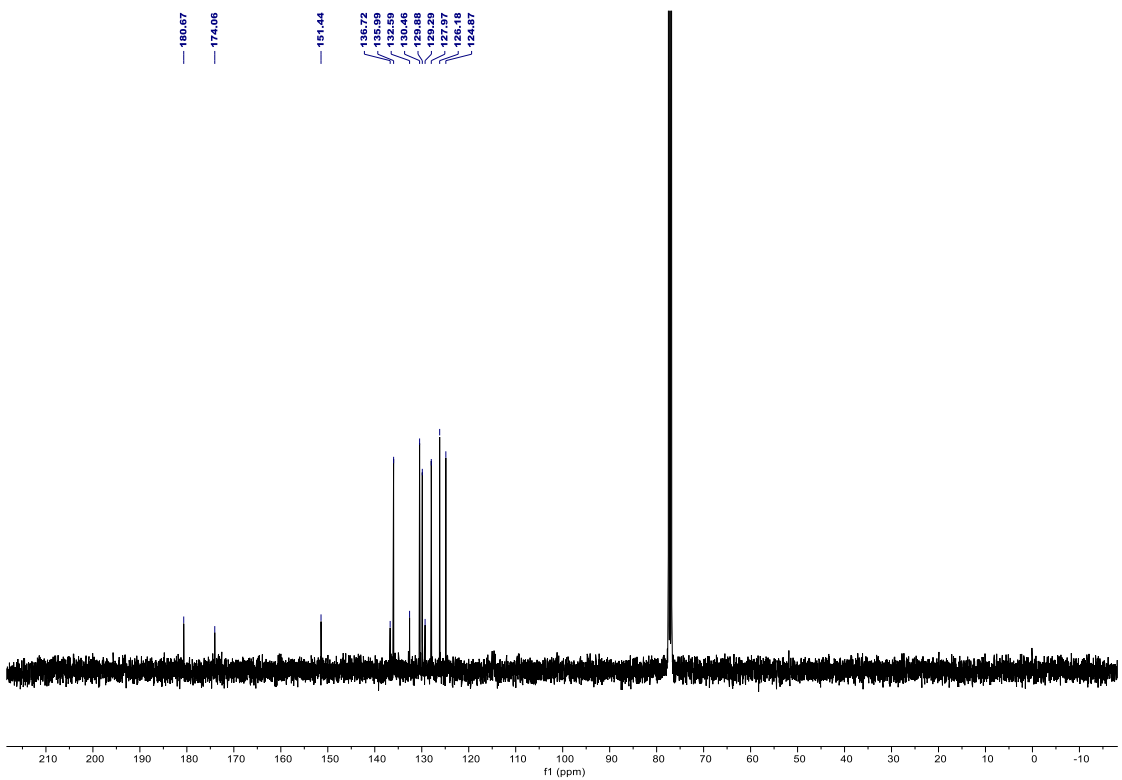
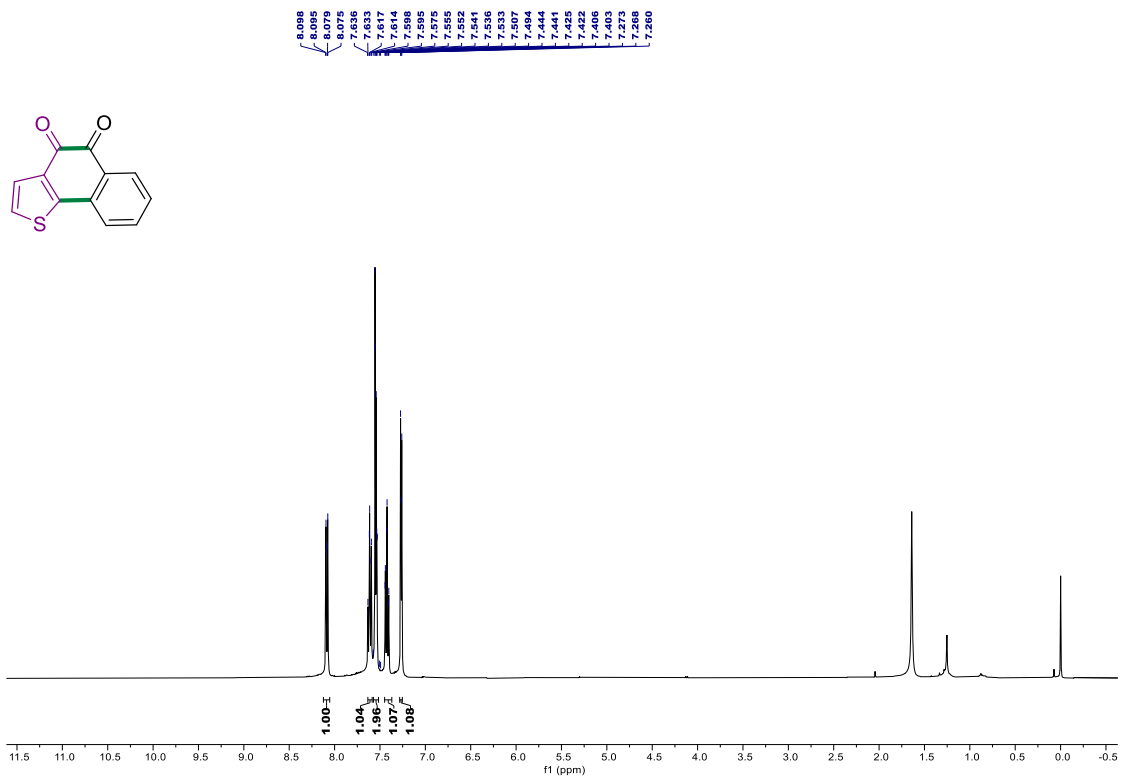
2,4-Dimethylphenanthrene-9,10-dione (3p)



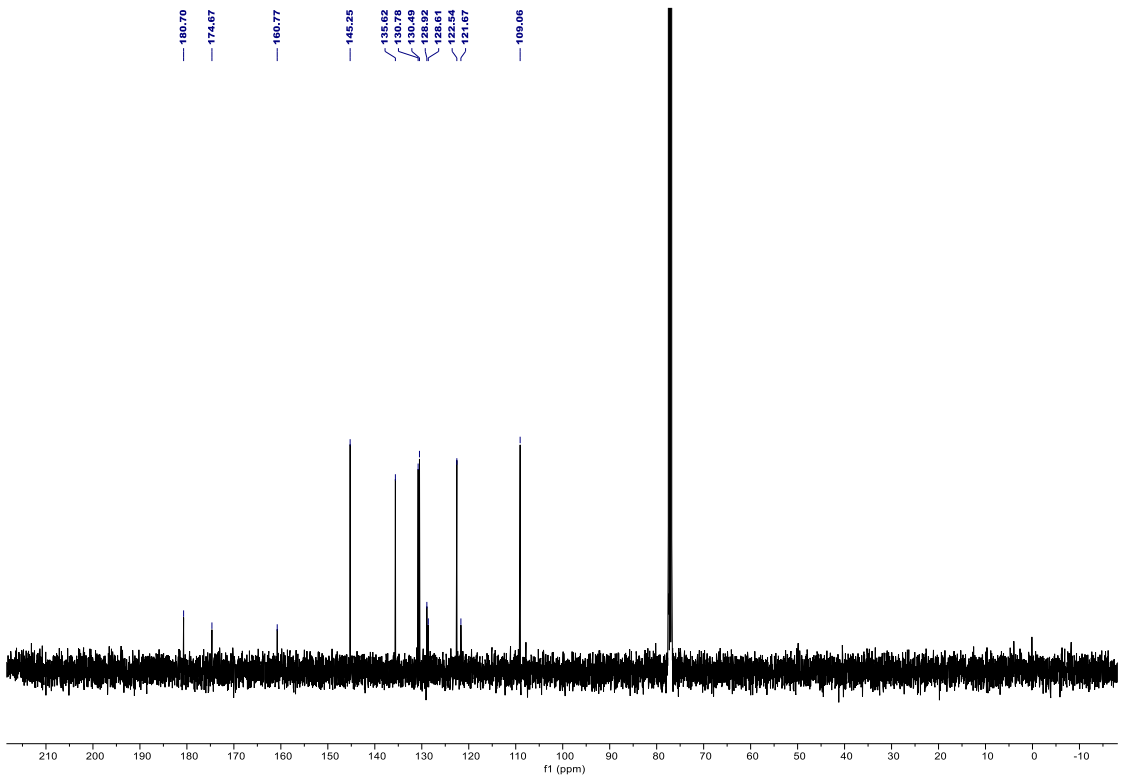
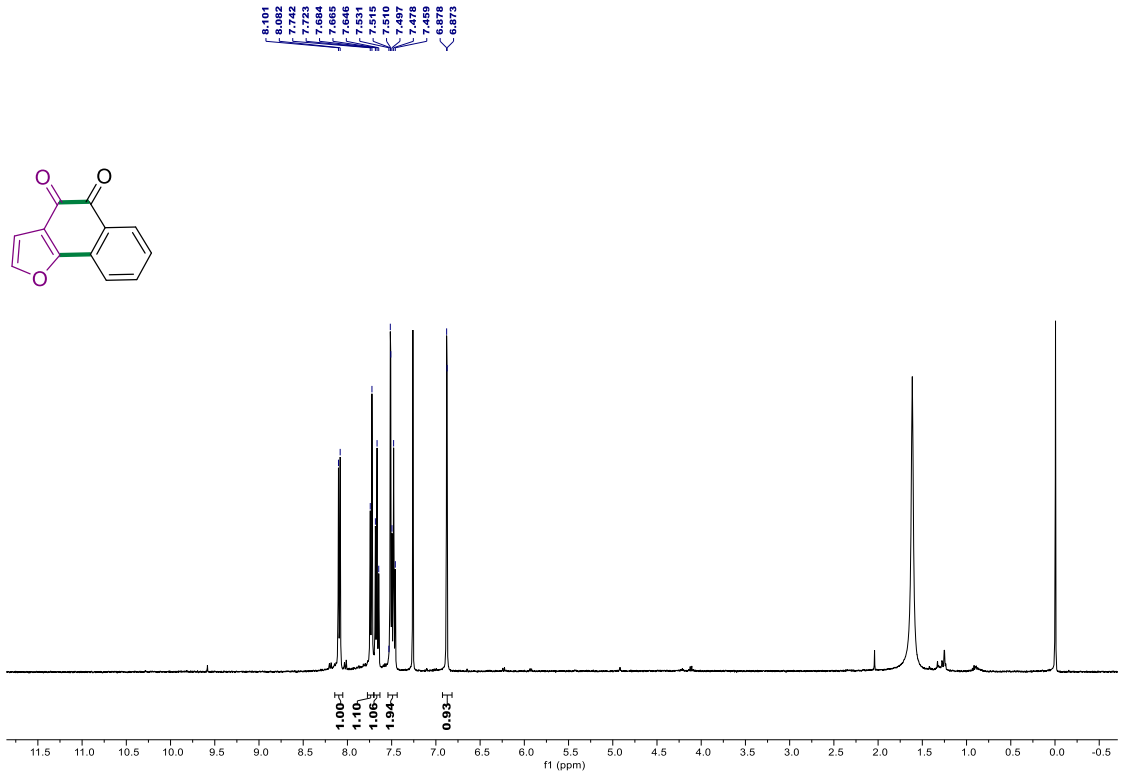
Benzo[c]phenanthrene-5,6-dione (3q)



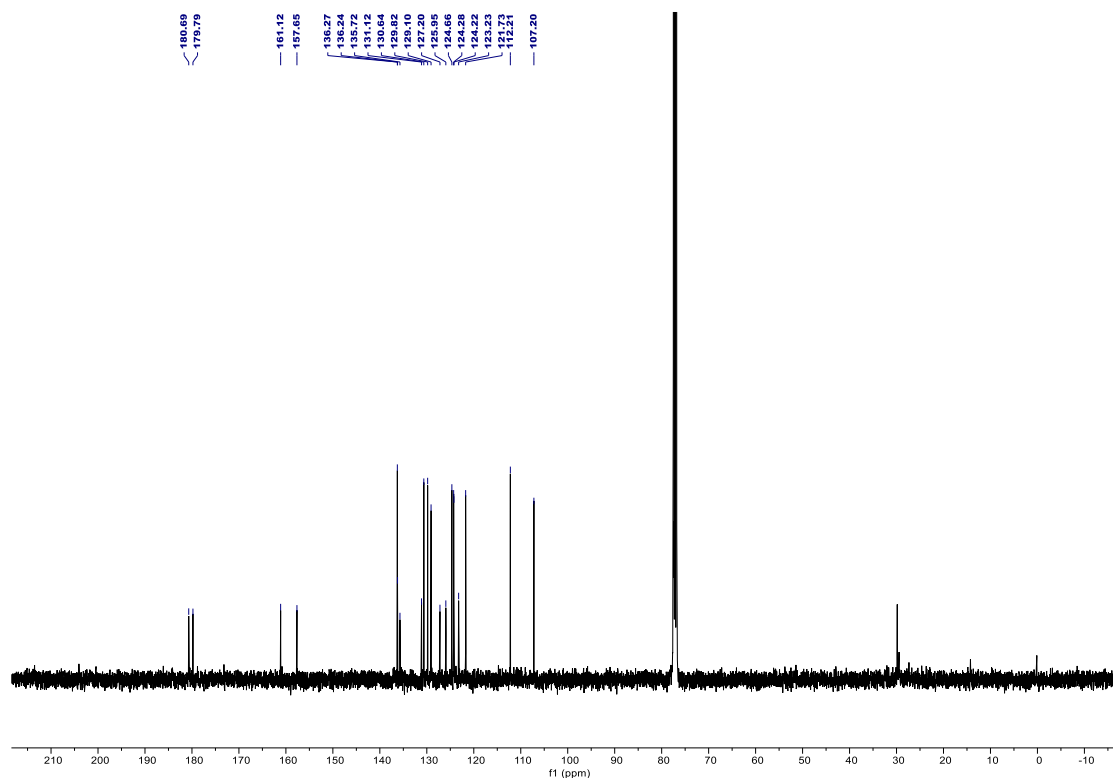
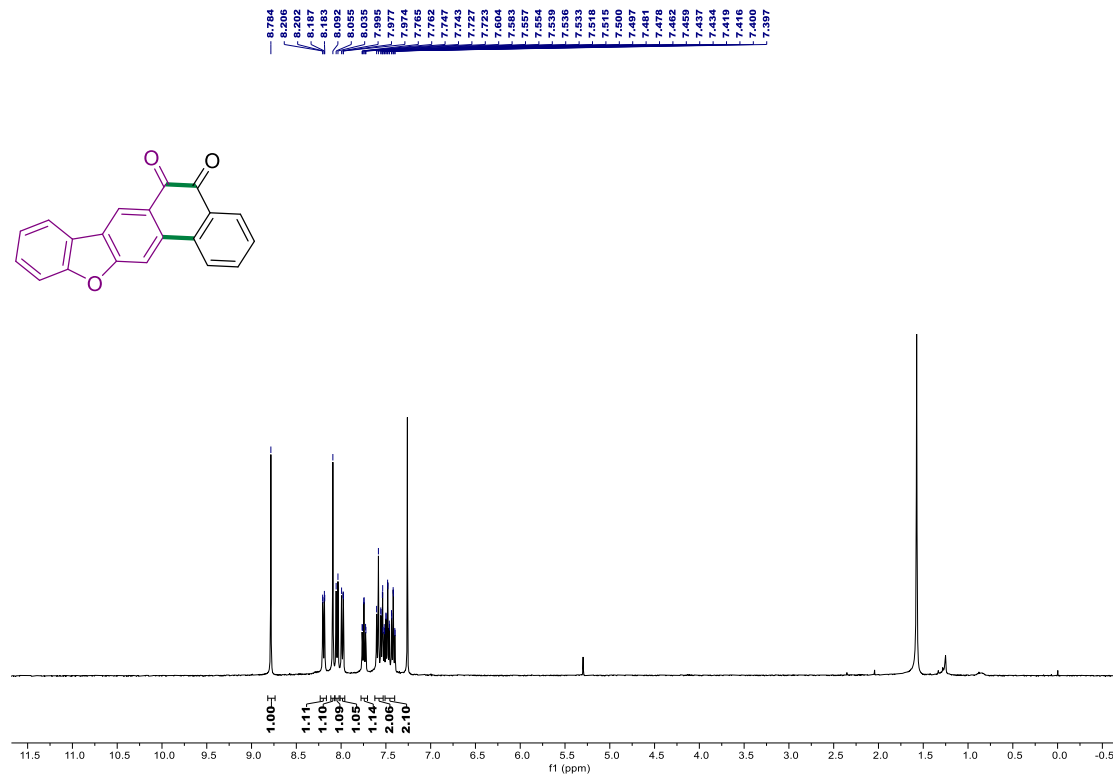
Naphtho[1,2-*b*]thiophene-4,5-dione (3r)



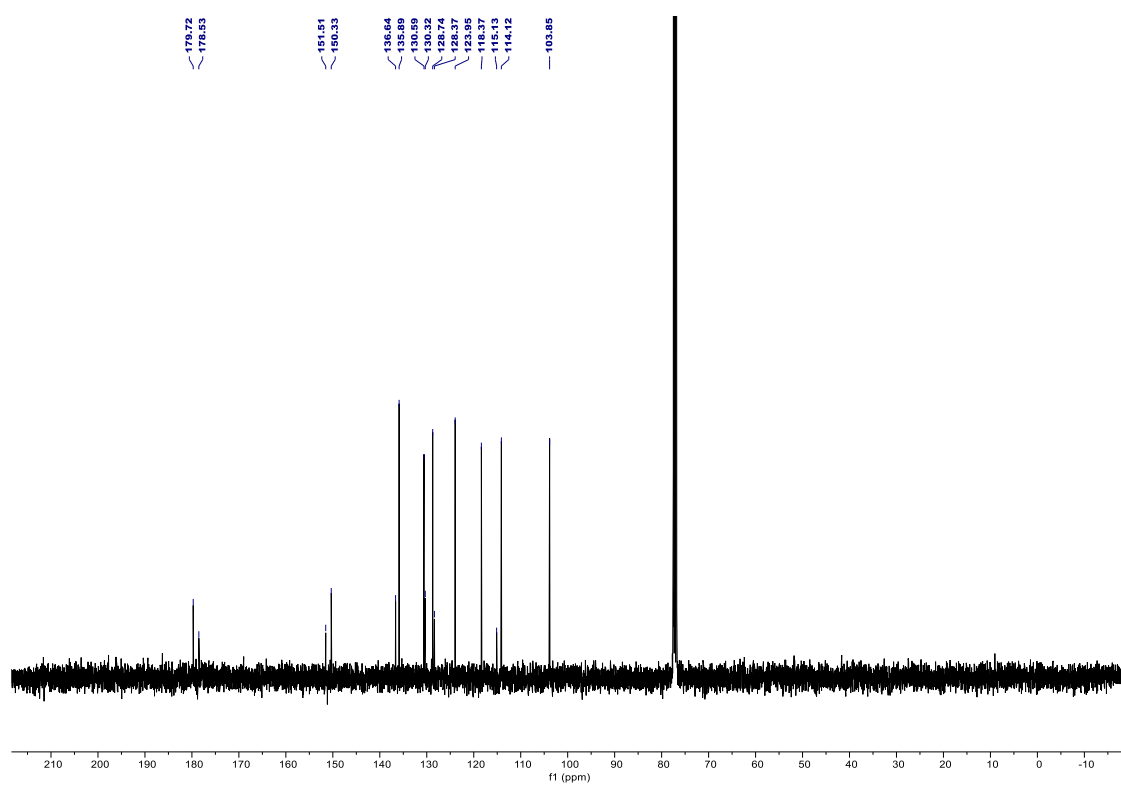
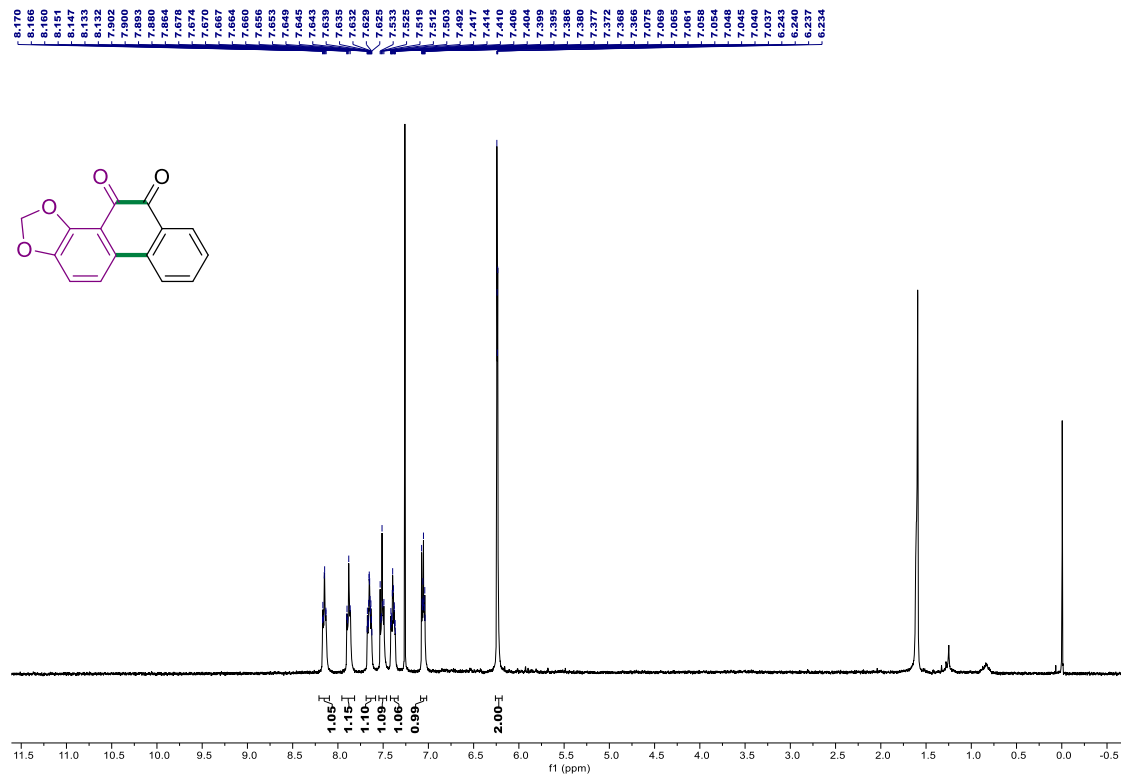
Naphtho[1,2-*b*]furan-4,5-dione (3s)



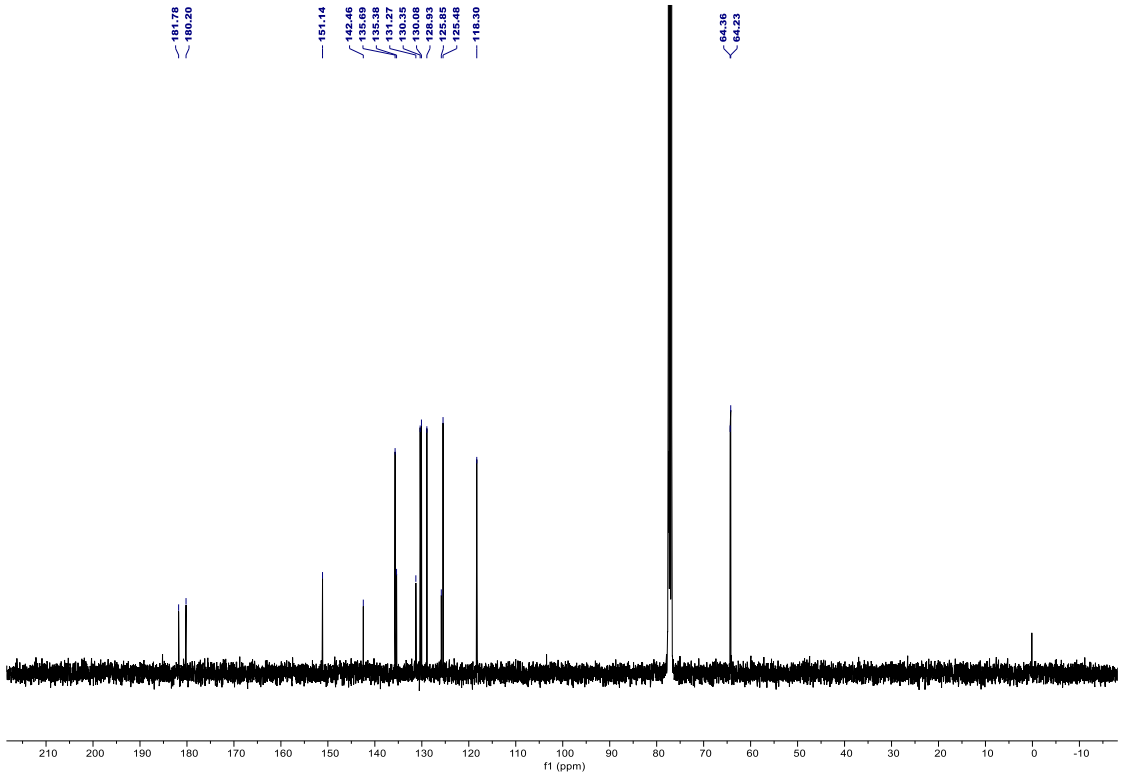
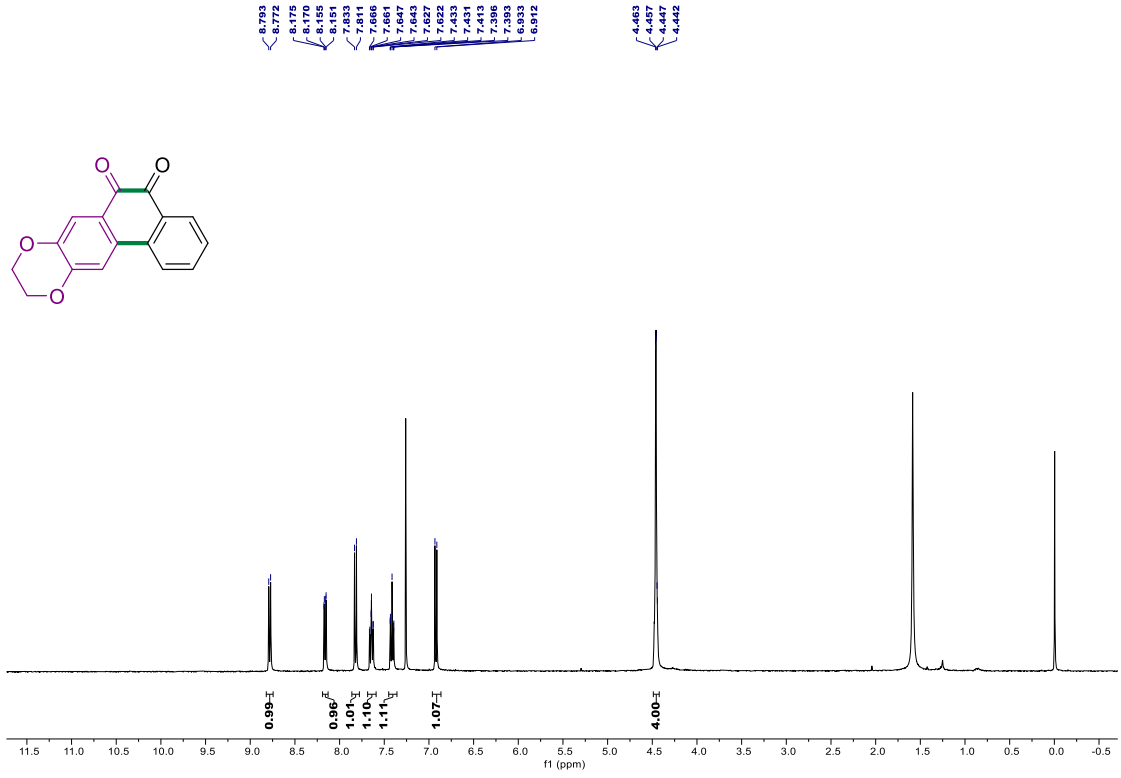
Phenanthro[3,2-*b*]benzofuran-5,6-dione (3t)



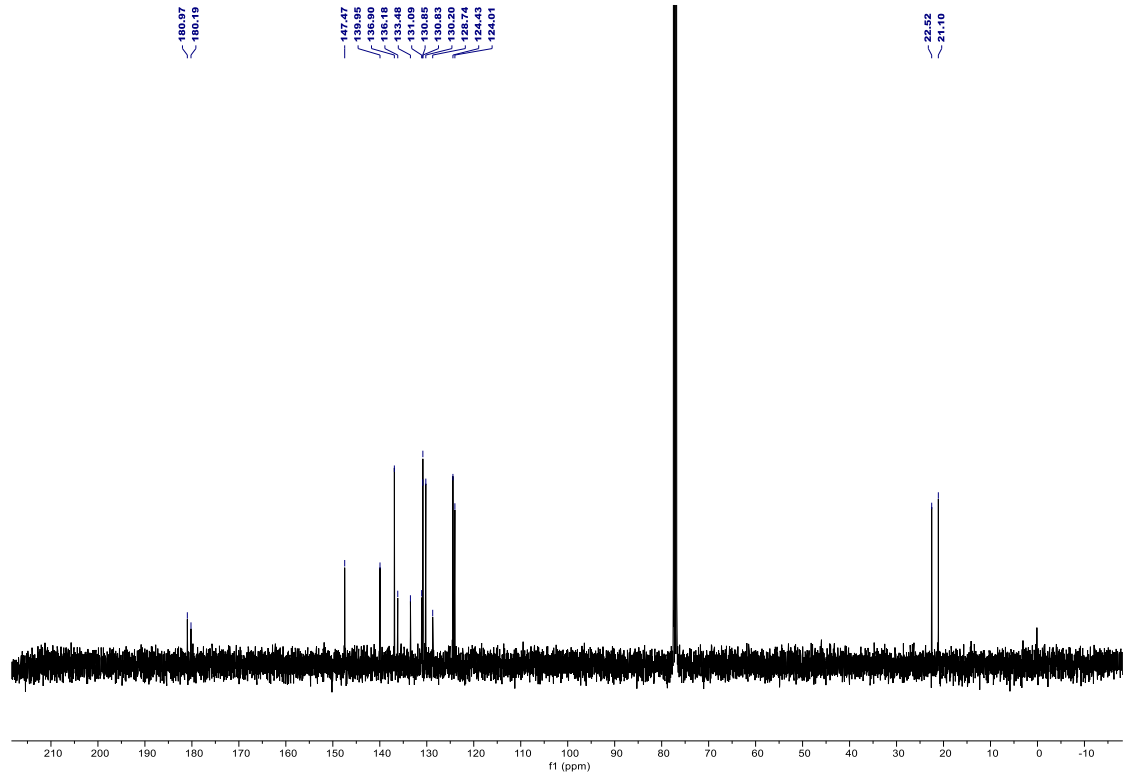
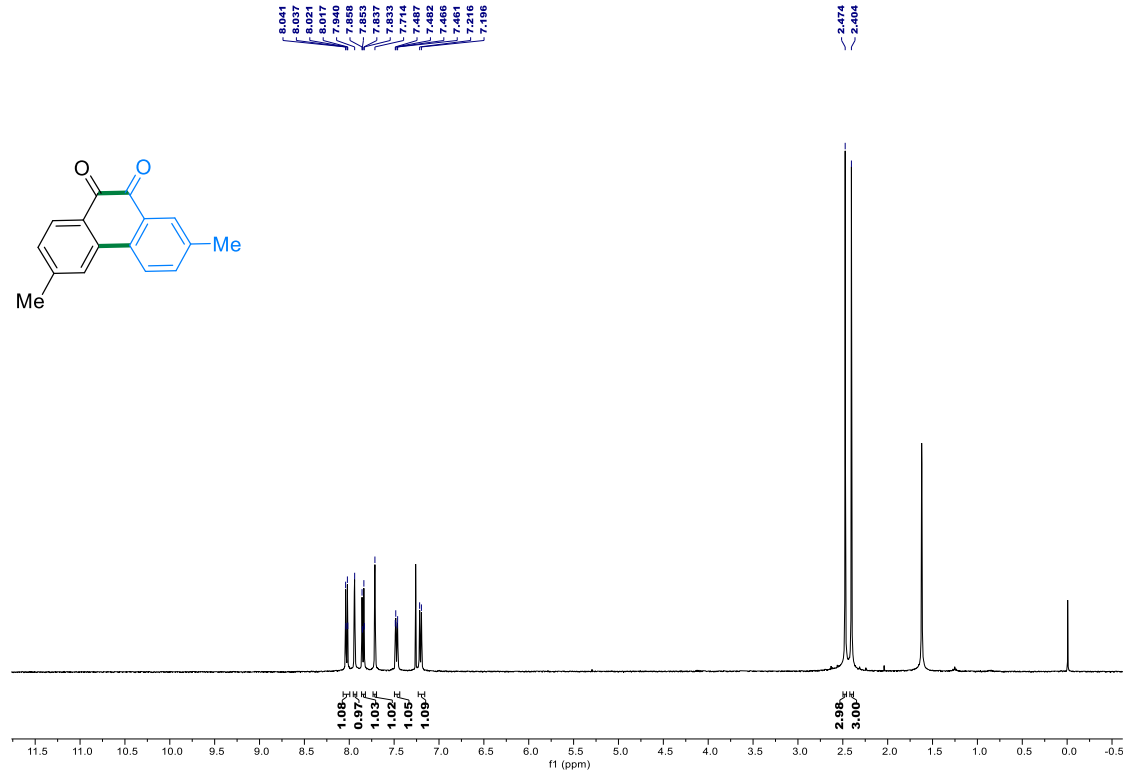
Phenanthro[1,2-d][1,3]dioxole-4,5-dione (3u)



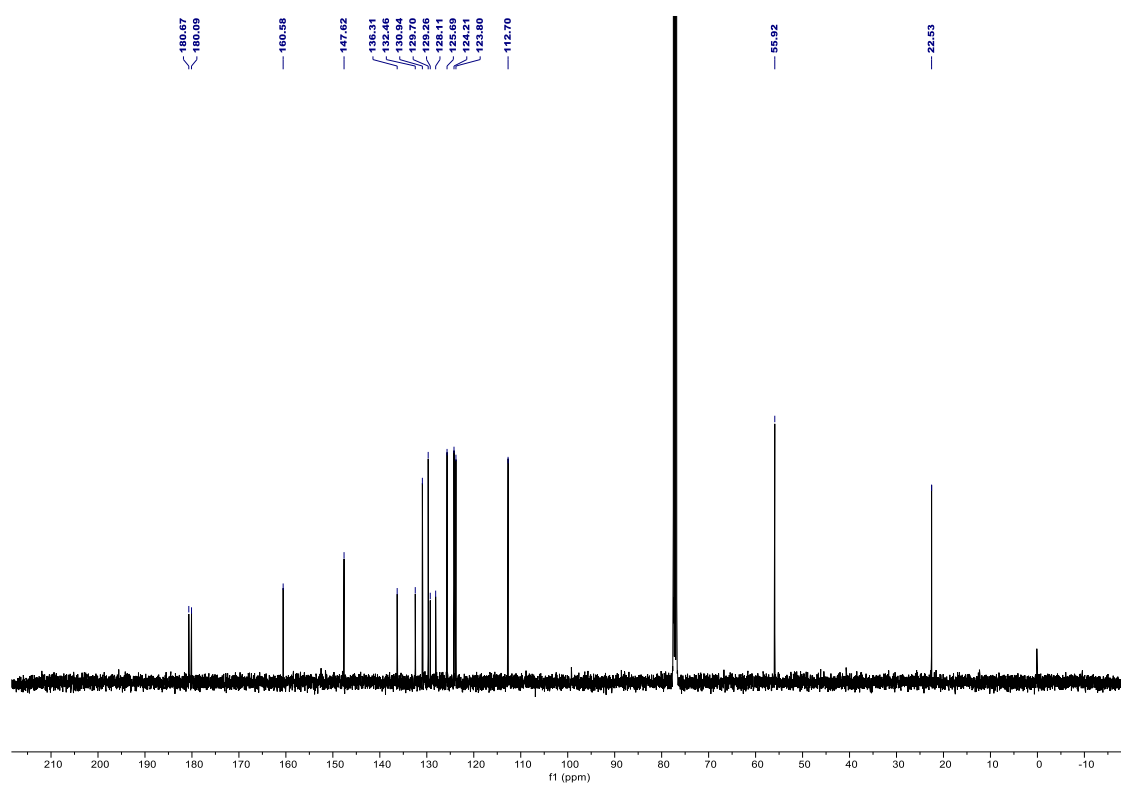
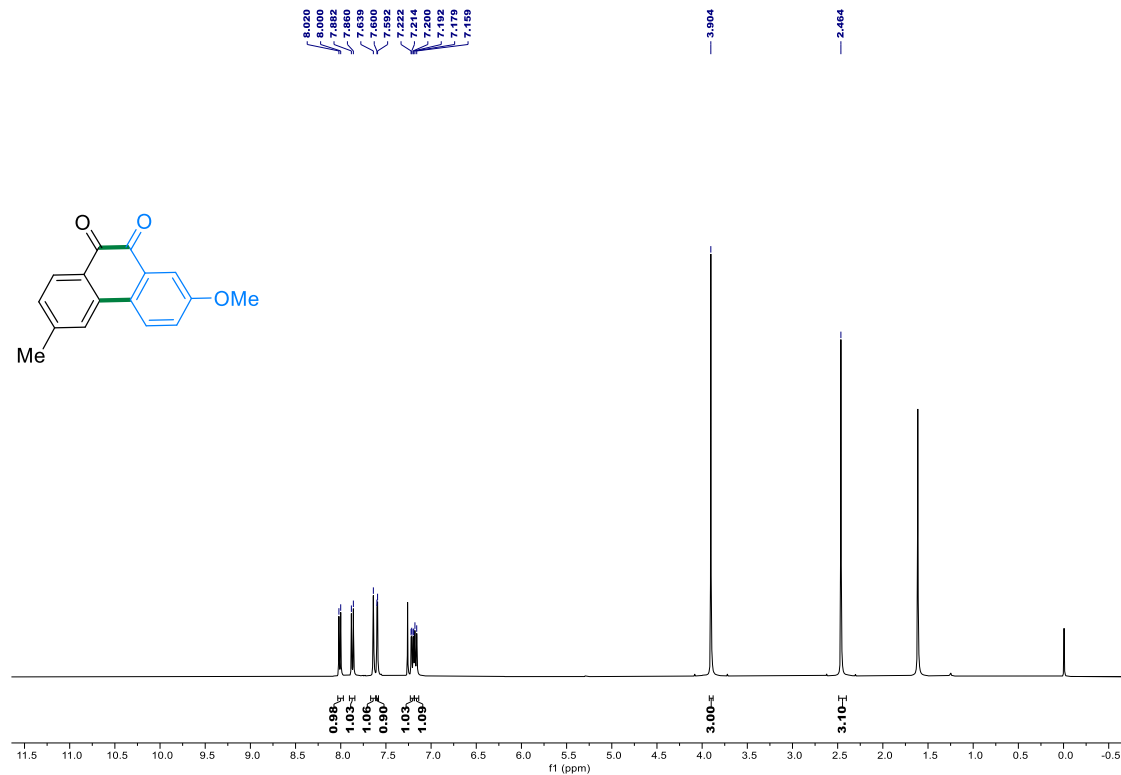
9,10-Dihydrophenanthro[2,3-*b*][1,4]dioxine-5,6-dione (3v)



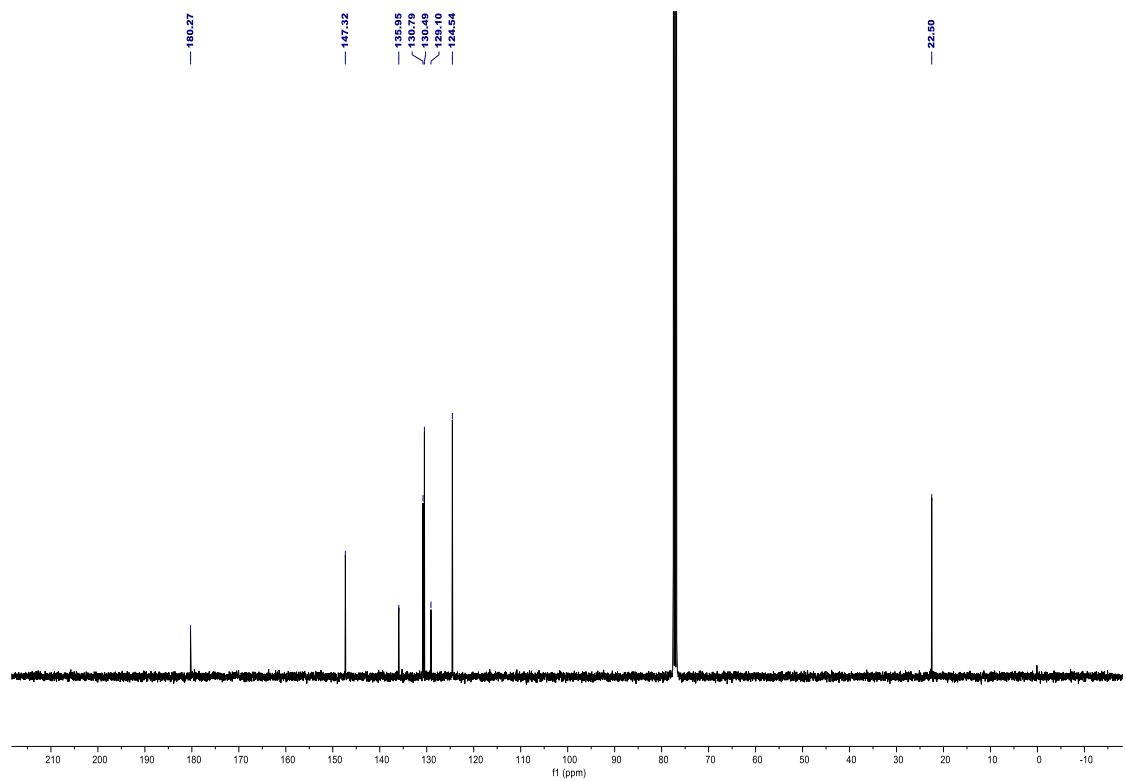
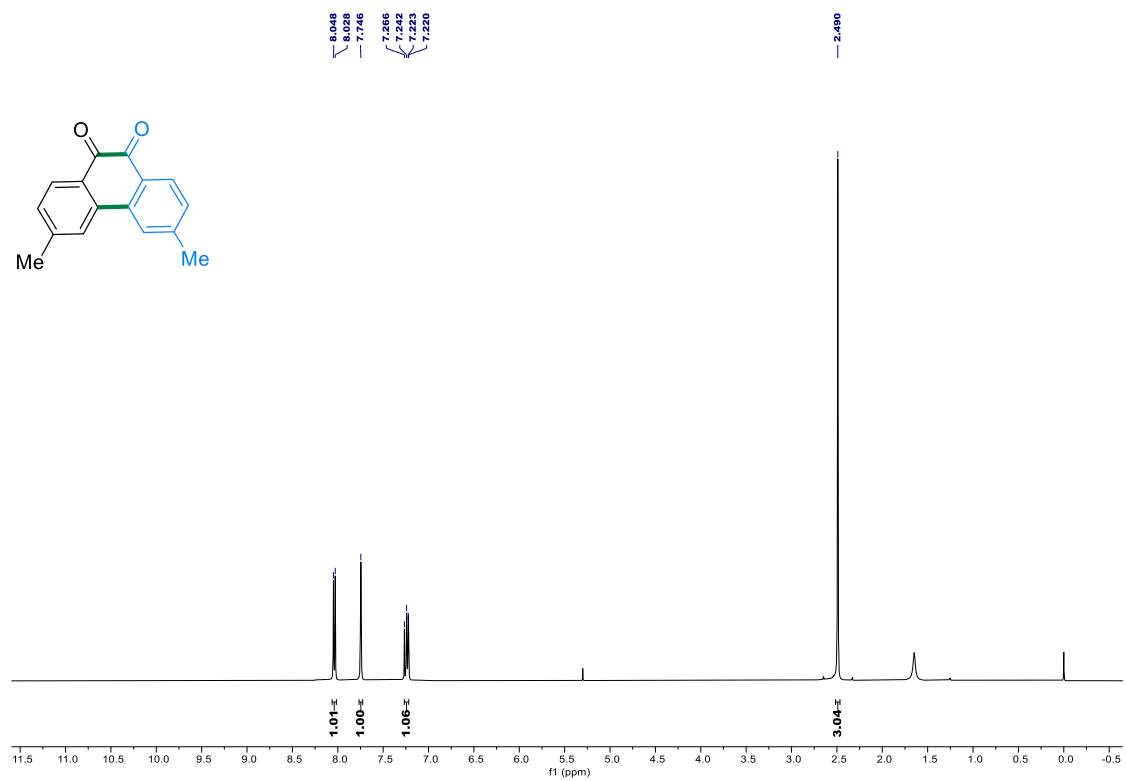
2,6-Dimethylphenanthrene-9,10-dione (4a)



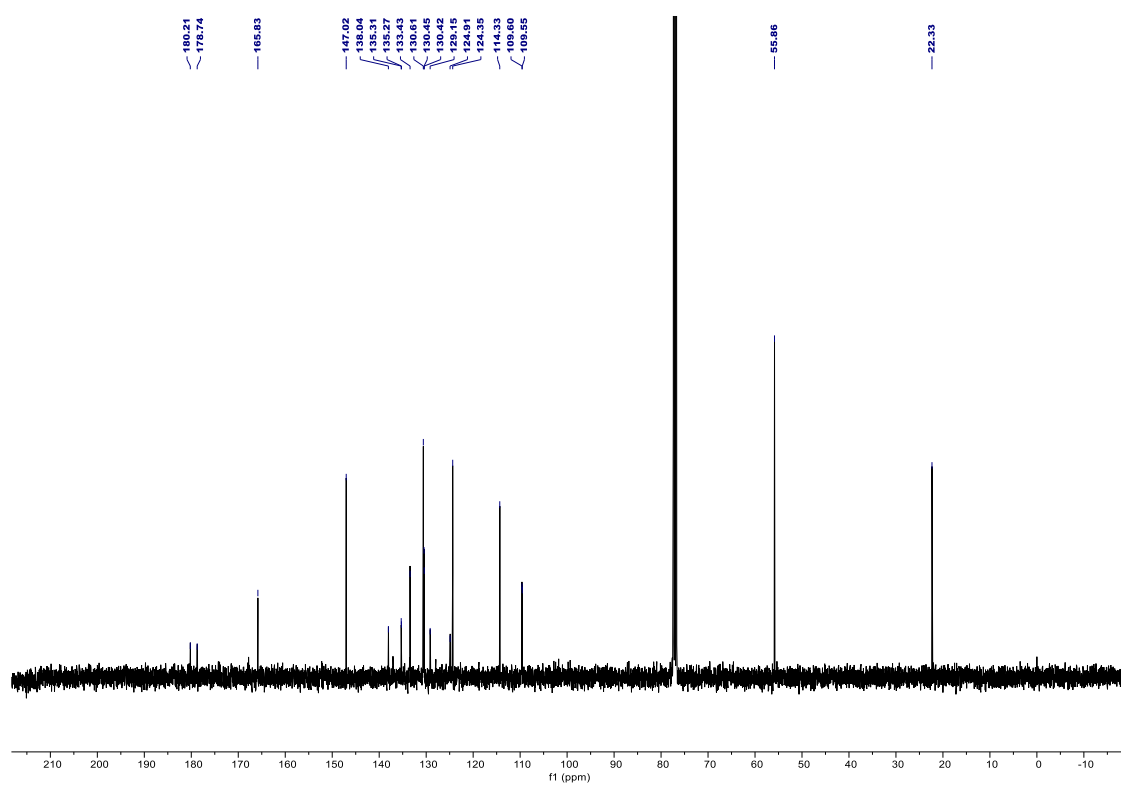
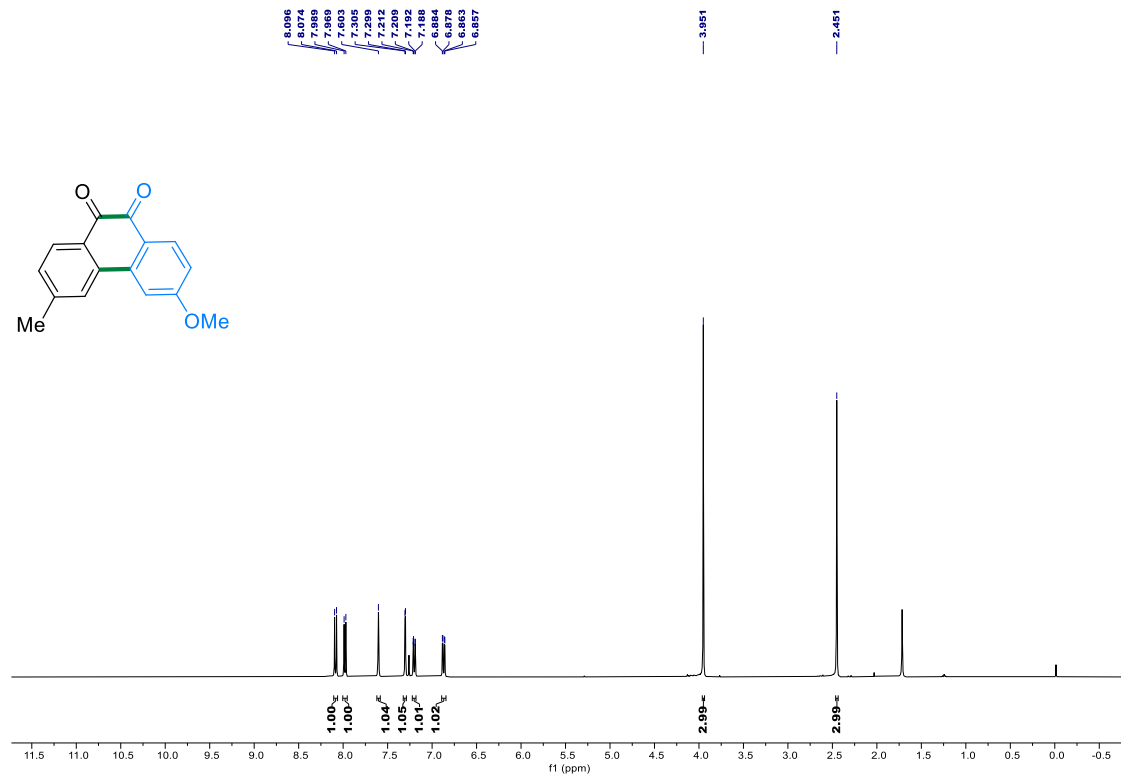
2-Methoxy-6-methylphenanthrene-9,10-dione (4b)



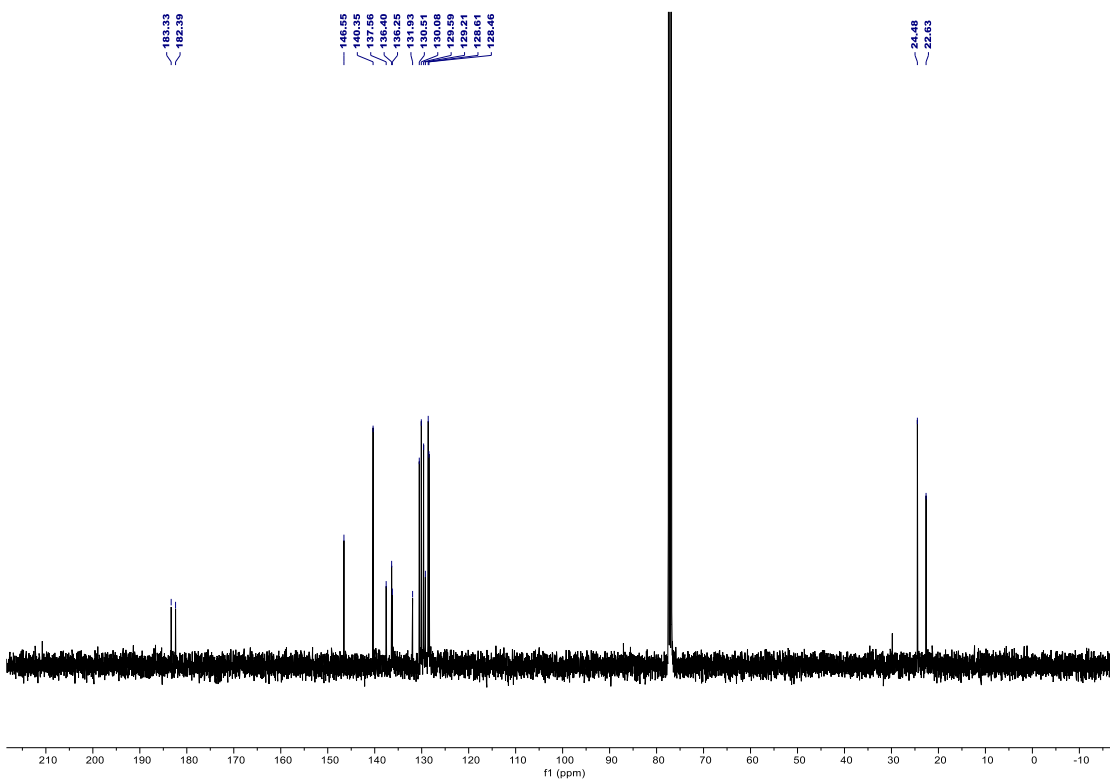
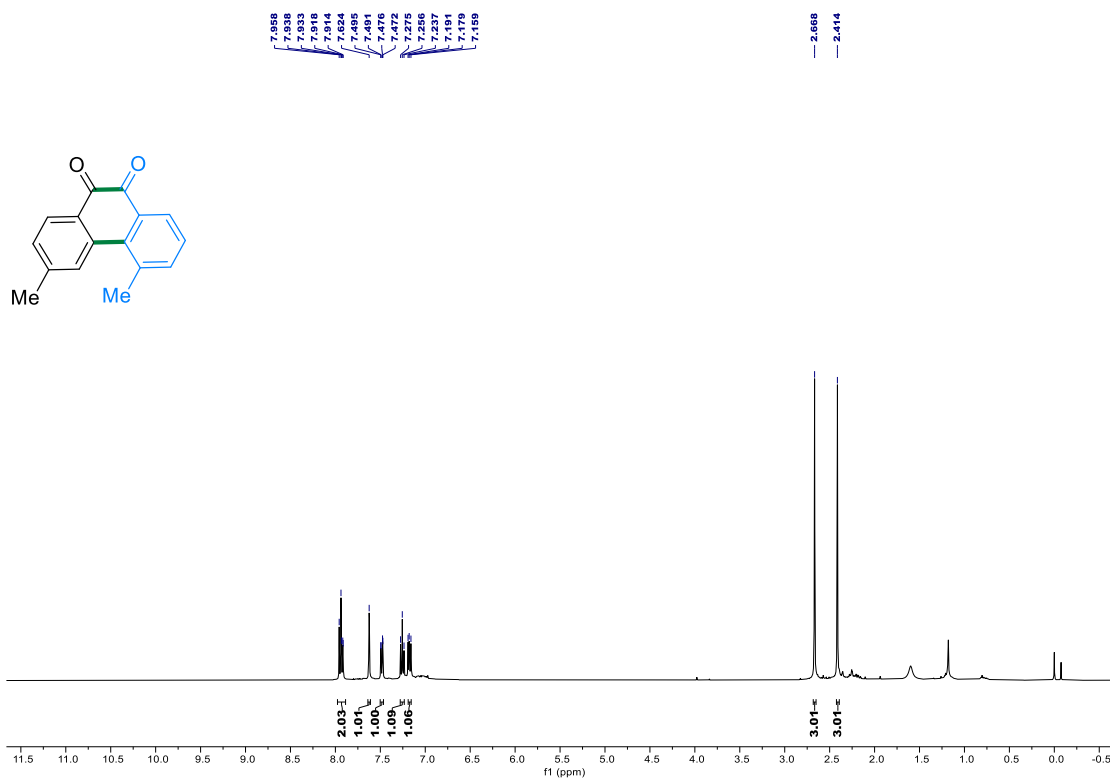
3,6-Dimethylphenanthrene-9,10-dione (4c)



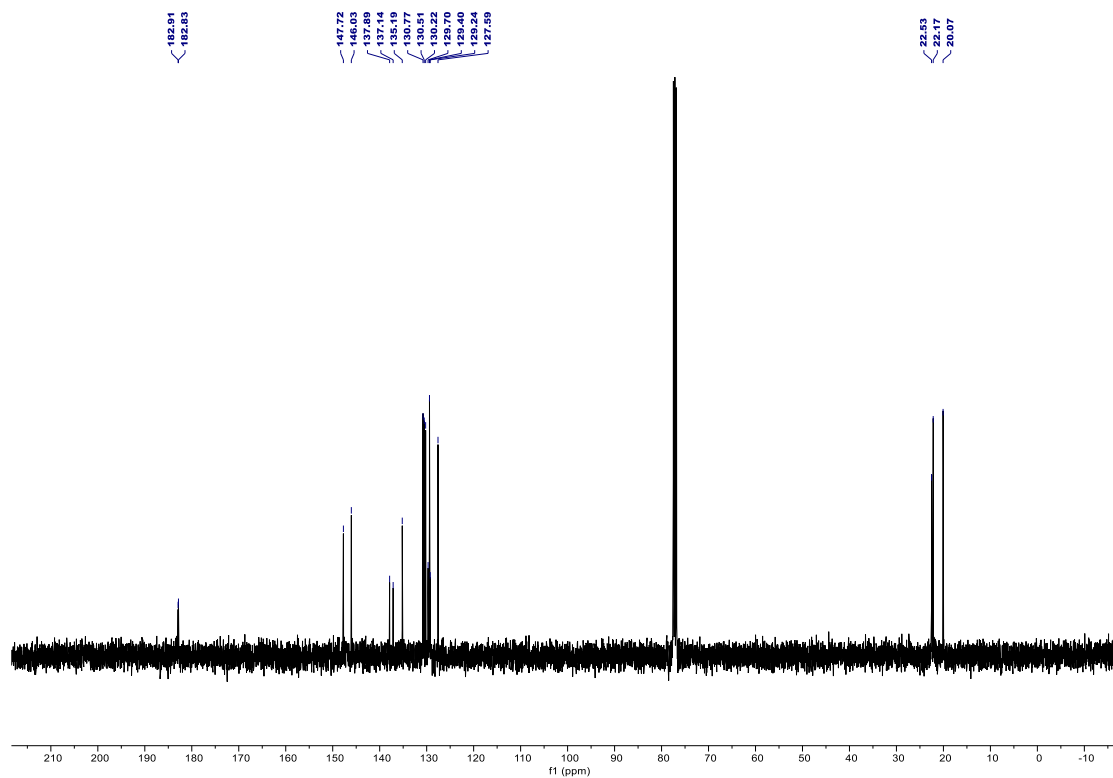
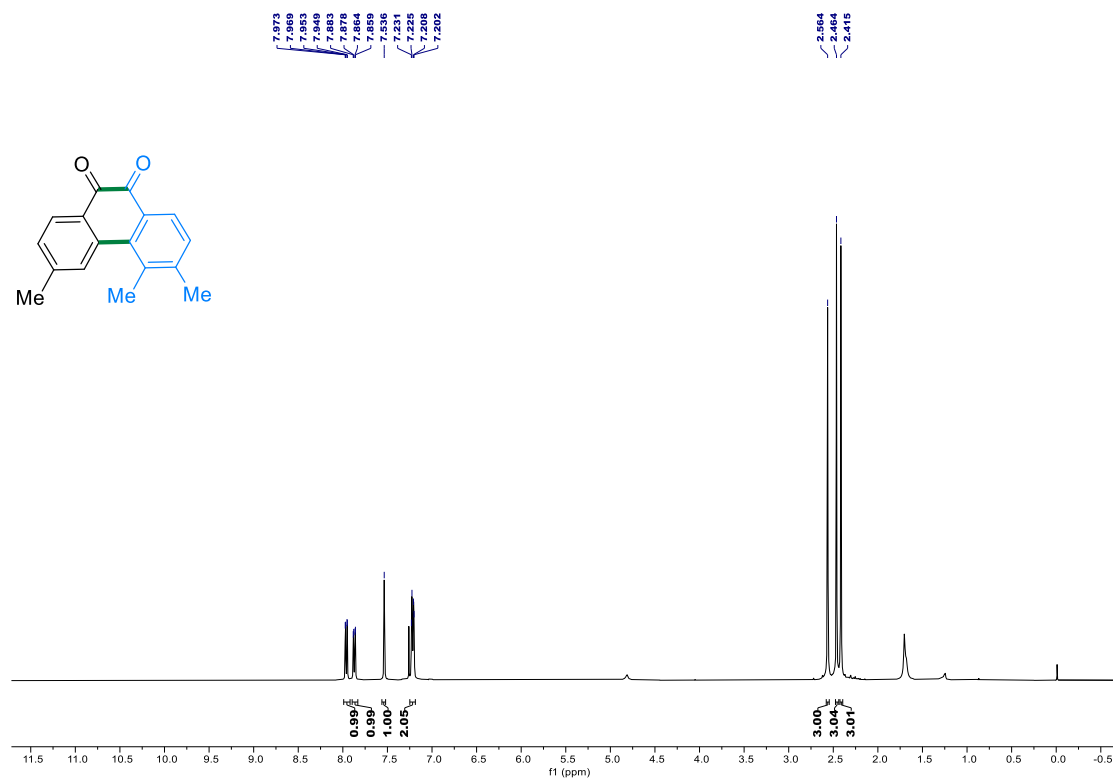
3-Methoxy-6-methylphenanthrene-9,10-dione (4d)



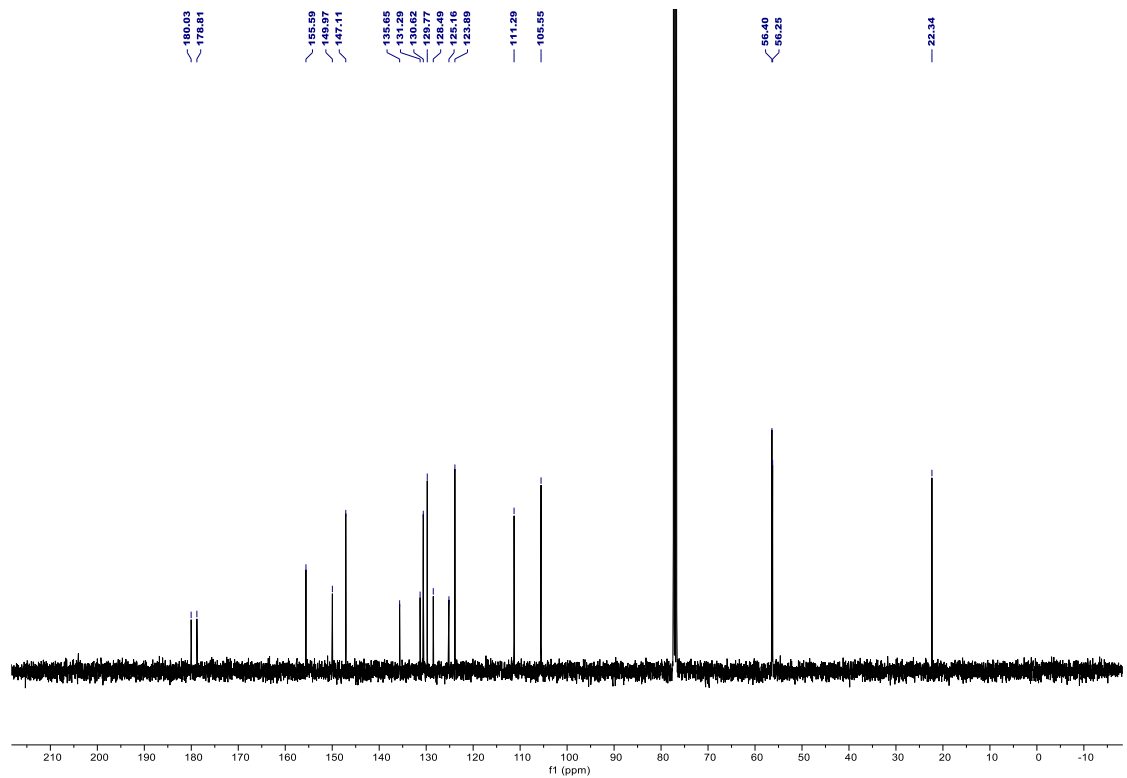
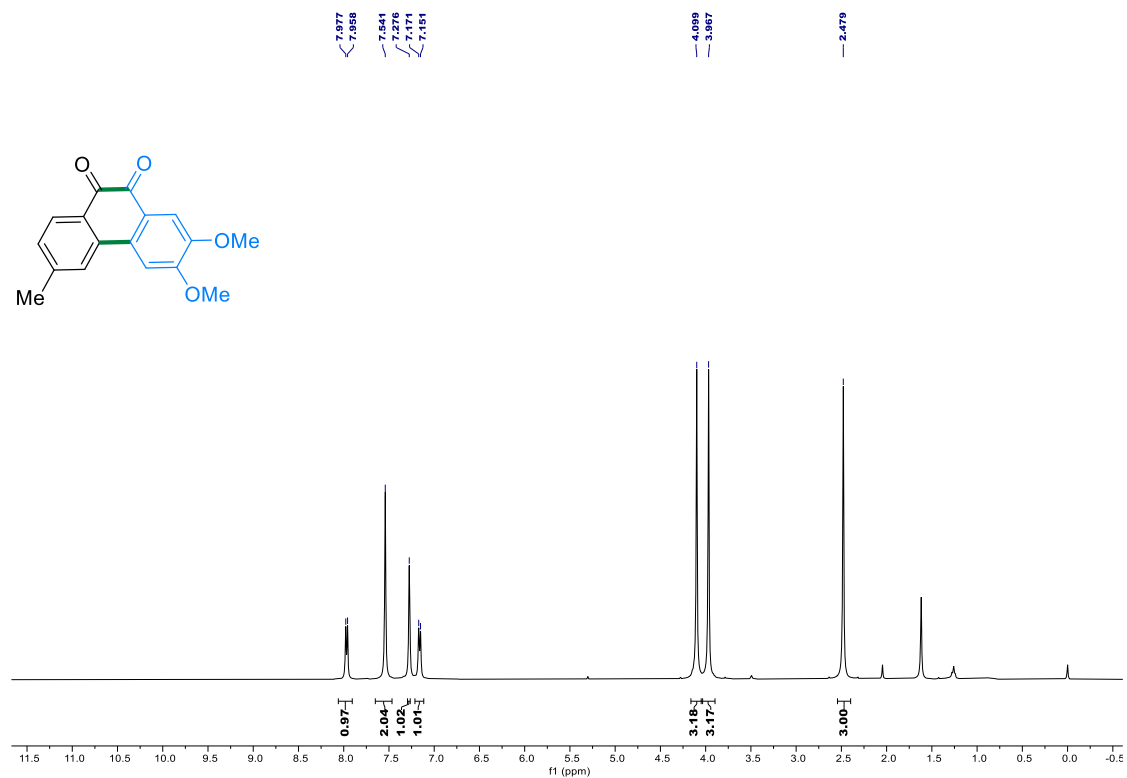
3,5-Dimethylphenanthrene-9,10-dione (4e)



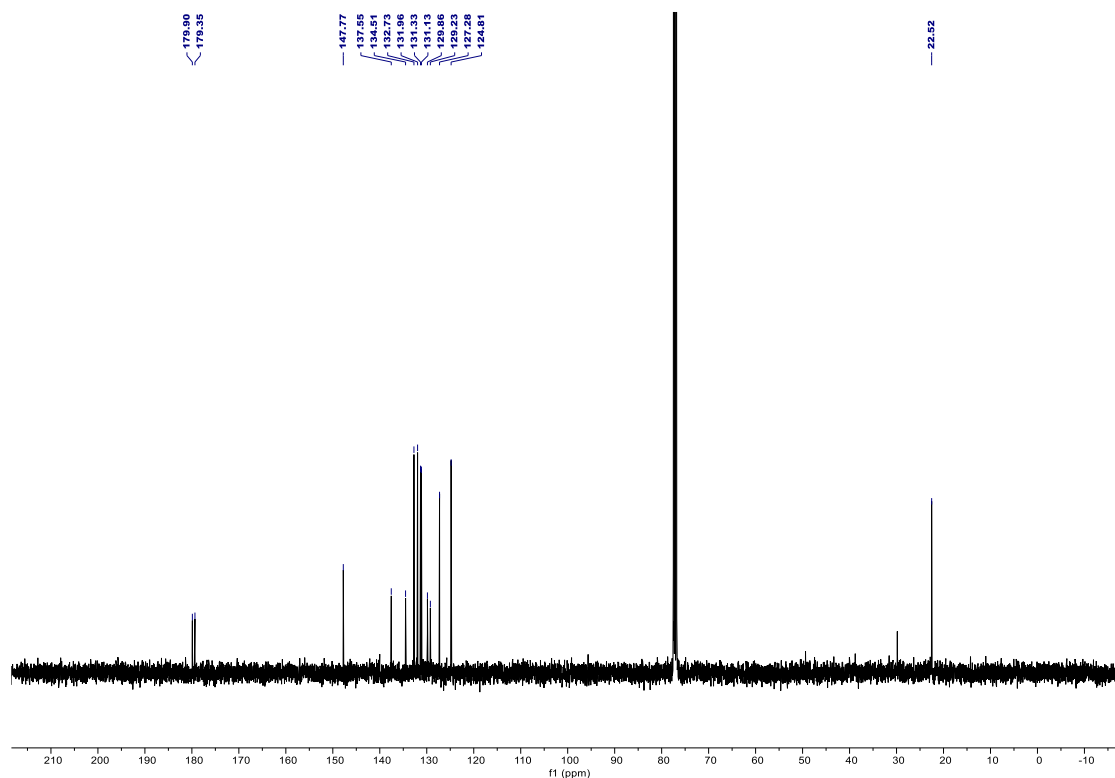
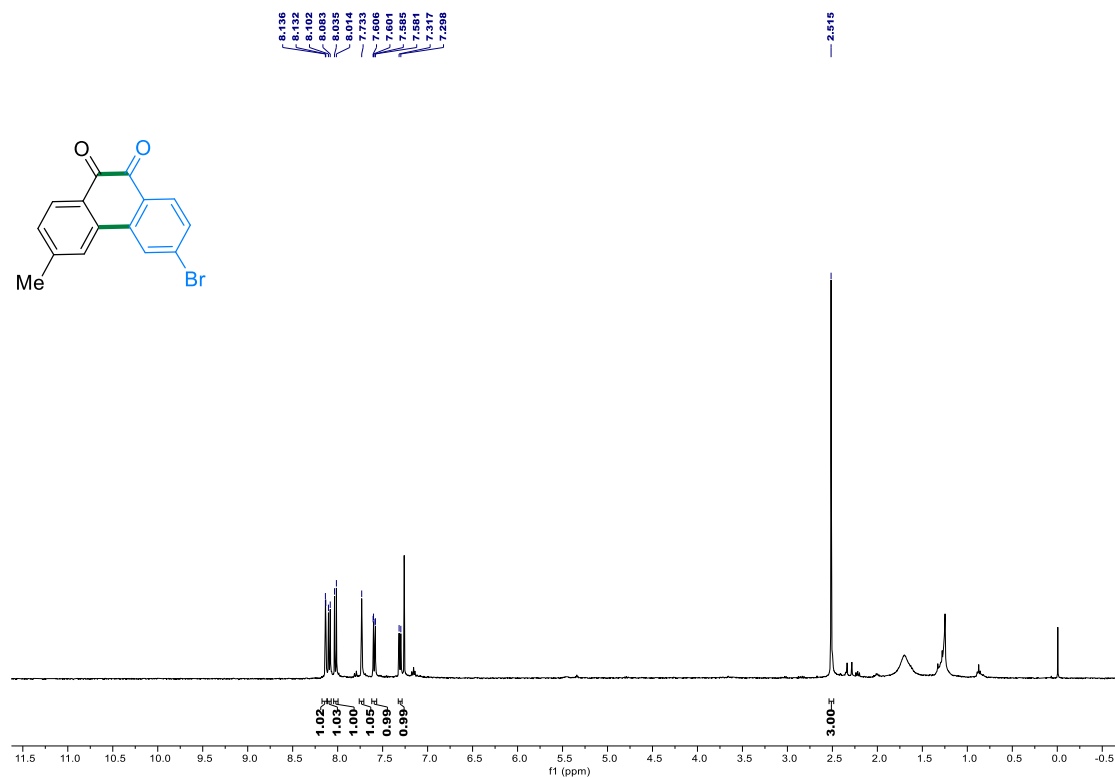
3,4,6-Trimethylphenanthrene-9,10-dione (4f)



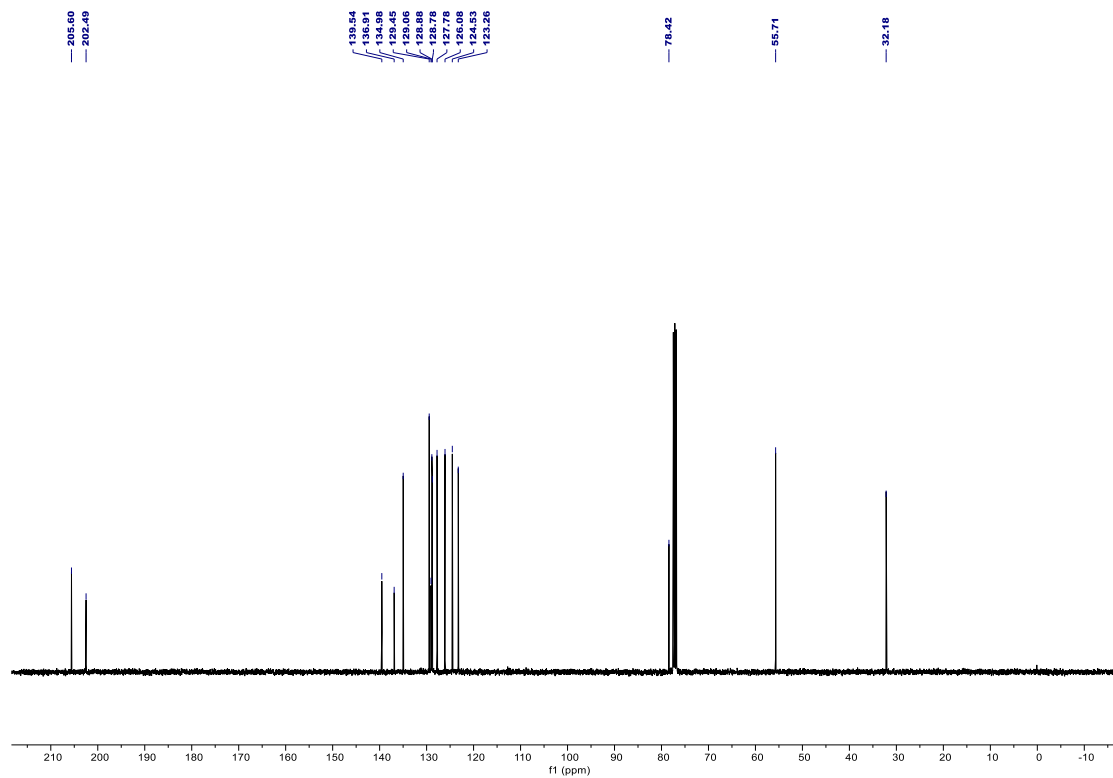
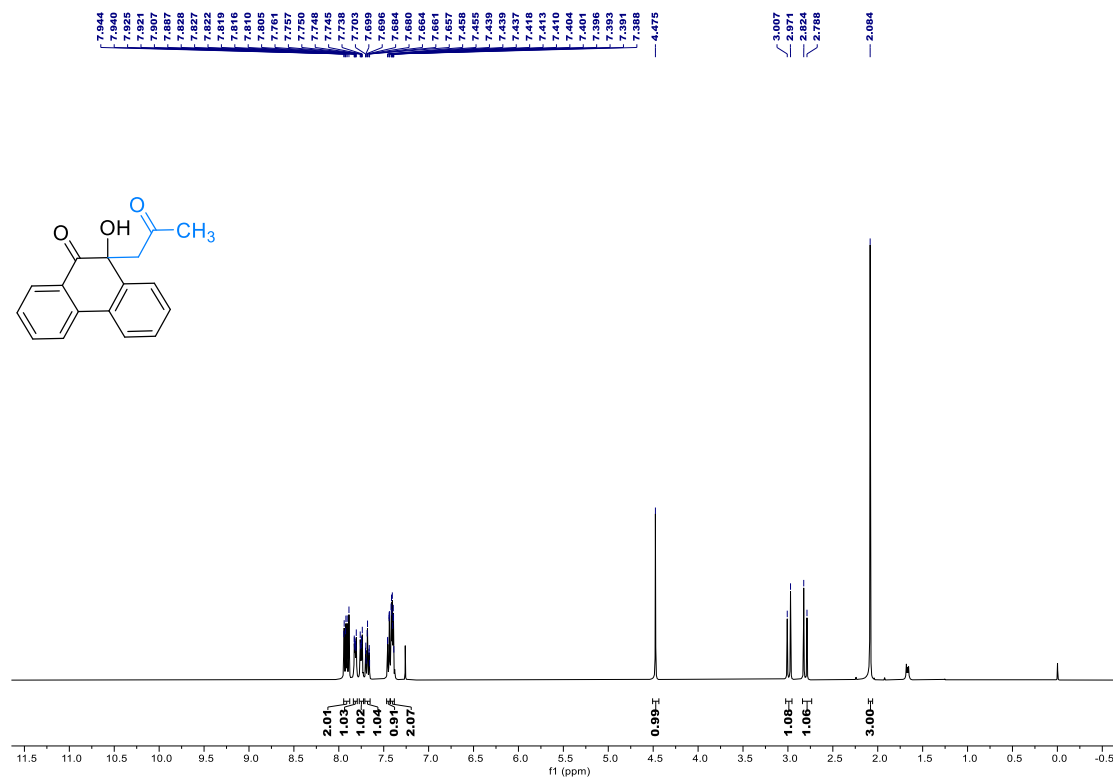
2,3-Dimethoxy-6-methylphenanthrene-9,10-dione (4g)



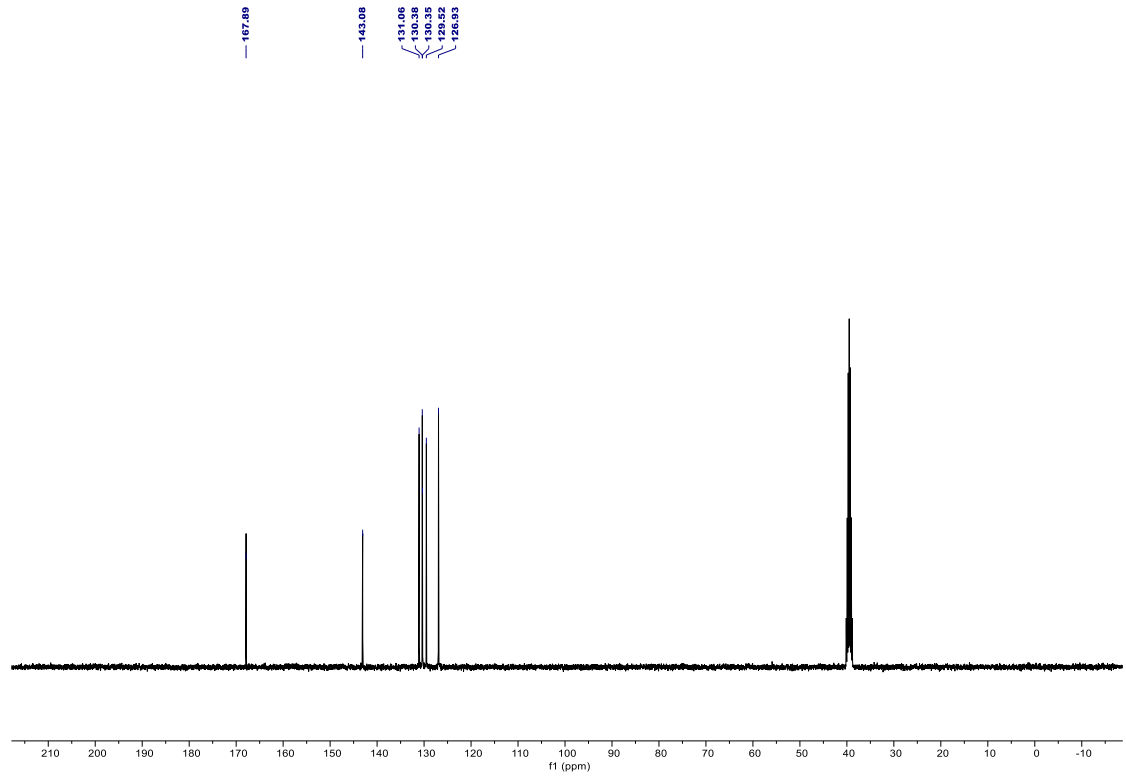
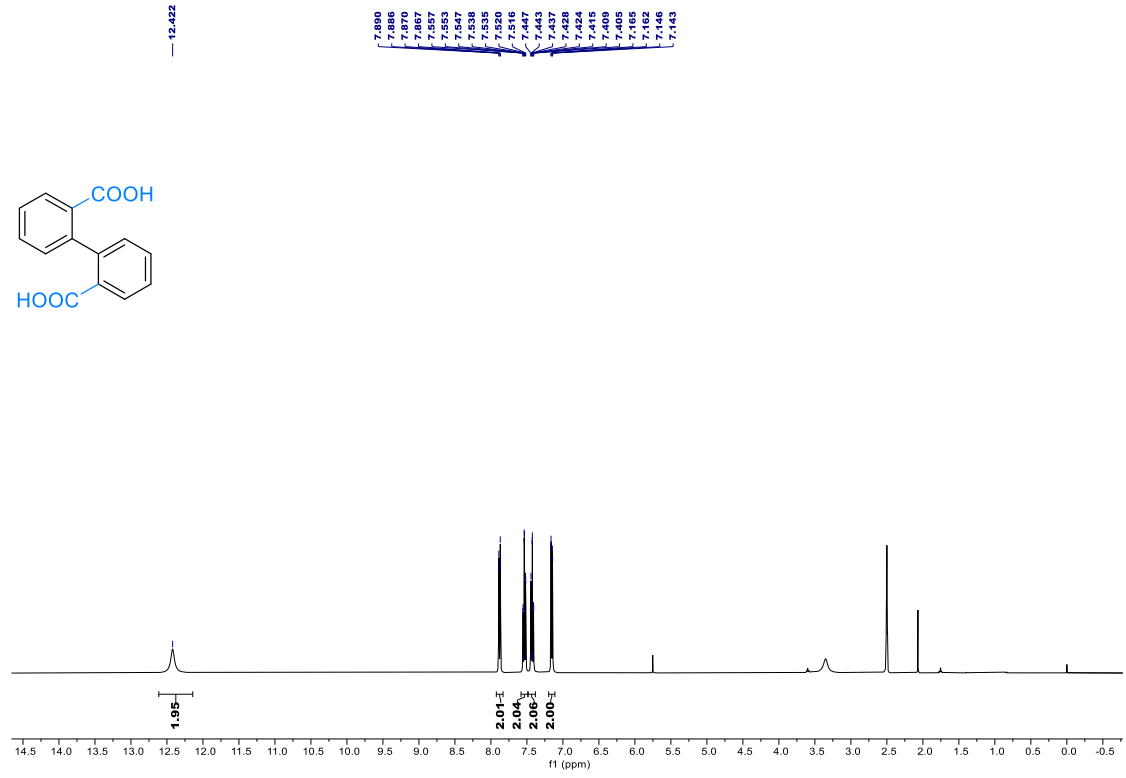
3-Bromo-6-methylphenanthrene-9,10-dione (4h)



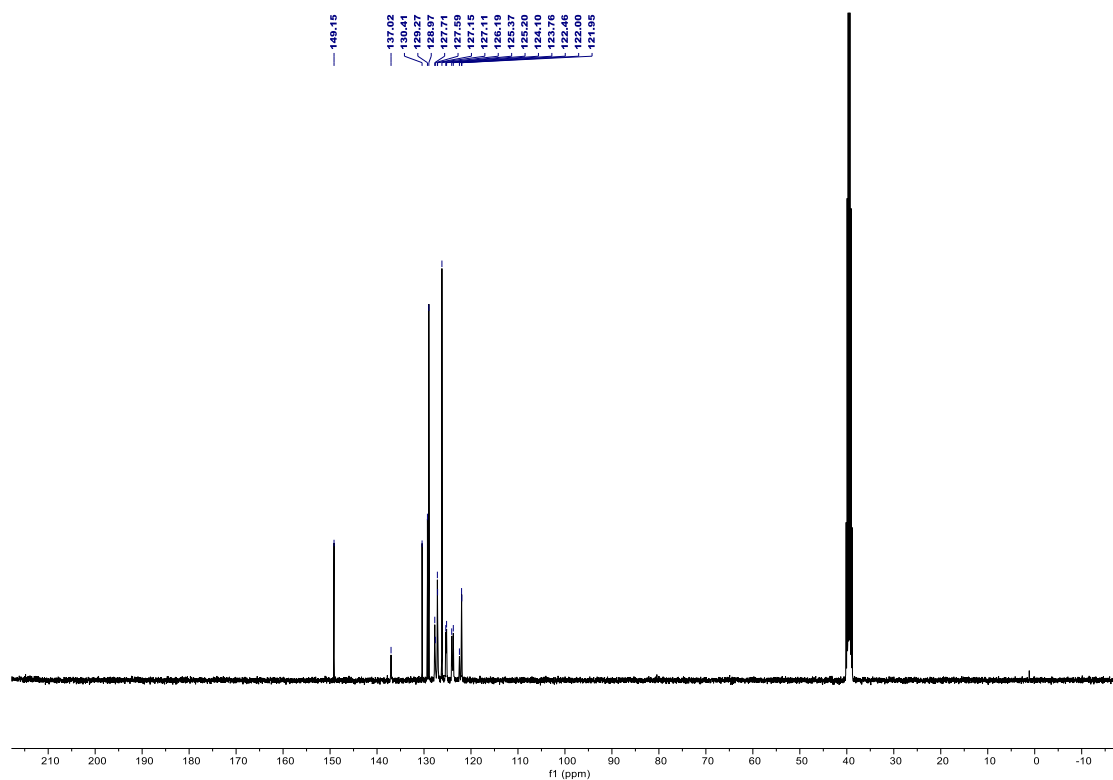
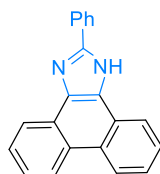
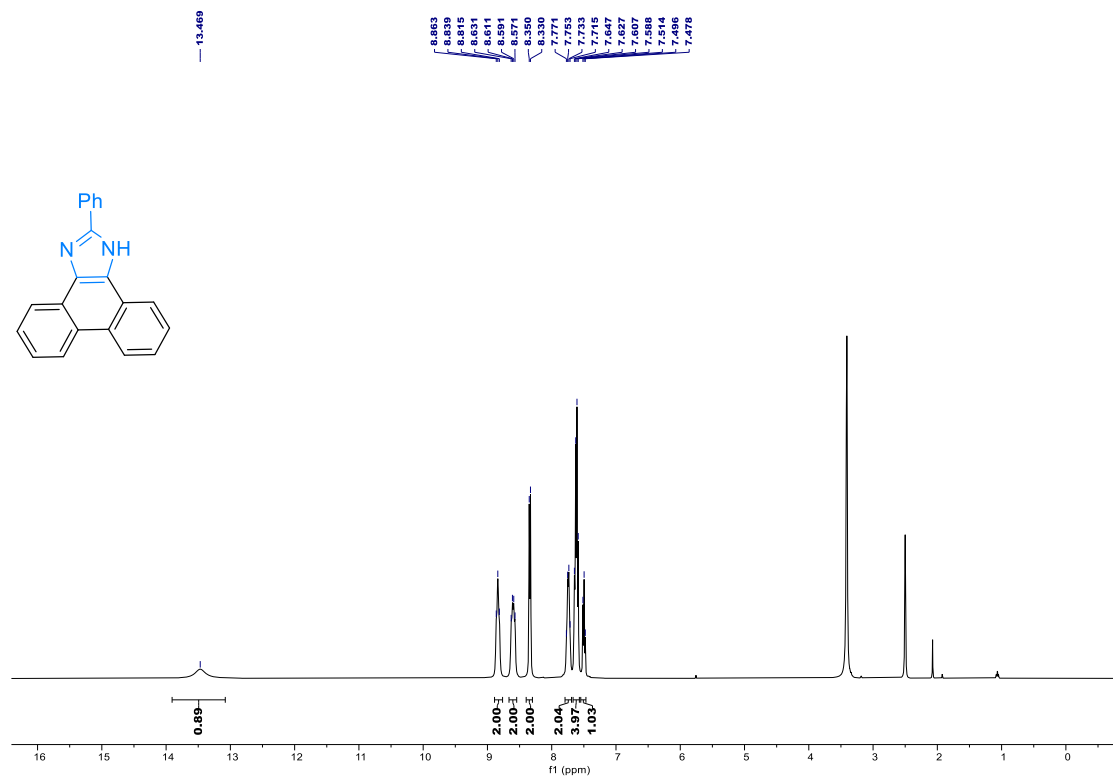
10-Hydroxy-10-(2-oxopropyl)phenanthren-9(10H)-one (6)



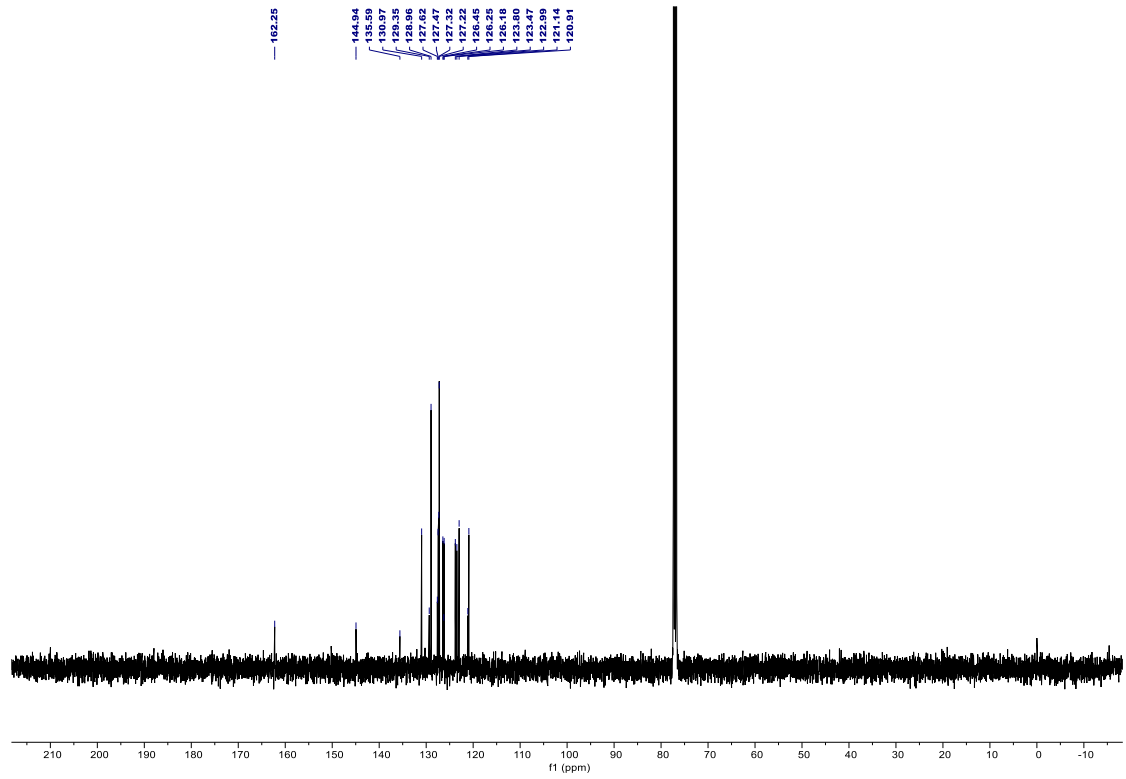
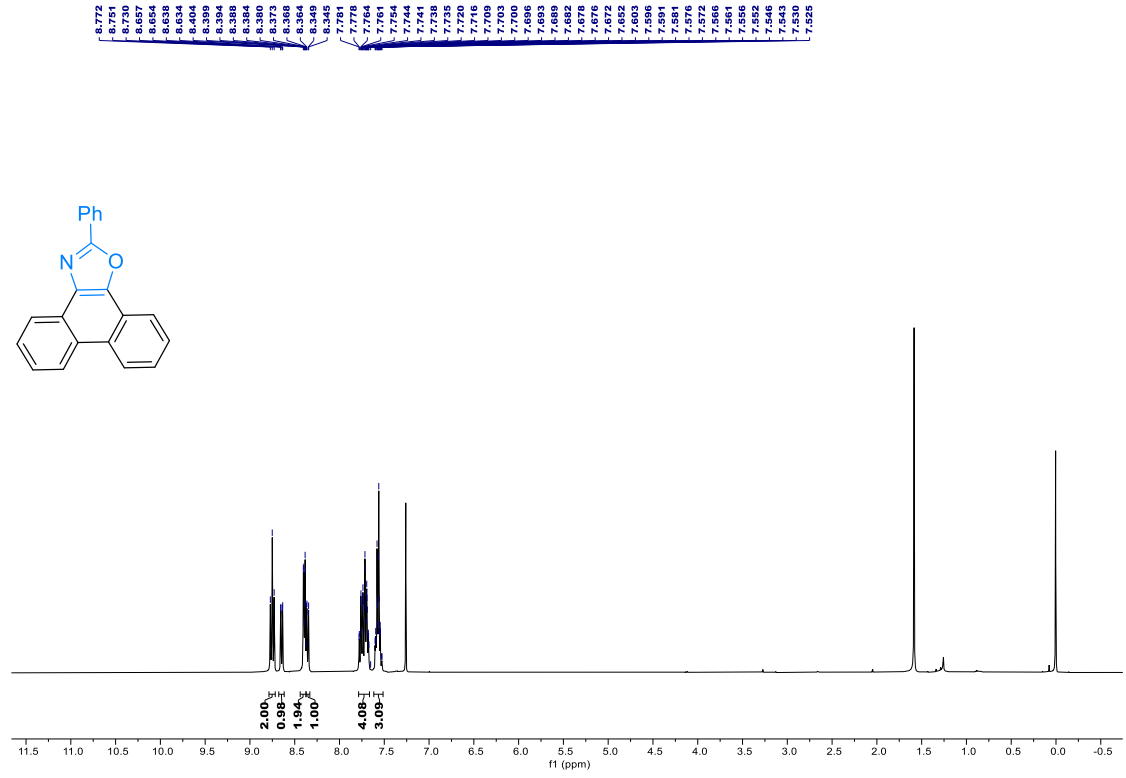
[1,1'-Biphenyl]-2,2'-dicarboxylic acid (8)



2-Phenyl-1*H*-phenanthro[9,10-*d*]imidazole (9)



2-Phenylphenanthro[9,10-d]oxazole (10)



Dibenzo[*a,c*]phenazine (12)

