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Supporting Information

Direct Electrochemical Synthesis of Quinones from Simple Aromatics and Heteroaromatics

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A: General Remarks

A1. Solvents.

The acetonitrile used in the experiment is chromatographic grade. Other solvents were from commercial sources and used without purification unless otherwise noted.

A2. Analytical methods.

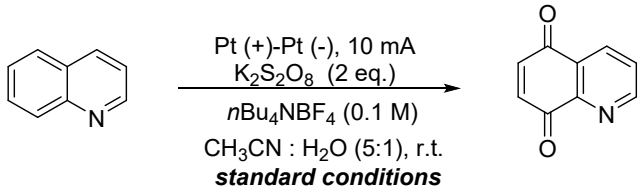
^{1}H NMR spectra, ^{13}C NMR spectra and ^{19}F NMR spectra were recorded on a Bruker AV-400/600 spectrometer (400/500 MHz and 100/125 MHz). Chemical shifts (δ) for protons are reported in parts per million (ppm) downfield from tetramethylsilane and are referenced to residual solvent peak. Chemical shifts (δ) for carbon are reported in parts per million (ppm) downfield from tetramethylsilane and are referenced to the carbon resonances of the solvent. ^{19}F spectra were calibrated in relation to the reference measurement of CF_3COOH (-78.5 ppm). Data are reported as follows: chemical shift, multiplicity (br = broad, s = singlet, d = doublet, dd = doublet of doublets, t = triplet, dt = doublet of triplets, q = quartet, quint = quintet, m = multiplet), coupling constants (J) in Hertz (Hz), integration; “app” is used to denote the apparent splitting of a signal.

High resolution mass spectrometry (HRMS) was carried out using MicroMass GCT CA 055 instrument, recorded on a MicroMass LCTTM spectrometer and analyzed by orthogonal acceleration time-of-flight (OA- TOF).

B: Optimization Tables

Other factors were screened in Table S1., such as temperature, electrolyte and electric current.

Table S1. Additional optimization for the reaction.



Entry	Variation from the standard conditions	Yield[a](%)
1	None	75
2	$LiClO_4$ as electrolyte	71
3	$LiPF_4$ as electrolyte	69
4	0.08 M nBu$_4$NBF$_4$ as electrolyte	72
5	0.06 M nBu$_4$NBF$_4$ as electrolyte	71
6	0.04 M nBu$_4$NBF$_4$ as electrolyte	68
7	40°C	61
8	10°C	67
9	8 mA	63
10	12 mA	71
11	N_2 atmosphere	70

Standard conditions: quinoline (65 mg, 0.5 mmol), $K_2S_2O_8$ (270 mg, 2 eq.), nBu$_4$NBF$_4$ (0.1 M), CH_3CN (2.5 mL), H_2O (0.5 mL), Pt anode, Pt cathode, constant current = 10 mA, under r.t. for 10 h; [a]Isolated yield.

C: General Procedure for the Electrolysis

C1: General procedure for the making of electrolytic cell

The cathode and anode are assembled by commercially available PTFE screws, nuts and Pt sheets.

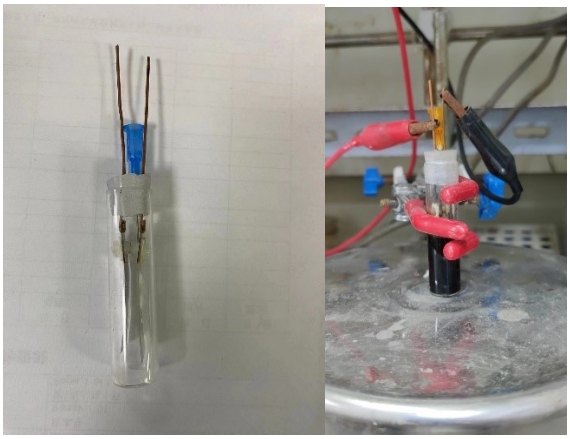


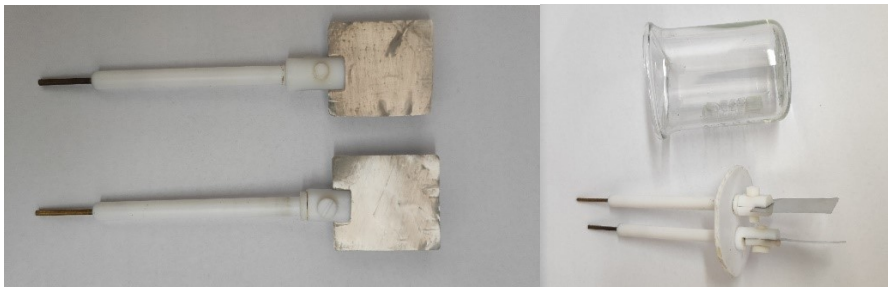
Figure S1. General procedure for the electrolysis: the materials used to make the electrolytic cell, the assemble of electrolytic cell and the electrolysis.

Two Pt elecrodes (10 mm×35 mm×1 mm) with the copper wires were cross the silica gel plug. Then elecrodes were placed into the cube (diameter 13 mm, length 70 mm) and the distance between two Pt sheets was almost 5 mm (Supplementary Figure S1).

C2: General procedure for electrolysis

An oven-dried undivided cell was equipped with a stir bar, substrate (0.5 mmol, 1 eq.), $K_2S_2O_8$ (270 mg, 1 mmol, 2 eq.), nBu$_4$NBF$_4$ (98 mg, 0.3 mmol, 0.1 M), CH_3CN (2.5 mL), H_2O (0.5 mL). Air has little effect on this reaction. Then the assembled electrodes were placed into the solution. The silica gel plug was sealed with film. The mixture was electrolyzed at a constant current of 10 mA until the substrates was completely consumed (Figure S1). The Pt electrodes were washed by water, ethanol and DCM in turn. Adding water dropwise to the reaction solution until all solids are dissolved. The aqueous layer was separated and extracted with EtOAc (3×10 mL), and the combined organic layers were washed with brine and dried over anhydrous Na_2SO_4. Following concentration in vacuo, the crude product was purified by column chromatography on silica gel to give pure product.

C3: Large scale general procedure for electrolysis

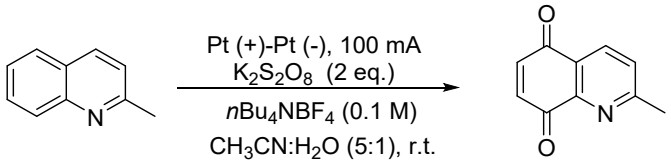


(a)

(b)

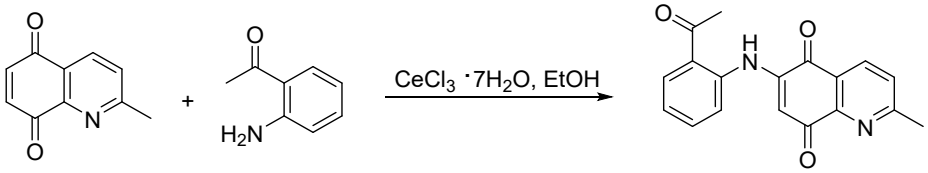
Figure S2. (a) The setup for large scale electrolysis; (b) The electrolysis

Two Pt elecrodes (65 mm×55 mm×1mm) were assembled into sealed cap. Then it was placed into the bake (diameter 35 mm, length 60 mm) and the distance between two Pt sheets was almost 24 mm (Figure S2, a)



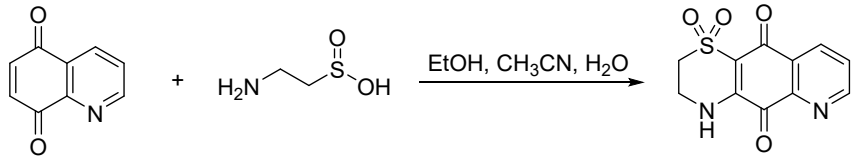
An oven-dried undivided cell was equipped with a stir bar, 2-methylquinoline (715 mg, 5 mmol, 1 eq.), $K_2S_2O_8$ (2.7 g, 10 mmol, 2 eq), nBu$_4$NBF$_4$ (987 mg, 3 mmol, 0.1 M), CH_3CN (25 mL), H_2O (5 mL). Then the assembled electrodes were placed into the solution. The silica gel plug was sealed with film. Air has little effect on this reaction. The mixture was electrolyzed at a constant current of 100 mA until the 2-methylquinoline was completely consumed. (Figure S2). The Pt electrodes were washed by water, ethanol and DCM in turn. Adding water dropwise to the reaction solution until all solids are dissolved and extracted with EtOAc (3×100 mL), and the combined organic layers were washed with brine and dried over anhydrous Na_2SO_4. Following concentration in vacuo, the crude product was purified by column chromatography on silica gel to give pure product (622 mg, 72%).

C4. Transformations of the product 1 and 2 [1-3]



2 **34** **35**, 76%

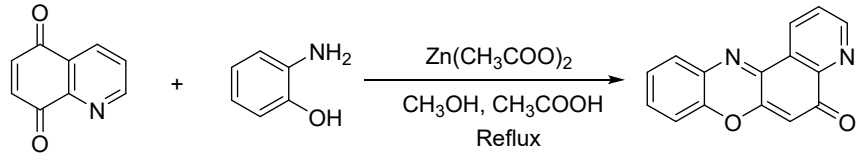
A solution of quinoline-5,8-dione (87 mg, 0.5 mmol, 1 eq.) in 10 mL ethanol was dropped into a solution of cerium (III) chloride (246 mg, 1 mmol, 2 eq.) and aminoacetophenone (203 mg, 1.5 mmol, 3 eq.) in 10 mL ethanol. The reaction media was stirred at room temperature overnight, hydrolyzed with 10% acetic acid. The mixture was then concentrated in vacuo and extracted with CH_2Cl_2. The organic layers were dried over Na_2SO_4 and concentrated to dryness. The crude product was purified by flash chromatography to give compound as red solid (116 mg, 76%)



1 **36** **37**, 51%

A solution of hypotaurine (50 mg, 0.46 mmol, 1 eq.) in water (4 mL) was added

to the quinone (109 mg, 0.69 mmol, 1.5 eq.) in 20 mL acetonitrile/ethanol (1:1) solution. The reaction mixture was stirred at room temperature for 18 h then the solvents were removed in vacuo to give an orange solid. Methanol was added, the mixture was sonicated for 1 min then the orange solid was isolated by filtration, then washed with methanol, providing bright yellow solid **37** (62 mg, 51%).

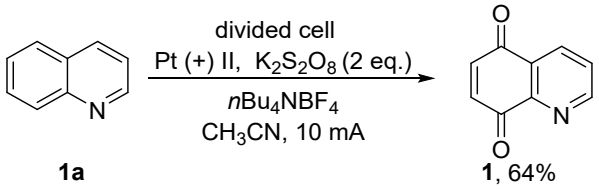


1 **38** **39**, 38%

2-Aminophenols (109 mg, 1 mmol) in methanol/acetic acid (50:50 v/v, 10 mL) were added dropwise to an equimolar mixture of 5,8-quinolinquinone (159 mg, 1 mmol) and Zn (II) acetate (183 mg, 1 mmol) in acetic acid (20 mL), and the mixture was stirred and refluxed for 2. The reaction mixture was evaporated in vacuo and acidified (6 N HCl) to break the Zn complex and extracted by chloroform. The organic layers were dried over Na_2SO_4 and concentrated to dryness. The crude product was purified by flash chromatography to give compound **39** as yellow solid (94 mg, 38%).

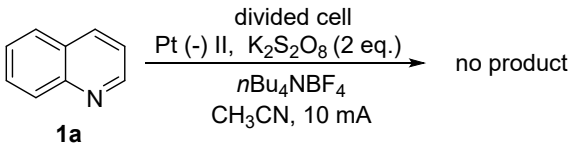
D. Mechanism research experiments

D1: Divided cell experiment



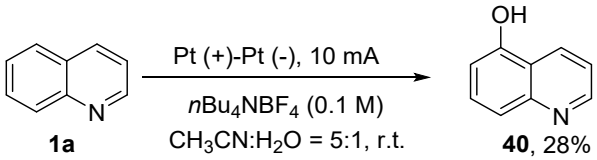
1a **1**, 64%

This control experiment was carried out in an H-type divided cell. The anodic chamber was equipped with quinoline (65 mg, 0.5 mmol, 1 eq.), $K_2S_2O_8$ (270 mg, 1 mmol, 2 eq), *n*Bu_4NBF_4 (98 mg, 0.3 mmol, 0.1 M) and CH_3CN (2.5 mL), H_2O (0.5 mL). The cathodic chamber was added *n*Bu_4NBF_4 (98 mg, 0.3 mmol, 0.1 M) and CH_3CN (2.5 mL), H_2O (0.5 mL). The mixture was electrolyzed at a constant current of 10 mA for 10 h. Water was dropped to the reaction solution until all solids were dissolved and extracted with EtOAc (3×10 mL), and the combined organic layers were washed with brine and dried over anhydrous Na_2SO_4. Following concentration in vacuo, the crude product was purified by column chromatography on silica gel to give pure product **1** (51 mg, 64%).

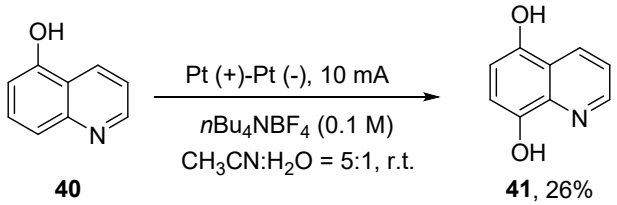


This control experiment was carried out in an H-type divided cell. The cathodic chamber was equipped with quinoline (65 mg, 0.5 mmol, 1 eq.), $K_2S_2O_8$ (270 mg, 1 mmol, 2 eq), nBu$_4$NBF$_4$ (98 mg, 0.3 mmol, 0.1 M) and CH_3CN (2.5 mL), H_2O (0.5 mL). The anodic chamber was added nBu$_4$NBF$_4$ (98 mg, 0.3 mmol, 0.1 M) and CH_3CN (2.5 mL), H_2O (0.5 mL). The mixture was electrolyzed at a constant current of 10 mA for 10 h. No product was detected using TLC, and large amount of quinoline was left.

D2: The determination of the intermediate

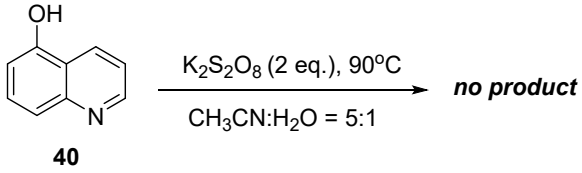


An oven-dried undivided cell was equipped with a stir bar, quinolone **1** (65 mg, 0.5 mmol, 1 eq.), nBu$_4$NBF$_4$ (98 mg, 0.3 mmol, 0.1 M), CH_3CN (2.5 mL), H_2O (0.5 mL). Then the assembled electrodes were placed into the solution. The silica gel plug was sealed with film. The mixture was electrolyzed at a constant current of 10 mA for 10 h. The Pt electrodes were washed by water, ethanol and DCM in turn. Water was dropped to the reaction solution until all solids were dissolved and extracted with EtOAc (3×10 mL) The aqueous layer was separated and extracted with EtOAc (3×10 mL), and the combined organic layers were washed with brine and dried over anhydrous Na_2SO_4. Following concentration in vacuo, the crude product was purified by column chromatography on silica gel to give pure product (20.3 mg, 28%).

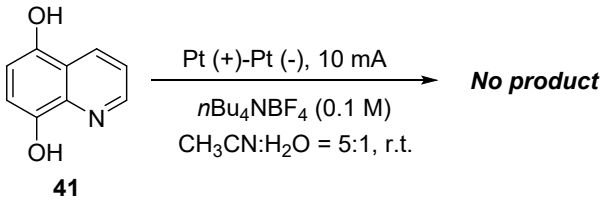


An oven-dried undivided cell was equipped with a stir bar, 5-hydroxyquinoline (72.5 mg, 0.5 mmol, 1 eq.), nBu$_4$NBF$_4$ (98 mg, 0.3 mmol, 0.1 M), CH_3CN (2.5 mL), H_2O (0.5 mL). Then the assembled electrodes were placed into the solution. The silica gel plug was sealed with film. The mixture was electrolyzed at a constant current of 10 mA for 10 h (Figure S1). The Pt electrodes were washed by water, ethanol and DCM in turn. Water was dropped to the reaction solution until all solids were dissolved and extracted with EtOAc (3×10 mL), and the combined organic layers were washed with

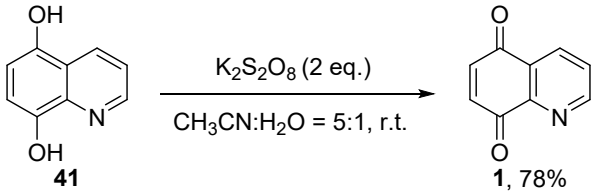
brine and dried over anhydrous Na_2SO_4. Following concentration in vacuo, the crude product was purified by column chromatography on silica gel to give pure product (21 mg, 26%).



A mixture of 5-hydroxyquinoline (65 mg, 0.5 mmol, 1 eq.) and $K_2S_2O_8$ (270 mg, 1 mmol, 2 eq.) in acetonitrile (2.5 mL), H_2O (0.5 mL) was heated at 90 °C for 10 h. No product was detected using TLC, and large amount of 5-hydroxyquinoline was left.



An oven-dried undivided cell was equipped with a stir bar, 5,8-dihydroxyquinoline (0.5 mmol, 80.5 mg, 1 eq.), *n*Bu_4NBF_4 (98 mg, 0.3 mmol, 0.1 M), CH_3CN (2.5 mL), H_2O (0.5 mL). Then the assembled electrodes were placed into the solution. The silica gel plug was sealed with film. The mixture was electrolyzed at a constant current of 10 mA for 10 h (Figure S1). No 5,8-quinolinequinone was detected using TLC, and large amount of 5,8-dihydroxyquinoline was left.



A mixture of 5,8-dihydroxyquinoline (80.5 mg, 0.5 mmol, 1 eq.) and $K_2S_2O_8$ (270 mg, 1 mmol, 2 eq.) in acetonitrile (2.5 mL) and H_2O (0.5 mL) were stired at room temperature for 10 h. After the reaction was finished, Water was dropped to the reaction solution until all solids were dissolved and extracted with EtOAc (3×100 mL), and the combined organic layers were washed with brine and dried over anhydrous Na_2SO_4. Following concentration in vacuo, the crude product was purified by column chromatography on silica gel to give pure product (62 mg, 78%).

D3: Cyclic voltammetry experiments for some substrates

The cyclic voltammograms were recorded in an electrolyte of *n*Bu_4NBF_4 (0.1 M) in

CH_3CN (3 mL) using a platinum disk working electrode, a Pt wire auxiliary and the Ag/AgCl reference electrode. The scan rate is 100 mV/s.

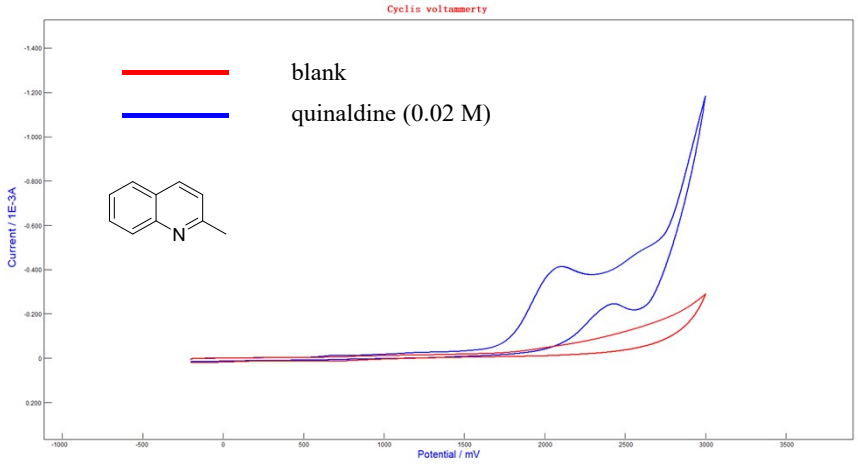


Figure S3 Red line: cyclic voltammogram of none in an electrolyte of nBu$_4$NBF$_4$ in CH_3CN; Blue line: cyclic voltammogram of quinaldine (0.02 M) in an electrolyte of nBu$_4$NBF$_4$ in CH_3CN, E_{ox}= 2.08 V.

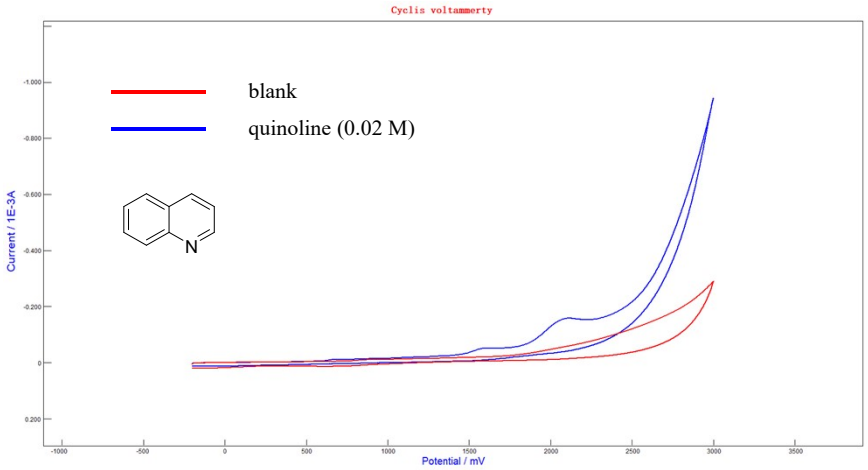


Figure S4 Red line: cyclic voltammogram of none in an electrolyte of nBu$_4$NBF$_4$ in CH_3CN; Blue line: cyclic voltammogram of quinoline (0.02 M) in an electrolyte of nBu$_4$NBF$_4$ in CH_3CN, E_{ox}= 2.09 V

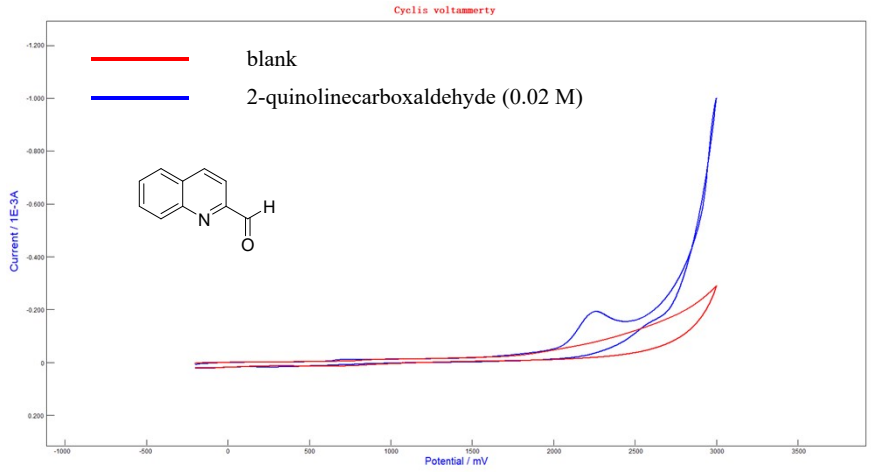


Figure S5 Red line: cyclic voltammogram of none in an electrolyte of nBu$_4$NBF$_4$ in CH$_3$CN; Blue line: cyclic voltammogram of 2-quinolinecarboxaldehyde (0.02 M) in an electrolyte of nBu$_4$NBF$_4$ in CH$_3$CN, E_{ox}= 2.27 V.

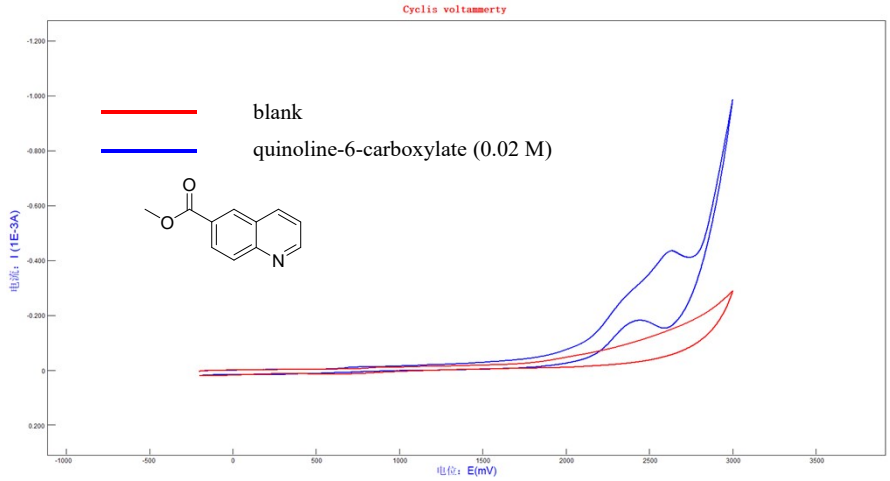


Figure S6 Red line: cyclic voltammogram of none in an electrolyte of nBu$_4$NBF$_4$ in CH$_3$CN; Blue line: cyclic voltammogram of methyl quinoline-6-carboxylate (0.02 M) in an electrolyte of nBu$_4$NBF$_4$ in CH$_3$CN, E_{ox}= 2.63 V.

D4: Cyclic voltammetry of quinolines under the conditions of different water content

In Figure S8, the first oxidative peak (1.73 V vs Ag/AgCl) of quinoline was not affected, but the second (2.16 V vs Ag/AgCl) increased with the increasing of water content. The oxidative peak of 2-formylquinoline (2.30 V vs Ag/AgCl) was not affected obviously until the amount of water increased to 4 equivalent. Therefore, the oxidations of water and arenes, especially the electron-deficient ones, were take place simultaneously.

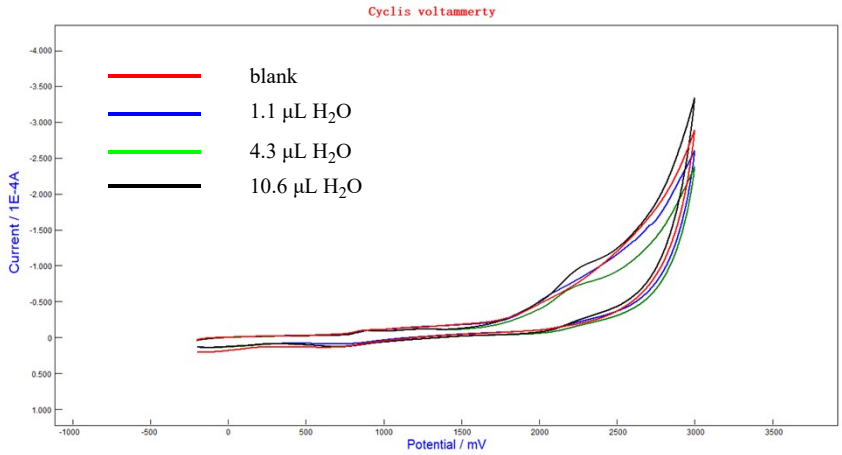


Figure S7. Red line: cyclic voltammogram of none in an electrolyte of nBu$_4$NBF$_4$ in CH$_3$CN; Blue line: cyclic voltammogram of 1.1 μL H$_2$O in an electrolyte of nBu$_4$NBF$_4$ in CH$_3$CN; Green line: cyclic voltammogram of 4.3 μL H$_2$O in an electrolyte of nBu$_4$NBF$_4$ in CH$_3$CN; Black line: cyclic voltammogram of 8.6 μL H$_2$O in an electrolyte of nBu$_4$NBF$_4$ in CH$_3$CN.

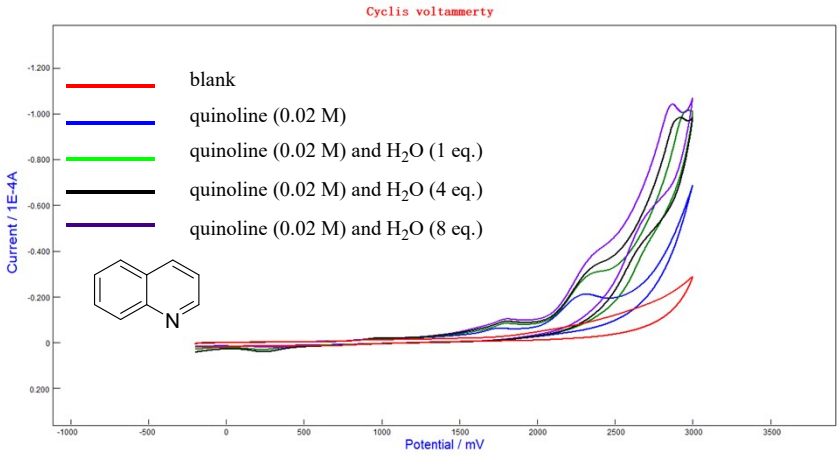


Figure S8. Red line: cyclic voltammogram of none in an electrolyte of nBu$_4$NBF$_4$ in CH$_3$CN; Blue line: cyclic voltammogram of quinoline (0.02 M) in an electrolyte of nBu$_4$NBF$_4$ in CH$_3$CN; Green line: cyclic voltammogram of quinoline (0.02 M) and 1.1 μL H$_2$O (1 eq.) in an electrolyte of nBu$_4$NBF$_4$ in CH$_3$CN; Black line: cyclic voltammogram of quinoline (0.02 M) and 4.3 μL H$_2$O (4 eq.) in an electrolyte of nBu$_4$NBF$_4$ in CH$_3$CN; Purple line: cyclic voltammogram of quinoline (0.02 M) and 8.6 μL H$_2$O (8 eq.) in an electrolyte of nBu$_4$NBF$_4$ in CH$_3$CN.

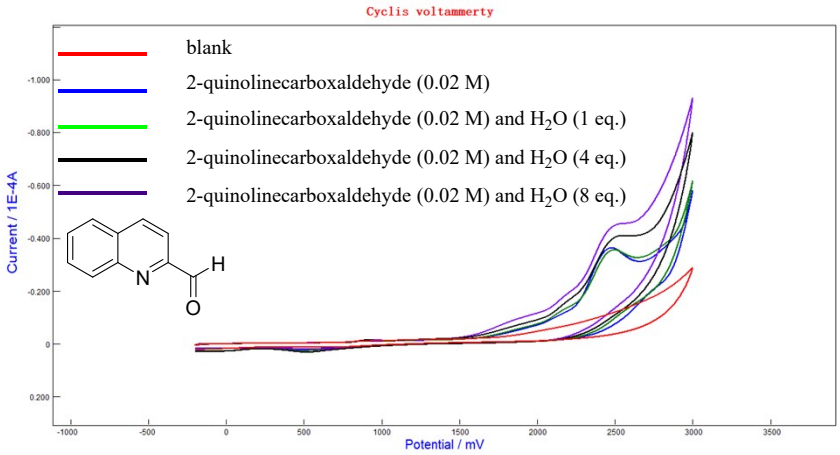


Figure S9. Red line: cyclic voltammogram of none in an electrolyte of nBu$_4$NBF$_4$ in CH$_3$CN; Blue line: cyclic voltammogram of 2-quinolinecarboxaldehyde (0.02 M) in an electrolyte of nBu$_4$NBF$_4$ in CH$_3$CN; Green line: cyclic voltammogram of 2-quinolinecarboxaldehyde (0.02 M) and 1.1 μL H$_2$O (1 eq.) in an electrolyte of nBu$_4$NBF$_4$ in CH$_3$CN; Purple line: cyclic voltammogram of 2-quinolinecarboxaldehyde (0.02 M) and 4.3 μL H$_2$O (4 eq.) in an electrolyte of nBu$_4$NBF$_4$ in CH$_3$CN; Black line: cyclic voltammogram of 2-quinolinecarboxaldehyde (0.02 M) and 8.6 μL H$_2$O (8 eq.) in an electrolyte of nBu$_4$NBF$_4$ in CH$_3$CN.

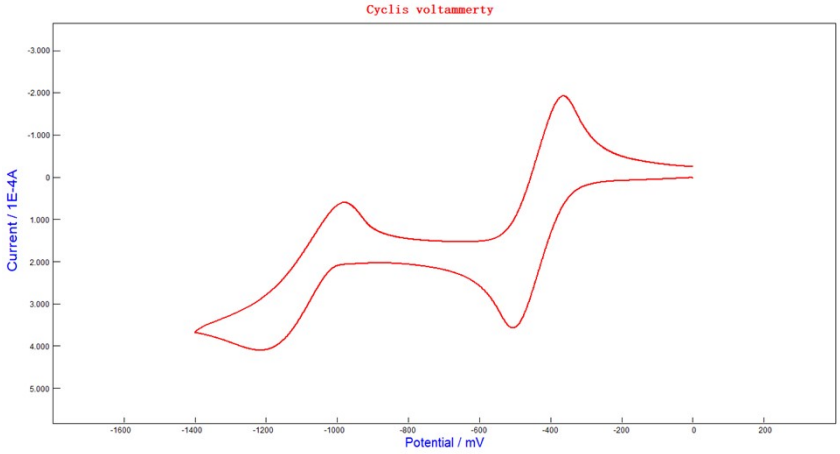
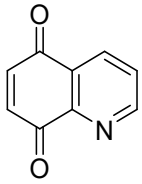


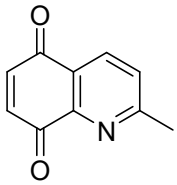
Figure S10. Cyclic voltammogram of **1** (0.02 M) in an electrolyte of nBu$_4$NBF$_4$ (0.1 M) in CH$_3$CN. E_{re1}= -0.51 V, E_{re2}= -1.21 V.

E: Characterization Data for the Electrolysis Products



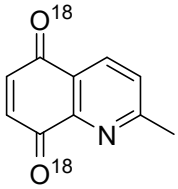
quinoline-5,8-dione

Yellow solid, 75% yield, Electricity = 5.0 F mol^{-1}. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.02 (d, *J* = 4.7 Hz, 1H), 8.39 (d, *J* = 7.8 Hz, 1H), 7.69 (dd, *J* = 7.9, 4.6 Hz, 1H), 7.13 (d, *J* = 10.4 Hz, 1H), 7.04 (d, *J* = 10.4 Hz, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 184.5, 183.2, 154.8, 147.4, 139.1, 138.1, 134.6, 129.1, 127.9.



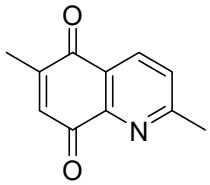
2-methylquinoline-5,8-dione

Yellow solid, 78% yield, Electricity = 4.8 F mol^{-1}. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.28 (d, *J* = 8.0 Hz, 1H), 7.54 (d, *J* = 8.0 Hz, 1H), 7.10 (d, *J* = 10.4 Hz, 1H), 7.01 (d, *J* = 10.4 Hz, 1H), 2.76 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 184.6, 183.5, 165.1, 146.9, 138.8, 137.8, 134.6, 127.8, 126.9, 25.3.



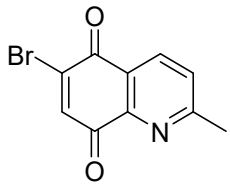
2-methylquinoline-5,8-dione

Yellow solid, 79% yield, Electricity = 4.7 F mol^{-1}. ^{1}H NMR (600 MHz, Acetone-d_6) δ 8.30 (d, *J* = 5.7 Hz, 1H), 7.74 (d, *J* = 5.6 Hz, 1H), 7.15 (d, *J* = 5.8 Hz, 1H), 7.11 (d, *J* = 10.6 Hz, 1H), 2.72 (s, 3H), ^{13}C NMR (151 MHz, Acetone-d_6) δ 185.2, 183.5, 164.9, 147.5, 139.5, 138.0, 134.5, 127.9, 127.6, 24.5. HRMS (EI): exact mass calculated for $C_{10}H_7NO_2$ $[M]^+$ require m/z = 177.0477, found m/z = 177.0479



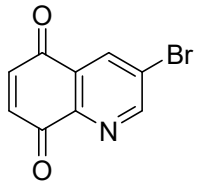
2,6-dimethylquinoline-5,8-dione

Yellow solid, 70% yield, Electricity = 5.3 F mol^{-1}. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.25 (d, *J* = 8.0 Hz, 1H), 7.47 (d, *J* = 8.0 Hz, 1H), 6.91 (q, *J* = 1.6 Hz, 1H), 2.71 (s, 3H), 2.16 (d, *J* = 1.6 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 184.9, 183.6, 164.7, 147.5, 147.1, 135.7, 134.6, 127.4, 126.9, 25.1, 16.1.



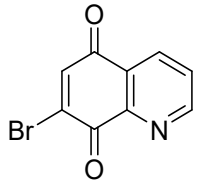
6-bromo-2-methylquinoline-5,8-dione

Yellow solid, 63% yield, Electricity = 5.9 F mol^{-1}. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.35 (d, *J* = 8.1 Hz, 1H), 7.61 (s, 1H), 7.54 (d, *J* = 8.1 Hz, 1H), 2.76 (s, 3H).^{13}C NMR (101 MHz, Chloroform-*d*) δ 180.9, 177.5, 165.7, 146.7, 140.2, 139.4, 135.6, 127.8, 126.1, 25.3.



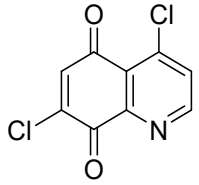
3-bromoquinoline-5,8-dione

Yellow solid, 68% yield, Electricity = 5.5 F mol^{-1}. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.07 (d, *J* = 2.3 Hz, 1H), 8.53 (d, *J* = 2.3 Hz, 1H), 7.20 (d, *J* = 10.4 Hz, 1H), 7.11 (d, *J* = 10.5 Hz, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 183.3, 182.3, 155.8, 145.3, 139.3, 137.7, 136.7, 129.5, 125.9. HRMS (EI): exact mass calculated for $C_9H_4BrNO_2$ $[M]^+$ require m/z = 236.9425, found m/z = 236.9427.



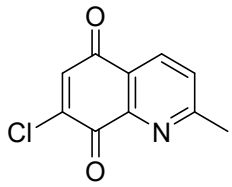
7-bromoquinoline-5,8-dione

Yellow solid, 57% yield, Electricity = 6.5 F mol^{-1}. ^{1}H NMR (400 MHz, Acetone-d_6) δ 9.09 (dd, *J* = 4.6, 1.7 Hz, 1H), 8.55 (dd, *J* = 7.9, 1.7 Hz, 1H), 7.92 (dd, *J* = 8.0, 4.6 Hz, 1H), 7.79 (s, 1H). ^{13}C NMR (101 MHz, Acetone-d_6) δ 181.2, 178.6, 155.3, 148.2, 141.5, 139.1, 135.6, 129.3, 128.5.



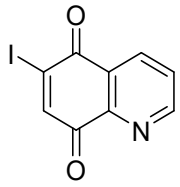
4,7-dichloroquinoline-5,8-dione

Yellow solid, 65% yield, Electricity = 5.7 F mol^{-1}. ^{1}H NMR (400 MHz, Acetone-d_6) δ 8.94 (d, *J* = 5.2 Hz, 1H), 7.96 (d, *J* = 5.2 Hz, 1H), 7.45 (s, 1H).^{13}C NMR (101 MHz, Acetone-d_6) δ 181.4, 175.7, 154.1, 150.4, 145.1, 144.3, 137.1, 131.3, 126.4. HRMS (EI): exact mass calculated for $C_9H_3Cl_2NO_2$ $[M]^+$ require m/z = 226.9541, found m/z = 226.9544.



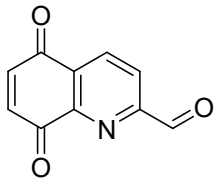
7-chloro-2-methylquinoline-5,8-dione

Yellow solid, 72% yield, Electricity = 5.2 F mol^{-1}. ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.23 (d, J = 8.0 Hz, 1H), 7.73 (d, J = 8.0 Hz, 1H), 7.50 (s, 1H), 2.66 (s, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 182.9, 176.4, 164.5, 147.2, 146.1, 135.3, 134.8, 128.3, 127.3, 25.0.



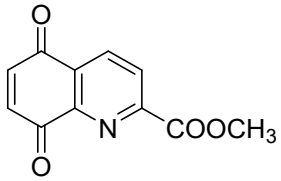
6-iodoquinoline-5,8-dione

Yellow solid, 74% yield, Electricity = 5.0 F mol^{-1}. ^{1}H NMR (400 MHz, Acetone-d_6) δ 9.08 (dd, J = 4.6, 1.7 Hz, 1H), 8.53 (dd, J = 7.9, 1.7 Hz, 1H), 8.12 (s, 1H), 7.89 (dd, J = 8.0, 4.6 Hz, 1H).^{13}C NMR (151 MHz, Acetone-d_6) δ 180.6, 179.7, 155.0, 149.1, 148.0, 135.7, 128.2, 127.7, 121.4. HRMS (EI): exact mass calculated for $C_9H_4INO_2$ $[M]^+$ require m/z = 284.9287, found m/z = 284.9286.



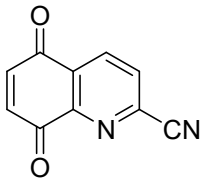
5,8-dioxo-5,8-dihydroquinoline-2-carbaldehyde

Yellow solid, 62% yield, Electricity = 6.0 F mol^{-1}. ^{1}H NMR (600 MHz, Acetone-d_6) δ 10.21 (s, 1H), 8.68 (d, J = 8.0 Hz, 1H), 8.35 (d, J = 8.0 Hz, 1H), 7.33 (d, J = 10.4 Hz, 1H), 7.26 (d, J = 10.5 Hz, 1H). ^{13}C NMR (151 MHz, Acetone-d_6) δ 192.5, 184.6, 182.7, 155.8, 148.3, 140.2, 138.5, 136.4, 131.9, 124.8. HRMS (EI): exact mass calculated for $C_{10}H_5NO_3$ $[M]^+$ require m/z = 187.0269, found m/z = 187.0266.



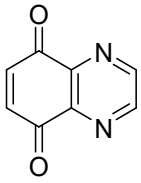
methyl 5,8-dioxo-5,8-dihydroquinoline-2-carboxylate

Yellow solid, 68% yield, Electricity = 5.5 F mol^{-1}. ^{1}H NMR (400 MHz, Acetone-d_6) δ 8.63 (d, J = 8.1 Hz, 1H), 8.50 (d, J = 8.0 Hz, 1H), 7.33-7.21 (m, 2H), 4.03 (s, 3H). ^{13}C NMR (151 MHz, Acetone-d_6) δ 184.6, 182.6, 164.8, 152.2, 147.9, 140.2, 138.3, 136.1, 131.3, 128.6, 52.8. HRMS (EI): exact mass calculated for $C_{11}H_7NO_4$ $[M]^+$ require m/z = 217.0375, found m/z = 217.0378.



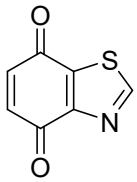
5,8-dioxo-5,8-dihydroquinoline-2-carbonitrile

Yellow solid, 71% yield, Electricity = 5.3 F mol^{-1}. ^{1}H NMR (400 MHz, Acetone-d_6) δ 8.71 (d, J = 8.0 Hz, 1H), 8.43 (d, J = 8.0 Hz, 1H), 7.31 (q, J = 10.5 Hz, 2H). ^{13}C NMR (101 MHz, Acetone-d_6) δ 184.1, 181.8, 148.8, 140.2, 138.7, 137.7, 136.7, 132.7, 131.3, 116.9. HRMS (EI): exact mass calculated for $C_{10}H_4N_2O_2$ $[M]^+$ require m/z = 184.0273, found m/z = 184.0270.



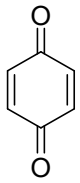
quinoxaline-5,8-dione

Yellow solid, 62% yield, Electricity = 6.0 F mol^{-1}. ^{1}H NMR (400 MHz, Acetone-d_6) δ 9.11 (s, 2H), 7.29 (s, 2H). ^{13}C NMR (101 MHz, Acetone-d_6) δ 183.5(×2), 149.3(×2), 144.8(×2), 139.1(×2).



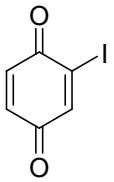
benzo[d]thiazole-4,7-dione

Yellow solid, 58% yield, Electricity = 6.4 F mol^{-1}. ^{1}H NMR (400 MHz, Chloroform-d) δ 9.13 (s, 1H), 6.91 (d, J = 2.9 Hz, 2H). ^{13}C NMR (101 MHz, Chloroform-d) δ 180.1, 179.2, 159.2, 152.9, 139.6, 137.6, 137.4.



benzoquinone

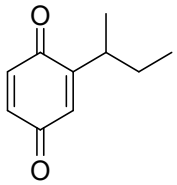
Yellow solid, 56% yield, Electricity = 6.6 F mol^{-1}. ^{1}H NMR (400 MHz, Acetone-d_6) δ 6.87 (s, 4H). ^{13}C NMR (101 MHz, Acetone-d_6) δ 187.9(×2), 137.1(×2).



2-iodocyclohexa-2,5-diene-1,4-dione

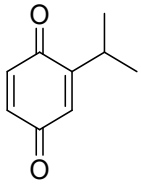
Yellow solid, 56% yield, Electricity = 6.6 F mol^{-1}. ^{1}H NMR (400 MHz, Acetone-d_6) δ

7.78 (d, *J* = 2.4 Hz, 1H), 7.12 (d, *J* = 10.1 Hz, 1H), 6.97 (dd, *J* = 10.1, 2.4 Hz, 1H). ^{13}C NMR (151 MHz, Acetone-d_6) δ 184.7, 181.0, 146.6, 137.1, 135.1, 119.4.



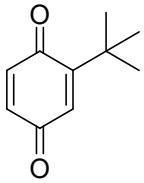
2-(sec-butyl) cyclohexa-2,5-diene-1,4-dione

Yellow solid, 58% yield, Electricity = 6.4 F mol^{-1}. ^{1}H NMR (600 MHz, Acetone-d_6) δ 7.67 (d, *J* = 10.1 Hz, 1H), 7.60 (dd, *J* = 10.1, 2.5 Hz, 1H), 7.39 (dd, *J* = 2.5, 1.0 Hz, 1H), 3.66 (hd, *J* = 7.0, 1.0 Hz, 1H), 2.47-2.39 (m, 1H), 2.31 (dp, *J* = 13.5, 7.3 Hz, 1H), 1.96 (d, *J* = 6.9 Hz, 3H), 1.71 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (151 MHz, Acetone-d_6) δ 188.2, 187.5, 153.9, 137.5, 136.3, 131.4, 33.7, 28.7, 18.7, 11.6.



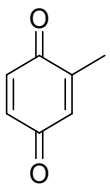
2-isopropylcyclohexa-2,5-diene-1,4-dione

Yellow solid, 30% yield, Electricity = 12.4 F mol^{-1}. ^{1}H NMR (600 MHz, Acetone-d_6) δ 8.03 – 7.95 (m, 2H), 7.65 – 7.59 (m, 1H), 7.51 (t, *J* = 7.8 Hz, 1.93H), 6.81 (d, *J* = 10.1 Hz, 0.83H), 6.75 (dd, *J* = 10.1, 2.6 Hz, 0.86H), 6.55 (dd, *J* = 2.6, 1.2 Hz, 0.86H), 2.99 (pd, *J* = 6.9, 1.2 Hz, 1H), 2.58 (s, 3H), 1.13 (d, *J* = 6.9 Hz, 6H), . ^{13}C NMR (151 MHz, Acetone-d_6) δ 205.5, 197.1, 187.9, 186.9, 154.5, 137.3, 137.1, 135.9, 132.9, 130.1, 128.6, 128.2, 29.0 (dp, *J* = 38.7, 19.4 Hz), 26.6, 25.9, 20.7(×2).



2-(tert-butyl)cyclohexa-2,5-diene-1,4-dione

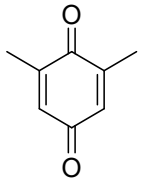
Yellow solid, 38% yield, Electricity = 9.8 F mol^{-1}. ^{1}H NMR (400 MHz, Acetone-d_6) δ 6.78 (d, *J* = 1.7 Hz, 2H), 6.61 (dd, *J* = 1.7, 0.7 Hz, 1H), 1.32 (s, 9H). ^{13}C NMR (101 MHz, Acetone-d_6) δ 187.9, 187.5, 155.3, 138.6, 134.9, 131.3, 34.8, 28.4(×3).



2-methylcyclohexa-2,5-diene-1,4-dione

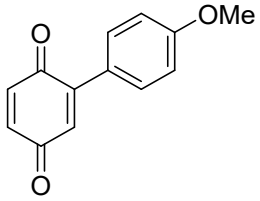
Yellow solid, 63% yield, Electricity = 5.9 F mol^{-1}. ^{1}H NMR (400 MHz, Acetone-d_6) δ 6.85 (d, *J* = 10.1 Hz, 1H), 6.79 (dd, *J* = 10.1, 2.5 Hz, 1H), 6.70 (dq, *J* = 3.1, 1.6 Hz, 1H), 2.05 (d, *J* = 1.7 Hz, 3H). ^{13}C NMR (151 MHz, Acetone-d_6) δ 187.9, 187.9, 146.2,

137.1, 136.8, 133.4, 15.2.



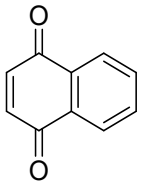
2,6-dimethylcyclohexa-2,5-diene-1,4-dione

Yellow solid, 36% yield, Electricity = 10.3 F mol^{-1}. ^{1}H NMR (600 MHz, Acetone-d_6) δ 6.62 (s, 2H), 2.05 (s, 6H). ^{13}C NMR (151 MHz, Acetone-d_6) δ 188.2, 187.7, 146.1(×2), 133.3(×2), 15.4(×2).



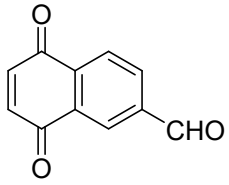
4'-methoxy-[1,1'-biphenyl]-2,5-dione

Yellow solid, 53% yield, Electricity = 7.0 F mol^{-1}. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.56 – 7.50 (m, 1H), 7.04 – 7.00 (m, 1H), 6.93 (s, 1H), 6.91 – 6.87 (m, 1H), 3.81 (s, 2H), 2.51 (p, J = 1.8 Hz, 1H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 188.2, 187.5, 161.2, 145.0, 137.8, 136.5, 131.5(×2), 131.1, 125.4, 114.3(×2), 55.8.



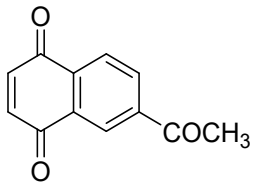
naphthalene-1,4-dione

Yellow solid, 40% yield, 57% yield, 37% yield, Electricity = 9.3 F mol^{-1}, 6.5 F mol^{-1}, 10.0 F mol^{-1}. ^{1}H NMR (400 MHz, Acetone-d_6) δ 8.12 – 8.01 (m, 2H), 7.98-7.85 (m, 2H), 7.07 (s, 2H). ^{13}C NMR (101 MHz, Acetone-d_6) δ 185.3(×2), 139.3(×2), 134.6(×2), 132.6(×2), 126.6(×2).



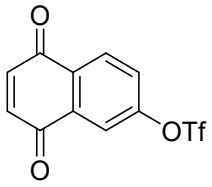
5,8-dioxo-5,8-dihydronaphthalene-2-carbaldehyde

Yellow solid, 62% yield, Electricity = 6.0 F mol^{-1}. ^{1}H NMR (400 MHz, Acetone-d_6) δ 10.31 (s, 1H), 8.58 (d, J = 1.7 Hz, 1H), 8.40 (dd, J = 7.9, 1.7 Hz, 1H), 8.27 (d, J = 7.9 Hz, 1H), 7.19 (d, J = 1.1 Hz, 2H). ^{13}C NMR (101 MHz, Acetone-d_6) δ 192.1, 184.8, 184.6, 140.6, 139.6, 139.5, 135.8, 133.9, 133.3, 127.7, 127.5.



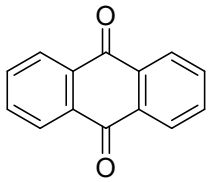
6-acetylnaphthalene-1,4-dione

Yellow solid, 67% yield, Electricity = 5.6 F mol^{-1}. ^{1}H NMR (400 MHz, Acetone-d_6) δ 8.56 (dd, J = 1.9, 0.6 Hz, 1H), 8.43 (dd, J = 8.1, 1.8 Hz, 1H), 8.18 (dd, J = 8.0, 0.5 Hz, 1H), 7.16 (d, J = 1.4 Hz, 2H), 2.77 (s, 3H). ^{13}C NMR (101 MHz, Acetone-d_6) δ 196.9, 184.8, 184.7, 141.6, 139.6, 139.46, 134.9, 133.4, 132.8, 127.2, 126.2, 26.8.



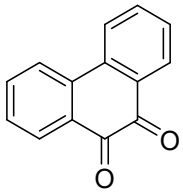
5,8-dioxo-5,8-dihydronaphthalen-2-yl trifluoromethanesulfonate

Yellow solid, 54% yield, Electricity = 6.9 F mol^{-1}. ^{1}H NMR (400 MHz, Acetone-d_6) δ 8.31 (d, J = 8.5 Hz, 1H), 8.06 (d, J = 2.6 Hz, 1H), 8.01 (dd, J = 8.6, 2.6 Hz, 1H), 7.20 (d, J = 3.0 Hz, 2H). ^{13}C NMR (101 MHz, Acetone-d_6) δ 183.9, 183.7, 153.5, 139.5, 139.4, 134.9, 132.4, 129.9, 127.4, 119.3 (q, J = 320.0 Hz), 119.5. ^{19}F NMR (376 MHz, Acetone-d_6) δ -73.98.



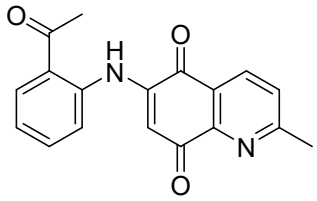
anthracene-9,10-dione

Yellow solid, 68% yield, Electricity = 5.5 F mol^{-1}. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.32 (dd, J = 5.8, 3.3 Hz, 4H), 7.81 (dd, J = 5.8, 3.3 Hz, 4H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 183.4(×2), 134.3(×2), 133.7(×2), 127.4(×2).



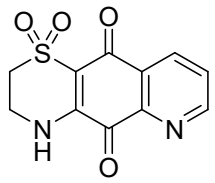
phenanthrene-9,10-dione

Yellow solid, 56% yield, Electricity = 6.7 F mol^{-1}. ^{1}H NMR (400 MHz, Acetone-d_6) δ 8.32 (d, J = 8.0 Hz, 2H), 8.17-8.10 (m, 2H), 7.85 (td, J = 7.7, 1.5 Hz, 2H), 7.60 (t, J = 7.5 Hz, 2H). ^{13}C NMR (151 MHz, Acetone-d_6) δ 180.2(×2), 136.3(×2), 136.2(×2), 131.9(×2), 129.9(×2), 129.9(×2), 124.9(×2).



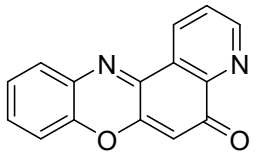
6-((2-acetylphenyl)amino)-2-methylquinoline-5,8-dione

Yellow solid, 76% yield,^{1}H NMR (400 MHz, Chloroform-*d*) δ 10.69 (s, 1H), 8.30 (d, *J* = 8.0 Hz, 1H), 8.05 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.60 – 7.49 (m, 2H), 7.44 (d, *J* = 8.0 Hz, 1H), 7.12 (ddd, *J* = 8.2, 6.9, 1.5 Hz, 1H), 6.82 (s, 1H), 3.93 (s, 3H), 2.74 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 183.1, 181.6, 167.6, 165.7, 148.1, 143.3, 140.5, 134.9, 134.1, 132.2, 126.7, 125.4, 123.5, 120.5, 119.1, 106.1, 52.6, 25.5. HRMS (EI): exact mass calculated for $C_{18}H_{14}N_2O_3$ $[M]^+$ require m/z = 306.1004, found m/z = 306.1007.



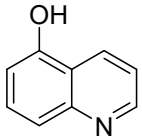
3,4-dihydro-2H-[1,4]thiazino[2,3-g]quinoline-5,10-dione 1,1-dioxide

Yellow solid, 51% yield, ^{1}H NMR (600 MHz, DMSO-d_6) δ 9.26 (d, *J* = 68.3 Hz, 1H), 8.98 (d, *J* = 46.7 Hz, 1H), 8.36 (d, *J* = 8.0 Hz, 1H), 7.93-7.71 (m, 1H), 3.87 (s, 2H), 3.39 (s, 2H). ^{13}C NMR (151 MHz, DMSO-d_6) δ 177.8, 175.0, 154.1, 148.3, 147.3, 134.9, 130.9, 129.9, 111.4, 49.2(×2).



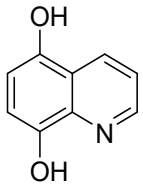
5H-pyrido[3,2-a]phenoxazin-5-one

Yellow solid, 38% yield, ^{1}H NMR (600 MHz, DMSO-d_6) δ 9.10 (dd, *J* = 4.5, 1.7 Hz, 1H), 9.03 (dd, *J* = 8.1, 1.7 Hz, 1H), 7.94 (dd, *J* = 8.1, 4.3 Hz, 2H), 7.73-7.66 (m, 1H), 7.59-7.54 (m, 1H), 7.54-7.49 (m, 1H), 6.60 (s, 1H). ^{13}C NMR (151 MHz, DMSO-d_6) δ 181.9, 153.6, 151.5, 147.1, 144.3, 133.3, 132.9, 132.7, 130.1, 128.3, 127.1, 126.2, 116.6, 108.2, 55.4.



quinolin-5-ol

Yellow solid, 28% yield, Electricity = 13.3 F mol^{-1}. ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.54-9.49 (m, 1H), 9.22 (dd, *J* = 8.5, 1.8 Hz, 1H), 8.20 (t, *J* = 8.0 Hz, 1H), 8.15-8.03 (m, 2H), 7.66 (d, *J* = 7.6 Hz, 1H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 155.7, 151.1, 150.0, 131.8, 130.9, 121.1, 120.5, 119.1, 109.4.

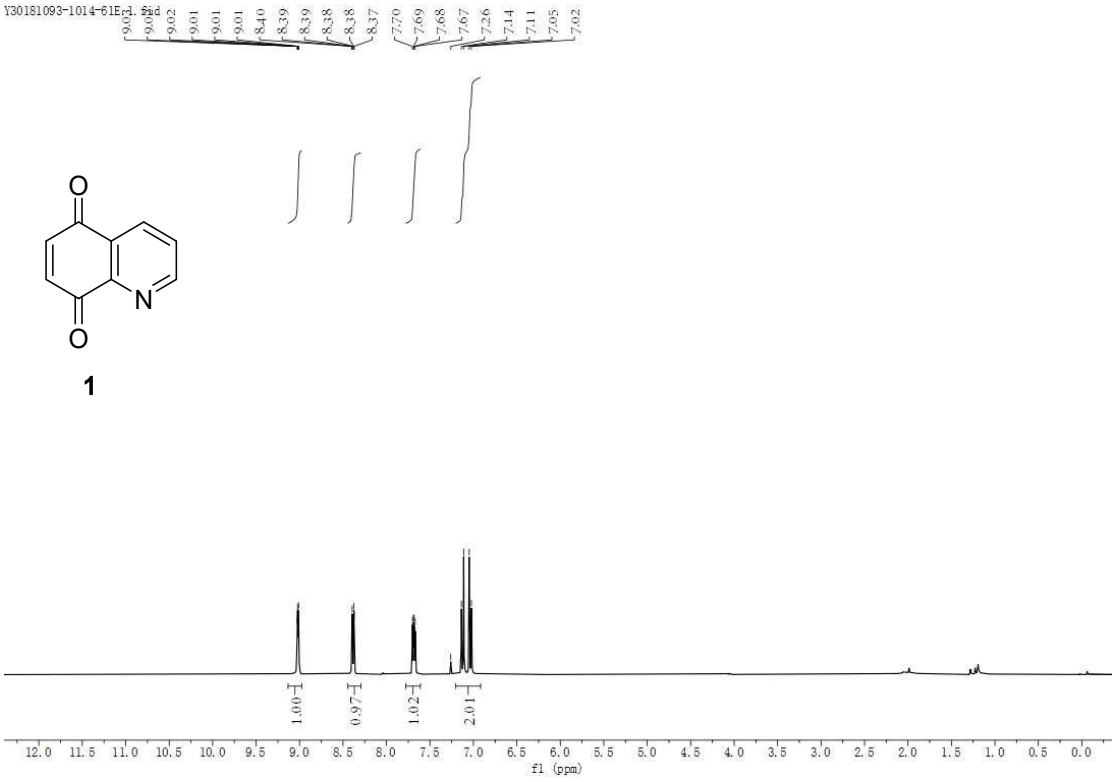


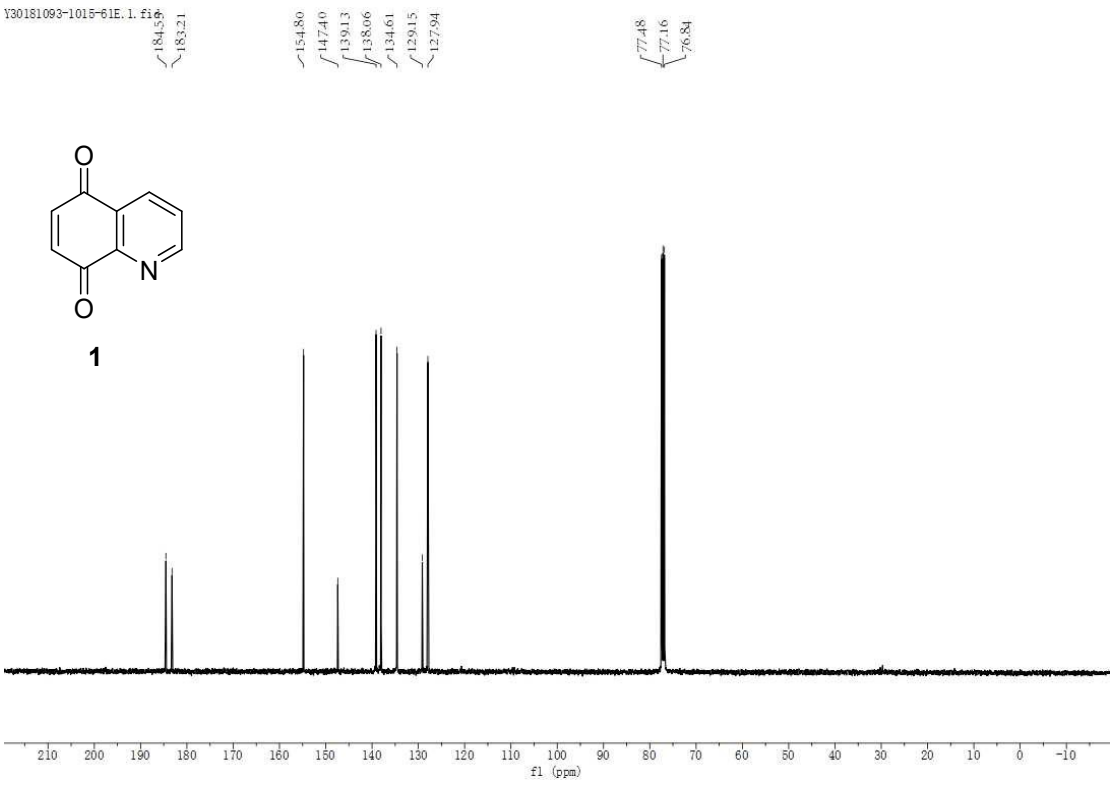
quinoline-5,8-diol

Yellow solid, 26% yield, Electricity = 14.3 F mol^{-1}. ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.81 (dd, J = 4.2, 1.7 Hz, 1H), 8.45 (dd, J = 8.5, 1.7 Hz, 1H), 7.48 (dd, J = 8.5, 4.2 Hz, 1H), 6.90 (d, J = 8.2 Hz, 1H), 6.79 (d, J = 8.2 Hz, 1H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 148.5, 145.6, 144.8, 138.7, 131.2, 120.7, 120.1, 110.9, 108.9. HRMS (EI): exact mass calculated for $C_9H_7NO_2$ $[M]^+$ require m/z = 161.0477, found m/z = 161.0478.

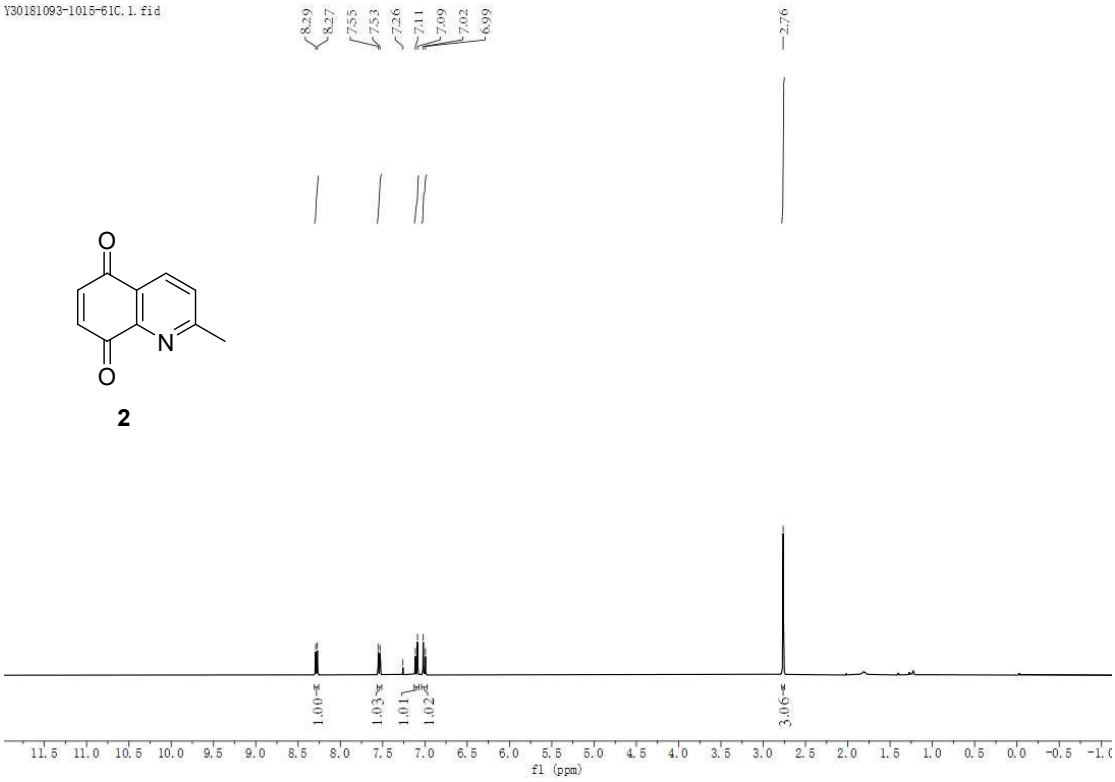
F: NMR Spectra of Products.

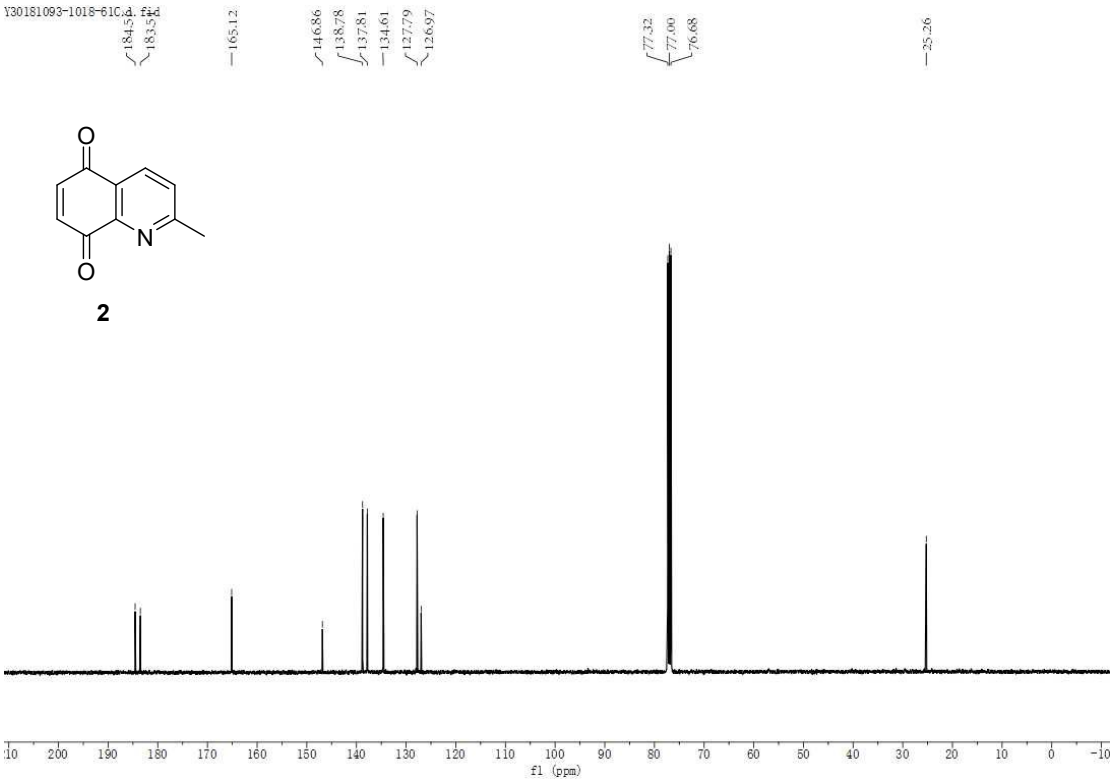
1: quinoline-5,8-dione



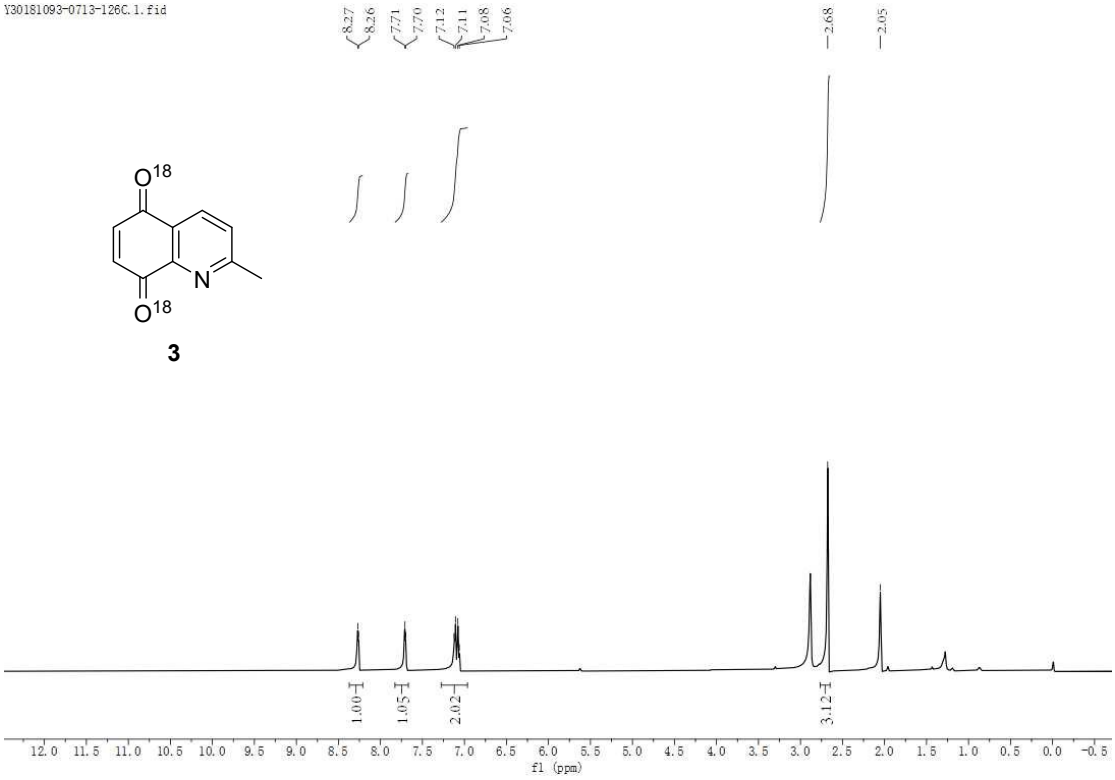


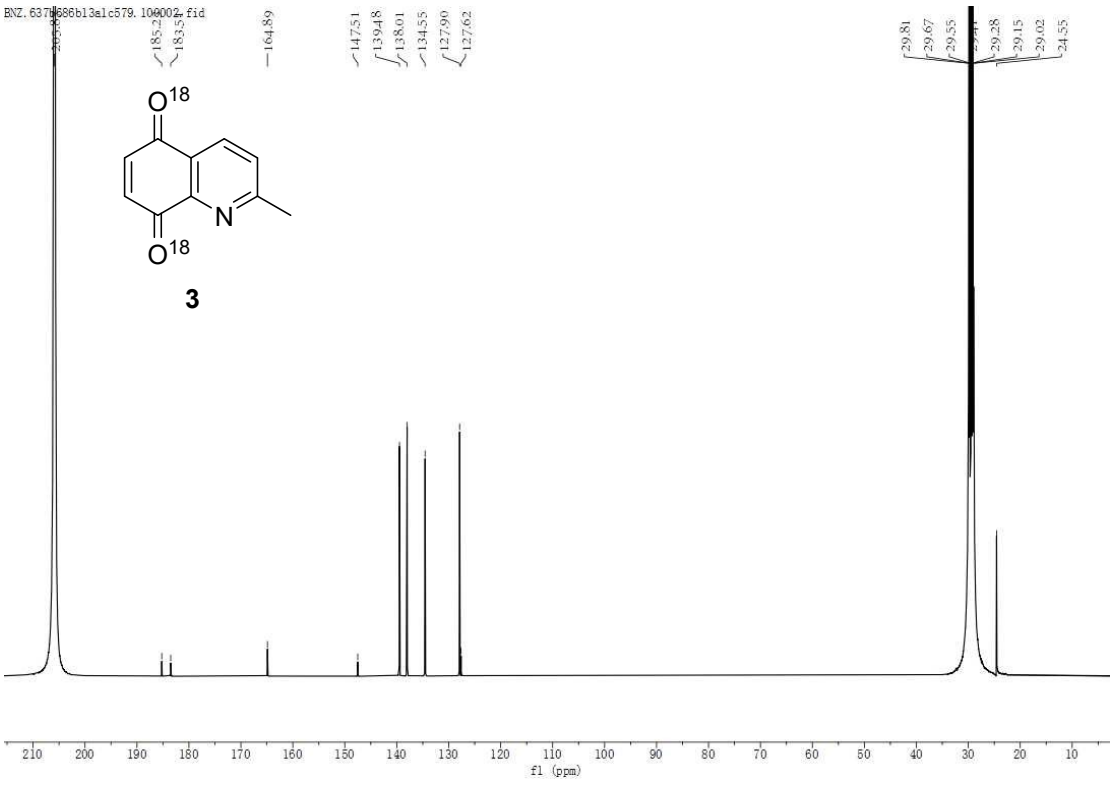
2: 2-methylquinoline-5,8-dione



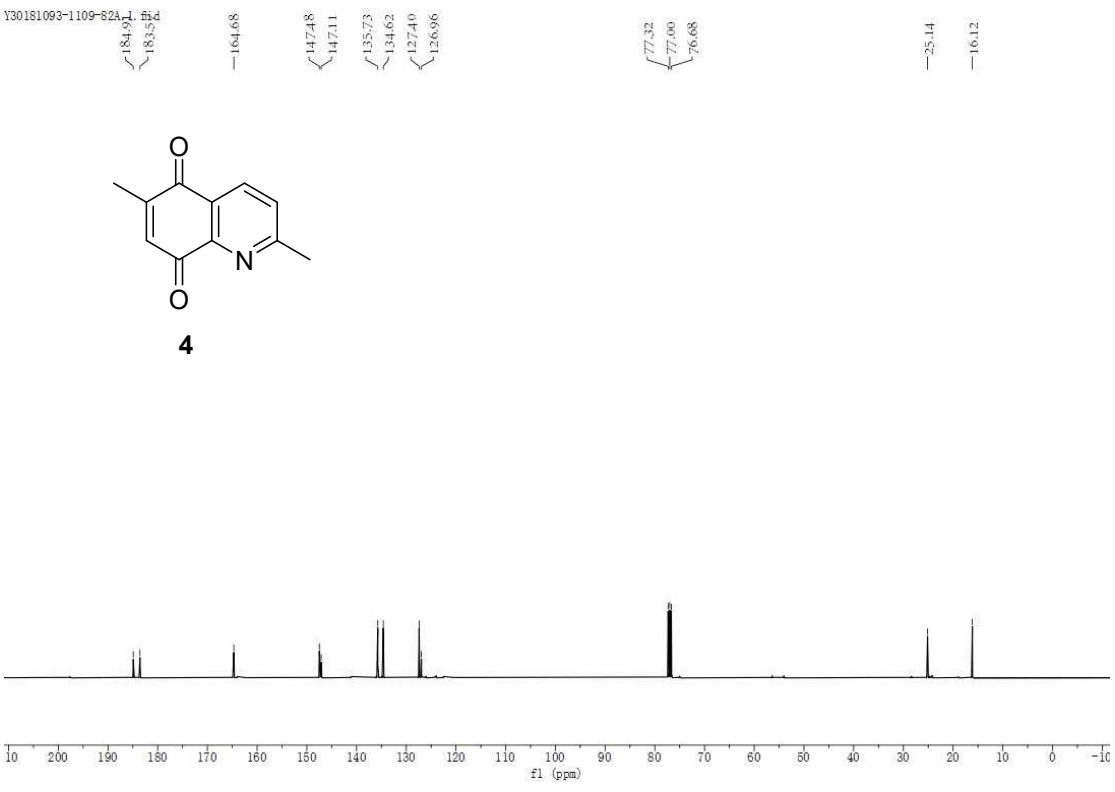


3: 2-methylquinoline-5,8-dione

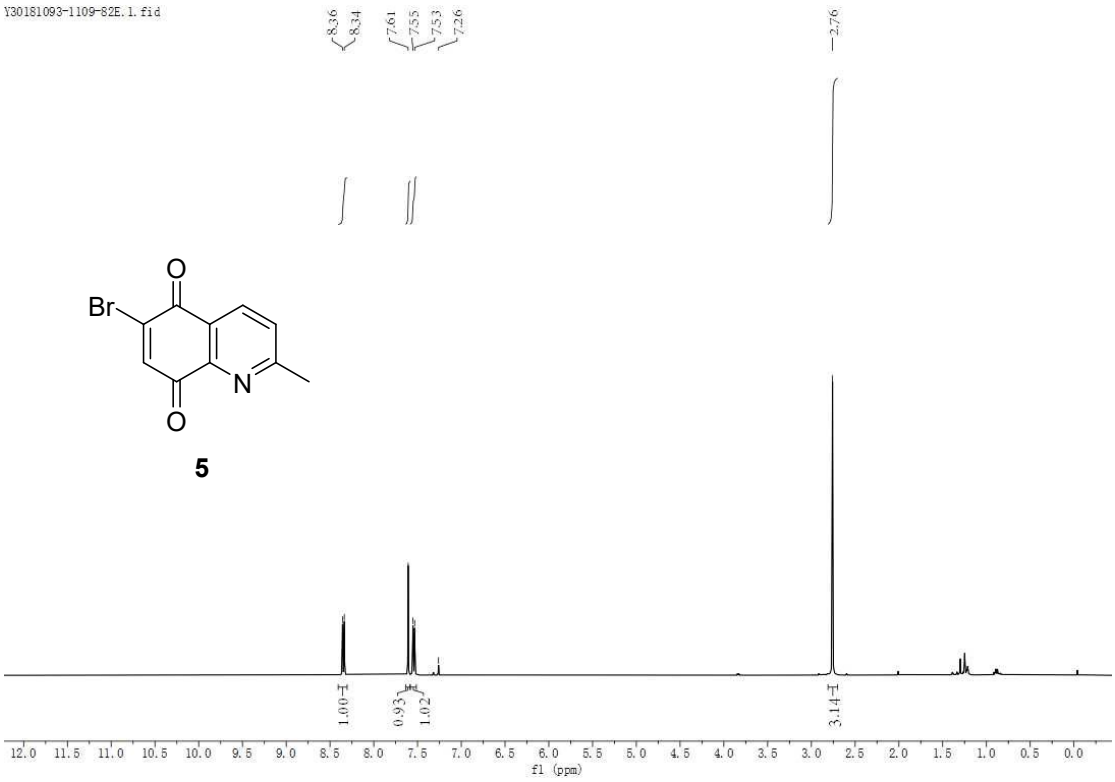




4: 2,6-dimethylquinoline-5,8-dione



5: 6-bromo-2-methylquinoline-5,8-dione



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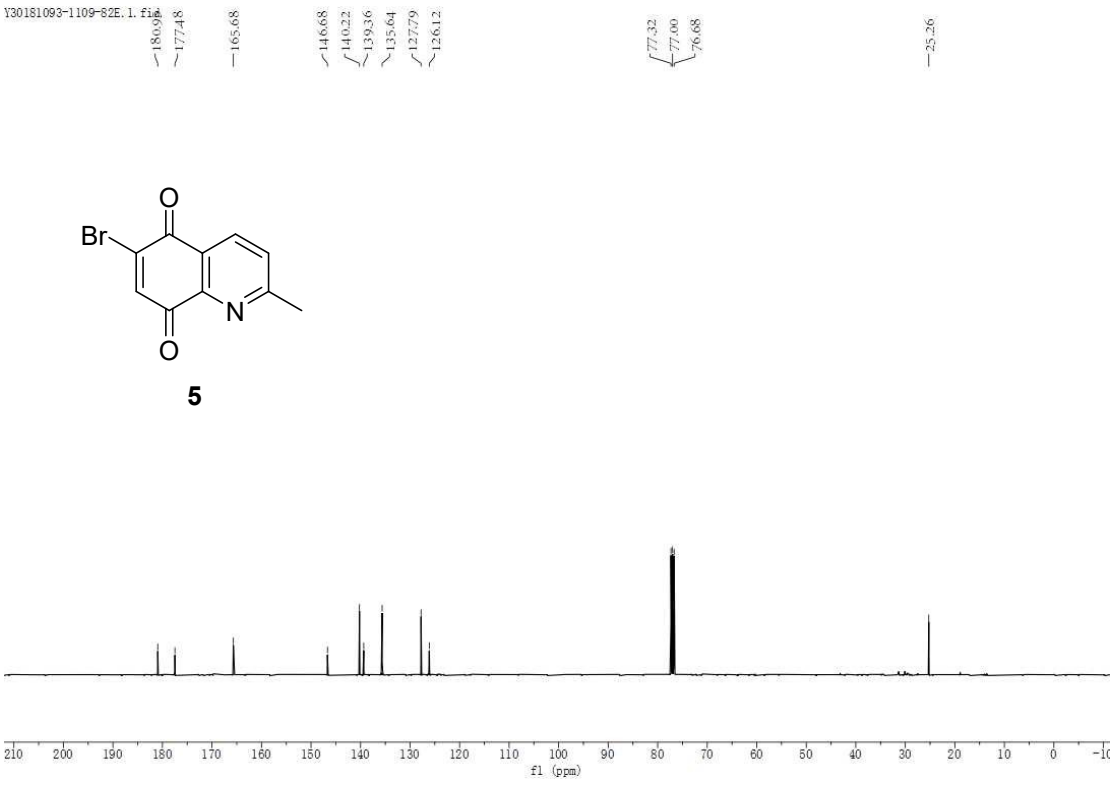
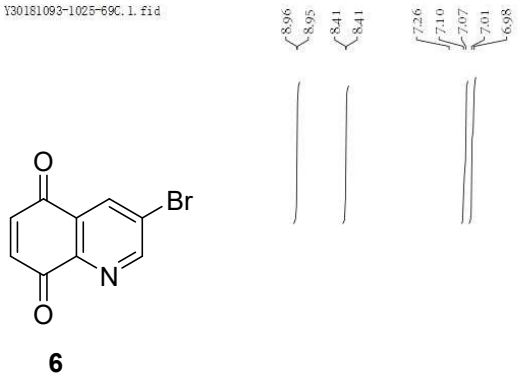


5

6. 3-bromoquinoline-5,8-dione



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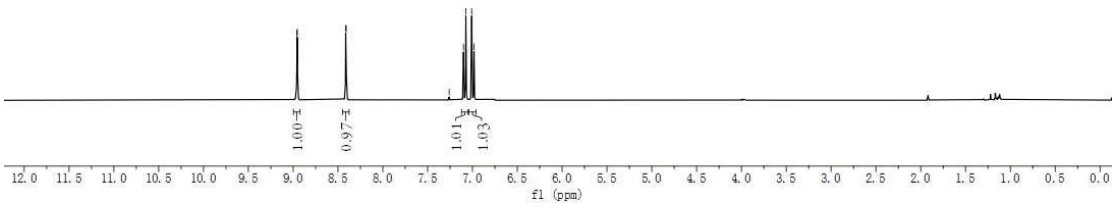

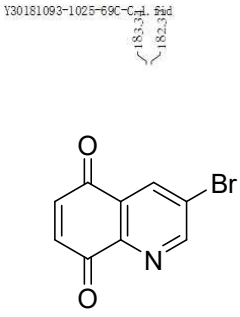

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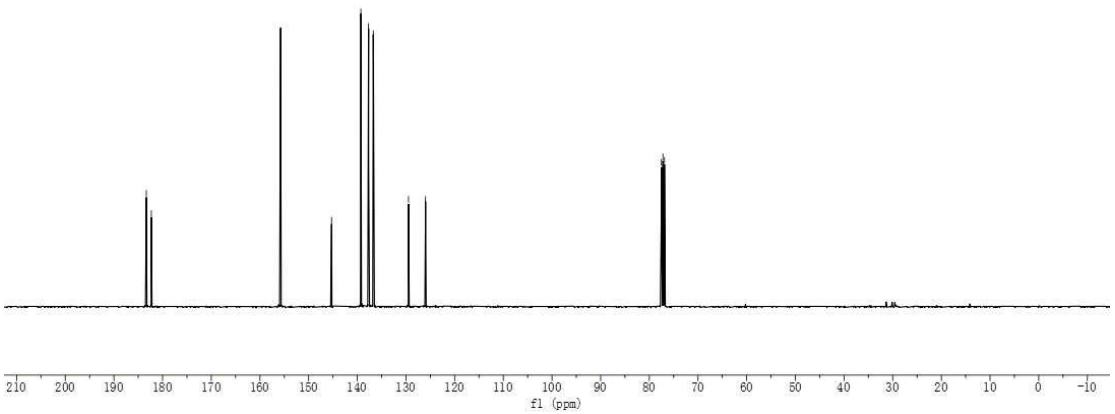
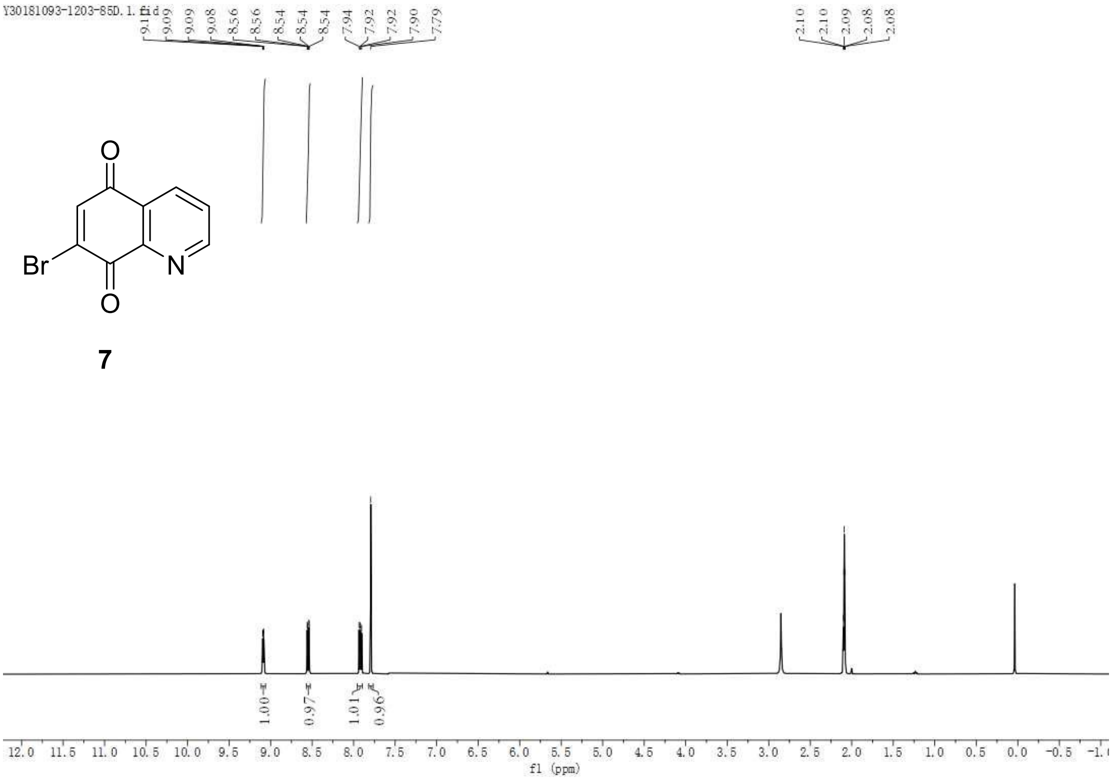
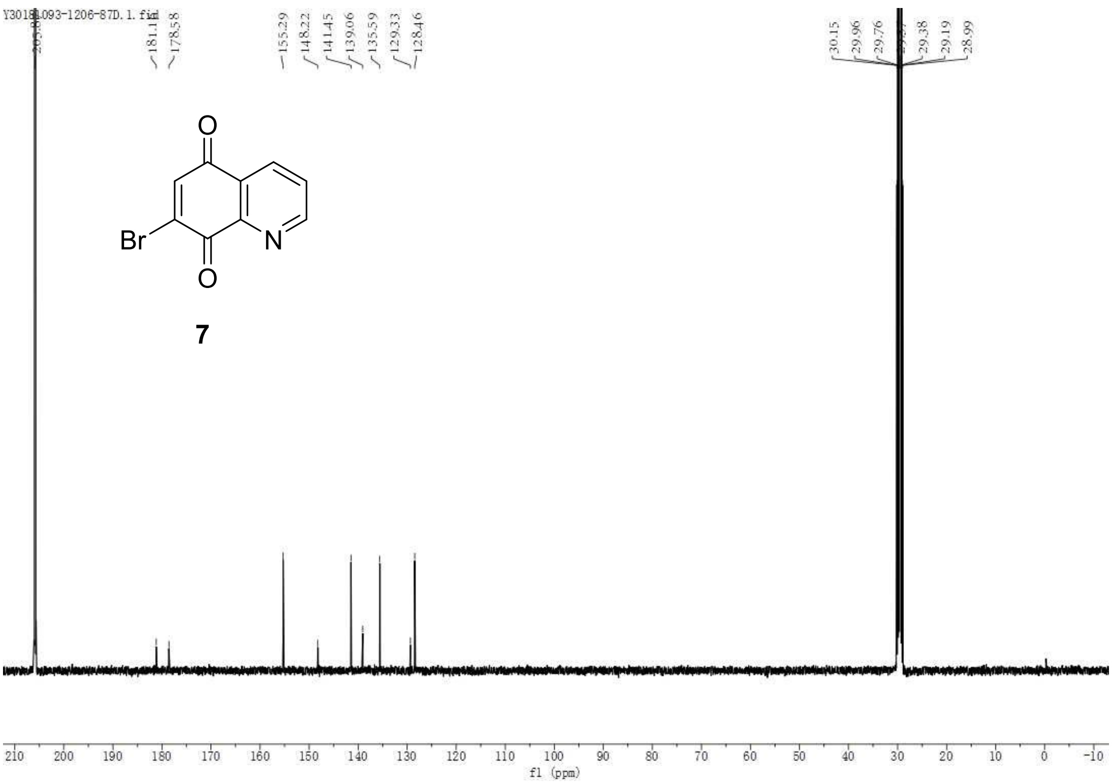
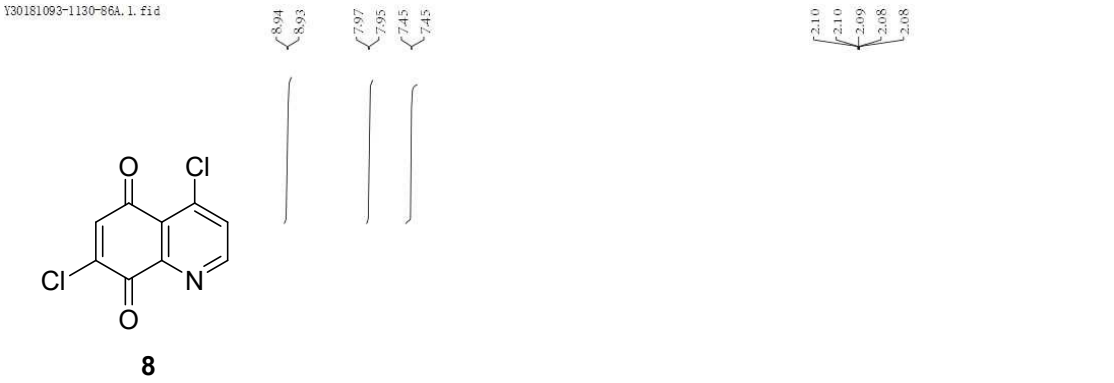


7: 7-bromoquinoline-5,8-dione





8. 4,7-dichloroquinoline-5,8-dione



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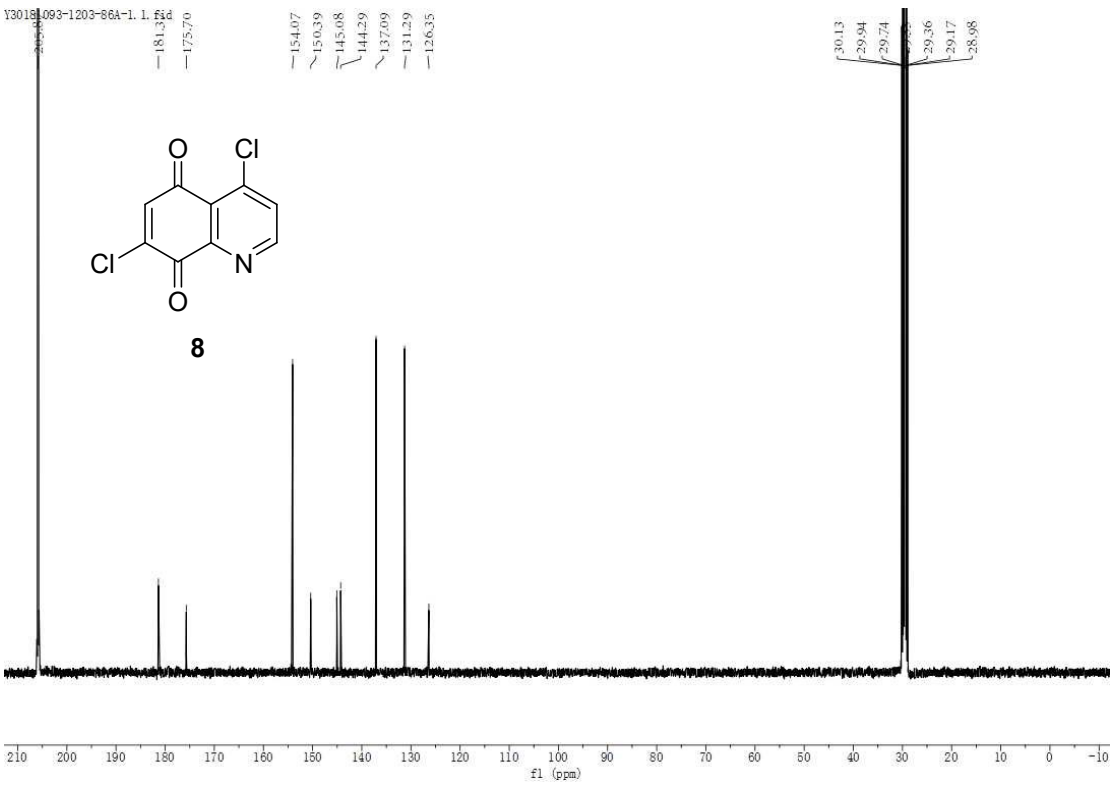
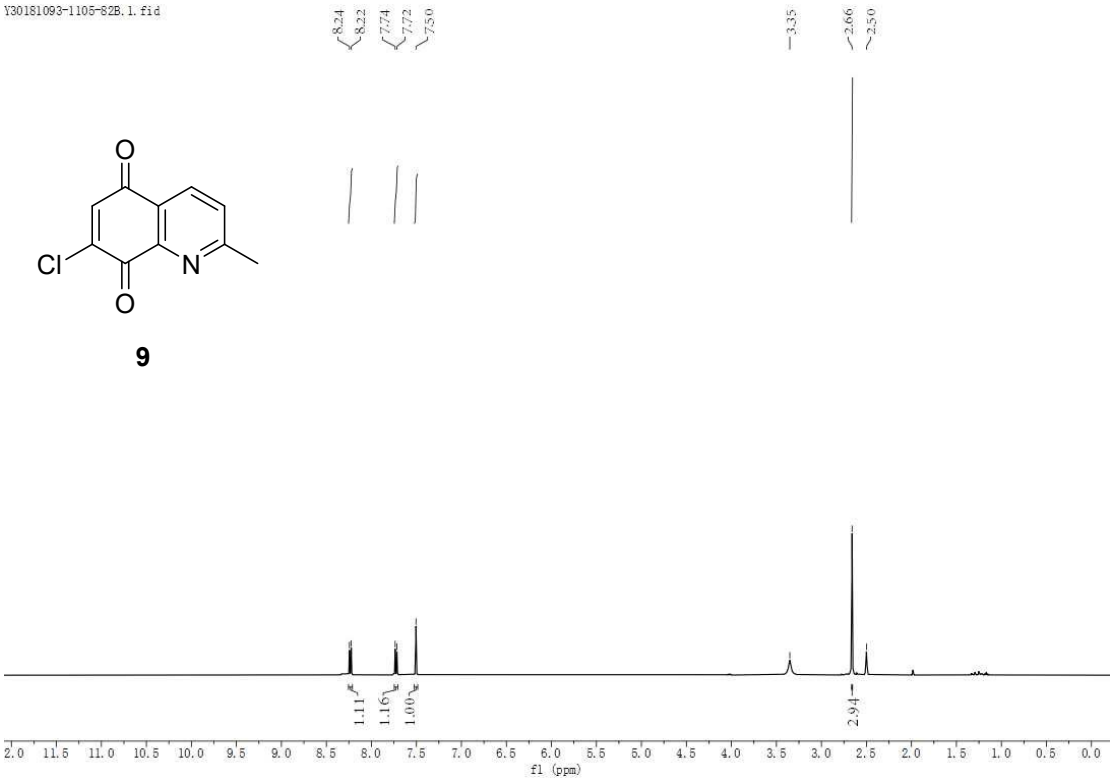


8

9: 7-chloro-2-methylquinoline-5,8-dione



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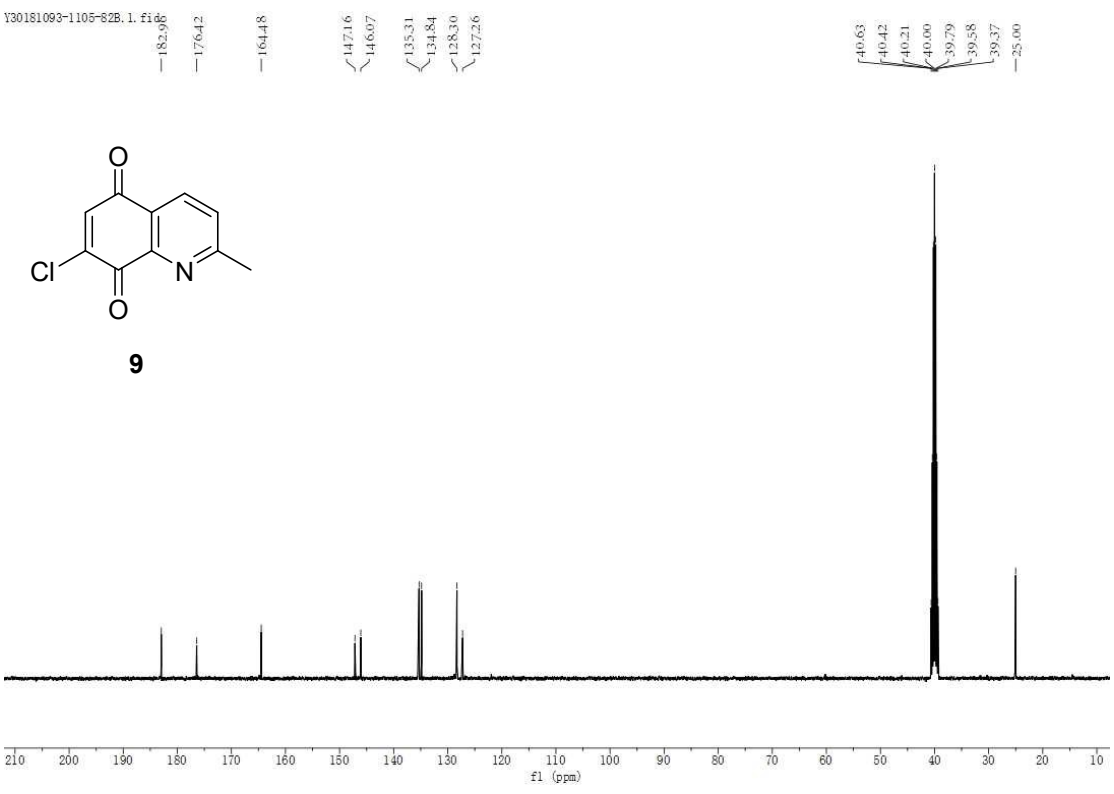
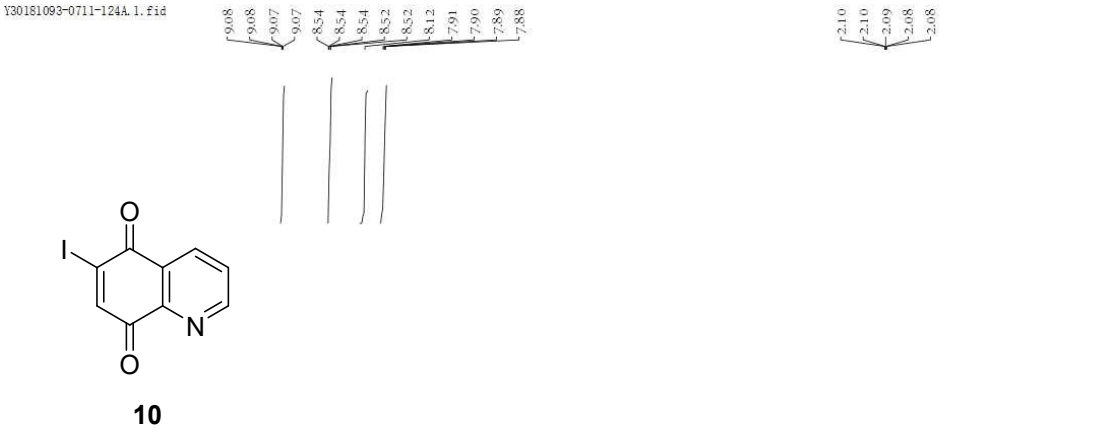


9

10: 6-iodoquinoline-5,8-dione



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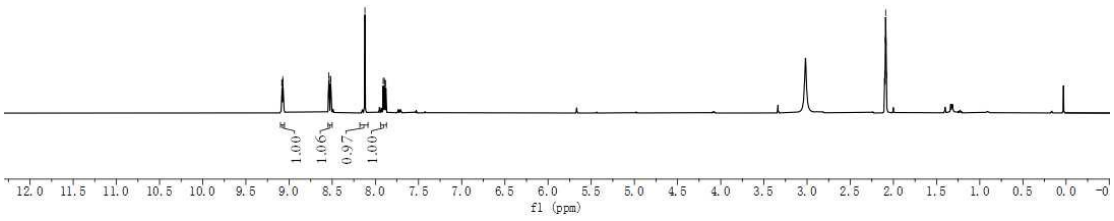
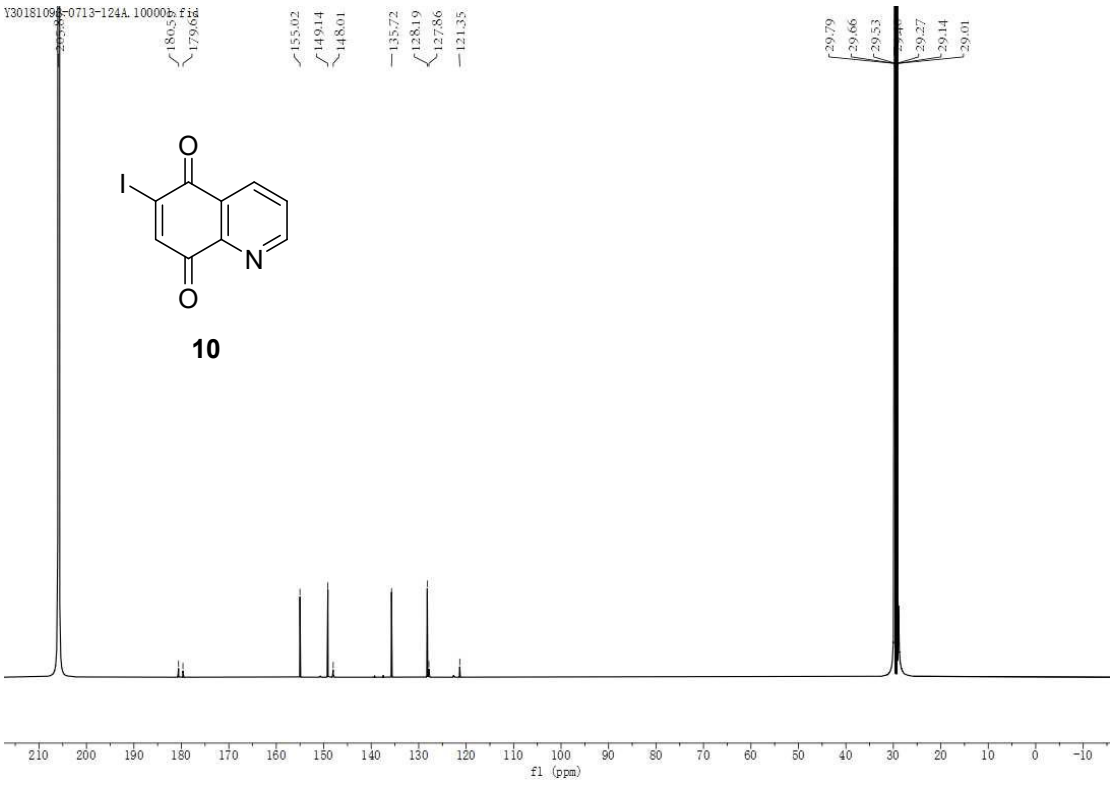
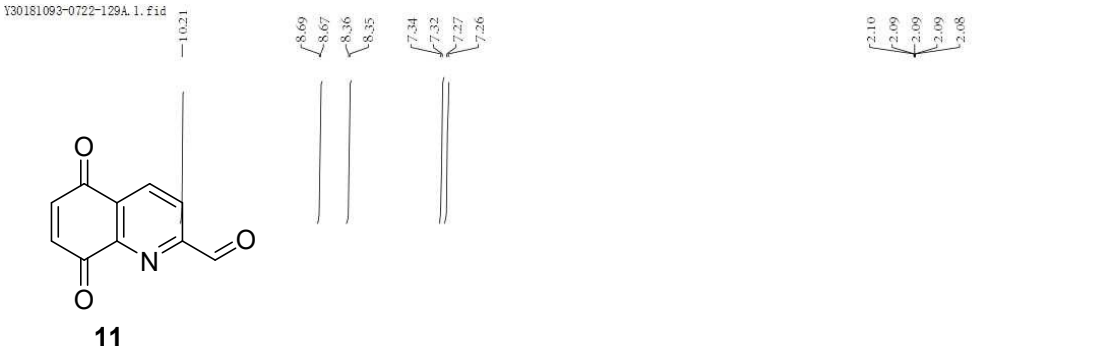
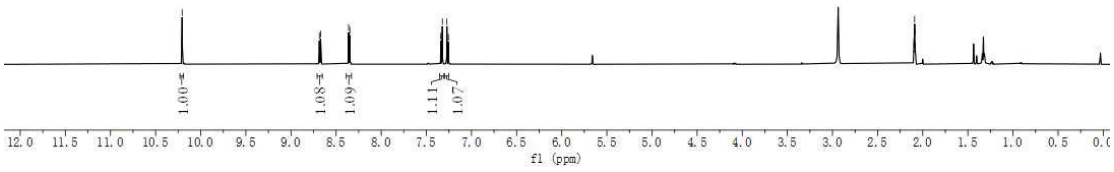




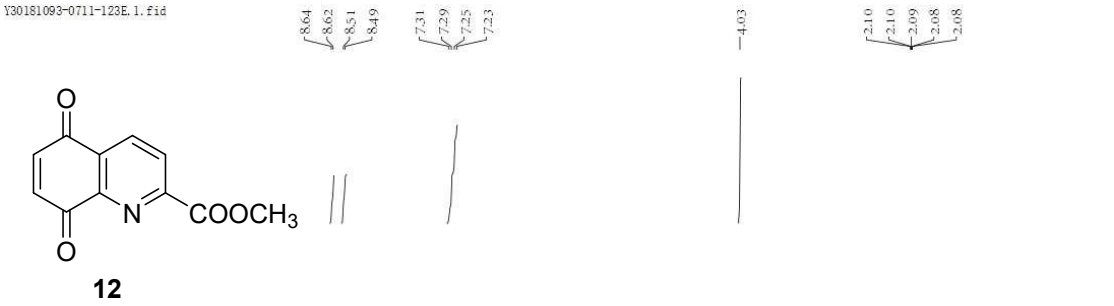
10

11: 5,8-dioxo-5,8-dihydroquinoline-2-carbaldehyde





12. methyl 5,8-dioxo-5,8-dihydroquinoline-2-carboxylate



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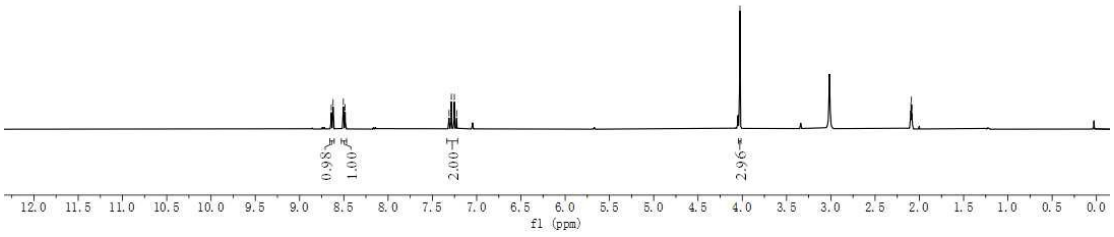
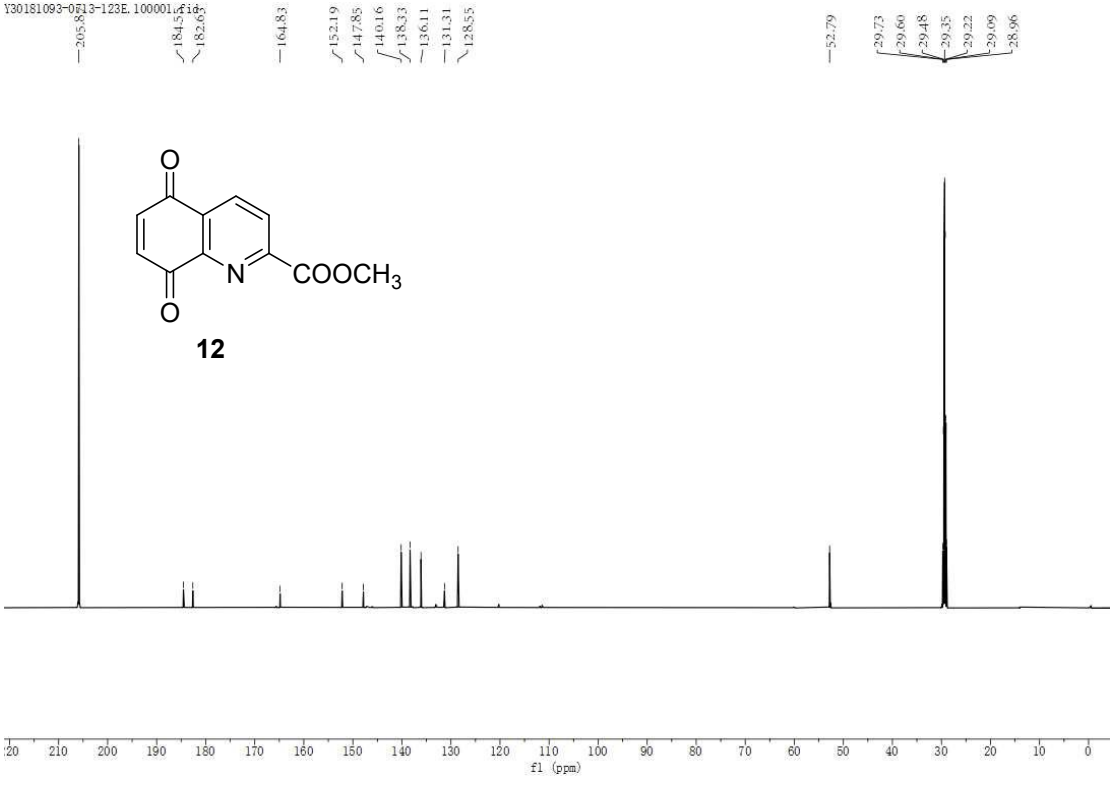
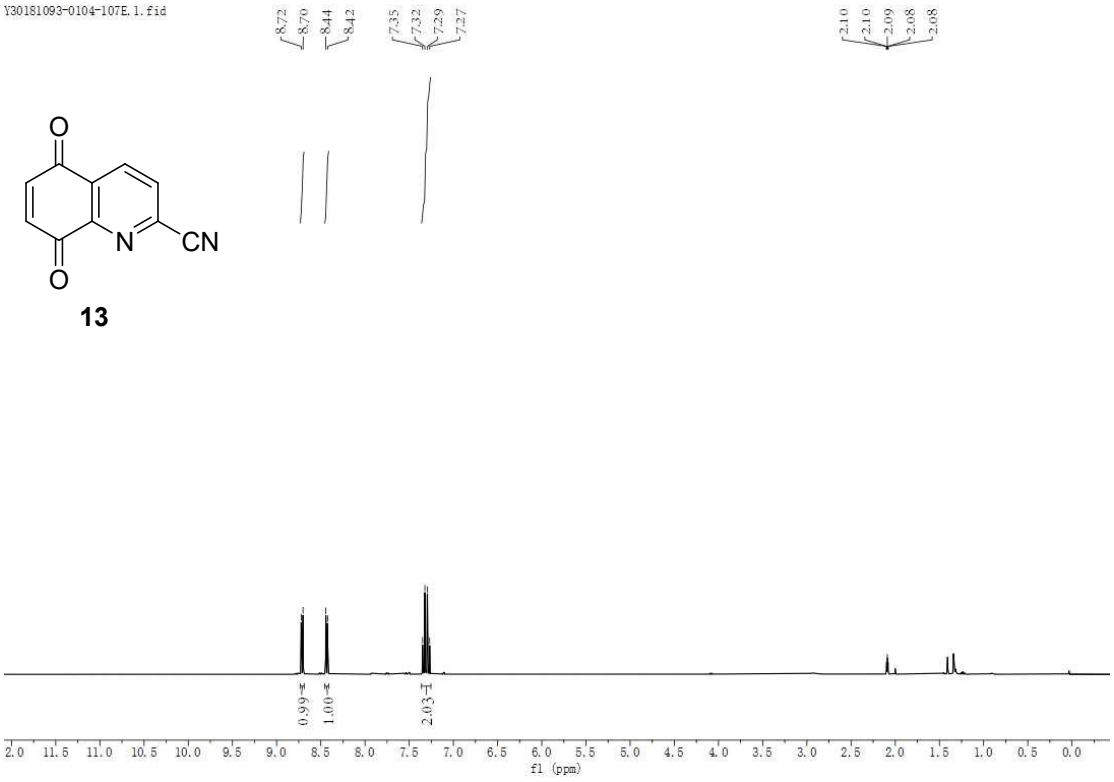
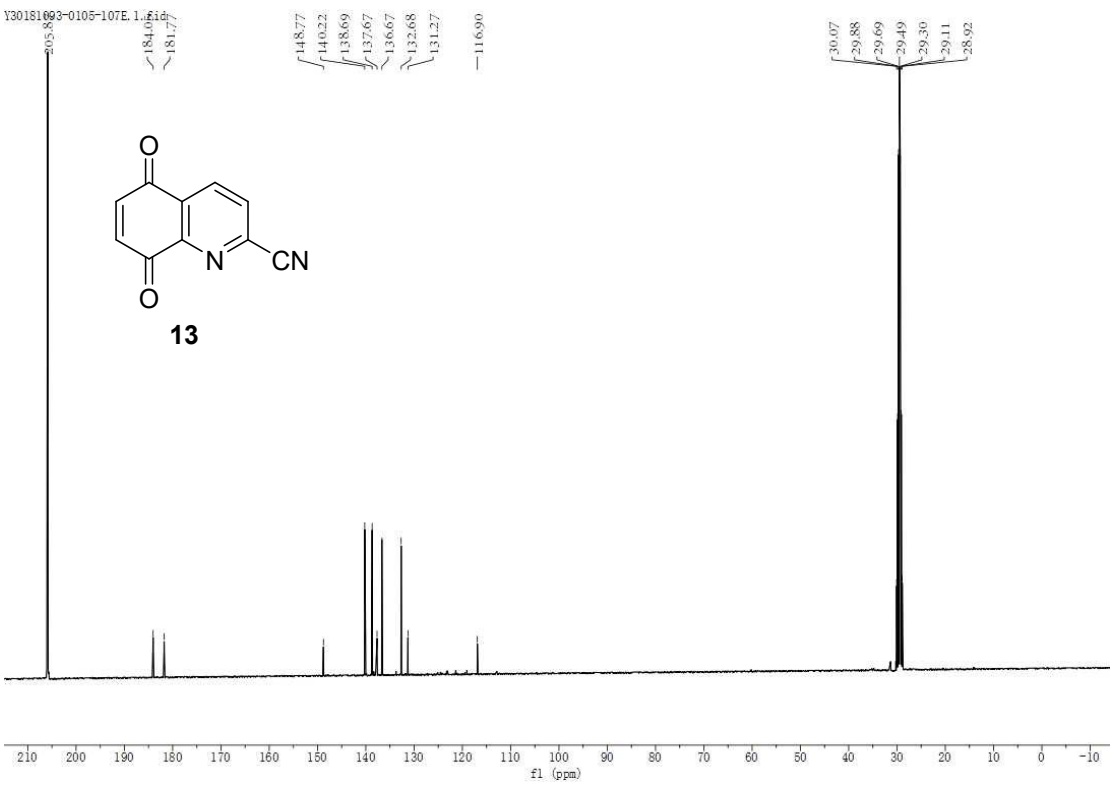




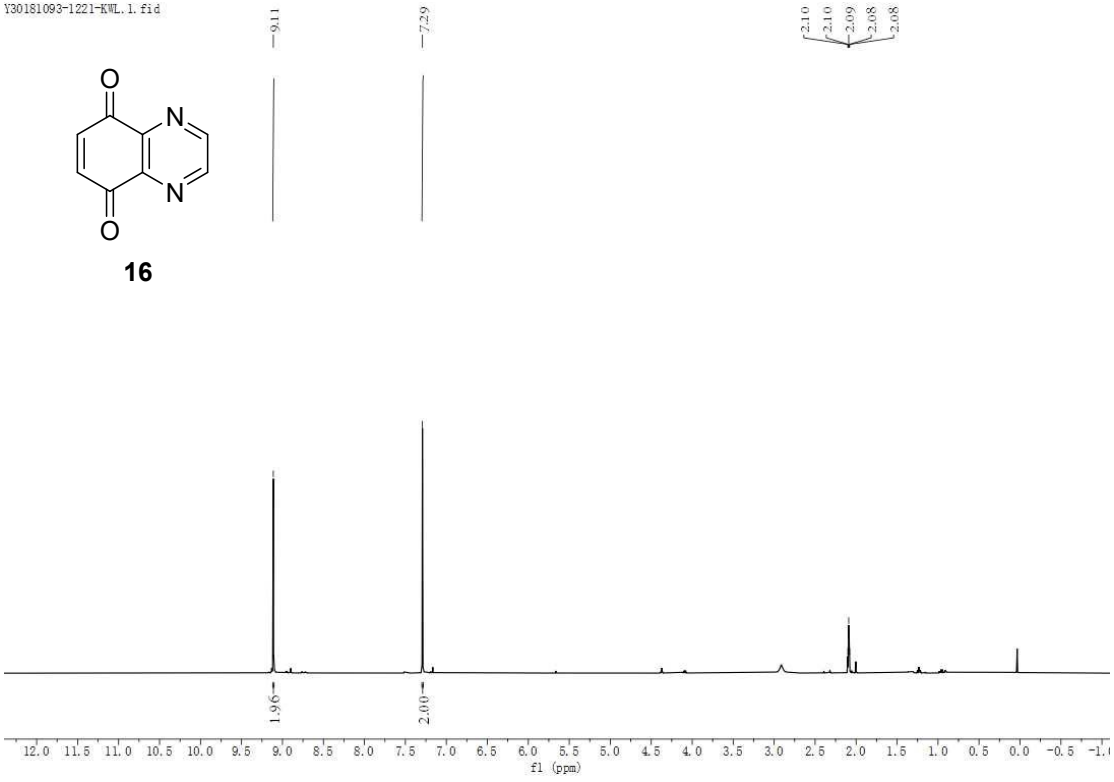
12

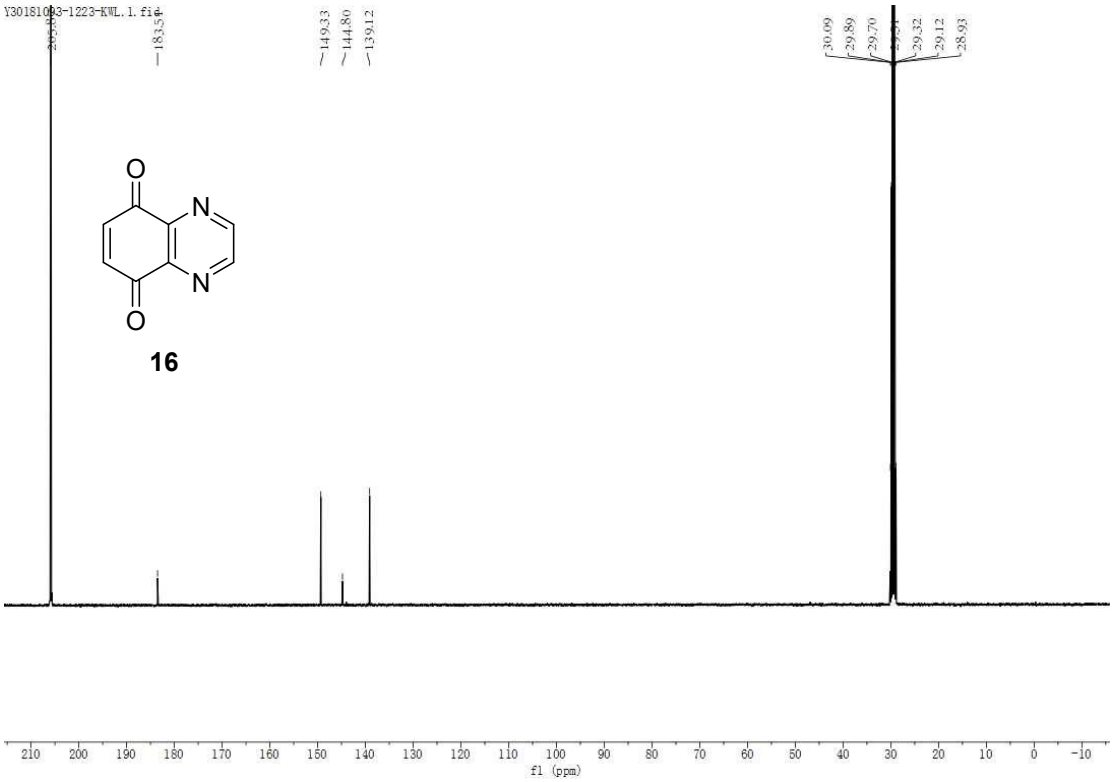
13: 5,8-dioxo-5,8-dihydroquinoline-2-carbonitrile



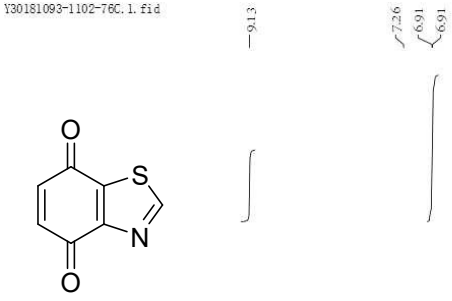


16: quinoxaline-5,8-dione





17: benzo[d]thiazole-4,7-dione



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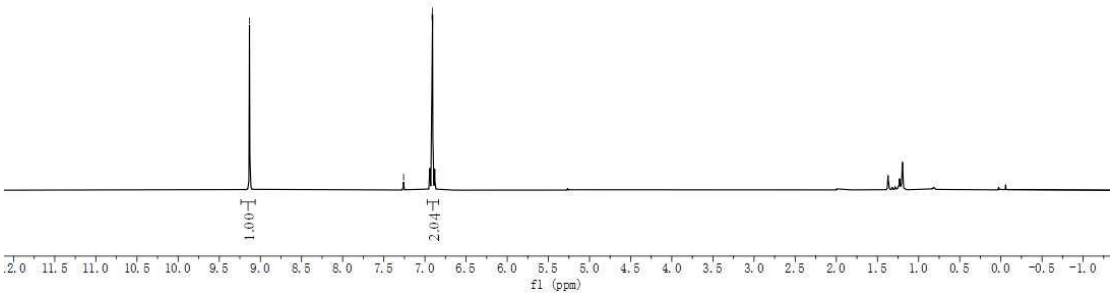

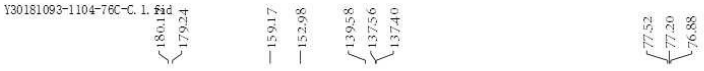

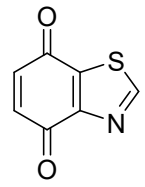

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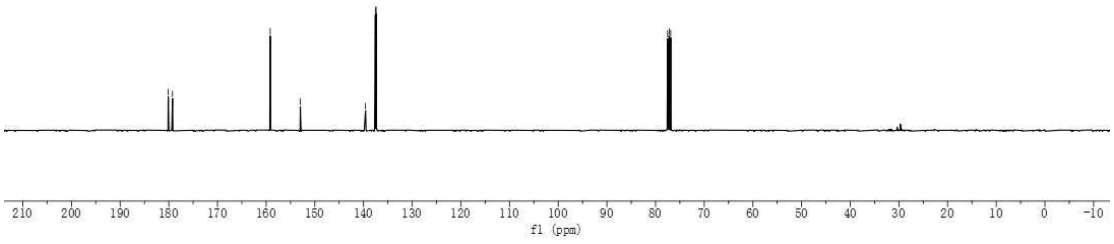
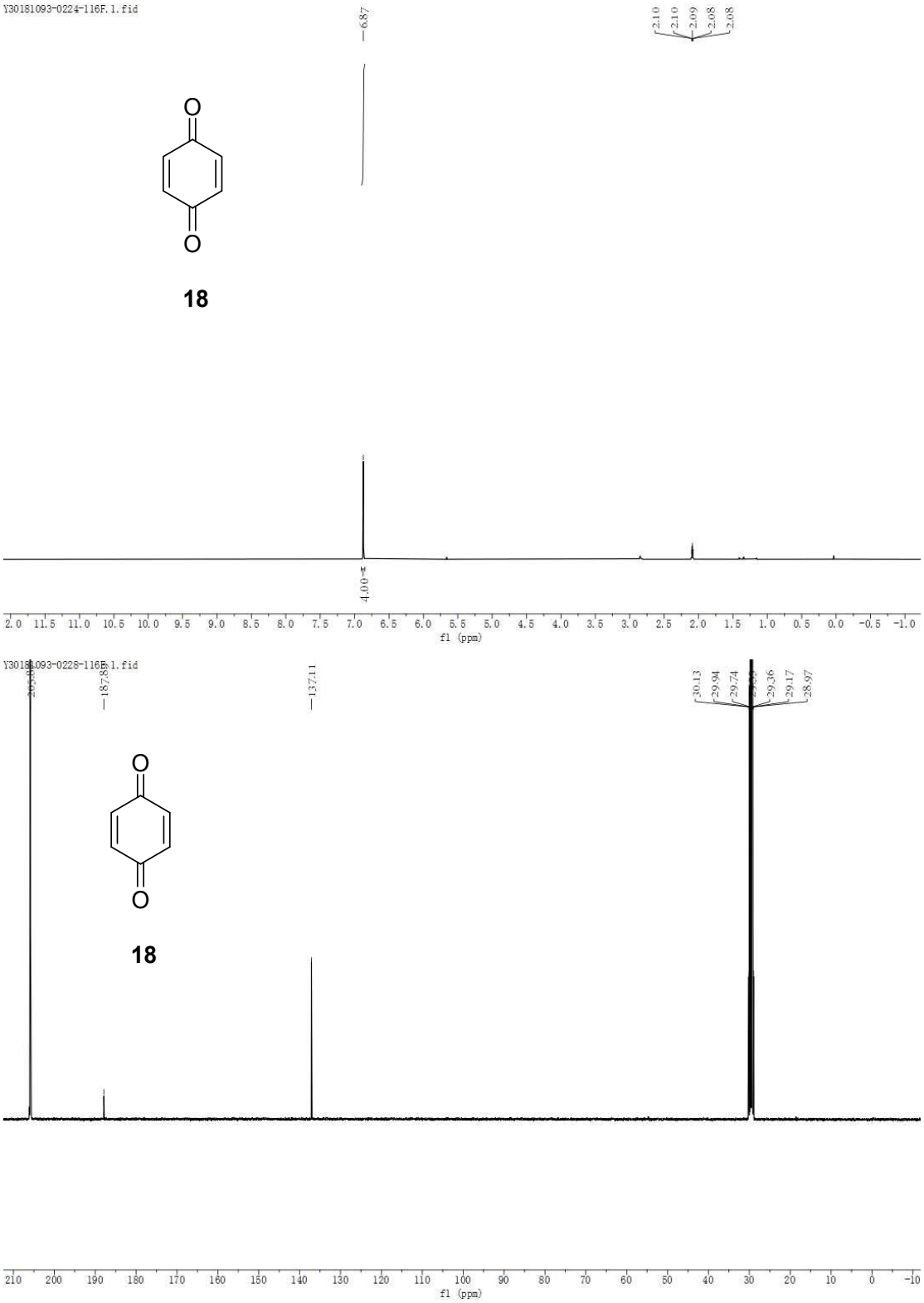


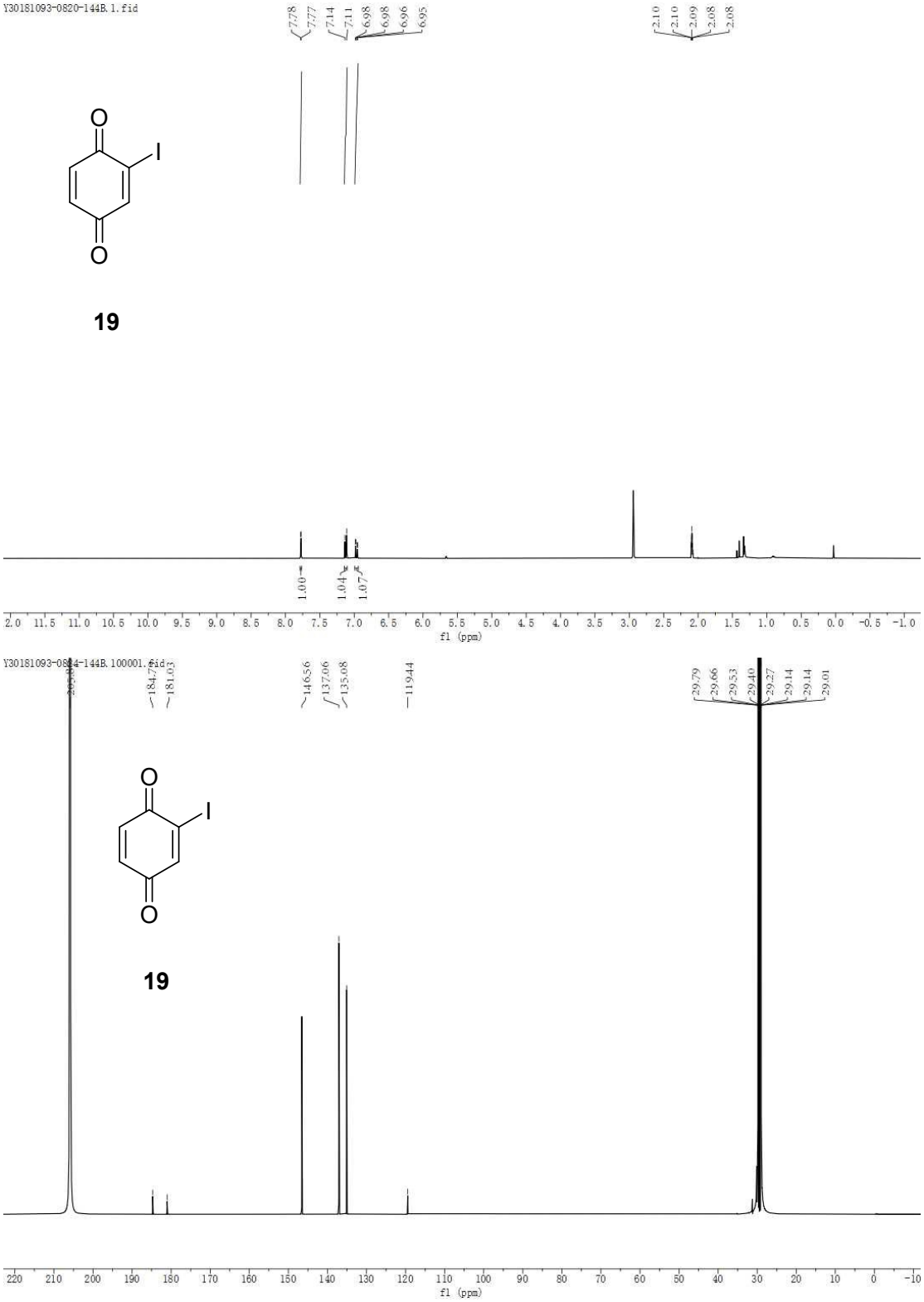
18: benzoquinone



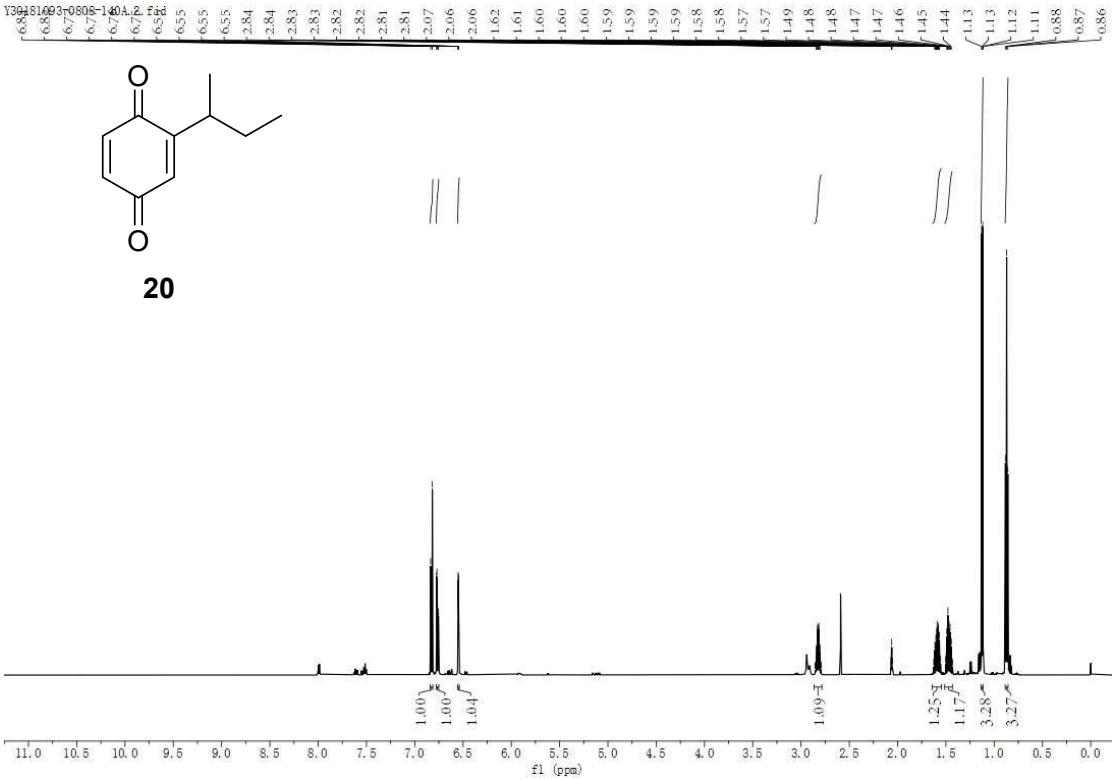
18

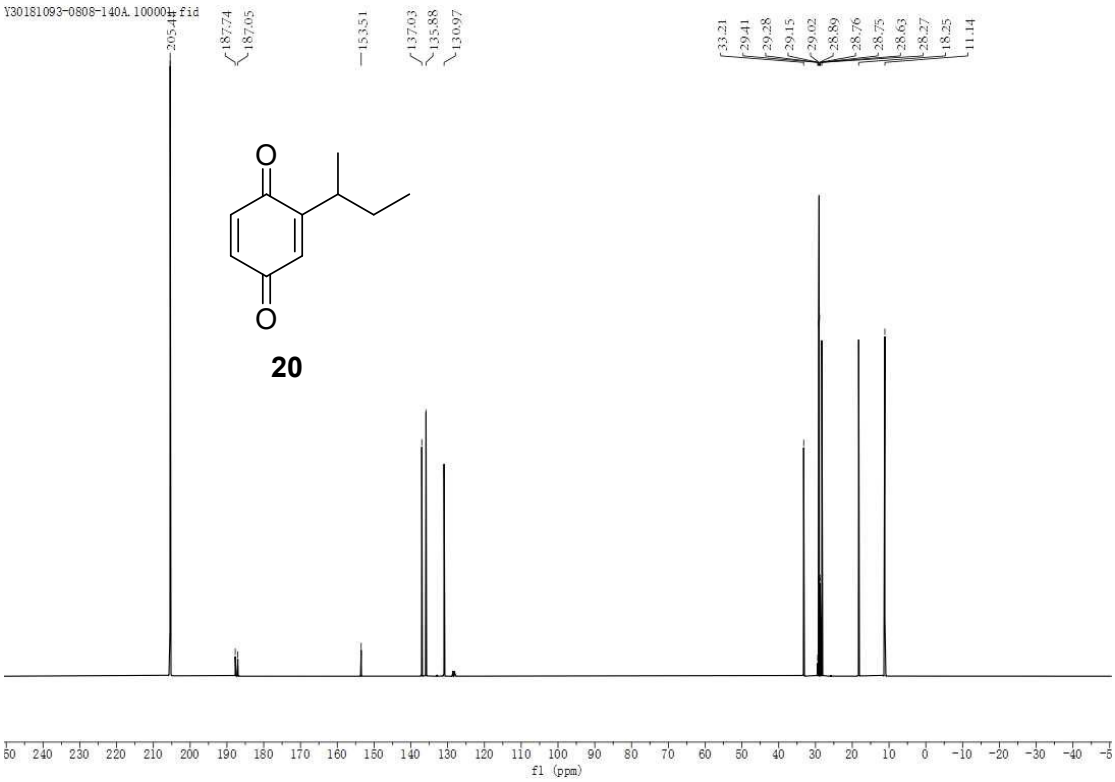
18

19: 2-iodocyclohexa-2,5-diene-1,4-dione

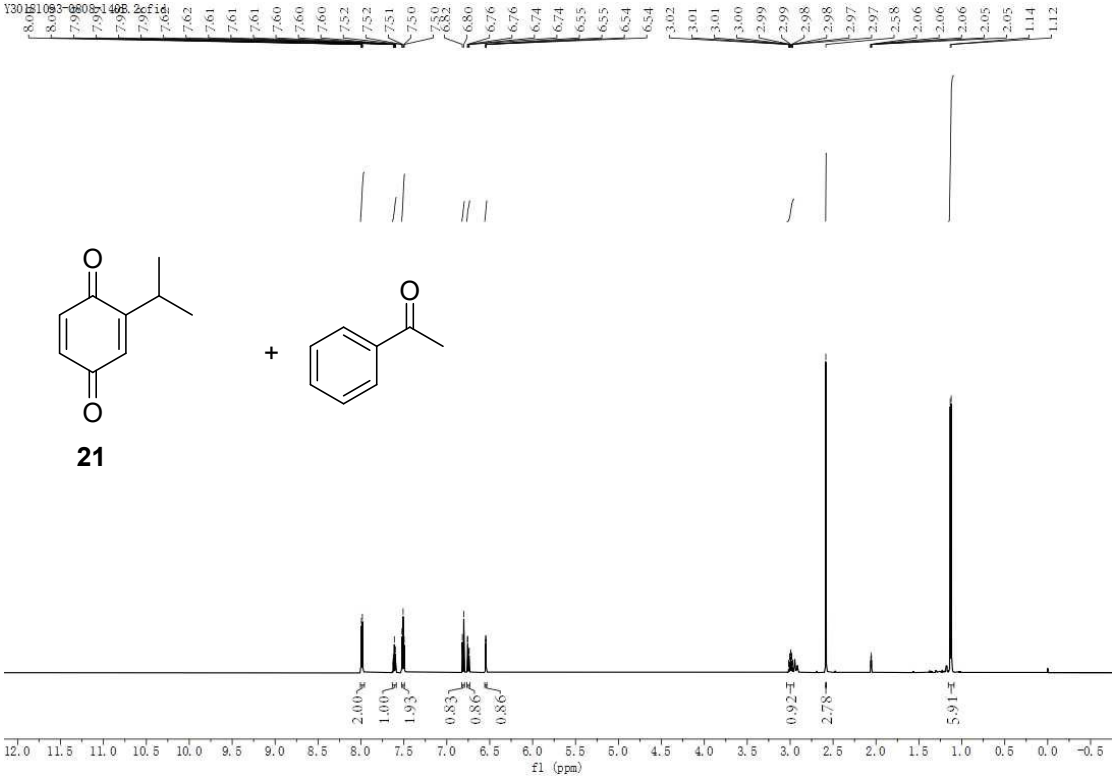


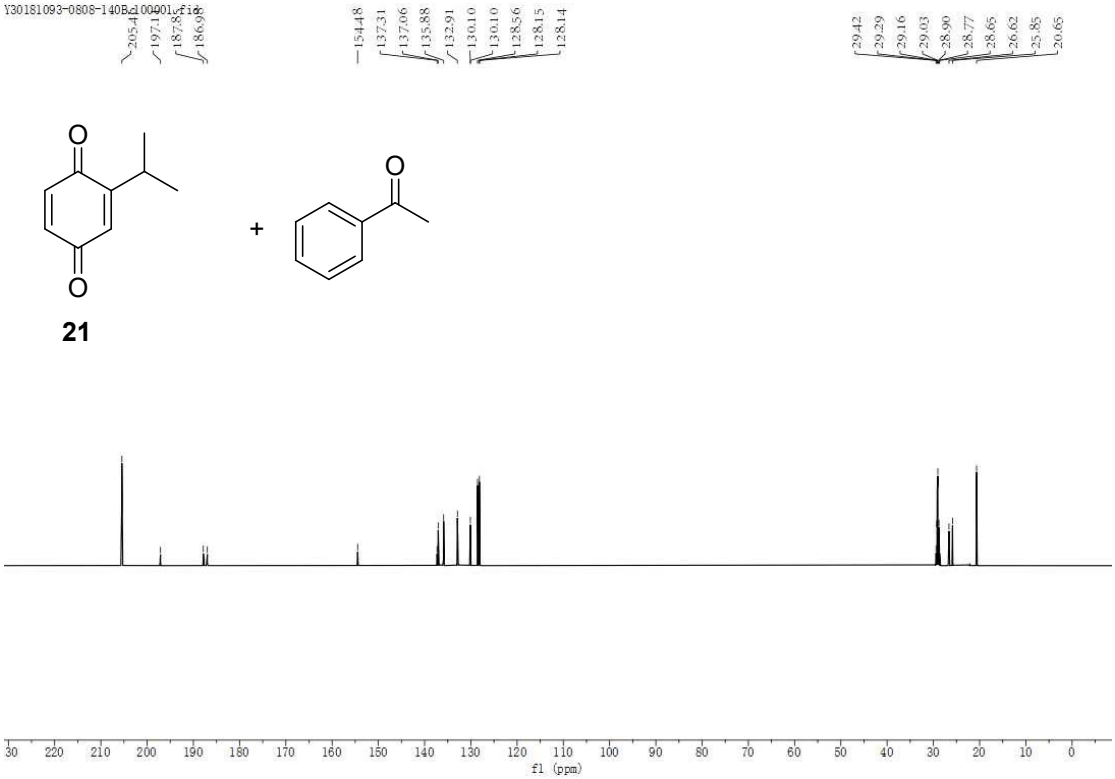
20: 2-(sec-butyl)cyclohexa-2,5-diene-1,4-dione



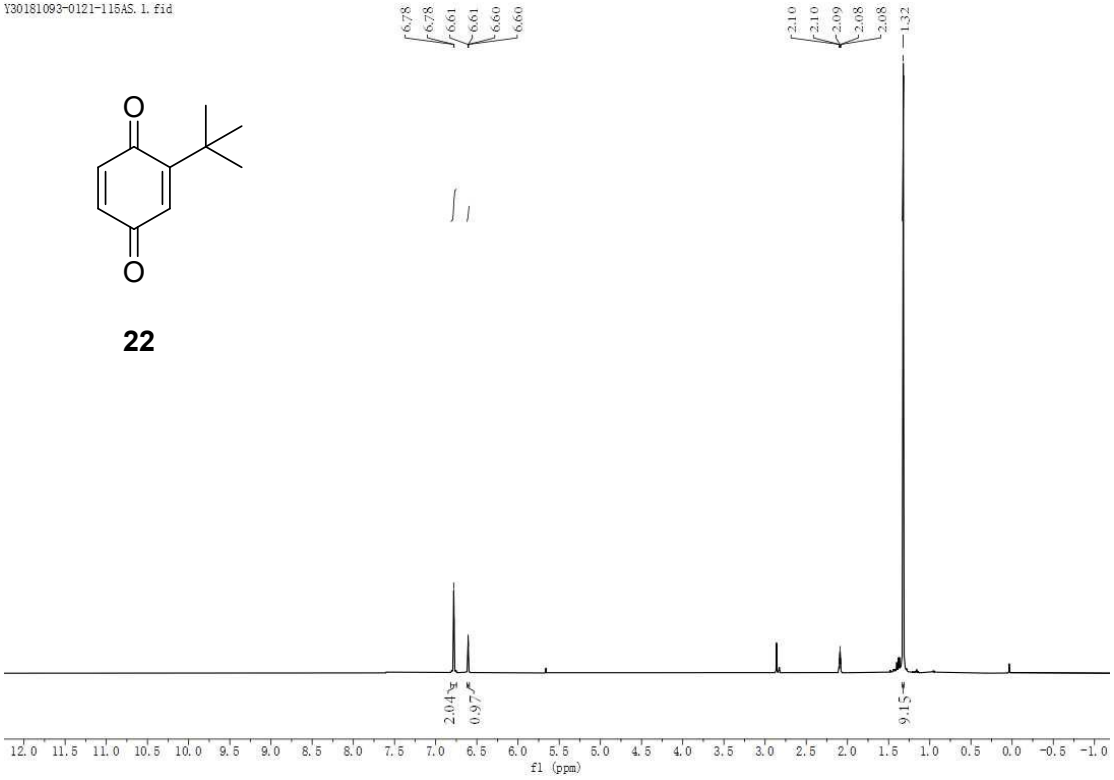


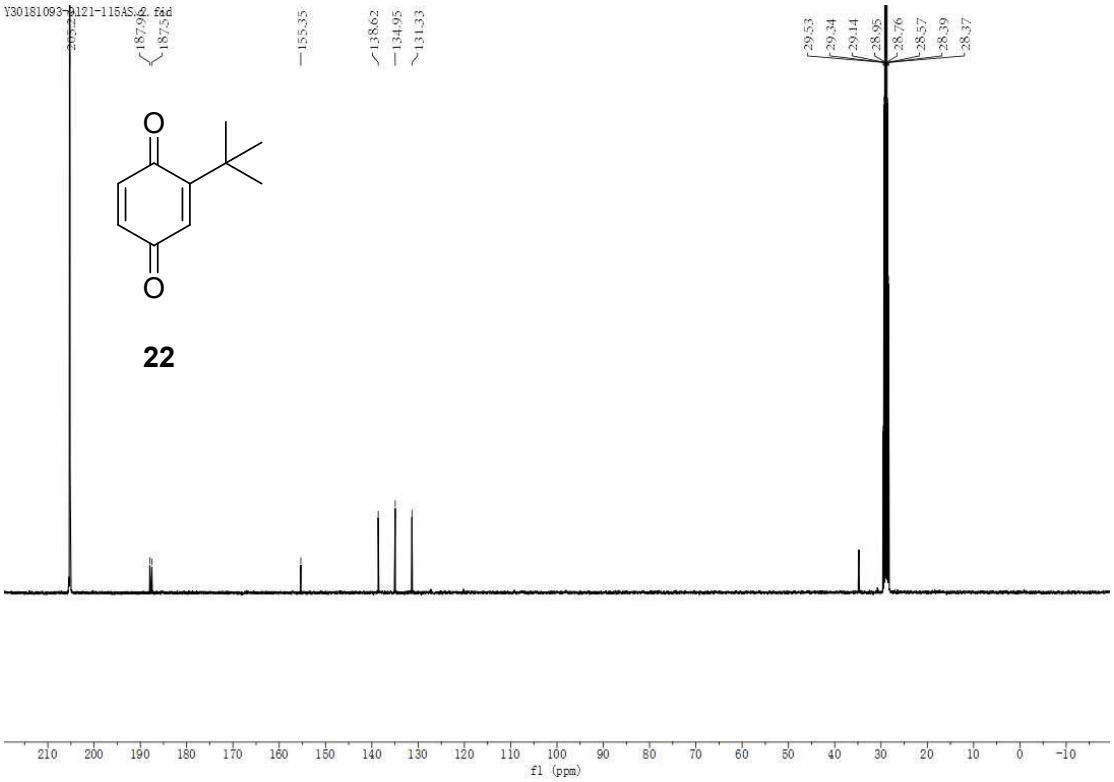
21: 2-isopropylcyclohexa-2,5-diene-1,4-dione and acetophenone



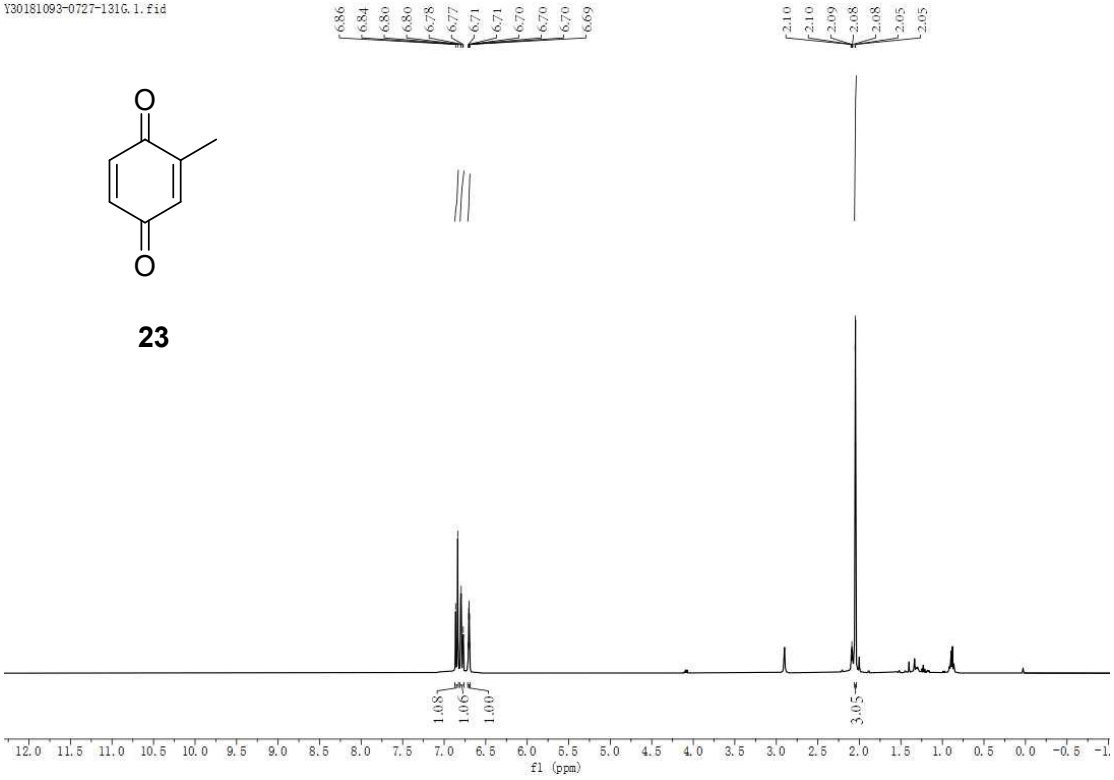


22: 2-(tert-butyl)cyclohexa-2,5-diene-1,4-dione



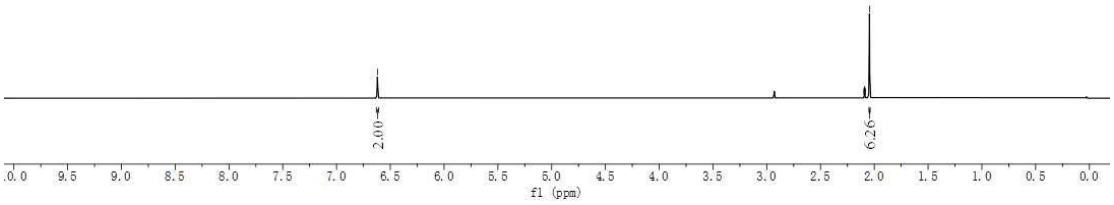


23: 2-methylcyclohexa-2,5-diene-1,4-dione



24: 2,6-dimethylcyclohexa-2,5-diene-1,4-dione

24



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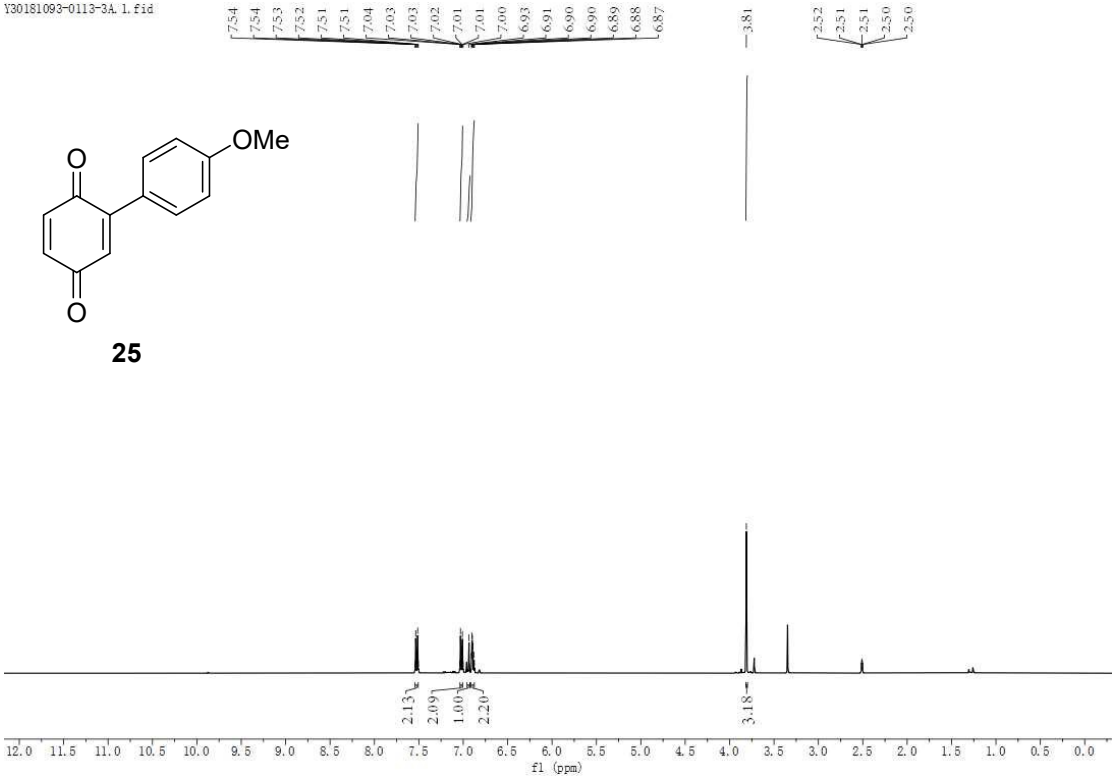
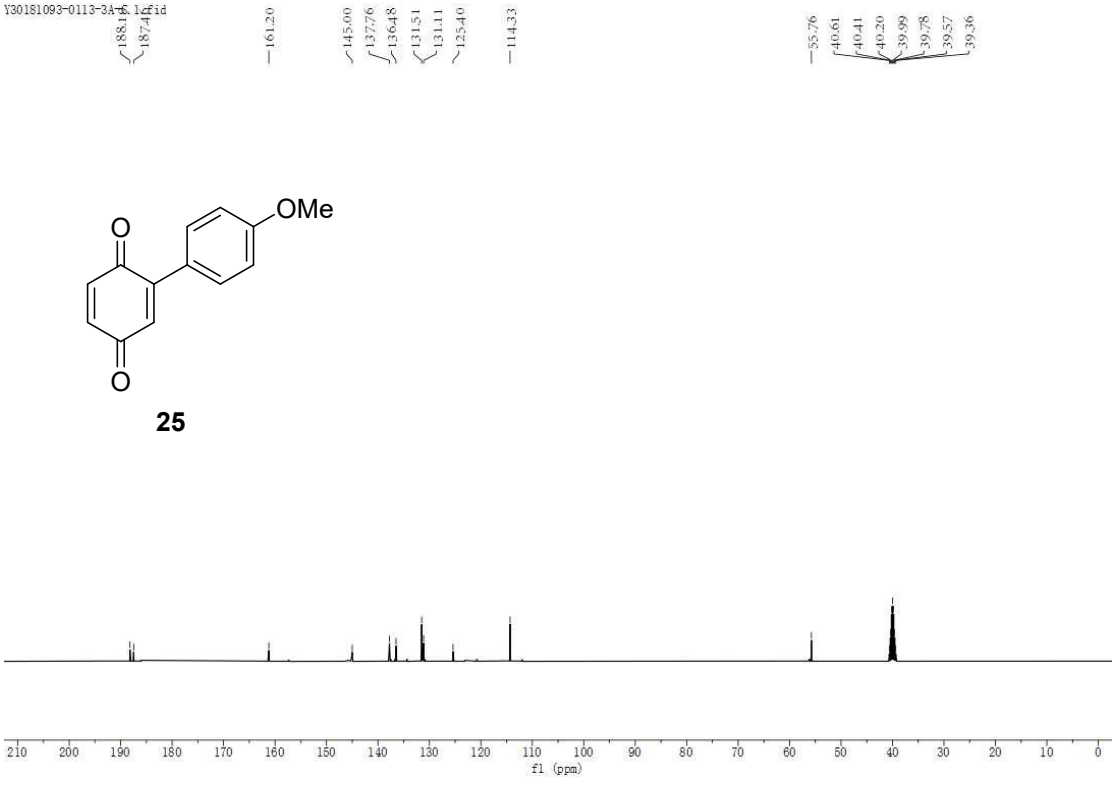
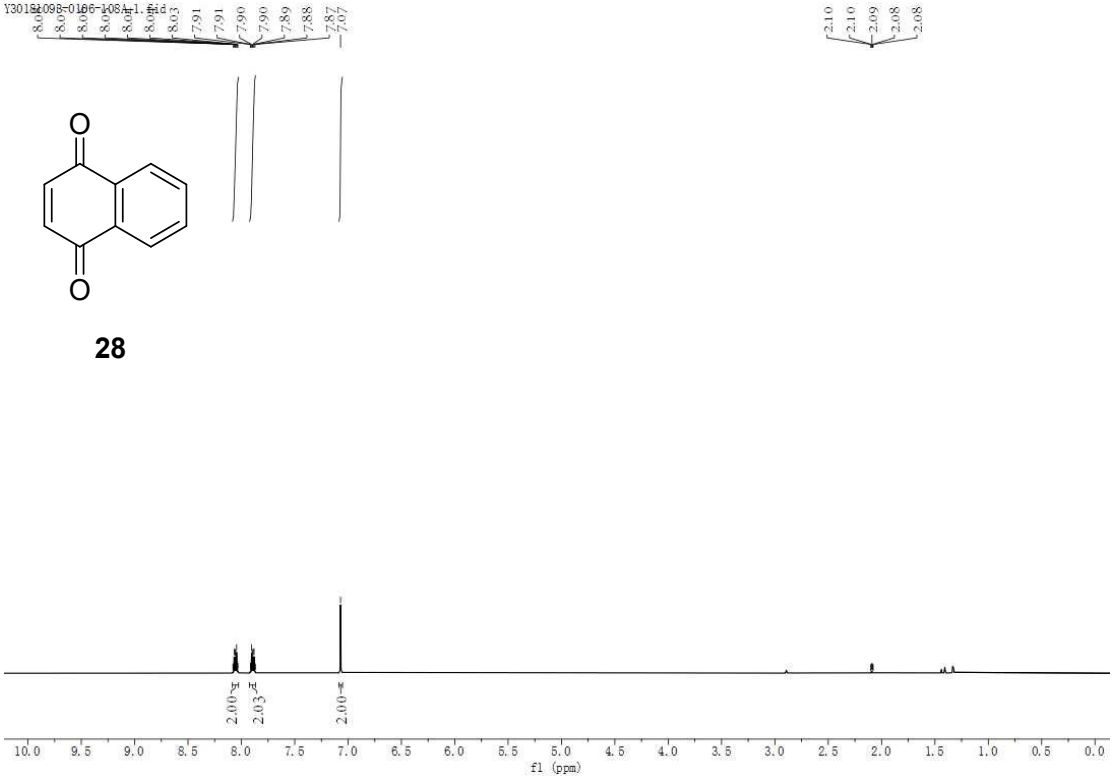
25: 4'-methoxy-[1,1'-biphenyl]-2,5-dione





28: naphthalene-1,4-dione



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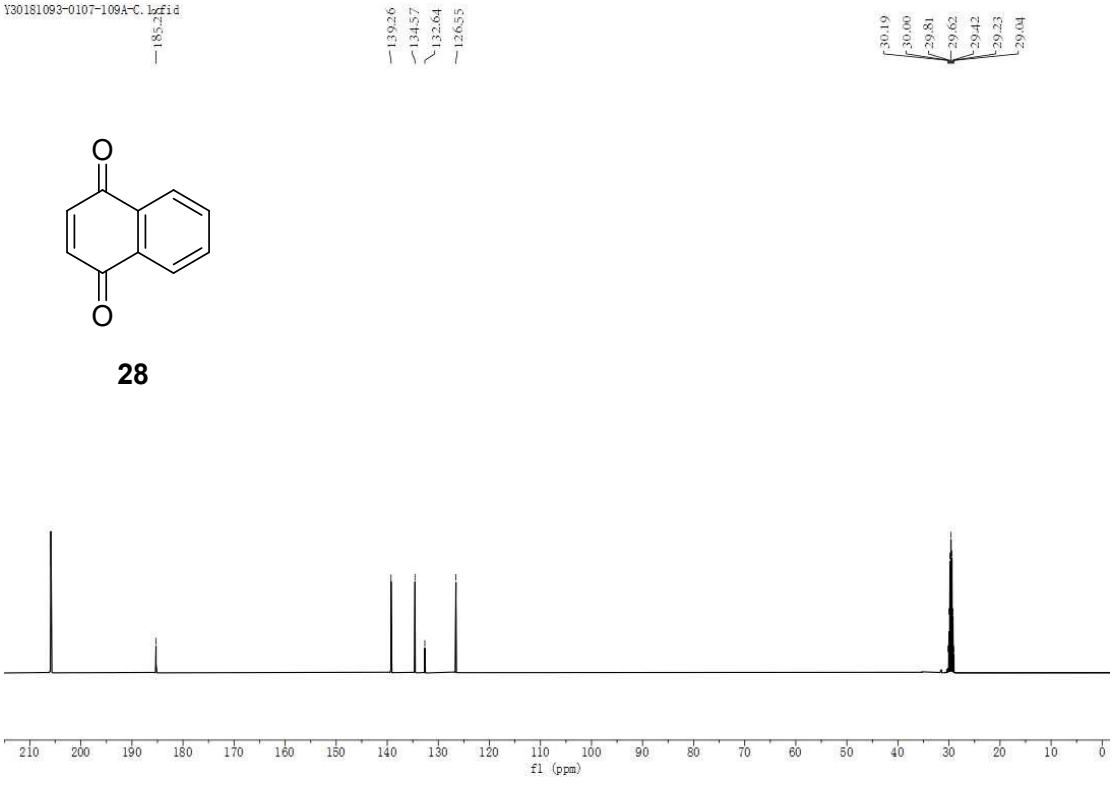
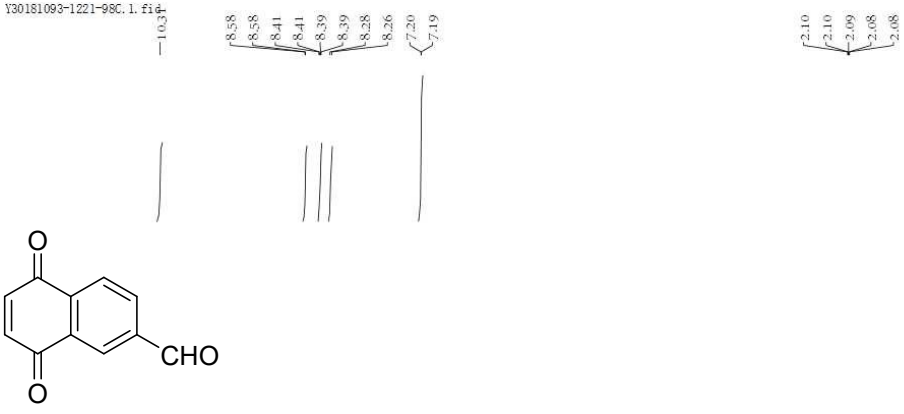


28

29: 5,8-dioxo-5,8-dihydronaphthalene-2-carbaldehyde



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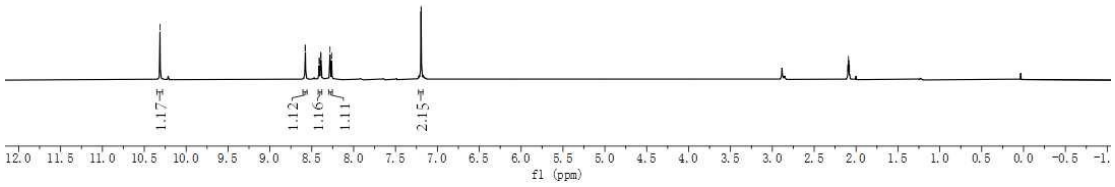
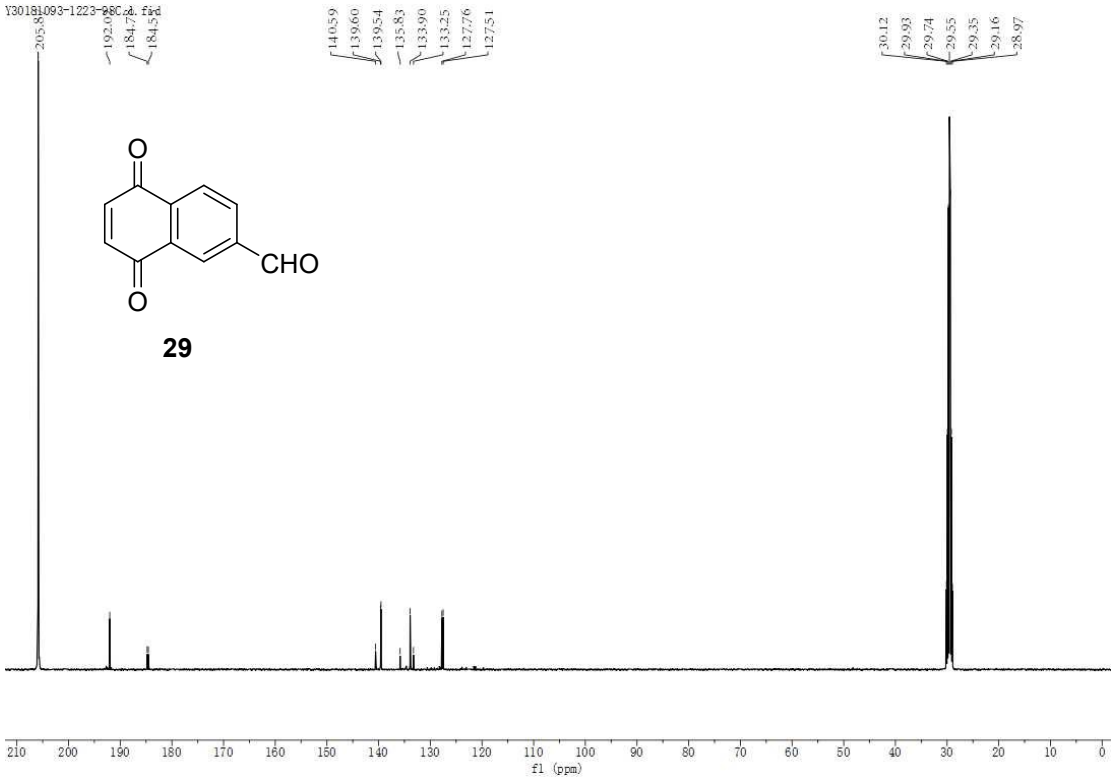
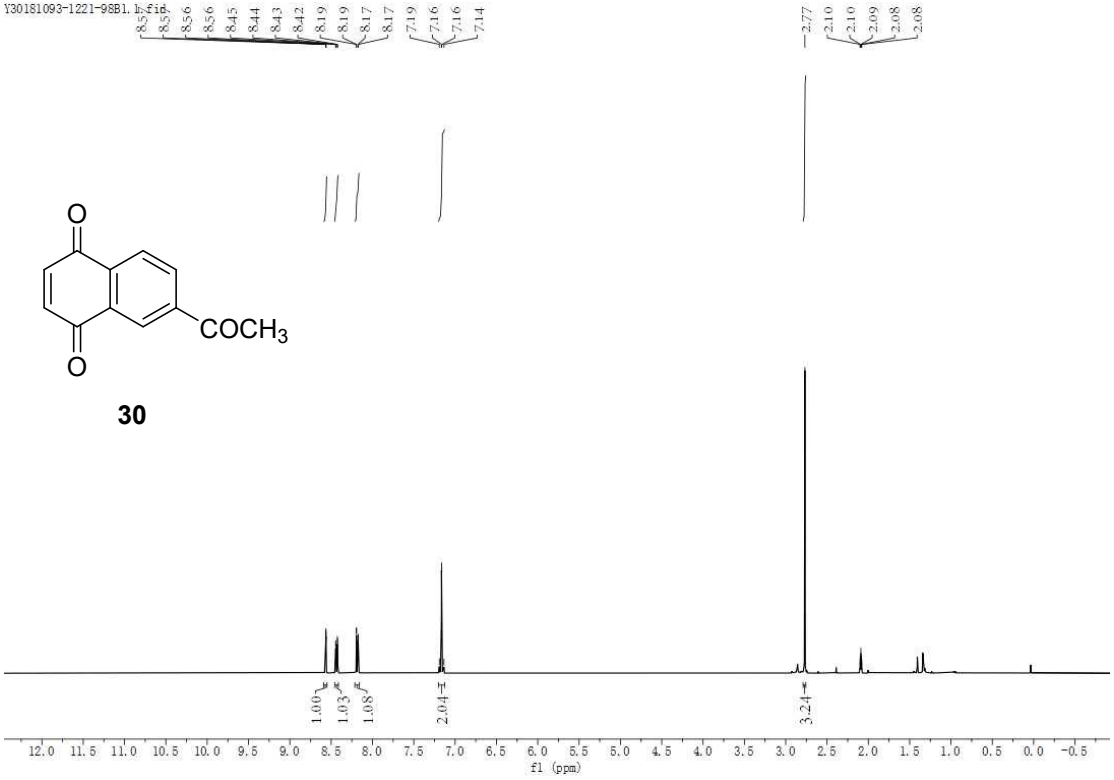




29

30: 6-acetylnaphthalene-1,4-dione



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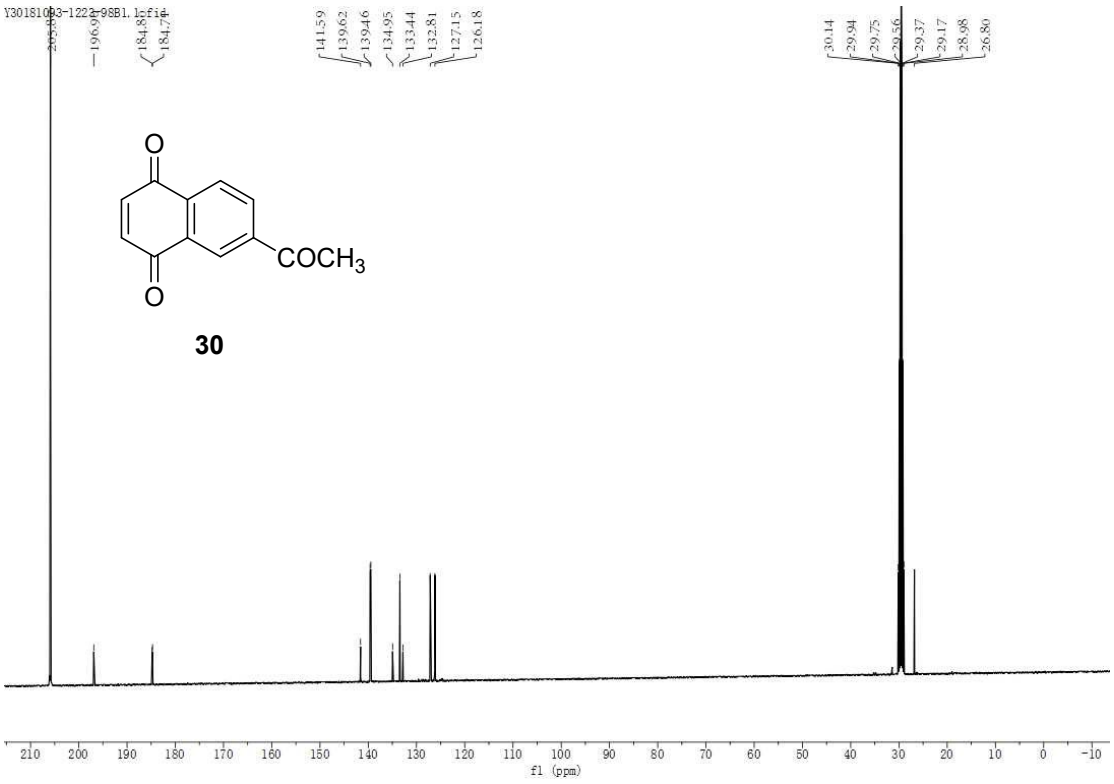
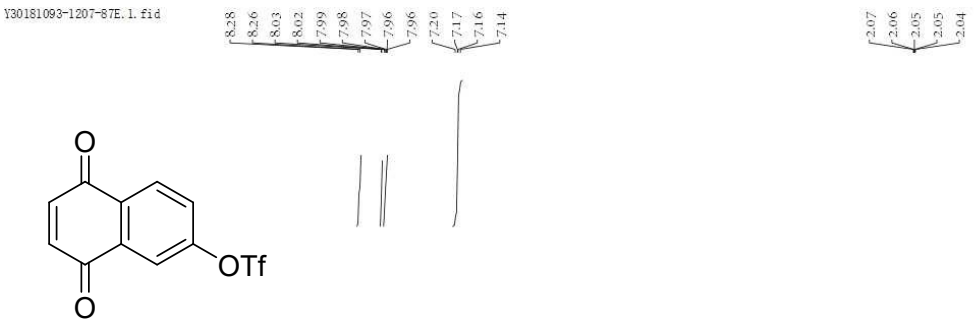


30

31: 5,8-dioxo-5,8-dihydronaphthalen-2-yl trifluoromethanesulfonate



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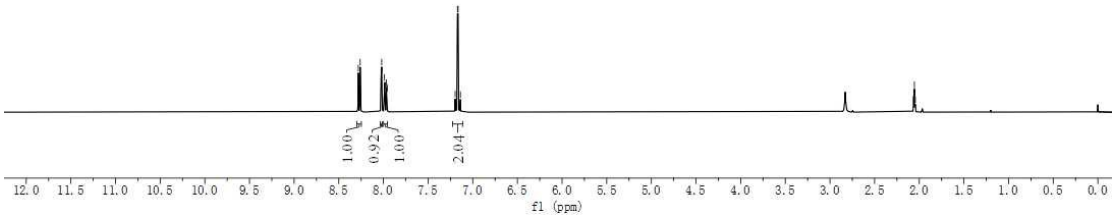

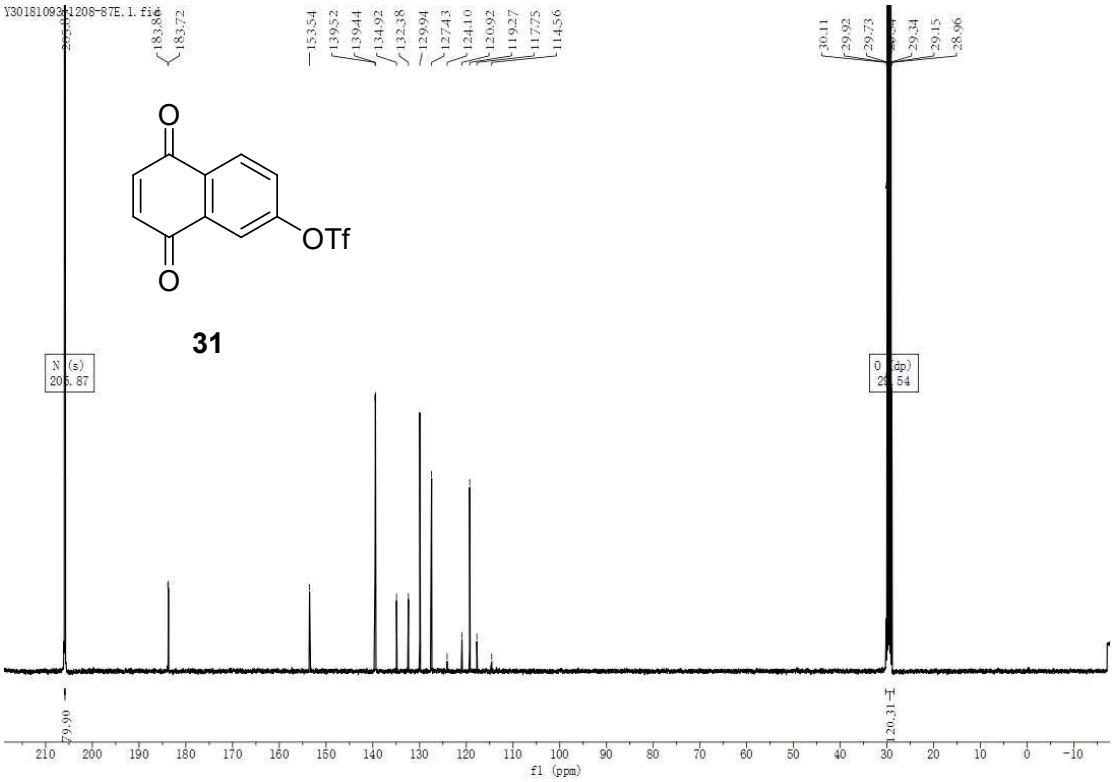

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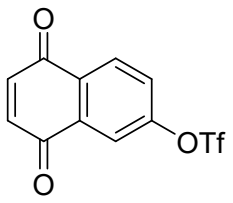

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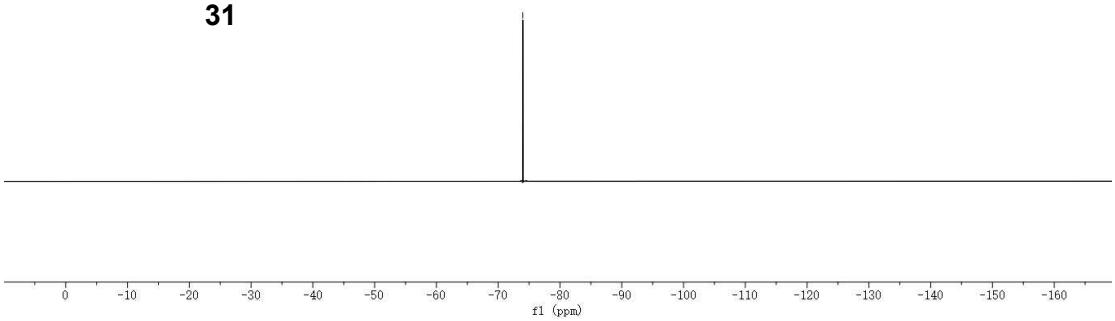
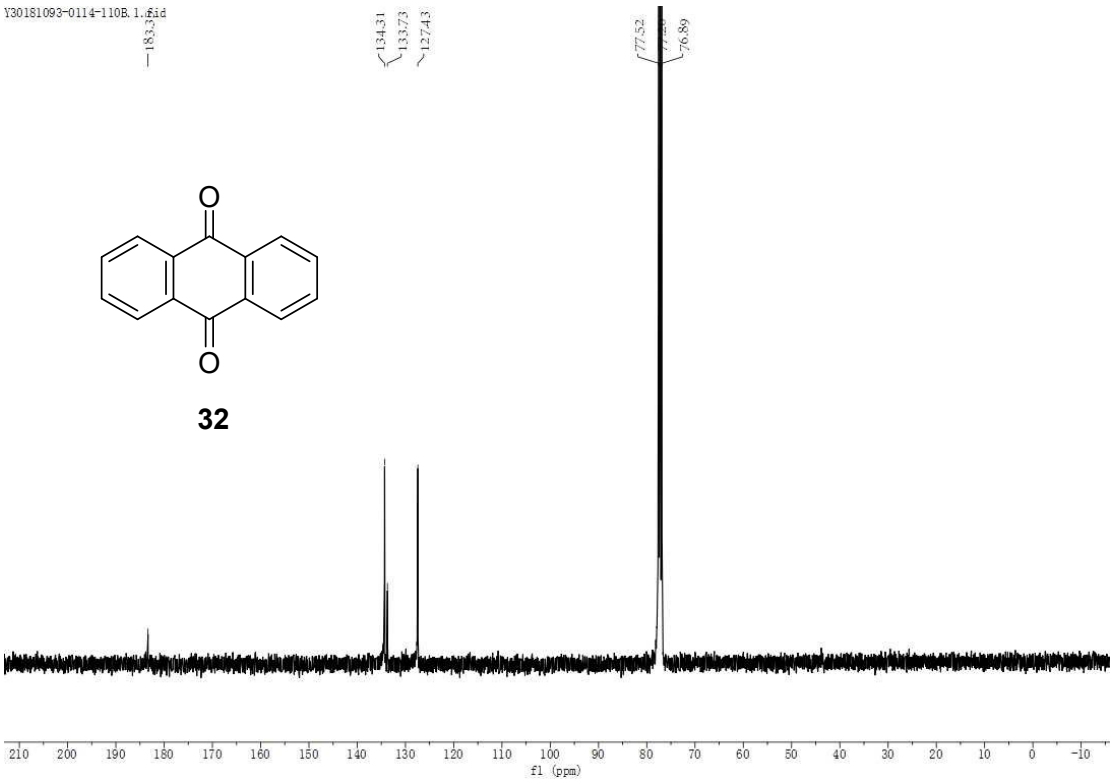


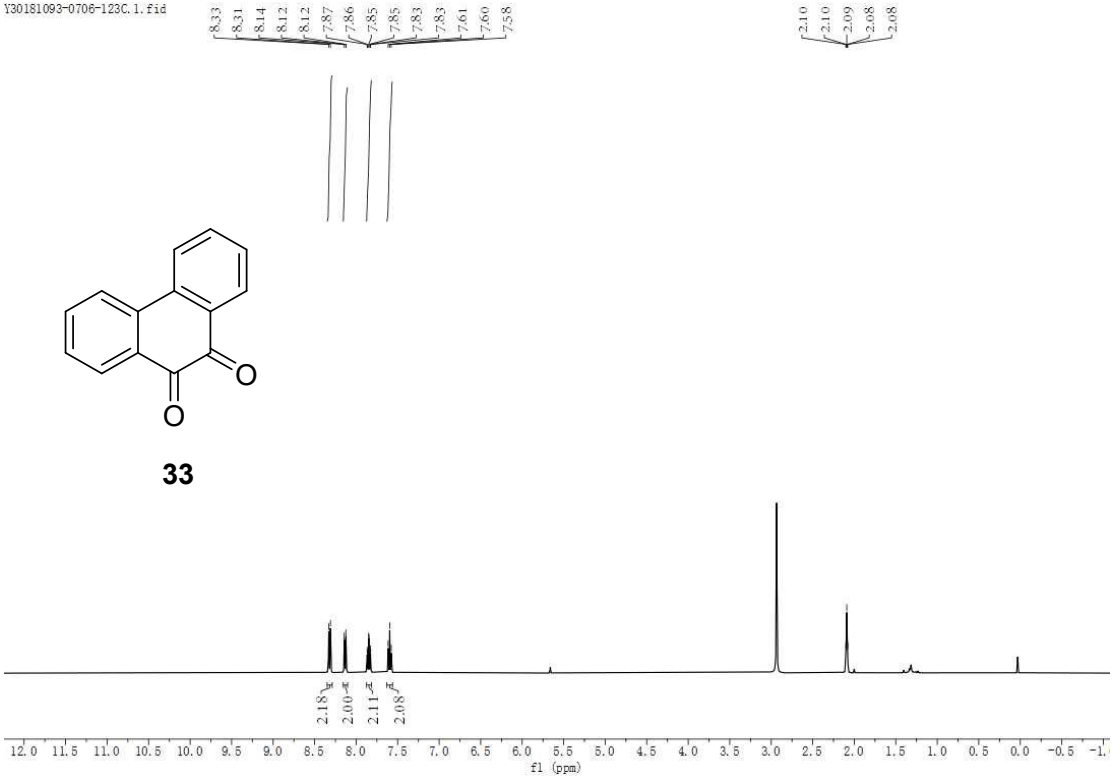
32: anthracene-9,10-dione

32

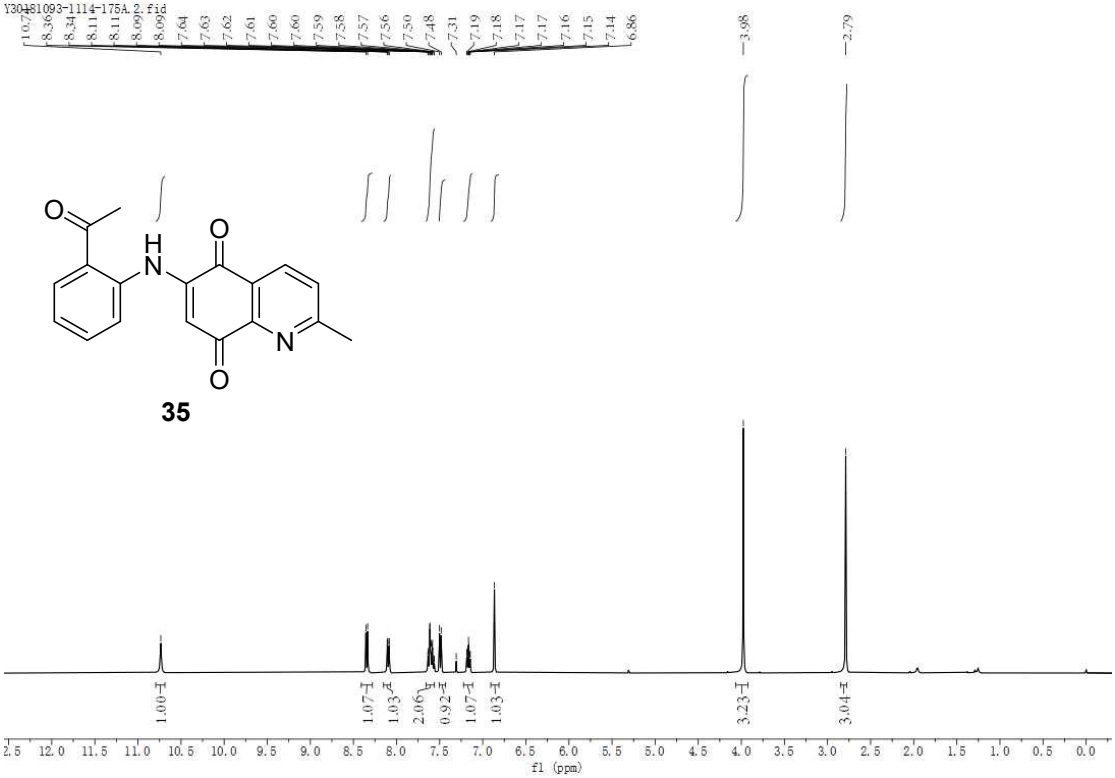


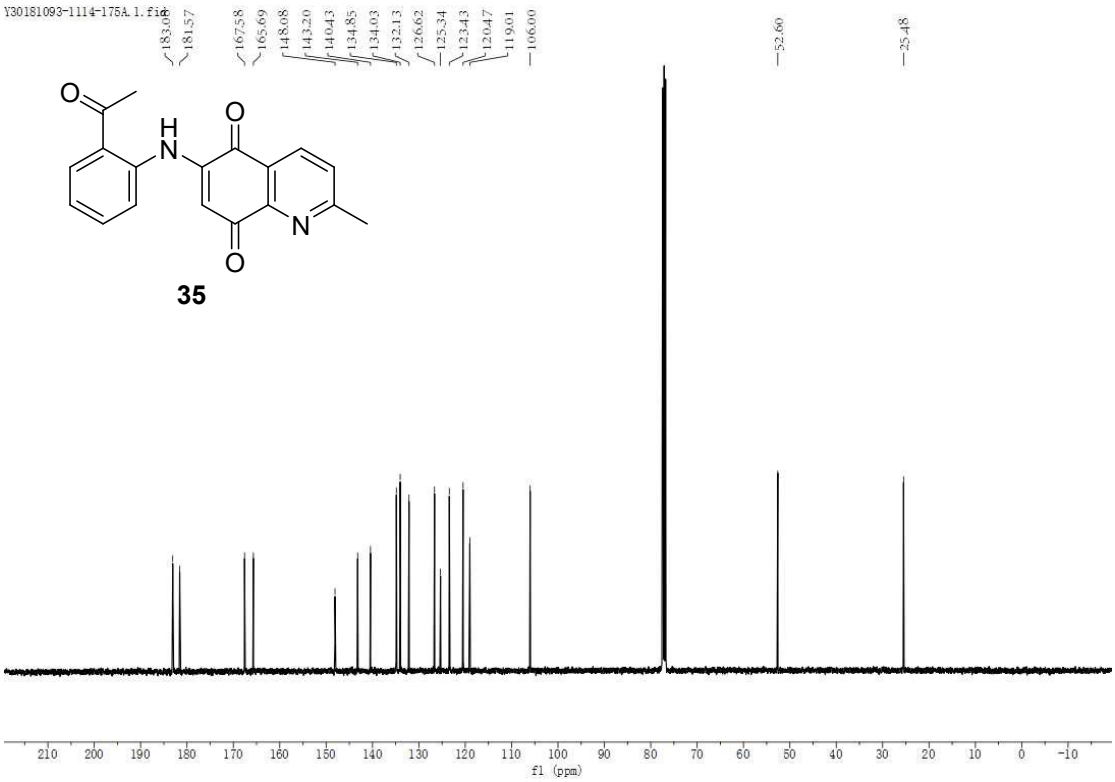
32

33: phenanthrene-9,10-dione

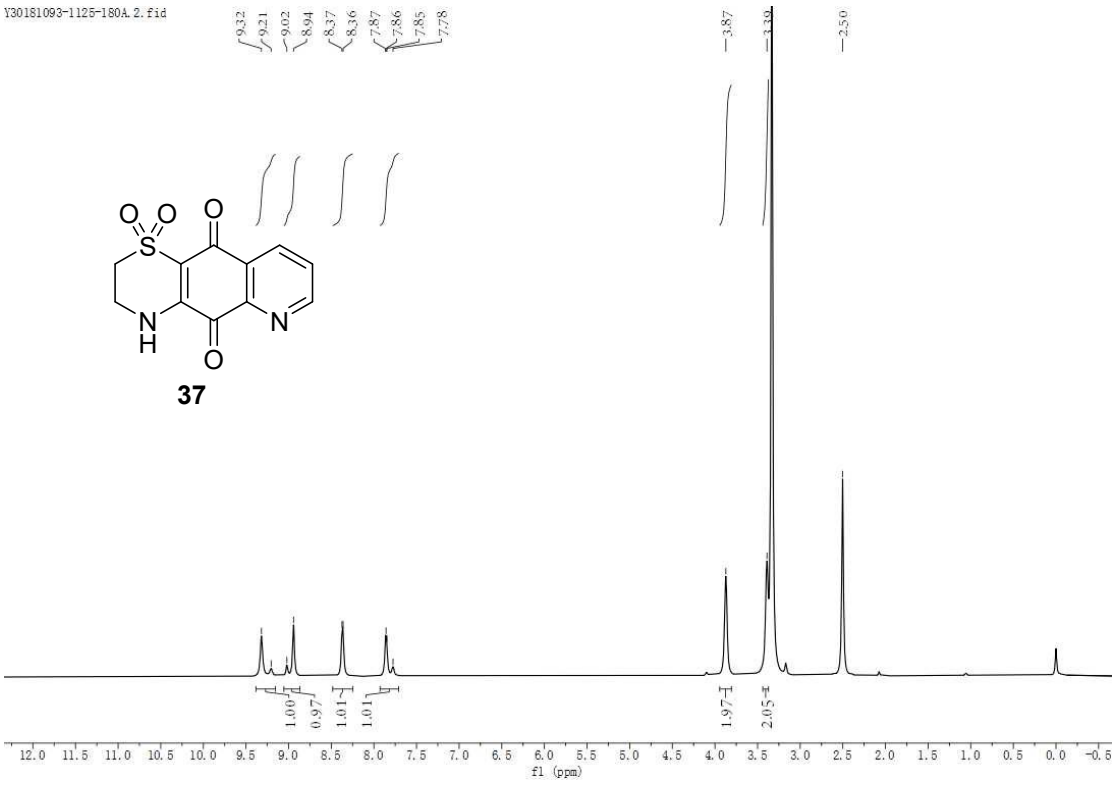


35: 6-((2-acetylphenyl)amino)-2-methylquinoline-5,8-dione





37: 3,4-dihydro-2H-[1,4]thiazino[2,3-g]quinoline-5,10-dione 1,1-dioxide



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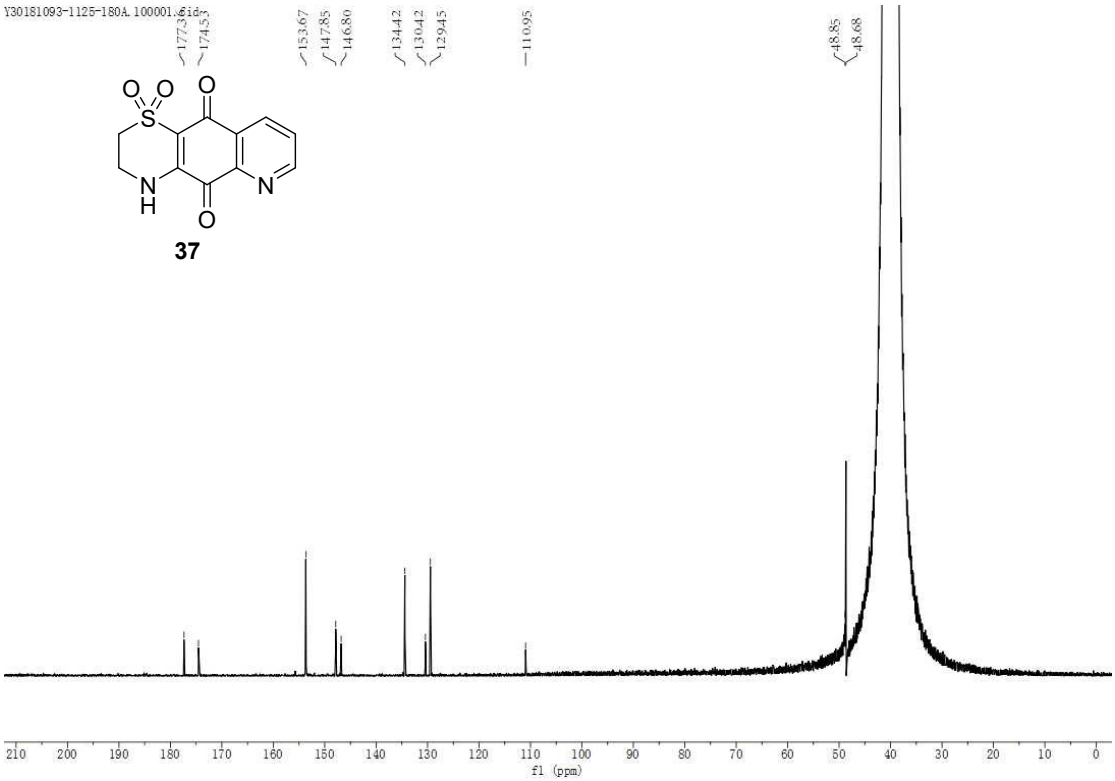
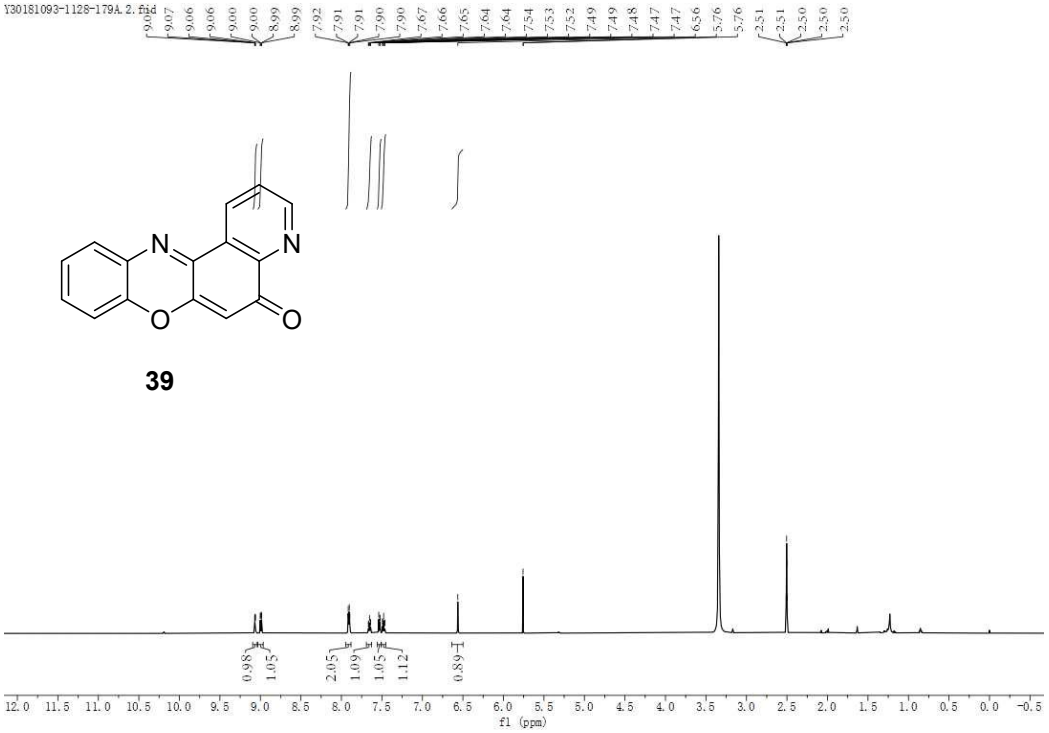
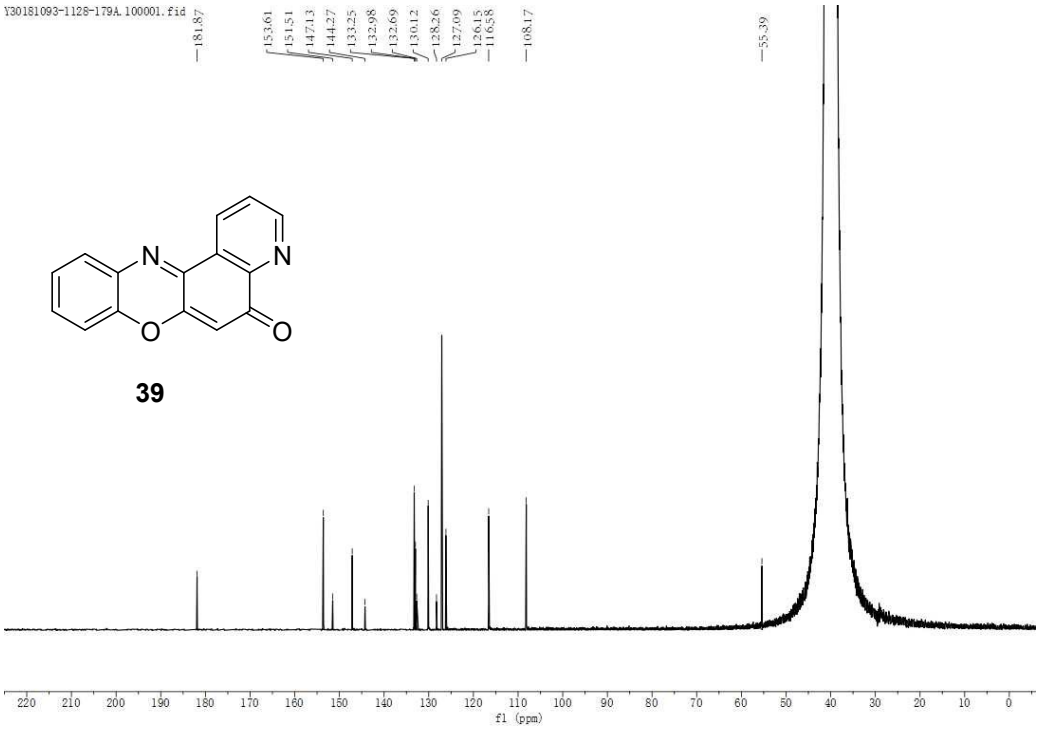


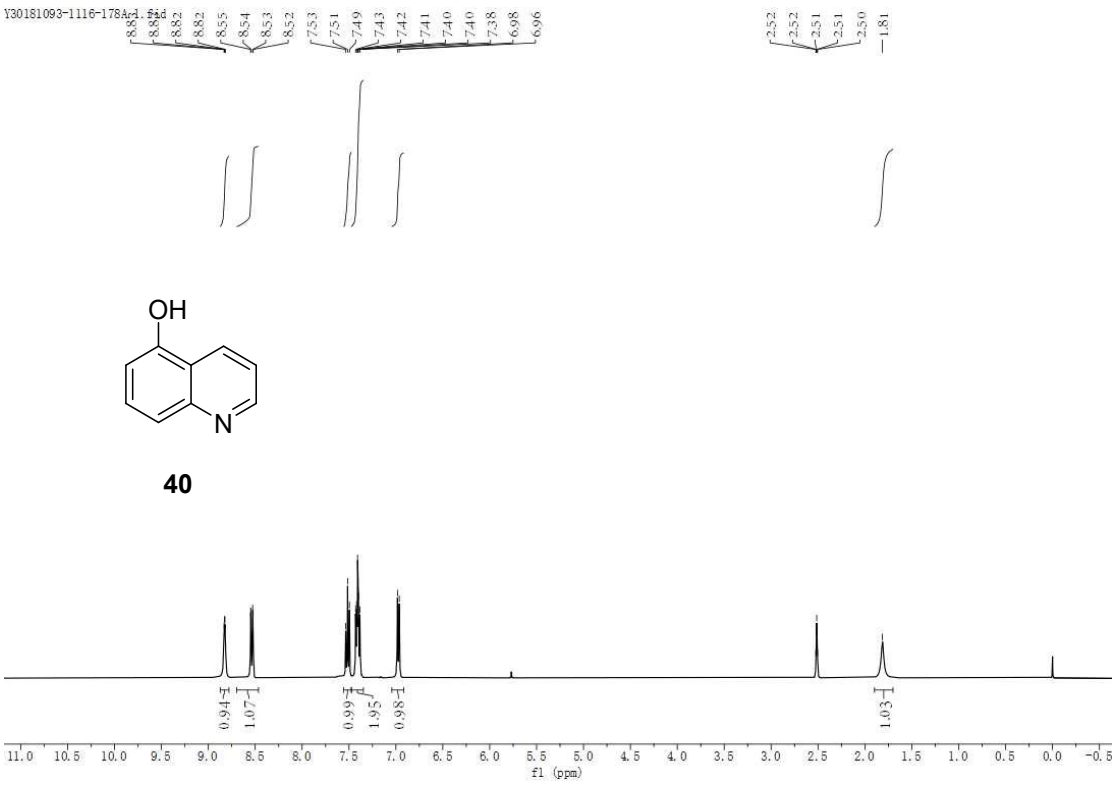
37

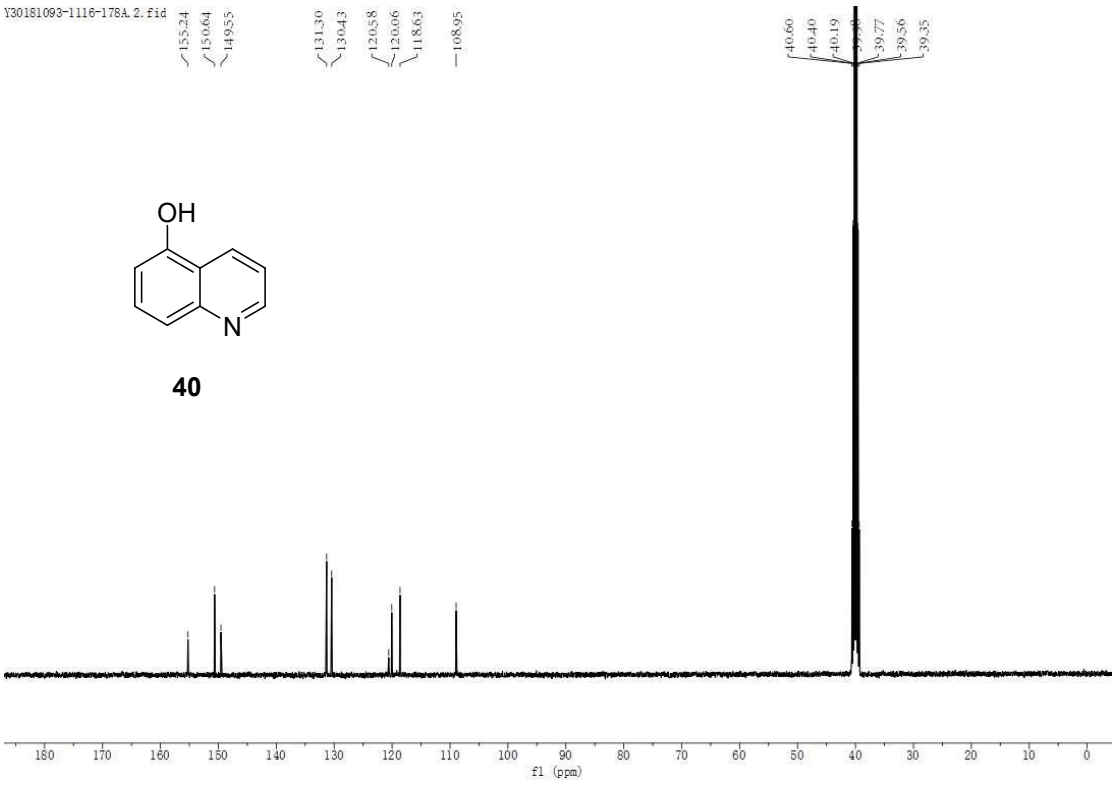
39: 5H-pyrido[3,2-a]phenoxazin-5-one



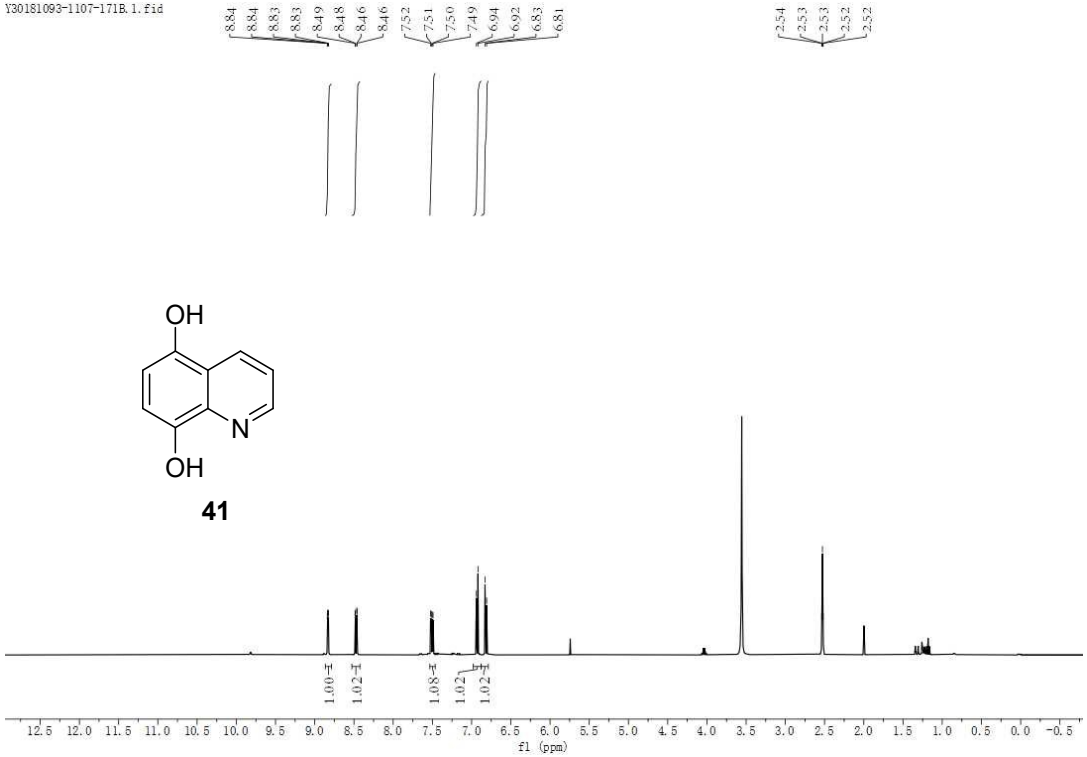


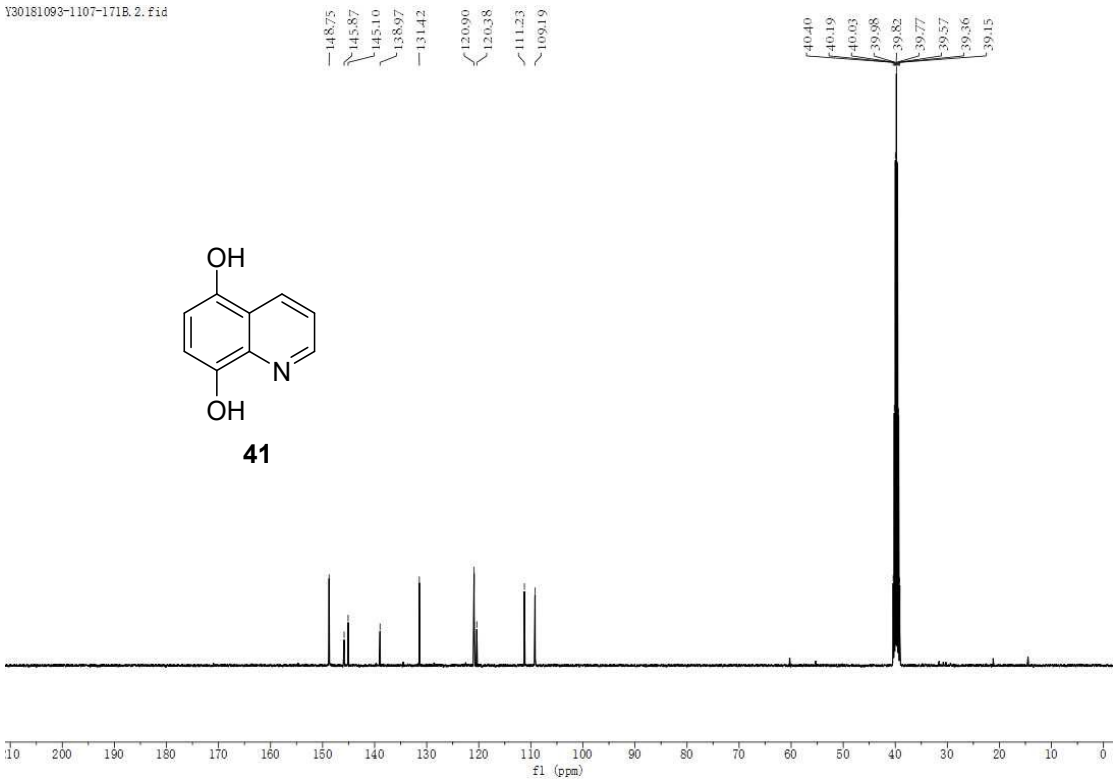
40: quinolin-5-ol





41: quinoline-5,8-diol





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3. A. Bolognese, G. Correale, M. Manfra, A. Lavecchia, O. Mazzoni, E. Novellino, V. Barone, P. La Colla, R. Loddo, *J. Med. Chem.,* 2002, **45**, 5217-5223.