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Iron catalyzed C-C dehydrogenative coupling reaction: synthesis of Arylquinones from Quinones/Hydroquinones

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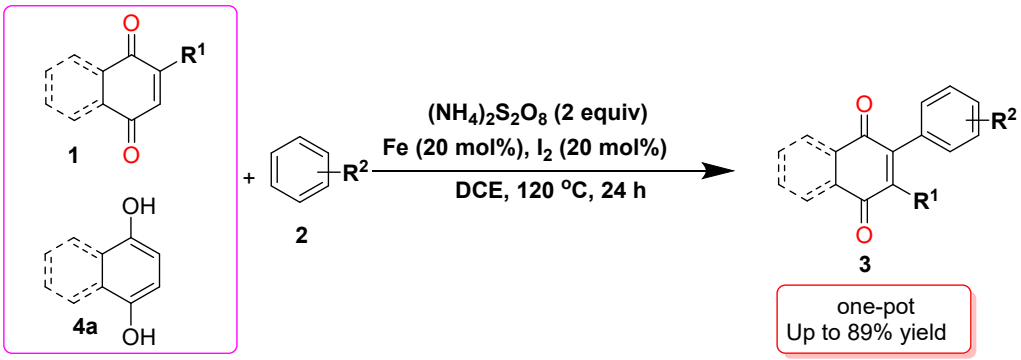
Table of Content

1. General information

Chemicals and analytical grade solvents were purchased from commercial suppliers and used without further purification unless otherwise stated. All reagents were weighed and handled in air at room temperature. Analytical thin–layer chromatography was performed on glass plates of Silica Gel GF–254 with detection by UV light (254 and 365 nm). Column chromatography was carried out on silica gel (200-300 mesh). ^{1}H NMR spectra were recorded at 400 MHz and ^{13}C NMR spectra were recorded at 101 MHz by using Agilent 400 MHz NMR spectrometer. Chemical shifts were calibrated using residual undeuterated solvent as an internal reference (^{1}H NMR: $CDCl_3$ 7.26 ppm, DMSO-d_6 2.50 ppm, ^{13}C NMR: $CDCl_3$ 77.16 ppm, DMSO-d_6 39.52 ppm). Data are reported as follows: chemical shift, multiplicity (s = singlet, br s = broad singlet, d = doublet, t = triplet, q = quartet, m = multiplet), Coupling constants (*J*) were reported in Hertz (Hz). HRMS were performed on a Thermo Scientific LTQ Orbitrap XL instrument. Melting points were measured with micro melting point apparatus.

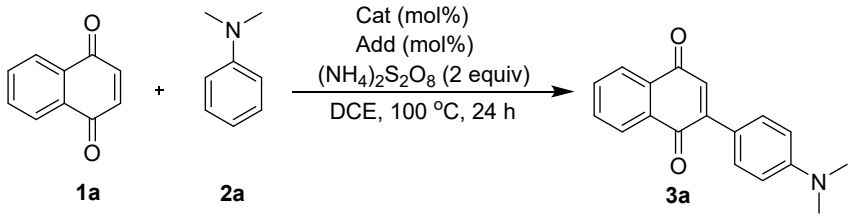
2. General procedure for the synthesis of the compounds



To a solution of DCE (2 mL) was added **1** or **4a** (0.3 mmol), **2** (0.8 mmol), Fe (0.06 mmol, 20 mol%), I_2 (0.06 mmol, 20 mol%), and $(NH4)_2S_2O_8$ (0.6 mmol, 2 equiv). The reaction mixture was stirred stirred at 120 °C for 24 h. After the completion of the reaction (monitored by TLC). The reaction was quenched with saturated salt water (2 ml) and the mixture was extracted with EtOAc (3 × 3 mL). The organic extracts were washed with brine, dried over Na_2SO_4, filtered and the solvent was removed in vacuo. The crude product was purified by silica gel column chromatography to give **3**.

3 Optimization of reaction conditions

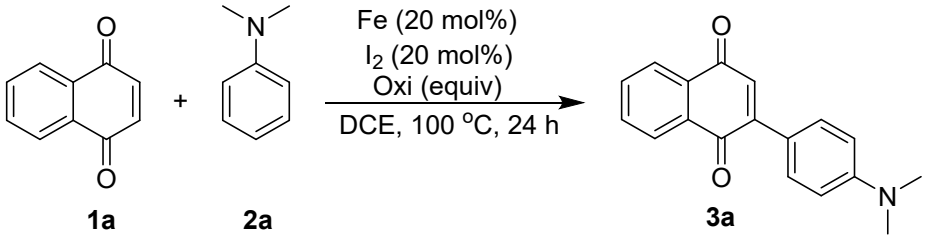
Table S1 Optimization of catalyst and additive [a]



Entry	[Cat] (mol%)	Additive (mol%)	Yield[b] (%)
1	CuI (10)	——	30
2	$Cu(OAc)_2$ (10)	——	Trace
3	$Cu(OAc)_2·H_2O$ (10)	——	Trace
4	$CuCl_2·2H_2O$ (10)	——	21
5	$Cu(acac)_2$ (10)	——	Trace
6	Zn (10)	——	41
7	Fe (10)	——	58
8	$CoCl_2$ (10)	——	24
9	$Pd(OTf)_2$ (10)	——	41
10	$Pd(OAc)_2$ (10)	——	34
11	$FeCl_3$ (10)	——	35
12	$FeSO_4·7H_2O$ (10)	——	23
13	Fe (20)	——	65
14	Fe (30)	——	53
15	Fe (40)	——	45
16	Fe (20)	CuBr (20)	24
17	Fe (20)	CuI (20)	31
18	Fe (20)	$Pd(OTf)_2$ (20)	34
19	Fe (20)	Zn (20)	14
20	Fe (20)	AgOAc (20)	20
21	Fe (20)	$CoCl_2$ (20)	14
22	Fe (20)	I_2 (20)	76
23	Fe (20)	I_2 (10)	59
24	Fe (20)	I_2 (30)	61
25	Fe (20)	I_2 (40)	65

[a] Reaction conditions: 1,4- naphthoquinone **1a** (0.30 mmol), *N*，*N*-dimethylaniline **2a** (2 equiv), catalysts (mol%), additive (mol%), $(NH_4)_2S_2O_8$ (2 equiv), 1,2-dichloroethane (2 mL) as solvent, 120 °C, sealed tube for 24 h. [b] Isolated yields.

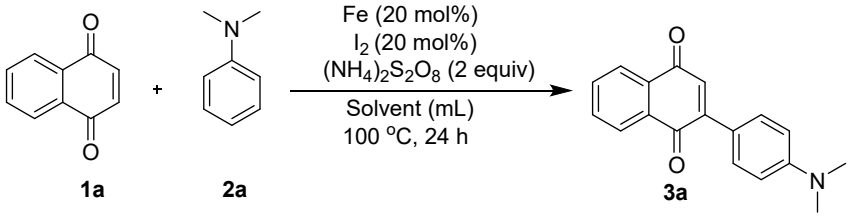
Table S2 Optimization of oxidants [a]



Entry	Oxidants (equiv)	Yield[b] (%)
1	——	37
2	$K_2S_2O_8$ (2)	45
3	H_2O_2 (2)	Trace
4	$KMnO_4$ (2)	40
5	BPO (2)	15
6	Oxone (2)	32
7	$(NH_4)_2S_2O_8$ (2)	76
8	$(NH_4)_2S_2O_8$ (1)	68
9	$(NH_4)_2S_2O_8$ (3)	66

[a] Reaction conditions: 1,4- naphthoquinone **1a** (0.30 mmol), *N, N*-dimethylaniline **2a** (2 equiv), 1,2-dichloroethane (2 mL) as solvent, Fe (20 mol%), I_2 (20 mol%), oxidants (equiv), 120 °C, sealed tube for 24 h.[b] Isolated yields.[c]

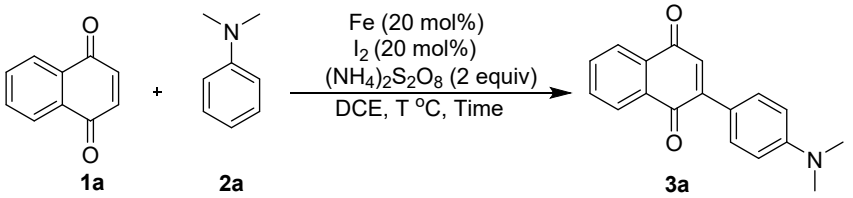
Table S3 Optimization of solvents [a]



Entry	Solvent (mL)	yield[b] (%)
1	DMF (2)	Trace
2	CH_3CN (2)	45
3	EtOH (2)	Trace
4	MeOH (2)	Trace
5	1,4-dioxane (2)	32
6	DCE (2)	76
7	DCE (1)	56
8	DCE (3)	68

[a] Reaction conditions: 1,4- naphthoquinone **1a** (0.30 mmol), *N. N*-dimethylaniline **2a** (2 equiv), Fe (20 mmol%), I_2 (20 mol%),$(NH_4)_2S_2O_8$ (2 equiv), solvent (mL), 120 °C, sealed tube for 24 h. [b] Isolated yields.

Table S4 Optimization of dosages [a]

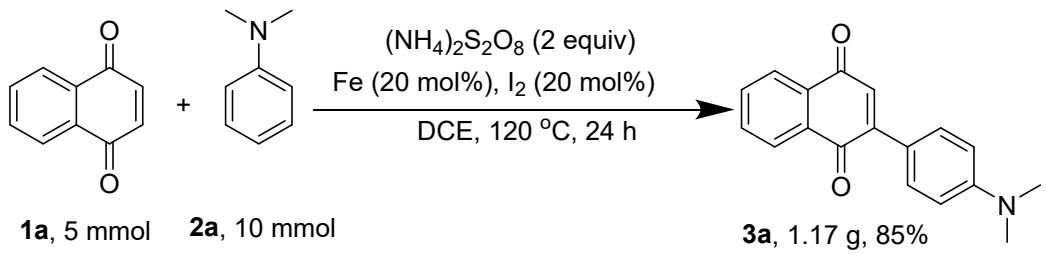


1a **2a** **3a**

Entry	**2a** (equiv)	t (h)	T (°C)	Yield[b] (%)
1	1	24	100	26
2	1.5	24	100	50
3	2	24	100	76
4	3	24	100	61
5	2	24	80	41
6	2	24	120	89
7	2	24	140	70
8	2	6	120	50
9	2	18	120	64
10	2	32	120	72

[a] Reaction conditions: 1,4- naphthoquinone **1a** (0.30 mmol), *N, N*-dimethylaniline **2a** (equiv), 1,2-dichloroethane (2 mL) as solvent , Fe (20 mol%), I_2 (20 mol%), $(NH_4)_2S_2O_8$ (2 equiv), T °C, sealed tube for time.[b] Isolated yields.

4 Procedure for gram-scale reaction

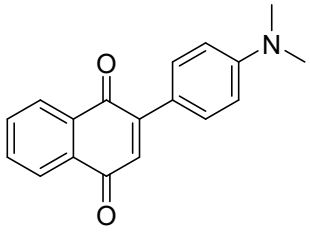


1a, 5 mmol **2a**, 10 mmol **3a**, 1.17 g, 85%

To a solution of DCE (32 mL) was added **1a** (5 mmol), **2** (10 mmol), Fe (20 mol%), I_2 (20 mol%), and $(NH4)_2S_2O_8$ (2 equiv). The reaction mixture was stirred stirred at 120 °C for 24 h. After the completion of the reaction (monitored by TLC). The reaction was quenched with saturated salt water (30 ml) and the mixture was extracted with EtOAc (3 × 30 mL). The organic extracts were washed with brine, dried over Na_2SO_4, filtered and the solvent was removed in vacuo. The crude product was purified by silica gel column chromatography to give **3a** in 85% yield.

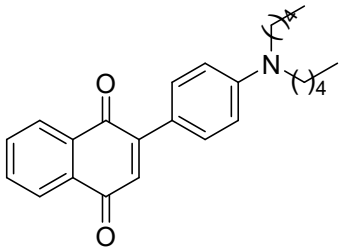
5 Characterization data of products

2-(4-(dimethylamino)phenyl)naphthalene-1,4-dione（3a）[1]



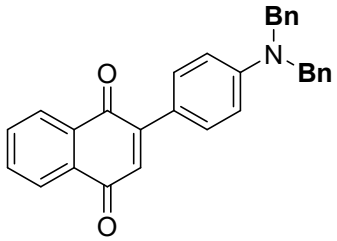
Purple solid, 89% yield; mp 96-98 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (dd, *J* = 5.6, 3.4 Hz, 1H), 8.11 (dd, *J* = 5.6, 3.3 Hz, 1H), 7.75 (dt, *J* = 7.4, 3.6 Hz, 2H), 7.62 (d, *J* = 8.8 Hz, 2H), 7.04 (s, 1H), 6.79 (d, *J* = 8.7 Hz, 2H), 3.07 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 185.40, 185.17, 151.80, 147.37, 133.50, 133.34, 132.91, 132.31, 131.21, 130.96, 126.88, 125.67, 111.85, 40.19.

2-(4-(diethylamino)phenyl)naphthalene-1,4-dione （3b）



Purple solid, 85% yield; mp 96-98 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 – 8.13 (m, 1H), 8.09 (d, *J* = 2.9 Hz, 1H), 7.77 – 7.70 (m, 2H), 7.59 (d, *J* = 8.5 Hz, 2H), 7.01 (s, 1H), 6.68 (d, *J* = 7.4 Hz, 2H), 3.33 (t, *J* = 7.4 Hz, 4H), 1.61 (s, 5H), 1.37 (d, *J* = 13.4 Hz, 8H), 0.93 (t, *J* = 6.8 Hz, 5H).^{13}C NMR (101 MHz, $CDCl_3$) δ 185.63, 185.16, 149.71, 147.26, 133.46, 133.24, 132.97, 132.38, 131.20, 130.37, 126.86, 125.63, 111.21, 77.31, 77.00, 76.68, 50.99, 29.68, 29.26, 26.94, 22.56, 14.07. For $C_{26}H_{32}NO_2^+$ $(M+H)^+$ 390.2433 found: 390.2437 .

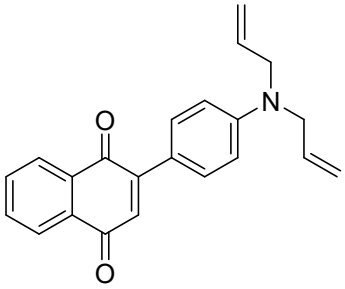
2-(4-(dibenzylamino)phenyl)naphthalene-1,4-dione（3c）[1]



Purple solid, 82% yield; mp 144-146 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 – 8.13 (m, 1H), 8.10 (dd, *J* = 5.1, 3.4 Hz, 1H), 7.73 (dd, *J* = 5.2, 3.3 Hz, 2H), 7.54 (d, *J* = 8.6 Hz, 2H), 7.36 (t, *J* = 7.3 Hz, 4H), 7.28 (dd, *J* = 15.0, 7.0 Hz, 7H), 7.00 (s, 1H), 6.82 (d, *J* = 8.6 Hz, 2H), 4.74 (s, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 185.39, 185.16, 150.82,

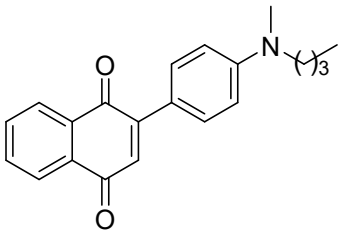
147.23, 137.61, 133.55, 133.39, 132.85, 132.29, 131.40, 131.17, 128.83, 128.56, 128.00, 127.21, 126.91, 126.51, 125.70, 121.26, 112.09, 111.19, 54.03.

2-(4-(diallylamino)phenyl)naphthalene-1,4-dione（3d）



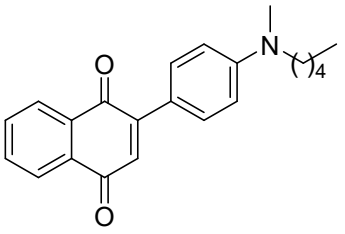
Purple solid, 75% yield; mp 96-98 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (d, *J* = 3.6 Hz, 1H), 8.09 (s, 1H), 7.77 – 7.71 (m, 2H), 7.56 (d, *J* = 8.4 Hz, 2H), 7.01 (s, 1H), 6.75 (d, *J* = 8.0 Hz, 2H), 5.93 – 5.81 (m, 2H), 5.23 – 5.15 (m, 4H), 3.99 (s, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 185.45, 185.19, 150.29, 147.31, 133.50, 133.33, 132.94, 132.31, 131.13, 131.00, 126.89, 125.67, 120.70, 118.75, 116.40, 111.87, 52.61, 29.68. For $C_{22}H_{20}NO_2^+$ $(M+H)^+$ 330.1494 found: 330.1497.

2-(4-(ethyl(methyl)amino)phenyl)naphthalene-1,4-dione（3e）



Purple solid, 78% yield; mp 96-98 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 – 8.14 (m, 1H), 8.12 – 8.06 (m, 1H), 7.73 (dd, *J* = 5.2, 3.2 Hz, 2H), 7.60 (d, *J* = 8.7 Hz, 2H), 7.02 (s, 1H), 6.73 (d, *J* = 8.2 Hz, 2H), 3.39 (t, *J* = 7.4 Hz, 2H), 3.02 (s, 3H), 1.63 – 1.58 (m, 2H), 1.37 (dd, *J* = 14.9, 7.4 Hz, 2H), 0.96 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 185.50, 185.17, 147.32, 133.48, 133.29, 132.94, 132.34, 131.09, 130.78, 126.87, 125.65, 111.47, 52.22, 38.41, 29.00, 20.29, 13.95. For $C_{21}H_{22}NO_2^+$ $(M+H)^+$ 320.1651 found: 320.1656.

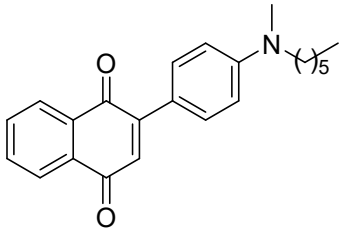
2-(4-(ethyl(methyl)amino)phenyl)naphthalene-1,4-dione（3f）[1]



Purple sticky solid, 76% yield; mp 96-98 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 – 8.12 (m, 1H), 8.11 – 8.04 (m, 1H), 7.73 (dd, *J* = 5.5, 3.3 Hz, 2H), 7.60 (d, *J* = 8.8 Hz, 2H), 7.02 (s, 1H), 6.73 (d, *J* = 8.2 Hz, 2H), 3.38 (t, *J* = 7.5 Hz, 2H), 3.02 (s, 3H), 1.61 (d, *J* = 6.8 Hz, 3H), 1.37 – 1.30 (m, 3H), 0.92 (t, *J* = 6.8 Hz, 3H).^{13}C NMR (101 MHz,

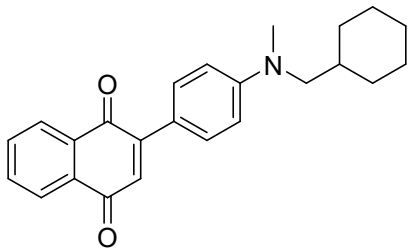
$CDCl_3$) δ 185.61, 185.17, 133.48, 133.29, 132.94, 132.34, 131.09, 130.77, 126.87, 125.65, 111.43, 51.69, 37.81, 29.24, 26.54, 22.56, 14.05.

2-(4-(ethyl(methyl)amino)phenyl)naphthalene-1,4-dione（3g）



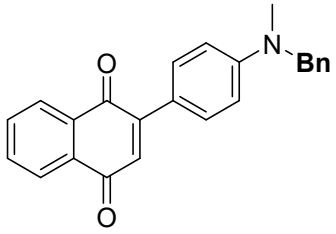
Purple solid, 76% yield; mp 96-98 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (dd, *J* = 5.4, 3.5 Hz, 1H), 8.09 (dd, *J* = 5.6, 3.3 Hz, 2H), 7.76 – 7.73 (m, 2H), 7.61 (s, 1H), 7.00 (d, *J* = 14.1 Hz, 2H), 6.72 (s, 1H), 3.40 – 3.35 (m, 2H), 3.02 (s, 3H), 1.61 (s, 4H), 1.32 (d, *J* = 2.5 Hz, 4H), 0.89 (d, *J* = 6.3 Hz, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 185.22, 185.17, 147.32, 138.65, 133.90, 133.48, 133.29, 132.89, 132.34, 132.30, 131.83, 131.09, 130.77, 126.87, 126.39, 125.65, 111.04, 109.56, 52.20, 38.16, 31.66, 29.63, 26.75, 22.63, 14.01. For $C_{23}H_{26}NO_2^+$ $(M+H)^+$ 348.1964 found: 348.1967.

2-(4-((cyclohexylmethyl)(methyl)amino)phenyl)naphthalene-1,4-dione（3h）



Purple solid, 70% yield; mp 96-98 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 – 8.13 (m, 1H), 8.12 – 8.05 (m, 1H), 7.77 – 7.69 (m, 2H), 7.59 (d, *J* = 9.0 Hz, 2H), 7.01 (s, 1H), 6.71 (d, *J* = 9.0 Hz, 2H), 3.21 (d, *J* = 6.9 Hz, 2H), 3.04 (s, 3H), 1.76 – 1.68 (m, 5H), 1.28 – 1.17 (m, 4H), 0.98 (t, *J* = 10.9 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 185.57, 185.16, 150.90, 147.32, 133.46, 133.27, 132.95, 132.35, 131.03, 130.63, 126.87, 125.63, 119.78, 111.30, 59.24, 39.79, 36.84, 31.19, 29.60, 26.45, 25.93. For $C_{24}H_{26}NO_2^+$ $(M+H)^+$ 360.1964 found: 360.1965.

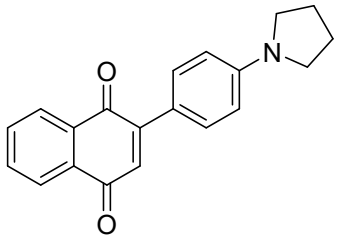
2-(4-(benzyl(methyl)amino)phenyl)naphthalene-1,4-dione（3i）



Purple solid, 72% yield; mp 96-98 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (dd, *J* = 4.9, 3.4 Hz, 1H), 8.09 (dd, *J* = 4.8, 3.4 Hz, 1H), 7.73 (dd, *J* = 4.9, 3.2 Hz, 2H), 7.58 (d,

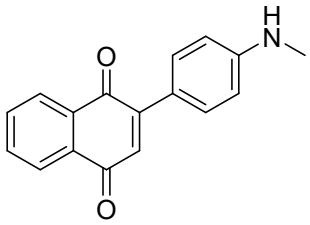
J = 8.4 Hz, 2H), 7.34 (t, *J* = 7.4 Hz, 2H), 7.29 – 7.21 (m, 3H), 7.01 (s, 1H), 6.80 (d, *J* = 8.5 Hz, 2H), 4.63 (s, 2H), 3.13 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 185.43, 185.16, 151.08, 147.29, 137.97, 133.52, 133.36, 132.88, 132.30, 131.21, 131.10, 128.73, 127.14, 126.89, 126.50, 125.68, 120.80, 111.76, 56.01, 38.62, 29.70. For $C_{24}H_{20}NO_2^+$ $(M+H)^+$ 354.1494 found: 354.1495.

2-(4-(pyrrolidin-1-yl)phenyl)naphthalene-1,4-dione（3j）[1]



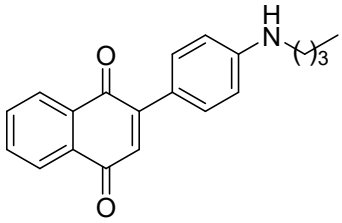
Purple solid, 86% yield; mp 193-195 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (dd, *J* = 5.8, 3.1 Hz, 1H), 8.09 (dd, *J* = 5.4, 3.5 Hz, 1H), 7.73 (dd, *J* = 5.7, 3.3 Hz, 2H), 7.61 (d, *J* = 8.8 Hz, 2H), 7.01 (s, 1H), 6.61 (d, *J* = 8.8 Hz, 2H), 3.37 (d, *J* = 6.3 Hz, 4H), 2.05 (d, *J* = 6.4 Hz, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 185.62, 185.17, 149.28, 147.49, 133.45, 133.25, 132.98, 132.36, 131.11, 130.55, 126.86, 125.62, 119.83, 111.58, 47.55, 29.69, 25.46.

2-(4-(methylamino)phenyl)naphthalene-1,4-dione（3k）[1]



Purple solid, 73% yield; mp 135-137 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (s, 1H), 8.09 (d, *J* = 1.9 Hz, 1H), 7.75 – 7.71 (m, 2H), 7.54 (d, *J* = 8.3 Hz, 2H), 7.00 (s, 1H), 6.65 (d, *J* = 8.3 Hz, 2H), 2.89 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 185.39, 185.23, 151.03, 147.49, 133.53, 133.40, 132.85, 132.26, 131.45, 131.13, 126.89, 125.68, 121.64, 112.01, 30.31.

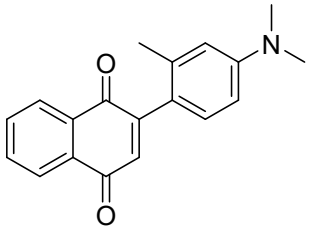
2-(4-(ethylamino)phenyl)naphthalene-1,4-dione（3l）



Purple solid, 71% yield; mp 96-98 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (s, 1H), 8.09 (s, 1H), 7.76 – 7.70 (m, 2H), 7.53 (d, *J* = 8.2 Hz, 2H), 7.01 (s, 1H), 6.66 (d, *J* = 7.9 Hz, 2H), 3.19 (t, *J* = 6.9 Hz, 2H), 1.64 (dt, *J* = 14.0, 6.9 Hz, 2H), 1.53 – 1.33 (m,

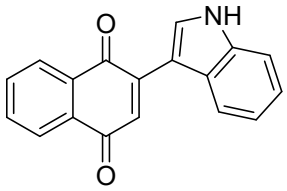
1H), 0.95 (dd, J = 25.4, 18.2 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 185.40, 185.22, 150.08, 147.46, 133.52, 133.38, 132.86, 132.25, 131.34, 131.18, 126.89, 125.68, 112.34, 43.30, 31.41, 20.21, 13.83. For $C_{20}H_{20}NO_2^+$ $(M+H)^+$ 306.1494 found: 306.1499.

2-(4-(dimethylamino)-2-methylphenyl)naphthalene-1,4-dione（3m）[2]



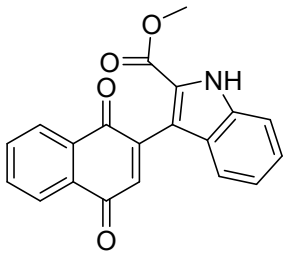
Purple solid, 69% yield; mp 158-159 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 – 8.11 (m, 2H), 7.75 (dd, J = 3.8, 2.6 Hz, 2H), 7.10 (d, J = 9.1 Hz, 1H), 6.90 (s, 1H), 6.62 (s, 2H), 3.00 (s, 6H), 2.23 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 185.37, 184.71, 151.14, 150.49, 137.52, 135.76, 133.57, 132.54, 132.26, 130.99, 126.98, 125.90, 114.09, 109.54, 40.30, 29.69, 21.33.

2-(1*H*-indol-3-yl)naphthalene-1,4-dione（3n）[1]



Red solid, 87% yield; mp 201-203 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.97 (s, 1H), 8.22 (t, J = 4.0 Hz, 1H), 8.09 – 8.04 (m, 1H), 8.00 – 7.95 (m, 1H), 7.88 – 7.79 (m, 3H), 7.50 (dd, J = 6.3, 2.4 Hz, 1H), 7.26 – 7.16 (m, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 185.39, 184.49, 142.50, 137.16, 134.31, 133.83, 132.89, 132.13, 128.09, 126.89, 125.58, 125.54, 122.91, 121.62, 120.34, 112.99, 107.77.

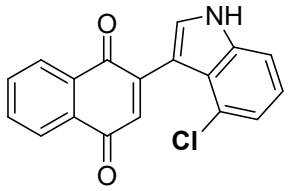
Methyl 3-(1,4-dioxo-1,4-dihydronaphthalen-2-yl)-1H-indole-2-carboxylate（3o）



Purple solid, 62% yield; mp 96-98 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.39 (s, 1H), 8.18 (d, J = 2.9 Hz, 2H), 7.81 – 7.77 (m, 2H), 7.63 (d, J = 8.2 Hz, 1H), 7.48 (d, J = 8.2 Hz, 1H), 7.37 (d, J = 7.9 Hz, 1H), 7.17 (s, 1H), 3.76 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 185.01, 183.51, 161.36, 143.92, 136.14, 135.91, 133.78, 133.71, 132.72,

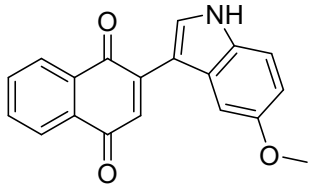
132.29, 126.99, 126.84, 126.13, 126.09, 125.87, 121.89, 120.49, 112.25, 52.11. For $C_{20}H_{14}NO_4^+$ $(M+H)^+$ 332.0923 found: 332.0921.

2-(4-chloro-1*H*-indol-3-yl)naphthalene-1,4-dione（3p）[3]



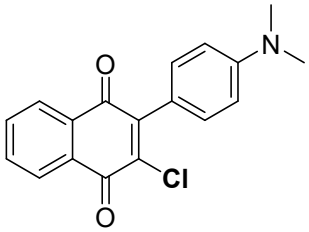
Red solid, 75% yield; mp 253-255 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.11 (s, 1H), 8.15 (ddd, J = 15.6, 5.5, 3.3 Hz, 2H), 7.99 (dd, J = 5.6, 3.3 Hz, 2H), 7.85 (d, J = 2.5 Hz, 1H), 7.57 (d, J = 8.0 Hz, 1H), 7.27 (t, J = 7.8 Hz, 1H), 7.19 (d, J = 7.6 Hz, 1H), 7.12 (s, 1H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 185.48, 184.77, 144.86, 138.36, 134.64, 134.57, 134.53, 132.54, 132.18, 129.80, 126.93, 125.97, 124.91, 123.93, 123.32, 121.35, 111.85, 109.07.

2-(5-methoxy-1*H*-indol-3-yl)naphthalene-1,4-dione（3q）[3]



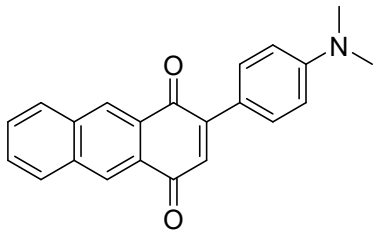
Black solid, 84% yield; mp 165-167 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.85 (s, 1H), 8.09 (d, J = 2.9 Hz, 1H), 8.00 – 7.96 (m, 1H), 7.92 – 7.88 (m, 1H), 7.77 – 7.74 (m, 2H), 7.35 (d, J = 8.8 Hz, 1H), 7.21 (d, J = 1.7 Hz, 1H), 7.11 (s, 1H), 6.81 (dd, J = 8.8, 2.1 Hz, 1H), 3.75 (s, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 185.47, 184.49, 155.41, 142.61, 134.41, 133.90, 133.41, 132.87, 132.12, 127.56, 126.90, 126.20, 125.53, 113.71, 112.48, 107.63, 102.97, 55.91.

2-chloro-3-(4-(dimethylamino)phenyl)naphthalene-1,4-dione（3r）[4]



Purple solid, 63% yield; mp 201-202 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (dd, J = 22.1, 2.9 Hz, 2H), 7.73 (d, J = 3.0 Hz, 1H), 7.59 (s, 1H), 7.37 (d, J = 8.6 Hz, 1H), 7.02 (s, 1H), 6.76 (d, J = 8.6 Hz, 2H), 3.05 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 185.42, 185.19, 147.35, 134.00, 133.83, 133.50, 133.35, 132.91, 132.31, 131.90, 131.16, 130.95, 127.24, 126.89, 125.67, 111.75, 110.93, 40.14.

2-(4-(dimethylamino)phenyl)anthracene-1,4-dione（3s）



Purple solid, 83% yield; mp 96-98 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.65 (s, 1H), 8.58 (s, 1H), 8.03 (s, 2H), 7.64 (d, *J* = 6.2 Hz, 4H), 7.10 (s, 1H), 6.75 (d, *J* = 7.6 Hz, 2H), 3.03 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 184.95, 184.77, 151.69, 148.59, 134.78, 132.82, 131.01, 130.10, 130.00, 129.58, 129.20, 129.06, 128.99, 127.64, 120.76, 111.69, 40.10, 29.70. For $C_{22}H_{18}NO_2^+$ $(M+H)^+$ 328.1338 found: 328.1341.

6 References

1 J. H. Jiang, S. S. K. Boominathan, W. P. Hu, C. Y. Chen, J. K. Vandavasi, Y. T. Lin and J. J. Wang, *Eur. J. Org. Chem.,* 2016, **2016**, 2284-2289.

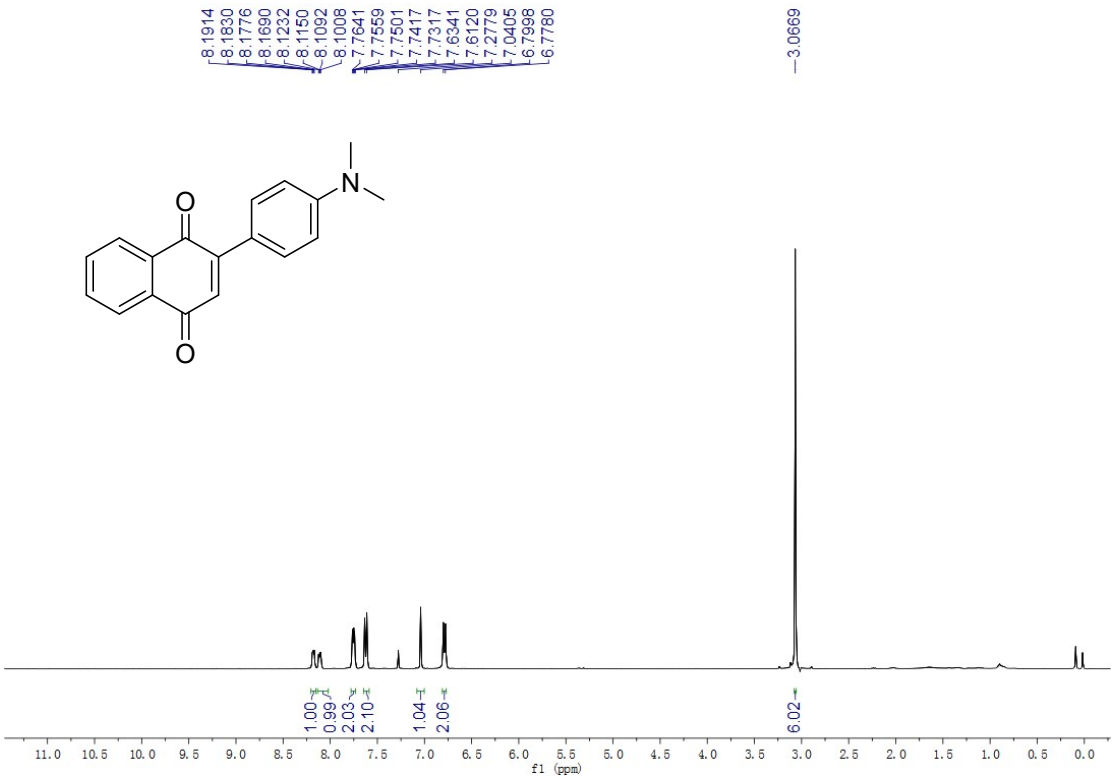
2 M. Janeczko, O. M. Demchuk, D. Strzelecka, K. Kubiński and M. Masłyk, *Eur. J. Org. Chem.,* 2016, **124**, 1019-1025.

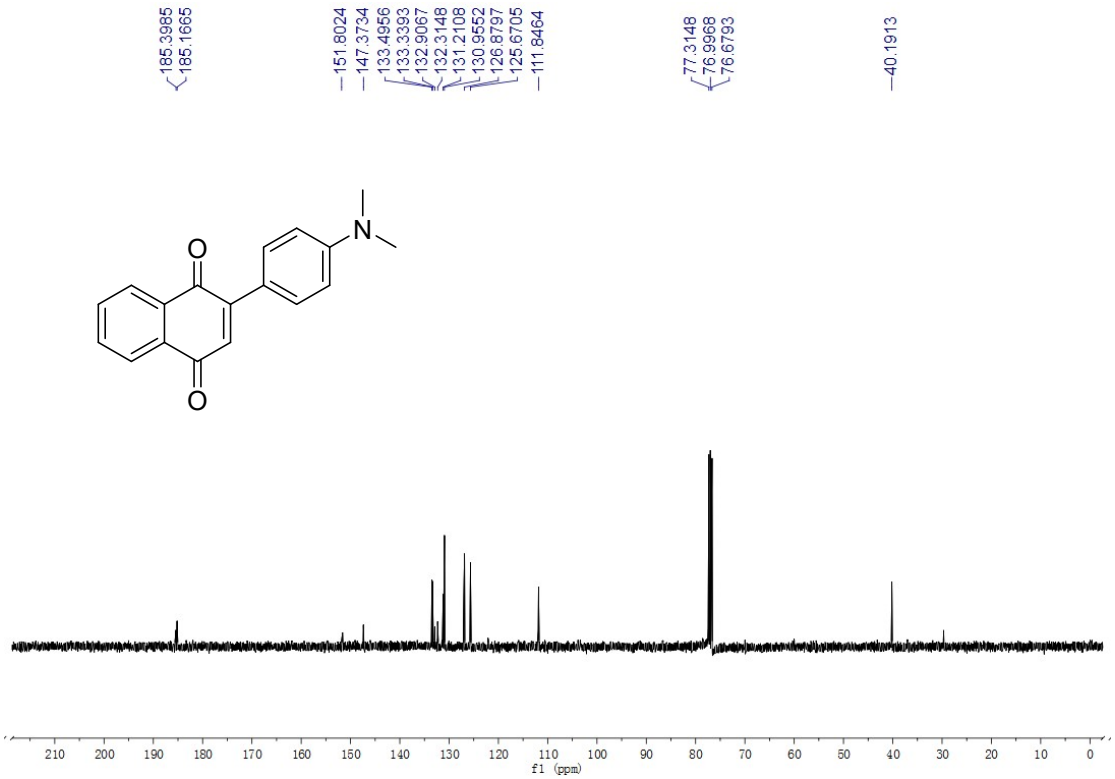
3 Y. Dong, H. Zhang, J. Yang, S. He, Z.-C. Shi, X.-M. Zhang and J.-Y. Wang, *ACS omega.,* 2019, **4**, 21567-21577.

4 C. Blackburn, J. Griffiths, *J. Chem. Res.,* 1982, **12**, 3457-3472.

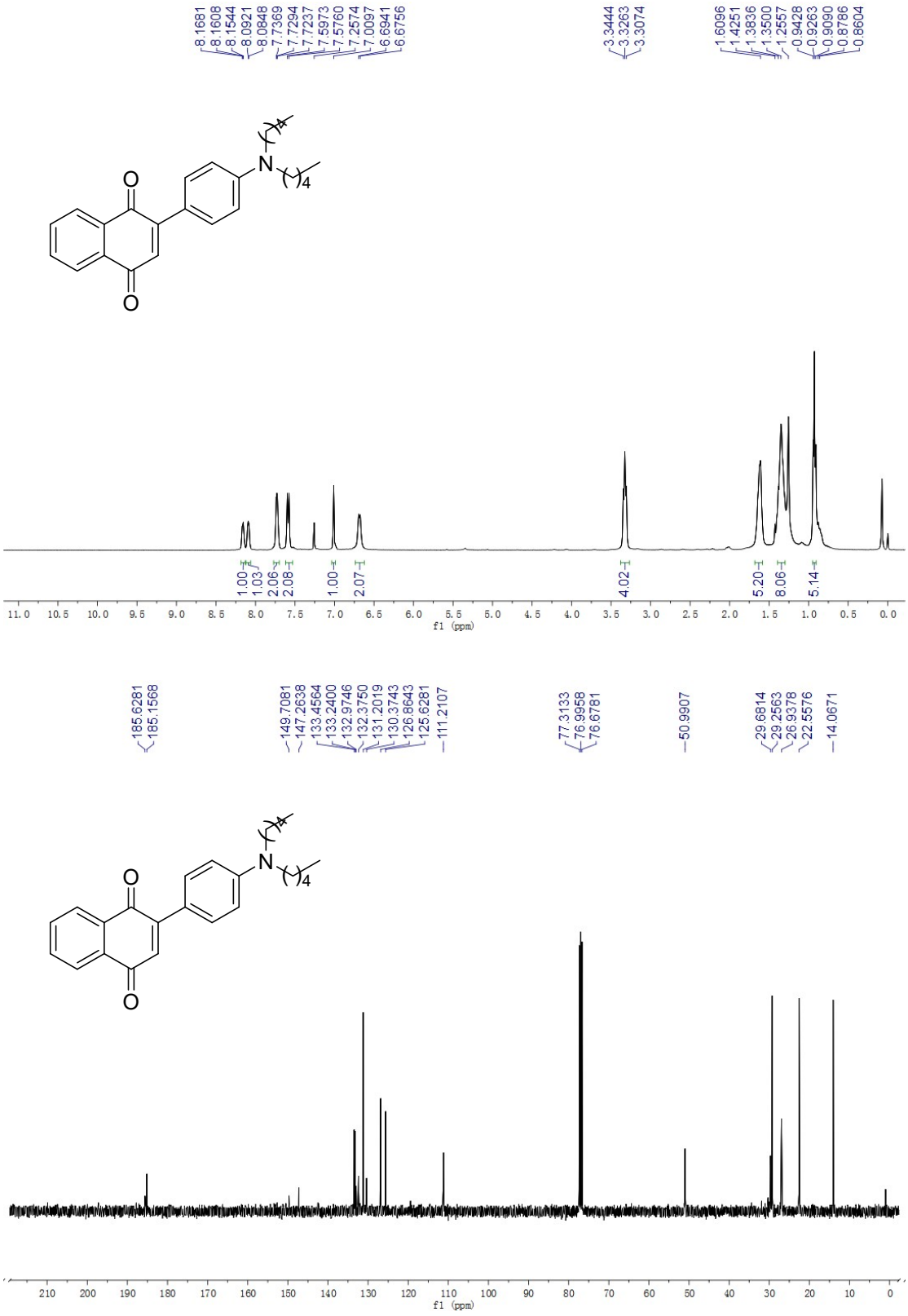
7 Copies of ^{1}H and ^{13}C spectra for all compounds

2-(4-(dimethylamino)phenyl)naphthalene-1,4-dione（3a）

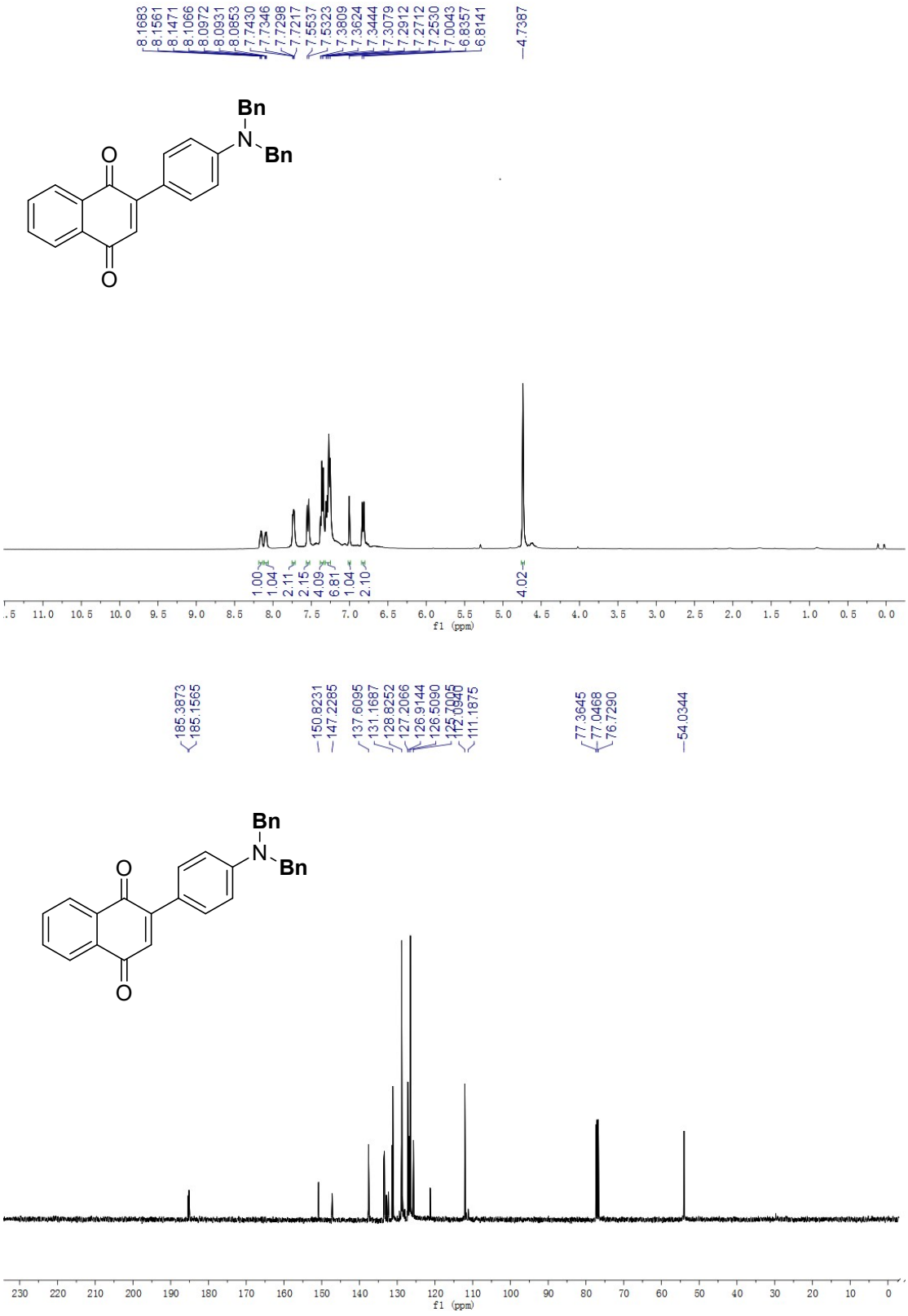




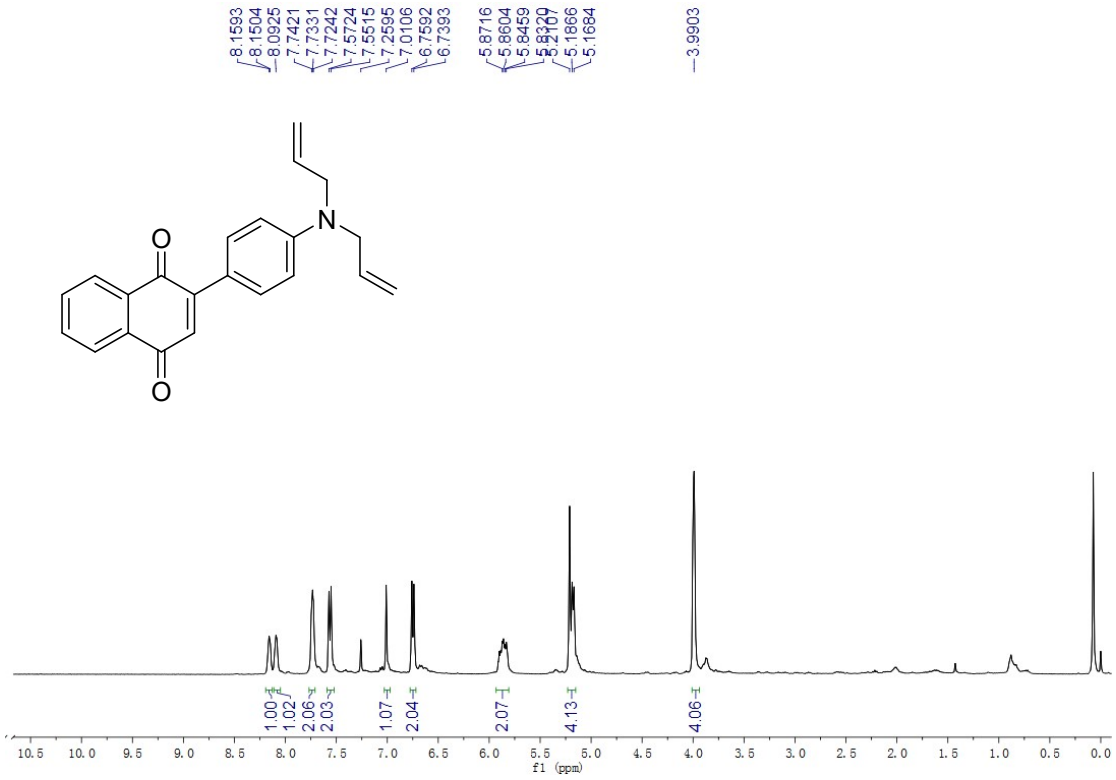
2-(4-(diethylamino)phenyl)naphthalene-1,4-dione（3b）

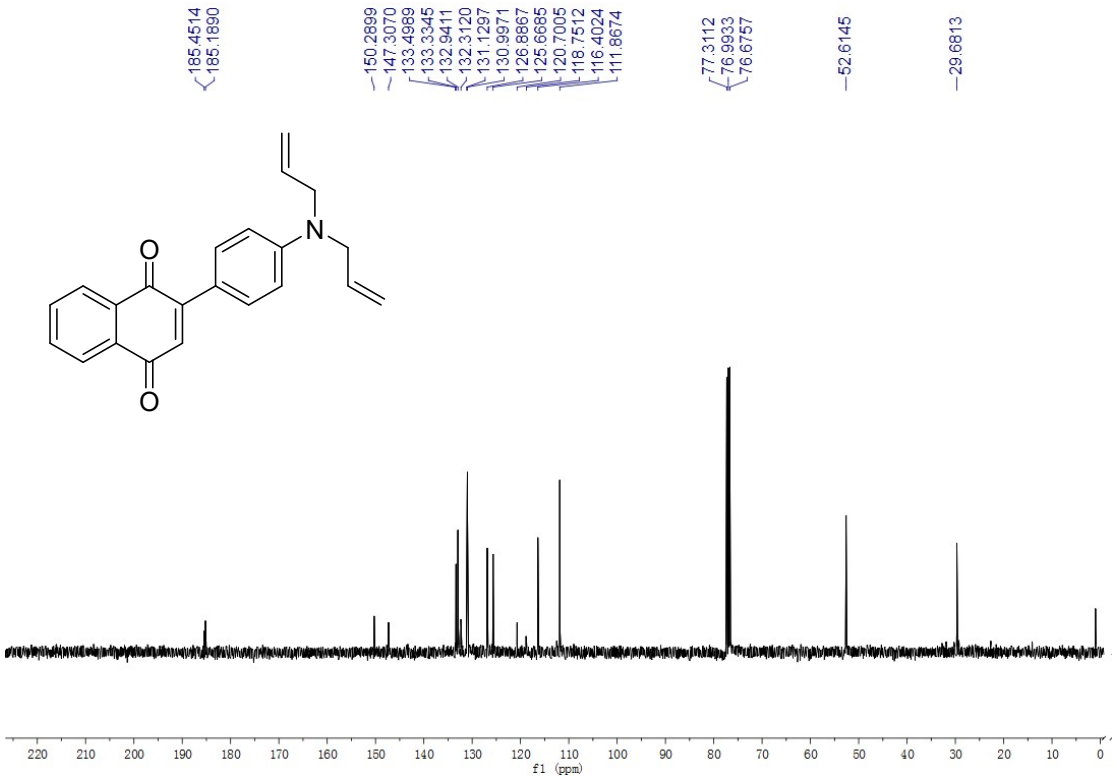


2-(4-(dibenzylamino)phenyl)naphthalene-1,4-dione（3c）



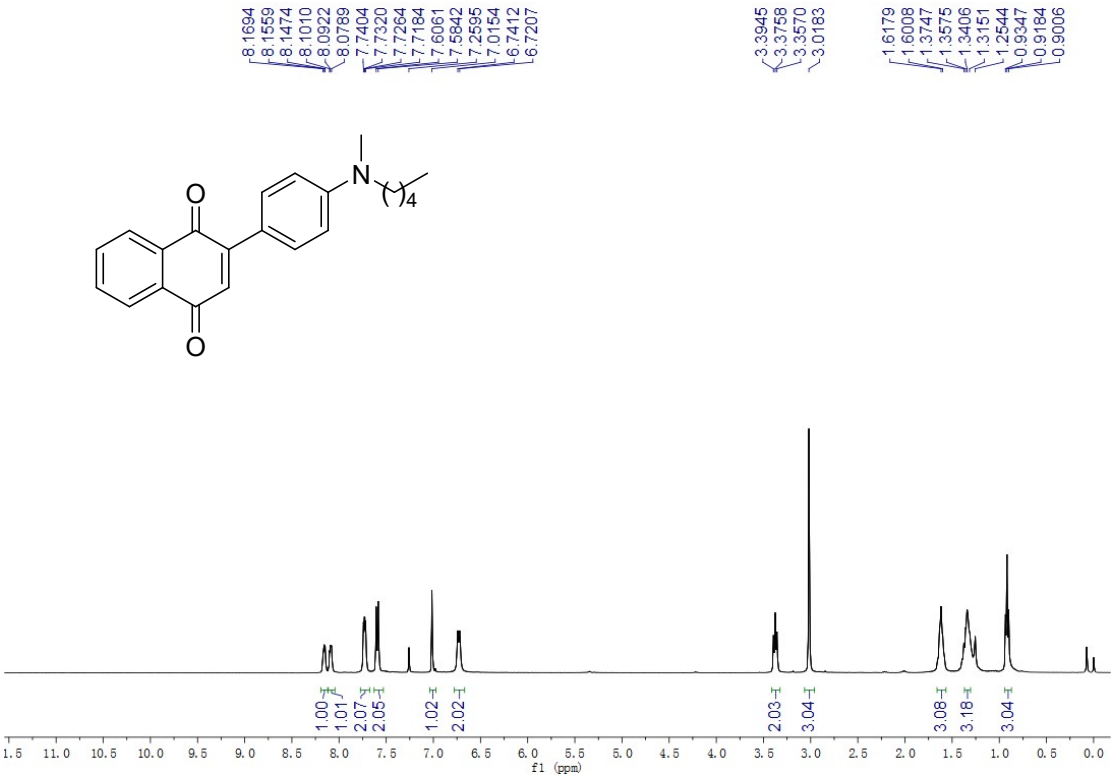
2-(4-(diallylamino)phenyl)naphthalene-1,4-dione（3d）

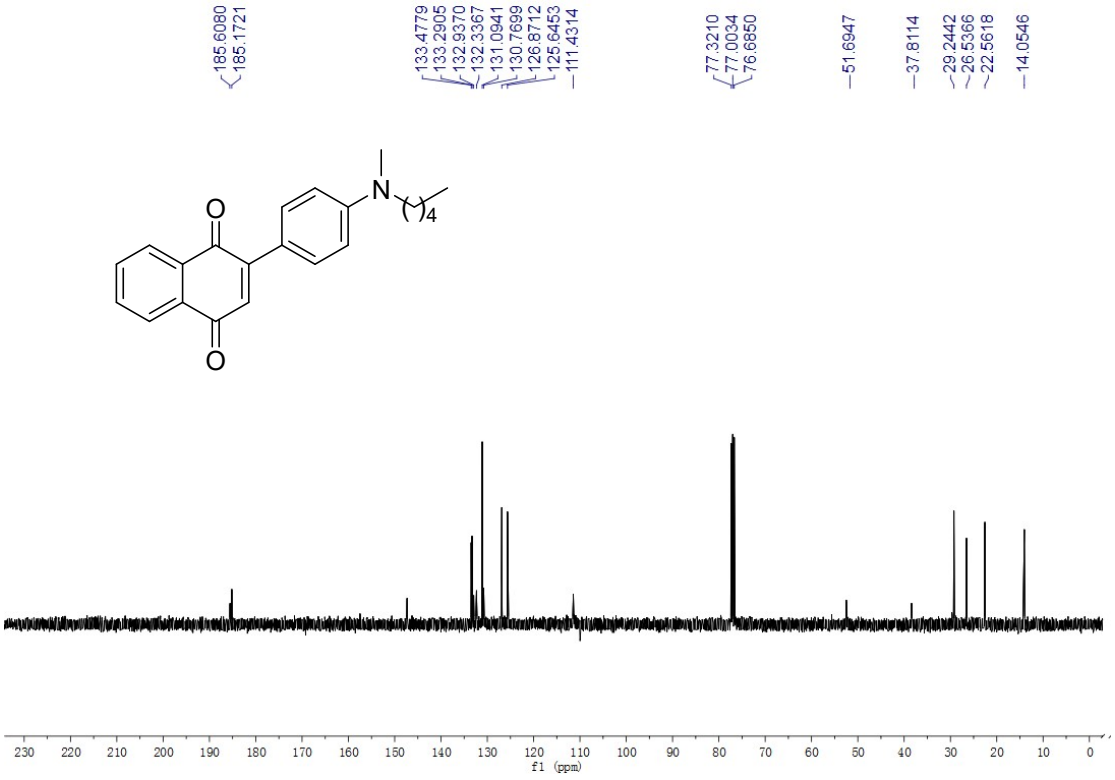




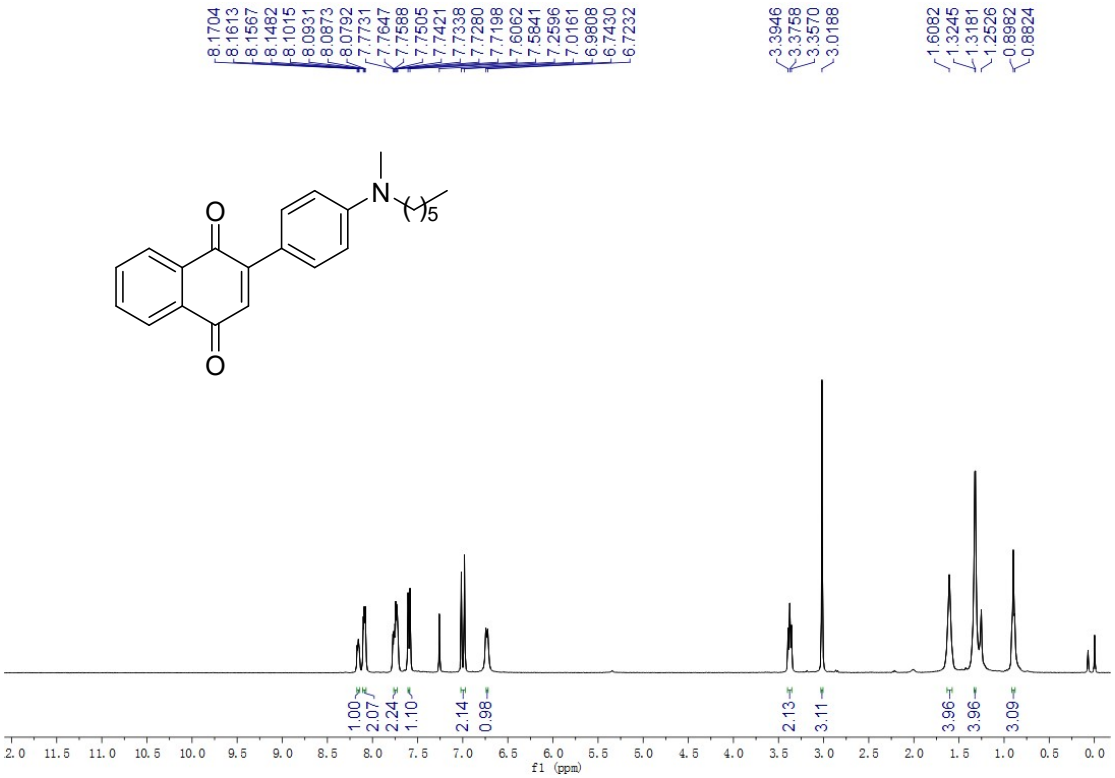
2-(4-(ethyl(methyl)amino)phenyl)naphthalene-1,4-dione（3e）

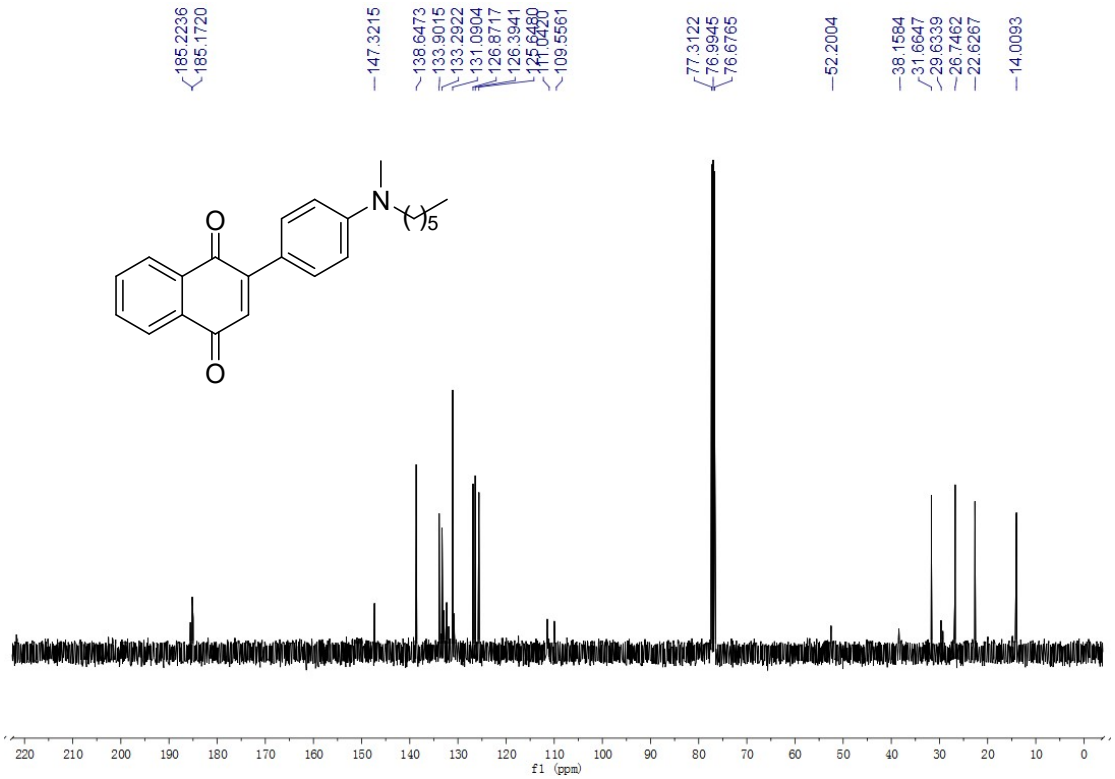
2-(4-(ethyl(methyl)amino)phenyl)naphthalene-1,4-dione（3f）



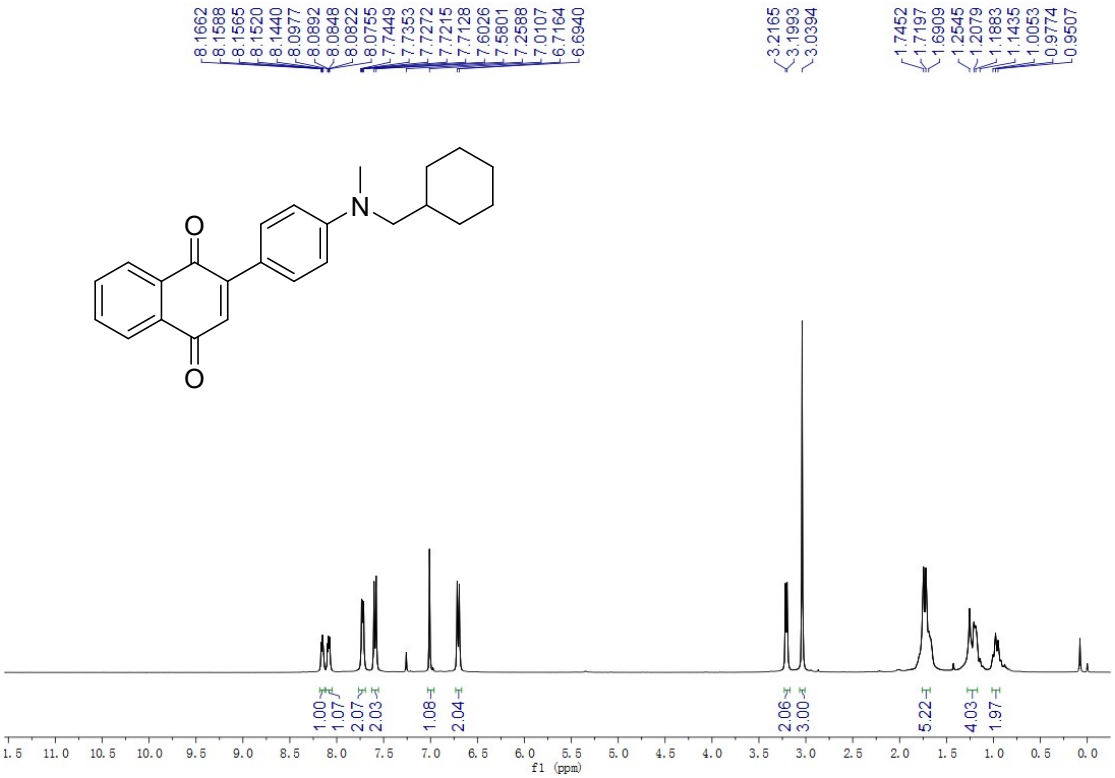


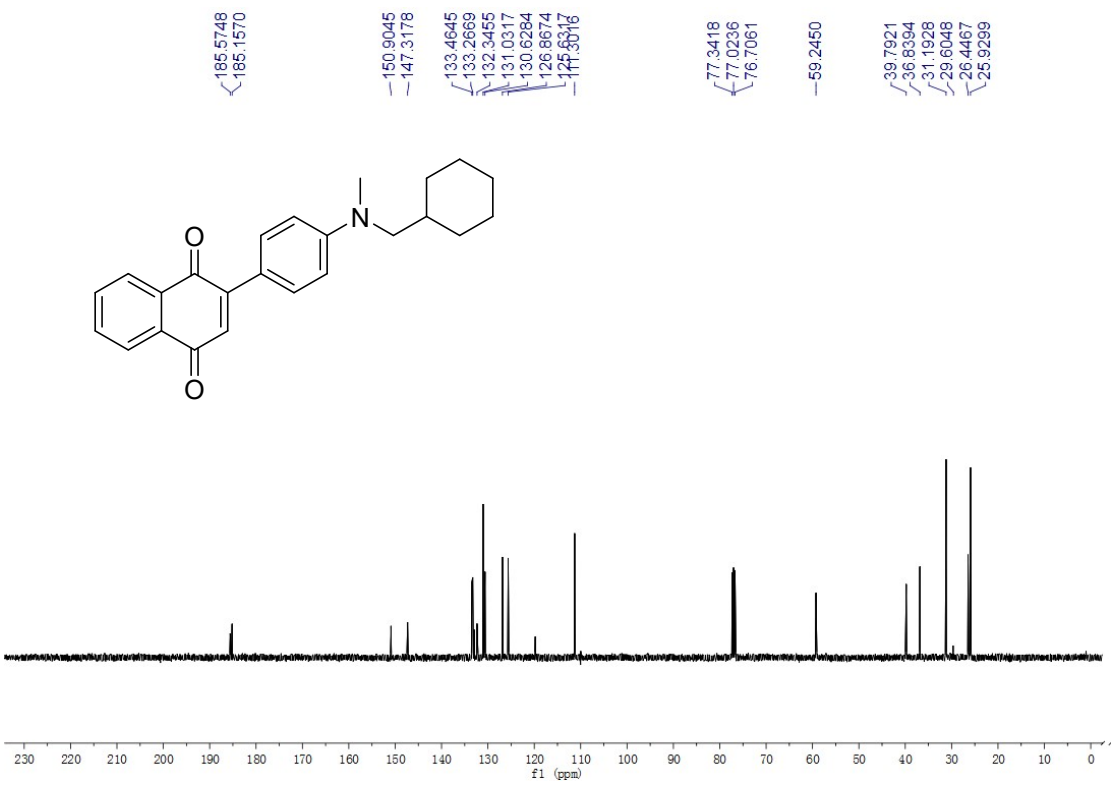
2-(4-(ethyl(methyl)amino)phenyl)naphthalene-1,4-dione（3g）



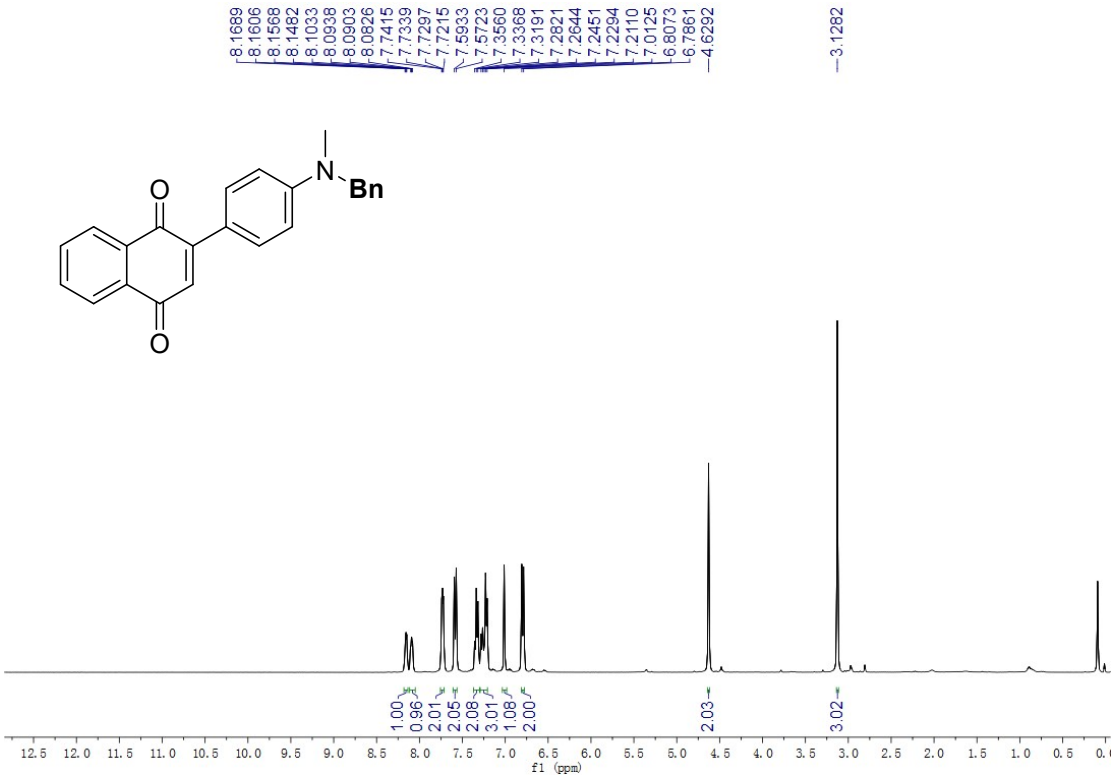


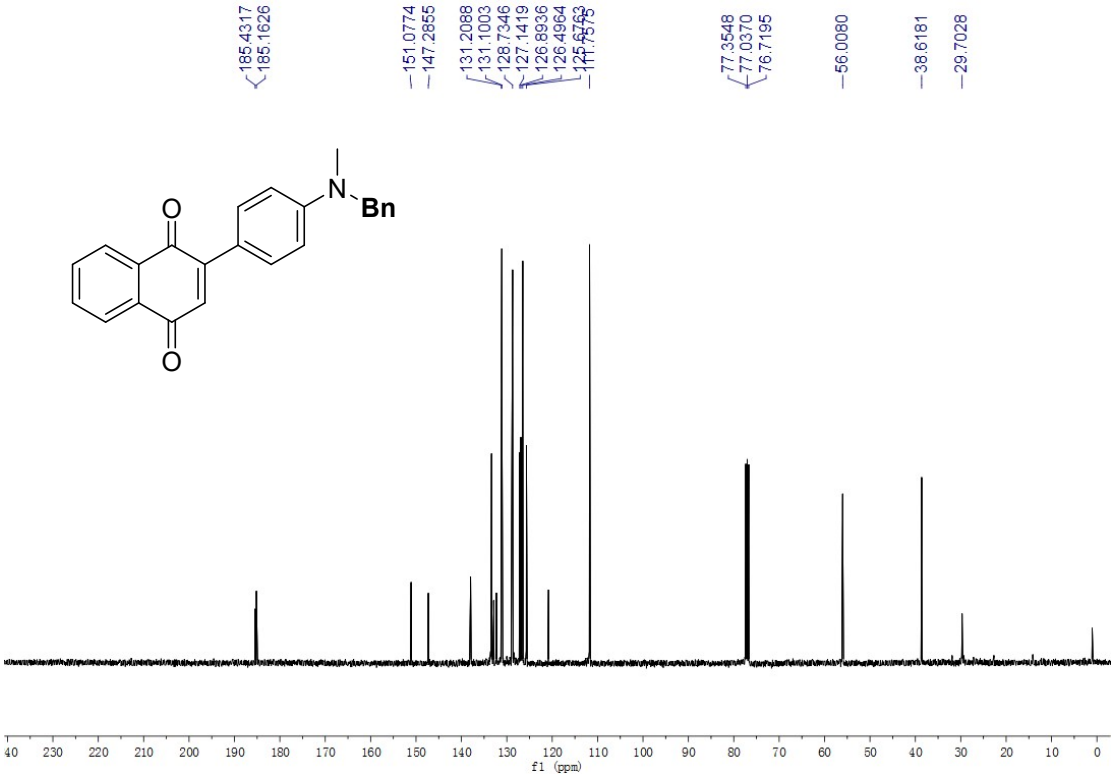
2-(4-((cyclohexylmethyl)(methyl)amino)phenyl)naphthalene-1,4-dione（3h）



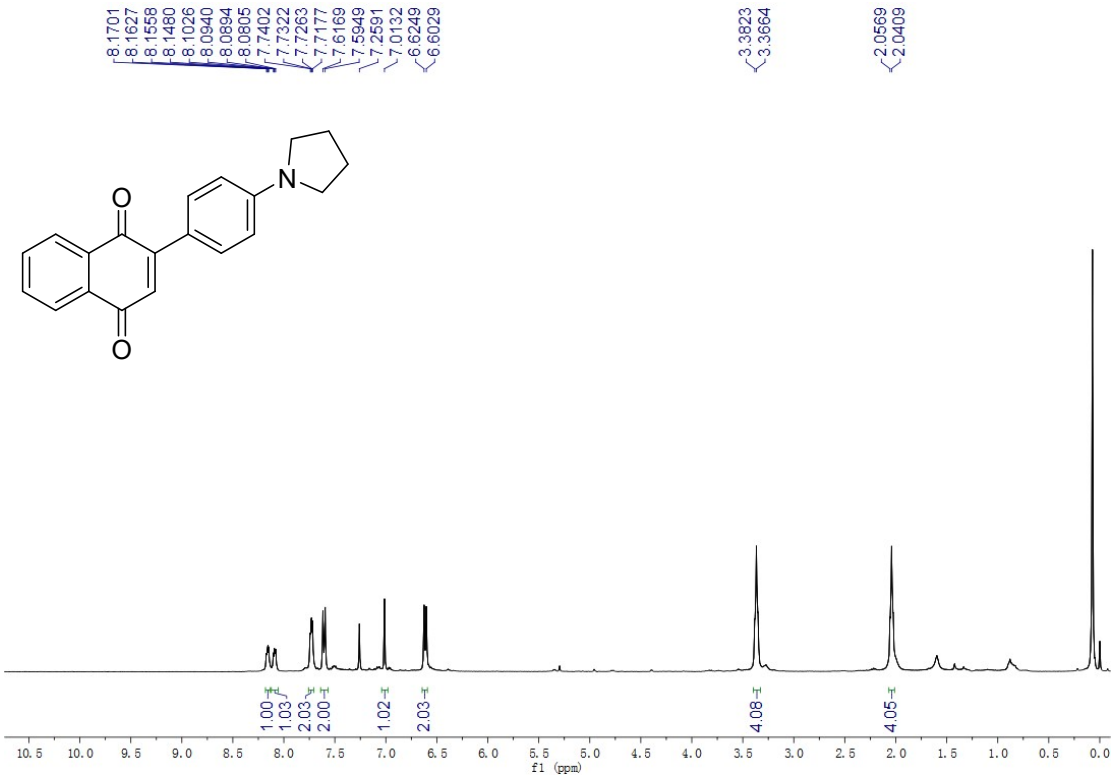


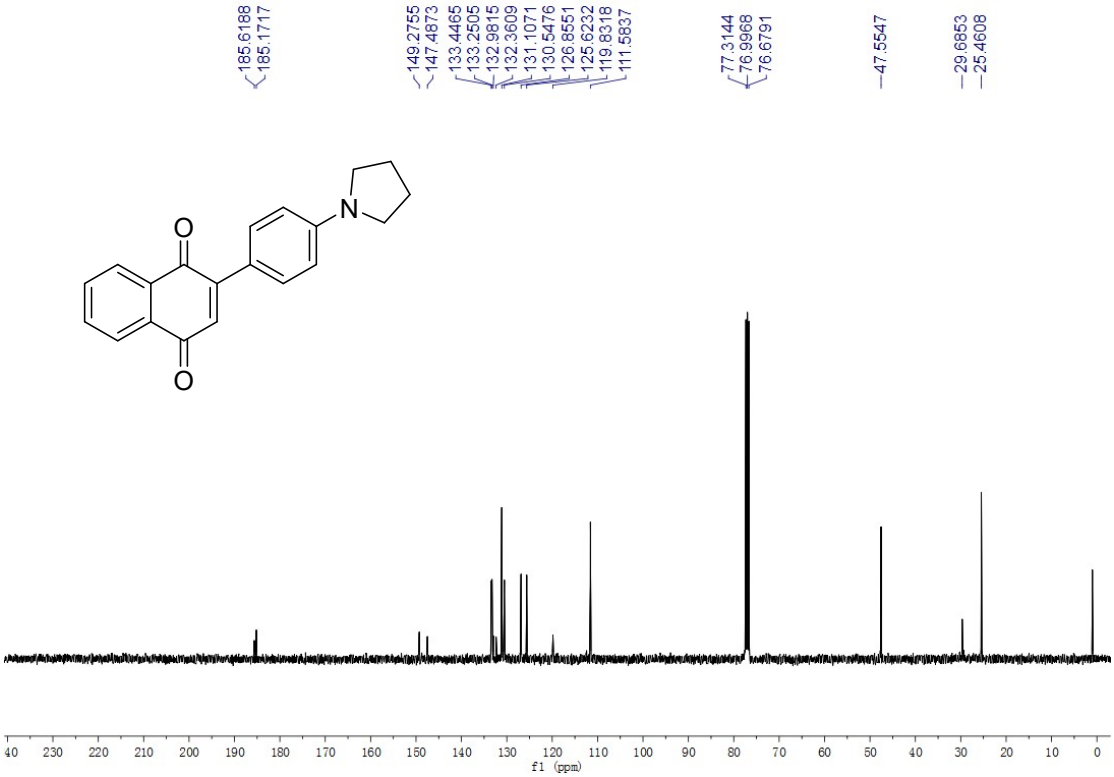
2-(4-(benzyl(methyl)amino)phenyl)naphthalene-1,4-dione（3i）



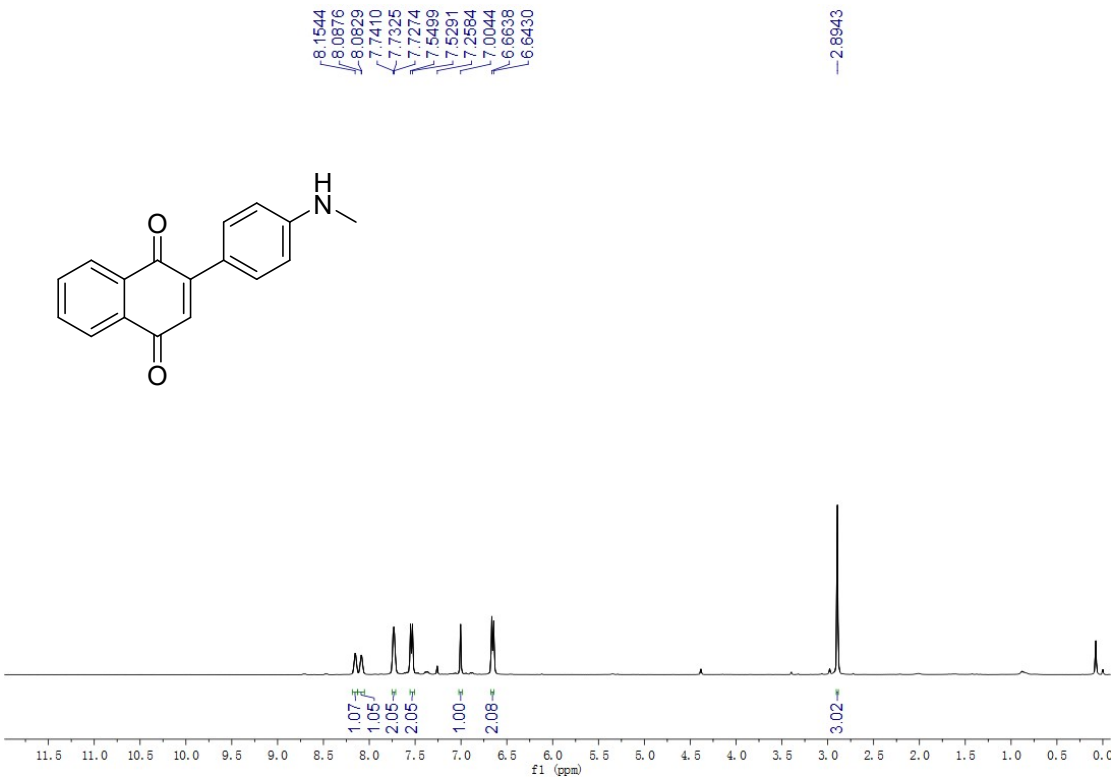


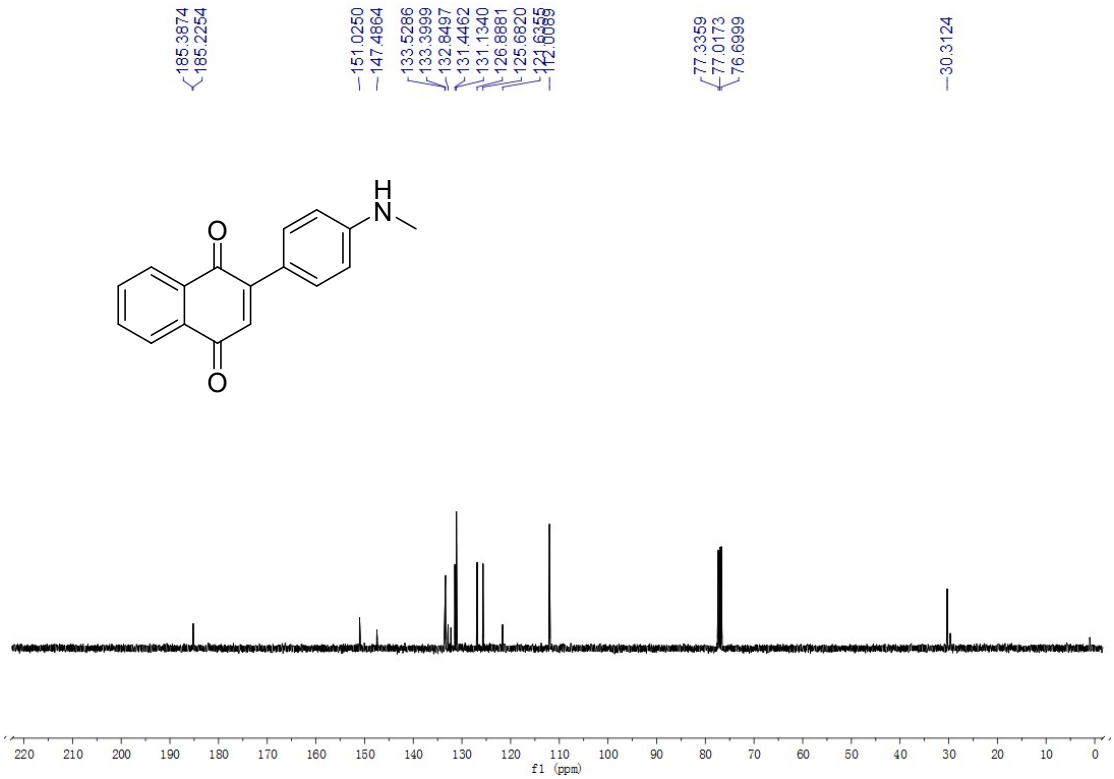
2-(4-(pyrrolidin-1-yl)phenyl)naphthalene-1,4-dione（3j）



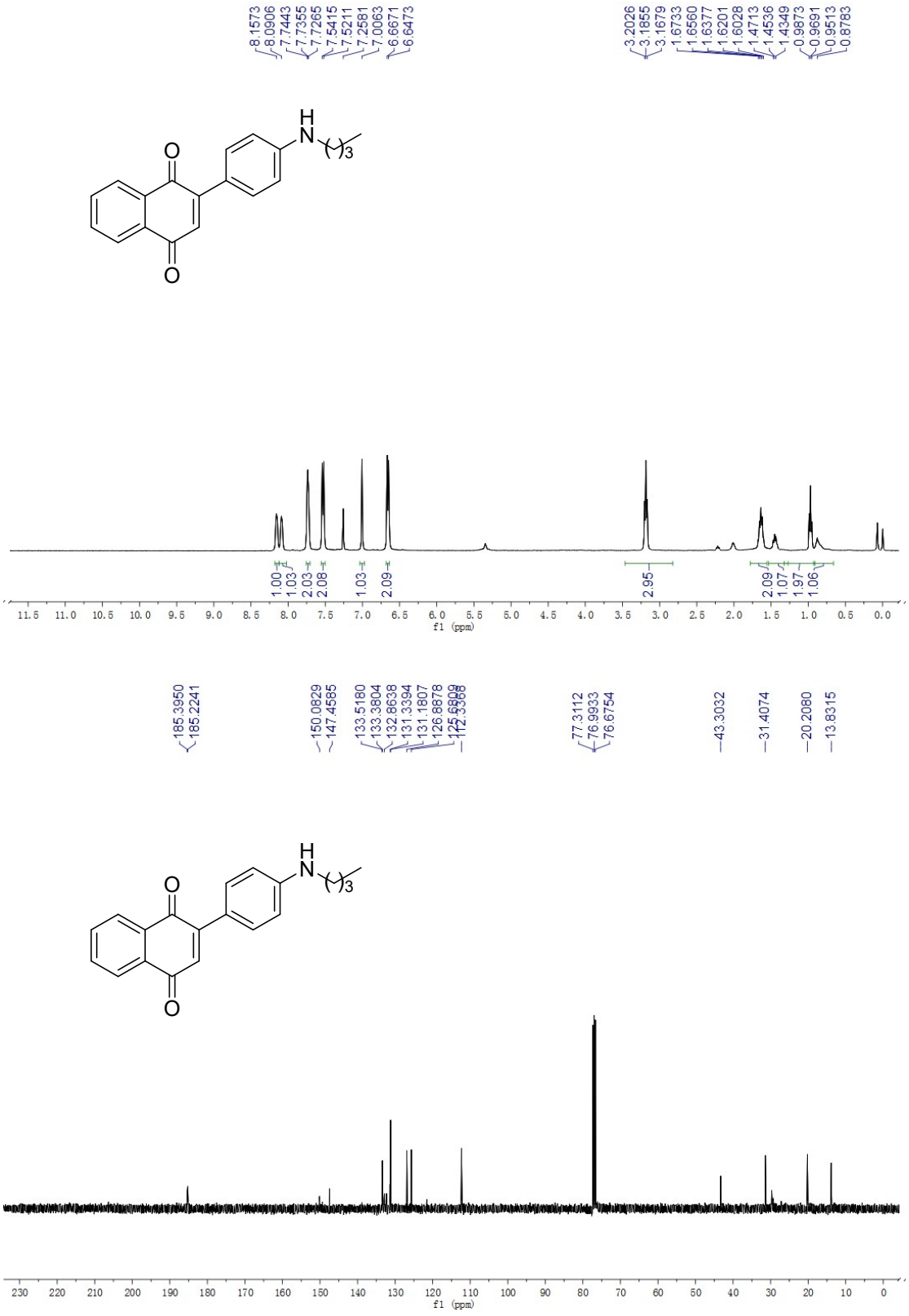


2-(4-(methylamino)phenyl)naphthalene-1,4-dione（3k）

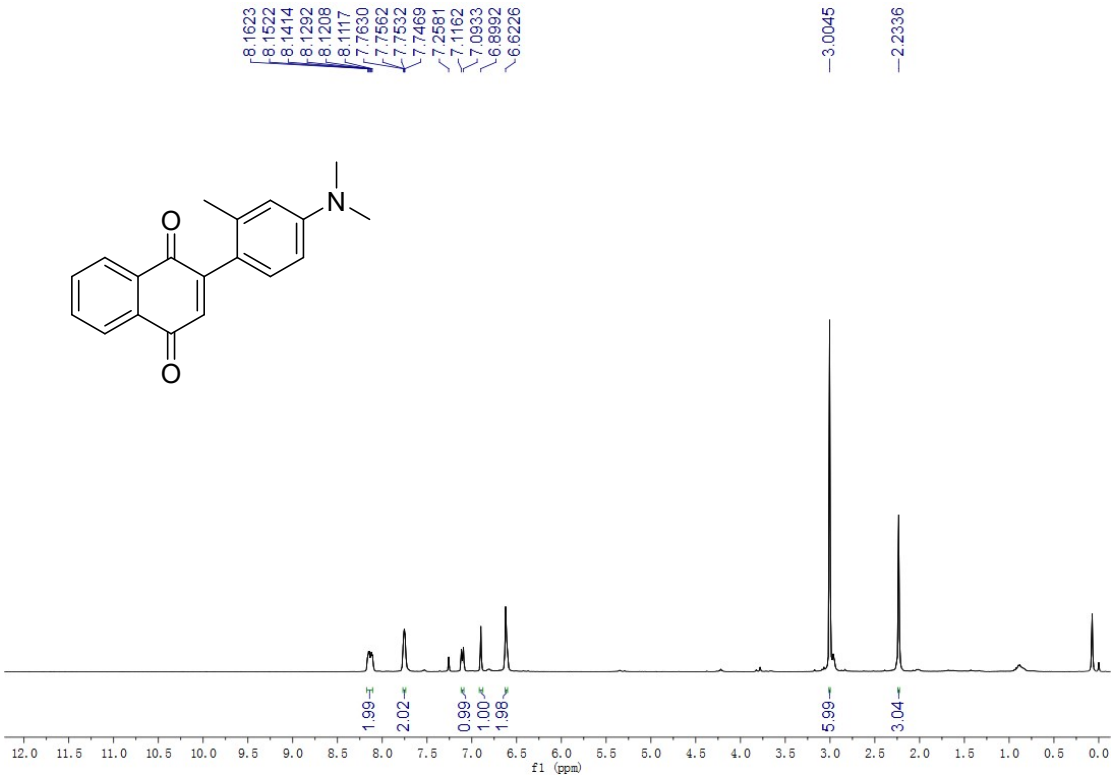


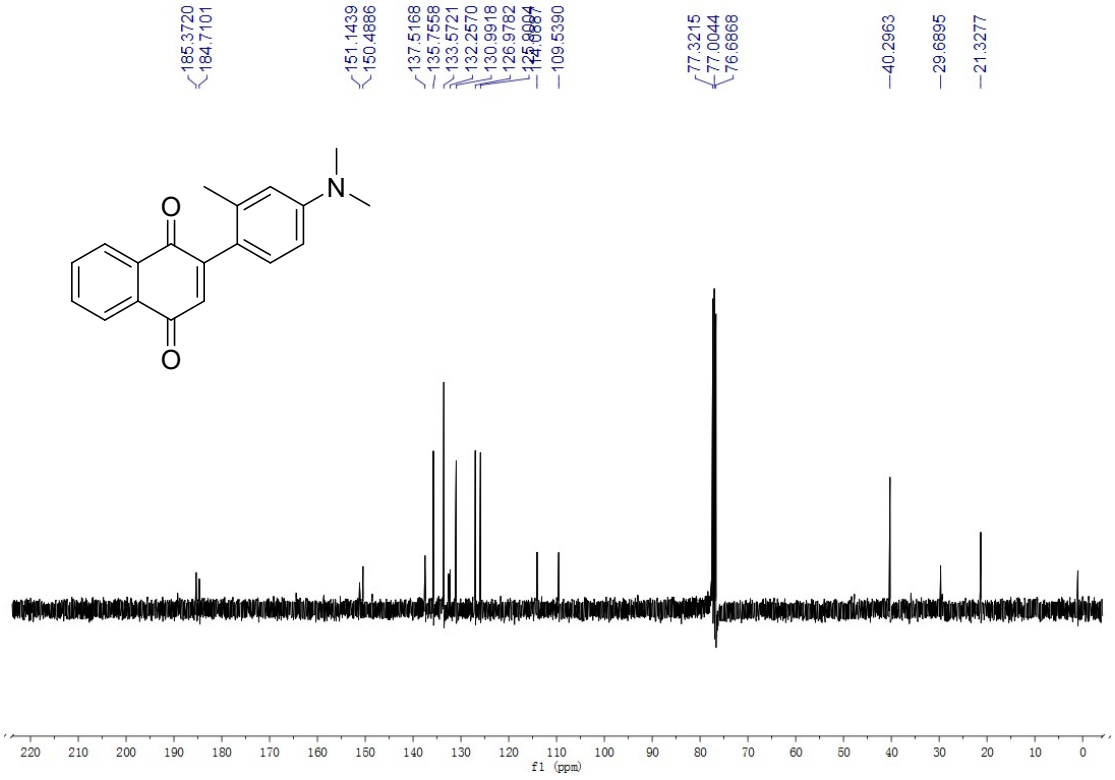


2-(4-(ethylamino)phenyl)naphthalene-1,4-dione（3l）

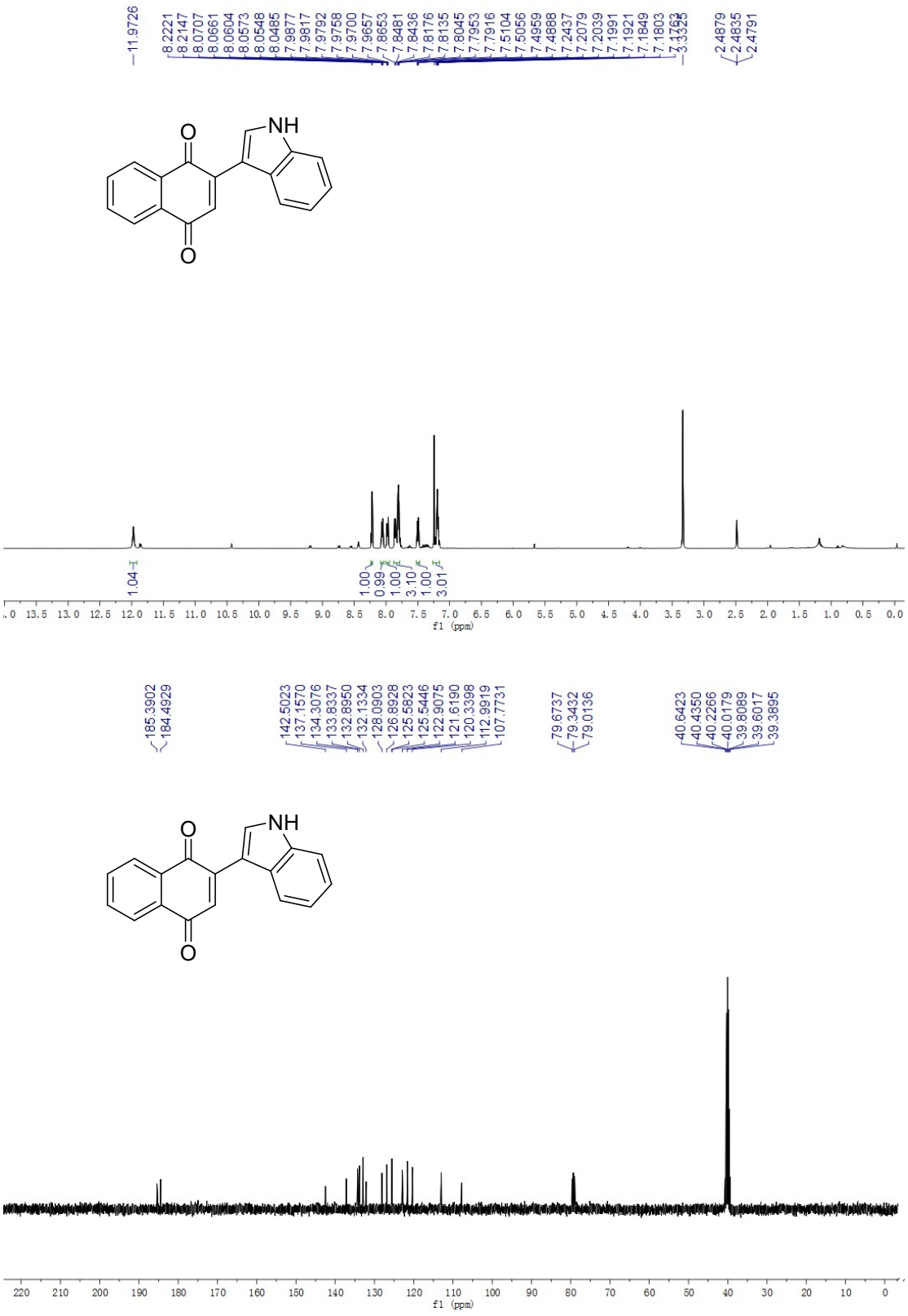


2-(4-(dimethylamino)-2-methylphenyl)naphthalene-1,4-dione（3m）

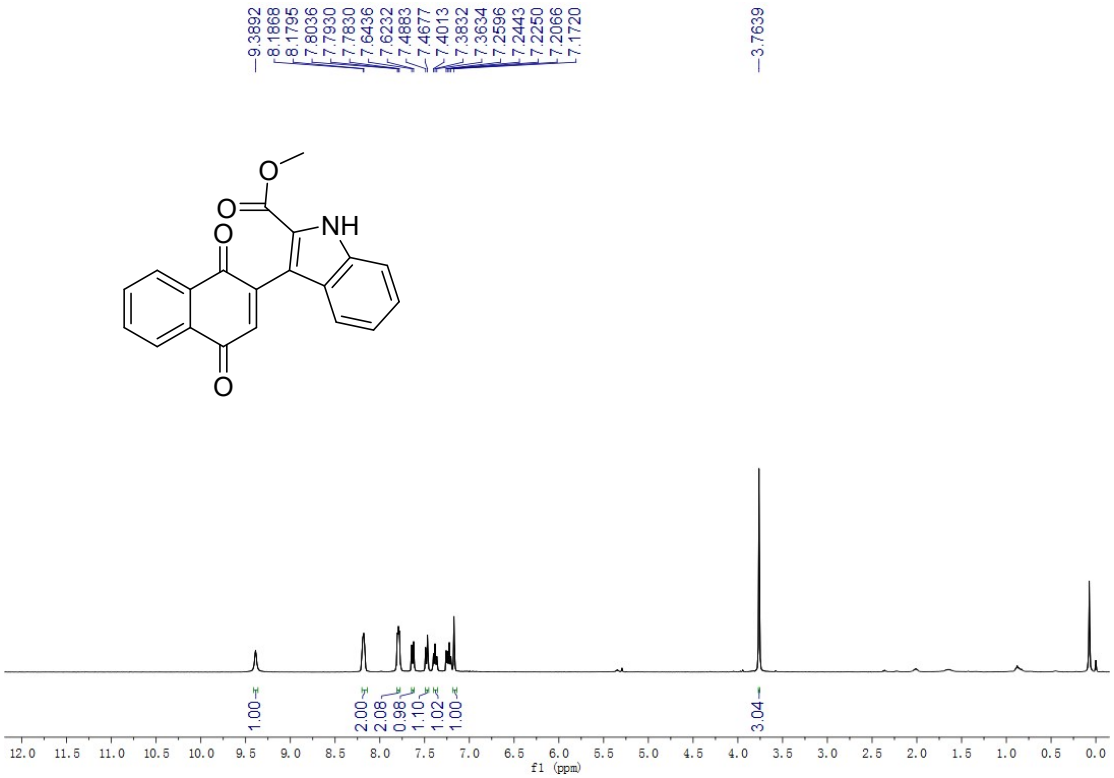


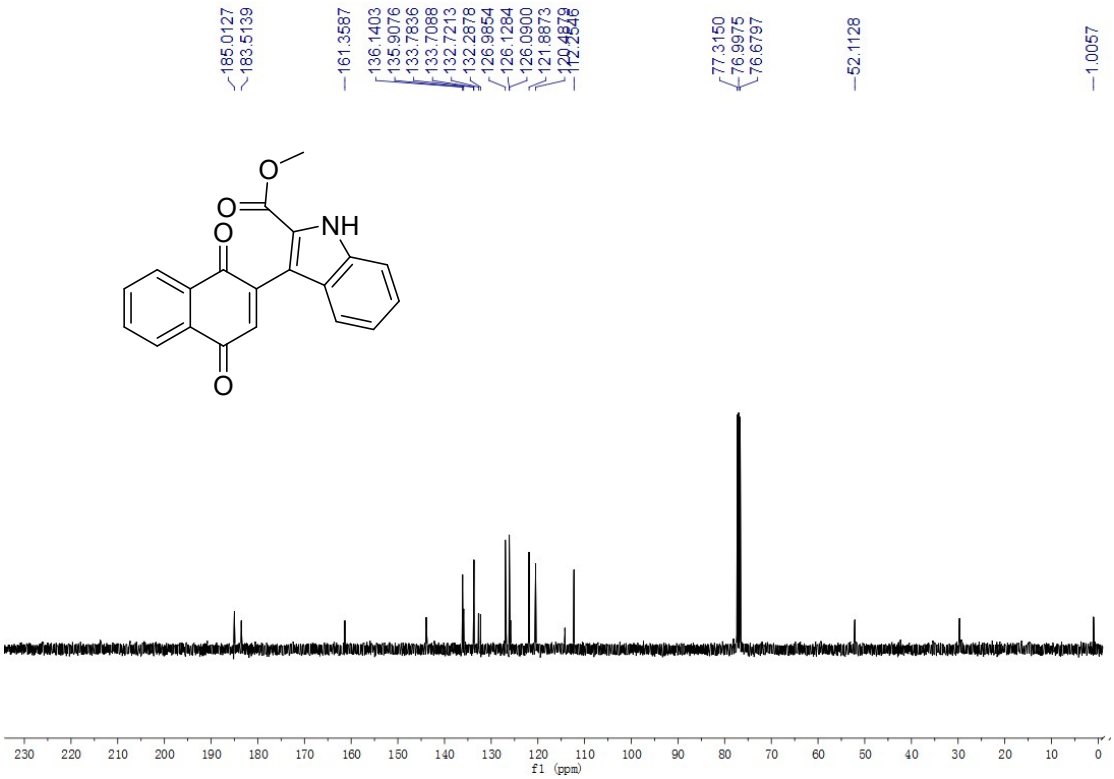


2-(1*H*-indol-3-yl)naphthalene-1,4-dione（3n）

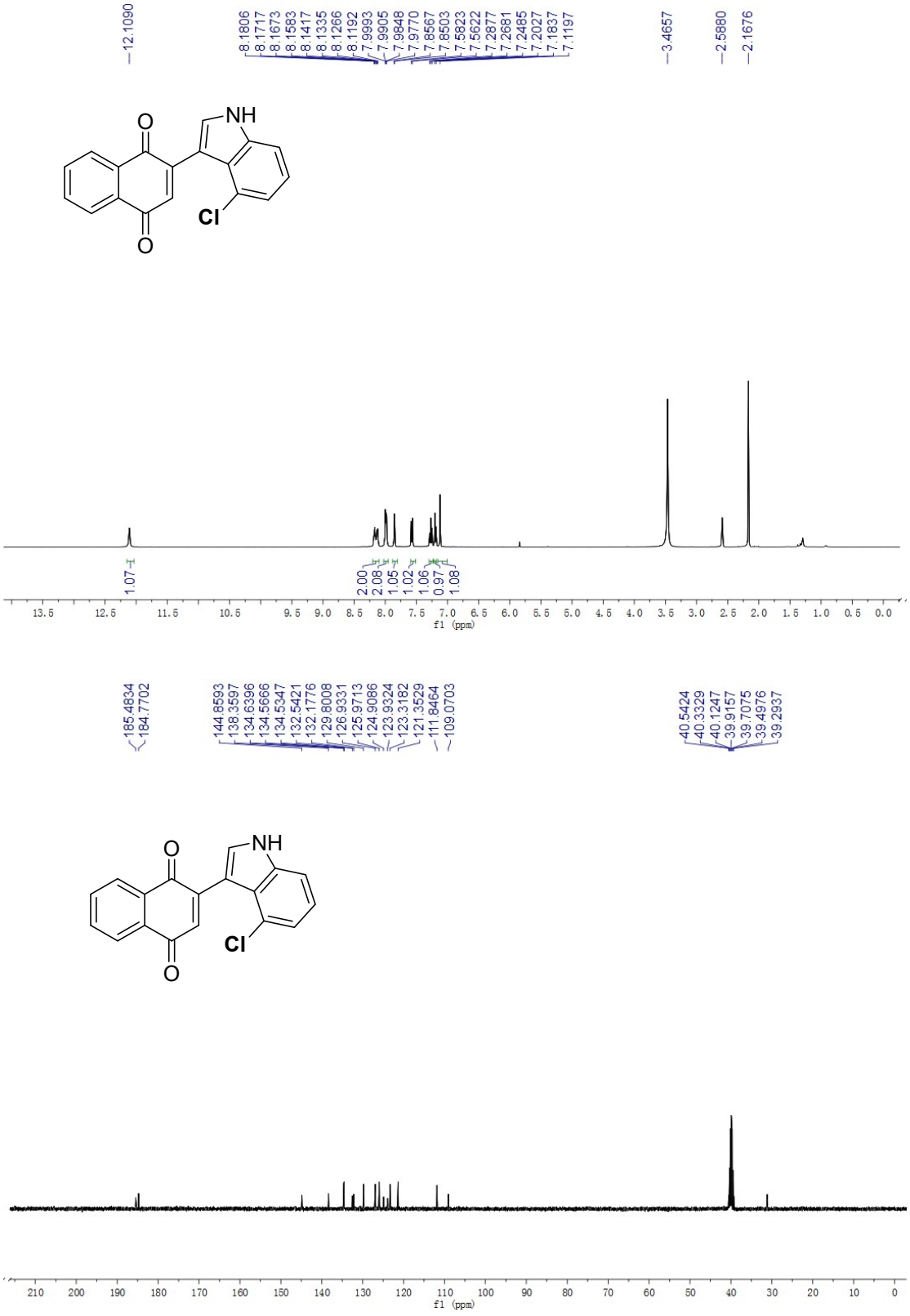


Methyl 3-(1,4-dioxo-1,4-dihydronaphthalen-2-yl)-1H-indole-2-carboxylate（3o）

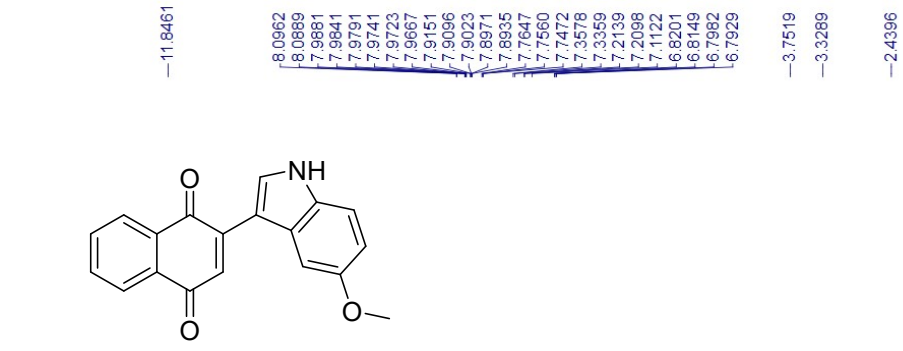


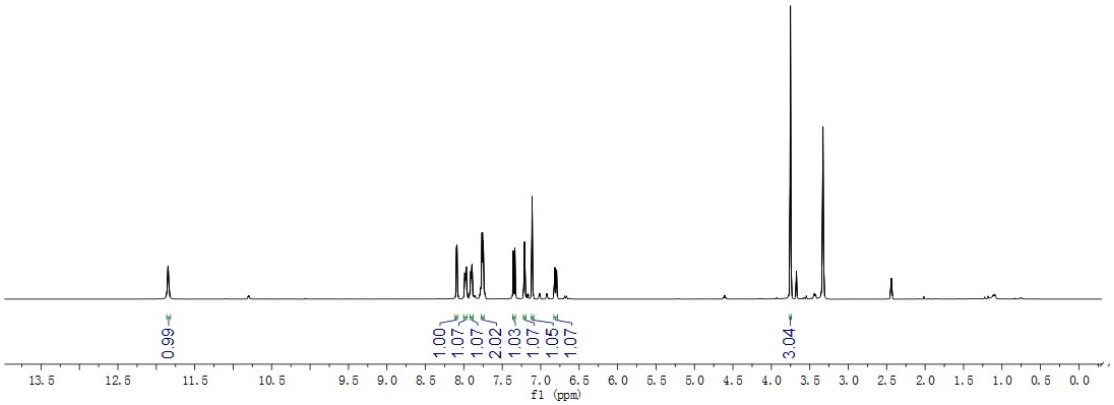


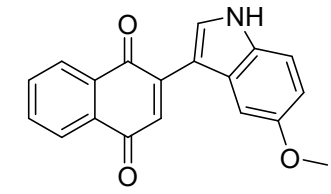
2-(4-chloro-1*H*-indol-3-yl)naphthalene-1,4-dione（3p）

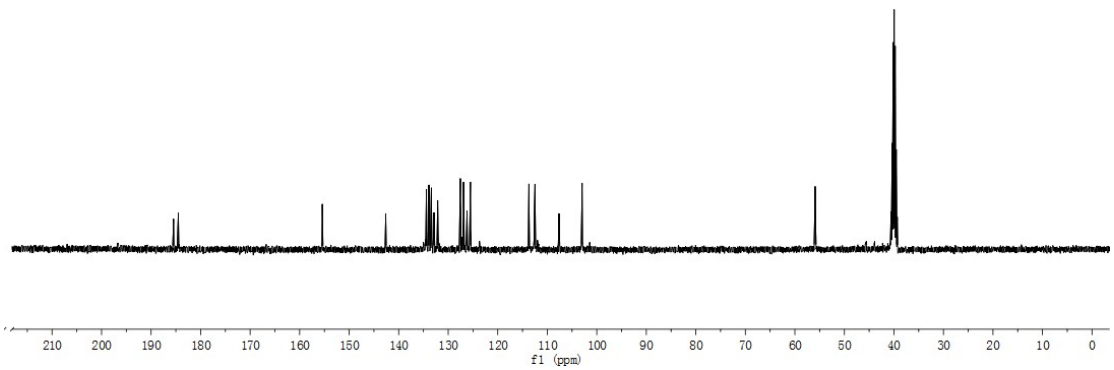


2-(5-methoxy-1*H*-indol-3-yl)naphthalene-1,4-dione（3q）

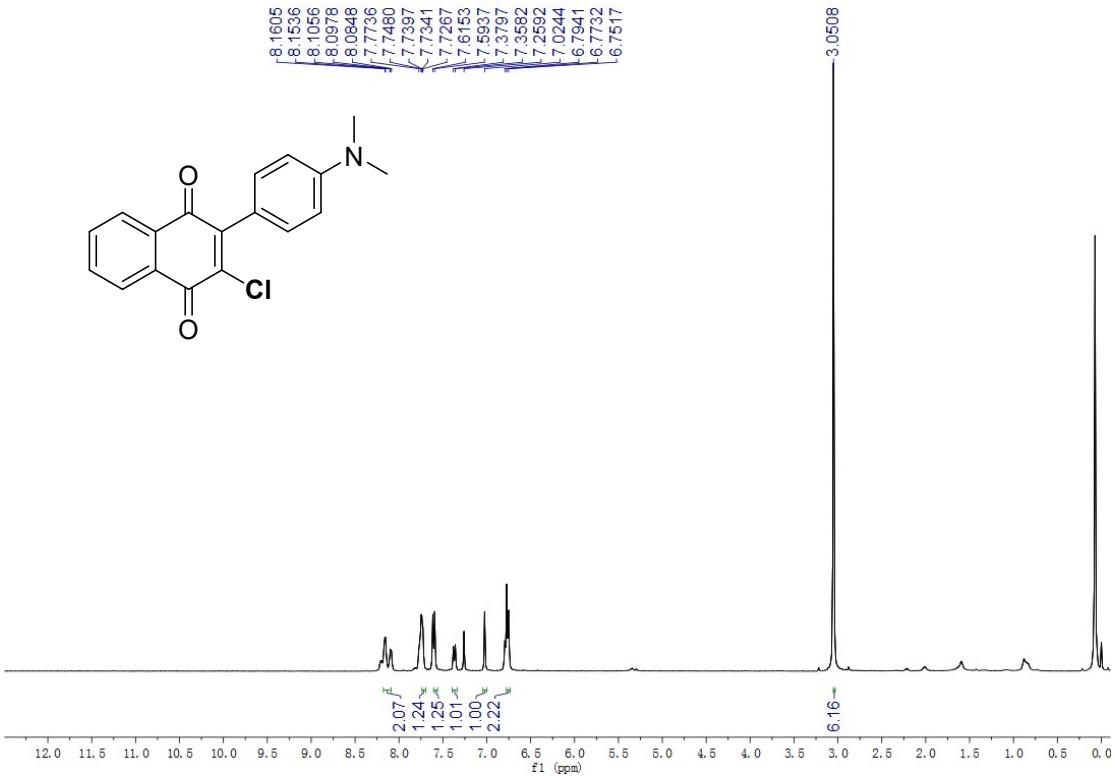


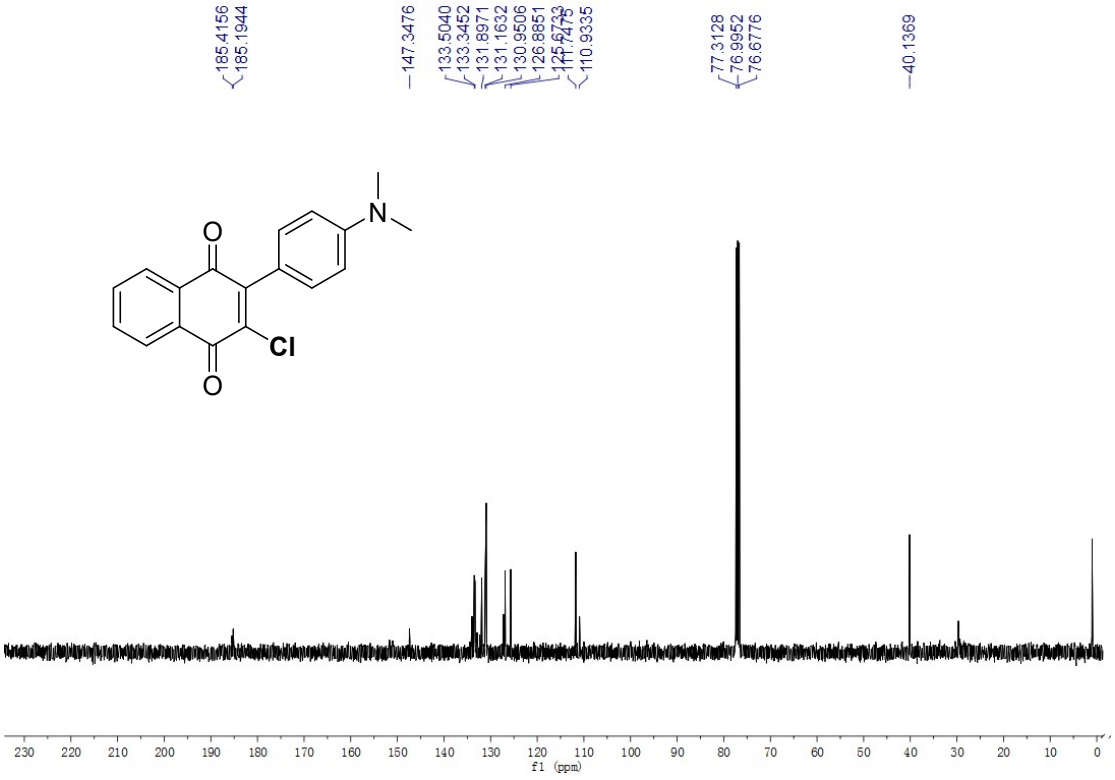






2-chloro-3-(4-(dimethylamino)phenyl)naphthalene-1,4-dione（3r）





2-(4-(dimethylamino)phenyl)anthracene-1,4-dione（3s）