Assembly of Polycyclic *N*-Heterocycles via Copper-Catalyzed Cycloamination of Indolylquinones and Aromatic amines

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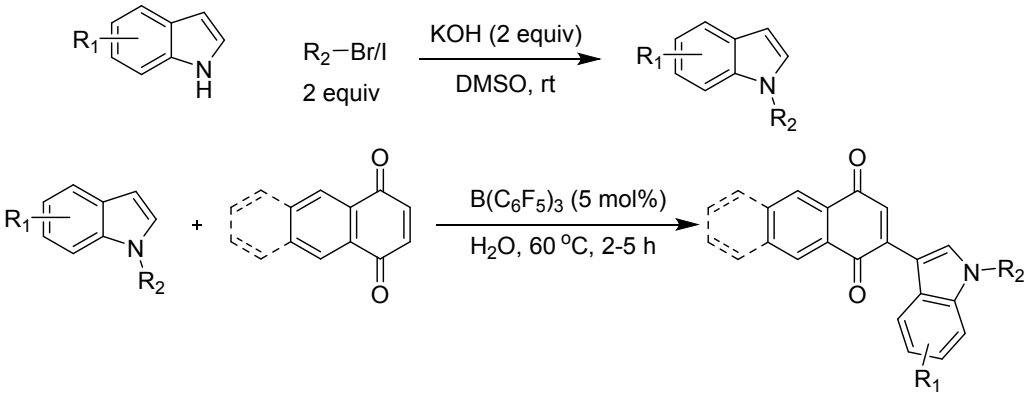
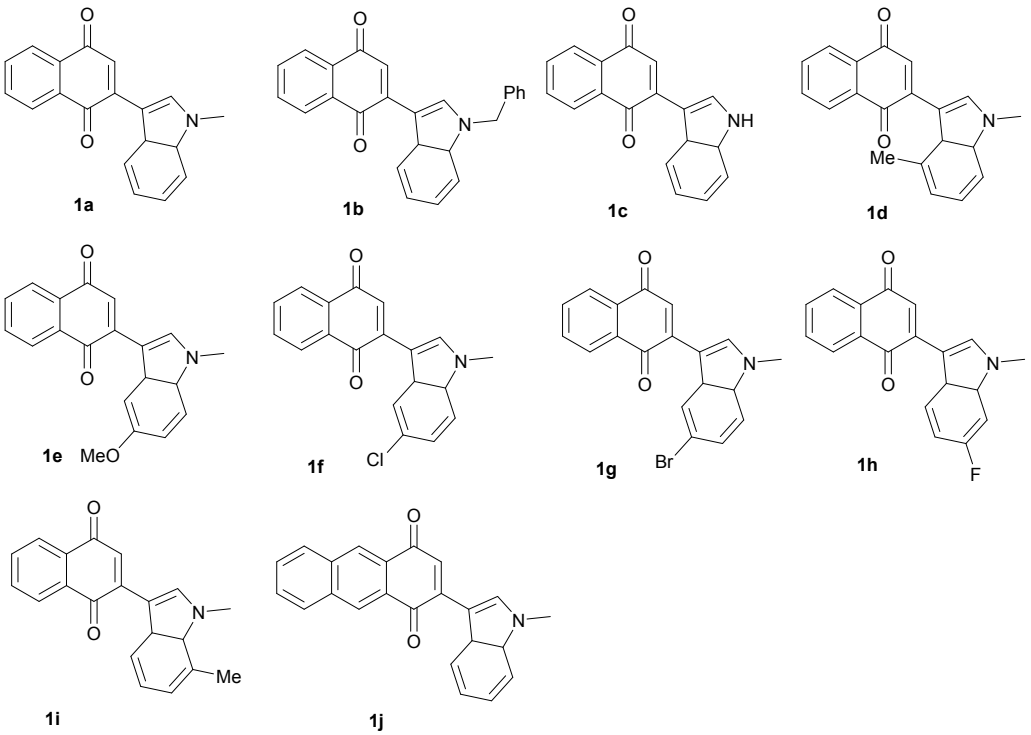
1. General information

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.

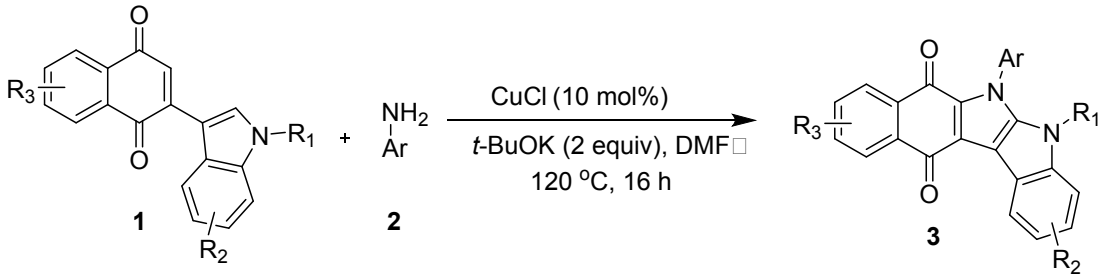
2. Preparation of the starting materials

For this study, *N*-Protected indoles were prepared from substituted indoles with alkyl bromides (iodomethane used for methyl-protected reagent).[1] Indoles-substituted quinones (**1a-1j**) were prepared from *N*-Protected indoles with quinones.[2]





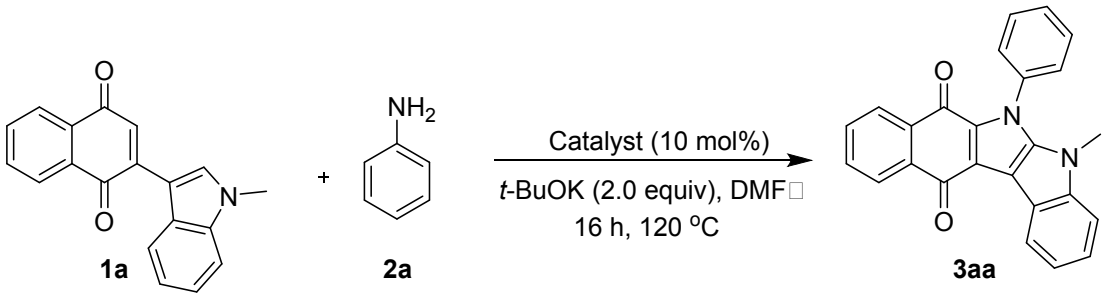
3. General procedure for the synthesis of compounds 3



To a solution of indolylquinone **1** (0.3 mmol), CuCl (0.03 mmol, 10 mol%), *t*-BuOK (0.6 mmol, 2 equiv) in DMF (2 mL) was added aromatic amine **2** (0.6 mmol, 2 equiv). The reaction mixture was stirred at 120 °C (oil bath) under air atmosphere for 16 h. After the completion of the reaction (monitored by TLC), and cooled down to room temperature. The reaction was quenched with saturated salt water (10 ml) and the mixture was extracted with EtOAc (3 × 5 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**.

4. Optimization of reaction conditions

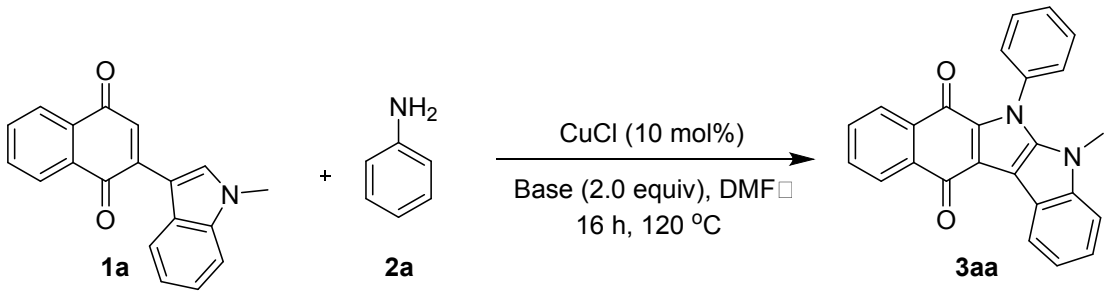
Table S1. Optimization of catalyst[a]



Entry	catalyst	Yield[b]
1	$Cu(OAc)_2$	42
2	$Cu(OTf)_2$	45
3	$CuSO_4.5H_2O$	36
4	$CuCl_2.2H_2O$	39
5	CuCl	87
6	$CuBr_2$	49
7	CuBr	43
8	CuI	61
9	No	15

[a]Reaction conditions: **1a** (0.3 mmol), **2a** (0.6 mmol), catalyst (10 mol%), *t*-BuOK (0.6 mmol), DMF (2.0 mL), 16 h, 120 °C. [b]Isolated yield.

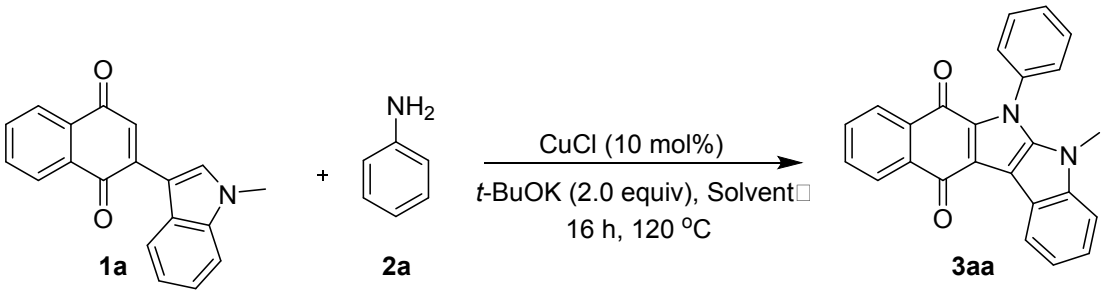
Table S2. Optimization of base[a]



Entry	Base	Yield[b]
1	*t*-BuOK	87
2	*t*-BuONa	60
3	K_2CO_3	32
4	Na_2CO_3	36
5	KOH	51
6	NaOH	63
7	CH_3ONa	41
8	Cs_2CO_3	46
9	Et_3N	NR
10	DMAP	NR
11	No	NR

[a]Reaction conditions: **1a** (0.3 mmol), **2a** (0.6 mmol), CuCl (10 mol%), Base (2.0 equiv), DMF (2.0 mL), 16 h, 120 °C. [b]Isolated yield. N.R. = no reaction.

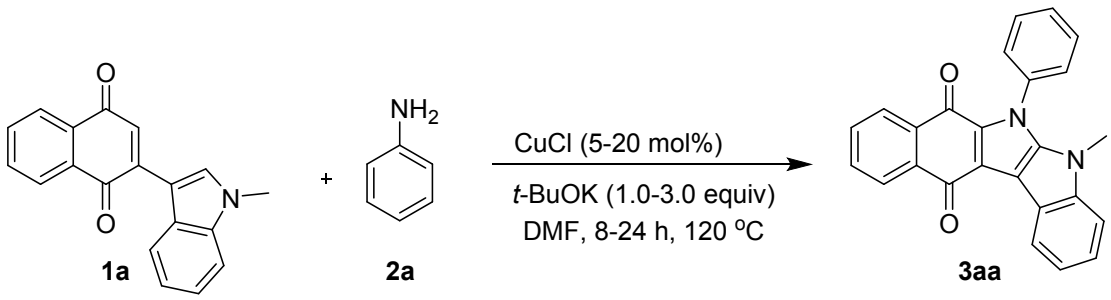
Table S3. Optimization of solvents[a]



Entry	Solvent	Yield[b]
1	DMF	87
2	DMAC	52
3	NMP	NR
4	EtOH	NR
5	CH_3NO_2	NR
6	Dioxane	NR
7	DCE	NR
8	CH_3CN	NR
9	Toluene	NR
10	$PhCF_3$	NR
11	DMSO	31

[a]Reaction conditions: **1a** (0.3 mmol), **2a** (0.6 mmol), CuCl (10 mol%), *t*-BuOK (2.0 equiv), Solvent (2.0 mL), 16 h, 120 °C. [b]Isolated yield. DMF = *N*,*N*-Dimethylformamide; DMAC = *N*,*N*-Dimethylacetamide; NMP = *N*-Methyl pyrrolidone; DMSO = Dimethyl sulfoxide; N.R. = no reaction.

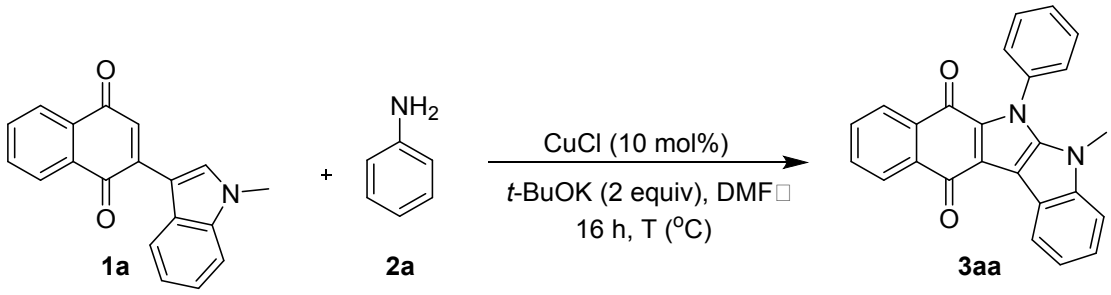
Table S4. Optimization of dosages[a]



Entry	2a (equiv)	CuCl (mol %)	*t*-BuOK (equiv)	t (h)	Yield[b]
1	2.0	5	2.0	16	75
2	2.0	10	2.0	16	87
3	2.0	20	2.0	16	81
4	2.0	10	1.0	16	65
5	2.0	10	3.0	16	78
6	1.0	10	2.0	16	71
7	1.5	10	2.0	16	78
8	3.0	10	2.0	16	79
9	2.0	10	2.0	24	85
10	2.0	10	2.0	8	62
11[c]	2.0	10	2.0	16	73
12[d]	2.0	10	2.0	16	82

[a]Reaction conditions: **1a** (0.3 mmol), **2a** (0.3-0.9 mmol), CuCl (5-20 mol%), *t*-BuOK (1.0-3.0 equiv), DMF (2.0 mL), 8-24 h, 120 °C. [b]Isolated yield. [c]DMF (1.0 mL). [d]DMF (3.0 mL).

Table S5. Optimization of temperature[a]

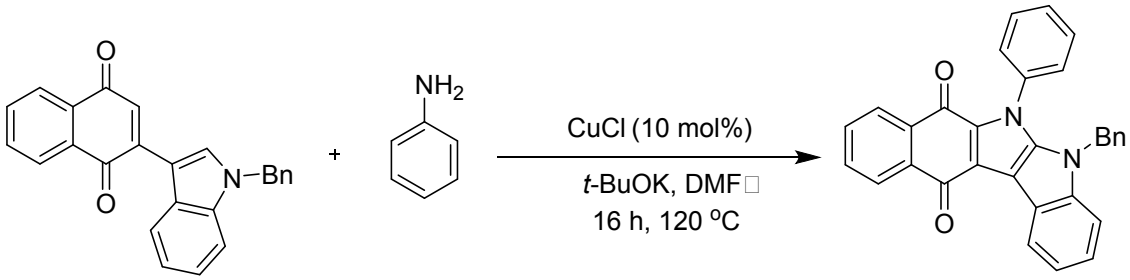


Entry	T (°C)	Yield[b]
1	80	55
2	100	70
3	110	76
4	120	87
5	140	81

[a]Reaction conditions: **1a** (0.3 mmol), **2a** (0.6 mmol), CuCl (10 mol%), *t*-BuOK

(2.0 equiv), DMF (2.0 mL), 16 h, 80-140 °C. [b]Isolated yield.

5. Procedure for gram-scale reaction

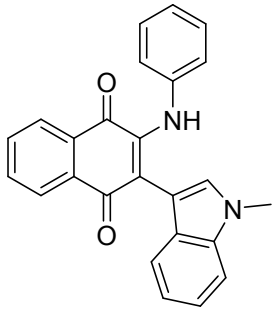


1b, 4 mmol **2a**, 8 mmol **3ba**, 1.29 g, 83%

To a solution of indolylnaphthoquinone **1b** (1.45 g), CuCl (39.6 mg, 10 mol%), *t*-BuOK (896 mg, 2.0 equiv) in DMF (26 mL) was added aniline **2a** (745 mg, 2.0 equiv). The reaction mixture was stirred at 120 °C (oil bath) under air atmosphere for 16 h. After the completion of the reaction (monitored by TLC), and cooled down to room temperature. The reaction was quenched with saturated salt water (100 ml) and the mixture was extracted with EtOAc (3 × 50 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 **3ba** in 83% yield.

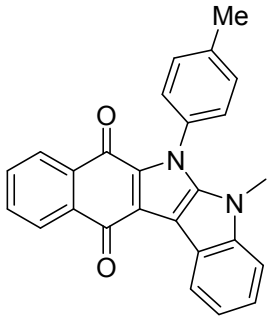
6. Characterization data of products

2-(1-methyl-1*H*-indol-3-yl)-3-(phenylamino)naphthalene-1,4-dione (4a)



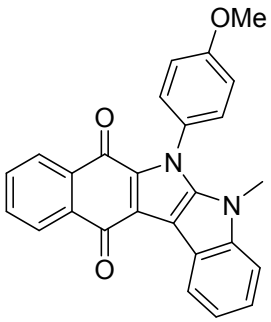
Black solid, 63% yield; mp 206-208 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.73 (s, 1H), 8.07 (dd, J = 16.0, 7.5 Hz, 2H), 7.83 (dt, J = 21.7, 7.4 Hz, 2H), 7.25 (s, 1H), 7.21 (d, J = 7.9 Hz, 1H), 7.16 (d, J = 8.1 Hz, 1H), 6.98 (t, J = 7.5 Hz, 1H), 6.89 (t, J = 7.4 Hz, 1H), 6.72 – 6.46 (m, 5H), 3.63 (s, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 182.8, 182.3, 141.1, 138.8, 136.4, 134.8, 133.4, 133.2, 132.4, 131.2, 129.8, 126.7, 126.5, 126.3, 126.1, 122.3, 121.5, 121.1, 120.9, 119.3, 114.8, 109.6, 107.0, 32.8. HRMS calcd. For $C_{25}H_{19}N_2O_2^+$ $(M+H)^+$ 379.1447 found: 379.1441.

5-methyl-6-(p-tolyl)-5,6-dihydrobenzo[f]indolo[2,3-b]indole-7,12-dione (3ab)[3]



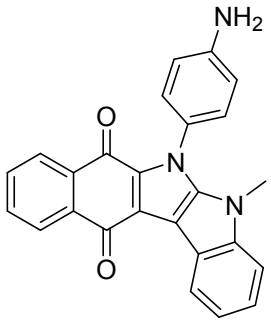
Red solid, 88% yield; mp 271-273 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.36 (d, *J* = 7.2 Hz, 1H), 8.16 (s, 1H), 7.97 (s, 1H), 7.59 (s, 2H), 7.46 (s, 2H), 7.41 (s, 2H), 7.33 – 7.27 (m, 2H), 7.20 (d, *J* = 7.5 Hz, 1H), 3.28 (s, 3H), 2.51 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 181.90, 174.12, 144.10, 143.59, 139.92, 134.77, 133.81, 133.19, 133.05, 132.25, 130.34, 130.10, 129.78, 127.78, 127.59, 126.01, 124.15, 122.70, 121.55, 121.09, 120.04, 109.25, 29.69, 21.45.

6-(4-methoxyphenyl)-5-methyl-5,6-dihydrobenzo[f]indolo[2,3-b]indole-7,12-dione (3ac)[3]



Red solid, 83% yield; mp 262-264 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.34 (d, *J* = 7.1 Hz, 1H), 8.15 (s, 1H), 7.95 (s, 1H), 7.58 (s, 2H), 7.51 (d, *J* = 7.5 Hz, 2H), 7.35 – 7.26 (m, 2H), 7.17 (d, *J* = 7.5 Hz, 1H), 7.10 (d, *J* = 7.6 Hz, 2H), 3.93 (s, 3H), 3.28 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 181.88, 174.14, 160.27, 143.51, 134.71, 133.05, 132.24, 128.93, 125.97, 124.12, 122.62, 121.04, 119.93, 114.57, 109.25, 55.58, 30.05.

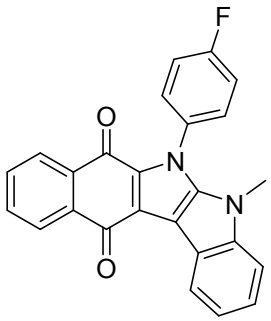
6-(4-aminophenyl)-5-methyl-5,6-dihydrobenzo[f]indolo[2,3-b]indole-7,12-dione (3ad)[3]



Red solid, 79% yield; mp 271-273 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.36 (d, *J* = 7.4 Hz, 1H), 8.19 – 8.14 (m, 1H), 8.01 – 7.95 (m, 1H), 7.59 (p, *J* = 6.8 Hz, 3H), 7.35 –

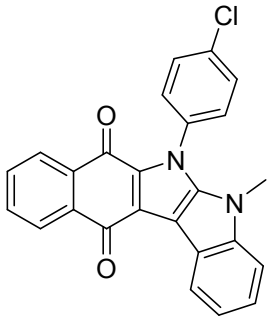
7.20 (m, 6H), 6.83 (d, J = 8.5 Hz, 2H), 3.34 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 181.93, 174.15, 147.65, 143.61, 134.85, 133.20, 132.99, 132.18, 130.51, 128.63, 126.68, 126.01, 125.95, 124.07, 122.65, 121.35, 120.99, 120.06, 115.23, 109.22, 30.01.

6-(4-fluorophenyl)-5-methyl-5,6-dihydrobenzo[f]indolo[2,3-b]indole-7,12-dione (3ae) [3]



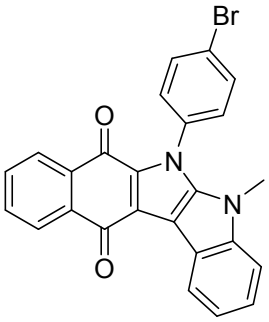
Red solid, 60% yield; mp 261-263 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.34 (d, J = 7.0 Hz, 1H), 8.17 – 8.11 (m, 1H), 7.96 – 7.90 (m, 1H), 7.62 – 7.56 (m, 4H), 7.35 – 7.24 (m, 5H), 7.17 (d, J = 7.8 Hz, 1H), 3.27 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 181.72, 174.10, 164.26, 161.77, 145.12, 143.46, 134.55, 133.07, 133.03, 132.43, 132.40, 132.29, 129.84, 129.75, 125.99, 125.93, 124.24, 122.64, 121.64, 121.17, 119.89, 116.64, 116.41, 109.26, 108.20, 30.11. ^{19}F NMR (376 MHz, $CDCl_3$) δ 110.36.

6-(4-chlorophenyl)-5-methyl-5,6-dihydrobenzo[f]indolo[2,3-b]indole-7,12-dione (3af) [3]



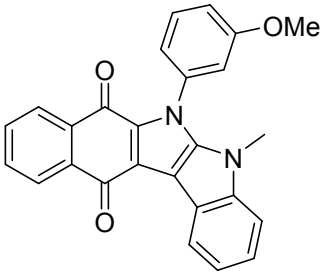
Red solid, 62% yield; mp 263-265 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.38 (d, J = 7.6 Hz, 1H), 8.20 – 8.14 (m, 1H), 7.98 (dd, J = 5.6, 3.3 Hz, 1H), 7.64 – 7.52 (m, 6H), 7.31 (dd, J = 15.0, 7.5 Hz, 2H), 7.22 (s, 1H), 3.32 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 181.82, 174.20, 145.05, 143.52, 135.88, 134.96, 134.56, 133.21, 132.45, 129.75, 129.27, 126.13, 126.01, 124.38, 122.76, 121.31, 119.92, 109.37, 30.29.

6-(4-bromophenyl)-5-methyl-5,6-dihydrobenzo[f]indolo[2,3-b]indole-7,12-dione (3ag) [3]



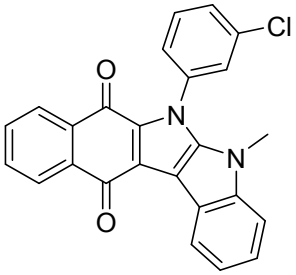
Red solid, 65% yield; mp 251-253 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.37 (d, *J* = 7.4 Hz, 1H), 8.19 – 8.15 (m, 1H), 7.99 – 7.95 (m, 1H), 7.76 – 7.72 (m, 2H), 7.63 – 7.60 (m, 2H), 7.50 – 7.46 (m, 2H), 7.36 – 7.29 (m, 2H), 7.21 (s, 1H), 3.32 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 181.76, 174.16, 144.93, 143.51, 135.51, 134.55, 133.18, 133.08, 132.72, 132.42, 130.15, 129.58, 126.11, 125.99, 124.36, 123.94, 123.86, 122.73, 121.29, 119.91, 109.35, 108.38, 29.68.

6-(3-methoxyphenyl)-5-methyl-5,6-dihydrobenzo[f]indolo[2,3-b]indole-7,12-dione (3ah) [3]



Red solid, 83% yield; mp 283-285 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.32 – 8.27 (m, 1H), 8.10 – 8.06 (m, 1H), 7.91 – 7.86 (m, 1H), 7.52 (ddd, *J* = 8.2, 4.7, 2.8 Hz, 3H), 7.27 – 7.08 (m, 6H), 3.90 (s, 3H), 3.24 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 181.69, 173.80, 160.29, 145.00, 143.43, 137.49, 134.60, 133.01, 132.91, 132.10, 130.26, 130.06, 125.91, 125.84, 124.03, 122.51, 121.39, 120.96, 120.12, 119.86, 115.60, 113.69, 109.19, 108.05, 55.61, 29.95.

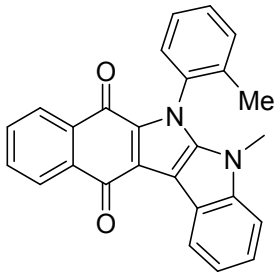
6-(3-chlorophenyl)-5-methyl-5,6-dihydrobenzo[f]indolo[2,3-b]indole-7,12-dione (3ai) [3]



Red solid, 66% yield; mp 275-277 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.48 (d, *J* = 7.7 Hz, 1H), 8.32 (dd, *J* = 5.7, 3.2 Hz, 1H), 8.13 (dd, *J* = 5.9, 3.0 Hz, 1H), 7.95 (s, 1H), 7.91 – 7.79 (m, 5H), 7.58 – 7.53 (m, 1H), 7.48 (dd, *J* = 12.7, 5.0 Hz, 2H), 3.54 (s,

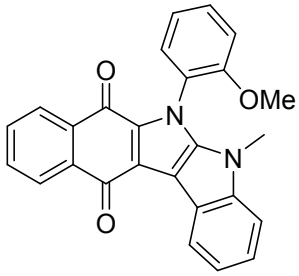
3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 181.57, 173.57, 143.52, 137.47, 134.62, 134.42, 133.26, 132.87, 132.45, 130.52, 130.05, 128.38, 126.60, 125.86, 124.34, 122.19, 121.01, 119.65, 109.99, 109.81, 107.94, 30.35.

5-methyl-6-(o-tolyl)-5,6-dihydrobenzo[f]indolo[2,3-b]indole-7,12-dione (3aj) [3]



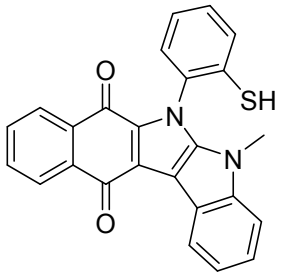
Red solid, 78% yield; mp 271-273 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.40 (d, J = 7.1 Hz, 1H), 8.23 – 8.17 (m, 1H), 8.03 – 7.96 (m, 1H), 7.64 – 7.59 (m, 2H), 7.53 – 7.41 (m, 4H), 7.38 – 7.30 (m, 2H), 7.24 (t, J = 3.7 Hz, 2H), 3.24 (s, 3H), 2.12 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 181.91, 174.16, 151.06, 143.61, 140.32, 136.38, 135.71, 134.60, 133.28, 133.07, 132.33, 131.06, 130.02, 127.94, 127.08, 126.10, 126.03, 124.59, 124.18, 122.70, 121.17, 120.16, 115.44, 109.30, 29.42, 17.40.

6-(2-methoxyphenyl)-5-methyl-5,6-dihydrobenzo[f]indolo[2,3-b]indole-7,12-dione (3ak) [3]



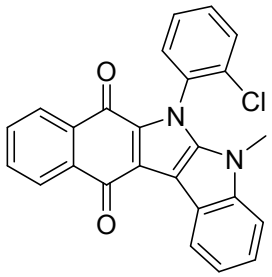
Red solid, 71% yield; mp 246-248 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.44 (d, J = 7.0 Hz, 1H), 8.26 – 8.22 (m, 1H), 8.08 – 8.03 (m, 1H), 7.67 – 7.61 (m, 4H), 7.41 – 7.19 (m, 6H), 3.82 (s, 3H), 3.37 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 181.95, 174.04, 155.65, 145.12, 143.48, 134.79, 134.14, 133.64, 133.45, 133.27, 132.94, 132.14, 131.18, 130.45, 129.74, 129.44, 127.69, 127.02, 126.74, 126.55, 126.47, 125.98, 125.96, 125.23, 123.91, 122.59, 122.12, 121.64, 120.94, 120.84, 120.16, 112.02, 111.97, 110.27, 109.18, 109.12, 108.13, 107.53, 55.88, 29.35.

6-(2-mercaptophenyl)-5-methyl-5,6-dihydrobenzo[f]indolo[2,3-b]indole-7,12-dione (3al) [3]



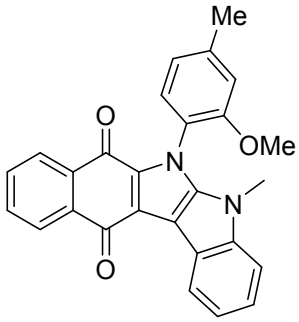
Red solid, 67% yield; mp 281-283 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.97 – 8.91 (m, 1H), 8.40 – 8.32 (m, 1H), 7.92 (dd, *J* = 8.0, 1.0 Hz, 1H), 7.79 – 7.71 (m, 2H), 7.44 – 7.38 (m, 2H), 7.35 (s, 1H), 7.31 – 7.23 (m, 4H), 7.13 (dd, *J* = 7.7, 1.0 Hz, 1H), 3.91 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 179.29, 145.30, 138.52, 137.16, 135.17, 134.79, 132.73, 132.57, 131.42, 131.10, 130.55, 129.40, 127.38, 126.33, 125.56, 125.51, 124.92, 124.84, 121.85, 121.39, 119.63, 109.92, 107.25 , 33.21.

6-(2-chlorophenyl)-5-methyl-5,6-dihydrobenzo[f]indolo[2,3-b]indole-7,12-dione (3am) [3]



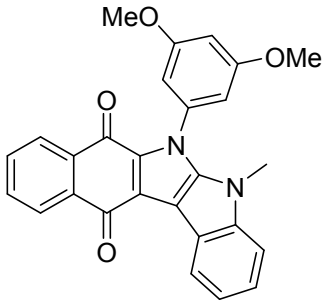
Red solid, 65% yield; mp 263-265 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.35 (d, *J* = 7.1 Hz, 1H), 8.15 (d, *J* = 6.9 Hz, 1H), 7.95 (d, *J* = 6.9 Hz, 1H), 7.76 (d, *J* = 7.1 Hz, 1H), 7.61 (dd, *J* = 30.5, 7.0 Hz, 5H), 7.29 (dd, *J* = 16.1, 8.1 Hz, 2H), 7.18 (d, *J* = 7.8 Hz, 1H), 3.27 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 181.78, 174.02, 144.53, 143.34, 134.56, 134.41, 134.11, 133.15, 133.05, 132.31, 131.14, 130.33, 130.15, 130.02, 127.87, 126.06, 125.95, 124.12, 122.60, 121.80, 121.14, 120.03, 109.31, 108.16, 29.47.

6-(2-methoxy-4-methylphenyl)-5-methyl-5,6-dihydrobenzo[f]indolo[2,3-b]indole-7,12-dione (3an) [3]



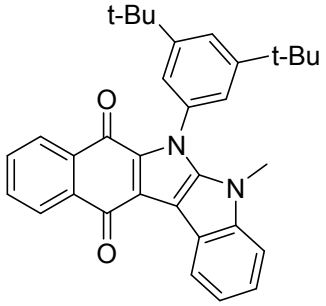
Red solid, 79% yield; mp 271-273 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.40 – 8.36 (m, 1H), 8.19 – 8.16 (m, 1H), 8.02 – 7.98 (m, 1H), 7.61 – 7.57 (m, 2H), 7.36 – 7.25 (m, 4H), 7.21 (d, *J* = 8.1 Hz, 1H), 7.02 (d, *J* = 9.0 Hz, 1H), 3.72 (s, 3H), 3.30 (s, 3H), 2.40 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 181.94, 173.99, 153.49, 145.16, 143.51, 134.83, 133.30, 132.91, 132.11, 131.56, 130.51, 130.41, 129.74, 125.96, 124.88, 123.87, 122.58, 121.57, 120.90, 120.19, 111.95, 109.17, 108.11, 55.97, 29.37, 20.50.

6-(3,5-dimethoxyphenyl)-5-methyl-5,6-dihydrobenzo[f]indolo[2,3-b]indole-7,12-dione (3ao) [3]



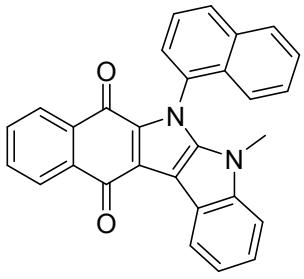
Red solid, 75% yield; mp 256-258 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.34 (d, *J* = 6.7 Hz, 1H), 8.16 – 8.10 (m, 1H), 7.99 – 7.90 (m, 1H), 7.56 (dt, *J* = 10.6, 3.6 Hz, 2H), 7.28 (ddd, *J* = 14.2, 10.2, 3.4 Hz, 2H), 7.16 (d, *J* = 7.7 Hz, 1H), 6.75 (d, *J* = 2.2 Hz, 2H), 6.70 – 6.64 (m, 1H), 3.85 (s, 6H), 3.32 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 181.79, 173.75, 161.15, 144.98, 143.48, 138.00, 134.64, 133.07, 132.98, 132.17, 130.28, 125.98, 125.93, 124.10, 122.59, 121.42, 121.03, 119.92, 109.24, 108.05, 106.36, 101.80, 55.66, 29.94.

6-(3,5-di-tert-butylphenyl)-5-methyl-5,6-dihydrobenzo[f]indolo[2,3-b]indole-7,12-dione (3ap) [3]



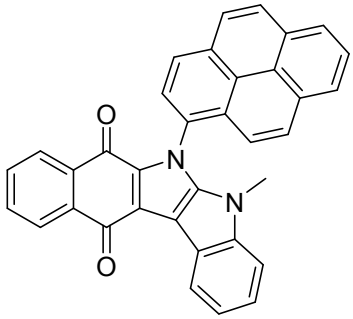
Red solid, 82% yield; mp 286-288 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.39 – 8.36 (m, 1H), 8.17 – 8.14 (m, 1H), 7.96 (dd, *J* = 5.3, 1.9 Hz, 1H), 7.62 (t, *J* = 1.7 Hz, 1H), 7.58 – 7.55 (m, 2H), 7.42 (d, *J* = 1.7 Hz, 2H), 7.32 – 7.24 (m, 3H), 7.14 (s, 1H), 3.18 (s, 3H), 1.40 (s, 18H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 181.88, 173.79, 152.13, 152.06, 145.16, 143.49, 135.76, 134.83, 133.17, 132.88, 132.05, 130.34, 126.06, 125.85, 123.93, 123.08, 122.57, 122.26, 121.25, 120.89, 120.01, 115.95, 109.13, 107.98, 35.11, 34.91, 31.42, 31.36, 29.82.

5-methyl-6-(naphthalen-1-yl)-5,6-dihydrobenzo[f]indolo[2,3-b]indole-7,12-dione (3aq) [3]



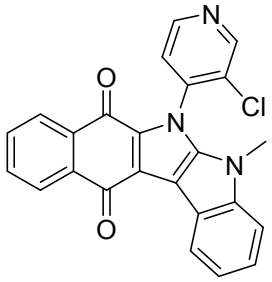
Red solid, 89% yield; mp 267-269 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.44 (dd, *J* = 6.2, 2.4 Hz, 1H), 8.20 (dd, *J* = 7.5, 1.1 Hz, 1H), 8.12 (d, *J* = 8.3 Hz, 1H), 8.01 (d, *J* = 8.3 Hz, 1H), 7.89 (dd, *J* = 7.5, 1.1 Hz, 1H), 7.81 (d, *J* = 7.3 Hz, 1H), 7.68 (d, *J* = 8.0 Hz, 1H), 7.62 – 7.54 (m, 3H), 7.43 (d, *J* = 8.3 Hz, 1H), 7.34 – 7.29 (m, 3H), 7.16 (dd, *J* = 6.5, 2.1 Hz, 1H), 2.99 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 181.74, 173.91, 143.48, 134.56, 134.06, 133.24, 133.12, 133.05, 132.30, 130.94, 130.26, 128.59, 128.04, 127.11, 126.09, 126.04, 125.87, 125.28, 124.18, 122.71, 121.98, 121.14, 120.09, 109.31, 108.09, 29.42.

5-methyl-6-(pyren-1-yl)-5,6-dihydrobenzo[f]indolo[2,3-b]indole-7,12-dione (3ar) [3]



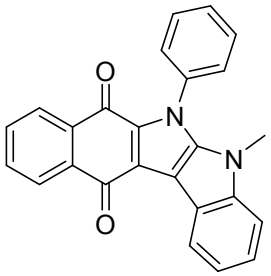
Red solid, 78% yield; mp 281-283 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.50 (dd, *J* = 6.2, 2.9 Hz, 1H), 8.38 (d, *J* = 8.1 Hz, 1H), 8.30 (d, *J* = 7.6 Hz, 1H), 8.28 – 8.13 (m, 6H), 8.10 – 8.03 (m, 2H), 7.87 (d, *J* = 6.5 Hz, 1H), 7.64 – 7.55 (m, 3H), 7.37 – 7.34 (m, 2H), 7.20 – 7.17 (m, 1H), 2.92 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 182.04, 174.08, 146.05, 143.56, 137.45, 134.60, 133.32, 133.09, 132.36, 131.58, 131.13, 130.84, 130.00, 129.74, 128.87, 128.65, 127.20, 126.71, 126.35, 126.15, 126.05, 125.63, 125.05, 124.92, 124.43, 124.24, 122.81, 121.86, 121.22, 120.87, 120.17, 111.39, 109.38, 108.17, 29.50.

6-(3-chloropyridin-4-yl)-5-methyl-5,6-dihydrobenzo[f]indolo[2,3-b]indole-7,12-dione (3as) [3]



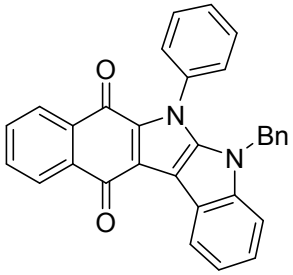
Red solid, 63% yield; mp 283-285 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.51 (d, *J* = 5.0 Hz, 1H), 9.00 (d, *J* = 7.1 Hz, 1H), 8.83 – 8.77 (m, 1H), 8.55 (dd, *J* = 7.3, 1.5 Hz, 1H), 8.48 (d, *J* = 5.0 Hz, 1H), 8.29 – 8.23 (m, 2H), 8.08 – 7.86 (m, 3H), 7.83 (d, *J* = 7.8 Hz, 1H), 3.95 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 181.56, 173.96, 150.93, 149.29, 143.84, 143.17, 142.38, 134.01, 133.24, 132.95, 132.54, 130.67, 129.83, 126.18, 125.92, 124.47, 124.43, 122.59, 122.28, 121.43, 119.78, 109.44, 108.55, 29.65.

5-methyl-6-phenyl-5,6-dihydrobenzo[f]indolo[2,3-b]indole-7,12-dione (3aa) [3]



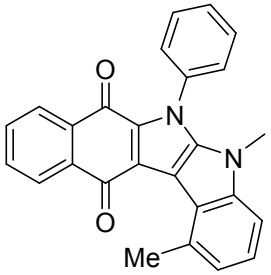
Red solid, 87% yield; mp 263-265 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.35 (d, *J* = 7.3 Hz, 1H), 8.14 (d, *J* = 5.9 Hz, 1H), 7.94 (d, *J* = 5.5 Hz, 1H), 7.60 (d, *J* = 15.9 Hz, 7H), 7.36 – 7.23 (m, 3H), 7.17 (d, *J* = 7.6 Hz, 1H), 3.24 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 181.88, 174.08, 143.50, 136.44, 134.64, 133.08, 132.28, 129.81, 129.49, 127.94, 125.99, 124.18, 122.63, 121.09, 119.90, 109.28, 30.09.

5-benzyl-6-phenyl-5,6-dihydrobenzo[f]indolo[2,3-b]indole-7,12-dione (3ba) [3]



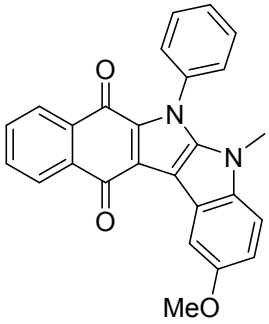
Red solid, 85% yield; mp 279-281 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.46 (s, 1H), 8.20 (d, *J* = 6.6 Hz, 1H), 7.97 (d, *J* = 7.0 Hz, 1H), 7.62 (d, *J* = 6.0 Hz, 2H), 7.50 (d, *J* = 7.1 Hz, 1H), 7.32 (ddd, *J* = 26.6, 15.2, 7.5 Hz, 7H), 7.18 (dd, *J* = 26.6, 7.1 Hz, 4H), 6.62 (d, *J* = 6.8 Hz, 2H), 4.95 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 181.94, 174.20, 144.55, 143.43, 136.06, 134.63, 133.15, 132.40, 130.59, 129.61, 129.18, 128.61, 127.61, 126.08, 125.50, 124.49, 122.86, 121.52, 120.13, 109.87, 108.70, 77.32, 77.01, 76.69, 46.74.

1,5-dimethyl-6-phenyl-5,6-dihydrobenzo[f]indolo[2,3-b]indole-7,12-dione (3da) [3]



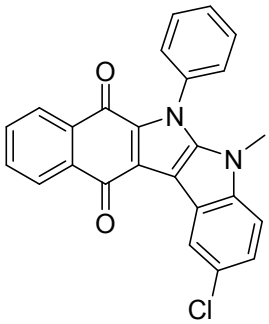
Red solid, 76% yield; mp 278-280 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 – 8.08 (m, 1H), 7.89 (dd, *J* = 7.3, 1.6 Hz, 1H), 7.62 – 7.50 (m, 7H), 7.19 (t, *J* = 7.7 Hz, 1H), 7.04 – 6.97 (m, 2H), 3.16 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 181.25, 174.55, 145.20, 143.72, 136.87, 134.06, 133.81, 133.64, 132.63, 132.38, 131.40, 129.75, 129.48, 129.06, 128.07, 126.35, 125.36, 124.09, 123.11, 121.20, 120.13, 106.65, 106.39, 30.04, 22.44.

2-methoxy-5-methyl-6-phenyl-5,6-dihydrobenzo[f]indolo[2,3-b]indole-7,12-dione (3ea) [3]



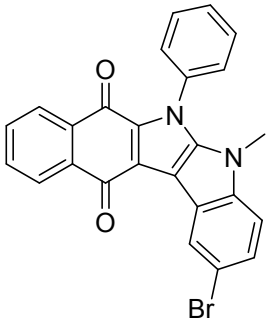
Red solid, 73% yield; mp 271-273 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.36 – 8.32 (m, 1H), 8.17 – 8.13 (m, 1H), 8.07 (d, *J* = 2.3 Hz, 1H), 7.86 (s, 5H), 7.81 – 7.78 (m, 2H), 7.23 (d, *J* = 8.8 Hz, 1H), 7.13 (dd, *J* = 8.8, 2.5 Hz, 1H), 4.18 (s, 3H), 3.42 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 181.85, 173.90, 154.87, 145.49, 138.24, 136.46, 134.65, 133.00, 132.12, 130.20, 129.70, 129.38, 127.98, 125.96, 125.75, 121.42, 120.34, 113.43, 109.97, 108.20, 105.02, 55.93, 30.06.

2-chloro-5-methyl-6-phenyl-5,6-dihydrobenzo[f]indolo[2,3-b]indole-7,12-dione (3fa) [3]



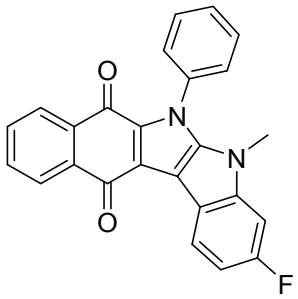
Red solid, 64% yield; mp 266-268 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.29 – 8.27 (m, 1H), 8.13 (dd, *J* = 4.0, 3.2 Hz, 1H), 7.92 (t, *J* = 3.4 Hz, 1H), 7.63 (s, 7H), 7.24 (d, *J* = 1.8 Hz, 2H), 7.08 (s, 1H), 3.25 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 181.22, 174.30, 141.68, 136.21, 134.43, 134.12, 133.12, 132.98, 132.47, 129.91, 129.52, 127.93, 126.55, 126.06, 126.03, 123.98, 122.02, 120.92, 110.18, 30.23.

2-bromo-5-methyl-6-phenyl-5,6-dihydrobenzo[f]indolo[2,3-b]indole-7,12-dione (3ga) [3]



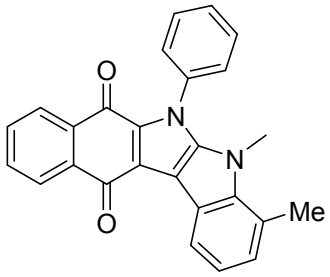
Red solid, 62% yield; mp 276-278 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.45 (s, 1H), 8.14 (d, *J* = 7.4 Hz, 1H), 7.94 (d, *J* = 7.3 Hz, 1H), 7.60 (d, *J* = 7.8 Hz, 7H), 7.38 (d, *J* = 8.7 Hz, 1H), 7.05 (d, *J* = 8.7 Hz, 1H), 3.27 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 181.42, 174.37, 142.02, 136.19, 134.42, 133.11, 132.96, 132.47, 129.91, 129.51, 127.94, 126.63, 126.06, 126.02, 124.94, 121.44, 113.97, 110.64, 30.24.

3-fluoro-5-methyl-6-phenyl-5,6-dihydrobenzo[f]indolo[2,3-b]indole-7,12-dione (3ha) [3]



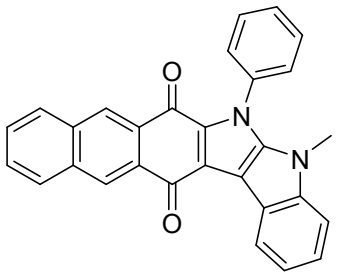
Red solid, 60% yield; mp 281-283 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.28 (dd, *J* = 8.6, 5.6 Hz, 1H), 8.17 – 8.13 (m, 1H), 7.99 – 7.94 (m, 1H), 7.64 – 7.58 (m, 7H), 7.04 – 6.99 (m, 1H), 6.90 (dd, *J* = 9.6, 2.2 Hz, 1H), 3.23 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 181.81, 174.18, 161.96, 159.39, 145.07, 143.29, 136.27, 134.64, 133.13, 133.08, 132.35, 129.89, 129.52, 127.88, 126.07, 126.01, 123.56, 123.46, 109.08, 108.85, 97.03, 96.75, 30.31. ^{19}F NMR (376 MHz, $CDCl_3$) δ 115.95.

4,5-dimethyl-6-phenyl-5,6-dihydrobenzo[f]indolo[2,3-b]indole-7,12-dione (3ia) [3]



Red solid, 79% yield; mp 276-278 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.29 (d, *J* = 7.6 Hz, 1H), 8.19 – 8.16 (m, 1H), 8.00 – 7.97 (m, 1H), 7.60 (t, *J* = 2.9 Hz, 7H), 7.17 (s, 1H), 7.04 (d, *J* = 7.4 Hz, 1H), 3.50 (s, 3H), 2.67 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 181.46, 173.71, 145.96, 142.52, 136.72, 136.32, 134.73, 133.16, 133.06, 132.27, 129.70, 129.47, 127.95, 126.03, 121.57, 121.47, 121.42, 121.03, 120.98, 120.68, 33.59, 19.87.

5-methyl-6-phenyl-5,6-dihydroindolo[2,3-b]naphtho[2,3-f]indole-7,14-dione (3ja)[3]



Red solid, 83% yield; mp 285-287 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.68 (s, 1H), 8.47 (s, 1H), 8.02 (d, *J* = 7.3 Hz, 1H), 7.89 (d, *J* = 7.1 Hz, 1H), 7.65 – 7.55 (m, 7H), 7.37 – 7.31 (m, 2H), 7.25 – 7.19 (m, 2H), 3.28 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 181.45, 173.91, 143.53, 142.95, 134.89, 134.40, 134.32, 131.54, 130.88, 130.35, 129.97, 129.79, 129.75, 129.43, 128.73, 128.58, 128.03, 128.00, 127.92, 127.09, 124.16, 123.97, 122.81, 121.50, 121.19, 109.99, 109.26, 104.96, 30.09.

7. References

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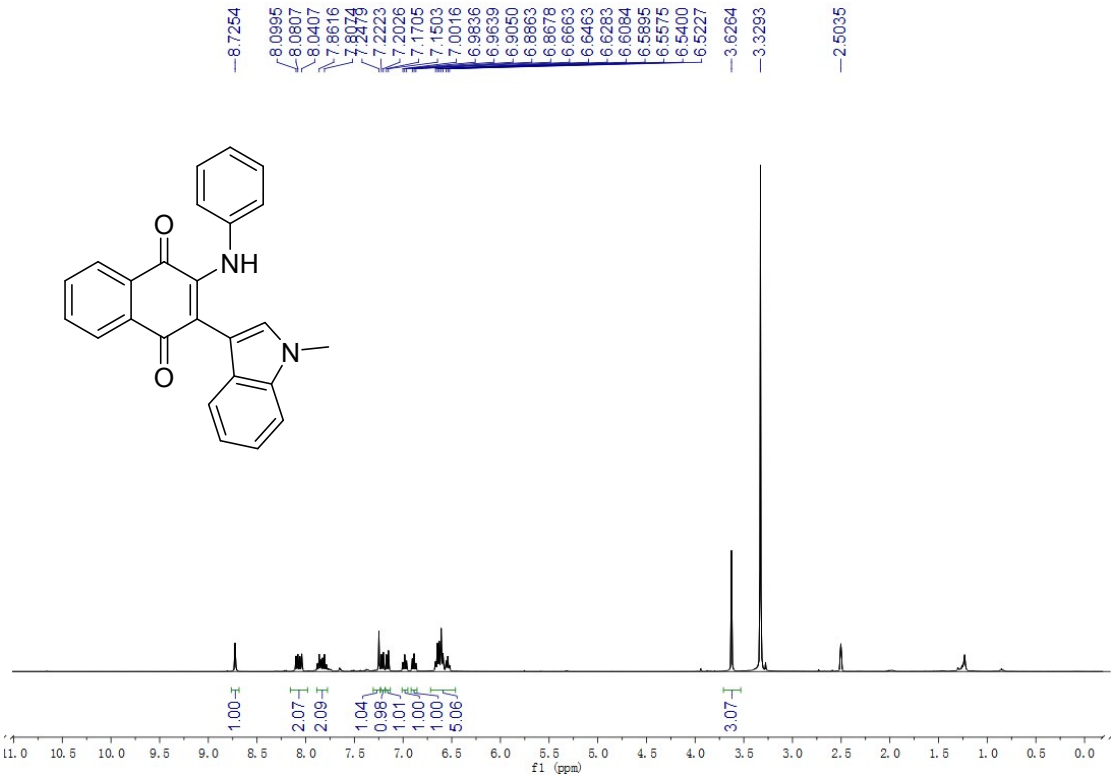
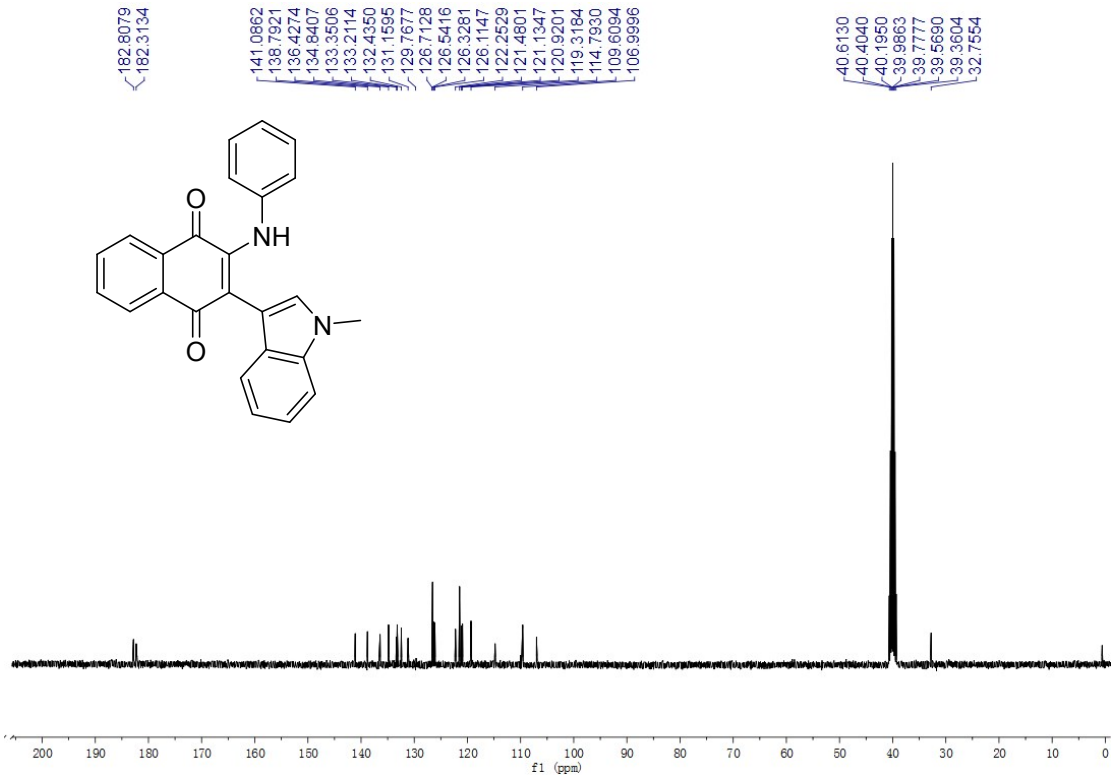
2. Y. Dong, H. Zhang, J. Yang, S. He, Z.-C. Shi, X.-M. Zhang and J.-Y. Wang, B (C6F5) 3-Catalyzed C–C Coupling of 1, 4-Naphthoquinones with the C-3 Position of Indole Derivatives in Water. *ACS omega,* 2019, **4**, 21567-21577.
3. Y. Dong, J. Yang, H, Zhang. X-Y Zhan. Z.-C. Shi, S. He, X.-M. Zhang and J.-Y. Wang, Cobalt-Catalyzed Cycloamination: Synthesis and Photophysical Properties of Polycyclic N-Heterocycles, *Org. Lett*., 2020, **22**, 5151-5156.

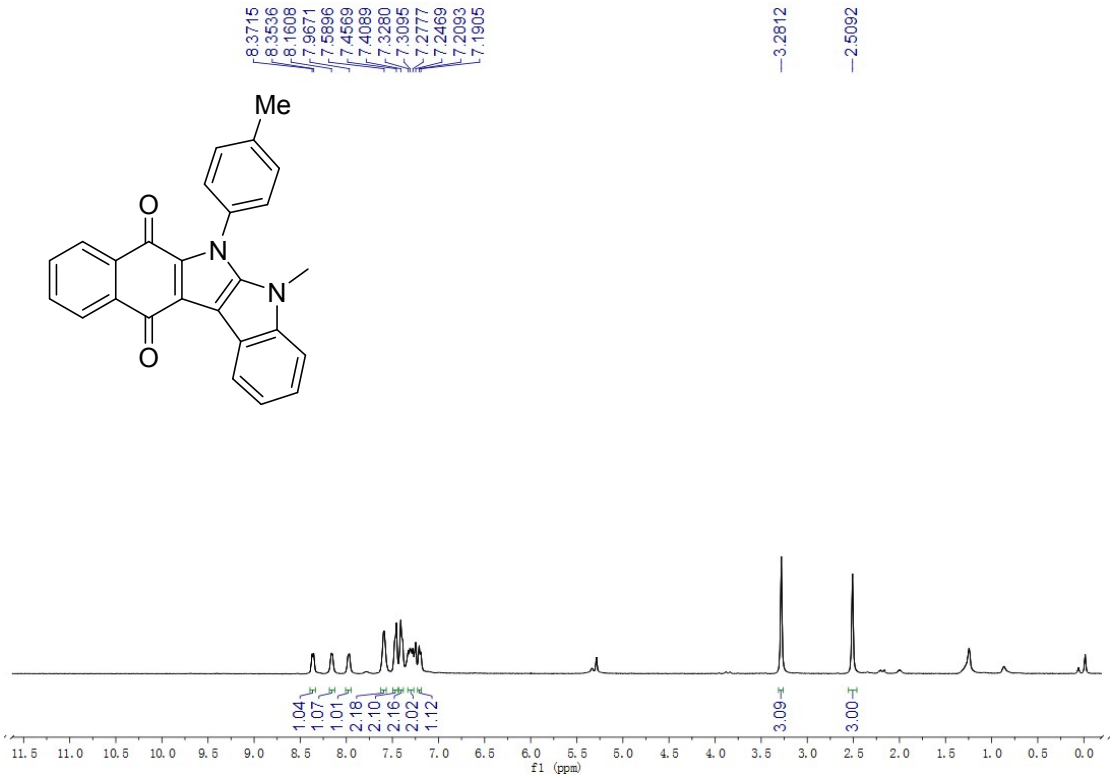
8. Copies of ^{1}H, ^{13}C and ^{19}F NMR spectra for all Compounds

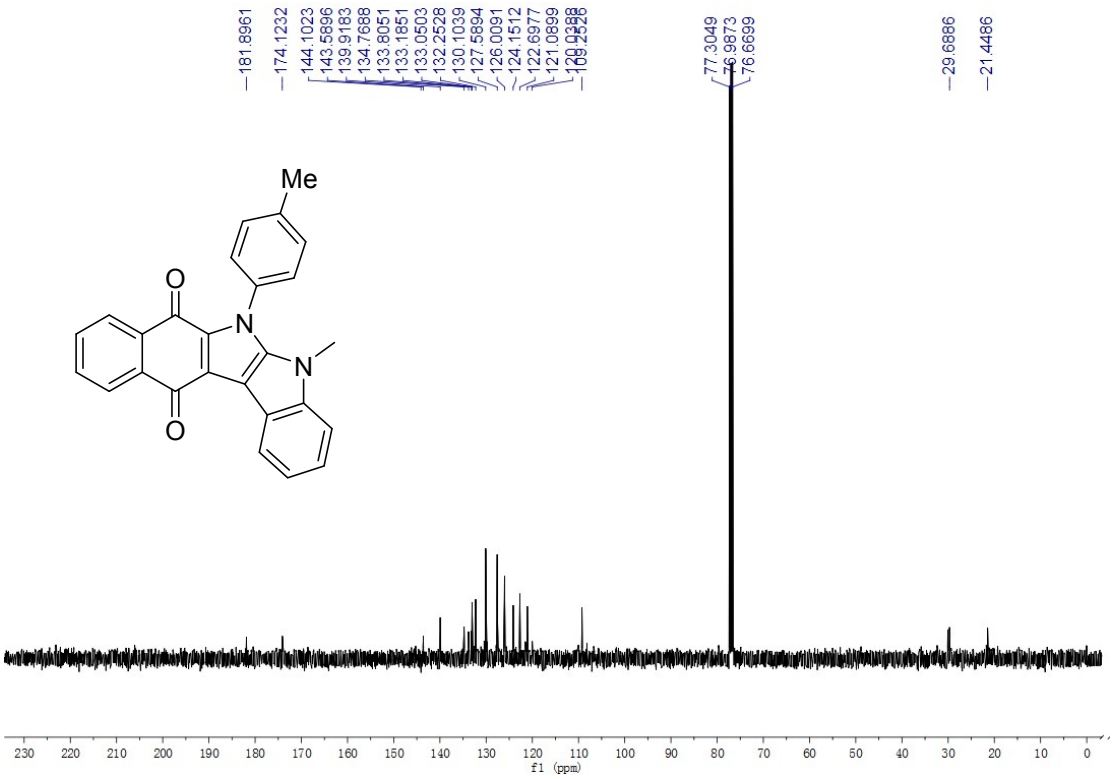
2-(1-methyl-1*H*-indol-3-yl)-3-(phenylamino)naphthalene-1,4-dione (4a)



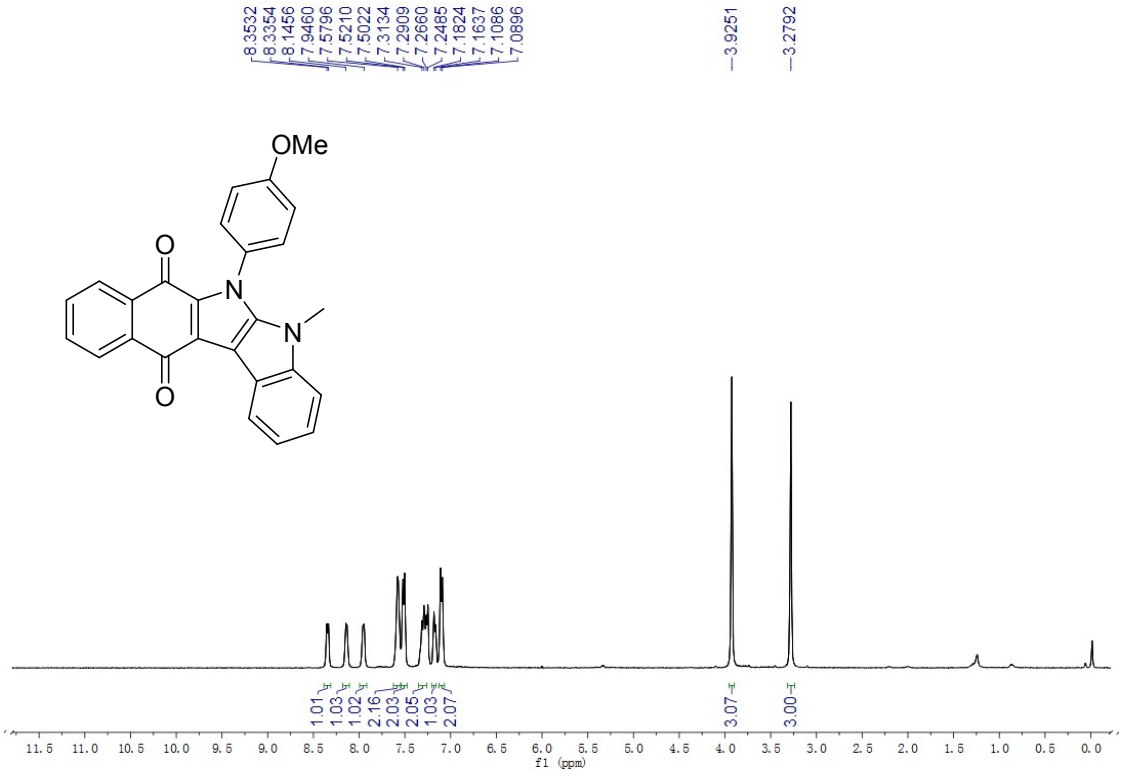


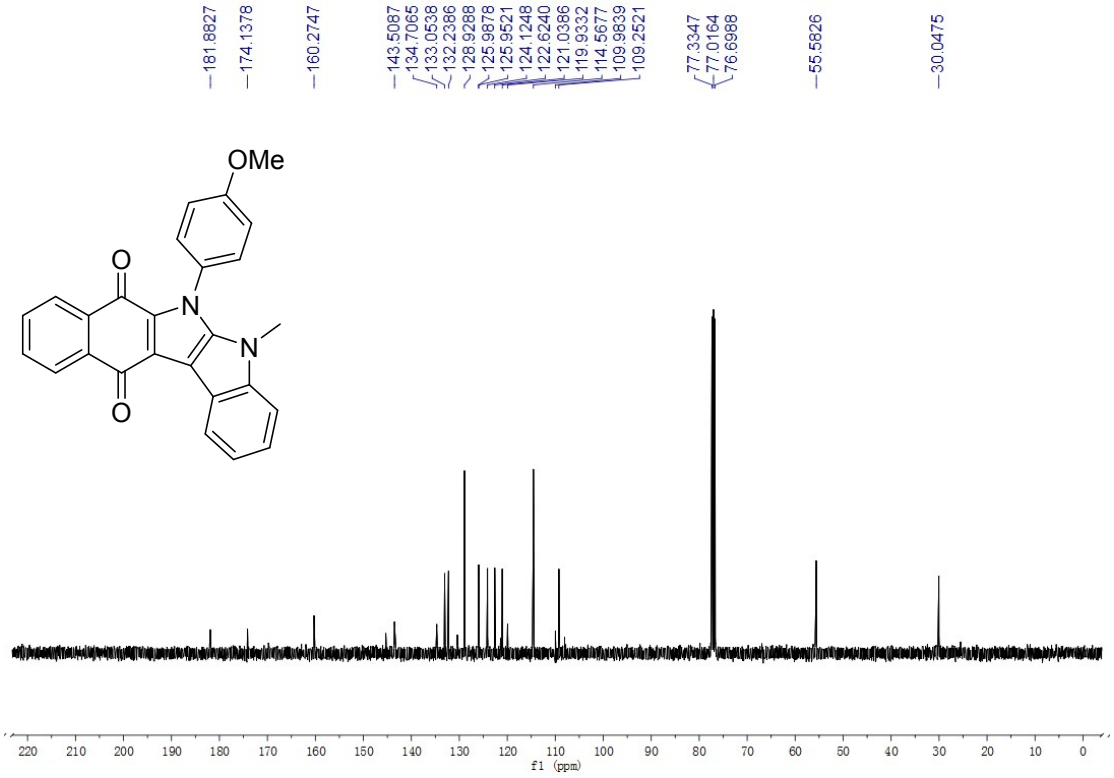
5-methyl-6-(p-tolyl)-5,6-dihydrobenzo[f]indolo[2,3-b]indole-7,12-dione (3ab)



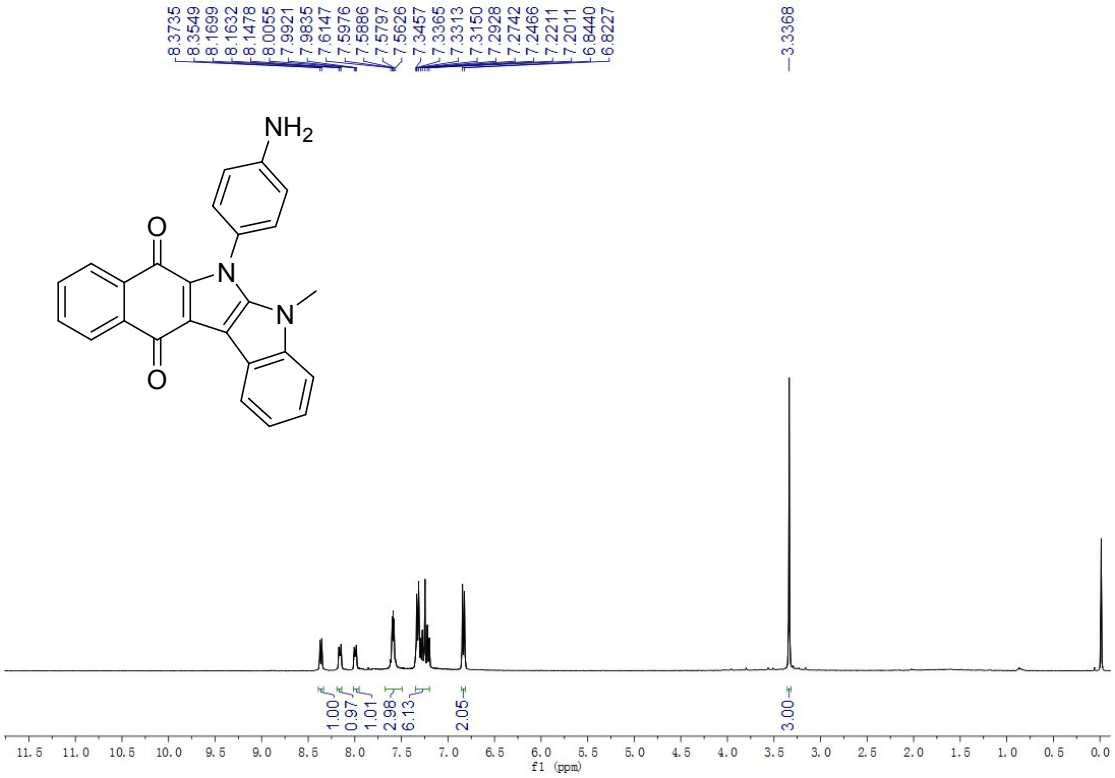


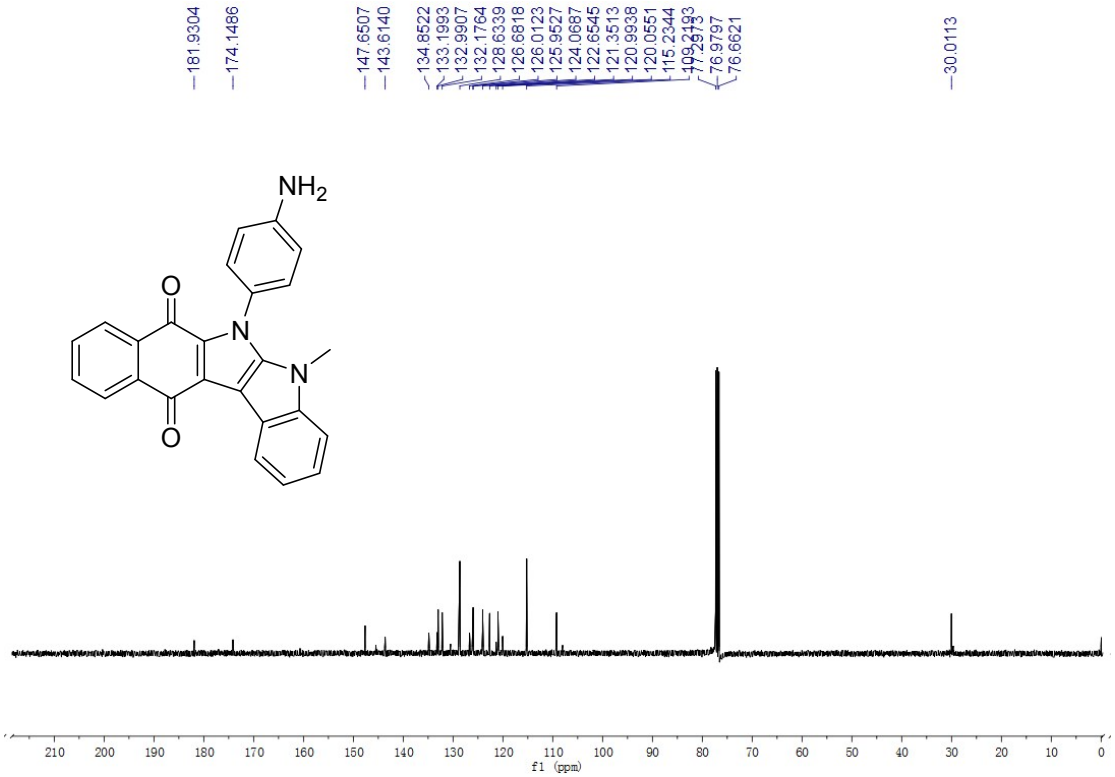
6-(4-methoxyphenyl)-5-methyl-5,6-dihydrobenzo[f]indolo[2,3-b]indole-7,12-dione (3ac)



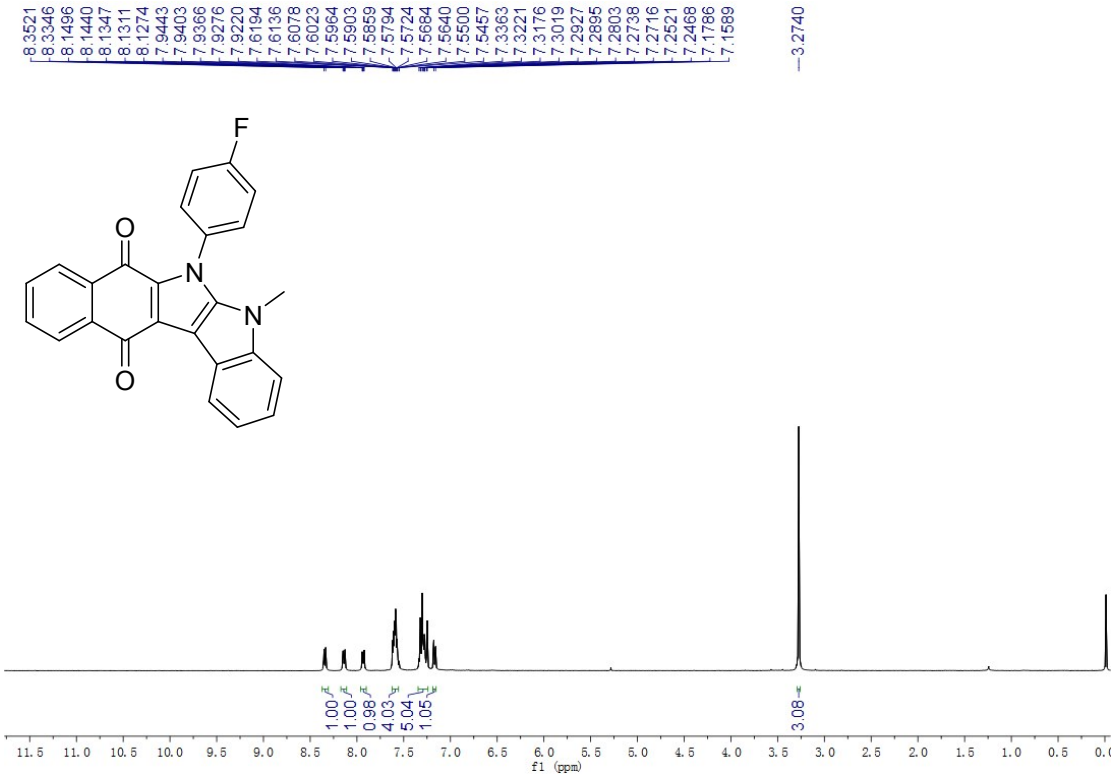


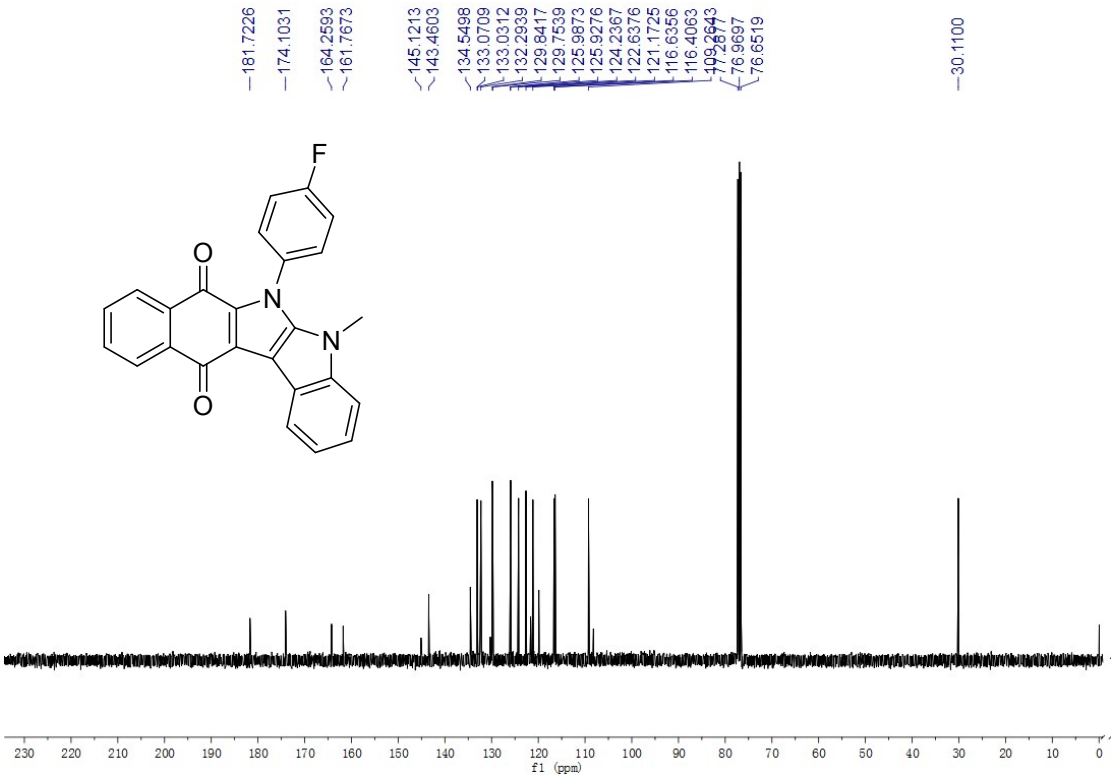
6-(4-aminophenyl)-5-methyl-5,6-dihydrobenzo[f]indolo[2,3-b]indole-7,12-dione (3ad)

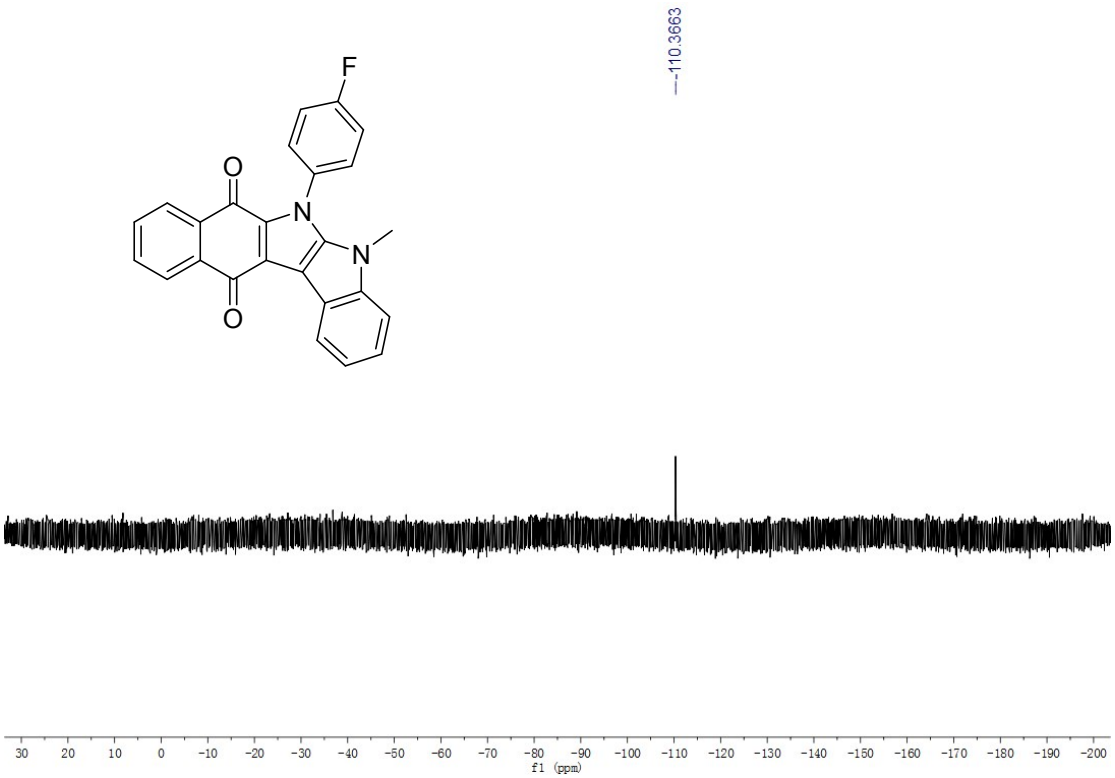




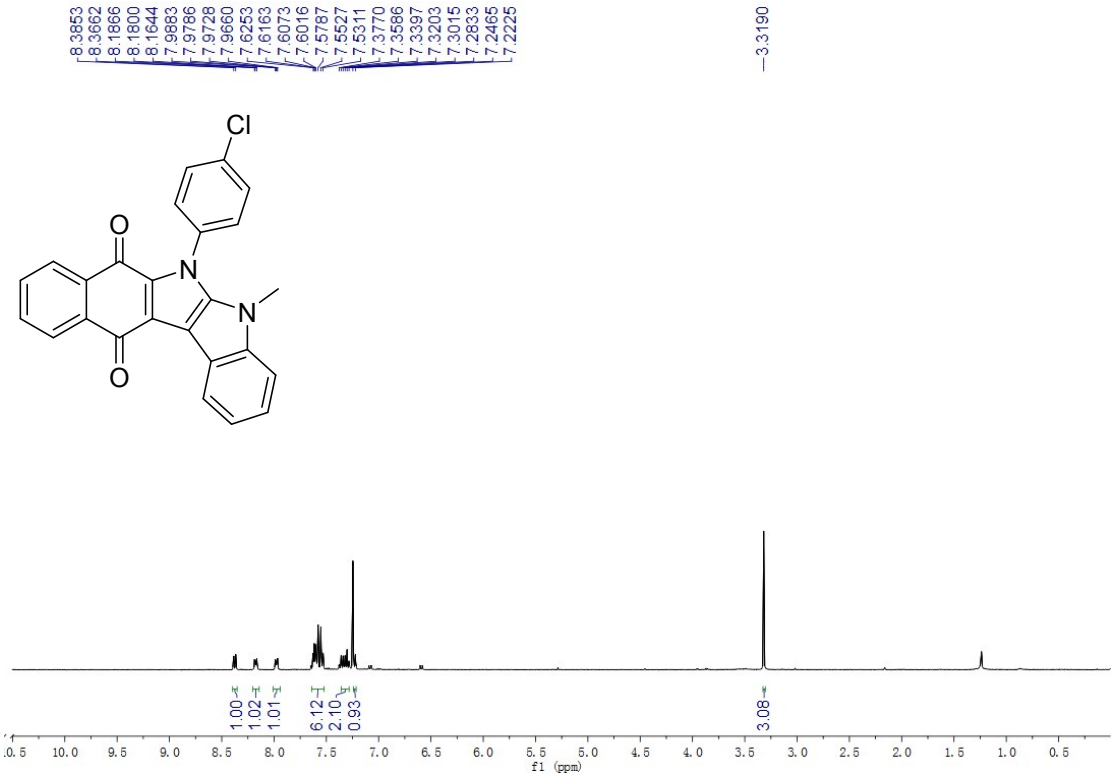
6-(4-fluorophenyl)-5-methyl-5,6-dihydrobenzo[f]indolo[2,3-b]indole-7,12-dione (3ae)

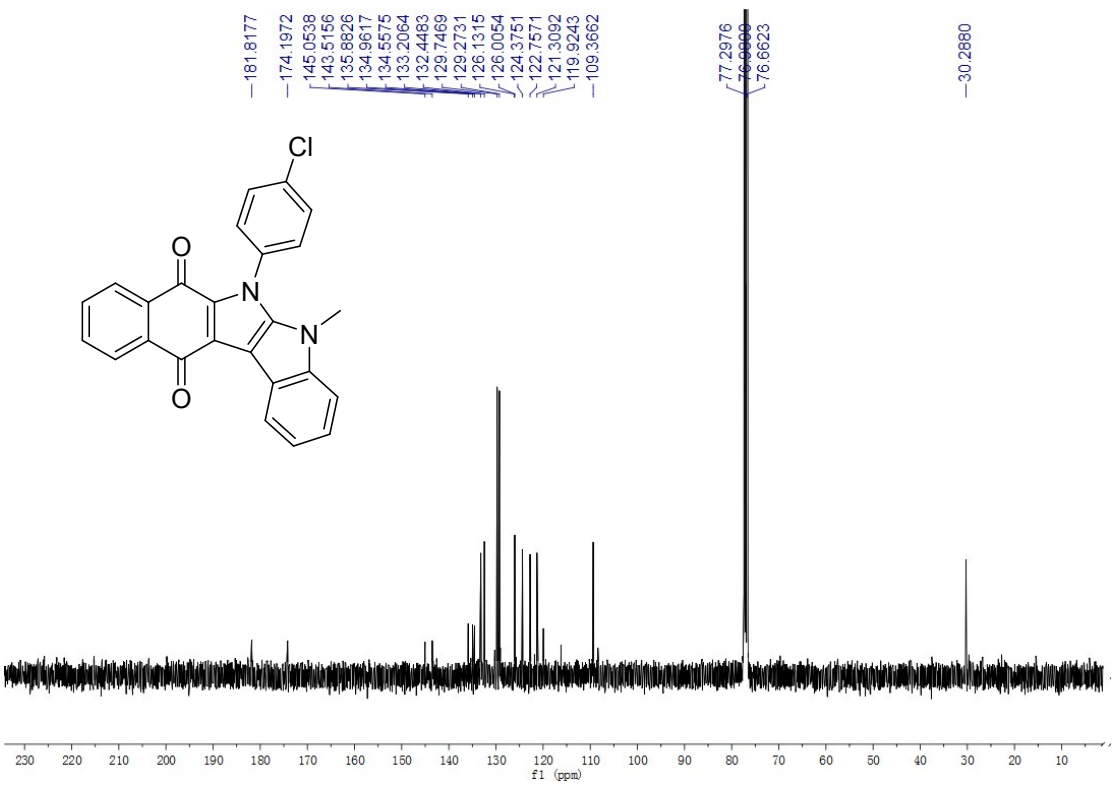




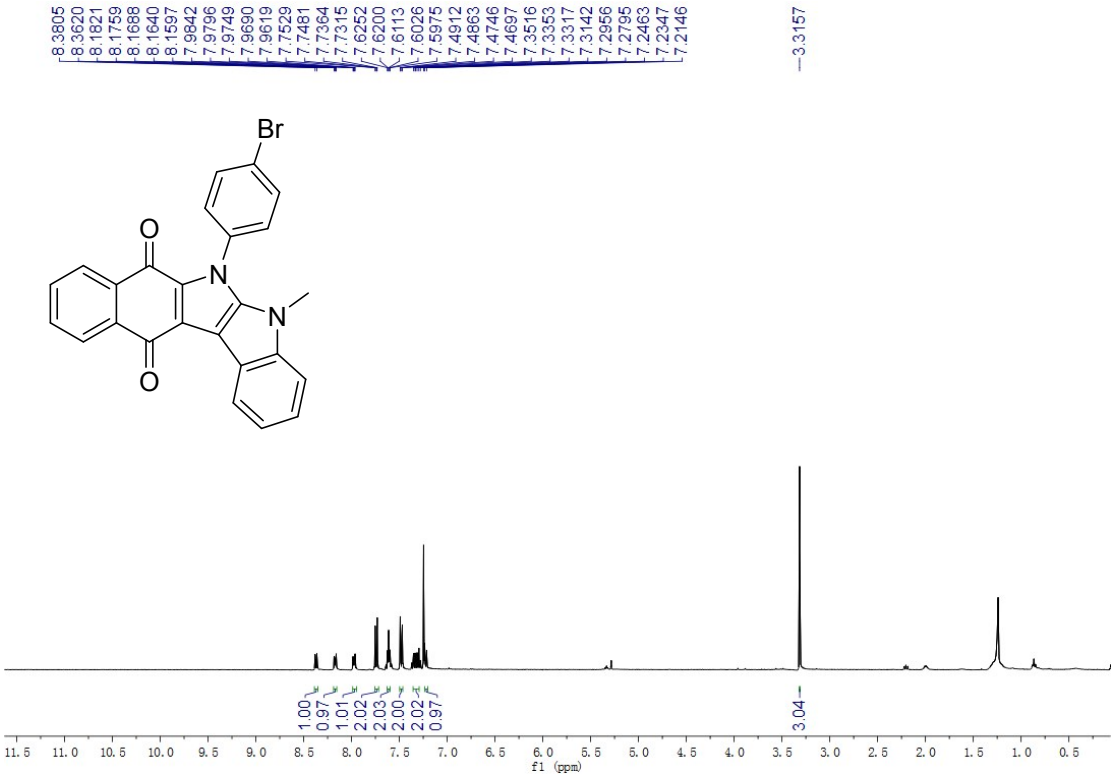

F
O
N
N
O
-110.3663
30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200
f1 (ppm)

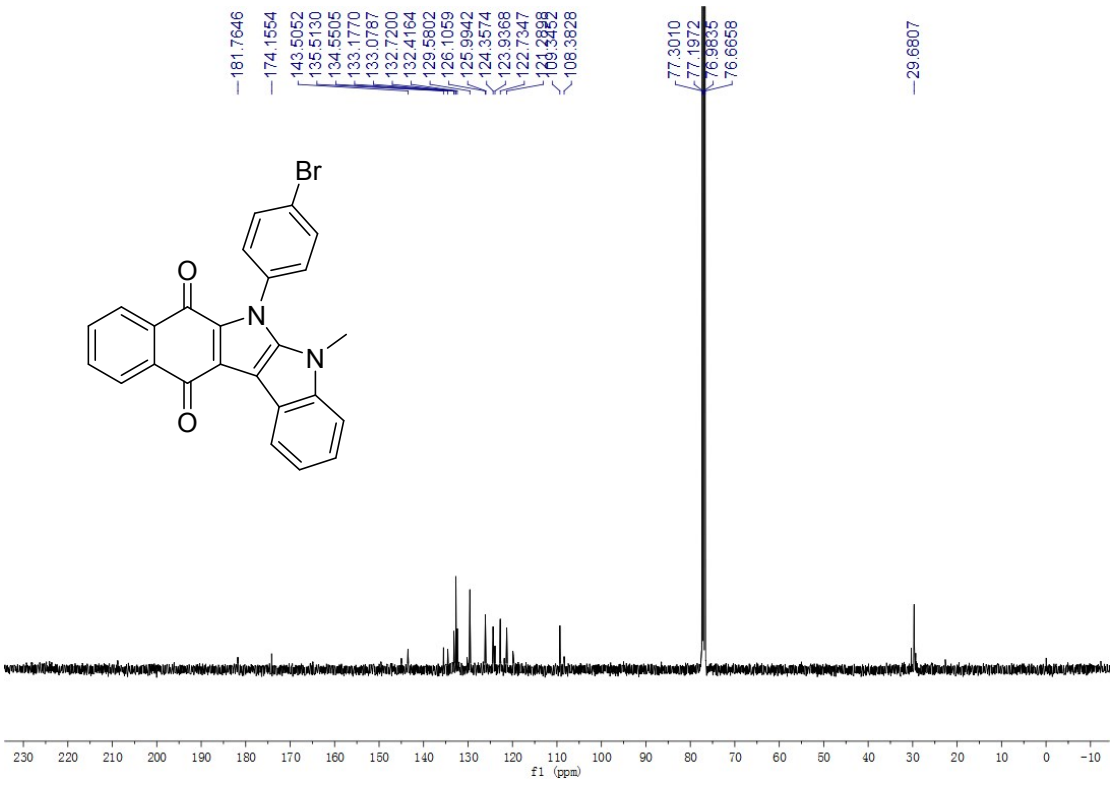
6-(4-chlorophenyl)-5-methyl-5,6-dihydrobenzo[f]indolo[2,3-b]indole-7,12-dione (3af)



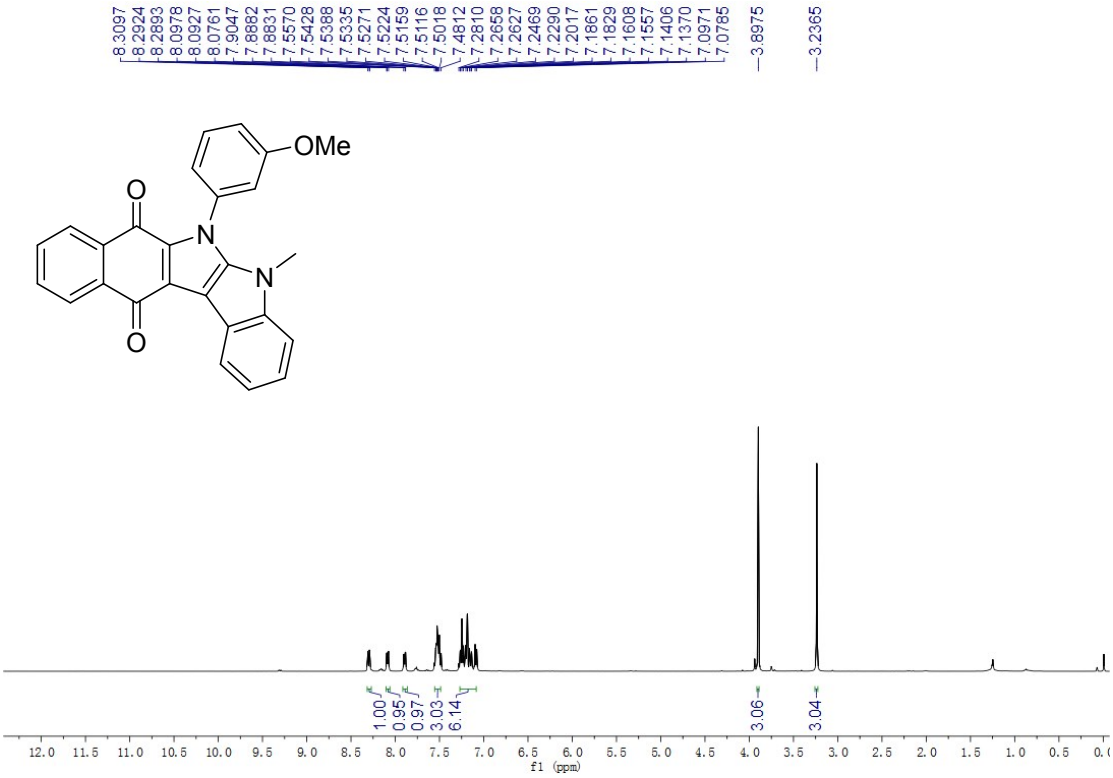


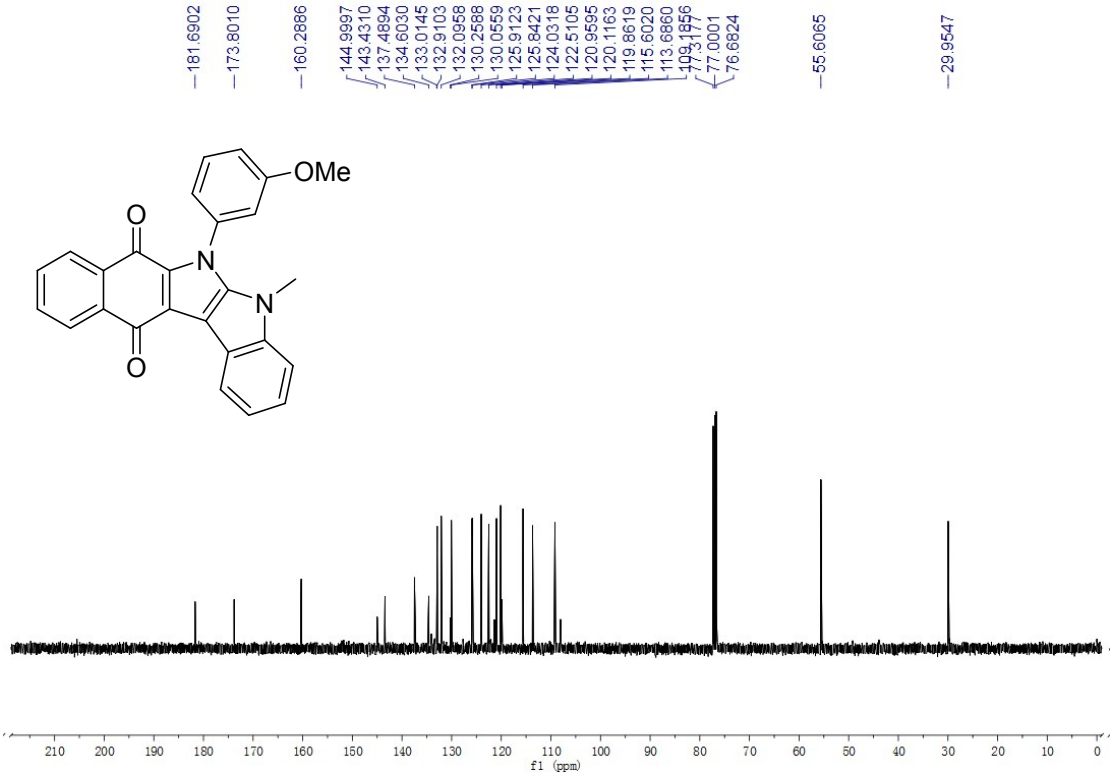
6-(4-bromophenyl)-5-methyl-5,6-dihydrobenzo[f]indolo[2,3-b]indole-7,12-dione (3ag)



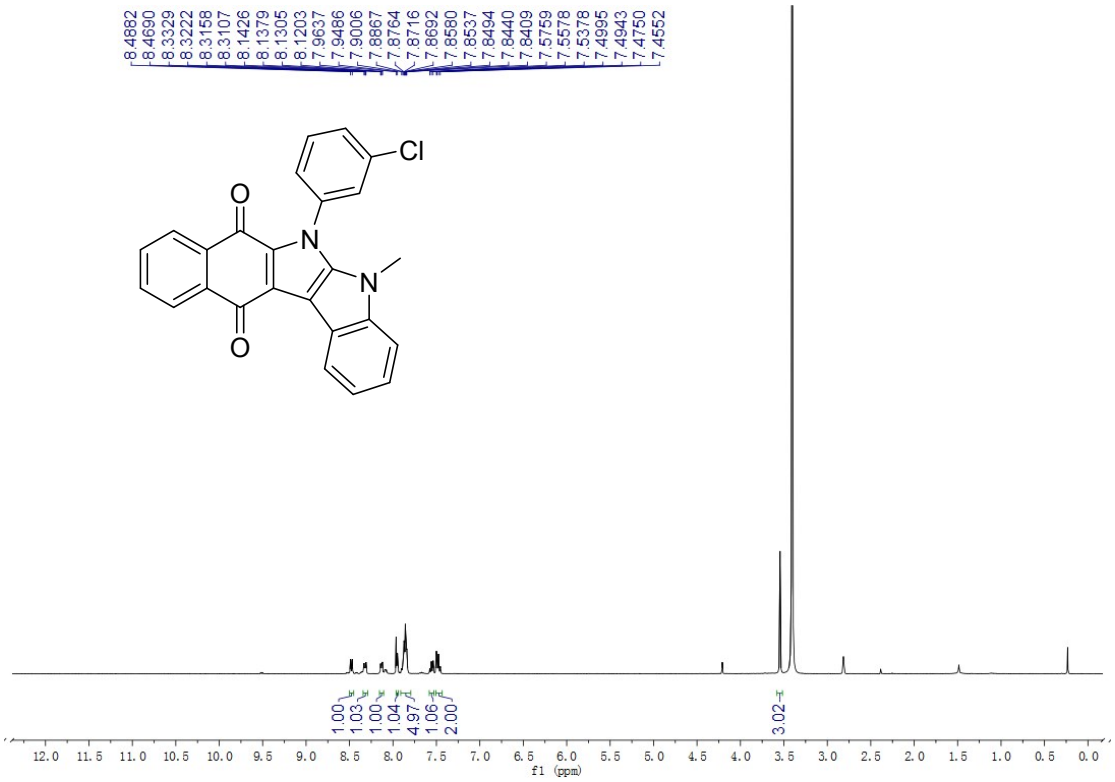


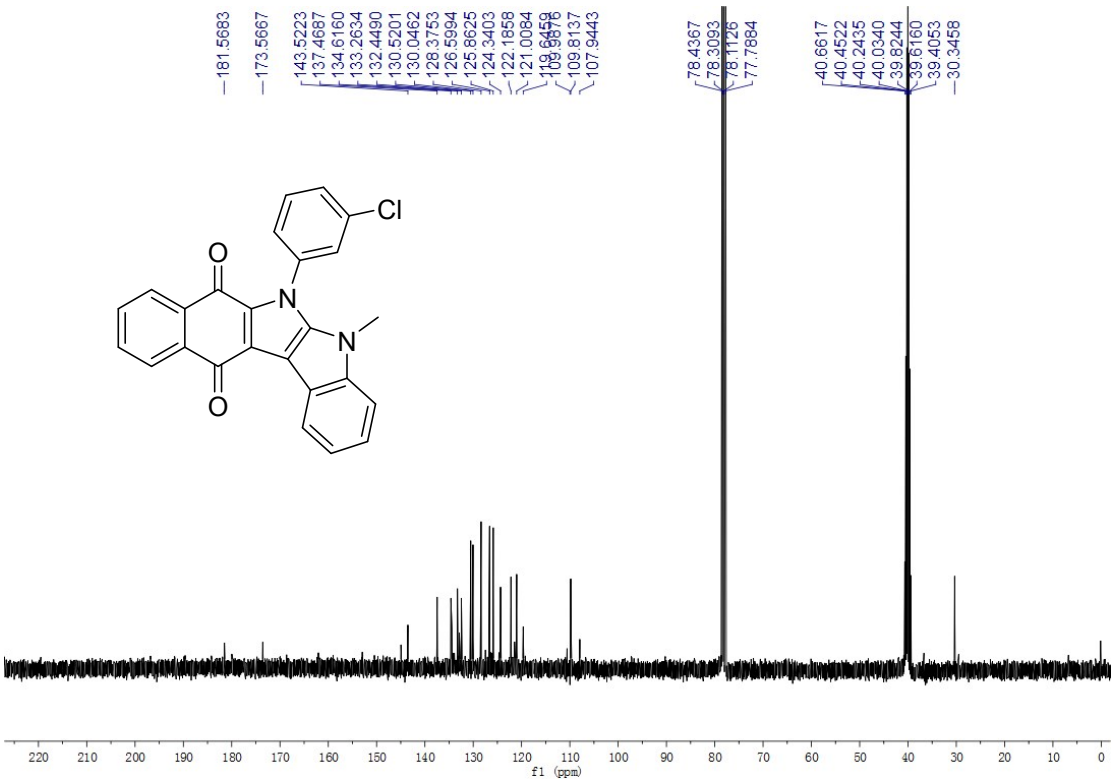
6-(3-methoxyphenyl)-5-methyl-5,6-dihydrobenzo[f]indolo[2,3-b]indole-7,12-dione (3ah)



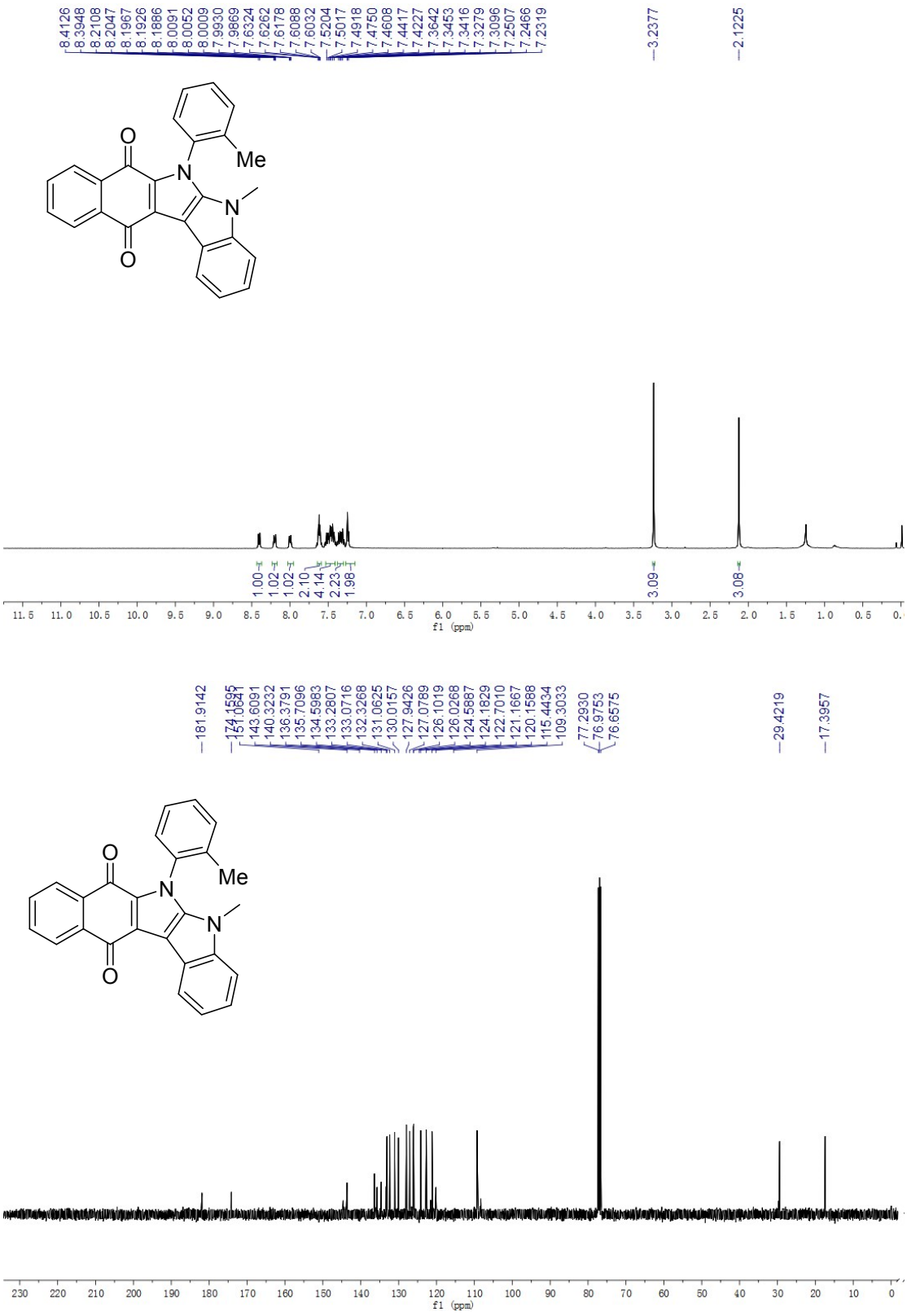


6-(3-chlorophenyl)-5-methyl-5,6-dihydrobenzo[f]indolo[2,3-b]indole-7,12-dione (3ai)

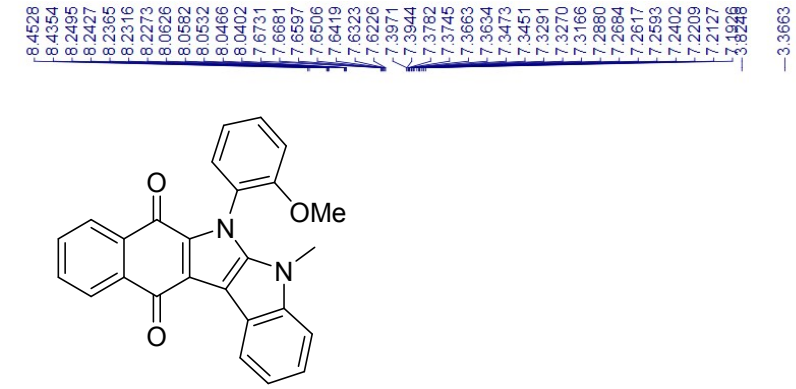


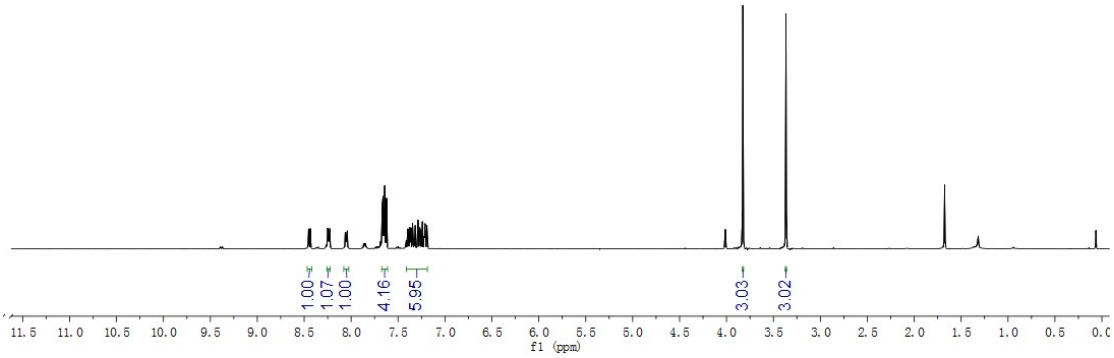


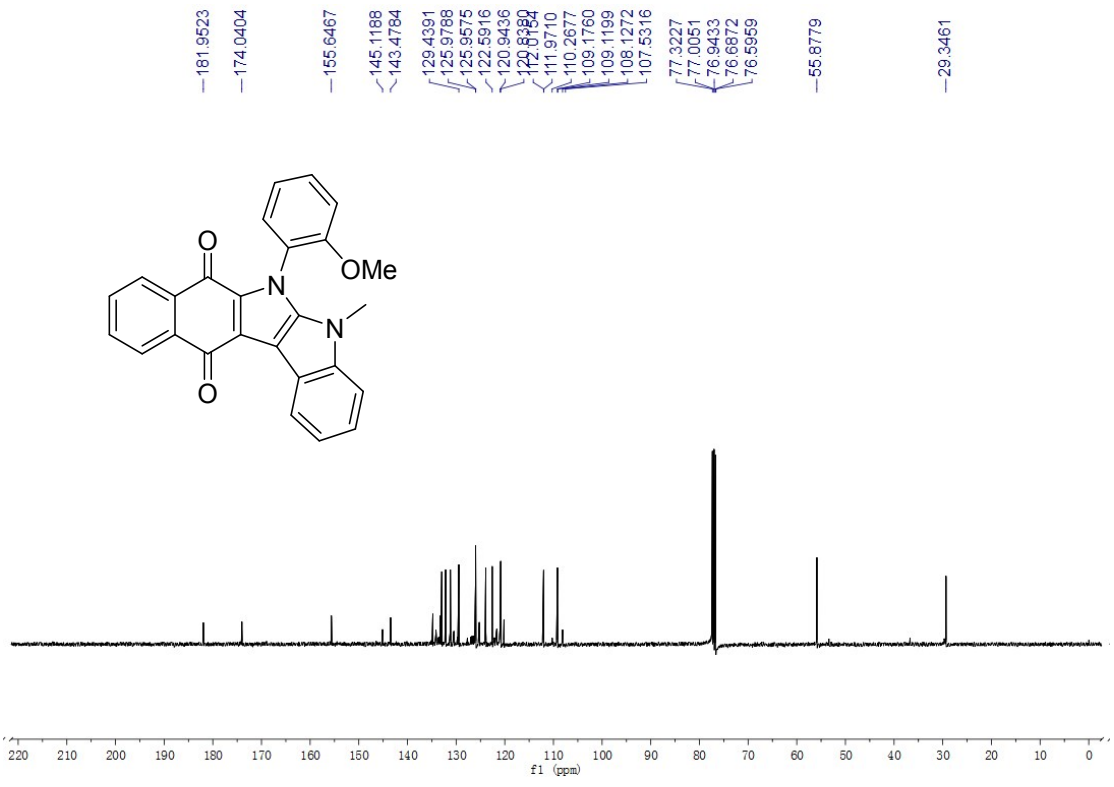
5-methyl-6-(o-tolyl)-5,6-dihydrobenzo[f]indolo[2,3-b]indole-7,12-dione (3aj)



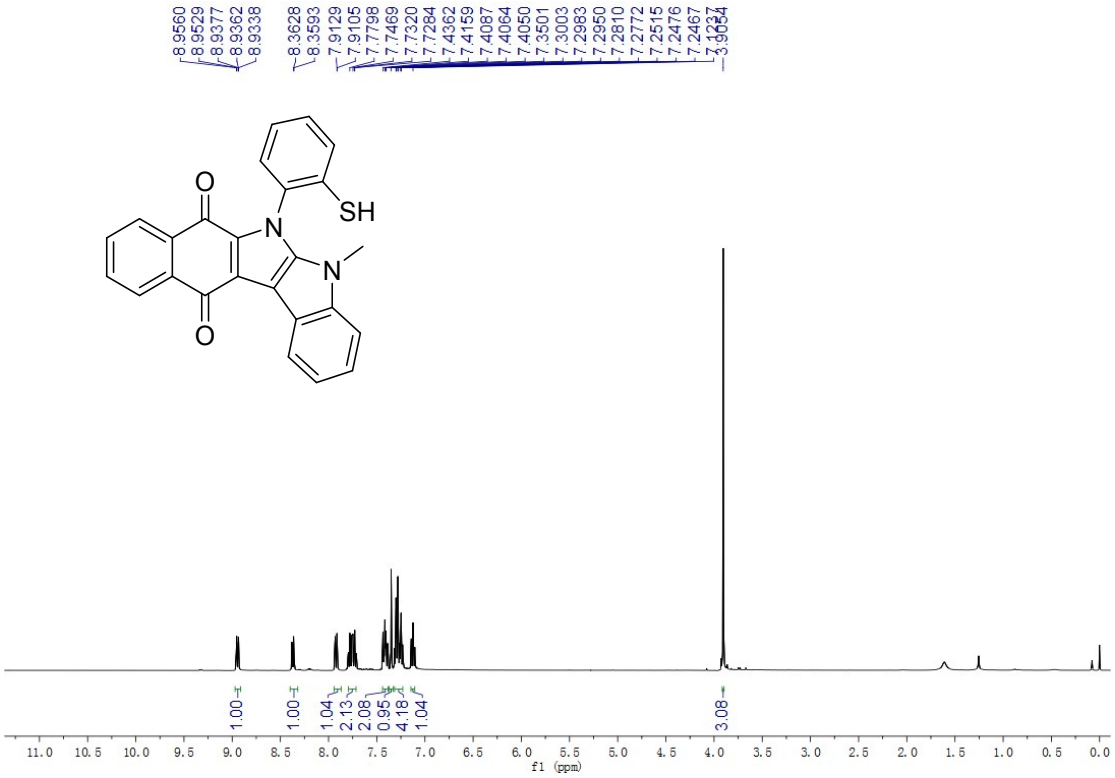
6-(2-methoxyphenyl)-5-methyl-5,6-dihydrobenzo[f]indolo[2,3-b]indole-7,12-dione (3ak)

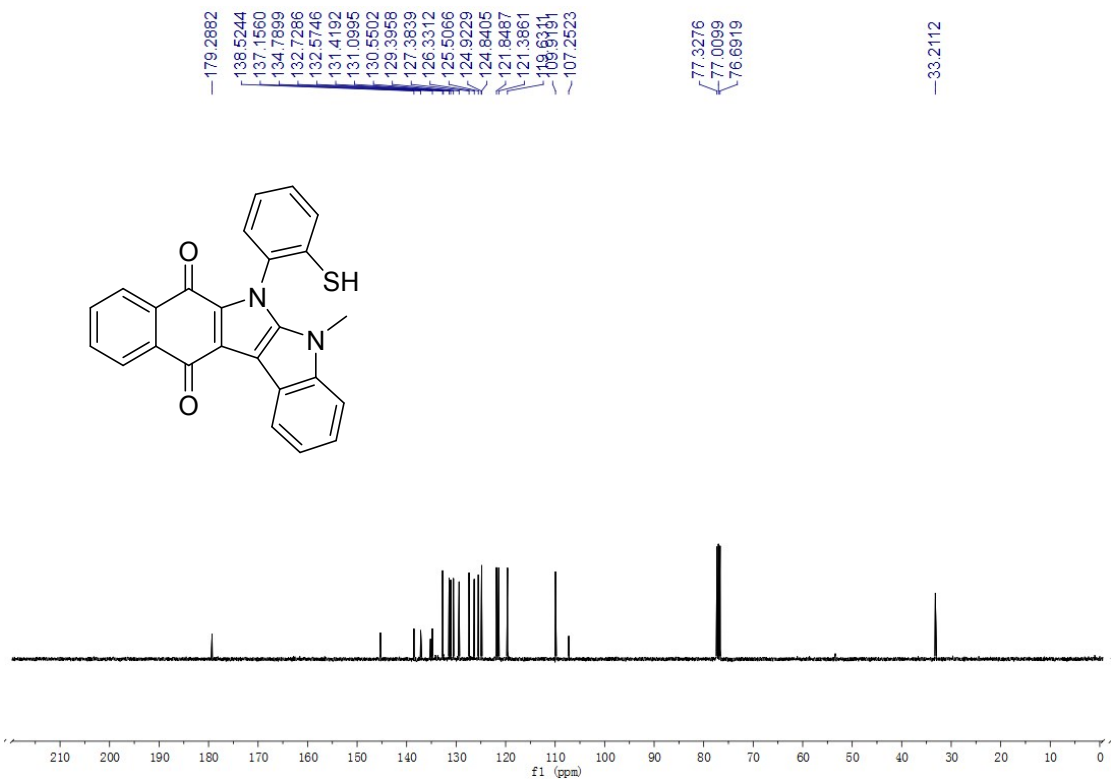




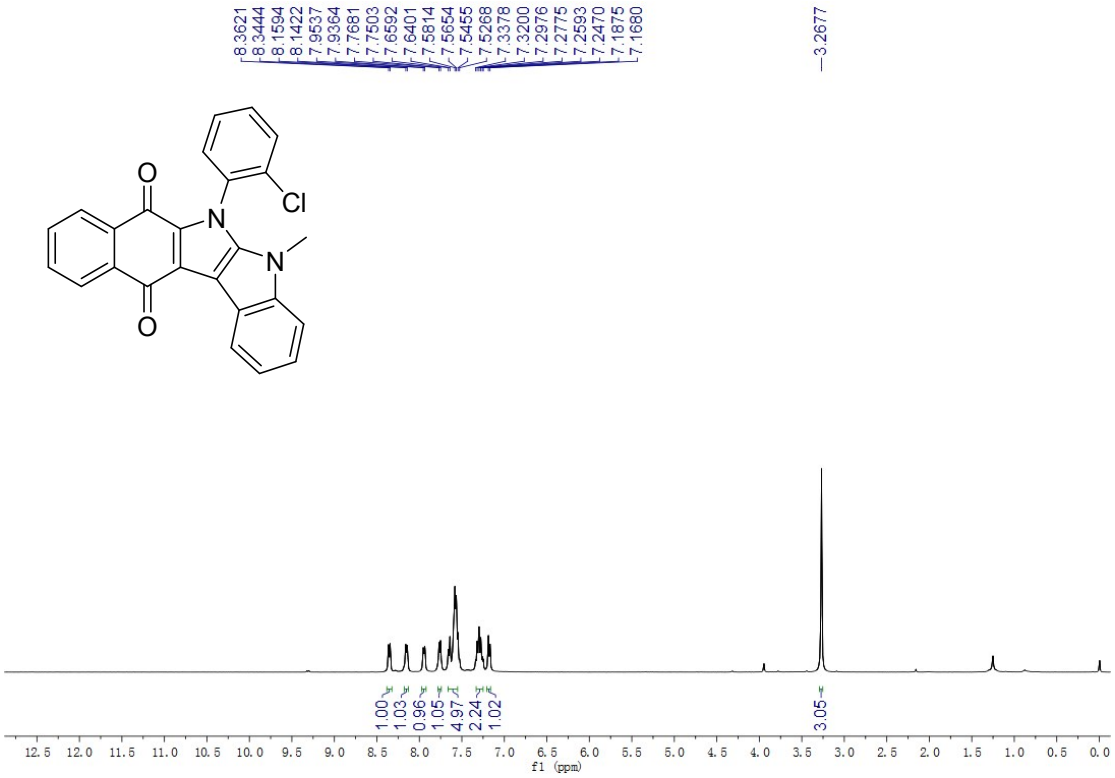


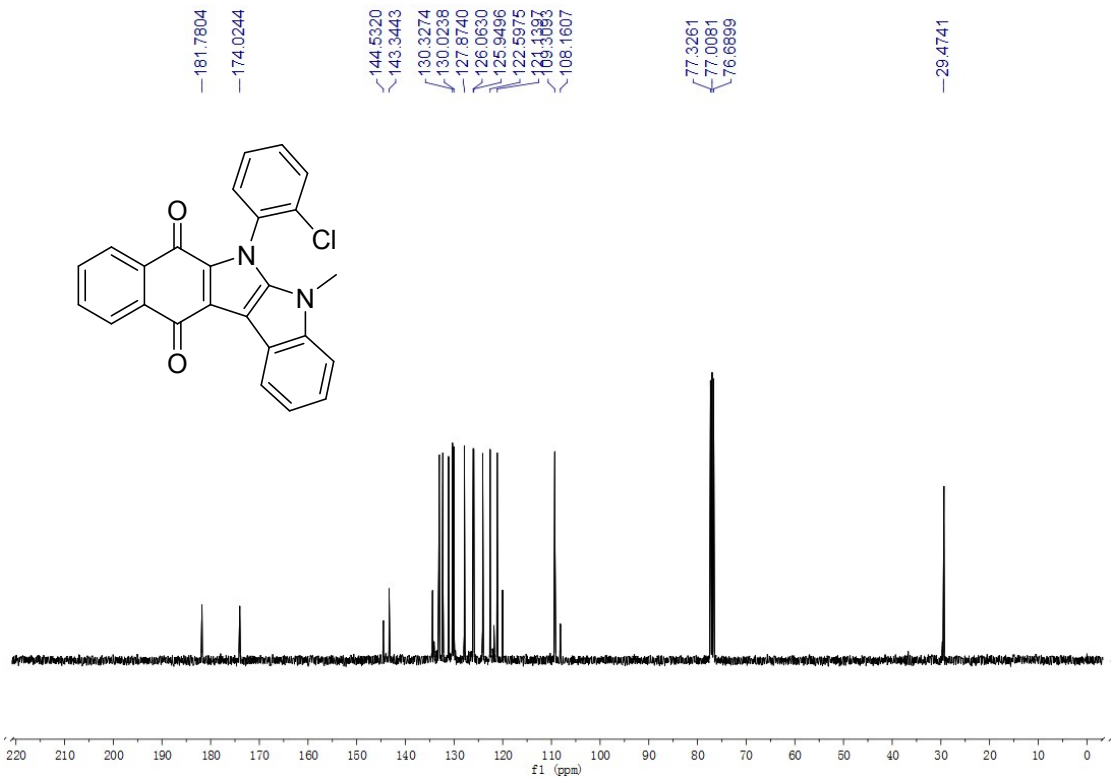
6-(2-mercaptophenyl)-5-methyl-5,6-dihydrobenzo[f]indolo[2,3-b]indole-7,12-dione (3al)



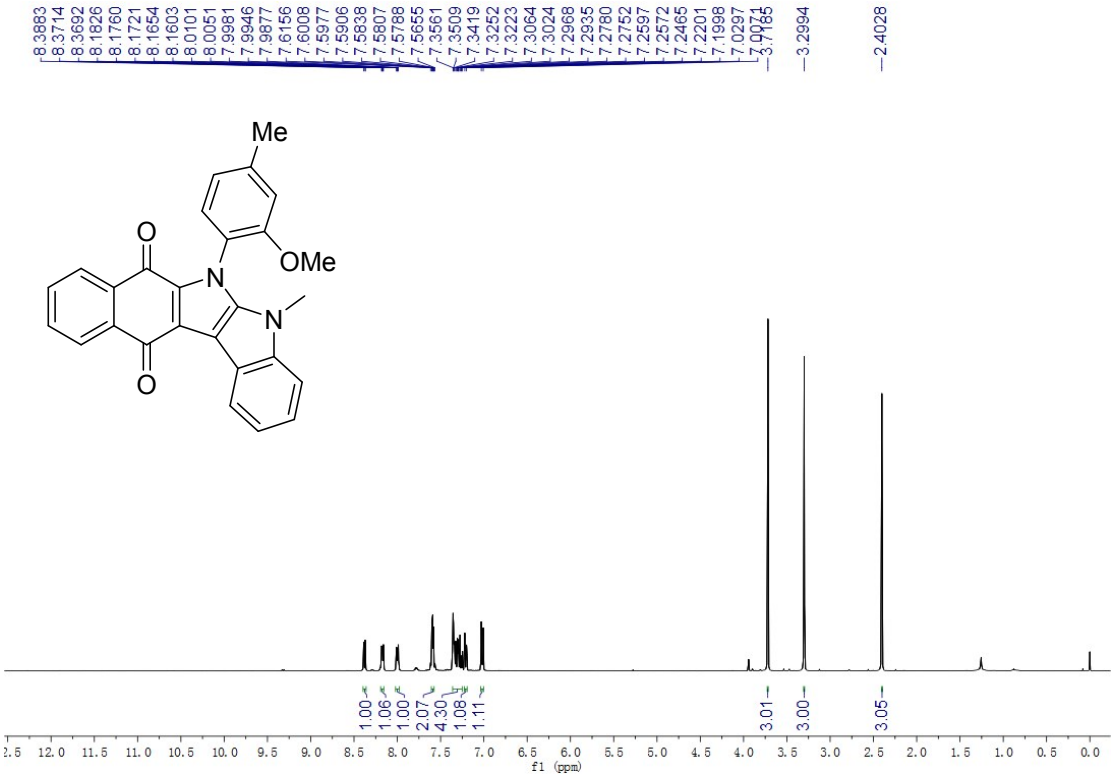


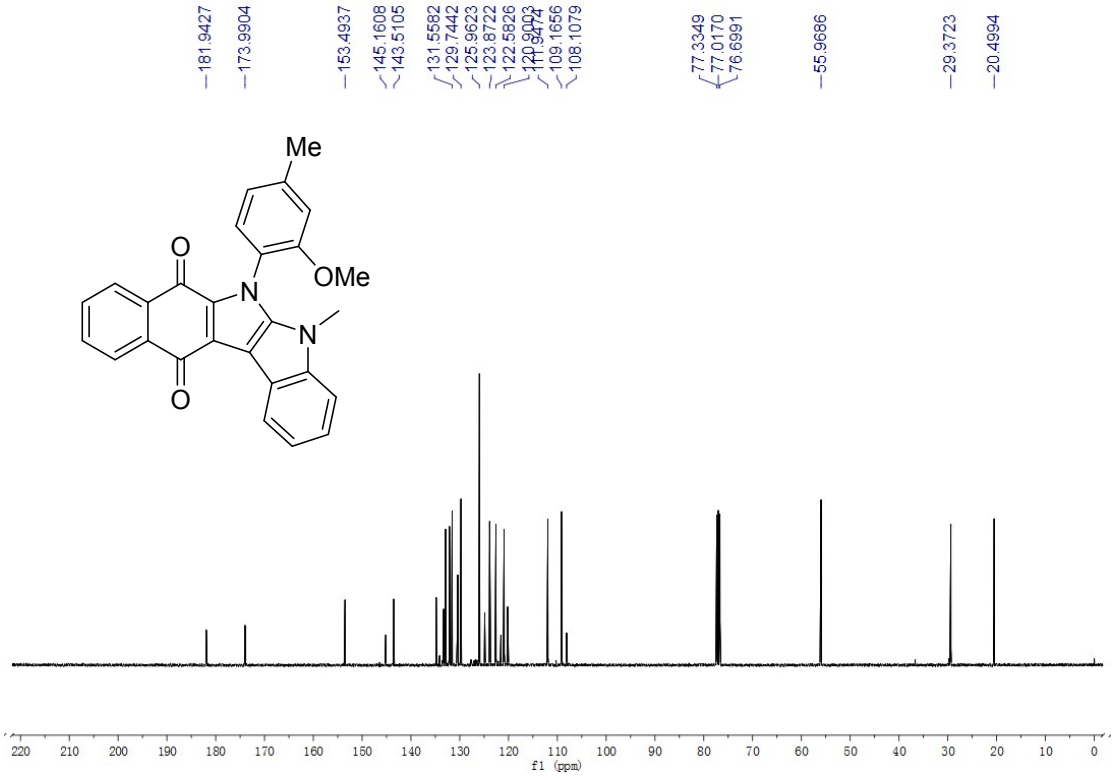
6-(2-chlorophenyl)-5-methyl-5,6-dihydrobenzo[f]indolo[2,3-b]indole-7,12-dione (3am)



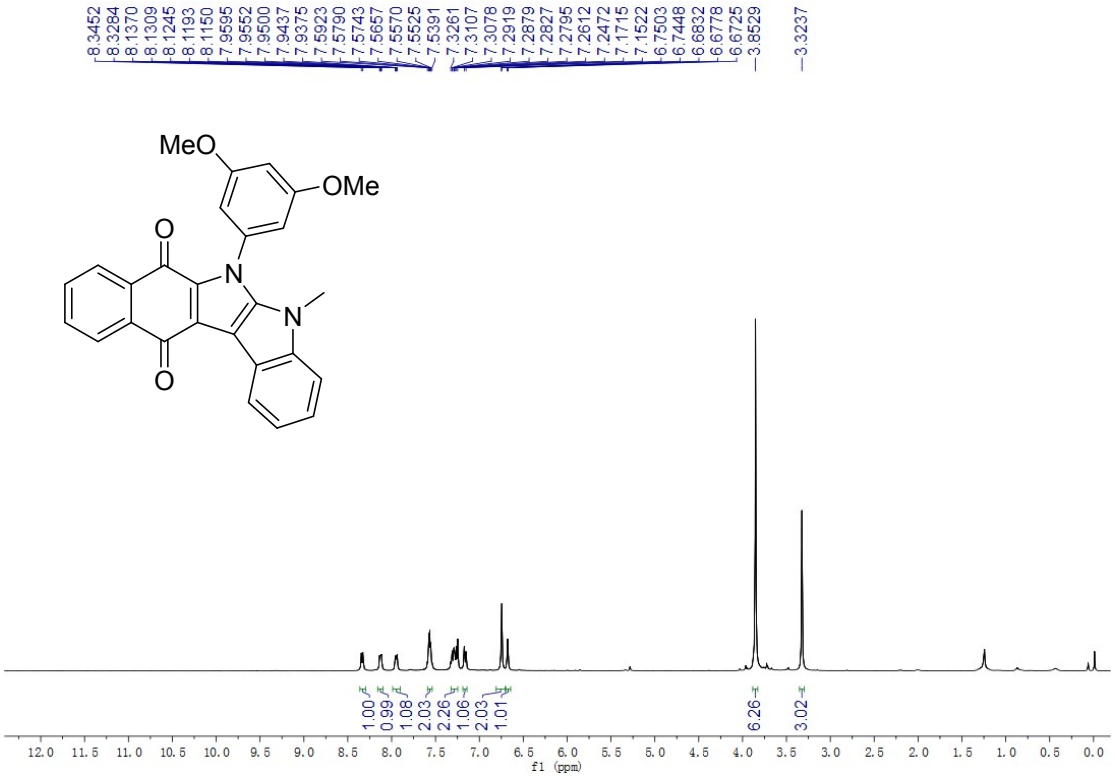


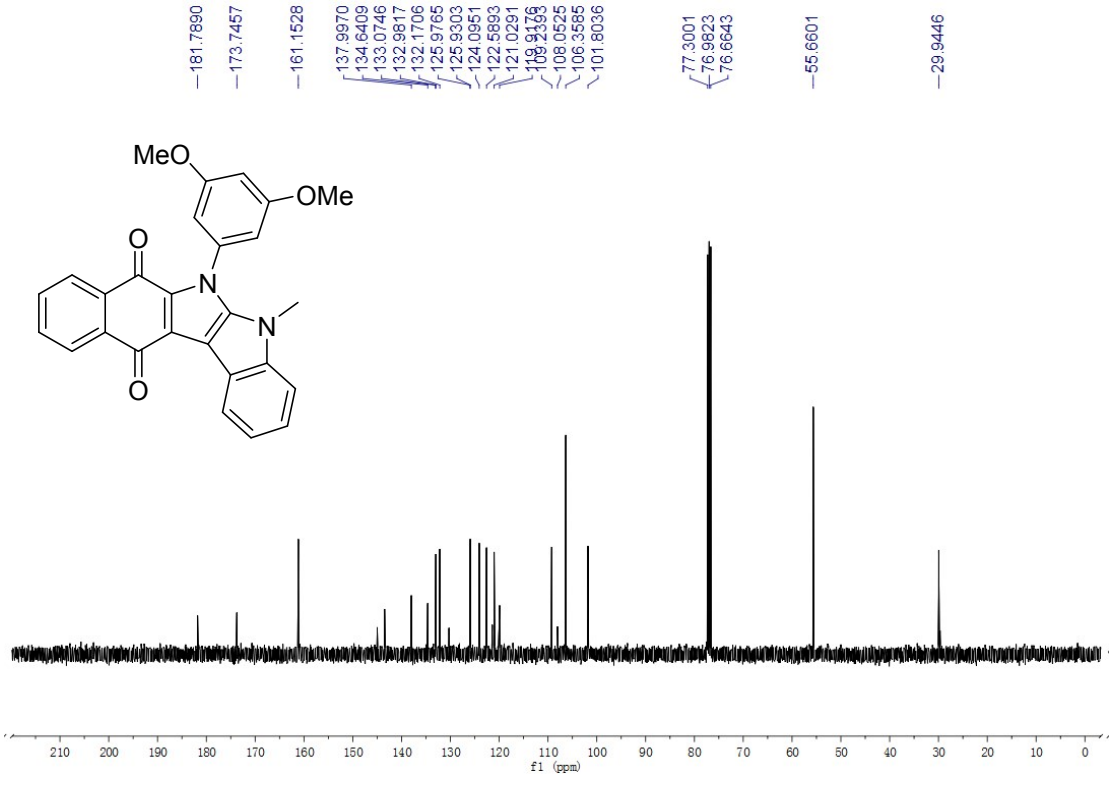
6-(2-methoxy-4-methylphenyl)-5-methyl-5,6-dihydrobenzo[f]indolo[2,3-b]indole-7,12-dione (3an)



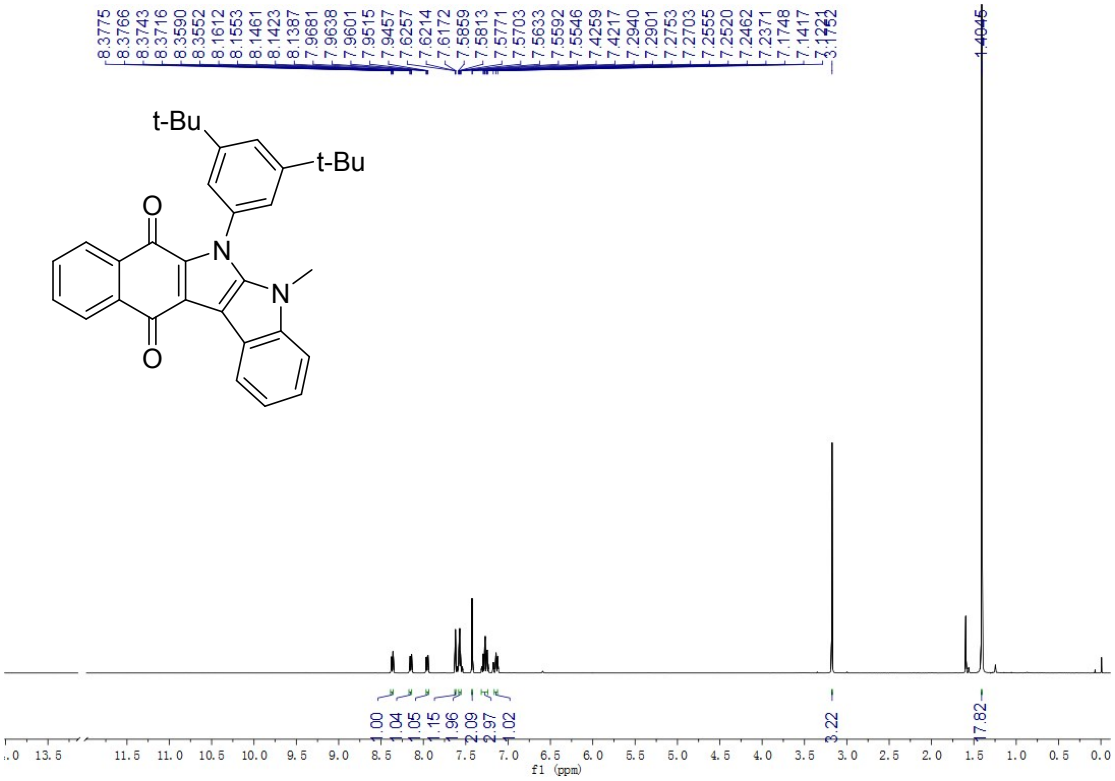


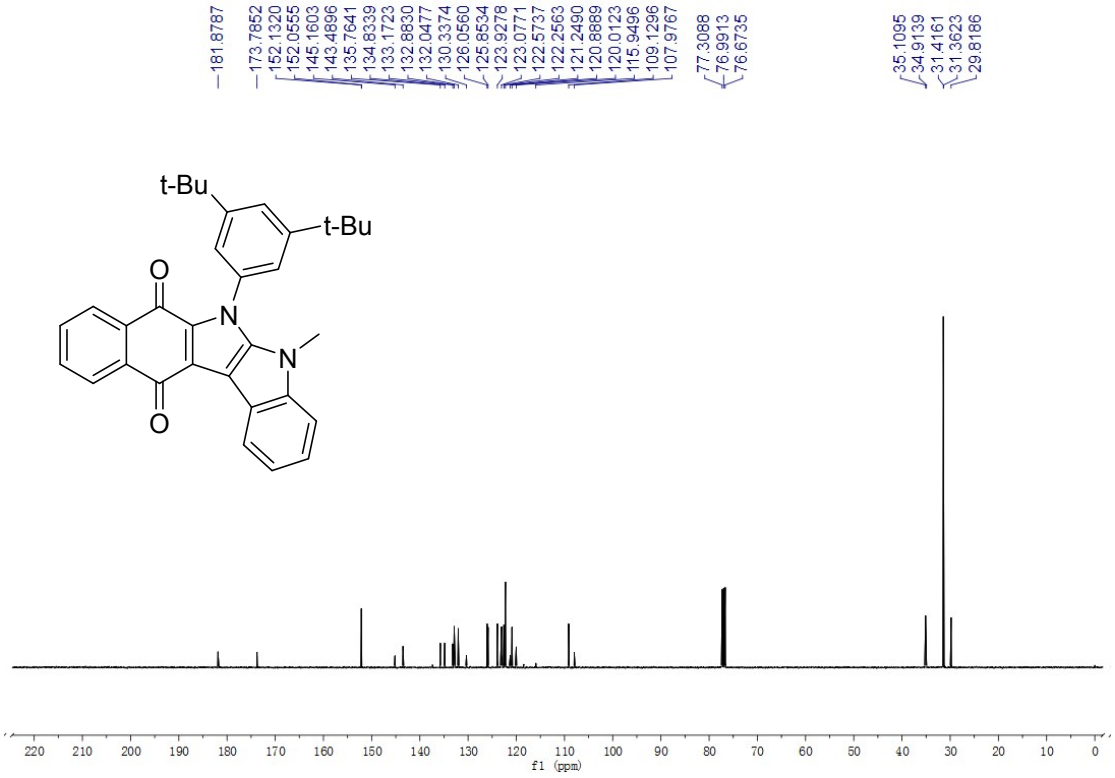
6-(3,5-dimethoxyphenyl)-5-methyl-5,6-dihydrobenzo[f]indolo[2,3-b]indole-7,12-dione (3ao)



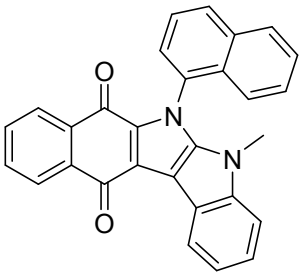


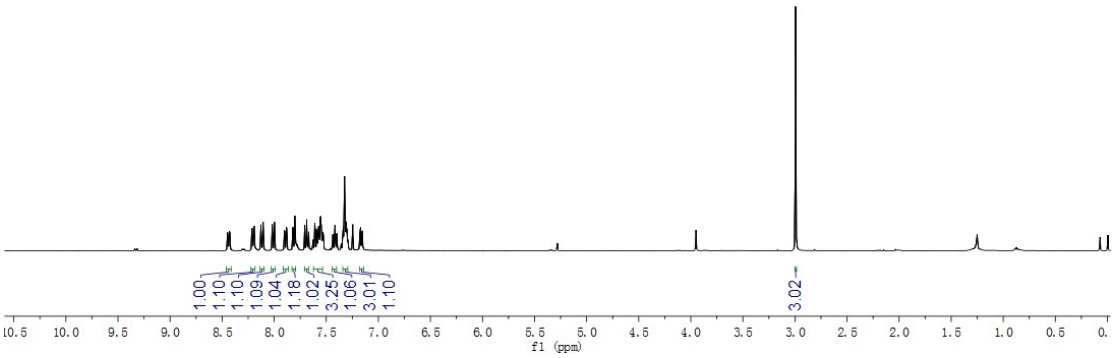
6-(3,5-di-tert-butylphenyl)-5-methyl-5,6-dihydrobenzo[f]indolo[2,3-b]indole-7,12-dione (3ap)

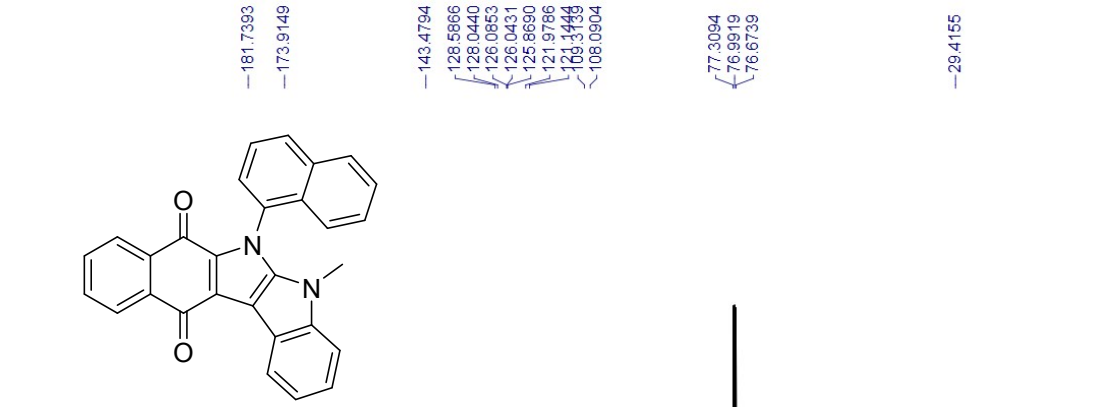


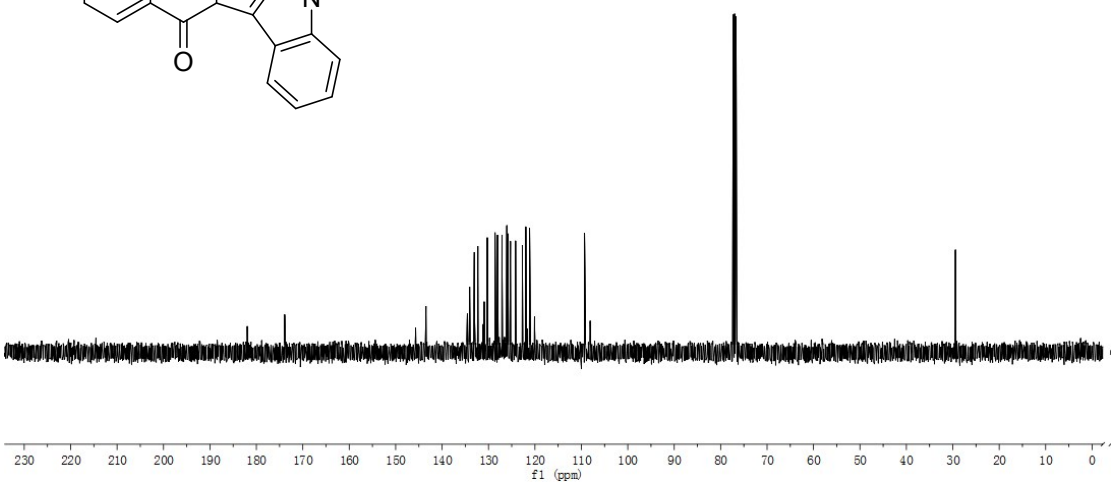


5-methyl-6-(naphthalen-1-yl)-5,6-dihydrobenzo[f]indolo[2,3-b]indole-7,12-dione (3aq)

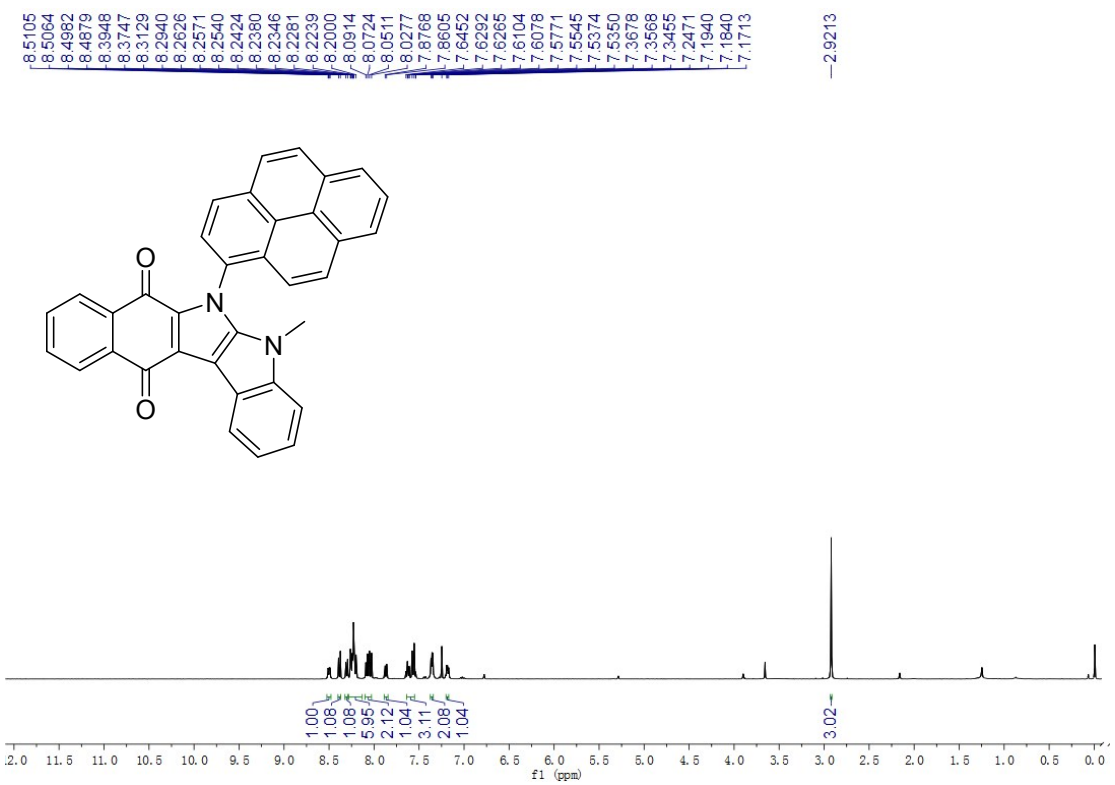


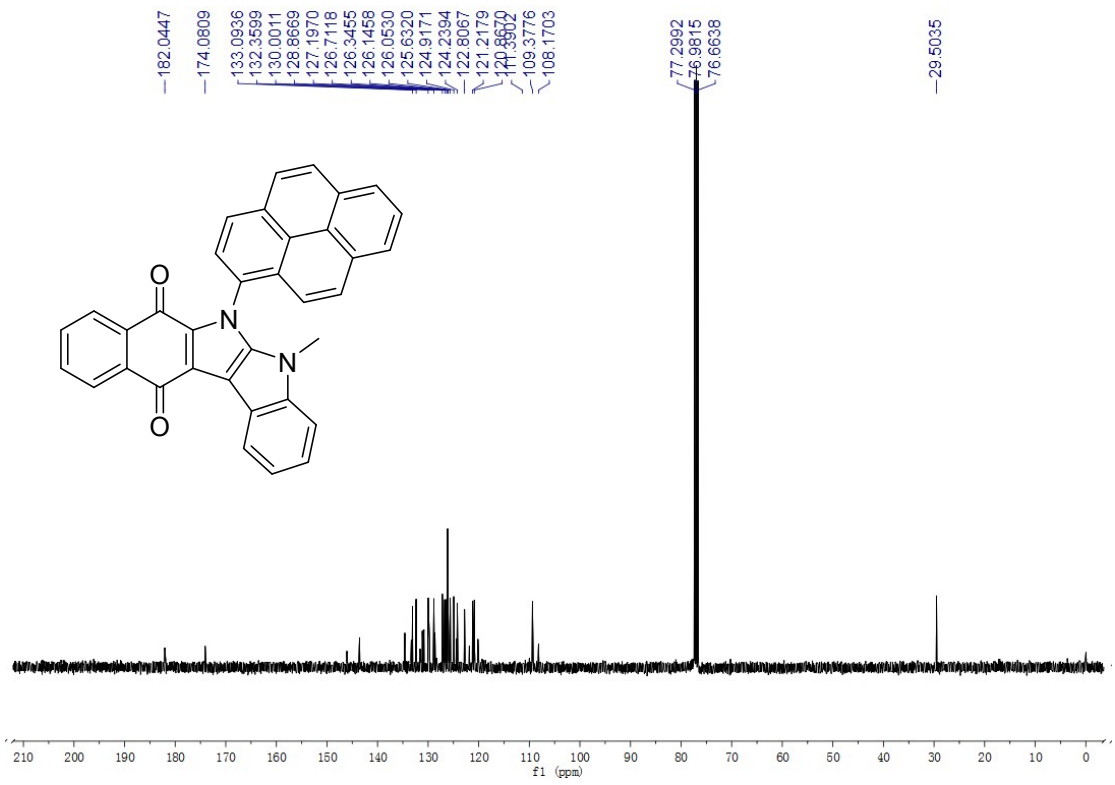




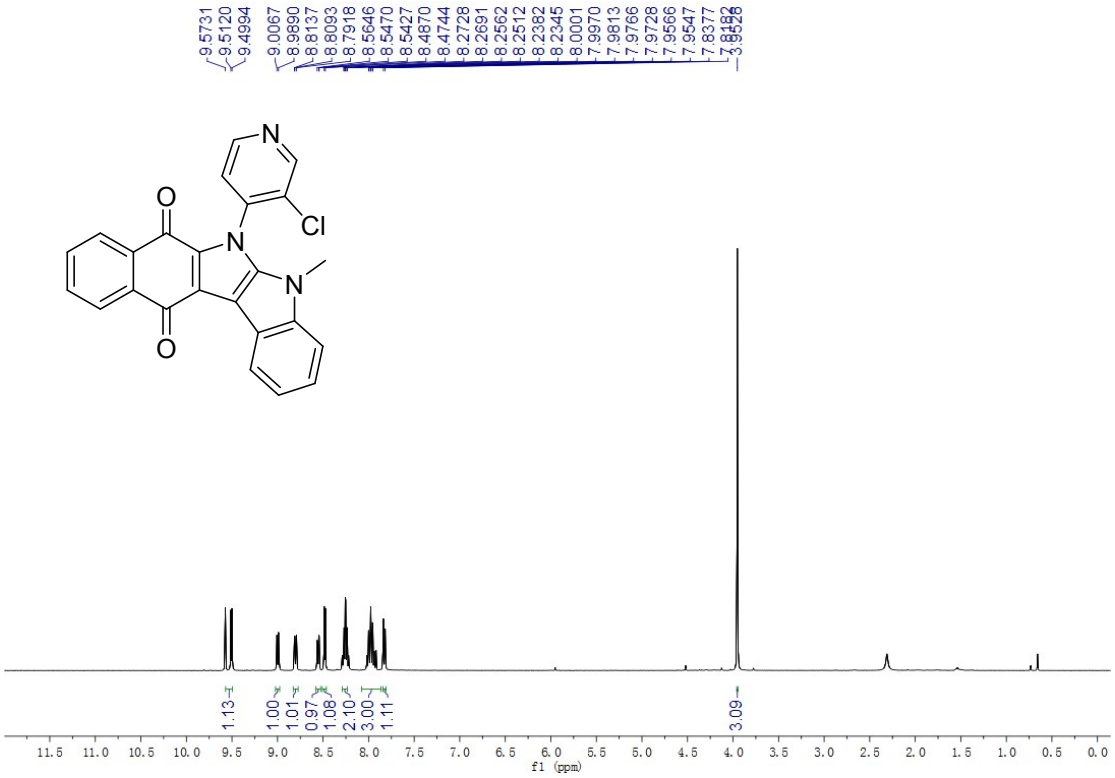


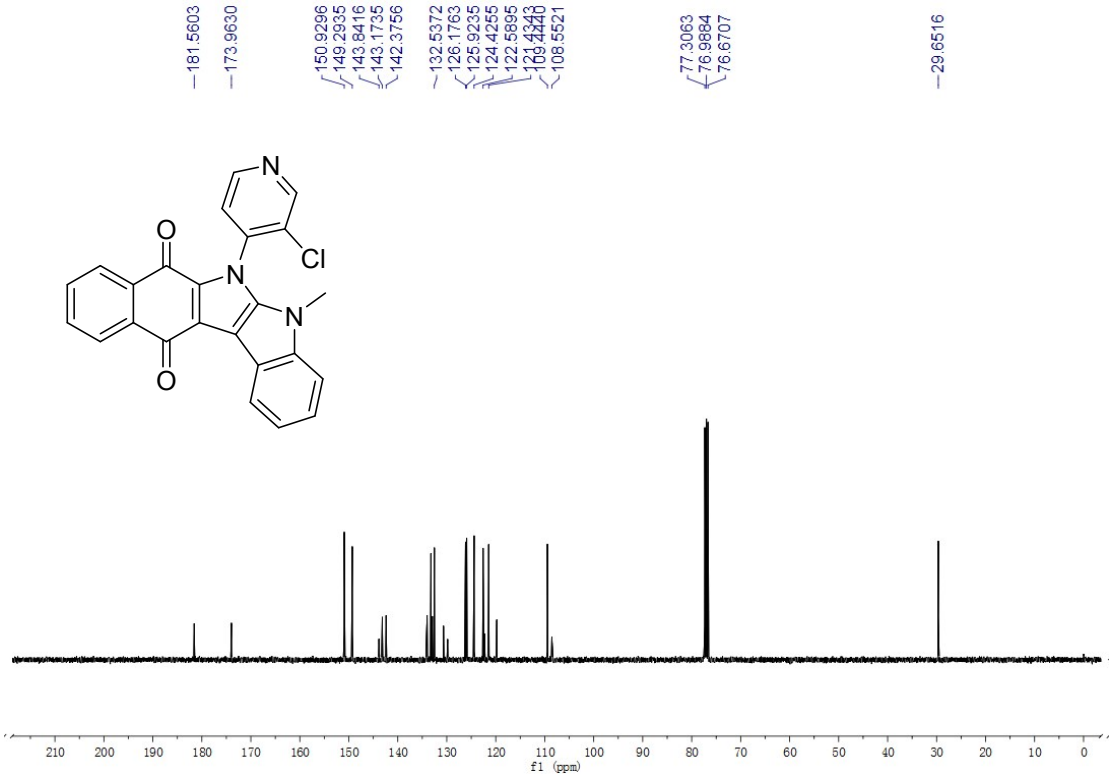
5-methyl-6-(pyren-1-yl)-5,6-dihydrobenzo[f]indolo[2,3-b]indole-7,12-dione (3ar)



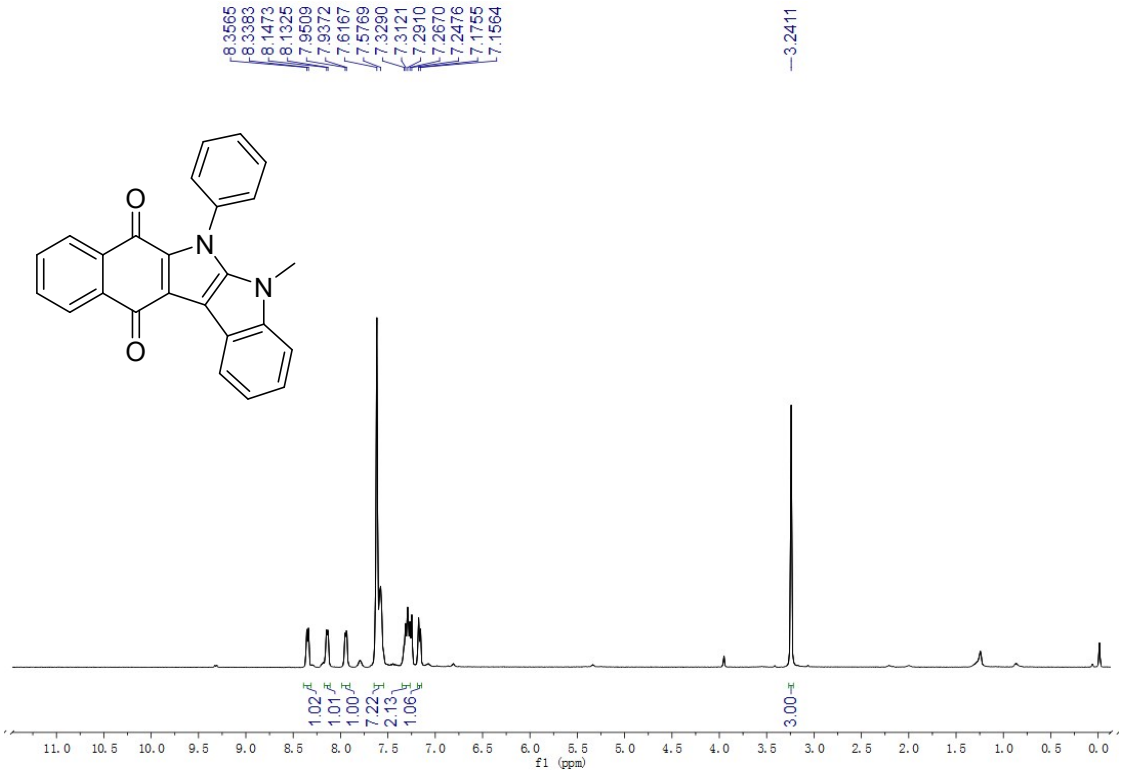


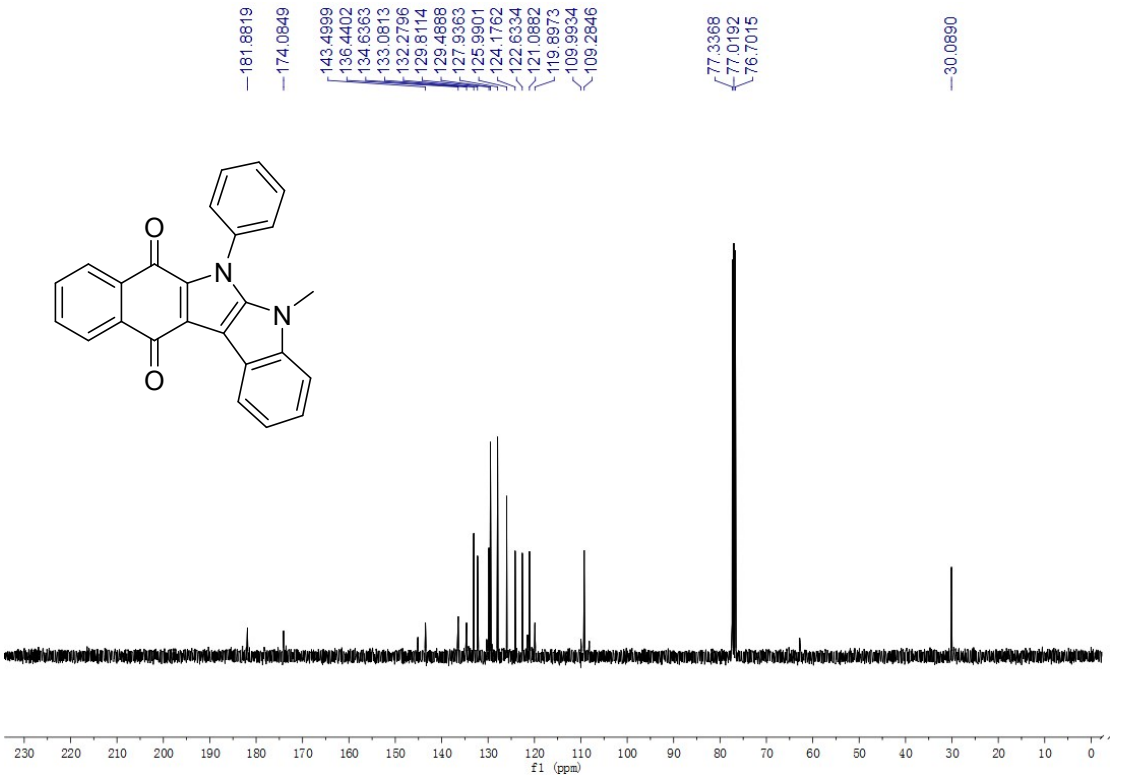
6-(3-chloropyridin-4-yl)-5-methyl-5,6-dihydrobenzo[f]indolo[2,3-b]indole-7,12-dione (3as)



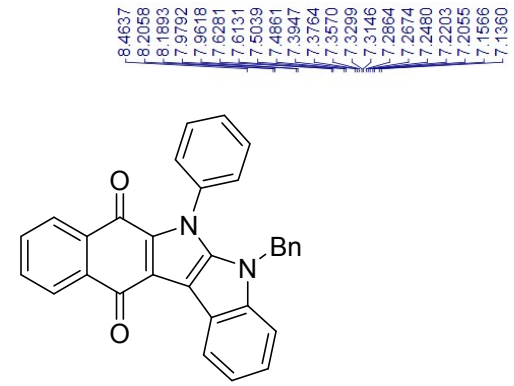


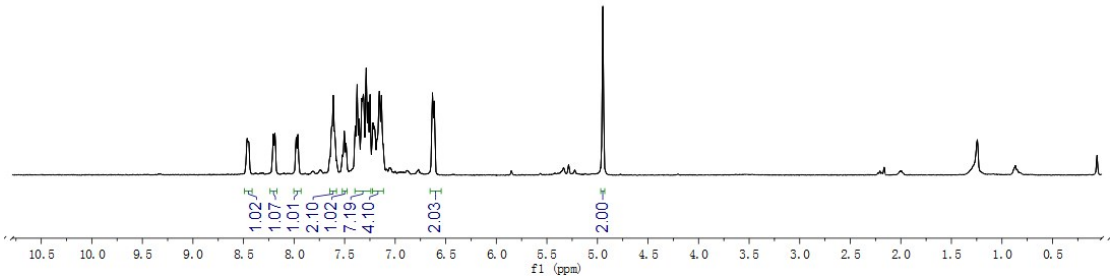
5-methyl-6-phenyl-5,6-dihydrobenzo[f]indolo[2,3-b]indole-7,12-dione (3aa)

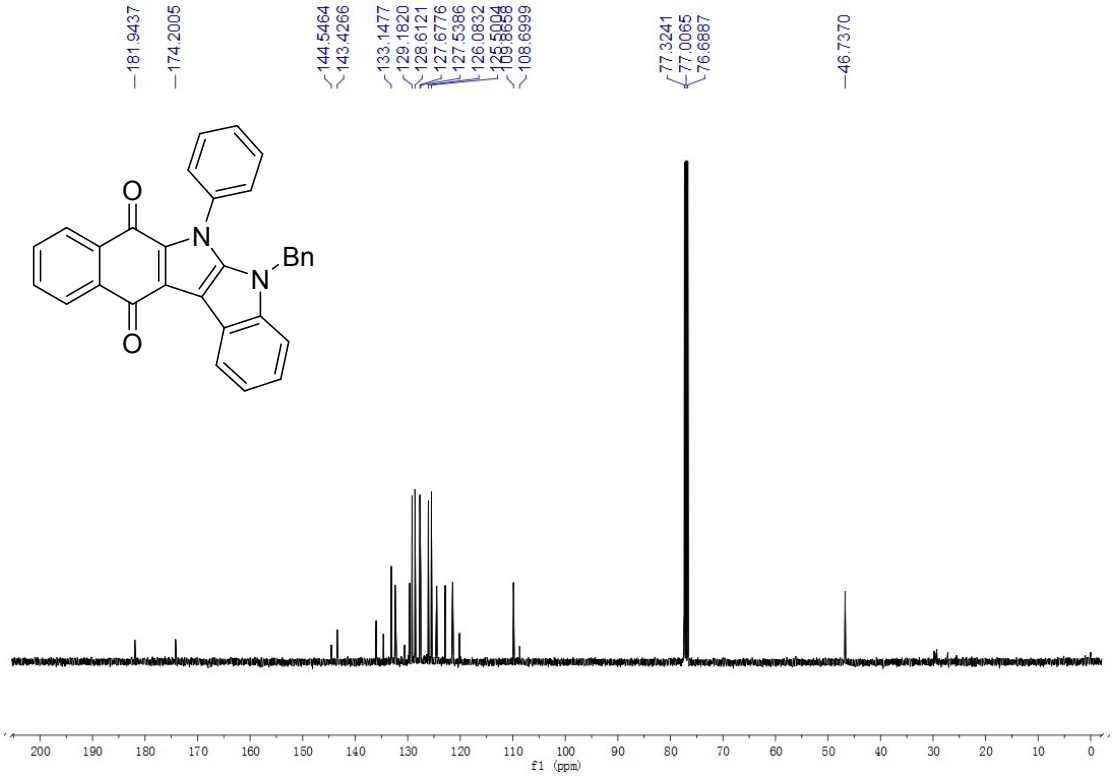




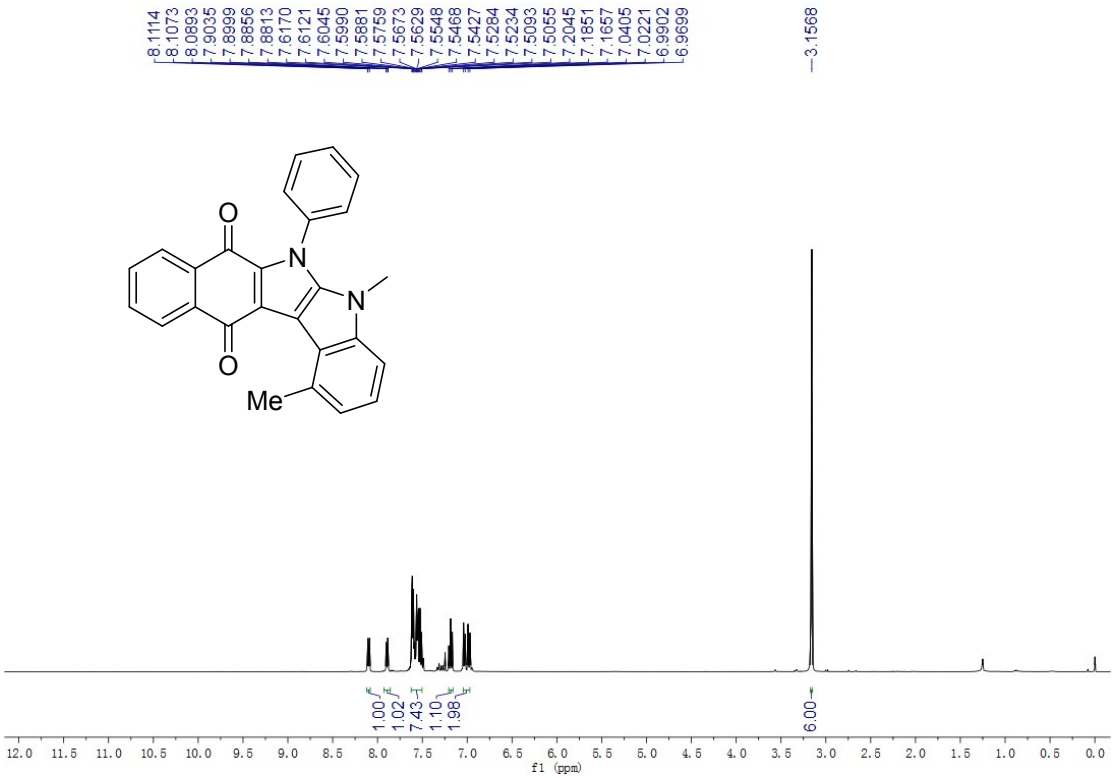
5-benzyl-6-phenyl-5,6-dihydrobenzo[f]indolo[2,3-b]indole-7,12-dione (3ba)

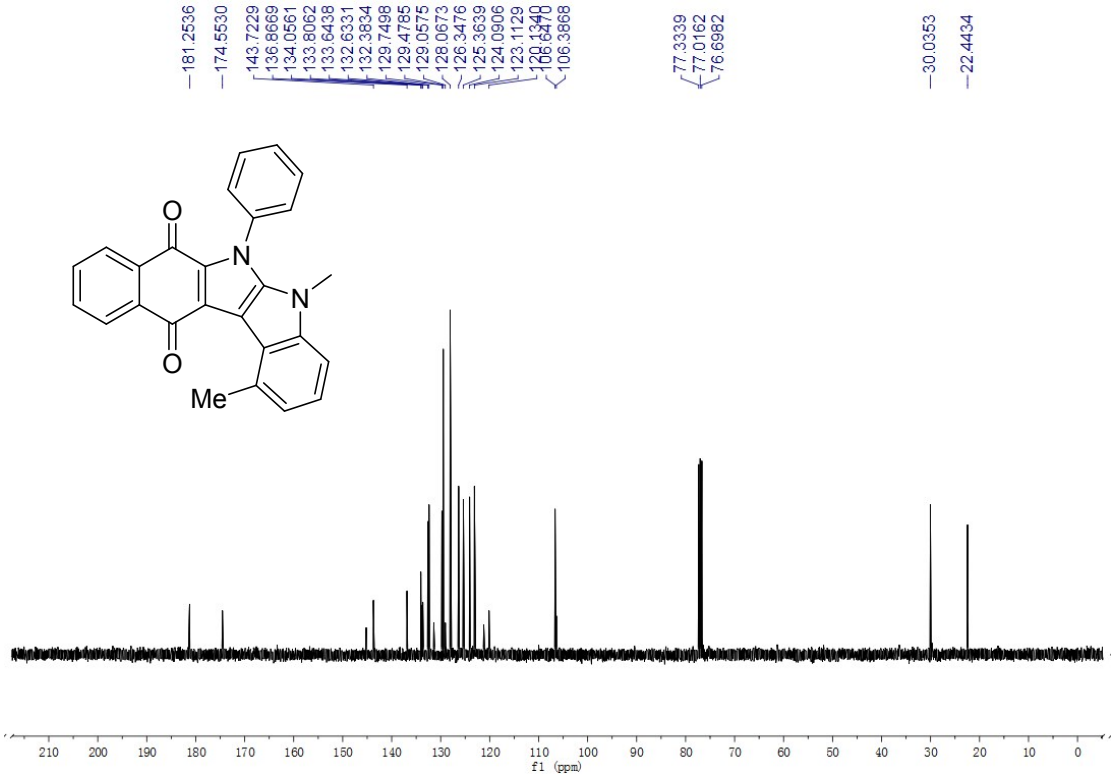




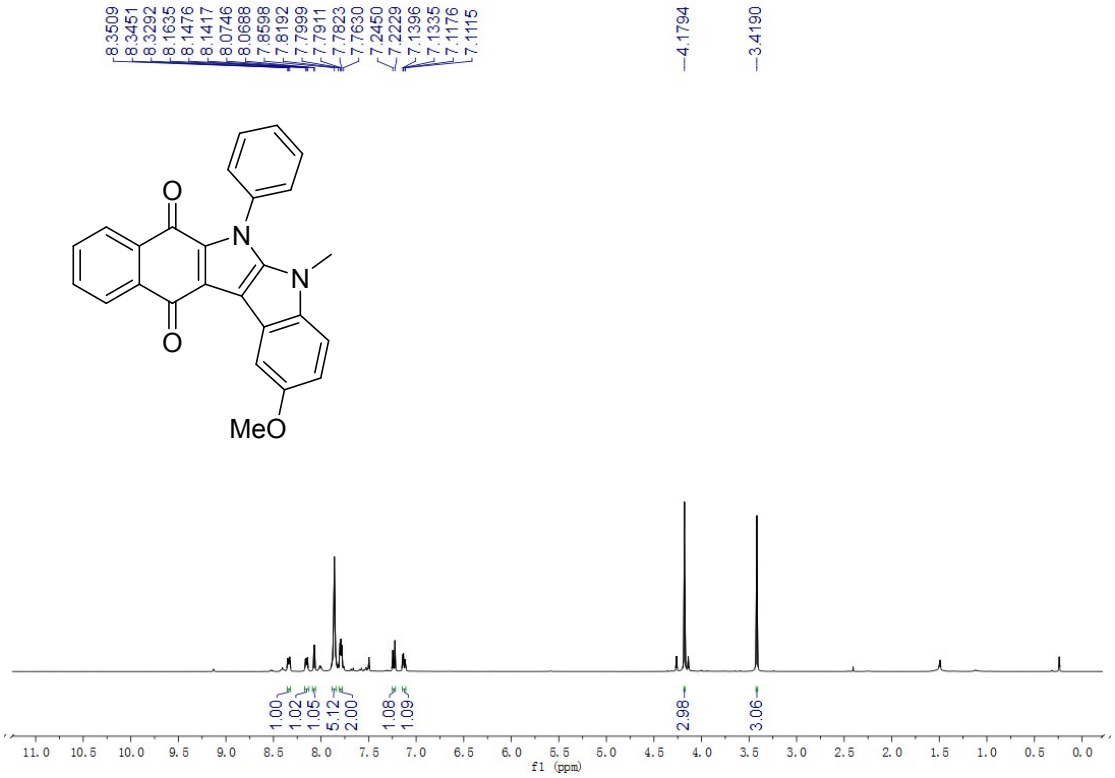


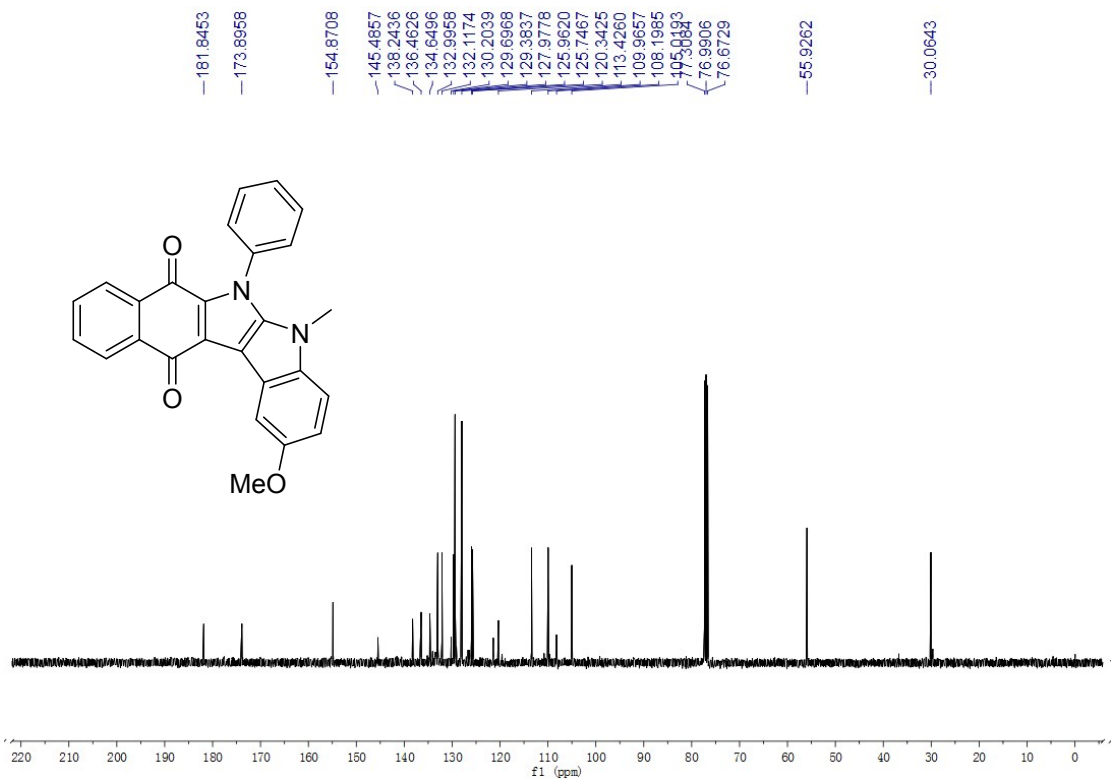
1,5-dimethyl-6-phenyl-5,6-dihydrobenzo[f]indolo[2,3-b]indole-7,12-dione (3da)





2-methoxy-5-methyl-6-phenyl-5,6-dihydrobenzo[f]indolo[2,3-b]indole-7,12-dione (3ea)





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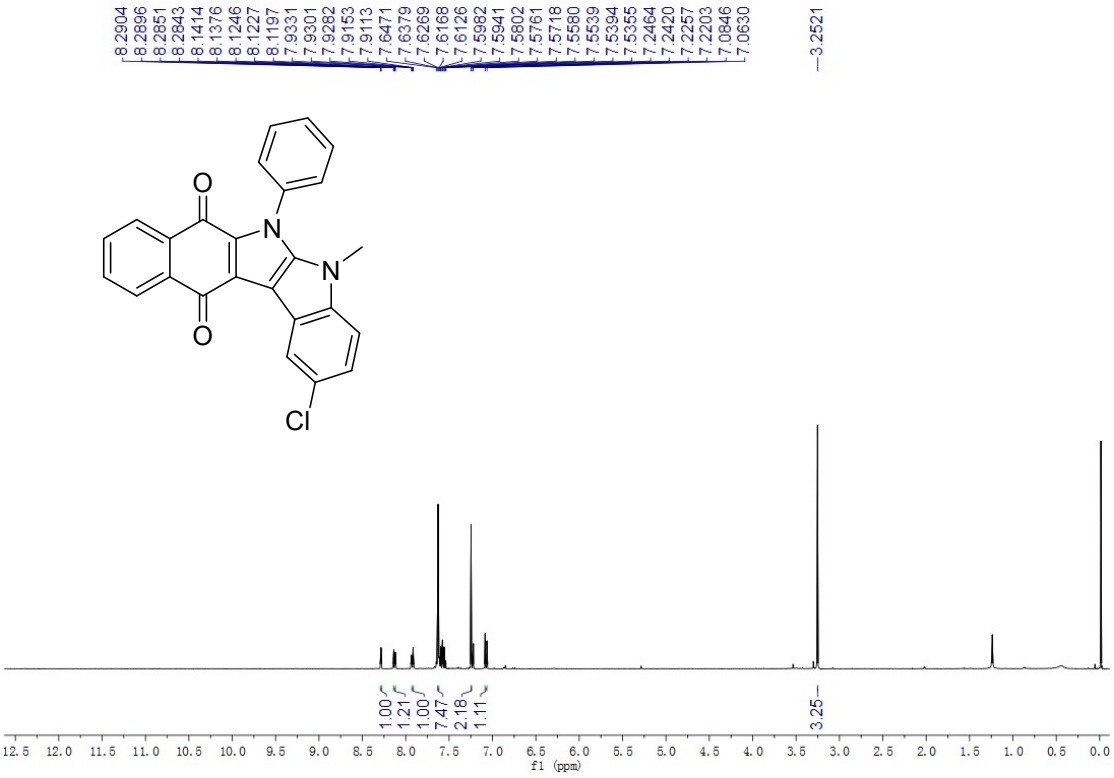
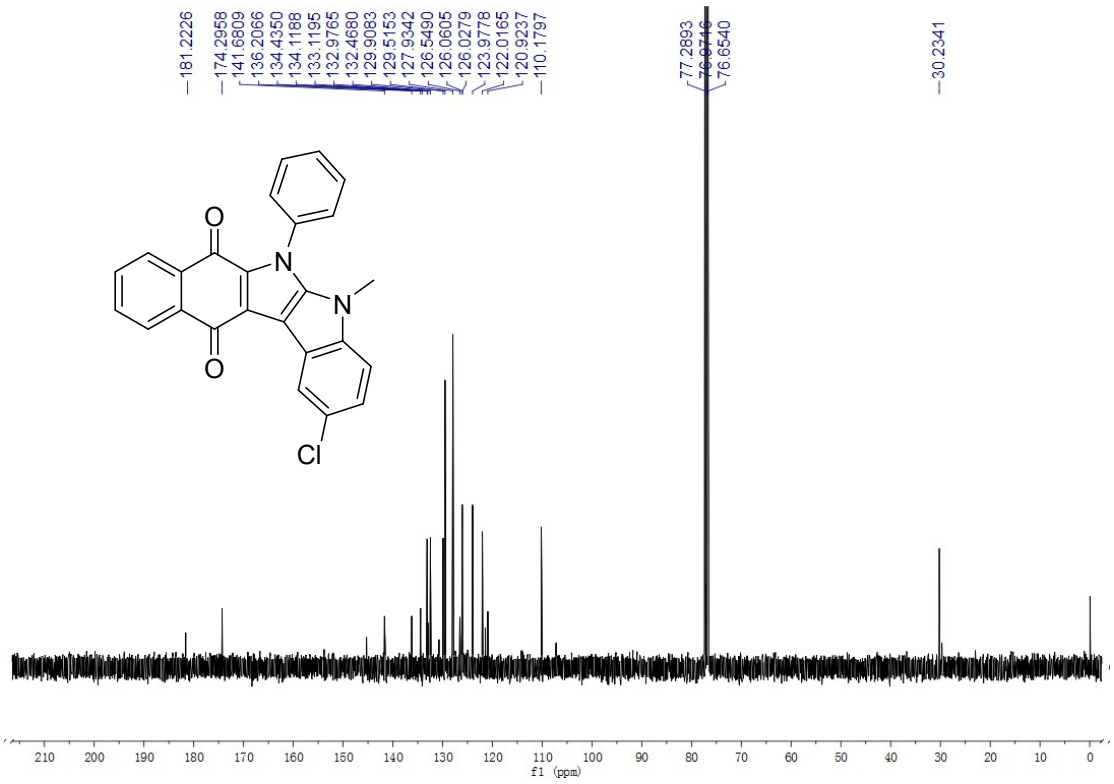
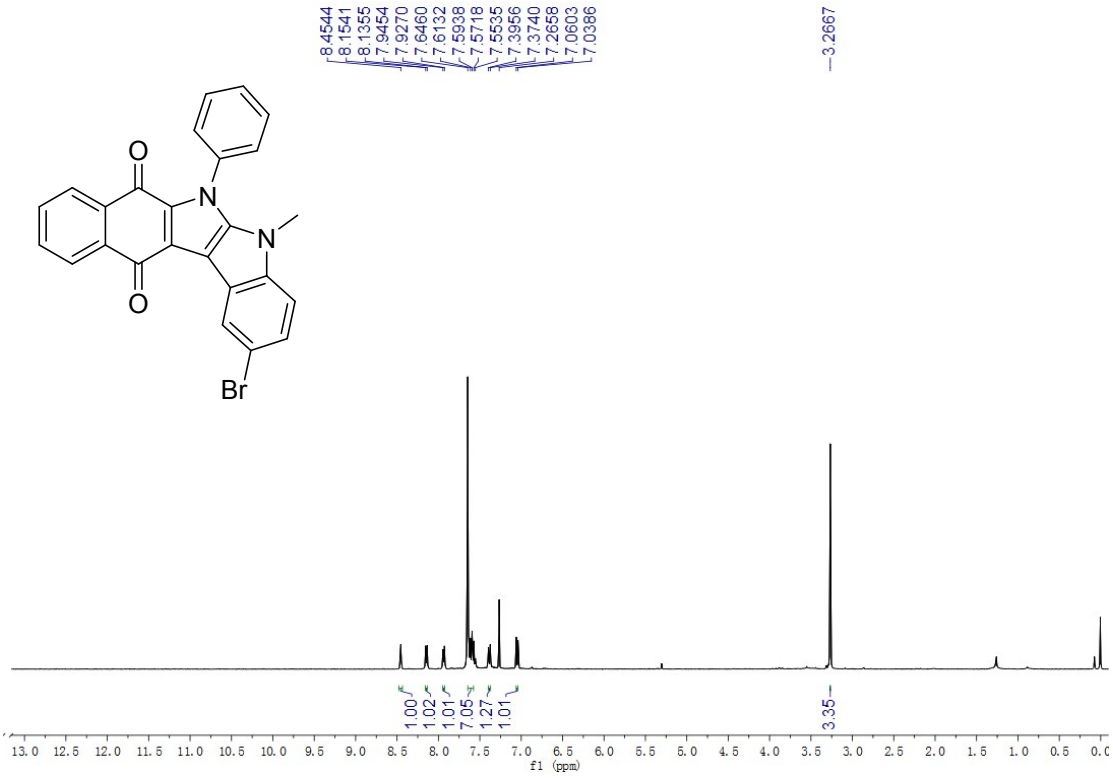
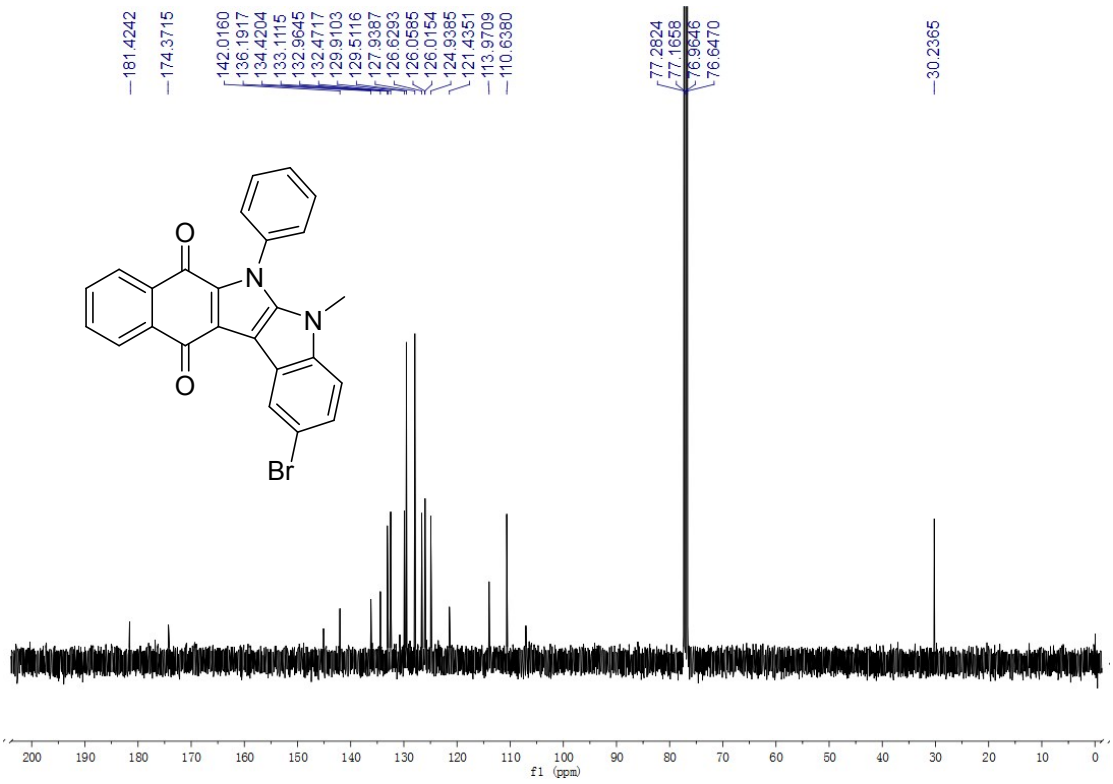


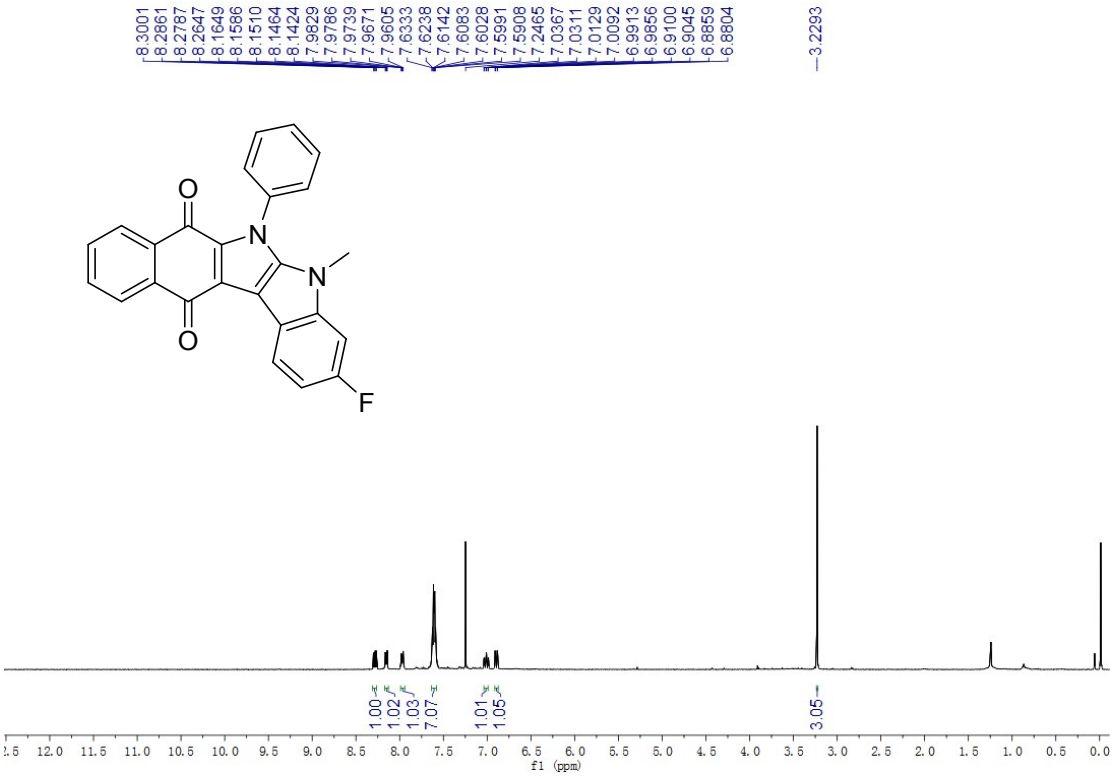


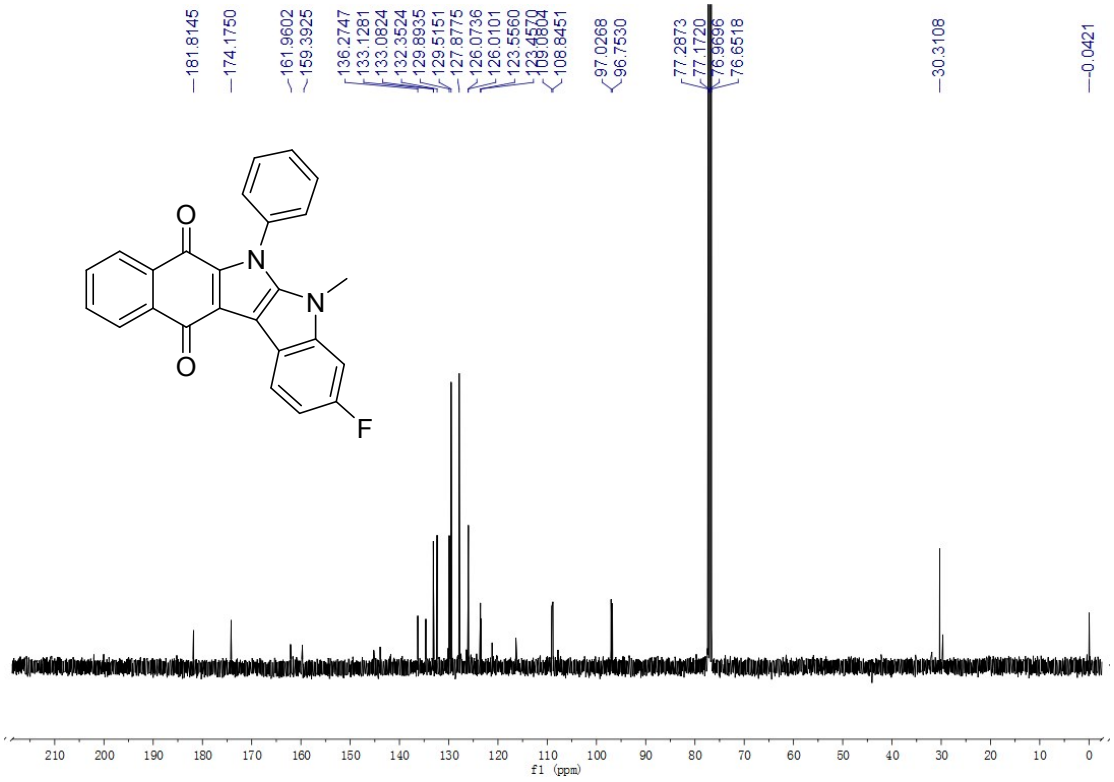
2-bromo-5-methyl-6-phenyl-5,6-dihydrobenzo[f]indolo[2,3-b]indole-7,12-dione (3ga)

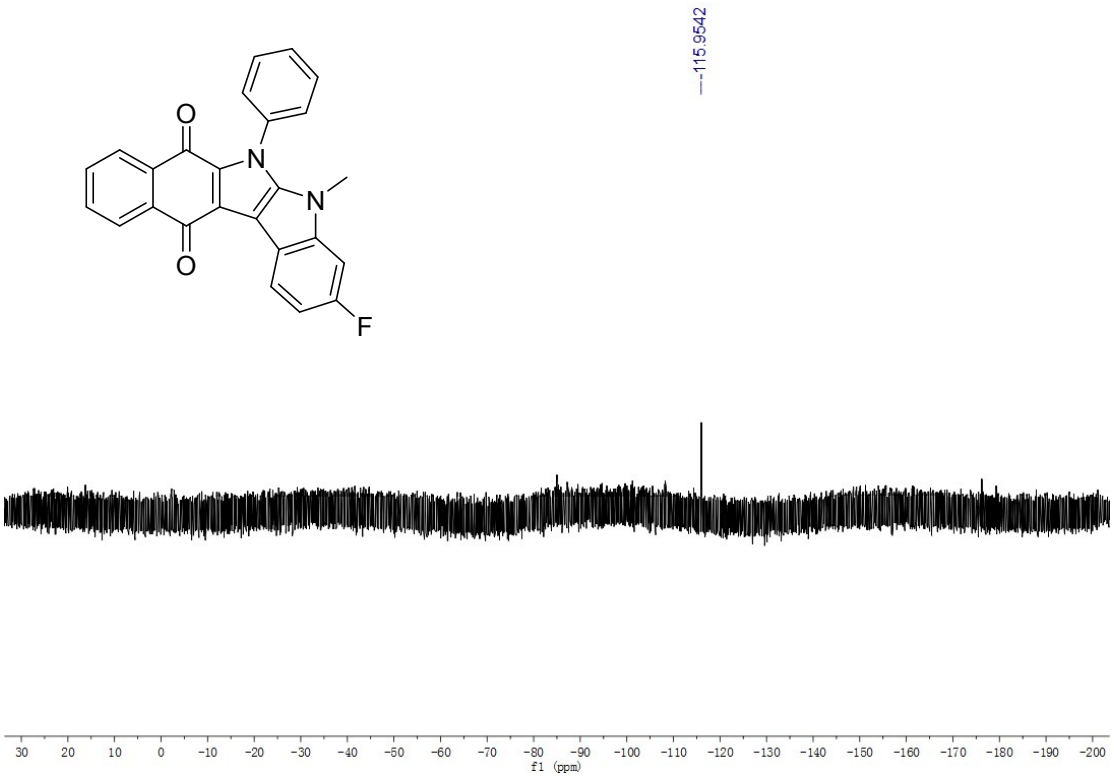




3-fluoro-5-methyl-6-phenyl-5,6-dihydrobenzo[f]indolo[2,3-b]indole-7,12-dione (3ha)



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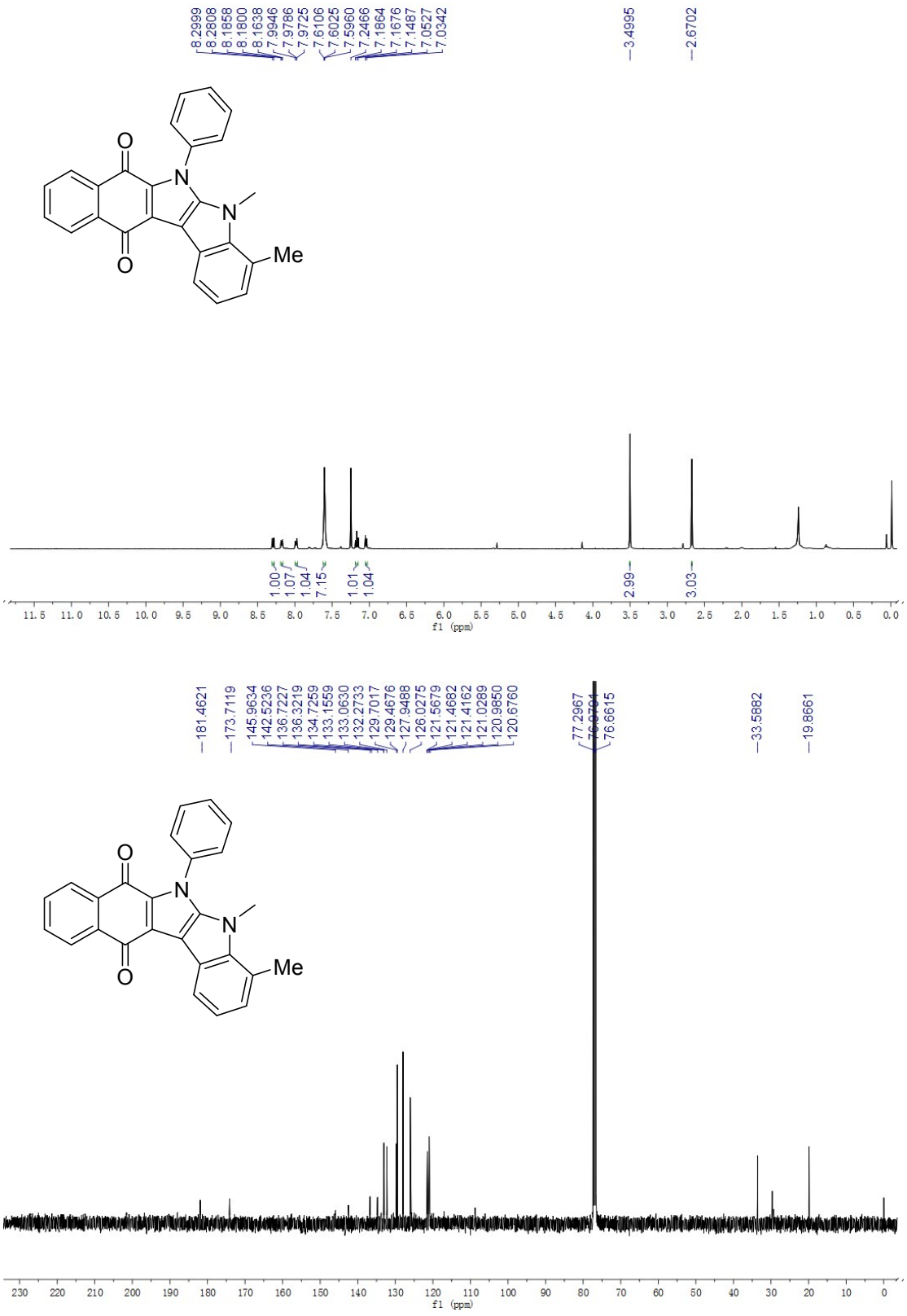
O
N
N
O
F
30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200
f1 (ppm)

4,5-dimethyl-6-phenyl-5,6-dihydrobenzo[f]indolo[2,3-b]indole-7,12-dione (3ia)



5-methyl-6-phenyl-5,6-dihydroindolo[2,3-b]naphtho[2,3-f]indole-7,14-dione (3ja)