Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

Copper-catalyzed switchable cyclization of alkyne-tethered *α*-bromocarbonyls: selective access to quinolin-2-ones and quinoline-2,4-diones

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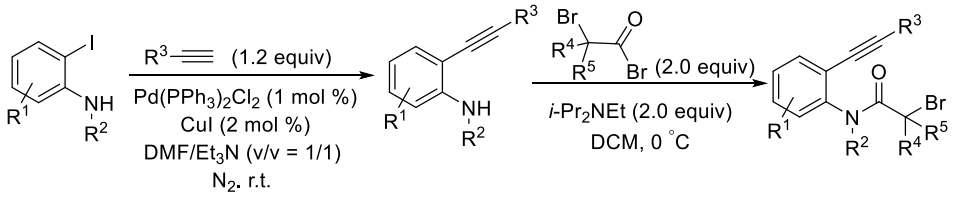
(A) General information

All chemicals including maleimides were obtained from commercial sources and were used as received unless otherwise noted. Alkyne-tethered α-bromocarbonyls was synthesized according to literature report.[1-2] The progress of the reactions was monitored by TLC with silica gel plates, and the visualization was carried out under UV light (254 nm). ^{1}H NMR, ^{13}C NMR, and ^{19}F NMR spectra were recorded on a Bruker 500 (500, 126, and 471 MHz) or a Bruker 400 (400, 101, and 376 MHz) advance spectrometer at room temperature in $CDCl_3$ (solvent signals, δ 7.26 and 77.0 ppm) using TMS as internal standard. HRMS spectra were recorded on an electrospray ionization quadrupole time-of-flight (ESI-Q-TOF) mass spectrometer.

(B) Typical experimental procedures

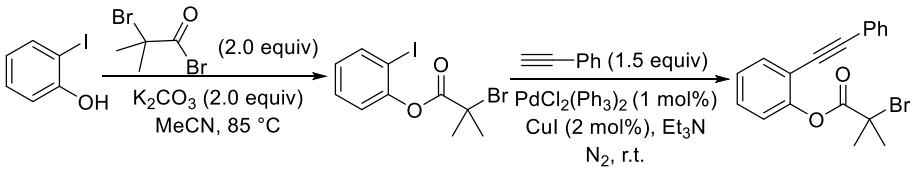
(1) General procedure for the synthesis of *N*-linked 1.[1]



$Pd(PPh_3)_2Cl_2$ (1 mol%), CuI (2 mol%), Et_3N (5.0 mL), and alkynes (1.2 equiv) were added to a solution of *o*-iodophenylamine derivatives (5.0 mmol) in DMF (5.0 mL). The mixture was stirred at the room temperature under nitrogen atmosphere and monitored by TLC. After the reaction went to completion, water (10.0 mL) was added to the reaction mixture, then extracted with ethyl acetate and washed with saturated NH_4Cl. The combined organic solution was washed with the saturated NaCl solution, dried over anhydrous $MgSO_4$, concentrated, used for next step without further purification.

A mixture of the above crude product and *N*-ethyl-*N*-isopropylpropan-2-amine (2.0 equiv) in DCM (10.0 mL) was cooled to 0 °C, and carbonyl bromides (2.0 equiv) were added dropwise. The mixture was allowed to warm up to room temperature over 30 min and was diluted with DCM. The organic phase was washed with water, saturated $NaHCO_3$, and brine. The resulting solution was dried over Na_2SO_4, concentrated and purified by column chromatography to give target compound **1** (hexane/ethyl acetate = 10:1).

(2) General procedure for the synthesis of *O*-linked 1.[2]

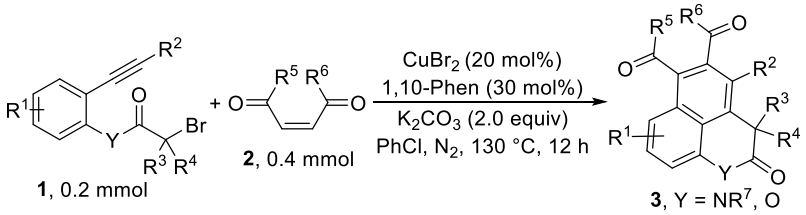


To a round bottom flask were added with 2-iodophenol (5.0 mmol), K_2CO_3 (2.0 equiv), MeCN (10.0 mL), and 2-bromo-2-methylpropanoyl bromide (2.0 equiv). The reaction mixture was stirred at 85 ^oC in an oil bath for 12 h. The solution was concentrated under reduced pressure, and the mixture was purified by flash column chromatography over silica gel to afford 2-iodophenyl 2-bromo-2-methylpropanoate (hexane/ethyl acetate = 10:1).

To a round bottom flask were added with 2-iodophenyl 2-bromo-2-methylpropanoate, $PdCl_2(PPh_3)_2$ (1 mol%), CuI (2 mol%), Et_3N (10.0 mL), and ethynylbenzene (1.5 equiv). The reaction mixture was stirred at room temperature under nitrogen atmosphere for 12 h. After the reaction was finished, the mixture was diluted with saturated NH_4Cl and extracted three times with EtOAc. The organic layer was dried over Na_2SO_4, filtration and evaporation of the solvent. The solution was

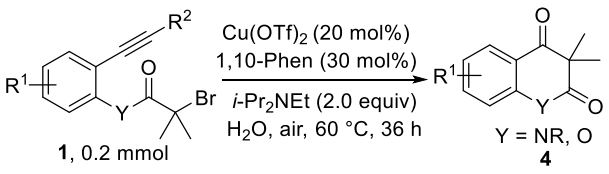
concentrated under reduced pressure, and the mixture was purified by flash column chromatography over silica gel to afford 2-(phenylethynyl)phenyl 2-bromo-2-methylpropanoate **1** (hexane/ethyl acetate = 8:1).

(3) General procedure for synthesis of compounds 3.



To a Schlenk tube were added alkyne-tethered *α*-bromocarbonyls **1** (0.2 mmol), maleimides **2** (0.4 mmol, 2.0 equiv), $CuBr_2$ (20 mol%), 1,10-Phen (30 mol%), and K_2CO_3 (2.0 equiv) in PhCl (1.0 mL). Then the tube was stirred at 130 °C sealed in nitrogen atmosphere for the indicated time until complete consumption of starting material as monitored by TLC and/or GC-MS analysis. After the reaction was finished, the mixture was extracted three times with EtOAc. The organic layer was dried over Na_2SO_4, filtration and evaporation of the solvent. The mixture was purified by flash column chromatography over silica gel (hexane/ethyl acetate = 5:1) to afford the desired products **3**.

(4) General procedure for synthesis of compounds 4.

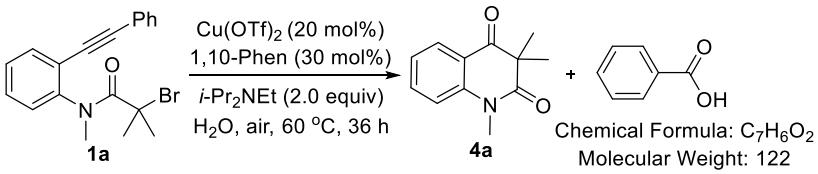


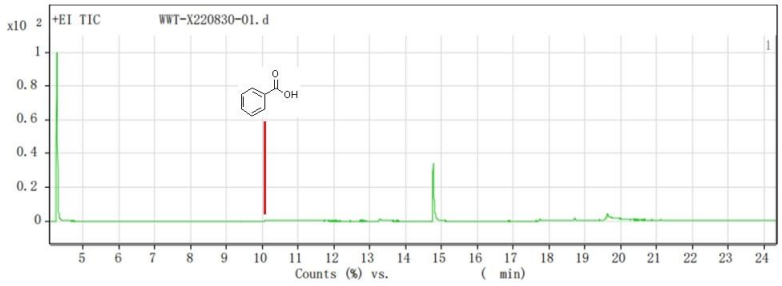
To a Schlenk tube were added alkyne-tethered *α*-bromocarbonyls **1** (0.2 mmol), $Cu(OTf)_2$ (20 mol%), 1,10-Phen (30 mol%), and *i*-Pr_2NEt (2.0 equiv) in H_2O (1.0 mL). Then the tube was stirred at 60 °C sealed in air for the indicated time until

complete consumption of starting material as monitored by TLC and/or GC-MS analysis. After the reaction was finished, the mixture was extracted three times with EtOAc. The organic layer was dried over Na_2SO_4, filtration and evaporation of the solvent. The mixture was purified by flash column chromatography over silica gel (hexane/ethyl acetate = 5:1) to afford the desired products **4**.

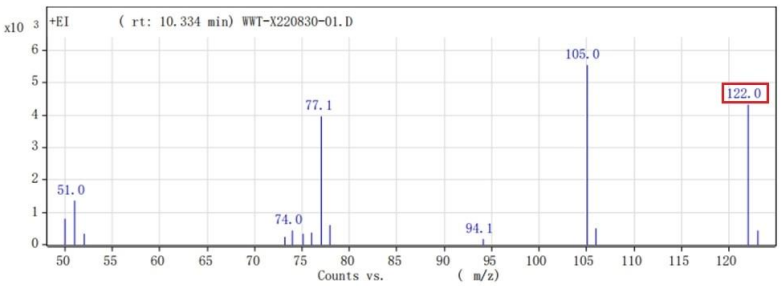
(C) GC-MS monitoring experiments

(1) Benzoic acid determined by GC-MS analysis.



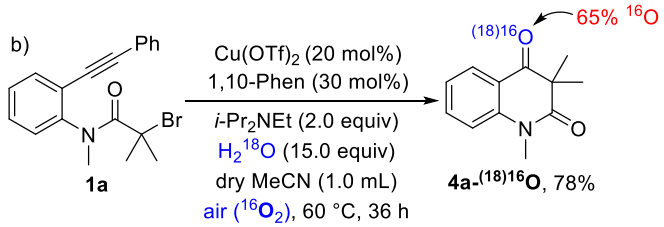


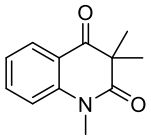
The reaction mixture was analyzed by Agilent 5977B GC/MSD during the whole process from 0 to 24 minutes.



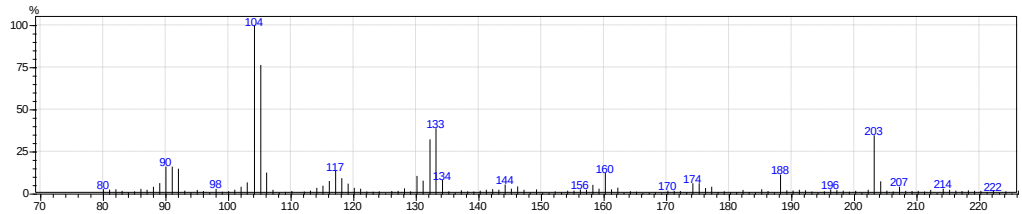
The reaction mixture was analyzed by Agilent 5977B GC/MSD at 10.334 minutes.

(2) The ^{18}O-labeled experiments determined by GC-MS analysis.



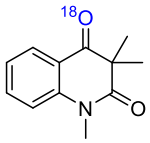


Chemical Formula: $C_{12}H_{13}NO_2$
Molecular Weight: 203

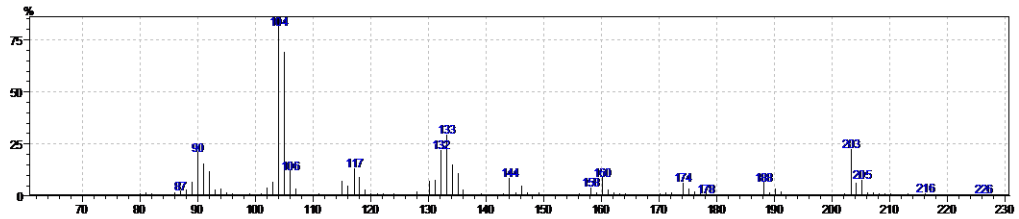


80.00	58	2.80	107.10	49	2.37	135.20	30	1.45
81.00	52	2.51	108.10	16	0.77	136.20	14	0.68
82.00	57	2.76	109.10	24	1.16	137.20	44	2.13
83.00	36	1.74	110.10	34	1.64	138.20	31	1.50
84.00	19	0.92	112.10	29	1.40	139.20	27	1.31
85.00	31	1.50	113.10	38	1.84	140.20	38	1.84
86.00	60	2.90	114.10	74	3.58	141.20	49	2.37
87.00	50	2.42	115.10	98	4.74	142.20	58	2.80
88.00	86	4.16	116.10	158	7.64	143.20	49	2.37
89.00	132	6.38	117.10	281	13.59	144.20	114	5.51
90.00	334	16.15	118.10	191	9.24	145.20	63	3.05
91.00	334	16.15	119.10	124	6.00	146.20	90	4.35
92.00	308	14.89	120.10	73	3.53	147.20	49	2.37
93.00	39	1.89	121.10	62	3.00	148.20	19	0.92
94.00	19	0.92	122.10	29	1.40	149.20	54	2.61
95.00	47	2.27	123.10	26	1.26	150.20	16	0.77
96.00	34	1.64	124.10	30	1.45	151.20	11	0.53
97.00	14	0.68	125.10	6	0.29	152.20	30	1.45
98.00	60	2.90	126.10	34	1.64	153.20	18	0.87
99.00	26	1.26	127.10	36	1.74	154.20	39	1.89
100.00	33	1.60	128.10	66	3.19	155.20	39	1.89
101.00	49	2.37	129.10	31	1.50	156.20	52	2.51
102.00	87	4.21	130.10	220	10.64	157.20	49	2.37
103.00	140	6.77	131.10	161	7.79	158.20	110	5.32
104.15	2068	100.00	132.20	668	32.30	159.20	63	3.05
105.15	1580	76.40	133.15	803	38.83	160.20	254	12.28
106.10	260	12.57	134.20	169	8.17	161.20	54	2.61

162.20	76	3.68	178.20	22	1.06	194.20	13	0.63
163.20	14	0.68	179.20	30	1.45	195.20	31	1.50
164.20	33	1.60	180.20	18	0.87	196.20	54	2.61
165.20	26	1.26	181.20	21	1.02	197.20	46	2.22
166.20	8	0.39	182.20	47	2.27	198.20	39	1.89
167.20	16	0.77	183.20	21	1.02	199.20	26	1.26
168.20	19	0.92	184.20	18	0.87	200.20	36	1.74
169.20	6	0.29	185.20	55	2.66	201.20	16	0.77
170.20	38	1.84	186.20	34	1.64	202.20	50	2.42
171.20	36	1.74	187.20	18	0.87	**203.15**	**717**	**34.67**
172.20	34	1.64	188.20	234	11.32	204.20	153	7.40
173.20	19	0.92	189.20	42	2.03	**205.20**	**38**	**1.84**
174.20	129	6.24	190.20	41	1.98	206.20	29	1.40
175.20	129	6.24	191.20	49	2.37	207.20	87	4.21
176.20	70	3.38	192.20	42	2.03			
177.20	86	4.16	193.20	27	1.31			

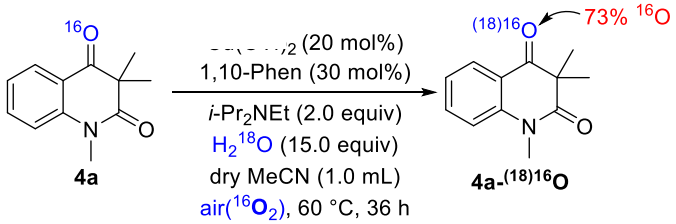


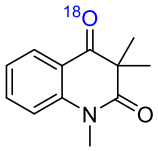
Chemical Formula: $C_{12}H_{13}N^{18}O_2$
Molecular Weight: 205



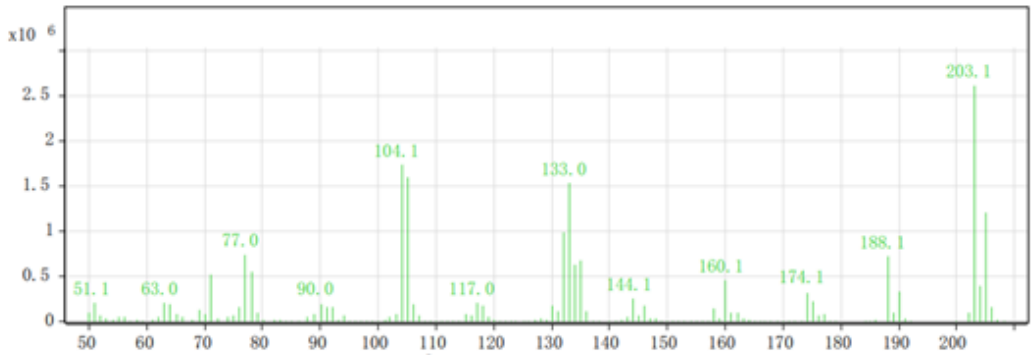
80.00	78	2.51	96.10	54	1.74	112.10	14	0.45
81.00	55	1.77	97.10	42	1.35	113.10	22	0.71
82.00	13	0.42	98.10	57	1.84	114.10	65	2.10
83.00	68	2.19	99.10	36	1.16	115.10	217	7.00
84.00	52	1.68	100.10	46	1.48	116.10	124	4.00
85.00	54	1.74	101.10	27	0.87	117.10	350	11.28
86.00	106	3.42	102.10	190	6.13	118.10	265	8.54
87.00	81	2.61	103.10	250	8.06	119.10	114	3.68
88.00	111	3.58	104.10	3102	100.00	120.10	14	0.45
89.00	263	8.48	105.10	2329	75.08	121.10	34	1.10
90.05	602	19.41	106.10	289	9.32	122.10	60	1.93
91.10	386	12.44	107.10	82	2.64	123.10	11	0.35
92.05	339	10.93	108.10	22	0.71	124.10	42	1.35
93.10	63	2.03	109.10	10	0.32	125.10	22	0.71
94.10	193	6.22	110.10	44	1.42	126.10	26	0.84
95.10	55	1.77	111.10	21	0.68	127.10	57	1.84

128.10	73	2.35	155.10	30	0.97	182.10	34	1.10
129.10	87	2.80	156.10	55	1.77	183.10	41	1.32
130.10	268	8.64	157.10	30	0.97	184.10	50	1.61
131.10	175	5.64	158.10	146	4.71	185.10	46	1.48
132.15	902	29.08	159.10	60	1.93	186.10	21	0.68
133.15	942	30.37	160.10	306	9.86	187.10	21	0.68
134.10	404	13.02	161.10	116	3.74	188.10	332	10.70
135.10	353	11.38	162.10	113	3.64	189.10	74	2.39
136.10	106	3.42	163.10	33	1.06	190.10	198	6.38
137.10	31	1.00	164.10	29	0.93	191.10	34	1.10
138.10	46	1.48	165.10	5	0.16	192.10	30	0.97
139.10	30	0.97	166.10	14	0.45	193.10	70	2.26
140.10	63	2.03	167.10	11	0.35	194.10	19	0.61
141.10	36	1.16	168.10	38	1.23	195.10	19	0.61
142.10	33	1.06	169.10	18	0.58	196.10	29	0.93
143.10	100	3.22	170.10	27	0.87	197.10	24	0.77
144.10	311	10.03	171.10	14	0.45	198.10	30	0.97
145.10	86	2.77	172.10	21	0.68	199.10	33	1.06
146.10	169	5.45	173.10	33	1.06	200.10	58	1.87
147.10	95	3.06	174.10	228	7.35	201.10	31	1.00
148.10	52	1.68	175.10	92	2.97	202.10	42	1.35
149.10	38	1.23	176.10	62	2.00	**203.20**	**721**	**23.24**
150.10	14	0.45	177.10	60	1.93	204.20	145	4.67
151.10	27	0.87	178.10	46	1.48	**205.15**	**431**	**13.89**
152.10	14	0.45	179.10	26	0.84	206.20	90	2.90
153.10	33	1.06	180.10	36	1.16	207.20	82	2.64
154.10	27	0.87	181.10	10	0.32			



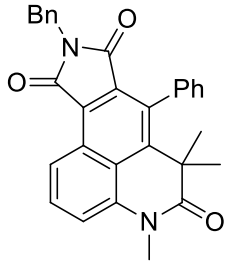


Chemical Formula: $C_{12}H_{13}NO_2$
Molecular Weight: 205.10



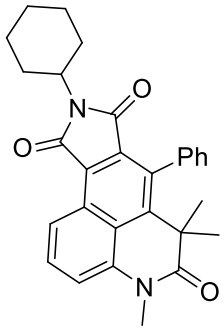
50	100190.98	3.83	92	155053.34	5.93	144.1	244455.75	9.34
51	198120.91	7.57	93	16069.07	0.61	145.1	65265.14	2.49
52	58675.89	2.24	94	58548.95	2.24	146.1	167321.91	6.39
53	33386.5	1.28	101.1	15411.32	0.59	147	39585.39	1.51
55	50724.87	1.94	102	51738.65	1.98	148	32476.92	1.24
56.1	53915.91	2.06	103	80869.54	3.09	158.1	135989.47	5.2
62	41142.84	1.57	104	1734626.62	66.29	159.1	35198.83	1.35
63	203127.92	7.76	105	1605298.88	61.35	160	448258.31	17.13
64	181644	6.94	106	181782.58	6.95	161.1	91464.99	3.5
65	85611.46	3.27	107	61863.84	2.36	162	95145.66	3.64
66.1	43926.67	1.68	115	86958.4	3.32	163	34636.37	1.32
69	120952.87	4.62	116	69589.55	2.66	164	16036.23	0.61
70	84415.38	3.23	117	208337.72	7.96	174.1	320585.34	12.25
71	522604.72	19.97	118	170662.77	6.52	175	227330.23	8.69
72.2	31218.86	1.19	119	42998.34	1.64	176.1	60715.17	2.32
74	53178.9	2.03	120	20185.79	0.77	177	81959.22	3.13
75	69755.23	2.67	128	30066.9	1.15	188	717316.25	27.41
76	153189.59	5.85	129.1	17711.96	0.68	189.1	91958.56	3.51
77	729908.44	27.89	130	177674.78	6.79	190.1	324259.94	12.39
78	555886.75	21.24	131.1	105693.2	4.04	191	39837.88	1.52
79	95996.92	3.67	132	992259.44	37.92	202.1	96255.05	3.68
80.1	893.11	0.57	133	1537641.12	58.76	**203.1**	**2616700.5**	**100**
82	14372.08	0.55	134	630867.25	24.11	204.1	399364.94	15.26
87.6	50694.01	1.94	135	667852.56	25.52	**205.1**	**1198819.88**	**45.81**
89	79632.59	3.04	136	109663.55	4.19	206.1	156766.58	5.99
90	196312.03	7.5	142.1	18642.74	0.71			
91	154541.97	5.91	143.1	47780.65	1.83			

(D) Analytical data

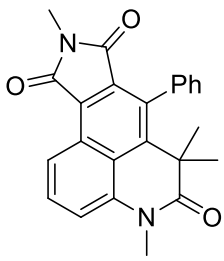


9-Benzyl-4,6,6-trimethyl-7-phenylisoindolo[6,5,4-*de*]quinoline-5,8,10(4*H*,6*H*,9*H*)-trione (3a), The product was purified by silica

gel column chromatography with petroleum ether/ethyl acetate (5:1, v/v). Light yellow solid (0.0810 g, 88% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.80 (d, J = 9.2 Hz, 1H), 7.69 (t, J = 8.0 Hz, 1H), 7.51-7.44 (m, 3H), 7.39-7.36 (m, 2H), 7.30-7.23 (m, 5H), 7.17-7.14 (m, 1H), 4.72 (s, 2H), 3.55 (s, 3H), 1.50 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 173.6, 168.5, 167.1, 145.1, 137.5, 137.4, 136.5, 134.8, 130.8, 130.3, 129.8, 128.7, 128.6, 128.2, 128.1, 127.7, 127.6, 125.2, 122.9, 119.3, 111.5, 46.7, 41.5, 30.6, 29.7; HRMS *m/z* (ESI) calcd for $C_{30}H_{25}N_2O_3$ ([M+H]$^+$) 461.1860, found 461.1866.

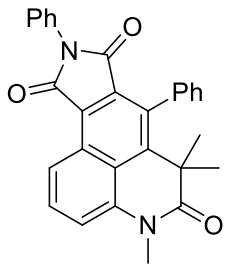


9-Cyclohexyl-4,6,6-trimethyl-7-phenylisoindolo[6,5,4-*de*]quinoline-5,8,10(4*H*,6*H*,9*H*)-trione (3b). The product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (5:1, v/v). Light yellow solid (0.0787 g, 87% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.83 (d, J = 8.5 Hz, 1H), 7.70 (t, J = 8.0 Hz, 1H), 7.51-7.45 (m, 3H), 7.32-7.30 (m, 2H), 7.17 (d, J = 7.5 Hz, 1H), 4.03-3.97 (m, 1H), 3.56 (s, 3H), 2.18-2.10 (m, 2H), 1.82-1.66 (m, 4H), 1.51 (s, 6H), 1.29-1.20 (m, 4H); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 173.7, 168.9, 167.6, 144.7, 137.5 (2), 134.6, 130.5, 130.3, 129.7, 128.1, 128.0, 127.5, 125.1, 122.8, 119.2, 111.4, 50.8, 46.7, 30.6, 29.9, 29.7, 26.1, 25.1; HRMS *m/z* (ESI) calcd for $C_{29}H_{29}N_2O_3$ ([M+H]$^+$) 453.2173, found 453.2167.

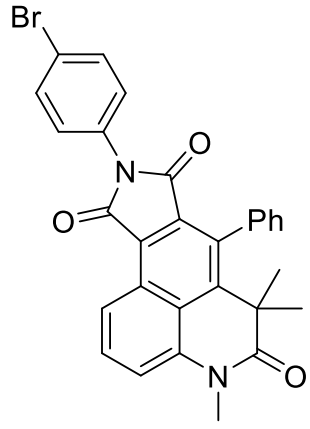


4,6,6,9-Tetramethyl-7-phenylisoindolo[6,5,4-*de*]quinoline-5,8,10(4*H*,6*H*,9*H*)-trione (3c). The product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (5:1, v/v). Light yellow solid (0.0522 g, 68% yield); ^{1}H NMR

(500 MHz, $CDCl_3$) δ: 8.80 (d, J = 8.5 Hz, 1H), 7.71 (t, J = 8.0 Hz, 1H), 7.53-7.45 (m, 3H), 7.31-7.29 (m, 2H), 7.17 (d, J = 7.5 Hz, 1H), 3.56 (s, 3H), 3.06 (s, 3H), 1.52 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 173.6, 168.8, 167.8, 144.9, 137.6, 137.5, 134.7, 130.9, 130.3, 129.8, 128.1(2), 127.6, 125.3, 122.9, 119.2, 111.4, 46.7, 30.6, 29.7, 23.8; HRMS *m/z* (ESI) calcd for $C_{24}H_{21}N_2O_3$ ($[M+H]^+$) 385.1547, found 385.1543.

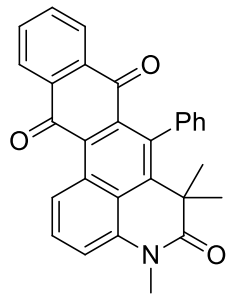


4,6,6-Trimethyl-7,9-diphenylisoindolo[6,5,4-*de*]quinoline-5,8,10(4*H*,6*H*,9*H*)-trione (3d). The product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (5:1, v/v). Light yellow solid (0.0687 g, 77% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.88 (d, J = 8.5 Hz, 1H), 7.75 (t, J = 8.0 Hz, 1H), 7.48-7.43 (m, 3H), 7.41-7.39 (m, 2H), 7.36-7.31 (m, 5H), 7.21 (d, J = 7.0 Hz, 1H), 3.57 (s, 3H), 1.54 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 173.6, 167.7, 166.5, 145.6, 137.6, 137.3, 135.0, 131.5, 130.4, 130.3, 130.1, 128.9, 128.3, 128.2, 127.9, 127.6, 126.9, 124.9, 123.1, 119.4, 111.7, 46.8, 30.7, 29.7; HRMS *m/z* (ESI) calcd for $C_{29}H_{23}N_2O_3$ ($[M+H]^+$) 447.1703, found 447.1709.

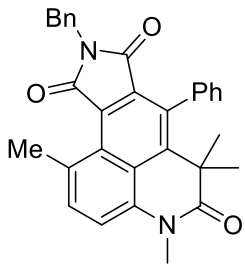


9-(4-Bromophenyl)-4,6,6-trimethyl-7-phenylisoindolo[6,5,4-*de*]quinoline-5,8,10(4*H*,6*H*,9*H*)-trione (3e). The product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (5:1, v/v). Light yellow solid (0.0702 g, 67% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.86 (d, J = 8.0 Hz, 1H), 7.75 (t, J = 8.0 Hz, 1H), 7.54-7.52 (m, 2H), 7.49-7.44 (m, 3H), 7.33-7.31 (m, 2H), 7.28-7.26 (m, 2H), 7.22 (d,

J = 7.5 Hz, 1H), 3.57 (s, 3H), 1.54 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 173.6, 167.3, 166.1, 145.9, 137.7, 137.2, 135.0, 132.0, 130.6, 130.3(2), 130.2, 128.3, 128.2(2), 127.7, 124.7, 123.1, 121.5, 119.3, 111.8, 46.9, 30.7, 29.7; HRMS *m/z* (ESI) calcd for $C_{29}H_{22}BrN_2O_3$ ($[M+H]^+$) 525.0808, found 525.0816.

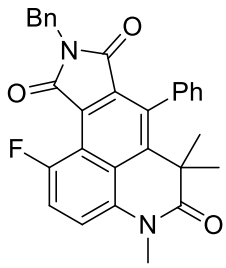


4,6,6-Trimethyl-7-phenyl-4*H*-anthra[3,2,1-*de*]quinoline-5,8,13(6*H*)-trione (3f). The product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (5:1, v/v). Brown solid (0.0742 g, 86% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.17 (d, *J* = 8.8 Hz,1H), 8.16 (d, *J* = 7.6 Hz, 1H), 7.80 (d, *J* = 7.6 Hz, 1H), 7.75-7.70 (m, 2H), 7.66-7.62 (m, 1H), 7.46-7.38 (m, 3H), 7.31-7.29 (m, 2H), 7.23 (d, *J* = 7.6 Hz, 1H), 3.56 (s, 3H), 1.31 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 186.7, 185.7, 173.5, 144.6, 139.9, 137.1, 137.0, 136.3, 134.3(2), 133.5, 133.4, 131.3, 130.4, 130.2, 129.4, 127.5, 126.8, 126.2(2), 123.1, 122.6, 112.1, 47.0, 31.0, 29.4; HRMS *m/z* (ESI) calcd for $C_{29}H_{22}NO_3$ ($[M+H]^+$) 432.1594, found 432.1586.

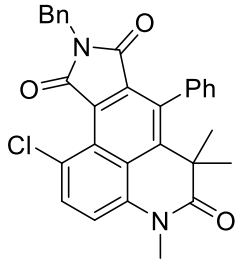


9-Benzyl-1,4,6,6-tetramethyl-7-phenylisoindolo[6,5,4-*de*]quinoline-5,8,10(4*H*,6*H*,9*H*)-trione (3g). The product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (5:1, v/v). Light yellow solid (0.0825 g, 87% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.52-7.43 (m, 4H), 7.37-7.34 (m, 2H), 7.30-7.23 (m, 5H), 7.10 (d, *J* = 8.0 Hz, 1H), 4.73 (s, 2H), 3.53 (s, 3H), 2.97 (s, 3H), 1.43 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 173.0, 167.4, 166.9, 145.7, 137.6, 136.6, 135.7, 134.4, 132.3, 132.2, 130.4, 130.0, 128.6 (2), 128.5,

128.0, 127.6, 127.4, 127.1, 124.9, 112.0, 46.6, 41.6, 31.0, 29.6, 25.0; HRMS *m/z* (ESI) calcd for $C_{31}H_{27}N_2O_3$ ($[M+H]^+$) 475.2016, found 475.2010.

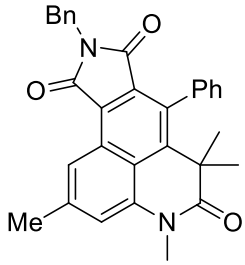


9-Benzyl-1-fluoro-4,6,6-trimethyl-7-phenylisoindolo[6,5,4-*de*]quinoline-5,8,10(4*H*,6*H*,9*H*)-trione (3h). The product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (5:1, v/v). Light yellow solid (0.0717 g, 75% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.53 (t, J = 7.2 Hz, 1H), 7.49-7.43 (m, 3H), 7.40-7.37 (m, 2H), 7.29-7.24 (m, 5H), 7.15-7.12 (m, 1H), 4.75 (s, 2H), 3.54 (s, 3H), 1.46 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 173.0, 166.4, 165.2, 153.5 (d, J_{C-F} = 258.5 Hz), 145.5, 137.1, 136.5, 136.1, 134.1, 132.8, 130.3, 128.9, 128.6, 128.3, 127.8, 127.6, 125.3 (d, J_{C-F} = 8.4 Hz), 124.2 (d, J_{C-F} = 4.8 Hz), 118.1 (d, J_{C-F} = 22.1 Hz), 114.3 (d, J_{C-F} = 22.7 Hz), 111.9 (d, J_{C-F} = 7.4 Hz), 46.5, 41.9, 31.1, 29.7; ^{19}F NMR (376 MHz, $CDCl_3$) δ: -109.5; HRMS *m/z* (ESI) calcd for $C_{30}H_{24}FN_2O_3$ ($[M+H]^+$) 479.1765, found 479.1757.

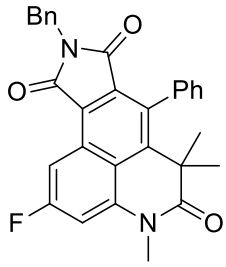


9-Benzyl-1-chloro-4,6,6-trimethyl-7-phenylisoindolo[6,5,4-*de*]quinoline-5,8,10(4*H*,6*H*,9*H*)-trione (3i). The product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (5:1, v/v). Light yellow solid (0.0743 g, 75% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.81 (d, J = 8.0 Hz, 1H), 7.70 (t, J = 8.0 Hz, 1H), 7.51-7.45 (m, 3H), 7.39-7.37 (m, 2H), 7.30-7.27 (m, 4H), 7.18-7.16 (m, 1H), 4.73 (s, 2H), 3.55 (s, 3H), 1.50 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 173.6, 168.5, 167.1, 145.0, 137.5, 137.3, 136.5, 134.7, 130.7, 130.3, 129.8, 128.7, 128.6, 128.1 (2),

127.7, 127.5, 125.1, 122.8, 119.2, 111.5, 46.7, 41.4, 30.6, 29.6; HRMS *m/z* (ESI) calcd for $C_{30}H_{24}ClN_2O_3$ ($[M+H]^+$) 495.1470, found 495.1478.

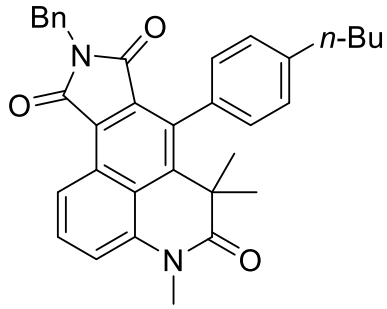


9-Benzyl-2,4,6,6-tetramethyl-7-phenylisoindolo[6,5,4-*de*]quinoline-5,8,10(4*H*,6*H*,9*H*)-trione (3j). The product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (5:1, v/v). Light yellow solid (0.0835 g, 88% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.59 (s, 1H), 7.50-7.44 (m, 3H), 7.39-7.36 (m, 2H), 7.30-7.23 (m, 5H), 6.99 (s, 1H), 4.71 (s, 2H), 3.54 (s, 3H), 2.60 (s, 3H), 1.49 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 173.9, 168.9, 167.3, 145.0, 140.5, 137.5, 137.3, 136.6, 133.9, 130.9, 130.5, 128.8, 128.7, 128.5, 128.1, 127.8, 127.6, 124.3, 121.4, 118.2, 113.8, 46.7, 41.5, 30.6, 29.7, 22.4; HRMS *m/z* (ESI) calcd for $C_{31}H_{27}N_2O_3$ ($[M+H]^+$) 475.2016, found 475.2012.

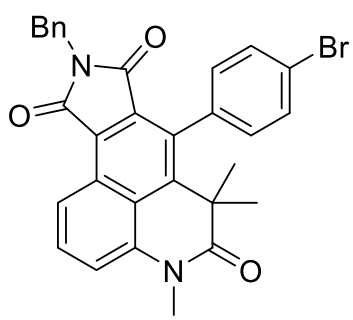


9-Benzyl-2-fluoro-4,6,6-trimethyl-7-phenylisoindolo[6,5,4-*de*]quinoline-5,8,10(4*H*,6*H*,9*H*)-trione (3k). The product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (5:1, v/v). Light yellow solid (0.0679 g, 71% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.42-8.39 (m, 1H), 7.52-7.45 (m, 3H), 7.39-7.36 (m, 2H), 7.29-7.23 (m, 5H), 6.92-6.89 (m, 1H), 4.71 (s, 2H), 3.52 (s, 3H), 1.50 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 173.8, 168.4, 166.9, 162.9 (d, $J_{C\text{-}F}$ = 250.8 Hz), 145.6, 140.1 (d, $J_{C\text{-}F}$ = 11.7 Hz), 137.1, 136.4, 134.2, 131.7, 130.4, 129.3 (d, $J_{C\text{-}F}$ = 12.8 Hz), 128.8, 128.7, 128.3, 127.8, 127.7, 124.6 (d, $J_{C\text{-}F}$ = 6.9 Hz), 120.2, 102.4 (d, $J_{C\text{-}F}$ = 7.7

Hz), 102.2 (d, $J_{C\text{-}F}$ = 16.0 Hz), 46.8, 41.6, 30.8, 29.8; ^{19}F NMR (376 MHz, $CDCl_3$) δ: -106.2; HRMS *m/z* (ESI) calcd for $C_{30}H_{24}FN_2O_3$ ($[M+H]^+$) 479.1765, found 479.1761.

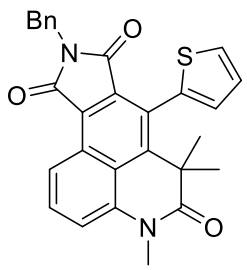


9-Benzyl-7-(4-butylphenyl)-4,6,6-trimethylisoindolo[6,5,4-*de*]quinoline-5,8,10(4*H*,6*H*,9*H*)-trione (3l). The product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (5:1, v/v). Light yellow solid (0.0857 g, 83% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.80 (d, J = 8.5 Hz, 1H), 7.68 (t, J = 8.0 Hz, 1H), 7.38-7.36 (m, 2H), 7.29-7.25 (m, 5H), 7.18-7.14 (m, 3H), 4.74 (s, 2H), 3.54 (s, 3H), 2.75 (t, J = 8.0 Hz, 2H), 1.75-1.69 (m, 2H), 1.49 (s, 6H), 1.45-1.41 (m, 2H), 0.98 (t, J = 7.0 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 173.7, 168.6, 167.2, 145.3, 142.8, 137.5, 136.5, 135.1, 134.4, 130.9, 130.1, 129.7, 128.6, 128.5, 128.1, 127.6, 127.5, 125.1, 122.9, 119.2, 111.4, 46.7, 41.4, 35.5, 33.4, 30.6, 29.6, 22.5, 14.0; HRMS *m/z* (ESI) calcd for $C_{34}H_{33}N_2O_3$ ($[M+H]^+$) 517.2486, found 517.2494.

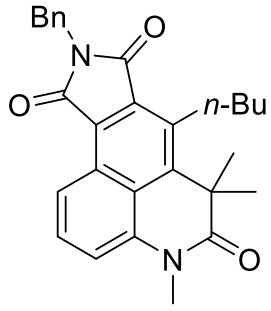


9-Benzyl-7-(4-bromophenyl)-4,6,6-trimethylisoindolo[6,5,4-*de*]quinoline-5,8,10(4*H*,6*H*,9*H*)-trione (3m). The product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (5:1, v/v). Light yellow solid (0.0830 g, 77% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.80 (d, J = 9.5 Hz, 1H), 7.71 (t, J = 8.0 Hz, 1H), 7.60-7.58 (m, 2H), 7.38-7.36 (m, 2H), 7.30-7.27 (m, 2H), 7.25-7.22 (m, 1H), 7.18-7.16 (m, 3H), 4.73 (s, 2H), 3.55 (s, 3H), 1.49 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 173.3, 168.3,

167.1, 145.2, 137.5, 136.3 (2), 133.2, 131.9, 130.8, 130.5, 130.0, 128.6 (2), 128.2, 127.7, 125.2, 122.8, 122.4, 119.2, 111.6, 46.6, 41.4, 30.6, 29.8; HRMS *m/z* (ESI) calcd for $C_{30}H_{24}BrN_2O_3$ ($[M+H]^+$) 539.0965, found 539.0969.

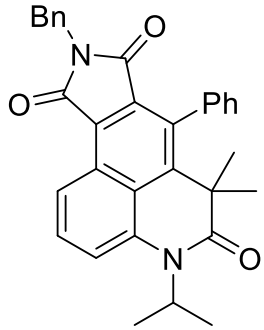


(B) 9-Benzyl-4,6,6-trimethyl-7-(thiophen-2-yl)isoindolo[6,5,4-*de*]quinoline-5,8,10(4*H*,6*H*,9*H*)-trione (3n). The product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (5:1, v/v). Light yellow solid (0.0561 g, 60% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.80 (d, *J* = 7.2 Hz, 1H), 7.71 (t, *J* = 8.0 Hz, 1H), 7.56-7.55 (m, 1H), 7.41-7.38 (m, 2H), 7.31-7.27 (m, 2H), 7.24-7.22 (m, 1H), 7.18-7.16 (m, 2H), 7.03-7.02 (m, 1H), 4.76 (s, 2H), 3.55 (s, 3H), 1.64 (s, 3H), 1.62 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 173.6, 168.4, 166.7, 147.9, 137.6, 137.2, 136.5, 131.8, 130.4, 129.8, 128.7, 128.6, 128.5, 127.8, 126.8, 126.7, 126.5, 125.2, 122.8, 119.3, 111.6, 46.9, 41.5, 30.6, 30.1, 28.9; HRMS *m/z* (ESI) calcd for $C_{28}H_{23}N_2O_3S$ ($[M+H]^+$) 467.1424, found 467.1430.

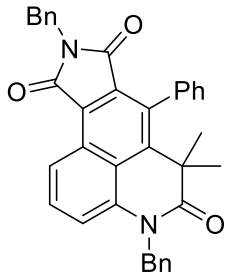


9-Benzyl-7-butyl-4,6,6-trimethylisoindolo[6,5,4-*de*]quinoline-5,8,10(4*H*,6*H*,9*H*)-trione (3o). The product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (5:1, v/v). Light yellow solid (0.0600 g, 68% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.72 (d, *J* = 8.5 Hz, 1H), 7.58 (t, *J* = 8.0 Hz, 1H), 7.46 (d, *J* = 7.5 Hz, 2H), 7.33 (t, *J* = 7.5 Hz, 2H), 7.28-7.26 (m, 1H), 7.06 (d, *J* = 7.5 Hz, 1H), 4.88 (s, 2H), 3.53 (s, 3H), 1.92 (s, 6H), 1.63-1.58 (m, 2H), 1.45-1.38 (m, 2H), 1.34-1.28 (m, 2H), 1.02 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (126 MHz,

$CDCl_3$) δ: 174.5, 168.7, 168.5, 144.7, 137.5, 136.8, 136.6, 130.7, 129.0, 128.7, 128.5, 127.7, 127.3, 126.0, 122.7, 119.2, 110.9, 45.1, 41.5, 34.9, 30.3, 30.2, 24.4, 23.5, 13.8; HRMS *m/z* (ESI) calcd for $C_{28}H_{29}N_2O_3$ ($[M+H]^+$) 441.2173, found 441.2179.

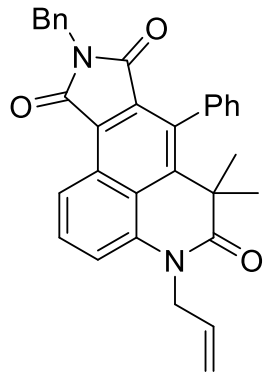


9-Benzyl-4-isopropyl-6,6-dimethyl-7-phenylisoindolo[6,5,4-*de*]quinoline-5,8,10(4*H*,6*H*,9*H*)-trione (3p). The product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (5:1, v/v). Light yellow solid (0.0840 g, 86% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.77 (d, *J* = 8.4 Hz, 1H), 7.66 (t, *J* = 8.0 Hz, 1H), 7.50-7.44 (m, 3H), 7.38-7.35 (m, 2H), 7.33-7.24 (m, 6H), 4.90-4.85 (m, 1H), 4.71 (s, 2H), 1.60 (s, 3H), 1.59 (s, 3H), 1.43 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 173.9, 168.7, 167.3, 145.3, 137.6, 137.3, 136.6, 134.4, 130.6, 130.3, 129.7, 128.7(2), 128.4, 128.2, 127.8, 127.6, 125.2, 124.1, 119.0, 111.9, 49.0, 47.4, 41.5, 29.4, 19.7; HRMS *m/z* (ESI) calcd for $C_{32}H_{29}N_2O_3$ ($[M+H]^+$) 489.2173, found 489.2167.

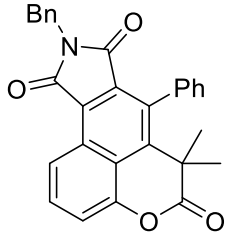


4,9-Dibenzyl-6,6-dimethyl-7-phenylisoindolo[6,5,4-*de*]quinoline-5,8,10(4*H*,6*H*,9*H*)-trione (3q). The product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (5:1, v/v). Light yellow solid (0.0761 g, 71% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.76 (d, *J* = 8.0 Hz, 1H), 7.56-7.46 (m, 4H), 7.38 (t, *J* = 4.0 Hz, 2H), 7.35-7.31 (m, 4H), 7.29-7.27 (m, 3H), 7.25-7.21 (m, 3H), 7.08 (d, *J* = 7.5 Hz, 1H), 5.37 (s, 2H), 4.72 (s, 2H), 1.57 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 173.8, 168.5, 167.1, 144.8, 137.4, 136.6, 136.5, 136.2, 134.7, 130.8, 130.2, 129.8,

129.0, 128.7, 128.6, 128.2(2), 127.7, 127.6, 127.4, 126.2, 125.3, 123.2, 119.5, 112.7, 47.1, 46.9, 41.5, 29.8; HRMS *m/z* (ESI) calcd for $C_{36}H_{29}N_2O_3$ ($[M+H]^+$) 537.2173, found 537.2179.

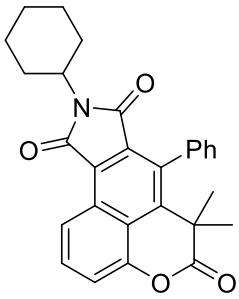


4-Allyl-9-benzyl-6,6-dimethyl-7-phenylisoindolo[6,5,4-*de*]quinoline-5,8,10(4*H*,6*H*,9*H*)-trione (3r). The product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (5:1, v/v). Light yellow solid (0.0710 g, 73% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.80 (d, J = 8.0 Hz, 1H), 7.66 (t, J = 8.0 Hz, 1H), 7.52-7.45 (m, 3H), 7.38-7.37 (m, 2H), 7.30-7.23 (m, 5H), 7.15 (d, J = 7.5 Hz, 1H), 5.98-5.91 (m, 1H), 5.27-5.22 (m, 2H), 4.77-4.76 (m, 2H), 4.73 (s, 2H), 1.49 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 173.2, 168.5, 167.1, 144.8, 137.4, 136.5 (2), 134.7, 131.5, 130.7, 130.2, 129.8, 128.7, 128.6, 128.2, 128.1, 127.7, 127.6, 125.3, 123.1, 119.4, 116.8, 112.4, 46.8, 45.7, 41.5, 29.7; HRMS *m/z* (ESI) calcd for $C_{32}H_{27}N_2O_3$ ($[M+H]^+$) 487.2016, found 487.2012.

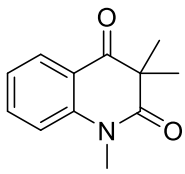


9-Benzyl-6,6-dimethyl-7-phenyl-5*H*-chromeno[5,4-*ef*]isoindole-5,8,10(6*H*,9*H*)-trione (3t). The product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (5:1, v/v). Light yellow solid (0.0689 g, 77% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.85 (d, J = 8.4 Hz, 1H), 7.74 (t, J = 8.0 Hz, 1H), 7.54-7.47 (m, 3H), 7.37 (t, J = 8.0 Hz, 3H), 7.30-7.26 (m, 5H), 4.74 (s, 2H), 1.53 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 171.5, 168.2, 167.0, 148.1, 141.7, 136.4 (2), 134.6, 131.1, 130.4,

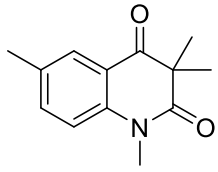
129.9, 128.8, 128.7, 128.6, 127.9 (2), 127.8, 126.2, 121.2, 120.9, 114.5, 46.1, 41.6, 29.1; HRMS *m/z* (ESI) calcd for $C_{29}H_{22}NO_4$ ([M+H]$^+$) 448.1543, found 448.1549.



9-Cyclohexyl-6,6-dimethyl-7-phenyl-5*H*-chromeno[5,4-*ef*]isoindole-5,8,10(6*H*,9*H*)-trione (3u). The product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (5:1, v/v). Light yellow solid (0.0729 g, 83% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.87 (d, J = 9.2 Hz, 1H), 7.75 (t, J = 8.0 Hz, 1H), 7.54-7.48 (m, 3H), 7.37-7.35 (m, 1H), 7.32-7.29 (m, 2H), 4.05-3.97 (m, 1H), 2.18-2.08 (m, 2H), 1.84-1.79 (m, 2H), 1.69-1.62 (m, 3H), 1.54 (s, 6H), 1.29-1.23 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 171.6, 168.6, 167.5, 148.1, 141.3, 136.6, 134.4, 130.8, 130.3, 129.9, 128.5, 127.9, 127.7, 126.0, 121.1, 120.9, 114.4, 51.0, 46.1, 29.9, 29.1, 26.1, 25.1; HRMS *m/z* (ESI) calcd for $C_{28}H_{26}NO_4$ ([M+H]$^+$) 440.1856, found 440.1864.

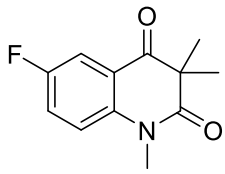


1,3,3-Trimethylquinoline-2,4(1*H*,3*H*)-dione (4a).[3] The product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (5:1, v/v). 0.0345 g, 85% yield; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.02-8.00 (m, 1H), 7.65-7.62 (m, 1H), 7.20-7.16 (m, 2H), 3.47 (s, 3H), 1.49 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 197.7, 174.3, 143.1, 135.8, 128.2, 123.0, 119.9, 114.7, 53.2, 29.9, 23.9; HRMS *m/z* (ESI) calcd for $C_{12}H_{14}NO_2$ ([M+H]$^+$) 204.1019, found 204.1011.

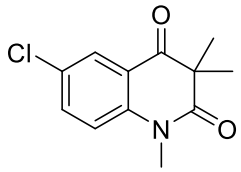


1,3,3,6-Tetramethylquinoline-2,4(1*H*,3*H*)-dione (4b). The product was purified by silica gel column chromatography with

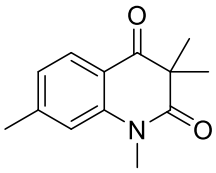
petroleum ether/ethyl acetate (5:1, v/v). Colorless oil (0.0369 g, 85% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.80 (s, 1H), 7.43 (d, J = 8.4 Hz, 1H), 7.07 (d, J = 8.4 Hz, 1H), 3.45 (s, 3H), 2.37 (s, 3H), 1.48 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 198.0, 174.2, 140.9, 136.6, 132.8, 128.1, 119.7, 114.7, 53.1, 29.9, 23.9, 20.4; HRMS *m/z* (ESI) calcd for $C_{13}H_{16}NO_2$ ($[M+H]^+$) 218.1176, found 218.1170.



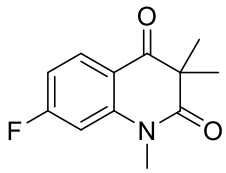
6-Fluoro-1,3,3-trimethylquinoline-2,4(1*H*,3*H*)-dione (4c). The product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (5:1, v/v). Colorless oil (0.0354 g, 80% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.69-7.66 (m, 1H), 7.37-7.32 (m, 1H), 7.18-7.14 (m, 1H), 3.47 (s, 3H), 1.49 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 196.9, 173.8, 158.5 (d, J_{C-F} = 245.9 Hz), 139.5, 122.8 (d, J_{C-F} = 23.5 Hz), 121.1 (d, J_{C-F} = 6.3 Hz), 116.6 (d, J_{C-F} = 7.1 Hz), 114.0 (d, J_{C-F} = 23.4 Hz), 53.1, 30.2, 23.9; ^{19}F NMR (376 MHz, $CDCl_3$) δ: -119.6; HRMS *m/z* (ESI) calcd for $C_{12}H_{13}FNO_2$ ($[M+H]^+$) 222.0925, found 222.0927.



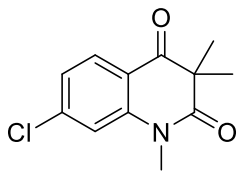
6-Chloro-1,3,3-trimethylquinoline-2,4(1*H*,3*H*)-dione (4d). The product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (5:1, v/v). Colorless oil (0.0384 g, 81% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.95 (s, 1H), 7.59-7.56 (m, 1H), 7.12 (d, J = 9.2 Hz, 1H), 3.46 (s, 3H), 1.49 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 196.6, 173.9, 141.6, 135.4, 128.8, 127.7, 121.0, 116.4, 53.3, 30.1, 23.8; HRMS *m/z* (ESI) calcd for $C_{12}H_{13}ClNO_2$ ($[M+H]^+$) 238.0629, found 238.0635.



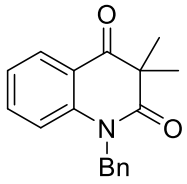
1,3,3,7-Tetramethylquinoline-2,4(1*H*,3*H*)-dione (4e). The product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (5:1, v/v). Colorless oil (0.0365 g, 84% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.90 (d, J = 7.6 Hz, 1H), 7.00 (d, J = 8.8 Hz, 1H), 6.97 (s, 1H), 3.46 (s, 3H), 2.46 (s, 3H), 1.48 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 197.3, 174.6, 147.2, 143.2, 128.3, 124.1, 117.6, 115.2, 52.9, 29.8, 24.0, 22.4; HRMS *m/z* (ESI) calcd for $C_{13}H_{16}NO_2$ ($[M+H]^+$) 218.1176, found 218.1170.



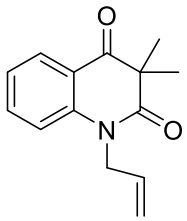
7-Fluoro-1,3,3-trimethylquinoline-2,4(1*H*,3*H*)-dione (4f). The product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (5:1, v/v). Colorless oil (0.0345 g, 78% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.06-8.02 (m, 1H), 6.90-6.86 (m, 2H), 3.45 (s, 3H), 1.49 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 196.2, 174.4, 167.4 (d, $J_{C\text{-}F}$ = 256.6 Hz), 145.4 (d, $J_{C\text{-}F}$ = 11.7 Hz), 131.2 (d, $J_{C\text{-}F}$ = 11.2 Hz), 116.4, 110.4 (d, $J_{C\text{-}F}$ = 22.3 Hz), 102.4 (d, $J_{C\text{-}F}$ = 27.6 Hz), 53.1, 30.1, 24.0; ^{19}F NMR (376 MHz, $CDCl_3$) δ: -99.5; HRMS *m/z* (ESI) calcd for $C_{12}H_{13}FNO_2$ ($[M+H]^+$) 222.0925, found 222.0931.



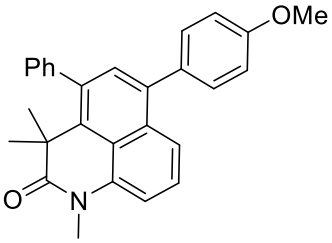
7-Chloro-1,3,3-trimethylquinoline-2,4(1*H*,3*H*)-dione (4g).[4] The product was purified by silica gel column chromatograp hy with petroleum ether/ethyl acetate (5:1, v/v). 0.0375 g, 7 9% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.95 (d, J = 8.0 Hz, 1H), 7.17-7.14 (m, 2H), 3.46 (s, 3H), 1.49 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 196.5, 174.3, 144.1, 142.1, 129.6, 123.3, 118.2, 115.0, 53.2, 30.0, 23.9; HRMS *m/z* (ESI) calcd for $C_{12}H_{13}ClNO_2$ ($[M+H]^+$) 238.0629, found 238.0635.



1-Benzyl-3,3-dimethylquinoline-2,4(1*H*,3*H*)-dione (4h). The product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (5:1, v/v). Colorless oil (0.0469 g, 84% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.01-7.99 (m, 1H), 7.48-7.45 (m, 1H), 7.33 (t, J = 7.5 Hz, 2H), 7.28-7.23 (m, 3H), 7.13 (t, J = 7.5 Hz, 1H), 7.05 (d, J = 8.0 Hz, 1H), 5.27 (s, 2H), 1.58 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 197.6, 174.6, 142.5, 136.2, 135.7, 129.0, 128.3, 127.5, 126.3, 123.2, 120.2, 115.6, 53.4, 46.3, 23.9; HRMS *m/z* (ESI) calcd for $C_{18}H_{18}NO_2$ ($[M+H]^+$) 280.1332, found 280.1338.



1-Allyl-3,3-dimethylquinoline-2,4(1*H*,3*H*)-dione (4i). The product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (5:1, v/v). Colorless oil (0.0371 g, 81% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.01-7.99 (m, 1H), 7.60-7.57 (m, 1H), 7.16 (t, J = 7.5 Hz, 1H), 7.12 (d, J = 8.5 Hz, 1H), 5.93-5.88 (m, 1H), 5.25-5.18 (m, 2H), 4.68-4.66 (m, 2H), 1.51 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 197.7, 174.0, 142.3, 135.7, 131.7, 128.2, 123.1, 120.1, 116.9, 115.4, 53.3, 44.9, 23.8; HRMS *m/z* (ESI) calcd for $C_{14}H_{16}NO_2$ ($[M+H]^+$) 230.1176, found 230.1172.



6-(4-Methoxyphenyl)-1,3,3-trimethyl-4-phenyl-1*H*-benzo[*de*]quinolin-2(3*H*)-one (6a).[1] The product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (5:1, v/v). White solid (0.0456 g, 56% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.64-7.62 (m, 1H), 7.43-7.40 (m, 2H), 7.39-7.38 (m, 2H), 7.37-7.35 (m, 2H), 7.34-7.32 (m, 2H), 7.17 (s, 1H), 7.06-7.04 (m, 1H), 7.00-6.97 (m,

2H), 3.86 (s, 3H), 3.56 (s, 3H), 1.51 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 174.5, 159.1, 144.2, 138.5, 137.5, 137.1, 134.9, 133.1, 132.5, 131.5, 131.2, 129.9, 127.5, 127.0, 126.1, 120.9, 120.1, 113.8, 109.3, 55.4, 45.3, 30.6, 29.9; HRMS *m/z* (ESI) calcd for $C_{28}H_{26}NO_2$ ($[M+H]^+$) 408.1958, found 408.1966.

(E) References

[1] B. Liu, J.-X. Yu, Y. Li, J.-H. Li and D.-L. He, Copper-catalyzed annulation cascades of alkyne-tethered *α*-bromocarbonyls with alkynes: an access to heteropolycycles, *Org. Lett.* 2018, **20**, 2129-2132.

[2] S. Xie, Y. Li, P. Liu and P. Sun, Visible light-induced radical addition/annulation to construct phenylsulfonyl-functionalized dihydrobenzofurans involving an intramolecular 1,5-hydrogen atom transfer process, *Org. Lett.* 2020, **22**, 8774-8779.

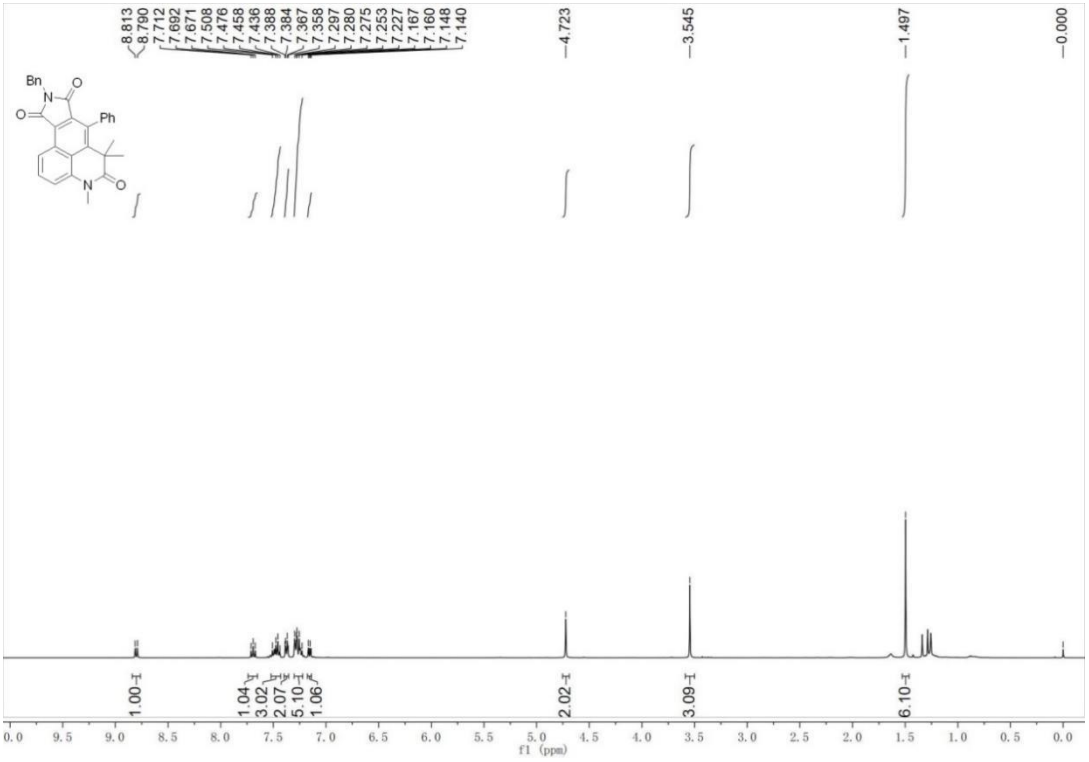
[3] N. Kise, K. Sasaki and T. Sakurai, Reductive coupling of isatins with ketones and aldehydes by low-valent titanium, *Tetrahedron* 2014, **70**, 9668-9675.

[4] A. B. Daruwala, J. E. Gearien, W. J. Dunn, P. S. Benoit and L. Bauer, *ß*-Amino ketones. synthesis and some biological activities in mice of 3,3-dialkyl-1,2,3,4-tetrahydro-4-quinolinones and related mannich bases, *J. Med. Chem.* 1974, **17**, 819-824.

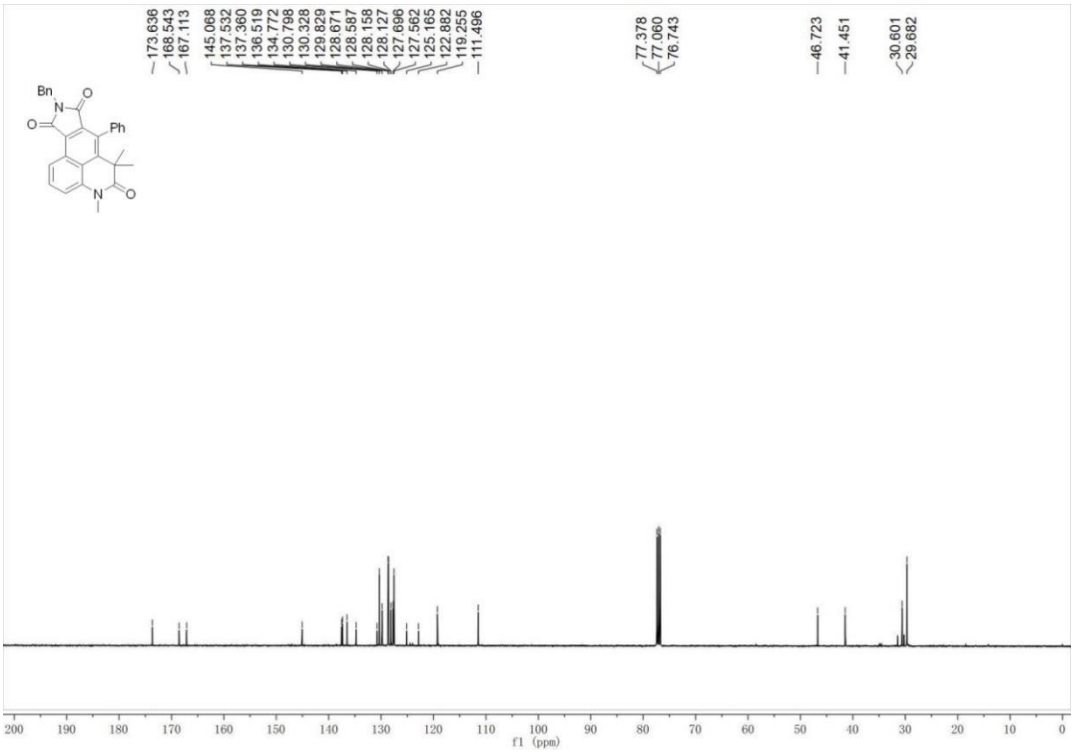
(F) Spectra

9-Benzyl-4,6,6-trimethyl-7-phenylisoindolo[6,5,4-*de*]quinoline-5,8,10(4*H*,6*H*,9*H*)-trione (3a)

^{1}H NMR-spectrum (400 MHz, $CDCl_3$) of **3a**

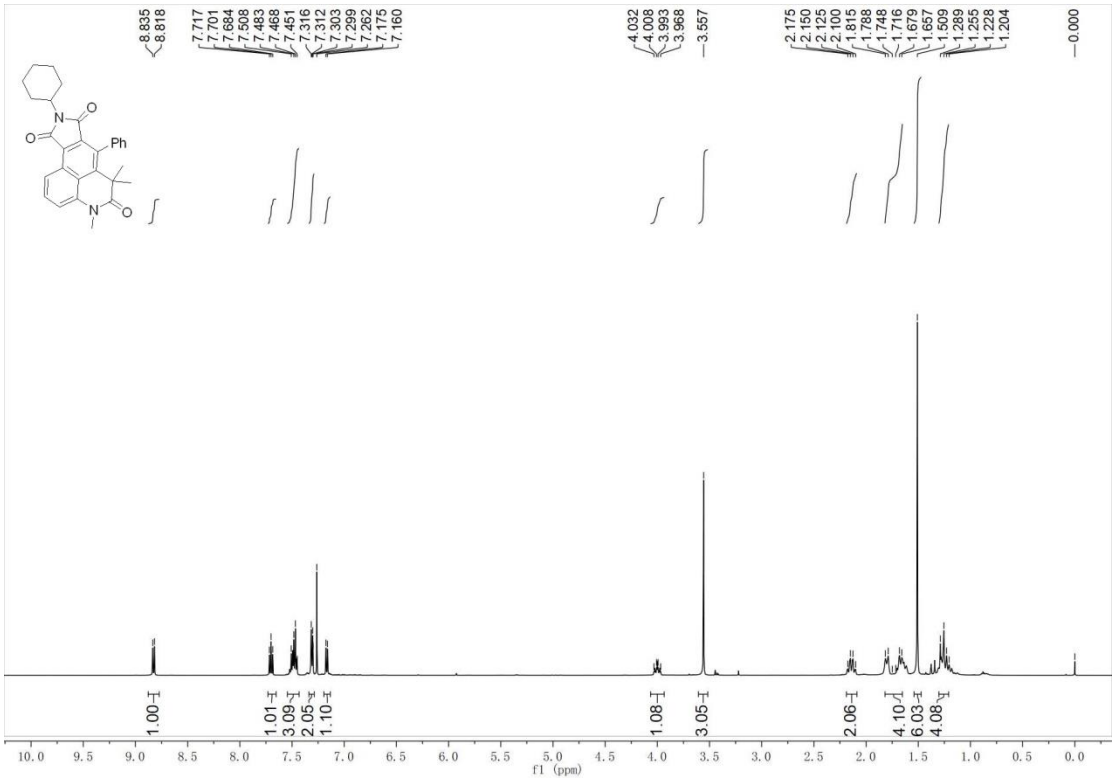


^{13}C NMR-spectrum (101 MHz, $CDCl_3$) of **3a**

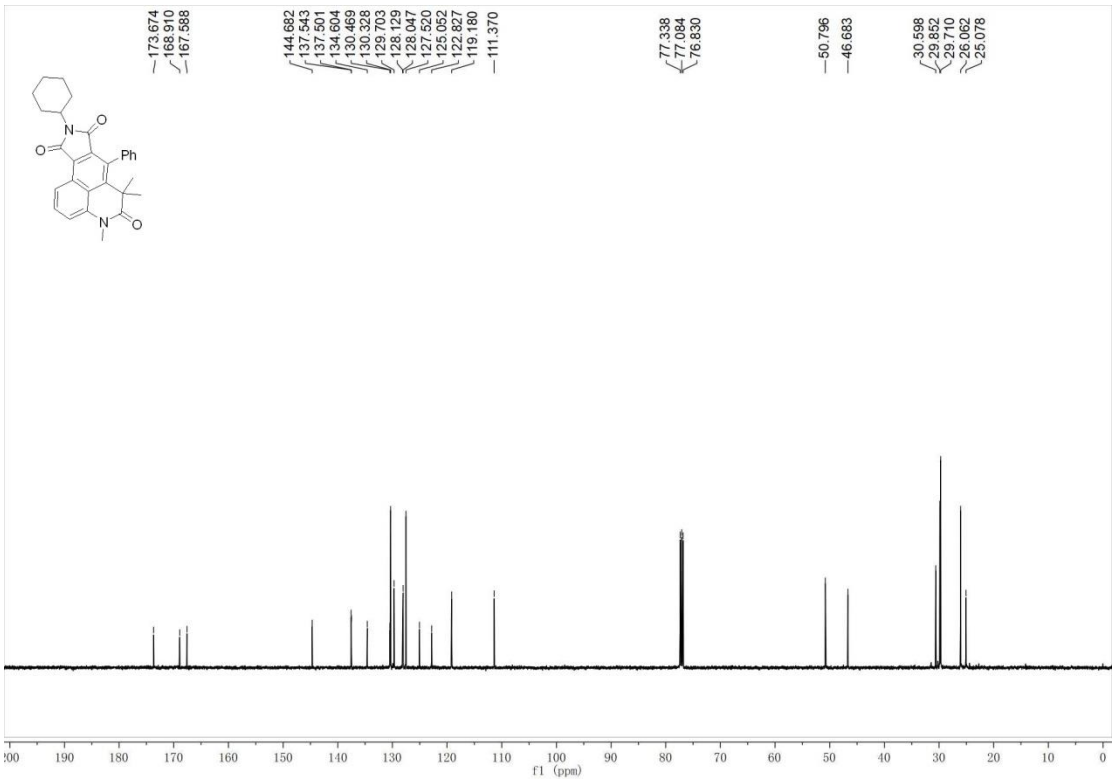


9-Cyclohexyl-4,6,6-trimethyl-7-phenylisoindolo[6,5,4-*de*]quinoline-5,8,10(4*H*,6*H*,9*H*)-trione (3b)

^{1}H NMR-spectrum (500 MHz, $CDCl_3$) of **3b**

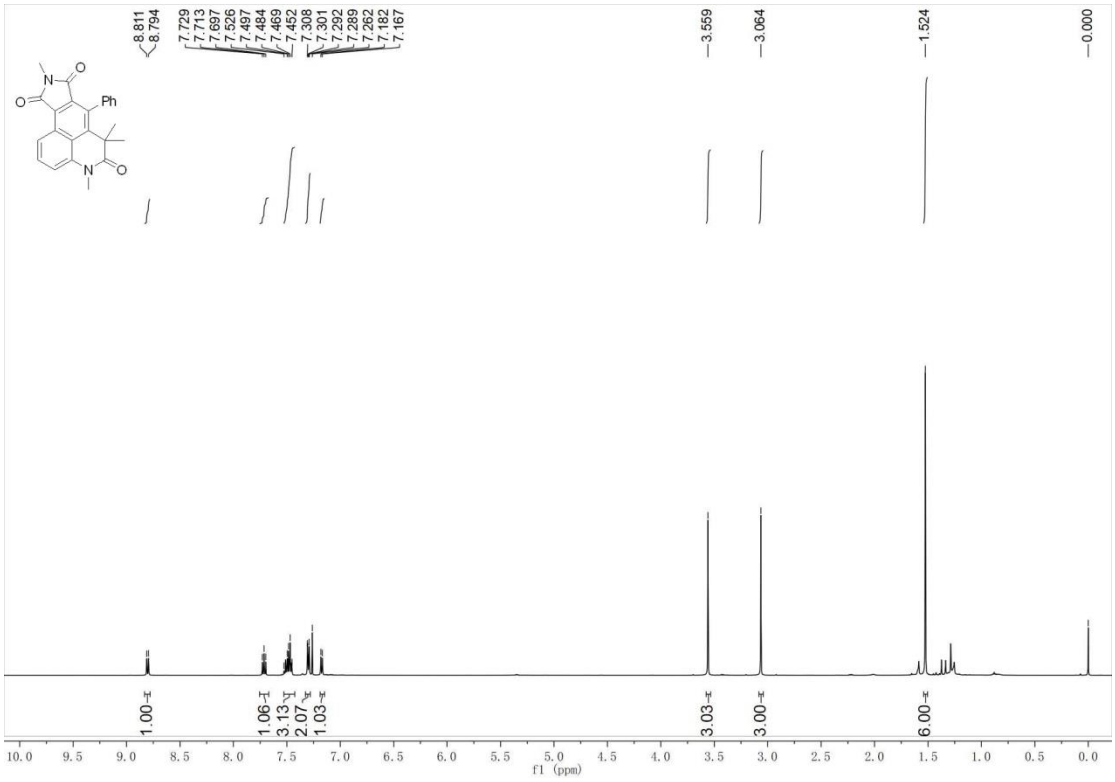


^{13}C NMR-spectrum (126 MHz, $CDCl_3$) of **3b**

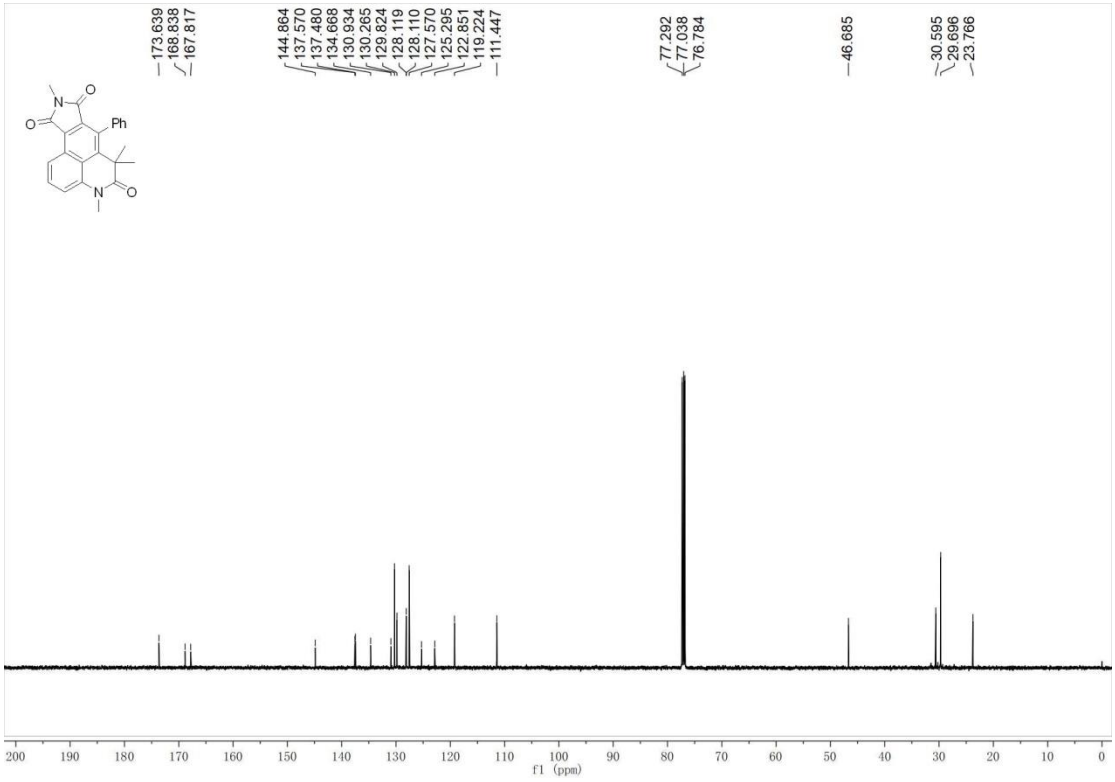


4,6,6,9-Tetramethyl-7-phenylisoindolo[6,5,4-*de*]quinoline-5,8,10(4*H*,6*H*,9*H*)-trione (3c)

^{1}H NMR-spectrum (500 MHz, $CDCl_3$) of **3c**

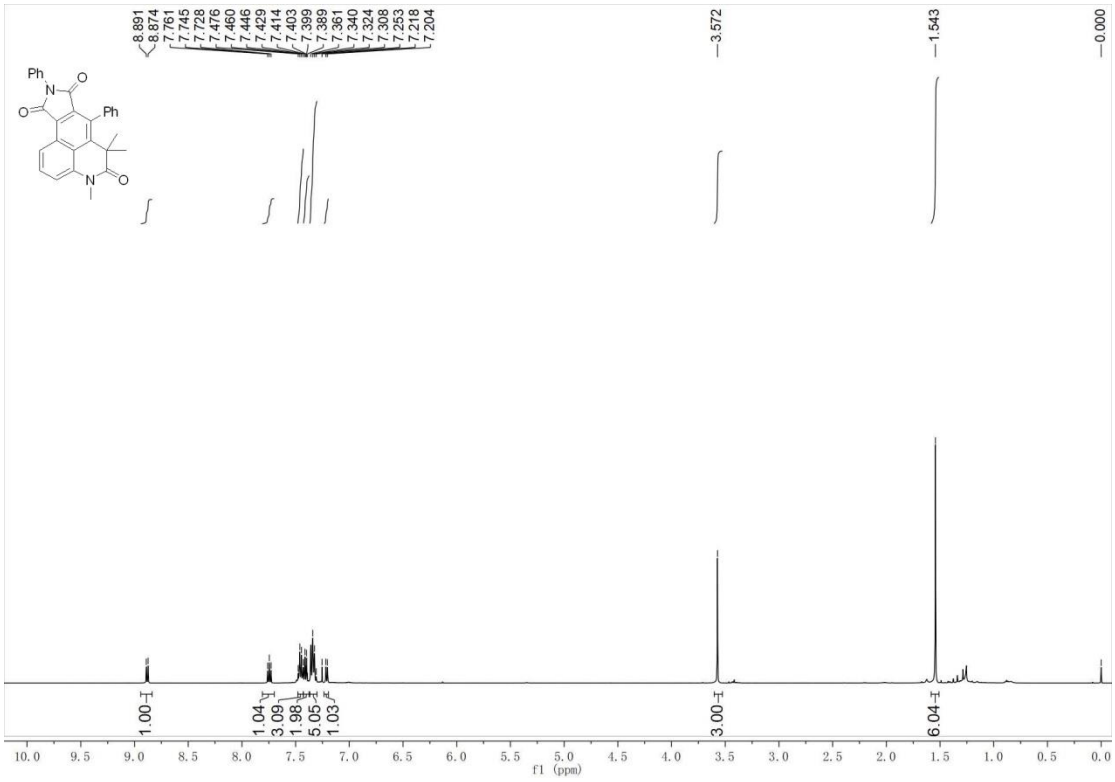


^{13}C NMR-spectrum (126 MHz, $CDCl_3$) of **3c**

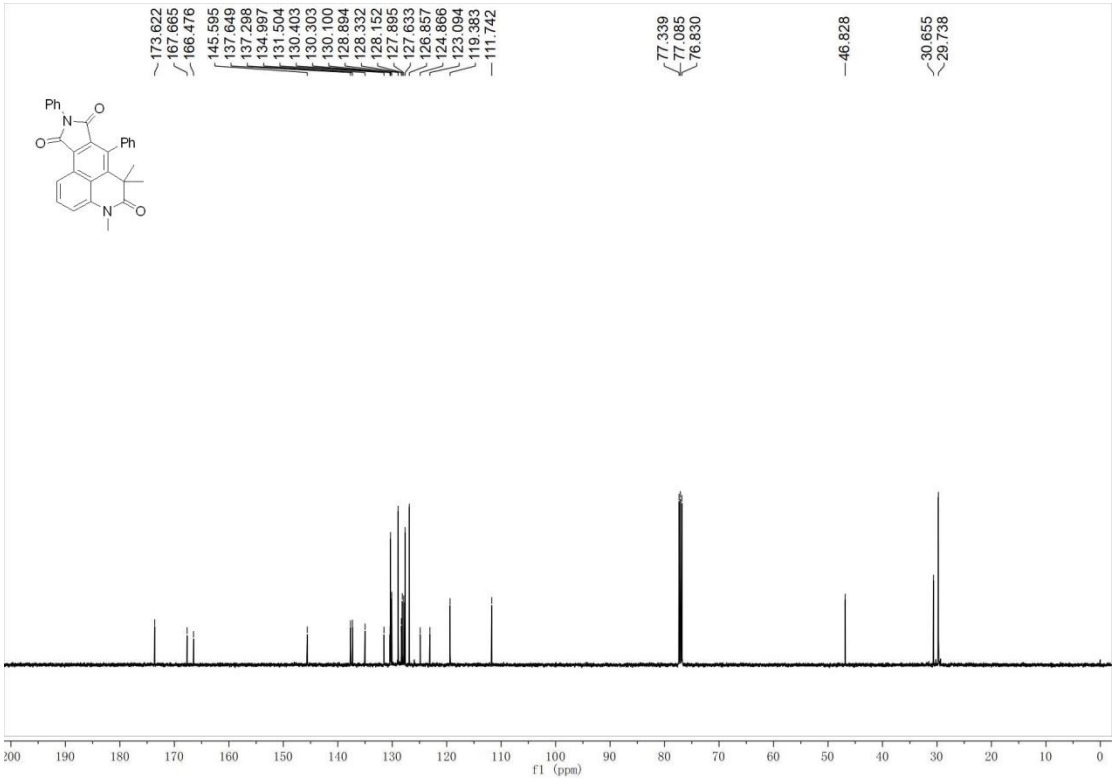


4,6,6-Trimethyl-7,9-diphenylisoindolo[6,5,4-*de*]quinoline-5,8,10(4*H*,6*H*,9*H*)-trione (3d)

^{1}H NMR-spectrum (500 MHz, $CDCl_3$) of **3d**

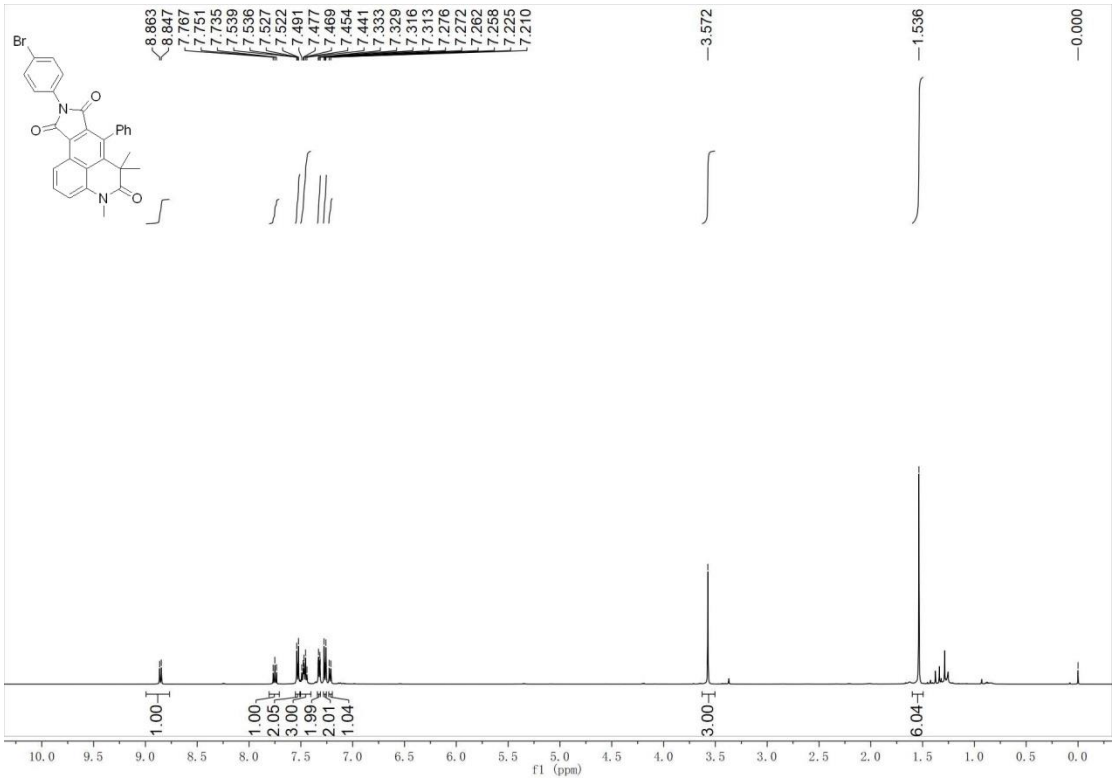


^{13}C NMR-spectrum (126 MHz, $CDCl_3$) of **3d**

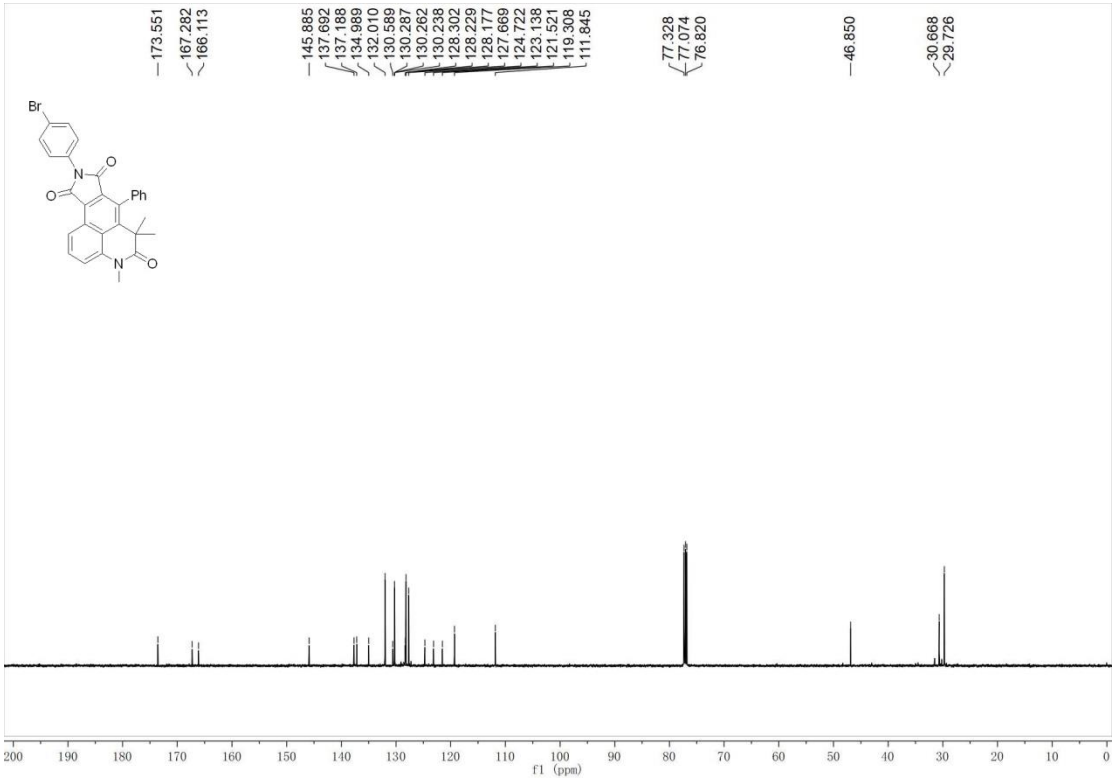


9-(4-Bromophenyl)-4,6,6-trimethyl-7-phenylisoindolo[6,5,4-*de*]quinoline-5,8,10(4*H*,6*H*,9*H*)-trione (3e)

^{1}H NMR-spectrum (500 MHz, $CDCl_3$) of **3e**

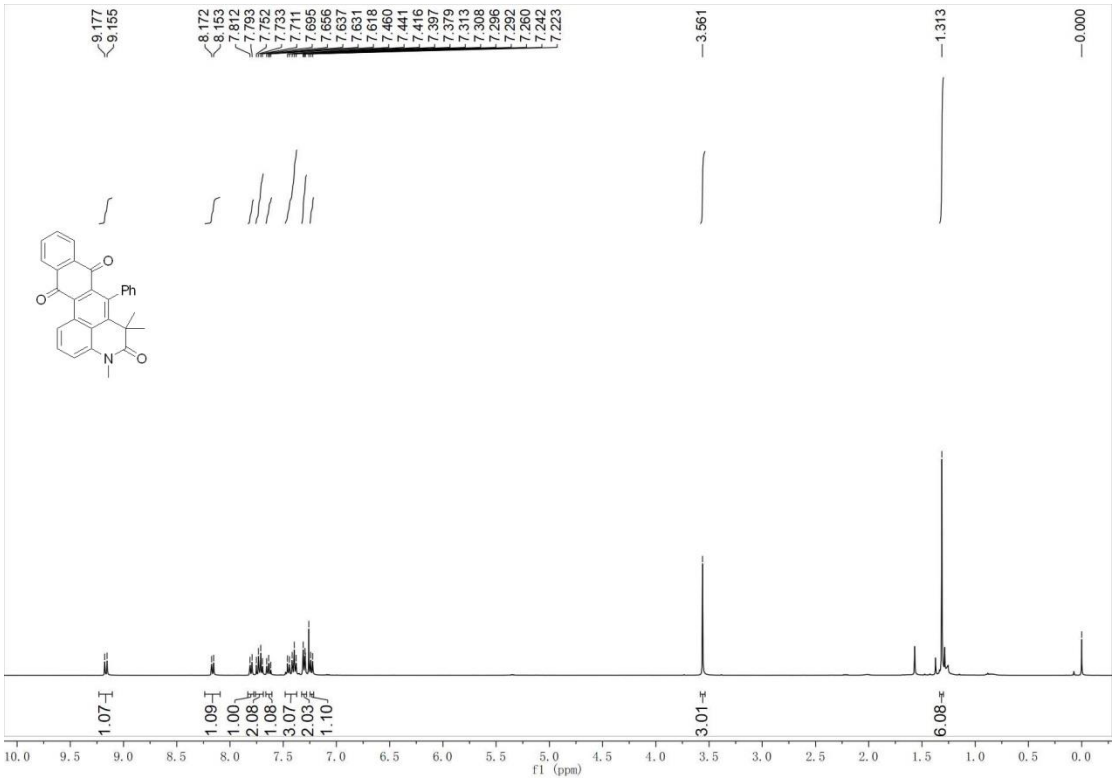


^{13}C NMR-spectrum (126 MHz, $CDCl_3$) of **3e**

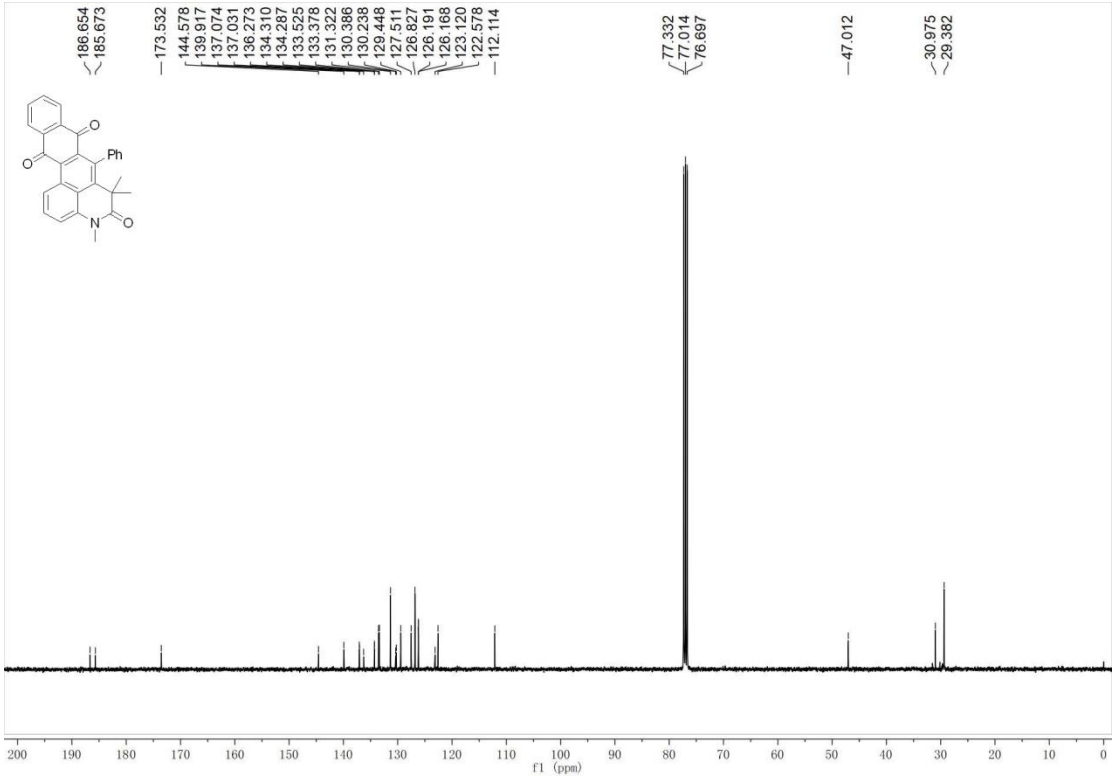


4,6,6-Trimethyl-7-phenyl-4*H*-anthra[3,2,1-*de*]quinoline-5,8,13(6*H*)-trione (3f)

^{1}H NMR-spectrum (400 MHz, $CDCl_3$) of **3f**

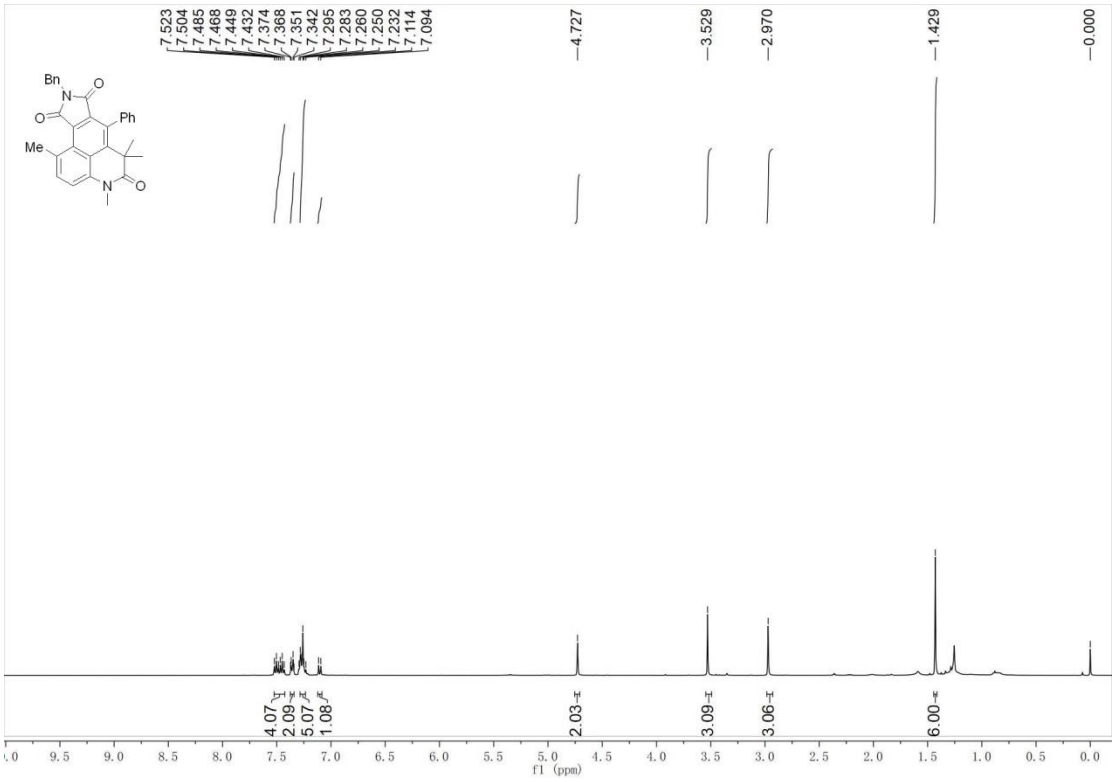


^{13}C NMR-spectrum (101 MHz, $CDCl_3$) of **3f**

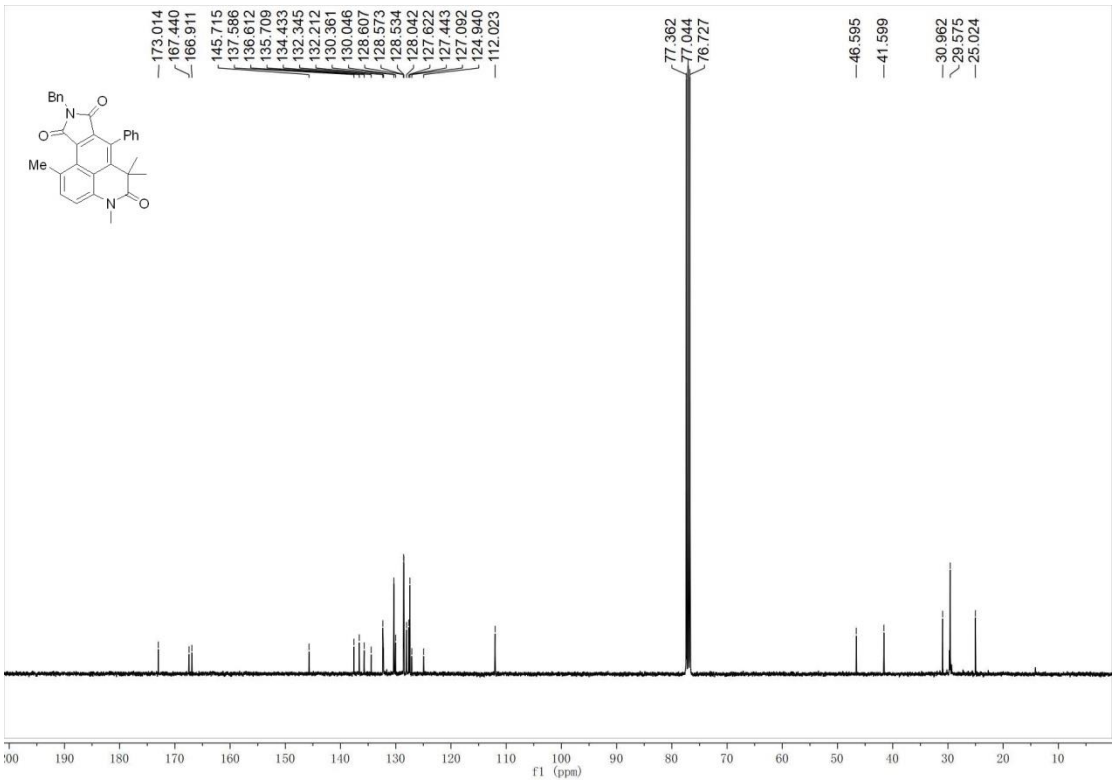


9-Benzyl-1,4,6,6-tetramethyl-7-phenylisoindolo[6,5,4-*de*]quinoline-5,8,10(4*H*,6*H*,9*H*)-trione (3g)

^{1}H NMR-spectrum (400 MHz, $CDCl_3$) of **3g**

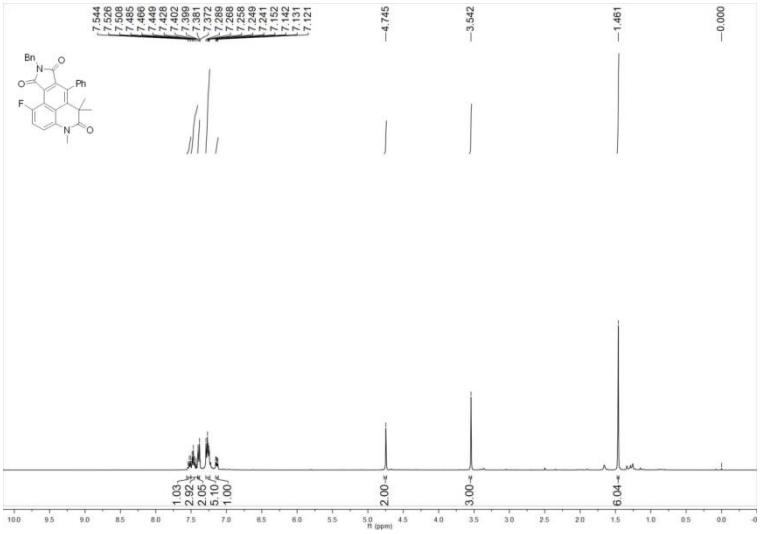


^{13}C NMR-spectrum (101MHz, $CDCl_3$) of **3g**

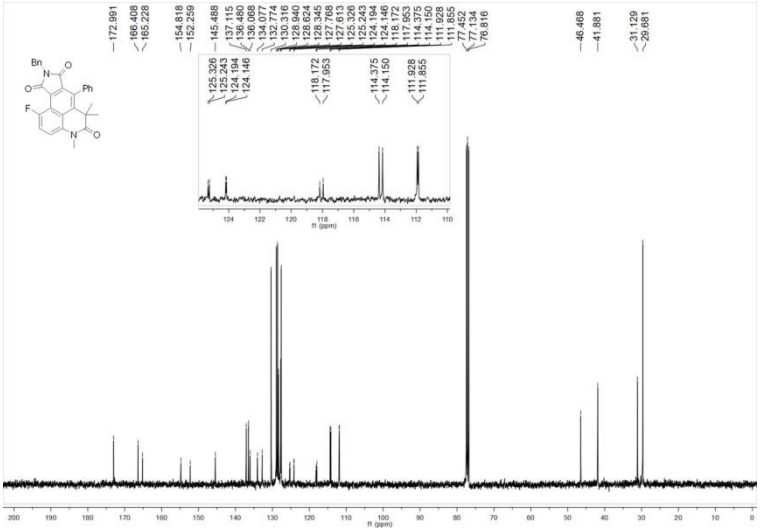


9-Benzyl-1-fluoro-4,6,6-trimethyl-7-phenylisoindolo[6,5,4-*de*]quinoline-5,8,10(4*H*,6*H*,9*H*)-trione (3h)

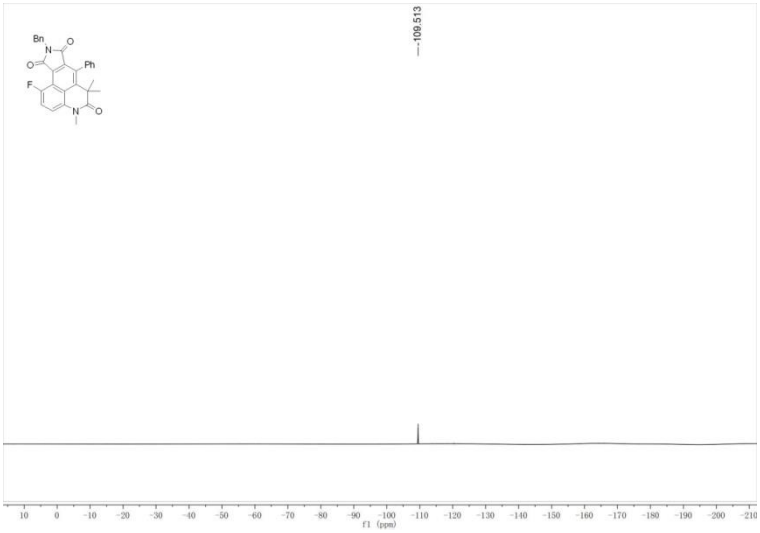
^{1}H NMR-spectrum (400 MHz, $CDCl_3$) of **3h**



^{13}C NMR-spectrum (101 MHz, $CDCl_3$) of **3h**

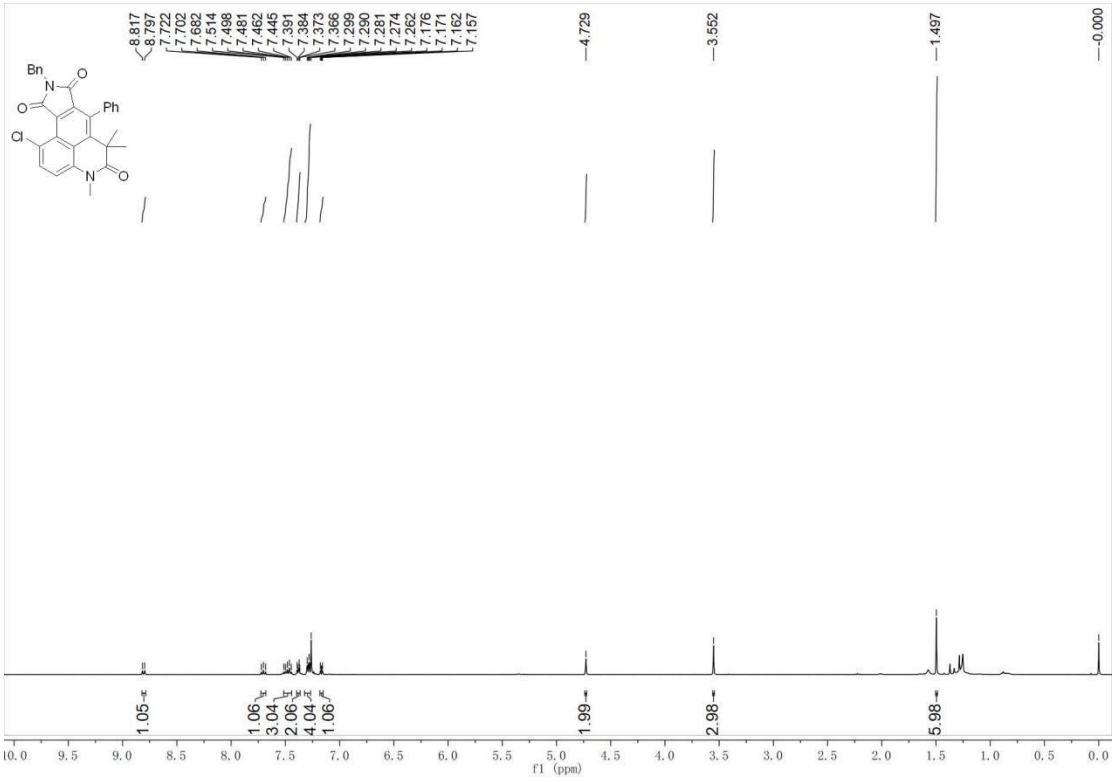


^{19}F NMR-spectrum (376 MHz, $CDCl_3$) of **3h**

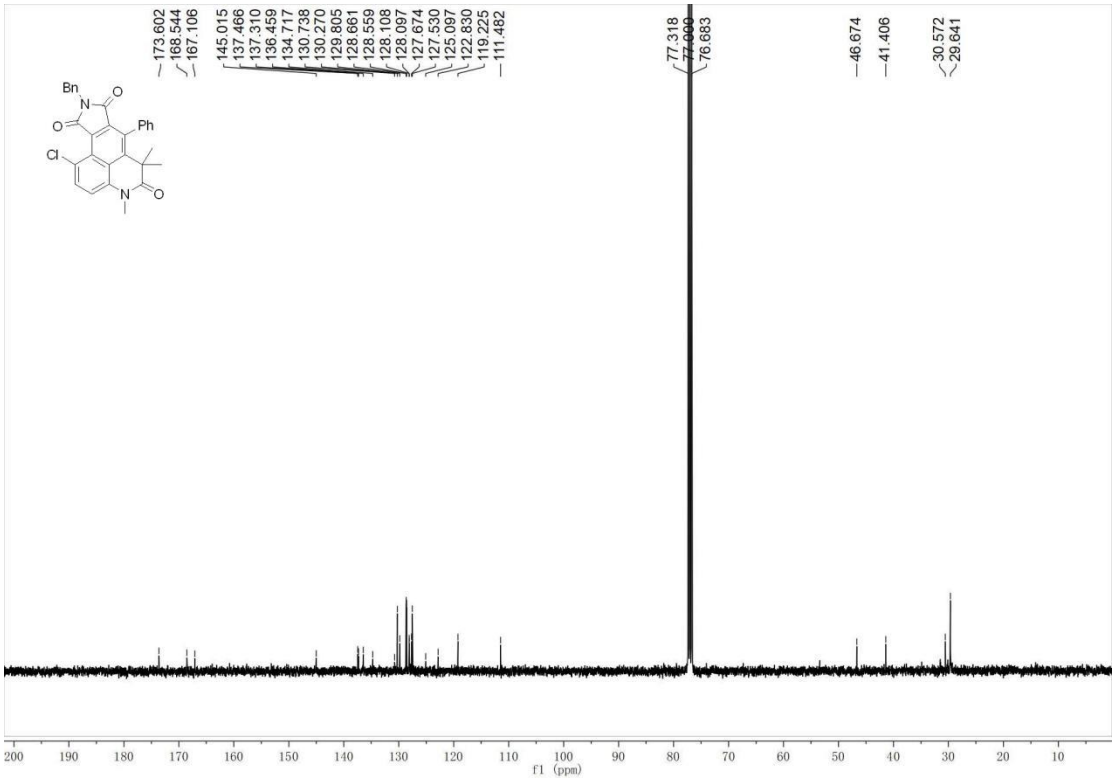


9-Benzyl-1-chloro-4,6,6-trimethyl-7-phenylisoindolo[6,5,4-*de*]quinoline-5,8,10(4*H*,6*H*,9*H*)-trione (3i)

^{1}H NMR-spectrum (400 MHz, $CDCl_3$) of **3i**

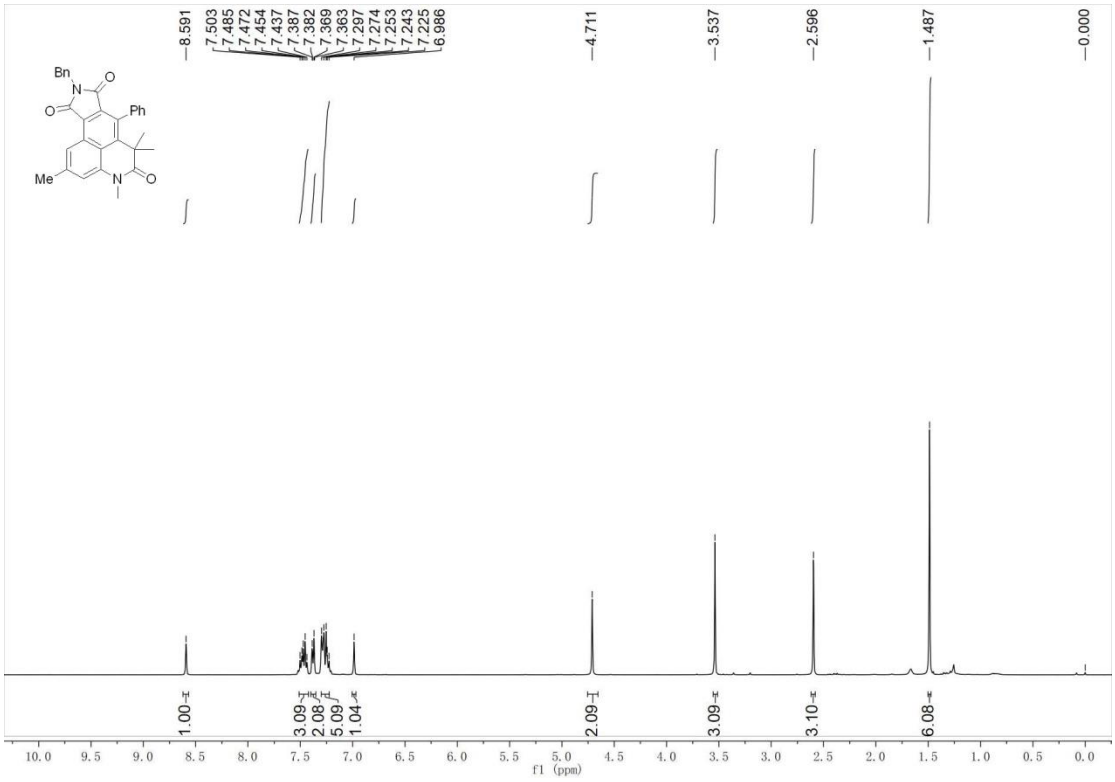


^{13}C NMR-spectrum (101 MHz, $CDCl_3$) of **3i**

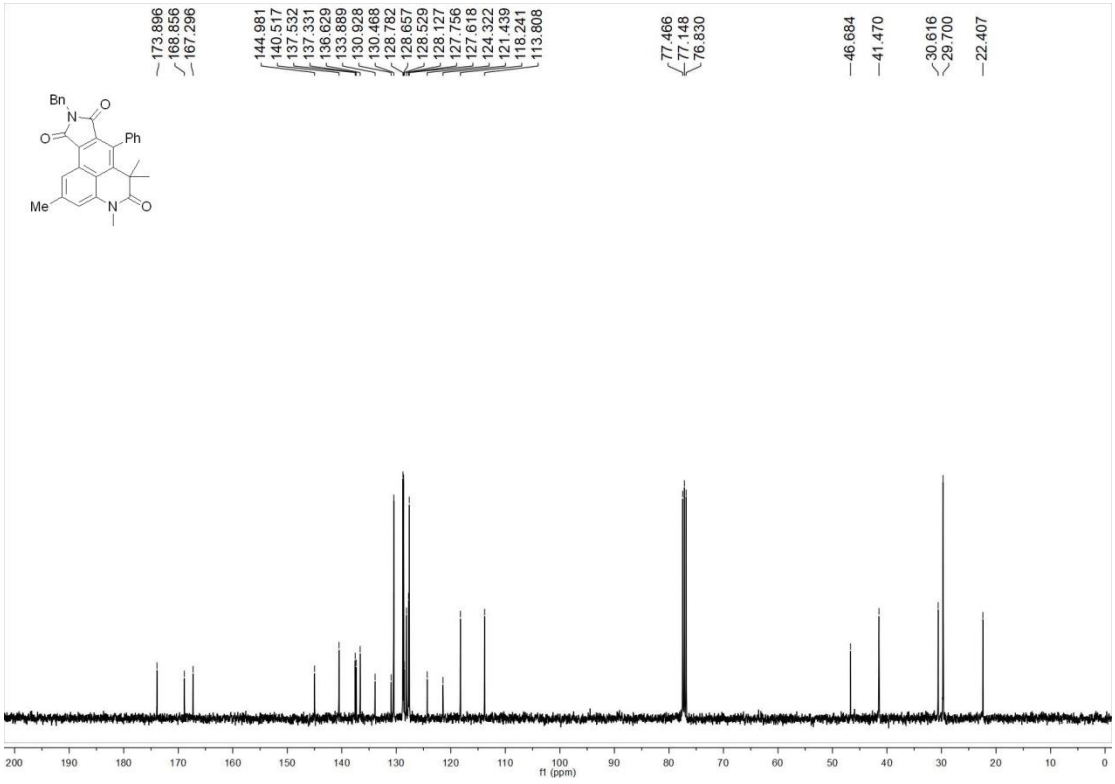


9-Benzyl-2,4,6,6-tetramethyl-7-phenylisoindolo[6,5,4-*de*]quinoline-5,8,10(4*H*,6*H*,9*H*)-trione (3j)

^{1}H NMR-spectrum (400 MHz, $CDCl_3$) of **3j**

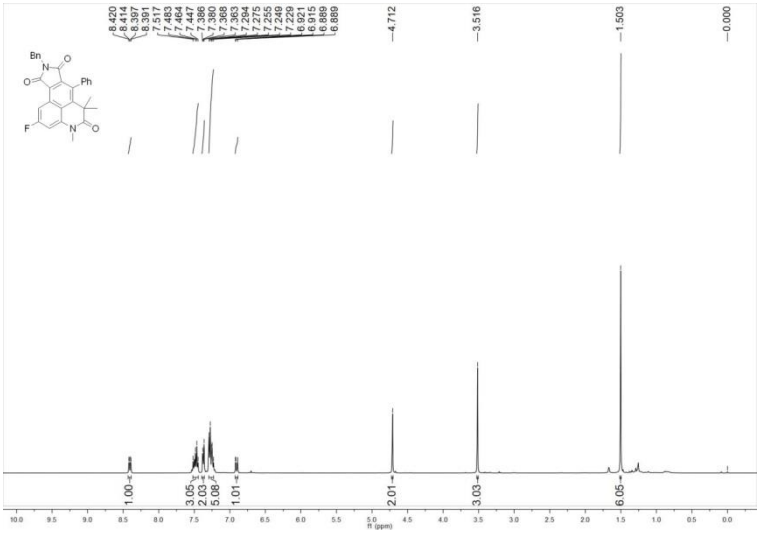


^{13}C NMR-spectrum (101 MHz, $CDCl_3$) of **3j**

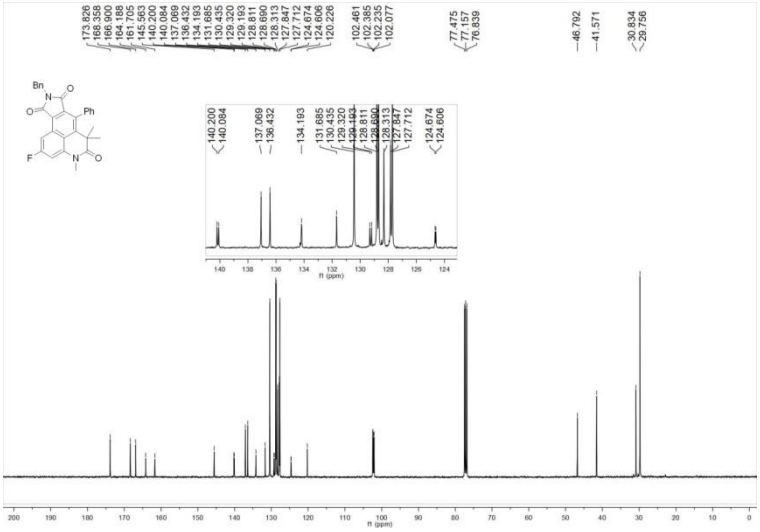


9-Benzyl-2-fluoro-4,6,6-trimethyl-7-phenylisoindolo[6,5,4-*de*]quinoline-5,8,10(4*H*,6*H*,9*H*)-trione (3k)

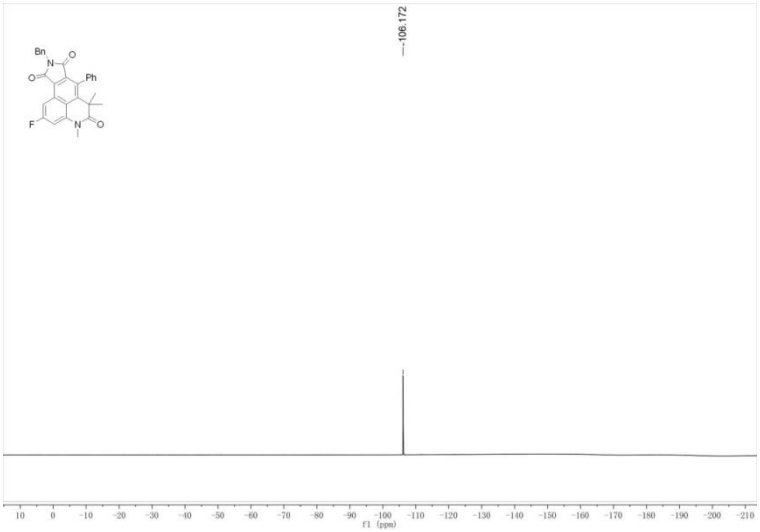
^{1}H NMR-spectrum (400 MHz, $CDCl_3$) of **3k**



^{13}C NMR-spectrum (101 MHz, $CDCl_3$) of **3k**

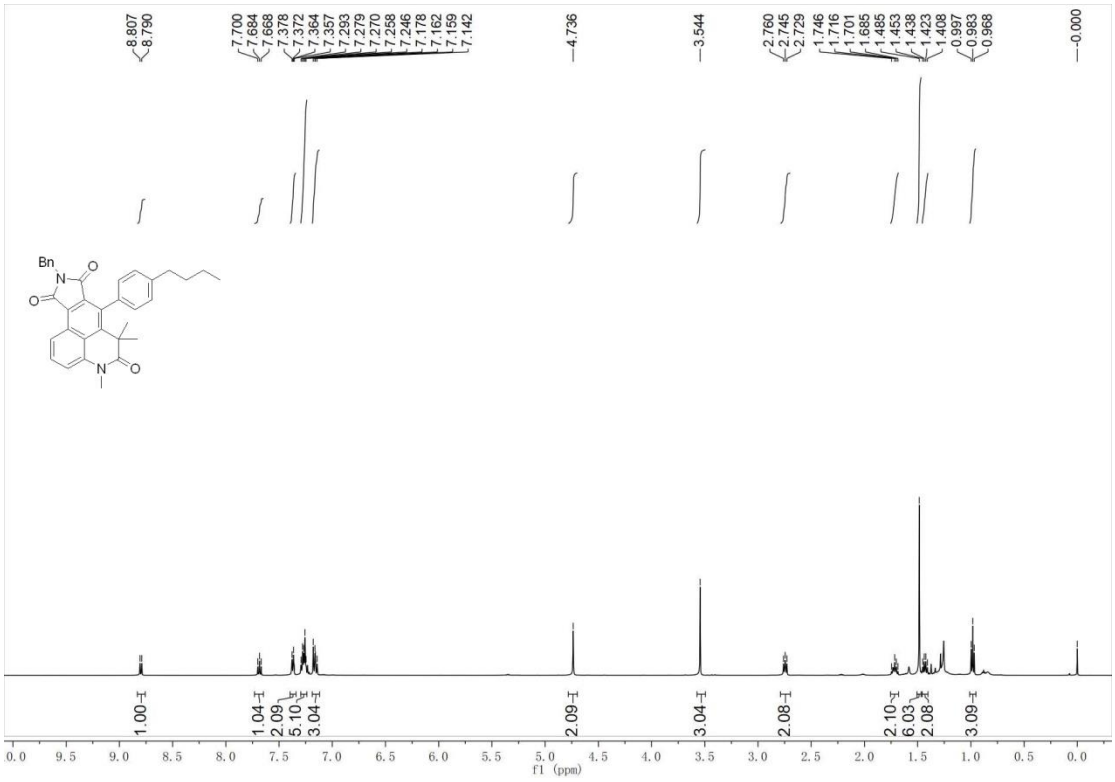


^{19}F NMR-spectrum (376 MHz, $CDCl_3$) of **3k**

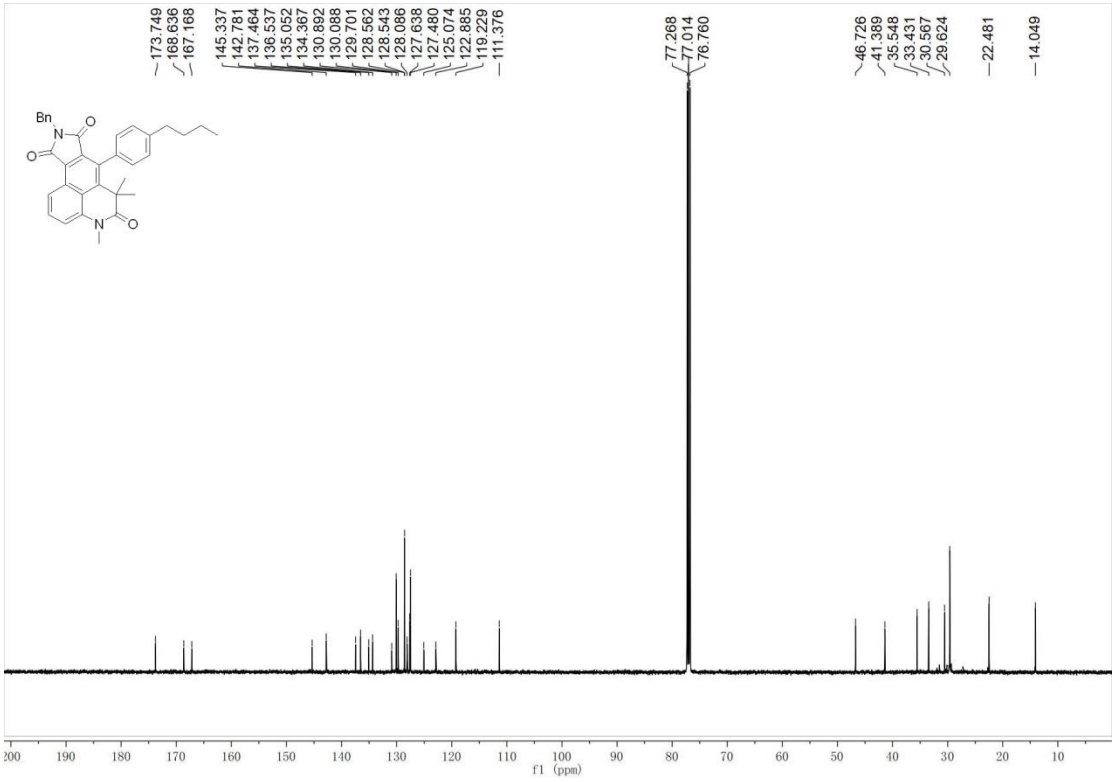


9-Benzyl-7-(4-butylphenyl)-4,6,6-trimethylisoindolo[6,5,4-*de*]quinoline-5,8,10(4*H*,6*H*,9*H*)-trione (3l)

^{1}H NMR-spectrum (500 MHz, $CDCl_3$) of **3l**

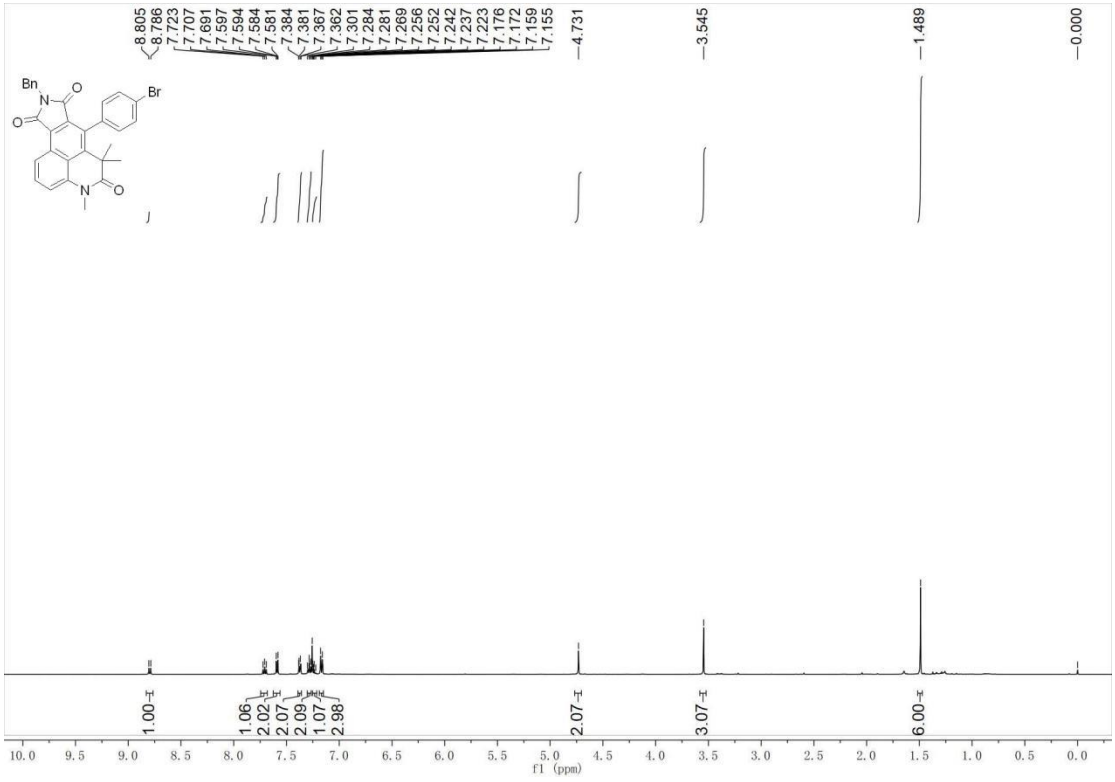


^{13}C NMR-spectrum (126 MHz, $CDCl_3$) of **3l**

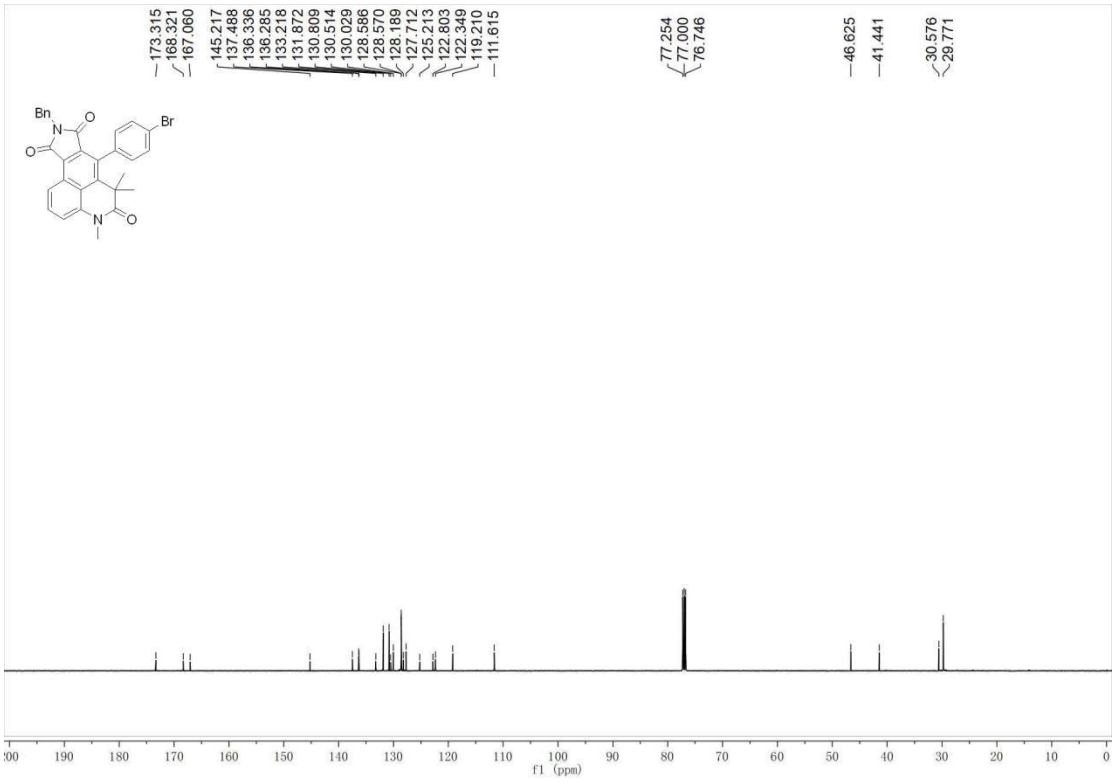


9-Benzyl-7-(4-bromophenyl)-4,6,6-trimethylisoindolo[6,5,4-*de*]quinoline-5,8,10(4*H*,6*H*,9*H*)-trione (3m)

^{1}H NMR-spectrum (500 MHz, $CDCl_3$) of **3m**

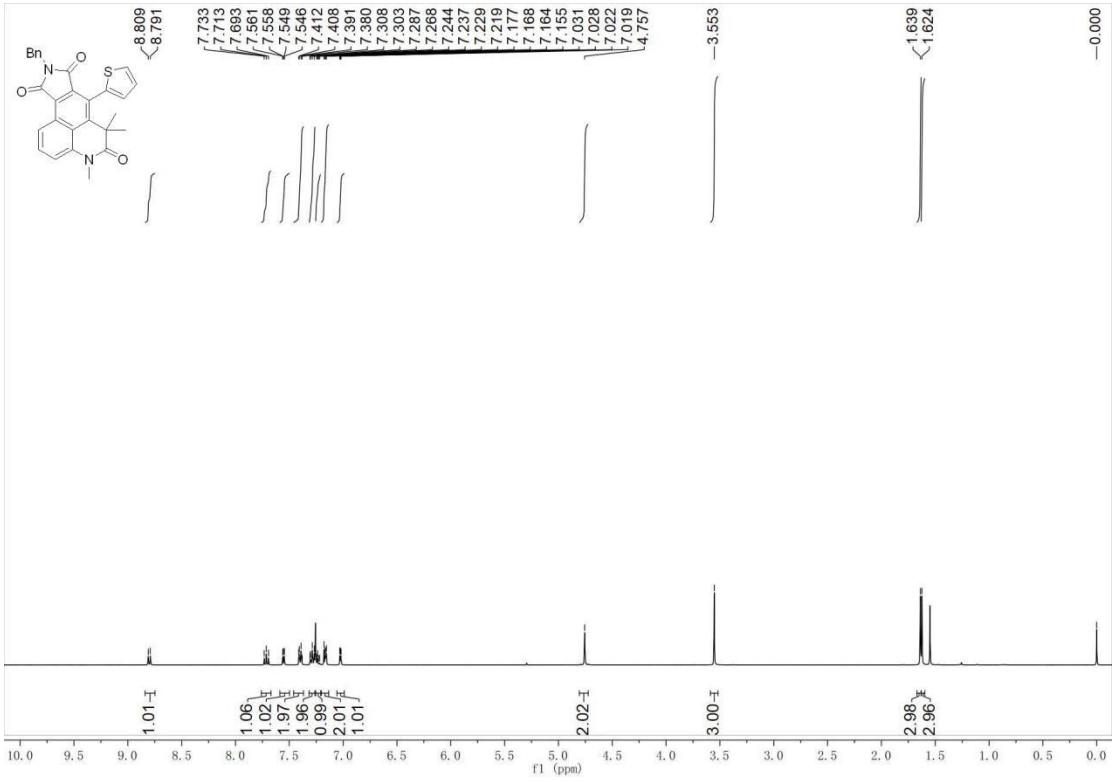


^{13}C NMR-spectrum (126 MHz, $CDCl_3$) of **3m**

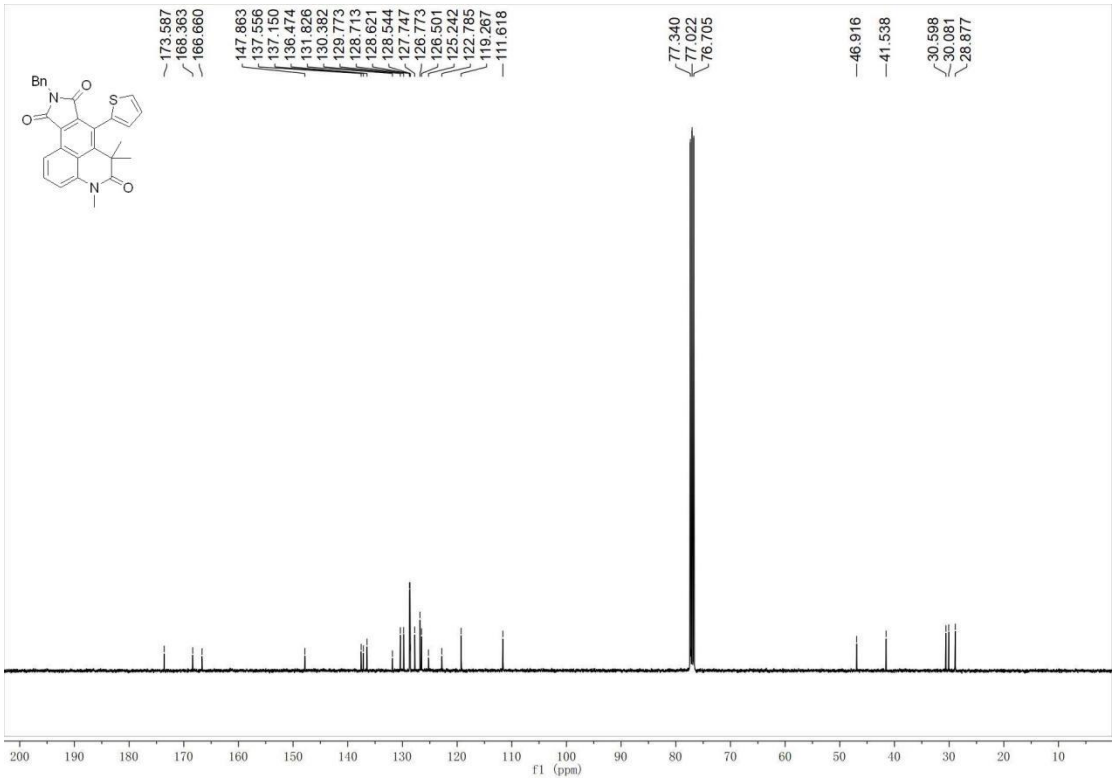


9-Benzyl-4,6,6-trimethyl-7-(thiophen-2-yl)isoindolo[6,5,4-*de*]quinoline-5,8,10(4*H*,6*H*,9*H*)-trione (3n)

^{1}H NMR-spectrum (400 MHz, $CDCl_3$) of **3n**

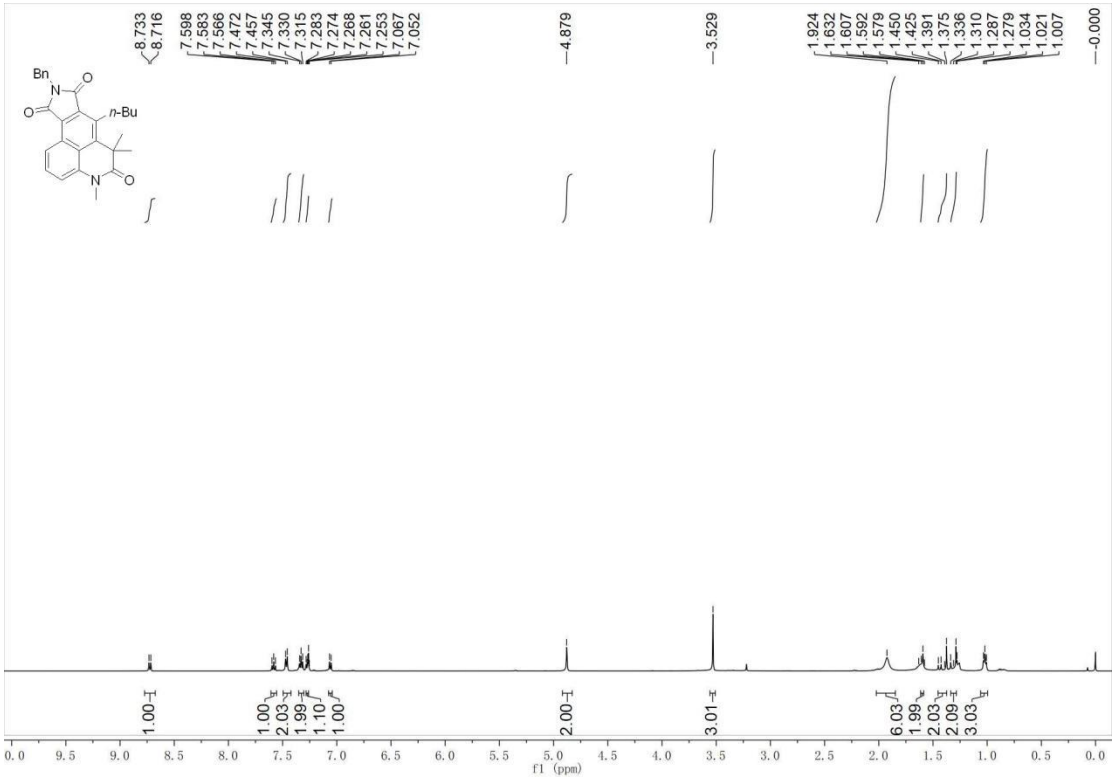


^{13}C NMR-spectrum (101 MHz, $CDCl_3$) of **3n**

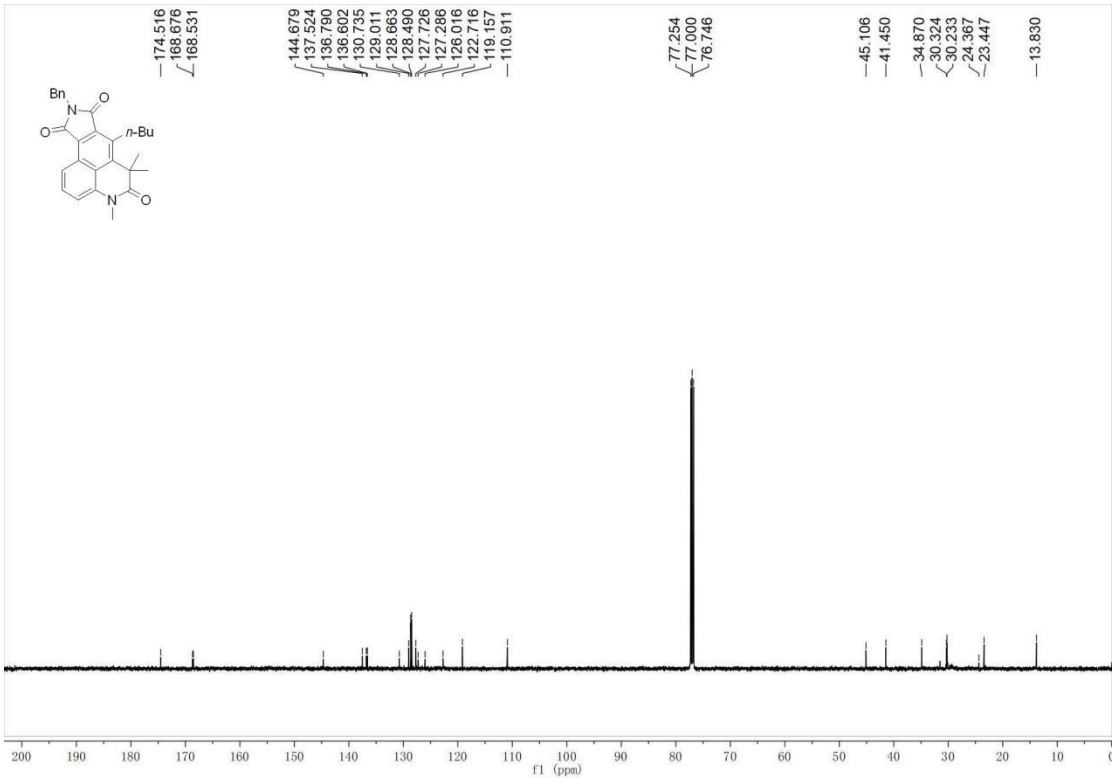


9-Benzyl-7-butyl-4,6,6-trimethylisoindolo[6,5,4-*de*]quinoline-5,8,10(4*H*,6*H*,9*H*)-trione (3o)

^{1}H NMR-spectrum (500 MHz, $CDCl_3$) of **3o**

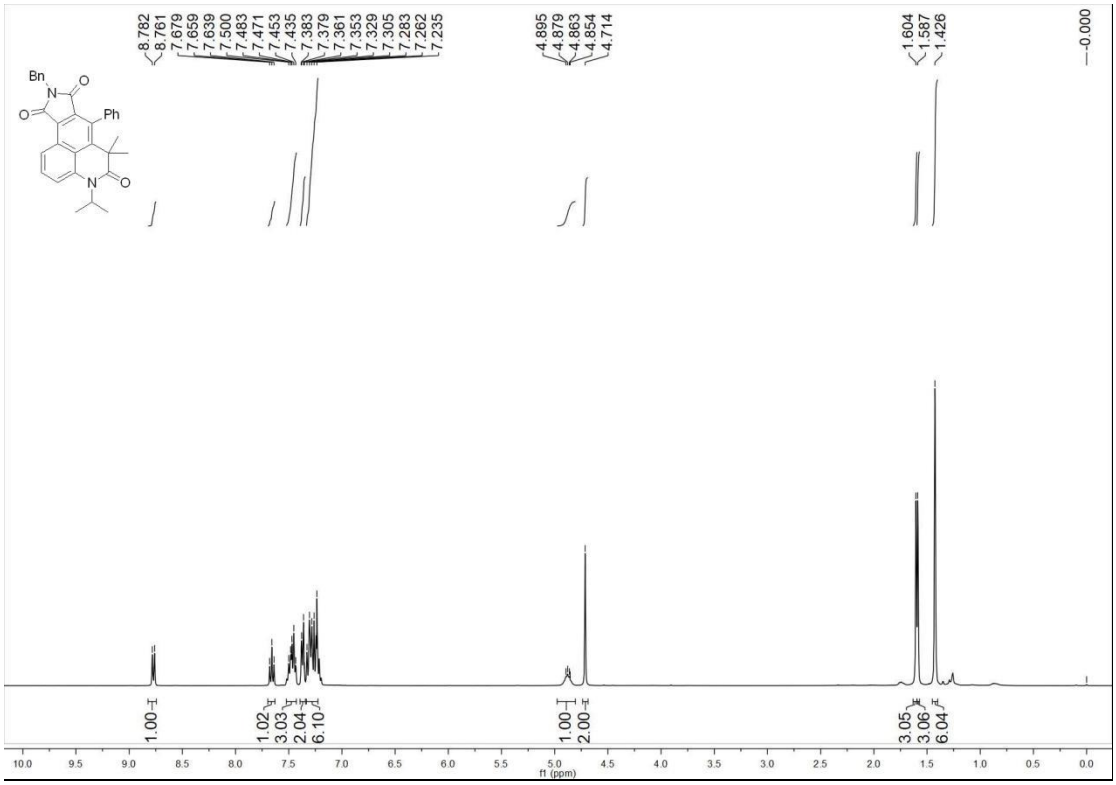


^{13}C NMR-spectrum (126 MHz, $CDCl_3$) of **3o**

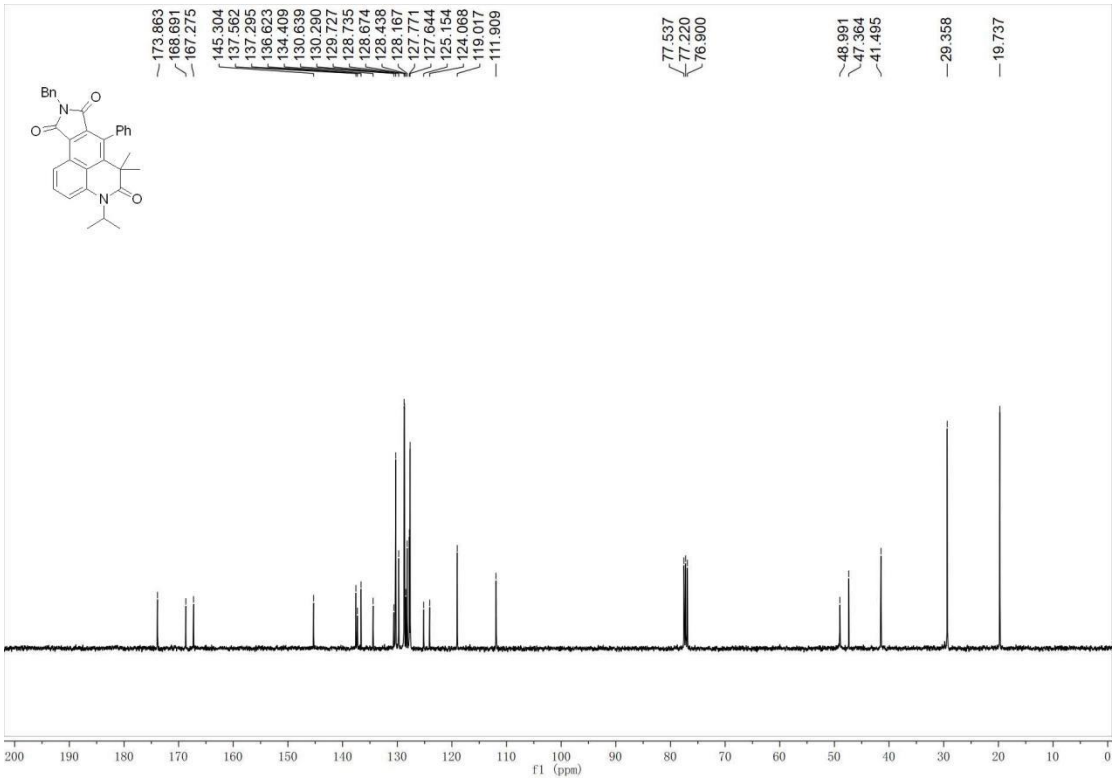


9-Benzyl-4-isopropyl-6,6-dimethyl-7-phenylisoindolo[6,5,4-*de*]quinoline-5,8,10(4*H*,6*H*,9*H*)-trione (3p)

^{1}H NMR-spectrum (400 MHz, $CDCl_3$) of **3p**

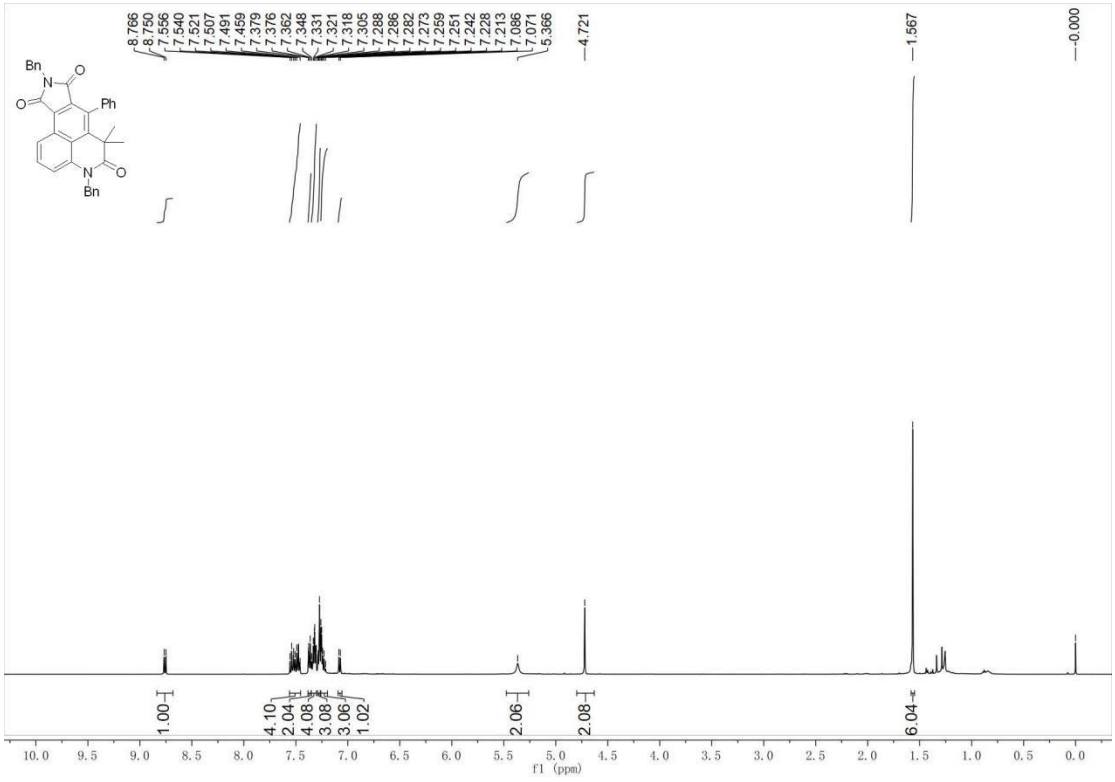


^{13}C NMR-spectrum (101 MHz, $CDCl_3$) of **3p**

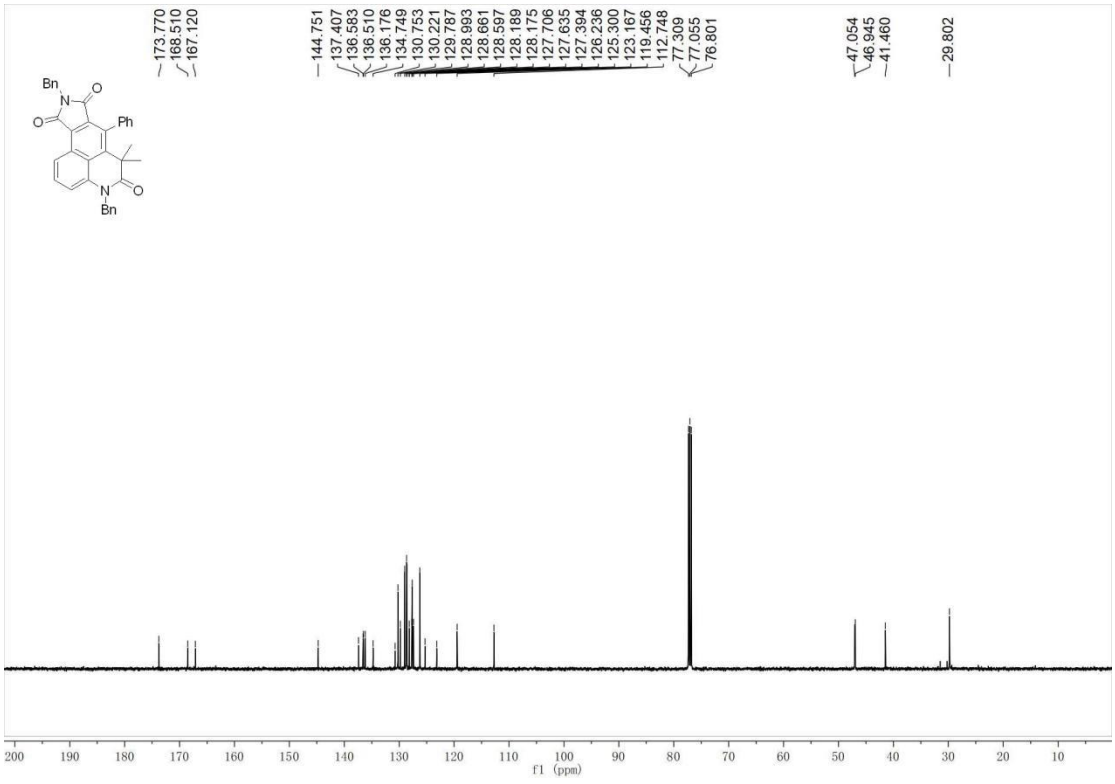


4,9-Dibenzyl-6,6-dimethyl-7-phenylisoindolo[6,5,4-*de*]quinoline-5,8,10(4*H*,6*H*,9*H*)-trione (3q)

^{1}H NMR-spectrum (500 MHz, $CDCl_3$) of **3q**

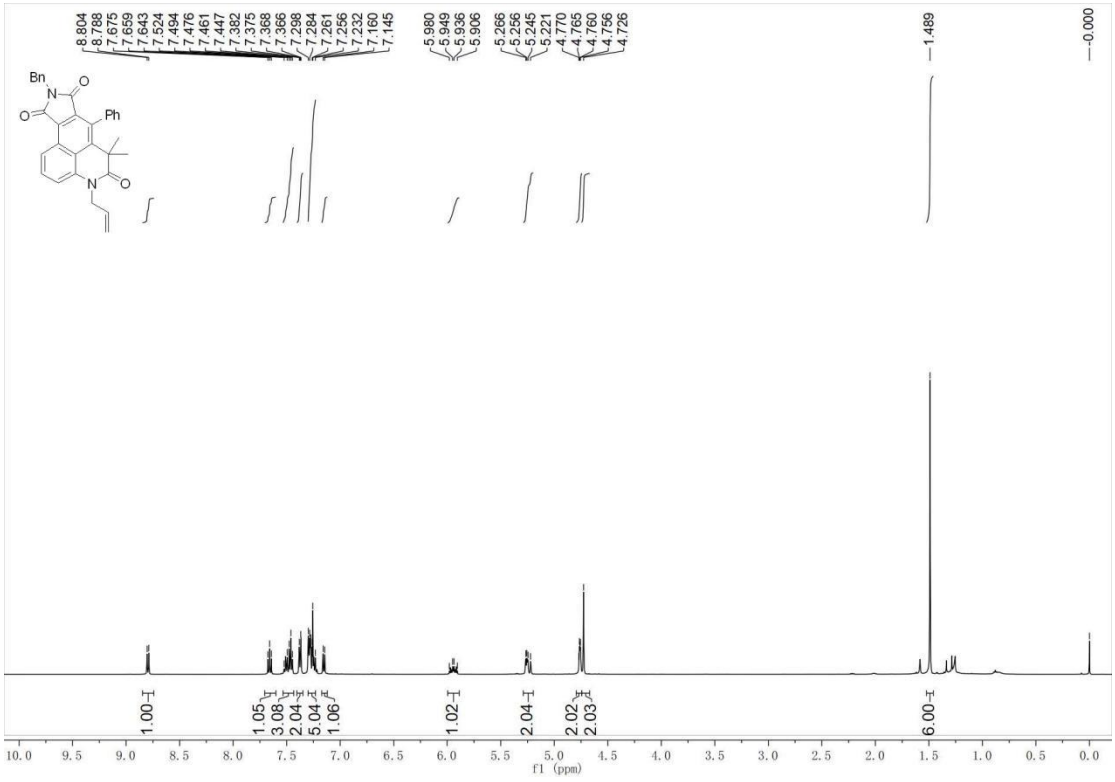


^{13}C NMR-spectrum (126 MHz, $CDCl_3$) of **3q**

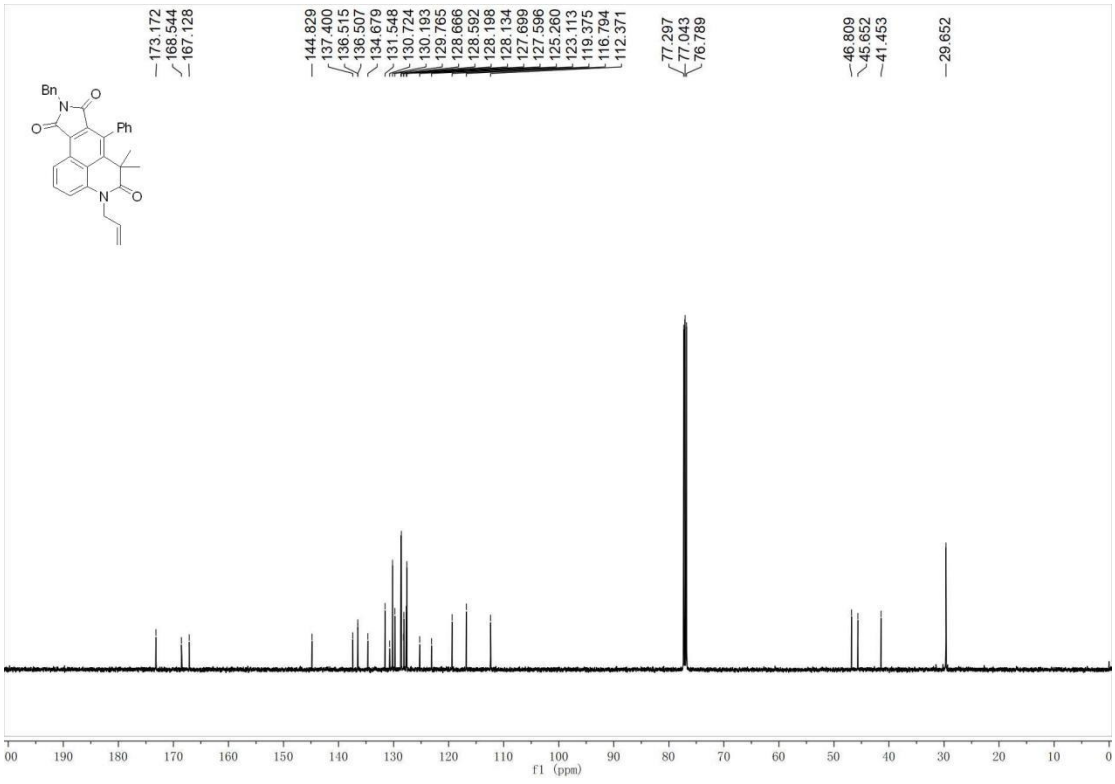


4-Allyl-9-benzyl-6,6-dimethyl-7-phenylisoindolo[6,5,4-*de*]quinoline-5,8,10(4*H*,6*H*,9*H*)-trione (3r)

^{1}H NMR-spectrum (500 MHz, $CDCl_3$) of **3r**

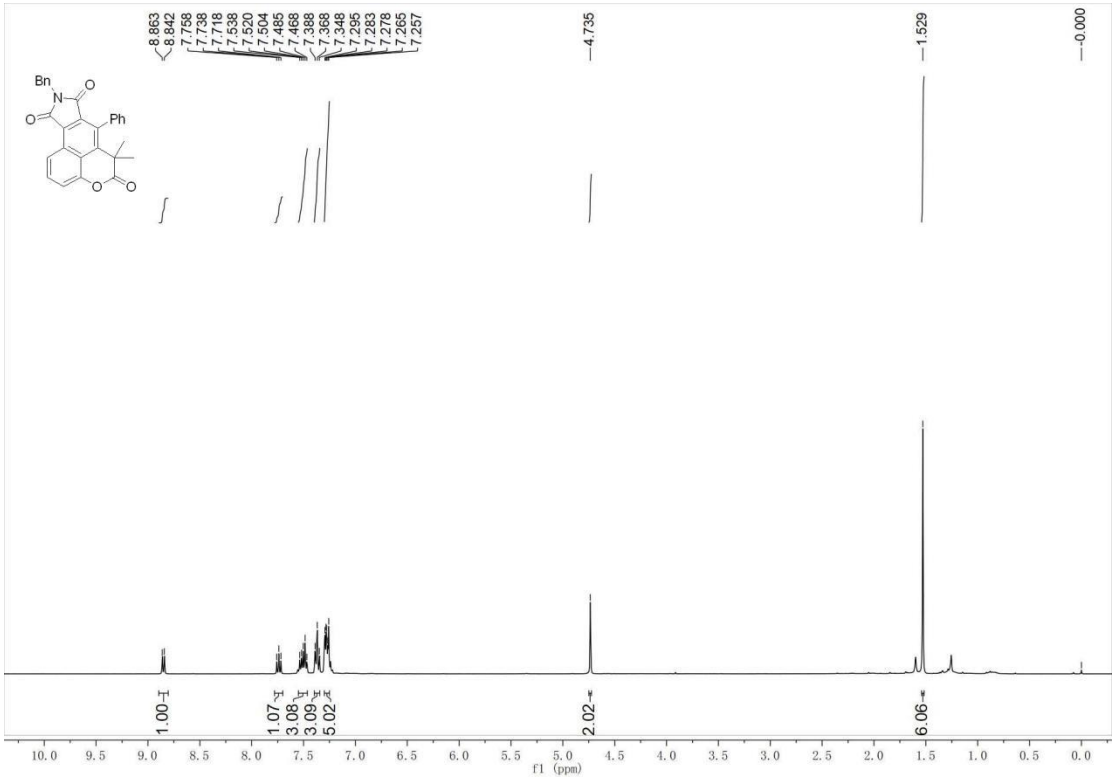


^{13}C NMR-spectrum (126 MHz, $CDCl_3$) of **3r**

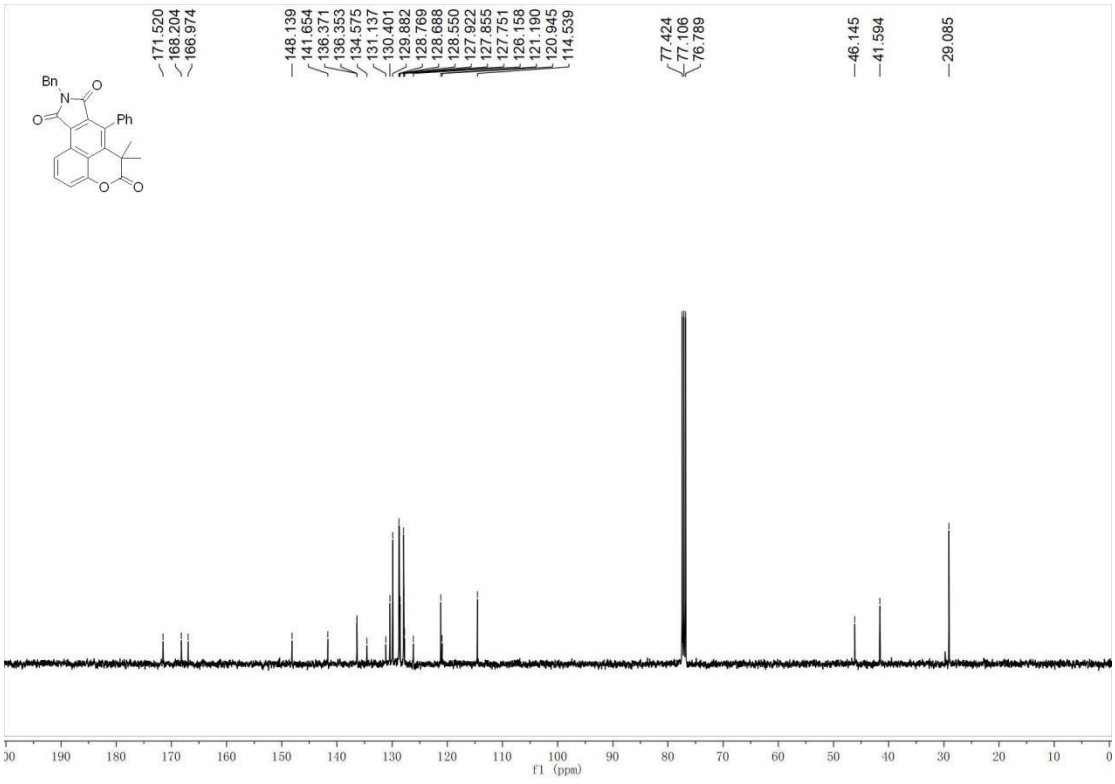


9-Benzyl-6,6-dimethyl-7-phenyl-5*H*-chromeno[5,4-*ef*]isoindole-5,8,10(6*H*,9*H*)-trione(3t)

^{1}H NMR-spectrum (400 MHz, $CDCl_3$) of **3t**

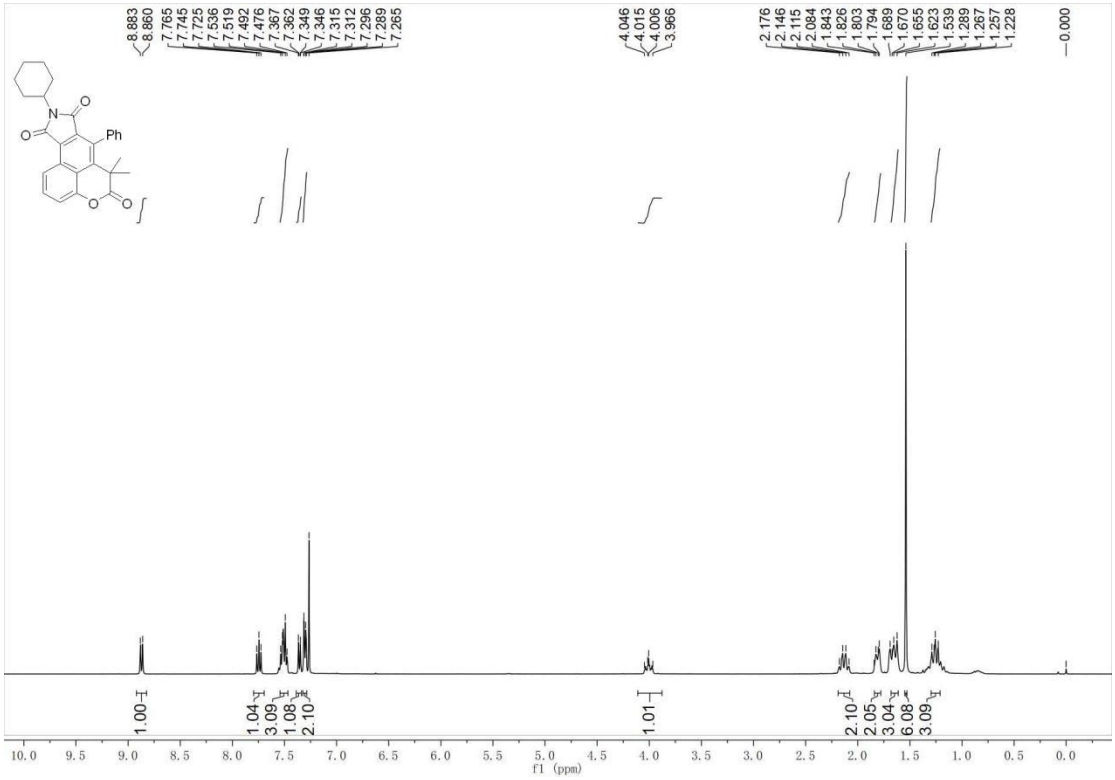


^{13}C NMR-spectrum (101 MHz, $CDCl_3$) of **3t**

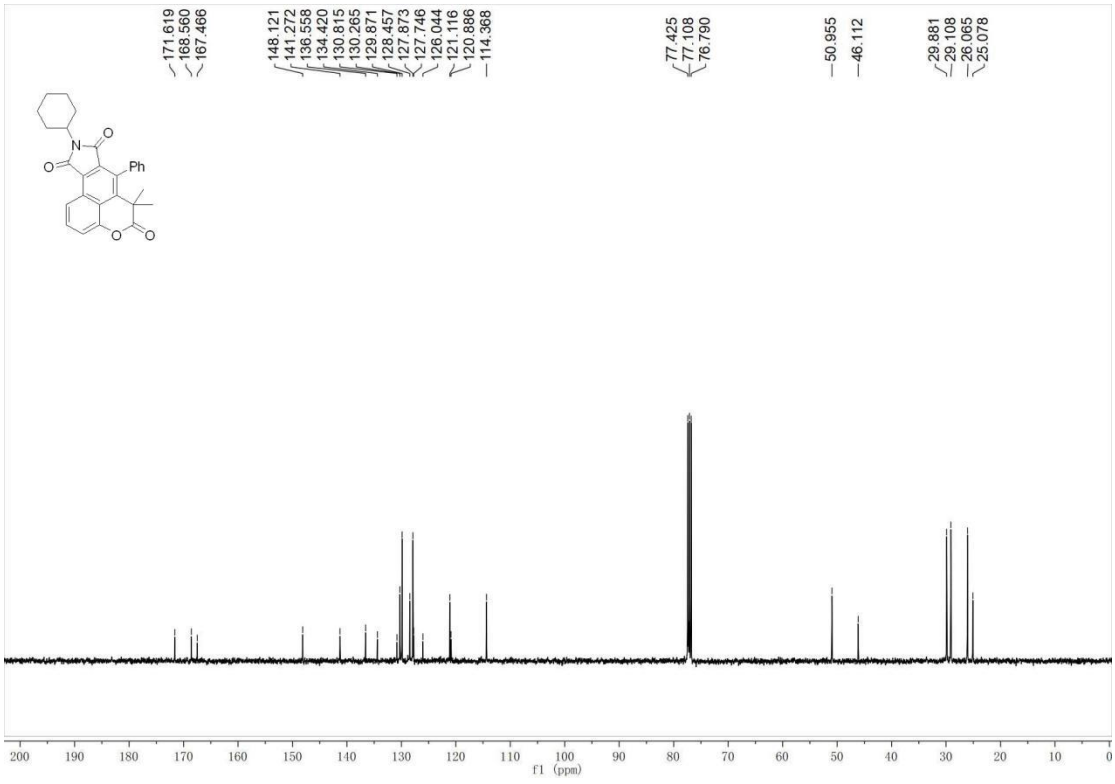


9-Cyclohexyl-6,6-dimethyl-7-phenyl-5*H*-chromeno[5,4-*ef*]isoindole-5,8,10(6*H*,9*H*)-trione (3u)

^{1}H NMR-spectrum (400 MHz, $CDCl_3$) of **3u**

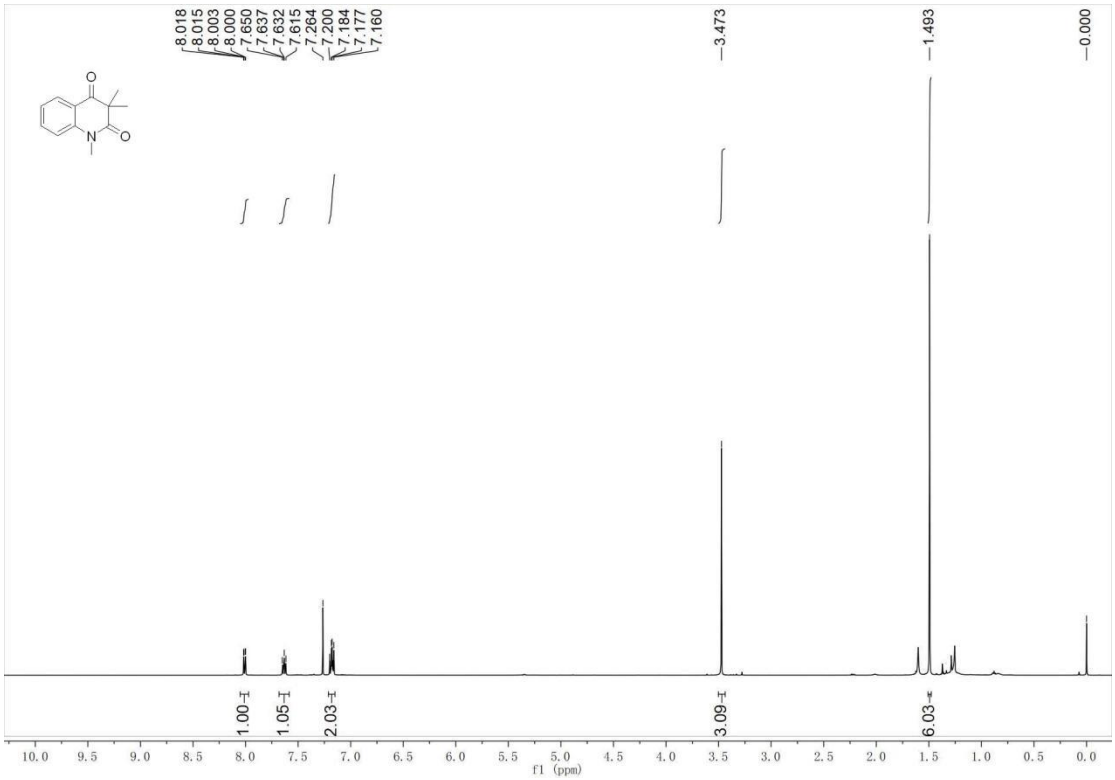


^{13}C NMR-spectrum (101 MHz, $CDCl_3$) of **3u**

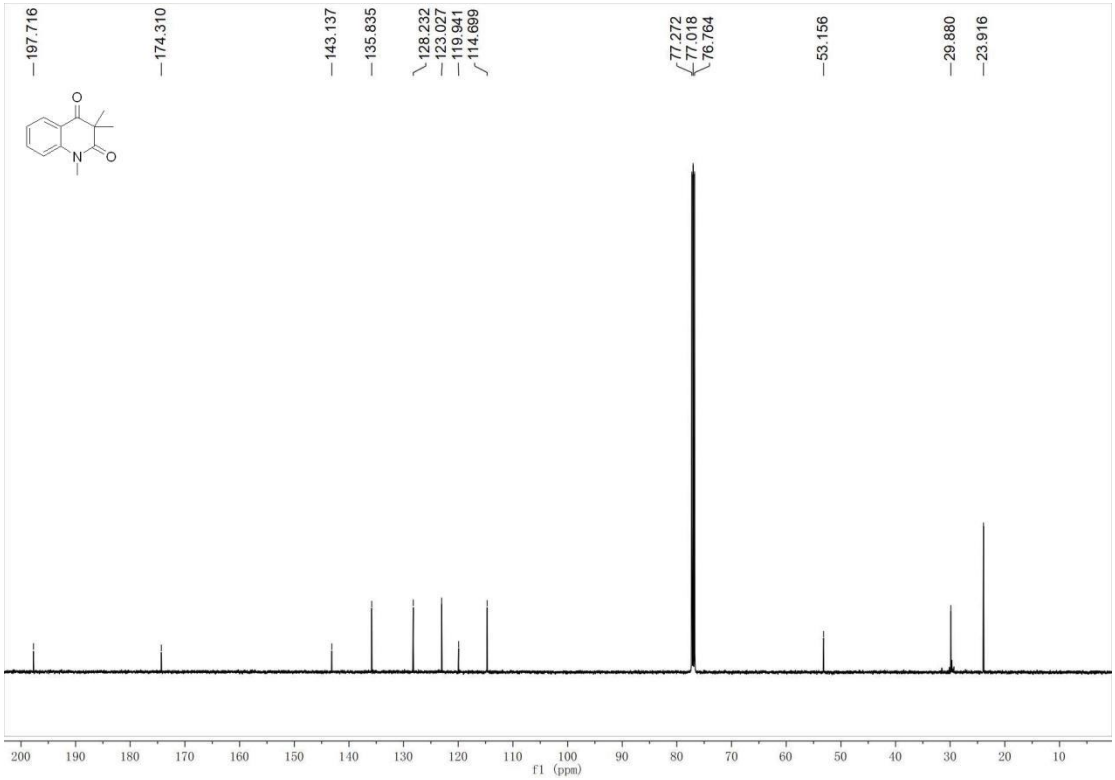


1,3,3-Trimethylquinoline-2,4(1*H*,3*H*)-dione (4a)

^{1}H NMR-spectrum (500 MHz, $CDCl_3$) of **4a**

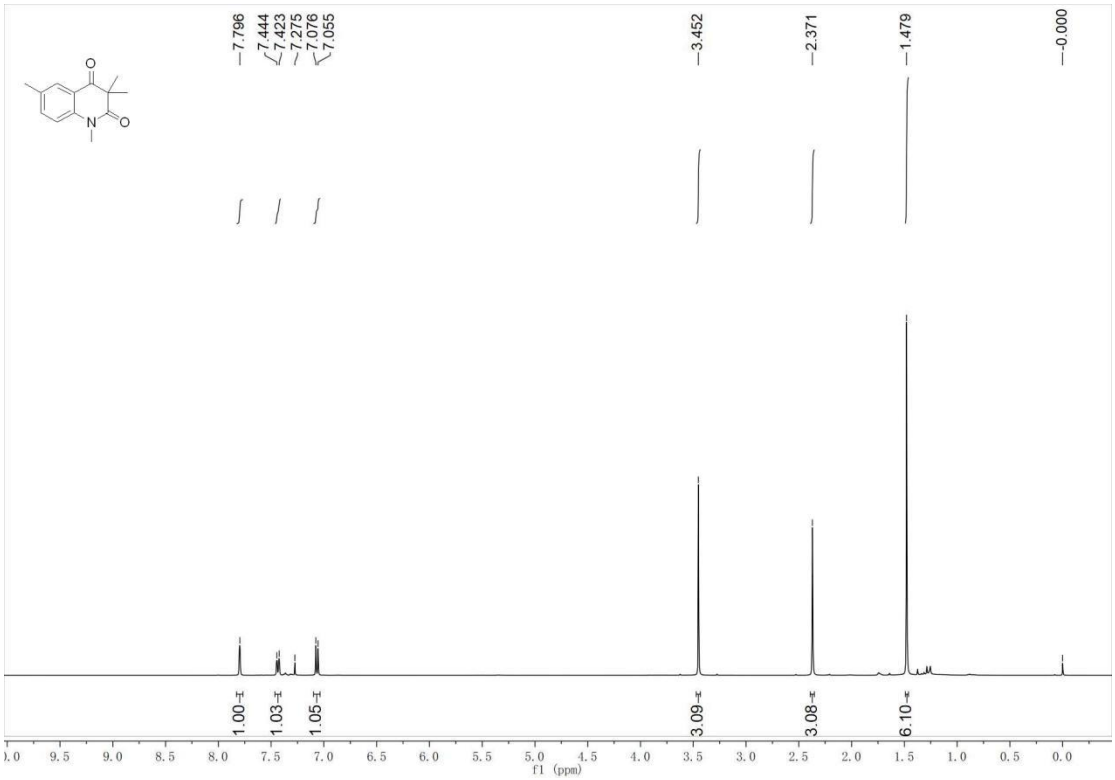


^{13}C NMR-spectrum (126 MHz, $CDCl_3$) of **4a**

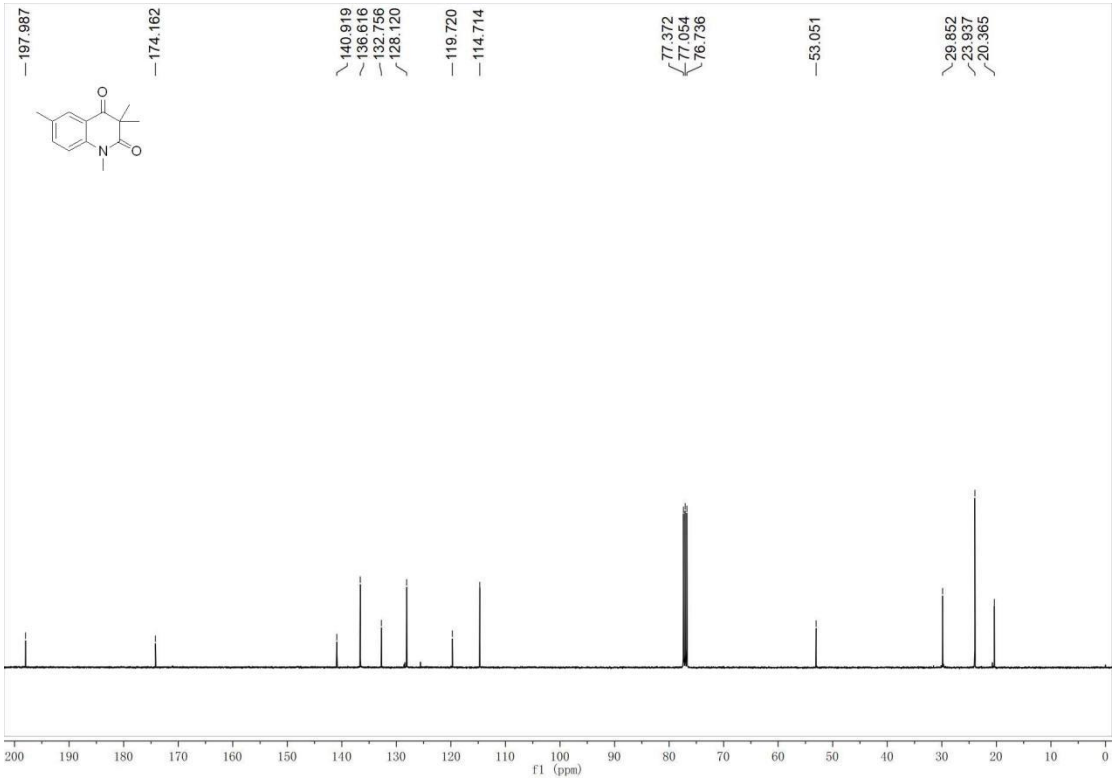


1,3,3,6-Tetramethylquinoline-2,4(1*H*,3*H*)-dione(4b)

^{1}H NMR-spectrum (400 MHz, $CDCl_3$) of **4b**

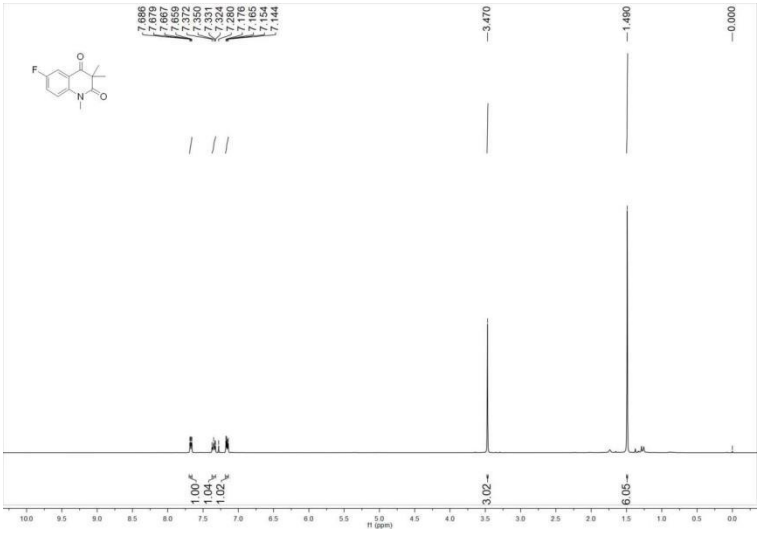


^{13}C NMR-spectrum (101 MHz, $CDCl_3$) of **4b**

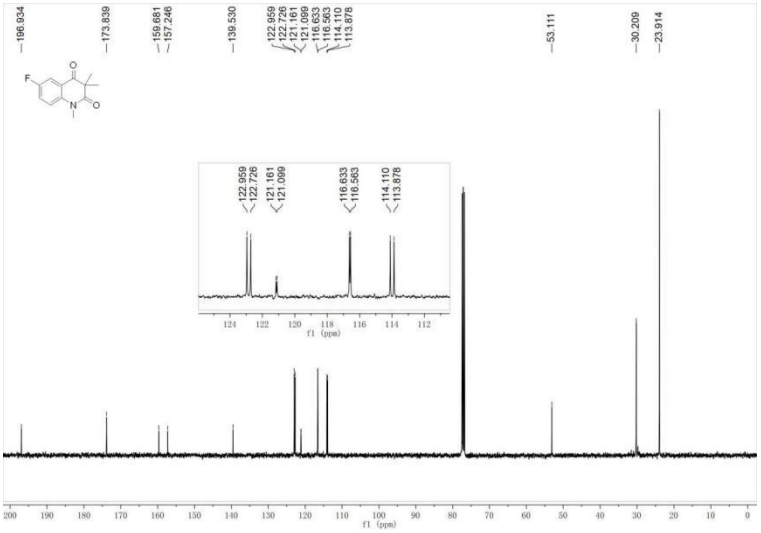


6-Fluoro-1,3,3-trimethylquinoline-2,4(1*H*,3*H*)-dione (4c)

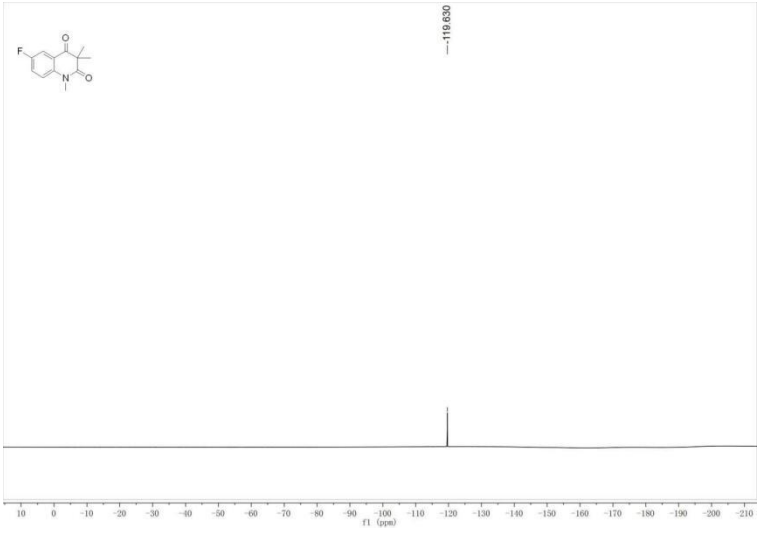
^{1}H NMR-spectrum (400 MHz, $CDCl_3$) of **4c**



^{13}C NMR-spectrum (101 MHz, $CDCl_3$) of **4c**

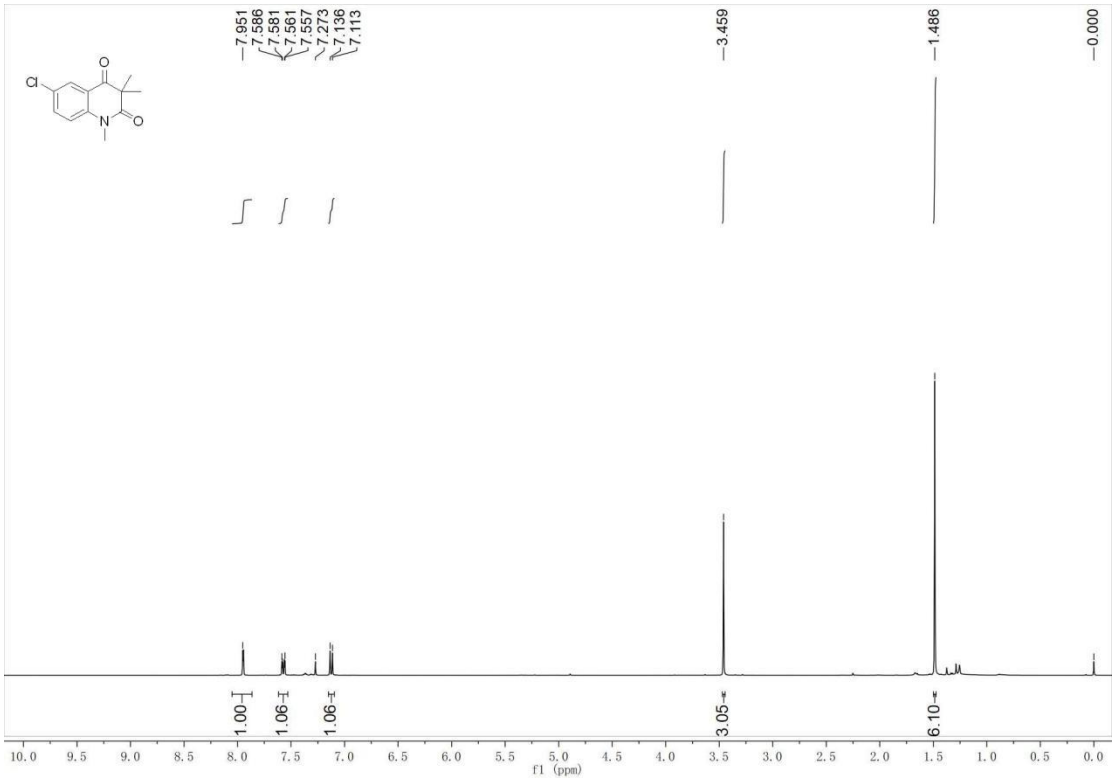


^{19}F NMR-spectrum (376 MHz, $CDCl_3$) of **4c**

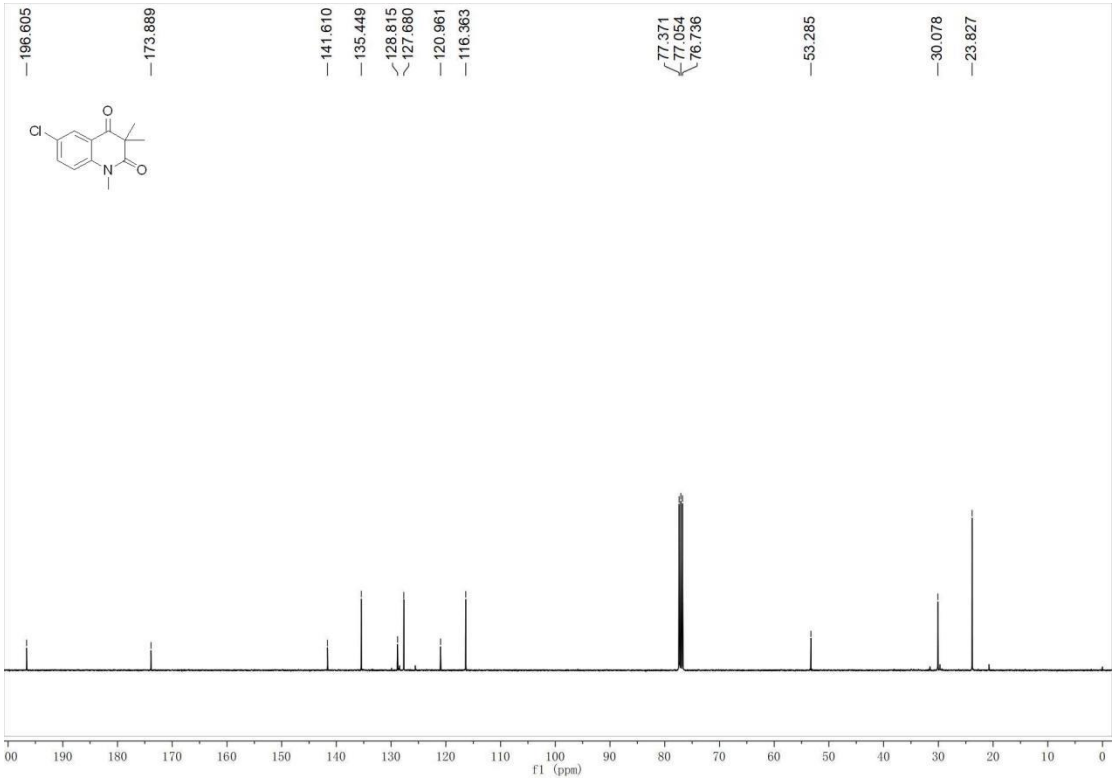


6-Chloro-1,3,3-trimethylquinoline-2,4(1*H*,3*H*)-dione (4d)

^{1}H NMR-spectrum (400 MHz, $CDCl_3$) of **4d**

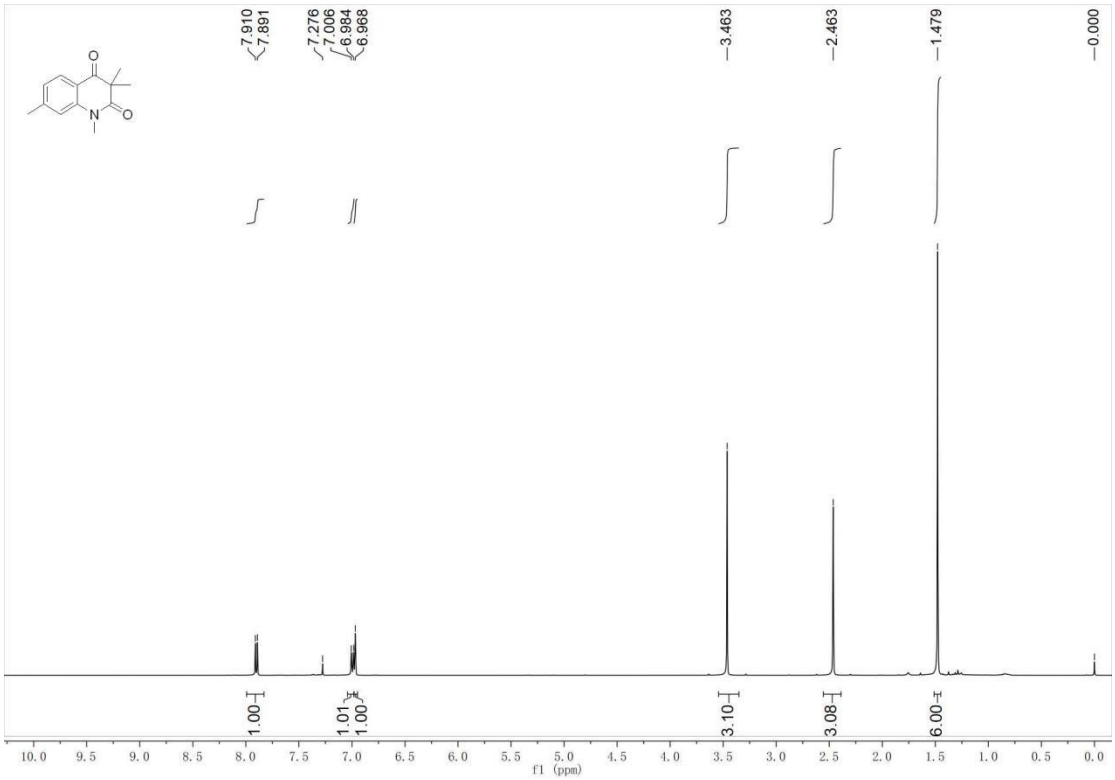


^{13}C NMR-spectrum (101 MHz, $CDCl_3$) of **4d**

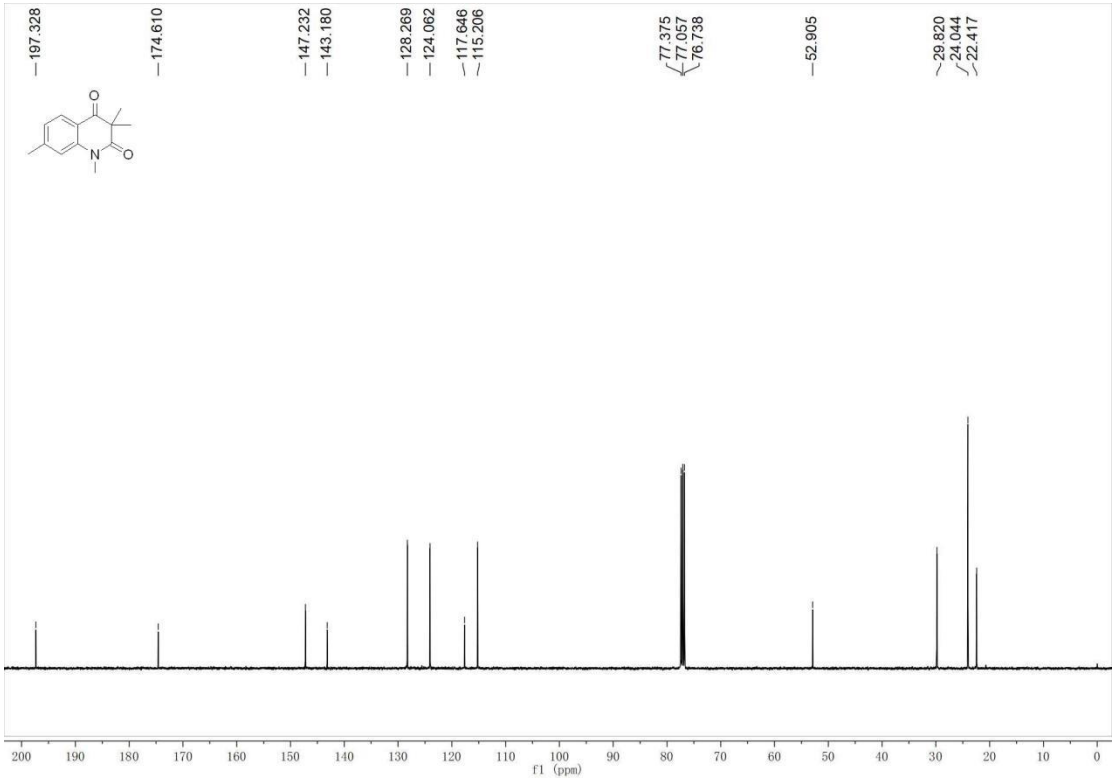


1,3,3,7-Tetramethylquinoline-2,4(1*H*,3*H*)-dione (4e)

^{1}H NMR-spectrum (400 MHz, $CDCl_3$) of **4e**

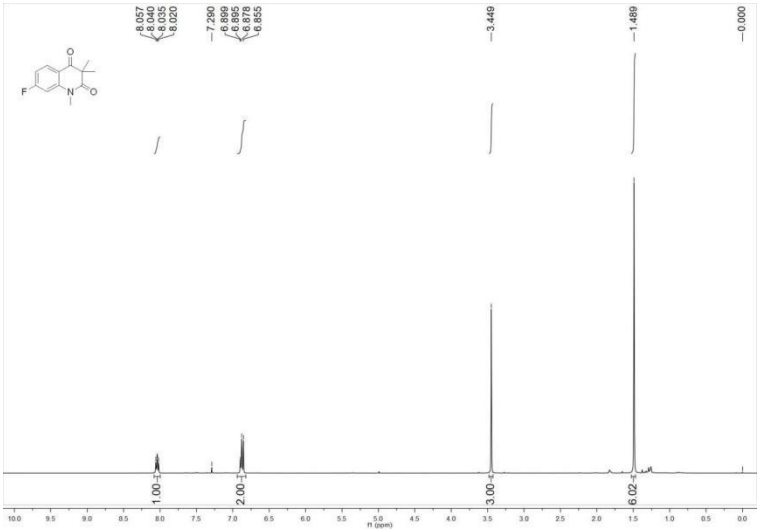


^{13}C NMR-spectrum (101 MHz, $CDCl_3$) of **4e**

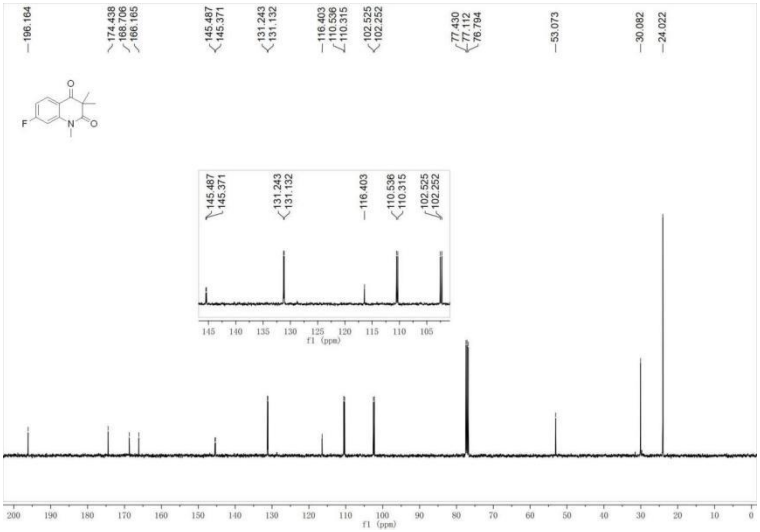


7-Fluoro-1,3,3-trimethylquinoline-2,4(1*H*,3*H*)-dione (4f)

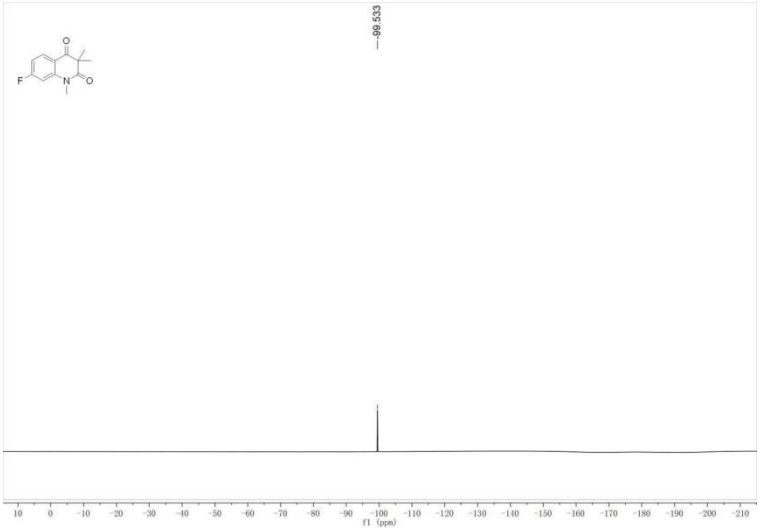
^{1}H NMR-spectrum (400 MHz, $CDCl_3$) of **4f**



^{13}C NMR-spectrum (101 MHz, $CDCl_3$) of **4f**

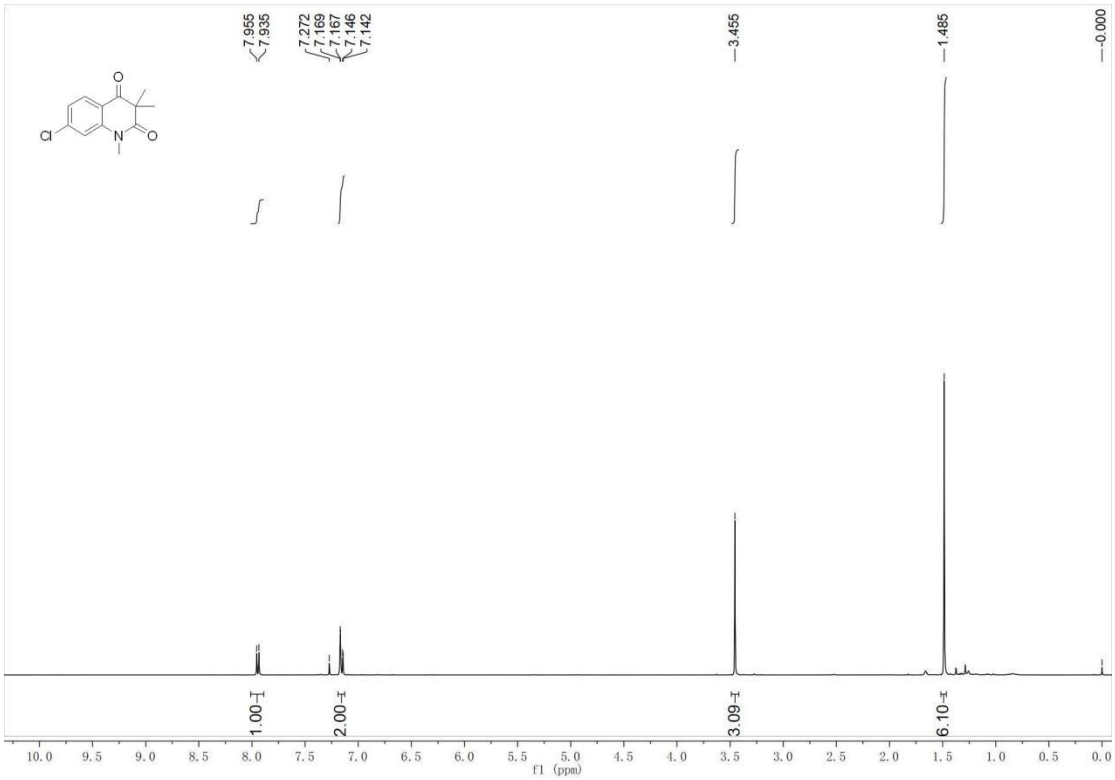


^{19}F NMR-spectrum (376 MHz, $CDCl_3$) of **4f**

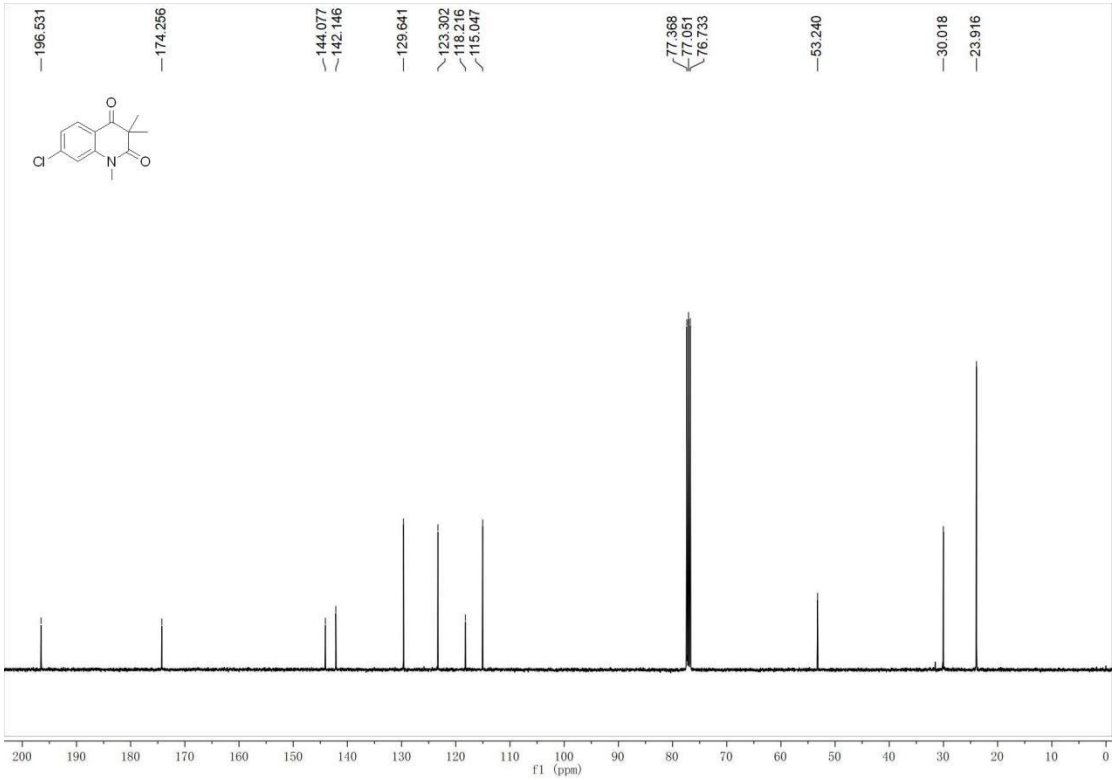


7-Chloro-1,3,3-trimethylquinoline-2,4(1*H*,3*H*)-dione (4g)

^{1}H NMR-spectrum (400 MHz, $CDCl_3$) of **4g**

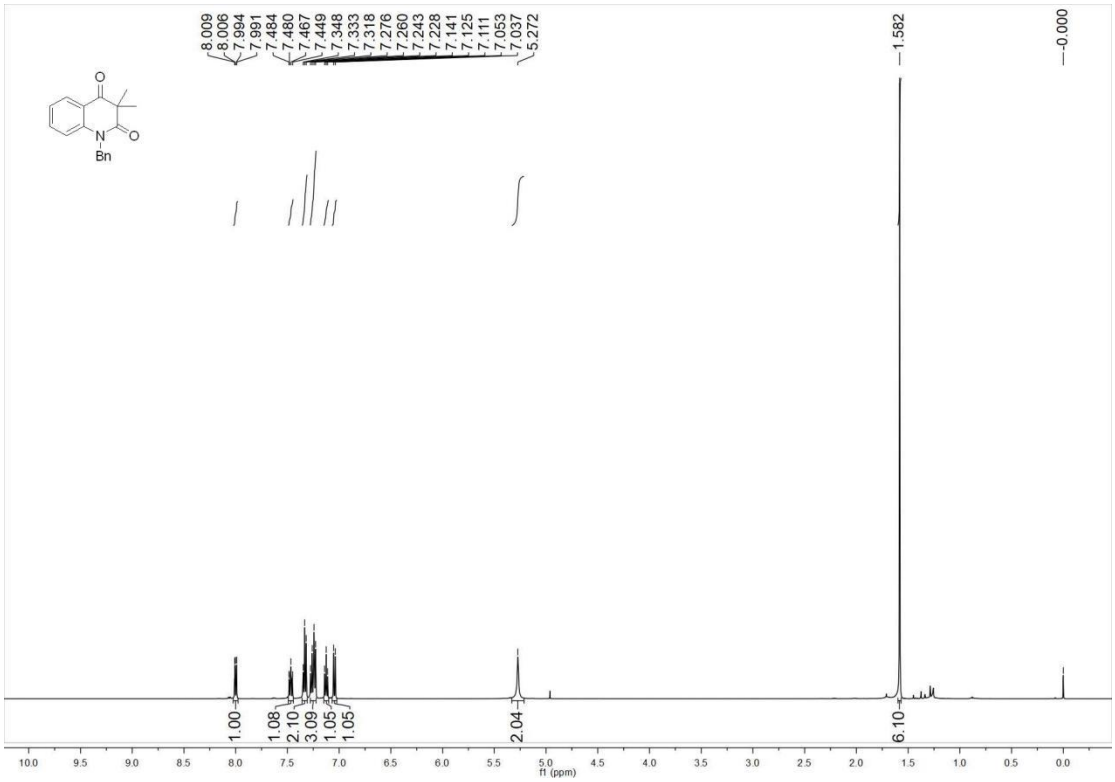


^{13}C NMR-spectrum (101 MHz, $CDCl_3$) of **4g**

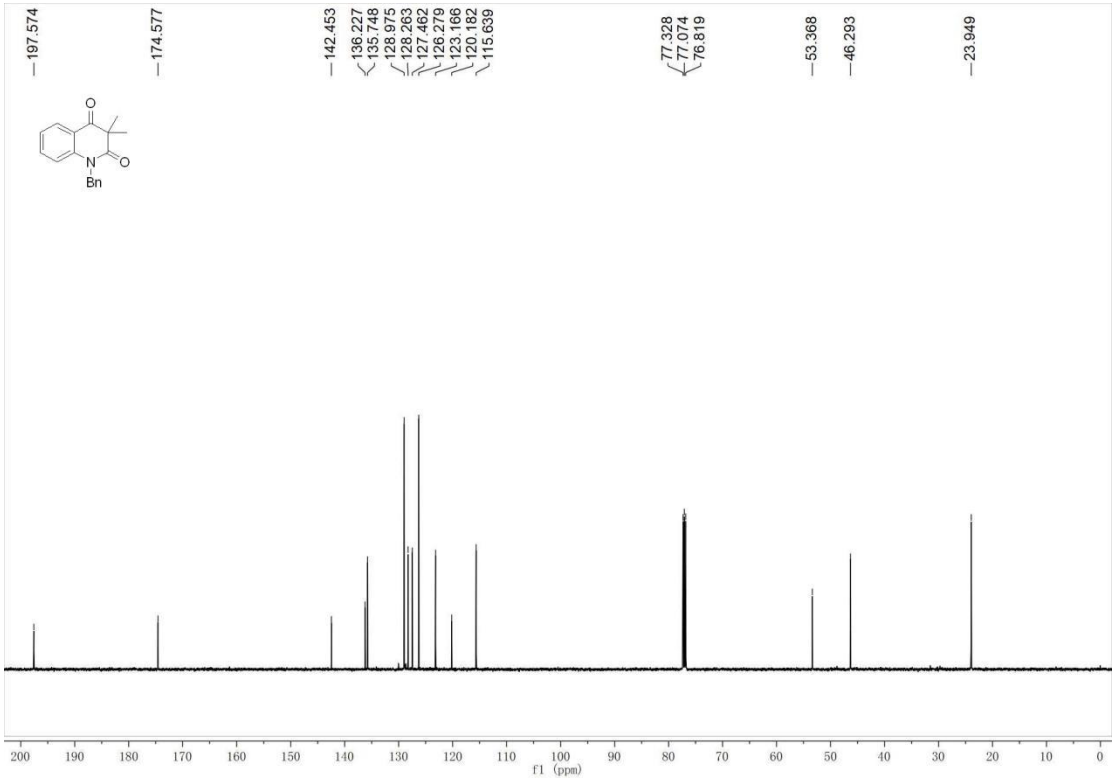


1-Benzyl-3,3-dimethylquinoline-2,4(1*H*,3*H*)-dione (4h)

^{1}H NMR-spectrum (500 MHz, $CDCl_3$) of **4h**

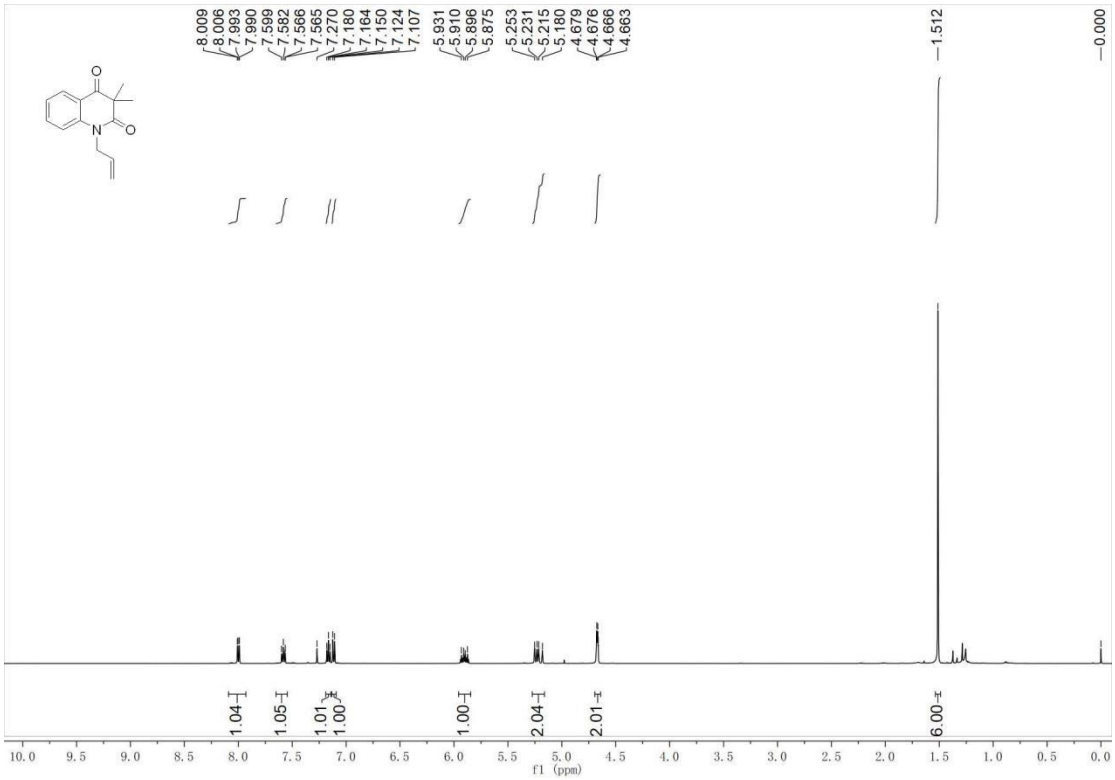


^{13}C NMR-spectrum (126 MHz, $CDCl_3$) of **4h**

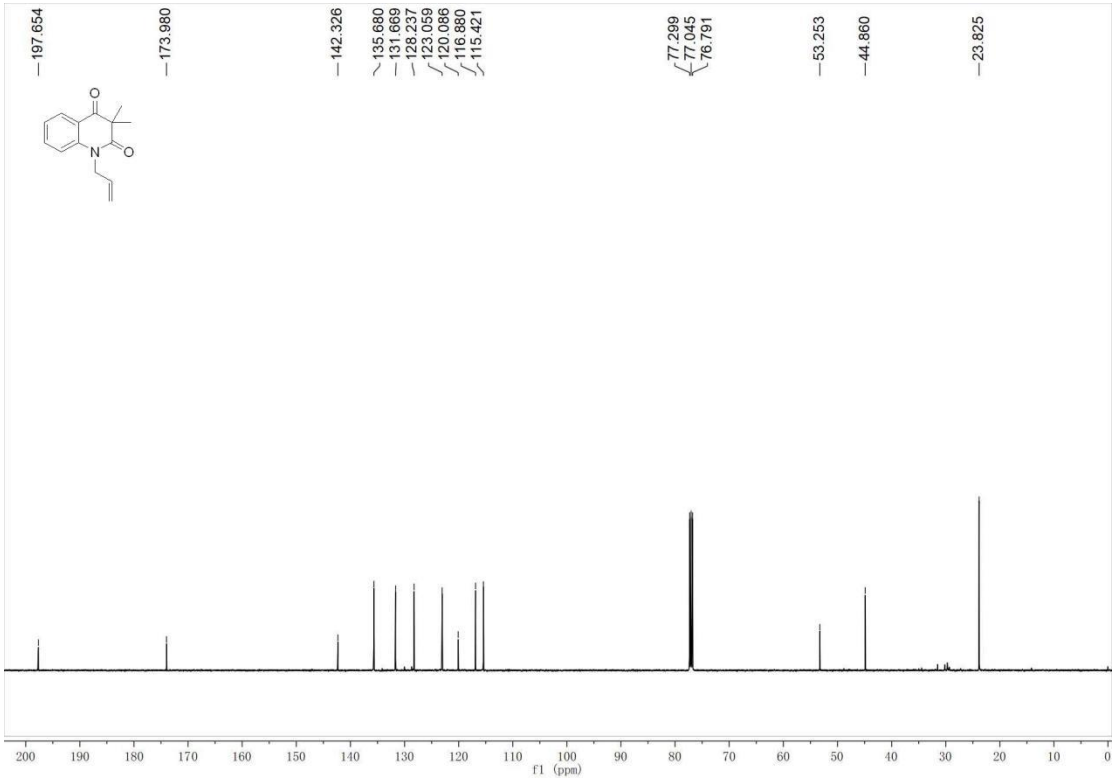


1-Allyl-3,3-dimethylquinoline-2,4(1*H*,3*H*)-dione (4i)

^{1}H NMR-spectrum (500 MHz, $CDCl_3$) of **4i**

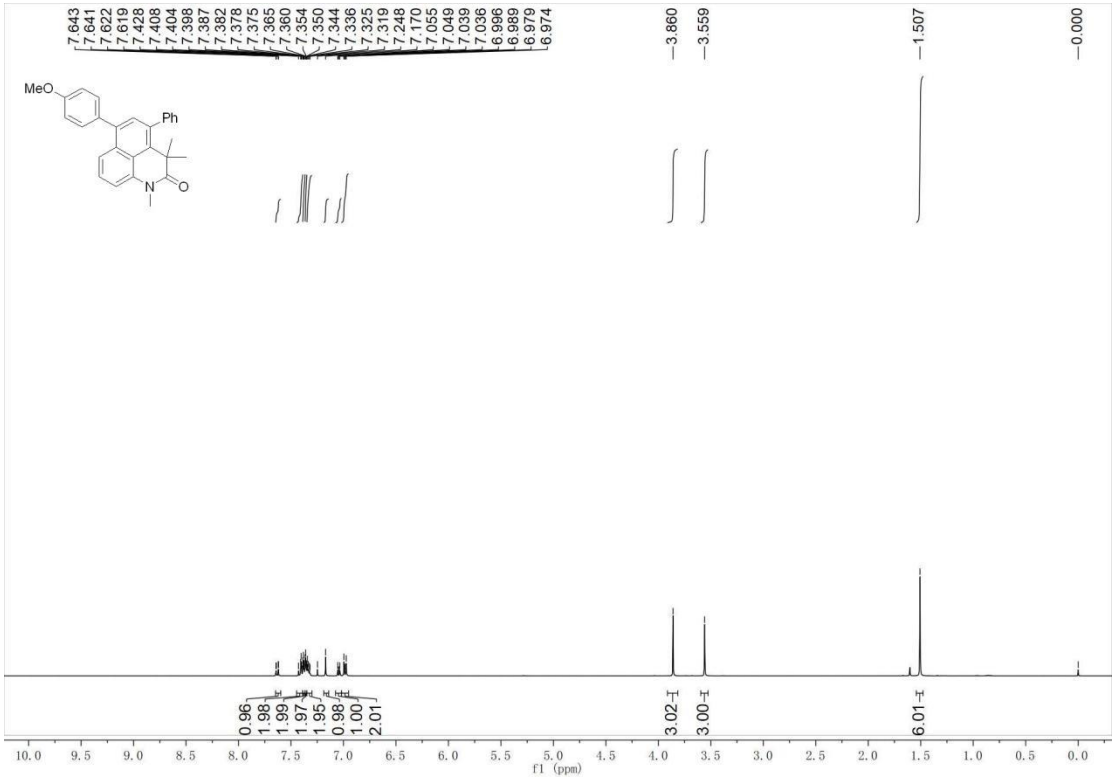


^{13}C NMR-spectrum (126 MHz, $CDCl_3$) of **4i**



6-(4-Methoxyphenyl)-1,3,3-trimethyl-4-phenyl-1*H*-benzo[*de*]quinolin-2(3*H*)-one (6a)

^{1}H NMR-spectrum (400 MHz, $CDCl_3$) of **6a**



^{13}C NMR-spectrum (101 MHz, $CDCl_3$) of **6a**