Electronic Supplementary Material (ESI) for ChemComm.

Palladium-Catalyzed Dearomatizative [2+2+1] Carboannulation of 1,7-Enynes with Aryl Diazonium Salts and H_2O: Facile Synthesis of Spirocyclohexadienone-Fused Cyclopenta[*c*]quinolin-4(5*H*)-ones

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Supporting Information

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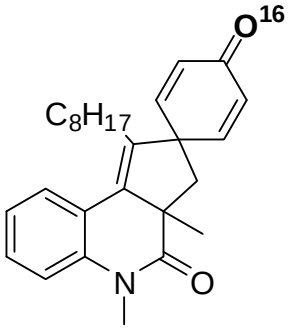
(A) Typical Experimental Procedure

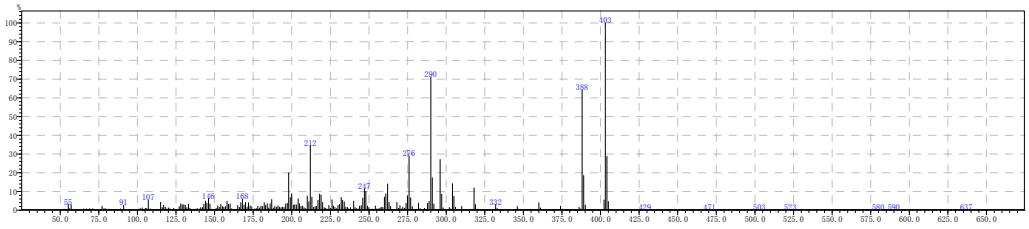
(a) Typical Experimental Procedure for $PdCl_2$-Catalyzed Dearomatizative [2+2+1] Carboannulation of 1,7-Enynes with Aryl Diazonium Salts and H2O:

To a Schlenk tube were added 1,7-enyne **1** (0.3 mmol), aryl diazonium salt **2** (0.6 mmol), $PdCl_2$ (10 mol%), Na_2CO_3 (2 equiv) and MeCN (2 mL). Then the tube was charged with argon, and was stirred at 80 ^oC for the indicated time until complete consumption of starting material as monitored by TLC analysis. After the reaction was finished, the reaction mixture was washed with brine. The aqueous phase was re-extracted with ethyl acetate. The combined organic extracts were dried over Na_2SO_4, concentrated in vacuum, and the resulting residue was purified by silica gel column chromatography (hexane/ethyl acetate = 5:1) to afford the desired products **3**.

(b) Figure S1 The O^{18}-Labelled Control Experiment:



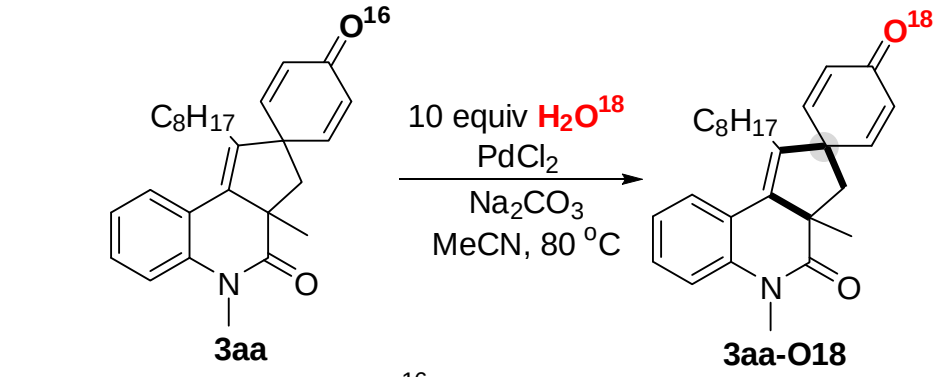
Chemical Formula: $C_{27}H_{33}NO_2$
Molecular Weight: 403



[MS Spectrum]
# of Peaks480
Raw Spectrum 30.320 (scan : 5365) Base Peak m/z 403.05 (Inten : 2,904,451)
Background No
Background Spectrum
m/z Absolute Intensity Relative Intensity

55.10	88910	3.06
56.10	24727	0.85
57.10	82678	2.85
77.05	62863	2.16
91.05	78079	2.69
107.00	155071	5.34
115.05	124811	4.30
144.05	143166	4.93
145.05	109936	3.79
146.00	182094	6.27
168.00	171178	5.89
197.00	107844	3.71
198.00	581201	20.01
199.00	197529	6.80
200.00	254615	8.77
201.00	80623	2.78
201.95	87390	3.01
202.95	81833	2.82
204.00	178162	6.13
210.00	220898	7.61
211.00	131818	4.54
212.00	1000756	34.46
213.00	203679	7.01
216.95	153715	5.29
217.95	248270	8.55
218.95	235023	8.09
219.95	122543	4.22
226.00	161506	5.56
231.95	199344	6.86
232.95	158600	5.46
233.95	127740	4.40
245.95	189150	6.51
247.00	335326	11.55
248.00	291902	10.05
259.95	205049	7.06
260.95	254002	8.75
262.00	407100	14.02
263.00	121617	4.19
274.95	224673	7.74
275.95	835130	28.75
277.00	191847	6.61
290.00	2061122	70.96
291.00	503876	17.35
292.00	98194	3.38
296.05	787257	27.11
297.05	247251	8.51
304.00	413498	14.24
305.00	216174	7.44
306.00	49172	1.69
310.05	61287	2.11
318.00	345330	11.89
388.05	1867112	64.28
389.05	536963	18.49
390.05	80043	2.76
402.15	160426	5.52
403.05	**2904451**	**100.00**
404.05	835017	28.75
405.05	**133736**	**4.60**
406.05	16067	0.55

The GC-MS analysis results showed that no exchange between substrate **3aa** and H_2O^{18}.



3aa

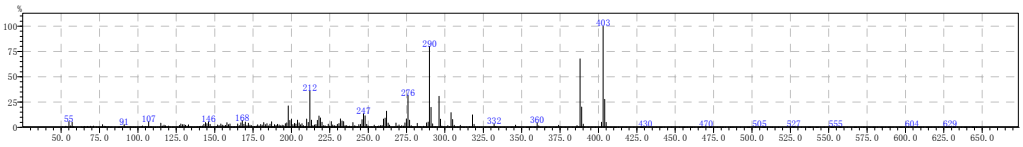
Chemical Formula: $C_{27}H_{33}N^{16}O_2$

Molecular Weight: 403

3aa-O18

Chemical Formula: $C_{27}H_{33}N^{16}O^{18}O$

Molecular Weight: 405



[MS Spectrum]

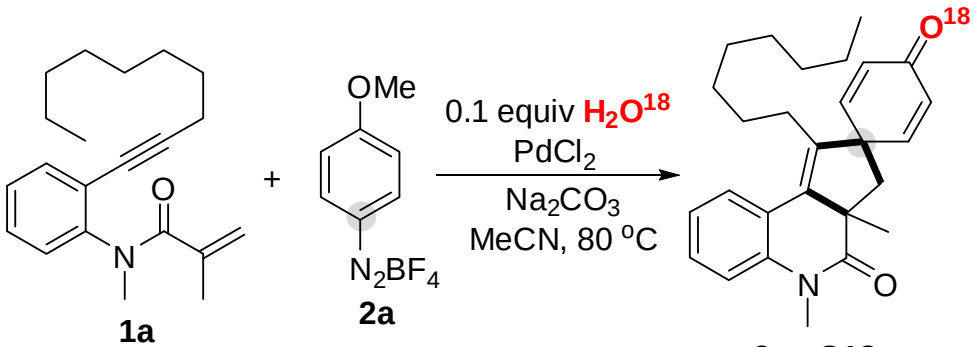
# of Peaks446

Raw Spectrum 29.920 (scan : 5285) Base Peak m/z 403.10 (Inten : 553,969)

Background No Background Spectrum

m/z	Absolute Intensity	Relative Intensity	m/z	Absolute Intensity	Relative Intensity	m/z	Absolute Intensity	Relative Intensity
55.10	31044	5.60	216.95	38169	6.89	276.95	39377	7.11
56.10	7830	1.41	217.95	62441	11.27	288.00	24841	4.48
57.10	28506	5.15	218.95	52161	9.42	289.00	29074	5.25
77.05	15068	2.72	219.95	28486	5.14	290.00	443028	79.97
91.00	15103	2.73	231.95	45898	8.29	291.00	109942	19.85
107.00	30678	5.54	232.95	35225	6.36	292.00	19948	3.60
115.00	22919	4.14	234.00	31514	5.69	296.10	169937	30.68
165.00	18674	3.37	244.00	14802	2.67	297.05	44736	8.08
167.00	25423	4.59	244.95	16268	2.94	304.00	80540	14.54
168.00	36697	6.62	246.00	42690	7.71	305.00	43102	7.78
169.00	17006	3.07	247.00	74666	13.48	318.00	68150	12.30
170.00	29273	5.28	248.00	63713	11.50	388.05	375107	67.71
196.00	20300	3.66	249.00	17306	3.12	389.05	111733	20.17
197.00	24786	4.47	259.95	45351	8.19	390.05	17772	3.21
198.00	117830	21.27	260.95	51140	9.23	402.05	28090	5.07
199.00	37463	6.76	262.00	88778	16.03	**403.10**	**553969**	**100.00**
200.00	45518	8.22	263.00	23694	4.28	404.05	153714	27.75
209.95	45658	8.24	264.00	12569	2.27	**405.05**	**27362**	**4.94**
211.00	27586	4.98	273.95	24466	4.42	406.05	3291	0.59
212.00	199551	36.02	274.95	46015	8.31	408.10	865	0.16
213.00	39825	7.19	275.95	174096	31.43			

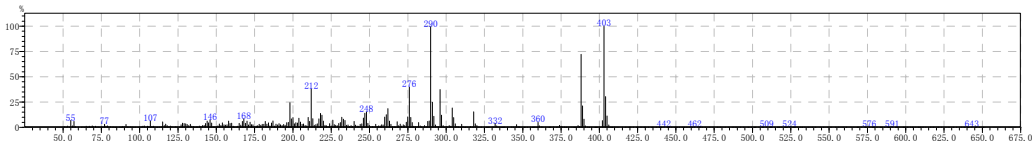
The GC-MS analysis results showed that the amount of O^{18} atom was increased in product **3aa-O18**.



1a **2a** **3aa-O18**

Chemical Formula: $C_{27}H_{33}N^{16}O^{18}O$

Molecular Weight: 405



[MS Spectrum]

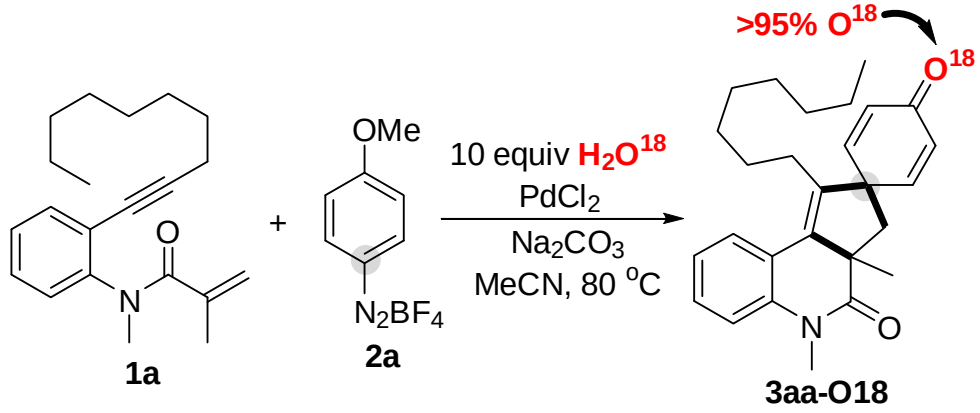
# of Peaks 399

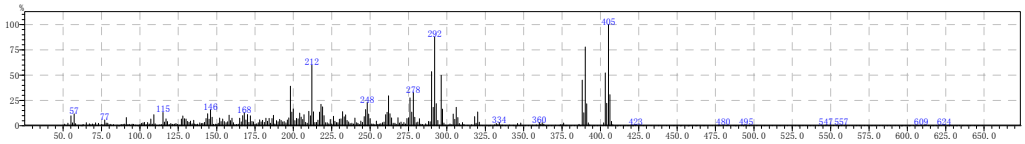
Raw Spectrum 29.935 (scan : 5288) Base Peak m/z 403.05 (Inten : 584,820)

Background 29.695 (scan : 5240)

m/z	Absolute Intensity	Relative Intensity	m/z	Absolute Intensity	Relative Intensity	m/z	Absolute Intensity	Relative Intensity
55.05	38909	6.65	218.95	69715	11.92	289.95	579596	99.11
56.10	8454	1.45	219.95	36300	6.21	291.00	145320	24.85
57.10	33160	5.67	220.95	11745	2.01	292.00	63633	10.88
77.00	14688	2.51	226.00	39970	6.83	293.00	13102	2.24
91.05	15096	2.58	230.95	27276	4.66	296.05	218807	37.41
107.00	35894	6.14	231.95	58637	10.03	297.05	70778	12.10
115.00	30109	5.15	232.95	46419	7.94	304.00	112404	19.22
196.00	26244	4.49	233.95	39570	6.77	305.00	55846	9.55
197.00	29065	4.97	240.00	34202	5.85	306.00	20790	3.55
198.00	141424	24.18	240.95	12390	2.12	318.00	89196	15.25
199.00	48452	8.28	245.95	52812	9.03	319.00	20625	3.53
200.00	56684	9.69	246.95	82254	14.06	388.05	421872	72.14
203.95	51553	8.82	247.95	87501	14.96	389.05	124287	21.25
204.95	30600	5.23	259.95	59580	10.19	390.05	46104	7.88
210.00	57078	9.76	260.95	72096	12.33	402.05	38011	6.50
211.00	33341	5.70	262.00	109178	18.67	**403.05**	**584820**	**100.00**
211.95	221586	37.89	263.00	35915	6.14	404.05	177430	30.34
213.00	48432	8.28	263.95	17681	3.02	**405.05**	**65745**	**11.24**
213.95	12271	2.10	274.95	60348	10.32	406.10	13863	2.37
216.95	48820	8.35	275.95	231172	39.53	**407.10**	**1427**	**0.24**
217.95	79013	13.51	276.95	57064	9.76	408.10	321	0.05

The GC-MS analysis results showed that product **3aa-O18** contained >95% O^{18} atom.





[MS Spectrum]

# of Peaks414

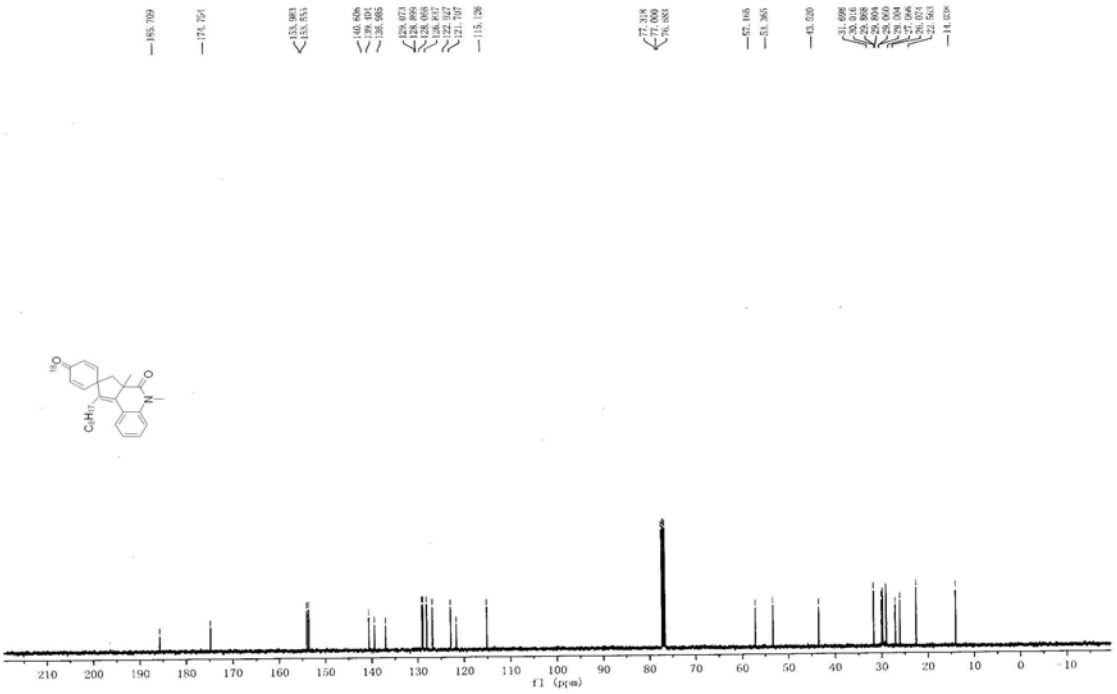
Raw Spectrum 29.750 (scan : 5251) Base Peak m/z 405.20 (Inten : 152,320)

Background 29.540 (scan : 5209)

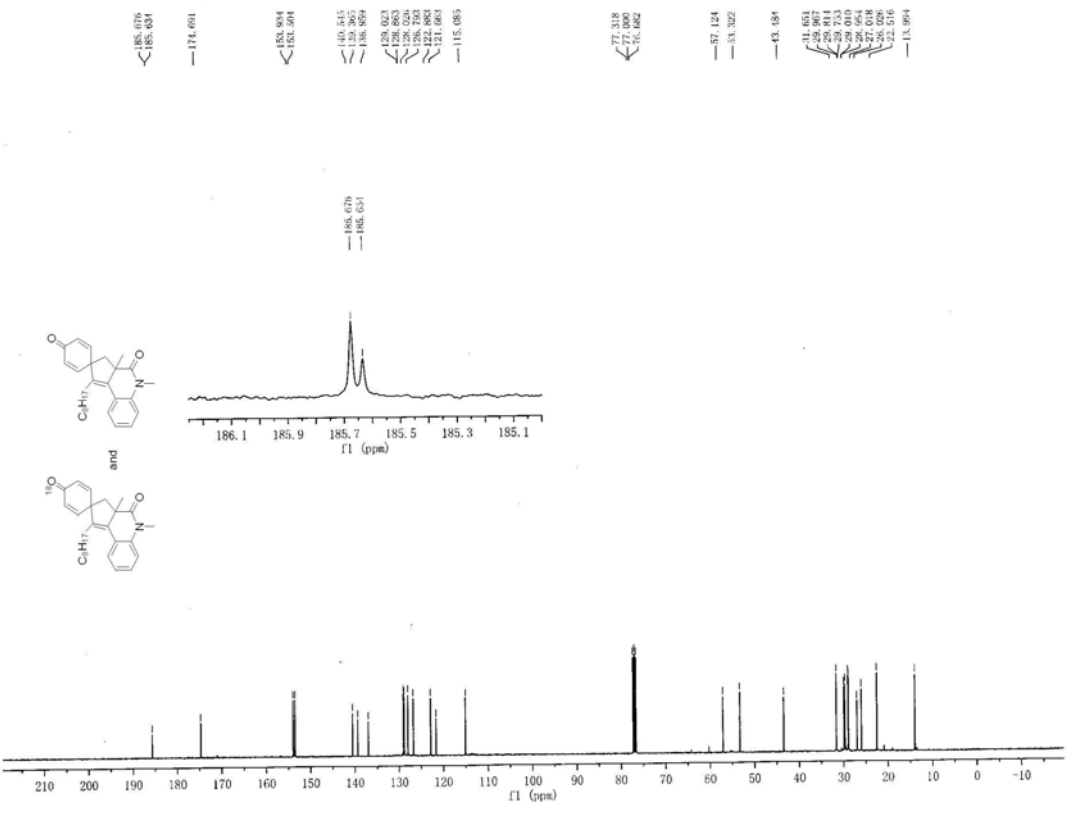
m/z	Absolute Intensity	Relative Intensity	m/z	Absolute Intensity	Relative Intensity	m/z	Absolute Intensity	Relative Intensity
55.10	14489	9.51	212.05	91285	59.93	278.10	49683	32.62
56.10	4322	2.84	213.00	20291	13.32	279.10	12684	8.33
57.10	17040	11.19	217.05	20461	13.43	282.10	10612	6.97
91.10	10785	7.08	218.00	31667	20.79	290.05	81345	53.40
109.05	15914	10.45	219.00	28519	18.72	291.10	27921	18.33
115.05	20045	13.16	220.00	15281	10.03	292.05	134114	88.05
144.10	17392	11.42	226.10	13696	8.99	293.10	32796	21.53
146.00	23677	15.54	232.00	21198	13.92	296.20	76102	49.96
158.10	15914	10.45	233.05	12909	8.47	297.15	25009	16.42
167.00	15216	9.99	234.05	16373	10.75	304.10	17855	11.72
168.00	19767	12.98	240.10	11515	7.56	306.10	27921	18.33
170.10	16815	11.04	246.10	13573	8.91	320.10	20040	13.16
186.05	10398	6.83	247.10	24487	16.08	388.10	68794	45.16
187.00	15729	10.33	248.10	34296	22.52	389.15	19599	12.87
197.05	11848	7.78	249.05	17727	11.64	390.15	118407	77.74
198.10	59472	39.04	250.00	10630	6.98	391.15	33074	21.71
199.05	20321	13.34	260.10	16340	10.73	**403.20**	**79982**	**52.51**
200.00	25588	16.80	261.05	20169	13.24	404.15	33845	22.22
204.05	18699	12.28	262.05	45160	29.65	**405.20**	**152320**	**100.00**
205.00	13282	8.72	263.00	17367	11.40	406.20	46929	30.81
210.05	21906	14.38	276.00	42030	27.59	**407.20**	**57653.78**	
211.05	14357	9.43	277.05	20393	13.39	408.05	14760.97	

^{13}C NMR spectra for product 3aa-O18 and a mixture of 3aa/3aa-O18

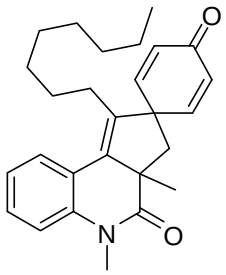
3aa-^{18}O:



3aa and 3aa-^{18}O:

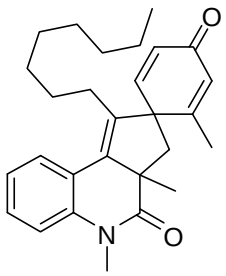


(B) Analytical data



3a',5'-Dimethyl-1'-octyl-3',3a'-dihydrospiro[cyclohexa[2,5]diene-1,2'-cyclopenta[*c*]quinoline]-4,4'(*5'H*)-dione (3aa):

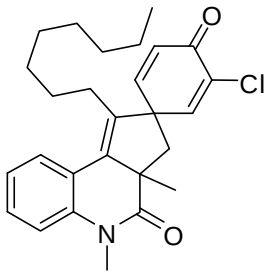
Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.41 (d, *J* = 7.6 Hz, 1H), 7.35 (t, *J* = 6.8 Hz, 1H), 7.15-7.08 (m, 2H), 6.90 (d, *J* = 10.0 Hz, 1H), 6.68 (d, *J* = 10.0 Hz, 1H), 6.33-6.27 (m, 2H), 3.39 (s, 3H), 2.88 (d, *J* = 14.8 Hz, 1H), 2.10 (d, *J* = 14.4 Hz, 1H), 2.08-2.00 (m, 2H), 1.30 (s, 3H), 1.27-1.20 (m, 12H), 0.86 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 185.8, 174.8, 154.0, 153.6, 140.6, 139.4, 137.0, 129.1, 128.9, 128.1, 126.9, 123.0, 121.7, 115.2, 57.2, 53.4, 43.5, 31.7, 30.1, 29.8, 29.7, 29.1, 29.0, 27.1, 26.1, 22.6, 14.1; IR (KBr, cm^{-1}): 1671, 1625; LRMS (EI 70 ev) *m*/z (%): 404 (M^++1, 29), 403 (M^+, 100), 388 (64), 290 (71); HRMS (ESI) for $C_{27}H_{34}NO_2$ ($[M+H]^+$): calcd 404.2584, found 404.2574.



2,3a',5'-Trimethyl-1'-octyl-3',3a'-dihydrospiro[cyclohexa[2,5]diene-1,2'-cyclopenta[*c*]quinoline]-4,4'(*5'H*)-dione (3ab):

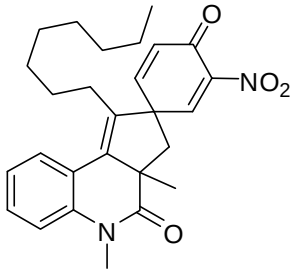
Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.36 (t, *J* = 7.6 Hz, 2H), 7.15-7.08 (m, 2H), 6.57 (d, *J* = 10.0 Hz, 1H), 6.26 (s, 1H), 6.19 (d, *J* = 9.6 Hz, 1H), 3.41 (s, 3H), 3.04 (d, *J* = 14.4 Hz, 1H), 2.04-1.87 (m, 6H), 1.25 (s, 3H), 1.27-1.17 (m, 12H), 0.86 (t,

J = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 186.5, 174.5, 161.0, 154.3, 141.4, 139.2, 137.8, 129.0, 128.8, 126.9, 126.8, 122.9, 122.6, 115.0, 60.6, 53.5, 41.1, 31.7, 30.3, 29.9, 29.6, 29.1, 29.0, 26.8, 25.7, 22.6, 21.1, 14.1; IR (KBr, cm^{-1}): 1677, 1636; HRMS (ESI) for $C_{28}H_{36}NO_2$ ($[M+H]^+$): calcd 418.2741, found 418.2726.



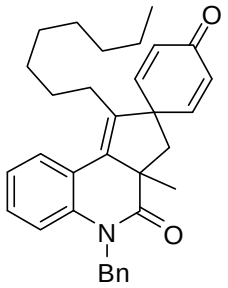
3-Chloro-3a',5'-dimethyl-1'-octyl-3',3a'-dihydrospiro[cyclohexa[2,5]diene-1,2'-cyclopenta[*c*]quinoline]-4,4'(*5'H*)-dione (3ac):

Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.42-7.35 (m, 2H), 7.16-7.08 (m, 2H), 7.58 (s, 0.68H), 6.92-6.87 (m, 0.70H), 6.69 (d, *J* = 9.6 Hz, 0.69H), 6.42-6.36 (m, 0.93H), 3.40 (s, 3H), 2.98-2.92 (m, 1H), 2.18-2.13 (m, 1H), 2.06-2.02 (m, 2H), 1.31-1.30 (m, 3H), 1.25-1.21 (m, 12H), 0.86 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 178.7, 174.4, 154.0, 153.6, 149.6, 149.4, 139.6, 139.5, 139.4, 137.8, 131.7, 129.2, 128.0, 126.9, 123.0 (2C), 121.5, 115.2, 59.4, 59.3, 53.6, 43.2, 43.0, 31.7, 30.1, 29.9, 29.8, 29.7, 29.0 (2C), 26.9, 26.0, 22.6, 14.0; IR (KBr, cm^{-1}): 1659, 1619; HRMS (ESI) for $C_{27}H_{33}{}^{35}ClNO_2$ ($[M+H]^+$): calcd 438.2194, found 438.2206.



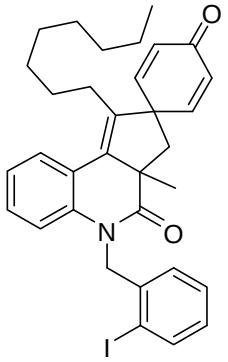
3a',5'-Dimethyl-3-nitro-1'-octyl-3',3a'-dihydrospiro[cyclohexa[2,5]diene-1,2'-cyclopenta[*c*]quinoline]-4,4'(*5'H*)-dione (3ae):

Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.50 (d, *J* = 6.8 Hz, 0.63H), 7.42-7.39 (m, 2H), 7.33 (s, 0.42H), 7.19-7.11 (m, 2H), 6.96 (d, *J* = 10.0 Hz, 0.39H), 6.75 (d, *J* = 9.6 Hz, 0.63H), 6.43 (t, *J* = 10.4 Hz, 0.90H), 3.41 (s, 3H), 3.09-3.01 (m, 1H), 2.29-2.18 (m, 1H), 2.10-2.02 (m, 2H), 1.33 (s, 3H), 1.31-1.22 (m, 12H), 0.87 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 174.5, 174.0, 173.9, 153.5, 152.9, 149.3, 148.8, 146.8, 139.5 (2C), 138.0, 129.6 (2C), 129.0, 127.9, 127.0, 123.2, 121.1, 115.4, 57.7, 57.6, 54.1, 53.9, 43.2, 43.0, 31.7, 30.2, 30.1, 30.0, 29.8, 29.0 (2C), 27.1, 26.0, 22.6, 14.1; IR (KBr, cm^{-1}): 1683, 1631; HRMS (ESI) for $C_{27}H_{33}N_2O_4$ ($[M+H]^+$): calcd 449.2435, found 449.2449.



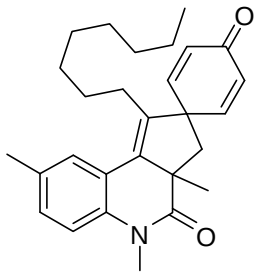
5'-Benzyl-3a'-methyl-1'-octyl-3',3a'-dihydrospiro[cyclohexa[2,5]diene-1,2'-cyclopenta[*c*]quinoline]-4,4'(*5'H*)-dione (3ba):

Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.43 (d, *J* = 7.6 Hz, 1H), 7.32 (d, *J* = 7.2 Hz, 2H), 7.26-7.19 (m, 4H), 7.09 (t, *J* = 7.2 Hz, 1H), 6.99-6.92 (m, 2H), 6.72 (d, *J* = 10.0 Hz, 1H), 6.36-6.30 (m, 2H), 5.61 (d, *J* = 16.4 Hz, 1H), 4.75 (d, *J* = 16.4 Hz, 1H), 3.00 (d, *J* = 14.4 Hz, 1H), 2.16 (d, *J* = 14.8 Hz, 1H), 2.11-2.04 (m, 2H), 1.45 (s, 3H), 1.28-1.22 (m, 12H), 0.87 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 185.7, 174.8, 153.9, 153.5, 140.8, 138.9, 136.9, 129.1, 128.9, 128.8, 128.2, 127.1, 126.9, 126.0, 123.1, 121.9, 115.9, 57.3, 53.5, 46.7, 43.3, 31.7, 29.9, 29.8, 29.0 (2C), 27.0, 26.1, 22.6, 14.0; IR (KBr, cm^{-1}): 1677, 1664; LRMS (EI 70 ev) *m*/z (%): 480 (M^++1, 20), 479 (M^+, 52), 372 (16), 91 (100); HRMS (ESI) for $C_{33}H_{38}NO_2$ ($[M+H]^+$): calcd 480.2897, found 480.2877.



5'-(2-Iodobenzyl)-3a'-methyl-1'-octyl-3',3a'-dihydrospiro[cyclohexa[2,5]diene-1,2'-cyclopenta[*c*]quinoline]-4,4'(*5'H*)-dione (3ca):

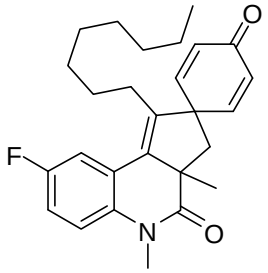
Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.90 (d, *J* = 7.6 Hz, 1H), 7.45 (d, *J* = 7.6 Hz, 1H), 7.23 (t, *J* = 8.0 Hz, 1H), 7.12 (t, *J* = 7.2 Hz, 1H), 6.99-6.93 (m, 2H), 6.82 (d, *J* = 7.6 Hz, 1H), 6.72 (d, *J* = 8.8 Hz, 1H), 6.37-6.31(m, 2H), 5.47(d, *J* = 17.2 Hz, 1H), 4.72(d, *J* = 17.2 Hz, 1H), 2.98 (d *J* = 14.8 Hz, 1H), 2.16 (d, *J* = 14.4 Hz, 1H), 2.17-2.03 (m, 2H), 1.48 (s, 3H), 1.26-1.22 (m, 12H), 0.87 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 185.7, 174.8, 153.8, 153.4, 141.2, 139.7, 138.5, 137.8, 136.7, 129.2, 129.1, 128.9, 128.6, 128.2, 127.0, 125.7, 123.4, 121.9, 116.0, 97.4, 57.3, 53.6, 52.5, 43.3, 31.7, 29.9, 29.8, 29.1, 29.0, 27.1, 26.2, 22.6, 14.1; IR (KBr, cm^{-1}): 1667, 1622; HRMS (ESI) for $C_{33}H_{37}INO_2$ ($[M+H]^+$): calcd 606.1864, found 606.1878.



3a',5',8'-Trimethyl-1'-octyl-3',3a'-dihydrospiro[cyclohexa[2,5]diene-1,2'-cyclopenta[*c*]quinoline]-4,4'(*5'H*)-dione (3ea):

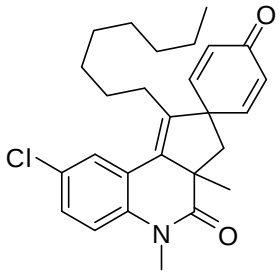
Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.22 (s, 1H), 7.15 (d, *J* = 9.6 Hz, 1H), 6.97 (d, *J* = 8.4 Hz, 1H), 6.90 (d, *J* = 10.0 Hz, 1H), 6.67 (d, *J* = 10.0 Hz, 1H), 6.33-

6.26 (m, 2H), 3.37 (s, 3H), 2.87 (d, *J* = 14.4 Hz, 1H), 2.35 (s, 3H), 2.10 (d, *J* = 14.8 Hz, 1H), 2.06-2.02 (m, 2H), 1.29 (s, 3H), 1.24-1.22 (m, 12H), 0.86 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 185.8, 174.6, 154.0, 153.6, 140.3, 137.2, 137.1, 132.4, 129.4, 129.1, 128.0, 127.5, 121.6, 115.0, 57.2, 53.4, 43.5, 31.7, 30.0, 29.9, 29.7, 29.1, 29.0, 27.0, 26.1, 22.6, 20.7, 14.0; IR (KBr, cm^{-1}): 1688, 1621; LRMS (EI 70 ev) *m*/z (%): 418 (M^++1, 32), 417 (M^+, 100), 402 (45), 304 (58); HRMS (ESI) for $C_{28}H_{36}NO_2$ ($[M+H]^+$): calcd 418.2741, found 418.2714.



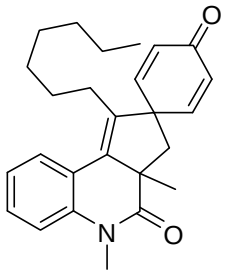
8'-Fluoro-3a',5'-dimethyl-1'-octyl-3',3a'-dihydrospiro[cyclohexa[2,5]diene-1,2'-cyclopenta[*c*]quinoline]-4,4'(*5'H*)-dione (3fa):

Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.10 (d, *J* = 10.4 Hz, 1H), 7.02 (t, *J* = 9.2 Hz, 2H), 6.86 (d, *J* = 10.0 Hz, 1H), 6.64 (d, *J* = 10.0 Hz, 1H), 6.32-6.26 (m, 2H), 3.36 (s, 3H), 2.86 (d, *J* = 14.4 Hz, 1H), 2.09 (d, *J* = 14.4 Hz, 1H), 2.05-1.99 (m, 2H), 1.28 (s, 3H), 1.27-1.19 (m, 12H), 0.84 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 185.6, 174.3, 158.4 (d, *J* = 241.5 Hz, 1C), 153.3 (d, *J* = 36.1 Hz, 1C), 142.2, 136.0 (d, *J* = 42.2 Hz, 1C), 129.3, 128.3, 123.2 (d, *J* = 7.8 Hz, 1C), 116.4 (d, *J* = 8.2 Hz, 1C), 115.3 (d, *J* = 22.4 Hz, 1C), 113.7 (d, *J* = 23.6 Hz, 1C), 57.2, 53.2, 43.5, 31.7, 30.3, 29.8 (2C), 29.1, 29.0, 27.0, 26.1, 22.6, 14.1; IR (KBr, cm^{-1}): 1679, 1622; LRMS (EI 70 ev) *m*/z (%): 422 (M^++1, 30), 421 (M^+, 100), 406 (69), 308 (62), 276 (100); HRMS (ESI) for $C_{27}H_{33}NO_2{}^{19}F$ ($[M+H]^+$): calcd 422.2490, found 422.2481.



8'-Chloro-3a',5'-dimethyl-1'-octyl-3',3a'-dihydrospiro[cyclohexa[2,5]diene-1,2'-cyclopenta[*c*]quinoline]-4,4'(*5'H*)-dione (3ga):

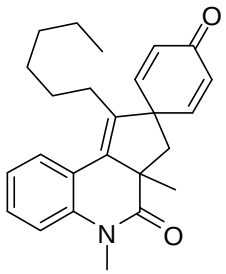
Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.36 (s, 1H), 7.29 (d, *J* = 8.8 Hz, 1H), 7.00 (t, *J* = 8.8 Hz, 1H), 6.86 (d, *J* = 10.0 Hz, 1H), 6.64 (d, *J* = 10.0 Hz, 1H), 6.33-6.27 (m, 2H), 3.36 (s, 3H), 2.86 (d, *J* = 14.4 Hz, 1H), 2.10 (d, *J* = 14.8 Hz, 1H), 2.05-2.00 (m, 2H), 1.29 (s, 3H), 1.26-1.22 (m, 12H), 0.85 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 185.5, 174.4, 153.4, 153.0, 142.3, 138.0, 135.8, 129.2, 128.5, 128.3, 128.2, 126.7, 123.1, 116.3, 57.1, 53.2, 43.5, 30.6, 30.1, 29.8, 29.6, 29.0, 28.9, 26.8, 26.1, 22.5, 14.0; IR (KBr, cm^{-1}): 1695, 1630; LRMS (EI 70 ev) *m*/z (%): 439 (M^{+}+2, 37), 438 (M^{+}+1, 30), 437 (100), 422 (70), 324 (65); HRMS (ESI) for $C_{27}H_{33}NO_2{}^{35}Cl$ ($[M+H]^{+}$): calcd 438.2194, found 438.2186.



1'-Heptyl-3a',5'-dimethyl-3',3a'-dihydrospiro[cyclohexa[2,5]diene-1,2'-cyclopenta[*c*]quinoline]-4,4'(*5'H*)-dione (3ha):

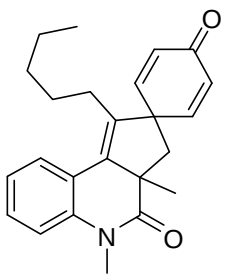
Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.41 (d, *J* = 7.6 Hz, 1H), 7.36 (t, *J* = 8.4 Hz, 1H), 7.15-7.08 (m, 2H), 6.90 (d, *J* = 10.0 Hz, 1H), 6.68 (d, *J* = 10.0 Hz, 1H), 6.34-6.27 (m, 2H), 3.40 (s, 3H), 2.89 (d, *J* = 14.4 Hz, 1H), 2.10 (d, *J* = 14.4 Hz, 1H), 2.07-2.03 (m, 2H), 1.30 (s, 3H), 1.28-1.14 (m, 10H), 0.85 (t, *J* = 6.8 Hz, 3H); ^{13}C

NMR (100 MHz, $CDCl_3$) δ: 185.8, 174.8, 154.0, 153.6, 140.6, 139.4, 137.0, 129.1, 128.9, 128.1, 126.9, 122.9, 121.7, 115.1, 57.2, 53.4, 43.5, 31.6, 30.0, 29.9, 29.8, 28.7, 27.1, 26.1, 22.5, 14.0; IR (KBr, cm^{-1}): 1673, 1665; LRMS (EI 70 ev) *m*/z (%): 390 (M^++1, 28), 389 (M^+, 100), 374 (64), 290 (67); HRMS (ESI) for $C_{26}H_{32}NO_2$ ($[M+H]^+$): calcd 390.2428, found 390.2411.



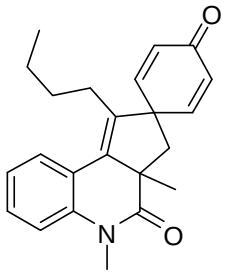
1'-Hexyl-3a',5'-dimethyl-3',3a'-dihydrospiro[cyclohexa[2,5]diene-1,2'-cyclopenta[*c*]quinoline]-4,4'(*5'H*)-dione (3ia):

Yellow oil; ^1H NMR (400 MHz, $CDCl_3$) δ: 7.40 (d, *J* = 7.2 Hz, 1H), 7.35 (t, *J* = 8.0 Hz, 1H), 7.15-7.07 (m, 2H), 6.90 (d, *J* = 9.6 Hz, 1H), 6.68 (d, *J* = 12.8 Hz, 1H), 6.33-6.27 (m, 2H), 3.39 (s, 3H), 2.88 (d, *J* = 14.4 Hz, 1H), 2.10 (d, *J* = 14.4 Hz, 1H), 2.06-2.02 (m, 2H), 1.29 (s, 3H), 1.24-1.20 (m, 8H), 0.84 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 185.7, 174.8, 154.0, 153.6, 140.6, 139.4, 137.0, 129.1, 128.9, 128.1, 126.8, 122.9, 121.7, 115.1, 57.2, 53.4, 43.5, 31.2, 30.0, 29.8, 29.5, 27.1, 26.1, 22.4, 13.9; IR (KBr, cm^{-1}): 1655, 1620; LRMS (EI 70 ev) *m*/z (%): 376 (M^++1, 28), 375 (M^+, 100), 360 (60), 290 (78); HRMS (ESI) for $C_{25}H_{30}NO_2$ ($[M+H]^+$): calcd 376.2271, found 376.2254.



3a’,5’-Dimethyl-1’-pentyl-3’,3a’-dihydrospiro[cyclohexa[2,5]diene-1,2'-cyclopenta[*c*]quinoline]-4,4'(*5'H*)-dione (3ja):

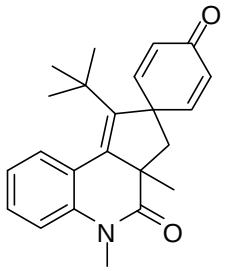
Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.40 (d, *J* = 7.6 Hz, 1H), 7.35 (t, *J* = 7.2 Hz, 1H), 7.14-7.07 (m, 2H), 6.90 (d, *J* = 10.0 Hz, 1H), 6.67 (d, *J* = 9.6 Hz, 1H), 6.32-6.26 (m, 2H), 3.39 (s, 3H), 2.87 (d, *J* = 14.4 Hz, 1H), 2.10 (d, *J* = 14.4 Hz, 1H), 2.06-2.02 (m, 2H), 1.29 (s, 3H), 1.25-1.22 (m, 6H), 0.82 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 185.7, 174.7, 154.0, 153.6, 140.6, 139.4, 137.0, 129.0, 128.9, 128.0, 126.8, 122.9, 121.7, 115.1, 57.2, 53.4, 43.5, 32.0, 30.0, 29.5, 27.0, 26.1, 22.1, 13.8; IR (KBr, cm^{-1}): 1673, 1668; LRMS (EI 70 ev) *m*/z (%): 362 (M^++1, 25), 361 (M^+, 100), 346 (53), 290 (71); HRMS (ESI) for $C_{24}H_{28}NO_2$ ($[M+H]^+$): calcd 362.2115, found 362.2100.



1'-Butyl-3a',5'-dimethyl-3',3a'-dihydrospiro[cyclohexa[2,5]diene-1,2'-cyclopenta[*c*]quinoline]-4,4'(*5'H*)-dione (3ka):

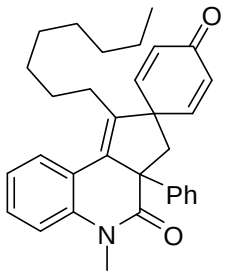
Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.41 (d, *J* = 7.6 Hz, 1H), 7.35 (t, *J* = 6.8 Hz, 1H), 7.15-7.08 (m, 2H), 6.90 (d, *J* = 10.0 Hz, 1H), 6.68 (d, *J* = 10.0 Hz, 1H), 6.33-6.27 (m, 2H), 3.39 (s, 3H), 2.89 (d, *J* = 14.8 Hz, 1H), 2.10 (d, *J* = 14.4 Hz, 1H), 2.07-2.03 (m, 2H), 1.30 (s, 3H), 1.28-1.24 (m, 4H), 0.84 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 185.8, 174.8, 154.0, 153.6, 140.6, 139.4, 137.0, 129.1, 128.9, 128.1, 126.9, 122.9, 121.7, 115.1, 57.2, 53.4, 43.5, 32.0, 30.0, 26.8, 26.1, 23.0, 13.7; IR (KBr, cm^{-1}): 1670, 1669; LRMS (EI 70 ev) *m*/z (%): 348 (M^++1, 21), 347 (M^+, 83),

332 (48), 290 (89), 276 (100); HRMS (ESI) for $C_{23}H_{26}NO_2$ ($[M+H]^+$): calcd 348.1958, found 348.1960.



1'-*tert*-Butyl-3a',5'-dimethyl-3',3a'-dihydrospiro[cyclohexa[2,5]diene-1,2'-cyclopenta[*c*]quinoline]-4,4'(*5'H*)-dione (3la):

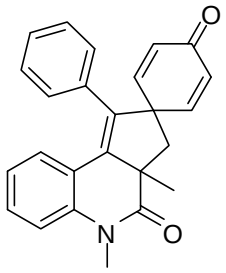
Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.54 (d, *J* = 7.6 Hz, 1H), 7.32 (t, *J* = 8.0 Hz, 1H), 7.12-7.03 (m, 3H), 6.94 (d, *J* = 3.2 Hz, 1H), 6.30 (d, *J* = 10.0 Hz, 1H), 6.17 (d, *J* = 10.0 Hz, 1H), 3.37 (s, 3H), 2.86 (d, *J* = 14.0 Hz, 1H), 1.94 (d, *J* = 14.0 Hz, 1H), 1.11 (s, 9H), 1.00 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 185.6, 174.6, 156.4, 155.9, 149.3, 139.2, 137.6, 129.5, 128.5, 127.8, 126.2, 125.7, 122.2, 114.9, 58.3, 53.4, 44.5, 36.0, 31.5, 30.2, 24.2; IR (KBr, cm^{-1}): 1695, 1633; LRMS (EI 70 ev) *m*/z (%): 348 (M^++1, 29), 347 (M^+, 66), 332 (50), 290 (79), 276 (100); HRMS (ESI) for $C_{23}H_{26}NO_2$ ($[M+H]^+$): calcd 348.1958, found 348.1948.



5'-Methyl-1'-octyl-3a'-phenyl-3',3a'-dihydrospiro[cyclohexa[2,5]diene-1,2'-cyclopenta[*c*]quinoline]-4,4'(*5'H*)-dione (3ma):

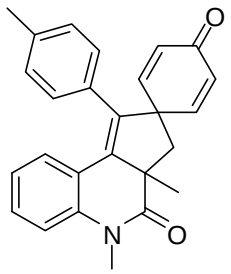
Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.59 (d, *J* = 7.6 Hz, 1H), 7.32-7.14 (m, 7H), 6.92 (d, *J* = 8.4 Hz, 1H), 6.74 (d, *J* = 10.0 Hz, 1H), 6.58 (d, *J* = 10.0 Hz, 1H), 6.35 (d, *J* = 10.0 Hz, 1H), 6.12 (d, *J* = 10.0 Hz, 1H), 3.36 (s, 3H), 3.25 (d, *J* = 14.4 Hz,

1H), 2.36 (d, *J* = 14.4 Hz, 1H), 2.29-2.18 (m, 2H), 1.32-1.25 (m, 12H), 0.86 (t, *J* = 6.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 185.7, 172.2, 153.0, 152.8, 144.6, 142.0, 139.3, 129.6, 128.9, 128.7, 128.0, 127.4, 126.5, 126.4, 123.1, 122.6, 115.5, 60.9, 57.4, 47.3, 31.7, 31.5, 30.3, 29.9, 29.1, 29.0, 27.5, 22.6, 14.0; IR (KBr, cm^{-1}): 1665, 1630; LRMS (EI 70 ev) *m*/z (%): 466 (M^++1, 29), 465 (M^+, 86), 358 (55), 274 (53), 260 (100); HRMS (ESI) for $C_{32}H_{36}NO_2$ ($[M+H]^+$): calcd 466.2741, found 466.2739.



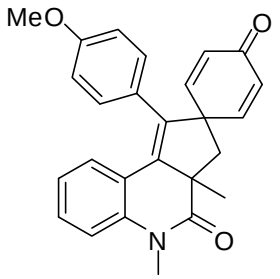
3a',5'-Dimethyl-1'-phenyl-3',3a'-dihydrospiro[cyclohexa[2,5]diene-1,2'-cyclopenta[*c*]quinoline]-4,4'(*5'H*)-dione (3oa):

Yellow solid, mp 143.2-144.1 °C (uncorrected); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.28-7.19 (m, 5H), 7.06 (t, *J* = 6.8 Hz, 3H), 6.87 (d, *J* = 7.6 Hz, 1H), 6.80 (t, *J* = 7.6 Hz, 1H), 6.65 (d, *J* = 10.0 Hz, 1H), 6.40 (d, *J* = 10.0 Hz, 1H), 6.08 (d, *J* = 10.0 Hz, 1H), 3.45 (s, 3H), 3.01 (d, *J* = 14.4 Hz, 1H), 2.28 (d, *J* = 14.4 Hz, 1H), 1.45 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 185.6, 174.5, 153.5, 153.3, 139.9, 138.7, 134.4, 129.4, 129.0, 128.7, 128.5, 128.2, 128.1, 128.0, 122.7, 120.5, 115.2, 57.3, 53.5, 44.7, 30.1, 25.9; IR (KBr, cm^{-1}): 1675, 1613; LRMS (EI 70 ev) *m*/z (%): 368 (M^++1, 13), 367 (M^+, 60), 352 (30), 291 (100); HRMS (ESI) for $C_{25}H_{22}NO_2$ ($[M+H]^+$): calcd 368.1645, found 368.1650.



3a',5'-Dimethyl-1'-*p*-tolyl-3',3a'-dihydrospiro[cyclohexa[2,5]diene-1,2'-cyclopenta[*c*]quinoline]-4,4'(*5'H*)-dione (3pa):

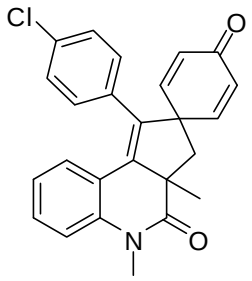
Yellow solid, mp 138.9-139.6 °C (uncorrected); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.26-7.22 (m, 2H), 7.07 (d, *J* = 7.6 Hz, 1H), 7.00 (d, *J* = 8.0 Hz, 2H), 6.95-6.92 (m, 3H), 6.82 (t, *J* = 7.6 Hz, 1H), 6.65 (d, *J* = 10.0 Hz, 1H), 6.37 (d, *J* = 10.0 Hz, 1H), 6.09 (d, *J* = 10.0 Hz, 1H), 3.45 (s, 3H), 3.00 (d, *J* = 14.4 Hz, 1H), 2.29-2.25 (m, 4H), 1.44 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 185.6, 174.5, 153.7, 153.5, 139.9, 138.8, 138.2, 138.0, 131.4, 129.2 (2C), 128.9, 128.6, 128.0, 127.9, 122.6, 120.8, 115.1, 57.3, 53.4, 44.8, 30.1, 25.8, 21.2; IR (KBr, cm^{-1}): 1661, 1618; LRMS (EI 70 ev) *m*/z (%): 382 (M^++1, 28), 381 (M^+, 99), 366 (76), 275 (100); HRMS (ESI) for $C_{26}H_{24}NO_2$ ($[M+H]^+$): calcd 382.1802, found 382.1788.



1'-(4-Methoxyphenyl)-3a',5'-dimethyl-3',3a'-dihydrospiro[cyclohexa[2,5]diene-1,2'-cyclopenta[*c*]quinoline]-4,4'(*5'H*)-dione (3qa):

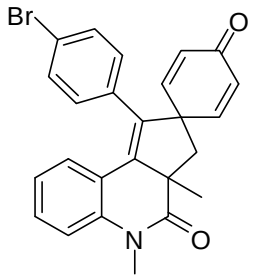
Yellow solid, mp 177.8-179.1 °C (uncorrected); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.29-7.23 (m, 2H), 7.07 (d, *J* = 8.0 Hz, 1H), 7.00-6.94 (m, 3H), 6.83 (t, *J* = 7.2 Hz, 1H), 6.73 (d, *J* = 6.8 Hz, 2H), 6.65 (d, *J* = 10.0 Hz, 1H), 6.38 (d, *J* = 10.0 Hz, 1H), 6.11 (d, *J* = 10.0 Hz, 1H), 3.77 (s, 3H), 3.45 (s, 3H), 3.00 (d, *J* = 14.4 Hz, 1H), 2.26 (d, *J* = 14.4 Hz, 1H), 1.43 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 185.6, 174.5, 159.4, 153.9, 153.6, 139.9, 138.4, 137.9, 129.3, 129.2, 128.9, 128.6, 128.0, 126.6, 122.7, 120.8, 115.2, 113.9, 57.3, 55.1, 53.3, 44.8, 30.1, 25.8; IR (KBr, cm^{-1}): 1677, 1618;

LRMS (EI 70 ev) *m*/z (%): 398 (M^++1, 19), 397 (M^+, 70), 382 (31), 291 (100); HRMS (ESI) for $C_{24}H_{26}NO_2$ ([M+H]$^+$): calcd 398.1751, found 398.1762.



1'-(4-Chlorophenyl)-3a',5'-dimethyl-3',3a'-dihydrospiro[cyclohexa[2,5]diene-1,2'-cyclopenta[*c*]quinoline]-4,4'(*5'H*)-dione (3ra):

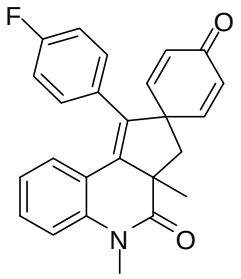
Yellow solid, mp 189.3-190.6 ºC (uncorrected); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.32-7.27 (m, 1H), 7.24-7.18 (m, 3H), 7.08 (d, *J* = 8.4 Hz, 1H), 7.01 (d, *J* = 9.2 Hz, 2H), 6.89-6.84 (m, 2H), 6.62 (d, *J* = 10.0 Hz, 1H), 6.39 (d, *J* = 10.0 Hz, 1H), 6.11 (d, *J* = 10.0 Hz, 1H), 3.45 (s, 3H), 3.00 (d, *J* = 14.4 Hz, 1H), 2.28 (d, *J* = 14.4 Hz, 1H), 1.45 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 185.3, 174.3, 153.1, 153.0, 139.9, 139.5, 137.2, 134.1, 132.9, 129.6, 129.5, 129.2, 128.8 (2C), 127.9, 122.8, 120.2, 115.3, 57.1, 53.5, 44.7, 30.1, 25.8 ; IR (KBr, cm^{-1}): 1665, 1620; LRMS (EI 70 ev) *m*/z (%):403 (M^++1, 34), 402 (M^+, 28), 401 (100), 386 (79), 295 (85); HRMS (ESI) for $C_{25}H_{21}{}^{35}ClNO_2$ ([M+H]$^+$): calcd 402.1255, found 402.1239.



1'-(4-Bromophenyl)-3a',5'-dimethyl-3',3a'-dihydrospiro[cyclohexa[2,5]diene-1,2'-cyclopenta[c]quinoline]-4,4'(5'H)-dione: (3sa)

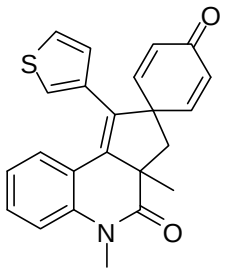
Yellow solid, mp 101.5-102.7 ºC (uncorrected); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.36-7.28 (m, 3H), 7.22 (d, *J* = 10.0 Hz, 1H), 7.08 (d, *J* = 8.4 Hz, 1H), 6.95 (d, *J* = 6.8

Hz, 2H), 6.88-6.84 (m, 2H), 6.62 (d, *J* = 10.0 Hz, 1H), 6.39 (d, *J* = 10.0 Hz, 1H), 6.11 (d, *J* = 10.0 Hz, 1H), 3.45 (s, 3H), 3.00 (d, *J* = 14.4 Hz, 1H), 2.28 (d, *J* = 14.4 Hz, 1H), 1.45 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 185.2, 174.2, 153.1, 153.0, 139.9, 139.6, 137.2, 133.4, 131.8, 129.7, 129.6, 129.2, 128.8, 127.9, 122.8, 122.4, 120.2, 115.3, 57.0, 53.5, 44.7, 30.0, 25.8; IR (KBr, cm^{-1}): 1672, 1629; LRMS (EI 70 ev) *m*/z (%):447 (M^++2, 25), 445 (M^+, 26), 433 (44), 417 (100), 320 (71); HRMS (ESI) for $C_{25}H_{21}BrNO_2$ ($[M+H]^+$): calcd 446.0750, found 446.0755.



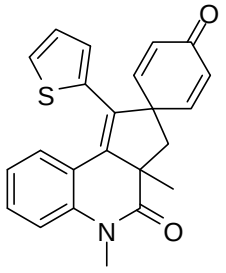
1'-(4-Fluorophenyl)-3a',5'-dimethyl-3',3a'-dihydrospiro[cyclohexa[2,5]diene-1,2'-cyclopenta[c]quinoline]-4,4'(5'H)-dione: (3ta)

Yellow solid, mp 112.7-113.8 ºC (uncorrected); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.31-7.27 (m, 1H), 7.22 (d, *J* = 10.0 Hz, 1H), 7.09-7.03 (m, 3H), 6.91 (t, *J* = 8.8 Hz, 2H), 6.86-6.83 (m, 2H), 6.63 (d, *J* = 10.0 Hz, 1H), 6.39 (d, *J* = 10.0 Hz, 1H), 6.11 (d, *J* = 10.0 Hz, 1H), 3.45 (s, 3H), 3.00 (d, *J* = 14.4 Hz, 1H), 2.29 (d, *J* = 14.0 Hz, 1H), 1.45 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 185.4, 174.3, 162.5 (d, *J* = 246.7 Hz, 1C), 153.3, 153.0, 140.0, 139.2, 137.5, 129.9, 129.5, 129.1, 128.8, 122.7, 120.4, 115.6 (t, *J* = 21.3 Hz, 1C), 98.4, 57.2, 53.5, 44.7, 30.1, 25.9; IR (KBr, cm^{-1}): 1683, 1631; LRMS (EI 70 ev) *m*/z (%): 386 (M^++1, 25), 385 (M^+, 100), 370 (90), 278 (63); HRMS (ESI) for $C_{25}H_{21}NO_2$ ($[M+H]^+$): calcd 386.1551, found 386.1549.



3a',5'-Dimethyl-1'-(thiophen-3-yl)-3',3a'-dihydrospiro[cyclohexa[2,5]diene-1,2'-cyclopenta[*c*]quinoline]-4,4'(*5'H*)-dione (3ua):

Yellow solid, mp 103.2-105.0 ºC (uncorrected); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.30 (t, *J* = 8.0 Hz, 1H), 7.23 (d, *J* = 10.0 Hz, 1H), 718-7.16 (m, 1H), 7.10-7.06 (m, 3H), 6.89 (t, *J* = 7.6 Hz, 1H), 6.79 (d, *J* = 4.8 Hz, 1H), 6.64 (d, *J* = 10.0 Hz, 1H), 6.40 (d, *J* = 10.0 Hz, 1H), 6.15 (d, *J* = 10.0 Hz, 1H), 3.44 (s, 3H), 2.99 (d, *J* = 14.4 Hz, 1H), 2.24 (d, *J* = 14.4 Hz, 1H), 1.41 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 185.3, 174.4, 153.8, 153.7, 139.9, 138.5, 134.2, 133.2, 129.5, 128.9, 128.7, 127.9, 127.2, 125.6, 123.3, 122.7, 120.7, 115.2, 56.9, 53.4, 44.6, 30.0, 25.6; IR (KBr, cm^{-1}): 1658, 1609; LRMS (EI 70 ev) *m*/z (%): 374 (M^{+}+1, 15), 373 (M^{+}, 57), 358 (36), 267 (100); HRMS (ESI) for $C_{23}H_{20}NO_2S$ ($[M+H]^{+}$): calcd 374.1209, found 373.1195.

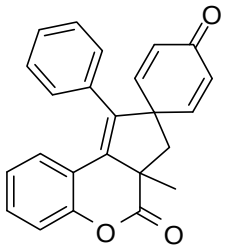


3a',5'-dimethyl-1'-(thiophen-2-yl)-3',3a'-dihydrospiro[cyclohexa[2,5]diene-1,2'-cyclopenta[c]quinoline]-4,4'(5'H)-dione: (3va)

Yellow solid, mp 99.5-101.0 ºC (uncorrected); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.32 (t, *J* = 7.6 Hz, 1H), 7.21-7.17 (m, 2H), 7.15-7.08 (m, 2H), 6.90-6.89 (m, 2H), 6.82-6.81 (m, 2H), 6.66 (d, *J* = 10.0 Hz, 1H), 6.42 (d, *J* = 10.0 Hz, 1H), 6.15 (d, *J* = 10.0 Hz, 1H), 3.45 (s, 3H), 3.01 (d, *J* = 14.4 Hz, 1H), 2.27 (d, *J* = 14.4 Hz, 1H), 1.42 (s,

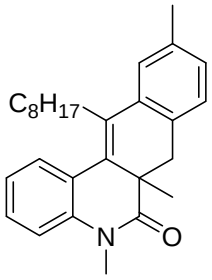
3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 185.5, 174.2, 153.2, 152.6, 140.2, 140.0, 134.6, 129.8, 129.5, 129.2, 128.6, 127.9, 127.1, 126.9, 126.2, 122.7, 115.3, 113.8, 57.2, 53.6, 44.4, 30.1, 25.8; IR (KBr, cm^{-1}): 1658, 1609; LRMS (EI 70 ev) *m*/z (%): 374 (M^++1, 15), 373 (M^+, 57), 358 (36), 267 (100); HRMS (ESI) for $C_{23}H_{20}NO_2S$ ($[M+H]^+$): calcd 374.1209, found 373.1195.

3a'-Methyl-1'-phenyl-3'*H*-spiro[cyclohexa[2,5]diene-1,2'-cyclopenta[c]chromene]-4,4'(3a'*H*)-dione: (3wa)



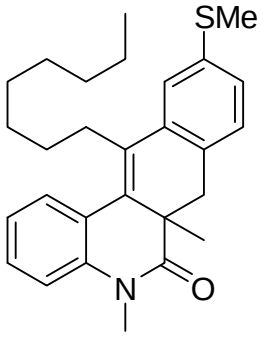
Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.32-7.26 (m, 4H), 7.21-7.18 (m, 1H), 7.14-7.12 (m, 1H), 7.10-7.07 (m, 2H), 6.89-6.86 (m, 2H), 6.50 (d, *J* = 10.0 Hz, 1H), 6.39 (d, *J* = 10.0 Hz, 1H), 6.80 (t, *J* = 7.6 Hz, 1H), 6.11 (d, *J* = 10.0 Hz, 1H), 3.06 (d, *J* = 14.0 Hz, 1H), 2.35 (d, *J* = 14.4 Hz, 1H), 1.58 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 185.1, 171.9, 152.4, 152.0, 151.3, 140.3, 133.6, 130.3, 129.3, 129.1, 128.6 (2C), 127.9, 127.4, 124.2, 118.2, 116.9, 57.2, 52.4, 44.0, 25.6; IR (KBr, cm^{-1}): 1664, 1602; LRMS (EI 70 ev) *m*/z (%): 355 (M^++1, 24), 354 (M^+, 95), 339 (100), 311 (97); HRMS (ESI) for $C_{22}H_{19}NO_3$ ($[M+H]^+$): calcd 355.1329, found 355.1336.

5,6a,10-Trimethyl-12-octyl-6a,7-dihydrobenzo[*j*]phenanthridin-6(5H)-one (4ah):



Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.42 (d, *J* = 7.6 Hz, 1H), 7.32-7.23 (m, 2H), 7.16-7.14 (m, 1H), 7.10-7.00 (m, 3H), 3.38 (s, 3H), 3.16-3.06 (m, 2H), 2.86-2.77

(m, 1H), 2.37 (s, 3H), 1.57-1.55 (m, 1H), 1.37-1.32 (m, 2H), 1.26-1.15 (m, 10H), 0.97-0.96 (m, 3H), 0.83 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 174.6, 139.9, 135.8, 134.5, 133.4, 132.0, 130.4, 128.4 (2C), 127.6, 127.1, 124.9, 124.2, 122.4, 114.3, 44.0, 43.9, 37.9, 37.5, 31.8, 30.2, 29.2, 29.1, 22.6, 21.5, 21.2, 20.4, 14.1; IR (KBr, cm^{-1}): 1675, 1460; HRMS (ESI) for $C_{28}H_{36}NO$ ($[M+H]^+$): calcd 402.2791, found 402.2799.

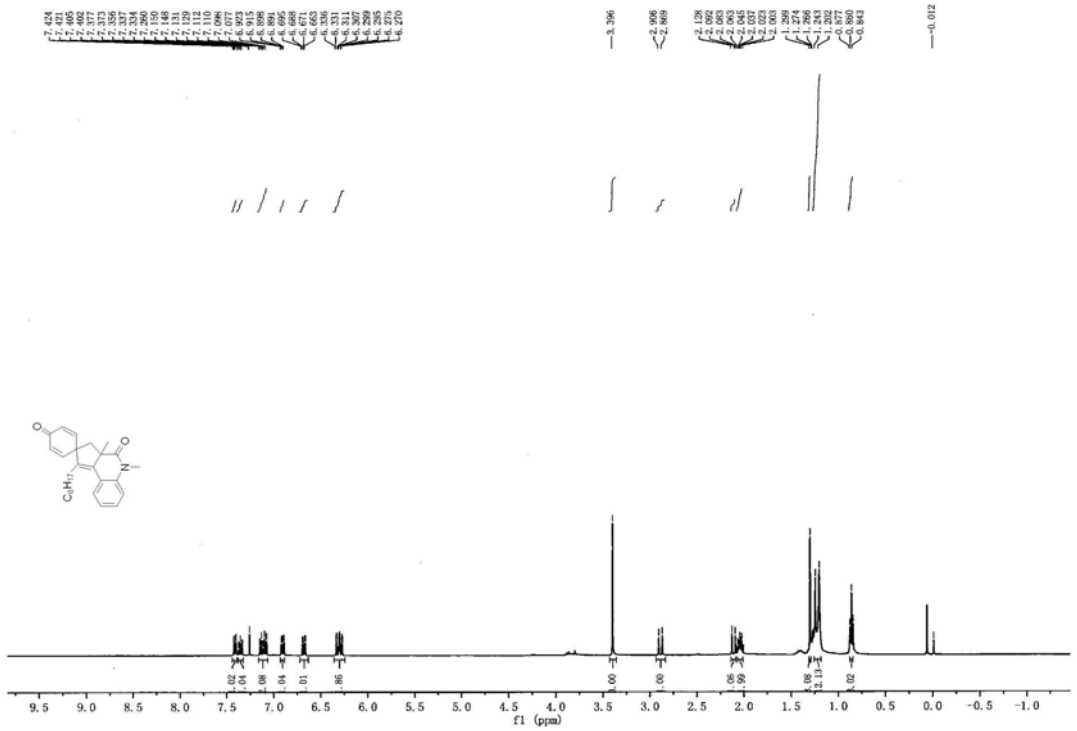


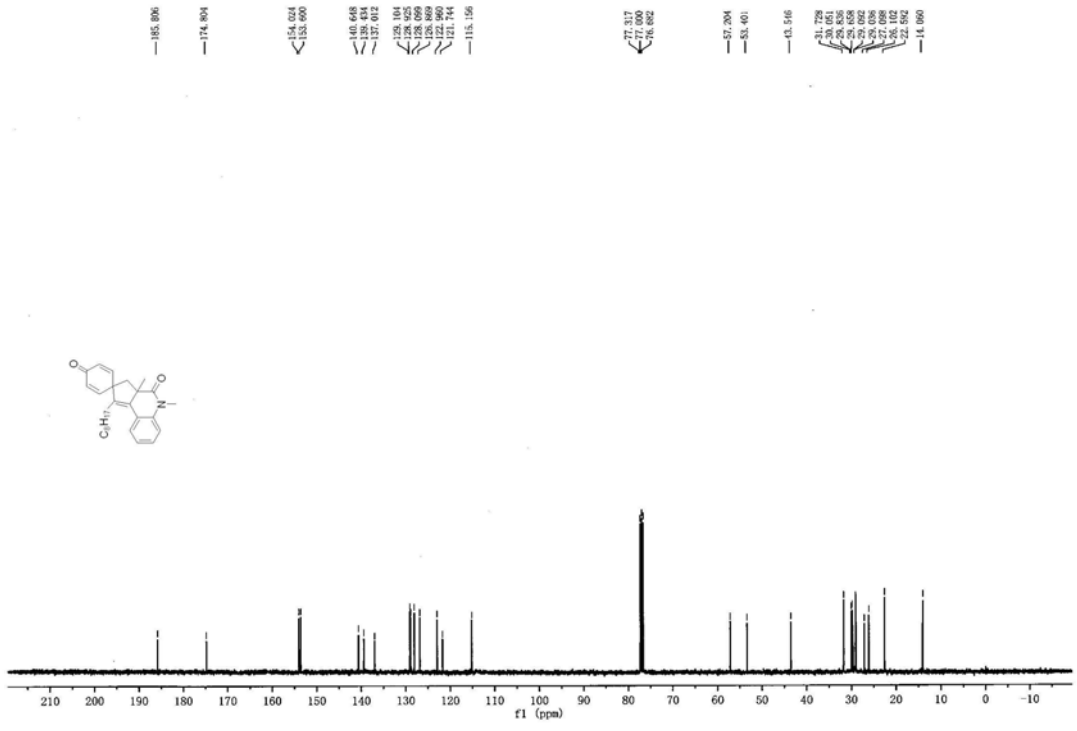
5,6a-dimethyl-10-(methylthio)-12-octyl-6a,7-dihydrobenzo[j]phenanthridin-6(5H)-one (4ak):

Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.42 (d, J = 7.6 Hz, 1H), 7.33-7.25 (m, 2H), 7.19 (d, J = 8.0 Hz, 1H), 7.14-7.07 (m, 2H), 7.03 (d, J = 8.0 Hz, 1H), 3.38 (s, 3H), 3.12-3.09 (m, 3H), 2.84-2.79 (m, 1H), 2.51 (s, 3H), 1.63-1.51 (m, 1H), 1.37-1.34 (m, 1H), 1.22-1.15 (m, 10H), 0.97 (s, 3H), 0.83 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 174.3, 139.9, 135.9, 135.3, 133.9, 133.0, 130.8, 130.4, 129.1, 128.6, 125.7, 123.5, 123.4, 122.4, 114.4, 44.1, 37.4, 31.7, 30.2, 29.2 (2C), 29.1, 29.0, 22.6, 20.5, 16.7, 14.1; IR (KBr, cm^{-1}): 1676, 1474; HRMS (ESI) for $C_{28}H_{36}NO_2S$ ($[M+H]^+$): calcd 434.2512, found 434.2531.

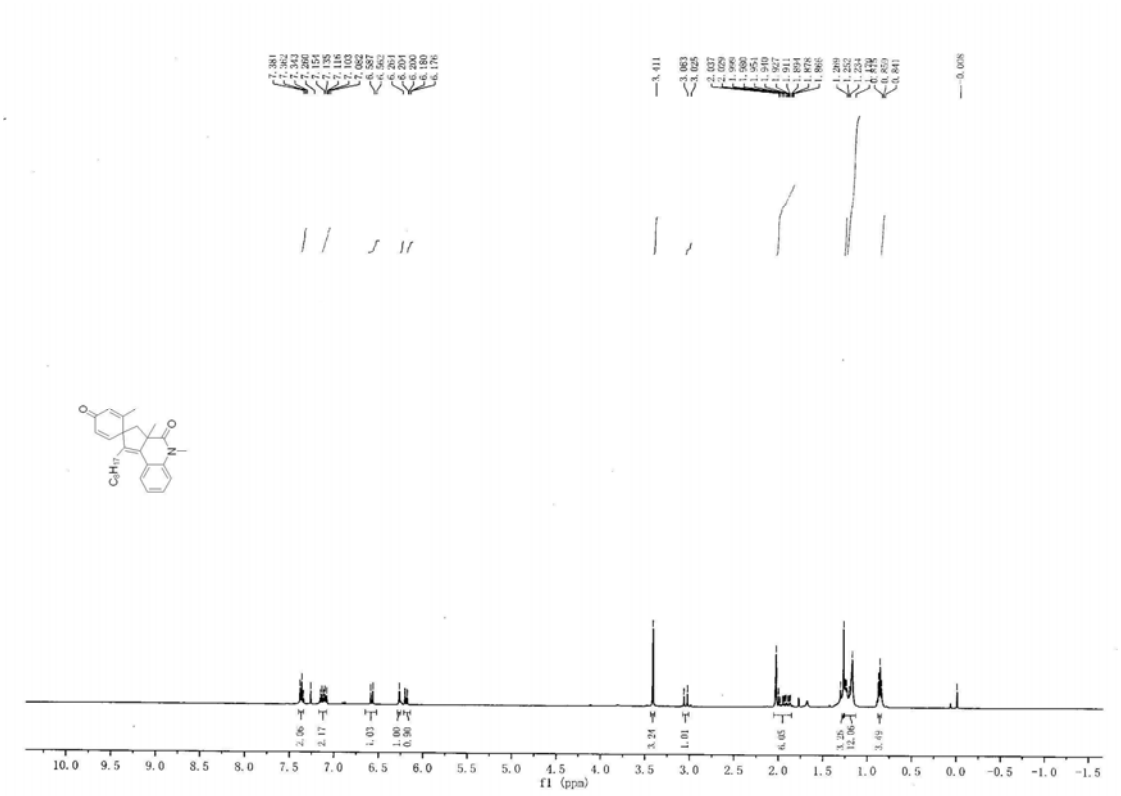
(D) Spectra

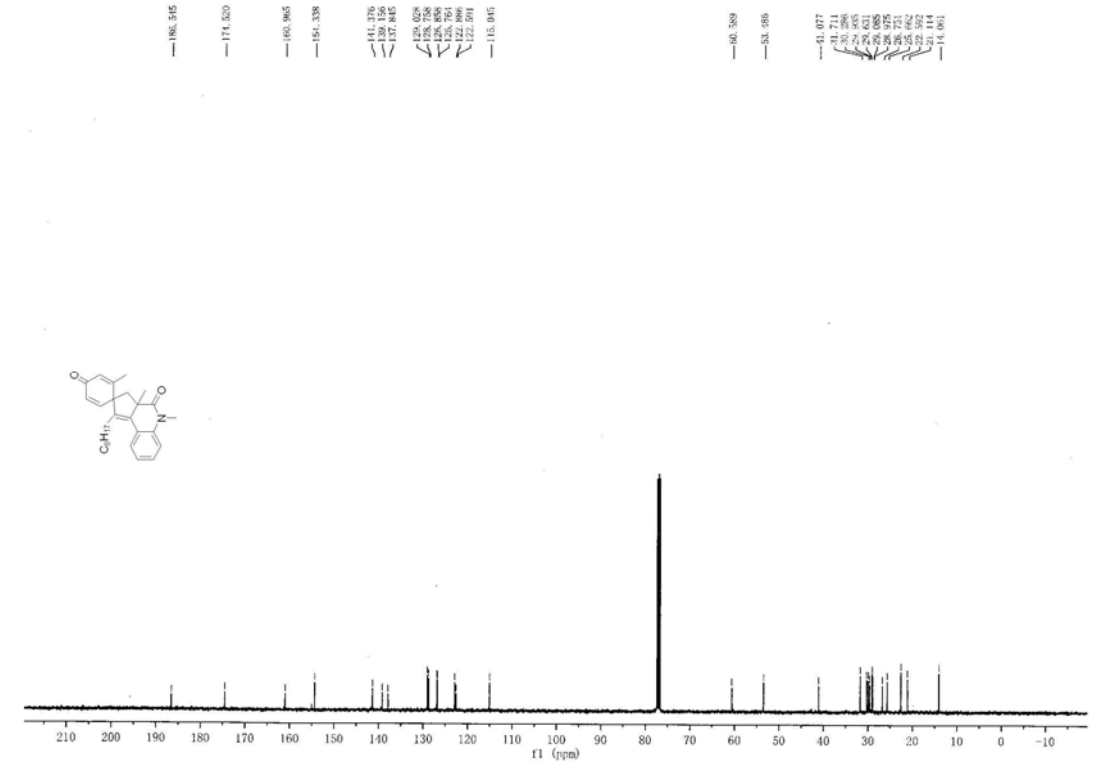
3a',5'-Dimethyl-1'-octyl-3',3a'-dihydrospiro[cyclohexa[2,5]diene-1,2'-cyclopenta[*c*]quinoline]-4,4'(*5'H*)-dione (3aa):



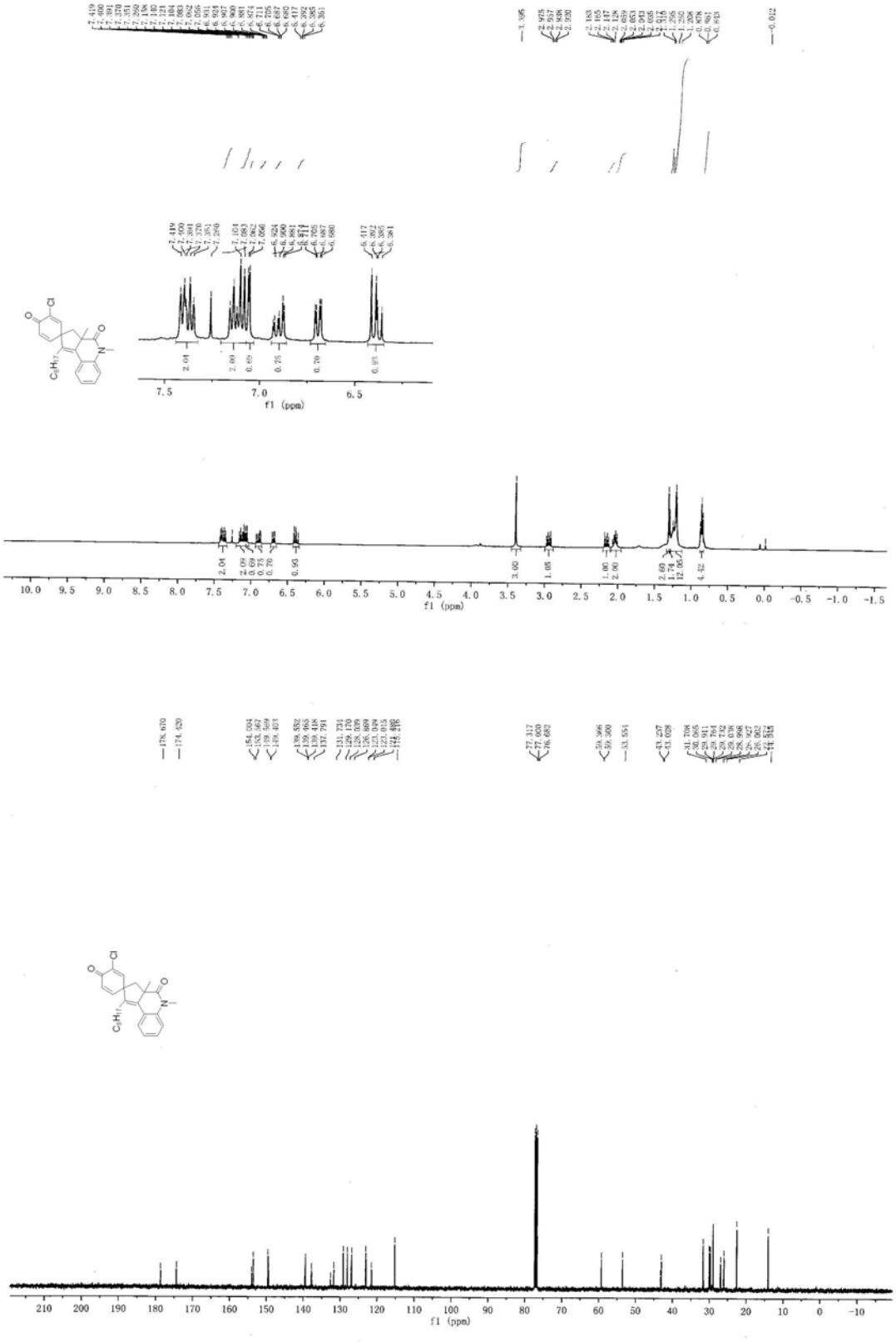


2,3a',5'-Trimethyl-1'-octyl-3',3a'-dihydrospiro[cyclohexa[2,5]diene-1,2'-cyclopenta[*c*]quinoline]-4,4'(*5'H*)-dione (3ab):

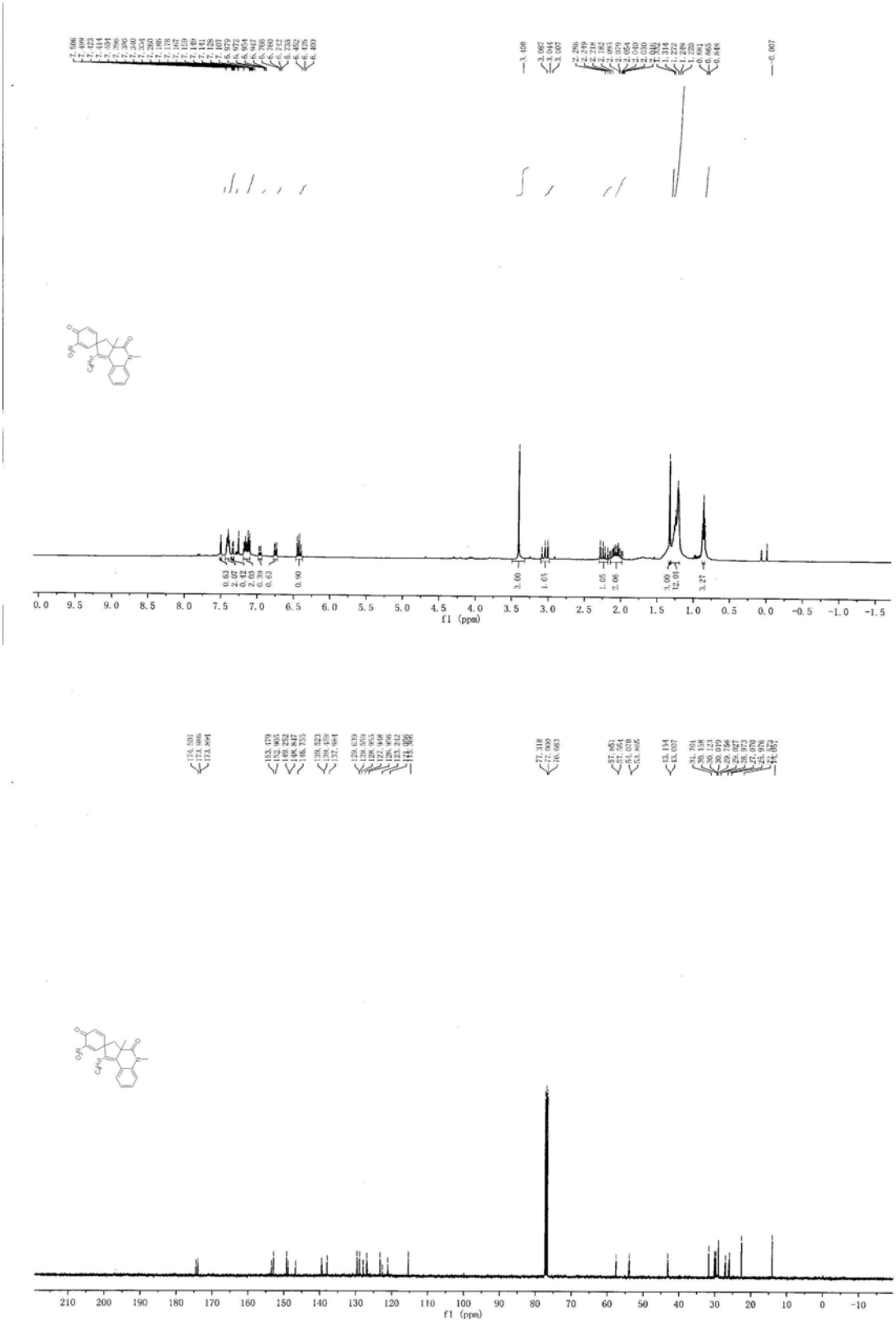




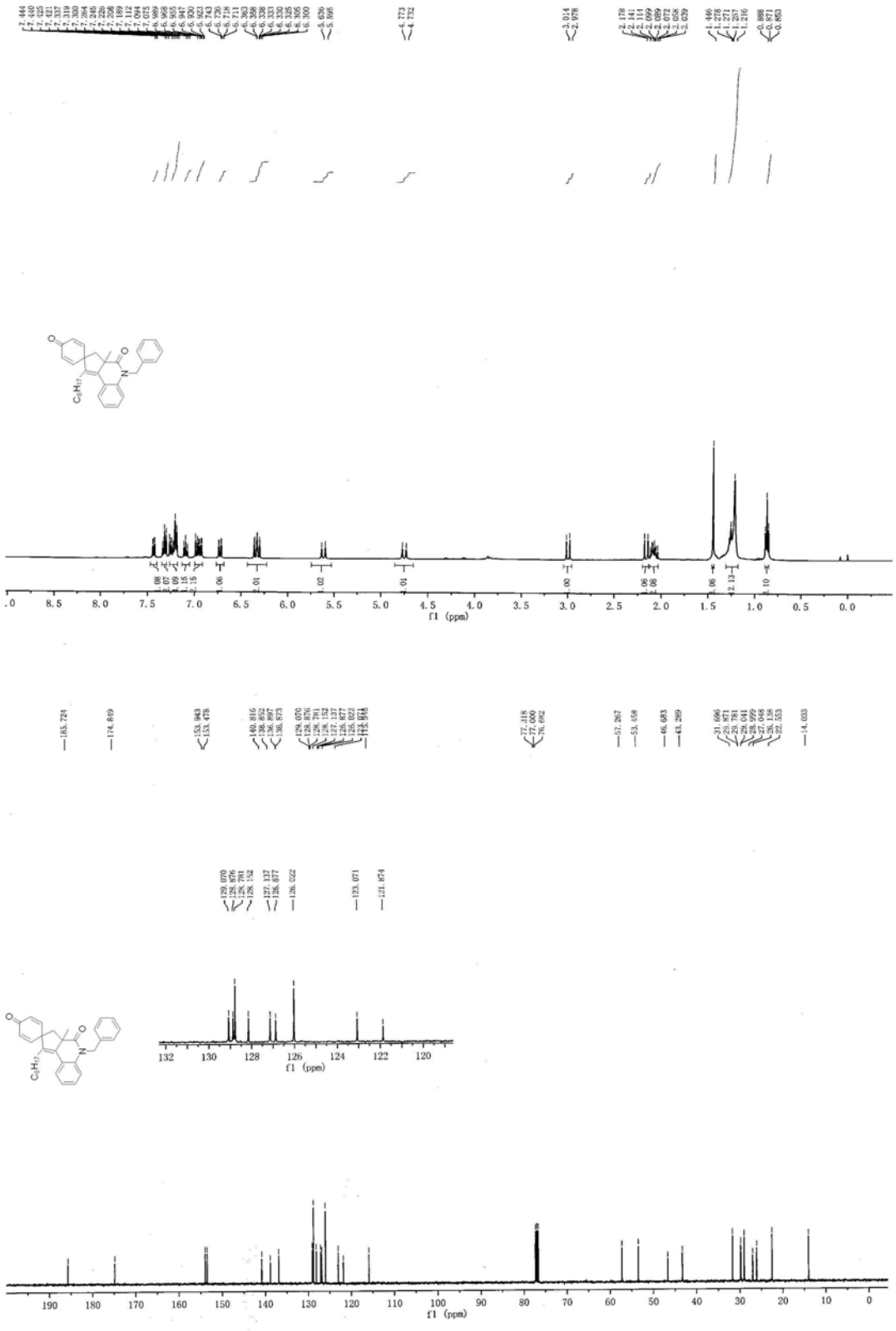
3-Chloro-3a',5'-dimethyl-1'-octyl-3',3a'-dihydrospiro[cyclohexa[2,5]diene-1,2'-cyclopenta[*c*]quinoline]-4,4'(*5'H*)-dione (3ac):



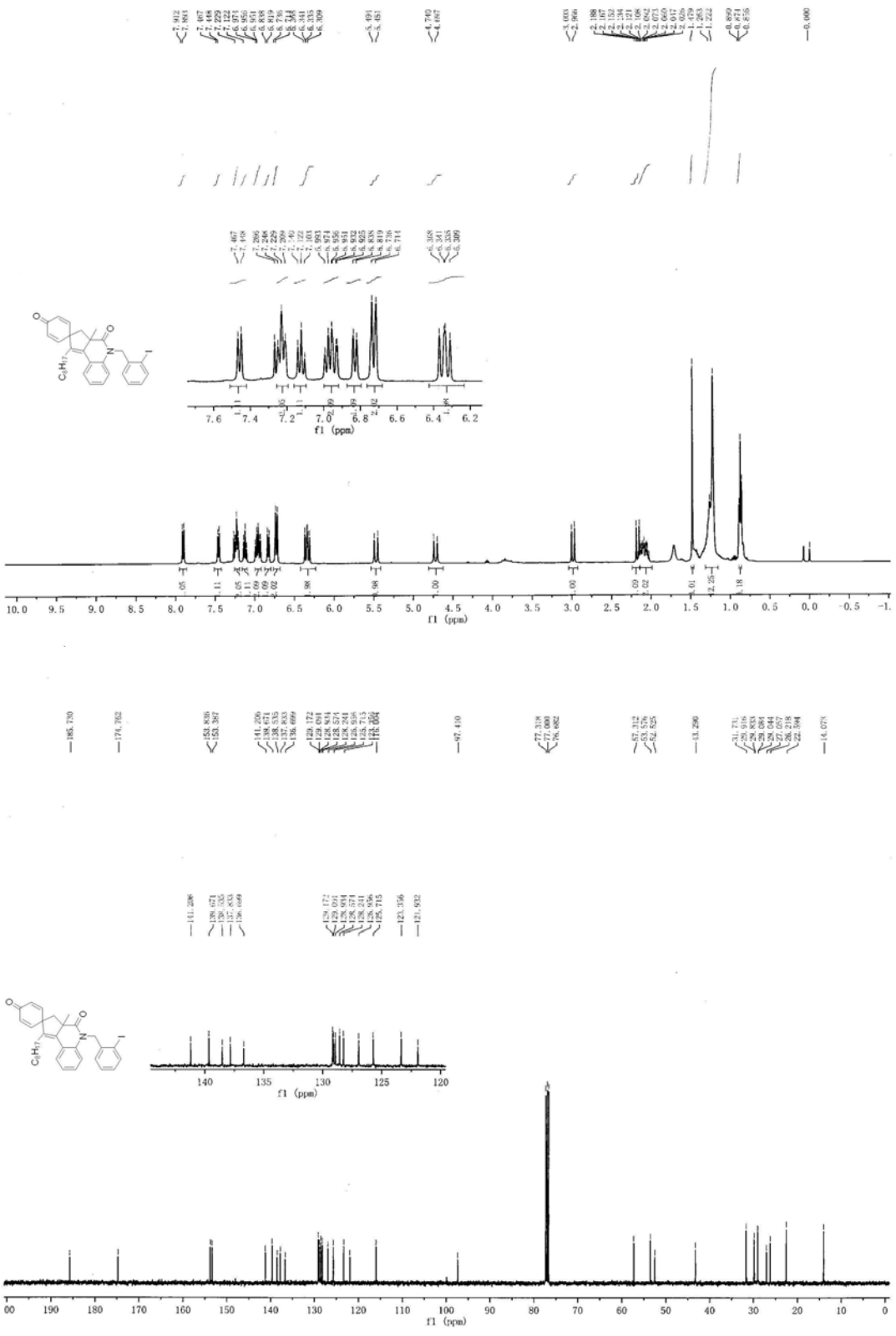
3a',5'-Dimethyl-3-nitro-1'-octyl-3',3a'-dihydrospiro[cyclohexa[2,5]diene-1,2'-cyclopenta[*c*]quinoline]-4,4'(*5'H*)-dione (3ae):



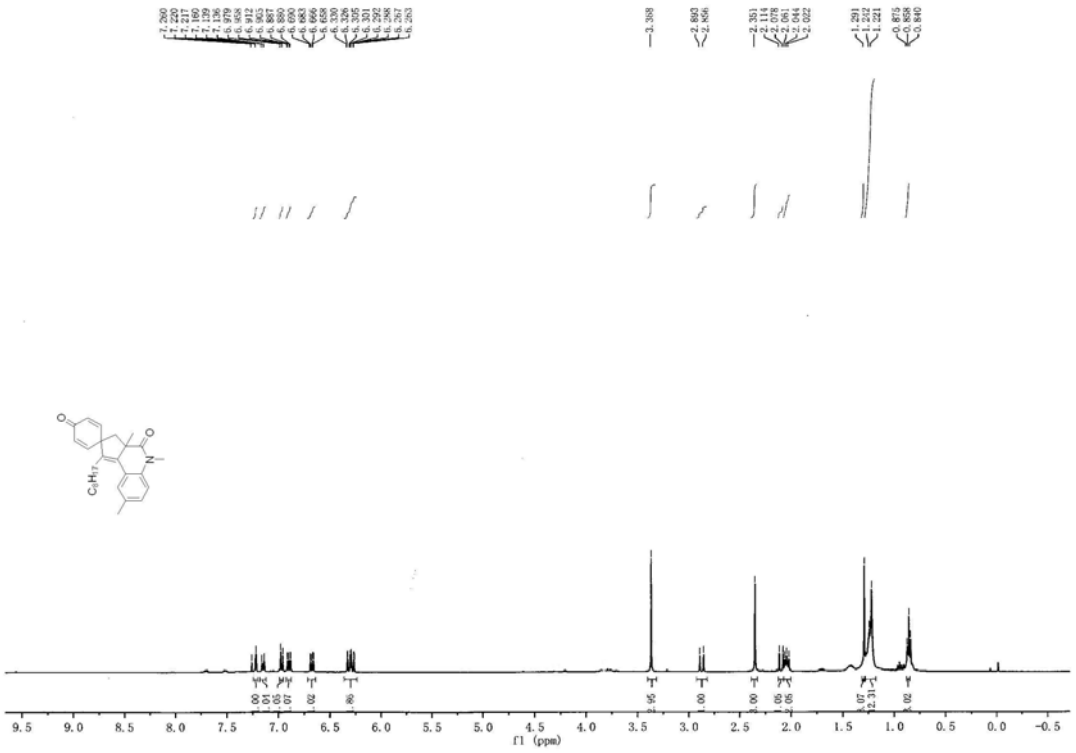
5'-Benzyl-3a'-methyl-1'-octyl-3',3a'-dihydrospiro[cyclohexa[2,5]diene-1,2'-cyclopenta[*c*]quinoline]-4,4'(*5'H*)-dione (3ba):

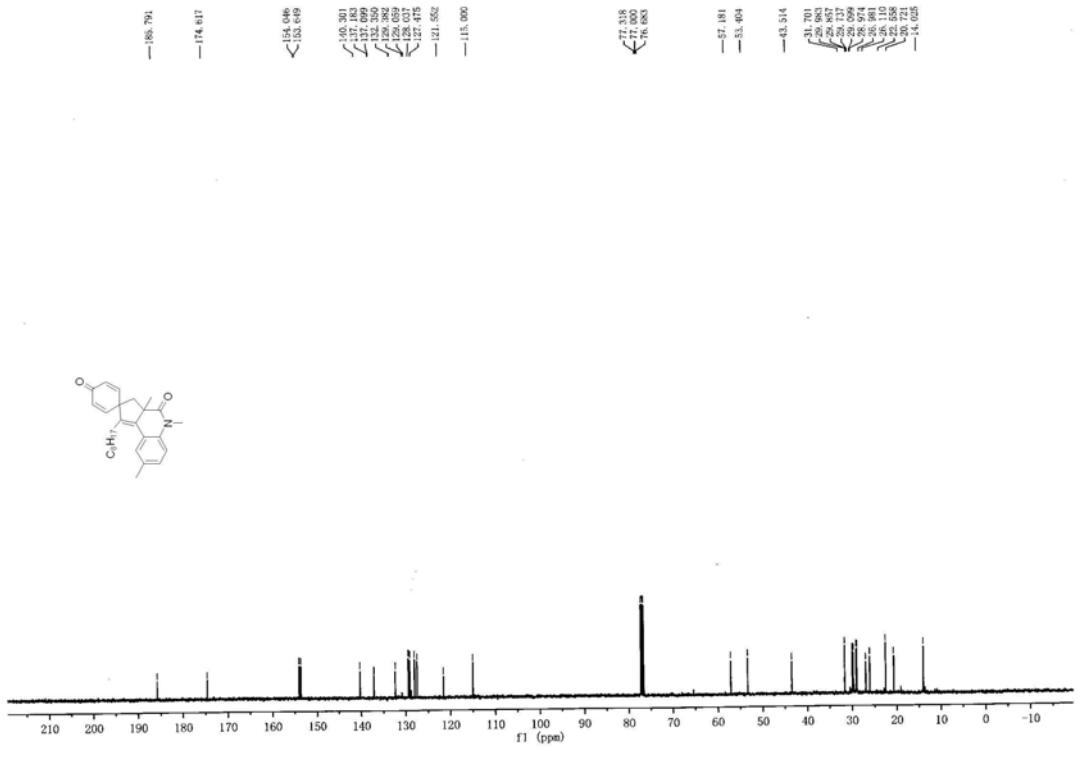


5'-(2-Iodobenzyl)-3a'-methyl-1'-octyl-3',3a'-dihydrospiro[cyclohexa[2,5]diene-1,2'-cyclopenta[*c*]quinoline]-4,4'(*5'H*)-dione (3ca):

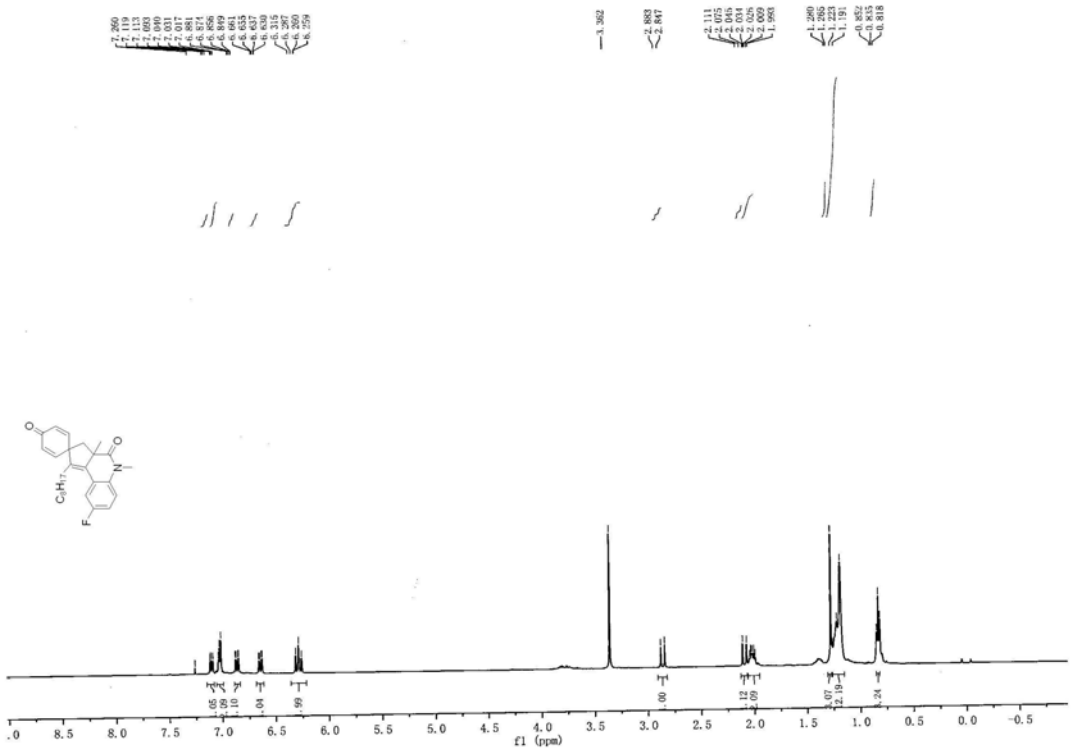


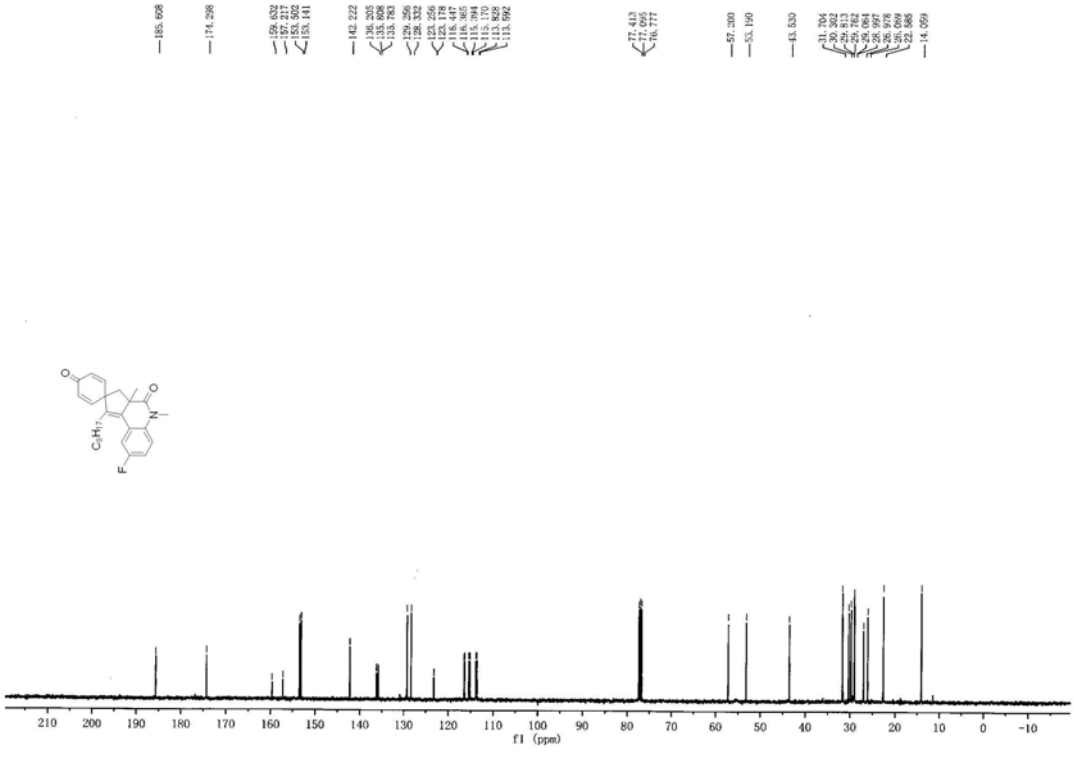
3a',5',8'-Trimethyl-1'-octyl-3',3a'-dihydrospiro[cyclohexa[2,5]diene-1,2'-cyclopenta[*c*]quinoline]-4,4'(*5'H*)-dione (3ea):



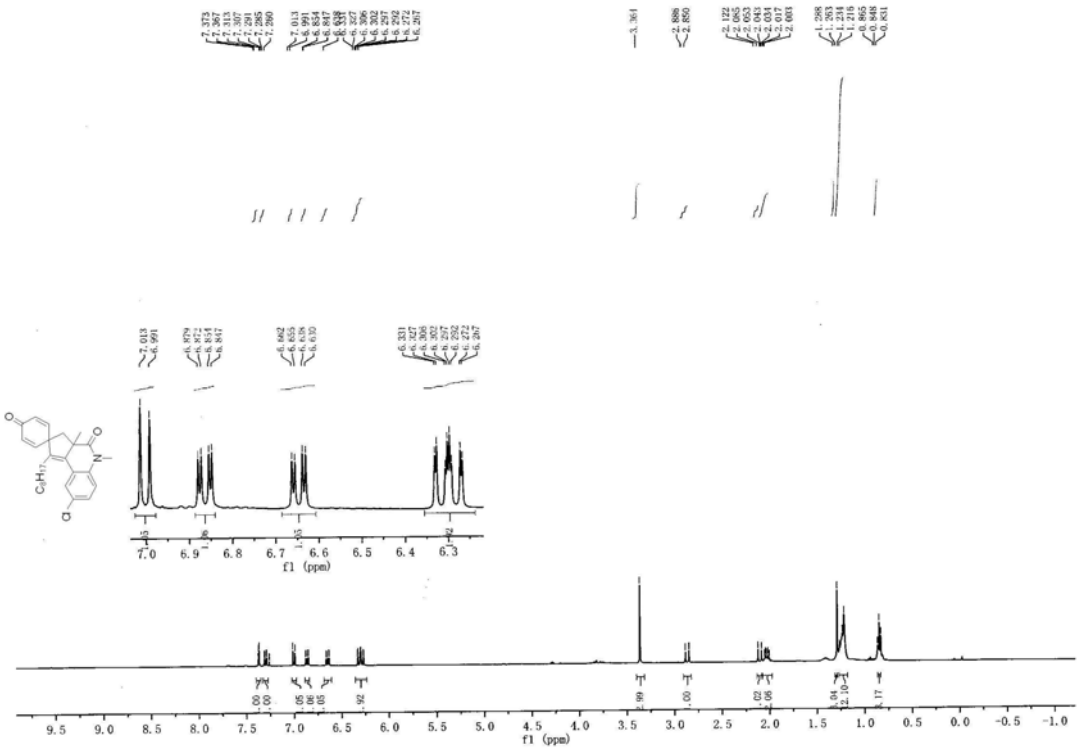


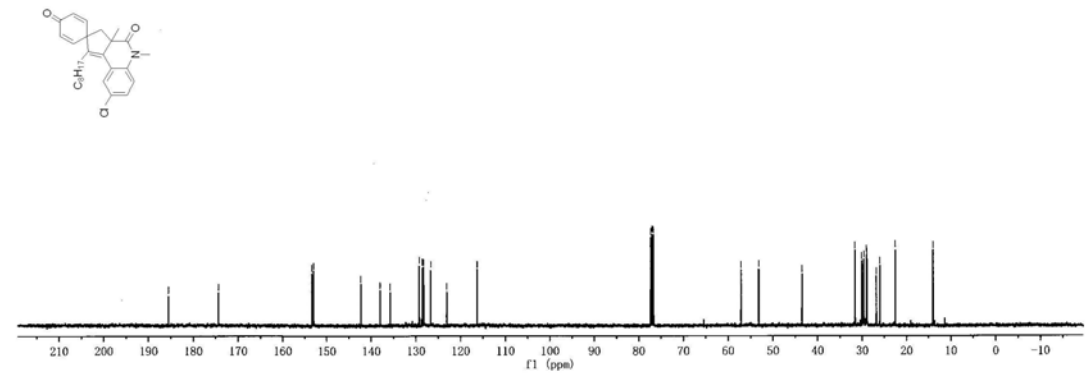
8'-Fluoro-3a',5'-dimethyl-1'-octyl-3',3a'-dihydrospiro[cyclohexa[2,5]diene-1,2'-cyclopenta[*c*]quinoline]-4,4'(*5'H*)-dione (3fa):



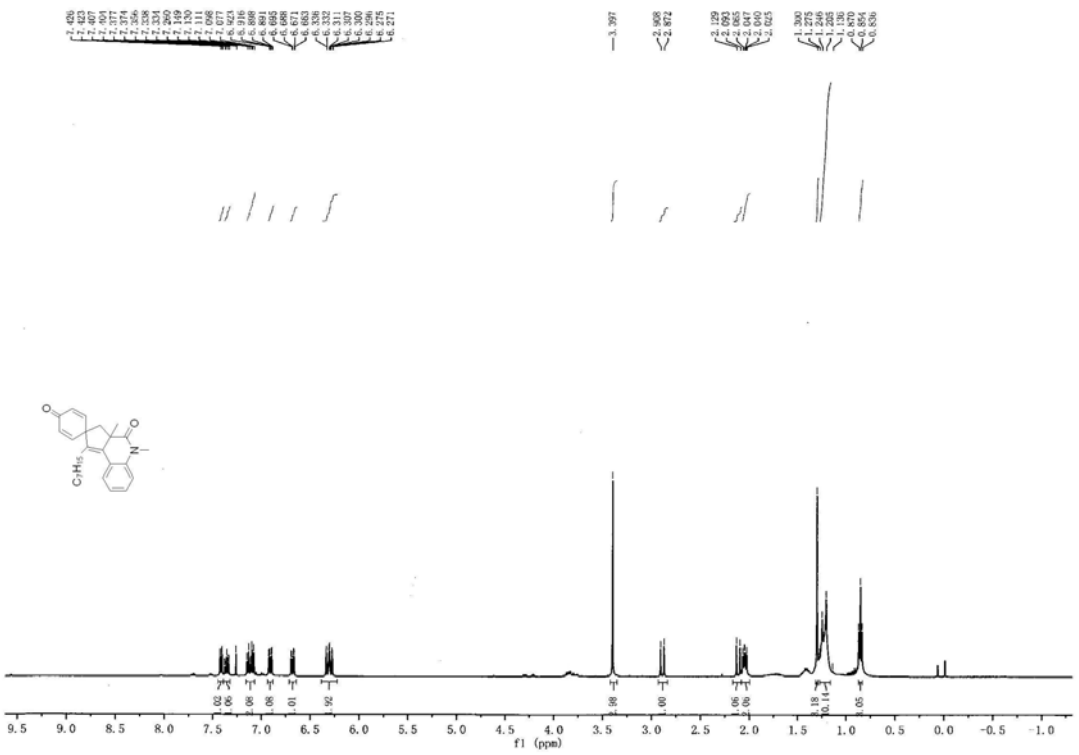


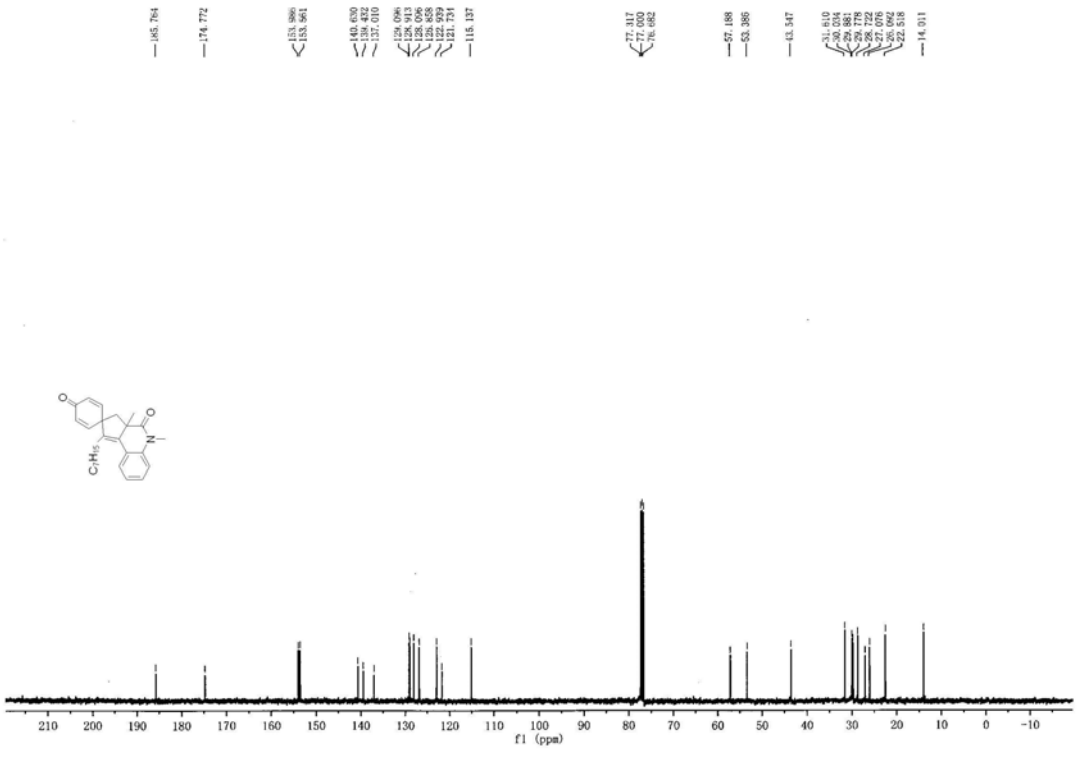
8'-Chloro-3a',5'-dimethyl-1'-octyl-3',3a'-dihydrospiro[cyclohexa[2,5]diene-1,2'-cyclopenta[*c*]quinoline]-4,4'(*5'H*)-dione (3ga):



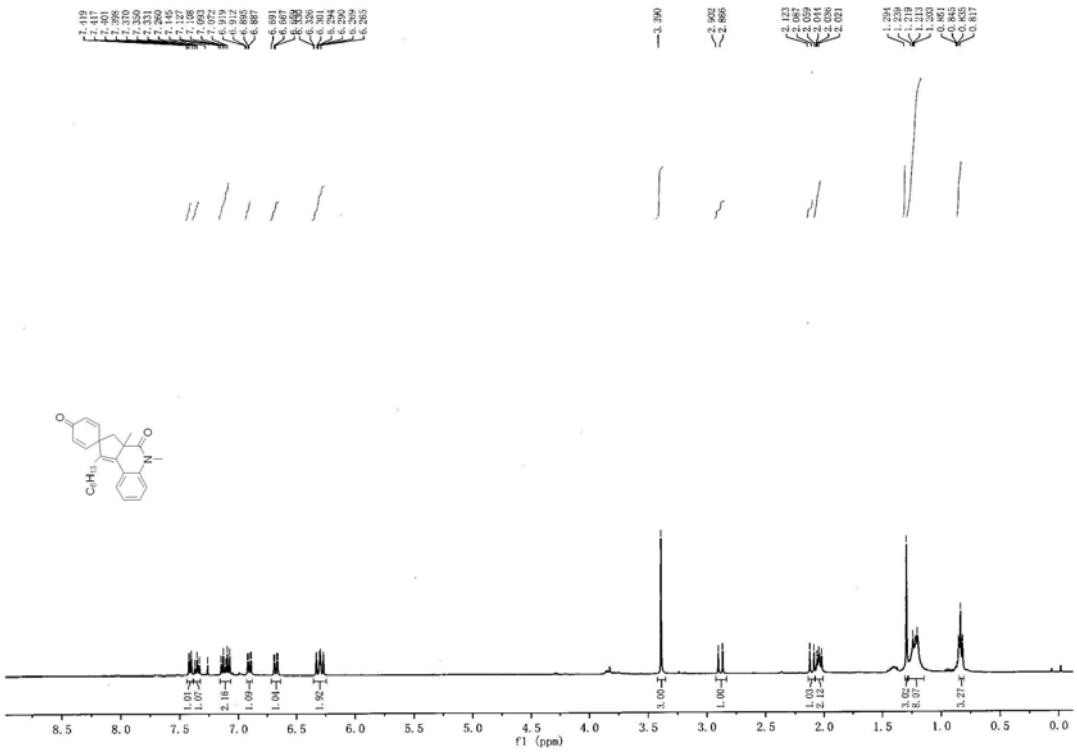


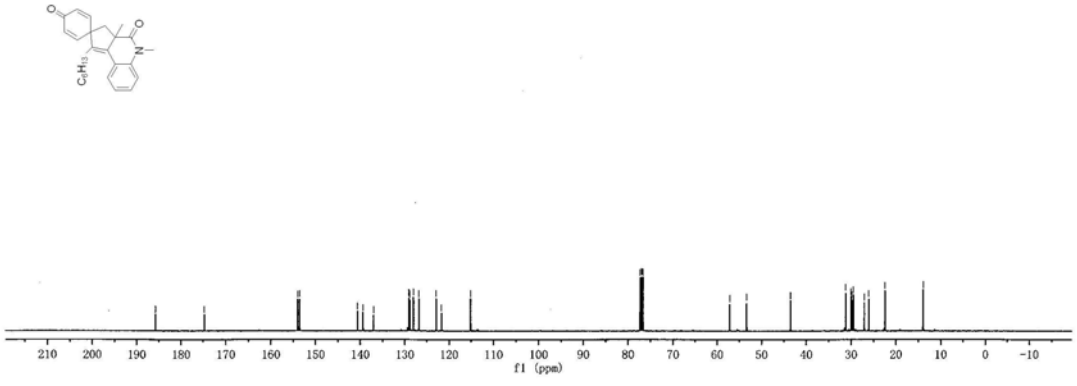
1'-Heptyl-3a',5'-dimethyl-3',3a'-dihydrospiro[cyclohexa[2,5]diene-1,2'-cyclopenta[*c*]quinoline]-4,4'(*5'H*)-dione (3ha):



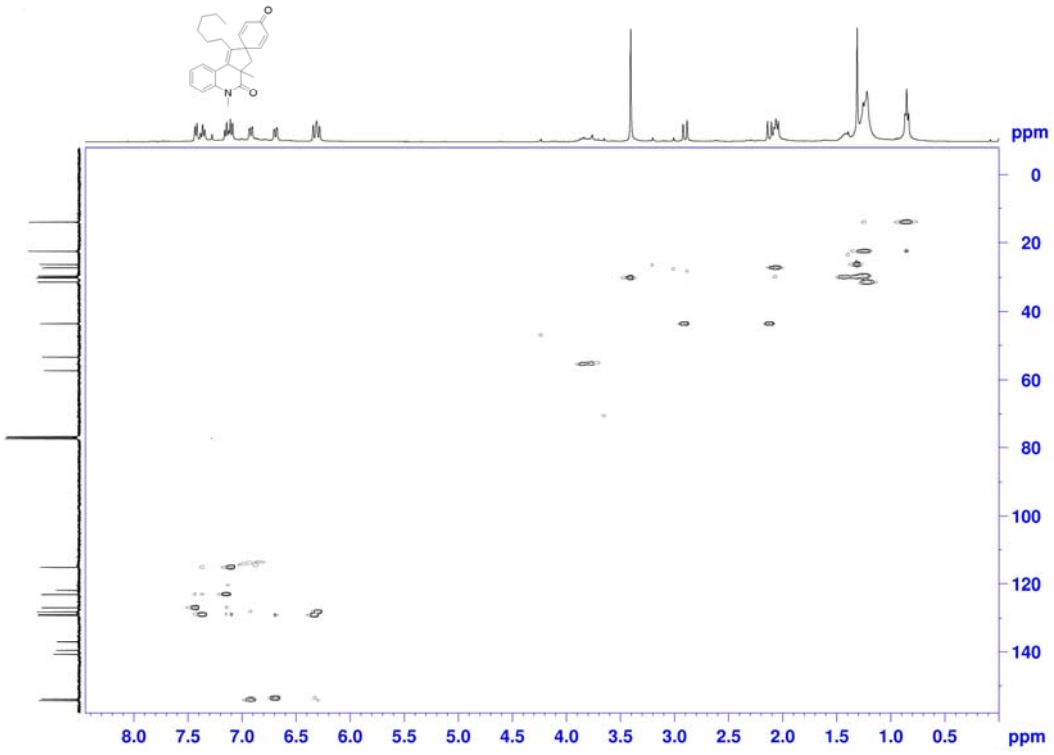


1'-Hexyl-3a',5'-dimethyl-3',3a'-dihydrospiro[cyclohexa[2,5]diene-1,2'-cyclopenta[*c*]quinoline]-4,4'(*5'H*)-dione (3ia):

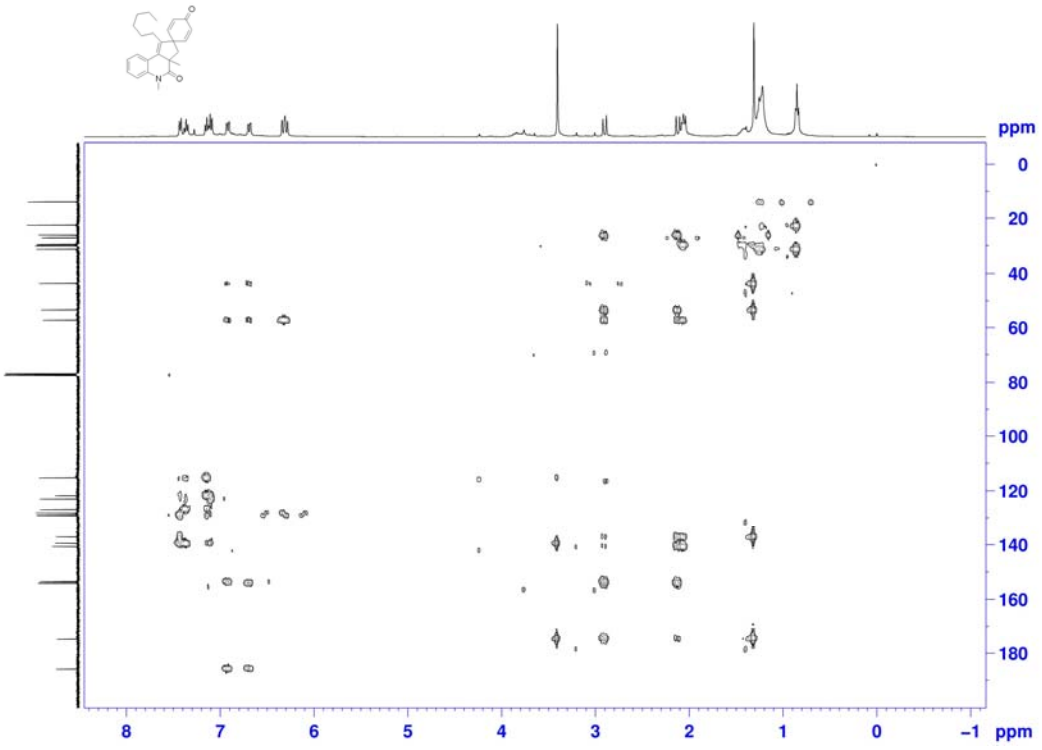




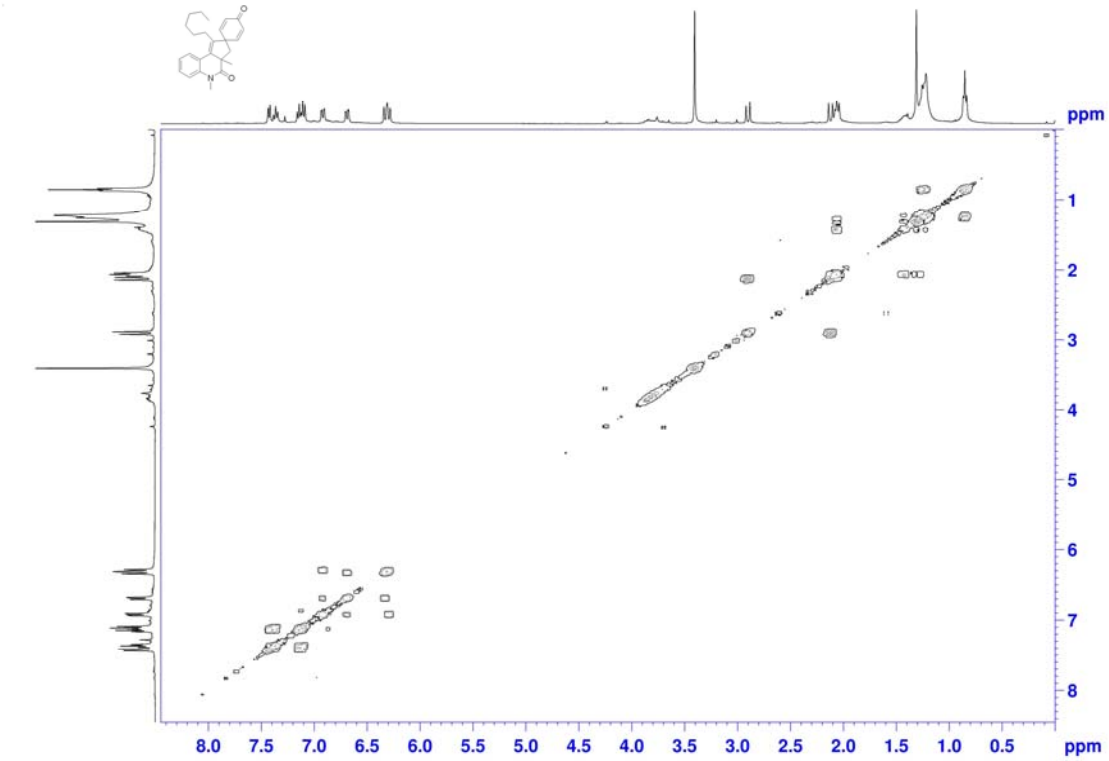
C-H HSQC



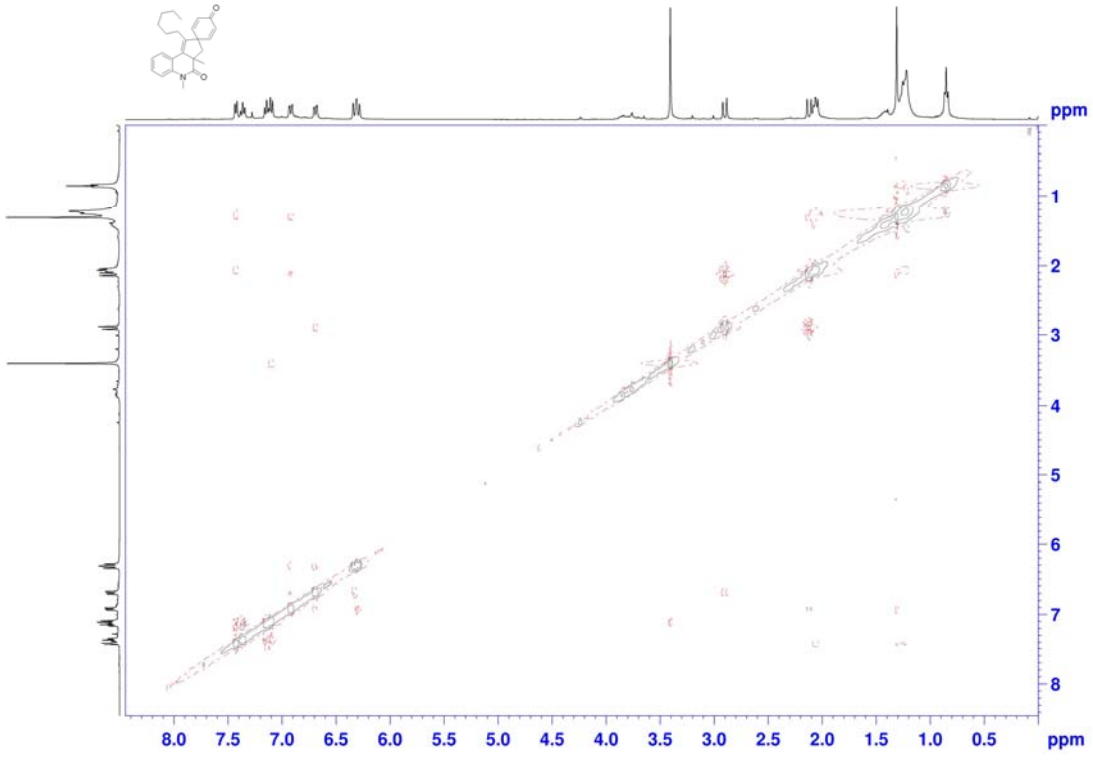
C-H HMBC



H-H COSY

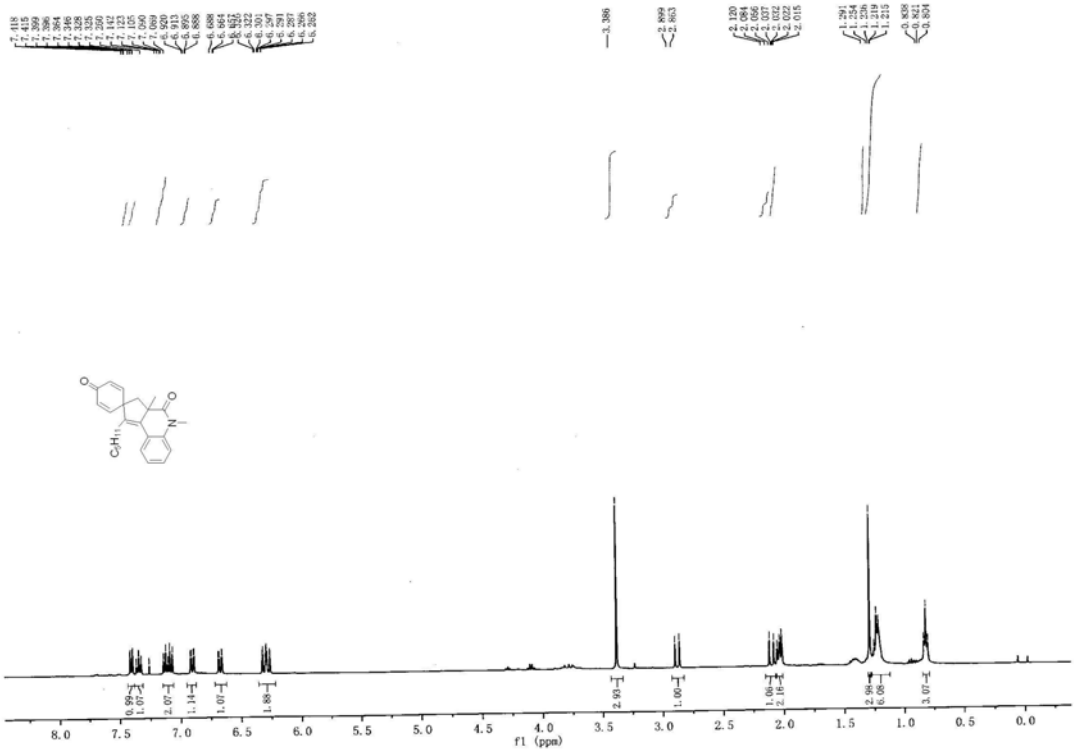


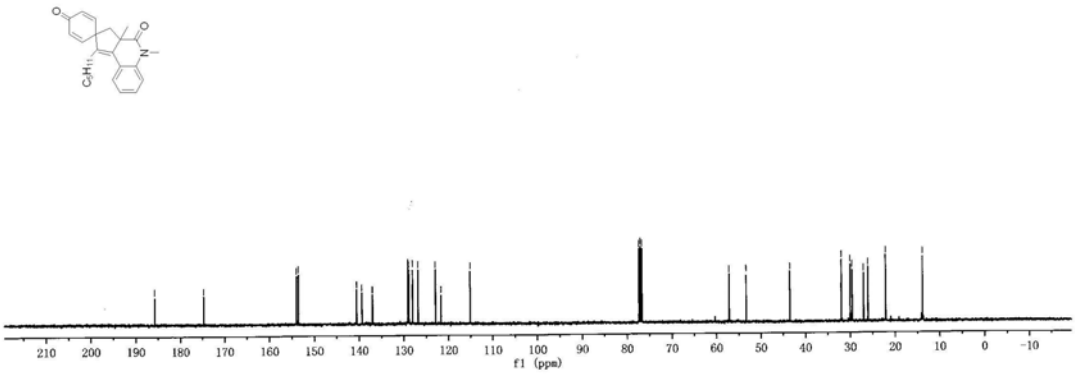
H-H NOESY



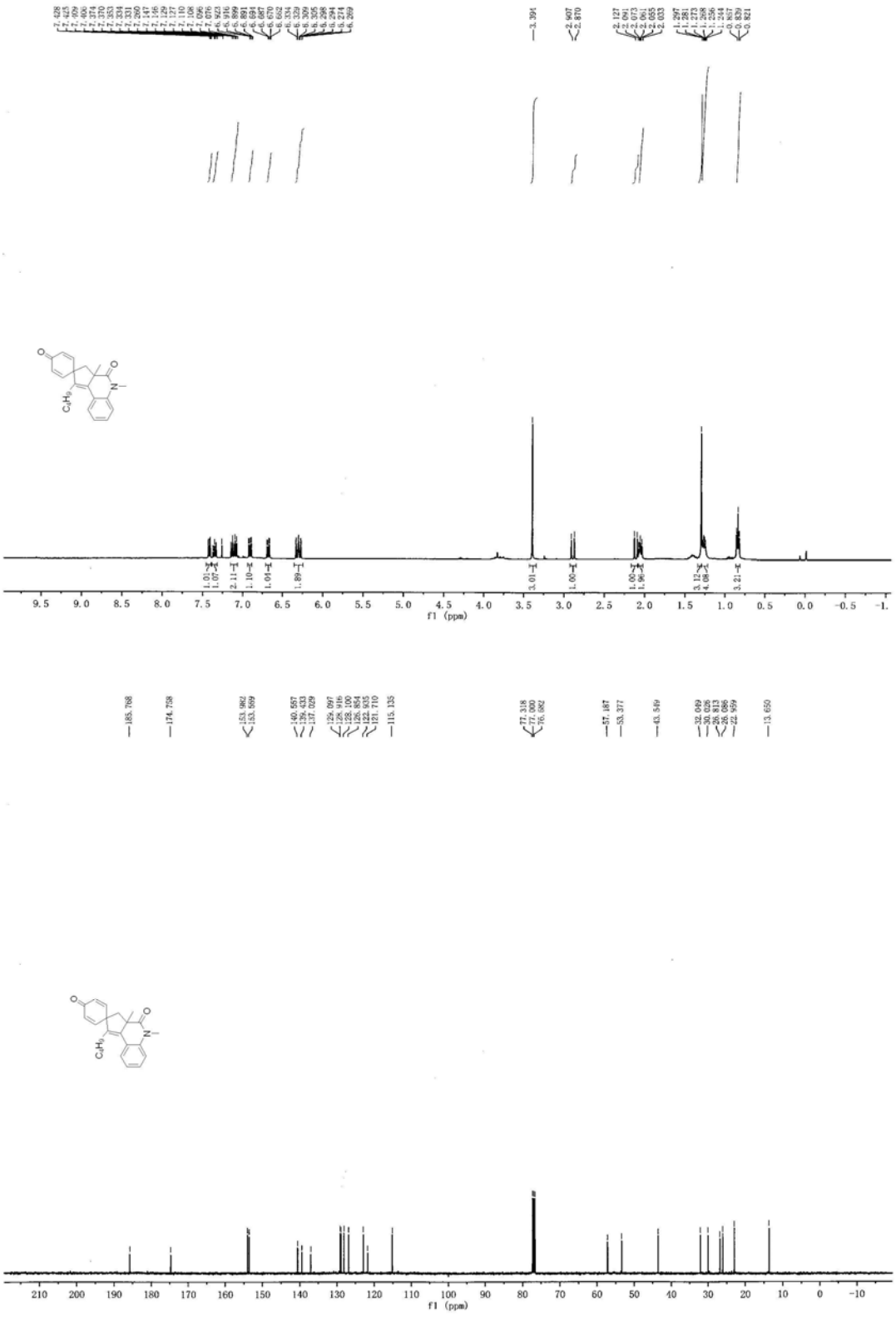
3a’,5’-Dimethyl-1’-pentyl-3’,3a’-dihydrospiro[cyclo

hexa[2,5]diene-1,2'-cyclopenta[*c*]quinoline]-4,4'(*5'H*)-dione (3ja):

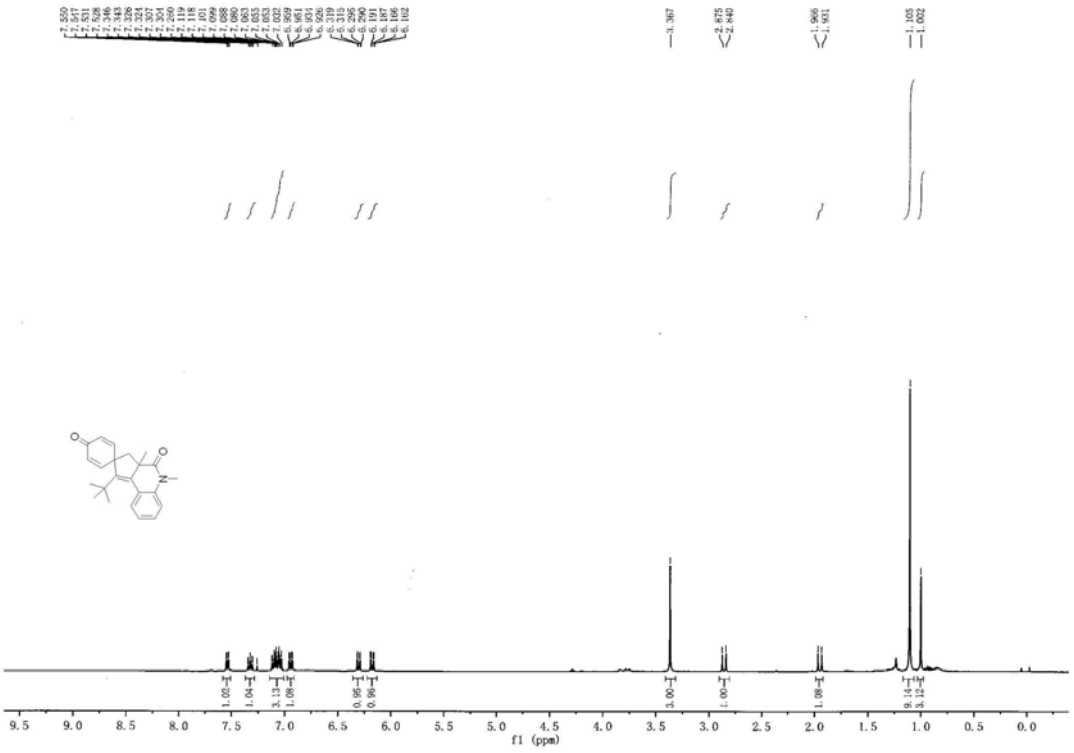


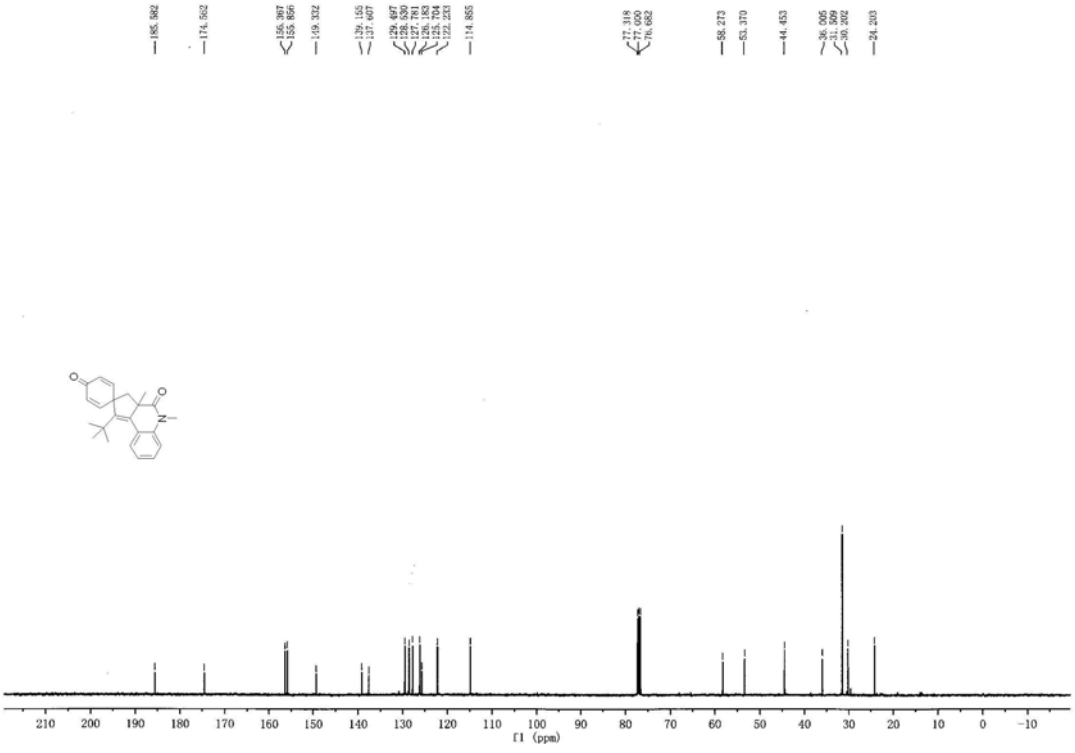


1'-Butyl-3a',5'-dimethyl-3',3a'-dihydrospiro[cyclohexa[2,5]diene-1,2'-cyclopenta[*c*]quinoline]-4,4'(*5'H*)-dione (3ka):

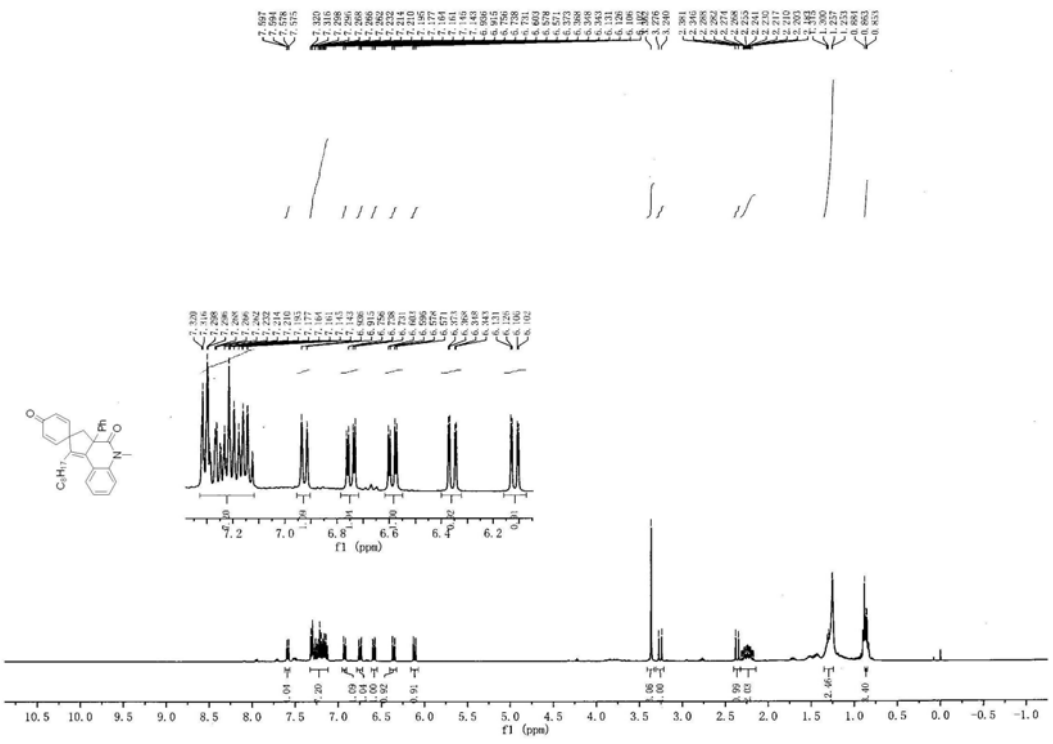


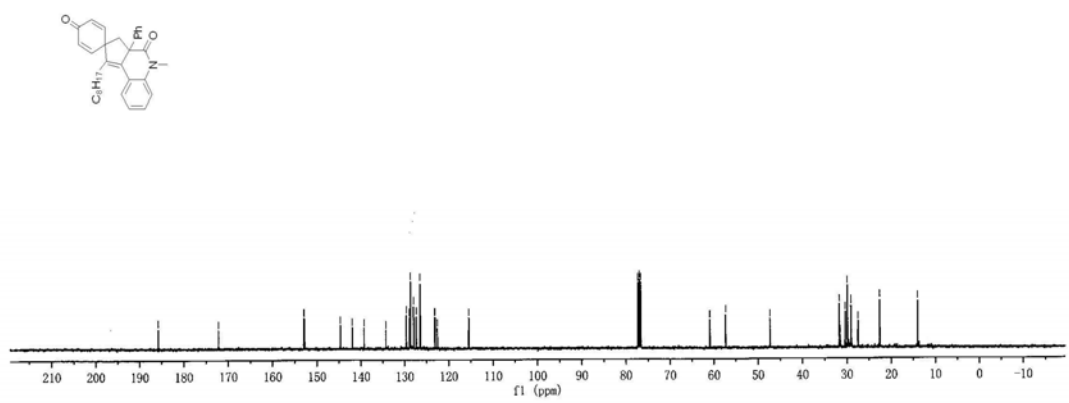
1'-*tert*-Butyl-3a',5'-dimethyl-3',3a'-dihydrospiro[cyclohexa[2,5]diene-1,2'-cyclopenta[*c*]quinoline]-4,4'(*5'H*)-dione (3la):



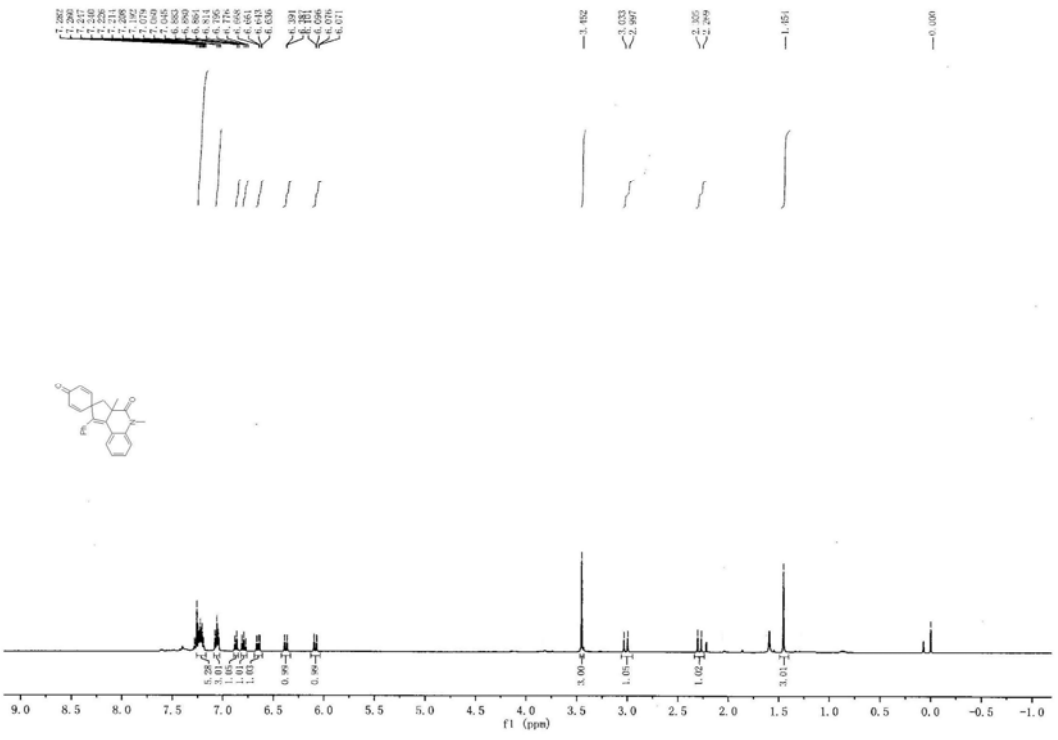


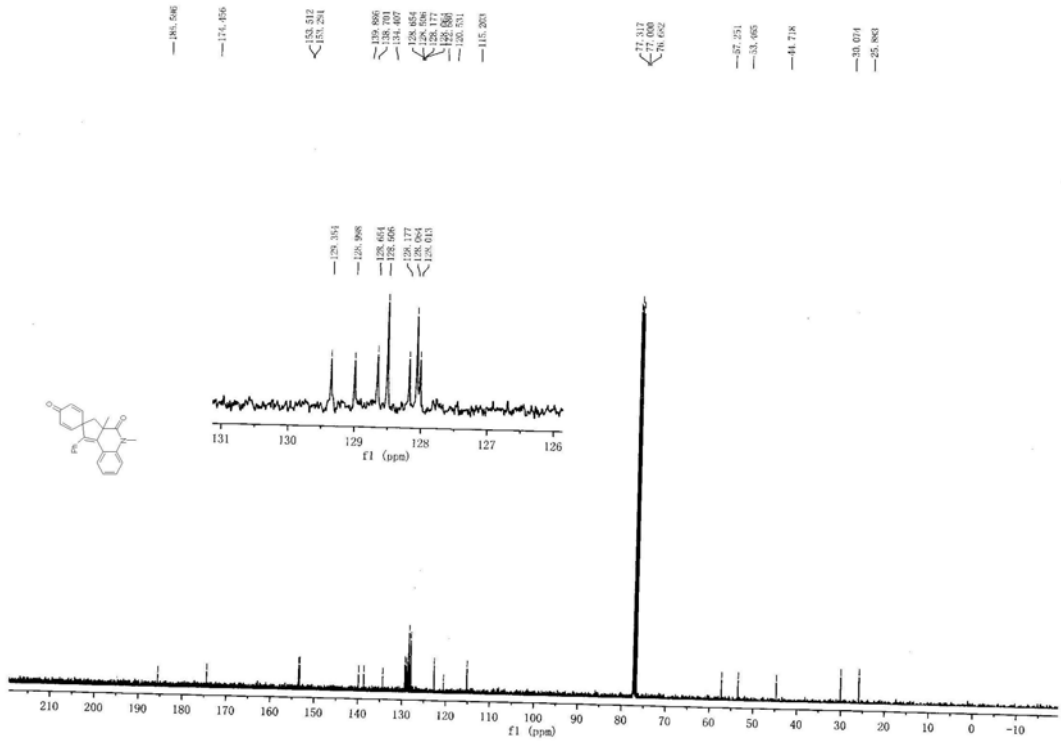
5'-Methyl-1'-octyl-3a'-phenyl-3',3a'-dihydrospiro[cyclohexa[2,5]diene-1,2'-cyclopenta[*c*]quinoline]-4,4'(*5'H*)-dione (3ma):



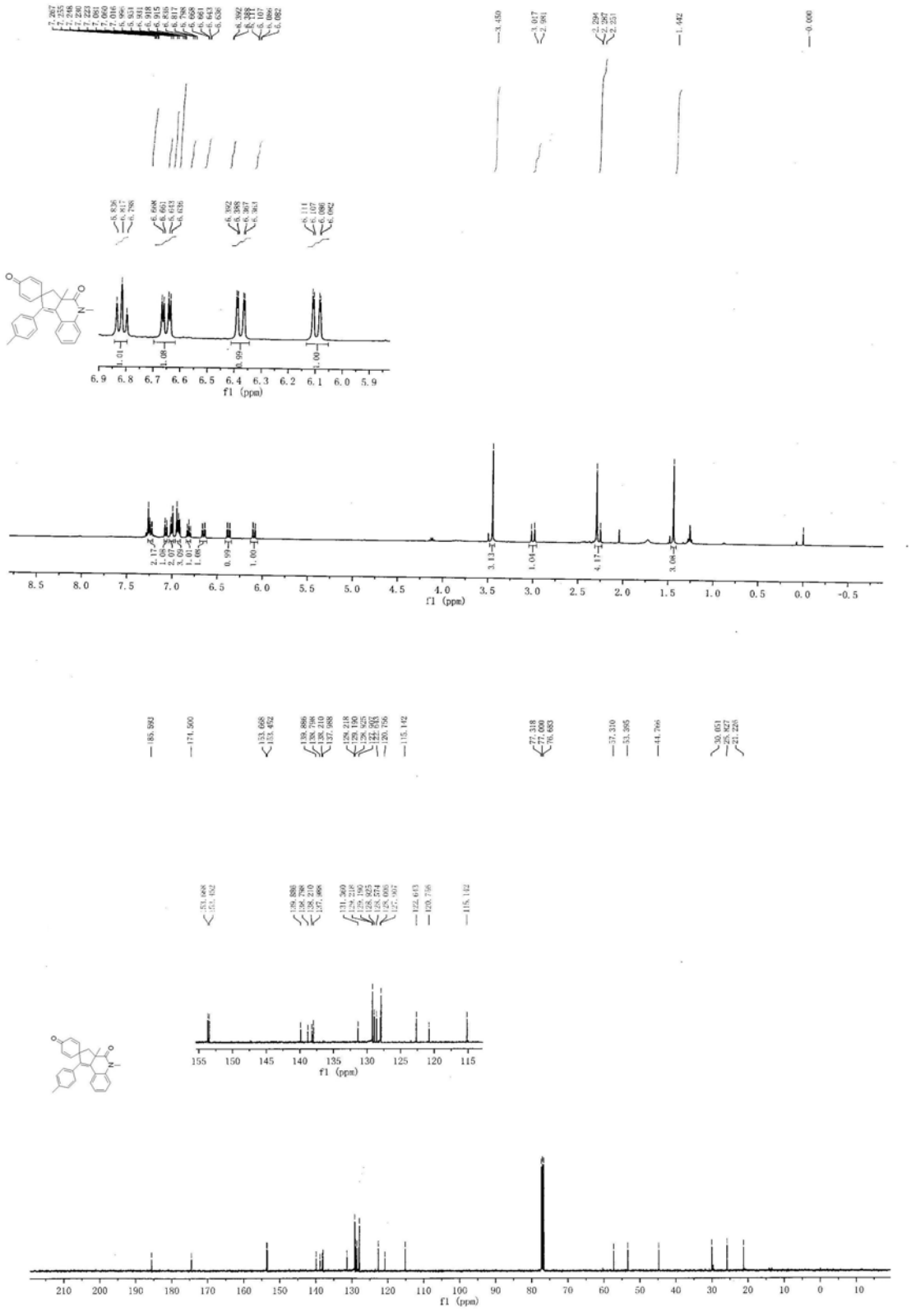


3a',5'-Dimethyl-1'-phenyl-3',3a'-dihydrospiro[cyclohexa[2,5]diene-1,2'-cyclopenta[*c*]quinoline]-4,4'(*5'H*)-dione (3oa):

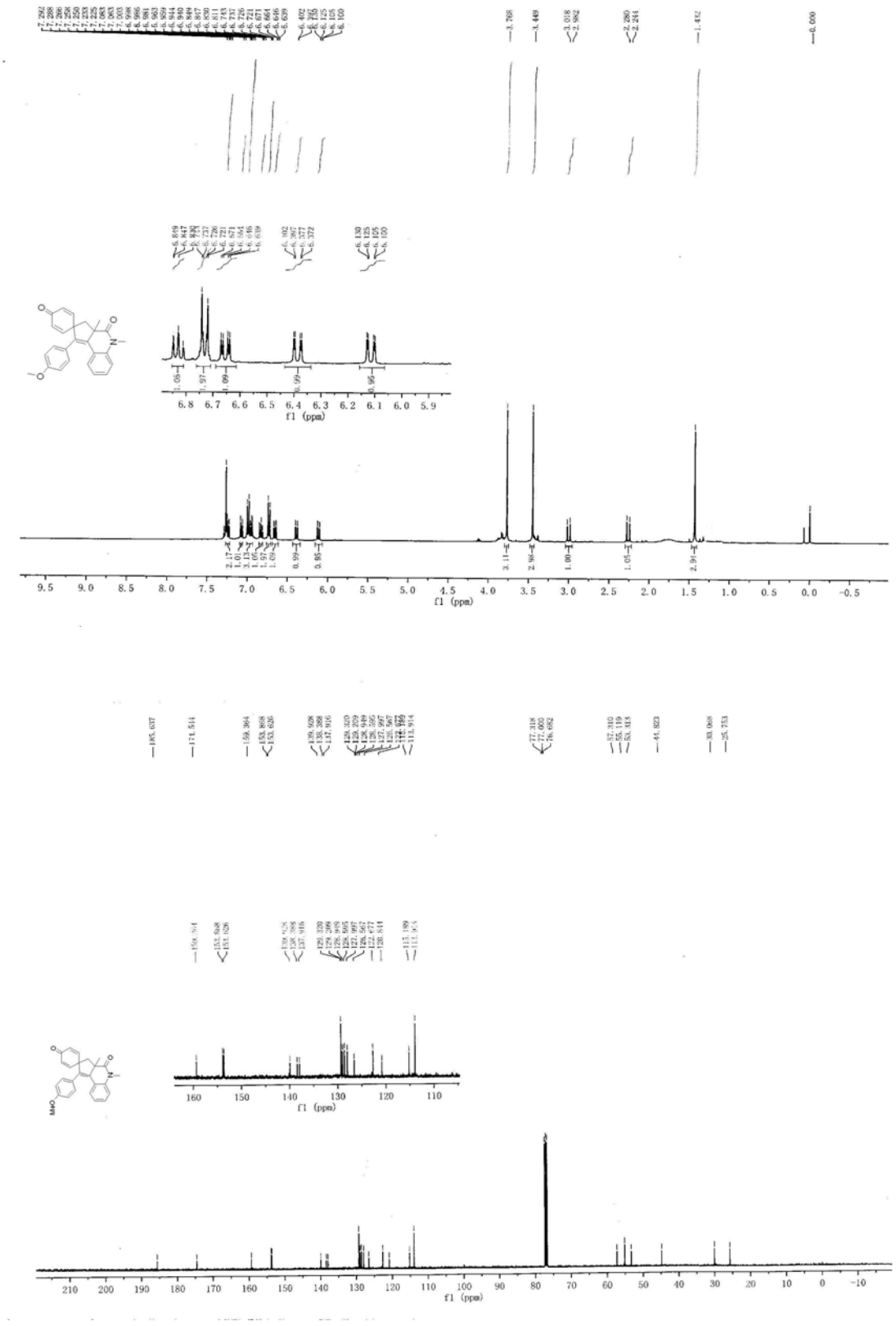




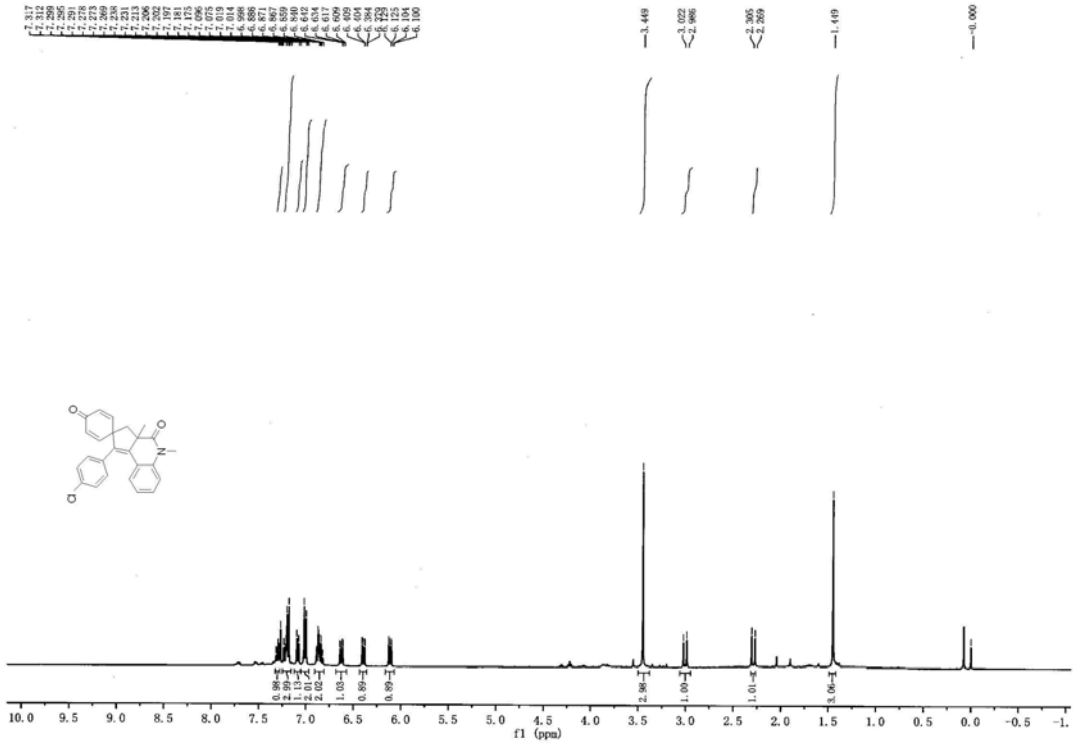
3a',5'-Dimethyl-1'-*p*-tolyl-3',3a'-dihydrospiro[cyclohexa[2,5]diene-1,2'-cyclopenta[*c*]quinoline]-4,4'(*5'H*)-dione (3pa):

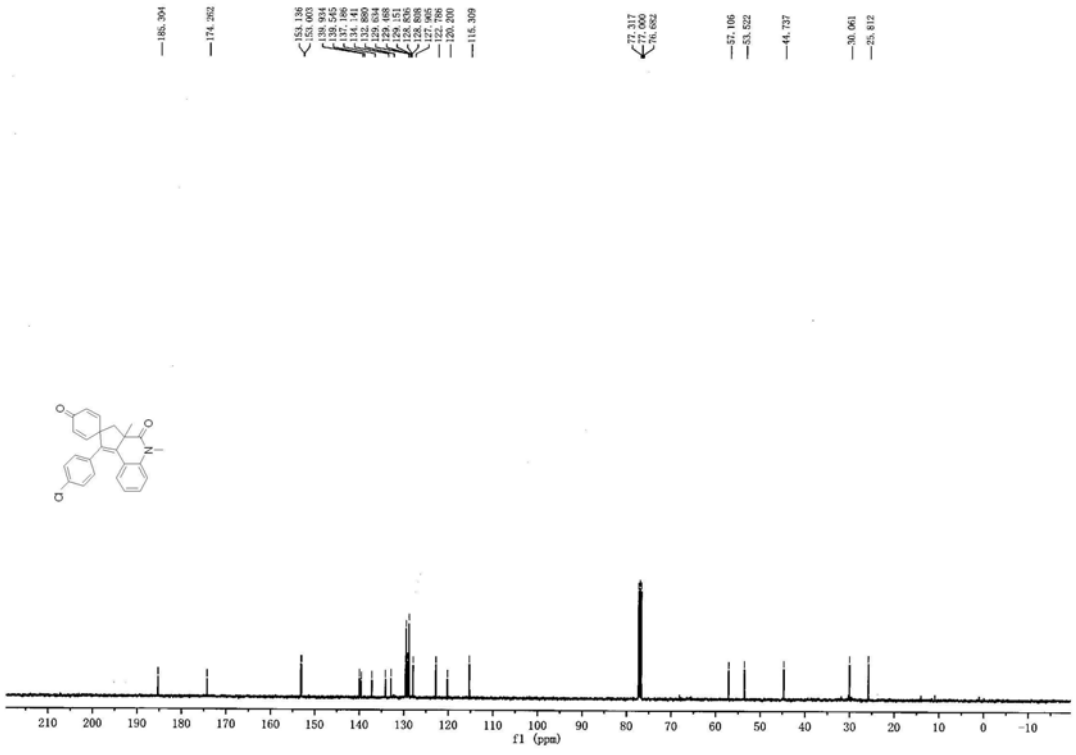


1'-(4-Methoxyphenyl)-3a',5'-dimethyl-3',3a'-dihydrospiro[cyclohexa[2,5]diene-1,2'-cyclopenta[*c*]quinoline]-4,4'(*5'H*)-dione (3qa):

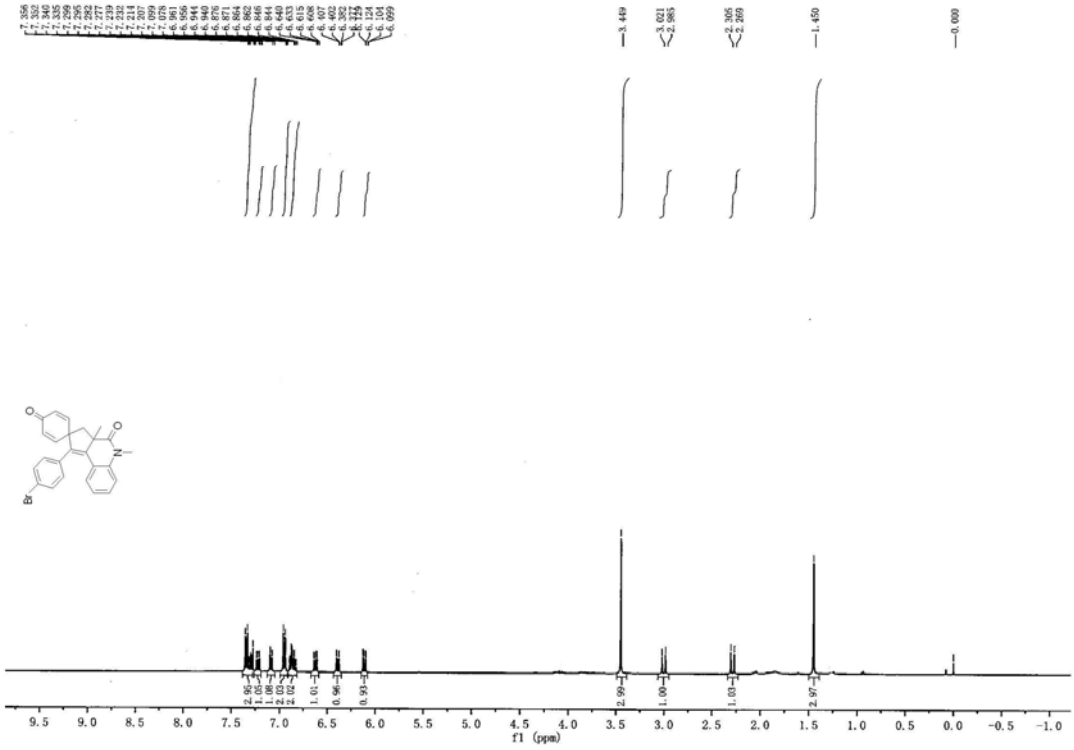


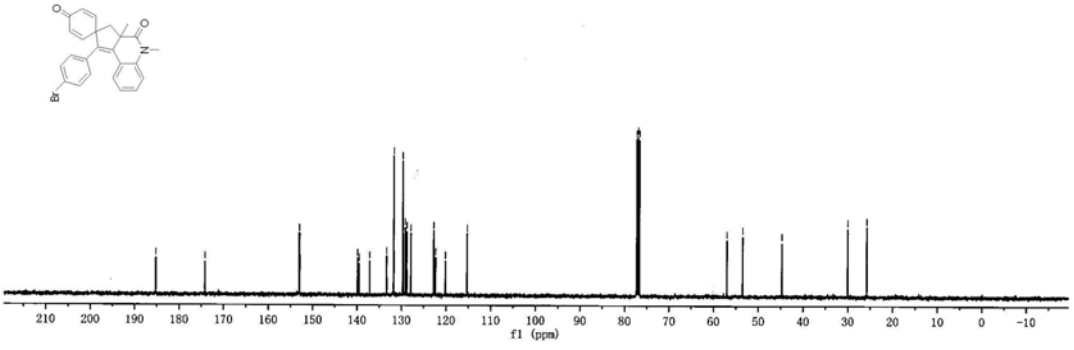
1'-(4-Chlorophenyl)-3a',5'-dimethyl-3',3a'-dihydrospiro[cyclohexa[2,5]diene-1,2'-cyclopenta[*c*]quinoline]-4,4'(*5'H*)-dione (3ra):



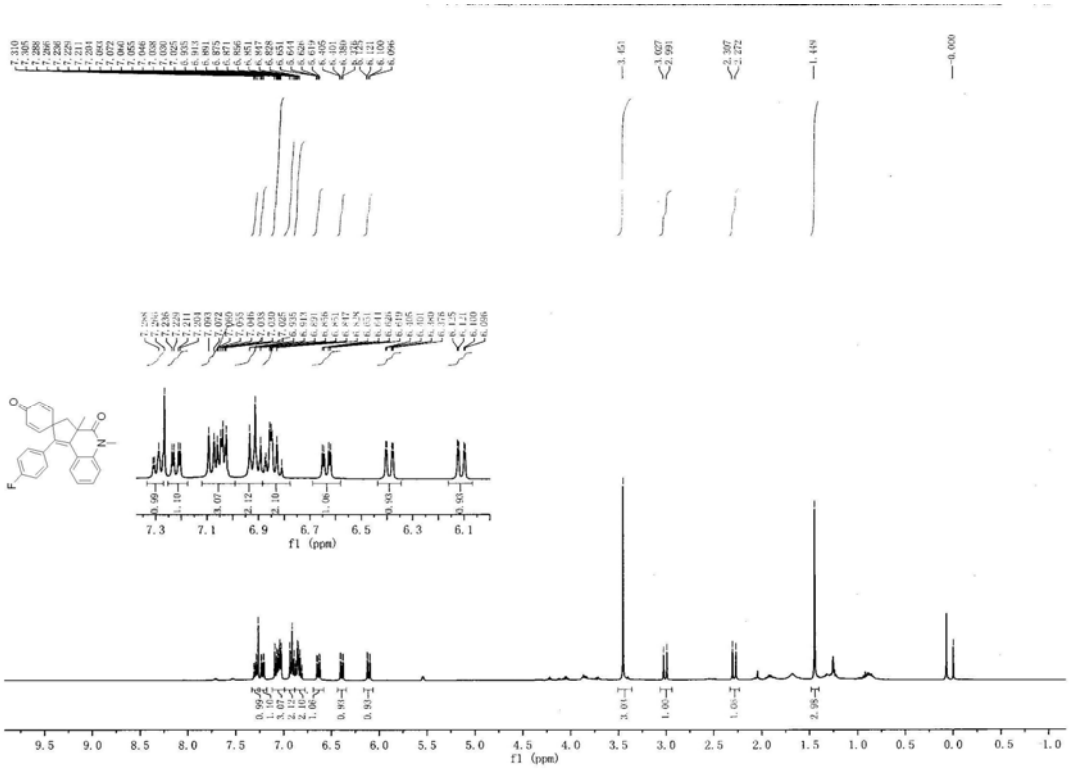


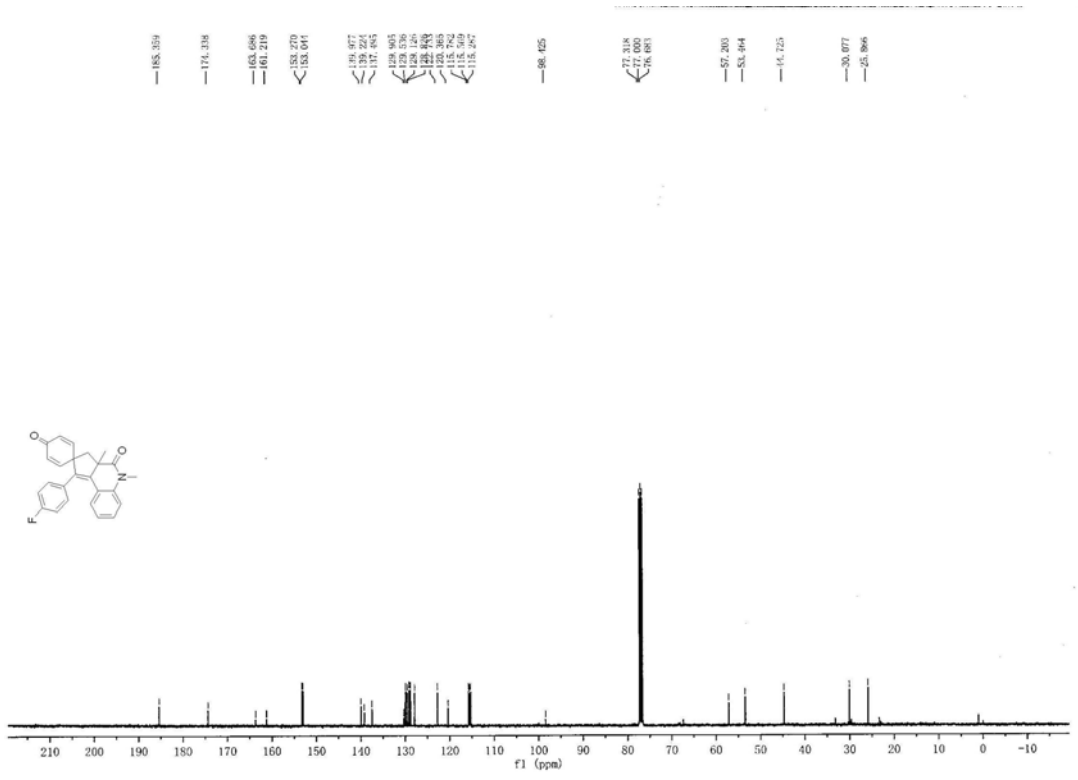
1'-(4-Bromophenyl)-3a',5'-dimethyl-3',3a'-dihydrospiro[cyclohexa[2,5]diene-1,2'-cyclopenta[c]quinoline]-4,4'(5'H)-dione: (3sa)



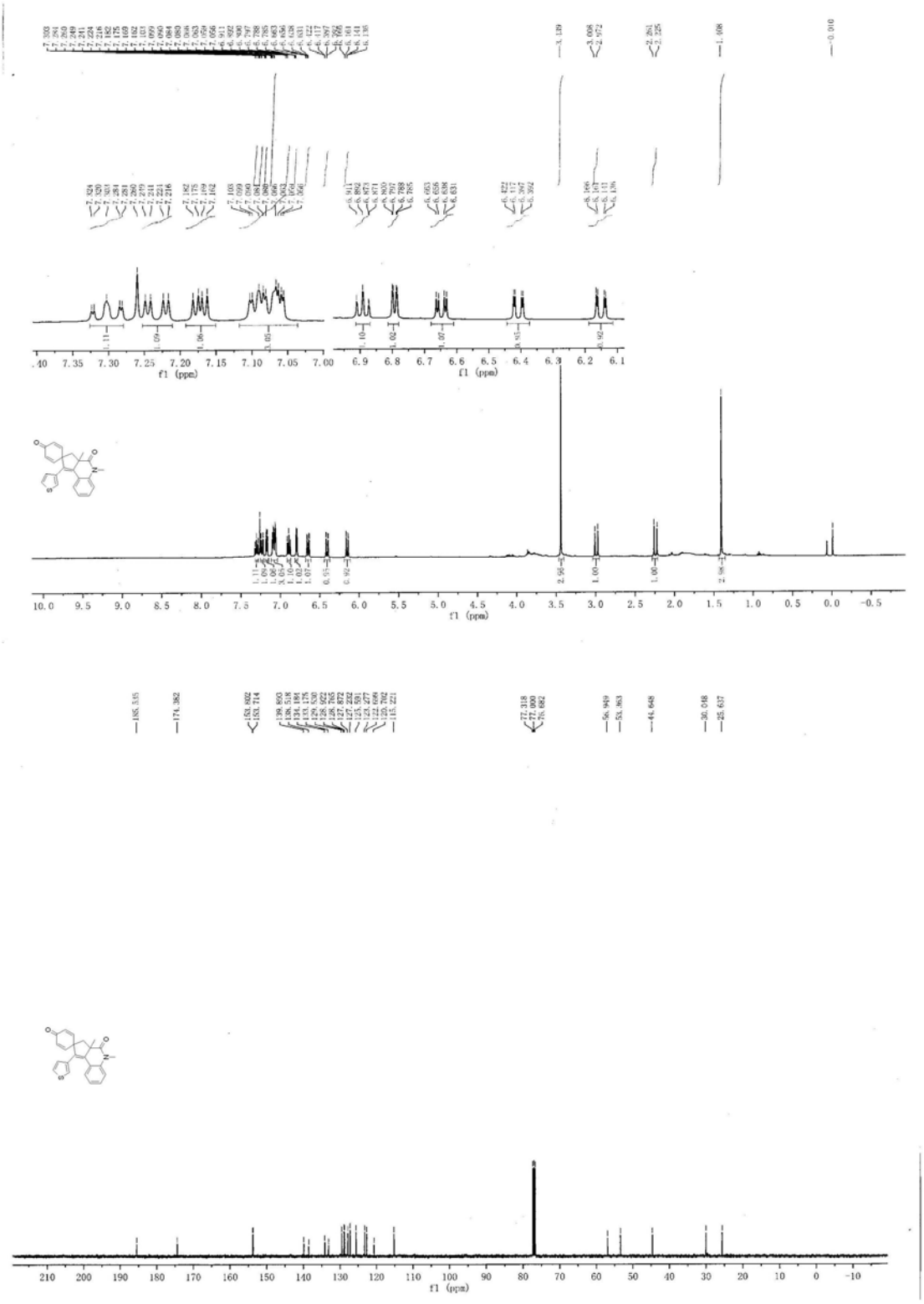


1'-(4-Fluorophenyl)-3a',5'-dimethyl-3',3a'-dihydrospiro[cyclohexa[2,5]diene-1,2'-cyclopenta[c]quinoline]-4,4'(5'H)-dione: (3ta)

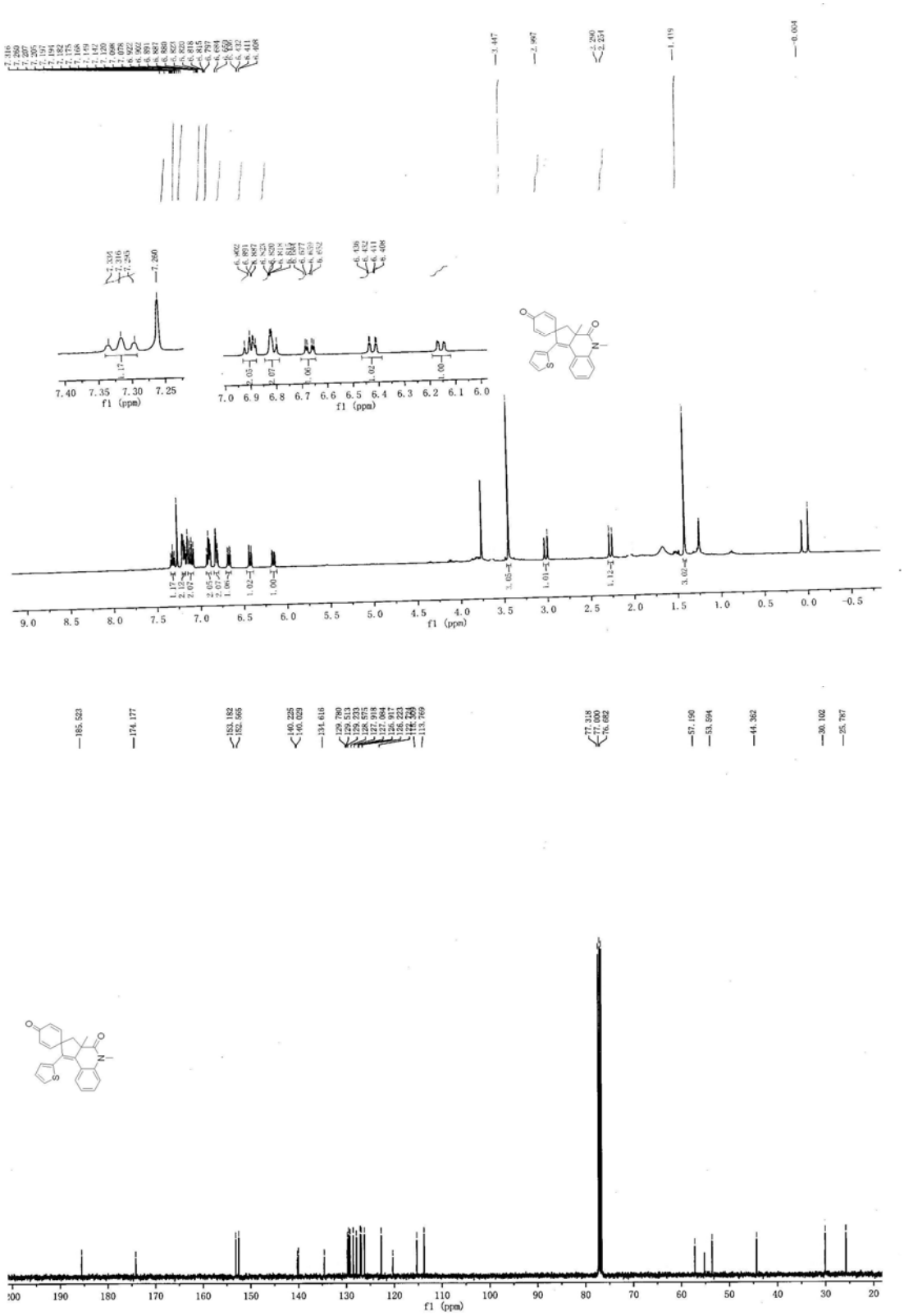




3a',5'-Dimethyl-1'-(thiophen-3-yl)-3',3a'-dihydrospiro[cyclohexa[2,5]diene-1,2'-cyclopenta[*c*]quinoline]-4,4'(*5'H*)-dione (3ua):

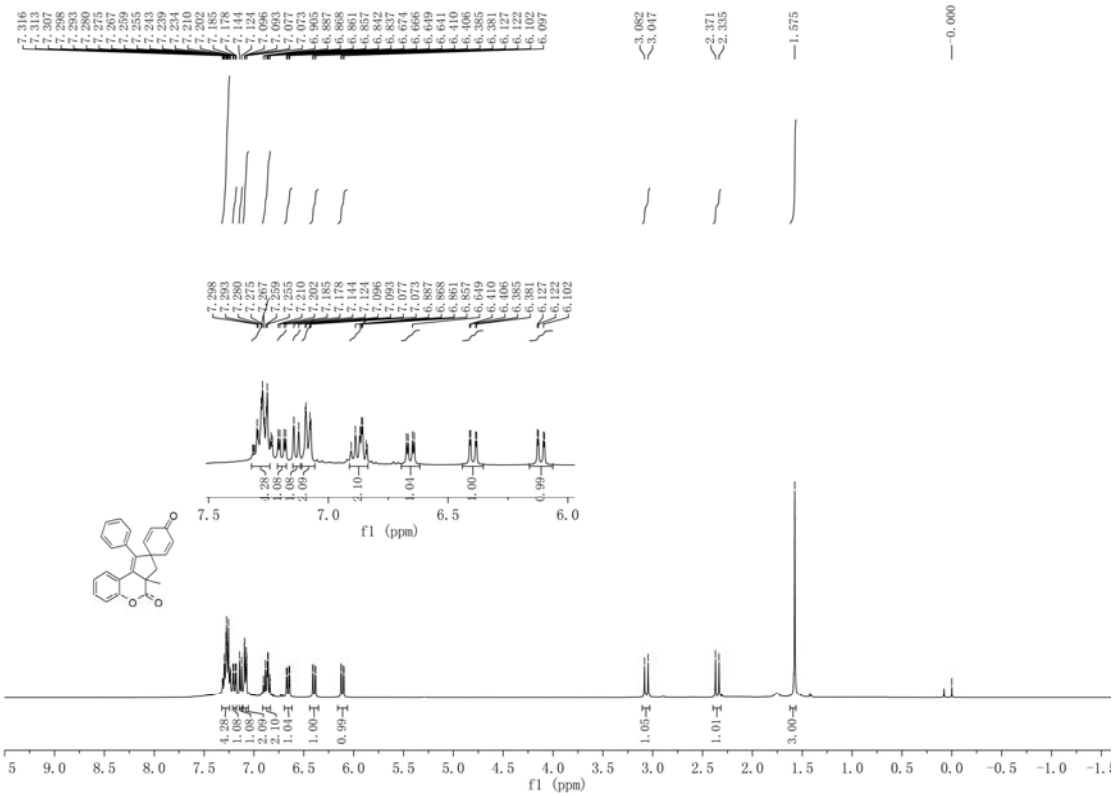


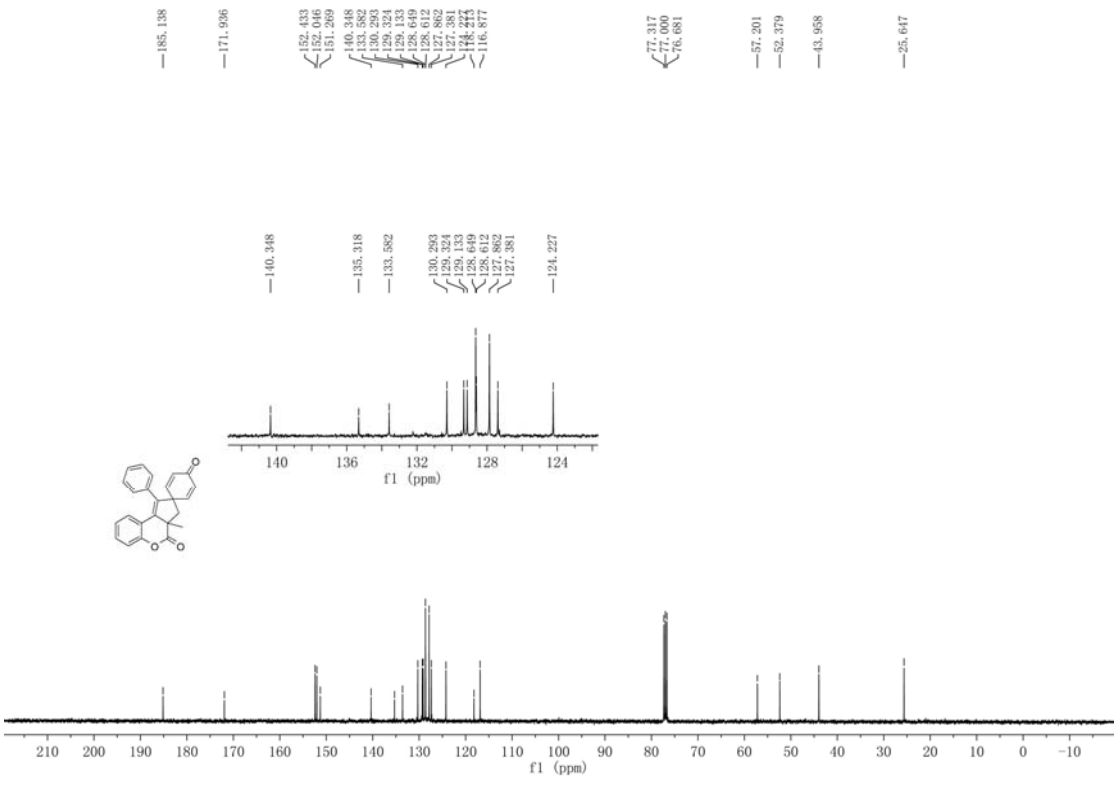
3a',5'-dimethyl-1'-(thiophen-2-yl)-3',3a'-dihydrospiro[cyclohexa[2,5]diene-1,2'-cyclopenta[c]quinoline]-4,4'(5'H)-dione: (3va)



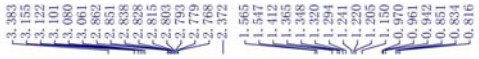
3a'-Methyl-1'-phenyl-3'H-spiro[cyclohexa[2,5]diene-1,2'-cyclopenta[c]chromene]

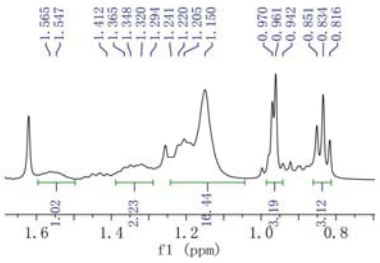
-4,4'(3a'H)-dione: (3wa)

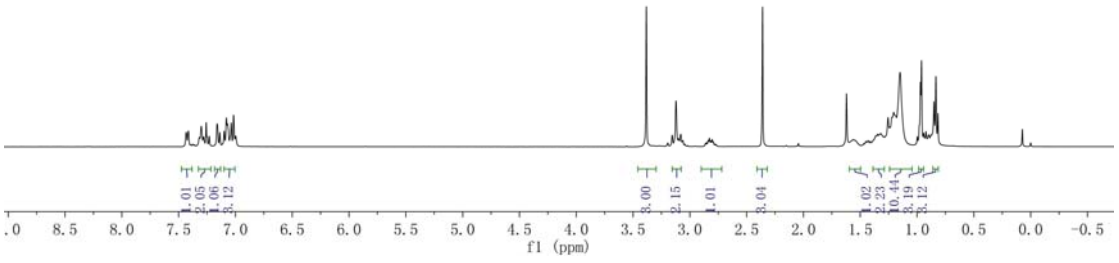


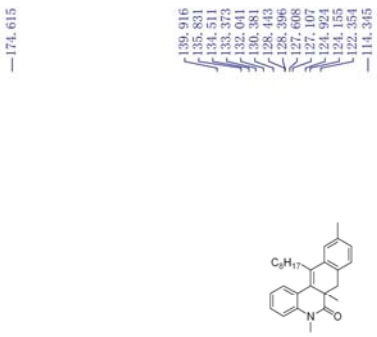


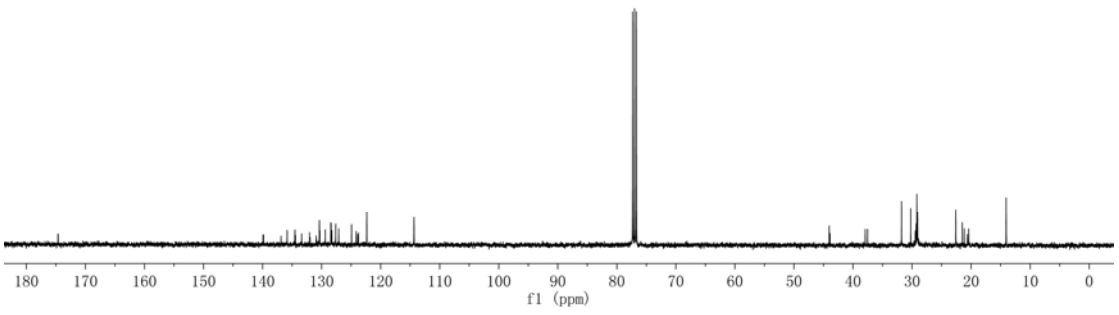
5,6a,10-Trimethyl-12-octyl-6a,7-dihydrobenzo[*j*]phenanthridin-6(5H)-one (4ah)



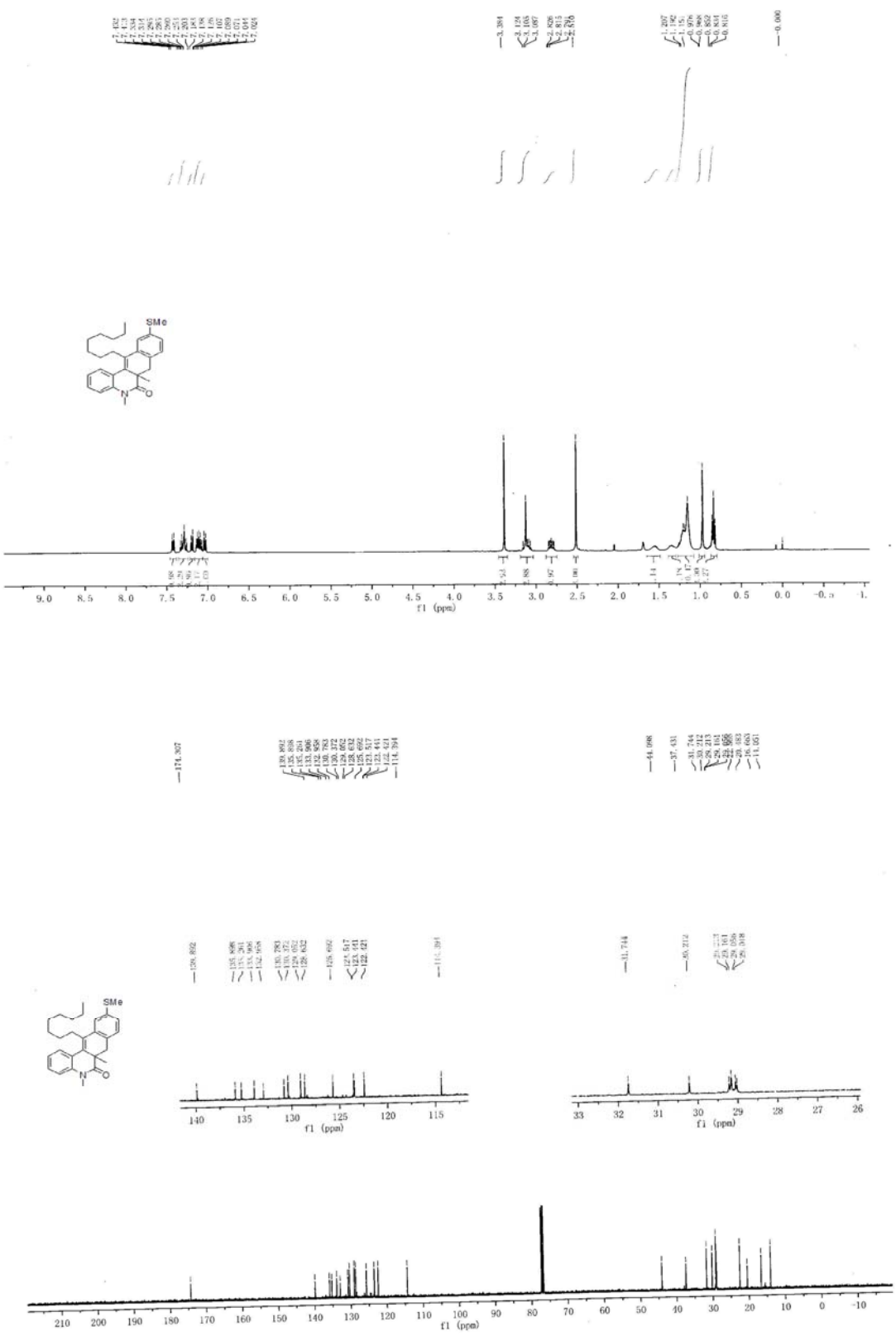




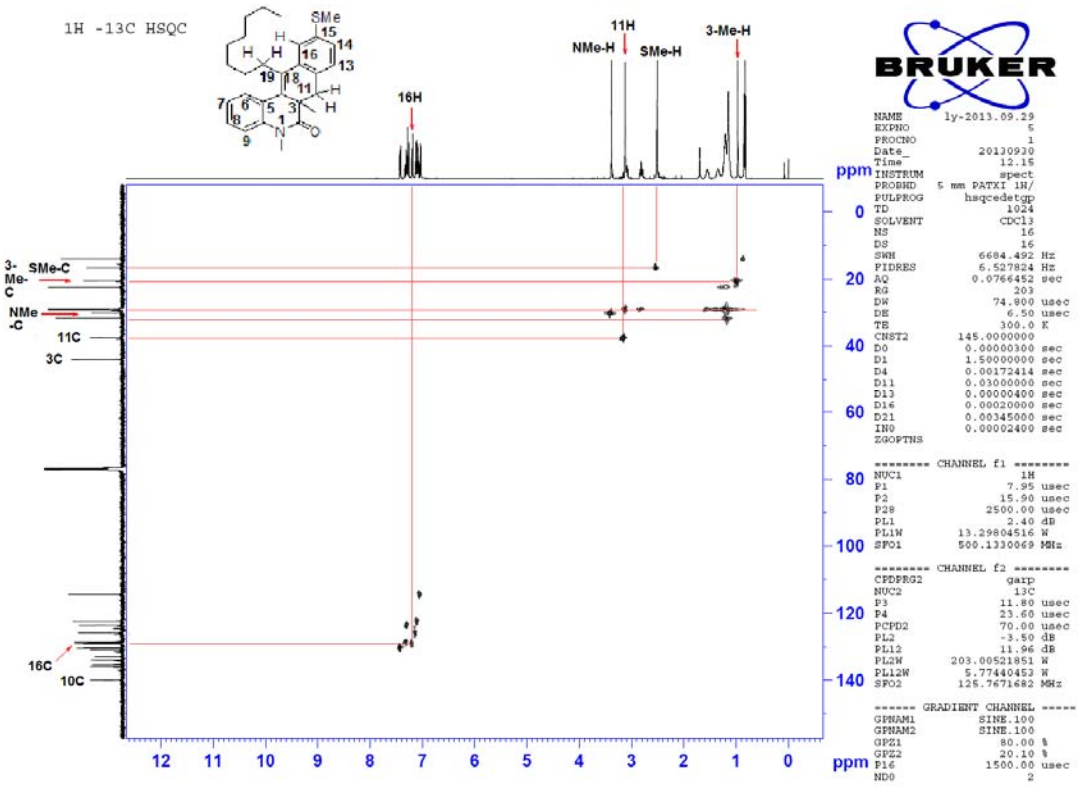




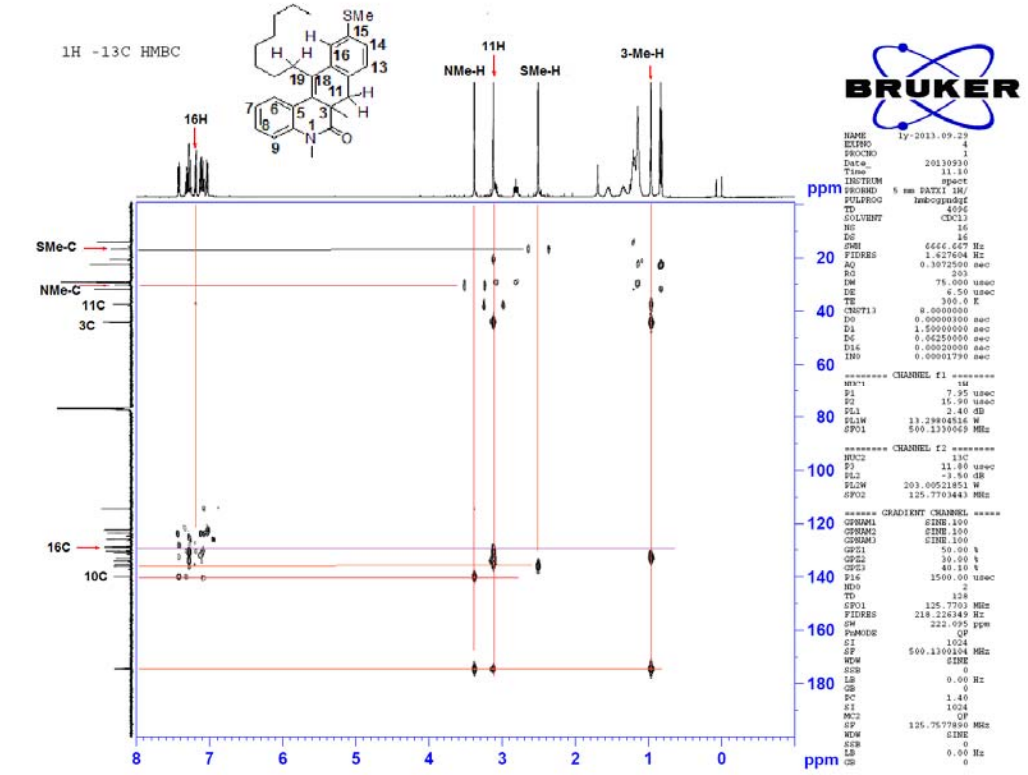
5,6a-dimethyl-10-(methylthio)-12-octyl-6a,7-dihydrobenzo[j]phenanthridin-6(5H)-one (4aj)



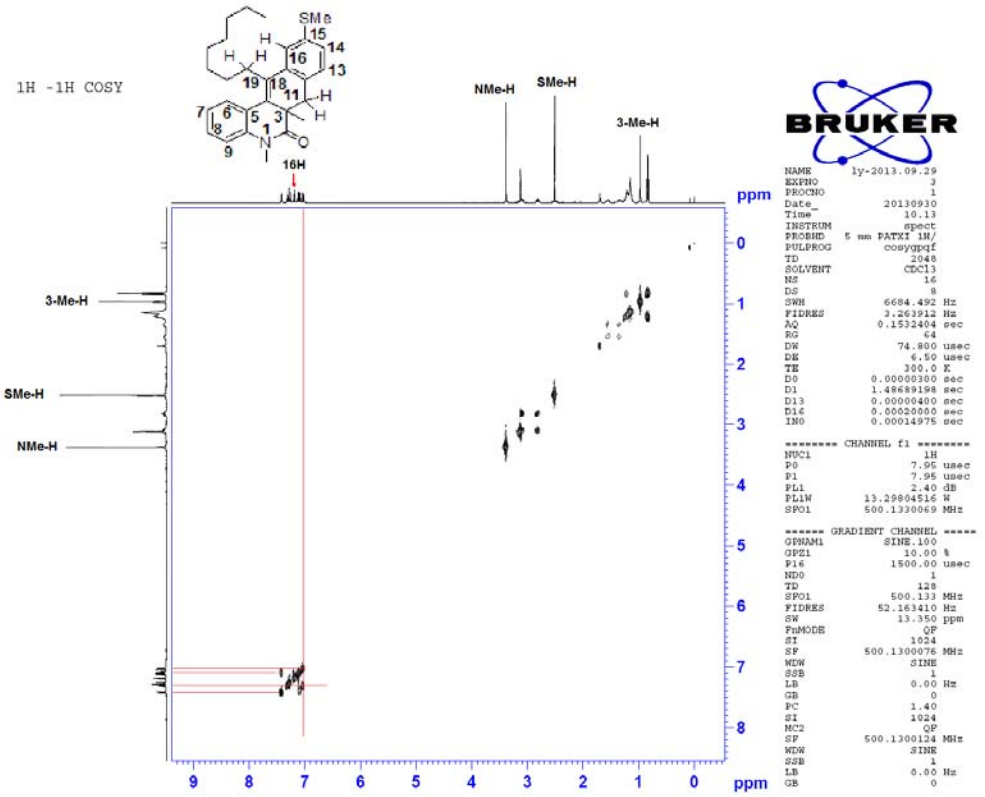
C-H HSQC



C-H HMBC



H-H Cosy



H-H Noesy