Supplementary Information

Oxidative Tandem Annulation of 1-(2-Ethynylaryl)prop-2-en-1-ones Catalyzed by Cooperative Iodine and TBHP

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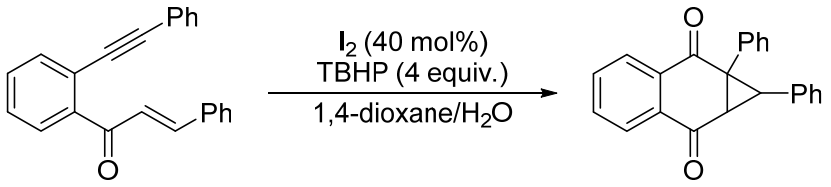
(A) Typical experimental procedures

(a) General

The ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ solvent on a NMR spectrometer using TMS as internal standard. HRMS was measured on an electrospray ionization (ESI) apparatus using time-of-flight (TOF) mass spectrometry. Melting points are uncorrected. The instrument for electrolysis is DC power source (PM3005B) (made in China). Cyclic voltammograms were obtained on a CHI 605E potentiostat. The anode electrode is graphite rod (Φ6mm×80mm) and cathode electrode is platinum electrodes (1.0×1.0 cm^2). Starting materials (1-(2-ethynylaryl)prop-2-en-1-ones) **1** were synthesized according to the literature procedures.[1-4].

(b) General procedure for the oxidative tandem annulation of 1-(2-ethynylaryl)prop-2-en-1-ones (1):



1a **2a**

To a 25 mL Schlenk tube were added I_2 (40 mol %), 1,6-enyne **1a** (0.2 mmol) , and 1,4-dioxane/H_2O (v/v=10/1; 3.3 mL). Then TBHP (70%w in water) 4 equiv. was added to the solution. The mixture was stirred at 80 °C under argon atmosphere for 14 h until complete consumption of starting material as monitored by TLC and/or GC-MS analysis. After the reaction was finished, the reaction mixture was cooled to room temperature, diluted with ethyl acetate, and washed with $Na_2S_2O_3$ and saturated NaCl. The aqueous phase was extracted twice with ethyl acetate and washed with saturated

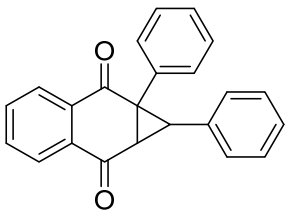
NaCl. The combined organic phases were dried over anhydrous Na_2SO_4 and concentrated, then purified by column chromatography (petroleum ether/ethyl acetate, v/v=15/1) to afford **2a** (86% yield, 55.7 mg).

1 mmol scale

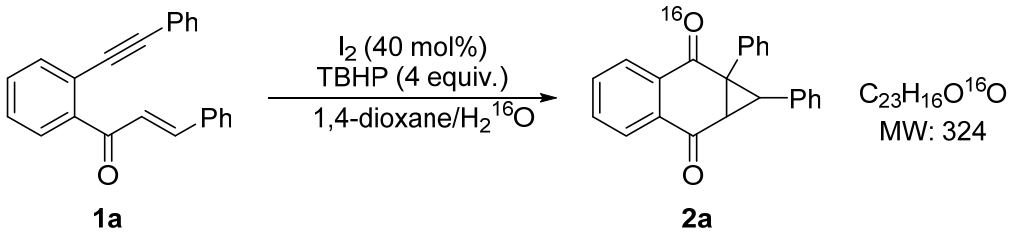
To a 25 mL Schlenk tube were added I_2 (40 mol %), 1,6-enyne **1a** (1 mmol) , and 1,4-dioxane/H_2O (v/v=10/1; 5.5 mL). Then TBHP (70% solution in water) 4 equiv. was added to the solution. The mixture was stirred at 80 °C under argon atmosphere for 14 h until complete consumption of starting material as monitored by TLC and/or GC-MS analysis. After the reaction was finished, the reaction mixture was cooled to room temperature, diluted with ethyl acetate, and washed with $Na_2S_2O_3$ and saturated NaCl. The aqueous phase was extracted twice with ethyl acetate and washed with saturated NaCl. The combined organic phases were dried over anhydrous Na_2SO_4 and concentrated, then purified by column chromatography (petroleum ether/ethyl acetate, v/v=15/1) to afford **2a** (90% yield, 290 mg).

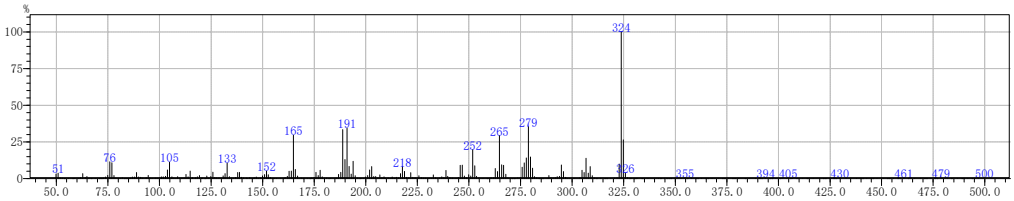
(B) Analytical data

1,1a-Diphenyl-1a,7a-dihydro-1*H*-cyclopropa[*b*]naphthalene-2,7-dione (2a)[5]



86% yield, 55.7mg; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 - 8.07 (m, 2H), 7.80 - 7.79 (m, 2H), 7.25 - 7.23 (m, 3H), 7.15 - 7.07 (m, 5H), 6.76 (d, J = 7.2 Hz, 2H), 3.67 (d, J = 5.6 Hz, 1H), 3.42 (d, J = 5.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.7, 191.0, 134.4, 134.2, 133.3, 132.5, 132.5, 131.8, 131.6, 128.1, 128.0, 128.0, 127.5, 126.8, 50.9, 43.0, 39.9; LRMS (EI, 70 eV) *m/z* (%): 324 (M^+, 100), 279 (35), 265 (29).





[MS Spectrum]

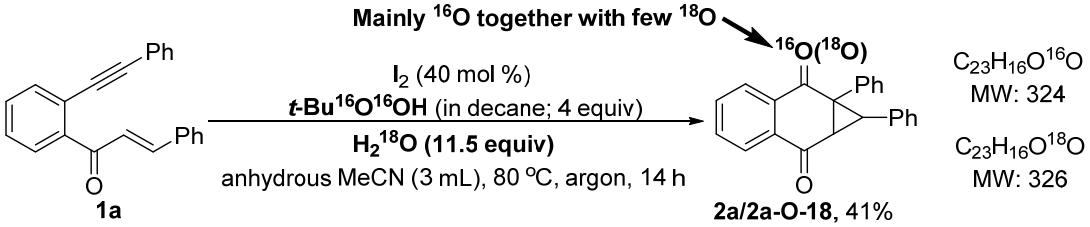
# of Peaks 355

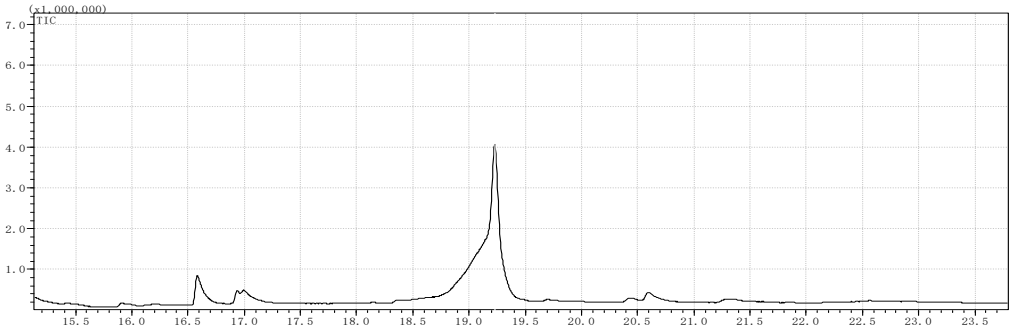
Raw Spectrum 21.190 (scan: 3539) Base Peak m/z 323.80 (Inten: 600,271)

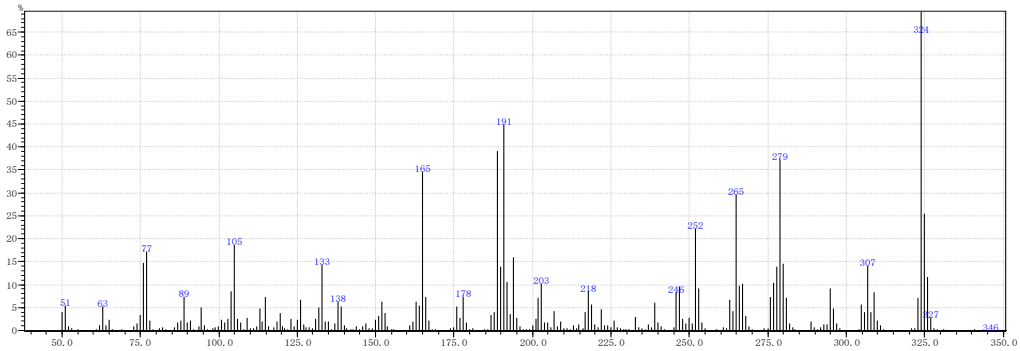
Background No Background Spectrum

m/z	Absolute Intensity	Relative Intensity	m/z	Absolute Intensity	Relative Intensity	m/z	Absolute Intensity	Relative Intensity
49.90	18330	3.05	119.40	12695	2.11	165.85	37295	6.21
50.90	22326	3.72	124.95	8651	1.44	166.90	10342	1.72
62.85	20419	3.40	125.90	25985	4.33	175.90	25602	4.27
74.90	13190	2.20	130.85	10613	1.77	176.95	12573	2.09
75.90	68526	11.42	131.75	20036	3.34	177.90	33713	5.62
76.90	64575	10.76	132.80	63236	10.53	186.85	16856	2.81
77.90	12158	2.03	133.85	7749	1.29	187.95	25220	4.20
87.95	6209	1.03	137.85	24615	4.10	188.85	200216	33.35
88.90	24804	4.13	138.85	25546	4.26	189.95	77938	12.98
94.50	13274	2.21	150.90	15892	2.65	190.90	206598	34.42
103.85	35828	5.97	151.90	30815	5.13	191.90	49271	8.21
104.85	66537	11.08	152.80	15529	2.59	192.95	18814	3.13
112.90	17210	2.87	161.95	9506	1.58	193.85	70114	11.68
113.85	7261	1.21	162.85	30461	5.07	194.85	11564	1.93
114.85	31311	5.22	163.95	30939	5.15	200.95	12372	2.06
118.35	7110	1.18	164.90	177426	29.56	201.85	35618	5.93

202.85	48457	8.07	264.80	176126	29.34	304.80	33825	5.63
206.80	14335	2.39	265.85	56345	9.39	305.85	24486	4.08
216.85	20343	3.39	266.80	53759	8.96	306.75	82405	13.73
217.80	48740	8.12	267.85	17565	2.93	307.85	22277	3.71
218.80	29214	4.87	275.80	46030	7.67	308.80	48942	8.15
221.80	24351	4.06	276.80	64530	10.75	309.80	11658	1.94
238.80	33607	5.60	277.85	84608	14.09	322.85	59601	9.93
245.80	54130	9.02	278.85	212884	35.46	**323.80**	**600271**	**100.00**
246.80	54606	9.10	279.80	88430	14.73	324.80	158519	26.41
251.80	118204	19.69	280.80	42150	7.02	**325.80**	**22094**	**3.68**
252.80	52425	8.73	288.80	12177	2.03	326.80	3698	0.62
262.80	40951	6.82	294.80	55617	9.27	327.80	130	0.02
263.85	28845	4.81	295.80	28553	4.76			





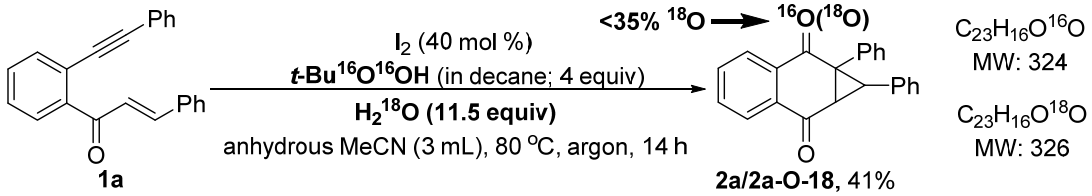


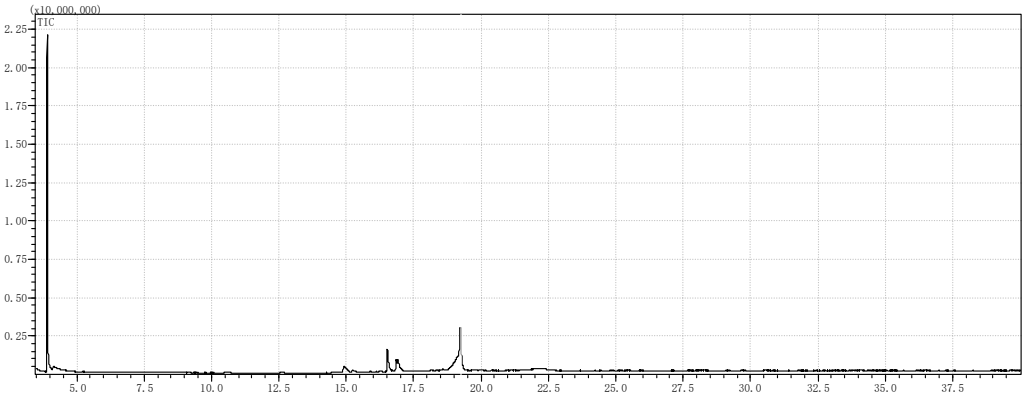
[MS Spectrum]# of Peaks 301

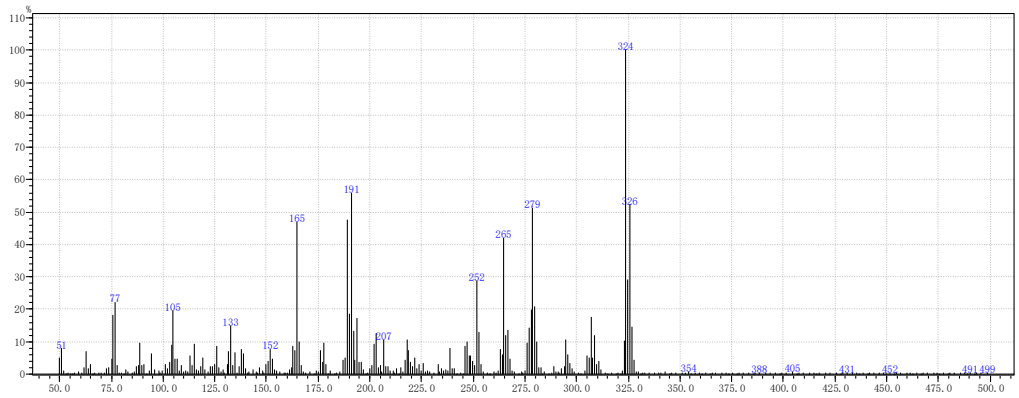
Raw Spectrum 19.225 (scan : 3146) Base Peak m/z 323.90 (Inten : 395,810)

Background 19.445 (scan : 3190)

m/z	Absolute Intensity	Relative Intensity	m/z	Absolute Intensity	Relative Intensity	m/z	Absolute Intensity	Relative Intensity
103.95	33656	8.50	201.95	28353	7.16	277.90	56691	14.32
104.95	72841	18.40	202.95	40051	10.12	278.95	149500	37.77
132.90	55141	13.93	217.90	33743	8.53	279.90	61387	15.51
164.95	139240	35.18	218.90	23316	5.89	294.90	37176	9.39
165.95	28554	7.21	245.85	34356	8.68	308.90	33366	8.43
177.95	29145	7.36	246.85	38966	9.84	309.90	8259	2.09
188.95	161143	40.71	251.90	86600	21.88	322.95	28594	7.22
189.95	57412	14.50	252.90	34767	8.78	**323.90**	**395810**	**100.00**
190.95	180596	45.63	264.90	119643	30.23	324.90	103563	26.16
191.95	41701	10.54	265.90	39259	9.92	**325.90**	**47484**	**12.00**
192.95	12070	3.05	266.90	40517	10.24	326.90	9842	2.49
193.95	63472	16.04	276.90	44764	11.31	327.85	1382	0.35







[MS Spectrum]

# of Peaks 287

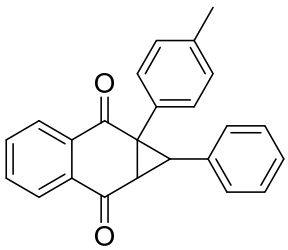
Raw Spectrum 19.230 (scan : 3147) Base Peak m/z 323.90 (Inten : 223,890)

Background 19.450 (scan : 3191)

m/z	Absolute Intensity	Relative Intensity						
49.90	10922	4.88	88.90	20321	9.08	163.95	16218	7.24
50.95	16690	7.45	103.90	18699	8.35	164.90	102989	46.00
61.95	3675	1.64	104.90	40581	18.13	165.95	22137	9.89
62.90	16224	7.25	114.90	19398	8.66	166.85	5179	2.31
75.90	39853	17.80	125.90	19111	8.54	175.95	14518	6.48
76.95	47783	21.34	162.90	18116	8.09	176.95	7857	3.51

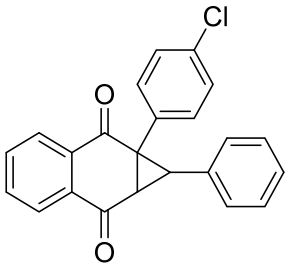
177.90	20952	9.36	245.85	19559	8.74	279.90	48336	21.59
179.00	6133	2.74	246.85	21391	9.55	280.90	15477	6.91
186.95	9000	4.02	247.80	13689	6.11	288.90	4966	2.22
187.95	10215	4.56	248.85	11297	5.05	294.85	25182	11.25
188.95	108560	48.49	249.85	8870	3.96	295.90	12866	5.75
189.95	41044	18.33	250.95	4874	2.18	296.90	7278	3.25
190.95	121895	54.44	251.90	65157	29.10	305.95	10900	4.87
191.95	29561	13.20	252.85	24889	11.12	306.90	40030	17.88
192.90	6788	3.03	253.85	5334	2.38	307.90	12230	5.46
193.90	38009	16.98	263.95	13098	5.85	308.85	25198	11.25
194.95	7379	3.30	264.85	95389	42.61	309.85	6322	2.82
195.85	8627	3.85	265.85	27590	12.32	310.85	9863	4.41
200.90	6558	2.93	266.90	29263	13.07	322.95	23033	10.29
201.90	20552	9.18	267.90	9329	4.17	**323.90**	**223890**	**100.00**
202.90	28249	12.62	275.90	22199	9.92	324.95	68170	30.45
217.90	23340	10.42	276.85	32022	14.30	**325.90**	**115300**	**51.50**
218.85	16237	7.25	277.95	44650	19.94	326.85	30403	13.58
219.85	8064	3.60	278.85	116895	52.21	**327.90**	**9166**	**4.09**

1-Phenyl-1a-(*p*-tolyl)-1a,7a-dihydro-1*H*-cyclopropa[*b*]naphthalene-2,7-dione (2b)



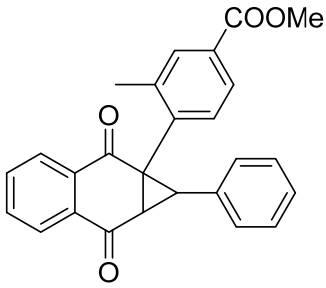
83% yield, 56.1 mg; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 - 8.09 (m, 2H), 7.79 - 7.77 (m, 2H), 7.14 - 7.08 (m, 3H), 7.05 - 7.00 (m, 4H), 6.77 (d, *J* = 7.2 Hz, 2H), 3.63 (d, *J* = 5.2 Hz, 1H), 3.40 (d, *J* = 5.2 Hz, 1H), 2.28 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.8, 191.3, 137.7, 134.4, 134.1, 133.5, 132.5, 131.6, 128.8, 128.5, 128.0, 128.0, 127.4, 126.7, 50.6, 43.1, 40.1, 21.2; LRMS (EI, 70 eV) *m/z* (%): 338 (M^+, 100), 323 (25), 279 (20); HRMS (ESI): calcd for $C_{24}H_{19}O_2$ [$M+H^+$] 339.1380, found 339.1387.

1a-(4-Chlorophenyl)-1-phenyl-1a,7a-dihydro-1*H*-cyclopropa[*b*]naphthalene-2,7-dione (2c)



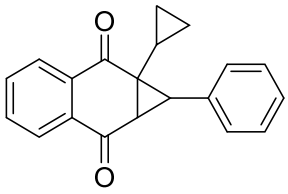
73% yield, 52.2 mg; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 - 8.09 (m, 2H), 7.79 - 7.78 (m, 2H), 7.21 (d, *J* = 7.2 Hz, 2H), 7.16 - 7.06 (m, 5H), 6.77 (d, *J* = 6.8 Hz, 2H), 3.64 (d, *J* = 4.8 Hz, 1H), 3.43 (d, *J* = 4.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.3, 190.7, 134.5, 134.3, 134.0, 133.1, 132.9, 132.4, 132.2, 130.2, 128.3, 128.2, 128.0, 127.9, 127.7, 126.8, 50.0, 42.9, 39.5; LRMS (EI, 70 eV) *m/z* (%): 360 (M^++2, 36), 358 (M^+, 100), 323 (37); HRMS (ESI): calcd for $C_{23}H_{16}{}^{35}ClO_2$ [M+H^+] 359.0833, found 359.0846.

Methyl 4-(2,7-dioxo-1-phenyl-1,2,7,7a-tetrahydro-1a*H*-cyclopropa[*b*]naphthalen-1a-yl)-3-methylbenzoate (2d)



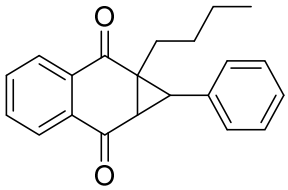
81% yield; 64.1 mg ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 - 8.07 (m, 2.8H), 7.91 (d, *J* = 8.8 Hz, 1.4H), 7.81 - 7.77 (m, 2.8H), 7.69 (s, 0.8H), 7.55 - 7.50 (m, 1.4H), 7.22 - 7.11 (m, 2.4H), 7.04 (t, *J* = 7.2 Hz, 2H), 6.82 (d, *J* = 7.6 Hz, 0.8H), 6.65 (d, *J* = 8.0 Hz, 2H), 6.57 (d, *J* = 8.0 Hz, 0.4H), 3.89 (s, 3H), 3.86 (s, 1.2H), 3.58 (d, *J* = 5.6 Hz, 1H), 3.53 (d, *J* = 5.6 Hz, 0.4H), 3.48 (d, *J* = 5.6 Hz, 1H), 3.39 (d, *J* = 5.6 Hz, 0.4H), 2.37 (s, 1.2H), 1.85 (s, 3H).^{13}C NMR (100 MHz, $CDCl_3$) δ 192.3, 191.2, 190.0, 166.8, 141.1, 138.7, 136.2, 135.6, 134.5, 134.4, 134.2, 133.5, 133.4, 133.3, 132.5, 132.4, 132.3, 132.2, 131.8, 131.5, 131.1, 130.0, 129.7, 128.3, 128.2, 127.9, 127.9, 127.9, 127.7, 127.4, 127.0, 126.8, 126.6, 126.0, 52.1, 52.0, 50.5, 48.6, 43.5, 43.1, 41.8, 41.1, 20.0, 19.6; LRMS (EI, 70 eV) *m/z* (%): 396 (M^+, 100), 337 (23), 293 (14); HRMS (ESI): calcd for $C_{26}H_{21}O_4$ [M+H^+] 397.1434, found 397.1432.

1a-Cyclopropyl-1-phenyl-1a,7a-dihydro-1*H*-cyclopropa[*b*]naphthalene-2,7-dione (2e)



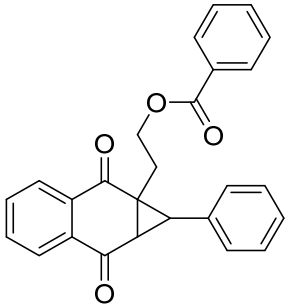
50% yield, 28.8 mg; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 (d, *J* = 7.2 Hz, 1H), 8.02 (d, *J* = 6.8 Hz, 1H), 7.79 - 7.72 (m, 2H), 7.34 - 7.25 (m, 5H), 3.24 (d, *J* = 5.6 Hz, 1H), 2.97 (d, *J* = 5.6 Hz, 1H), 1.29 - 1.22 (m, 1H), 0.82 - 0.74 (m, 1H), 0.31 - 0.20 (m, 2H), 0.15 - 0.08 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.2, 193.4, 134.2, 134.0, 133.7, 132.5, 132.1, 128.9, 128.3, 127.5, 127.5, 126.6, 45.4, 42.7, 36.5, 8.6, 4.4; LRMS (EI, 70 eV) *m/z* (%): 288 (M^+, 52), 273 (23), 91 (100); HRMS (ESI): calcd for $C_{20}H_{17}O_2$ [$M+H^+$] 289.1223, found 289.1237.

1a-Butyl-1-phenyl-1a,7a-dihydro-1*H*-cyclopropa[*b*]naphthalene-2,7-dione (2f)



80% yield; 48.6 mg ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (d, *J* = 6.8 Hz, 1H), 8.03 (d, *J* = 7.2 Hz, 1H), 7.78 - 7.72 (m, 2H), 7.35 - 7.27 (m, 3H), 7.22 (d, *J* = 7.2 Hz, 2H), 3.25 (d, *J* = 5.6 Hz, 1H), 3.06 (d, *J* = 5.6 Hz, 1H), 2.37 - 2.30 (m, 1H), 1.52 - 1.17 (m, 4H), 0.81 (t, *J* = 7.2 Hz, 3H), 0.76 - 0.68 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.8, 193.8, 134.1, 134.0, 133.6, 132.6, 132.5, 128.8, 128.5, 127.7, 127.4, 126.6, 44.6, 42.7, 38.3, 29.3, 27.0, 22.7, 13.9; LRMS (EI, 70 eV) *m/z* (%): 304 (M^+, 100), 247 (47), 203 (62); HRMS (ESI): calcd for $C_{21}H_{21}O_2$ [$M+H^+$] 305.1536, found 305.1543.

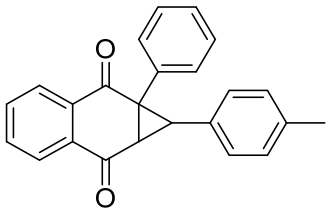
2-(2,7-Dioxo-1-phenyl-1,2,7,7a-tetrahydro-1a*H*-cyclopropa[*b*]naphthalen-1a-yl)ethyl benzoate (2g)



73% yield, 57.8 mg; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (d, *J* = 7.2 Hz, 1H), 8.04 (d, *J* = 6.8 Hz, 1H), 7.91 (d, *J* = 7.6 Hz, 2H), 7.78 - 7.73 (m, 2H), 7.52 (t, *J* = 7.2 Hz, 1H), 7.41 - 7.28 (m, 5H), 7.24 (d, *J* = 7.6 Hz, 2H), 4.59 - 4.53 (m, 1H), 4.42 - 4.36 (m, 1H), 3.28 (d, *J* = 5.6 Hz, 1H), 3.22 (d, *J* = 5.6 Hz, 1H),

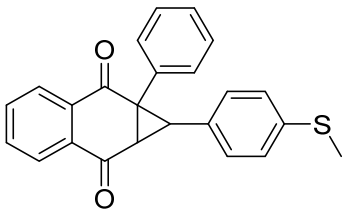
2.84 - 2.78 (m, 1H), 1.26 - 1.17 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.1, 192.8, 166.4, 134.2, 134.1, 133.0, 132.9, 132.4, 132.3, 129.8, 129.5, 128.8, 128.7, 128.3, 128.0, 127.4, 126.7, 62.2, 41.3, 41.3, 38.0, 26.9; LRMS (EI, 70 eV) *m/z* (%): 396 (M^+, 3), 274 (100), 229 (16); HRMS (ESI): calculated for $C_{26}H_{21}O_4$ [$M+H^+$] 397.1434, found 397.1440.

1a-Phenyl-1-(p-tolyl)-1a,7a-dihydro-1*H*-cyclopropa[*b*]naphthalene-2,7-dione (2h)[5]



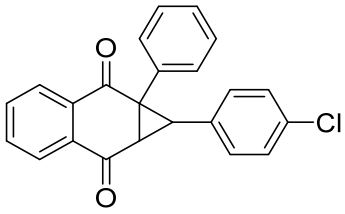
89% yield, 60.1 mg; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 - 8.09 (m, 2H), 7.78 - 7.77 (m, 2H), 7.24 - 7.15(m, 5H), 6.88 (d, *J* = 7.6 Hz, 2H), 6.62 (d, *J* = 7.6 Hz, 2H), 3.63 (d, *J* = 5.2 Hz, 1H), 3.39 (d, *J* = 5.2 Hz, 1H), 2.21 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.8, 191.1, 137.3, 134.4, 134.1, 132.5, 131.8, 131.7, 130.3, 128.7, 128.0, 128.0, 127.9, 127.8, 126.7, 50.9, 43.0, 40.1, 21.0; LRMS (EI, 70 eV) *m/z* (%): 338 (M^+, 100), 279 (53), 293 (23).

1-(4-(Methylthio)phenyl)-1a-phenyl-1a,7a-dihydro-1*H*-cyclopropa[*b*]-naphthalene-2,7-dione (2i)



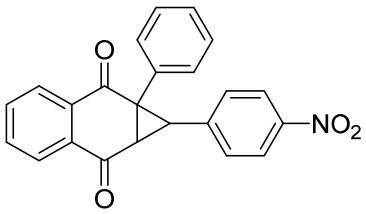
84 yield%; 62.2 mg ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 - 8.10 (m, 2H), 7.81 - 7.79 (m, 2H), 7.27 - 7.25 (m, 3H), 7.15 - 7.14 (m, 2H), 6.95 (d, *J* = 7.6 Hz, 2H), 6.65 (d, *J* = 7.6 Hz, 2H), 3.61 (d, *J* = 5.6 Hz, 1H), 3.37 (d, *J* = 5.2 Hz, 1H), 2.39 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.6, 190.9, 138.1, 134.5, 134.2, 132.4, 131.8, 131.5, 130.0, 128.4, 128.2, 128.1, 126.8, 125.7, 50.9, 42.7, 40.2, 15.4; LRMS (EI, 70 eV) *m/z* (%): 370 (M^+, 100), 326 (18), 279 (51); HRMS (ESI): calculated for $C_{24}H_{19}O_2S$ [$M+H^+$] 371.1100, found 371.1113.

1-(4-Chlorophenyl)-1a-phenyl-1a,7a-dihydro-1*H*-cyclopropa[*b*]naphthalene-2,7-dione (2j)



95% yield, 68.0 mg; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 - 8.09 (m, 2H), 7.80 - 7.78 (m, 2H), 7.26 - 7.13 (m, 5H), 7.06 (d, *J* = 8.0 Hz, 2H), 6.67 (d, *J* = 8.0 Hz, 2H), 3.61 (d, *J* = 5.2 Hz, 1H), 3.38 (d, *J* = 5.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.3, 190.7, 134.5, 134.3, 133.4, 132.3, 132.3, 132.0, 131.8, 131.2, 129.2, 128.2, 128.2, 128.2, 128.1, 126.8, 50.6, 42.1, 39.9; LRMS (EI, 70 eV) *m/z* (%): 360 (M^++2, 36), 358 (M^+, 100), 323 (15); HRMS (ESI): calculated for $C_{23}H_{16}{}^{35}ClO_2$ [M+H^+] 359.0833, found 359.0841.

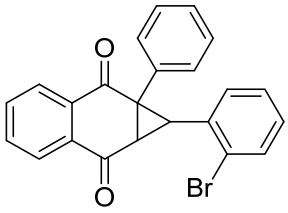
1-(4-Nitrophenyl)-1a-phenyl-1a,7a-dihydro-1*H*-cyclopropa[*b*]naphthalene-2,7-dione (2k)



54% yield, 39.8 mg; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 - 8.12 (m, 2H), 7.95 (d, *J* = 8.4 Hz, 2H), 7.84 - 7.82 (m, 2H), 7.28 - 7.27 (m, 3H), 7.14 - 7.12 (m, 2H), 6.91 (d, *J* = 8.8 Hz, 2H), 3.72 (d, *J* = 5.6 Hz, 1H), 3.48 (d, *J* = 5.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.6, 190.1, 147.0, 141.1, 134.8, 134.5, 132.2, 132.1, 131.7, 130.6, 128.7, 128.6, 128.4, 128.2, 126.9, 123.2, 50.8, 41.5, 40.0; LRMS (EI, 70 eV) *m/z* (%): 369 (M^+, 100), 339 (10), 278 (39); HRMS (ESI): calculated for $C_{23}H_{16}NO_4$ [M+H^+] 370.1074, found 370.1080.

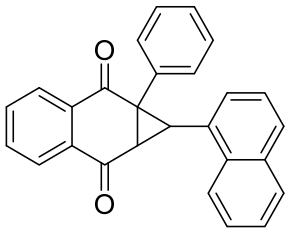
1-(2-Bromophenyl)-1a-phenyl-1a,7a-dihydro-1*H*-cyclopropa[*b*]naphthalene-2,7-dione (2l)

84 yield%, 67.5 mg; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (d, *J* = 6.4 Hz, 1H), 8.11 (d, *J* = 7.6 Hz, 1H), 7.83 - 7.77 (m, 2H), 7.51 (d, *J* = 7.2 Hz, 1H), 7.25 - 7.18 (m, 5H), 7.01 - 6.94 (m, 2H), 6.64 (d, *J* = 7.6 Hz, 1H), 3.81 (d, *J* = 6.0 Hz, 1H), 3.74 (d, *J* = 6.0 Hz,



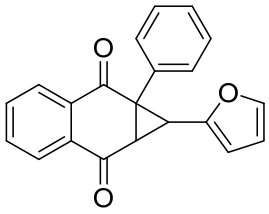
1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.7, 190.8, 134.6, 134.2, 132.7, 132.6, 132.5, 132.4, 131.5, 131.2, 129.0, 128.1, 128.0, 128.0, 127.6, 127.1, 126.7, 126.3, 49.4, 43.6, 37.7; LRMS (EI, 70 eV) *m/z* (%): 404 (M^++2, 96), 402 (M^+, 100), 323 (60), 265 (58); HRMS (ESI): calculated for $C_{23}H_{16}{}^{79}BrO_2$ [M+H^+] 403.0328, found 403.0335.

1-(Naphthalen-1-yl)-1a-phenyl-1a,7a-dihydro-1*H*-cyclopropa[*b*]naphthalene-2,7-dione (2m)[5]



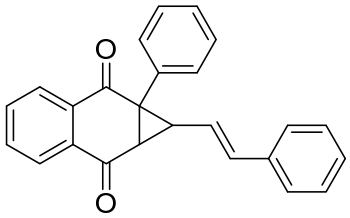
86% yield, 64.3 mg; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.30 (d, *J* = 7.2 Hz, 1H), 8.14 (d, *J* = 7.2 Hz, 1H), 8.03 (d, *J* = 8.0 Hz, 1H), 7.85 - 7.78 (m, 3H), 7.61 (d, *J* = 8.4 Hz, 1H), 7.57 (t, *J* = 7.6 Hz, 1H), 7.49 (t, *J* = 7.6 Hz, 1H), 7.13 (t, *J* = 7.6 Hz, 1H), 7.06 – 6.96 (m, 6H), 4.01 (d, *J* = 5.6 Hz, 1H), 3.97 (d, *J* = 6.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.0, 191.5, 134.5, 134.3, 133.3, 132.7, 132.6, 132.5, 131.7, 130.9, 128.8, 128.8, 128.5, 128.1, 127.8, 127.7, 126.8, 126.8, 126.0, 125.0, 124.3, 123.0, 50.2, 41.1, 37.5; LRMS (EI, 70 eV) *m/z* (%): 374 (M^+, 100), 357 (10), 329 (51).

1-(Furan-2-yl)-1a-phenyl-1a,7a-dihydro-1*H*-cyclopropa[*b*]naphthalene-2,7-dione (2n)



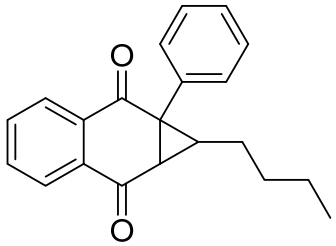
38% yield, 23.9 mg; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 - 8.09 (m, 2H), 7.79 - 7.78 (m, 2H), 7.28 - 7.21 (m, 5H), 7.10 (s, 1H), 6.14 - 6.13 (m, 1H), 5.88 - 5.86 (m, 1H), 3.64 (d, *J* = 5.6 Hz, 1H), 3.44 (d, *J* = 5.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.1, 190.6, 147.6, 142.2, 134.5, 134.3, 132.4, 132.2, 131.1, 128.1, 128.0, 126.8, 110.6, 108.9, 49.4, 38.9, 35.8; LRMS (EI, 70 eV) *m/z* (%): 314 (M^+, 100), 285 (16), 257 (24); HRMS (ESI): calculated for $C_{21}H_{15}O_3$ [M+H^+] 315.1016, found 315.1028.

(*E*)-1a-phenyl-1-styryl-1a,7a-dihydro-1*H*-cyclopropa[*b*]naphthalene-2,7-dione (2o)



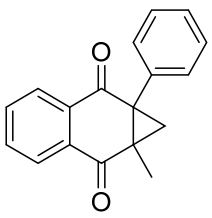
80% yield, 56.0 mg ; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 - 8.09 (m, 2H), 7.79 - 7.76 (m, 2H), 7.44 - 7.37 (m, 5H), 7.25 - 7.17 (m, 3H), 7.11 (d, *J* = 7.2 Hz, 2H), 6.61 (d, *J* = 15.6 Hz, 1H), 5.32 (dd, *J* = 15.6, 9.2 Hz, 1H), 3.28 (d, *J* = 4.8 Hz, 1H), 3.06 (t, *J* = 9.2, 4.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.0, 191.1, 136.1, 134.4, 134.2, 132.5, 132.4, 132.4, 131.5, 128.6, 128.4, 128.3, 127.9, 126.7, 126.2, 125.1, 49.1, 42.6, 41.5; LRMS (EI, 70 eV) *m/z* (%): 350 (M^+, 100), 331 (14), 259 (53); HRMS (ESI): calculated for $C_{25}H_{19}O_2$ [M+H^+] 351.1380, found 351.1387.

1-Butyl-1a-phenyl-1a,7a-dihydro-1*H*-cyclopropa[*b*]naphthalene-2,7-dione (2p)



40% yield, 24.3 mg; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 - 8.04 (m, 2H), 7.75 - 7.71 (m, 2H), 7.44 - 7.35 (m, 5H), 2.92 (d, *J* = 5.2 Hz, 1H), 2.23 - 2.18 (m, 1H), 1.60 - 1.52 (m, 1H), 1.42 - 1.35 (m, 2H), 1.26 - 1.17 (m, 2H), 0.90 - 0.78 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.6, 192.2, 134.1, 133.9, 132.8, 132.6, 132.4, 131.2, 128.2, 128.0, 127.8, 126.5, 48.4, 40.7, 40.4, 30.9, 29.9, 22.2, 13.8; LRMS (EI, 70 eV) *m/z* (%): 304 (M^+, 100), 261 (42), 247 (47); HRMS (ESI): calculated for $C_{21}H_{21}O_2$ [M+H^+] 305.1536, found 305.1543

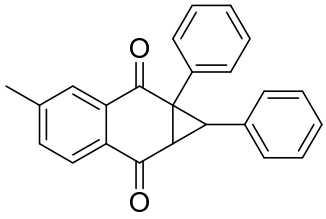
1a-Methyl-7a-phenyl-1a,7a-dihydro-1*H*-cyclopropa[*b*]naphthalene-2,7-dione (2q)



79% yield; 41.4 mg ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, *J* = 7.2 Hz, 1H), 7.99 (d, *J* = 7.2 Hz, 1H), 7.75 - 7.68 (m, 2H), 7.43 - 7.35 (m, 3H), 7.25 (d, *J* = 7.2 Hz, 2H), 2.22 (d, *J* = 4.8 Hz, 1H), 2.01 (d, *J* = 4.8 Hz, 1H), 1.23 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.6, 194.4, 134.0, 133.9, 133.7, 132.5, 132.1, 128.6, 128.1, 127.0, 126.7, 48.4, 38.9, 32.3, 15.4; LRMS (EI, 70 eV) *m/z* (%): 262 (M^+, 75), 247 (100), 233 (46); HRMS (ESI):

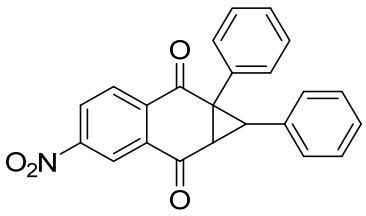
calculated for $C_{18}H_{15}O_2$ [M+H$^+$] 263.1067, found 263.1073.

4-Methyl-1,1a-diphenyl-1a,7a-dihydro-1*H*-cyclopropa[*b*]naphthalene-2,7-dione (2r)



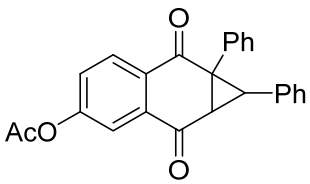
94 yield%, 63.5 mg; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, *J* = 8.0 Hz, 1H), 7.96 (s, 1H), 7.59 (d, *J* = 8.0 Hz, 1H), 7.24 - 7.23 (m, 3H), 7.14 - 7.06 (m, 5H), 6.74 (d, *J* = 7.2 Hz, 2H), 3.63 (d, *J* = 5.6 Hz, 1H), 3.39 (d, *J* = 5.6 Hz, 1H), 2.51 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.7, 191.3, 145.7, 135.1, 133.4, 132.4, 131.9, 131.7, 130.1, 128.2, 128.0, 128.0, 127.9, 127.4, 126.9, 50.8, 43.2, 39.8, 21.9; LRMS (EI, 70 eV) *m/z* (%): 338 (M$^+$, 100), 323 (16), 279 (35); HRMS (ESI): calculated for $C_{24}H_{19}O_2$ [M+H$^+$] 339.1380, found 339.1395.

5-Nitro-1,1a-diphenyl-1a,7a-dihydro-1*H*-cyclopropa[*b*]naphthalene-2,7-dione (2s)



82% yield, 60.7 mg; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.92 (s, 1H), 8.57 (d, *J* = 8.4 Hz, 1H), 8.37 (d, *J* = 8.4 Hz, 1H), 7.27 - 7.26 (m, 3H), 7.17 - 7.09 (m, 5H), 6.75 (d, *J* = 7.6 Hz, 2H), 3.78 (d, *J* = 5.2 Hz, 1H), 3.44 (d, *J* = 5.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.3, 189.4, 151.4, 136.3, 133.8, 132.4, 131.7, 130.7, 130.2, 128.4, 128.3, 128.2, 128.2, 128.0, 127.9, 122.4, 51.4, 42.7, 40.3; LRMS (EI, 70 eV) *m/z* (%): 369 (M$^+$, 100), 322 (19), 265 (29); HRMS (ESI): calculated for $C_{23}H_{16}NO_4$ [M+H$^+$] 370.1074, found 370.1081.

2,7-Dioxo-1,7a-diphenyl-1a,2,7,7a-tetrahydro-1*H*-cyclopropa[*b*]naphthalen-4-yl acetate (2t)



76% yield, 58.0 mg; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (d, *J* = 8.4 Hz, 1H), 7.82 (s, 1H), 7.50 (d, *J* = 8.8 Hz, 1H), 7.26 - 7.23 (m, 3H), 7.14 - 7.07 (m, 5H), 6.75 (d, *J* = 7.2 Hz, 2H),

3.66 (d, J = 5.6 Hz, 1H), 3.46 (d, J = 5.6 Hz, 1H), 2.36 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.6, 190.0, 168.6, 155.3, 134.2, 133.1, 131.8, 131.4, 130.2, 130.0, 128.0, 128.0, 127.8, 127.6, 119.6, 50.8, 42.9, 40.1, 21.0; LRMS (EI, 70 eV) *m/z* (%): 382 (M^+, 100), 340 (93), 295 (31); HRMS (ESI): calculated for $C_{25}H_{19}O_4$ [M+H^+] 383.1278, found 383.1290.

(C) References

(1) Wang, Z.-Q.; Zhang, W.-W.; Gong, L.-B.; Tang, R.-Y.; Yang, X.-H.; Liu, Y.; Li, J.-H. *Angew. Chem. Int. Ed.* **2011**, *50*, 8968.

(2) Wang, Y.-H.; Zhu, L.-L.; Zhang, Y.-X.; Chen, Z. *Chem. Commun.* **2010**, *46*, 577.

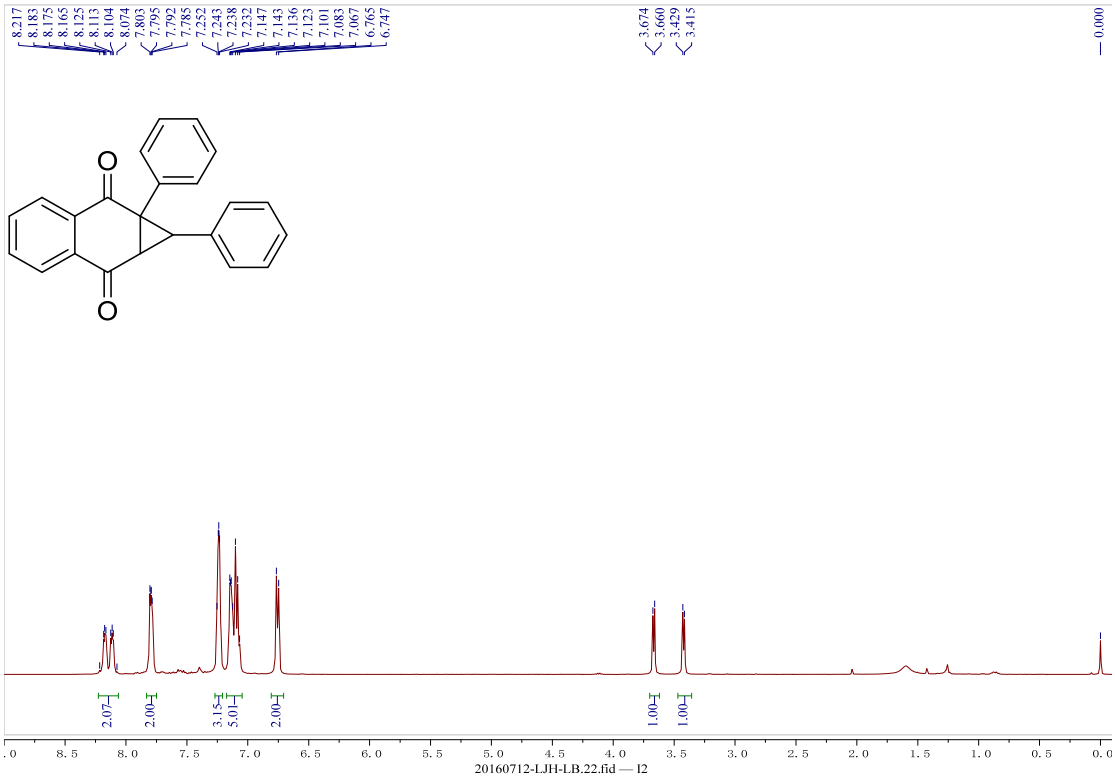
(3) Liang, G.; Xu, Y.; Seiple, I. B.; Trauner, D. *J. Am. Chem. Soc.* **2006**, *128*, 11022.

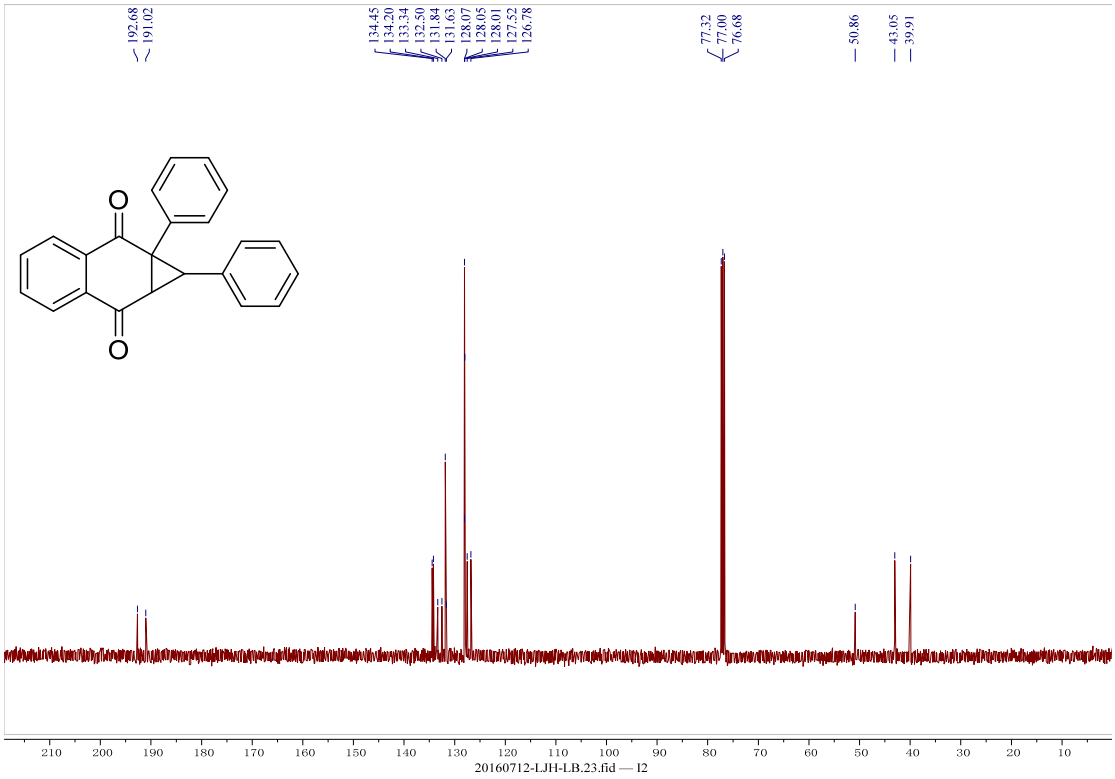
(4) Petrone, D. A.; Malik, H. A.; Clemenceau, A.; Lautens, M. *Org. Lett.* **2012**, *14*, 4806.

(5) Zheng, L.; Zhou, B.; Jin, H.; Li, T.; Liu, Y. *Org. Lett.* **2018**, *20*, DOI: 10.1021/acs.orglett.8b03007.

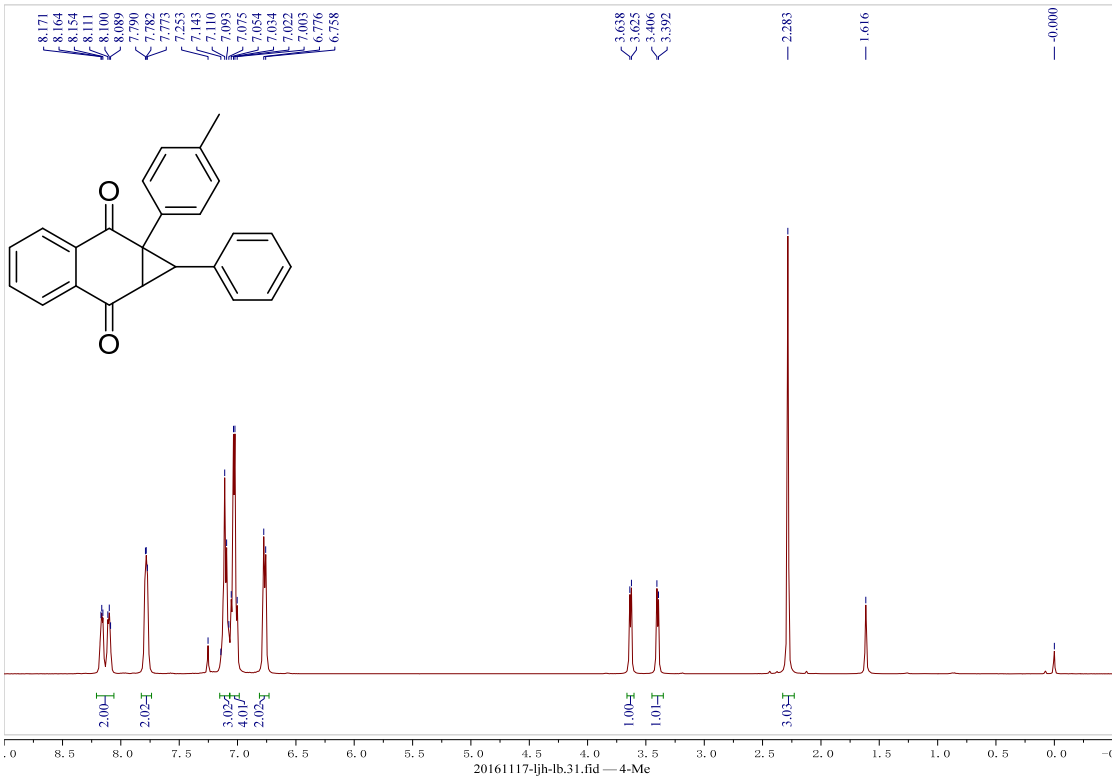
(D) Spectra

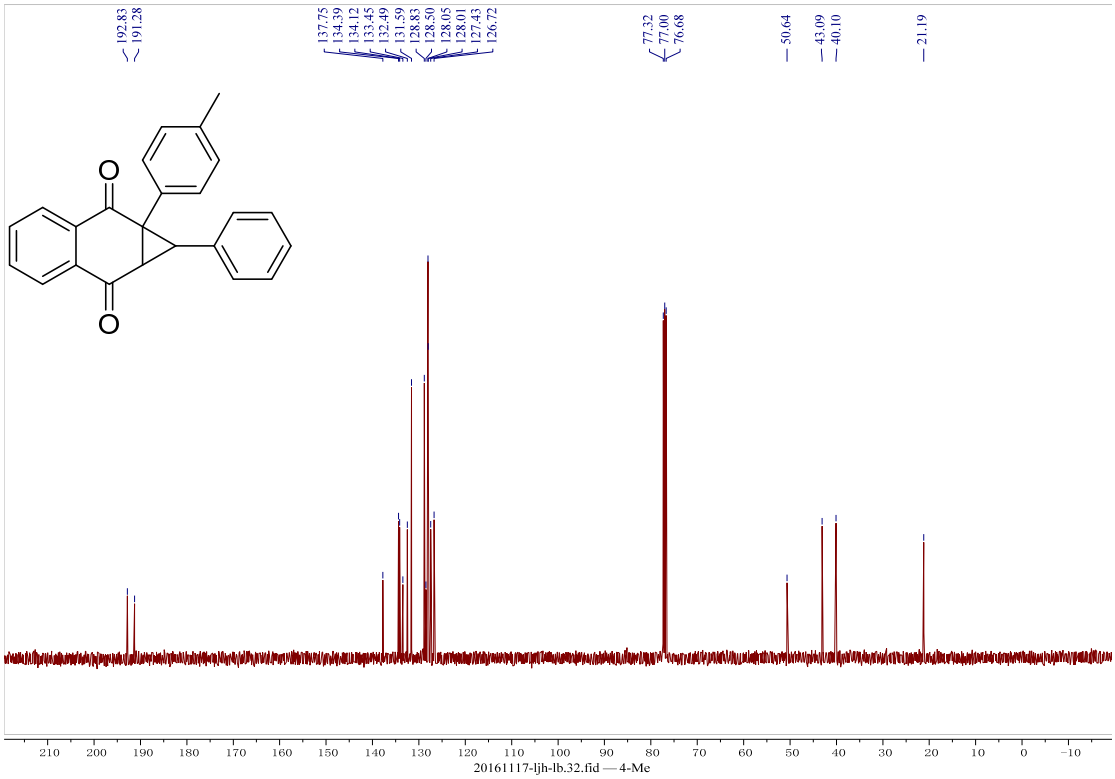
1,1a-Diphenyl-1a,7a-dihydro-1*H*-cyclopropa[*b*]naphthalene-2,7-dione (2a)



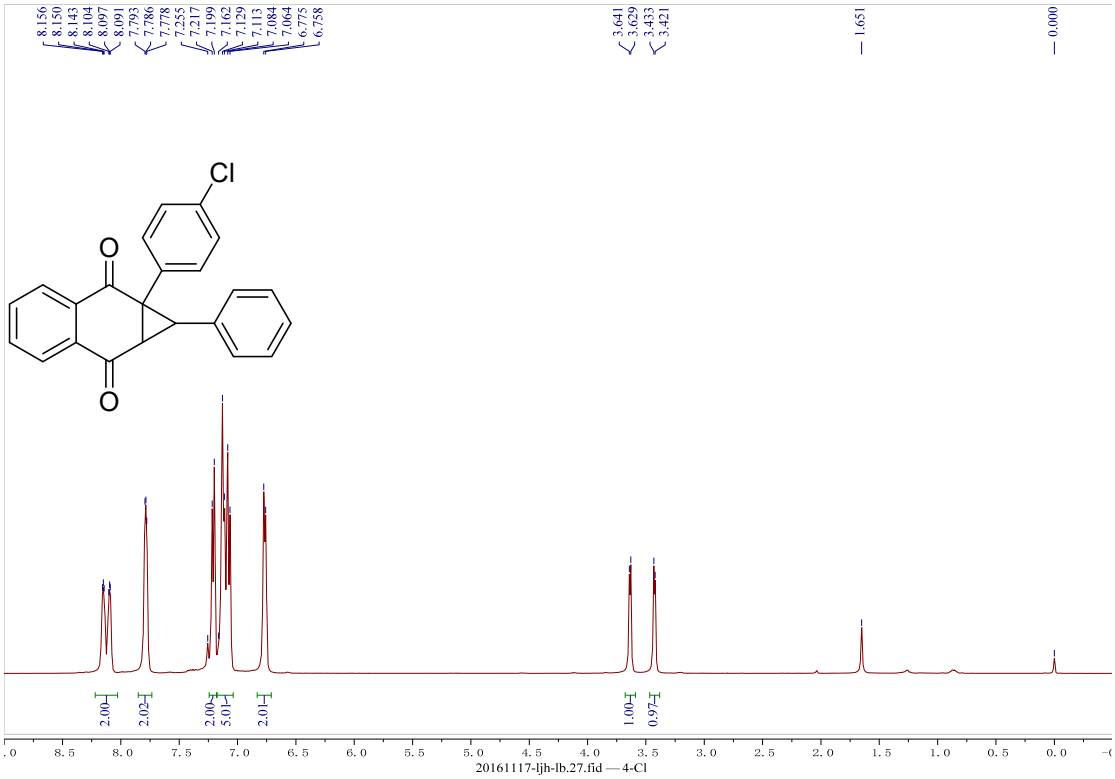


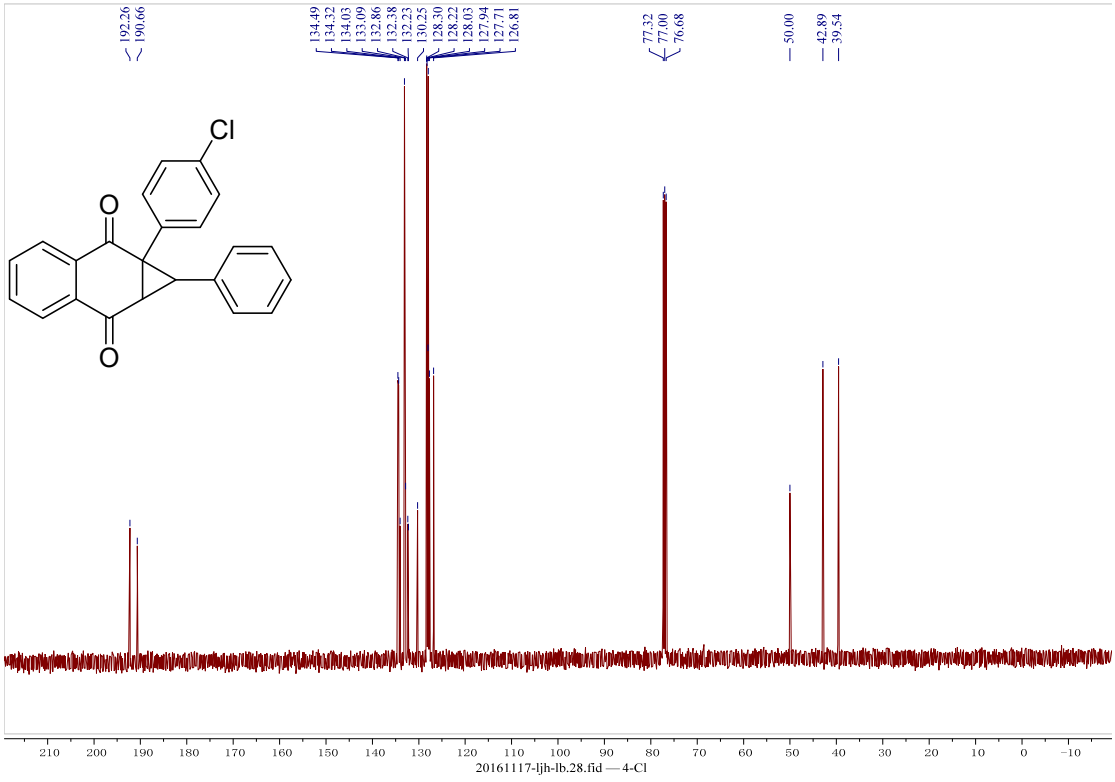
Phenyl-1a-(*p*-tolyl)-1a,7a-dihydro-1*H*-cyclopropa[*b*]naphthalene-2,7-dione (2b)



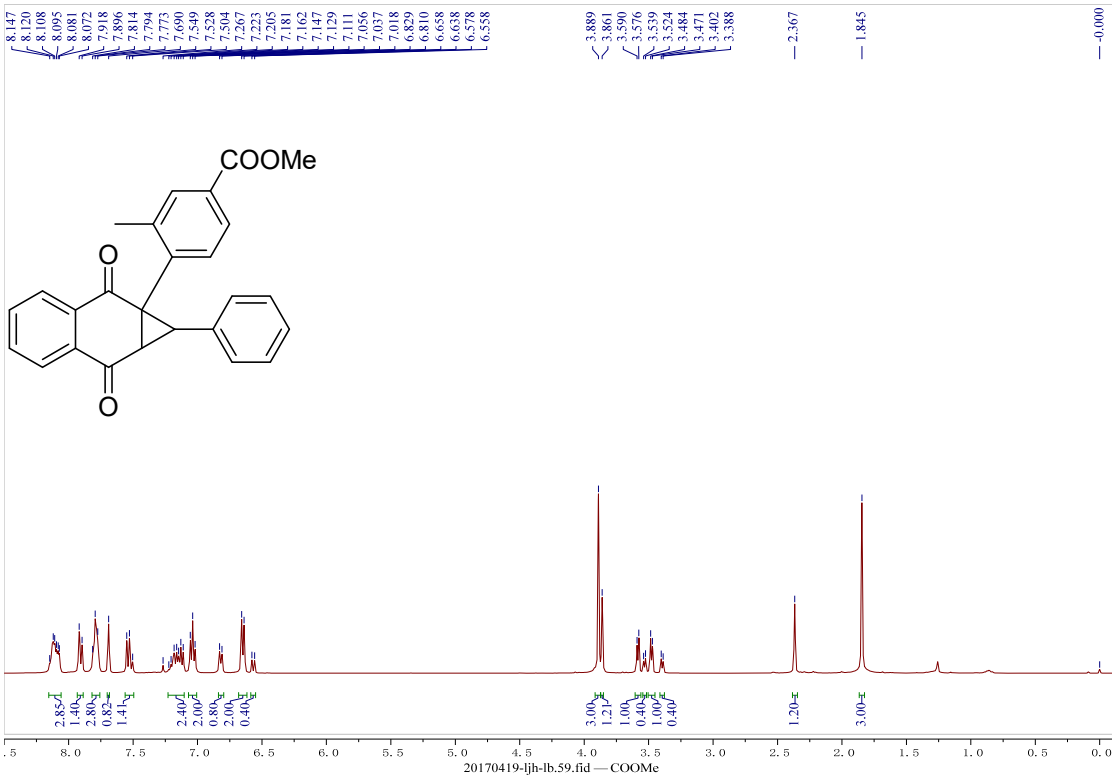


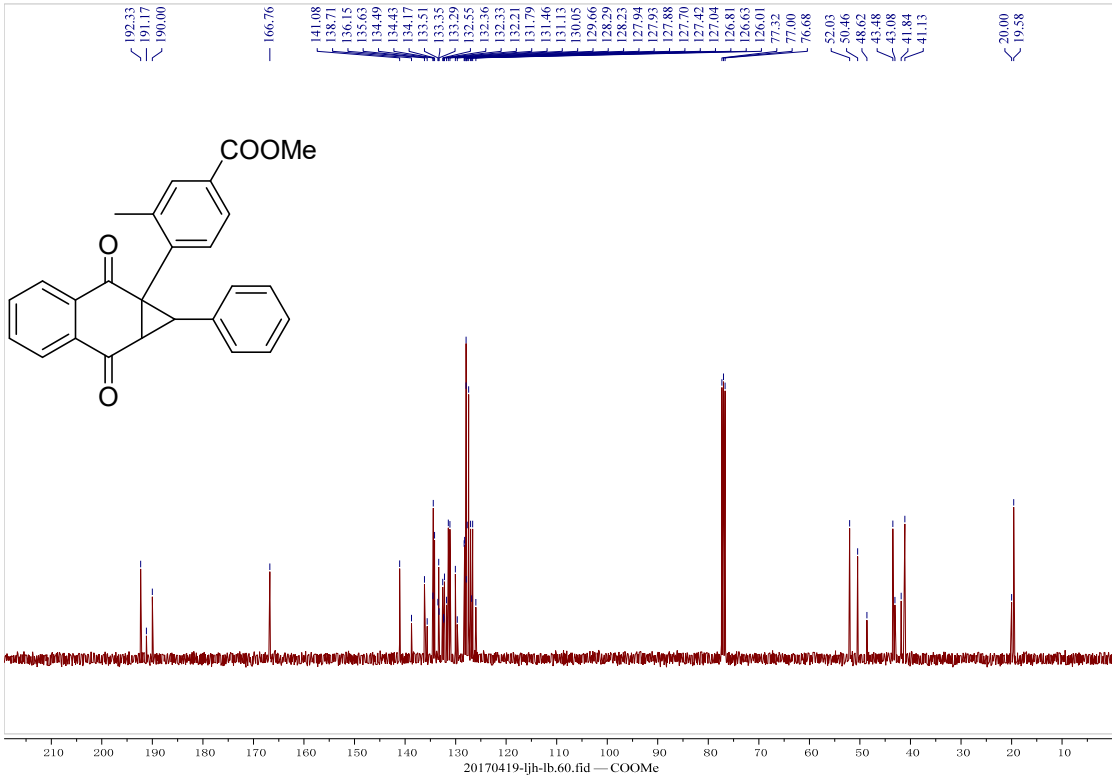
1a-(4-Chlorophenyl)-1-phenyl-1a,7a-dihydro-1*H*-cyclopropa[*b*]naphthalene-2,7-dione (2c)



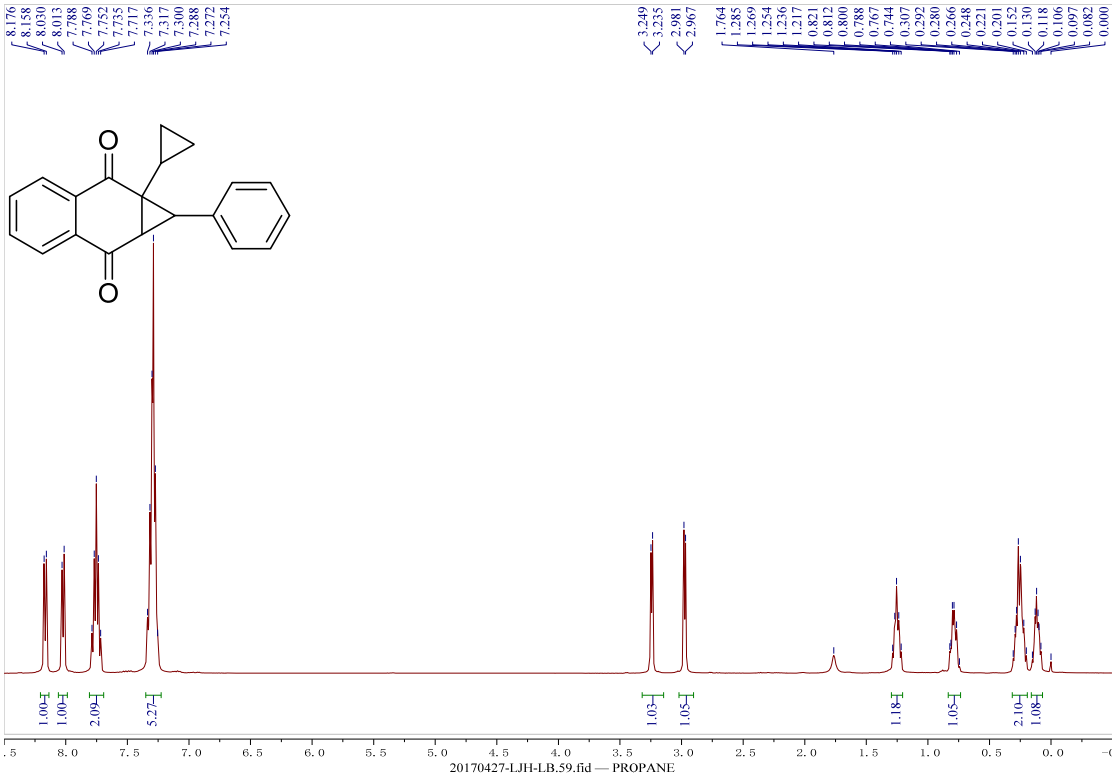


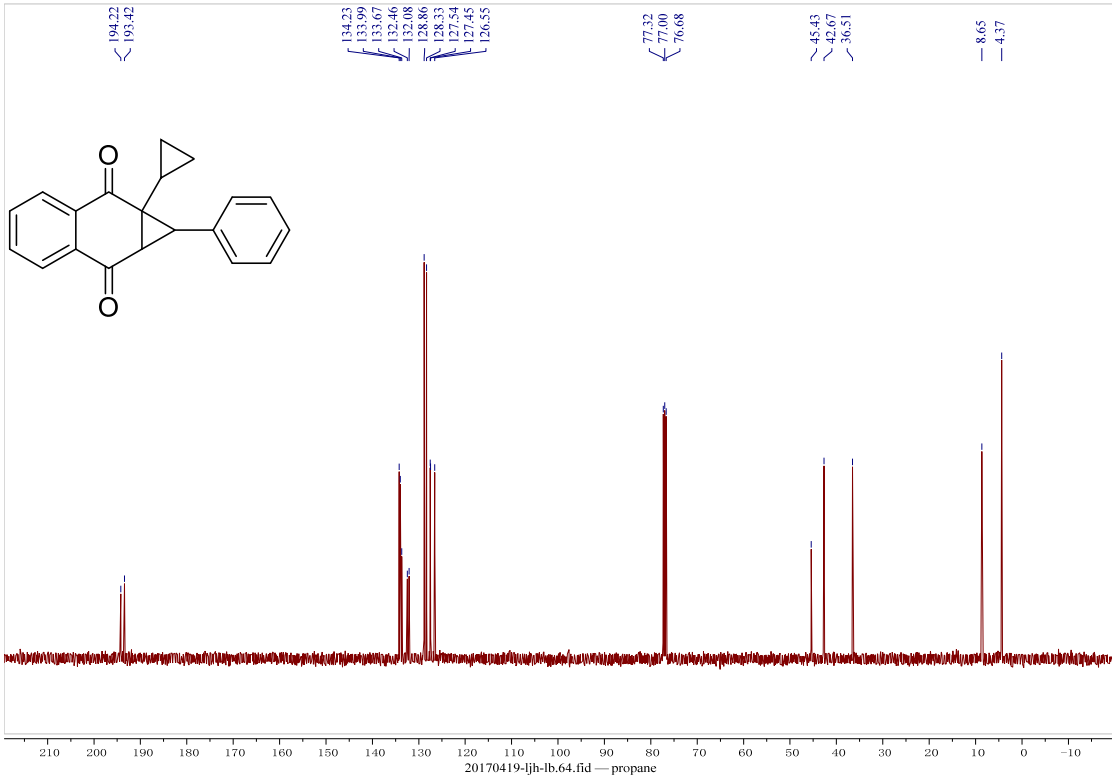
Methyl 4-(2,7-dioxo-1-phenyl-1,2,7,7a-tetrahydro-1a*H*-cyclopropa[*b*]naphthalen-1a-yl)-3-methylbenzoate (2d)



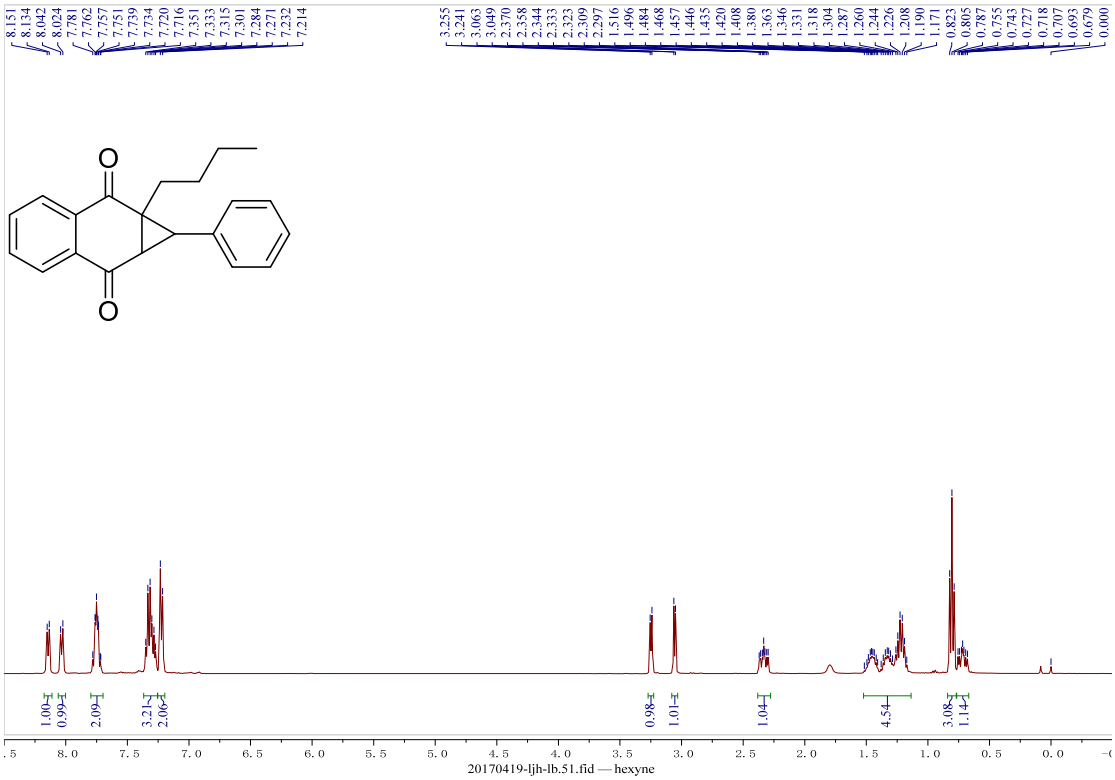


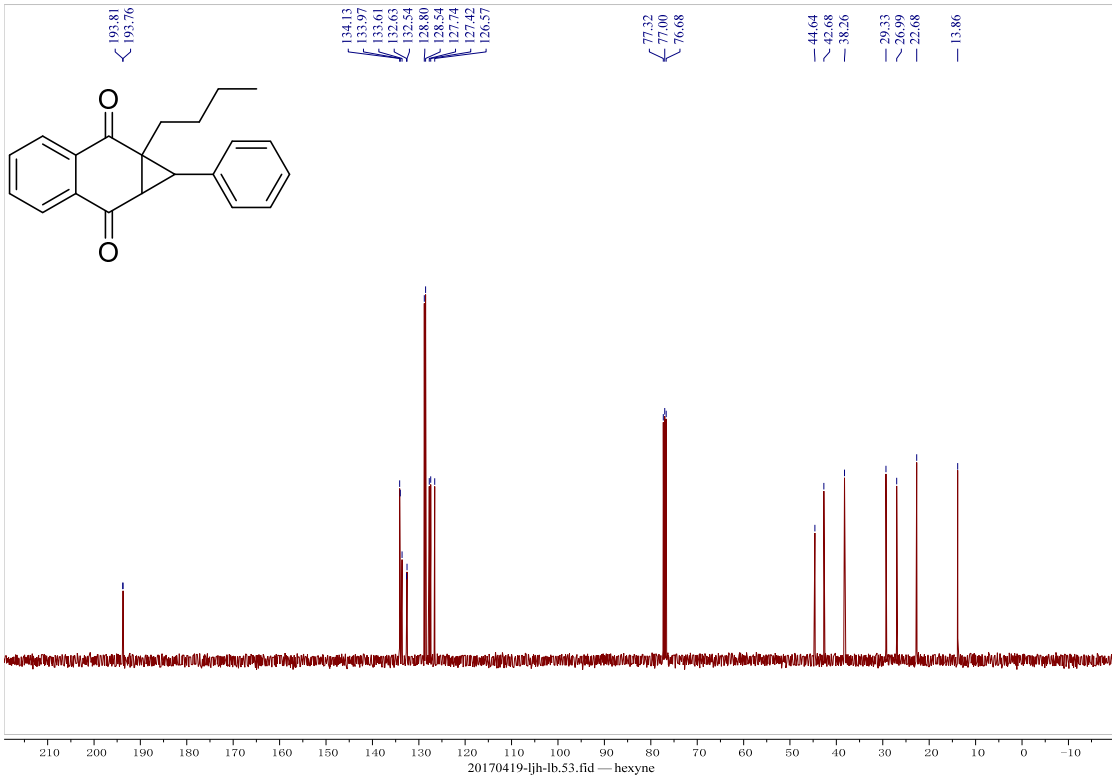
1a-Cyclopropyl-1-phenyl-1a,7a-dihydro-1*H*-cyclopropa[*b*]naphthalene-2,7-dione (2e)



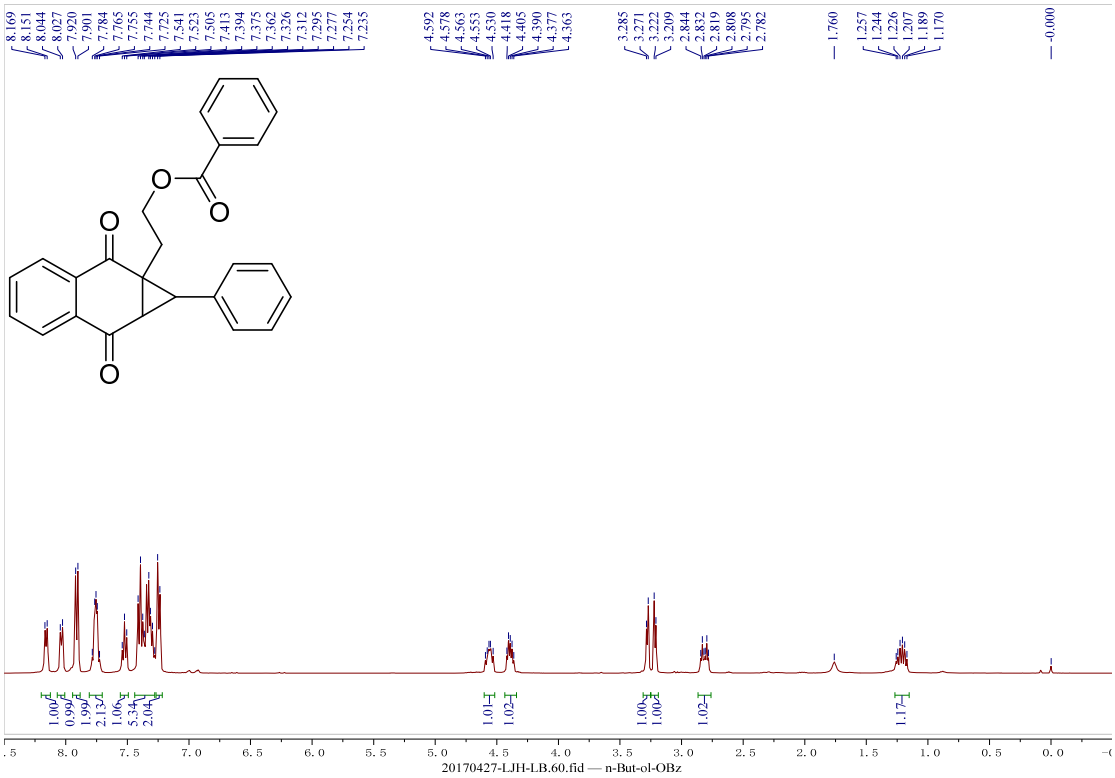


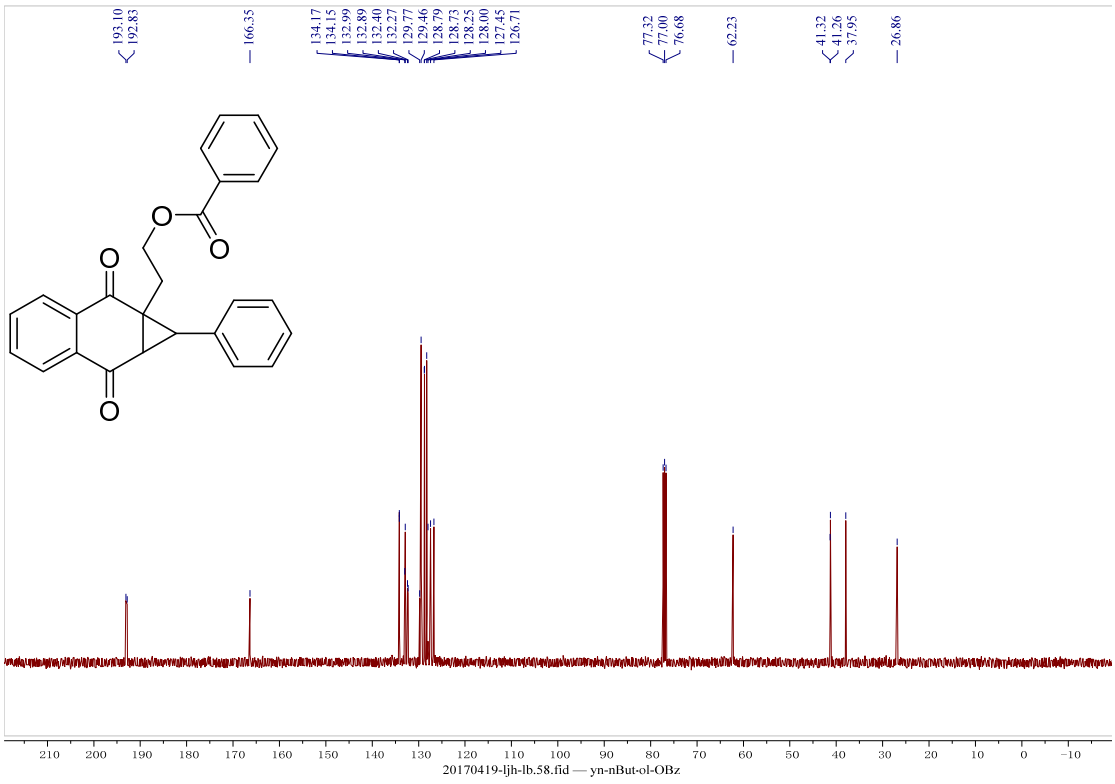
1a-Butyl-1-phenyl-1a,7a-dihydro-1*H*-cyclopropa[*b*]naphthalene-2,7-dione (2f)



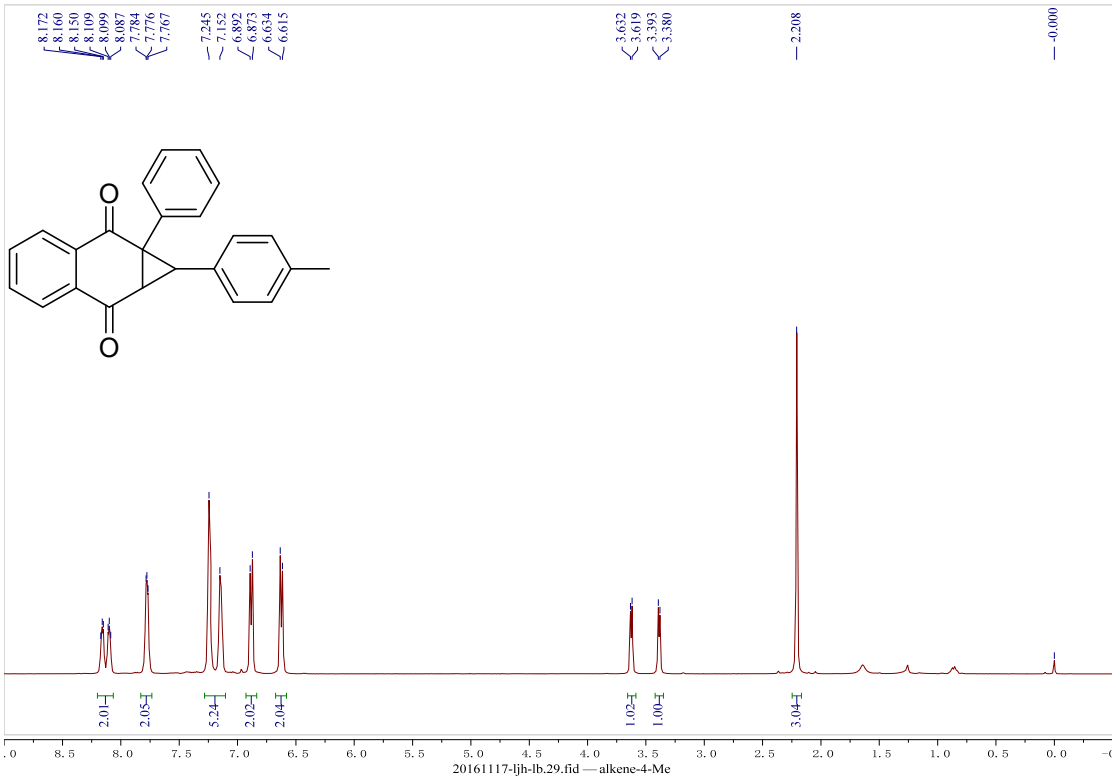


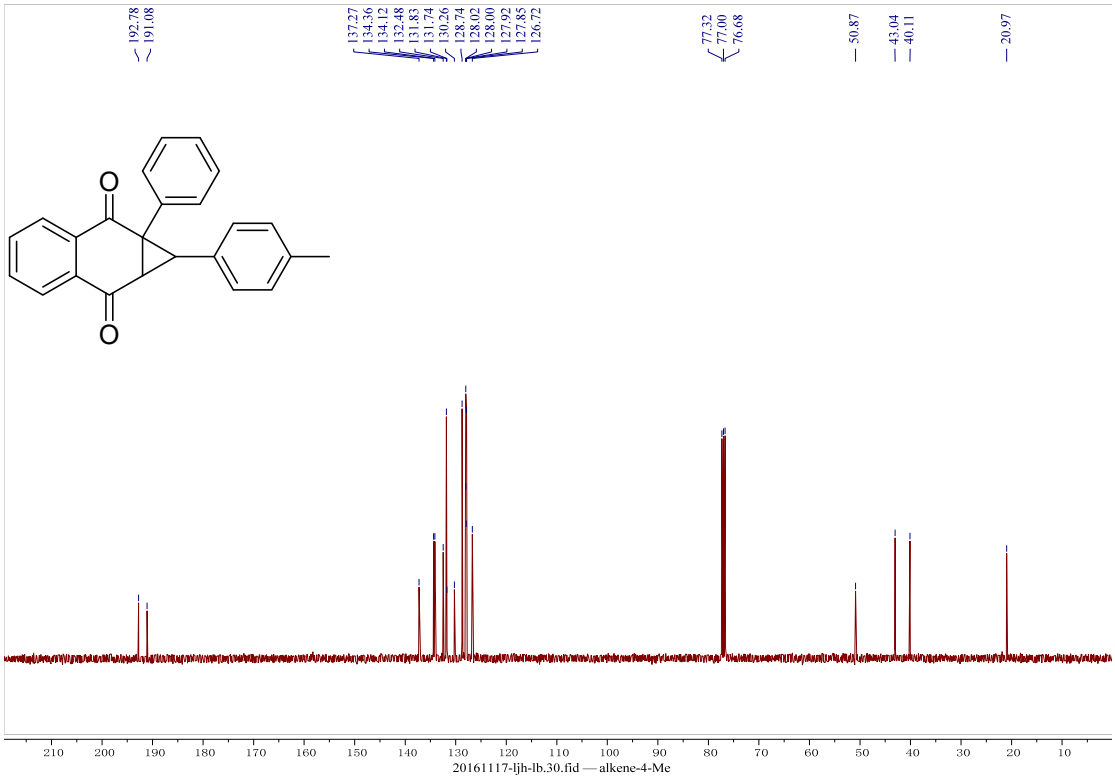
2-(2,7-Dioxo-1-phenyl-1,2,7,7a-tetrahydro-1a*H*-cyclopropa[*b*]naphthalen-1a-yl)ethyl benzoate (2g)



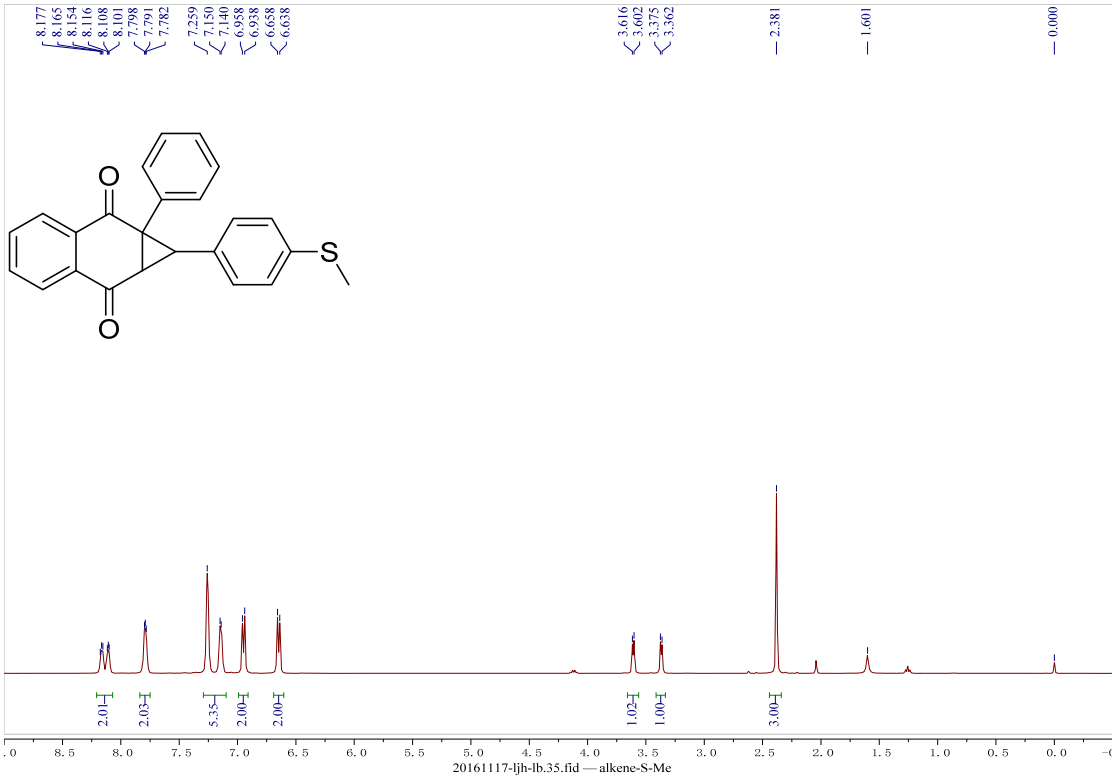


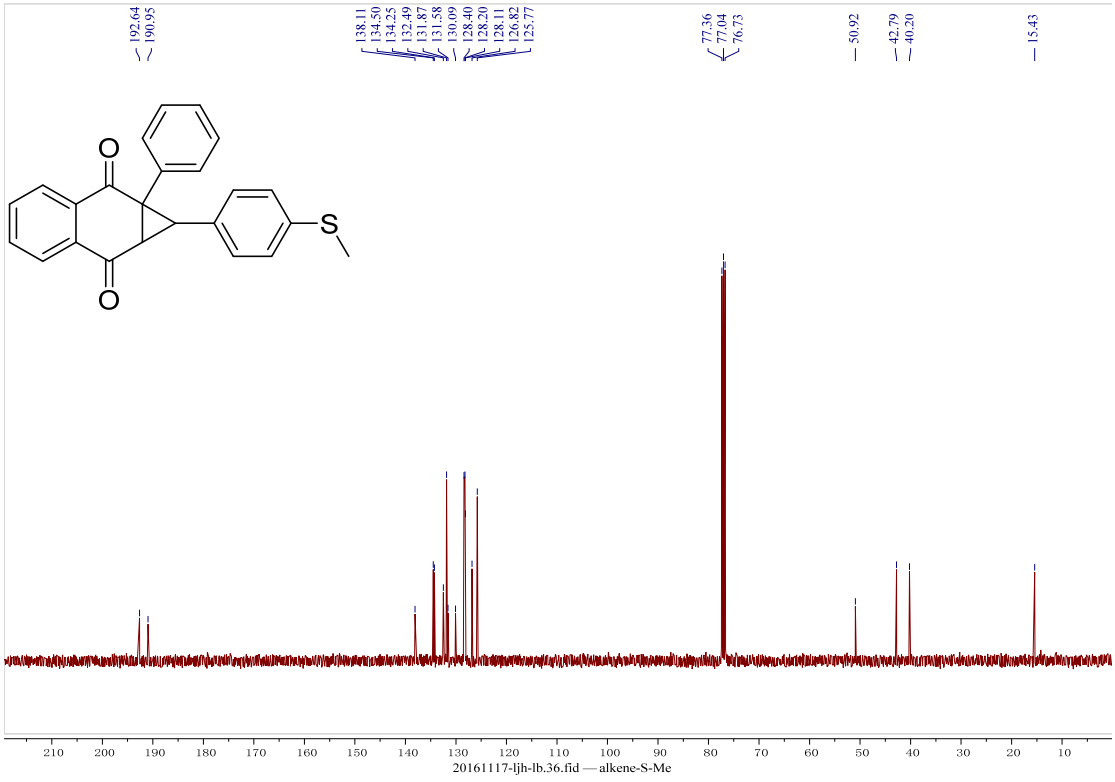
1a-Phenyl-1-(*p*-tolyl)-1a,7a-dihydro-1*H*-cyclopropa[*b*]naphthalene-2,7-dione (2h)



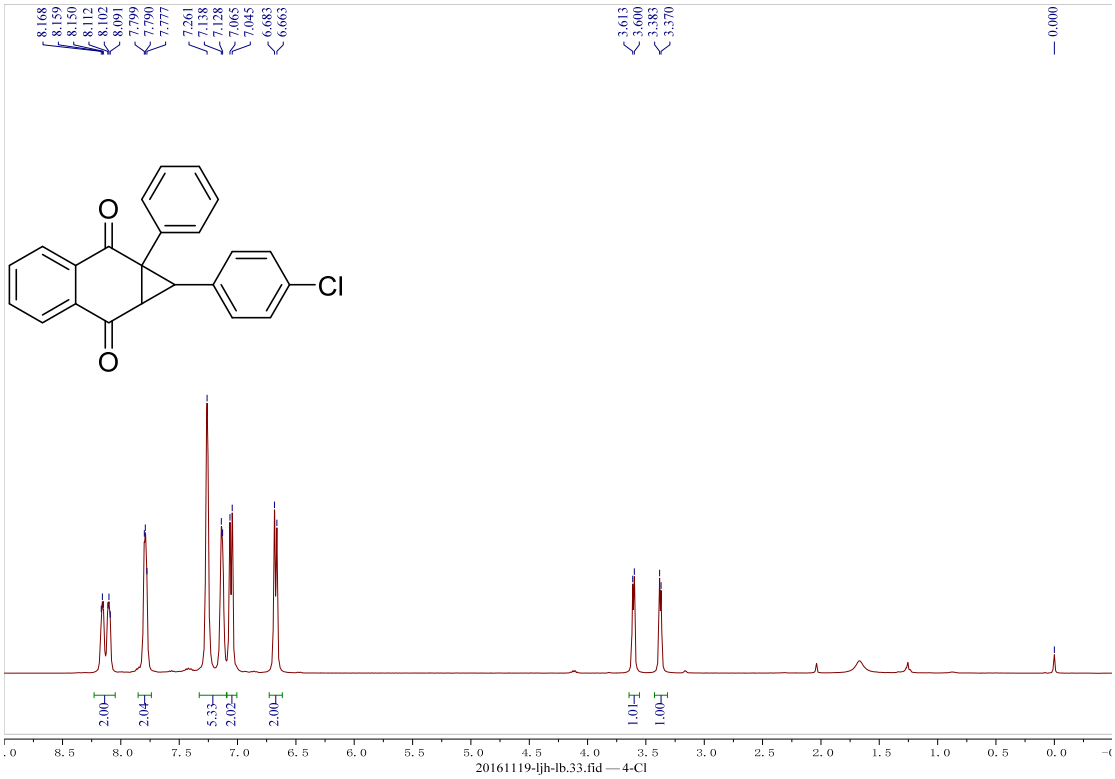


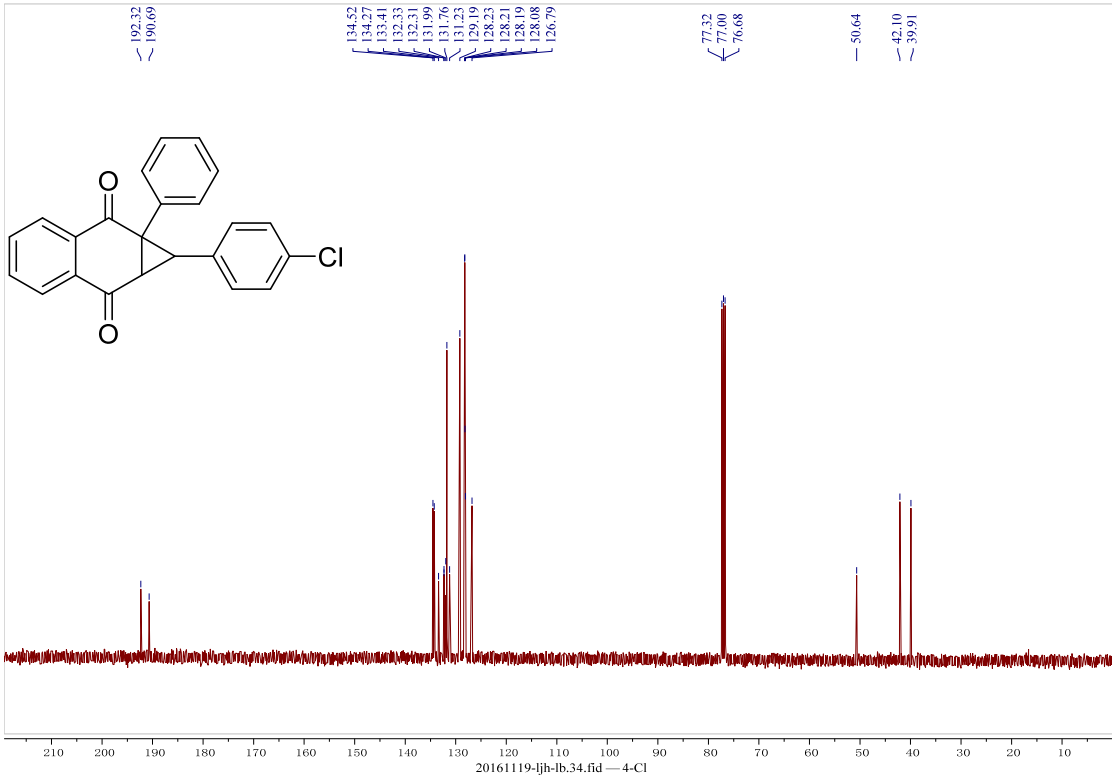
1-(4-(Methylthio)phenyl)-1a-phenyl-1a,7a-dihydro-1*H*-cyclopropa[*b*]naphthalene-2,7-dione (2i)



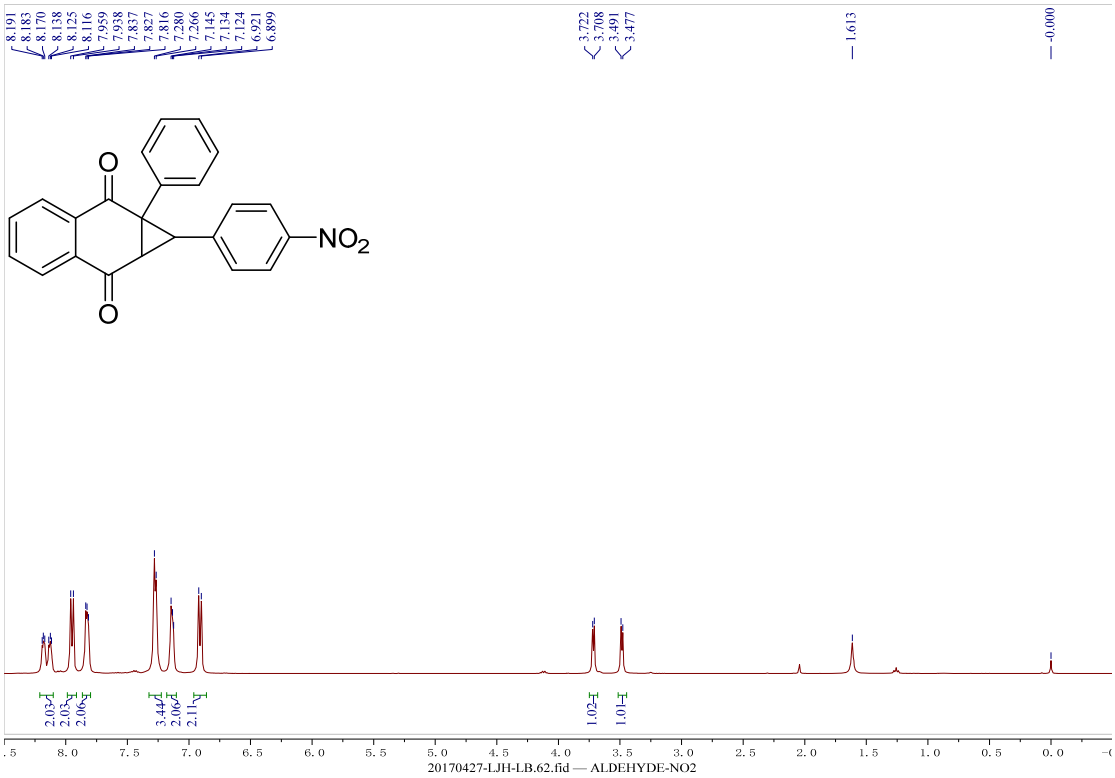


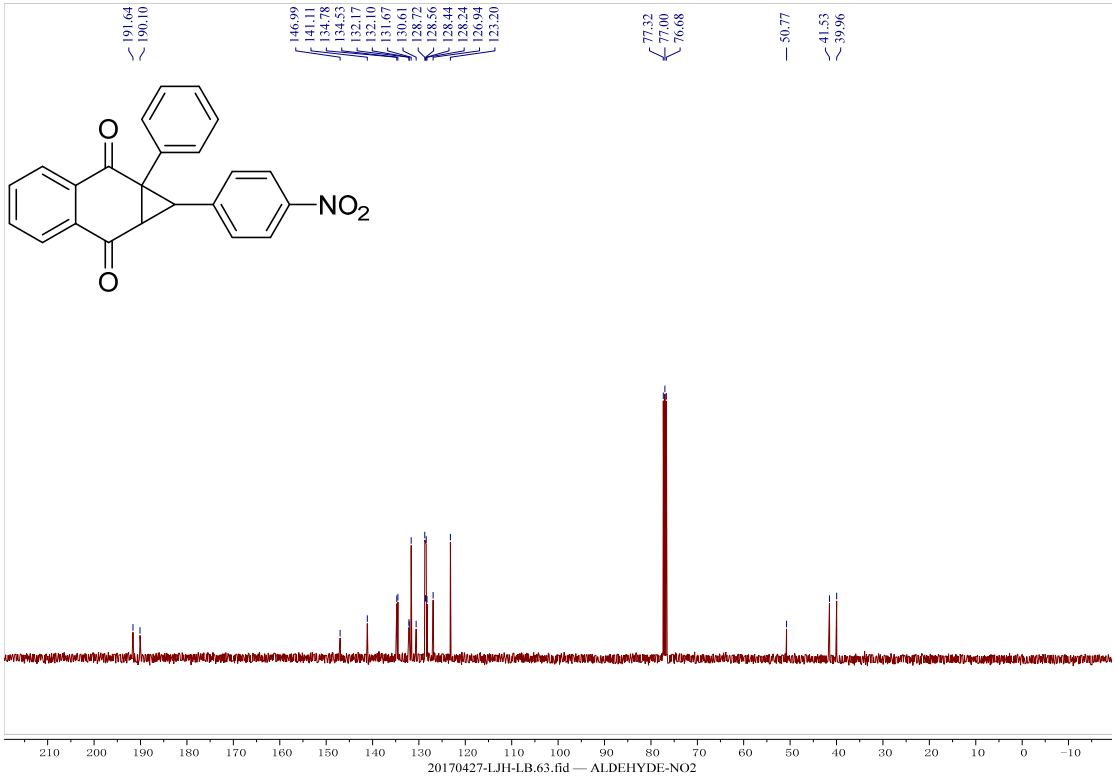
1-(4-Chlorophenyl)-1a-phenyl-1a,7a-dihydro-1*H*-cyclopropa[*b*]naphthalene-2,7-dione (2j)



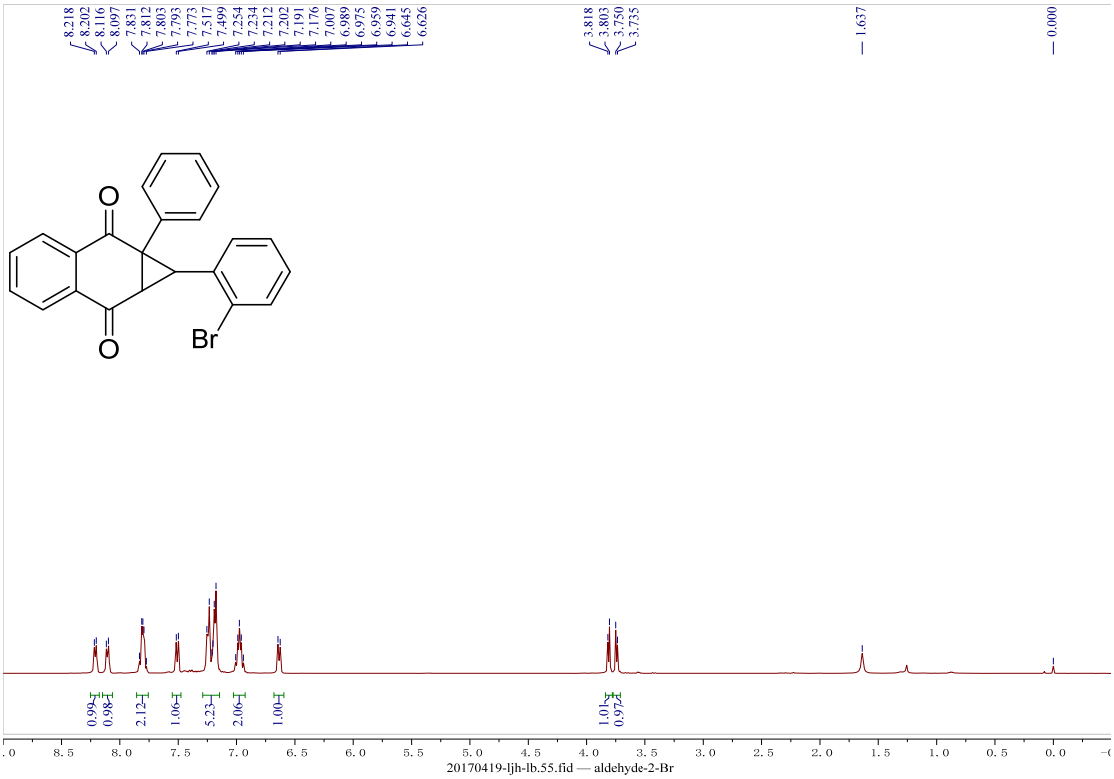


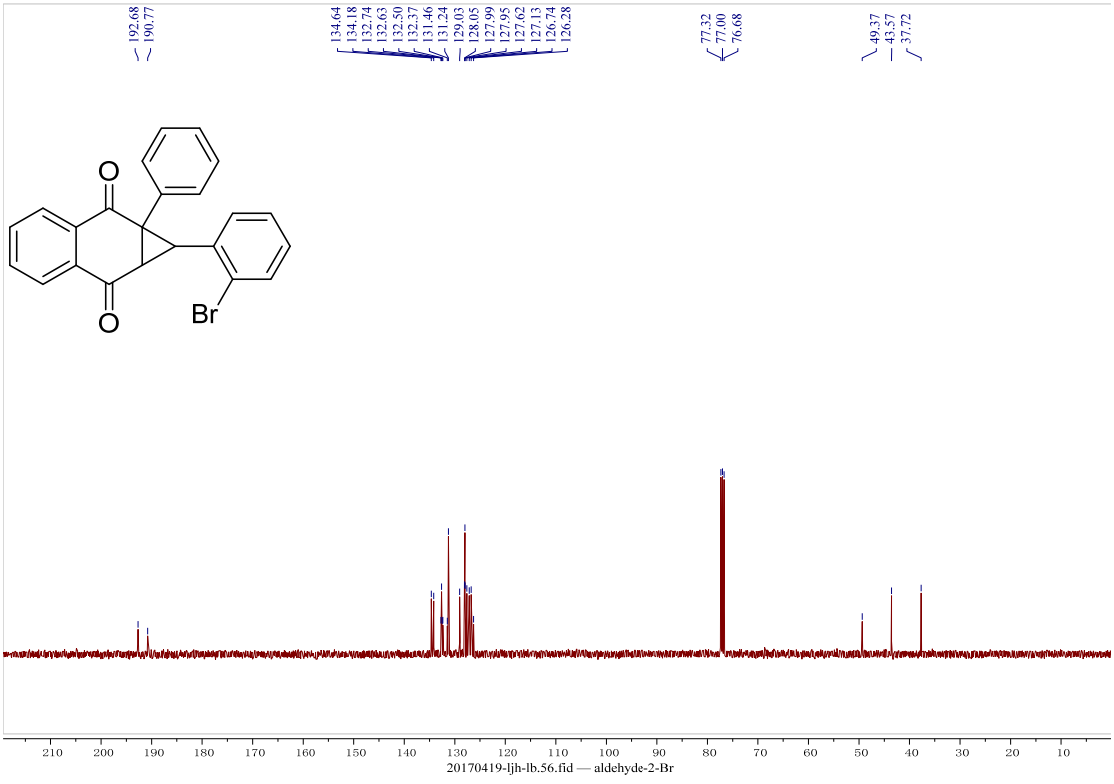
1-(4-Nitrophenyl)-1a-phenyl-1a,7a-dihydro-1*H*-cyclopropa[*b*]naphthalene-2,7-dione (2k)



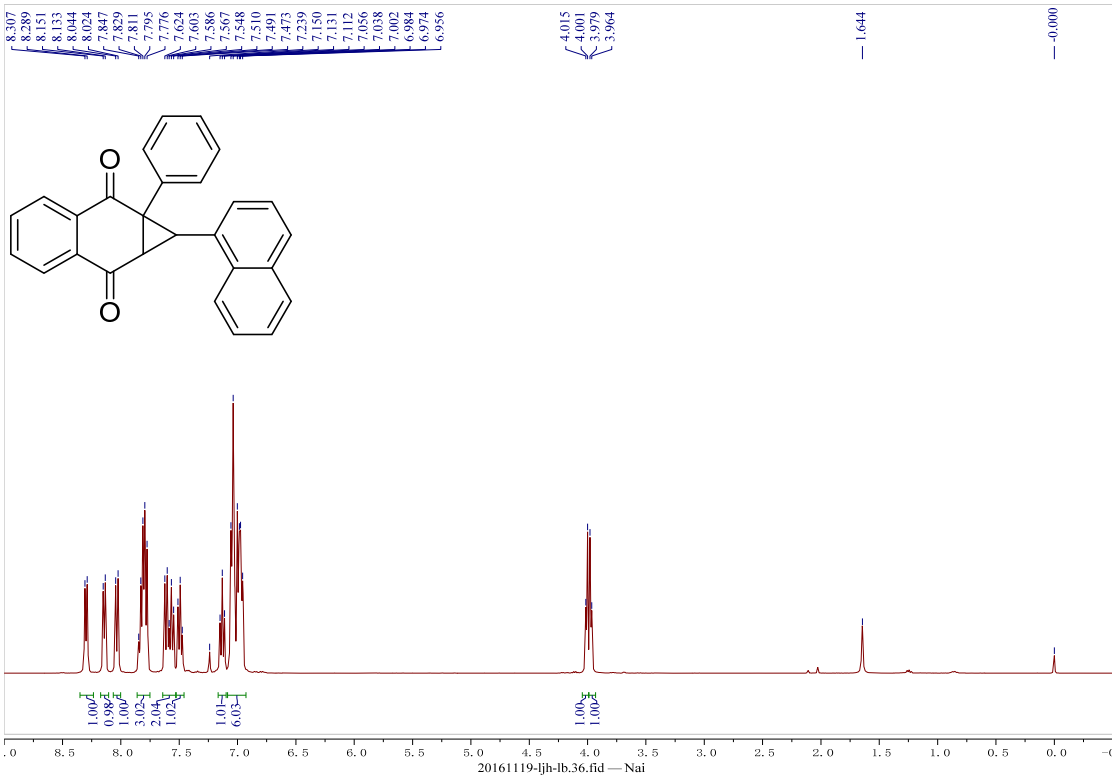


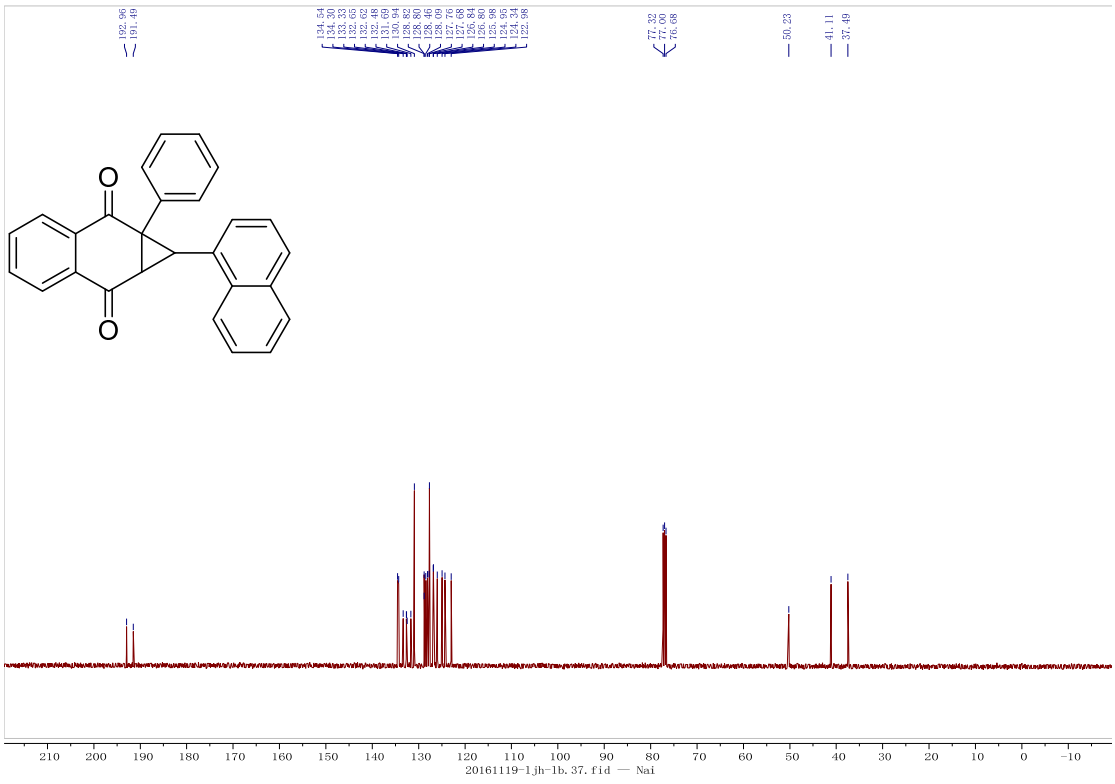
1-(2-Bromophenyl)-1a-phenyl-1a,7a-dihydro-1*H*-cyclopropa[*b*]naphthalene-2,7-dione (2l)



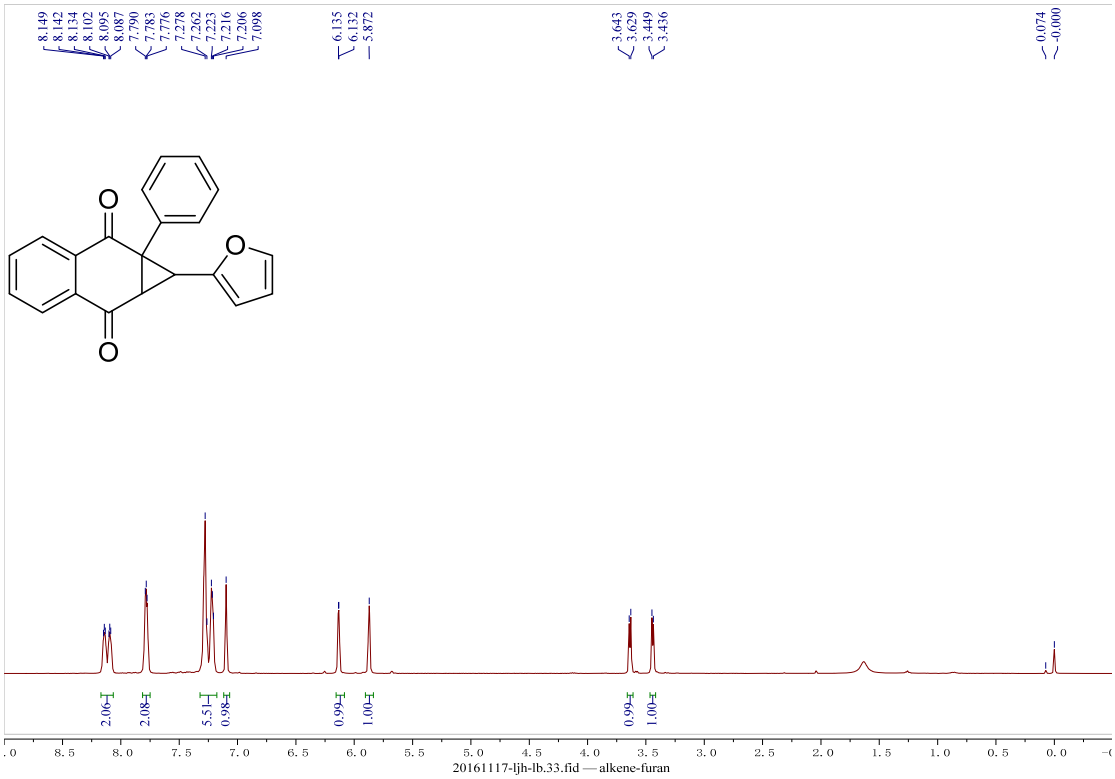


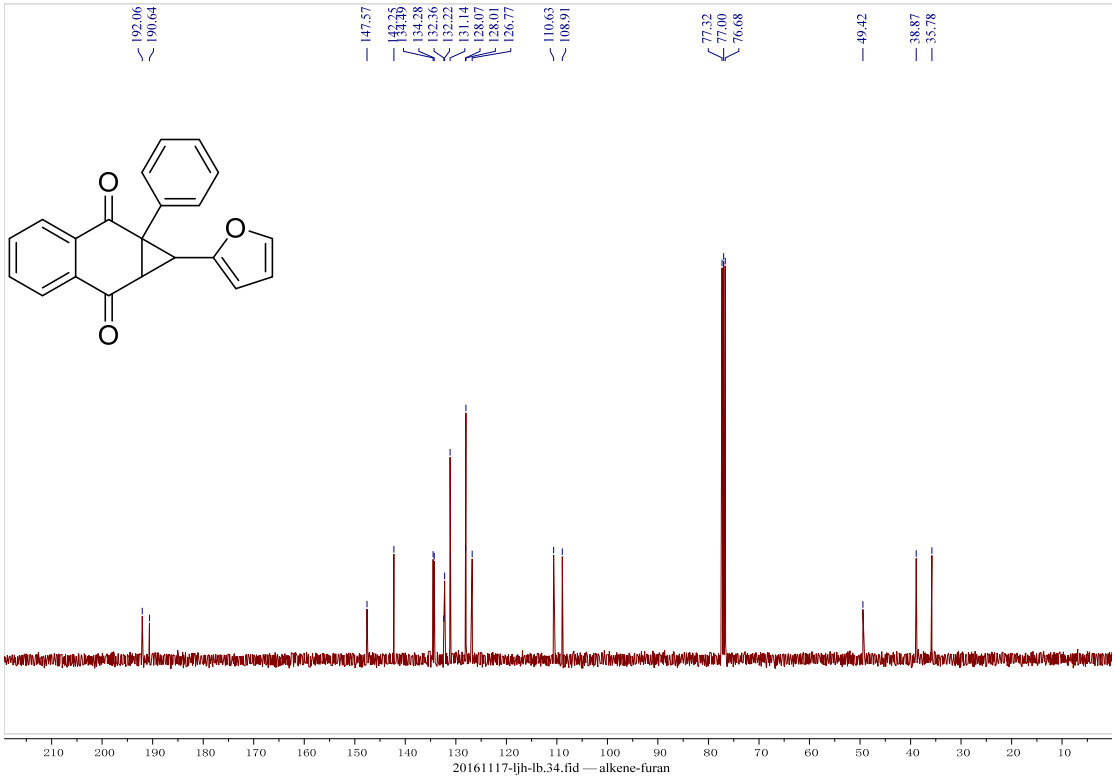
1-(Naphthalen-1-yl)-1a-phenyl-1a,7a-dihydro-1*H*-cyclopropa[*b*]naphthalene-2,7-dione (2m)





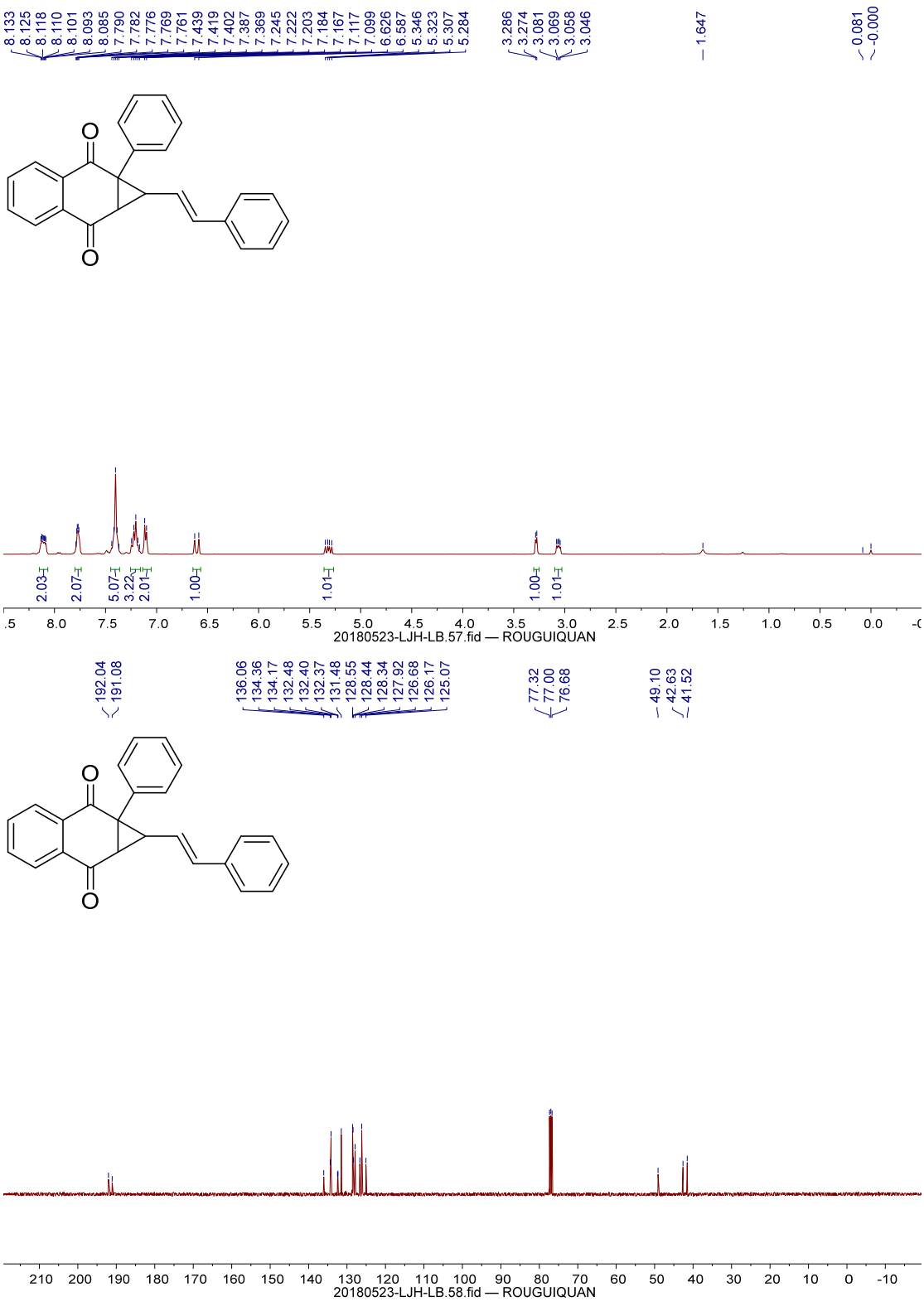
1-(Furan-2-yl)-1a-phenyl-1a,7a-dihydro-1*H*-cyclopropa[*b*]naphthalene-2,7-dione (2n)



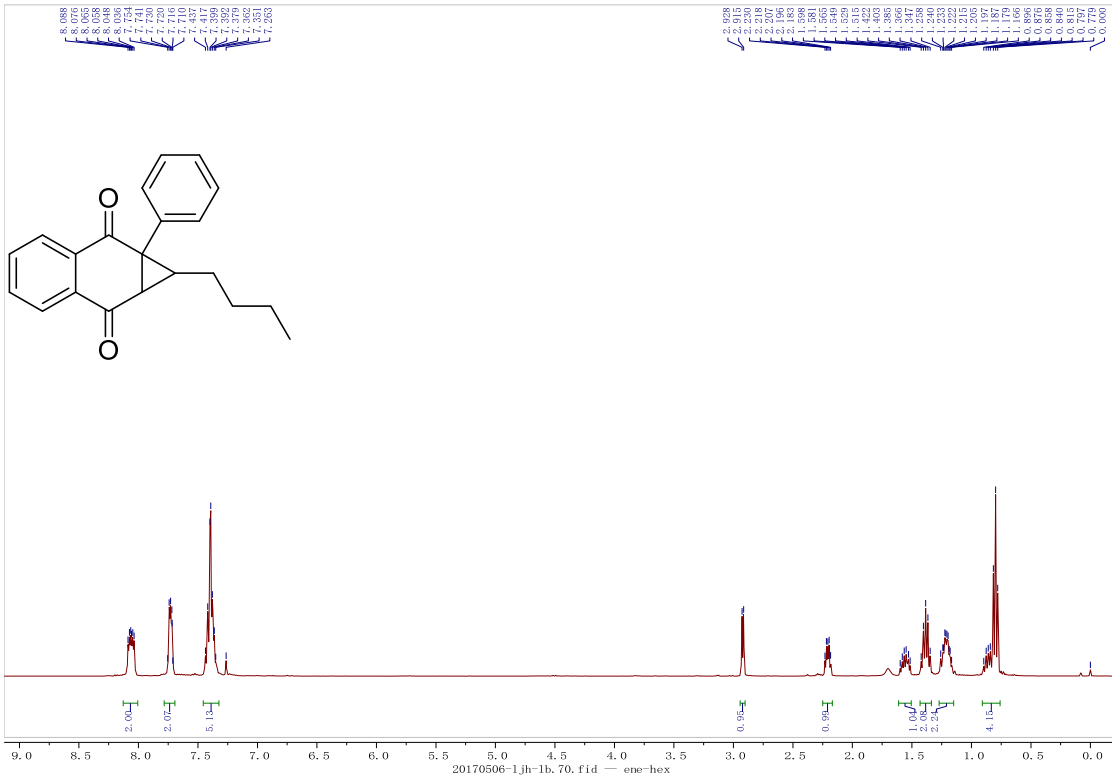


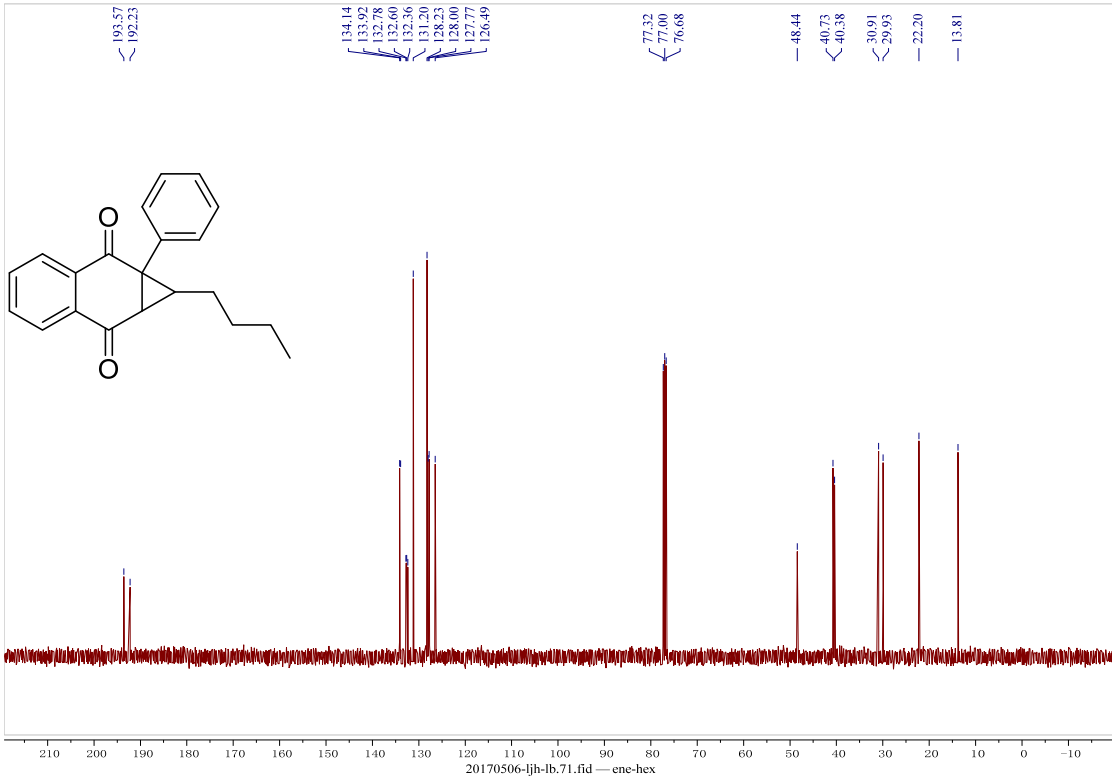
(*E*)-1a-phenyl-1-styryl-1a,7a-dihydro-1*H*-cyclopropa[*b*]naphthalene-2,7-dione

(2o)

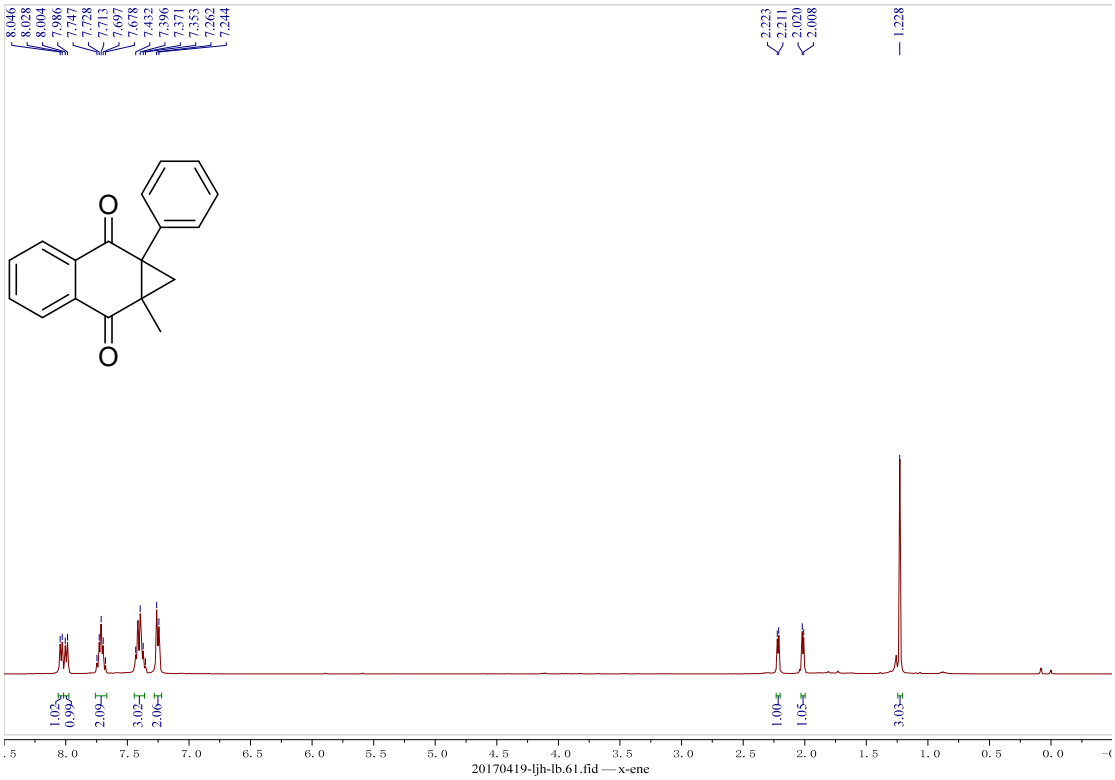


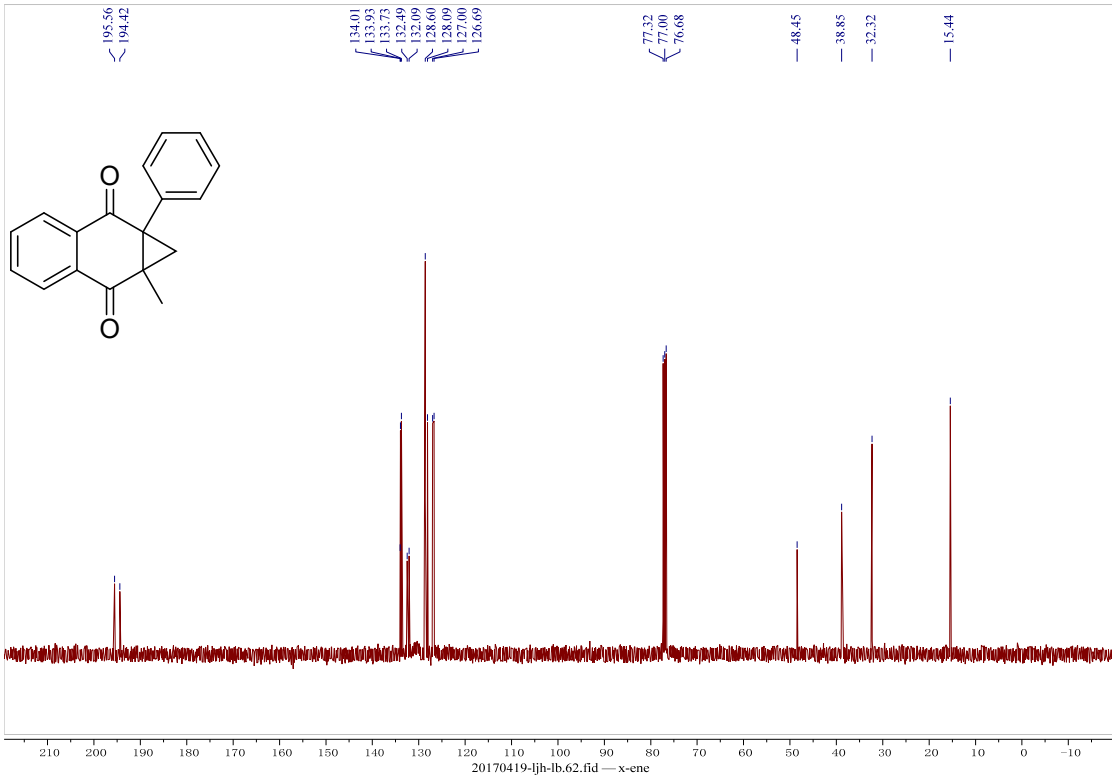
1-Butyl-1a-phenyl-1a,7a-dihydro-1*H*-cyclopropa[*b*]naphthalene-2,7-dione (2p)



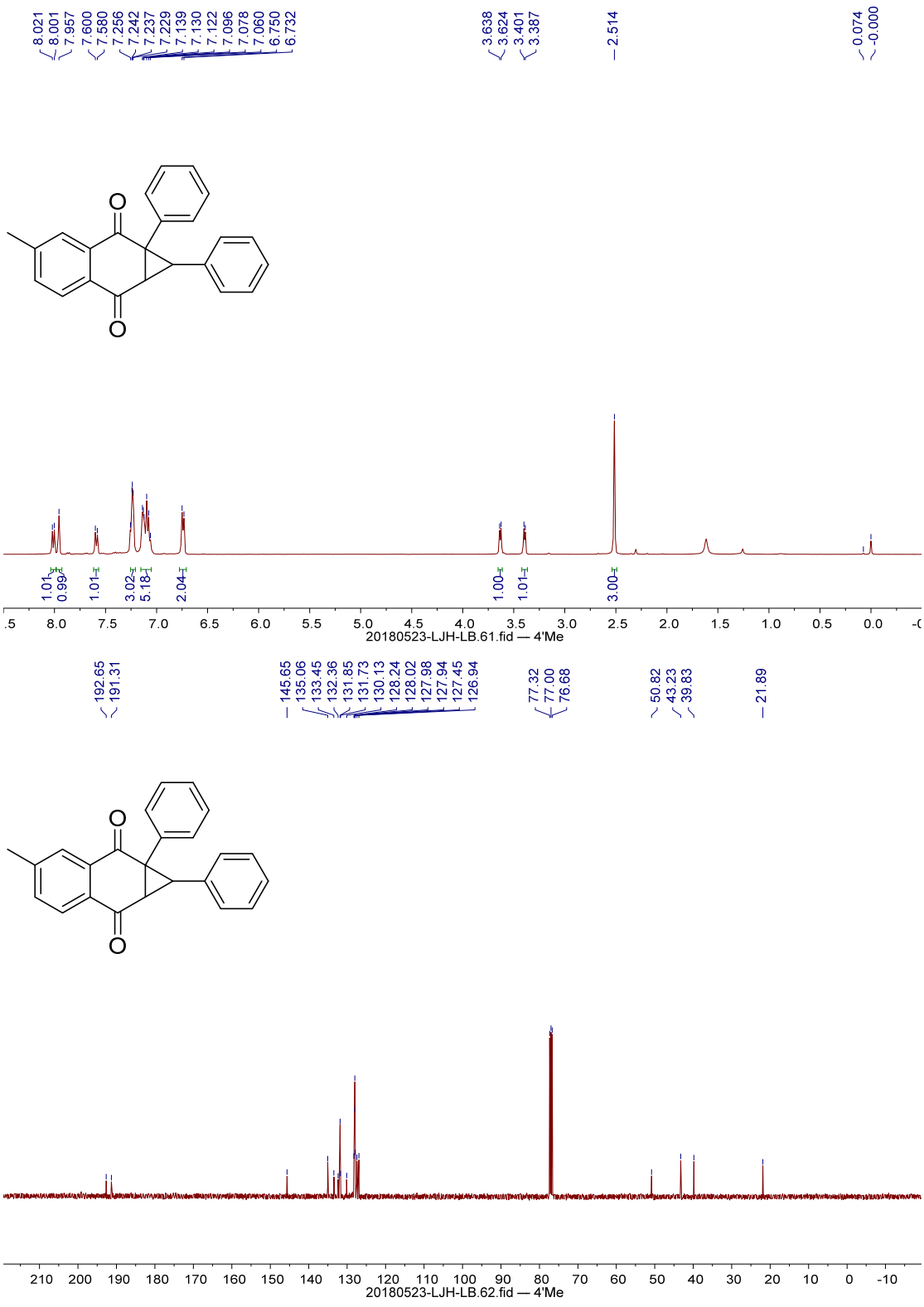


1a-Methyl-7a-phenyl-1a,7a-dihydro-1*H*-cyclopropa[*b*]naphthalene-2,7-dione (2q)

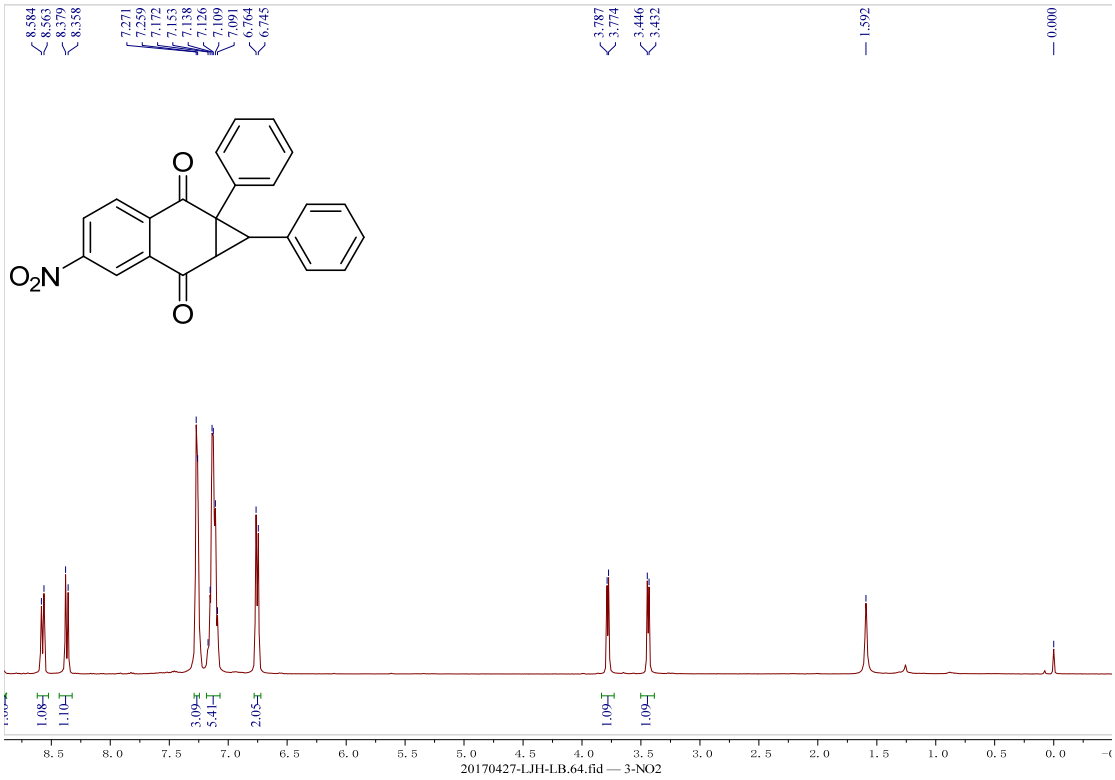


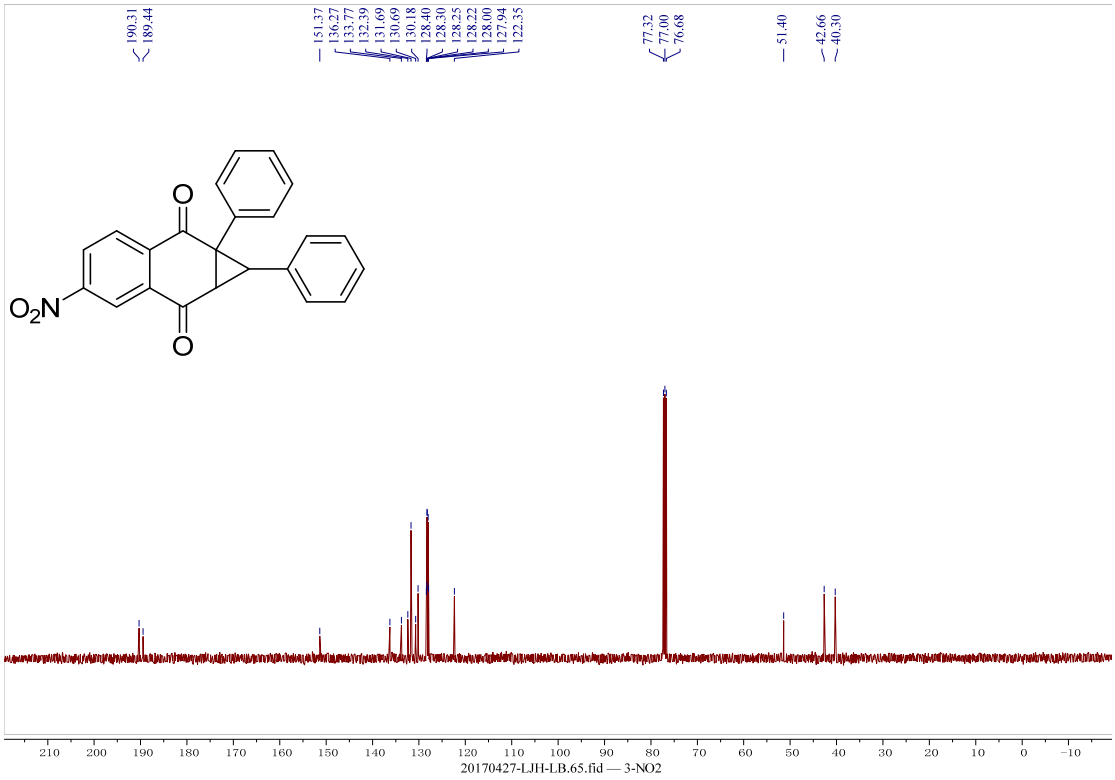


4-Methyl-1,1a-diphenyl-1a,7a-dihydro-1*H*-cyclopropa[*b*]naphthalene-2,7-dione (2r)

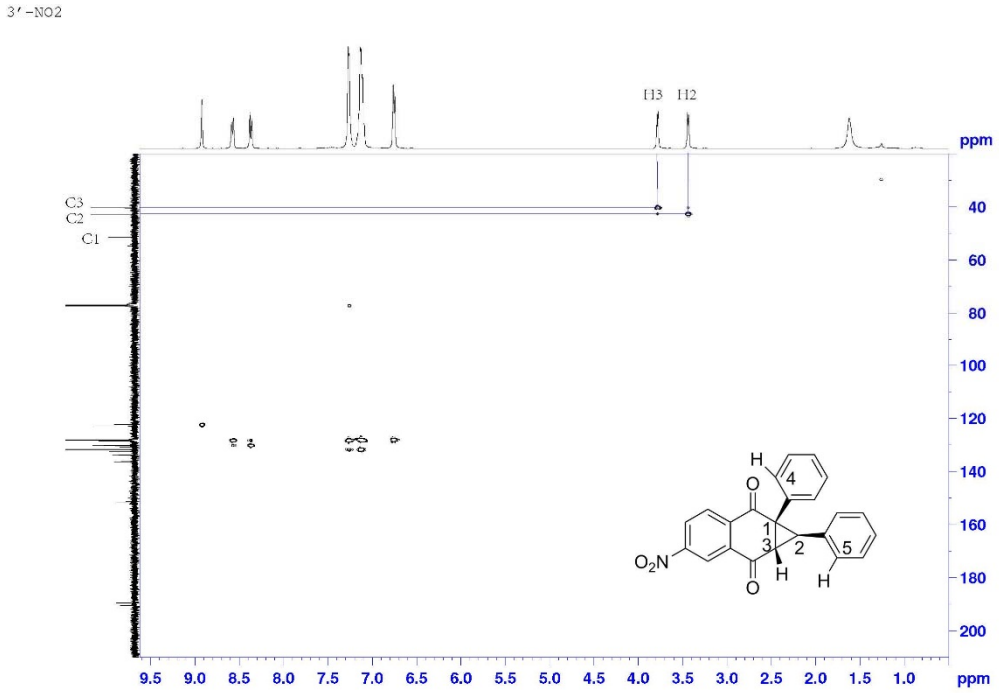


5-Nitro-1,1a-diphenyl-1a,7a-dihydro-1*H*-cyclopropa[*b*]naphthalene-2,7-dione (2s)

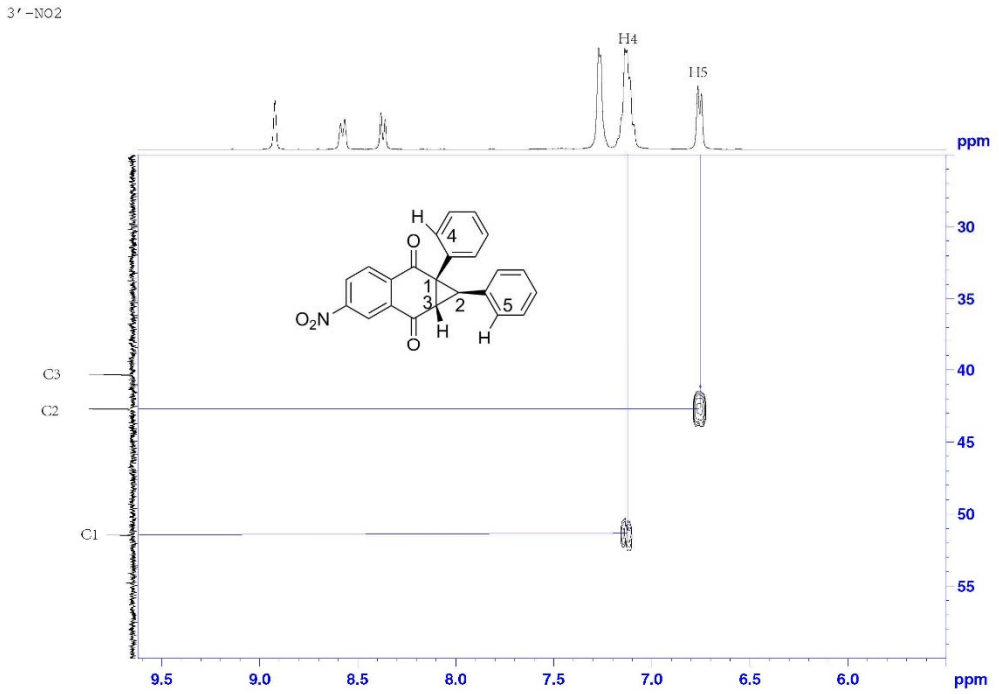




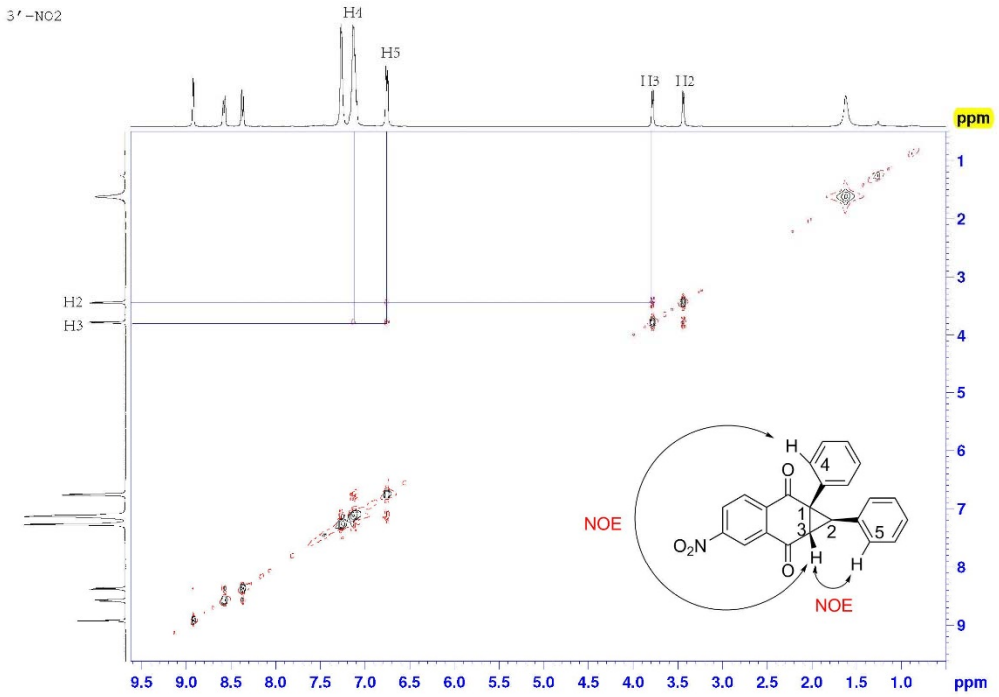
HSQC


3′-NO2
H3
H2
C3
C2
C1
ppm
40
60
80
100
120
140
160
180
200
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
H
O
4
1
3
2
5
O_2N
H
H
O

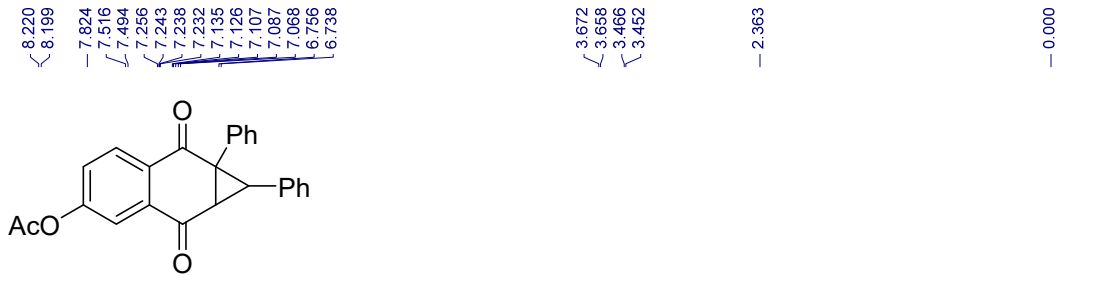
HMBC

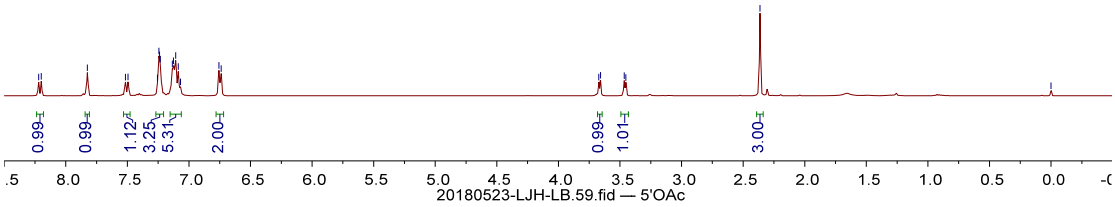

3′-NO2
H4
H5
ppm
30
35
40
45
50
55
H
O
4
1
3
2
5
O_2N
H
H
O
C3
C2
C1
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
ppm

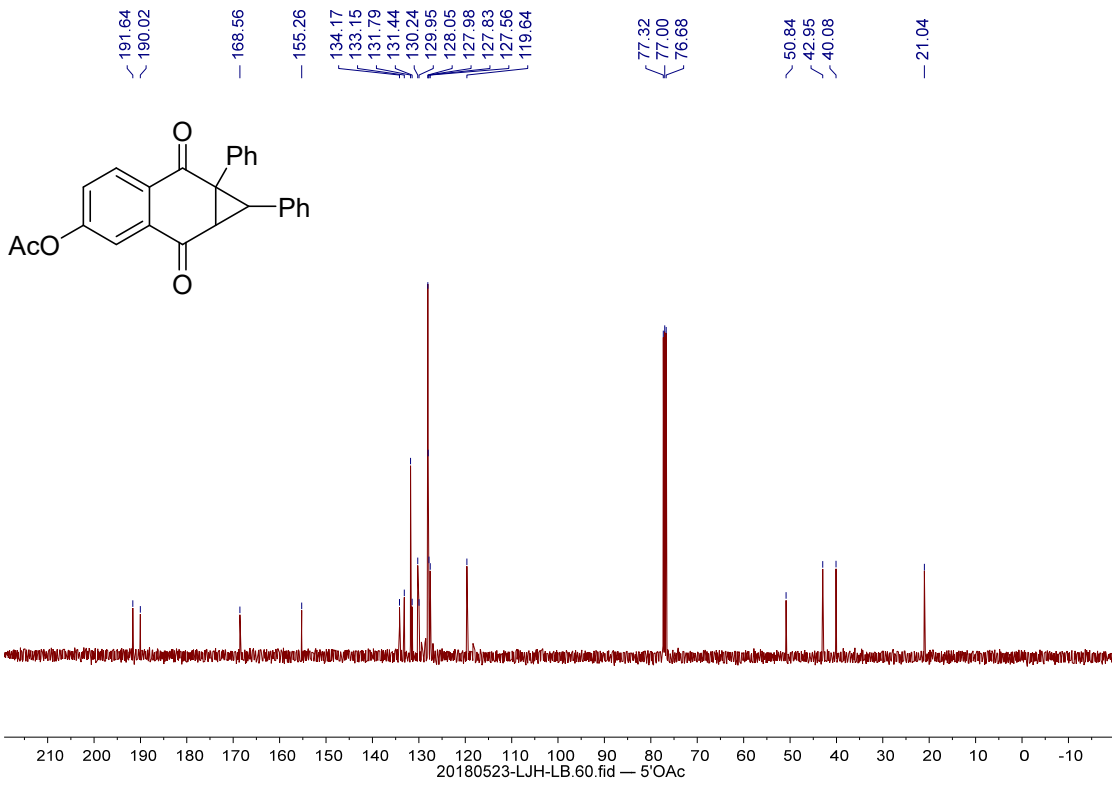
NOE


3′-NO2
H4
H5
H3
H2
ppm
H2
H3
NOE
O
H
4
1
3
2
5
O
H
H
NOE
O2N
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm

2,7-Dioxo-1,7a-diphenyl-1a,2,7,7a-tetrahydro-1*H*-cyclopropa[*b*]naphthalen-4-yl acetate (2t)







(E) The X-ray single-crystal diffraction analysis of 2m (CCDC 1875958):

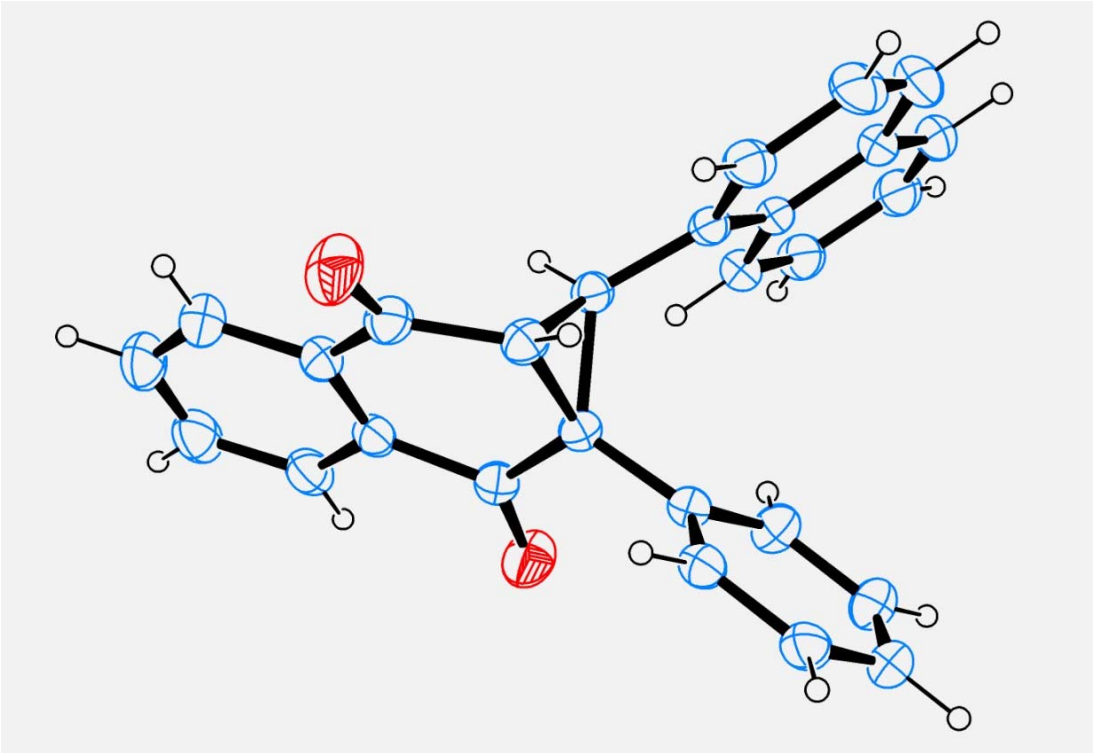


Table S1. Crystal data and structure refinement for ljh053_0m.

Identification code	ljh053_0m	
Empirical formula	C27 H18 O2	
Formula weight	374.41	
Temperature	296(2) K	
Wavelength	0.71073 A	
Crystal system, space group	Monoclinic, P2(1)/c	
Unit cell dimensions	a = 12.883(2) A	alpha = 90 deg.
	b = 10.655(2) A	beta = 93.427(3) deg.
	c = 13.918(3) A	gamma = 90 deg.
Volume	1907.1(6) A^3	
Z, Calculated density	4, 1.304 Mg/m^3	
Absorption coefficient	0.081 mm^-1	
F(000)	784	
Crystal size	0.23 x 0.21 x 0.20 mm	

Theta range for data collection	1.58 to 27.27 deg.
Limiting indices	-16<=h<=16, -13<=k<=13, -17<=l<=10
Reflections collected / unique	10897 / 4242 [R(int) = 0.0258]
Completeness to theta = 27.27	99.0 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9840 and 0.9816
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4242 / 0 / 263
Goodness-of-fit on F^2	1.026
Final R indices [I>2sigma(I)]	R1 = 0.0421, wR2 = 0.1004
R indices (all data)	R1 = 0.0662, wR2 = 0.1122
Extinction coefficient	0.0062(9)
Largest diff. peak and hole	0.158 and -0.165 e.A^-3

Table S2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for ljh053_0m.

U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
O(2)	1136(1)	-690(1)	782(1)	75(1)
O(1)	4295(1)	2270(1)	1950(1)	72(1)
C(24)	3464(2)	6066(2)	-1609(1)	62(1)
C(23)	2416(2)	6064(2)	-1732(1)	60(1)
C(22)	1801(1)	5149(1)	-1303(1)	49(1)
C(27)	2302(1)	4203(1)	-721(1)	40(1)
C(18)	1684(1)	3277(1)	-287(1)	40(1)
C(3)	2221(1)	2221(1)	241(1)	38(1)
C(2)	2556(1)	2265(1)	1319(1)	38(1)
C(1)	3598(1)	1684(1)	1539(1)	43(1)
C(11)	3772(1)	372(1)	1220(1)	44(1)

C(10)	4779(1)	-101(2)	1304(1)	55(1)
C(9)	4970(2)	-1328(2)	1067(1)	66(1)
C(21)	713(2)	5132(2)	-1443(1)	65(1)
C(20)	142(1)	4251(2)	-1027(1)	65(1)
C(19)	627(1)	3308(2)	-441(1)	52(1)
C(4)	1687(1)	1397(1)	941(1)	42(1)
C(5)	1861(1)	34(2)	868(1)	49(1)
C(6)	2956(1)	-410(1)	895(1)	46(1)
C(8)	4173(2)	-2086(2)	729(1)	73(1)
C(7)	3168(2)	-1644(2)	643(1)	63(1)
C(12)	2300(1)	3380(1)	1918(1)	39(1)
C(17)	1569(1)	3291(1)	2602(1)	45(1)
C(16)	1372(1)	4306(2)	3189(1)	53(1)
C(15)	1905(1)	5404(2)	3100(1)	57(1)
C(14)	2635(1)	5508(2)	2421(1)	59(1)
C(13)	2830(1)	4503(2)	1834(1)	52(1)
C(26)	3398(1)	4230(1)	-615(1)	45(1)
C(25)	3957(1)	5130(2)	-1048(1)	54(1)

Table S3. Bond lengths [A] and angles [deg] for ljh053_0m.

O(2)-C(5)	1.2120(18)
O(1)-C(1)	1.2082(17)
C(24)-C(23)	1.351(3)
C(24)-C(25)	1.397(2)
C(24)-H(24)	0.9300
C(23)-C(22)	1.411(2)
C(23)-H(23)	0.9300
C(22)-C(21)	1.403(2)
C(22)-C(27)	1.424(2)

C(27)-C(26)	1.411(2)
C(27)-C(18)	1.424(2)
C(18)-C(19)	1.366(2)
C(18)-C(3)	1.4913(19)
C(3)-C(4)	1.507(2)
C(3)-C(2)	1.5373(19)
C(3)-H(3)	0.9800
C(2)-C(1)	1.494(2)
C(2)-C(12)	1.4985(19)
C(2)-C(4)	1.5213(19)
C(1)-C(11)	1.488(2)
C(11)-C(10)	1.390(2)
C(11)-C(6)	1.395(2)
C(10)-C(9)	1.374(2)
C(10)-H(10)	0.9300
C(9)-C(8)	1.368(3)
C(9)-H(11)	0.9300
C(21)-C(20)	1.345(3)
C(21)-H(21)	0.9300
C(20)-C(19)	1.415(2)
C(20)-H(20)	0.9300
C(19)-H(19)	0.9300
C(4)-C(5)	1.474(2)
C(4)-H(4)	0.9800
C(5)-C(6)	1.487(2)
C(6)-C(7)	1.392(2)
C(8)-C(7)	1.377(3)
C(8)-H(8)	0.9300
C(7)-H(7)	0.9300

C(12)-C(17)	1.382(2)
C(12)-C(13)	1.387(2)
C(17)-C(16)	1.388(2)
C(17)-H(17)	0.9300
C(16)-C(15)	1.366(2)
C(16)-H(16)	0.9300
C(15)-C(14)	1.377(2)
C(15)-H(15)	0.9300
C(14)-C(13)	1.378(2)
C(14)-H(14)	0.9300
C(13)-H(13)	0.9300
C(26)-C(25)	1.361(2)
C(26)-H(26)	0.9300
C(25)-H(25)	0.9300
C(23)-C(24)-C(25)	119.18(16)
C(23)-C(24)-H(24)	120.4
C(25)-C(24)-H(24)	120.4
C(24)-C(23)-C(22)	122.01(16)
C(24)-C(23)-H(23)	119.0
C(22)-C(23)-H(23)	119.0
C(21)-C(22)-C(23)	122.12(16)
C(21)-C(22)-C(27)	118.99(16)
C(23)-C(22)-C(27)	118.89(15)
C(26)-C(27)-C(22)	117.50(14)
C(26)-C(27)-C(18)	123.45(13)
C(22)-C(27)-C(18)	119.05(13)
C(19)-C(18)-C(27)	119.62(14)
C(19)-C(18)-C(3)	121.59(14)
C(27)-C(18)-C(3)	118.48(12)

C(18)-C(3)-C(4)	122.83(12)
C(18)-C(3)-C(2)	123.58(12)
C(4)-C(3)-C(2)	59.95(9)
C(18)-C(3)-H(3)	113.4
C(4)-C(3)-H(3)	113.4
C(2)-C(3)-H(3)	113.4
C(1)-C(2)-C(12)	116.06(11)
C(1)-C(2)-C(4)	116.94(12)
C(12)-C(2)-C(4)	119.49(12)
C(1)-C(2)-C(3)	112.59(11)
C(12)-C(2)-C(3)	120.57(11)
C(4)-C(2)-C(3)	59.04(9)
O(1)-C(1)-C(11)	120.39(14)
O(1)-C(1)-C(2)	121.07(14)
C(11)-C(1)-C(2)	118.53(12)
C(10)-C(11)-C(6)	119.47(15)
C(10)-C(11)-C(1)	118.15(14)
C(6)-C(11)-C(1)	122.28(13)
C(9)-C(10)-C(11)	120.25(17)
C(9)-C(10)-H(10)	119.9
C(11)-C(10)-H(10)	119.9
C(8)-C(9)-C(10)	120.25(17)
C(8)-C(9)-H(11)	119.9
C(10)-C(9)-H(11)	119.9
C(20)-C(21)-C(22)	121.12(16)
C(20)-C(21)-H(21)	119.4
C(22)-C(21)-H(21)	119.4
C(21)-C(20)-C(19)	120.64(16)
C(21)-C(20)-H(20)	119.7

C(19)-C(20)-H(20)	119.7
C(18)-C(19)-C(20)	120.57(16)
C(18)-C(19)-H(19)	119.7
C(20)-C(19)-H(19)	119.7
C(5)-C(4)-C(3)	116.92(13)
C(5)-C(4)-C(2)	120.75(13)
C(3)-C(4)-C(2)	61.01(9)
C(5)-C(4)-H(4)	115.7
C(3)-C(4)-H(4)	115.7
C(2)-C(4)-H(4)	115.7
O(2)-C(5)-C(4)	121.04(15)
O(2)-C(5)-C(6)	121.60(15)
C(4)-C(5)-C(6)	117.36(13)
C(7)-C(6)-C(11)	119.39(15)
C(7)-C(6)-C(5)	119.62(15)
C(11)-C(6)-C(5)	120.90(13)
C(9)-C(8)-C(7)	120.68(17)
C(9)-C(8)-H(8)	119.7
C(7)-C(8)-H(8)	119.7
C(8)-C(7)-C(6)	119.93(18)
C(8)-C(7)-H(7)	120.0
C(6)-C(7)-H(7)	120.0
C(17)-C(12)-C(13)	118.40(14)
C(17)-C(12)-C(2)	120.73(13)
C(13)-C(12)-C(2)	120.78(13)
C(12)-C(17)-C(16)	120.56(15)
C(12)-C(17)-H(17)	119.7
C(16)-C(17)-H(17)	119.7
C(15)-C(16)-C(17)	120.24(15)

C(15)-C(16)-H(16)	119.9
C(17)-C(16)-H(16)	119.9
C(16)-C(15)-C(14)	119.91(15)
C(16)-C(15)-H(15)	120.0
C(14)-C(15)-H(15)	120.0
C(15)-C(14)-C(13)	120.02(16)
C(15)-C(14)-H(14)	120.0
C(13)-C(14)-H(14)	120.0
C(14)-C(13)-C(12)	120.86(15)
C(14)-C(13)-H(13)	119.6
C(12)-C(13)-H(13)	119.6
C(25)-C(26)-C(27)	121.40(14)
C(25)-C(26)-H(26)	119.3
C(27)-C(26)-H(26)	119.3
C(26)-C(25)-C(24)	121.03(16)
C(26)-C(25)-H(25)	119.5
C(24)-C(25)-H(25)	119.5

Symmetry transformations used to generate equivalent atoms:

Table S4. Anisotropic displacement parameters (A^2 x 10^3) for ljh053_0m.

The anisotropic displacement factor exponent takes the form:

-2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
O(2)	66(1)	52(1)	107(1)	-3(1)	1(1)	-22(1)
O(1)	50(1)	66(1)	98(1)	-22(1)	-24(1)	3(1)
C(24)	88(1)	47(1)	50(1)	4(1)	2(1)	-9(1)
C(23)	94(1)	40(1)	46(1)	5(1)	-5(1)	9(1)
C(22)	63(1)	44(1)	40(1)	-5(1)	-6(1)	13(1)
C(27)	48(1)	37(1)	34(1)	-5(1)	-4(1)	7(1)

C(18)	39(1)	43(1)	36(1)	-8(1)	-3(1)	7(1)
C(3)	37(1)	39(1)	37(1)	-3(1)	0(1)	2(1)
C(2)	38(1)	38(1)	38(1)	-1(1)	1(1)	-1(1)
C(1)	43(1)	44(1)	43(1)	0(1)	-1(1)	0(1)
C(11)	51(1)	44(1)	36(1)	5(1)	2(1)	6(1)
C(10)	57(1)	59(1)	48(1)	5(1)	1(1)	14(1)
C(9)	72(1)	67(1)	60(1)	6(1)	7(1)	27(1)
C(21)	68(1)	65(1)	60(1)	4(1)	-12(1)	24(1)
C(20)	44(1)	85(1)	64(1)	-8(1)	-10(1)	23(1)
C(19)	42(1)	61(1)	50(1)	-6(1)	-2(1)	7(1)
C(4)	38(1)	44(1)	45(1)	-3(1)	1(1)	-4(1)
C(5)	56(1)	44(1)	47(1)	1(1)	1(1)	-10(1)
C(6)	59(1)	40(1)	40(1)	3(1)	2(1)	2(1)
C(8)	98(2)	51(1)	70(1)	-2(1)	8(1)	26(1)
C(7)	84(1)	44(1)	60(1)	-2(1)	0(1)	3(1)
C(12)	41(1)	41(1)	36(1)	0(1)	-3(1)	2(1)
C(17)	49(1)	46(1)	39(1)	4(1)	1(1)	3(1)
C(16)	64(1)	59(1)	38(1)	2(1)	6(1)	15(1)
C(15)	80(1)	46(1)	46(1)	-8(1)	-2(1)	14(1)
C(14)	73(1)	42(1)	60(1)	-8(1)	-1(1)	-5(1)
C(13)	55(1)	48(1)	52(1)	-6(1)	6(1)	-5(1)
C(26)	50(1)	43(1)	42(1)	1(1)	-2(1)	3(1)
C(25)	59(1)	53(1)	51(1)	0(1)	4(1)	-6(1)

Table S5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for ljh053_0m.

	x	y	z	U(eq)
H(24)	3852	6683	-1895	74
H(23)	2089	6685	-2110	73

H(3)	2709	1765	-145	45
H(10)	5326	415	1521	66
H(11)	5643	-1643	1136	80
H(21)	382	5741	-1829	78
H(20)	-578	4262	-1125	78
H(19)	223	2704	-158	62
H(4)	982	1652	1083	51
H(8)	4312	-2910	556	87
H(7)	2631	-2169	416	76
H(17)	1206	2545	2671	54
H(16)	875	4239	3644	64
H(15)	1776	6080	3498	69
H(14)	2996	6256	2357	70
H(13)	3324	4580	1377	62
H(26)	3746	3621	-241	54
H(25)	4679	5121	-969	65

Table S6. Torsion angles [deg] for ljh053_0m.

C(25)-C(24)-C(23)-C(22)	0.5(3)
C(24)-C(23)-C(22)-C(21)	-178.86(16)
C(24)-C(23)-C(22)-C(27)	0.3(2)
C(21)-C(22)-C(27)-C(26)	178.49(14)
C(23)-C(22)-C(27)-C(26)	-0.7(2)
C(21)-C(22)-C(27)-C(18)	-0.8(2)
C(23)-C(22)-C(27)-C(18)	-179.97(13)
C(26)-C(27)-C(18)-C(19)	-178.89(14)
C(22)-C(27)-C(18)-C(19)	0.4(2)
C(26)-C(27)-C(18)-C(3)	-5.1(2)
C(22)-C(27)-C(18)-C(3)	174.14(12)

C(19)-C(18)-C(3)-C(4)	-23.3(2)
C(27)-C(18)-C(3)-C(4)	163.10(12)
C(19)-C(18)-C(3)-C(2)	-96.60(17)
C(27)-C(18)-C(3)-C(2)	89.78(16)
C(18)-C(3)-C(2)-C(1)	-139.60(13)
C(4)-C(3)-C(2)-C(1)	108.82(13)
C(18)-C(3)-C(2)-C(12)	3.37(19)
C(4)-C(3)-C(2)-C(12)	-108.20(14)
C(18)-C(3)-C(2)-C(4)	111.58(15)
C(12)-C(2)-C(1)-O(1)	-21.2(2)
C(4)-C(2)-C(1)-O(1)	-170.89(15)
C(3)-C(2)-C(1)-O(1)	123.54(16)
C(12)-C(2)-C(1)-C(11)	160.18(13)
C(4)-C(2)-C(1)-C(11)	10.50(19)
C(3)-C(2)-C(1)-C(11)	-55.07(17)
O(1)-C(1)-C(11)-C(10)	-7.6(2)
C(2)-C(1)-C(11)-C(10)	171.02(13)
O(1)-C(1)-C(11)-C(6)	168.77(16)
C(2)-C(1)-C(11)-C(6)	-12.6(2)
C(6)-C(11)-C(10)-C(9)	0.1(2)
C(1)-C(11)-C(10)-C(9)	176.60(15)
C(11)-C(10)-C(9)-C(8)	1.2(3)
C(23)-C(22)-C(21)-C(20)	-179.98(17)
C(27)-C(22)-C(21)-C(20)	0.9(3)
C(22)-C(21)-C(20)-C(19)	-0.5(3)
C(27)-C(18)-C(19)-C(20)	0.0(2)
C(3)-C(18)-C(19)-C(20)	-173.55(14)
C(21)-C(20)-C(19)-C(18)	0.1(3)
C(18)-C(3)-C(4)-C(5)	135.25(14)

C(2)-C(3)-C(4)-C(5)	-111.97(14)
C(18)-C(3)-C(4)-C(2)	-112.78(14)
C(1)-C(2)-C(4)-C(5)	4.4(2)
C(12)-C(2)-C(4)-C(5)	-144.17(14)
C(3)-C(2)-C(4)-C(5)	105.82(15)
C(1)-C(2)-C(4)-C(3)	-101.39(13)
C(12)-C(2)-C(4)-C(3)	110.00(14)
C(3)-C(4)-C(5)-O(2)	-126.26(16)
C(2)-C(4)-C(5)-O(2)	163.03(15)
C(3)-C(4)-C(5)-C(6)	53.14(18)
C(2)-C(4)-C(5)-C(6)	-17.6(2)
C(10)-C(11)-C(6)-C(7)	-1.2(2)
C(1)-C(11)-C(6)-C(7)	-177.54(14)
C(10)-C(11)-C(6)-C(5)	175.28(13)
C(1)-C(11)-C(6)-C(5)	-1.1(2)
O(2)-C(5)-C(6)-C(7)	11.9(2)
C(4)-C(5)-C(6)-C(7)	-167.45(15)
O(2)-C(5)-C(6)-C(11)	-164.52(16)
C(4)-C(5)-C(6)-C(11)	16.1(2)
C(10)-C(9)-C(8)-C(7)	-1.5(3)
C(9)-C(8)-C(7)-C(6)	0.4(3)
C(11)-C(6)-C(7)-C(8)	1.0(3)
C(5)-C(6)-C(7)-C(8)	-175.56(16)
C(1)-C(2)-C(12)-C(17)	-108.69(15)
C(4)-C(2)-C(12)-C(17)	40.18(19)
C(3)-C(2)-C(12)-C(17)	109.55(15)
C(1)-C(2)-C(12)-C(13)	67.81(18)
C(4)-C(2)-C(12)-C(13)	-143.32(14)
C(3)-C(2)-C(12)-C(13)	-73.96(17)

C(13)-C(12)-C(17)-C(16)	0.2(2)
C(2)-C(12)-C(17)-C(16)	176.73(13)
C(12)-C(17)-C(16)-C(15)	-0.5(2)
C(17)-C(16)-C(15)-C(14)	0.6(2)
C(16)-C(15)-C(14)-C(13)	-0.3(3)
C(15)-C(14)-C(13)-C(12)	0.0(3)
C(17)-C(12)-C(13)-C(14)	0.1(2)
C(2)-C(12)-C(13)-C(14)	-176.47(14)
C(22)-C(27)-C(26)-C(25)	0.3(2)
C(18)-C(27)-C(26)-C(25)	179.60(14)
C(27)-C(26)-C(25)-C(24)	0.4(2)
C(23)-C(24)-C(25)-C(26)	-0.9(3)

Symmetry transformations used to generate equivalent atoms: