Supplementary Material

The Diels-Alder reaction of 1,4-quinones in hexafluoroisopropanol

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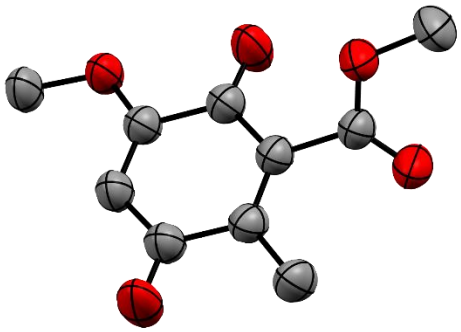


Figure S1. X-ray structure of quinone **1j**.
CCDC 2088944

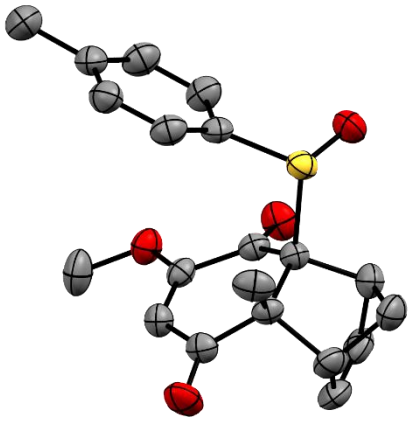


Figure S2. X-ray structure of cycloadduct **α-3a**.
CCDC 1865848

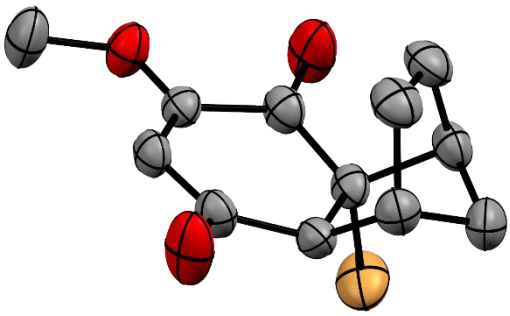


Figure S4. X-ray structure of cycloadduct **3f**.
CCDC 1865849

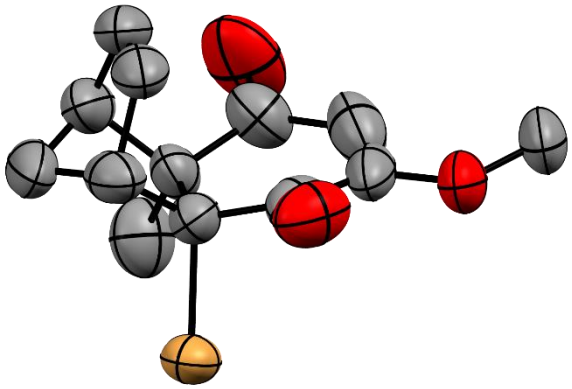


Figure S3. X-ray structure of cycloadduct **3g**.
CCDC 1865850

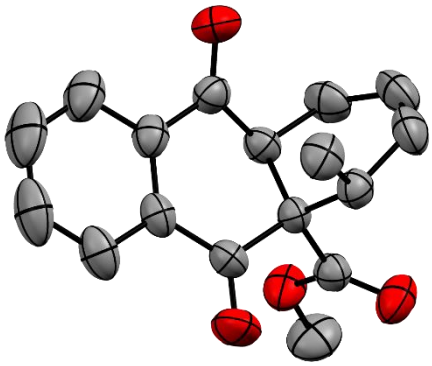


Figure S5. X-ray structure of cycloadduct **5i**.
CCDC 1865851

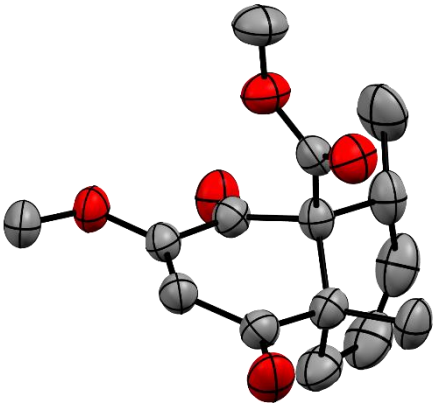


Figure S6. X-ray structure of cycloadduct **5j**.
CCDC 2088945

Table S1. Crystal data and structure refinement for **1j**

Chemical formula	$C_{10}H_{10}O_5$
M_r	210.18
Crystal system, space group	Monoclinic, $P2_1/n$
Temperature (K)	295
a, *b*, *c* (Å)	3.9749 (3), 14.4461 (8), 17.1695 (8)
β (°)	91.309 (5)
V (Å^3)	985.64 (10)
Z	4
F(000)	440
D_x (Mg m^{-3})	1.416
Radiation type	Cu *K*α
No. of reflections for cell measurement	1756
θ range (°) for cell measurement	4.0-66.6
μ (mm^{-1})	0.98
Crystal size (mm)	0.58 × 0.10 × 0.04
Data collection	
Diffractometer	Oxford Diffraction Xcalibur, Ruby, Gemini Ultra
Absorption correction	Analytical *CrysAlis PRO* 1.171.40.53 (Rigaku Oxford Diffraction, 2019) Analytical numeric absorption correction using a multifaceted crystal model based on expressions derived by R.C. Clark & J.S. Reid. (Clark, R. C. & Reid, J. S. (1995). Acta Cryst. A51, 887-897) Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm.
T_{min}, T_{max}	0.835, 0.975
No. of measured, independent and observed [$I > 2s(I)$] reflections	5108, 1747, 1389
R_{int}	0.044
θ values (°)	θ_{max} = 67.1, θ_{min} = 4.0
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.597
Range of *h*, *k*, *l*	*h* = -4→4, *k* = -17→16, *l* = -18→20

Refinement	
Refinement on	F^2
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.059, 0.173, 1.06
No. of reflections	1747
No. of parameters	139
No. of restraints	0
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.24, -0.25

Table S2. Atomic coordinates for **1j**

Label	x	y	z
O1	0.5454	0.3878	0.8131
O2	0.8604	0.2634	0.8383
O3	0.3265	0.1191	0.5774
O4	0.7713	0.4135	0.5244
O5	0.9013	0.4285	0.6738
C1	0.5808	0.4161	0.8936
H1A	0.4700	0.4744	0.9006
H1B	0.8153	0.4223	0.9073
H1C	0.4808	0.3703	0.9263
C2	0.6995	0.3106	0.7939
C3	0.6435	0.2885	0.7088
C4	0.5170	0.2063	0.6849
C5	0.4260	0.1280	0.7369
H5A	0.5687	0.0760	0.7267
H5B	0.1954	0.1110	0.7271
H5C	0.4552	0.1467	0.7903
C6	0.4524	0.1916	0.5994
C7	0.5344	0.2634	0.5439
H7	0.4895	0.2542	0.4911
C8	0.6748	0.3434	0.5683
C9	0.7266	0.4038	0.4414
H9A	0.8178	0.4570	0.4159
H9B	0.4910	0.3986	0.4285
H9C	0.8412	0.3491	0.4244
C10	0.7465	0.3602	0.6530

Table S3. Crystal data and structure refinement for **α-3a**

Chemical formula	$C_{20}H_{20}O_4S$
M_r	356.42
Crystal system, space group	Orthorhombic, $P2_12_12_1$
Temperature (K)	295
a, *b*, *c* (Å)	7.9696(4), 10.2226(4), 21.4477(8)
V (Å^3)	1747.34(13)
Z	4
F(000)	752
D_x (Mg m^{-3})	1.355
Radiation type	Mo *K*α
No. of reflections for cell measurement	2740
θ range (°) for cell measurement	2.8–27.1
μ (mm^{-1})	0.21
Crystal size (mm)	0.59 × 0.35 × 0.13
Data collection	
Diffractometer	Oxford Diffraction Xcalibur, Ruby, Gemini ultra
Absorption correction	Analytical *CrysAlis PRO* 1.171.38.46 (Rigaku Oxford Diffraction, 2015) Analytical numeric absorption correction using a multifaceted crystal model based on expressions derived by R.C. Clark & J.S. Reid. (Clark, R. C. & Reid, J. S. (1995). Acta Cryst. A51, 887-897) Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm.
T_{min}, T_{max}	0.921, 0.976
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	9652, 5330, 3841
R_{int}	0.026
θ values (°)	θ_{max} = 30.5, θ_{min} = 2.2
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.714
Range of *h*, *k*, *l*	*h* = -11→11, *k* = -14→11, *l* = -30→18
Refinement	

Refinement on	F^2
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.049, 0.108, 1.02
No. of reflections	5330
No. of parameters	229
No. of restraints	0
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.35, -0.24
Absolute structure	Flack x determined using 1164 quotients [(I+)-(I-)]/[(I+)+(I-)] (Parsons, Flack and Wagner, Acta Cryst. B69 (2013) 249-259).
Absolute structure parameter	-0.01 (4)

Table S4. Atomic coordinates for **α-3a**

Label	x	y	z
S1	0.57744(8)	0.50319(8)	0.71009(3)
O1	0.8948(2)	0.5527(2)	0.53262(10)
O2	0.8499(2)	0.3733(2)	0.61831(10)
O3	0.3163(2)	0.5181(3)	0.49338(9)
O4	0.6953(3)	0.4249(2)	0.74862(9)
C1	0.9226(4)	0.6280(3)	0.47698(16)
H1A	0.876733	0.582272	0.441791
H1B	1.040.849	0.640523	0.470995
H1C	0.868604	0.711559	0.480986
C2	0.7358(3)	0.5208(3)	0.54596(12)
C3	0.5989(3)	0.5513(3)	0.51326(13)
H3	0.610685	0.603619	0.478065
C4	0.4315(3)	0.5062(3)	0.53030(12)
C5	0.3962(3)	0.4521(3)	0.59491(12)
C6	0.3057(4)	0.3155(3)	0.58994(14)
H6	0.187510	0.318654	0.577365
C7	0.4163(5)	0.2285(3)	0.55099(15)
H7	0.395097	0.201435	0.510350
C8	0.5500(5)	0.1972(3)	0.58524(15)
H8	0.638913	0.144139	0.573000
C9	0.5302(4)	0.2643(3)	0.64787(14)
H9	0.595889	0.228199	0.682434
C10	0.5589(3)	0.4133(3)	0.63267(12)
C11	0.7260(3)	0.4309(3)	0.60091(12)
C12	0.2763(4)	0.5508(3)	0.62563(15)
H12A	0.325957	0.636387	0.624721
H12B	0.256158	0.525564	0.668077
H12C	0.172004	0.552233	0.603246
C13	0.3389(4)	0.2598(3)	0.65506(15)
H13A	0.296145	0.171598	0.660263

H13B	0.298055	0.315937	0.688192
C14	0.9538(5)	1.0119(4)	0.66065(16)
H14A	0.961424	1.030.637	0.616876
H14B	1.064.601	1.005.121	0.677907
H14C	0.893963	1.081.102	0.681184
C15	0.8618(4)	0.8846(3)	0.67002(13)
C16	0.9466(4)	0.7697(3)	0.68219(15)
H16	1.063.110	0.771238	0.684460
C17	0.8634(4)	0.6519(3)	0.69114(14)
H17	0.923349	0.575574	0.698849
C18	0.6894(3)	0.6499(3)	0.68840(12)
C19	0.6016(4)	0.7643(3)	0.67826(14)
H19	0.484884	0.763526	0.678266
C20	0.6868(4)	0.8801(3)	0.66810(14)
H20	0.626747	0.956100	0.659858

Table S5. Crystal data and structure refinement for **3f**

Chemical formula	$C_{12}H_{11}BrO_3$
M_r	283.12
Crystal system, space group	Triclinic, $P\bar{1}$
Temperature (K)	295
a, *b*, *c* (Å)	7.5195 (5), 9.1616 (5), 9.3920 (6)
α, β, γ (°)	104.395 (5), 97.604 (5), 111.966 (6)
V (Å^3)	562.63 (7)
Z	2
F(000)	284
D_x (Mg m^{-3})	1.671
Radiation type	Mo *K*α
No. of reflections for cell measurement	2271
θ range (°) for cell measurement	3.3–29.4
μ (mm^{-1})	3.64
Crystal size (mm)	0.47 × 0.35 × 0.13
Data collection	
Diffractometer	Oxford Diffraction Xcalibur, Ruby, Gemini ultra
Absorption correction	Analytical *CrysAlis PRO* 1.171.38.46 (Rigaku Oxford Diffraction, 2015) Analytical numeric absorption correction using a multifaceted crystal model based on expressions derived by R.C. Clark & J.S. Reid. (Clark, R. C. & Reid, J. S. (1995). Acta Cryst. A51, 887-897) Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm.
T_{min}, T_{max}	0.330, 0.697
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	5591, 3020, 2214
R_{int}	0.021
θ values (°)	θ_{max} = 29.1, θ_{min} = 2.3
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.685
Range of *h*, *k*, *l*	*h* = -9→10, *k* = -10→12, *l* = -12→12

Refinement	
Refinement on	F^2
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.036, 0.085, 1.01
No. of reflections	3020
No. of parameters	146
No. of restraints	0
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.31, -0.43

Table S6. Atomic coordinates for **3f**

Label	x	y	z
Br1	0.38572(5)	0.39080(3)	0.14318(3)
O1	0.2471(3)	0.8535(3)	0.0501(3)
O2	0.6985(3)	0.7107(3)	0.4260(2)
O3	0.8740(2)	0.9219(2)	0.2941(2)
C1	0.5618(4)	0.8893(3)	0.1611(2)
H1	0.621627	0.975513	0.123558
C2	0.3483(4)	0.8046(3)	0.1203(3)
C3	0.2462(3)	0.6491(3)	0.1600(2)
H3	0.176566	0.556330	0.064852
C4	0.0913(4)	0.6596(3)	0.2519(3)
H4	-0.026023	0.664205	0.197398
C5	0.0535(4)	0.5049(3)	0.3005(3)
H5A	-0.037873	0.490160	0.365225
H5B	0.010492	0.403927	0.215305
C6	0.2692(4)	0.5689(3)	0.3879(3)
H6	0.299152	0.499746	0.443105
C7	0.3780(3)	0.5989(3)	0.2604(2)
C8	0.5940(4)	0.7183(3)	0.3216(3)
C9	0.6772(3)	0.8496(3)	0.2503(2)
C10	0.2027(4)	0.7954(3)	0.4010(3)
H10	0.198210	0.898398	0.431045
C11	0.3082(4)	0.7431(3)	0.4821(3)
H11	0.391120	0.802319	0.579214
C12	0.9773(4)	1.0547(3)	0.2379(3)
H12A	0.942837	1.014.211	0.128880
H12B	1.117.626	1.093.590	0.275343
H12C	0.940315	1.144.500	0.271984

Table S7. Crystal data and structure refinement for **3g**

Chemical formula	$C_{13}H_{13}BrO_3$
M_r	297.14
Crystal system, space group	Monoclinic, $P2_1/c$
Temperature (K)	295
a, *b*, *c* (Å)	13.5152 (7), 6.4284 (2), 14.2521 (7)
β (°)	103.413 (5)
V (Å^3)	1204.47 (10)
Z	4
F(000)	600
D_x (Mg m^{-3})	1.639
Radiation type	Cu $K\alpha$
No. of reflections for cell measurement	4617
θ range (°) for cell measurement	3.4–67.1
μ (mm^{-1})	4.61
Crystal size (mm)	0.18 × 0.07 × 0.02
Data collection	
Diffractometer	Oxford Diffraction Xcalibur, Ruby, Gemini ultra
Absorption correction	Analytical *CrysAlis PRO* 1.171.40.16b (Rigaku Oxford Diffraction, 2018) Analytical numeric absorption correction using a multifaceted crystal model based on expressions derived by R.C. Clark & J.S. Reid. (Clark, R. C. & Reid, J. S. (1995). Acta Cryst. A51, 887-897) Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm.
T_{min}, T_{max}	0.565, 0.883
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	12143, 2128, 1877
R_{int}	0.047
θ values (°)	θ_{max} = 66.9, θ_{min} = 3.4
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.597
Range of *h*, *k*, *l*	*h* = -16→16, *k* = -7→6, *l* = -16→17

Refinement	
Refinement on	F^2
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.078, 0.189, 1.08
No. of reflections	2128
No. of parameters	193
No. of restraints	47
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.51, -0.46

Table S8. Atomic coordinates for **3g**

Label	x	y	z
Br1A	0.18304(10)	0.03632(18)	0.32092(8)
C13A	0.3217(16)	0.068(3)	0.1804(16)
H13A	0.272640	-0.041838	0.172858
H13B	0.372281	0.048777	0.239284
H13C	0.353751	0.067388	0.126873
O1A	0.3293(5)	0.6409(10)	0.4389(4)
C1A	0.4217(11)	0.762(3)	0.4704(9)
H1A	0.479747	0.674654	0.472172
H1B	0.424770	0.816692	0.533718
H1C	0.421776	0.874676	0.426254
O2	0.4089(6)	0.4668(14)	0.1546(7)
O3	0.1361(5)	0.5099(10)	0.3582(4)
C2	0.3057(7)	0.5399(12)	0.3548(5)
C3	0.3730(7)	0.5420(15)	0.3039(7)
H3	0.433591	0.613732	0.326476
C4	0.3557(7)	0.4331(14)	0.2111(7)
C5	0.2690(5)	0.2750(10)	0.1837(5)
C6	0.2039(7)	0.3125(12)	0.0802(5)
H6	0.236136	0.274326	0.027714
C7	0.1651(8)	0.5288(12)	0.0774(5)
H7	0.185669	0.639865	0.044700
C8	0.0967(6)	0.5356(12)	0.1295(6)
H8	0.060534	0.652558	0.140566
C9	0.0872(6)	0.3191(12)	0.1682(6)
H9	0.024178	0.287622	0.188190
C10	0.1080(7)	0.1927(14)	0.0836(6)
H10A	0.120758	0.046779	0.099016
H10B	0.054885	0.207620	0.025112
C11	0.1871(5)	0.2873(10)	0.2442(4)
C12	0.2058(6)	0.4530(12)	0.3238(5)
Br1A	0.81696(10)	0.53632(18)	0.17908(8)
C13A	0.6783(16)	0.568(3)	0.3196(16)

H13A	0.727360	0.458162	0.327142
H13B	0.627719	0.548777	0.260716
H13C	0.646249	0.567388	0.373127
O1A	0.6707(5)	1.1409(10)	0.0611(4)
C1A	0.5783(11)	1.262(3)	0.0296(9)
H1A	0.520253	1.174.654	0.027828
H1B	0.575230	1.316.692	-0.033718
H1C	0.578224	1.374.676	0.073746
O2	0.5911(6)	0.9668(14)	0.3454(7)
O3	0.8639(5)	1.0099(10)	0.1418(4)
C2	0.6943(7)	1.0399(12)	0.1452(5)
C3	0.6270(7)	1.0420(15)	0.1961(7)
H3	0.566409	1.113.732	0.173524
C4	0.6443(7)	0.9331(14)	0.2889(7)
C5	0.7310(5)	0.7750(10)	0.3163(5)
C6	0.7961(7)	0.8125(12)	0.4198(5)
H6	0.763864	0.774326	0.472286
C7	0.8349(8)	1.0288(12)	0.4226(5)
H7	0.814331	1.139.865	0.455300
C8	0.9033(6)	1.0356(12)	0.3705(6)
H8	0.939466	1.152.558	0.359434
C9	0.9128(6)	0.8191(12)	0.3318(6)
H9	0.975822	0.787622	0.311810
C10	0.8920(7)	0.6927(14)	0.4164(6)
H10A	0.879242	0.546779	0.400984
H10B	0.945115	0.707620	0.474888
C11	0.8129(5)	0.7873(10)	0.2558(4)
C12	0.7942(6)	0.9530(12)	0.1762(5)
Br1A	0.81696(10)	0.96368(18)	0.67908(8)
C13A	0.6783(16)	0.932(3)	0.8196(16)
H13A	0.727360	1.041.838	0.827142
H13B	0.627719	0.951223	0.760716
H13C	0.646249	0.932612	0.873127
O1A	0.6707(5)	0.3591(10)	0.5611(4)
C1A	0.5783(11)	0.238(3)	0.5296(9)
H1A	0.520253	0.325346	0.527828
H1B	0.575230	0.183308	0.466282
H1C	0.578224	0.125324	0.573746
O2	0.5911(6)	0.5332(14)	0.8454(7)
O3	0.8639(5)	0.4901(10)	0.6418(4)
C2	0.6943(7)	0.4601(12)	0.6452(5)
C3	0.6270(7)	0.4580(15)	0.6961(7)
H3	0.566409	0.386268	0.673524
C4	0.6443(7)	0.5669(14)	0.7889(7)
C5	0.7310(5)	0.7250(10)	0.8163(5)
C6	0.7961(7)	0.6875(12)	0.9198(5)
H6	0.763864	0.725674	0.972286
C7	0.8349(8)	0.4712(12)	0.9226(5)
H7	0.814331	0.360135	0.955300

C8	0.9033(6)	0.4644(12)	0.8705(6)
H8	0.939466	0.347442	0.859434
C9	0.9128(6)	0.6809(12)	0.8318(6)
H9	0.975822	0.712378	0.811810
C10	0.8920(7)	0.8073(14)	0.9164(6)
H10A	0.879242	0.953221	0.900984
H10B	0.945115	0.792380	0.974888
C11	0.8129(5)	0.7127(10)	0.7558(4)
C12	0.7942(6)	0.5470(12)	0.6762(5)
Br1A	0.18304(10)	0.46368(18)	0.82092(8)
C13A	0.3217(16)	0.432(3)	0.6804(16)
H13A	0.272640	0.541838	0.672858
H13B	0.372281	0.451223	0.739284
H13C	0.353751	0.432612	0.626873
O1A	0.3293(5)	-0.1409(10)	0.9389(4)
C1A	0.4217(11)	-0.262(3)	0.9704(9)
H1A	0.479747	-0.174654	0.972172
H1B	0.424770	-0.316692	1.033.718
H1C	0.421776	-0.374676	0.926254
O2	0.4089(6)	0.0332(14)	0.6546(7)
O3	0.1361(5)	-0.0099(10)	0.8582(4)
C2	0.3057(7)	-0.0399(12)	0.8548(5)
C3	0.3730(7)	-0.0420(15)	0.8039(7)
H3	0.433591	-0.113732	0.826476
C4	0.3557(7)	0.0669(14)	0.7111(7)
C5	0.2690(5)	0.2250(10)	0.6837(5)
C6	0.2039(7)	0.1875(12)	0.5802(5)
H6	0.236136	0.225674	0.527714
C7	0.1651(8)	-0.0288(12)	0.5774(5)
H7	0.185669	-0.139865	0.544700
C8	0.0967(6)	-0.0356(12)	0.6295(6)
H8	0.060534	-0.152558	0.640566
C9	0.0872(6)	0.1809(12)	0.6682(6)
H9	0.024178	0.212378	0.688190
C10	0.1080(7)	0.3073(14)	0.5836(6)
H10A	0.120758	0.453221	0.599016
H10B	0.054885	0.292380	0.525112
C11	0.1871(5)	0.2127(10)	0.7442(4)
C12	0.2058(6)	0.0470(12)	0.8238(5)
Br1B	0.3503(5)	0.0188(11)	0.2112(6)
C13B	0.162(3)	0.078(5)	0.287(4)
H13D	0.150000	-0.026690	0.238218
H13E	0.217929	0.037420	0.338816
H13F	0.102014	0.094605	0.312200
H2	0.323131	0.599077	0.415940
O1B	0.4544(12)	0.629(4)	0.3645(15)
C1B	0.445(3)	0.756(10)	0.446(3)
H1D	0.511560	0.802189	0.479759
H1E	0.403170	0.874216	0.423556

H1F	0.415169	0.675352	0.488893
Br1B	0.6497(5)	0.5188(11)	0.2888(6)
C13B	0.838(3)	0.578(5)	0.213(4)
H13D	0.850000	0.473310	0.261782
H13E	0.782071	0.537420	0.161184
H13F	0.897986	0.594605	0.187800
H2	0.676869	1.099.077	0.084060
O1B	0.5456(12)	1.129(4)	0.1355(15)
C1B	0.555(3)	1.256(10)	0.054(3)
H1D	0.488440	1.302.189	0.020241
H1E	0.596830	1.374.216	0.076444
H1F	0.584831	1.175.352	0.011107
Br1B	0.6497(5)	0.9812(11)	0.7888(6)
C13B	0.838(3)	0.922(5)	0.713(4)
H13D	0.850000	1.026.690	0.761782
H13E	0.782071	0.962580	0.661184
H13F	0.897986	0.905395	0.687800
H2	0.676869	0.400923	0.584060
O1B	0.5456(12)	0.371(4)	0.6355(15)
C1B	0.555(3)	0.244(10)	0.554(3)
H1D	0.488440	0.197811	0.520241
H1E	0.596830	0.125784	0.576444
H1F	0.584831	0.324648	0.511107
Br1B	0.3503(5)	0.4812(11)	0.7112(6)
C13B	0.162(3)	0.422(5)	0.787(4)
H13D	0.150000	0.526690	0.738218
H13E	0.217929	0.462580	0.838816
H13F	0.102014	0.405395	0.812200
H2	0.323131	-0.099077	0.915940
O1B	0.4544(12)	-0.129(4)	0.8645(15)
C1B	0.445(3)	-0.256(10)	0.946(3)
H1D	0.511560	-0.302189	0.979759
H1E	0.403170	-0.374216	0.923556
H1F	0.415169	-0.175352	0.988893

Table S9. Crystal data and structure refinement for **5i**

Chemical formula	$C_{15}H_{18}O_5$
M_r	278.29
Crystal system, space group	Monoclinic, $P2_1/c$
Temperature (K)	295
a, *b*, *c* (Å)	10.6822 (6), 11.3107 (4), 12.8714 (6)
β (°)	114.202 (6)
V (Å^3)	1418.48 (13)
Z	4
F(000)	592
D_x (Mg m^{-3})	1.303
Radiation type	Mo *K*α
No. of reflections for cell measurement	5034
θ range (°) for cell measurement	2.1-32.4
μ (mm^{-1})	0.10
Crystal size (mm)	0.81 × 0.28 × 0.20
Data collection	
Diffractometer	Oxford Diffraction Xcalibur, Ruby, Gemini Ultra
Absorption correction	Gaussian *CrysAlis PRO* 1.171.40.53 (Rigaku Oxford Diffraction, 2019) Numerical absorption correction based on gaussian integration over a multifaceted crystal model Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm.
T_{min}, T_{max}	0.393, 1.000
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	12540, 4808, 3497
R_{int}	0.018
θ values (°)	θ_{max} = 32.7, θ_{min} = 2.1
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.761
Range of *h*, *k*, *l*	*h* = -15→15, *k* = -12→17, *l* = -19→18
Refinement	

Refinement on	F^2
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.047, 0.140, 1.04
No. of reflections	4808
No. of parameters	185
No. of restraints	0
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.17, -0.22

Table S10. Atomic coordinates for **5i**

Label	x	y	z
O1	0.5830	0.6937	0.5553
O2	0.1722	0.5039	0.5147
O3	0.3815	0.5879	0.2510
O4	0.1861	0.5154	0.2471
O5	0.0487	0.6820	0.3720
C1	0.0273	0.7447	0.1370
H1A	0.0463	0.6742	0.1045
H1B	-0.0131	0.8028	0.0784
H1C	-0.0353	0.7265	0.1710
C2	0.1608	0.7932	0.2279
H2	0.2191	0.8128	0.1882
C3	0.1392	0.9068	0.2785
H3	0.0701	0.9570	0.2320
C4	0.2116	0.9400	0.3843
H4	0.1914	1.0127	0.4074
C5	0.3242	0.8681	0.4696
H5A	0.2915	0.8321	0.5222
H5B	0.4005	0.9196	0.5130
C6	0.3748	0.7701	0.4121
C7	0.4655	0.8271	0.3593
H7A	0.5522	0.8487	0.4187
H7B	0.4209	0.8965	0.3175
H7C	0.4800	0.7718	0.3087
C8	0.4592	0.6837	0.5058
C9	0.3873	0.5911	0.5388
H9	0.4379	0.5386	0.5964
C10	0.2502	0.5796	0.4882
C11	0.2415	0.4176	0.6009
H11A	0.2955	0.3671	0.5756
H11B	0.1750	0.3711	0.6152
H11C	0.3003	0.4570	0.6698
C12	0.2823	0.5980	0.2711
C13	0.2025	0.4091	0.1913
H13A	0.2103	0.4298	0.1218
H13B	0.1242	0.3587	0.1743
H13C	0.2840	0.3681	0.2406
C14	0.2450	0.7059	0.3240
C15	0.1659	0.6591	0.3911

Table S11. Crystal data and structure refinement for **5j**

Chemical formula	$C_{17}H_{16}O_4$
M_r	284.30
Crystal system, space group	Monoclinic, $P2_1/c$
Temperature (K)	295
a, *b*, *c* (Å)	7.5455 (3), 14.8987 (5), 12.7722 (4)
β (°)	90.430 (3)
V (Å^3)	1435.79 (8)
Z	4
F(000)	600
D_x (Mg m^{-3})	1.315
Radiation type	Mo *K*α
No. of reflections for cell measurement	3865
θ range (°) for cell measurement	2.7–29.3
μ (mm^{-1})	0.09
Crystal size (mm)	0.52 × 0.44 × 0.26
Data collection	
Diffractometer	Oxford Diffraction Xcalibur, Ruby, Gemini ultra
Absorption correction	Analytical *CrysAlis PRO* 1.171.39.46 (Rigaku Oxford Diffraction, 2018) Analytical numeric absorption correction using a multifaceted crystal model based on expressions derived by R.C. Clark & J.S. Reid. (Clark, R. C. & Reid, J. S. (1995). Acta Cryst. A51, 887-897) Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm.
T_{min}, T_{max}	0.969, 0.980
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	9000, 2620, 2047
R_{int}	0.022
θ values (°)	θ_{max} = 25.4, θ_{min} = 2.1
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.602
Range of *h*, *k*, *l*	*h* = -9→9, *k* = -17→17, *l* = -15→15

Refinement	
Refinement on	F^2
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.041, 0.115, 1.04
No. of reflections	2620
No. of parameters	192
No. of restraints	0
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.16, -0.17

Table S12. Atomic coordinates for **5j**

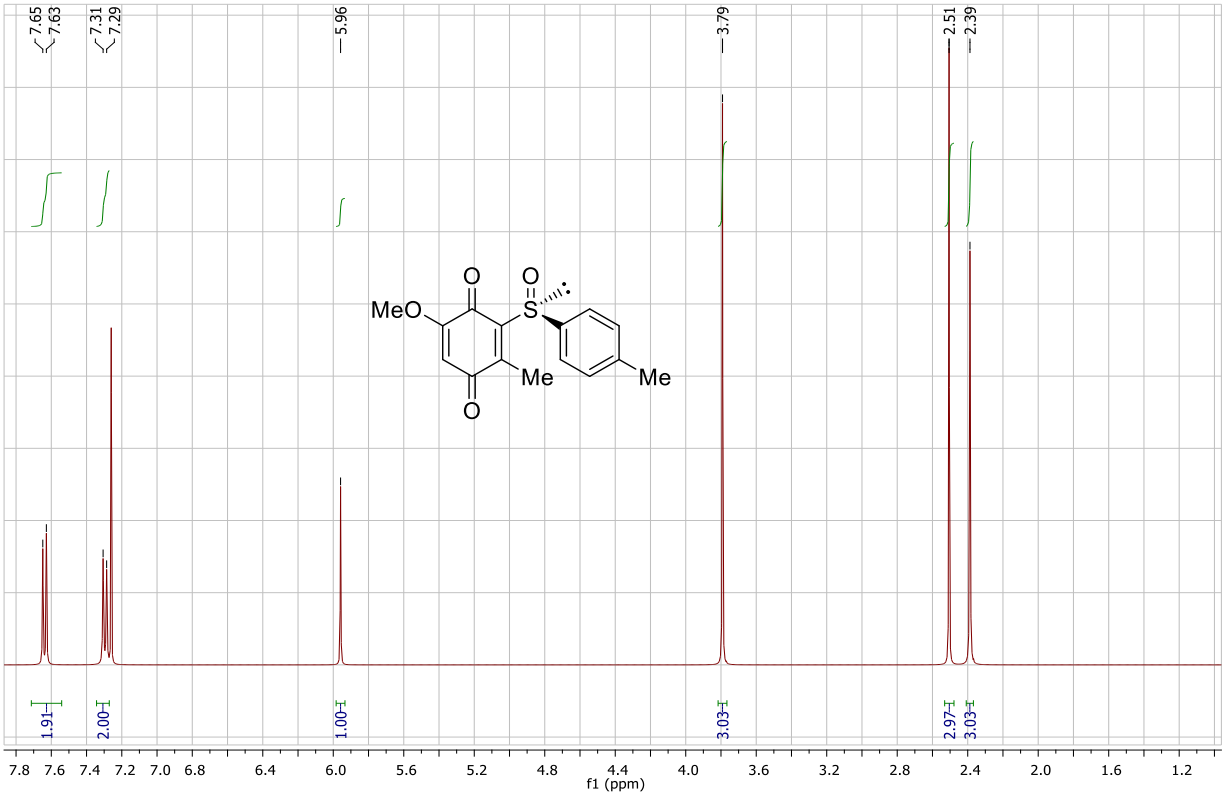
Label	x	y	z
O1	0.91421(18)	0.85282(8)	0.63908(9)
O2	0.86375(19)	0.85640(9)	0.46715(10)
O3	0.76586(19)	0.51905(8)	0.67536(10)
O4	0.50005(19)	0.84481(9)	0.61453(11)
C1	1.0335(3)	0.92800(14)	0.63068(18)
H1A	1.139.786	0.909319	0.596104
H1B	1.062.459	0.949825	0.699424
H1C	0.977537	0.974933	0.590924
C2	0.8397(2)	0.82267(11)	0.55108(12)
C3	0.7268(2)	0.73977(10)	0.57324(11)
C4	0.6656(2)	0.69791(11)	0.46743(12)
H4	0.636117	0.747871	0.420523
C5	0.5016(3)	0.63751(13)	0.47223(14)
H5A	0.524171	0.588432	0.519182
H5B	0.475487	0.614560	0.403601
H5C	0.402507	0.671668	0.496919
C6	0.8163(3)	0.64761(13)	0.41808(14)
H6	0.805786	0.633459	0.347392
C7	0.9617(3)	0.62206(13)	0.46696(16)
H7	1.045.365	0.590044	0.429036
C8	1.0008(2)	0.64105(13)	0.57864(15)
H8A	1.091.834	0.686897	0.583012
H8B	1.047.178	0.587119	0.611397
C9	0.8384(2)	0.67252(11)	0.63887(12)
H9	0.882506	0.705498	0.700130
C10	0.7241(2)	0.59779(11)	0.67957(12)
C11	0.5594(2)	0.62657(12)	0.73268(12)
C12	0.4816(3)	0.56986(15)	0.80569(15)
H12	0.529657	0.513454	0.818782
C13	0.3336(4)	0.5977(2)	0.85820(18)
H43	0.283995	0.560571	0.908710
C14	0.2576(3)	0.6794(2)	0.83725(17)

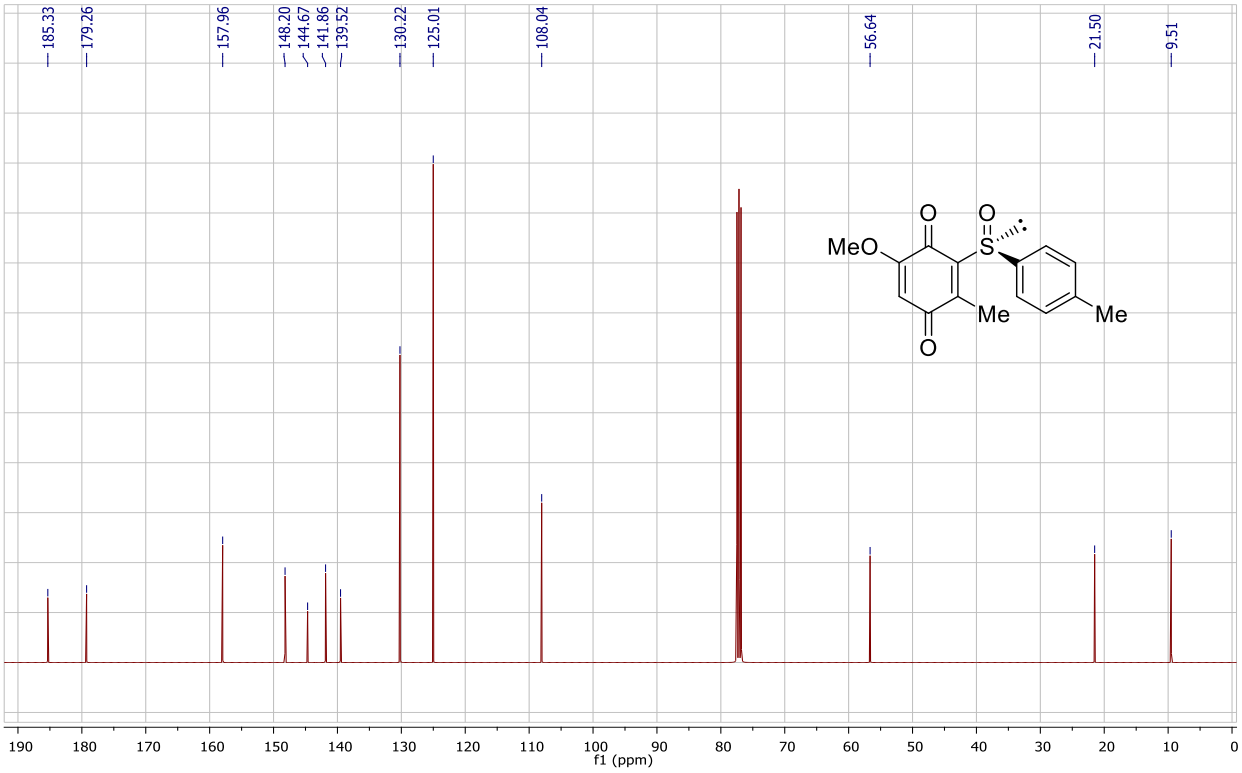
H14	0.155270	0.696515	0.872164
C15	0.3321(2)	0.73663(15)	0.76461(14)
H15	0.280243	0.792021	0.750636
C16	0.4857(2)	0.71074(12)	0.71236(11)
C17	0.5637(2)	0.77184(11)	0.63348(12)
O1	0.91421(18)	0.64718(8)	0.13908(9)
O2	0.86375(19)	0.64360(9)	-0.03285(10)
O3	0.76586(19)	0.98095(8)	0.17536(10)
O4	0.50005(19)	0.65519(9)	0.11453(11)
C1	1.0335(3)	0.57200(14)	0.13068(18)
H1A	1.139.786	0.590681	0.096104
H1B	1.062.459	0.550175	0.199424
H1C	0.977537	0.525067	0.090924
C2	0.8397(2)	0.67733(11)	0.05108(12)
C3	0.7268(2)	0.76023(10)	0.07324(11)
C4	0.6656(2)	0.80209(11)	-0.03257(12)
H4	0.636117	0.752129	-0.079477
C5	0.5016(3)	0.86249(13)	-0.02777(14)
H5A	0.524171	0.911568	0.019182
H5B	0.475487	0.885440	-0.096399
H5C	0.402507	0.828332	-0.003081
C6	0.8163(3)	0.85239(13)	-0.08192(14)
H6	0.805786	0.866541	-0.152608
C7	0.9617(3)	0.87794(13)	-0.03304(16)
H7	1.045.365	0.909956	-0.070964
C8	1.0008(2)	0.85895(13)	0.07864(15)
H8A	1.091.834	0.813103	0.083012
H8B	1.047.178	0.912881	0.111397
C9	0.8384(2)	0.82748(11)	0.13887(12)
H9	0.882506	0.794502	0.200130
C10	0.7241(2)	0.90221(11)	0.17957(12)
C11	0.5594(2)	0.87343(12)	0.23268(12)
C12	0.4816(3)	0.93014(15)	0.30569(15)
H12	0.529657	0.986546	0.318782
C13	0.3336(4)	0.9023(2)	0.35820(18)
H43	0.283995	0.939429	0.408710
C14	0.2576(3)	0.8206(2)	0.33725(17)
H14	0.155270	0.803485	0.372164
C15	0.3321(2)	0.76337(15)	0.26461(14)
H15	0.280243	0.707979	0.250636
C16	0.4857(2)	0.78926(12)	0.21236(11)
C17	0.5637(2)	0.72816(11)	0.13348(12)

^{1}H and ^{13}C NMR spectroscopic data of synthesized compounds

Synthesized quinones and sulfinylquinones

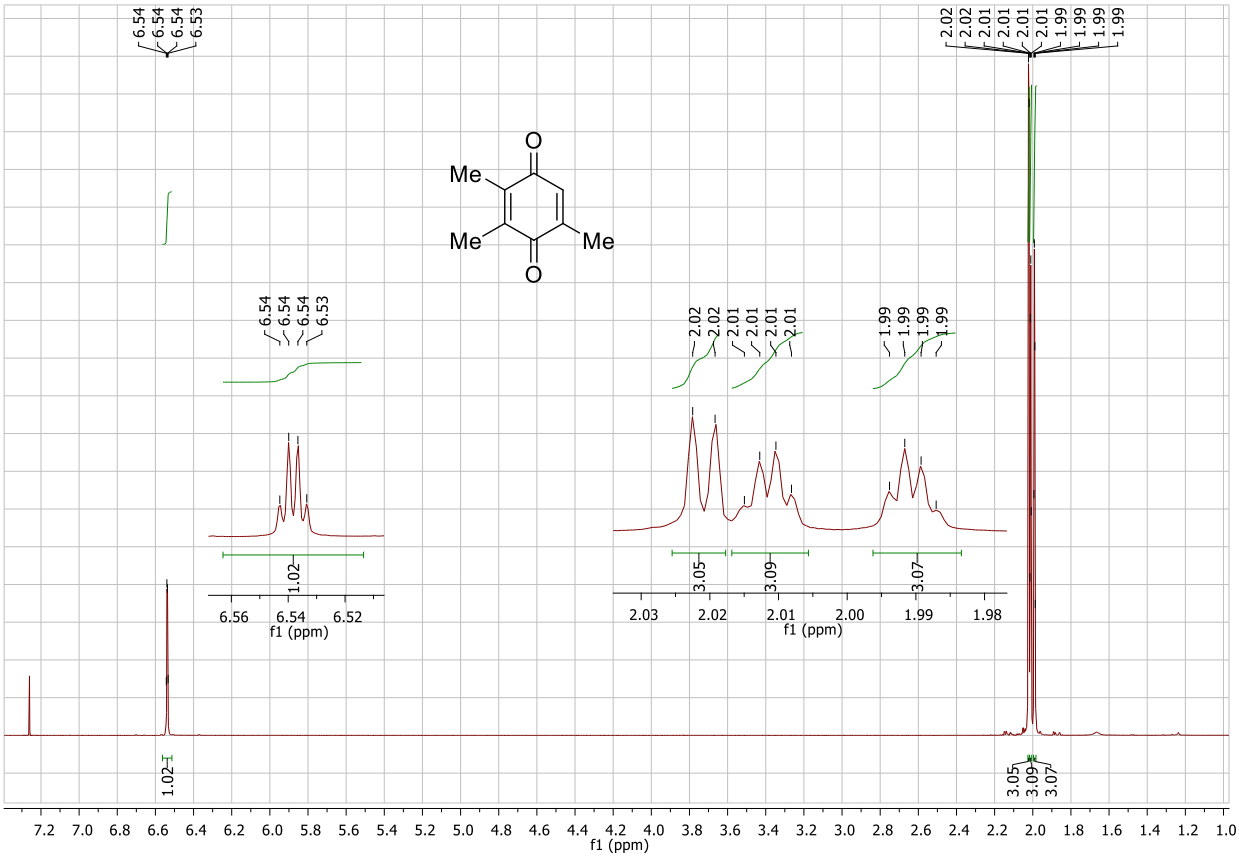
^{1}H and ^{13}C NMR spectra for (+)-(*S*)-5-methoxy-2-methyl-3-(*p*-tolylsulfinyl)cyclohexa-2,5-diene-1,4-dione (**1a**) in $CDCl_3$ (500 and 125 MHz)

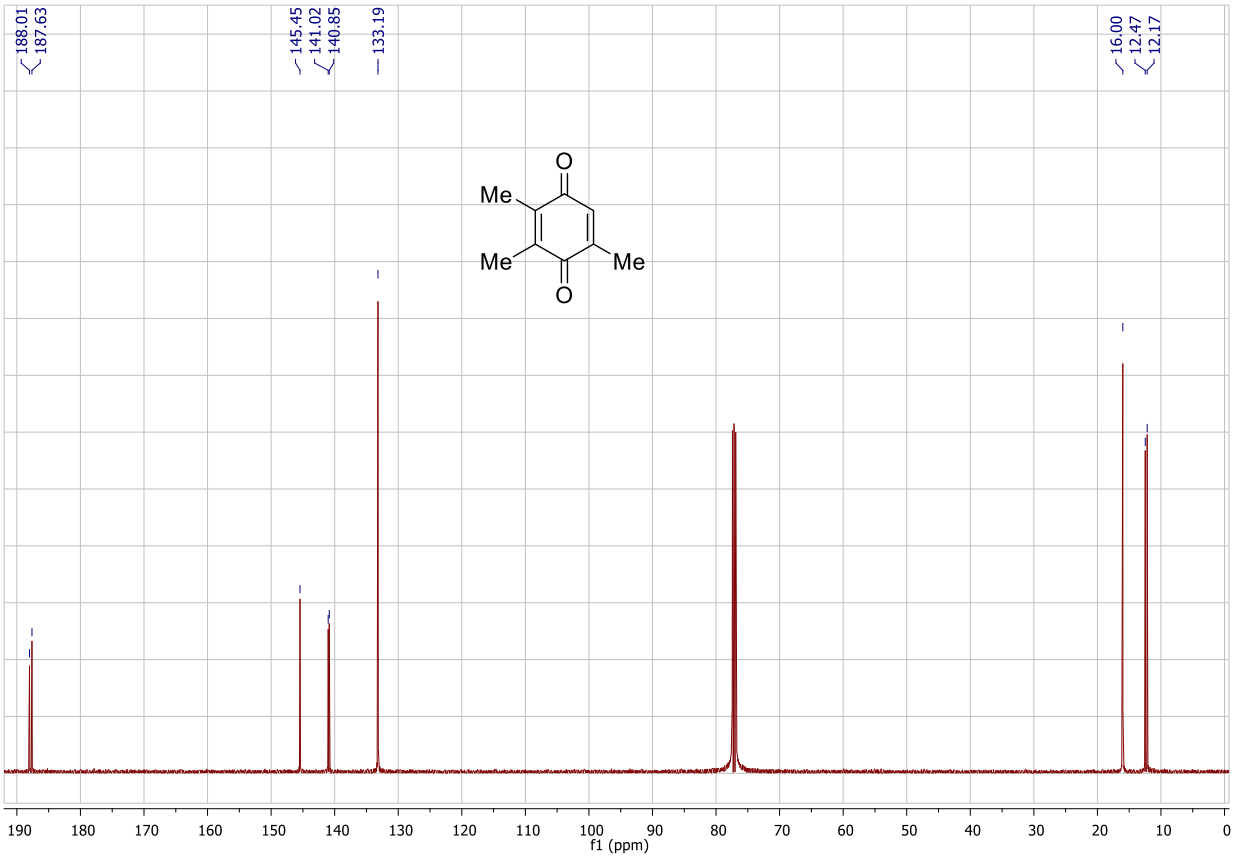




Experimental data for compound **1a** were in agreement with those found in the literature.[1,2]

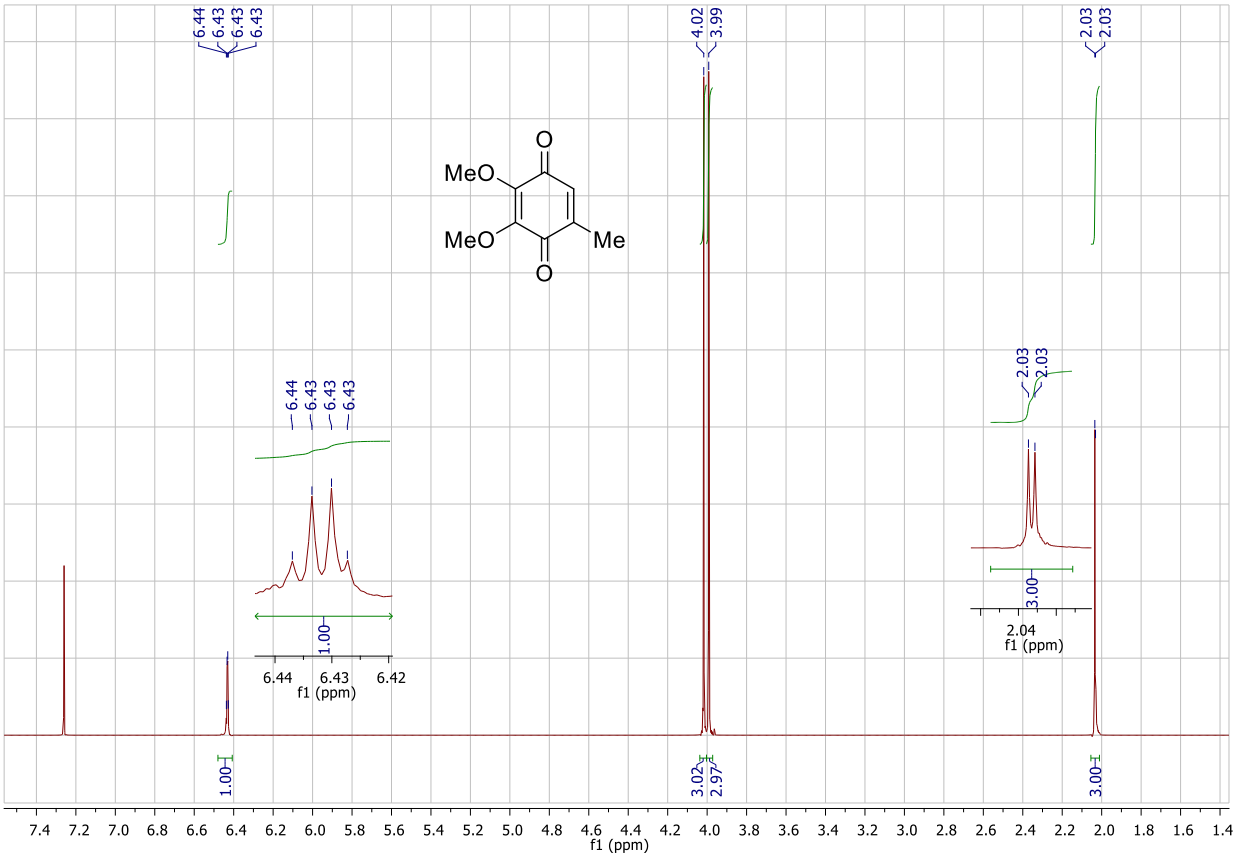
^{1}H and ^{13}C NMR spectra for 2,3,5-trimethylcyclohex-2,5-diene-1,4-dione (**1d**) in $CDCl_3$ (500 and 125 MHz)

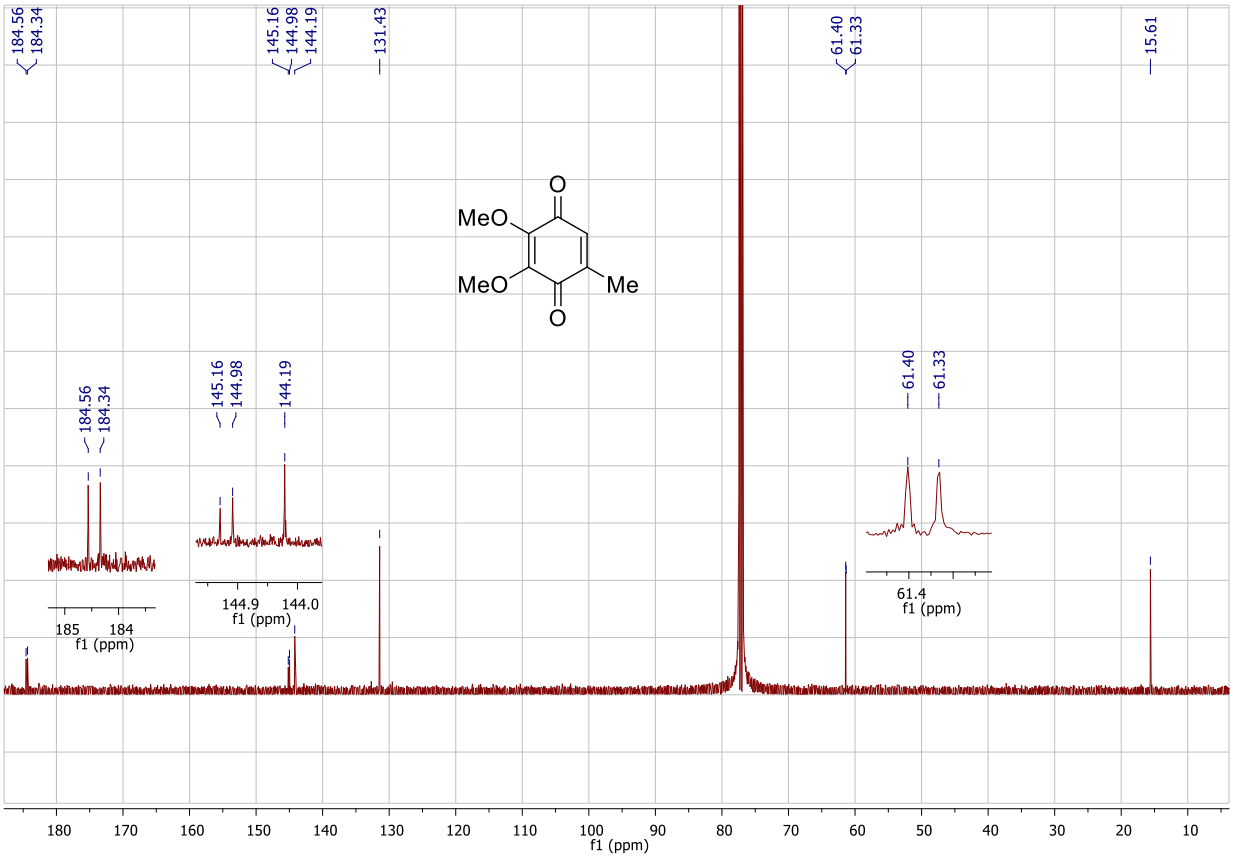




Experimental data for compound **1d** were in agreement with those found in the literature.[3]

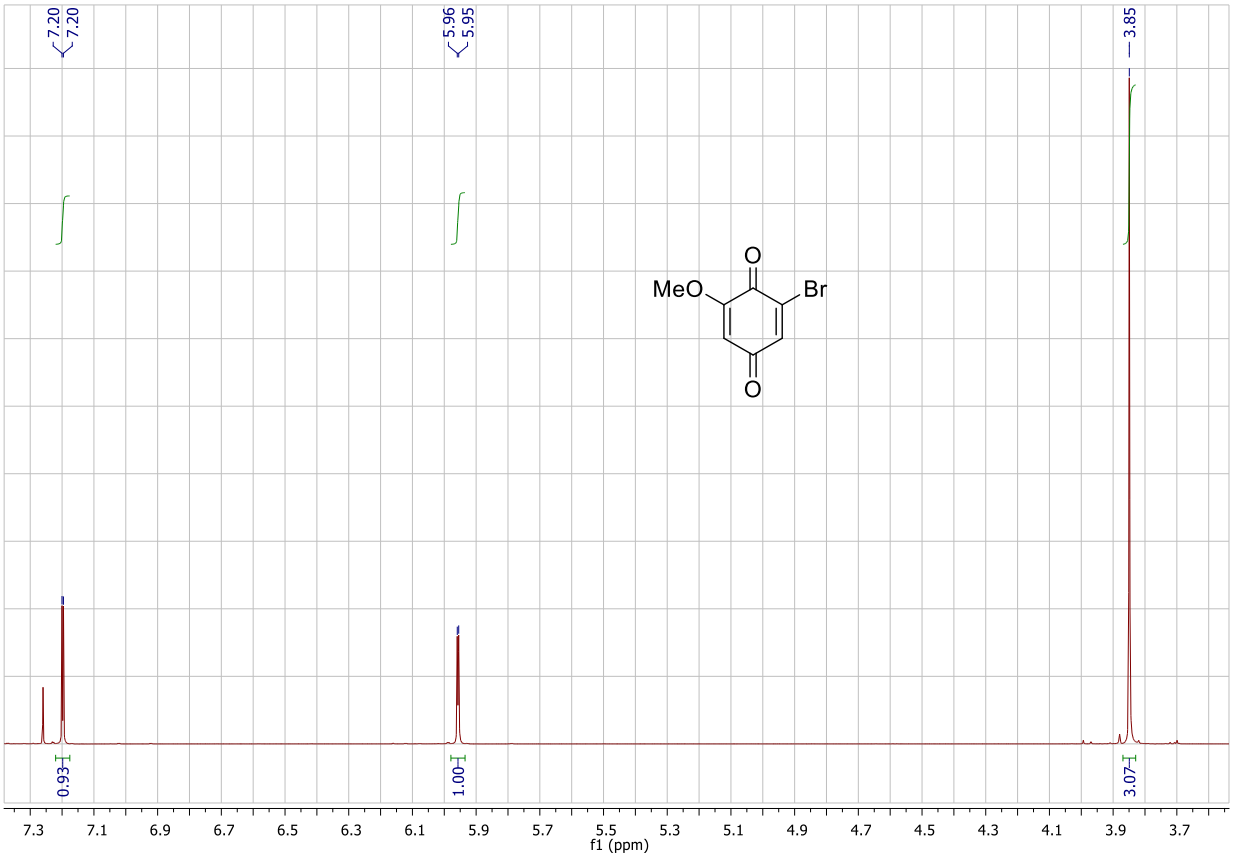
^{1}H and ^{13}C NMR spectra for 2,3-dimethoxy-5-methylcyclohexa-2,5-diene-1,4-dione (**1e**) in $CDCl_3$ (500 and 125 MHz)

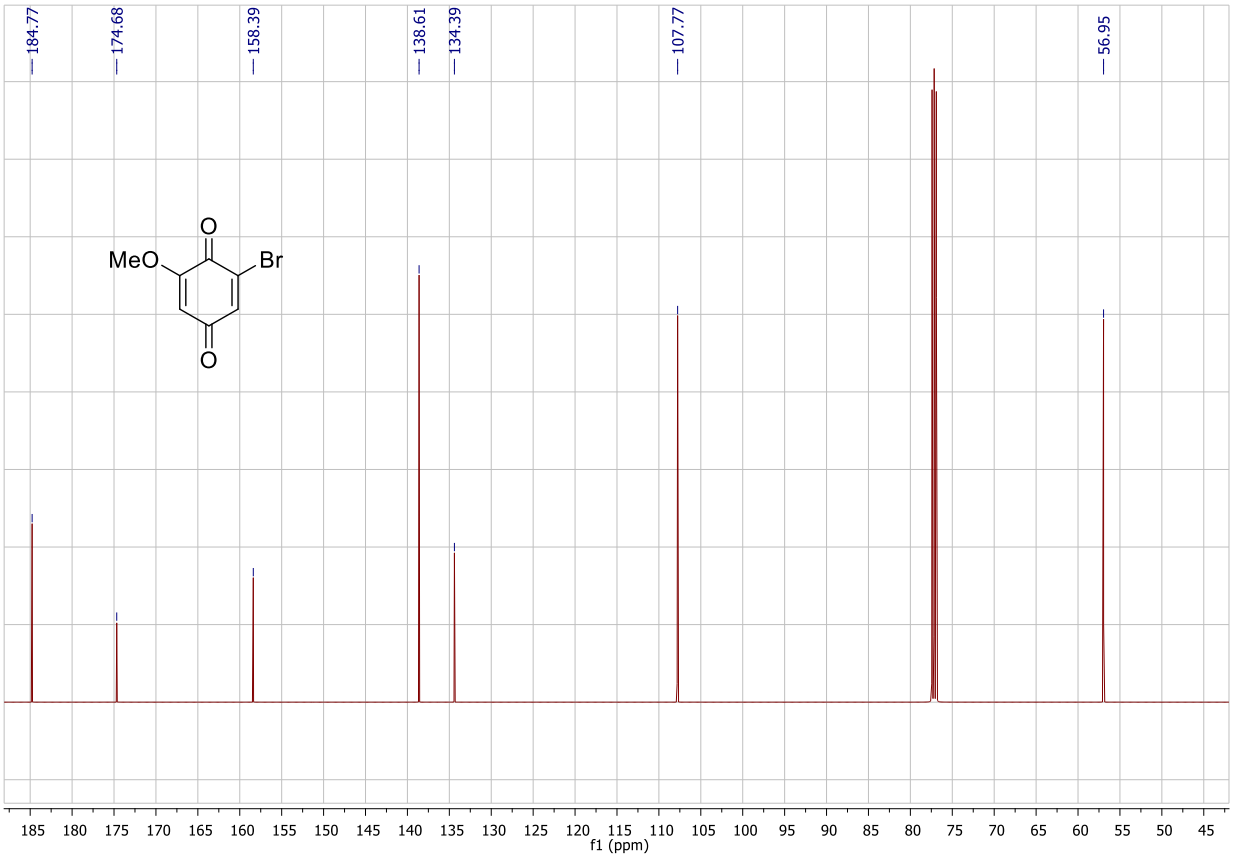




Experimental data for compound **1e** were in agreement with those found in the literature.[4]

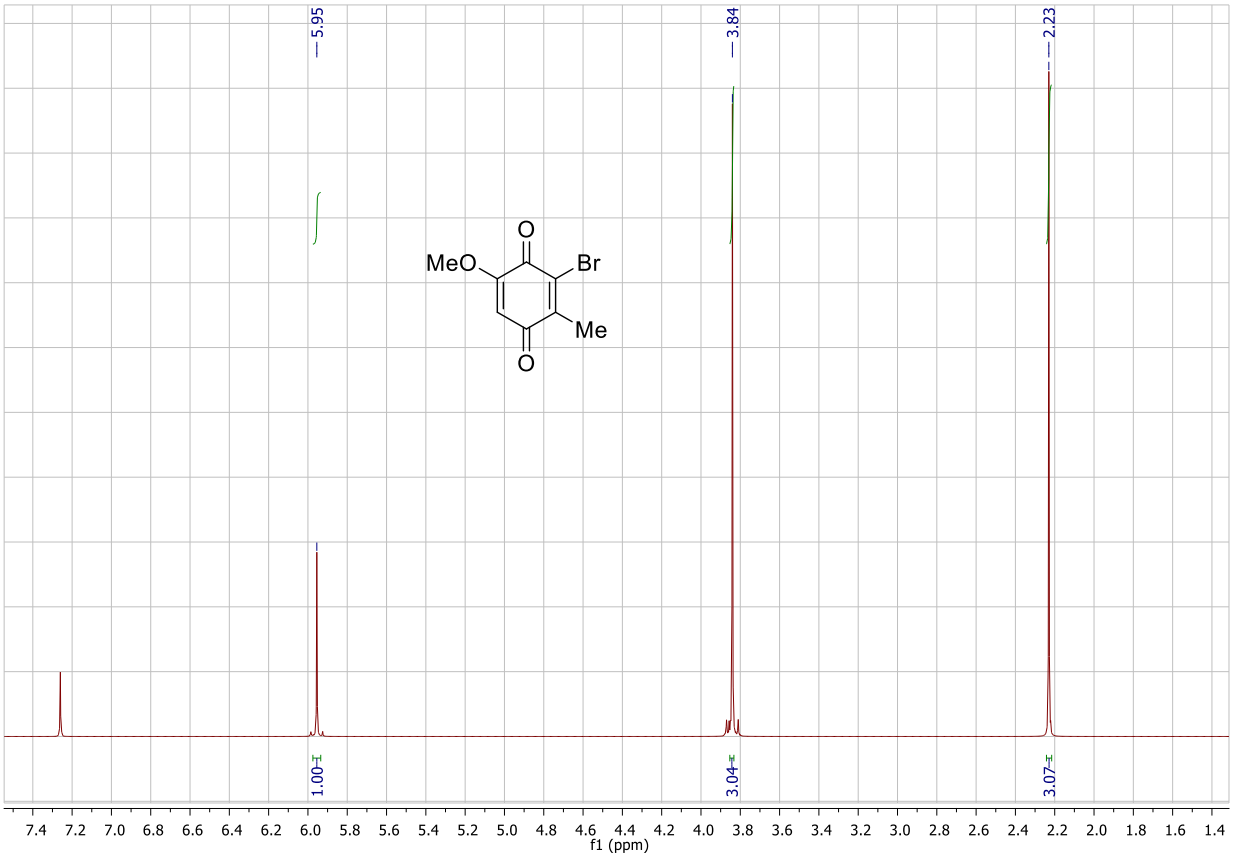
^{1}H and ^{13}C NMR spectra for 2-bromo-5-methoxycyclohexa-2,5-diene-1,4-dione (**1f**) in $CDCl_3$ (500 and 125 MHz)

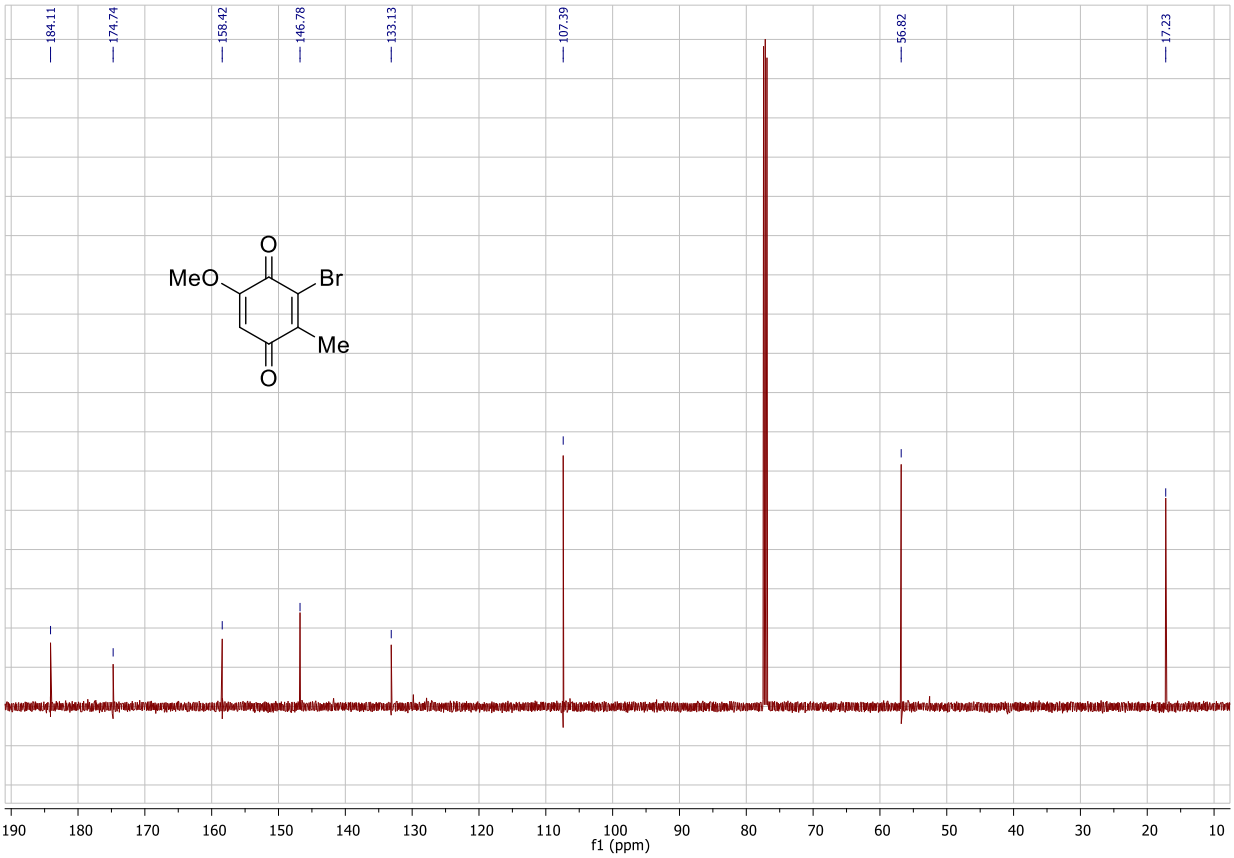




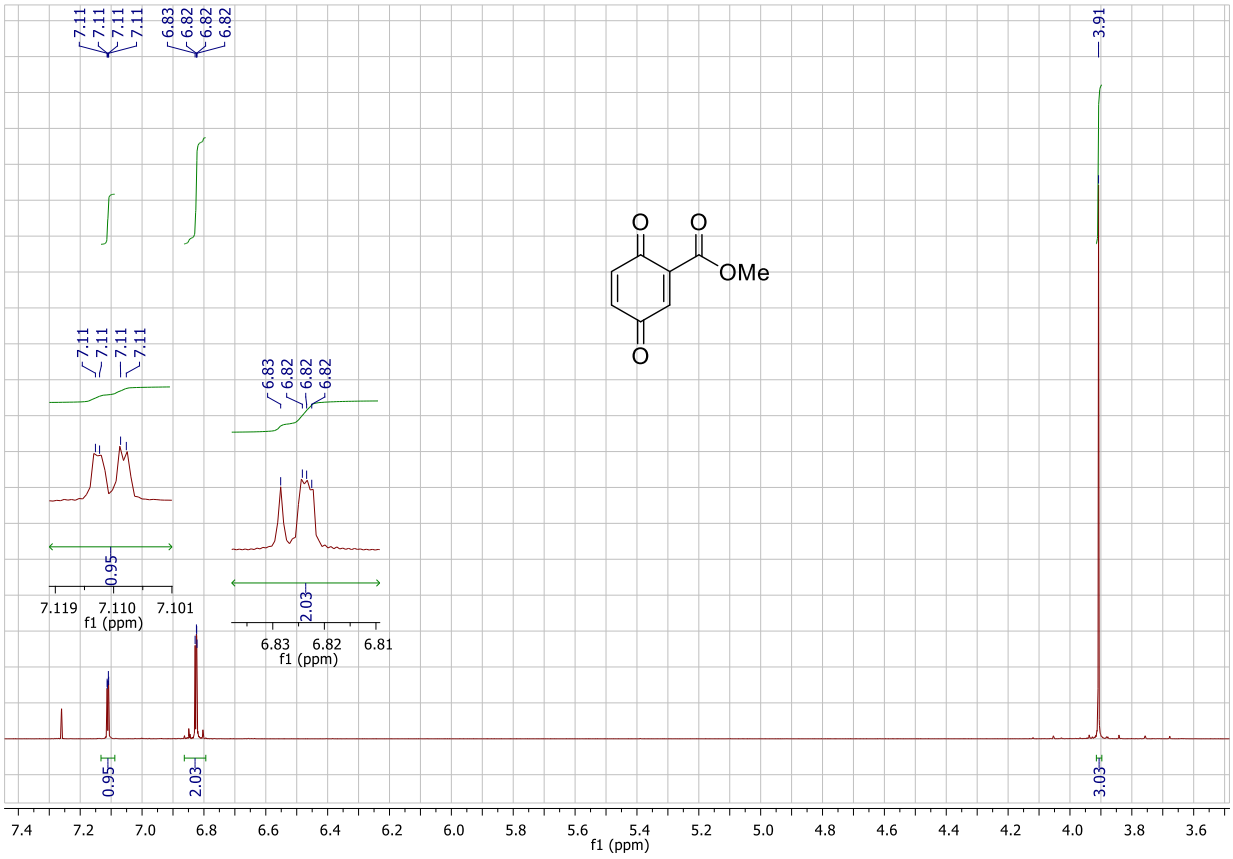
Experimental data for compound **1f** were in agreement with those found in the literature.[5]

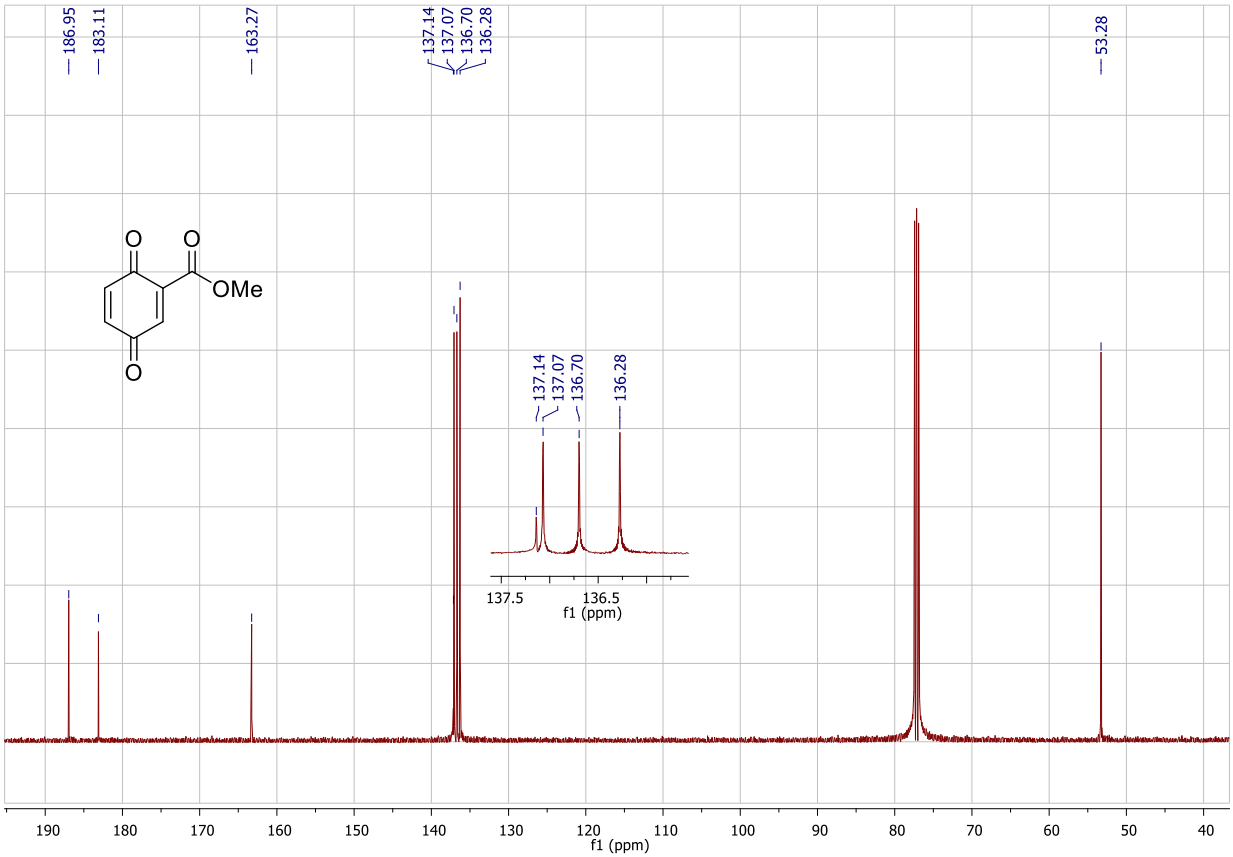
^{1}H and ^{13}C NMR spectra for 3-bromo-5-methoxy-2-methylcyclohexa-2,5-diene-1,4-dione (**1g**) in $CDCl_3$ (500 and 125 MHz)





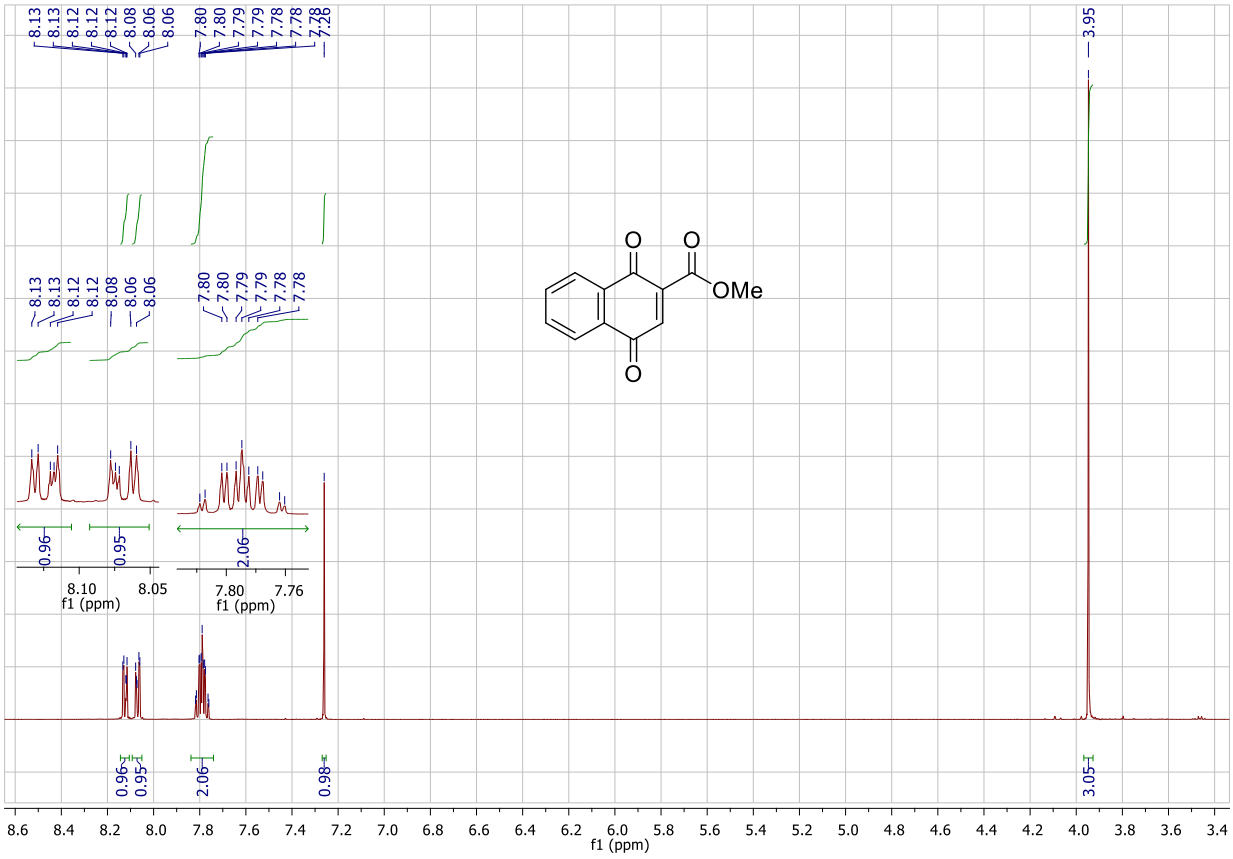
^{1}H and ^{13}C NMR spectra for methyl 3,6-dioxocyclohexa-1,4-diene-1-carboxylate (**1h**) in $CDCl_3$ (500 and 125 MHz)

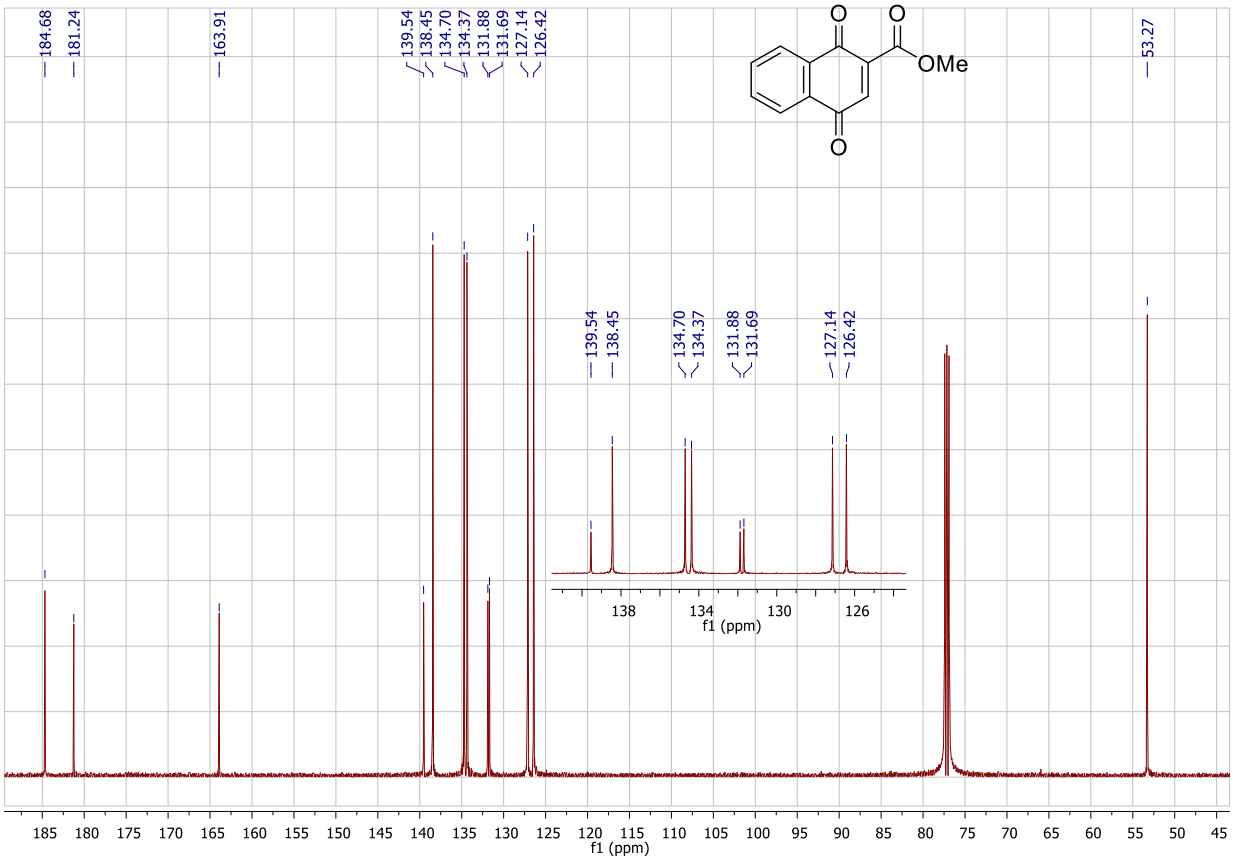




Experimental data for compound **1h** were in agreement with those found in the literature.[6]

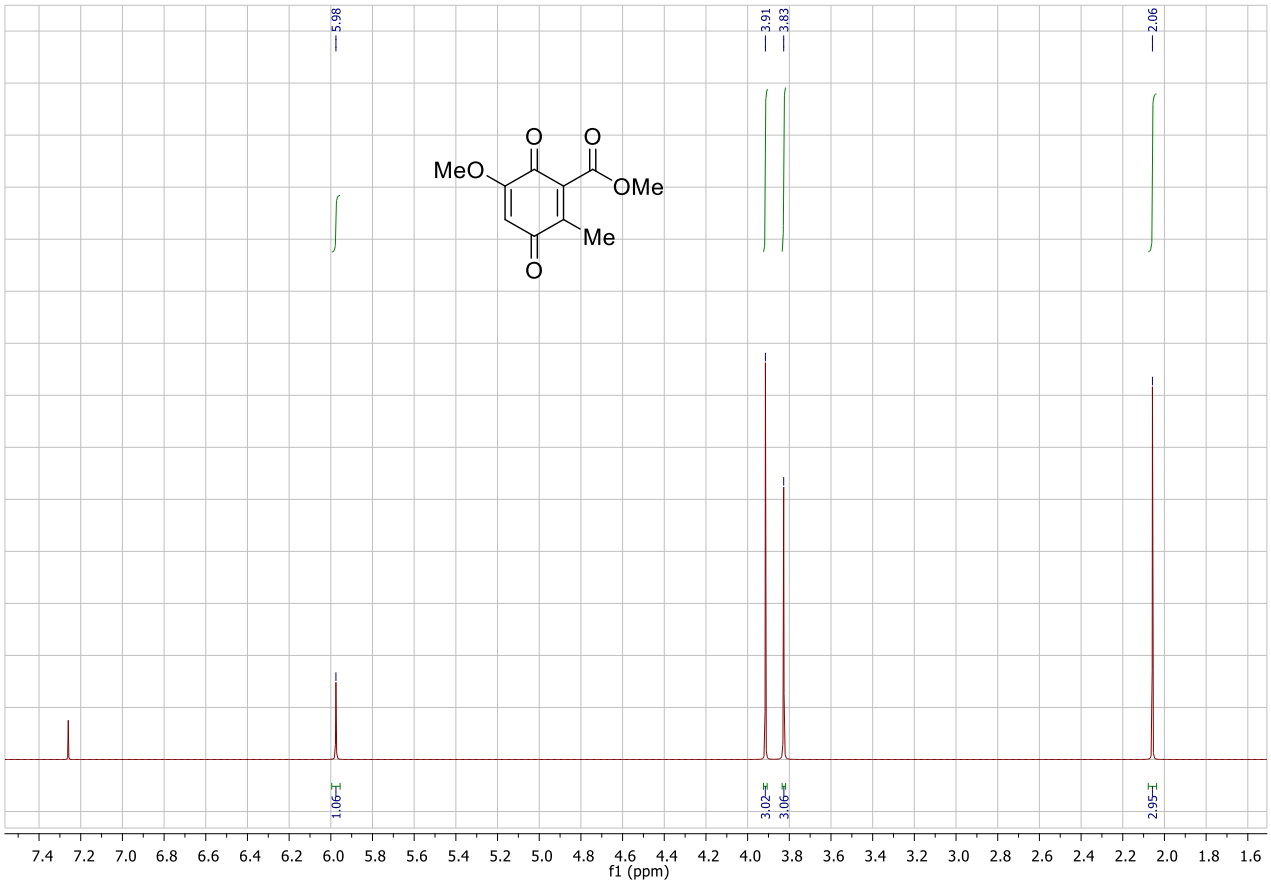
^{1}H and ^{13}C NMR spectra for methyl 1,4-dioxonaphthalene-2-carboxylate (**1i**) in $CDCl_3$ (500 and 125 MHz)

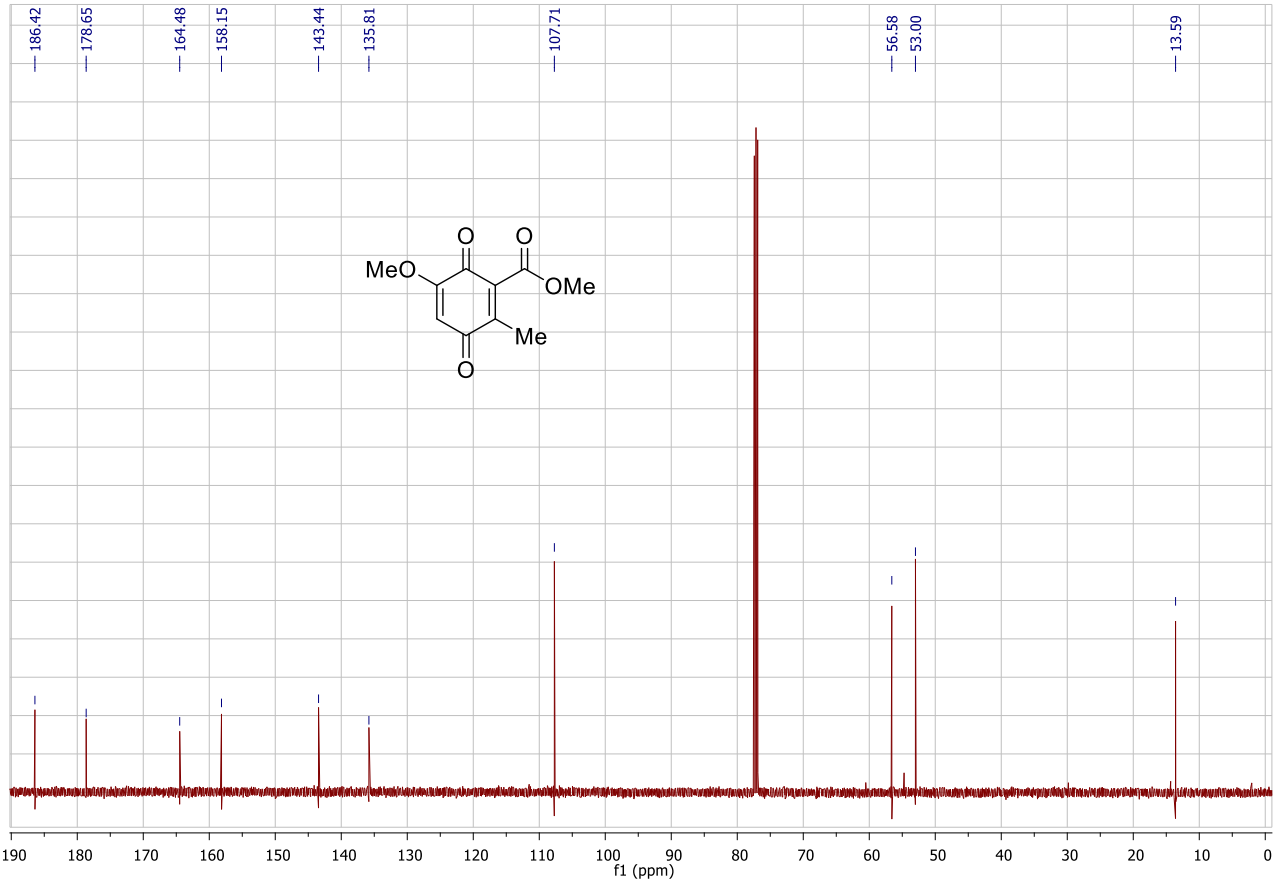




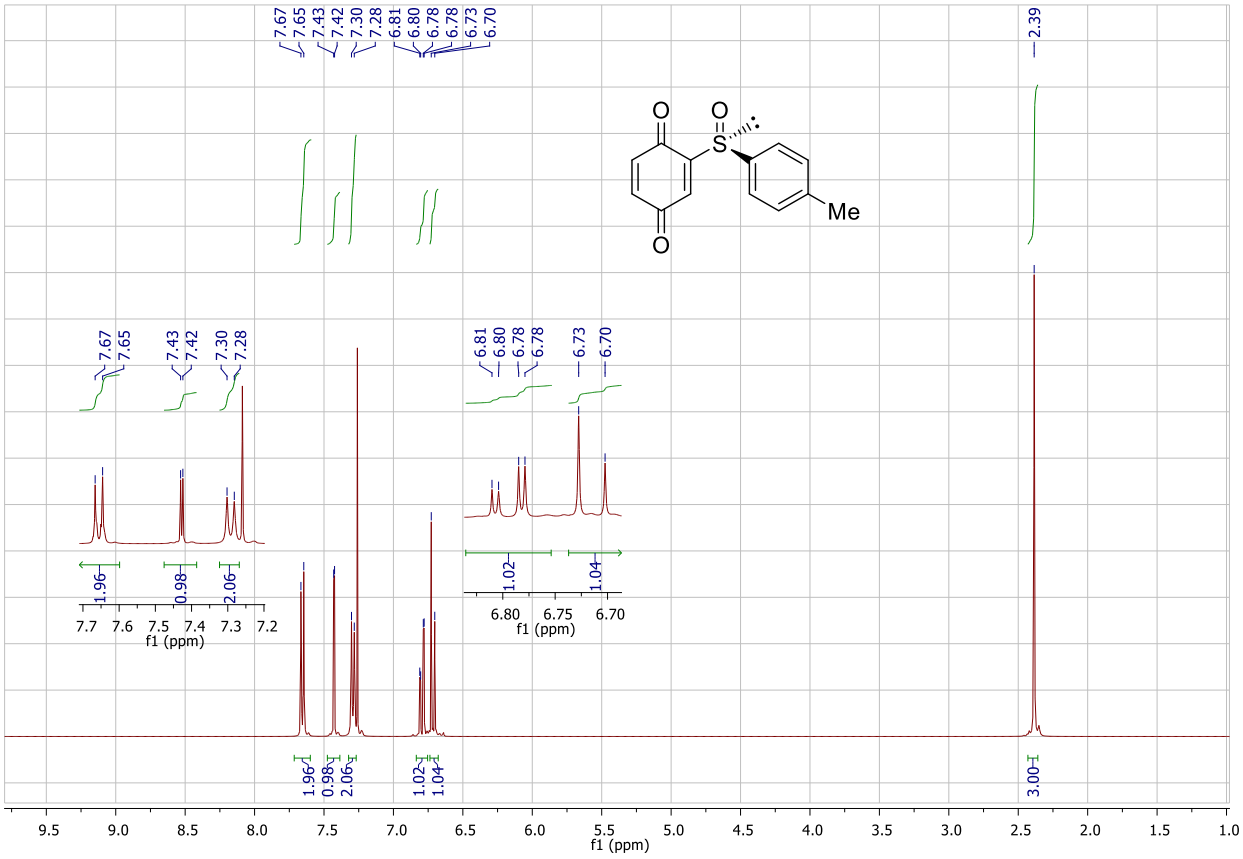
Experimental data for compound **1i** were in agreement with those found in the literature.[7]

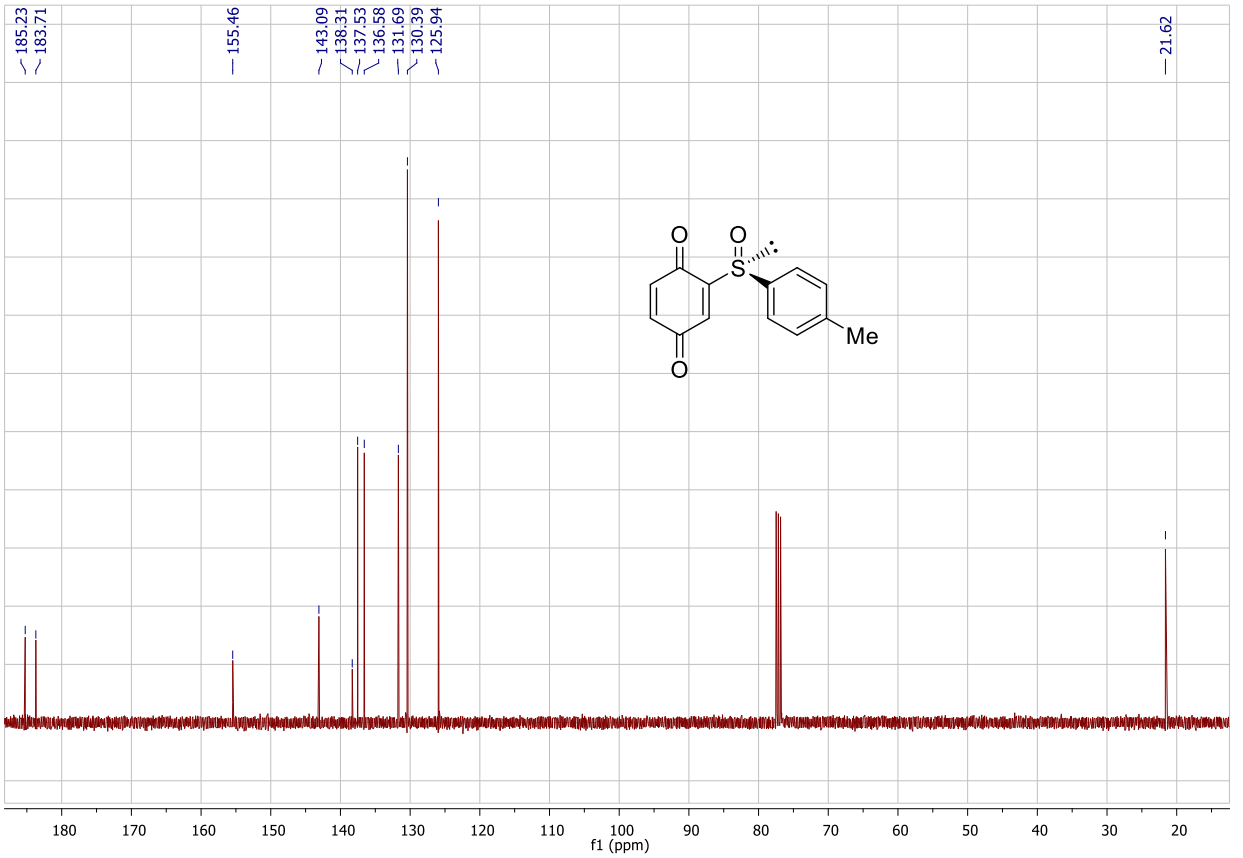
^{1}H and ^{13}C NMR spectra for methyl 5-methoxy-2-methyl-3,6-dioxocyclohexa-1,4-diene-1-carboxylate (**1j**) in $CDCl_3$ (500 and 125 MHz)





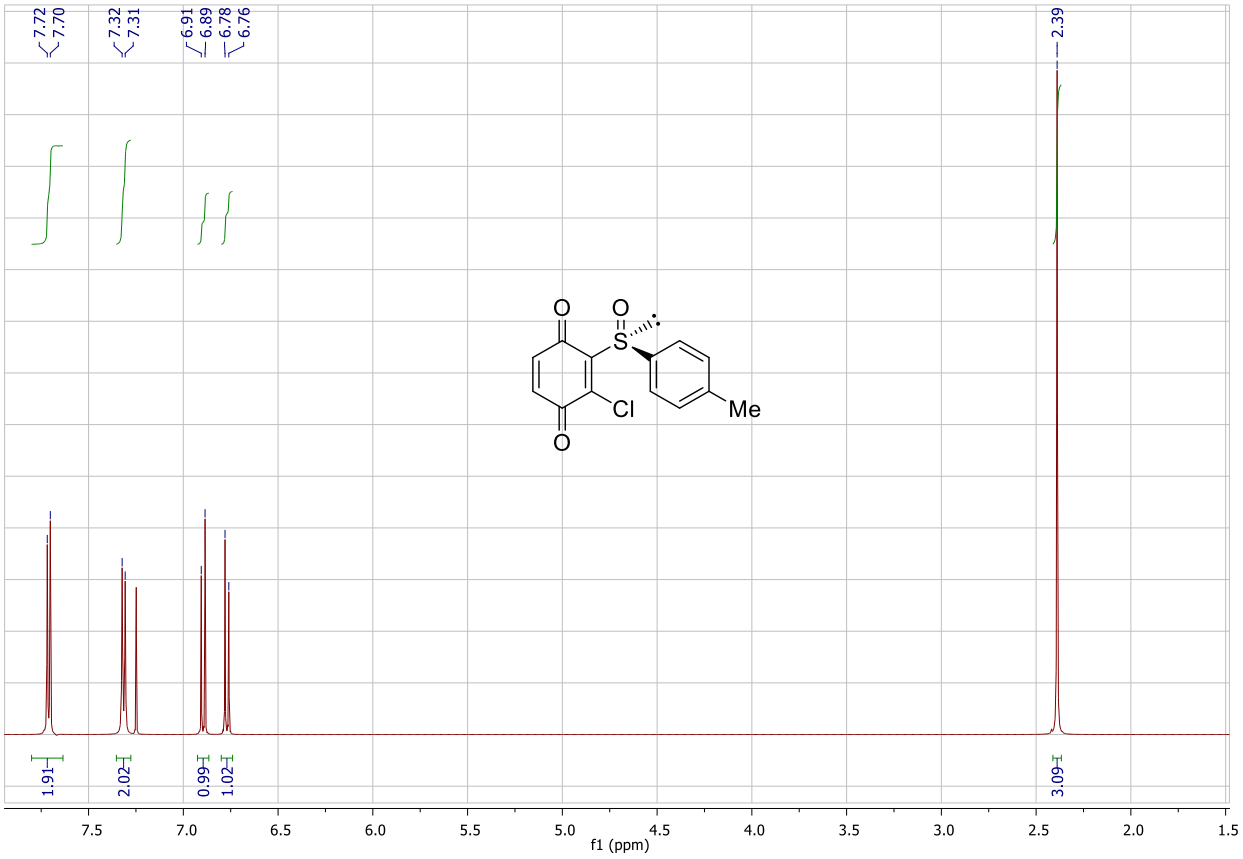
^{1}H and ^{13}C NMR spectra for (+)-(*S*)-2-(*p*-tolylsulfinyl)cyclohexa-2,5-diene-1,4-dione (**1k**) in $CDCl_3$ (400 and 100 MHz)

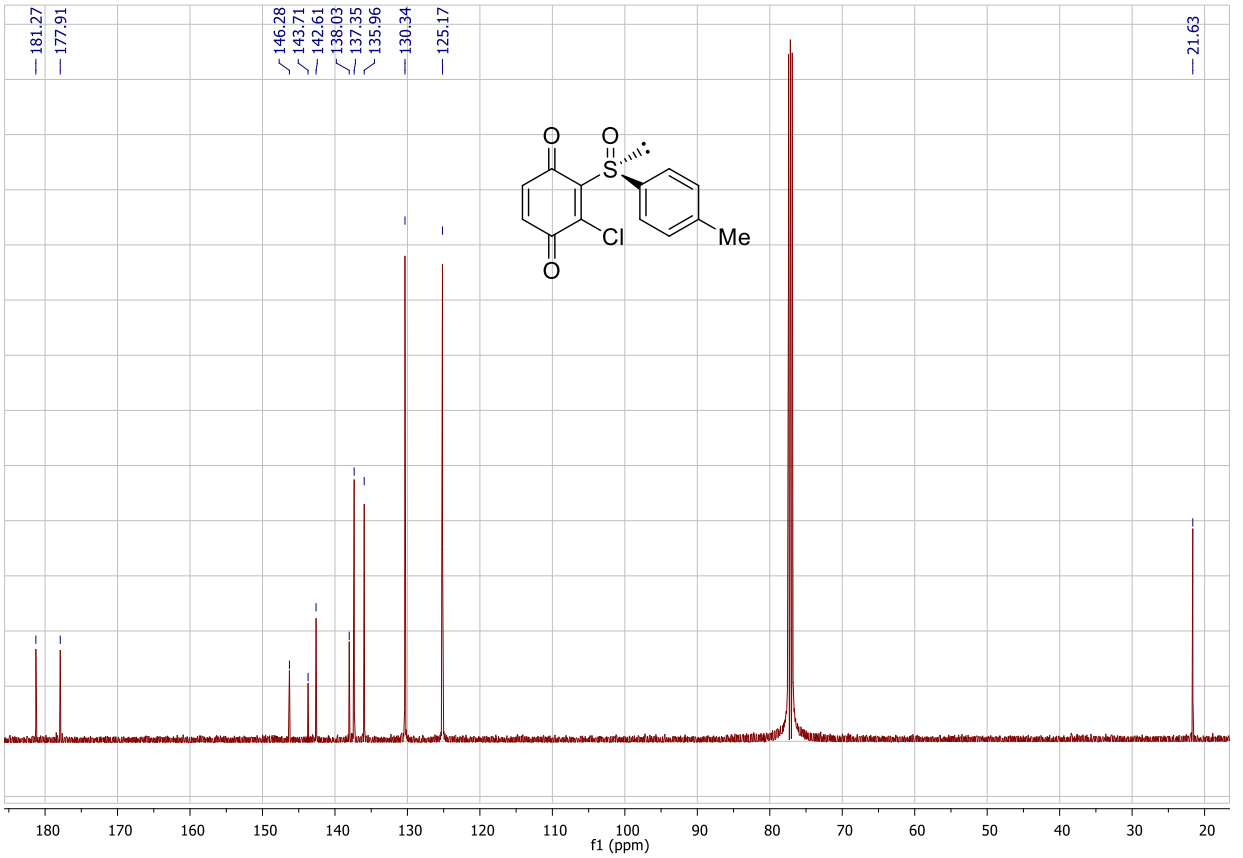




Experimental data for compound **1k** were in agreement with those found in the literature.[8]

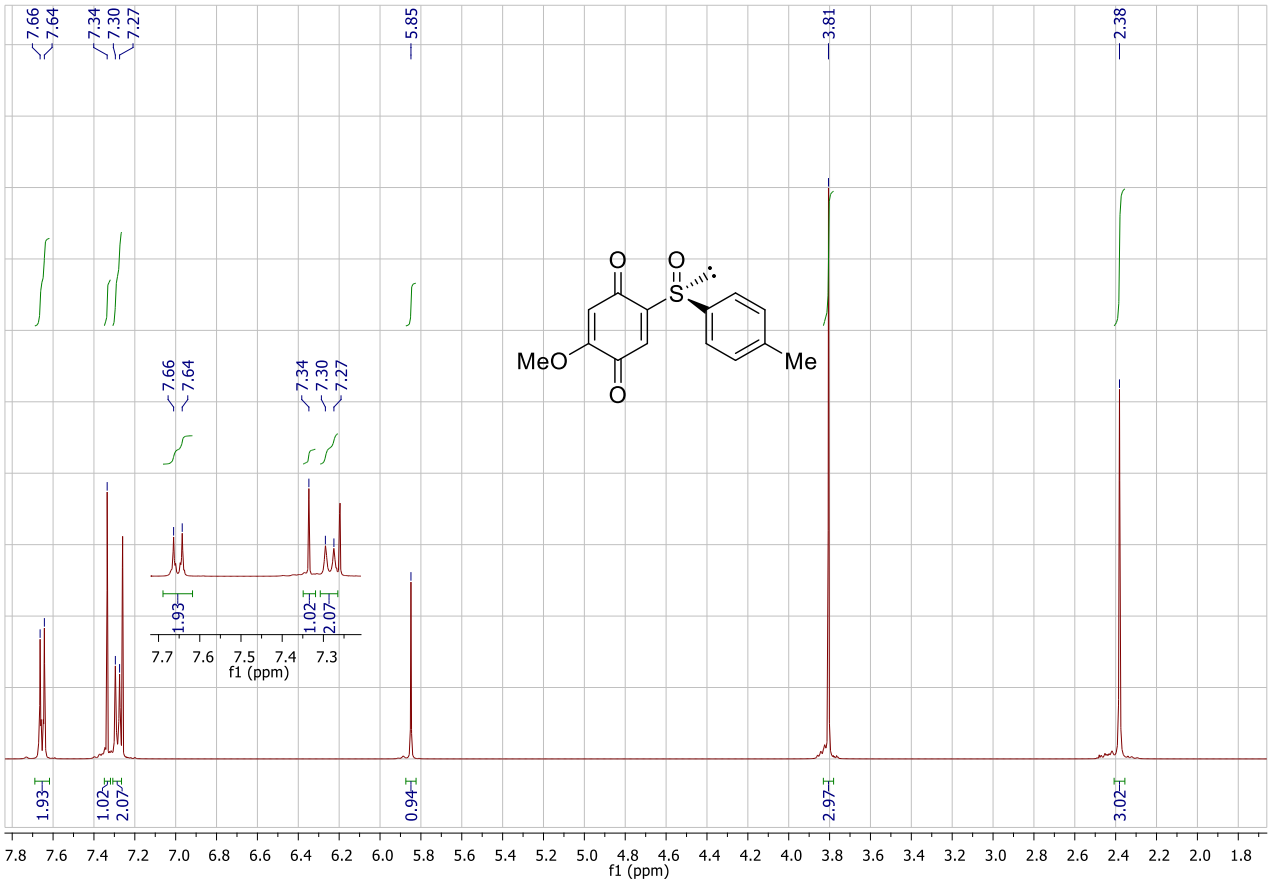
^{1}H and ^{13}C NMR spectra for (+)-(*S*)-2-chloro-3-(*p*-tolylsulfinyl)cyclohexa-2,5-diene-1,4-dione (**1l**) in $CDCl_3$ (500 and 125 MHz)

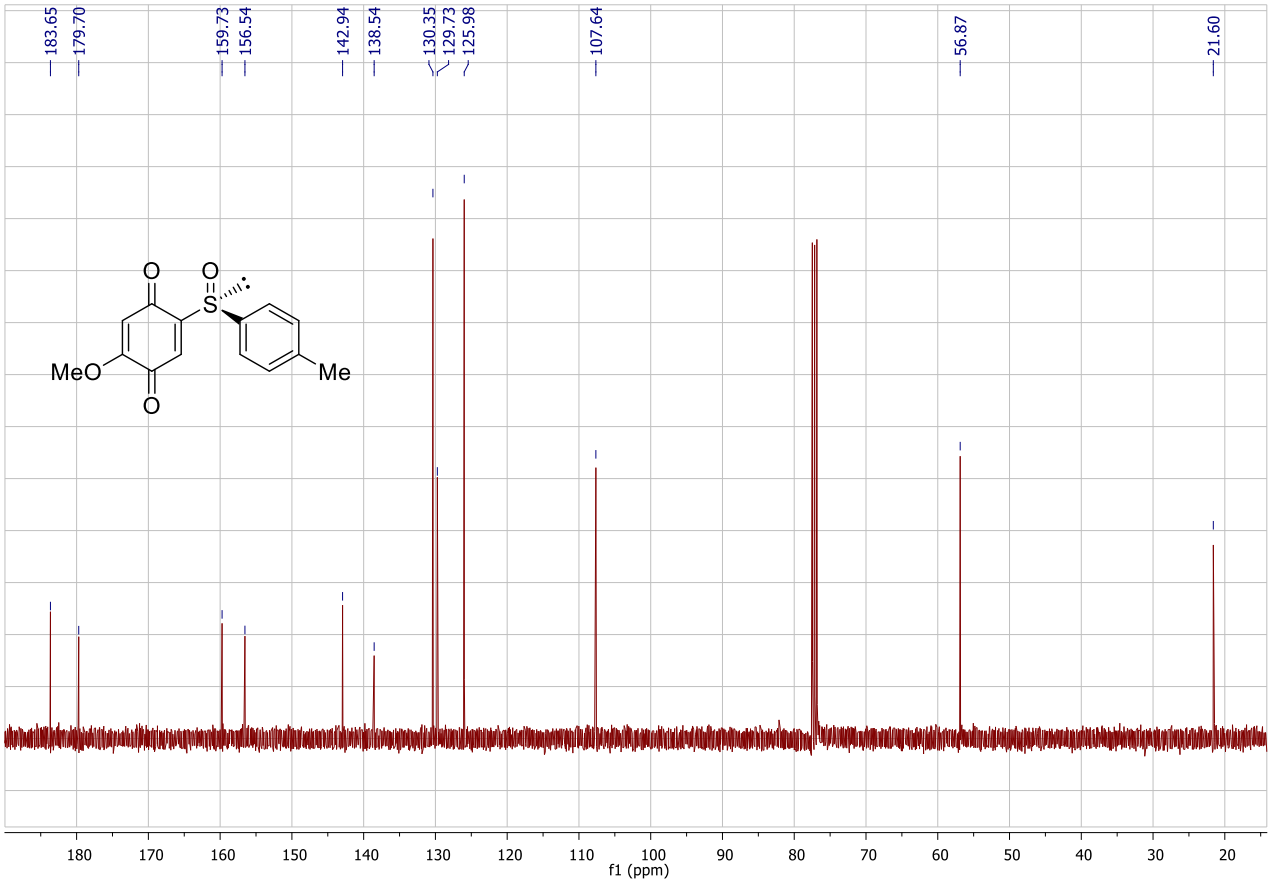




Experimental data for compound **1l** were in agreement with those found in the literature.[9]

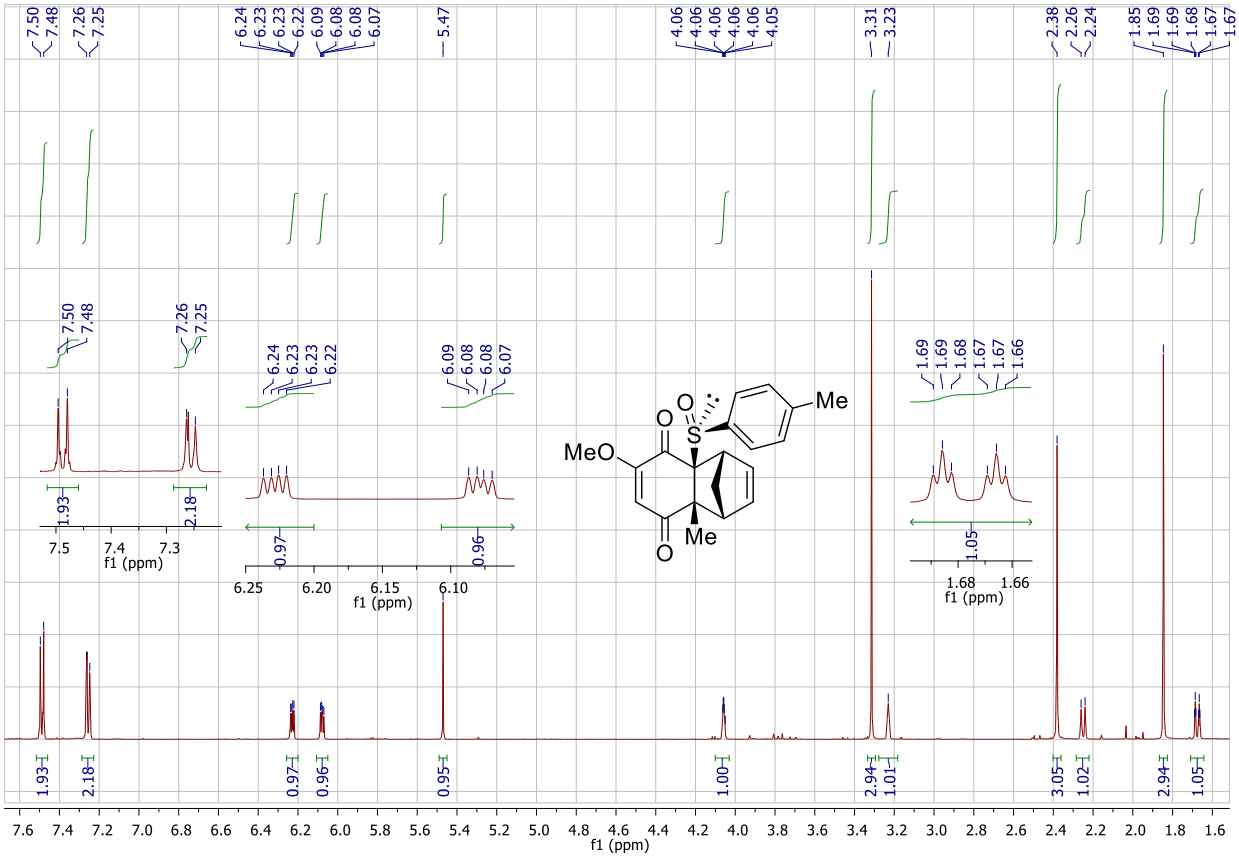
^{1}H and ^{13}C NMR spectra for (+)-(*S*)-2-methoxy-5-(*p*-tolylsulfinyl)cyclohexa-2,5-diene-1,4-dione (**1m**) in $CDCl_3$ (500 and 125 MHz)

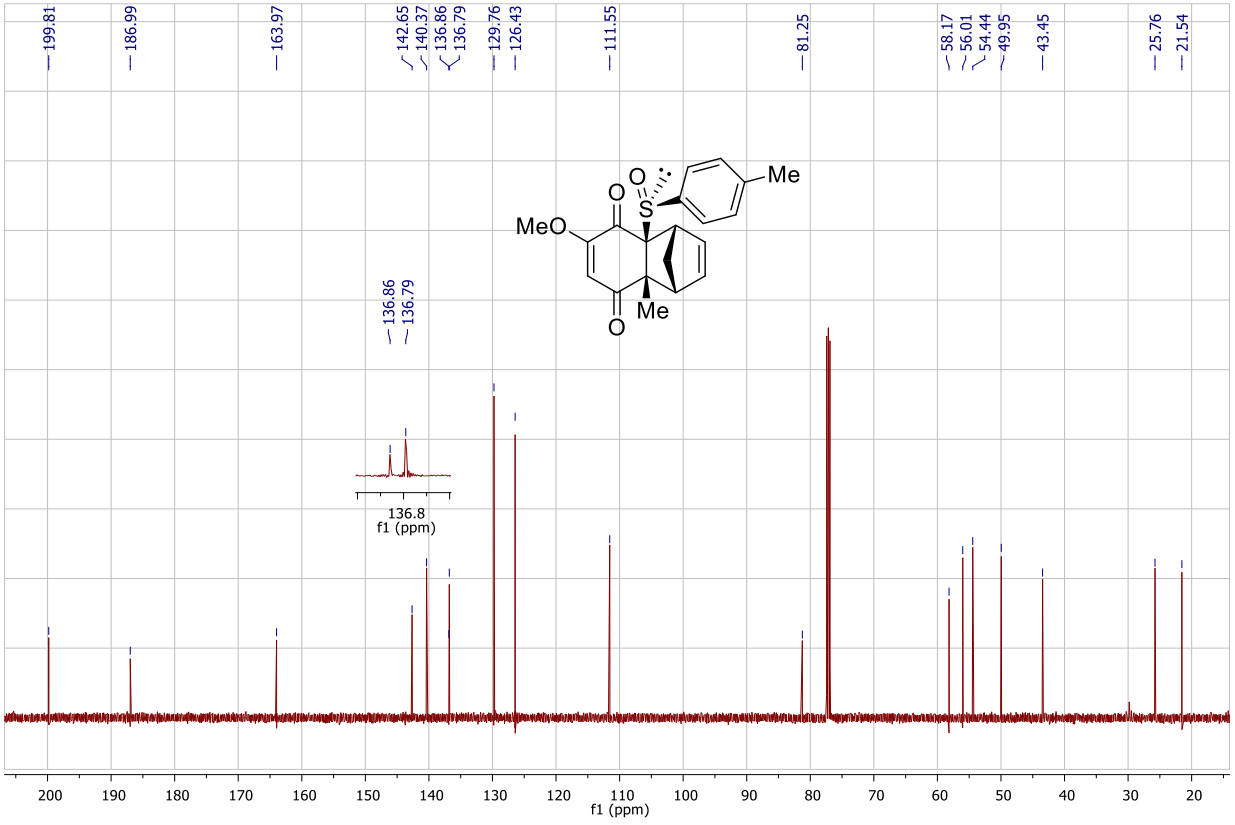




Synthesized cycloadducts and derivatives

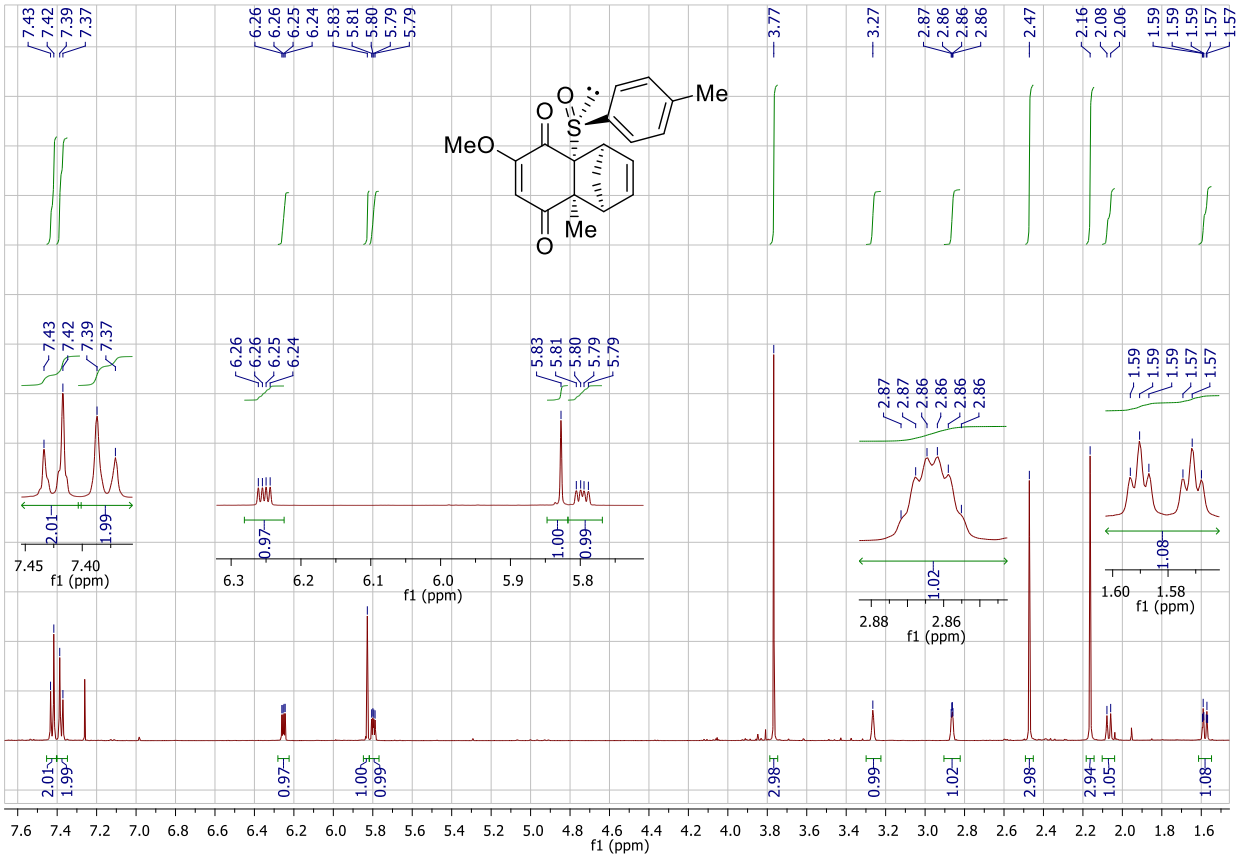
^{1}H and ^{13}C NMR spectra for (-)-(1*R*,4*S*,4a*S*,8a*R*)-6-methoxy-8a-methyl-4a-((*S*)-*p*-tolylsulfinyl)-1,4,4a,8a-tetrahydro-1,4-methanonaphthalene-5,8-dione (**α-3a**) in $CDCl_3$ (500 and 125 MHz)

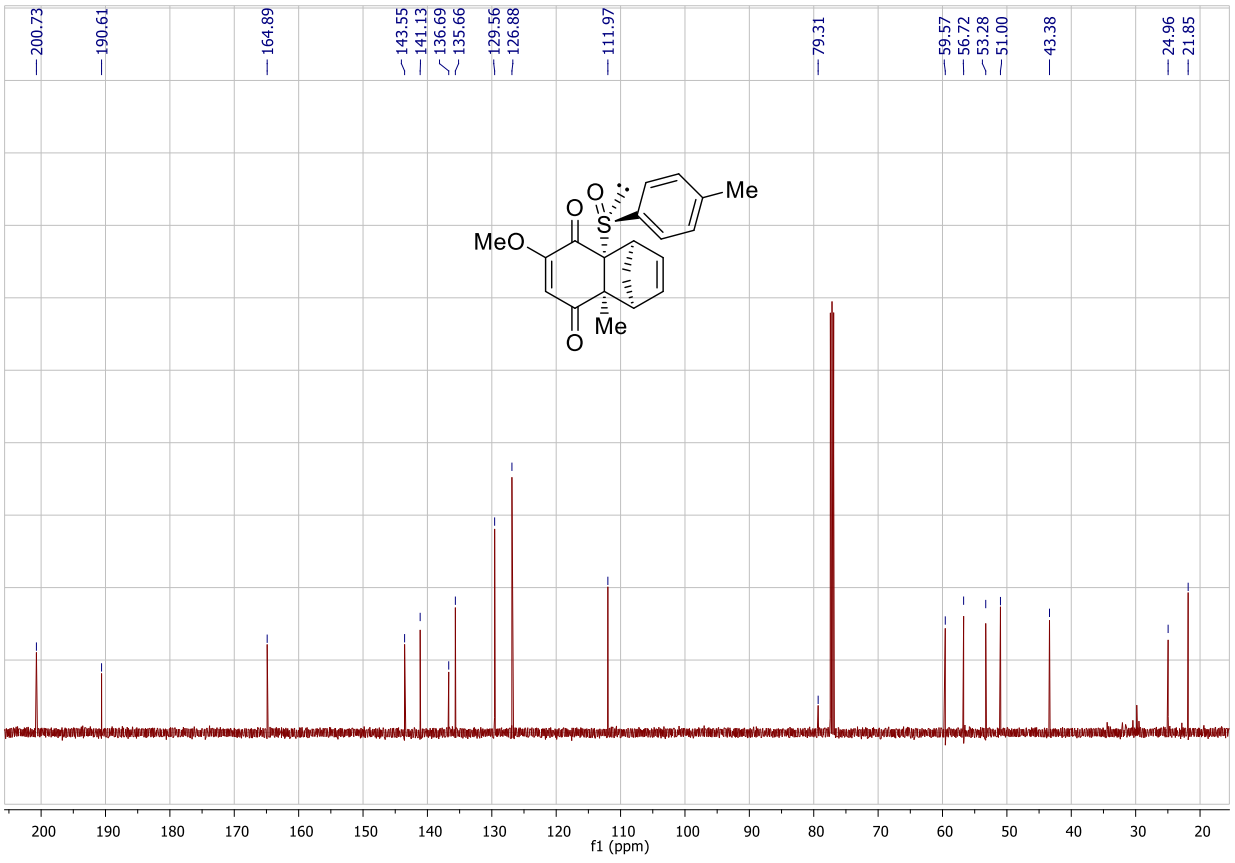




Experimental data for compound **α-3a** were in agreement with those found in the literature.[1]

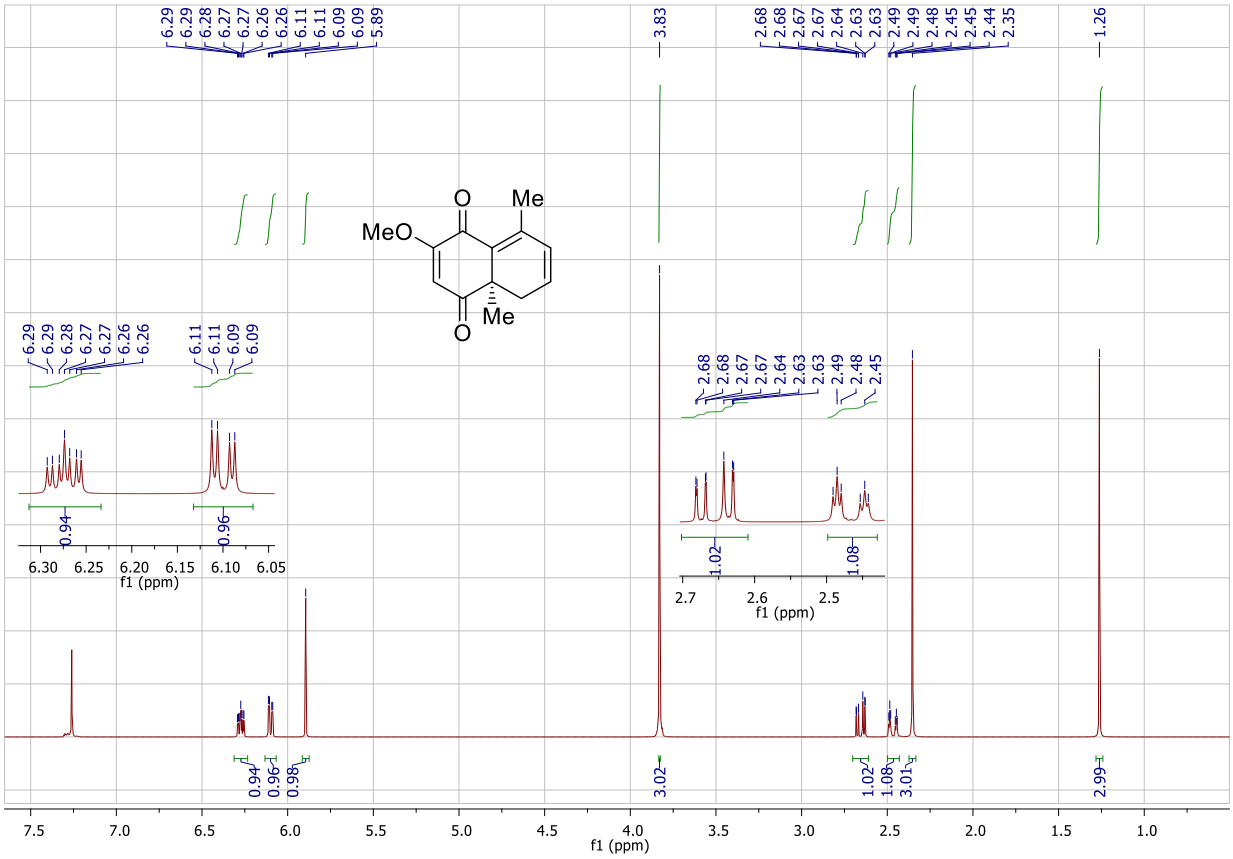
^{1}H and ^{13}C NMR spectra for (+)-(1*S*,4*R*,4a*R*,8a*S*)-6-methoxy-8a-methyl-4a-((*S*)-*p*-tolylsulfinyl)-1,4,4a,8a-tetrahydro-1,4-methanonaphthalene-5,8-dione (**β-3a**) in $CDCl_3$ (500 and 125 MHz)

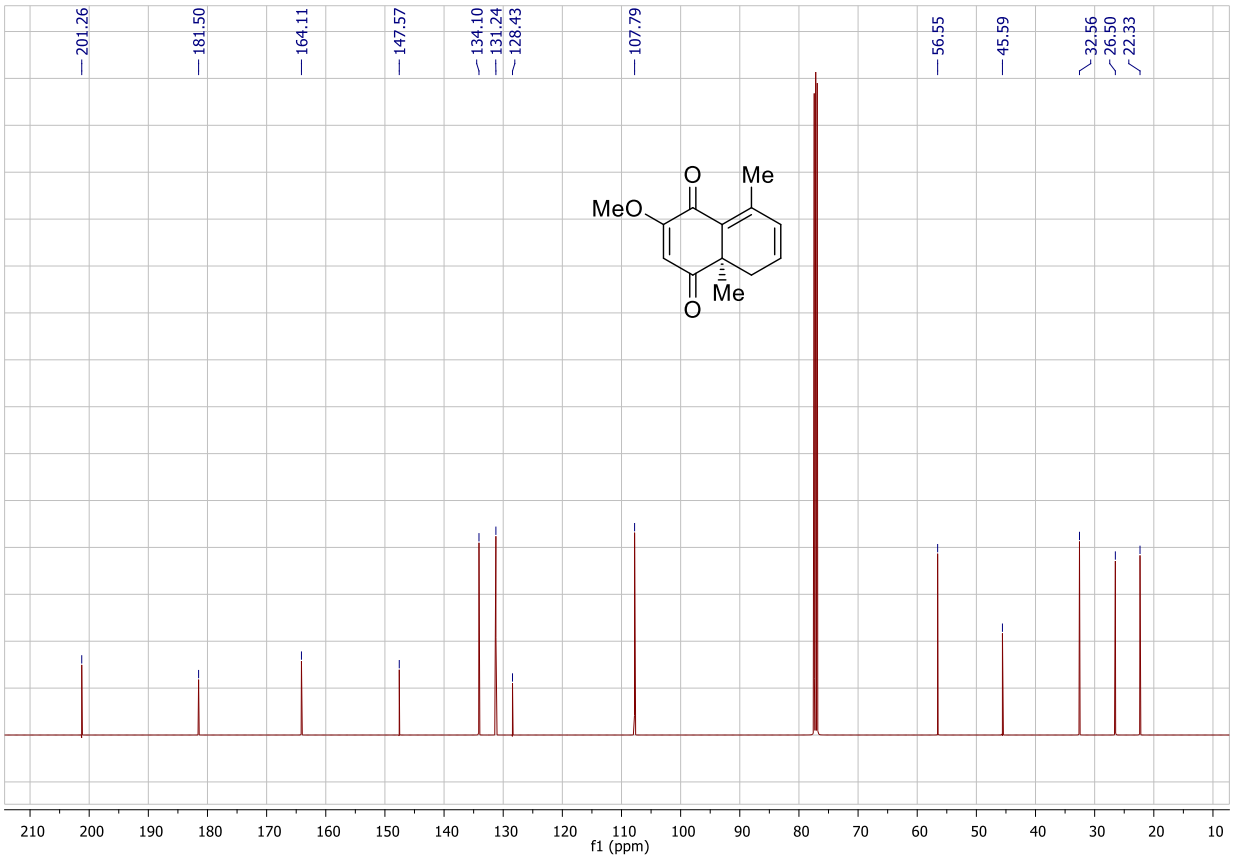




Experimental data for compound **β-3a** were in agreement with those found in the literature.[1]

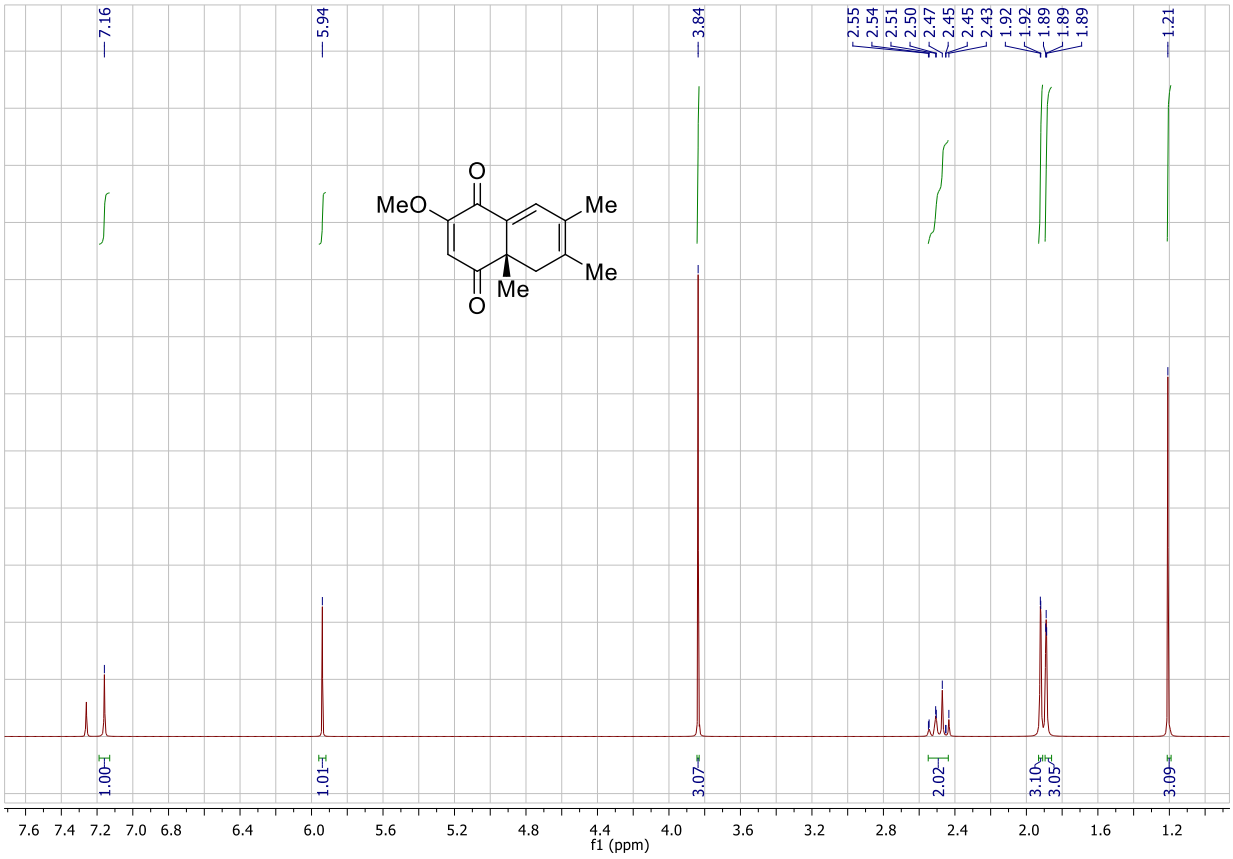
^{1}H and ^{13}C NMR spectra for (-)-(*R*)-2-methoxy-4a,8-dimethyl-4a,5-dihydronaphthalene-1,4-dione (**β-9a**) in $CDCl_3$ (400 and 100 MHz)

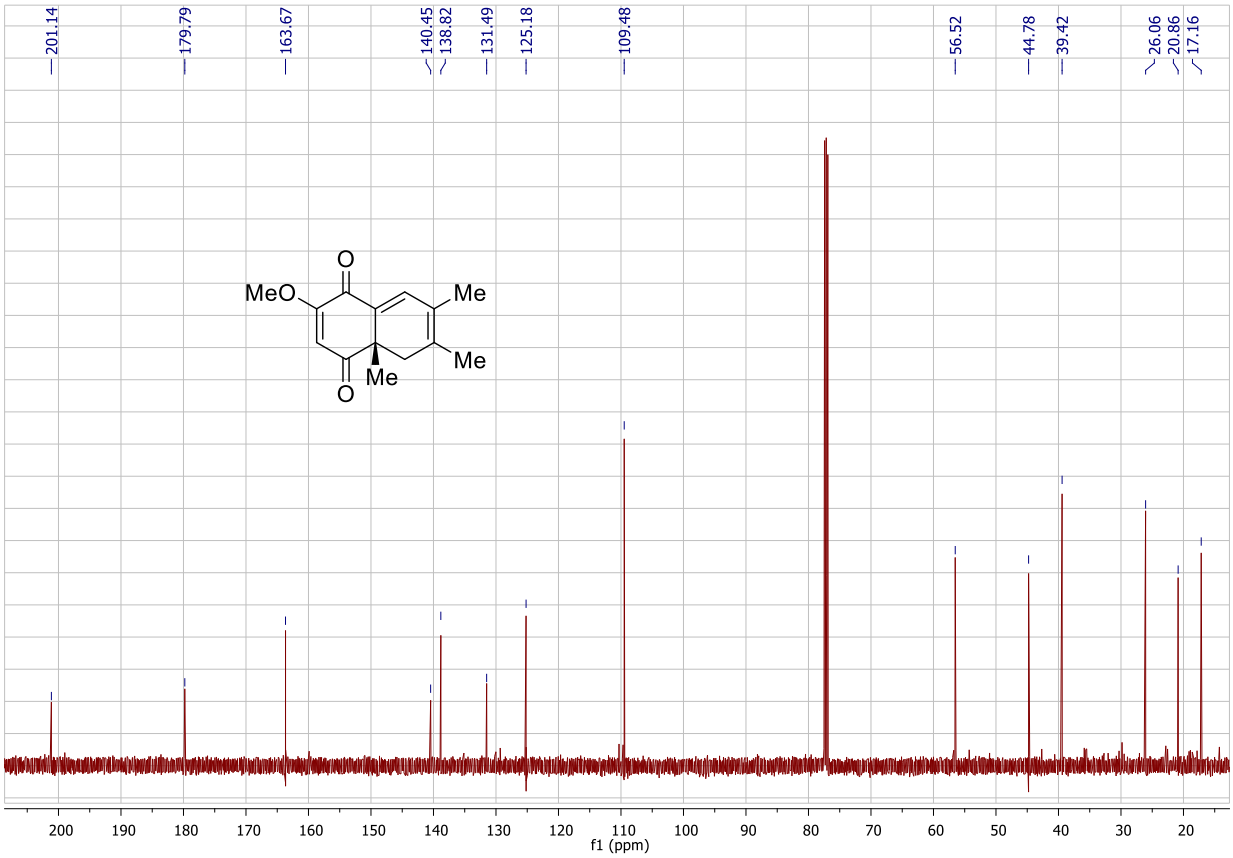




Experimental data for compound **β-9a** were in agreement with those found in the literature.[1]

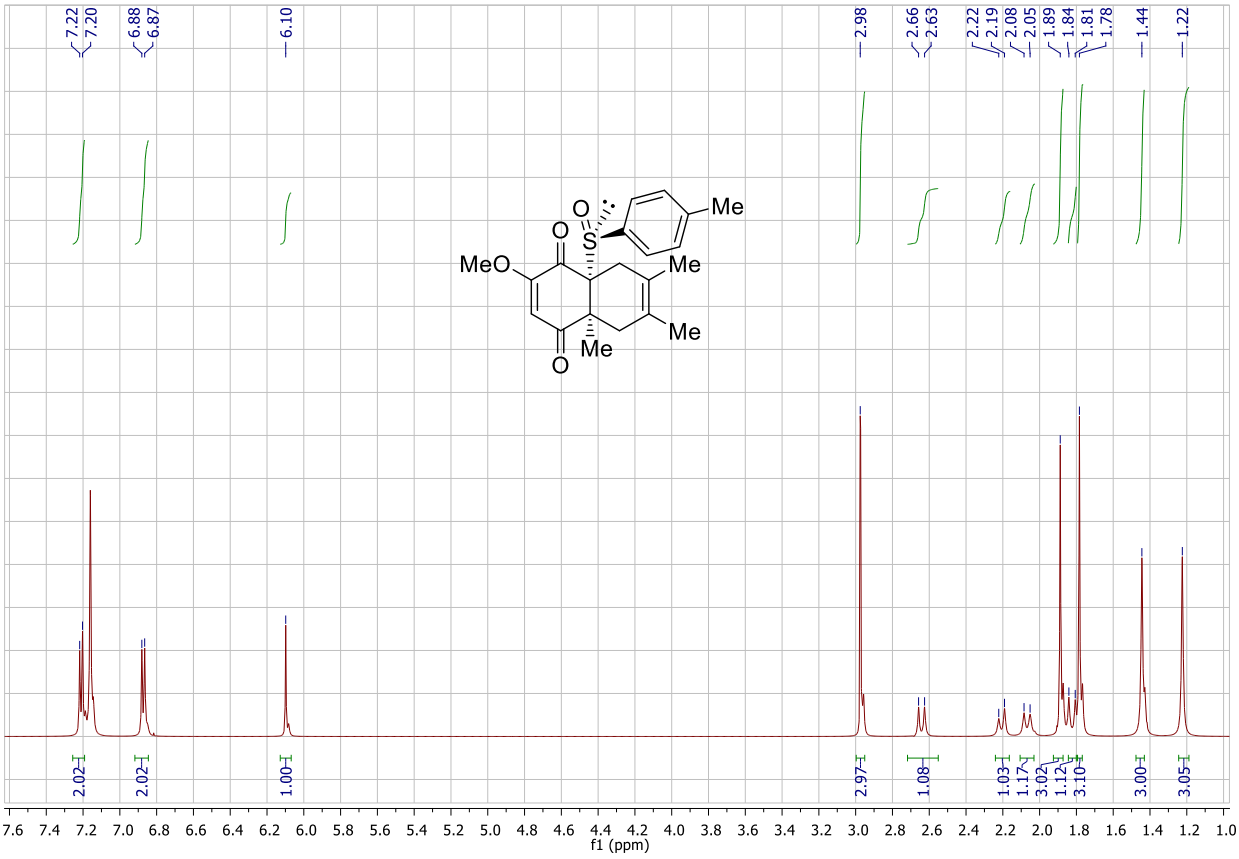
^{1}H and ^{13}C NMR spectra for (+)-(*S*)-2-methoxy-4a,6,7-trimethyl-4a,5-dihydrobaphthalene-1,4-dione (**α-10a**) in $CDCl_3$ (500 and 125 MHz)

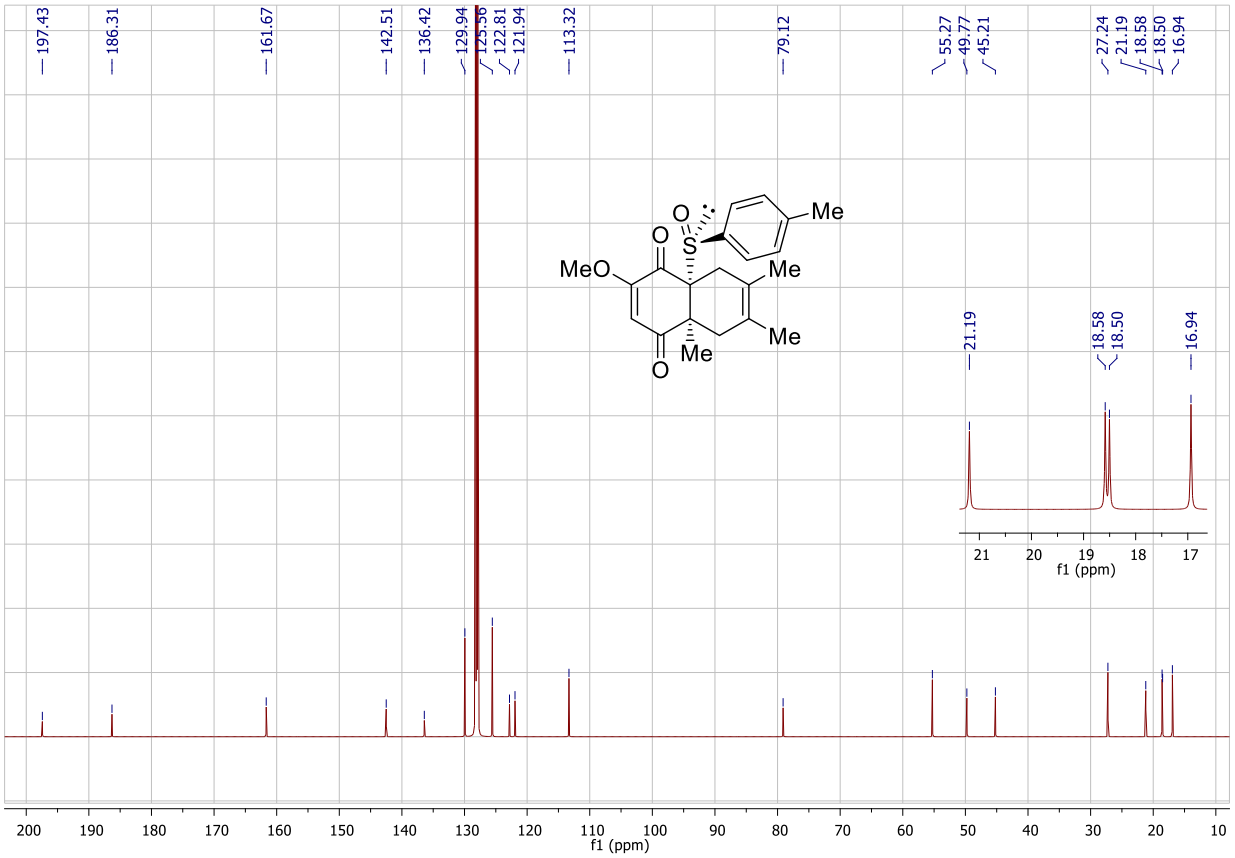




Experimental data for compound **α-10a** were in agreement with those found in the literature.[1]

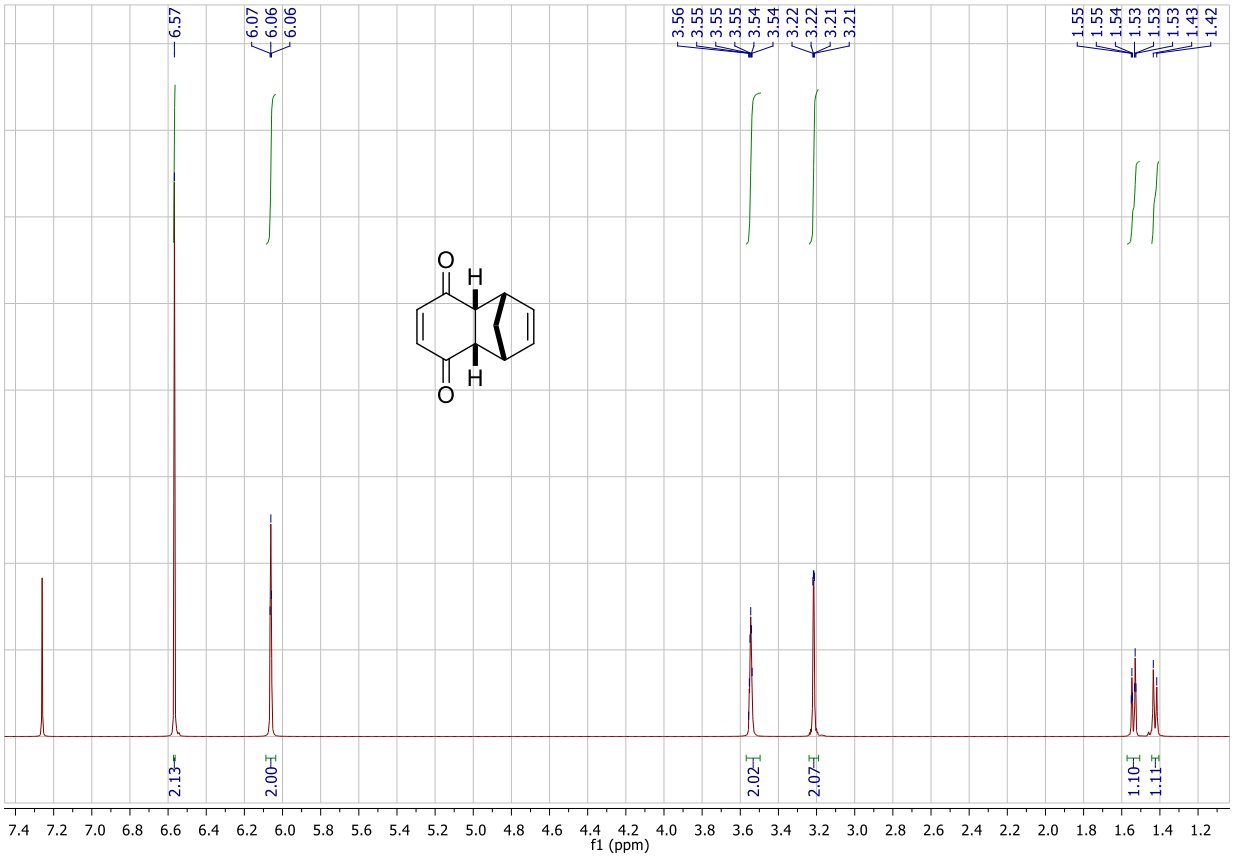
^{1}H and ^{13}C NMR spectra for (-)-(4a*S*,8a*R*)-2-methoxy-4a,6,7-trimethyl-8a-((*S*)-*p*-tolylsulfinyl)-4a-5,8,8a-tetrahydronaphthalene-1,4-dione (**β-6a**) in C_6D_6 (500 and 125 MHz)

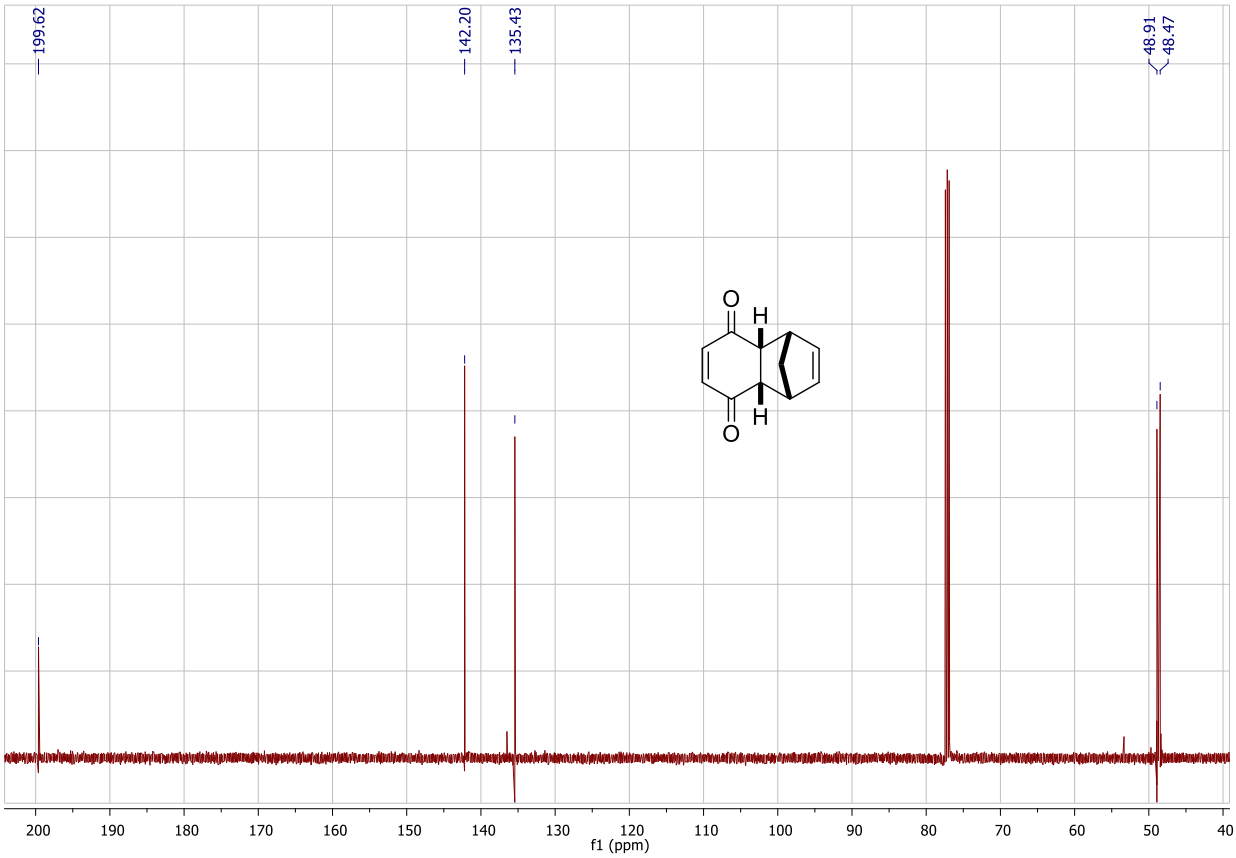




Experimental data for compound **β-6a** were in agreement with those found in the literature.[1]

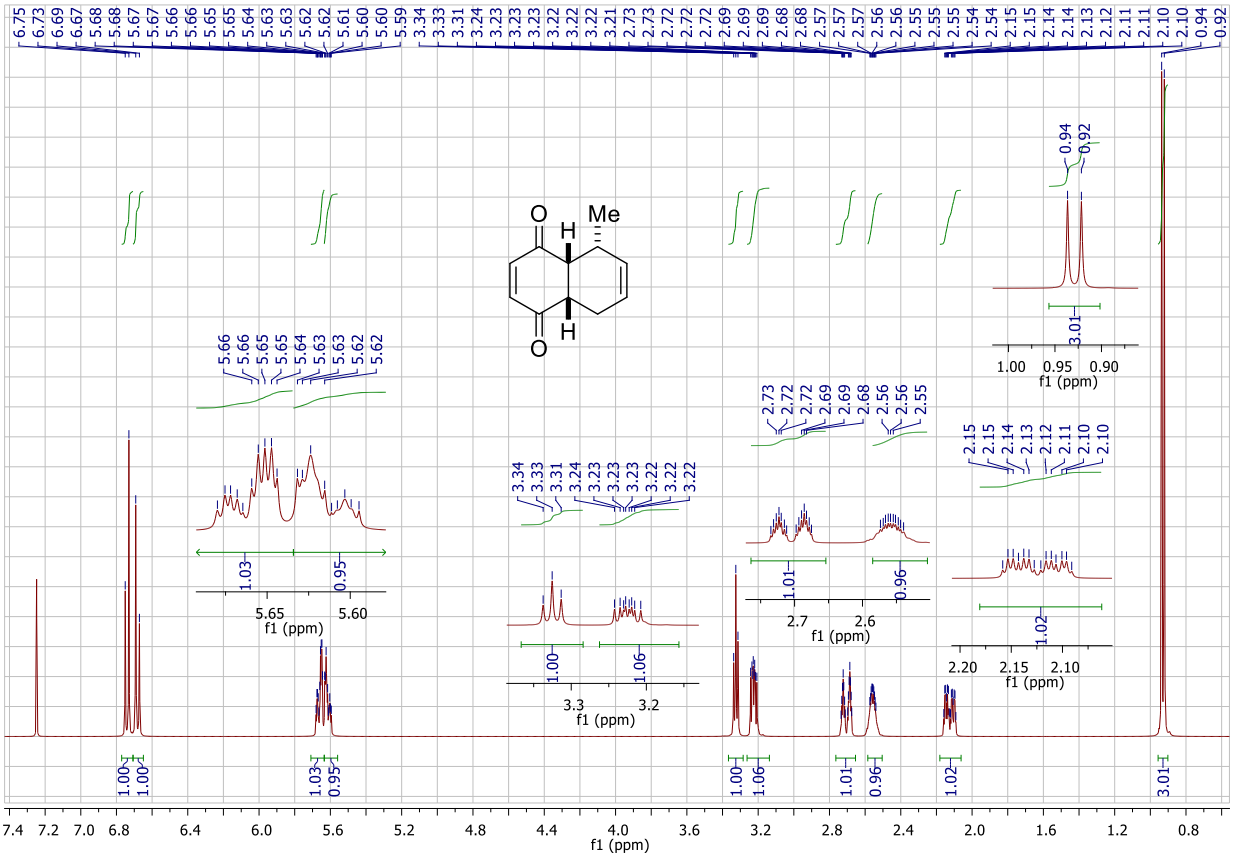
^{1}H and ^{13}C NMR spectra for (1*R*,4*S*,4a*R*,8a*S*)-1,4,4a,8a-tetrahydro-1,4-methanonaphthalene-5,8-dione (**3b**) in $CDCl_3$ (500 and 125 MHz)

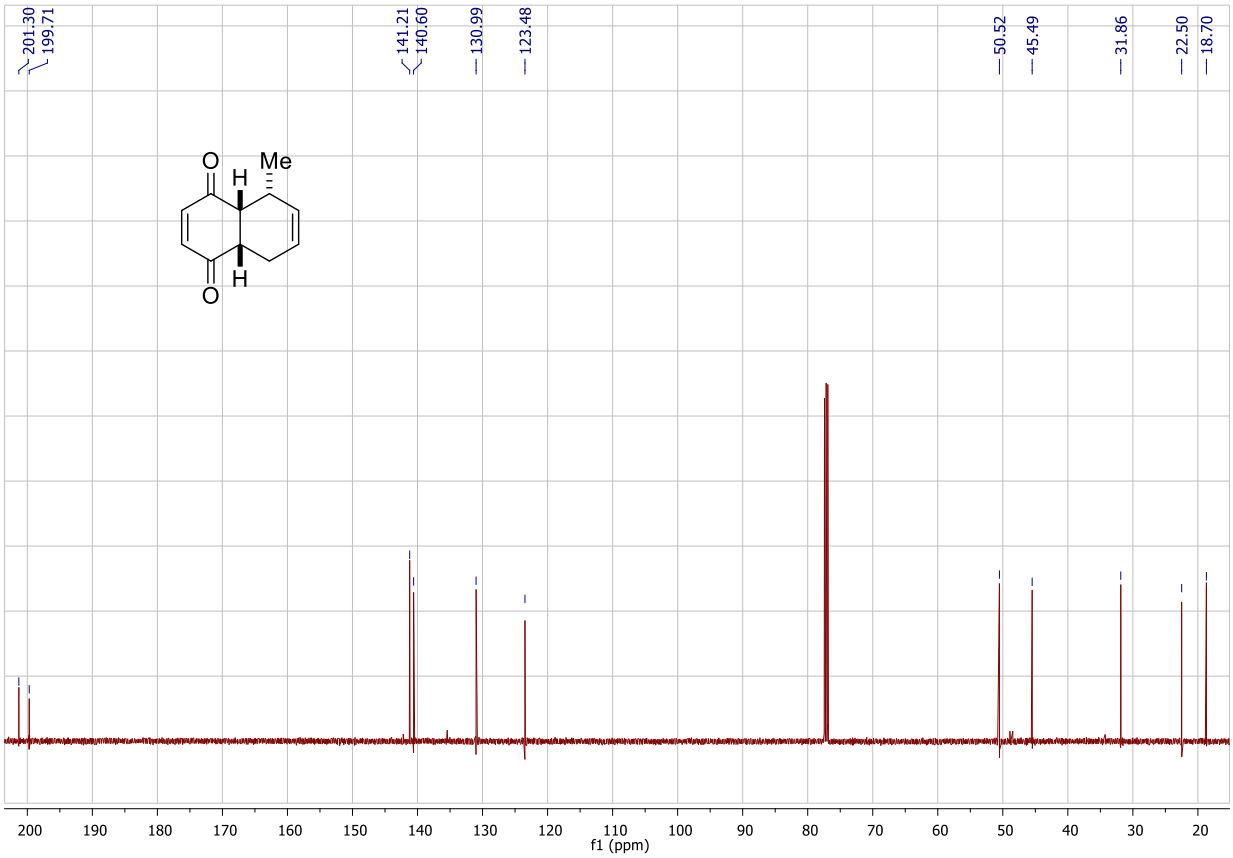




Experimental data for compound **3b** were in agreement with those found in the literature.[10]

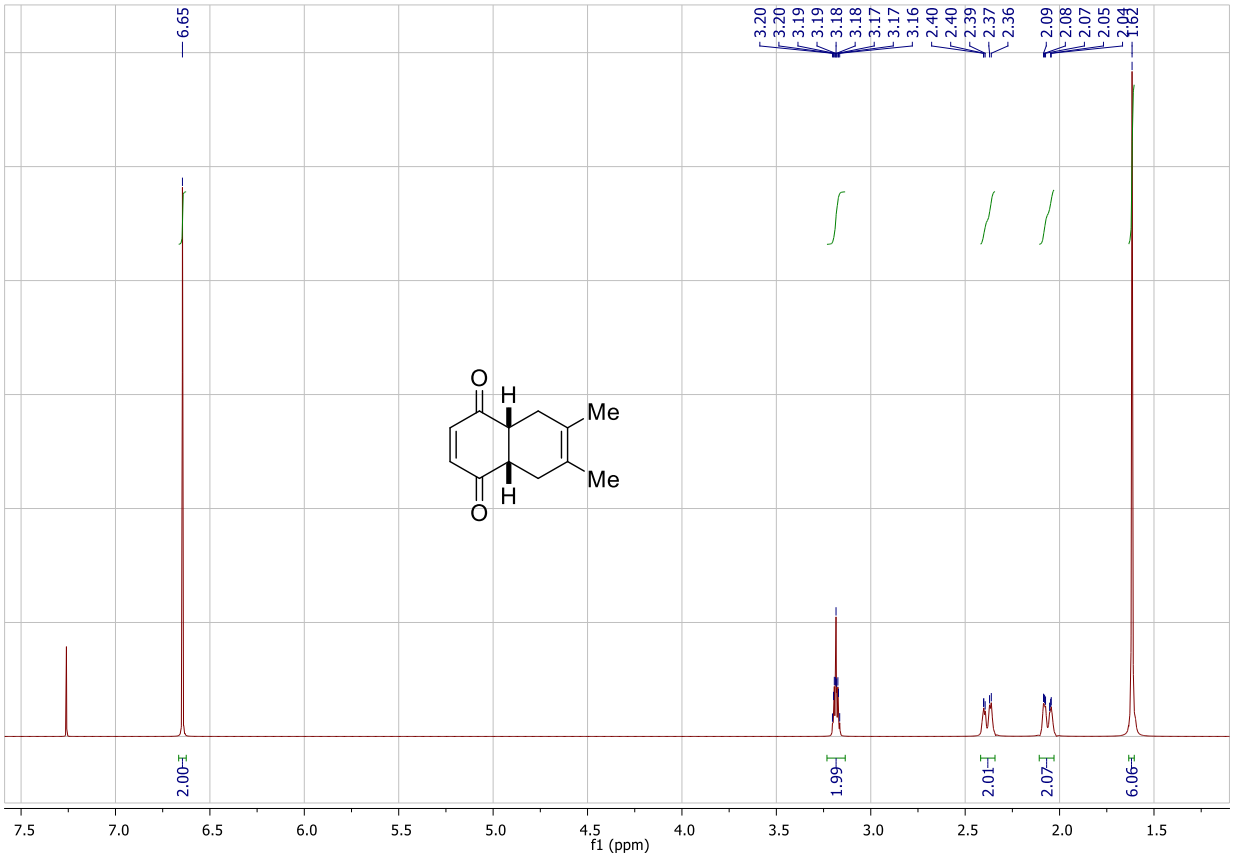
^{1}H and ^{13}C NMR spectra for (±)-*rel*-(4a*R*,5*R*,8a*S*)-5-methyl-4a,5,8,8a-tetrahydronaphthalene-1,4-dione (**5b**) in $CDCl_3$ (500 and 125 MHz)

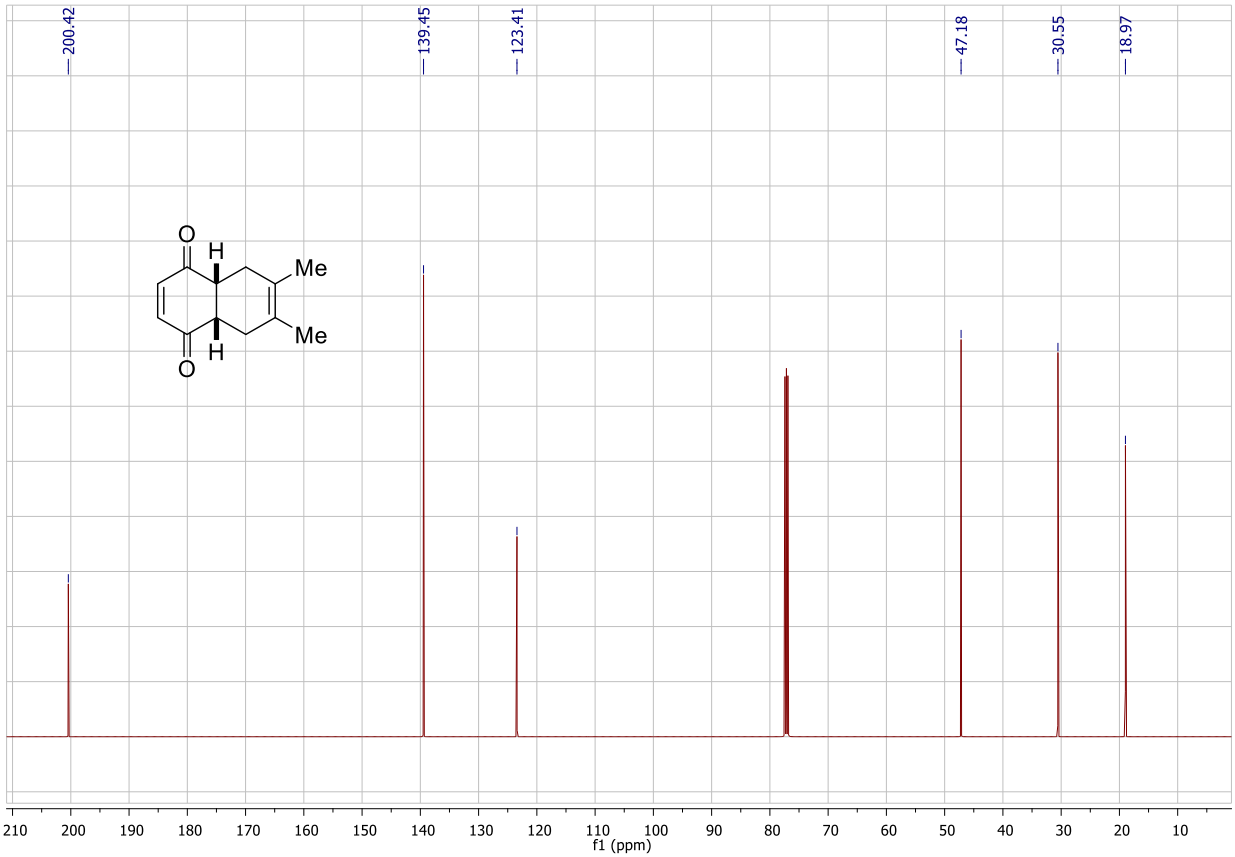




Experimental data for compound **5b** were in agreement with those found in the literature.[11]

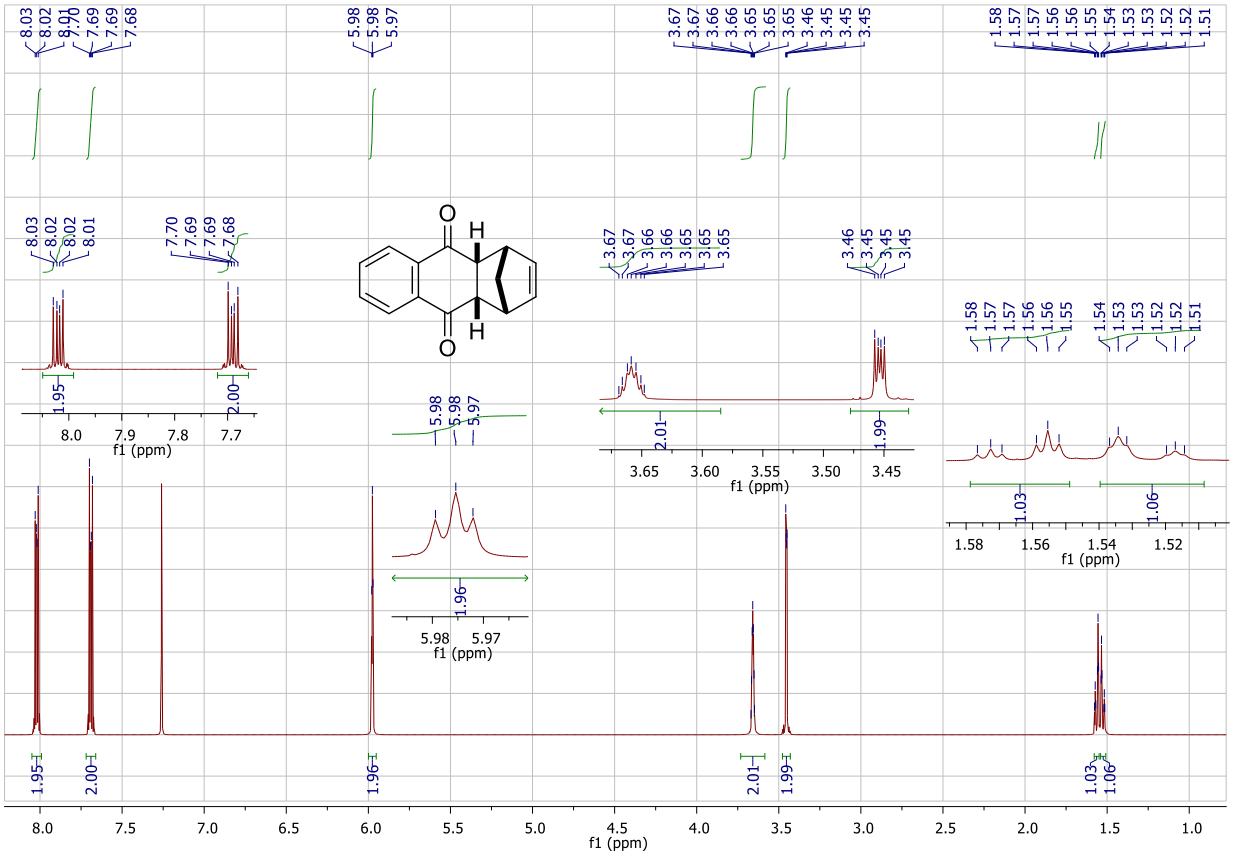
^{1}H and ^{13}C NMR spectra for (4a*R*,8a*S*)-6,7-dimethyl-4a,5,8,8a-tetrahydronaphthalene-1,4-dione (**6b**) in $CDCl_3$ (500 and 125 MHz)

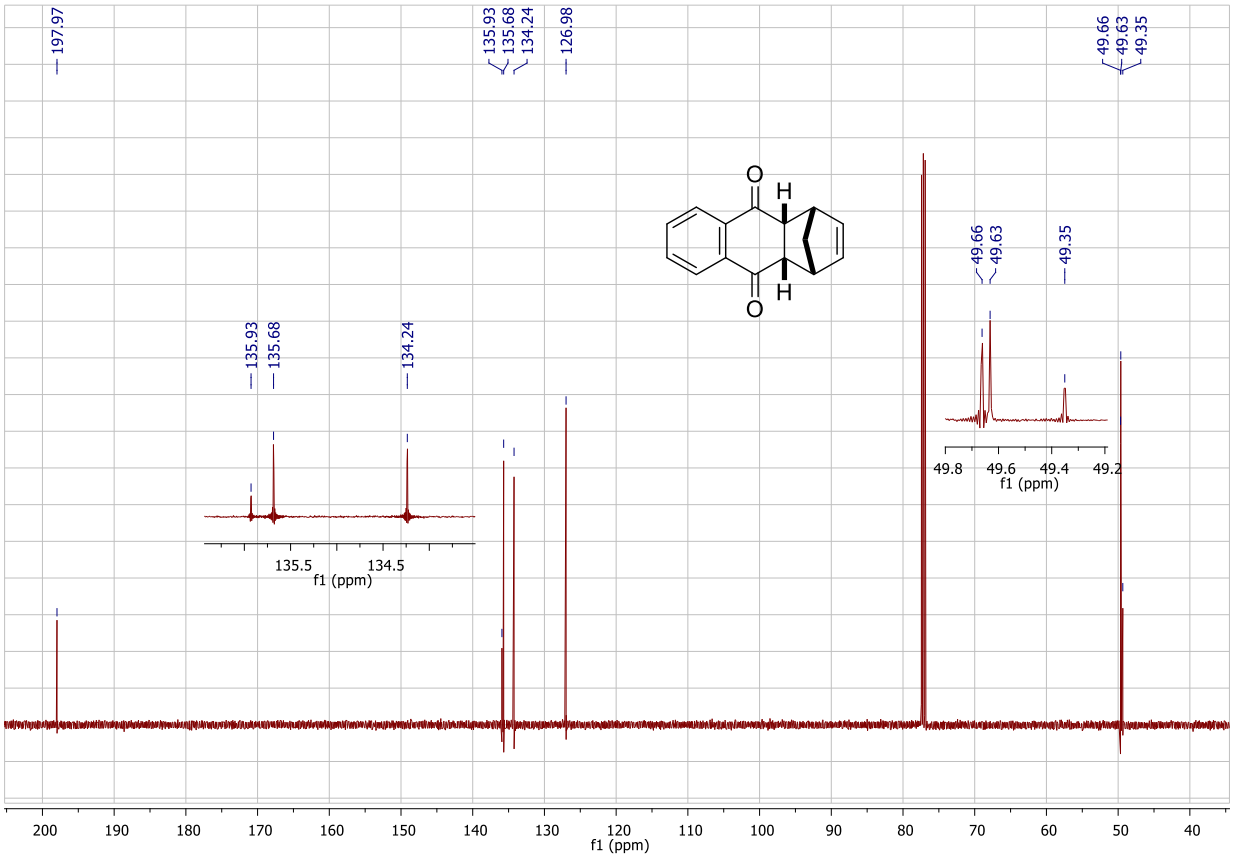




Experimental data for compound **6b** were in agreement with those found in the literature.[12]

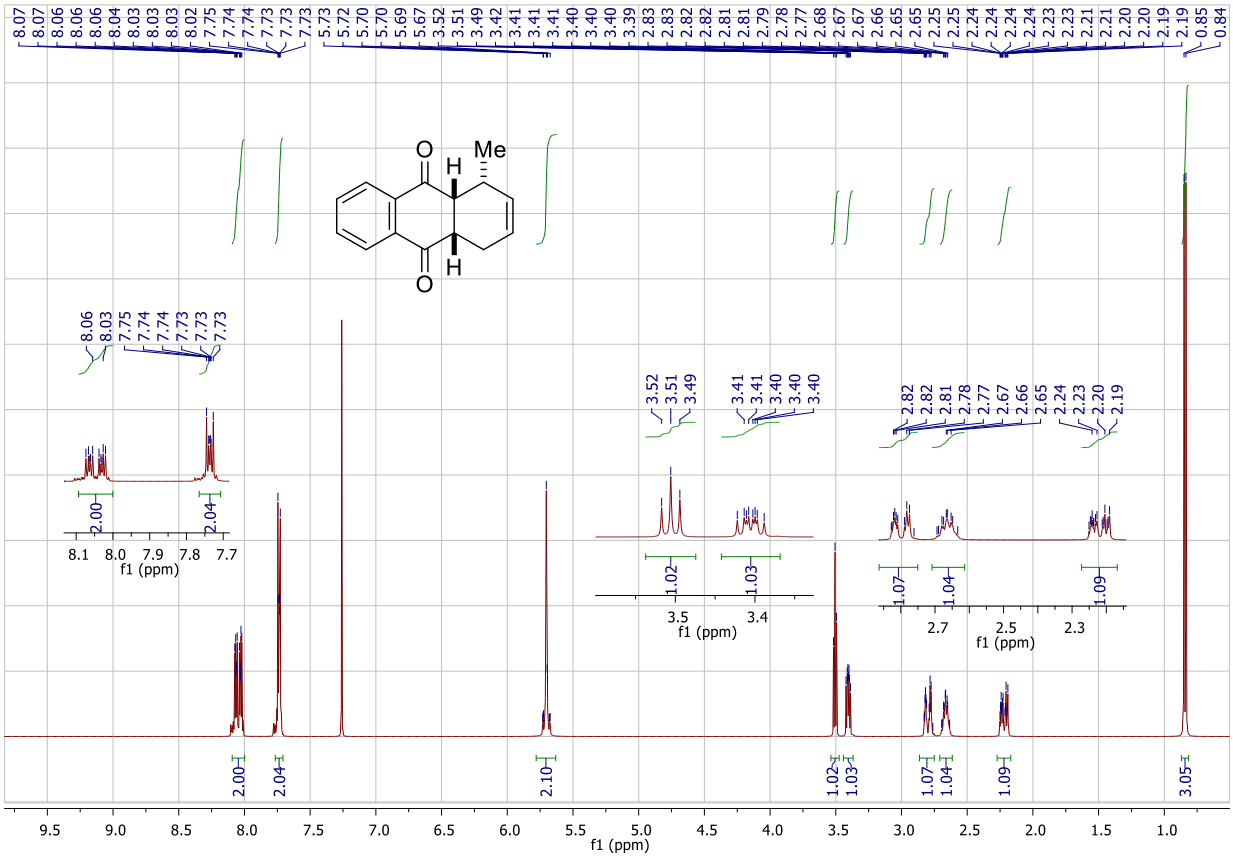
^{1}H and ^{13}C NMR spectra for (1*R*,4*S*,4a*R*,9a*S*)-1,4,4a,9a-tetrahydro-1,4-methanoanthracene-9,10-dione (**3c**) in $CDCl_3$ (500 and 125 MHz)

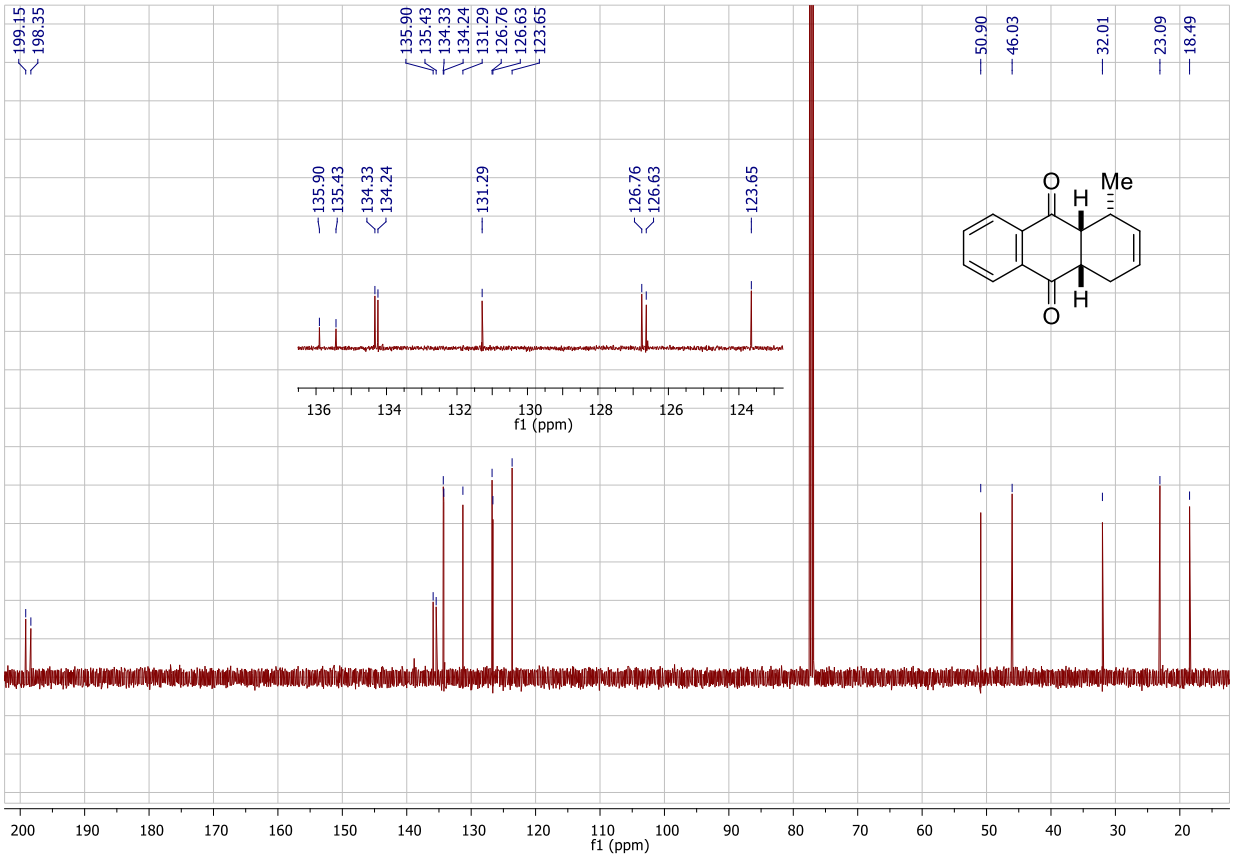




Experimental data for compound **3c** were in agreement with those found in the literature.[13]

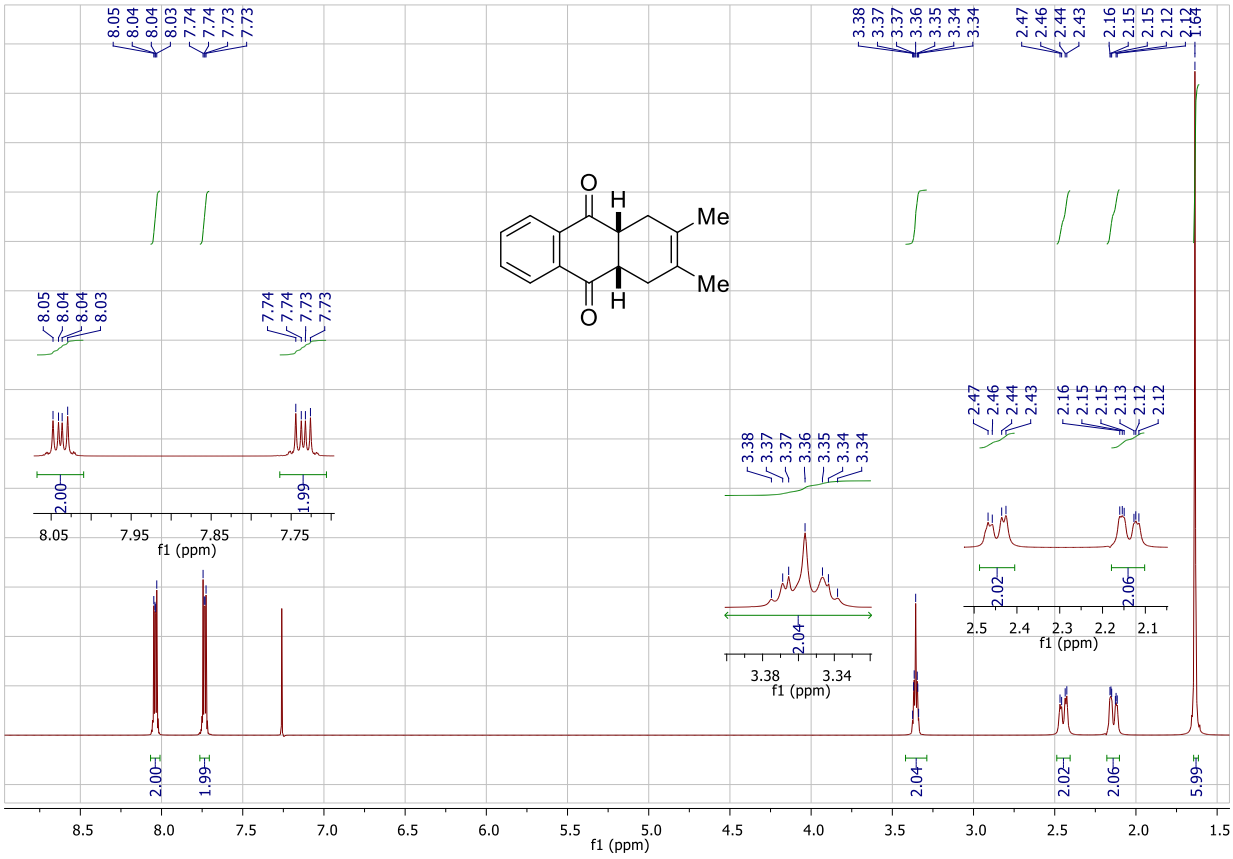
^{1}H and ^{13}C NMR spectra for (±)-*rel*-(1*R*,4a*S*,9a*R*)-1-methyl-1,4,4a,9a-tetrahydroanthracene-9,10-dione (**5c**) in $CDCl_3$ (500 and 125 MHz)

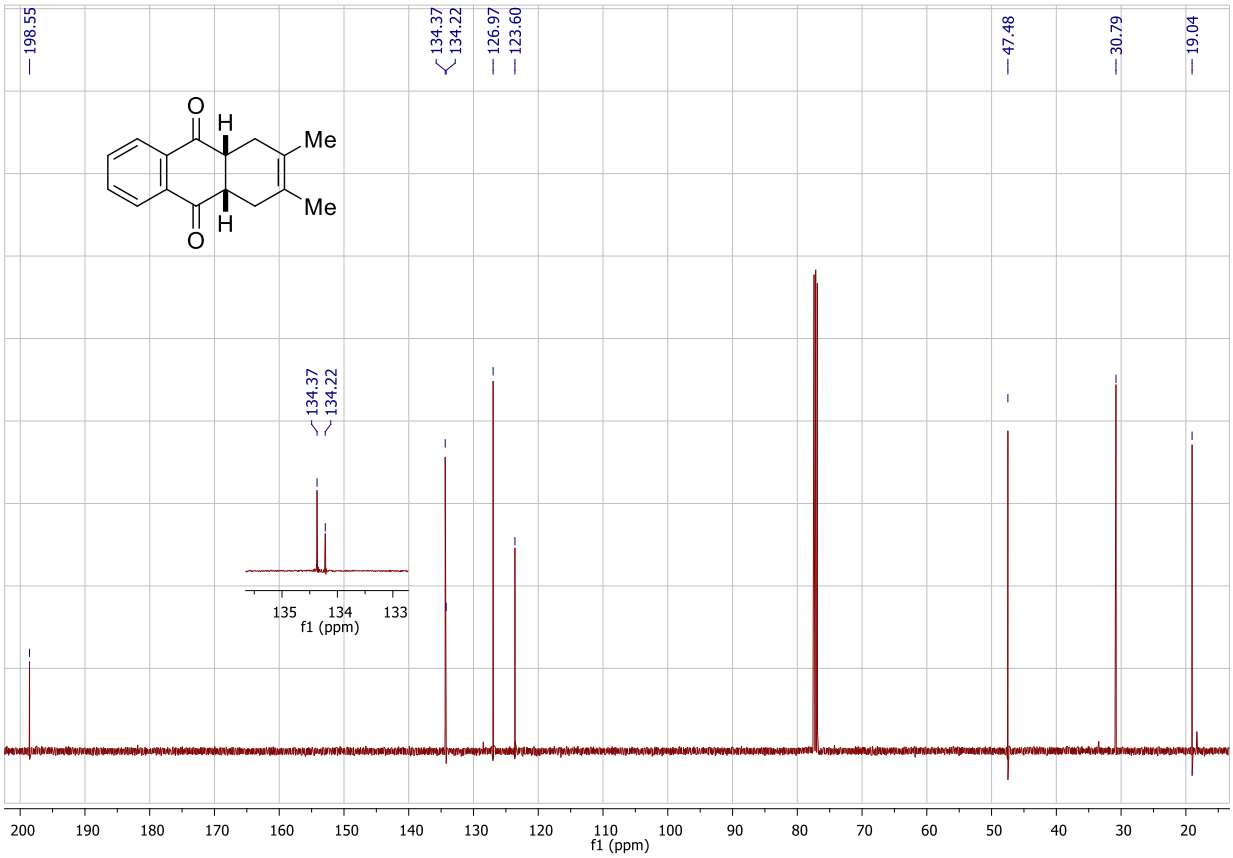




Experimental data for compound **5c** were in agreement with those found in the literature.[14]

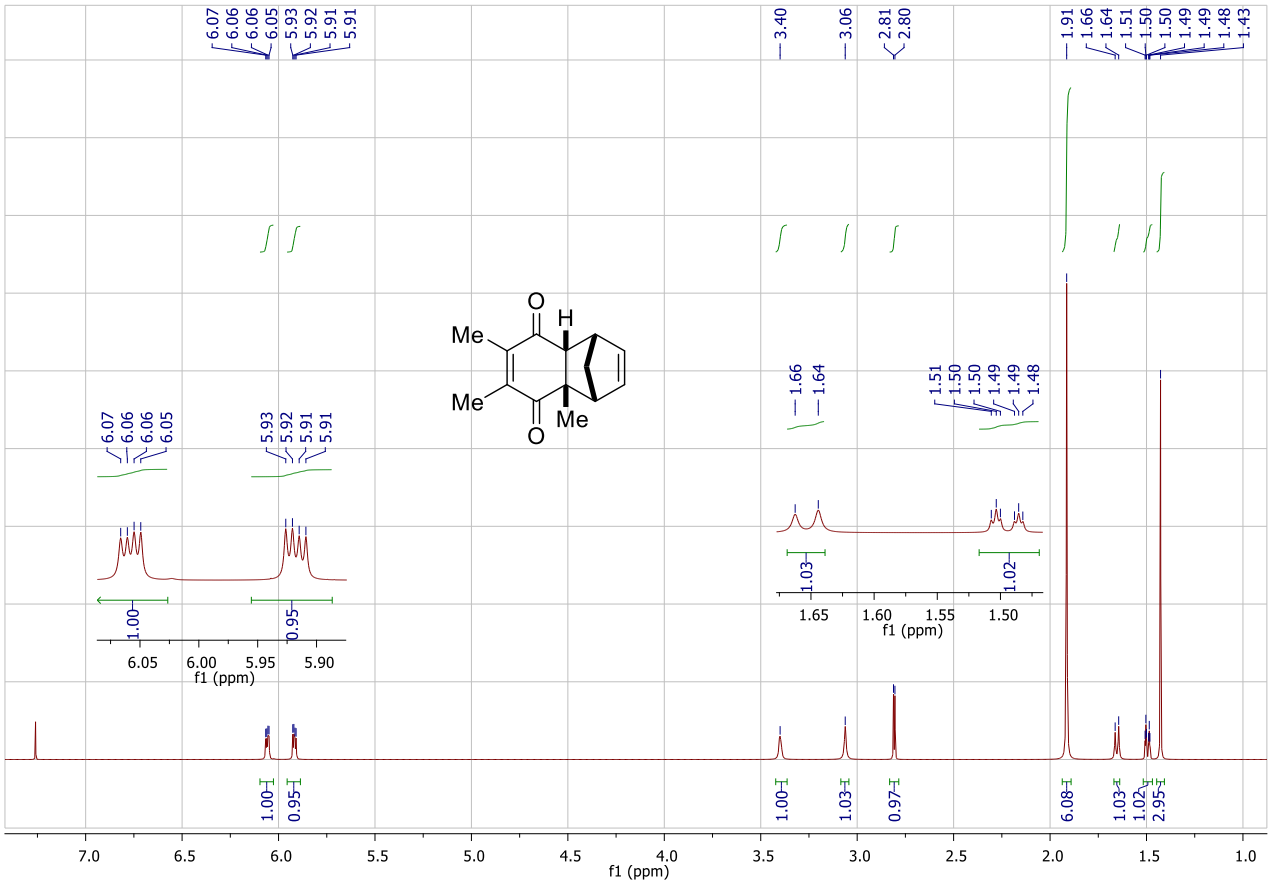
^{1}H and ^{13}C NMR spectra for (4a*R*,9a*S*)-2,3-dimethyl-1,4,4a,9a-tetrahydroanthracene-9,10-dione (**6c**) in $CDCl_3$ (500 and 125 MHz)

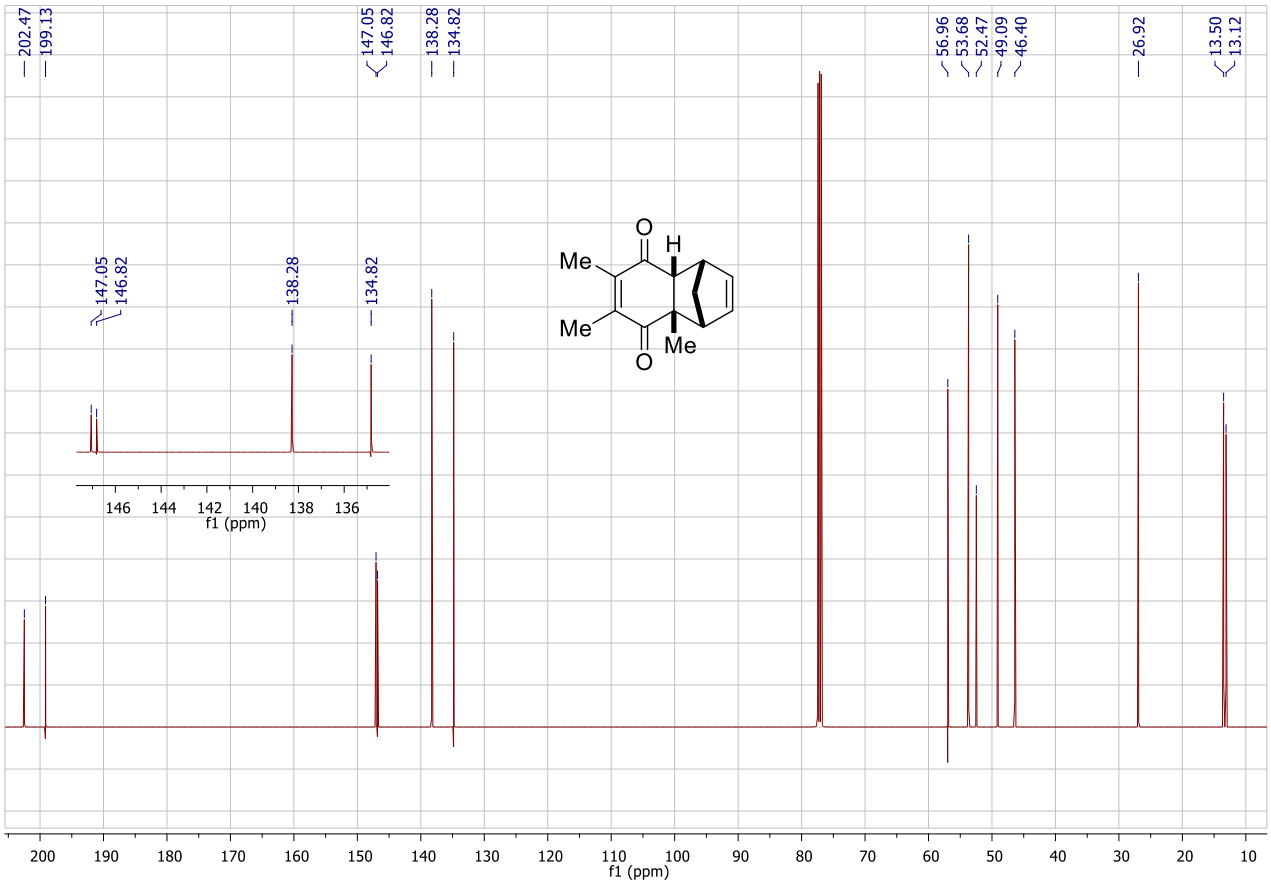




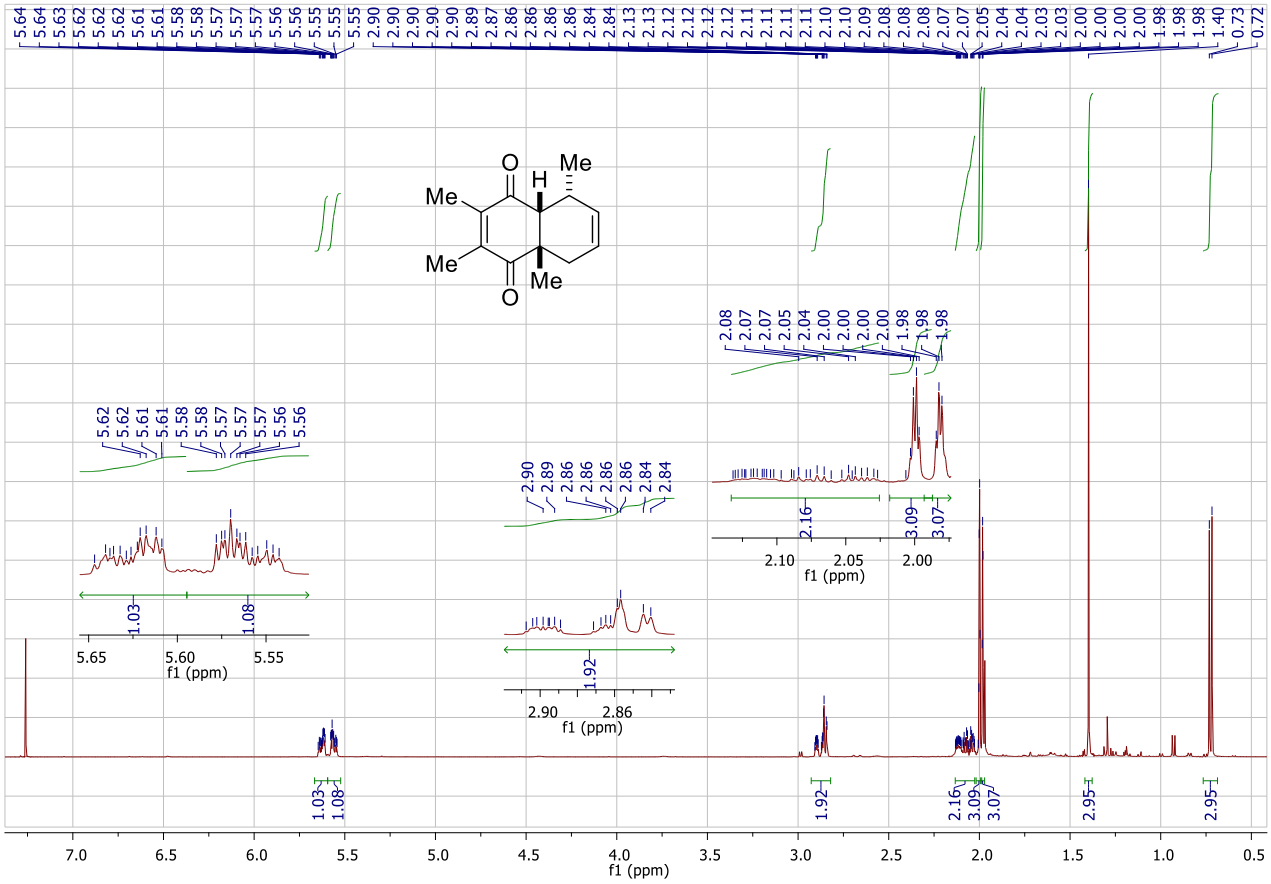
Experimental data for compound **6c** were in agreement with those found in the literature.[12]

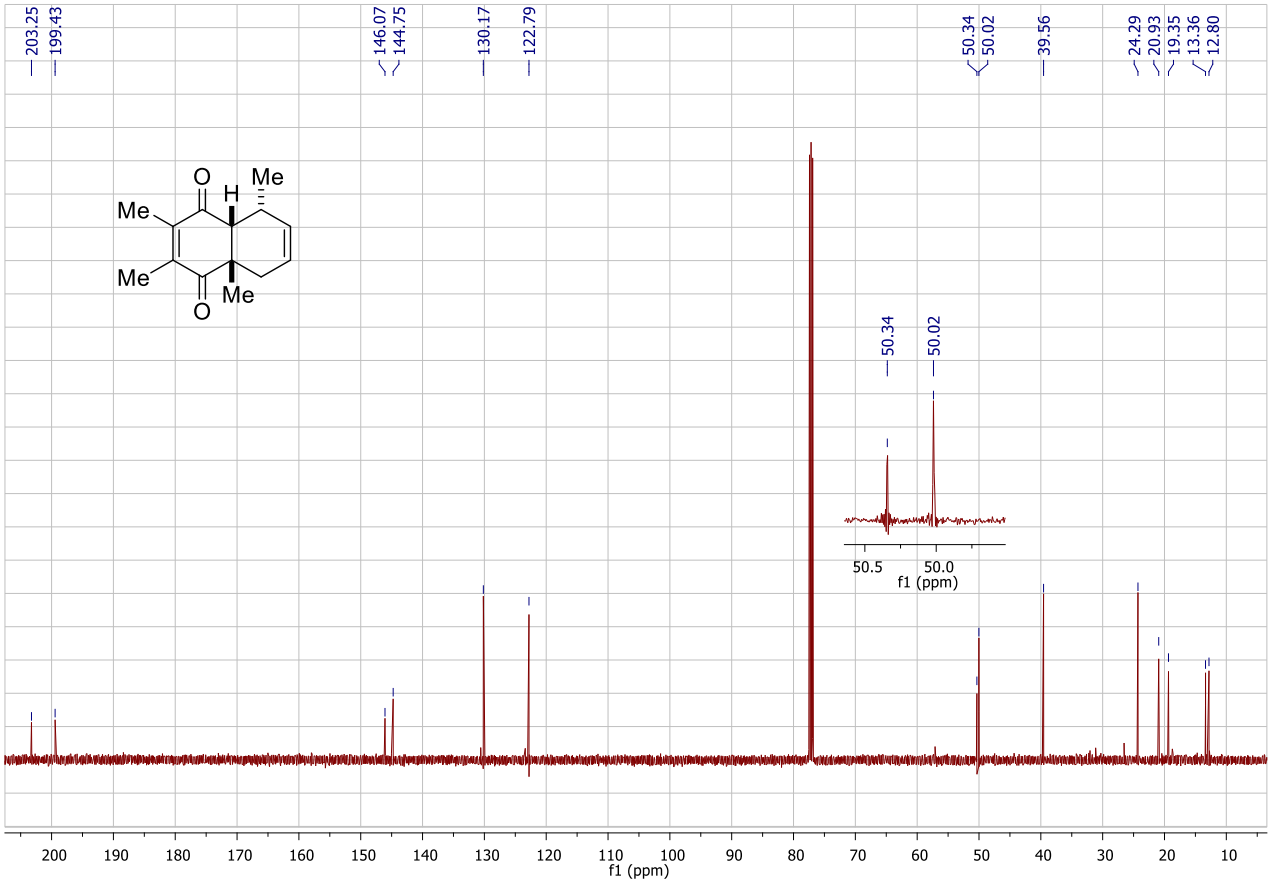
^{1}H and ^{13}C NMR spectra of (±)-*rel*-(1*R*,4*S*,4a*R*,8a*S*)-4a,6,7-trimethyl-1,4,4a,4a,8a-tetrahydro-1,4-methanonaphthalene-5,8-dione (**3d**) in $CDCl_3$ (500 and 125 MHz)



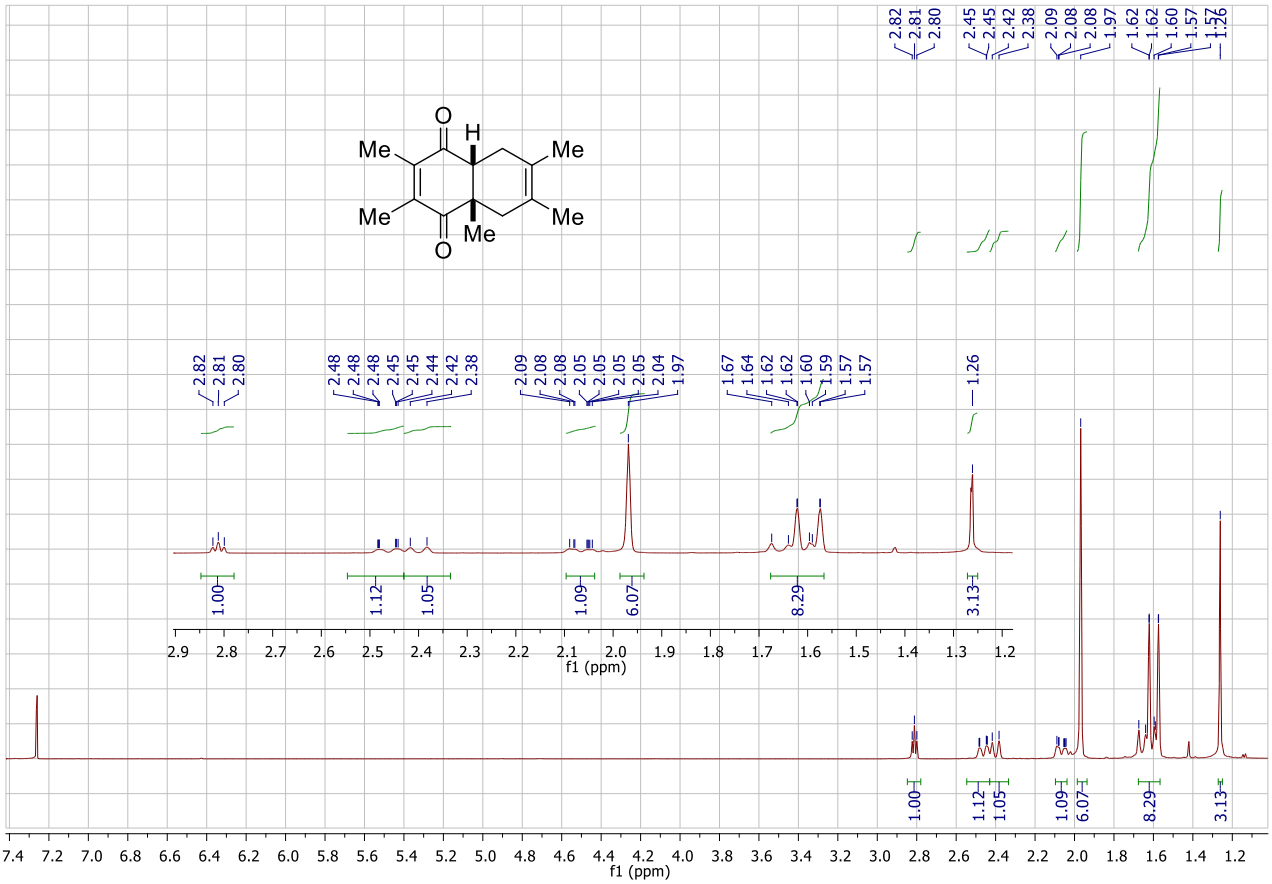


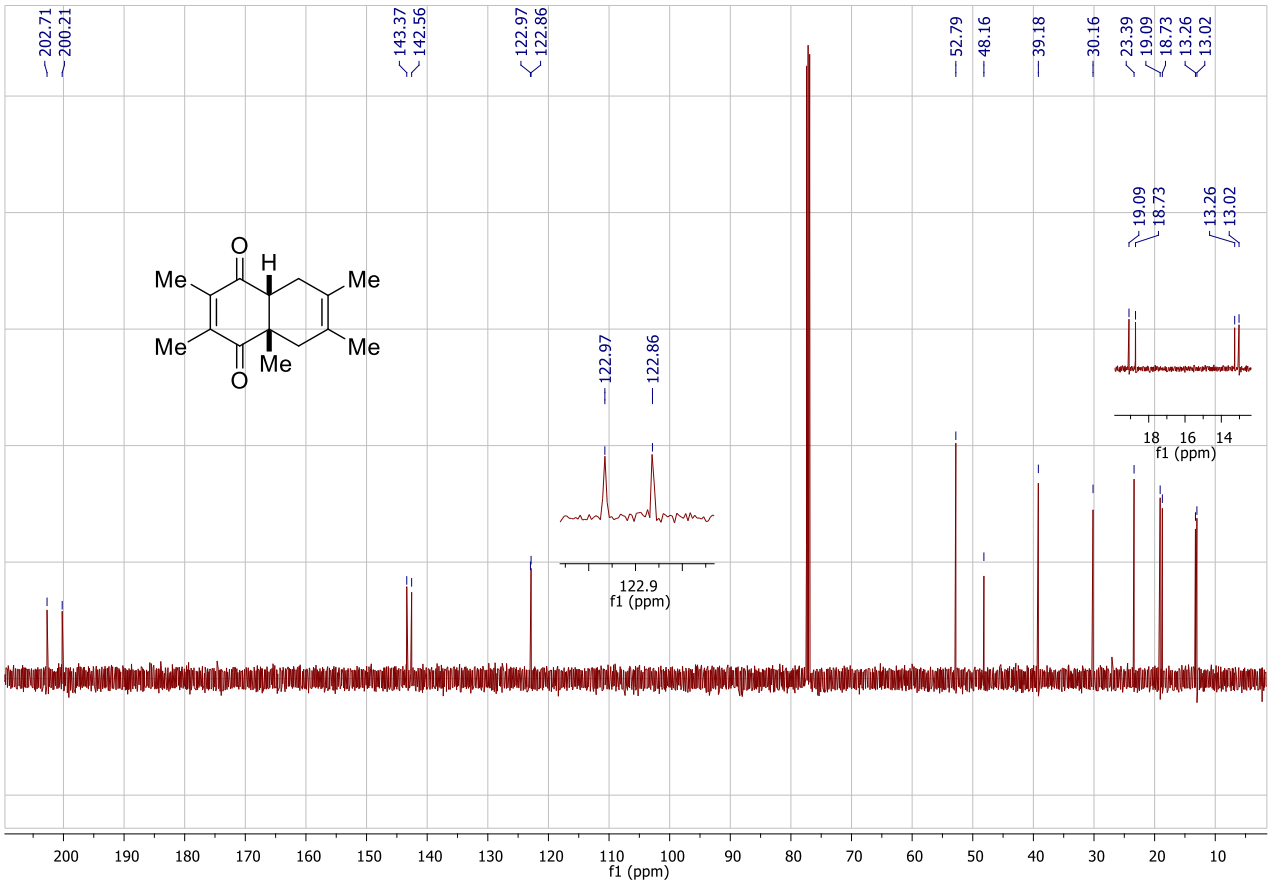
^{1}H and ^{13}C NMR spectra for (±)-*rel*-(4a*R*,8*S*,8a*S*)-2,3,4a,8-tetramethyl-4a,5,8,8a-tetrahydronaphthalene-1,4-dione (**5d**) in $CDCl_3$ (500 and 125 MHz)



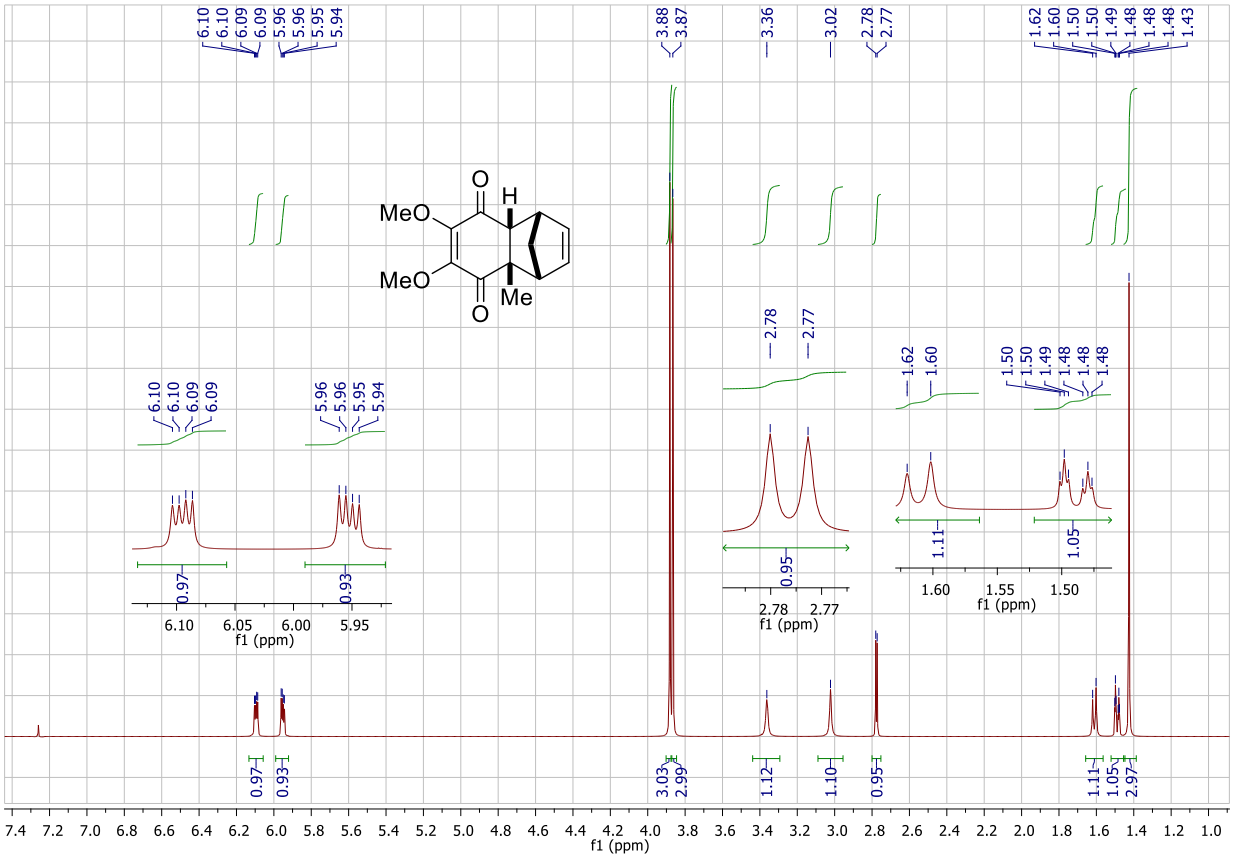


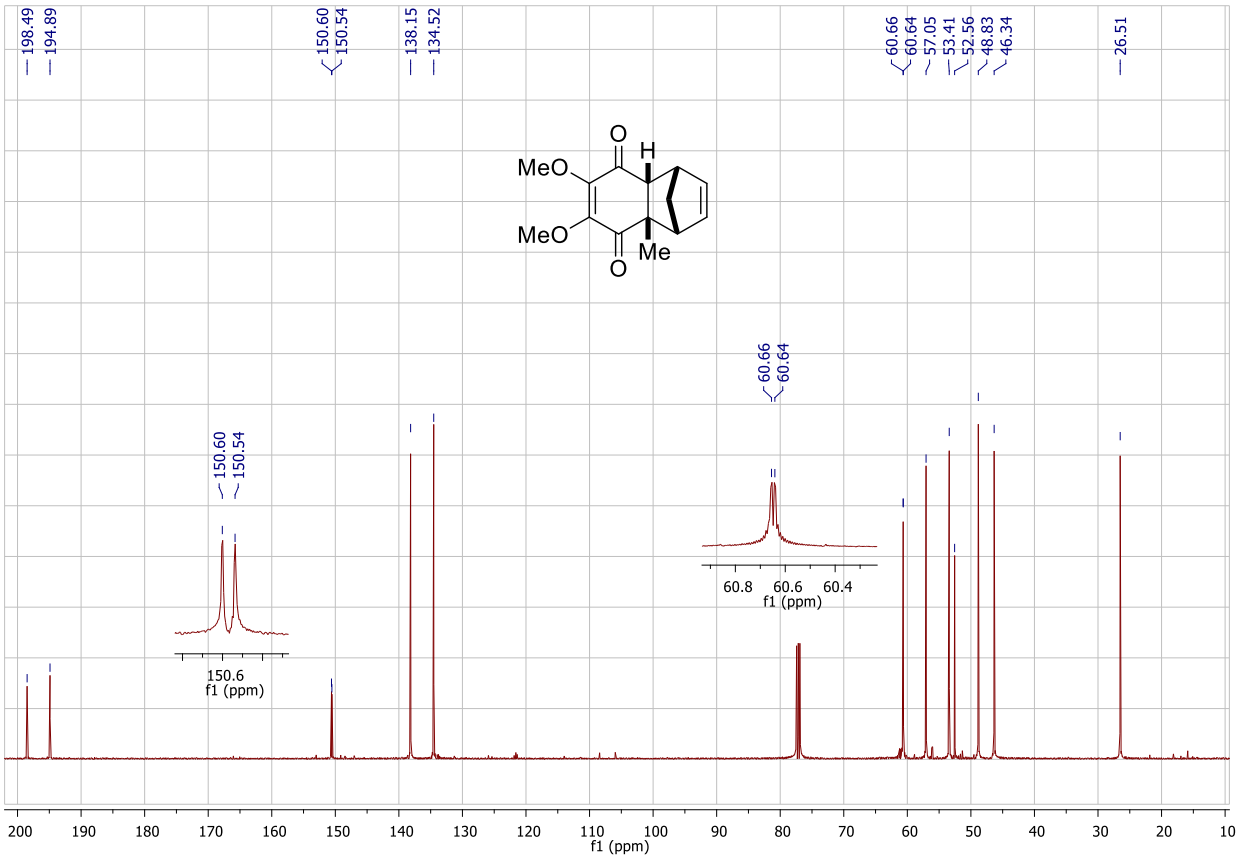
^{1}H and ^{13}C NMR spectra for (±)-*cis*-2,3,4a,6,7-pentamethyl-4a,5,8,8a-tetrahydronaphthalene-1,4-dione (**6d**) in $CDCl_3$ (500 and 125 MHz)





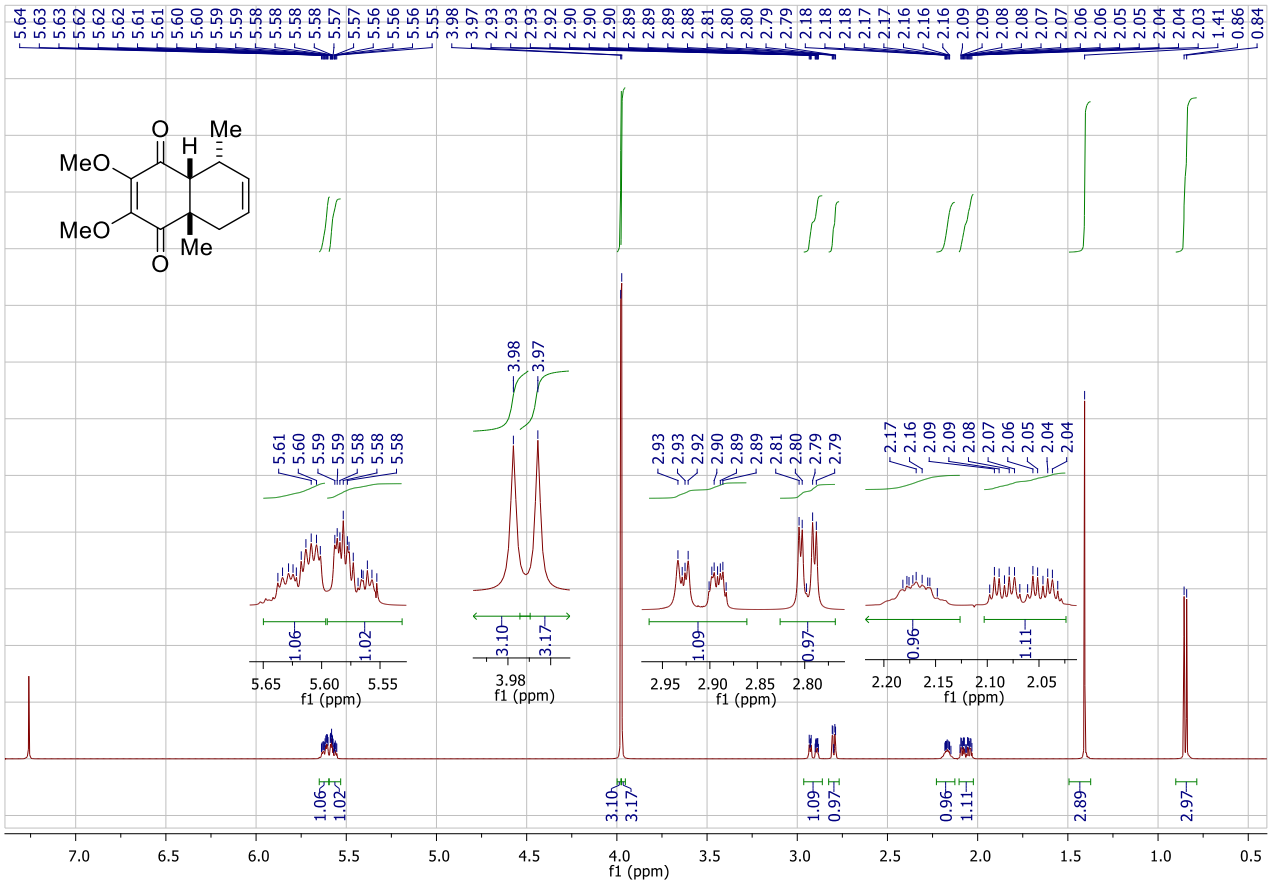
^{1}H and ^{13}C NMR spectra for (±)-*rel*-(1*R*,4*S*,4a*R*,8a*S*)-6,7-dimethoxy-4a-methyl-1,4,4a,8a-tetrahydro-1,4-methanonaphthalene-5,8-dione (**3e**) in $CDCl_3$ (500 and 125 MHz)

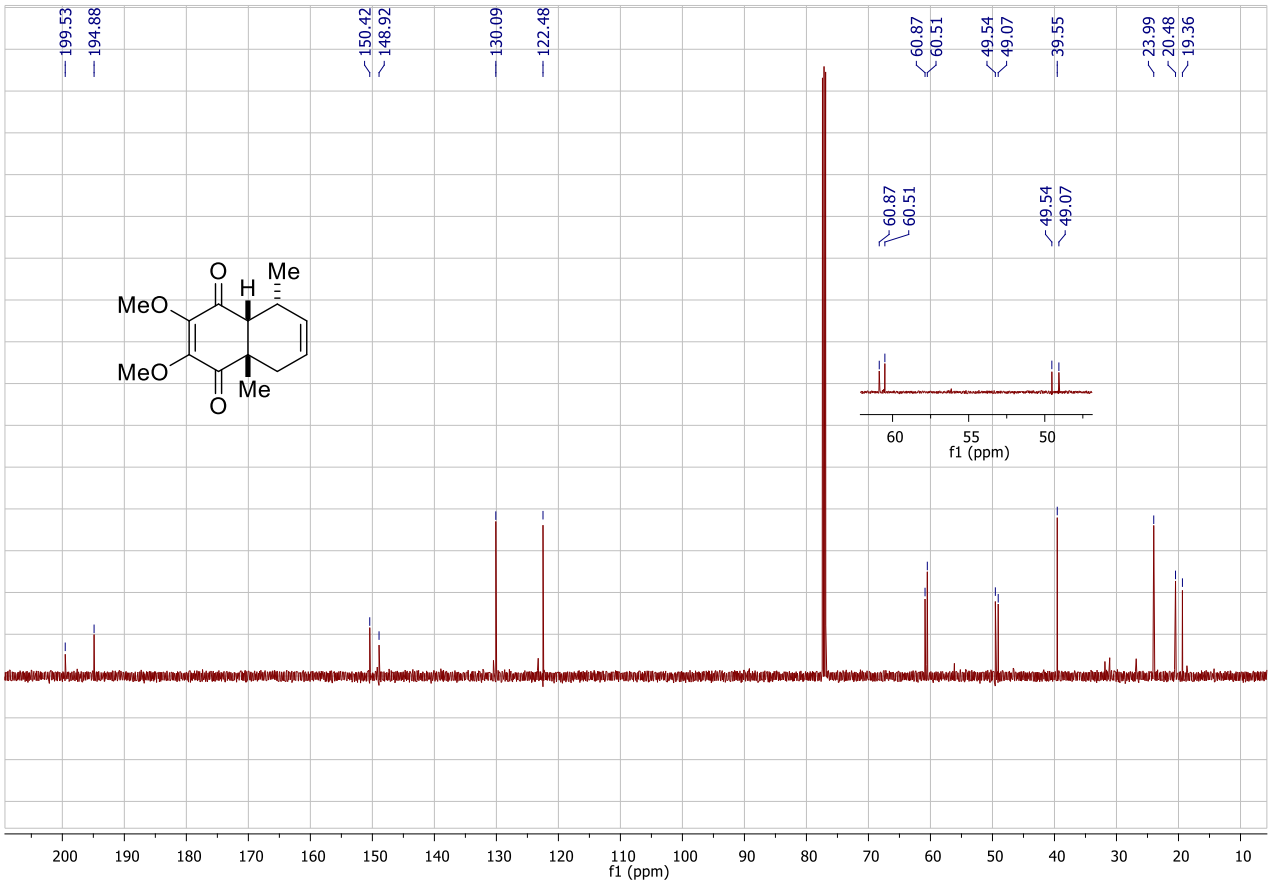




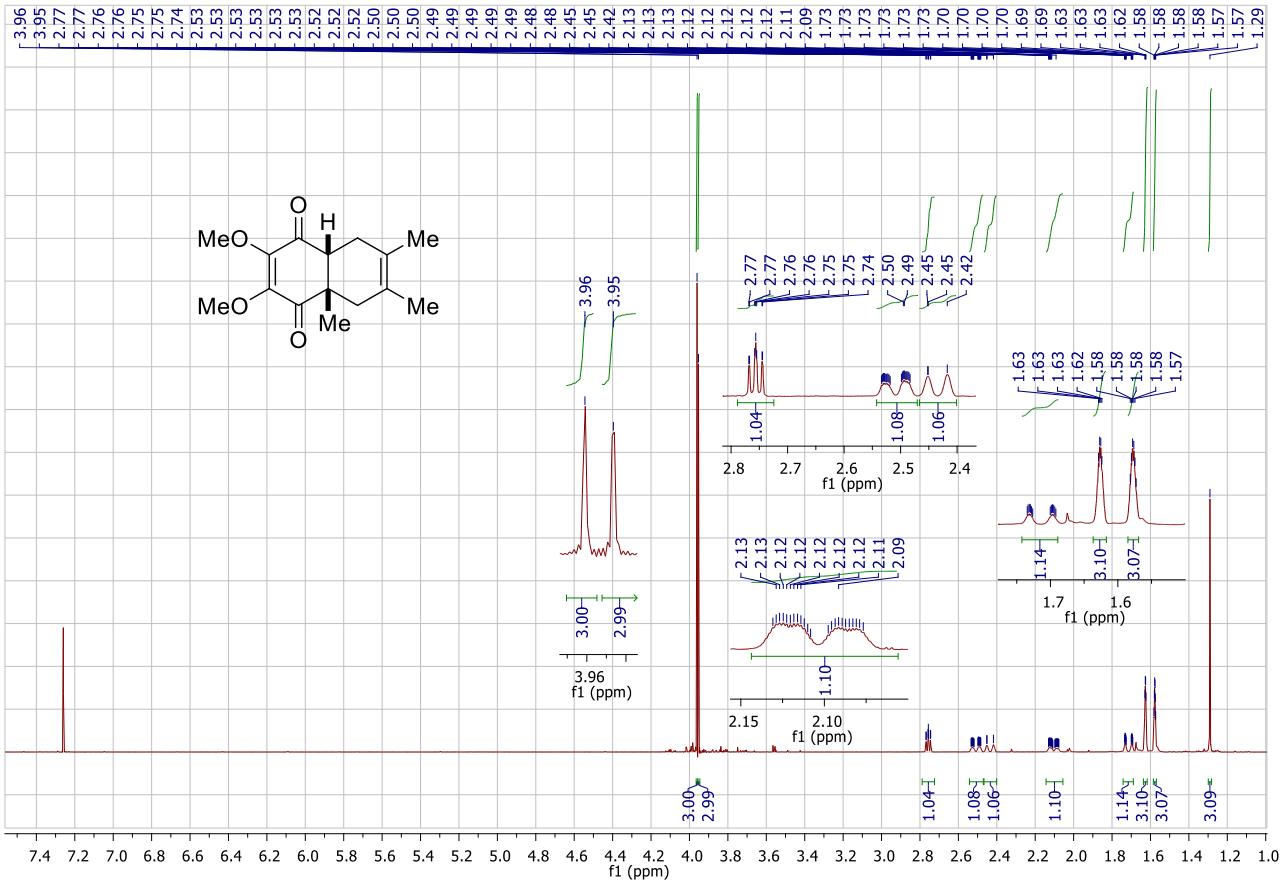
Experimental data for compound **3e** were in agreement with those found in the literature.[4]

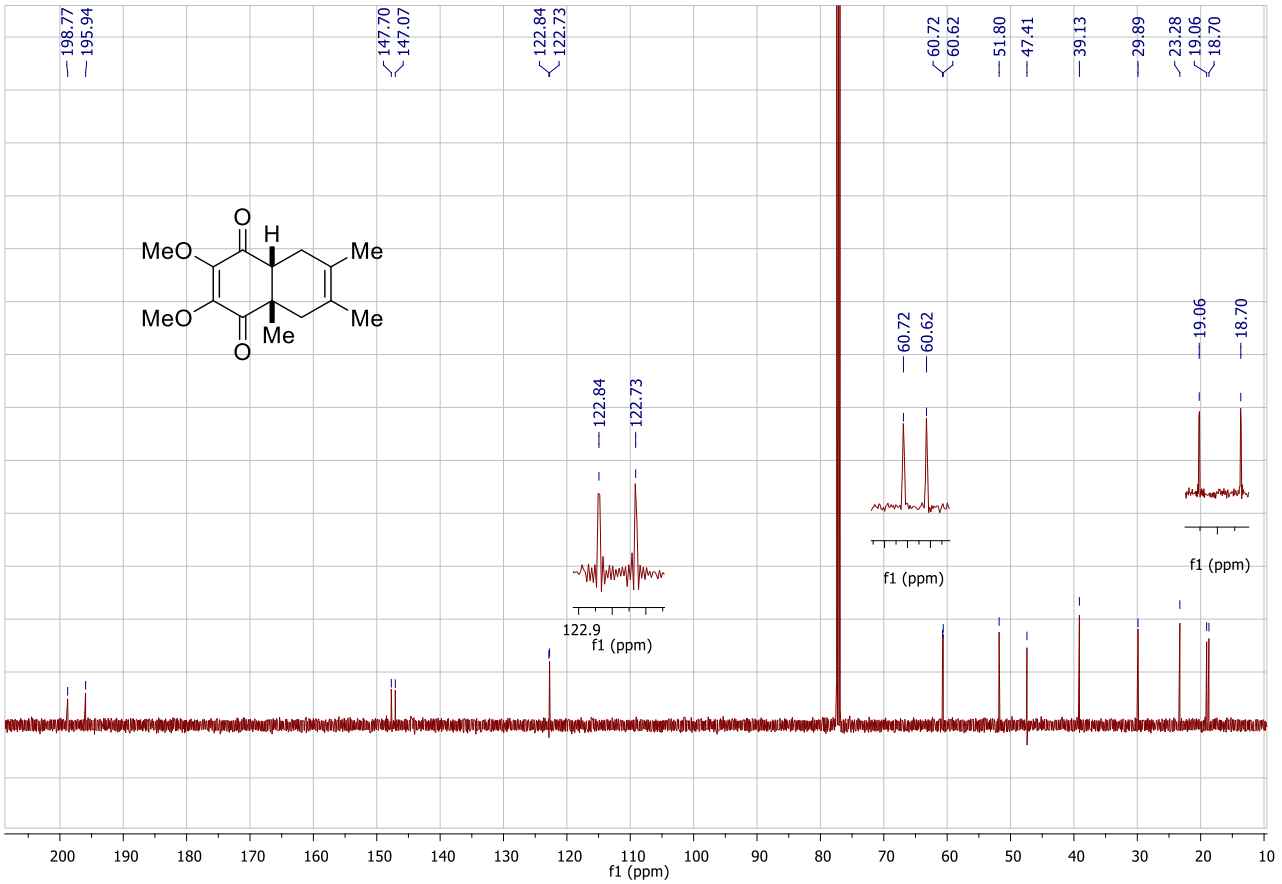
^{1}H and ^{13}C NMR spectra for (±)-*rel*-(4a*R*,8*S*,8a*S*)-2,3-dimethoxy-4a,8-dimethyl-4a,5,8,8a-tetrahydronaphthalene-1,4-dione (**5e**) in $CDCl_3$ (500 and 125 MHz)



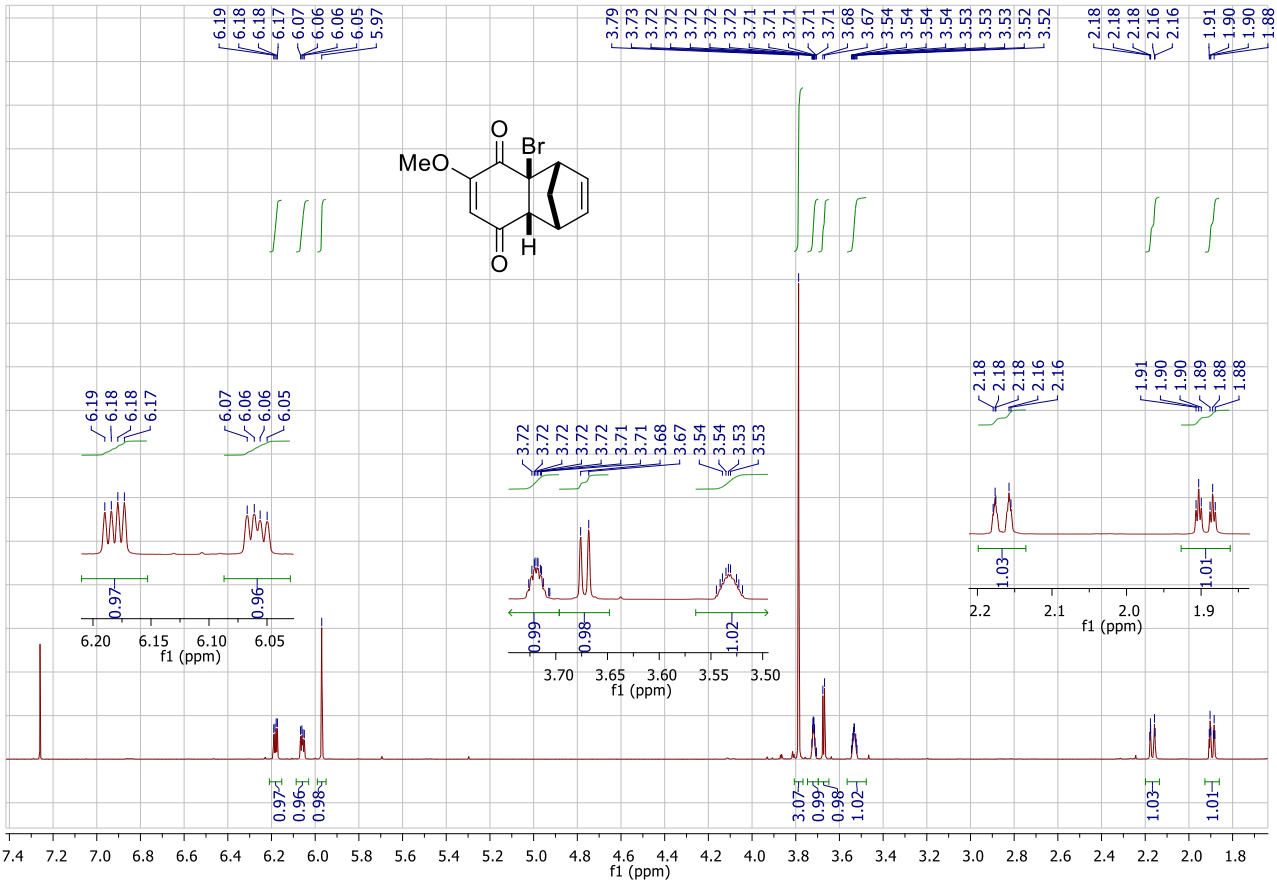


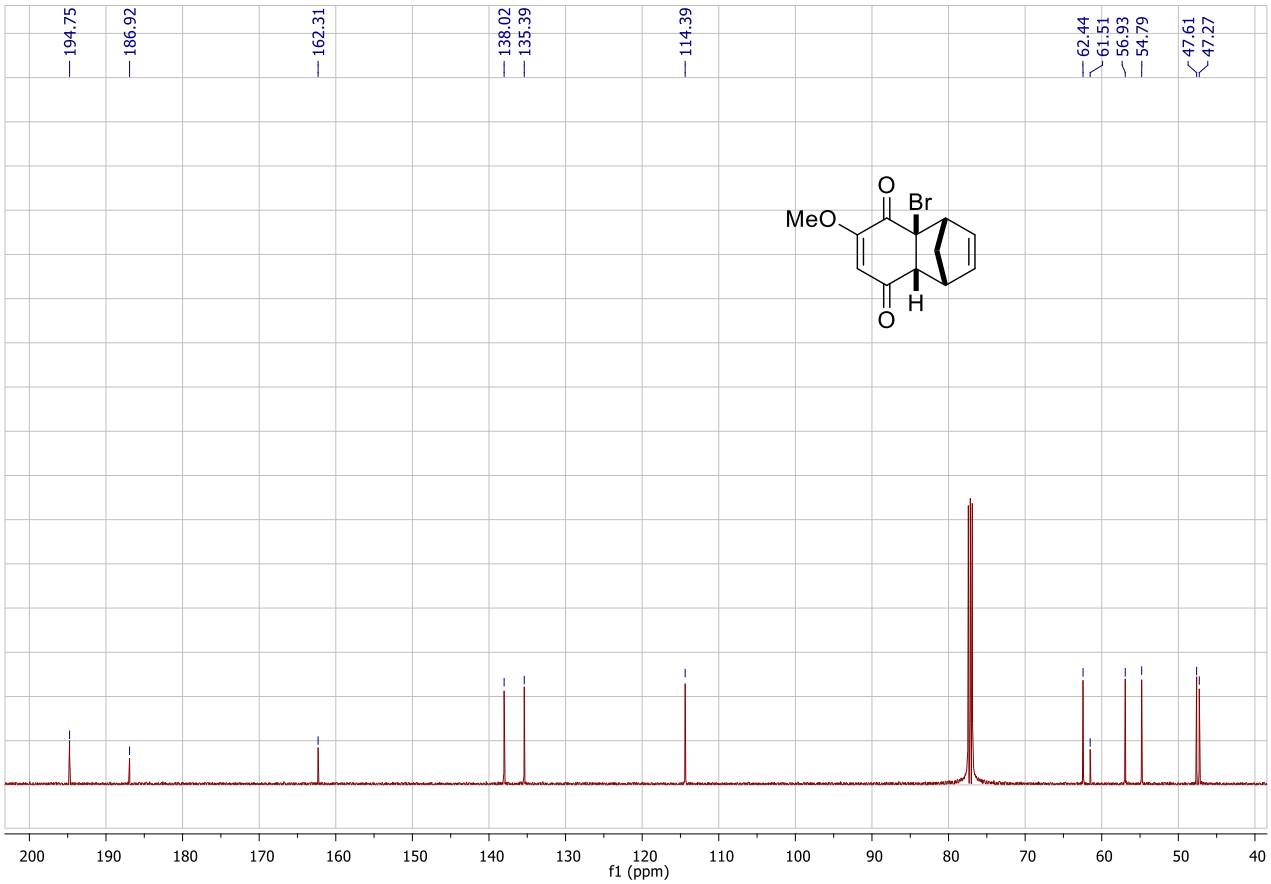
^{1}H and ^{13}C NMR spectra for (±)-*cis*-2,3-dimethyoxy-4a,6,7-trimethyl-4a,5,8,8a-tetrahydronaphthalene-1,4,-dione (**6e**) in $CDCl_3$ (500 and 125 MHz)



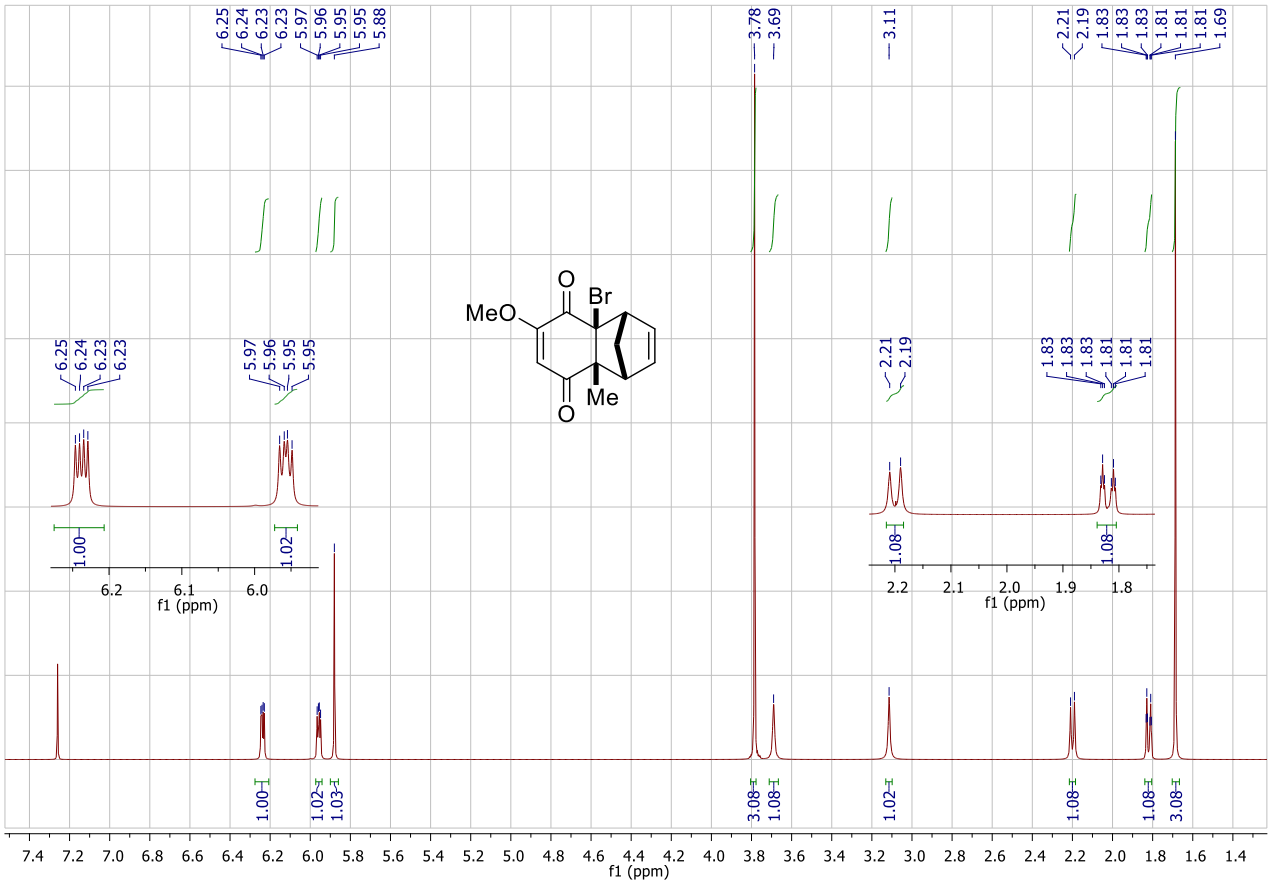


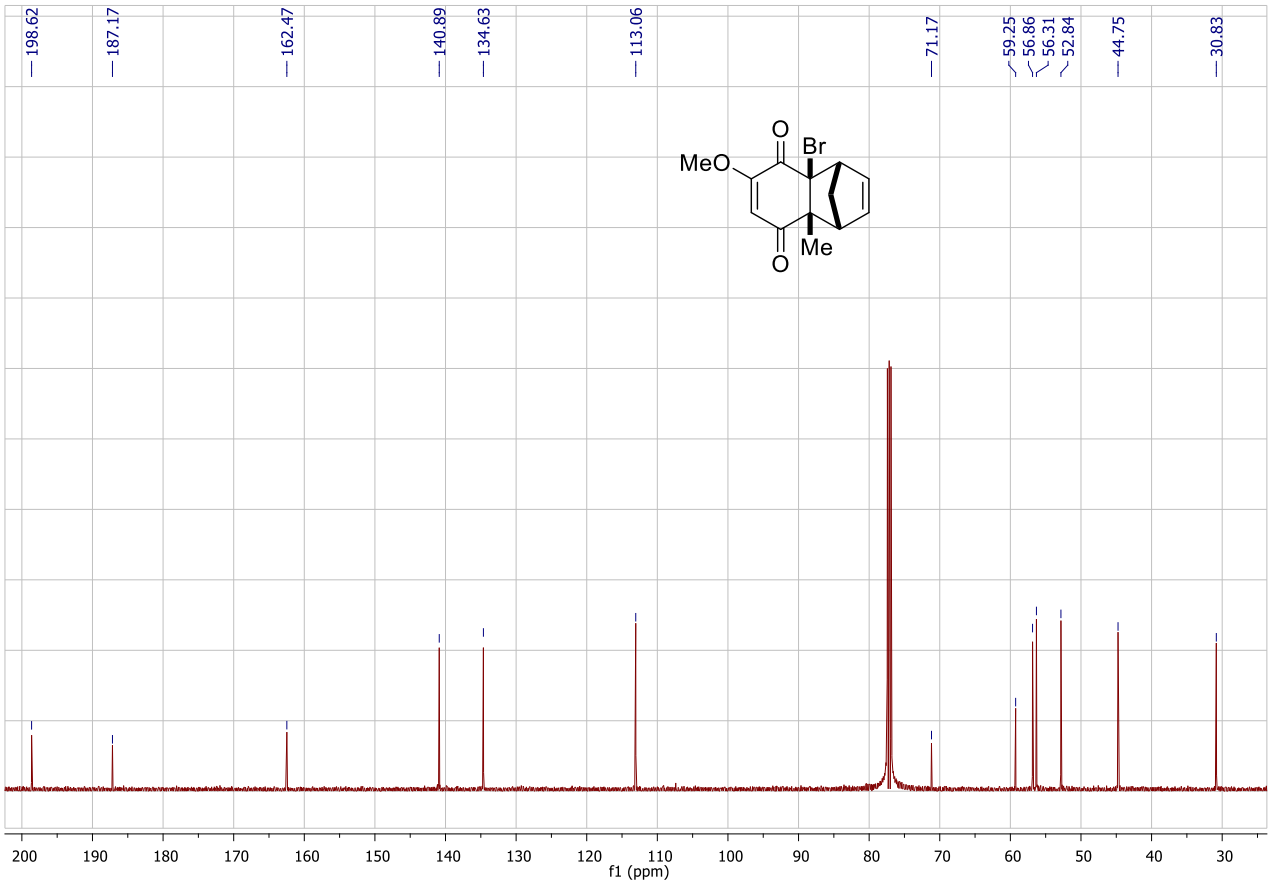
^{1}H and ^{13}C NMR spectra for (±)-*rel*-(1*R*,4*S*,4a*S*,8a*R*)-4a-bromo-6-methoxy-1,4,4a,8a-tetrahydromethanonaphthalene-5,8-dione (**3f**) in $CDCl_3$ (500 and 125 MHz)



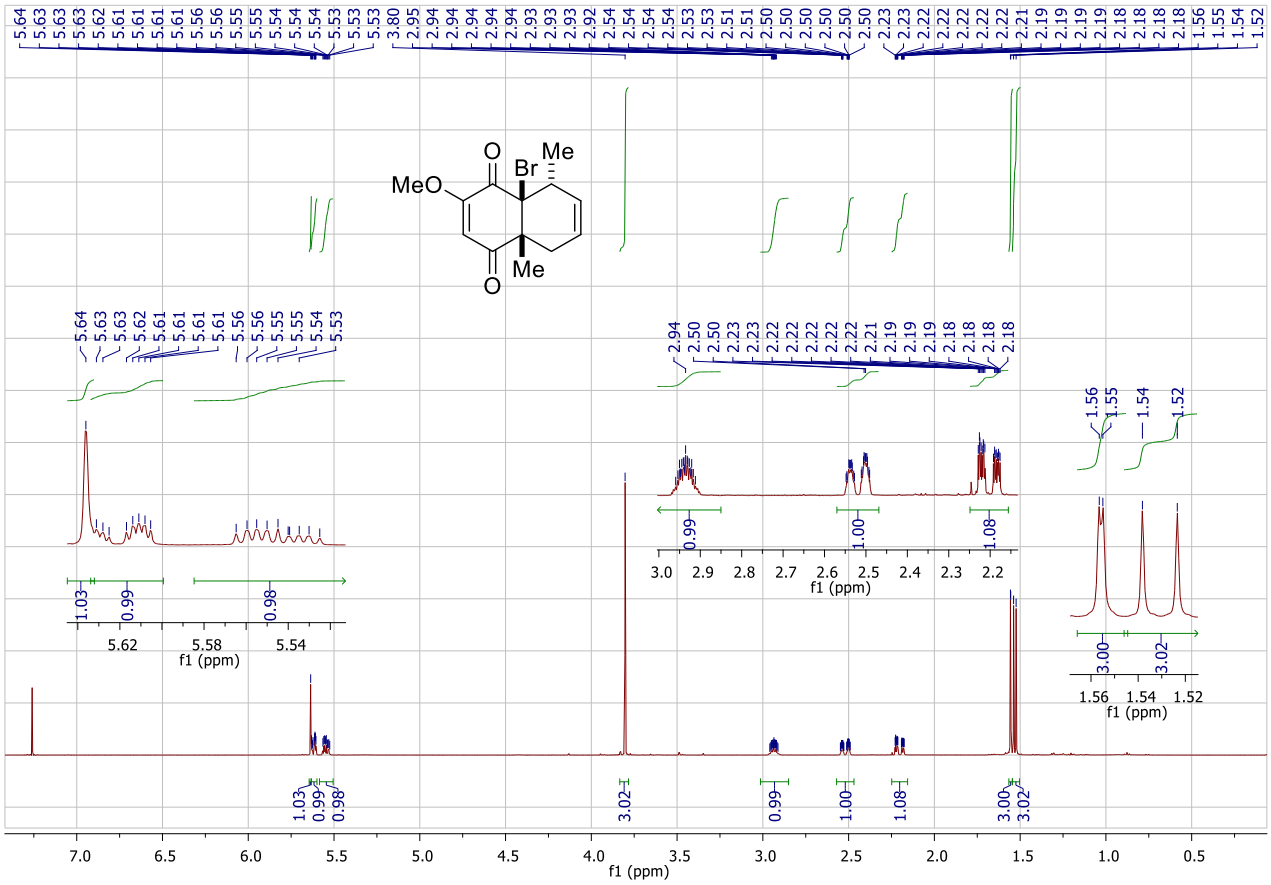


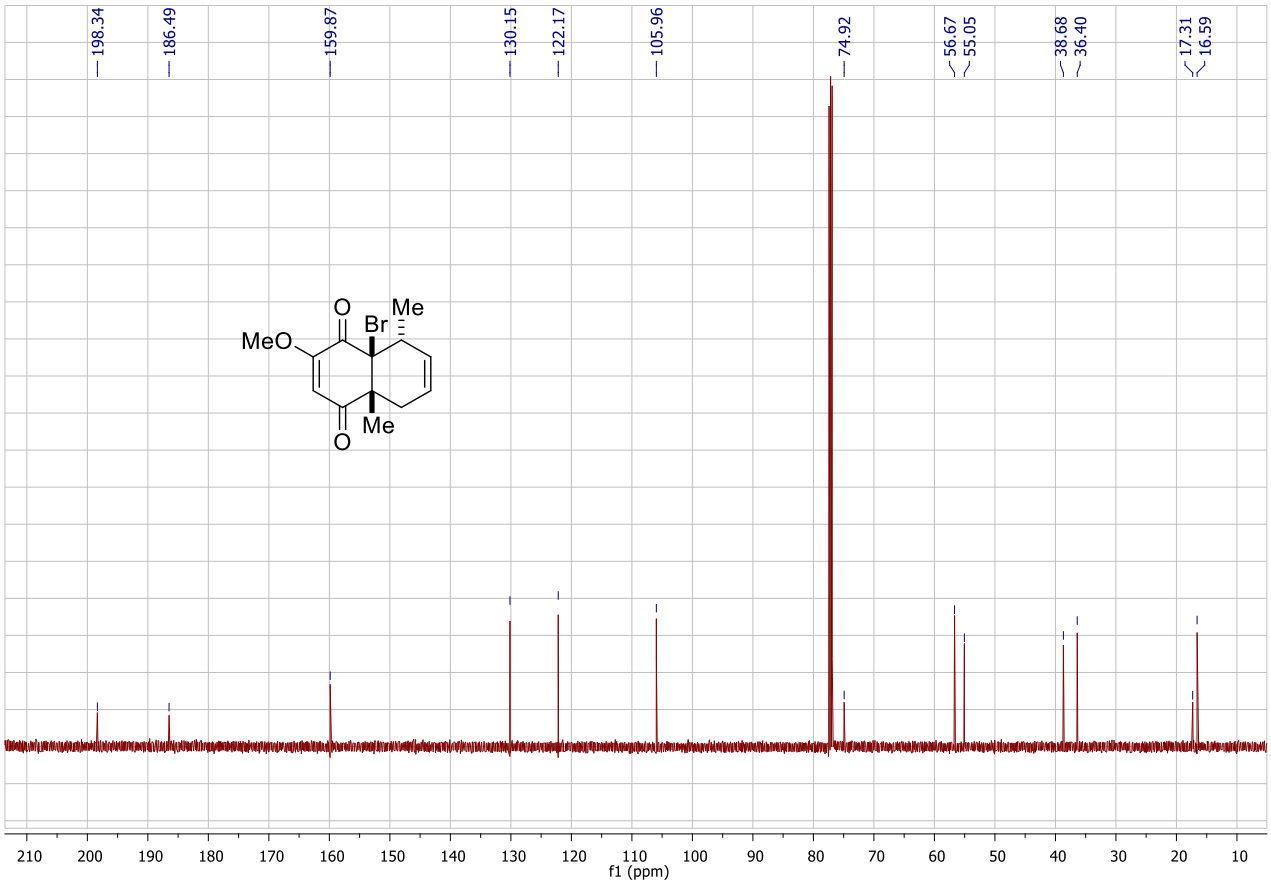
^{1}H and ^{13}C NMR sperctra for (±)-*rel*-(1*R*,4*S*,4a*S*,8a*R*)-4a-bromo-6-methoxy-8a-methyl-1,4,4a,8a-tetrahydro-1,4-methanonaphthalene-5,8-dione (**3g**) in $CDCl_3$ (500 and 125 MHz)



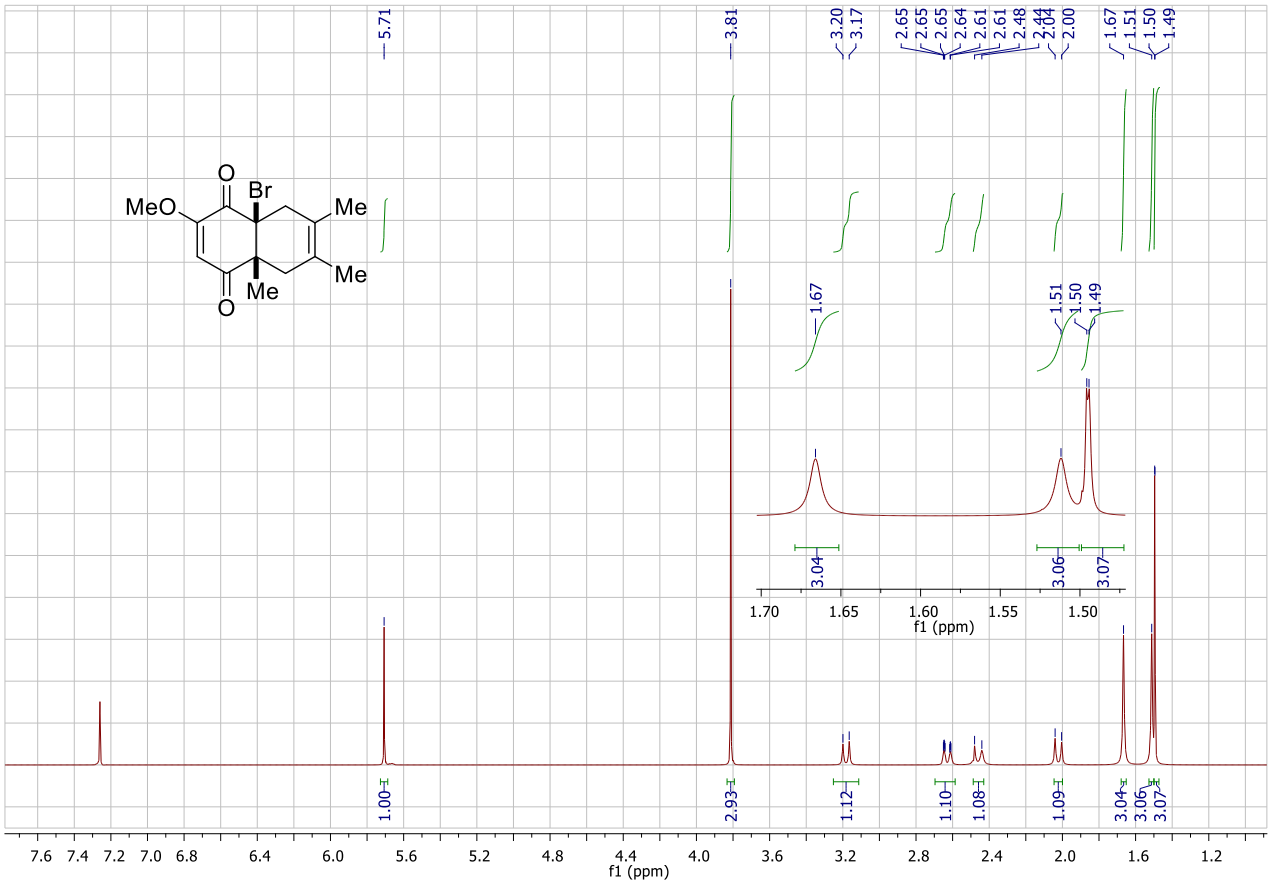


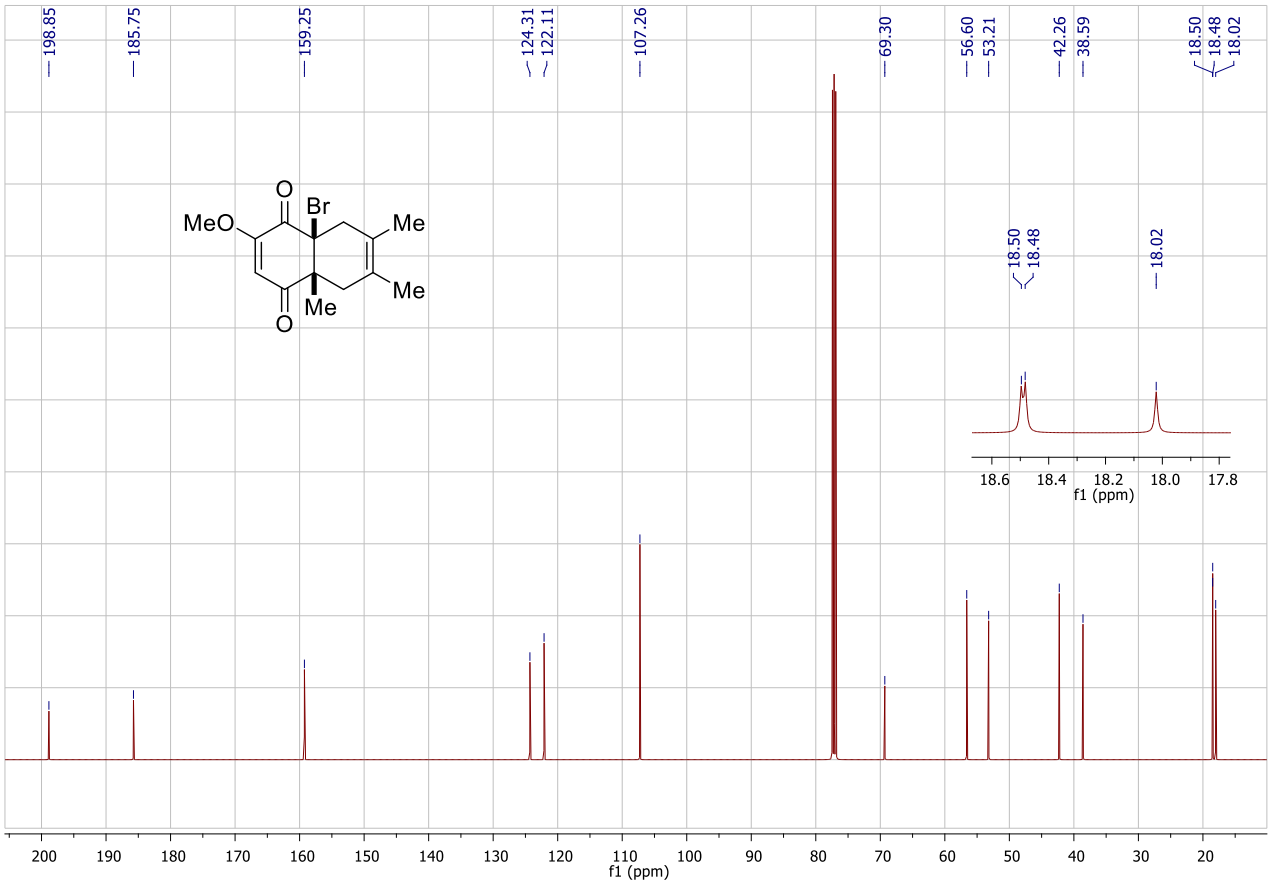
^{1}H and ^{13}C NMR spectra for (±)-*rel*-(4a*R*,8*R*,8a*S*)-8a-bromo-2-methoxy-4a,8-dimethyl-4a,5,8,8a-tetrahydronaphthalene-1,4-dione (**5g**) in $CDCl_3$ (500 and 125 MHz)



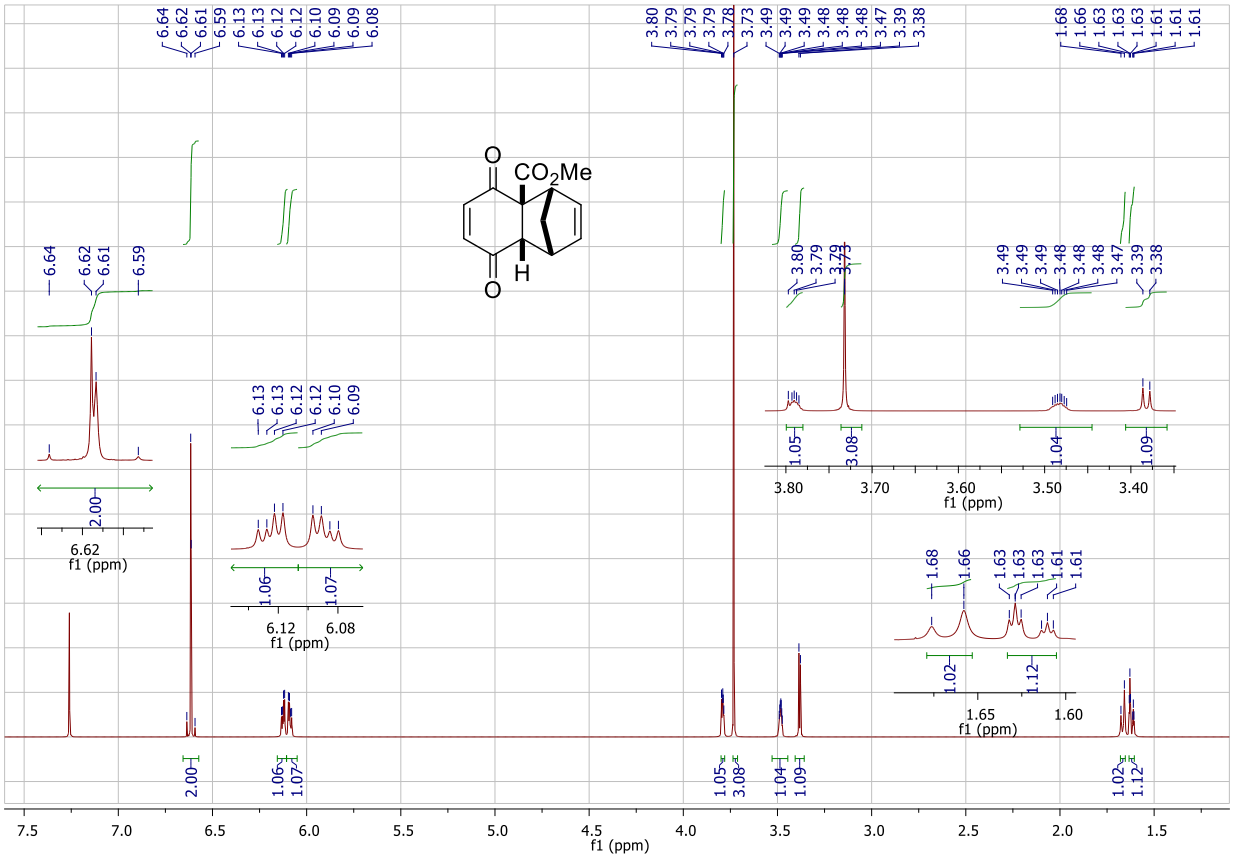


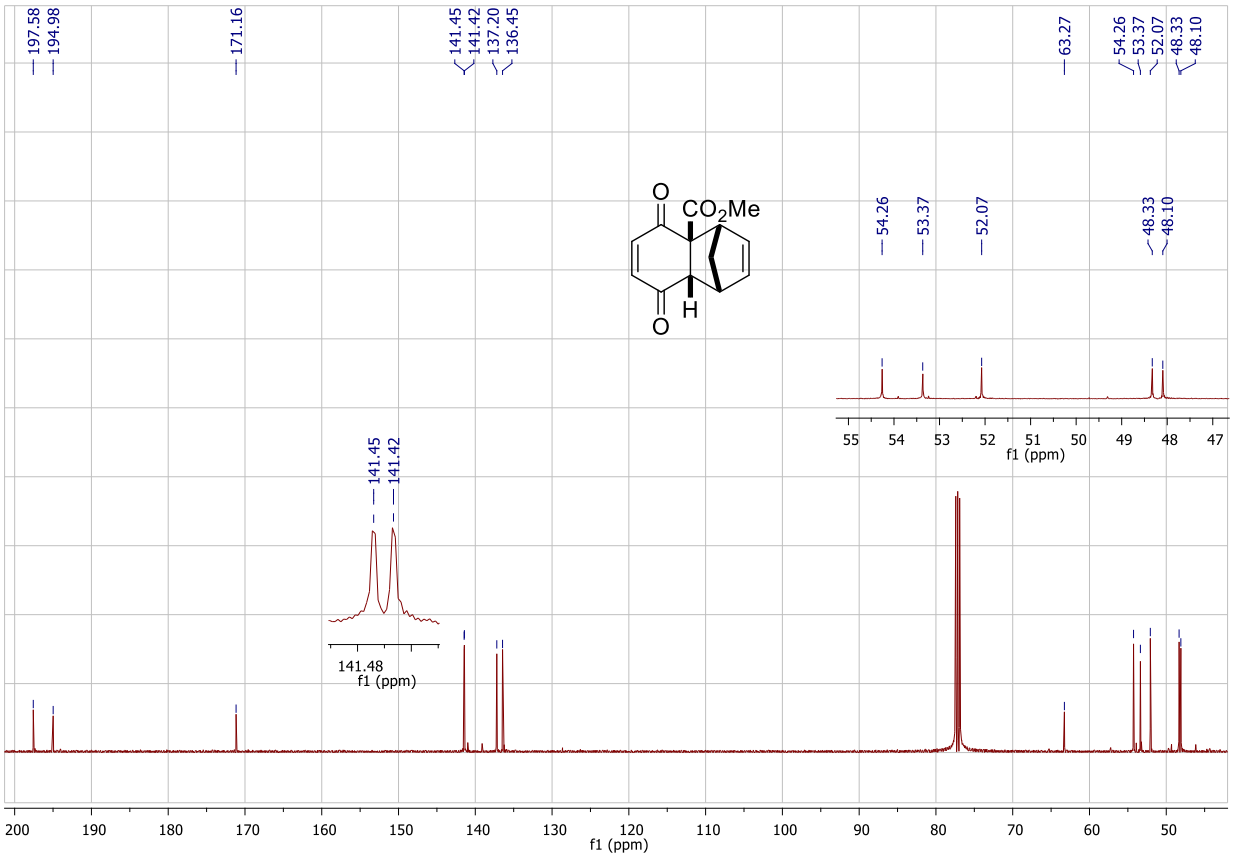
^{1}H and ^{13}C NMR spectra for (±)-*cis*-8a-bromo-2-methoxy-4a,6,7-trimethyl-4a,5,8,8a-tetrahydronaphthalene-1,4-dione (**6g**) in $CDCl_3$ (500 and 125 MHz)





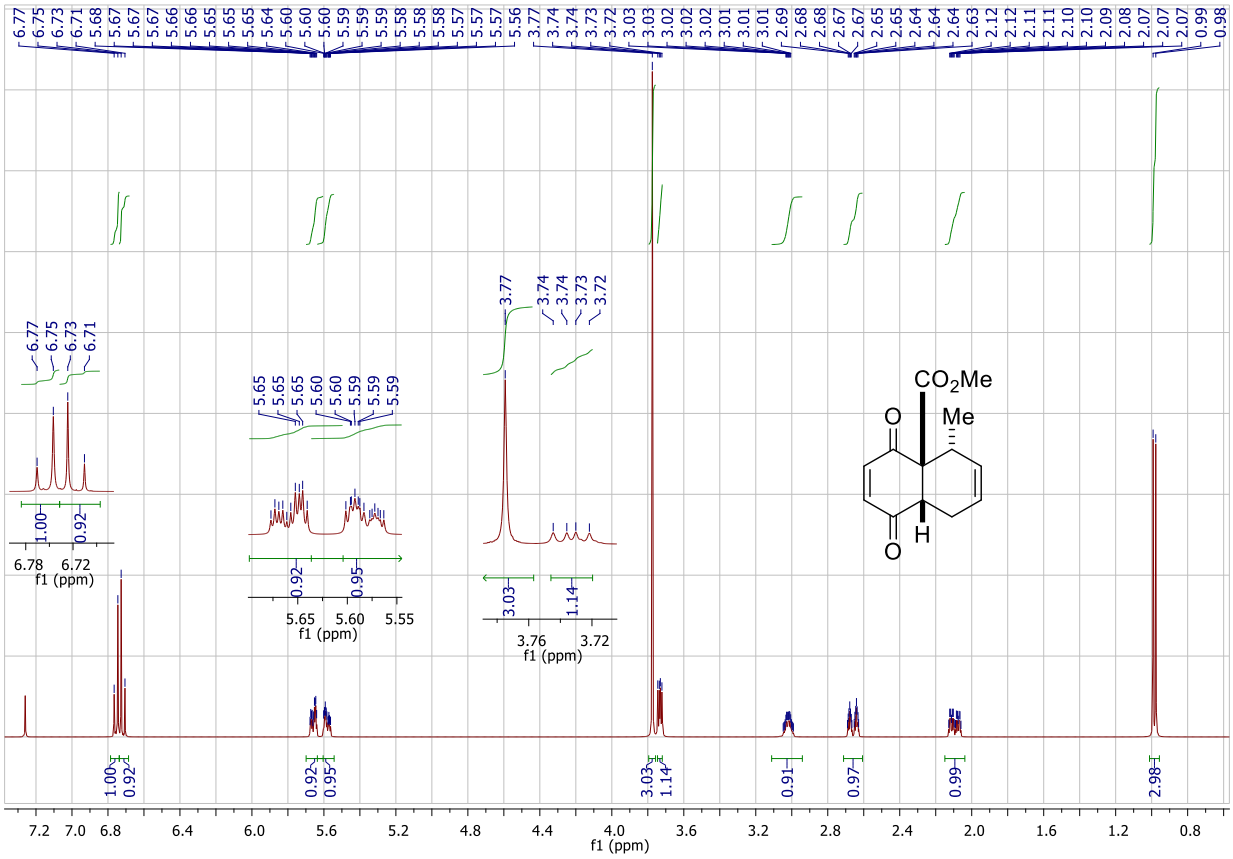
^{1}H and ^{13}C NMR spectra for methyl (±)-*rel*-(1*R*,4*S*,4a*S*,8a*S*)-5,8-dioxo-1,5,8,8a-tetrahydro-1,4-methanonaphthalene-4a(4*H*)-carboxylate (**3h**) in $CDCl_3$ (500 and 125 MHz)

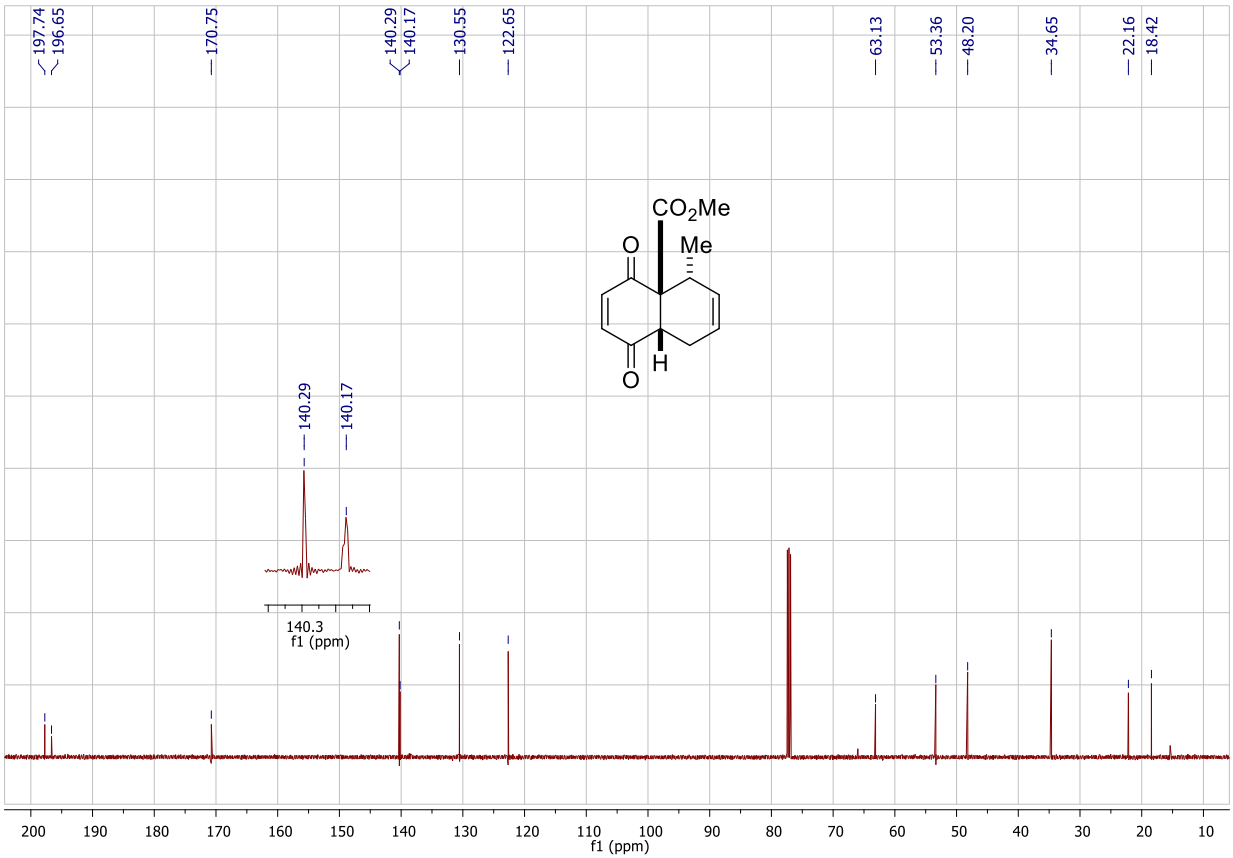




Experimental data for compound **3h** were in agreement with those found in the literature.[15]

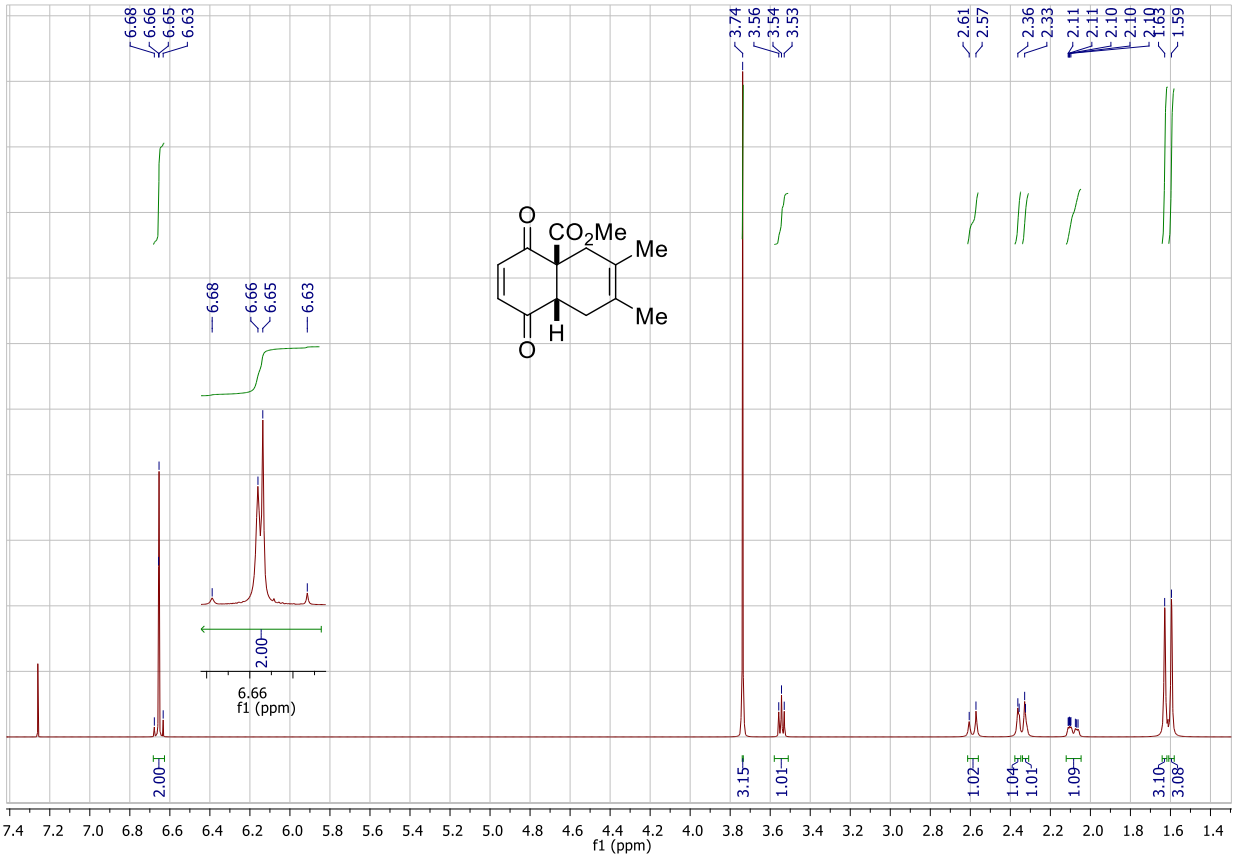
^{1}H and ^{13}C NMR spectra for methyl (±)-*rel*-(4a*R*,5*S*,8a*R*)-5-methyl-1,4-dioxo-1,5,8,8a-tetrahydronaphthalene-4a(4*H*)-carboxylate (**5h**) in $CDCl_3$ (500 and 125 MHz)

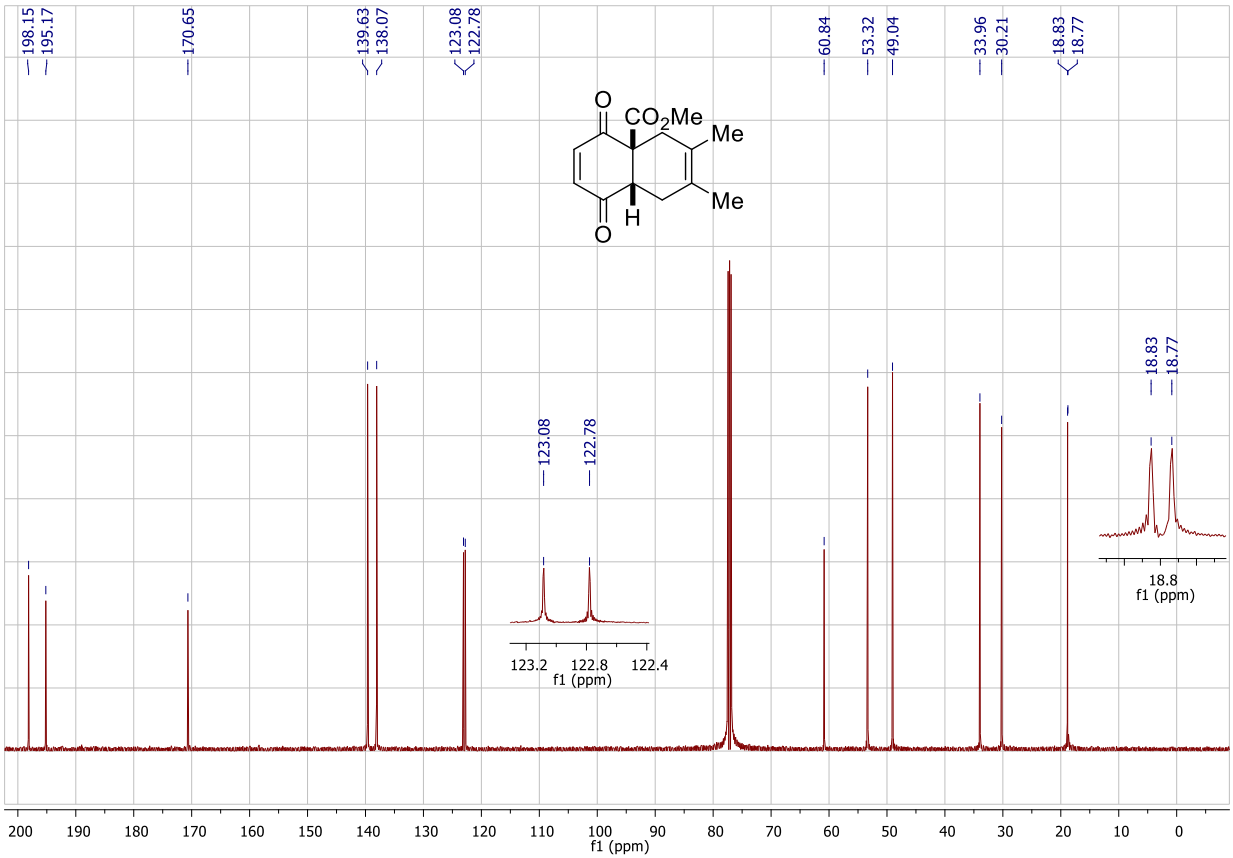




Experimental data for compound **5h** were in agreement with those found in the literature.[16]

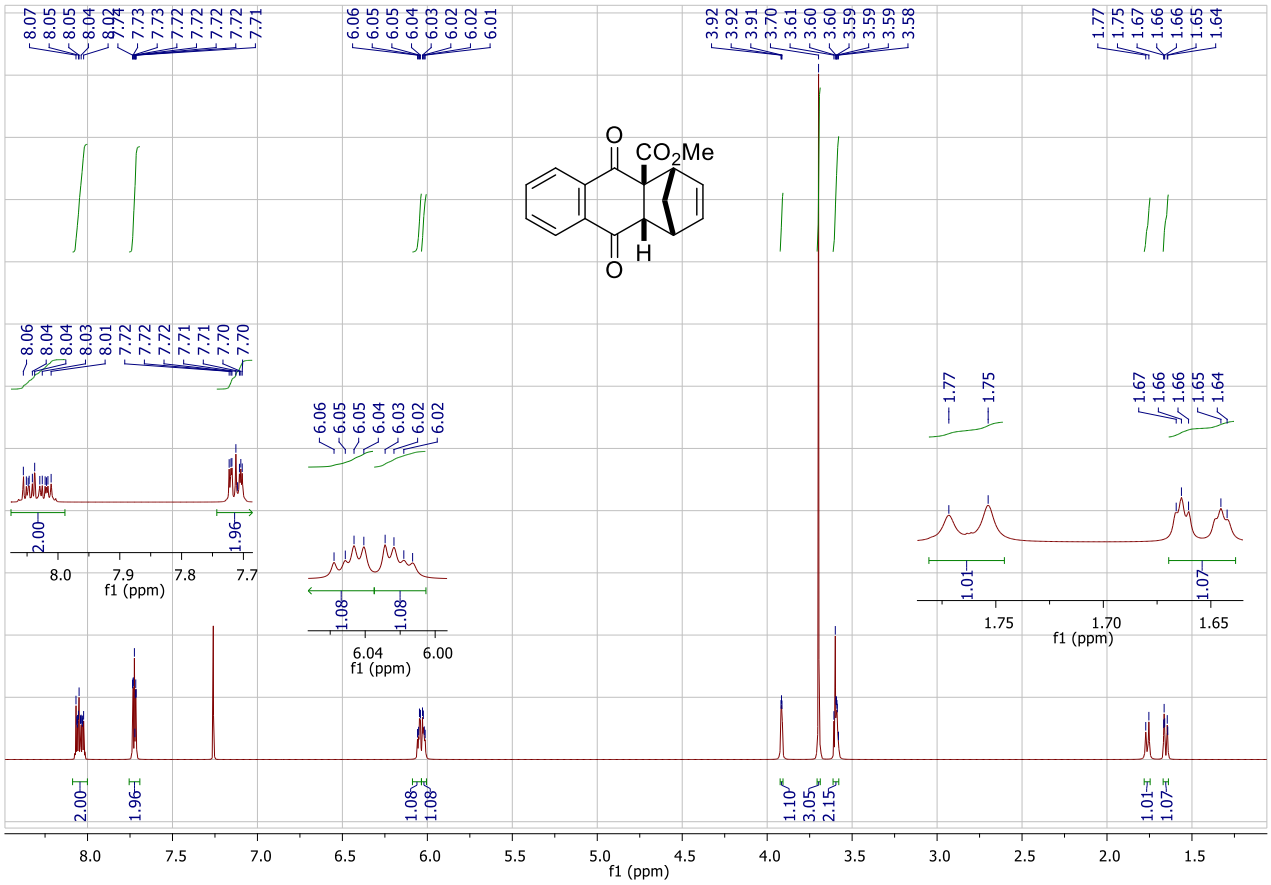
^{1}H and ^{13}C NMR spectra for methyl (±)-*cis*-6,7-dimethyl-1,4-dioxo-1,5,8,8a-tetrahydronphthalene-4a(4*H*)-carboxylate (**6h**) in $CDCl_3$ (500 and 125 MHz)

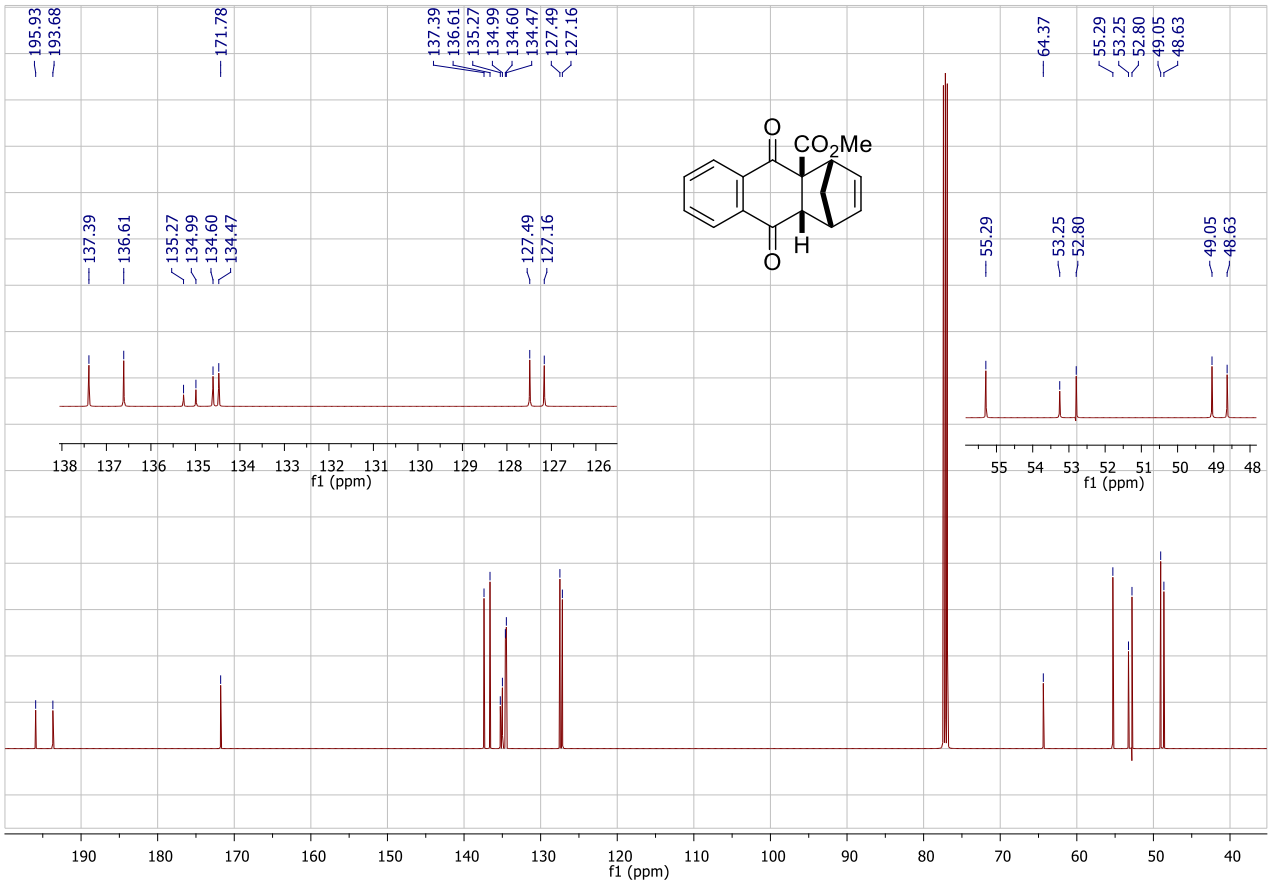




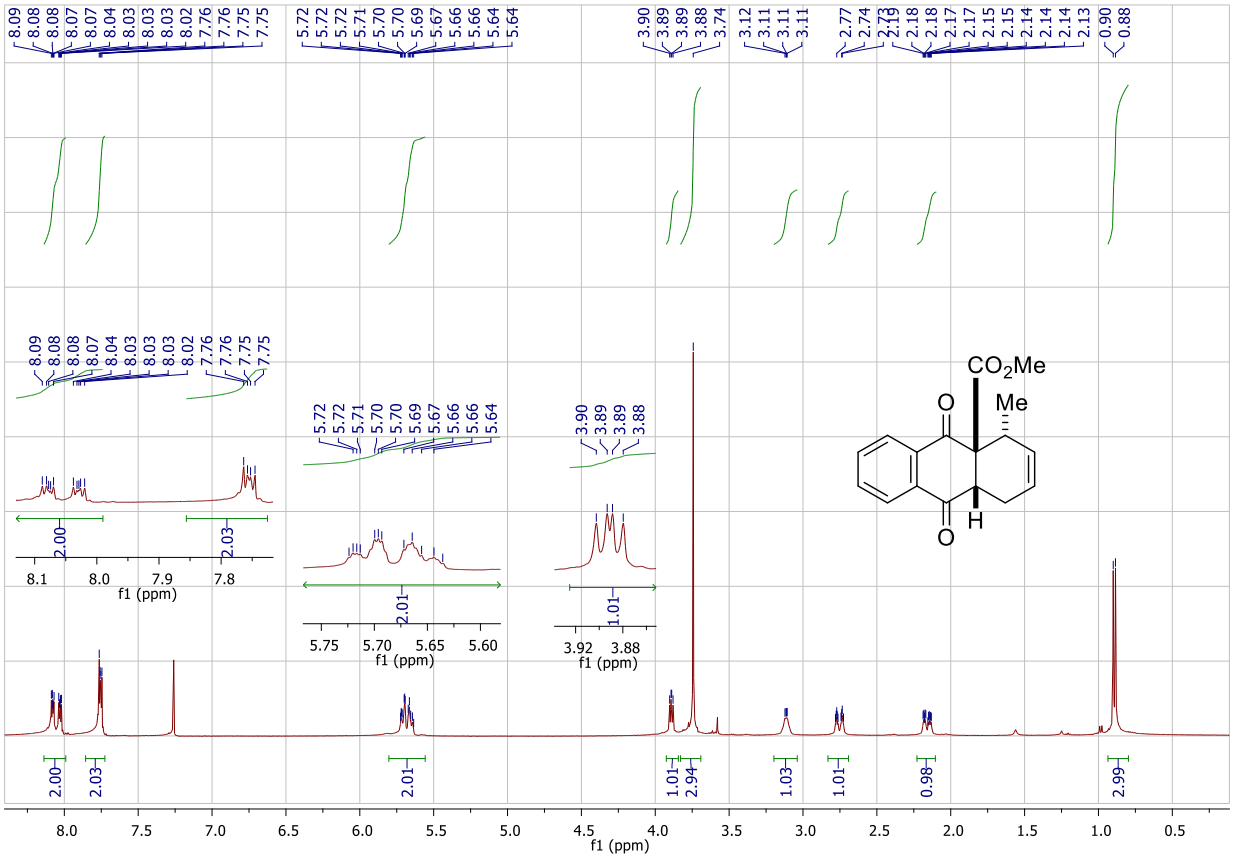
Experimental data for compound **6h** were in agreement with those found in the literature.[17]

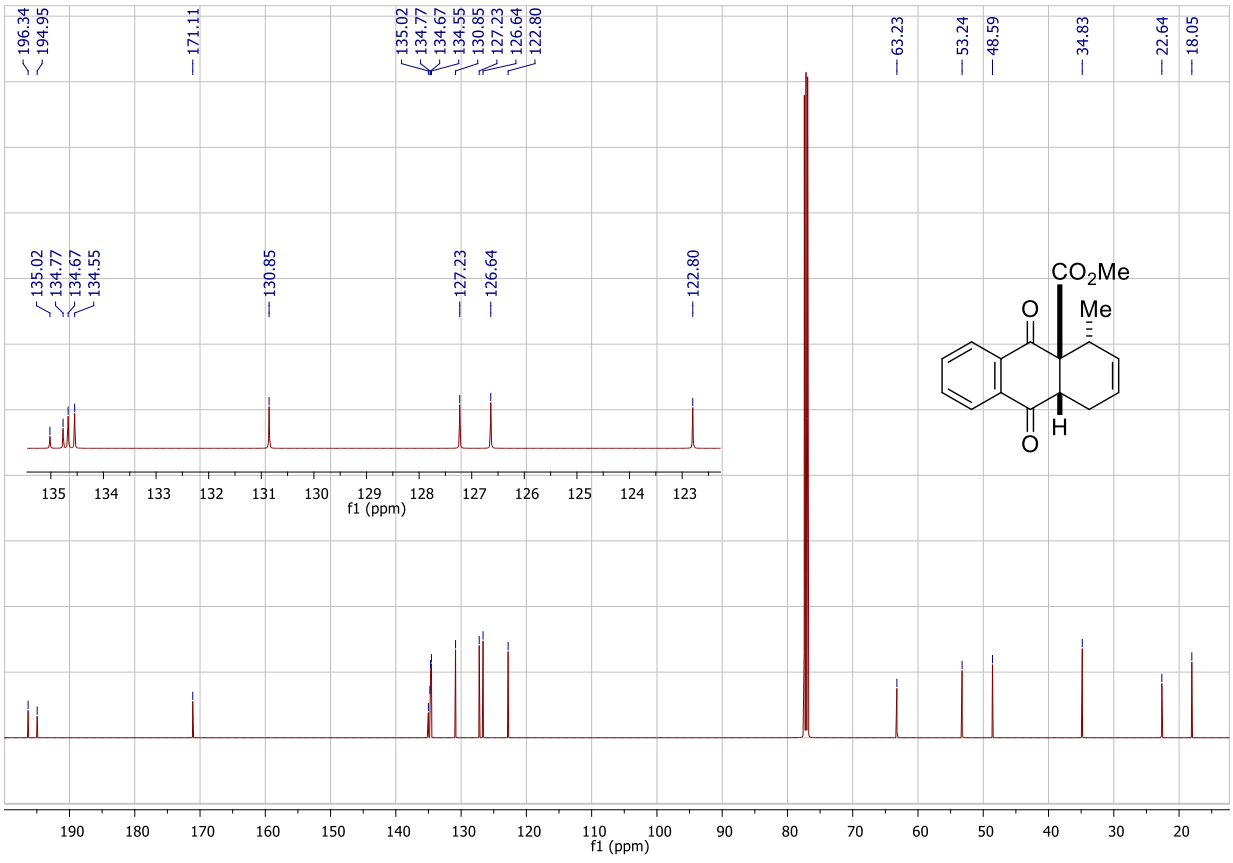
^{1}H and ^{13}C NMR spectra for methyl (±)-*rel*-(1*R*,4*S*,4a*S*,9a*S*)-9,10-dioxo-1,9,9a,10-tetrahydro-1,4-methanoanthracene-4a(4*H*)-carboxylate (**3i**) in $CDCl_3$ (500 and 125 MHz)





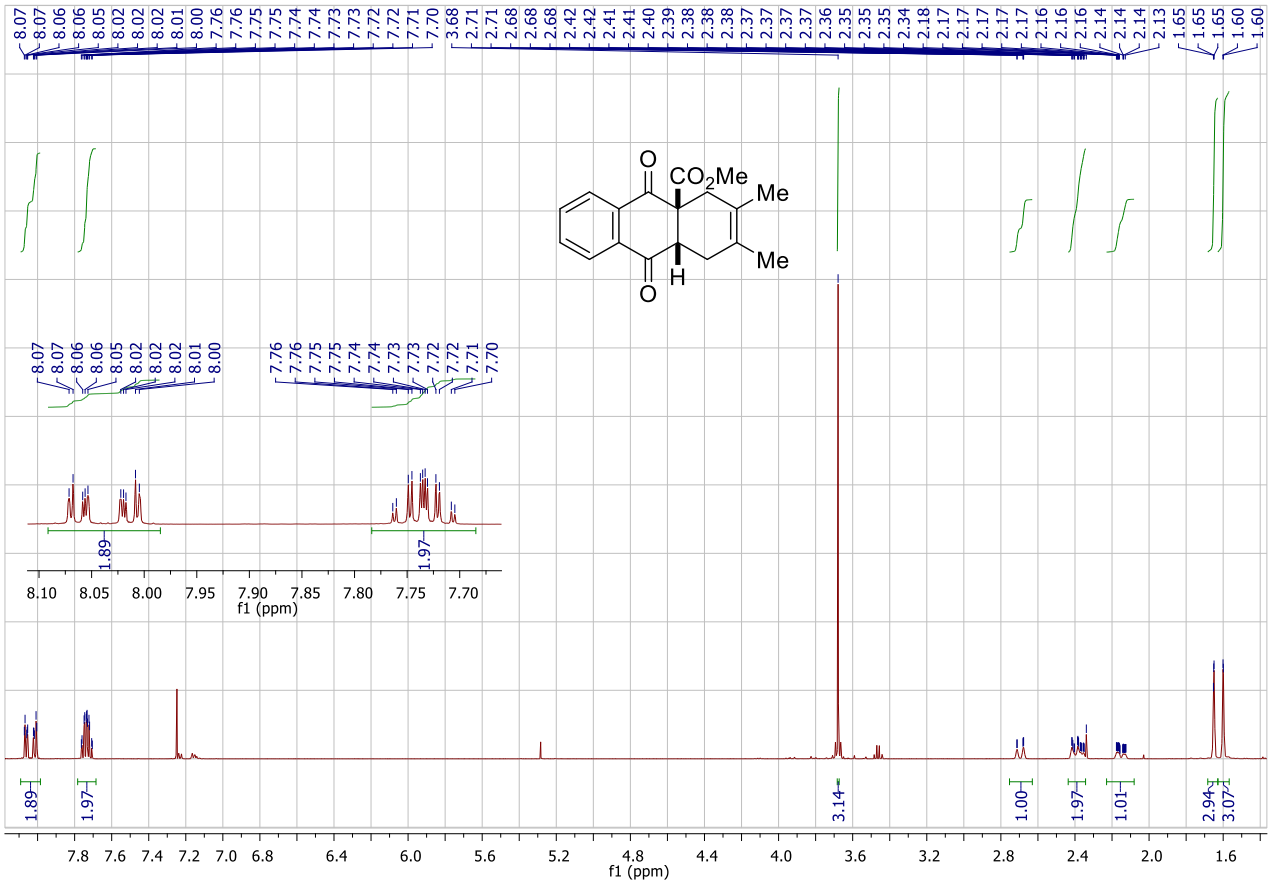
^{1}H and ^{13}C NMR spectra for methyl (±)-*rel*-(4*R*,4a*S*,9a*S*)-4-methyl-9,10-dioxo1,9,9a,10-tetrahydroanthracene-4a(4*H*)-carboxylate (**5i**) in $CDCl_3$ (500 and 125 MHz)

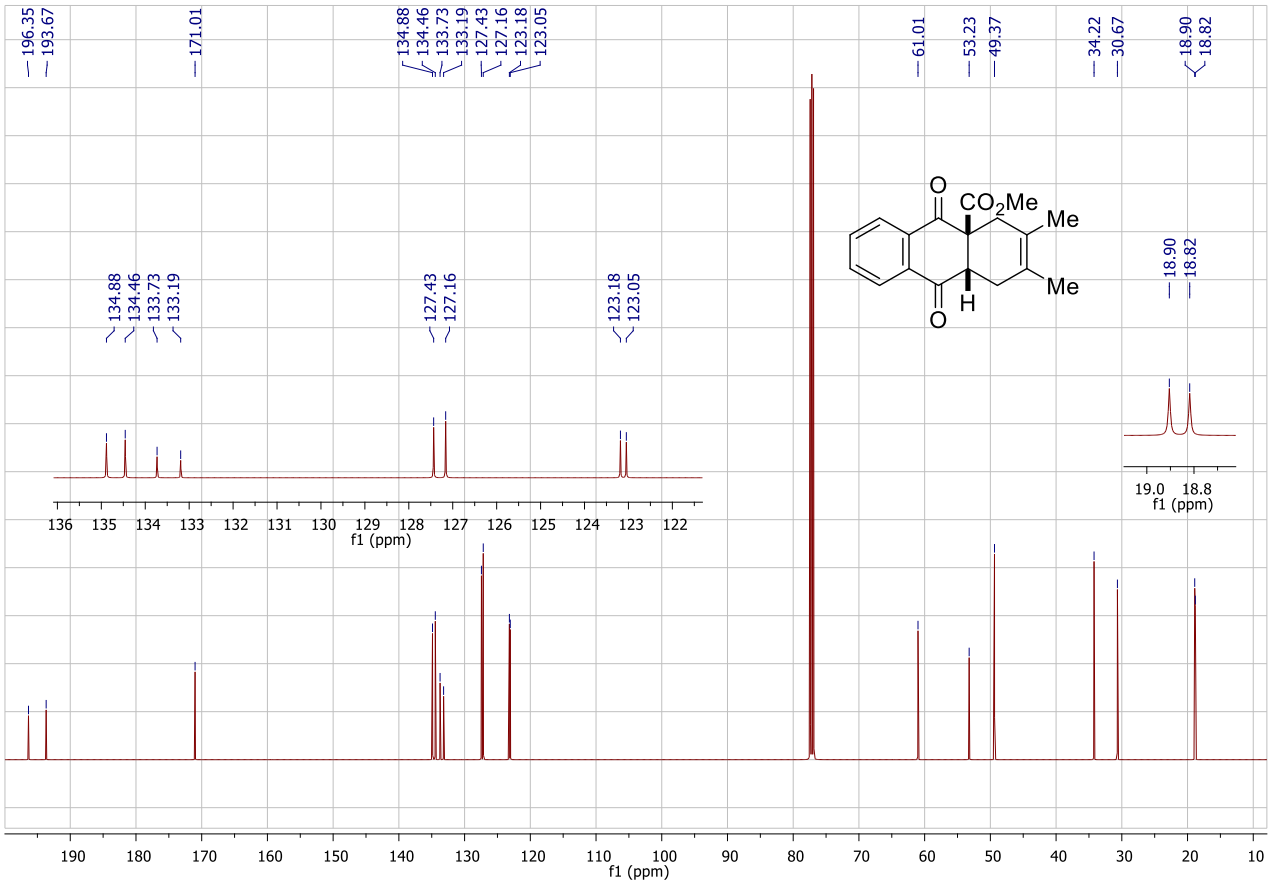




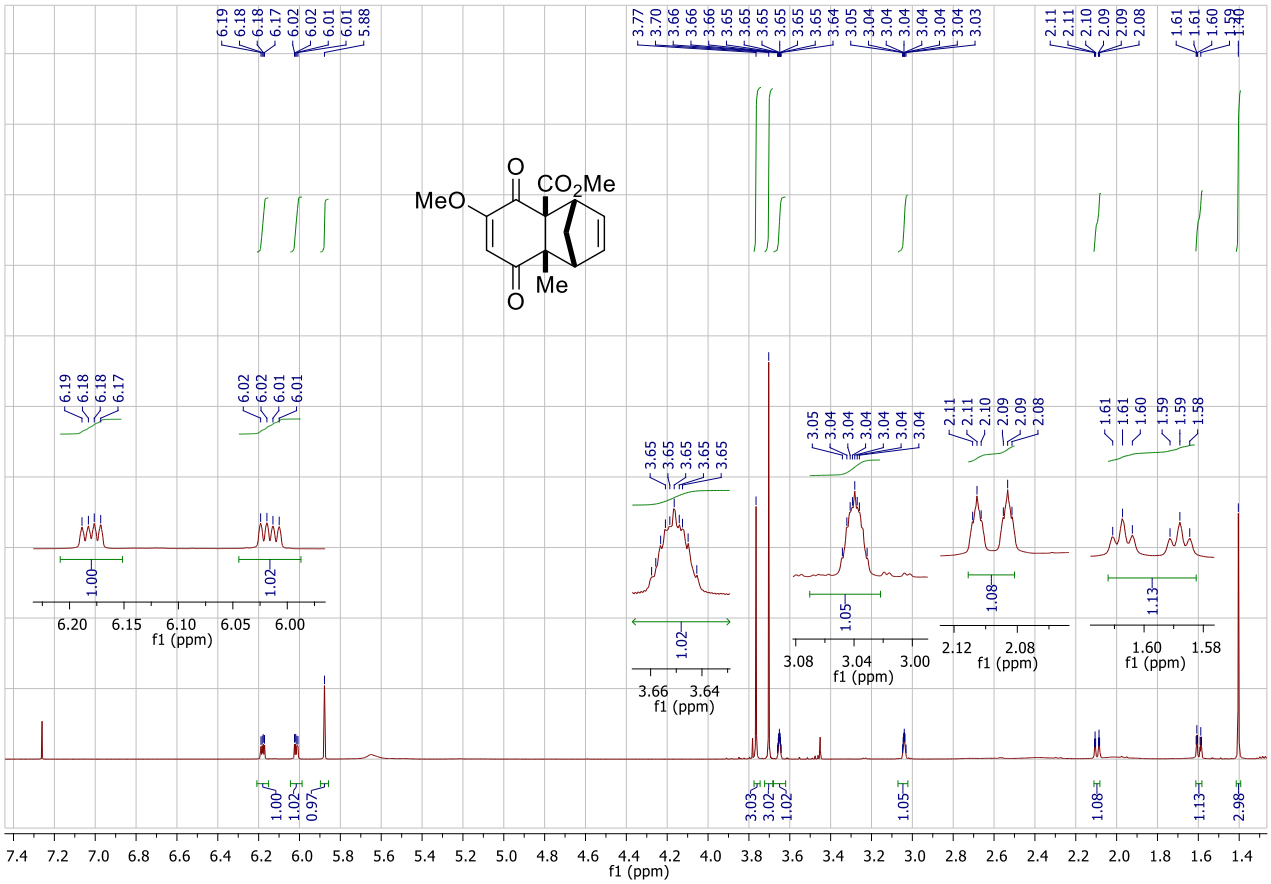
Experimental data for compound **5i** were in agreement with those found in the literature.[16]

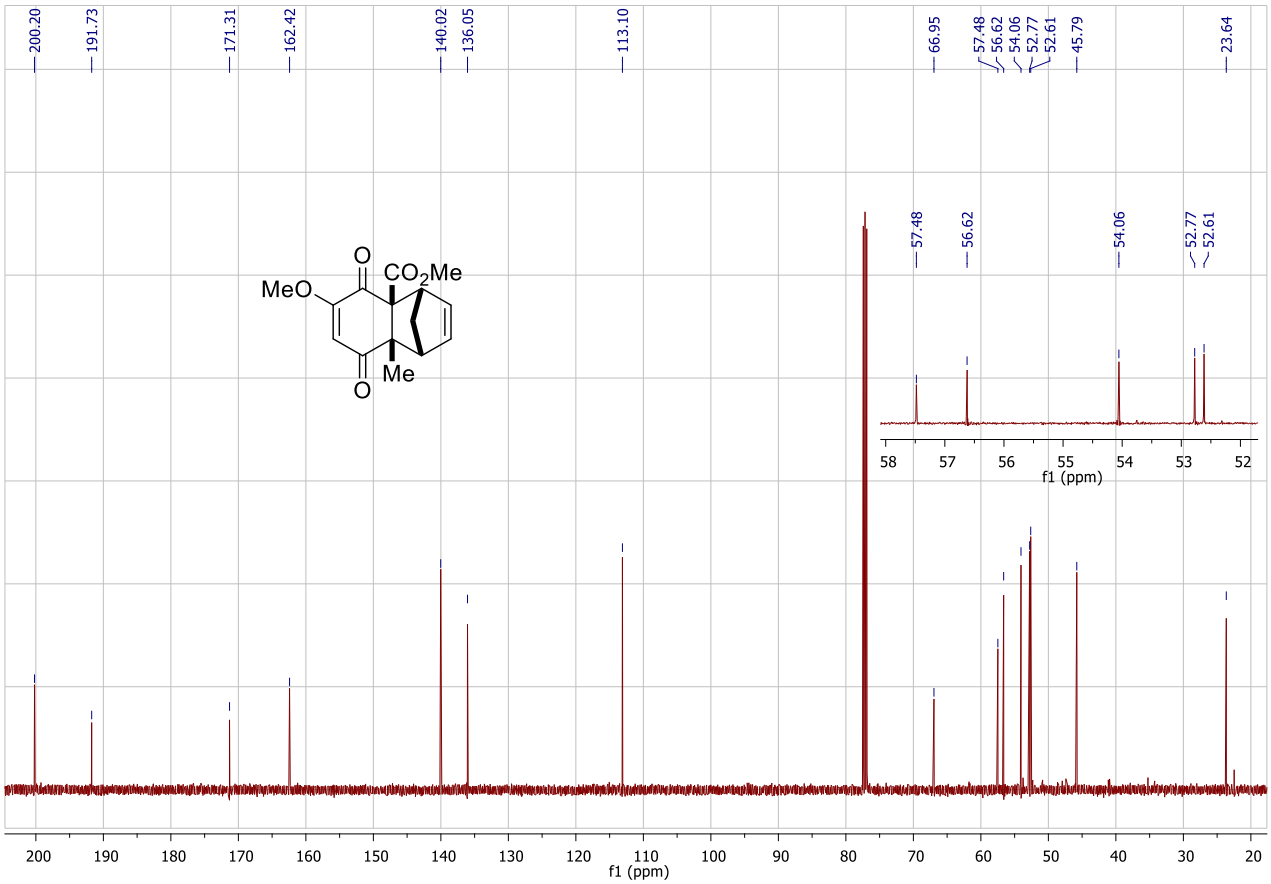
^{1}H and ^{13}C NMR spectra for methyl (±)-*cis*-2,3—dimethyl-9,10-dioxo-1,9,9a,10-tetrahydroanthracene-4a(4*H*)-carboxylate (**6i**) in $CDCl_3$ (500 and 125 MHz)



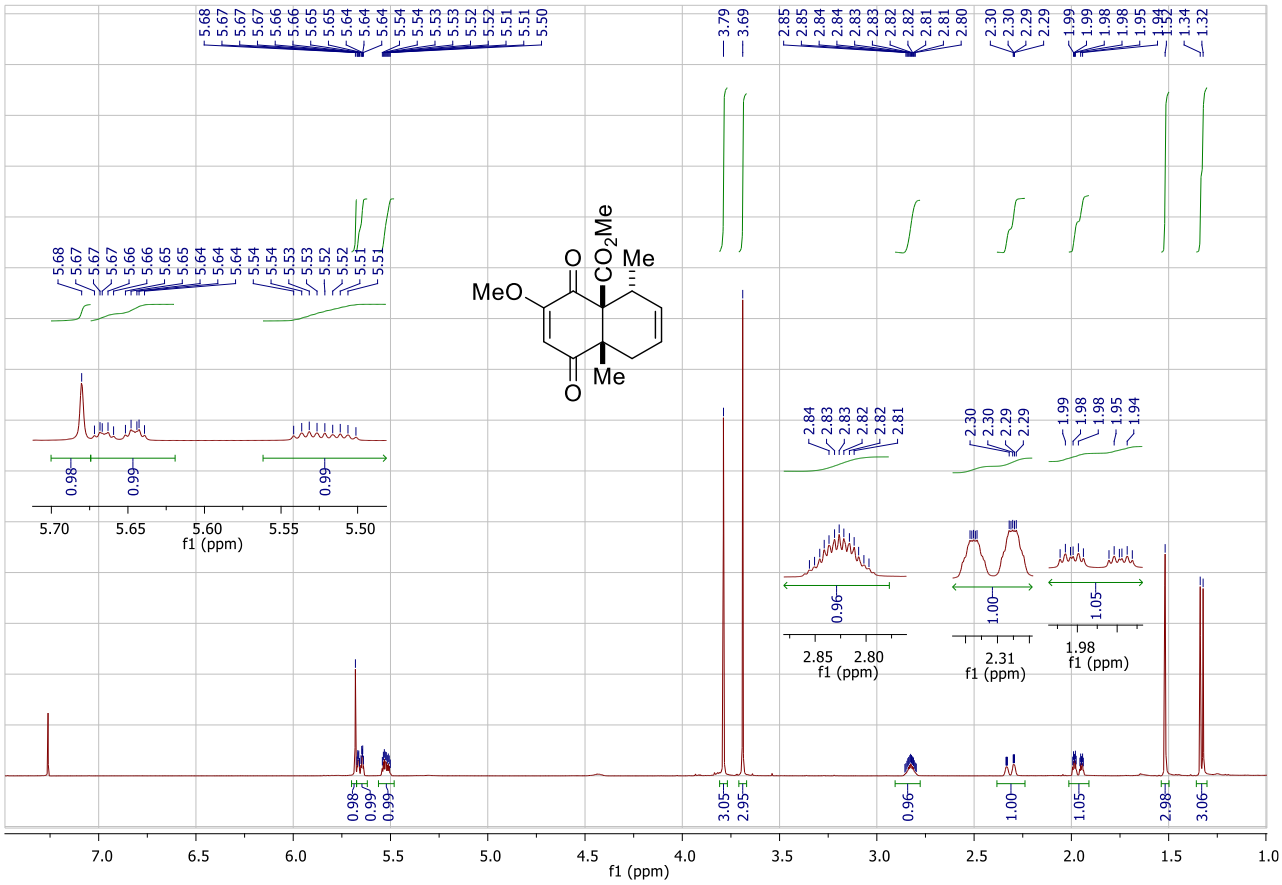


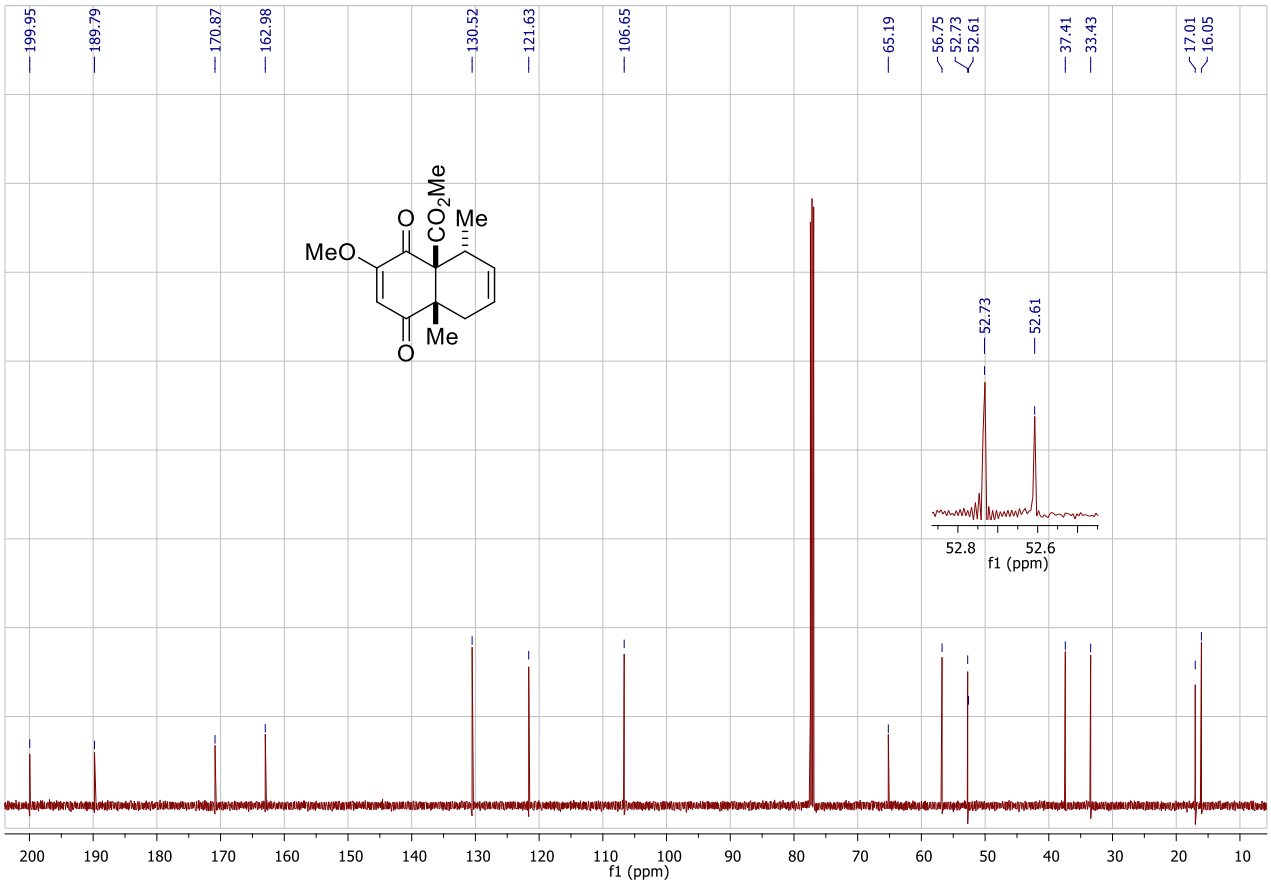
^{1}H and ^{13}C NMR spectra for methyl (±)-*rel*-(1*R*,4*S*,4a*S*,8a*S*)-6-methoxy-8a-methyl-5,8-dioxo1,5,8,8a-tetrahydro-1,4-methanonaphthalene-4a(4*H*)-carboxylate (**3j**) in $CDCl_3$ (500 and 125 MHz)



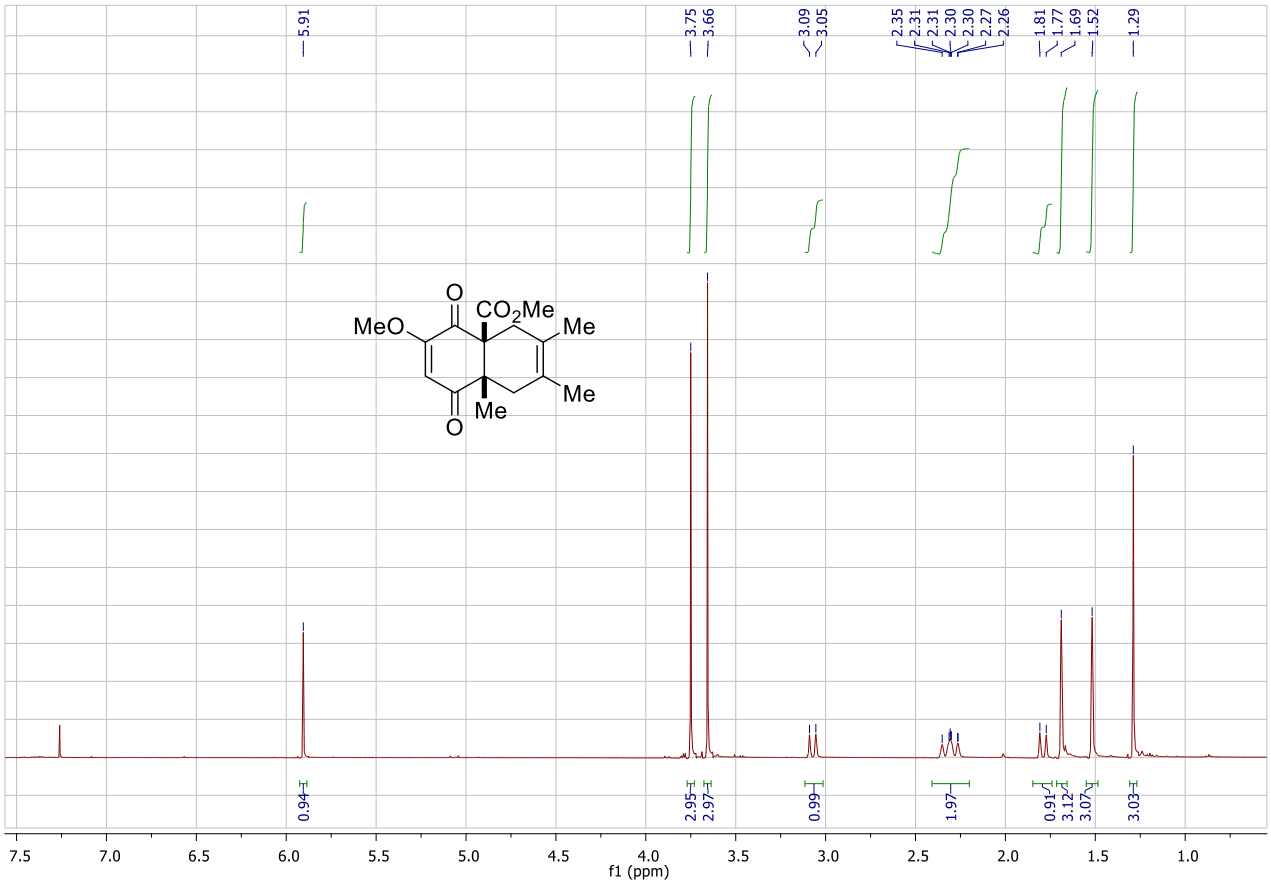


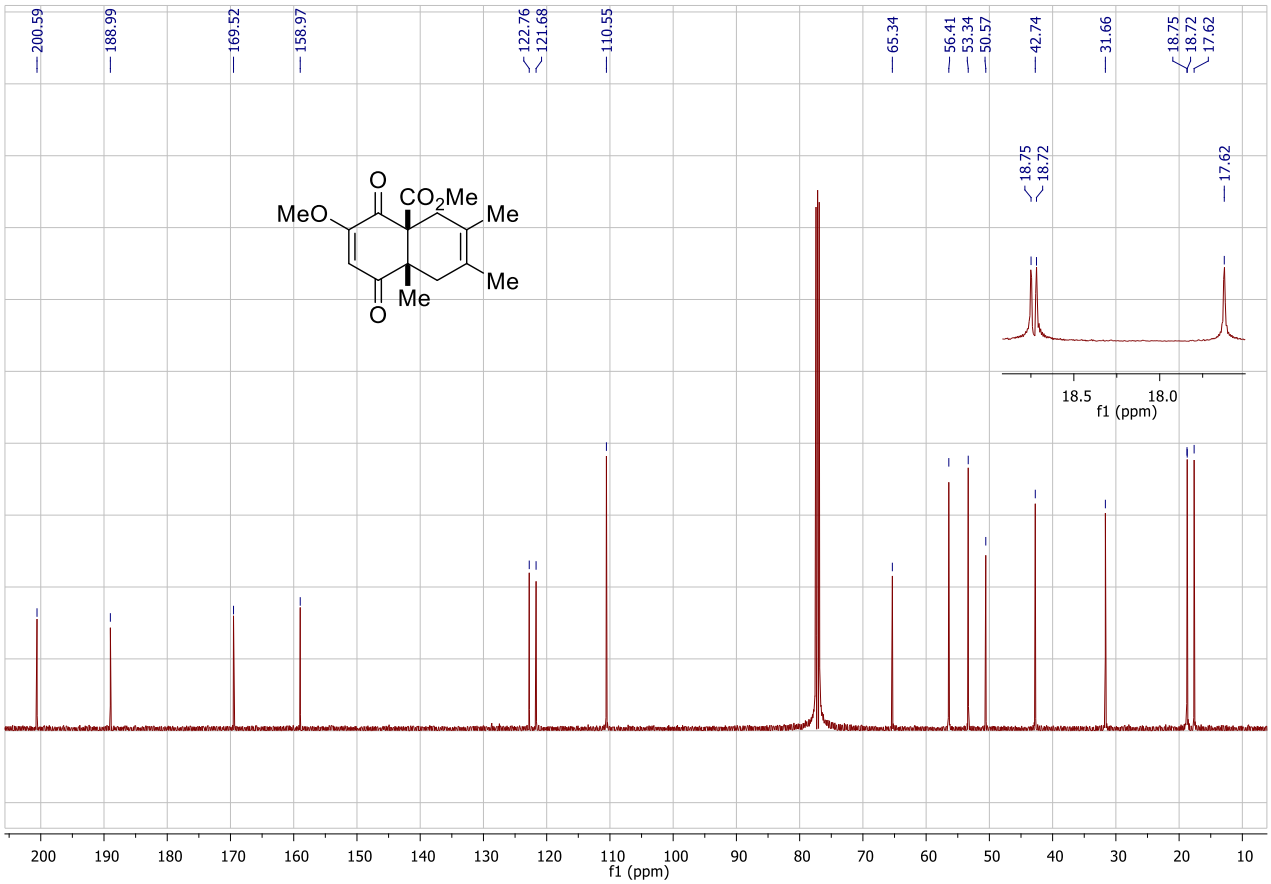
^{1}H and ^{13}C NMR spectra for methyl (±)-*rel*-(4a*R*,5*S*,8a*R*)-3-methoxy-5,8a-dimethyl-1,4-dioxo-1,5,8,8a-tetrahydronaphthalene-4a(4*H*)-carboxylate (**5j**) in $CDCl_3$ (500 and 125 MHz)



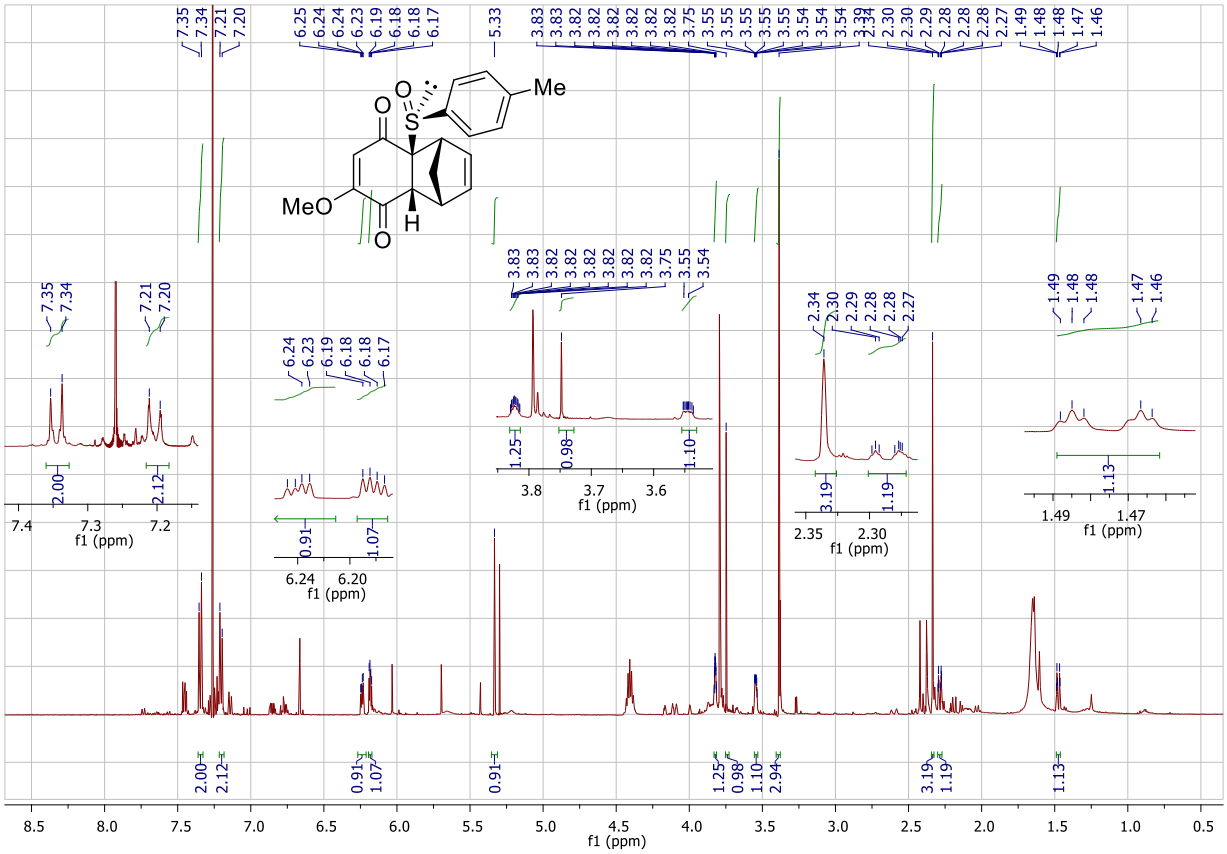


^{1}H and ^{13}C NMR spectra for Methyl (±)-*cis*-6,7,8a-trimethyl-1,4-dioxo-1,5,8,8a-tetrahydronaphthalene-4a(4*H*)-carboxylate (**6j**) in $CDCl_3$ (500 and 125 MHz)

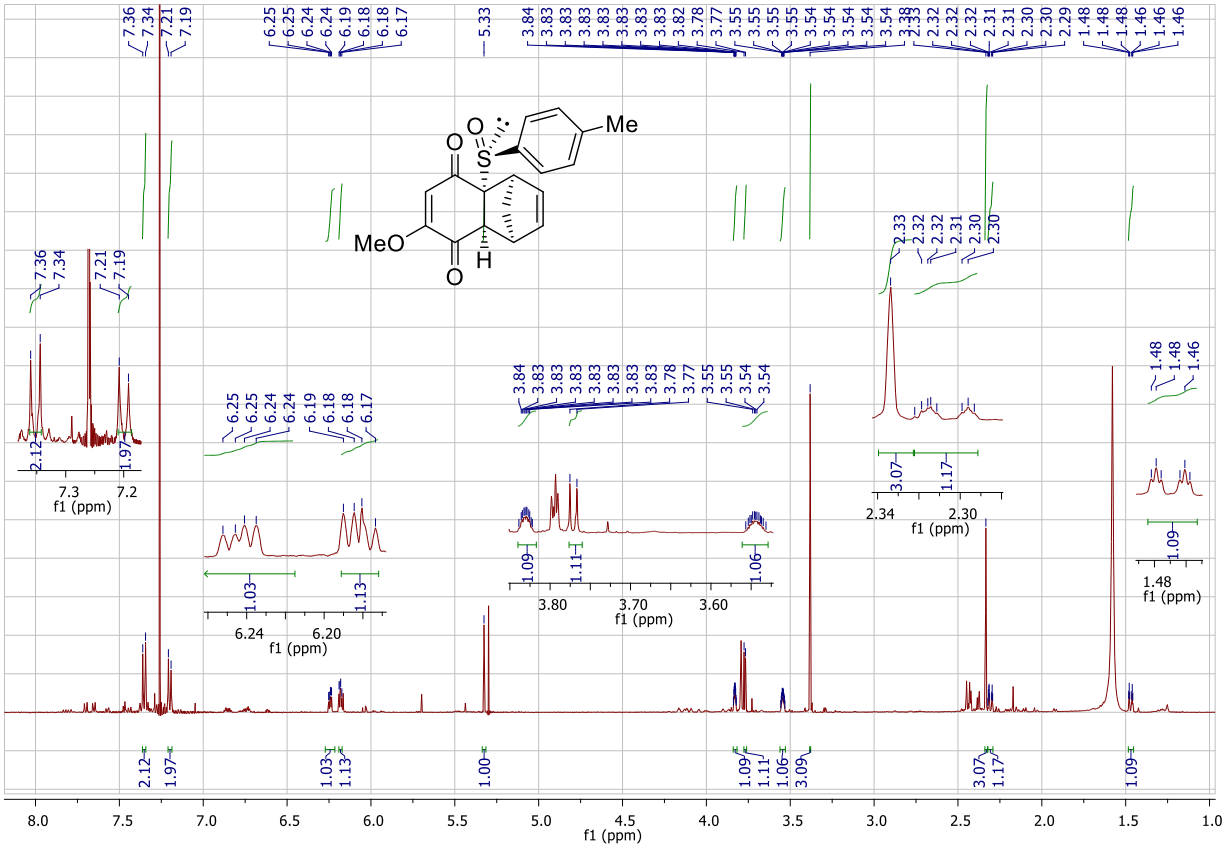




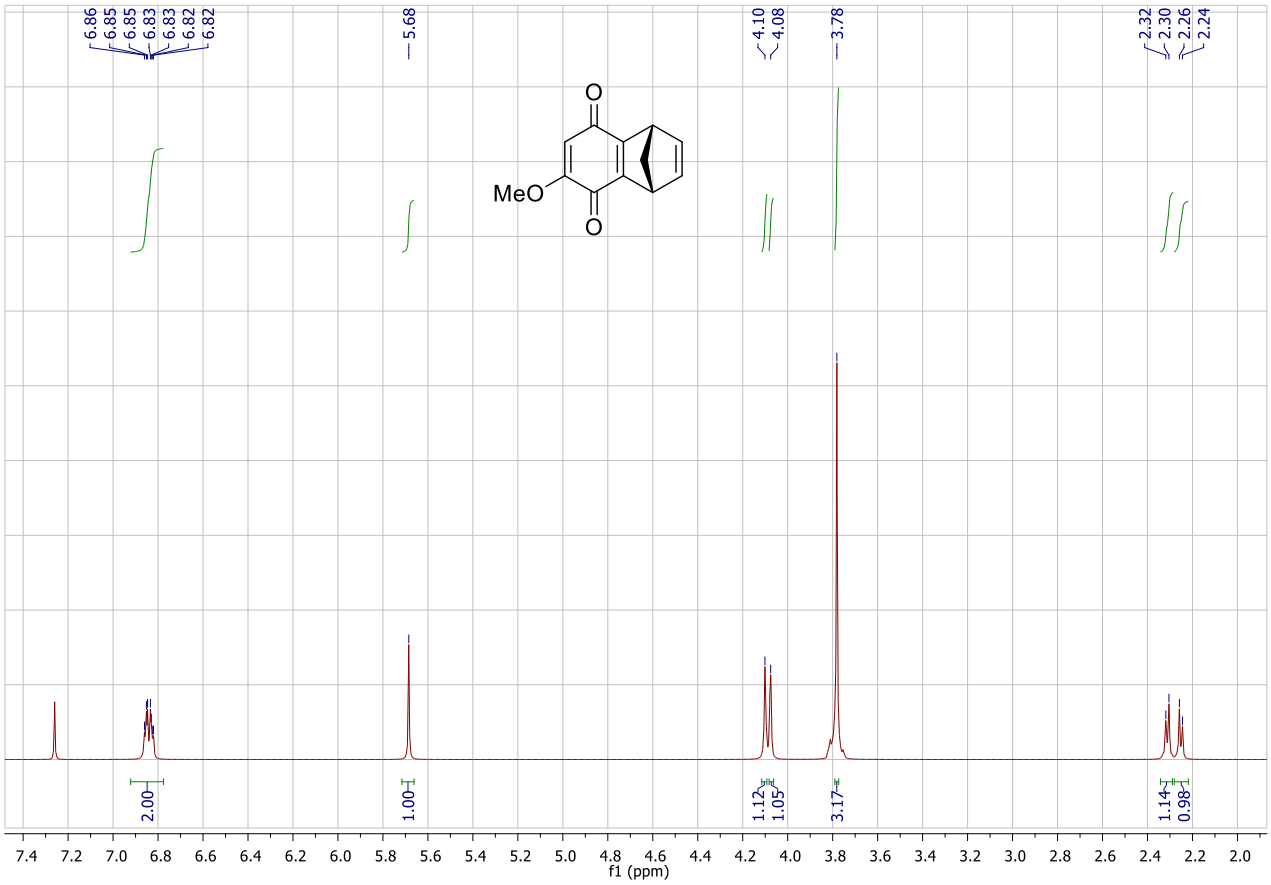
^{1}H NMR spectrum of the crude mixture for (1*R*,4*S*,4a*S*,8a*R*)-7-methoxy-4a-((*S*)-*p*-tolylsulfinyl)-1,4,4a,8a-tetrahydro-1,4-methanonaphthalene-5,8-dione (**α-3m**) in $CDCl_3$ (500 MHz)

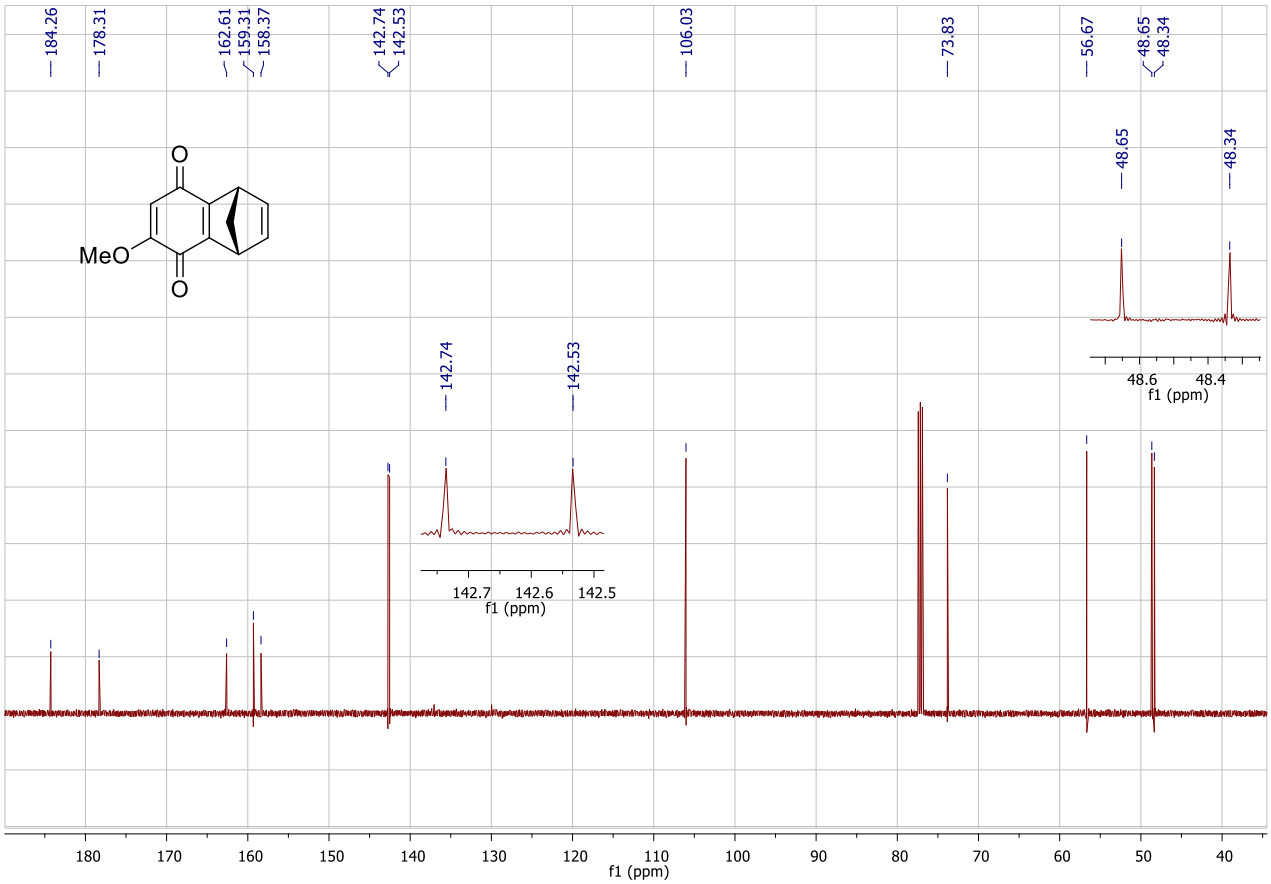


^{1}H NMR spectrum of the crude mixture for (1*S*,4*R*,4a*R*,8a*S*)-7-methoxy-4a-((*S*)-*p*-tolylsulfinyl)-1,4,4a,8a-tetrahydro-1,4-methanonaphthalene-5,8-dione (**β-3m**) in $CDCl_3$ (500 MHz)

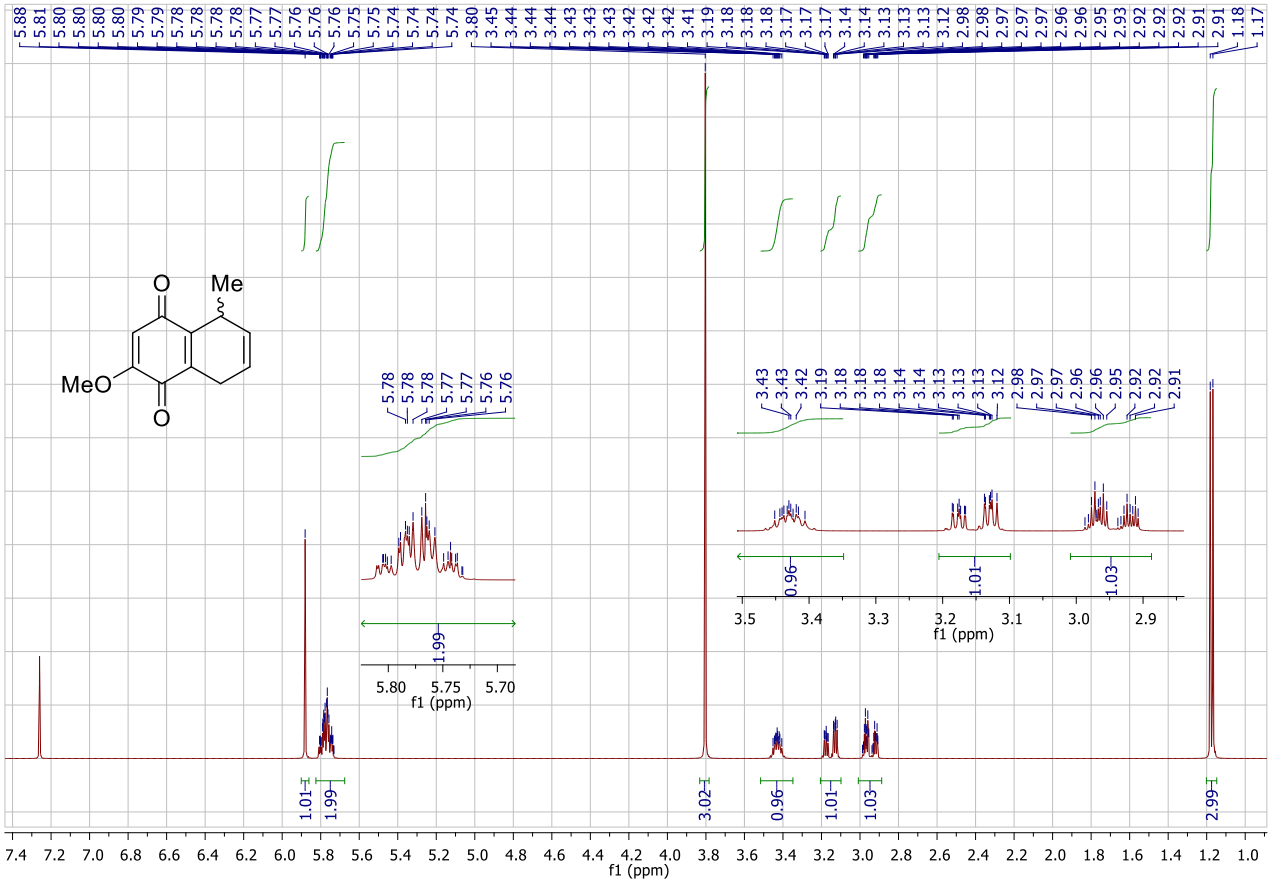


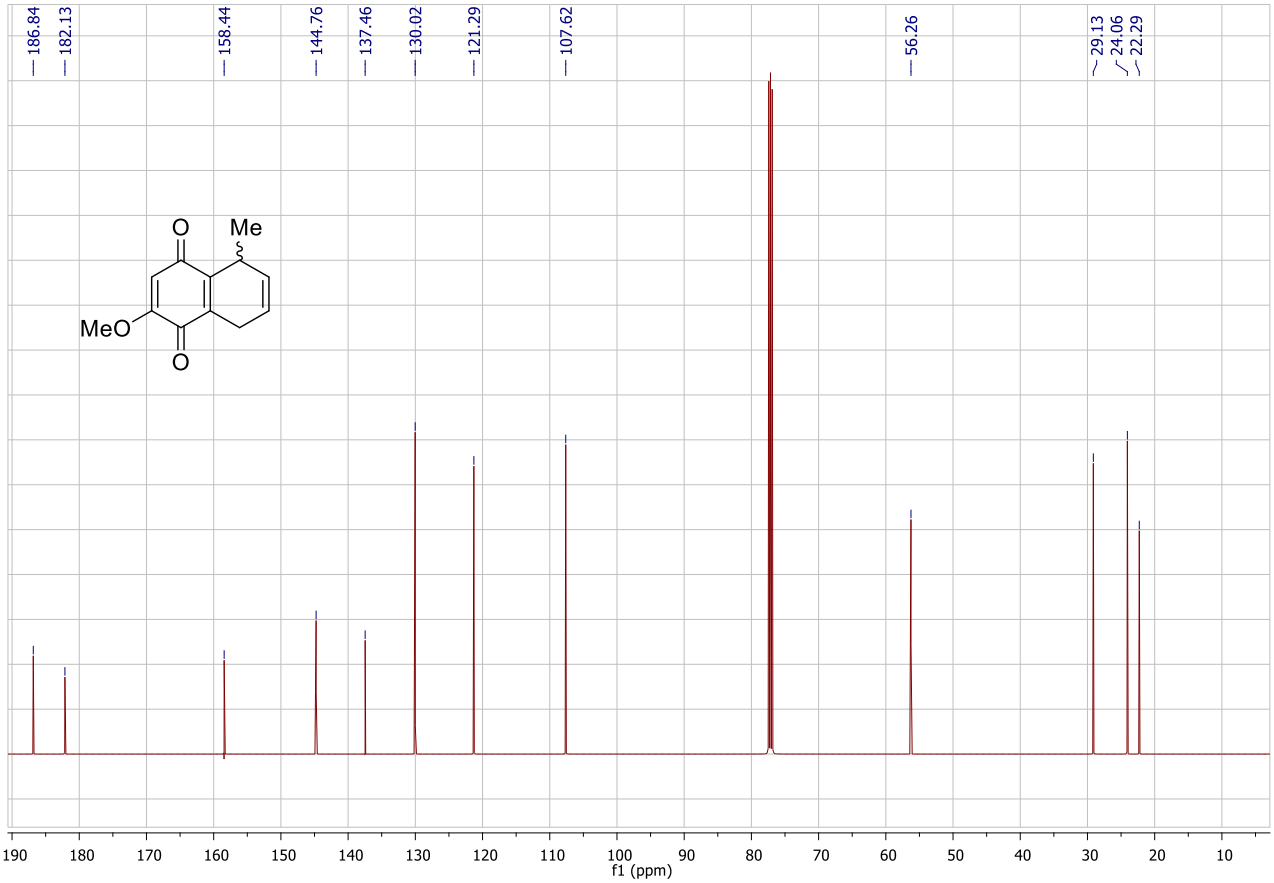
^{1}H and ^{13}C NMR spectra for (+)-(1*S*,4*R*)-6-methoxy-1,4-dihydro-1,4-methanonaphthalene-5,8-dione (**α-4m**) in $CDCl_3$ (500 and 125 MHz) (same spectra for **β-4m**)



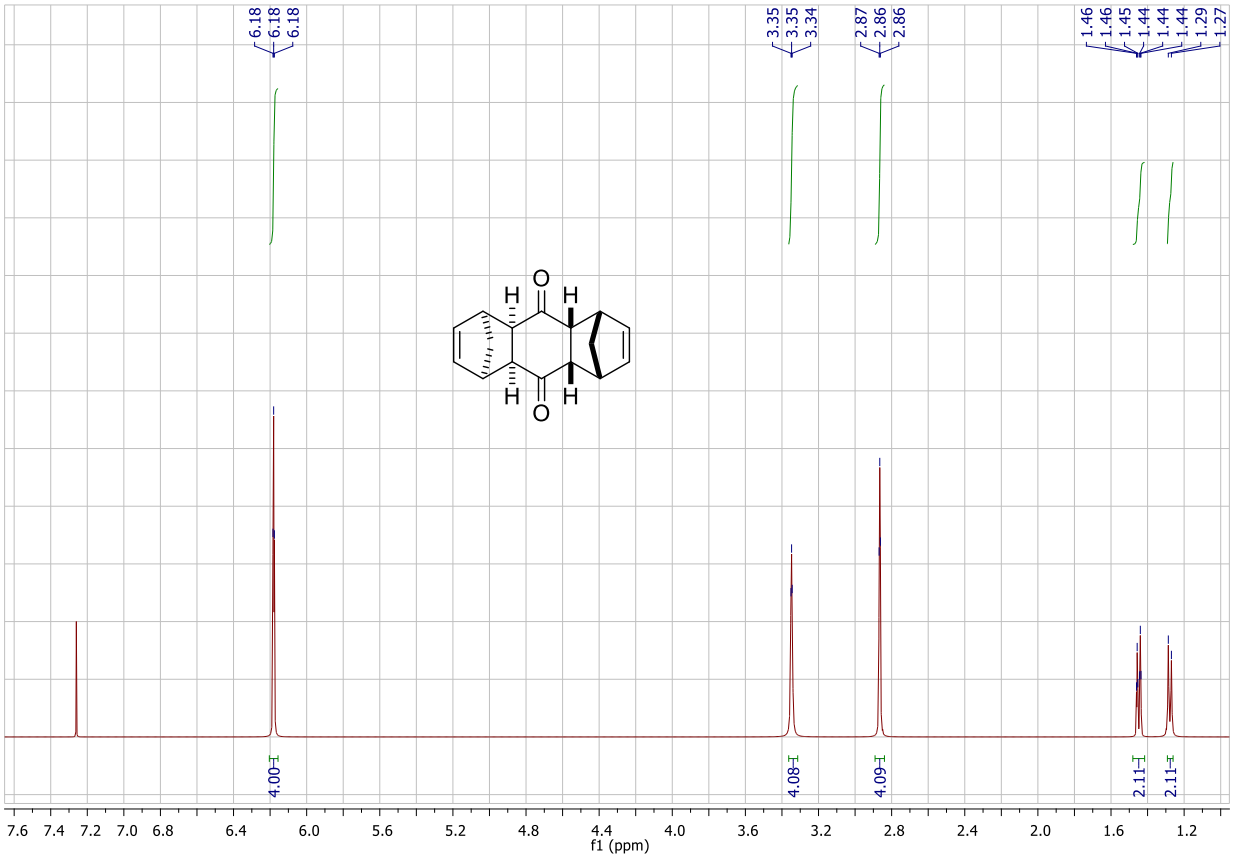


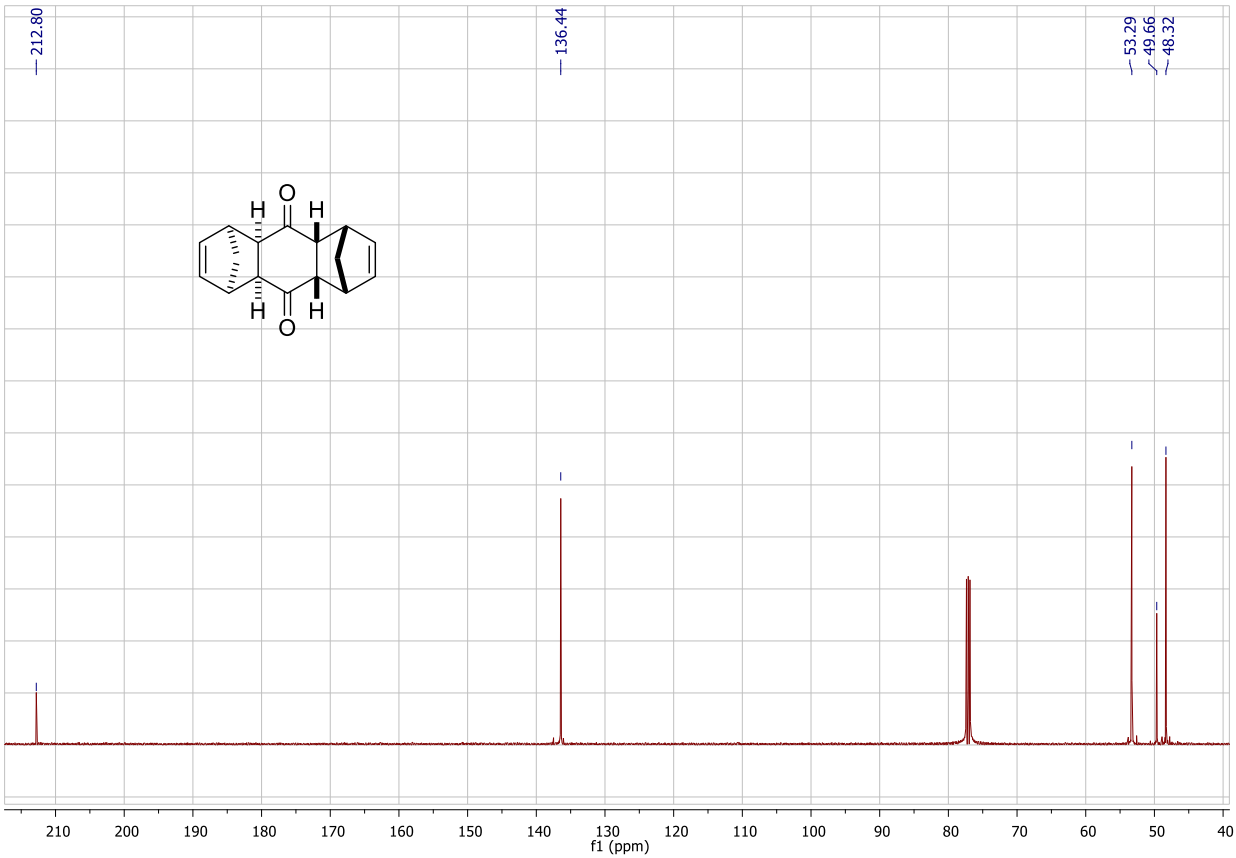
^{1}H and ^{13}C NMR spectra for 2-methoxy-5-methyl-5,8-dihydronaphthalene-1,4-dione (**7m**) in $CDCl_3$ (500 and 125 MHz)





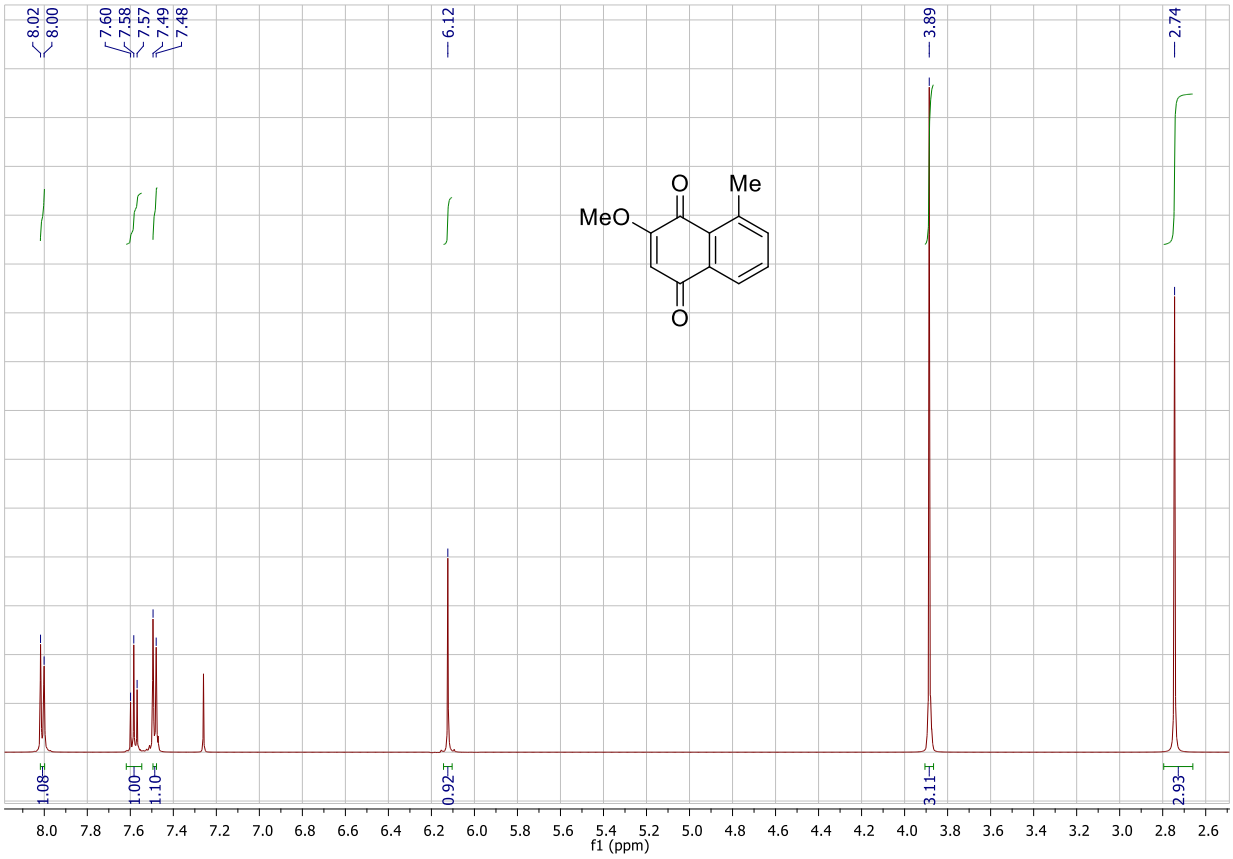
^{1}H and ^{13}C NMR spectra for (1*R*,4*S*,4a*R*,5*S*,8*R*,8a*S*,9a*S*,10a*R*)-1,4,4a,5,8,8a,9a,10a-octahydro1,4:5,8-dimethanoanthracene-9,10-dione (**11**) in $CDCl_3$ (500 and 125 MHz)

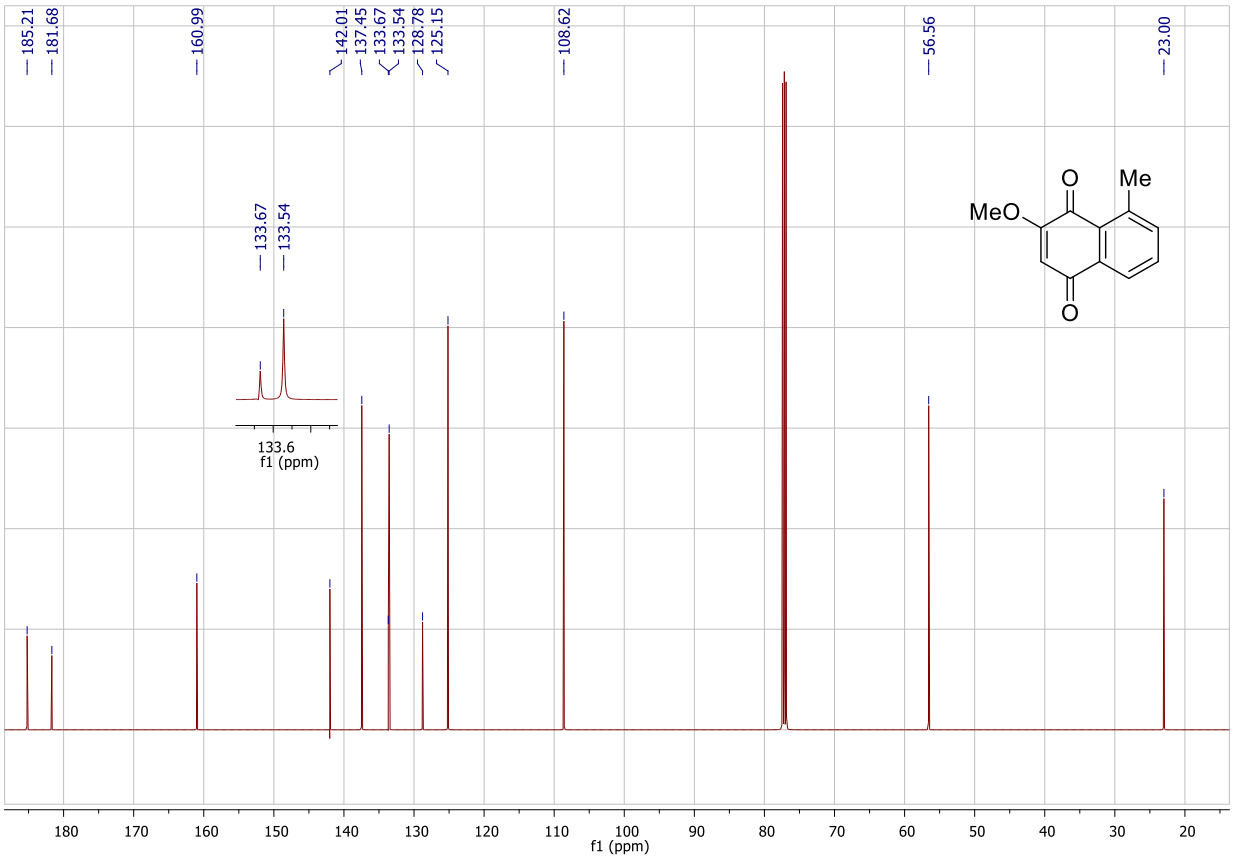




Experimental data for compound **11** were in agreement with those found in the literature.[18]

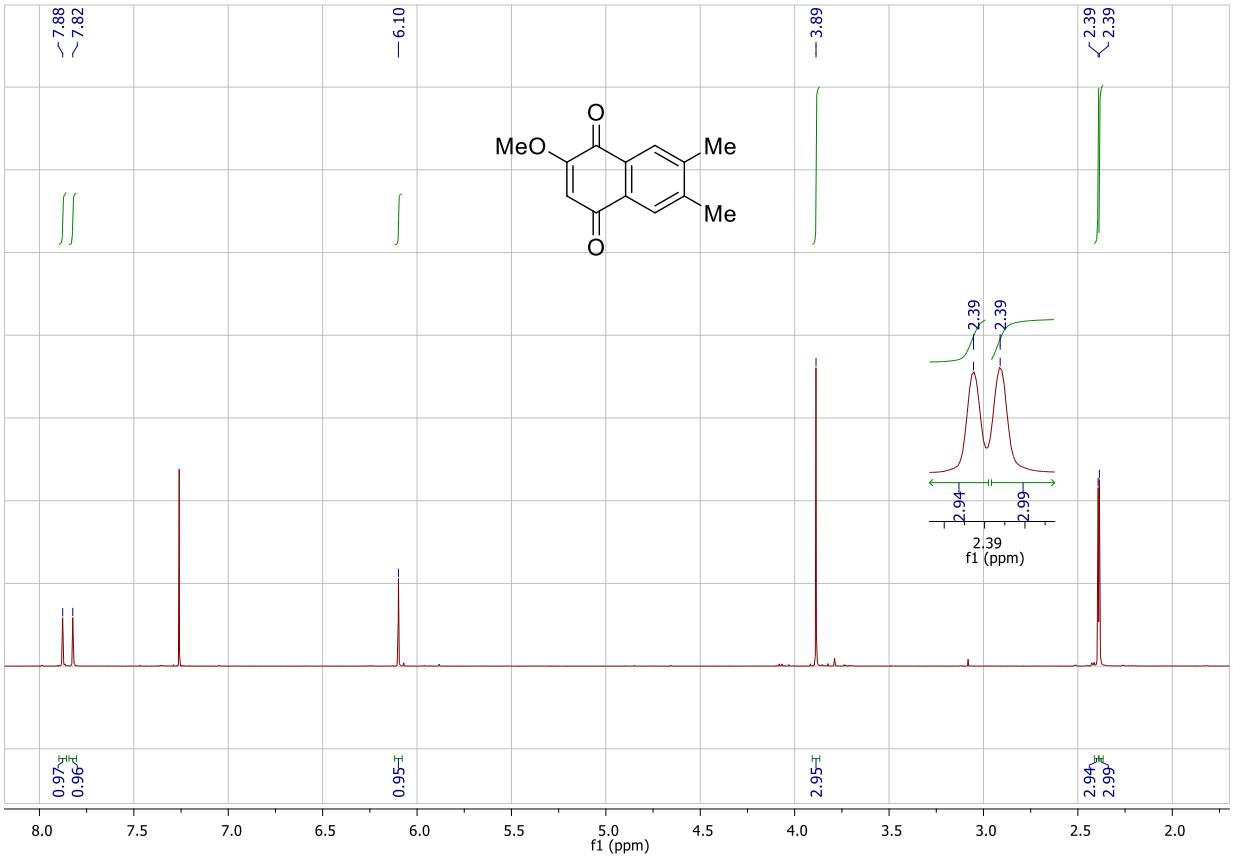
^{1}H and ^{13}C NMR spectra for 2-methoxy-8-methylnapthalene-1,4-dione (**12**) in $CDCl_3$ (500 and 125 MHz)

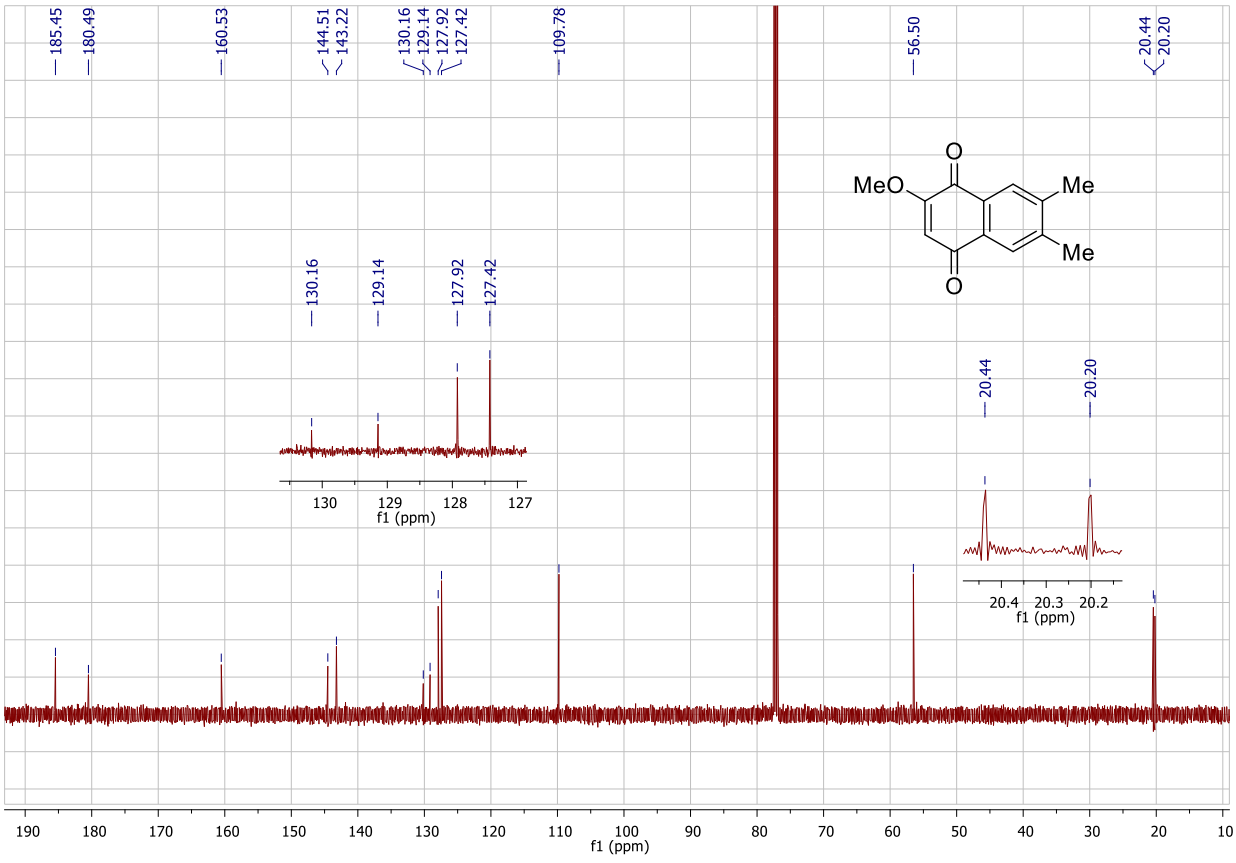




Experimental data for compound **12** were in agreement with those found in the literature.[19]

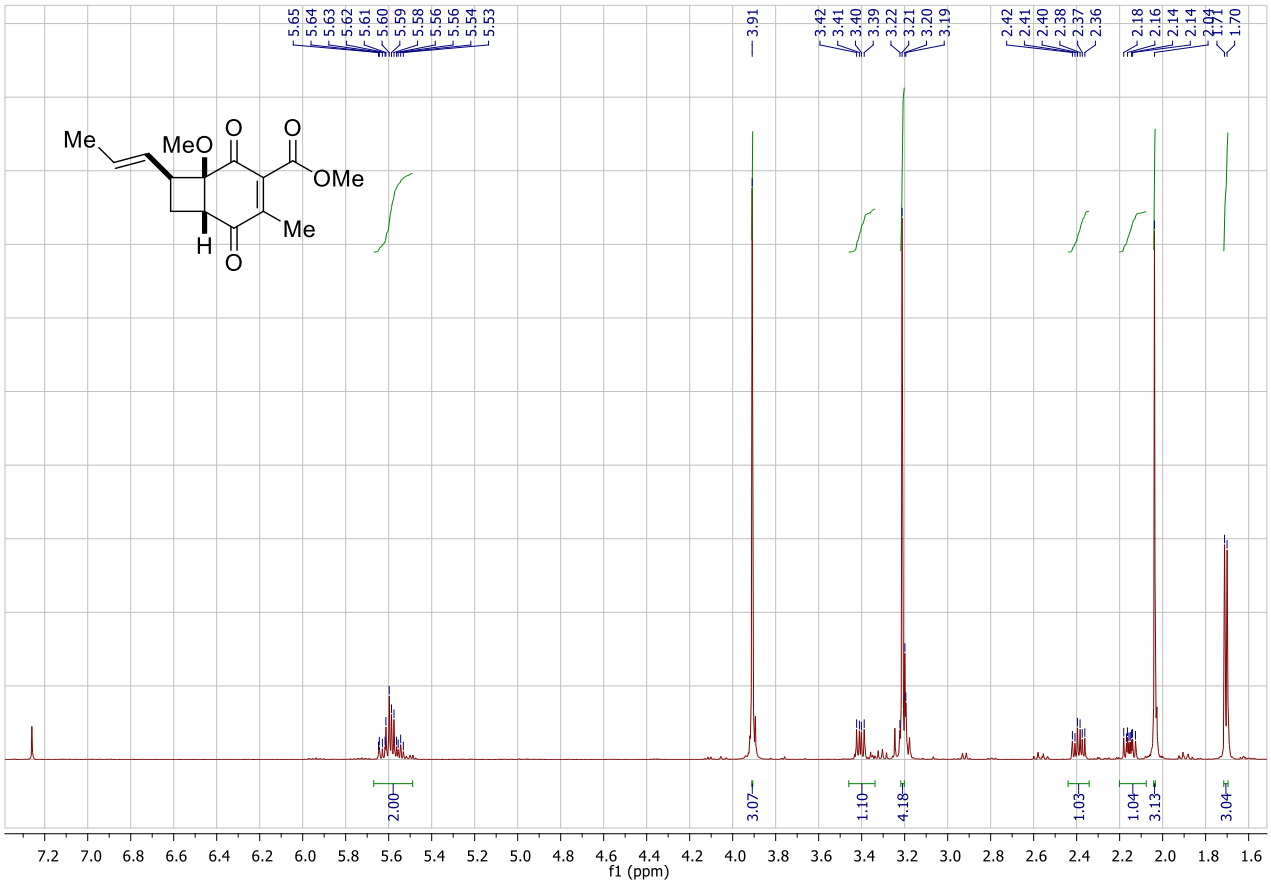
^{1}H and ^{13}C NMR spectra for 2-methoxy-6,7-dimethylnaphthalene-1,4-dione (**13**) in $CDCl_3$ (500 and 125 MHz)

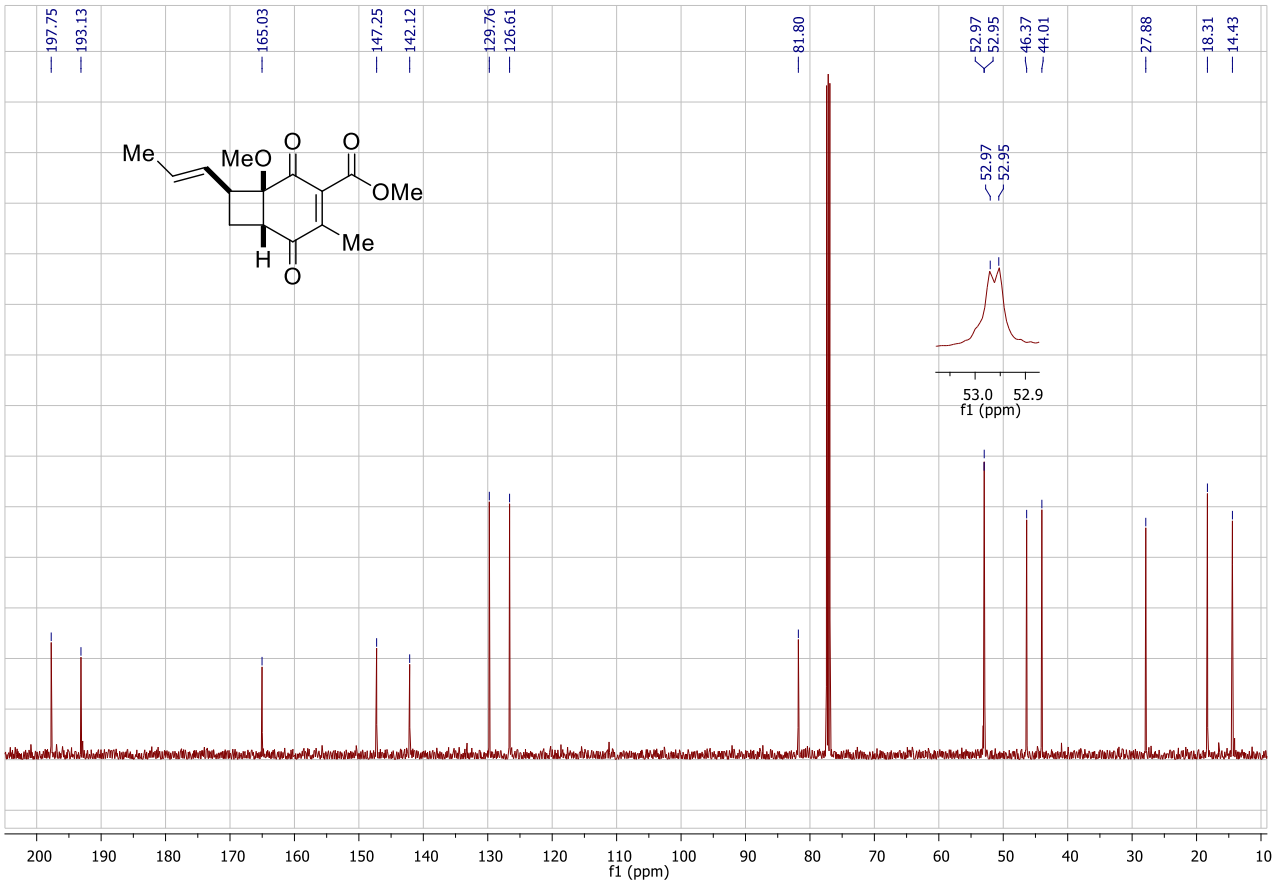




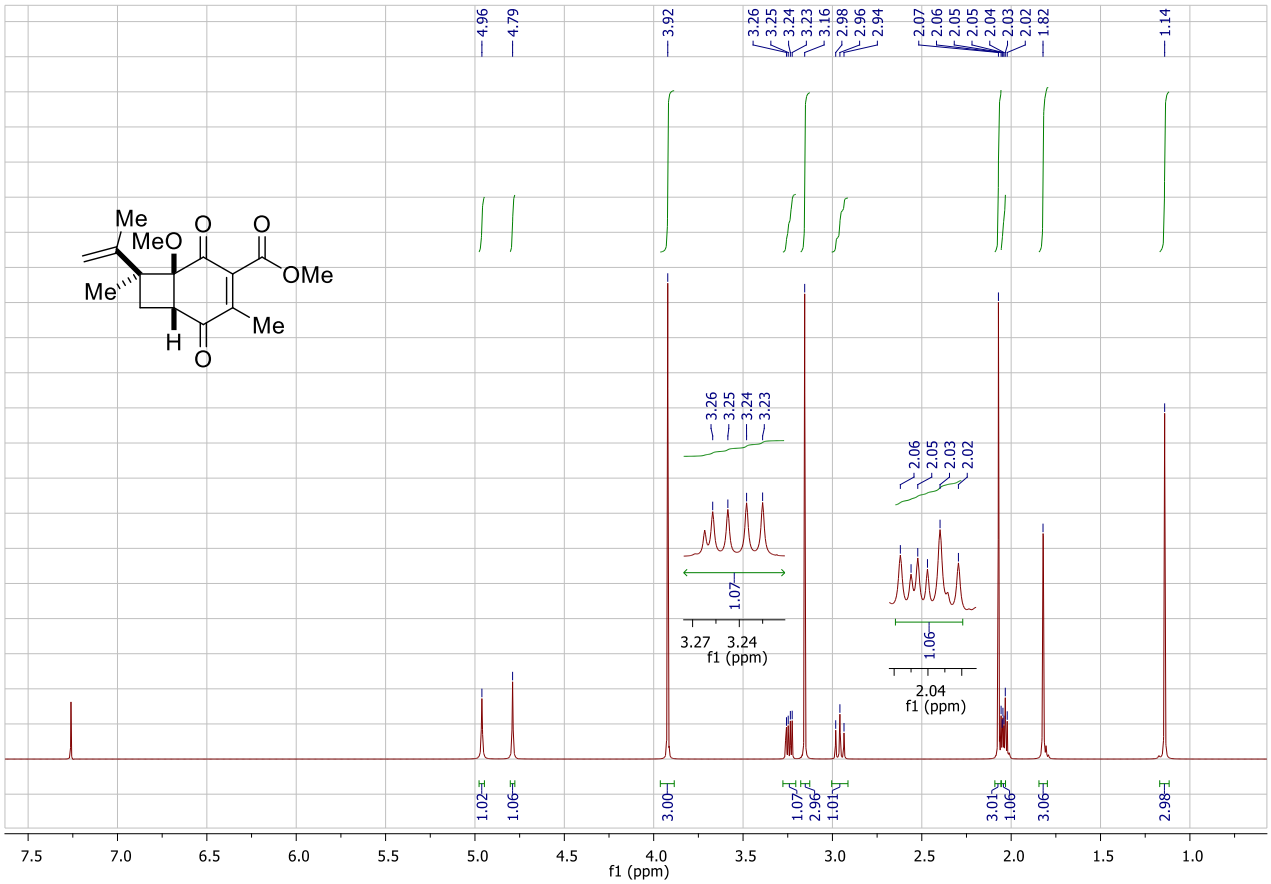
Experimental data for compound **13** were in agreement with those found in the literature.[20]

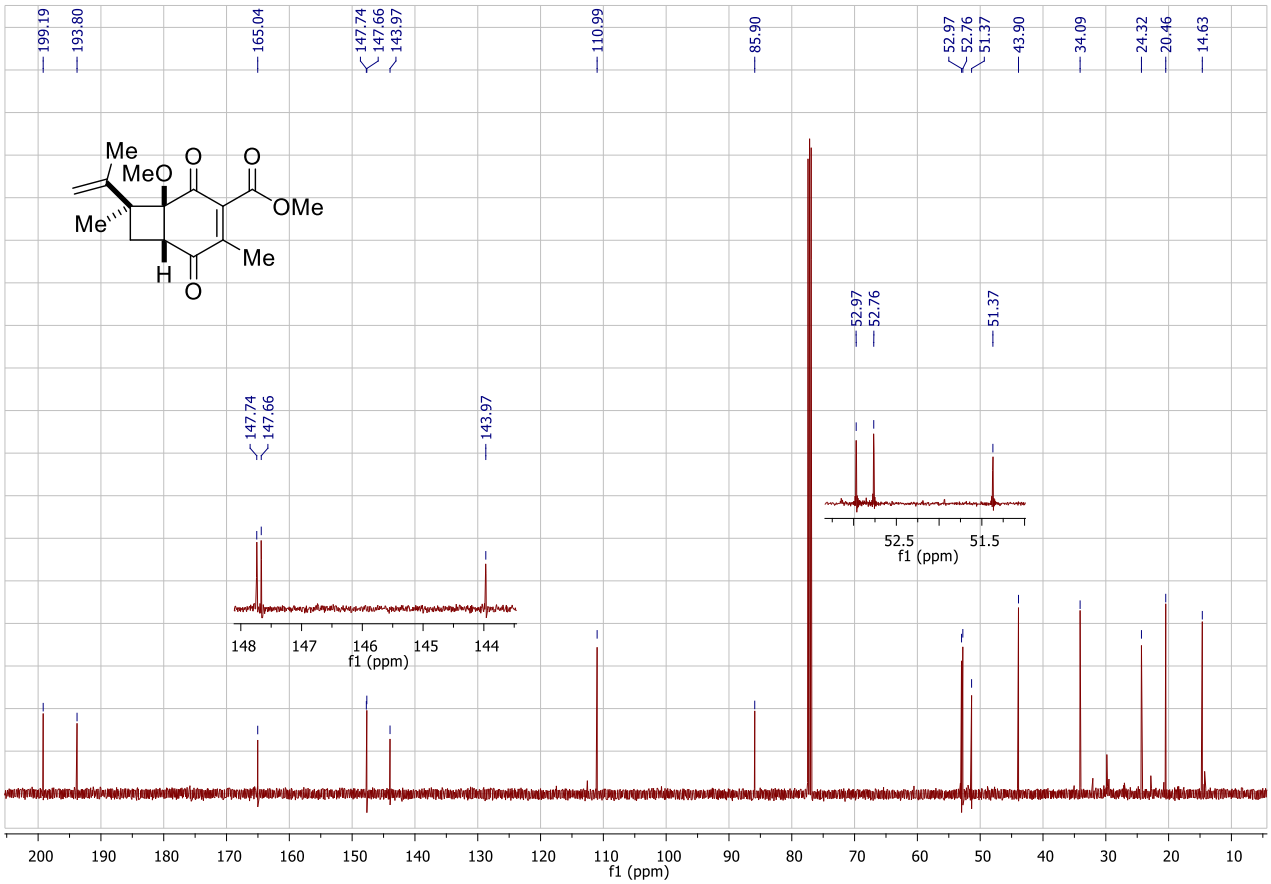
^{1}H and ^{13}C NMR spectra for Methyl (±)-*rel*-(1*R*,6*R*,8*S*)-1-methoxy-4,6-dimethyl-2,5-dioxo-8-((*E*)-prop-1-en-1-yl)bicyclo[4.2.0]oct-3-ene-3-carboxylate (**14**) in $CDCl_3$ (500 and 125 MHz)



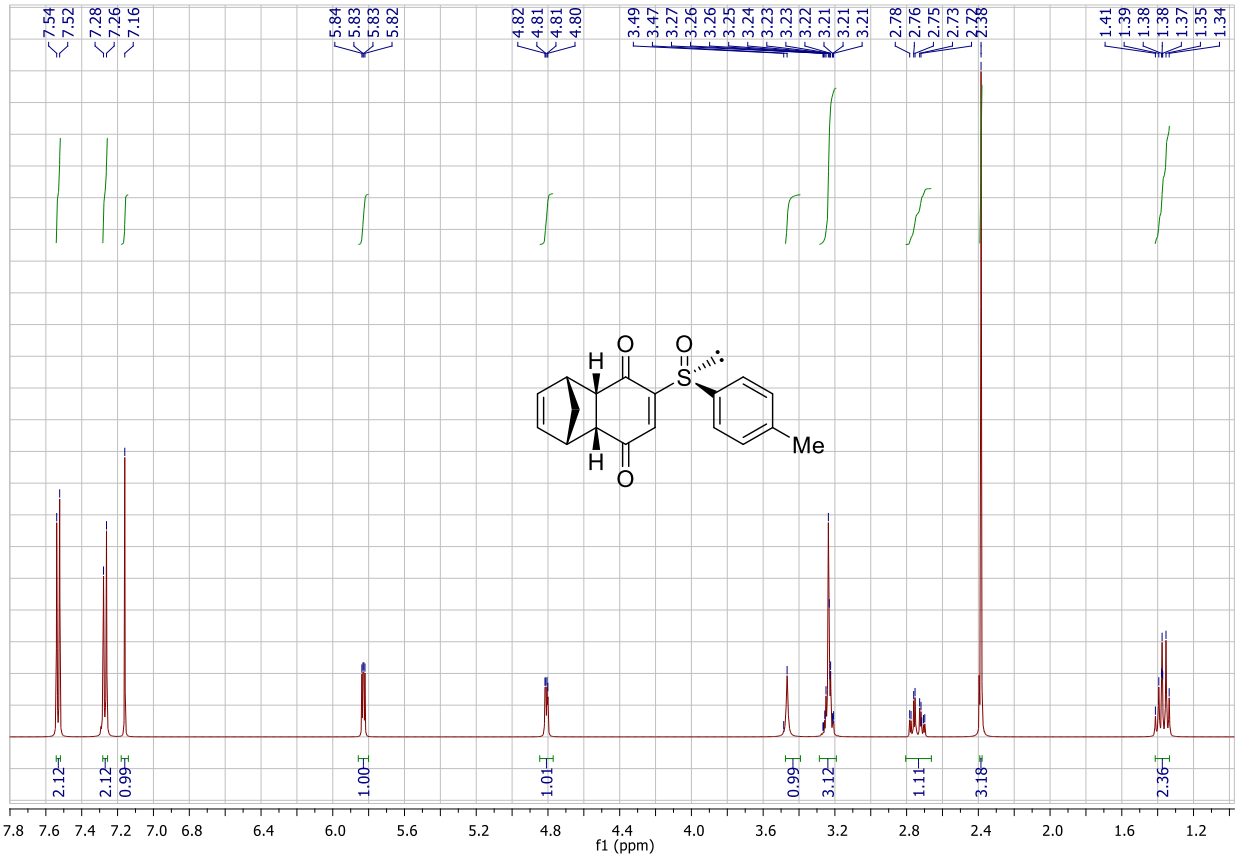


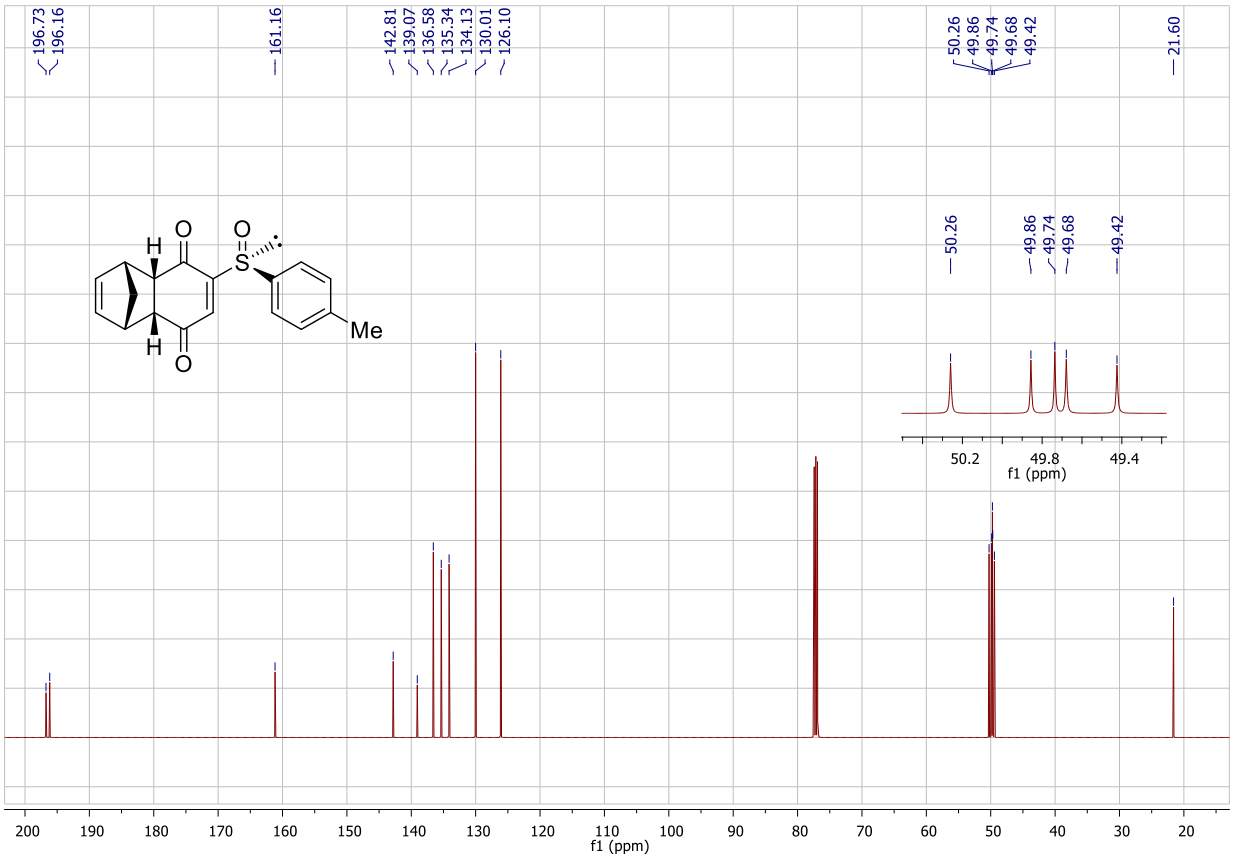
^{1}H and ^{13}C NMR spectra for Methyl (±)-*rel*-(1*R*,6*S*,8*R*)-1-methoxy-4,6,8-trimethyl-2,5-dioxo-8-(prop-1-en-2-yl)bicycle[4.2.0]oct-3-ene-3-carboxylate (**15**) in $CDCl_3$ (500 and 125 MHz)





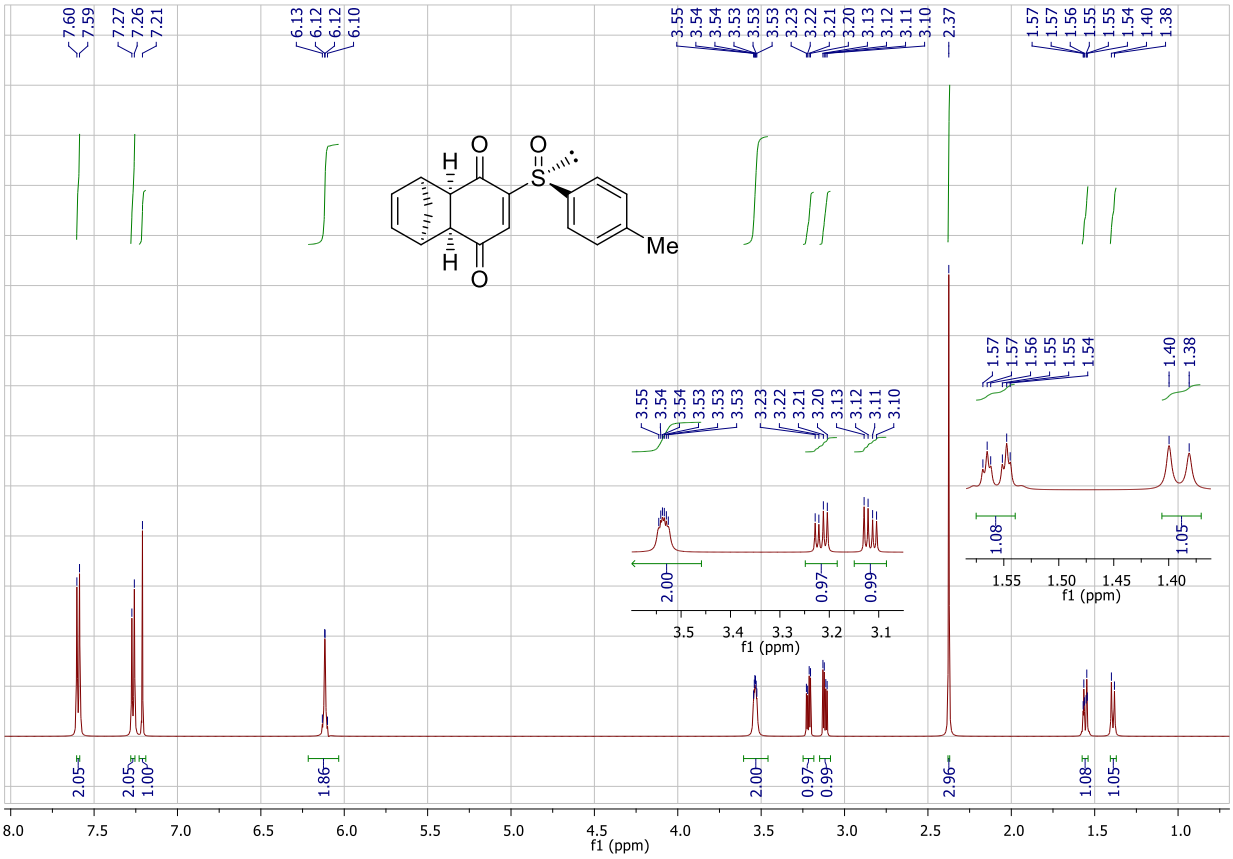
^{1}H and ^{13}C NMR spectra for (+)-(1*S*,4*R*,4a*S*,8a*R*)-6-((*S*)-*p*-tolylsulfinyl)-1,4,4a,8a-tetrahydro-1,4-methanonaphthalene-5,8-dione (**α-16**) in $CDCl_3$ (500 and 125 MHz)

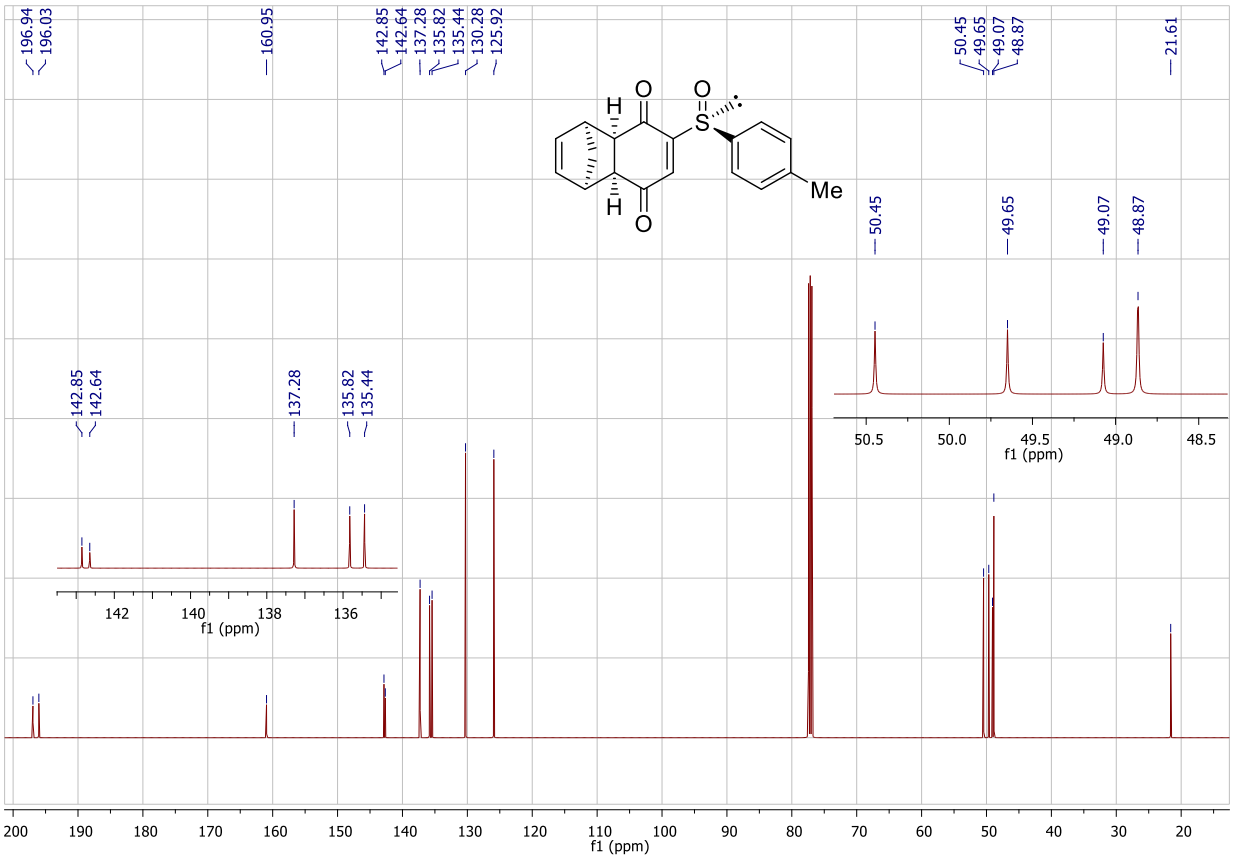




Experimental data for compound **α-16** were in agreement with those found in the literature.[8]

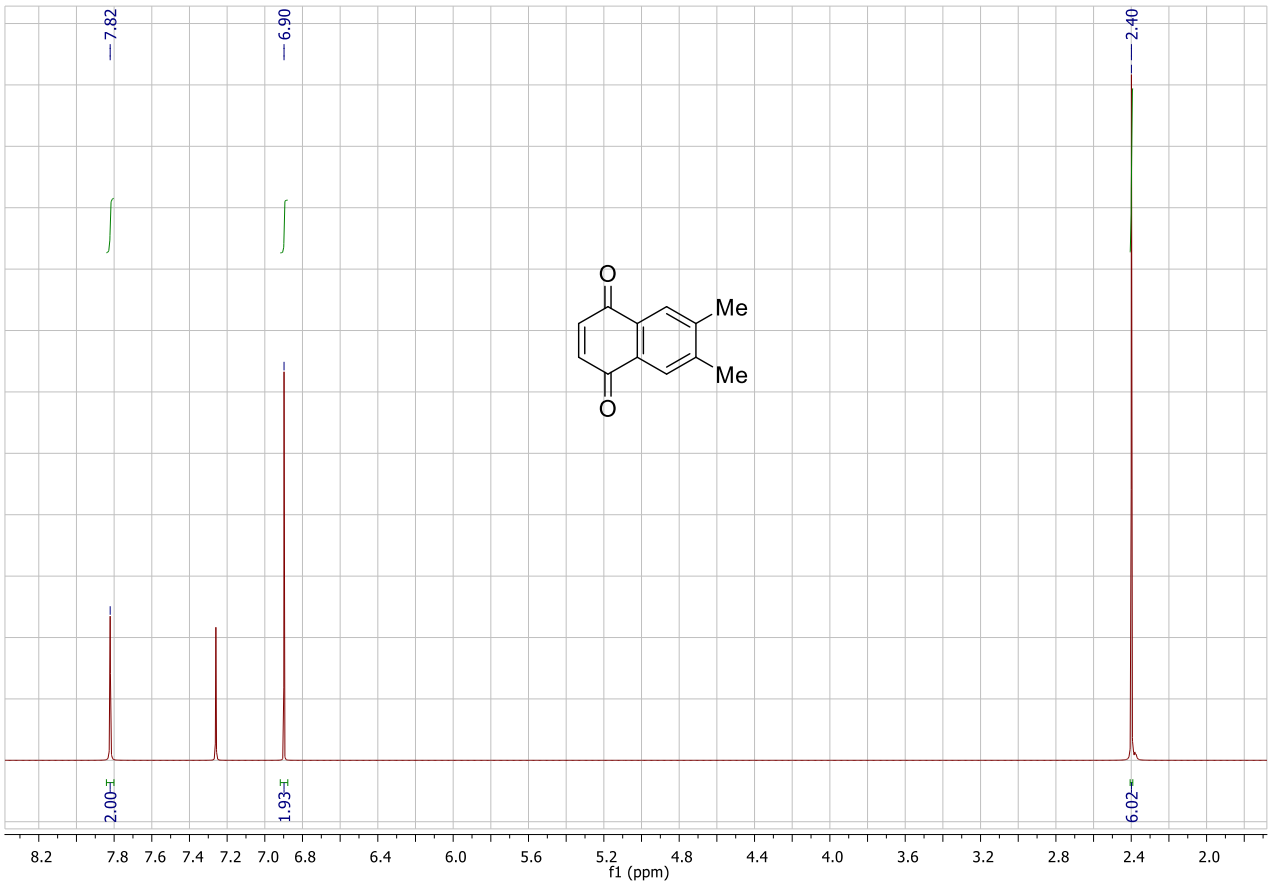
^{1}H and ^{13}C NMR spectra for (+)-(1*R*,4*S*,4a*R*,8a*S*)-6-((*S*)-*p*-tolylsulfinyl)-1,4,4a,8a-tetrahydro-1,4-methanonaphthalene-5,8-dione (**β-16**) in $CDCl_3$ (500 and 125 MHz)

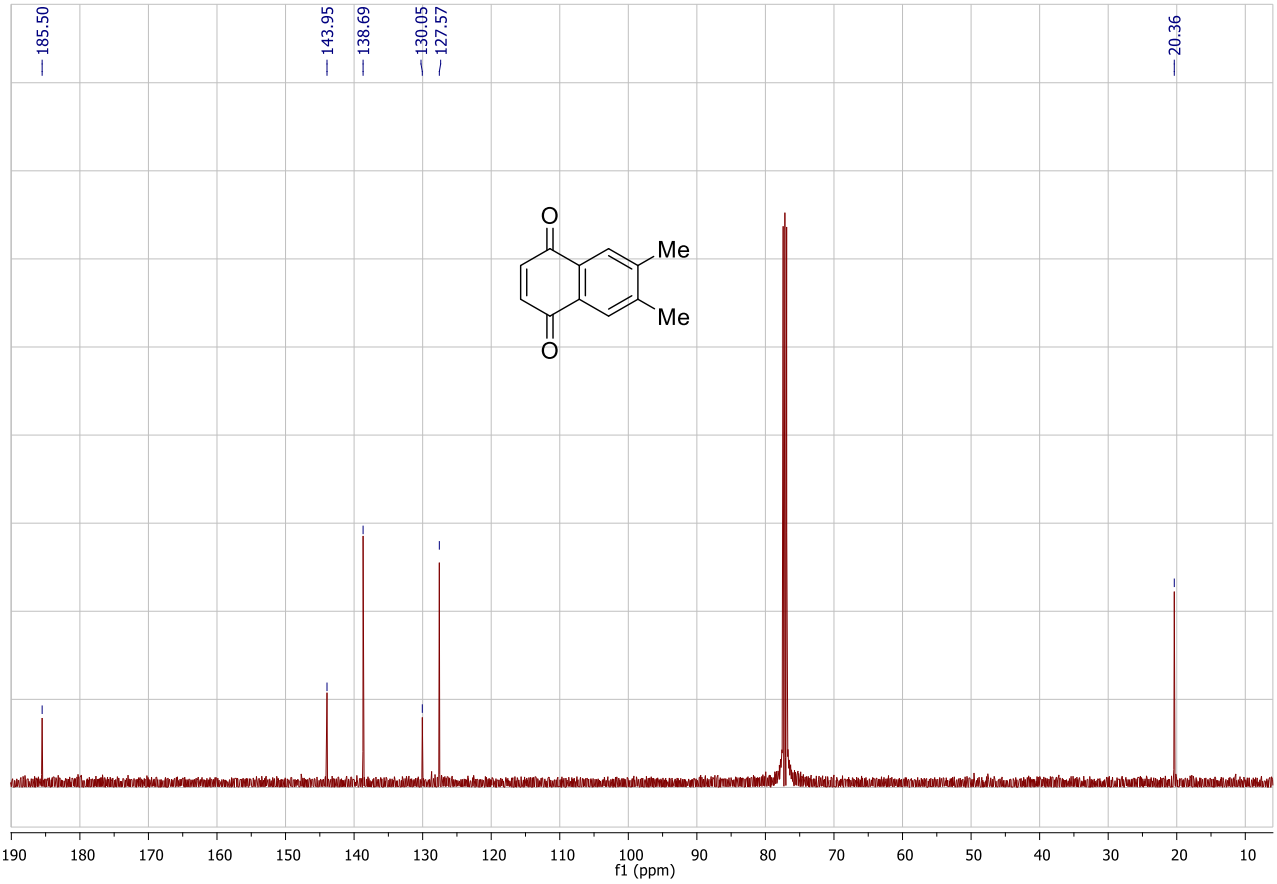




Experimental data for compound **β-16** were in agreement with those found in the literature.[8]

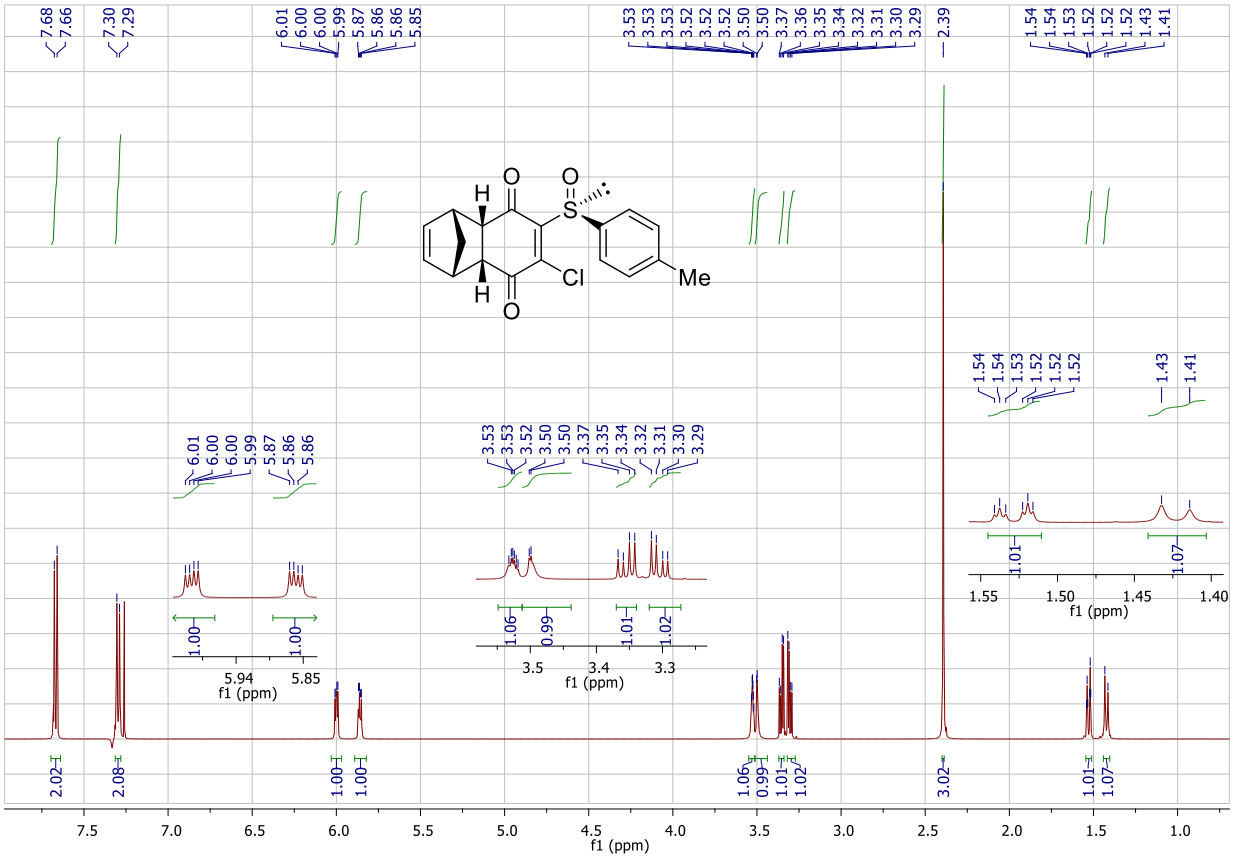
^{1}H and ^{13}C NMR spectra for 6,7-dimethylnaphthalene-1,4-dione (**17**) in $CDCl_3$ (500 and 125 MHz)

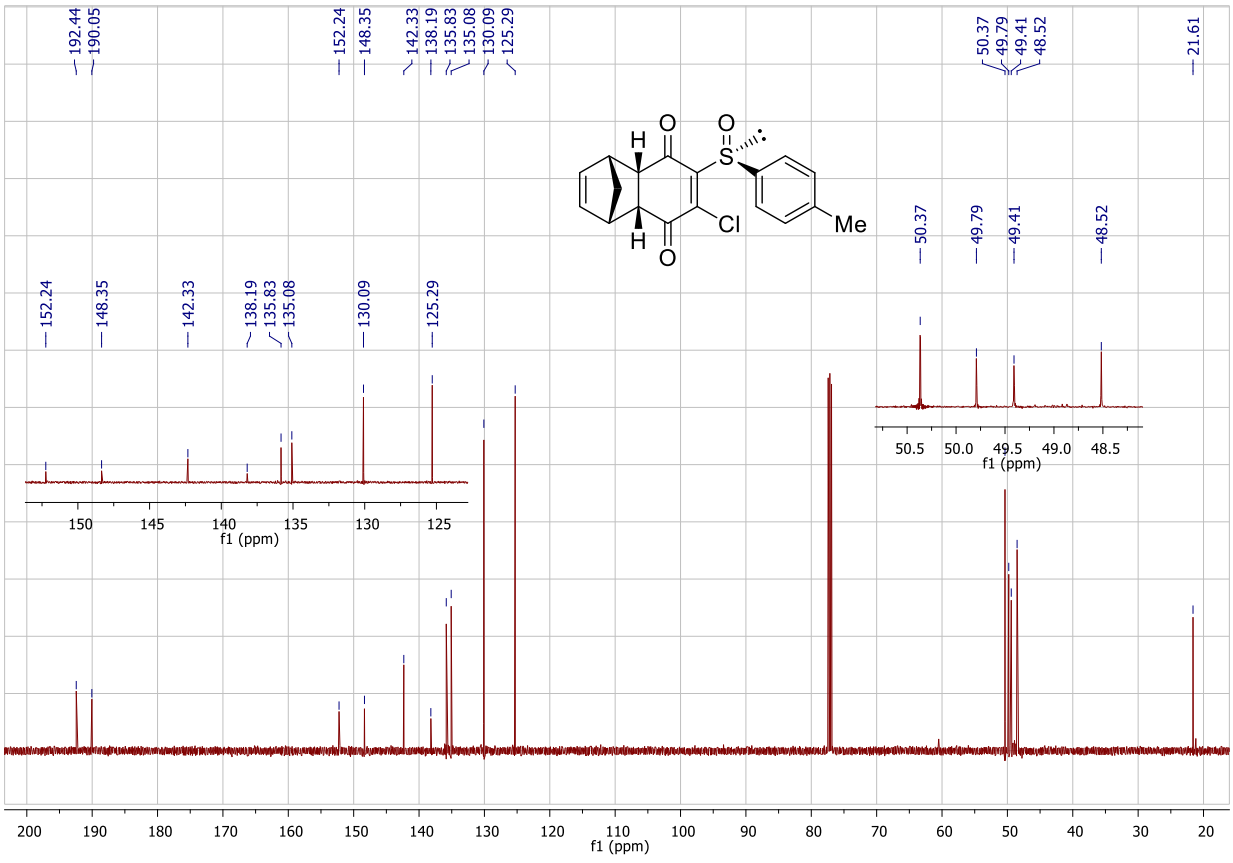




Experimental data for compound **17** were in agreement with those found in the literature.[21]

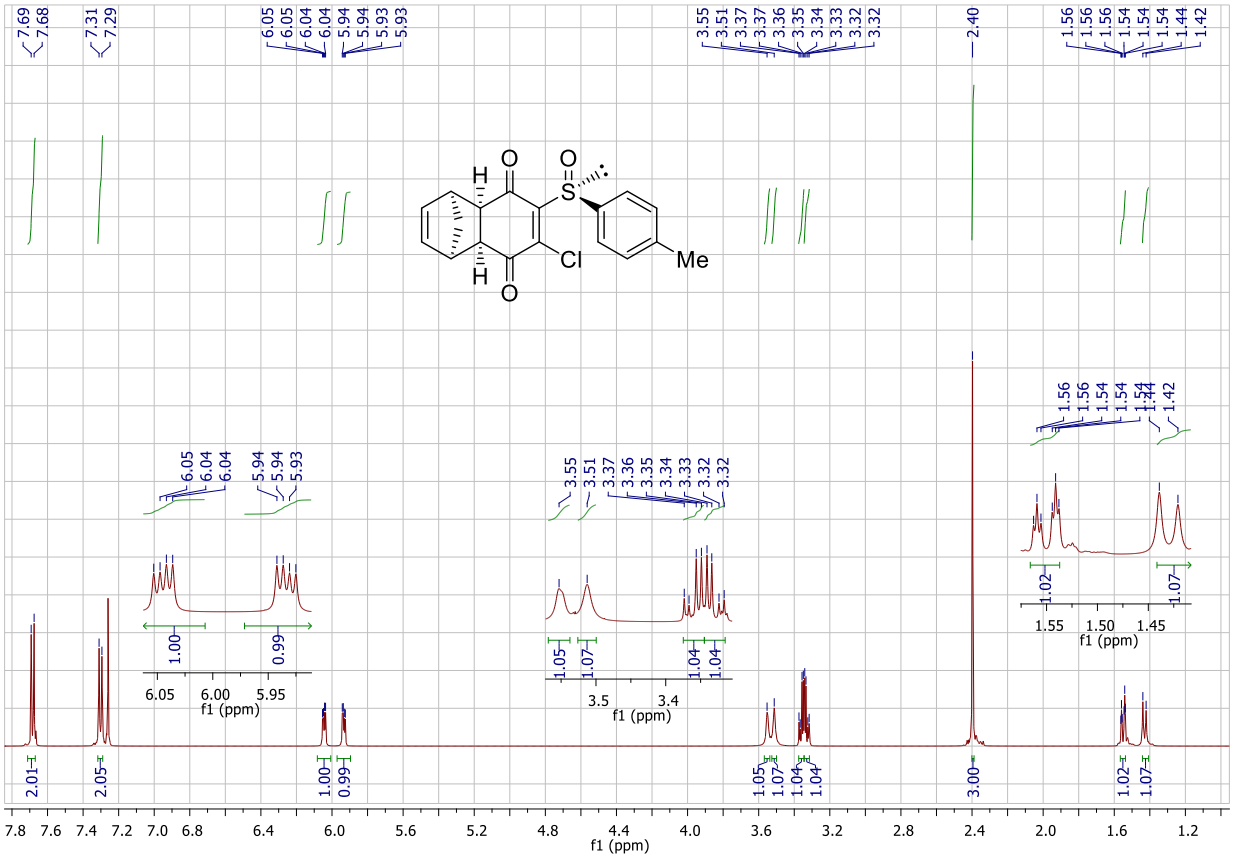
^{1}H and ^{13}C NMR spectra for (+)-(1*R*,4*S*,4a*R*,8a*S*)-6-chloro-7-((*S*)-*p*-tolylsulfinyl)-1,4,4a,8a-tetrahydro1,4-methanonaphthalene-5,8-dione (**α-18**) in $CDCl_3$ (500 and 125 MHz)

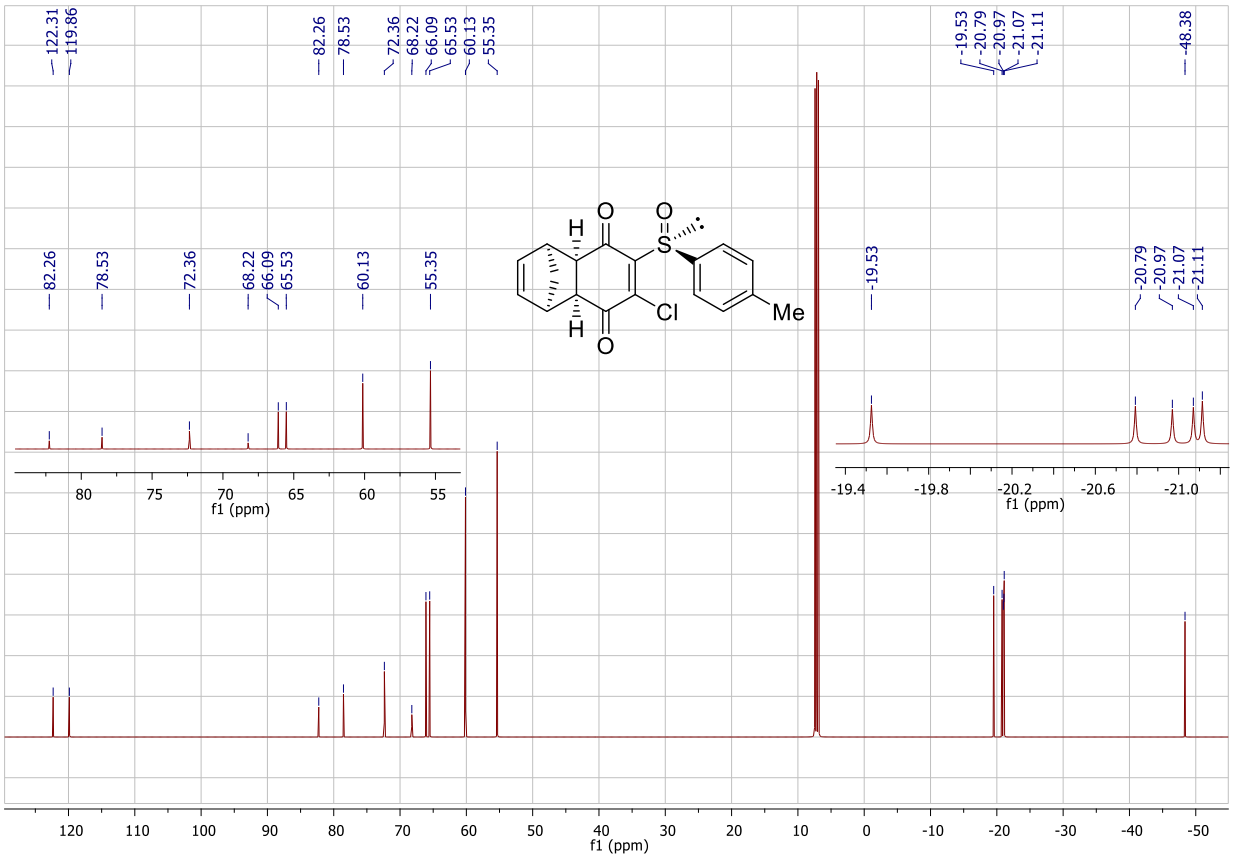




Experimental data for compound **α-18** were in agreement with those found in the literature.[9]

^{1}H and ^{13}C NMR spectra for (+)-(1*S*,4*R*,4a*S*,8a*R*)-6-chloro-7-((*S*)-*p*-tolylsulfinyl)-1,4,4a,8a-tetrahydro1,4-methanonaphthalene-5,8-dione (**β-18**) in $CDCl_3$ (500 and 125 MHz)





Experimental data for compound **β-18** were in agreement with those found in the literature.[9]

References

1. Lanfranchi, D. A.; Hanquet, G. *J. Org. Chem.* **2006**, *71*, 4854-4861. https://doi.org/10.1021/jo060486n
2. Lanfranchi, D .A.; Bour, C.; Hanquet, G. *Eur. J. Org. Chem.* **2011**, 2818-2826. https://doi.org/10.1002/ejoc.201100207
3. Möller, K.; Wienhöfer, G.; Schröder, K.; Join, B.; Junge, K.; Beller, M. *Chem. Eur. J.* **2010**, *16*, 10300-10303. https://doi.org/10.1002/chem.201001429
4. Lu, L.; Chen, F. *Synth. Commun.* **2004**, *34*, 4049-4053. https://doi.org/10.1081/SCC-200036578
5. Inman, M.; Moody, C. J. *J. Org. Chem.* **2010**, *75*, 6023-6026. https://doi.org/10.1021/jo101071c
6. Brimble, M. A.; Burgess, C.; Halim, R.; Petersson, M.; Ray, J. *Tetrahedron* **2004**, *60*, 5751-5758. https://doi.org/10.1016/j.tet.2004.05.008
7. Xia, L.; Idhayadhulla, A.; Lee, Y. R. *Mol. Divers* **2016**, *20*, 17-28. https://doi.org/10.1007/s11030-015-9630-2
8. Carreño, M. C.; García Ruano, J. L.; Urbano, A. *Tetrahedron Lett.* **1989**, *30*, 4003-4006. https://doi.org/10.1016/S0040-4039(00)99307-9
9. Carreño, M. C.; García Ruano, J. L.; Toledo, M. A.; Urbano, A. T*etrahedron Lett.* **1994**, *35*, 9759-9762. https://doi.org/10.1016/0040-4039(94)88379-3
10. Mal, D.; Ray, S. *Eur. J. Org. Chem.* **2008**, 3014-3020. https://doi.org/10.1002/ejoc.200800218
11. Wright, M. W.; Smalley, Jr., T. L.; Welker, M. E.; Rheingold, A. L. *J. Am. Chem. Soc.* **1994**, *116*, 6777-6791. https://doi.org/10.1021/ja00094a037
12. Seymour, C. P.; Tohda, R.; Tsubaki, M.; Hayashi, M.; Matsubara, R. *J. Org. Chem.* **2017**, *82*, 9647-9654. https://doi.org/10.1021/acs.joc.7b01709
13. Katoh, T.; Monma, H.; Wakasugi, J.; Koichi, N.; Katoh, T. *Eur. J. Org. Chem.* **2014**, 7099-7103. https://doi.org/10.1002/ejoc.201403064
14. Martì-Centelles, V.; Lawrence, A. L.; Lusby, P. J. *J. Am. Chem. Soc.* **2018**, *140*, 2862-2868. https://doi.org/10.1021/jacs.7b12146
15. Yoshida, N.; Konno, H.; Kamikubo, T.; Takahashi, M.; Ogasawara, K. *Tetrahedron: Asymmetry* **1999**, *10*, 3849-3857. https://doi.org/10.1016/S0957-4166(99)00414-0
16. Evans, D. A.; Wu, J. *J. Am. Chem. Soc.* **2003**, *125*, 10162-10163. https://doi.org/10.1021/ja0367602
17. Nishimoto, K.; Okada, Y.; Kim, S.; Chiba, K. *Electrochim. Acta* **2011**, *56*, 10626-10631. https://doi.org/10.1016/j.electacta.2011.02.087
18. Halterman, R. L.; Jan, S. T. *J. Org. Chem.* **1991**, *56*, 5253-5254. https://doi.org/10.1021/jo00018a008
19. Bohlmann, F.; Mathar, W.; Schwarz, H. *Chem. Ber.* **1977**, *110*, 2028-2045.

https://doi.org/10.1002/cber.19771100603
20. Hayakawa, K.; Ueyama, K.; Kanematsu, K. *J. Org. Chem.* **1985**, *50*, 1963-1969. https://doi.org/10.1021/jo00211a034
21. Catir, M.; Hamdullah, K. *Synlett* **2004**, 2151-2154. https://doi.org/10.1055/s-2004-832843

