Supporting Information

Synthesis of Dispiro-Orthoester *via* an Acetal Oxo-Carbenium Ion

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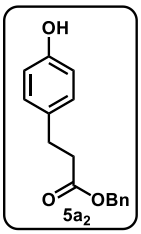
Content:

(I) General Information

All the chemicals were purchased commercially and used without further purification. All reactions were carried out in oven-dried glassware before use. Solvents were dried and distilled by standard laboratory purification techniques. Reactions were monitored by thin-layer chromatography (TLC) carried out on 0.25 mm Merck silica gel plates (60F-254) using UV light as a visualizing agent and Phosphomolybdic acid ($H_3[Mo_{12}PO_{40}]\cdot 12H_2O$), $KMnO_4$, *p*-anisaldehyde, Iodine and heat as developing agents. Flash column chromatography was performed using silica gel (size 100-200 and 230-400 mesh) and Alumina (basic). Yields refer to chromatographically pure material unless otherwise stated. ^1H and ^{13}C NMR spectra were recorded on Bruker Advance 500 and Bruker Advance 400 in Benzene-d_6, DMSO-d_6, and $CDCl_3$, having TMS 0.03% as the internal standard. Mass spectrometric data were obtained using WATERS-Q-T and Agilent of Premier-ESI-MS. Neat compounds were used to record all IR spectra. Melting points were obtained using a capillary melting point apparatus. Optical rotation was measured using a polarimeter (AUTOPOL II) at 20 °C. The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublet, ddd = doublet of doublet of doublet, m = multiplet. For plotting the graphs, Origin 2019 pro and Excel were used. Structure drawing was done using ChemDraw 20.1.1.

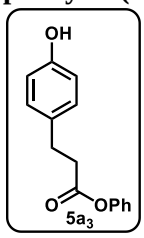
(II) Starting material preparation

benzyl 3-(4-hydroxyphenyl)propanoate ($5a_2$)



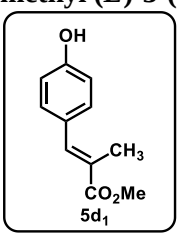
To a stirred solution of 3-(4-hydroxyphenyl)propanoic acid (500 mg, 3.00 mmol, 1 equiv.) in acetone (15 mL) was added ethyl (bromomethyl)benzene (615.7 mg, 3.6 mmol, 1.2 equiv.) and $KHCO_3$ (375.5 mg, 3.75 mmol, 1.25 equiv.) under nitrogen atmosphere and it was heated at 150 ℃ for 12 h. The reaction progress was monitored by TLC. Upon the completion of the reaction, it was concentrated in vacuo to remove acetone followed by flash chromatography R_f (Hexane/EtOAc, 80:20) = 0.3 to provide benzyl 3-(4-hydroxyphenyl)propanoate **$5a_2$** (169 mg, 22%) as a white solid. **^{1}H NMR** (396 MHz, CHLOROFORM-*D*) δ 7.36 (dtd, *J* = 15.9, 6.6, 4.2 Hz, 5H), 7.04 (d, *J* = 8.5 Hz, 2H), 6.78 – 6.72 (m, 2H), 5.14 (s, 2H), 2.92 (t, *J* = 7.7 Hz, 2H), 2.68 (t, *J* = 7.6 Hz, 2H). **^{13}C{^{1}H} NMR** (101 MHz, CHLOROFORM-*D*) δ 173.5, 154.3, 135.8, 132.1, 129.4, 128.6, 128.3, 128.3, 115.4, 66.5, 36.3, 30.1.

phenyl 3-(4-hydroxyphenyl)propanoate ($5a_3$)



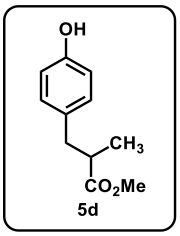
To a stirred solution of 3-(4-hydroxyphenyl)propanoic acid (500 mg, 3.00 mmol, 1 equiv.) in ethyl acetate (30 mL) was added phenol (847 mg, 9.0 mmol, 3 equiv.), DCC (796 mg, 3.86 mmol, 1.28 equiv.), DMAP (472 mg, 3.86 mmol, 1.28 equiv.) at room temperature under a nitrogen atmosphere and was stirred for 12 h. The reaction progress was monitored by TLC. Upon the completion of the reaction, it was concentrated in vacuo to remove ethyl acetate followed by flash chromatography R_f (Hexane/EtOAc, 70:30) = 0.5 to provide phenyl 3-(4-hydroxyphenyl)propanoate **$5a_3$** (196 mg, 27%) as a white solid. **^{1}H NMR** (500 MHz, CHLOROFORM-*D*) δ 7.37 (dd, *J* = 8.6, 7.3 Hz, 2H), 7.23 (t, *J* = 7.4 Hz, 1H), 7.12 (d, *J* = 6.9 Hz, 2H), 7.05 – 6.98 (m, 2H), 6.79 – 6.72 (m, 2H), 5.27 (-OH broad peak, 1H), 3.01 (t, *J* = 7.6 Hz, 2H), 2.86 (t, *J* = 7.7 Hz, 2H). **^{13}C{^{1}H} NMR** (126 MHz, CHLOROFORM-*D*) δ 172.0, 154.3, 150.7, 132.1, 129.6, 129.5, 126.0, 121.6, 115.5, 36.4, 30.2.

methyl (*E*)-3-(4-hydroxyphenyl)-2-methylacrylate[26] ($5d_1$)



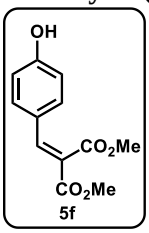
It was prepared by following known literature.
^{1}H NMR (500 MHz, CHLOROFORM-*D*) δ 7.66 (s, 1H), 7.32 (d, *J* = 8.7 Hz, 2H), 6.91 (d, *J* = 8.6 Hz, 2H), 3.83 (s, 3H), 2.13 (d, *J* = 1.4 Hz, 3H). **^{13}C{^{1}H} NMR** (101 MHz, CHLOROFORM-*D*) δ 170.4, 156.6, 139.6, 131.8, 128.1, 125.5, 115.6, 52.4, 14.1.

methyl 3-(4-hydroxyphenyl)-2-methylpropanoate (5d)



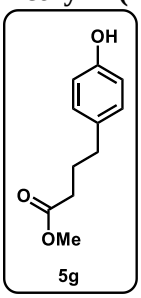
To a stirred solution of methyl (*E*)-3-(4-hydroxyphenyl)-2-methylacrylate **5d**$_1$ (2.0 g, 10.4 mmol, 1 equiv.) in ethanol (20 mL) was added Pd-charcoal (5% Pd on carbon) (10 mol%) at room temperature under hydrogen atmosphere and it was stirred for 12 h. The reaction progress was monitored by TLC. Upon the completion of the reaction, it was filtered through a pad of Celite using ethyl acetate followed by a concentration of filtrate in vacuo to obtain methyl 3-(4-hydroxyphenyl)-2-methylpropanoate **5d** (1.98 g, 98%) as yellow oil. **^{1}H NMR** (500 MHz, CHLOROFORM-*D*) δ 6.99 (d, *J* = 8.5 Hz, 2H), 6.74 (dd, *J* = 8.5, 1.4 Hz, 2H), 3.64 (s, 3H), 2.92 (dd, *J* = 13.5, 7.2 Hz, 1H), 2.71 (h, *J* = 7.0 Hz, 1H), 2.62 (dd, *J* = 13.5, 7.4 Hz, 1H), 1.15 (d, *J* = 6.9 Hz, 3H). **^{13}C{^{1}H} NMR** (126 MHz, CHLOROFORM-*D*) δ 177.6, 154.6, 131.0, 130.1, 115.4, 51.9, 41.9, 39.0, 16.8.

dimethyl 2-(4-hydroxybenzylidene)malonate[27] **(5f)**



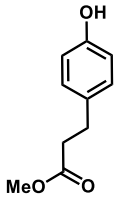
It was prepared by following known literature.
^{1}H NMR (500 MHz, CHLOROFORM-*D*) δ 7.70 (OH peak, 1H), 7.31 (d, *J* = 8.7 Hz, 2H), 6.81 (d, *J* = 8.8 Hz, 2H), 6.02 (s, 1H), 3.87 (s, 3H), 3.83 (s, 3H). **^{13}C{^{1}H} NMR** (101 MHz, CHLOROFORM-*D*) δ 168.0, 165.1, 158.5, 143.0, 131.9, 125.2, 122.6, 116.1, 52.9, 52.7

methyl 4-(4-hydroxyphenyl)butanoate (5g)

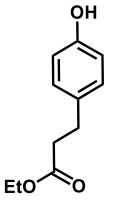


To a 250 mL round bottom flask charged with magnetic pallet was added 4-(4-methoxyphenyl)butanoic acid (2g, 10.2 mmol), HBr (20 mL, 48%) and glacial acetic acid (32 mL). After addition, it was fitted with a water condenser and stirred at 150 °C. Progress of the reaction was monitored by TLC and upon completion (6 h) it was poured into 150 mL of water and extracted with ethyl acetate to obtain 4-(4-hydroxyphenyl)butanoic acid (1.94 g, 98%) as a yellow solid.
A mixture of 4-(4-hydroxyphenyl)butanoic acid (1.80 g, 5.0 mmol, 1 equiv.), concentrated H_2SO_4 (0.1 mL), and CH_3OH (30 mL) were refluxed overnight. After the mixture was concentrated, water (25 mL) was added followed by $NaHCO_3$ until pH became 8. The mixture was extracted with ethyl acetate (2*25 mL) and the extracts were washed with saturated NaCl (10 mL), dried with anhydrous $MgSO_4$, and purified by filtering through silica gel to give methyl 4-(4-hydroxyphenyl)butanoate **5g** (1.90 g, 98% yield) as a yellow oil. **^{1}H NMR** (396 MHz, CHLOROFORM-*D*) δ 7.01 (d, *J* = 8.6 Hz, 2H), 6.78 (dd, *J* = 8.6, 2.2 Hz, 2H), 3.68 (s, 3H), 2.56 (d, *J* = 7.5 Hz, 2H), 2.34 (t, *J* = 7.5 Hz, 2H), 1.92 (p, *J* = 7.5 Hz, 2H). **^{13}C{^{1}H} NMR** (101 MHz, CHLOROFORM-*D*) δ 175.0, 154.2, 133.0, 129.5, 115.3, 51.8, 34.2, 33.4, 26.7.

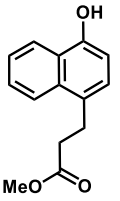
Commercial and known ester substrates:



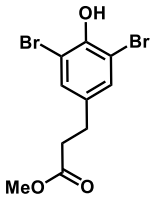
5a
Commercial
Methyl 3-(4-hydroxyphenyl) propanoate
CAS No.: **5597-50-2**



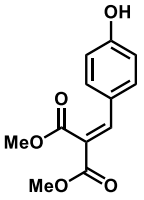
5a$_1$
Commercial
Ethyl 3-(4-hydroxyphenyl) propanoate,
CAS No.: **23795-02-0**



5b
methyl 3-(4-hydroxynaphthalen-1-yl) propanoate
Prepared by following
J. Am. Chem. Soc., 2021, **143,** 6363–6369.

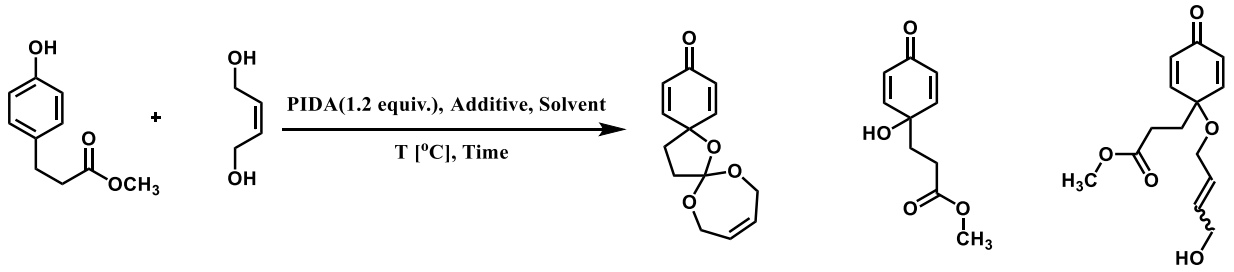


5e
Methyl 3-(3,5-dibromo-4-hydroxyphenyl)propanoate
Prepared by following
ACS Med. Chem. Lett., 2017, **8,** 947–952.



5f
dimethyl 2-(4-hydroxybenzylidene)malonate
Prepared by following
Tetrahedron Lett., 2017, **58,** 3219–3222.

(III) Detailed optimization



5a (1 equiv.) **6a** **7a** **8a** **9a**

S.No.	6a (equiv.)	Solvent	Additive (equiv.)	Temp. (°C)	Time	Isolated Yield (%) 7a	Isolated Yield (%) 8a	Isolated Yield (%) 9a
1	12	-	-	0 to rt	24 h	30	-	31
2	12	CH_3CN (0.1 M)	-	rt	12 h	nr[a]	-	-
3	12	DCM (0.1 M)	-	rt	12 h	nr[a]	-	-
4	12	DCM (0.1 M)	-	0	12 h	nr[a]	-	-
5	12	DCM (0.1 M)	PTSA (0.5 eq.)	0	12 h	nr[a]	-	-
6	12	THF (0.1 M)	-	rt	12 h	nr[a]	-	-
7	12	Toluene (0.1 M)	-	rt	12 h	15	27	-
8	2.2	DMSO (0.1 M)	-	rt	12 h	23	24	-
9	2.2	HFIP (0.25 M)	-	rt	24 h	30	15	-
10	2.2	HFIP (0.25 M)	-	rt	1 min	71	14	-
11	2.2	HFIP (0.25 M)	-	rt	5 min	59	22	-
12	2.2	HFIP (2.5 M)	-	rt	5 min	52	19	-
13	2.2	HFIP (0.25 M)	-	rt	1 h	35	12	-
14	2.2	HFIP (0.25 M)	-	45	1 min	30	30	-

15	2.2	HFIP (0.25 M)		0	15 min	76	22	-
16	2.2	HFIP (0.25 M)	-	rt	30 min	15	52	-
17	2.2	HFIP (0.25 M)	Molecular sieves (10 mol %)	rt	10 min	41	19	-
18	2.2	HFIP (0.25 M)	Na_2SO_4 (3)	rt	1 min	11	20	-
19	2.2	HFIP (0.25 M)	Na_2CO_3 (2.2)	rt	15 min	39	15	-
20	2.2	HFIP (0.25 M)	$NaHCO_3$ (2.2)	rt	15 min	35	22	-
21	2.2	HFIP (0.25 M)	K_2CO_3 (2.2)	rt	15 min	55	30	-
22	2.2	HFIP (0.25 M)	DMAP (2.2)	rt	15 min	50	35	-
23	2.2	HFIP (0.25 M)	DABCO (2.2)	rt	15 min	45	38	-
24	2.2	HFIP (0.25 M)	2,6-lutidine (2.2)	rt	12 h	67	35	-
25	2.2	HFIP (0.25 M)	Et_3N (2.2)	rt	1 min	73		-
26	2.2	HFIP (0.25 M)	TEMPO (2.2)	rt	1 min	67	28	-
27	2.2	HFIP (0.25 M)	DBU (2.2)	rt	12 h	77	traces	-
28	2.2	HFIP (0.25 M)	DBU (5)	rt	12 h	72	7	-
29	2.2	HFIP (0.25 M)	DBU (1.2)	rt	12 h	56	16	-
30	2.2	HFIP: DCM (1:1) (0.25 M)	DBU (2.2)	rt	12 h	nr[a]	-	-
31	2.2	HFIP (0.25 M) CF_3CH_2OH (1:1)	-	rt	10 min	37	45	-
32	2.2	HFIP: THF (1:1) (0.25 M)	DBU (2.2)	rt	12 h	nr[a]	-	-
33	2.2	HFIP (0.25 M)	DBU (2.2)	0 to rt	12 h	83	traces	-
34	2.2	CF_3CH_2OH (0.25 M)	-	rt	12 h	22	17	-
35	PIFA (2.2)	HFIP (0.25 M)	-	rt	12 h	0	34	-
36	PhI (20 mol%) and *m*cpba (1.2 equiv.)	HFIP (0.25 M)	-	rt	12 h	-	-	-
37	2.2	HFIP (0.25 M)	DBU (2.2)	0 to rt	1 h	72	traces	-
38	2.2	HFIP (0.25 M)	DBU (2.2)	0 to rt	3 h	74	traces	-
39	2.2	HFIP (0.25 M)	DBU (2.2)	0 to rt	6 h	75	traces	-
40	2.2	HFIP (0.25 M)	DBU (2.2)	0 to rt	9 h	77	traces	-

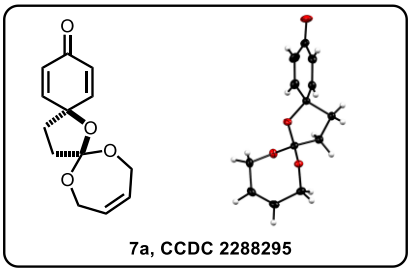
[a]**complex mixture**

(IV) General procedure A

It involved adding $PhI(OAc)_2$ (PIDA, 1.2 equiv.) in a single portion to a stirred solution of HFIP (0.25 M) at 0 ºC under an N_2 atmosphere followed by the addition of DBU (2.2 equiv.). The mixture was stirred at 0 ºC until PIDA dissolved completely. Afterward, a phenol derivative (1 equiv.) was added, and the diol was introduced upon observing a color change. The resulting mixture was allowed to warm to room temperature and stirred for 12 hours. Subsequently, it was diluted with ethyl acetate, and the reaction mixture was evaporated under reduced pressure. The residue was purified using column chromatography to isolate the desired product.

(V) Experimental Data

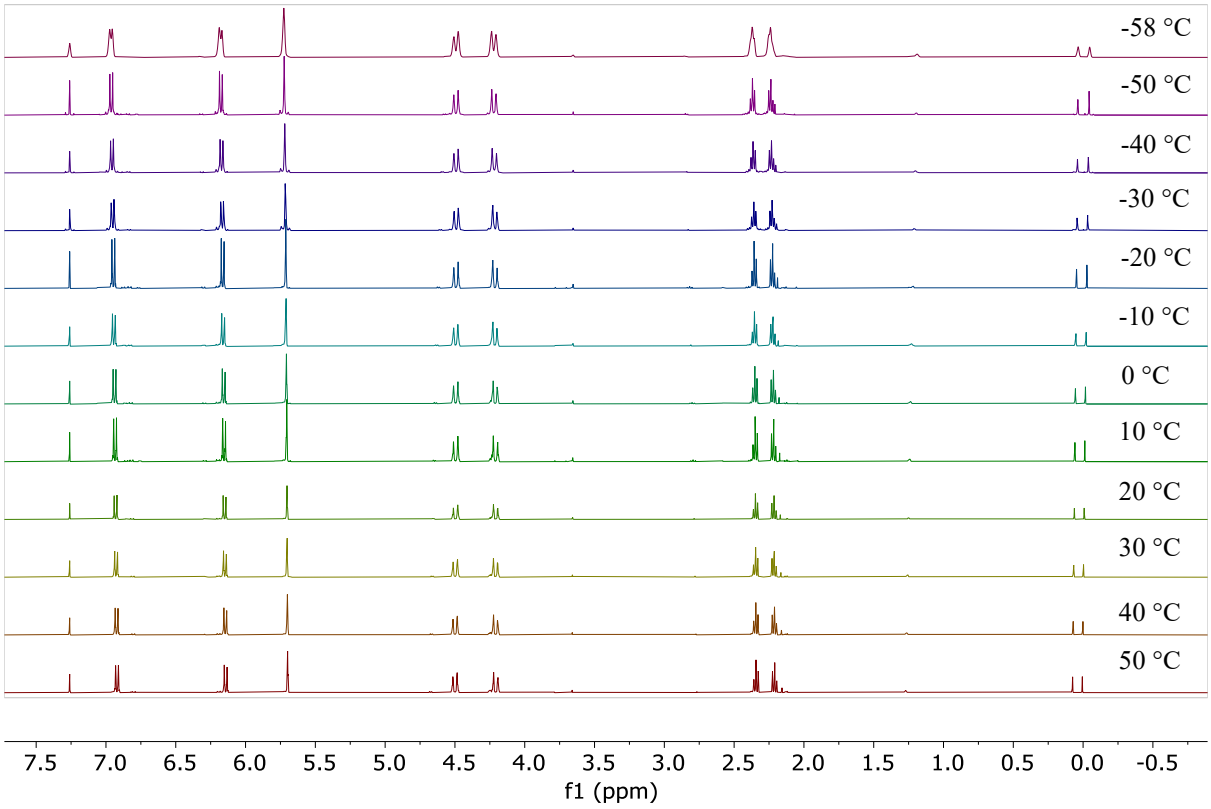
7,9,14-trioxadispiro[5.1.68.26]hexadeca-1,4,11-trien-3-one (7a)

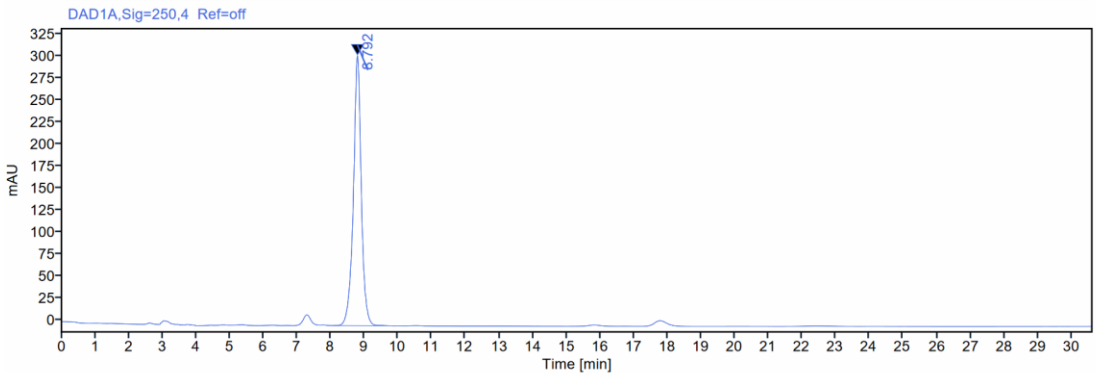


The general procedure **A** was followed using methyl 3-(4-hydroxyphenyl)propanoate (100 mg, 0.555 mmol, 1 equiv.) and (*Z*)-but-2-ene-1,4-diol (185.73 mg, 1.22 mmol, 2.2 equiv.) to obtain crude product **7a**. Purification by column chromatography R_f(Hexane/EtOAc 50/50, UV active, PMA stain active) = 0.5 yielded **7a** (107.8 mg, 83%) as a colorless white solid. **^{1}H NMR** (500 MHz, CHLOROFORM-*D*) δ 6.92 (d, *J* = 10.0 Hz, 2H), 6.14 (d, *J* = 9.9 Hz, 2H), 5.70 (t, 2H), 4.49 (t, 2H), 4.20 (t, 2H), 2.34 (t, *J* = 7.6 Hz, 2H), 2.21 (t, *J* = 7.6 Hz, 2H). **^{13}C{^{1}H} NMR** (100 MHz, CHLOROFORM-*D*) δ 185.1, 149.3, 128.5, 127.4, 125.1, 77.4, 62.8, 34.7, 33.1. **IR υ (cm-1)** 2921, 2853, 1725, 1668, 1628, 1438, 1381, 1315, 1209, 1167, 1074, 1046, 998, 961, 885, 913, 850, 804, 643, 612. **HRMS** (ESI-TOF) m/z: [M+H]- Calcd for $C_{13}H_{15}O_4$ 235.0970; Found 235.0965. **mp:** 91-93 °C.

VT-NMR and **chiral HPLC** analyses for **7a**

We performed the VT ^{1}H NMR in $CDCl_3$ from -58 °C to 50 °C. The ^{1}H NMR spectra revealed no change in either the splitting pattern or chemical shift of the spectra at various temperatures. Further, we have also performed the HPLC analysis on the chiral stationary phase using three different chiral columns (Chiralcel-ODH, Chiralpak-IC3, Chiralpak-IA) and it showed a single peak. Moreover, the result of the specific rotation showed zero value without any deviation. These results suggest that there are no other optical and non-optical isomers present. Molecule **7a** is achiral.

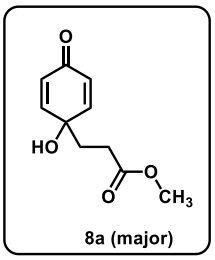




Signal:	DAD1A,Sig=250,4 Ref=off	
RT [min]	**Area**	**Area%**
8.792	5031.64	100.00
Sum	**5031.64**	

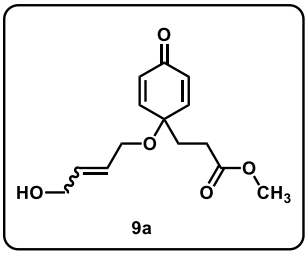
HPLC profile: 50% IPA and 50% hexane with a flow rate of 1.0 mL/min using CHIRALPAK IC-3

Methyl-3-(1-((4-hydroxybut-2-en-1-yl)oxy)-4-oxocyclohexa-2,5-dien-1-yl)propanoate (8a)



The general procedure **A** was followed using methyl 3-(4-hydroxyphenyl)propanoate (100 mg, 0.555 mmol, 1 equiv.) and (Z)-but-2-ene-1,4-diol (185.73 mg, 1.22 mmol, 2.2 equiv.) to obtain crude product **8a**. Purification by column chromatography R_f (Hexane/EtOAc 50/50, UV active, PMA stain active) = 0.2 yielded **8a** (10.8 mg, 10%) as a yellow oil. **^{1}H NMR** (500 MHz, CHLOROFORM-*D*) δ 6.81 (d, *J* = 10.4 Hz, 2H), 6.18 (d, *J* = 9.9 Hz, 2H), 3.66 (s, 3H), 2.73 (s, OH broad peak, 1H), 2.45 – 2.21 (m, 2H), 2.10 (t, *J* = 7.7 Hz, 2H). **^{13}C{^{1}H} NMR** (126 MHz, CHLOROFORM-*D*) δ 185.3, 173.5, 150.4, 128.7, 69.3, 52.1, 34.6, 28.7.

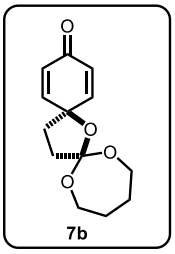
Methyl-3-(1-((4-hydroxybut-2-en-1-yl)oxy)-4-oxocyclohexa-2,5-dien-1-yl)propanoate (9a)



9a

The general procedure **A** was followed using methyl 3-(4-hydroxyphenyl)propanoate (100 mg, 0.555 mmol, 1 equiv.) and (Z)-but-2-ene-1,4-diol (185.73 mg, 1.22 mmol, 2.2 equiv.) to obtain crude product **9a**. Purification by column chromatography R_f (Hexane/EtOAc 50/50, UV active, PMA stain active) = 0.5 yielded **9a** (7.4 mg, 5%) as a yellow oil. **^{1}H NMR** (500 MHz, CHLOROFORM-*D*) δ 6.72 (d, *J* = 10.4 Hz, 2H), 6.29 (d, *J* = 10.3 Hz, 2H), 5.74 – 5.62 (m, 1H), 5.54 (dddt, *J* = 11.2, 6.3, 3.0, 1.5 Hz, 1H), 4.10 – 4.02 (m, 2H), 3.90 – 3.82 (m, 2H), 3.57 (s, *J* = 1.5 Hz, 3H), 2.27 (qd, *J* = 7.6, 3.4 Hz, 2H), 2.11 – 1.94 (m, 2H). **^{13}C{^{1}H} NMR** (126 MHz, CHLOROFORM-*D*) δ 185.1, 173.1, 150.2, 132.2, 131.5, 127.9, 74.9, 61.3, 58.5, 51.9, 34.2, 28.5. **IR υ (cm^{-1})** 3636, 3553, 3464, 2985, 2942, 2909, 2878, 1889, 1741, 1554, 1479, 1465, 1447, 1374, 1240, 1160, 1098, 1047. **HRMS (ESI):** m/z Calcd for [$C_{14}H_{18}O_5$, M+Na]: 289.1052.; Found: 289.1051.

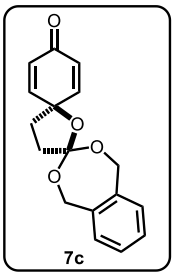
7,9,14-trioxadispiro[5.1.68.26]hexadeca-1,4-dien-3-one (7b)



7b

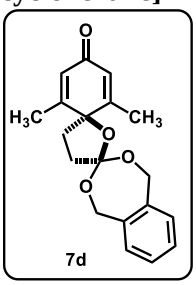
The general procedure **A** was followed using methyl 3-(4-hydroxyphenyl)propanoate (100 mg, 0.555 mmol, 1 equiv.) and butane-1,4-diol (110 mg, 1.22 mmol, 2.2 equiv.) to obtain crude product **7b**. Purification by column chromatography R_f (Hexane/EtOAc 60/40, UV active, PMA stain active) = 0.3 yielded **7b** (97 mg, 74%) as a colorless oil. **^{1}H NMR** (396 MHz, BENZENE-D_6) δ 6.57 (d, 2H), 5.99 (d, *J* = 10.2 Hz, 2H), 3.78 (ddd, *J* = 12.2, 7.4, 2.6 Hz, 2H), 3.39 (ddd, *J* = 12.2, 7.1, 2.8 Hz, 2H), 1.84 (t, *J* = 7.6 Hz, 2H), 1.70 – 1.58 (m, 2H), 1.31 (qd, *J* = 6.0, 3.5 Hz, 4H). **^{13}C{^{1}H} NMR** (100 MHz, BENZENE-D_6) δ 184.58, 149.6, 127.4, 124.9, 77.2, 64.0, 34.7, 34.1, 29.2. **IR υ (cm^{-1})** 2959, 2926, 1732, 1671, 1630, 1458, 1375, 1341, 1286,1244, 1178, 1150, 1080, 1006, 958, 933, 873, 852, 766, 690, 565, 461, 429. **HRMS** (ESI-TOF) m/z: [M+H]- Calcd for $C_{13}H_{17}O_4$ 237.1127; Found 237.1123.

1,3',4',5-tetrahydrodispiro[benzo[e][1,3]dioxepine-3,2'-furan-5',1''-cyclohexane]-2'',5''-dien-4''-one (7c)



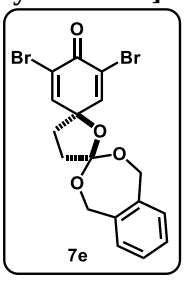
The general procedure **A** was followed using methyl 3-(4-hydroxyphenyl)propanoate (100 mg, 0.555 mmol, 1 equiv.) and 1,2-phenylenedimethanol (168.6 mg, 1.22 mmol, 2.2 equiv.) to obtain crude product **7c**. Purification by column chromatography R_f ($CHCl_3$/EtOAc 80/20) = 0.7 yielded **7c** (110 mg, 70%) as a colorless oil. **^{1}H NMR** (396 MHz, CHLOROFORM-*D*) δ 7.20 (dd, *J* = 5.6, 3.4 Hz, 2H), 7.08 (dd, *J* = 5.5, 3.4 Hz, 2H), 6.97 (d, *J* = 10.1 Hz, 2H), 6.17 (d, *J* = 10.2 Hz, 2H), 5.13 (d, *J* = 14.7 Hz, 2H), 4.77 (d, *J* = 14.8 Hz, 2H), 2.41 (t, *J* = 6.7 Hz, 2H), 2.26 (t, *J* = 6.8 Hz, 2H). **^{13}C{^{1}H} NMR** (100 MHz, CHLOROFORM-*D*) δ 185.2, 149.2, 137.0, 127.7, 127.1, 126.3, 125.2, 77.8, 66.4, 34.8, 33.4. **IR υ (cm^{-1})** 2958, 2924, 1730, 1671, 1633, 1447, 1381, 1317, 1289, 1215, 1088, 1059, 1035, 946, 914, 784, 645, 614, 475. **HRMS** (ESI-TOF) m/z: [M+H]- Calcd for $C_{17}H_{17}O_4$ 285.1127; Found 285.1123.

2'',6''-dimethyl-1,3',4',5-tetrahydrodispiro[benzo[e][1,3]dioxepine-3,2'-furan-5',1''-cyclohexane]-2'',5''-dien-4''-one (7d)



The general procedure **A** was followed using methyl ethyl 3-(4-hydroxy-2,6-dimethylphenyl)propanoate (100 mg, 0.550 mmol, 1 equiv.) and 1,2-phenylenedimethanol (167.1 mg, 1.21 mmol, 2.2 equiv.) to obtain crude product **7d**. Purification by column chromatography R_f (Hexane/EtOAc 70/30, UV active, PMA stain active) = 0.5 yielded **10d** (116 mg, 67%) as a colorless oil. **^{1}H NMR** (396 MHz, CHLOROFORM-*D*) δ 6.97 (dd, *J* = 5.8, 3.3 Hz, 2H), 6.73 (dd, *J* = 5.4, 3.3 Hz, 2H), 6.05 (s, 2H), 4.89 (d, *J* = 14.7 Hz, 2H), 4.43 (d, *J* = 14.5 Hz, 2H), 2.07 – 1.94 (m, 2H), 1.85 (s, 6H), 1.71 (dd, *J* = 9.3, 7.1 Hz, 2H). **^{13}C{^{1}H} NMR** (100 MHz, BENZENE-D_6) δ 184.6, 160.3, 137.7, 127.9, 127.1, 126.4, 84.5, 66.2, 35.2, 34.7, 18.6. **IR υ (cm^{-1})** 2958, 2923, 2870, 1730, 1671, 1632, 1447, 1381, 1317, 1263, 1228, 1172, 1087, 1058, 1034, 946, 914, 885, 748, 645, 613, 475, 430. **HRMS** (ESI-TOF) m/z: [M+H]- Calcd for $C_{19}H_{21}O_4$ 313.1440; Found 313.1429.

3'',5''-dibromo-1,3',4',5-tetrahydrodispiro[benzo[e][1,3]dioxepine-3,2'-furan-5',1''-cyclohexane]-2'',5''-dien-4''-one (7e)

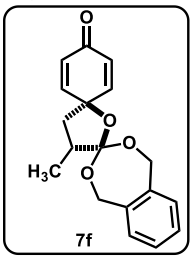


The general procedure **A** was followed using methyl methyl 3-(3,5-dibromo-4-hydroxyphenyl)propanoate (100 mg, 0.296 mmol, 1 equiv.) and 1,2-phenylenedimethanol (89.9 mg, 0.651 mmol, 2.2 equiv.) to obtain crude product **7e**. Purification using (basic Al_2O_3) column chromatography R_f (Hexane/EtOAc 80/20 UV active, PMA stain active) = 0.5 yielded **7e** (91.6 mg, 70%) as a colorless solid. **^{1}H NMR** (396 MHz, CHLOROFORM-*D*) δ 7.01 (s, 2H), 6.99 – 6.95 (m, 2H), 6.71 (dd, *J* = 5.6, 3.4 Hz, 2H), 4.88 (d, *J* = 14.6 Hz, 2H), 4.38 (d, *J* = 14.6 Hz, 2H), 1.70 (t, *J* = 7.7 Hz, 2H), 1.37 (dd, *J* = 8.3, 7.0 Hz, 2H).**^{13}C{^{1}H} NMR** (100 MHz, CHLOROFORM-*D*) δ 171.5, 149.6,

137.4, 127.2, 126.5, 125.3, 121.6, 81.1, 66.4, 33.6, 32.6.**IR υ (cm^{-1})** 3043, 2952, 2917, 1737, 1680, 1601, 1495, 1456,1374, 1317, 1285, 1221, 1102, 1043, 917, 880, 745, 694, **HRMS** (ESI-TOF) m/z: [M+Na]- Calcd for $C_{17}H_{14}Br_2NaO_4$ 462.9157; Found 462.9146.

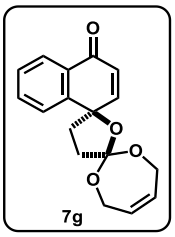
Note: If silica is used for purification compound decomposes.

3'-methyl-1,3',4',5-tetrahydrodispiro[benzo[e][1,3]dioxepine-3,2'-furan-5',1''-cyclohexane]-2'',5''-dien-4''-one (7f)



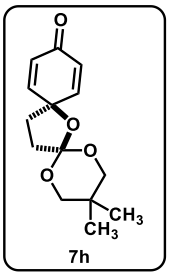
The general procedure **A** was followed using methyl (**±**) 3-(4-hydroxyphenyl)-2-methylpropanoate (100 mg, 0.515 mmol, 1 equiv.) and 1,2-phenylenedimethanol (156.1 mg, 1.13 mmol, 2.2 equiv.) to obtain crude product **7f**. Purification by column chromatography R_f (Hexane/EtOAc 50/50, UV active, PMA stain active) = 0.7 yielded **7f** (92.1 mg, *dr* 45:55, 60%) as a colorless oil. **^{1}H NMR** (396 MHz, DMSO-D_6) δ 7.21 (tt, *J* = 8.0, 3.9 Hz, 8H), 7.10 (dd, *J* = 10.2, 3.1 Hz, 2H), 7.01 (dd, *J* = 10.1, 3.0 Hz, 2H), 6.11 (ddd, *J* = 10.2, 4.7, 2.1 Hz, 4H), 5.09 (dd, *J* = 14.9, 4.9 Hz, 4H), 4.78 (dd, *J* = 14.8, 7.0 Hz, 4H), 2.71 (q, *J* = 7.2 Hz, 2H), 2.36 (dd, *J* = 13.2, 7.8 Hz, 2H), 1.94 (dd, *J* = 12.9, 7.0 Hz, 2H), 1.12 (d, *J* = 6.9 Hz, 6H). **^{13}C{^{1}H} NMR** (100 MHz, DMSO-D_6) δ 184.6, 150.9, 150.8, 137.5, 127.0, 126.9, 126.7, 126.4, 126.3, 126.1, 123.9, 75.1, 65.0, 64.8, 41.4, 15.0. **IR υ (cm^{-1})** 2950, 1631, 1087, 751, 467. **HRMS** (ESI-TOF) m/z: [M+H]- Calcd for $C_{18}H_{19}O_4$ 299.1283; Found 299.1280.

3',4',4'',7''-tetrahydro-4H-dispiro[naphthalene-1,2'-furan-5',2''-[1,3]dioxepin]-4-one (7g)



The general procedure **A** was followed using ethyl 3-(4-hydroxynaphthalen-1-yl)propanoate (100 mg, 0.409 mmol, 1 equiv.) and (*Z*)-but-2-ene-1,4-diol (79.2 mg, 0.90 mmol, 2.2 equiv.) to obtain crude product **7g**. Purification by column chromatography R_f (Hexane/EtOAc 80/20 UV active, PMA stain active) = 0.7 yielded **7g** (48.8 mg, 42%) as a brownish oil. **^{1}H NMR** (396 MHz, BENZENE-D_6) δ 8.31 (dd, *J* = 7.7, 1.4 Hz, 1H), 7.88 (d, *J* = 8.0 Hz, 1H), 7.22 – 7.19 (m, 1H), 7.02 (t, *J* = 7.5 Hz, 1H), 6.81 (d, *J* = 10.4 Hz, 1H), 6.18 (d, *J* = 10.4 Hz, 1H), 5.36 (d, *J* = 1.8 Hz, 2H), 4.51 – 4.39 (m, 1H), 4.30 (dq, *J* = 16.5, 2.4 Hz, 1H), 4.01 (dt, *J* = 17.1, 2.9 Hz, 1H), 3.96 – 3.82 (m, 1H), 2.10 – 2.00 (m, 1H), 1.99 – 1.85 (m, 2H), 1.83 – 1.72 (m, 1H).**^{13}C{^{1}H} NMR** (100 MHz, BENZENE-D_6) δ 183.5, 150.5, 146.2, 132.9, 130.8, 129.1, 128.9, 127.0, 126.5, 125.7, 80.0, 63.1, 62.9, 40.0, 33.2. **IR υ (cm^{-1})** 2956, 2918, 2850, 1732,1668, 1601, 1457, 1377, 1220, 1075, 1044, 1068, 976, 893, 867, 807, 766, 473. **HRMS** (ESI-TOF) m/z: [M+]- Calcd for $C_{17}H_{16}O_4$ 284.1048; Found 284.1043.

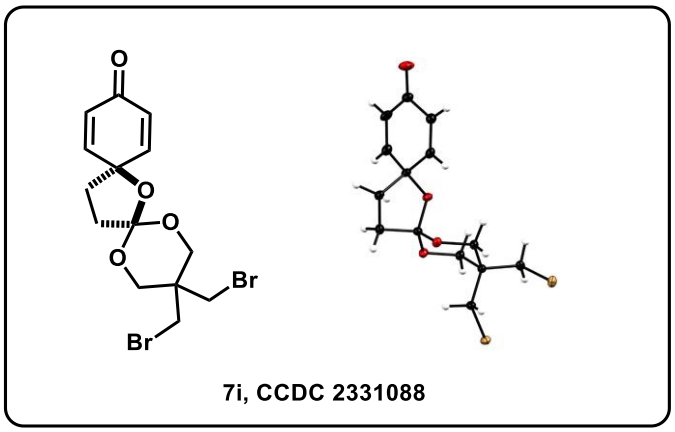
3,3-dimethyl-1,5,7-trioxadispiro[5.1.58.26]pentadeca-9,12-dien-11-one (7h)



7h

The general procedure **A** was followed using methyl 3-(4-hydroxyphenyl)propanoate (100 mg, 0.555 mmol, 1 equiv.) and 2,2-dimethylpropane-1,3-diol (127.0 mg, 1.22 mmol, 2.2 equiv.) to obtain crude product **7h**. Purification by column chromatography R_f (Hexane/EtOAc 80/20) = 0.6 yielded **7h** (95 88.9 mg, 64%) as a colorless solid.**^{1}H NMR** (400 MHz, DMSO-D_6) δ 6.98 (d, J = 9.8 Hz, 2H), 6.09 (d, J = 9.7 Hz, 2H), 3.77 (d, J = 10.8 Hz, 2H), 3.36 (d, J = 10.9 Hz, 2H), 2.22 (t, J = 7.6 Hz, 2H), 2.11 (t, J = 7.5 Hz, 2H), 1.11 (s, 3H), 0.72 (s, 3H). **^{13}C{^{1}H} NMR** (100 MHz, DMSO-D_6) δ 184.6, 150.4, 126.5, 119.7, 77.0, 70.3, 35.2, 33.3, 28.9, 22.3, 21.3. **IR υ (cm^{-1})** 3046, 2958, 2883, 1711, 1671, 1630, 1517, 1475, 1459, 1398, 1365, 1347, 1316, 1293, 1180, 1167, 1102, 1047, 1009, 935, 917, 898, 765, 721, 688, 588, 554, 530, 462, 431. **HRMS** (ESI-TOF) m/z: [M+H]- Calcd for $C_{14}H_{19}O_4$ 251.1283; Found 251.1277.

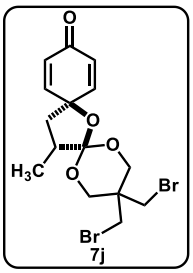
3,3-bis(bromomethyl)-1,5,7-trioxadispiro[5.1.58.26]pentadeca-9,12-dien-11-one (7i)



7i, CCDC 2331088

The general procedure **A** was followed using methyl 3-(4-hydroxyphenyl)propanoate (100 mg, 0.555 mmol, 1 equiv.) and 2,2-bis(bromomethyl)propane-1,3-diol (317.3 mg, 1.22 mmol, 2.2 equiv.) to obtain crude product **7i**. Purification by column chromatography R_f (Hexane/EtOAc 90/10, UV active, PMA stain active) = 0.5 yielded **7i** (140.3 mg, 62%) as a colorless solid. **^{1}H NMR** (396 MHz, DMSO-D_6) δ 7.01 (d, J = 10.0 Hz, 2H), 6.12 (d, J = 10.0 Hz, 2H), 4.08 (d, J = 11.4 Hz, 2H), 3.86 (s, 2H), 3.73 (d, 2H), 3.46 (s, 2H), 2.30 (dd, J = 8.5, 6.7 Hz, 2H), 2.15 (t, J = 7.7 Hz, 2H). **^{13}C{^{1}H} NMR** (100 MHz, DMSO-D_6) δ 184.5, 149.9, 126.7, 119.9, 77.7, 64.5, 36.4, 35.0, 34.8, 33.2. **IR u (cm^{-1})** 3028, 2971, 2897, 1705, 1673, 1634, 1609, 1459, 1430, 1363, 1347, 1283, 1167, 1116, 1080, 1018, 1005, 908, 859, 693, 562, 461. **HRMS** (ESI-TOF) m/z: [M+H]- Calcd for $C_{14}H_{17}O_4Br_2$ 408.9473; Found 408.9480. **mp:** 75-78 °C.

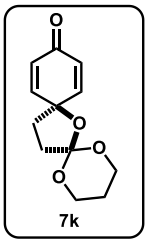
3,3-bis(bromomethyl)-15-methyl-1,5,7-trioxadispiro[5.1.58.26]pentadeca-9,12-dien-11-one (7j)



7j

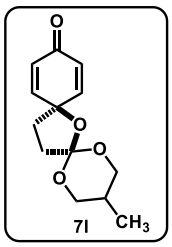
The general procedure **A** was followed using methyl (**±**) 3-(4-hydroxyphenyl)-2-methylpropanoate (100 mg, 0.515 mmol, 1 equiv.) and 2,2-bis(bromomethyl)propane-1,3-diol (296.7 mg, 1.13 mmol, 2.2 equiv.) to obtain crude product **7j**. Purification by column chromatography R_f (Hexane/EtOAc 60/40, UV active, PMA stain active) = 0.5 yielded **7j** (115.2 mg, *dr* 1:1, 50%) as a colorless solid. **^{1}H NMR** (500 MHz, DMSO-D_6) δ 7.11 (dd, J = 10.1, 3.0 Hz, 2H), 6.87 (dd, J = 10.0, 3.0 Hz, 2H), 6.10 (ddd, J = 18.0, 10.0, 2.1 Hz, 4H), 4.10 (dd, J = 25.2, 11.4 Hz, 4H), 3.85 (d, J = 3.7 Hz, 4H), 3.75 (td, J = 11.9, 2.9 Hz, 4H), 3.45 (s, 4H), 2.58 – 2.51 (m, 2H), 2.20 (dd, J = 12.8, 7.8 Hz, 2H), 1.92 (dd, J = 12.8, 11.7 Hz, 2H), 1.04 (s, 6H). **^{13}C{^{1}H} NMR** (126 MHz, DMSO-D_6) δ 184.6, 151.1, 149.8, 127.0, 126.2, 118.7, 75.4, 65.3, 63.3, 40.4, 36.5, 36.2, 34.8, 12.5. **IR υ (cm^{-1})** 3025, 2978, 2895, 1704, 1673, 1637, 1602, 1455, 1433, 1362, 1343, 1280, 1165, 1115, 1081, 1019, 1002, 909, 858, 693, 561, 460. **HRMS** (ESI-TOF) m/z: [M+H]- Calcd for $C_{15}H_{19}O_4Br_2$ 420.9650; Found 420.9639.

1,5,7-trioxadispiro[5.1.58.26]pentadeca-9,12-dien-11-one (7k)



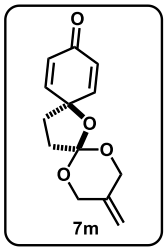
The general procedure **A** was followed using methyl 3-(4-hydroxyphenyl)propanoate (100 mg, 0.555 mmol, 1 equiv.) and propane-1,3-diol (92.8 mg, 1.22 mmol, 2.2 equiv.) to obtain crude product **7k**. Purification by column chromatography R_f (Hexane/EtOAc 50/50) = 0.6 yielded **7k** (95 mg, 77%) as a colorless oil. **^{1}H NMR** (500 MHz, DMSO-D_6) δ 6.99 (d, J = 10.0 Hz, 2H), 6.10 (d, J = 10.0 Hz, 2H), 4.07 (td, J = 12.3, 2.9 Hz, 2H), 3.79 (td, J = 11.0, 5.3 Hz, 2H), 2.22 – 2.15 (m, 2H), 2.14 – 2.07 (m, 2H), 2.01 – 1.89 (m, 1H), 1.49 – 1.41 (m, 1H). **^{13}C{^{1}H} NMR** (126 MHz, DMSO-D_6) δ 188.0, 154.0, 128.5, 70.0, 62.9, 58.8, 35.0, 31.8. **IR u (cm^{-1})** 3050, 2975, 2930, 2860, 1772, 1630, 1465, 1451, 1397, 1360, 1344, 1230, 1168, 1087, 1072, 932, 765, 620. **HRMS** (ESI-TOF) m/z: [M+H]- Calcd for $C_{12}H_{15}O_4$ 223.0970; Found 223.0972.

3-methyl-1,5,7-trioxadispiro[5.1.58.26]pentadeca-9,12-dien-11-one (7l)



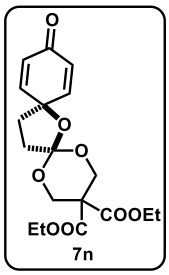
The general procedure **A** was followed using methyl 3-(4-hydroxyphenyl)propanoate (100 mg, 0.555 mmol, 1 equiv.) and 2-methylpropane-1,3-diol (110.0 mg, 1.22 mmol, 2.2 equiv.) to obtain crude product **7l**. Purification by column chromatography R_f (Hexane/EtOAc 80/20) = 0.6 yielded **7l** (102 mg, 78%) as a colorless oil. **^{1}H NMR** (500 MHz, BENZENE-D_6) δ 6.49 – 6.42 (m, 2H), 6.01 (d, J = 10.0 Hz, 2H), 3.67 (td, J = 11.3, 1.2 Hz, 2H), 3.60 – 3.38 (m, 2H), 2.05 (t, J = 7.8 Hz, 2H), 2.02 – 1.81 (m, 1H), 1.68 – 1.58 (m, 2H), 0.26 (ddd, J = 6.6, 4.4, 2.0 Hz, 3H). **^{13}C{^{1}H} NMR** (126 MHz, BENZENE-D_6) δ 184.5, 149.3, 127.4, 120.6, 77.8, 67.0, 36.3, 34.2 2, 18.5, 12.1. **IR u (cm^{-1})** 2962, 2878, 1732, 1699, 1672, 1632, 1460, 1394, 1375, 1349, 1286, 1242, 1164, 1104, 1020, 1008, 952, 933, 902, 853, 766, 721, 690, 576, 554, 461, 436. **HRMS** (ESI-TOF) m/z: [M+H]- Calcd for $C_{13}H_{17}O_4$ 237.1126; Found 237.1122.

3-methylene-1,5,7-trioxadispiro[5.1.58.26]pentadeca-9,12-dien-11-one (7m)



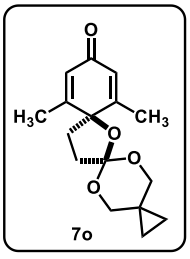
The general procedure **A** was followed using methyl 3-(4-hydroxyphenyl)propanoate (100 mg, 0.555 mmol, 1 equiv.) and 2-methylenepropane-1,3-diol (107.5 mg, 1.22 mmol, 2.2 equiv.) to obtain crude product **7m**. Purification by column chromatography R_f (Hexane/EtOAc 80/20) = 0.4 yielded **7m** (89.6 mg, 69%) as a colorless solid. **^{1}H NMR** (396 MHz, DMSO-D_6) δ 7.02 (d, *J* = 10.2 Hz, 2H), 6.11 (d, *J* = 10.1 Hz, 2H), 4.98 (s, 2H), 4.56 (d, *J* = 13.3 Hz, 2H), 4.20 (d, *J* = 13.0 Hz, 2H), 2.24 (ddd, *J* = 8.2, 6.6, 1.3 Hz, 2H), 2.20 – 2.09 (m, 2H). **^{13}C{^{1}H} NMR** (101 MHz, DMSO-D_6) δ 184.6, 150.2, 138.1, 126.7, 120.4, 109.9, 77.4, 64.1, 34.9, 33.4. **IR υ (cm^{-1})** 2976, 2926, 2867, 1704, 1669, 1628, 1469, 1453, 1400, 1361, 1344, 1290, 1184, 1169, 1031, 1006, 956, 930, 901, 876, 855, 765, 692, 619, 556, 485, 446. **HRMS** (ESI-TOF) m/z: [M+H]- Calcd for $C_{13}H_{15}O_4$ 235.0970; Found 235.0966. **mp:** 80-83 °C.

diethyl 11-oxo-1,5,7-trioxadispiro[5.1.58.26]pentadeca-9,12-diene-3,3-dicarboxylate (7n)



The general procedure **A** was followed using methyl 3-(4-hydroxyphenyl)propanoate (100 mg, 0.555 mmol, 1 equiv.) and diethyl 2,2-bis(hydroxymethyl)malonate (268.8 mg, 1.22 mmol, 2.2 equiv.) to obtain crude product **7n**. Purification by column chromatography R_f (Hexane/EtOAc 60/40) = 0.5 yielded **7n** (98 mg, 48%) as a colorless oil. **^{1}H NMR** (396 MHz, BENZENE-D_6) δ 6.32 (d, *J* = 10.3 Hz, 2H), 5.96 (d, *J* = 10.1 Hz, 2H), 4.82 – 4.72 (m, 2H), 4.61 (dt, *J* = 11.7, 3.8 Hz, 2H), 4.05 (q, *J* = 7.0 Hz, 2H), 3.76 (q, *J* = 7.1 Hz, 2H), 2.00 (t, *J* = 7.8 Hz, 2H), 1.54 (t, *J* = 7.7 Hz, 2H), 0.94 (t, *J* = 7.1 Hz, 3H), 0.76 (t, *J* = 7.1 Hz, 3H). **^{13}C{^{1}H} NMR** (100 MHz, BENZENE-D_6) δ 184.5, 167.9, 166.7, 148.5, 127.6, 120.5, 78.4, 63.5, 62.1, 61.9, 53.0, 35.9, 34.1, 13.9, 13.7. **IR u (cm^{-1})** 2956, 2919, 1732, 1671, 1632, 1447, 1365, 1345, 1220, 1091, 1007, 906, 853, 772. **HRMS** (ESI-TOF) m/z: [M+H]- Calcd for $C_{18}H_{23}O_8$ 367.1393; Found 367.1387.

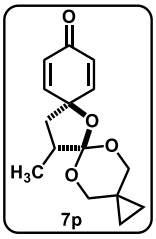
9,13-dimethyl-5,7,16-trioxatrispiro[2.2.1.58.26.23]heptadeca-9,12-dien-11-one (7o)



The general procedure **A** was followed using methyl ethyl 3-(4-hydroxy-2,6-dimethylphenyl)propanoate (100 mg, 0.550 mmol, 1 equiv.) and cyclopropane-1,1-diyldimethanol (123.5 mg, 1.21 mmol, 2.2 equiv.) to obtain crude product **7o**. Purification by column chromatography R_f (Hexane/EtOAc 70/30, UV active, PMA stain active) = 0.5 yielded **7o** (100 mg, 66%) as a yellow oil. **^{1}H NMR** (400 MHz, BENZENE-D_6) δ 6.03 (d, *J* = 16.1 Hz, 2H), 4.33 (d, *J* = 10.9 Hz, 2H), 2.67 (d, *J* = 10.7 Hz, 2H), 2.36 – 2.05 (m, 2H), 1.79 (s, 6H), 1.64 (t, 2H), 0.40 (t, *J* = 7.5 Hz, 2H), -0.11 (t, *J*

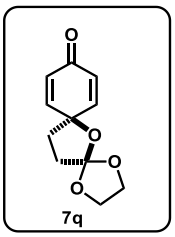
= 7.5 Hz, 2H). **^{13}C{^{1}H} NMR** (101 MHz, BENZENE-D_6) δ 184.3, 160.3, 125.8, 122.7, 84.9, 67.6, 37.6, 34.2, 18.1, 16.1, 13.4, 4.2 **IR υ (cm^{-1})** 3070, 2961, 2924, 2873, 2280, 1731, 1672, 1632, 1464, 1438, 1365, 1224, 1170, 1076, 891, 606, 504, 476. **HRMS** (ESI-TOF) m/z: [M+Na]- Calcd for $C_{16}H_{20}NaO_4$ 299.1259; Found 299.1256.

15-methyl-5,7,16-trioxatrispiro[2.2.1.58.26.23]heptadeca-9,12-dien-11-one (7p)



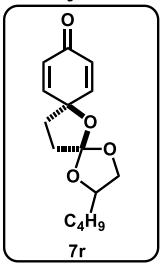
The general procedure **A** was followed using (**±**) methyl 3-(4-hydroxyphenyl)-2-methylpropanoate (100 mg, 0.515 mmol, 1 equiv.) and 1,2-phenylenedimethanol (115.4 mg, 1.13 mmol, 2.2 equiv.) to obtain crude product **7p**. Purification by column chromatography R_f (Hexane/EtOAc 60/40, UV active, PMA stain active) = 0.4 yielded **7p** (68.9 mg, *dr* 1:1, 51%) as a colorless solid.**^{1}H NMR** (396 MHz, DMSO-D_6) δ 7.09 (dd, *J* = 9.9, 3.0 Hz, 2H), 6.86 (dd, *J* = 9.8, 3.0 Hz, 2H), 6.11 (d, *J* = 2.3 Hz, 1H), 6.08 (t, *J* = 1.9 Hz, 2H), 6.06 (d, *J* = 1.9 Hz, 1H), 4.68 – 4.25 (m, 4H), 3.07 (ddd, *J* = 11.2, 7.8, 2.1 Hz, 4H), 2.51 – 2.40 (m, 2H), 2.19 (dd, *J* = 12.7, 7.9 Hz, 2H), 1.90 (dd, *J* = 12.7, 11.0 Hz, 2H), 1.04 (d, *J* = 6.8 Hz, 6H), 0.72 – 0.55 (m, 4H), 0.48 – 0.22 (m, 4H).**^{13}C{^{1}H} NMR** (126 MHz, DMSO-D_6) δ 185.3, 149.3, 137.1, 127.8, 127.2, 126.3, 125.3, 77.9, 66.4, 34.9, 33.5. **IR υ (cm^{-1})** 2961, 1625, 1487, 750, 468. **HRMS** (ESI-TOF) m/z: [M+H]- Calcd for $C_{15}H_{19}O_4$ 263.1283; Found 263.1277. **mp**: 101-103 °C.

1,4,6-trioxadispiro[4.1.57.25]tetradeca-8,11-dien-10-one (7q)



The general procedure **A** was followed using methyl 3-(4-hydroxyphenyl)propanoate (100 mg, 0.555 mmol, 1 equiv.) and ethane-1,2-diol (75.7 mg, 1.22 mmol, 2.2 equiv.) to obtain crude product **7q**. Purification by column chromatography R_f (Hexane/EtOAc 60/40, UV active, PMA stain active) = 0.4 yielded **7q** (72 mg, 62%) as a colorless oil. **^{1}H NMR** (500 MHz, BENZENE-D_6) δ 6.47 (d, *J* = 9.9 Hz, 2H), 5.98 (d, *J* = 9.9 Hz, 2H), 3.64 (t, 2H), 3.41 (t, 2H), 2.03 (t, 2H), 1.58 (t, 2H). **^{13}C{^{1}H} NMR** (126 MHz, BENZENE-D_6) δ 184.4, 149.1, 129.8, 127.5, 76.8, 64.3, 34.5, 32.5. **IR u** (cm^{-1}) 2958, 2912, 1732, 1670, 1628, 1457, 1397, 1341, 1286, 1248, 1251, 1179, 1079, 1057, 954, 935, 913, 856, 809, 758, 721, 689, 590, 541, 464. **HRMS** (ESI-TOF) m/z: [M+H]- Calcd for $C_{11}H_{13}O_4$ 209.0814; Found 209.0808.

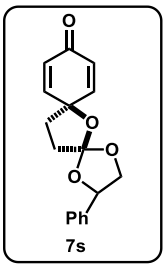
2-butyl-1,4,6-trioxadispiro[4.1.57.25]tetradeca-8,11-dien-10-one (7r)



The general procedure **A** was followed using methyl 3-(4-hydroxyphenyl)propanoate (100 mg, 0.555 mmol, 1 equiv.) and (**±**) hexane-1,2-diol (144 mg, 1.22 mmol, 2.2 equiv.) to obtain crude product **7r**. Purification by column chromatography R_f (Hexane/EtOAc 80/20) = 0.6 yielded **7r** (102.7 mg, *dr*:1:1

70%) as a colorless oil. **^{1}H NMR** (500 MHz, CHLOROFORM-*D*) δ 6.59 – 6.47 (m, 4H), 6.04 – 5.93 (m, 4H), 4.12 (qd, *J* = 6.8, 5.0 Hz, 1H), 3.96 – 3.87 (m, 1H), 3.85 (ddt, *J* = 11.8, 8.0, 3.6 Hz, 1H), 3.80 – 3.70 (m, 1H), 3.50 (t, *J* = 8.0 Hz, 1H), 3.27 (t, *J* = 7.1 Hz, 1H), 2.07 (dtd, *J* = 13.4, 8.0, 2.0 Hz, 4H), 1.64 (dddt, *J* = 10.1, 7.9, 6.0, 3.5 Hz, 4H), 1.47 – 1.36 (m, 2H), 1.25 (dddd, *J* = 13.8, 7.9, 5.5, 3.3 Hz, 2H), 1.19 – 0.96 (m, 8H), 0.84 – 0.76 (m, 6H). **^{13}C{^{1}H} NMR** (126 MHz, CHLOROFORM-*D*) δ 184.8, 149.8, 129.9, 127.4, 77.8, 76.7, 76.2, 69.4, 33.2, 33.0, 27.8, 22.8, 14.1. **IR u (cm^{-1})** 2957, 2934, 2873, 1734, 1672, 1632, 1459, 1396, 1342, 1284, 1245, 1179, 1077, 1010, 937, 854, 758, 721, 689, 554. **HRMS** (ESI-TOF) m/z: [M+H]- Calcd for $C_{15}H_{21}O_4$ 265.1440; Found 265.1434.

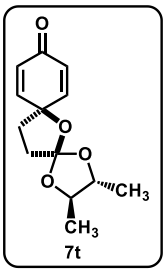
2-phenyl-1,4,6-trioxadispiro[4.1.57.25]tetradeca-8,11-dien-10-one (7s)



7s

The general procedure **A** was followed using methyl 3-(4-hydroxyphenyl)propanoate (100 mg, 0.555 mmol, 1 equiv.) and (±) Phenyl-1,2-ethanediol (117 mg, 1.22 mmol, 2.2 equiv.) to obtain crude product **7s**. Purification by column chromatography R_f (Hexane/EtOAc 80/20) = 0.6 yielded **7s** (92 mg, *dr*:1:1), 66%) as a colorless oil. **^{1}H NMR** (500 MHz, BENZENE-D_6) δ 7.35 (d, *J* = 8.1 Hz, 2H), 7.14 – 6.95 (m, 8H), 6.50 (ddq, *J* = 13.7, 7.7, 3.7 Hz, 4H), 6.15 – 5.95 (m, 4H), 5.09 (td, *J* = 6.8, 2.3 Hz, 1H), 4.80 (t, *J* = 8.1 Hz, 1H), 4.09 (td, *J* = 7.3, 3.3 Hz, 1H), 3.96 – 3.86 (m, 1H), 3.74 (t, *J* = 9.1 Hz, 1H), 3.52 (t, *J* = 7.2 Hz, 1H), 2.31 – 2.04 (m, 4H), 1.63 (ddd, *J* = 14.4, 7.8, 4.9 Hz, 4H). **^{13}C{^{1}H} NMR** (126 MHz, BENZENE-D_6) δ 184.7, 149.2, 138.8, 130.5, 128.8, 127.1, 126.4, 79.9, 77.6, 71.6, 33.2, 32.8. **IR u (cm^{-1})** 3036, 2954, 1967, 1735, 1671, 1496, 1457, 1310, 1285, 1245, 1216, 1177, 1078, 1010, 951, 855, 701, 602, 459. **HRMS** (ESI-TOF) m/z: [M+H]- Calcd for $C_{17}H_{17}O_4$ 285.1127; Found 285.1126.

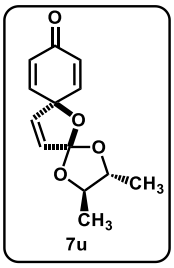
2,3-dimethyl-1,4,6-trioxadispiro[4.1.57.25]tetradeca-8,11-dien-10-one (7t)



7t

The general procedure **A** was followed using methyl 3-(4-hydroxyphenyl)propanoate (100 mg, 0.555 mmol, 1 equiv.) and (±)-2,3-Butanediol (110 mg, 1.22 mmol, 2.2 equiv.) to obtain crude product **7t**. Purification by column chromatography R_f (Hexane/EtOAc 80/20, UV active, PMA stain active) = 0.7 yielded **7t** (76 mg, 58%) as a colorless oil. **^{1}H NMR** (396 MHz, CHLOROFORM-*D*) δ 6.84 (ddd, *J* = 9.4, 7.7, 3.5 Hz, 2H), 6.19 (d, *J* = 10.0 Hz, 2H), 4.88 (qd, *J* = 6.6, 3.1 Hz, 1H), 3.87 (qd, *J* = 6.5, 3.2 Hz, 1H), 2.44 – 2.31 (m, 2H), 2.11 (td, *J* = 7.3, 5.3 Hz, 2H), 1.18 (d, *J* = 6.5 Hz, 3H), 1.15 (d, *J* = 6.5 Hz, 3H). **^{13}C{^{1}H} NMR** (100 MHz, CHLOROFORM-*D*) δ 185.3, 172.73, 150.5, 150.3, 128.6, 74.9, 69.3, 34.7, 29.4, 17.8, 14.2. **IR u (cm^{-1})** 2918, 2850, 1725, 1669, 1626, 1377, 1194, 1081, 863, 720. **HRMS** (ESI-TOF) m/z: [M+H]- Calcd for $C_{13}H_{17}O_4$ 237.1127; Found 237.1126.

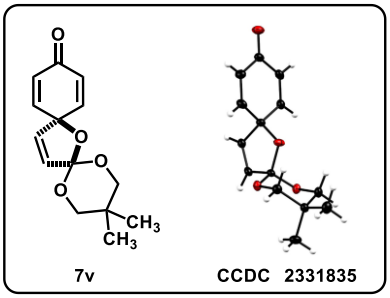
2,3-dimethyl-1,4,6-trioxadispiro[4.1.57.25]tetradeca-8,11,13-trien-10-one (7u)



7u

The general procedure **A** was followed using ethyl (Z)-3-(4-hydroxyphenyl)acrylate (100 mg, 0.520 mmol, 1 equiv.) and (**±**)-2,3-Butanediol (103.1 mg, 1.14 mmol, 2.2 equiv.) to obtain crude product **7u**. Purification by column chromatography R_f (Hexane/EtOAc 60/40, UV active, PMA stain active) = 0.5 yielded **7u** (54.8 mg, 45%) as a white solid. **^{1}H NMR** (500 MHz, DMSO-D_6) δ 6.65 (d, J = 10.1 Hz, 2H), 6.33 – 6.12 (m, 3H), 6.08 (d, J = 5.5 Hz, 1H), 5.09 – 4.35 (m, 2H), 1.11 (d, J = 6.1 Hz, 6H).**^{13}C{^{1}H} NMR** (126 MHz, DMSO-D_6) δ 184.3, 148.4, 134.8, 130.1, 129.4, 128.2, 81.4, 74.39 14.4. **IR υ (cm^{-1})** 2926, 1671, 1630, 1456, 1382, 1366, 1342, 1283, 1240, 1170, 1137, 1083, 1037, 1014, 917, 873, 815, 785, 735, 633, 610, 520, 440. **HRMS** (ESI-TOF) m/z: [M+H]- Calcd for $C_{13}H_{15}O_4$ 235.0970; Found 235.0973.

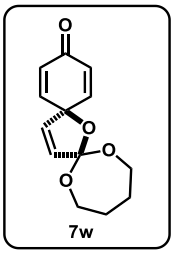
3,3-dimethyl-1,5,7-trioxadispiro[5.1.58.26]pentadeca-9,12,14-trien-11-one (7v)



7v CCDC 2331835

The general procedure **A** was followed using ethyl (Z)-3-(4-hydroxyphenyl)acrylate (100 mg, 0.520 mmol, 1 equiv.) and 2,2-dimethylpropane-1,3-diol (118.7 mg, 1.14 mmol, 2.2 equiv.) to obtain crude product **7v**. Purification by column chromatography R_f (Hexane/EtOAc 70/30, UV active, PMA stain active) = 0.5 yielded **7v** (51.6 mg, 40%) as a white solid. **^{1}H NMR** (400 MHz, DMSO-D_6) 6.70 (d, J = 10.0 Hz, 2H), 6.23 (d, J = 5.5 Hz, 1H), 6.19 (d, J = 10.0 Hz, 2H), 6.14 (d, J = 5.5 Hz, 1H), 3.86 (d, J = 10.9 Hz, 2H), 3.46 (d, J = 11.2 Hz, 2H), 1.13 (s, 3H), 0.77 (s, 3H). **^{13}C{^{1}H} NMR** (100 MHz, DMSO-D6) δ 184.3, 148.3, 134.0, 130.0, 128.3, 122.4, 83.0, 70.6, 29.0, 22.2 (methyl peak), 21.5 (methyl peak). **IR υ (cm^{-1})** 3080, 2926, 2854, 1777, 1672, 1631, 1604, 1459, 1389, 1352, 1284, 1164, 1134, 1081, 1026, 933, 877, 850, 813, 781, 665, 565, 441. **HRMS** (ESI-TOF) m/z: [M+Na]- Calcd for $C_{14}H_{16}NaO_4$ 271.0946; Found 271.0938. **mp:** 51-53 °C.

7,9,14-trioxadispiro[5.1.68.26]hexadeca-1,4,15-trien-3-one (7w)

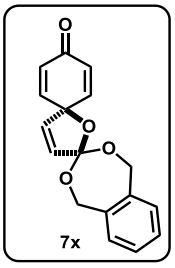


7w

The general procedure **A** was followed using ethyl (*Z*)-3-(4-hydroxyphenyl)acrylate (100 mg, 0.520 mmol, 1 equiv.) and butane-2,3-diol (102.7 mg, 1.14 mmol, 2.2 equiv.) to obtain crude product **7w**. Purification by column chromatography R_f (Hexane/EtOAc 65/35, UV active, PMA stain active) = 0.4 yielded **7w** (59.6 mg, 49%) as a white solid.**^{1}H NMR** (500 MHz, DMSO-D_6) 6.69 (d, J = 10.1 Hz, 2H),

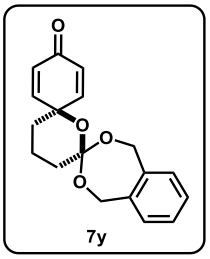
6.41 (d, *J* = 5.7 Hz, 1H), 6.17 (d, *J* = 10.1 Hz, 2H), 6.02 (d, *J* = 5.7 Hz, 1H), 3.92 – 3.83 (m, 2H), 3.77 – 3.69 (m, 2H), 1.63 (t, *J* = 2.4 Hz, 4H).**^{13}C{^{1}H} NMR** (126 MHz, DMSO-D_6) δ 184.3, 148.4, 132.0, 129.7, 128.1, 126.6, 82.1, 63.6, 28.5. **IR υ (cm^{-1})** 3078, 2947, 2852, 1776, 1668, 1628, 1468, 1429, 1391, 1282, 1238, 1215, 1147, 1066, 1045, 1036, 978, 868, 849, 799, 693, 544, 525, 443, 423. **HRMS** (ESI-TOF) m/z: [M+H]- Calcd for $C_{13}H_{15}O_4$ 235.0970; Found 235.0965. **mp:** 60-63 °C

1,5-dihydrodispiro[benzo[e][1,3]dioxepine-3,2'-furan-5',1''-cyclohexane]-2'',5''-dien-4''-one (7x)



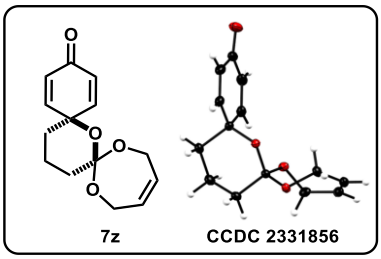
The general procedure **A** was followed using ethyl (*Z*)-3-(4-hydroxyphenyl)acrylate (100 mg, 0.520 mmol, 1 equiv.) and 1,2-phenylenedimethanol (157.5 mg, 1.14 mmol, 2.2 equiv.) to obtain crude product **7x**. Purification by column chromatography R_f (Hexane/EtOAc 70/30, UV active, PMA stain active) = 0.4 yielded **7x** (69 mg, 49%) as a white solid.**^{1}H NMR** (500 MHz, BENZENE-D_6) δ 6.96 (dd, *J* = 5.6, 3.3 Hz, 2H), 6.76 – 6.67 (m, 2H), 6.40 (dd, *J* = 9.7, 1.2 Hz, 2H), 6.00 (dd, *J* = 10.0, 1.4 Hz, 2H), 5.84 (dd, *J* = 5.7, 2.1 Hz, 1H), 5.14 (d, *J* = 5.7 Hz, 1H), 5.05 (d, *J* = 14.7 Hz, 2H), 4.61 (d, *J* = 14.6 Hz, 2H). **^{13}C{^{1}H} NMR** (126 MHz, BENZENE-D_6) δ 184.2, 147.1, 142.1, 137.4, 133.9, 129.0, 128.3, 127.2, 126.4, 83.4, 66.3. **IR υ (cm^{-1})** 2918, 2338, 1669, 1629, 1451, 1376, 1218, 1147, 1058, 851, 749, 607. **HRMS** (ESI-TOF) m/z: [M+Na]- Calcd for $C_{17}H_{14}NaO_4$ 305.0784; Found 305.0775.

1,4',5,5'-tetrahydro-3'H-dispiro[benzo[e][1,3]dioxepine-3,2'-pyran-6',1''-cyclohexane]-2'',5''-dien-4''-one (7y)



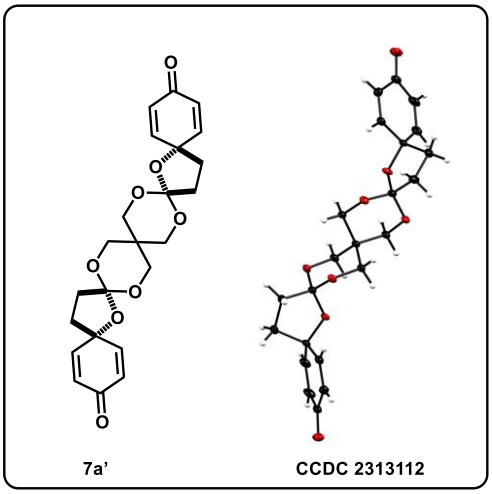
The general procedure **A** was followed using methyl 4-(4-hydroxyphenyl)butanoate (100 mg, 0.515 mmol, 1 equiv.) and 1,2-phenylenedimethanol (156.5 mg, 1.13 mmol, 2.2 equiv.) to obtain crude product **7y**. Purification by column chromatography R_f (Hexane/EtOAc 65/35, UV active, PMA stain active) = 0.6 yielded **7y** (53.8 mg, 35%) as a white solid. **^{1}H NMR** (500 MHz, DMSO-D_6) δ 7.28 (d, J = 10.3 Hz, 2H), 7.23 – 7.18 (m, 2H), 7.17 – 7.10 (m, 2H), 6.14 (d, J = 10.3 Hz, 2H), 4.95 (d, J = 15.0 Hz, 2H), 4.70 (d, J = 15.0 Hz, 2H), 1.98 (dd, J = 7.8, 4.5 Hz, 2H), 1.87 (ddt, J = 12.4, 8.7, 4.7 Hz, 2H), 1.73 (dd, J = 7.6, 4.6 Hz, 2H). **^{13}C{^{1}H} NMR** (101 MHz, DMSO-D_6) δ 184.6, 150.2, 137.3, 127.0, 126.8, 126.1, 113.4, 72.3, 63.6, 32.8, 29.5, 17.3. **IR υ (cm^{-1})** 3063, 2938, 2875, 1702, 1670, 1630, 1498, 1453, 1399, 1286, 1247, 1217,, 1124, 1104, 1051946, 906, 744, 685, 626, 605, 466. **HRMS** (ESI-TOF) m/z: [M+H]- Calcd for $C_{18}H_{19}O_4$ 299.1283; Found 299.1280.

7,9,14-trioxadispiro[5.1.68.36]heptadeca-1,4,11-trien-3-one (7z)



The general procedure **A** was followed using methyl 4-(4-hydroxyphenyl)butanoate (100 mg, 0.515 mmol, 1 equiv.) and (*Z*)-but-2-ene-1,4-diol (99.8 mg, 1.13 mmol, 2.2 equiv.) to obtain crude product **7z**. Purification by column chromatography R_f (Hexane/EtOAc 65/35, UV active, PMA stain active) = 0.5 yielded **7z** (48.6 mg, 38%) as a white solid. **^{1}H NMR** (500 MHz, DMSO-D_6) δ 7.22 (d, J = 10.3 Hz, 2H), 6.10 (d, J = 10.3 Hz, 2H), 5.64 (t, J = 1.9 Hz, 2H), 4.28 (dt, J = 16.6, 2.5 Hz, 2H), 4.18 – 3.98 (m, 2H), 1.90 (dd, J = 7.9, 4.4 Hz, 2H), 1.85 – 1.78 (m, 2H), 1.68 (dd, J = 7.5, 4.6 Hz, 2H). **^{13}C{^{1}H} NMR** (100 MHz, CHLOROFORM-*D*) δ 185.0, 150.9, 129.1, 127.2, 113.9, 72.7, 61.1, 33.2, 29.6, 17.8. **IR u (cm^{-1})** 2962, 2926, 2855, 1740, 1668, 1630, 1445, 1458, 1400, 1391, 1368, 1304, 1249, 1206, 1133, 1058, 961, 856, 647, 524, 440. **HRMS** (ESI-TOF) m/z: [M+H]- Calcd for $C_{14}H_{17}O_4$ 249.1126; Found 249.1120. **mp**: 65-68 °C

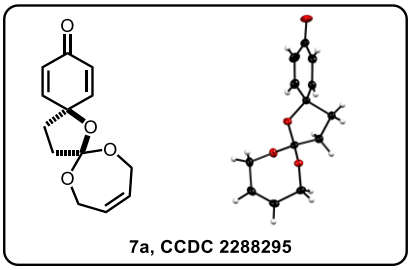
7,9,13,15,24,27-hexaoxapentaspiro[5.1.2.2.1.516.214.211.28.26]nonacosa-1,4,17,20-tetraene-3,19-dione (7a')



The general procedure A was followed. To a stirred solution of PIDA (214.9 mg, 0.666 mmol 1.2 equiv.) in HFIP (0.25 M) was added DBU (185.9 mg, 1.22 mmol, 2.2 equiv.) followed by the addition of methyl 3-(4-hydroxyphenyl)propanoate (100 mg, 0.555 mmol, 1 equiv.) and 2,2-bis(hydroxymethyl)propane-1,3-diol (37.8 mg, 0.5 mmol, 0.5 equiv.) dissolved in 0.2 mL of DMSO at 0 ºC under N_2 atmosphere to obtain crude product **7a'**. Purification by column chromatography R_f (Hexane/EtOAc 70/30, UV active, PMA stain active) = 0.4 yielded **7a'** (53.4 mg, 45%) as a colorless solid. **^{1}H NMR** (400 MHz, BENZENE-D_6) δ 6.34 (ddd, J = 12.2, 9.5, 2.5 Hz, 4H), 6.01 (d, J = 9.6 Hz, 4H), 4.46 (d, J = 9.7 Hz, 2H), 4.02 (d, J = 11.0 Hz, 2H), 3.54 (d, J = 11.2 Hz, 2H), 2.95 (dd, J = 11.5, 2.4 Hz, 2H), 1.95 (qt, J = 13.1, 7.7 Hz, 4H), 1.62 – 1.50 (m, 4H). **^{13}C{^{1}H} NMR** (101 MHz, BENZENE-D_6) δ 184.2, 148.6, 148.5, 120.8, 78.1, 64.5, 64.1, 36.0, 34.2. **DEPT-135** (100 MHz, BENZENE-D_6) δ 148.4, 148.3, 128.1, 127.5, 64.3, 63.9, 35.8, 34.0. **IR υ (cm^{-1})** 2956.12, 2918, 2850, 1674, 1631, 1458, 1380, 1245, 1163, 1102, 1049, 1022, 936, 910, 872, 852, 617.3, 463. **HRMS** (ESI-TOF) m/z: [M+H]- Calcd for $C_{23}H_{25}O_8$ 429.1549; Found 429.1532. **mp:** 160-163 °C.

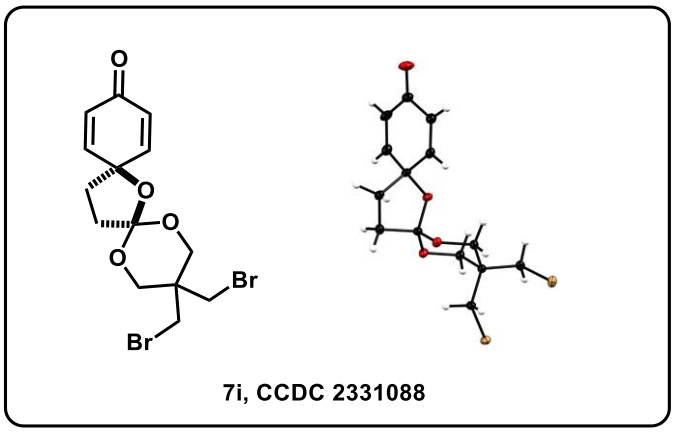
(VI) XRD Data

7,9,14-trioxadispiro[5.1.68.26]hexadeca-1,4,11-trien-3-one (7a)



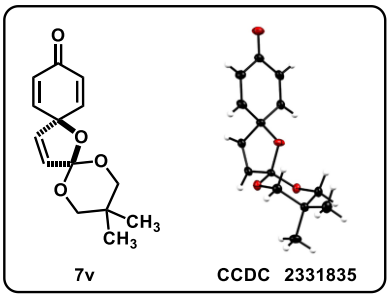
Structure of compound **7a** (CCDC 2288295) in solid state. The anisotropic displacement parameters are drawn at the 50% probability displacement level. Red = Oxygen atom; Black = Carbon atom; White - Hydrogen atom. Crystal was grown in acetone (slow evaporation). X-Ray Crystal Structure Analysis of **7a:** Molecular formula = $C_{13}H_{14}O_4$, Mr. = 234.24 $gmol^{-1}$, colorless crystal, space group: $P2_1/n$, Hall group: -P 2yn, a = 11.6135(4) Å, b = 5.8166(2) Å, c = 16.6086(5) Å, α = 90°, β = 92.064(1)°, γ = 90°, Volume: 1121.20(6) $Å^3$, Temperature: 296 K, Z = 4, D_{calc} = 1.388 g cm^{-3}, D_{report} = 1.388 g cm^{-3}, λ = 0.71073 Å, m(Cu-Kα) = 0.103 mm^{-1}, empirical absorption correction(T_{min} = 0.652, T_{max} = 0.746), CCD Bruker SMART APEX diffractometer, structure was solved by direct methods and refined (SHELXL-97) by full matrix least squares based on F^2 to R(reflections)= 0.0378(1790) [I > 20(1)], wR_2 (reflections) = 0.0988 (2065), S = 1.050.

3,3-bis(bromomethyl)-1,5,7-trioxadispiro[5.1.58.26]pentadeca-9,12-dien-11-one (7i)



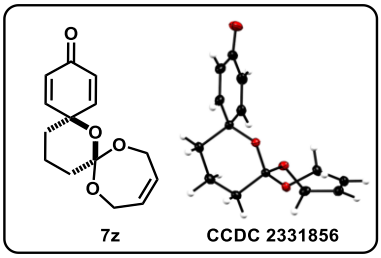
Structure of compound **7i (CCDC 2331088)** in solid state. The anisotropic displacement parameters are drawn at the 50% probability displacement level. Red = Oxygen atom; Black = Carbon atom; White - Hydrogen atom. Crystal was grown in acetone (slow evaporation). X-Ray Crystal Structure Analysis of **7i:** Molecular formula = $C_{14}H_{16}Br_2O_4$, Mr. = 408.09 $gmol^{-1}$, colorless crystal, space group: $P2_1/c$, Hall group: -P 2ybc, a = 11.1660(3) Å , b = 10.3032(3) Å, c = 13.0230(3) Å, α = 90°, β = 96.244(1)°, γ = 90°, Volume: 1489.35(7) $Å^3$, Temperature: 296 K, Z = 4, D_{calc} = 1.820 g cm^{-3}, D_{report} = 1.820 g cm^{-3}, λ = 0.71073 Å, m(Cu-Ka) = 5.452 mm^{-1}, empirical absorption correction(T_{min} = 0.522, T_{max} = 0.746), CCD Bruker SMART APEX diffractometer, structure was solved by direct methods and refined (SHELXL-97) by full matrix least squares based on F^2 to R(reflections)= 0.0194(3421) [I > 20(1)], wR_2 (reflections) = 0.0443(3720), S = 1.028.

3,3-dimethyl-1,5,7-trioxadispiro[5.1.58.26]pentadeca-9,12,14-trien-11-one (7v)



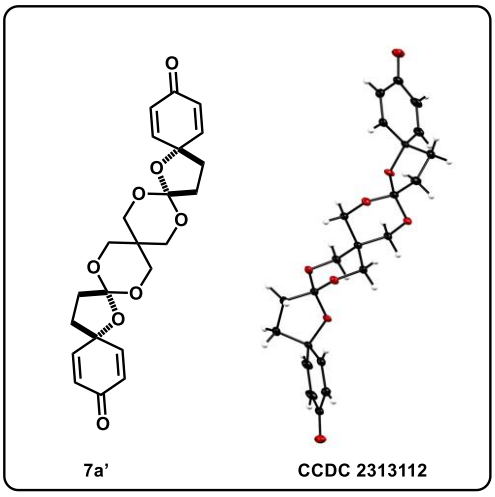
Structure of compound **7v (CCDC 2331835)** in solid state. The anisotropic displacement parameters are drawn at the 50% probability displacement level. Red = Oxygen atom; Black = Carbon atom; White - Hydrogen atom. Crystal was grown in acetone (slow evaporation). X-Ray Crystal Structure Analysis of **7v:** Molecular formula = $C_{14}H_{16}O_4$, Mr. = 248.27gmol^{-1}, colorless crystal, space group: C2/c, Hall group: -C 2yc, a = 27.5396(8) Å , b = 5.7677(1) Å, c = 20.9082(6) Å, α = 90°, β = 129.818(2) °, γ = 90°, Volume: 2550.85(13) Å^3, Temperature: 296 K, Z = 8, D_{calc} = 1.293 g cm^{-3}, D_{report} = 1.293 g cm^{-3}, λ = 0.71073 Å, m(Cu-Ka) = 0.094 mm^{-1}, empirical absorption correction(T_{min} = 0.552, T_{max} = 0.746), CCD Bruker SMART APEX diffractometer, structure was solved by direct methods and refined (SHELXL-97) by full matrix least squares based on F² to R(reflections)= 0.0396(2686) [I > 20(1)], wR_2 (reflections) = 0.1035(3226), S = 1.029.

7,9,14-trioxadispiro[5.1.68.36]heptadeca-1,4,11-trien-3-one (7z)



Structure of compound **7z (CCDC 2331856)** in solid state. The anisotropic displacement parameters are drawn at the 50% probability displacement level. Red = Oxygen atom; Black = Carbon atom; White - Hydrogen atom. Crystal was grown in acetone (slow evaporation). X-Ray Crystal Structure Analysis of **7z:** Molecular formula = $C_{14}H_{16}O_4$, Mr. = 248.27gmol^{-1}, colorless crystal, space group: $P2_1/n$, Hall group: -P 2yn, a = a=6.6173(1) Å , b = 18.0893(4) Å, c =10.0300(2) Å, α = 90°, β = 92.580(1)°, γ = 90°, Volume: 1199.40(4) Å^3, Temperature: 296 K, Z = 4, D_{calc} = 1.375 g cm^{-3}, D_{report} = 1.375 g cm^{-3}, λ = 0.71073 Å, m(Cu-Ka) = 0.100 mm^{-1}, empirical absorption correction(T_{min} = 0.517, T_{max} = 0.746), CCD Bruker SMART APEX diffractometer, structure was solved by direct methods and refined (SHELXL-97) by full matrix least squares based on F² to R(reflections)= 0.0369(2736) [I > 20(1)], wR_2 (reflections) = 0.1005(2973), S = 1.037.

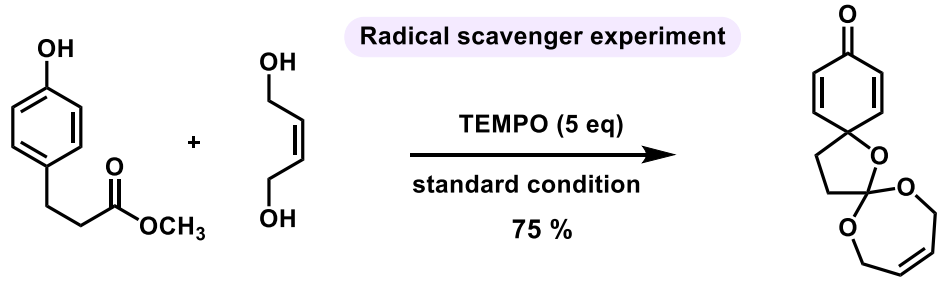
7,9,13,15,24,27-hexaoxapentaspiro[5.1.2.2.1.516.214.211.28.26]nonacosa-1,4,17,20-tetraene-3,19-dione (7a')



Structure of compound **7a' (CCDC 2313112)** in solid state. The anisotropic displacement parameters are drawn at the 50% probability displacement level. Red = Oxygen atom; Black = Carbon atom; White - Hydrogen atom. Crystal was grown in acetone (slow evaporation). X-Ray Crystal Structure Analysis of **7a':** Molecular formula = $C_{23}H_{24}O_8$, Mr. = 428.42 $gmol^{-1}$, colorless crystal, space group: C2/c, Hall group: -C 2yc, a = 34.4820(15) Å , b = 5.8066(3) Å, c = c=10.1971(5) Å, α = 90°, β = 102.891(2)°, γ = 90°, Volume: 1990.24(17) $Å^3$, Temperature: 296 K, Z = 4, D_{calc} = 1.430 g cm^{-3}, D_{report} = 1.430 g cm^{-3}, λ = 0.71073 Å, μ(Cu–Kα) = 0.108 mm^{-1}, empirical absorption correction(T_{min} = 0.575, T_{max} = 0.746), CCD Bruker SMART APEX diffractometer, structure was solved by direct methods and refined (SHELXL-97) by full matrix least squares based on F^2 to R(reflections)= 0.0382(2199) [I > 20(1)], wR_2 (reflections) = 0.0986(2492), S = 1.051.

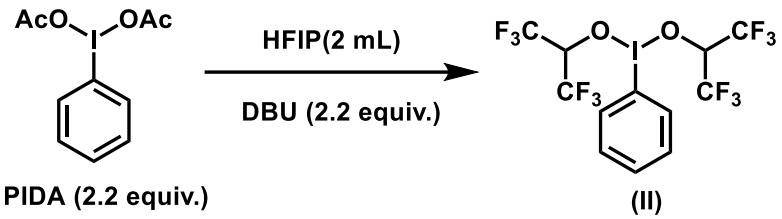
(VII) Mechanstic investigation:

1) **Radical scavenger experiment:** The general procedure **A** was followed using methyl 3-(4-hydroxyphenyl)propanoate (100 mg, 0.555 mmol, 1 equiv.), (*Z*)-but-2-ene-1,4-diol (185.73 mg, 1.22 mmol, 2.2 equiv.) and TEMPO (86.7 mg, 2.77 mmol, 5 equiv) to obtain crude product **7a**. Purification by column chromatography R_f (Hexane/EtOAc 50/50, UV active, PMA stain active) = 0.5 yielded **7a** (97.5 mg, 75%) as a colorless white solid.



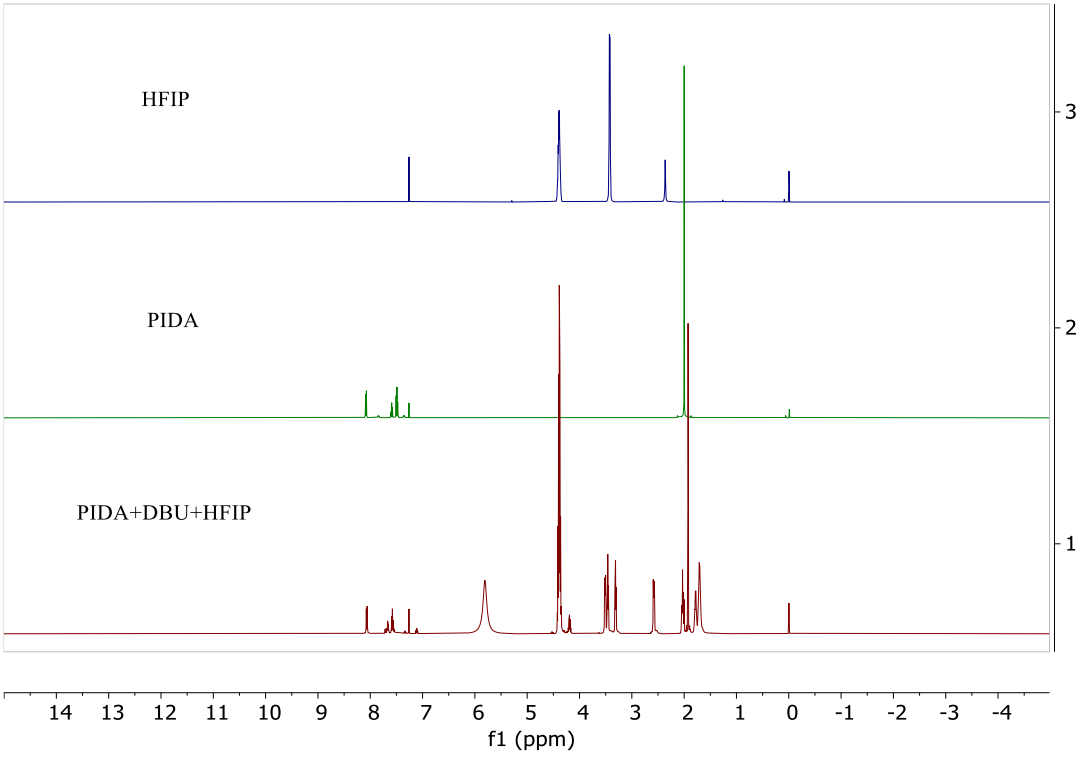
2) **NMR study for the exchange of HFIP with acetate (*in situ* generation of Compound II):** To a stirred solution of HFIP (2 mL) was added DBU (2.2 equiv.) and PIDA (1.2 equiv.) at 0 °C and it was stirred for 5 minutes followed by recording of NMR using 0.4 mL of $CDCl_3$. NMR data for compound 2 matches with the previously reported data in *Angew. Chemie Int. Ed.* **2019**, *58*, 9811–9815.

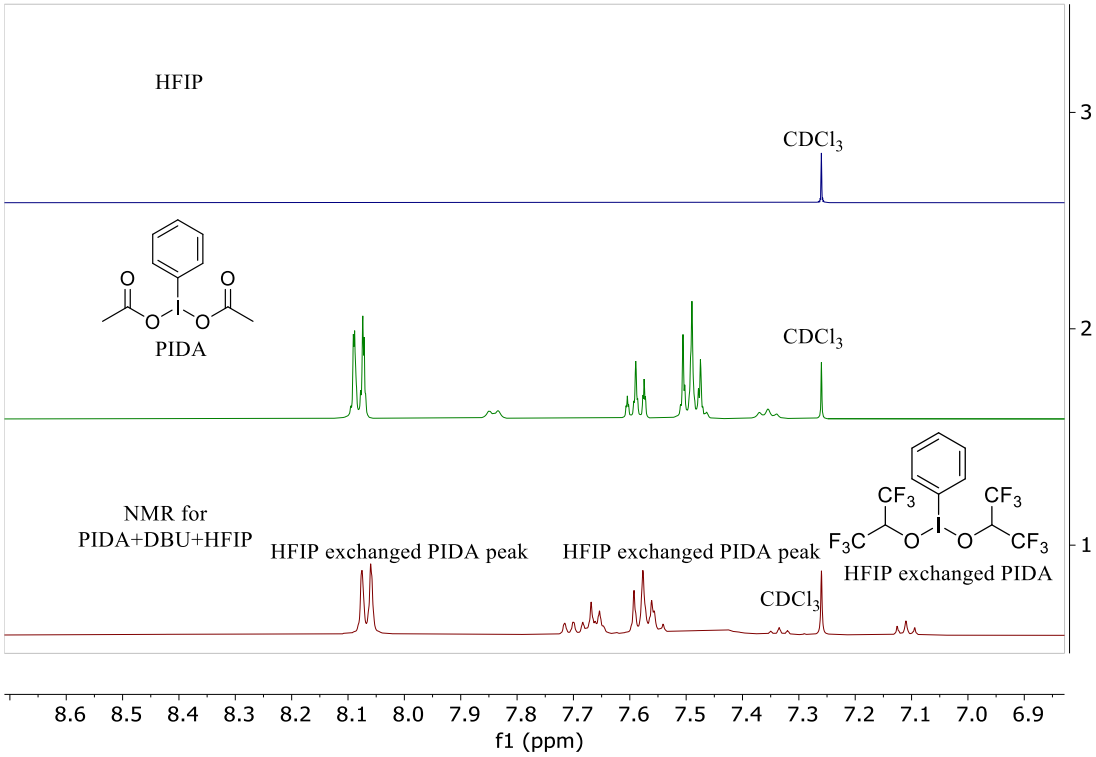
NMR analysis

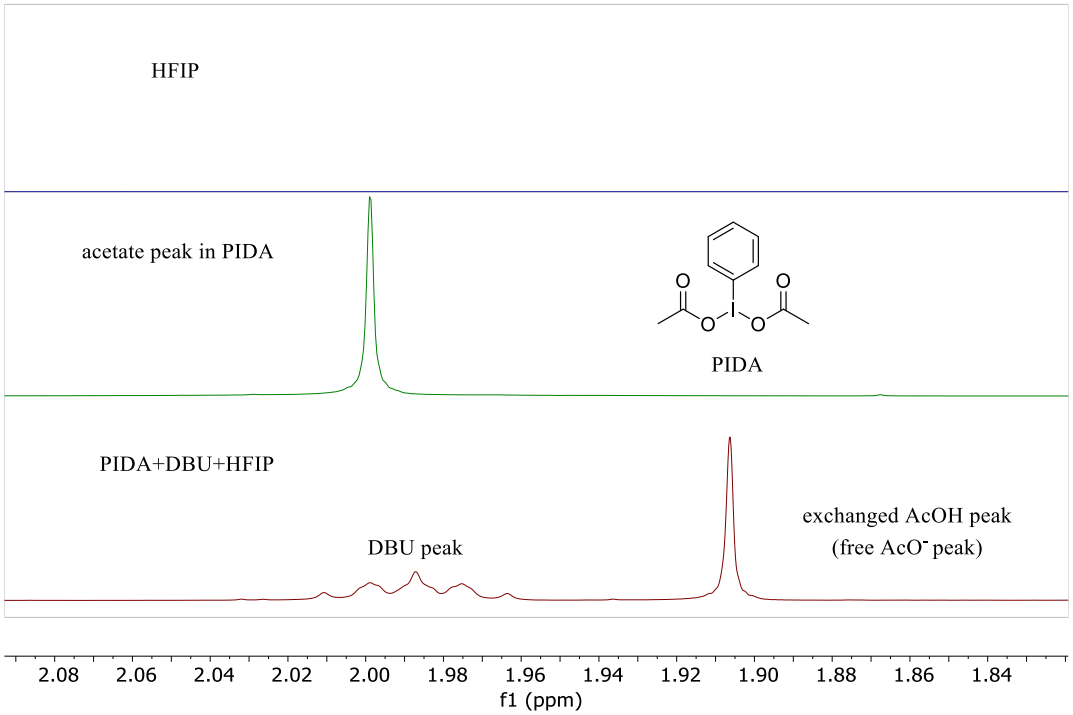


PIDA (2.2 equiv.) (II)

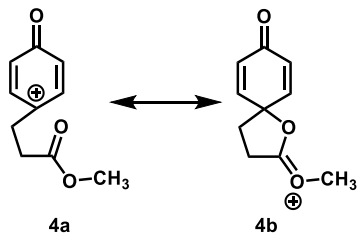
1) NMR spectra shown here are for Hexafluoroisopropanol (HFIP), phenyliodine(III) diacetate (PIDA), and the mixture of PIDA, DBU, and HFIP (reaction mixture before adding the diol and phenolic ester starting material) in $CDCl_3$. Once PIDA, DBU, and HFIP are mixed together, PIDA gets consumed and very little amount of it remains (after 5 min) as clearly visible from NMR.
2) There is a slight shift in the acetate ion peak towards the shielding region indicating the removal of acetate from Iodine (+3).







3) **HRMS (ESI-TOF) analysis for 4a or 4b:**

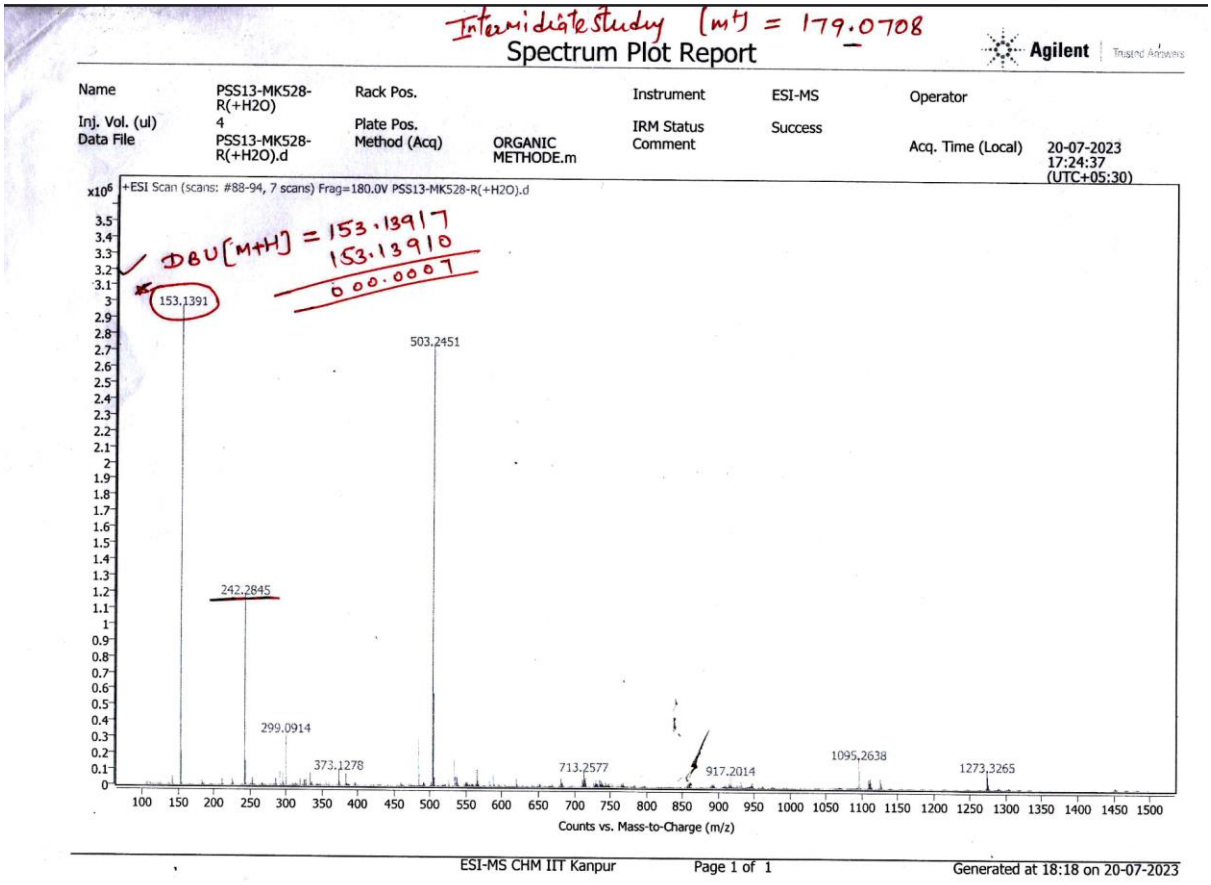


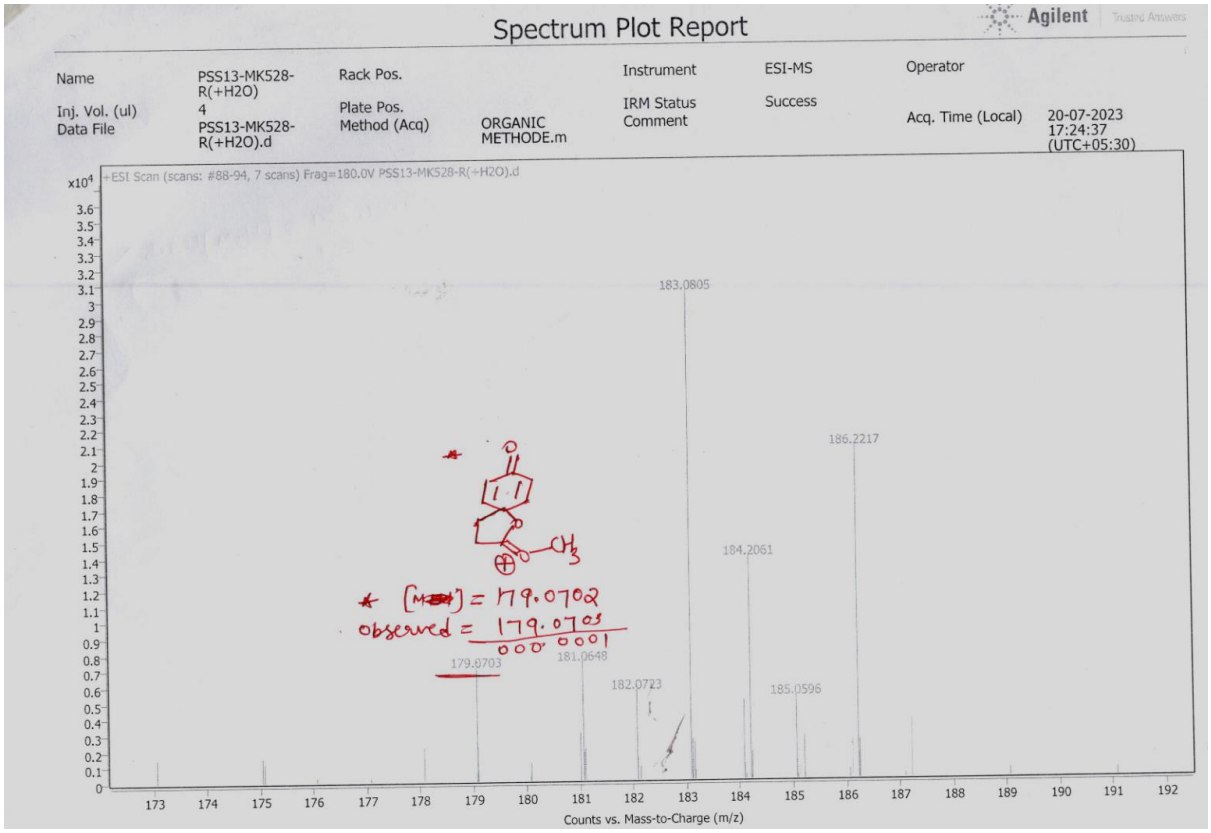
4a **4b**

HRMS (ESI-TOF) m/z: [M+] Calcd for $C_{10}H_{11}O_3$ 179.0702; Found 179.0703.

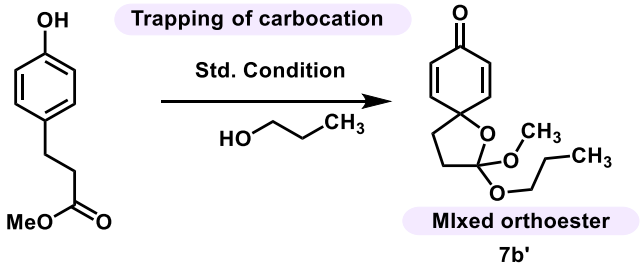
Full High-resolution mass spectra: DBU concentration is very high with respect to intermediate that suppresses the peak intensity of intermediate.

Further confirmation was done by trapping the intermediate using *n*-propanol (**7b'**).





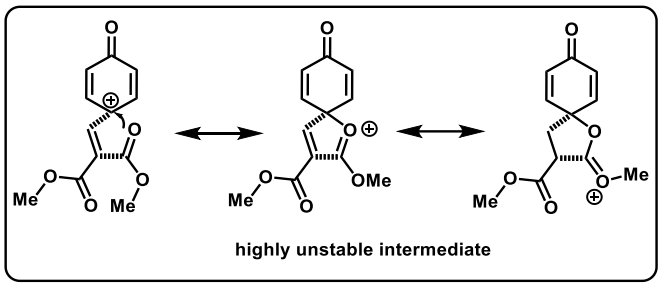
4) **Trapping of carbocation (2-methoxy-2-propoxy-1-oxaspiro[4.5]deca-6,9-dien-8-one (7b'))**



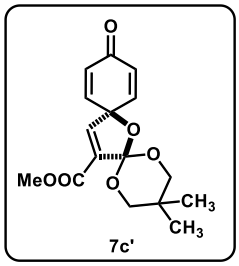
The general procedure **A** was followed using methyl 3-(4-hydroxyphenyl)propanoate (100 mg, 0.555 mmol, 1 equiv.) and 1-propanol (73.3 mg, 1.22 mmol, 2.2 equiv.) to obtain crude product **7b'**. Purification by column chromatography R_f (Hexane/EtOAc 80/20, UV active, PMA stain active) = 0.5 yielded **7b'** (60 mg, 45%) as a colorless liquid. **^{1}H NMR** (396 MHz, BENZENE-D_6) δ 6.17 – 5.98 (m, 4H), 3.30 (s, 3H), 2.91 (t, J = 6.4 Hz, 2H), 2.02 (dd, J = 8.9, 6.9 Hz, 2H), 1.85 (dd, J = 8.8, 6.9 Hz, 2H), 1.44 – 1.28 (m, 2H), 0.76 (t, J = 7.3 Hz, 3H). **^{13}C{^{1}H} NMR** (101 MHz, CHLOROFORM-D) δ 184.3, 172.6, 150.0, 131.5, 74.2, 66.8, 51.1, 34.7, 28.4, 23.8, 10.7. **IR υ (cm^{-1})** 3055, 2956, 2919, 2870, 2851, 1775, 1674, 1632, 1561, 1465, 1378, 1264, 1237, 1165, 1109, 1026, 80, 814, 747, 690, 618, 592, 538, 457. **HRMS** (ESI-TOF) m/z: [M+Na]- Calcd for $C_{13}H_{18}NaO_4$ 261.1103; Found 261.1099.

5) **Stability of carbocation** (preparation of orthoester with electron-withdrawing group)

Further involvement of carbocation was confirmed by using a diester starting material which gave only 10% of the Ortho ester (**7c'**) due to destabilization of tertiary carbocation due to conjugation (as shown below) with the ester group through pi-bond.

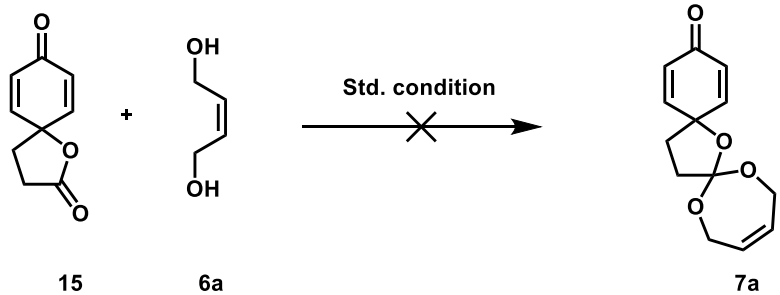


methyl 3,3-dimethyl-11-oxo-1,5,7-trioxadispiro[5.1.58.26]pentadeca-9,12,14-triene-15-carboxylate (7c')



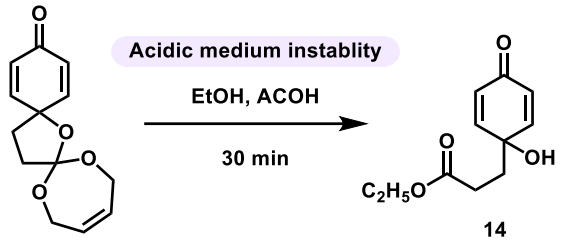
The general procedure **A** was followed using dimethyl 2-(4-hydroxybenzylidene)malonate (100 mg, 0.423 mmol, 1 equiv.) and 2,2-dimethylpropane-1,3-diol (97 mg, 0.931 mmol, 2.2 equiv.) to obtain crude product **7c'**. Purification by column chromatography R_f (Hexane/EtOAc 60/40, UV active, $KMnO_4$ stain active) = 0.3 yielded **7c'** (13 mg, 10%) as a colorless liquid. **^{1}H NMR** (400 MHz, DMSO-D_6) δ 7.13 (s, 1H), 6.72 (d, J = 10.2 Hz, 2H), 6.25 (d, J = 9.9 Hz, 2H), 3.88 (d, J = 10.6 Hz, 2H), 3.73 (s, 3H), 3.50 (d, J = 10.8 Hz, 2H), 1.25 (s, 3H), 0.76 (s, 3H). **^{13}C{^{1}H} NMR** (100 MHz, DMSO-D_6) δ 184.0, 167.3, 148.0, 146.3, 144.5, 129.2, 80.6, 79.1, 70.7, 51.9, 29.1, 22.0, 21.2. **IR u (cm^{-1})** 3050, 2965, 2921, 2866, 1776, 1739, 1670, 1622, 1563, 1460, 1350, 1274, 1227, 1155, 1107, 1016, 810, 740, 699, 612, 593, 530, 456. **HRMS** (ESI-TOF) m/z: [M+Na]- Calcd for $C_{16}H_{19}NaO_6$ 306.1103; Found 306.1099.

6) **Checking another possible intermediate:**



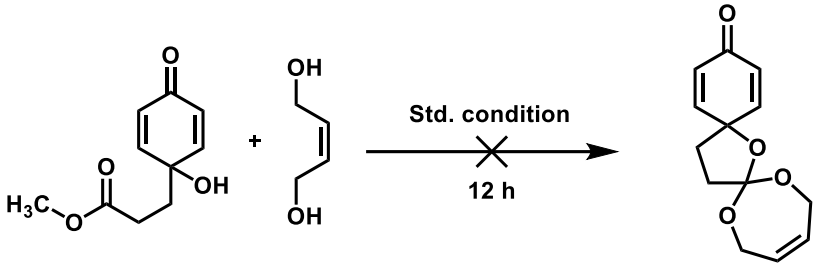
The general procedure **A** was followed using 1-oxaspiro[4.5]deca-6,9-diene-2,8-dione (100 mg, 0.609 mmol, 1 equiv.) and (*Z*)-but-2-ene-1,4-diol (185.73 mg, 1.22 mmol, 2.2 equiv.). There was no product formation indicating the reaction did not proceed through neutral lactone.

7) **Decomposition study of compound 7a:**



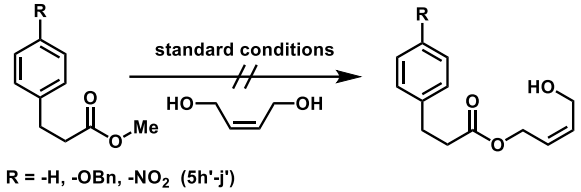
To a stirred solution of compound **7a (**50 mg, 0.213 mmol, 1 equiv.**)** in ethanol (2 mL) was added AcOH (0.5 equiv.) at room temperature under a nitrogen atmosphere. It was stirred for 30 minutes. The reaction progress was monitored by TLC. Upon the completion of the reaction, it was concentrated in vacuo to remove ethanol followed by column chromatography R_f (Hexane/EtOAc, 60:40) = 0.4 to provide **14** ethyl 3-(1-hydroxy-4-oxocyclohexa-2,5-dien-1-yl)propanoate (42.6 mg, 95%) as a yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.80 (d, *J* = 10.2 Hz, 2H), 6.14 (d, *J* = 10.2 Hz, 2H), 4.09 (q, *J* = 7.2 Hz, 2H), 3.25 (s, -OH peak, 1H), 2.31 (t, *J* = 7.7 Hz, 2H), 2.12 – 2.03 (t, *J* = 7.7 Hz, 2H), 1.22 (t, *J* = 7.2 Hz, 3H).

8) **Interconversion study of compound 14 to 7a:**



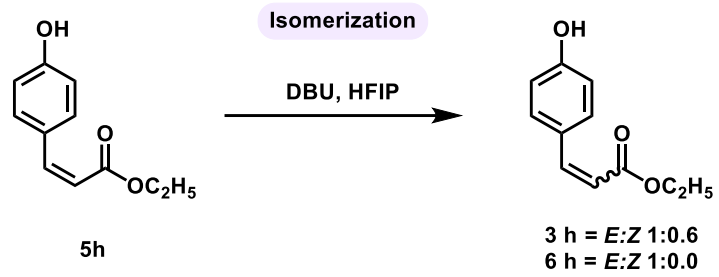
General procedure A was followed using methyl 3-(1-hydroxy-4-oxocyclohexa-2,5-dien-1-yl)propanoate **(**50 mg, 0.254 mmol, 1 equiv.) and (*Z*)-but-2-ene-1,4-diol (185.73 mg, 1.22 mmol, 2.2 equiv.). There was no product formation indicating that compounds **14** and **7a** are not inconvertible.

9) ***trans*-esterification experiment:**

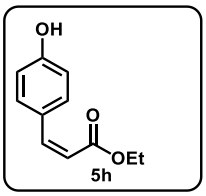


The general procedure **A** was followed using the known compound 8i to 8k (100 mg, 1 equiv.) and (*Z*)-but-2-ene-1,4-diol (185.73 mg, 1.22 mmol, 2.2 equiv.). There was no product formation and the starting material was isolated as such Indicating that the reaction is not going through the trans-esterification pathway.

10) **Isomaratization study for the compound 5h:** To a stirred solution DBU (174 mg, 1.14 mmol, 2.2 equiv.) in HFIP (2 mL) was added ethyl (*z*)-3-(4-hydroxyphenyl)acrylate (100 mg, 0.520 mmol, 1 equiv.). It was stirred for three hours and six hours (two different reactions) followed by filtration through a small pad of silica using pure ethyl acetate to obtain the mixture of compound 8g/8g' and the *E/Z* ratio was calculated using ^{1}H NMR.

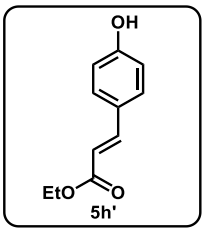


preparation of compound **ethyl (*z*)-3-(4-hydroxyphenyl)acrylate (5h)**



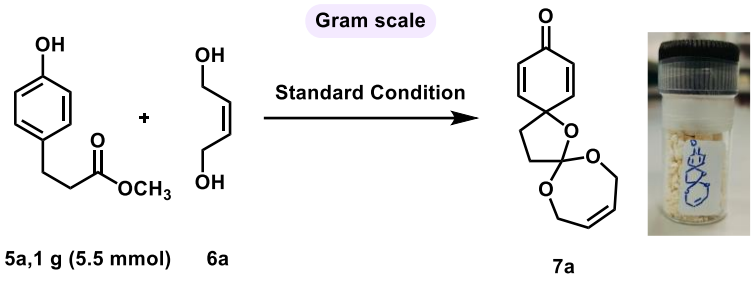
To a stirred solution of 4-hydroxybenzaldehyde (10.0 g, 0.082 mol, 1 equiv.) in DCM (100 ml) was added ethyl 2-(triphenyl-l5-phosphaneylidene)acetate (34.2 g, 0.098 mol, 1.2 equiv.) at room temperature under nitrogen atmosphere. The reaction progress was monitored by TLC. Upon the completion of the reaction, it was concentrated in vacuo to remove DCM followed by column chromatography R_f (Hexane/EtOAc, 90:10) = 0.3 to provide ethyl (*z*)-3-(4-hydroxyphenyl)acrylate (1.5 g, 10%) as a colorless solid. **^{1}H NMR** (500 MHz, CHLOROFORM-*D*) δ 7.59 (d, *J* = 8.6 Hz, 2H), 6.87 (d, *J* = 12.6 Hz, 1H), 6.78 (d, *J* = 8.7 Hz, 2H), 5.83 (d, *J* = 12.7 Hz, 1H), 4.21 (q, *J* = 7.1 Hz, 2H), 1.30 (t, *J* = 7.1 Hz, 3H). **^{13}C{^{1}H} NMR** (126 MHz, CHLOROFORM-*D*) δ 167.3, 157.2, 144.2, 132.4, 127.3, 117.0, 115.3, 60.6, 14.3.

ethyl (*E*)-3-(4-hydroxyphenyl)acrylate (5h-*trans*)



To a stirred solution of 4-hydroxybenzaldehyde (10.0 g, 0.082 mol, 1 equiv.) in DCM (100 mL) was added ethyl 2-(triphenyl-l5-phosphaneylidene)acetate (34.2 g, 0.098 mol, 1.2 equiv.) at room temperature under nitrogen atmosphere. The reaction progress was monitored by TLC. Upon the completion of the reaction, it was concentrated in vacuo to remove DCM followed by purification using column chromatography R_f (Hexane/EtOAc, 90:10) = 2.9 to provide ethyl (*E*)-3-(4-hydroxyphenyl)acrylate (13.4 g, 85%) as a colorless solid. **^{1}H NMR** (500 MHz, CHLOROFORM-*D*) δ 7.62 (d, *J* = 15.9 Hz, 1H), 7.40 (d, *J* = 8.6 Hz, 2H), 6.86 (d, *J* = 8.6 Hz, 2H), 6.56 (broad signal, s, 1H), 6.28 (d, *J* = 15.9 Hz, 1H), 4.26 (q, *J* = 7.2 Hz, 2H), 1.32 (t, *J* = 7.1 Hz, 3H).**^{13}C{^{1}H} NMR** (101 MHz, CHLOROFORM-*D*) δ 168.3, 158.4, 145.1, 130.2, 127.0, 116.1, 115.3, 60.9, 14.4.

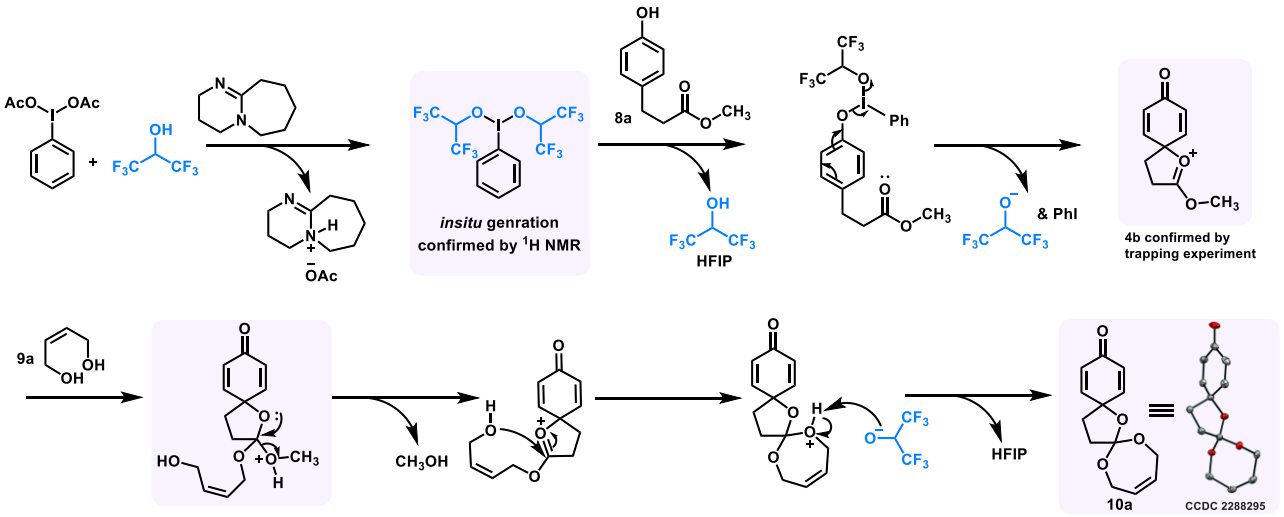
11) **Gram-scale reaction:**



Several batches of this study gave the product in the yield range of 77 to 83%

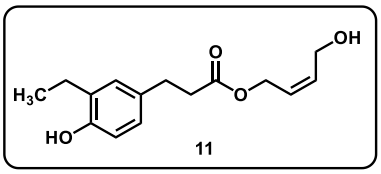
The general procedure **A** was followed using methyl 3-(4-hydroxyphenyl)propanoate (1000 mg, 5.549 mmol, 1 equiv.) and (*Z*)-but-2-ene-1,4-diol (1.07 g, 12.2 mmol, 2.2 equiv.) and 8 mL of HFIP to obtain crude product **7a**. Purification by column chromatography R_f (Hexane/EtOAc 50/50, UV active, PMA stain active) = 0.5 yielded **7a** (1 g, 77%) as a colorless white solid.

(VIII) Proposed Reaction Mechanism



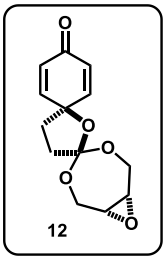
(IX) Product Scope

(Z)-4-hydroxybut-2-en-1-yl 3-(3-ethyl-4-hydroxyphenyl)propanoate (11)



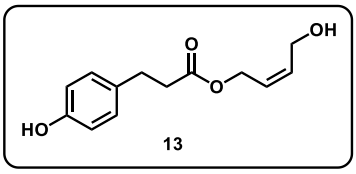
To a stirred solution of the 7,9,14-trioxadispiro[5.1.6$^{8.26}$]hexadeca-1,4,11-trien-3-one (**7a**) (30 mg, 0.13 mmol, 1 equiv.) in THF (0.04 M) was added EtMgBr (1.0 M in THF) (0.26 mL, 0.26 mmol, 2 equiv.) at -78 °C. After 2 h of stirring when TLC showed complete consumption, it was quenched by the addition of saturated ammonium chloride solution followed by extraction using DCM. The collected DCM layer was washed with brine followed by drying over Na_2SO_4 to obtain the crude mixture after *invacuo* removal of solvent. Purification by column chromatography R_f (Hexane/EtOAc 50/50, UV active, PMA stain active, $KMNO_4$ active) = 0.5 yielded **11** (26 mg, 77%) as a colorless oil. **^{1}H NMR** (400 MHz, CHLOROFORM-*D*) δ 7.02 (d, *J* = 8.5 Hz, 2H), 6.73 (d, *J* = 8.5 Hz, 2H), 5.82 (dt, *J* = 12.0, 6.8 Hz, 1H), 5.57 (dq, *J* = 12.1, 6.2 Hz, 2H, alkene, phenolic OH peak), 4.64 (d, *J* = 7.1 Hz, 2H), 4.22 (d, *J* = 6.7 Hz, 2H), 2.85 (t, *J* = 7.6 Hz, 2H), 2.58 (t, *J* = 7.6 Hz, 2H), 2.25 (s, 1H, OH peak).**^{13}C{^{1}H} NMR** (100 MHz, CHLOROFORM-*D*) δ 173.5, 152.1, 133.4, 130.2, 129.3, 126.7, 125.8, 116.3, 115.3, 60.2, 58.5, 36.4, 30.3, 23.1, 14.2. **IR υ (cm^{-1})** 3442, 1736, 1612, 1442, 1267, 1255, 1201, 1062, 875, 839 . **HRMS** (ESI-TOF) m/z: [M+Na]- Calcd for $C_{13}H_{16}O_4Na$ 259.0946; Found 259.0945.

3',4'-dihydro-3,5,8-trioxadispiro[bicyclo[5.1.0]octane-4,2'-furan-5',1"-cyclohexane]-2",5"-dien-4"-one (12)



To a stirred solution of the 7,9,14-trioxadispiro[5.1.6$^{8.26}$]hexadeca-1,4,11-trien-3-one (**7a**) (30 mg, 0.13 mmol, 1 equiv.) in 5 mL DCM was added $NaHCO_3$ (53.7 mg, 0.64 mmol, 5 equiv.) and *m*-CPBA (67.3 mg, 0.39 mmol, 3 equiv.). After 72 h of stirring, it was filtered through the plug of cotton using DCM. After filtration DCM layer was washed with brine followed by drying over Na_2SO_4 to obtain the crude mixture after invacuo removal of solvent. Purification by column chromatography R_f (Hexane/EtOAc 50/50, UV active, PMA stain active, $KMNO_4$ active) = 0.4 yielded **12** (23 mg, 69%) as a colorless oil. **^{1}H NMR** (400 MHz, BENZENE-D_6) δ 6.35 (d, *J* = 9.8 Hz, 2H), 5.97 (d, *J* = 10.1 Hz, 2H), 3.88 (dd, *J* = 14.1, 2.3 Hz, 2H), 3.60 (dd, *J* = 14.3, 1.7 Hz, 2H), 2.62 (d, *J* = 2.3 Hz, 2H), 1.69 (t, *J* = 7.6 Hz, 2H), 1.47 (t, *J* = 7.6 Hz, 2H). **^{13}C{^{1}H} NMR** (100 MHz, CHLOROFORM-*D*) δ 184.3, 148.5, 128.8, 125.1, 77.9, 61.6, 55.4, 34.6, 34.3. **IR υ (cm^{-1})** 2923, 2850, 1722, 1670, 1630, 1432, 1372, 1310, 1202, 1165, 1072, 1042, 970, 913, 850, 835, 804, 643, 612. **HRMS** (ESI-TOF) m/z: [M+Na]- Calcd for $C_{13}H_{14}O_5Na$ 273.0738; Found 273.0733.

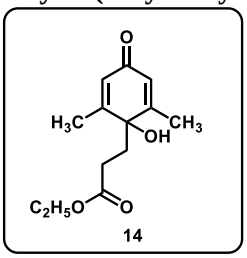
(Z)-4-hydroxybut-2-en-1-yl 3-(4-hydroxyphenyl)propanoate (13)



13

To a stirred solution of the 7,9,14-trioxadispiro[5.1.6$^{8.26}$]hexadeca-1,4,11-trien-3-one (**7a**) (30 mg, 0.13 mmol, 1 equiv.) in THF (0.04 M) was added DIBAL (1.0 M in Toluene) (0.26 mL, 0.26 mmol, 2 equiv.) at -40 °C. After 2 h of stirring when TLC showed complete consumption, it was quenched by the addition of Rochelle salt solution followed by extraction using DCM. The collected DCM layer was washed with brine followed by drying over Na_2SO_4 to obtain the crude mixture after invacuo removal of solvent. Purification by column chromatography R_f (Hexane/EtOAc 50/50, UV active, PMA stain active, $KMNO_4$ active) = 0.3 yielded **13** (25 mg, 82%) as a colorless oil. **^{1}H NMR** (400 MHz, CHLOROFORM-*D*) δ 7.02 (d, *J* = 8.5 Hz, 2H), 6.73 (d, *J* = 8.5 Hz, 2H), 5.82 (dt, *J* = 12.0, 6.8 Hz, 1H), 5.57 (dq, *J* = 12.1, 6.2 Hz, 2H, alkene, phenolic OH peak), 4.64 (d, *J* = 7.1 Hz, 2H), 4.22 (d, *J* = 6.7 Hz, 2H), 2.85 (t, *J* = 7.6 Hz, 2H), 2.58 (t, *J* = 7.6 Hz, 2H), 2.25 (s, 1H, OH peak).**^{13}C{^{1}H} NMR** (101 MHz, CHLOROFORM-*D*) δ 173.3, 154.3, 133.4, 132.5, 129.6, 125.8, 115.5, 60.2, 58.6, 36.4, 30.2.**IR υ (cm^{-1})** 3315, 1702 1620, 1516, 1422, 1392, 1316, 1263, 1208, 1151, 1102, 1065, 998, 902, 832. **HRMS** (ESI-TOF) m/z: [M+Na]- Calcd for $C_{13}H_{16}O_4Na$ 259.0946; Found 259.0945.

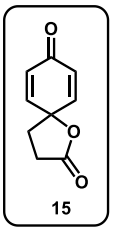
ethyl 3-(1-hydroxy-2,6-dimethyl-4-oxocyclohexa-2,5-dien-1-yl)propanoate (14)



14

To a stirred solution of compound **7d (**100 mg, 0.320 mmol, 1 equiv.**)** in ethanol (2 mL) was added AcOH (0.5 equiv.) at room temperature under a nitrogen atmosphere. It was stirred for 30 minutes. The reaction progress was monitored by TLC. Upon the completion of the reaction, it was concentrated in vacuo to remove ethanol followed by column chromatography R_f (Hexane/EtOAc, 60:40) = 0.4 to provide **14** ethyl 3-(1-hydroxy-4-oxocyclohexa-2,5-dien-1-yl)propanoate (72.5 mg, 95%) as a yellow oil. **^{1}H NMR** (500 MHz, CHLOROFORM-*D*) δ 6.03 (s, 2H), 4.06 (q, *J* = 7.0 Hz, 2H), 2.16 (t, *J* = 16.3 Hz, 2H), 2.05 (s, 6H), 1.94 – 1.84 (m, 2H), 1.20 (t, *J* = 6.9 Hz, 3H). **^{13}C{^{1}H} NMR** (126 MHz, CHLOROFORM-*D*) δ 185.6, 172.3, 160.8, 128.0, 74.2, 60.8, 31.5, 28.8, 18.19, 18.16. **IR υ (cm^{-1})** 3428, 2960, 2923, 2853, 1730, 1666, 1626, 1444, 1377, 1300, 1261, 1189, 1014, 8992, 798, 723, 625, 586. **HRMS** (ESI-TOF) m/z: [M+H]- Calcd for $C_{13}H_{19}O_4$ 239.1283; Found 239.175.

ethyl 3-(1-hydroxy-2,6-dimethyl-4-oxocyclohexa-2,5-dien-1-yl)propanoate (15)



A stirred solution of the 7,9,14-trioxadispiro[5.1.6$^{8.26}$]hexadeca-1,4,11-trien-3-one (**10a**) (30 mg, 0.13 mmol, 1 equiv.) in moist Ac_2O (0.06 M) was heated at 140 °C in a sealed tube. After 1 h of stirring when TLC showed complete consumption, water was added to the reaction followed by extraction using DCM. The collected DCM layer was washed with brine followed by drying over Na_2SO_4 to obtain the crude mixture after invacuo removal of solvent. Purification by column chromatography R_f (Hexane/EtOAc 50/50, UV active, PMA stain active, $KMNO_4$ active) = 0.6 yielded **15** (20 mg, 95%) as a colorless solid. **^{1}H NMR** (396 MHz, CHLOROFORM-*D*) δ 6.85 (d, *J* = 10.2 Hz, 2H), 6.27 (d, *J* = 10.2 Hz, 2H), 2.77 (t, *J* = 8.3 Hz, 2H), 2.37 (t, *J* = 8.4 Hz, 2H). **^{13}C{^{1}H} NMR** (126 MHz, CHLOROFORM-*D*) δ 184.1, 175.2, 145.6, 129.3, 78.4, 32.4, 28.0.

(X) References

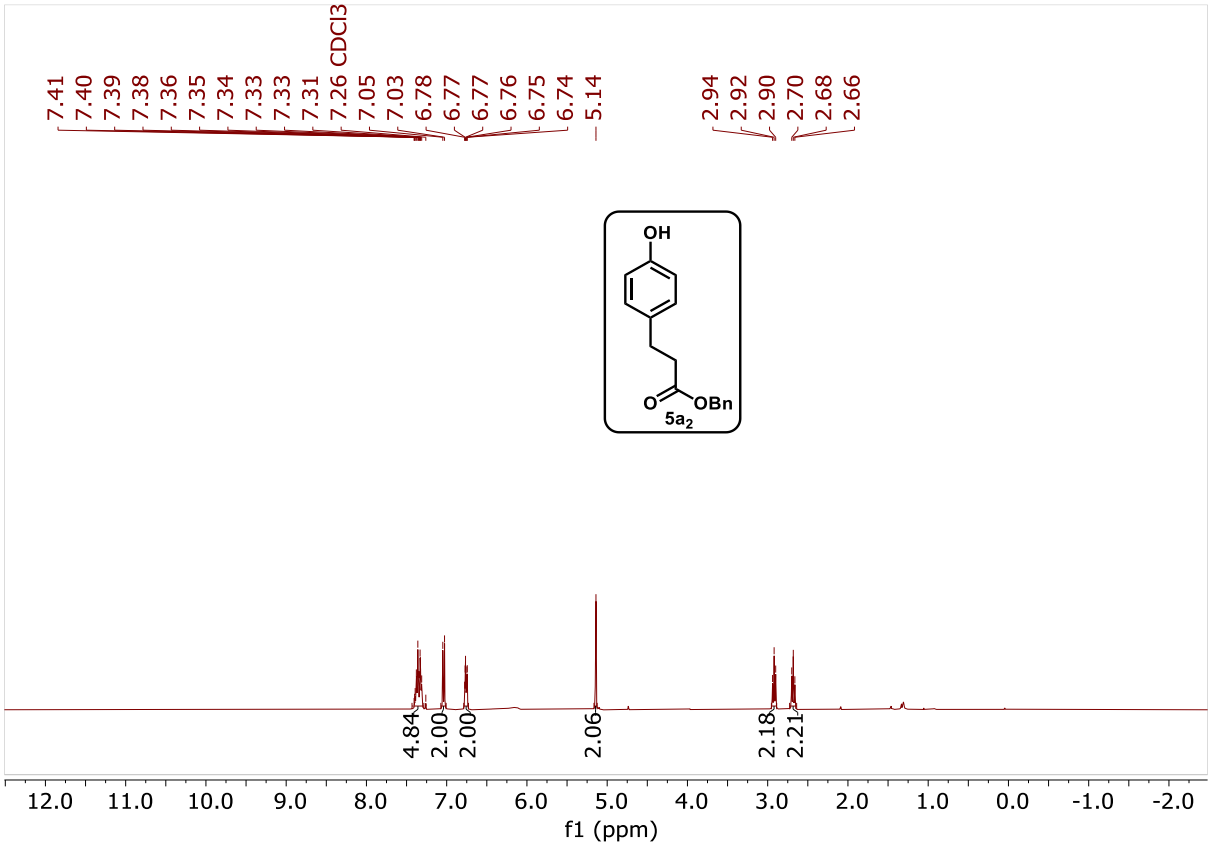
(26) J. G. Buchanan, D. G. Hill, R. H. Wightman, I. K. Boddy and B. D. Hewitt, *Tetrahedron*, 1995, **51**, 6033–6050.

(27) M. G. Donahue, N. G. Jentsch and E. C. Realini, *Tetrahedron Lett.*, 2017, **58**, 3219–3222.

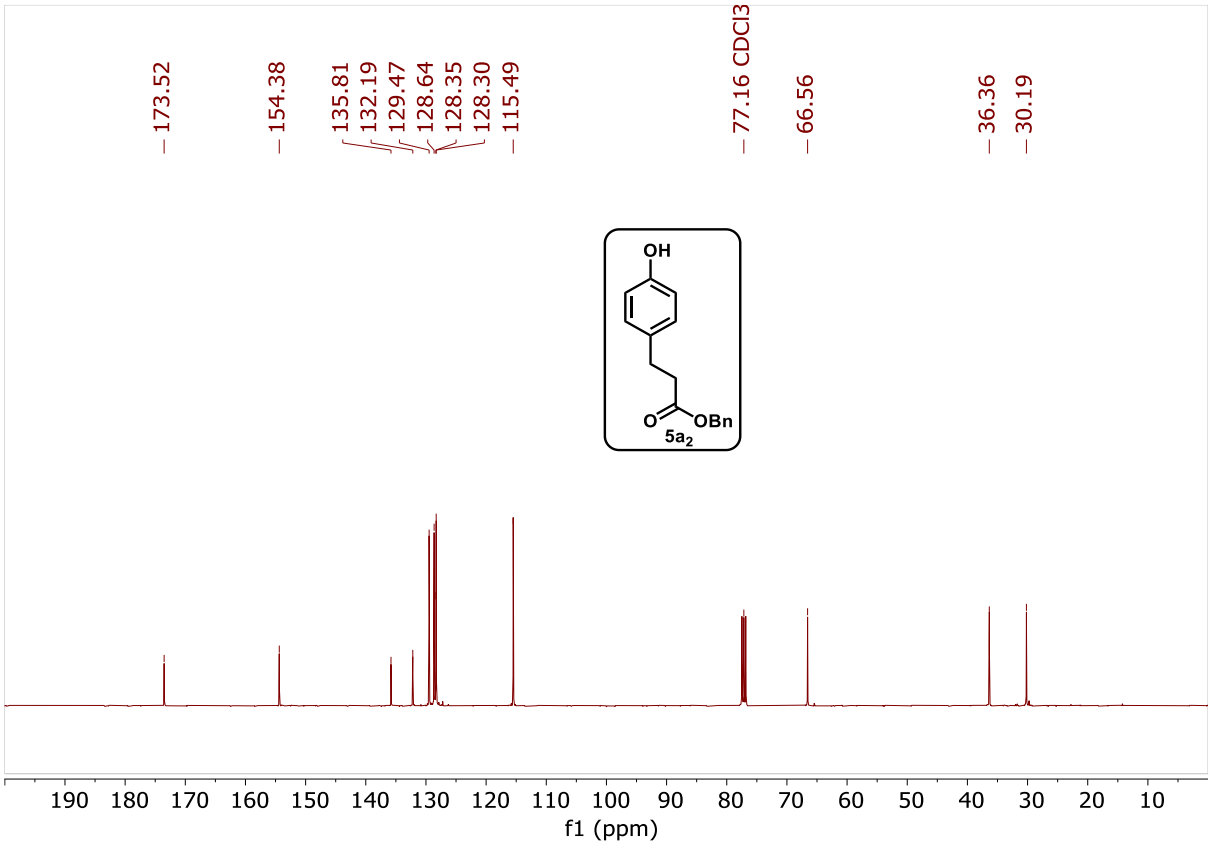
(28) M. Elsherbini, B. Winterson, H. Alharbi, A. A. Folgueiras-Amador, C. Génot and T. Wirth, *Angew. Chemie Int. Ed.*, 2019, **58**, 9811–9815.

(XI) NMR spectra

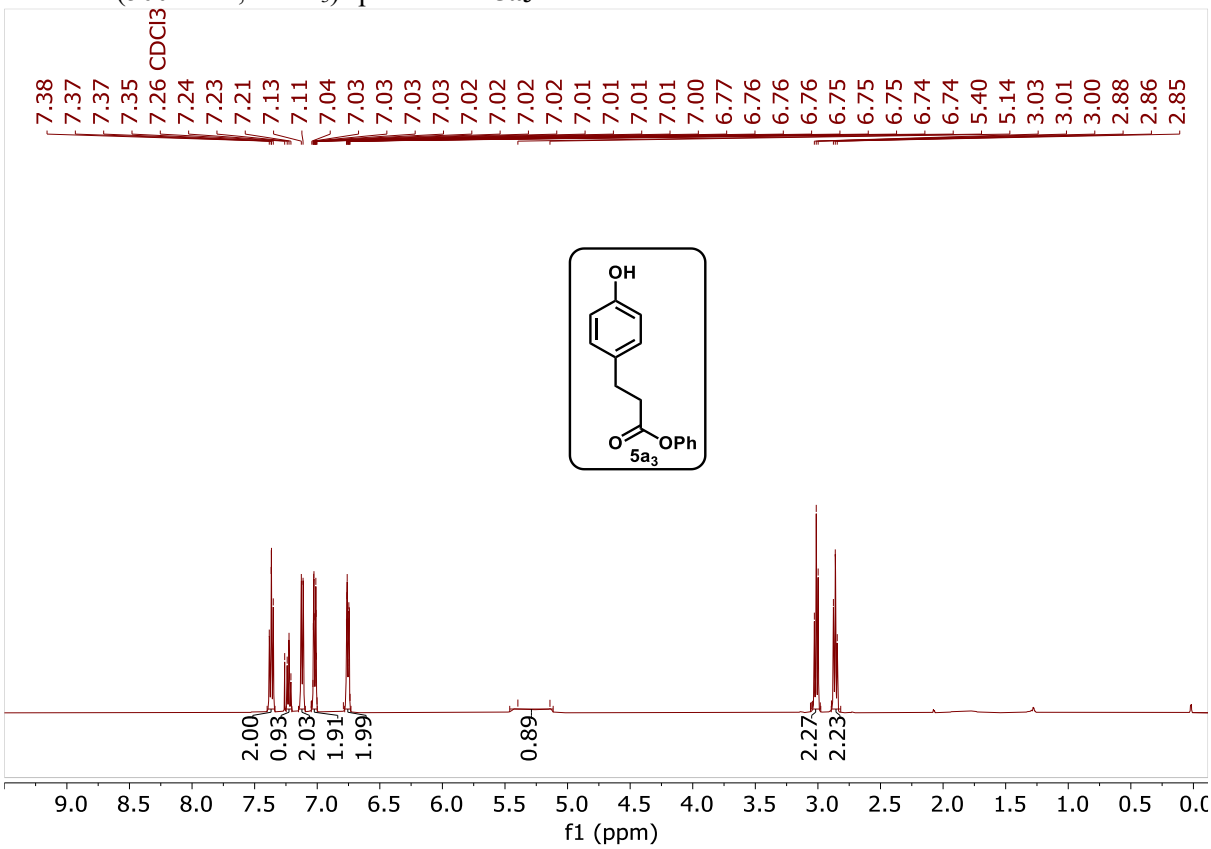
^{1}H NMR (396 MHz, $CDCl_3$) spectrum of **$5a_2$**



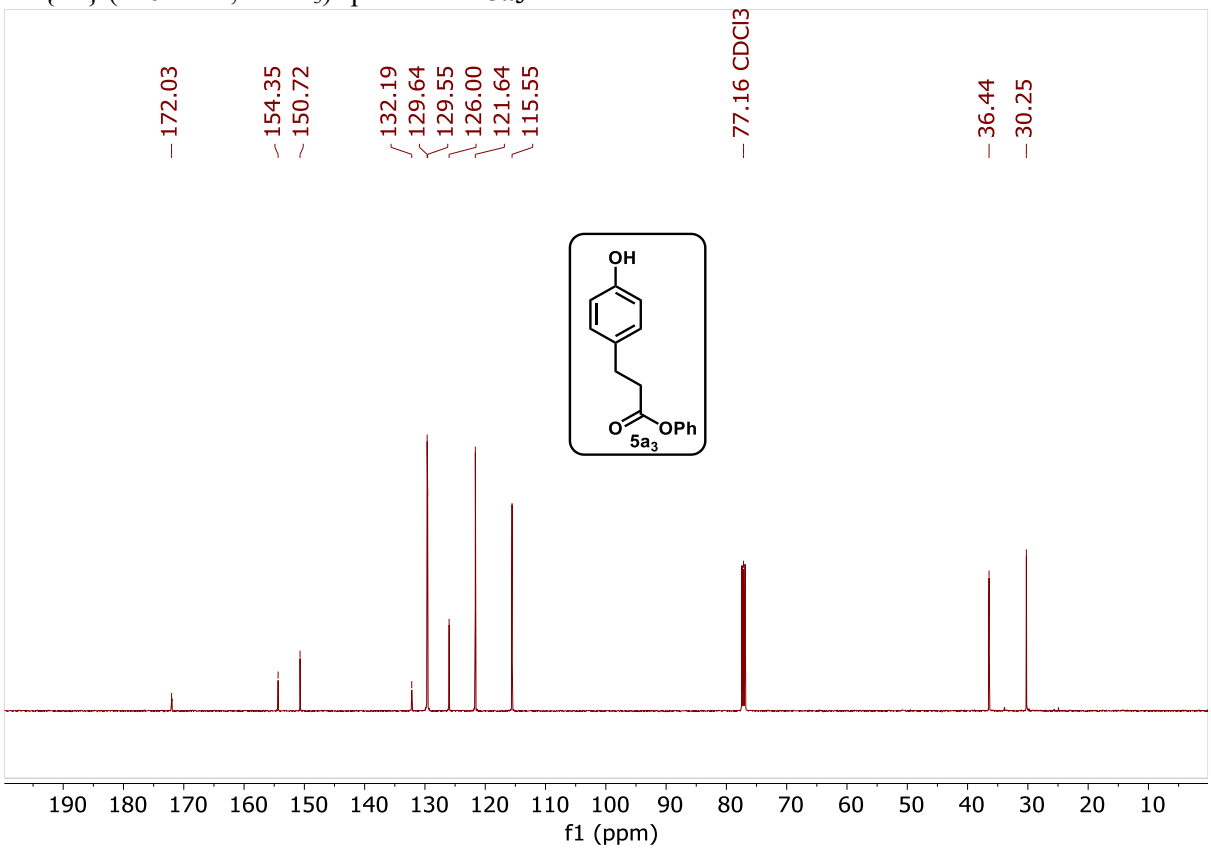
^{13}C{^{1}H} (101 MHz, $CDCl_3$) spectrum of **$5a_2$**



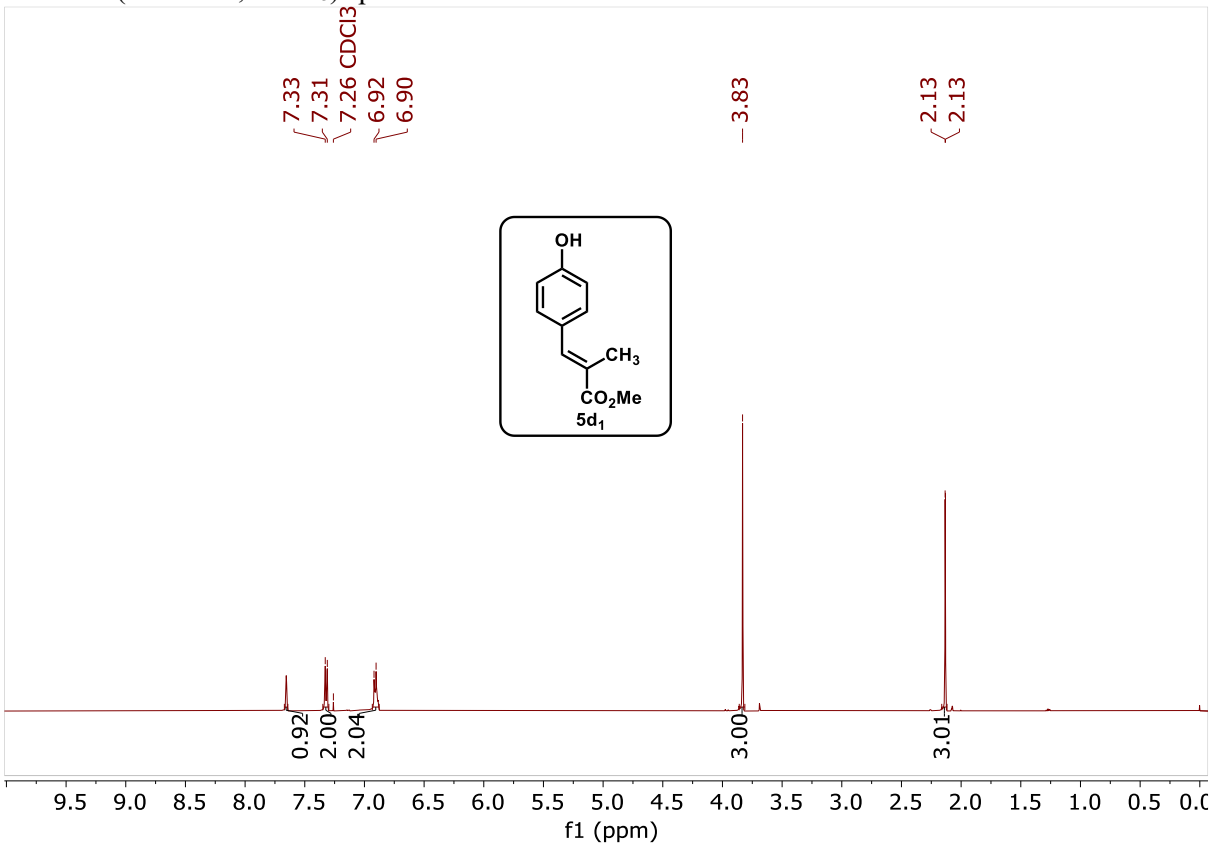
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **5a$_3$**



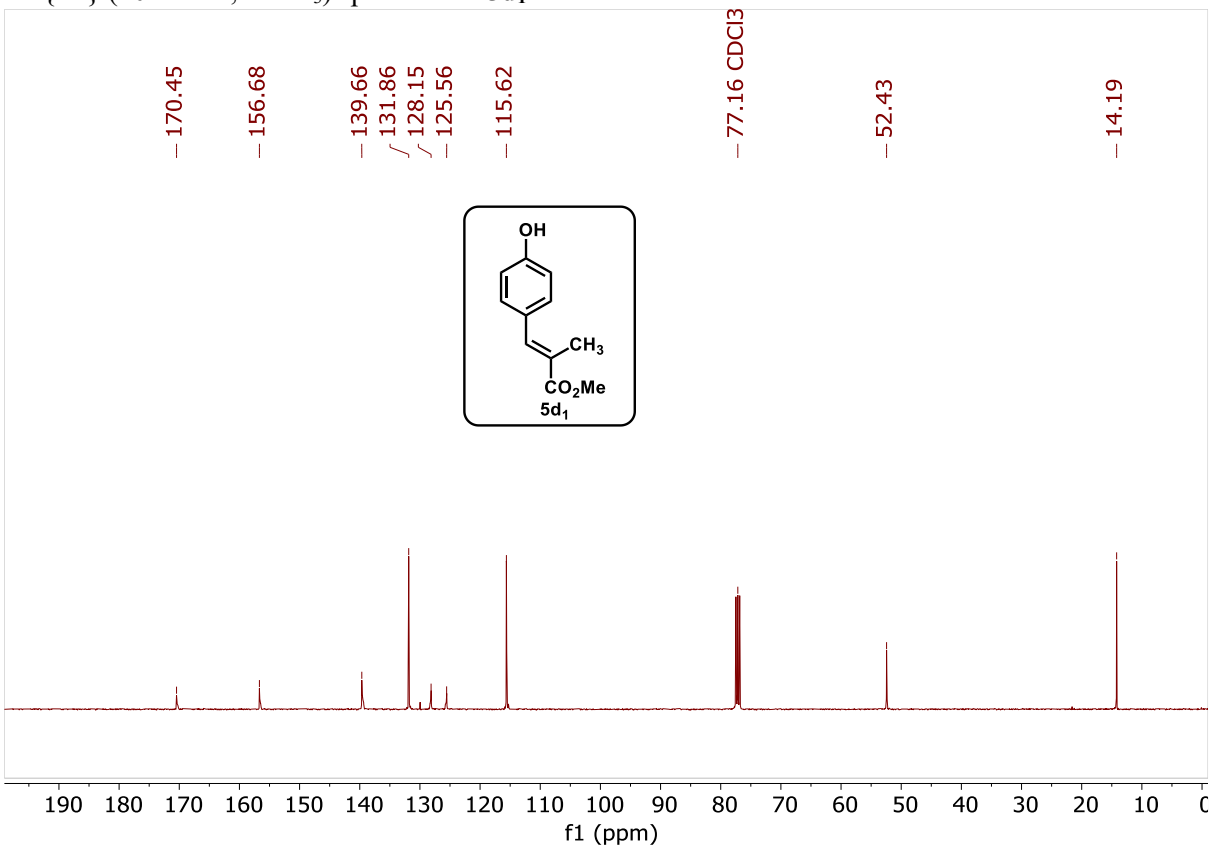
^{13}C{^{1}H} (126 MHz, $CDCl_3$) spectrum of **5a$_3$**



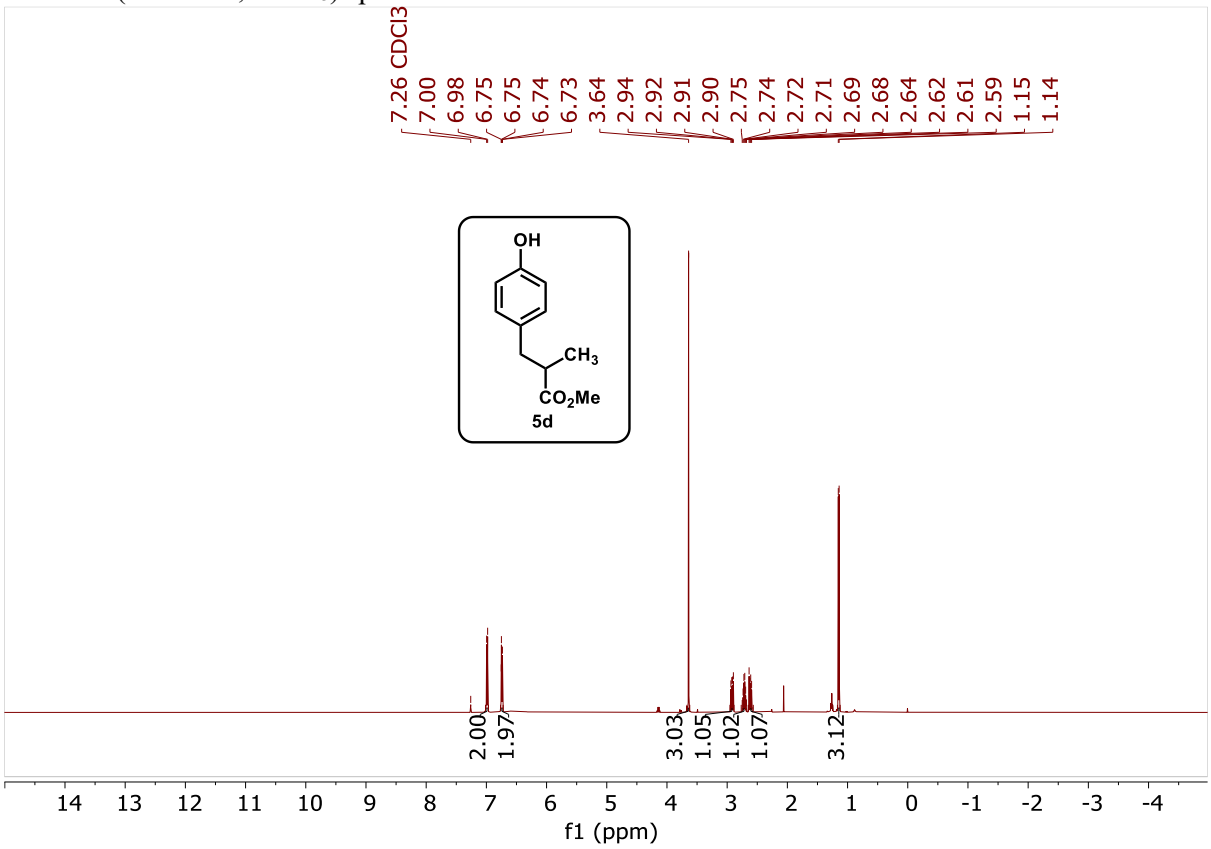
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **$5d_1$**



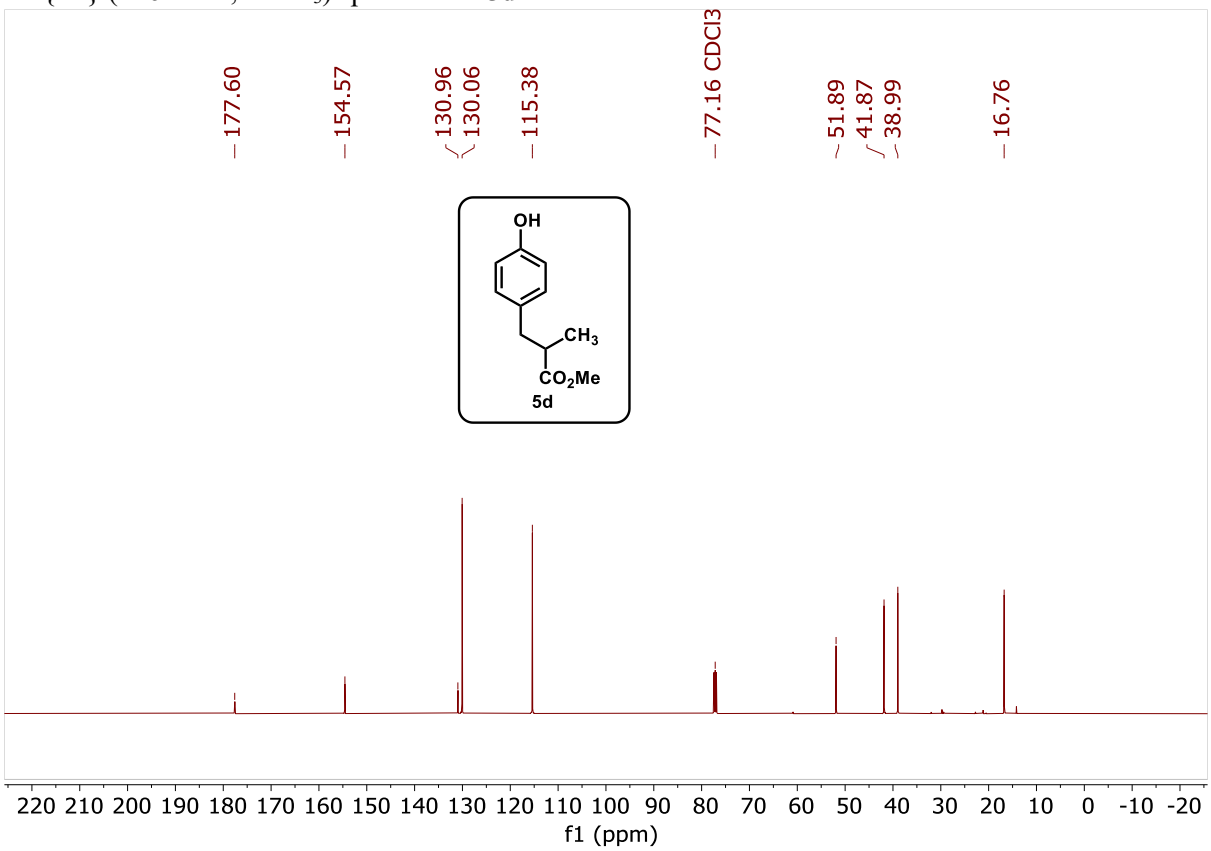
^{13}C{^{1}H} (101 MHz, $CDCl_3$) spectrum of **$5d_1$**



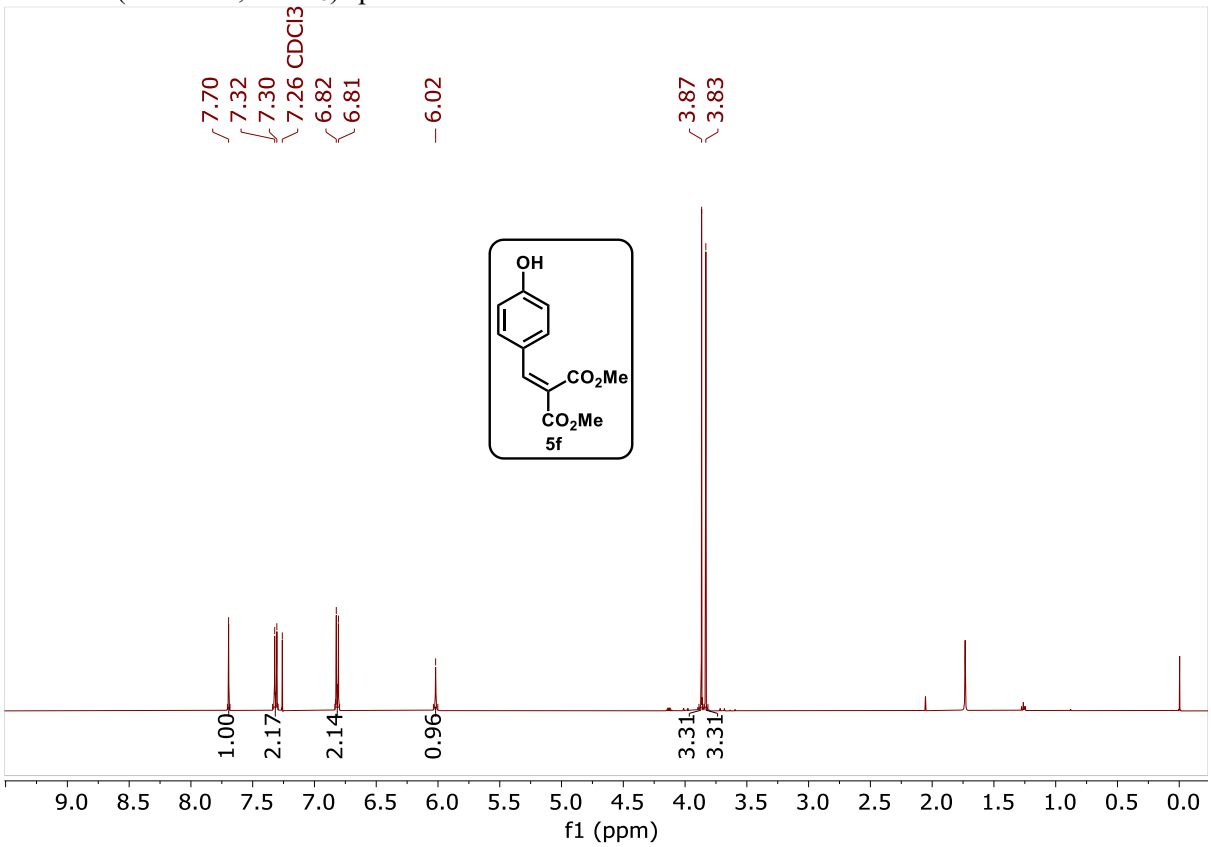
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **5d**



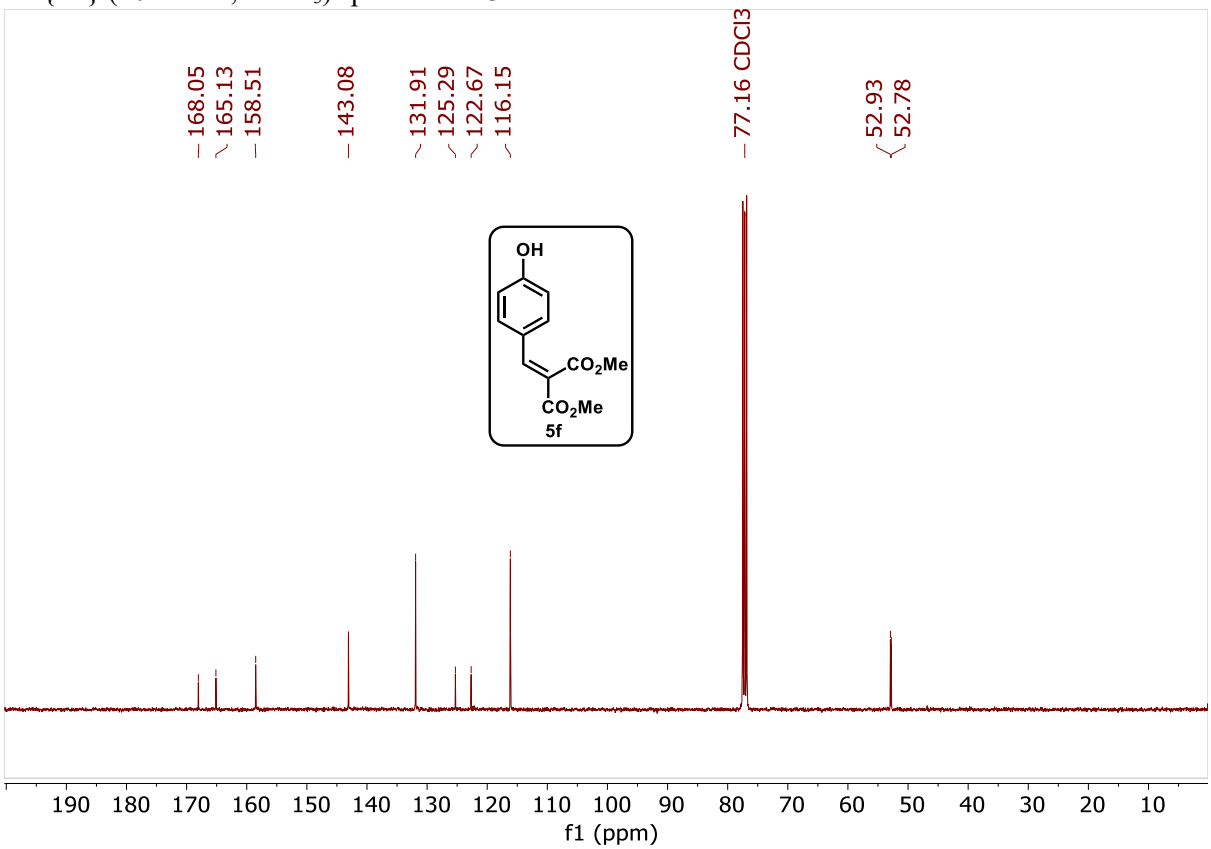
^{13}C{^{1}H} (126 MHz, $CDCl_3$) spectrum of **5d**



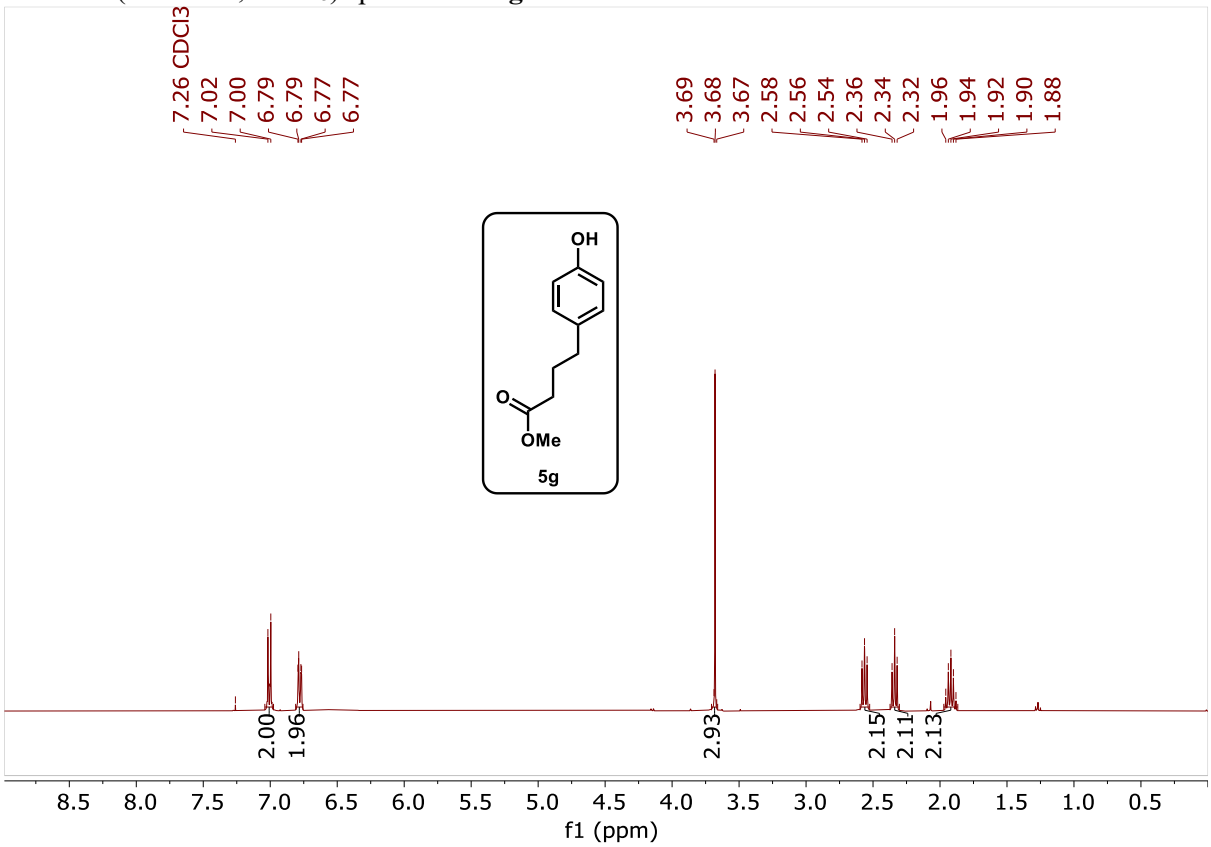
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **5f**



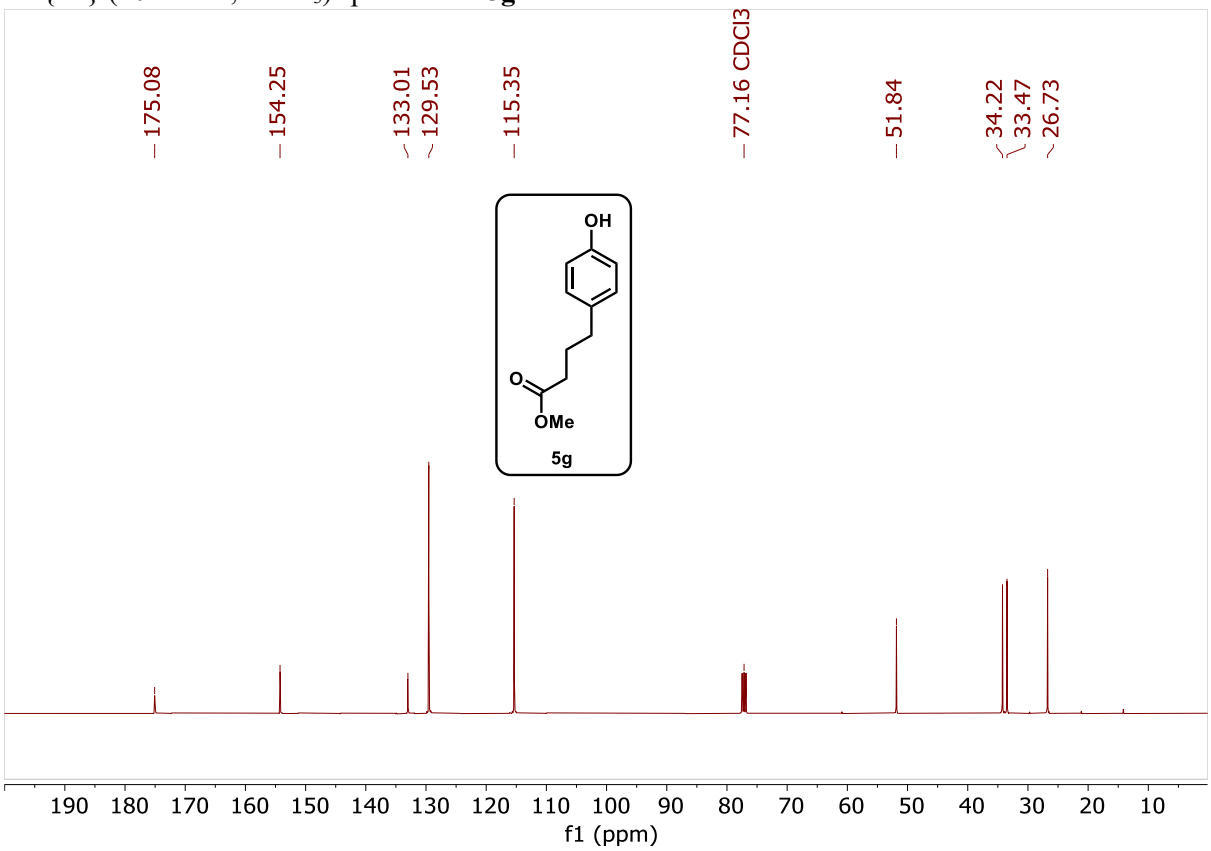
^{13}C{^{1}H} (101 MHz, $CDCl_3$) spectrum of **5f**



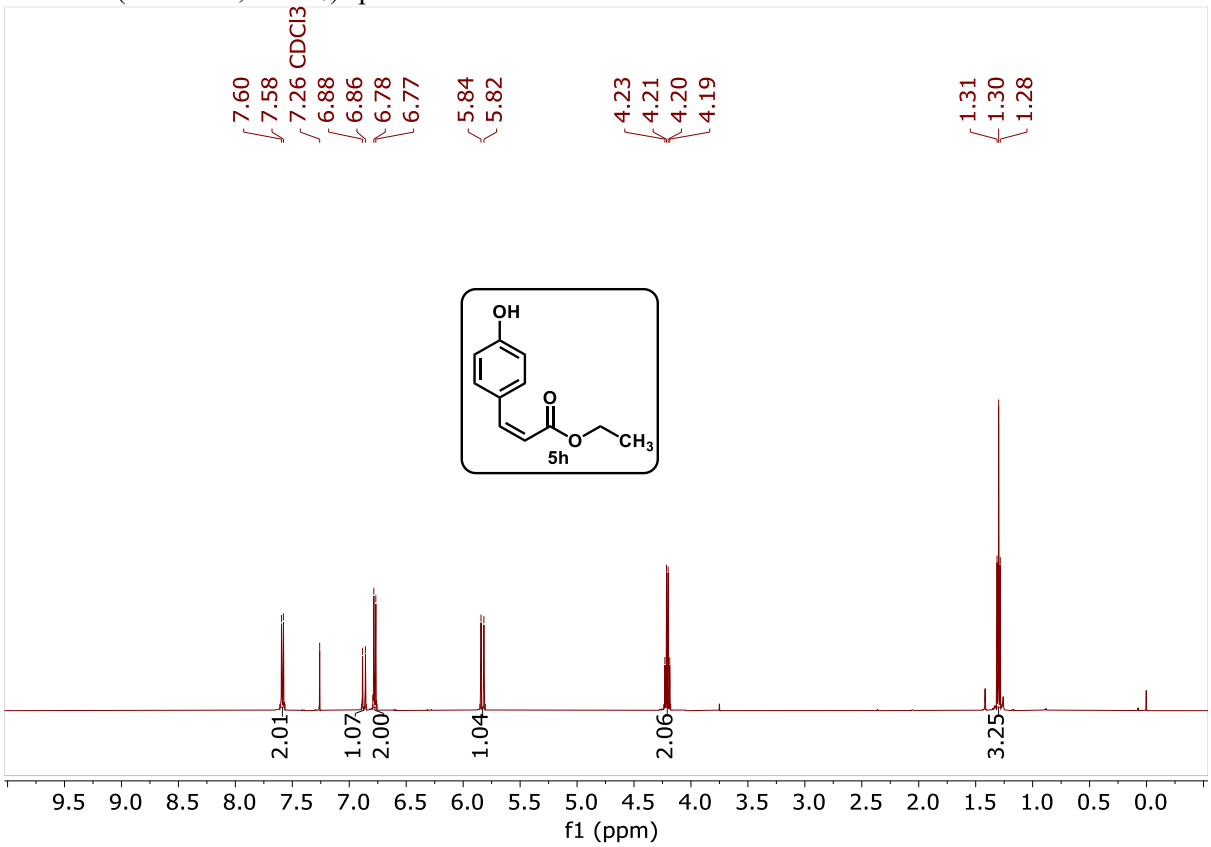
^{1}H NMR (396 MHz, $CDCl_3$) spectrum of **5g**



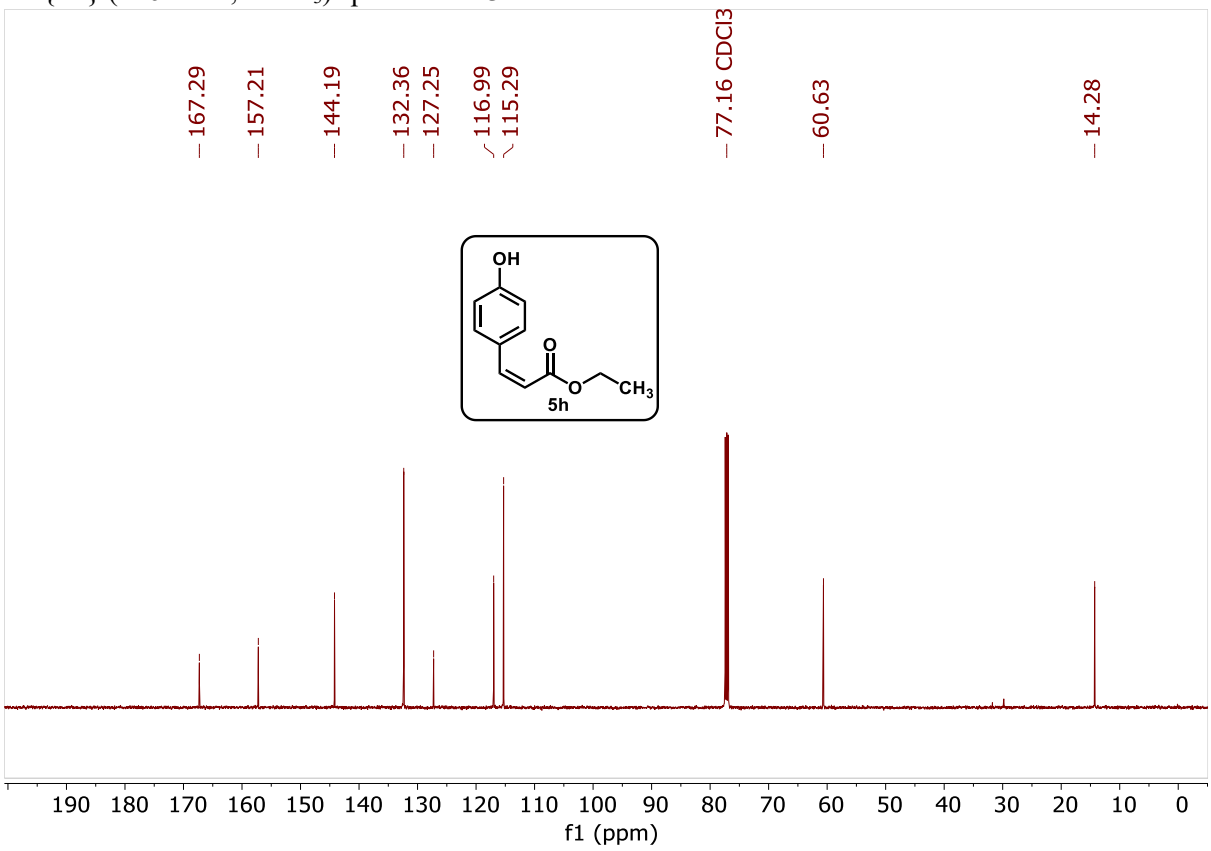
^{13}C{^{1}H} (101 MHz, $CDCl_3$) spectrum of **5g**



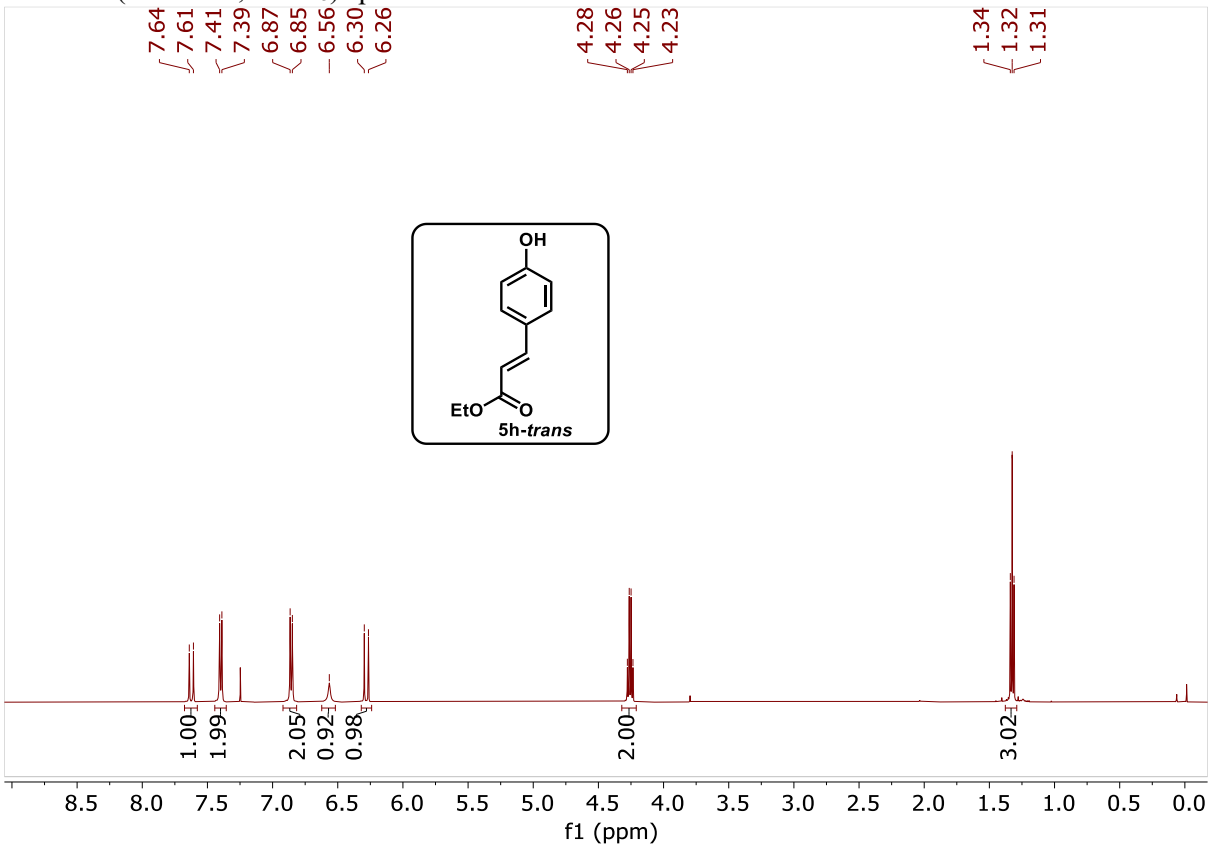
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **5h**



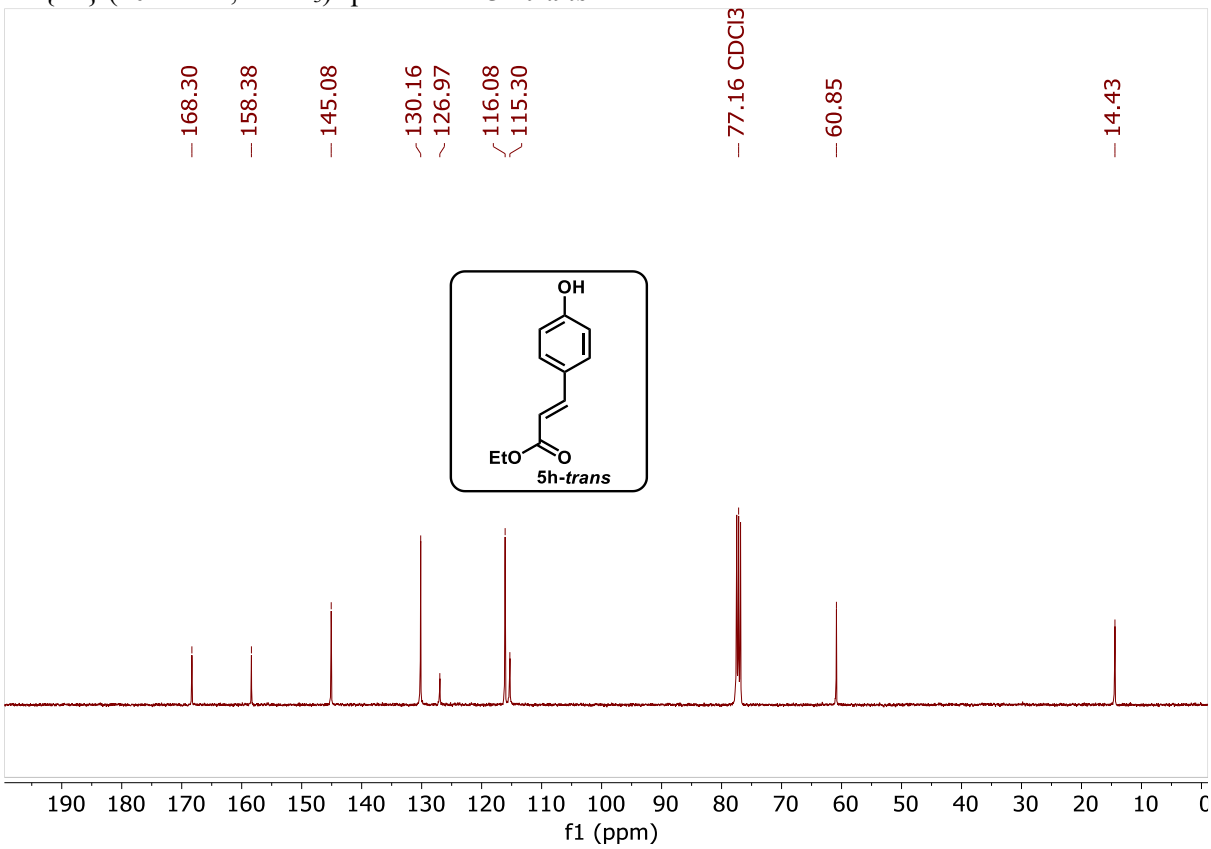
^{13}C{^{1}H} (126 MHz, $CDCl_3$) spectrum of **5h**



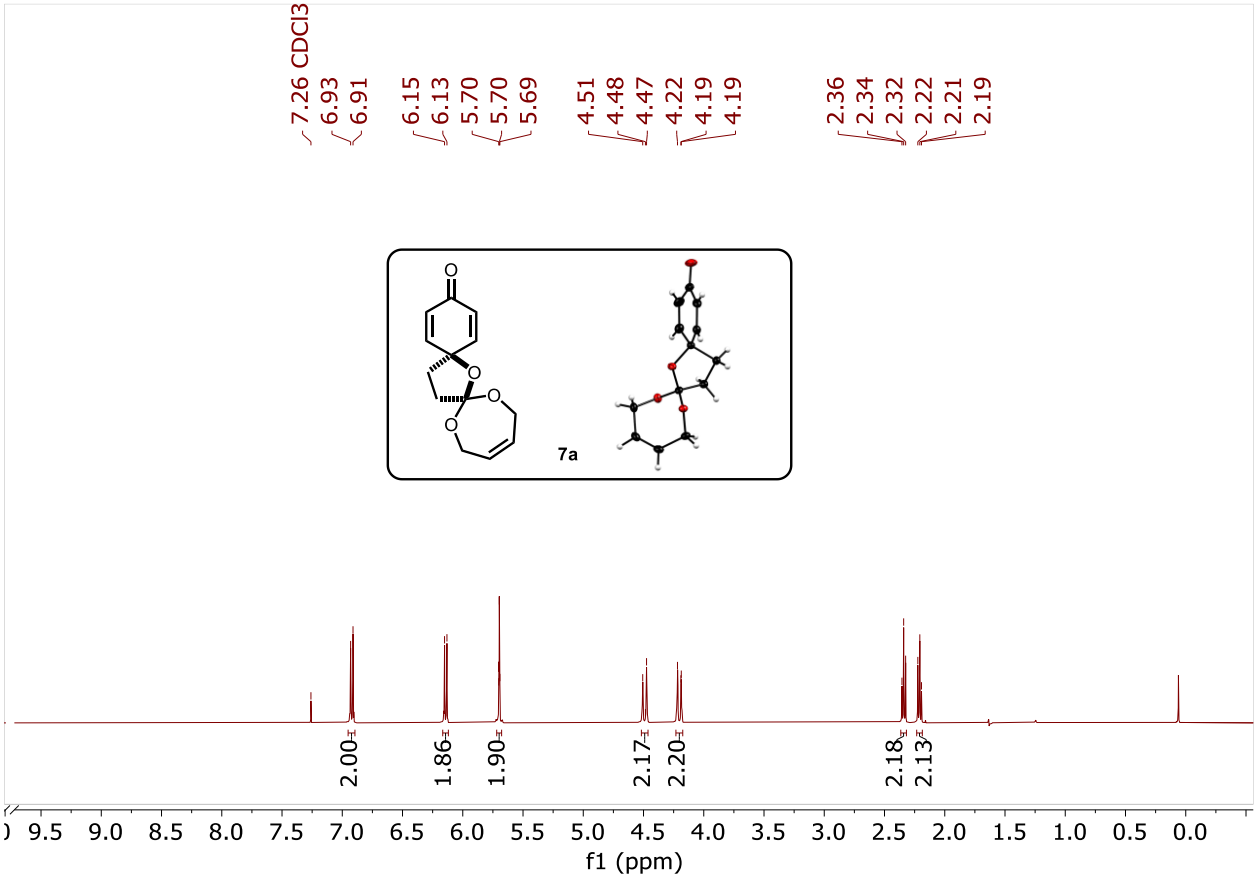
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **5h-*trans***



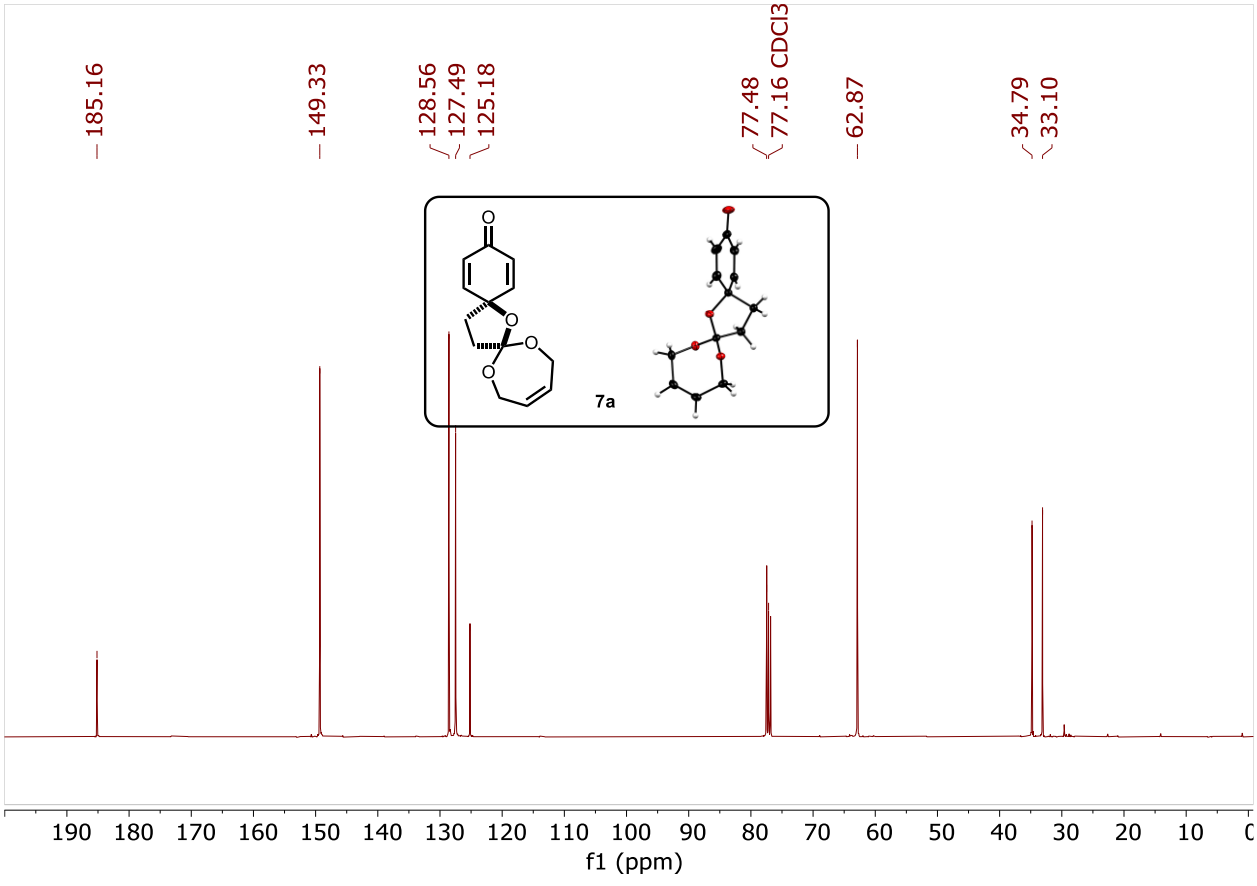
^{13}C{^{1}H} (101 MHz, $CDCl_3$) spectrum of **5h-*trans***



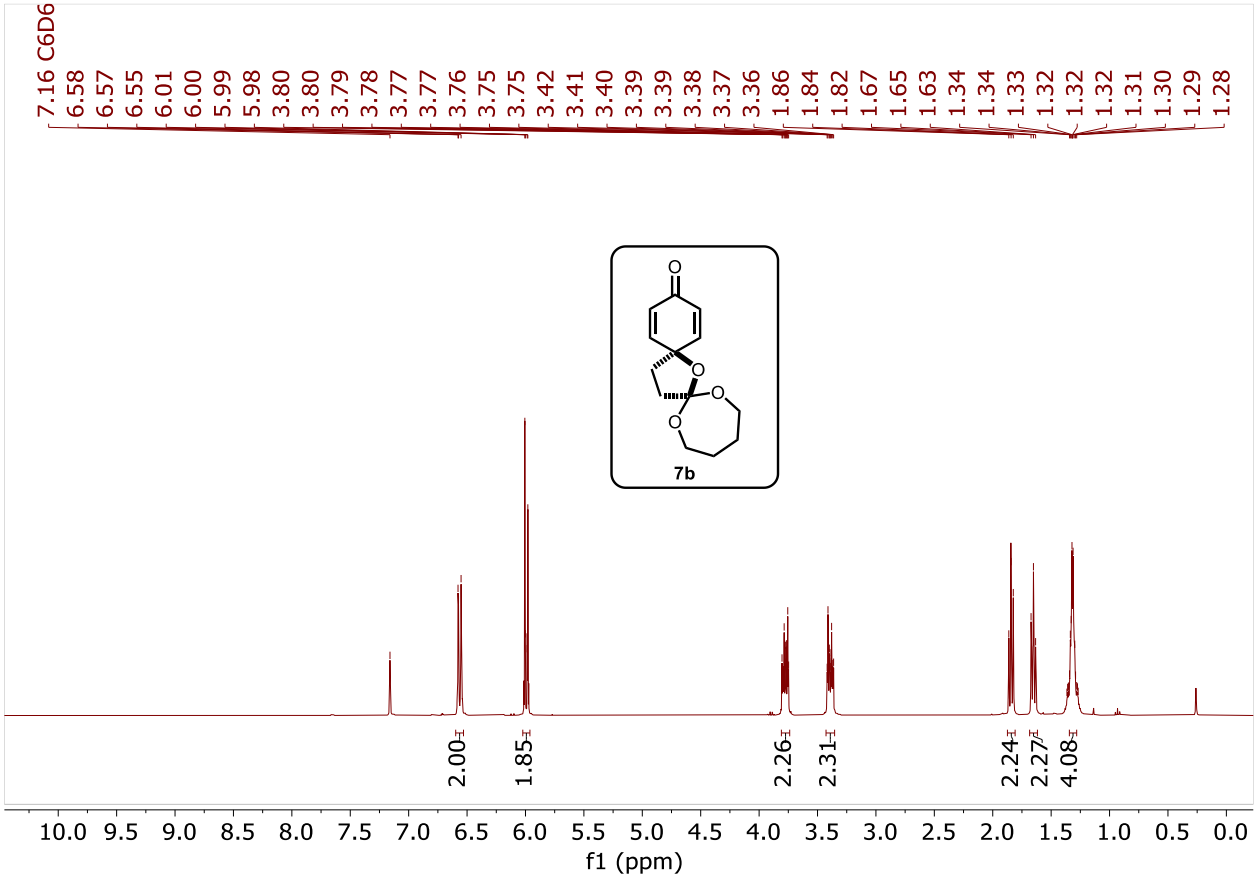
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **7a**



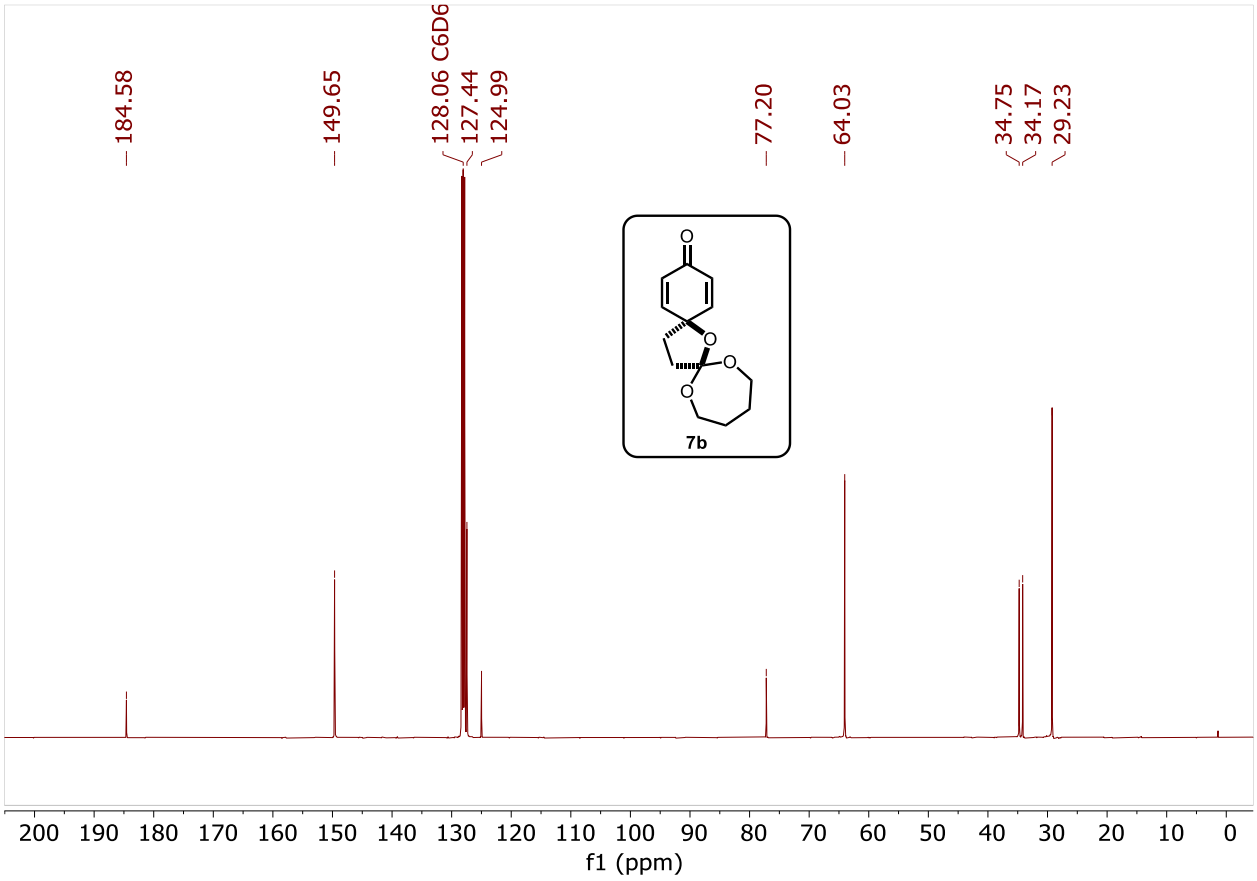
^{13}C{^{1}H} (101 MHz, $CDCl_3$) spectrum of **7a**



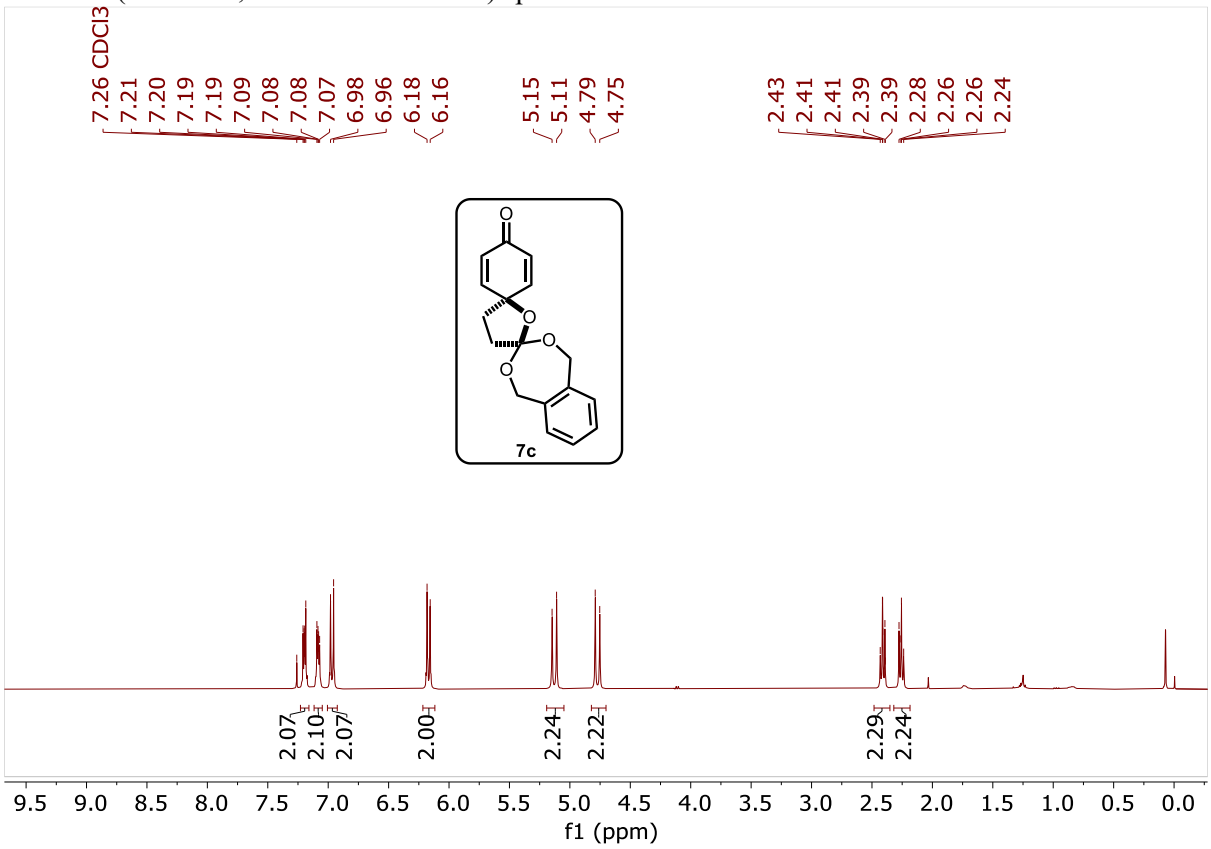
^{1}H NMR (396 MHz, BENZENE-D_6) spectrum of **7b**



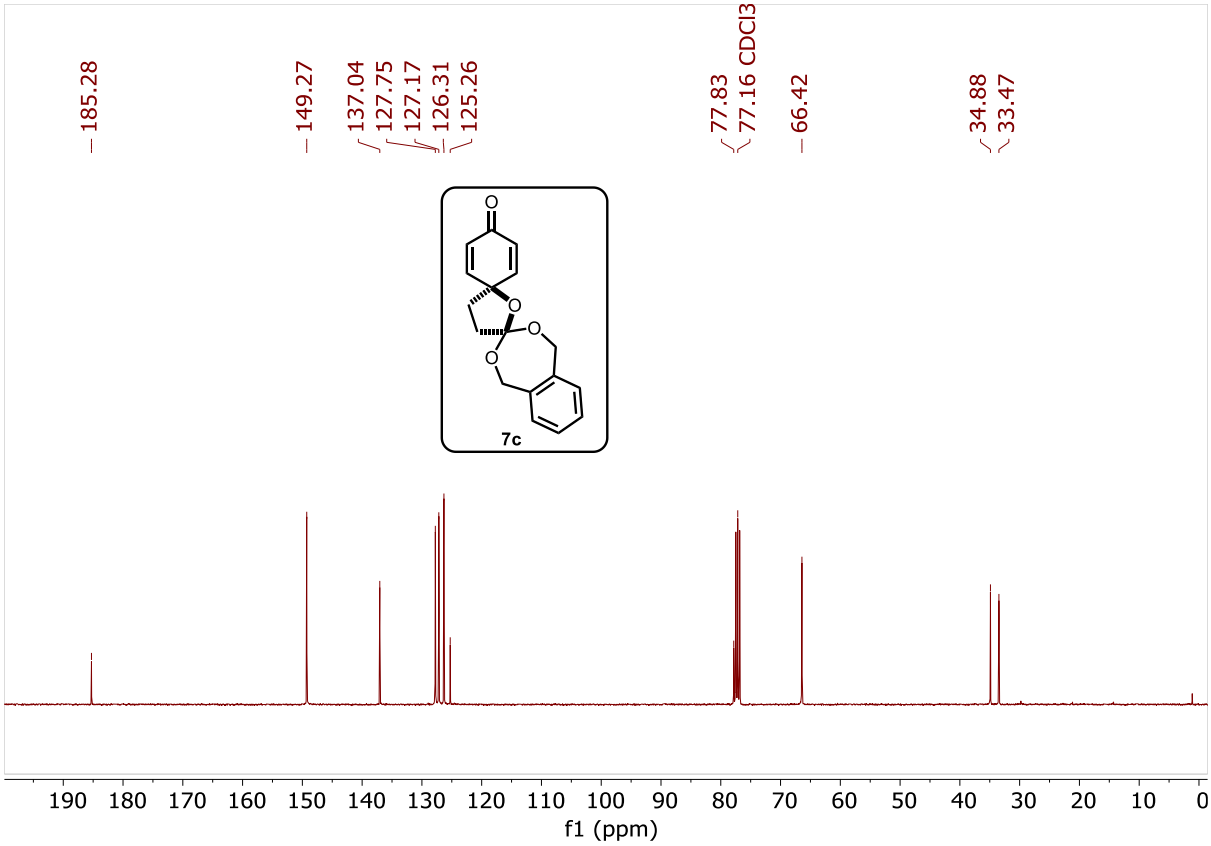
^{13}C{^{1}H} (100 MHz, BENZENE-D6) spectrum of **7b**



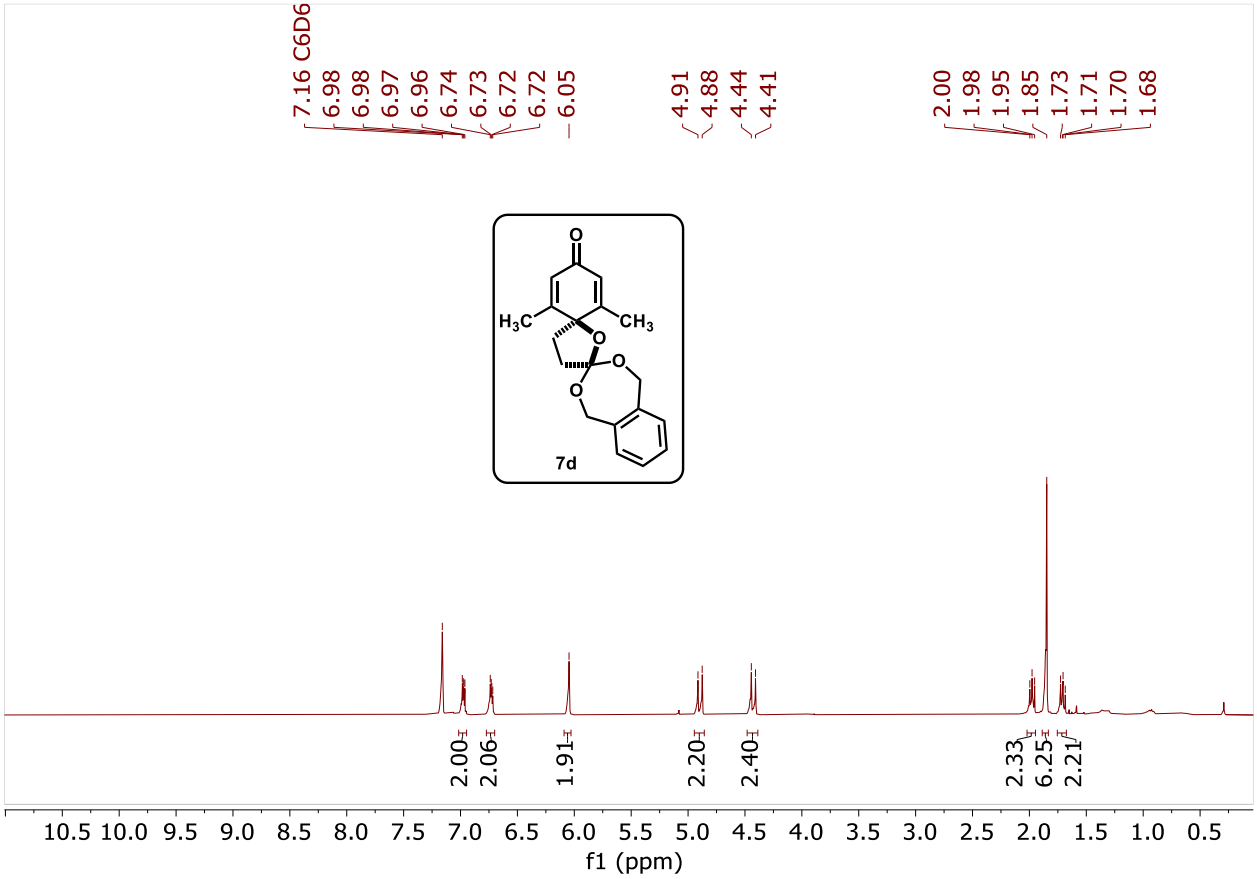
^{1}H NMR (396 MHz, CHLOROFORM-D) spectrum of **7c**



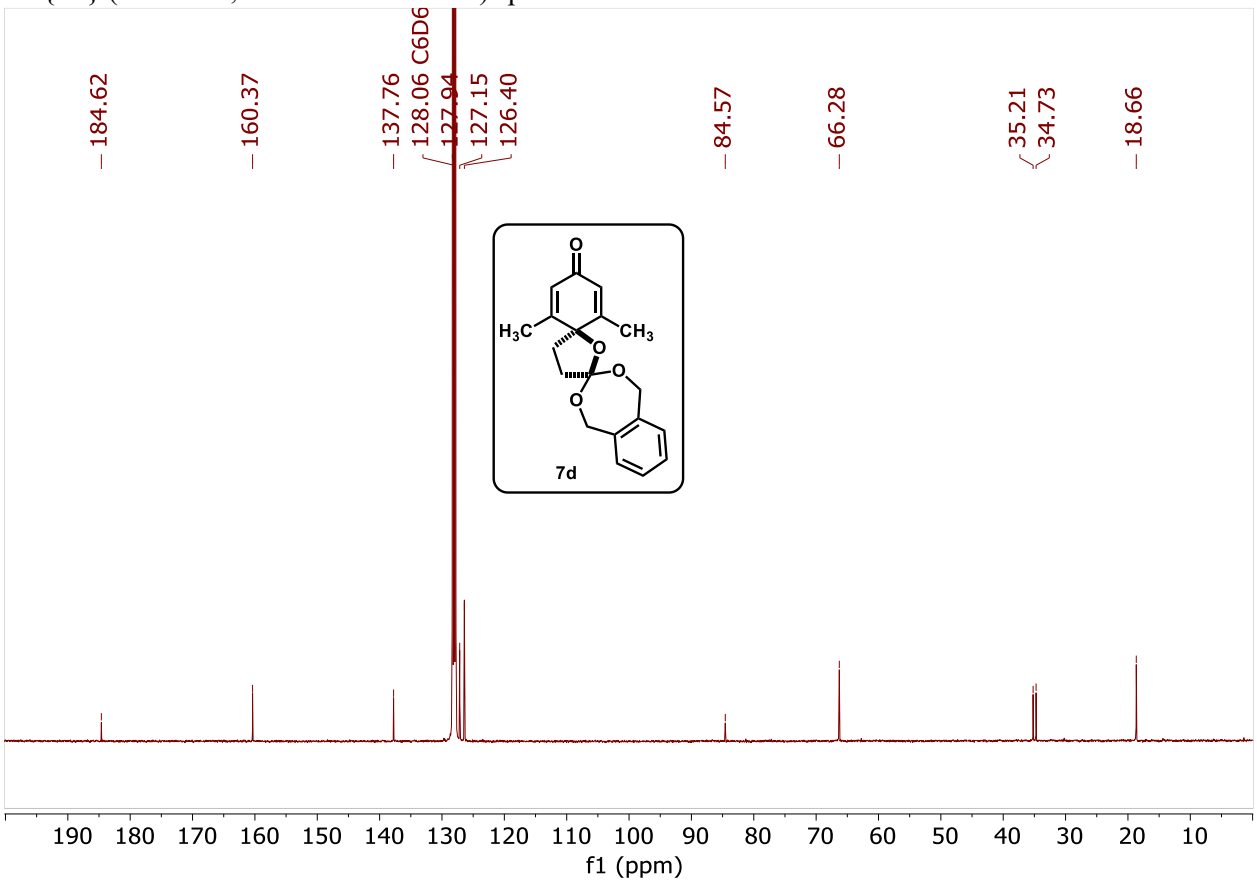
^{13}C{^{1}H} (100 MHz, CHLOROFORM-D) spectrum of **7c**



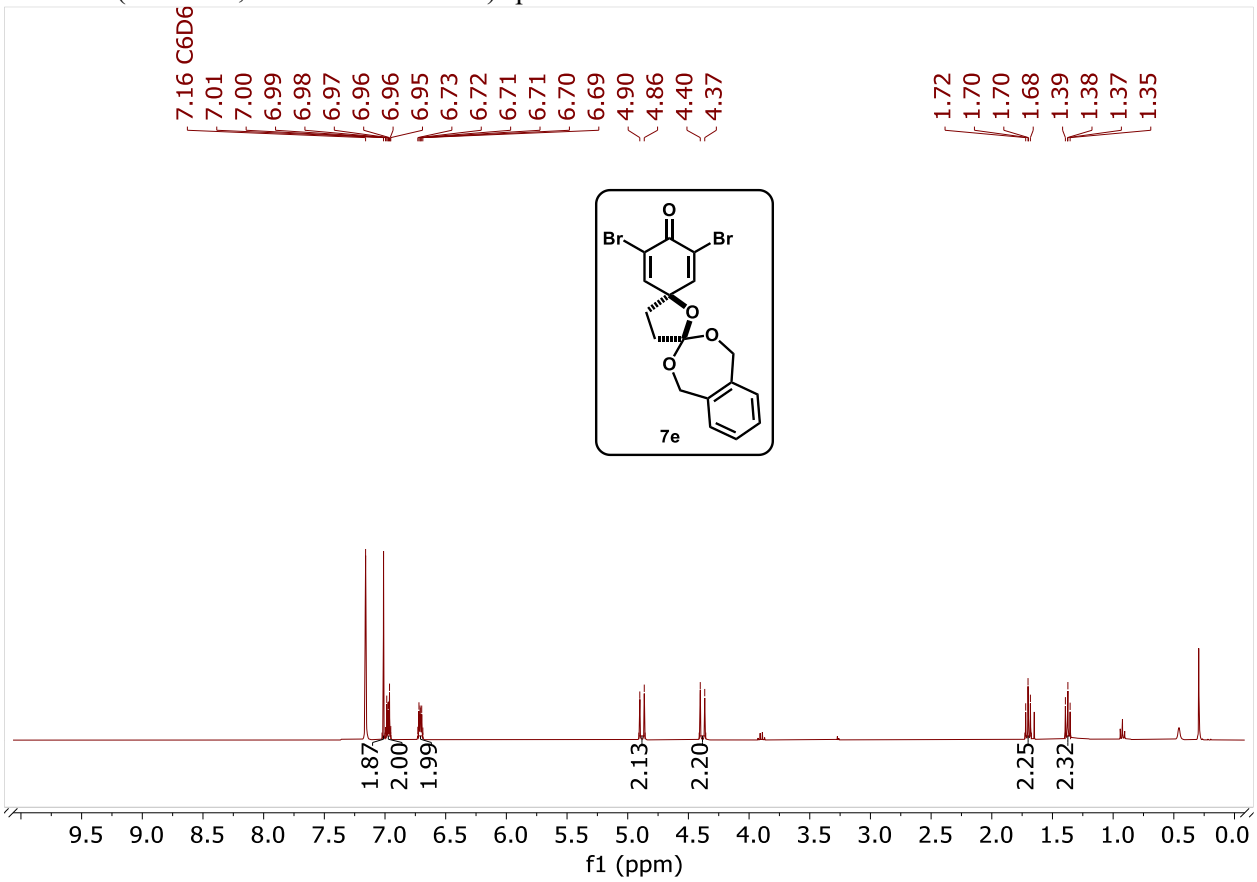
^{1}H NMR (396 MHz, CHLOROFORM-D) spectrum of **7d**



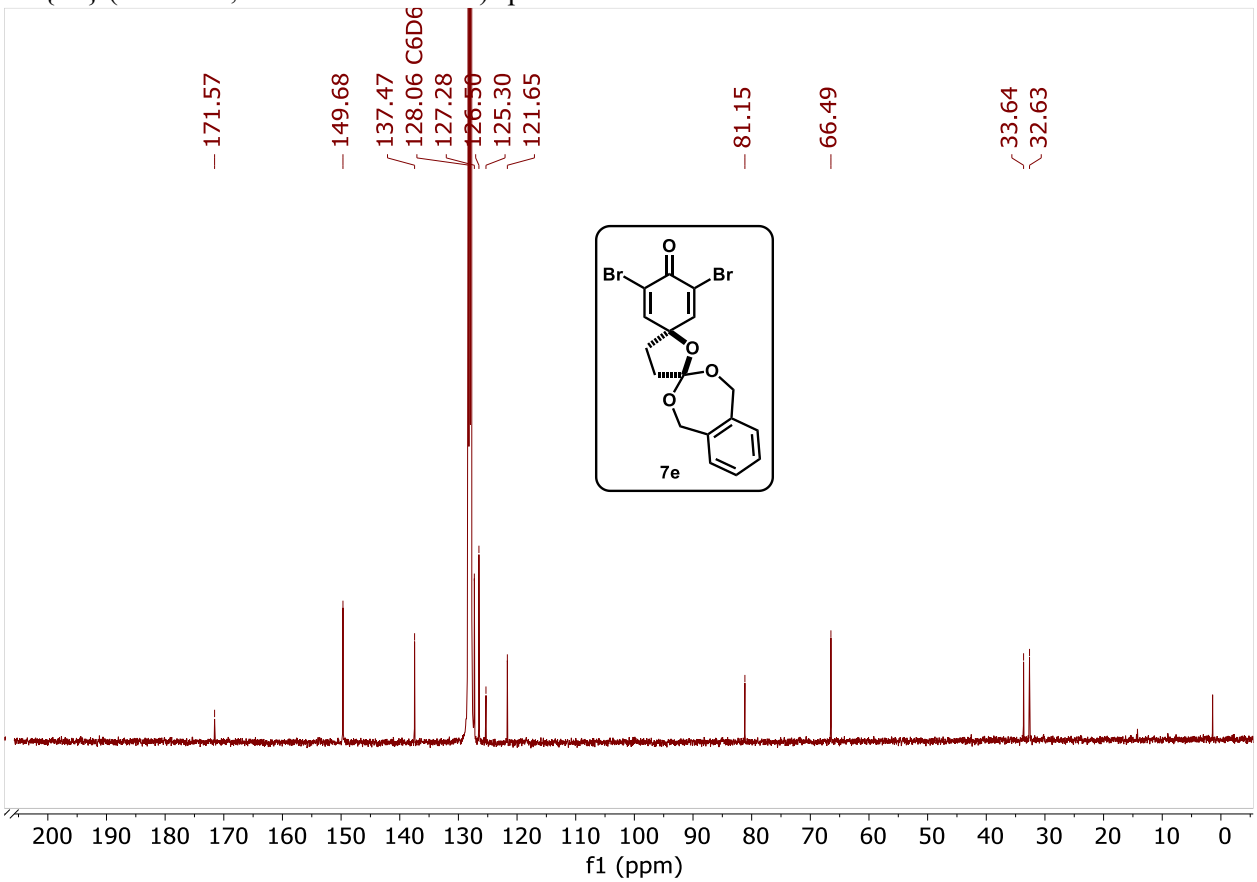
^{13}C{^{1}H} (100 MHz, CHLOROFORM-D) spectrum of **7d**



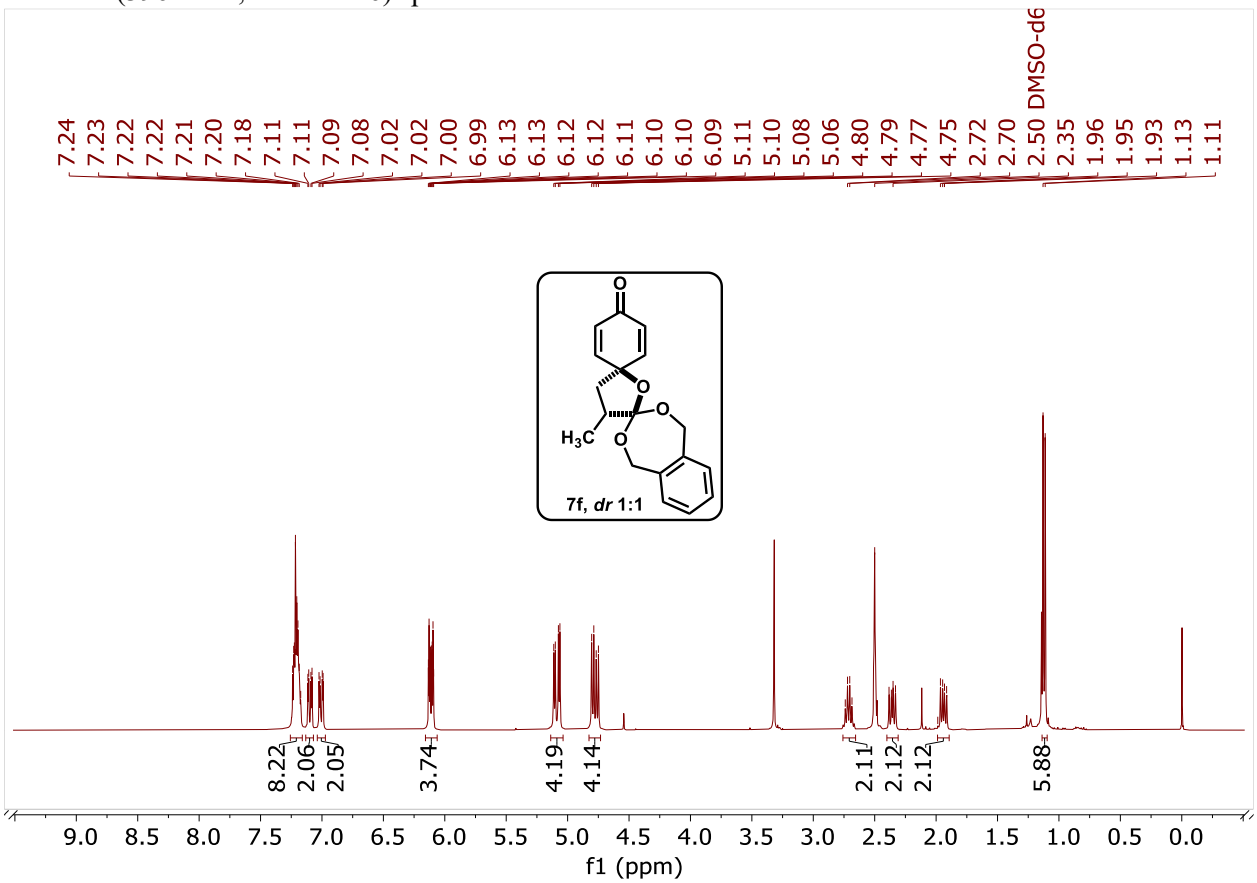
^{1}H NMR (396 MHz, CHLOROFORM-D) spectrum of **7e**



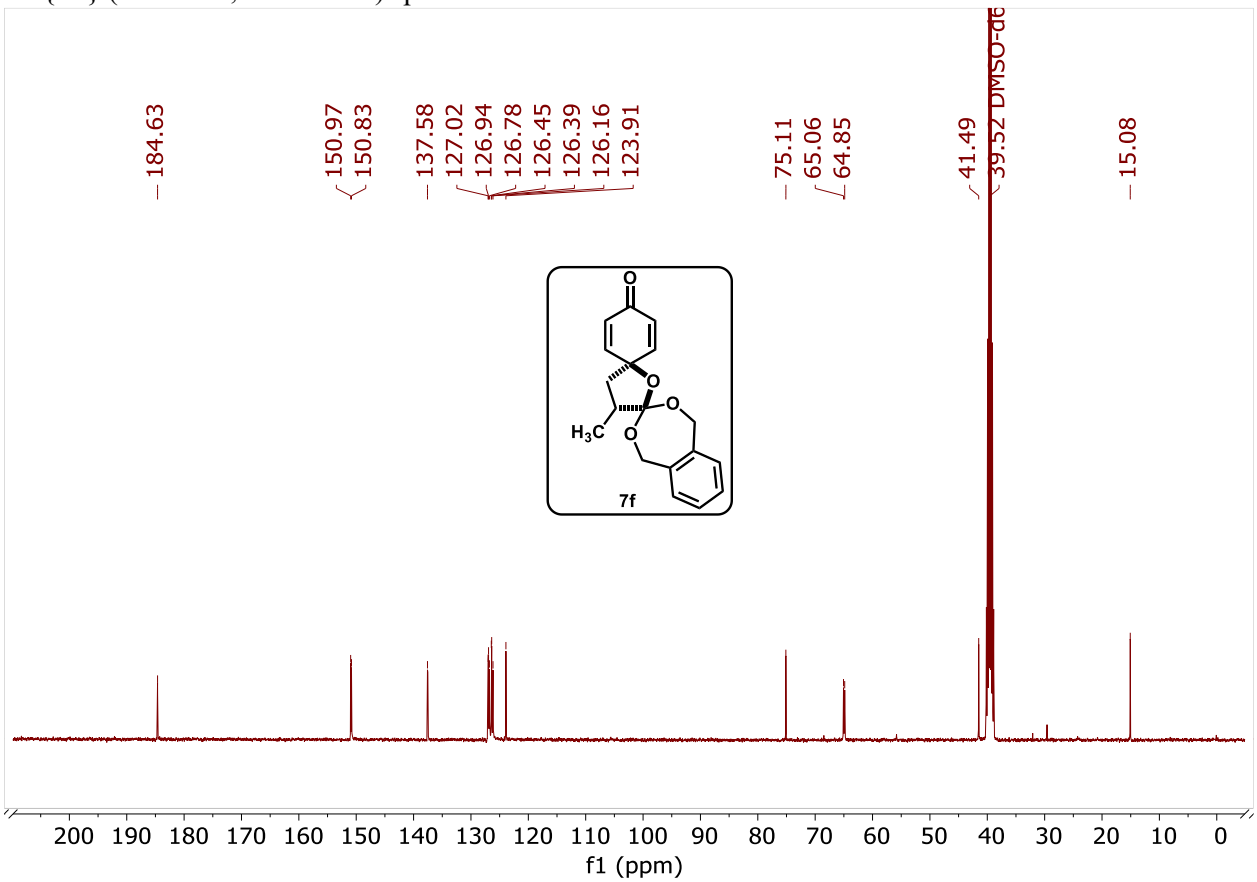
^{13}C{^{1}H} (100 MHz, CHLOROFORM-D) spectrum of **7e**



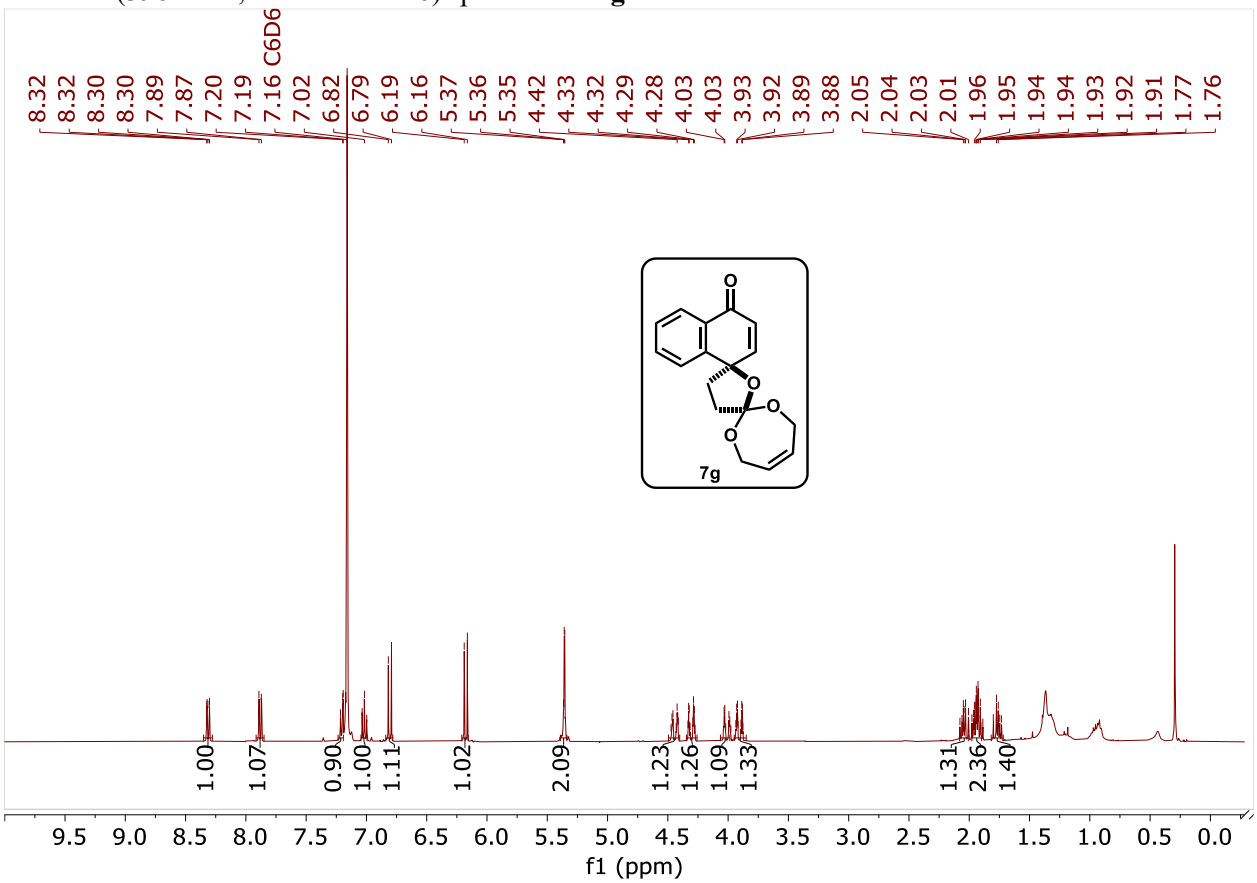
^{1}H NMR (396 MHz, DMSO-D6) spectrum of **7f**



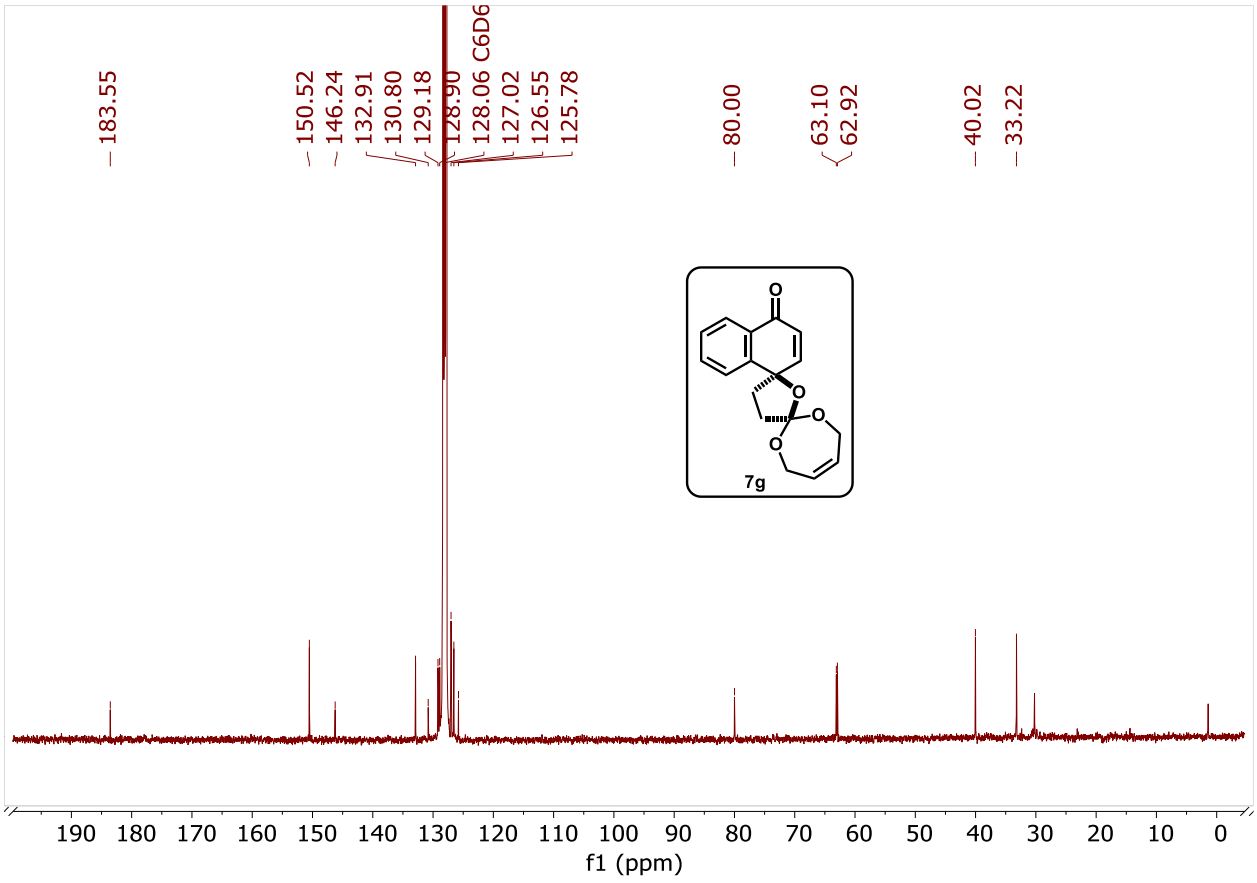
^{13}C{^{1}H} (100 MHz, DMSO-D6) spectrum of **7f**



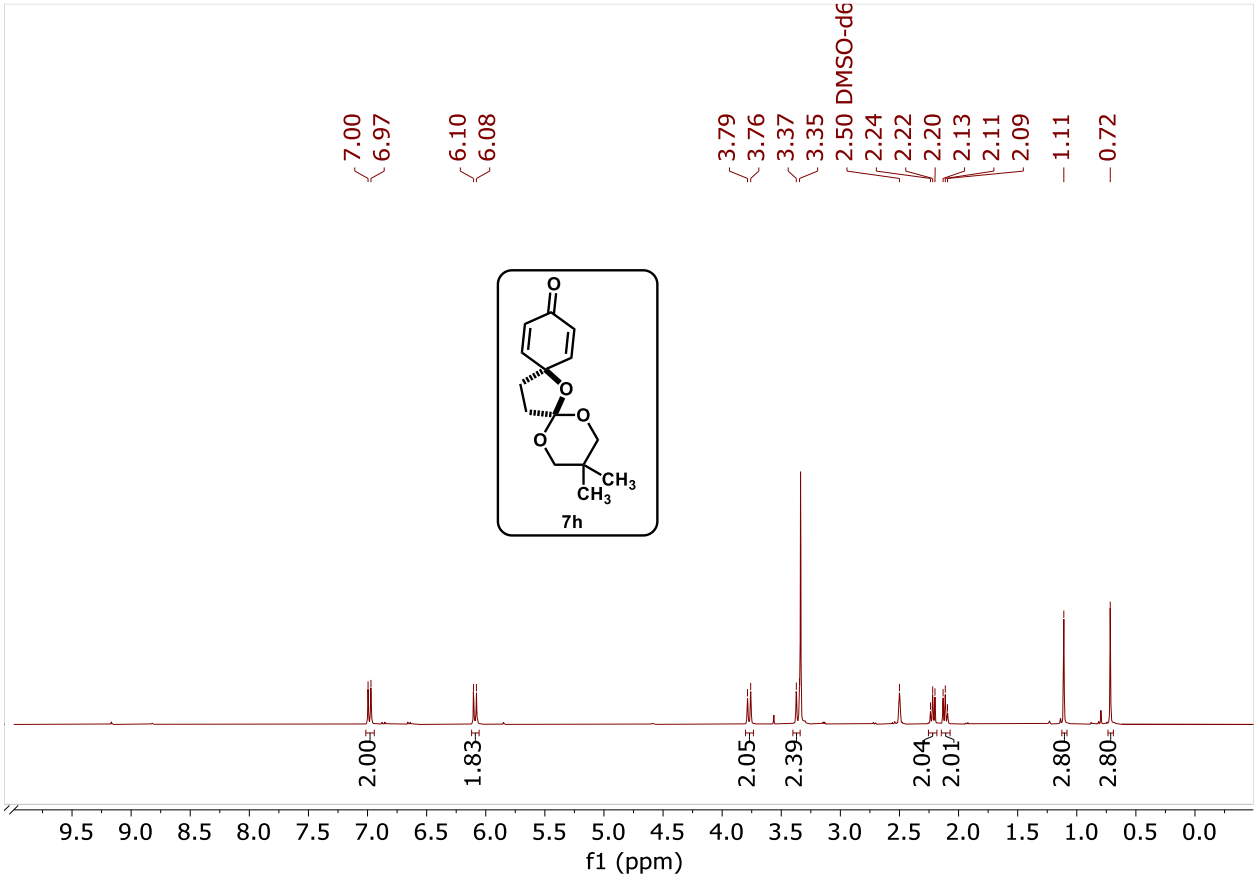
^{1}H NMR (396 MHz, BENZENE-D6) spectrum of **7g**



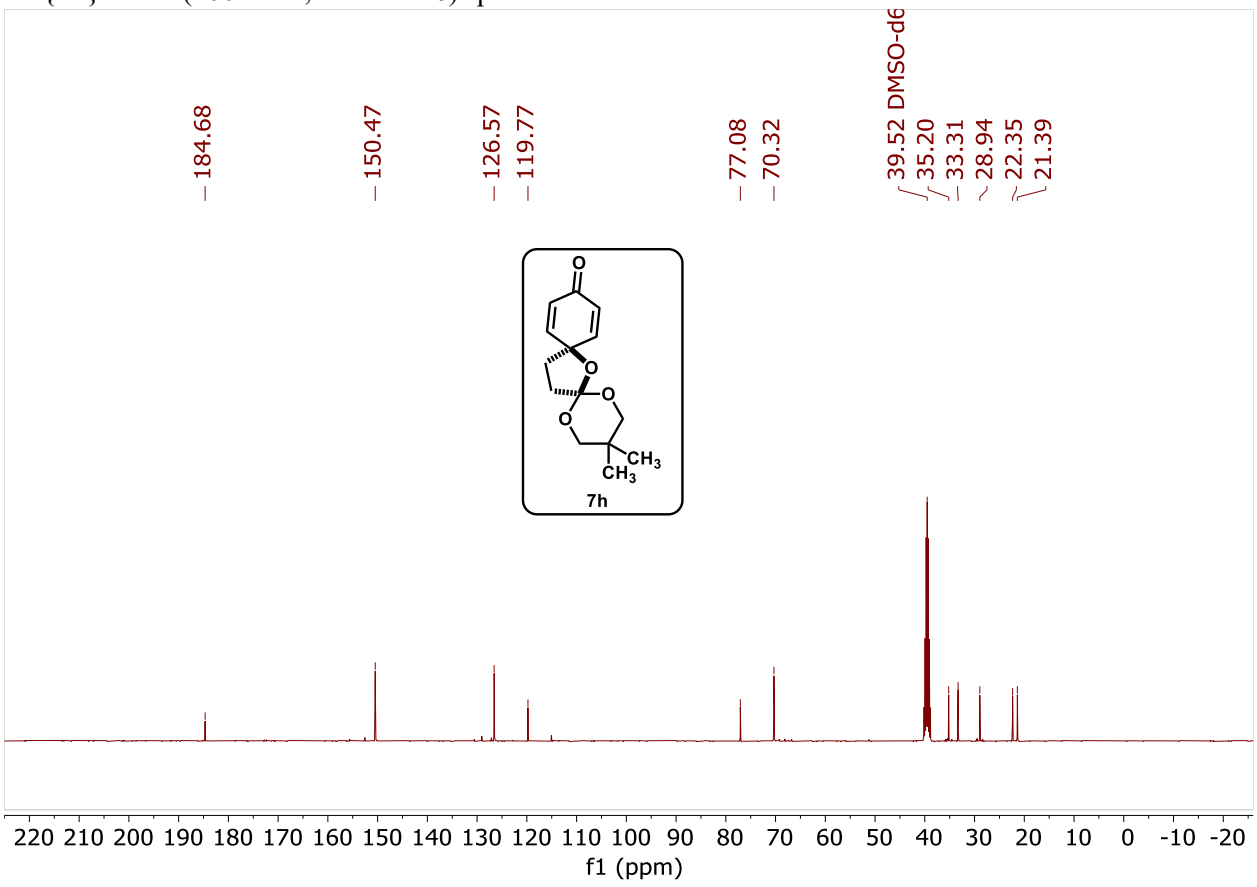
^{13}C{^{1}H} (100 MHz, BENZENE-D6) spectrum of **7g**



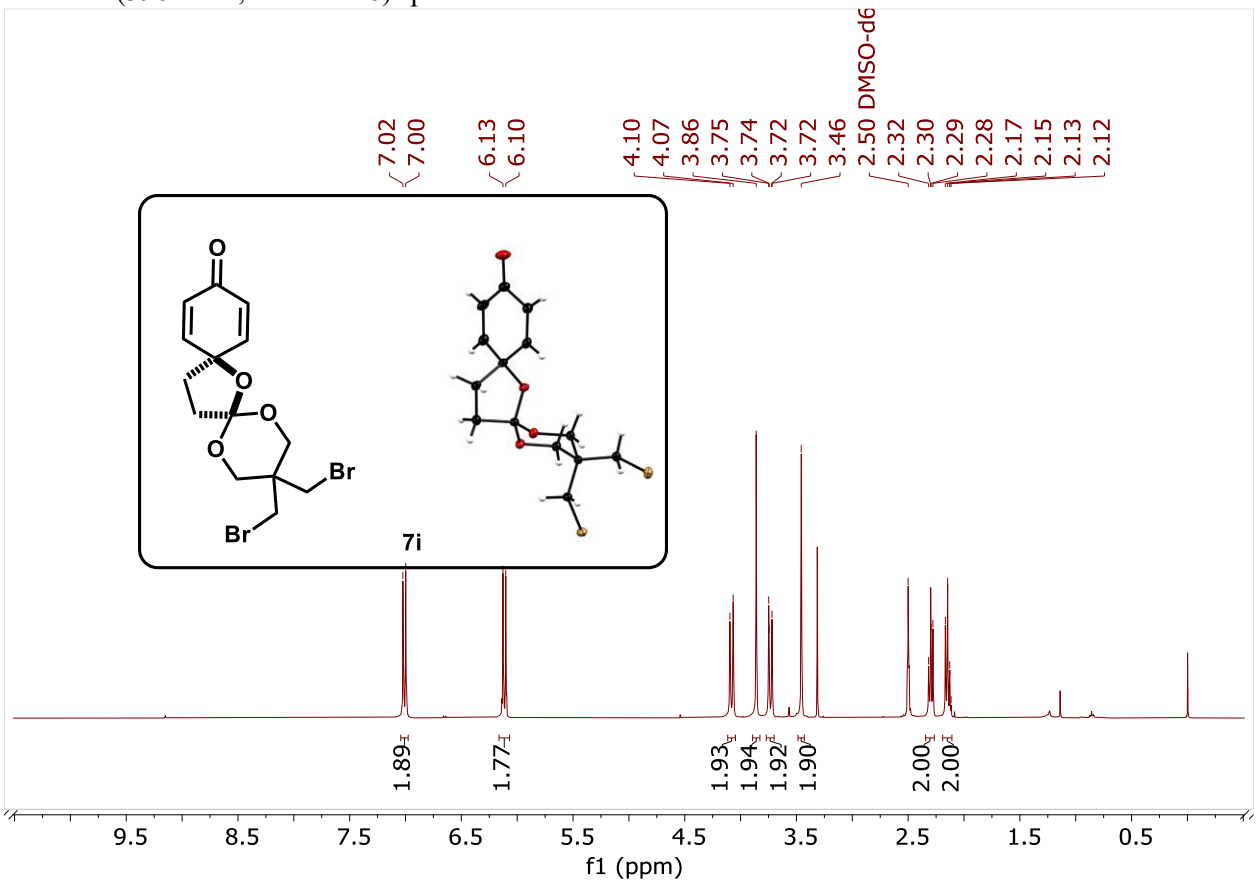
^{1}H NMR (400 MHz, DMSO-D6) spectrum of **7h**



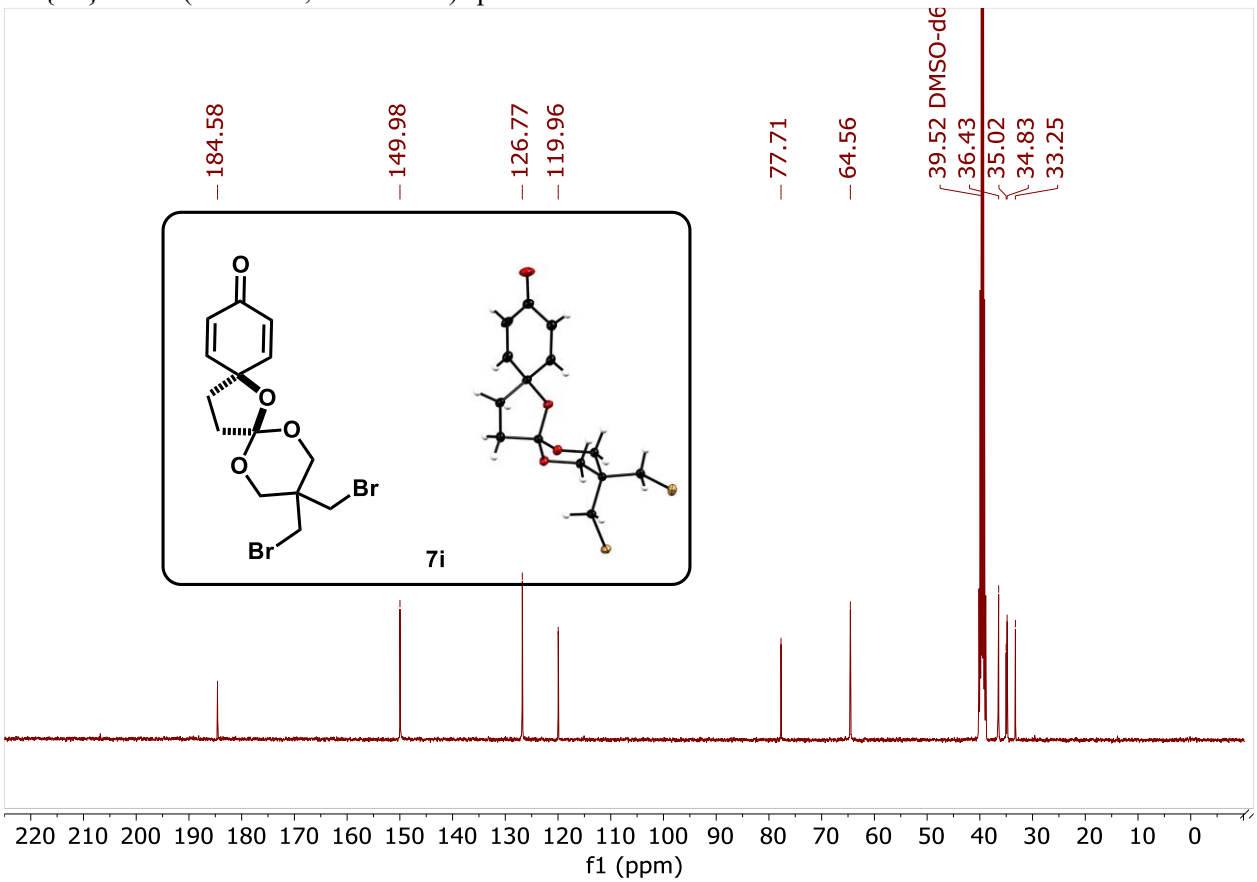
^{13}C{^{1}H} NMR (100 MHz, DMSO-D6) spectrum of **7h**



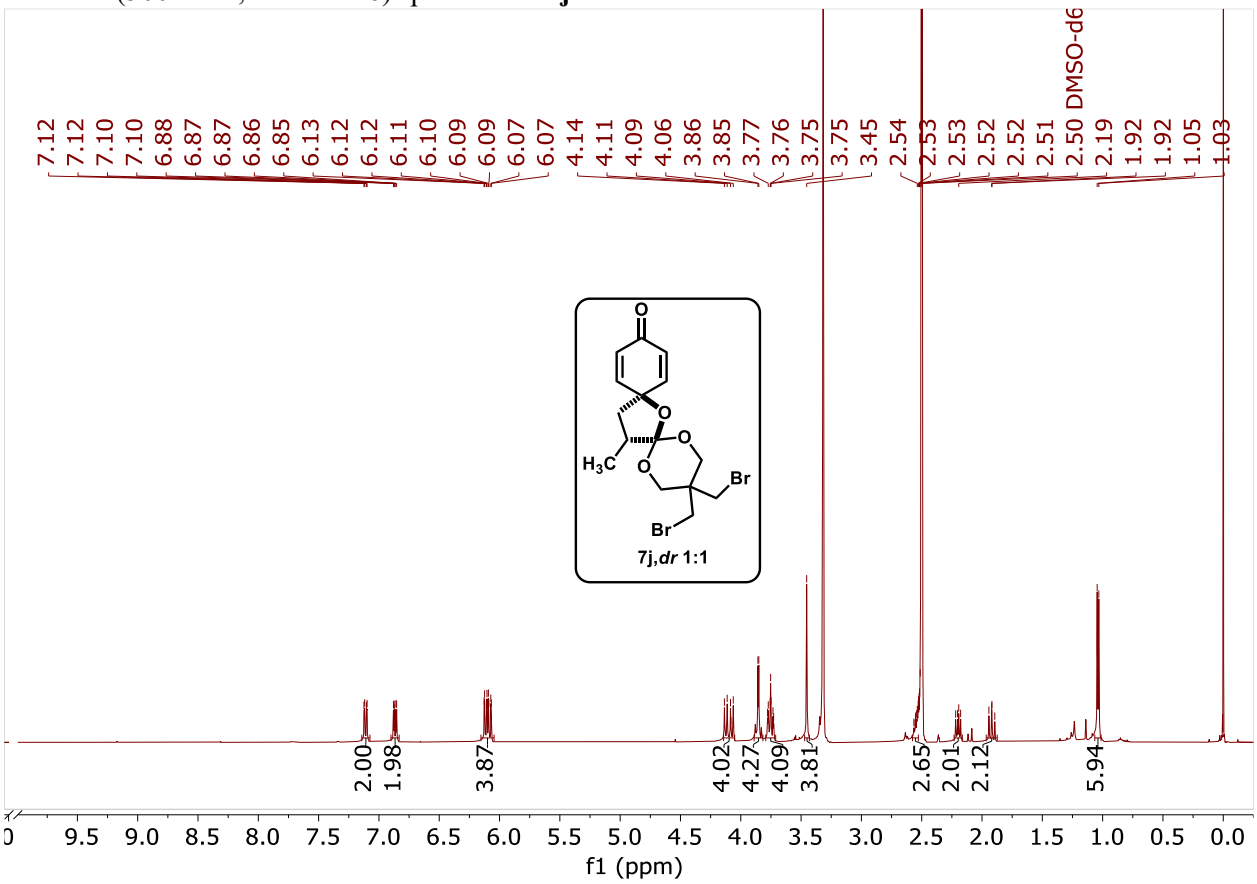
^{1}H NMR (396 MHz, DMSO-D6) spectrum of **7i**



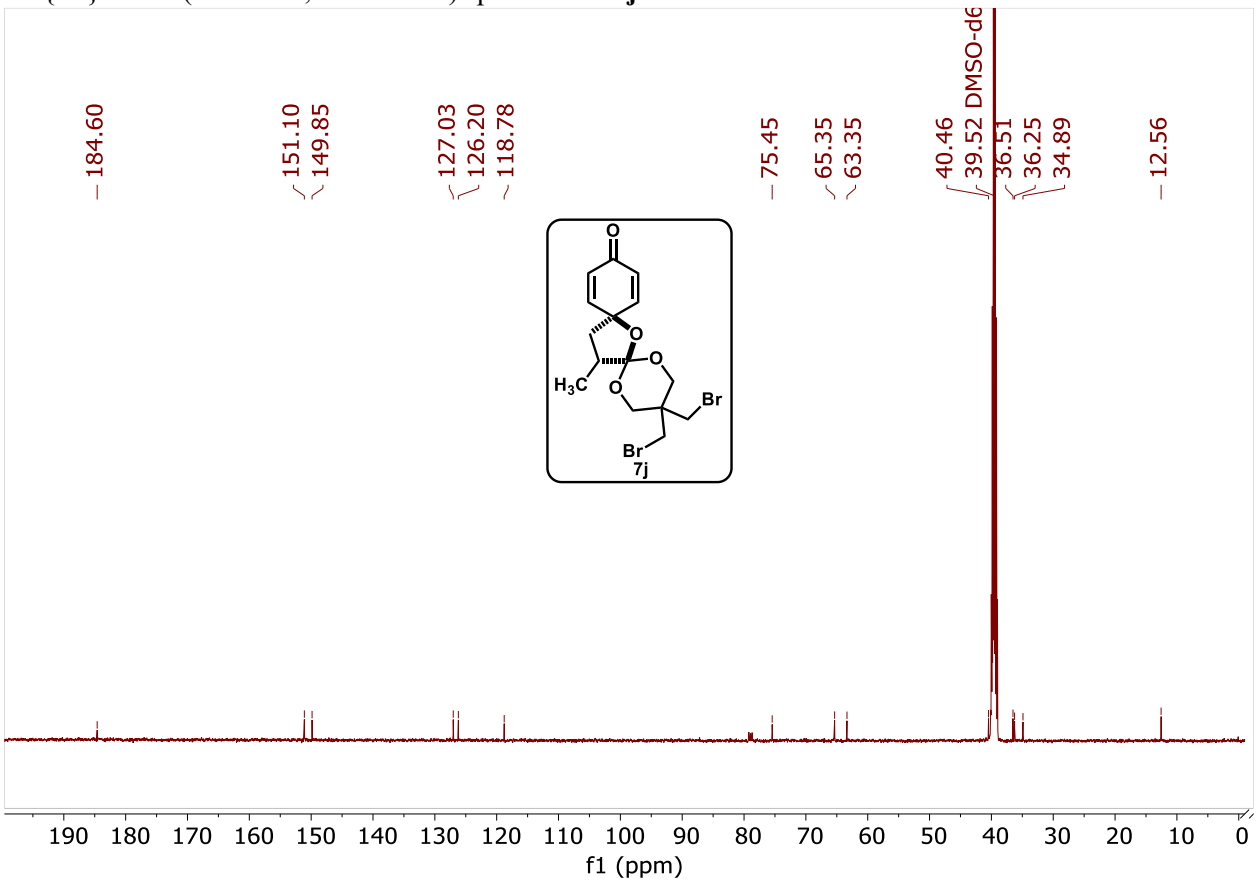
^{13}C{^{1}H} NMR (100 MHz, DMSO-D6) spectrum of **7i**



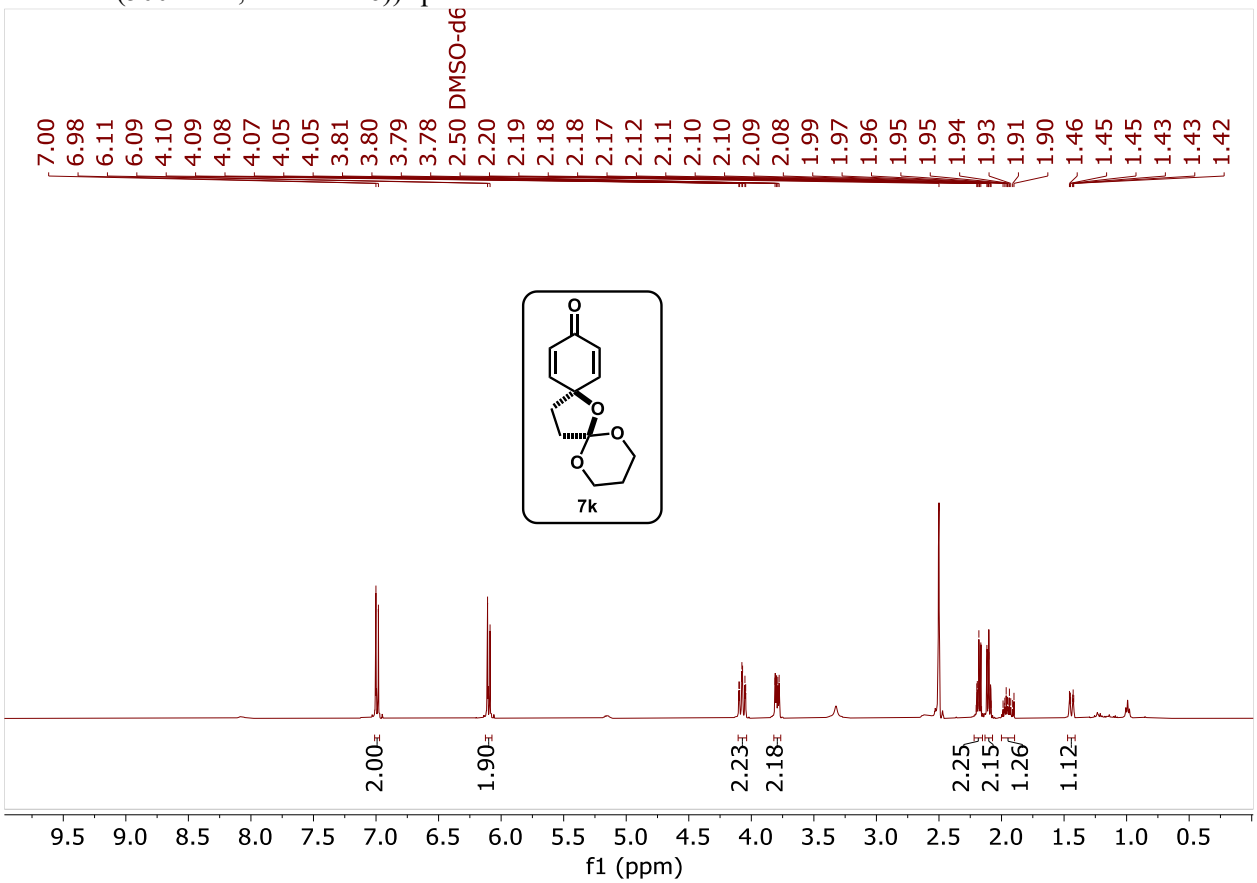
^{1}H NMR (500 MHz, DMSO-D6) spectrum of **7j**



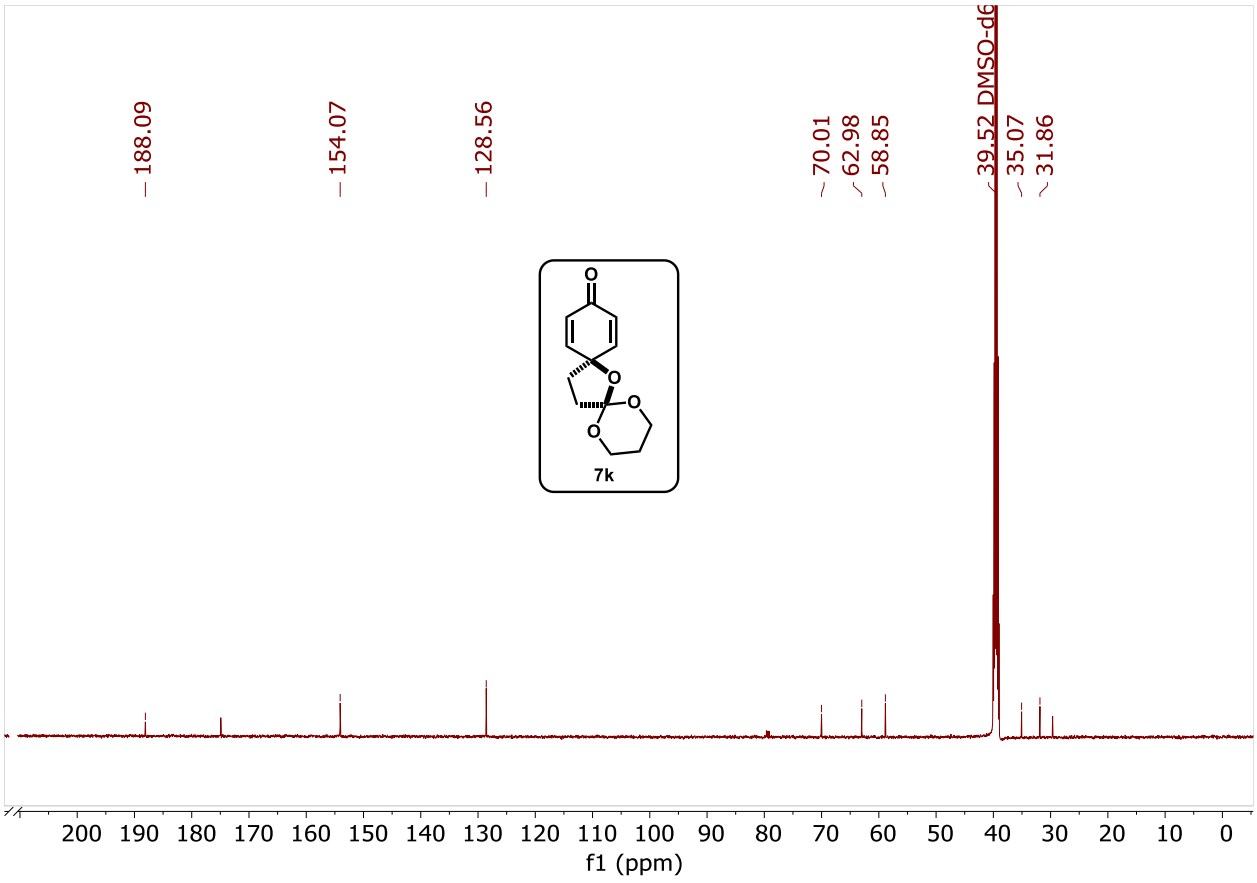
^{13}C{^{1}H} NMR (126 MHz, DMSO-D6) spectrum of **7j**



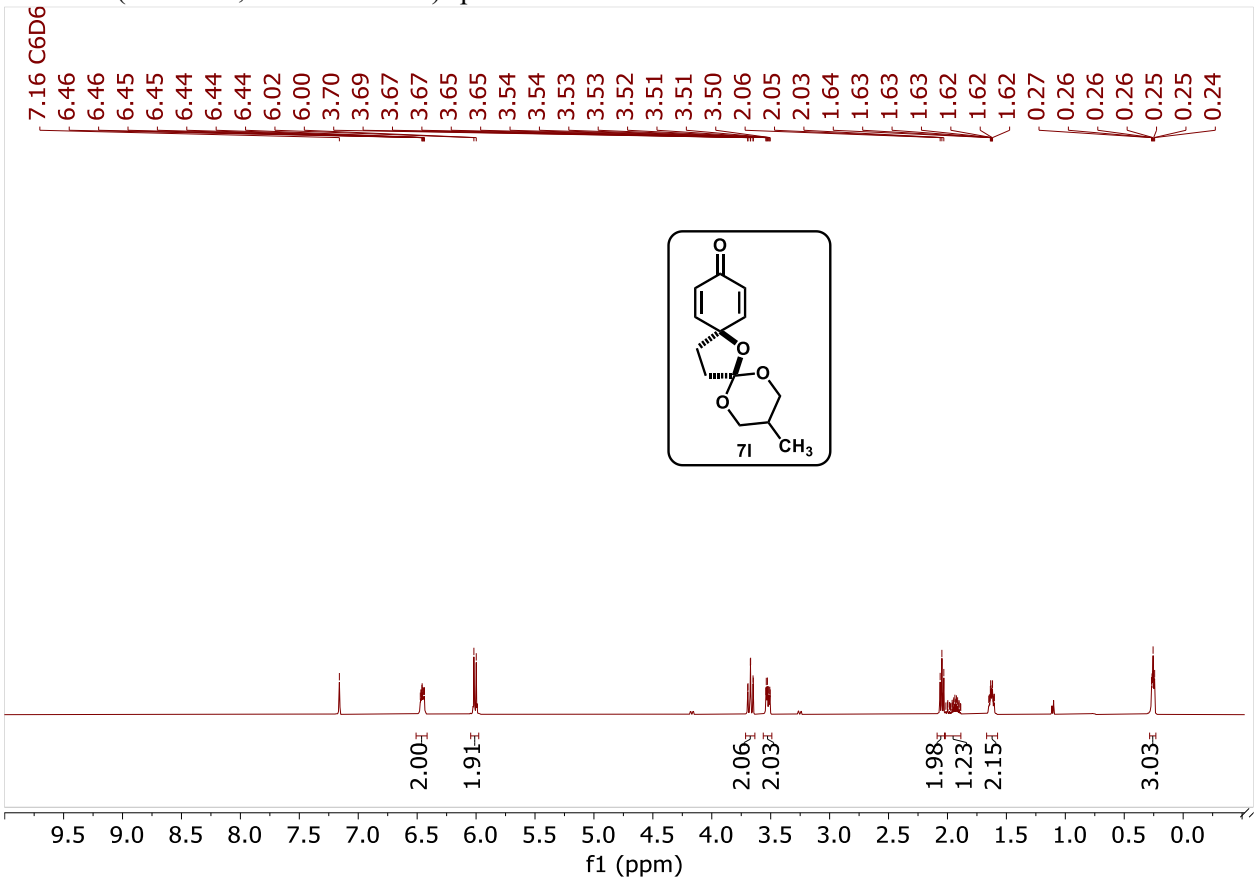
^{1}H NMR (500 MHz, DMSO-D6)) spectrum of **7k**



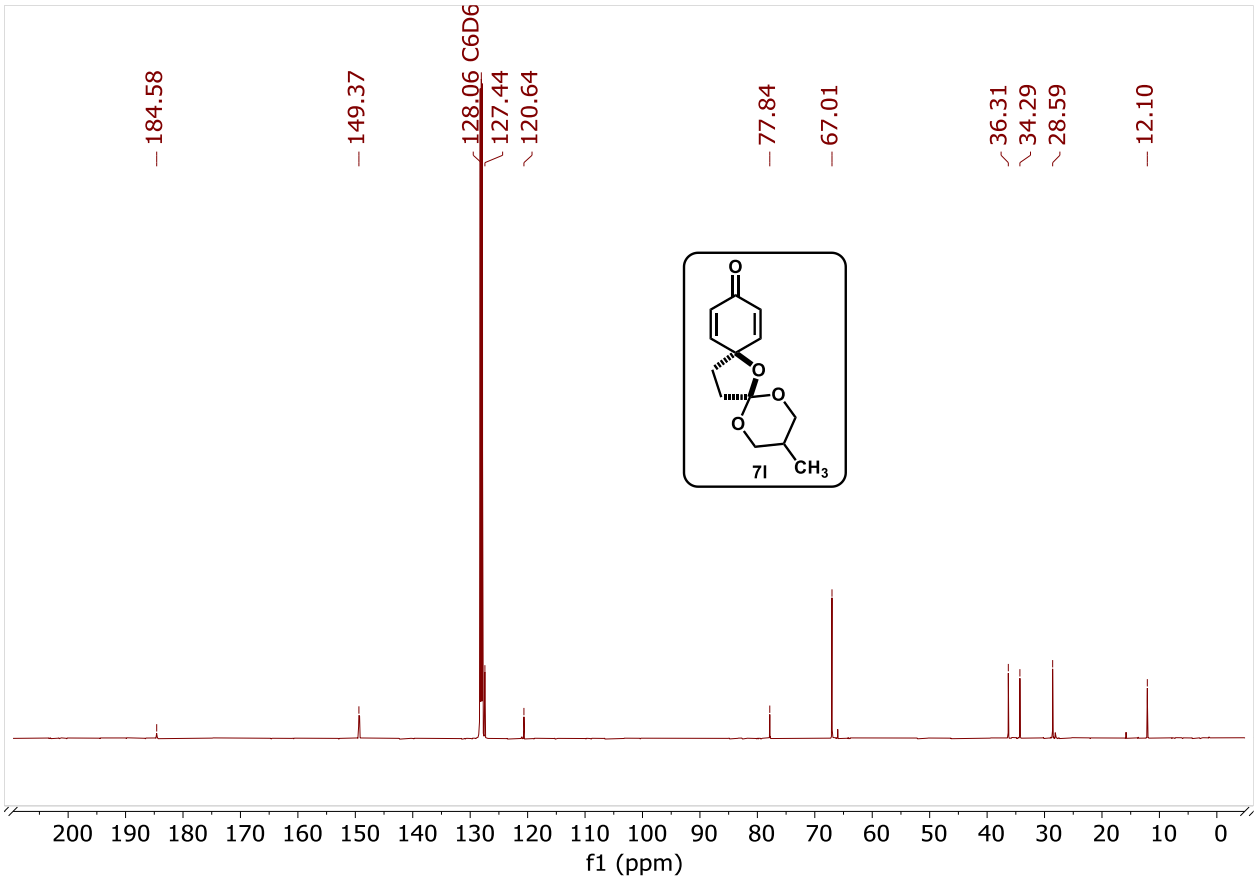
^{13}C{^{1}H} (126 MHz, DMSO-D6) spectrum of **7k**



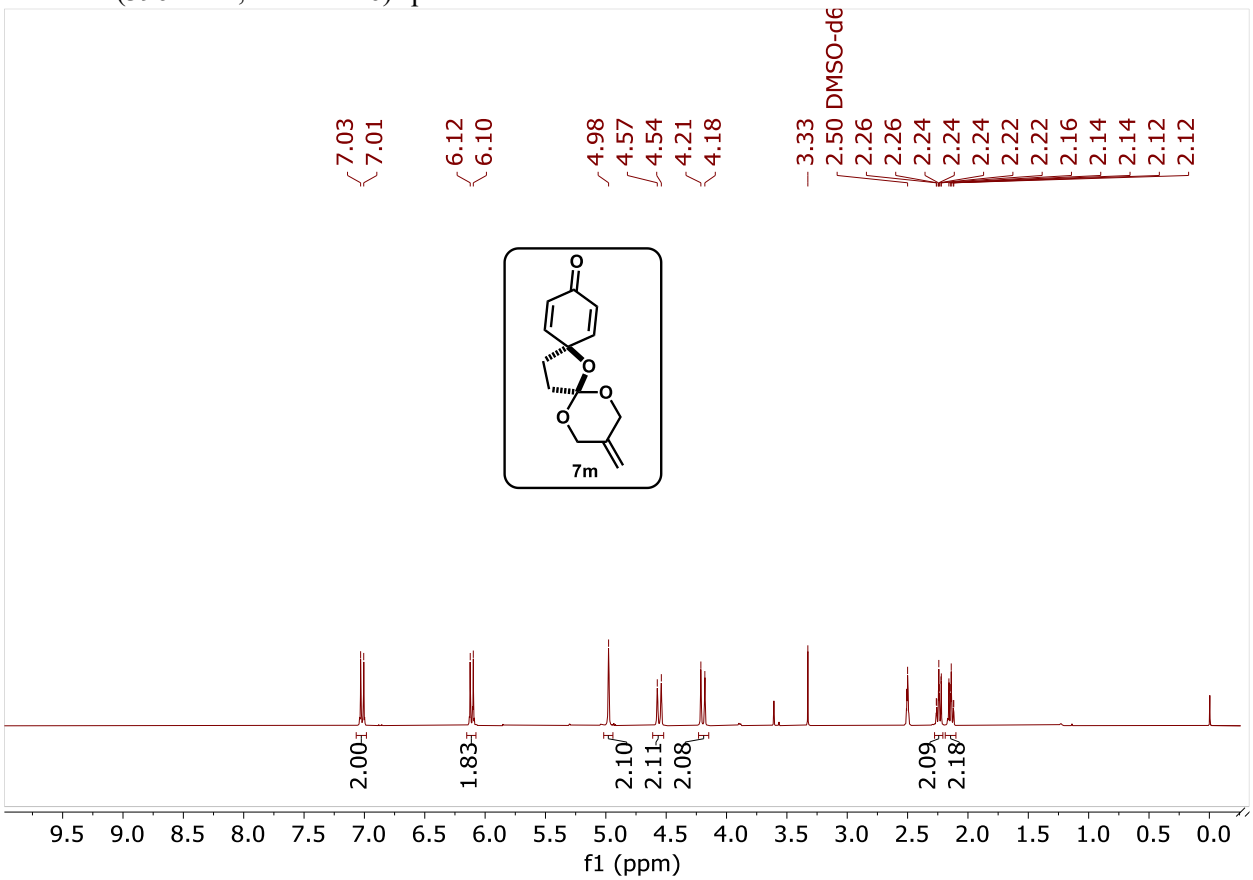
^{1}H NMR (500 MHz, BENZENE-D6) spectrum of **7l**



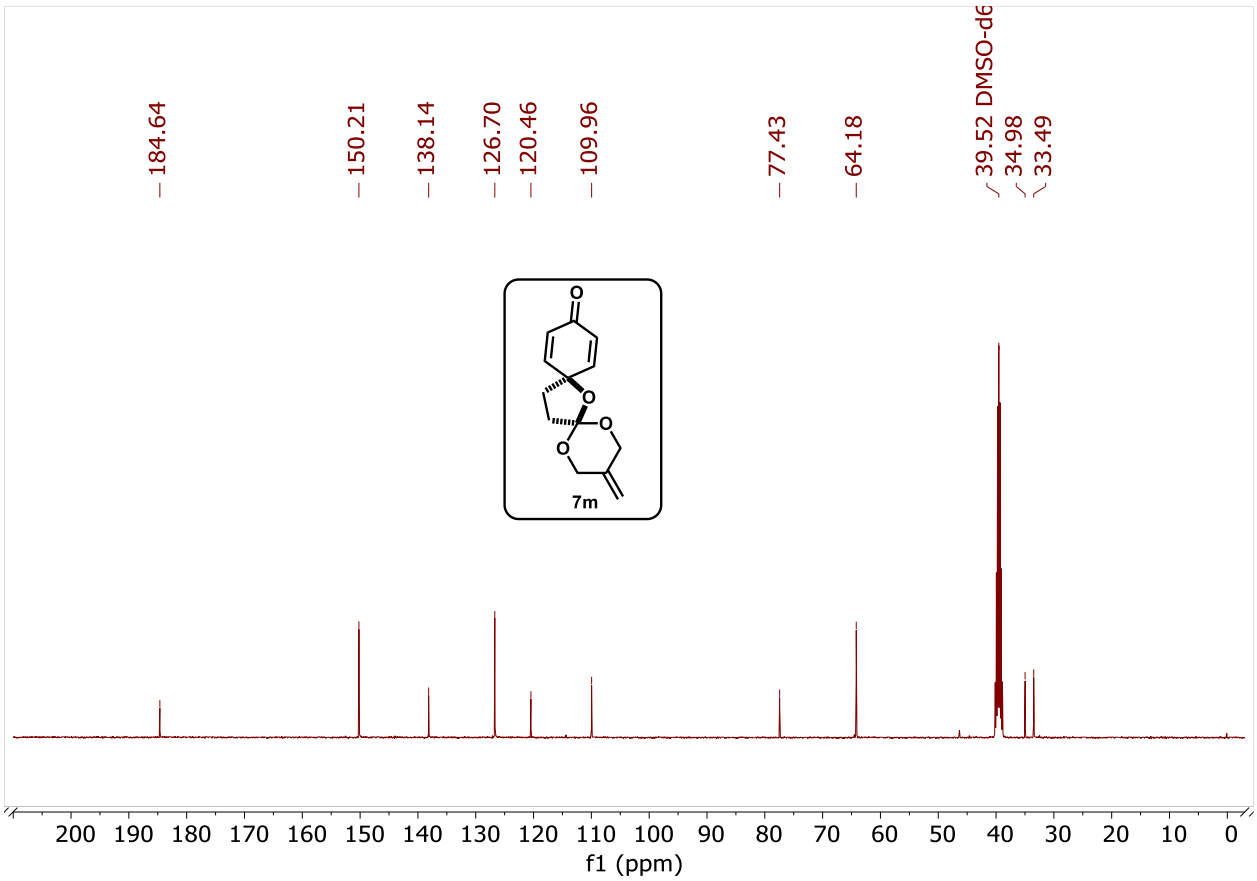
^{13}C{^{1}H} (126 MHz, BENZENE-D6) spectrum of **7l**



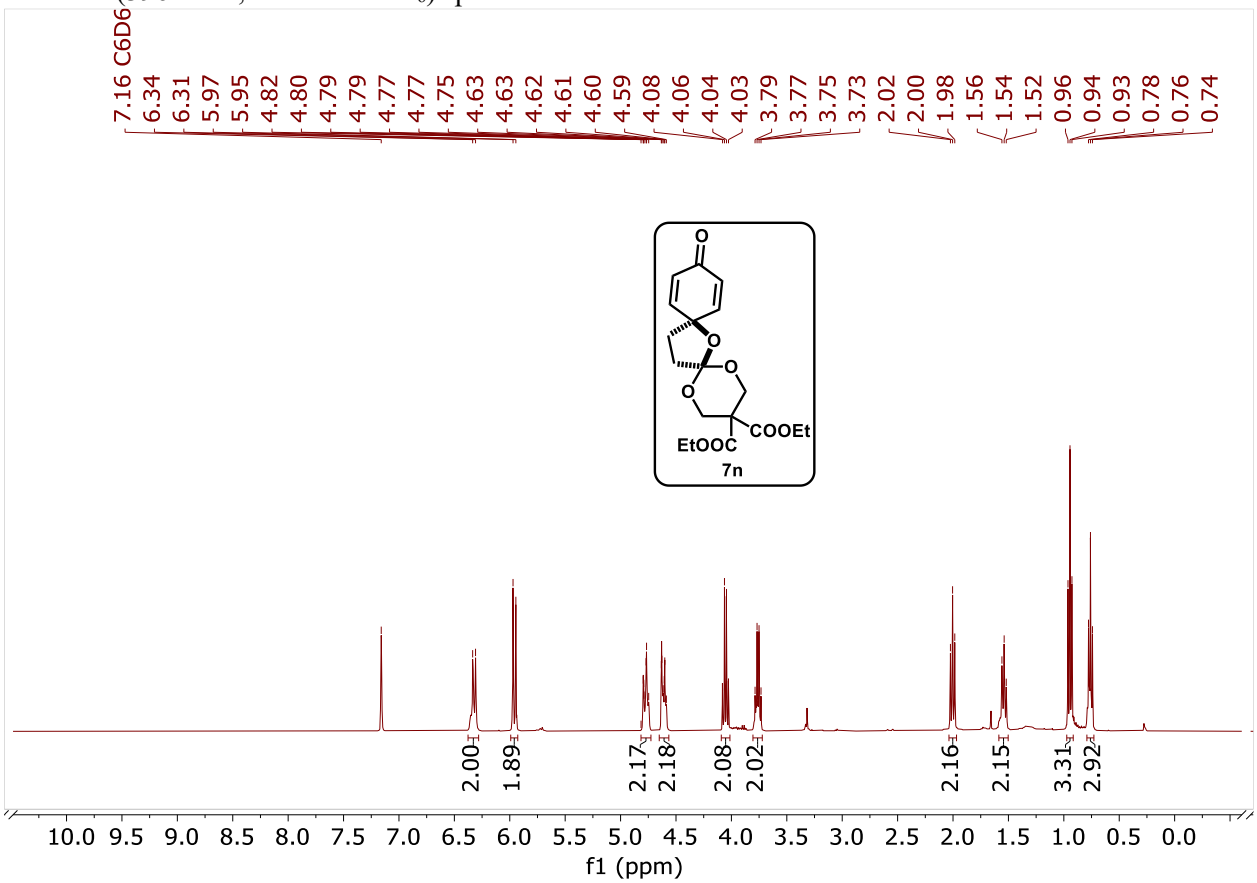
^{1}H NMR (396 MHz, DMSO-D6) spectrum of **7m**



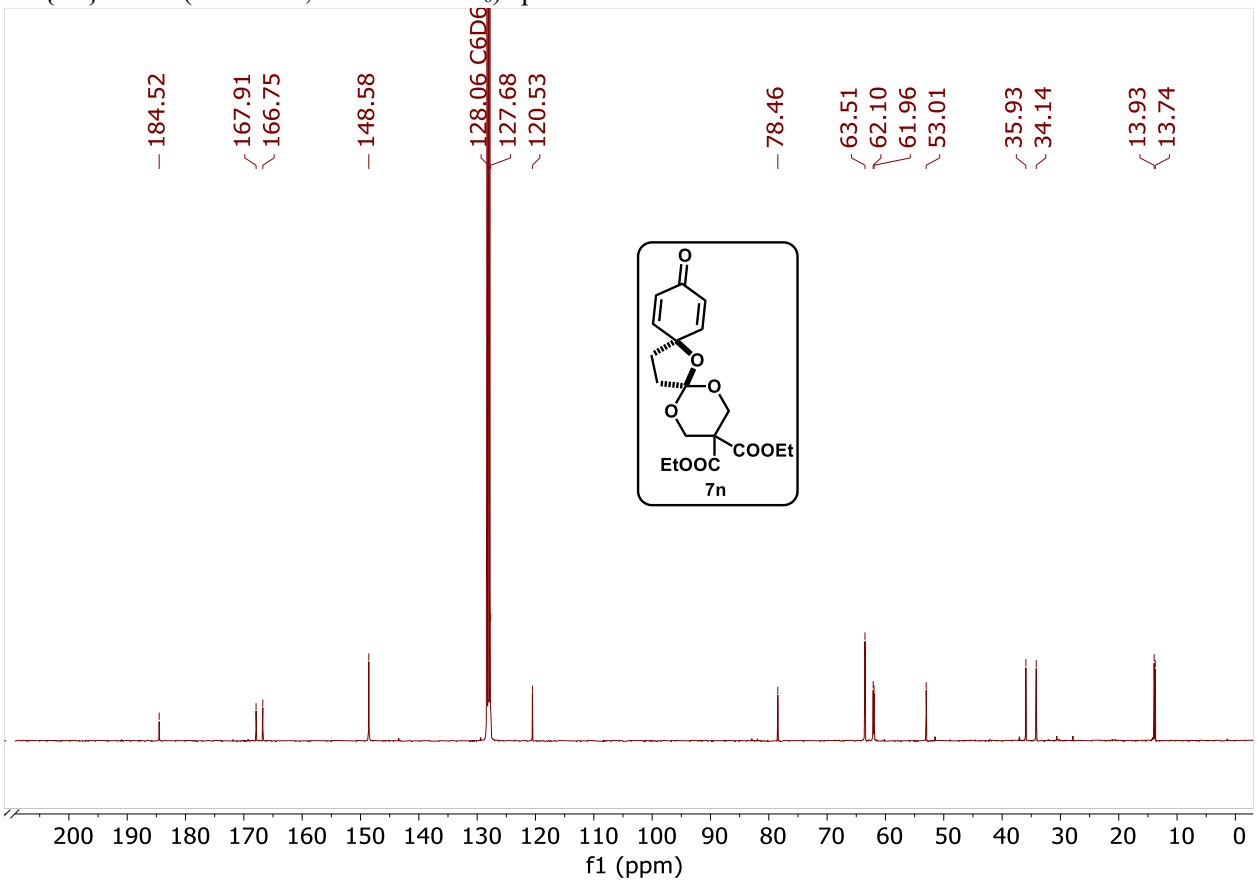
^{13}C{^{1}H} (101 MHz, DMSO-D6) spectrum of **7m**



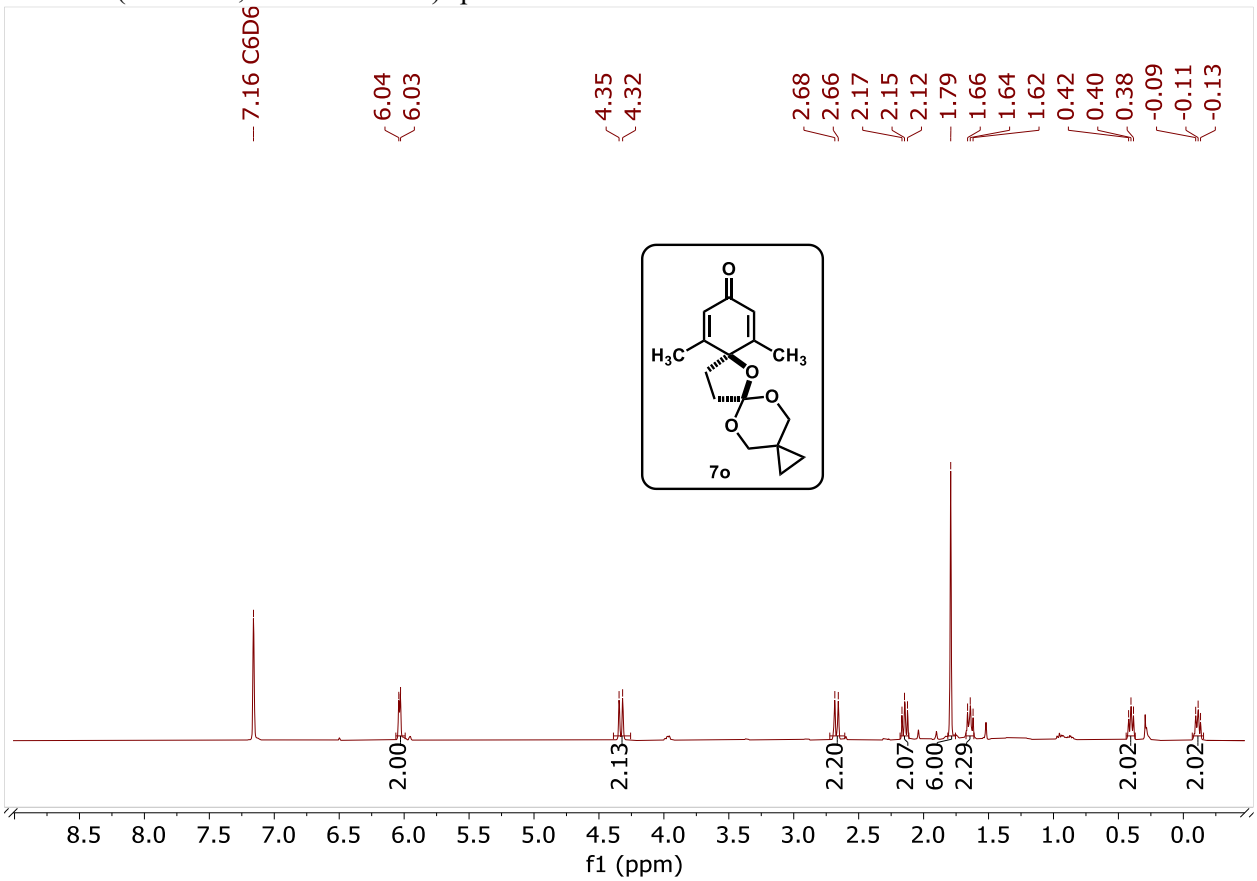
^{1}H NMR (396 MHz, BENZENE-D_6) spectrum of **7n**



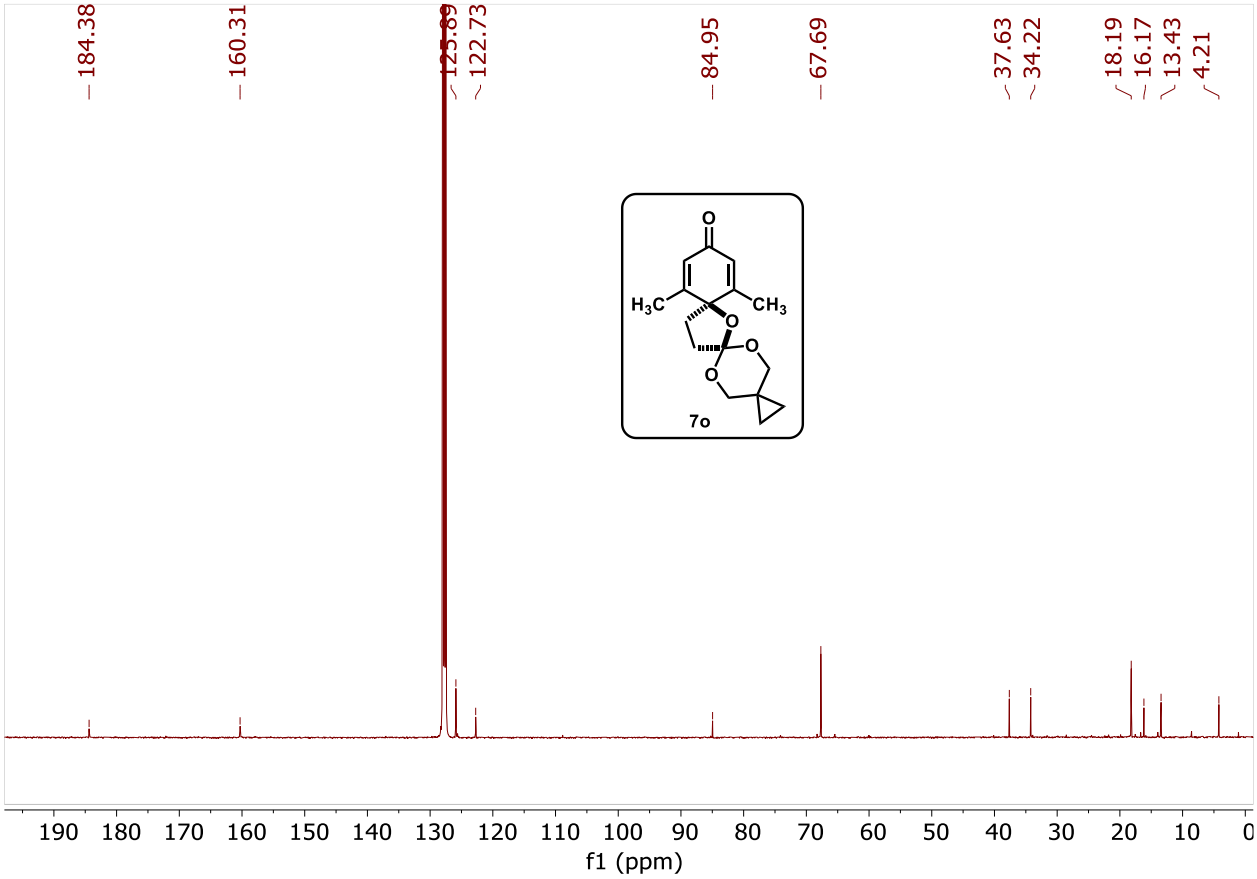
^{13}C{^{1}H} NMR (100 MHz, BENZENE-D_6) spectrum of **7n**



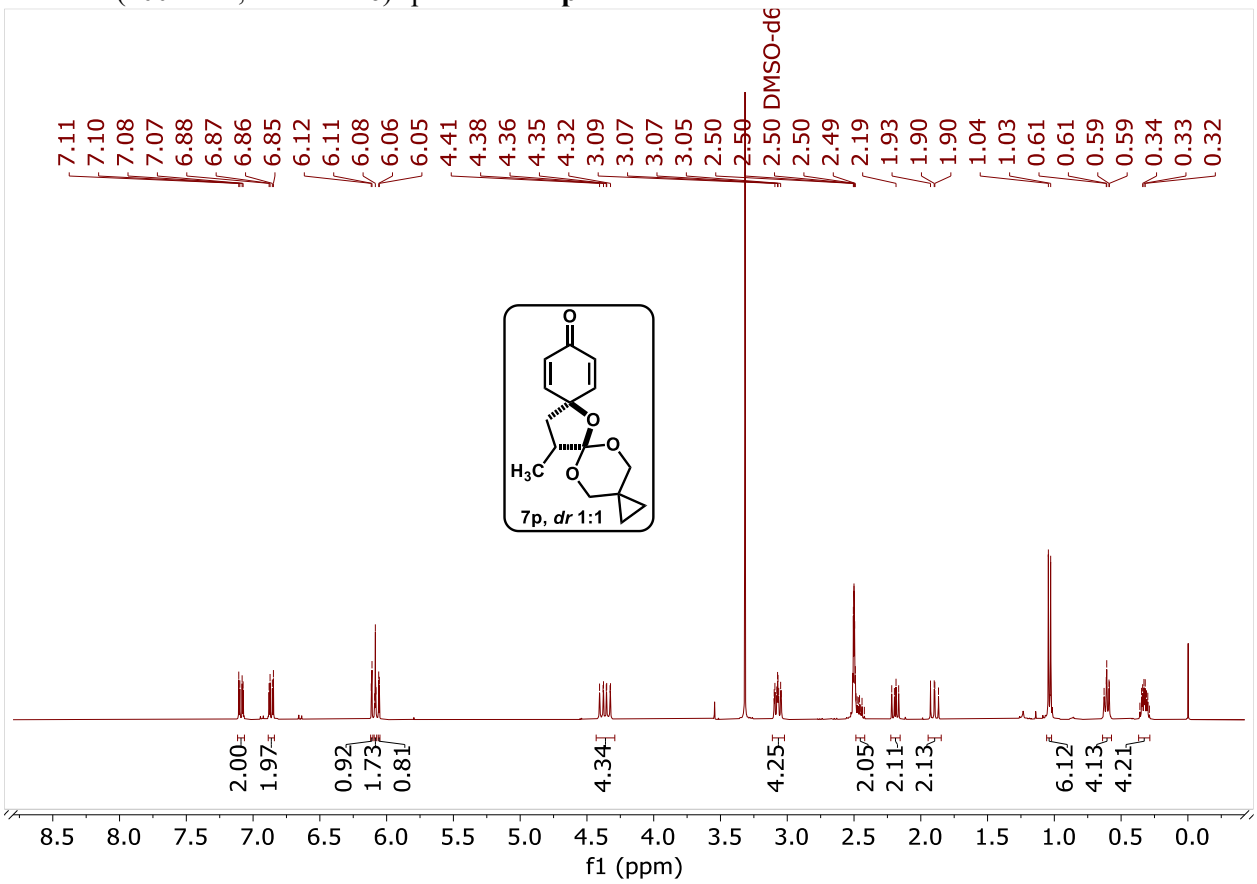
^{1}H NMR (400 MHz, BENZENE-D6) spectrum of **7o**



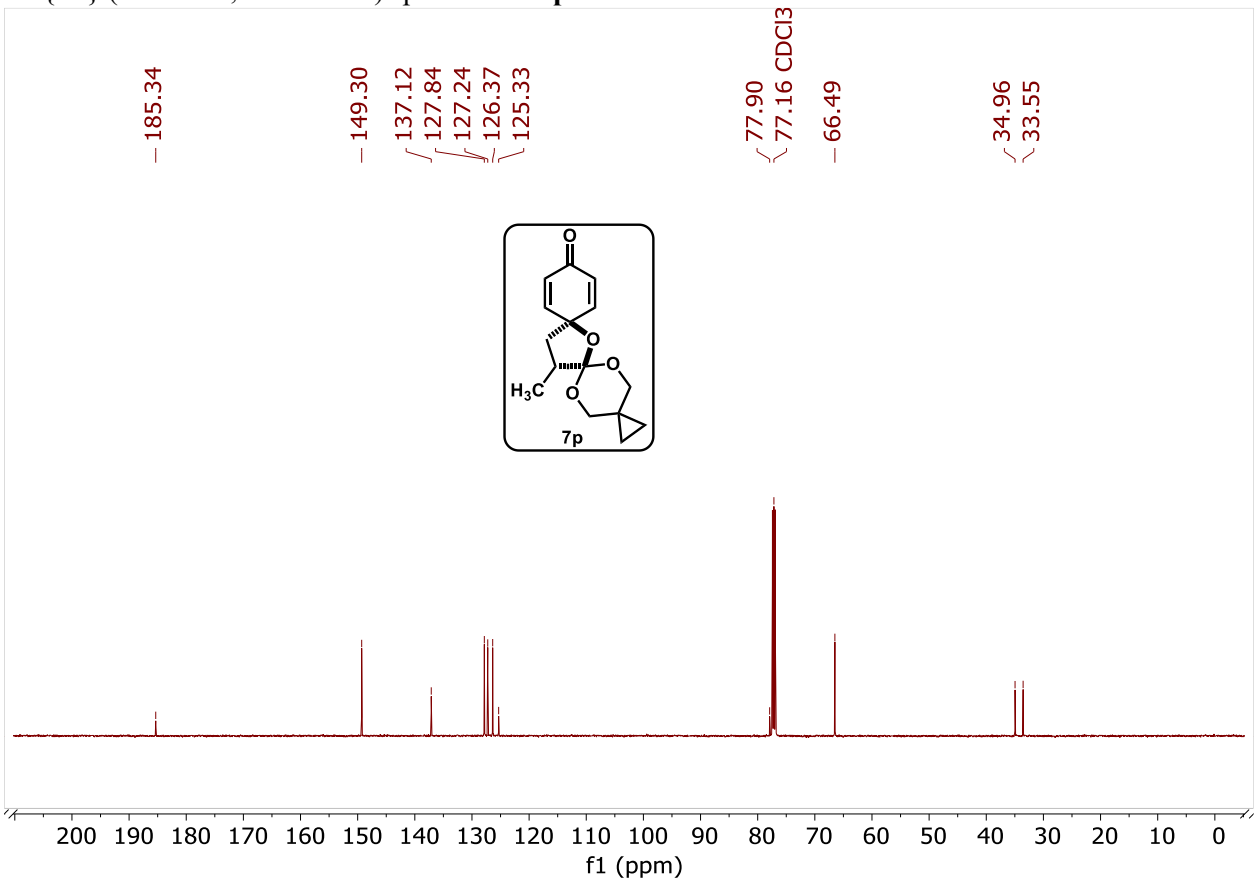
^{13}C{^{1}H} (101 MHz, BENZENE-D6) spectrum of **7o**



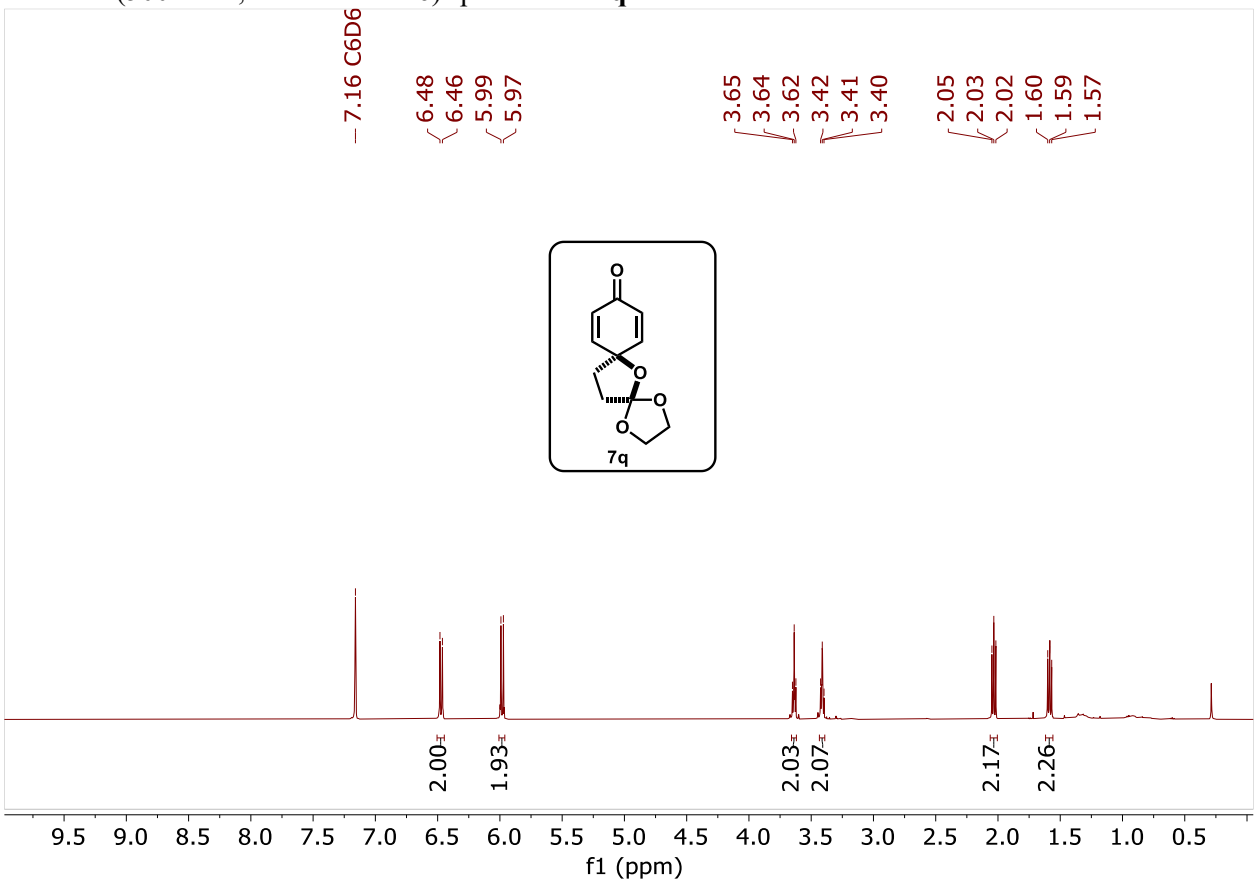
^{1}H NMR (400 MHz, DMSO-D6) spectrum of **7p**



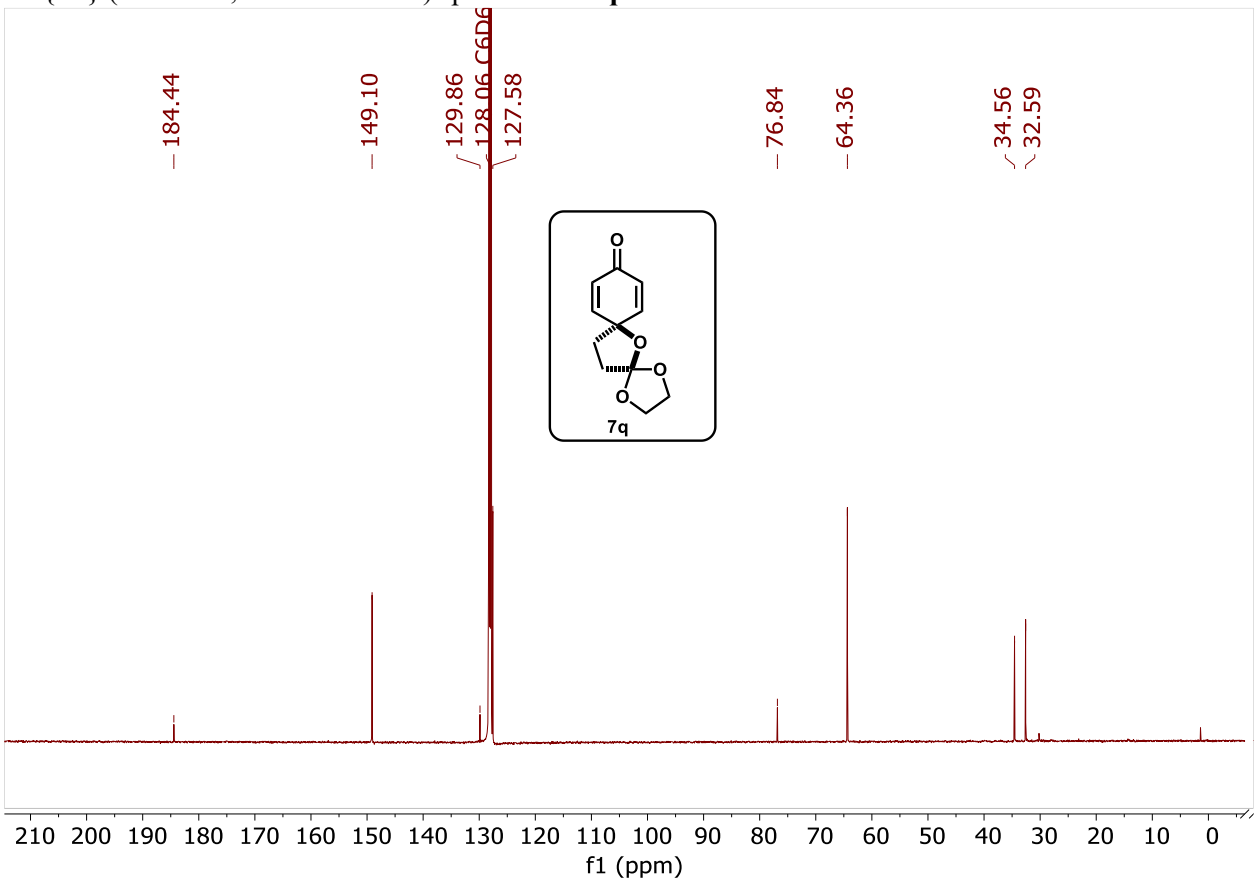
^{13}C{^{1}H} (101 MHz, DMSO-D6) spectrum of **7p**



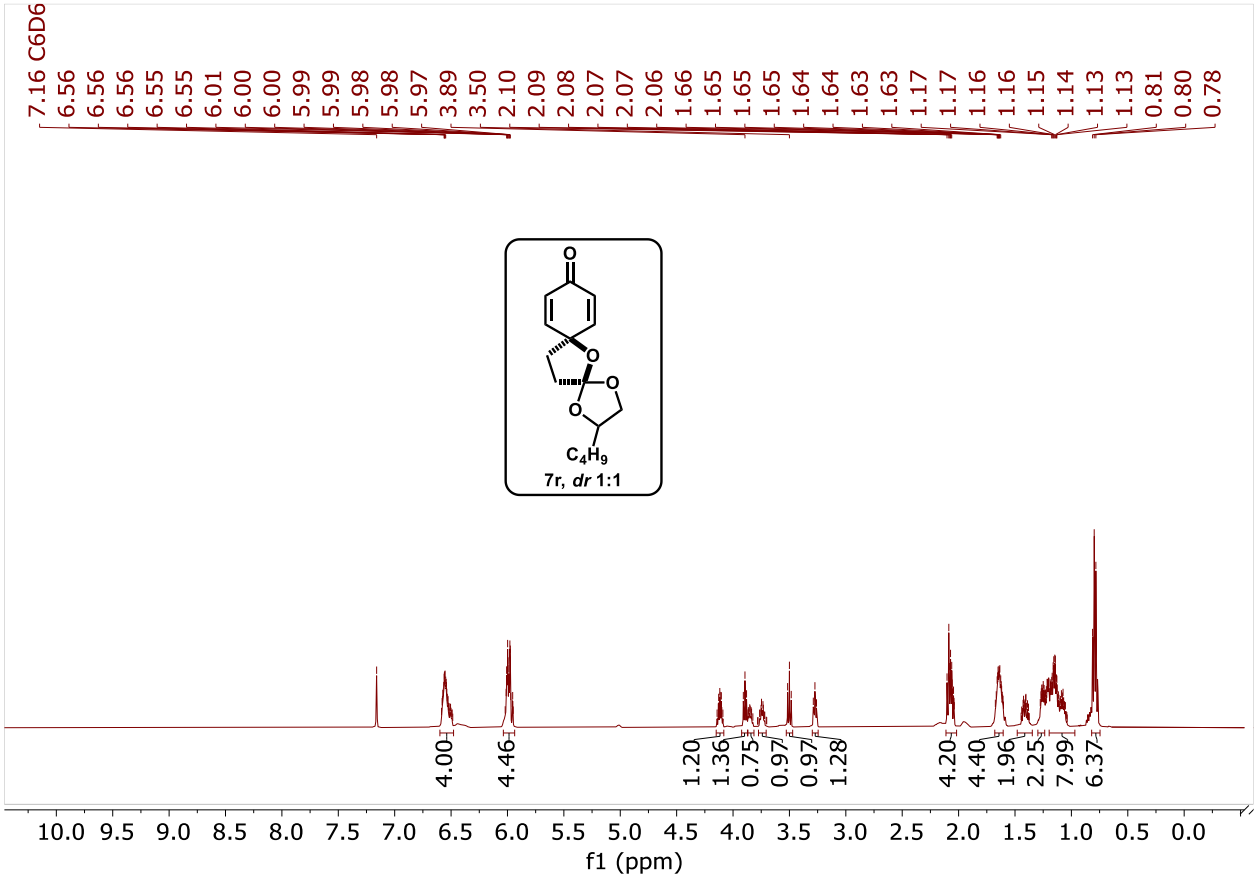
^{1}H NMR (500 MHz, BENZENE-D6) spectrum of **7q**



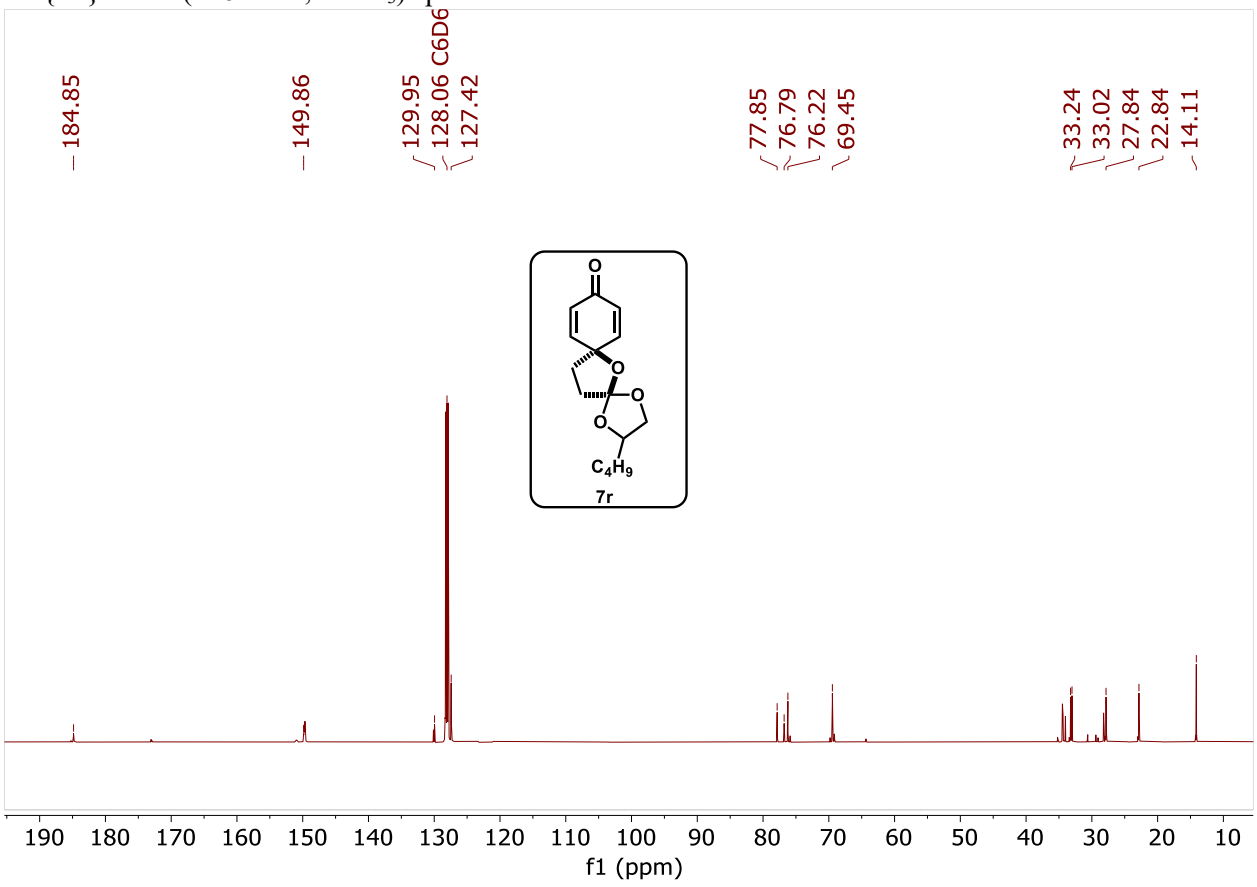
^{13}C{^{1}H} (126 MHz, BENZENE-D6) spectrum of **7q**



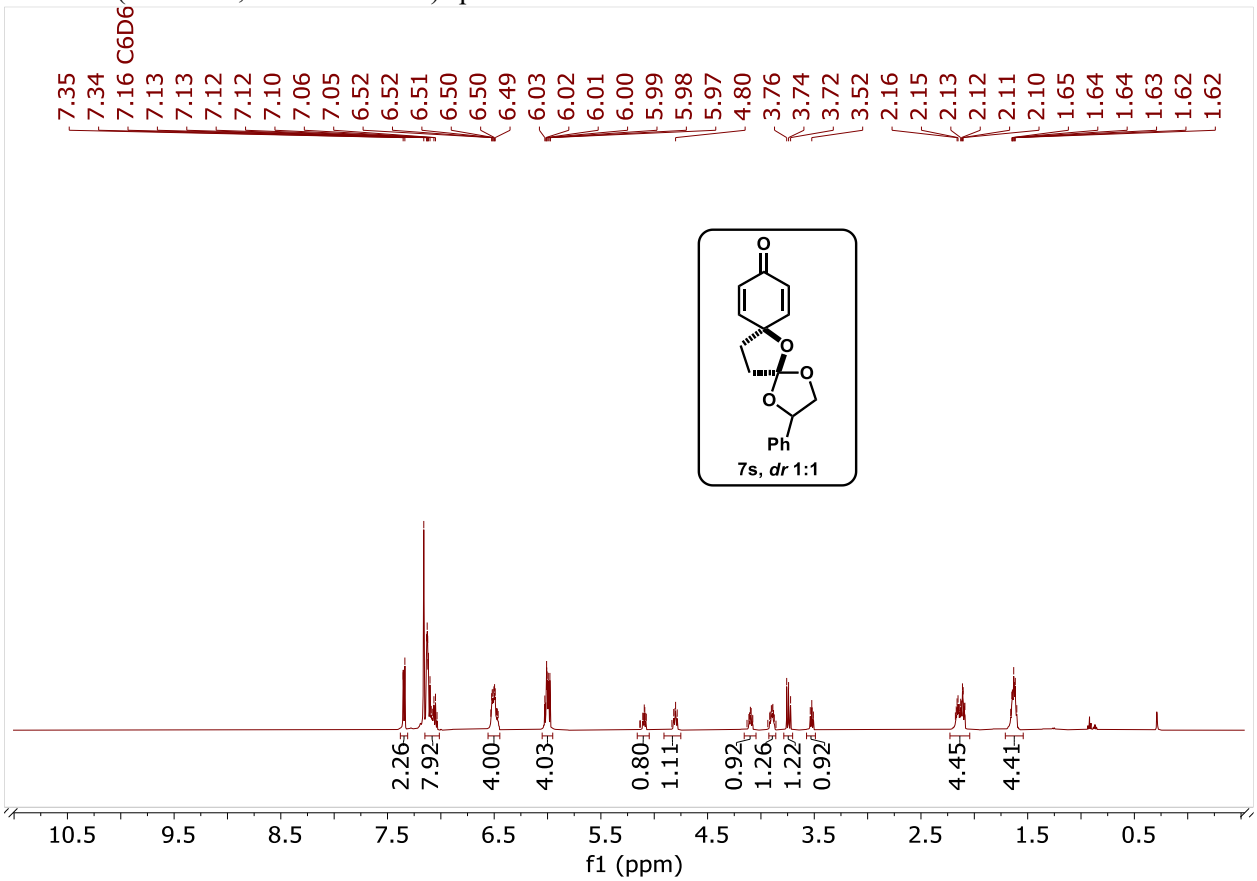
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **7r**



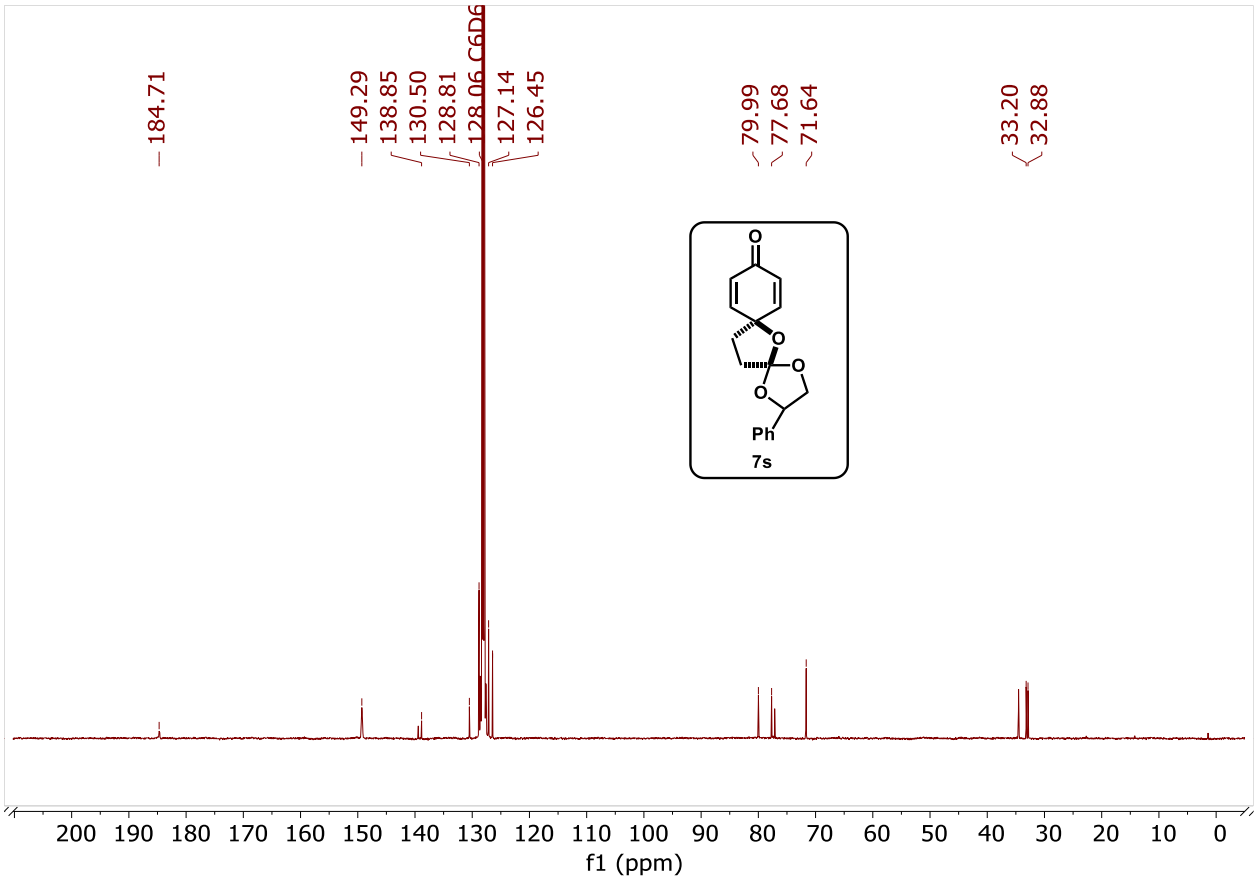
^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) spectrum of **7r**



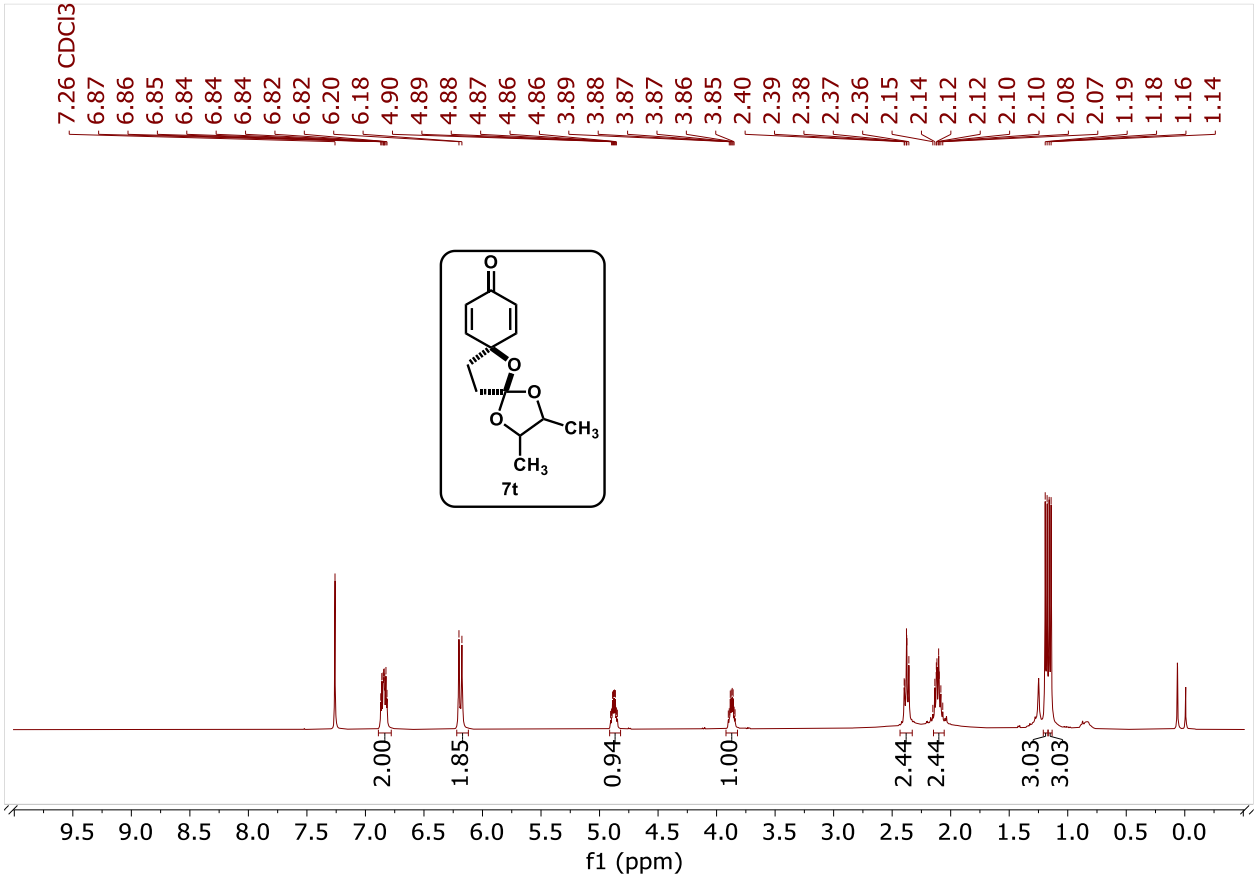
^{1}H NMR (500 MHz, BENZENE-D6) spectrum of **7s**



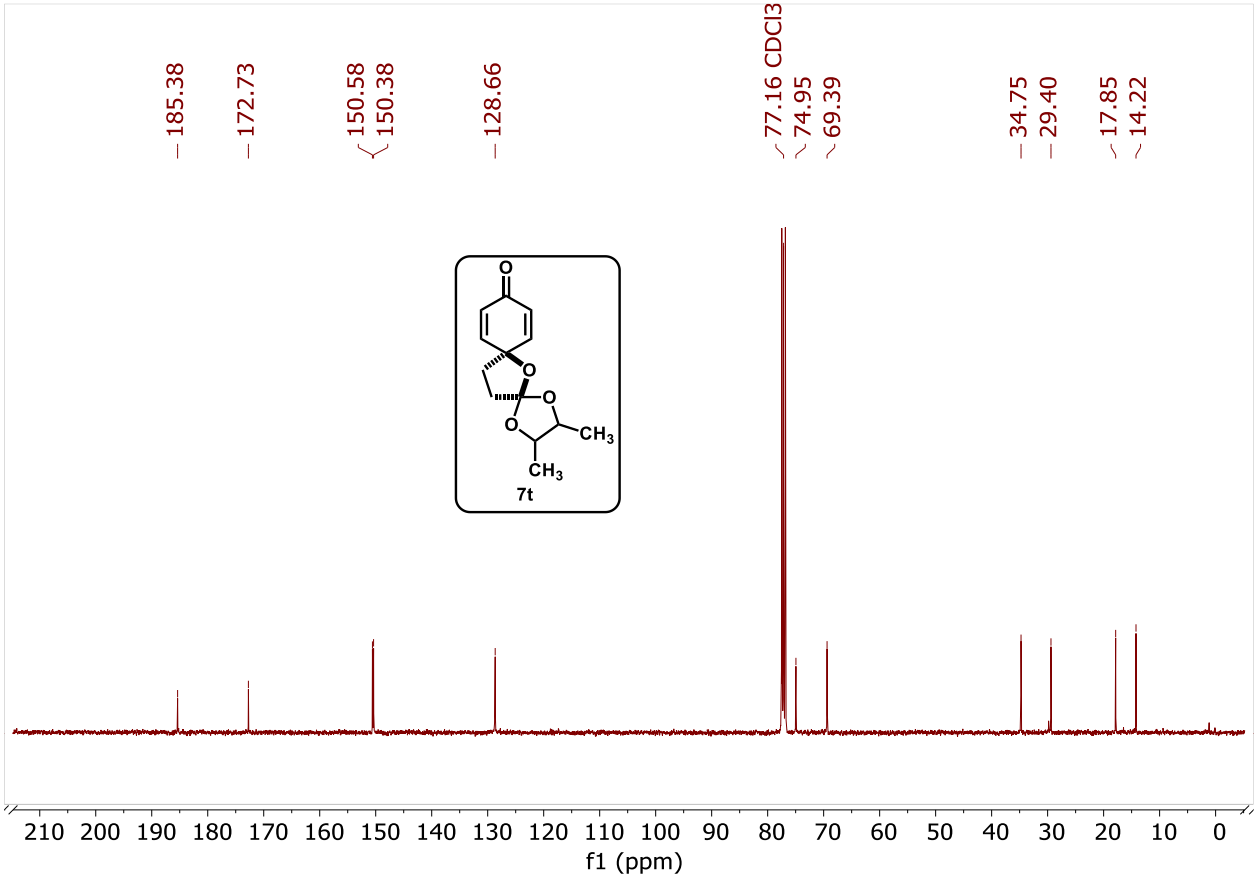
^{13}C{^{1}H} NMR (126 MHz, BENZENE-D6) spectrum of **7s**



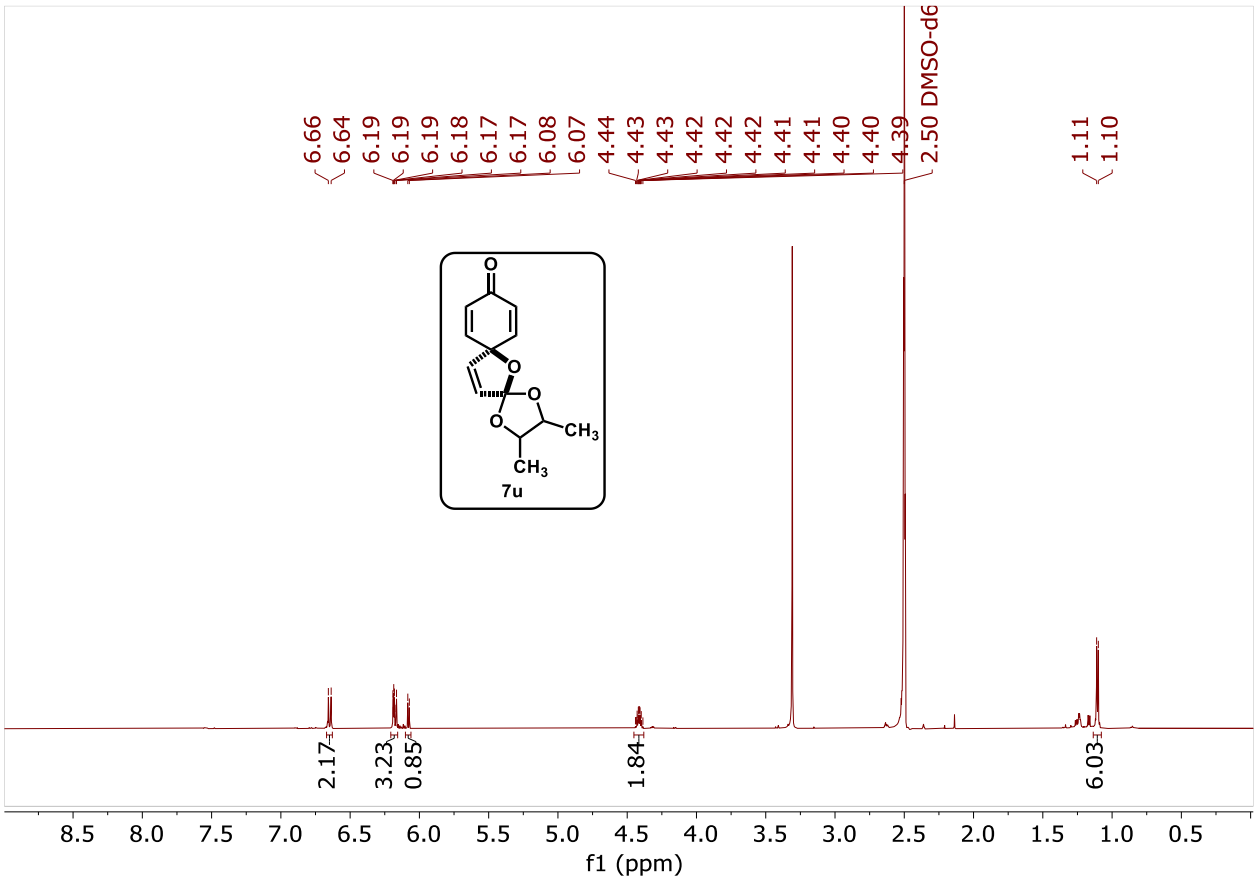
^{1}H NMR (396 MHz, 126 MHz, $CDCl_3$) spectrum of **7t**



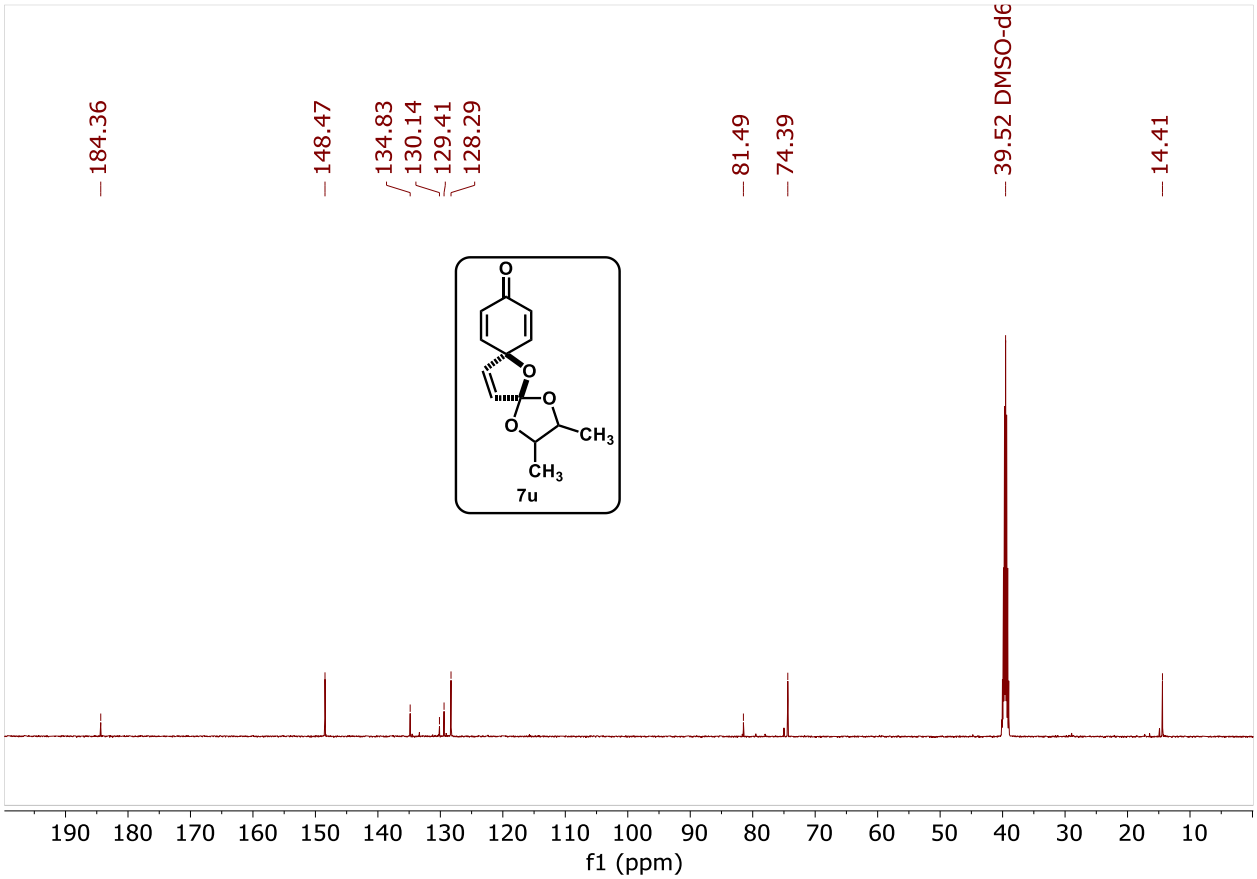
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) spectrum of 7**t**



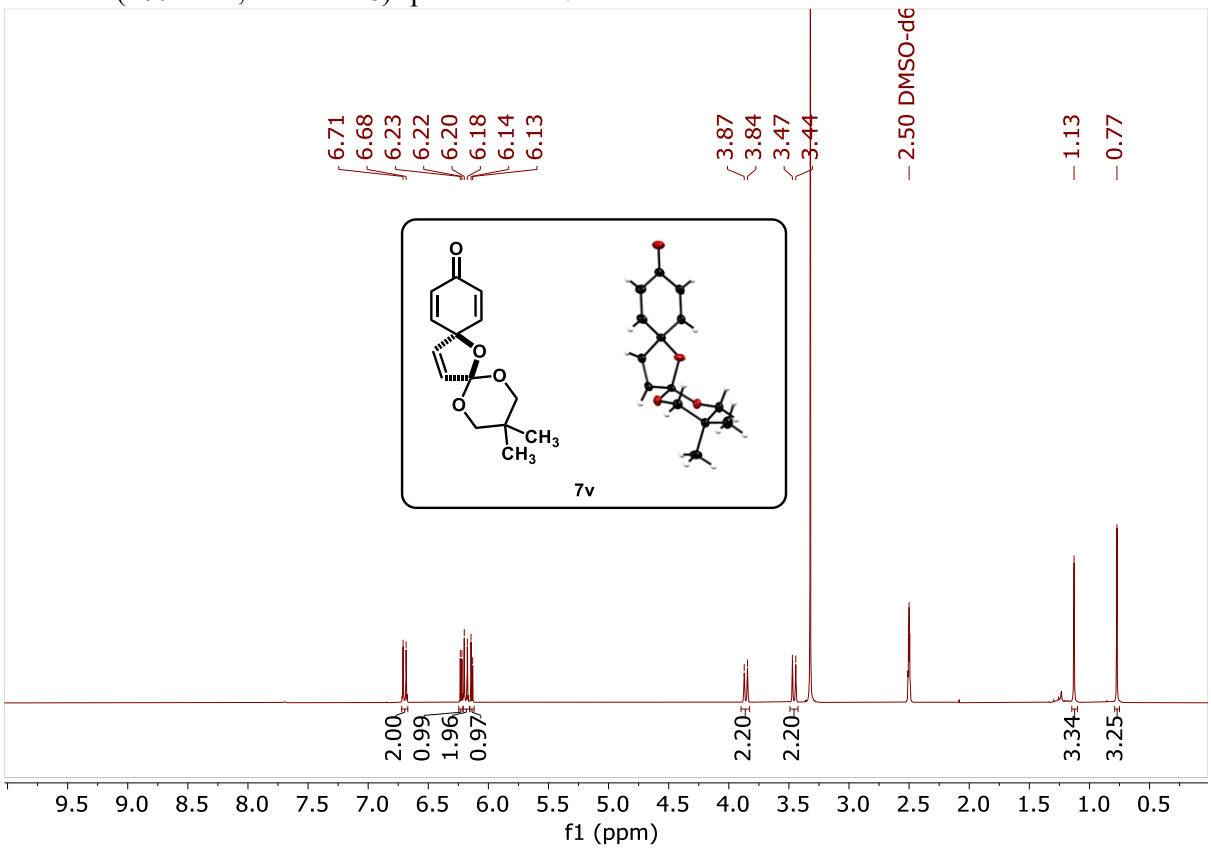
^{1}H NMR (500 MHz, DMSO-D6) spectrum of **7u**



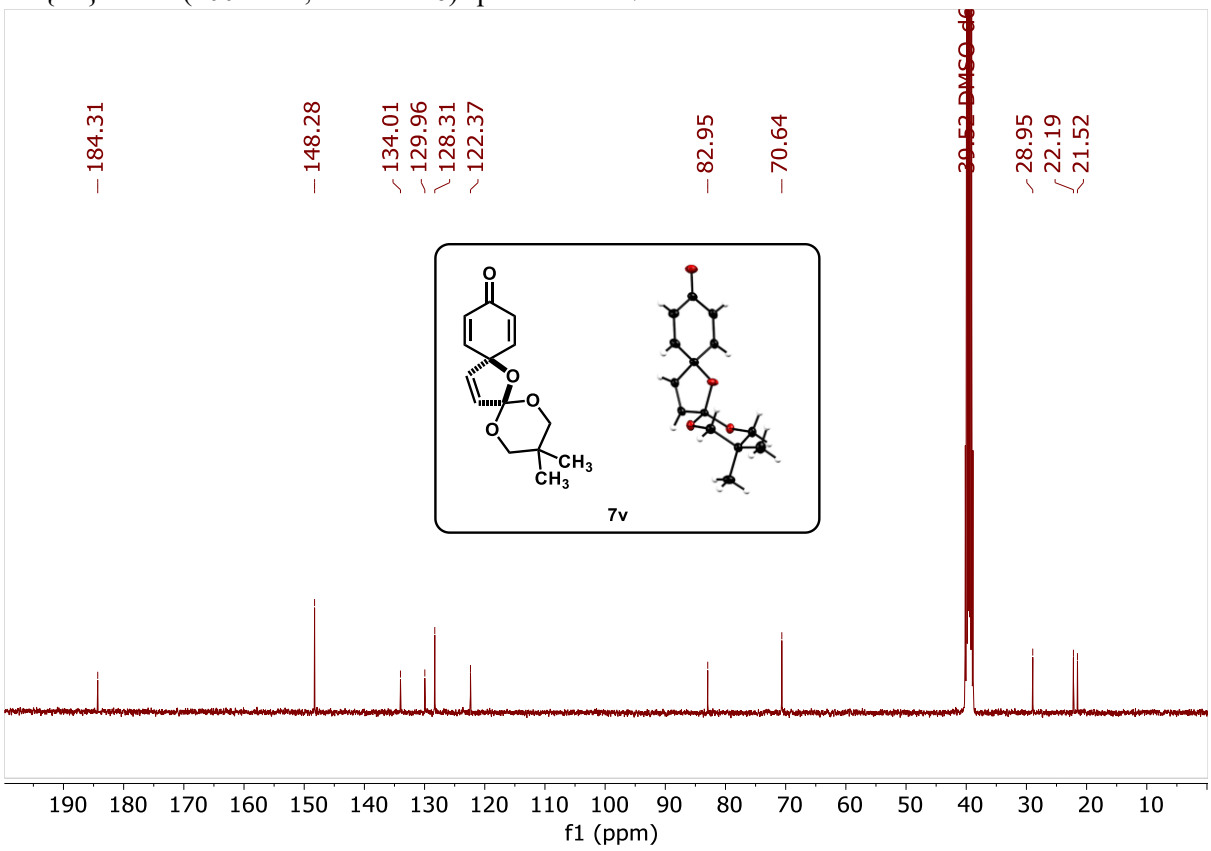
^{13}C{^{1}H} NMR (126 MHz, DMSO-D6) spectrum of **7u**



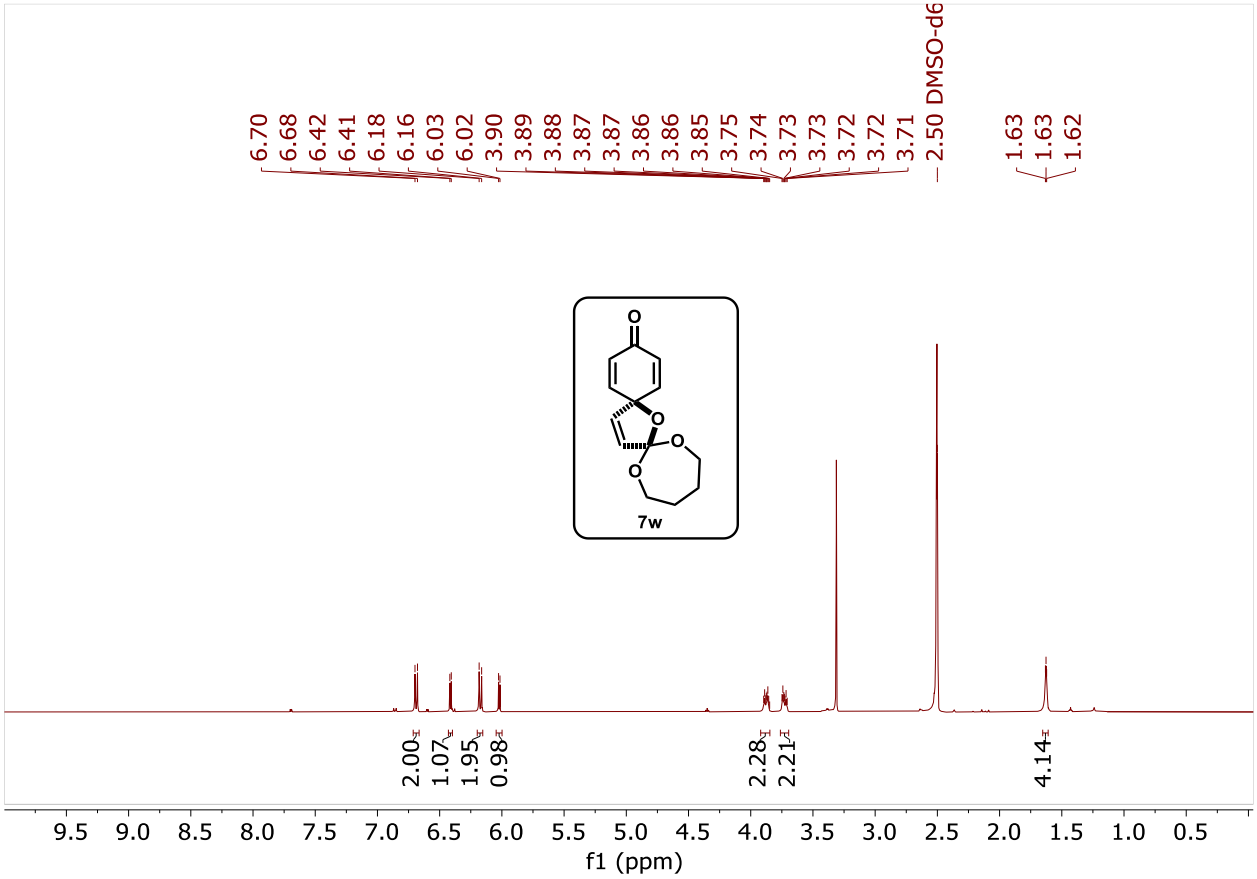
^{1}H NMR (400 MHz, DMSO-D6) spectrum of **7v**



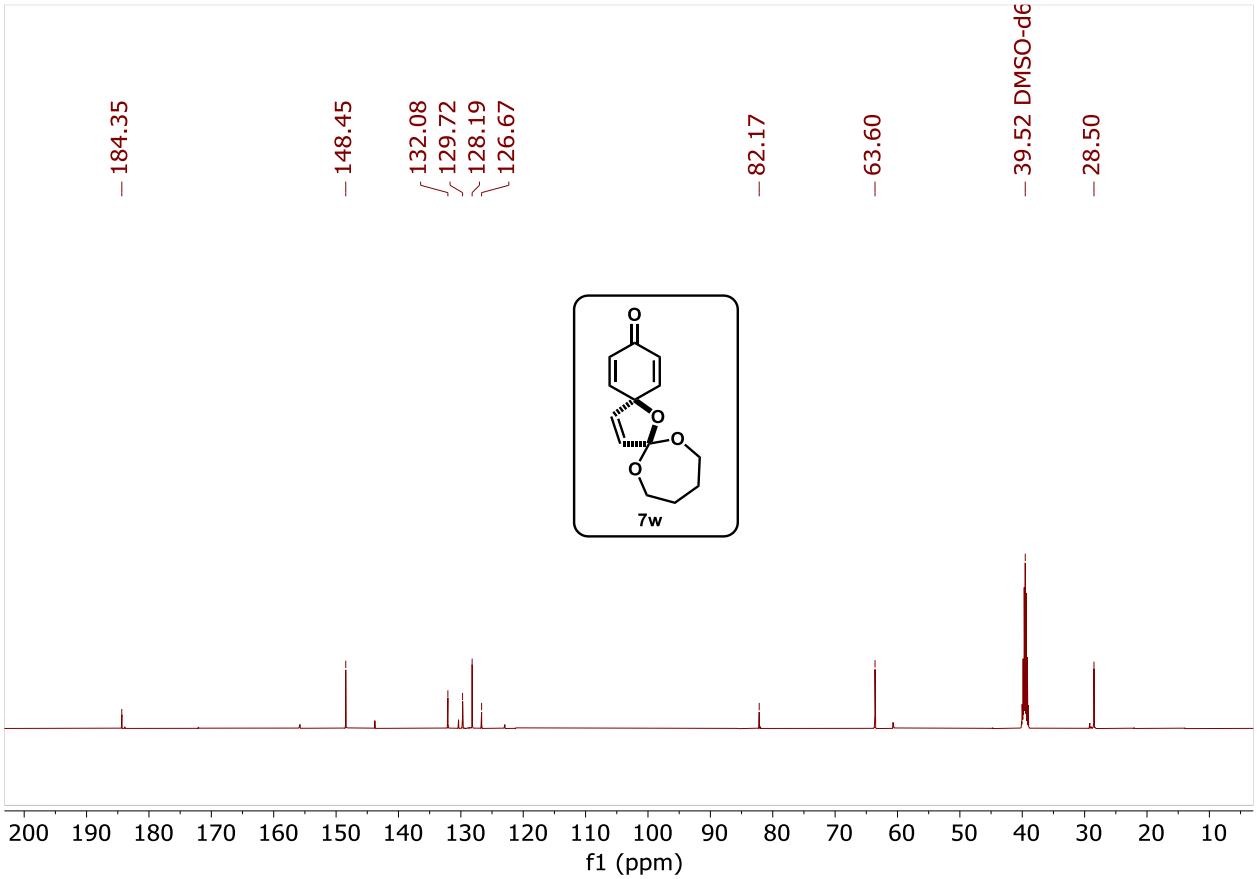
^{13}C{^{1}H} NMR (100 MHz, DMSO-D6) spectrum of **7v**



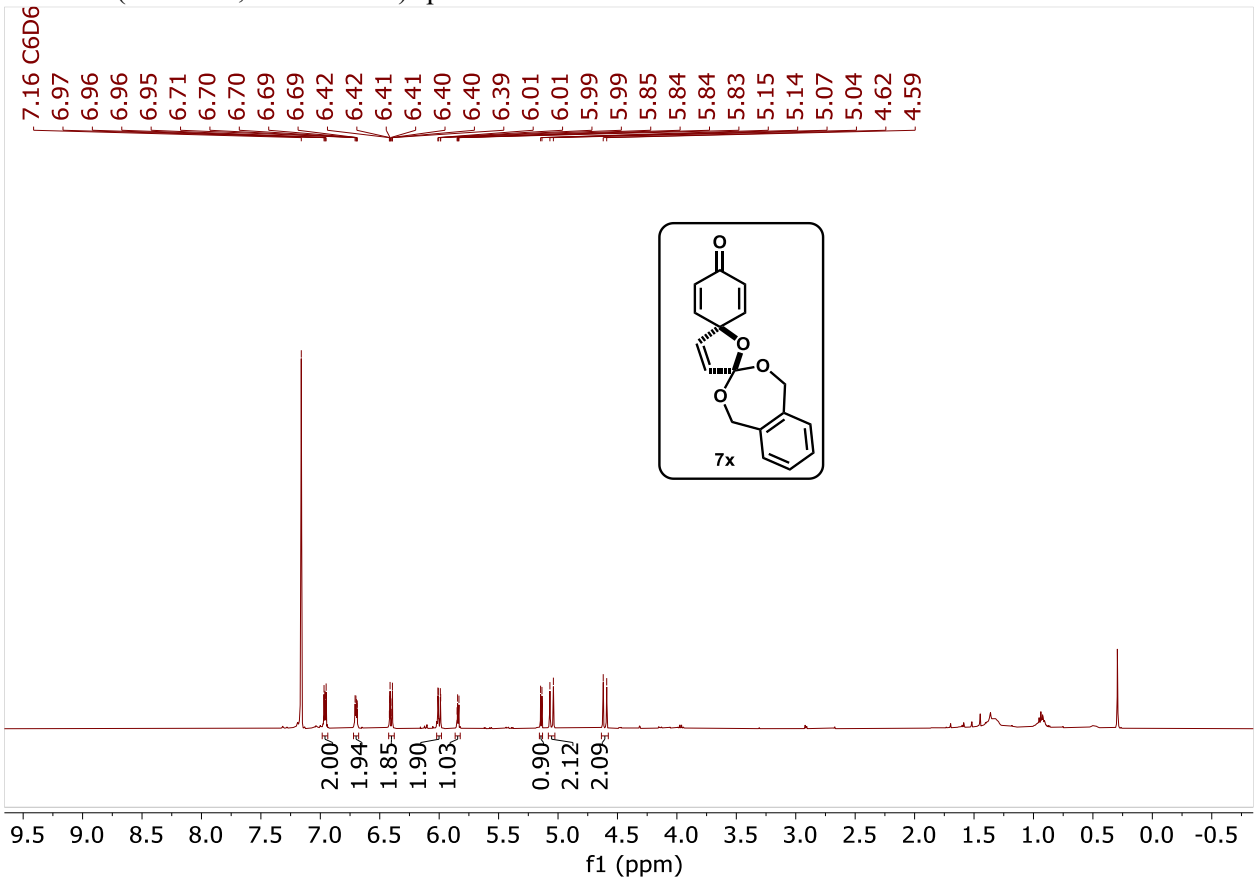
^{1}H NMR (500 MHz, DMSO-D6) spectrum of **7w**



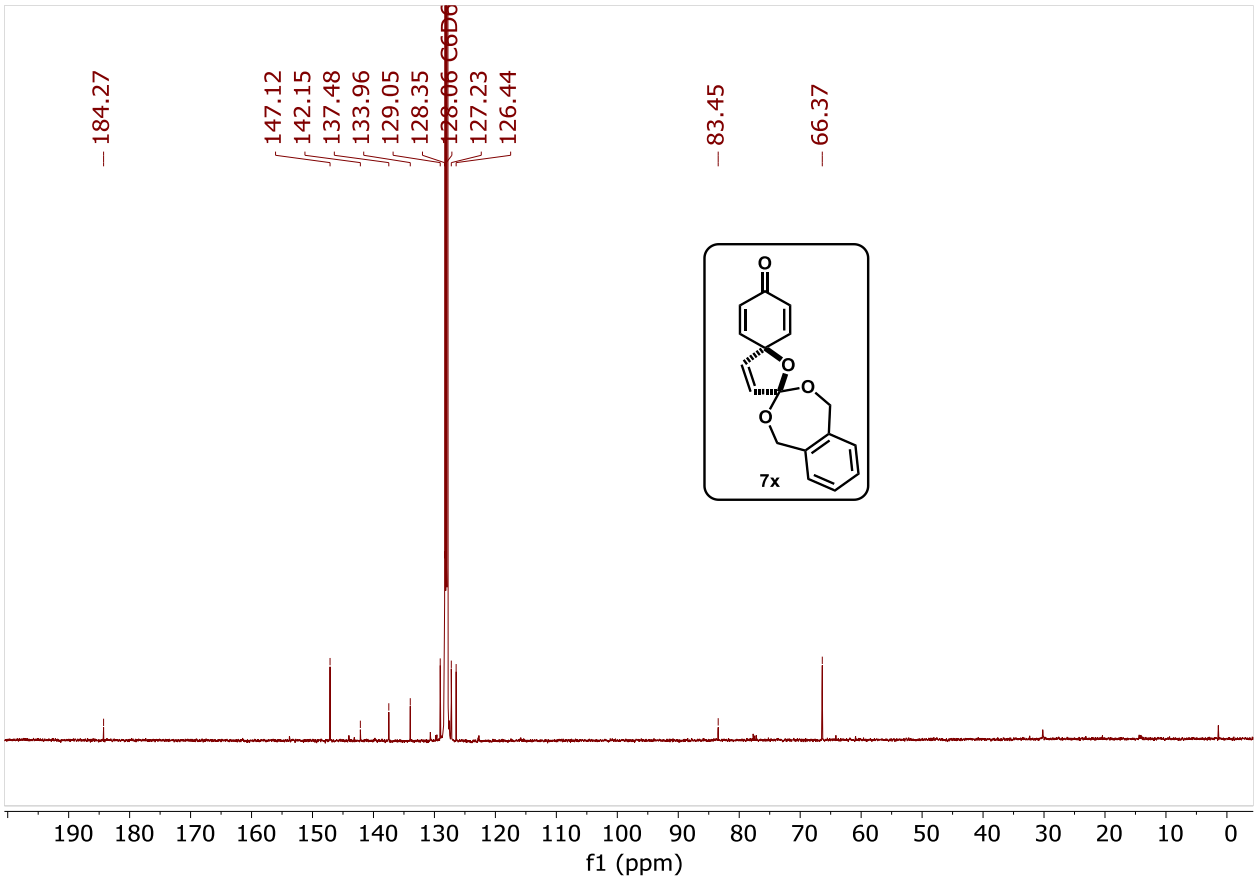
^{13}C{^{1}H} NMR (126 MHz, DMSO-D6) spectrum of **7w**



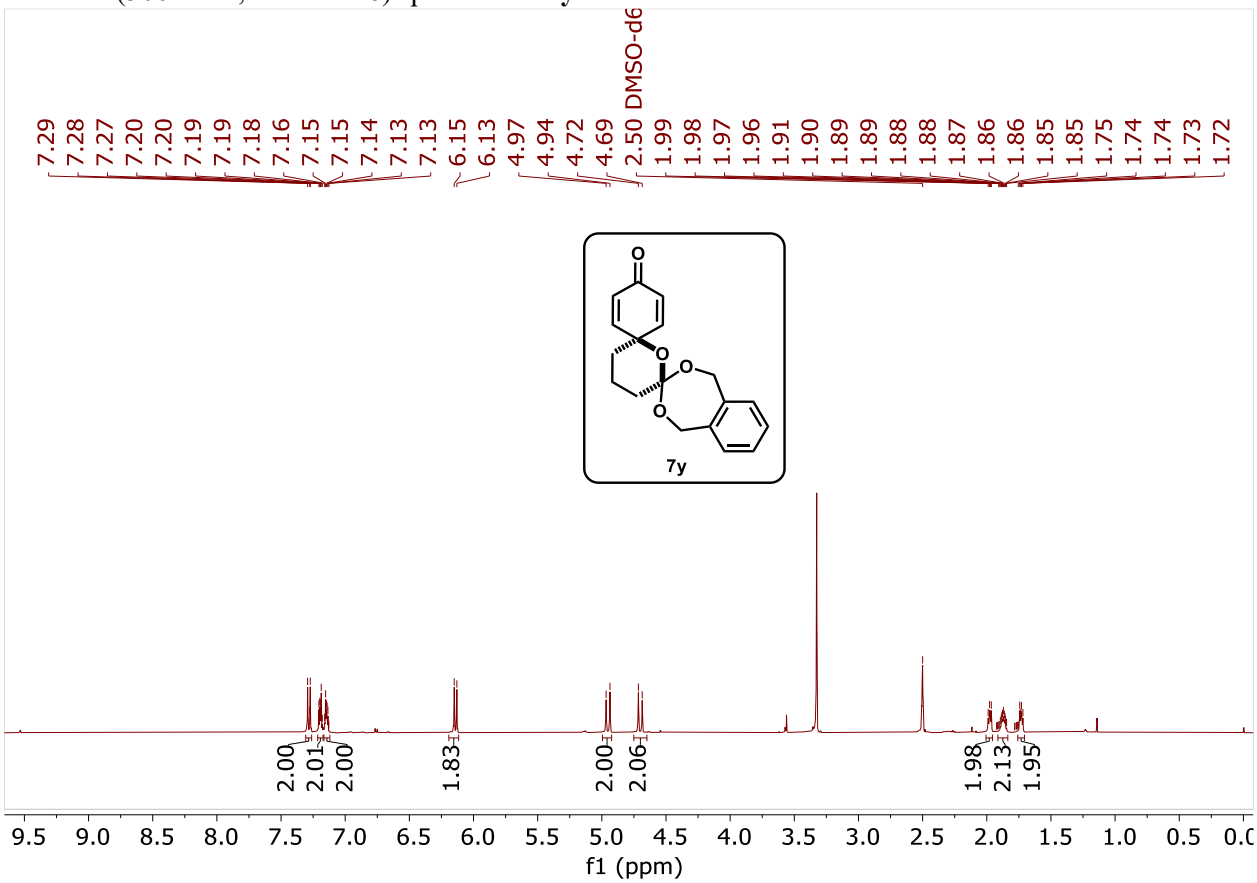
^{1}H NMR (500 MHz, Benzene-D6) spectrum of **7x**



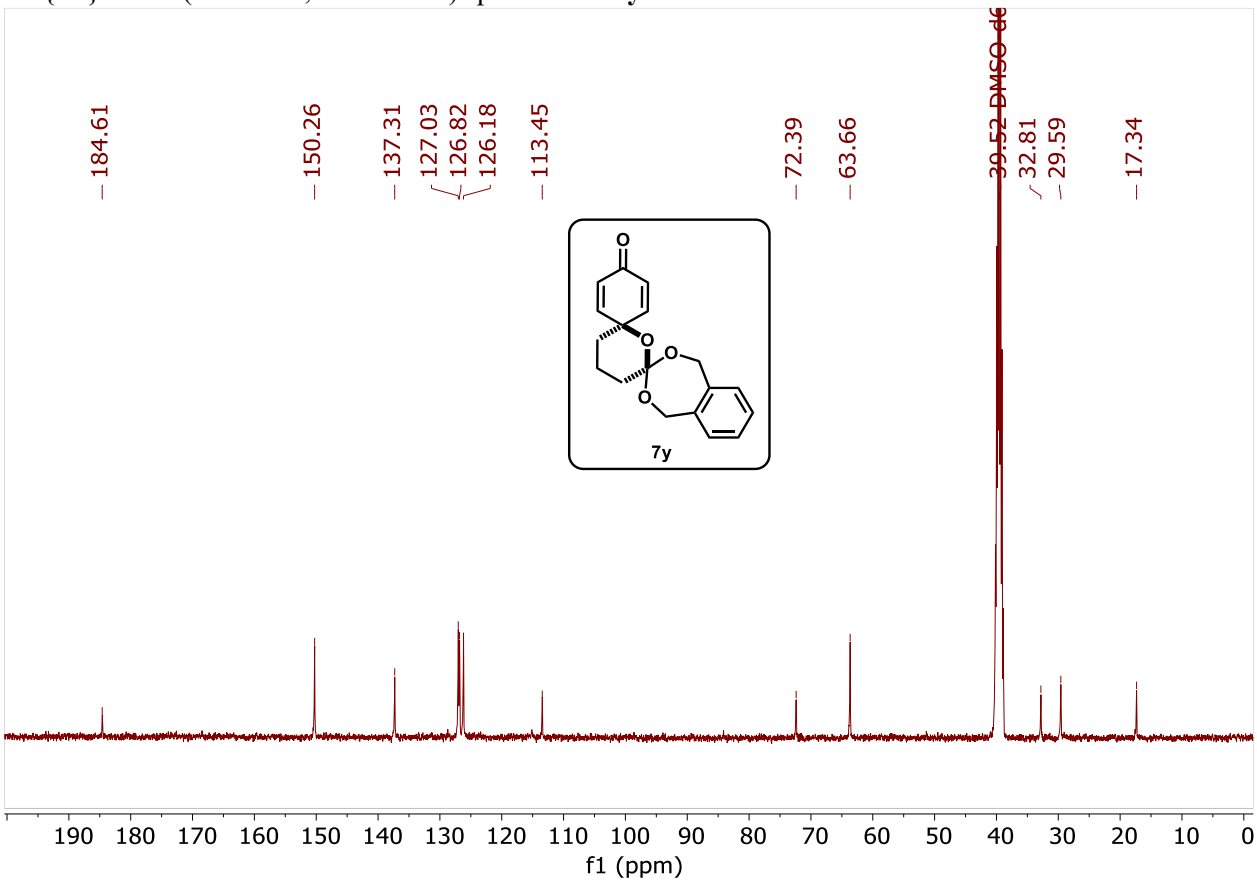
^{13}C{^{1}H} NMR (126 MHz, Benzene-D6) spectrum of **7x**



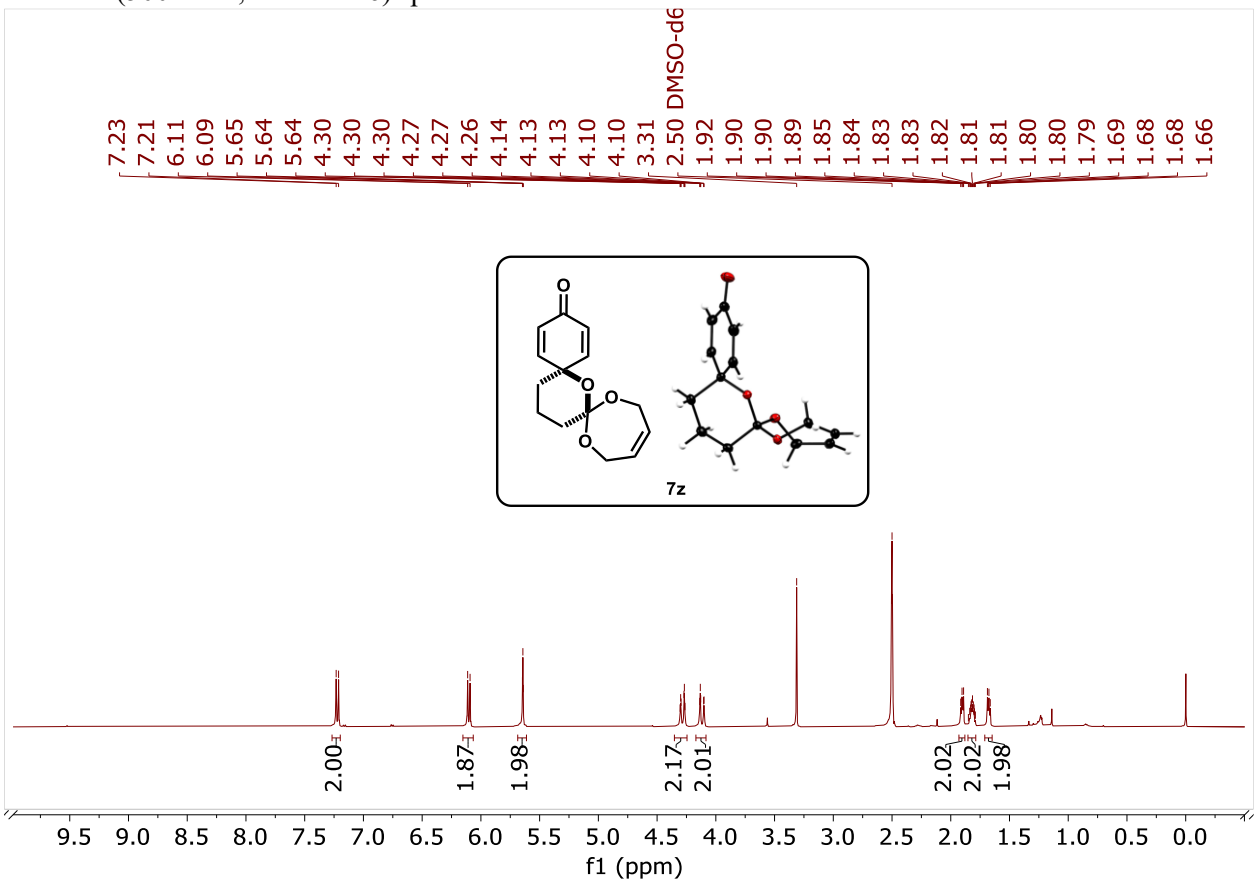
^{1}H NMR (500 MHz, DMSO-D6) spectrum of **7y**



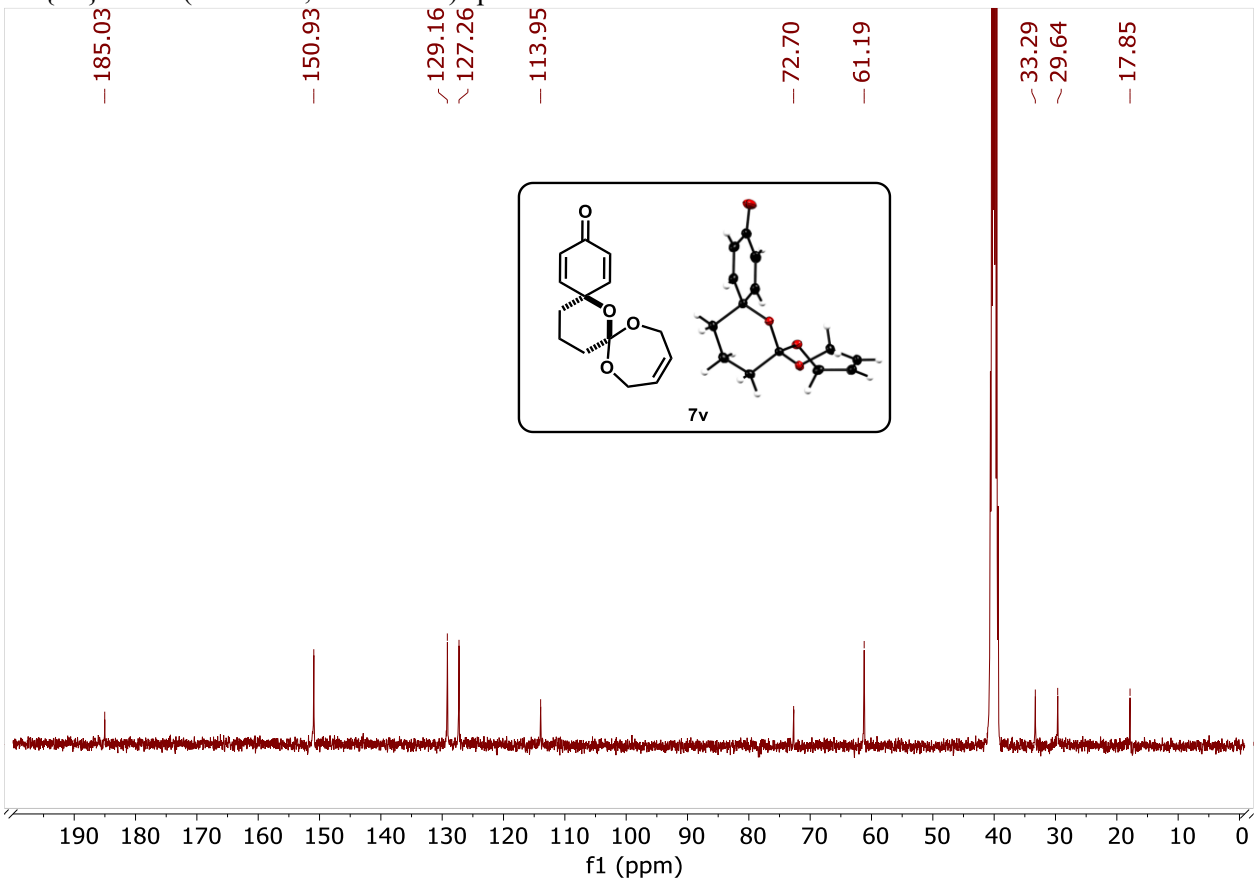
^{13}C{^{1}H} NMR (101 MHz, DMSO-D6) spectrum of **7y**



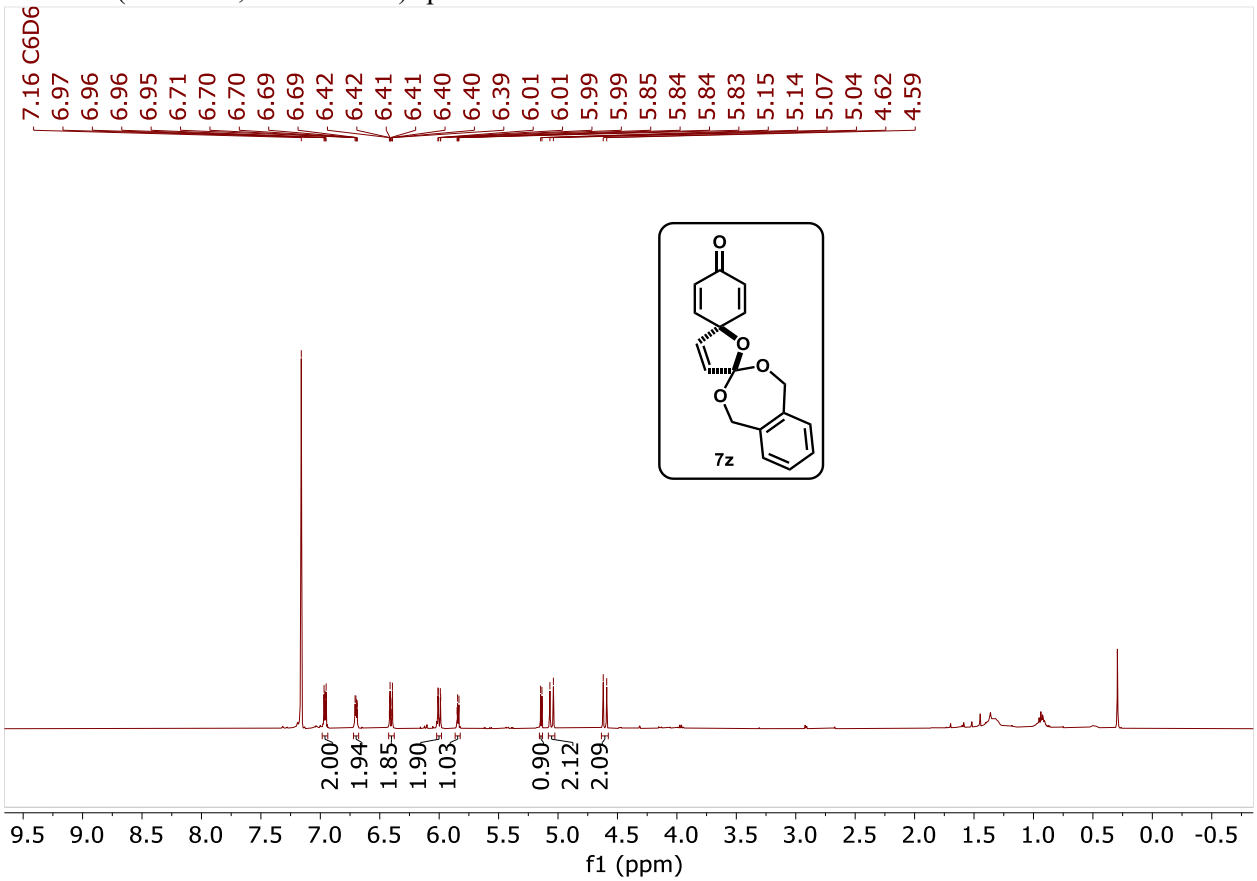
^{1}H NMR (500 MHz, DMSO-D6) spectrum of **7z**



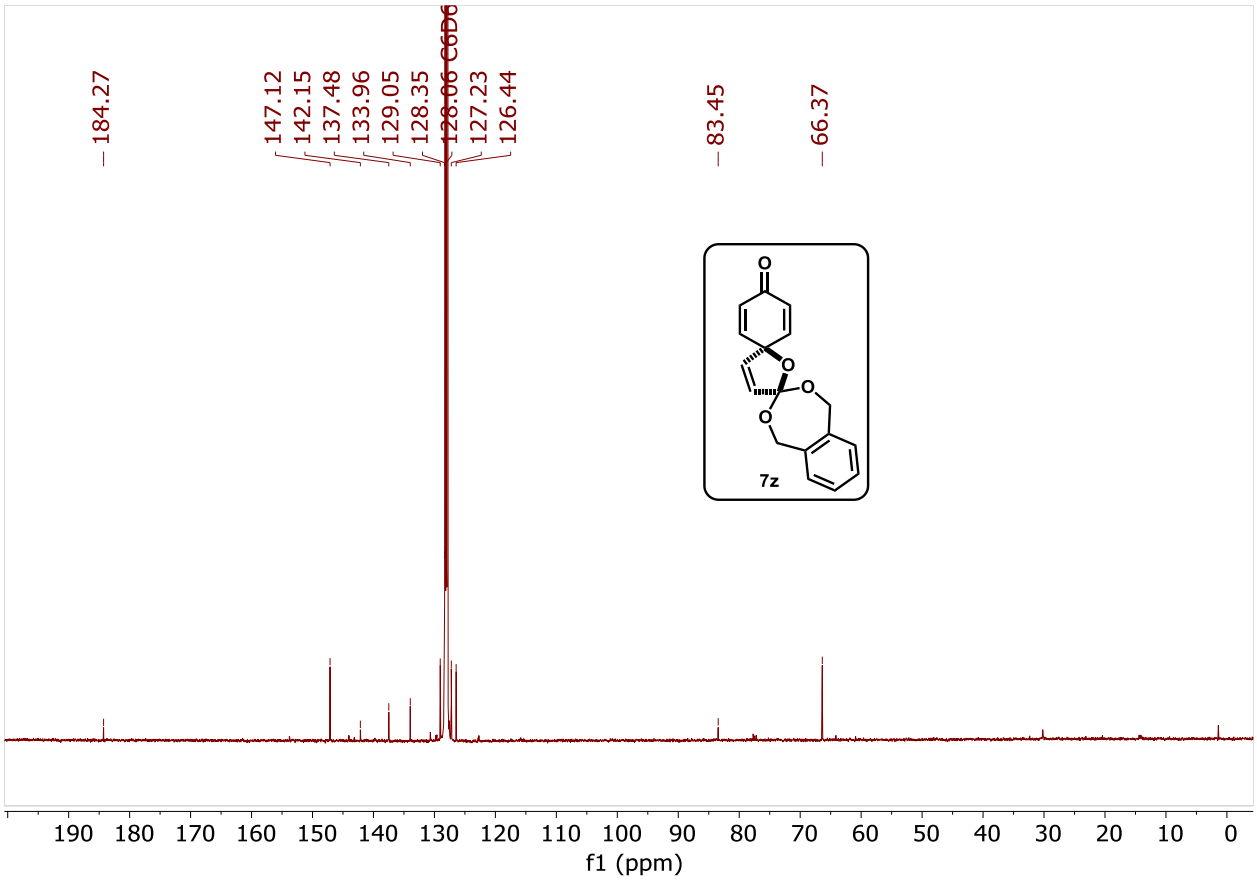
^{13}C{^{1}H} NMR (101 MHz, DMSO-D6) spectrum of **7z**



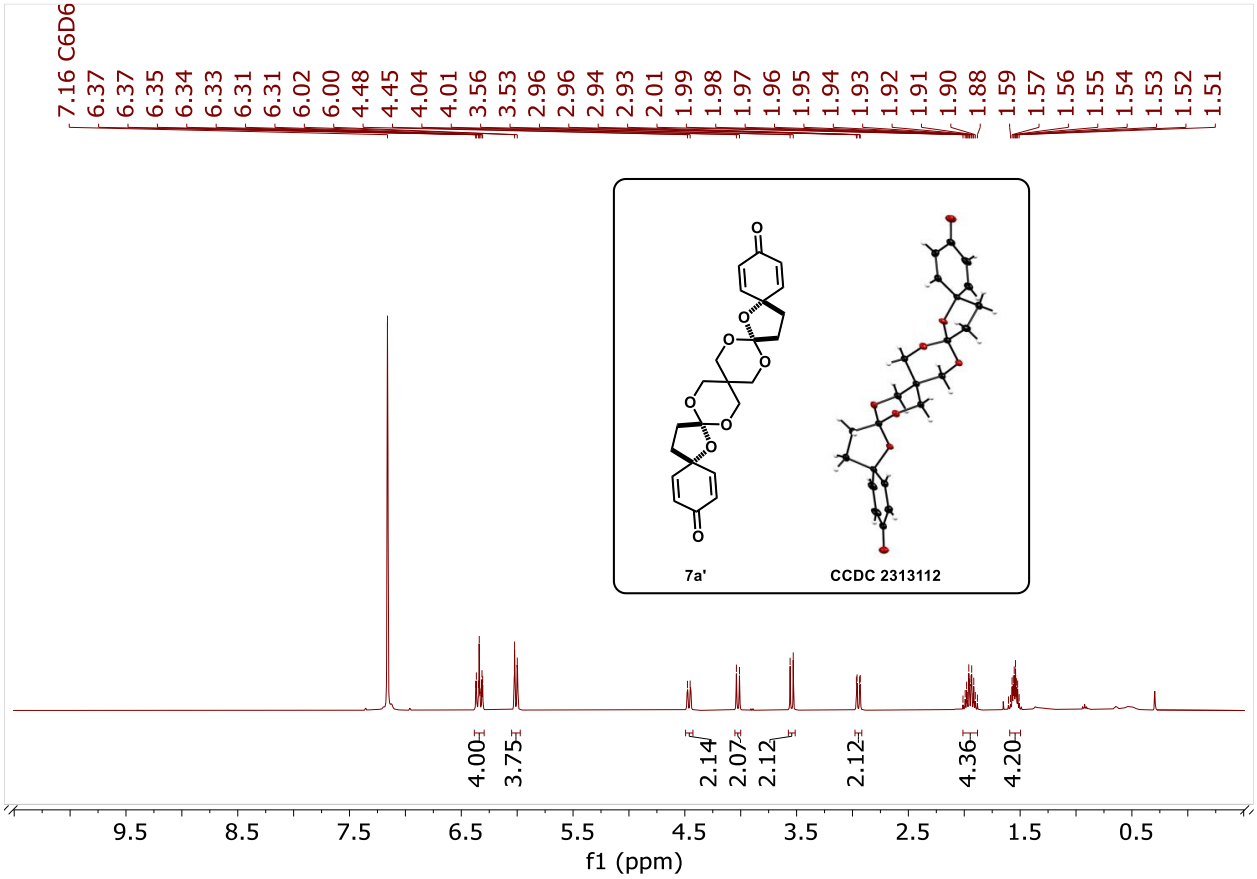
^{1}H NMR (500 MHz, Benzene-D6) spectrum of **7z**



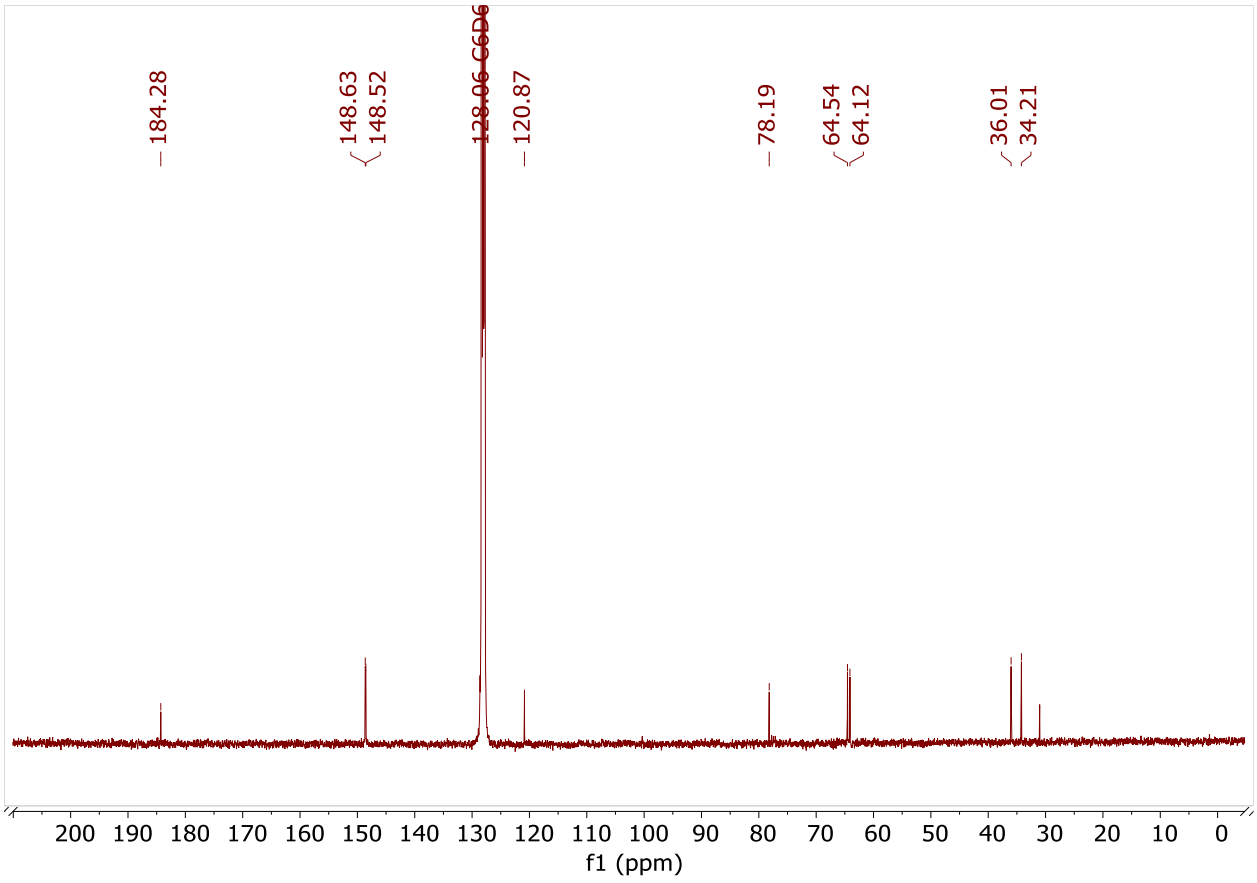
^{13}C{^{1}H} NMR (126 MHz, Benzene-D6) spectrum of **7z**



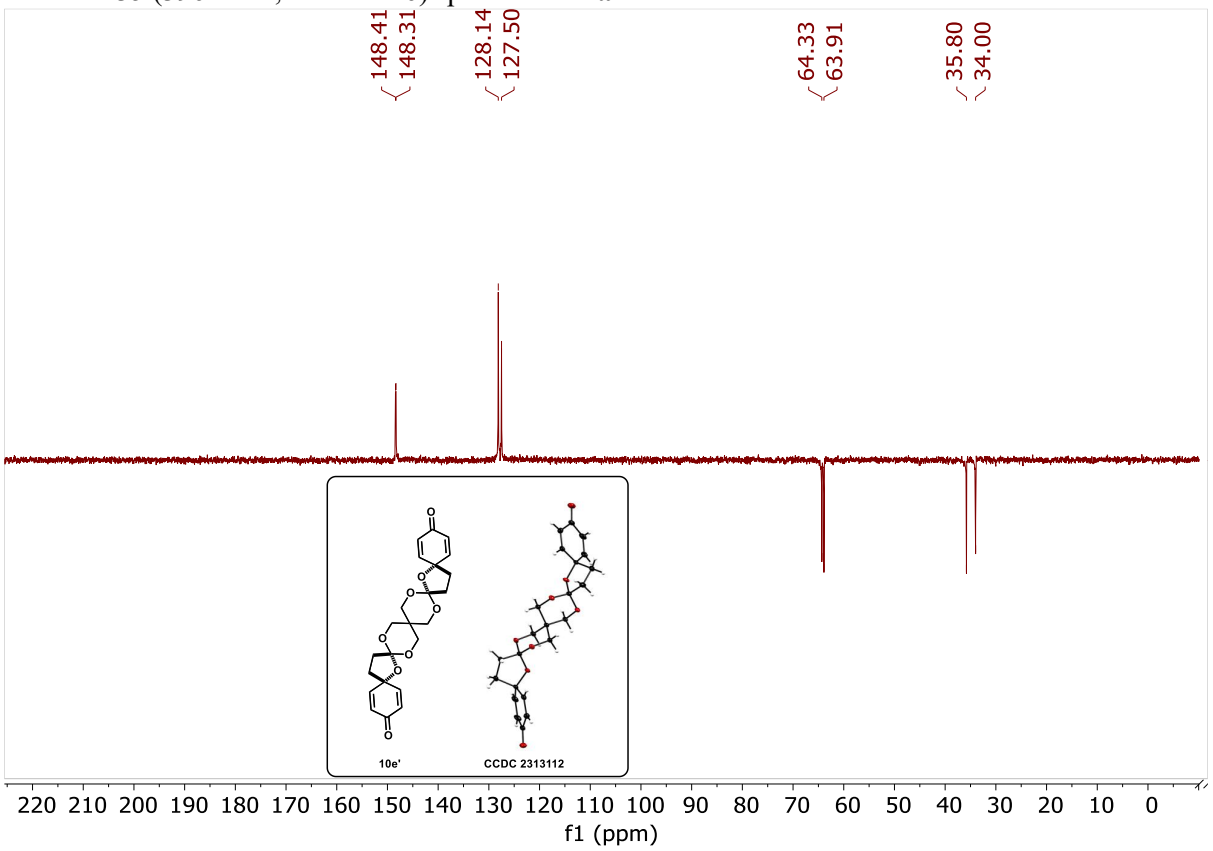
^{1}H NMR (400 MHz, BENZENE-D6) spectrum of **7a'**



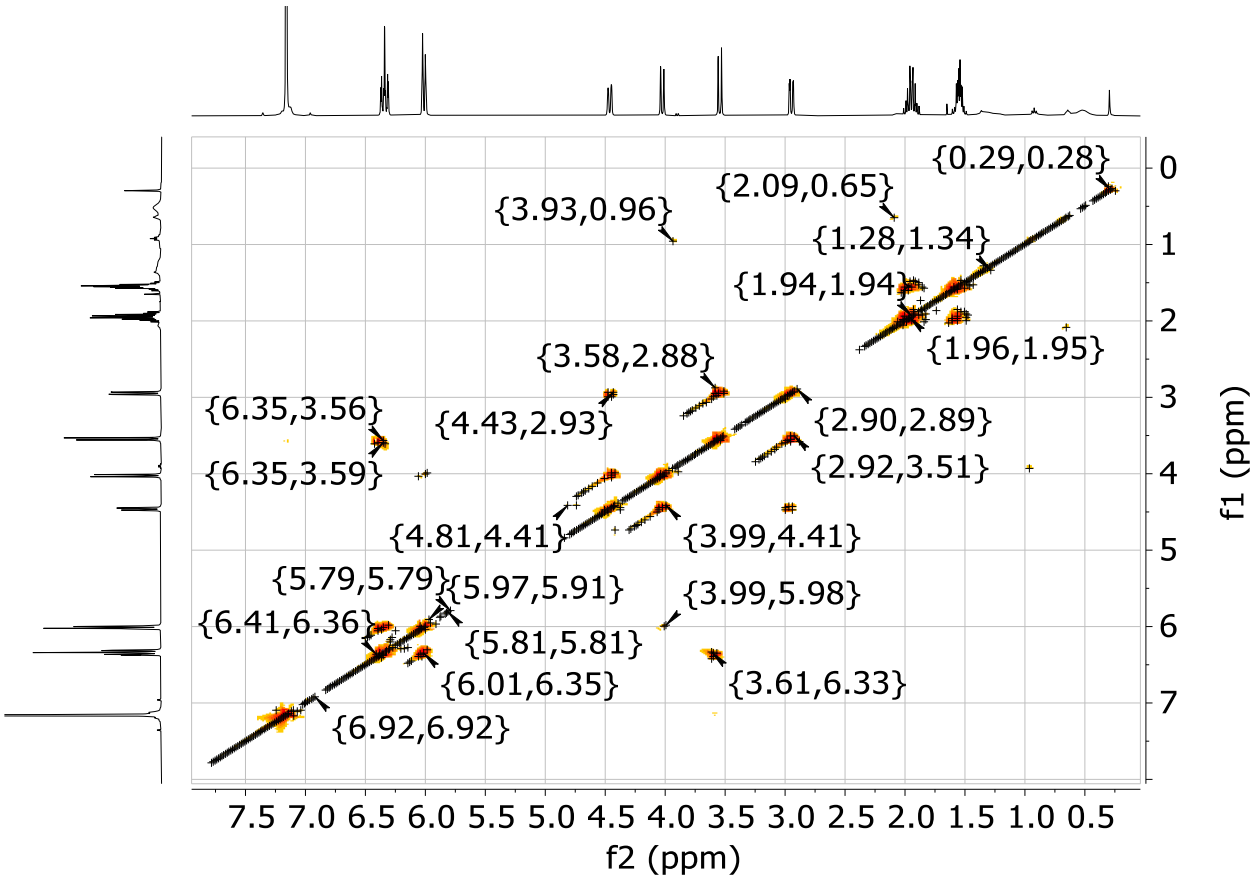
^{13}C{^{1}H} NMR (101 MHz, BENZENE-D6) spectrum of **7a'**



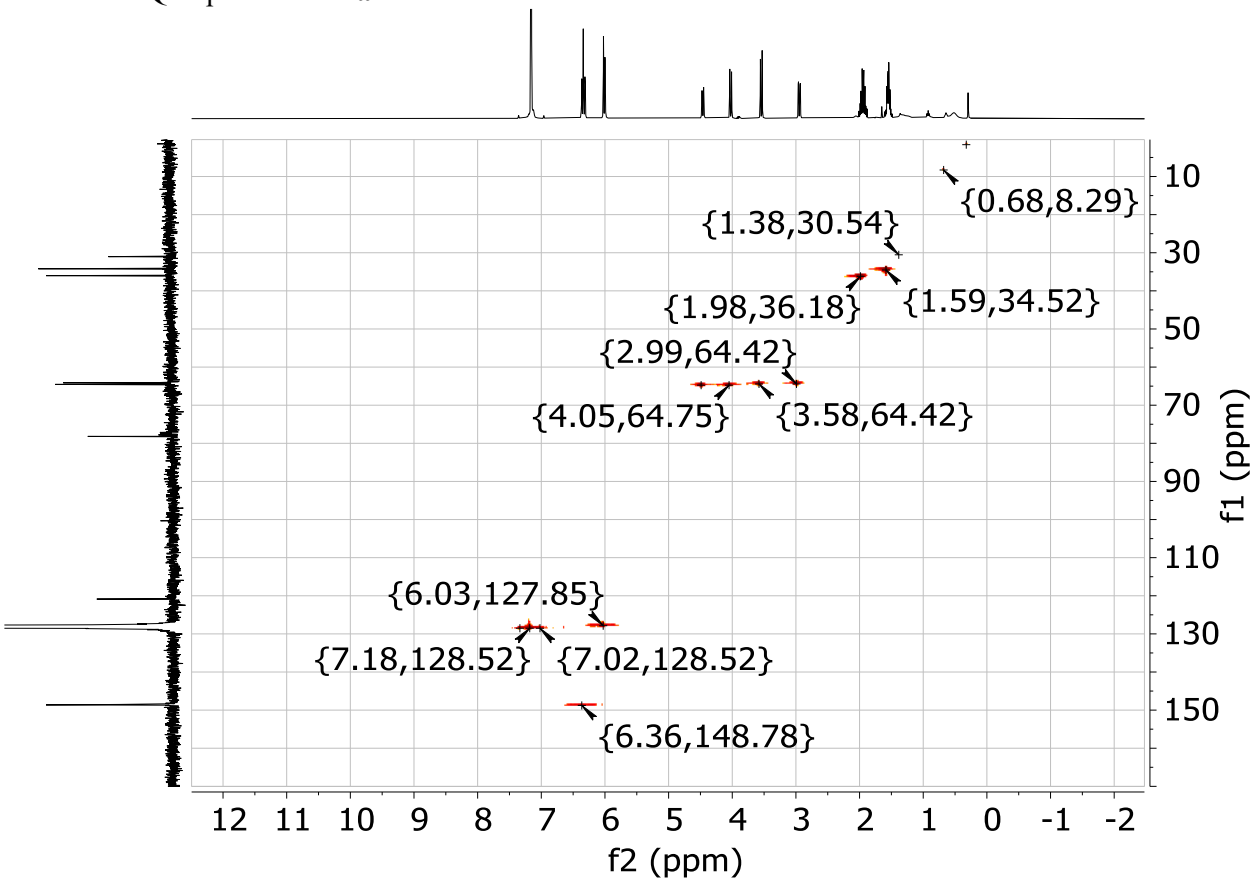
DEPT - 135 (396 MHz, DMSO-D6) spectrum of **7a'**



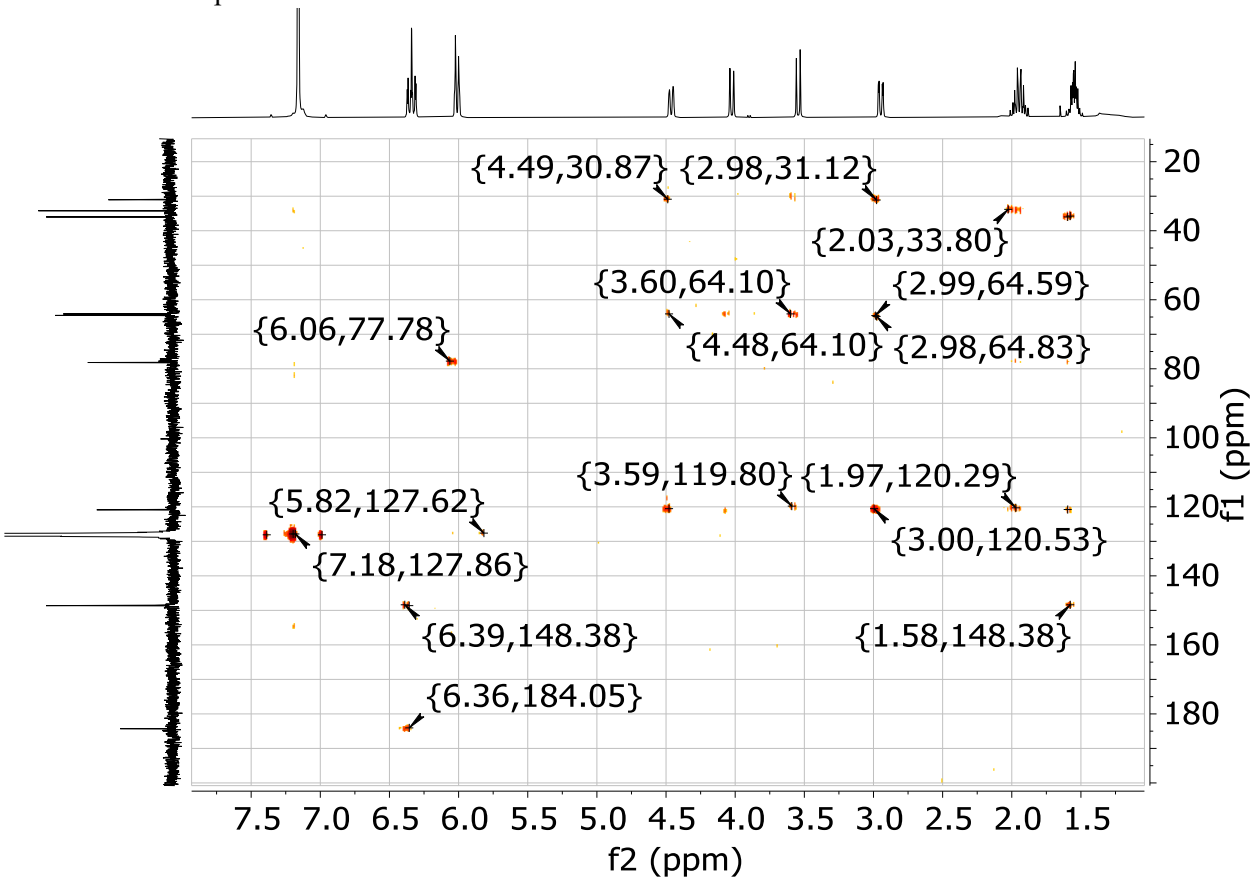
^{1}H - ^{1}H COSY NMR spectrum of **7a'**



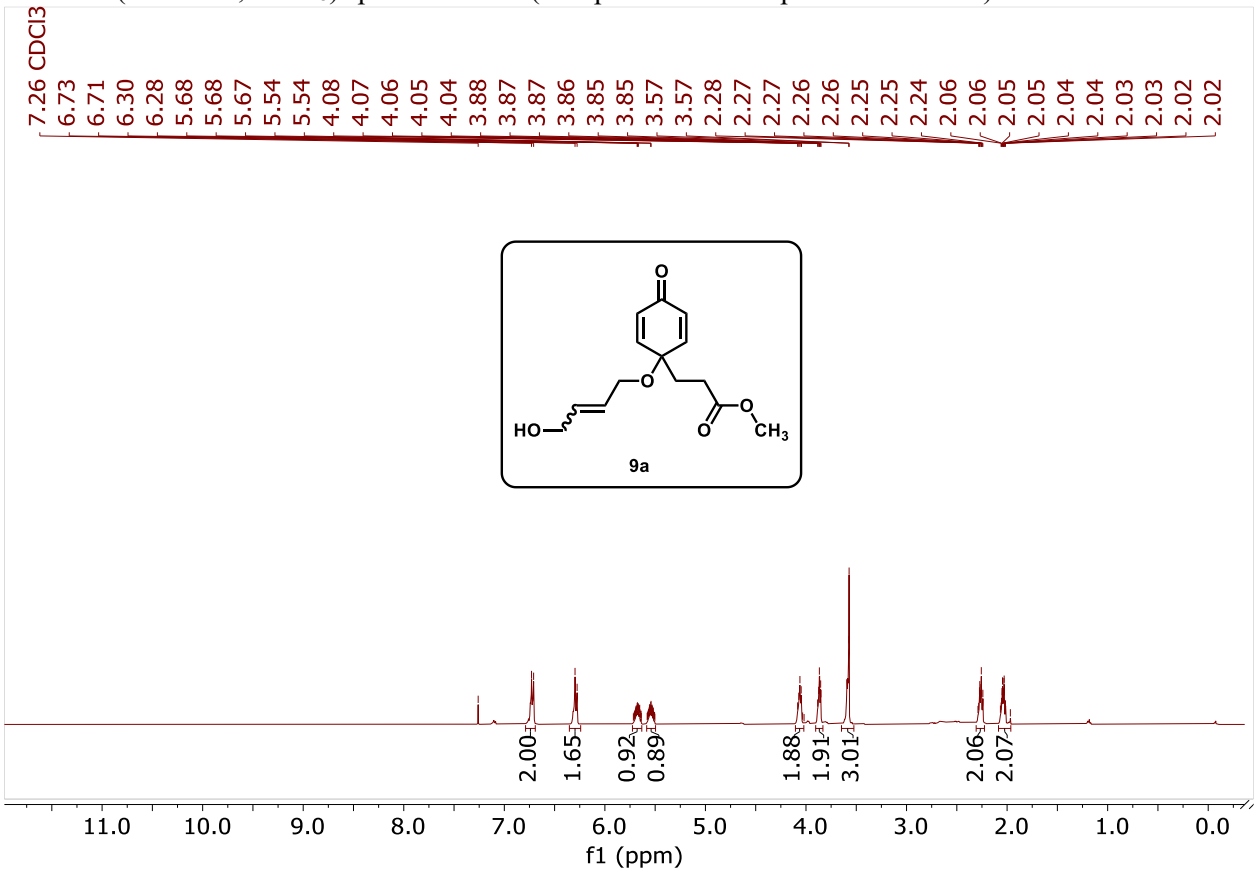
$^{1}H - ^{13}C$ HSQC spectrum of **7a'**



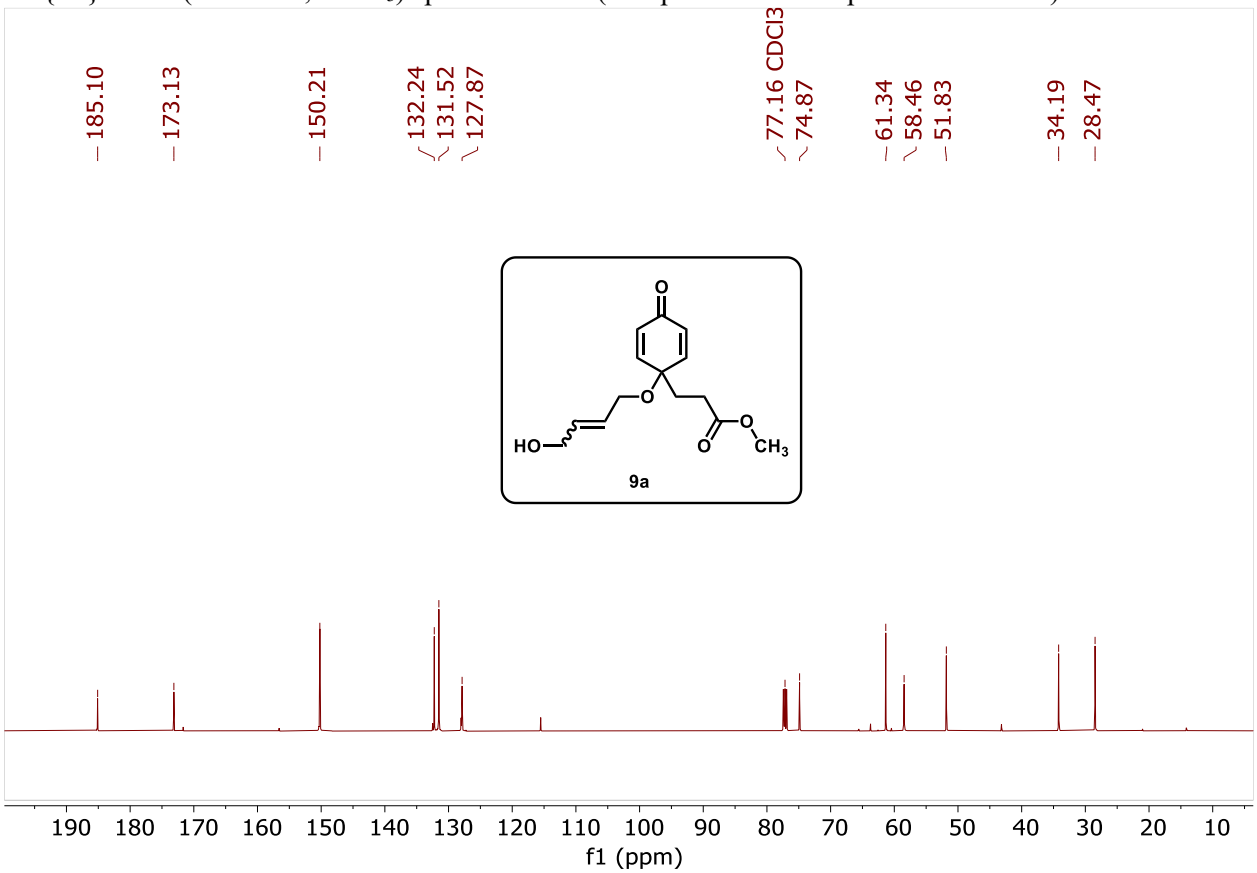
$^{1}H - ^{13}C$ HMBC spectrum of **7a'**



^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **9a** (side product of the optimised reaction)

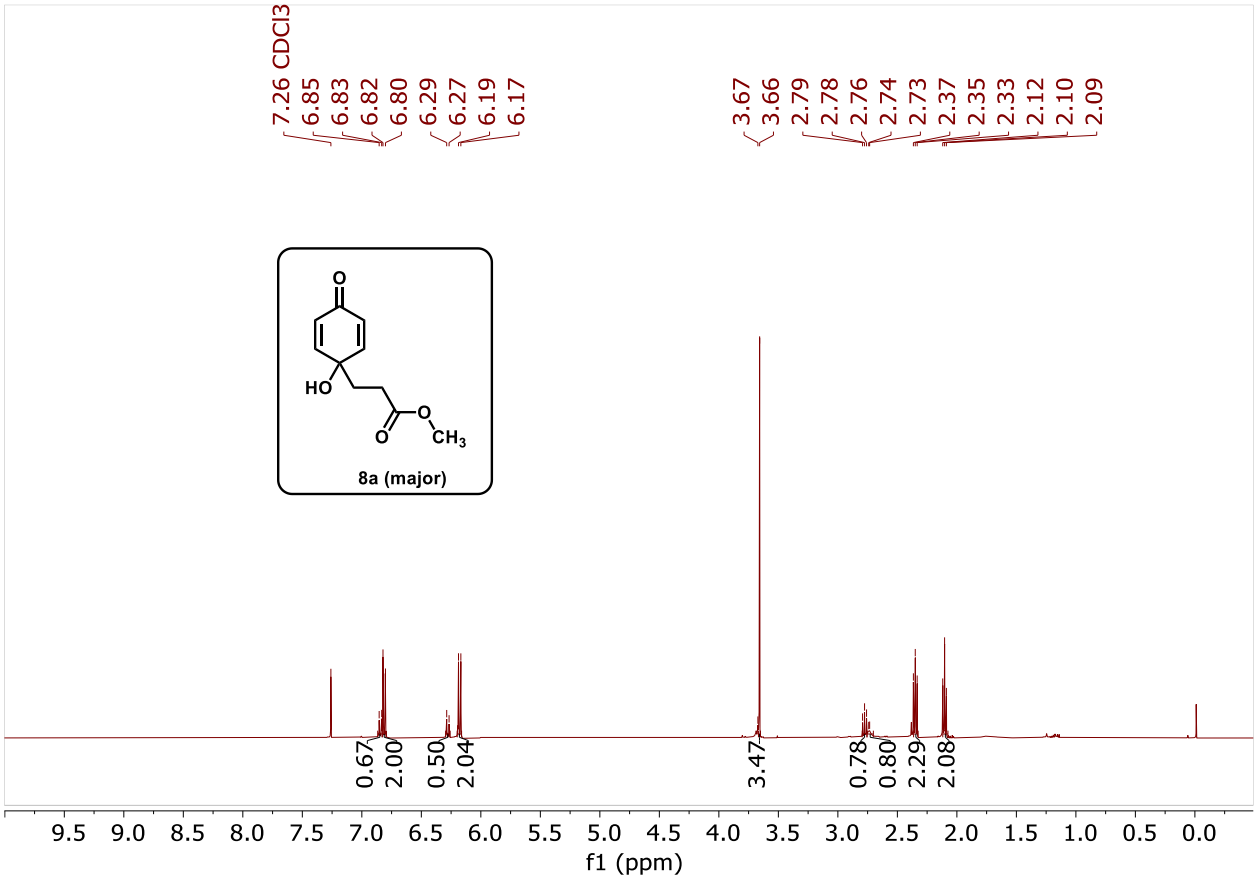


^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) spectrum of **9a** (side product of the optimised reaction)

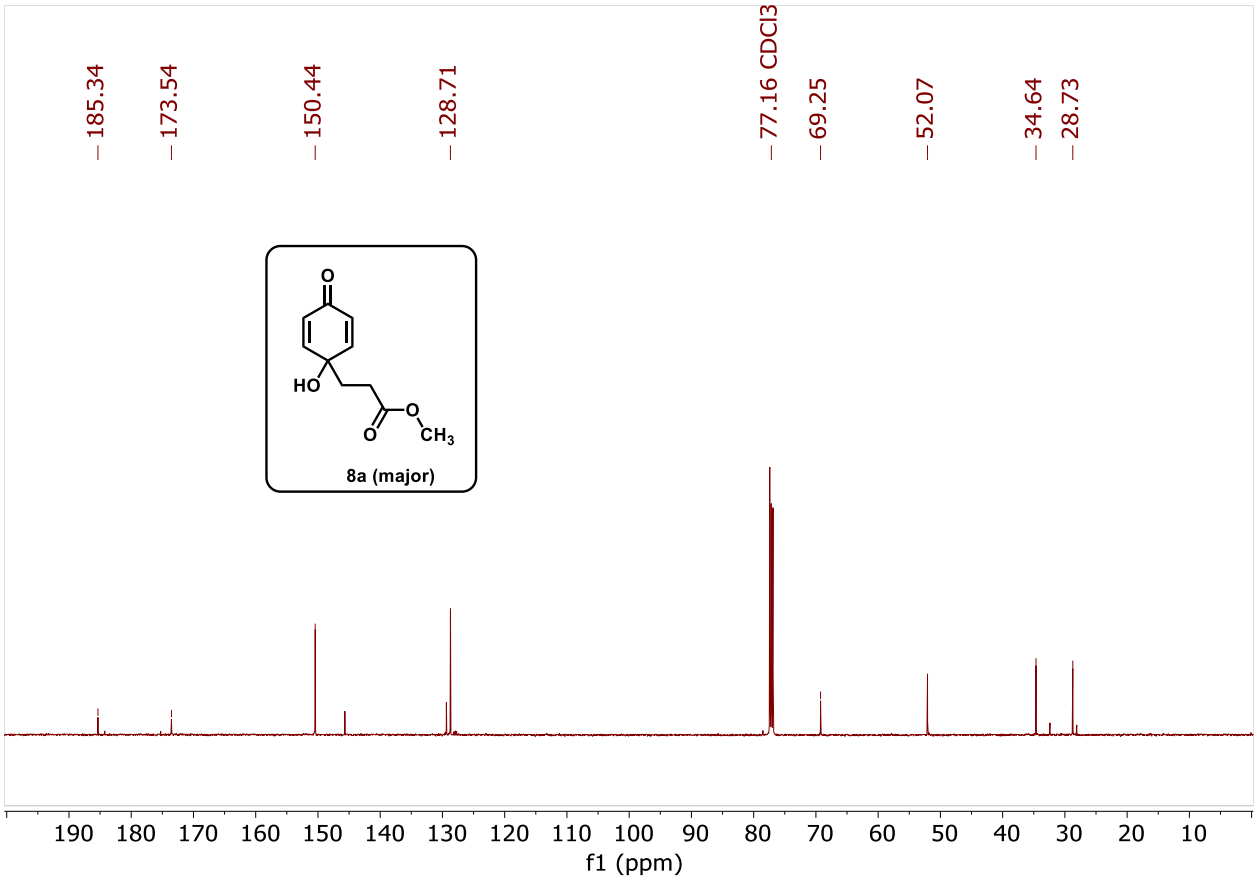


^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **8a**

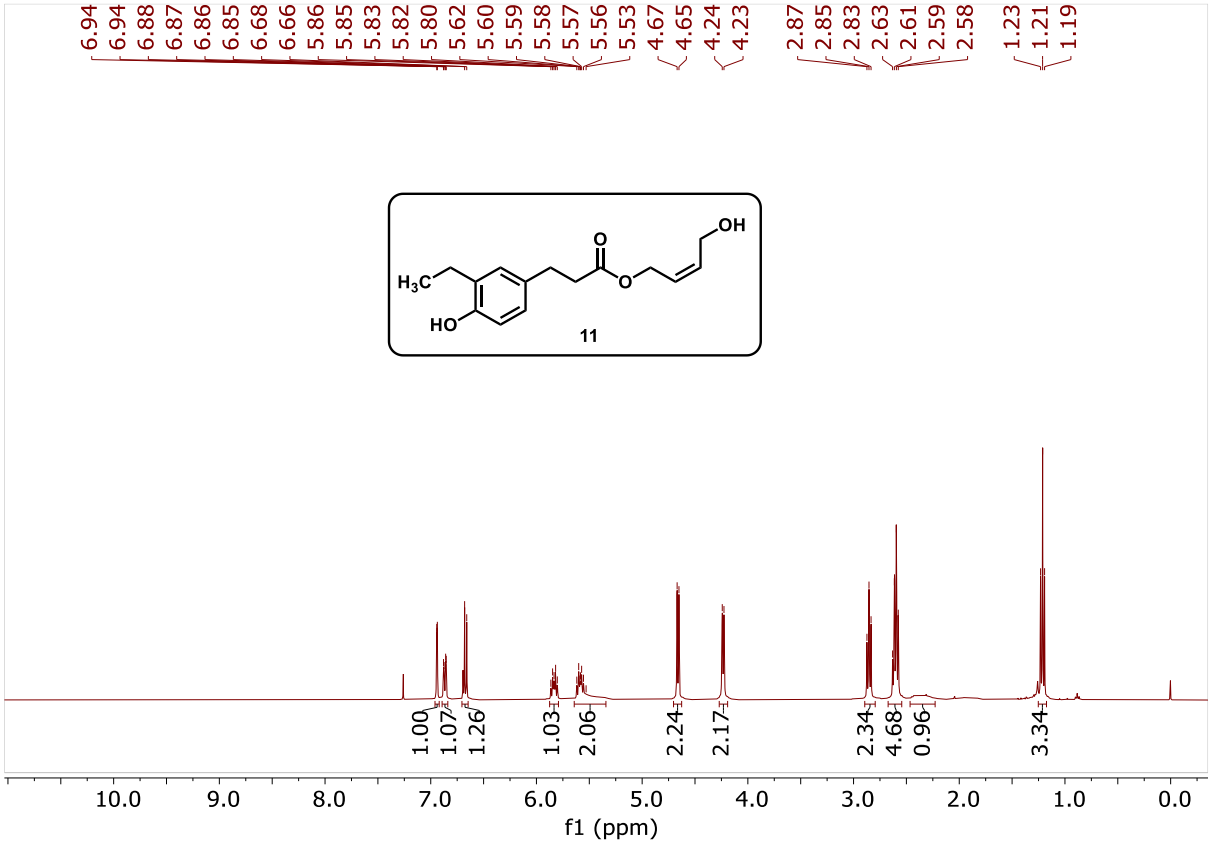
(side product of the optimized reaction)



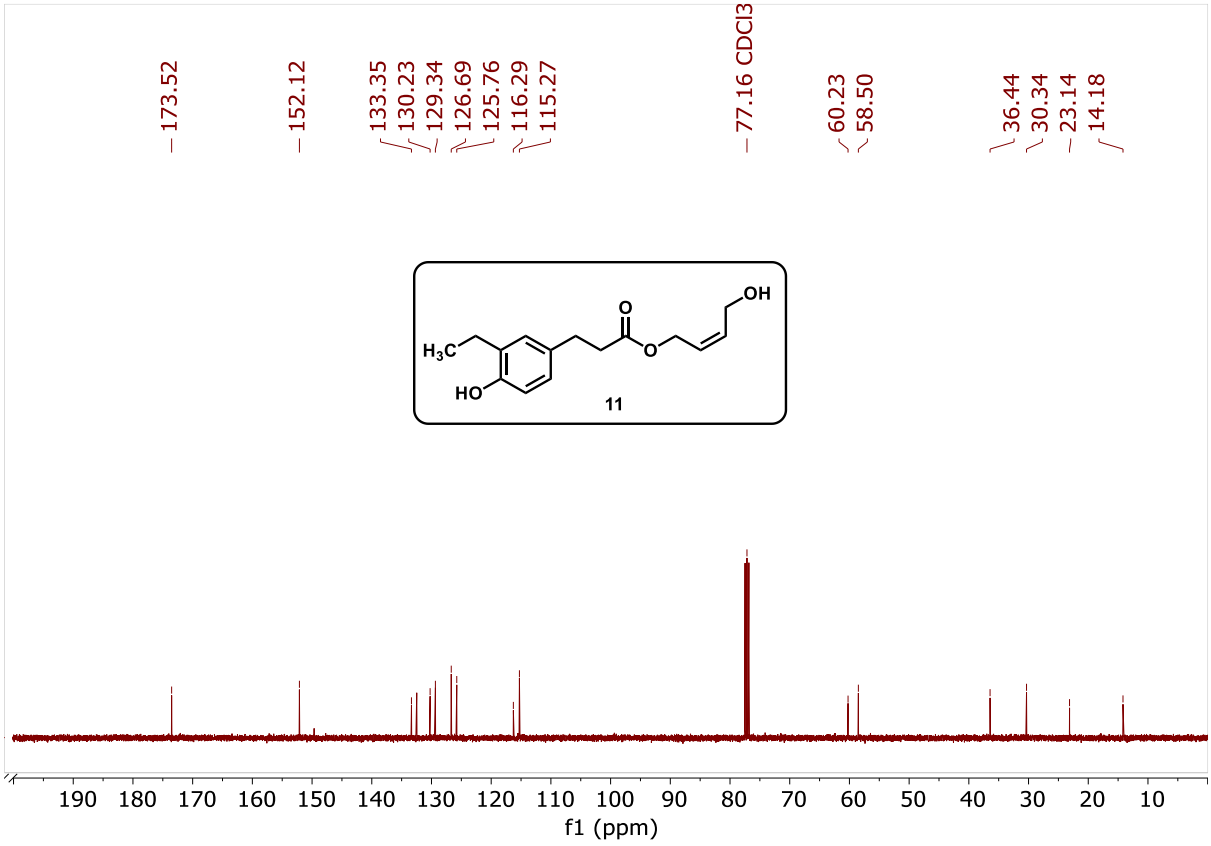
$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) spectrum of **8a** (side product of the optimized reaction)



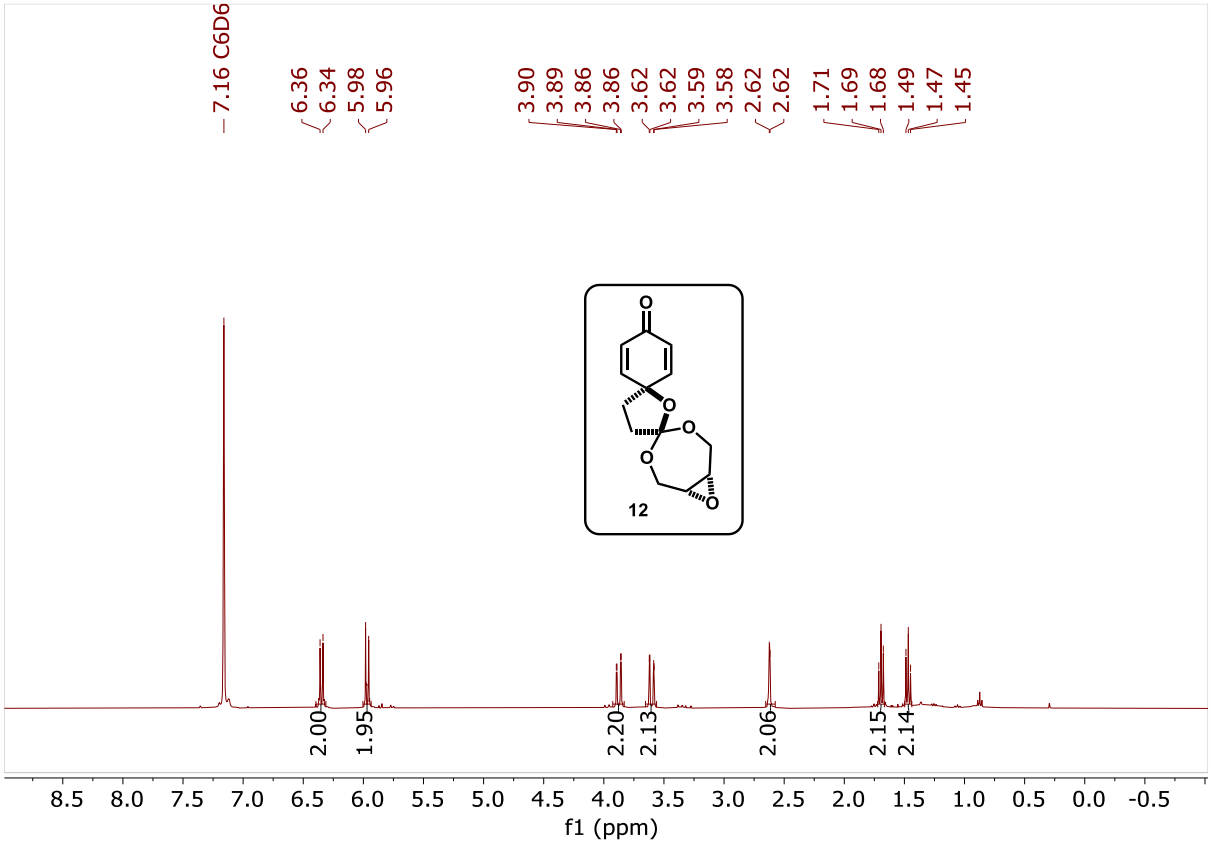
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **11**



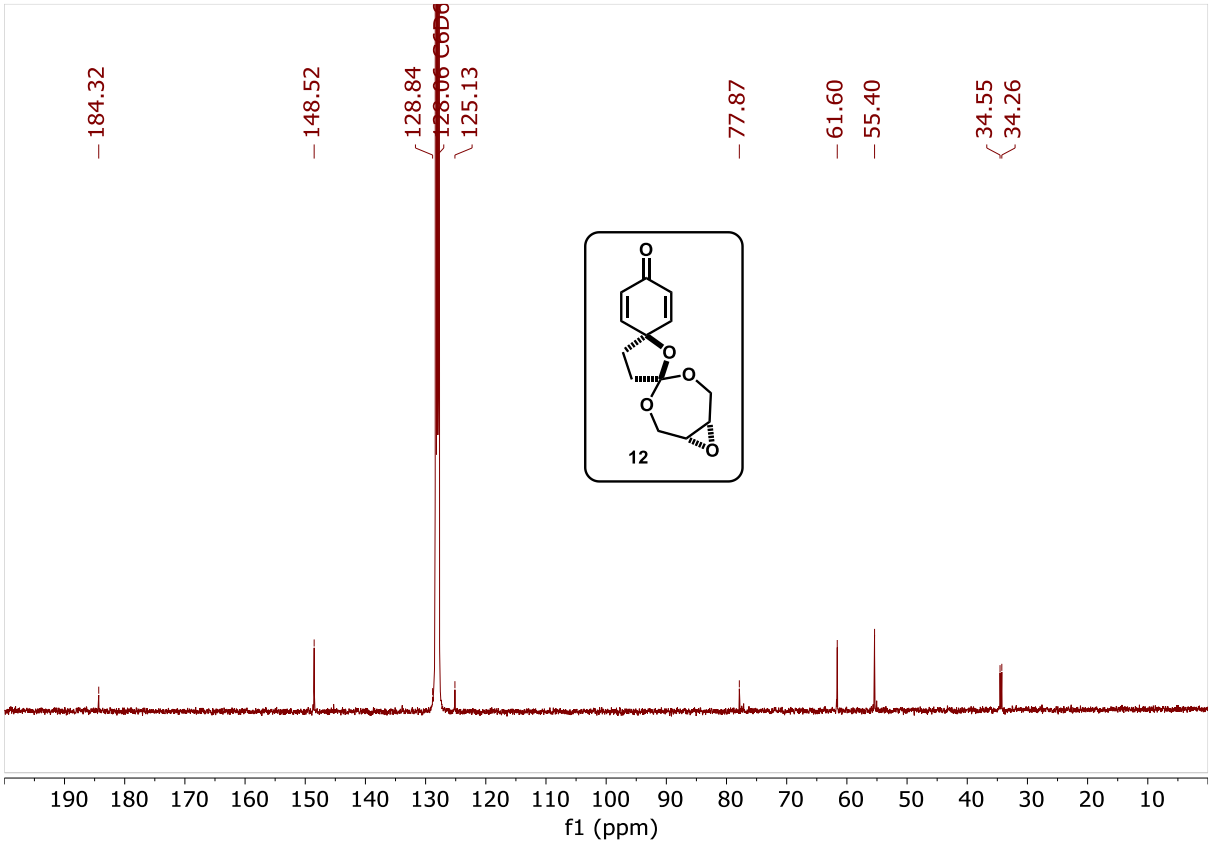
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) spectrum of **11**



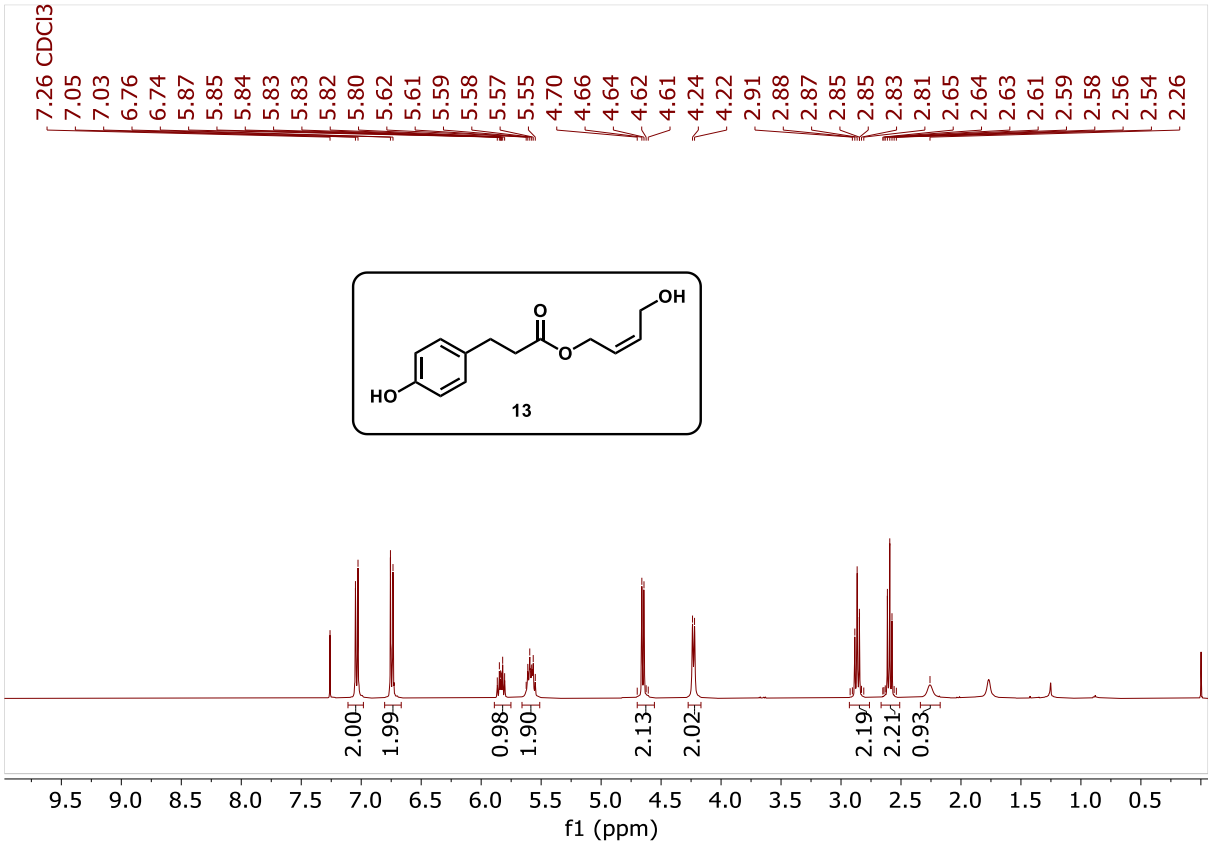
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **12**



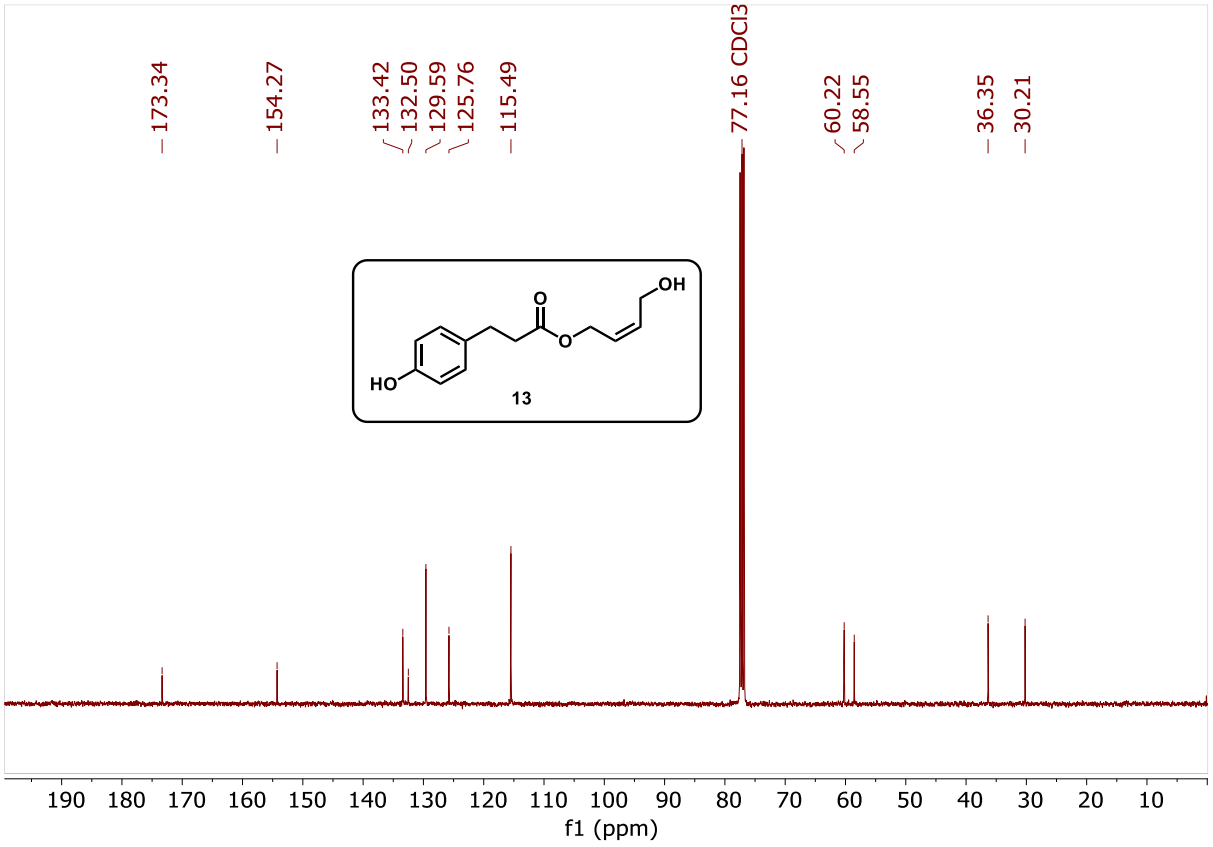
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) spectrum of **12**



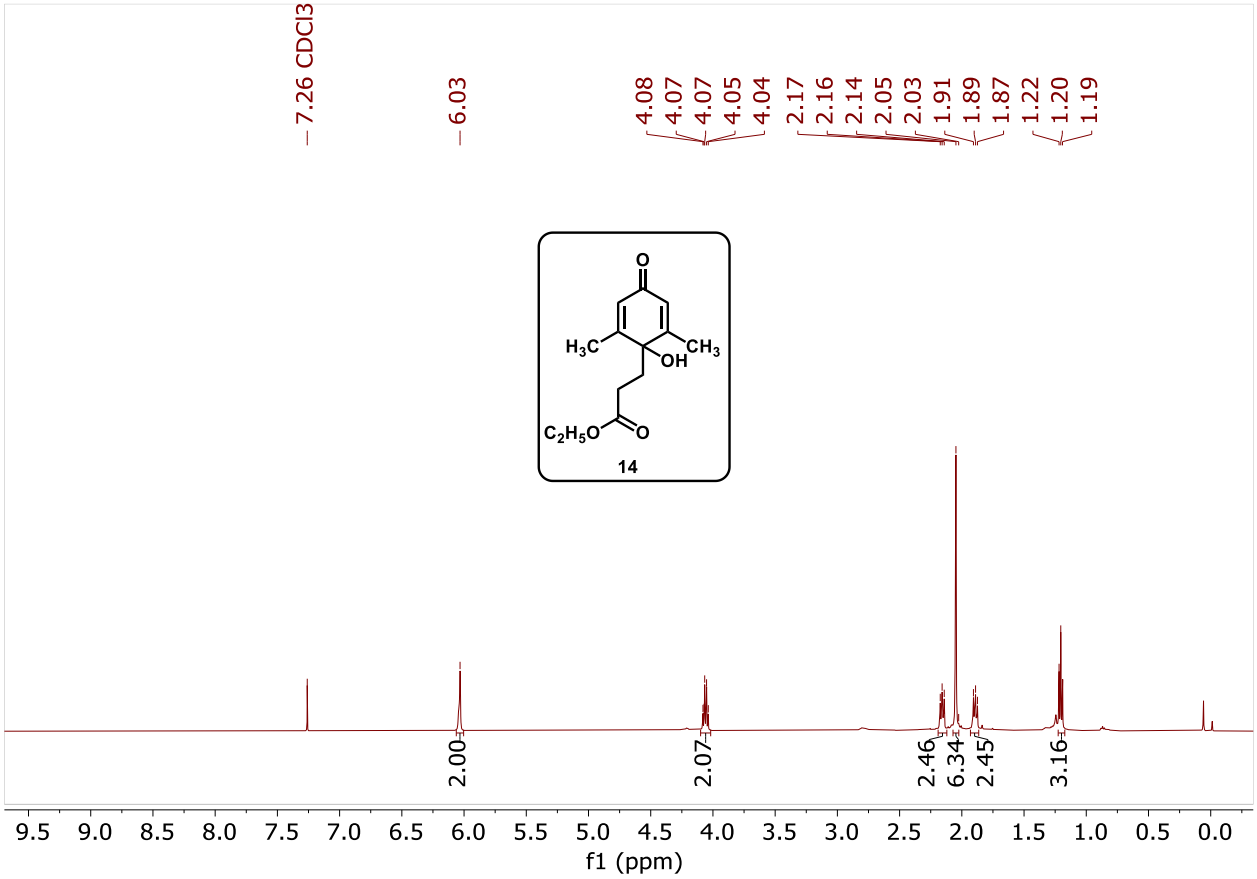
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **13**



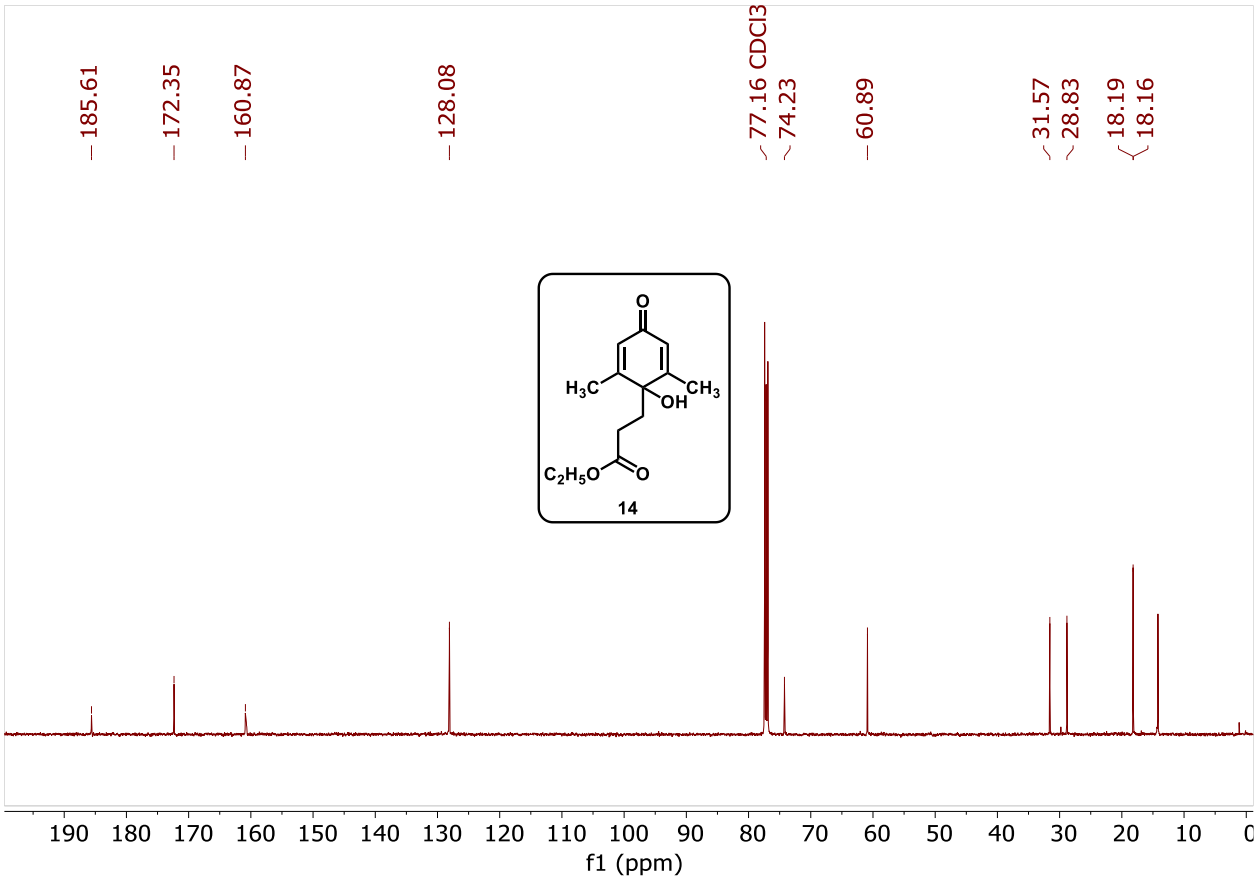
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) spectrum of **13**



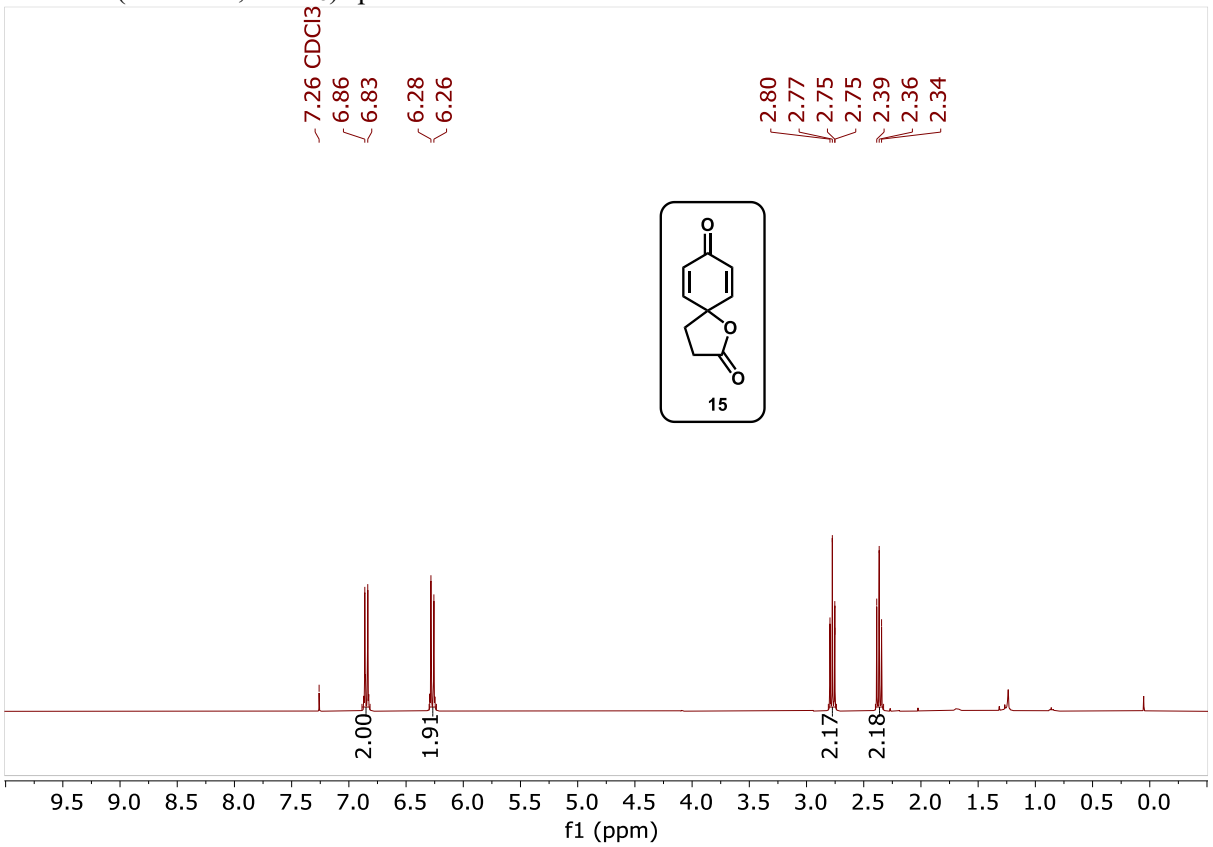
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **14**



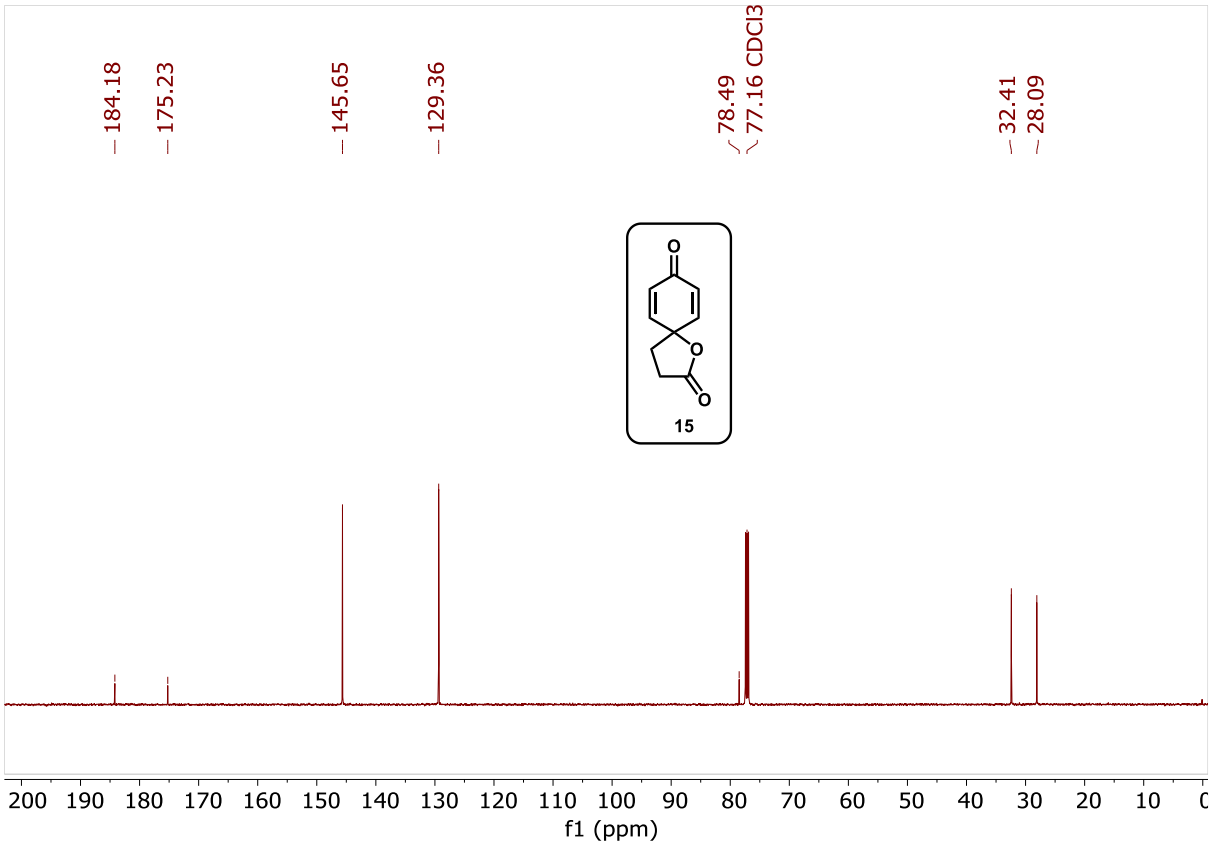
^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) spectrum of **14**



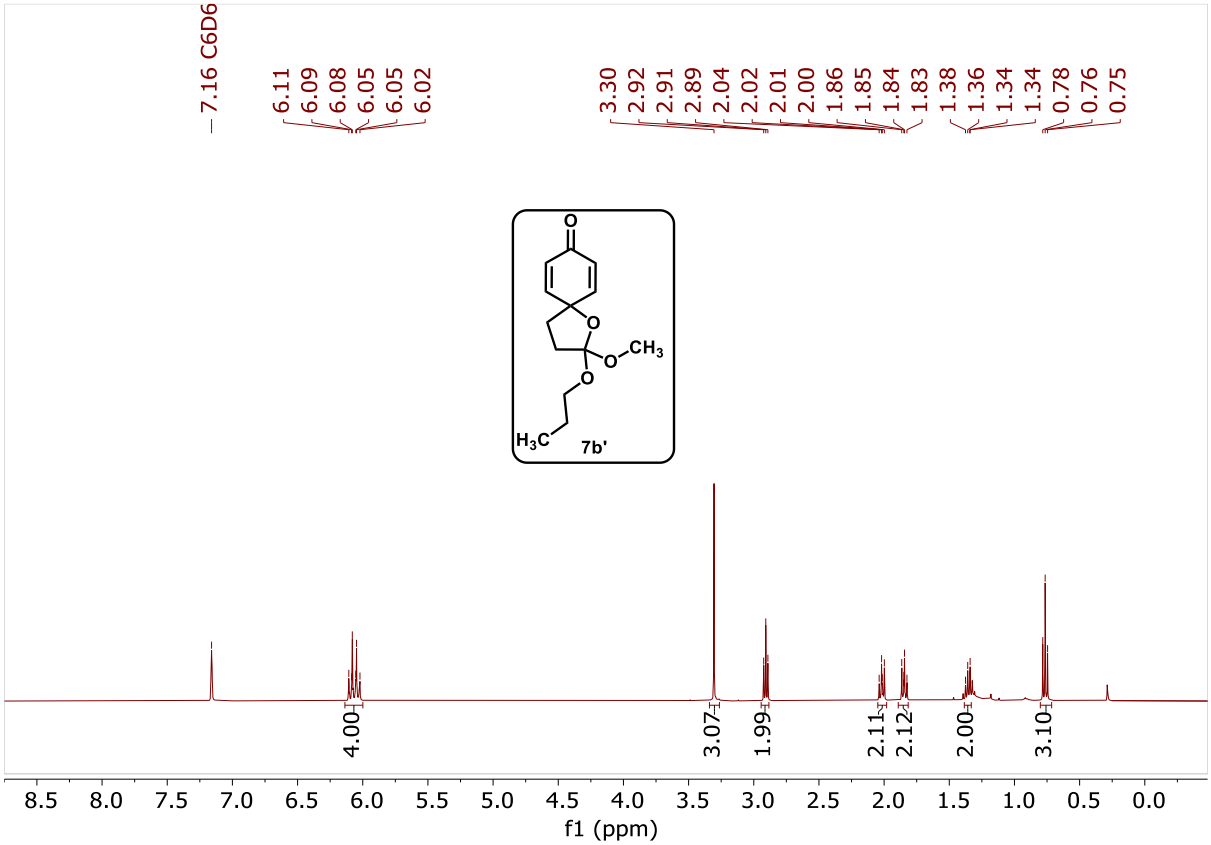
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **15**



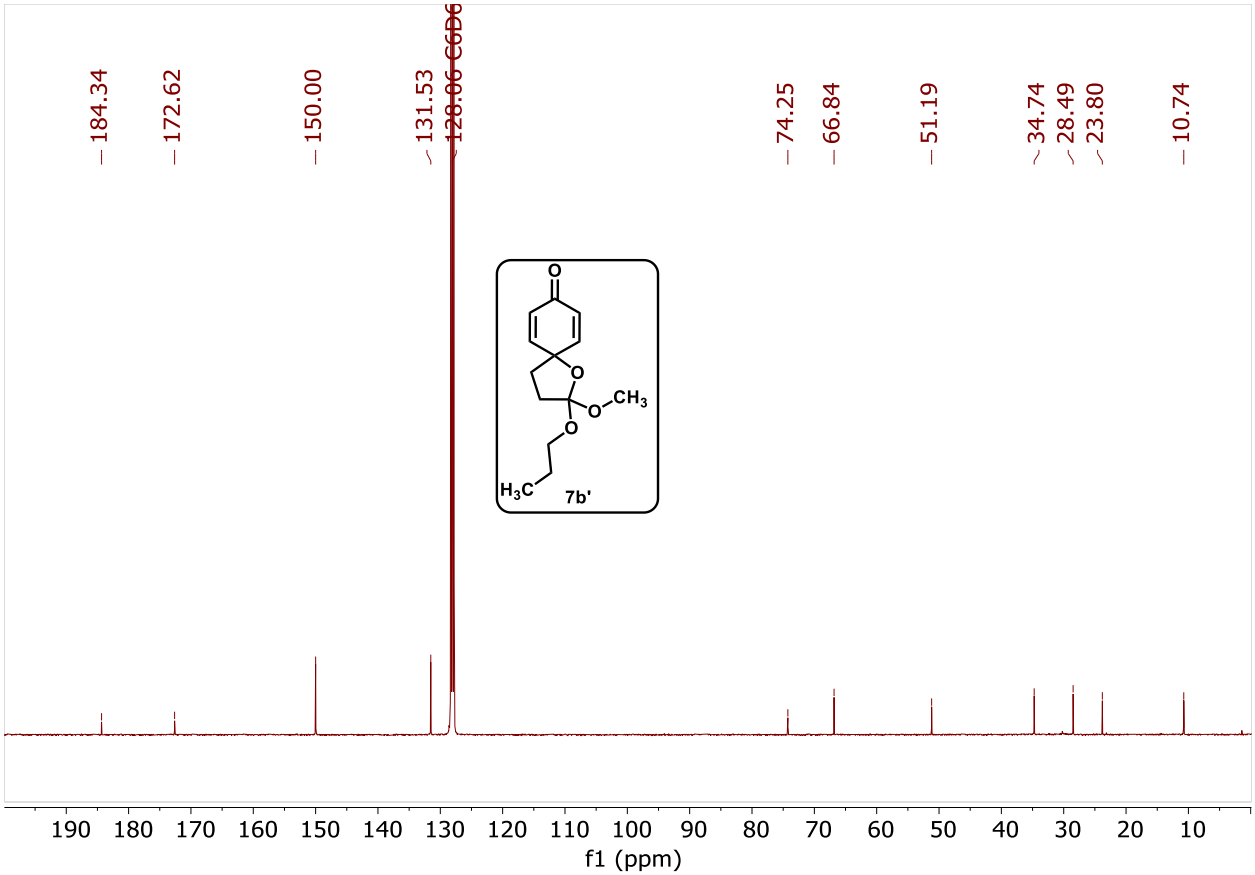
^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) spectrum of **15**



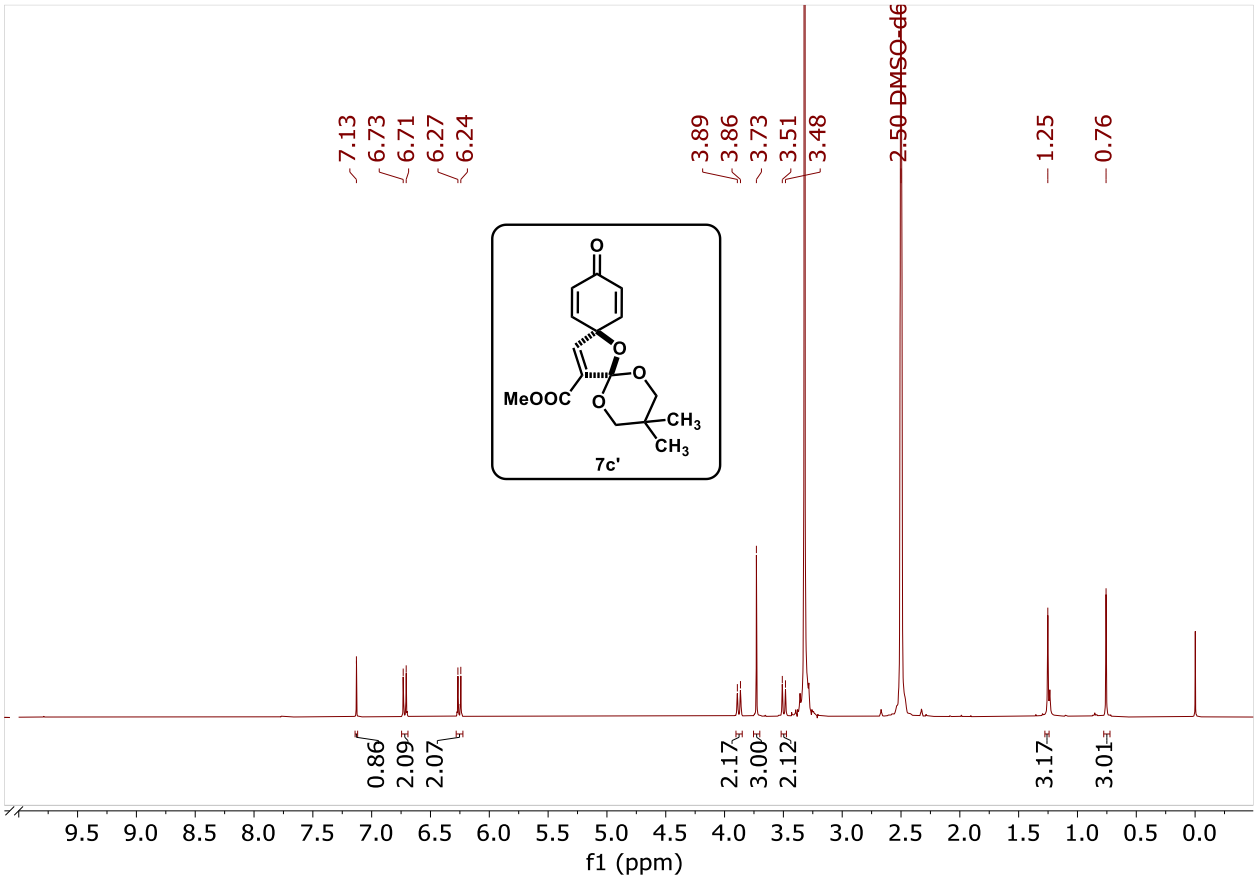
^{1}H NMR (396 MHz, BENZENE-D_6) spectrum of **7b'**



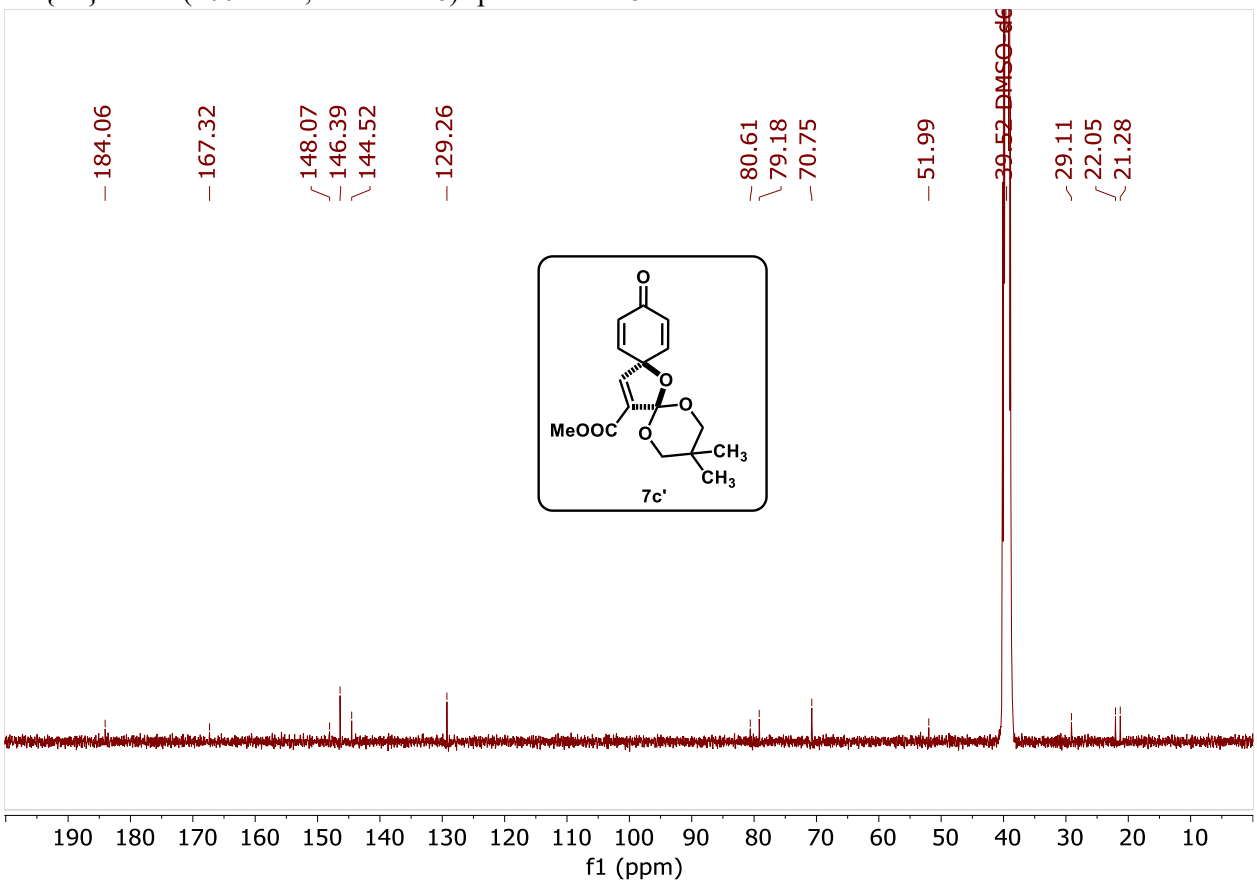
^{13}C{^{1}H} NMR (396 MHz, BENZENE-D_6) spectrum of **7b'**



^{1}H NMR (400 MHz, DMSO-D6) spectrum of **7c'**



^{13}C{^{1}H} NMR (100 MHz, DMSO-D6) spectrum of **7c'**



^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **11a'**