Laccase-catalyzed phenol oxidation. Rapid assignment of ring-proton deficient polycyclic benzofuran regioisomers by experimental ^{1}H-^{13}C long-range coupling constants and DFT-predicted product formation.

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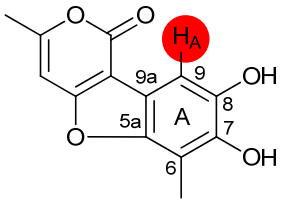
Supplementary Information

1. Computational studies.

1.1 Calculated and experimental ^{13}C NMR chemical shifts of selected A-ring carbons of 4a in DMSO (δ in ppm).



4a

C	C-9a	C-5a	C-7	C-8
Experimental	112.31	148.09	143.36	143.78
ACD/CNMR in DMSO	118.43 (6.22) [a]	156.61 (3.28) [a]	143.73 (4.57) [a]	145.93 (3.74) [a]
DFT GIAO calculations [b]				
B3LYP/6-311+G(2d,p)//B3LYP/6-31G(d) with TMS as reference compound	120.47	156.01	151.23	149.05
B3LYP/6-311+G(2d,p)//B3LYP/6-31G(d) with benzene as reference compound	114.19	149.73	144.95	142.77
mPW1PW91/6-311+G(2d,p)// mPW1PW91/6-31G(d) with TMS as reference compound	118.34	152.98	148.61	146.70
mPW1PW91/6-311+G(2d,p)// mPW1PW91/6-31G(d) with benzene as reference compound	113.03	147.67	143.30	141.43

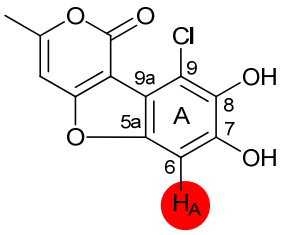
[a] Confidence limits.

[b] Theoretical ^{13}C NMR chemical shifts (δ_a) were derived by the following equation:

$\delta_a = \sigma_{ref} - \sigma_a + \delta_{ref}$

where σ_{ref} and σ_a are the calculated NMR isotropic magnetic shielding tensors of the reference compound and carbon a of the compound of interest: σ_{TMS} = 187.509 ppm and $\sigma_{benzene}$ = 53.933 ppm at the mPW1PW91/6-311+G(2d,p)// mPW1PW91/6-31G(d) level; σ_{TMS} = 182.941 ppm and $\sigma_{benzene}$ = 48.390 ppm at the B3LYP/6-311+G(2d,p)//B3LYP/6-31G(d) level. δ_{ref} represents the chemical shift of the reference compound in deuterated DMSO: δ_{TMS} = 0 ppm; $\delta_{benzene}$ = 128.27 ppm.

1.2 Calculated and experimental ^{13}C NMR chemical shifts of selected A-ring carbons of 3d in DMSO (δ in ppm).



3d

C	C-9a	C-5a	C-7	C-8
Experimental	112.83	147.77	146.19	141.12
ACD/CNMR in DMSO	117.32 (12.99) [a]	152.54 (3.75) [a]	147.45 (3.64) [a]	143.59 (4.58) [a]
DFT GIAO calculations [b]				
B3LYP/6-311+G(2d,p)//B3LYP/6-31G(d) with TMS as reference compound	120.79	156.74	152.84	146.57
B3LYP/6-311+G(2d,p)//B3LYP/6-31G(d) with benzene as reference compound	114.51	150.46	146.56	140.30
mPW1PW91/6-311+G(2d,p)// mPW1PW91/6-31G(d) with TMS as reference compound	119.32	152.82	149.09	146.25
mPW1PW91/6-311+G(2d,p)// mPW1PW91/6-31G(d) with benzene as reference compound	114.01	147.56	143.78	140.94

[a] Confidence limits.

[b] Theoretical ^{13}C NMR chemical shifts (δ_a) were derived by the following equation:

$\delta_a = \sigma_{ref} - \sigma_a + \delta_{ref}$

where σ_{ref} and σ_a are the calculated NMR isotropic magnetic shielding tensors of the reference compound and carbon a of the compound of interest: σ_{TMS} = 187.509 ppm and $\sigma_{benzene}$ = 53.933 ppm at the mPW1PW91/6-311+G(2d,p)// mPW1PW91/6-31G(d) level; σ_{TMS} = 182.941 ppm and $\sigma_{benzene}$ = 48.390 ppm at the B3LYP/6-311+G(2d,p)//B3LYP/6-31G(d) level. δ_{ref} represents the chemical shift of the reference compound in deuterated DMSO: δ_{TMS} = 0 ppm; $\delta_{benzene}$ = 128.27 ppm.

1.3 Cartesian coordinates of 4a of the NMR GIAO mPW1PW91/6-311+G(2d,p)// mPW1PW91/6-31G(d) calculation.

C	0.38547	0.50808	0.00003
C	0.81574	-0.82384	0.00004
C	2.14521	-1.22596	-0.00001
C	3.06703	-0.17961	0.
C	2.66209	1.17319	-0.00002
C	1.32827	1.53828	0.00003
O	3.70661	2.0597	0.00013
O	4.38948	-0.47799	-0.00027
C	-1.0478	0.43057	0.0001
C	-1.36543	-0.90888	0.00003
O	-0.26308	-1.68636	-0.00003
C	-2.07484	1.42633	0.00013
O	-3.37472	0.88375	0.00005
C	-3.66066	-0.43567	0.00005
C	-2.69414	-1.38981	-0.00001
O	-1.9672	2.62641	-0.00011
C	-5.12758	-0.68864	-0.00014
C	2.58922	-2.65651	0.00014
H	1.01508	2.57707	0.00001
H	3.36536	2.96209	-0.00001
H	4.87271	0.36244	-0.00045
H	-2.93565	-2.44318	0.00002
H	-5.59257	-0.23543	0.88097
H	-5.59239	-0.23522	-0.88124
H	-5.33721	-1.75921	-0.00028
H	1.73235	-3.3317	-0.00059
H	3.20338	-2.87317	0.87948
H	3.2047	-2.8729	-0.87834

1.4 Cartesian coordinates of 4a of the NMR GIAO B3LYP/6-311+G(2d,p)//B3LYP/6-31G(d) calculation.

C	0.3873720	0.5069360	-0.0000570
C	0.8214010	-0.8287320	0.0000040
C	2.1543860	-1.2306540	0.0000290
C	3.0783570	-0.1798340	0.0000230
C	2.6705630	1.1759500	-0.0000570
C	1.3322540	1.5403200	-0.0000520
O	3.7192140	2.0721940	0.0001550
O	4.4095850	-0.4812930	-0.0001010
C	-1.0508080	0.4310130	-0.0000340
C	-1.3747000	-0.9113350	-0.0000830

O	-0.2665400	-1.6967880	-0.0000380
C	-2.0752600	1.4337510	0.0000060
O	-3.3904460	0.8909690	-0.0000270
C	-3.6786920	-0.4365740	-0.0001340
C	-2.7073120	-1.3912170	-0.0000680
O	-1.9644480	2.6376890	0.0000880
C	-5.1518620	-0.6907880	0.0001320
C	2.5993790	-2.6684060	0.0001430
H	1.0183020	2.5800480	-0.0001690
H	3.3722010	2.9767600	-0.0001190
H	4.8960580	0.3614680	-0.0003230
H	-2.9471360	-2.4463200	-0.0002560
H	-5.6190970	-0.2377870	0.8824830
H	-5.6193660	-0.2377970	-0.8820780
H	-5.3609240	-1.7633600	0.0001770
H	1.7402730	-3.3431910	-0.0007750
H	3.2143290	-2.8874930	0.8805290
H	3.2159580	-2.8870860	-0.8791900

1.5 Cartesian coordinates of 3d of the NMR GIAO mPW1PW91/6-311+G(2d,p)// mPW1PW91/6-31G(d) calculation.

C	3.75019	-0.4329	0.00024
C	2.91039	-1.49703	0.00034
C	1.53668	-1.18189	-0.00003
C	1.02171	0.10264	-0.00032
C	1.93268	1.21018	-0.00011
O	3.28144	0.83495	-0.00013
O	0.56742	-2.11454	0.00001
C	-0.62637	-1.43527	-0.00019
C	-0.41837	-0.04901	-0.00044
C	-1.8619	-2.05803	-0.00008
C	-2.96918	-1.2245	0.
C	-2.82742	0.18421	0.00004
C	-1.56221	0.76482	-0.00047
O	-3.92055	0.97433	0.0008
O	-4.25292	-1.64831	-0.00005
Cl	-1.46925	2.49485	-0.00064
O	1.71398	2.401	0.0002
C	5.23524	-0.48889	0.00065
H	3.27444	-2.51883	0.00072
H	-1.96147	-3.14116	0.00001
H	-4.7242	0.41876	0.00297
H	-4.30632	-2.6327	0.00043
H	5.63596	0.02031	0.88326
H	5.57875	-1.52412	0.00107
H	5.63642	0.01972	-0.8821

1.6 Cartesian coordinates of 3d of the NMR GIAO B3LYP/6-311+G(2d,p)//B3LYP/6-31G(d) calculation.

C	0.4155750	-0.0697660	-0.0000230
C	0.6207730	-1.4637720	-0.0000550
C	1.8559960	-2.0929880	-0.0000400
C	2.9719690	-1.2642540	-0.0000330
C	2.8252270	0.1434390	0.0000040
C	1.5649200	0.7387260	-0.0000010
O	4.0027820	0.8392310	-0.0000240
O	4.2189110	-1.8042850	0.0000800
C	-1.0248060	0.0931470	-0.0000780
C	-1.5527380	-1.1869960	-0.0000090
O	-0.5855290	-2.1374630	0.0000050
C	-1.9147950	1.2285490	-0.0001130
O	-3.2939890	0.8600410	-0.0000540
C	-3.7682990	-0.4083830	0.0000340
C	-2.9360000	-1.4838810	0.0000180
O	-1.6736000	2.4092320	0.0000010
C	-5.2619310	-0.4565470	0.0000770
Cl	1.5000220	2.4896710	0.0000480
H	1.9620170	-3.1708100	-0.0001150
H	3.8050190	1.7924580	-0.0000240
H	4.8572330	-1.0694660	0.0001370
H	-3.3094030	-2.4991140	0.0001220
H	-5.6611360	0.0575820	-0.8819300
H	-5.6170080	-1.4897910	-0.0002000
H	-5.6610580	0.0570570	0.8824300

1.7 Cartesian coordinates of 3f of the NMR GIAO mPW1PW91/6-311+G(2d,p)// mPW1PW91/6-31G(d) calculation

C	-4.1189	-0.36232	-0.05032
C	-3.71808	0.93033	0.03038
C	-2.32214	1.13166	0.03092
C	-1.38045	0.12035	-0.02646
C	-1.83126	-1.23198	-0.16776
O	-3.22578	-1.37376	-0.13873
O	-1.75035	2.34896	0.08286
C	-0.39084	2.13897	0.05796
C	-0.08658	0.77178	0.00324
C	0.54124	3.16032	0.07014
C	1.87259	2.7736	0.02917
C	2.22272	1.40447	-0.01386
C	1.26968	0.38324	-0.02009

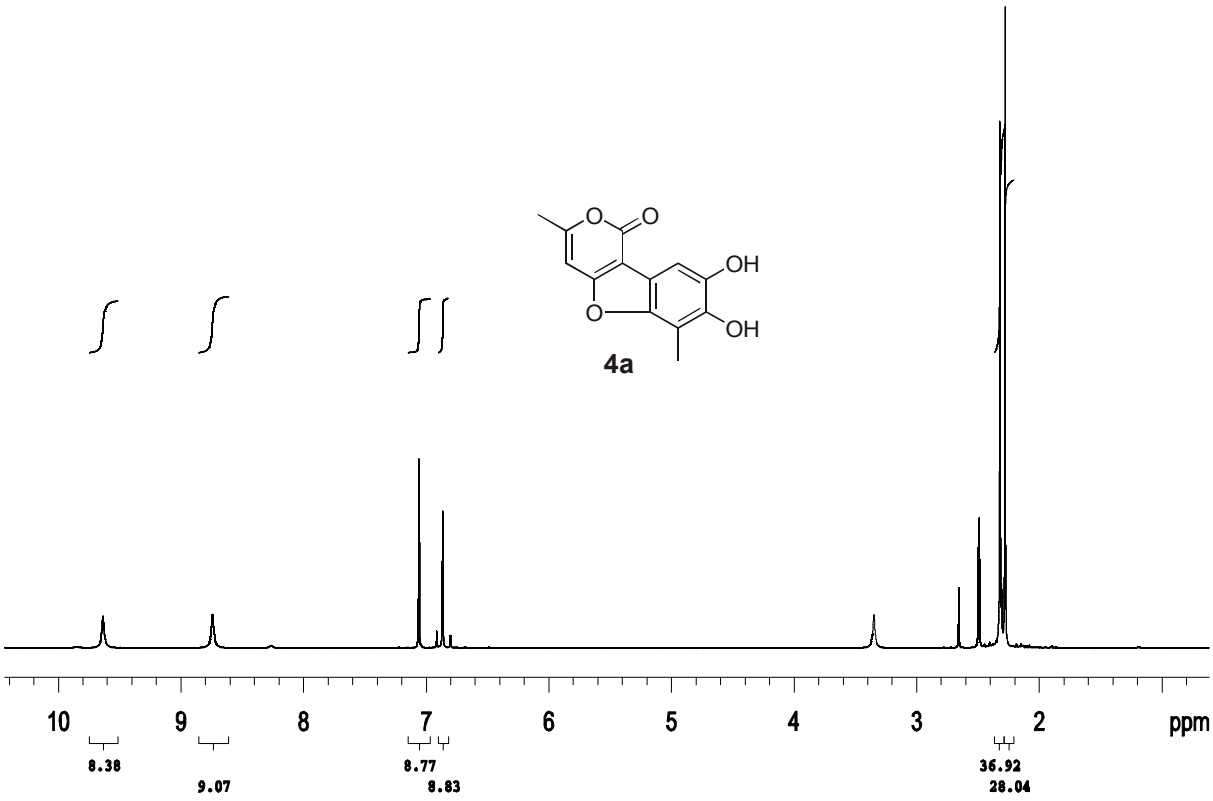
C	-5.52462	-0.84566	-0.05866
O	-1.19536	-2.25147	-0.31583
C	1.7426	-1.0241	0.01438
C	2.4925	-1.54876	-1.04648
C	2.99404	-2.84775	-0.98385
C	2.75982	-3.63255	0.14196
C	2.01911	-3.11565	1.20407
C	1.51536	-1.82139	1.14223
O	3.56628	1.18942	-0.01476
O	2.8334	3.7243	0.0479
H	-4.42608	1.74992	0.0906
H	0.26057	4.20885	0.11146
H	-5.69998	-1.52495	0.7821
H	-6.21827	-0.00683	0.01298
H	-5.73205	-1.40206	-0.97862
H	2.66742	-0.94101	-1.93319
H	3.56747	-3.24451	-1.819
H	3.15416	-4.64522	0.19321
H	1.83511	-3.72401	2.08715
H	0.94444	-1.41792	1.97557
H	3.7665	0.23746	0.01332
H	3.71448	3.30311	0.0312

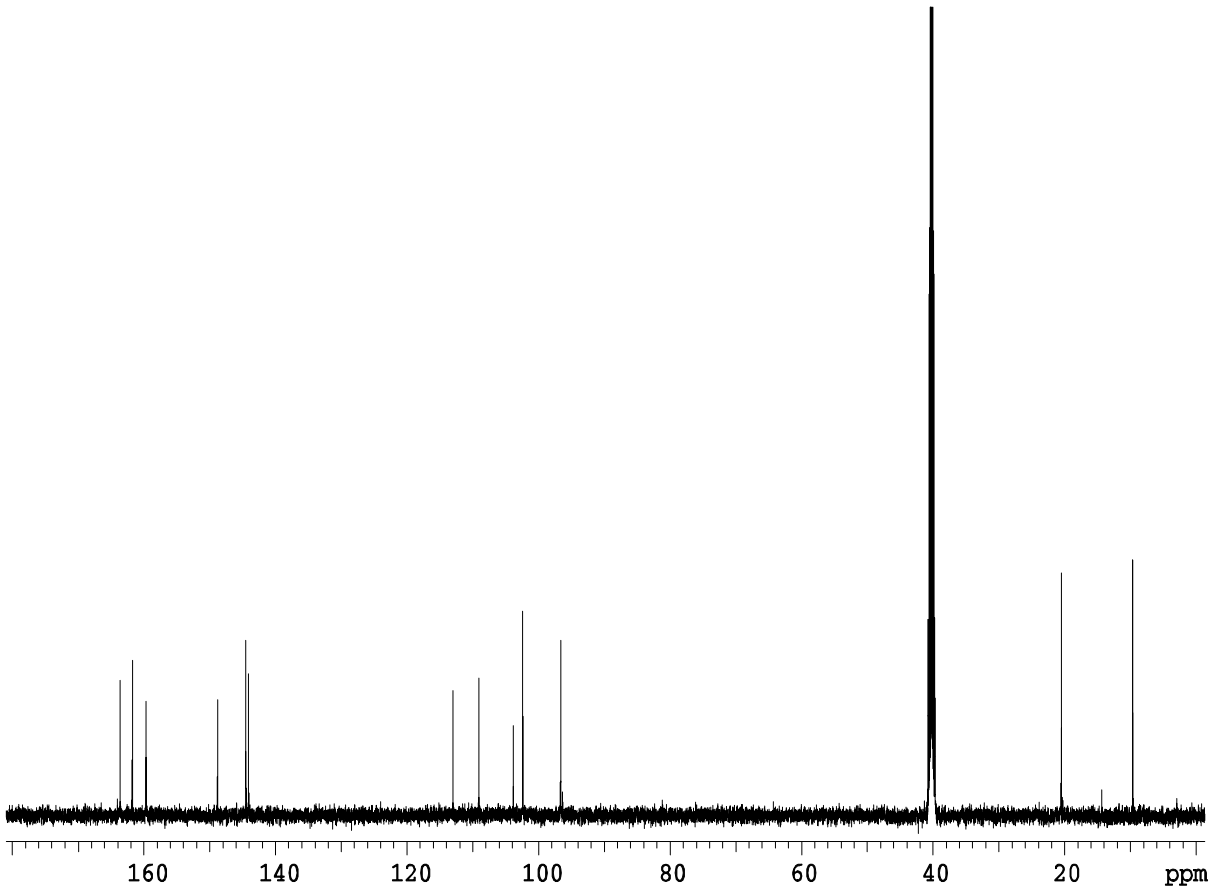
1.8 Cartesian coordinates of 4f of the NMR GIAO mPW1PW91/6-311+G(2d,p)// mPW1PW91/6-31G(d) calculation

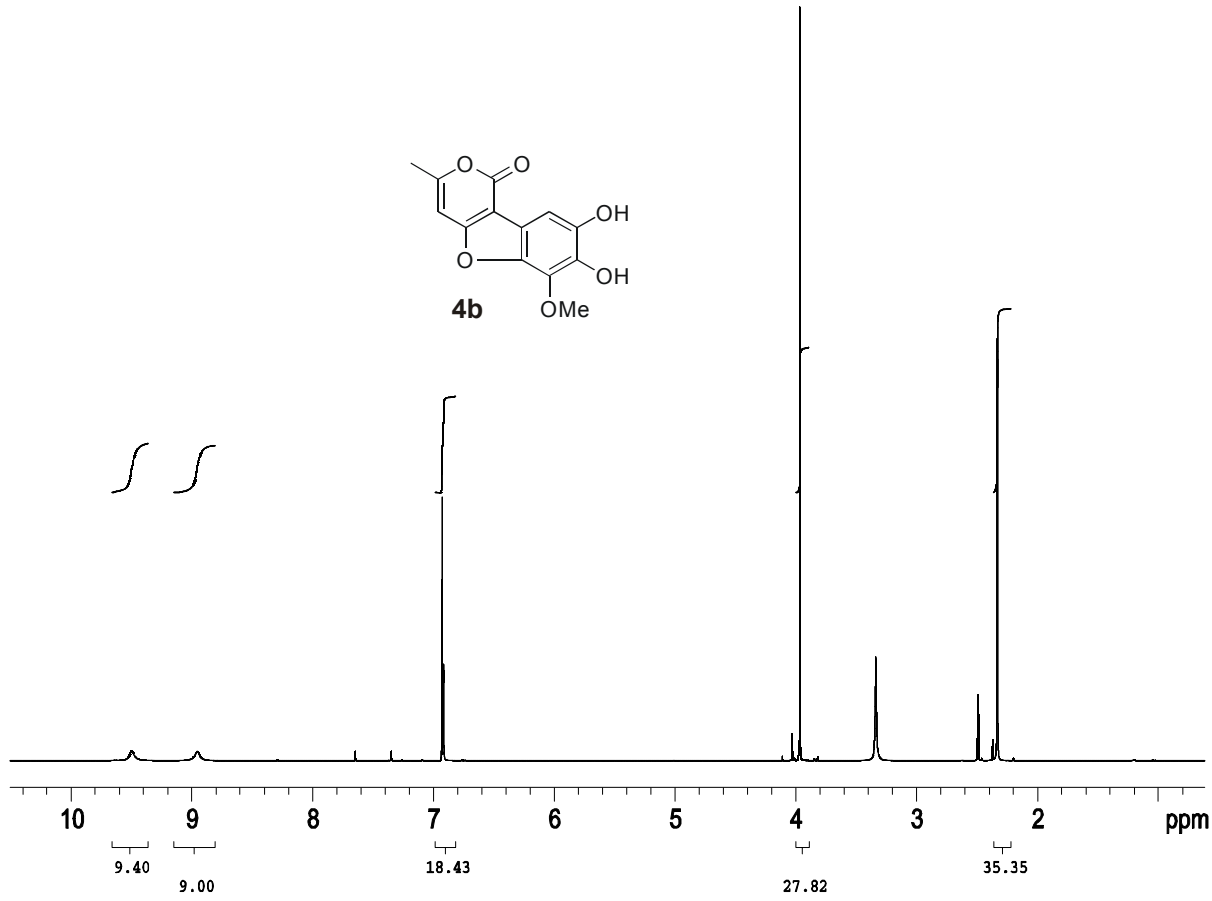
C	4.00891	-1.53843	0.09497
C	2.71406	-1.94594	0.06474
C	1.7553	-0.91183	0.02119
C	2.07824	0.4294	0.00729
C	3.444	0.83553	0.03937
O	4.34884	-0.22644	0.08265
O	0.42271	-1.10451	-0.01068
C	-0.15012	0.15232	-0.05034
C	0.83278	1.14862	-0.03612
C	-1.52235	0.39942	-0.05899
C	-1.86831	1.75612	-0.08477
C	-0.89607	2.7835	-0.0802
C	0.46018	2.4934	-0.04853
O	3.90735	1.95763	0.03358
C	5.20096	-2.42507	0.14412
C	-2.53169	-0.68457	-0.02447
C	-2.45722	-1.75989	-0.91932
C	-3.39664	-2.78542	-0.87073
C	-4.42198	-2.75337	0.0725
C	-4.50312	-1.6887	0.96797
C	-3.56609	-0.66076	0.92121

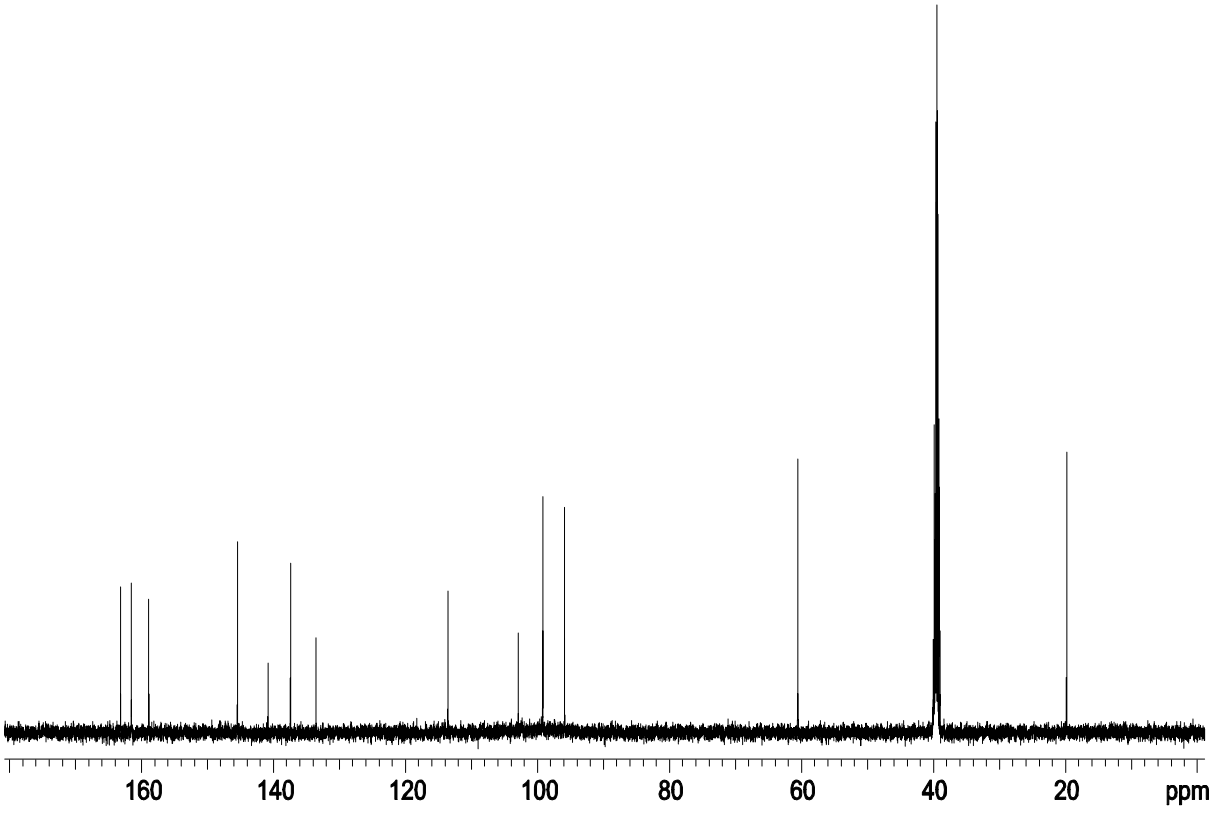
O	-1.29532	4.07624	-0.11385
O	-3.15985	2.20213	-0.08565
H	2.4464	-2.99711	0.07494
H	1.19123	3.29552	-0.04696
H	5.79324	-2.21895	1.04172
H	4.89854	-3.47307	0.15156
H	5.8455	-2.24643	-0.72279
H	-1.66456	-1.78739	-1.66278
H	-3.32789	-3.61163	-1.57514
H	-5.15549	-3.55586	0.10978
H	-5.2969	-1.65904	1.71131
H	-3.62823	0.16179	1.62887
H	-2.26882	4.09727	-0.19837
H	-3.70794	1.68859	-0.71989

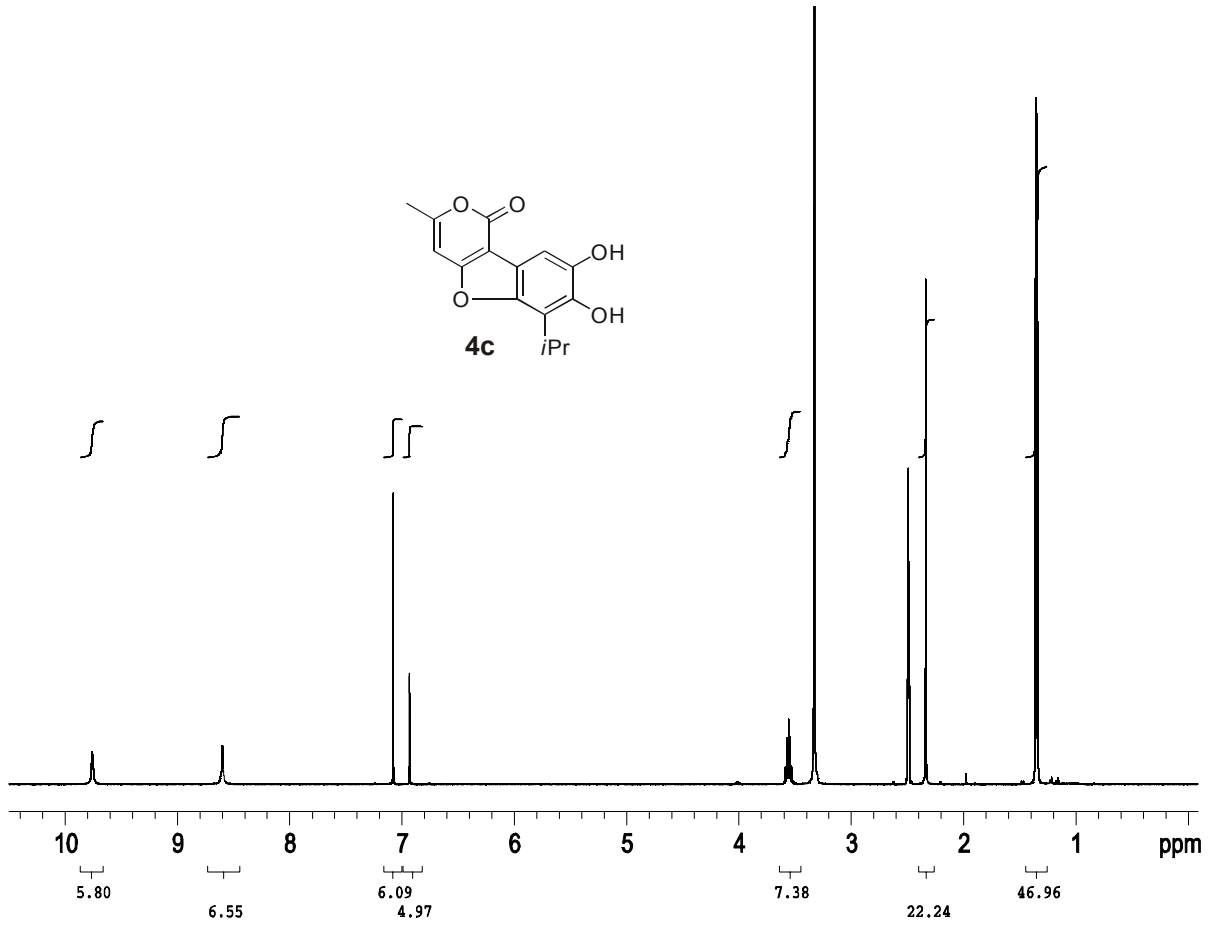
2. Spectra of compounds 3, 4, 5 and 6.

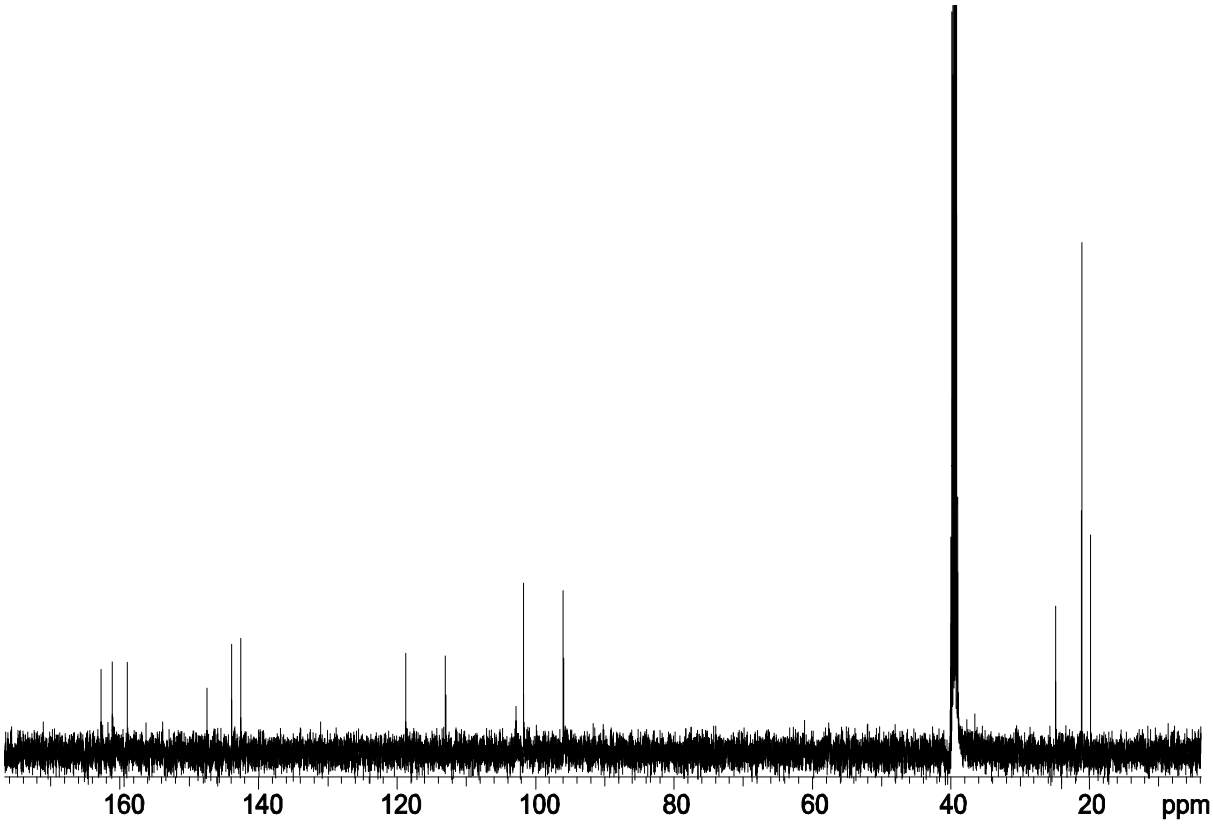


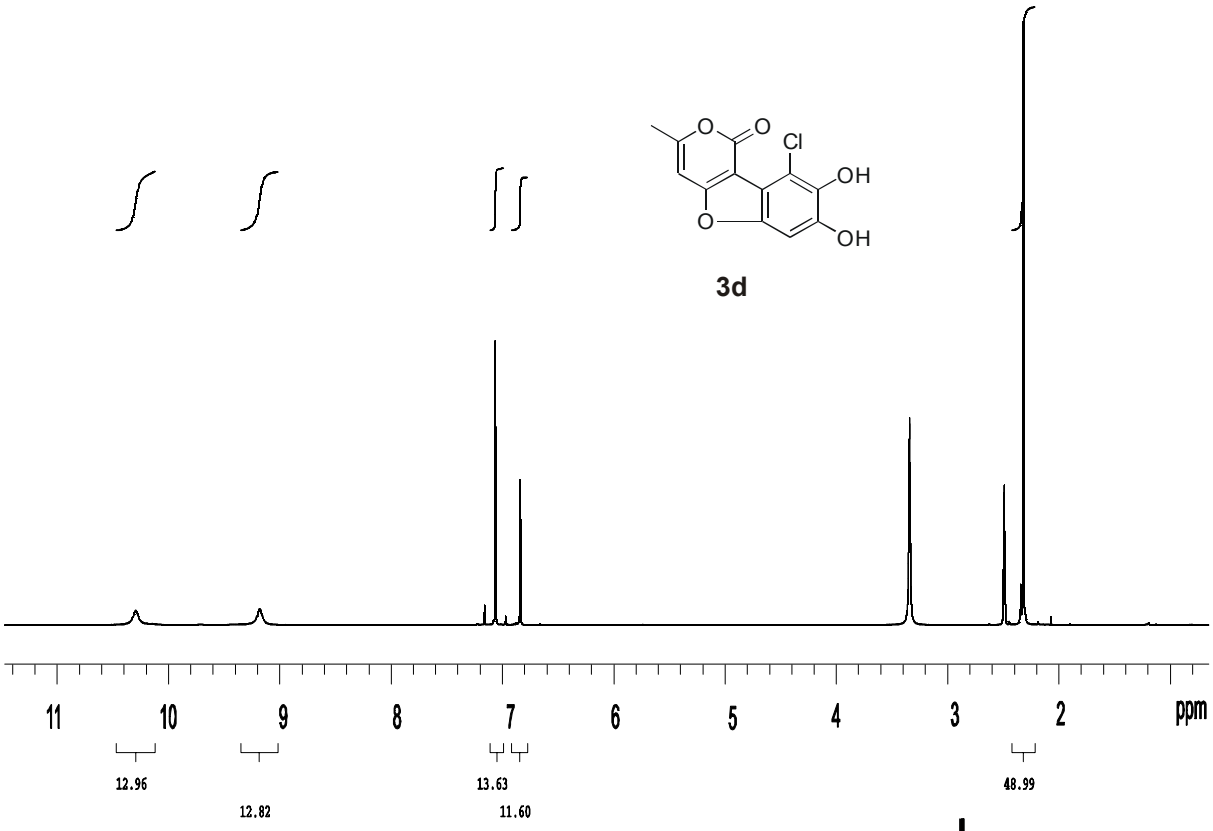












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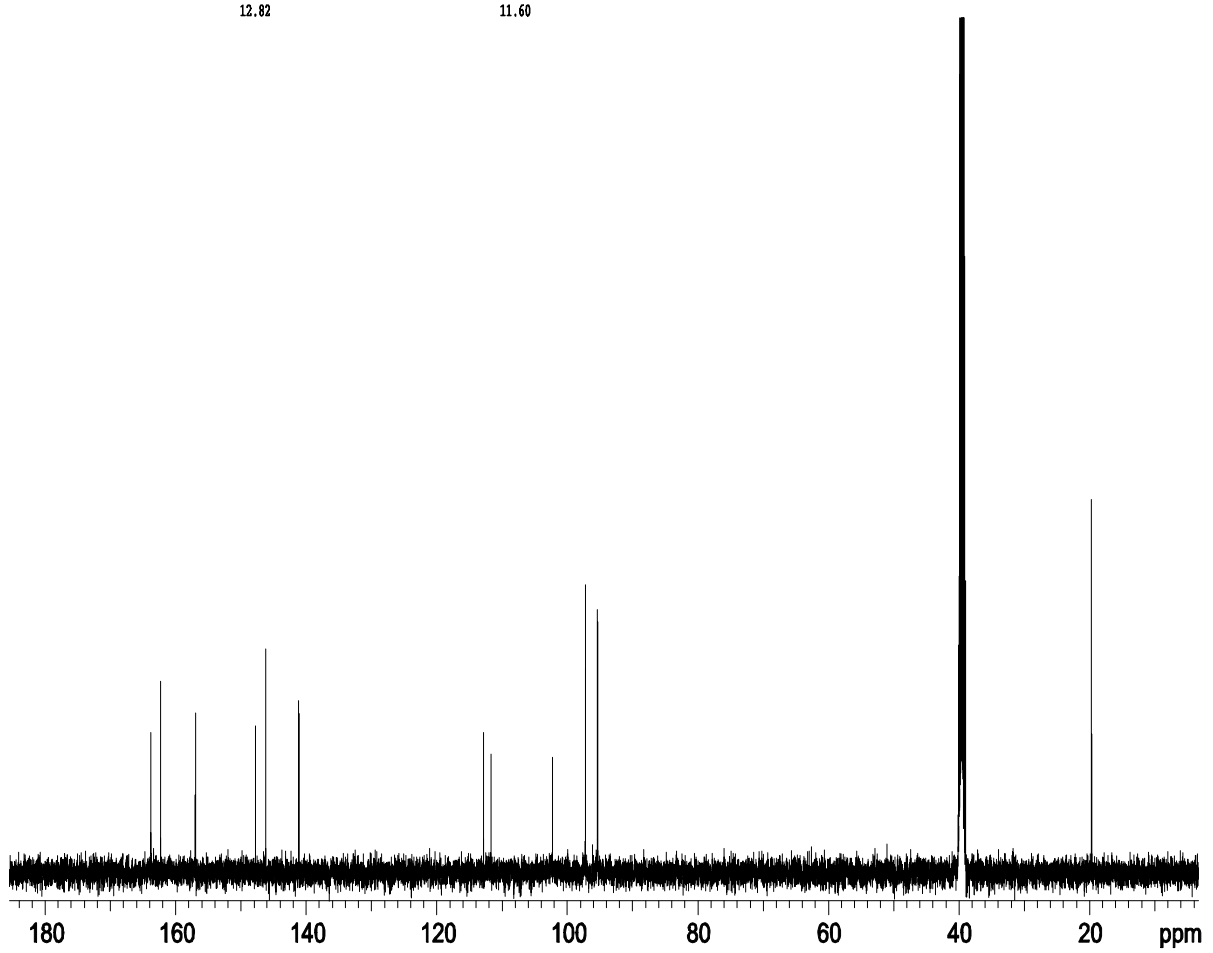

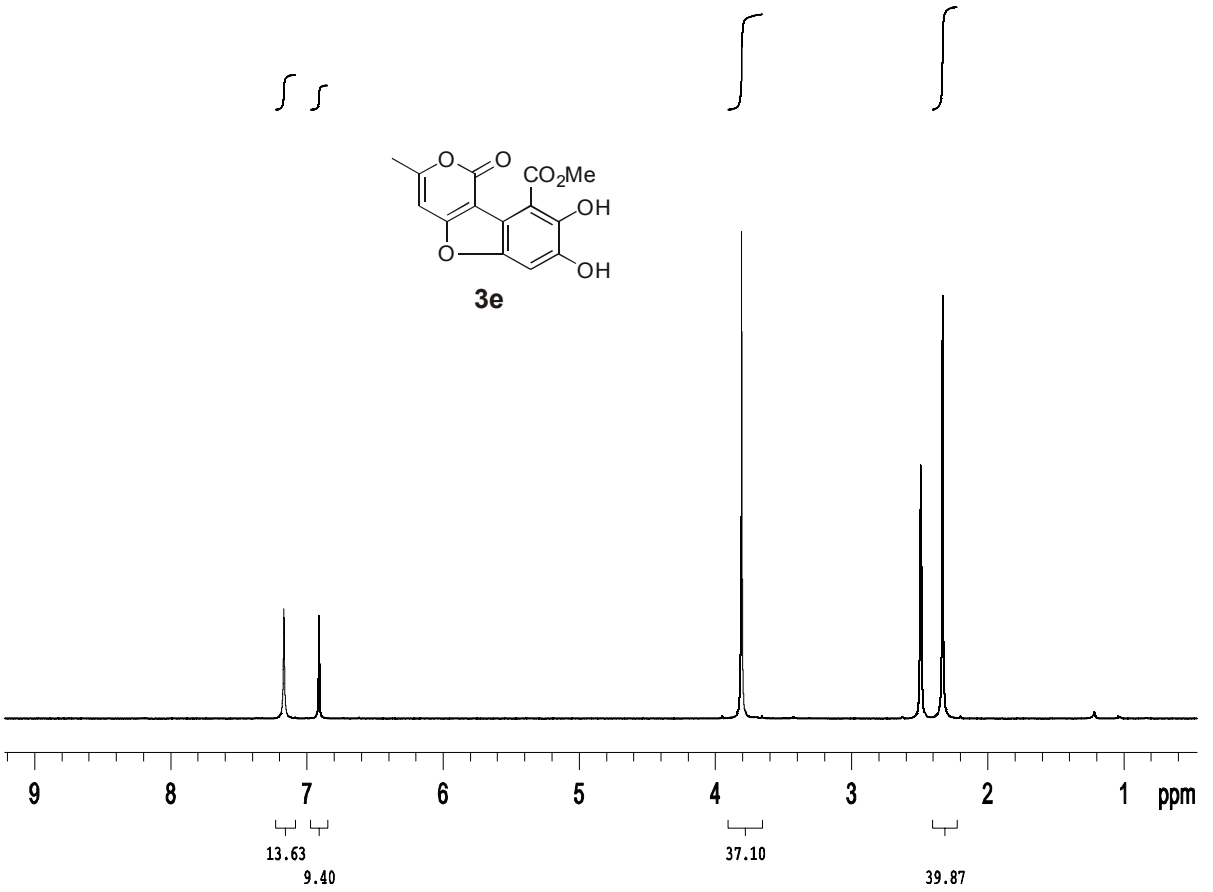

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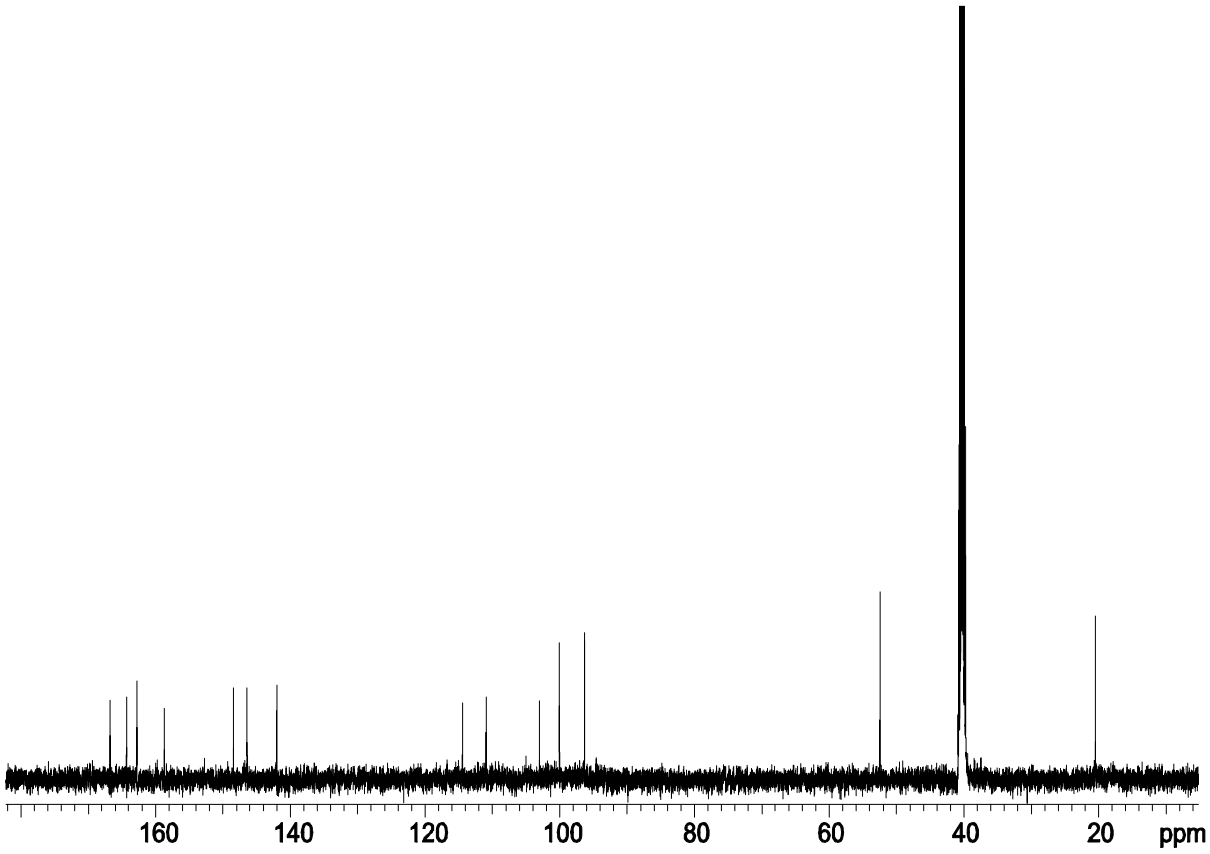

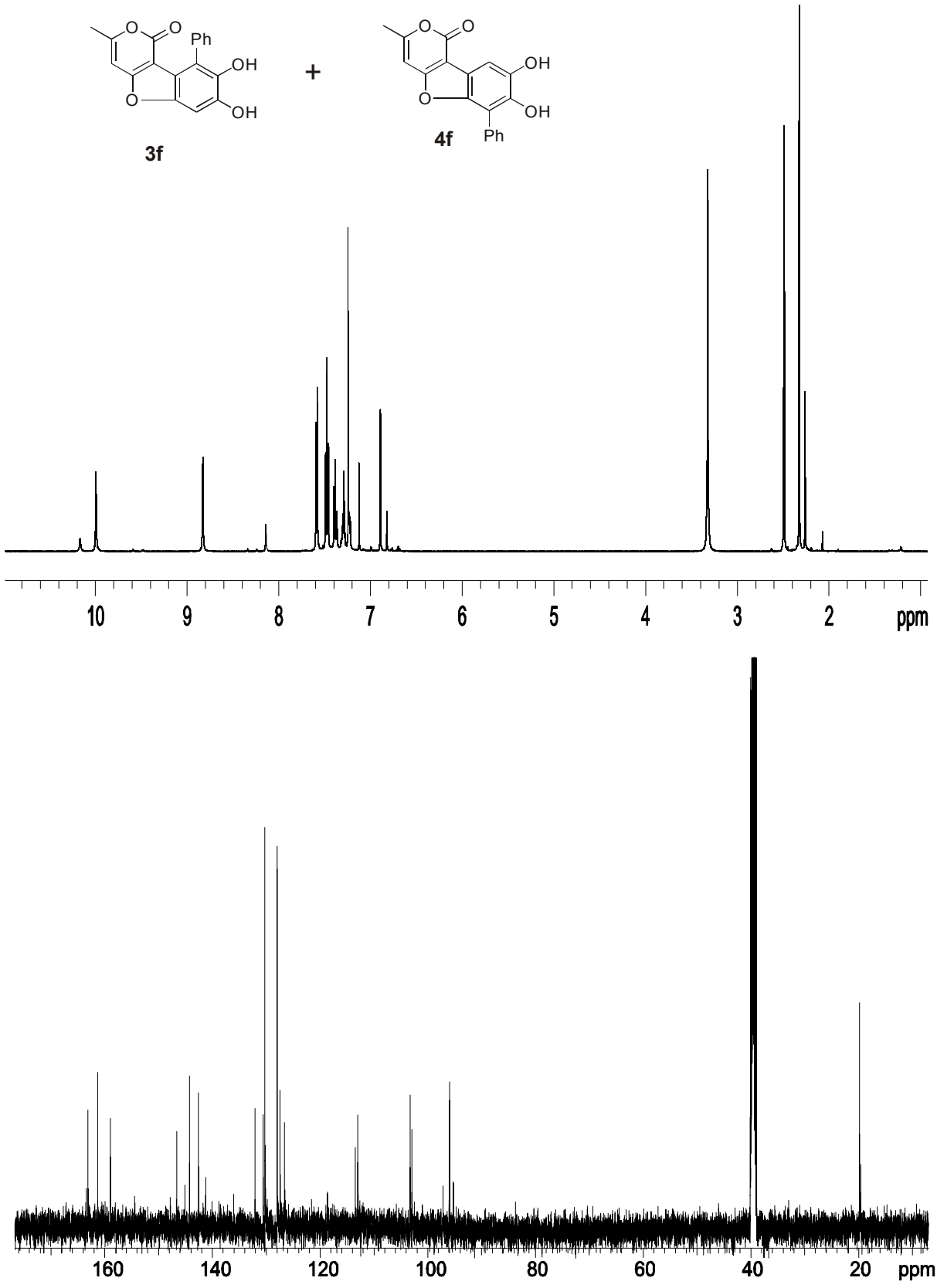

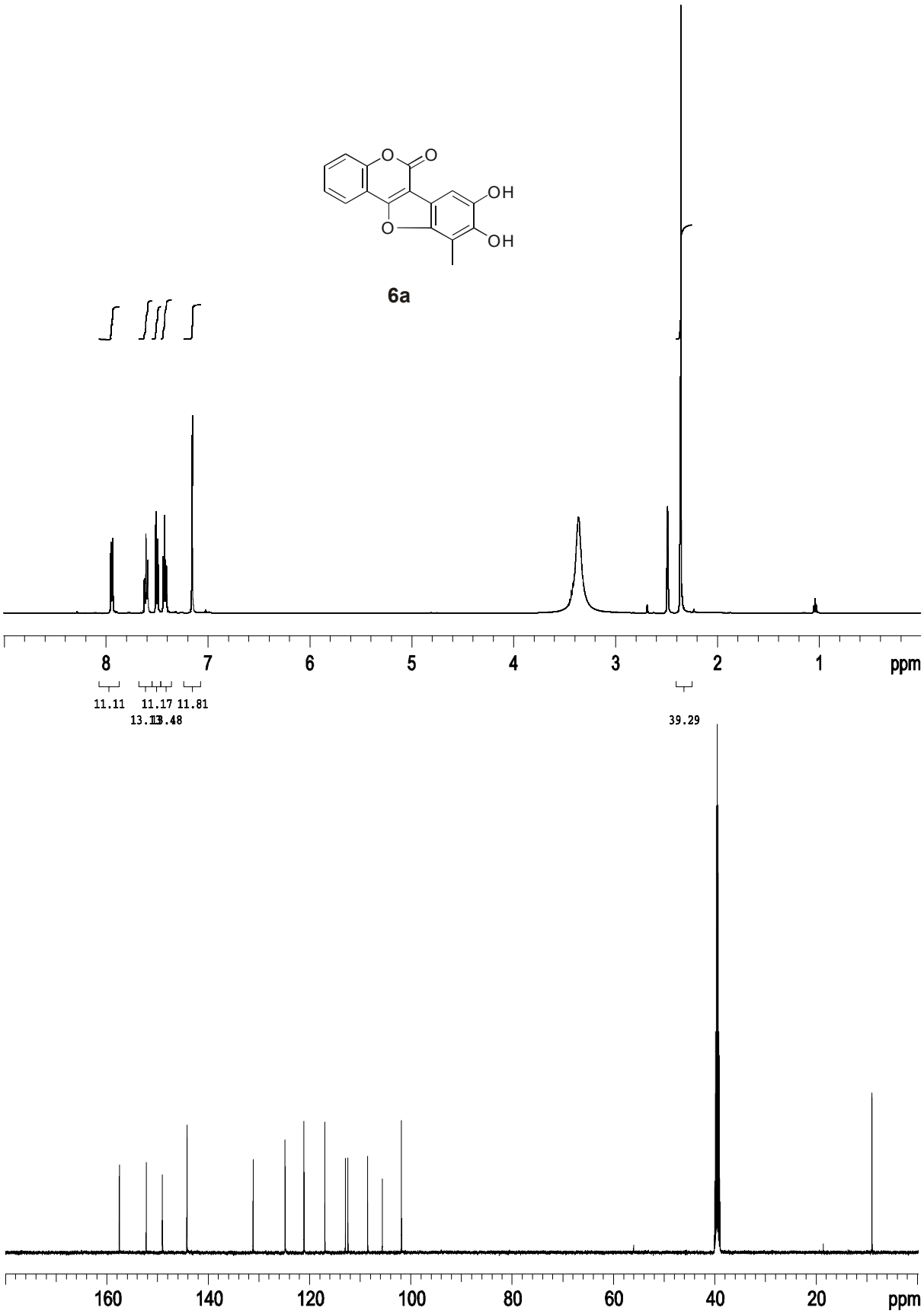
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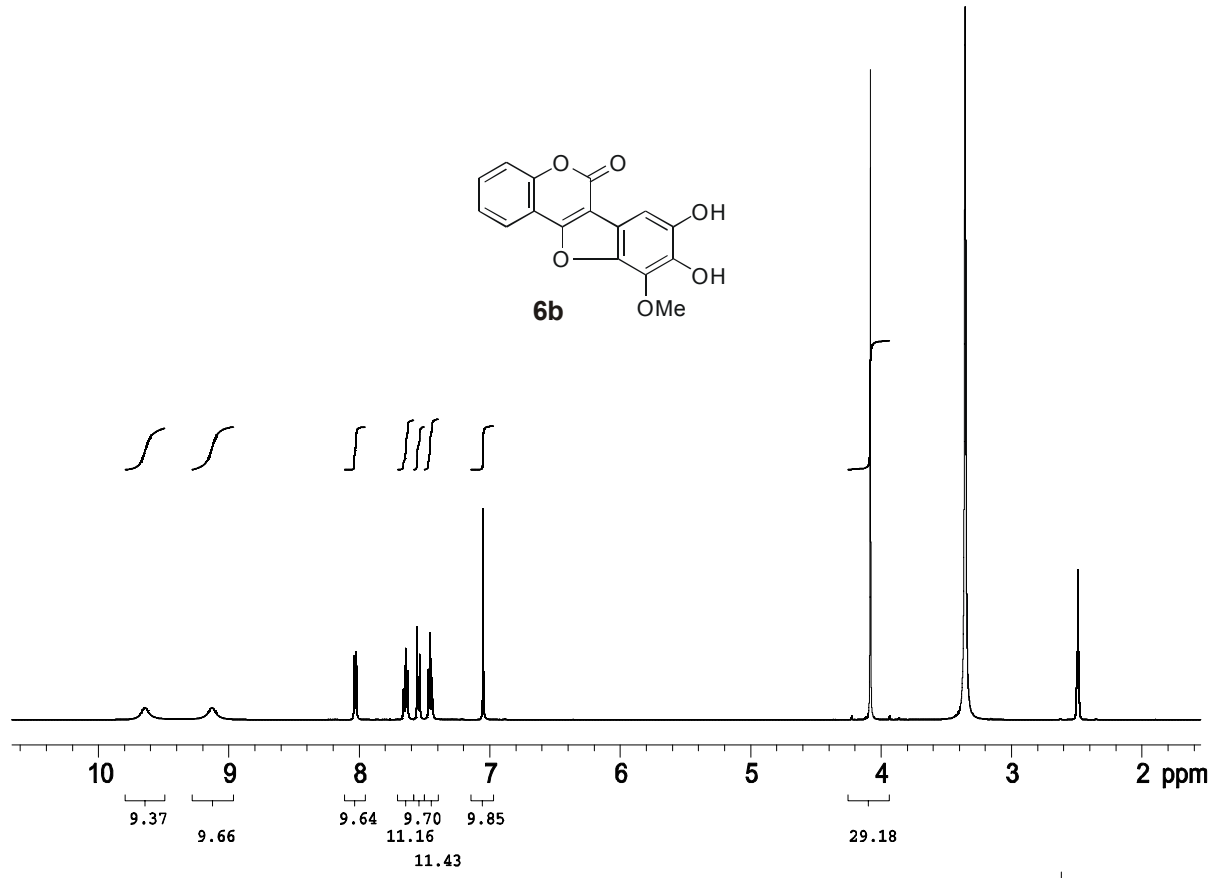

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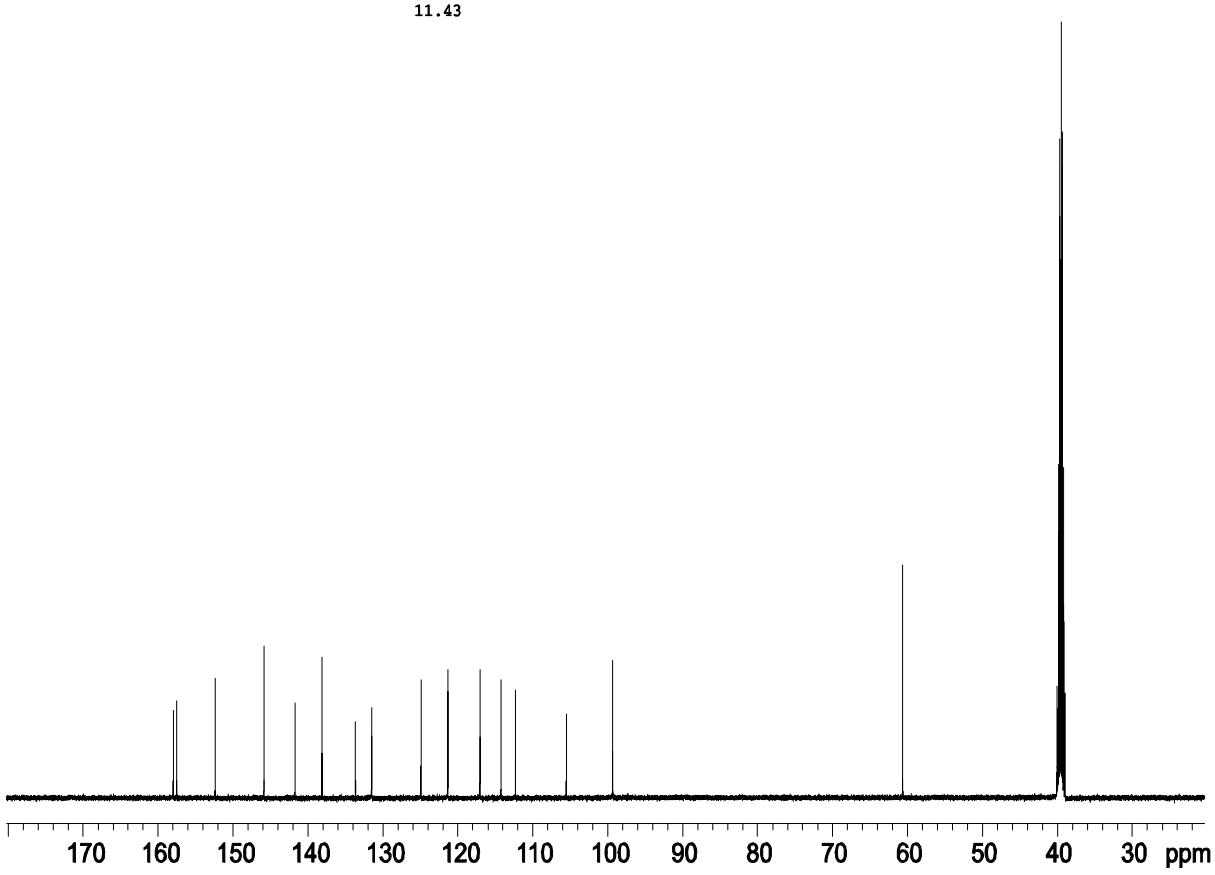

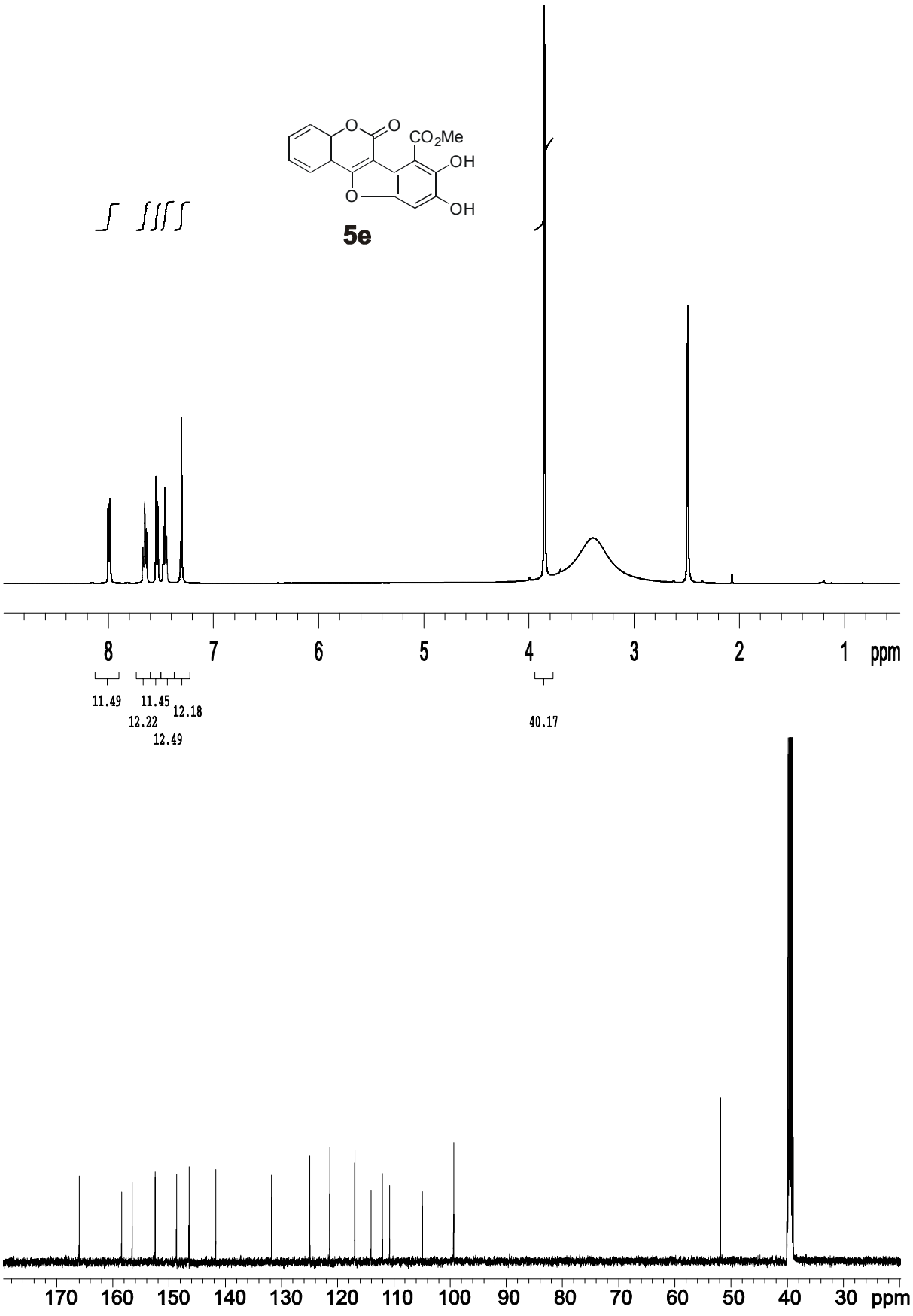
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ppm