

Supplementary Material for

Synthesis of Highly Enantio-Enriched Heliespirones A and C by a Diastereoselective Aromatic Claisen Rearrangement

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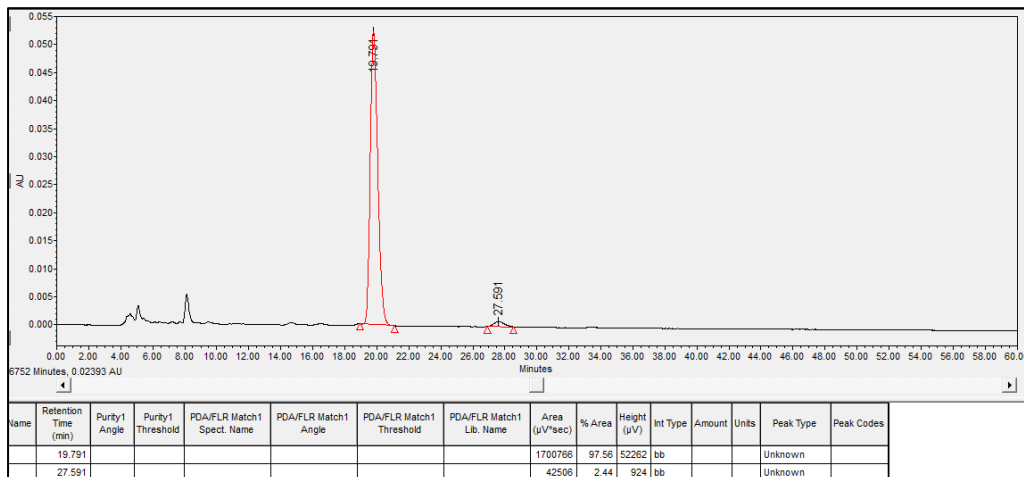
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Comparison of reported specific rotation values for the heliespirones.

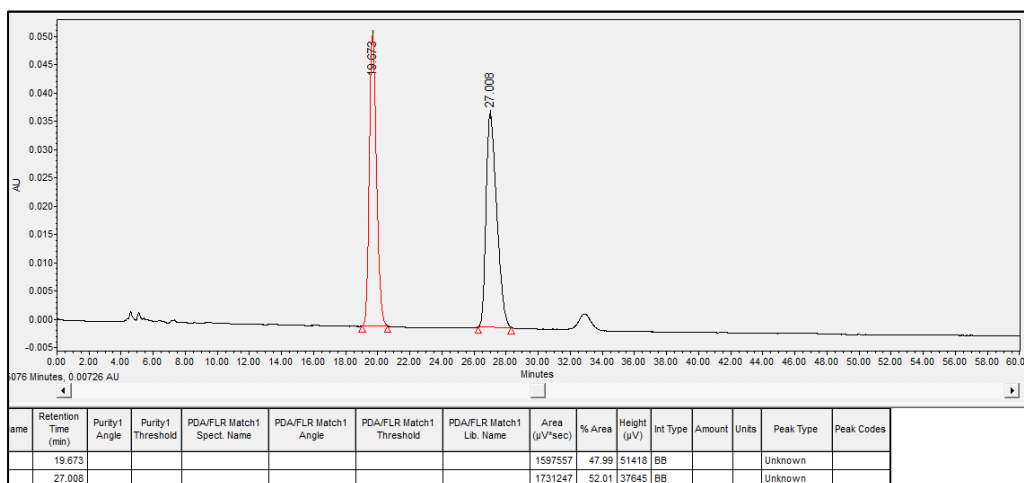
Compound ^[a]	Reported [α] _D	Reference
heliespirone A	-29.0 (c 0.1, CHCl ₃)	A. Macías, R. M. Varela, A. Torres, J. G. Molinillo, <i>Tetrahedron Lett.</i> 1998 , 39, 427–430.
ent-heliespirone A	+17.6 (c 0.09, CHCl ₃)	C. Huang, B. Liu, <i>Chem. Commun.</i> 2010 , 46, 5280–5282.
ent-heliespirone A	+23.2 (c 0.09, CHCl ₃)	W.-J. Bai, J. C. Green, T. R. R. Pettus, <i>J. Org. Chem.</i> 2011 , 77, 379–387.
heliespirone A	-55.2 (c 0.13, CHCl ₃)	A. Miyawaki, D. Kikuchi, M. Niki, Y. Manabe, M. Kanematsu, H. Yokoe, M. Yoshida, K. Shishido, <i>J. Org. Chem.</i> 2012 , 77, 8231–8243.
heliespirone A	-28.0 (c 0.1, CHCl ₃)	P. Norcott, C. S. P. McErlean, <i>Eur. J. Org. Chem.</i> 2014 , 5056–5062
heliespirone C	+14.4 (c 0.1, CHCl ₃)	A. Macías, R. M. Varela, A. Torres, J. G. Molinillo, <i>Tetrahedron Lett.</i> 1998 , 39, 427–430.
ent-heliespirone C	-31.8 (c 0.11, CHCl ₃)	C. Huang, B. Liu, <i>Chem. Commun.</i> 2010 , 46, 5280–5282.
ent-heliespirone C	-24.9 (c 0.10, CHCl ₃)	W.-J. Bai, J. C. Green, T. R. R. Pettus, <i>J. Org. Chem.</i> 2011 , 77, 379–387.
heliespirone C	+50.4 (c 0.4 CHCl ₃)	A. Miyawaki, D. Kikuchi, M. Niki, Y. Manabe, M. Kanematsu, H. Yokoe, M. Yoshida, K. Shishido, <i>J. Org. Chem.</i> 2012 , 77, 8231–8243.
heliespirone C	+13.0 (c 0.1 CHCl ₃)	P. Norcott, C. S. P. McErlean, <i>Eur. J. Org. Chem.</i> 2014 , 5056–5062

Enantioselective HPLC traces for (-)-heliespirone A

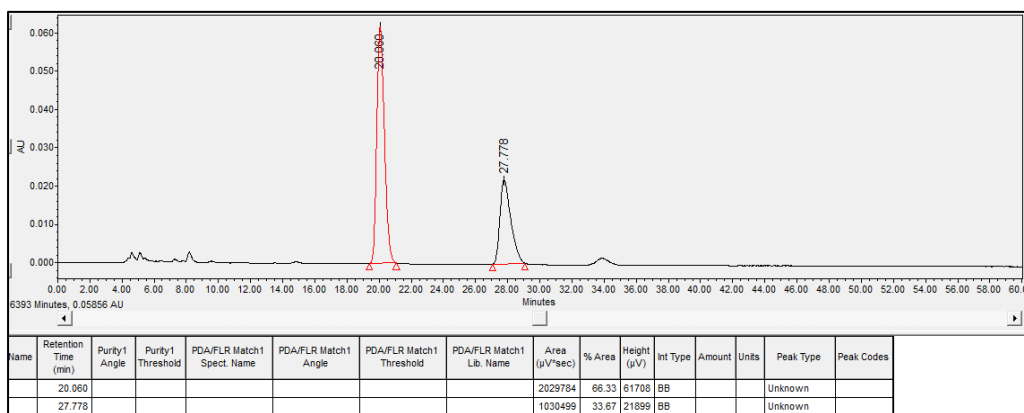
Enantioenriched



Racemate

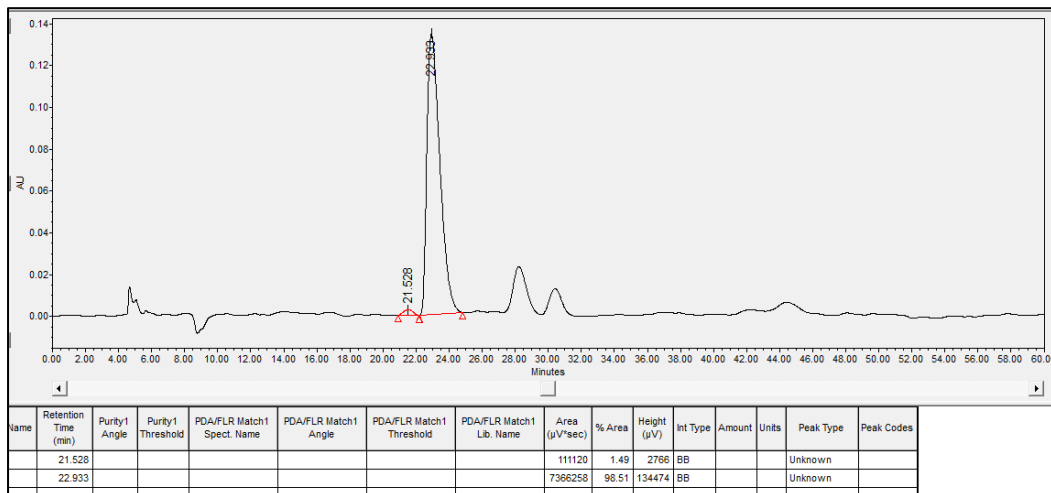


Co-injection

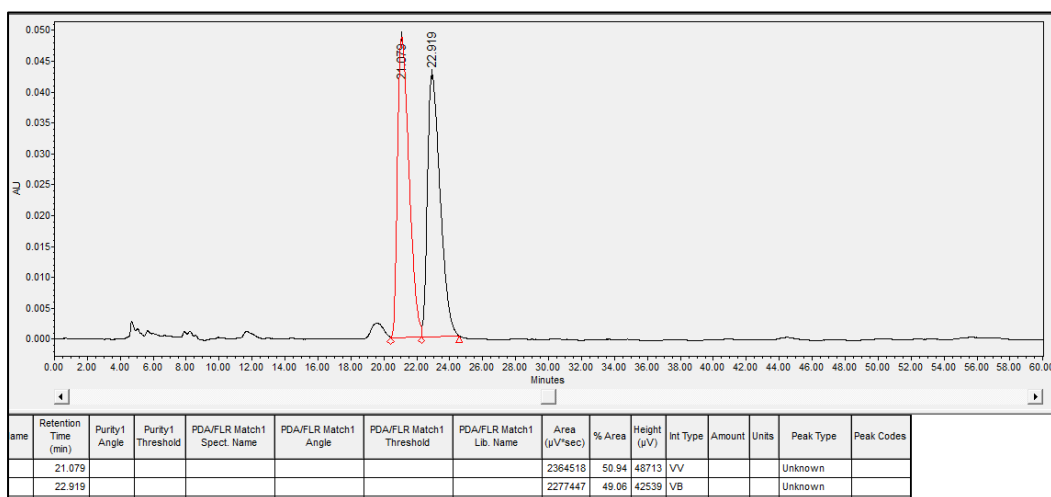


Enantioselective HPLC traces for (+)-heliespirone C

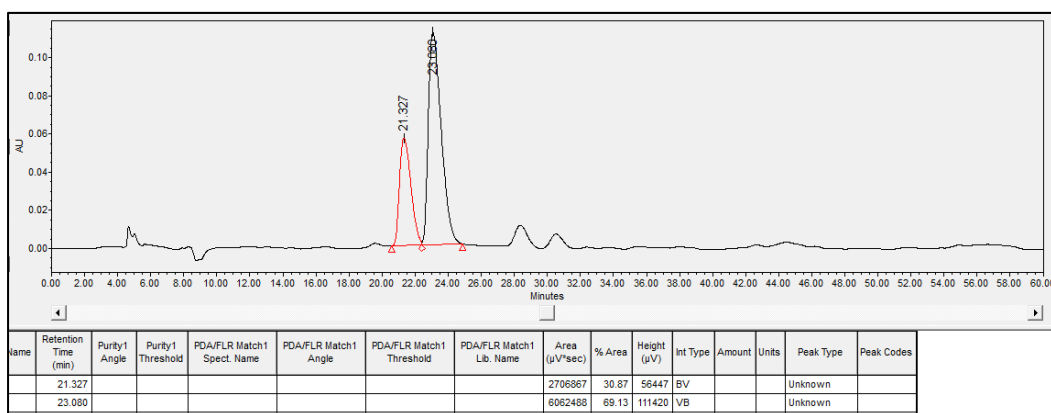
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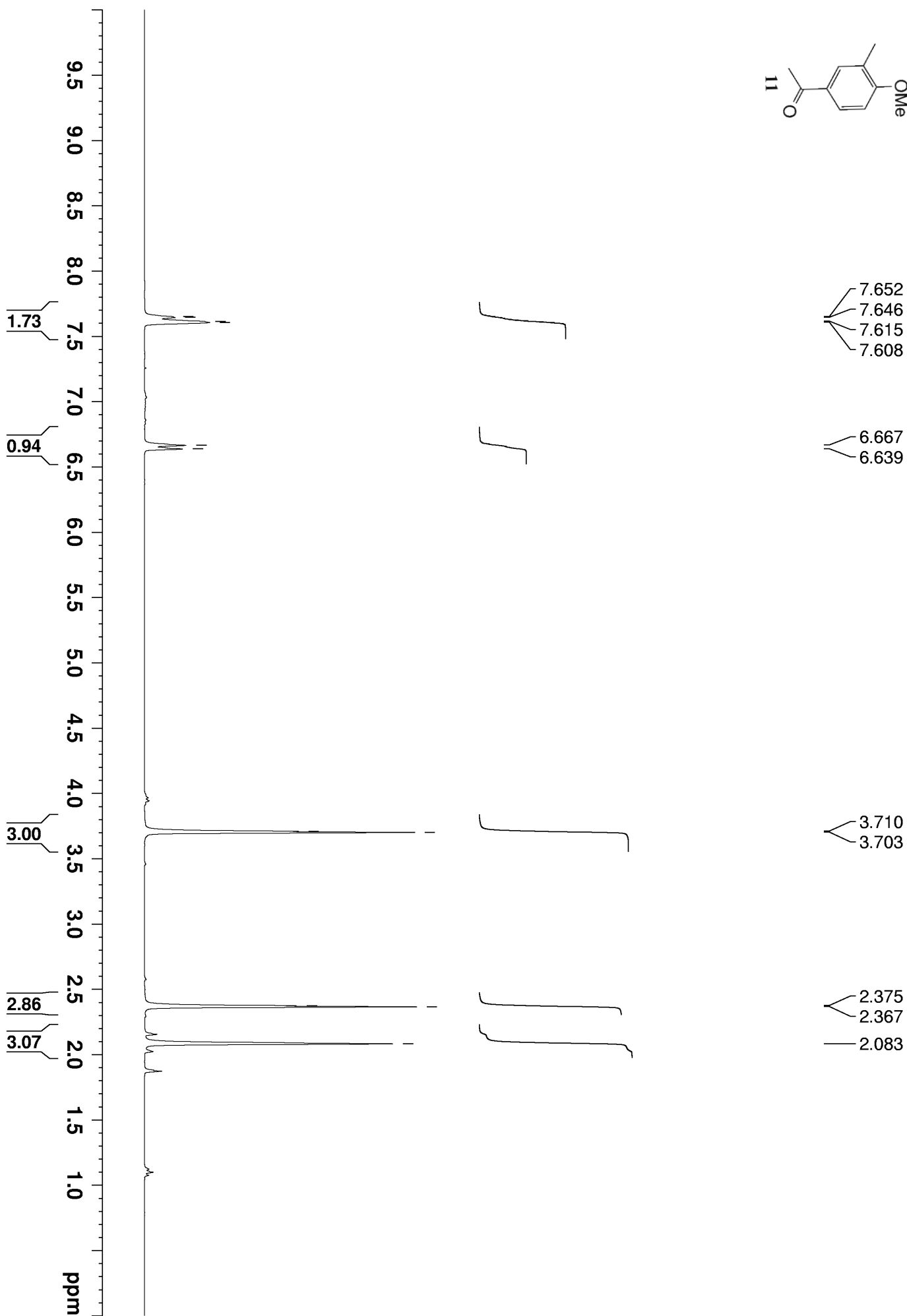
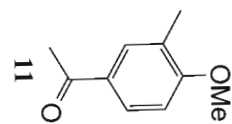


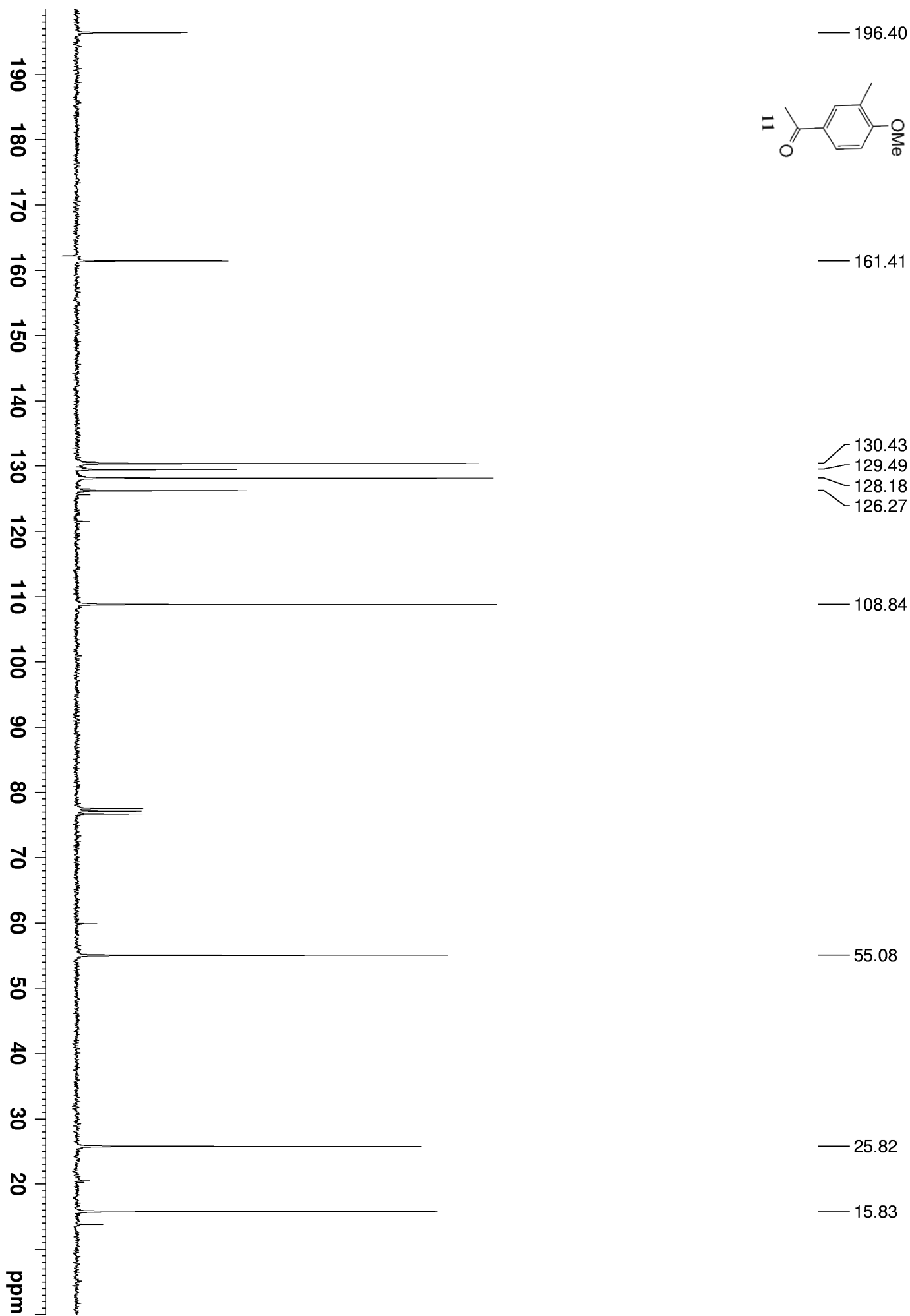
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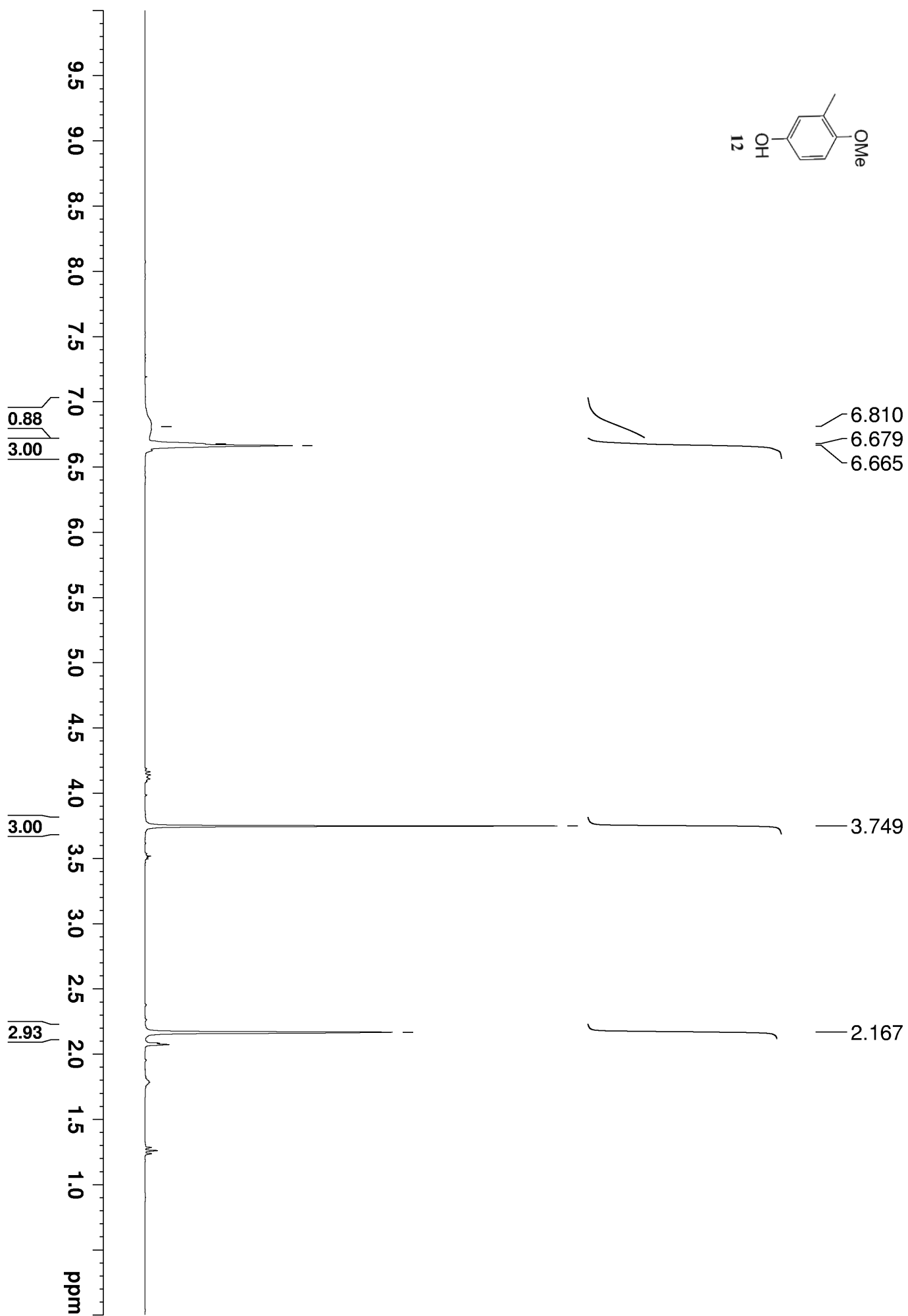
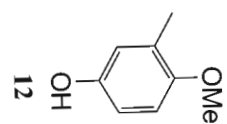


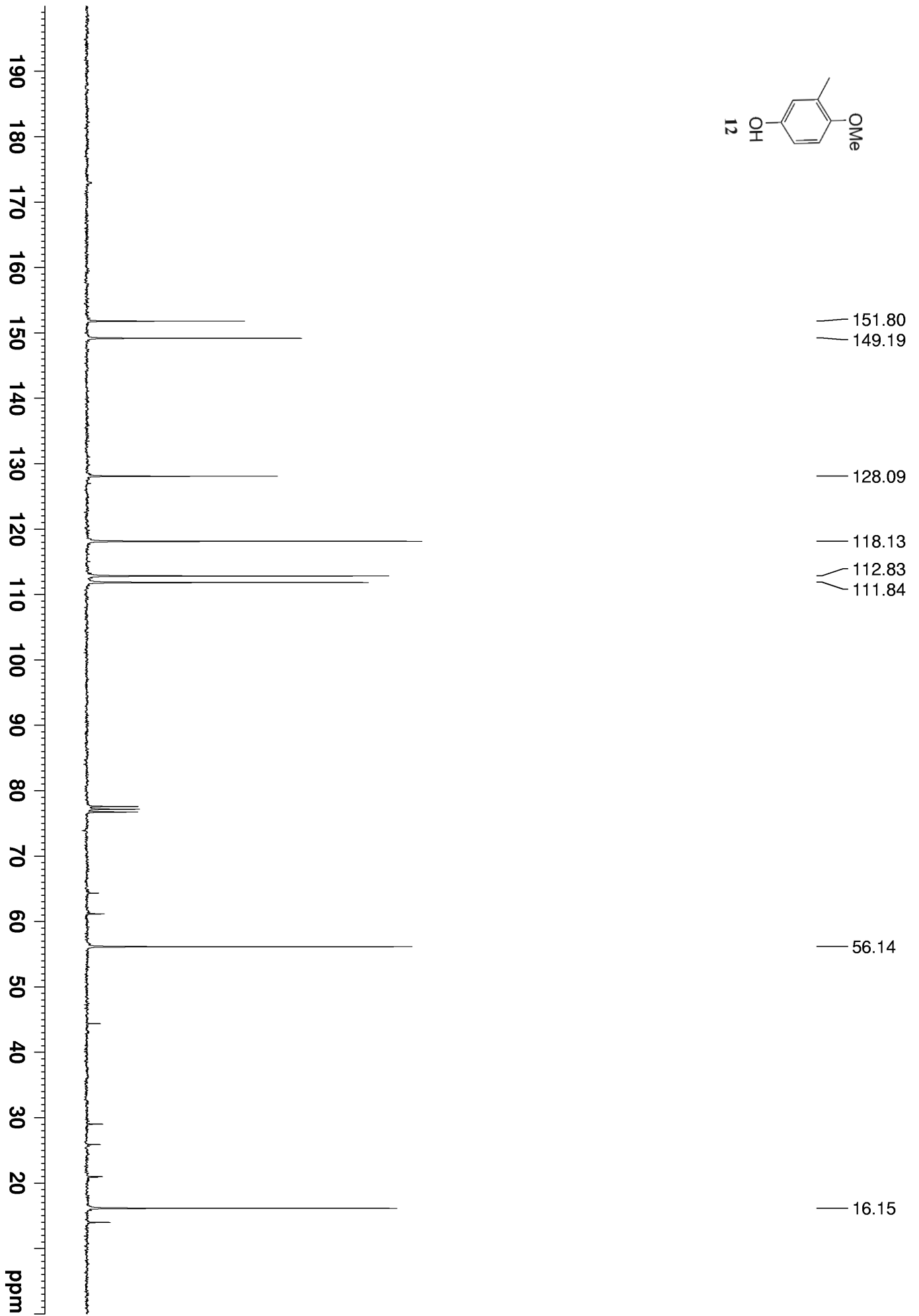
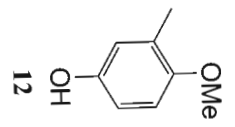
Co-injection

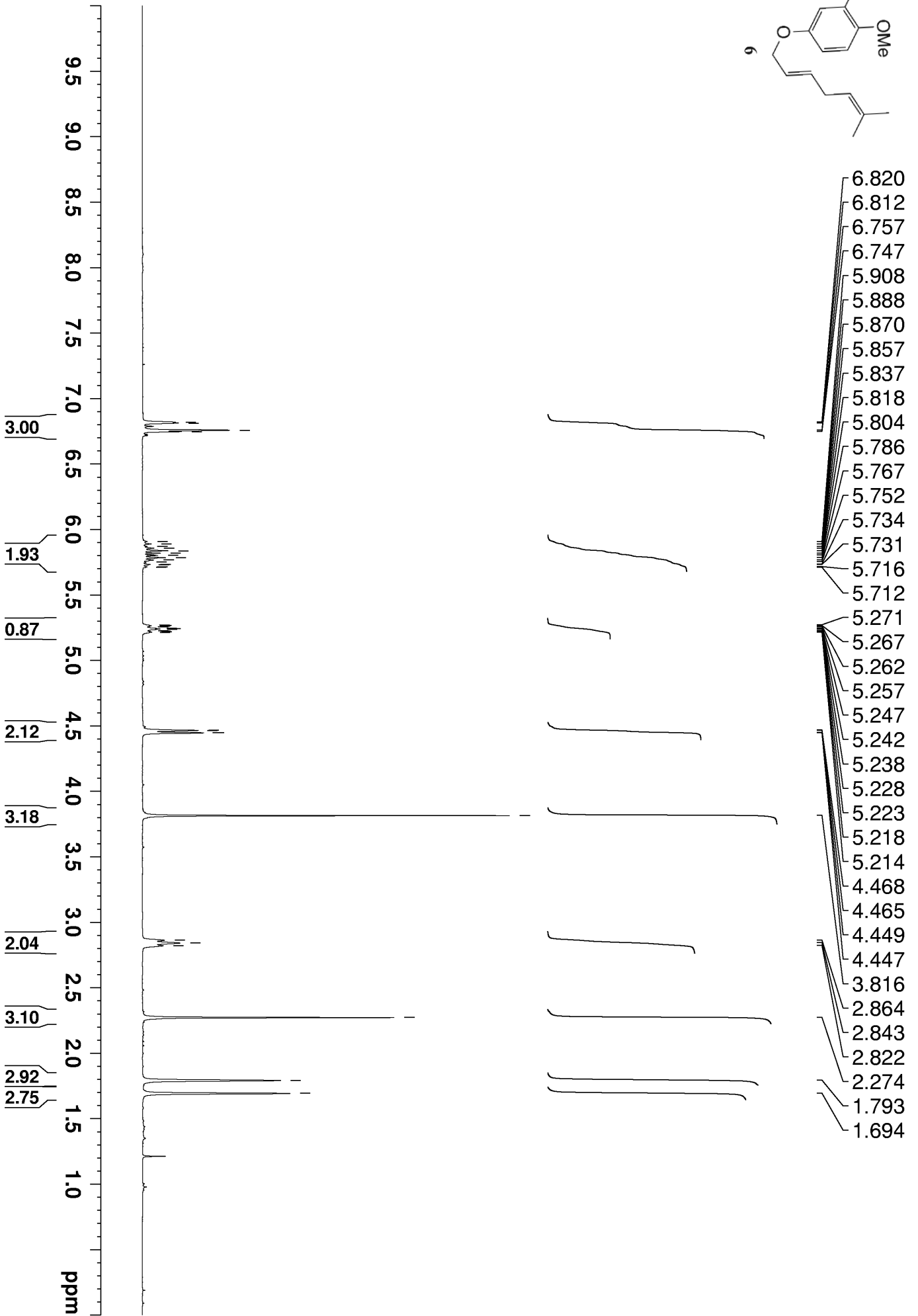
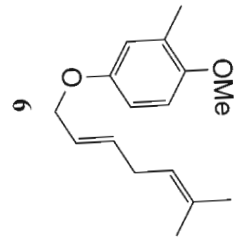


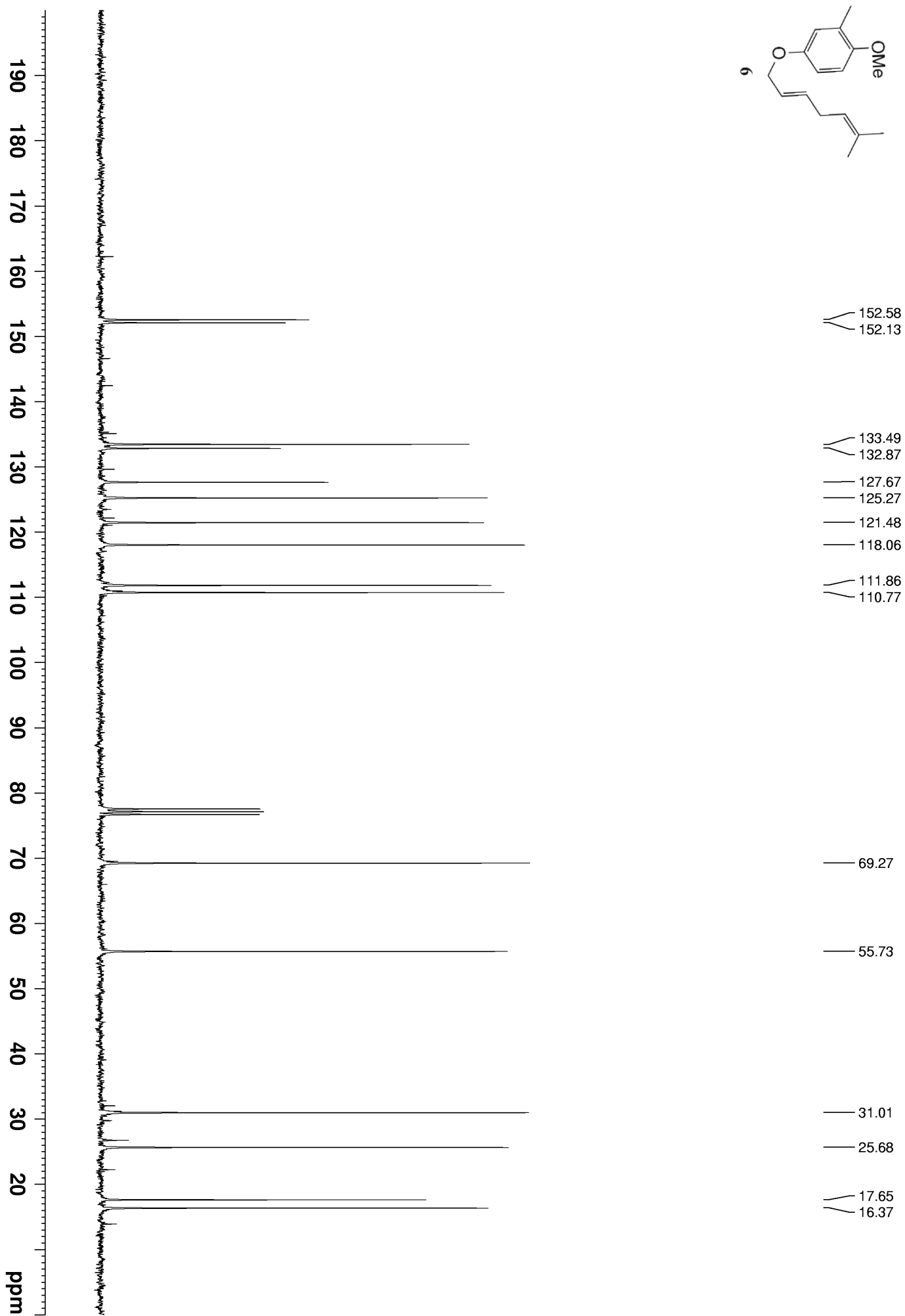
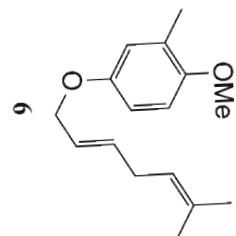


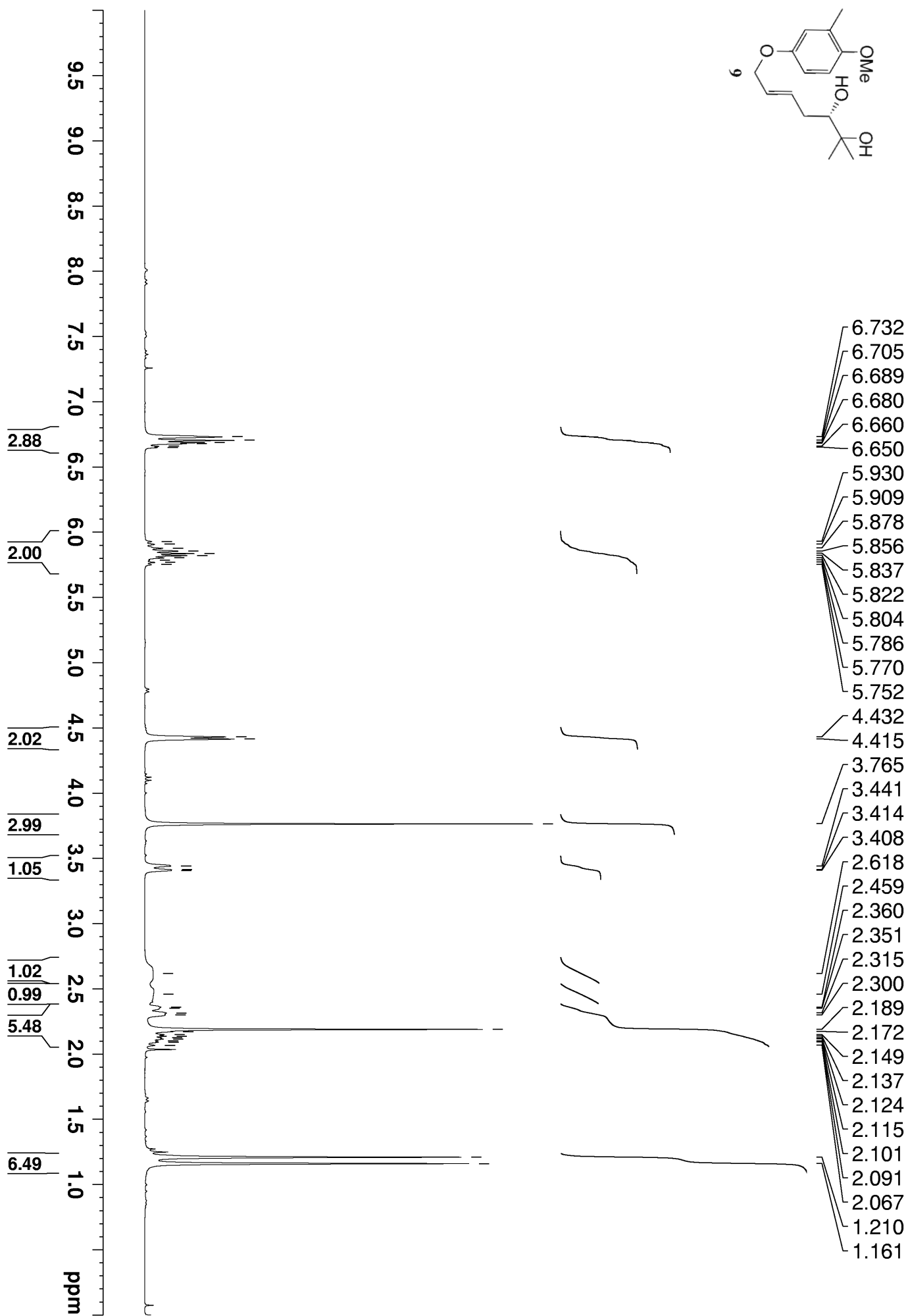
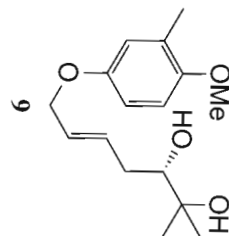


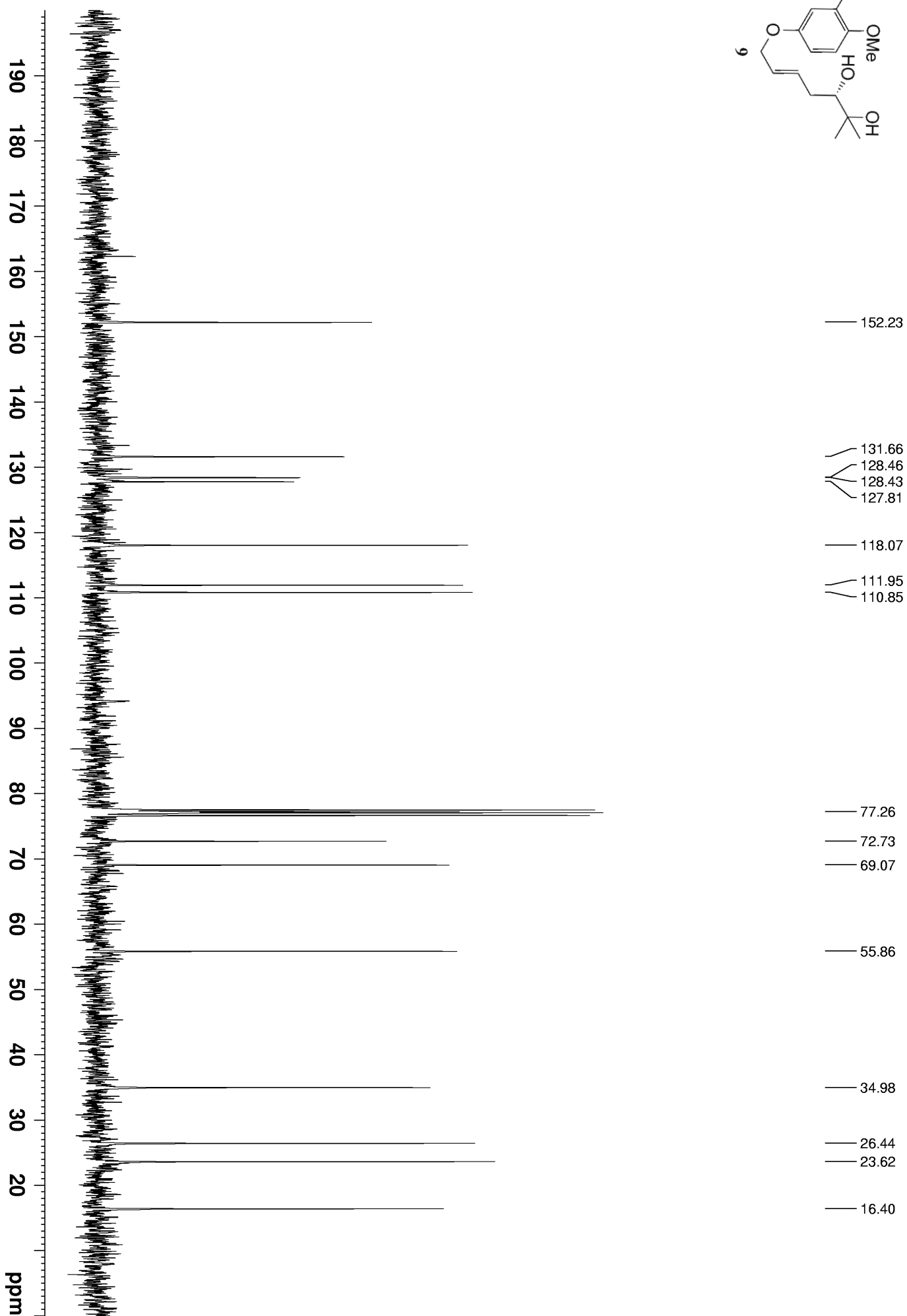
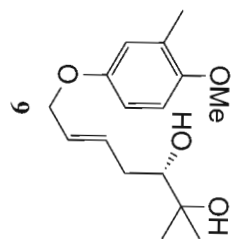


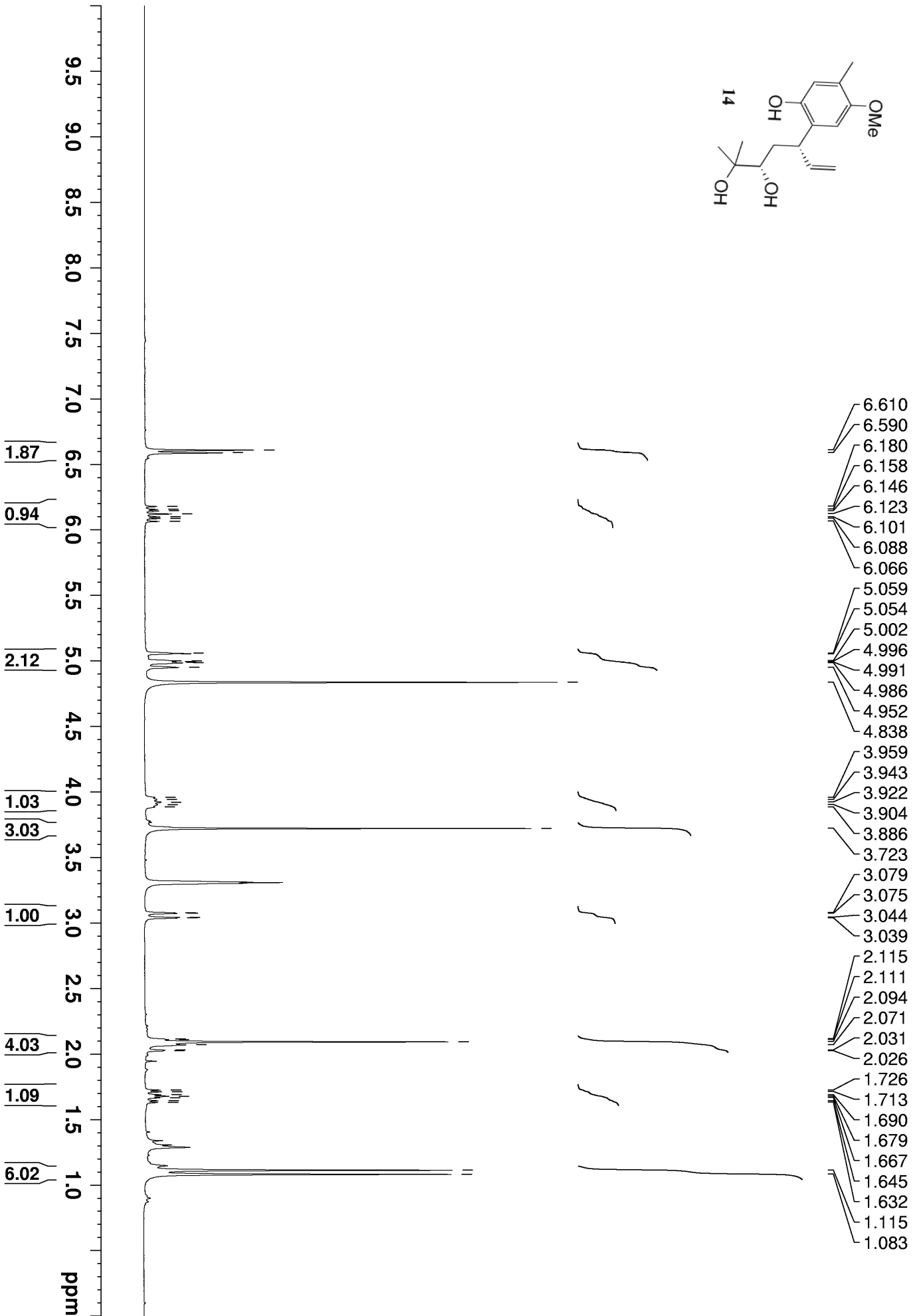
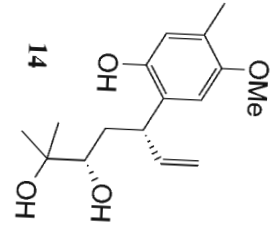


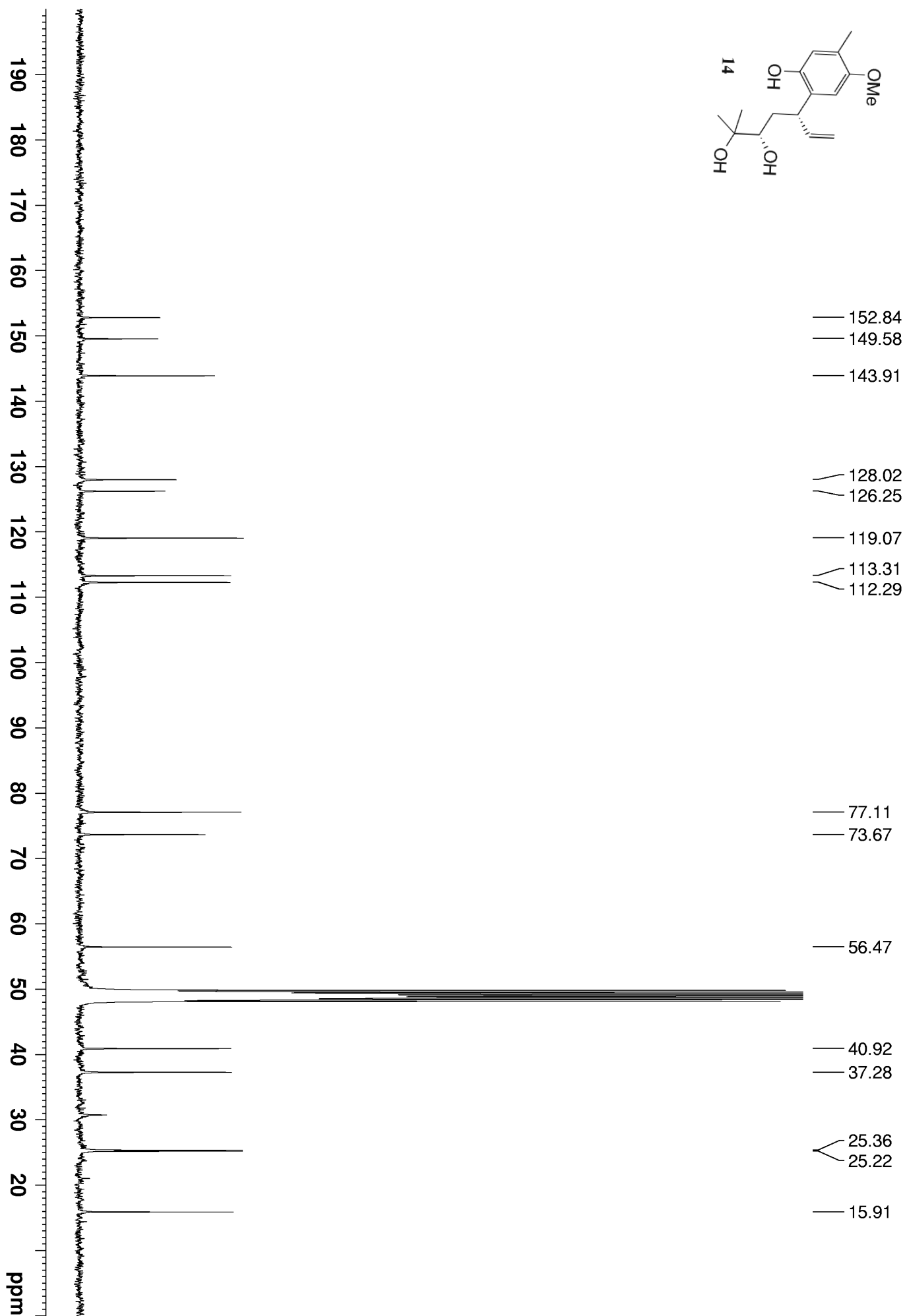
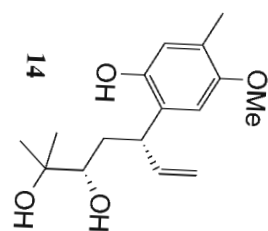


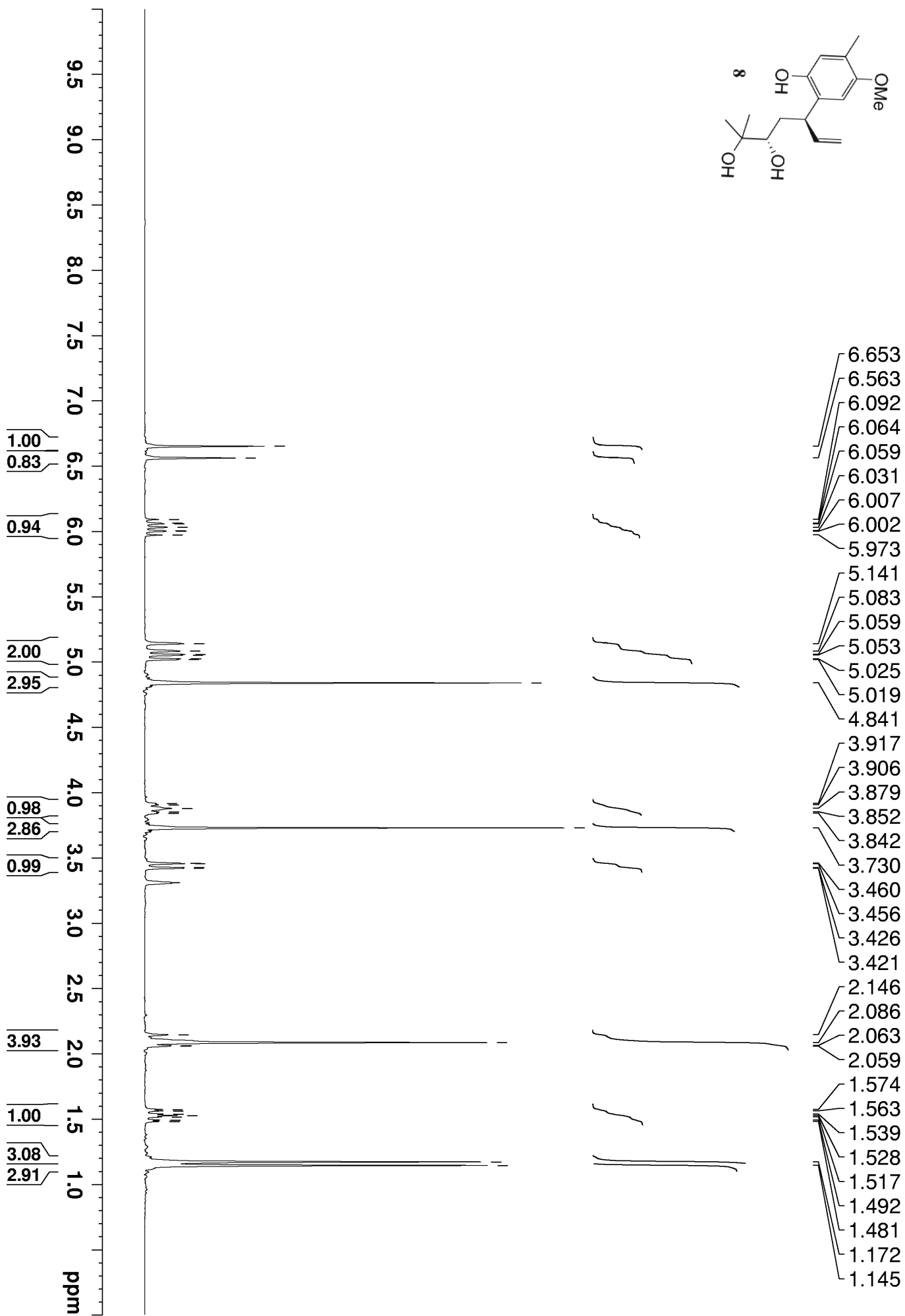
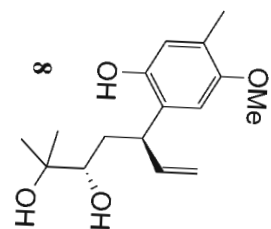


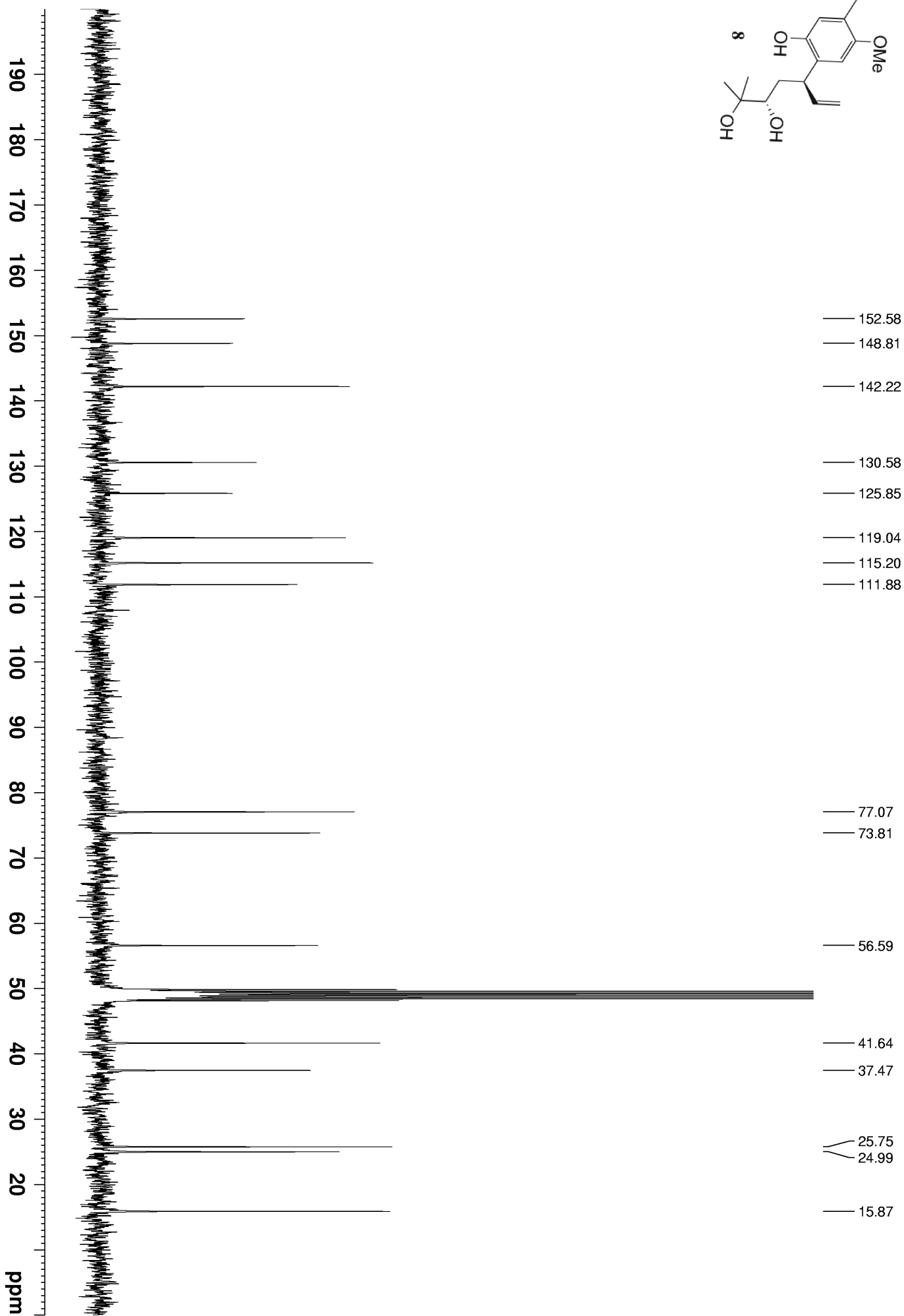
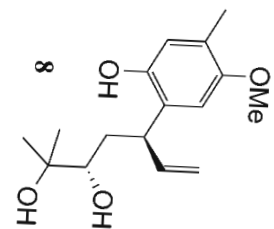


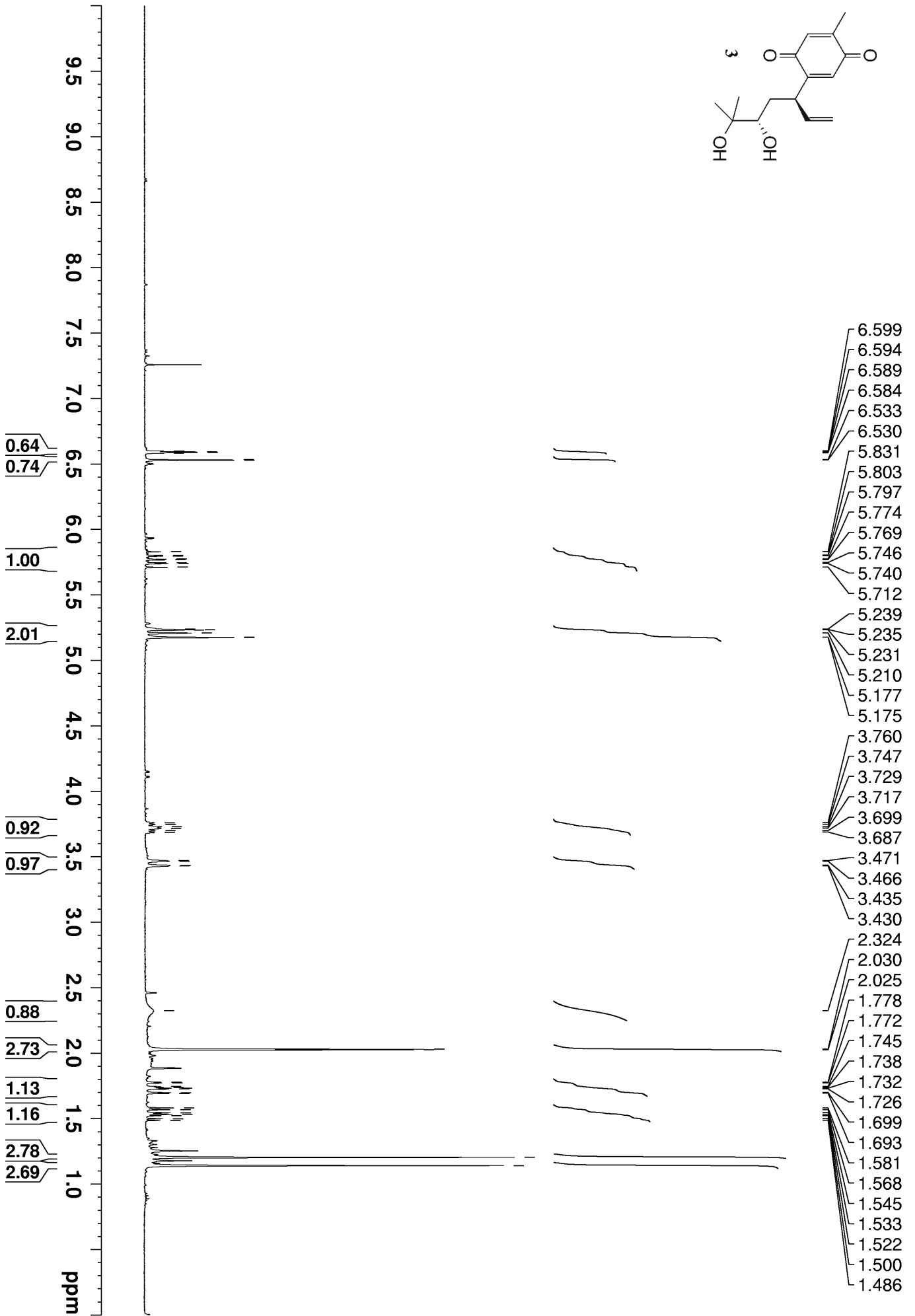
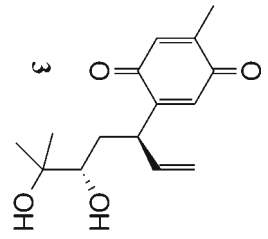


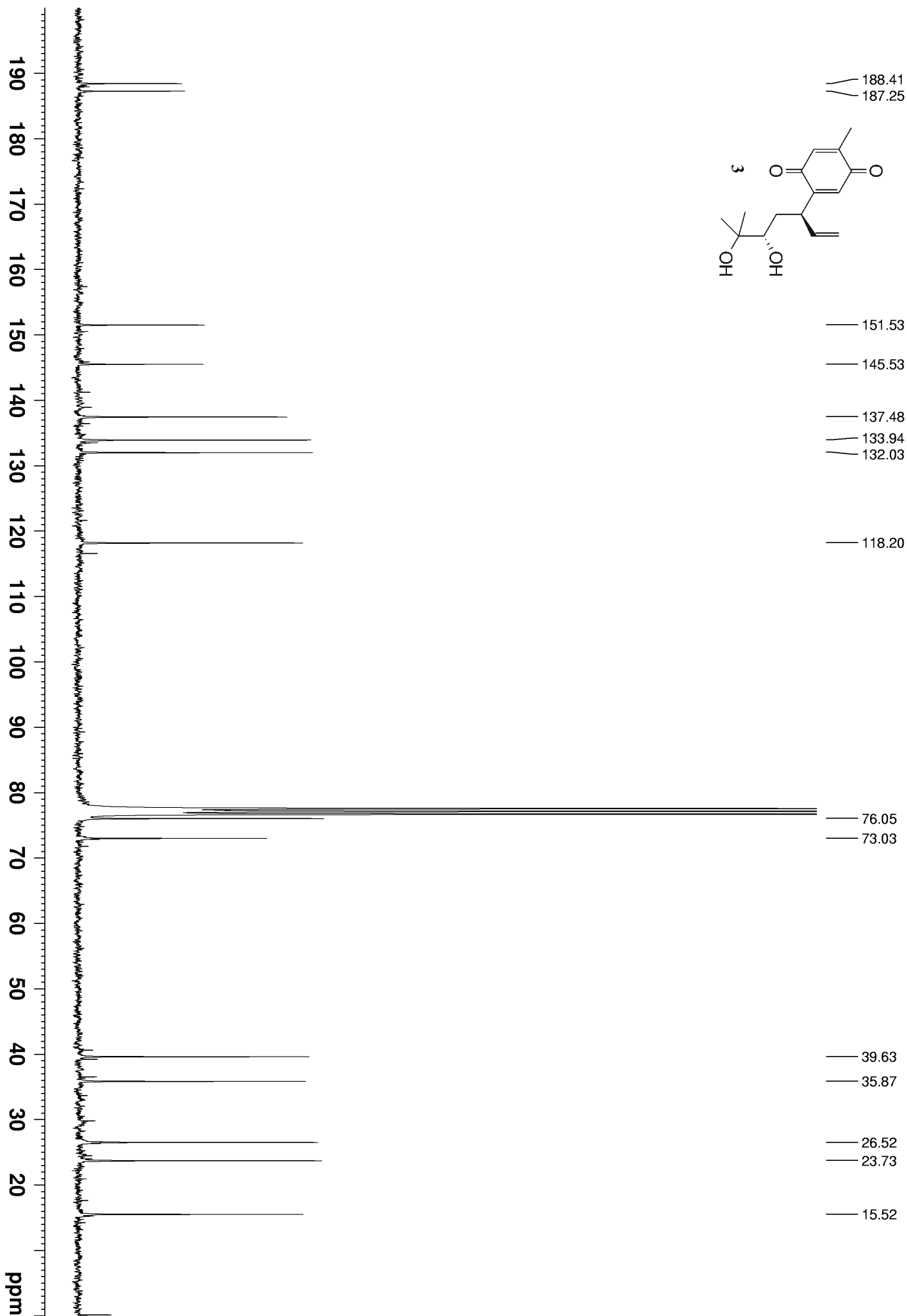


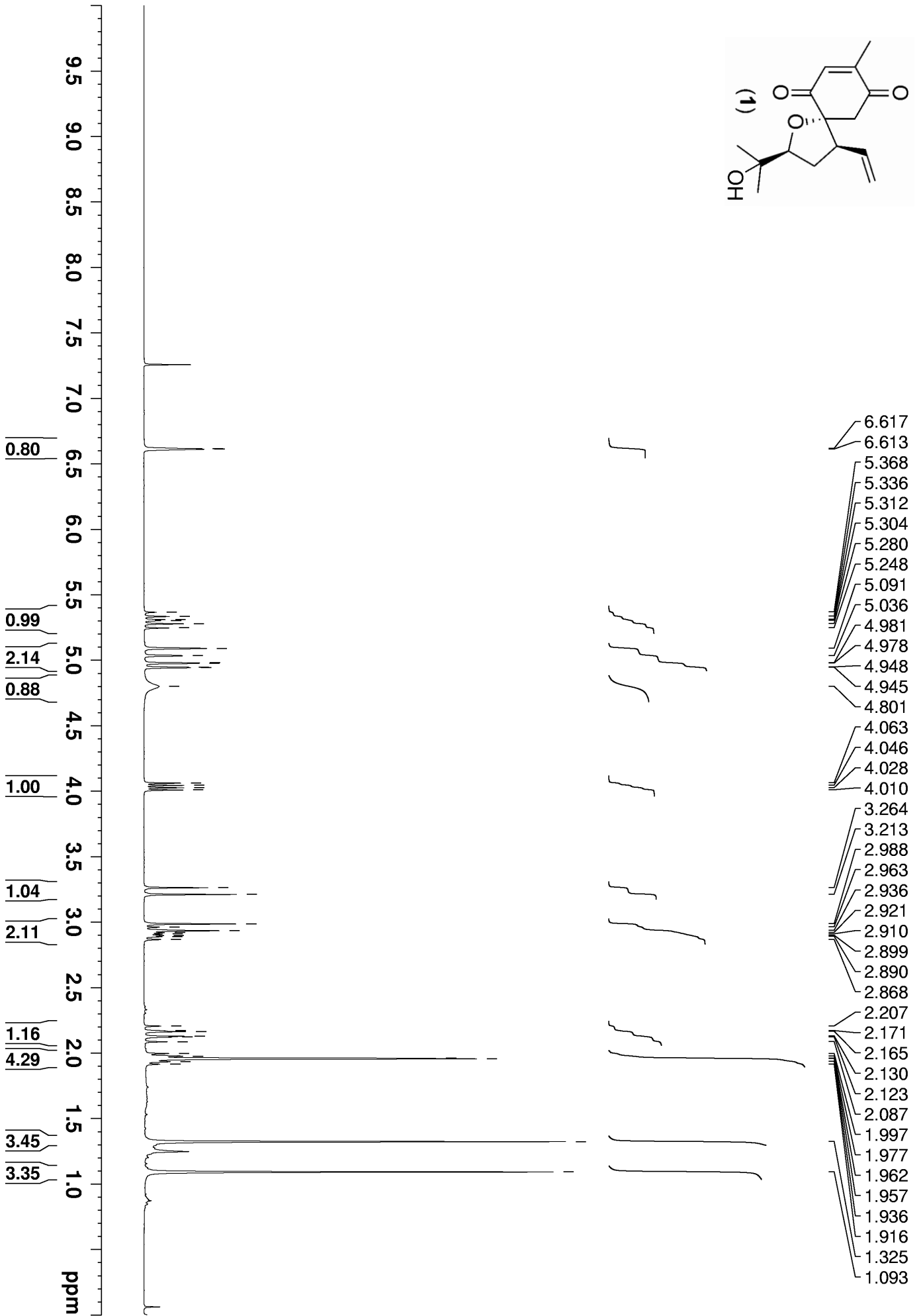
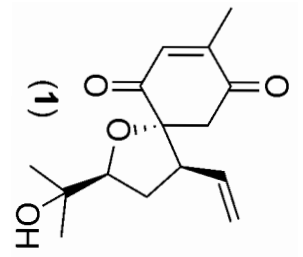


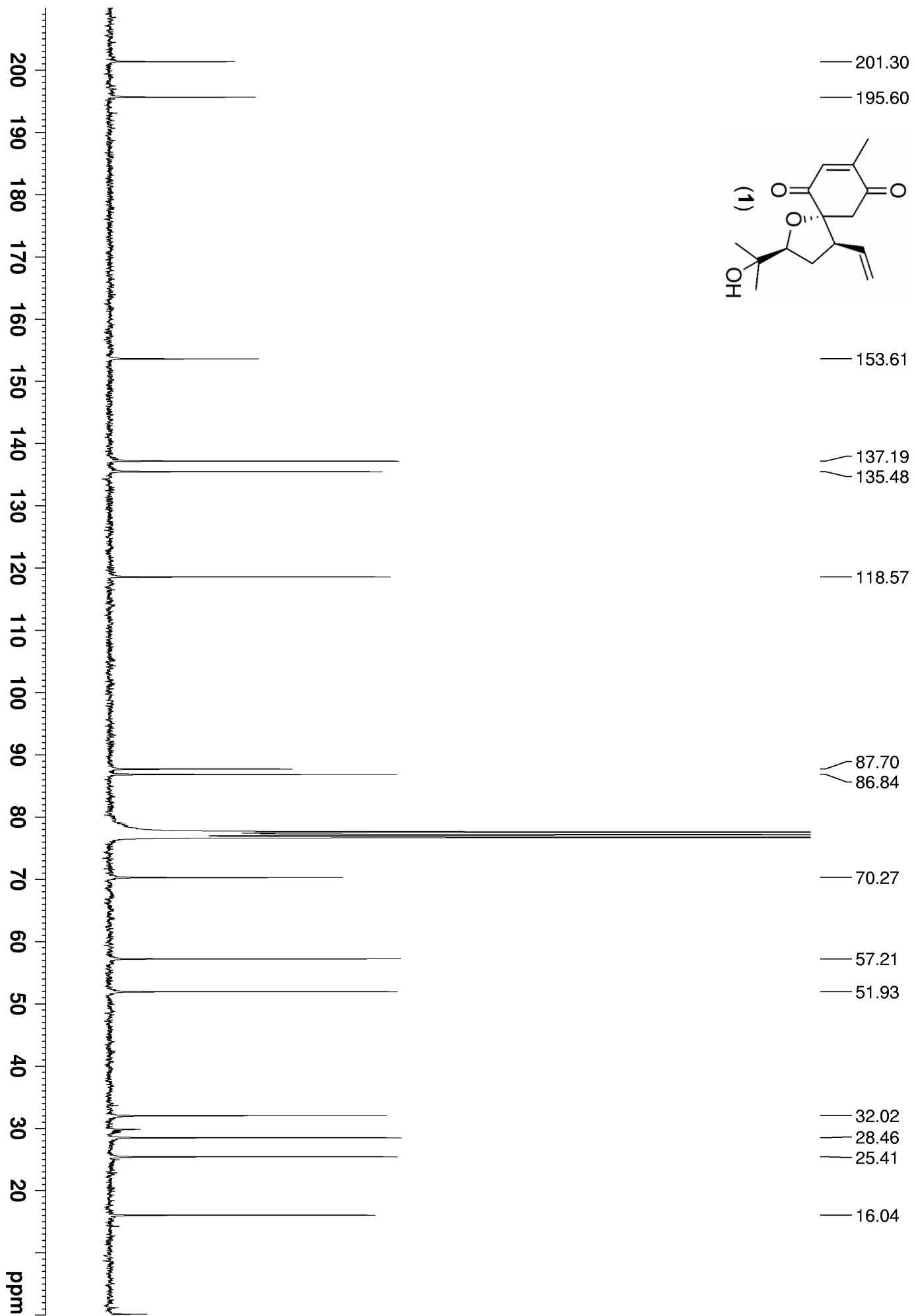


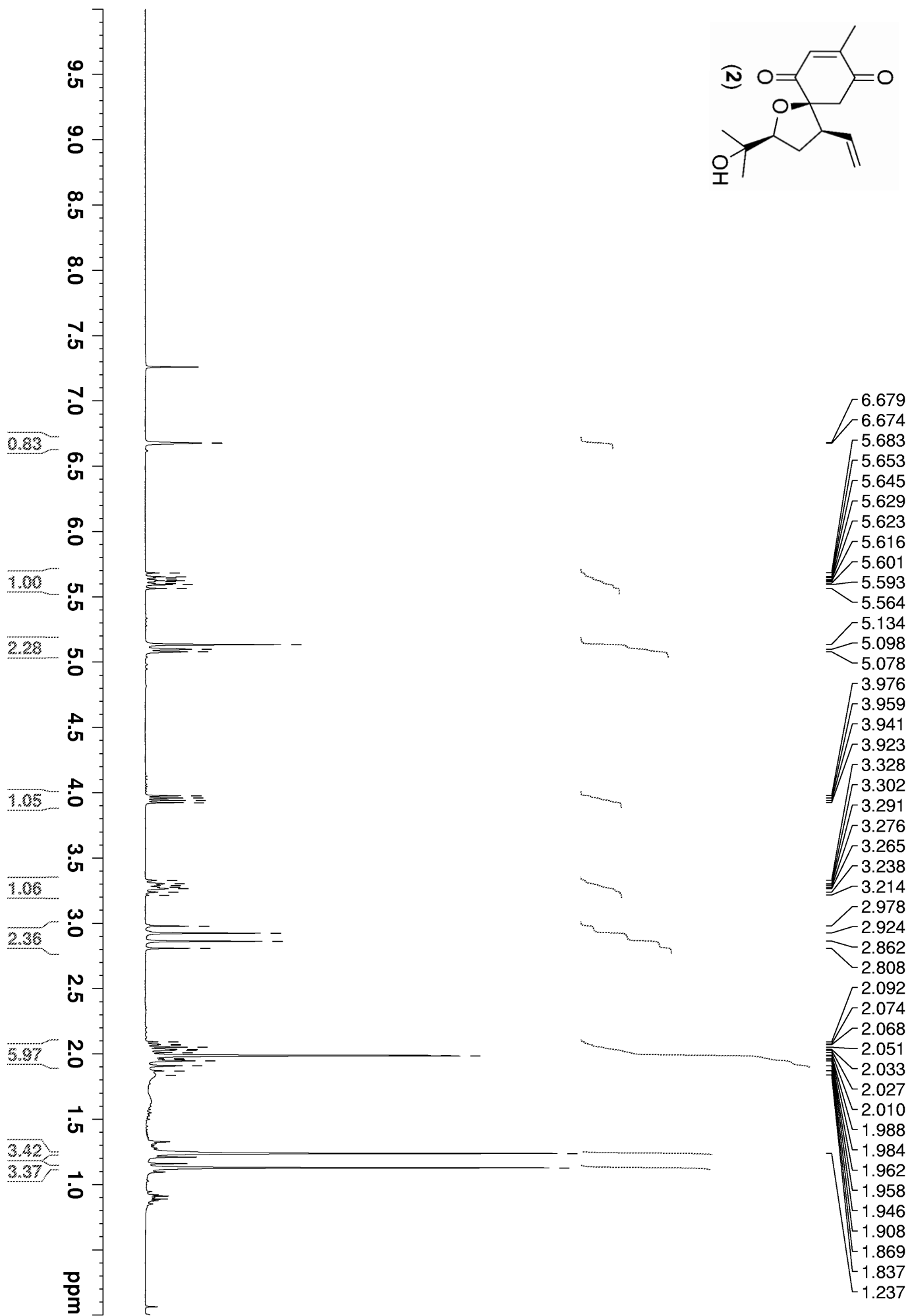
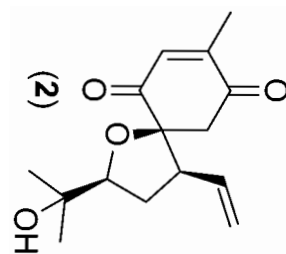


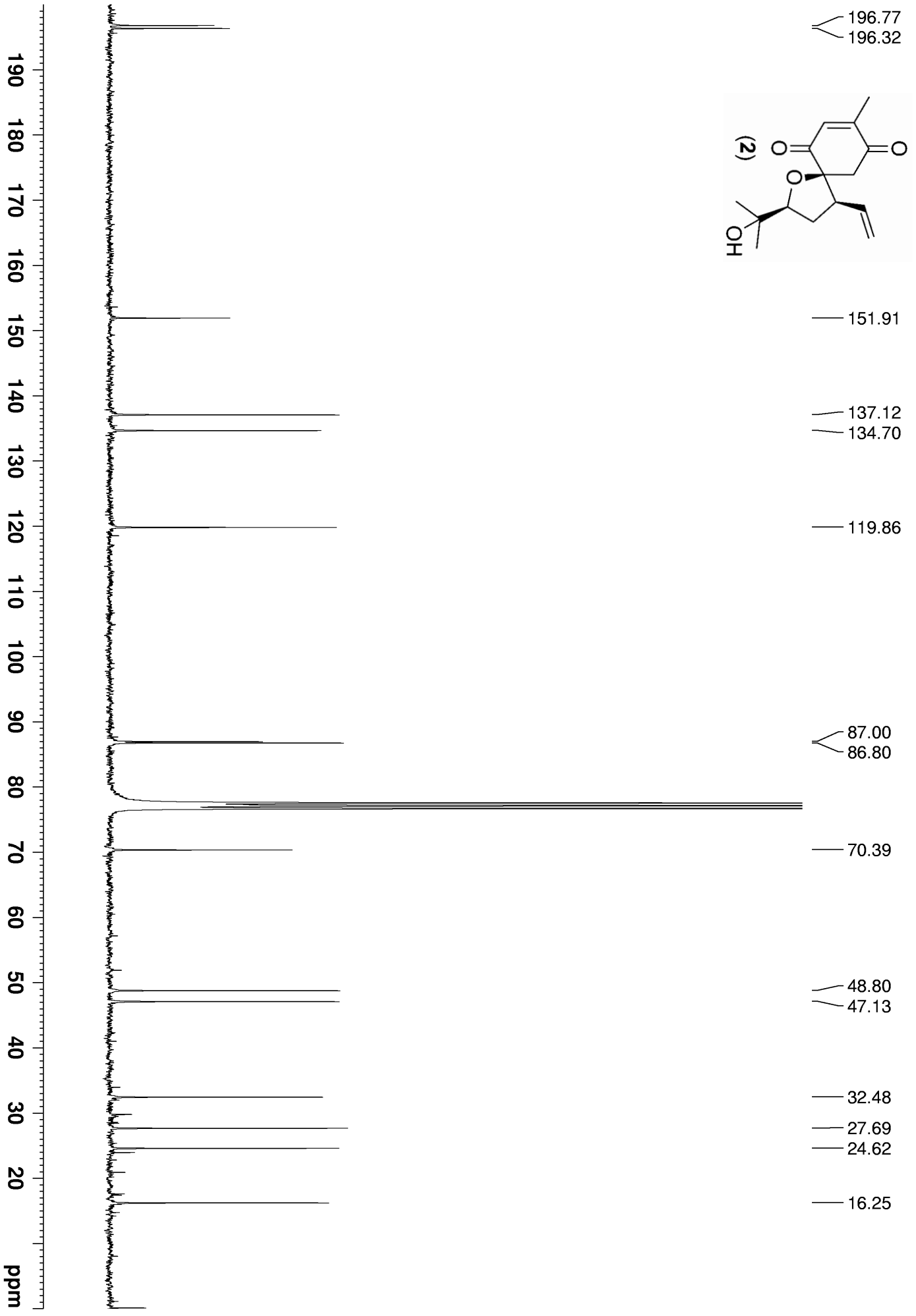












Absolute energies for calculated structures

B3LYP/6-31G* pentane

Compound	G(au)	$\Delta G(\text{au})$	$\Delta G(\text{kJmol}^{-1})$
15	-1246.38675	0	0
TS15a	-1246.32215	0.0646	169.575
TS15b	-1246.31761	0.06914	181.4925
TS15c	-1246.32388	0.06287	165.0337
TS15d	-1246.32534	0.06141	161.2012

Cartesian co-ordinates for calculated structures

Compound 15

C	-0.519334	4.051311	0.684818
C	-1.051481	1.947913	2.459120
C	0.228815	3.944961	1.879003
C	-1.508850	3.114615	0.392136
C	-1.777126	2.057141	1.274525
C	-0.053201	2.893376	2.743909
C	1.298421	4.960065	2.194256
O	-0.190459	5.112444	-0.121089
C	-0.914081	5.282831	-1.330427
O	-1.222270	0.974339	3.415553
C	-2.277903	0.029271	3.268433
C	-1.932649	-1.159079	2.407225
C	-0.717526	-1.449366	1.934845
C	-0.392989	-2.669400	1.115267
C	-0.181326	-2.476839	-0.406271
C	1.041120	-1.586454	-0.811244
C	0.776586	-0.085990	-0.754012
C	2.337692	-1.980379	-0.107278

O	1.185513	-1.925917	-2.263306
O	-0.032923	-3.752344	-0.976766
Al	0.575957	-3.789091	-2.650510
H	2.049421	-1.624176	-2.591603
C	2.211919	-4.862703	-2.945082
C	-0.767402	-3.643959	-4.093416
H	-2.085020	3.183905	-0.523543
H	-2.534463	1.329476	1.007582
H	0.500610	2.791529	3.673463
H	2.073005	4.978544	1.417833
H	0.882874	5.973753	2.243037
H	1.775699	4.736409	3.152772
H	-0.504467	6.177728	-1.802841
H	-1.985784	5.429277	-1.141691
H	-0.782995	4.424849	-2.003257
H	-2.496606	-0.307148	4.290151
H	-3.187537	0.525061	2.901075
H	-2.769274	-1.831617	2.208397
H	0.099738	-0.770693	2.173735
H	0.498643	-3.167494	1.517227
H	-1.213127	-3.391884	1.190937
H	-1.078055	-1.970727	-0.807007
H	1.615831	0.466765	-1.194033
H	0.659103	0.257224	0.276295
H	-0.133291	0.168036	-1.305838
H	3.198164	-1.483485	-0.573400
H	2.310828	-1.667035	0.941072

H	2.489951	-3.062222	-0.144888
H	1.980712	-5.935765	-3.003378
H	2.947688	-4.743426	-2.138317
H	2.716862	-4.605764	-3.887530
H	-0.321157	-3.344983	-5.052645
H	-1.266951	-4.607319	-4.269727
H	-1.556898	-2.915562	-3.863566

TS15a

C	-1.888457	-1.166130	3.113438
C	-2.785545	1.384387	2.244162
C	-3.282346	-0.962803	2.830944
C	-0.974544	-0.154018	2.954327
C	-1.376084	1.113050	2.432384
C	-3.690293	0.272326	2.385412
C	-4.259728	-2.086054	3.065882
O	-1.506107	-2.386738	3.641178
C	-0.873879	-3.275717	2.718352
O	-3.196913	2.531306	1.866334
C	-2.752164	2.538051	-0.270452
C	-1.402172	2.314952	-0.149510
C	-0.866552	1.080109	0.262070
C	0.632085	0.901953	0.273694
C	1.174281	0.518742	-1.133060
C	2.485565	1.296409	-1.508040
C	2.177704	2.699473	-2.023043
C	3.553258	1.288647	-0.416057

O	3.010118	0.517682	-2.670189
O	1.392345	-0.864818	-1.223073
Al	2.119307	-1.275617	-2.805241
H	3.982195	0.529178	-2.667296
C	3.546430	-2.639636	-2.811719
C	0.917479	-1.080520	-4.359977
H	0.063716	-0.331989	3.221613
H	-0.721235	1.966782	2.572559
H	-4.741616	0.465893	2.184888
H	-3.999177	-2.977773	2.483530
H	-4.261418	-2.389495	4.119507
H	-5.273830	-1.780656	2.792395
H	-1.564478	-3.581470	1.920621
H	-0.574848	-4.155109	3.293873
H	0.013352	-2.817361	2.263676
H	-3.451442	1.716590	-0.382473
H	-3.137657	3.527114	-0.493690
H	-0.738845	3.179975	-0.128702
H	-1.455054	0.181664	0.086690
H	1.086834	1.834950	0.625624
H	0.939738	0.104987	0.956071
H	0.425534	0.832438	-1.881161
H	3.092718	3.225996	-2.316622
H	1.679683	3.292267	-1.247722
H	1.514302	2.644266	-2.892125
H	4.490399	1.721237	-0.790185
H	3.233241	1.903040	0.430492

H	3.746611	0.274224	-0.053227
H	3.139332	-3.627294	-2.553052
H	4.359544	-2.440124	-2.100838
H	3.999540	-2.742750	-3.807825
H	1.470252	-1.072637	-5.309843
H	0.190163	-1.901535	-4.424526
H	0.338660	-0.147444	-4.320069

TS15b

C	-0.390536	-0.044232	-3.459730
C	-2.924603	-0.687324	-2.321416
C	-1.582052	0.616404	-3.940806
C	-0.456807	-0.972274	-2.445225
C	-1.693261	-1.236598	-1.788814
C	-2.783355	0.317345	-3.357143
C	-1.467367	1.590041	-5.084415
O	0.748432	0.312881	-4.122387
C	1.989199	-0.185172	-3.641626
O	-4.056073	-1.014793	-1.868873
C	-4.152761	-0.118209	0.341517
C	-2.958697	0.539384	0.274804
C	-1.716753	-0.136041	0.244212
C	-0.421713	0.625025	0.388911
C	0.327474	0.316054	1.713265
C	1.254851	-0.956686	1.674426
C	0.499718	-2.266394	1.879351
C	2.184684	-1.008299	0.466298

O	2.112849	-0.786736	2.892198
O	1.099525	1.427599	2.088017
Al	1.936904	1.072752	3.629271
H	3.017834	-1.085042	2.698476
C	3.742395	1.837855	3.833524
C	0.778052	0.790182	5.204217
H	0.430314	-1.511552	-2.133178
H	-1.786474	-2.155144	-1.219020
H	-3.698272	0.783919	-3.714103
H	-2.446891	2.005292	-5.336996
H	-0.787172	2.414360	-4.840910
H	-1.057794	1.099126	-5.975664
H	2.758040	0.269897	-4.268189
H	2.048024	-1.277753	-3.728200
H	2.148596	0.104138	-2.594804
H	-5.096443	0.412173	0.274949
H	-4.204443	-1.175907	0.571497
H	-2.955125	1.610624	0.073656
H	-1.732078	-1.141244	0.651229
H	0.241600	0.475994	-0.470445
H	-0.638067	1.698126	0.417248
H	-0.438498	0.109191	2.482038
H	1.196498	-3.110756	1.937145
H	-0.184635	-2.453860	1.045504
H	-0.081815	-2.232161	2.806845
H	2.900953	-1.834394	0.565831
H	1.607832	-1.193762	-0.442501

H	2.730269	-0.067198	0.342787
H	3.700150	2.933160	3.752136
H	4.460739	1.495348	3.076255
H	4.171757	1.612975	4.819487
H	1.343439	0.348140	6.036997
H	0.339527	1.724525	5.579011
H	-0.057758	0.109021	4.993344

TS15c

C	-1.053580	-2.483840	-1.952699
C	-2.941273	-0.403310	-2.428516
C	-2.451140	-2.709108	-1.676776
C	-0.612033	-1.270612	-2.429833
C	-1.522213	-0.178150	-2.579504
C	-3.337603	-1.684943	-1.889114
C	-2.893994	-4.063480	-1.185576
O	-0.259152	-3.573581	-1.719037
C	1.136938	-3.452465	-1.950066
O	-3.793678	0.512352	-2.655771
C	-3.642944	1.803378	-0.839943
C	-2.295713	2.048988	-0.935863
C	-1.325456	1.053022	-0.714074
C	0.143605	1.410987	-0.684691
C	0.729834	1.438220	0.758717
C	1.678639	0.231229	1.069340
C	0.914978	-1.061139	1.330894
C	2.810724	0.056603	0.058187

O	2.297161	0.641328	2.367043
O	1.422992	2.635601	0.997877
Al	2.104459	2.623116	2.652164
H	3.182651	0.249023	2.452011
C	3.907188	3.395492	2.861794
C	0.782569	2.716215	4.118937
H	0.434135	-1.119498	-2.672789
H	-1.216331	0.671670	-3.180026
H	-4.399456	-1.835269	-1.708273
H	-3.975598	-4.082186	-1.025246
H	-2.636430	-4.847344	-1.908141
H	-2.395530	-4.330296	-0.246179
H	1.566492	-4.425494	-1.705121
H	1.582738	-2.684911	-1.304520
H	1.352645	-3.208937	-2.997842
H	-4.372003	2.558154	-1.114845
H	-4.024015	0.946345	-0.295927
H	-1.966591	2.975725	-1.404772
H	-1.620032	0.199837	-0.106065
H	0.718116	0.728673	-1.314873
H	0.285836	2.415352	-1.095195
H	-0.113683	1.343231	1.465833
H	1.597029	-1.876533	1.598307
H	0.360030	-1.363666	0.436914
H	0.203226	-0.923089	2.150542
H	3.547540	-0.670346	0.424314
H	2.426816	-0.333300	-0.888717

H	3.312983	1.008034	-0.138757
H	3.876280	4.483047	2.704613
H	4.644563	2.997128	2.152118
H	4.306142	3.240058	3.873814
H	1.232641	2.475097	5.092212
H	0.334447	3.714253	4.214823
H	-0.044951	2.009337	3.968298

TS15d

C	-0.190342	3.293138	-1.151231
C	-2.804799	2.171793	-1.150047
C	-0.881942	3.100479	-2.396436
C	-0.757989	2.917307	0.041773
C	-2.026158	2.273048	0.068932
C	-2.129090	2.522844	-2.378368
C	-0.230547	3.548389	-3.680661
O	1.076171	3.851405	-1.195738
C	1.145476	5.214990	-0.774151
O	-3.990007	1.723183	-1.146657
C	-3.838903	-0.508890	-0.519764
C	-2.475259	-0.580999	-0.567019
C	-1.638555	0.026788	0.392329
C	-0.150521	-0.155597	0.295020
C	0.281926	-1.546521	0.839016
C	1.528359	-2.116307	0.073937
C	1.102451	-2.834362	-1.202479
C	2.642379	-1.101257	-0.163341

O	2.054597	-3.167595	0.998723
O	0.534223	-1.484761	2.216873
Al	1.157686	-3.060703	2.792098
H	3.026003	-3.137205	1.014968
C	2.579902	-3.030932	4.160050
C	-0.140156	-4.549596	2.754516
H	-0.215529	3.091381	0.967708
H	-2.579515	2.242554	1.001184
H	-2.684084	2.381868	-3.302948
H	0.007482	4.618724	-3.653013
H	0.715923	3.023276	-3.855431
H	-0.890986	3.368497	-4.533852
H	0.547490	5.863678	-1.428127
H	2.196877	5.505233	-0.837456
H	0.796110	5.333416	0.259123
H	-4.358350	-0.184095	0.373965
H	-4.451422	-0.903340	-1.323297
H	-2.004728	-0.927256	-1.488338
H	-2.041450	0.165153	1.392118
H	0.145009	-0.037929	-0.753652
H	0.386159	0.598953	0.875831
H	-0.536174	-2.258578	0.636760
H	1.966460	-3.227152	-1.748621
H	0.563815	-2.144807	-1.861770
H	0.433293	-3.666170	-0.960556
H	3.524037	-1.592400	-0.595661
H	2.316380	-0.341831	-0.880010

H	2.929426	-0.595747	0.764219
H	2.189172	-2.651296	5.114637
H	3.444944	-2.404900	3.903825
H	2.955910	-4.043931	4.361540
H	0.349157	-5.522508	2.901066
H	-0.895695	-4.452972	3.546149
H	-0.684617	-4.606458	1.802259

B3LYP/6-31G* pentane

Compound	G(au)
TS16a	-1246.70941
TS16b	-1246.69853
TS16c	-1246.69347
TS16d	-1246.70856

B3LYP/6-31G* CH₂Cl₂

Compound	G(au)
1	-884.506068
2	-884.508059