

Electronic Supplementary Information

Total synthesis and stereochemical assignment of cryptolatifolione

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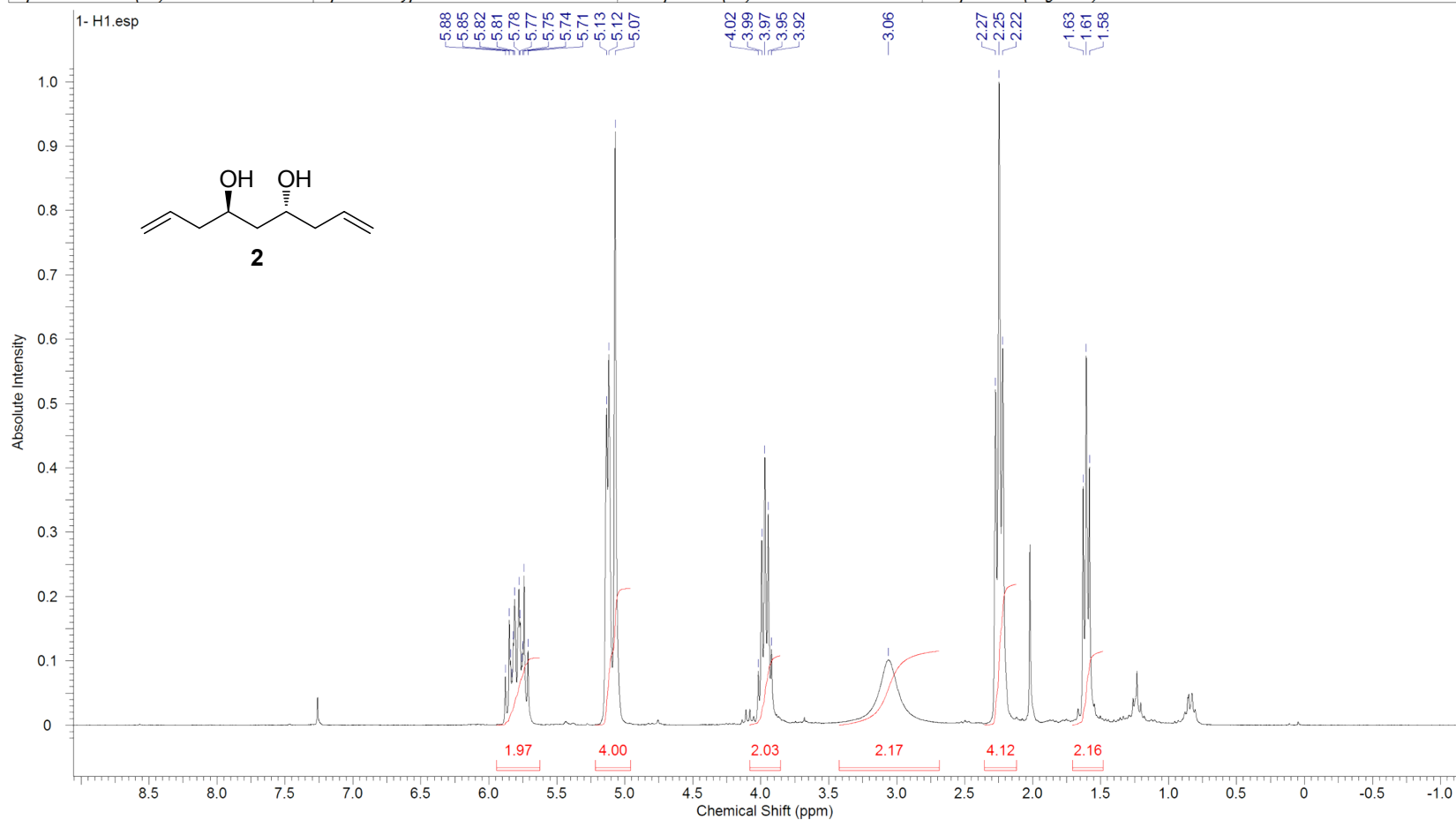
Homepage: <http://www.pilli.iqm.unicamp.br>

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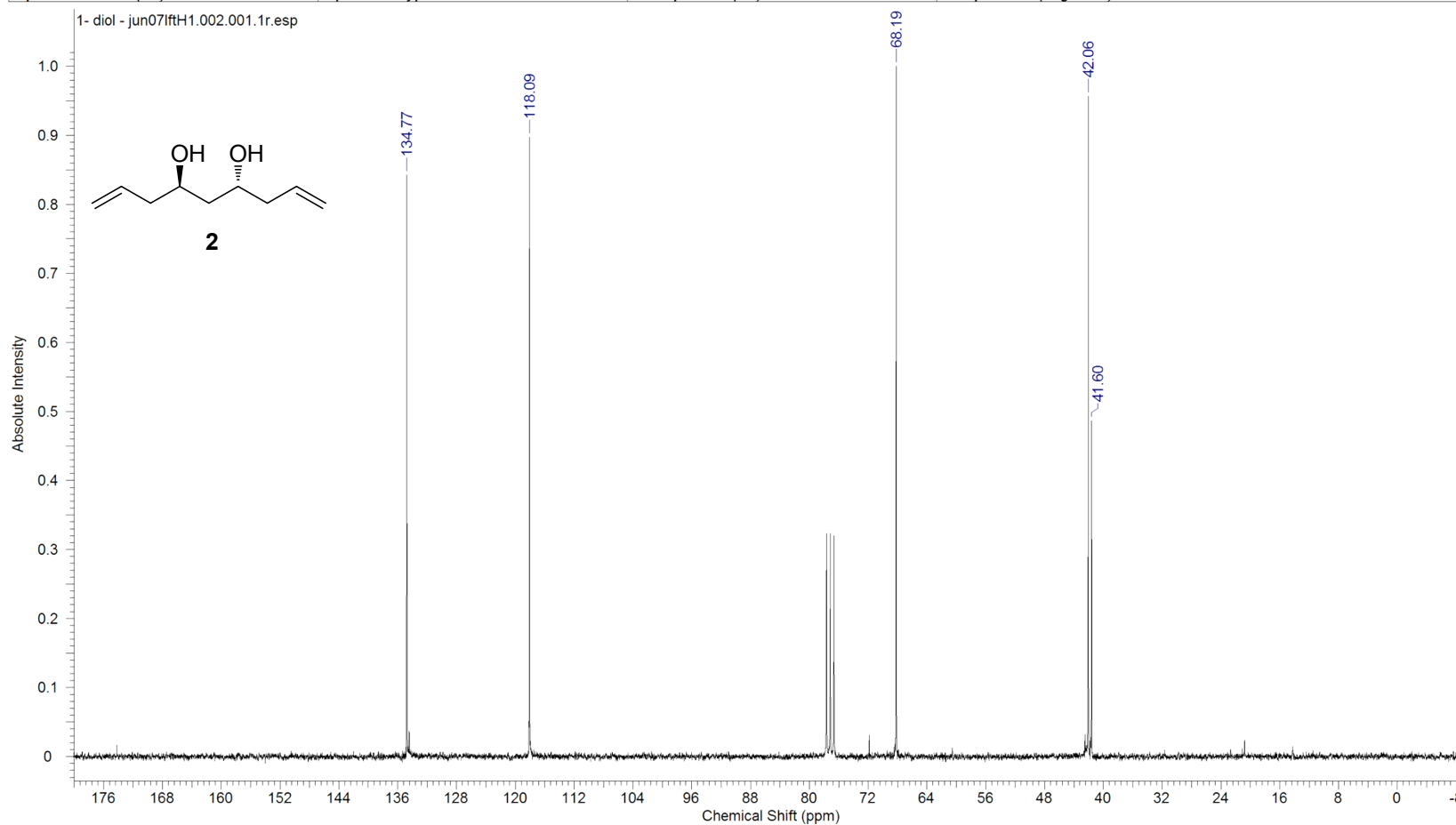
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I. Spectral data and chromatograms.

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Spectrum Offset (Hz)	1750.6281	Spectrum Type	STANDARD	Sweep Width (Hz)	5175.83
				Temperature (degree C)	25.160

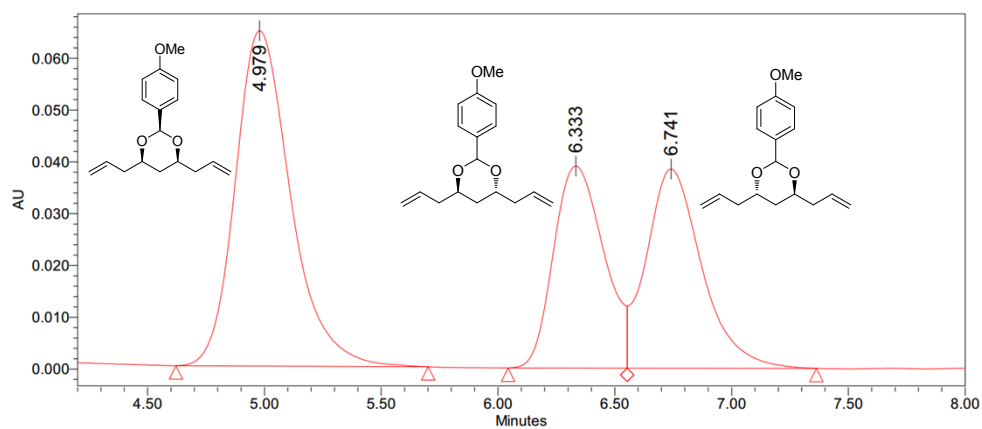


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Spectrum Offset (Hz)	6297.2959	Spectrum Type	STANDARD	Sweep Width (Hz)	15059.78
				Temperature (degree C)	25.160



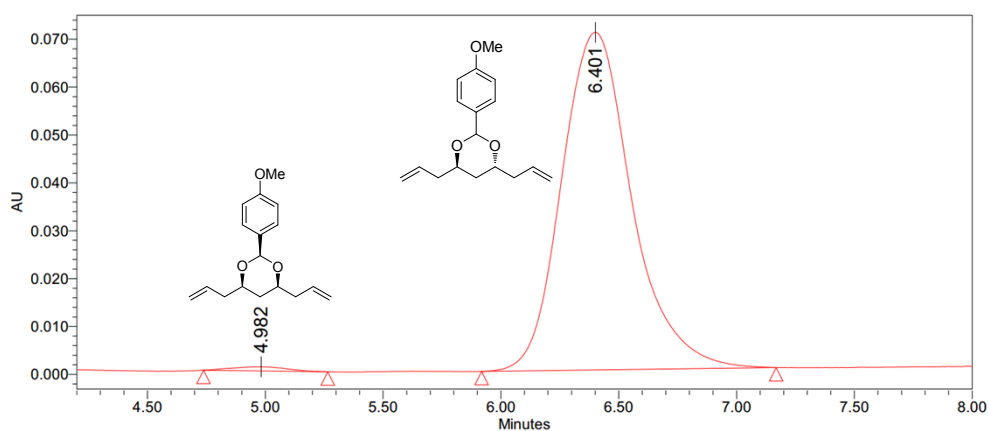
HPLC: Chiralpak® IA column, hexanes:*i*-PrOH 98:2, 1.0 mL/min, 224.0 nm

HPLC of racemic and *meso* compound derivative:



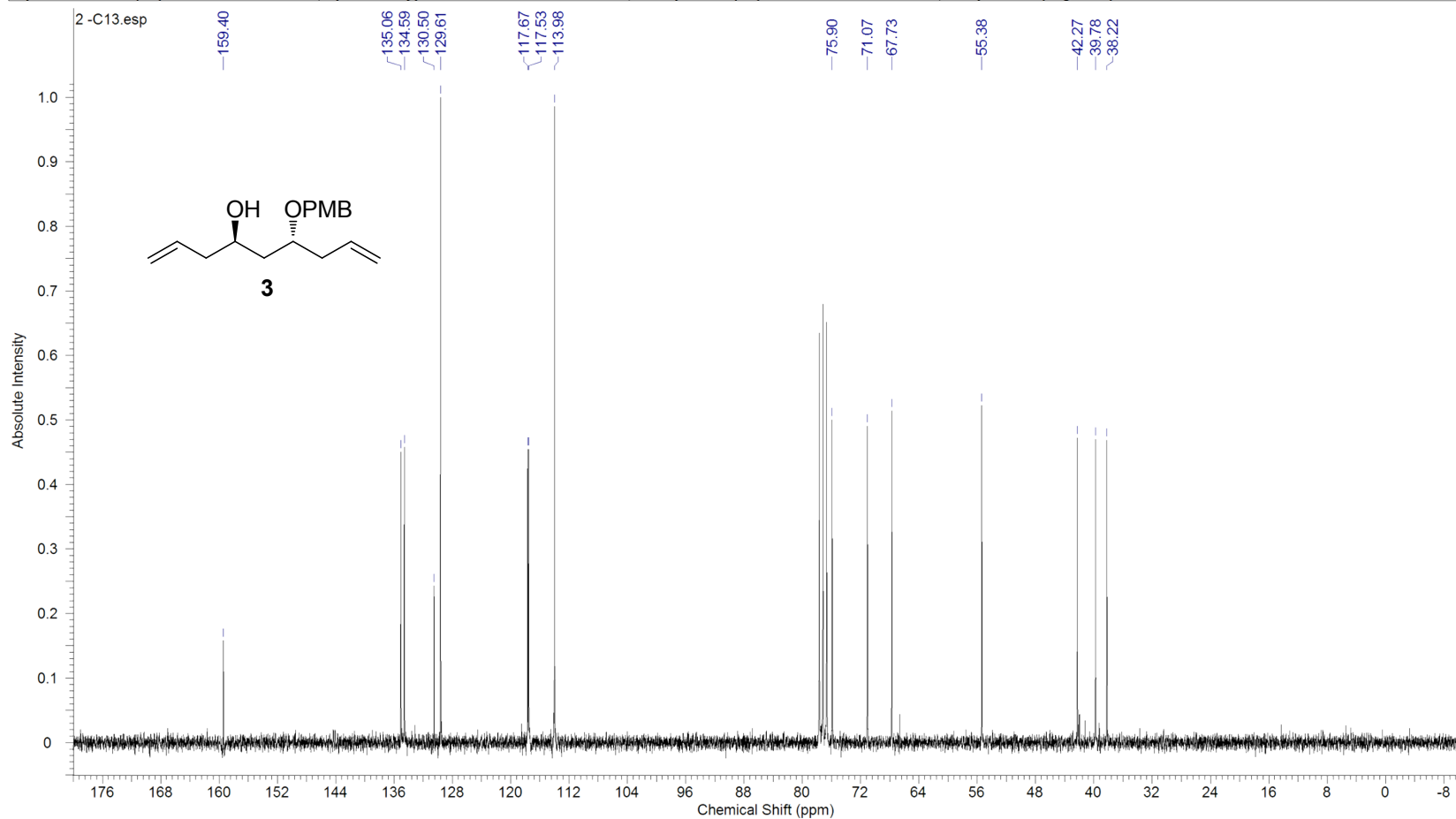
Compound	Retention time (min)	Area %
<i>meso</i>	4.98	46.6
<i>R,R</i>	6.33	25.5
<i>S,S</i>	6.74	27.9

Enantioenriched compound derivative:

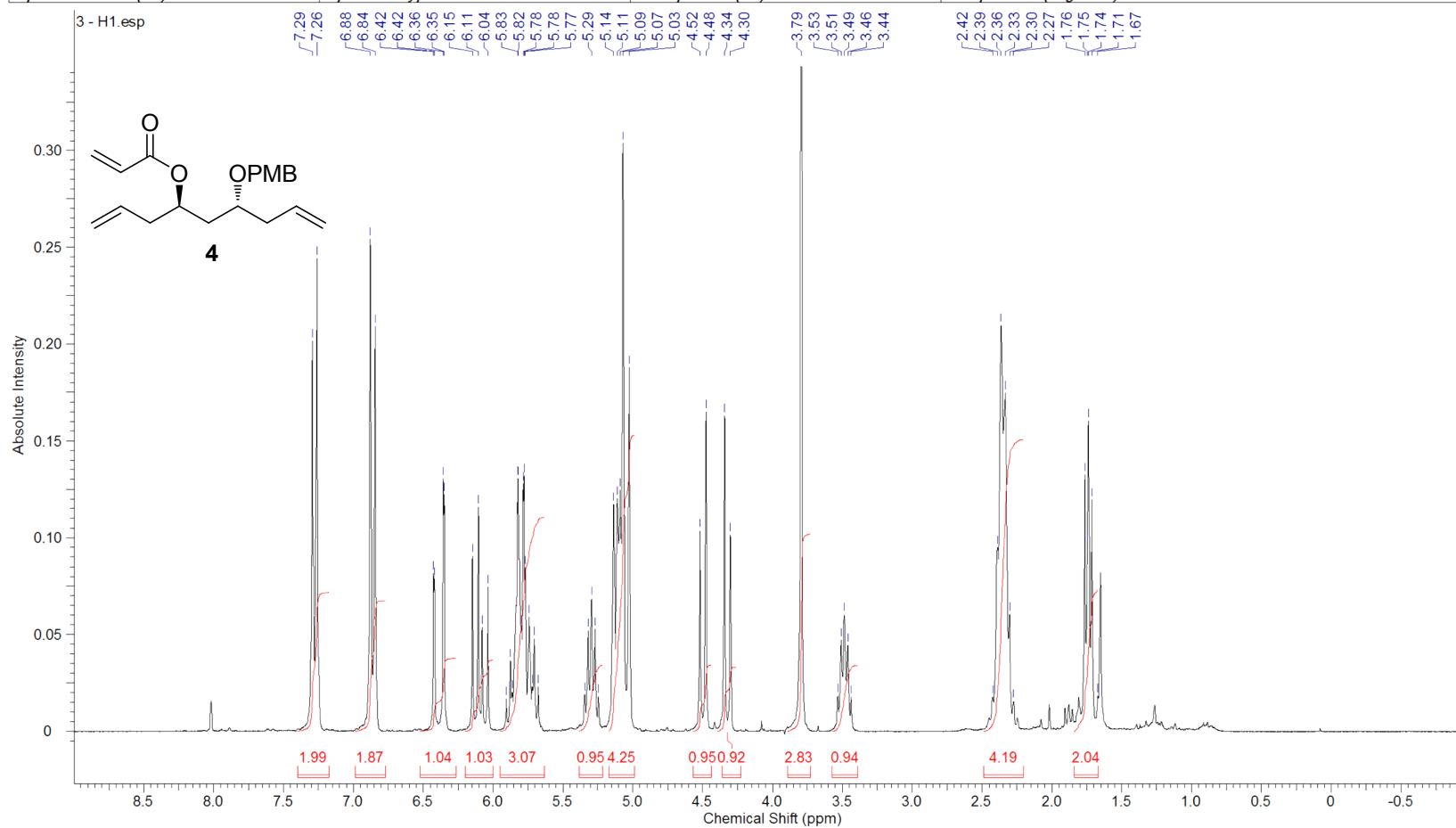


Compound	Retention time (min)	Area %
<i>meso</i>	4.98	0.9
<i>R,R</i>	6.40	99.1

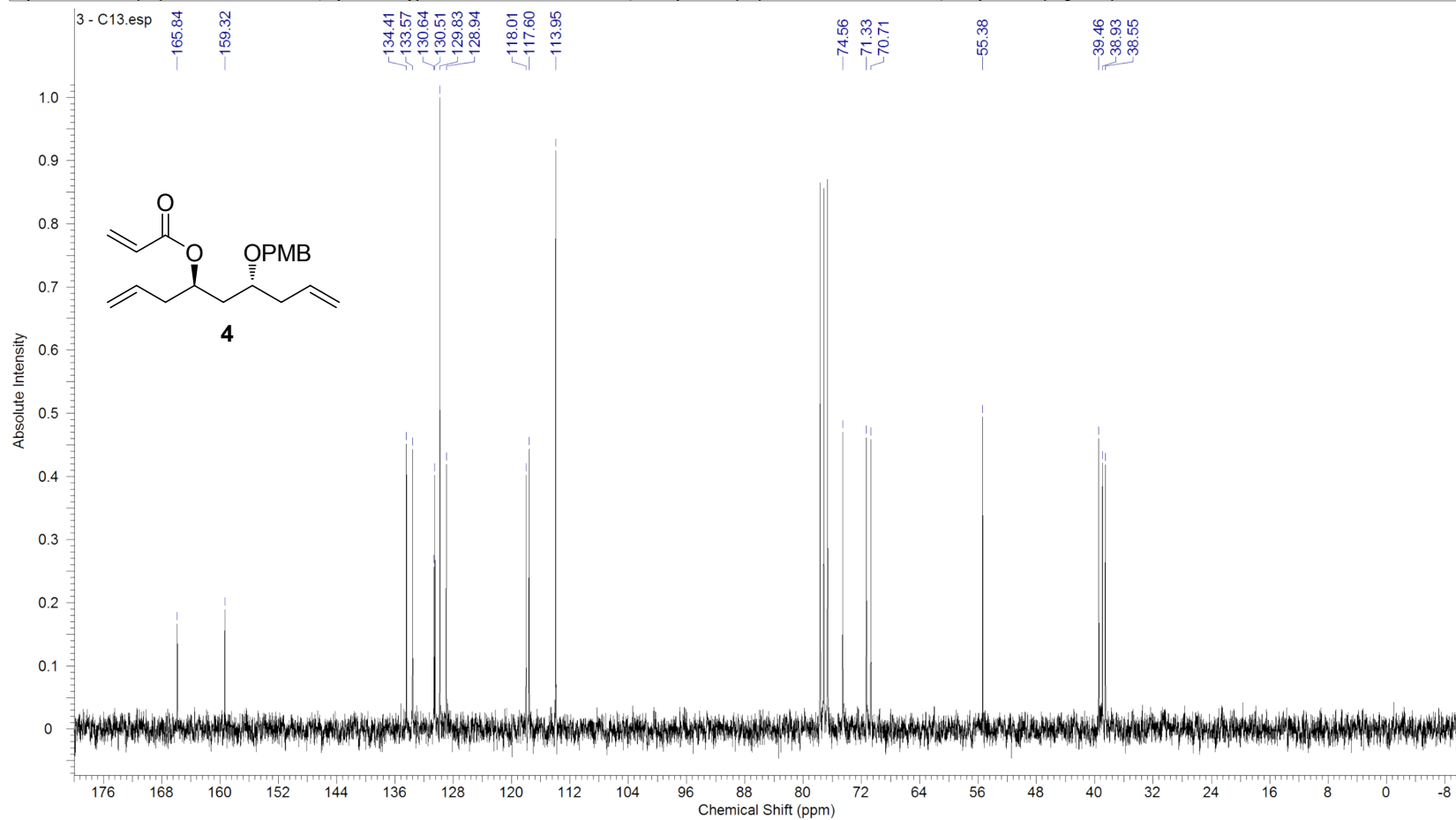
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Frequency (MHz)	62.90	Nucleus	13C	Number of Transients	512
Original Points Count	8192	Owner	root	Points Count	32768
Receiver Gain	724.10	SW(cyclical) (Hz)	15060.24	Solvent	CHLOROFORM-d
Spectrum Offset (Hz)	6297.2959	Spectrum Type	STANDARD	Sweep Width (Hz)	15059.78
				Temperature (degree C)	25.260



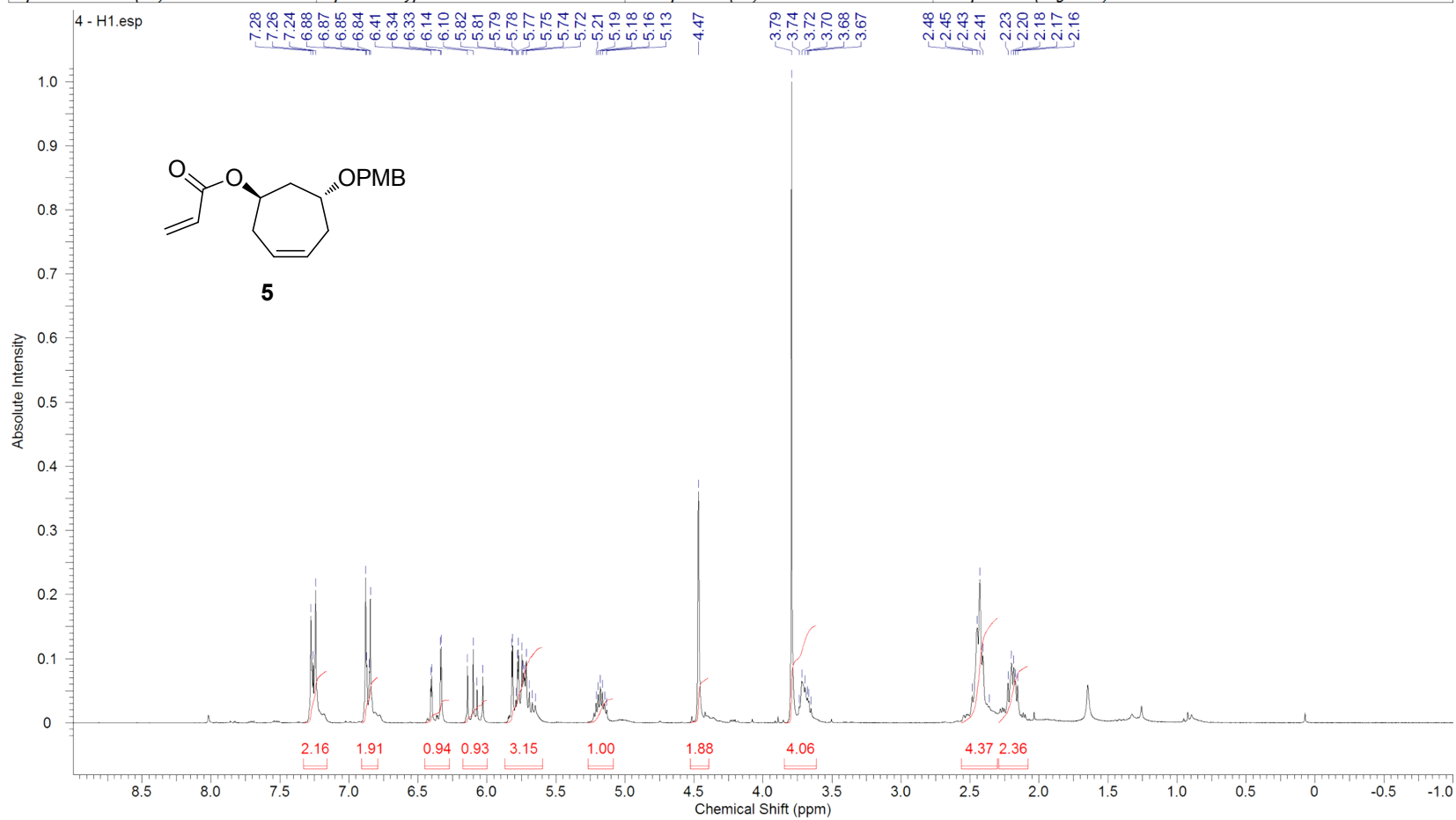
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Spectrum Offset (Hz)	1751.7339	Spectrum Type	STANDARD	Sweep Width (Hz)	5175.83
				Temperature (degree C)	25.160



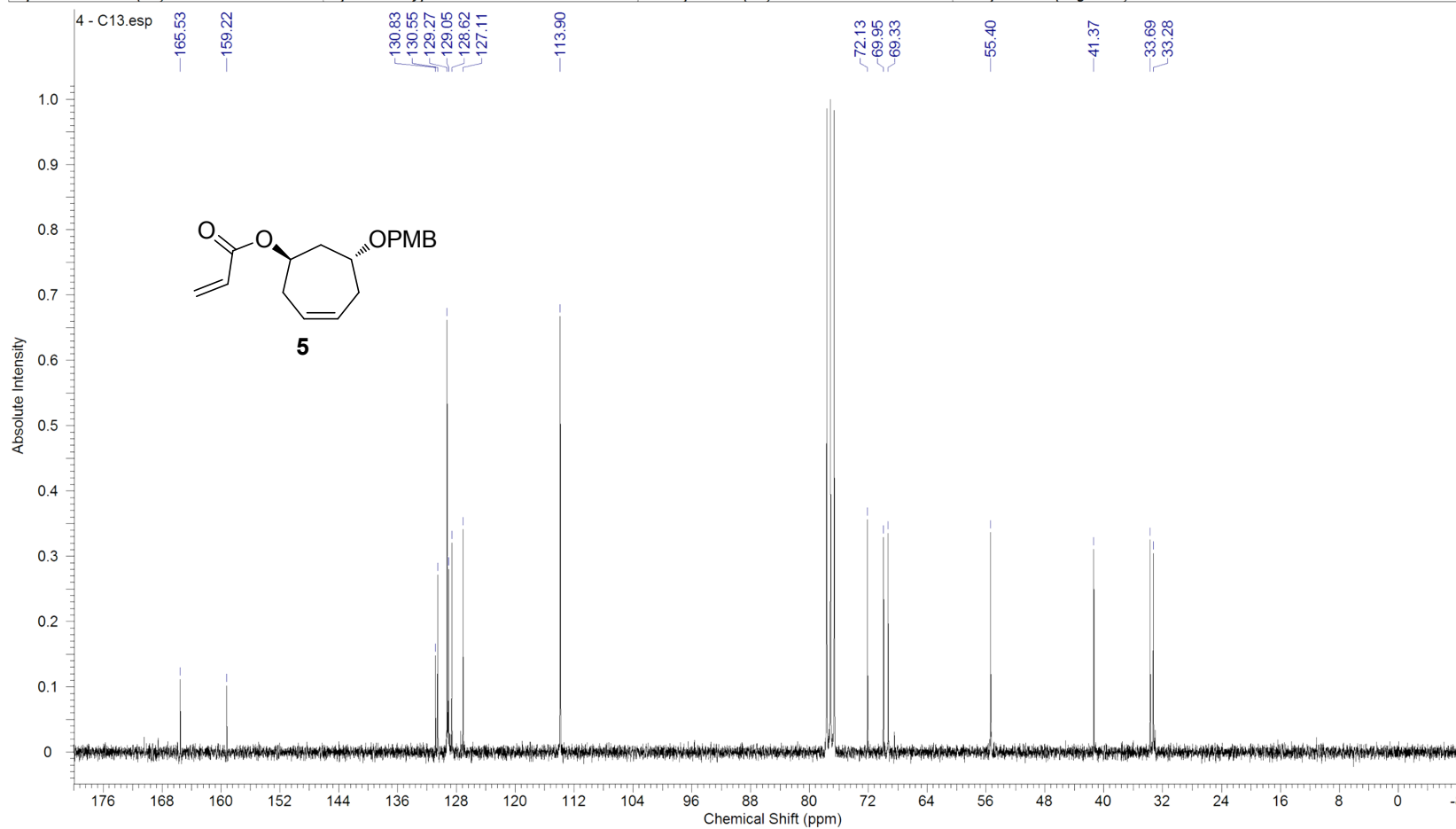
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Original Points Count	8192	Owner	root	Points Count	32768
Receiver Gain	1024.00	SW(cyclical) (Hz)	15060.24	Solvent	CHLOROFORM-d
Spectrum Offset (Hz)	6298.2158	Spectrum Type	STANDARD	Sweep Width (Hz)	15059.78
				Temperature (degree C)	25.160



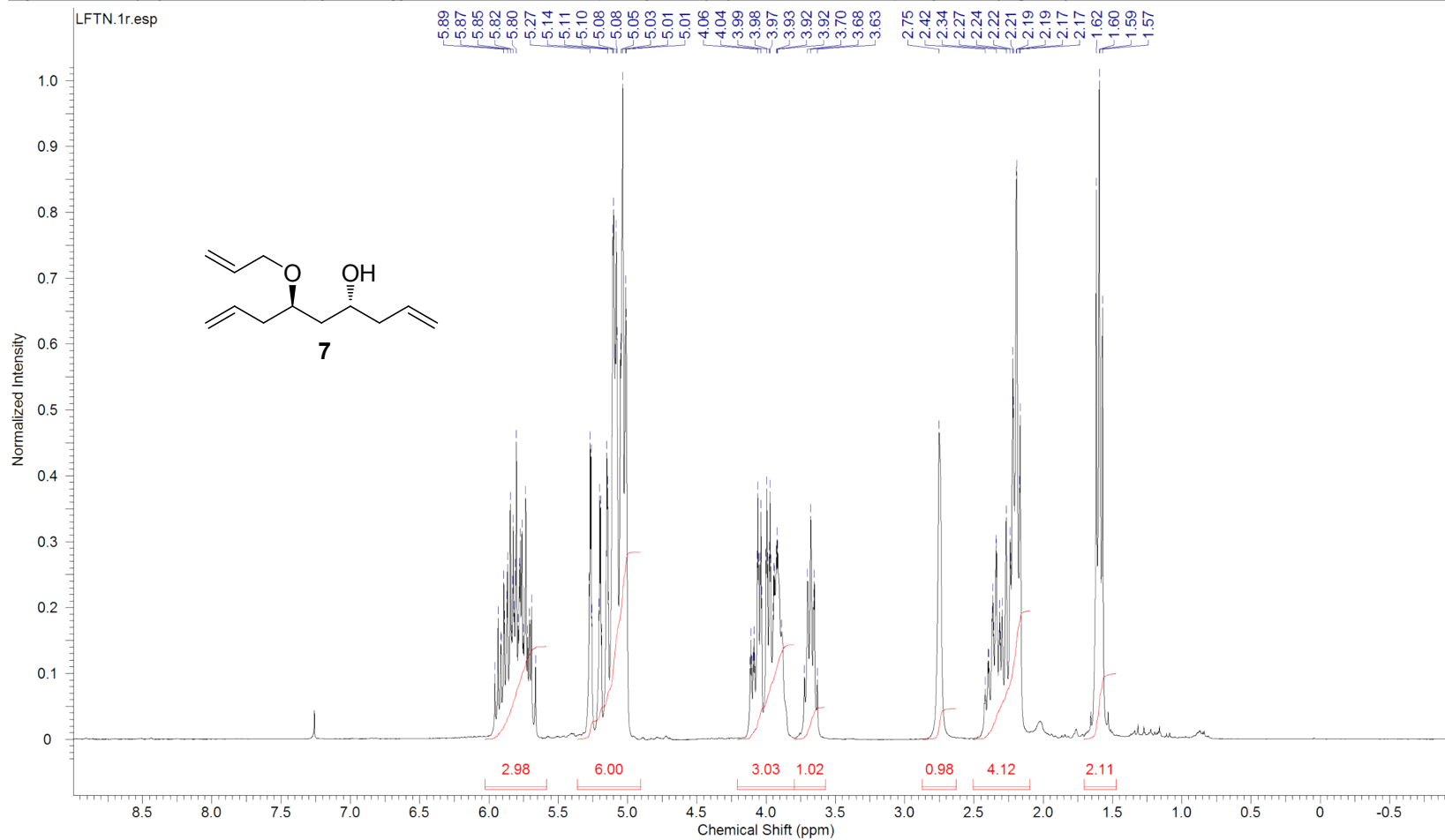
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Frequency (MHz)	250.13	Nucleus	1H	Number of Transients	17
Original Points Count	16384	Owner	root	Points Count	32768
Receiver Gain	574.70	SW(cyclical) (Hz)	5175.98	Solvent	CHLOROFORM-d
Spectrum Offset (Hz)	1750.4702	Spectrum Type	STANDARD	Sweep Width (Hz)	5175.83
				Temperature (degree C)	25.160



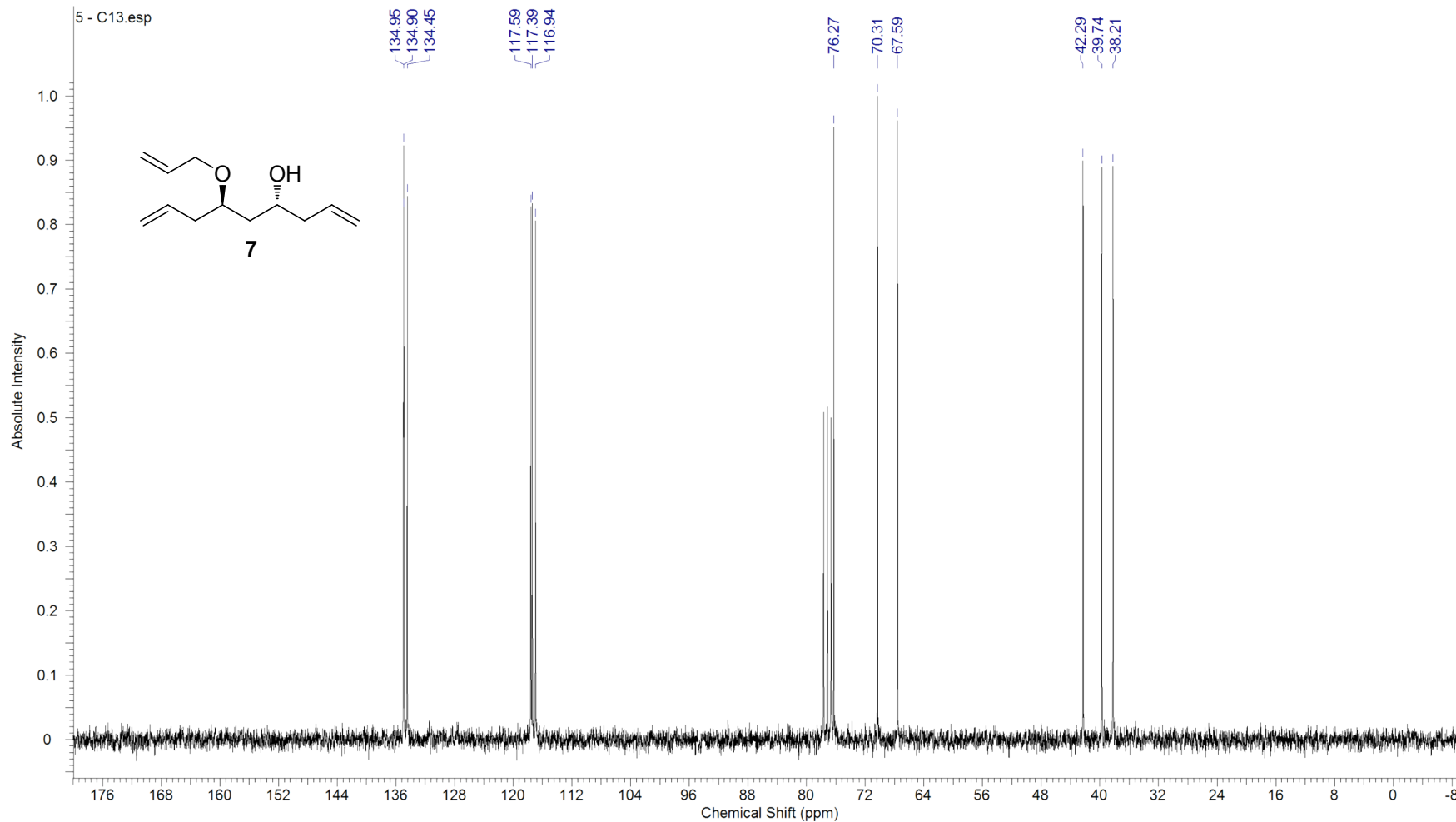
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Frequency (MHz)	62.90	Nucleus	13C	Number of Transients	1024
Original Points Count	8192	Owner	root	Points Count	32768
Receiver Gain	724.10	SW(cyclical) (Hz)	15060.24	Solvent	CHLOROFORM-d
Spectrum Offset (Hz)	6298.2158	Spectrum Type	STANDARD	Sweep Width (Hz)	15059.78
				Temperature (degree C)	25.160



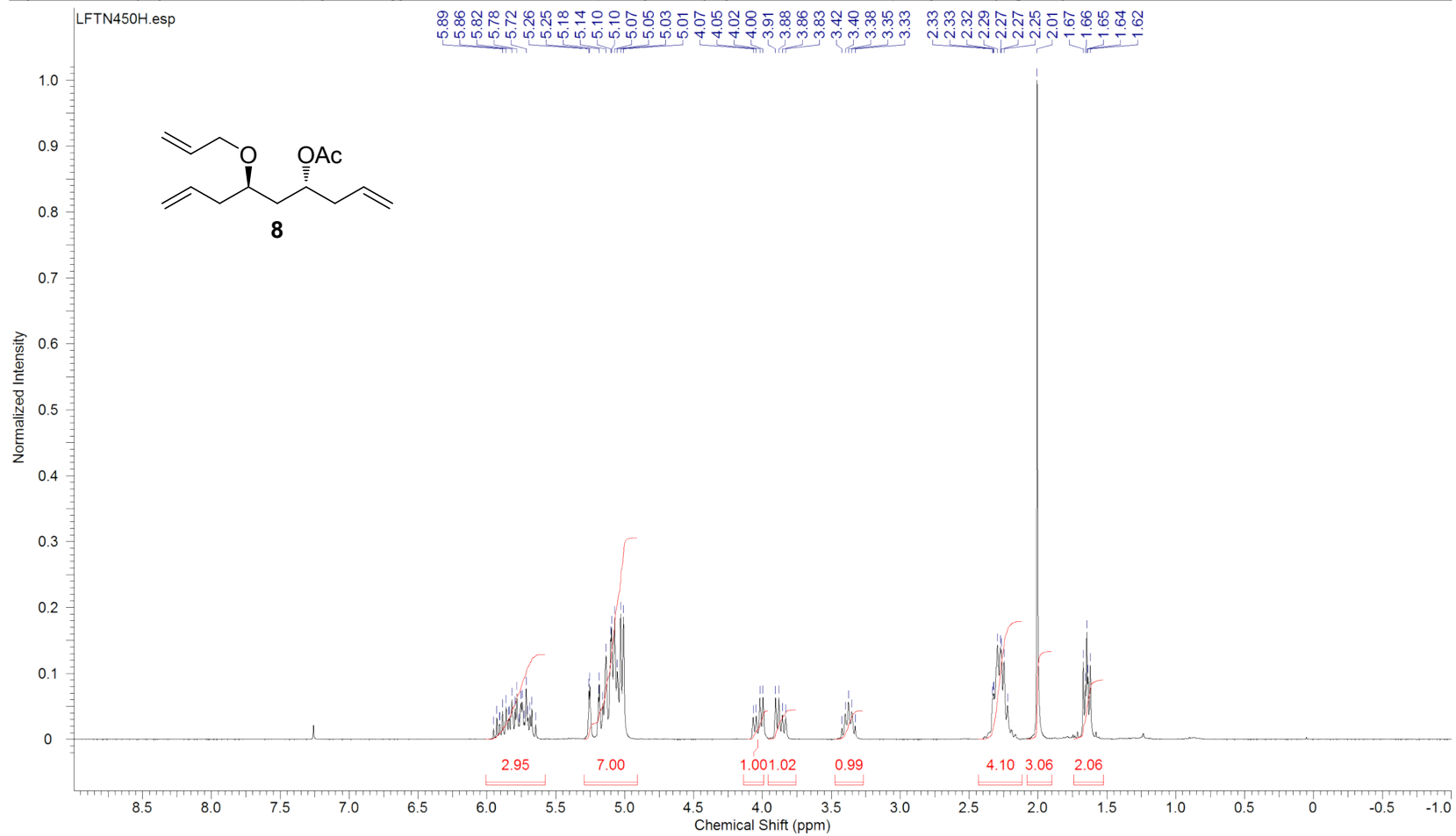
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Frequency (MHz)	250.13	Nucleus	1H	Number of Transients	17
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Receiver Gain	101.60	SW(cyclical) (Hz)	5175.98	Solvent	CHLOROFORM-d
Spectrum Offset (Hz)	1750.9441	Spectrum Type	STANDARD	Sweep Width (Hz)	5175.83
				Temperature (degree C)	25.160



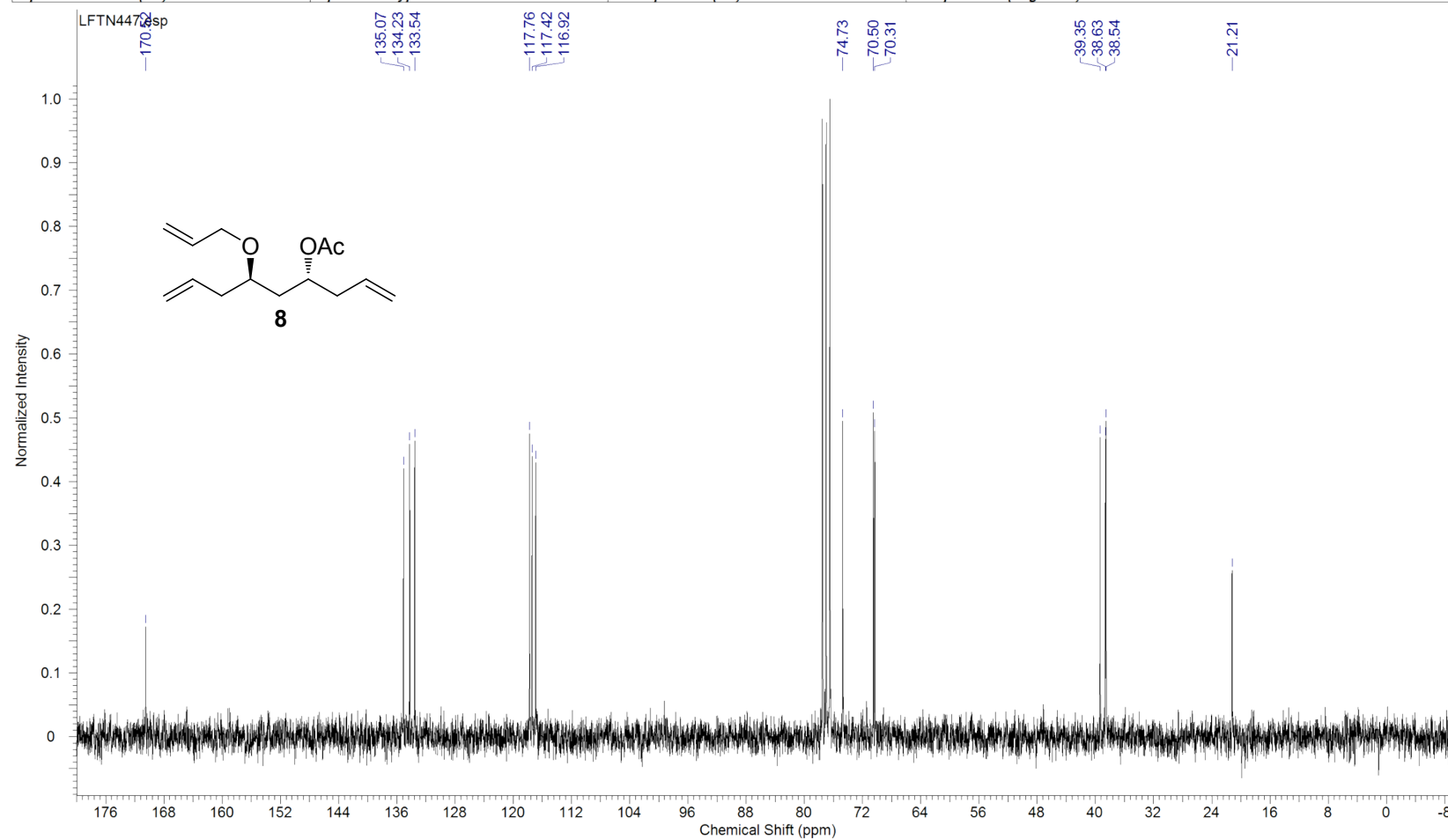
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Frequency (MHz)	62.90	Nucleus	13C	Number of Transients	100
Original Points Count	8192	Owner	root	Points Count	32768
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				Temperature (degree C)	25.260



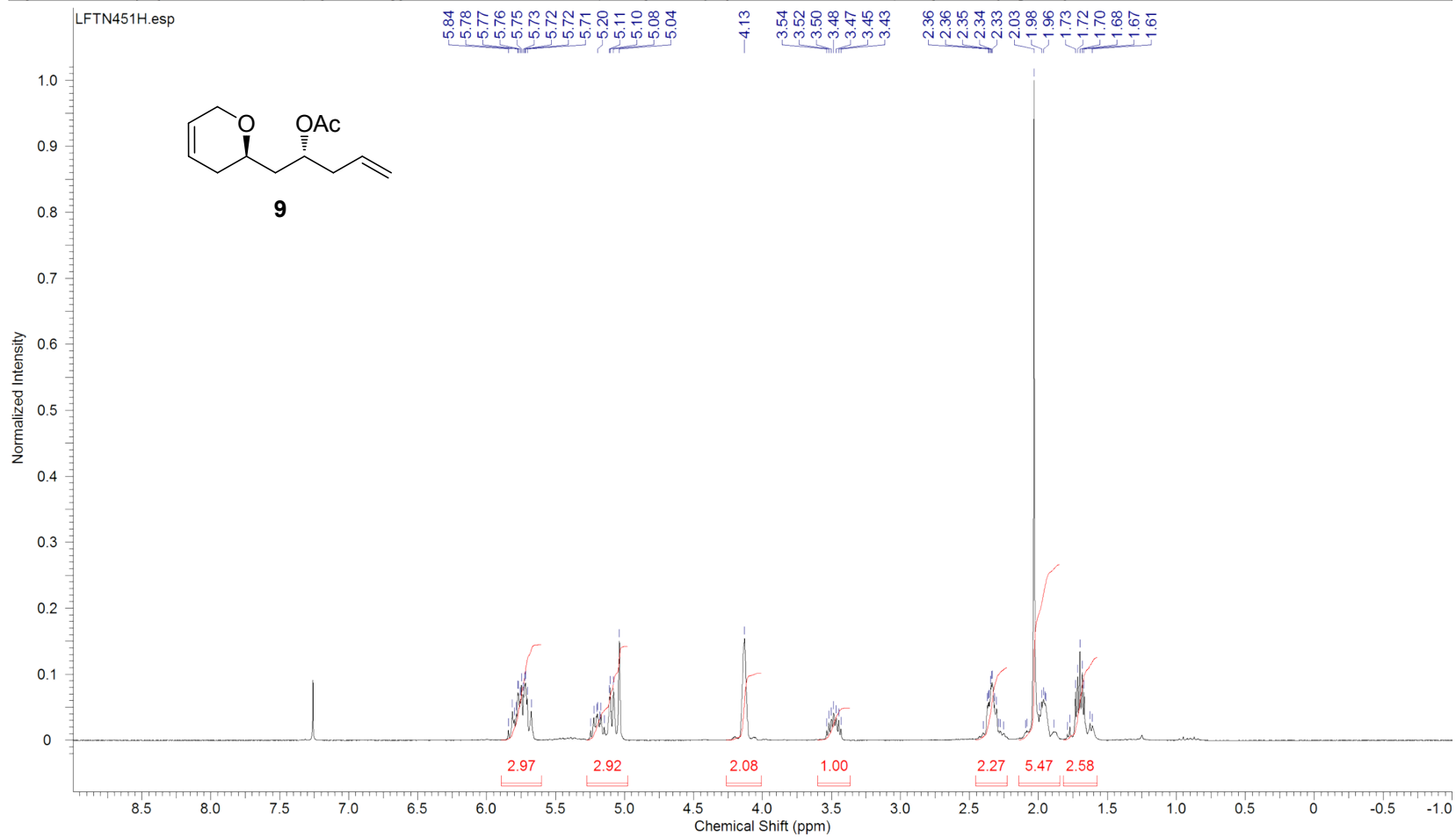
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Receiver Gain	181.00	SW(cyclical) (Hz)	5175.98	Solvent	CHLOROFORM-d
Spectrum Offset (Hz)	1750.4702	Spectrum Type	STANDARD	Sweep Width (Hz)	5175.83
				Temperature (degree C)	23.960



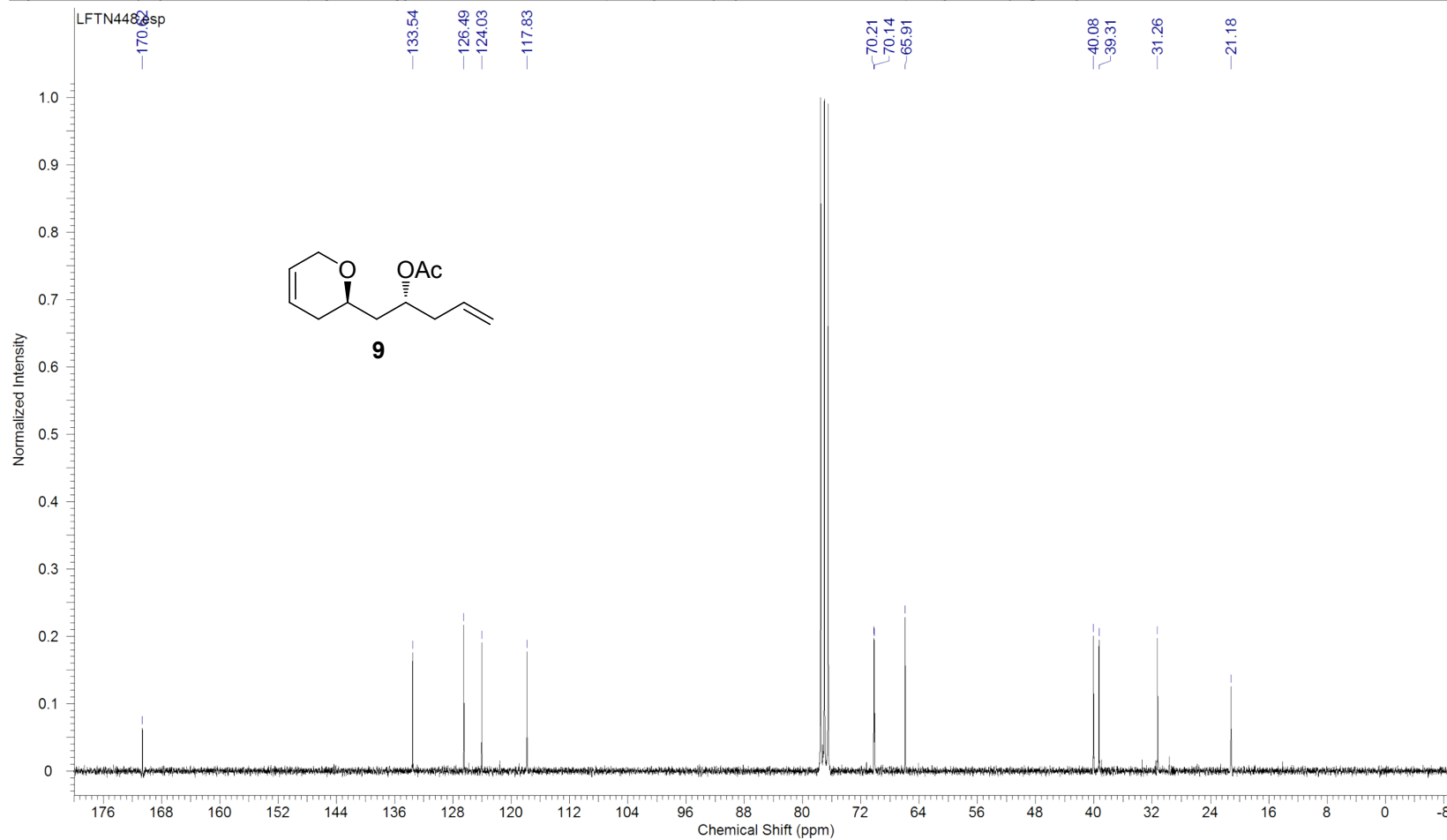
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Original Points Count	8192	Owner	root	Points Count	32768
Receiver Gain	574.70	SW(cyclical) (Hz)	15060.24	Solvent	CHLOROFORM-d
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				Temperature (degree C)	23.860



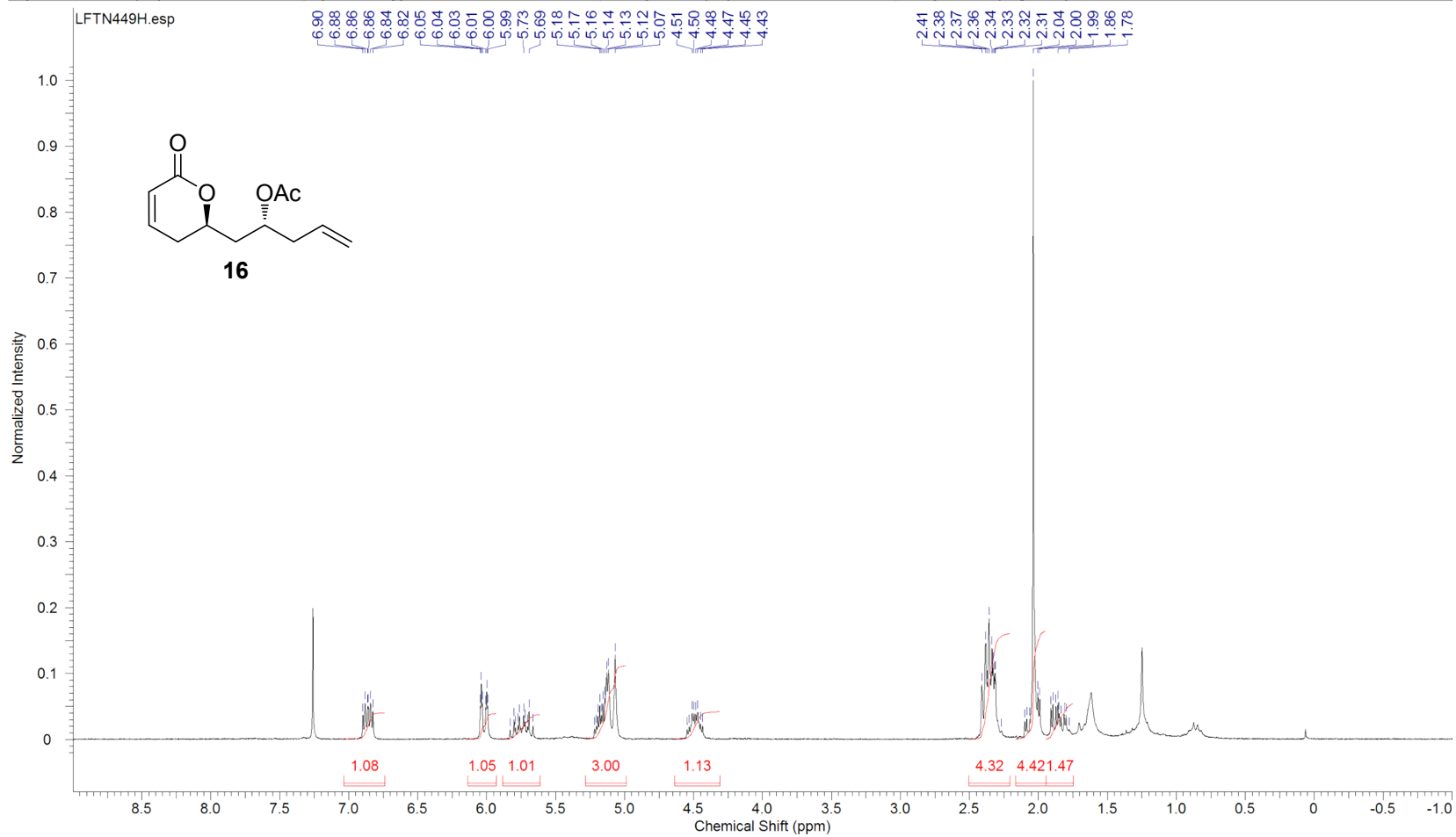
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Frequency (MHz)	250.13	Nucleus	1H	Number of Transients	17
Original Points Count	16384	Owner	root	Points Count	32768
Receiver Gain	912.30	SW(cyclical) (Hz)	5175.98	Solvent	CHLOROFORM-d
Spectrum Offset (Hz)	1750.4702	Spectrum Type	STANDARD	Sweep Width (Hz)	5175.83
				Temperature (degree C)	25.160



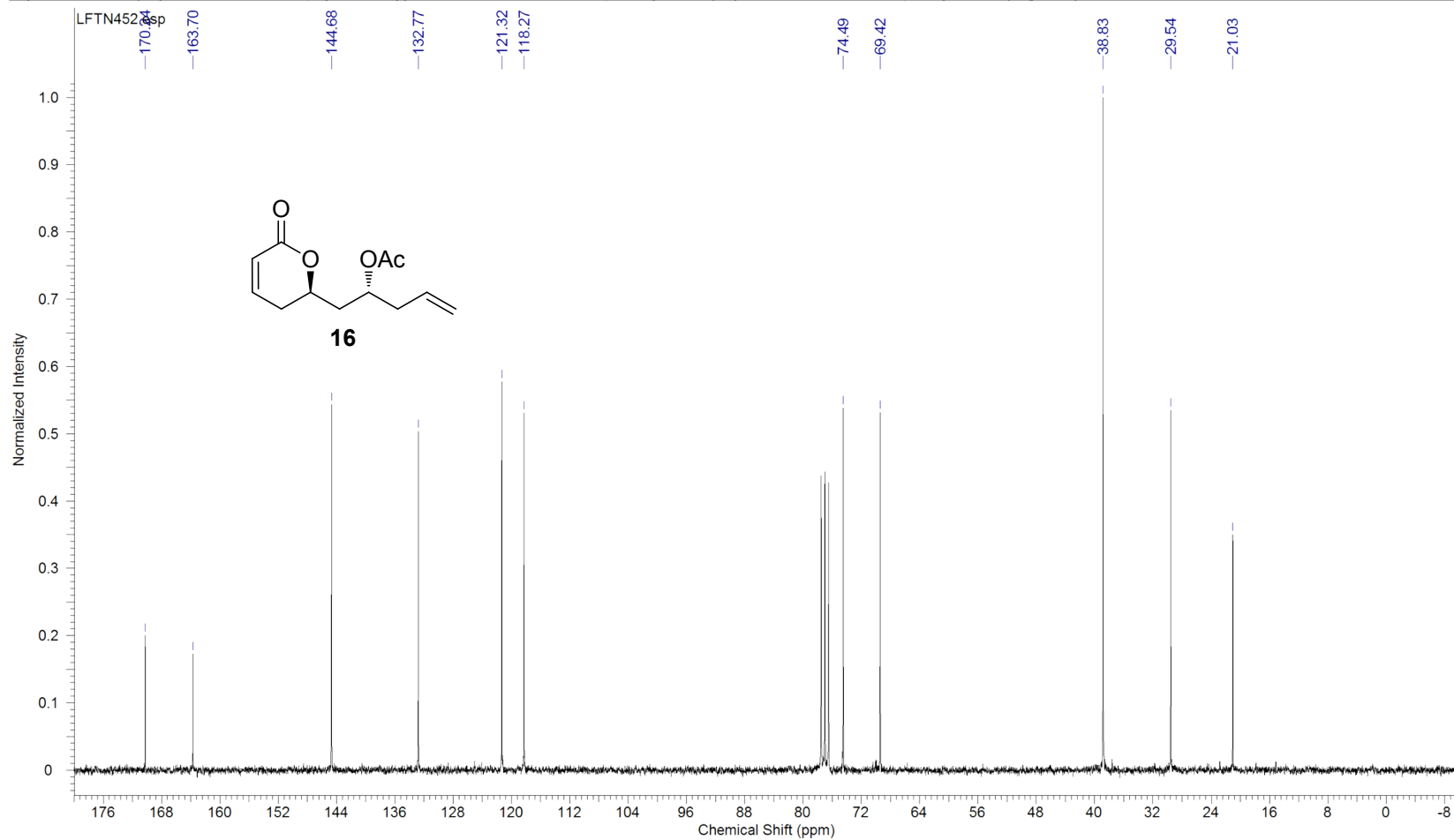
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Frequency (MHz)	62.90	Nucleus	13C	Number of Transients	4000	Origin	spect
Original Points Count	8192	Owner	root	Points Count	32768	Pulse Sequence	zgpg30
Receiver Gain	512.00	SW(cyclical) (Hz)	15060.24	Solvent	CHLOROFORM-d		
Spectrum Offset (Hz)	6289.5313	Spectrum Type	STANDARD	Sweep Width (Hz)	15059.78	Temperature (degree C)	23.960



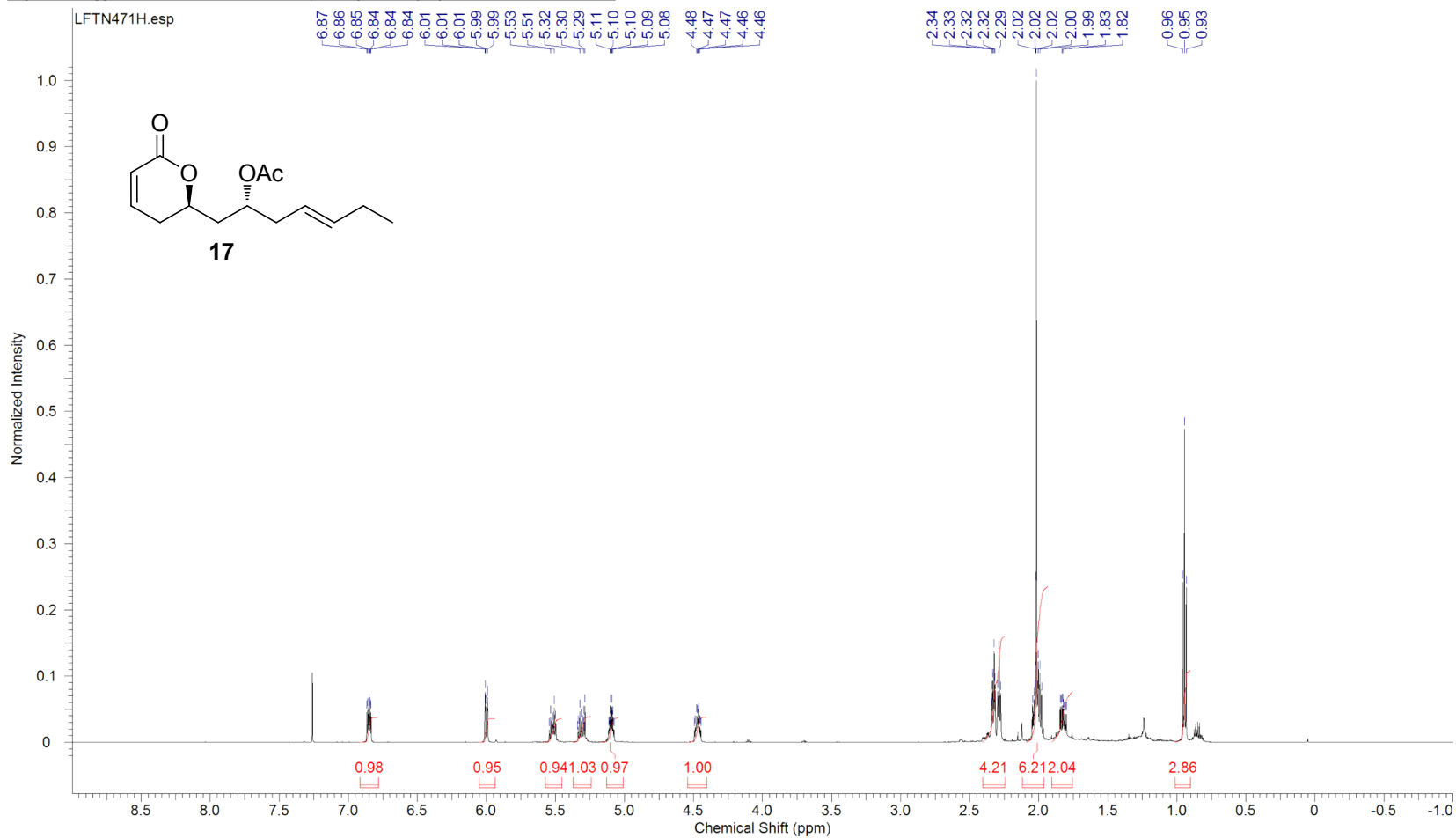
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Frequency (MHz)	250.13	Nucleus	1H	Number of Transients	17
Original Points Count	16384	Owner	root	Points Count	32768
Receiver Gain	1625.50	SW(cyclical) (Hz)	5175.98	Solvent	CHLOROFORM-d
Spectrum Offset (Hz)	1750.4702	Spectrum Type	STANDARD	Sweep Width (Hz)	5175.83
				Temperature (degree C)	23.560



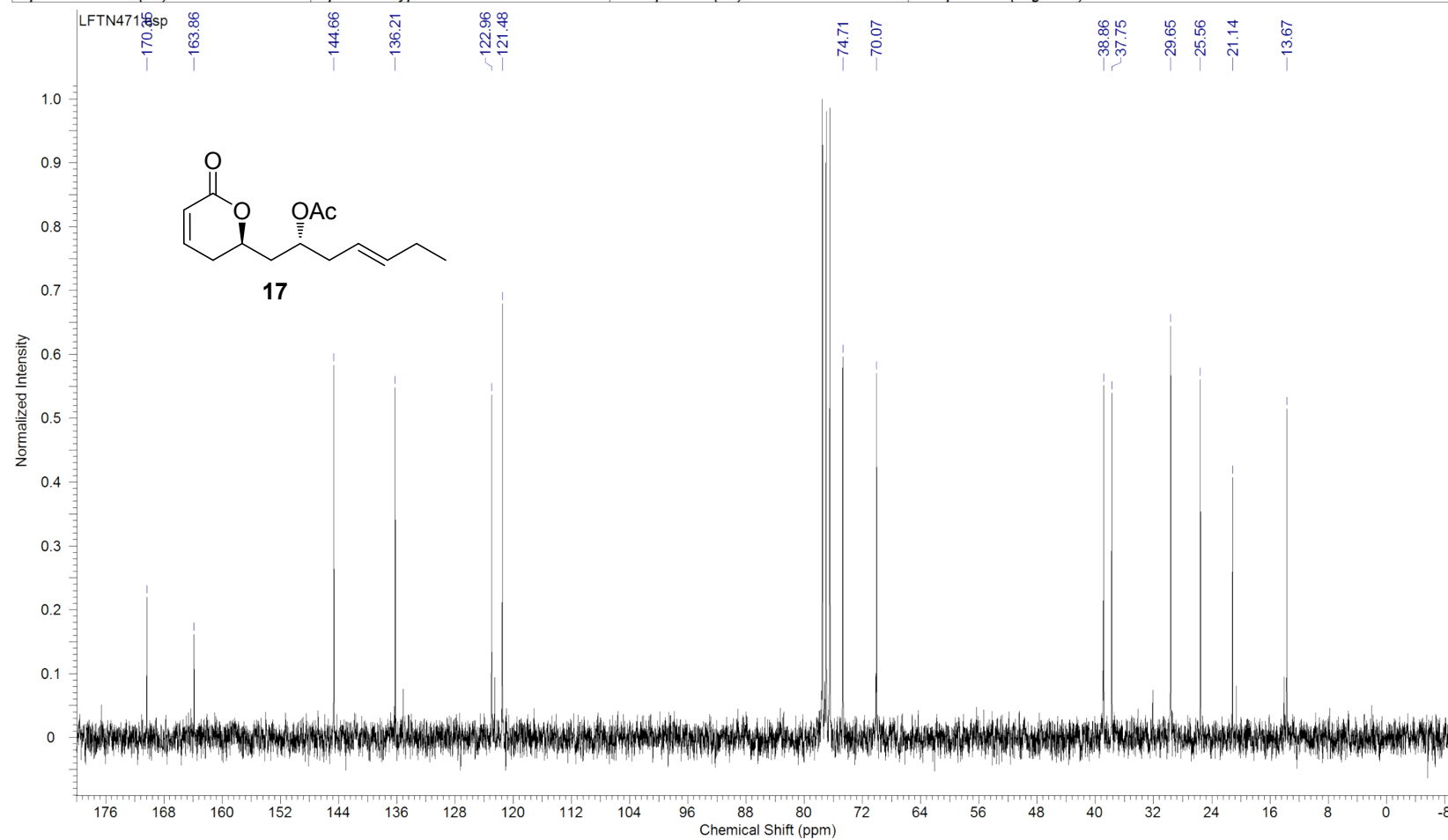
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Frequency (MHz)	62.90	Nucleus	13C	Number of Transients	965
Original Points Count	8192	Owner	root	Points Count	32768
Receiver Gain	362.00	SW(cyclical) (Hz)	15060.24	Solvent	CHLOROFORM-d
Spectrum Offset (Hz)	6284.0161	Spectrum Type	STANDARD	Sweep Width (Hz)	15059.78
				Temperature (degree C)	25.160



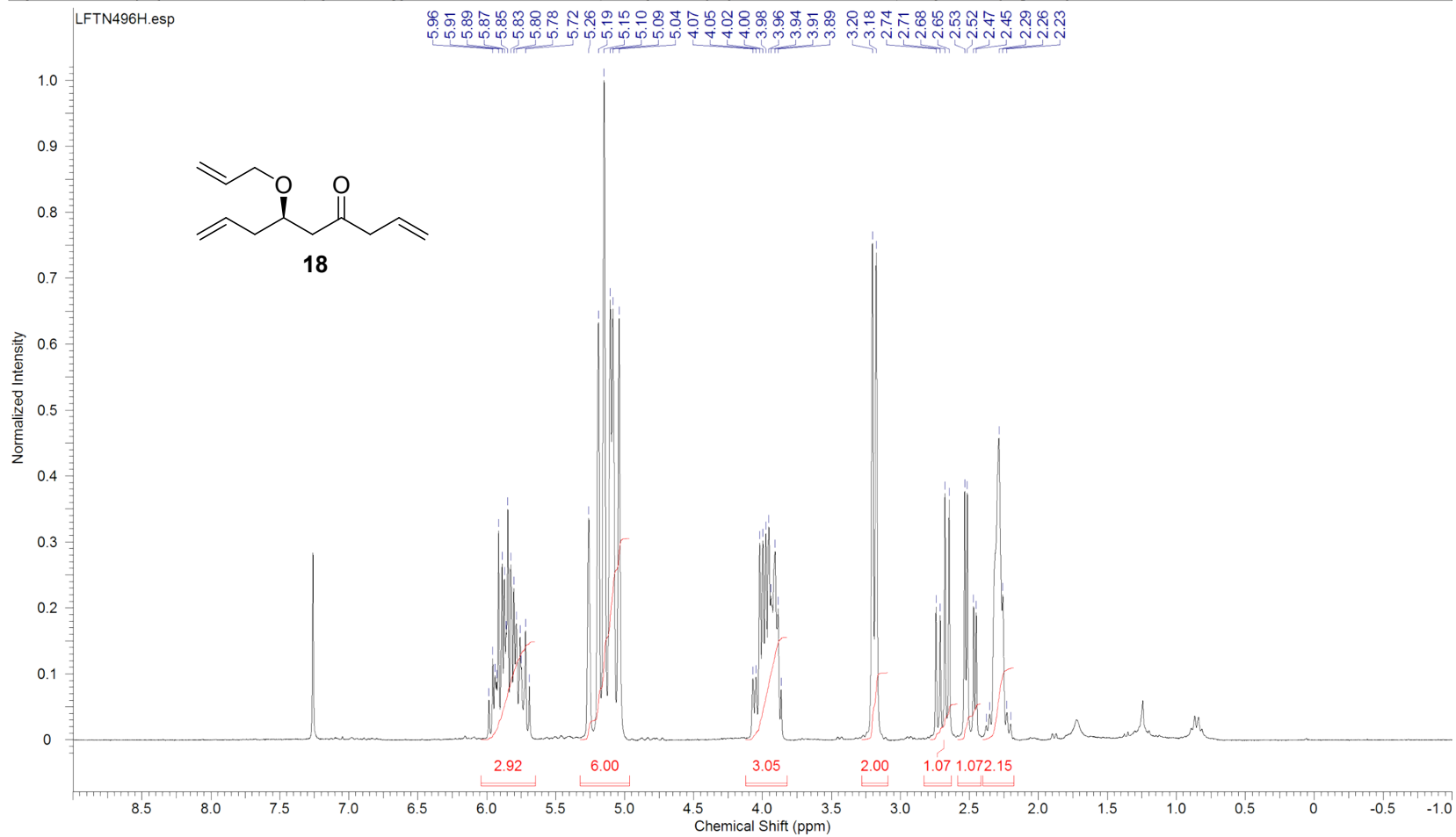
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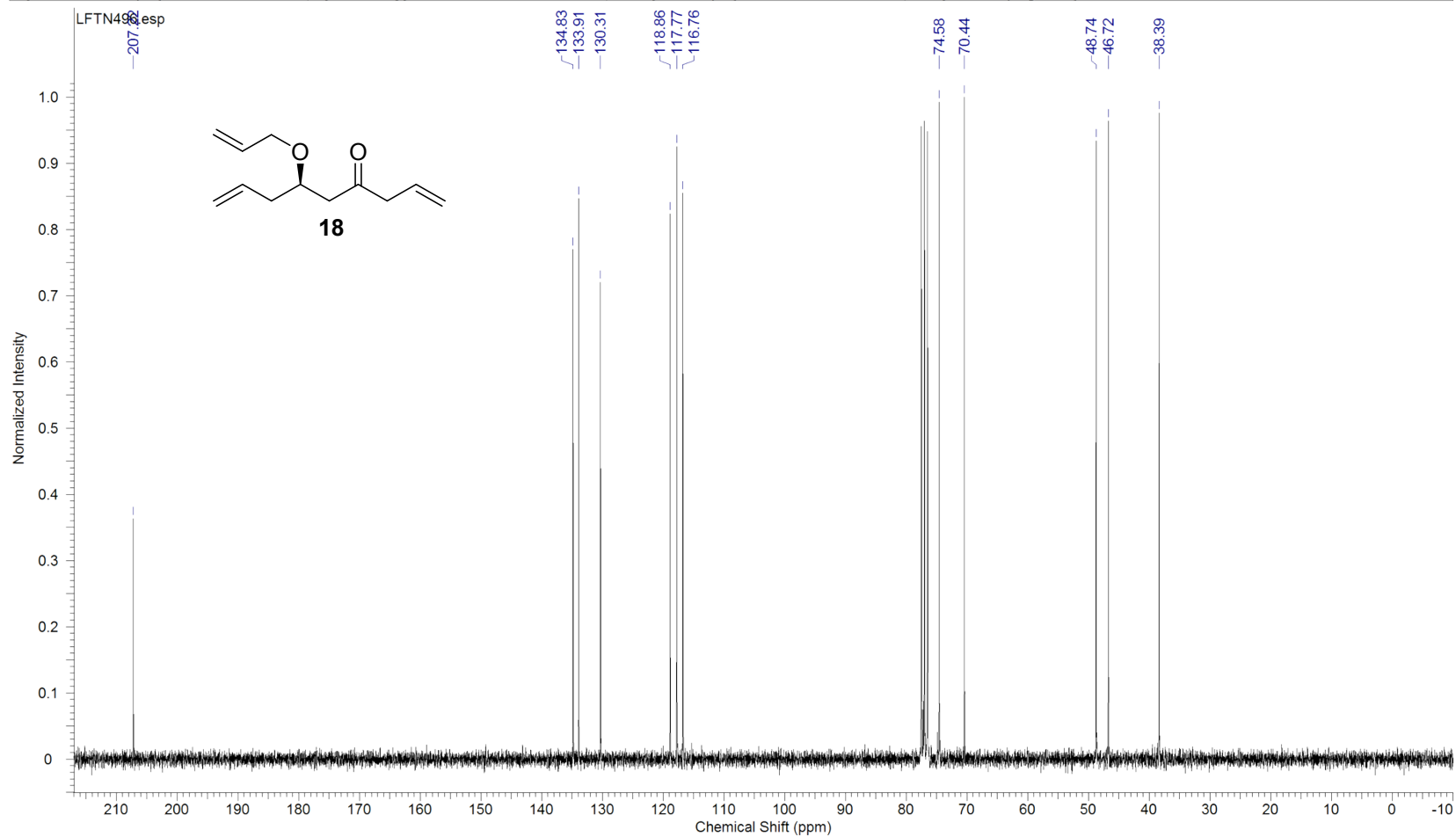
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Original Points Count	8192	Owner	root	Points Count	32768	Pulse Sequence	zgpg30
Receiver Gain	287.40	SW(cyclical) (Hz)	15060.24	Solvent	CHLOROFORM-d		
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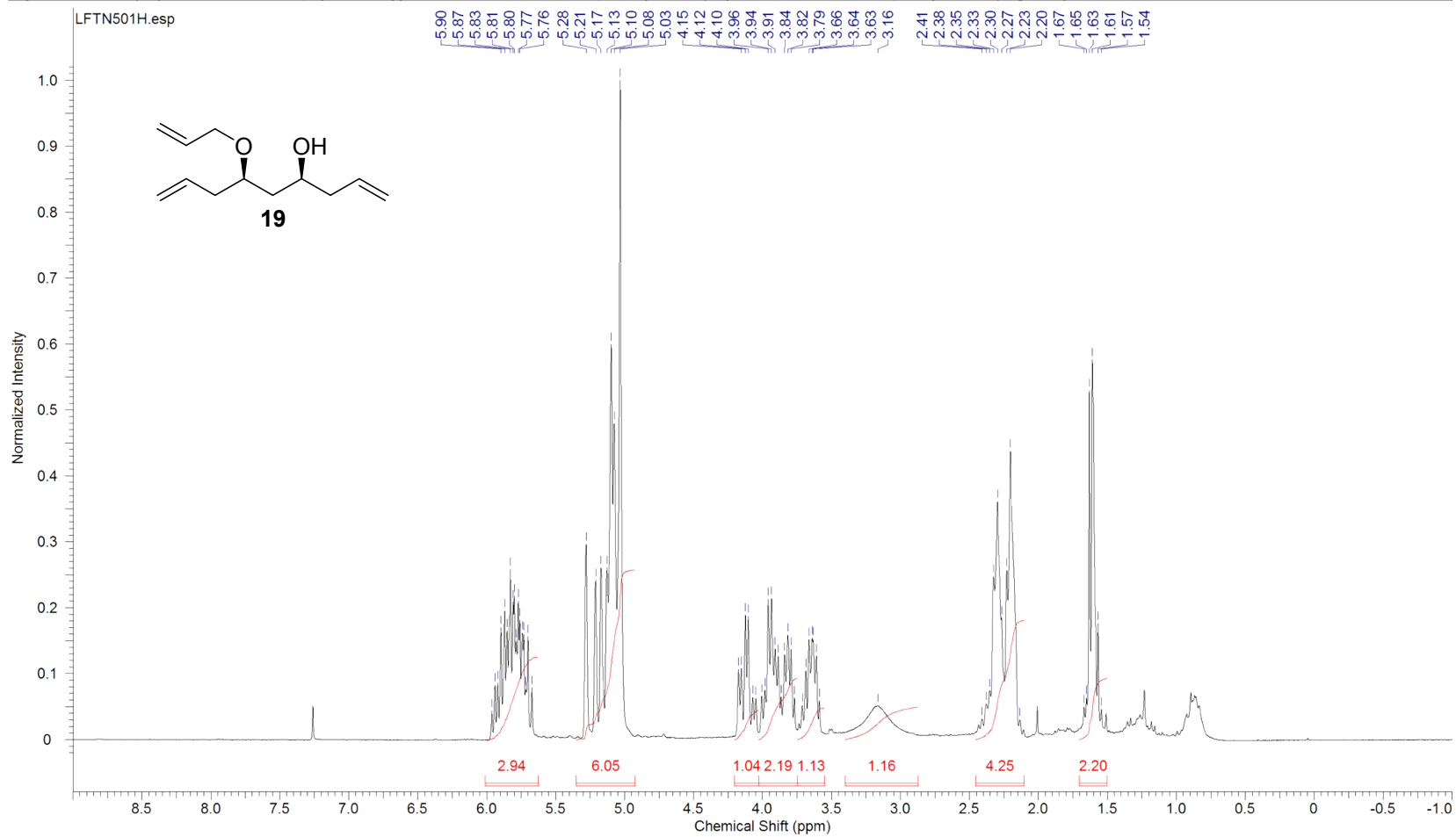
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Frequency (MHz)	250.13	Nucleus	1H	Number of Transients	17	Origin	spect
Original Points Count	16384	Owner	root	Points Count	32768	Pulse Sequence	zg30
Receiver Gain	256.00	SW(cyclical) (Hz)	5175.98	Solvent	CHLOROFORM-d		
Spectrum Offset (Hz)	1750.6281	Spectrum Type	STANDARD	Sweep Width (Hz)	5175.83	Temperature (degree C)	25.160



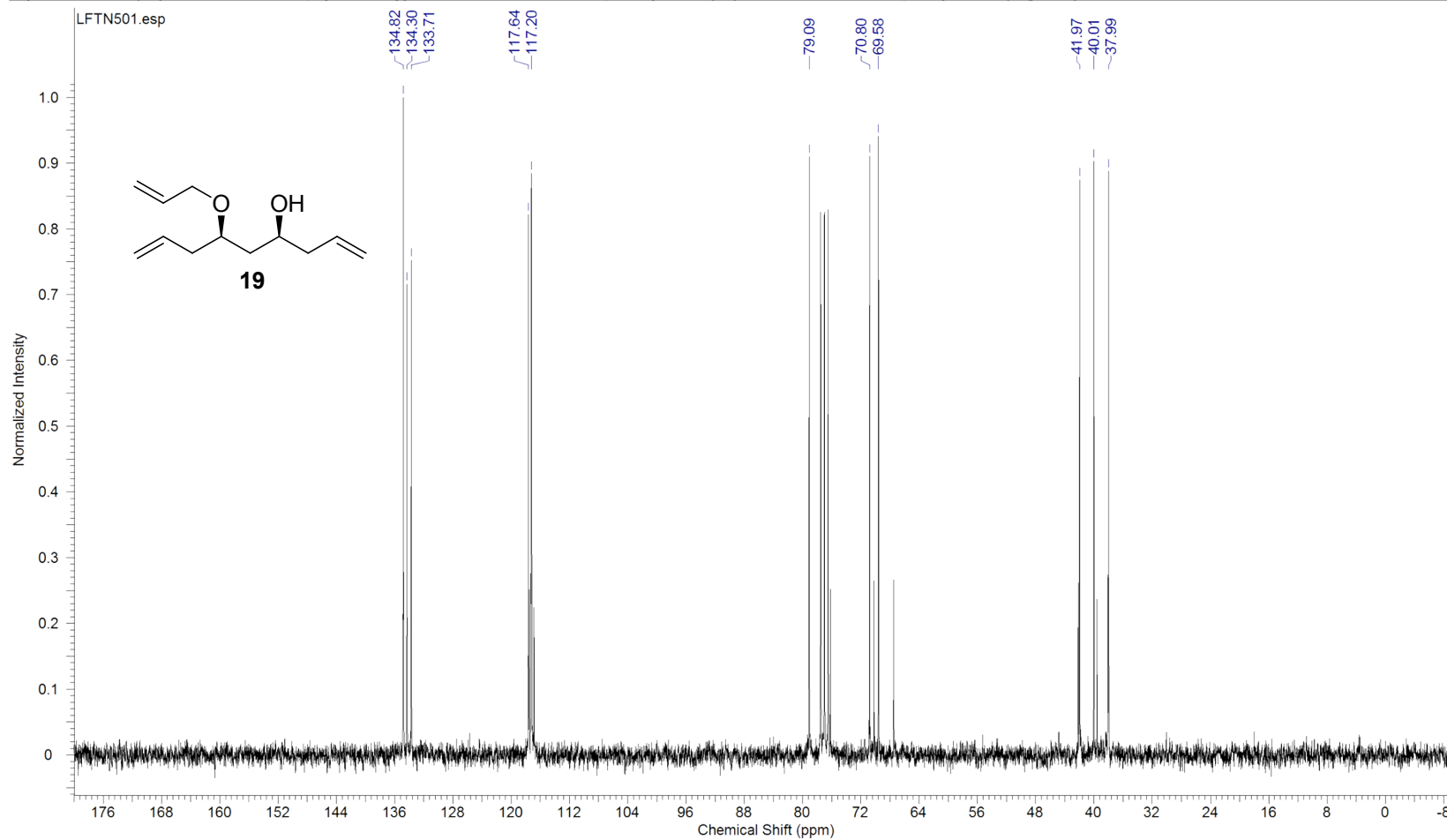
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Original Points Count	8192	Owner	root	Points Count	32768	Pulse Sequence
Receiver Gain	512.00	SW(cyclical) (Hz)	15060.24	Solvent	CHLOROFORM-d	
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						25.260



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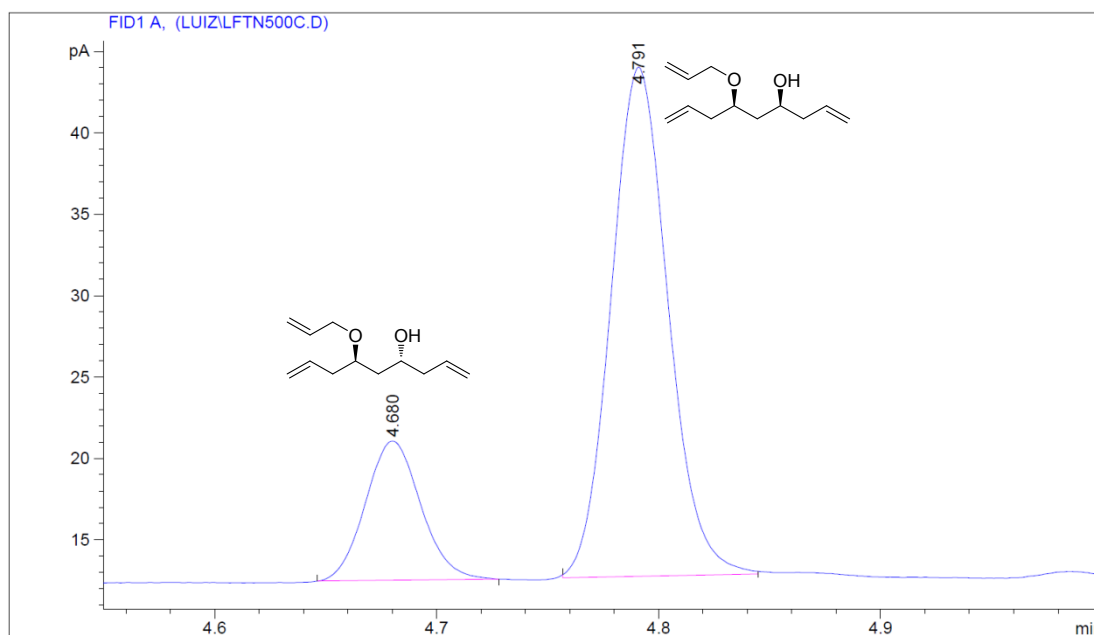


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Frequency (MHz)	62.90	Nucleus	13C	Number of Transients	256	Origin spect
Original Points Count	8192	Owner	root	Points Count	32768	Pulse Sequence zgpg30
Receiver Gain	645.10	SW(cyclical) (Hz)	15060.24	Solvent	CHLOROFORM-d	
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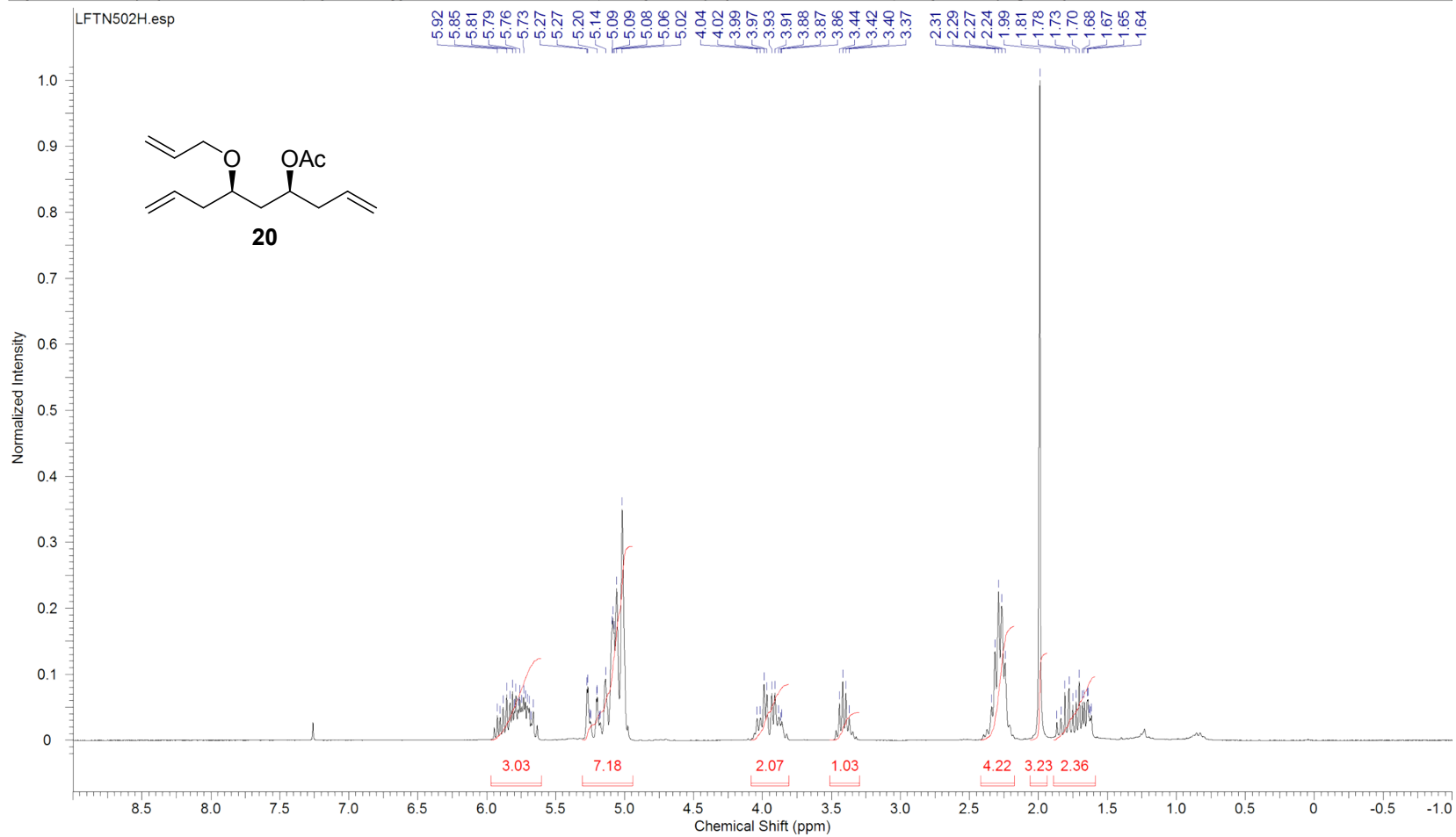
GC: HP-5 Crosslinked 5% PH ME Siloxane column (30 m x 0.32 mm x 0.25 μ m), temperature ramp: 120 $^{\circ}$ C for 1 min, 10 $^{\circ}$ C/min to 150 $^{\circ}$ C, 150 $^{\circ}$ C for 2 min.

GC analysis after chromatographic purification:

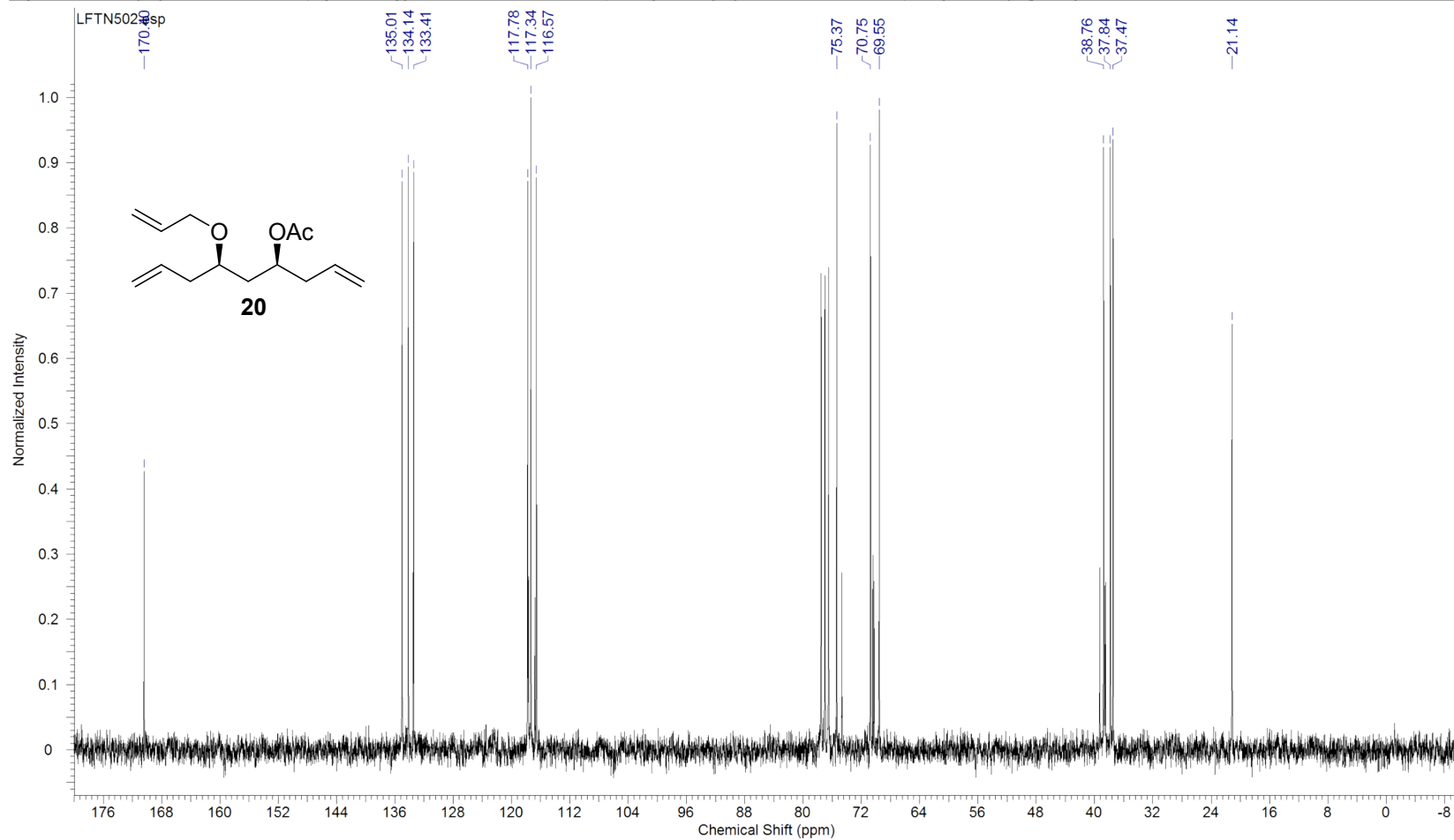


Compound	Retention time (min)	Area %
<i>anti</i>	4.68	21.0
<i>syn</i>	4.79	79.0

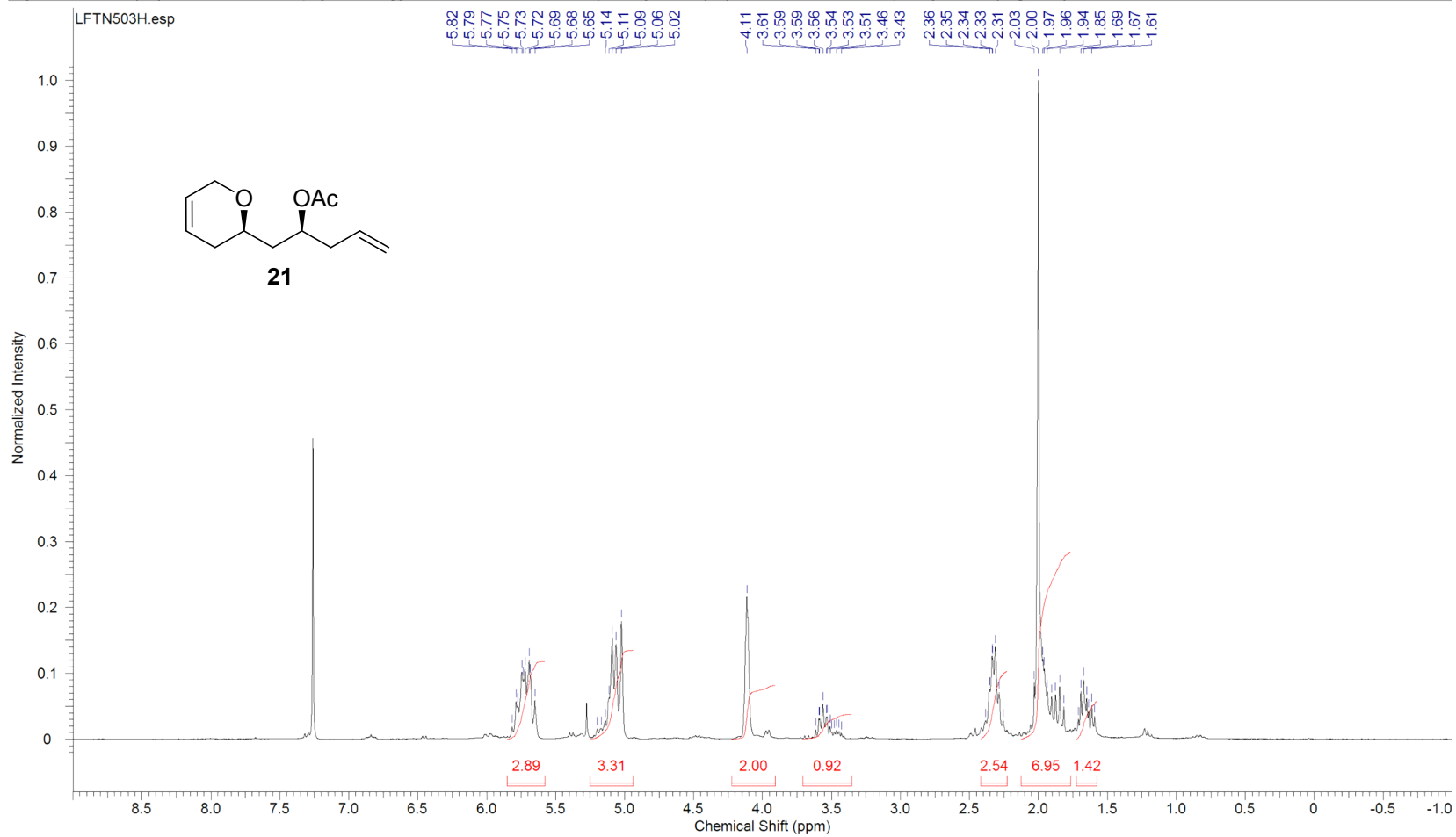
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Original Points Count	16384	Owner	root	Points Count	32768
Receiver Gain	143.70	SW(cyclical) (Hz)	5175.98	Solvent	CHLOROFORM-d
Spectrum Offset (Hz)	1750.6281	Spectrum Type	STANDARD	Sweep Width (Hz)	5175.83
				Temperature (degree C)	25.160



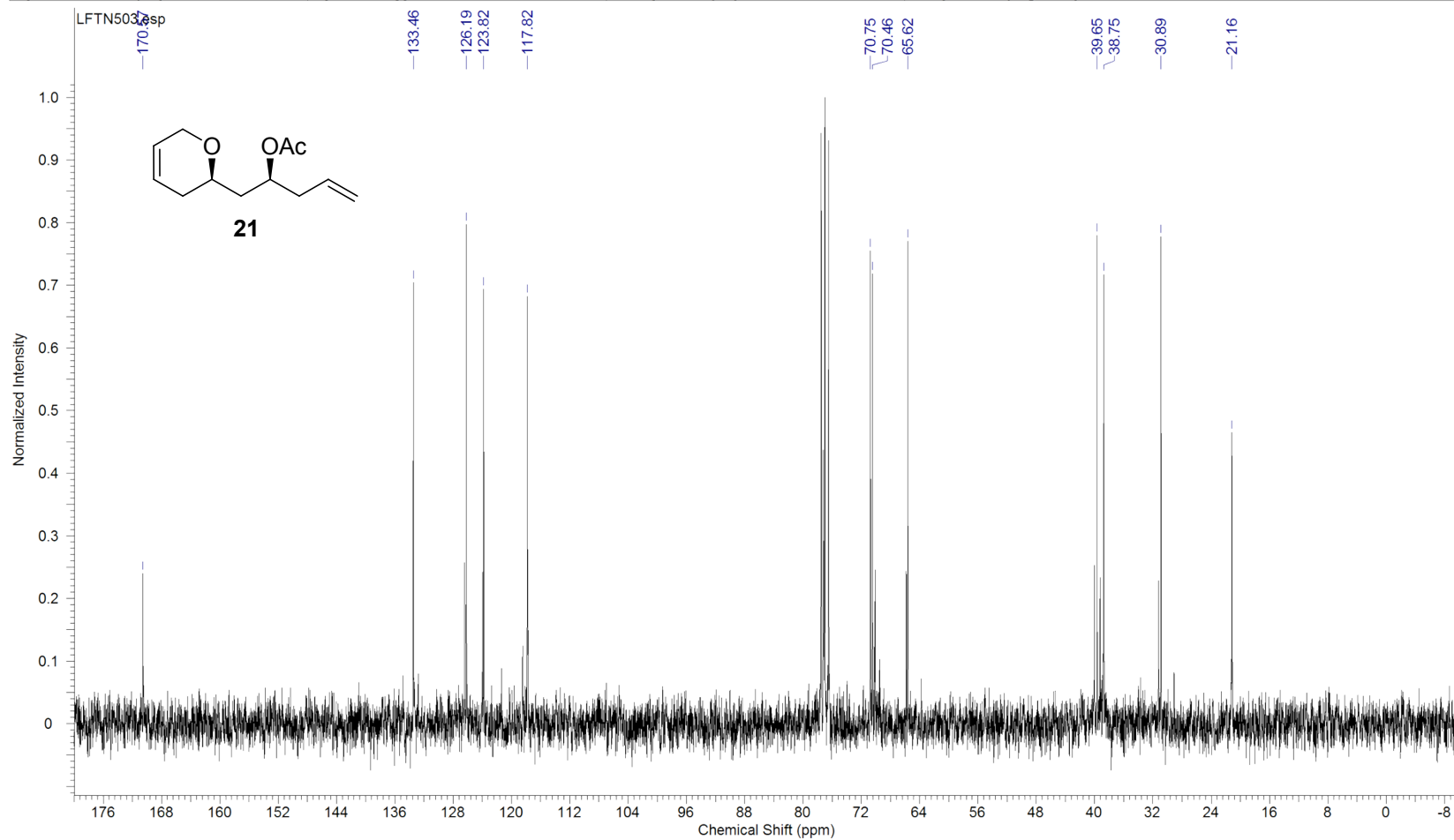
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Original Points Count	8192	Owner	root	Points Count	32768	Pulse Sequence	zgpg30
Receiver Gain	512.00	SW(cyclical) (Hz)	15060.24	Solvent	CHLOROFORM-d		
Spectrum Offset (Hz)	6286.7734	Spectrum Type	STANDARD	Sweep Width (Hz)	15059.78	Temperature (degree C)	25.160



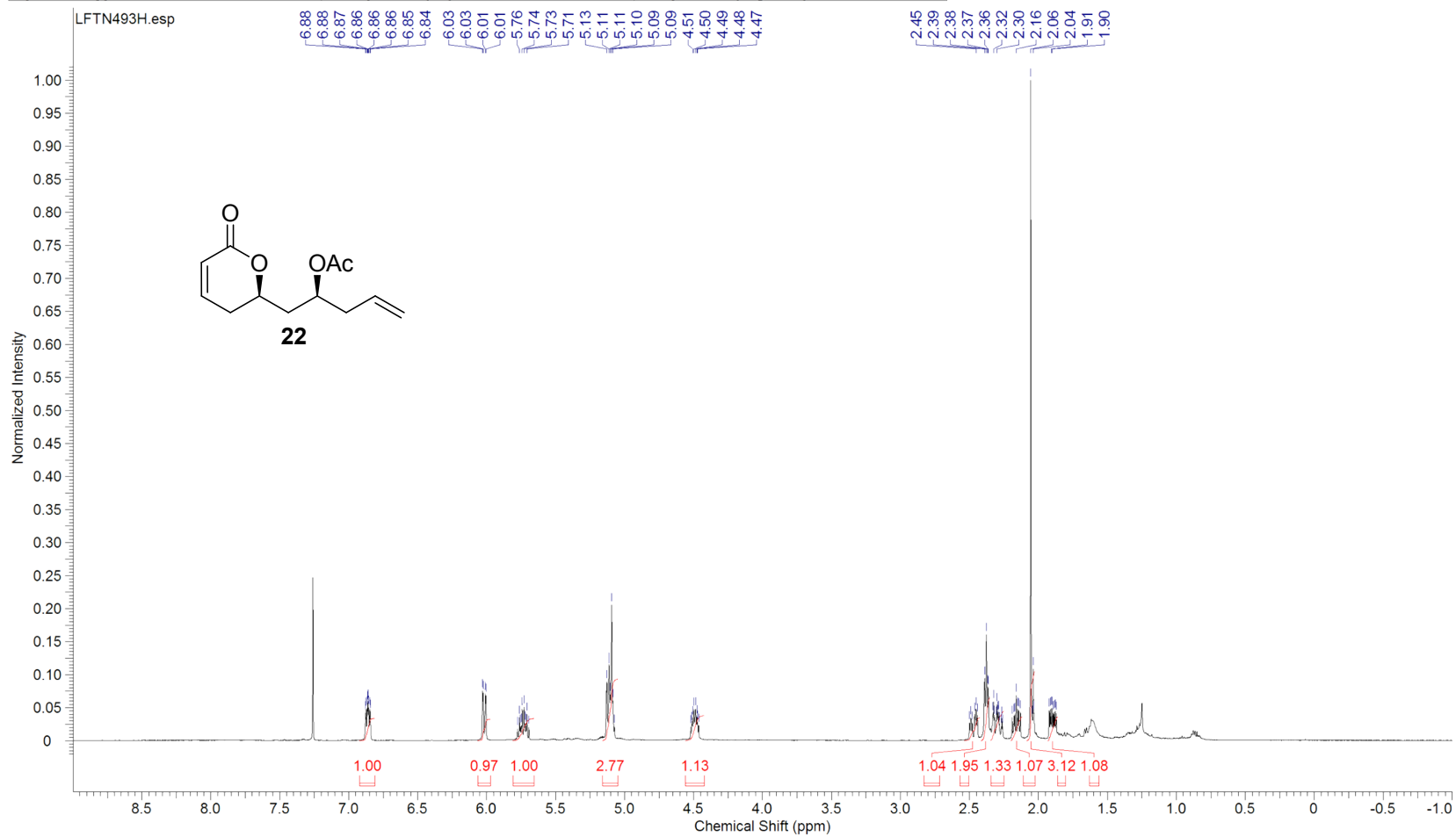
Acquisition Time (sec)	3.1654	Comment	LFTN503	Date	23 Jan 2015 18:01:04
Date Stamp	23 Jan 2015 18:01:04	File Name	\\nmrparc.iqm.unicamp.br\spectros\bruker250\2015\jan15\data\Pill\inmr\jan23\ftH1\1\PDATA\1\1r		
Frequency (MHz)	250.13	Nucleus	1H	Number of Transients	17
Original Points Count	16384	Owner	root	Points Count	32768
Receiver Gain	203.20	SW(cyclical) (Hz)	5175.98	Solvent	CHLOROFORM-d
Spectrum Offset (Hz)	1750.6281	Spectrum Type	STANDARD	Sweep Width (Hz)	5175.83
				Temperature (degree C)	25.160



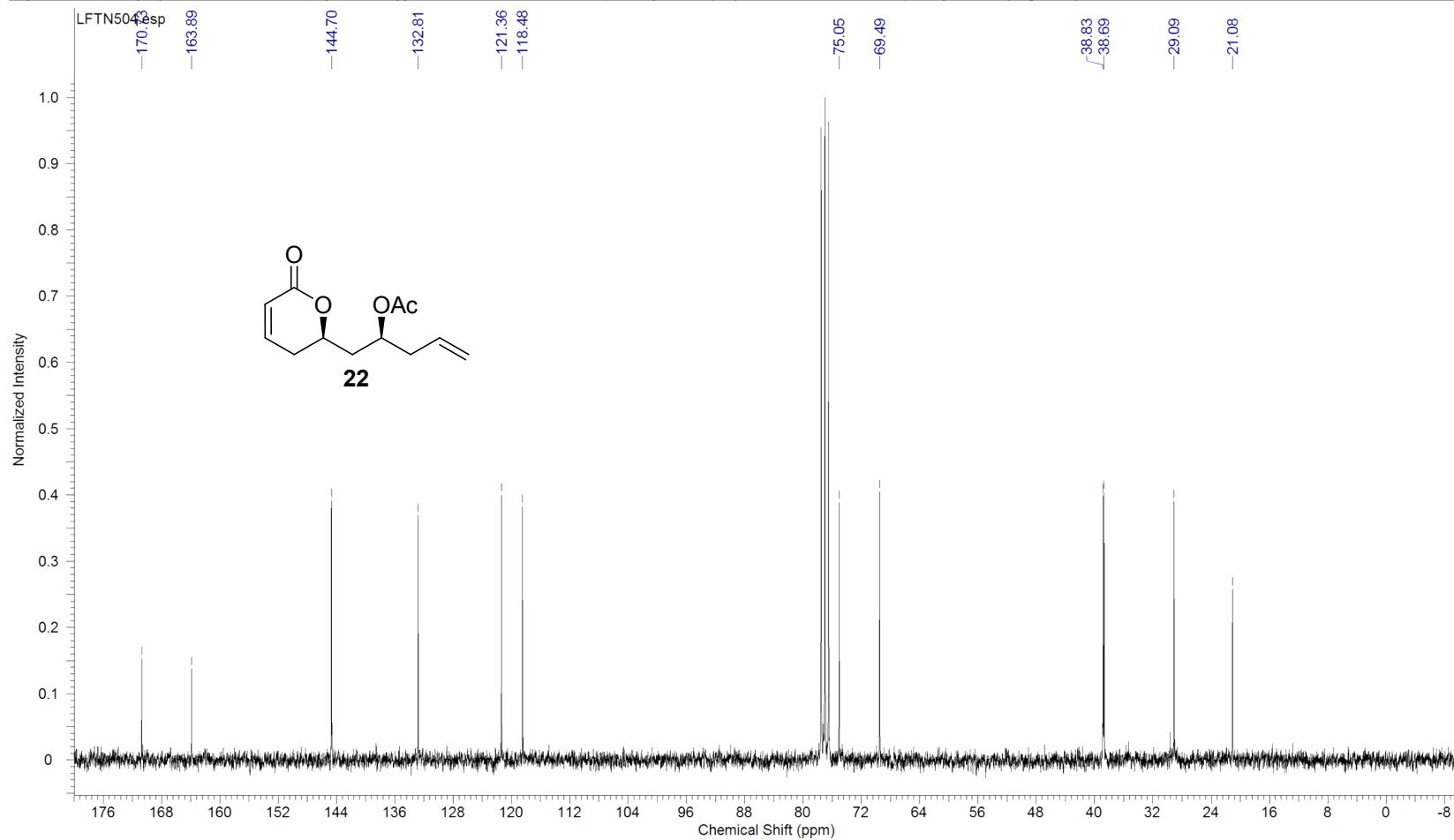
Acquisition Time (sec)	0.5439	Comment	LFTN503	Date	23 Jan 2015 18:07:28		
Date Stamp	23 Jan 2015 18:07:28			File Name	\\nmrparc.iqm.unicamp.br\spectros\bruker250\2015\jan15\data\Pill\nmr\jan23\ftH1\3\PDATA\1\1r		
Frequency (MHz)	62.90	Nucleus	13C	Number of Transients	128	Origin	spect
Original Points Count	8192	Owner	root	Points Count	32768	Pulse Sequence	zgpg30
Receiver Gain	406.40	SW(cyclical) (Hz)	15060.24	Solvent	CHLOROFORM-d		
Spectrum Offset (Hz)	6287.6929	Spectrum Type	STANDARD	Sweep Width (Hz)	15059.78	Temperature (degree C)	25.260



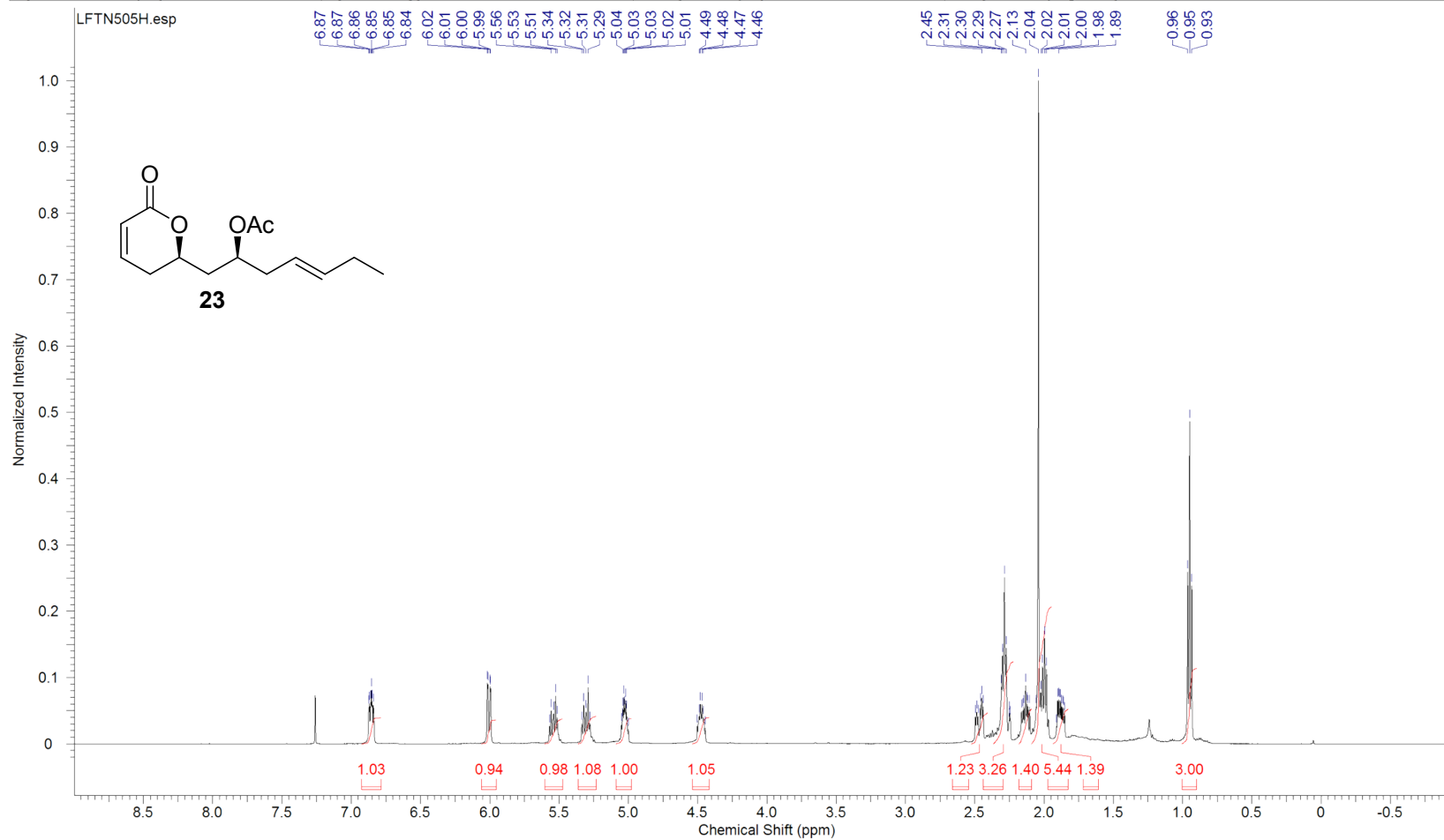
Acquisition Time (sec)	1.6384	Comment	Luiz - LFTN 493 - CDCI3 - Avance 500 MHz - dez19lftH1		Date	19 Dec 2014 07:16:48	
Date Stamp	19 Dec 2014 07:16:48		File Name	\\nmrsparc.iqm.unicamp.br\spectros\avance500\2014\dez14\Pill\dez19lftH1\1\PDATA\1\1r			
Frequency (MHz)	499.87	Nucleus	1H	Number of Transients	16	Origin	spect
Original Points Count	16384	Owner	nmrsu	Points Count	65536	Pulse Sequence	zg30
Receiver Gain	161.00	SW(cyclical) (Hz)	10000.00	Solvent	CHLOROFORM-d	Spectrum Offset (Hz)	3069.7451
Spectrum Type	STANDARD	Sweep Width (Hz)	9999.85	Temperature (degree C)	25.146		



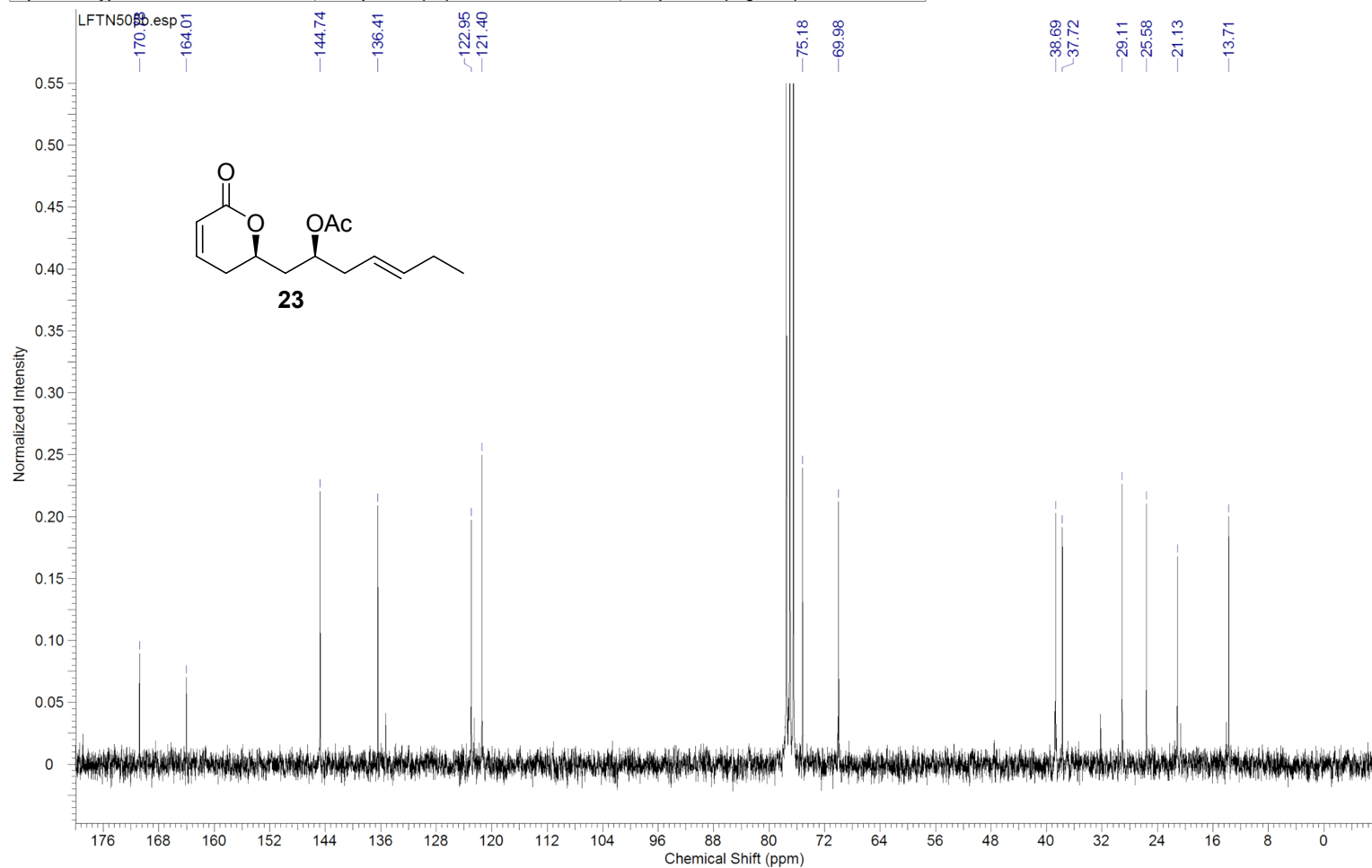
Acquisition Time (sec)	0.5439	Comment	LFTN504	Date	25 Jan 2015 14:46:56		
Date Stamp	25 Jan 2015 14:46:56			File Name	\\nmrsparc.iqm.unicamp.br\spectros\bruker250\2015\jan15\data\Pill\nmr\jan25\ftH1\3\PDATA\1\1r		
Frequency (MHz)	62.90	Nucleus	13C	Number of Transients	598	Origin	spect
Original Points Count	8192	Owner	root	Points Count	32768	Pulse Sequence	zgpg30
Receiver Gain	574.70	SW(cyclical) (Hz)	15060.24	Solvent	CHLOROFORM-d		
Spectrum Offset (Hz)	6287.6929	Spectrum Type	STANDARD	Sweep Width (Hz)	15059.78	Temperature (degree C)	25.160



Acquisition Time (sec)	1.6384	Comment	Luiz - LFTN 505 - CDCl3 - Avance 500 MHz - jan27ftH1			Date	27 Jan 2015 08:27:12
Date Stamp	27 Jan 2015 08:27:12			File Name	\\nmrsparc.igmm.unicamp.br\spectros\avance500\2015\jan15\Pillij\jan27ftH1\1\data\1\1r		
Frequency (MHz)	499.87	Nucleus	1H	Number of Transients	16	Origin	spect
Original Points Count	16384	Owner	nmrsu	Points Count	65536	Pulse Sequence	zg30
Receiver Gain	90.50	SW(cyclical) (Hz)	10000.00	Solvent	CHLOROFORM-d		
Spectrum Offset (Hz)	3069.4402	Spectrum Type	STANDARD	Sweep Width (Hz)	9999.85	Temperature (degree C)	25.135



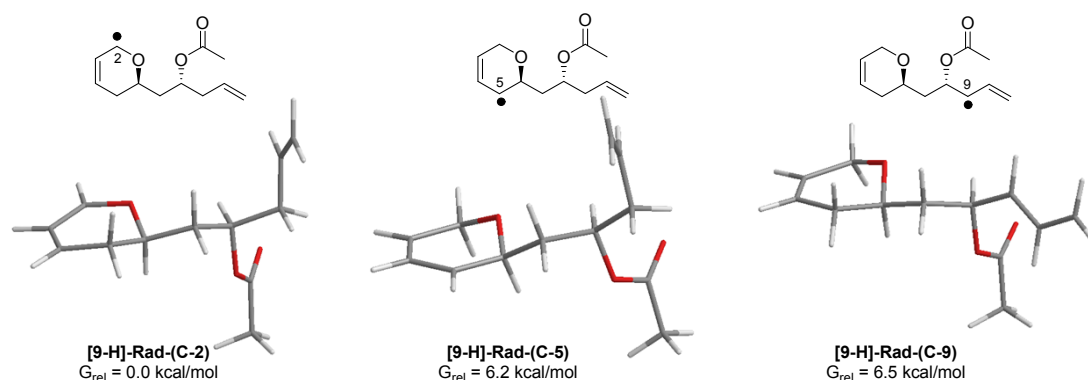
Acquisition Time (sec)	0.5439	Comment	LFTN505	Date	04 Feb 2015 08:08:00
Date Stamp	04 Feb 2015 08:08:00				
File Name	\nmrsparc.iqm.unicamp.br\spectros\bruker250\2015\fev15\data\Pill\nmr\fev03\ftH1\2\PDATA\1\1r			Frequency (MHz)	62.90
Nucleus	13C	Number of Transients	1256	Origin	spect
Owner	root	Points Count	32768	Pulse Sequence	zgpg30
SW(cyclical) (Hz)	15060.24	Solvent	CHLOROFORM-d	Spectrum Offset (Hz)	6289.0713
Spectrum Type	STANDARD	Sweep Width (Hz)	15059.78	Temperature (degree C)	25.160



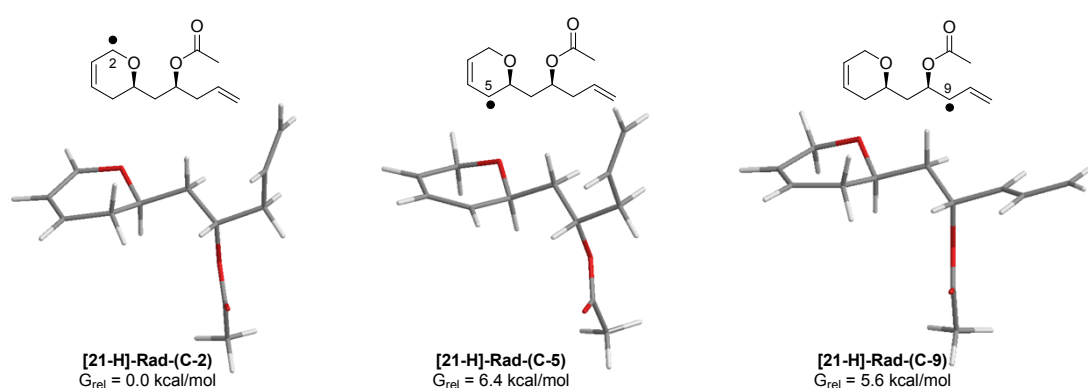
III. Computational methods

All DFT calculations were performed using Gaussian 09.¹ Density functional theory (DFT) calculations were carried out with the UB3LYP functional² and the 6-31+G** basis set. Geometries for all structures were fully optimized and the nature of the stationary points found was confirmed by frequency calculations. Reported thermochemical properties include zero-point energies (ZPEs) and Gibbs free energies, computed at 1 atm and 298.15 K and were not scaled.

Conformational searches were performed to locate the minimum energy conformers of all the structures. Initially, a large number of geometries were generated using the conformational search module of Hyperchem³ with the MM+ method.⁴ Selected structures were then successively reoptimized at the UB3LYP/6-31G* and UB3LYP/6-31+G** levels of theory.



UB3LYP/6-31+G** optimized geometries (global minima) found for the three allylic radicals derived from compound 9.



UB3LYP/6-31+G** optimized geometries (global minima) found for the three allylic radicals derived from compound 21.

[9-H]-Rad-(C-2)

UB3LYP/6-31+G** Geometry

C 0	1.788390	0.486261	-1.320965
O 0	0.828616	-0.008160	0.895679
C 0	0.598584	-0.082471	-0.536943
C 0	-0.711101	0.647535	-0.809307
C 0	-1.935840	0.027657	-0.142095
C 0	-3.217660	0.858129	-0.332417
C 0	-3.204370	2.147451	0.444065
C 0	-3.352121	3.366645	-0.082736
O 0	-2.120956	-1.280531	-0.763498
C 0	-2.731305	-2.246275	-0.035290
O 0	-3.147609	-2.081335	1.093581
C 0	-2.809299	-3.540402	-0.808884
C 0	3.075687	-0.115264	-0.829631
C 0	3.138858	-0.555786	0.485500
C 0	2.038769	-0.456153	1.327844
H 0	1.632742	0.278652	-2.387342
H 0	1.804122	1.584238	-1.218348
H 0	0.494893	-1.148269	-0.781843
H 0	-0.618198	1.683375	-0.464632
H 0	-0.874369	0.677672	-1.894184
H 0	-1.753342	-0.133464	0.923183
H 0	-3.369983	1.055387	-1.400837
H 0	-4.057859	0.244603	0.015460
H 0	-3.077123	2.049654	1.523077
H 0	-3.352738	4.257639	0.538353
H 0	-3.485824	3.514393	-1.152404
H 0	-3.414459	-4.257639	-0.254688
H 0	-1.802078	-3.945581	-0.951422
H 0	-3.237330	-3.368402	-1.800421
H 0	3.942229	-0.156487	-1.480997
H 0	4.057859	-0.960581	0.898967
H 0	2.047645	-0.682011	2.387342

Number of Imaginary Frequencies = 0

Energy = -693.175351303

ZPE = -692.906662

G = -692.953385

[9-H]-Rad-(C-5)

UB3LYP/6-31+G** Geometry

O 0	0.735381	-0.394376	0.876333
C 0	1.922805	-1.072548	1.279588
C 0	0.468477	-0.463705	-0.531125
C 0	-0.773744	0.392154	-0.791428
C 0	-2.031503	-0.101326	-0.083709
C 0	-3.226433	0.858504	-0.221654
C 0	-3.050270	2.133842	0.558202
C 0	-3.104431	3.366164	0.044388
O 0	-2.376786	-1.377564	-0.706633
C 0	-3.050303	-2.285980	0.037554
O 0	-3.394072	-2.100501	1.187645
C 0	-3.307803	-3.547131	-0.752194
C 0	3.120925	-0.647089	0.482000
C 0	2.935551	-0.113796	-0.786680
C 0	1.661537	-0.012966	-1.331779
H 0	1.773757	-2.167315	1.201947
H 0	2.048620	-0.840967	2.342449
H 0	0.232697	-1.513728	-0.791660
H 0	-0.566318	1.415146	-0.460223
H 0	-0.961107	0.425965	-1.872149
H 0	-1.826270	-0.291823	0.972236
H 0	-3.399012	1.078425	-1.282539
H 0	-4.111572	0.332435	0.157052
H 0	-2.879582	2.014375	1.628957
H 0	-2.987394	4.247330	0.668465
H 0	-3.274751	3.535905	-1.016748
H 0	-2.358056	-4.002016	-1.050597
H 0	-3.859629	-3.312523	-1.667435
H 0	-3.877525	-4.247330	-0.141616
H 0	4.111572	-0.784161	0.904842
H 0	3.795625	0.216069	-1.364616
H 0	1.505253	0.352785	-2.342449

Number of Imaginary Frequencies = 0

Energy = -693.164701594

ZPE = -692.896559

G = -692.943460

[9-H]-Rad-(C-9)

UB3LYP/6-31+G** Geometry

C 0	2.664750	-1.703051	1.106031
O 0	1.998571	-0.757039	-1.032025
C 0	4.222649	-0.246055	-0.170086
C 0	3.130964	0.097741	-1.147651
C 0	4.017679	-1.086357	0.849572
C 0	1.576397	-0.958188	0.322230
C 0	0.255403	-1.719902	0.268943
C 0	-0.900356	-0.924627	-0.360735
C 0	-2.103711	-1.781216	-0.628288
C 0	-3.241186	-1.852475	0.165544
C 0	-4.330694	-2.674115	-0.084965
O 0	-1.220625	0.147887	0.571481
C 0	-1.582853	1.350703	0.055251
O 0	-1.626486	1.597026	-1.131216
C 0	-1.932442	2.323678	1.155774
H 0	2.430235	-1.667870	2.178464
H 0	2.670548	-2.766471	0.824094
H 0	5.192749	0.220789	-0.328487
H 0	2.822911	1.151833	-1.024422
H 0	3.484833	-0.015854	-2.178464
H 0	4.831447	-1.337452	1.526682
H 0	1.415899	0.026013	0.792573
H 0	0.407727	-2.632171	-0.319699
H 0	-0.036834	-2.027449	1.279995
H 0	-0.558031	-0.468807	-1.294274
H 0	-2.031499	-2.417286	-1.509528
H 0	-3.280038	-1.210885	1.044600
H 0	-5.192749	-2.682332	0.572771
H 0	-4.355249	-3.331212	-0.949889
H 0	-1.198431	2.279774	1.964402
H 0	-2.906869	2.055144	1.578024
H 0	-1.988424	3.331212	0.743527

Number of Imaginary Frequencies = 0

Energy = -693.164281959

ZPE = -692.896120

G = -692.942963

[21-H]-Rad-(C-2)

UB3LYP/6-31+G** Geometry

C 0	-0.881349	-0.164174	0.957116
O 0	-1.483488	0.682391	-1.277966
C 0	-0.475714	-0.030948	-0.518378
C 0	0.823547	0.732876	-0.766122
C 0	2.073775	0.065111	-0.201399
C 0	3.359209	0.876193	-0.448083
C 0	3.408454	2.157536	0.339527
C 0	3.492071	3.380061	-0.186984
C 0	2.812607	-2.220391	-0.189120
O 0	3.258573	-2.102013	0.931634
C 0	2.857644	-3.482183	-1.019385
C 0	-2.282405	-0.698776	1.064772
C 0	-3.168076	-0.439998	0.029751
C 0	-2.766883	0.277828	-1.086911
O 0	2.195507	-1.223190	-0.869323
H 0	-0.167843	-0.824862	1.466304
H 0	-0.795815	0.820326	1.448938
H 0	-0.405002	-1.037056	-0.952310
H 0	0.943716	0.861901	-1.848788
H 0	0.740813	1.736121	-0.332401
H 0	1.975522	-0.128179	0.870716
H 0	4.203950	0.239694	-0.154125
H 0	3.455379	1.081286	-1.521422
H 0	3.379844	2.047733	1.425053
H 0	3.537566	4.269205	0.436086
H 0	3.527537	3.538293	-1.263042
H 0	1.842364	-3.800145	-1.278484
H 0	3.360796	-4.269205	-0.456779
H 0	3.389691	-3.295884	-1.958025
H 0	-2.594209	-1.230137	1.958025
H 0	-4.203950	-0.763992	0.080817
H 0	-3.426718	0.604447	-1.882605

Number of Imaginary Frequencies = 0

Energy = -693.173867334

ZPE = -692.905066

G = -692.952144

[21-H]-Rad-(C-5)

UB3LYP/6-31+G** Geometry

O 0	-1.452208	0.025143	-1.560979
C 0	-2.716785	-0.592878	-1.362826
C 0	-0.419629	-0.461391	-0.697447
C 0	0.814572	0.392510	-1.018486
C 0	2.117940	-0.100326	-0.399023
C 0	3.310837	0.835191	-0.671734
C 0	3.202281	2.153234	0.045911
C 0	3.182201	3.349893	-0.542557
C 0	3.110570	-2.283039	-0.251596
O 0	3.530263	-2.052268	0.861939
C 0	3.300644	-3.578997	-1.005461
C 0	-3.157476	-0.554252	0.071712
C 0	-2.198520	-0.438460	1.065899
C 0	-0.848100	-0.402228	0.746045
O 0	2.395553	-1.401578	-0.991686
H 0	-2.692309	-1.638894	-1.729974
H 0	-3.415850	-0.048252	-2.008220
H 0	-0.194531	-1.510672	-0.969744
H 0	0.925004	0.418862	-2.109067
H 0	0.633742	1.420501	-0.686359
H 0	2.024159	-0.247258	0.681265
H 0	4.214868	0.313684	-0.331391
H 0	3.405378	0.993081	-1.753140
H 0	3.147257	2.096295	1.134508
H 0	3.116752	4.269175	0.033197
H 0	3.238179	3.456720	-1.624073
H 0	2.328029	-4.024275	-1.239736
H 0	3.888216	-4.269175	-0.399216
H 0	3.809696	-3.390408	-1.956272
H 0	-4.214868	-0.644682	0.302417
H 0	-2.504537	-0.391783	2.109067
H 0	-0.090759	-0.368744	1.523527

Number of Imaginary Frequencies = 0

Energy = -693.162951718

ZPE = -692.894726

G = -692.941998

[21-H]-Rad-(C-9)

UB3LYP/6-31+G** Geometry

C 0	1.843884	-0.780506	0.875862
O 0	2.608833	-1.755858	-1.211488
C 0	4.186695	-0.455080	0.117916
C 0	3.859791	-1.086899	-1.208663
C 0	3.271088	-0.335758	1.081078
C 0	1.558803	-0.986483	-0.619011
C 0	0.269217	-1.752669	-0.918083
C 0	-1.008434	-1.097618	-0.395348
C 0	-2.238625	-1.887384	-0.714829
C 0	-3.278547	-2.090190	0.184531
C 0	-4.424547	-2.817082	-0.086406
C 0	-1.707912	1.207460	-0.358499
O 0	-2.144089	1.084342	0.766174
C 0	-1.779643	2.471805	-1.184501
O 0	-1.089887	0.220994	-1.049719
H 0	1.156977	-0.029988	1.289973
H 0	1.651601	-1.714198	1.426934
H 0	5.205354	-0.097331	0.257428
H 0	3.890681	-0.324195	-2.010000
H 0	4.605917	-1.848422	-1.467768
H 0	3.534602	0.102550	2.041920
H 0	1.516524	0.000185	-1.107159
H 0	0.192629	-1.888311	-2.003588
H 0	0.346445	-2.754317	-0.476684
H 0	-0.954112	-0.916932	0.680373
H 0	-2.313583	-2.296514	-1.722161
H 0	-3.180006	-1.635982	1.170141
H 0	-5.205354	-2.941453	0.656320
H 0	-4.580305	-3.285710	-1.054653
H 0	-2.166306	3.285710	-0.570129
H 0	-2.442942	2.312990	-2.041920
H 0	-0.792391	2.731035	-1.578887

Number of Imaginary Frequencies = 0

Energy = -693.164661124

ZPE = -692.896341

G = -692.943207

IV. References.

1 - Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J. A., Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, O.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J. and Fox, D. J. Gaussian 09, Gaussian, Inc., Wallingford CT, 2009.

2 - (a) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785-789. (b) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 1372-1377. (c) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648-5652.

3 - Hyperchem Professional Release 7.52, Hypercube, Inc., 2005.

4- Allinger, N. L. *J. Am. Chem. Soc.* **1977**, *99*, 8127-8134.