

Stereochemical Study of a Transannular Michael Reaction Cascade

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SUPPORTING INFORMATION

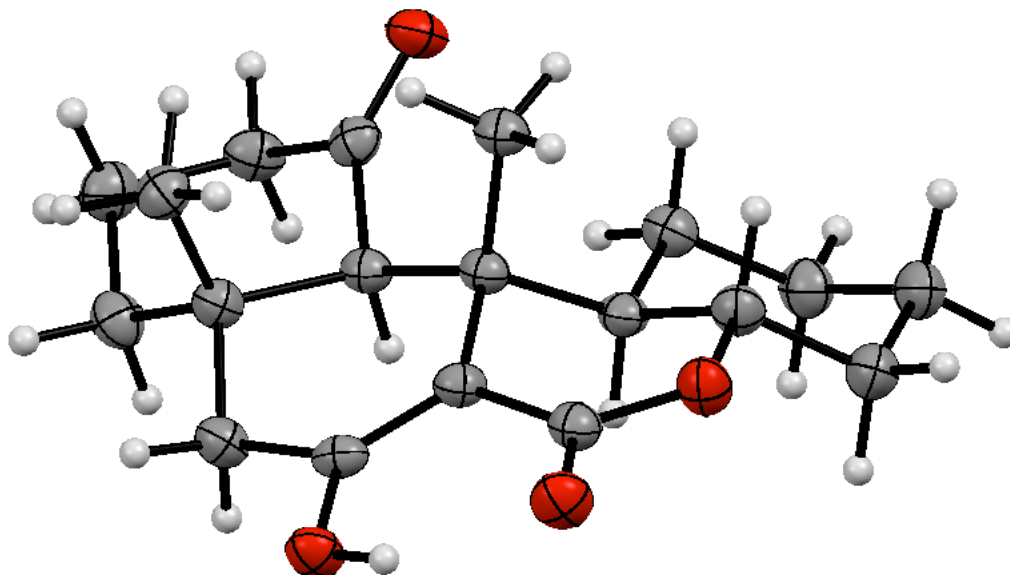
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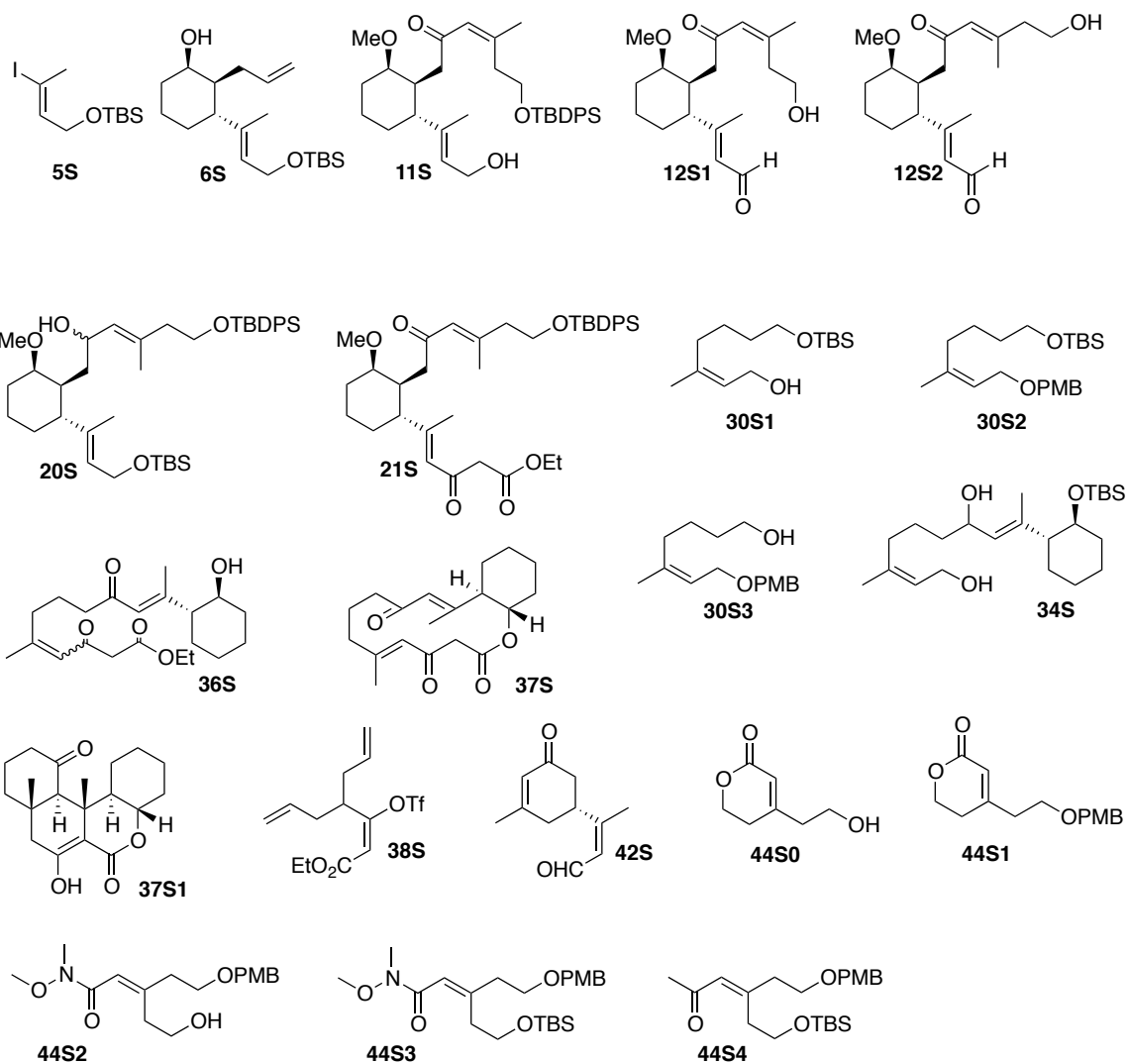
1. General Experimental Procedure:

All non-aqueous reactions were carried out in flame-dried glasswares under a N₂ atmosphere. Dichloromethane and diethyl ether were purified by passage through an activated molecular sieve solvent purification system. Tetrahydrofuran was freshly distilled over sodium and benzophenone. All other commercial reagents were used as received. ¹H NMR chemical shifts are reported as δ values in ppm relative to CDCl₃ (7.26 ppm), coupling constants (*J*) are reported in Hertz (Hz), and multiplicity follows convention. Deuteriochloroform (CDCl₃, 77.0 ppm) served as the internal standard for ¹³C NMR spectra. Flash column chromatography was performed using 60Å silica gel (Silicycle, 230-400 mesh) as the stationary phase. A Q-TOF premier mass spectrometer with an electrospray source was used for high-resolution mass spectra (HRMS). Thin layer chromatography (TLC) was performed using pre-coated glass-backed TLC plates of 250 μ m thickness.

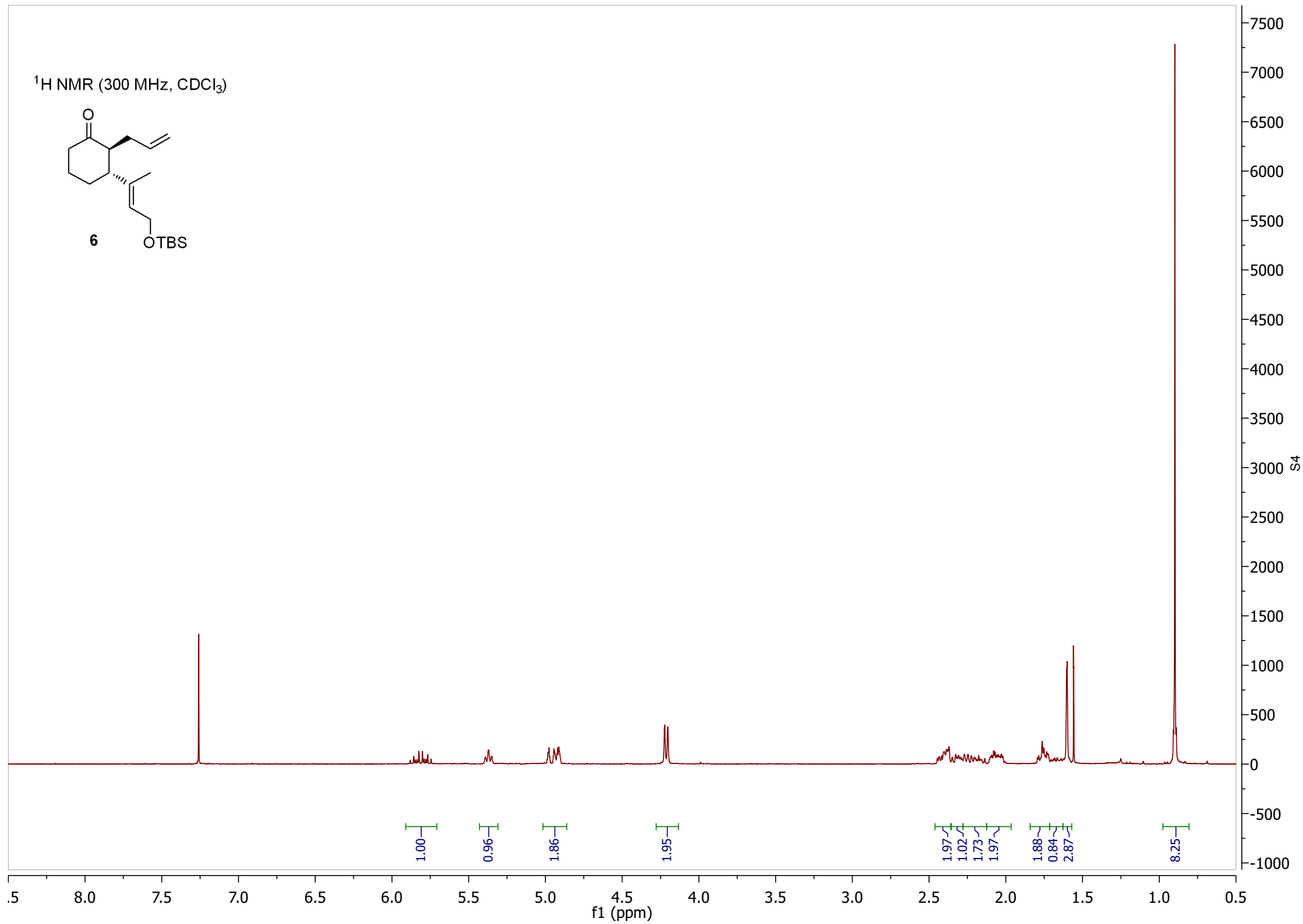
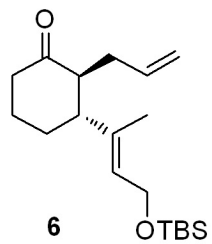
2. Thermal ellipsoid plot for 37S1

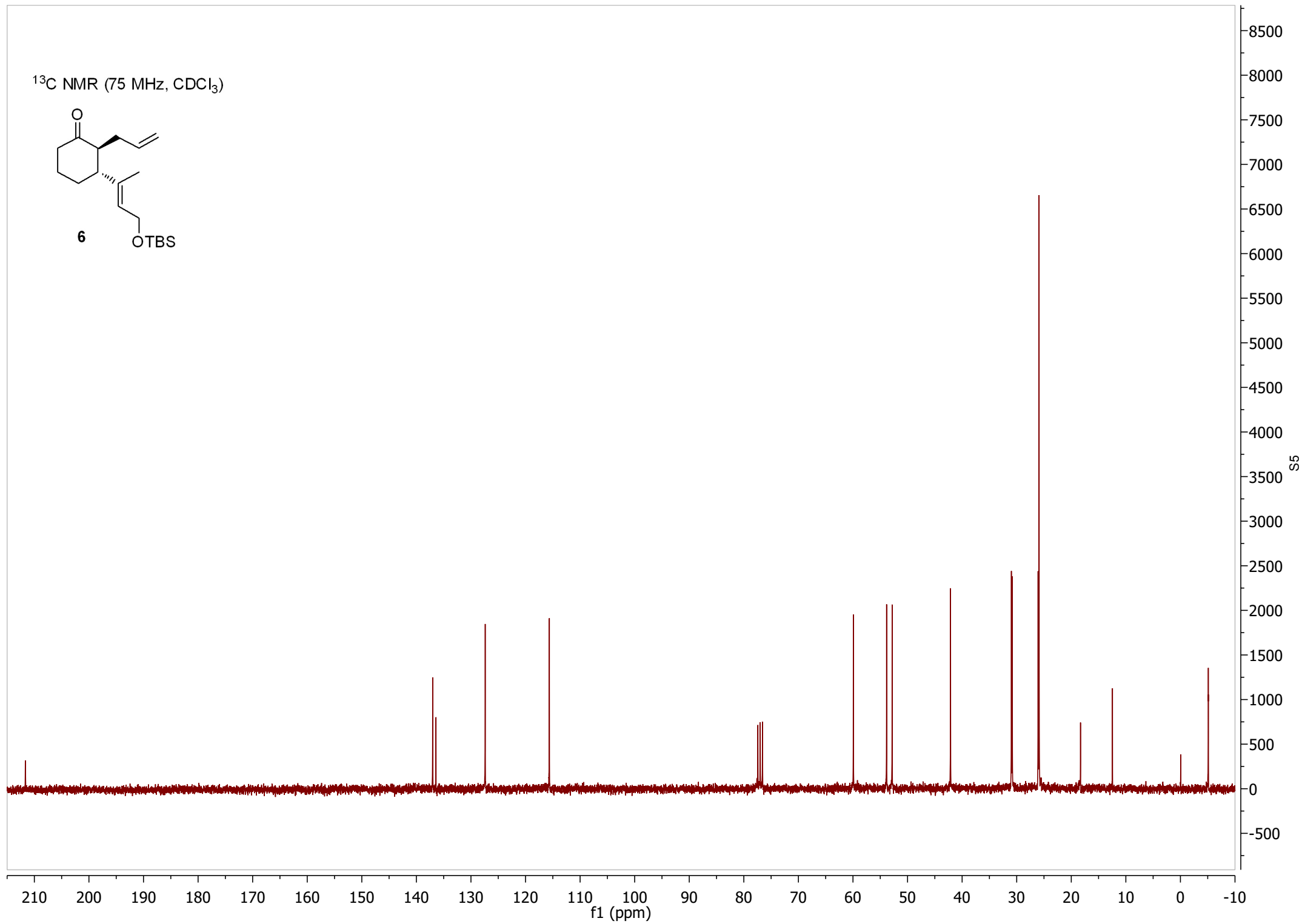
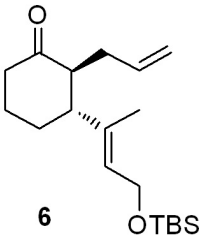


3. List of additional compounds

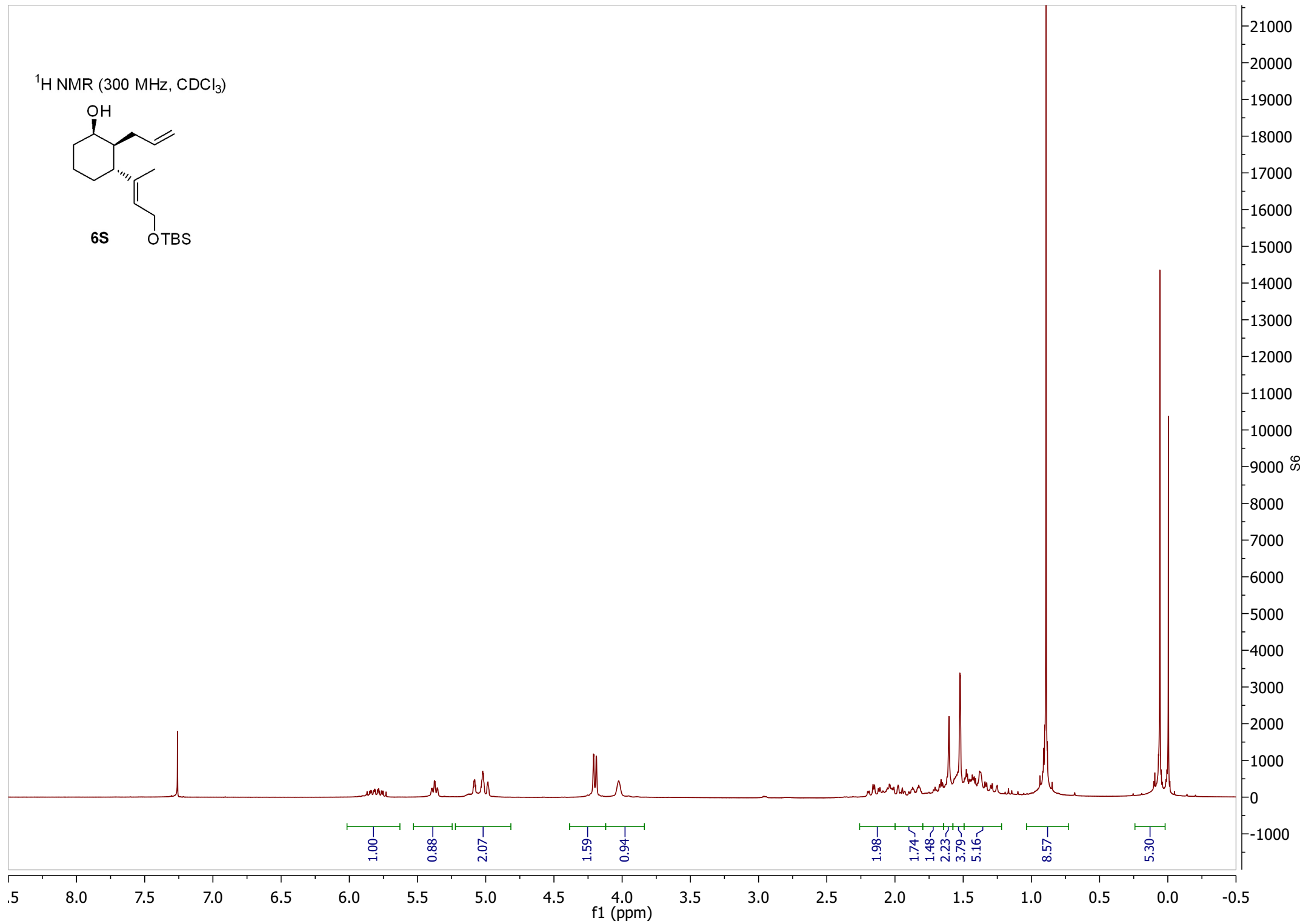
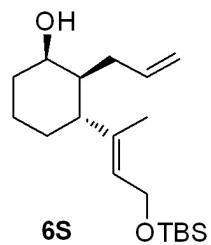


4. ^1H and ^{13}C NMR Spectra of New Compounds

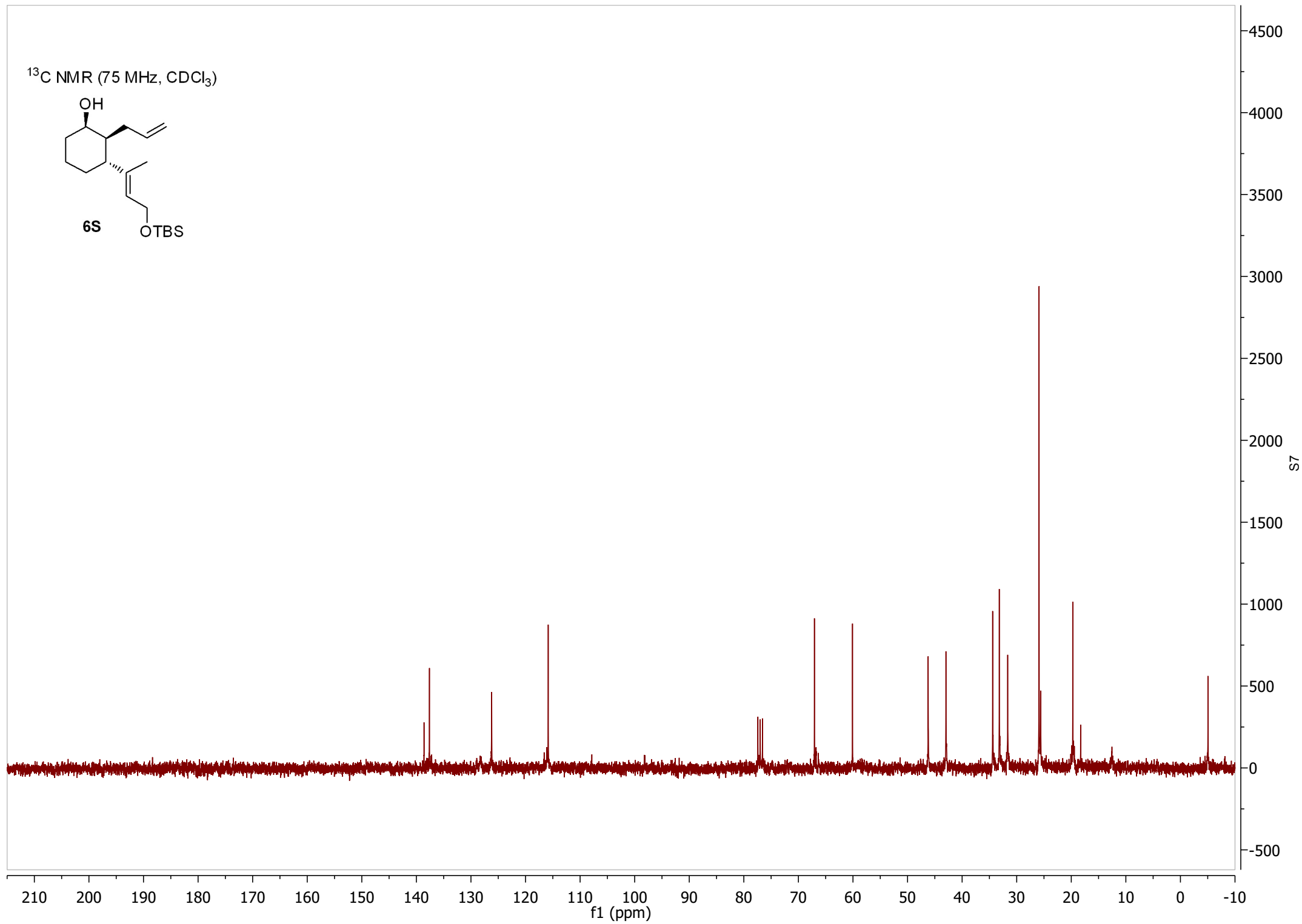
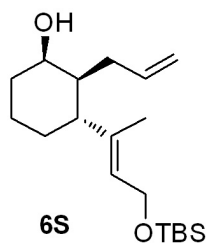
¹H NMR (300 MHz, CDCl₃)

^{13}C NMR (75 MHz, CDCl_3)

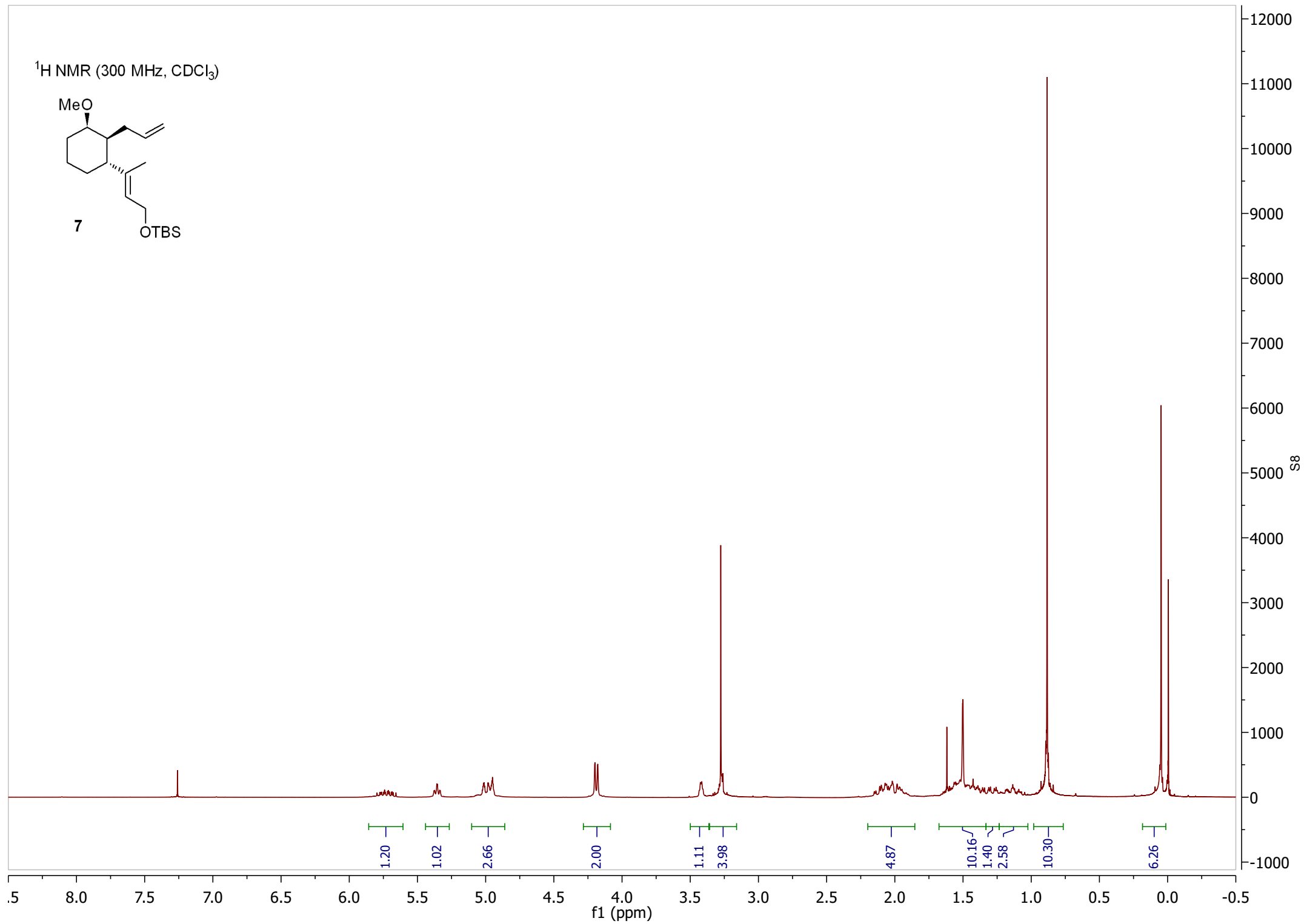
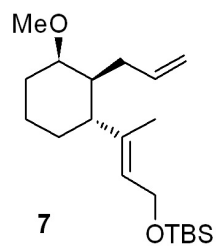
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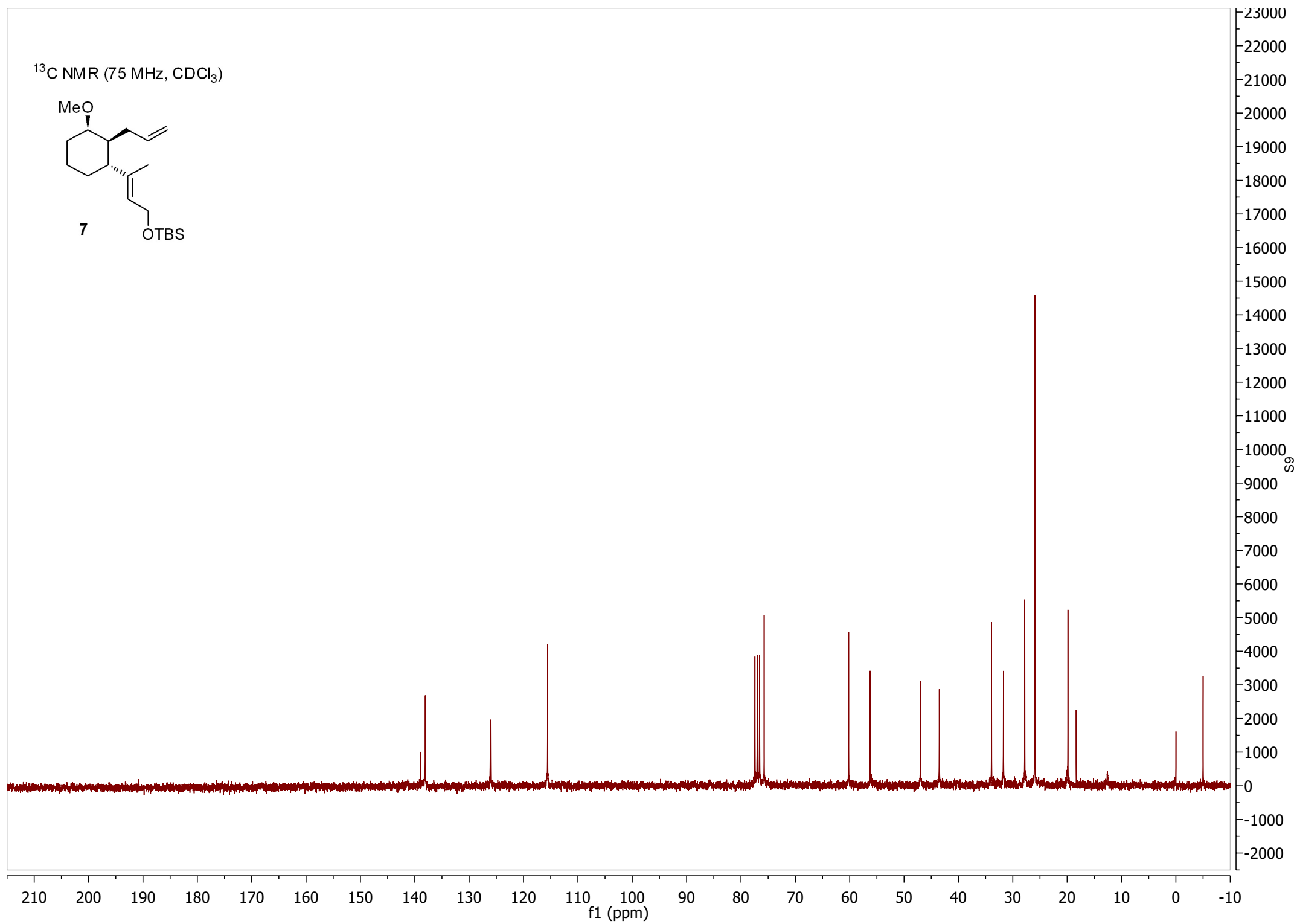
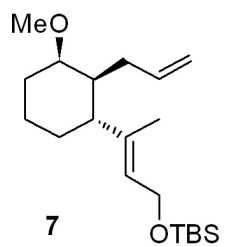
^{13}C NMR (75 MHz, CDCl_3)



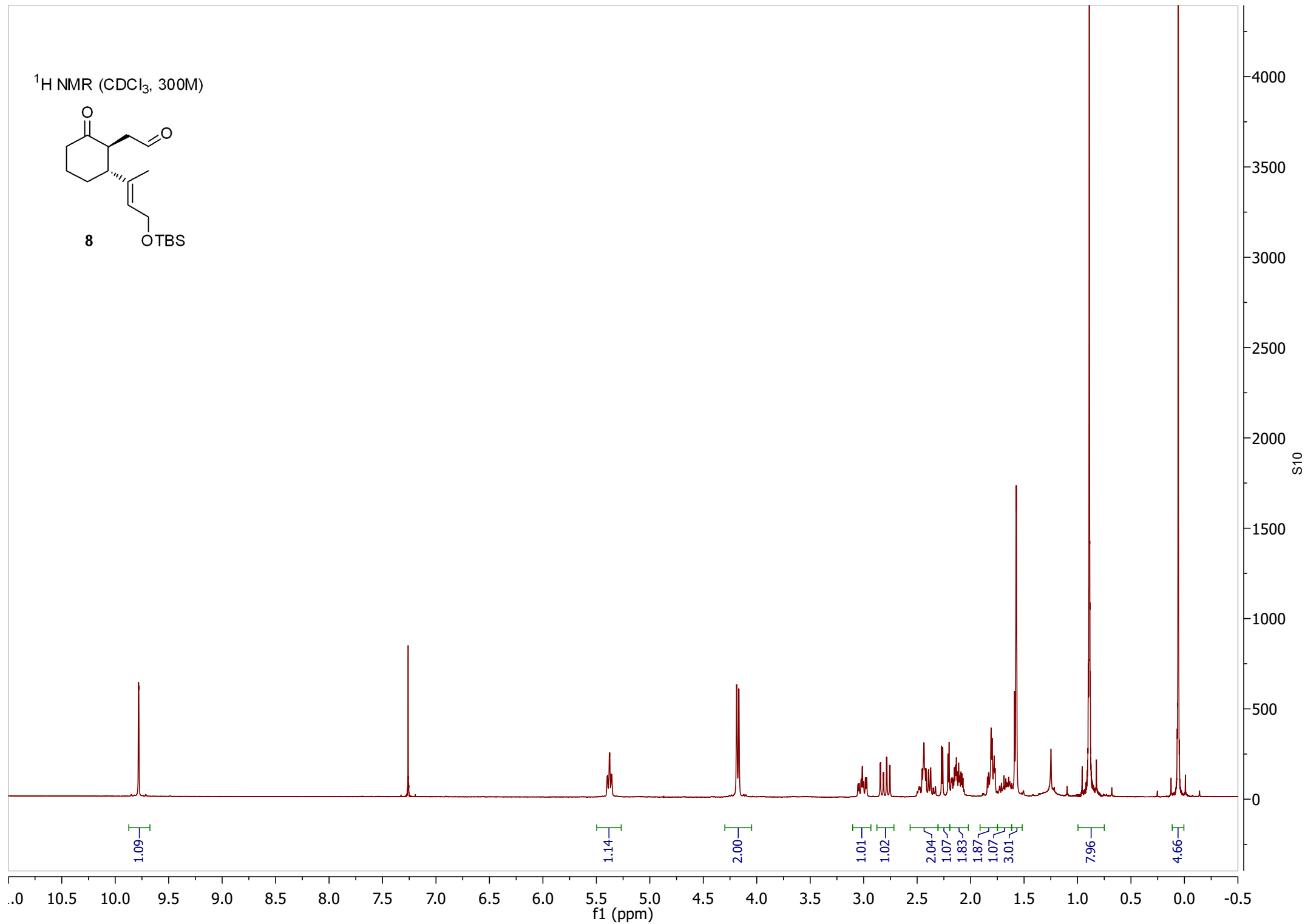
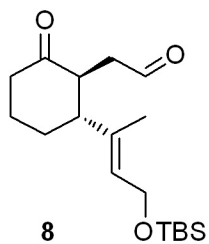
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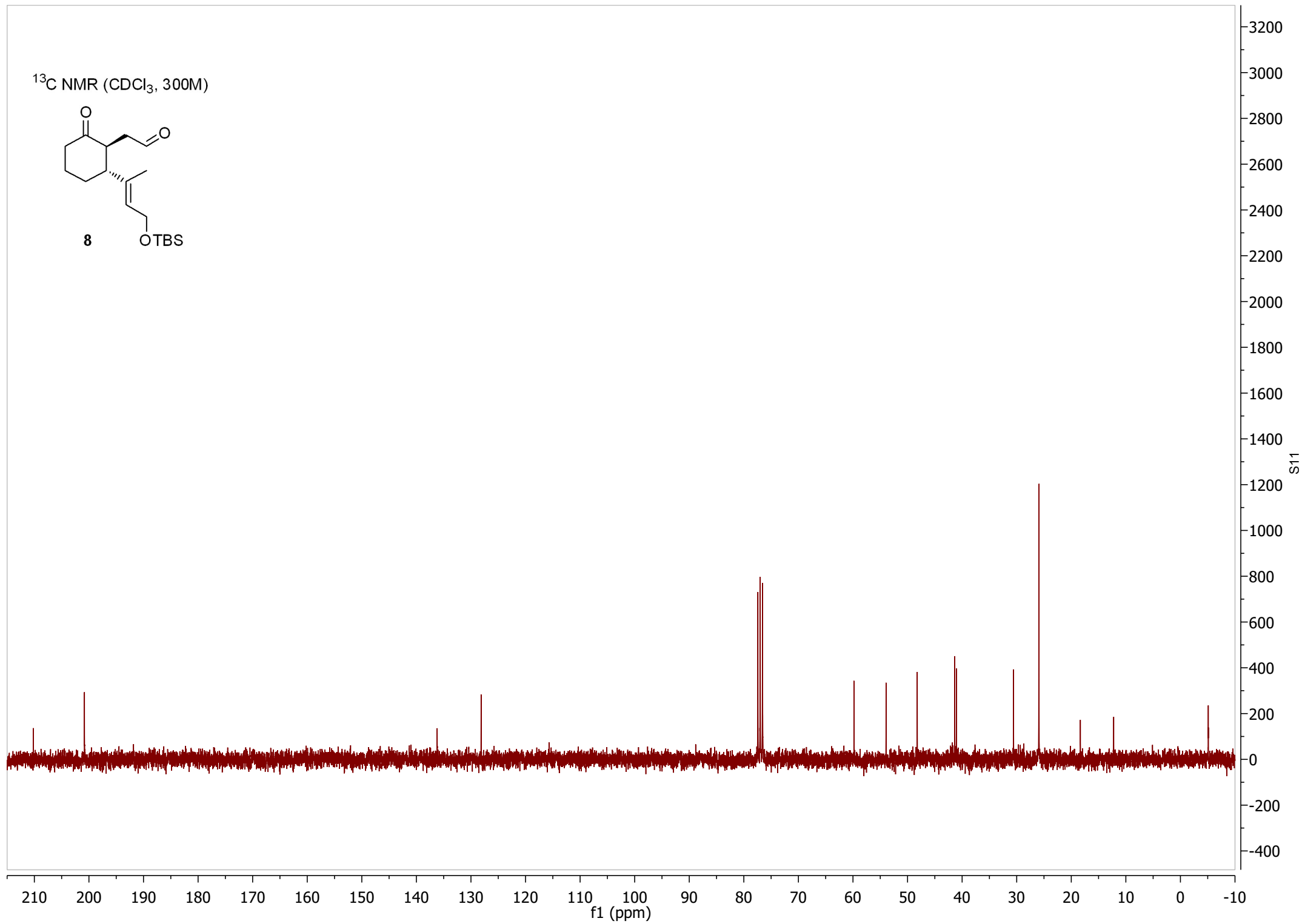
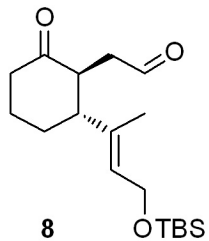
^{13}C NMR (75 MHz, CDCl_3)



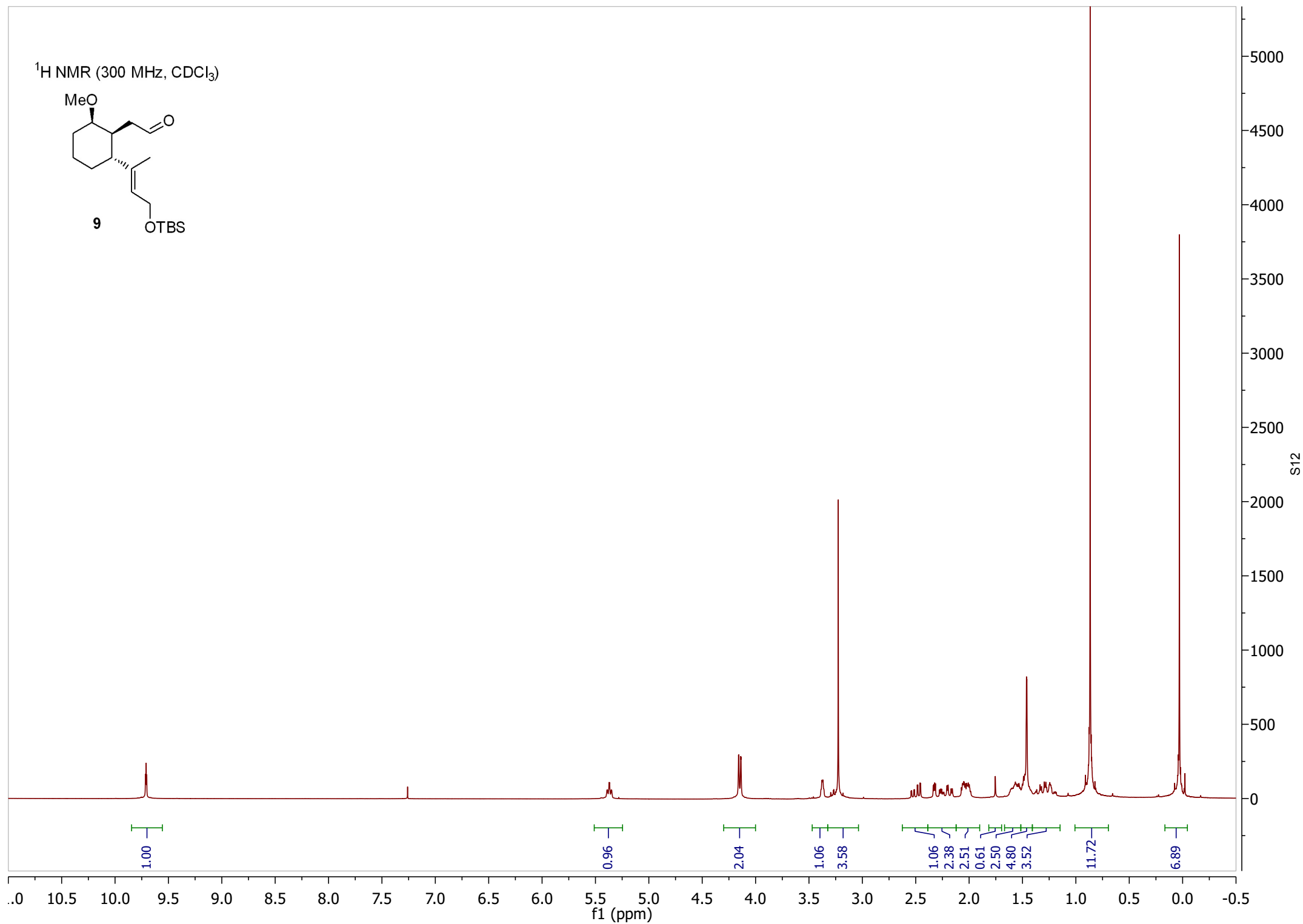
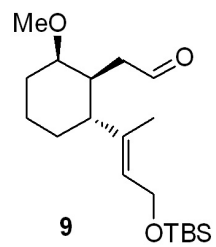
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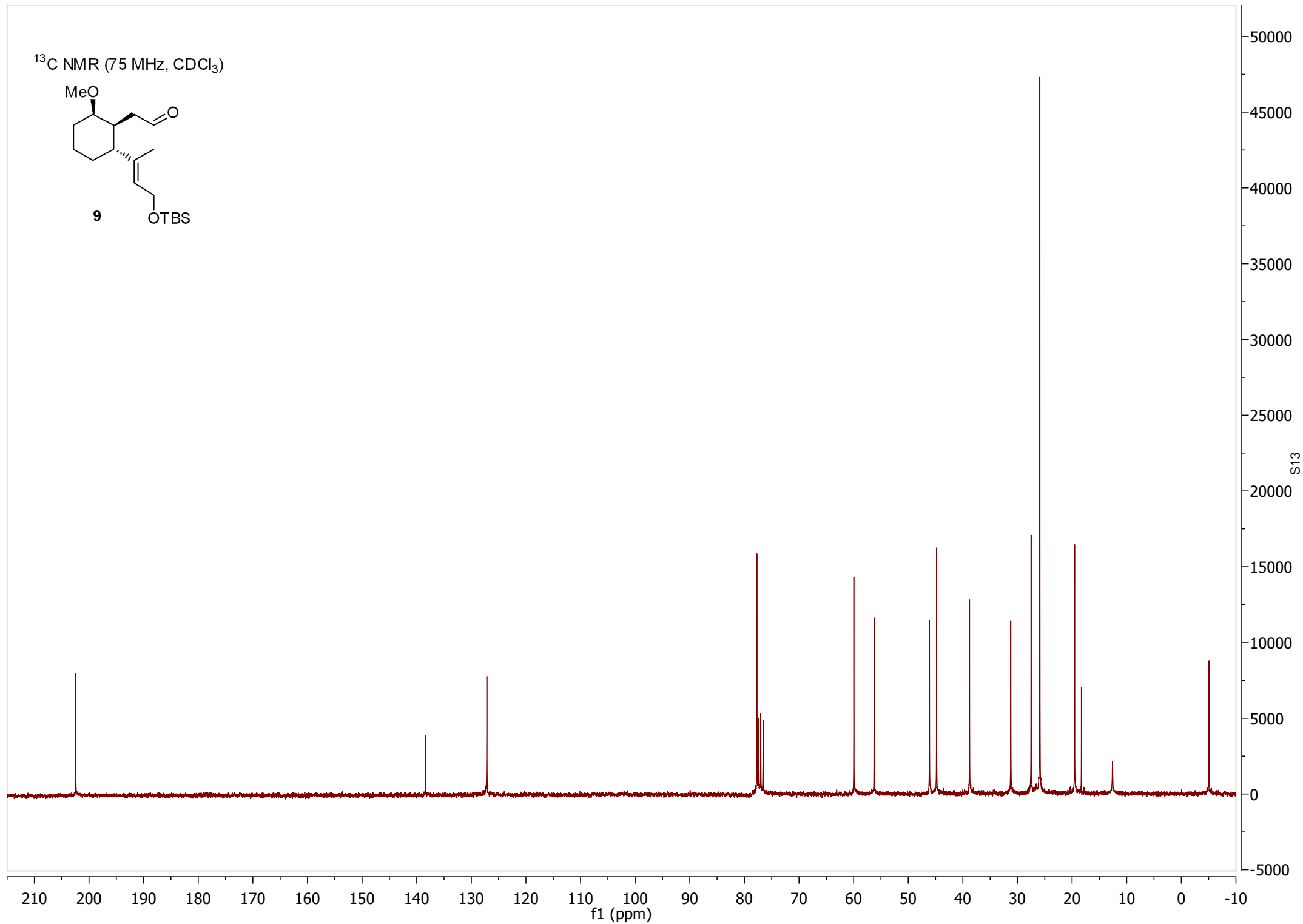
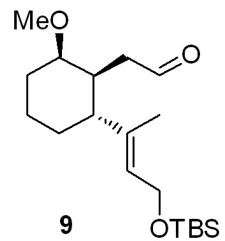
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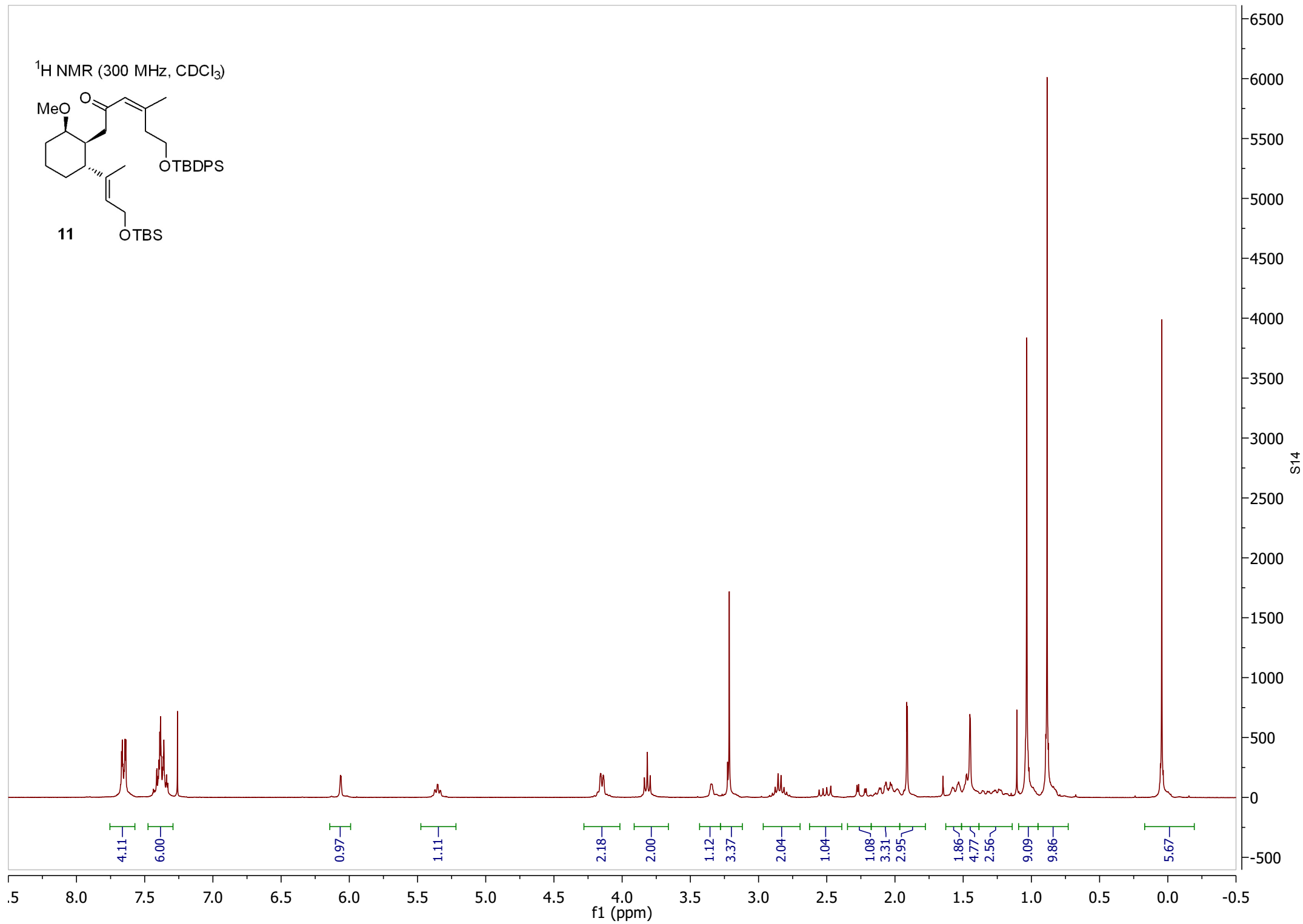
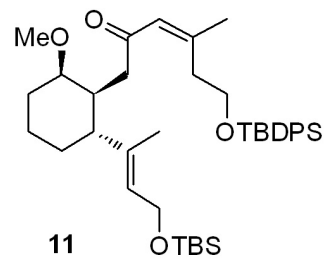
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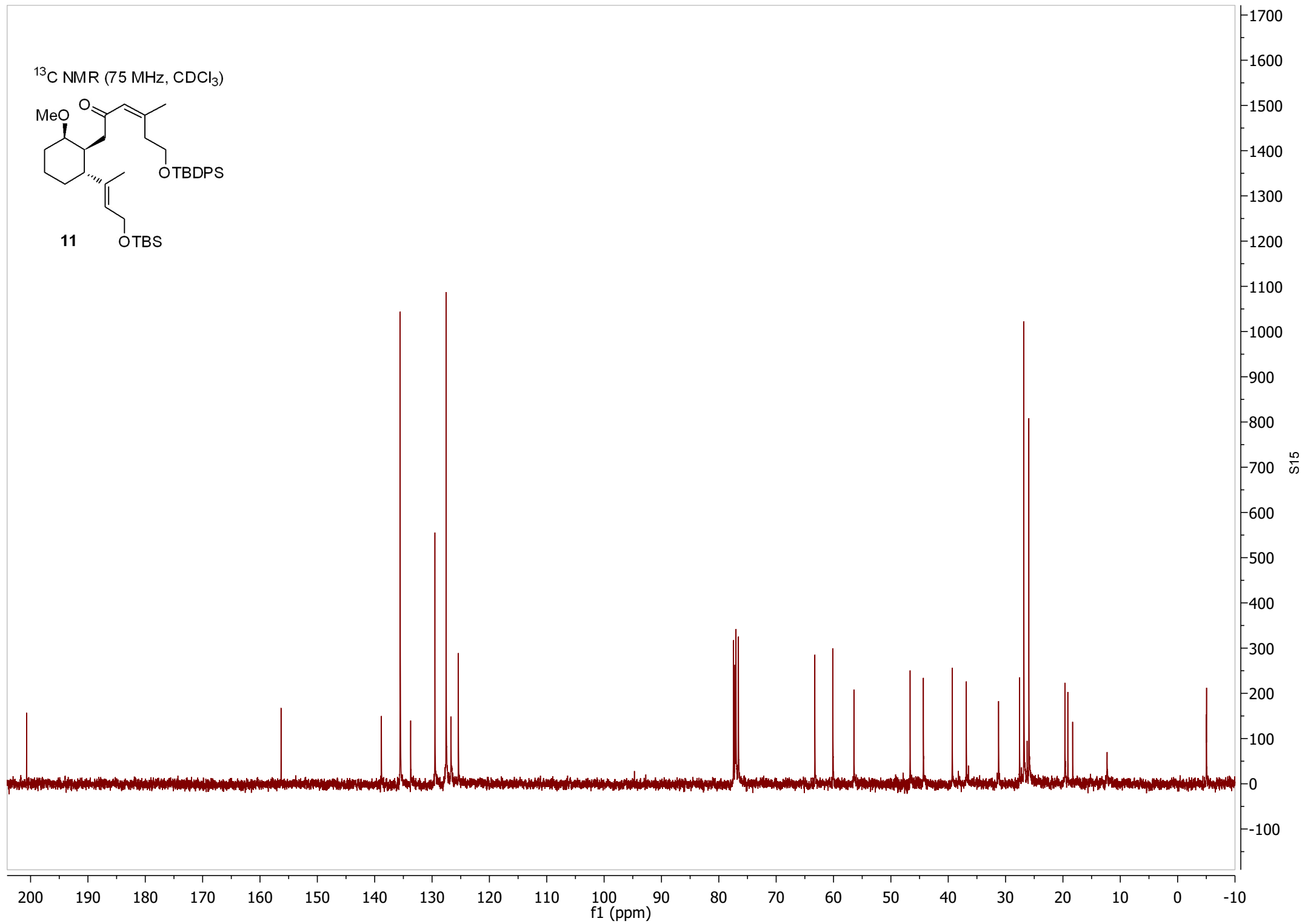
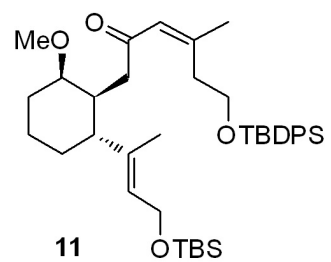
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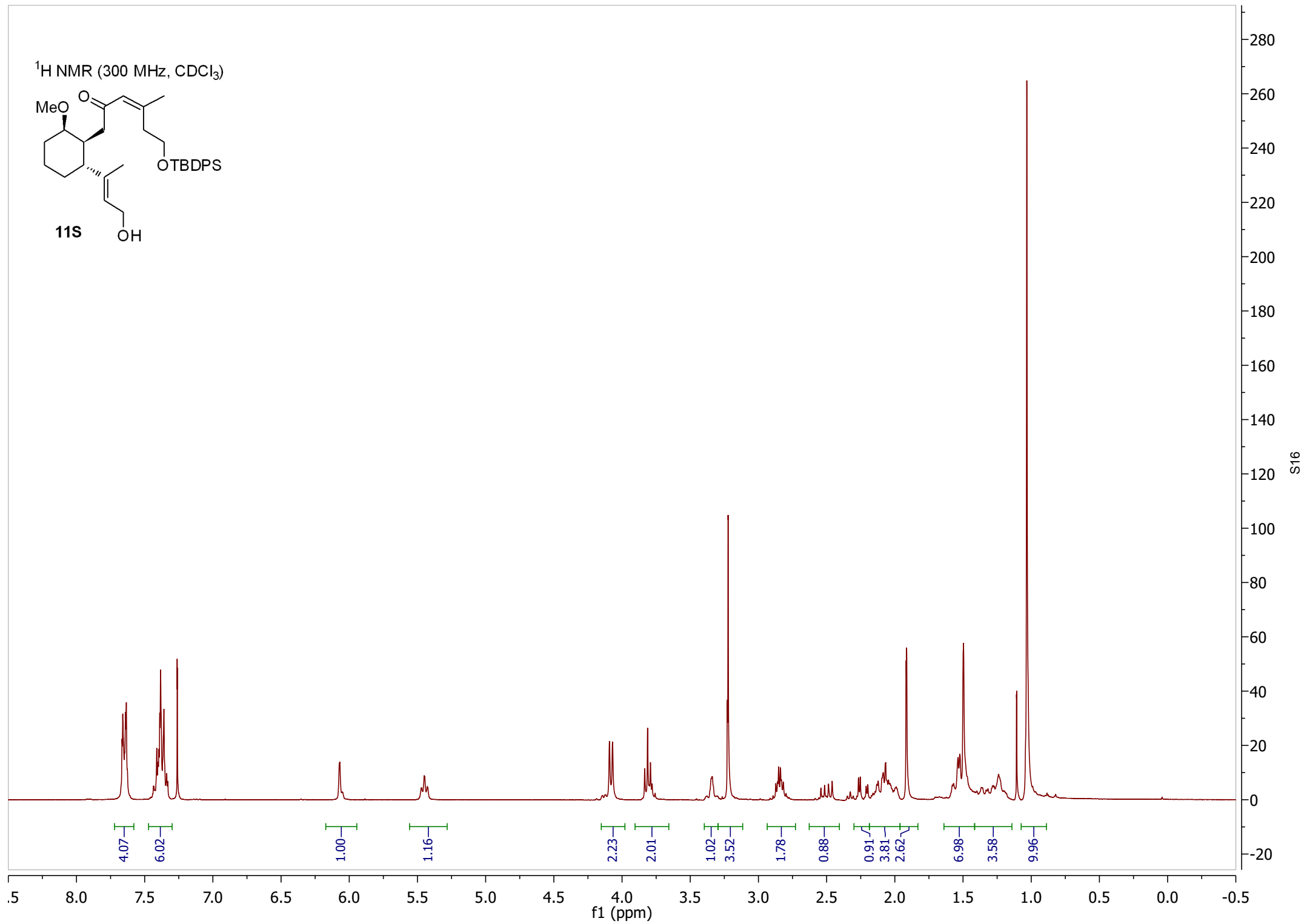
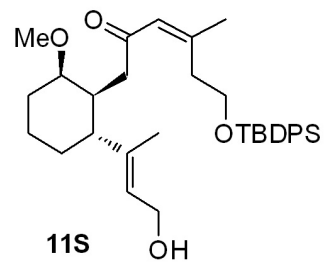
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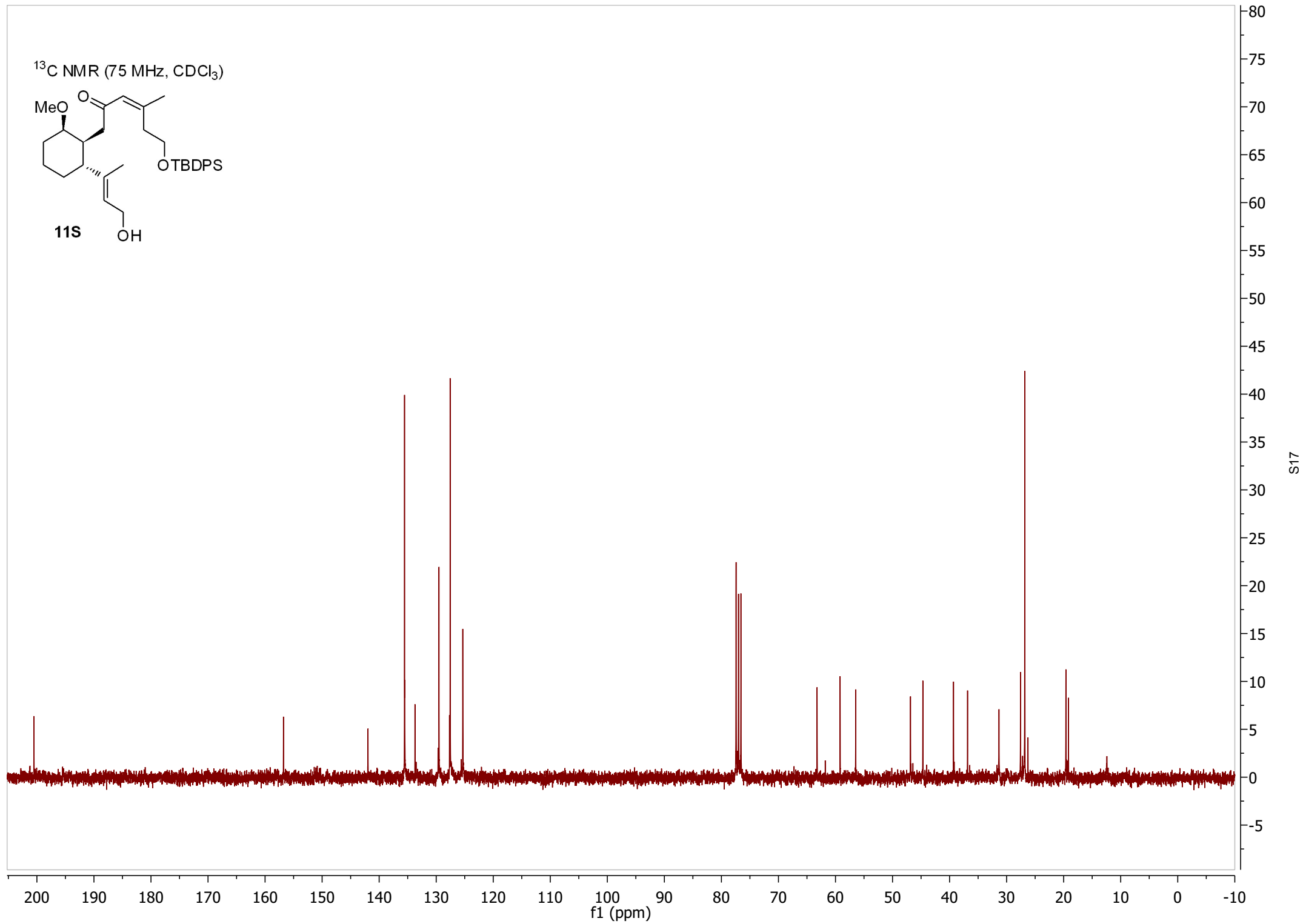
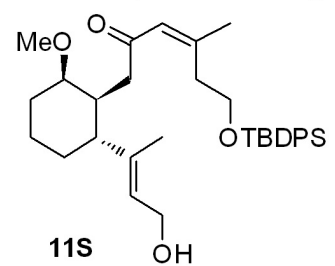
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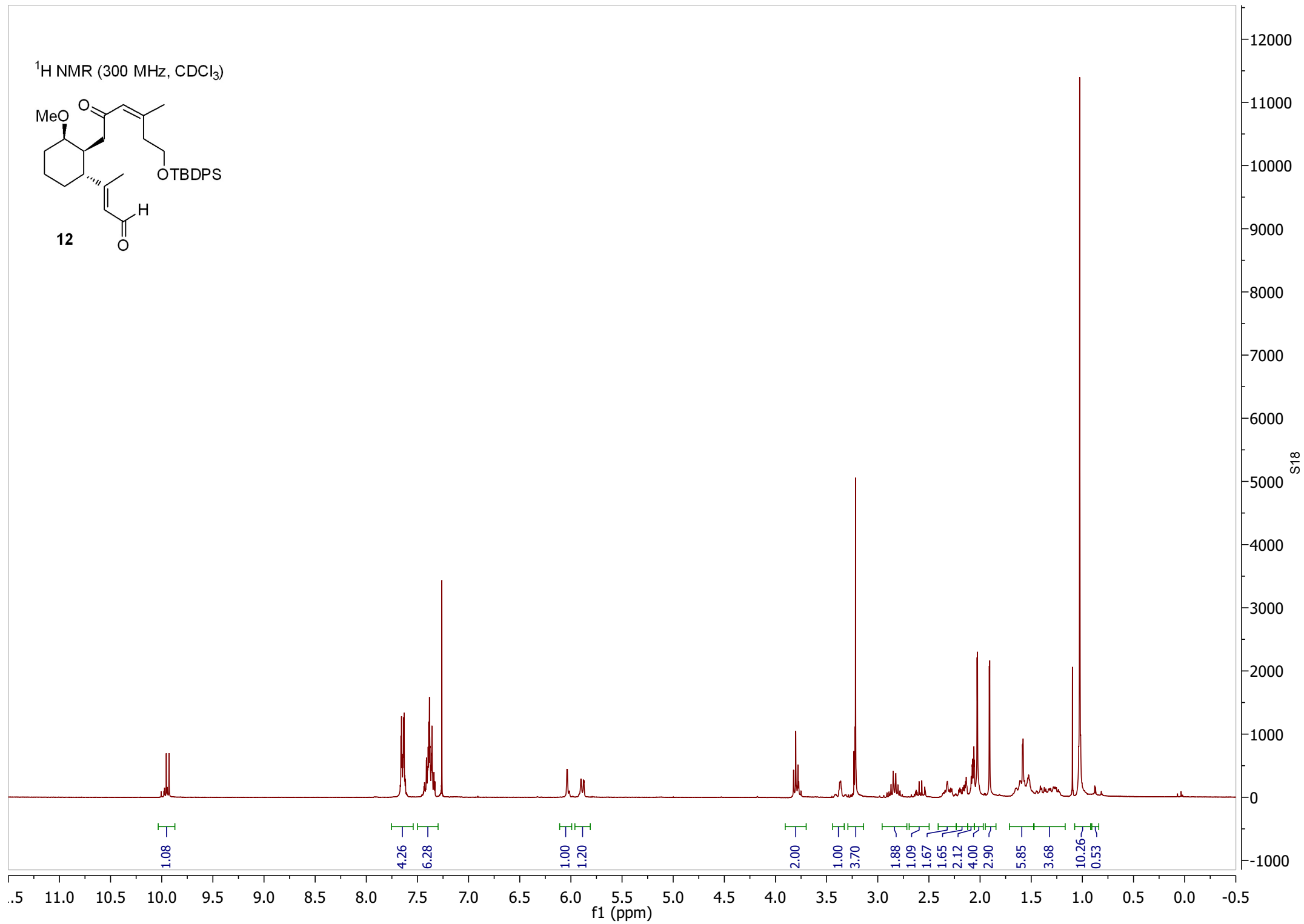
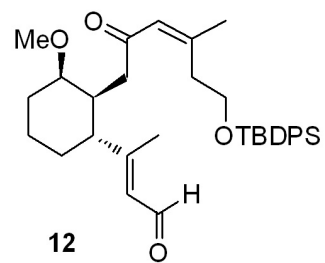
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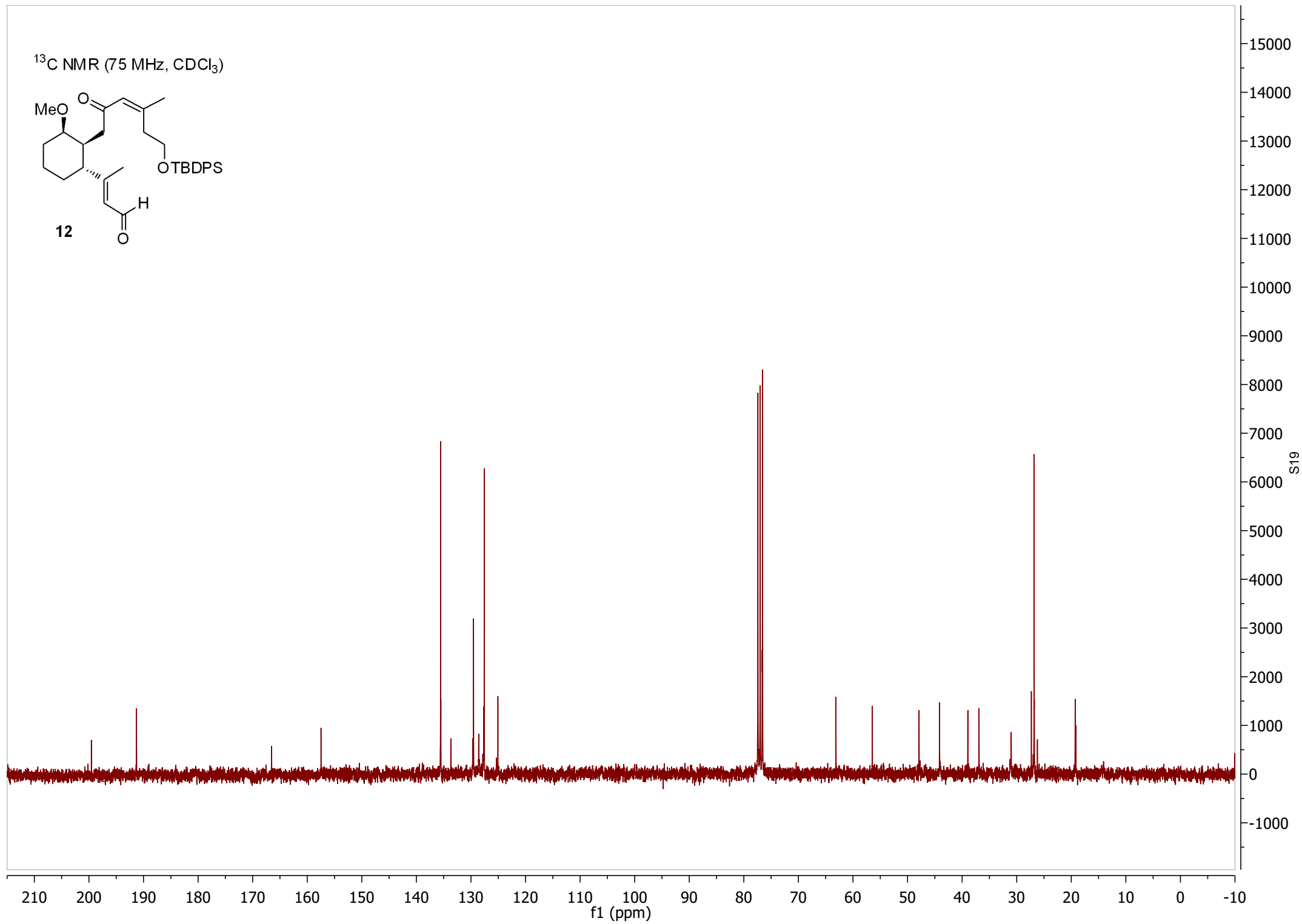
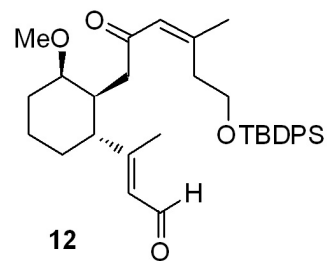
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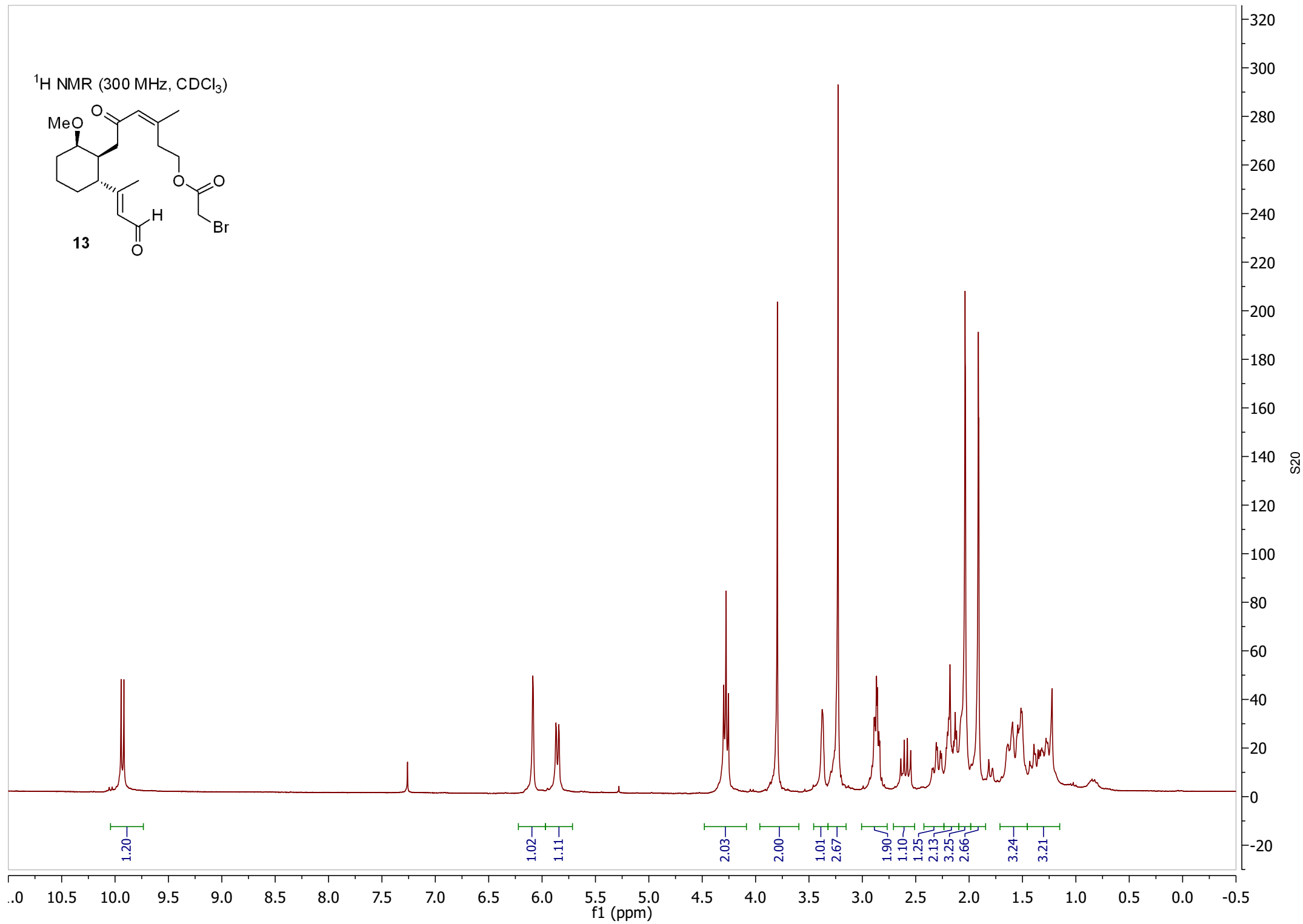
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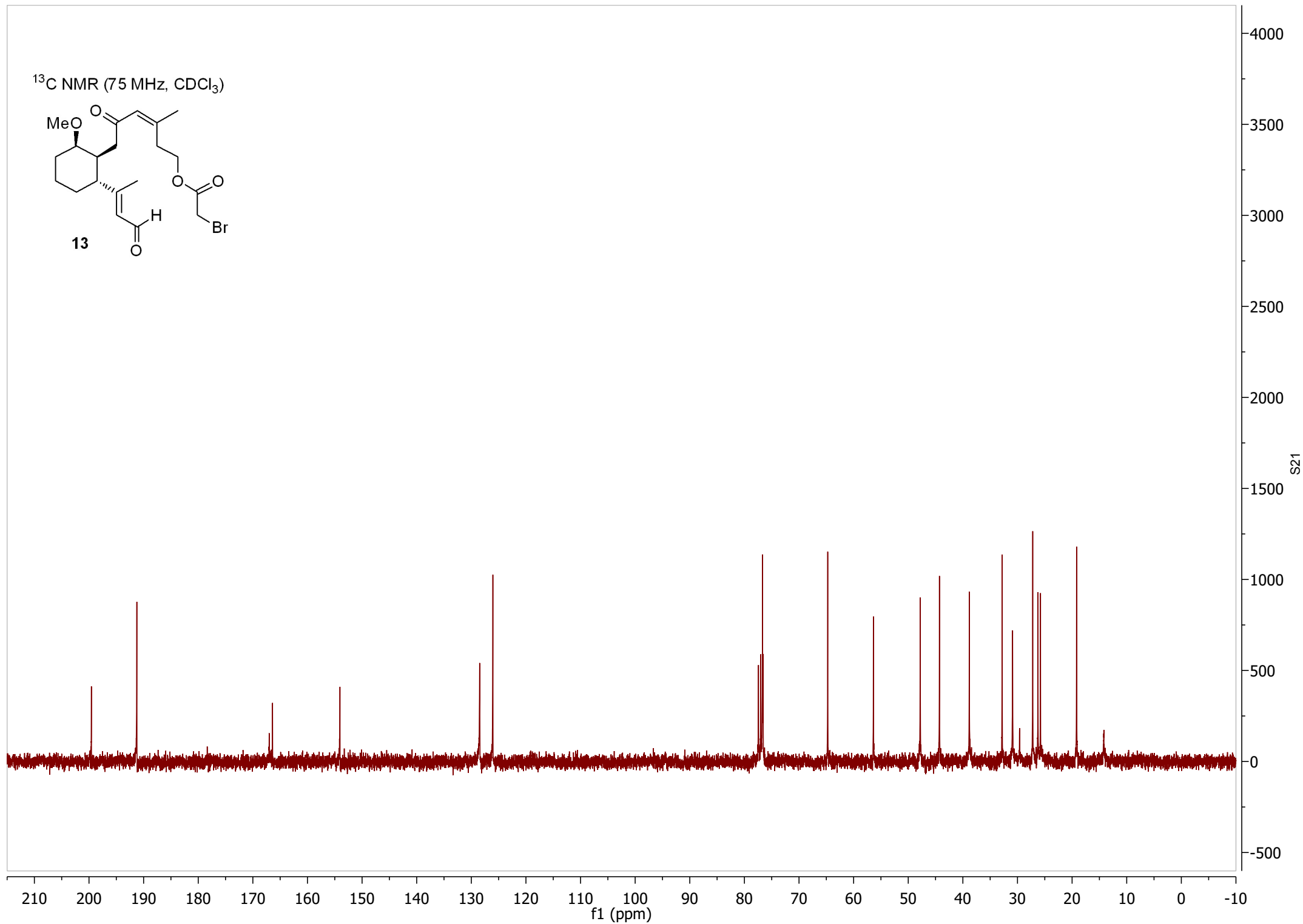
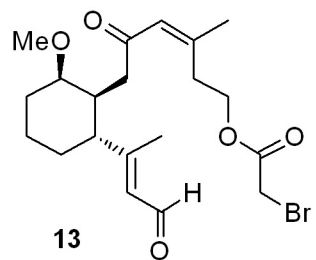
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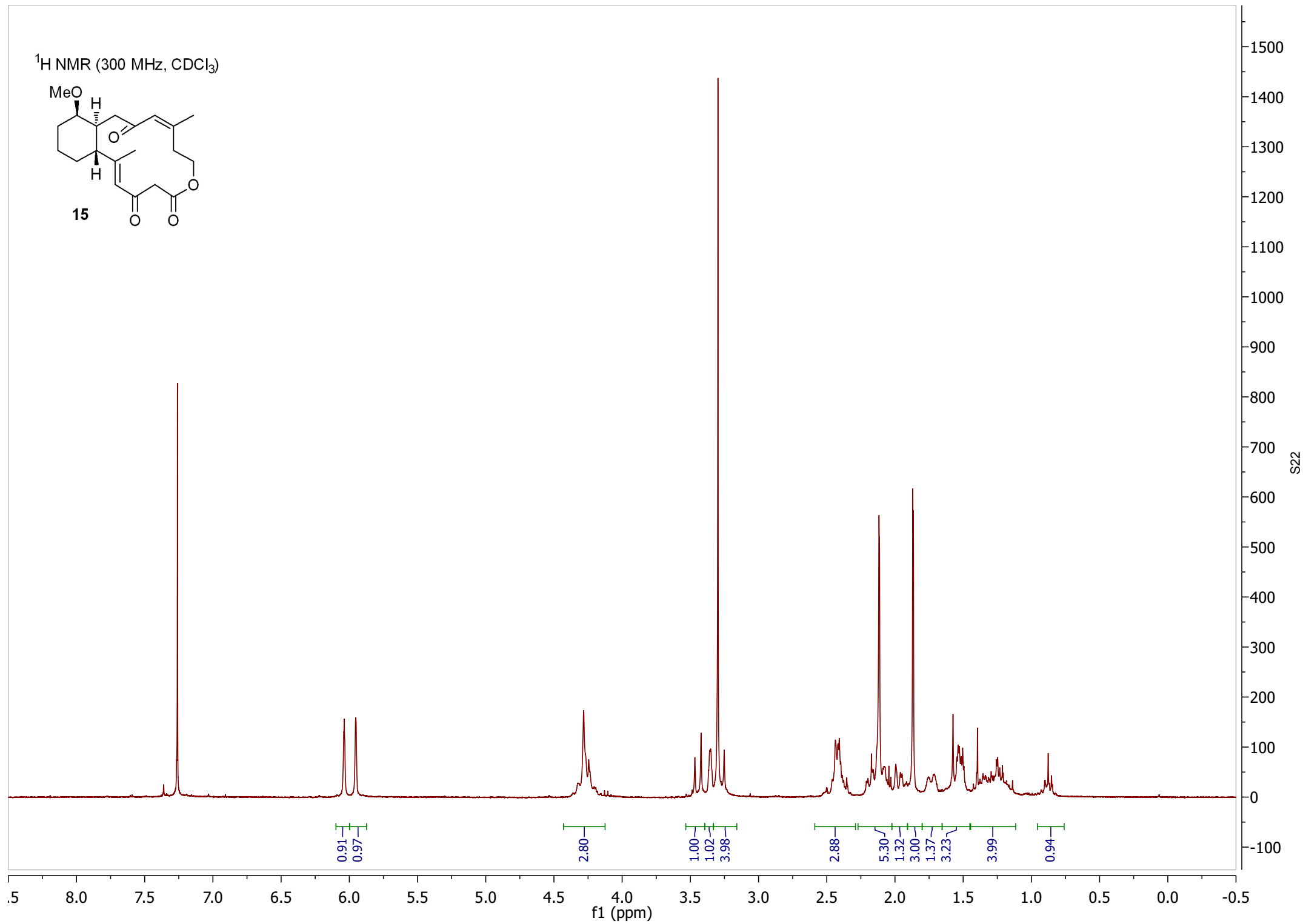
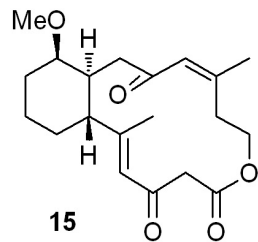
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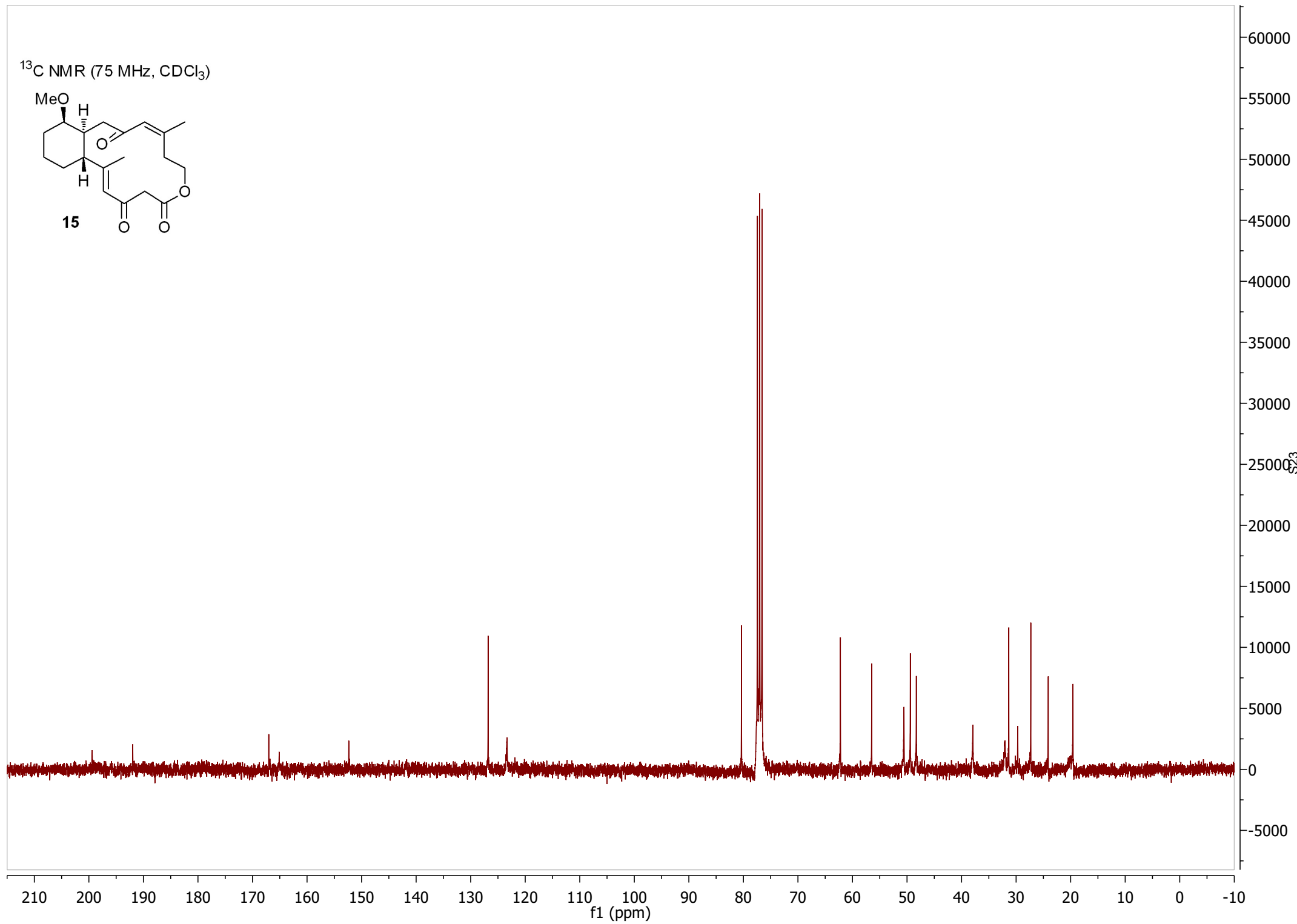
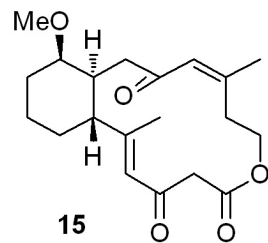
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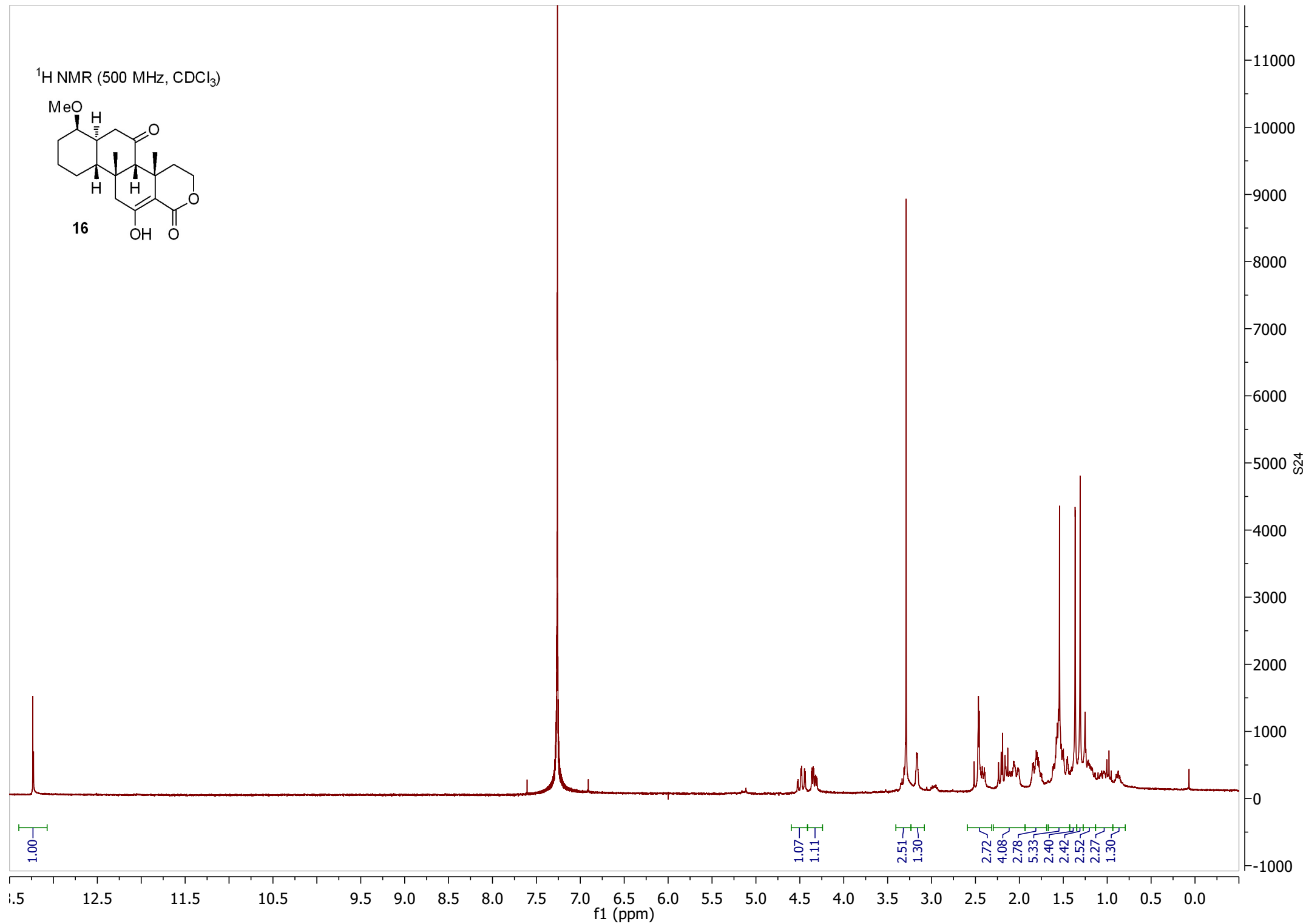
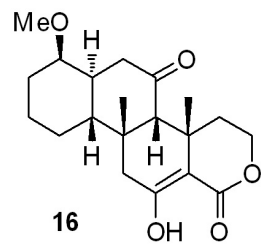
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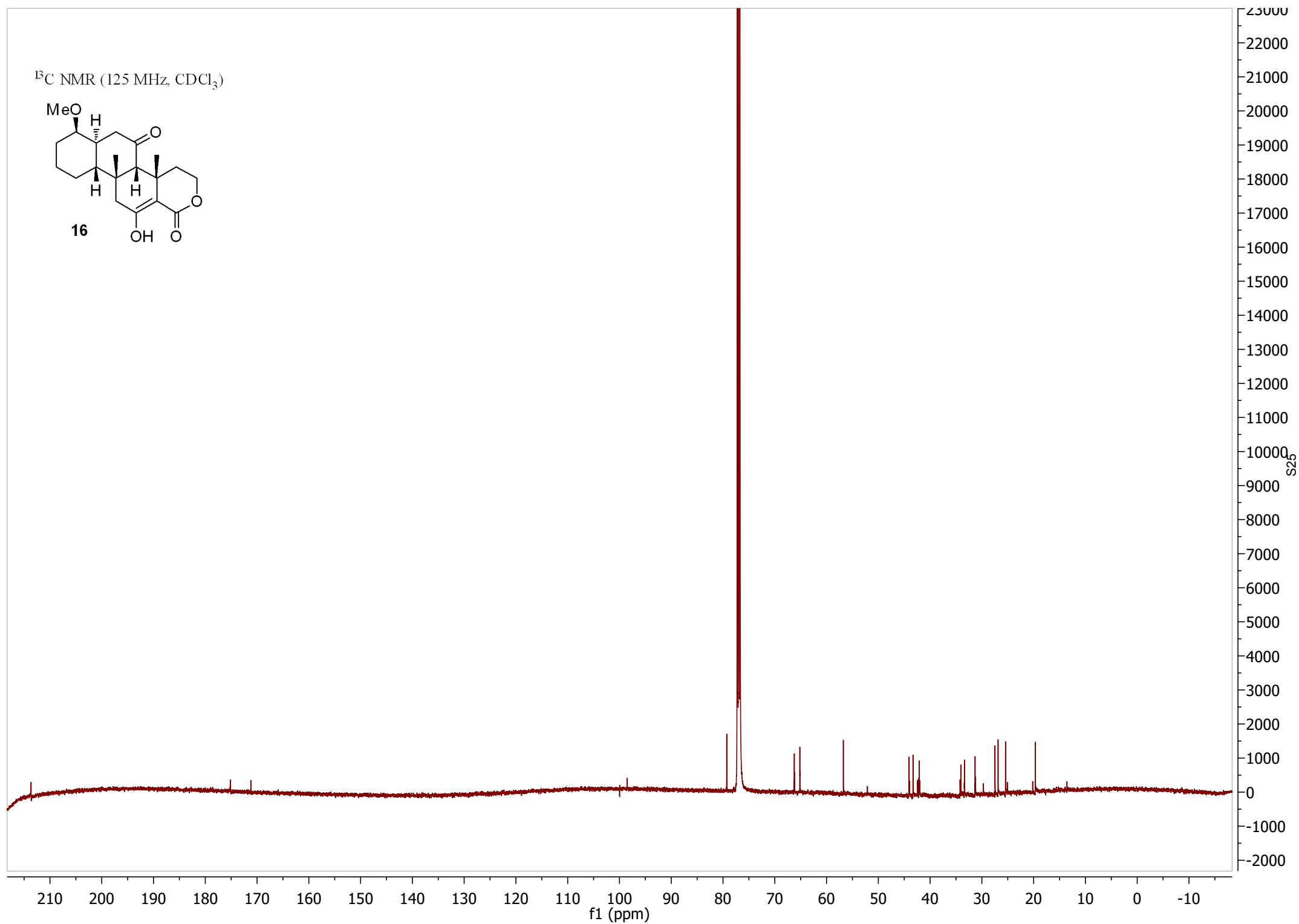
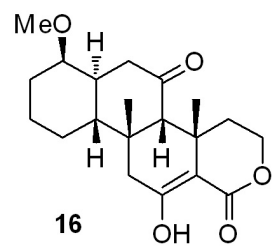
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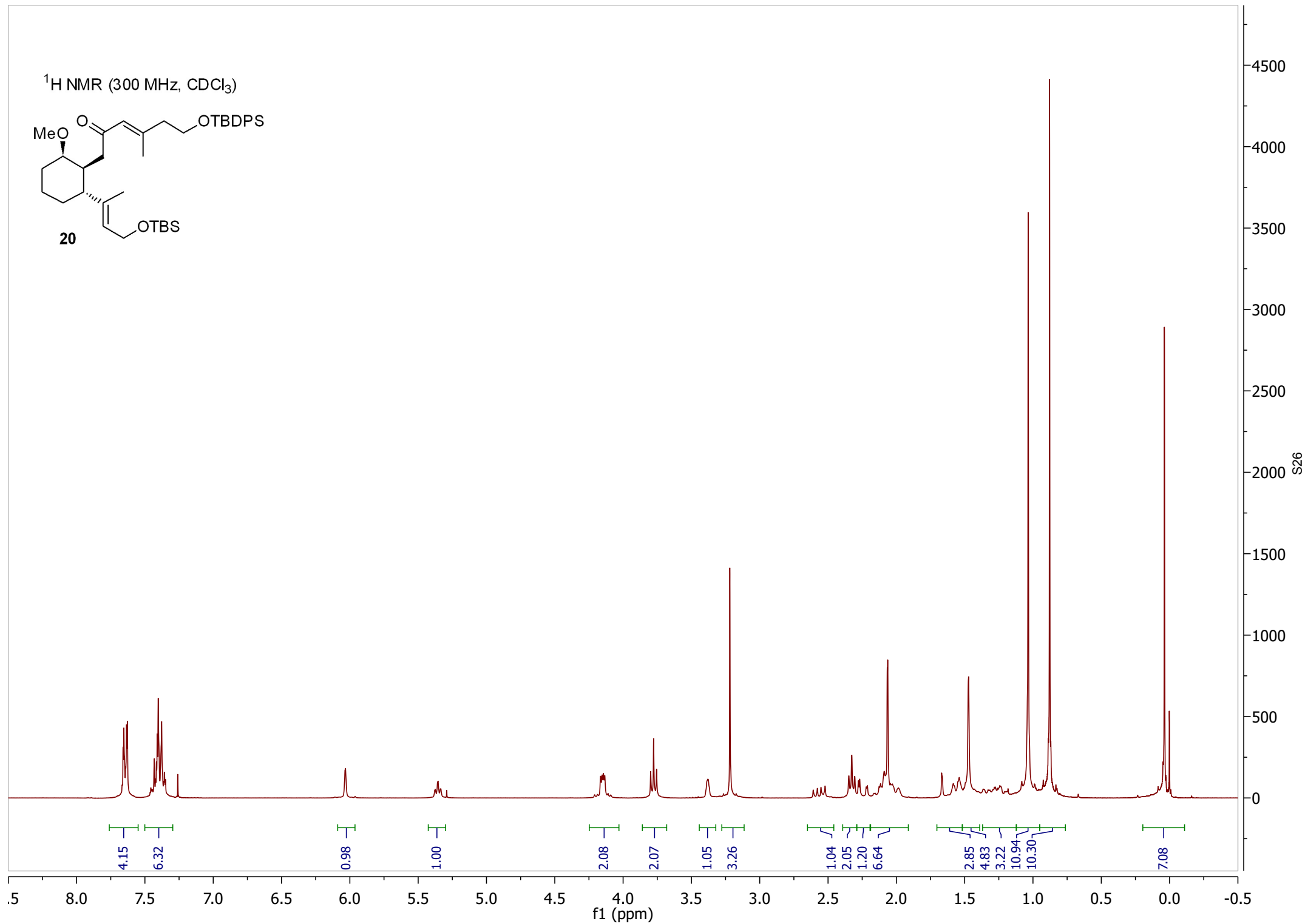
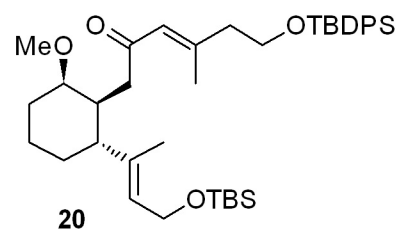
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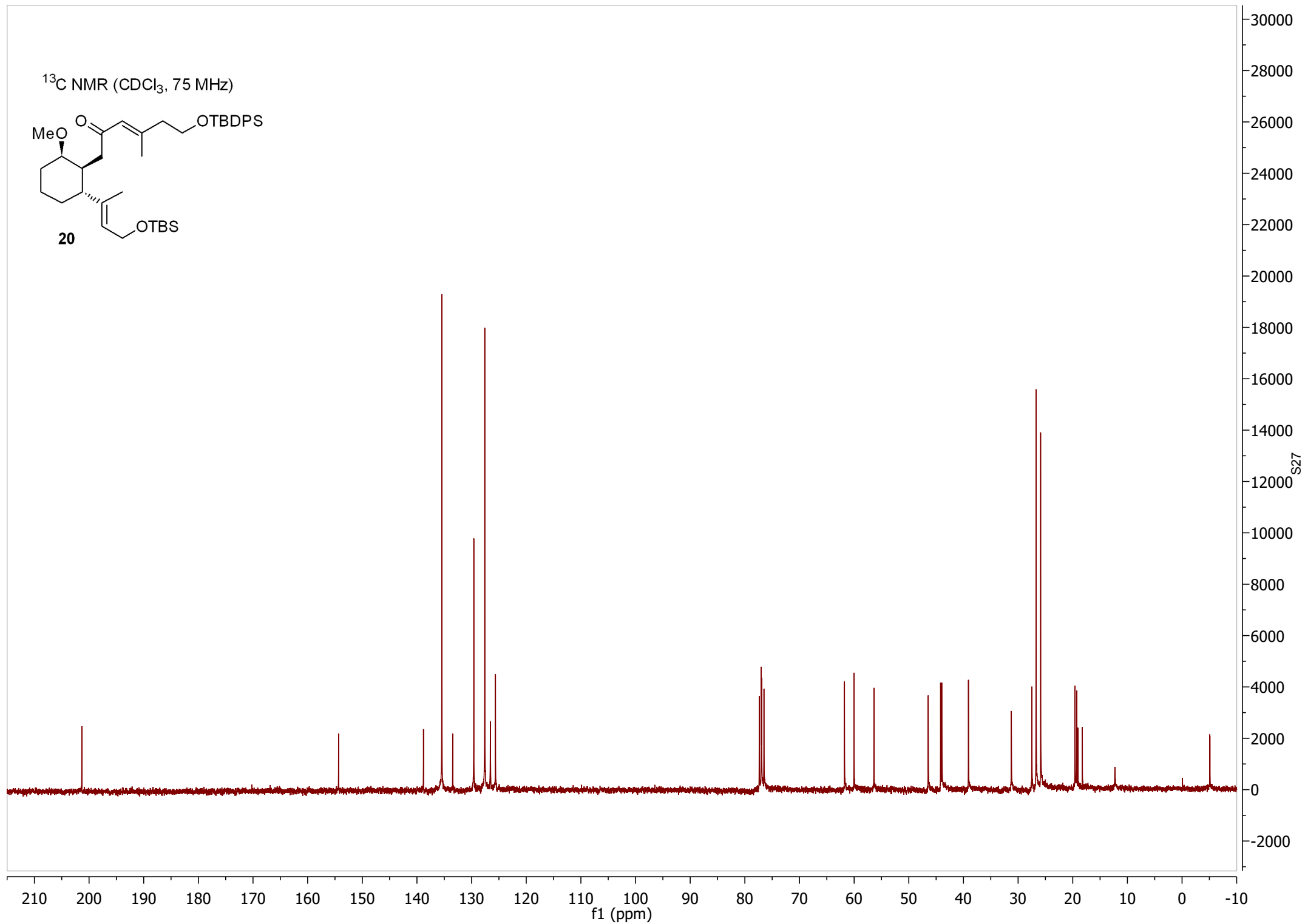
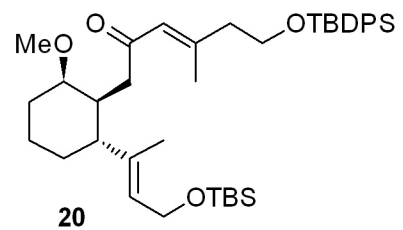
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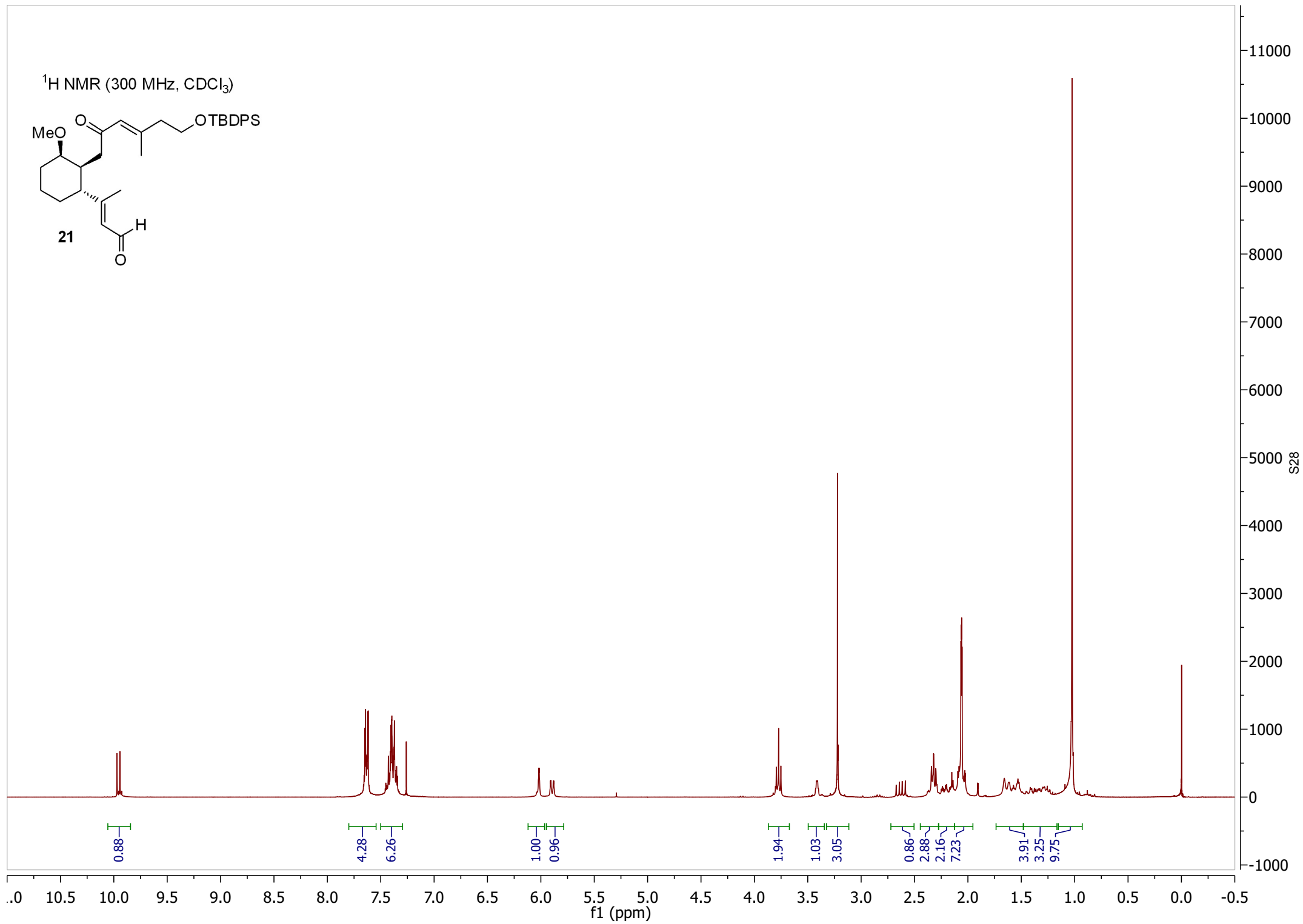
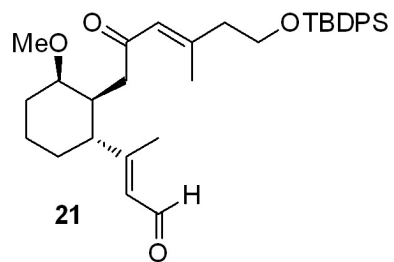
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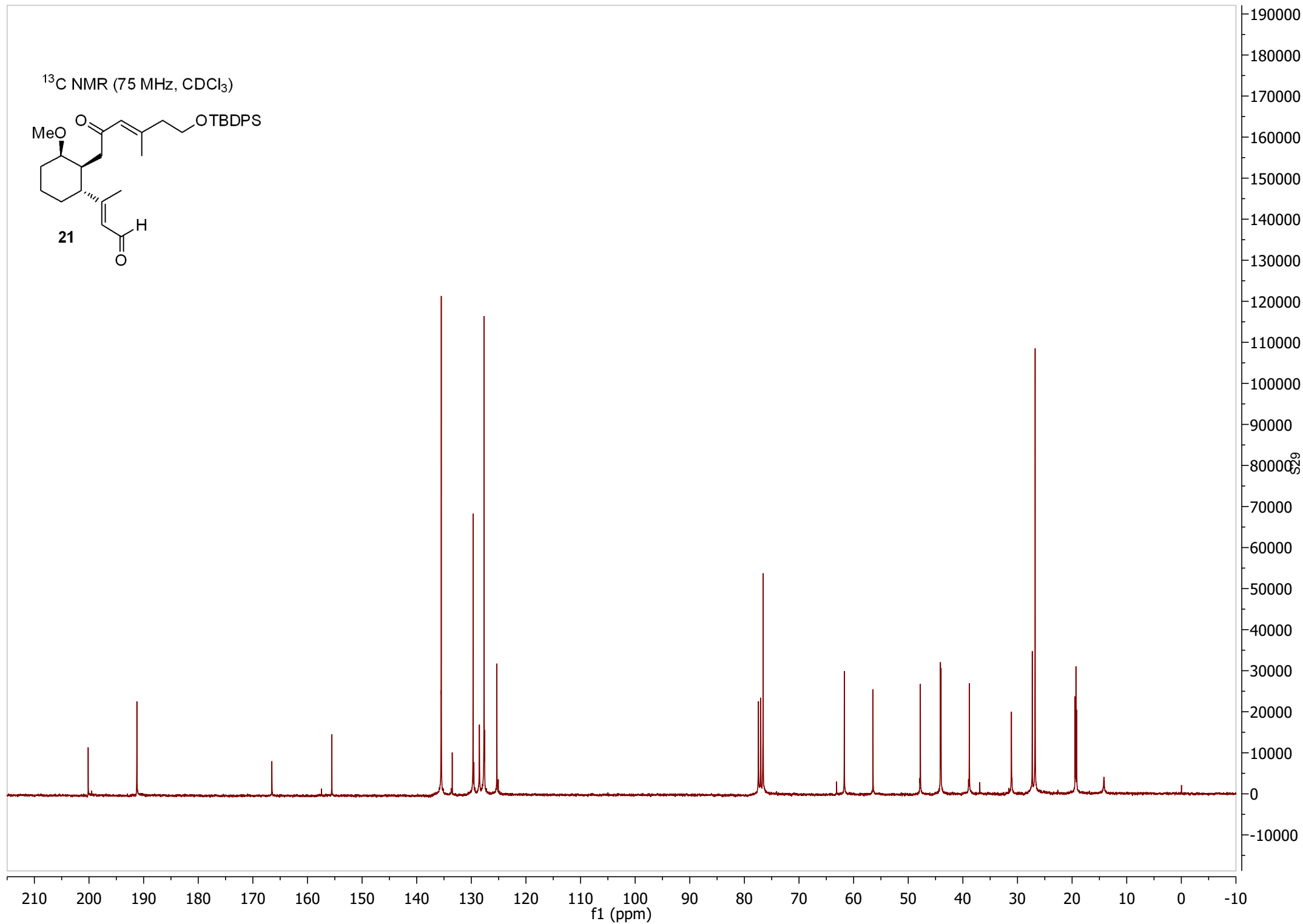


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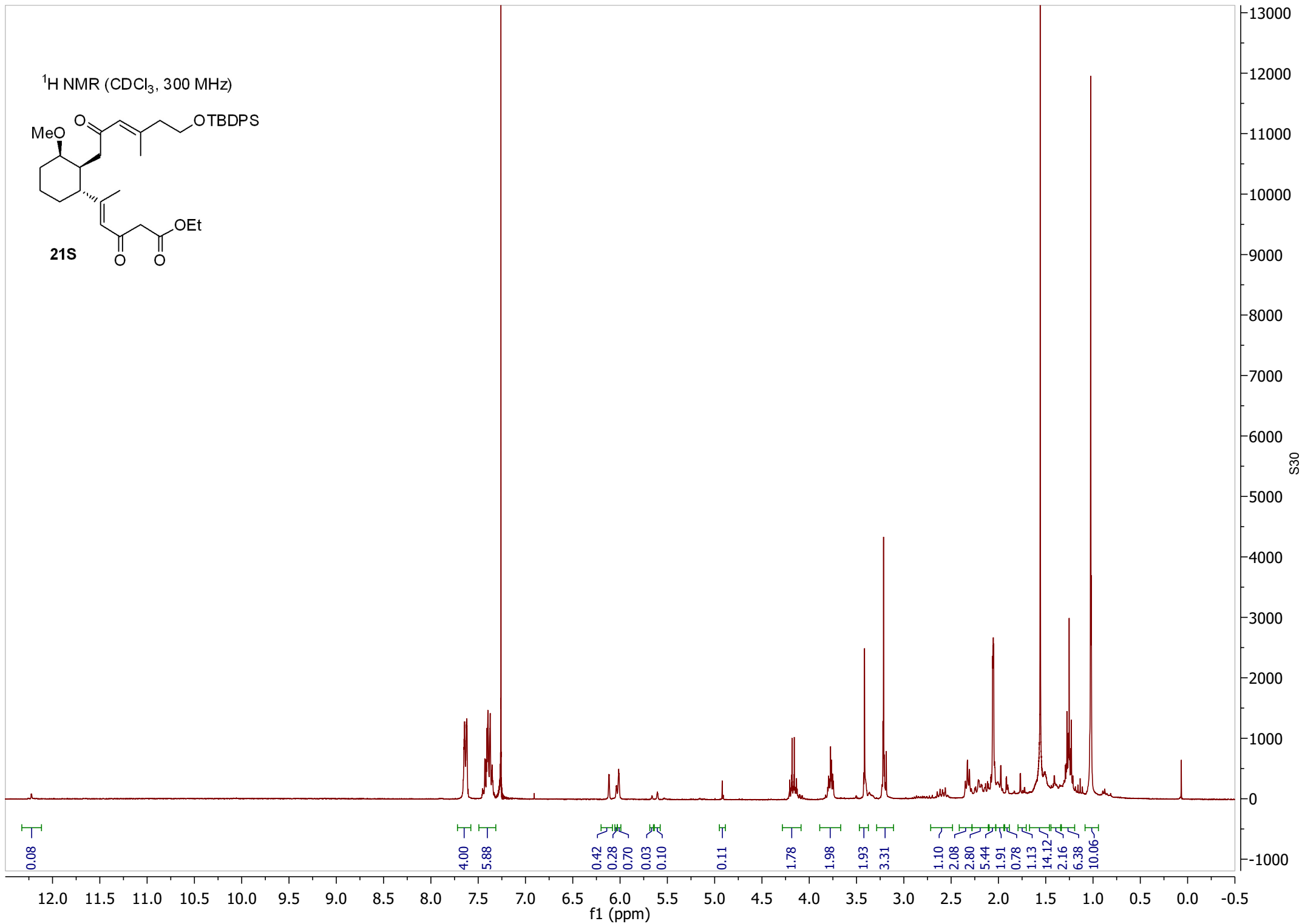
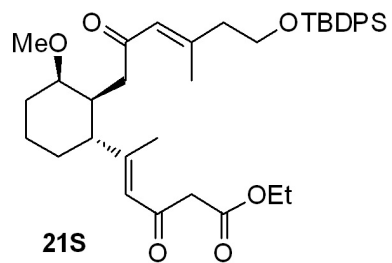


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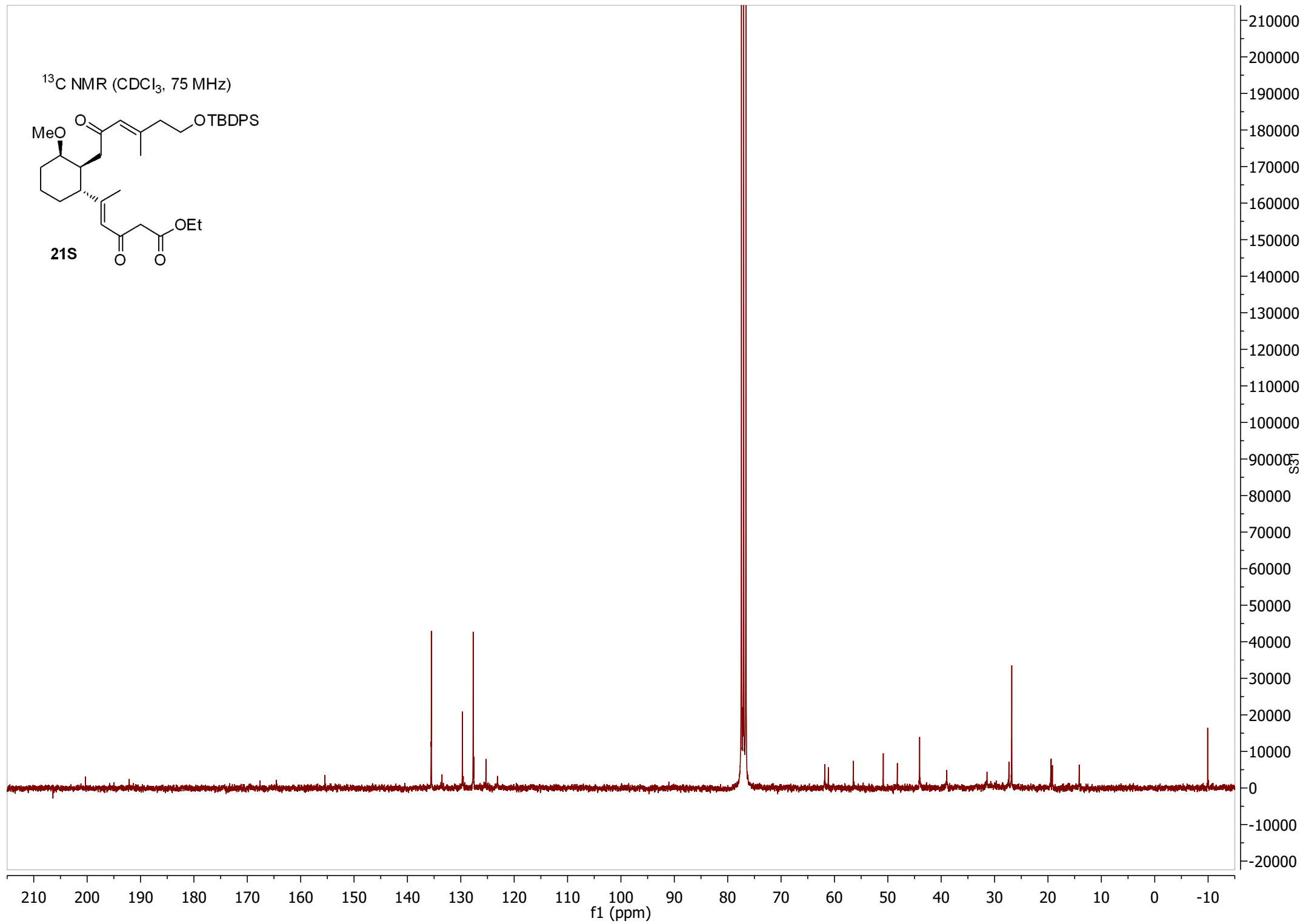
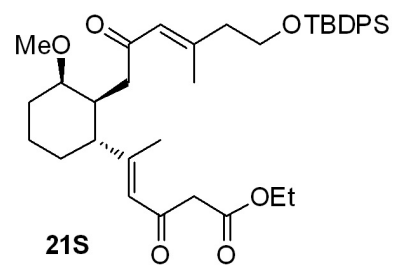




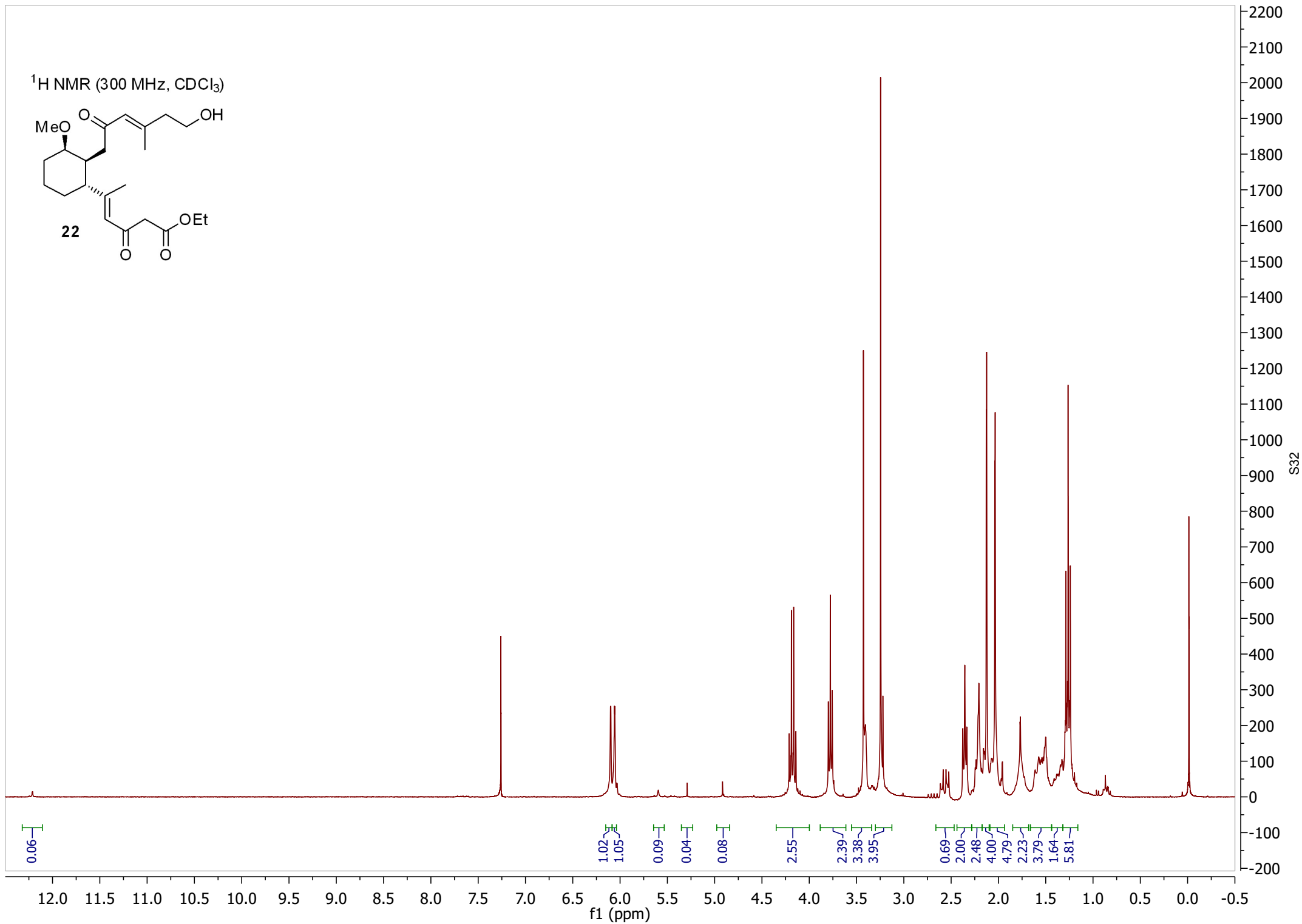
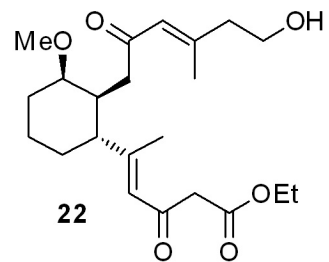
¹H NMR (CDCl₃, 300 MHz)



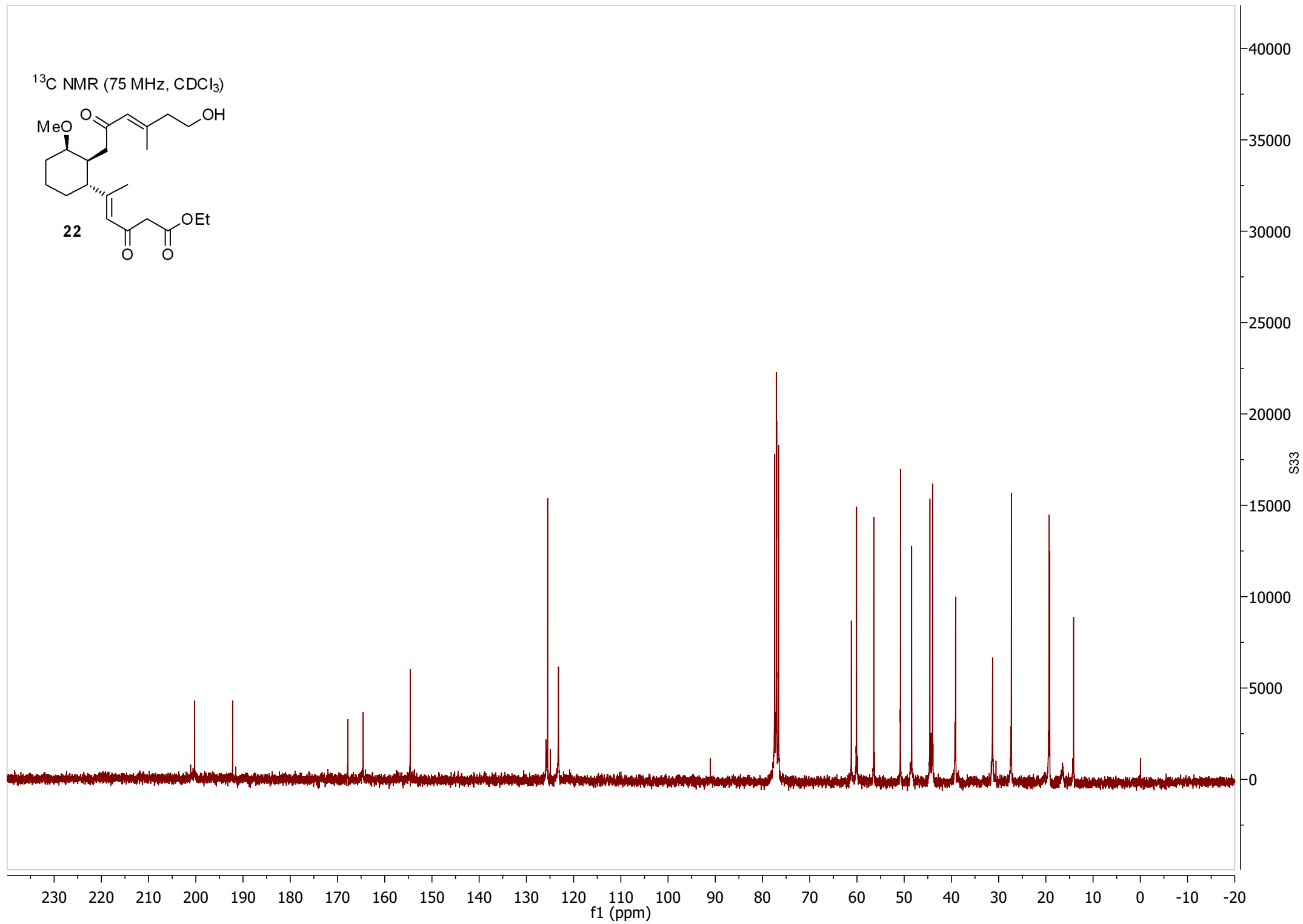
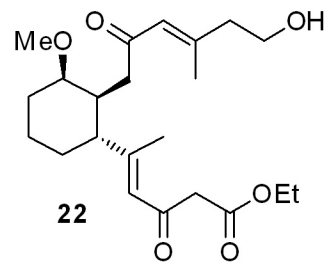
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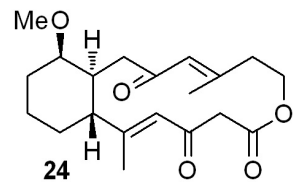
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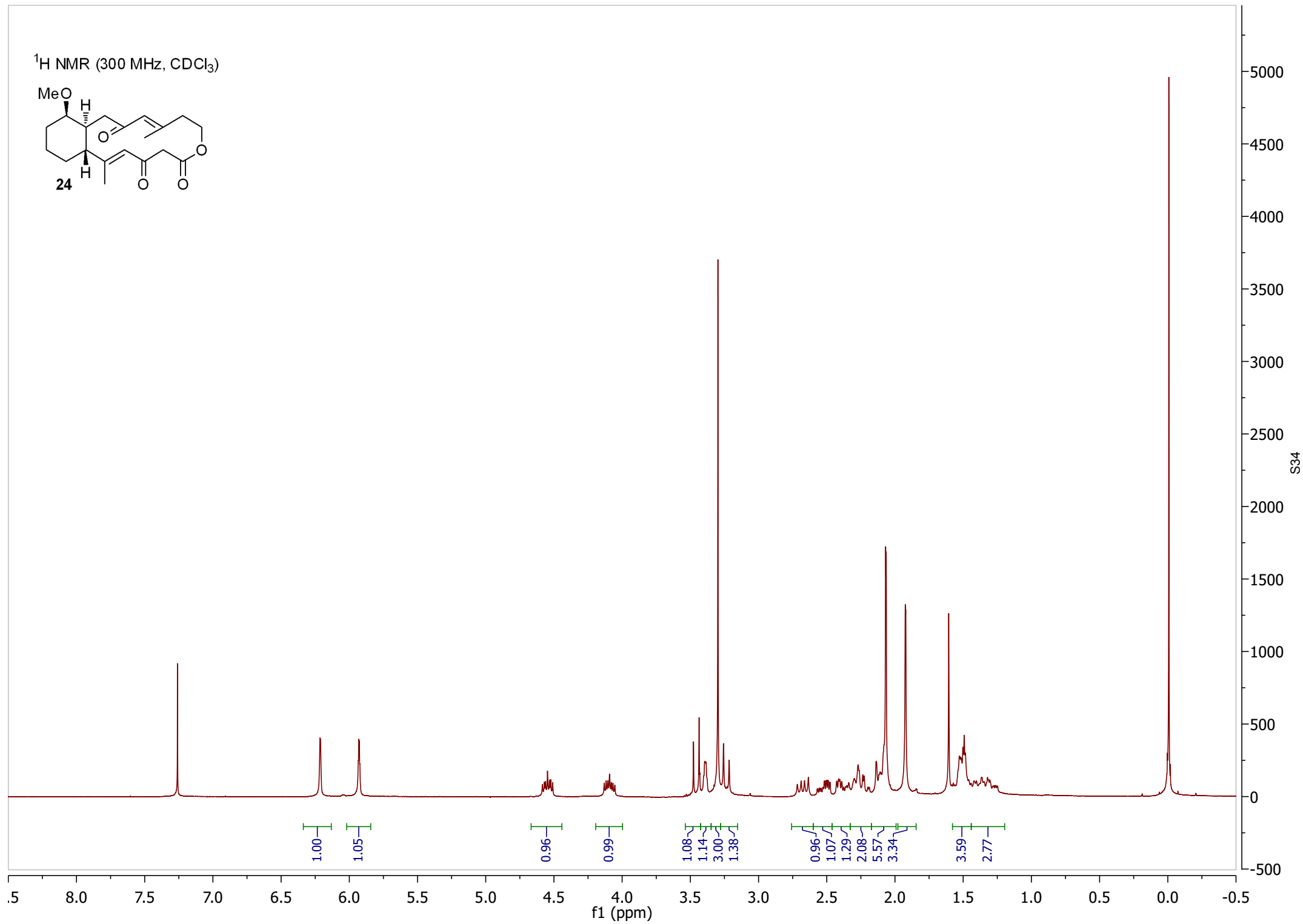
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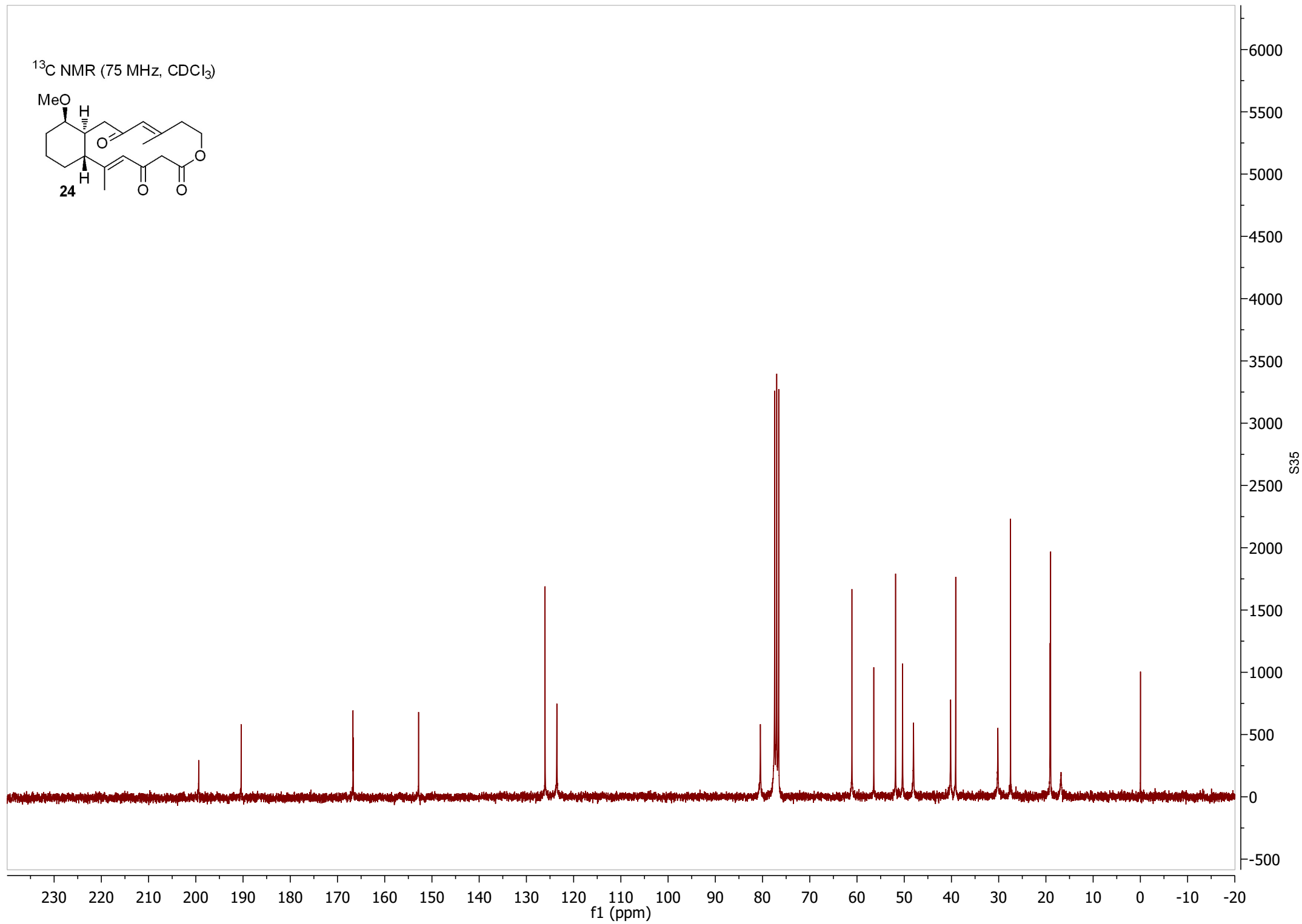
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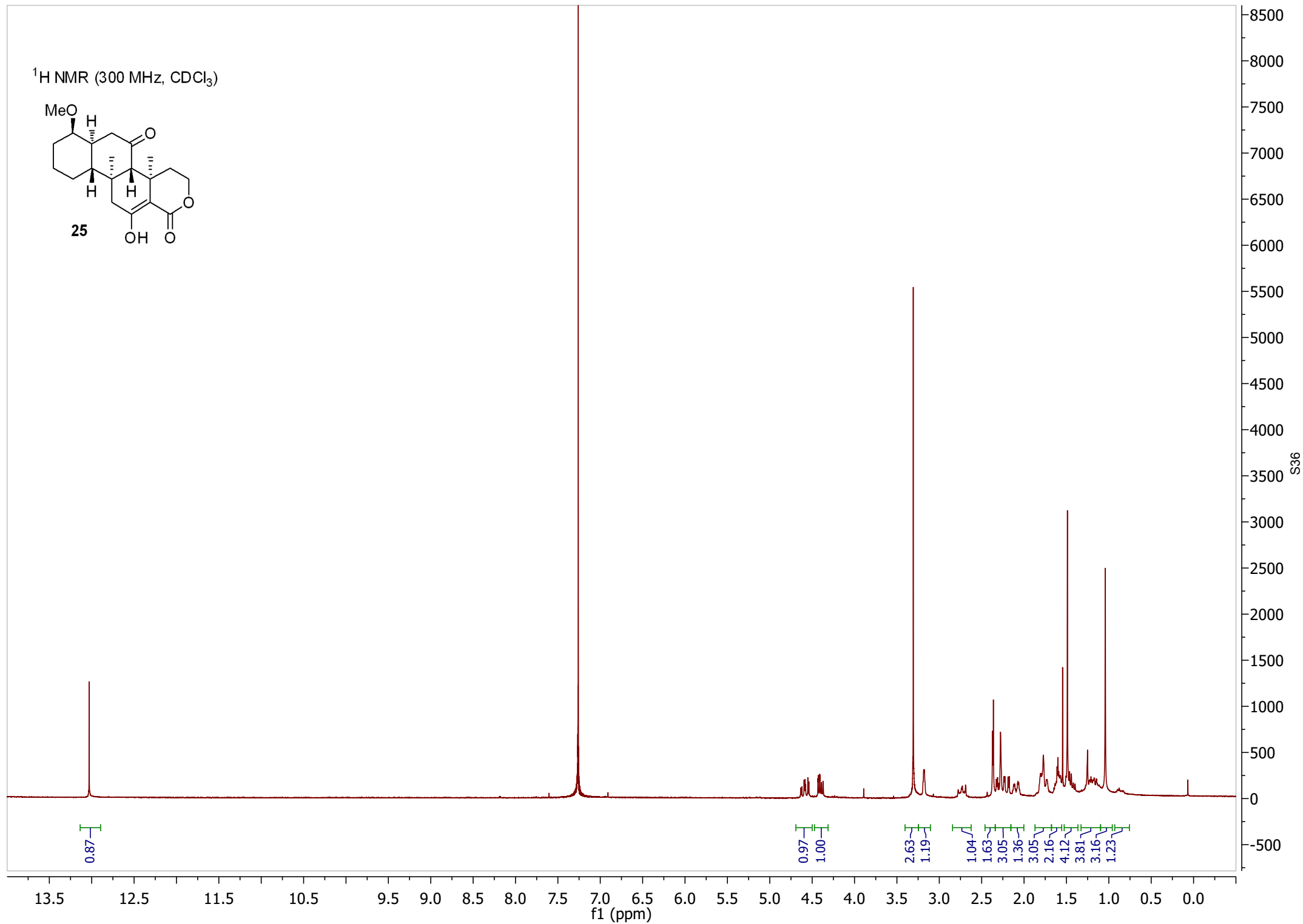
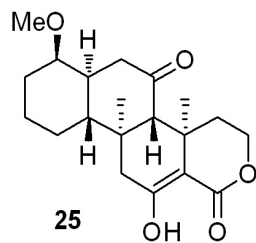
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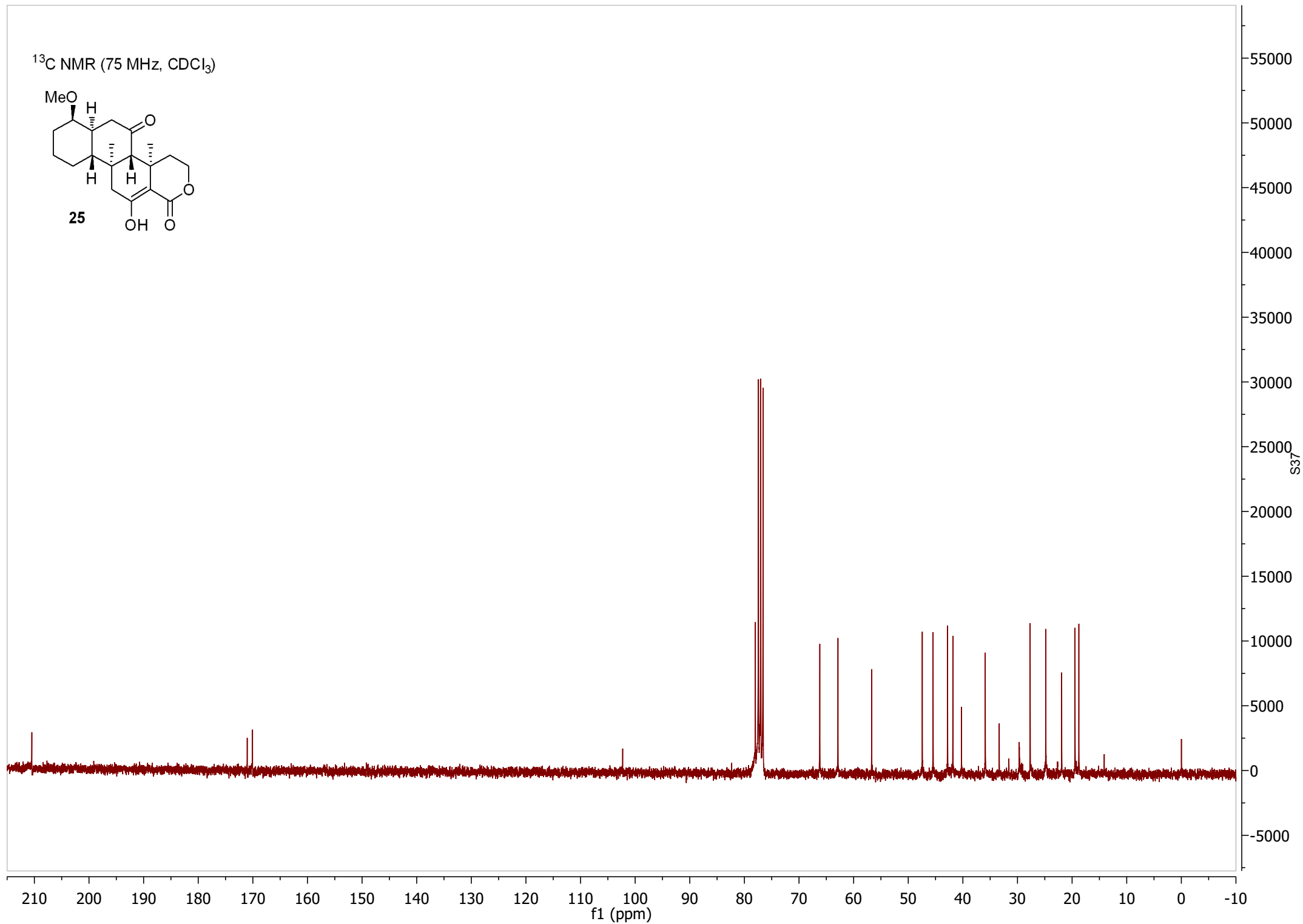
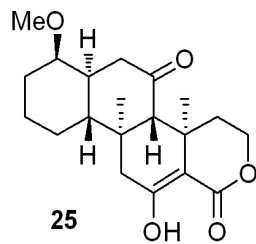
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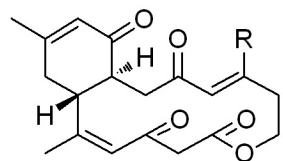
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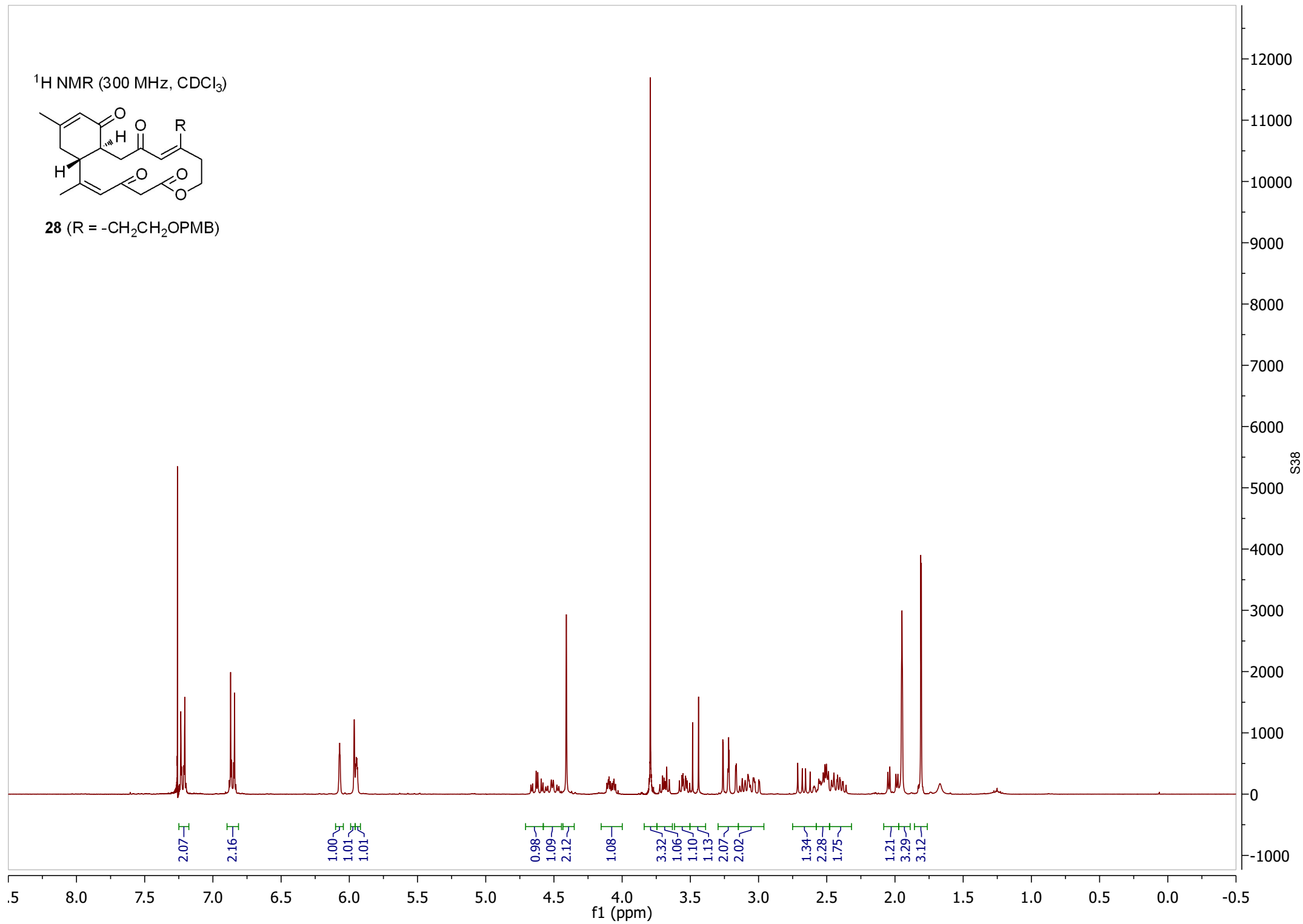
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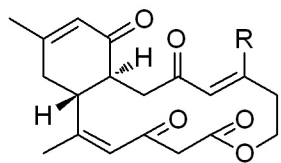
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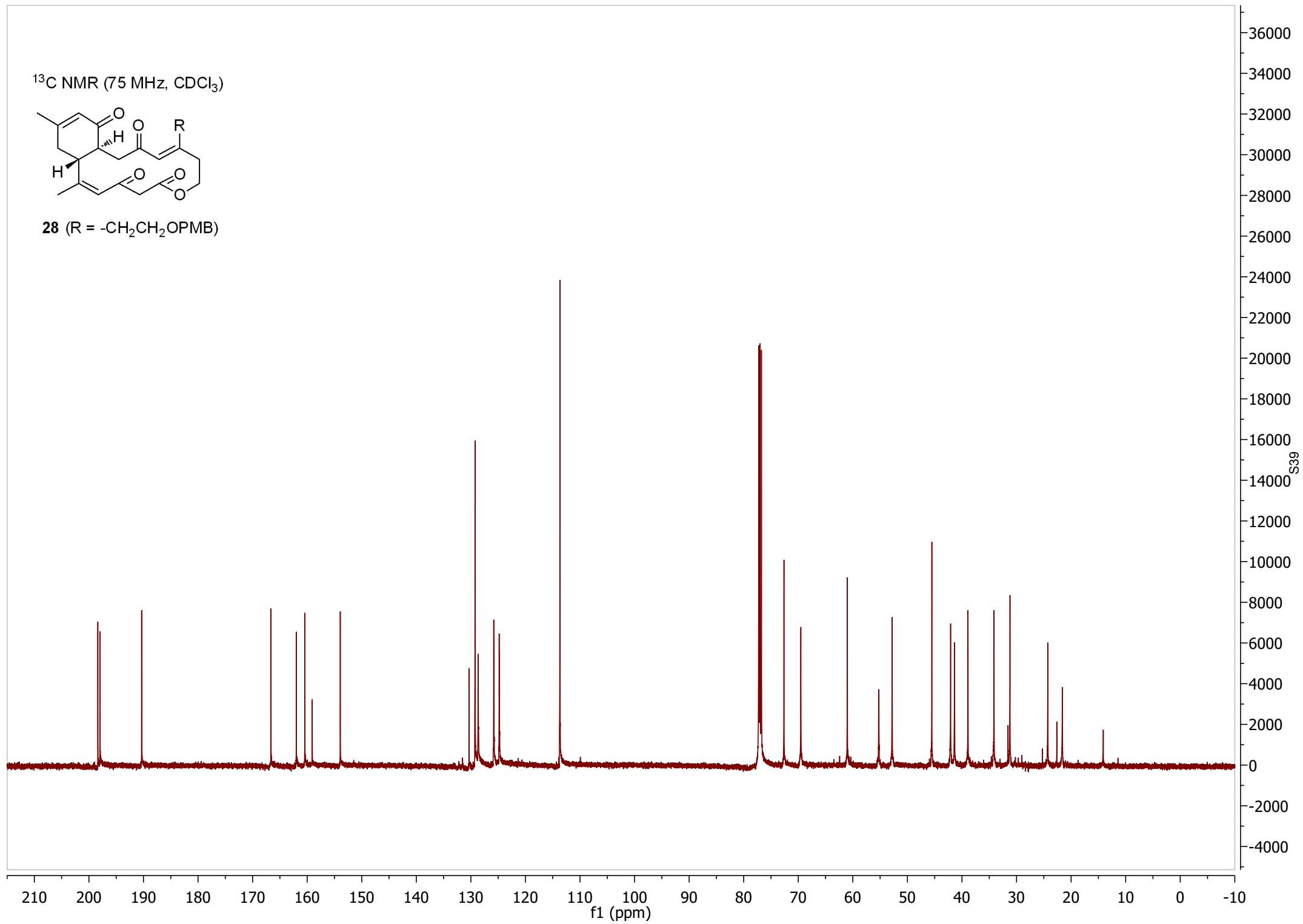
28 ($\text{R} = -\text{CH}_2\text{CH}_2\text{OPMB}$)



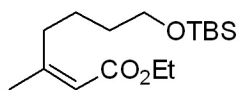
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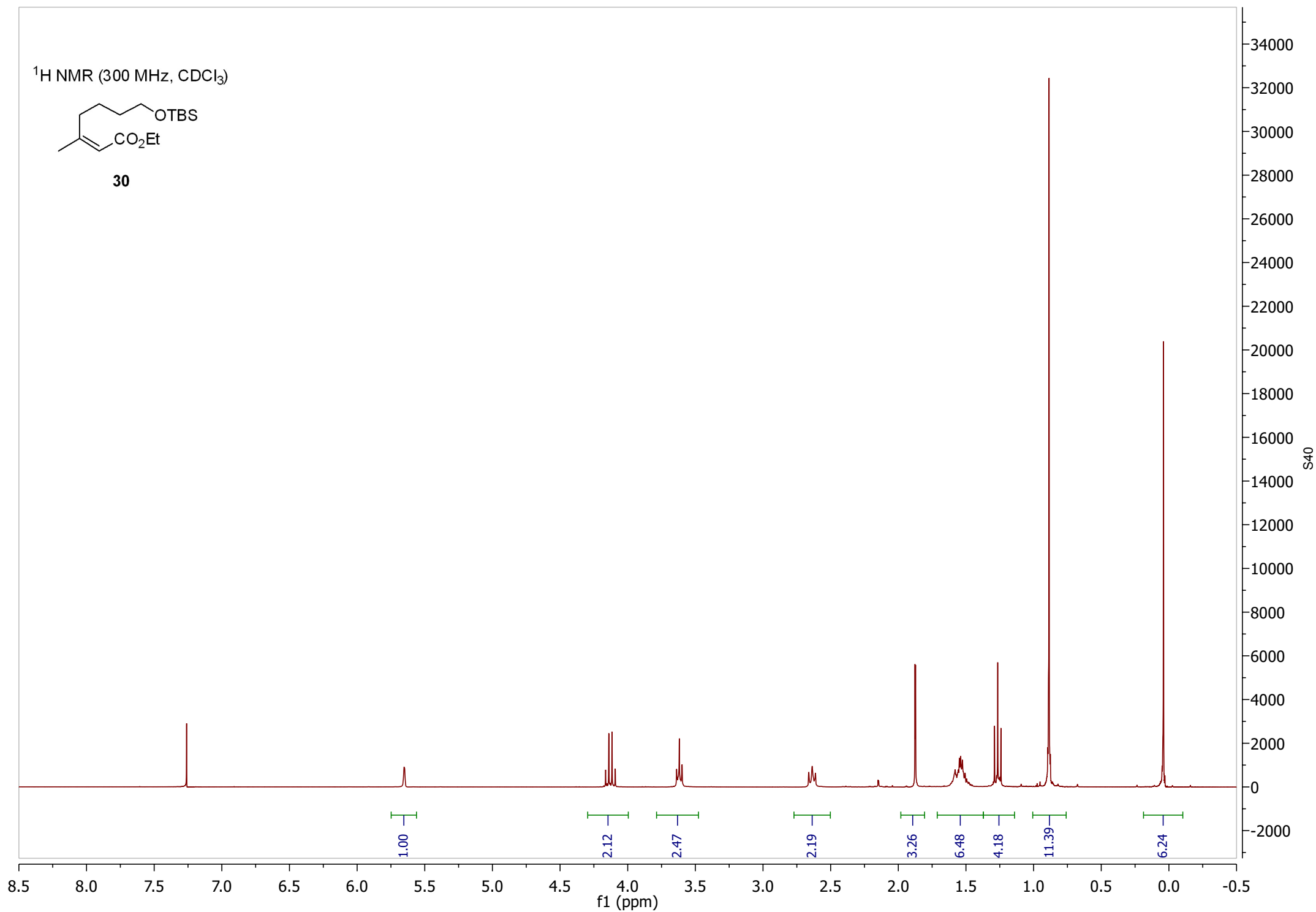
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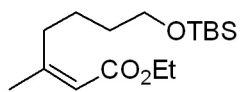
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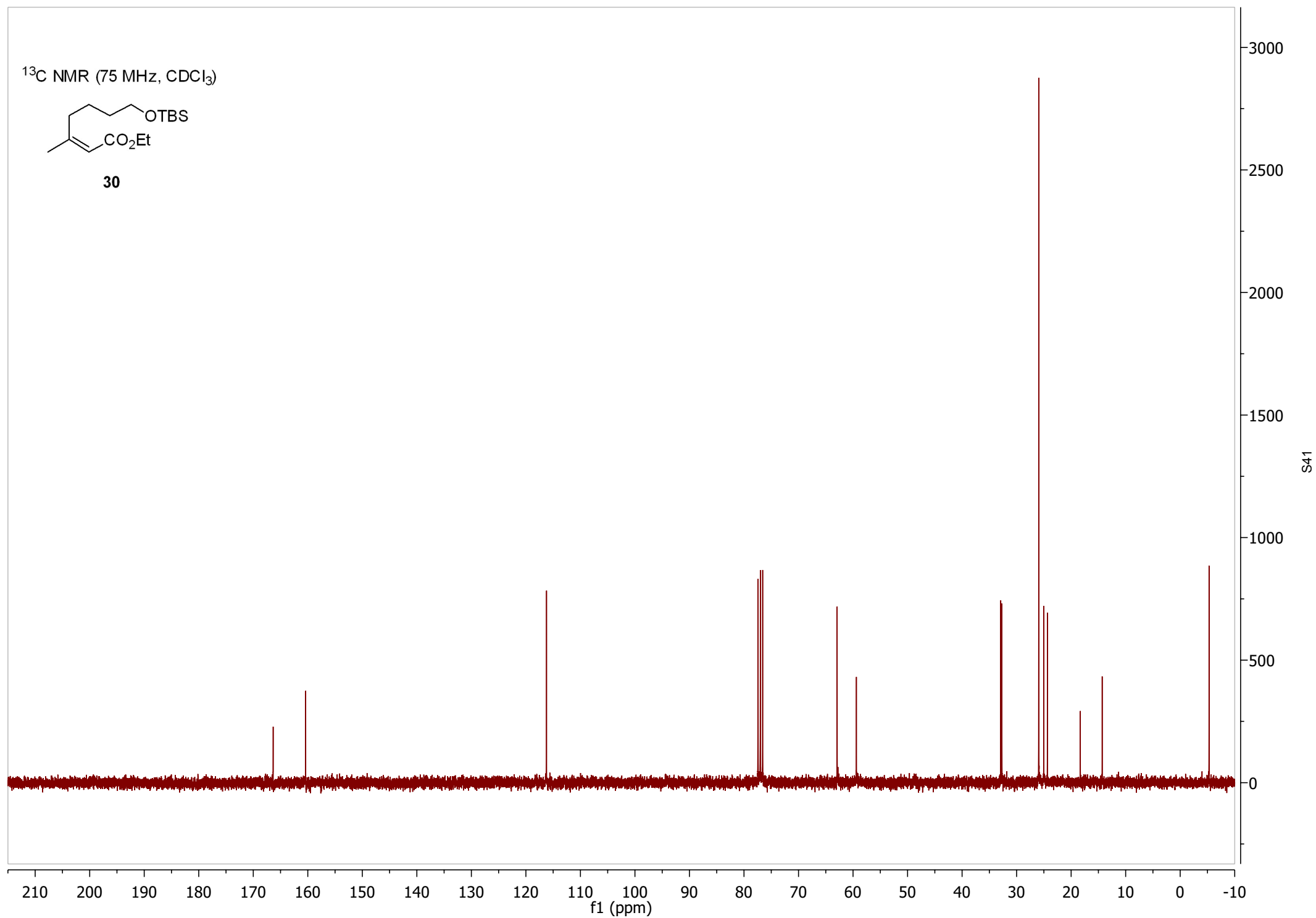
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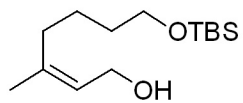
^{13}C NMR (75 MHz, CDCl_3)



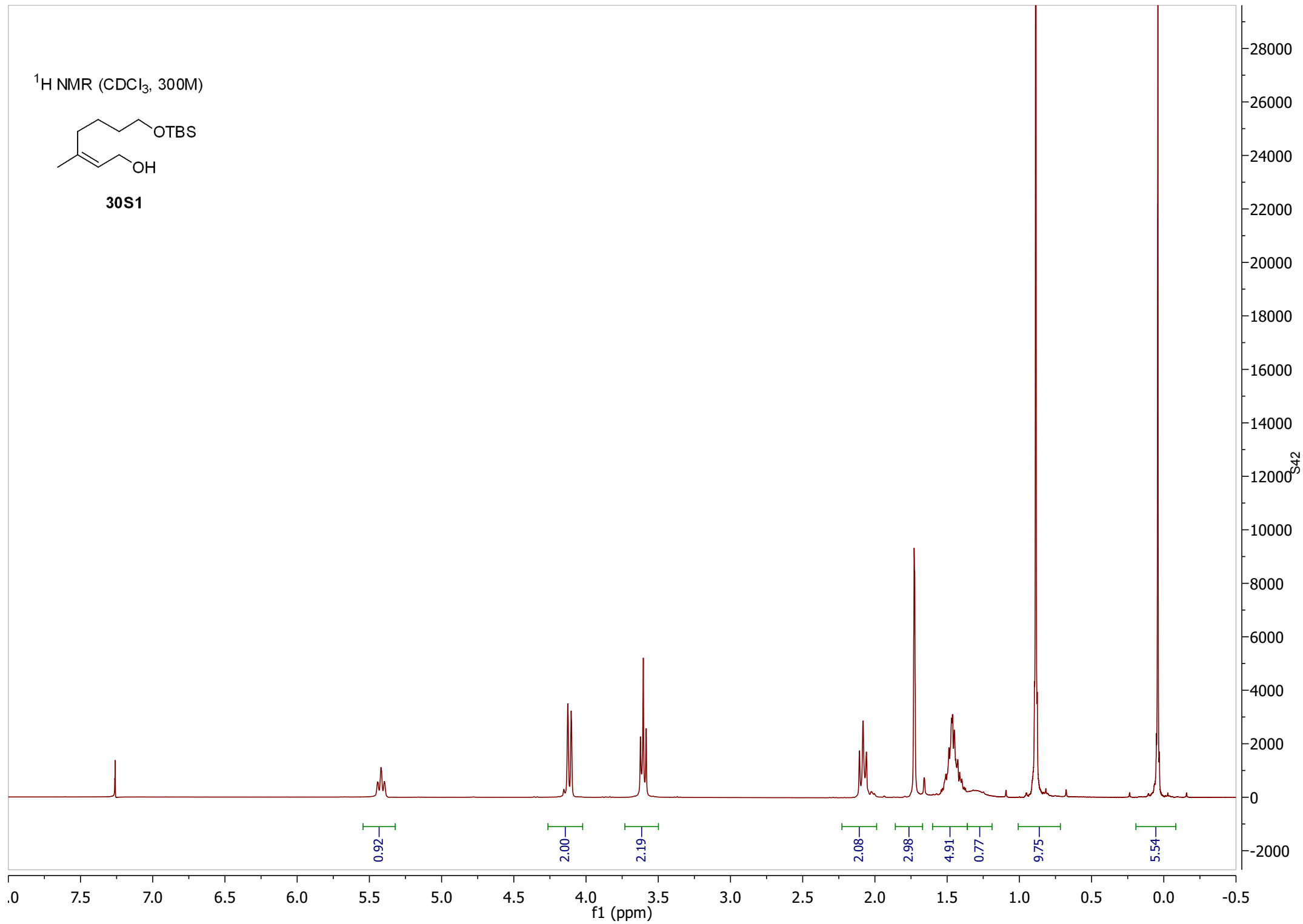
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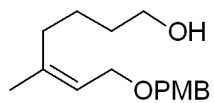
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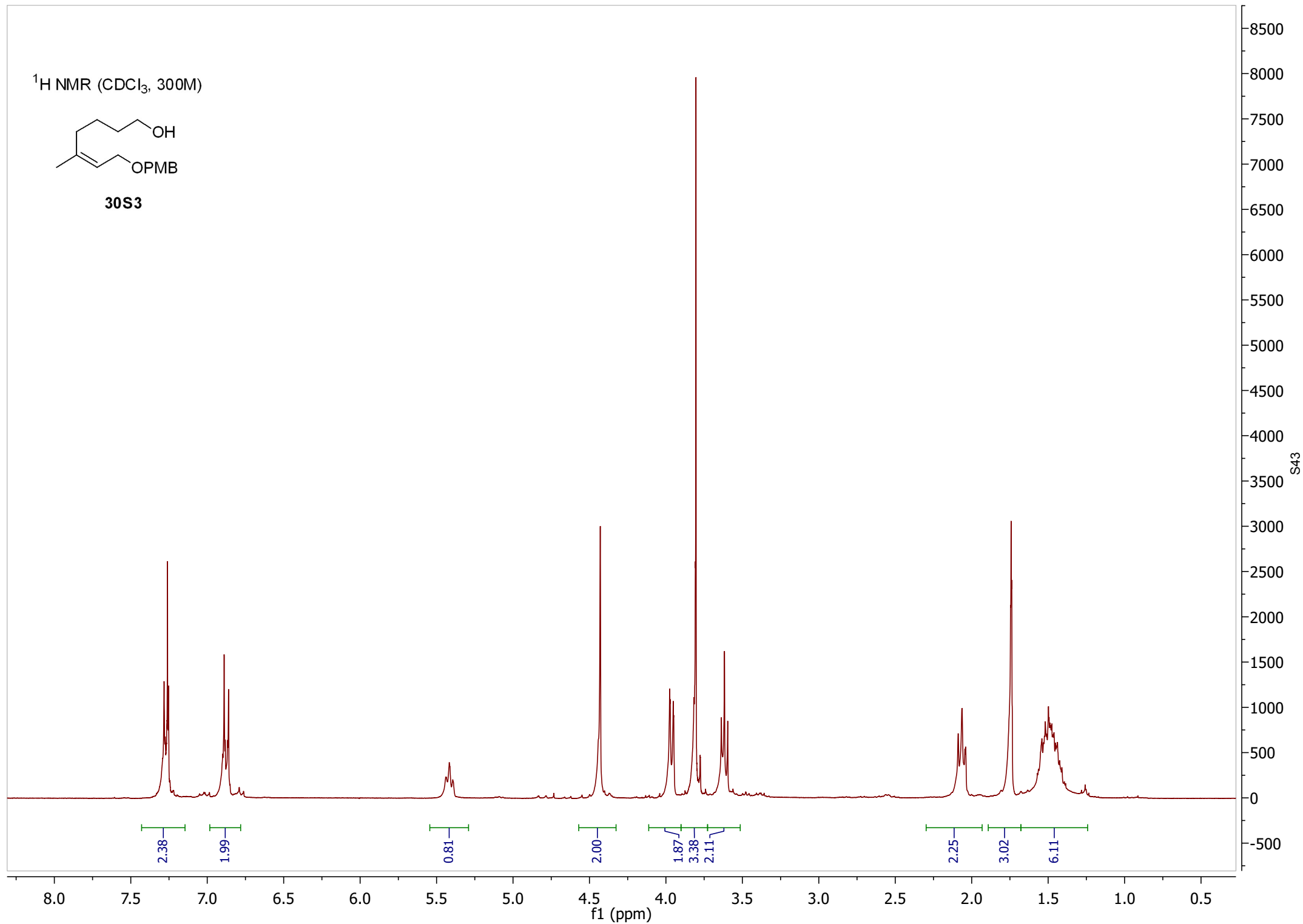
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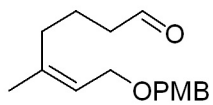
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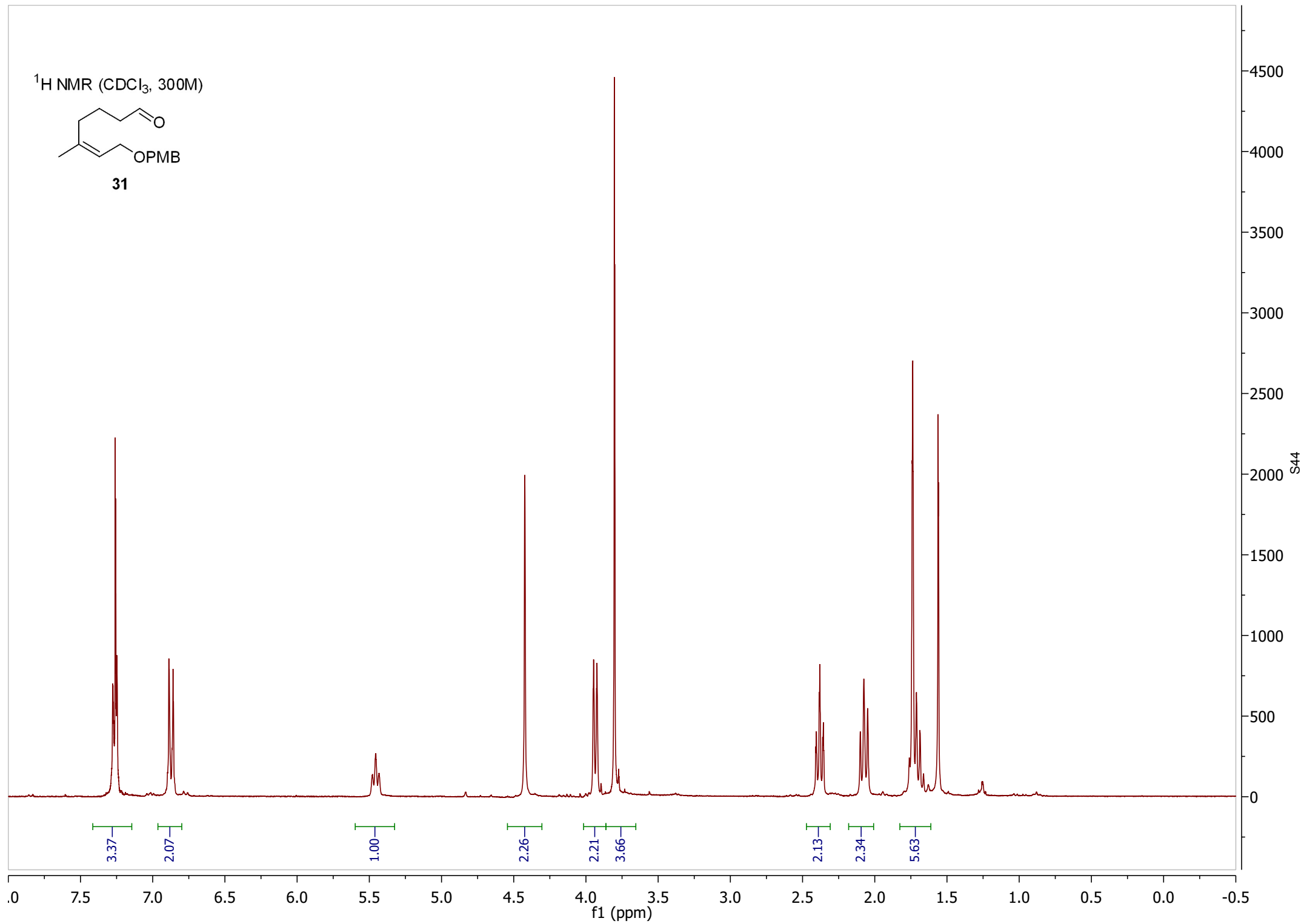
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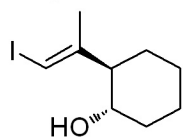
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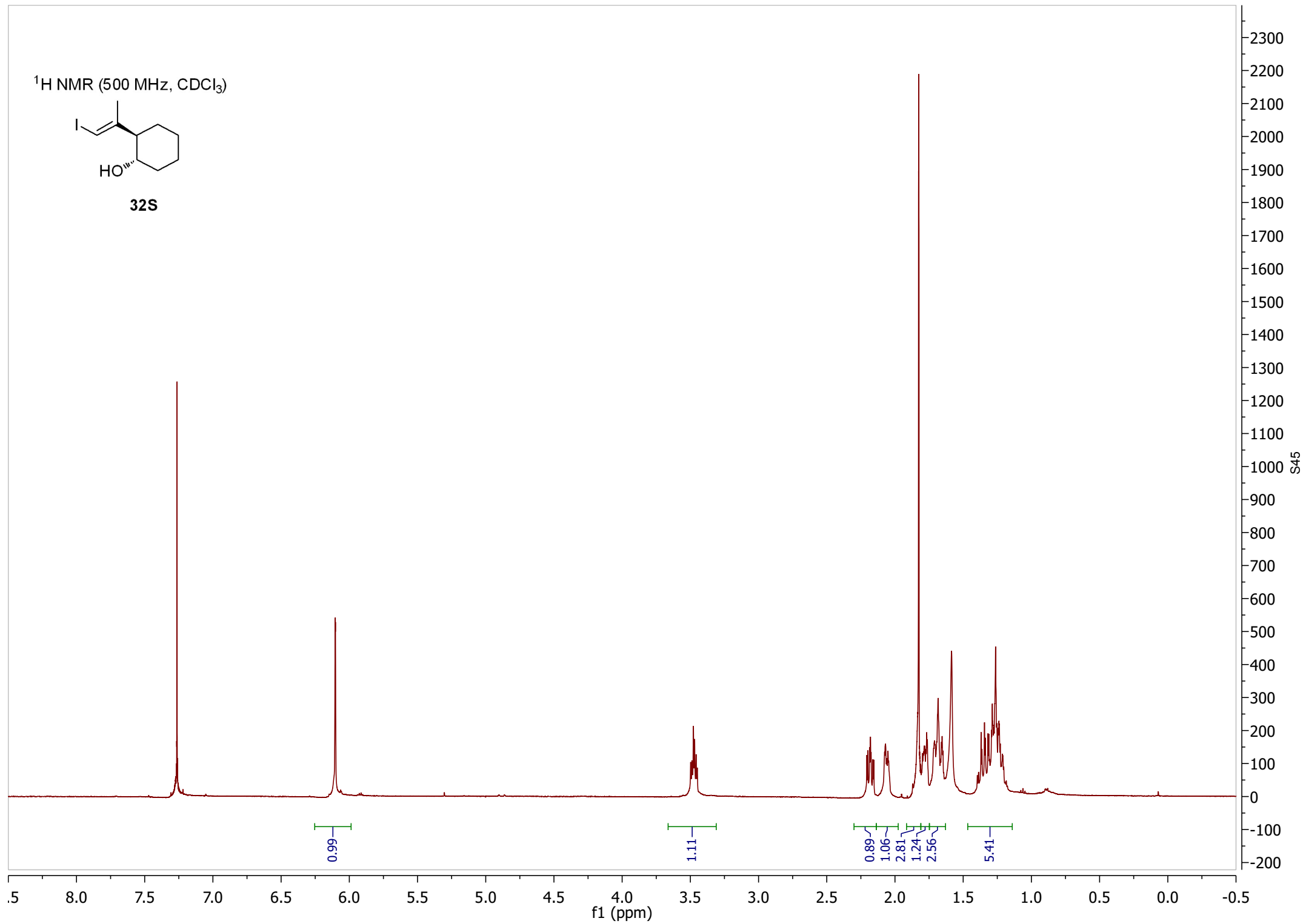
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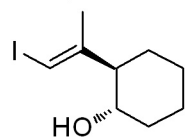
¹H NMR (500 MHz, CDCl₃)



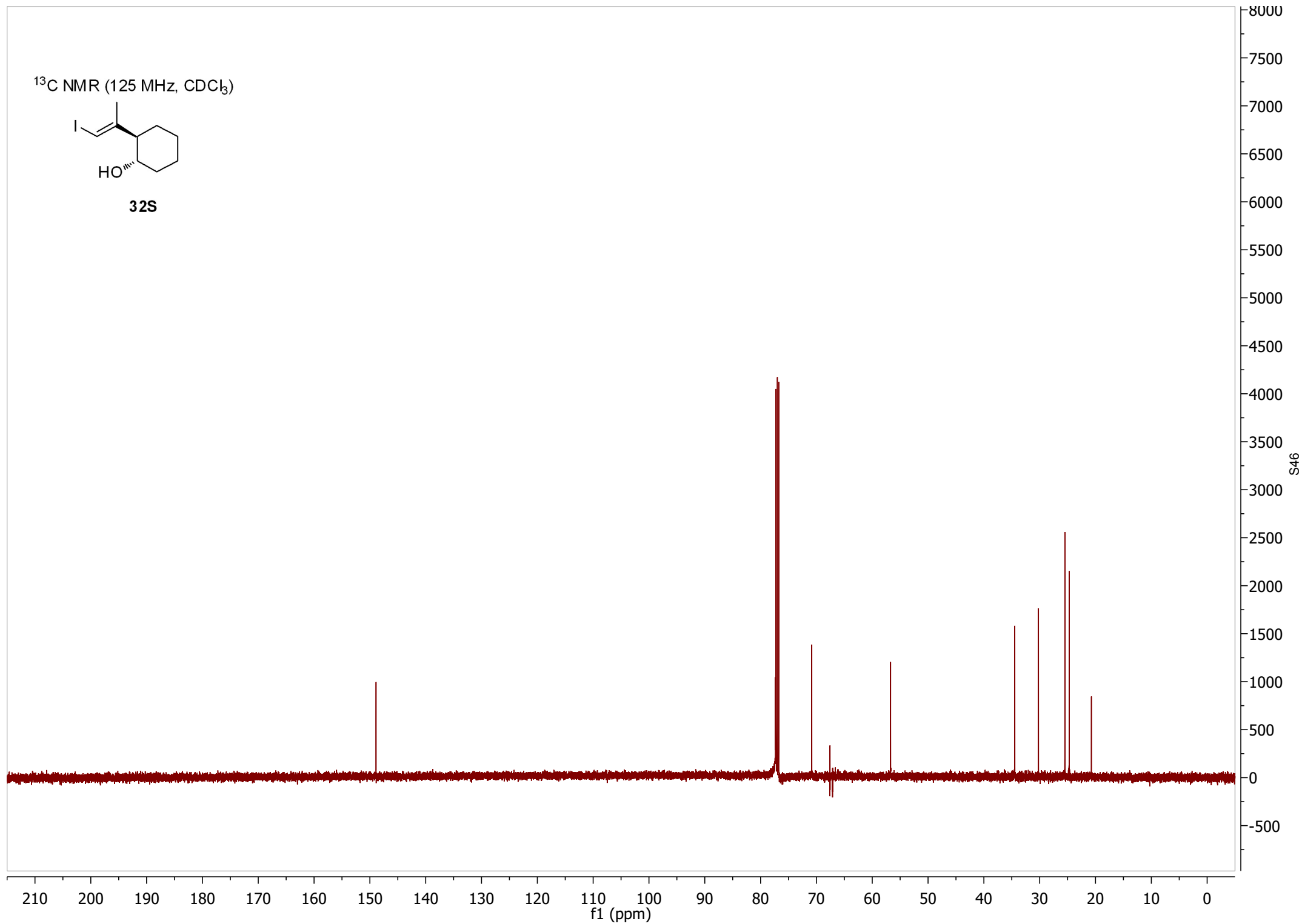
32S



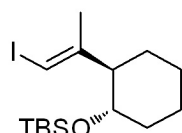
^{13}C NMR (125 MHz, CDCl_3)



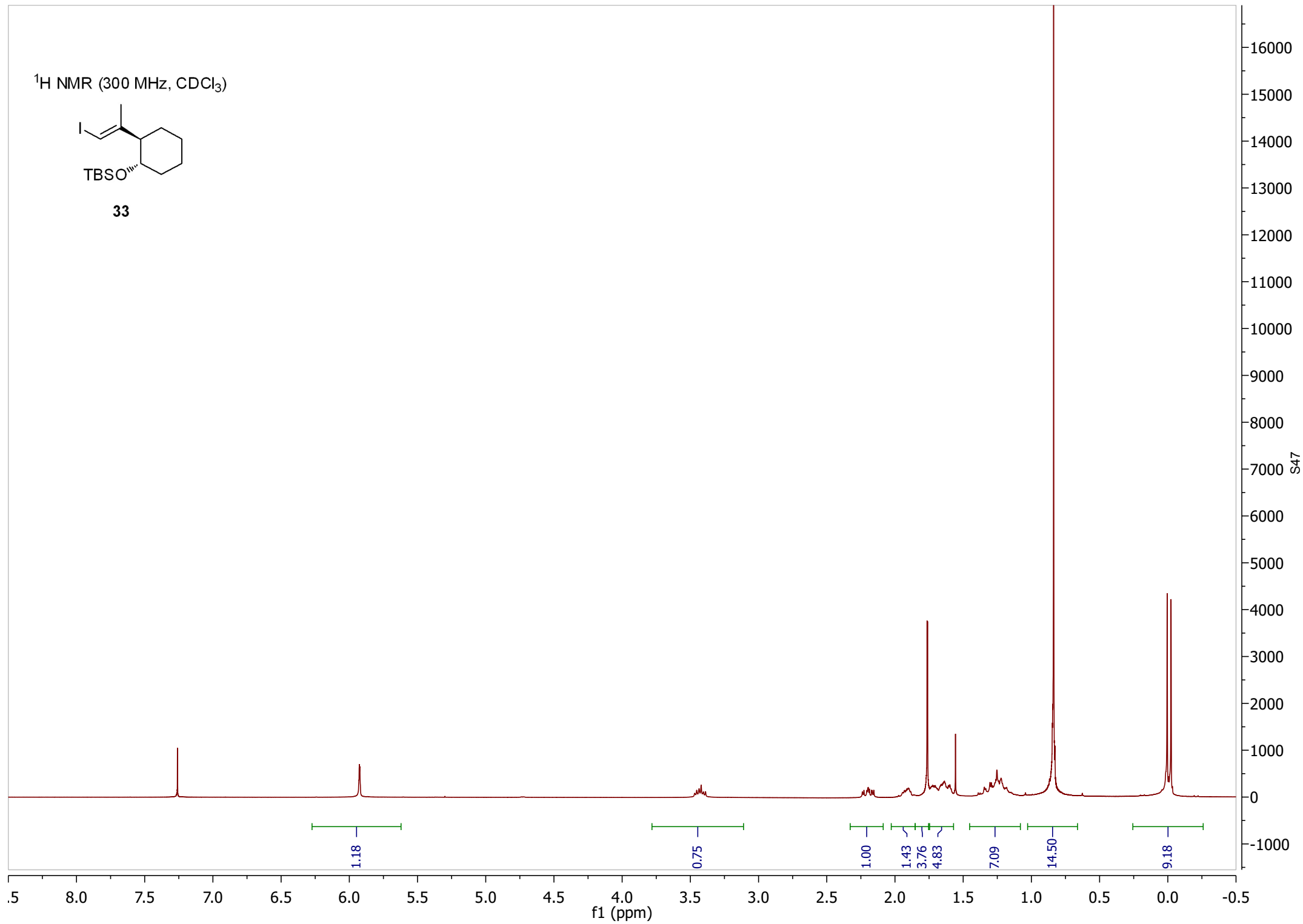
32S



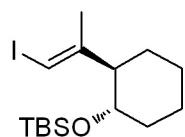
¹H NMR (300 MHz, CDCl₃)



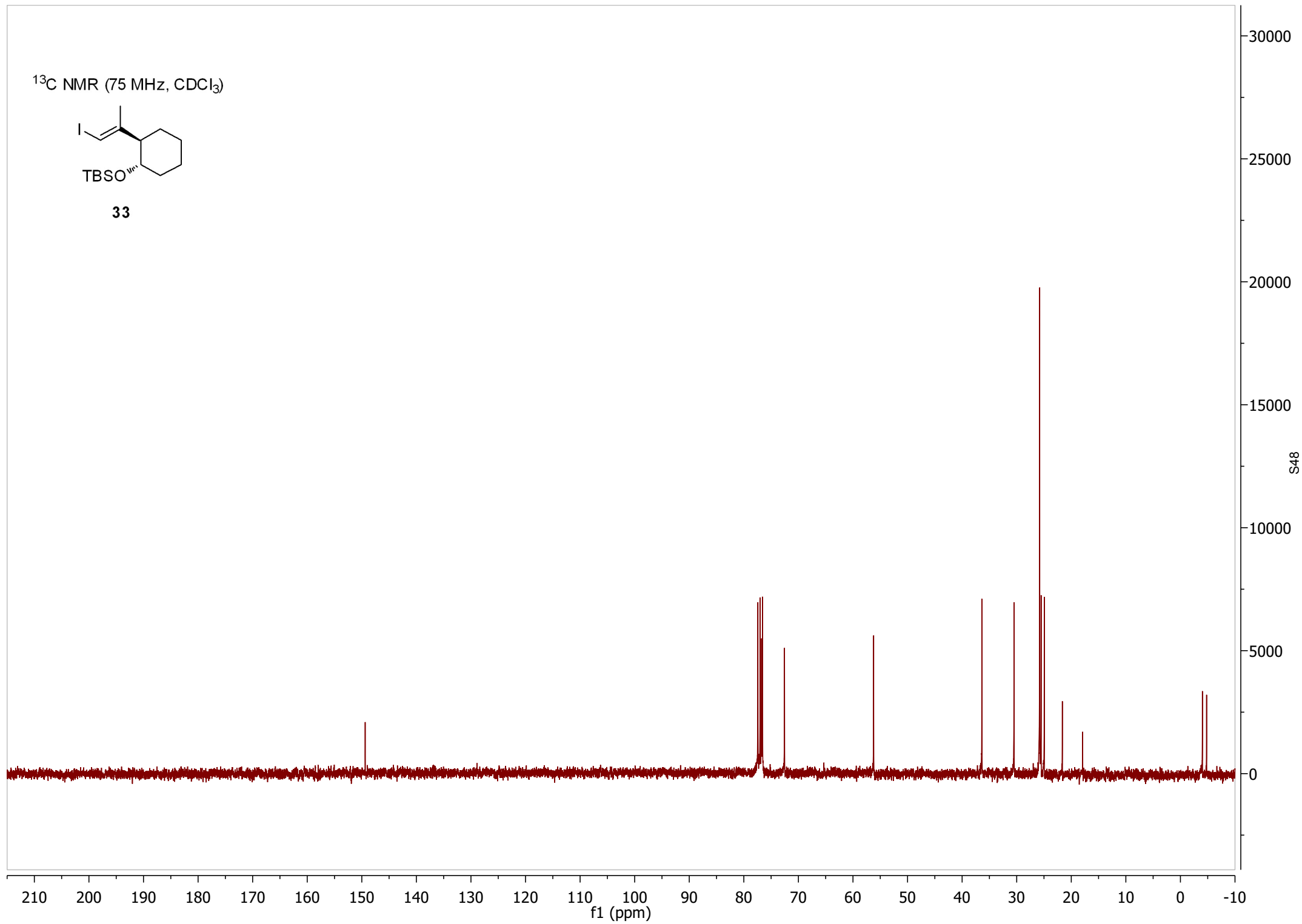
33



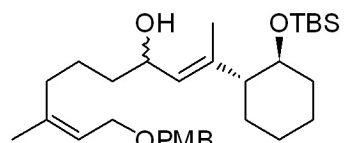
^{13}C NMR (75 MHz, CDCl_3)



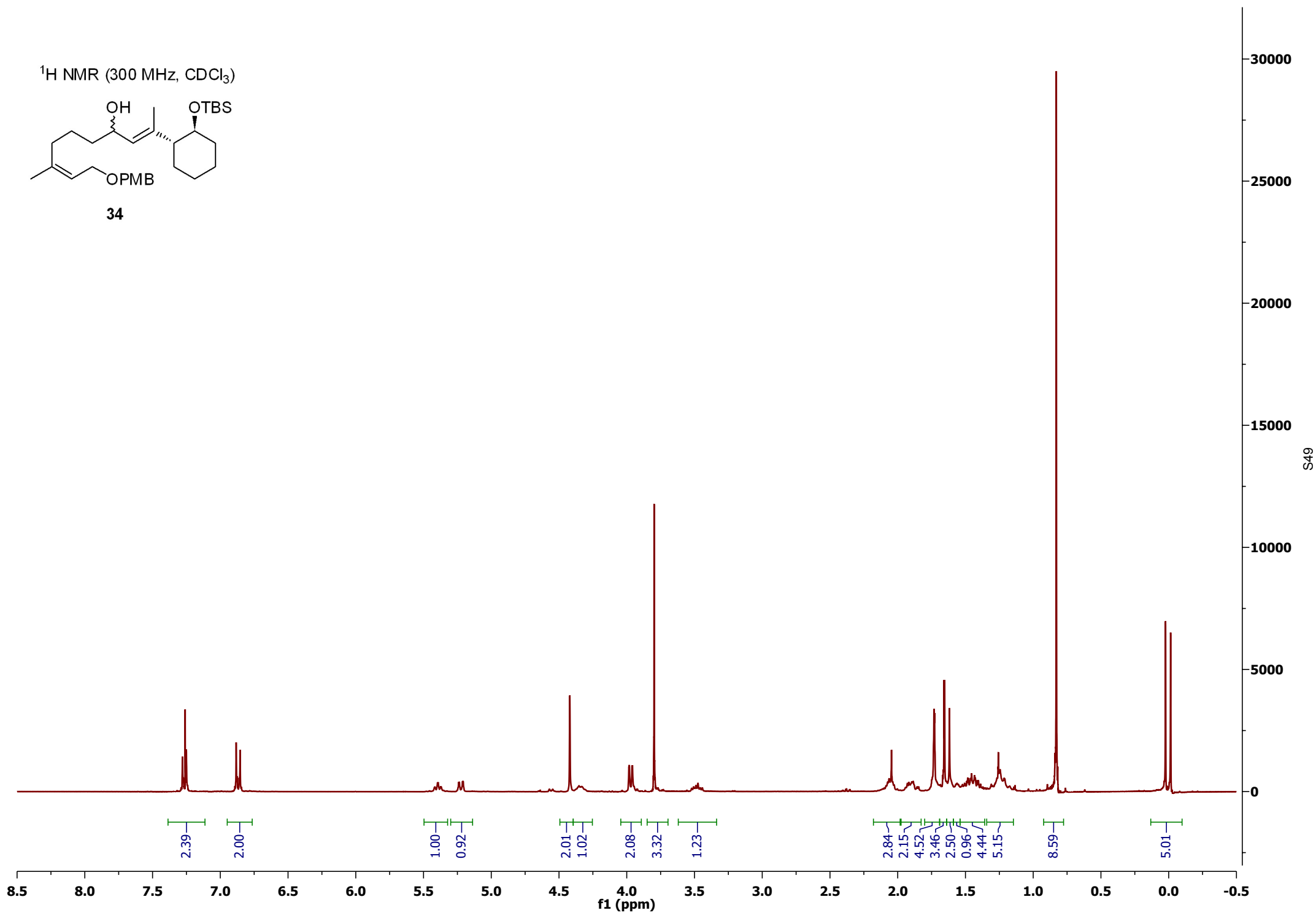
33



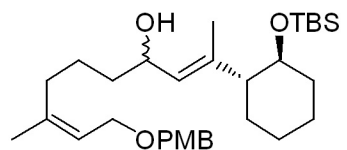
¹H NMR (300 MHz, CDCl₃)



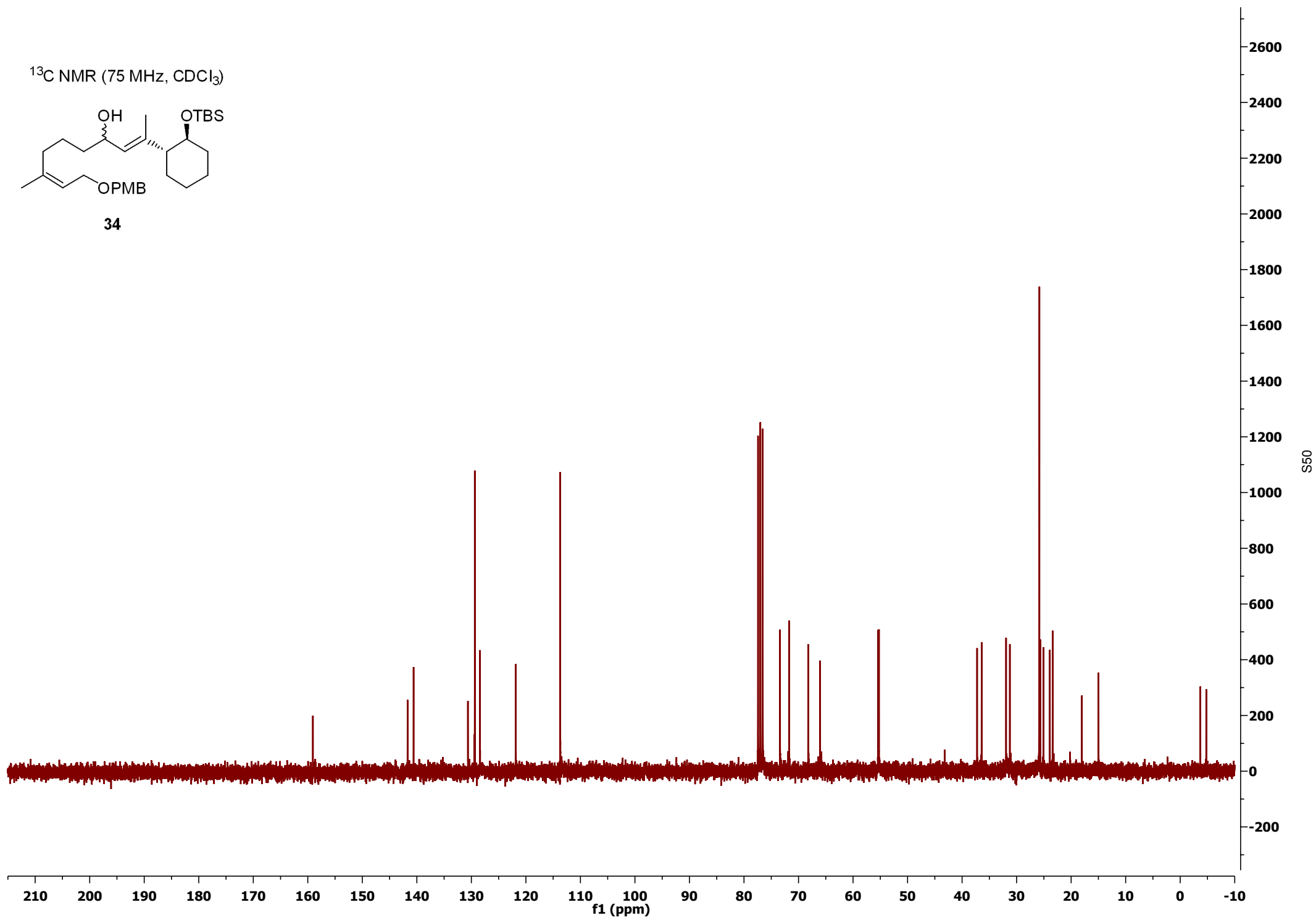
34



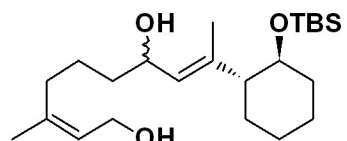
^{13}C NMR (75 MHz, CDCl_3)



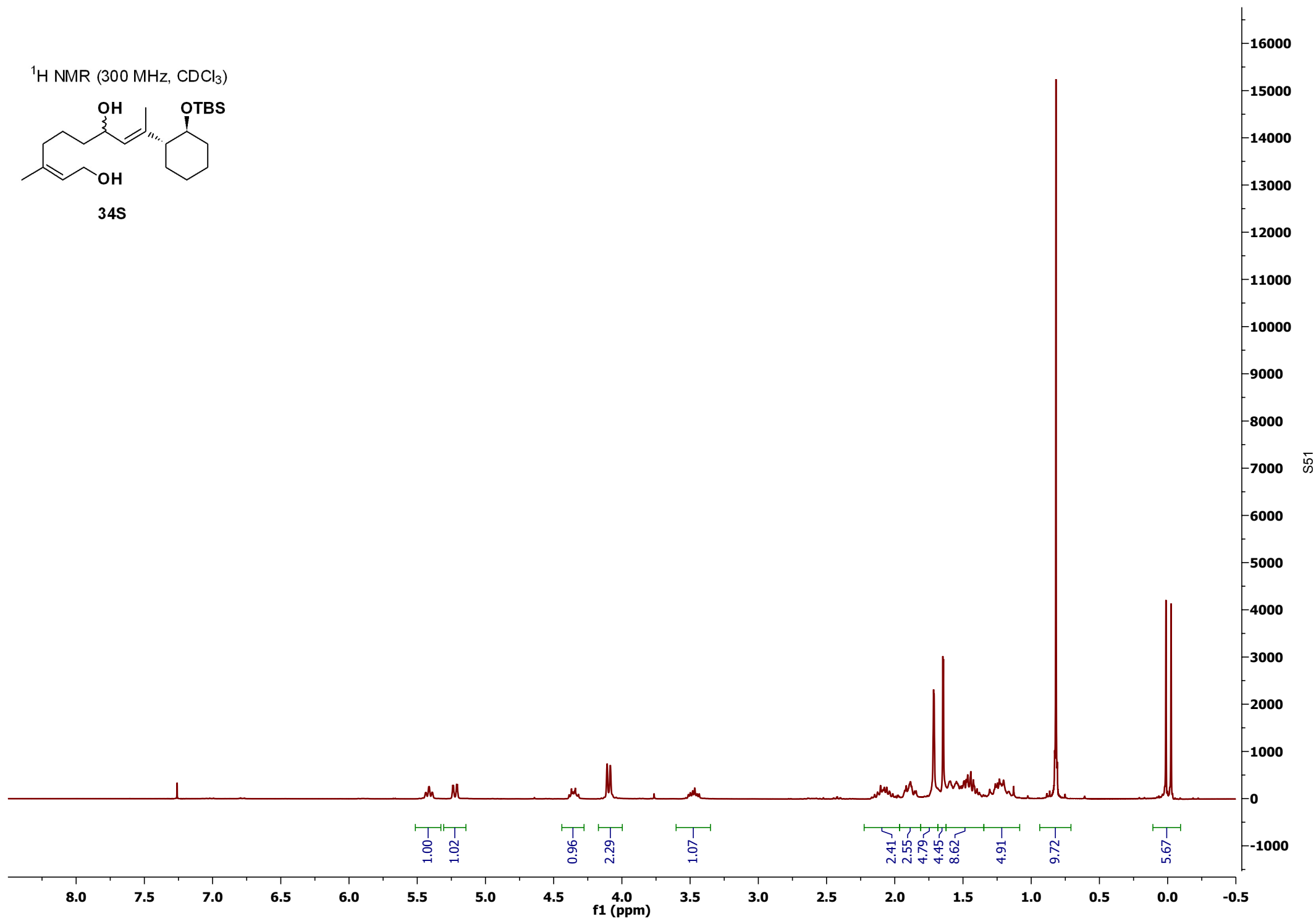
34



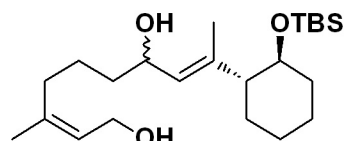
¹H NMR (300 MHz, CDCl₃)



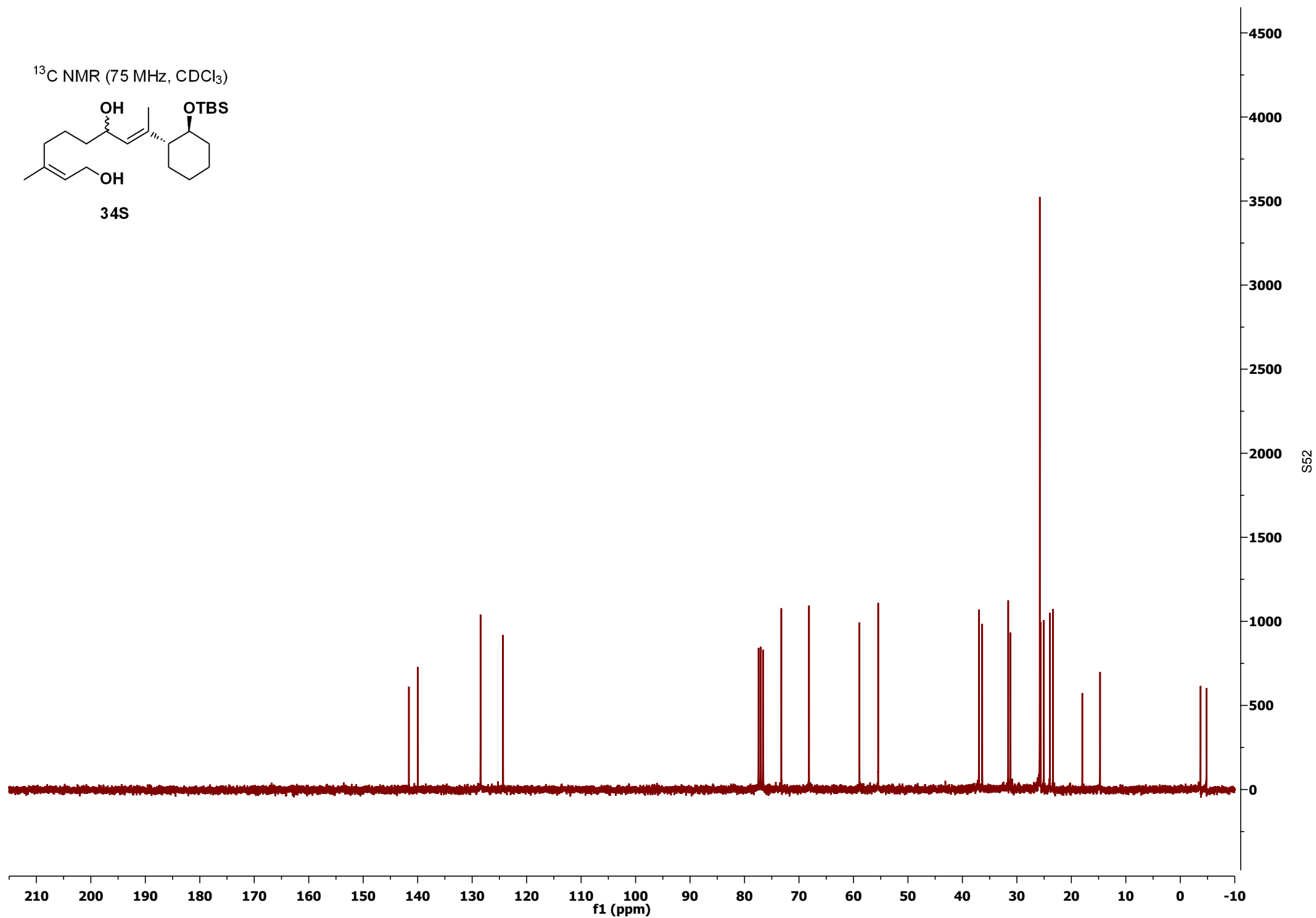
34S



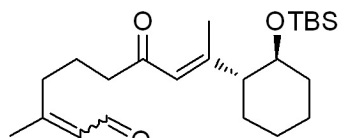
¹³C NMR (75 MHz, CDCl₃)



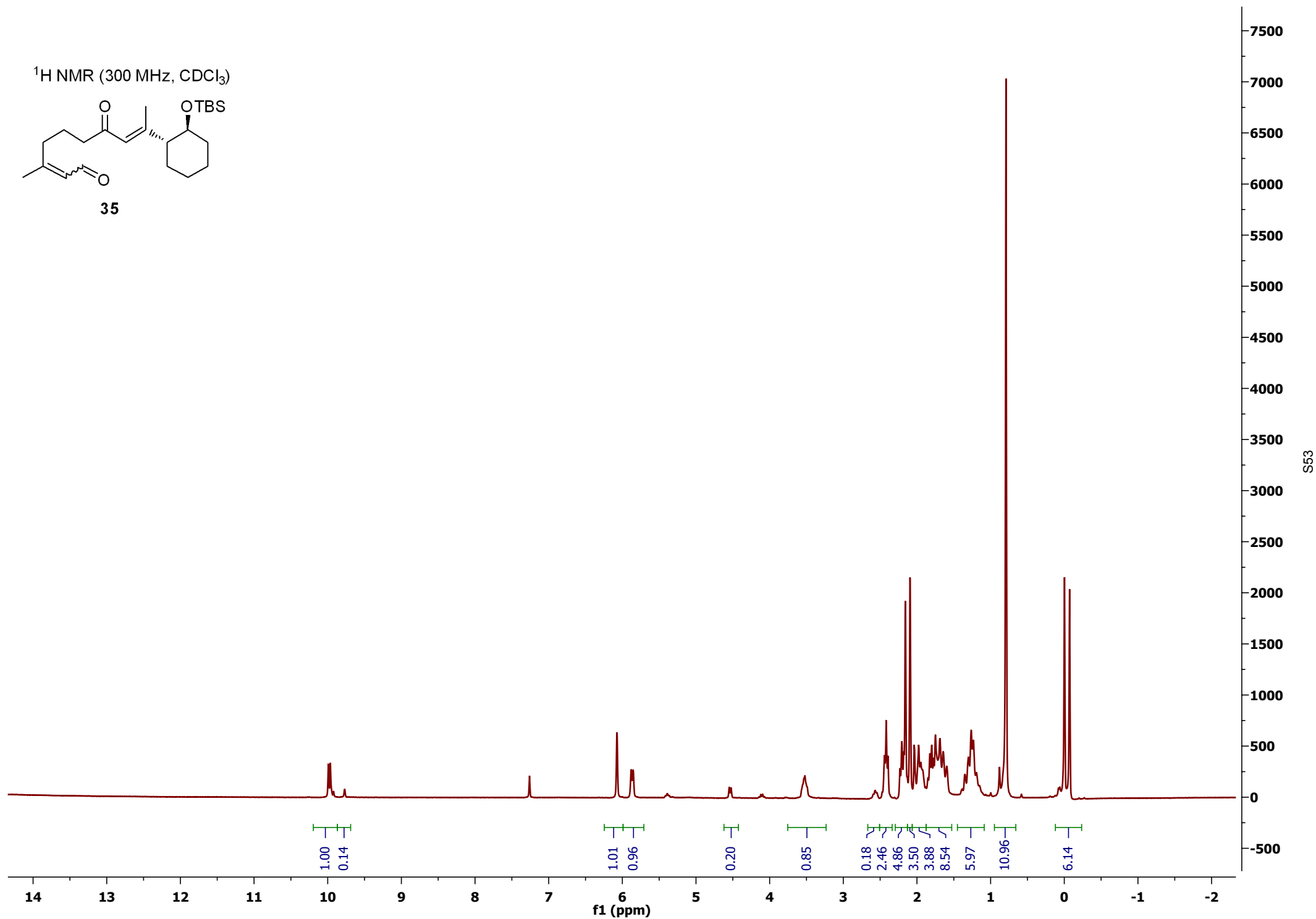
34S



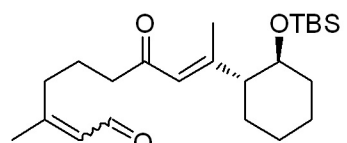
¹H NMR (300 MHz, CDCl₃)



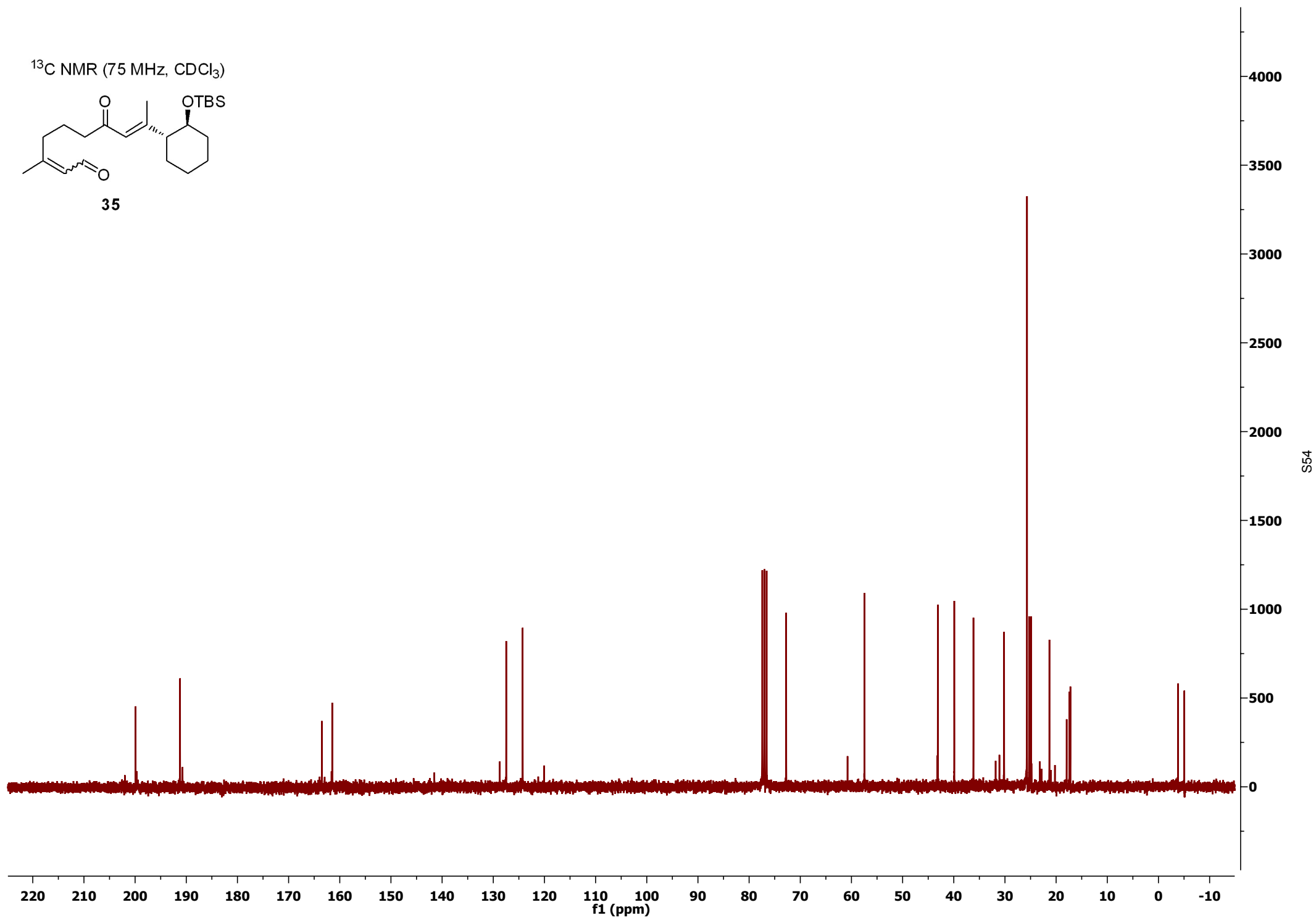
35



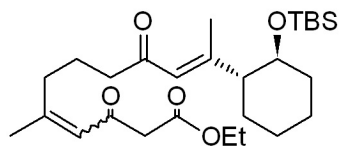
^{13}C NMR (75 MHz, CDCl_3)



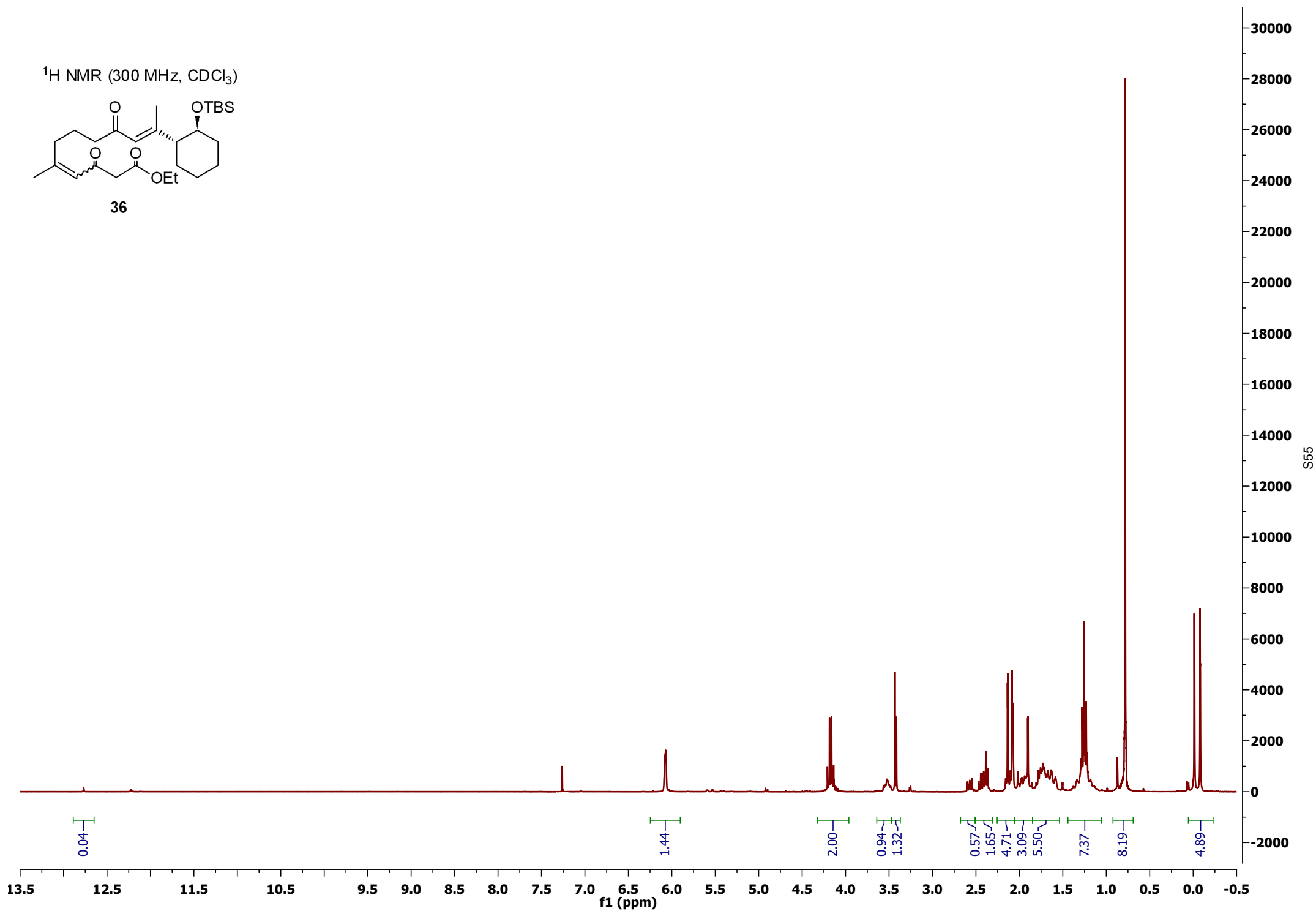
35



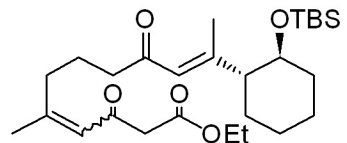
^1H NMR (300 MHz, CDCl_3)



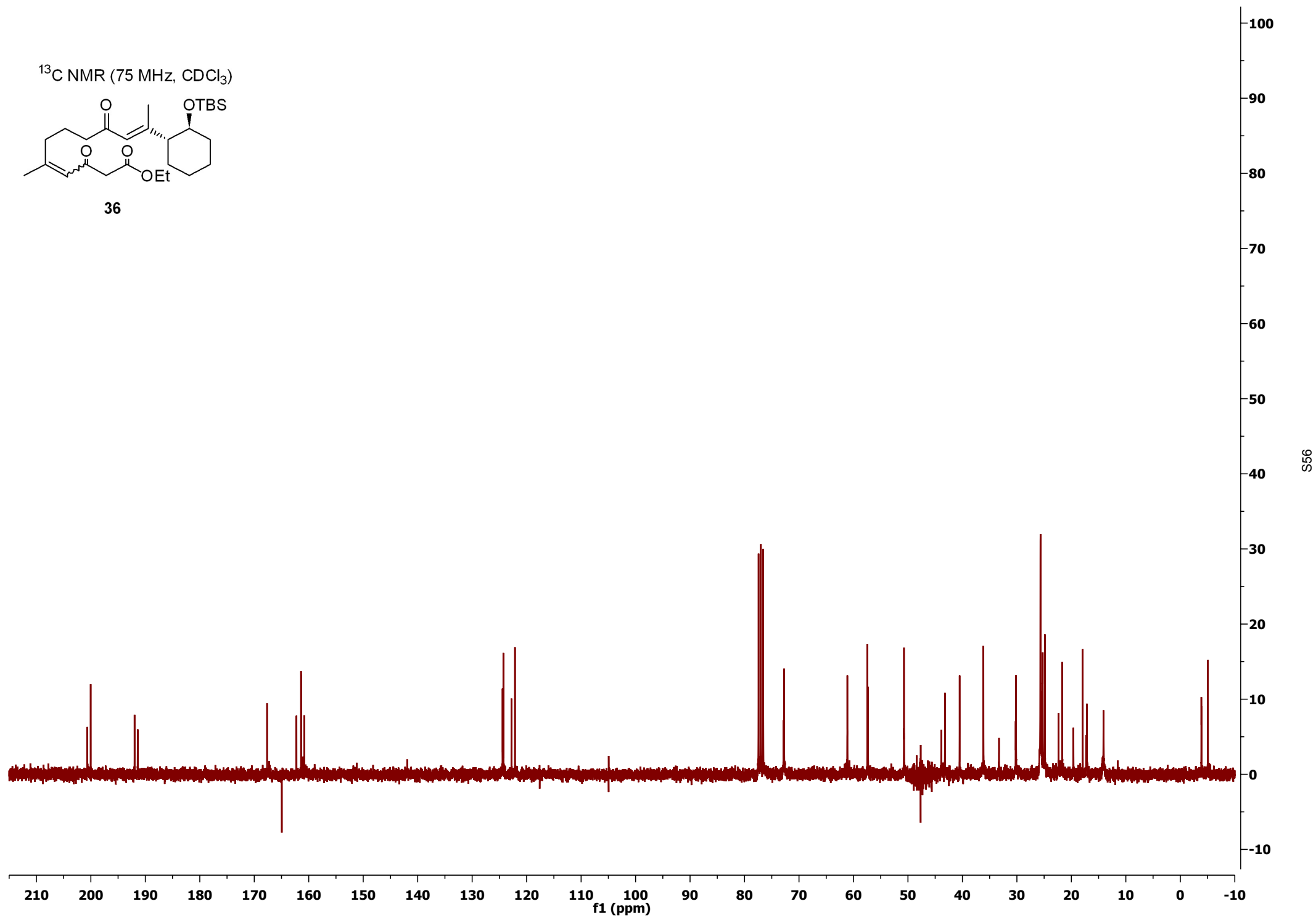
36



^{13}C NMR (75 MHz, CDCl_3)



36



¹H NMR (300 MHz, CDCl₃)

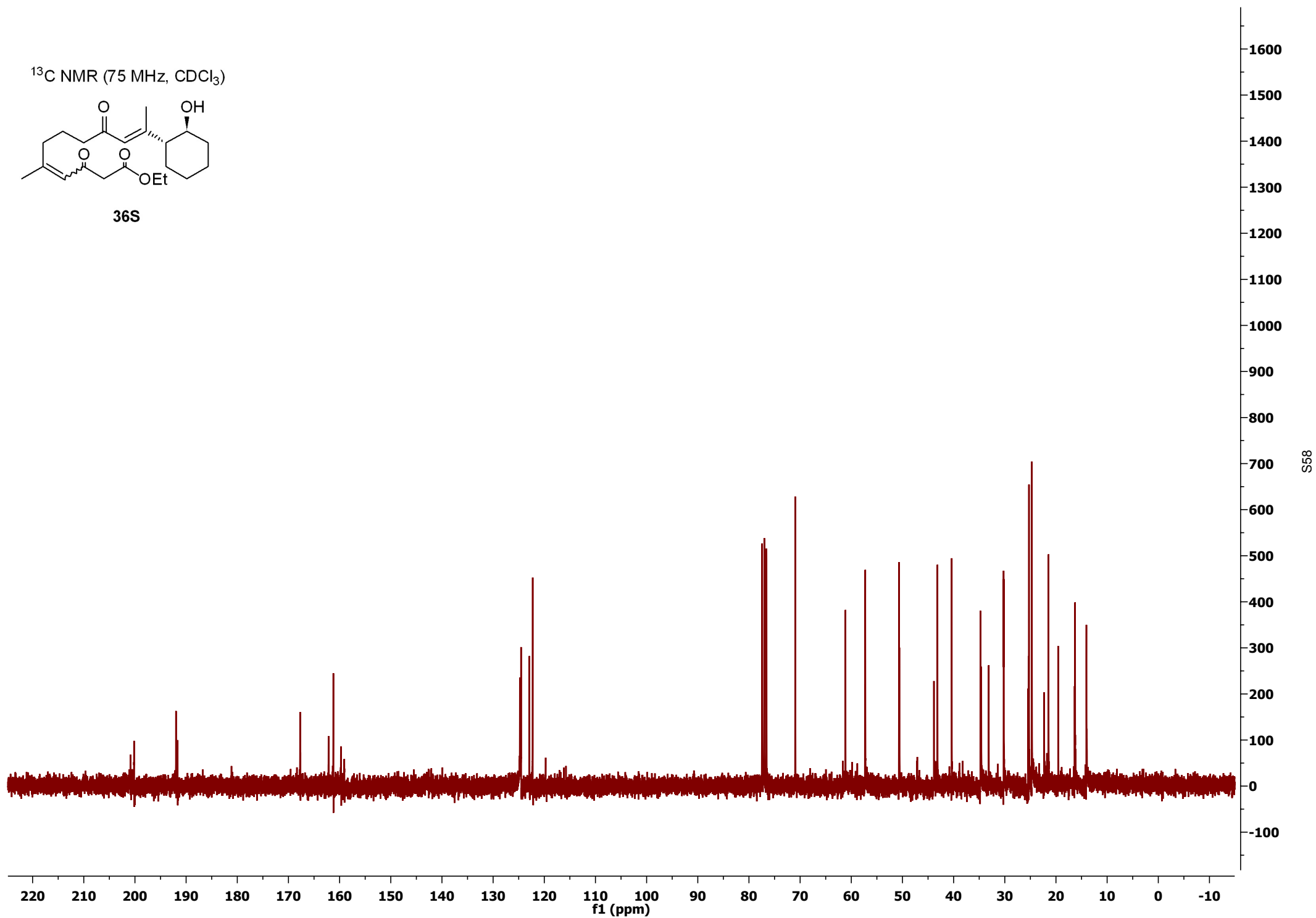
36S

Chemical structure of **36S** is shown in the top left corner. The structure is a complex molecule featuring a cyclohexane ring with a hydroxyl group, a ketone, and an ester linkage, connected to a side chain containing a double bond and a methyl group.

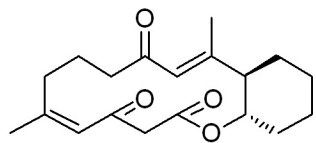
The ¹H NMR spectrum (300 MHz, CDCl₃) displays the following peaks and integrations:

Chemical Shift (ppm)	Integration
12.7	0.17
6.1	1.00
6.0	0.81
4.2	2.40
3.5	1.31
3.4	1.61
2.5	0.63
2.4	2.34
2.3	5.90
2.1	2.31
2.0	3.27
1.8	6.76
1.2	8.71

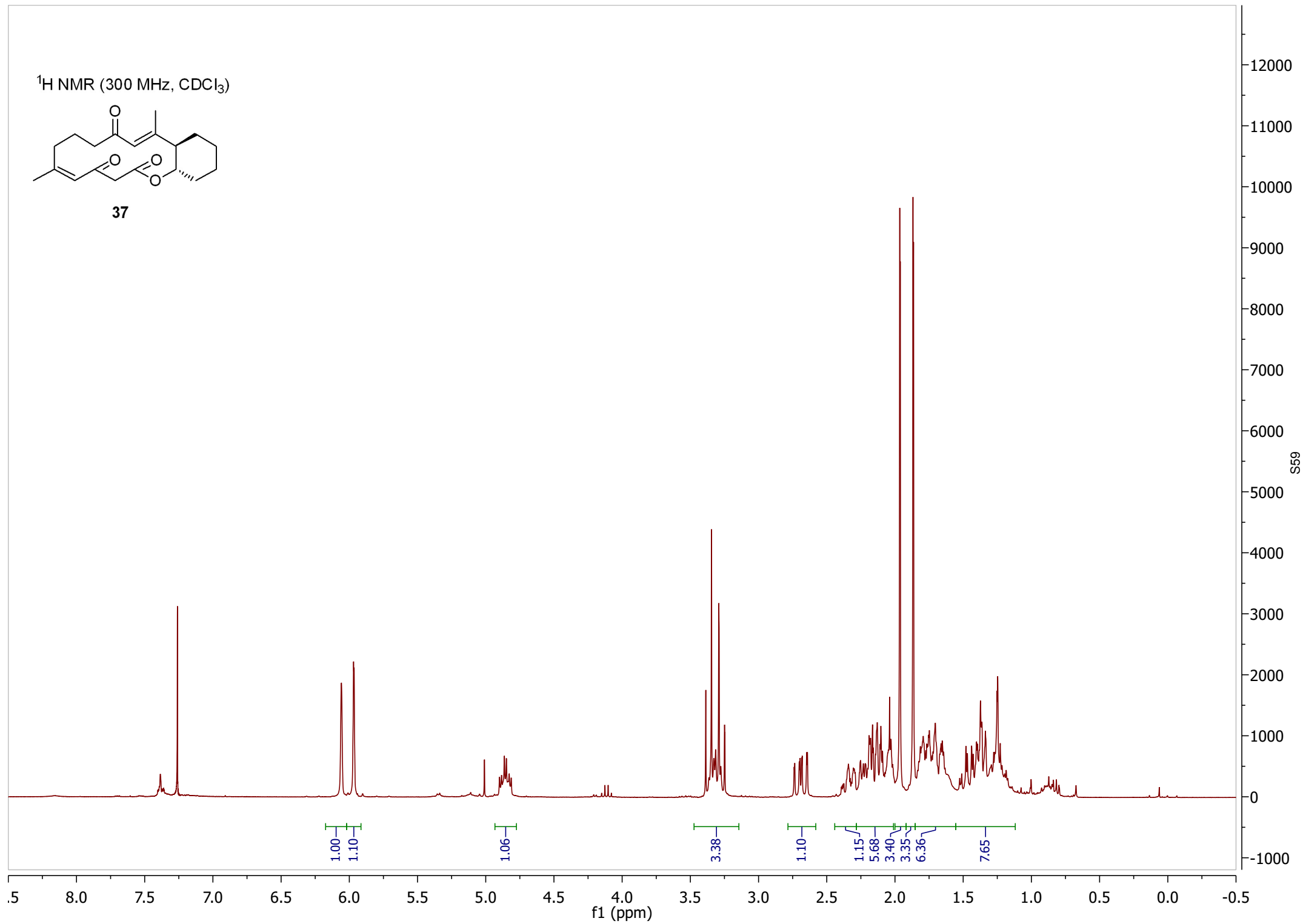
36S



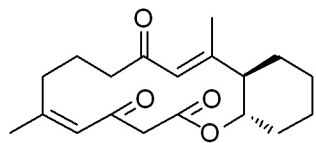
¹H NMR (300 MHz, CDCl₃)



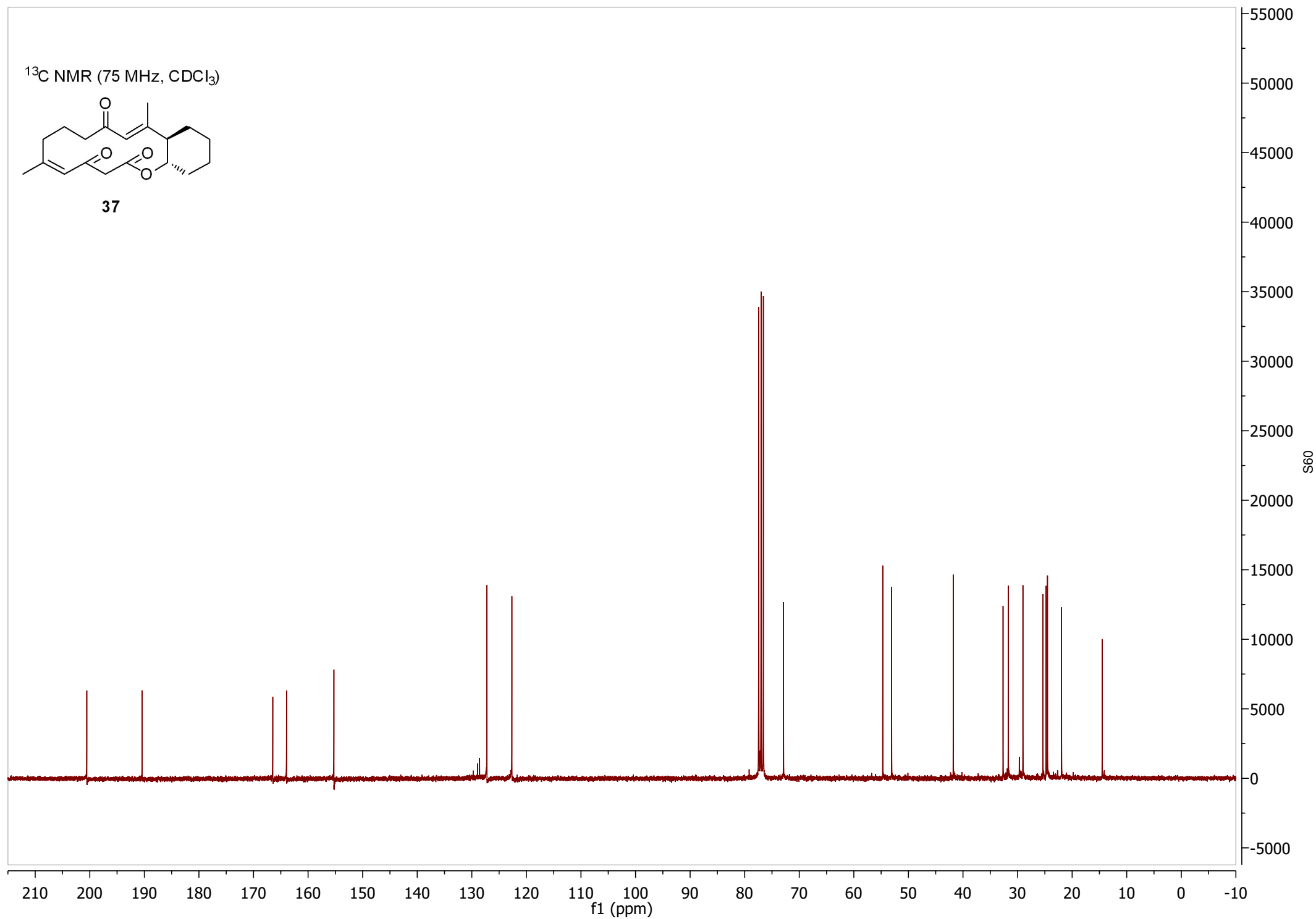
37



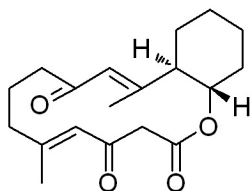
^{13}C NMR (75 MHz, CDCl_3)



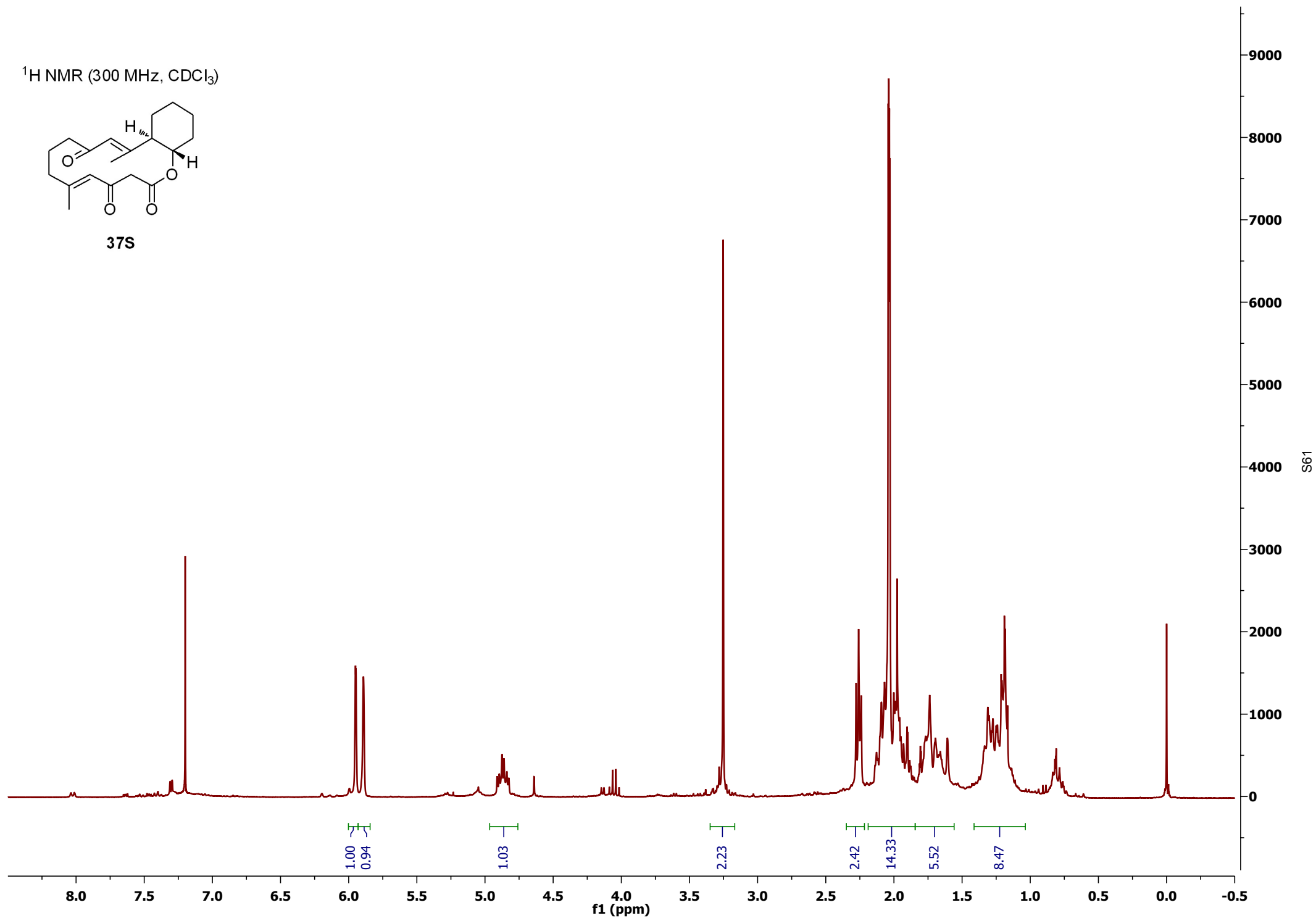
37



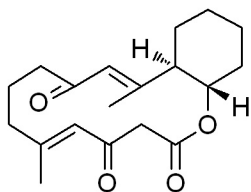
¹H NMR (300 MHz, CDCl₃)



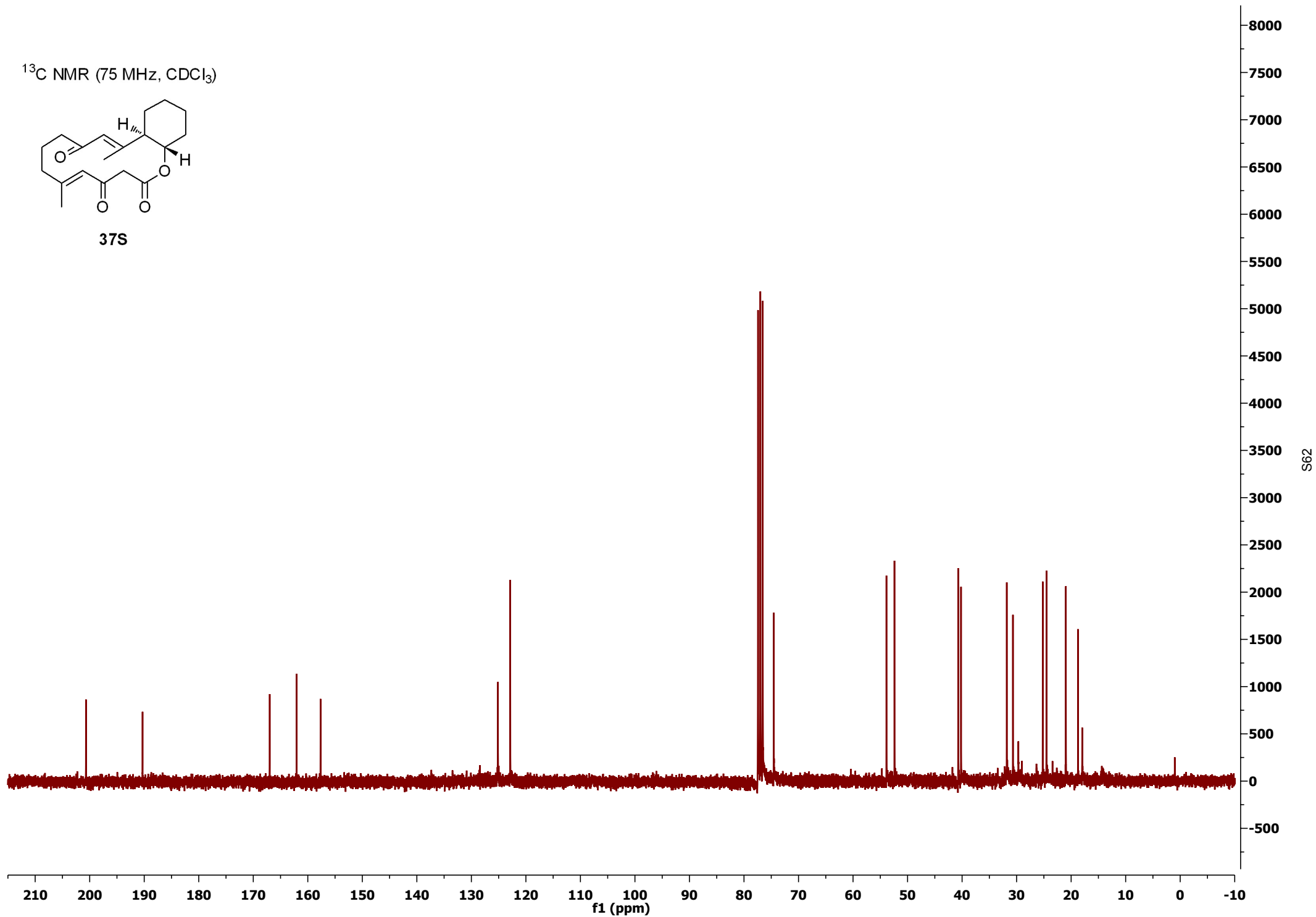
37S



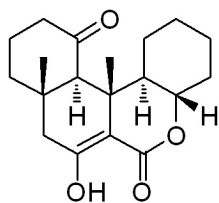
^{13}C NMR (75 MHz, CDCl_3)



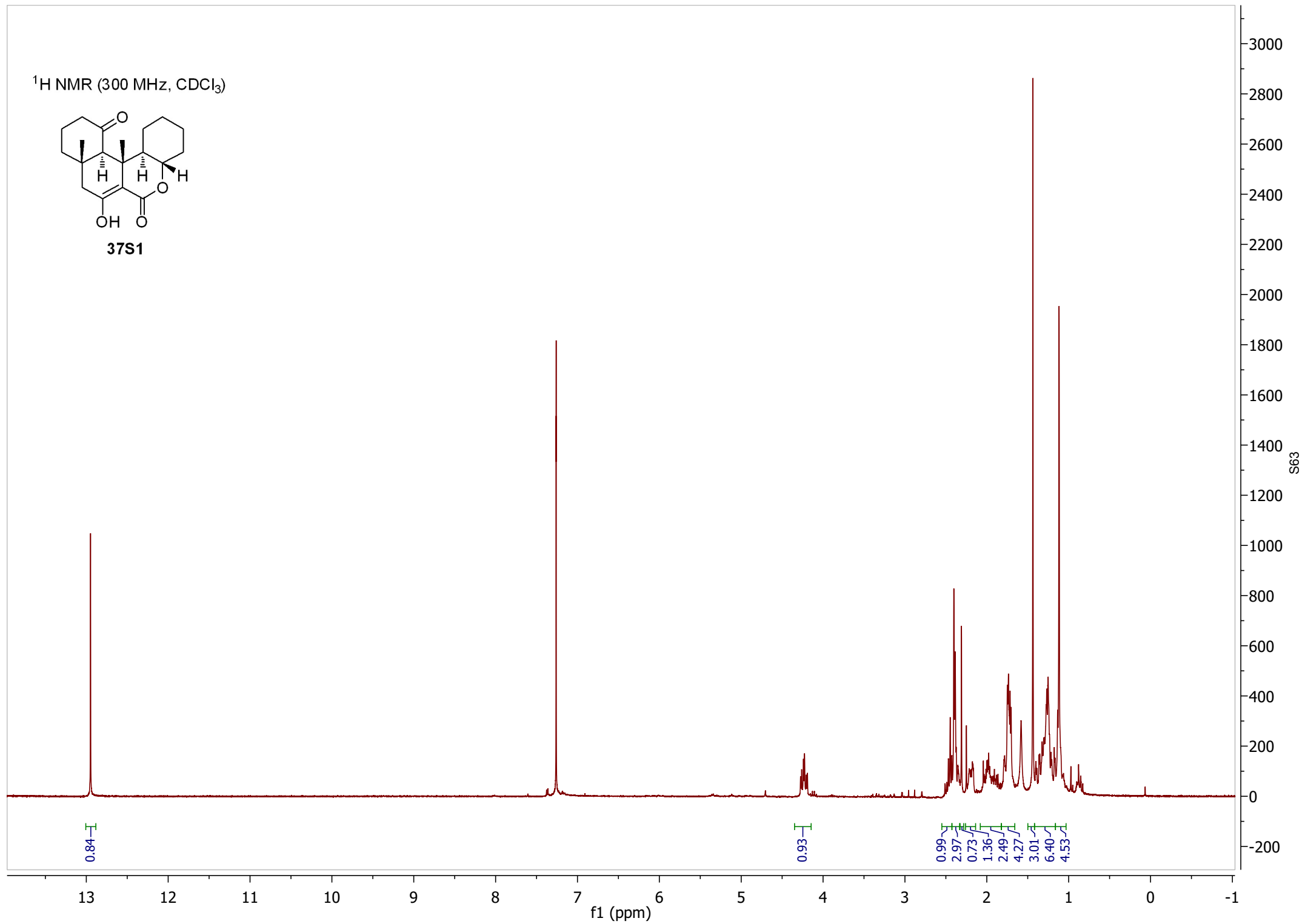
37S



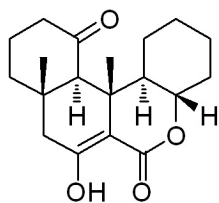
¹H NMR (300 MHz, CDCl₃)



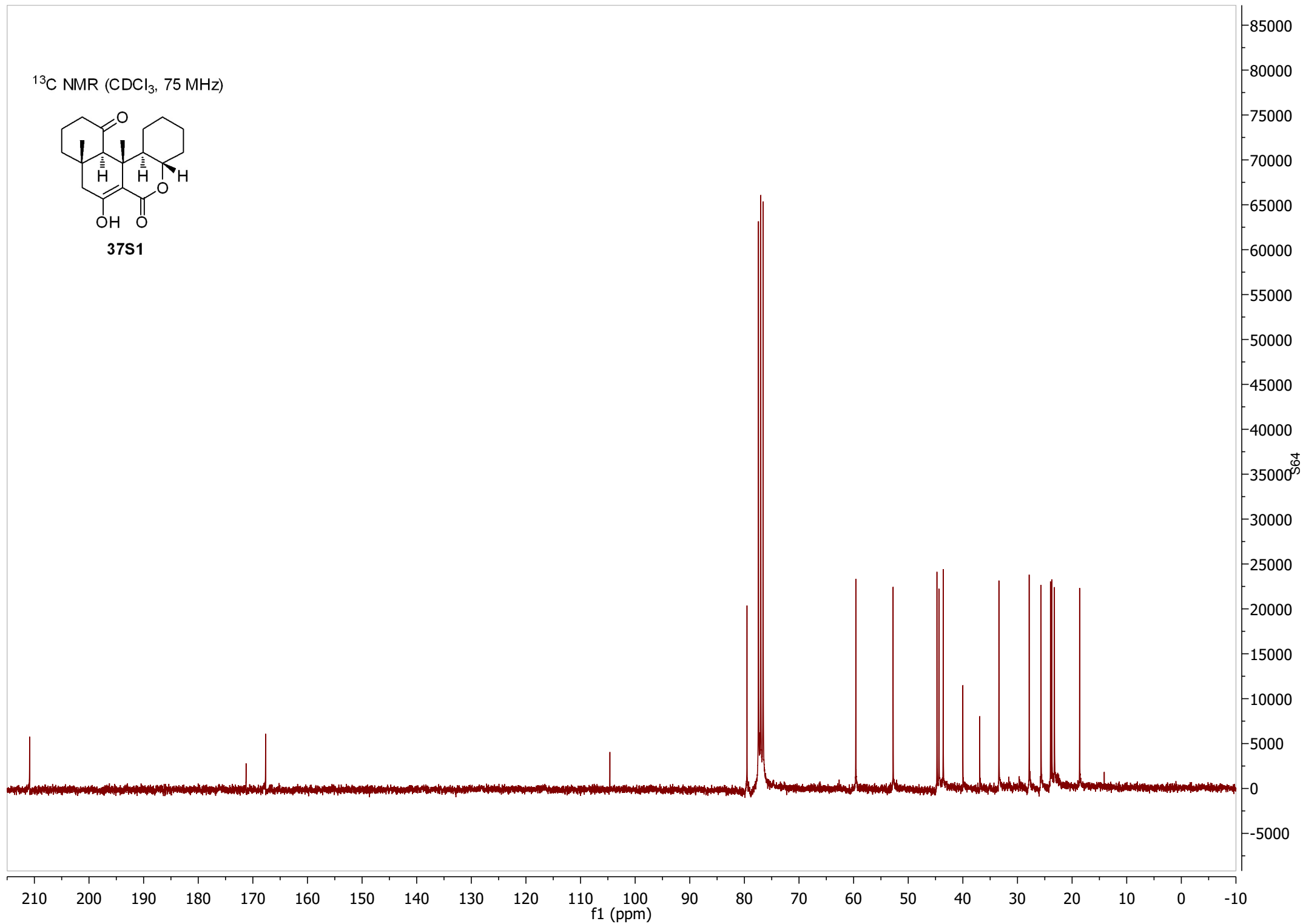
37S1



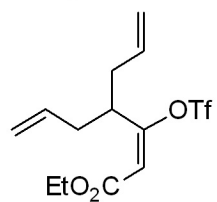
^{13}C NMR (CDCl_3 , 75 MHz)



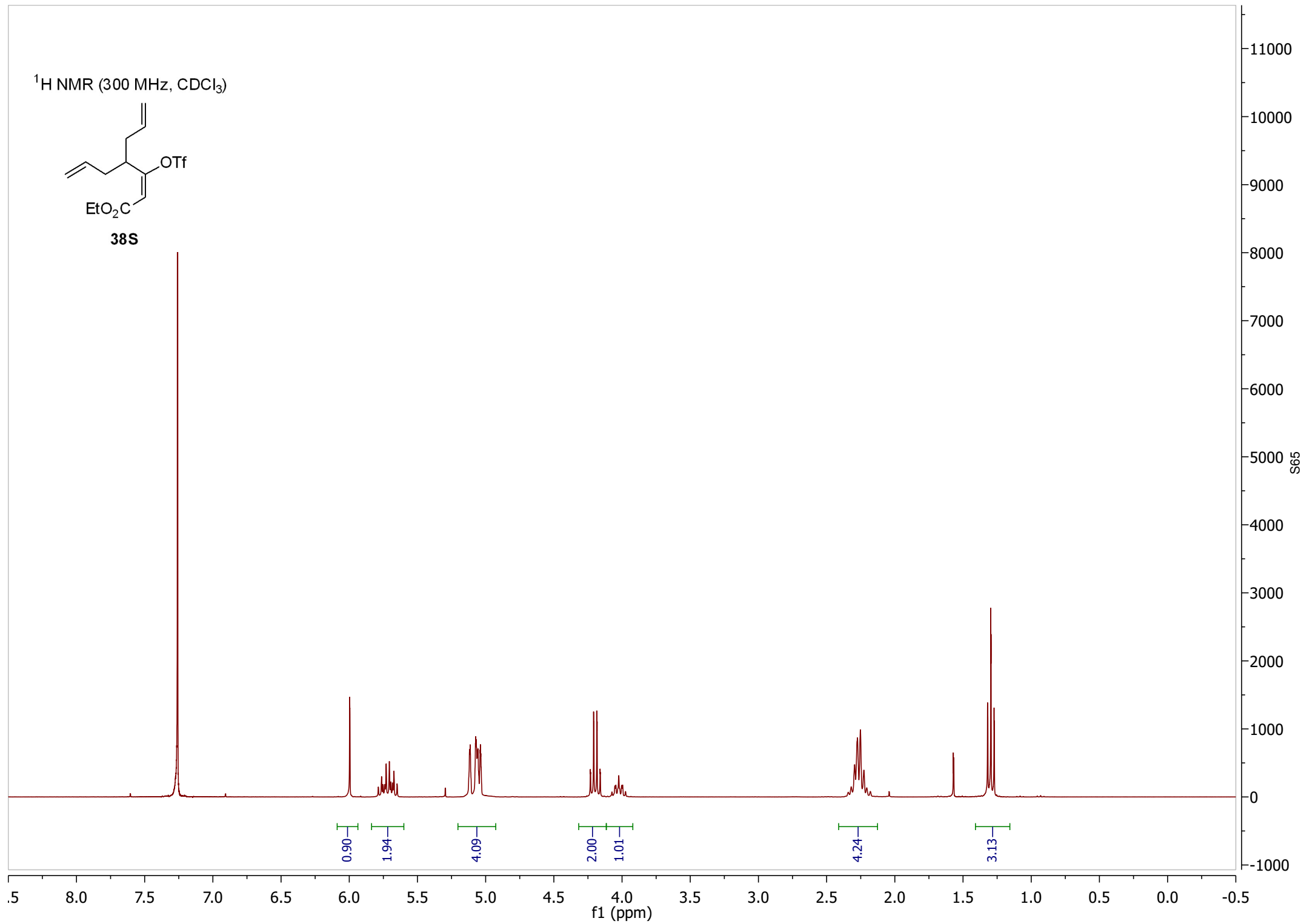
37S1



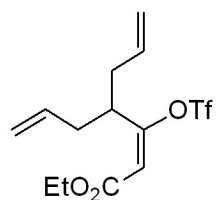
^1H NMR (300 MHz, CDCl_3)



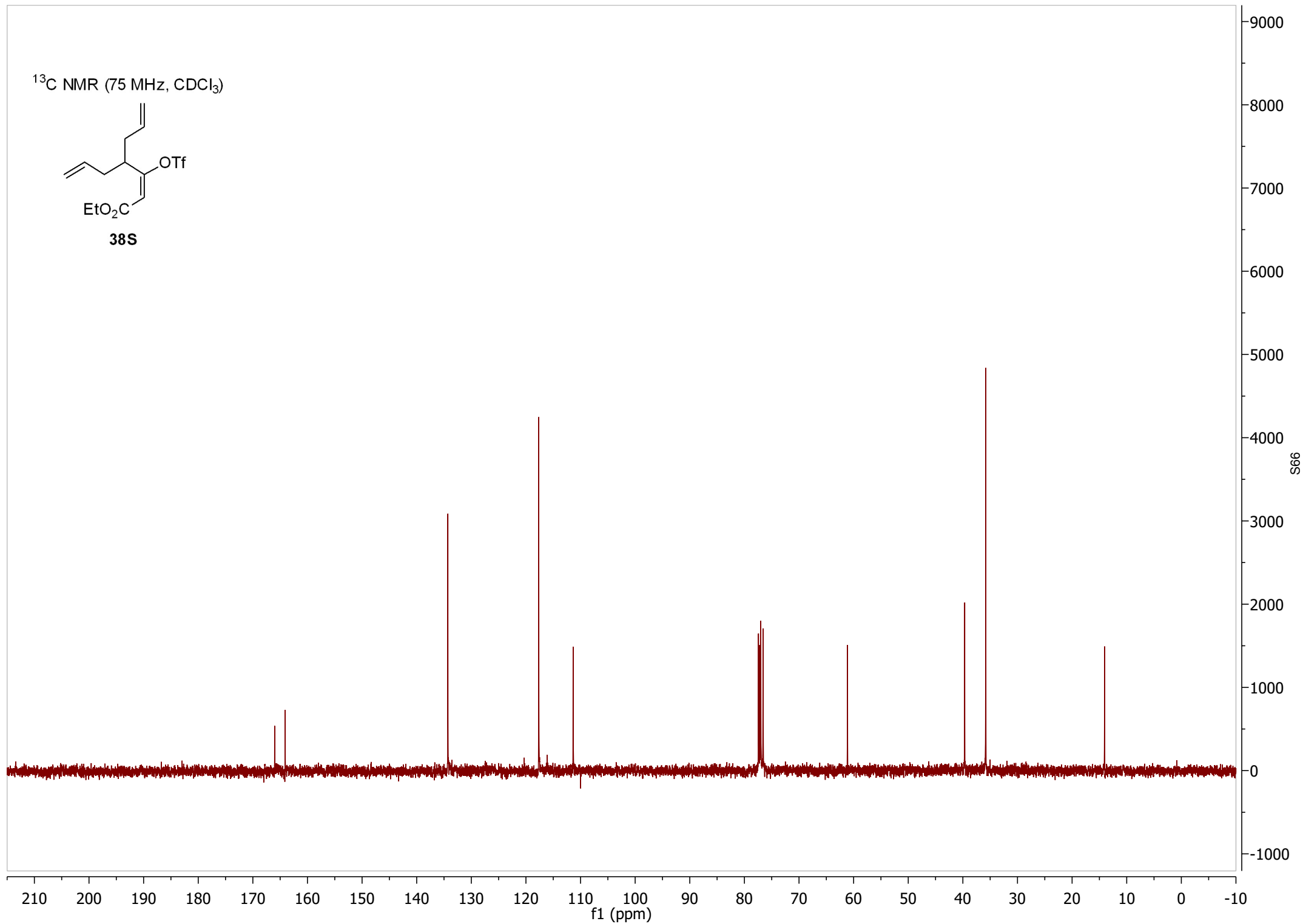
38S



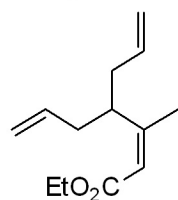
^{13}C NMR (75 MHz, CDCl_3)



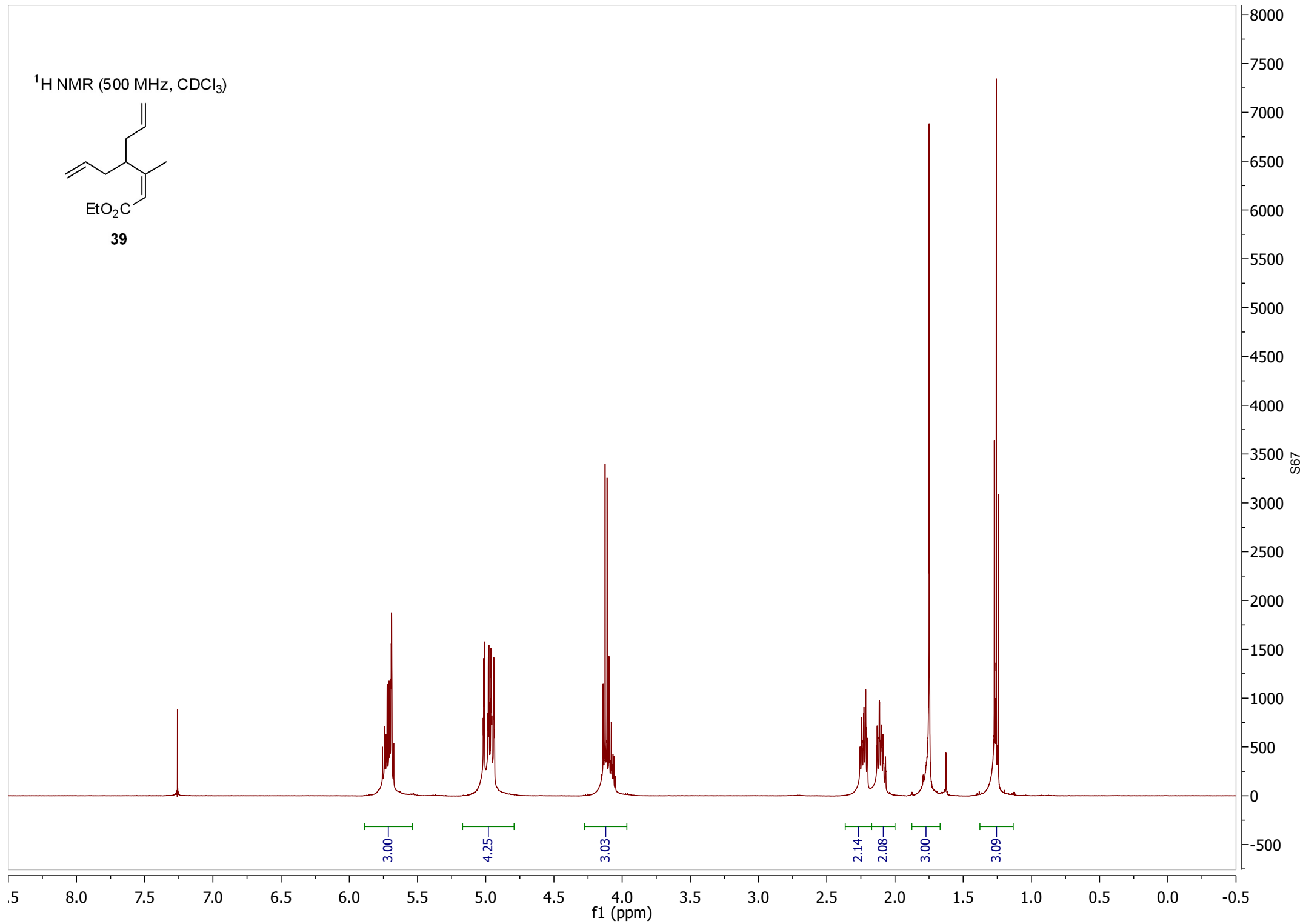
38S



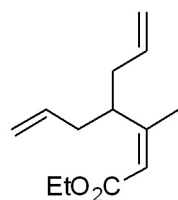
^1H NMR (500 MHz, CDCl_3)



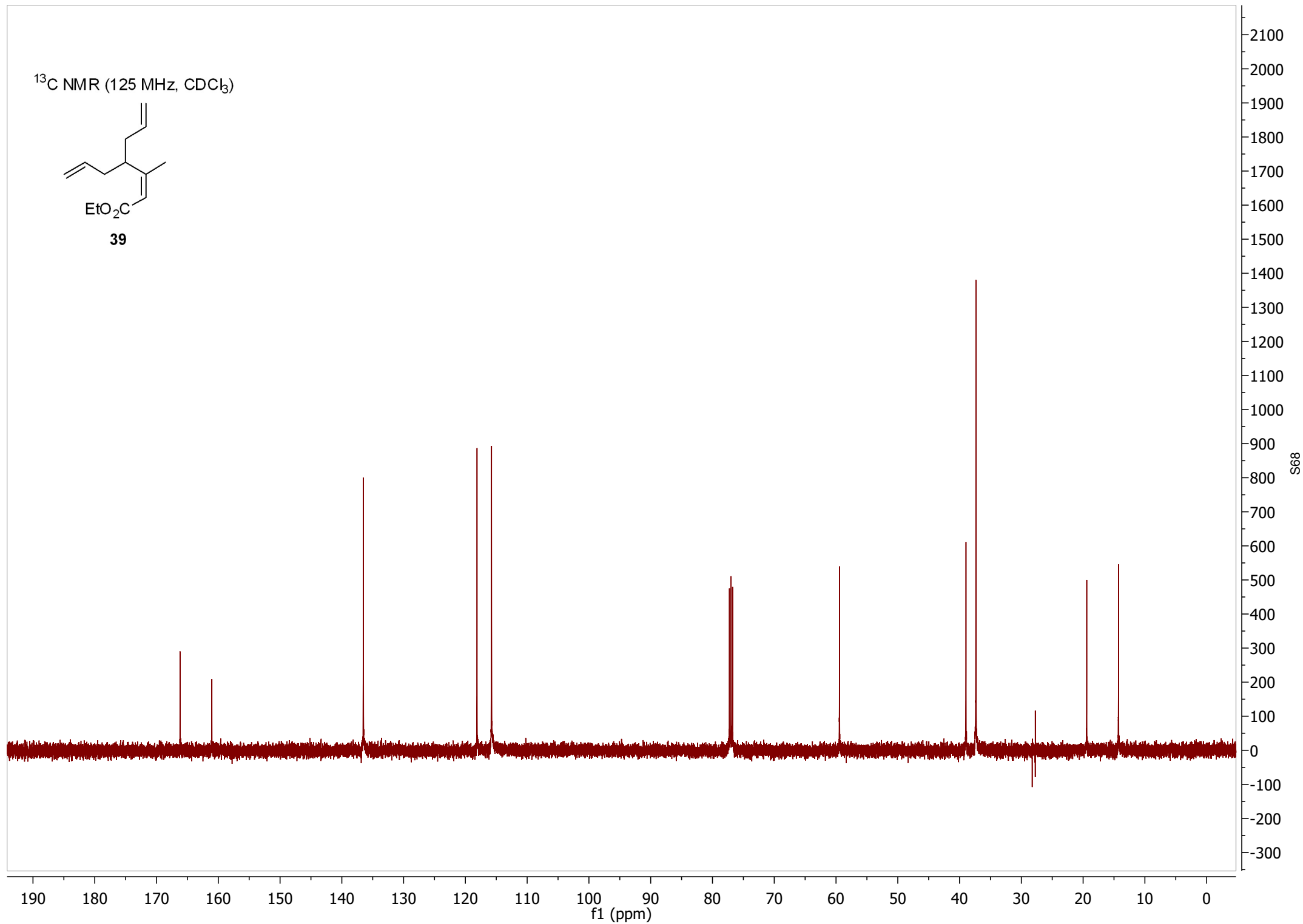
39



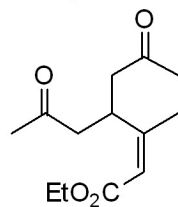
^{13}C NMR (125 MHz, CDCl_3)



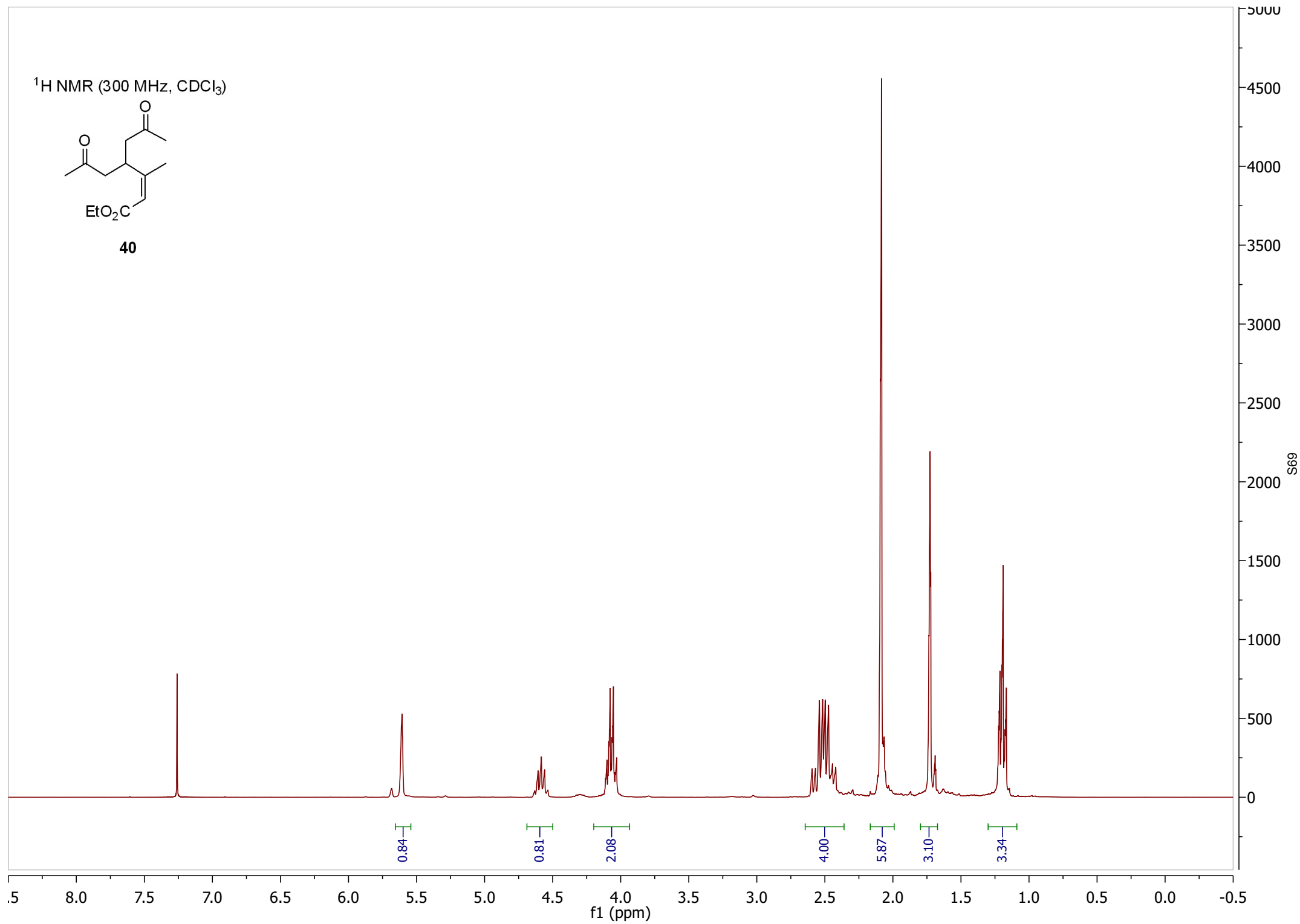
39



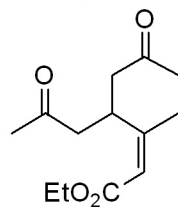
^1H NMR (300 MHz, CDCl_3)



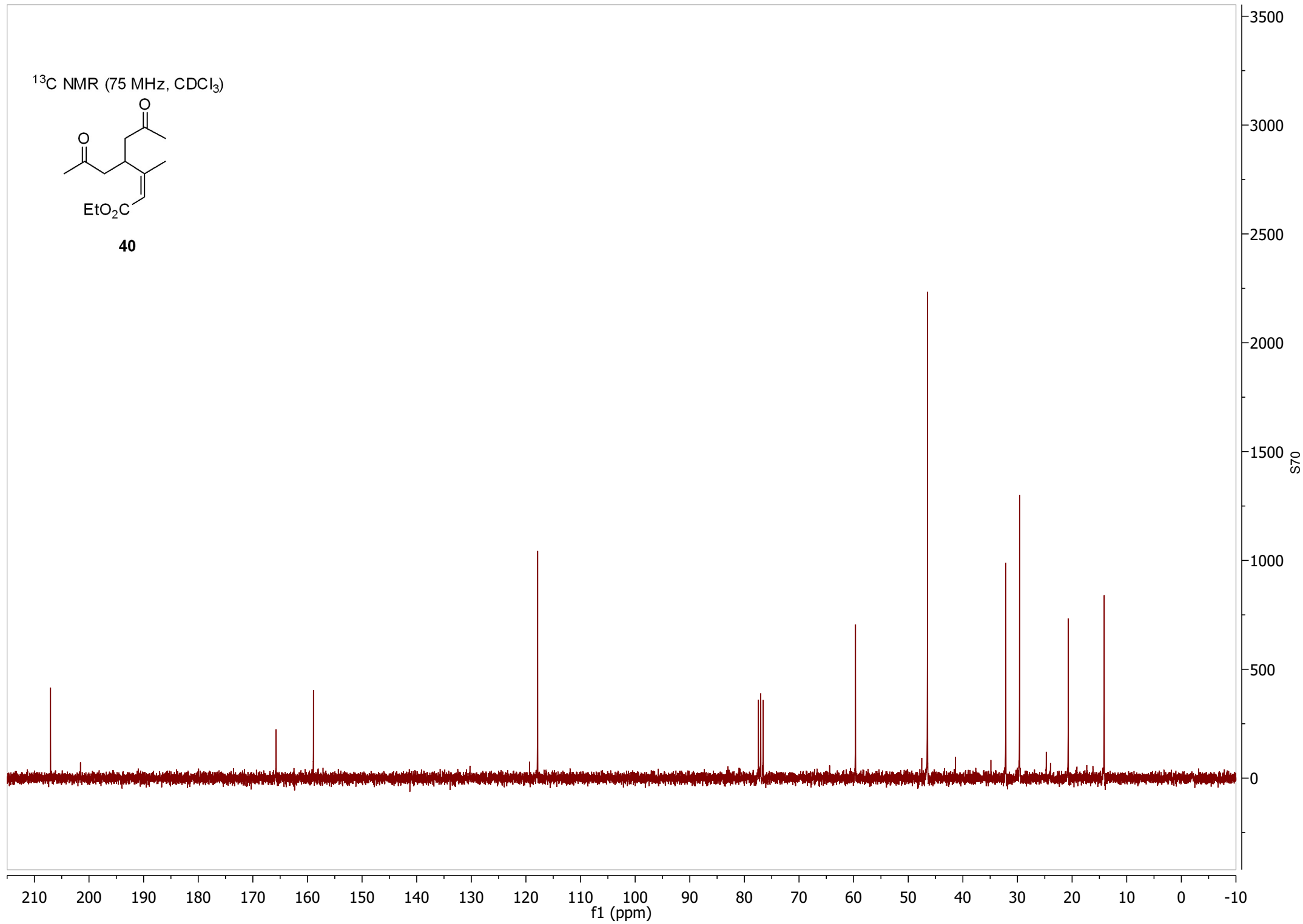
40



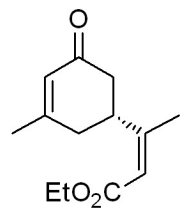
^{13}C NMR (75 MHz, CDCl_3)



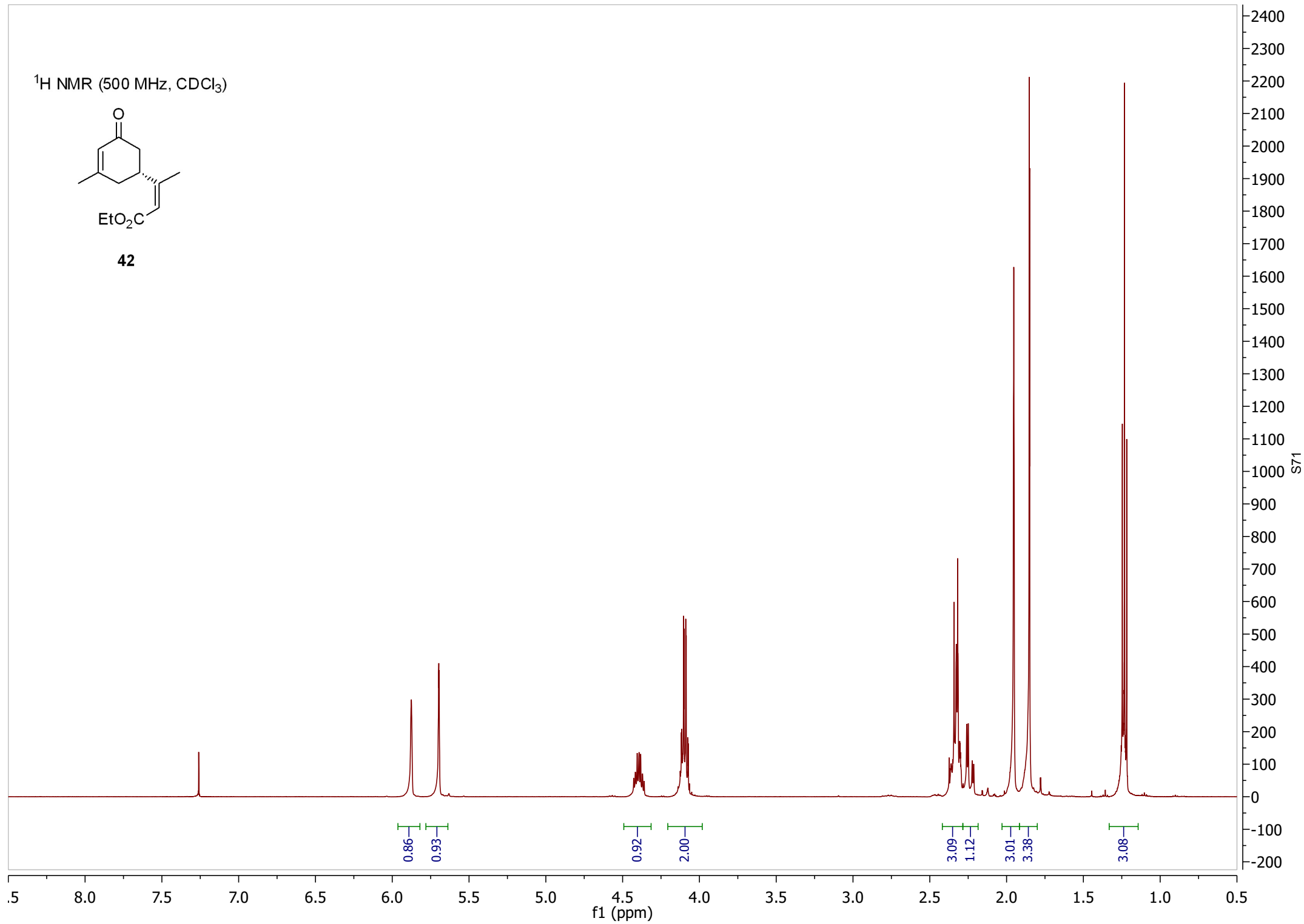
40



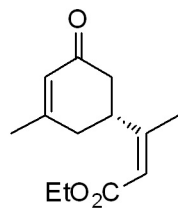
^1H NMR (500 MHz, CDCl_3)



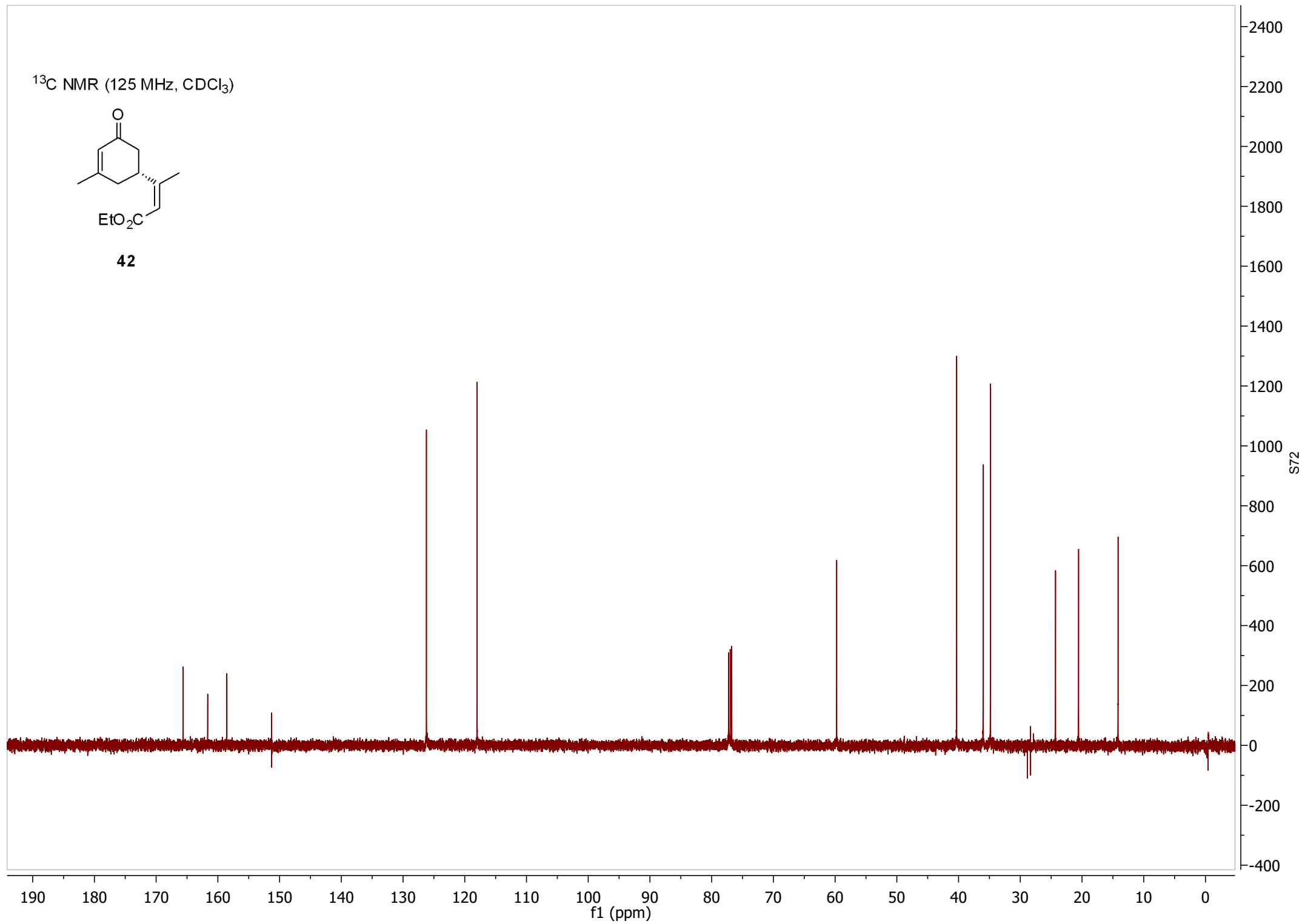
42



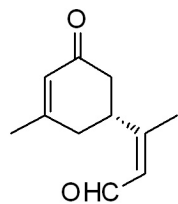
^{13}C NMR (125 MHz, CDCl_3)



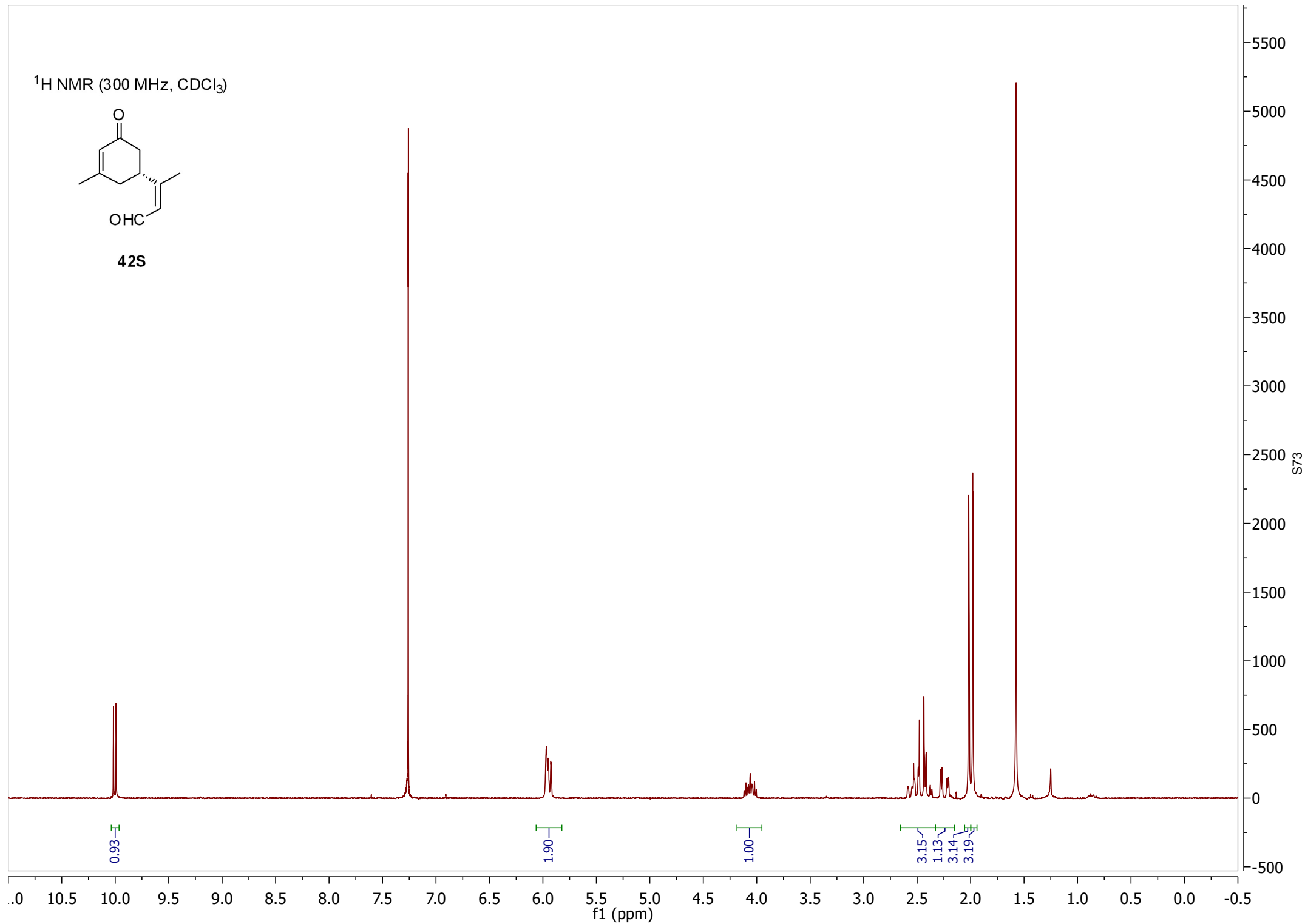
42



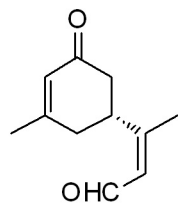
¹H NMR (300 MHz, CDCl₃)



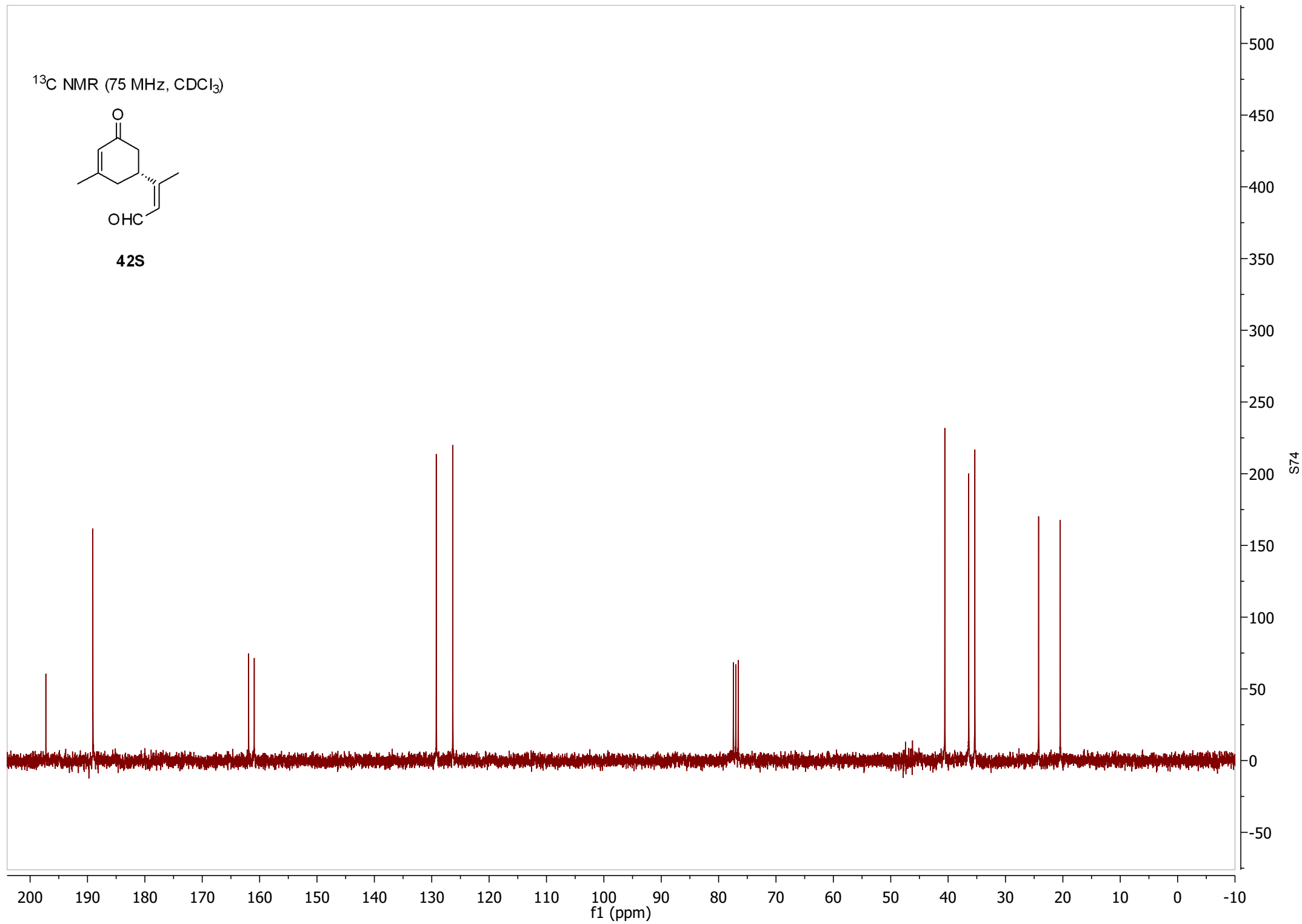
42S



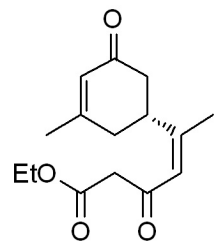
^{13}C NMR (75 MHz, CDCl_3)



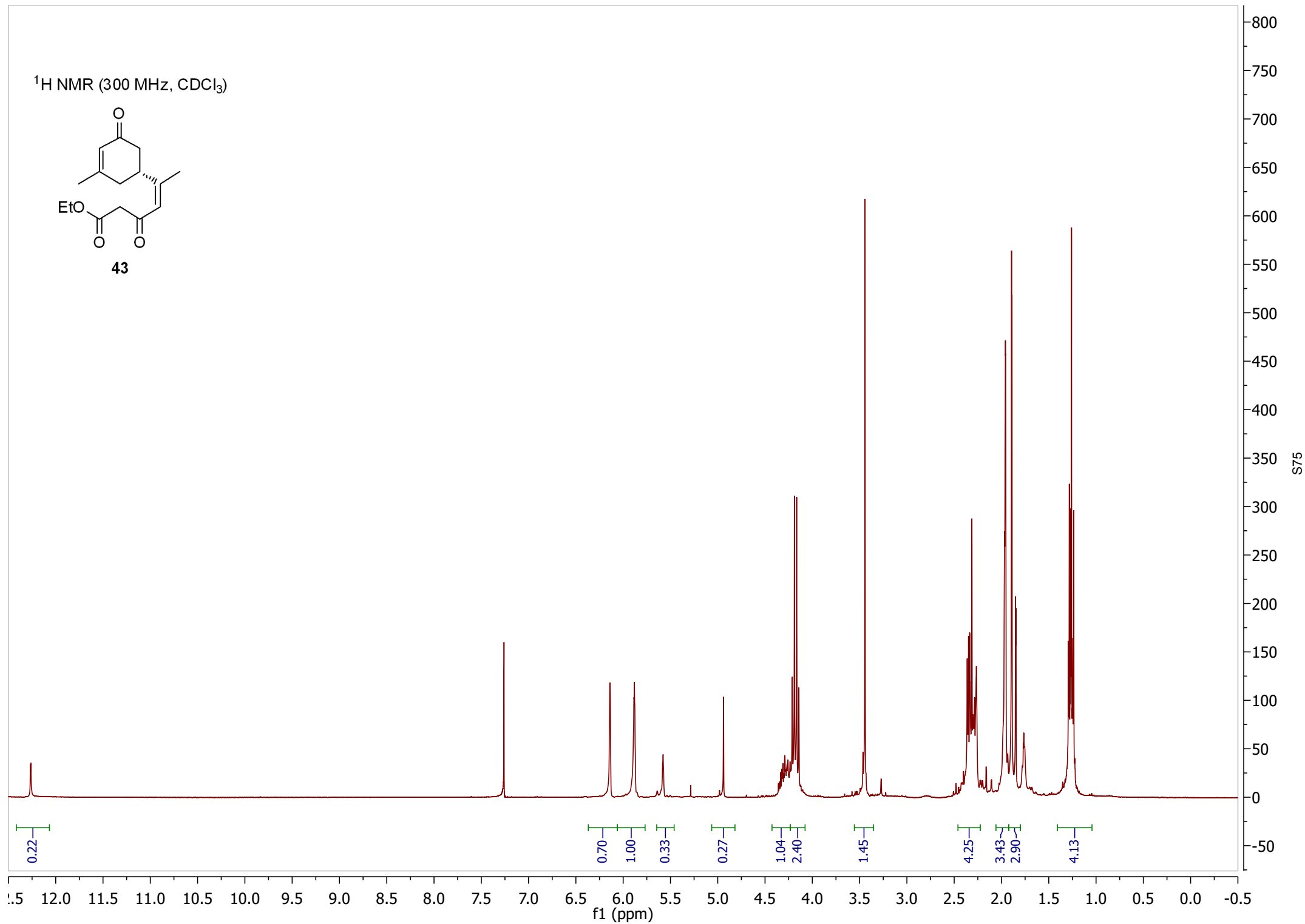
42S



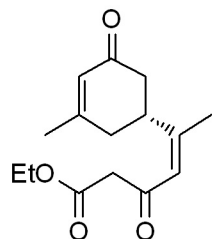
¹H NMR (300 MHz, CDCl₃)



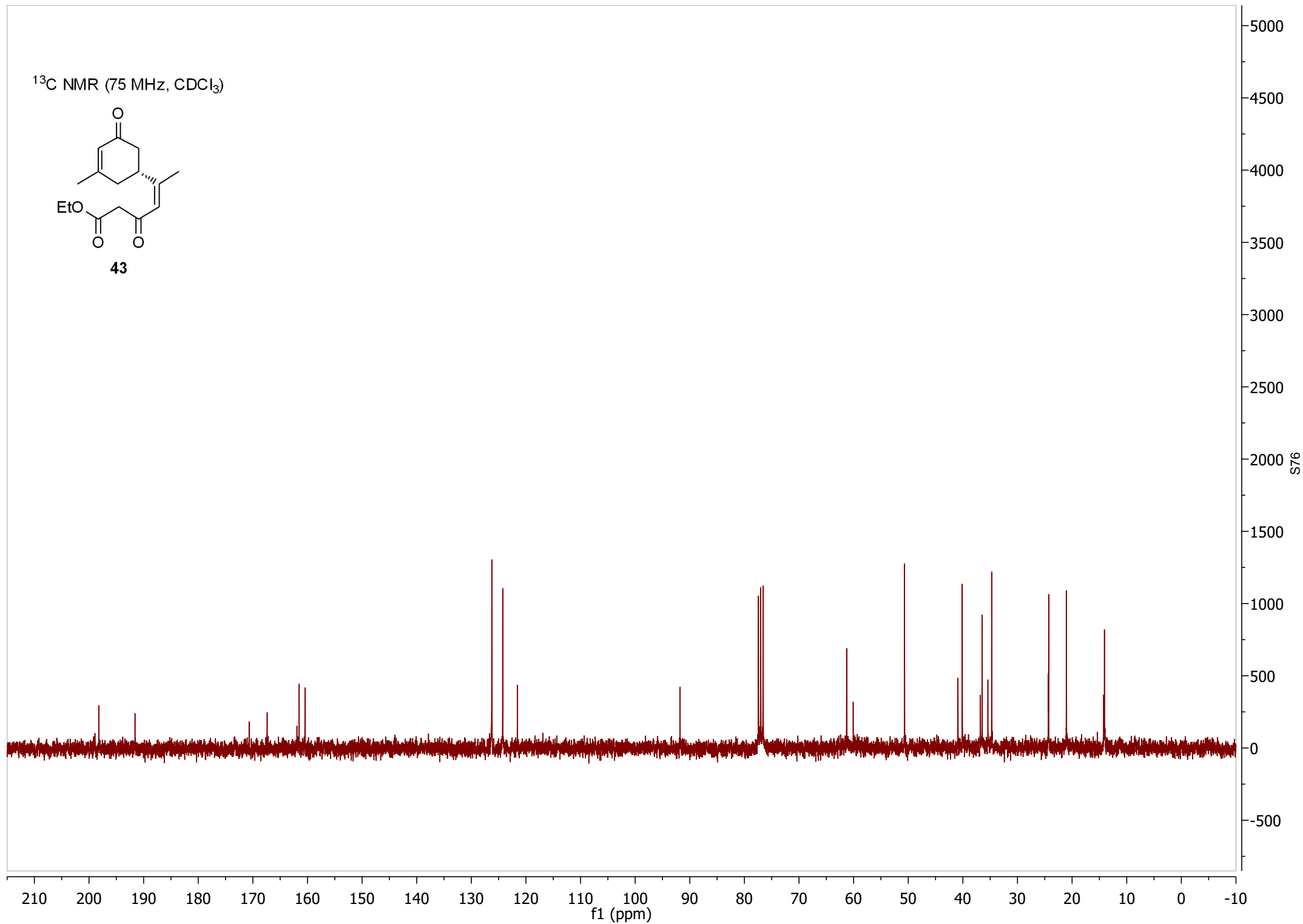
43



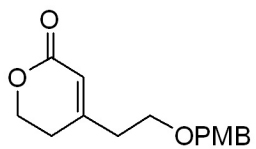
^{13}C NMR (75 MHz, CDCl_3)



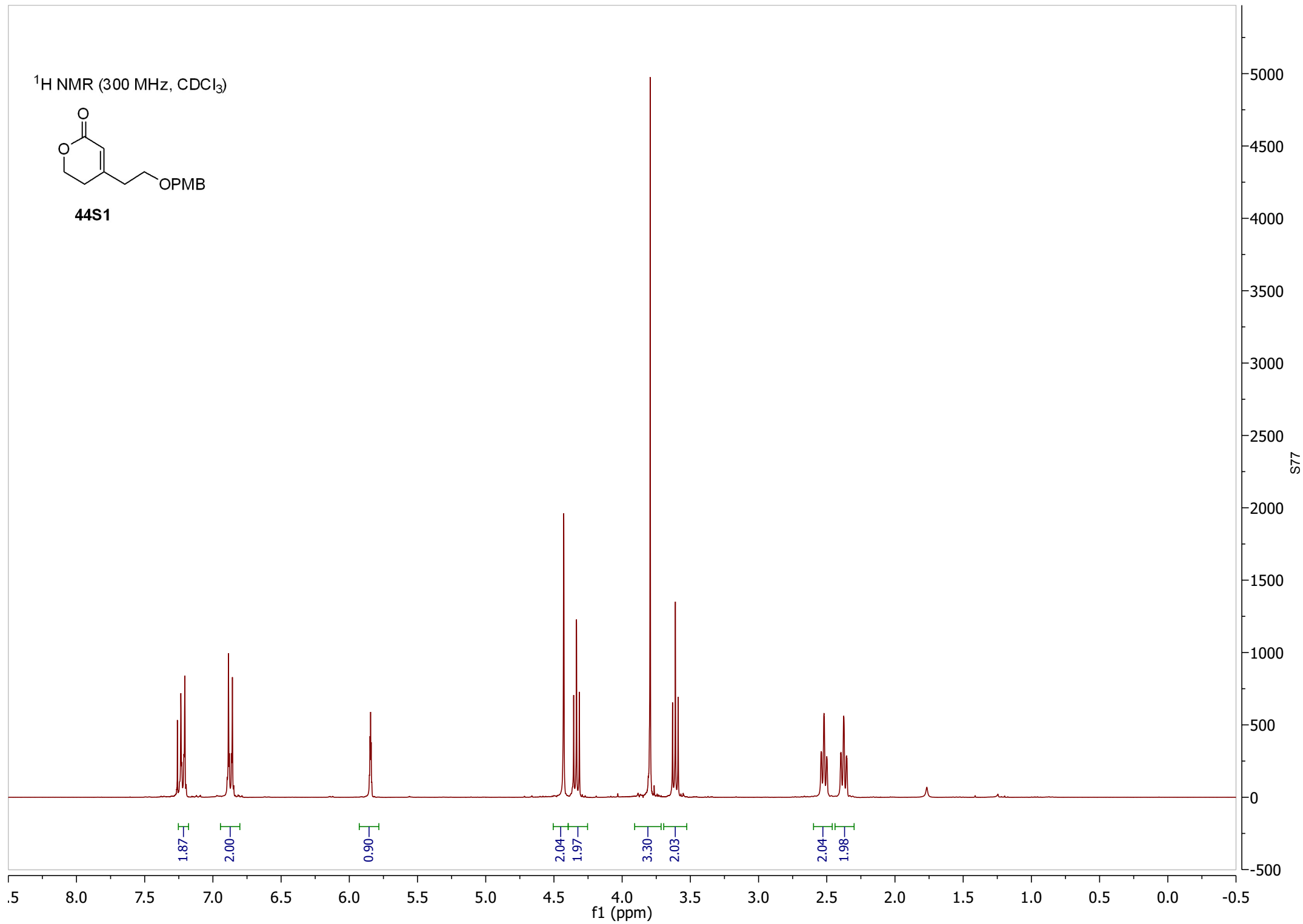
43



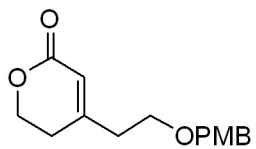
¹H NMR (300 MHz, CDCl₃)



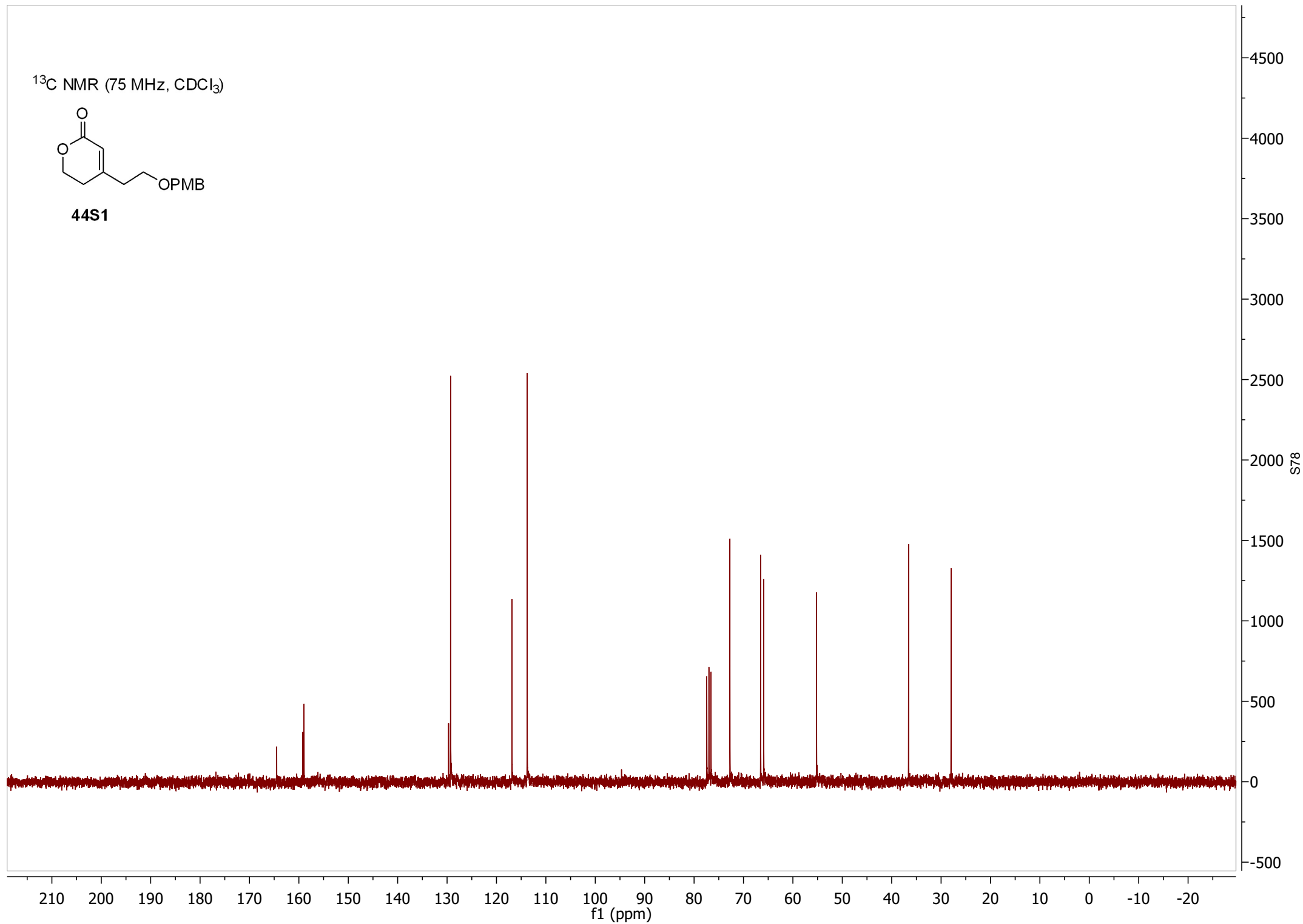
44S1



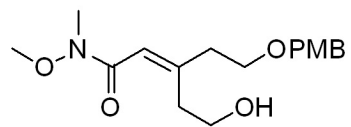
^{13}C NMR (75 MHz, CDCl_3)



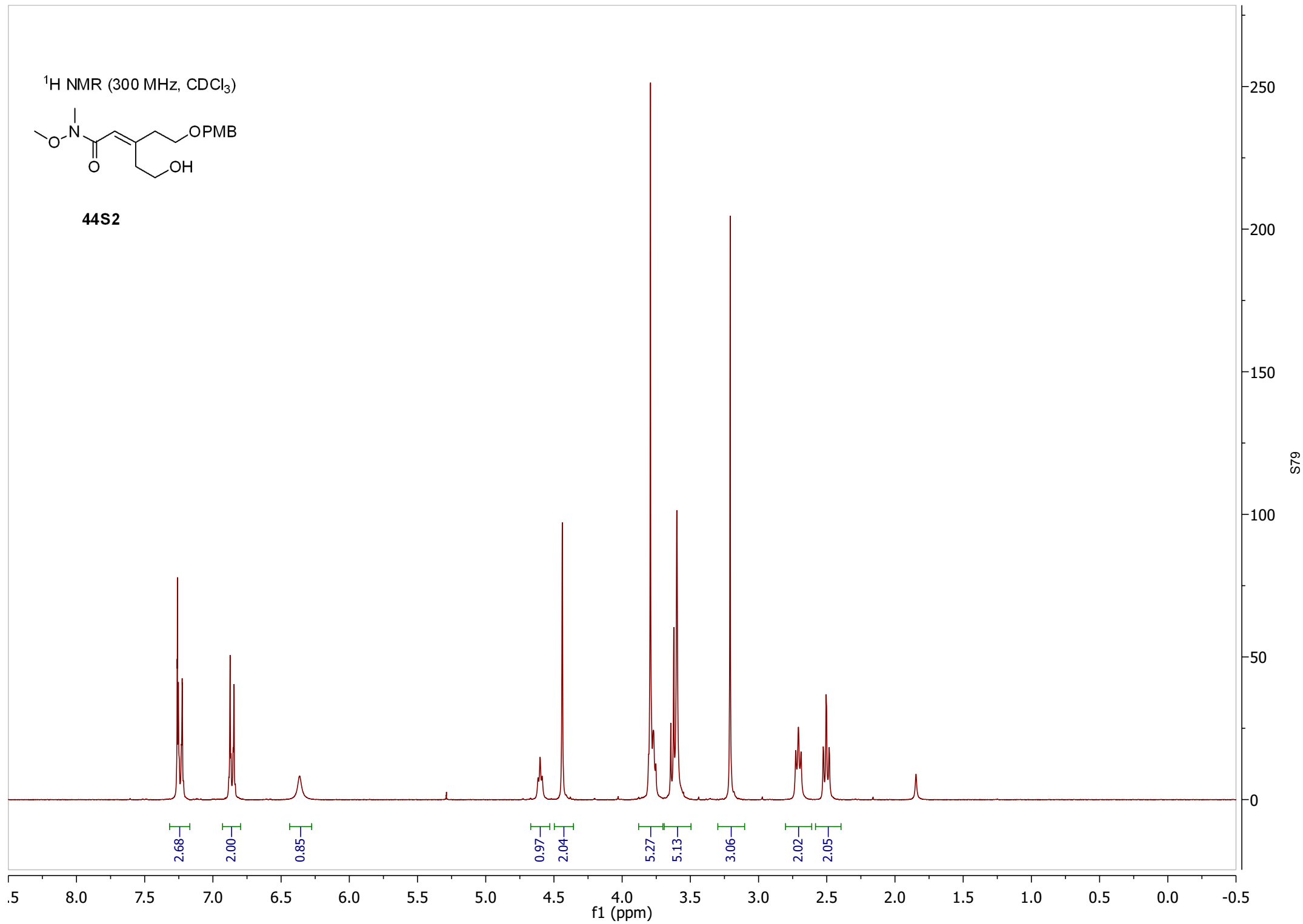
44S1



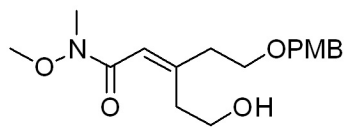
¹H NMR (300 MHz, CDCl₃)



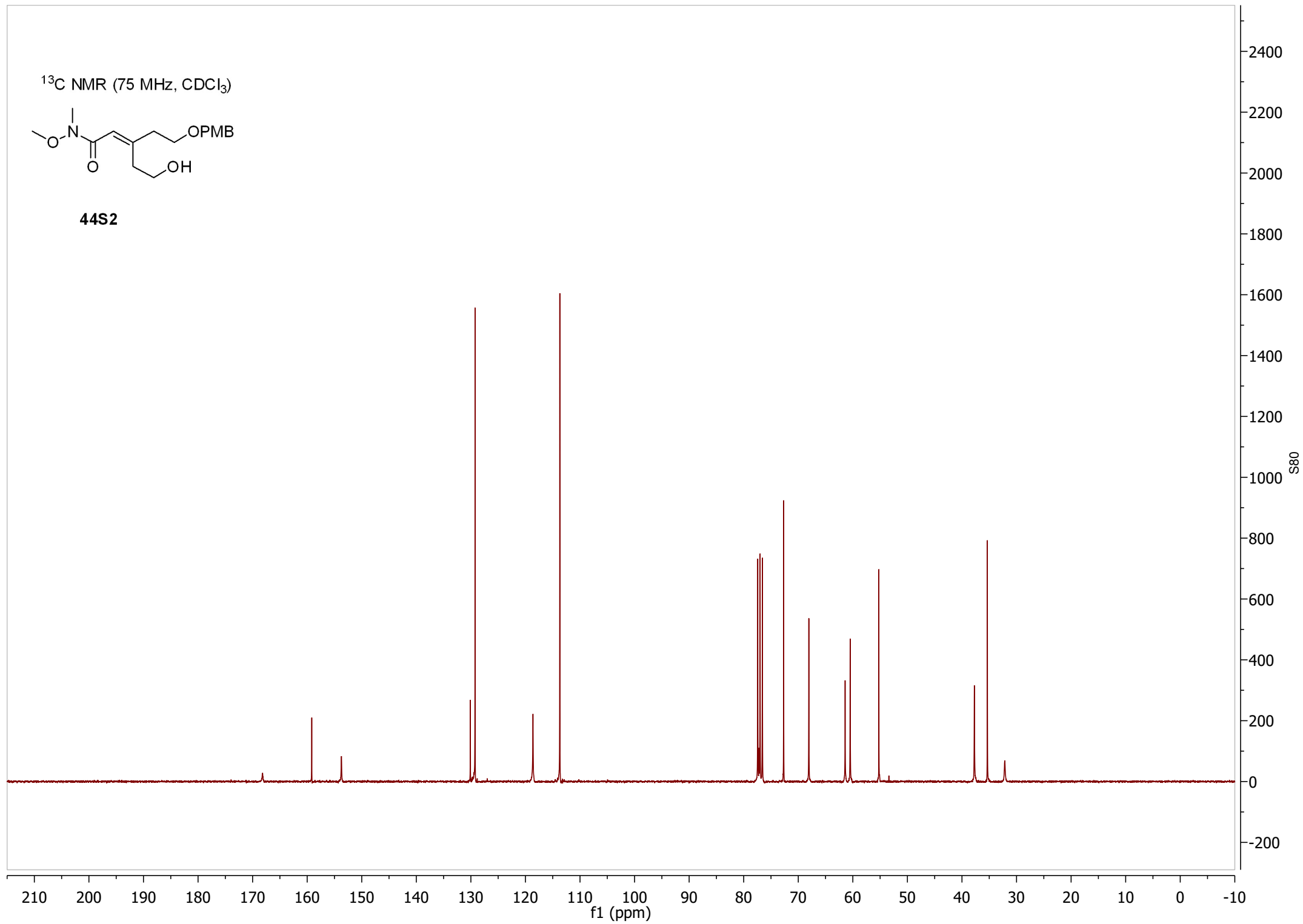
44S2



^{13}C NMR (75 MHz, CDCl_3)

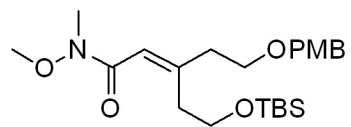


44S2

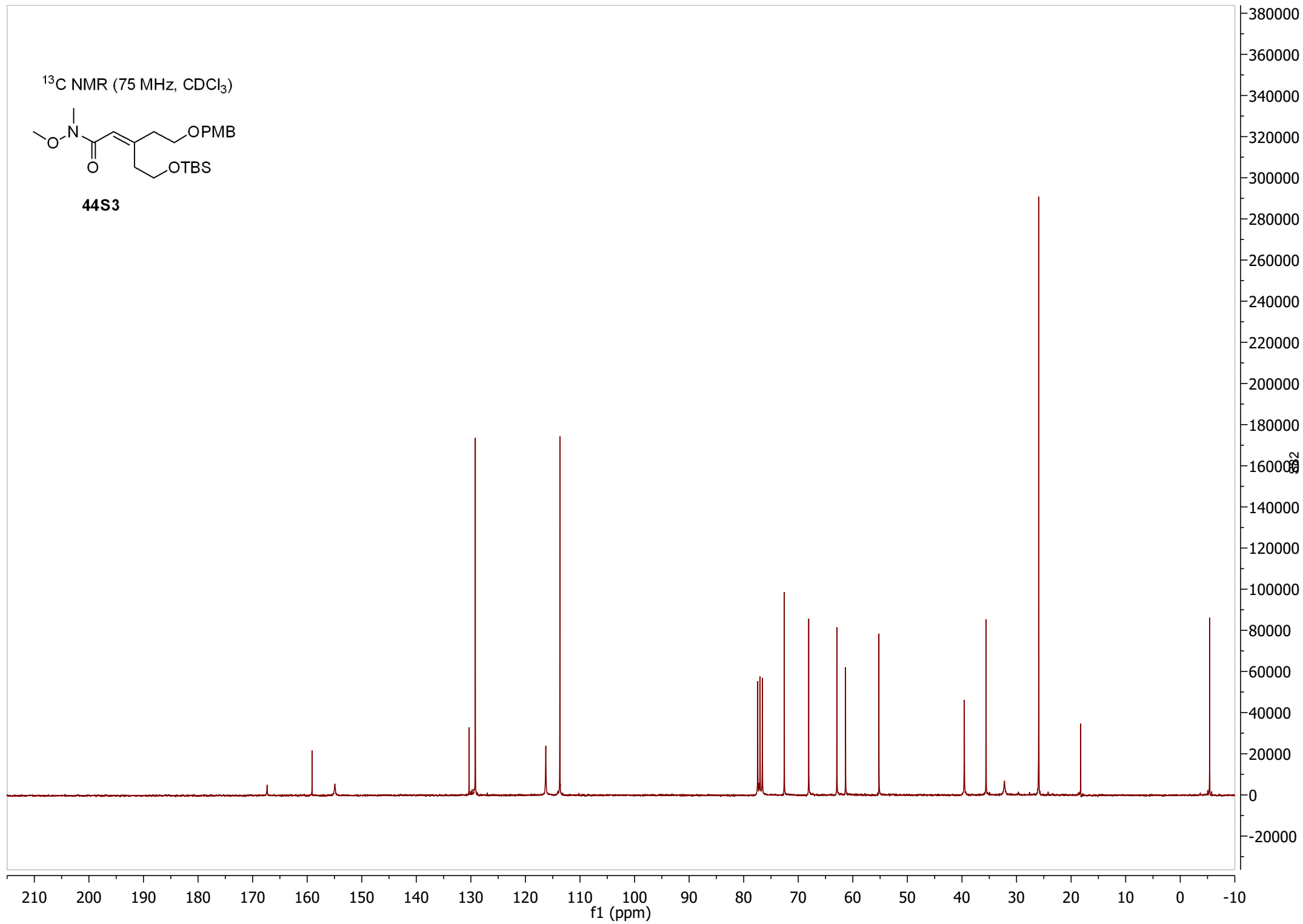


CN(C)C(=O)C(=C)CCOPMB[illegible]

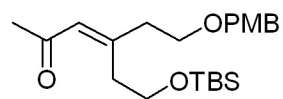
¹³C NMR (75 MHz, CDCl₃)



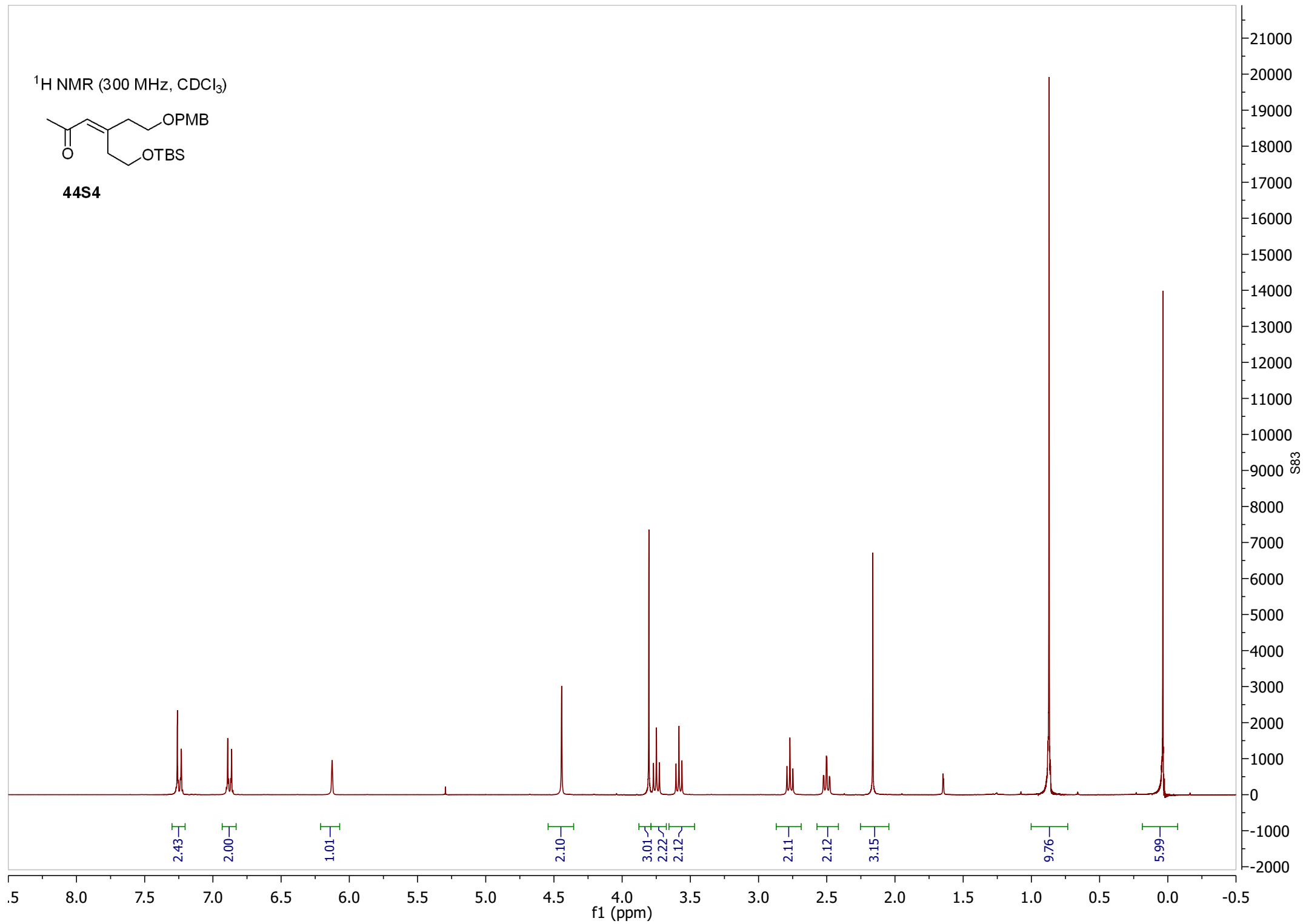
44S3



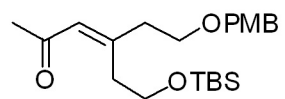
¹H NMR (300 MHz, CDCl₃)



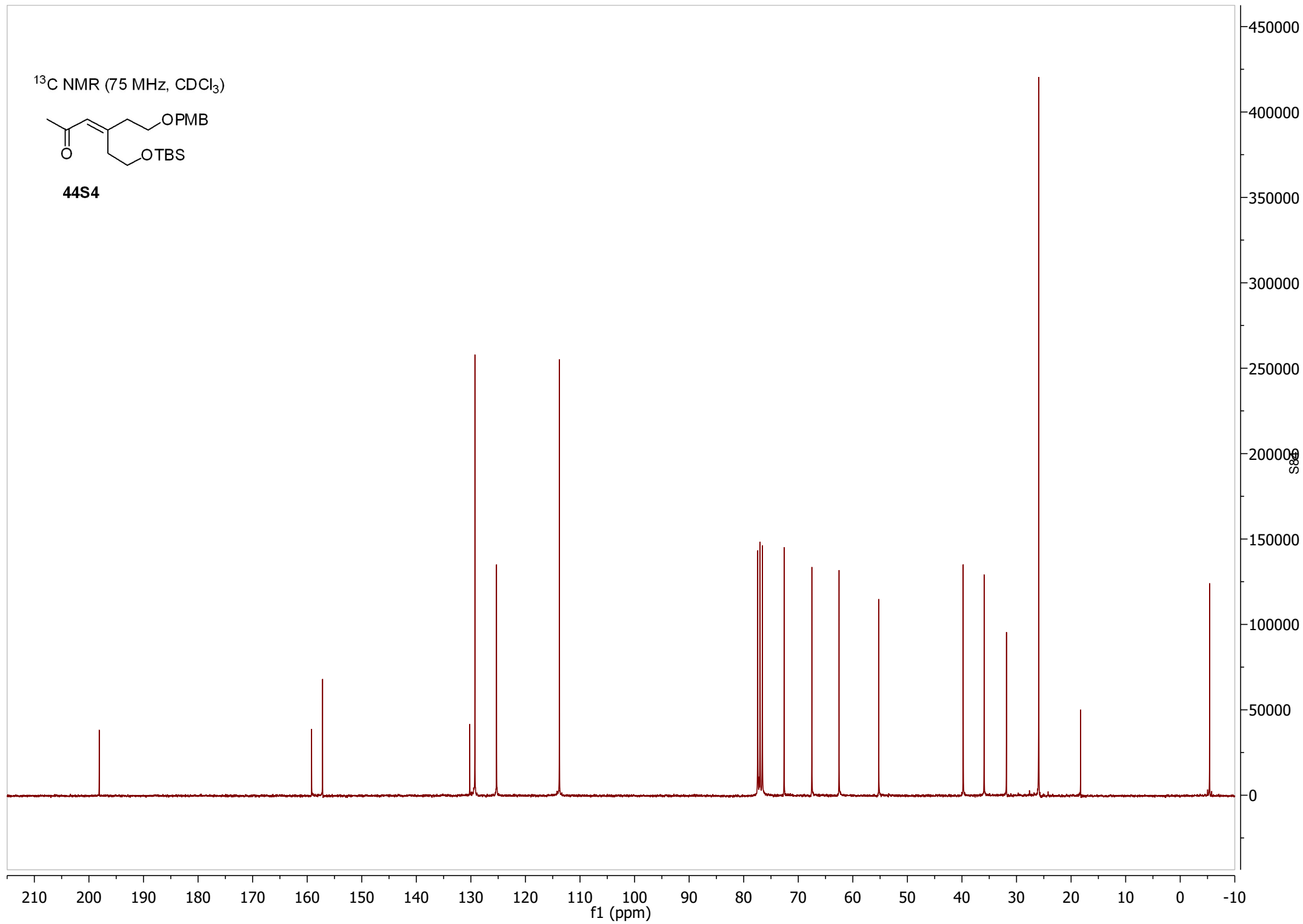
44S4



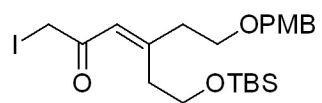
^{13}C NMR (75 MHz, CDCl_3)



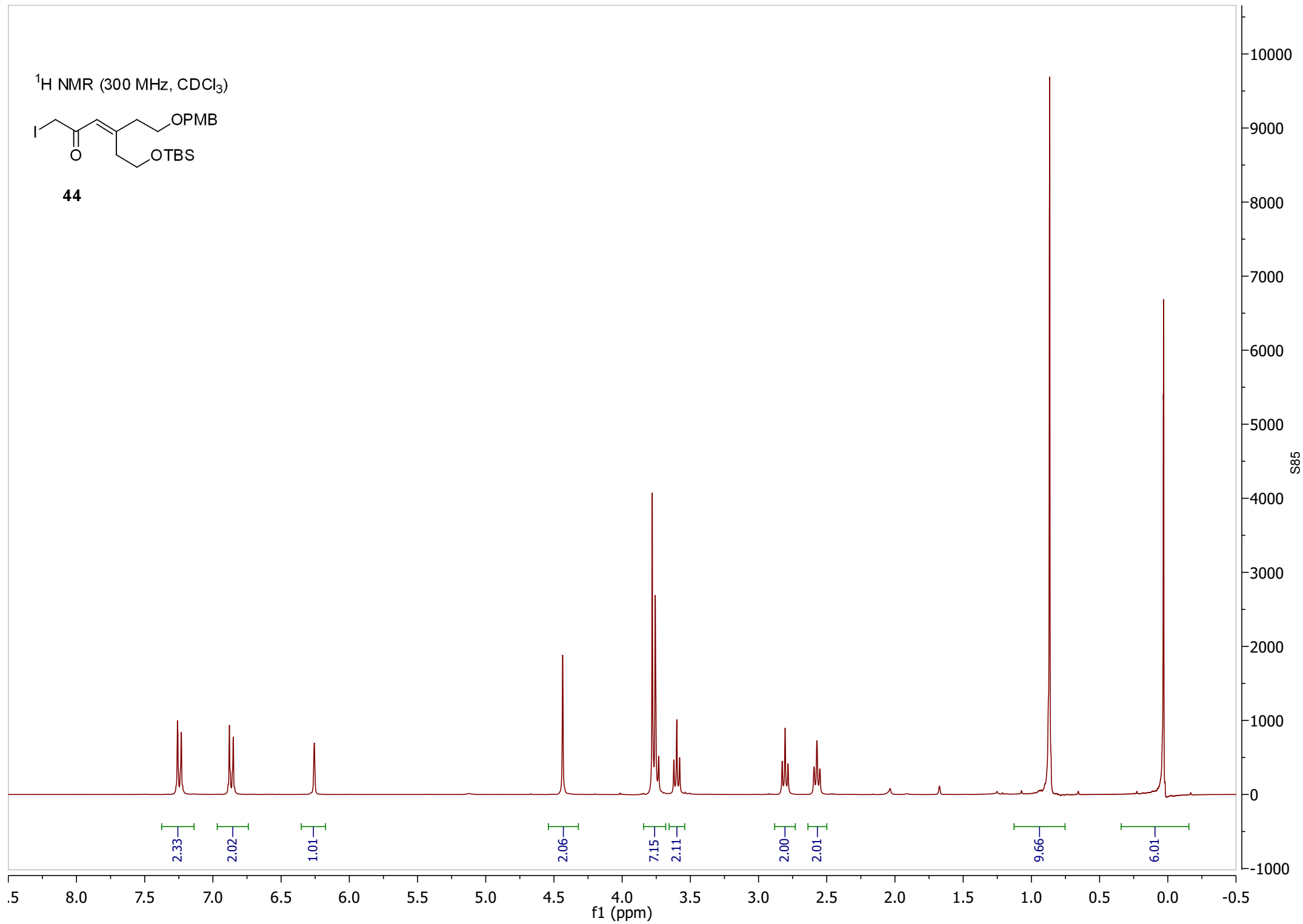
44S4



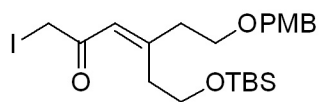
¹H NMR (300 MHz, CDCl₃)



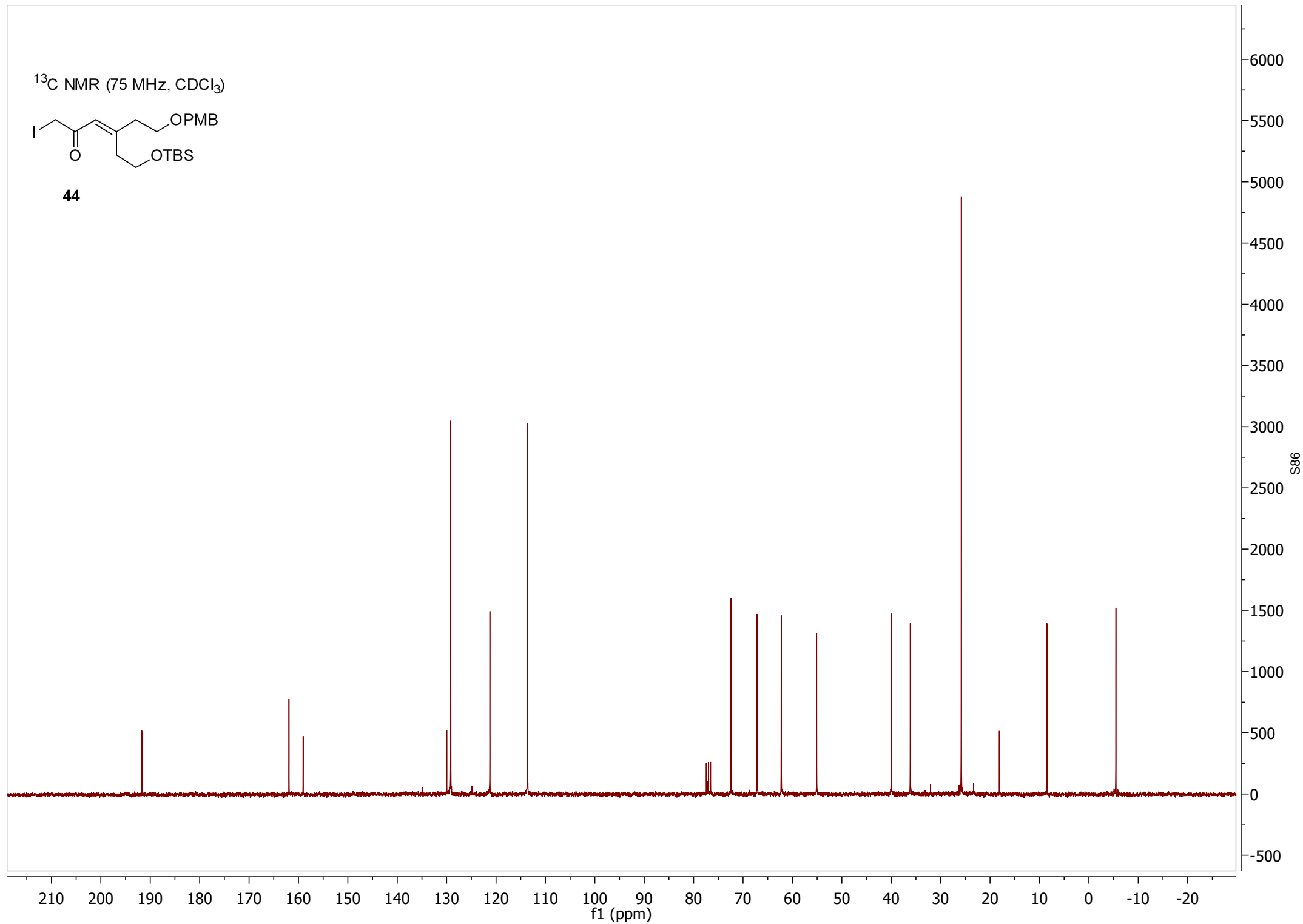
44

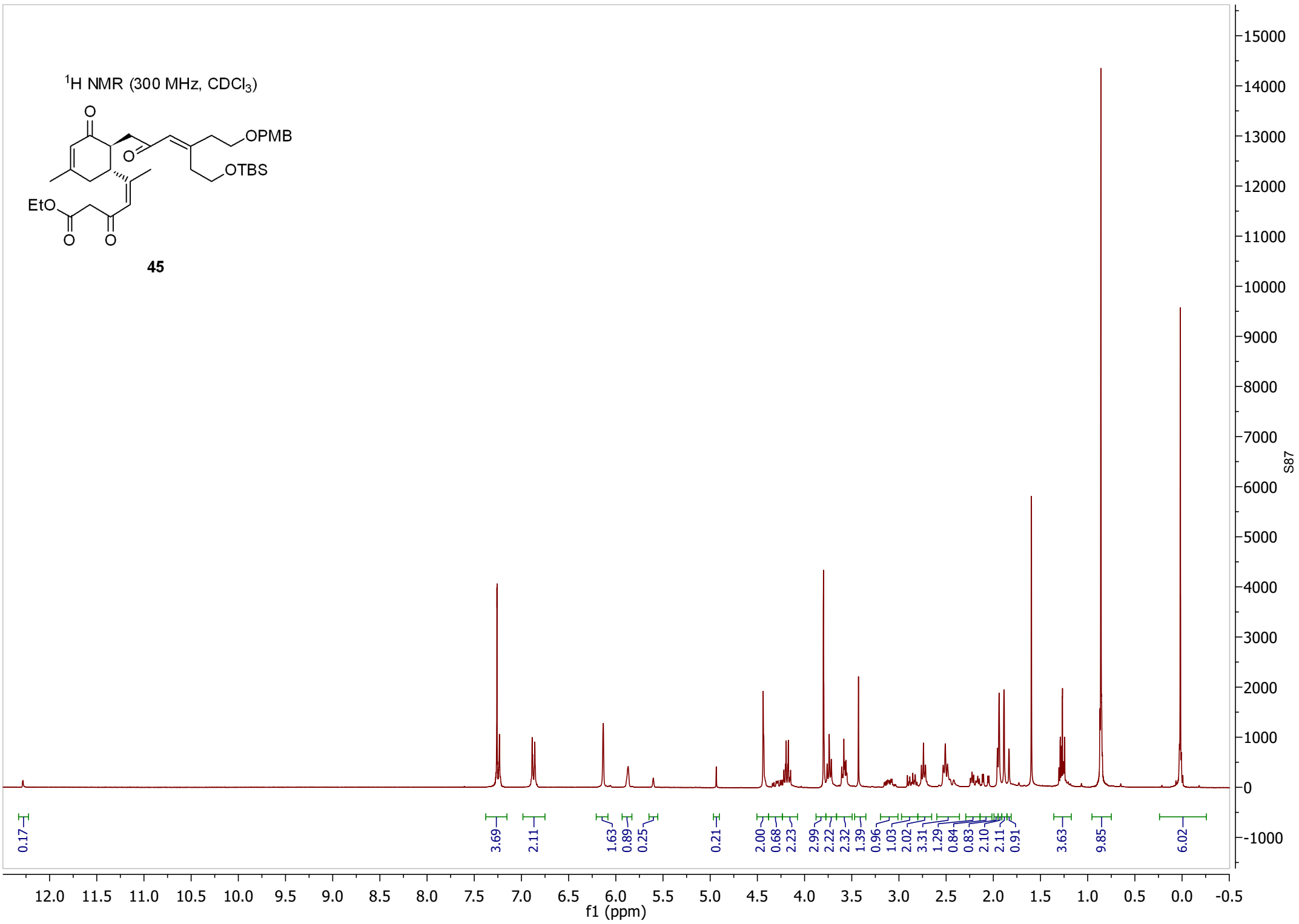
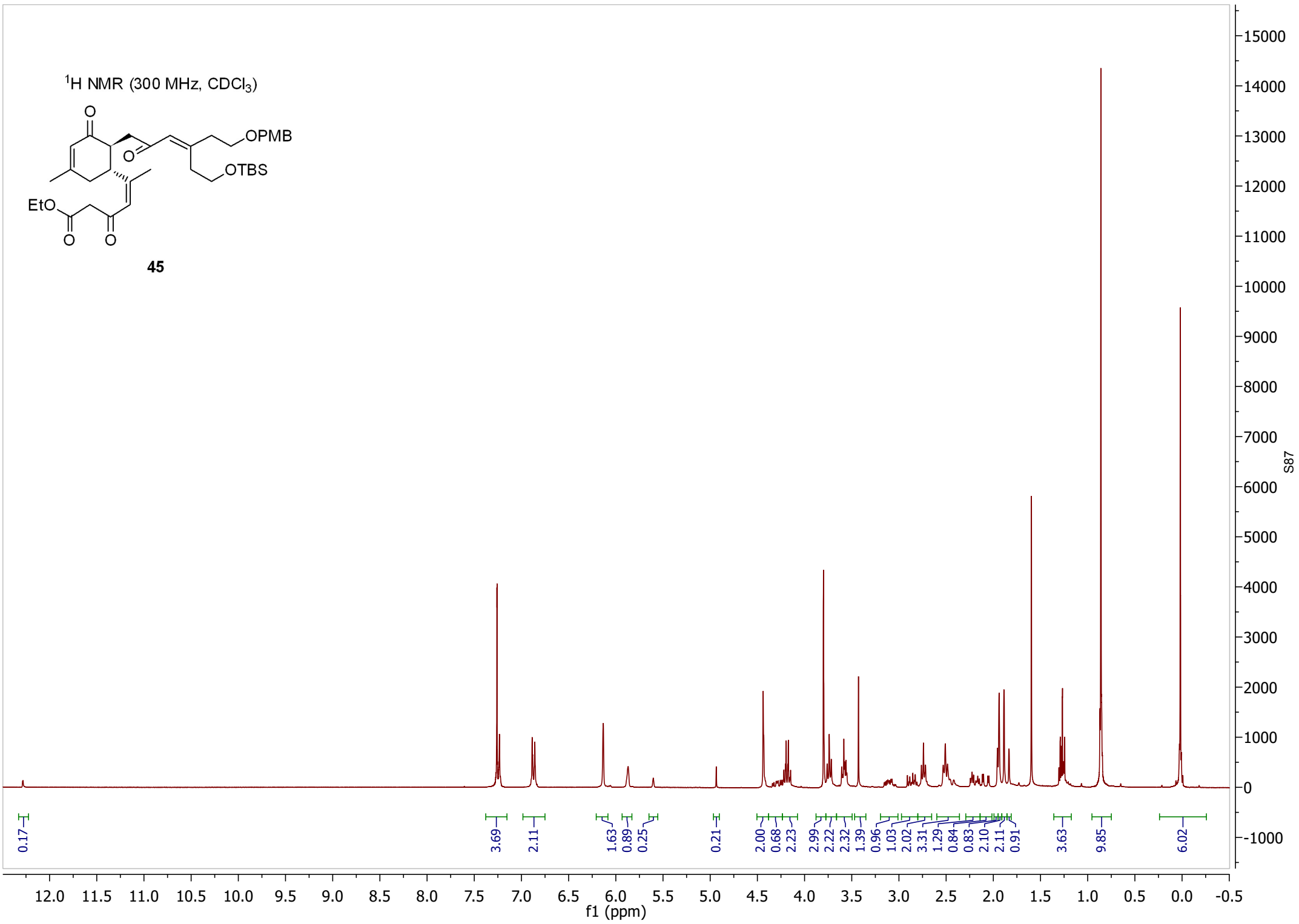


^{13}C NMR (75 MHz, CDCl_3)



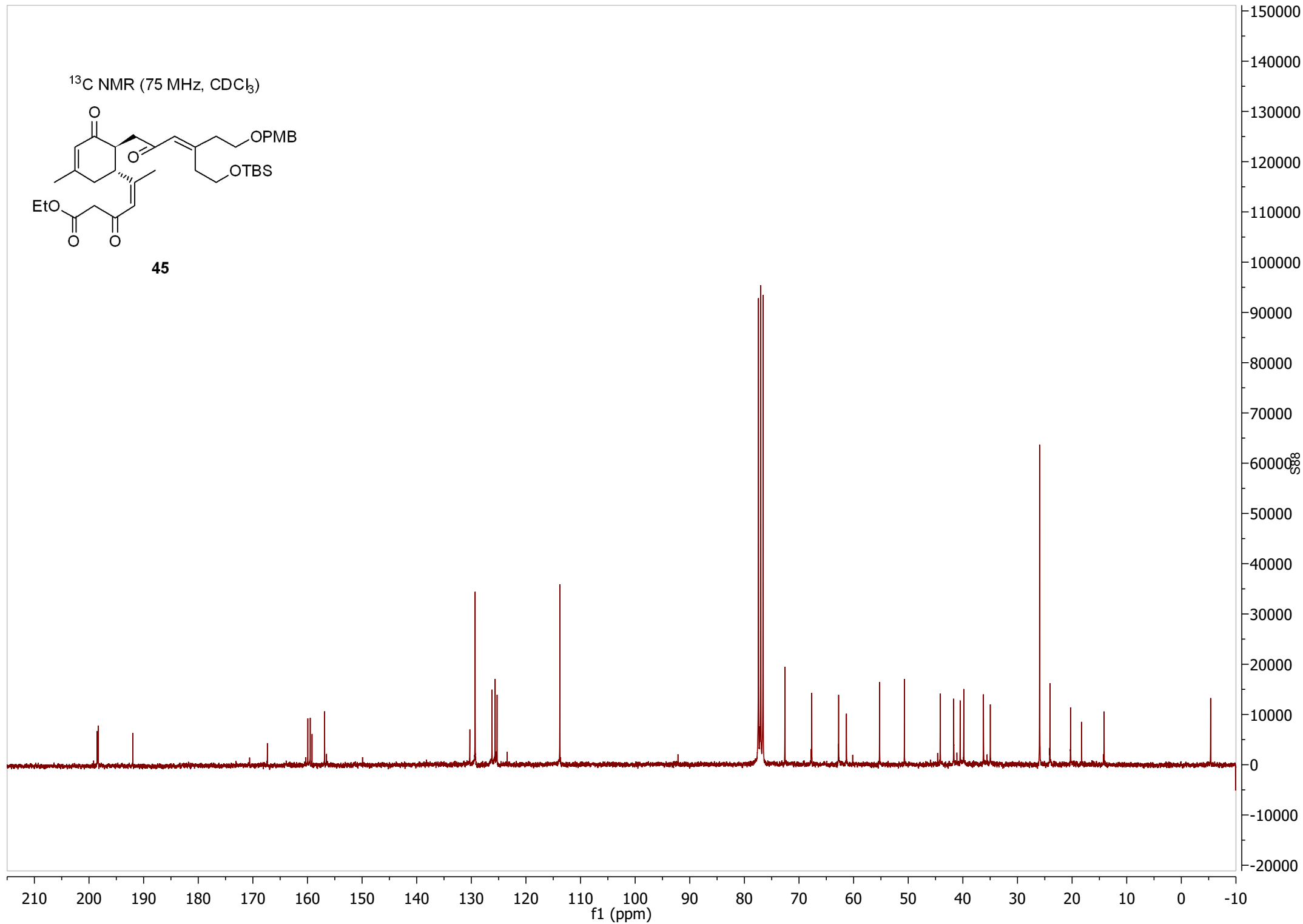
44

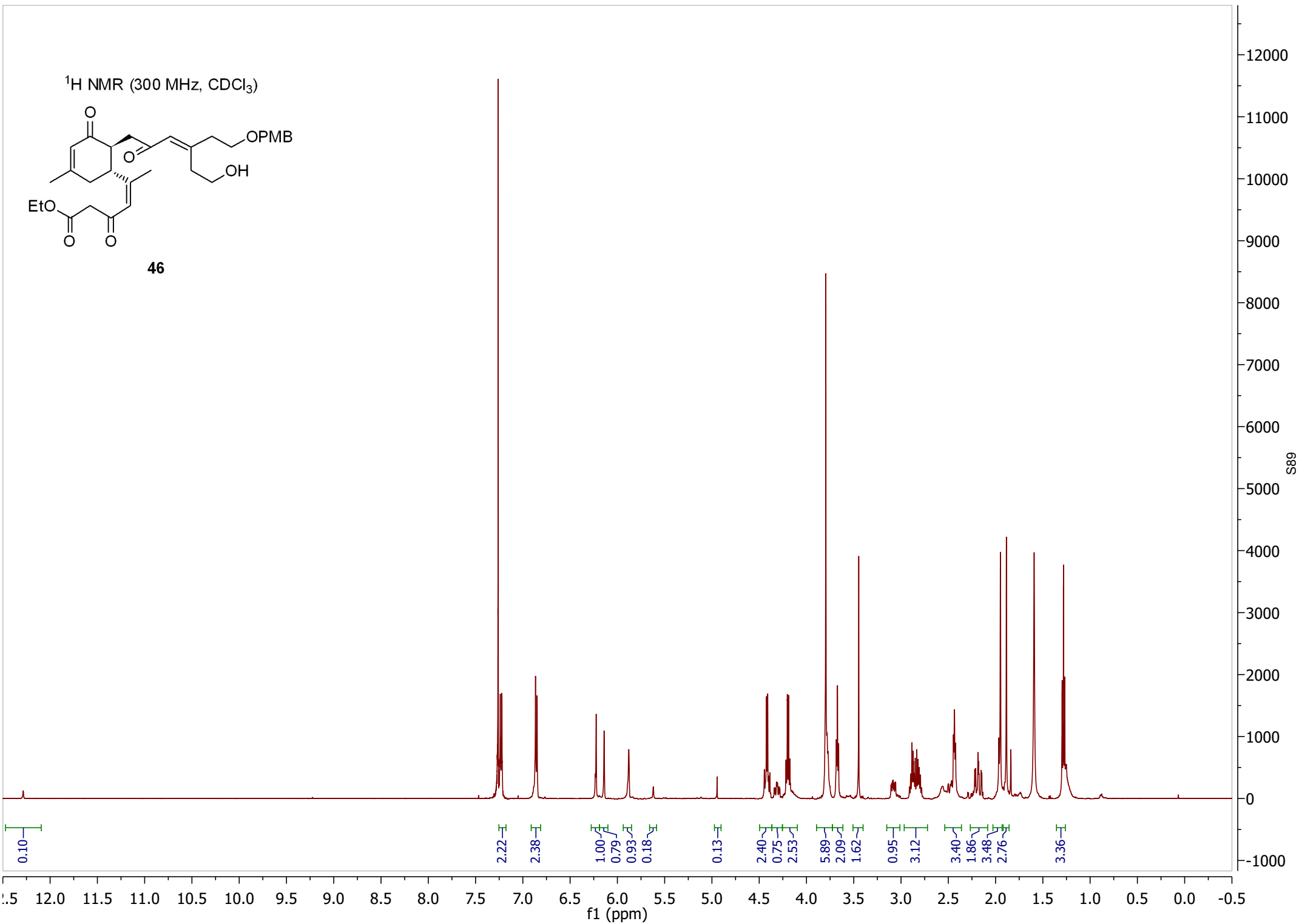




[illegible]

45





CC1=C(C)C(=O)C2=C(C1)OC(=C(C2)C=C(C)C(=O)CC(=O)OCC)C=C(C3CC(O)CC3COP(=O)(OC)OC)C4=CC=CC=C4

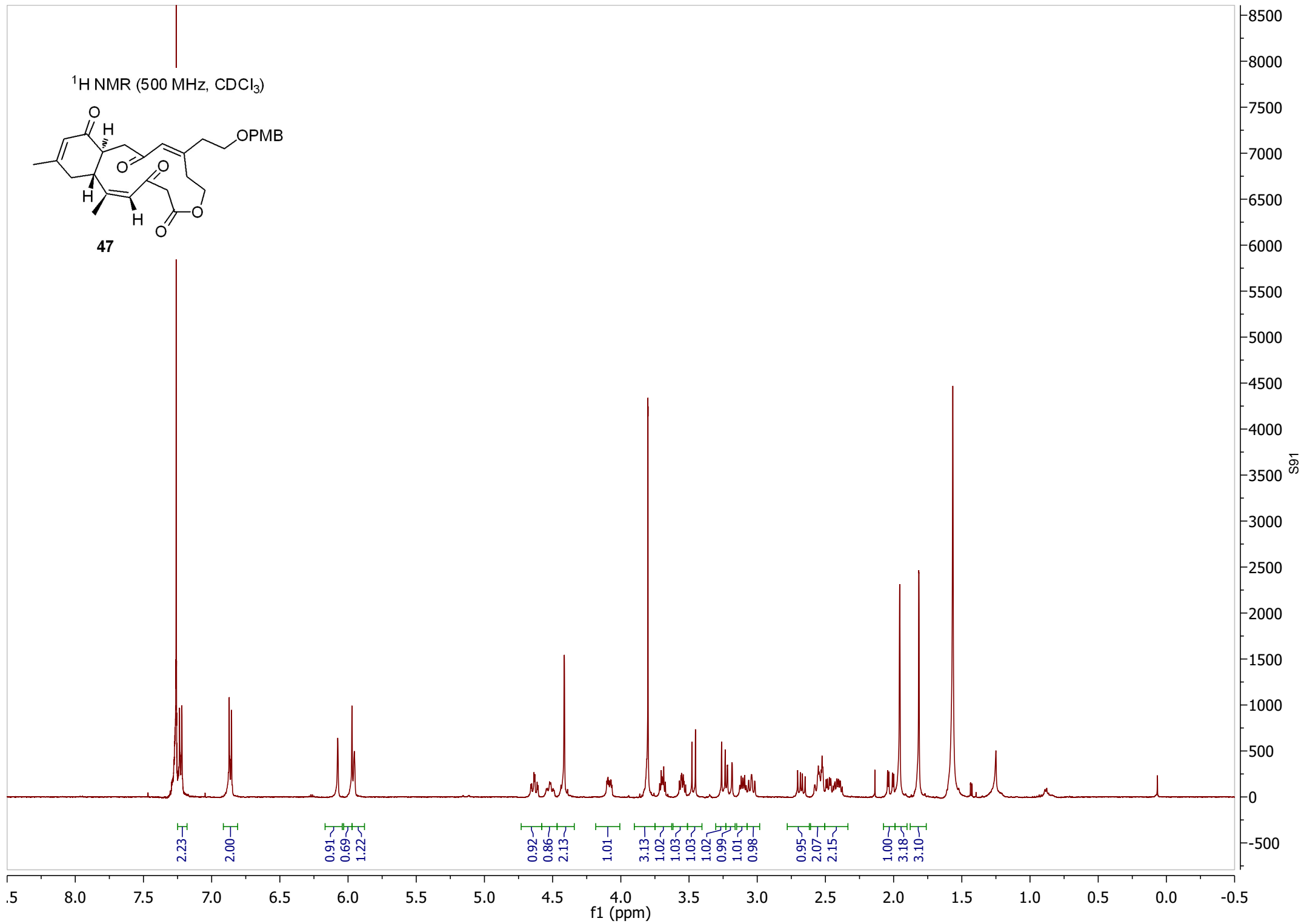
¹³C NMR (75 MHz, CDCl₃)

46

Chemical structure of compound **46** is shown in the top left corner. It is a complex molecule featuring a cyclohexanone ring with a methyl group, an ethyl ester group, and a side chain containing a double bond, a hydroxyl group, and a p-methoxybenzyl (PMB) ether group.

The ¹³C NMR spectrum displays the following peak assignments (approximate chemical shifts in ppm):

- Carbonyl carbons: ~205, ~200, ~195, ~165, ~160, ~155
- Alkene carbons: ~130, ~125, ~115
- Solvent (CDCl₃): ~77 (triplet)
- Aliphatic carbons: ~65, ~60, ~55, ~50, ~45, ~40, ~35, ~30, ~25, ~20, ~15



^{13}C NMR (125 MHz, CDCl_3)

