

**Supplementary Information**

**Hydroformylation of Olefinic Derivatives of Isosorbide and Isomannide**

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## General details

<sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR spectra were recorded at 400.1 and 100.6 MHz, respectively. For compounds **12**, **13**, and **14**, some of the <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR spectra were recorded at 800.1 and 201.2 MHz, respectively. For compound **15**, some of the <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR spectra were recorded at 700.1 and 176.1 MHz, respectively. All NMR measurements with the 400 and 700 MHz NMR spectrometers were carried out at 25 °C and NMR measurements with the 800 MHz NMR spectrometer were carried out at 15 °C. The chemical shifts for the NMR spectra are given in ppm, and are calibrated using residual solvent signals (for <sup>1</sup>H, CDCl<sub>3</sub> δ = 7.26 ppm, or toluene methyl group δ = 2.16 ppm; for <sup>13</sup>C, CDCl<sub>3</sub> δ = 77.0 ppm). The following abbreviations are used for multiplicities: s, singlet; d, doublet; t, triplet; dd, doublet of doublets; bs, broad signal. For selected compounds, NMR signals were assigned from HSQC, HMBC, NOESY and TOCSY spectra.

An FTIR spectrophotometer (ATR) was used for IR analysis.

For HRMS analysis, an LTQ Orbitrap analyzer was used.

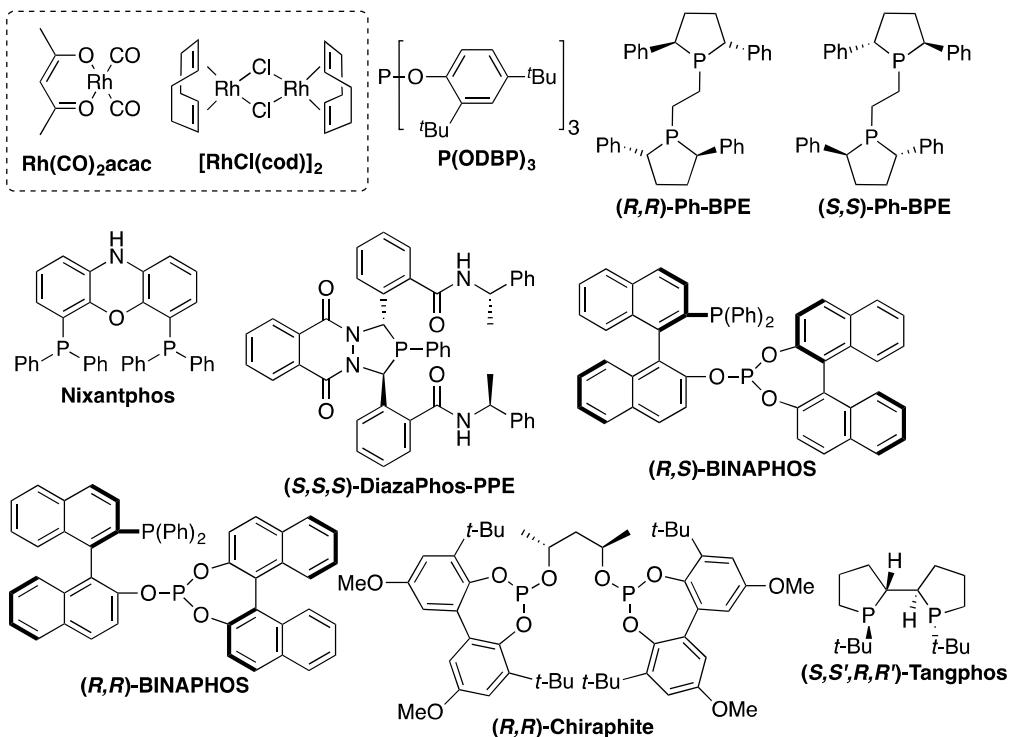
All reagents and solvents were obtained from commercial sources and were used without further purification.

Hydroformylation reactions were carried out in a high-pressure reactor (stainless steel vessel, 450 mL) in a 4 mL open glass vial using a synthetic gas mixture of 1:1 CO/H<sub>2</sub> under pressures 10–40 bar. The reactor was heated inside a rigid heating jacket with a temperature controller and a thermocouple. The gas inlet was controlled by internal analog pressure gage.

Reactions were monitored by thin-layer chromatography (TLC), and TLC plates were visualized either by UV detection or by staining with KMnO<sub>4</sub> or phosphomolybdic acid solution.

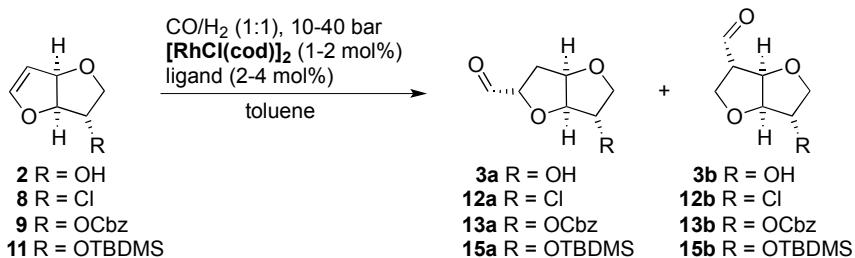
Purification of reaction products was done by flash chromatography using silica gel 60 (0.040–0.063 mm, 230–400 mesh).

## Hydroformylation of alkenes **2** and **9-10**. Screening of Rh-ligand complexes.



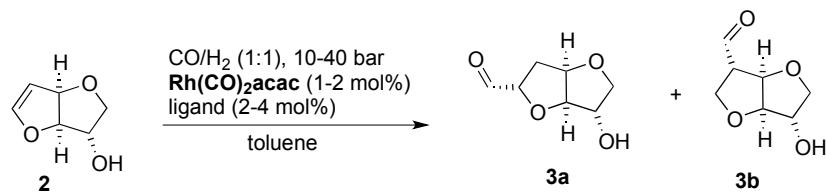
**Figure S1.** Rhodium precatalysts and ligands screened in this study.

**Table S1.** Hydroformylation of alkenes **2**, **8**, **9** and **11** with precatalyst **[RhCl(cod)]<sub>2</sub>**



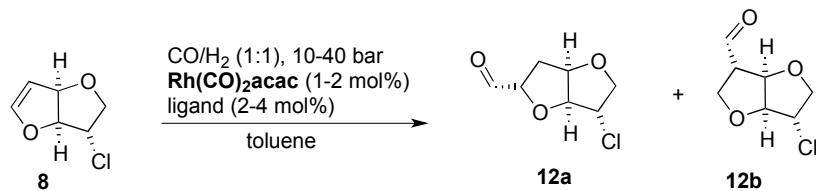
No	alkene	ligand	Temp. (°C)	P (bar)	Time (h)	a:b	Conversion (%)	Yield (a+b)%
1	<b>9</b>	BIPHEP, Nixantphos	50	20	18	n.d.	n.d.	traces
2	<b>9</b>	BIPHEP, Nixantphos	90	20	18	n.d.	<5	traces
3	<b>2</b>	Xantphos	90	20	16	-	n.d.	decomposed
4	<b>2</b>	Nixantphos	80	40	15	n.d.	n.d.	traces
5	<b>8</b>	(S,S)-Ph-BPE	80	10	4	n.d.	>95%	Cycle open, no SM
6	<b>11</b>	Nixantphos	80	40	16	n.d.	n.d.	<42% + cycle open
7	<b>11</b>	P(ODBP) <sub>3</sub>	40	30	20	n.d.	n.d.	traces
8	<b>11</b>	(R)-BINAP	40	30	20	n.d.	n.d.	traces
9	<b>11</b>	P(ODBP) <sub>3</sub>	80	40	16	n.d.	n.d.	traces

**Table S2.** Hydroformylation of alkene **2** with precatalyst Rh(CO)<sub>2</sub>acac



No	alkene	ligand	Temp. (°C)	P (bar)	time	product	a:b	Conversion (%)	Yield (a+b)%
1	<b>2</b>	P(ODBP) <sub>3</sub>	60	40	16	<b>3a/b</b>	1:2	50	12
2	<b>2</b>	P(ODBP) <sub>3</sub>	60	40	2	<b>3a/b</b>	1:1.6	99	30
3	<b>2</b>	P(ODBP) <sub>3</sub>	60	20	2	<b>3a/b</b>	1:1.3	50	30
4	<b>2</b>	P(ODBP) <sub>3</sub>	80	10	2	<b>3a/b</b>	n.d.	>80	<10
5	<b>2</b>	(R,R)-Ph-BPE	60	40	2	<b>3a/b</b>	n.d.	<5	Traces, mostly SM
6	<b>2</b>	(R,R)-Ph-BPE	60	40	19	<b>3a/b</b>	n.d.	n.d.	decomposition
7	<b>2</b>	-	60	20	14	<b>3a/b</b>	n.d.	n.d.	decomposition

**Table S3.** Hydroformylation of alkene **8** with precatalyst Rh(CO)<sub>2</sub>acac

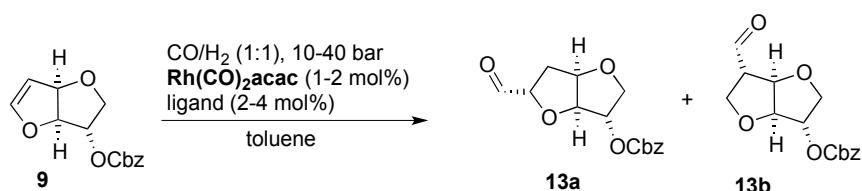


No	alkene	ligand	Temp. (°C)	P (bar)	Time (h)	product	a:b	Conversion (%)	Yield (a+b)%
1	<b>8</b>	P(ODBP) <sub>3</sub>	50	40	15	<b>12a/b</b>	n.d.	n.d.	decomposition
2	<b>8</b>	P(ODBP) <sub>3</sub>	60	40	12	<b>12a/b</b>	1:2	83	74
3	<b>8</b>	P(ODBP) <sub>3</sub>	60	10	2	<b>12a/b</b>	1:2	>99	65
4	<b>8</b>	P(ODBP) <sub>3</sub>	80	40	13	<b>12a/b</b>	n.d.	n.d.	traces
5	<b>8</b>	-	60	20	14	<b>12a/b</b>	n.d.	n.d.	Starting material
6	<b>8</b>	P(ODBP) <sub>3</sub>	80	10	3	<b>12a/b</b>	2.4:1	n.d.	68
7	<b>8</b>	P(ODBP) <sub>3</sub>	80	10	4	<b>12a/b</b>	2.8:1	n.d.	70
8	<b>8</b>	(S,S)-Ph-BPE	50	30	4	<b>12a/b</b>	1:1.8	39	7
9	<b>8</b>	(R,R)-Chiraphite	50	30	4	<b>12a/b</b>	4.3:1	71	15
10	<b>8</b>	(R,R)-Ph-BPE	50	40	15	<b>12a/b</b>	n.d.	n.d.	Traces, decomposition
11	<b>8</b>	(R,R)-Ph-BPE	60	40	27	<b>12a/b</b>	n.d.	<5	Traces, mostly starting material
12	<b>8</b>	(R,R)-Ph-BPE	60	40	48	<b>12a/b</b>	n.d.	n.d.	decomposition
13	<b>8</b>	(R,R)-Ph-BPE	60	20	16	<b>12a/b</b>	n.d.	n.d.	Unidentified sideproduct
14	<b>8</b>	(R,R)-Ph-BPE	80	40	16	<b>12a/b</b>	1.6:1	n.d.	<99
15	<b>8</b>	(S,S)-Ph-BPE	80	10	2	<b>12a/b</b>	1:8	n.d.	24
16	<b>8</b>	(S,S)-Ph-BPE	80	40	4	<b>12a/b</b>	3.5:1	n.d.	22
17	<b>8</b>	(S,S,S)-diazaPhos-PPE	80	10	2	<b>12a/b</b>	1:2	50	50
18	<b>8</b>	(S,S,S)-diazaPhos-PPE	80	40	4	<b>12a/b</b>	1:1.6	>99	60
19	<b>8</b>	(S,S',R,R')-Tangphos	80	10	4	<b>12a/b</b>	n.d.	n.d.	-
20	<b>8</b>	(R,R)-Chiraphite	80	40	4	<b>12a/b</b>	n.d.	n.d.	<99

No	alkene	ligand	Temp. (°C)	P (bar)	Time (h)	product	a:b	Conversion (%)	Yield (a+b)%
21	<b>8</b>	( <i>R,S</i> )-BINAPHOS	80	10	4	<b>12a/b</b>	mix <sup>a</sup>	n.d.	40
22	<b>8</b>	( <i>R,R</i> )-BINAPHOS	80	10	4	<b>12a/b</b>	mix <sup>a</sup>	n.d.	36
23	<b>8</b>	( <i>R,R</i> )-Ph-BPE	80	40	4	<b>12a/b</b>	1:1.5	70	64
24	<b>8</b>	( <i>R,R</i> )-Ph-BPE	80	30	5	<b>12a/b</b>	1:1.1	89	86
25	<b>8</b>	( <i>S,S</i> )-Ph-BPE	80	30	4	<b>12a/b</b>	1:6.3	89	60
26	<b>8 (0.8 g)</b>	( <i>S,S</i> )-Ph-BPE	80	30	5	<b>12a/b</b>	1:46	70	47

<sup>a</sup>Mixture of 3 or more isomeric aldehyde products (regiosomers together with at least one additional diastereomer in significant amount)

**Table S4.** Hydroformylation of alkene **9** with precatalyst Rh(CO)<sub>2</sub>acac



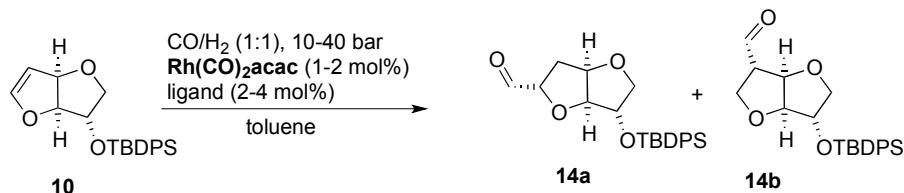
No	alkene	ligand	Temp. (°C)	P (bar)	Time (h)	product	a:b	Conversion (%)	Yield (a+b)%
1	<b>9</b>	-	60	20	14	<b>13a/b</b>	4:1	<5	Traces, mostly starting material
2	<b>9</b>	P(ODBP) <sub>3</sub>	60	40	14	<b>13a/b</b>	1:2	95	79
3	<b>9</b>	P(ODBP) <sub>3</sub>	80	10	2	<b>13a/b</b>	3.4:1	n.d.	92
4	<b>9</b>	P(ODBP) <sub>3</sub>	80	10	2	<b>13a/b</b>	3:1	n.d.	83
5	<b>9</b>	P(ODBP) <sub>3</sub>	80	1	2	<b>13a/b</b>	n.d.	<5	traces
6	<b>9</b>	( <i>R,R</i> )-Ph-BPE	60	40	15	<b>13a/b</b>	14:1 <sup>b</sup>	n.d.	54
7	<b>9</b>	( <i>R,R</i> )-Ph-BPE	60	40	48	<b>13a/b</b>	n.d.	80	decomposition
8	<b>9</b>	( <i>R,R</i> )-Ph-BPE	80	40	16	<b>13a/b</b>	1.6:1	n.d.	<99
9	<b>9</b>	( <i>S,S</i> )-Ph-BPE	80	40	4	<b>13a/b</b>	poor	n.d.	90
10	<b>9</b>	( <i>S,S</i> )-Ph-BPE	80	10	2	<b>13a/b</b>	1:13	n.d.	30
11	<b>9 (1 g)</b>	( <i>S,S</i> )-Ph-BPE	80	10	2	<b>13a/b</b>	1.20	40	38
12	<b>9 (0.5 g)</b>	( <i>S,S</i> )-Ph-BPE	80	10	4	<b>13a/b</b>	mix <sup>a</sup>	50	49
13	<b>9 (1 g)</b>	( <i>S,S</i> )-Ph-BPE	80	10	2.75	<b>13a/b</b>	1:17.3	70	68
15	<b>9</b>	( <i>S,S,S</i> )-diazaPhos-PPE	80	10	2	<b>13a/b</b>	1:2	60	54%
16	<b>9</b>	( <i>S,S,S</i> )-diazaPhos-PPE	80	40	4	<b>13a/b</b>	mix <sup>a</sup>	<99	<99
17	<b>9</b>	( <i>S,S',R,R'</i> )-Tangphos	80	10	2	<b>13a/b</b>	n.d.	n.d.	9
18	<b>9</b>	( <i>R,R</i> )-Chiraphite	80	10	2	<b>13a/b</b>	n.d.	n.d.	41
19	<b>9</b>	( <i>R,R</i> )-Chiraphite	80	10	2	<b>13a/b</b>	2:1	n.d.	48
20	<b>9</b>	( <i>R,R</i> )-Chiraphite	80	10	16	<b>13a/b</b>	n.d.	82	80

No	alkene	ligand	Temp. (°C)	P (bar)	Time (h)	product	a:b	Conversion (%)	Yield (a+b)%
21	<b>9</b>	( <i>R,R</i> )-Chiraphite	80	40	4	<b>13a/b</b>	1.5:1	75	37
22	<b>9</b>	( <i>R,R</i> )-Chiraphite	50	30	4	<b>13a/b</b>	1.8:1	n.d.	21
23	<b>9</b>	Nixantphos	80	20	2	<b>13a/b</b>	n.d.	<5	Traces, mostly starting material
24	<b>9</b>	( <i>R,S</i> )-BINAPHOS	80	10	4	<b>13a/b</b>	1:2.7	66	38
25	<b>9</b>	( <i>R,R</i> )-BINAPHOS	80	10	4	<b>13a/b</b>	1:2	60	59

<sup>a</sup>Mixture of 3 or more isomeric aldehyde products (regiosomers together with at least one additional diastereomer in significant amount);

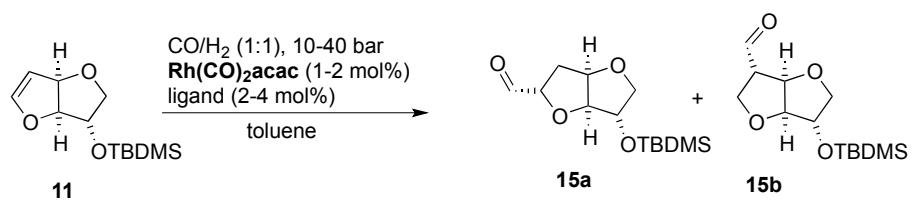
<sup>b</sup>Repeating this experiment gave lower regioselectivity

**Table S5.** Hydroformylation of alkene **10** with precatalyst Rh(CO)<sub>2</sub>acac



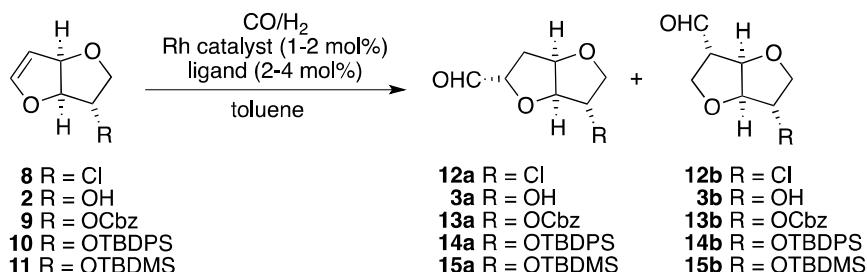
No	alkene	ligand	Temp. (°C)	P (bar)	Time (h)	product	a:b	Conversion (%)	Yield (a+b)%
1	<b>10</b>	P(ODBP) <sub>3</sub>	60	40	2	<b>14a/b</b>	1:1	70	67
2	<b>10</b>	P(ODBP) <sub>3</sub>	60	10	16	<b>14a/b</b>	2:1	55	51
3	<b>10</b>	P(ODBP) <sub>3</sub>	60	20	2	<b>14a/b</b>	1.4:1	n.d.	20
4	<b>10</b>	-	60	20	2	<b>14a/b</b>	n.d.	>95	decomposition
5	<b>10</b>	P(ODBP) <sub>3</sub>	80	10	2	<b>14a/b</b>	3.7:1	n.d.	60
6	<b>10</b>	P(ODBP) <sub>3</sub>	80	10	2	<b>14a/b</b>	3.8:1	<99	<99
7	<b>10</b>	P(ODBP) <sub>3</sub>	80	10	2	<b>14a/b</b>	4:1	<99	<99
8	<b>10</b>	( <i>R,R</i> )-Ph-BPE	60	40	19	<b>14a/b</b>	1.3:1	<5	Traces, mostly starting material
9	<b>10</b>	( <i>S,S</i> )-Ph-BPE	50	30	4	<b>14a/b</b>	1:1.2	n.d.	10
10	<b>10</b>	( <i>S,S</i> )-Ph-BPE	80	10	2	<b>14a/b</b>	>1:20 (dm 7:1)	n.d.	70
11	<b>10</b>	( <i>S,S</i> )-Ph-BPE	80	10	2	<b>14a/b</b>	1:1.1	n.d.	52
12	<b>10</b>	( <i>S,S</i> )-Ph-BPE	80	10	4	<b>14a/b</b>	1:1.3	n.d.	61
13	<b>10</b>	( <i>S,S</i> )-Ph-BPE	80	10	16	<b>14a/b</b>	1.6:1	<99	<99
14	<b>10</b>	( <i>S,S</i> )-Ph-BPE	80	40	4	<b>14a/b</b>	1:1.4	n.d.	<99
15	<b>10</b>	( <i>S,S,S</i> )-diazaPhos-PPE	80	10	2	<b>14a/b</b>	1.9:1	76	75
16	<b>10</b>	( <i>S,S',R,R'</i> )-Tangphos	80	10	2	<b>14a/b</b>	n.d.	60	57
17	<b>10</b>	( <i>R,R</i> )-Chiraphite	80	10	2	<b>14a/b</b>	1.2:1	51	21
18	<b>10</b>	( <i>R,R</i> )-BINAPHOS	80	10	4	<b>14a/b</b>	1.3:1	51	35

**Table S6.** Hydroformylation of alkene **11** with precatalyst Rh(CO)<sub>2</sub>acac



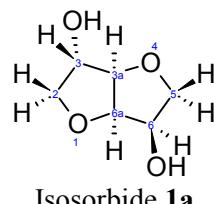
No	alkene	ligand	Temp. (°C)	P (bar)	Time (h)	product	a:b	Conversion (%)	Yield (a+b)%
1	<b>11</b>	P(ODBP) <sub>3</sub>	60	40	14	<b>15a/b</b>	1:1	>95	64
2	<b>11</b>	P(ODBP) <sub>3</sub>	80	10	4	<b>15a/b</b>	3.7:1	90	86

## Elucidation of regio- and diastereoisomers



For the determination of relative configurations of the obtained formyl derivatives **12-14** (Scheme S1) with bicyclic hexahydrofuran[3,2-*b*]furan (synonymous with 2,6-dioxabicyclo[3.3.0]octane or 1,4:3,6-dianhydro-2,5-dideoxyhexitol) skeleton, related to isosorbide **1a** structure, the latter is a good starting point for this analysis.

In a recent report on NMR of unsubstituted isosorbide 300 MHz <sup>1</sup>H spectrum is reported without detailed assignment.<sup>1</sup> At 800 MHz 18 2-5 bond <sup>1</sup>H-<sup>1</sup>H spin spin coupling constants can be measured and all *exo* and *endo* protons can be assigned via these coupling constants and NOE correlations.



**Table S7.** NMR chemical shifts and <sup>1</sup>H spin-spin coupling constants of isosorbide at 298K in CDCl<sub>3</sub> solution

	<i>Chemical shifts (ppm)</i>		<i>Coupling constants (Hz)</i>									
	$\delta^1\text{H}$	$\delta^{13}\text{C}$	$2_{\text{exo}}$	$2_{\text{endo}}$	$3_{\text{endo}}$	$3a_{\text{exo}}$	$6a_{\text{exo}}$	$6_{\text{exo}}$	$5_{\text{exo}}$	$5_{\text{endo}}$	$\text{OH-}3_{\text{exo}}$	$\text{OH-}6_{\text{endo}}$
<b>2<sub>exo</sub></b>	3.96	75.7										
<b>2<sub>endo</sub></b>	3.91		10.0									
<b>3<sub>endo</sub></b>	4.36	76.5	0.4	3.4								
<b>3a<sub>exo</sub></b>	4.39	88.1	0.9	0.3	1.2							
<b>6a<sub>exo</sub></b>	4.65	81.6	0.9			4.4						
<b>6<sub>exo</sub></b>	4.29	72.2	0.4				5.4					
<b>5<sub>exo</sub></b>	3.85							6.0				
<b>5<sub>endo</sub></b>	3.55	73.5					0.6	5.8	9.5			
<b>OH-3<sub>exo</sub></b>	2.61	—		0.3	4.8							
<b>OH-6<sub>endo</sub></b>	2.84	—						6.9	0.3			

The results of Table S7 are based on various 1D and 2D FT experiments, including 2D NOESY correlations. The most useful NOESY correlation peaks were observed between *endo* protons at C2 and C5 and *exo* protons from these carbons to bridgehead protons. From the two hydroxyl protons in isosorbide the *exo* hydroxyl at C3 has about 3 times larger temperature shift value compared to *endo*-OH at C6 (14.5 vs 5.1 Hz/deg), confirming strong intramolecular hydrogen bond of *endo* OH group.

Further illustration of segmental motion of isosorbide molecule is demonstrated by spin-lattice relaxation times of its carbon atoms. Intermolecular interactions are favored with *exo* hydroxyl groups and thus the effective anchor group is 3-OH, resulting in faster relaxation of C3 as compared to C6 (2.63 and 3.08 s). This segmental motion is also reflected on adjacent to OH groups carbon atoms: C2 and C5 1.44 s and 2.18 s, respectively, and C3a and C6a 2.67 s and 2.76 s, respectively, with mean standard deviation less than 0.01 s.

In addition to <sup>1</sup>H - <sup>1</sup>H spin spin coupling constants, one bond <sup>13</sup>C-<sup>13</sup>C coupling constants were measured from the satellites of proton decoupled <sup>13</sup>C NMR spectrum. The following 5 different <sup>1</sup>J<sub>C-C</sub> coupling constants (in Hz) were obtained: C2-C3 38.3, C5-C6 36.8, C3-C3a 35.9, C6-C6a 41.1 and C3a-C6a 34.2.

<sup>1</sup> Tundo, P.; Aricò, F.; Gauthier, G.; Rossi, L.; Rosamilia, A., E.; Bevinakatti, H., S.; Sievert, R., L.; Newman, C., P. *ChemSusChem* **2010**, 3, 566–570.

Differences in first and second pair of values illustrate the remarkable dependence of these coupling constants on the configuration of substituents in this bicyclic molecule.

Following regularities in NMR spectra of **12-14** should be noted.  $^3J$   $^1\text{H}$ - $^1\text{H}$  coupling constants from bridgehead to adjacent *exo* (5.4 Hz) or *endo* (1.2 Hz) protons are most informative for the determination of the configuration of substituents on these positions. This regularity is characteristic for many bicyclic molecules. In  $^{13}\text{C}$  spectra *endo* substituents induce high field shifts on the routes of  $\gamma$ -gauche interactions. Regularities in the NMR spectra of isosorbide were used for the determination of configurations of synthesized formyl derivatives.

In cases of formyl substituted derivatives 2D NOESY correlations were used for the determination of isomeric configurations. The regioisomers (C2- or C3-formyl-substituted derivatives) could be easily distinguished by looking at the  $^3J_{\text{HH}}$  coupling constant between the CHO group hydrogen and the adjacent CH group hydrogen. In the case of 2-*exo*-formyl derivative the  $^3J(\text{CH-2} - \text{CHO})$  was found to be around 2.0 Hz, while in the case of 3-*exo*-formyl derivative the  $^3J(\text{CH-3} - \text{CHO})$  was around 1.0 Hz. For the 3-*endo*-formyl derivative the  $^3J(\text{CH-3} - \text{CHO})$  was around 1.5 Hz. In addition, the chemical shifts of the protons at C3 were very characteristic: for the 2-formyl derivative the two protons at C3 had well-separated signals between 1.3–2.4 ppm, while for the 3-formyl derivative the proton at C3 had a signal around 2.5–3.2 ppm. Also, the  $^{13}\text{C}$  chemical shift of the C3 carbon was a source to give information about the regioisomers: the 2-formyl derivative the C3 carbon had chemical shift around 35 ppm, while the 3-formyl derivative the C3 carbon had chemical shift around 59 ppm.

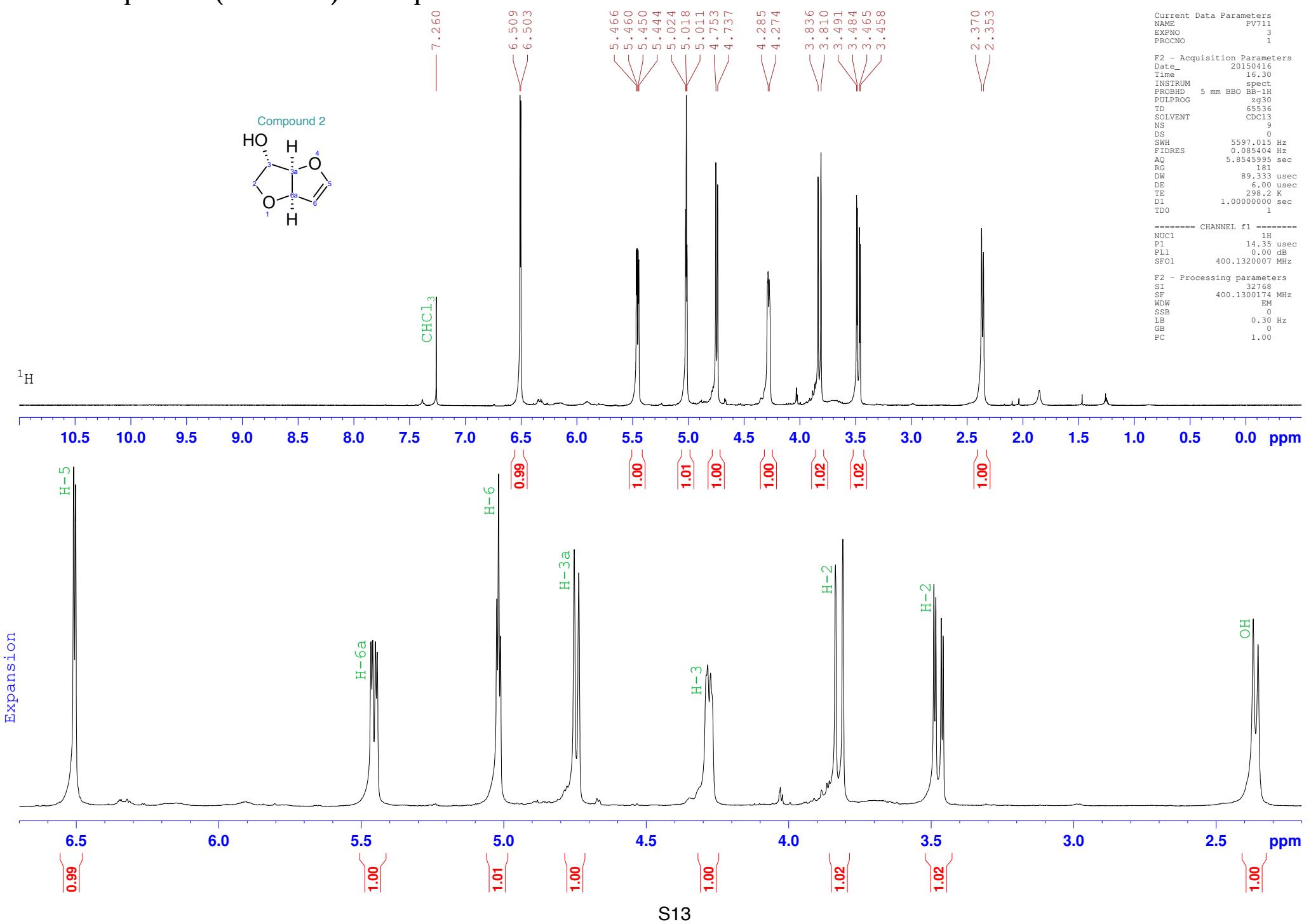
## Determination of regioisomeric ratios by analogy from crude $^1\text{H}$ spectra

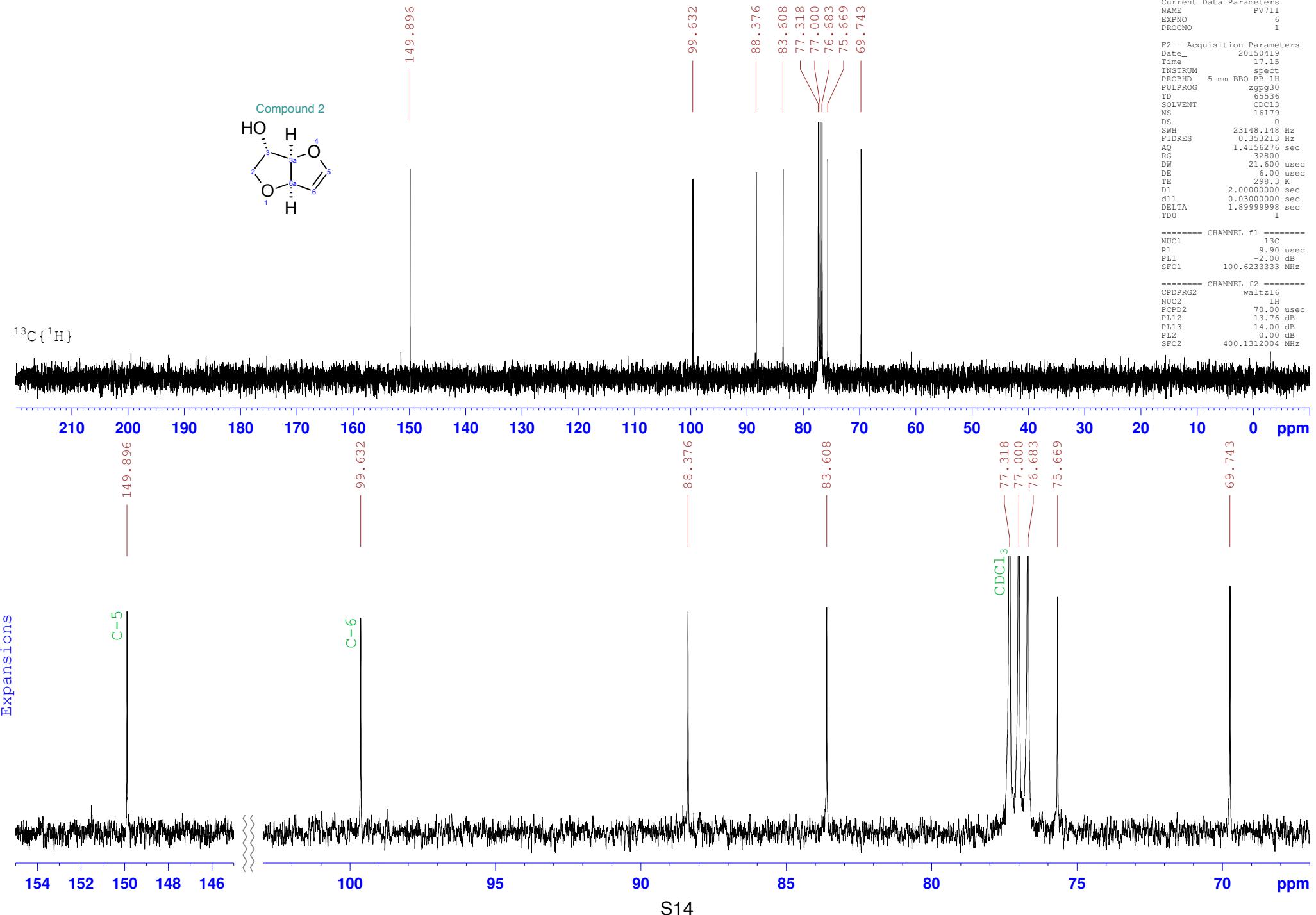
Due to epimerization of hydroformylation products on silica gel, regioisomeric ratios for the hydroformylation products were determined from the crude  $^1\text{H}$  NMR spectra of the reaction mixtures.

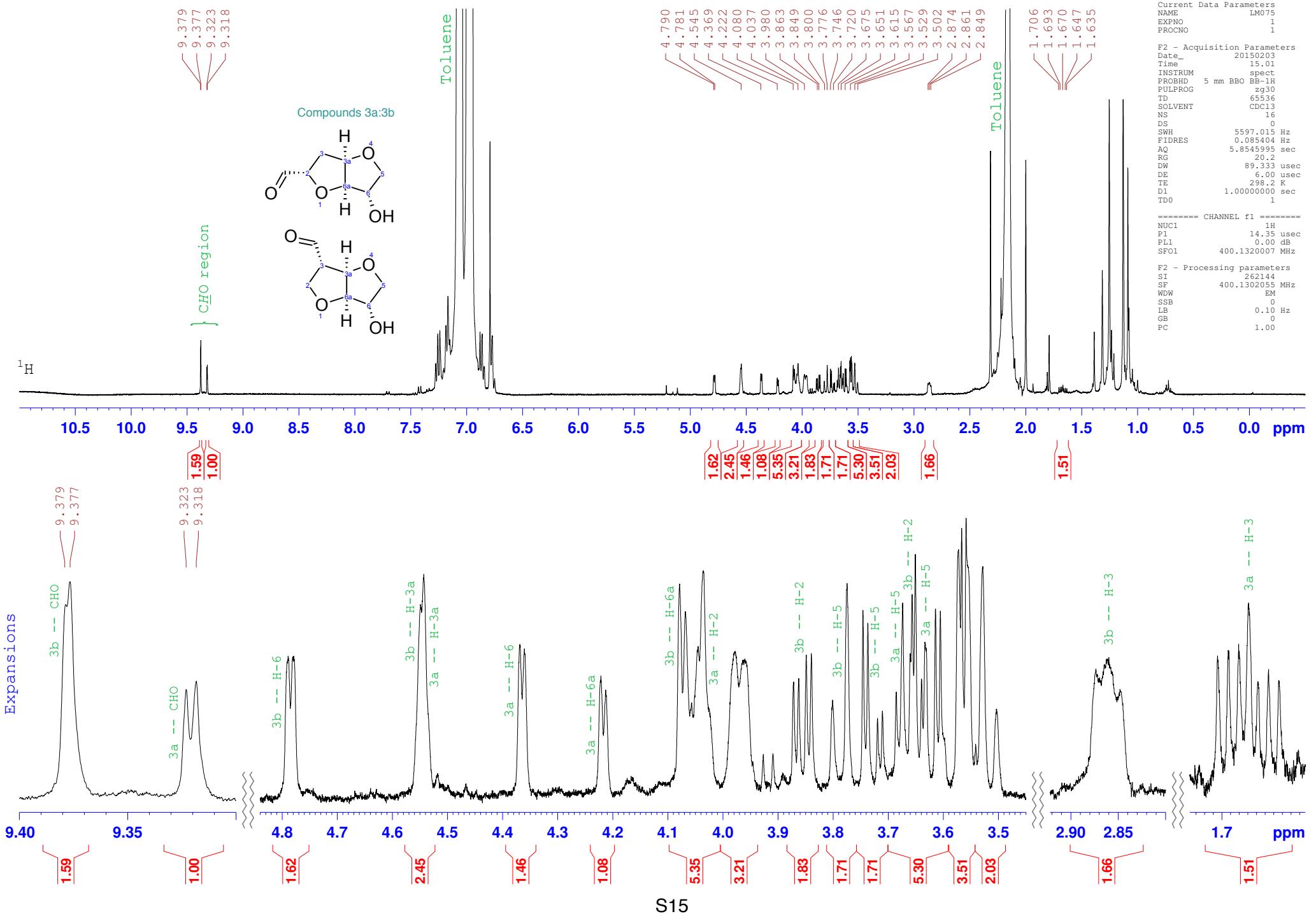
However, in all cases of potential interest, the ratio of isomers was also verified on corresponding alcohol obtained after reduction and purification. No change on isomeric composition was detected during the reduction.

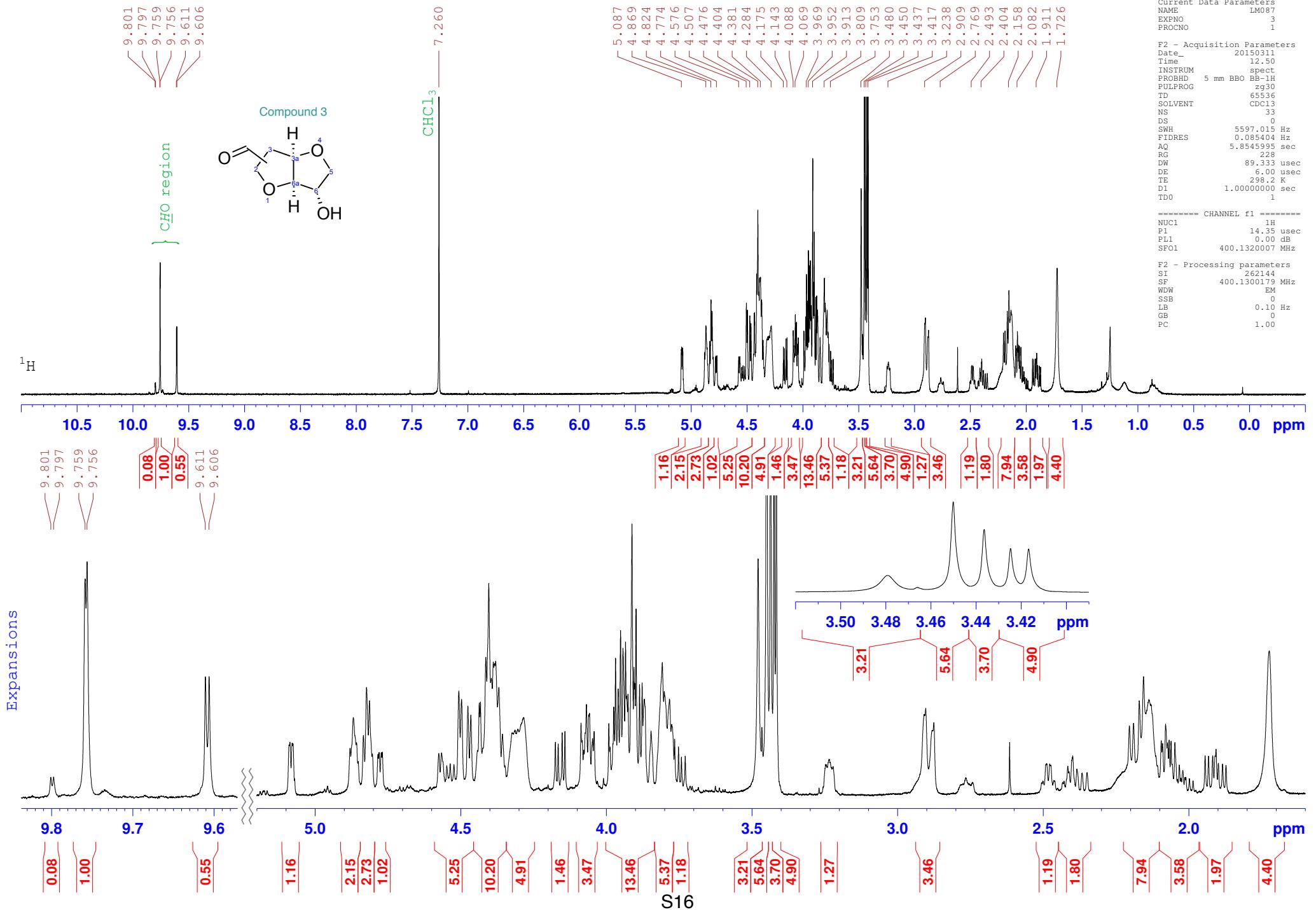
## Spectra

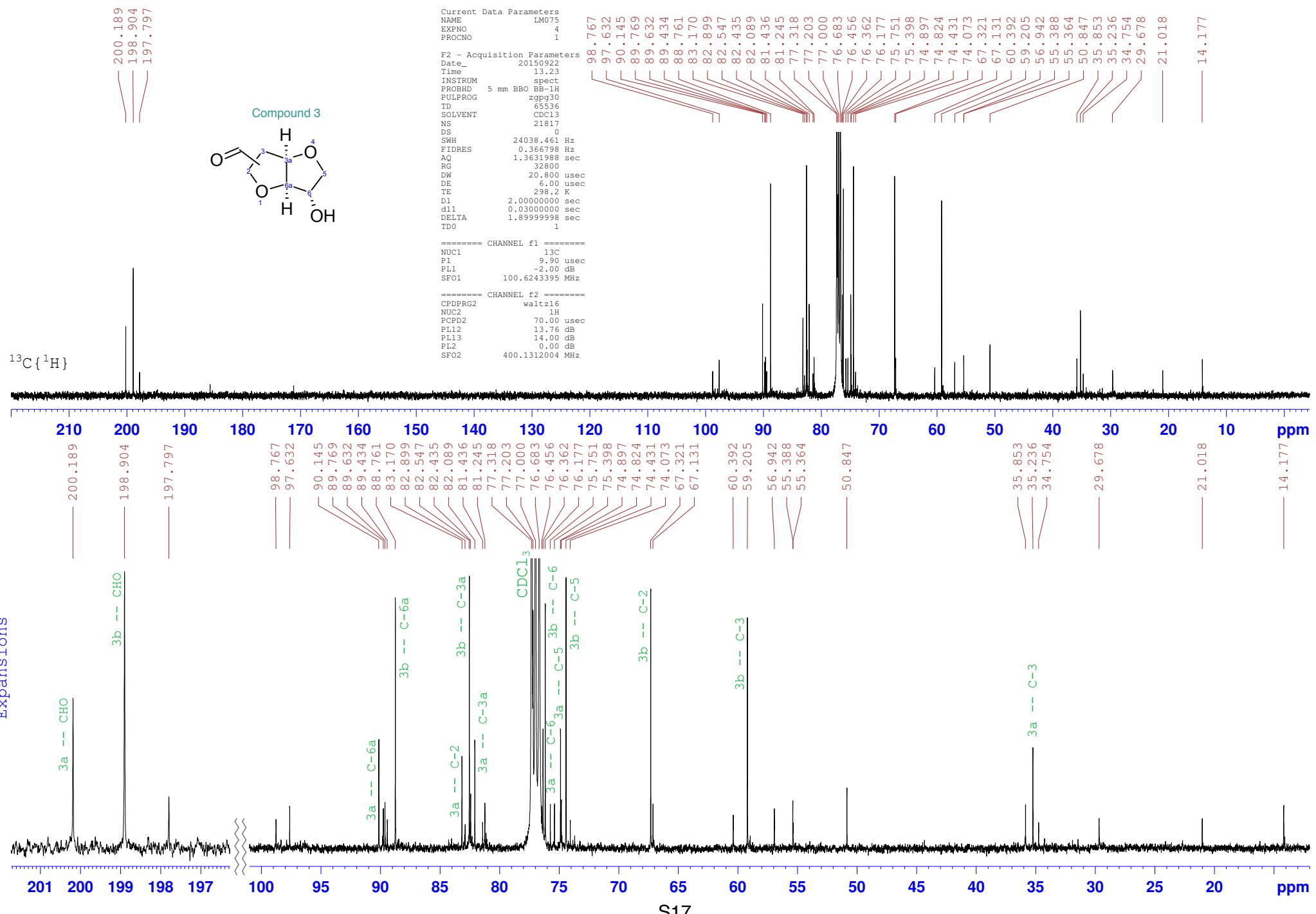
Copies of NMR spectra.

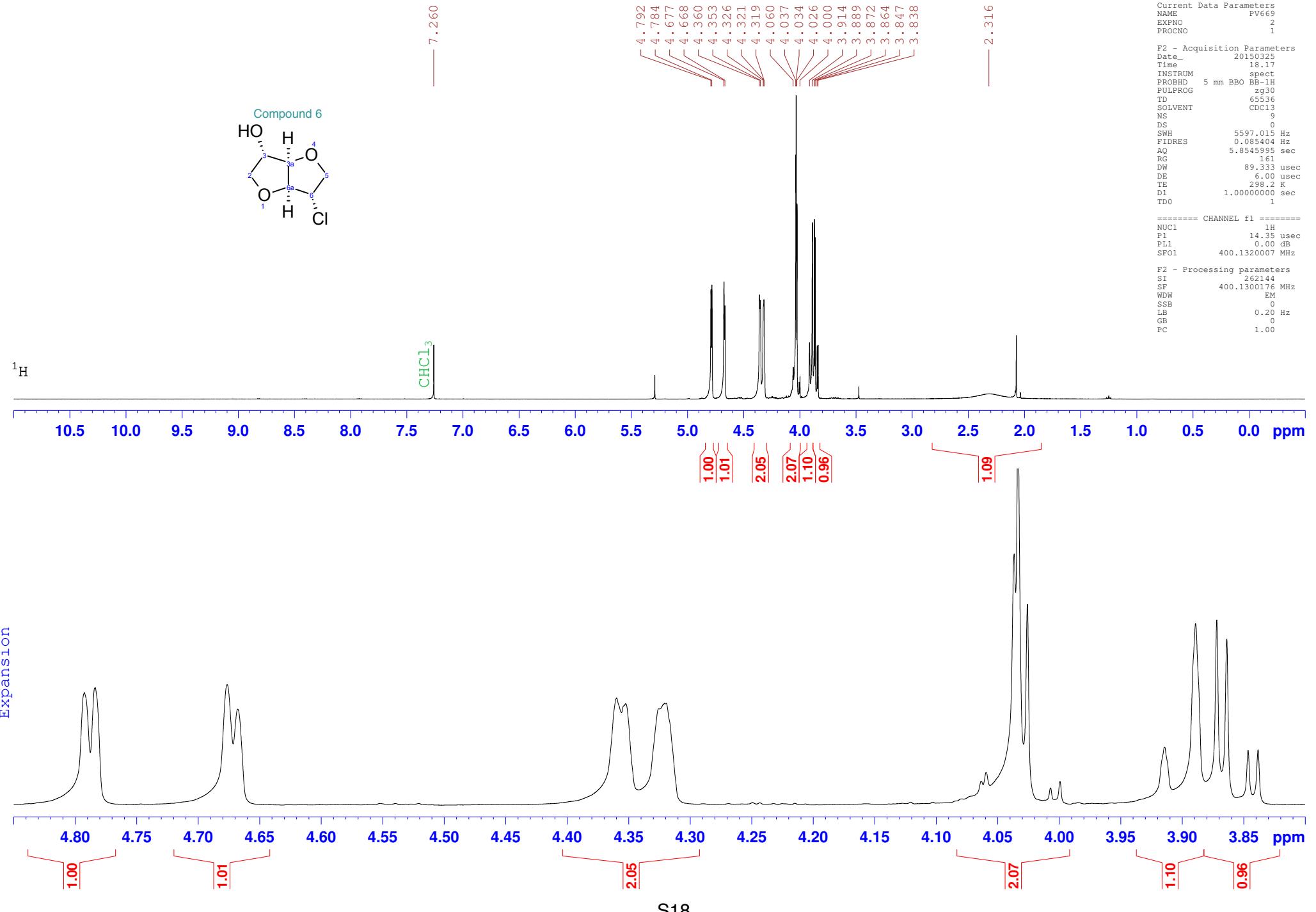
<sup>1</sup>H NMR spectrum (400.1 MHz) of compound 2

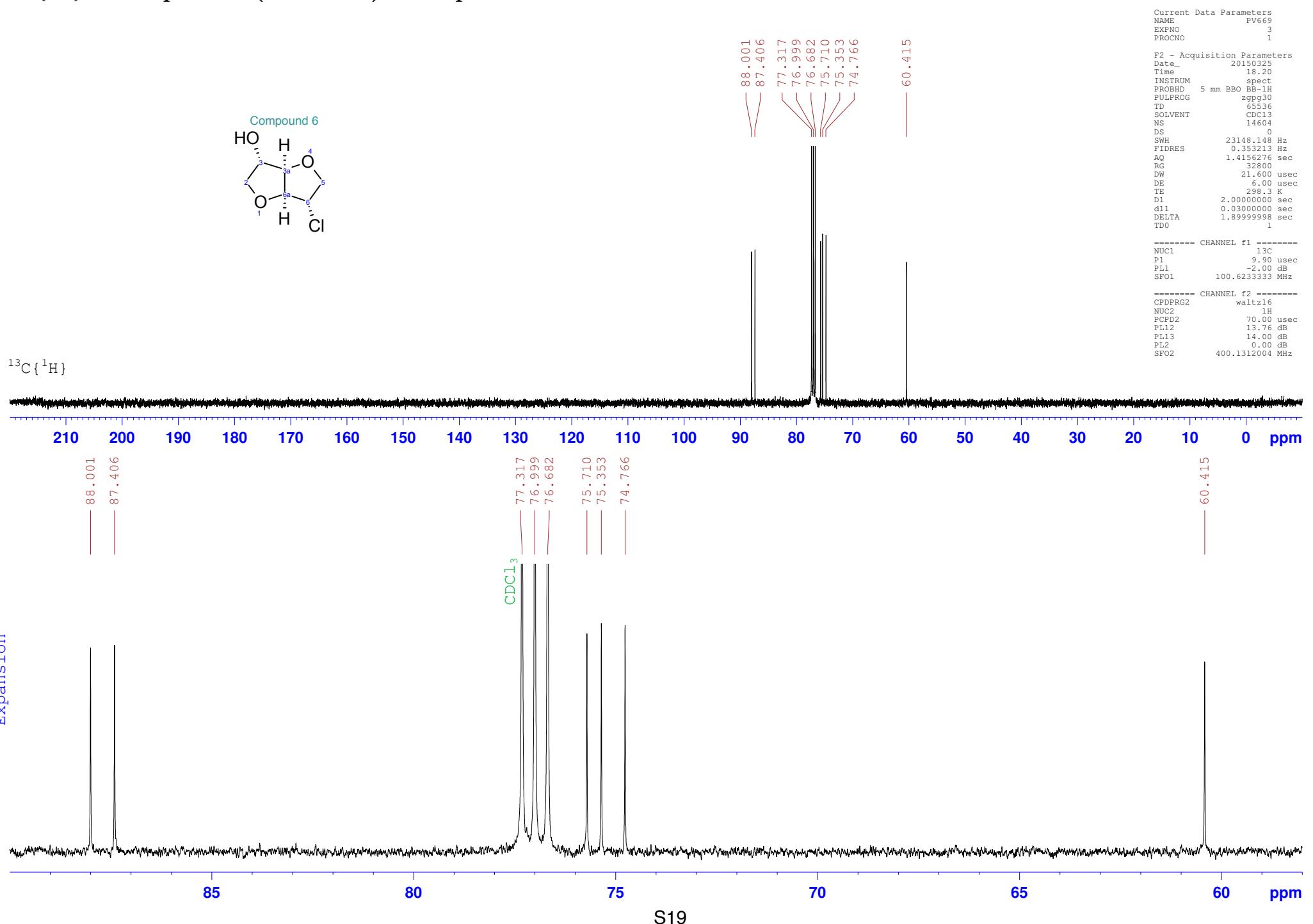
<sup>13</sup>C{<sup>1</sup>H} NMR spectrum (100.6 MHz) of compound 2

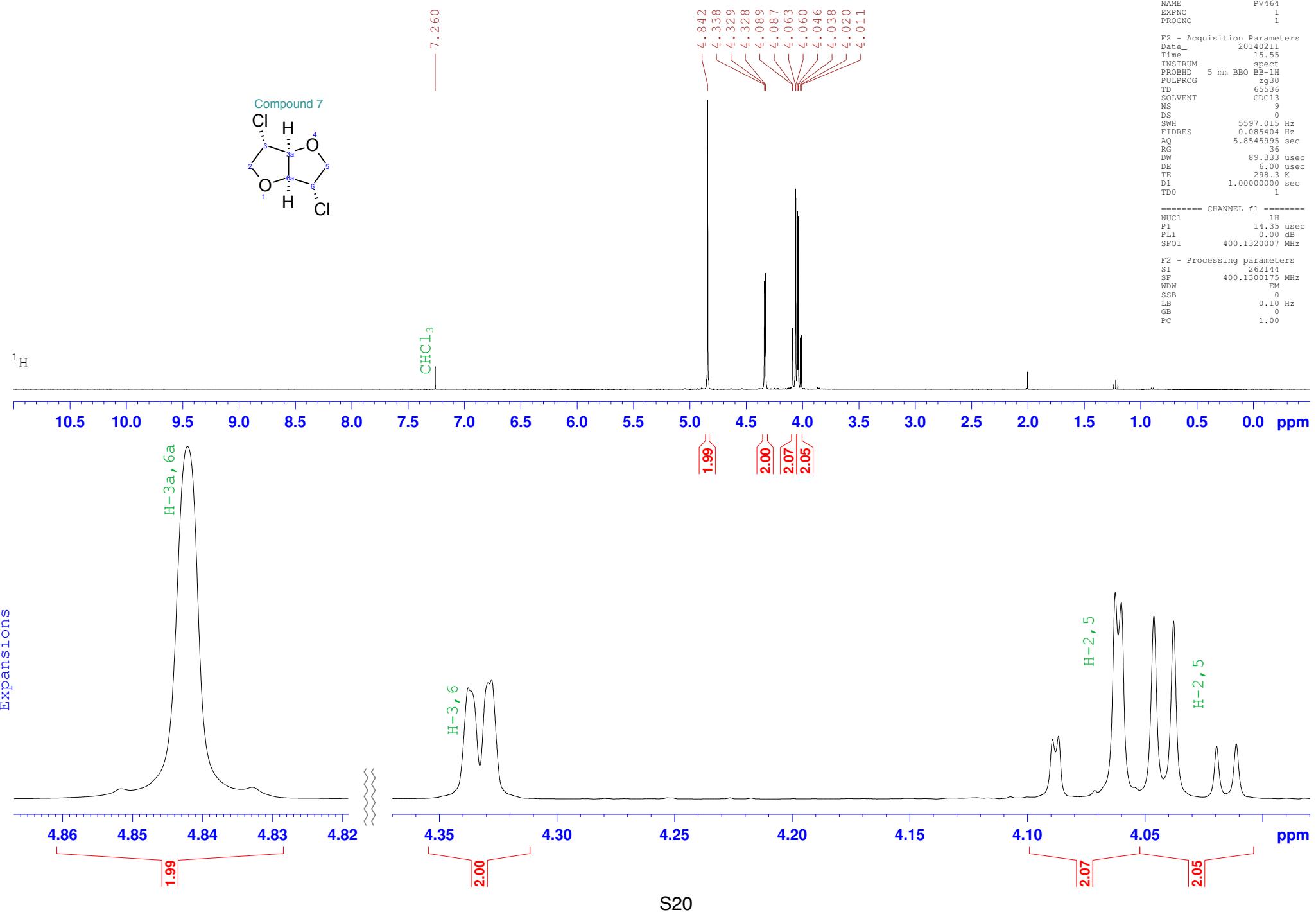
<sup>1</sup>H NMR spectrum (400.1 MHz) of compound 3 (crude)

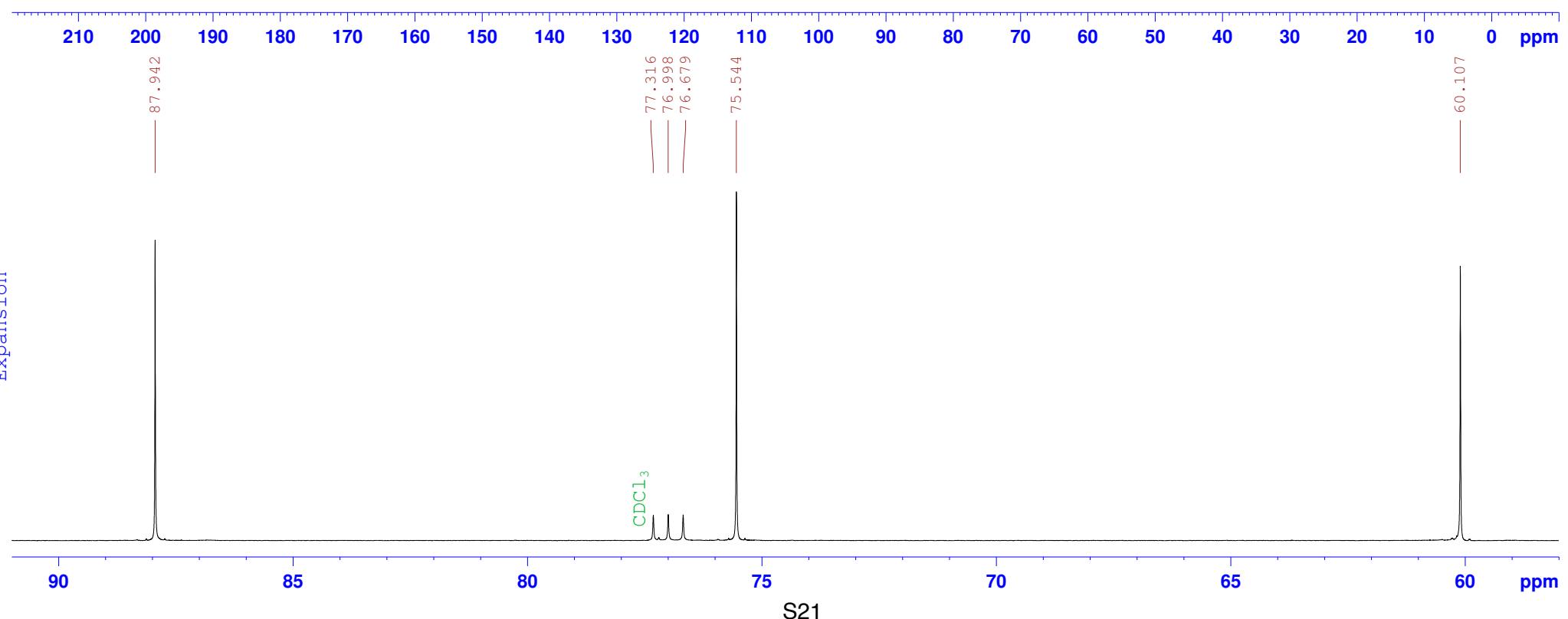
<sup>1</sup>H NMR spectrum (400.1 MHz) of compound 3 (purified)

<sup>13</sup>C{<sup>1</sup>H} NMR spectrum (100.6 MHz) of compound 3 (purified)

<sup>1</sup>H NMR spectrum (400.1 MHz) of compound 6

<sup>13</sup>C{<sup>1</sup>H} NMR spectrum (100.6 MHz) of compound 6

<sup>1</sup>H NMR spectrum (400.1 MHz) of compound 7

<sup>13</sup>C{<sup>1</sup>H} NMR spectrum (100.6 MHz) of compound 7<sup>13</sup>C{<sup>1</sup>H}

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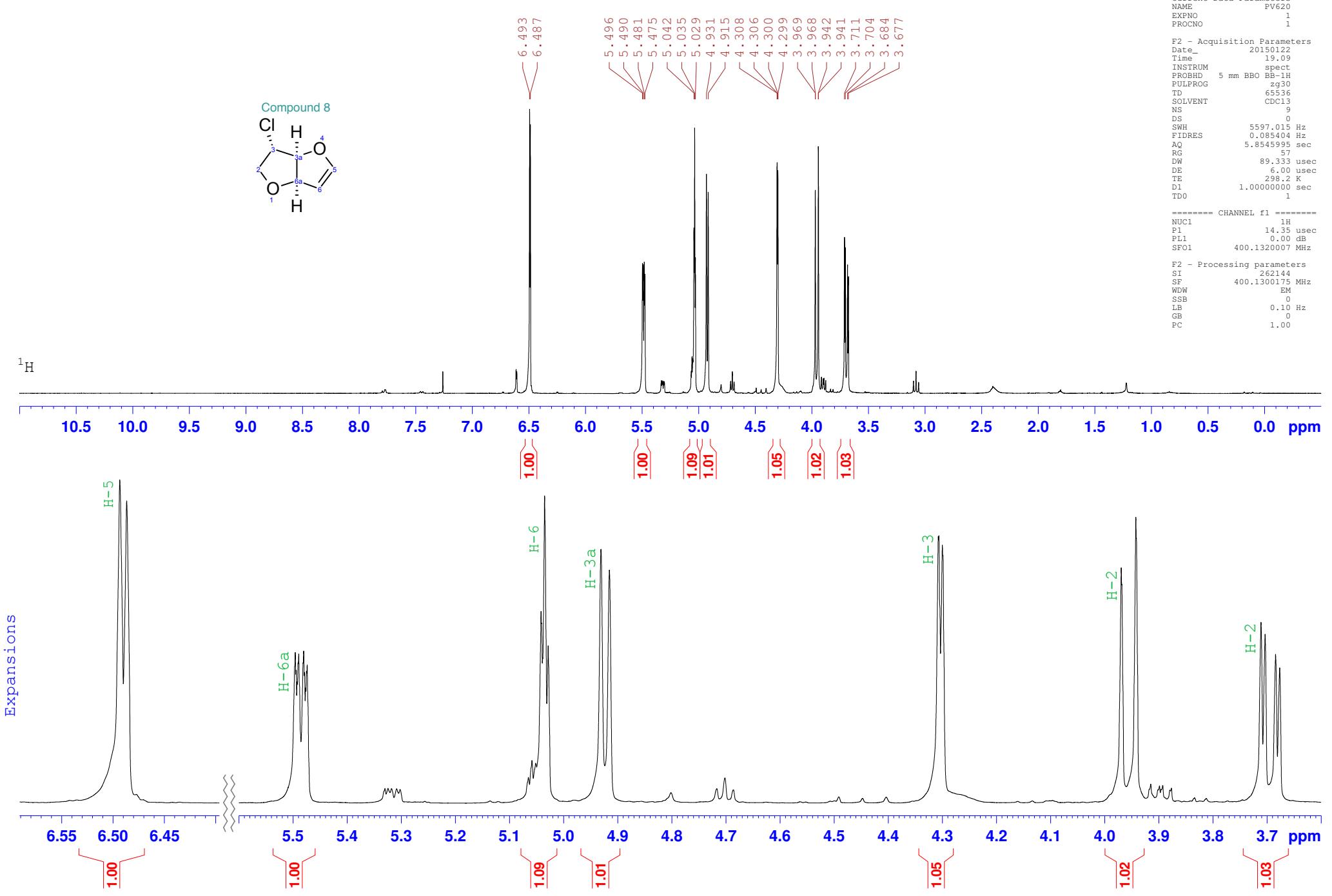
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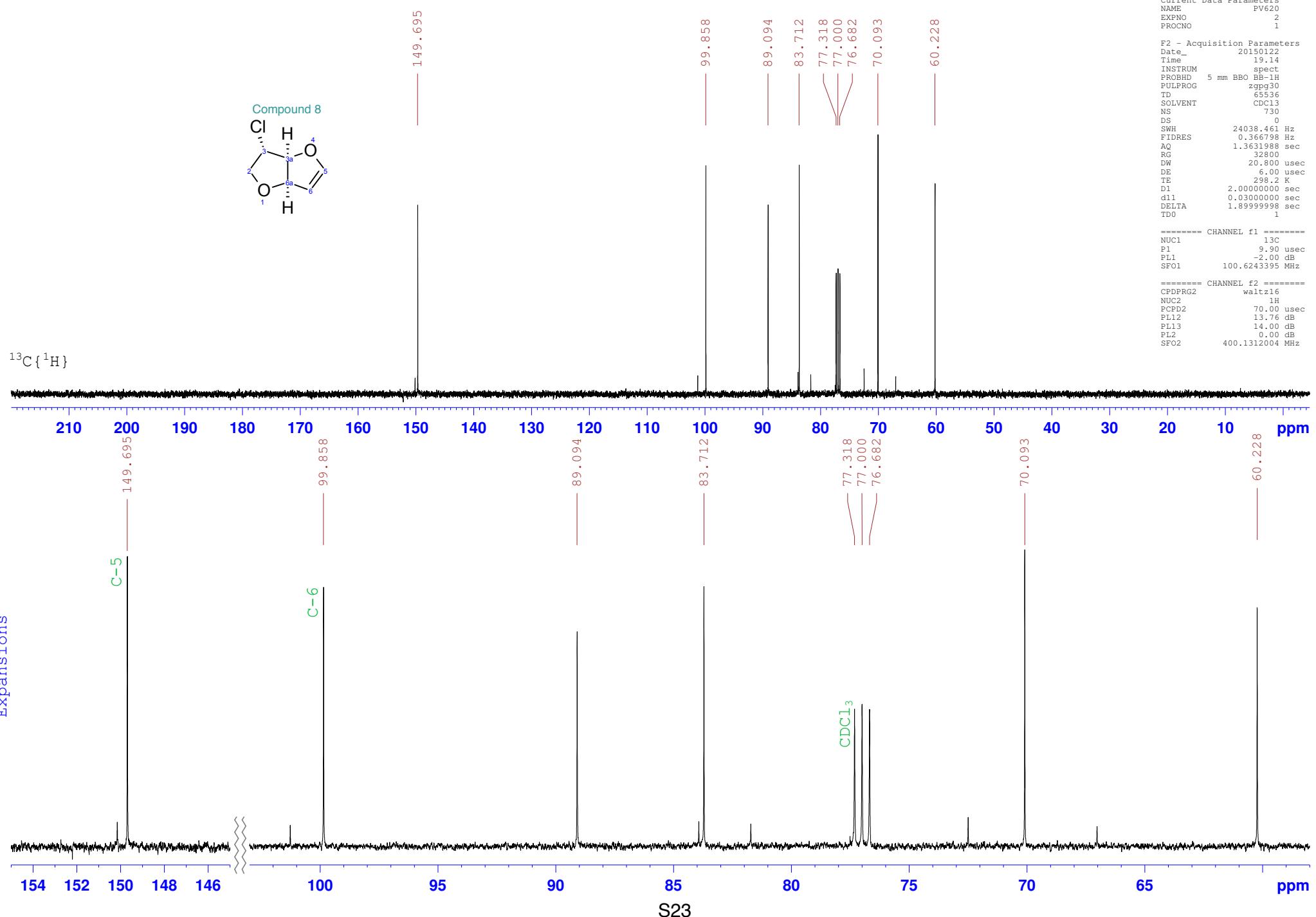
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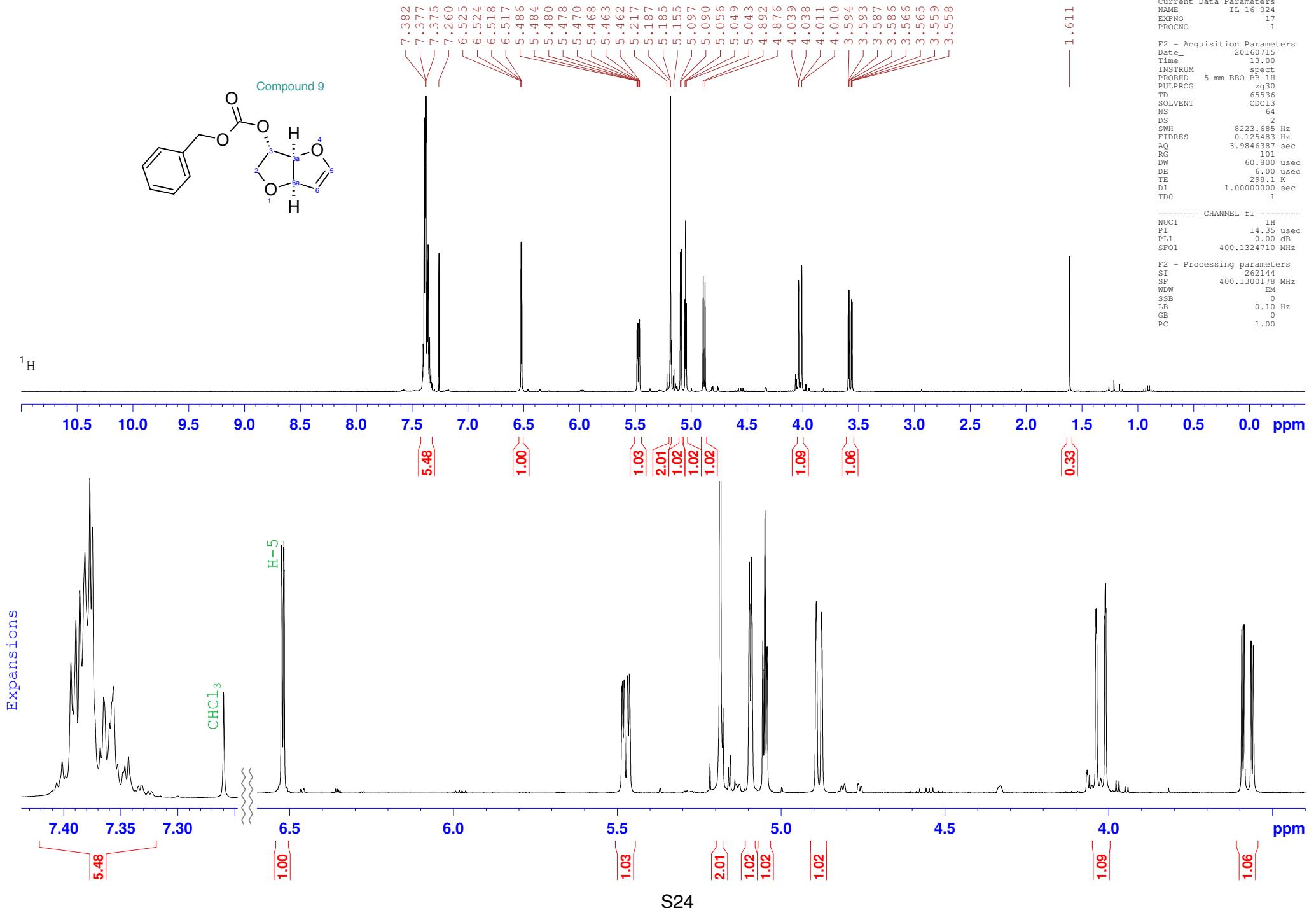
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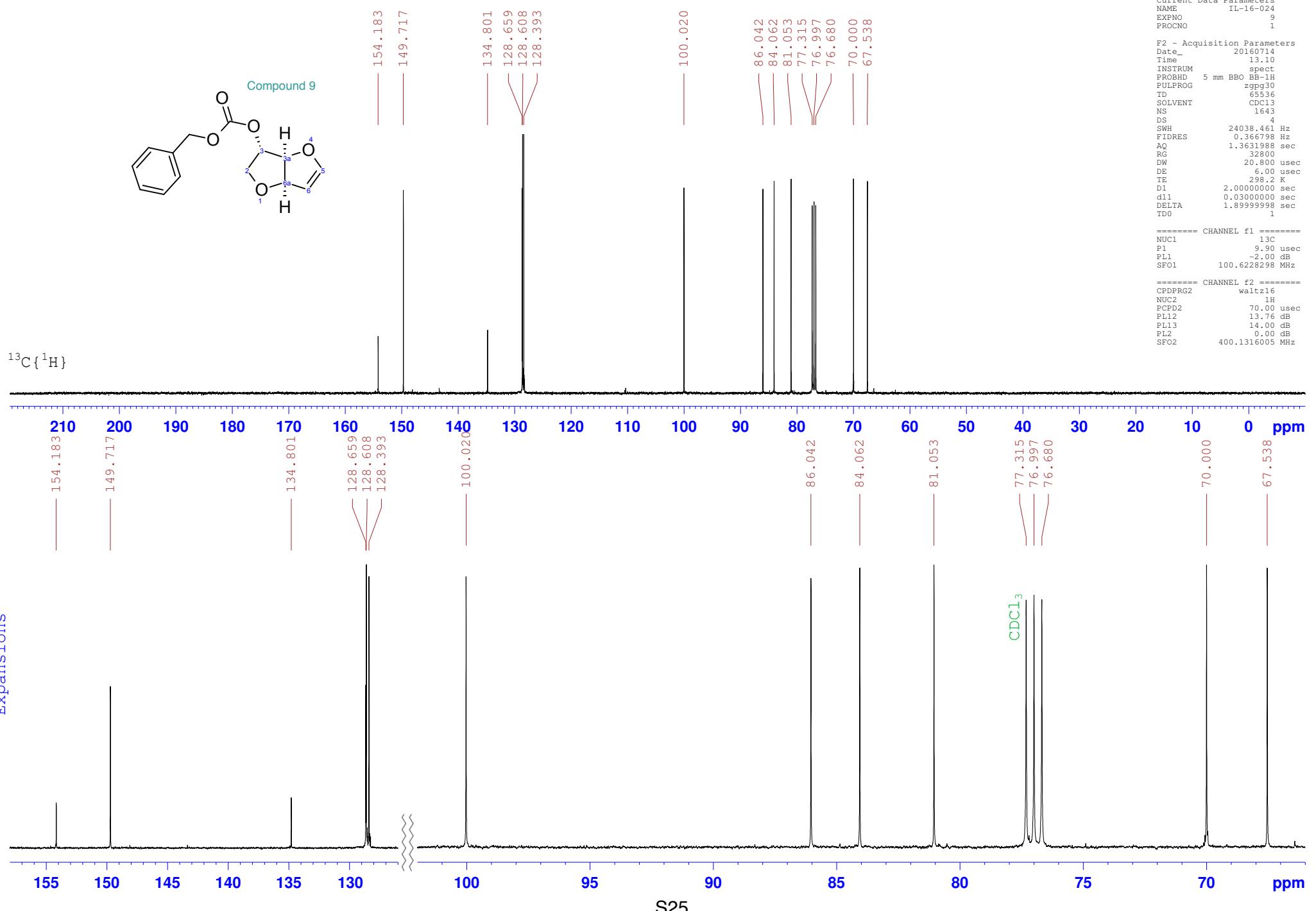
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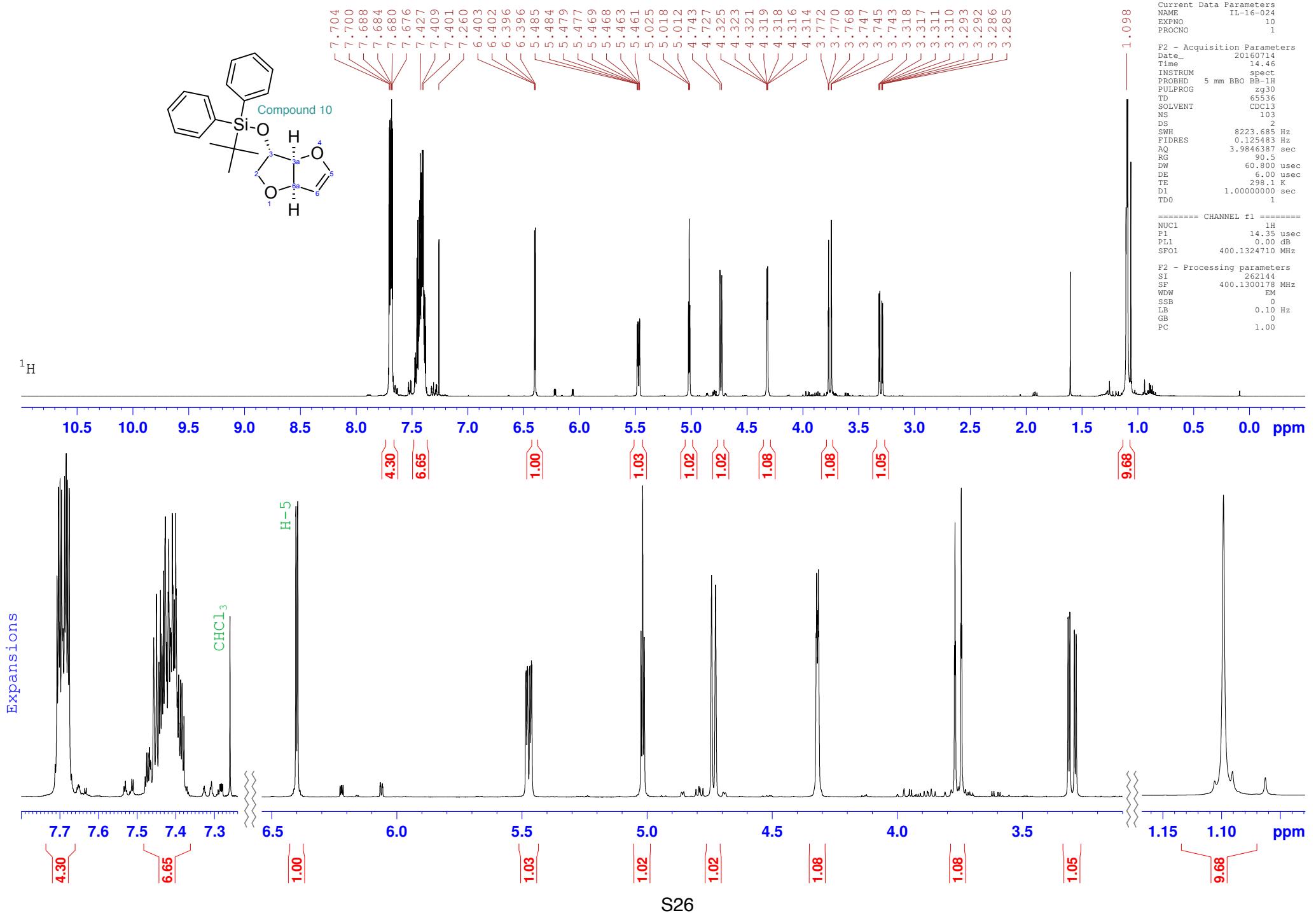
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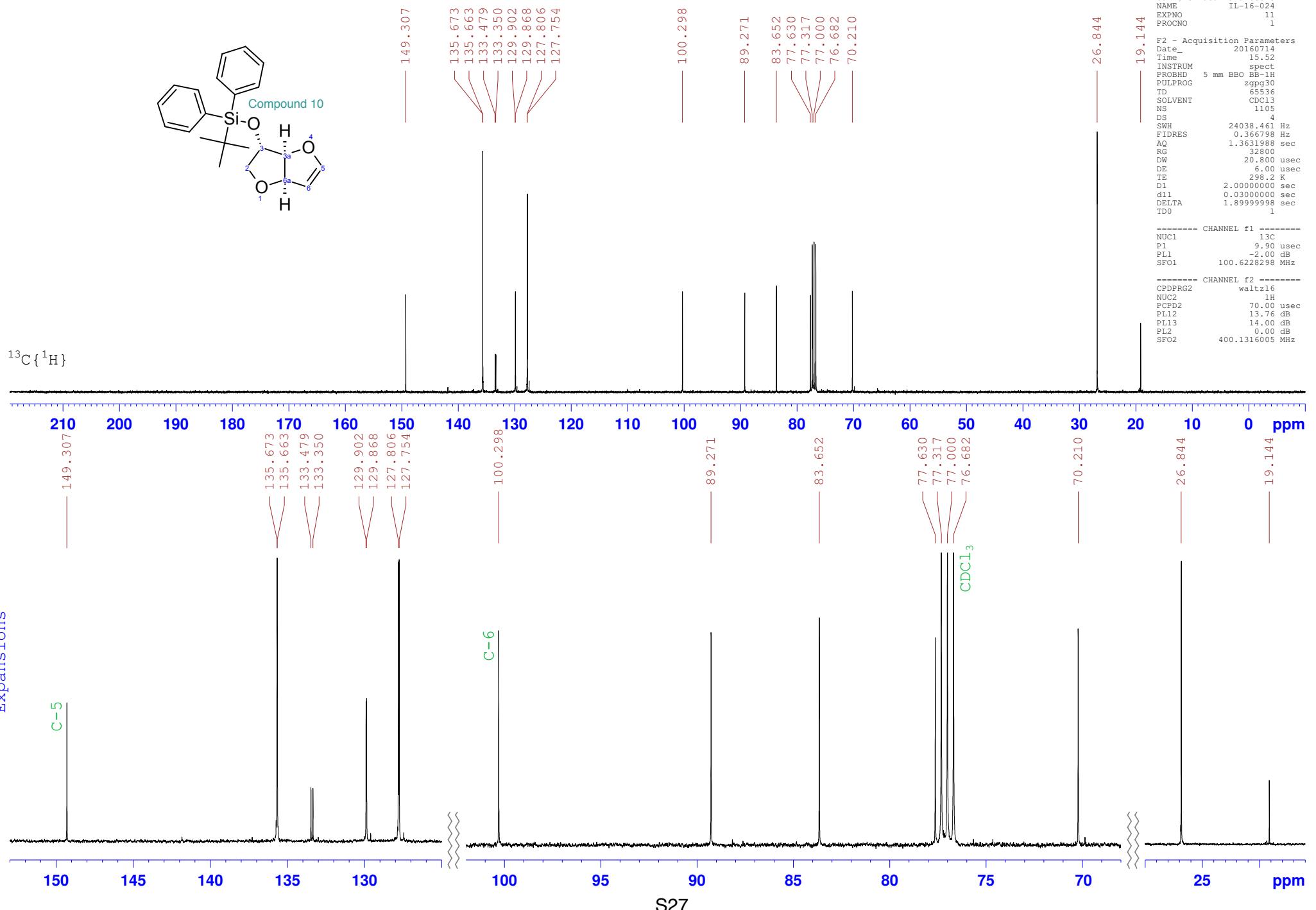
<sup>1</sup>H NMR spectrum (400.1 MHz) of compound 8

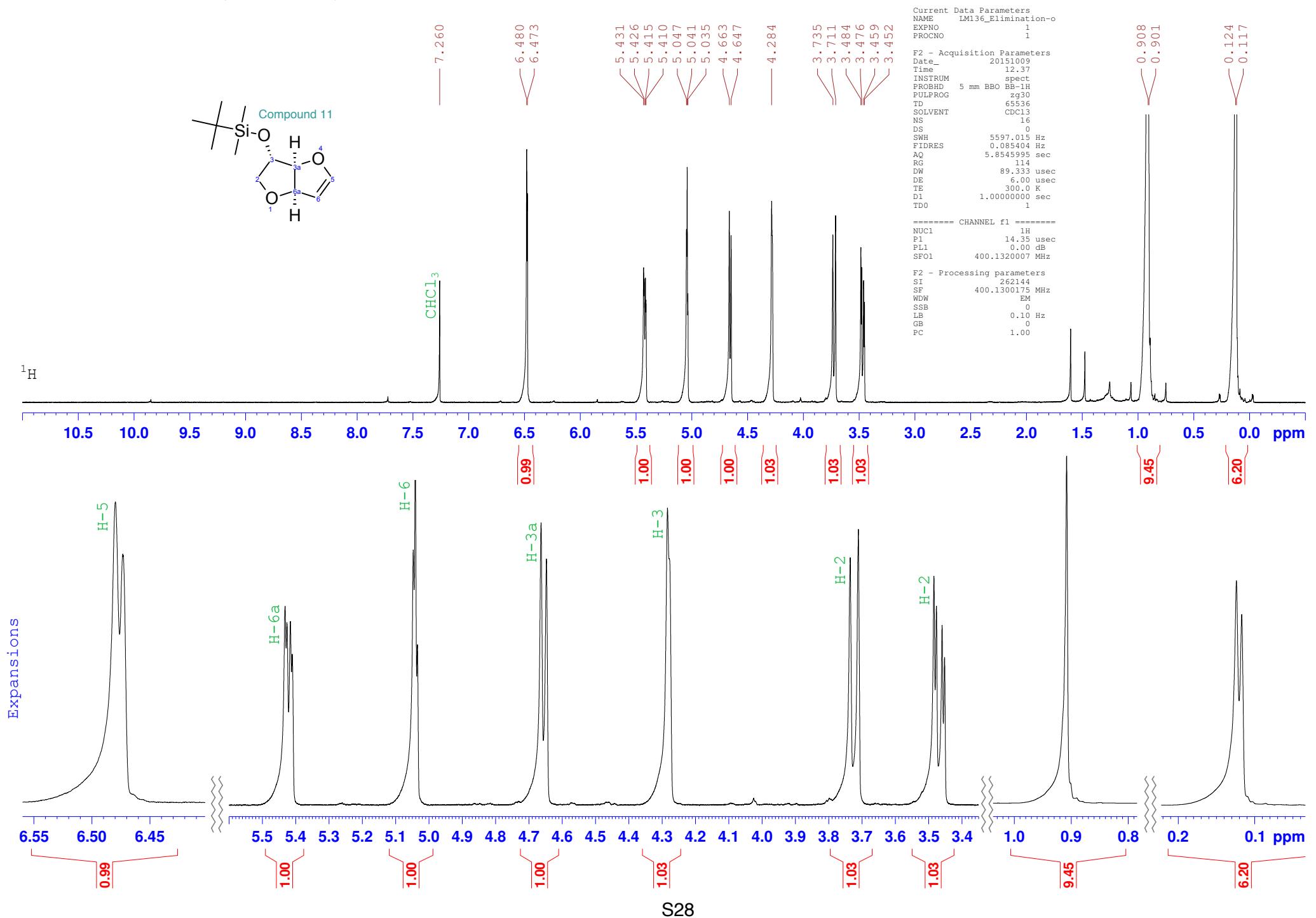
<sup>13</sup>C{<sup>1</sup>H} NMR spectrum (100.6 MHz) of compound 8

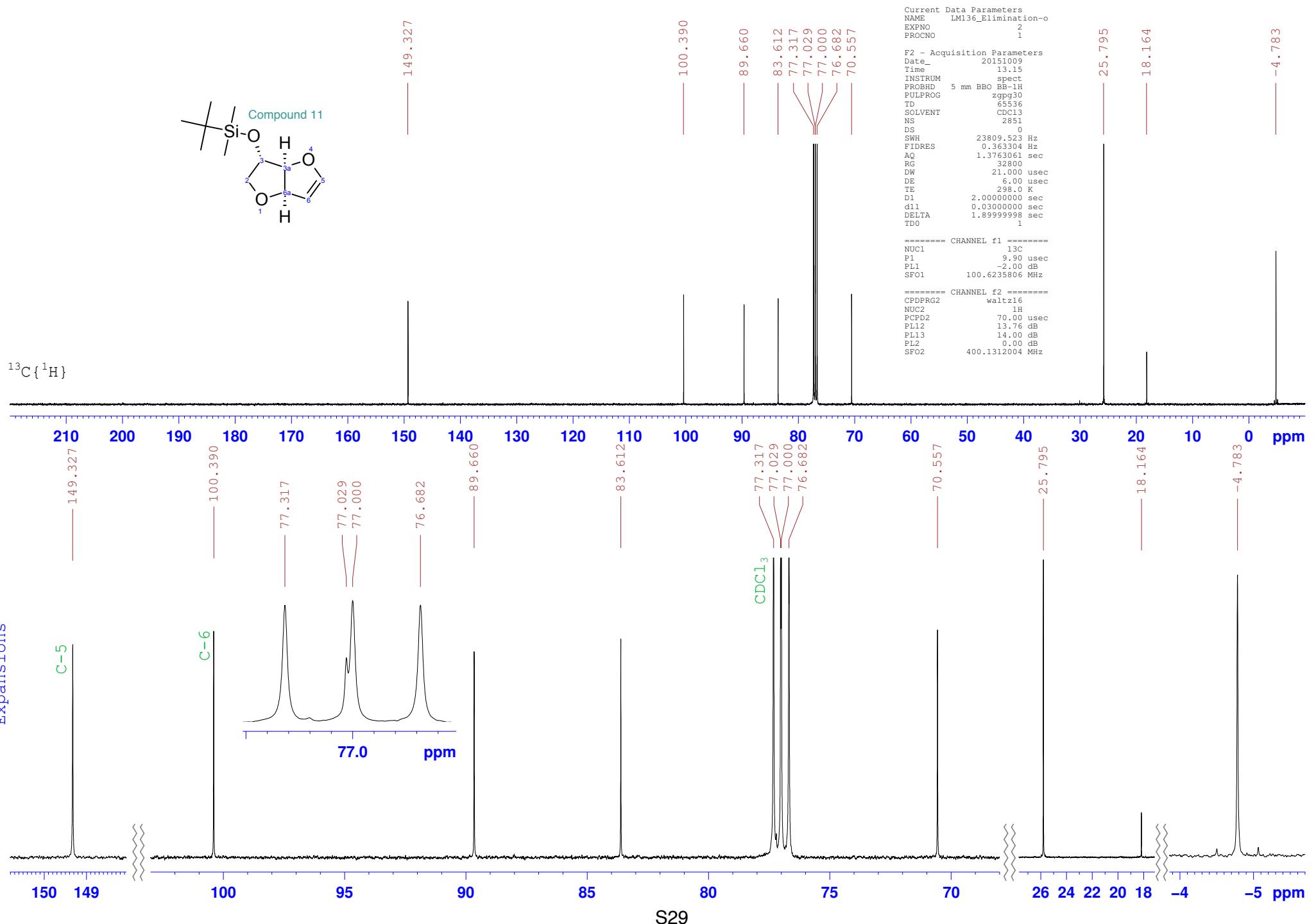
<sup>1</sup>H NMR spectrum (400.1 MHz) of compound 9

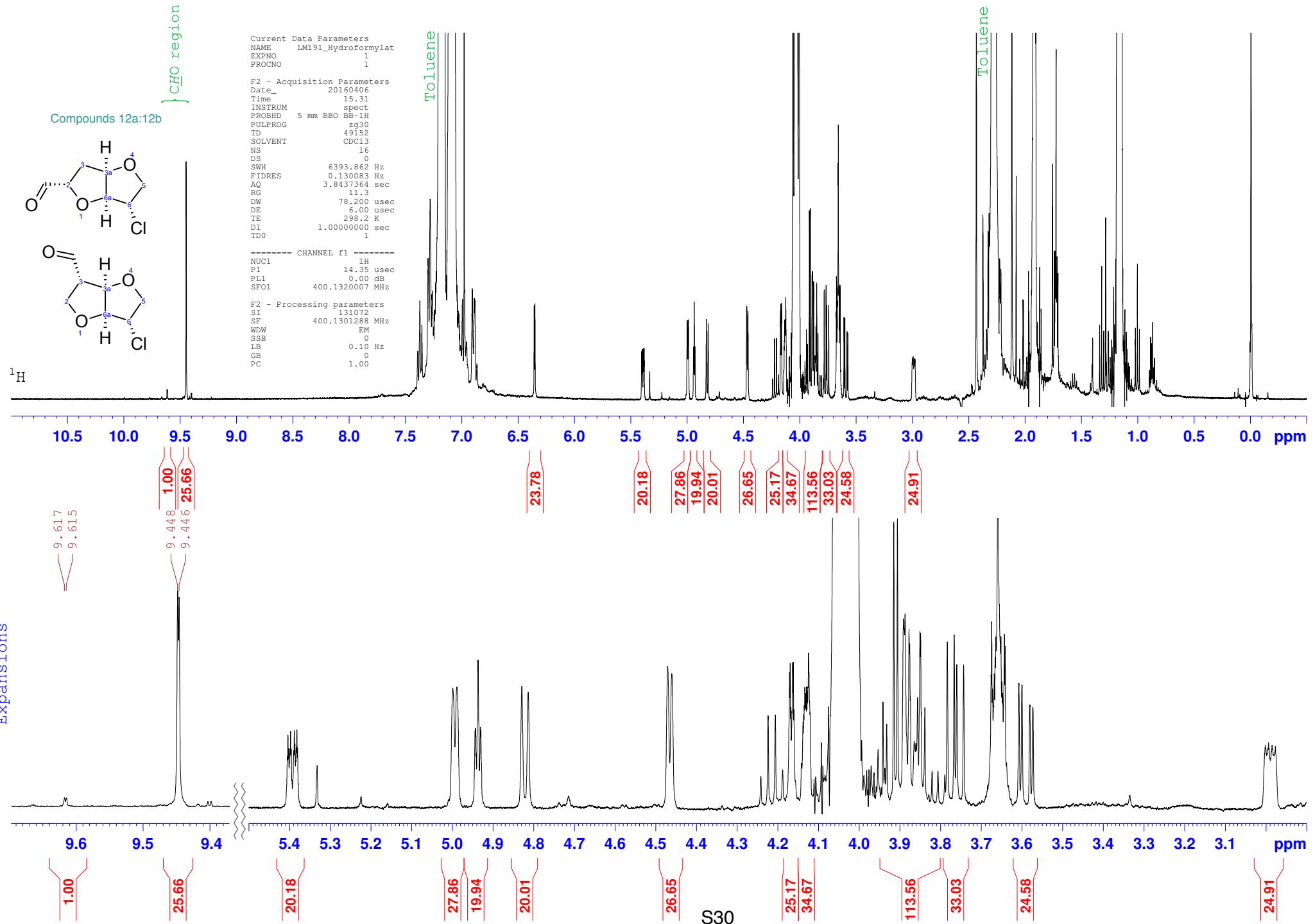
<sup>13</sup>C{<sup>1</sup>H} NMR spectrum (100.6 MHz) of compound 9

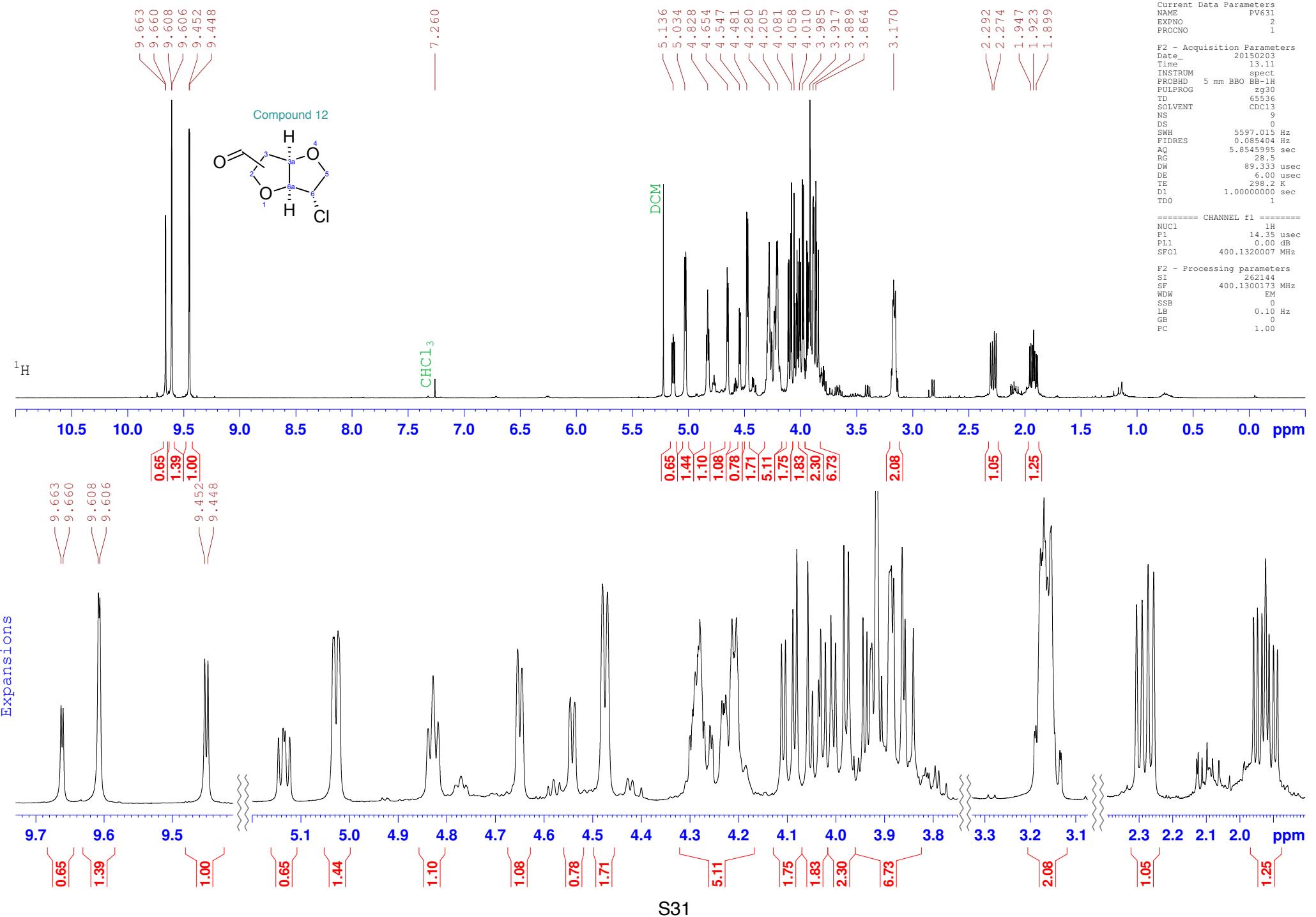
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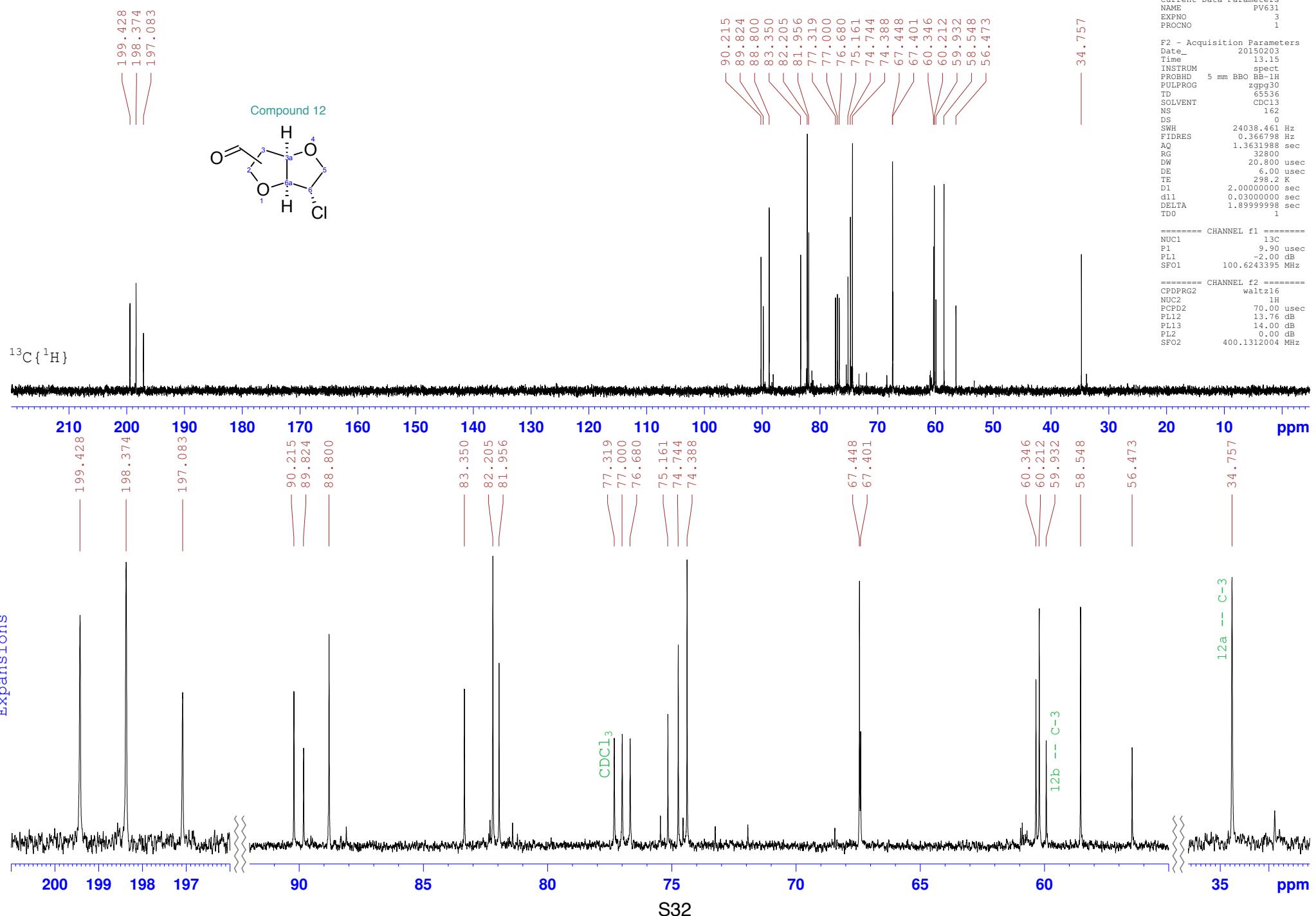
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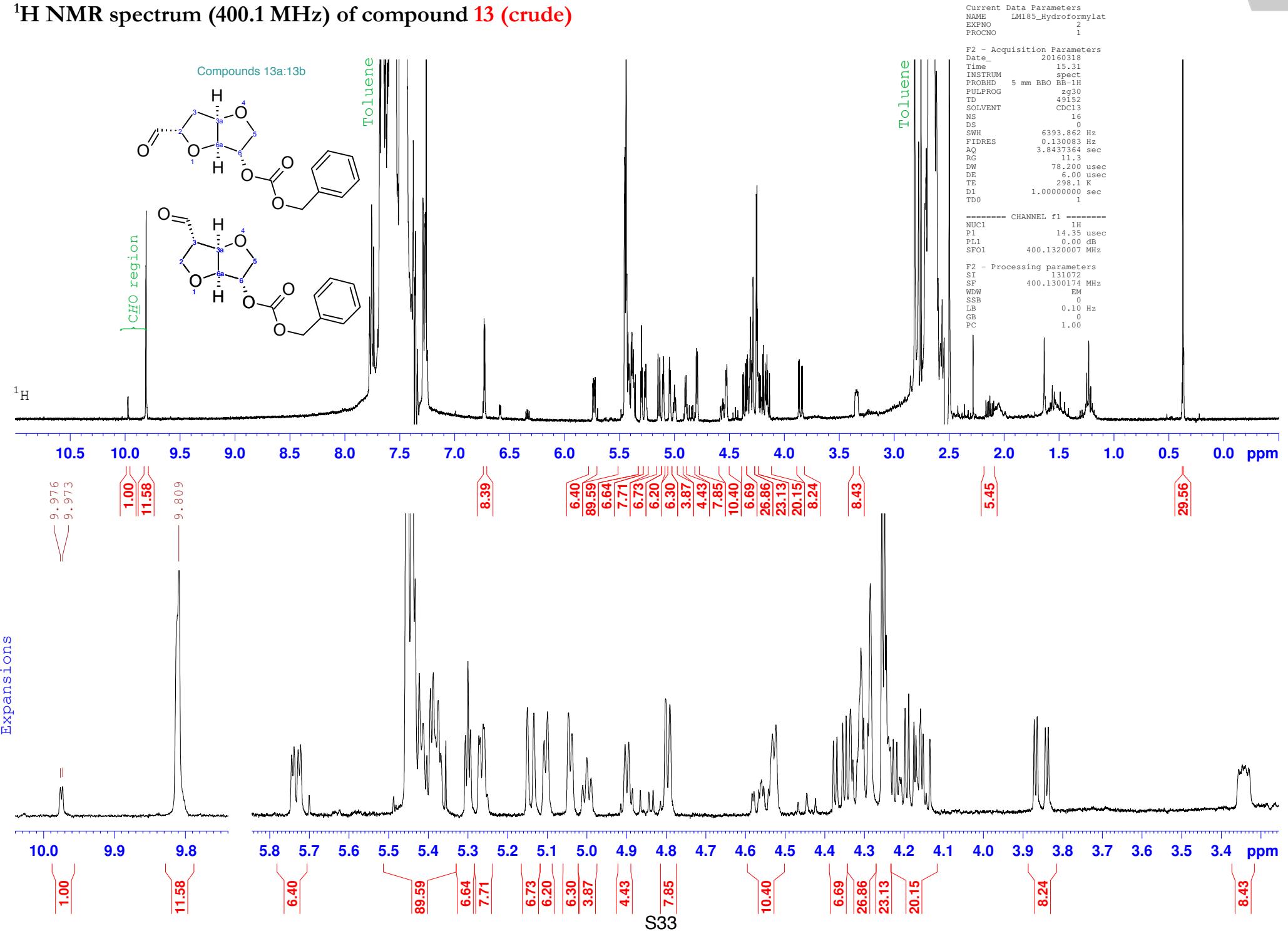
<sup>1</sup>H NMR spectrum (400.1 MHz) of compound 11

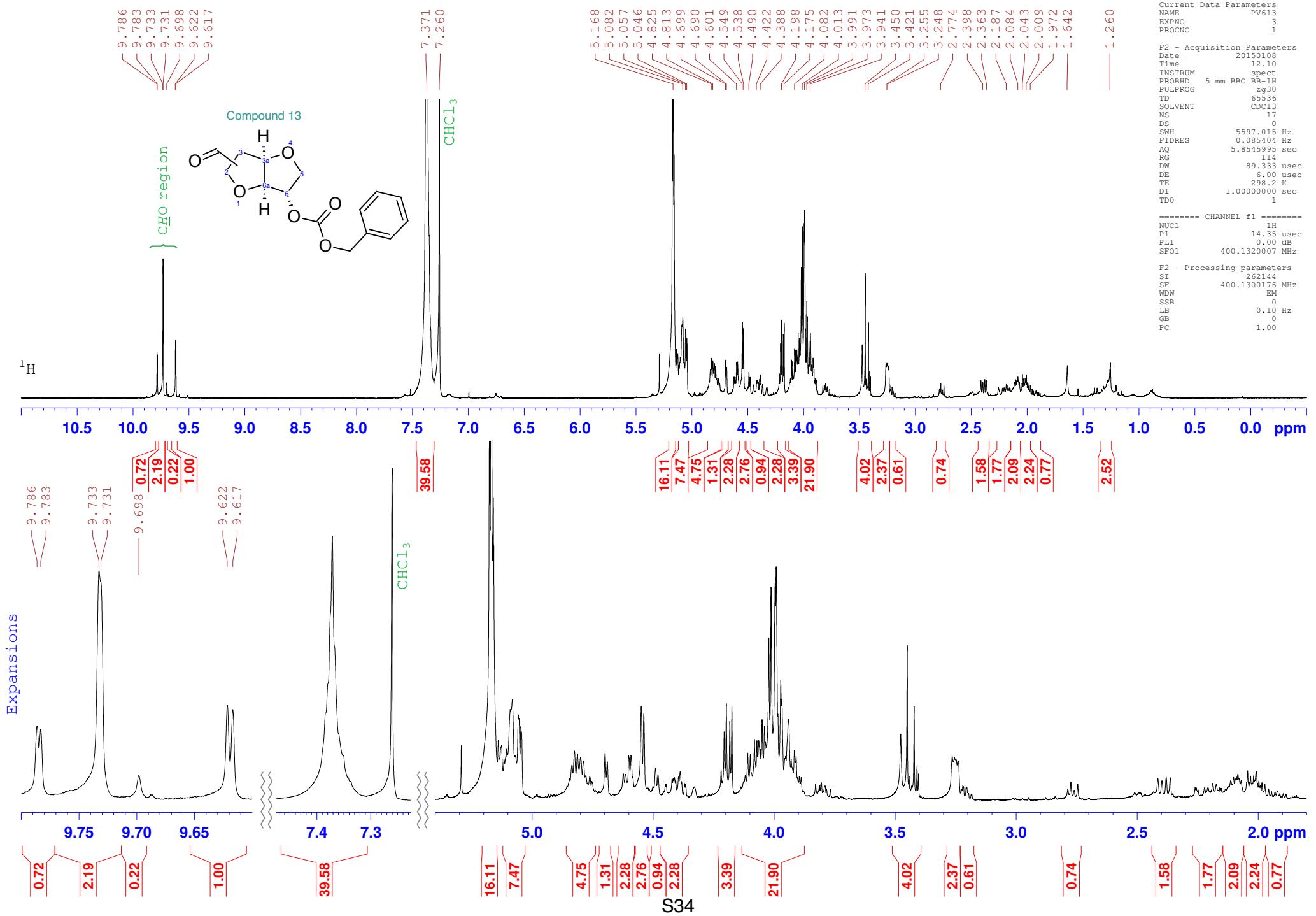
<sup>13</sup>C{<sup>1</sup>H} NMR spectrum (100.6 MHz) of compound 11

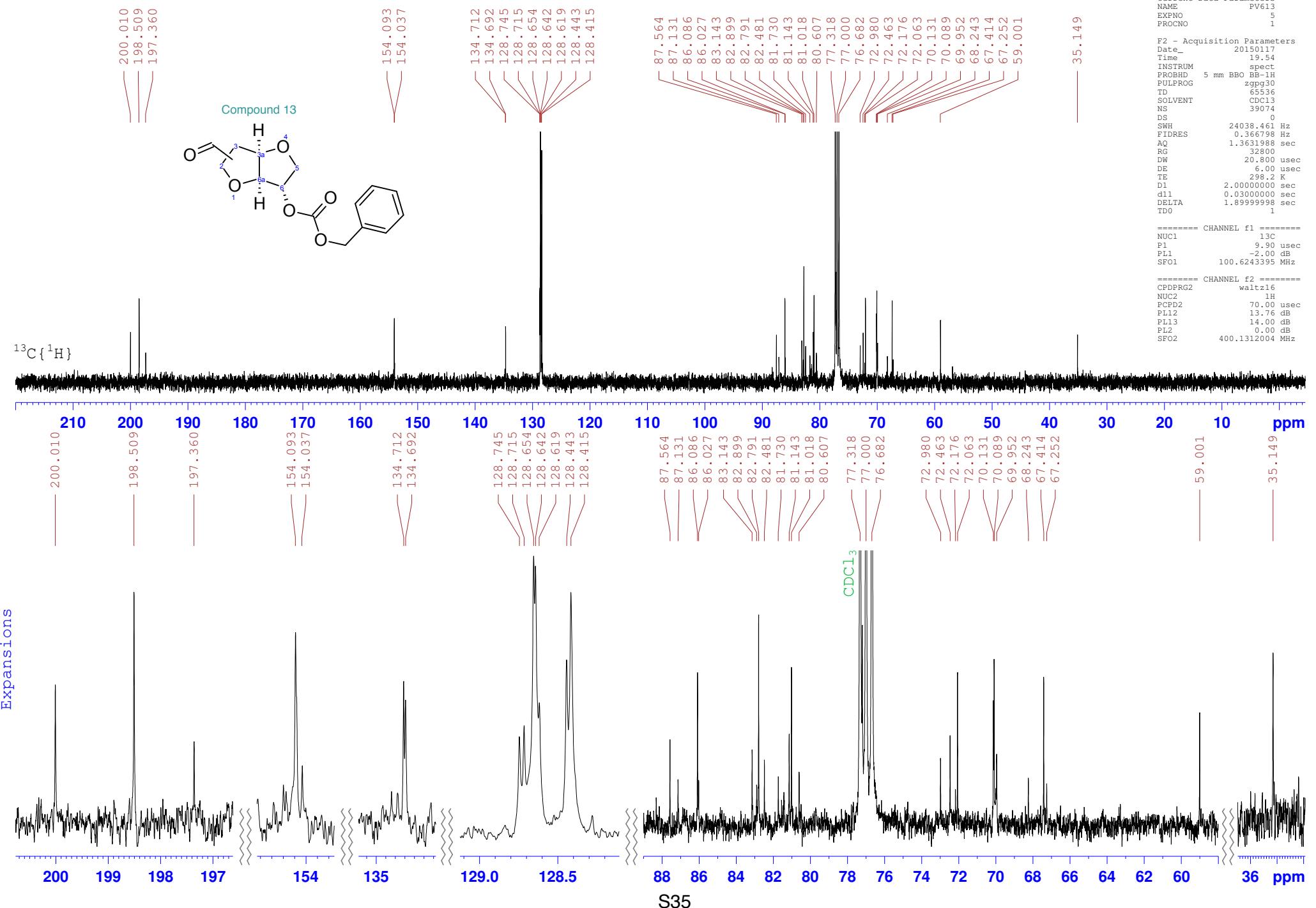
<sup>1</sup>H NMR spectrum (400.1 MHz) of compound 12 (crude)

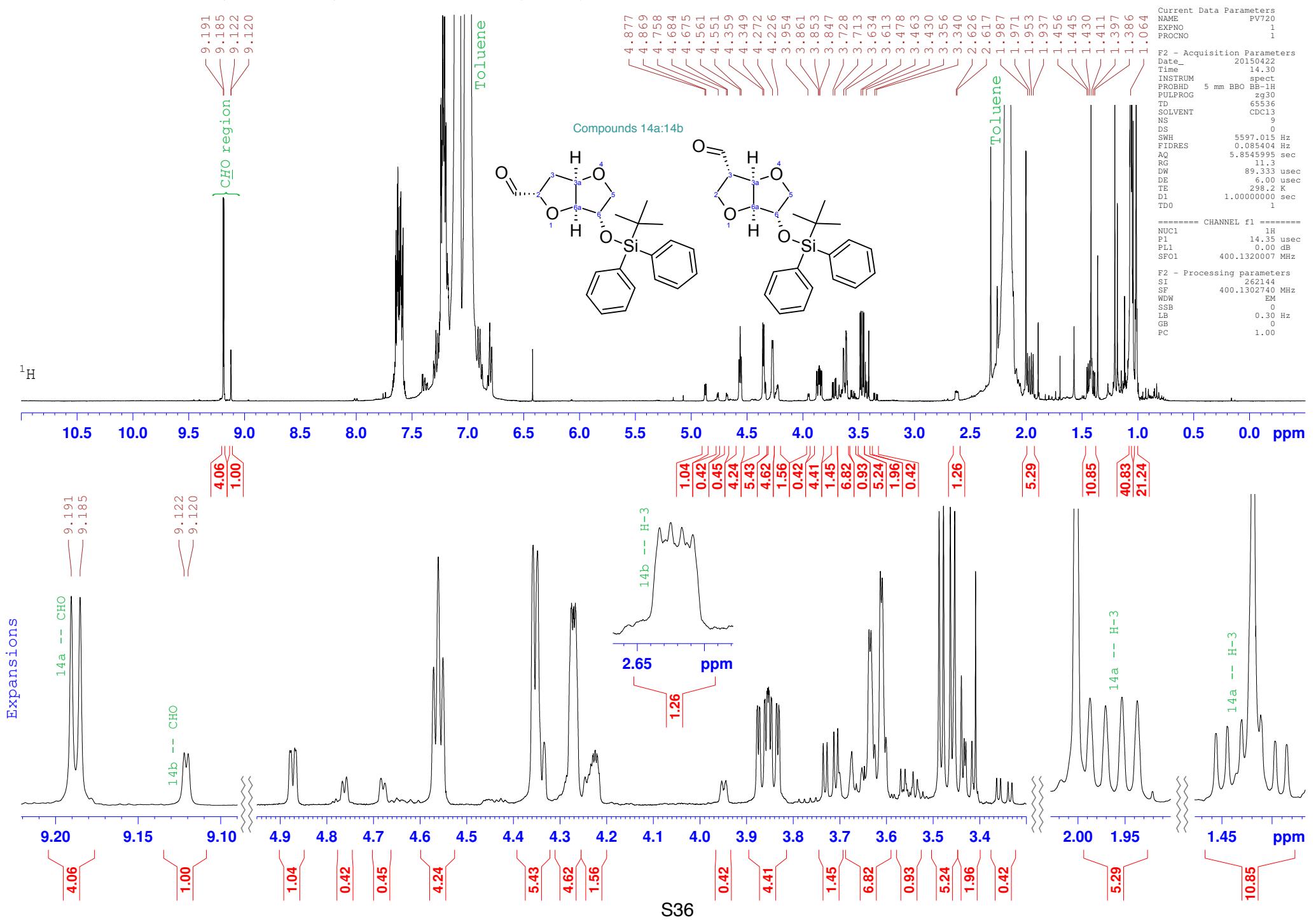
<sup>1</sup>H NMR spectrum (400.1 MHz) of compound 12 (purified)

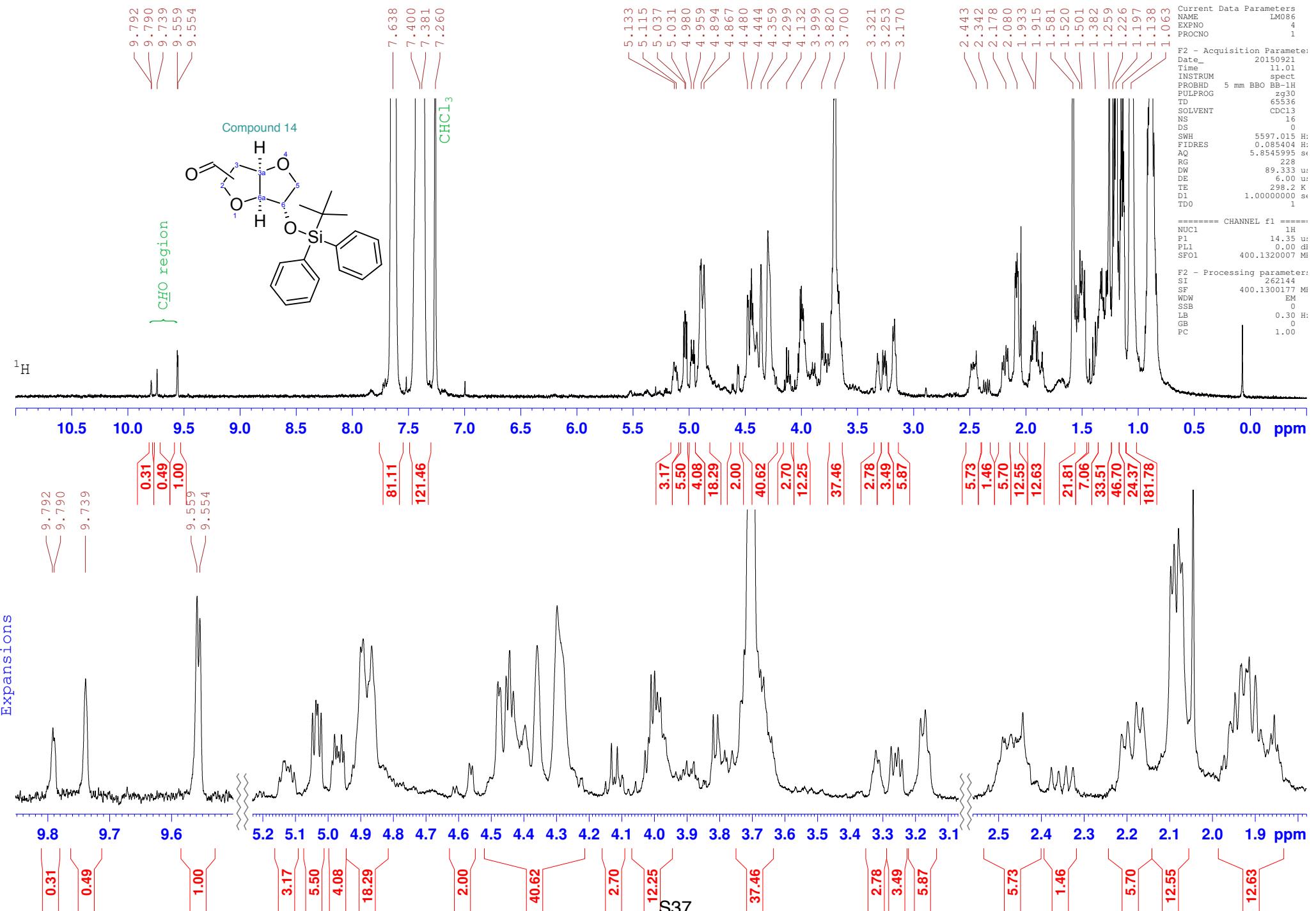
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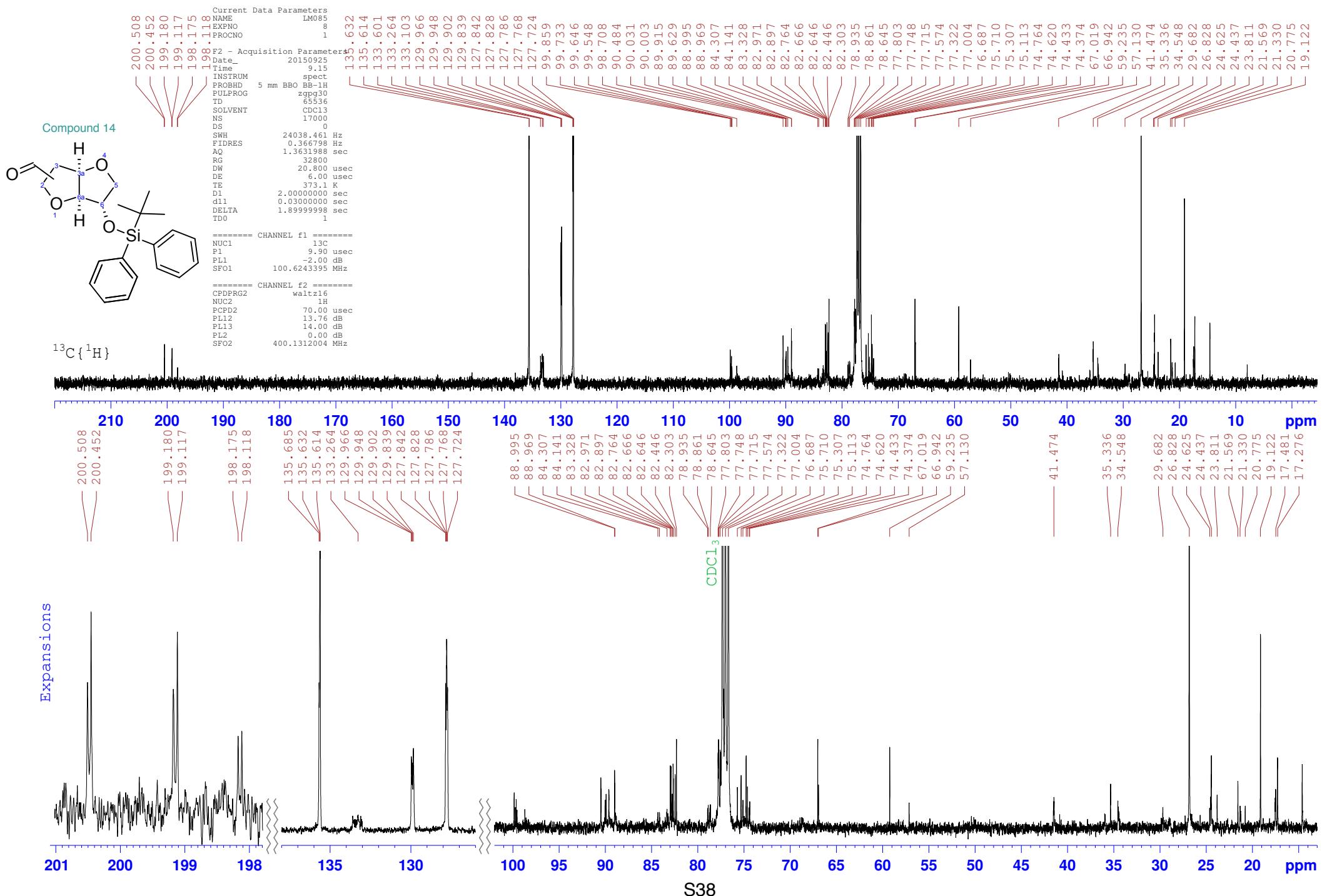
<sup>1</sup>H NMR spectrum (400.1 MHz) of compound 13 (crude)

<sup>1</sup>H NMR spectrum (400.1 MHz) of compound 13 (purified)

<sup>13</sup>C{<sup>1</sup>H} NMR spectrum (100.6 MHz) of compound 13 (purified)

<sup>1</sup>H NMR spectrum (400.1 MHz) of compound 14 (crude)

<sup>1</sup>H NMR spectrum (400.1 MHz) of compound 14 (purified)

<sup>13</sup>C{<sup>1</sup>H} NMR spectrum (100.6 MHz) of compound 14 (purified)

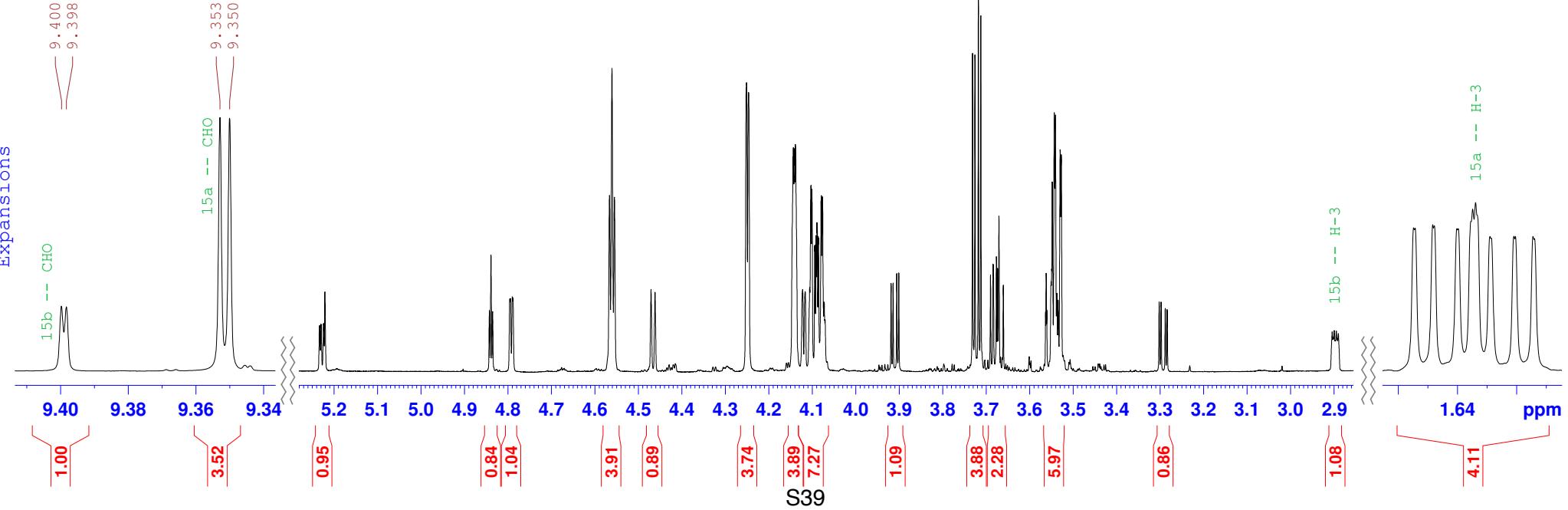
<sup>1</sup>H NMR spectrum (700.1 MHz) of compound 15 (crude)

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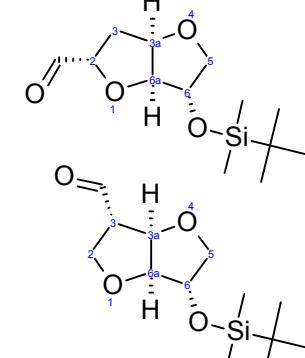
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 GB 0  
 PC 1.00

<sup>1</sup>H

Expansions



Compounds 15a:15b

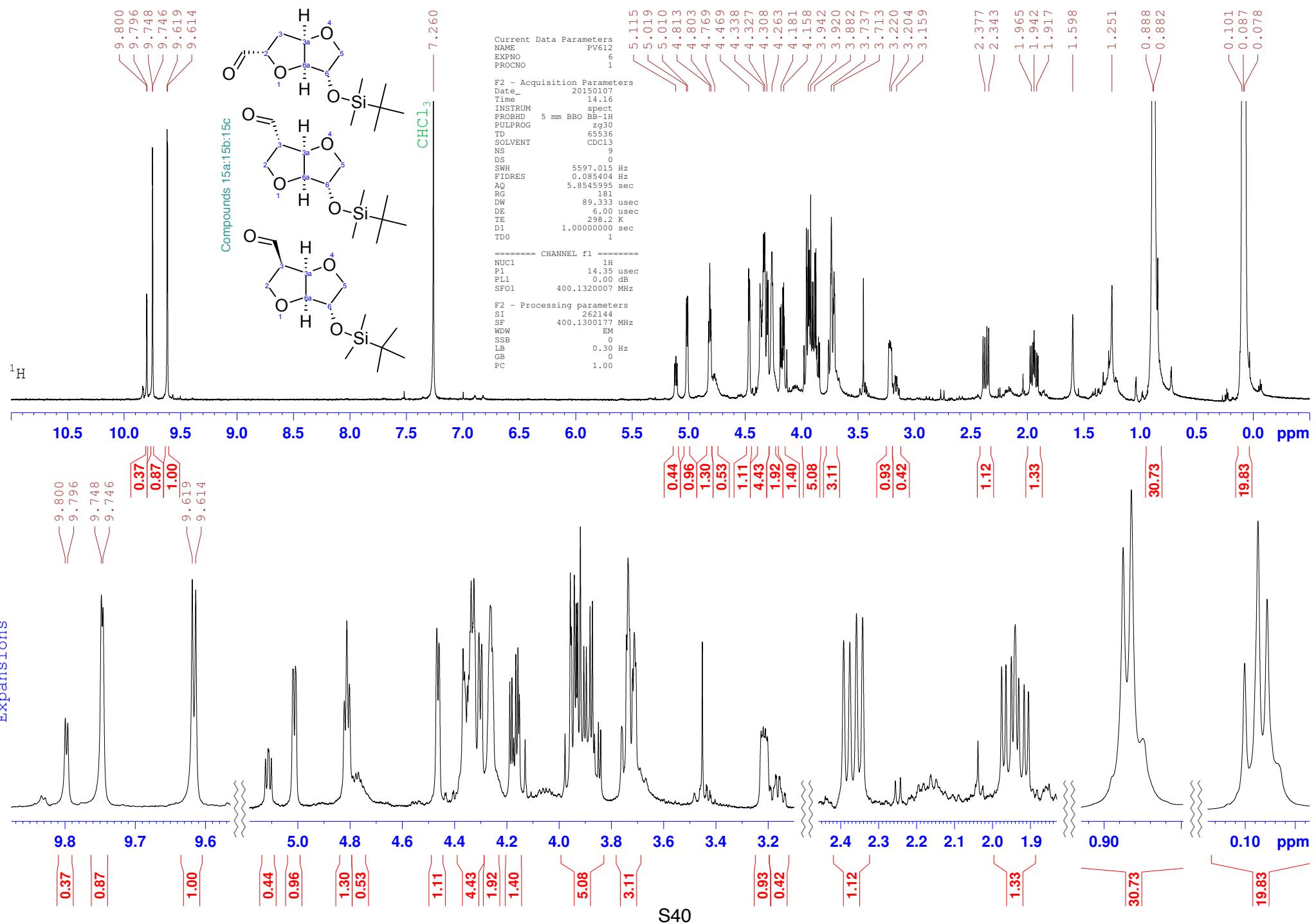


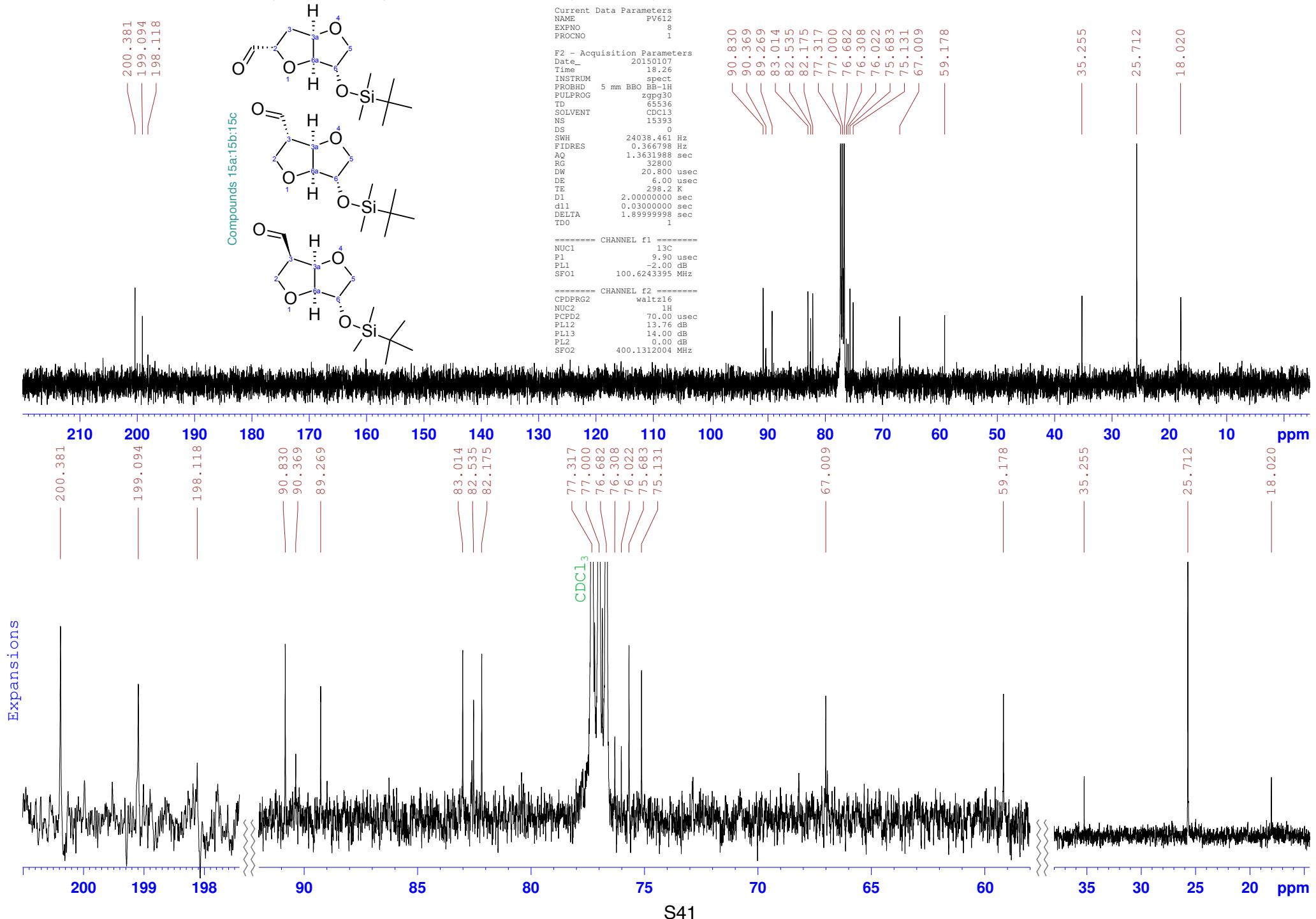
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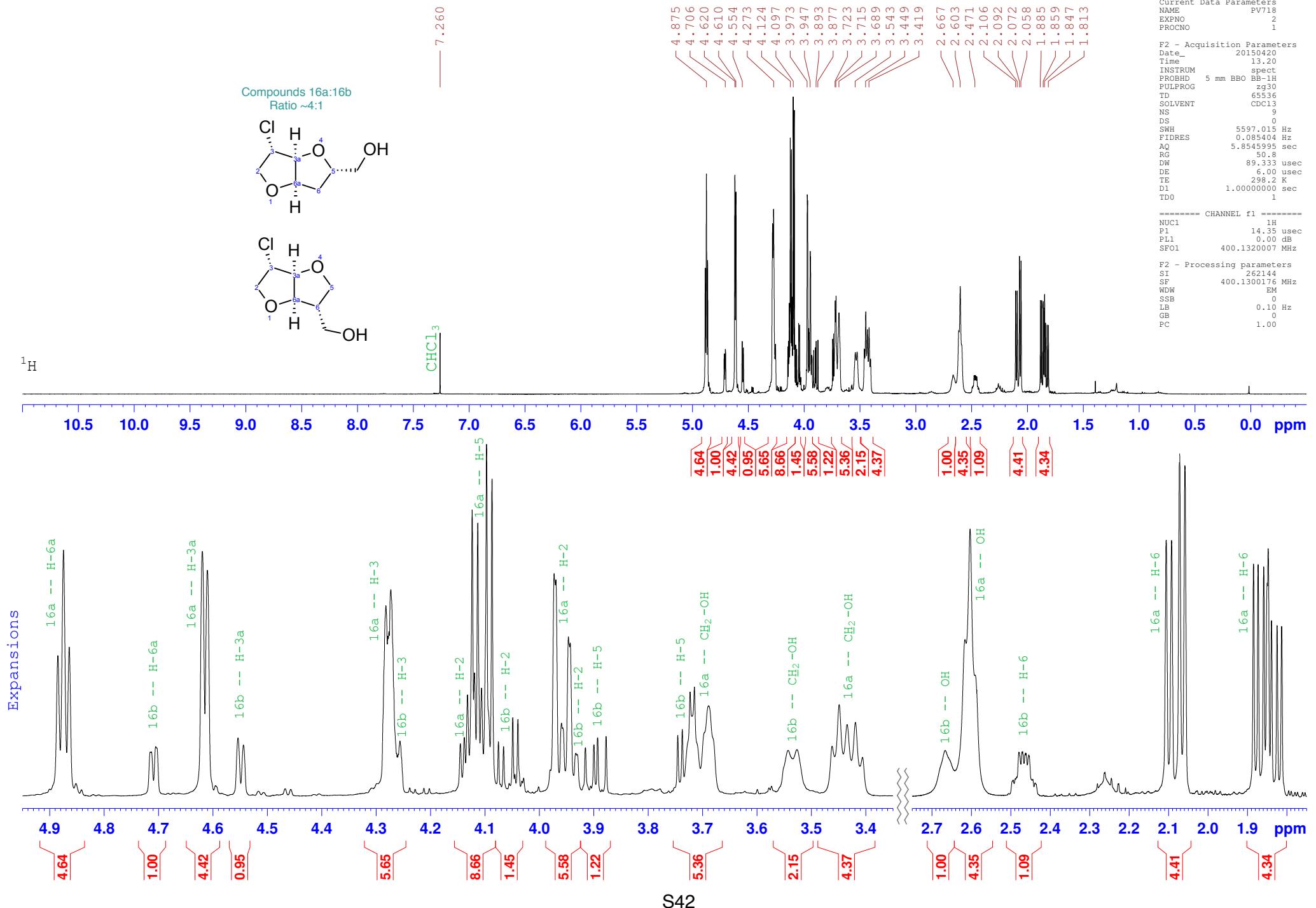
Toluene

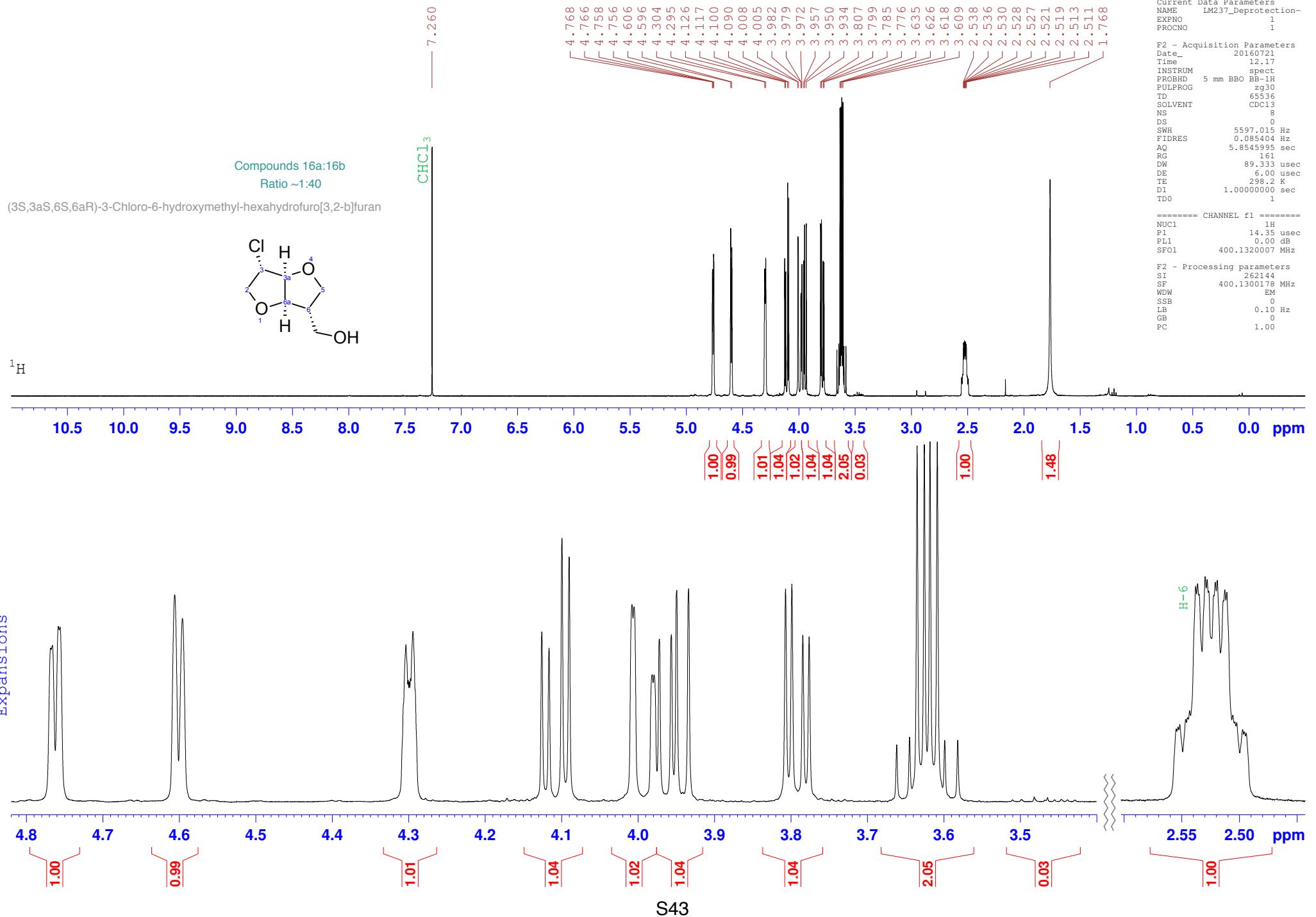
9.400 9.398 9.353 9.350 5.230 5.224 4.839 4.795 4.790 4.561 4.471 4.462 4.252 4.247 4.141 4.122 4.103 4.089 4.079 3.914 3.906 3.726 3.718 3.684 3.670 3.562 3.543 3.530 3.297 3.288 3.289 2.895 2.899 1.655 1.648 1.634 1.621 1.614 1.117 0.743 0.736 -0.061 -0.079

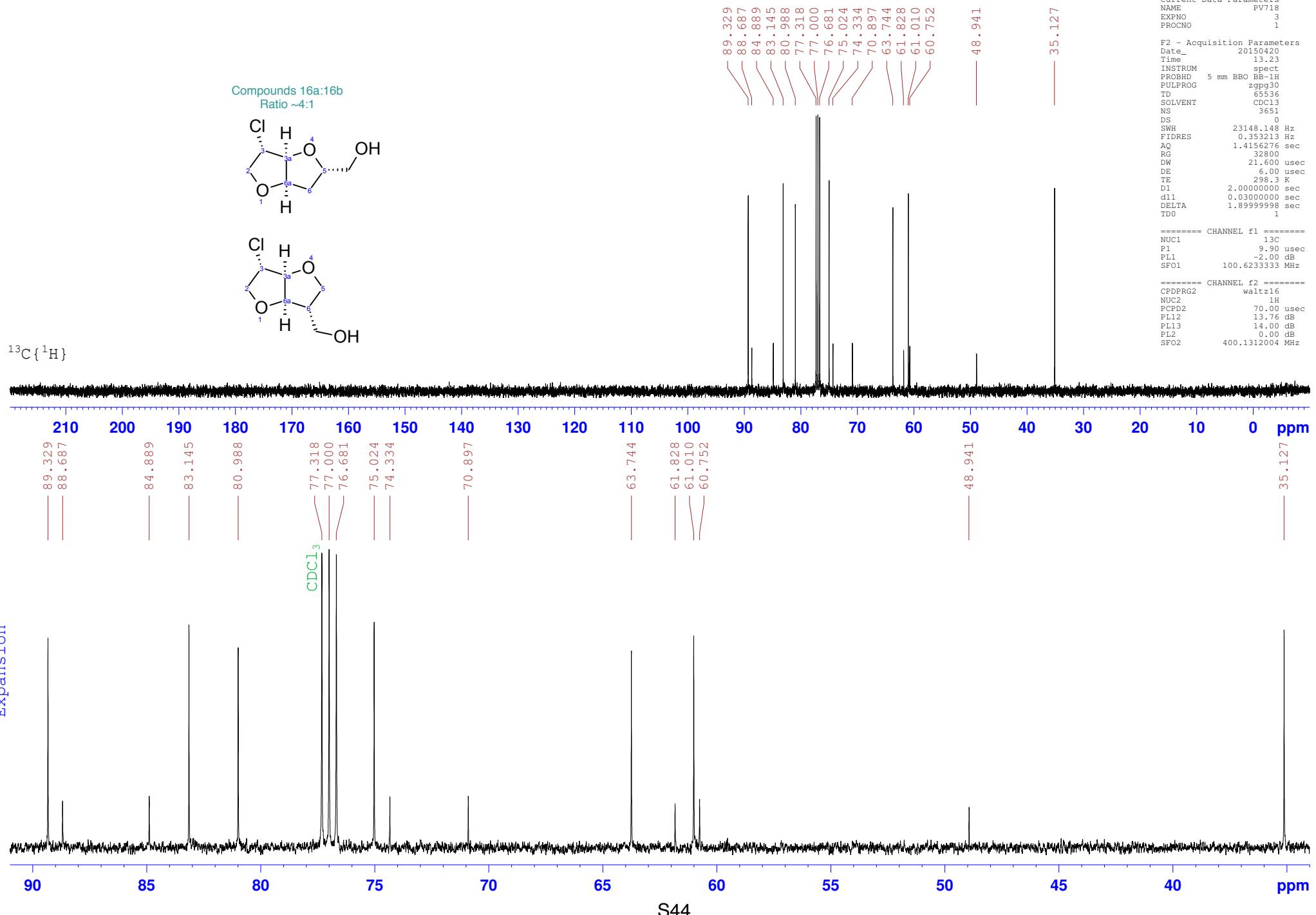
S39

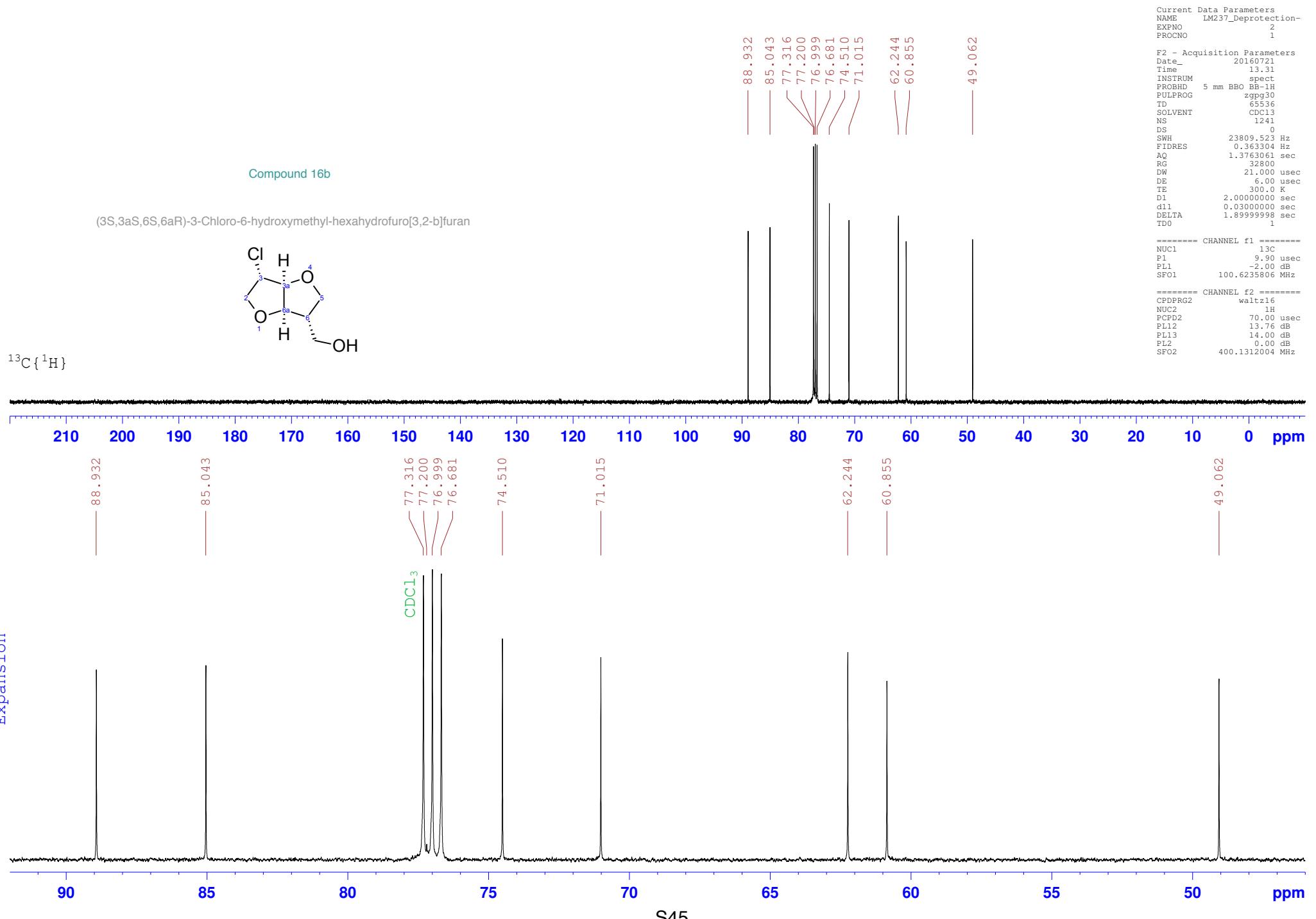
<sup>1</sup>H NMR spectrum (400.1 MHz) of compound 15 (purified)

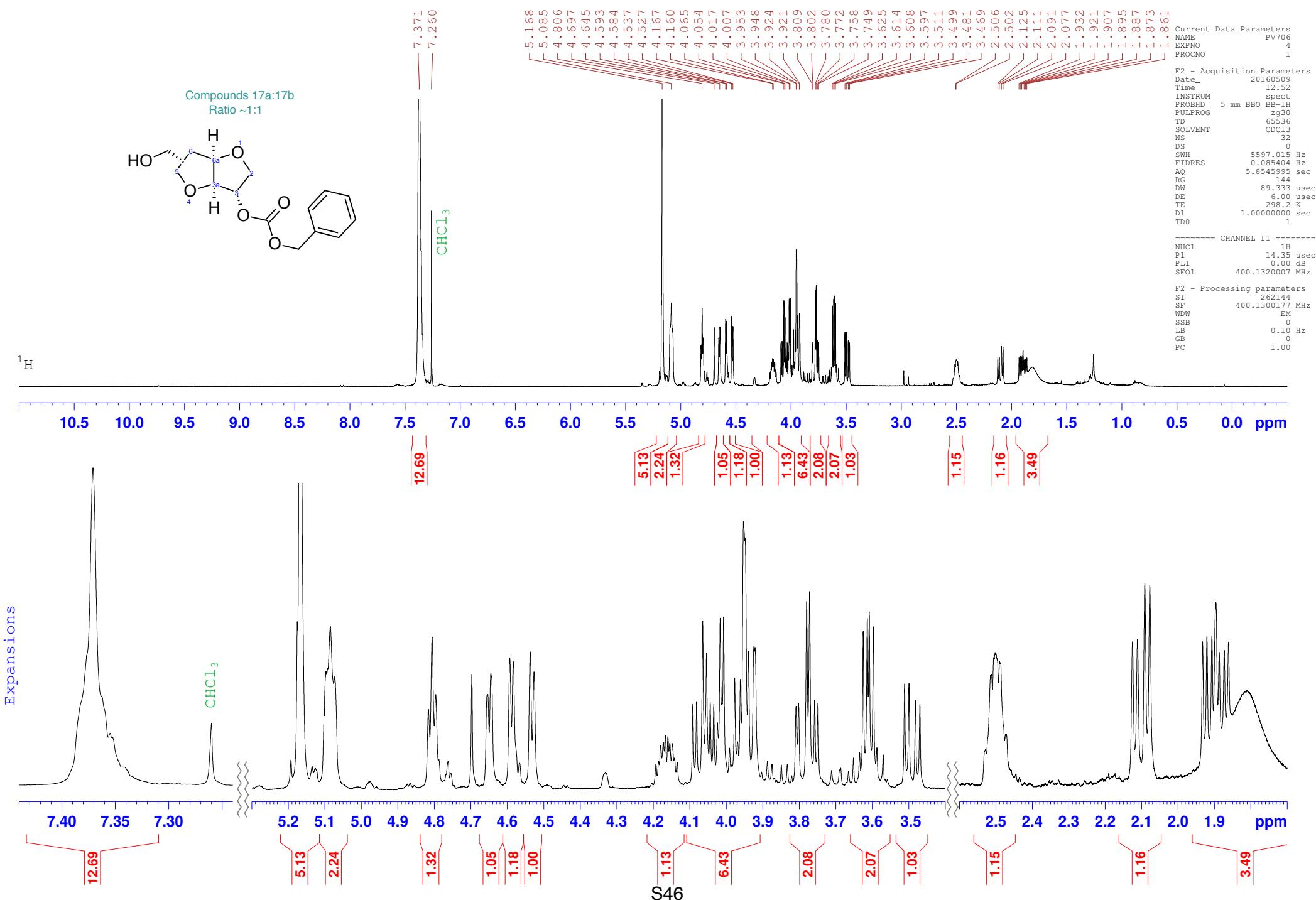
<sup>13</sup>C{<sup>1</sup>H} NMR spectrum (100.6 MHz) of compound 15 (purified)

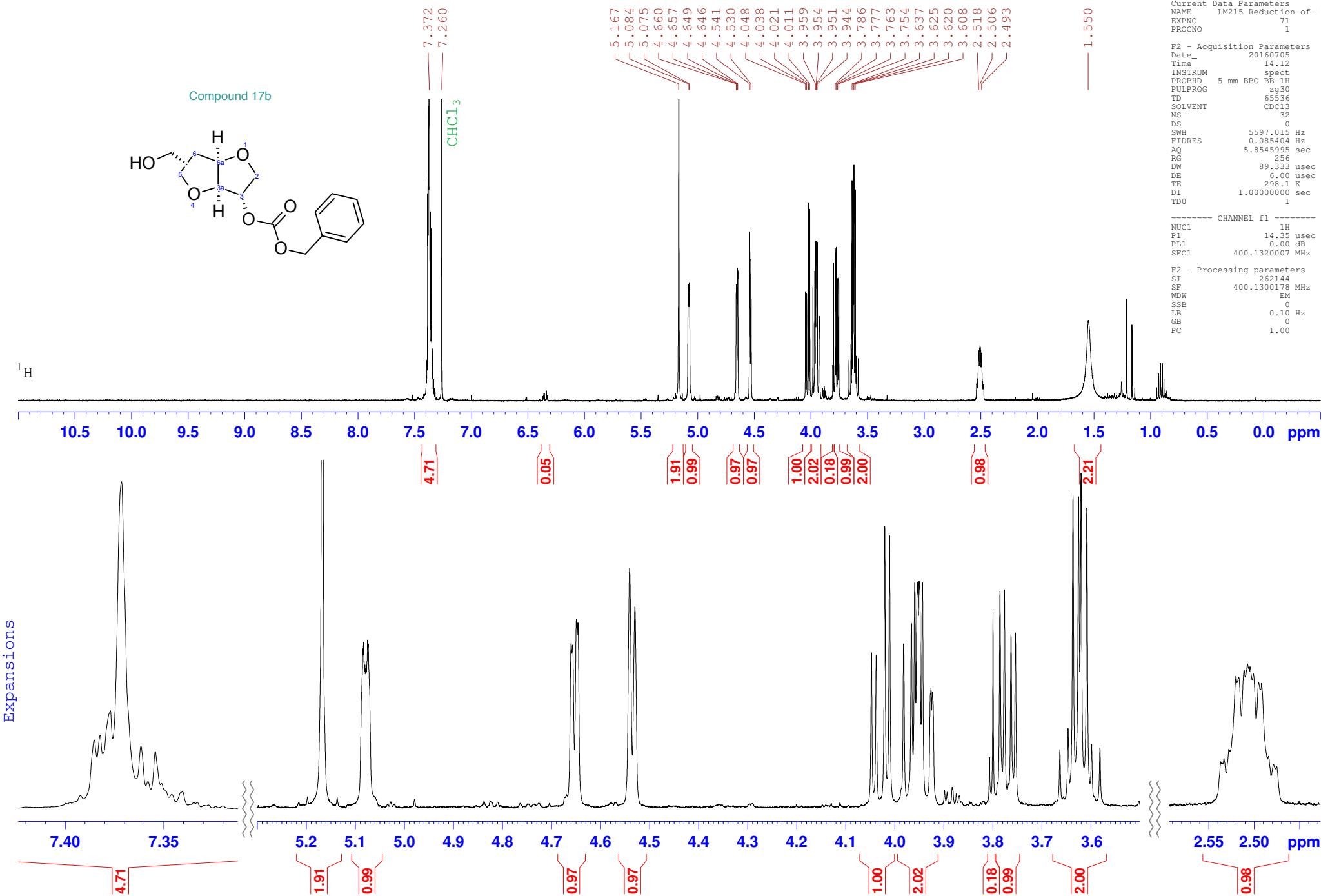
<sup>1</sup>H NMR spectrum (400.1 MHz) of compound 16

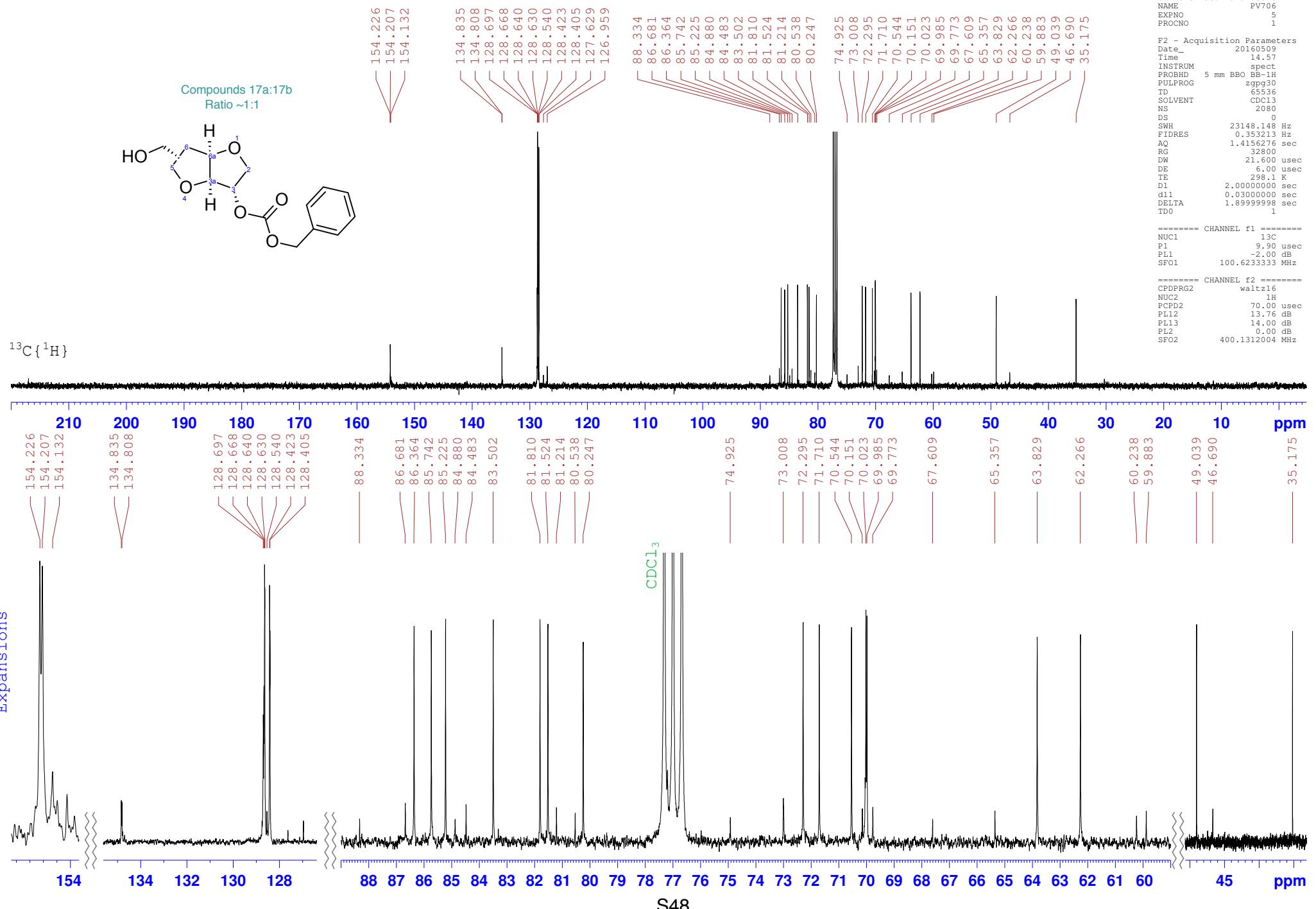
<sup>1</sup>H NMR spectrum (400.1 MHz) of compound 16

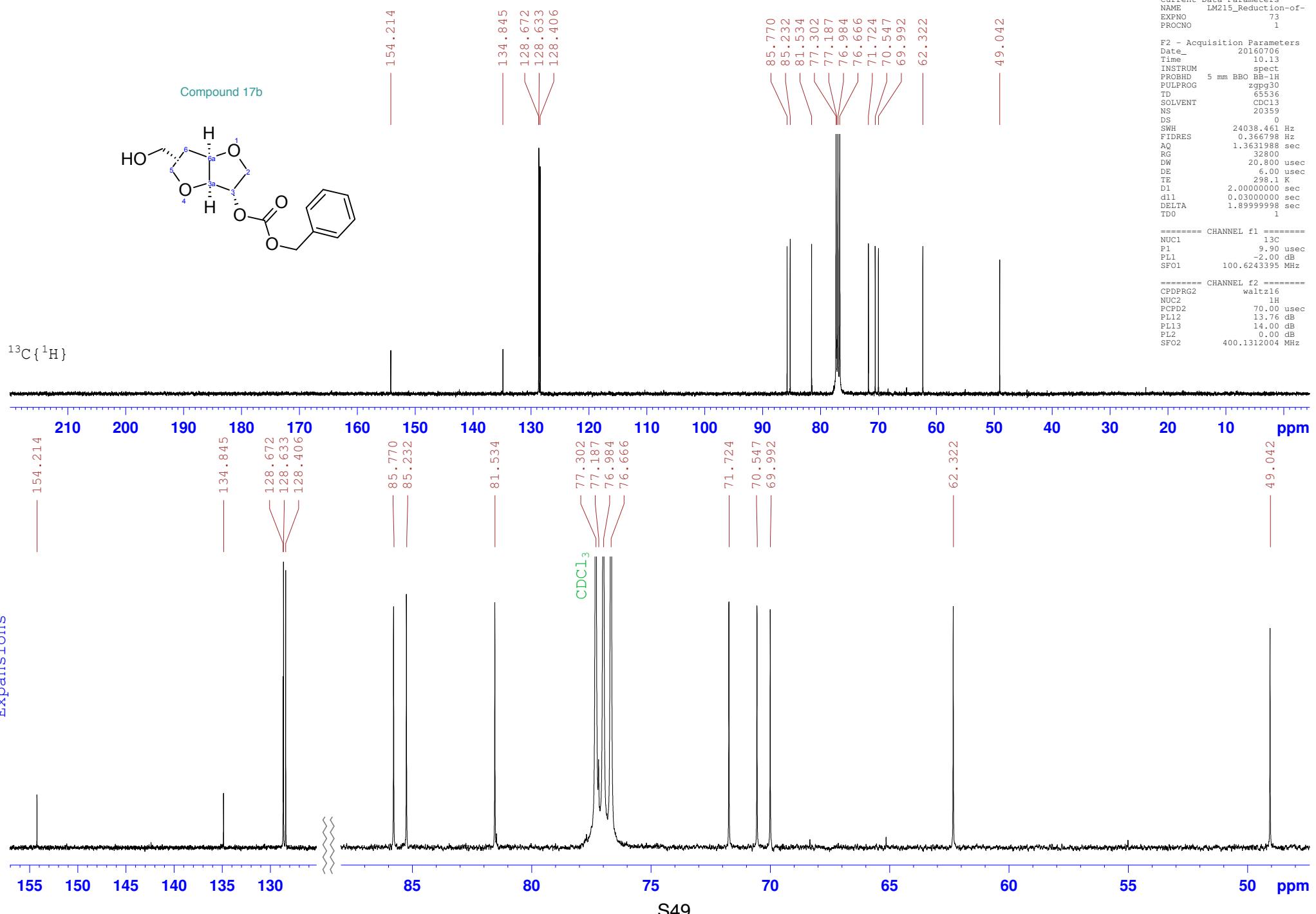
<sup>13</sup>C{<sup>1</sup>H} NMR spectrum (100.6 MHz) of compound 16

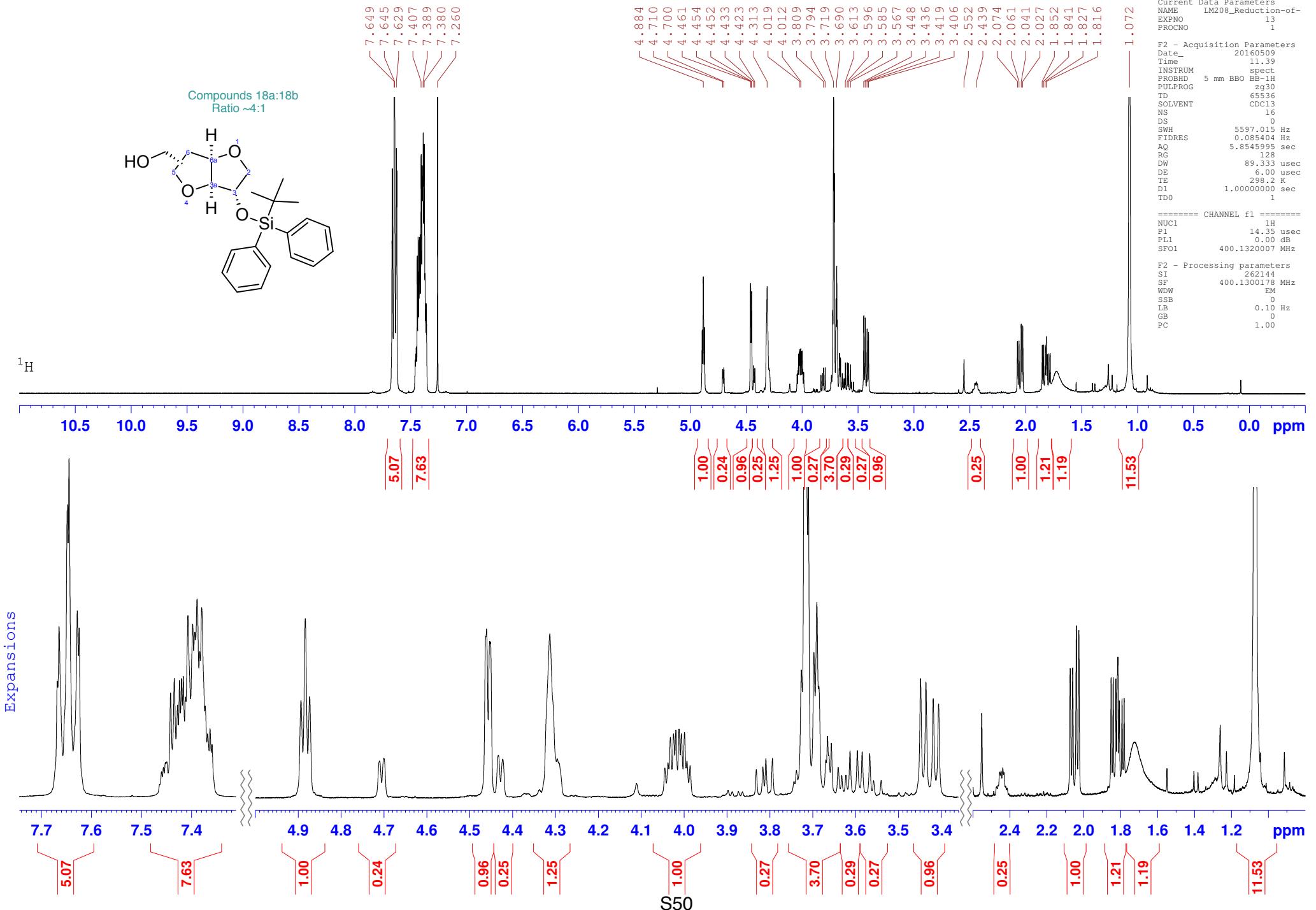
<sup>13</sup>C{<sup>1</sup>H} NMR spectrum (100.6 MHz) of compound 16

<sup>1</sup>H NMR spectrum (400.1 MHz) of compound 17

<sup>1</sup>H NMR spectrum (400.1 MHz) of compound 17

<sup>13</sup>C{<sup>1</sup>H} NMR spectrum (100.6 MHz) of compound 17

<sup>13</sup>C{<sup>1</sup>H} NMR spectrum (100.6 MHz) of compound 17

<sup>1</sup>H NMR spectrum (400.1 MHz) of compound 18

<sup>13</sup>C{<sup>1</sup>H} NMR spectrum (100.6 MHz) of compound 18