

## Supplementary Information

### Copper-Catalyzed Formal Transfer Hydrogenation/Deuteration of Aryl Alkynes

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## I. General Information

The following chemicals were purchased from commercial vendors and were used as received: Cu(OAc)<sub>2</sub> (99.999% from Alfa Aesar); (*R*)-(-)-4,4'-bis[di(3,5-di-*tert*-butyl-4-methoxyphenyl)phosphino]-3,3'-bi(1,2-methylenedioxybenzene) ((*R*)-DTBM-SEGPPOS) and (*S*)-(+)-4,4'-bis[di(3,5-di-*tert*-butyl-4-methoxyphenyl)phosphino]-3,3'-bi(1,2-methylenedioxybenzene) ((*S*)-DTBM-SEGPPOS) (TCI), dimethoxy(methyl)silane (TCI); 2-propanol-OD (Millipore Sigma); 2-propanol-*d*<sub>8</sub> (Acros Organic); ethanol (Oakwood Chemical); *tert*-butyldimethylsilyl chloride (TBSCl); D<sub>2</sub>O (Oakwood Chemical).

Anhydrous tetrahydrofuran (THF) was purified by an MBRAUN solvent purification system (MB-SPS). Prior to use, triethylamine (Et<sub>3</sub>N) was distilled over CaH<sub>2</sub> and stored over 3Å molecular sieves. Chloroform-*d* (CDCl<sub>3</sub>) was stored over 3Å molecular sieves. Thin-layer chromatography (TLC) was conducted with Silicycle silica gel 60Å F254 pre-coated plates (0.25 mm) and visualized with UV, Iodine and KMnO<sub>4</sub> stains. Flash chromatography was performed using Silia Flash® P60, 40-60 μm (230-400 mesh), purchased from Silicycle. For reactions that required heating (optimization, transfer hydrogenation and deuteration reactions), a PolyBlock for 2 dram vials was used on top of a Heidolph heating/stir plate.

<sup>1</sup>H NMR spectra were recorded on a Varian 300 or 400 MHz spectrometer and are reported in ppm using solvent as an internal standard (CDCl<sub>3</sub> at 7.26 ppm). Data reported as: s = singlet, d = doublet, t = triplet, q = quartet, p = pentet, sxt = sextet, hep = heptet, sep = septet, oct = octet, m = multiplet, br = broad; coupling constant(s) in Hz; integration. <sup>13</sup>C NMR spectra were recorded on a Varian 76 MHz or 101 MHz spectrometer and are reported in ppm using solvent as an internal standard (CDCl<sub>3</sub> at 77.16 ppm). <sup>19</sup>F NMR spectra were recorded on a Varian 376 MHz spectrometer. <sup>2</sup>H NMR spectra were recorded on a Varian 61 MHz spectrometer. Labeled solvent impurities were calculated out when reporting isolated yields.

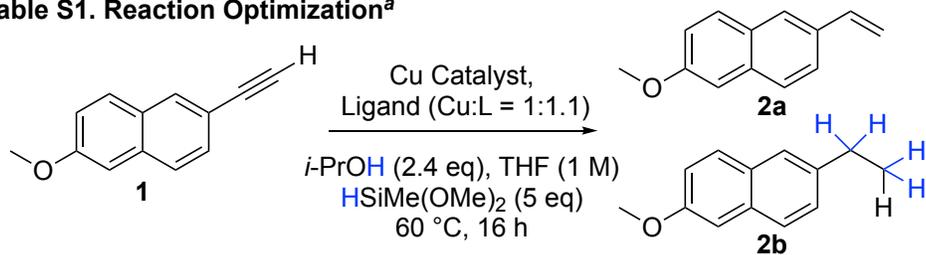
High-resolution mass spectra were obtained for all new compounds not previously reported using the resources of the Chemistry Instrument Center (CIC), University at Buffalo, SUNY, Buffalo, NY. Specifically, high resolution accurate mass analysis was conducted using the following instruments: 12T Bruker SolarixR 12 Hybrid FTMS, provided through funding from the National Institutes of Health, NIH S10 RR029517; a Thermo Q-Exactive Focus Orbitrap Liquid Chromatograph Tandem Mass Spectrometer and a Thermo Q-Exactive Orbitrap Gas Chromatograph Tandem Mass Spectrometer, provided through funding from the National Science Foundation, MRI-1919594.

## II. Optimization Studies

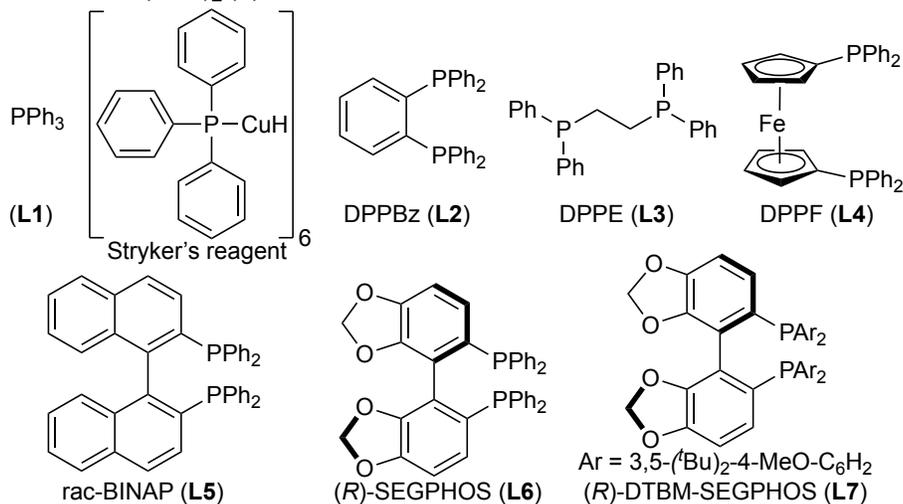
### General procedure A for optimization studies in Table S1.

In a N<sub>2</sub> filled glovebox, ligand, Cu catalyst (Cu:L = 1:1.1), and THF were added to an oven-dried 2-dram vial followed by dropwise addition of dimethoxy(methyl)silane (123  $\mu$ L, 1 mmol, 5 eq.). A color change from green/blue to orange was observed while stirring for 15 minutes. In a separate oven-dried 1-dram vial was added 2-ethynyl-6-methoxynaphthalene (36.4 mg, 0.2 mmol, 1 eq.), THF (0.1 mL), and 2-propanol (37  $\mu$ L, 0.48 mmol, 2.4 eq.). The solution in the 1-dram vial was added dropwise over 20 seconds to the 2-dram vial. The total volume of THF was calculated based on having a final reaction concentration of 1M based on the alkyne substrate. The 2-dram vial was capped with a red pressure relief cap, taken out of the glovebox, and stirred for 16 h at 60 °C at which point the reaction was filtered through a 1" silica plug with 20 mL of Et<sub>2</sub>O or CH<sub>2</sub>Cl<sub>2</sub> followed by an additional 80 mL of the appropriate solvent to elute the crude product into a 200 mL round bottom flask. The solvent was removed by rotary evaporation, and the product was analyzed by <sup>1</sup>H NMR using 1,3,5-trimethylbenzene as an internal standard. Yields for all entries were obtained by isolating the product after flash column chromatography if greater than 5% NMR yield was observed for **2b** in the crude <sup>1</sup>H NMR.

**Table S1. Reaction Optimization<sup>a</sup>**



Entry	Cu Catalyst (mol%) <sup>b</sup>	Ligand	Yield of <b>2a</b> (%)	Yield of <b>2b</b> (%)	RSM <b>1</b> (%)
1	Cu(OAc) <sub>2</sub> (5)	L1	11	trace <sup>c</sup>	48
2	Stryker's Reagent (5)	N/A	53	trace <sup>c</sup>	6
3	Cu(OAc) <sub>2</sub> (5)	L2	5	trace <sup>c</sup>	82
4	Cu(OAc) <sub>2</sub> (5)	L3	8	trace <sup>c</sup>	75
5	Cu(OAc) <sub>2</sub> (5)	L4	11	trace <sup>c</sup>	72
6	Cu(OAc) <sub>2</sub> (5)	L5	12	trace <sup>c</sup>	49
7	Cu(OAc) <sub>2</sub> (5)	L6	30	4 <sup>d</sup>	45
8	Cu(OAc) <sub>2</sub> (5)	L7	0	98 <sup>d</sup>	0
9	Cu(OAc) <sub>2</sub> (1)	L7	3.5	87 <sup>d</sup>	0
10	Cu(OAc) <sub>2</sub> (2)	L7	0	91 <sup>d</sup>	0
11	N/A	N/A	4	0 <sup>c</sup>	86
12	Cu(OAc) <sub>2</sub> (2)	N/A	3	0 <sup>c</sup>	80
13 <sup>e</sup>	Cu(OAc) <sub>2</sub> (2)	L7	0	95 <sup>d</sup>	0
14 <sup>f</sup>	Cu(OAc) <sub>2</sub> (2)	L7	0	93 <sup>d</sup>	0



<sup>a</sup>Reactions were conducted using 0.2 mmol of substrate. <sup>b</sup>Cu(OAc)<sub>2</sub> was used in the reactions as a 0.2 M solution in THF. <sup>c</sup>Yield was determined by <sup>1</sup>H NMR analysis of the crude reaction mixture, using 1,3,5-trimethylbenzene as an internal standard. <sup>d</sup>Yield determined after purification by flash column chromatography. <sup>e</sup>Poly(methylhydrosiloxane) (5 eq) was used instead of dimethoxy(methyl)silane. <sup>f</sup>Diethoxy(methyl)silane (5 eq) was used instead of dimethoxy(methyl)silane.

**Entry 1.** According to the general procedure A for optimization studies, a stirring solution of triphenylphosphine **L1** (5.8 mg, 0.022 mmol, 0.11 eq.), Cu(OAc)<sub>2</sub> (50  $\mu$ L of a 0.2 M solution in THF, 0.01 mmol, 0.05 eq.), and dimethoxy(methyl)silane (123  $\mu$ L, 1.0 mmol, 5 eq.) in THF (0.05 mL) was prepared, and to this was added a solution of 2-ethynyl-6-methoxynaphthalene (36.4 mg, 0.2 mmol, 1 eq.) and 2-propanol (37  $\mu$ L, 0.48 mmol, 2.4 eq.) in THF (0.1 mL) dropwise. The reaction stirred for 16 h at 60°C, after which it was filtered through a silica plug with Et<sub>2</sub>O (20 mL) and eluted with Et<sub>2</sub>O (80 mL). The solvent was removed by rotary evaporation, and the crude product was analyzed by <sup>1</sup>H NMR with 1,3,5-trimethylbenzene as an internal standard, (11% **2a**, trace **2b**, 48% RSM **1**).

**Entry 2.** According to the general procedure A for optimization studies, a stirring solution of (triphenylphosphine)copper hydride hexamer (Stryker's Reagent) (3.3 mg, 0.0017 mmol, 0.00083 eq.), and dimethoxy(methyl)silane (123  $\mu$ L, 1.0 mmol, 5 eq.) in THF (0.1 mL) was prepared, and to this was added a solution of 2-ethynyl-6-methoxynaphthalene (36.4 mg, 0.2 mmol, 1 eq.) and 2-propanol (37  $\mu$ L, 0.48 mmol, 2.4 eq.) in THF (0.1 mL) dropwise. The reaction stirred for 16 h at 60°C, after which it was filtered through a silica plug with Et<sub>2</sub>O (20 mL) and eluted with Et<sub>2</sub>O (80 mL). The solvent was removed by rotary evaporation, and the crude product was analyzed by <sup>1</sup>H NMR with 1,3,5-trimethylbenzene as an internal standard (53% **2a**, 2.5% **2b**, 6% RSM **1**).

**Entry 3.** According to the general procedure A for optimization studies, a stirring solution of 1,2-bis(diphenylphosphino)benzene **L2** (4.9 mg, 0.011 mmol, 0.055 eq.), Cu(OAc)<sub>2</sub> (50  $\mu$ L of a 0.2 M solution in THF, 0.01 mmol, 0.05 eq.), and dimethoxy(methyl)silane (123  $\mu$ L, 1.0 mmol, 5 eq.) in THF (0.05 mL) was prepared, and to this was added a solution of 2-ethynyl-6-methoxynaphthalene (36.4 mg, 0.2 mmol, 1 eq.) and 2-propanol (37  $\mu$ L, 0.48 mmol, 2.4 eq.) in THF (0.1 mL) dropwise. The reaction stirred for 16 h at 60°C, after which it was filtered through a silica plug with Et<sub>2</sub>O (20 mL) and eluted with Et<sub>2</sub>O (80 mL). The solvent was removed by rotary evaporation, and the crude product was analyzed by <sup>1</sup>H NMR with 1,3,5-trimethylbenzene as an internal standard (5% **2a**, trace **2b**, 82% RSM **1**).

**Entry 4.** According to the general procedure A for optimization studies, a stirring solution of 1,2-bis(diphenylphosphino)ethane **L3** (4.4 mg, 0.011 mmol, 0.055 eq.), Cu(OAc)<sub>2</sub> (50  $\mu$ L of a 0.2 M solution in THF, 0.01 mmol, 0.05 eq.), and dimethoxy(methyl)silane (123  $\mu$ L, 1.0 mmol, 5 eq.) in THF (0.05 mL) was prepared, and to this was added a solution of 2-ethynyl-6-methoxynaphthalene (36.4 mg, 0.2 mmol, 1 eq.) and 2-propanol (37  $\mu$ L, 0.48 mmol, 2.4 eq.) in THF (0.1 mL) dropwise. The reaction stirred for 16 h at 60°C, after which it was filtered through a silica plug with Et<sub>2</sub>O (20 mL) and eluted with Et<sub>2</sub>O (80 mL). The solvent was removed by rotary evaporation, and the crude product was analyzed by <sup>1</sup>H NMR with 1,3,5-trimethylbenzene as an internal standard (8% **2a**, trace **2b**, 75% RSM **1**).

**Entry 5.** According to the general procedure A for optimization studies, a stirring solution of 1,1'-bis(diphenylphosphino)-ferrocene **L4** (6.1 mg, 0.011 mmol, 0.055 eq.), Cu(OAc)<sub>2</sub> (50  $\mu$ L of a 0.2 M solution in THF, 0.01 mmol, 0.05 eq.), and dimethoxy(methyl)silane (123  $\mu$ L, 1.0 mmol, 5 eq.) in THF (0.05 mL) was prepared, and to this was added a solution of 2-ethynyl-6-methoxynaphthalene (36.4 mg, 0.2 mmol, 1 eq.) and 2-propanol (37  $\mu$ L, 0.48 mmol, 2.4 eq.) in THF (0.1 mL) dropwise. The reaction stirred for 16 h at 60°C, after which it was filtered through a silica plug with Et<sub>2</sub>O (20 mL) and eluted with Et<sub>2</sub>O (80 mL). The solvent was removed by rotary evaporation, and the crude product was analyzed by <sup>1</sup>H NMR with 1,3,5-trimethylbenzene as an internal standard (11% **2a**, trace **2b**, 72% RSM **1**).

**Entry 6.** According to the general procedure A for optimization studies, a stirring solution of ( $\pm$ )-2,2'-bis(diphenylphosphino)-1,1'-binaphthalene **L5** (6.8 mg, 0.011 mmol, 0.055 eq.), Cu(OAc)<sub>2</sub> (50  $\mu$ L of a 0.2 M solution in THF, 0.01 mmol, 0.05 eq.), and dimethoxy(methyl)silane (123  $\mu$ L, 1.0 mmol, 5 eq.) in THF (0.05 mL) was prepared, and to this was added a solution of 2-ethynyl-6-methoxynaphthalene (36.4 mg, 0.2 mmol, 1 eq.) and 2-propanol (37  $\mu$ L, 0.48 mmol, 2.4 eq.) in THF (0.1 mL) dropwise. The reaction stirred for 16 h at 60°C, after which it was filtered through a silica plug with Et<sub>2</sub>O (20 mL) and eluted with Et<sub>2</sub>O (80 mL). The solvent was removed by rotary evaporation, and the crude product was analyzed by <sup>1</sup>H NMR with 1,3,5-trimethylbenzene as an internal standard (12% **2a**, trace **2b**, 49% RSM **1**).

**Entry 7.** According to the general procedure A for optimization studies, a stirring solution of (*R*)-(+)-5,5'-bis(diphenylphosphino)-4,4'-bi-1,3-benzodioxole **L6** (6.7 mg, 0.011 mmol, 0.055 eq.), Cu(OAc)<sub>2</sub> (50 μL of a 0.2 M solution in THF, 0.01 mmol, 0.05 eq.), and dimethoxy(methyl)silane (123 μL, 1.0 mmol, 5 eq.) in THF (0.05 mL) was prepared, and to this was added a solution of 2-ethynyl-6-methoxynaphthalene (36.4 mg, 0.2 mmol, 1 eq.) and 2-propanol (37 μL, 0.48 mmol, 2.4 eq.) in THF (0.1 mL) dropwise. The reaction stirred for 16 h at 60°C, after which it was filtered through a silica plug with Et<sub>2</sub>O (20 mL) and eluted with Et<sub>2</sub>O (80 mL). The solvent was removed by rotary evaporation, and the crude product was analyzed by <sup>1</sup>H NMR with 1,3,5-trimethylbenzene as an internal standard. The crude product was dry loaded onto silica gel, and was purified by flash column chromatography using gradient elution (50 mL of hexane, 100 mL of 2% ethyl acetate in hexane, and 50 mL of 5% ethyl acetate in hexane) to yield a white solid (28.8 mg, 30% **2a**, 4% **2b**, 45% RSM **1**).

**Entry 8.** According to the general procedure A for optimization studies, a stirring solution of (*R*)-(-)-5,5'-bis[di(3,5-*tert*-butyl-4-methoxyphenyl)phosphino]-4,4'-bi-1,3-benzodioxole **L7** (13.0 mg, 0.011 mmol, 0.055 eq.), Cu(OAc)<sub>2</sub> (50 μL of a 0.2 M solution in THF, 0.01 mmol, 0.05 eq.), and dimethoxy(methyl)silane (123 μL, 1.0 mmol, 5 eq.) in THF (0.05 mL) was prepared, and to this was added a solution of 2-ethynyl-6-methoxynaphthalene (36.4 mg, 0.2 mmol, 1 eq.) and 2-propanol (37 μL, 0.48 mmol, 2.4 eq.) in THF (0.1 mL) dropwise. The reaction stirred for 16 h at 60°C, after which it was filtered through a silica plug with Et<sub>2</sub>O (20 mL) and eluted with Et<sub>2</sub>O (80 mL). The solvent was removed by rotary evaporation, and the crude product was analyzed by <sup>1</sup>H NMR with 1,3,5-trimethylbenzene as an internal standard. The crude product was dry loaded onto silica gel, and was purified by column chromatography using gradient elution (50 mL of hexanes, 100 mL of 2% ethyl acetate in hexane, and 50 mL of 5% ethyl acetate in hexane) to yield a white solid (36.4 mg, 0.195 mmol, 98% yield).

**Entry 9.** According to the general procedure A for optimization studies, a stirring solution of (*R*)-(-)-5,5'-bis[di(3,5-*tert*-butyl-4-methoxyphenyl)phosphino]-4,4'-bi-1,3-benzodioxole **L7** (2.6 mg, 0.0022 mmol, 0.011 eq.), Cu(OAc)<sub>2</sub> (10 μL of a 0.2 M solution in THF, 0.002 mmol, 0.01 eq.), and dimethoxy(methyl)silane (123 μL, 1.0 mmol, 5 eq.) in THF (0.09 mL) was prepared, and to this was added a solution of 2-ethynyl-6-methoxynaphthalene (36.4 mg, 0.2 mmol, 1 eq.) and 2-propanol (37 μL, 0.48 mmol, 2.4 eq.) in THF (0.1 mL) dropwise. The reaction stirred for 16 h at 60°C, after which it was filtered through a silica plug with Et<sub>2</sub>O (20 mL) and eluted with Et<sub>2</sub>O (80 mL). The solvent was removed by rotary evaporation, and the crude product was analyzed by <sup>1</sup>H NMR with 1,3,5-trimethylbenzene as an internal standard. The crude product was dry loaded onto silica gel, and was purified by column chromatography using gradient elution (50 mL of hexane, 100 mL of 2% ethyl acetate in hexane, and 50 mL of 5% ethyl acetate in hexane) to yield a white solid (33.8 mg, 3.5% **2a**, 87% **2b**).

**Entry 10.** According to the general procedure A for optimization studies, a stirring solution of (*R*)-(-)-5,5'-bis[di(3,5-*tert*-butyl-4-methoxyphenyl)phosphino]-4,4'-bi-1,3-benzodioxole **L7** (5.2 mg, 0.0044 mmol, 0.022 eq.), Cu(OAc)<sub>2</sub> (20 μL of a 0.2 M solution in THF, 0.004 mmol, 0.02 eq.), and dimethoxy(methyl)silane (123 μL, 1.0 mmol, 5 eq.) in THF (0.08 mL) was prepared, and to this was added a solution of 2-ethynyl-6-methoxynaphthalene (36.4 mg, 0.2 mmol, 1 eq.) and 2-propanol (37 μL, 0.48 mmol, 2.4 eq.) in THF (0.1 mL) dropwise. The reaction stirred for 16 h at 60°C, after which it was filtered through a silica plug with Et<sub>2</sub>O (20 mL) and eluted with Et<sub>2</sub>O (80 mL). The solvent was removed by rotary evaporation, and the crude product was analyzed by <sup>1</sup>H NMR with 1,3,5-trimethylbenzene as an internal standard. The crude product was dry loaded onto silica gel, and was purified by column chromatography using gradient elution (50 mL of hexane, 100 mL of 2% ethyl acetate in hexane, and 50 mL of 5% ethyl acetate in hexane) to yield a white solid (33.8 mg, 0.182 mmol, 91% yield).

**Entry 11.** According to the general procedure A for optimization studies, a stirring solution of dimethoxy(methyl)silane (123 μL, 1.0 mmol, 5 eq.) in THF (0.1 mL) was prepared, and to this was added a solution of 2-ethynyl-6-methoxynaphthalene (36.4 mg, 0.2 mmol, 1 eq.) and 2-propanol (37 μL, 0.48 mmol, 2.4 eq.) in THF (0.1 mL) dropwise. The reaction stirred for 16 h at 60°C, after which it was filtered through a silica plug with Et<sub>2</sub>O (20 mL) and eluted with Et<sub>2</sub>O (80 mL). The solvent was removed by rotary evaporation, and the crude product was analyzed by <sup>1</sup>H NMR with 1,3,5-trimethylbenzene as an internal standard (4% **2a**, 86% RSM **1**).

**Entry 12.** According to the general procedure A for optimization studies, a stirring solution of  $\text{Cu}(\text{OAc})_2$  (20  $\mu\text{L}$  of a 0.2 M solution in THF, 0.004 mmol, 0.02 eq.) and dimethoxy(methyl)silane (123  $\mu\text{L}$ , 1.0 mmol, 5 eq.) in THF (0.08 mL) was prepared, and to this was added a solution of 2-ethynyl-6-methoxynaphthalene (36.4 mg, 0.2 mmol, 1 eq.) and 2-propanol (37  $\mu\text{L}$ , 0.48 mmol, 2.4 eq.) in THF (0.1 mL) dropwise. The reaction stirred for 16 h at 60°C, after which it was filtered through a silica plug with  $\text{Et}_2\text{O}$  (20 mL) and eluted with  $\text{Et}_2\text{O}$  (80 mL). The solvent was removed by rotary evaporation, and the crude product was analyzed by  $^1\text{H}$  NMR with 1,3,5-trimethylbenzene as an internal standard (3% **2a**, 80% RSM **1**).

**Entry 13.** According to the general procedure A for optimization studies, a stirring solution of (*S*)-(-)-5,5'-bis[di(3,5-di-*tert*-butyl-4-methoxyphenyl)phosphino]-4,4'-bi-1,3-benzodioxole **L7** (5.2 mg, 0.0044 mmol, 0.022 eq.),  $\text{Cu}(\text{OAc})_2$  (20  $\mu\text{L}$  of a 0.2 M solution in THF, 0.004 mmol, 0.02 eq.), and poly(methylhydrosiloxane) (67  $\mu\text{L}$ , 1.0 mmol, 5 eq.) in THF (0.08 mL) was prepared, and to this was added a solution of 2-ethynyl-6-methoxynaphthalene (36.4 mg, 0.2 mmol, 1 eq.) and 2-propanol (37  $\mu\text{L}$ , 0.48 mmol, 2.4 eq.) in THF (0.1 mL) dropwise. The reaction stirred for 16 h at 60°C, after which it was filtered through a silica plug with  $\text{Et}_2\text{O}$  (20 mL) and eluted with  $\text{Et}_2\text{O}$  (80 mL). The solvent was removed by rotary evaporation, and the crude product was analyzed by  $^1\text{H}$  NMR with 1,3,5-trimethylbenzene as an internal standard. The crude product was dry loaded onto silica gel, and was purified by column chromatography using gradient elution (50 mL of hexane, 100 mL of 2% ethyl acetate in hexane, and 50 mL of 5% ethyl acetate in hexane) to yield a white solid (35.4 mg, 0.19 mmol, 95% yield).

**Entry 14.** According to the general procedure A for optimization studies, a stirring solution of (*S*)-(-)-5,5'-bis[di(3,5-di-*tert*-butyl-4-methoxyphenyl)phosphino]-4,4'-bi-1,3-benzodioxole **L7** (5.2 mg, 0.0044 mmol, 0.022 eq.),  $\text{Cu}(\text{OAc})_2$  (20  $\mu\text{L}$  of a 0.2 M solution in THF, 0.004 mmol, 0.02 eq.), and diethoxy(methyl)silane (160  $\mu\text{L}$ , 1.0 mmol, 5 eq.) in THF (0.08 mL) was prepared, and to this was added a solution of 2-ethynyl-6-methoxynaphthalene (36.4 mg, 0.2 mmol, 1 eq.) and 2-propanol (37  $\mu\text{L}$ , 0.48 mmol, 2.4 eq.) in THF (0.1 mL) dropwise. The reaction stirred for 16 h at 60°C, after which it was filtered through a silica plug with  $\text{Et}_2\text{O}$  (20 mL) and eluted with  $\text{Et}_2\text{O}$  (80 mL). The solvent was removed by rotary evaporation, and the crude product was analyzed by  $^1\text{H}$  NMR with 1,3,5-trimethylbenzene as an internal standard. The crude product was dry loaded onto silica gel, and was purified by column chromatography using gradient elution (50 mL of hexane, 100 mL of 2% ethyl acetate in hexane, and 50 mL of 5% ethyl acetate in hexane) to yield a white solid (34.7 mg, 0.186 mmol, 93% yield).

### III. Transfer Hydrogenation Reaction Scope

#### General procedure for transfer hydrogenation (B)

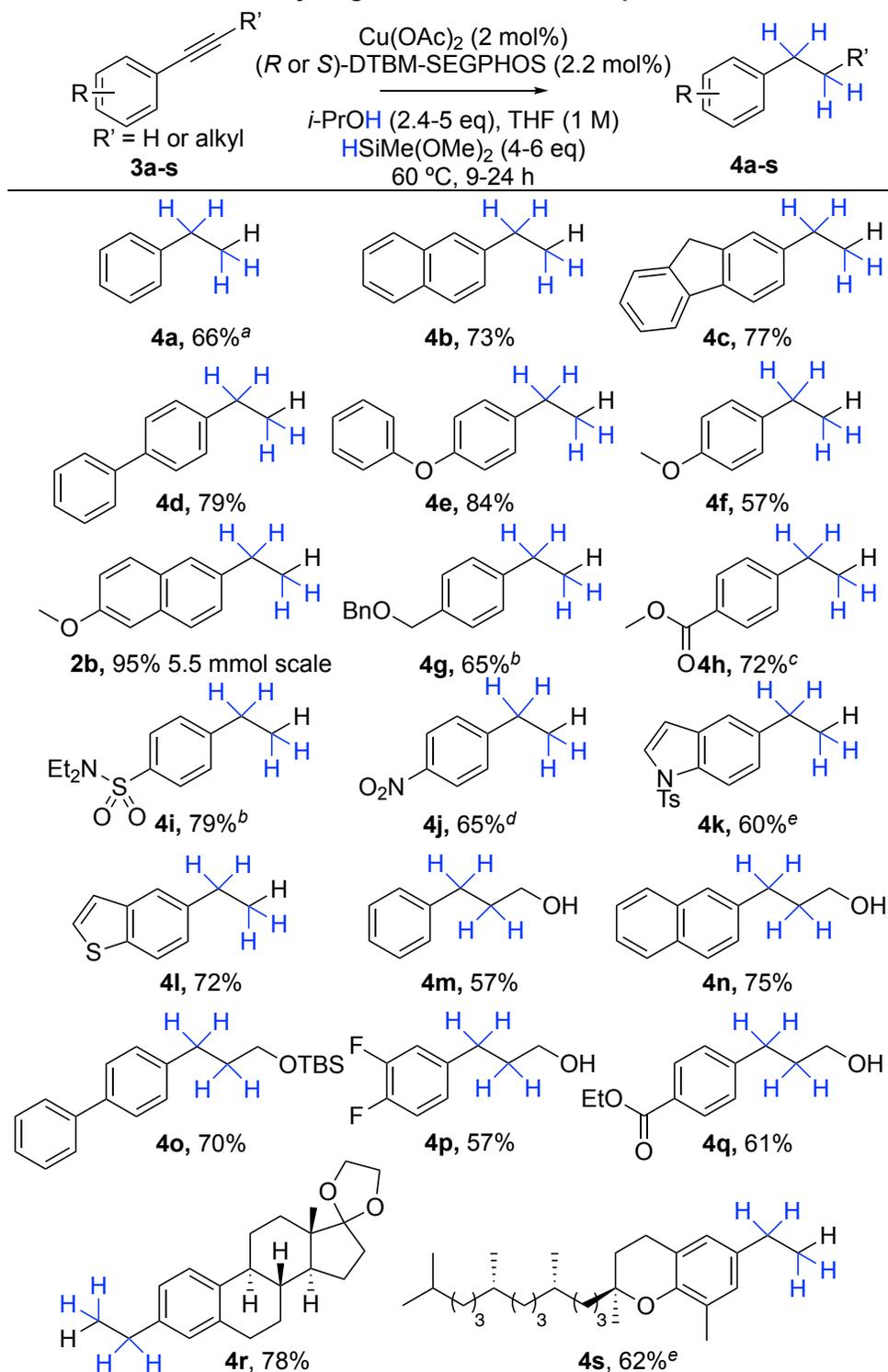
In a  $\text{N}_2$  filled glovebox, (*R* or *S*)-DTBM-SEGPPOS (10.4 mg, 0.0088 mmol, 0.022 eq.),  $\text{Cu}(\text{OAc})_2$  (40  $\mu\text{L}$  of a 0.2 M solution in THF, 0.008 mmol, 0.02 eq.), and THF (0.16 mL) were added to an oven-dried 2-dram vial followed by dropwise addition of dimethoxy(methyl)silane (247  $\mu\text{L}$ , 2 mmol, 5 eq.). A color change from green/blue to orange was observed while stirring for 15 minutes. In a separate oven-dried 1-dram vial was added the alkyne substrate (0.4 mmol, 1 eq.), THF (0.2 mL), and either ethanol or 2-propanol (2.4-5 eq. based on substrate). The solution in the 1-dram vial was added dropwise over 20 seconds to the 2-dram vial. The total volume of THF was calculated based on having a final reaction concentration of 1M based on the alkyne substrate. The 2-dram vial was capped with a red pressure relief cap, taken out of the glovebox, and stirred for 9-24 h at the appropriate temperature at which point the reaction was filtered through a 1" silica plug with 20 mL of  $\text{Et}_2\text{O}$  followed by 80 mL of  $\text{Et}_2\text{O}$  to elute the remaining product into a 200 mL round bottom flask. After removing the  $\text{Et}_2\text{O}$  by rotary evaporation, the crude product was isolated by flash column chromatography.

#### General purification for alcohol containing substrates after transfer hydrogenation reaction (C)

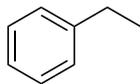
The crude product was dissolved in THF (1.6 mL) and tetrabutylammonium fluoride (0.8 mL of 1.0 M in THF solution, 2 eq.) was added. The reaction was stirred at room temperature for 1-2 hours until complete by TLC analysis. Upon completion, reaction mixture was diluted with  $\text{Et}_2\text{O}$  (10 mL) and quenched with saturated aqueous  $\text{NH}_4\text{Cl}$  (5 mL). The aqueous layer was extracted with  $\text{Et}_2\text{O}$  (3 x 10 mL) and the combined organic layers were washed with water (10 mL) and brine (10 mL), then dried over

anhydrous Na<sub>2</sub>SO<sub>4</sub>. The mixture was filtered, and the solvent was removed by rotary evaporation. The crude product was purified by flash column chromatography to give the desired product.

**Scheme S1. Transfer Hydrogenation Substrate Scope**



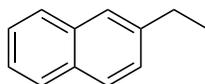
<sup>a</sup>Yield determined by <sup>1</sup>H NMR analysis using 1,3,5-trimethylbenzene as an internal standard. <sup>b</sup>2.4-2.6 eq of EtOH used. <sup>c</sup>Reaction performed at 40 °C. <sup>d</sup>Reaction performed at 23 °C. <sup>e</sup>5 mol% Cu(OAc)<sub>2</sub> and 5.5 mol% DTBM-SEGPPOS used.



**Ethyl Benzene [4a].** According to the general transfer hydrogenation procedure B, (S)-DTBM-SEGPPOS (10.4 mg, 0.0088 mmol, 0.022 eq.), Cu(OAc)<sub>2</sub> (40  $\mu$ L of a 0.2 M solution in THF, 0.008 mmol, 0.02 eq.), THF (0.16 mL), then dimethoxy(methyl)silane (247  $\mu$ L, 2 mmol, 5 eq.) were combined in a 2-dram vial followed by addition of a solution of ethynylbenzene (40.9 mg, 0.4 mmol, 1 eq.), THF (0.2 mL), and 2-propanol (74  $\mu$ L, 0.96 mmol, 2.4 eq.). The 2-dram vial was capped with a red pressure relief cap, and the reaction stirred for 10 h at 60 °C. After silica plug filtration using diethyl ether (100 mL) as the eluent, the solvent was concentrated, and 18.5  $\mu$ L of 1,3,5-trimethylbenzene was used as an internal standard to determine the <sup>1</sup>H NMR crude yield (66% crude yield by <sup>1</sup>H NMR).

<sup>1</sup>H NMR: (400 MHz, CDCl<sub>3</sub>)

$\delta$  7.29 (t, *J* = 7.6 Hz, 2H), 7.25 – 7.16 (m, 3H), 2.66 (q, *J* = 7.6 Hz, 2H), 1.27 (t, *J* = 7.6 Hz, 3H).



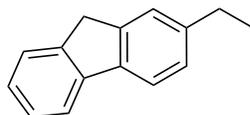
**2-Ethylnaphthalene [4b].** According to the general transfer hydrogenation procedure B, (S)-DTBM-SEGPPOS (10.4 mg, 0.0088 mmol, 0.022 eq.), Cu(OAc)<sub>2</sub> (40  $\mu$ L of a 0.2 M solution in THF, 0.008 mmol, 0.02 eq.), THF (0.16 mL), then dimethoxy(methyl)silane (247  $\mu$ L, 2 mmol, 5 eq.) were combined in a 2-dram vial followed by addition of a solution of 2-ethynyl-naphthalene (60.9 mg, 0.4 mmol, 1 eq.), THF (0.2 mL), and 2-propanol (74  $\mu$ L, 0.96 mmol, 2.4 eq.). The 2-dram vial was capped with a red pressure relief cap, and the reaction stirred for 14 h at 60 °C. After silica plug filtration using diethyl ether (100 mL) as the eluent, the solvent was concentrated, and the crude brown oil was dry loaded onto a silica gel column. Flash chromatography using 350 mL of hexanes as eluent gave the pure product as a clear, colorless oil (45.8 mg, 0.29 mmol, 73% yield). The spectra for the title compound matched previously reported spectra.<sup>1</sup>

<sup>1</sup>H NMR: (400 MHz, CDCl<sub>3</sub>)

$\delta$  7.86 – 7.76 (m, 3H), 7.65 (s, 1H), 7.51 – 7.39 (m, 2H), 7.38 (d, *J* = 8.4 Hz, 1H), 2.84 (q, *J* = 7.6 Hz, 2H), 1.36 (t, *J* = 7.6 Hz, 3H).

<sup>13</sup>C NMR: (101 MHz, CDCl<sub>3</sub>)

$\delta$  141.9, 133.9, 132.1, 127.9, 127.7, 127.6, 127.2, 126.0, 125.7, 125.1, 29.20, 15.7.



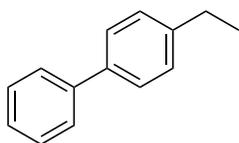
**2-Ethyl-9H-fluorene [4c].** According to the general transfer hydrogenation procedure B, (S)-DTBM-SEGPPOS (10.4 mg, 0.0088 mmol, 0.022 eq.), Cu(OAc)<sub>2</sub> (40  $\mu$ L of a 0.2 M solution in THF, 0.008 mmol, 0.02 eq.), THF (0.16 mL), then dimethoxy(methyl)silane (247  $\mu$ L, 2 mmol, 5 eq.) were combined in a 2-dram vial followed by addition of a solution of 2-ethynyl-9H-Fluorene (76.1 mg, 0.4 mmol, 1 eq.), THF (0.2 mL), and 2-propanol (74  $\mu$ L, 0.96 mmol, 2.4 eq.). The 2-dram vial was capped with a red pressure relief cap, and the reaction stirred for 9 h at 60 °C. After silica plug filtration using diethyl ether (100 mL) as the eluent, the solvent was concentrated. The crude brown oil was dry loaded onto a silica gel column. Flash chromatography using 100 mL of hexanes as eluent gave the pure product as a yellow solid (60.0 mg, 0.309 mmol, 77% yield). The spectra for the title compound matched previously reported spectra.<sup>2</sup>

<sup>1</sup>H NMR: (400 MHz, CDCl<sub>3</sub>)

$\delta$  7.77 (d, *J* = 7.6, 1H), 7.71 (d, *J* = 7.8 Hz, 1H), 7.56 – 7.52 (m, 1H), 7.42 – 7.34 (m, 2H), 7.31 – 7.26 (m, 1H), 7.25 – 7.21 (m, 1H), 3.89 (s, 2H), 2.75 (q, *J* = 7.6 Hz, 2H), 1.31 (t, *J* = 7.6 Hz, 3H).

<sup>13</sup>C NMR: (101 MHz, CDCl<sub>3</sub>)

δ 143.7, 143.3, 143.3, 141.9, 139.5, 126.8, 126.6, 126.3, 125.1, 124.7, 119.8, 119.7, 37.0, 29.2, 16.1.



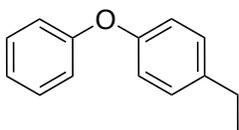
**4-Ethyl-1,1'-biphenyl [4d].** According to the general transfer hydrogenation procedure B, (S)-DTBM-SEGPPOS (10.4 mg, 0.0088 mmol, 0.022 eq.), Cu(OAc)<sub>2</sub> (40 μL of a 0.2 M solution in THF, 0.008 mmol, 0.02 eq.), THF (0.16 mL), then dimethoxy(methyl)silane (247 μL, 2 mmol, 5 eq.) were combined in a 2-dram vial followed by addition of a solution of 4-ethynyl-1,1'-Biphenyl (71.3 mg, 0.4 mmol, 1 eq.), THF (0.2 mL), and 2-propanol (74 μL, 0.96 mmol, 2.4 eq.). The 2-dram vial was capped with a red pressure relief cap, and the reaction stirred for 9 h at 60 °C. After silica plug filtration using diethyl ether (100 mL) as the eluent, the solvent was concentrated, and the crude brown oil was dry loaded onto a silica gel column. Flash chromatography using 100 mL of hexanes as eluent gave the pure product as a clear, yellow oil (57.5 mg, 0.316 mmol, 79% yield). The spectra for the title compound matched previously reported spectra.<sup>1</sup>

<sup>1</sup>H NMR: (400 MHz, CDCl<sub>3</sub>)

δ 7.63 – 7.60 (m, 2H), 7.58 – 7.53 (m, 2H), 7.48 – 7.43 (m, 2H), 7.38 – 7.33 (m, 1H), 7.31 (d, J = 8.1 Hz, 2H), 2.73 (q, J = 7.6 Hz, 2H), 1.32 (t, J = 7.6 Hz, 3H).

<sup>13</sup>C NMR: (101 MHz, CDCl<sub>3</sub>)

δ 143.5, 141.4, 138.8, 128.8, 128.4, 127.2, 127.2, 127.1, 28.7, 15.7.



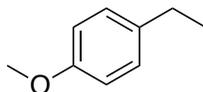
**1-Ethyl-4-phenoxybenzene [4e].** According to the general transfer hydrogenation procedure B, (S)-DTBM-SEGPPOS (10.4 mg, 0.0088 mmol, 0.022 eq.), Cu(OAc)<sub>2</sub> (40 μL of a 0.2 M solution in THF, 0.008 mmol, 0.02 eq.), THF (0.16 mL), then dimethoxy(methyl)silane (247 μL, 2 mmol, 5 eq.) were combined in a 2-dram vial followed by addition of a solution of 1-ethynyl-4-phenoxy-benzene (77.7 mg, 0.4 mmol, 1 eq.), THF (0.2 mL), and 2-propanol (74 μL, 0.96 mmol, 2.4 eq.). The 2-dram vial was capped with a red pressure relief cap, and the reaction stirred for 9 h at 60 °C. After silica plug filtration using diethyl ether (100 mL) as the eluent, the solvent was concentrated, and the crude brown oil was dry loaded onto a silica gel column. Flash chromatography using 100 mL of hexanes as eluent gave the pure product as a clear, yellow oil (66.5 mg, 0.335 mmol, 84% yield). The spectra for the title compound matched previously reported spectra.<sup>3</sup>

<sup>1</sup>H NMR: (400 MHz, CDCl<sub>3</sub>)

δ 7.37 – 7.30 (m, 2H), 7.18 (d, J = 8.5 Hz, 2H), 7.12 – 7.06 (m, 1H), 7.04 – 6.99 (m, 2H), 6.98 – 6.94 (m, 2H), 2.66 (q, J = 7.6 Hz, 2H), 1.26 (t, J = 7.6 Hz, 3H).

<sup>13</sup>C NMR: (101 MHz, CDCl<sub>3</sub>)

δ 157.9, 155.0, 139.4, 129.8, 129.2, 123.0, 119.2, 118.6, 28.3, 15.9.



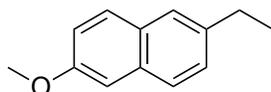
**1-Ethyl-4-methoxybenzene [4f].** According to the general transfer hydrogenation procedure B, (S)-DTBM-SEGPHOS (10.4 mg, 0.0088 mmol, 0.022 eq.), Cu(OAc)<sub>2</sub> (40  $\mu$ L of a 0.2 M solution in THF, 0.008 mmol, 0.02 eq.), THF (0.16 mL), then dimethoxy(methyl)silane (247  $\mu$ L, 2.0 mmol, 5 eq.) were combined in a 2-dram vial followed by addition of a solution of 1-ethynyl-4-methoxybenzene (52.9 mg, 0.4 mmol, 1 eq.), THF (0.2 mL), and 2-propanol (153  $\mu$ L, 2.0 mmol, 5 eq.). The 2-dram vial was capped with a red pressure relief cap, and the reaction stirred for 12 h at 60 °C. After silica plug filtration using diethyl ether (100 mL) as the eluent, the solvent was concentrated, and the crude colorless liquid was dry loaded onto a silica gel column. Flash chromatography using 100 mL of hexanes as eluent gave the pure product as a clear and colorless liquid (30.9 mg, 0.227 mmol, 57% yield). The spectra for the title compound matched previously reported spectra.<sup>4</sup>

<sup>1</sup>H NMR: (300 MHz, CDCl<sub>3</sub>)

$\delta$  7.12 (d,  $J$  = 8.5 Hz, 2H), 6.84 (d,  $J$  = 8.5 Hz, 2H), 3.79 (s, 3H), 2.60 (q,  $J$  = 7.6 Hz, 2H), 1.22 (t,  $J$  = 7.5 Hz, 3H).

<sup>13</sup>C NMR: (75 MHz, CDCl<sub>3</sub>)

$\delta$  157.7, 136.5, 128.9, 113.9, 55.4, 28.1, 16.0.



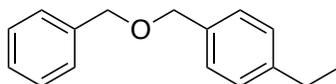
**2-Ethyl-6-methoxynaphthalene [2b].** According to the general transfer hydrogenation procedure B, (S)-DTBM-SEGPHOS (142.4 mg, 0.12 mmol, 0.022 eq.), Cu(OAc)<sub>2</sub> (0.549 mL of a 0.2 M solution in THF, 0.11 mmol, 0.02 eq.), THF (2.5 mL), then dimethoxy(methyl)silane (3.39 mL, 27.45 mmol, 5 eq.) were combined in a 20-dram vial followed by addition of a solution of 2-ethynyl-6-methoxynaphthalene (1.0 g, 5.49 mmol, 1 eq.), THF (2.5 mL), and 2-propanol (1.01 mL, 13.18 mmol, 2.4 eq.). The 20-dram vial was capped with a red pressure relief cap, and the reaction stirred for 15 h at 60 °C. After silica plug filtration using diethyl ether (200 mL) as the eluent, the solvent was concentrated under vacuum. Purification by flash chromatography using gradient elution (100 mL of hexanes, 200 mL of 5% of ethyl acetate in hexanes, 500 mL of 8% ethyl acetate in hexanes) gave the pure product as a cream colored solid (0.97 g, 5.21 mmol, 95% yield). The spectra for the title compound matched previously reported spectra.<sup>1</sup>

<sup>1</sup>H NMR: (400 MHz, CDCl<sub>3</sub>)

$\delta$  7.70 – 7.64 (m, 2H), 7.57 – 7.54 (m, 1H), 7.32 (dd,  $J$  = 8.4, 1.8 Hz, 1H), 7.15 – 7.09 (m, 2H), 3.91 (s, 3H), 2.78 (q,  $J$  = 7.6 Hz, 2H), 1.31 (t,  $J$  = 7.6, 3H).

<sup>13</sup>C NMR: (101 MHz, CDCl<sub>3</sub>)

$\delta$  157.2, 139.6, 133.0, 129.3, 129.0, 127.7, 126.8, 125.6, 118.7, 105.8, 55.4, 29.0, 15.8.



**1-((Benzyloxy)methyl)-4-ethylbenzene [4g].** According to the general transfer hydrogenation procedure B, (S)-DTBM-SEGPHOS (10.4 mg, 0.0088 mmol, 0.022 eq.), Cu(OAc)<sub>2</sub> (40  $\mu$ L of a 0.2 M solution in THF, 0.008 mmol, 0.02 eq.), THF (0.16 mL), then dimethoxy(methyl)silane (296  $\mu$ L, 2.4 mmol, 6 eq.) were combined in a 2-dram vial followed by addition of a solution of 1- ethynyl- 4- [(phenylmethoxy) methyl] - benzene (88.9 mg, 0.4 mmol, 1 eq.), THF (0.2 mL), and ethanol (61  $\mu$ L, 1.04 mmol, 2.6 eq.). The 2-dram vial was capped with a red pressure relief cap, and the reaction stirred for 18 h at 60 °C. After silica plug filtration using diethyl ether (100 mL) as the eluent, the solvent was concentrated, and the crude brown oil

was dry loaded onto a silica gel column. Flash chromatography using gradient elution (75 mL of hexanes, 100 mL of 1% ethyl acetate in hexanes, 100 mL of 2% ethyl acetate in hexanes, 200 mL of 5% ethyl acetate in hexanes) gave the pure product as a clear, yellow oil (58.5 mg, 0.26 mmol, 65% yield).

$^1\text{H NMR}$ : (400 MHz,  $\text{CDCl}_3$ )

$\delta$  7.43 – 7.35 (m, 4H), 7.34 – 7.28 (m, 3H), 7.22 (d,  $J = 7.9$  Hz, 2H), 4.57 (d,  $J = 7.6$  Hz, 4H), 2.68 (q,  $J = 7.6$  Hz, 2H), 1.26 (t,  $J = 7.6$  Hz, 3H).

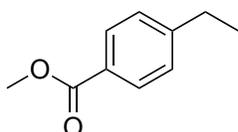
$^{13}\text{C NMR}$ : (101 MHz,  $\text{CDCl}_3$ )

$\delta$  143.9, 138.6, 135.6, 128.5, 128.1, 128.0, 127.9, 127.7, 72.2, 72.1, 28.8, 15.8.

ATR-IR ( $\text{cm}^{-1}$ ):

3029, 2964, 2929, 2856, 1718, 1090, 1072.

HRMS: ( $\text{ESI}^+$ )  $m/z$ :  $[\text{M}+\text{Na}]^+$  Calcd for  $\text{C}_{16}\text{H}_{18}\text{NaO}$  249.1250; Found 249.1257.



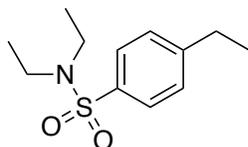
**Methyl 4-ethylbenzoate [4h]**. According to the general transfer hydrogenation procedure B, (S)-DTBM-SEGPPOS (10.4 mg, 0.0088 mmol, 0.022 eq.),  $\text{Cu}(\text{OAc})_2$  (40  $\mu\text{L}$  of a 0.2 M solution in THF, 0.008 mmol, 0.02 eq.), THF (0.16 mL), then dimethoxy(methyl)silane (247  $\mu\text{L}$ , 2 mmol, 5 eq.) were combined in a 2-dram vial followed by addition of a solution of methyl 4-ethynylbenzoate (64.1 mg, 0.4 mmol, 1 eq.), THF (0.2 mL), and 2-propanol (74  $\mu\text{L}$ , 0.96 mmol, 2.4 eq.). The 2-dram vial was capped with a red pressure relief cap, and the reaction stirred for 22 h at 40  $^\circ\text{C}$ . After silica plug filtration using diethyl ether (100 mL) as the eluent, the solvent was concentrated under vacuum. Purification by flash chromatography using gradient elution (100 mL of hexanes, 200 mL of 10% of DCM in hexanes, 200 mL of 20% DCM in hexanes, 200 mL of 30% DCM in hexanes) gave the pure product as a clear colorless liquid (47.0 mg, 0.286 mmol, 72% yield). The spectra for the title compound matched previously reported spectra.<sup>5</sup>

$^1\text{H NMR}$ : (400 MHz,  $\text{CDCl}_3$ )

$\delta$  7.95 (d,  $J = 8.2$  Hz, 2H), 7.25 (d,  $J = 8.1$  Hz, 2H), 3.89 (s, 3H), 2.70 (q,  $J = 7.6$  Hz, 2H), 1.25 (t,  $J = 7.6$  Hz, 3H).

$^{13}\text{C NMR}$ : (101 MHz,  $\text{CDCl}_3$ )

$\delta$  167.3, 149.9, 129.8, 128.0, 127.8, 52.1, 29.1, 15.3.



**N,N,4-Triethylbenzenesulfonamide [4i]**. According to the general transfer hydrogenation procedure B, (S)-DTBM-SEGPPOS (10.4 mg, 0.0088 mmol, 0.022 eq.),  $\text{Cu}(\text{OAc})_2$  (40  $\mu\text{L}$  of a 0.2 M solution in THF, 0.008 mmol, 0.02 eq.), THF (0.16 mL), then dimethoxy(methyl)silane (247  $\mu\text{L}$ , 2 mmol, 5 eq.) were combined in a 2-dram vial followed by addition of a solution of *N,N*-diethyl-4-ethynyl-benzenesulfonamide (95 mg, 0.4 mmol, 1 eq.), THF (0.2 mL), and ethanol (56  $\mu\text{L}$ , 0.96 mmol, 2.4 eq.). The 2-dram vial was capped with a red pressure relief cap, and the reaction stirred for 20 h at 60  $^\circ\text{C}$ . After silica plug filtration using diethyl ether (100 mL) as the eluent, the solvent was concentrated, and the crude brown oil was dry

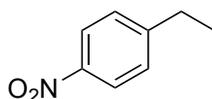
loaded onto a silica gel column. Flash chromatography using gradient elution (100 mL of hexanes, 100 mL of 5% ethyl acetate in hexanes, 100 mL of 6% ethyl acetate in hexanes, 200 mL of 8% ethyl acetate in hexanes, 200 mL of 10% ethyl acetate in hexanes, 200 mL of 12% ethyl acetate in hexanes) gave the pure product as a clear, yellow oil (76.4 mg, 0.317 mmol, 79% yield). The spectra for the title compound matched previously reported spectra.<sup>6</sup>

<sup>1</sup>H NMR: (400 MHz, CDCl<sub>3</sub>)

δ 7.70 (d, *J* = 8.3 Hz, 2H), 7.29 (d, *J* = 8.1 Hz, 2H), 3.21 (q, *J* = 7.2 Hz, 4H), 2.69 (q, *J* = 7.6 Hz, 2H), 1.24 (t, *J* = 7.6 Hz, 3H), 1.11 (t, *J* = 7.2 Hz, 6H).

<sup>13</sup>C NMR: (101 MHz, CDCl<sub>3</sub>)

δ 149.2, 137.7, 128.5, 127.2, 42.2, 28.8, 15.2, 14.3.



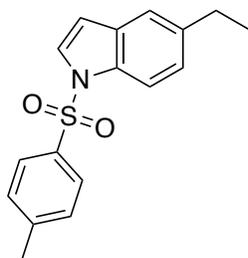
**4-Ethylnitrobenzene [4j].** According to the general transfer hydrogenation procedure B, (S)-DTBM-SEGPPOS (10.4 mg, 0.0088 mmol, 0.022 eq.), Cu(OAc)<sub>2</sub> (40 μL of a 0.2 M solution in THF, 0.008 mmol, 0.02 eq.), THF (0.16 mL), then dimethoxy(methyl)silane (247 μL, 2 mmol, 5 eq.) were combined in a 2-dram vial followed by addition of a solution of methyl-4-ethynynitrobenzene (58.9 mg, 0.4 mmol, 1 eq.), THF (0.2 mL), and 2-propanol (74 μL, 0.96 mmol, 2.4 eq.). The 2-dram vial was capped with a red pressure relief cap, and the reaction stirred for 24 h at room temperature. After silica plug filtration using diethyl ether (100 mL) as the eluent, the solvent was concentrated, under vacuum. Purification by flash chromatography using gradient elution (100 mL of hexanes, 200 mL of 5% ethyl acetate in hexanes 200 mL of 10% of ethyl acetate in hexanes, 200 mL of 20% ethyl acetate in hexanes) gave the pure product as a clear brown liquid (39.4 mg, 0.26 mmol, 65% yield). The spectra for the title compound matched previously reported spectra.<sup>7</sup>

<sup>1</sup>H NMR: (400 MHz, CDCl<sub>3</sub>)

δ 8.13 (d, *J* = 8.7 Hz, 2H), 7.33 (d, *J* = 8.5 Hz, 2H), 2.75 (q, *J* = 7.6 Hz, 2H), 1.27 (t, *J* = 7.6 Hz, 3H).

<sup>13</sup>C NMR: (101 MHz, CDCl<sub>3</sub>)

δ 152.2, 146.3, 128.7, 123.7, 29.0, 15.2.



**5-Ethyl-1-tosyl-1H-indole [4k].** According to the general transfer hydrogenation procedure B, (S)-DTBM-SEGPPOS (13.0 mg, 0.011 mmol, 0.055 eq.), Cu(OAc)<sub>2</sub> (50 μL of a 0.2 M solution in THF, 0.01 mmol, 0.05 eq.), THF (0.05 mL), then dimethoxy(methyl)silane (123 μL, 1.0 mmol, 5 eq.) were combined in a 2-dram vial followed by addition of a solution of 5-ethynyl-1-tosyl-1H-indole (59.1 mg, 0.2 mmol, 1 eq.), THF (0.1 mL), and 2-propanol (77 μL, 1.0 mmol, 5 eq.). The 2-dram vial was capped with a red pressure relief cap, and the reaction stirred for 24 h at 60 °C. After silica plug filtration using diethyl ether (100 mL) as the eluent, the solvent was concentrated, and the crude brown liquid was dry loaded onto a silica gel column. Flash chromatography using gradient elution (100 mL of 10% ethyl acetate in hexanes, 100 mL of 20%

ethyl acetate in hexanes followed by 200 mL of 30% ethyl acetate in hexanes) gave the pure product as a clear and colorless oil (36.1 mg, 0.12 mmol, 60% yield).

**<sup>1</sup>H NMR:** (400 MHz, CDCl<sub>3</sub>)

δ 7.90 (d, *J* = 8.5 Hz, 1H), 7.76 (d, *J* = 8.3 Hz, 2H), 7.53 (d, *J* = 3.6 Hz, 1H), 7.33 (s, 1H), 7.20 (d, *J* = 8.2 Hz, 2H), 7.16 (d, *J* = 8.5 Hz, 1H), 6.59 (d, *J* = 3.6 Hz, 1H), 2.70 (q, *J* = 7.6 Hz, 2H), 2.33 (s, 3H), 1.25 (t, *J* = 7.6 Hz, 3H).

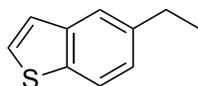
**<sup>13</sup>C NMR:** (101 MHz, CDCl<sub>3</sub>)

δ 144.9, 139.5, 135.5, 133.3, 131.1, 130.0, 126.9, 126.5, 125.1, 120.1, 113.4, 109.1, 28.8, 21.7, 16.1.

**ATR-IR (cm<sup>-1</sup>):**

2962, 2926, 2873, 1596, 1367, 1130.

**HRMS:** (ESI<sup>+</sup>) *m/z*: [M+Na]<sup>+</sup> Calcd for C<sub>17</sub>H<sub>17</sub>NNaO<sub>2</sub>S 322.0872; Found 322.0882.



**5-Ethylbenzo[*b*]thiophene [4I].** According to the general transfer hydrogenation procedure B, (S)-DTBM-SEGPHOS (10.4 mg, 0.0088 mmol, 0.022 eq.), Cu(OAc)<sub>2</sub> (40 μL of a 0.2 M solution in THF, 0.008 mmol, 0.02 eq.), THF (0.16 mL), then dimethoxy(methyl)silane (247 μL, 2 mmol, 5 eq.) were combined in a 2-dram vial followed by addition of a solution of 5-ethynylbenzo[*b*]thiophene (63 mg, 0.4 mmol, 1 eq.), THF (0.2 mL), and 2-propanol (74 μL, 0.96 mmol, 2.4 eq.). The 2-dram vial was capped with a red pressure relief cap, and the reaction stirred for 13 h at 60 °C. After silica plug filtration using diethyl ether (100 mL) as the eluent, the solvent was concentrated under vacuum. Purification by flash chromatography using gradient elution (100 mL of hexanes, 200 mL of 5% ethyl acetate in hexanes) gave the pure product as a clear red oil (46.9 mg, 0.289 mmol, 72% yield).

**<sup>1</sup>H NMR:** (400 MHz, CDCl<sub>3</sub>)

δ 7.82 (d, *J* = 8.1 Hz, 1H), 7.69 – 7.66 (m, 1H), 7.43 (d, *J* = 5.4 Hz, 1H), 7.31 (dd, *J* = 5.4, 0.8 Hz, 1H), 7.24 (dd, *J* = 8.2, 1.7 Hz, 1H), 2.80 (q, *J* = 7.6 Hz, 2H), 1.33 (t, *J* = 7.6 Hz, 3H).

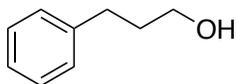
**<sup>13</sup>C NMR:** (101 MHz, CDCl<sub>3</sub>)

δ 140.6, 140.1, 137.3, 126.5, 125.1, 123.8, 122.4, 122.3, 29.0, 16.2.

**ATR-IR (cm<sup>-1</sup>):**

2962, 2928, 2868, 1738, 808, 691.

**HRMS:** (EI<sup>+</sup>) *m/z*: [M]<sup>+</sup> Calcd for C<sub>10</sub>H<sub>10</sub>S 162.0503; Found 162.0496.



**3-Phenyl-1-propanol [4m].** According to the general transfer hydrogenation procedure B, (S)-DTBM-SEGPHOS (10.4 mg, 0.0088 mmol, 0.022 eq.), Cu(OAc)<sub>2</sub> (40 μL of a 0.2 M solution in THF, 0.008 mmol, 0.02 eq.), THF (0.16 mL), then dimethoxy(methyl)silane (247 μL, 2.0 mmol, 5 eq.) were combined in a 2-dram vial followed by addition of a solution of 3-phenyl-2-propyn-1-ol (52.9 mg, 0.4 mmol, 1 eq.), THF (0.2 mL), and 2-propanol (74 μL, 0.96 mmol, 2.4 eq.). The 2-dram vial was capped with a red pressure relief cap, and the reaction stirred for 18 h at 60 °C. After silica plug filtration using diethyl ether (100 mL) as the eluent, the solvent was concentrated. The clear crude oil was treated with tetrabutylammonium fluoride

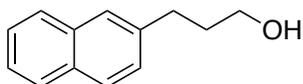
following the general procedure C. Flash chromatography using gradient elution (100 mL of hexanes, 100 mL of 5% ethyl acetate in hexanes, 100 mL of 10% ethyl acetate in hexanes, 200 mL of 15% ethyl acetate in hexanes) gave the pure product as a clear and colorless oil (31 mg, 0.227 mmol, 57% yield). The spectra for the title compound matched previously reported spectra.<sup>8</sup>

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)

δ 7.33 – 7.27 (m, 2H), 7.24 – 7.17 (m, 3H), 3.68 (t, *J* = 6.5 Hz, 2H), 2.72 (t, *J* = 7.64 Hz, 2H), 1.95 – 1.86 (m, 2H), 1.64 (s, 1H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)

δ 141.9, 128.5, 128.5, 126.0, 62.4, 34.3, 32.2.



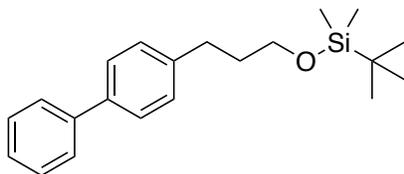
**2-Naphthalenepropanol [4n].** According to the general transfer hydrogenation procedure B, (S)-DTBM-SEGPHOS (10.4 mg, 0.0088 mmol, 0.022 eq.), Cu(OAc)<sub>2</sub> (40 μL of a 0.2 M solution in THF, 0.008 mmol, 0.02 eq.), THF (0.16 mL), then dimethoxy(methyl)silane (247 μL, 2.0 mmol, 5 eq.) were combined in a 2-dram vial followed by addition of a solution of 3-(2-Naphthalenyl)-2-propyn-1-ol (72.8 mg, 0.4 mmol, 1 eq.), THF (0.2 mL), and 2-propanol (74 μL, 0.96 mmol, 2.4 eq.). The 2-dram vial was capped with a red pressure relief cap, and the reaction stirred for 18 h at 60 °C. After silica plug filtration using diethyl ether (100 mL) as the eluent, the solvent was concentrated. The clear crude oil was treated with tetrabutylammonium fluoride following the general procedure C. Flash chromatography using gradient elution (100 mL of hexanes, 100 mL of 5% ethyl acetate in hexanes, 200 mL of 10% ethyl acetate in hexanes, 200 mL of 15% ethyl acetate in hexanes) gave the pure product as a white solid (56 mg, 0.30 mmol, 75% yield). The spectra for the title compound matched previously reported spectra.<sup>9</sup>

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)

δ 7.85 – 7.74 (m, 3H), 7.65 (s, 1H), 7.50 – 7.40 (m, 2H), 7.36 (d, *J* = 8.4 Hz, 1H), 3.72 (t, *J* = 6.4 Hz, 2H), 2.89 (t, *J* = 7.6 Hz, 2H), 2.03 – 1.93 (m, 2H), 1.76 (s, 1H).

<sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)

δ 139.4, 133.7, 132.1, 128.1, 127.7, 127.5, 127.4, 126.5, 126.0, 125.3, 62.3, 34.1, 32.3.



**(3-([1,1'-Biphenyl]-4-yl)propoxy)(tert-butyl)dimethylsilane [4o].** According to the general transfer hydrogenation procedure B, (S)-DTBM-SEGPHOS (8.0 mg, 0.0068 mmol, 0.022 eq.), Cu(OAc)<sub>2</sub> (31 μL of a 0.2 M solution in THF, 0.0628 mmol, 0.02 eq.), THF (0.12 mL), then dimethoxy(methyl)silane (191 μL, 1.55 mmol, 5 eq.) were combined in a 2-dram vial followed by addition of a solution of ((3-([1,1'-biphenyl]-4-yl)prop-2-yn-1-yl)oxy)(tert-butyl)dimethylsilane (100 mg, 0.31 mmol, 1 eq.), THF (0.15 mL), and 2-propanol (119 μL, 1.55 mmol, 5 eq.). The 2-dram vial was capped with a red pressure relief cap, and the reaction stirred for 10 h at 60 °C. After silica plug filtration using diethyl ether (100 mL) as the eluent, the solvent was concentrated. Flash chromatography using gradient elution (100 mL of hexanes, 100 mL of 2% ethyl acetate in hexanes, 100 mL of 5% ethyl acetate in hexanes) gave the pure product as a white crystalline solid (71 mg, 0.217 mmol, 70% yield).

<sup>1</sup>H NMR: (400 MHz, CDCl<sub>3</sub>)

$\delta$  7.59 (d,  $J = 7.2$  Hz, 2H), 7.52 (d,  $J = 8.2$  Hz, 2H), 7.44 (t,  $J = 7.6$  Hz, 2H), 7.36 – 7.30 (m, 1H), 7.30 – 7.26 (m, 2H), 3.68 (t,  $J = 6.3$  Hz, 2H), 2.76 – 2.70 (m, 2H), 1.95 – 1.83 (m, 2H), 0.93 (s, 9H), 0.08 (s, 6H).

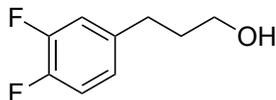
$^{13}\text{C}$  NMR: (75 MHz,  $\text{CDCl}_3$ )

$\delta$  141.6, 141.3, 138.8, 129.0, 128.8, 127.2, 127.1, 127.1, 62.5, 34.6, 31.9, 26.1, 18.5, -5.1.

FT-IR (thin film,  $\text{cm}^{-1}$ ):

2930, 2925, 2854, 1250, 1098, 1077.

HRMS: (ESI<sup>+</sup>)  $m/z$ :  $[\text{M}+\text{Na}]^+$  Calcd for  $\text{C}_{21}\text{H}_{30}\text{NaOSi}$  349.1958; Found 349.1968.



**3,4-Difluorobenzyl alcohol [4p].** According to the general transfer hydrogenation procedure B, (S)-DTBM-SEGPHOS (10.4 mg, 0.0088 mmol, 0.022 eq.),  $\text{Cu}(\text{OAc})_2$  (40  $\mu\text{L}$  of a 0.2 M solution in THF, 0.008 mmol, 0.02 eq.), THF (0.16 mL), then dimethoxy(methyl)silane (247  $\mu\text{L}$ , 2.0 mmol, 5 eq.) were combined in a 2-dram vial followed by addition of a solution of 3,4-difluorobenzyl alcohol (67.3 mg, 0.4 mmol, 1 eq.), THF (0.2 mL), and 2-propanol (74  $\mu\text{L}$ , 0.96 mmol, 2.4 eq.). The 2-dram vial was capped with a red pressure relief cap, and the reaction stirred for 19 h at 60 °C. After silica plug filtration using diethyl ether (100 mL) as the eluent, the solvent was concentrated. The clear crude oil was treated with tetrabutylammonium fluoride following the general procedure C. Flash chromatography using gradient elution (100 mL of hexanes, 100 mL of 5% ethyl acetate in hexanes, 100 mL of 10% ethyl acetate in hexanes, 200 mL of 15% ethyl acetate in hexanes) gave the pure product as a clear oil (39.0 mg, 0.227 mmol, 57% yield).

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )

$\delta$  7.10 – 6.95 (m, 2H), 6.92 – 6.86 (m, 1H), 3.66 (q,  $J = 5.9$  Hz, 2H), 2.67 (t,  $J = 7.4$ , 2H), 1.90 – 1.81 (m, 2H), 1.31 (s, 1H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )

$\delta$  150.8 (dd,  $J = 144.6, 12.6$  Hz), 148.3 (dd,  $J = 142.6, 12.7$  Hz), 138.9 (dd,  $J = 5.5, 3.9$  Hz), 124.3 (dd,  $J = 6.0, 3.5$  Hz), 117.2 (d,  $J = 16.6$  Hz), 117.1 (d,  $J = 16.8$  Hz), 61.9, 34.1, 31.3.

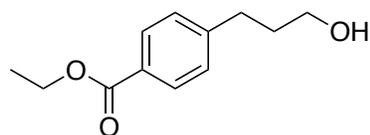
$^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )

$\delta$  -138.53, -142.39.

ATR-IR ( $\text{cm}^{-1}$ ):

3319, 2934, 2868, 1717, 1510, 1209, 1116, 1048.

HRMS: (ESI<sup>+</sup>)  $m/z$ :  $[\text{M}+\text{H}]^+$  Calcd for  $\text{C}_9\text{H}_{11}\text{OF}_2$  173.0778; Found 173.0780.



**Ethyl 4-(3-hydroxypropyl)benzoate [4q].** According to the general transfer hydrogenation procedure B, (S)-DTBM-SEGPHOS (10.4 mg, 0.0088 mmol, 0.022 eq.),  $\text{Cu}(\text{OAc})_2$  (40  $\mu\text{L}$  of a 0.2 M solution in THF, 0.008 mmol, 0.02 eq.), THF (0.16 mL), then dimethoxy(methyl)silane (247  $\mu\text{L}$ , 2.0 mmol, 5 eq.) were combined in a 2-dram vial followed by addition of a solution of ethyl 4-(3-hydroxypropyl)benzoate (81.8 mg, 0.4 mmol, 1 eq.), THF (0.2 mL), and 2-propanol (73.9  $\mu\text{L}$ , 0.96 mmol, 2.4 eq.). The 2-dram vial was capped with a red pressure relief cap, and the reaction stirred for 18 h at 60 °C. After silica plug filtration using diethyl ether (100 mL) as the eluent, the solvent was concentrated. The clear crude oil was treated

with tetrabutylammonium fluoride following the general procedure C. Flash chromatography using gradient elution (100 mL of hexanes, 100 mL of 5% ethyl acetate in hexanes, 100 mL of 10% ethyl acetate in hexanes, 200 mL of 15% ethyl acetate in hexanes) gave the pure product as a clear yellow oil (51 mg, 0.244 mmol, 61% yield).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)

δ 7.95 (d, *J* = 8 Hz, 2H), 7.25 (d, *J* = 7.7 Hz, 2H), 4.35 (q, *J* = 7 Hz, 2H), 3.66 (t, *J* = 6.3 Hz, 2H), 2.76 (t, *J* = 8, 2H), 1.90 (p, 2H), 1.65 (s, 1H), 1.37 (t, *J* = 7.1 Hz, 3H).

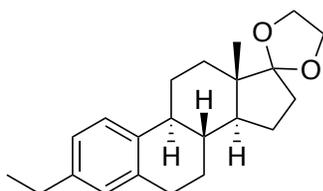
<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)

δ 166.8, 147.5, 129.8, 128.5, 128.2, 62.0, 60.9, 33.9, 32.2, 14.4.

ATR-IR (cm<sup>-1</sup>):

3412, 2986, 2933, 2873, 1713, 1610, 1272, 1102, 1041, 1020.

HRMS: (ESI<sup>+</sup>) *m/z*: [M+Na]<sup>+</sup> Calcd for C<sub>12</sub>H<sub>16</sub>NaO<sub>3</sub> 231.0992; Found 231.0999.



**(8*R*,9*S*,13*S*,14*S*)-3-Ethyl-13-methyl-6,7,8,9,11,12,13,14,15,16-**

**decahydrospiro[cyclopenta[*a*]phenanthrene-17,2'-[1,3]dioxolane] [4r]**. According to the general procedure B, (S)-DTBM-SEGPHOS (5.7 mg, 0.00486 mmol, 0.022 eq.), Cu(OAc)<sub>2</sub> (22 μL of a 0.2 M solution in THF, 0.0044 mmol, 0.02 eq.), THF (0.1 mL), then dimethoxy(methyl)silane (136 μL, 1.1 mmol, 5 eq.) were combined in a 2-dram vial followed by addition of a solution of (8*R*,9*S*,13*S*,14*S*)-3-(ethynyl)-13-methyl-6,7,8,9,11,12,13,14,15,16 decahydrospiro[cyclopenta[*a*]phenanthrene-17,2'-[1,3]dioxolane] (71.3 mg, 0.22 mmol, 1 eq.), THF (0.1 mL), and 2-propanol (85 μL, 1.1 mmol, 5 eq.). The 2-dram vial was capped with a red pressure relief cap, and the reaction stirred for 19 h at 60 °C. After silica plug filtration using dichloromethane as the eluent (100 mL), the solvent was concentrated, and the crude brown oil was dry loaded onto a silica gel column. Flash chromatography using gradient elution (100 mL of hexanes, 100 mL of 3% ethyl acetate in hexanes, 100 mL of 5% ethyl acetate in hexanes, 100 mL of 8% ethyl acetate in hexanes, 200 mL of 9% ethyl acetate in hexanes, 100 mL of 10% ethyl acetate in hexanes) gave the pure product as a clear, yellow oil (56.2 mg, 0.172 mmol, 78% yield).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)

δ 7.25 (d, *J* = 7.9 Hz, 1H), 7.00 (d, *J* = 8.0 Hz, 1H), 6.95 (s, 1H), 4.02 – 3.86 (m, 4H), 2.94 – 2.80 (m, 2H), 2.60 (q, *J* = 7.6 Hz, 2H), 2.41 – 2.23 (m, 2H), 2.11 – 2.00 (m, 1H), 1.96 – 1.73 (m, 4H), 1.71 – 1.60 (m, 1H), 1.59 – 1.30 (m, 5H), 1.24 (t, *J* = 7.6 Hz, 3H), 0.90 (s, 3H).

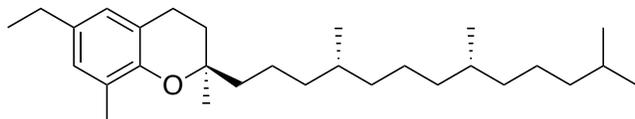
<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)

δ 141.6, 137.8, 136.7, 128.6, 125.5, 125.3, 119.6, 65.4, 64.7, 49.6, 46.3, 44.1, 39.1, 34.4, 30.9, 29.7, 28.4, 27.2, 26.1, 22.5, 15.8, 14.5.

ATR-IR (cm<sup>-1</sup>):

2965, 2933, 2872, 1735, 1693, 1610, 1103, 1040.

HRMS: (ESI<sup>+</sup>) *m/z*: [M+H]<sup>+</sup> Calcd for C<sub>22</sub>H<sub>31</sub>O<sub>2</sub> 327.2319; Found 327.2329.



**(R)-6-Ethyl-2,8-dimethyl-2-((4R,8R)-4,8,12-trimethyltridecyl)chromane [4s].** According to the general procedure B, (S)-DTBM-SEGPPOS (13 mg, 0.011 mmol, 0.055 eq.), Cu(OAc)<sub>2</sub> (50  $\mu$ L of a 0.2 M solution in THF, 0.01 mmol, 0.05 eq.), THF (0.05 mL), then dimethoxy(methyl)silane (99  $\mu$ L, 0.8 mmol, 4 eq.) were combined in a 2-dram vial followed by addition of a solution of (R)-6-ethynyl-2,8-dimethyl-2-((4R,8R)-4,8,12-trimethyltridecyl)chromane (82.1 mg, 0.2 mmol, 1 eq.), THF (0.1 mL), and 2-propanol (77  $\mu$ L, 1.0 mmol, 5 eq.). The 2-dram vial was capped with a red pressure relief cap, and the reaction stirred for 16 h at 60 °C. After silica plug filtration using diethyl ether (100 mL) as the eluent, the solvent was concentrated, and the crude colorless liquid was dry loaded onto a silica gel column. Flash chromatography using gradient elution (100 mL of hexanes followed by 200 mL of 2% ethyl acetate in hexanes) gave the pure product as a clear and colorless liquid (51.2 mg, 0.124 mmol, 62% yield).

<sup>1</sup>H NMR: (400 MHz, CDCl<sub>3</sub>)

$\delta$  6.80 (s, 1H), 6.73 (s, 1H), 2.80 – 2.66 (m, 2H), 2.53 (q, *J* = 7.6 Hz, 2H), 2.15 (s, 3H), 1.87 – 1.68 (m, 2H), 1.62 – 1.47 (m, 3H), 1.46 – 1.01 (m, 24H), 0.92 – 0.81 (m, 12H).

<sup>13</sup>C NMR: (101 MHz, CDCl<sub>3</sub>)

$\delta$  150.2, 134.5, 128.0, 126.1, 126.0, 120.3, 75.9, 40.4, 39.5, 37.6, 37.6, 37.4, 33.0, 32.9, 31.5, 28.1, 28.1, 25.0, 24.6, 24.5, 22.9, 22.8, 22.5, 21.2, 19.9, 19.8, 16.2, 16.1.

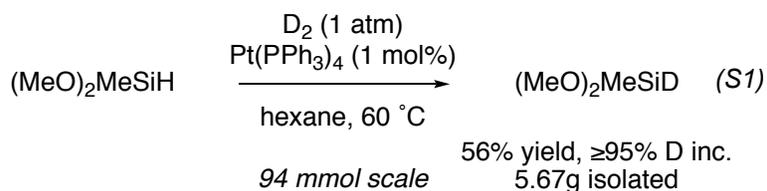
ATR-IR (cm<sup>-1</sup>):

2957, 2924, 2854, 1733, 1598, 1220, 1151.

HRMS: (ESI<sup>+</sup>) *m/z*: [M+H]<sup>+</sup> Calcd for C<sub>29</sub>H<sub>51</sub>O 415.3934; Found 415.3946.

#### IV. Transfer Deuteration Reaction Scope

##### Procedure for the synthesis of dimethoxy(methyl)silane-*d*



The procedure was adapted from a previously reported method.<sup>10</sup> To an oven-dried 500 mL Schlenk flask equipped with a Teflon stir bar in a N<sub>2</sub> filled glovebox was added the Pt(PPh<sub>3</sub>)<sub>4</sub> (1.17 g, 0.941 mmol, 0.01 eq.), dimethoxy(methyl)silane (11.6 mL, 94.1 mmol, 1 eq.), and 5.0 mL of degassed anhydrous hexanes. The Schlenk flask was sealed with a rubber septa and removed from the glovebox, connected to a manifold line, and cooled to -78 °C. A single freeze-pump-thaw cycle was performed, and the Schlenk flask was backfilled with D<sub>2</sub> gas from a D<sub>2</sub> purged balloon at room temperature. The flask was sealed with parafilm and heated to 60 °C. After 2 hours, the reaction was cooled to room temperature and then a single freeze-pump-thaw was performed again, backfilling with D<sub>2</sub> gas. The process was repeated 6 times or until the <sup>1</sup>H NMR showed  $\geq 95\%$  D incorporation. It is important to maintain a N<sub>2</sub> (g) inert atmosphere while obtaining a minimal quantity of sample for <sup>1</sup>H NMR analysis.

The solution was purified through a distillation apparatus; the set up consisted of a flame-dried 25 mL round-bottom receiving flask and a cannula. The 25 mL round-bottom receiving flask was flame-dried, and then filled with N<sub>2</sub>. Once the receiving flask reached room temperature, the cannula was inserted, maintaining positive pressure, and tightly sealed with parafilm to prevent condensation from entering. Upon confirmation of positive N<sub>2</sub> flow, the open end of the cannula was inserted into the Schlenk

reaction flask. The 25 mL round-bottom receiving flask was cooled to  $-78\text{ }^{\circ}\text{C}$  and closed to the manifold line, and then the Schlenk flask was heated to  $80\text{ }^{\circ}\text{C}$ . The heat initiated the distillation of the dimethoxy(methyl)silane-*d* and the hexane through the cannula which were trapped in the cold 25 mL round-bottom receiving flask. Vacuum was also applied to the 25 mL round-bottom receiving flask to promote this process. Once all of the silane and hexane were trapped in the 25 mL round-bottom receiving flask, the flask was removed from the heat and the manifold was closed to vacuum line while the 25 mL round-bottom receiving flask warmed to room temperature. Under positive nitrogen flow, the cannula was removed from the 25 mL round-bottom receiving flask, while keeping it inserted in the Schlenk reaction flask. The 25 mL round-bottom receiving flask was tightly sealed with Parafilm, and stored in the  $-4\text{ }^{\circ}\text{C}$  freezer. The final product was in a solution of hexane, and the molarity was calculated by  $^1\text{H}$  NMR using 1,3,5-trimethylbenzene as an internal standard, and used for the transfer deuteration reactions (5.67 g in a 5.29 M hexane solution, 52.9 mmol, 56% yield).

\*Note: it is important to monitor that the end of the cannula does not get clogged by frozen solvent/silane. If this occurs, remove the Schlenk reaction flask from heat and close manifold to vacuum line. Warm the 25 mL round-bottom receiving flask until the solids on the tip of the cannula melt, and then distillation can be resumed.

### General procedure for transfer deuteration. (D)

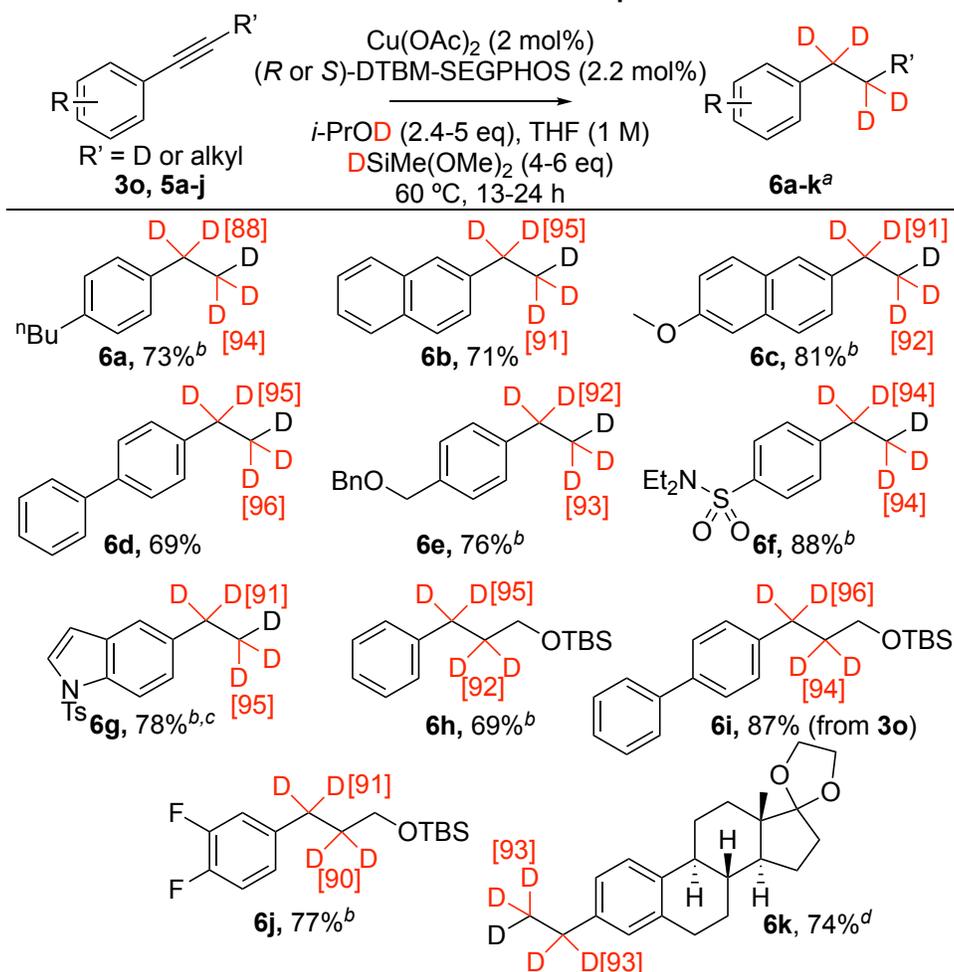
In a  $\text{N}_2$  filled glovebox, (*R* or *S*)-DTBM-SEGPPOS (10.4 mg, 0.0088 mmol, 0.022 eq.),  $\text{Cu}(\text{OAc})_2$  (40  $\mu\text{L}$  of a 0.2 M solution in THF, 0.008 mmol, 0.02 eq.), and THF (0.16 mL) were added to an oven-dried 2-dram vial followed by dropwise addition of dimethoxy(methyl)silane-*d* in hexanes (2 mmol, 5 eq.). A color change from green/blue to orange was observed while stirring for 15 minutes. In a separate 1-dram vial was added the alkyne substrate (0.4 mmol, 1 eq.), THF (0.2 mL), and either 2-propanol-OD or 2-propanol- $d_8$  (2.4-5 eq. based on substrate). The solution in the 1-dram vial was added dropwise over 20 seconds to the 2-dram vial. The total volume of THF was calculated based on having a final reaction concentration of 1M based on the alkyne substrate. The 2-dram vial was capped with a red pressure relief cap, taken out of the glovebox, and stirred for 13-24 h at  $60\text{ }^{\circ}\text{C}$  at which point the reaction was filtered through a 1" silica plug with 20 mL of  $\text{Et}_2\text{O}$  followed by 80 mL of  $\text{Et}_2\text{O}$  to elute the remaining product into a 200 mL round bottom flask. After removing the  $\text{Et}_2\text{O}$  by rotary evaporation, the crude product was isolated by flash chromatography.

Method for calculating deuterium incorporation at each labeled carbon of each substrate:

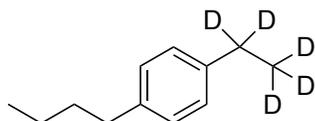
In the  $^1\text{H}$  NMR spectra, if both benzylic and homobenzylic peaks were clearly visible and no overlap with other peaks was observed, then the deuterium incorporation was calculated from the integration of the protonated peak. If overlap of other peaks or overlap with an impurity such as water or grease was observed in the homobenzylic region of the  $^1\text{H}$  NMR spectra, a  $^2\text{H}$  NMR spectra was obtained. The ratio of the two peaks that appear in the  $^2\text{H}$  NMR spectra was correlated to the calculated deuterium incorporation at the benzylic peak in the  $^1\text{H}$  NMR spectra.

\*2-propanol- $d_8$  was used due to a 2-propanol-OD backorder from the supplier during COVID-19.

### Scheme S2. Transfer Deuteration Substrate Scope



<sup>a</sup>Deuterium incorporation measured by <sup>1</sup>H NMR and/or <sup>2</sup>H NMR. <sup>b</sup>2-propanol-*d*<sub>8</sub> used and found to be equally effective as *i*-PrOD. <sup>c</sup>5 mol% Cu(OAc)<sub>2</sub> and 5.5 mol% DTBM SEGPPOS used. <sup>d</sup>Reaction run for 38 h.



**1-Butyl-4-(ethyl-*d*<sub>5</sub>)benzene [6a].** According to the general procedure D, (S)-DTBM-SEGPPOS (5.2 mg, 0.0044 mmol, 0.022 eq.), Cu(OAc)<sub>2</sub> (20 μL of a 0.2 M solution in THF, 0.004 mmol, 0.02 eq.), THF (0.08 mL), then dimethoxy(methyl)silane-*d* (0.17 mL of a 5.9 M solution in hexanes, 1.0 mmol, 5 eq.) were combined in a 2-dram vial followed by addition of a solution of 1-butyl-4-(ethynyl-*d*)benzene (31.8 mg, 0.2 mmol, 1 eq.), THF (0.1 mL), and 2-propanol-*d*<sub>8</sub> (77 μL, 1.0 mmol, 5 eq.). The 2-dram vial was capped with a red pressure relief cap, and the reaction stirred for 17 h at 60 °C. After silica plug filtration using diethyl ether (100 mL) as the eluent, the solvent was concentrated, and the crude yellow liquid was dry loaded onto a silica gel column. Flash chromatography using 200 mL of hexanes as eluent gave the pure product as a colorless oil (24.4 mg, 0.146 mmol, 73% yield).

<sup>1</sup>H NMR: (400 MHz, CDCl<sub>3</sub>)

δ 7.12 (s, 4H), 2.62 – 2.57 (m, 2.24H due to overlap of two benzylic sites), 1.65 – 1.55 (m, 2H), 1.43 – 1.31 (m, 2H), 1.19 (br s, integration not determined due to overlap with grease), 0.94 (t, *J* = 7.3 Hz, 3H).

$^2\text{H}$  NMR: (61 MHz,  $\text{CHCl}_3$ )

$\delta$  2.58 (br s, 1.76D), 1.19 (br s, 2.82D).

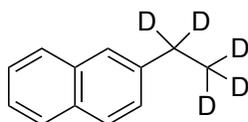
$^{13}\text{C}$  NMR: (101 MHz,  $\text{CDCl}_3$ )

$\delta$  141.4, 140.2, 128.5, 127.8, 35.4, 34.0, 28.3 – 27.2 (m), 22.6, 15.5 – 14.6 (m), 14.1.

ATR-IR ( $\text{cm}^{-1}$ ):

2956, 2927, 2857, 2222, 2079, 1514.

HRMS: ( $\text{EI}^+$ )  $m/z$ :  $[\text{M}]^+$  Calcd for  $\text{C}_{12}\text{H}_{13}\text{D}_5$  168.1722; Found 167.1716.



**2-(Ethyl- $d_5$ )naphthalene [6b].** According to the general procedure D, (*S*)-DTBM-SEGPHOS (10.4 mg, 0.0088 mmol, 0.022 eq.),  $\text{Cu}(\text{OAc})_2$  (40  $\mu\text{L}$  of a 0.2 M solution in THF, 0.008 mmol, 0.02 eq.), THF (0.16 mL), then dimethoxy(methyl)silane- $d$  (0.38 mL of 5.3 M solution in hexanes, 2 mmol, 5 eq.) were combined in a 2-dram vial followed by addition of a solution of 2-(ethynyl- $d$ )naphthalene (61.2 mg, 0.4 mmol, 1 eq.), THF (0.2 mL), and 2-propanol-OD (74  $\mu\text{L}$ , 0.96 mmol, 2.4 eq.). The 2-dram vial was capped with a red pressure relief cap, and the reaction stirred for 21 h at 60  $^\circ\text{C}$ . After silica plug filtration using diethyl ether (100 mL) as the eluent, the solvent was concentrated, and the crude brown oil was dry loaded onto a silica gel column. Flash chromatography using 350 mL of hexanes as eluent gave the pure product as a clear, yellow oil (46.0 mg, 0.285 mmol, 71% yield).

$^1\text{H}$  NMR: (400 MHz,  $\text{CDCl}_3$ )

$\delta$  7.85 – 7.75 (m, 3H), 7.64 (s, 1H), 7.51 – 7.40 (m, 2H), 7.37 (d,  $J = 8.4$ , 1H), 2.80 (br s, 0.11H), 1.30 (br s, integration not determined due to overlap with grease).

$^2\text{H}$  NMR: (61 MHz,  $\text{CHCl}_3$ )

$\delta$  2.80 (br s, 1.89D), 1.31 (br s, 2.72D).

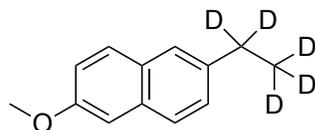
$^{13}\text{C}$  NMR: (101 MHz,  $\text{CDCl}_3$ )

$\delta$  141.9, 133.9, 132.1, 127.9, 127.7, 127.6, 127.2, 126.0, 125.7, 125.1, 29.0 – 27.7 (m), 15.5 – 13.9 (m).

FT-IR (thin film,  $\text{cm}^{-1}$ ):

2961, 2922, 2851, 2221, 1508, 1462.

HRMS: ( $\text{EI}^+$ )  $m/z$ :  $[\text{M}]^+$  Calcd for  $\text{C}_{12}\text{H}_7\text{D}_5$  161.1253; Found 161.1247.



**2-(Ethyl- $d_5$ )-6-methoxynaphthalene [6c].** According to the general procedure D, (*R*)-DTBM-SEGPHOS (5.2 mg, 0.0044 mmol, 0.022 eq.),  $\text{Cu}(\text{OAc})_2$  (20  $\mu\text{L}$  of a 0.2 M solution in THF, 0.004 mmol, 0.02 eq.), THF (0.08 mL), then dimethoxy(methyl)silane- $d$  (0.17 mL of a 5.9 M solution in hexanes, 1.0 mmol, 5 eq.) were combined in a 2-dram vial followed by addition of a solution of 2-(ethynyl- $d$ )-6-methoxynaphthalene (36.6 mg, 0.2 mmol, 1 eq.), THF (0.10 mL), and 2-propanol- $d_8$  (77  $\mu\text{L}$ , 1.0 mmol, 5 eq.). The 2-dram vial was capped with a red pressure relief cap, and the reaction stirred for 17 h at 60  $^\circ\text{C}$ . After silica plug filtration using diethyl ether (100 mL) as the eluent, the solvent was concentrated and the crude colorless

solid was dry loaded onto a silica gel column. Flash chromatography using elution (50 mL of hexanes, 200 mL of 2% ethyl acetate in hexanes) gave the pure product as a white solid (31.0 mg, 0.162 mmol, 81% yield).

**<sup>1</sup>H NMR:** (400 MHz, CDCl<sub>3</sub>)

δ 7.72 – 7.67 (m, 2H), 7.58 (d, *J* = 0.9 Hz, 1H), 7.34 (dd, *J* = 8.4, 1.7 Hz, 1H), 7.17 – 7.12 (m, 2H), 3.93 (s, 3H), 2.77 (br s, 0.18H), 1.29 (br s, integration not determined due to overlap with grease).

**<sup>2</sup>H NMR:** (61 MHz, CHCl<sub>3</sub>)

δ 2.77 (br s, 1.82D), 1.30 (br s, 2.77D).

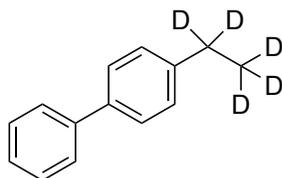
**<sup>13</sup>C NMR:** (101 MHz, CDCl<sub>3</sub>)

δ 157.2, 139.5, 133.0, 129.3, 129.0, 127.7, 126.8, 125.6, 118.7, 105.7, 55.4, 28.6 – 27.7 (m), 15.2 – 14.5 (m).

**ATR-IR (cm<sup>-1</sup>):**

2961, 2938, 2838, 2218, 2062, 1161.

**HRMS:** (ESI<sup>+</sup>) *m/z*: [M+H]<sup>+</sup> Calcd for C<sub>13</sub>H<sub>10</sub>D<sub>5</sub>O 192.1436; Found 192.1426.



**4-(Ethyl-*d*<sub>5</sub>)-1,1'-biphenyl [6d].** According to the general procedure D, (*S*)-DTBM-SEGPHOS (10.4 mg, 0.0088 mmol, 0.022 eq.), Cu(OAc)<sub>2</sub> (40 μL of a 0.2 M solution in THF, 0.008 mmol, 0.02 eq.), THF (0.16 mL), then dimethoxy(methyl)silane-*d* (0.51 mL of 3.9 M solution in hexanes, 2 mmol, 5 eq.) were combined in a 2-dram vial followed by addition of a solution of 4-ethynyl-*d*-1,1'-biphenyl (71.6 mg, 0.4 mmol, 1 eq.), THF (0.2 mL), and 2-propanol-OD (74 μL, 0.96 mmol, 2.4 eq.). The 2-dram vial was capped with a red pressure relief cap, and the reaction stirred for 13 h at 60 °C. After silica plug filtration using diethyl ether (100 mL) as the eluent, the solvent was concentrated, and the crude brown oil was dry loaded onto a silica gel column. Flash chromatography using 350 mL of hexanes as eluent gave the pure product as a clear, yellow oil (51.6 mg, 0.276 mmol, 69% yield).

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>)

δ 7.68 – 7.59 (m, 2H), 7.59 – 7.52 (m, 2H), 7.50 – 7.42 (m, 2H), 7.40 – 7.33 (m, 1H), 7.33 – 7.29 (m, 2H), 2.70 (br s, 0.10H), 1.27 (br s, integration not determined due to overlap with grease).

**<sup>2</sup>H NMR:** (61 MHz, CHCl<sub>3</sub>)

δ 2.70 (br s, 1.90D), 1.28 (br s, 2.87D).

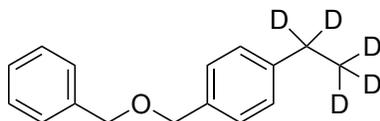
**<sup>13</sup>C NMR** (75 MHz, CDCl<sub>3</sub>)

δ 143.5, 141.3, 138.7, 128.8, 128.4, 127.2, 127.2, 127.1, 28.6 – 27.0 (m), 15.7 – 14.1 (m).

**ATR-IR (cm<sup>-1</sup>):**

3054, 3028, 2936, 2221, 2067.

**HRMS:** (EI<sup>+</sup>) *m/z*: [M+H]<sup>+</sup> Calcd for C<sub>14</sub>H<sub>9</sub>D<sub>5</sub> 187.1409; Found 187.1404.



**1-((Benzyloxy)methyl)-4-(ethyl-*d*<sub>5</sub>)benzene [6e].** According to the general procedure D, (*S*)-DTBM-SEGPPOS (5.2 mg, 0.0044 mmol, 0.022 eq.), Cu(OAc)<sub>2</sub> (20 μL of a 0.2 M solution in THF, 0.004 mmol, 0.02 eq.), THF (0.08 mL), then dimethoxy(methyl)silane-*d* (0.20 mL of a 5.9 M solution in hexanes, 1.2 mmol, 6 eq.) were combined in a 2-dram vial followed by addition of a solution of 1-((benzyloxy)methyl)-4-(ethynyl-*d*)benzene (45 mg, 0.2 mmol, 1 eq.), THF (0.1 mL), and 2-propanol-*d*<sub>8</sub> (77 μL, 1.0 mmol, 5 eq.). The 2-dram vial was capped with a red pressure relief cap, and the reaction stirred for 18 h at 60 °C. After silica plug filtration using diethyl ether (100 mL) as the eluent, the solvent was concentrated, and the crude brown oil was dry loaded onto a silica gel column. Flash chromatography using gradient elution (50 mL of hexanes, 100 mL of 3% ethyl acetate in hexanes, 200 mL of 5% ethyl acetate in hexanes) gave the pure product as a colorless oil (35.0 mg, 0.151 mmol, 76% yield).

<sup>1</sup>H NMR: (400 MHz, CDCl<sub>3</sub>)

δ 7.42 – 7.35 (m, 4H), 7.34 – 7.29 (m, 3H), 7.22 (d, *J* = 8.1 Hz, 2H), 4.58 (s, 2H), 4.56 (s, 2H), 2.64 (br s, 0.17H), 1.21 (br s, integration not determined due to overlap with grease).

<sup>2</sup>H NMR: (61 MHz, CHCl<sub>3</sub>)

δ 2.64 (br s, 1.83D), 1.22 (br s, 2.78D).

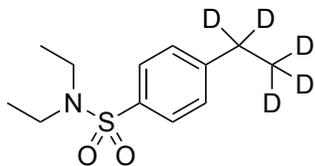
<sup>13</sup>C NMR: (101 MHz, CDCl<sub>3</sub>)

δ 143.8, 138.5, 135.6, 128.5, 128.1, 128.0, 127.9, 127.7, 72.1, 72.1, 28.4 – 27.3 (m), 15.5 – 14.3 (m).

ATR-IR (cm<sup>-1</sup>):

3029, 2853, 2222, 2081, 1615, 1090, 1071.

HRMS: (ESI<sup>+</sup>/FTICR) *m/z*: [M+Na]<sup>+</sup> Calcd for C<sub>16</sub>H<sub>13</sub>D<sub>5</sub>NaO 254.1564; Found 254.1570.



***N,N*-Diethyl-4-(ethyl-*d*<sub>5</sub>)benzenesulfonamide [6f].** According to the general procedure D, (*S*)-DTBM-SEGPPOS (10.4 mg, 0.0088 mmol, 0.022 eq.), Cu(OAc)<sub>2</sub> (40 μL of a 0.2 M solution in THF, 0.008 mmol, 0.02 eq.), THF (0.16 mL), then dimethoxy(methyl)silane-*d* (0.38 mL of 5.3 M solution in hexanes, 2 mmol, 5 eq.) were combined in a 2-dram vial followed by addition of a solution of *N,N*-diethyl-4-(ethynyl-*d*)benzenesulfonamide (95 mg, 0.4 mmol, 1 eq.), THF (0.2 mL), and 2-propanol-*d*<sub>8</sub> (153 μL, 2.0 mmol, 5 eq.). The 2-dram vial was capped with a red pressure relief cap, and the reaction stirred for 24 h at 60 °C. After silica plug filtration using diethyl ether (100 mL) as the eluent, the solvent was concentrated, and the crude brown oil was dry loaded onto a silica gel column. Flash chromatography using gradient elution (100 mL of hexanes, 100 mL 4% ethyl acetate in hexane, 300 mL of 8% ethyl acetate in hexanes) gave the pure product as a clear, yellow oil (86.1 mg, 0.35 mmol, 88% yield).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)

δ 7.68 (d, *J* = 8.3 Hz, 2H), 7.27 (d, *J* = 8.2 Hz, 2H), 3.19 (q, *J* = 7.2 Hz, 4H), 2.63 (br s, 0.12H), 1.16 (br s, integration not determined due to overlap with grease), 1.09 (t, *J* = 7.2 Hz, 6H).

<sup>2</sup>H NMR: (61 MHz, CHCl<sub>3</sub>)

δ 2.63 (br s, 1.88D), 1.17 (br s, 2.83D).

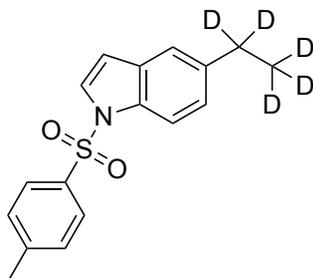
<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)

δ 149.0, 137.6, 128.4, 127.1, 42.1, 32.3 – 31.6 (m), 28.5 – 27.4 (m), 14.2.

ATR-IR (cm<sup>-1</sup>):

2976, 2936, 2870, 2225, 2079, 1332, 1150.

**HRMS:** (ESI<sup>+</sup>/FTICR) *m/z*: [M+Na]<sup>+</sup> Calcd for C<sub>12</sub>H<sub>14</sub>D<sub>5</sub>NNaO<sub>2</sub>S 269.1343; Found 269.1351.



**5-(Ethyl-*d*<sub>5</sub>)-1-tosyl-1H-indole [6g].** According to the general procedure D, (*S*)-DTBM-SEGPHOS (13.0 mg, 0.011 mmol, 0.055 eq.), Cu(OAc)<sub>2</sub> (50 μL of a 0.2 M solution in THF, 0.01 mmol, 0.05 eq.), THF (0.05 mL), then dimethoxy(methyl)silane-*d* (0.17 mL of a 5.9 M solution in hexanes, 1.0 mmol, 5 eq.) were combined in a 2-dram vial followed by addition of a solution of 5-(ethynyl-*d*)-1-tosyl-1H-indole (59.3 mg, 0.2 mmol, 1 eq.), THF (0.1 mL), and 2-propanol-*d*<sub>8</sub> (77 μL, 1.0 mmol, 5 eq.). The 2-dram vial was capped with a red pressure relief cap, and the reaction stirred for 24 h at 60 °C. After silica plug filtration using diethyl ether (100 mL) as the eluent, the solvent was concentrated, and the crude brown liquid was dry loaded onto a silica gel column. Flash chromatography using gradient elution (100 mL of hexanes, 100 mL of 5% ethyl acetate in hexanes, 200 mL of 10% ethyl acetate in hexanes) gave the pure product as a colorless oil (47.7 mg, 0.156 mmol, 78% yield).

**<sup>1</sup>H NMR:** (400 MHz, CDCl<sub>3</sub>)

δ 7.90 (d, *J* = 8.5 Hz, 1H), 7.76 (d, *J* = 8.3 Hz, 2H), 7.53 (d, *J* = 3.6 Hz, 1H), 7.33 (d, *J* = 1.4 Hz, 1H), 7.20 (d, *J* = 8.4 Hz, 2H), 7.16 (dd, *J* = 8.5, 1.4 Hz, 1H), 6.60 (d, *J* = 3.6 Hz, 1H), 2.66 (br s, 0.18H), 2.32 (s, 3H), 1.20 (br s, integration not determined due to overlap with grease).

**<sup>2</sup>H NMR:** (61 MHz, CHCl<sub>3</sub>)

δ 2.66 (br s, 1.82D), 1.21 (br s, 2.84D).

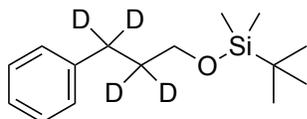
**<sup>13</sup>C NMR:** (101 MHz, CDCl<sub>3</sub>)

δ 144.9, 139.4, 135.4, 133.3, 131.1, 129.9, 126.9, 126.5, 125.1, 120.1, 113.4, 109.1, 28.5 – 27.4 (m), 21.7, 15.9 – 14.6 (m).

**ATR-IR (cm<sup>-1</sup>):**

3038, 2922, 2221, 2081, 1367, 1130.

**HRMS:** (ESI<sup>+</sup>/FTICR) *m/z*: [M+Na]<sup>+</sup> Calcd for C<sub>17</sub>H<sub>12</sub>D<sub>5</sub>NNaO<sub>2</sub>S 327.1186; Found 327.1195.



**tert-Butyldimethyl(3-phenylpropoxy-2,2,3,3-*d*<sub>4</sub>)silane [6h].** According to the general procedure D, (*R*)-DTBM-SEGPHOS (7.8 mg, 0.0066 mmol, 0.022 eq.), Cu(OAc)<sub>2</sub> (30 μL of a 0.2 M solution in THF, 0.006 mmol, 0.02 eq.), THF (0.12 mL), then dimethoxy(methyl)silane-*d* (0.28 mL, 1.5 mmol, 5.3 M solution in hexanes, 5 eq.) were combined in a 2-dram vial followed by addition of a solution of ((3-(phenyl)prop-2-yn-1-yl)oxy)(tert-butyl)dimethylsilane (73.8 mg, 0.3 mmol, 1 eq.), THF (0.15 mL), and 2-propanol-*d*<sub>8</sub> (115 μL, 1.5 mmol, 5.0 eq.). The 2-dram vial was capped with a red pressure relief cap, and the reaction stirred for 19 h at 60 °C. After silica plug filtration using diethyl ether (100 mL) as the eluent, the solvent was concentrated, and the crude brown oil was dry loaded onto a silica gel column. Flash chromatography using gradient elution (100 mL of hexanes) gave the pure product as a clear and colorless oil (53.0 mg, 0.208 mmol, 69% yield).

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)

δ 7.38 – 7.26 (m, 2H), 7.22 – 7.19 (m, 3H), 3.65 (s, 2H), 2.67 (br s, 0.11H), 1.83 (br s, 0.16H), 0.94 (s, 9H), 0.08 (s, 6H).

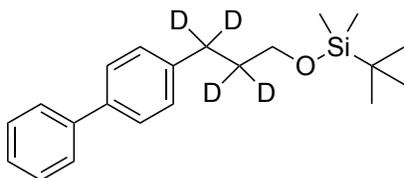
<sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)

δ 142.3, 128.6, 128.4, 125.8, 62.4, 34.5 – 33.1 (m), 32.2 – 30.7 (m), 26.1, 18.5, -5.1.

ATR-IR (cm<sup>-1</sup>):

2928, 2894, 2856, 2211, 2116, 1085.

HRMS: (ESI<sup>+</sup>) m/z: [M+H]<sup>+</sup> Calcd for C<sub>15</sub>H<sub>23</sub>D<sub>4</sub>OSi 255.2082; Found 255.2072.



**(3-([1,1'-Biphenyl]-4-yl)propoxy-2,2,3,3-d<sub>4</sub>)(tert-butyl)dimethylsilane [6i]**. According to the general procedure D, (S)-DTBM-SEGPPOS (8 mg, 0.0068 mmol, 0.022 eq.), Cu(OAc)<sub>2</sub> (31 μL of a 0.2 M solution in THF, 0.0062 mmol, 0.02 eq.), THF (0.13 mL), then dimethoxy(methyl)silane-*d* (0.29 mL, 1.55 mmol, 5.3M solution in hexanes, 5 eq.) were combined in a 2-dram vial followed by addition of a solution of ((3-([1,1'-biphenyl]-4-yl)prop-2-yn-1-yl)oxy)(tert-butyl)dimethylsilane (100 mg, 0.31 mmol, 1 eq.), THF (0.15 mL), and 2-propanol-OD (119 μL, 1.55 mmol, 5 eq.). The 2-dram vial was capped with a red pressure relief cap, and the reaction stirred for 24 h at 60 °C. After silica plug filtration using diethyl ether (100 mL) as the eluent, the solvent was concentrated. Flash chromatography using gradient elution (100 mL of hexanes, 100 mL of 2% ethyl acetate in hexanes, 100 mL of 5% ethyl acetate in hexanes) gave the pure product as a white crystalline solid (89 mg, 0.27 mmol, 87% yield).

<sup>1</sup>H NMR: (400 MHz, CDCl<sub>3</sub>)

δ 7.64 – 7.59 (m, 2H), 7.55 (d, *J* = 8.2 Hz, 2H), 7.46 (t, *J* = 8.4 Hz, 2H), 7.38 – 7.32 (m, 1H), 7.32 – 7.27 (m, 2H), 3.69 (s, 2H), 2.73 (br s, 0.08 H), 1.88 (t, *J* = 6.6 Hz, 0.13 H), 0.96 (d, *J* = 2.6 Hz, 9H), 0.11 (d, *J* = 1.3 Hz, 6H).

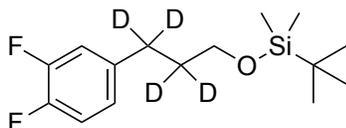
<sup>13</sup>C NMR: (101 MHz, CDCl<sub>3</sub>)

δ 141.5, 141.3, 138.8, 129.0, 128.8, 127.2, 127.1, 127.1, 62.4, 34.3 – 33.2 (m), 31.5 – 30.7 (m), 26.1, 18.5, -5.1.

ATR-IR (cm<sup>-1</sup>):

2953, 2926, 2854, 2203, 2115, 1251, 1110, 1065.

HRMS: (ESI<sup>+</sup>/FTICR) m/z: [M + Na]<sup>+</sup> Calcd for C<sub>21</sub>H<sub>26</sub>D<sub>4</sub>NaOSi 353.2209; Found 353.2219.



**tert-Butyl(3-(3,4-difluorophenyl)propoxy-2,2,3,3-d<sub>4</sub>)dimethylsilane [6j]**. According to the general procedure D, (S)-DTBM-SEGPPOS (5.2 mg, 0.0044 mmol, 0.022 eq.), Cu(OAc)<sub>2</sub> (20 μL of a 0.2 M solution in THF, 0.004 mmol, 0.02 eq.), THF (0.08 mL), then dimethoxy(methyl)silane-*d* (0.14 mL of a 5.9

M solution in hexanes, 0.8 mmol, 4 eq.) were combined in a 2-dram vial followed by addition of a solution of 1-((benzyloxy)methyl)-4-(ethynyl-*d*)benzene (56.5 mg, 0.2 mmol, 1 eq.), THF (0.1 mL), and 2-propanol-*d*<sub>8</sub> (77 μL, 1.0 mmol, 5 eq.). The 2-dram vial was capped with a red pressure relief cap, and the reaction stirred for 24 h at 60 °C. After silica plug filtration using diethyl ether (100 mL) as the eluent, the solvent was concentrated, and the crude colorless oil was dry loaded onto a silica gel column. Flash chromatography using gradient elution (100 mL of hexanes followed by 200 mL of 1% ethyl acetate in hexanes) gave the pure product as a clear and colorless oil (44.6 mg, 0.154 mmol, 77% yield).

<sup>1</sup>H NMR: (400 MHz, CDCl<sub>3</sub>)

δ 7.08 – 6.95 (m, 2H), 6.90 – 6.85 (m, 1H), 3.60 (s, 2H), 2.61 (br s, 0.19H), 1.76 (br s, 0.20H), 0.91 (s, 9H), 0.05 (s, 6H).

<sup>13</sup>C NMR: (75 MHz, CDCl<sub>3</sub>)

δ 150.3 (dd, *J* = 247.1, 12.6 Hz), 148.8 (dd, *J* = 245.1, 12.6 Hz), 139.3 (dd, *J* = 4.3 Hz), 124.3 (dd, *J* = 5.7, 3.5 Hz), 117.3 (d, *J* = 16.6 Hz), 117.0 (d, *J* = 16.9 Hz), 61.9, 34.2 – 32.8 (m), 31.3 – 30.1 (m), 26.1, 18.5, -5.2.

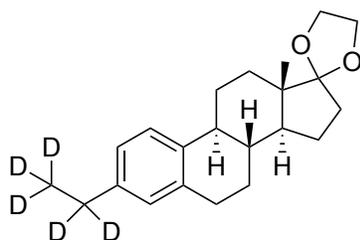
<sup>19</sup>F NMR: (376 MHz, CDCl<sub>3</sub>)

δ -138.80, -142.71.

ATR-IR (cm<sup>-1</sup>):

2955, 2929, 2857, 2211, 2119, 1607, 1518, 1254, 1087.

HRMS: (ESI<sup>+</sup>) *m/z*: [M+H]<sup>+</sup> Calcd for C<sub>15</sub>H<sub>21</sub>D<sub>4</sub>F<sub>2</sub>OSi 291.1894; Found 291.1881.



**(8*R*,9*S*,13*S*,14*S*)-3-(Ethyl-*d*<sub>5</sub>)-13-methyl-6,7,8,9,11,12,13,14,15,16-decahydrospiro[cyclopenta[*a*]phenanthrene-17,2'-[1,3]dioxolane] [6k].** According to the general procedure D, (*R*)-DTBM-SEGPPOS (5.2 mg, 0.0044 mmol, 0.022 eq.), Cu(OAc)<sub>2</sub> (20 μL of a 0.2 M solution in THF, 0.004 mmol, 0.02 eq.), THF (0.08 mL), then dimethoxy(methyl)silane-*d* (0.19 mL of 5.3 M solution in hexanes, 1 mmol, 5 eq.) were combined in a 2-dram vial followed by addition of a solution of (8*R*,9*S*,13*S*,14*S*)-3-(ethynyl-*d*)-13-methyl-6,7,8,9,11,12,13,14,15,16-decahydrospiro[cyclopenta[*a*]phenanthrene-17,2'-[1,3]dioxolane] (64.6 mg, 0.2 mmol, 1 eq.), THF (0.1 mL), and 2-propanol-OD (77 μL, 1.0 mmol, 5 eq.). The 2-dram vial was capped with a red pressure relief cap, and the reaction stirred for 38 h at 60 °C. After silica plug filtration using diethyl ether (100 mL) as the eluent, the solvent was concentrated, and the crude brown oil was dry loaded onto a silica gel column. Flash chromatography using gradient elution (100 mL of hexanes, 100 mL of 3% ethyl acetate in hexane, 100 mL of 5% ethyl acetate in hexanes, 100 mL of 8% ethyl acetate in hexanes, 200 mL of 9% ethyl acetate in hexanes, 100 mL of 10% ethyl acetate in hexanes) gave the pure product as a clear, yellow oil (48.7 mg, 0.147 mmol, 74% yield).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)

δ 7.25 (d, *J* = 8.0 1H), 7.01 (d, *J* = 8.0, 1H), 6.95 (s, 1H), 4.08 – 3.83 (m, 4H), 2.92 – 2.83 (m, 2H), 2.58 (br s, 0.15H), 2.41 – 2.24 (m, 2H), 2.11 – 2.00 (m, 1H), 1.96 – 1.74 (m, 4H), 1.71 – 1.61 (m, 1H), 1.60 – 1.30 (m, 5H), 1.20 (br s, 0.20H), 0.90 (s, 3H).

<sup>2</sup>H NMR: (61 MHz, CHCl<sub>3</sub>)

δ 2.58 (br s, 1.85D), 1.21 (br s, 2.80D).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )

$\delta$  141.5, 137.8, 136.7, 128.6, 125.5, 125.3, 119.6, 65.4, 64.7, 49.6, 46.3, 44.1, 39.1, 34.4, 30.9, 29.7, 28.1 – 27.4 (m), 27.2, 26.1, 22.5, 15.5 – 14.2 (m), 14.5.

ATR-IR ( $\text{cm}^{-1}$ ):

2966, 2936, 2872, 2221, 2075, 1700, 1610, 1103, 1042.

HRMS: (ESI<sup>+</sup>) m/z:  $[\text{M} + \text{Na}]^+$  Calcd for  $\text{C}_{22}\text{H}_{25}\text{D}_5\text{NaO}_2$  354.2452; Found 354.2462.

## V. Synthesis of Alkyne Substrates

### General TBS protection of internal alkynes (E)

To a flame-dried round bottom flask was added the alcohol substrate (2.5 mmol, 1 eq.), dry DCM (7.5 mL) followed by imidazole (340 mg, 5.0 mmol, 2 eq.) and *tert*-butyldimethylsilyl chloride (414 mg, 2.75 mmol, 1.1 eq.). The reaction was stirred at room temperature overnight. Upon completion, the reaction mixture was quenched with water (20 mL) and extracted with diethyl ether (2 x 15 mL). The combined organic layers were washed with brine (15 mL) and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. The mixture was filtered, and the solvent was removed by rotary evaporation. The crude product was purified by flash column chromatography to give the desired TBS protected alcohol.

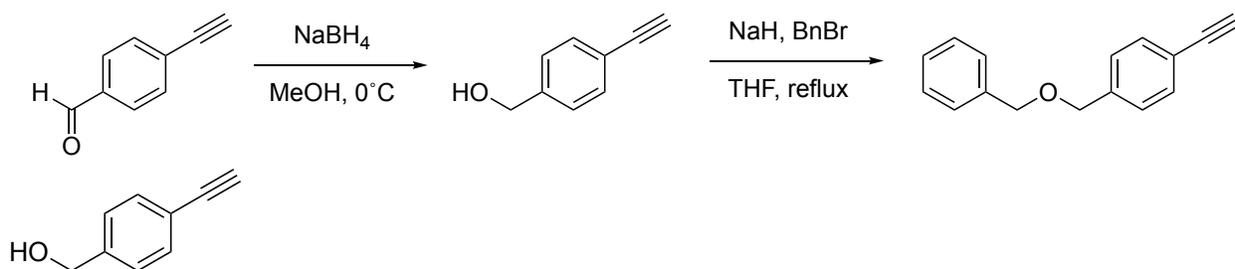
### General Sonogashira Coupling for the synthesis of internal alkynes<sup>11</sup> (F)

To a flame-dried round bottom flask under N<sub>2</sub> was added triethylamine (15 mL), which was degassed for 10 minutes. The aryl halide (3.0 mmol, 1 eq.), Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> (42 mg, 0.06 mmol, 0.02 eq.) and CuI (23 mg, 0.12 mmol, 0.04 eq.) were then sequentially added at room temperature. The mixture was stirred for 10 minutes followed by the addition of propargyl alcohol (3.3 mmol, 1.1 eq.). After 16 h of stirring at room temperature, the reaction was quenched with water (10 mL) and extracted with ethyl acetate (3 x 15 mL). The organic layers were washed with water (4 x 10 mL) and then dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. The mixture was filtered, and the solvent was removed by rotary evaporation. The crude product was purified by flash column chromatography to give the desired aryl substituted propargyl alcohol.

### General Aryl Finkelstein procedure<sup>12</sup> (G)

In a N<sub>2</sub> filled glovebox, a 25 mL dry Schlenk tube was charged with CuI (46.1 mg, 0.242 mmol, 0.05 eq.), aryl bromide compound (4.83 mmol, 1 eq.), and NaI (1.45g, 9.66 mmol, 2 eq.), followed by addition of *trans*-*N,N'*-dimethyl-1,2-cyclohexane diamine (0.076 mL, 0.483 mmol, 0.1 eq.) and anhydrous dioxane (4.83 mL). The Schlenk tube was equipped with a cold finger condenser, sealed and removed from the glovebox. The reaction was stirred at reflux in an oil bath under N<sub>2</sub> for 24 hours. Upon completion, the reaction was cooled to room temperature and was quenched with ammonia aqueous solution (prepared by diluting 0.5 mL of 0.5 M NH<sub>3</sub>/dioxane solution in 40 mL of water). The aqueous layer was then extracted with CH<sub>2</sub>Cl<sub>2</sub> (3 x 15 mL). The combined organic layers were washed with water (1 x 20 mL), dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered, and concentrated under vacuum. The crude product was purified by column chromatography to give the desired aryl iodide.

### Scheme S3: Synthesis of 1-((benzyloxy)methyl)-4-ethynylbenzene

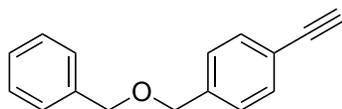


#### 4-Ethynylbenzyl alcohol

To a flame dried 500 mL round bottom flask equipped with a Teflon stir bar was added 4-ethynylbenzaldehyde (3.94 g, 30.3 mmol, 1 eq.), NaBH<sub>4</sub> (2.29 g, 60.6 mmol, 2 eq.), and anhydrous methanol (235 mL). Reaction was stirred in ice bath until completion, monitored by TLC. Upon completion, the reaction was quenched with saturated NaHCO<sub>3</sub> aqueous solution and extracted with CH<sub>2</sub>Cl<sub>2</sub> (4 x 100 mL). The combined organic layers were washed with water, dried over Na<sub>2</sub>SO<sub>4</sub>, and concentrated under vacuum. Excess solvent was removed by vacuum, and pure product was afforded as a yellow solid (3.38 g, 25.6 mmol, 85% yield). The spectra for the title compound matched previously reported spectra.<sup>13</sup>

#### <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)

δ 7.49 (d, *J* = 8.0 Hz, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 4.70 (s, 2H), 3.07 (s, 1H), 1.75 (s, 1H).



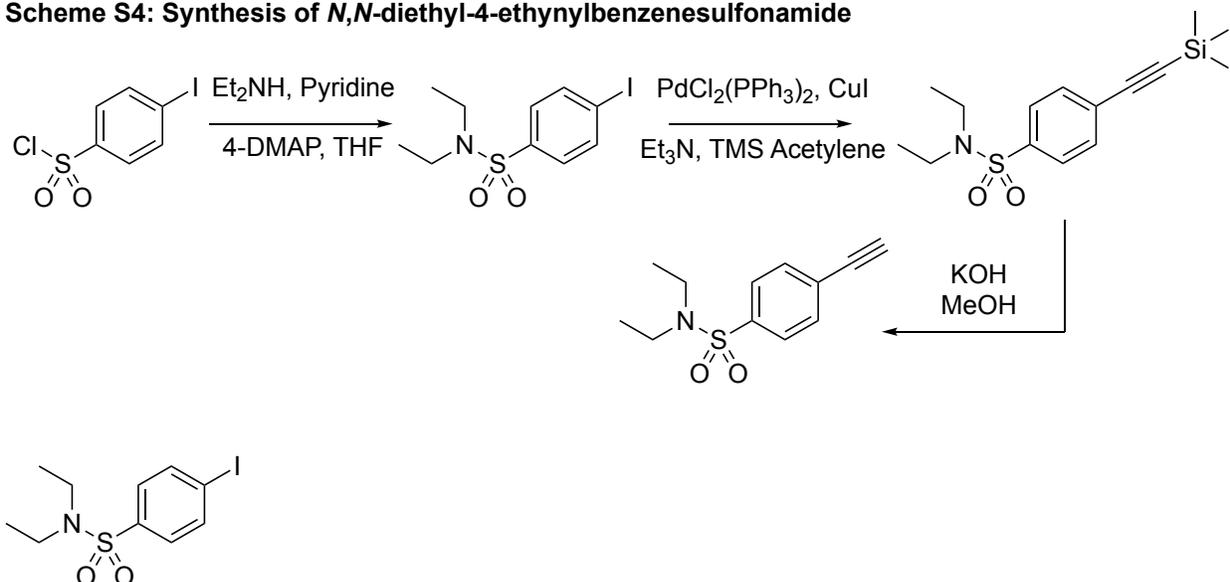
#### 1-((Benzyloxy)methyl)-4-ethynylbenzene [3g]

The benzyl protection was performed using a procedure adapted from the literature<sup>14</sup>, a flame dried 300 mL round bottom flask was equipped with a Teflon stir bar and to this was added 4-ethynylbenzyl alcohol (1.0 g, 7.57 mmol, 1 eq.), THF (7.8 mL), and NaH (60% dispersion in mineral oil) (0.303 g, 7.57 mmol, 1 eq.). Reaction was heated to reflux in an oil bath for 30 minutes, then cooled to room temperature. Benzyl bromide (0.89 mL, 7.5 mmol, 0.99 eq.) was added, and reaction was heated to reflux for 48 hours. Reaction was monitored by TLC and when reaction reached completion, reaction was cooled to room temperature followed by addition of water (10 mL). Solvent was removed by rotary evaporation, and 3M KOH was added into the round bottom flask until pH = 12 was reached. The crude reaction mixture was transferred to a separatory funnel with DCM and extracted with DCM (3 x 10 mL). The combined organic layers were washed with brine (2 x 10 mL), dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, and concentrated under vacuum. Crude product was dry loaded onto a column, and the pure product was purified by flash column chromatography with elution gradient (100 mL of hexanes, 200 mL of 10% ethyl acetate in hexanes, 400 mL of 25% ethyl acetate in hexanes), the title compound was afforded as a colorless oil (1.15 g, 5.17 mmol, 68% yield). The spectra for the title compound matched previously reported spectra.<sup>15</sup>

#### <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)

δ 7.49 (d, *J* = 8.1 Hz, 2H), 7.39 – 7.28 (m, 7H), 4.56 (s, 2H), 4.55 (s, 2H), 3.07 (s, 1H).

#### Scheme S4: Synthesis of *N,N*-diethyl-4-ethynylbenzenesulfonamide

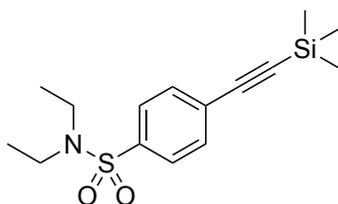


#### *N,N*-Diethyl-4-iodobenzenesulfonamide

To a flame-dried round bottom flask was added pyridine (11 mL) and 4-iodo-benzenesulfonylchloride (2.0 g, 6.6 mmol, 1 eq.), followed by addition of diethyl amine (0.75 mL, 7.27 mmol, 1.1 eq.) in THF (4 mL). The reaction flask was cooled over an ice bath and was added 4-DMAP (4-dimethylaminopyridine) (6.5 mg, 0.053 mmol, 0.008 eq.). The reaction was then warmed to room temperature and stirred for 48 hours. Reaction was monitored by TLC and upon completion, the mixture was poured into water (30 mL). The resulting precipitate was collected by vacuum filtration and rinsed with water (2 x 10 mL). The solid was dissolved in ethyl acetate (15 mL) and washed with 5% HCl (3 x 10 mL), water (2 x 10 mL), and brine (10 mL). The ethyl acetate solution was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and concentrated under vacuum. The crude product was dry loaded onto a column, and the pure product was eluted out through flash column chromatography (200 mL of hexanes, 300 mL of 5% ethyl acetate in hexanes, 300 mL of 10% ethyl acetate in hexanes, 300 mL of 15% ethyl acetate in hexanes, and 300 mL of 20% ethyl acetate in hexanes) to afford the pure product (1.40 g, 4.14 mmol, 63% yield). The spectra for the title compound matched previously reported spectra.<sup>16</sup>

#### <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)

δ 7.74 (d, *J* = 8.6 Hz, 2H), 7.41 (d, *J* = 8.6 Hz, 2H), 3.10 (q, *J* = 7.2 Hz, 4H), 0.99 (t, *J* = 7.2 Hz, 6H).



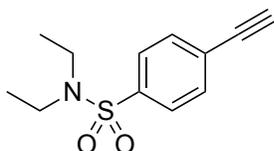
#### *N,N*-Diethyl-4-trimethylsilylethynylbenzenesulfonamide

Under N<sub>2</sub> atmosphere, to a stirred solution of *N,N*-diethyl-4-iodo-benzenesulfonamide (1.40 g, 4.14 mmol, 1 eq.) in degassed triethylamine (7 mL) was added Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> (58 mg, 0.083 mmol, 0.02 eq.) and CuI (39 mg, 0.21 mmol, 0.05 eq.) at room temperature. The mixture was then stirred for 10 minutes followed by the addition of trimethylsilyl acetylene (0.86 mL, 6.21 mmol, 1.5 eq.). Reaction was stirred at 60 °C in an oil bath overnight, and upon completion, was quenched with water (10 mL) and extracted with diethyl ether (3 x 15 mL). The combined organic layers were washed with 1 M HCl (100 mL) and water (4 x 10 mL), dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered, and concentrated under vacuum. The crude product was purified by flash column chromatography (100 mL of hexanes, 200 mL of 5% ethyl acetate in hexanes, 300 mL of 10% ethyl acetate in hexanes, 200 mL of 20% ethyl acetate in hexanes) to afford the pure

orange solid product. Quantitative yield was assumed, and product was taken immediately to the TMS-deprotection step.

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)

δ 7.72 (d, *J* = 8.5 Hz, 2H), 7.54 (d, *J* = 8.5 Hz, 2H), 3.21 (q, *J* = 7.2 Hz, 4H), 1.09 (t, *J* = 7.2 Hz, 6H), 0.24 (s, 9H).



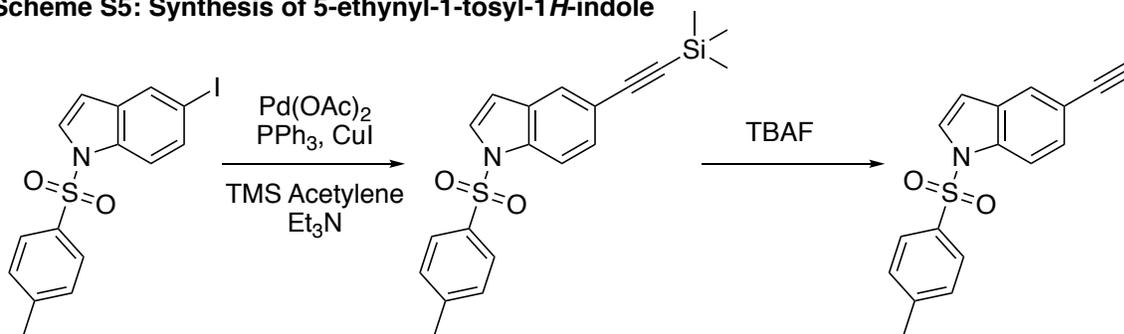
#### ***N,N*-Diethyl-4-ethynylbenzenesulfonamide [3i].**

The mixture of the TMS-protected sulfonamide (1.28 g, 4.14 mmol, 1 eq.), KOH (4.55 mL of 1 M aqueous solution, 4.55 mmol, 1.1 eq.), and MeOH (26 mL) were stirred at room temperature for 14 hours. The reaction progress was monitored by TLC. Upon completion, the reaction mixture was diluted with water (10 mL) and extracted with Et<sub>2</sub>O (3 x 15 mL). The combined organic layers were washed with 1 M HCl (20 mL), water (20 mL) and brine (20 mL), dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, and filtered. The solvent was then removed by rotary evaporation. The crude product was dry loaded onto a column, and purified by flash column chromatography (100 mL of hexanes, 200 mL of 5% ethyl acetate in hexanes, 800 mL of 10% ethyl acetate in hexanes, 200 mL of 20% ethyl acetate in hexanes) to afford the pure orange solid product (703 mg, 2.96 mmol, 72% yield). The spectra for the title compound matched previously reported spectra.<sup>17</sup>

<sup>1</sup>H NMR: (400 MHz, CDCl<sub>3</sub>)

δ 7.74 (d, *J* = 8.3 Hz, 2H), 7.57 (d, *J* = 8.2 Hz, 2H), 3.27 – 3.17 (m, 5H), 1.10 (t, *J* = 7.2 Hz, 6H).

#### **Scheme S5: Synthesis of 5-ethynyl-1-tosyl-1*H*-indole**

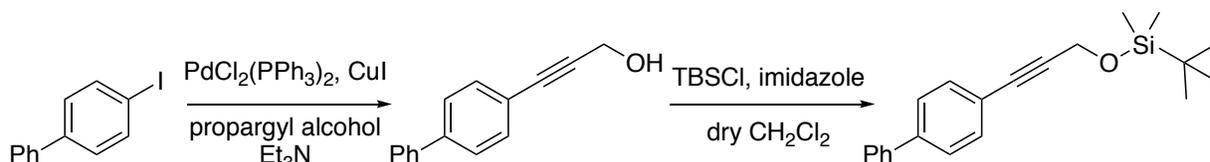


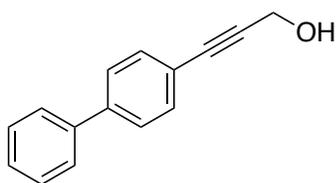
**5-Ethynyl-1-tosyl-1*H*-indole [3k].** Following a previously reported method, from 5-iodo-1-tosyl-1*H*-indole (0.863 g, 2.17 mmol), the title compound was obtained as a yellow solid (0.492 g, 1.67 mmol, 77% yield). The spectra for the title compound matched previously reported spectra.<sup>18</sup>

<sup>1</sup>H NMR: (300 MHz, CDCl<sub>3</sub>)

δ 7.96 (d, *J* = 8.6 Hz, 1H), 7.75 (d, *J* = 8.3 Hz, 2H), 7.67 (d, *J* = 1.4 Hz, 1H), 7.59 (d, *J* = 3.7 Hz, 1H), 7.44 (dd, *J* = 8.6, 1.4 Hz, 1H), 7.19 (d, *J* = 8.3 Hz, 2H), 6.61 (d, *J* = 3.7, 1H), 3.05 (s, 1H), 2.29 (s, 3H).

#### **Scheme S6: Synthesis of ((3-([1,1'-biphenyl]-4-yl)prop-2-yn-1-yl)oxy)(*tert*-butyl)dimethylsilane**

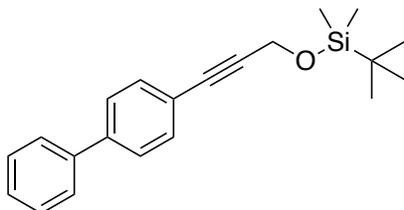




**((3-([1,1'-Biphenyl]-4-yl)prop-2-yn-1-yl)).** Synthesized according to the general procedure F from 4-iodo-1,1'-biphenyl (1.00 g, 3.57 mmol), the title compound was obtained as a light yellow solid (633 mg, 3.04 mmol, 85%). The spectra for the title compound matched previously reported spectra.<sup>19</sup>

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)

δ 7.63 – 7.48 (m, 6H), 7.45 (t, 2H), 7.40 – 7.32 (m, 1H), 4.53 (d, *J* = 6.2, 2H), 1.66 (t, *J* = 6.1 Hz, 1H).



**((3-([1,1'-Biphenyl]-4-yl)prop-2-yn-1-yl)oxy)(tert-butyl)dimethylsilane [30].** Following the general procedure E, the alcohol substrate (500 mg, 2.4 mmol, 1 eq.) in dry DCM (7.5 mL) followed by imidazole (327 mg, 4.8 mmol, 2 eq.) and *tert*-butyldimethylsilyl chloride (398 mg, 2.64 mmol, 1.1 eq.). Purified with flash column chromatography using gradient elution (100 mL of hexanes, 100 mL of 3% ethyl acetate in hexanes, 300 mL of 5% of ethyl acetate in hexanes), the title compound was obtained as a light yellow solid (633 mg, 1.96 mmol, 82% yield). The spectra for the title compound matched previously reported spectra.<sup>20</sup>

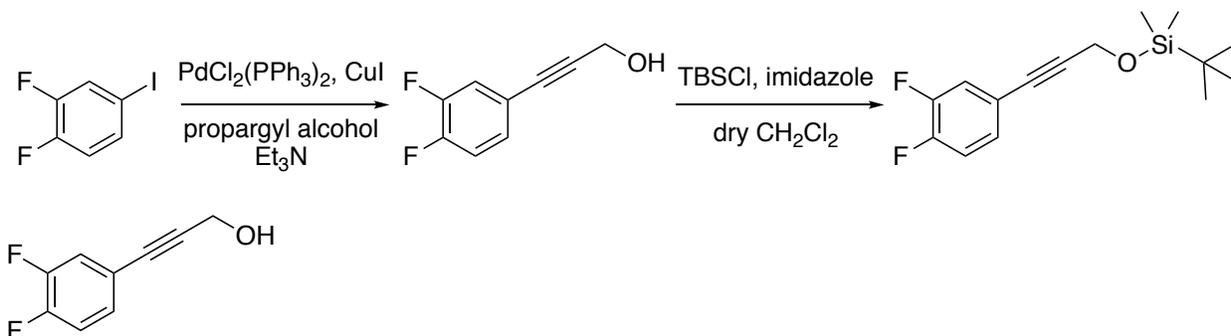
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)

δ 7.61 – 7.56 (m, 2H), 7.54 (d, *J* = 8.4 Hz, 2H), 7.50 (d, *J* = 8.0 Hz, 2H), 7.44 (t, *J* = 7.7 Hz, 2H), 7.36 (t, *J* = 7.4 Hz, 1H), 4.57 (s, 2H), 0.95 (s, 9H), 0.19 (s, 6H).

<sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)

δ 141.1, 140.4, 132.1, 128.9, 127.7, 127.1, 127.0, 122.0, 88.7, 84.8, 52.4, 26.0, 18.5, -4.9.

#### Scheme S7: Synthesis of tert-butyl((3-(3,4-difluorophenyl)prop-2-yn-1-yl)oxy)dimethylsilane



**3-(3,4-Difluorophenyl)-2-propyn-1-ol [3p].** Following the general procedure F, Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> (117 mg, 0.167 mmol, 0.02 eq.) and CuI (63 mg, 0.33 mmol, 0.04 eq.) were sequentially added to a solution of 1,2-difluoro-4-iodobenzene (2.0 g, 8.34 mmol, 1 eq.) in degassed triethylamine (42 mL) under nitrogen at room temperature. To the reaction mixture was added propargyl alcohol (0.53 mL, 9.17 mmol, 1.1 eq.). The reaction mixture was stirred for 22 hr. Crude product was purified with flash chromatography using

gradient elution (100 mL of hexanes, 100 mL of 5% ethyl acetate in hexanes, 100 mL of 10% of ethyl acetate in hexanes, 400 mL of 15% of ethyl acetate in hexanes), **3u** was obtained as a clear dark yellow oil (0.959 g, 5.70 mmol, 68.4% yield).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)

δ 7.25 – 7.18 (m, 1H), 7.17 – 7.12 (m, 1H), 7.11 – 7.03 (m, 1H), 4.47 (s, 2H), 2.34 (br s, 1H).

<sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)

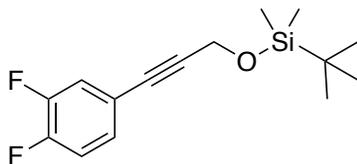
δ 152.1 (dd, *J* = 58.5, 12.8 Hz), 148.7 (dd, *J* = 55.8, 12.7 Hz), 128.5 (dd, *J* = 6.5, 3.6 Hz), 119.5 (dd, *J* = 7.6, 4.2 Hz), 121.1 – 116.9 (m), 87.9, 83.7, 51.5.

<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>)

δ -135.60, -137.11.

ATR-IR (cm<sup>-1</sup>): 3321, 2927, 2866, 2232, 1734, 1512, 1216, 1167.

HRMS: (EI<sup>+</sup>) *m/z*: [M]<sup>+</sup> Calcd for C<sub>9</sub>H<sub>6</sub>OF<sub>2</sub> 168.0400; Found 168.0380.



**tert-Butyl((3-(3,4-difluorophenyl)prop-2-yn-1-yl)oxy)dimethylsilane [5i]**. According to the general procedure E, from alcohol **3u** (0.330g, 1.96 mmol) the title compound was obtained as a clear and colorless oil (0.47 g, 1.66 mmol, 85% yield).

<sup>1</sup>H NMR: (300 MHz, CDCl<sub>3</sub>)

δ 7.26 – 7.03 (m, 3H), 4.51 (s, 2H), 0.94 (s, 9H), 0.16 (s, 6H).

<sup>13</sup>C NMR: (101 MHz, CDCl<sub>3</sub>)

δ 150.7 (dd, *J* = 251.3, 12.5 Hz), 150.1 (dd, *J* = 249.1, 13.1 Hz), 128.3 (dd, *J* = 5.8, 3.9 Hz), 120.7 (d, *J* = 18.4 Hz), 120.0 (dd, *J* = 7.4, 4.3 Hz), 117.5 (d, *J* = 17.8 Hz), 88.7, 82.8, 52.2, 26.0, 18.5, -5.0.

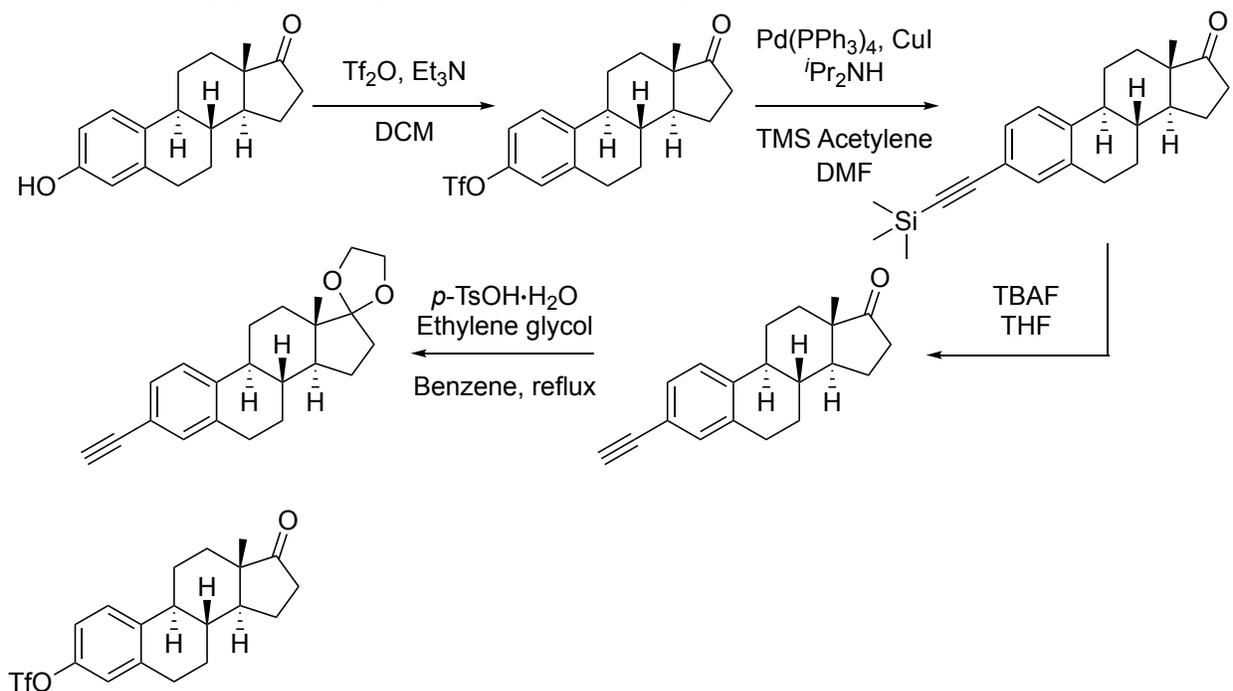
<sup>19</sup>F NMR: (376 MHz, CDCl<sub>3</sub>)

δ -136.07, -137.28.

ATR-IR (cm<sup>-1</sup>): 2954, 2856, 2215, 1513, 1251, 1217, 1080.

HRMS: (ESI<sup>+</sup>) *m/z*: [M+Na]<sup>+</sup> Calcd for C<sub>15</sub>H<sub>20</sub>F<sub>2</sub>NaOSi 305.1144; Found 305.1147.

**Scheme S8: Synthesis of (8*R*,9*S*,13*S*,14*S*)-3-ethynyl-13-methyl-6,7,8,9,11,12,13,14,15,16-decahydrospiro[cyclopenta[*a*]phenanthrene-17,2'-[1,3]dioxolane]**

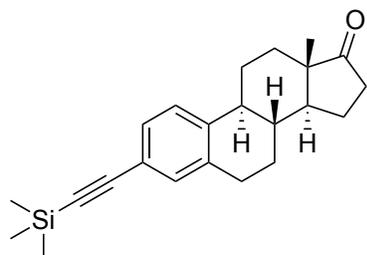


**(8*R*,9*S*,13*S*,14*S*)-13-Methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6*H*-cyclopenta[*a*]phenanthren-3-yl trifluoromethanesulfonate.**

In a 100 mL flame dried round bottom flask equipped with a Teflon stir bar was added estrone (1 g, 3.7 mmol, 1 eq.),  $\text{Et}_3\text{N}$  (1.03 mL, 7.4 mmol, 2 eq.), and  $\text{DCM}$  (18 mL), and was stirred in an ice bath for 15 minutes. Triflic anhydride (0.685 mL, 4.07 mmol, 4 eq.) was added dropwise, and a brown color persisted in the reaction flask. The reaction was stirred at room temperature for 8 hours and progress was monitored by TLC. Upon completion the reaction was quenched with saturated aqueous  $\text{NaHCO}_3$  (10 mL). The aqueous layer was extracted with  $\text{DCM}$  (3 x 20 mL), the combined organic layers were washed with brine (20 mL), dried over  $\text{Na}_2\text{SO}_4$  and concentrated under vacuum. The crude product was dry loaded onto a column, and purified by flash column chromatography (100 mL of hexanes, 100 mL of 5% ethyl acetate in hexanes, 100 mL of 7% ethyl acetate in hexanes, 100 mL of 10% ethyl acetate in hexanes, 300 mL of 12% ethyl acetate in hexanes, 300 mL of 15% ethyl acetate in hexanes, and 300 mL of 17% ethyl acetate in hexanes) to afford the pure, white solid product (1.36 g, 3.38 mmol, 91% yield). The spectra for the title compound matched previously reported spectra.<sup>21</sup>

**$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )**

$\delta$  7.34 (d, 1H), 7.07 – 6.97 (m, 2H), 2.99 – 2.88 (m, 2H), 2.52 (dd,  $J = 18.8, 8.7$  Hz, 1H), 2.46 – 2.36 (m, 1H), 2.35 – 2.27 (m, 1H), 2.23 – 1.94 (m, 4H), 1.72 – 1.40 (m, 6H), 0.92 (s, 3H).



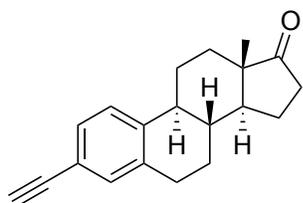
**(8*R*,9*S*,13*S*,14*S*)-13-Methyl-3-((trimethylsilyl)ethynyl)-6,7,8,9,11,12,13,14,15,16-decahydro-17*H*-cyclopenta[*a*]phenanthren-17-one.**

In a 100 mL oven dried Schlenk tube equipped with a Teflon stir bar was added (8*R*,9*S*,13*S*,14*S*)-13-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6*H*-

cyclopenta[*a*]phenanthren-3-yl trifluoromethanesulfonate (1 g, 2.49 mmol, 1 eq.), DMF (30 mL), Pd(PPh<sub>3</sub>)<sub>4</sub> (287 mg, 0.249 mmol, 0.1 eq.), CuI (47 mg, 0.249 mmol, 0.1 eq.), and <sup>i</sup>Pr<sub>2</sub>NH (1.05 mL, 7.46 mmol, 3 eq.). The reaction mixture was degassed with N<sub>2</sub> for 20 minutes, followed by addition of trimethylsilyl acetylene (0.414 mL, 2.99 mmol, 1.2 eq.). Using a cold finger condenser, the reaction was heated to reflux in an oil bath for 24 hours. The reaction progress was monitored by TLC. Upon completion, reaction was diluted with Et<sub>2</sub>O, washed with brine (3 x 10 mL), dried over Na<sub>2</sub>SO<sub>4</sub>, and concentrated under vacuum. The crude product was dry loaded onto a column, and purified by flash column chromatography (200 mL of hexanes, 100 mL of 2% ethyl acetate in hexanes, 300 mL 4% ethyl acetate in hexanes, 600 mL of 6% ethyl acetate in hexanes, 500 mL of 7% ethyl acetate in hexanes, and 600 mL of 8% ethyl acetate in hexanes) to afford the pure white solid product (474 mg, 1.35 mmol, 54% yield). The spectra for the title compound matched previously reported spectra.<sup>22</sup>

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)

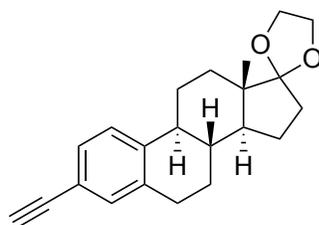
δ 7.25 – 7.18 (m, 3H), 2.92 – 2.83 (m, 2H), 2.51 (dd, *J* = 18.8, 8.7 Hz, 1H), 2.45 – 2.35 (m, 1H), 2.34 – 2.24 (m, 1H), 2.21 – 1.91 (m, 4H), 1.70 – 1.36 (m, 6H), 0.91 (s, 3H), 0.24 (s, 9H).



**(8*R*,9*S*,13*S*,14*S*)-3-Ethynyl-13-methyl-6,7,8,9,11,12,13,14,15,16-decahydro-17*H*-cyclopenta[*a*]phenanthren-17-one.** In a round bottom flask, (8*R*,9*S*,13*S*,14*S*)-13-methyl-3-((trimethylsilyl)ethynyl)-6,7,8,9,11,12,13,14,15,16-decahydro-17*H*-cyclopenta[*a*]phenanthren-17-one (514 mg, 1.47 mmol, 1 eq.), TBAF (1.62 mL of 1 M TBAF in THF, 1.1 eq.) and THF (6.6 mL) were combined and stirred for 5 hours, reaction progress was monitored by TLC. Upon completion, the reaction was quenched with distilled water (20 mL), extracted with DCM (3 x 10 mL), dried over Na<sub>2</sub>SO<sub>4</sub>, and concentrated under vacuum. The crude product was dry loaded onto a column, and purified by flash column chromatography (100 mL of hexanes, 100 mL of 2% ethyl acetate in hexanes, 100 mL 4% ethyl acetate in hexanes, 300 mL of 6% ethyl acetate in hexanes, and 600 mL of 8% ethyl acetate in hexanes) to afford the white solid product (310 mg, 1.11 mmol, 76% yield). The spectra for the title compound matched previously reported spectra.<sup>22</sup>

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)

δ 7.30 – 7.19 (m, 3H), 3.02 (s, 1H), 2.94 – 2.85 (m, 2H), 2.51 (dd, *J* = 18.8, 8.7 Hz, 1H), 2.45 – 2.37 (m, 1H), 2.36 – 2.25 (m, 1H), 2.21 – 1.92 (m, 4H), 1.69 – 1.38 (m, 6H), 0.91 (s, 3H).



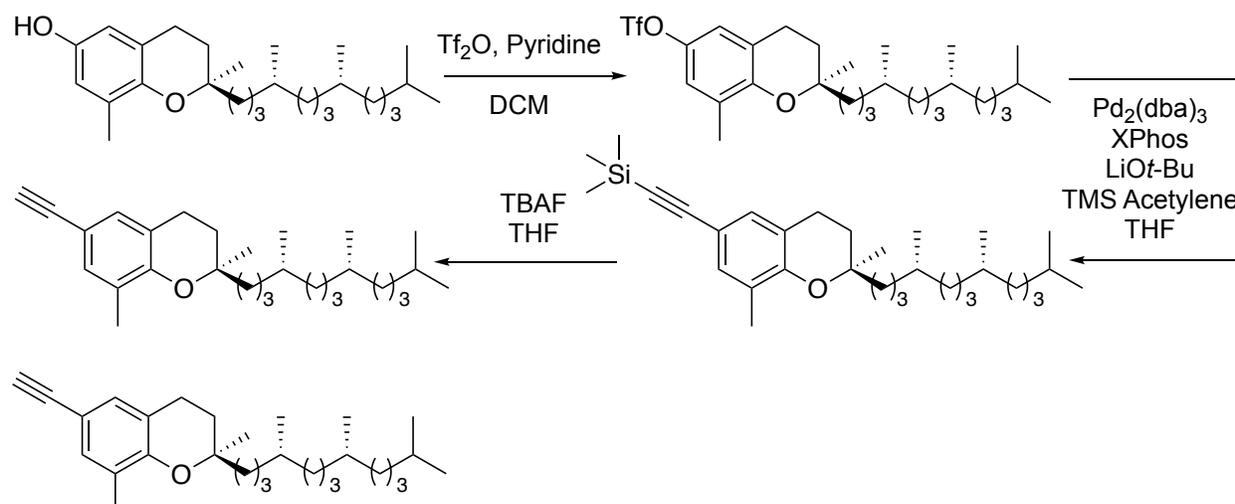
**(8*R*,9*S*,13*S*,14*S*)-3-Ethynyl-13-methyl-6,7,8,9,11,12,13,14,15,16-decahydrospiro[cyclopenta[*a*]phenanthrene-17,2'-[1,3]dioxolane] [3*r*]** To a 100 mL round bottom flask equipped with a Teflon stir bar was added (8*R*,9*S*,13*S*,14*S*)-3-ethynyl-13-methyl-6,7,8,9,11,12,13,14,15,16-decahydro-17*H*-cyclopenta[*a*]phenanthren-17-one (307 mg, 1.1 mmol, 1 eq.), *p*-TsOH•H<sub>2</sub>O (19 mg, 0.10 mmol, 0.091 eq.), ethylene glycol (1.23 mL, 22 mmol, 20 eq.), and benzene (8 mL). The reaction flask was fitted with a condenser equipped with a Dean Stark trap for the removal of water, and heated to reflux in an oil bath. Progress was monitored by TLC, and upon completion, reaction was poured into 10 mL of water, and extracted with DCM (3 x 10 mL). The combined organic layers were

washed with water (10 mL), brine (10 mL), and dried over Na<sub>2</sub>SO<sub>4</sub>. Solvent was removed by rotary evaporation, and the crude product was dry loaded onto a column, and purified by flash column chromatography (80 mL of hexanes, 100 mL of 3% ethyl acetate in hexanes, 100 mL of 5% ethyl acetate in hexanes, 100 mL of 6% ethyl acetate in hexanes, 100 mL of 8% ethyl acetate in hexanes, and 500 mL of 9% ethyl acetate in hexanes) to afford the white solid product (148 mg, 0.459 mmol, 42% yield). The spectra for the title compound matched previously reported spectra.<sup>18</sup>

<sup>1</sup>H NMR: (400 MHz, CDCl<sub>3</sub>)

δ 7.28 – 7.21 (m, 3H), 4.01 – 3.84 (m, 4H), 3.00 (s, 1H), 2.87 – 2.80 (m, 2H), 2.37 – 2.22 (m, 2H), 2.08 – 1.98 (m, 1H), 1.96 – 1.71 (m, 4H), 1.69 – 1.59 (m, 1H), 1.59 – 1.28 (m, 5H), 0.88 (s, 3H).

#### Scheme S9: Synthesis of (*R*)-6-Ethynyl-2,8-dimethyl-2-((4*R*,8*R*)-4,8,12-trimethyltridecyl)chromane

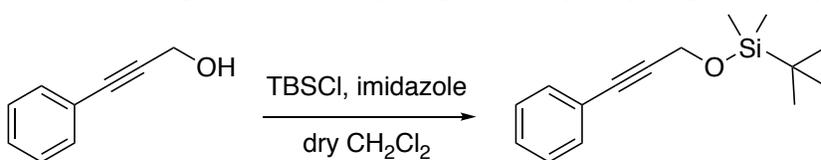


**(*R*)-6-Ethynyl-2,8-dimethyl-2-((4*R*,8*R*)-4,8,12-trimethyltridecyl)chromane [3s].** Following a previously reported method, from (*R*)-2,8-dimethyl-2-((4*R*,8*R*)-4,8,12-trimethyltridecyl)chroman-6-yl trifluoromethanesulfonate (1.07 g, 2.00 mmol), the title compound was obtained as a pale yellow oil (0.41 g, 1.00 mmol, 50% yield). The spectra for the title compound matched previously reported spectra.<sup>18</sup>

<sup>1</sup>H NMR: (300 MHz, CDCl<sub>3</sub>)

δ 7.17 – 7.06 (m, 2H), 2.94 (s, 1H), 2.79 – 2.67 (m, 2H), 2.16 (s, 3H), 1.90 – 1.70 (m, 2H), 1.67 – 1.04 (m, 24H), 0.97 – 0.81 (m, 12H).

#### Scheme S10: Synthesis of ((3-(phenyl)prop-2-yn-1-yl)oxy)(*tert*-butyl)dimethylsilane



**((3-(Phenyl)prop-2-yn-1-yl)oxy)(*tert*-butyl)dimethylsilane [5h].** The compound was synthesized according to the general procedure E. 3-phenylprop-2-yn-1-ol (2.0 g, 15.1 mmol, 1 eq.) and dry DCM (45 mL) were added to a flame dried 200 mL round bottom flask equipped with a Teflon stir bar, followed by imidazole (1.87 g, 30.2 mmol, 2 eq.) and *tert*-butyldimethylsilyl chloride (2.50 g, 16.6 mmol, 1.1 eq.). The reaction was allowed to stir at room temperature overnight. The mixture was then transferred to a separatory funnel and extracted with diethyl ether (2 x 30 mL). The combined organic layers were washed with brine (15 mL) and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. The mixture was filtered, and the solvent was removed by rotary evaporation. The crude oil was purified by flash chromatography (250 mL of hexanes,

200 mL of 2% ethyl acetate in hexanes) to afford a clear oil (3.6 g, 14.6 mmol, 97%). The spectra for the title compound matched previously reported spectra.<sup>23</sup>

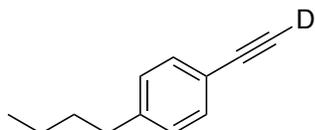
<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)

δ 7.50 – 7.36 (m, 2H), 7.35 – 7.27 (m, 3H), 4.55 (s, 2H), 0.95 (s, 9H), 0.18 (s, 6H).

## VI. Synthesis of D-alkyne Substrates

### General Procedure for Preparation of D-alkynes (H)

Following a previously reported procedure for the terminal deuteration of alkynes<sup>24</sup>, a flame dried round bottom flask equipped with a Teflon stir bar was purged with N<sub>2</sub> and to this was added, aryl alkyne (1 eq.), anhydrous K<sub>2</sub>CO<sub>3</sub> (1.5 eq.), and anhydrous CH<sub>3</sub>CN sequentially. After stirring for 30 minutes, D<sub>2</sub>O (50 eq.) was added to the round bottom flask and the reaction was stirred at room temperature for 12 – 48 hours. Reaction progress was followed by <sup>1</sup>H NMR. Upon completion, the mixture was extracted with dichloromethane or diethyl ether. The combined organic extracts were dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered, and concentrated under vacuum. The products were used in the next step without further purification.



**1-Butyl-4-(ethynyl-d)benzene [5a].** Following the general procedure H, in a N<sub>2</sub> filled glovebox, 1-butyl-4-ethynylbenzene (0.63 g, 4.0 mmol, 1 eq.), anhydrous K<sub>2</sub>CO<sub>3</sub> (0.83 g, 6.0 mmol, 1.5 eq.) and anhydrous CH<sub>3</sub>CN (12.0 mL) were stirred for 30 min. D<sub>2</sub>O (3.61 mL, 200 mmol, 50 eq.) was added to the reaction, and the mixture was stirred for 36 h at room temperature under nitrogen atmosphere. Upon completion, the reaction was extracted with diethyl ether (3 x 10 mL). The combined extracts were dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered, and concentrated under vacuum to afford the title compound as a light yellow liquid (0.52 g, 3.27 mmol, 82% yield).

<sup>1</sup>H NMR: (400 MHz, CDCl<sub>3</sub>)

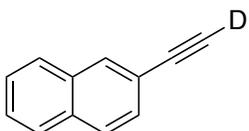
δ 7.44 (d, *J* = 8.1 Hz, 2H), 7.15 (d, *J* = 8.1 Hz, 2H), 3.05 (br s, 0.07H), 2.63 (t, *J* = 7.5 Hz, 2H), 1.67 – 1.55 (m, 2H), 1.44 – 1.30 (m, 2H), 0.95 (t, *J* = 7.3 Hz, 3H).

<sup>13</sup>C NMR: (101 MHz, CDCl<sub>3</sub>)

δ 144.0, 132.1, 128.5, 119.3, 83.5 (t, *J* = 7.6 Hz, 1C), 76.8 – 75.9 (multiplet overlapping with CDCl<sub>3</sub> signal, 1C), 35.7, 33.5, 22.4, 14.1.

ATR-IR (cm<sup>-1</sup>): 3296, 3081, 3028, 2957, 2929, 2871, 2859, 2584, 1910, 1508, 1466, 821.

HRMS: (EI<sup>+</sup>) *m/z*: [M]<sup>+</sup> Calcd for C<sub>12</sub>H<sub>13</sub>D 159.1200; Found 159.1153.



**2-(Ethynyl-d)naphthalene [5b].** Following the general procedure H, in a N<sub>2</sub> filled glovebox, 2-ethynyl-naphthalene (200 mg, 1.31 mmol, 1 eq.), K<sub>2</sub>CO<sub>3</sub> (272 mg, 1.97 mmol, 1.5 eq.), and CH<sub>3</sub>CN (2.0 mL) were added to a flame dried 200 mL round bottom flask equipped with a Teflon stir bar. After stirring for 30 minutes, deuterium oxide (1.18 mL, 66.5 mmol, 50 eq.) was added to round bottom flask. After stirring at room temperature for 12 h, the reaction was quenched with distilled water (10 mL), and extracted with dichloromethane (3 x 10 mL). The organic layers were combined, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and concentrated to afford the white solid (200 mg, 1.31 mmol, >99% yield).

<sup>1</sup>H NMR: (400 MHz, CDCl<sub>3</sub>)

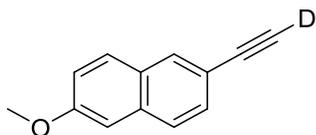
δ 8.04 (s, 1H), 7.87 – 7.76 (m, 3H), 7.57 – 7.47 (m, 3H), 3.15 (br s, 0.09H).

<sup>13</sup>C NMR: (75 MHz, CDCl<sub>3</sub>)

δ 133.2, 132.9, 132.4, 128.7, 128.2, 127.9 (+ 1 overlapping signal), 127.0, 126.7, 119.5, 83.7 (t, *J* = 7.3 Hz, 1C), 77.9 – 77.3 (multiplet overlapping with CDCl<sub>3</sub> signal, 1C).

ATR-IR (cm<sup>-1</sup>): 3276, 3049, 2922, 2572, 1971, 1593.

HRMS: (EI<sup>+</sup>) *m/z*: [M]<sup>+</sup> Calcd for C<sub>12</sub>H<sub>7</sub>D 153.0700; Found 153.0680.



**2-(Ethynyl-*d*)-6-methoxynaphthalene [5c].** Following the general procedure H, in a N<sub>2</sub> filled glovebox, 2-ethynyl-6-methoxynaphthalene, (0.18 g, 0.99 mmol, 1 eq.) anhydrous K<sub>2</sub>CO<sub>3</sub> (0.205 g, 1.49 mmol, 1.5 eq.) and anhydrous CH<sub>3</sub>CN (3.0 mL) were stirred for 30 min. D<sub>2</sub>O (0.90 mL, 50 mmol, 50 eq.) was added to the reaction. The reaction mixture was stirred for 36 h at room temperature under nitrogen atmosphere. Upon completion, the reaction was extracted with diethyl ether (3 x 5 mL). The combined extracts were dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered, and concentrated under vacuum to afford the title compound as a light yellow solid (0.18 g, 0.98 mmol, 99% yield).

<sup>1</sup>H NMR: (400 MHz, CDCl<sub>3</sub>)

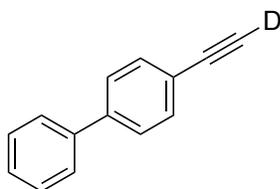
δ 7.96 (s, 1H), 7.69 (t, *J* = 8.8 Hz, 2H), 7.50 (dd, *J* = 8.2, 1.0 Hz, 1H), 7.17 (dd, *J* = 8.9, 2.3 Hz, 1H), 7.10 (d, *J* = 2.2 Hz, 1H), 3.92 (s, 3H), 3.13 (br s, 0.06H).

<sup>13</sup>C NMR: (75 MHz, CDCl<sub>3</sub>)

δ 158.6, 134.5, 132.2, 129.5, 129.3, 128.4, 127.0, 119.6, 117.0, 105.9, 83.9 (t, *J* = 7.2 Hz, 1C), 77.0 – 76.2 (multiplet overlapping with CDCl<sub>3</sub> signal, 1C), 55.5.

ATR-IR (cm<sup>-1</sup>): 3257, 3059, 3002, 2967, 2938, 2903, 2841, 2564, 1225, 1028.

HRMS: (EI<sup>+</sup>) *m/z*: [M]<sup>+</sup> Calcd for C<sub>13</sub>H<sub>9</sub>DO 183.0800; Found 183.0788.



**4-(Ethynyl-*d*)-1,1'-biphenyl [5d].** Following the general procedure H, in a N<sub>2</sub> filled glovebox, 4-ethynyl-1,1'-biphenyl (200 mg, 1.12 mmol, 1 eq.), K<sub>2</sub>CO<sub>3</sub> (0.698 g, 5.05 mmol, 4.5 eq.), and CH<sub>3</sub>CN (1.5 mL) were combined. After stirring for 30 minutes, D<sub>2</sub>O (75 μL, 4.14 mmol, 3.7 eq.) was added to round bottom flask and the reaction was stirred at room temperature for 12 h. The reaction was quenched with distilled water, and extracted with dichloromethane (3 x 10 mL). The organic layers were combined and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> then concentrated. The reaction was repeated three times to allow for full deuterium incorporation. The title compound was afforded as an orange solid product (200 mg, 1.12 mmol, >99% yield).

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)

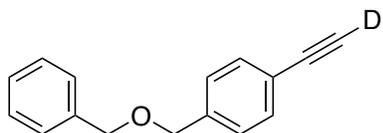
δ 7.65 – 7.52 (m, 6H), 7.50 – 7.41 (m, 2H), 7.41 – 7.32 (m, 1H), 3.14 (br s, 0.09H).

<sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)

δ 141.7, 140.4, 132.7, 129.0, 127.9, 127.2, 127.1, 121.1, 83.2 (t, *J* = 6.9 Hz, 1C), 78.3 – 77.3 (multiplet overlapping with CDCl<sub>3</sub> signal, 1C).

ATR-IR (cm<sup>-1</sup>): 3272, 3056, 3028, 2922, 2851, 2572.

HRMS: (EI<sup>+</sup>) *m/z*: [M]<sup>+</sup> Calcd for C<sub>14</sub>H<sub>9</sub>D 179.0800; Found 179.0837.



**1-((Benzyloxy)methyl)-4-(ethynyl-d)benzene [5e]**. Following the general procedure H, in a N<sub>2</sub> filled glovebox, 1-((benzyloxy)methyl)-4-ethynylbenzene (1.11 g, 4.99 mmol, 1 eq.), anhydrous K<sub>2</sub>CO<sub>3</sub> (1.04 g, 7.49 mmol, 1.5 eq.) in anhydrous CH<sub>3</sub>CN (15.0 mL) were stirred for 30 min. D<sub>2</sub>O (4.51 mL, 250 mmol, 50 eq.) was added to the reaction. The reaction mixture was stirred for 36 h at room temperature under nitrogen atmosphere. Upon completion, the reaction was extracted with diethyl ether (3 x 15 mL). The combined extracts were dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered, and concentrated under vacuum to afford the title compound as a white solid (1.05 g, 4.70 mmol, 94% yield).

<sup>1</sup>H NMR: (300 MHz, CDCl<sub>3</sub>)

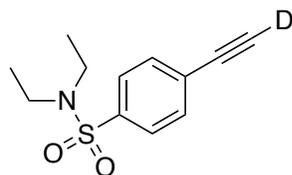
δ 7.55 (d, *J* = 8.4 Hz, 2H), 7.48 – 7.33 (m, 7H), 4.61 (s, 2H), 4.60 (s, 2H), 3.13 (s, 0.00H).

<sup>13</sup>C NMR: (75 MHz, CDCl<sub>3</sub>)

δ 139.2, 138.1, 132.2, 128.5, 127.8, 127.6, 121.3, 83.2 (t, *J* = 7.1 Hz, 1C), 77.4 – 76.6 (multiplet overlapping with CDCl<sub>3</sub> signal), 72.3, 71.6.

ATR-IR (cm<sup>-1</sup>): 3287, 3087, 3063, 3031, 2925, 2856, 2580, 1702, 1087, 1070

HRMS: (ESI<sup>+</sup>) *m/z*: [M+Na]<sup>+</sup> Calcd for C<sub>16</sub>H<sub>13</sub>DNaO 246.1000; Found 246.1002.



***N,N*-Diethyl-4-(ethynyl-d)benzenesulfonamide [5f]**. Following the general procedure H, in a N<sub>2</sub> filled glovebox, *N,N*-diethyl-4-(ethynyl)-benzenesulfonamide (500 mg, 2.11 mmol, 1 eq.), K<sub>2</sub>CO<sub>3</sub> (0.437 g, 3.16 mmol, 1.5 eq.), and CH<sub>3</sub>CN (3.24 mL) were added to a 200 mL flame dried round bottom flask equipped with a Teflon stirbar. After stirring for 30 minutes, D<sub>2</sub>O (1.91 mL, 106 mmol, 50 eq.) was added to the reaction and stirred at room temperature for 12 h. The reaction was quenched with distilled water (10 mL), and extracted with dichloromethane (3 x 10 mL). The organic layers were combined and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, then concentrated to afford the product as a yellow solid (470 mg, 1.97 mmol, 93% yield).

<sup>1</sup>H NMR: (400 MHz, CDCl<sub>3</sub>)

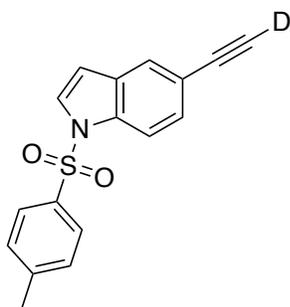
δ 7.75 (d, *J* = 8.5 Hz, 2H), 7.58 (d, *J* = 8.5 Hz, 2H), 3.22 (q, *J* = 7.1 Hz, 4.1H), 1.11 (t, *J* = 7.2 Hz, 6H).

<sup>13</sup>C NMR: (101 MHz, CDCl<sub>3</sub>)

δ 140.5, 132.7, 127.0, 126.4, 81.8 (t, *J* = 7.1 Hz, 1C), 80.6 (t, *J* = 19.7 Hz, 1C), 42.1, 14.2.

ATR-IR (cm<sup>-1</sup>): 3253, 2977, 2923, 2565, 1963, 1331, 1154.

HRMS: (ESI<sup>+</sup>) *m/z*: [M+Na]<sup>+</sup> Calcd for C<sub>12</sub>H<sub>14</sub>DNNaO<sub>2</sub>S 261.0778; Found 261.0781.



**5-(Ethynyl-*d*)-1-tosyl-1H-indole [5g].** Following the general procedure H, in a N<sub>2</sub> filled glovebox, 5-(ethynyl)-1-tosyl-1H-indole (0.40 g, 1.35 mmol, 1 eq.), anhydrous K<sub>2</sub>CO<sub>3</sub> (0.280 g, 2.03 mmol, 1.5 eq.) in anhydrous CH<sub>3</sub>CN (4.0 mL) were stirred for 30 min. D<sub>2</sub>O (1.22 mL, 67.5 mmol, 50 eq.) was added to the reaction. The reaction mixture was stirred for 36 h at room temperature under nitrogen atmosphere. Upon completion, the reaction was extracted with ethyl acetate (3 x 10 mL). The combined extracts were dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered, and concentrated under vacuum to afford the title compound as a white solid (0.38 g, 1.28 mmol, 95% yield).

**<sup>1</sup>H NMR:** (400 MHz, CDCl<sub>3</sub>)

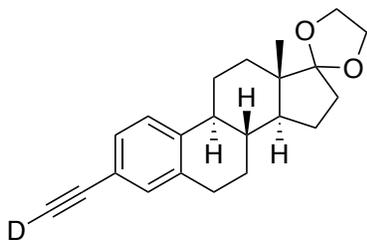
δ 7.97 (d, *J* = 8.6 Hz, 1H), 7.75 (d, *J* = 8.3 Hz, 2H), 7.67 (d, *J* = 1.6 Hz, 1H), 7.59 (d, *J* = 3.7 Hz, 1H), 7.45 (dd, *J* = 8.6, 1.6 Hz, 1H), 7.18 (d, *J* = 8.3 Hz, 2H), 6.61 (d, *J* = 3.7 Hz, 1H), 3.07 (br s, 0.05H), 2.27 (s, 3H).

**<sup>13</sup>C NMR:** (75 MHz, CDCl<sub>3</sub>)

δ 145.3, 134.9, 134.5, 130.6, 130.0, 128.4, 127.4, 126.8, 125.5, 117.1, 113.5, 108.8, 83.4 (t, *J* = 5.5 Hz, 1C), 76.4 (t, *J* = 38.4 Hz, 1C), 21.5.

**ATR-IR (cm<sup>-1</sup>):** 3117, 2920, 2573, 1370, 1116.

**HRMS:** (ESI<sup>+</sup>) *m/z*: [M+Na]<sup>+</sup> Calcd for C<sub>17</sub>H<sub>12</sub>DNNaO<sub>2</sub>S 319.0622; Found 319.0626.



**(8*R*,9*S*,13*S*,14*S*)-3-(Ethynyl-*d*)-13-methyl-6,7,8,9,11,12,13,14,15,16-decahydrospiro[cyclopenta[*a*]phenanthrene-17,2'-[1,3]dioxolane] [5j].** Following the general procedure H, in a N<sub>2</sub> filled glovebox, (8*R*,9*S*,13*S*,14*S*)-3-(ethynyl)-13-methyl-6,7,8,9,11,12,13,14,15,16-decahydrospiro[cyclopenta[*a*]phenanthrene-17,2'-[1,3]dioxolane] (213 mg, 0.661 mmol, 1 eq.), K<sub>2</sub>CO<sub>3</sub> (0.137 g, 0.991 mmol, 1.5 eq.), and CH<sub>3</sub>CN (2 mL) were added to a flame dried 300 mL round bottom flask equipped with a Teflon stir bar. After stirring for 30 minutes, D<sub>2</sub>O (0.597 mL, 33.1 mmol, 50 eq.) was added to round bottom flask. After stirring at room temperature for 24 h, reaction was quenched with distilled water, and extracted with dichloromethane (3 x 10 mL). The organic layers were combined and dried over Na<sub>2</sub>SO<sub>4</sub>, then concentrated to afford a white solid (215 mg, 0.665 mmol, >99% yield).

**<sup>1</sup>H NMR:** (400 MHz, CDCl<sub>3</sub>)

δ 7.25 – 7.22 (m, 2H), 7.22 – 7.19 (m, 1H), 3.99 – 3.81 (m, 4H), 2.99 (br s, 0.07H), 2.88 – 2.79 (m, 2H), 2.36 – 2.21 (m, 2H), 2.07 – 1.97 (m, 1H), 1.95 – 1.70 (m, 4H), 1.69 – 1.59 (m, 1H), 1.59 – 1.24 (m, 5H), 0.87 (s, 3H).

**<sup>13</sup>C NMR:** (101 MHz, CDCl<sub>3</sub>)

$\delta$  141.6, 137.0, 132.6, 129.3, 125.5, 119.4, 119.2, 83.6 (br s), 76.6 –75.3 (multiplet overlapping with CDCl<sub>3</sub> signal, 1C), 65.3, 64.7, 49.5, 46.2, 44.2, 38.7, 34.3, 30.7, 29.3, 26.8, 25.9, 22.4, 14.4.

ATR-IR (cm<sup>-1</sup>):

2978, 2939, 2875, 2587, 2249, 1735, 1620, 1590, 1179, 1044.

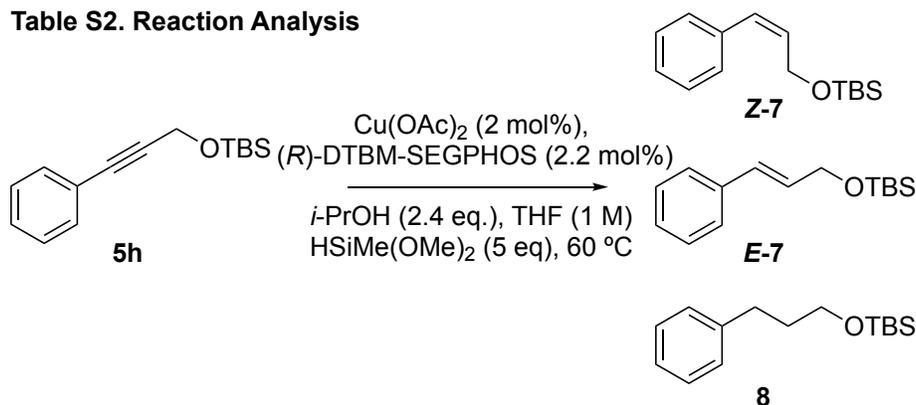
HRMS: (ESI<sup>+</sup>) m/z: [M + H]<sup>+</sup> Calcd for C<sub>22</sub>H<sub>26</sub>DO<sub>2</sub> 324.2068; Found 324.2075.

## VII. Mechanistic Studies

### General Procedure for Time Reaction Analysis

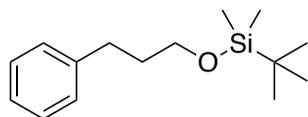
In a N<sub>2</sub> filled glovebox, (*R*)-DTBM-SEGPPOS (5.2 mg, 0.0044mmol, 0.022 eq.), Cu(OAc)<sub>2</sub> (20 μL of a 0.2 M solution in THF, 0.004 mmol, 0.02 eq.), and THF (0.08 mL) were added to an oven-dried 2-dram vial followed by dropwise addition of dimethoxy(methyl)silane (123 μL, 1 mmol, 5 eq.). A color change from green/blue to orange was observed while stirring for 15 minutes. In a separate oven-dried 1-dram vial was added the ((3-(phenyl)prop-2-yn-1-yl)oxy)(*tert*-butyl)dimethylsilane (49 mg, 0.2 mmol, 1 eq.), THF (0.1 mL), and 2-propanol (37 μL, 0.48 mmol, 2.4 eq.). The solution in the 1-dram vial was added dropwise over 20 seconds to the 2-dram vial. The total volume of THF was calculated based on having a final reaction concentration of 1M based on the alkyne substrate. The 2-dram vial was capped with a red pressure relief cap, taken out of the glovebox, and stirred at 60 °C for the designated time. The reaction mixture was then filtered through a 1" silica plug with 20 mL of Et<sub>2</sub>O followed by 80 mL of Et<sub>2</sub>O to elute the remaining product into a 200 mL round bottom flask. After removing the Et<sub>2</sub>O by rotary evaporation, the crude product was isolated by flash column chromatography using gradient elution (100 mL of hexanes followed by 200 mL of 5% ethyl acetate in hexanes) to give *tert*-butyldimethyl(3-phenylpropoxy)silane as a clear, colorless oil. The spectra for the title compound matched previously reported spectra.<sup>25</sup>

Table S2. Reaction Analysis



Entry	Reaction Time (min)	Z-7 <sup>a</sup> (%)	E-7 <sup>a</sup> (%)	8 <sup>a</sup> (%)
1	15	74	0	6
2	30	48	2	25
3	45	40	5	36
4	90	17	7	54
5	180	7	5	61
6	9 h	0	0	79

<sup>a</sup>Yields of each product were determined by <sup>1</sup>H NMR of the combined products after purification.



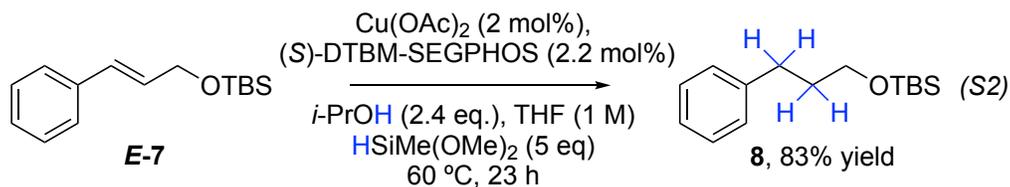
**tert-Butyldimethyl(3-phenylpropoxy)silane (8)**

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)

δ 7.33 – 7.25 (m, 2H), 7.23 – 7.16 (m, 3H), 3.65 (t, *J* = 6.3 Hz, 2H), 2.69 (t, *J* = 7.9 Hz, 2H), 1.90 – 1.80 (m, 2H), 0.93 (s, 9H), 0.07 (s, 6H).

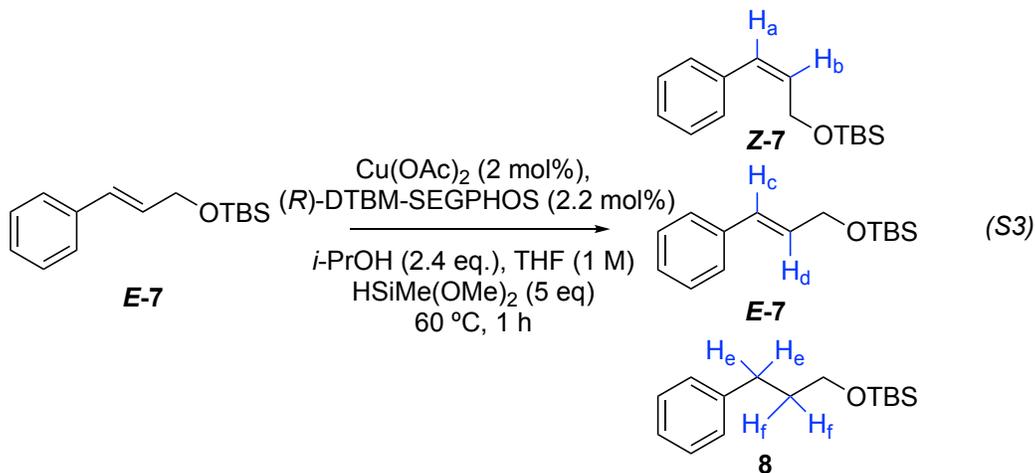
<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)

δ 142.4, 128.6, 128.4, 125.8, 62.5, 34.6, 32.2, 26.1, 18.5, -5.1



**tert-Butyldimethyl(3-phenylpropoxy)silane (8)**

In a N<sub>2</sub> filled glovebox, (*S*)-DTBM-SEGPPOS (7.8 mg, 0.0066mmol, 0.022 eq.), Cu(OAc)<sub>2</sub> (30 μL of a 0.2 M solution in THF, 0.006 mmol, 0.02 eq.), and THF (0.12 mL) were added to an oven-dried 2-dram vial followed by dropwise addition of dimethoxy(methyl)silane (185 μL, 1.5 mmol, 5 eq.). A color change from green/blue to orange was observed while stirring for 15 minutes. In a separate oven-dried 1-dram vial was added the **E-7** (74.5 mg, 0.3 mmol, 1 eq.), THF (0.15 mL), and 2-propanol (55 μL, 0.72 mmol, 2.4 eq.). The solution in the 1-dram vial was added dropwise over 20 seconds to the 2-dram vial. The total volume of THF was calculated based on having a final reaction concentration of 1M based on the alkyne substrate. The 2-dram vial was capped with a red pressure relief cap, taken out of the glovebox, and stirred at 60 °C for 23 h. The reaction mixture was then filtered through a 1" silica plug with 20 mL of Et<sub>2</sub>O followed by 80 mL of Et<sub>2</sub>O to elute the remaining product into a 200 mL round bottom flask. After removing the Et<sub>2</sub>O by rotary evaporation, the crude product was isolated by flash column chromatography using gradient elution (100 mL of hexanes followed by 100 mL of 2% ethyl acetate in hexanes) to give *tert*-butyldimethyl(3-phenylpropoxy)silane as a clear, colorless oil (62 mg, 0.248 mmol, 83% yield). The spectra for the title compound matched previously reported spectra.<sup>25</sup>



### **tert-Butyldimethyl(3-phenylpropoxy)silane (8)**

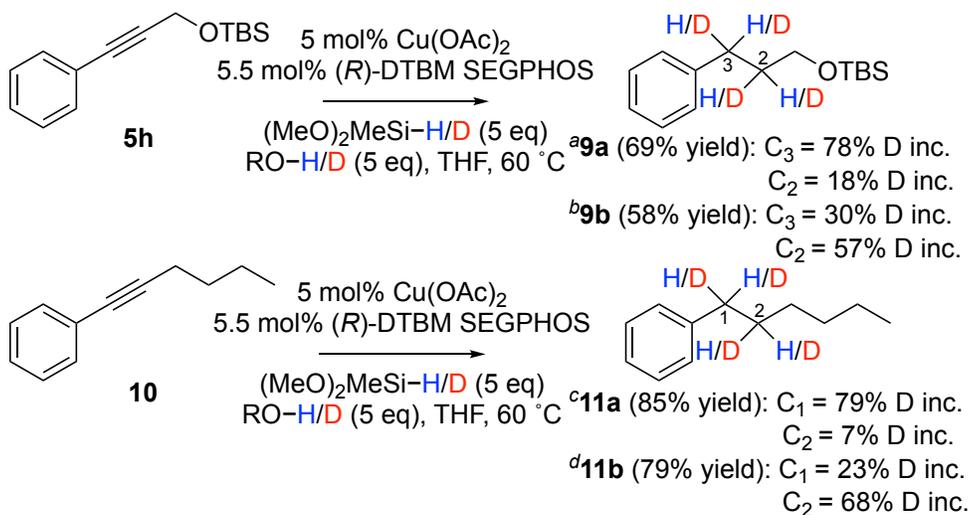
In a N<sub>2</sub> filled glovebox, (S)-DTBM-SEGPHOS (7.8 mg, 0.0066mmol, 0.022 eq.), Cu(OAc)<sub>2</sub> (30 μL of a 0.2 M solution in THF, 0.006 mmol, 0.02 eq.), and THF (0.12 mL) were added to an oven-dried 2-dram vial followed by dropwise addition of dimethoxy(methyl)silane (185 μL, 1.5 mmol, 5 eq.). A color change from green/blue to orange was observed while stirring for 15 minutes. In a separate oven-dried 1-dram vial was added the **E-7** (74.5 mg, 0.3 mmol, 1 eq.), THF (0.15 mL), and 2-propanol (55 μL, 0.72 mmol, 2.4 eq.). The solution in the 1-dram vial was added dropwise over 20 seconds to the 2-dram vial. The total volume of THF was calculated based on having a final reaction concentration of 1M based on the alkyne substrate. The 2-dram vial was capped with a red pressure relief cap, taken out of the glovebox, and stirred at 60 °C for 1 h. The reaction mixture was then filtered through a 1" silica plug with 20 mL of Et<sub>2</sub>O followed by 80 mL of Et<sub>2</sub>O to elute the remaining product into a 200 mL round bottom flask. After removing the Et<sub>2</sub>O by rotary evaporation, the crude product was isolated by flash column chromatography using gradient elution (100 mL of hexanes followed by 100 mL of 2% ethyl acetate in hexanes) to give *tert*-butyldimethyl(3-phenylpropoxy)silane as a clear, colorless oil (61 mg combination of all products, 42% alkane **8**, 39% **E-7**, trace **Z-7**).

### **Transfer Hydrodeuteration Experiments:**

Method for calculating deuterium incorporation at each carbon:

In the <sup>1</sup>H NMR spectra, if both benzylic and homobenzylic peaks were clearly visible and no overlap with other peaks was observed, then the deuterium incorporation was calculated from the integration of the protonated peak. If overlap of other peaks or overlap with an impurity such as water or grease was observed in the homobenzylic region of the <sup>1</sup>H NMR spectra, a <sup>2</sup>H NMR spectra was obtained. The ratio of the two peaks that appear in the <sup>2</sup>H NMR spectra was correlated to the calculated deuterium incorporation at the benzylic peak in the <sup>1</sup>H NMR spectra.

### **Scheme S11: Regioselective Transfer Hydrodeuteration**



All reactions performed with Cu(OAc)<sub>2</sub> (5 mol%), (R)-DTBM-SEGPHOS (5.5 mol%), THF (0.2 M, based on alkyne substrate), 60 °C. All yields are isolated and %D inc. was determined using <sup>1</sup>H NMR and/or <sup>2</sup>H NMR. <sup>a</sup>5 eq (MeO)<sub>2</sub>MeSi-H, 5 eq EtOD, 24 h. <sup>b</sup>5 eq (MeO)<sub>2</sub>MeSi-D, 5 eq EtOH, 24 h. **9b** was isolated as a mixture with alkene (23% yield) present due to incomplete conversion. See SI for details. <sup>c</sup>5 eq (MeO)<sub>2</sub>MeSi-H, 5 eq 2-propanol-d<sub>8</sub>, 21 h. <sup>d</sup>5 eq (MeO)<sub>2</sub>MeSi-D, 5 eq *i*-PrOH, 21 h.



#### ***Tert*-butyldimethyl(3-phenylpropoxy)silane-*d*<sub>2</sub> [9a].**

In a N<sub>2</sub> filled glovebox, (*R*)-DTBM-SEGPPOS (13 mg, 0.011 mmol, 0.055 eq.), Cu(OAc)<sub>2</sub> (50 μL of a 0.2 M solution in THF, 0.01 mmol, 0.05 eq.), and THF (0.05 mL) were added to an oven-dried 2-dram vial followed by dropwise addition of dimethoxy(methyl)silane (123 μL, 1 mmol, 5 eq.). A color change from green/blue to orange was observed while stirring for 15 minutes. In a separate oven-dried 1-dram vial was added the ((3-(phenyl)prop-2-yn-1-yl)oxy)(*tert*-butyl)dimethylsilane (49 mg, 0.2 mmol, 1 eq.), THF (0.10 mL), and ethanol-OD (58 μL, 1 mmol, 5 eq.). The solution in the 1-dram vial was added dropwise over 20 seconds to the 2-dram vial. The 2-dram vial was capped with a red pressure relief cap, taken out of the glovebox, and stirred at 60 °C for 24 h. The reaction mixture was then filtered through a 1" silica plug with 20 mL of Et<sub>2</sub>O followed by 80 mL of Et<sub>2</sub>O to elute the remaining product into a 200 mL round bottom flask. After removing the Et<sub>2</sub>O by rotary evaporation, the crude product was isolated by flash column chromatography using gradient elution (100 mL of hexanes followed by 100 mL of 2% ethyl acetate in hexanes) to give *tert*-butyldimethyl(3-phenylpropoxy)silane-*d*<sub>2</sub> as a clear, colorless oil (34.9 mg, 0.138 mmol, 69% yield).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):

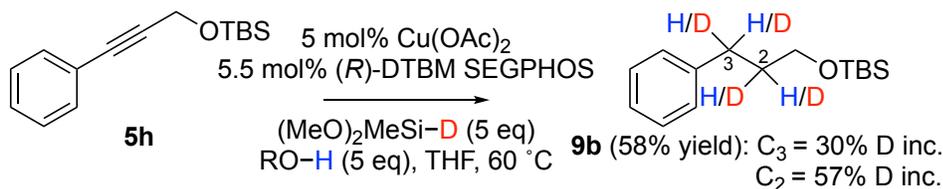
δ 7.31 – 7.26 (m, 2H), 7.21 – 7.17 (m, 3H), 3.66 – 3.63 (m, 2H), 2.69 – 2.65 (m, 0.44H), 1.87-1.82 (m, 1.65H), 0.92 (s, 9H), 0.06 (s, 6H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>):

δ 142.3, 128.6, 128.4, 125.8, 62.5, 34.5– 34.0 (m), 32.3 – 31.2 (m), 26.1, 18.5, -5.1.

ATR-IR (cm<sup>-1</sup>): 3084, 3062, 3026, 2953, 2928, 2894, 2856, 2132, 1091.

HRMS: (ESI<sup>+</sup>) m/z: [M+Na]<sup>+</sup> Calcd for C<sub>15</sub>H<sub>24</sub>D<sub>2</sub>NaOSi 275.1771; Found 275.1773.



#### ***Tert*-butyldimethyl(3-phenylpropoxy)silane-*d*<sub>2</sub> [9b].**

In a N<sub>2</sub> filled glovebox, (*R*)-DTBM-SEGPPOS (13 mg, 0.011 mmol, 0.055 eq.), Cu(OAc)<sub>2</sub> (50 μL of a 0.2 M solution in THF, 0.01 mmol, 0.05 eq.), and THF (0.05 mL) were added to an oven-dried 2-dram vial followed by dropwise addition of dimethoxy(methyl)silane-*d* (0.14 mL, 1 mmol, 7.1 M solution in hexanes, 5 eq.). A color change from green/blue to orange was observed while stirring for 15 minutes. In a separate oven-dried 1-dram vial was added the ((3-(phenyl)prop-2-yn-1-yl)oxy)(*tert*-butyl)dimethylsilane (49 mg, 0.2 mmol, 1 eq.), THF (0.1 mL), and ethanol (58 μL, 1 mmol, 5 eq.). The solution in the 1-dram vial was added dropwise over 20 seconds to the 2-dram vial. The 2-dram vial was capped with a red pressure relief cap, taken out of the glovebox, and stirred at 60 °C for 24 h. The reaction mixture was then filtered through a 1" silica plug with 20 mL of Et<sub>2</sub>O followed by 80 mL of Et<sub>2</sub>O to elute the remaining product into a 200 mL round bottom flask. After removing the Et<sub>2</sub>O by rotary evaporation, the crude product was isolated by flash column chromatography using gradient elution (100 mL of

hexanes followed by 100 mL of 2% ethyl acetate in hexanes) to give *tert*-butyldimethyl(3-phenylpropoxy)silane-*d*<sub>2</sub> as a clear, colorless oil (40.5 mg, 58% alkane, 23% alkene).

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)

δ 7.42 – 7.14 (m, 7.2H, overlap with alkene aromatic protons), 6.61 (d, *J* = 14.1 Hz, 0.12H), 6.50 (s, 0.14H), 6.35 – 6.23 (m, 0.11H), 5.89 – 5.78 (m, 0.10H), 4.50 – 4.41 (m, 0.4H), 4.40 – 4.33 (m, 0.38H), 3.73 – 3.55 (m, 2H), 2.75 – 2.55 (m, 1.4H), 1.92 – 1.74 (m, 0.87H), 0.96 (s, 1.79H), 0.92 (s, 10.5H), 0.13 (s, 1.24H), 0.06 (s, 6.76H).

ATR-IR (cm<sup>-1</sup>): 3085, 3062, 3027, 2954, 2928, 2895, 2856, 2153, 1087.

HRMS: (EI<sup>+</sup>) *m/z*: [M-H]<sup>+</sup> Calcd for C<sub>15</sub>H<sub>24</sub>D<sub>2</sub>OSi 251.1830; Found 251.1795.



#### Hexylbenzene-*d*<sub>2</sub> [11a].

In a N<sub>2</sub> filled glovebox, (R)-DTBM-SEGPHOS (13 mg, 0.011 mmol, 0.055 eq.), Cu(OAc)<sub>2</sub> (50 μL of a 0.2 M solution in THF, 0.01 mmol, 0.05 eq.), and THF (0.05 mL) were added to an oven-dried 2-dram vial followed by dropwise addition of dimethoxy(methyl)silane (123 μL, 1 mmol, 5 eq.). A color change from green/blue to orange was observed while stirring for 15 minutes. In a separate oven-dried 1-dram vial was added the 1-hexyn-1-yl-benzene (31.7 mg, 0.2 mmol, 1 eq.), THF (0.1 mL), and 2-propanol-*d*<sub>8</sub> (77 μL, 1 mmol, 5 eq.). The solution in the 1-dram vial was added dropwise over 20 seconds to the 2-dram vial. The 2-dram vial was capped with a red pressure relief cap, taken out of the glovebox, and stirred at 60 °C for 21 h. The reaction mixture was then filtered through a 1" silica plug with 20 mL of Et<sub>2</sub>O followed by 80 mL of Et<sub>2</sub>O to elute the remaining product into a 200 mL round bottom flask. After removing the Et<sub>2</sub>O by rotary evaporation, the crude product was isolated by flash column chromatography using 200 mL of hexanes to give hexylbenzene-*d*<sub>2</sub> as a clear, colorless oil (28 mg, 0.17 mmol, 85% yield).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)

δ 7.32 – 7.24 (m, 2H), 7.22 – 7.13 (m, 3H), 2.64 – 2.55 (m, 0.42H), 1.66 – 1.54 (m, 1.94H, overlaps with H<sub>2</sub>O), 1.40 – 1.21 (m, 6H, overlaps with grease), 0.89 (t, *J* = 6.7 Hz, 3H).

<sup>2</sup>H NMR: (61 MHz, CHCl<sub>3</sub>)

δ 2.59 (br s, 1.58D), 1.62 (br s, 0.13D).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)

δ 143.1, 128.5, 128.4, 125.7, 36.4 – 35.3 (m), 31.9, 31.8 – 30.9 (m), 29.2, 22.8, 14.2.

ATR-IR (cm<sup>-1</sup>): 3084, 3061, 3025, 2956, 2923, 2855, 2191, 1074.

HRMS: (EI<sup>+</sup>) *m/z*: [M]<sup>+</sup> Calcd for C<sub>12</sub>H<sub>16</sub>D<sub>2</sub> 164.1500; Found 164.1528.



#### Hexylbenzene-*d*<sub>2</sub> [11b].

In a N<sub>2</sub> filled glovebox, (*R*)-DTBM-SEPHOS (26 mg, 0.022 mmol, 0.055 eq.), Cu(OAc)<sub>2</sub> (100 μL of a 0.2 M solution in THF, 0.02 mmol, 0.05 eq.), and THF (0.15 mL) were added to an oven-dried 2-dram vial followed by dropwise addition of dimethoxy(methyl)silane-*d* (288 μL, 2 mmol, 7.1 M solution in hexanes, 5 eq.). A color change from green/blue to orange was observed while stirring for 15 minutes. In a separate oven-dried 1-dram vial was added the 1-hexyn-1-yl-benzene (63 mg, 0.4 mmol, 1 eq.), THF (0.15 mL), and 2-propanol (153 μL, 2 mmol, 5 eq.). The solution in the 1-dram vial was added dropwise over 20 seconds to the 2-dram vial. The 2-dram vial was capped with a red pressure relief cap, taken out of the glovebox, and stirred at 60 °C for 21 h. The reaction mixture was then filtered through a 1" silica plug with 20 mL of Et<sub>2</sub>O followed by 80 mL of Et<sub>2</sub>O to elute the remaining product into a 200 mL round bottom flask. After removing the Et<sub>2</sub>O by rotary evaporation, the crude product was isolated by flash column chromatography using 200 mL of hexanes to give hexylbenzene-*d*<sub>2</sub> as a clear, colorless oil (52.0 mg, 0.317 mmol, 79% yield).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)

δ 7.33 – 7.27 (m, 2H), 7.24 – 7.17 (m, 3H), 2.66 – 2.58 (m, 1.54H), 1.69 – 1.56 (m, 0.76H, overlaps with H<sub>2</sub>O), 1.42 – 1.24 (m, 6H, overlaps with grease), 0.92 (t, *J* = 6.8 Hz, 3H).

<sup>2</sup>H NMR: (61 MHz, CHCl<sub>3</sub>)

δ 2.61 (br s, 0.46D), 1.60 (br s, 1.34D).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)

δ 143.1, 128.5, 128.4, 125.7, 36.2-35.3 (m), 31.9, 31.7 – 30.9 (m), 29.1, 22.8, 14.3.

ATR-IR (cm<sup>-1</sup>): 3085, 3063, 3026, 2956, 2921, 2871, 2855, 2361, 2150, 1077.

HRMS: (EI<sup>+</sup>) *m/z*: [M]<sup>+</sup> Calcd for C<sub>12</sub>H<sub>16</sub>D<sub>2</sub> 164.1500; Found 164.1528.

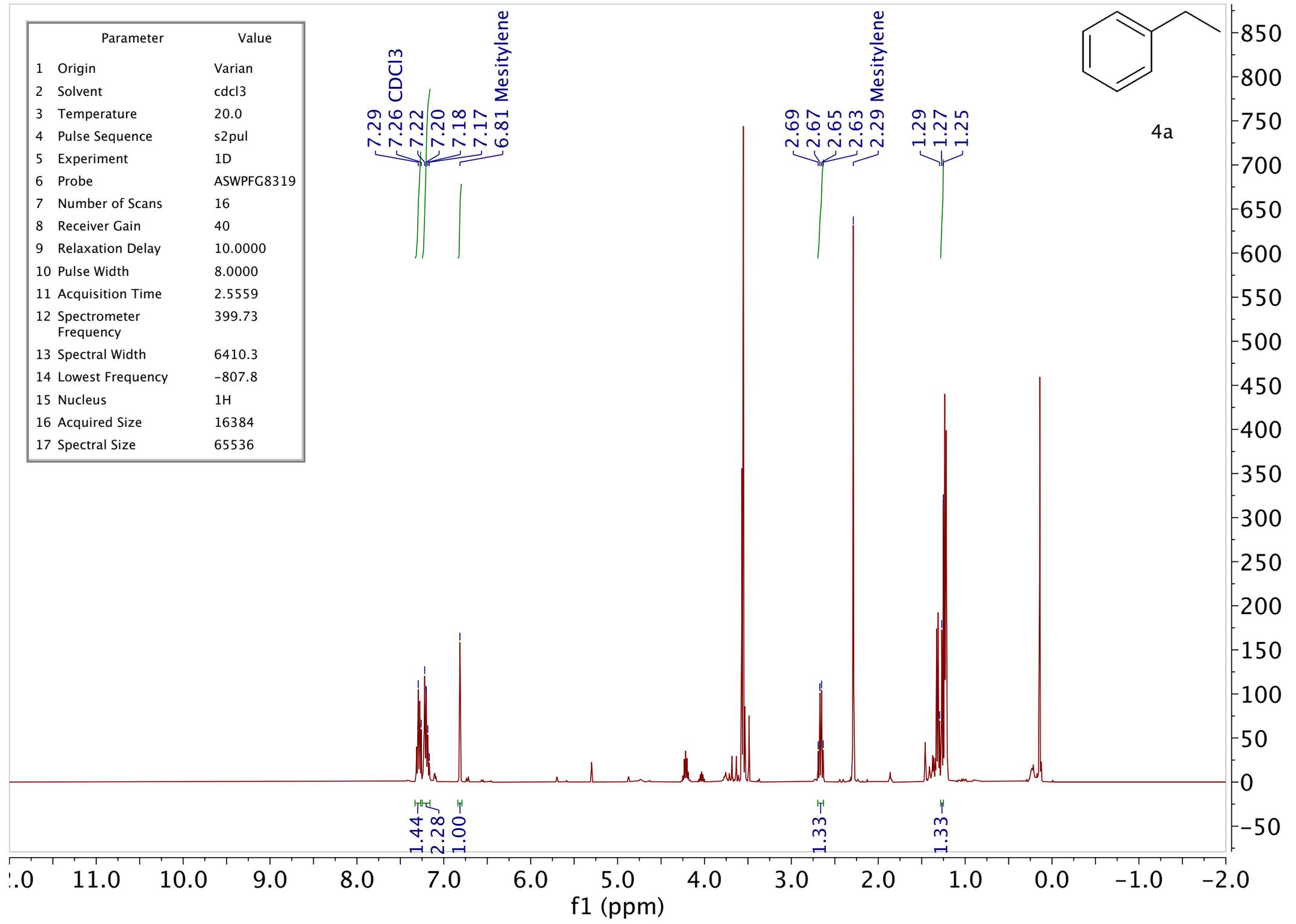
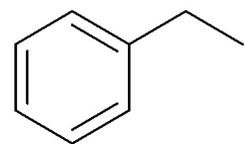
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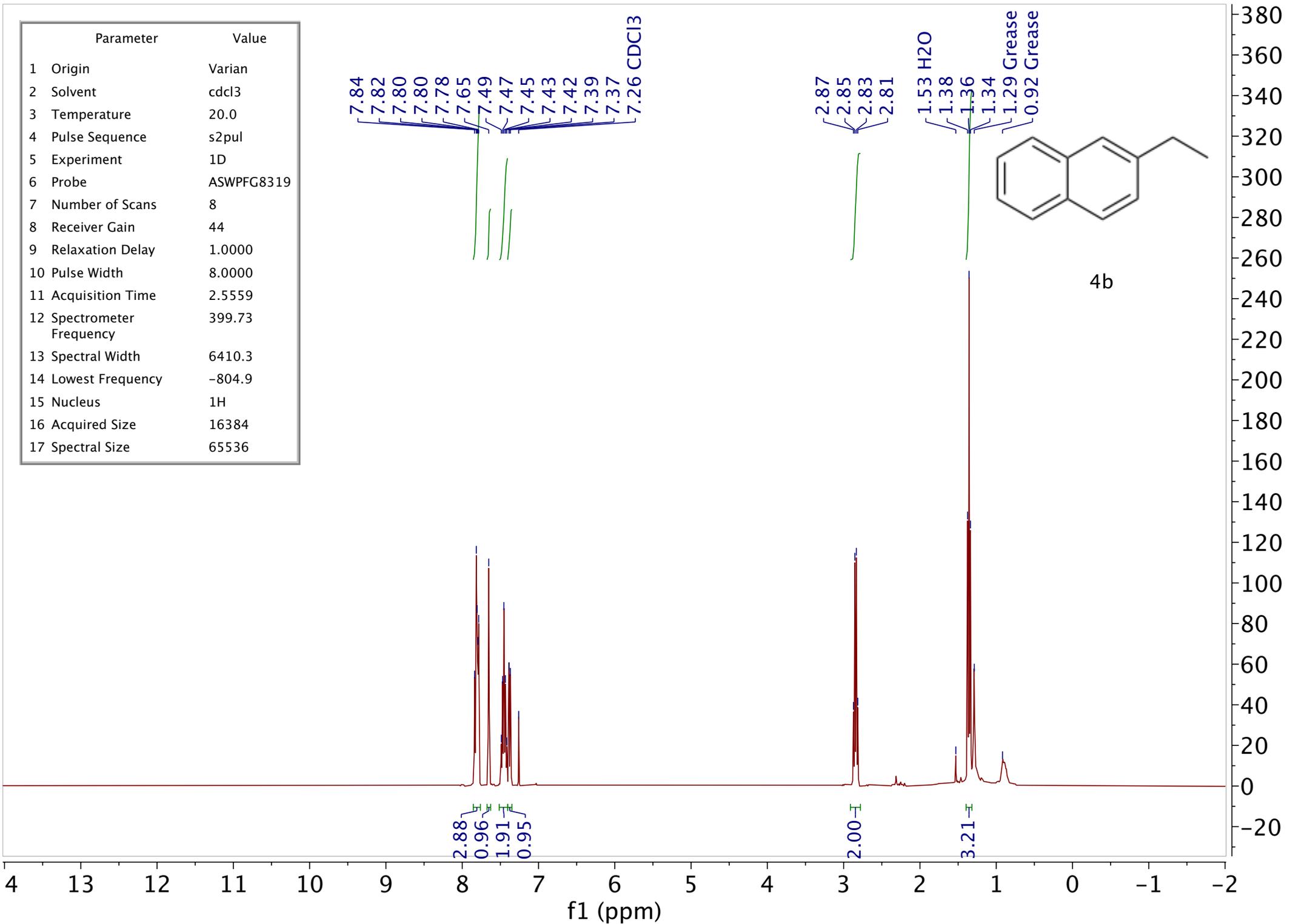
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## IX. Spectra

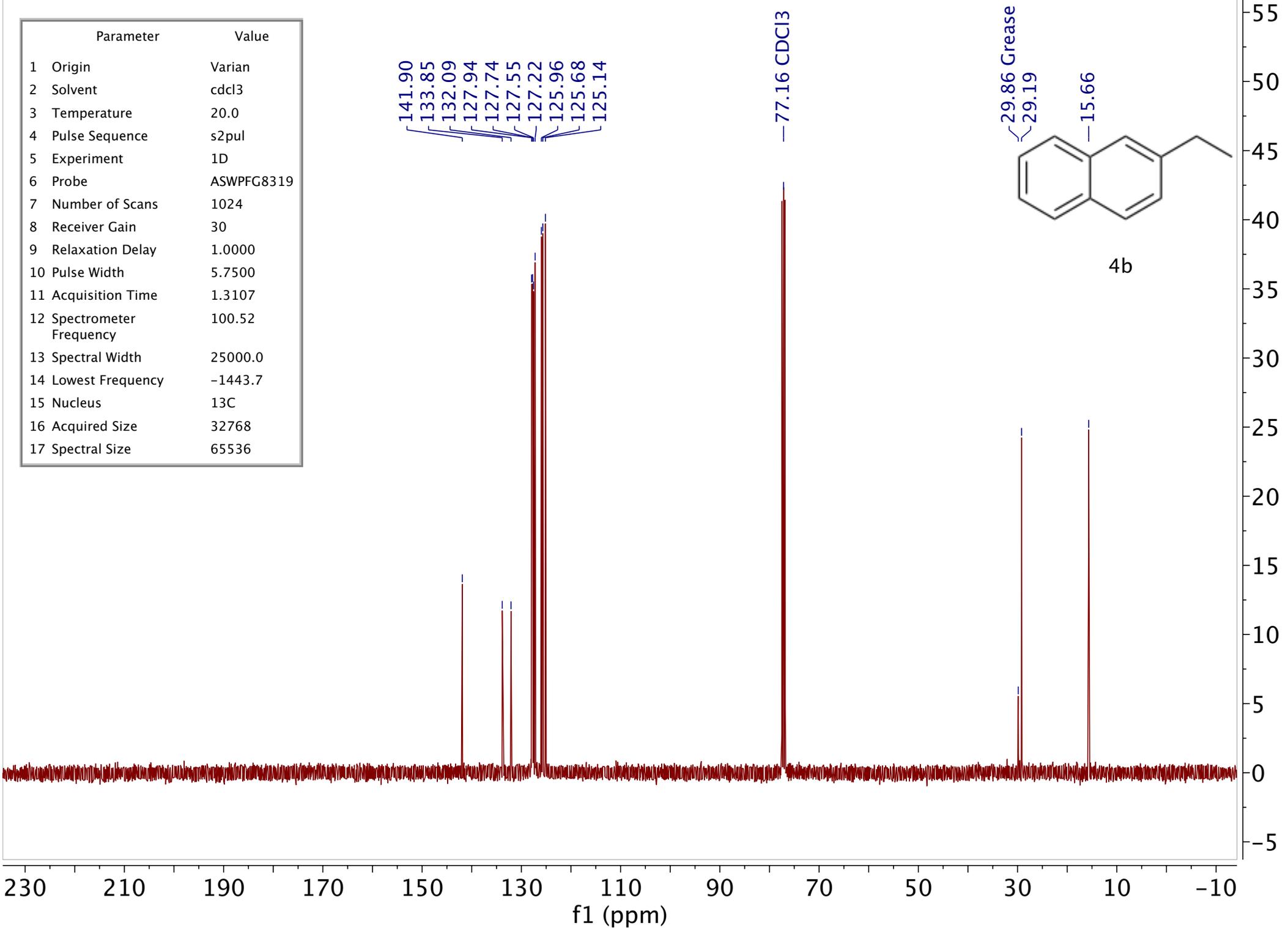
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2 Solvent	cdcl3
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5 Experiment	1D
6 Probe	ASWPG8319
7 Number of Scans	16
8 Receiver Gain	40
9 Relaxation Delay	10.0000
10 Pulse Width	8.0000
11 Acquisition Time	2.5559
12 Spectrometer Frequency	399.73
13 Spectral Width	6410.3
14 Lowest Frequency	-807.8
15 Nucleus	1H
16 Acquired Size	16384
17 Spectral Size	65536



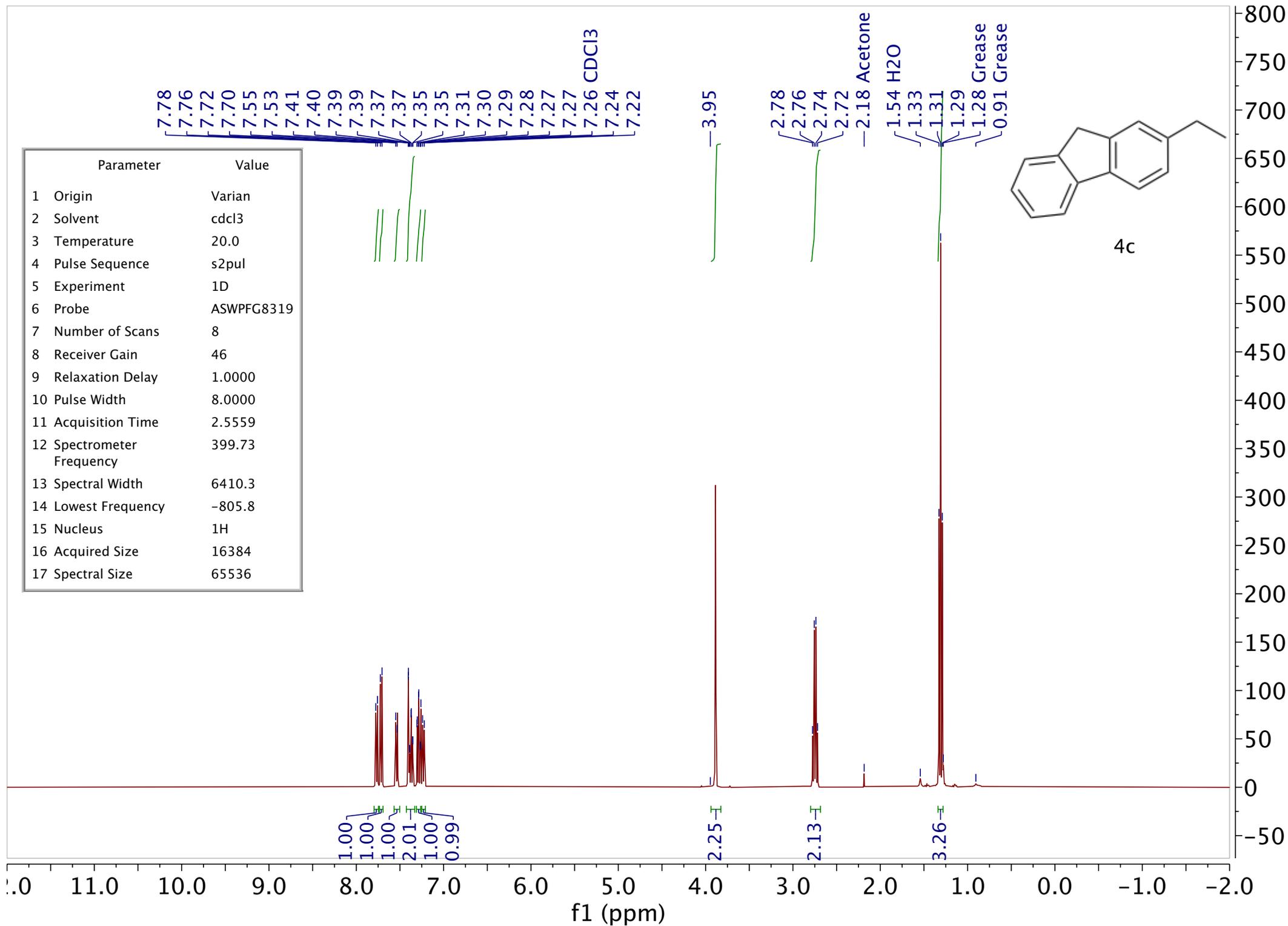
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4 Pulse Sequence	s2pul
5 Experiment	1D
6 Probe	ASWPG8319
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8 Receiver Gain	44
9 Relaxation Delay	1.0000
10 Pulse Width	8.0000
11 Acquisition Time	2.5559
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13 Spectral Width	6410.3
14 Lowest Frequency	-804.9
15 Nucleus	1H
16 Acquired Size	16384
17 Spectral Size	65536



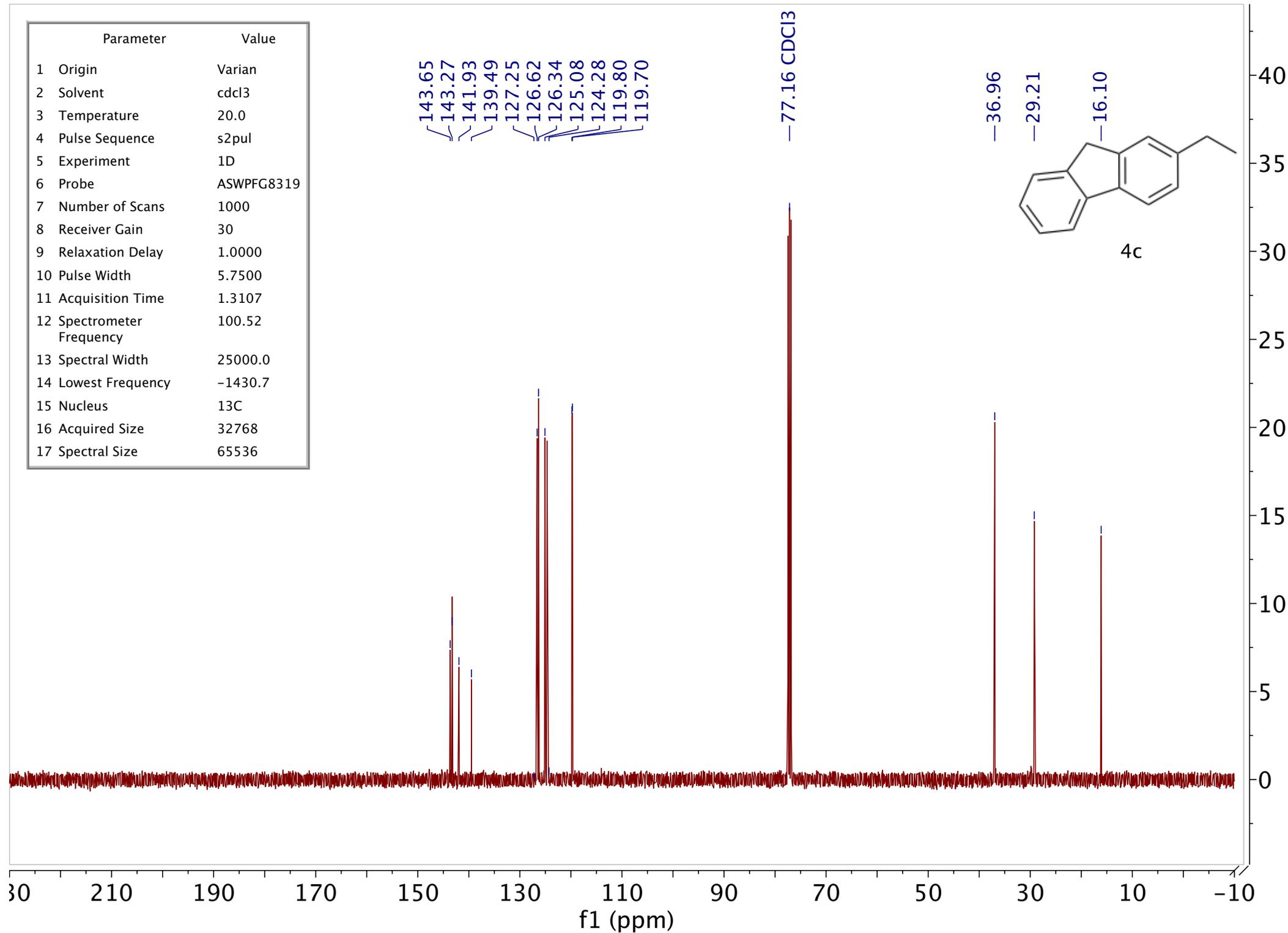
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5 Experiment	1D
6 Probe	ASWPG8319
7 Number of Scans	1024
8 Receiver Gain	30
9 Relaxation Delay	1.0000
10 Pulse Width	5.7500
11 Acquisition Time	1.3107
12 Spectrometer Frequency	100.52
13 Spectral Width	25000.0
14 Lowest Frequency	-1443.7
15 Nucleus	<sup>13</sup> C
16 Acquired Size	32768
17 Spectral Size	65536



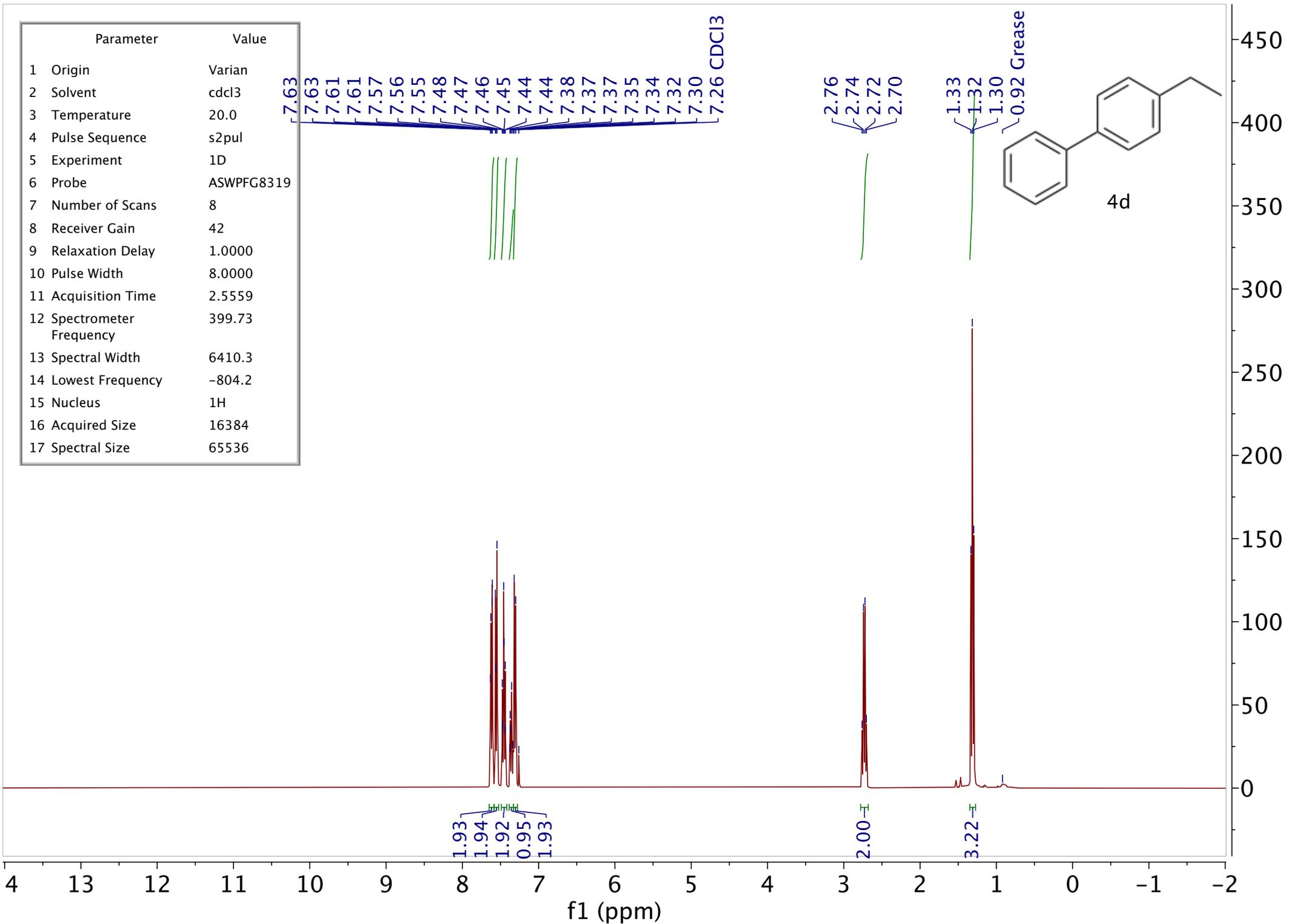
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10 Pulse Width	8.0000
11 Acquisition Time	2.5559
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14 Lowest Frequency	-805.8
15 Nucleus	1H
16 Acquired Size	16384
17 Spectral Size	65536



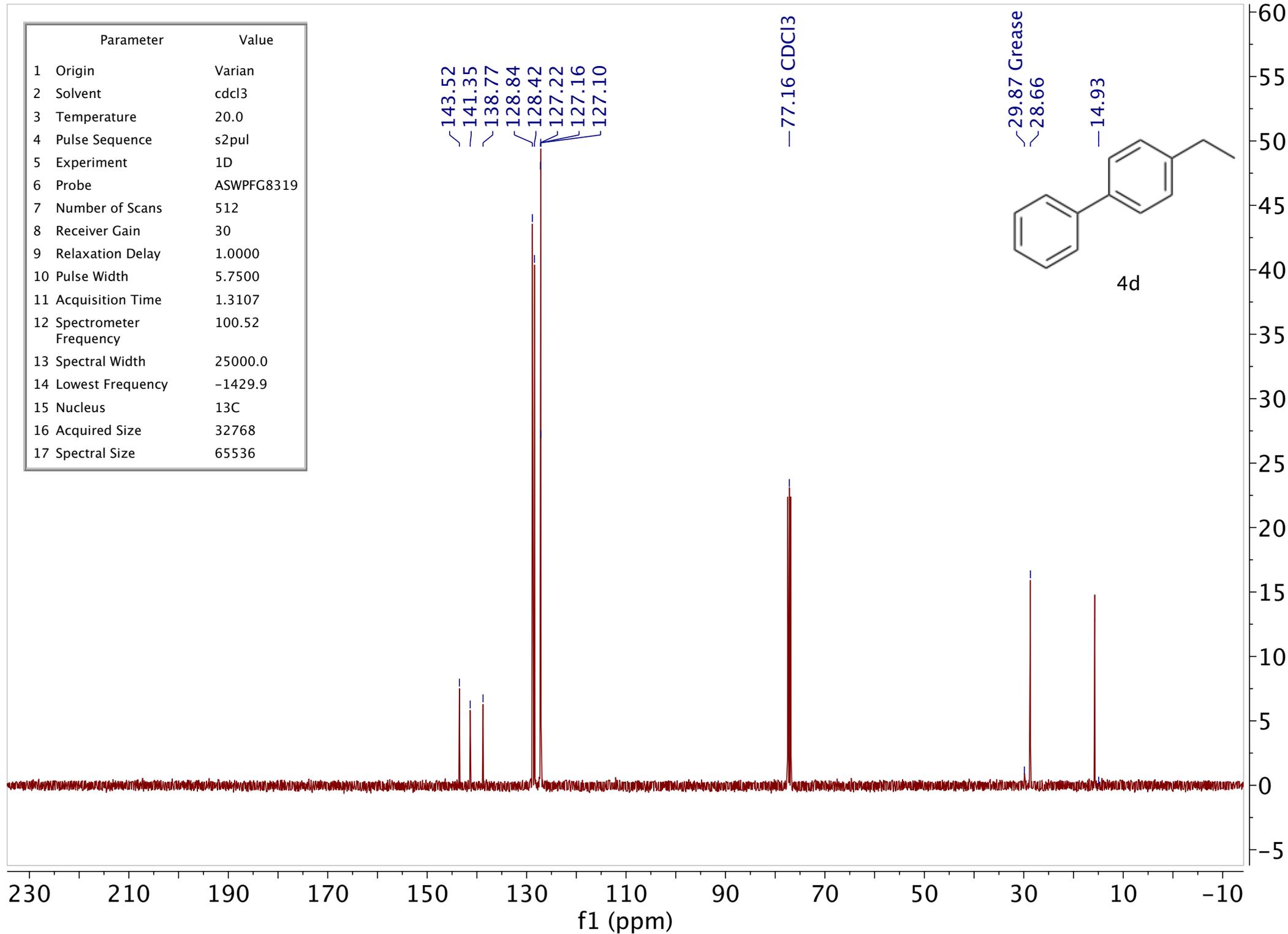
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10 Pulse Width	5.7500
11 Acquisition Time	1.3107
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15 Nucleus	13C
16 Acquired Size	32768
17 Spectral Size	65536

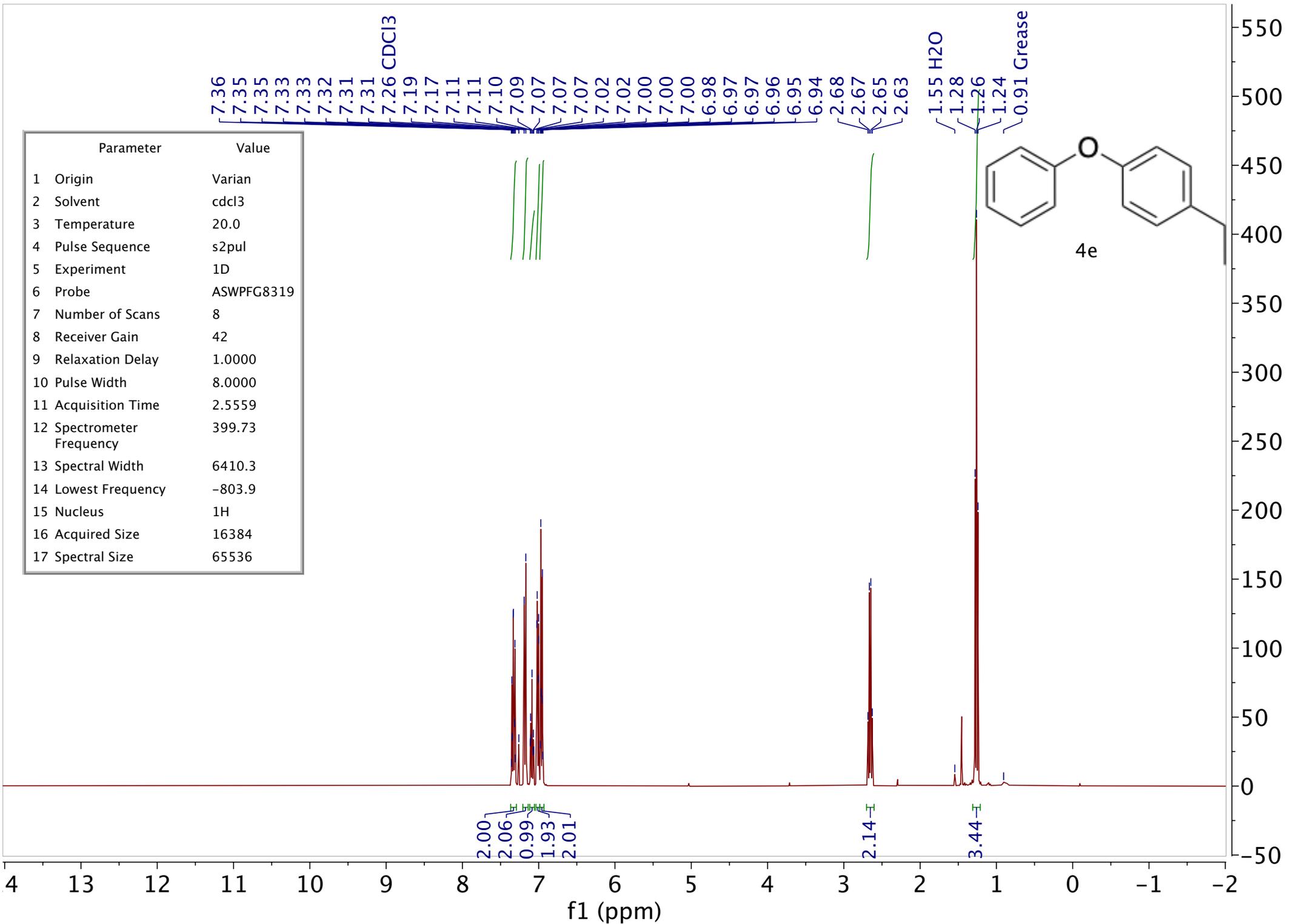


Parameter	Value
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5 Experiment	1D
6 Probe	ASWPG8319
7 Number of Scans	8
8 Receiver Gain	42
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10 Pulse Width	8.0000
11 Acquisition Time	2.5559
12 Spectrometer Frequency	399.73
13 Spectral Width	6410.3
14 Lowest Frequency	-804.2
15 Nucleus	1H
16 Acquired Size	16384
17 Spectral Size	65536



Parameter	Value
1 Origin	Varian
2 Solvent	cdcl3
3 Temperature	20.0
4 Pulse Sequence	s2pul
5 Experiment	1D
6 Probe	ASWPG8319
7 Number of Scans	512
8 Receiver Gain	30
9 Relaxation Delay	1.0000
10 Pulse Width	5.7500
11 Acquisition Time	1.3107
12 Spectrometer Frequency	100.52
13 Spectral Width	25000.0
14 Lowest Frequency	-1429.9
15 Nucleus	<sup>13</sup> C
16 Acquired Size	32768
17 Spectral Size	65536





Parameter	Value
1 Origin	Varian
2 Solvent	cdcl3
3 Temperature	20.0
4 Pulse Sequence	s2pul
5 Experiment	1D
6 Probe	ASWPFG8319
7 Number of Scans	8
8 Receiver Gain	42
9 Relaxation Delay	1.0000
10 Pulse Width	8.0000
11 Acquisition Time	2.5559
12 Spectrometer Frequency	399.73
13 Spectral Width	6410.3
14 Lowest Frequency	-803.9
15 Nucleus	1H
16 Acquired Size	16384
17 Spectral Size	65536

7.36  
7.35  
7.35  
7.33  
7.33  
7.32  
7.31  
7.31  
7.26 CDCl3  
7.19  
7.17  
7.11  
7.11  
7.10  
7.09  
7.07  
7.07  
7.07  
7.02  
7.02  
7.00  
7.00  
7.00  
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6.97  
6.96  
6.95  
6.94  
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2.65  
2.63

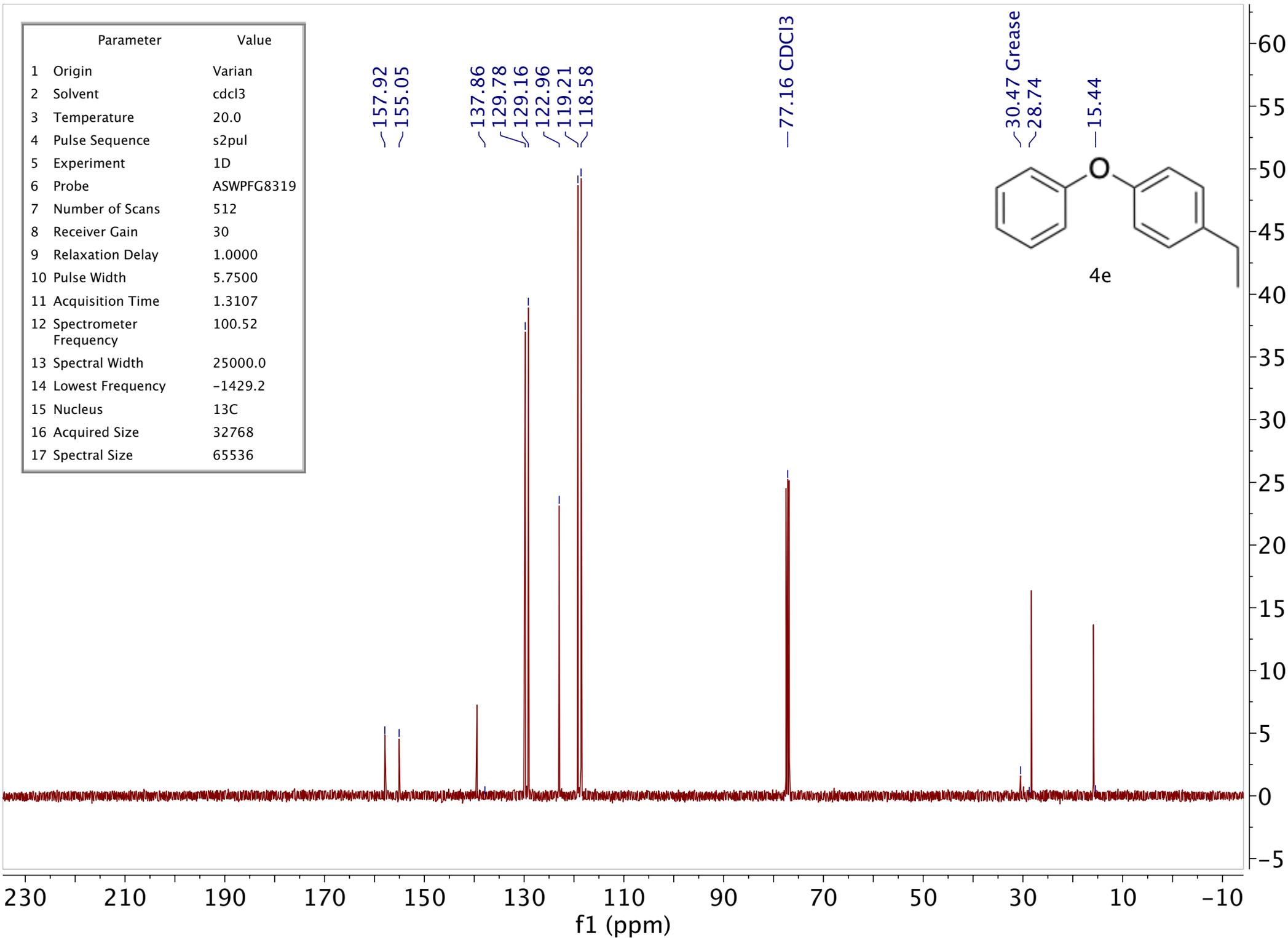
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1.28  
1.26  
1.24  
0.91 Grease

2.00  
2.06  
0.99  
1.93  
2.01

2.14  
3.44

4 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2  
f1 (ppm)  
550  
500  
450  
400  
350  
300  
250  
200  
150  
100  
50  
0  
-50

Parameter	Value
1 Origin	Varian
2 Solvent	cdcl3
3 Temperature	20.0
4 Pulse Sequence	s2pul
5 Experiment	1D
6 Probe	ASWPF8319
7 Number of Scans	512
8 Receiver Gain	30
9 Relaxation Delay	1.0000
10 Pulse Width	5.7500
11 Acquisition Time	1.3107
12 Spectrometer Frequency	100.52
13 Spectral Width	25000.0
14 Lowest Frequency	-1429.2
15 Nucleus	13C
16 Acquired Size	32768
17 Spectral Size	65536

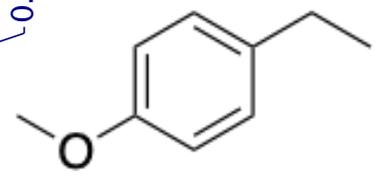


Parameter	Value
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4 Pulse Sequence	s2pul
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6 Number of Scans	8
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9 Pulse Width	6.2000
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11 Probe	ATB_300
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17 Spectral Size	65536

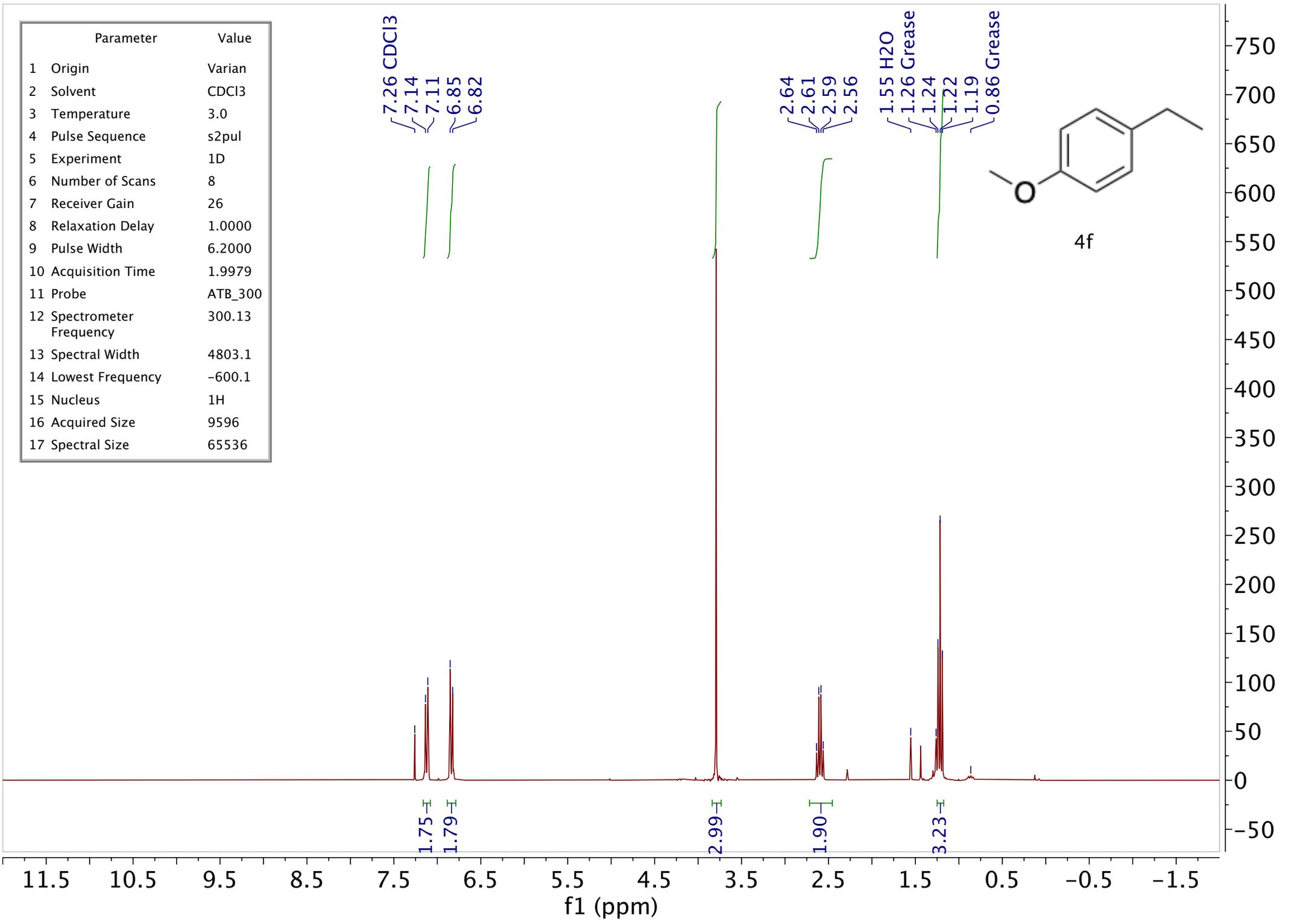
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 6.82

2.64  
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 2.59  
 2.56

1.55 H2O  
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 1.24  
 1.22  
 1.19  
 0.86 Grease



4f



1.75  
 1.79

2.99

1.90

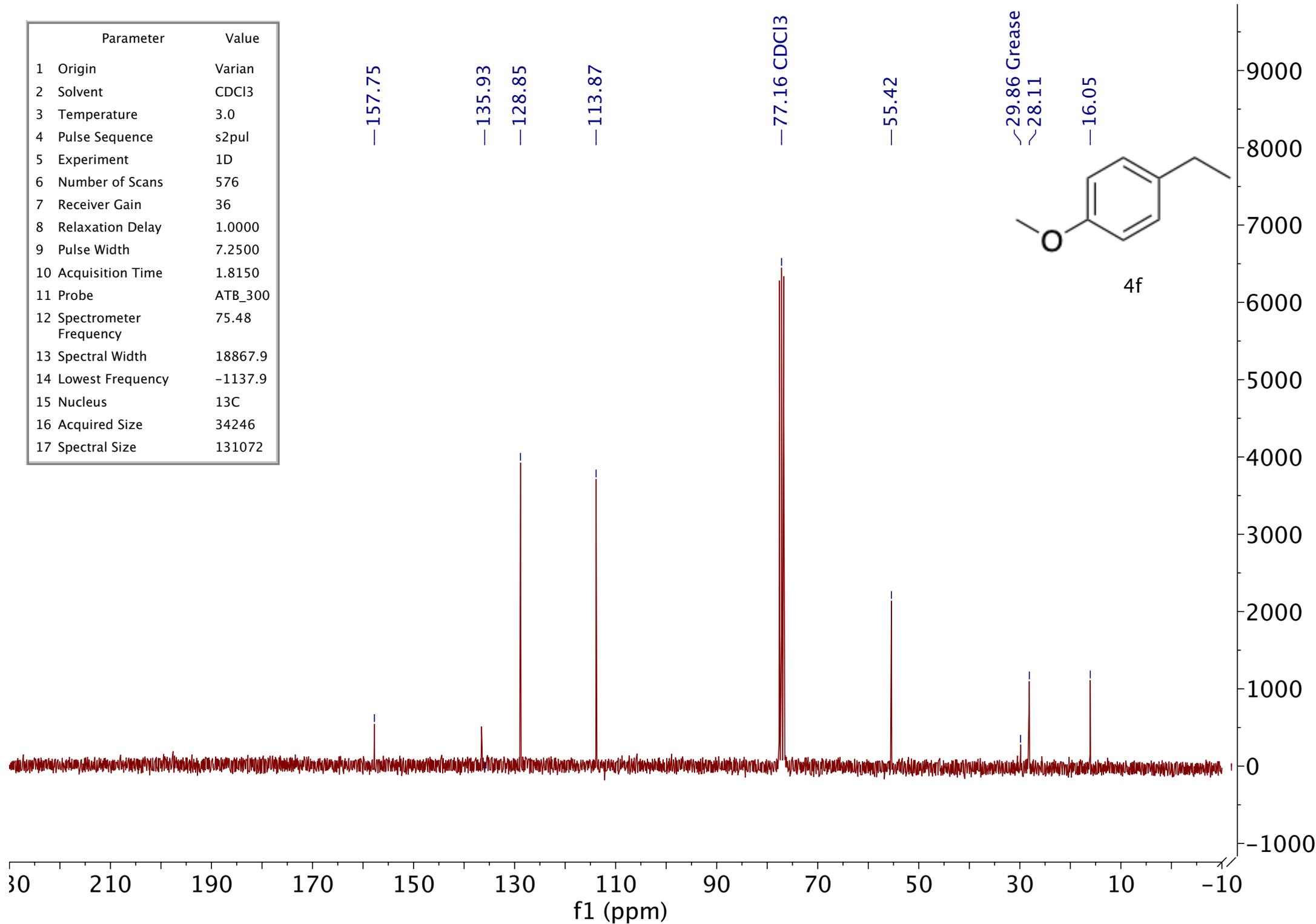
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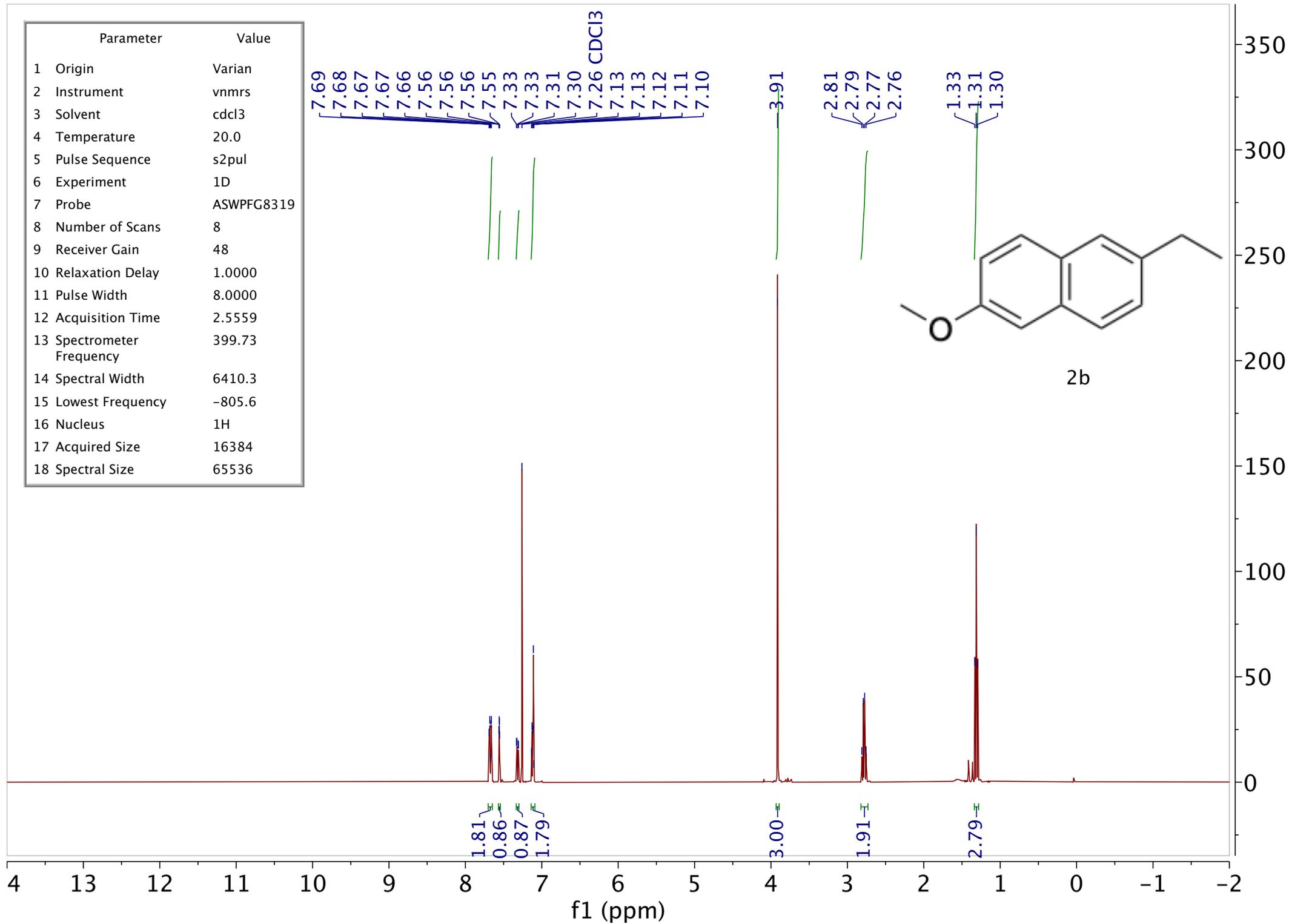
f1 (ppm)

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 500  
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 250  
 200  
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 100  
 50  
 0  
 -50

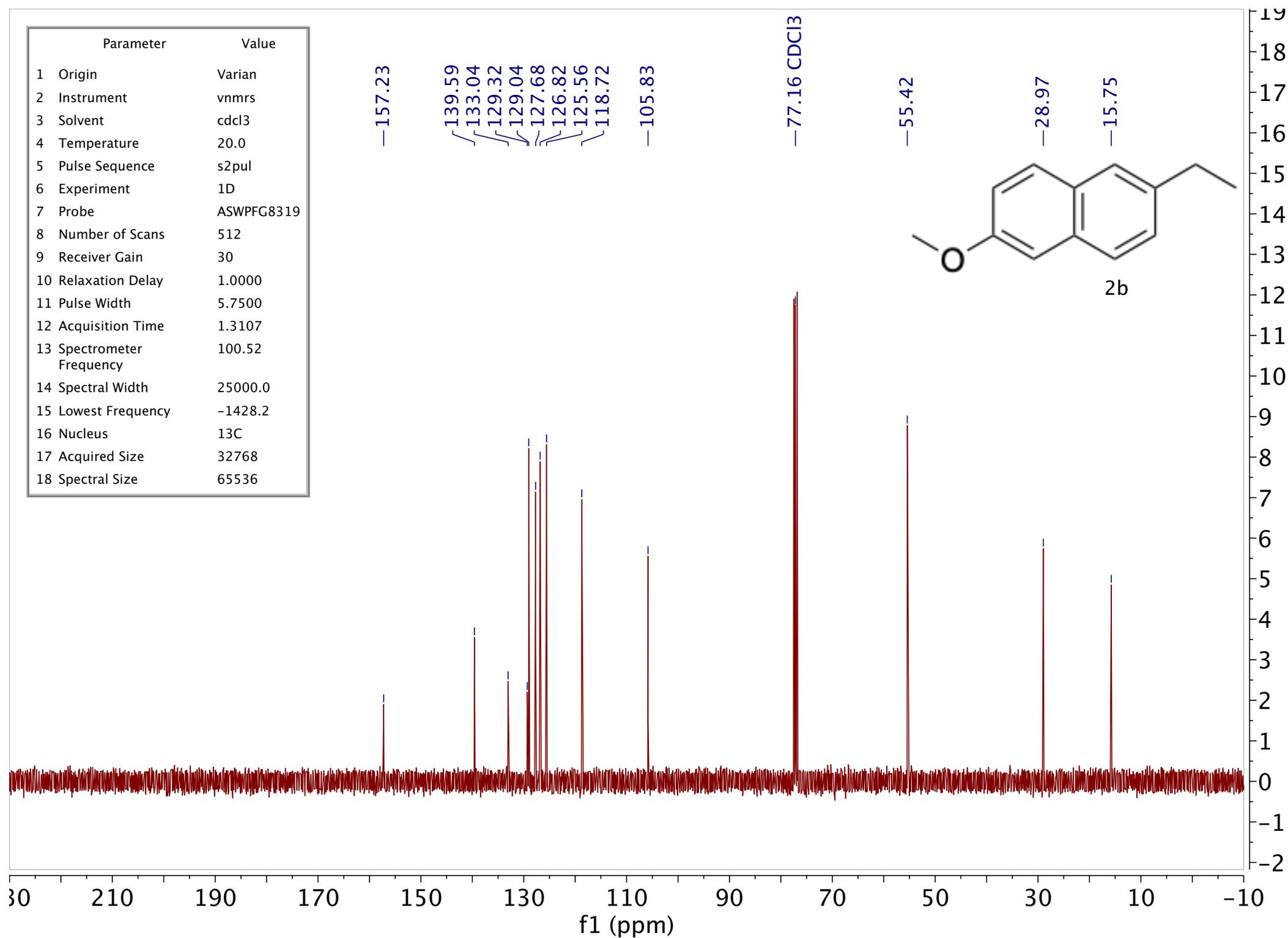
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8 Relaxation Delay	1.0000
9 Pulse Width	7.2500
10 Acquisition Time	1.8150
11 Probe	ATB_300
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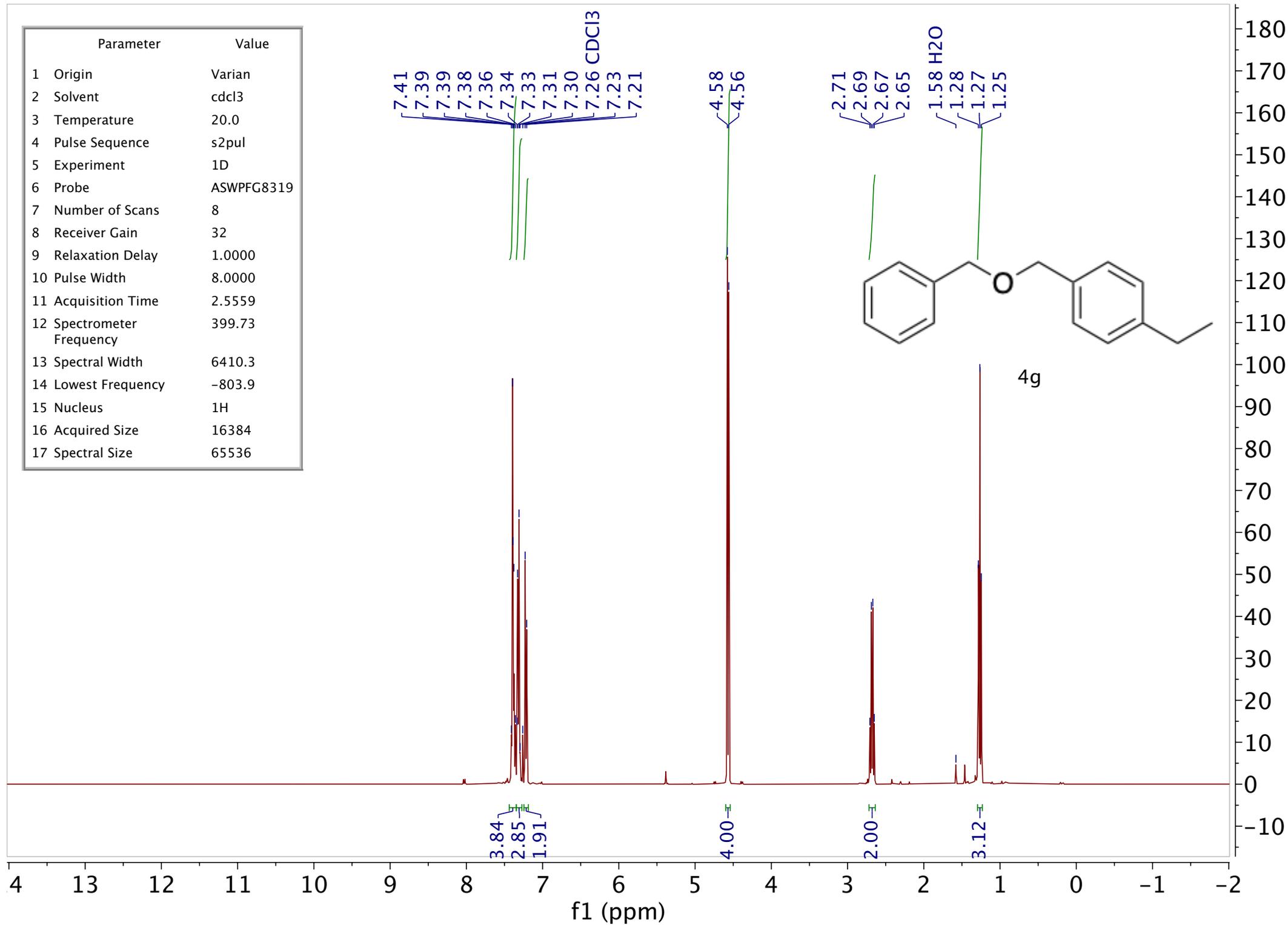
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5 Pulse Sequence	s2pul
6 Experiment	1D
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8 Number of Scans	8
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11 Pulse Width	8.0000
12 Acquisition Time	2.5559
13 Spectrometer Frequency	399.73
14 Spectral Width	6410.3
15 Lowest Frequency	-805.6
16 Nucleus	1H
17 Acquired Size	16384
18 Spectral Size	65536



Parameter	Value
1 Origin	Varian
2 Instrument	vnmrs
3 Solvent	cdcl3
4 Temperature	20.0
5 Pulse Sequence	s2pul
6 Experiment	1D
7 Probe	ASWPG8319
8 Number of Scans	512
9 Receiver Gain	30
10 Relaxation Delay	1.0000
11 Pulse Width	5.7500
12 Acquisition Time	1.3107
13 Spectrometer Frequency	100.52
14 Spectral Width	25000.0
15 Lowest Frequency	-1428.2
16 Nucleus	<sup>13</sup> C
17 Acquired Size	32768
18 Spectral Size	65536



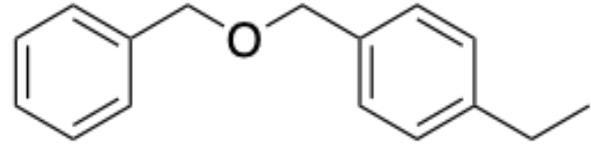
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5 Experiment	1D
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8 Receiver Gain	32
9 Relaxation Delay	1.0000
10 Pulse Width	8.0000
11 Acquisition Time	2.5559
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13 Spectral Width	6410.3
14 Lowest Frequency	-803.9
15 Nucleus	1H
16 Acquired Size	16384
17 Spectral Size	65536



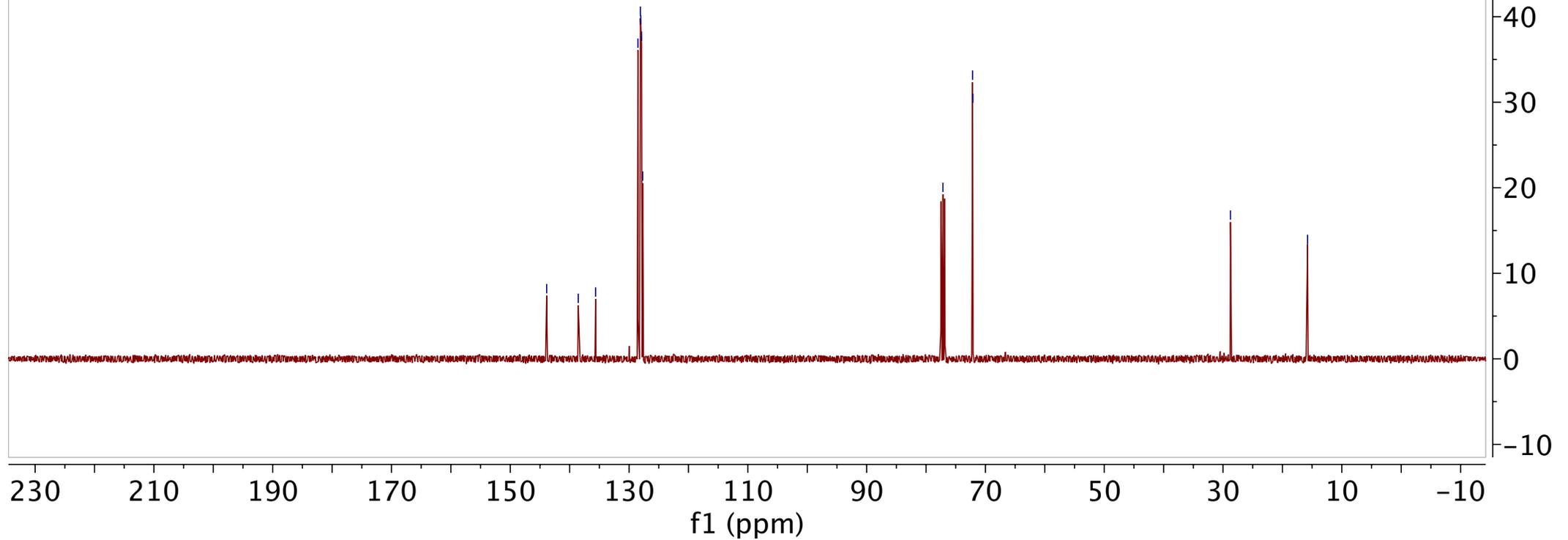
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5 Experiment	1D
6 Probe	ASWPF8319
7 Number of Scans	512
8 Receiver Gain	30
9 Relaxation Delay	1.0000
10 Pulse Width	5.7500
11 Acquisition Time	1.3107
12 Spectrometer Frequency	100.52
13 Spectral Width	25000.0
14 Lowest Frequency	-1430.7
15 Nucleus	<sup>13</sup> C
16 Acquired Size	32768
17 Spectral Size	65536

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135.64  
128.51  
128.09  
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127.70

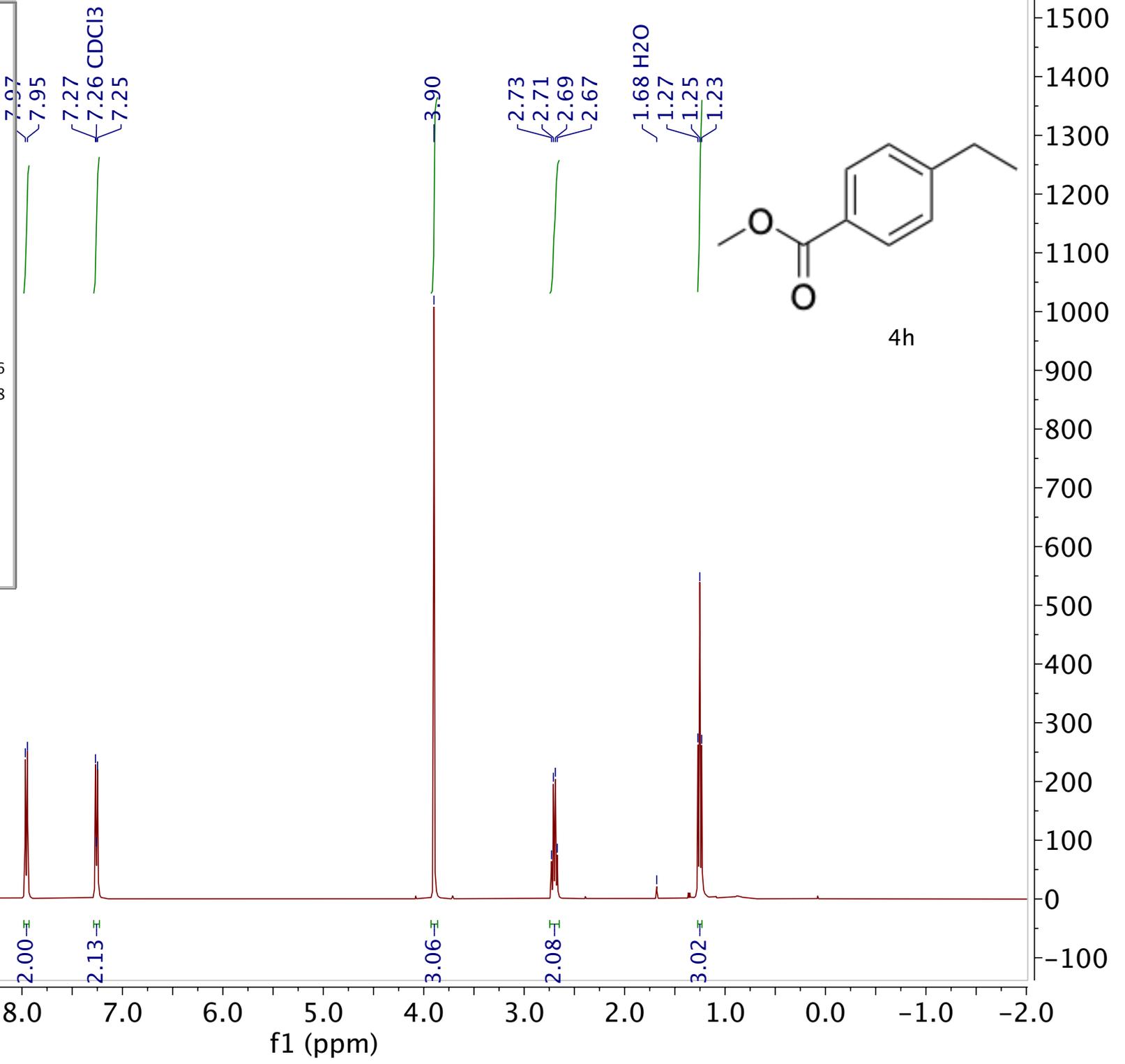
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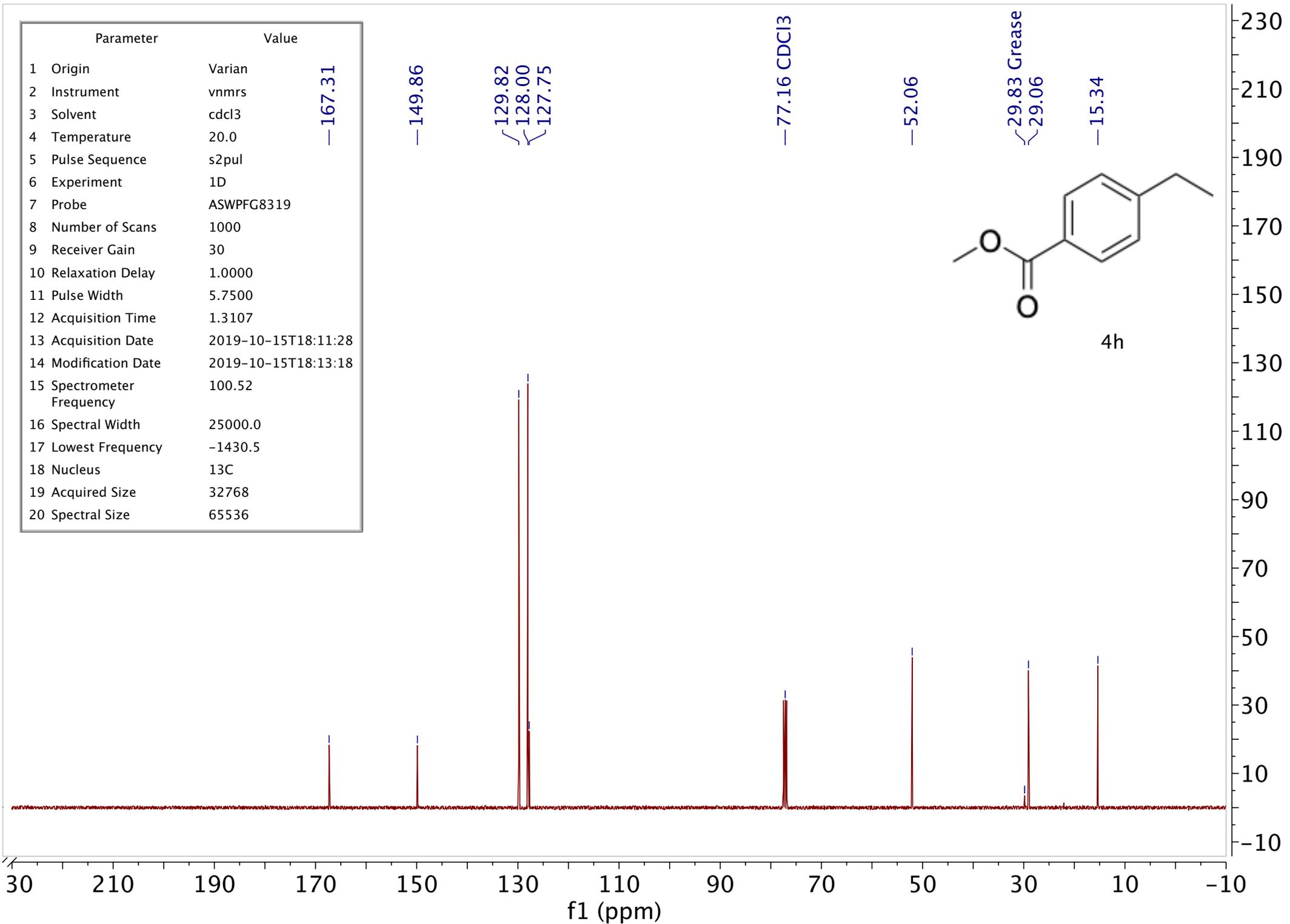
4g



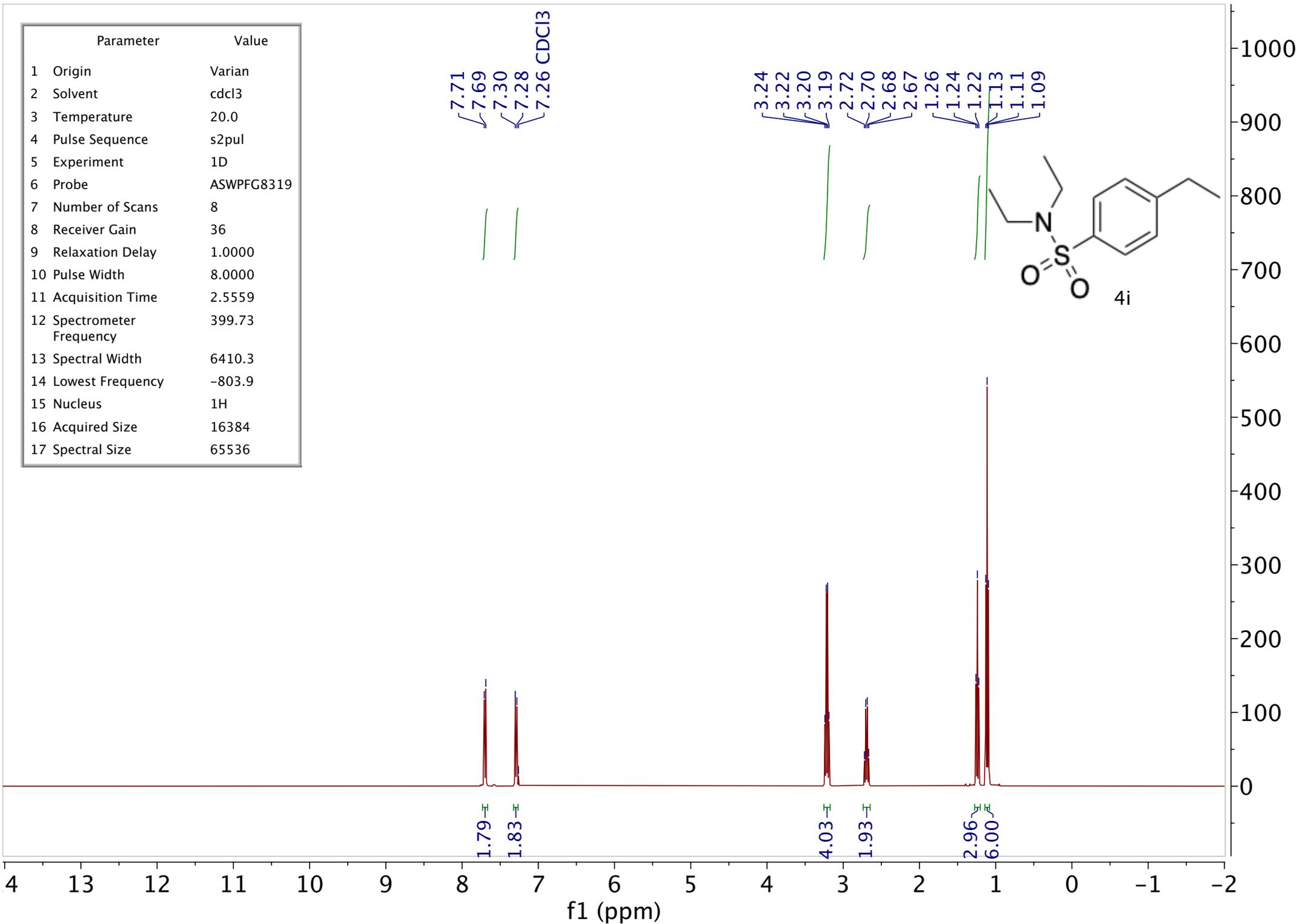
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18 Nucleus	1H
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20 Spectral Size	65536



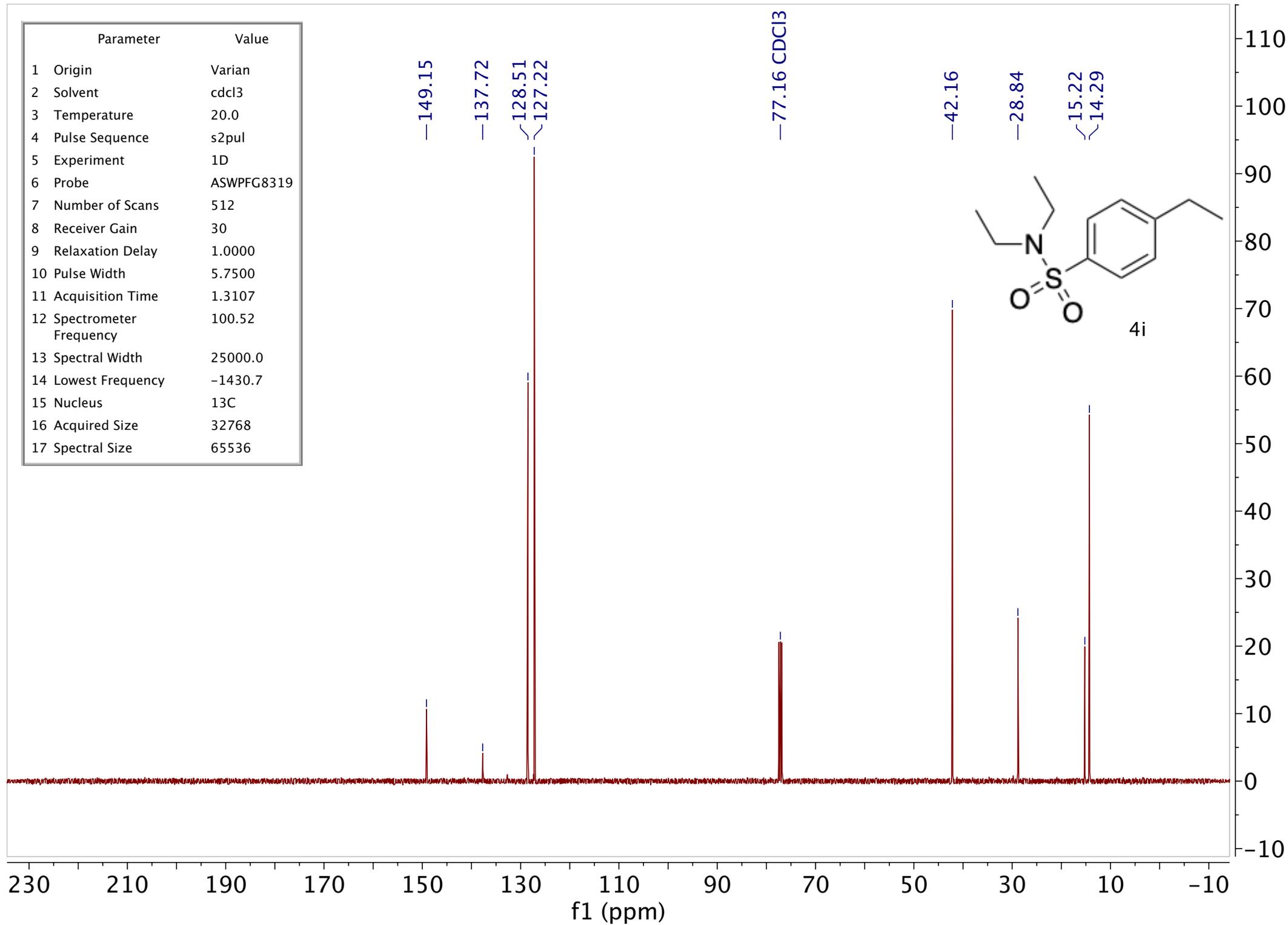
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18 Nucleus	13C
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20 Spectral Size	65536



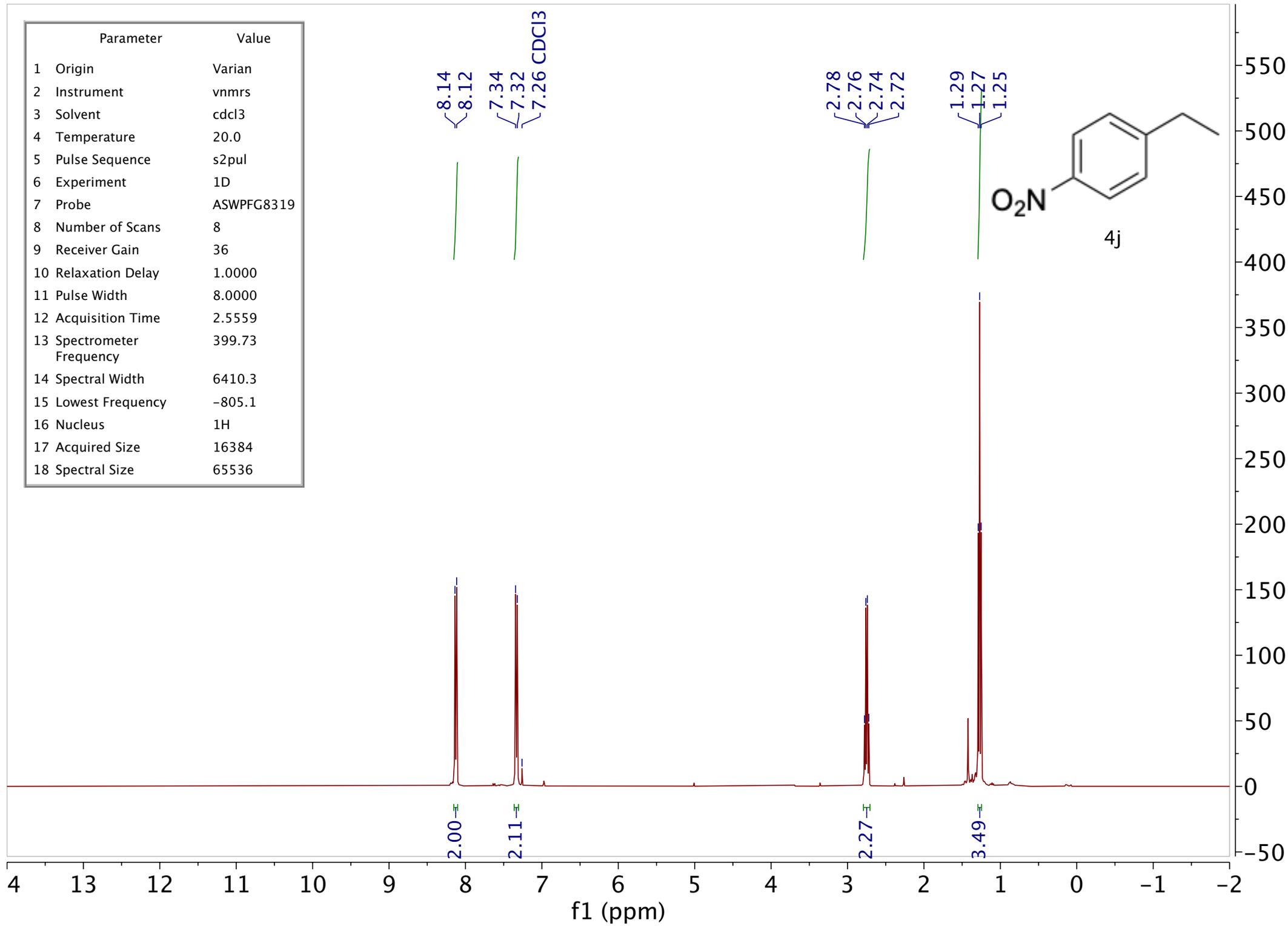
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10 Pulse Width	8.0000
11 Acquisition Time	2.5559
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14 Lowest Frequency	-803.9
15 Nucleus	1H
16 Acquired Size	16384
17 Spectral Size	65536



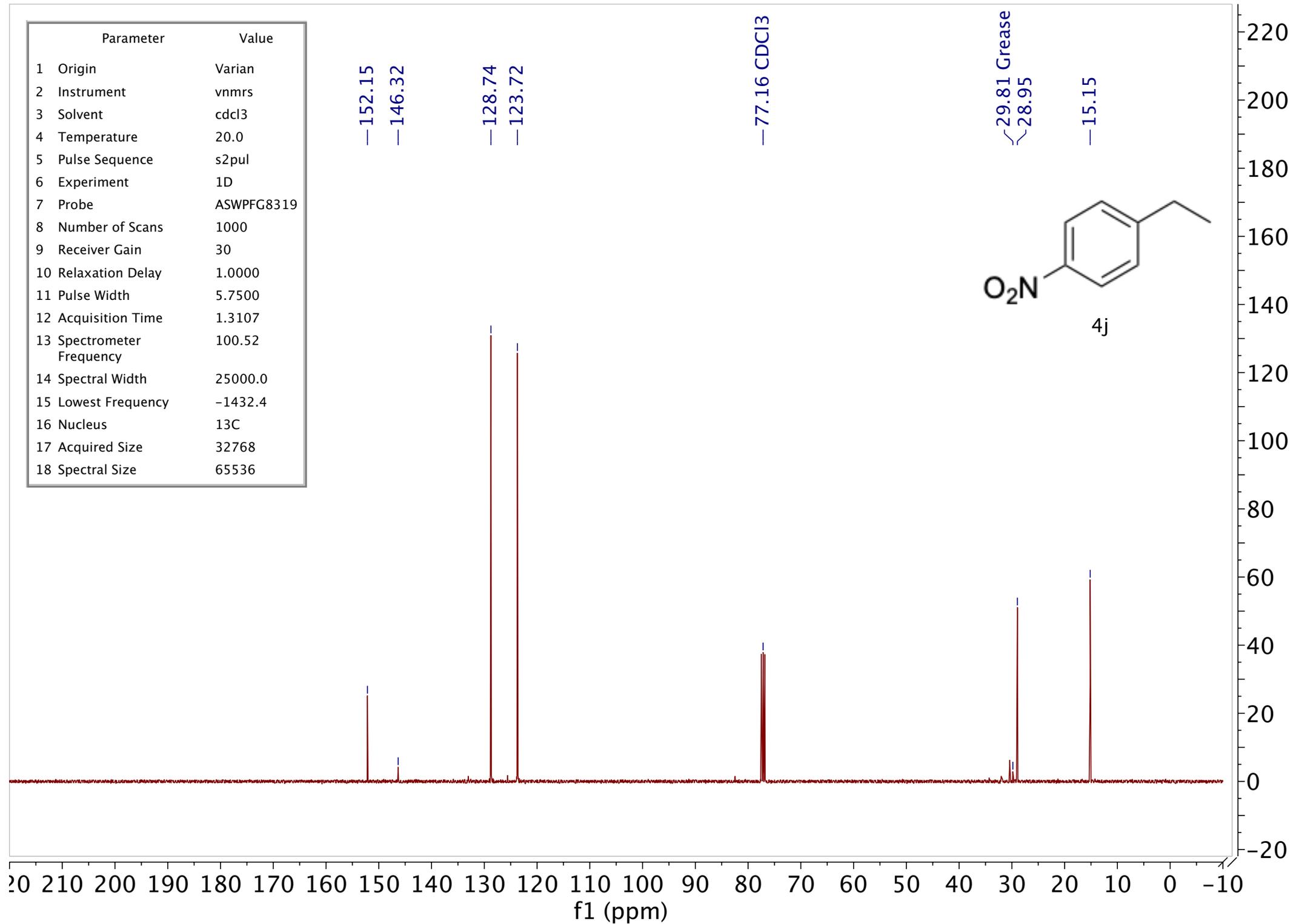
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10 Pulse Width	5.7500
11 Acquisition Time	1.3107
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16 Acquired Size	32768
17 Spectral Size	65536

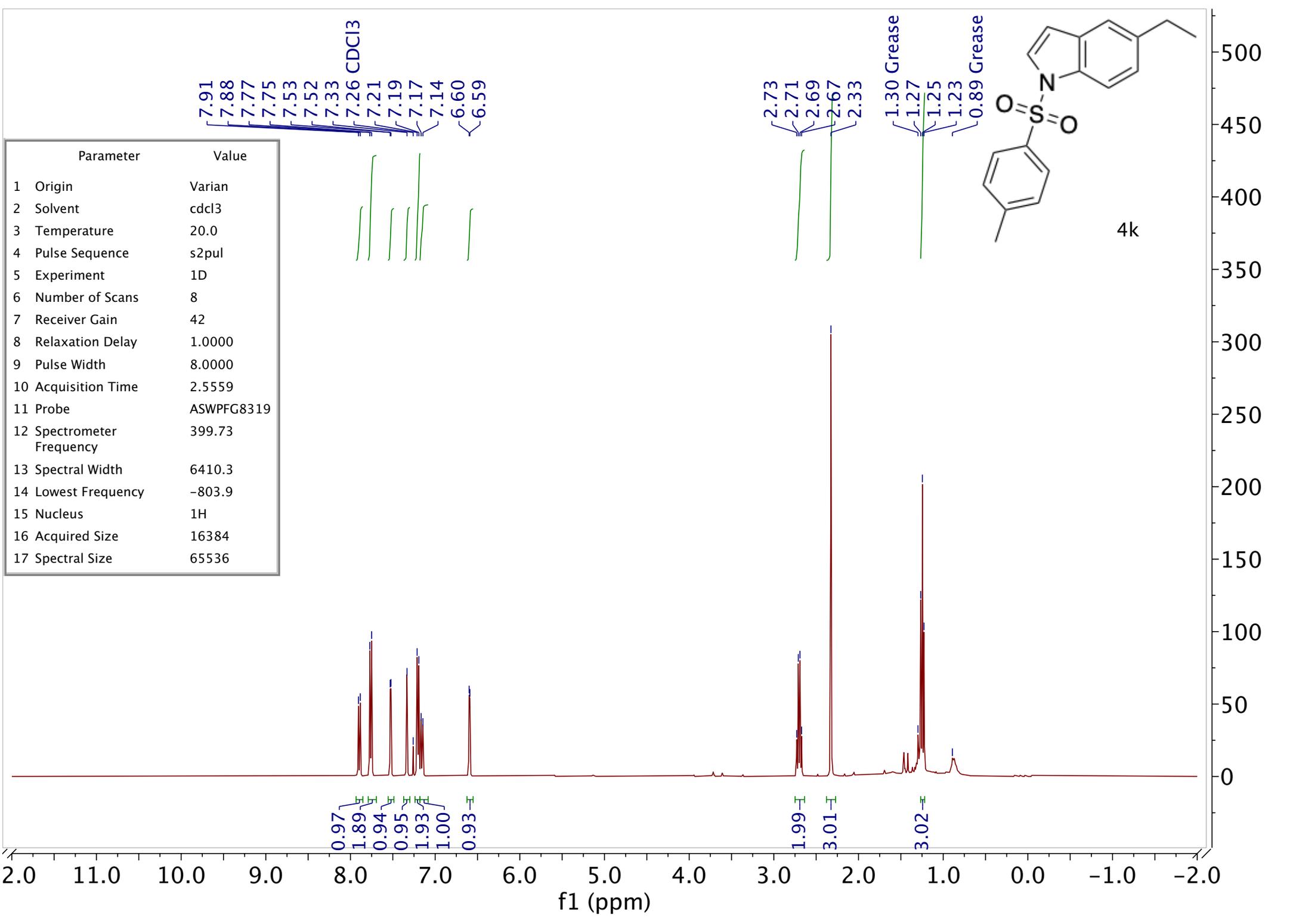


Parameter	Value
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2 Instrument	vnmrs
3 Solvent	cdcl3
4 Temperature	20.0
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6 Experiment	1D
7 Probe	ASWPG8319
8 Number of Scans	8
9 Receiver Gain	36
10 Relaxation Delay	1.0000
11 Pulse Width	8.0000
12 Acquisition Time	2.5559
13 Spectrometer Frequency	399.73
14 Spectral Width	6410.3
15 Lowest Frequency	-805.1
16 Nucleus	1H
17 Acquired Size	16384
18 Spectral Size	65536



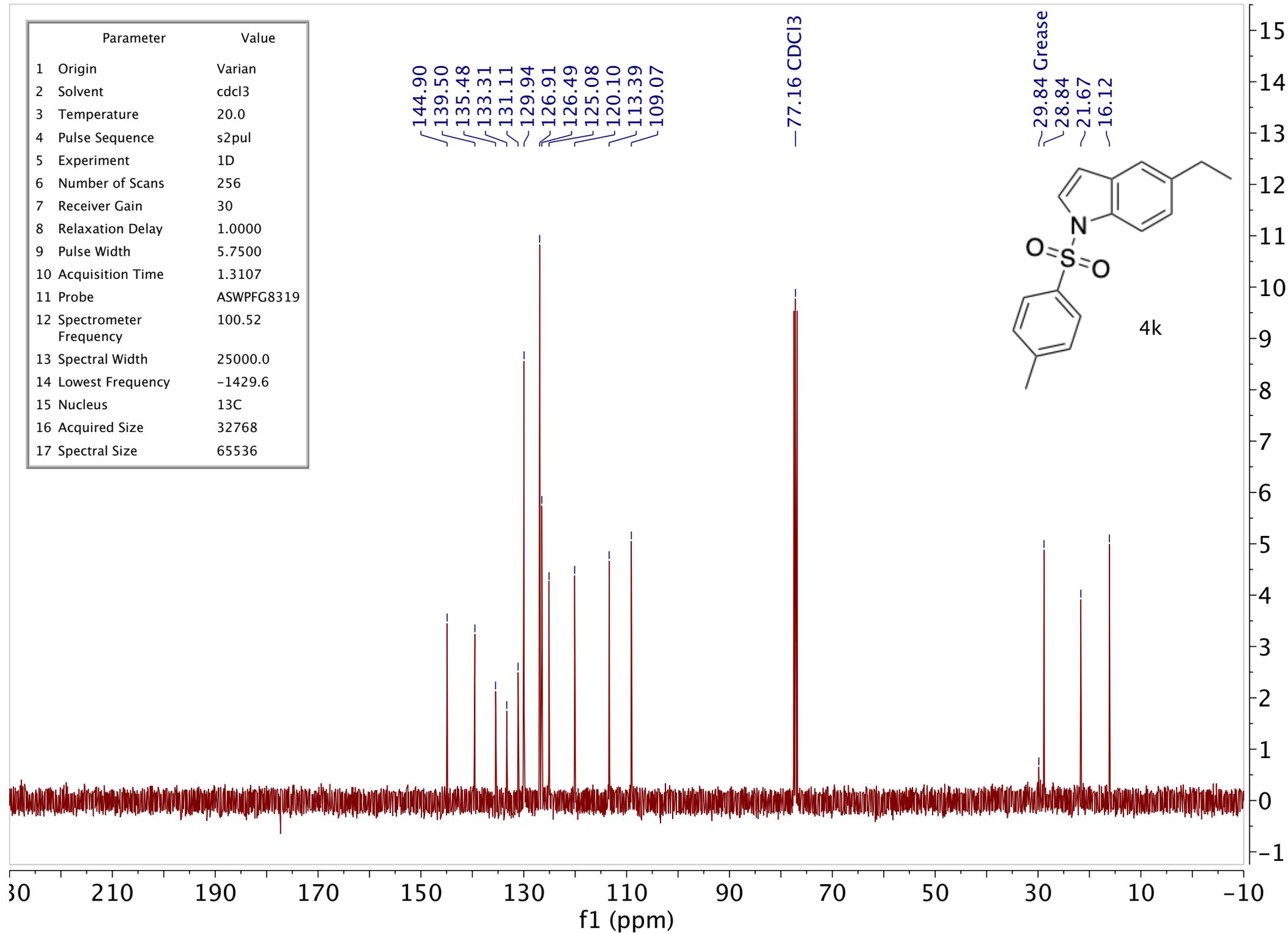
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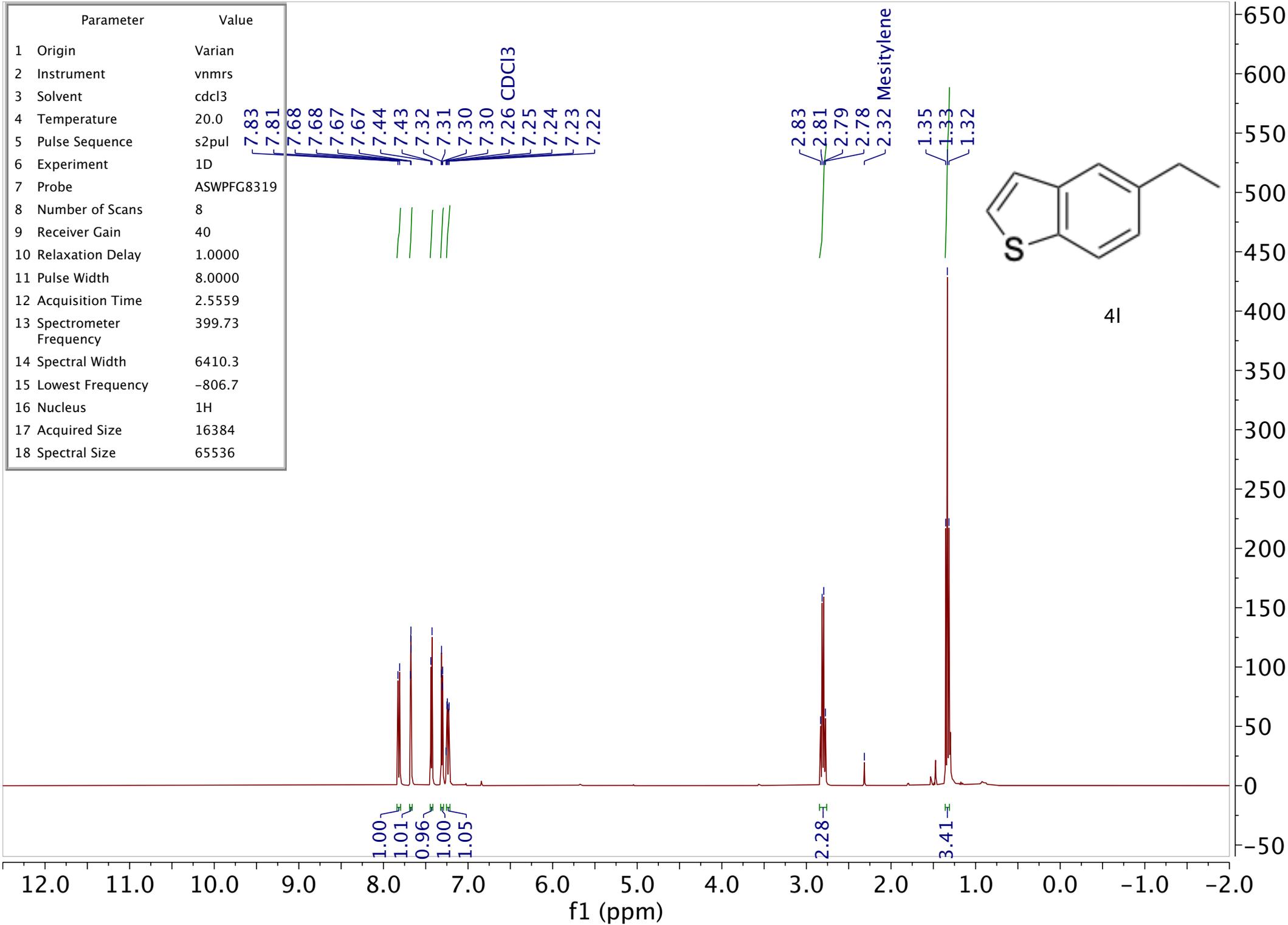


Parameter	Value
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2 Solvent	cdcl3
3 Temperature	20.0
4 Pulse Sequence	s2pul
5 Experiment	1D
6 Number of Scans	8
7 Receiver Gain	42
8 Relaxation Delay	1.0000
9 Pulse Width	8.0000
10 Acquisition Time	2.5559
11 Probe	ASWPFG8319
12 Spectrometer Frequency	399.73
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14 Lowest Frequency	-803.9
15 Nucleus	1H
16 Acquired Size	16384
17 Spectral Size	65536

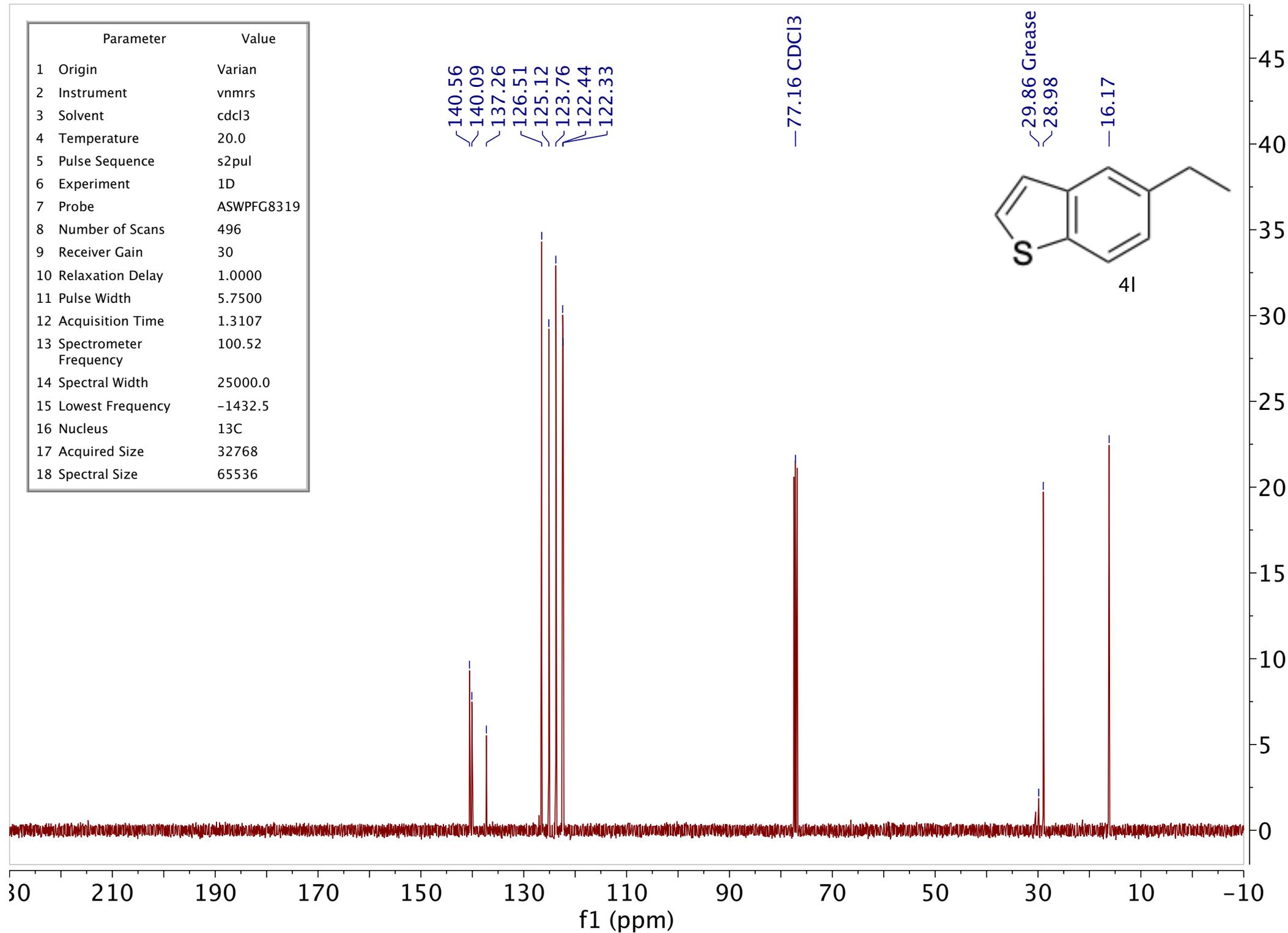
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10 Acquisition Time	1.3107
11 Probe	ASWPG8319
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15 Nucleus	13C
16 Acquired Size	32768
17 Spectral Size	65536



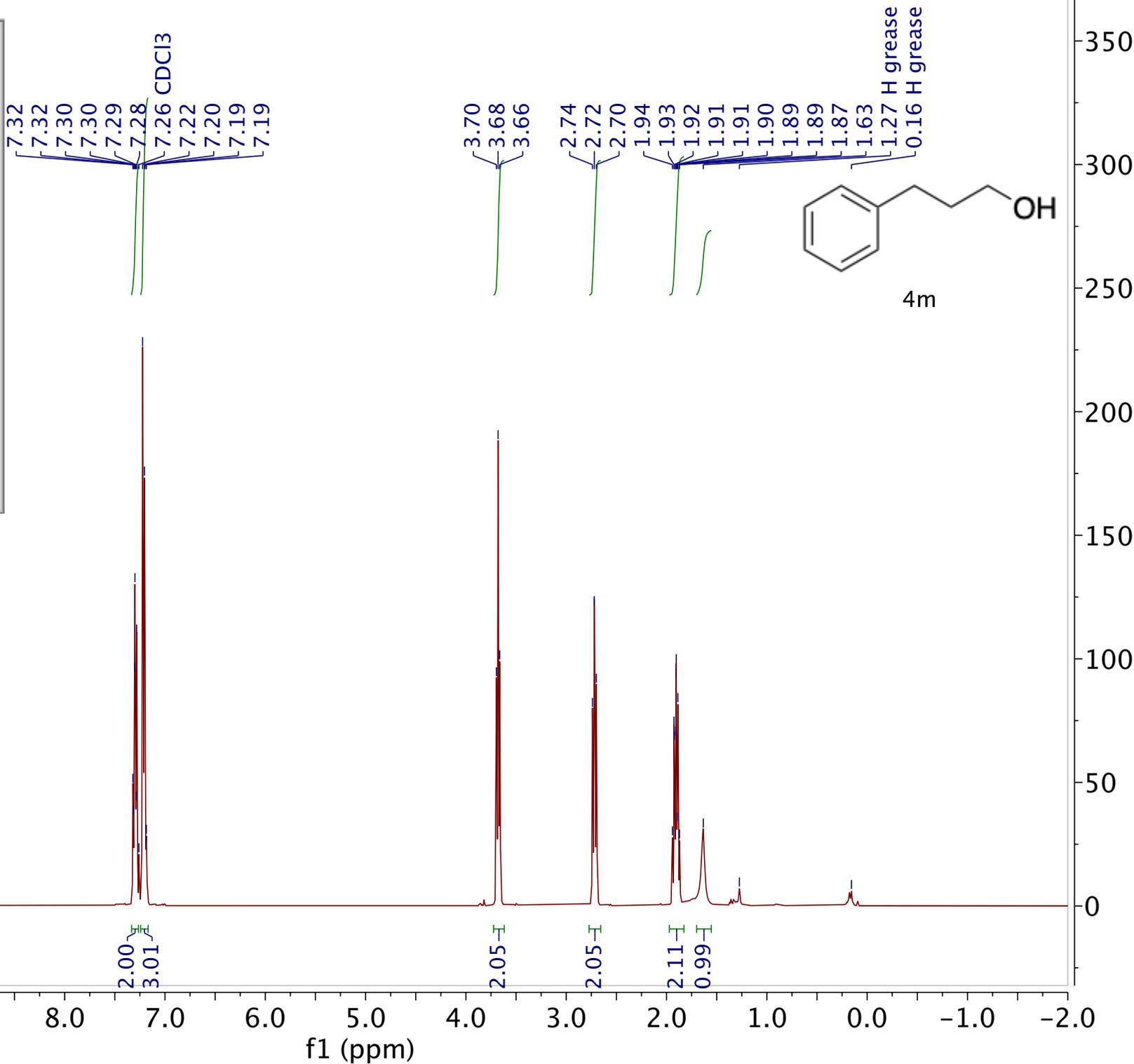
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7 Probe	ASWPFG8319
8 Number of Scans	8
9 Receiver Gain	40
10 Relaxation Delay	1.0000
11 Pulse Width	8.0000
12 Acquisition Time	2.5559
13 Spectrometer Frequency	399.73
14 Spectral Width	6410.3
15 Lowest Frequency	-806.7
16 Nucleus	1H
17 Acquired Size	16384
18 Spectral Size	65536



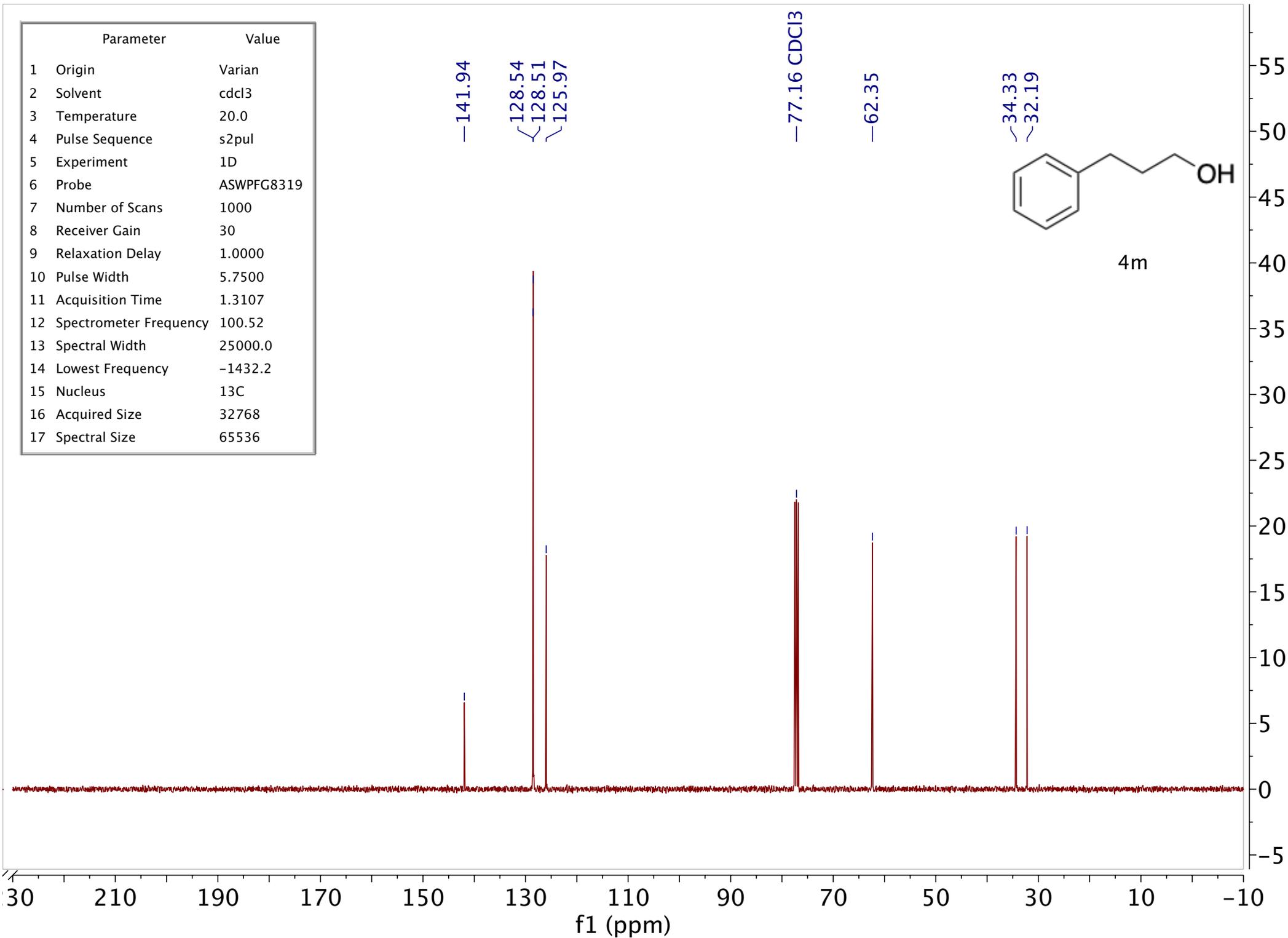
Parameter	Value
1 Origin	Varian
2 Instrument	vnmrs
3 Solvent	cdcl3
4 Temperature	20.0
5 Pulse Sequence	s2pul
6 Experiment	1D
7 Probe	ASWPF8319
8 Number of Scans	496
9 Receiver Gain	30
10 Relaxation Delay	1.0000
11 Pulse Width	5.7500
12 Acquisition Time	1.3107
13 Spectrometer Frequency	100.52
14 Spectral Width	25000.0
15 Lowest Frequency	-1432.5
16 Nucleus	<sup>13</sup> C
17 Acquired Size	32768
18 Spectral Size	65536

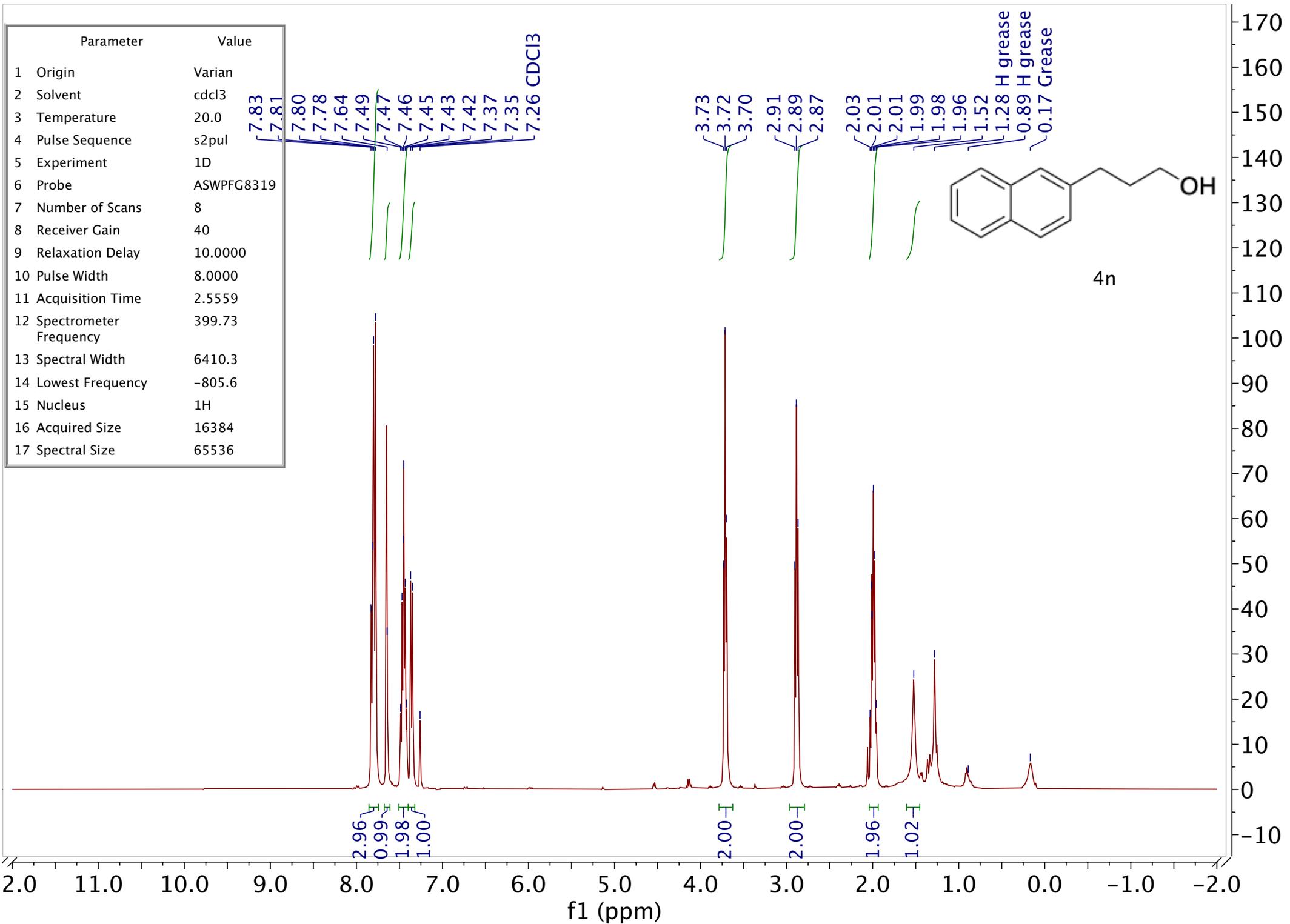


Parameter	Value
1 Origin	Varian
2 Solvent	cdcl3
3 Temperature	20.0
4 Pulse Sequence	s2pul
5 Experiment	1D
6 Probe	ASWPFG8319
7 Number of Scans	8
8 Receiver Gain	38
9 Relaxation Delay	10.0000
10 Pulse Width	8.0000
11 Acquisition Time	2.5559
12 Spectrometer Frequency	399.73
13 Spectral Width	6410.3
14 Lowest Frequency	-806.0
15 Nucleus	1H
16 Acquired Size	16384
17 Spectral Size	65536

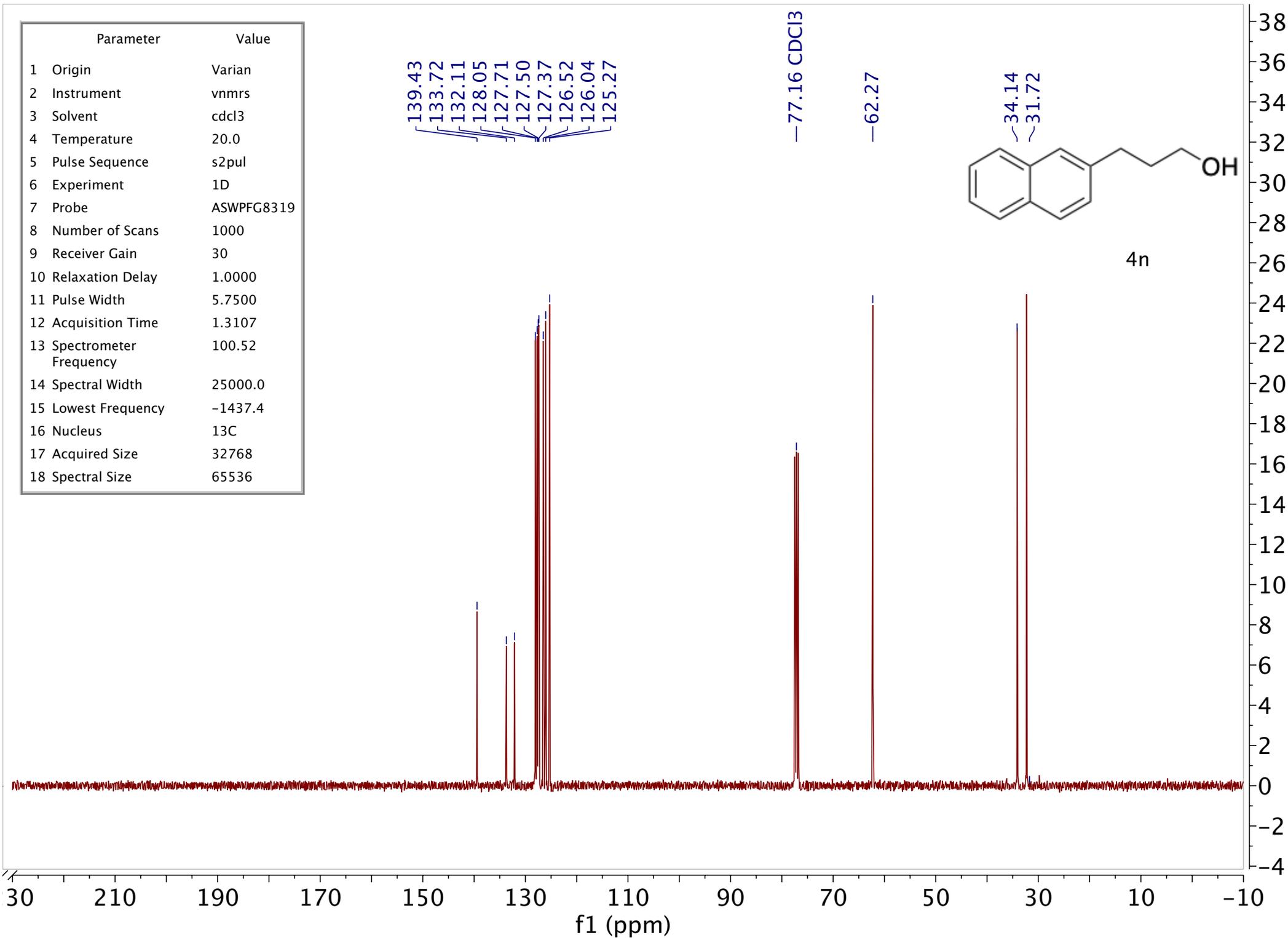


Parameter	Value
1 Origin	Varian
2 Solvent	cdcl3
3 Temperature	20.0
4 Pulse Sequence	s2pul
5 Experiment	1D
6 Probe	ASWPFG8319
7 Number of Scans	1000
8 Receiver Gain	30
9 Relaxation Delay	1.0000
10 Pulse Width	5.7500
11 Acquisition Time	1.3107
12 Spectrometer Frequency	100.52
13 Spectral Width	25000.0
14 Lowest Frequency	-1432.2
15 Nucleus	13C
16 Acquired Size	32768
17 Spectral Size	65536

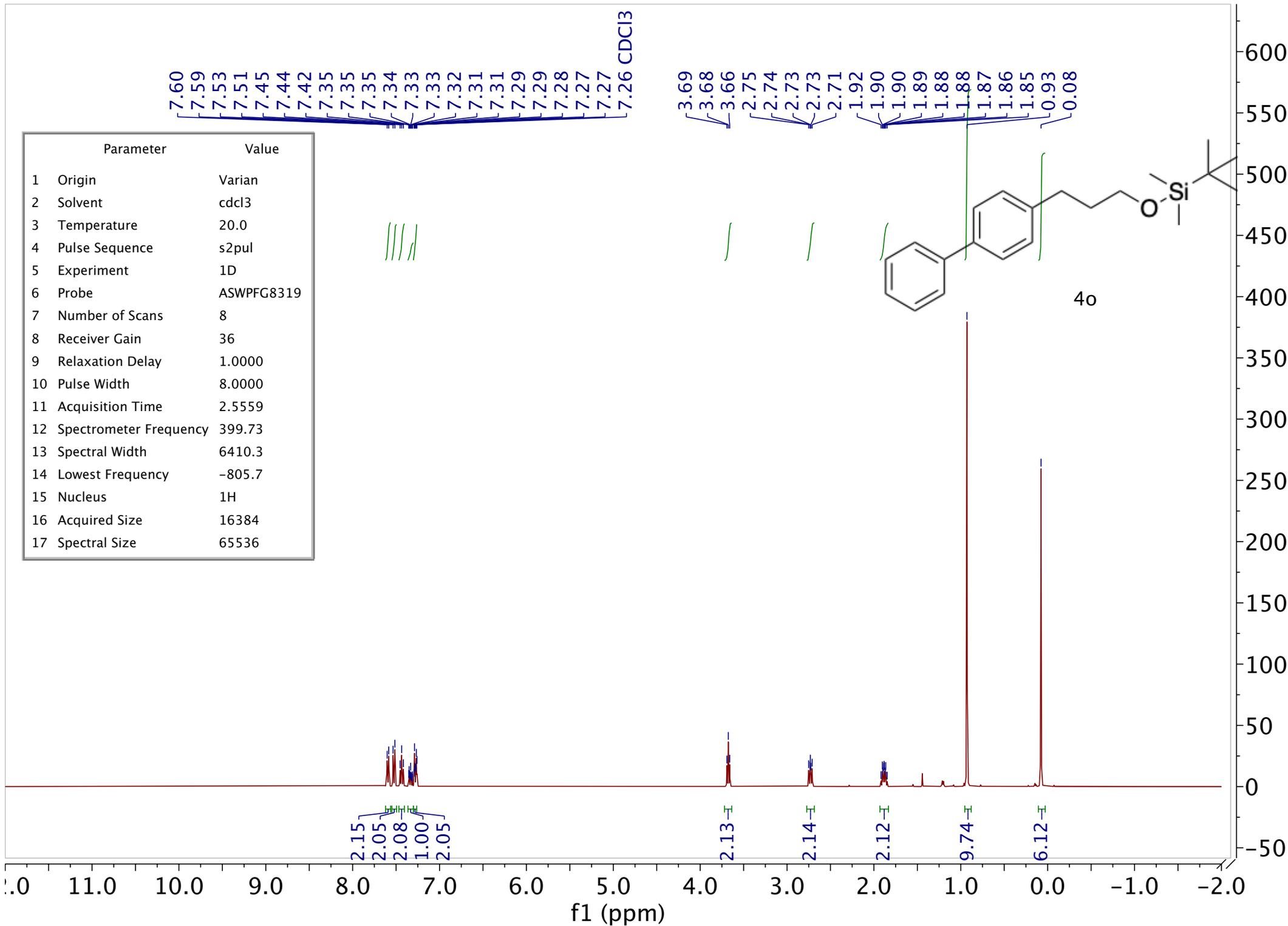




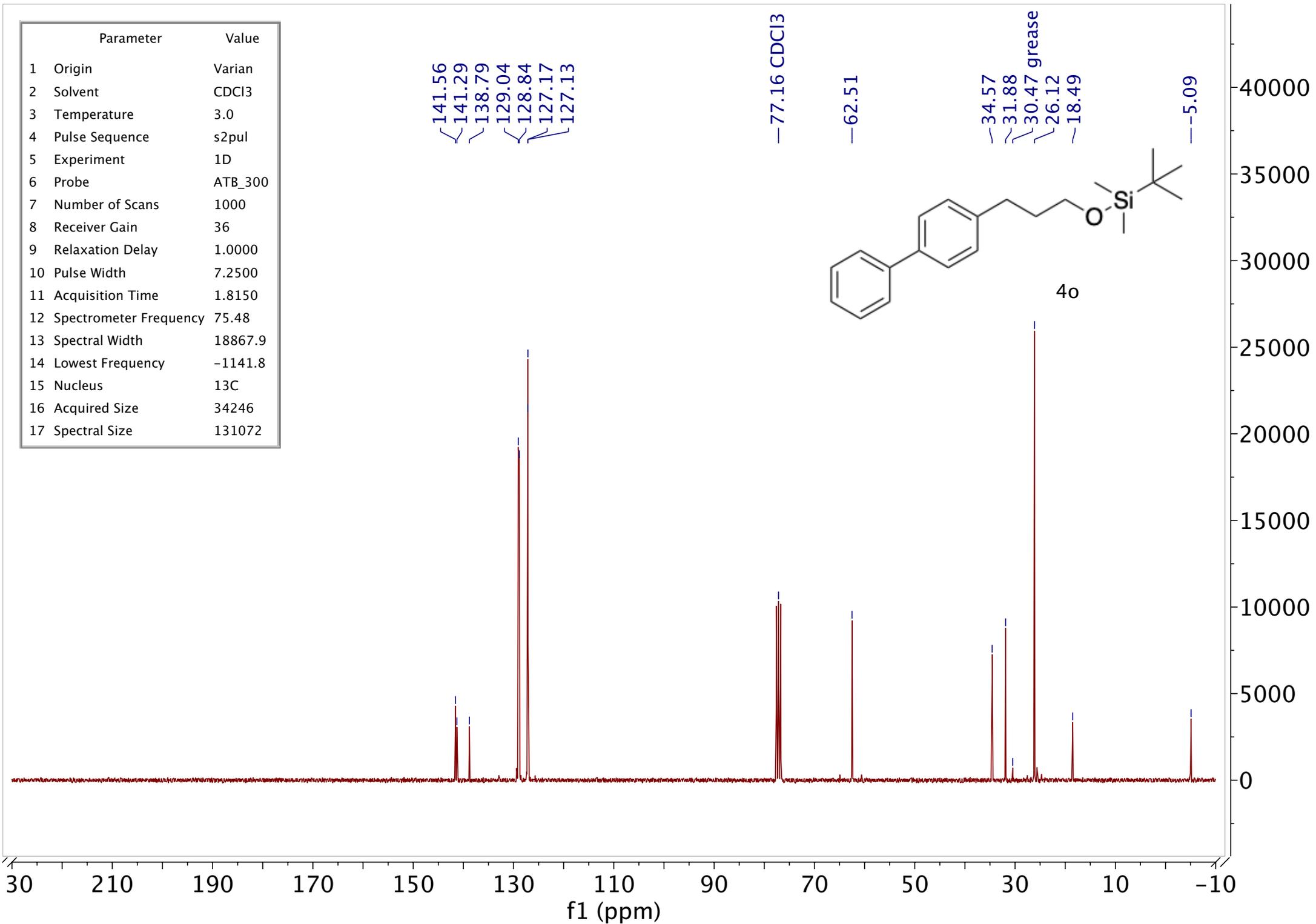
Parameter	Value
1 Origin	Varian
2 Instrument	vnmrs
3 Solvent	cdcl3
4 Temperature	20.0
5 Pulse Sequence	s2pul
6 Experiment	1D
7 Probe	ASWPG8319
8 Number of Scans	1000
9 Receiver Gain	30
10 Relaxation Delay	1.0000
11 Pulse Width	5.7500
12 Acquisition Time	1.3107
13 Spectrometer Frequency	100.52
14 Spectral Width	25000.0
15 Lowest Frequency	-1437.4
16 Nucleus	13C
17 Acquired Size	32768
18 Spectral Size	65536



Parameter	Value
1 Origin	Varian
2 Solvent	cdcl3
3 Temperature	20.0
4 Pulse Sequence	s2pul
5 Experiment	1D
6 Probe	ASWPFG8319
7 Number of Scans	8
8 Receiver Gain	36
9 Relaxation Delay	1.0000
10 Pulse Width	8.0000
11 Acquisition Time	2.5559
12 Spectrometer Frequency	399.73
13 Spectral Width	6410.3
14 Lowest Frequency	-805.7
15 Nucleus	1H
16 Acquired Size	16384
17 Spectral Size	65536



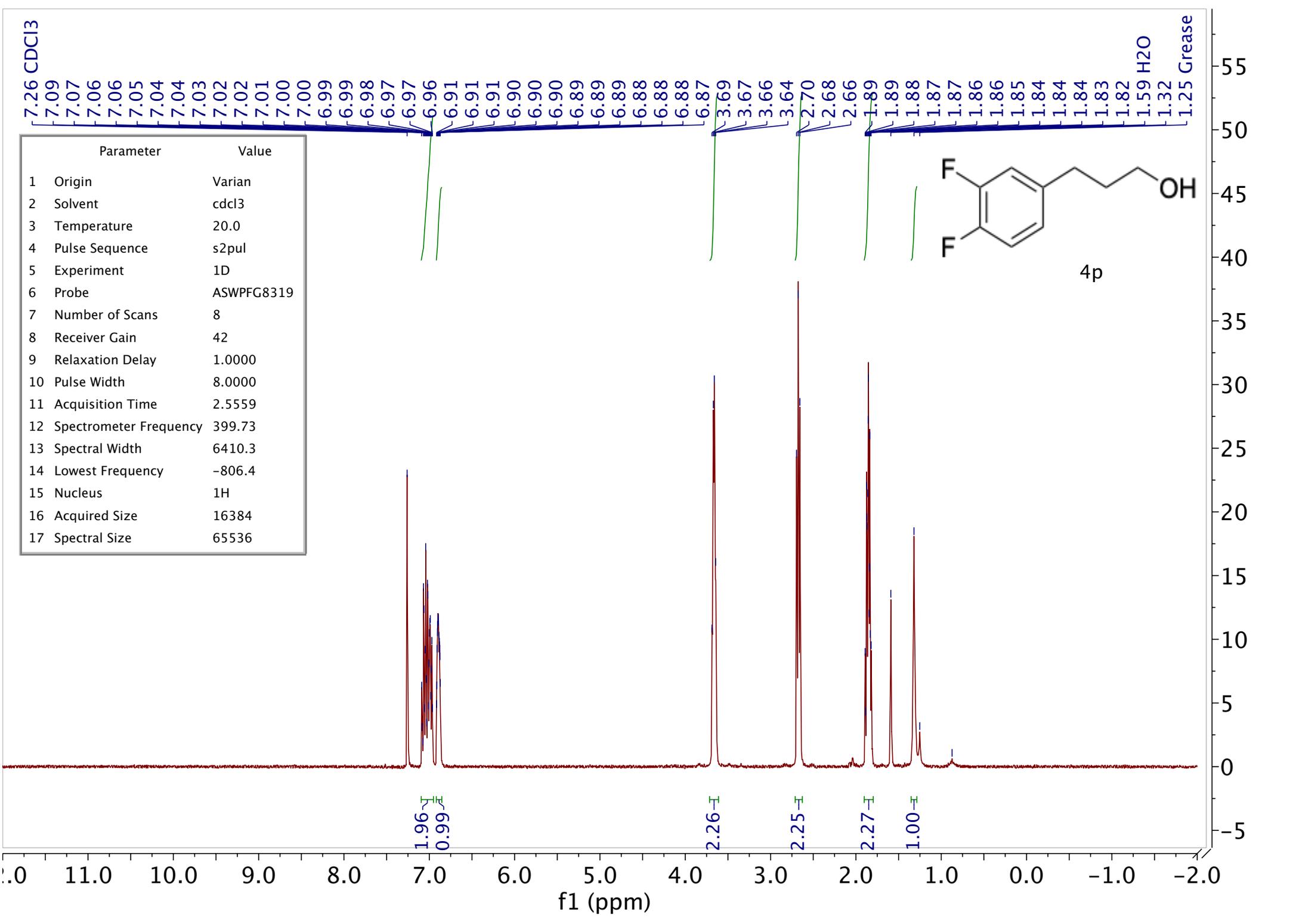
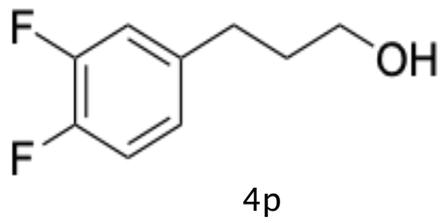
Parameter	Value
1 Origin	Varian
2 Solvent	CDCl3
3 Temperature	3.0
4 Pulse Sequence	s2pul
5 Experiment	1D
6 Probe	ATB_300
7 Number of Scans	1000
8 Receiver Gain	36
9 Relaxation Delay	1.0000
10 Pulse Width	7.2500
11 Acquisition Time	1.8150
12 Spectrometer Frequency	75.48
13 Spectral Width	18867.9
14 Lowest Frequency	-1141.8
15 Nucleus	13C
16 Acquired Size	34246
17 Spectral Size	131072



7.26 CDCl3

Parameter	Value
1 Origin	Varian
2 Solvent	cdcl3
3 Temperature	20.0
4 Pulse Sequence	s2pul
5 Experiment	1D
6 Probe	ASWPFG8319
7 Number of Scans	8
8 Receiver Gain	42
9 Relaxation Delay	1.0000
10 Pulse Width	8.0000
11 Acquisition Time	2.5559
12 Spectrometer Frequency	399.73
13 Spectral Width	6410.3
14 Lowest Frequency	-806.4
15 Nucleus	1H
16 Acquired Size	16384
17 Spectral Size	65536

- 7.09
- 7.07
- 7.06
- 7.06
- 7.05
- 7.04
- 7.04
- 7.03
- 7.02
- 7.02
- 7.01
- 7.00
- 7.00
- 6.99
- 6.99
- 6.98
- 6.97
- 6.97
- 6.96
- 6.91
- 6.91
- 6.91
- 6.90
- 6.90
- 6.90
- 6.89
- 6.89
- 6.89
- 6.88
- 6.88
- 6.88
- 6.87
- 3.69
- 3.67
- 3.66
- 3.64
- 2.70
- 2.68
- 2.66
- 1.89
- 1.89
- 1.88
- 1.87
- 1.87
- 1.86
- 1.86
- 1.85
- 1.84
- 1.84
- 1.84
- 1.83
- 1.82
- 1.59 H2O
- 1.32
- 1.25 Grease



1.96

0.99

2.26

2.25

2.27

1.00

f1 (ppm)

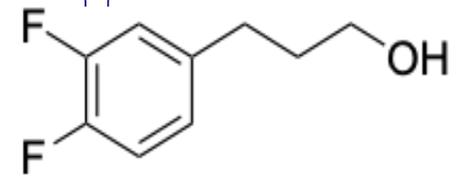
Parameter	Value
1 Origin	Varian
2 Solvent	cdcl3
3 Temperature	20.0
4 Pulse Sequence	s2pul
5 Experiment	1D
6 Probe	ASWPFG8319
7 Number of Scans	1000
8 Receiver Gain	30
9 Relaxation Delay	1.0000
10 Pulse Width	5.7500
11 Acquisition Time	1.3107
12 Spectrometer Frequency	100.52
13 Spectral Width	25000.0
14 Lowest Frequency	-1429.2
15 Nucleus	13C
16 Acquired Size	32768
17 Spectral Size	65536

151.57  
151.45  
150.14  
150.01  
149.11  
148.99  
147.69  
147.57  
138.92  
138.89  
138.87  
138.83  
124.36  
124.32  
124.30  
124.26  
117.31  
117.19  
117.14  
117.02

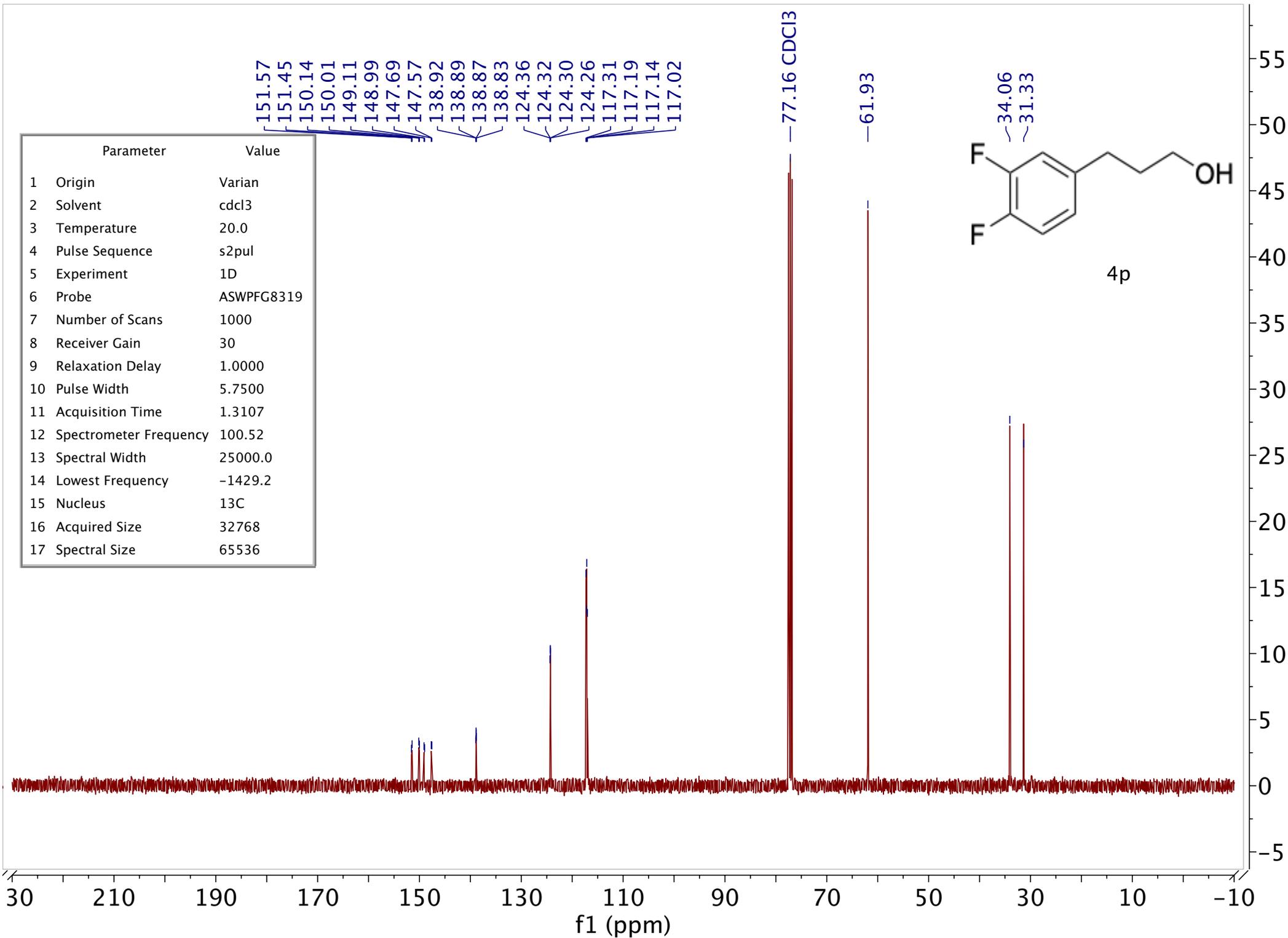
77.16 CDC13

61.93

34.06  
31.33

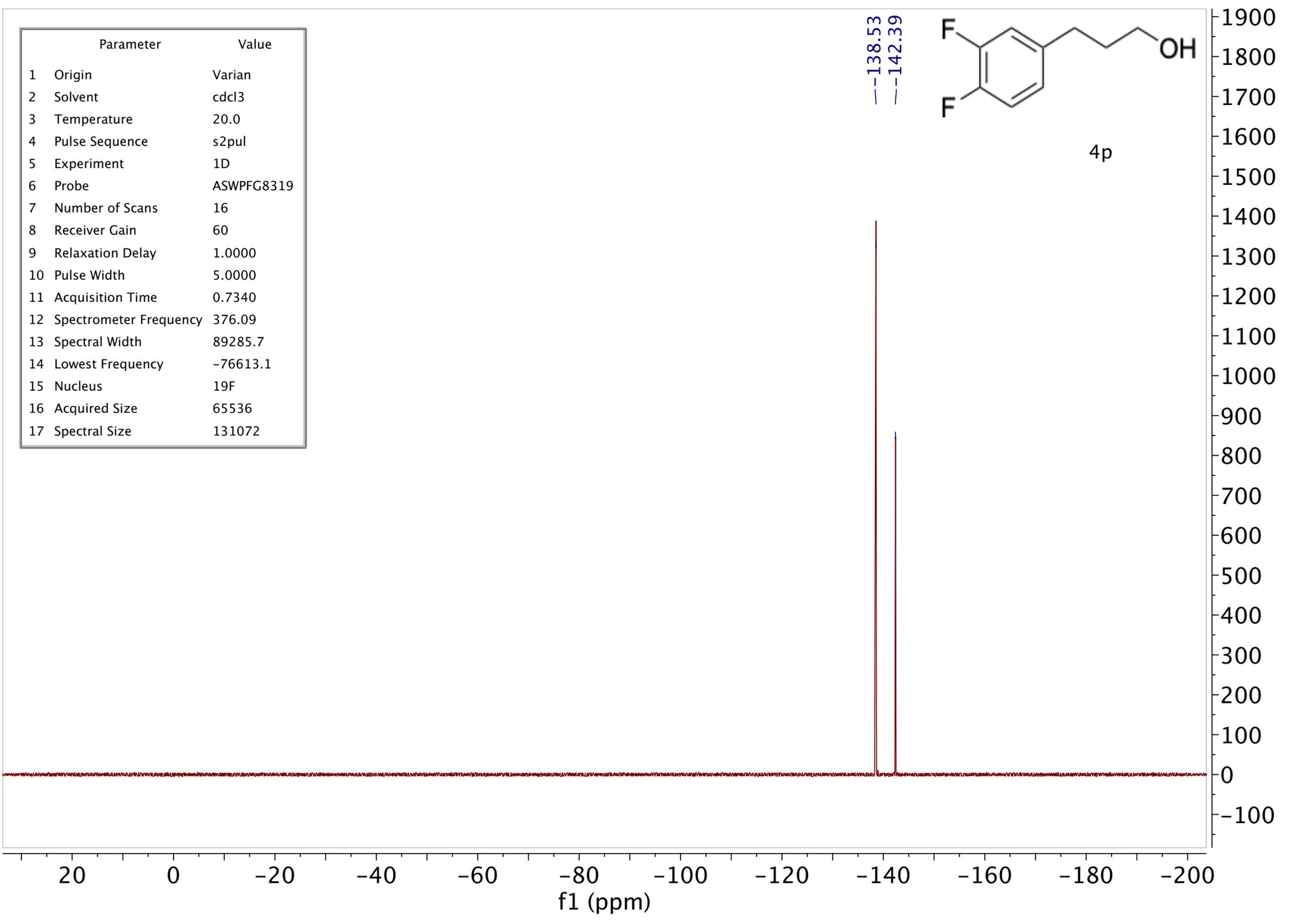
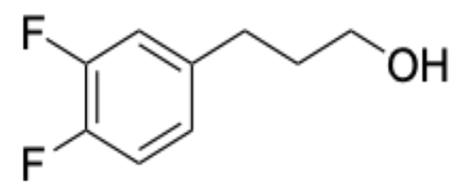


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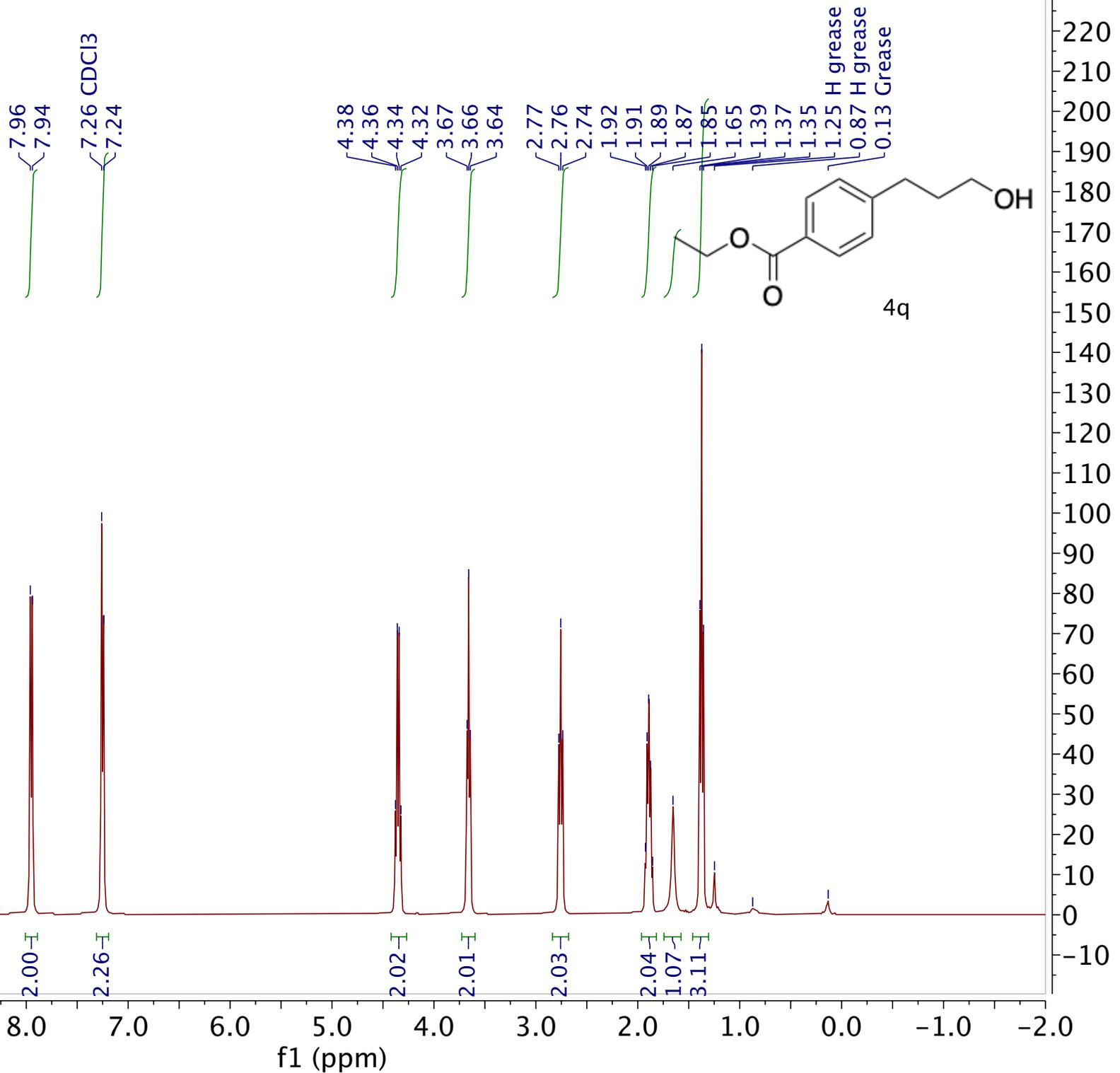


Parameter	Value
1 Origin	Varian
2 Solvent	cdcl3
3 Temperature	20.0
4 Pulse Sequence	s2pul
5 Experiment	1D
6 Probe	ASWPFG8319
7 Number of Scans	16
8 Receiver Gain	60
9 Relaxation Delay	1.0000
10 Pulse Width	5.0000
11 Acquisition Time	0.7340
12 Spectrometer Frequency	376.09
13 Spectral Width	89285.7
14 Lowest Frequency	-76613.1
15 Nucleus	19F
16 Acquired Size	65536
17 Spectral Size	131072

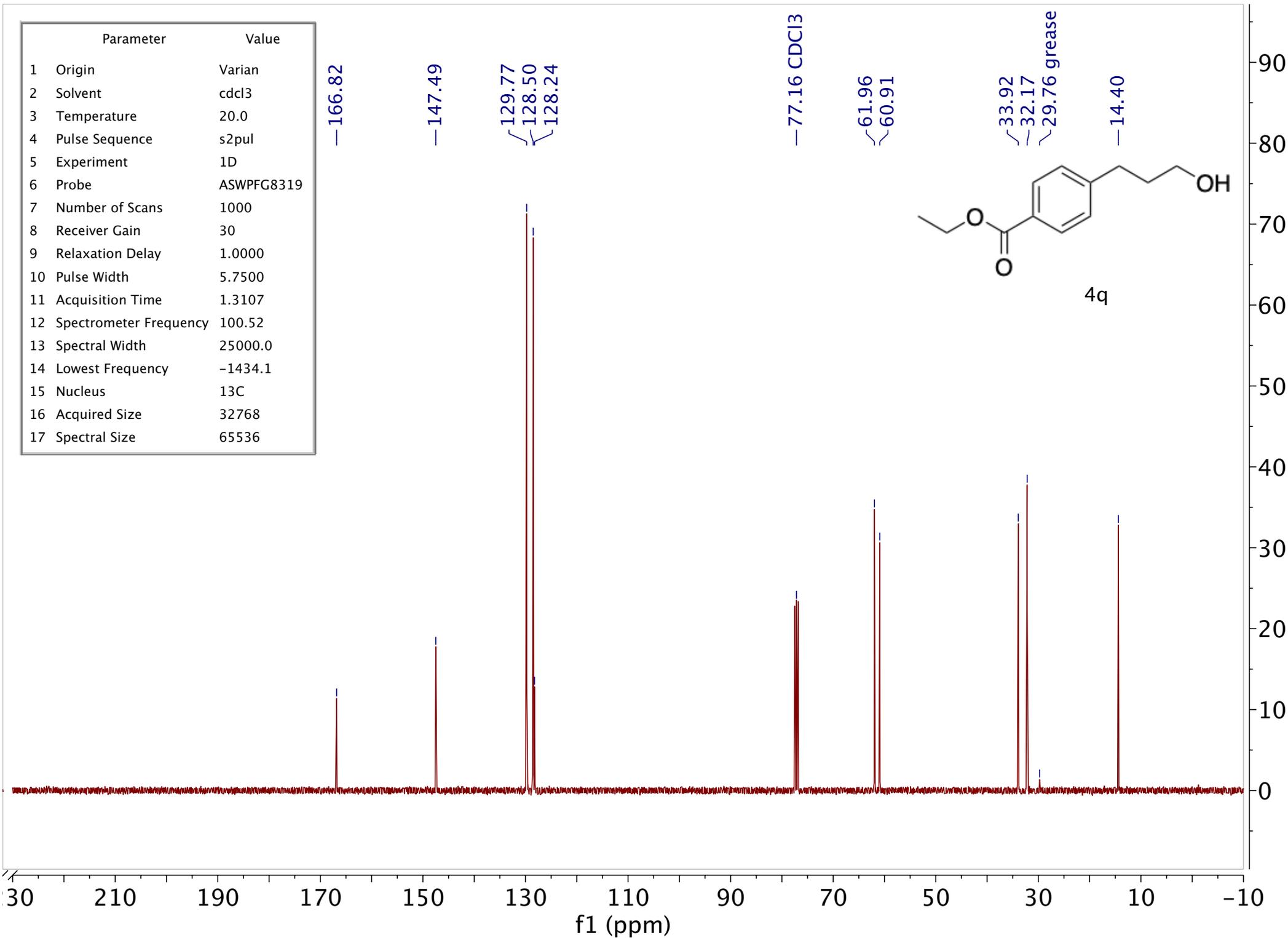
--138.53  
--142.39

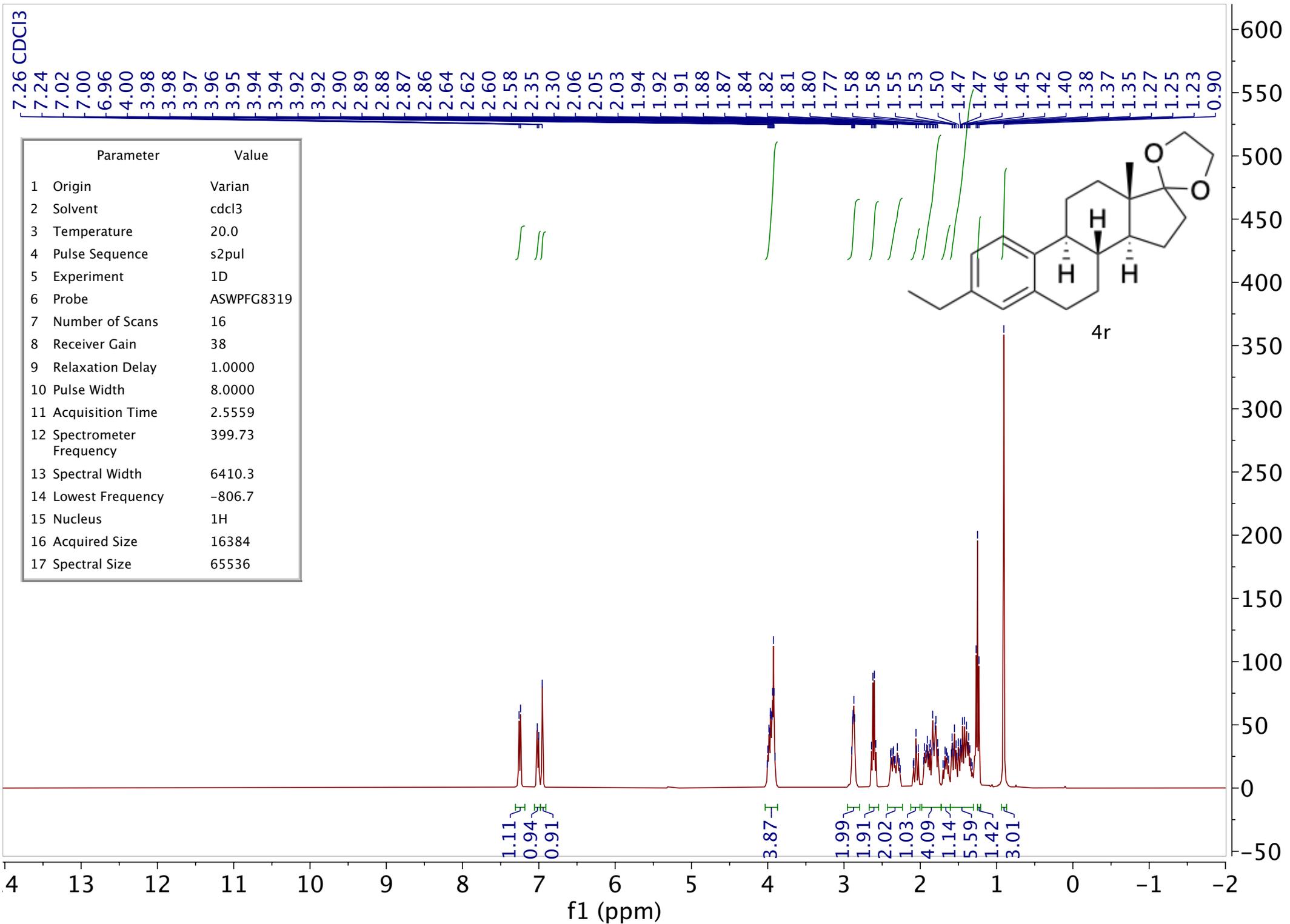


Parameter	Value
1 Origin	Varian
2 Solvent	cdcl3
3 Temperature	20.0
4 Pulse Sequence	s2pul
5 Experiment	1D
6 Probe	ASWPF8319
7 Number of Scans	8
8 Receiver Gain	38
9 Relaxation Delay	10.0000
10 Pulse Width	8.0000
11 Acquisition Time	2.5559
12 Spectrometer Frequency	399.73
13 Spectral Width	6410.3
14 Lowest Frequency	-806.3
15 Nucleus	1H
16 Acquired Size	16384
17 Spectral Size	65536



Parameter	Value
1 Origin	Varian
2 Solvent	cdcl3
3 Temperature	20.0
4 Pulse Sequence	s2pul
5 Experiment	1D
6 Probe	ASWPFG8319
7 Number of Scans	1000
8 Receiver Gain	30
9 Relaxation Delay	1.0000
10 Pulse Width	5.7500
11 Acquisition Time	1.3107
12 Spectrometer Frequency	100.52
13 Spectral Width	25000.0
14 Lowest Frequency	-1434.1
15 Nucleus	13C
16 Acquired Size	32768
17 Spectral Size	65536



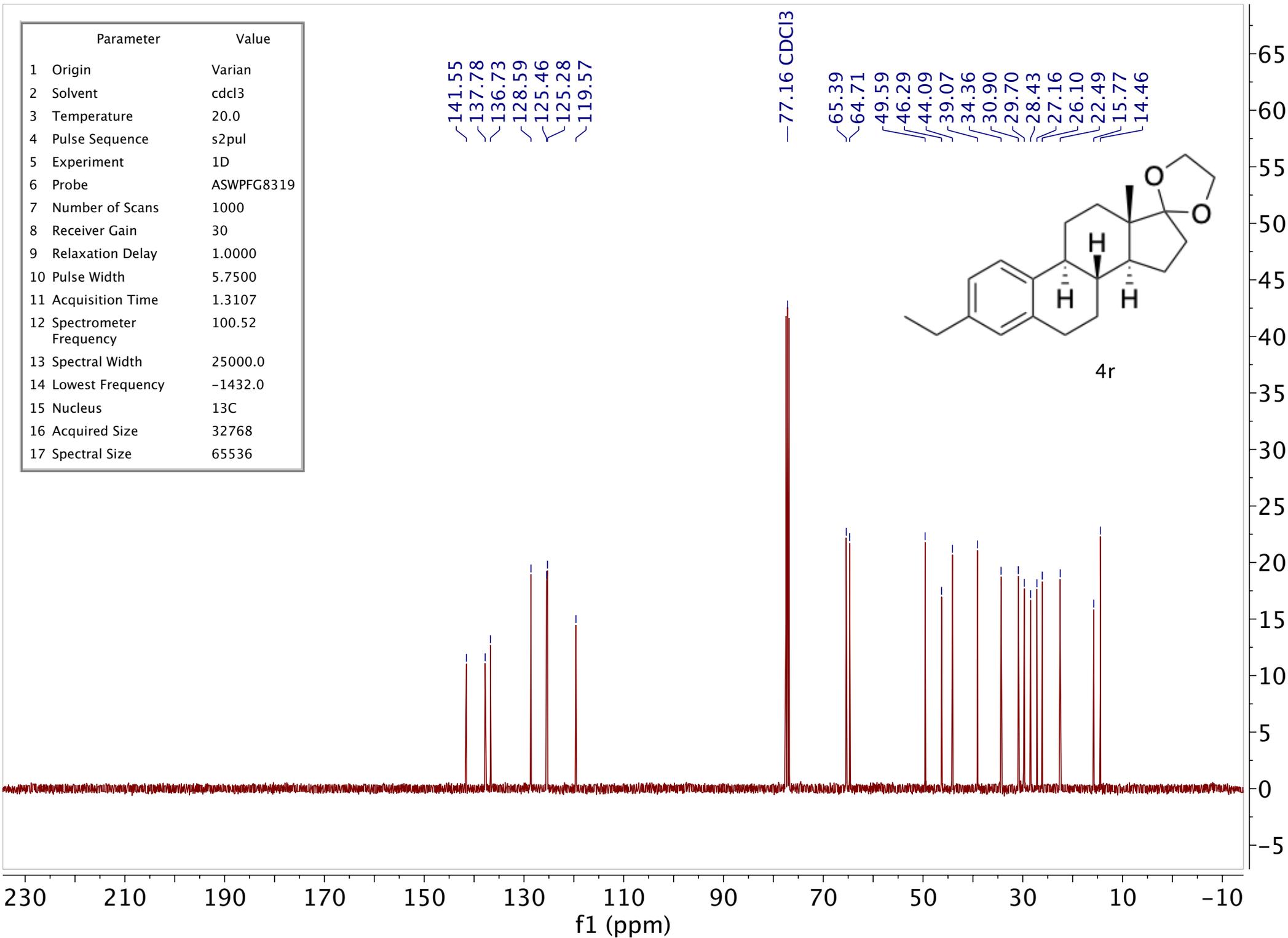
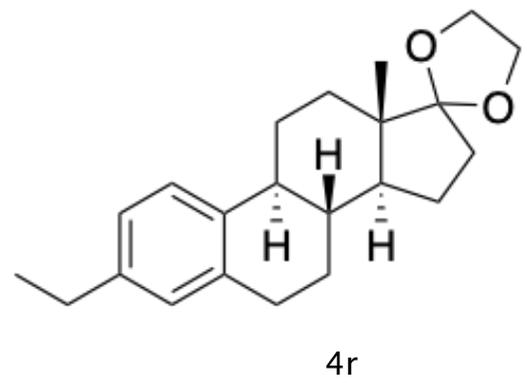


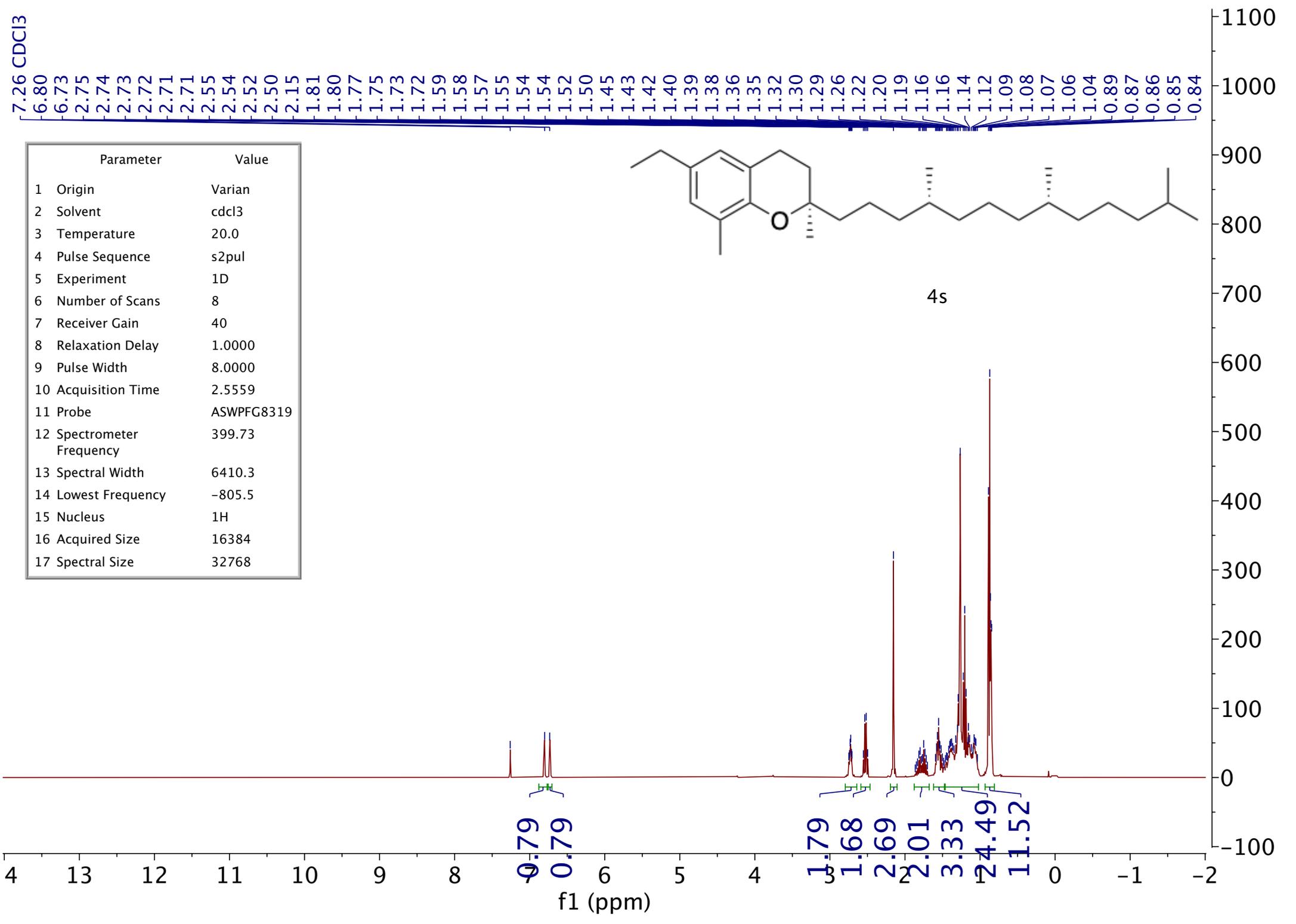
Parameter	Value
1 Origin	Varian
2 Solvent	cdcl3
3 Temperature	20.0
4 Pulse Sequence	s2pul
5 Experiment	1D
6 Probe	ASWPG8319
7 Number of Scans	1000
8 Receiver Gain	30
9 Relaxation Delay	1.0000
10 Pulse Width	5.7500
11 Acquisition Time	1.3107
12 Spectrometer Frequency	100.52
13 Spectral Width	25000.0
14 Lowest Frequency	-1432.0
15 Nucleus	<sup>13</sup> C
16 Acquired Size	32768
17 Spectral Size	65536

141.55  
137.78  
136.73  
128.59  
125.46  
125.28  
119.57

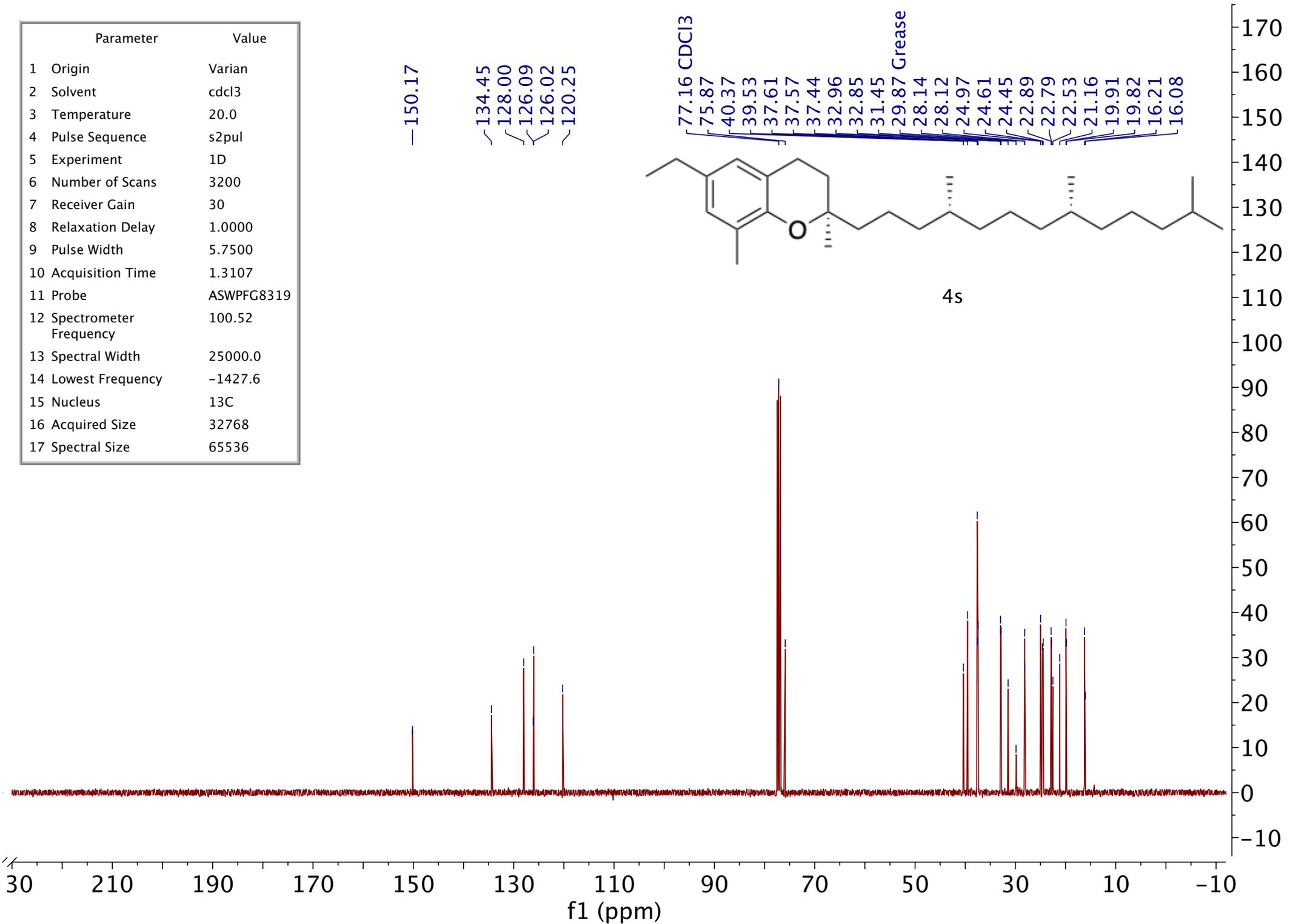
77.16 CDCl3

65.39  
64.71  
49.59  
46.29  
44.09  
39.07  
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30.90  
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28.43  
27.16  
26.10  
22.49  
15.77  
14.46

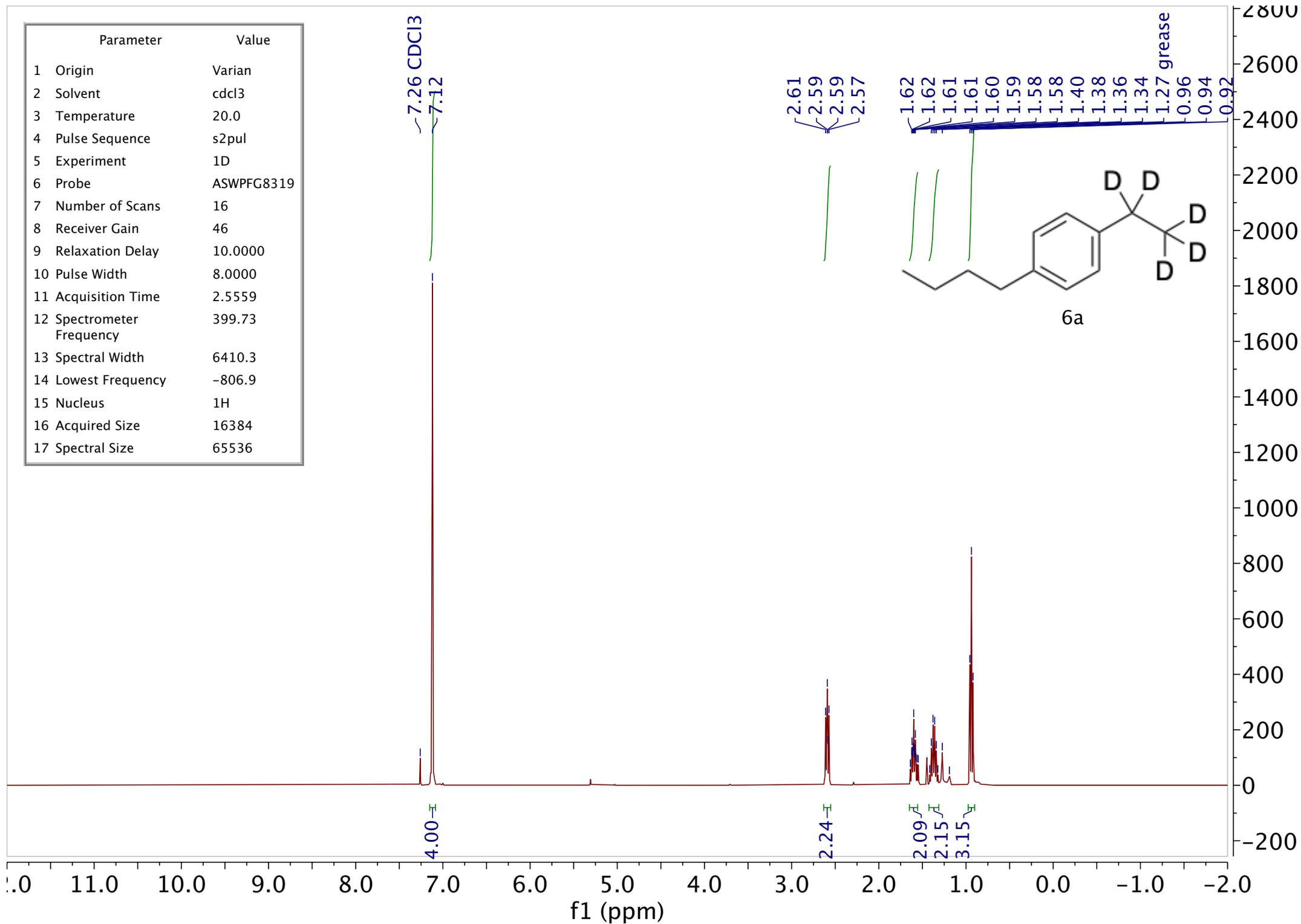




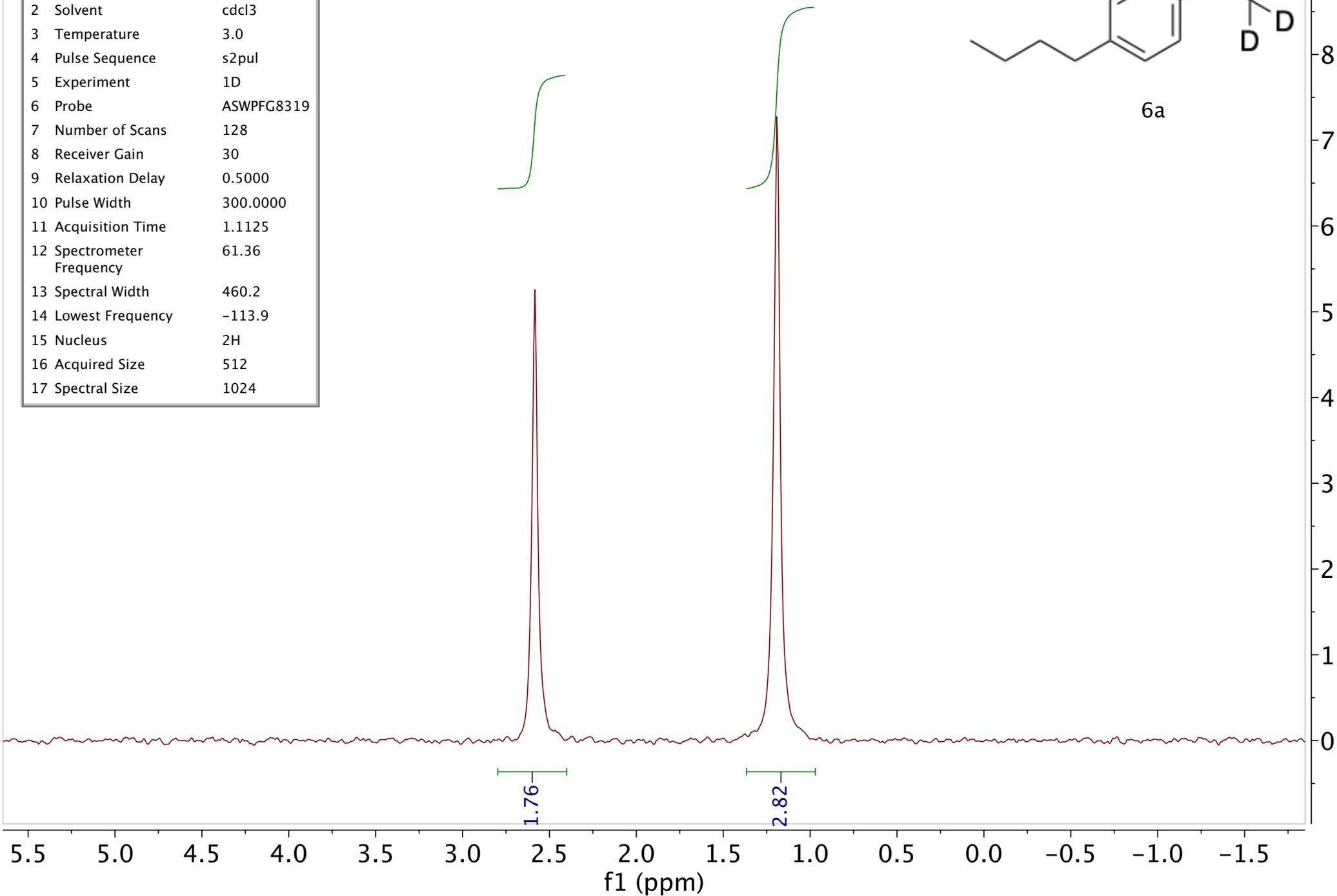
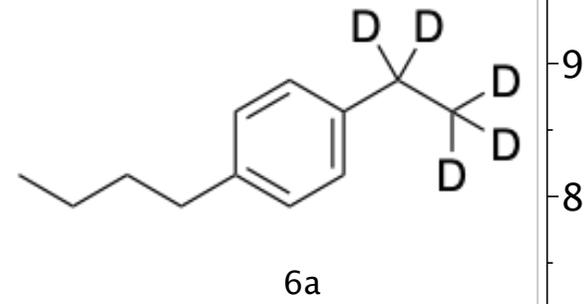
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1 Origin	Varian
2 Solvent	cdcl3
3 Temperature	20.0
4 Pulse Sequence	s2pul
5 Experiment	1D
6 Number of Scans	3200
7 Receiver Gain	30
8 Relaxation Delay	1.0000
9 Pulse Width	5.7500
10 Acquisition Time	1.3107
11 Probe	ASWPG8319
12 Spectrometer Frequency	100.52
13 Spectral Width	25000.0
14 Lowest Frequency	-1427.6
15 Nucleus	13C
16 Acquired Size	32768
17 Spectral Size	65536



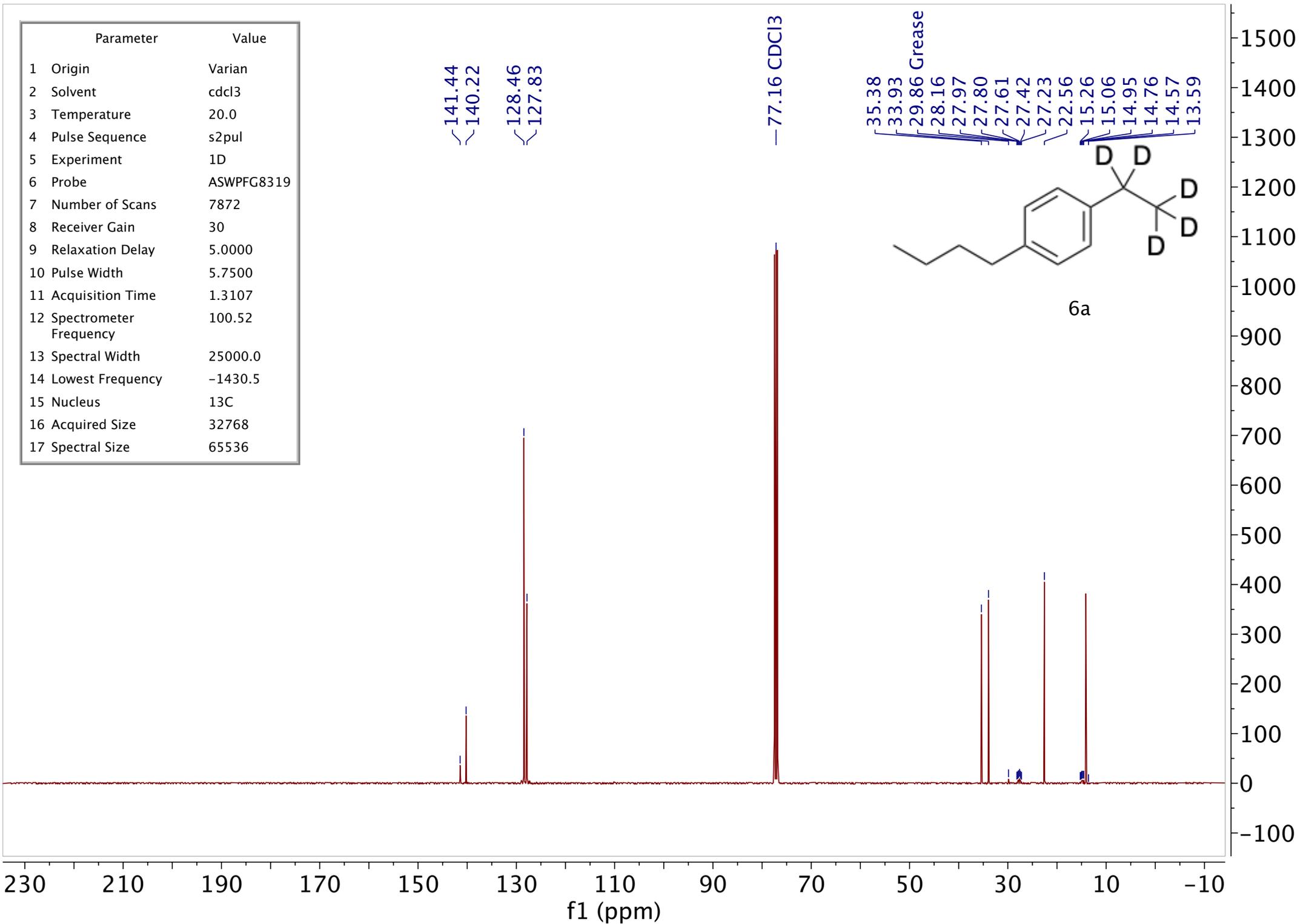
Parameter	Value
1 Origin	Varian
2 Solvent	cdcl3
3 Temperature	20.0
4 Pulse Sequence	s2pul
5 Experiment	1D
6 Probe	ASWPG8319
7 Number of Scans	16
8 Receiver Gain	46
9 Relaxation Delay	10.0000
10 Pulse Width	8.0000
11 Acquisition Time	2.5559
12 Spectrometer Frequency	399.73
13 Spectral Width	6410.3
14 Lowest Frequency	-806.9
15 Nucleus	1H
16 Acquired Size	16384
17 Spectral Size	65536



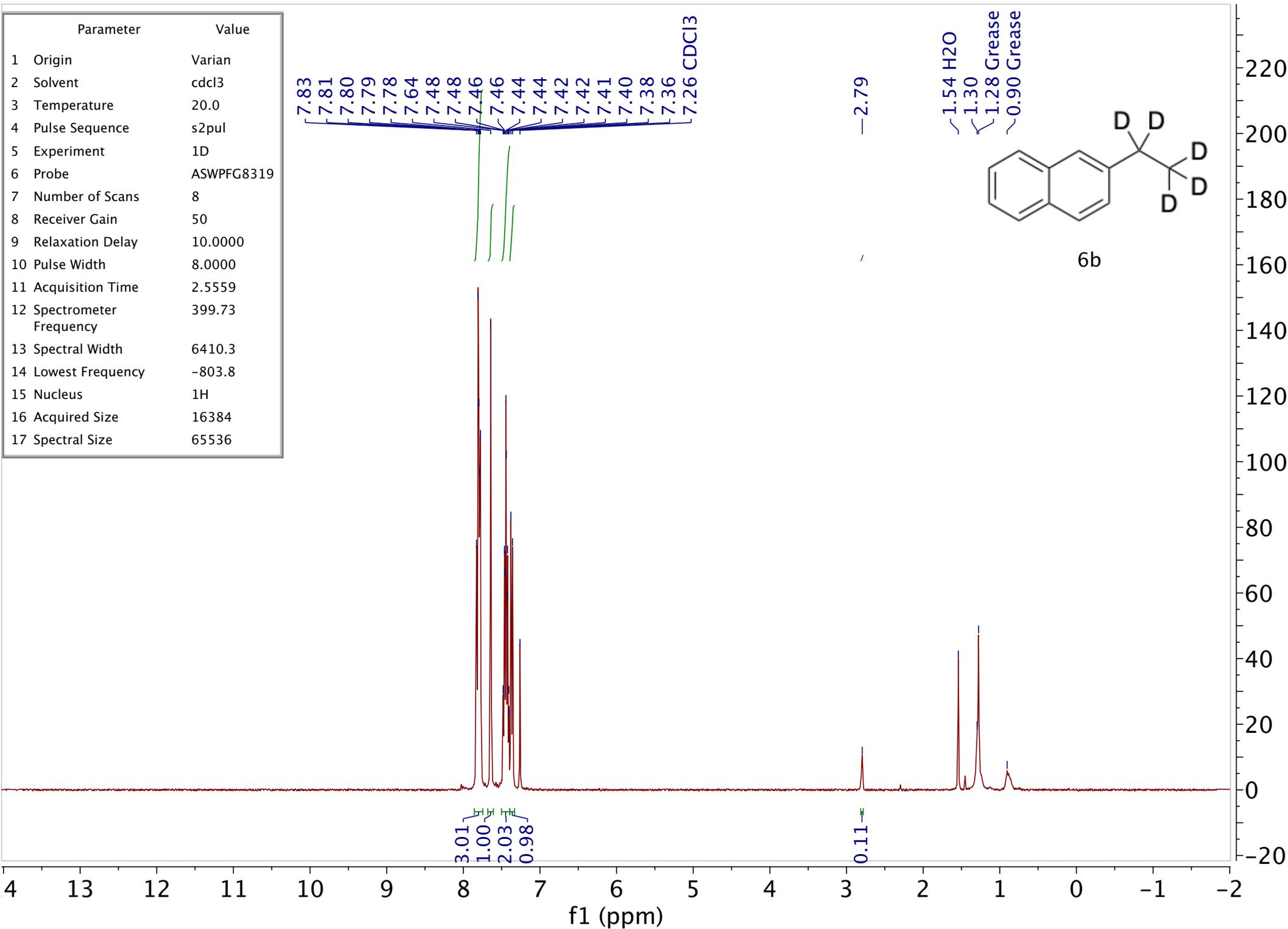
Parameter	Value
1 Origin	Varian
2 Solvent	cdcl3
3 Temperature	3.0
4 Pulse Sequence	s2pul
5 Experiment	1D
6 Probe	ASWPG8319
7 Number of Scans	128
8 Receiver Gain	30
9 Relaxation Delay	0.5000
10 Pulse Width	300.0000
11 Acquisition Time	1.1125
12 Spectrometer Frequency	61.36
13 Spectral Width	460.2
14 Lowest Frequency	-113.9
15 Nucleus	2H
16 Acquired Size	512
17 Spectral Size	1024



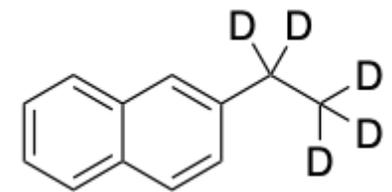
Parameter	Value
1 Origin	Varian
2 Solvent	cdcl3
3 Temperature	20.0
4 Pulse Sequence	s2pul
5 Experiment	1D
6 Probe	ASWPG8319
7 Number of Scans	7872
8 Receiver Gain	30
9 Relaxation Delay	5.0000
10 Pulse Width	5.7500
11 Acquisition Time	1.3107
12 Spectrometer Frequency	100.52
13 Spectral Width	25000.0
14 Lowest Frequency	-1430.5
15 Nucleus	<sup>13</sup> C
16 Acquired Size	32768
17 Spectral Size	65536



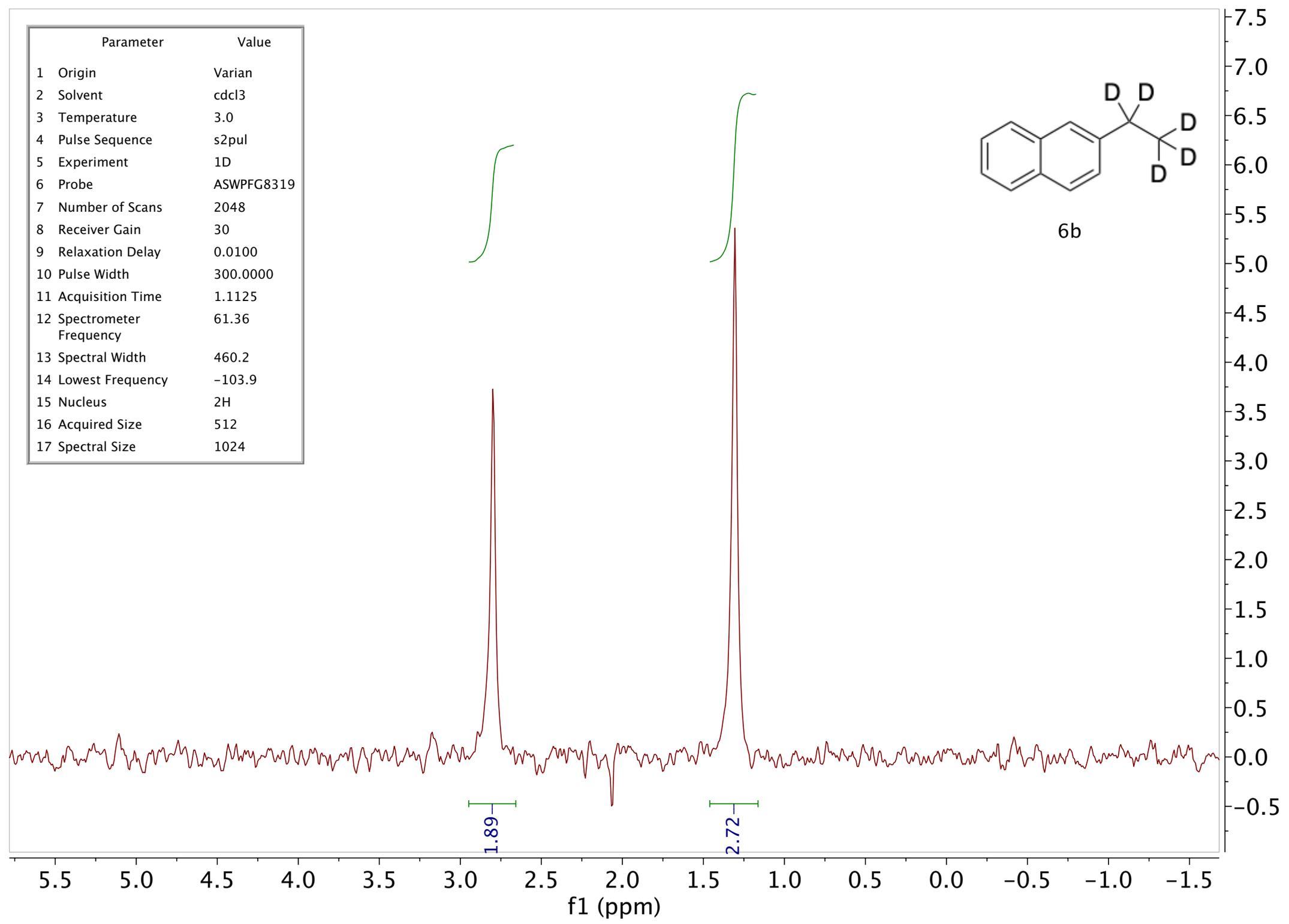
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1 Origin	Varian
2 Solvent	cdcl3
3 Temperature	20.0
4 Pulse Sequence	s2pul
5 Experiment	1D
6 Probe	ASWPFG8319
7 Number of Scans	8
8 Receiver Gain	50
9 Relaxation Delay	10.0000
10 Pulse Width	8.0000
11 Acquisition Time	2.5559
12 Spectrometer Frequency	399.73
13 Spectral Width	6410.3
14 Lowest Frequency	-803.8
15 Nucleus	1H
16 Acquired Size	16384
17 Spectral Size	65536



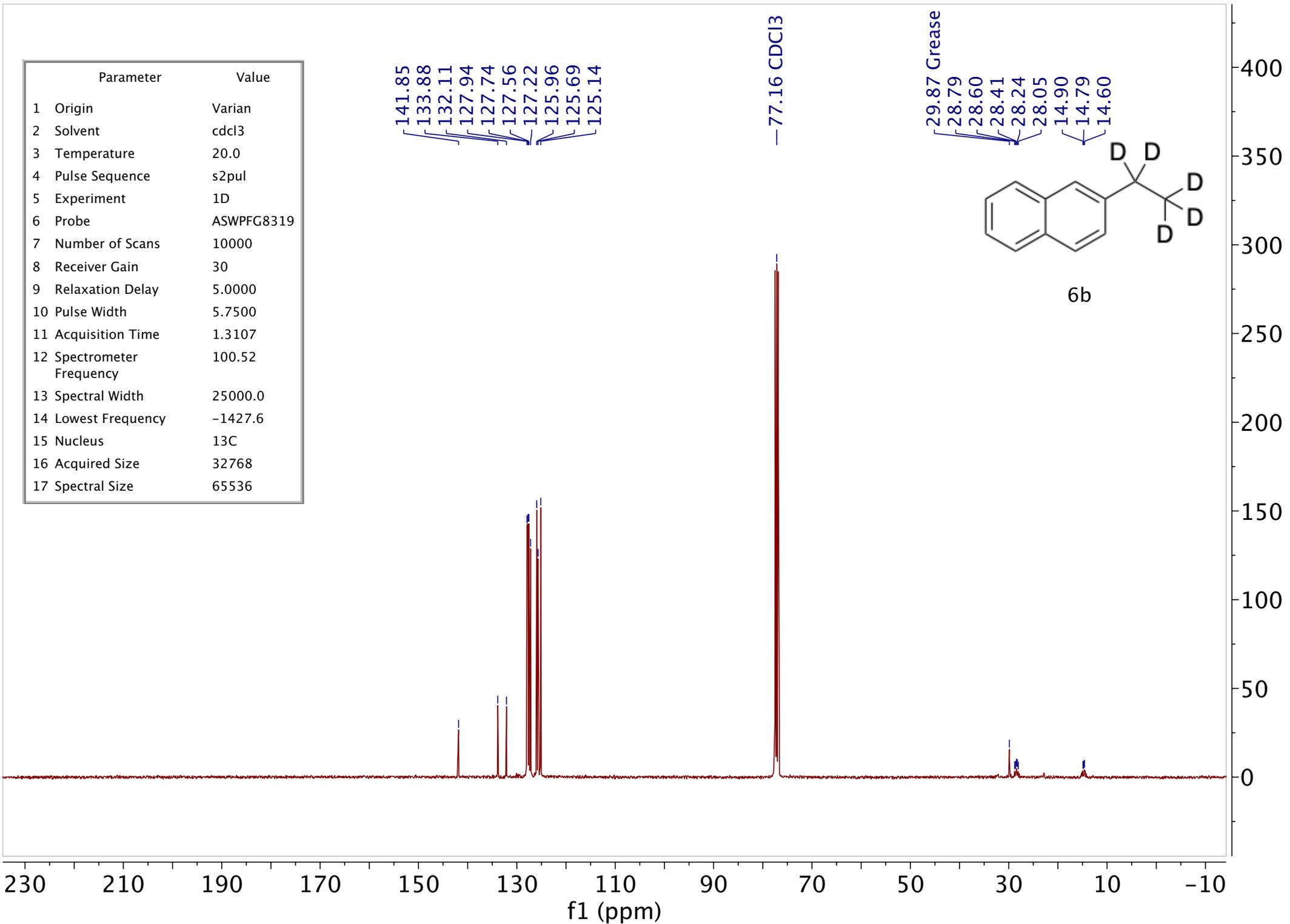
Parameter	Value
1 Origin	Varian
2 Solvent	cdcl3
3 Temperature	3.0
4 Pulse Sequence	s2pul
5 Experiment	1D
6 Probe	ASWPG8319
7 Number of Scans	2048
8 Receiver Gain	30
9 Relaxation Delay	0.0100
10 Pulse Width	300.0000
11 Acquisition Time	1.1125
12 Spectrometer	61.36
Frequency	
13 Spectral Width	460.2
14 Lowest Frequency	-103.9
15 Nucleus	2H
16 Acquired Size	512
17 Spectral Size	1024



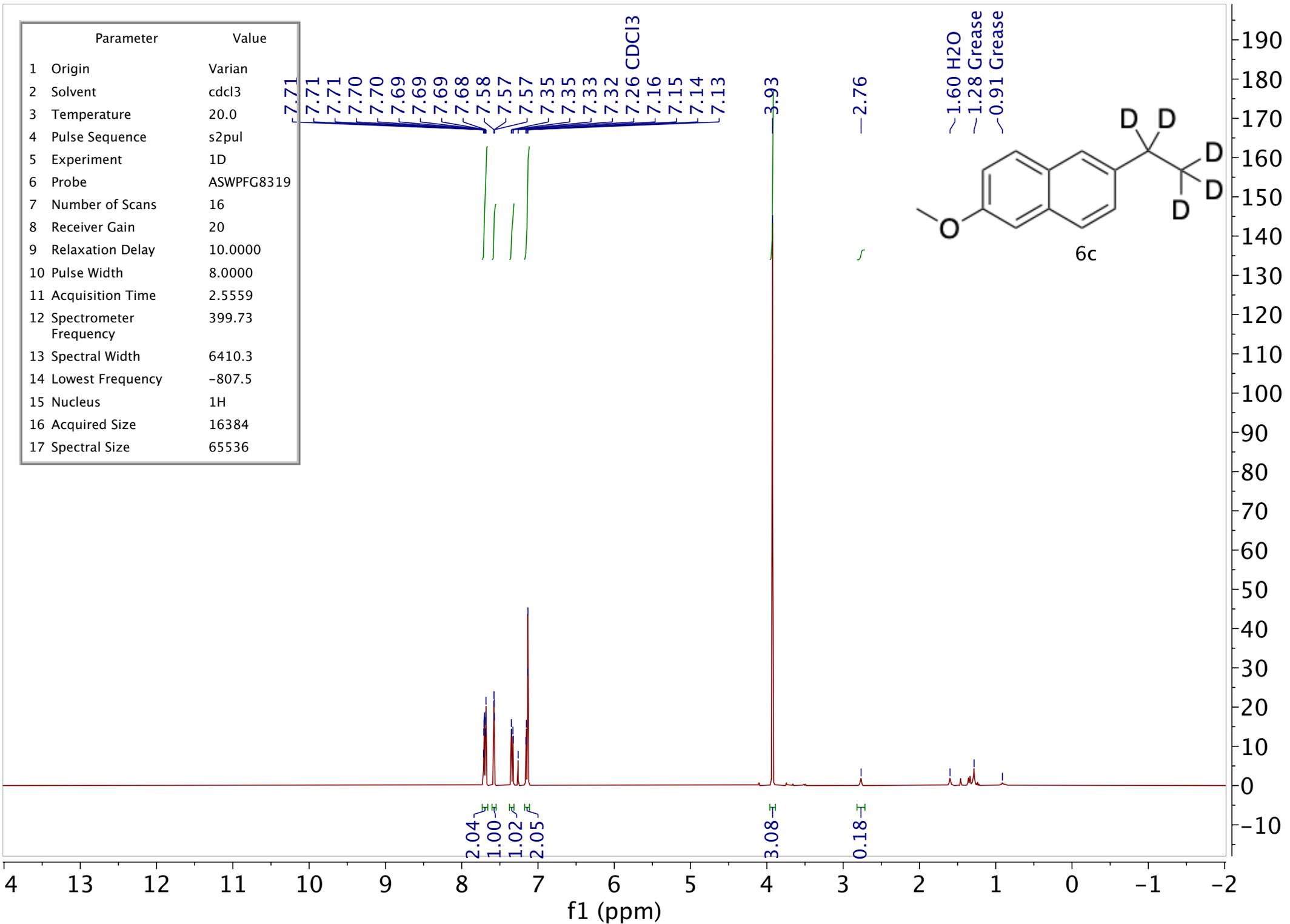
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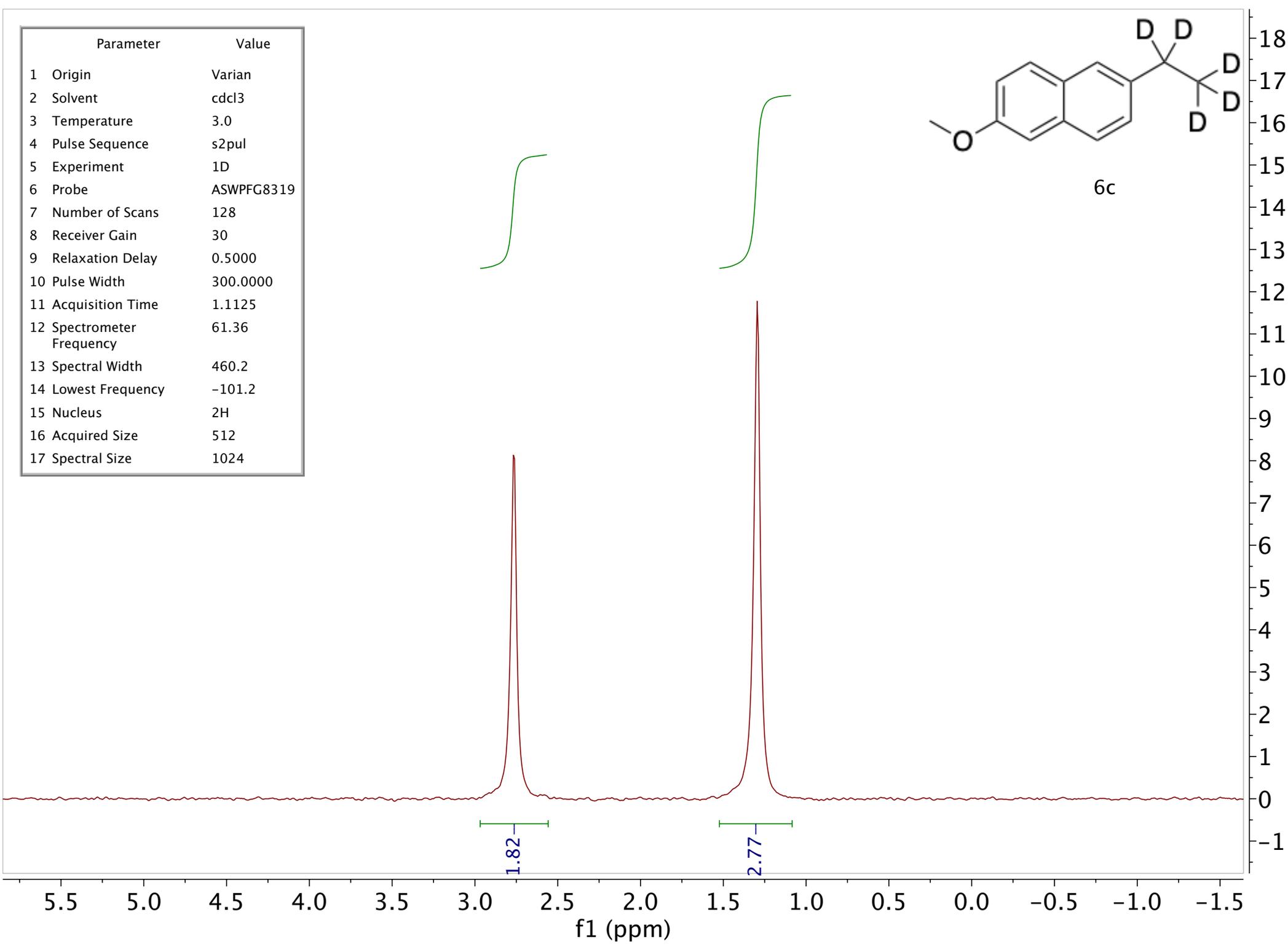
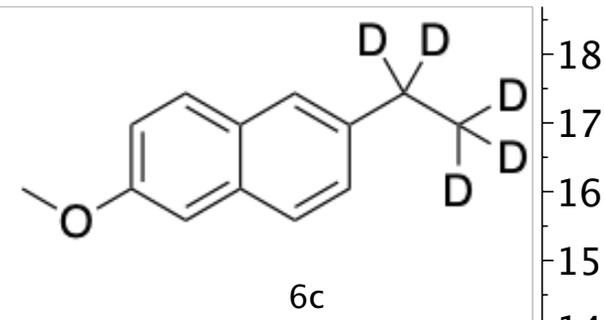
Parameter	Value
1 Origin	Varian
2 Solvent	cdcl3
3 Temperature	20.0
4 Pulse Sequence	s2pul
5 Experiment	1D
6 Probe	ASWPFG8319
7 Number of Scans	10000
8 Receiver Gain	30
9 Relaxation Delay	5.0000
10 Pulse Width	5.7500
11 Acquisition Time	1.3107
12 Spectrometer Frequency	100.52
13 Spectral Width	25000.0
14 Lowest Frequency	-1427.6
15 Nucleus	13C
16 Acquired Size	32768
17 Spectral Size	65536



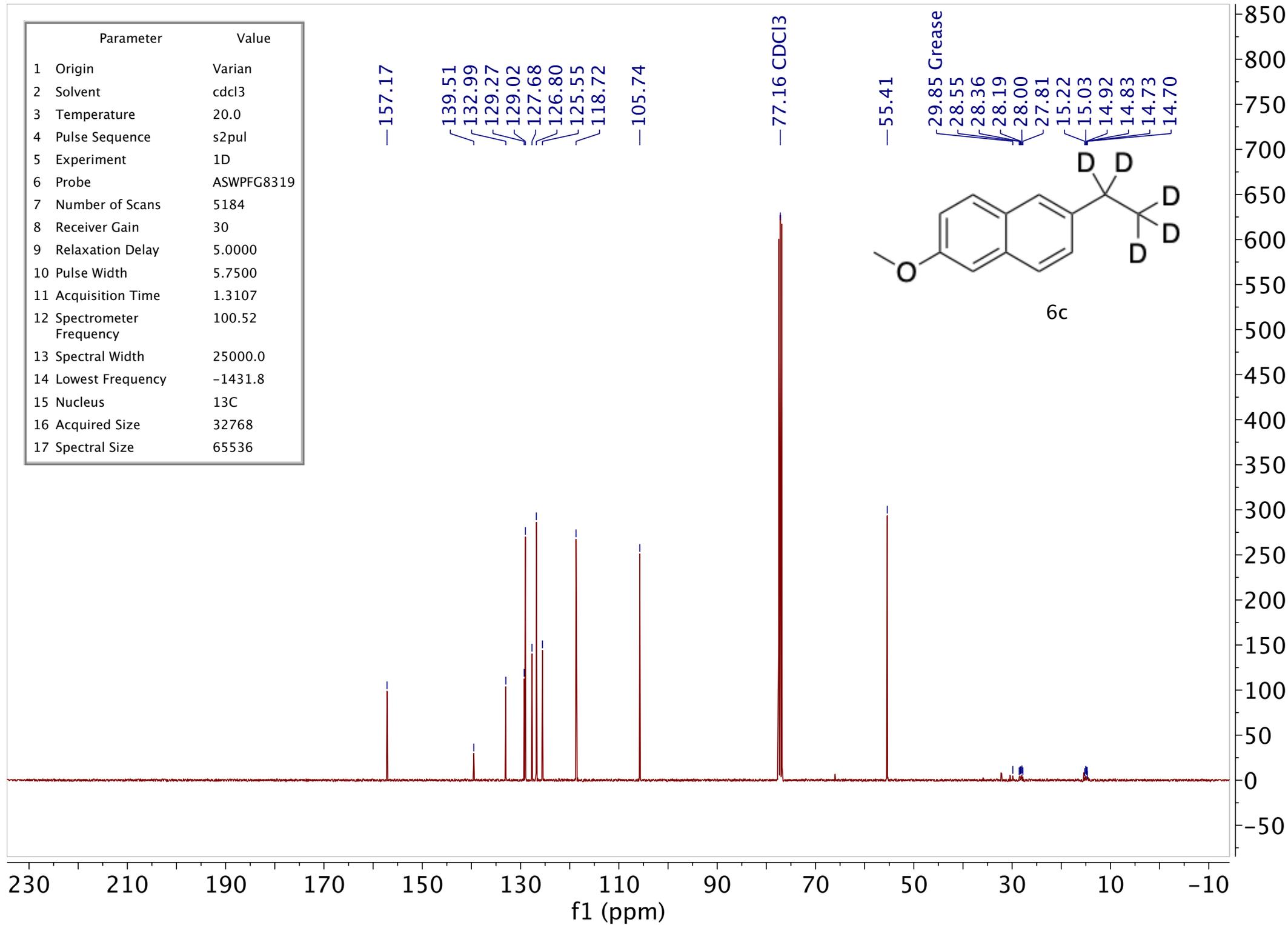
Parameter	Value
1 Origin	Varian
2 Solvent	cdcl3
3 Temperature	20.0
4 Pulse Sequence	s2pul
5 Experiment	1D
6 Probe	ASWPG8319
7 Number of Scans	16
8 Receiver Gain	20
9 Relaxation Delay	10.0000
10 Pulse Width	8.0000
11 Acquisition Time	2.5559
12 Spectrometer Frequency	399.73
13 Spectral Width	6410.3
14 Lowest Frequency	-807.5
15 Nucleus	1H
16 Acquired Size	16384
17 Spectral Size	65536

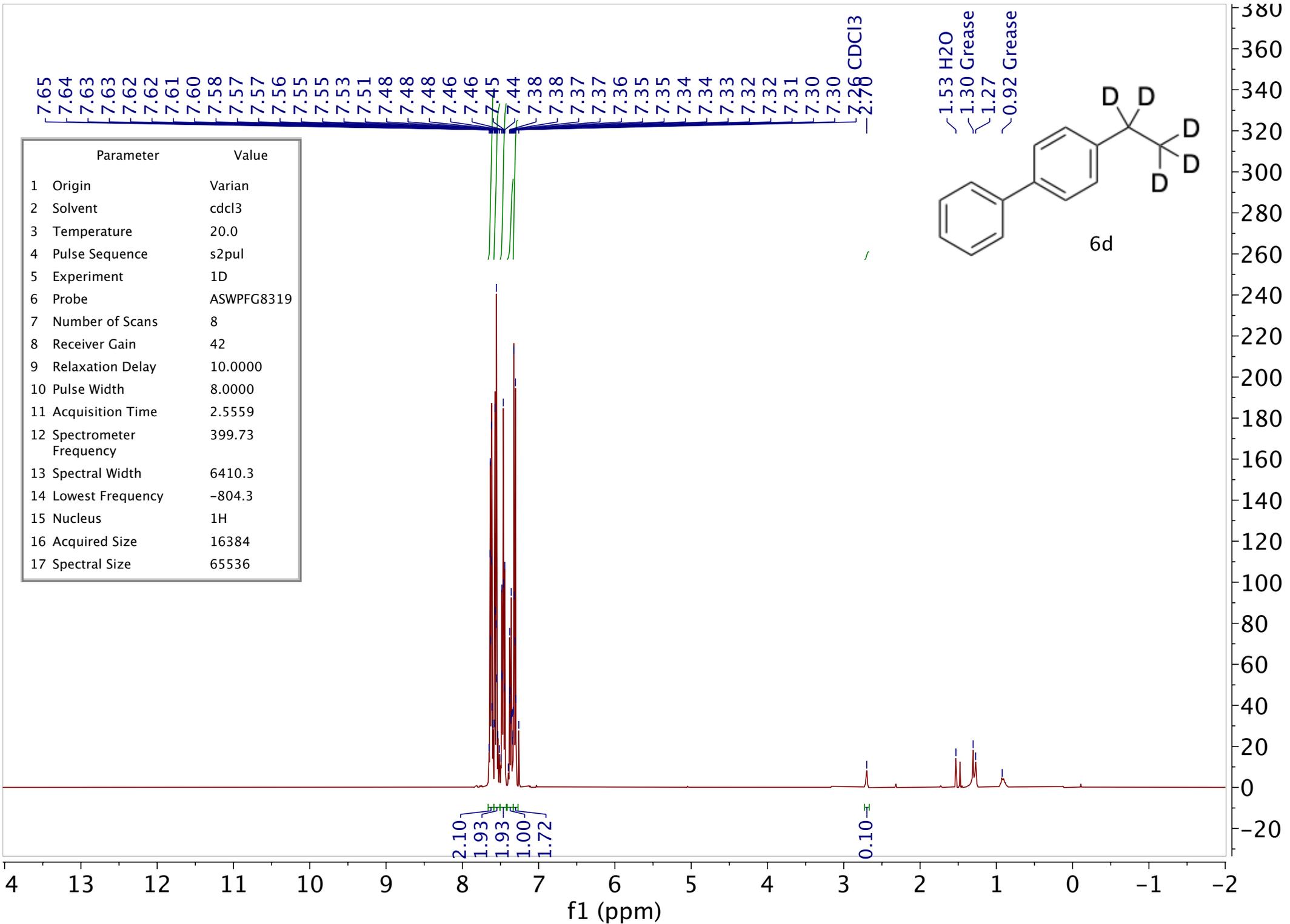


Parameter	Value
1 Origin	Varian
2 Solvent	cdcl3
3 Temperature	3.0
4 Pulse Sequence	s2pul
5 Experiment	1D
6 Probe	ASWPG8319
7 Number of Scans	128
8 Receiver Gain	30
9 Relaxation Delay	0.5000
10 Pulse Width	300.0000
11 Acquisition Time	1.1125
12 Spectrometer Frequency	61.36
13 Spectral Width	460.2
14 Lowest Frequency	-101.2
15 Nucleus	2H
16 Acquired Size	512
17 Spectral Size	1024

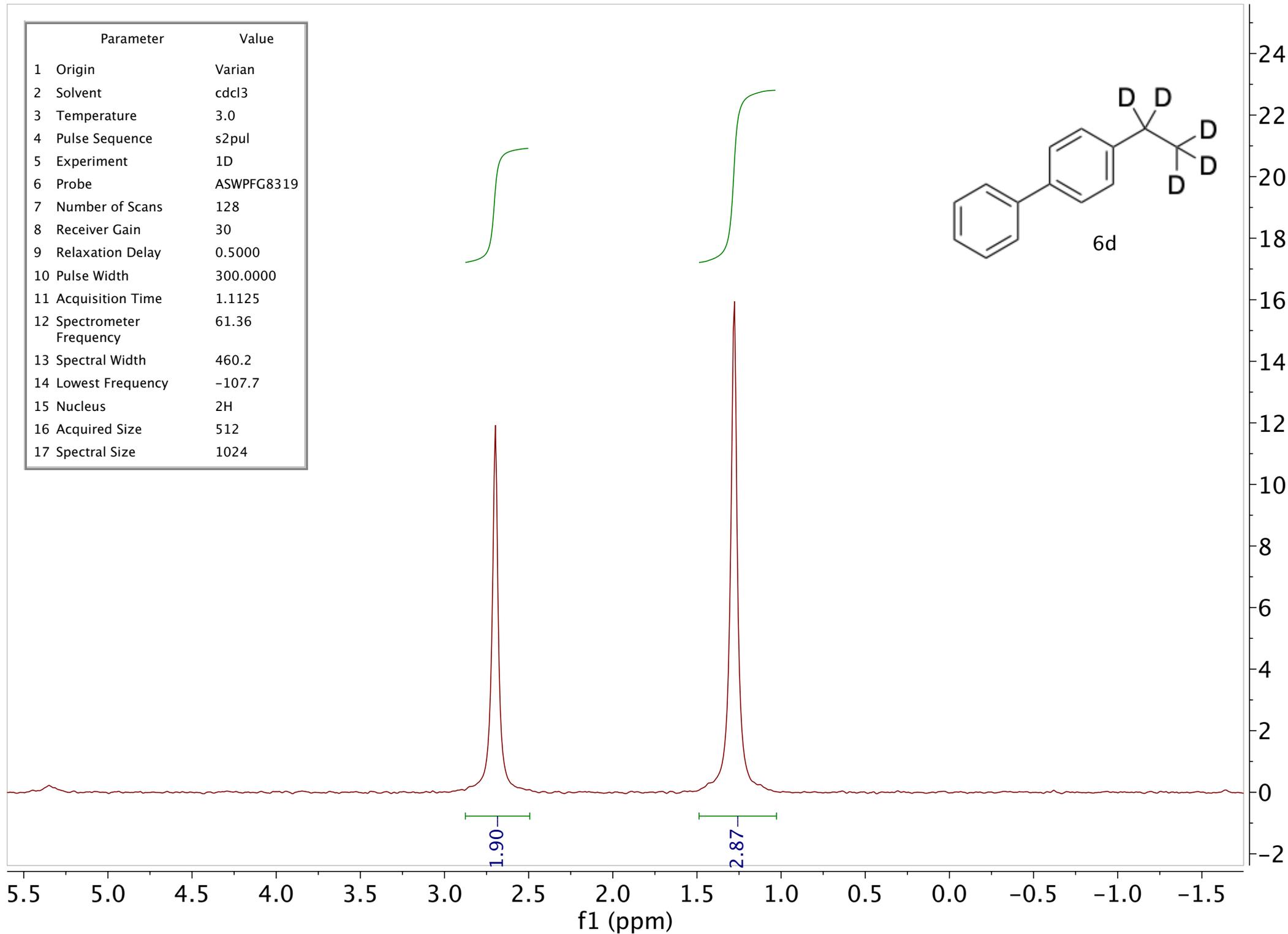


Parameter	Value
1 Origin	Varian
2 Solvent	cdcl3
3 Temperature	20.0
4 Pulse Sequence	s2pul
5 Experiment	1D
6 Probe	ASWPG8319
7 Number of Scans	5184
8 Receiver Gain	30
9 Relaxation Delay	5.0000
10 Pulse Width	5.7500
11 Acquisition Time	1.3107
12 Spectrometer Frequency	100.52
13 Spectral Width	25000.0
14 Lowest Frequency	-1431.8
15 Nucleus	13C
16 Acquired Size	32768
17 Spectral Size	65536

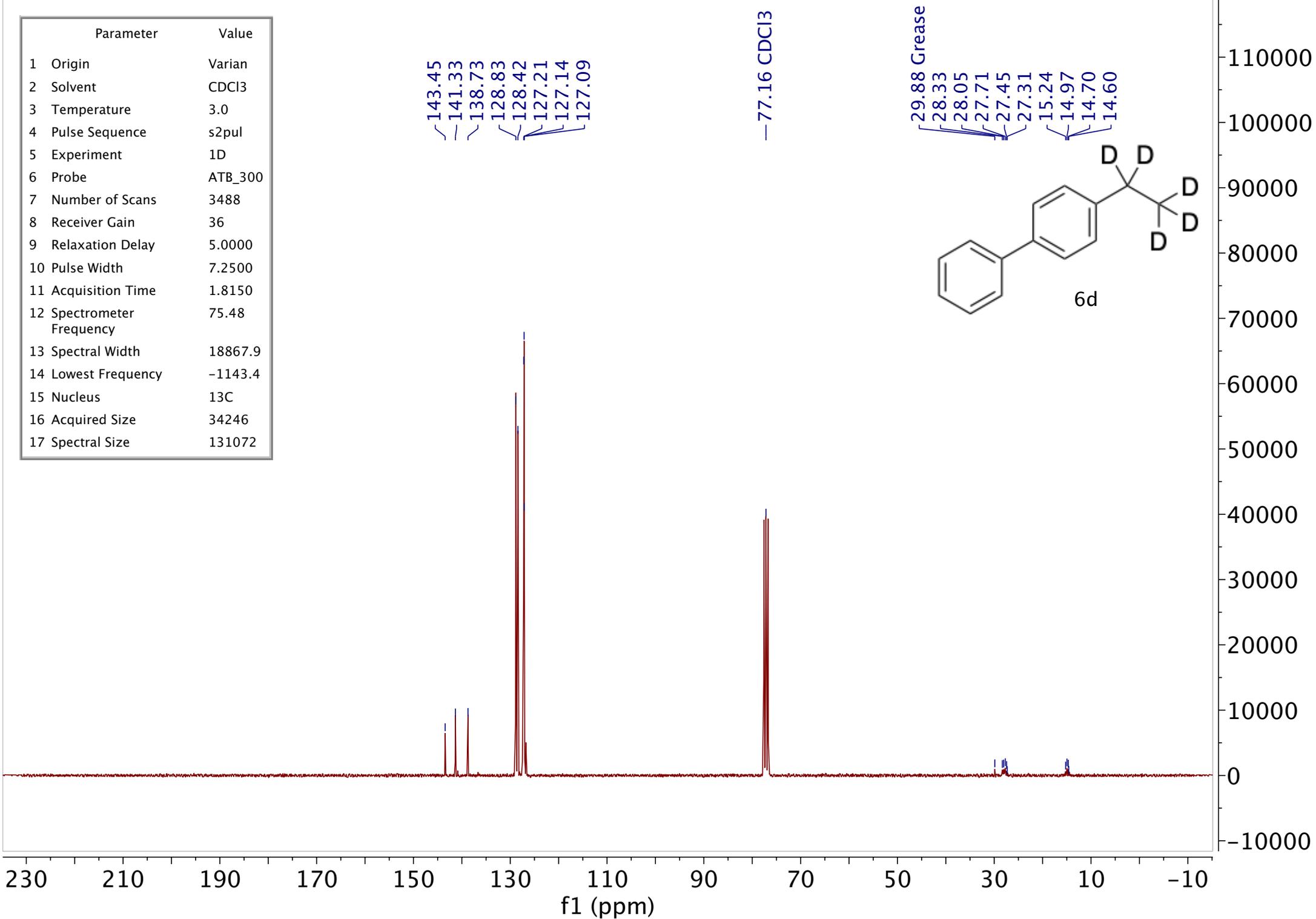




Parameter	Value
1 Origin	Varian
2 Solvent	cdcl3
3 Temperature	3.0
4 Pulse Sequence	s2pul
5 Experiment	1D
6 Probe	ASWPG8319
7 Number of Scans	128
8 Receiver Gain	30
9 Relaxation Delay	0.5000
10 Pulse Width	300.0000
11 Acquisition Time	1.1125
12 Spectrometer Frequency	61.36
13 Spectral Width	460.2
14 Lowest Frequency	-107.7
15 Nucleus	2H
16 Acquired Size	512
17 Spectral Size	1024



Parameter	Value
1 Origin	Varian
2 Solvent	CDCl3
3 Temperature	3.0
4 Pulse Sequence	s2pul
5 Experiment	1D
6 Probe	ATB_300
7 Number of Scans	3488
8 Receiver Gain	36
9 Relaxation Delay	5.0000
10 Pulse Width	7.2500
11 Acquisition Time	1.8150
12 Spectrometer Frequency	75.48
13 Spectral Width	18867.9
14 Lowest Frequency	-1143.4
15 Nucleus	13C
16 Acquired Size	34246
17 Spectral Size	131072



143.45  
141.33  
138.73  
128.83  
128.42  
127.21  
127.14  
127.09

77.16 CDCl3

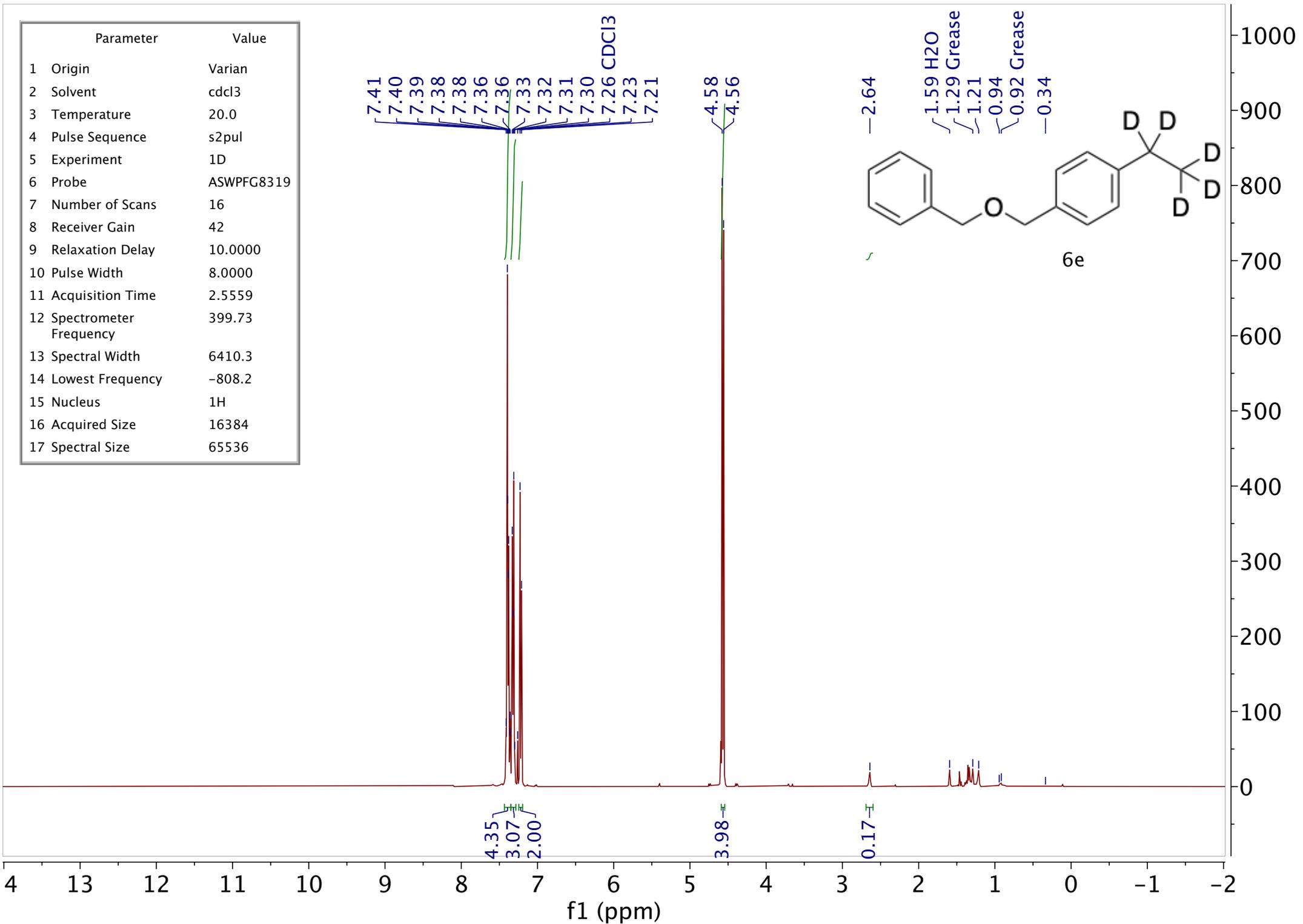
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6d

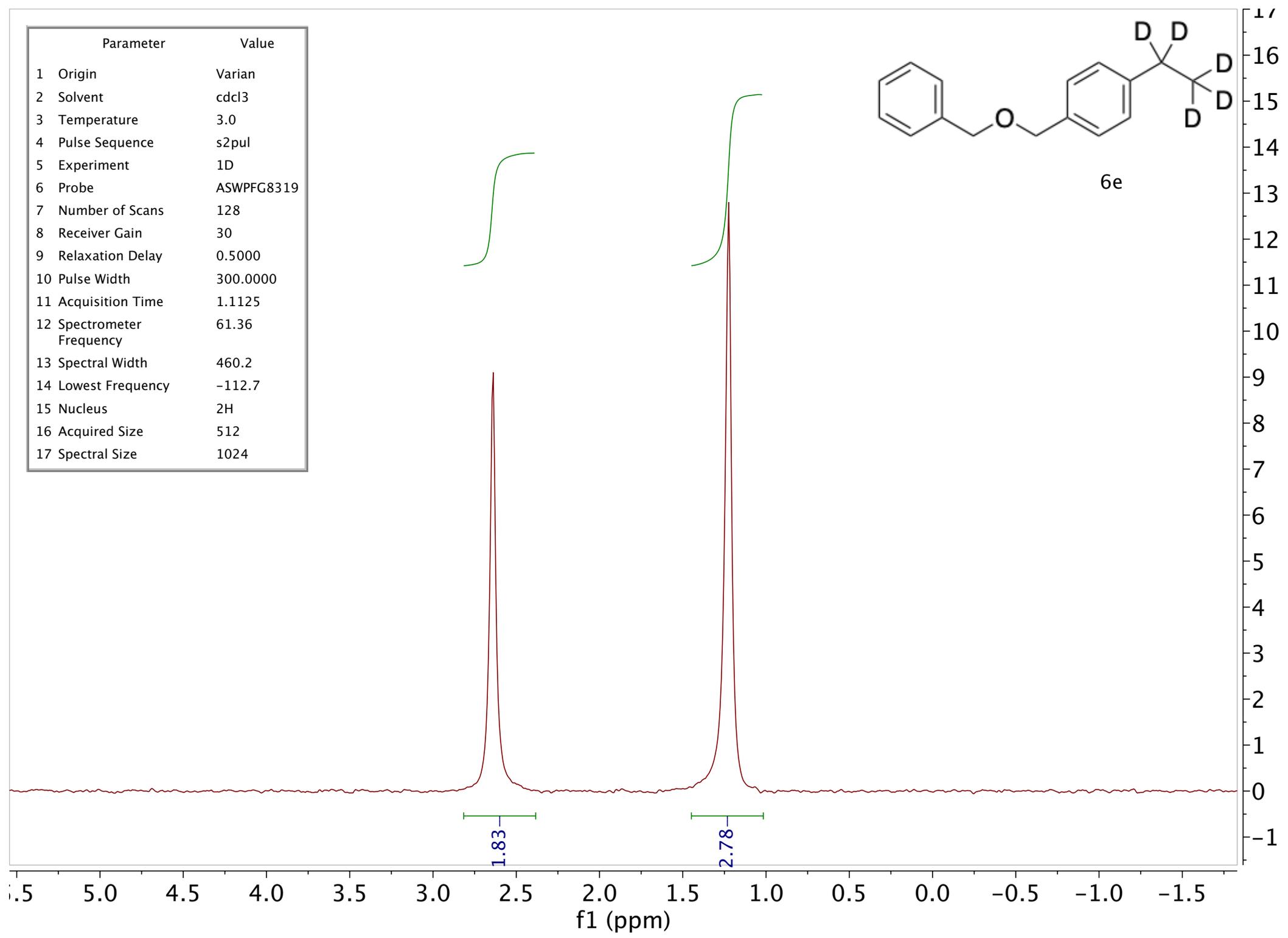
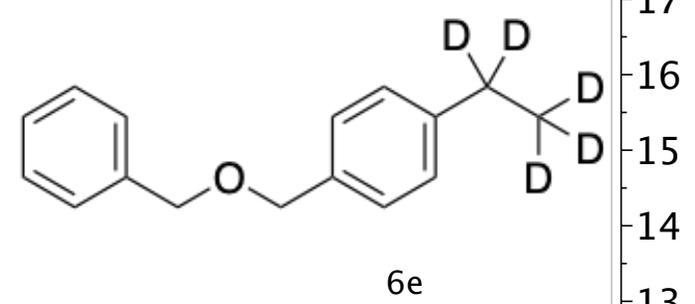
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f1 (ppm)

110000  
100000  
90000  
80000  
70000  
60000  
50000  
40000  
30000  
20000  
10000  
0  
-10000

Parameter	Value
1 Origin	Varian
2 Solvent	cdcl3
3 Temperature	20.0
4 Pulse Sequence	s2pul
5 Experiment	1D
6 Probe	ASWPG8319
7 Number of Scans	16
8 Receiver Gain	42
9 Relaxation Delay	10.0000
10 Pulse Width	8.0000
11 Acquisition Time	2.5559
12 Spectrometer Frequency	399.73
13 Spectral Width	6410.3
14 Lowest Frequency	-808.2
15 Nucleus	1H
16 Acquired Size	16384
17 Spectral Size	65536

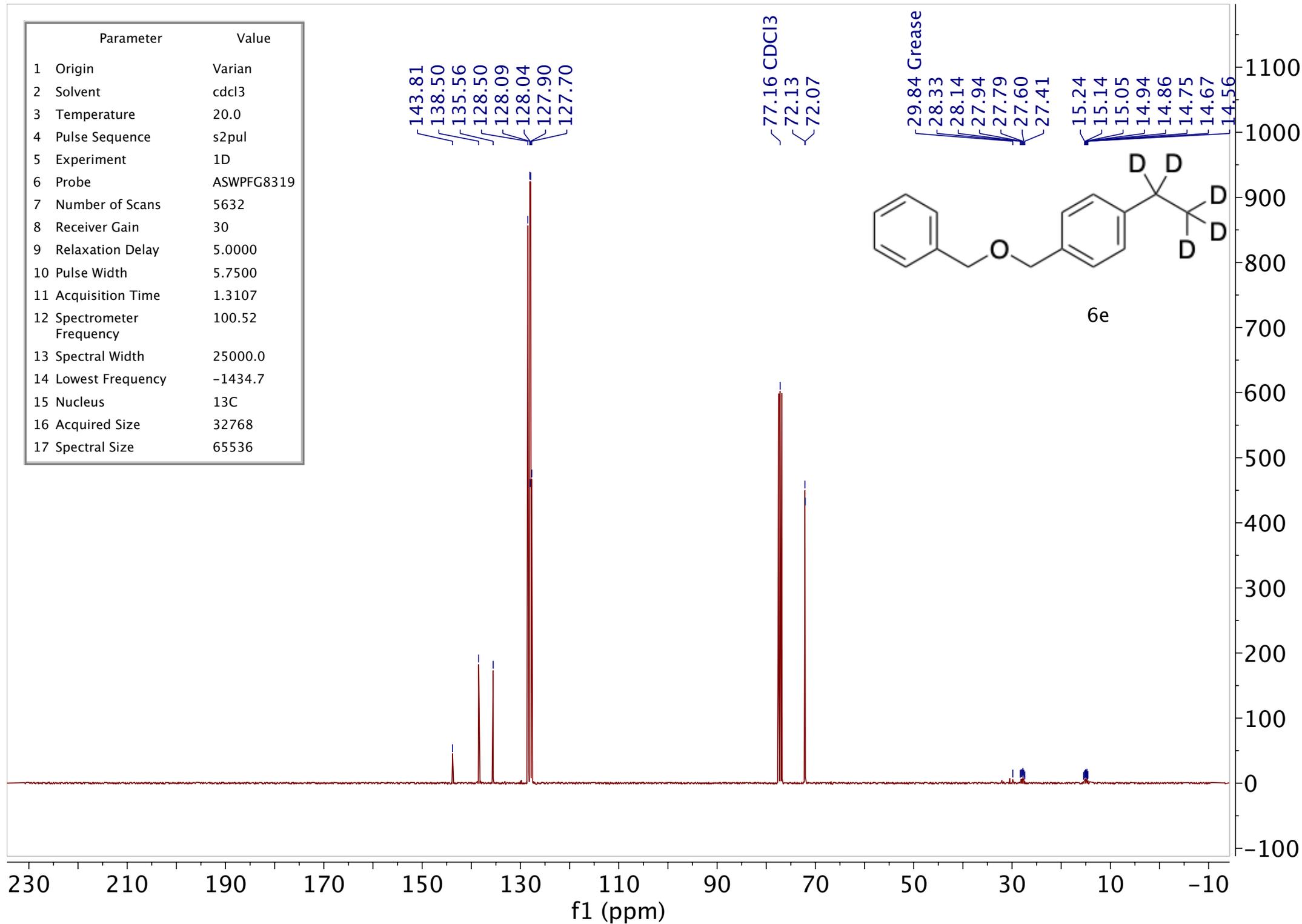


Parameter	Value
1 Origin	Varian
2 Solvent	cdcl3
3 Temperature	3.0
4 Pulse Sequence	s2pul
5 Experiment	1D
6 Probe	ASWPG8319
7 Number of Scans	128
8 Receiver Gain	30
9 Relaxation Delay	0.5000
10 Pulse Width	300.0000
11 Acquisition Time	1.1125
12 Spectrometer Frequency	61.36
13 Spectral Width	460.2
14 Lowest Frequency	-112.7
15 Nucleus	2H
16 Acquired Size	512
17 Spectral Size	1024

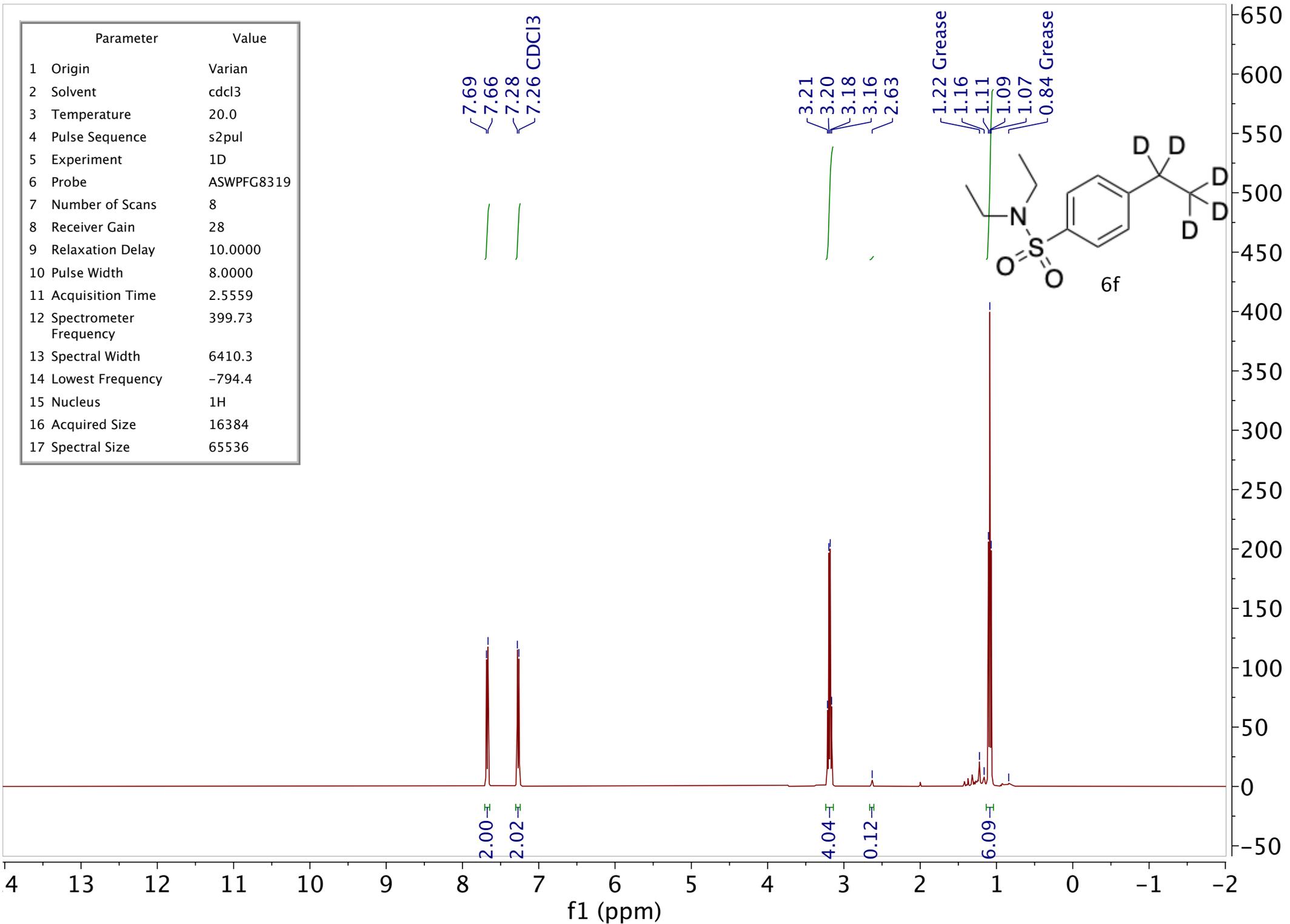


f1 (ppm)

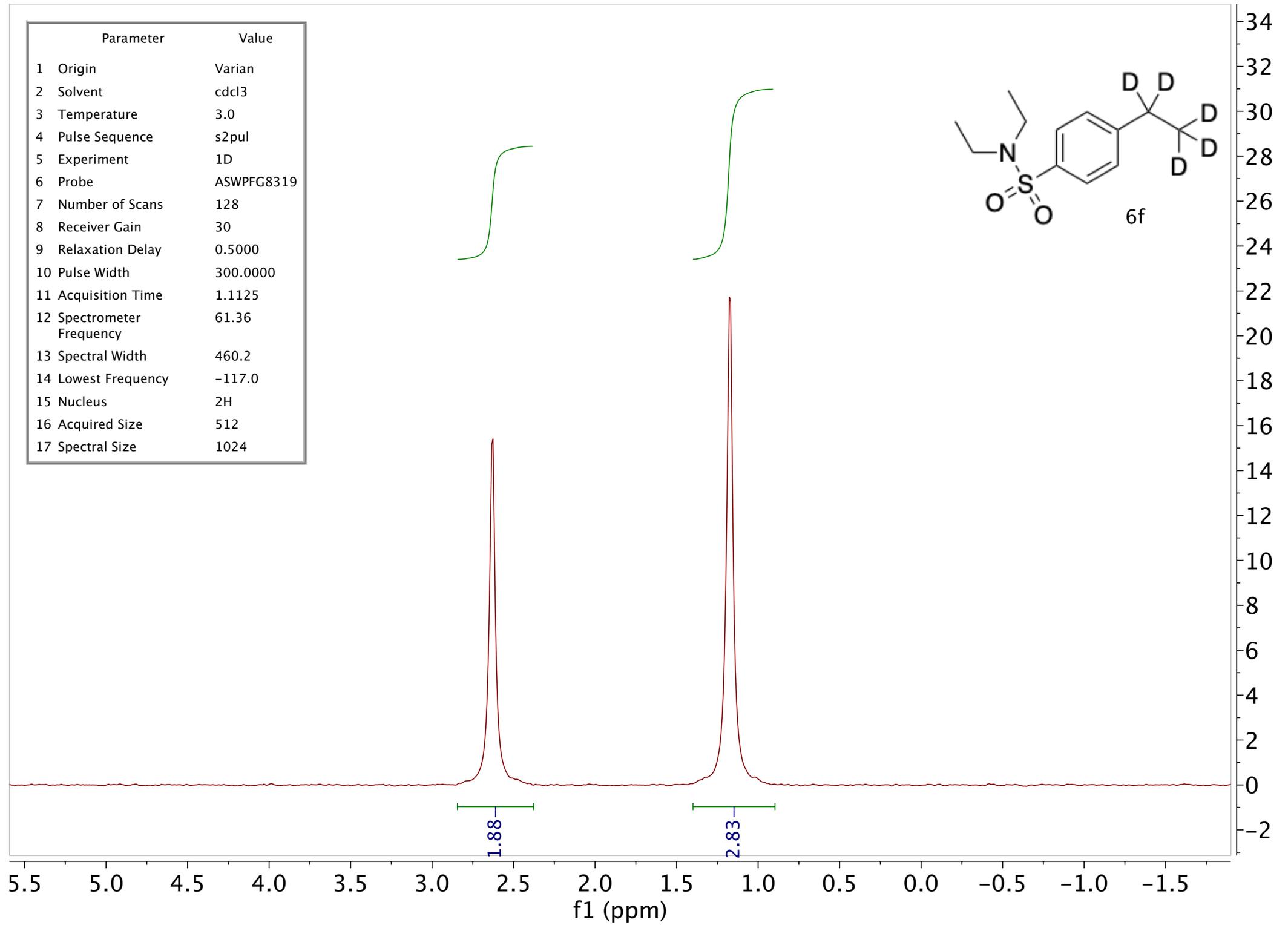
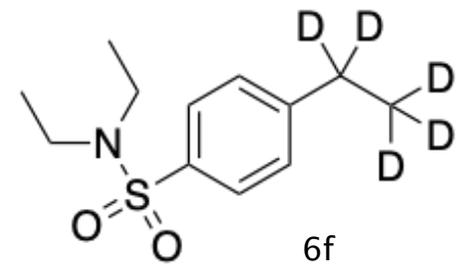
Parameter	Value
1 Origin	Varian
2 Solvent	cdcl3
3 Temperature	20.0
4 Pulse Sequence	s2pul
5 Experiment	1D
6 Probe	ASWPFG8319
7 Number of Scans	5632
8 Receiver Gain	30
9 Relaxation Delay	5.0000
10 Pulse Width	5.7500
11 Acquisition Time	1.3107
12 Spectrometer Frequency	100.52
13 Spectral Width	25000.0
14 Lowest Frequency	-1434.7
15 Nucleus	13C
16 Acquired Size	32768
17 Spectral Size	65536



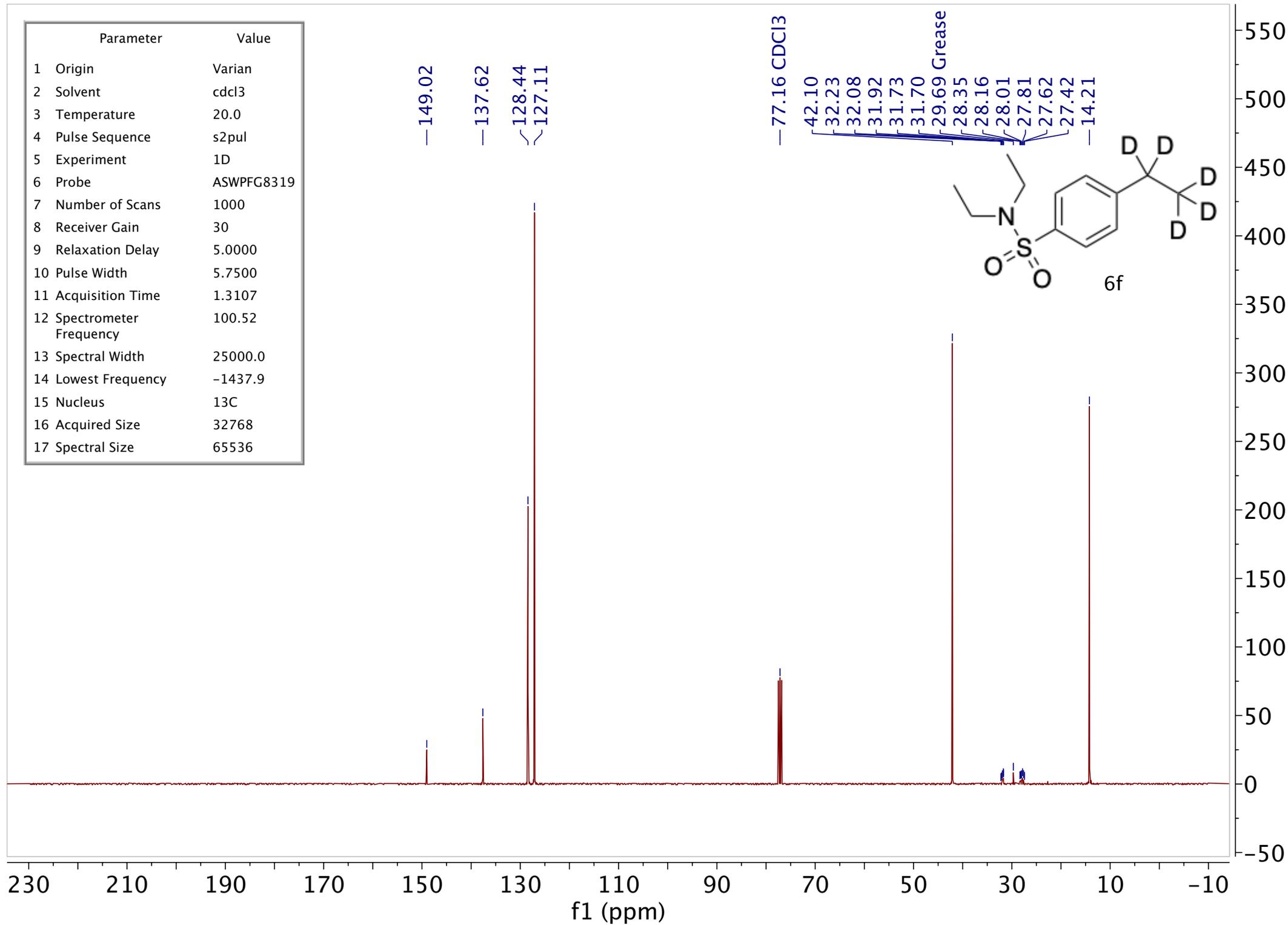
Parameter	Value
1 Origin	Varian
2 Solvent	cdcl3
3 Temperature	20.0
4 Pulse Sequence	s2pul
5 Experiment	1D
6 Probe	ASWPG8319
7 Number of Scans	8
8 Receiver Gain	28
9 Relaxation Delay	10.0000
10 Pulse Width	8.0000
11 Acquisition Time	2.5559
12 Spectrometer Frequency	399.73
13 Spectral Width	6410.3
14 Lowest Frequency	-794.4
15 Nucleus	1H
16 Acquired Size	16384
17 Spectral Size	65536



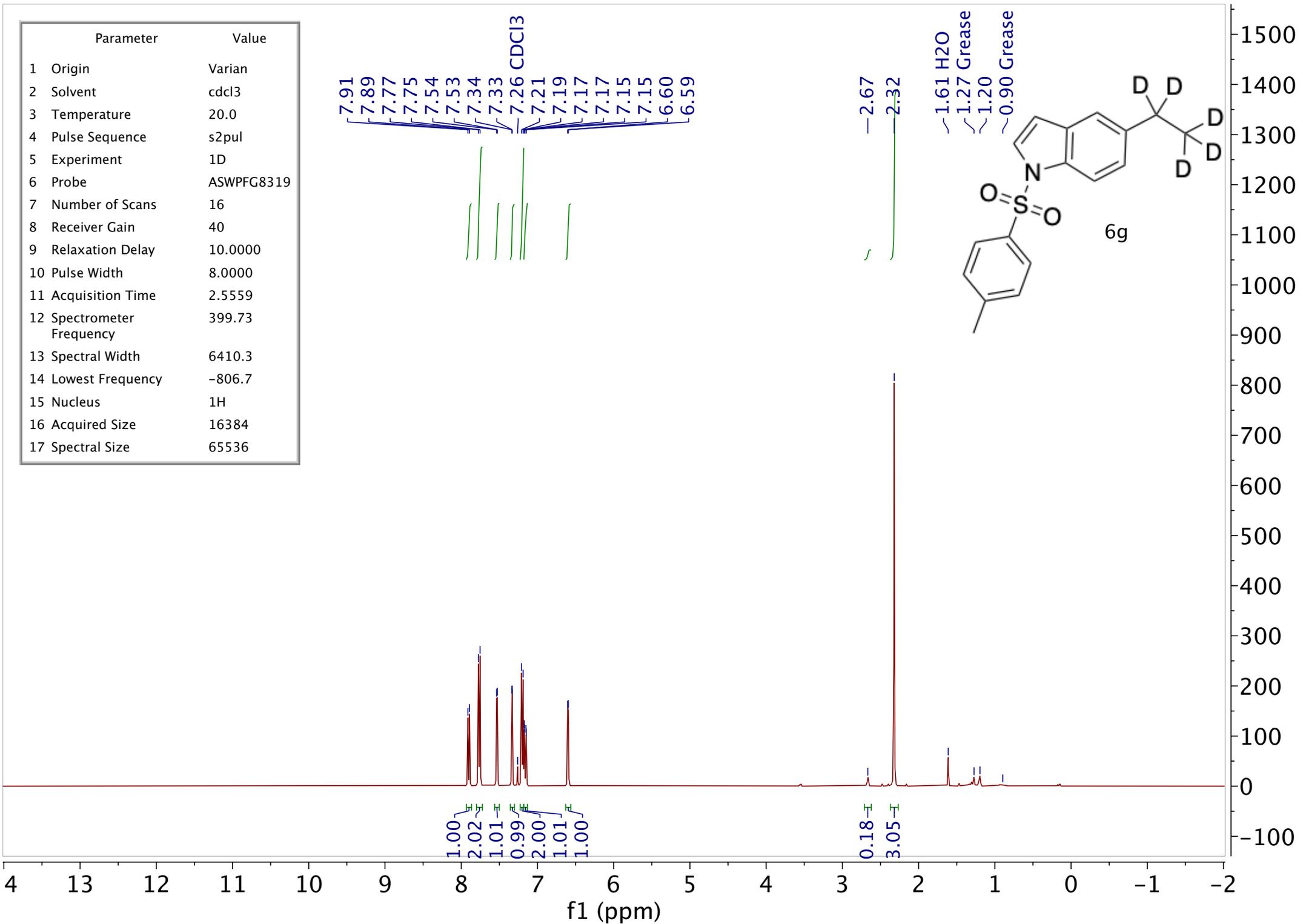
Parameter	Value
1 Origin	Varian
2 Solvent	cdcl3
3 Temperature	3.0
4 Pulse Sequence	s2pul
5 Experiment	1D
6 Probe	ASWPG8319
7 Number of Scans	128
8 Receiver Gain	30
9 Relaxation Delay	0.5000
10 Pulse Width	300.0000
11 Acquisition Time	1.1125
12 Spectrometer Frequency	61.36
13 Spectral Width	460.2
14 Lowest Frequency	-117.0
15 Nucleus	2H
16 Acquired Size	512
17 Spectral Size	1024



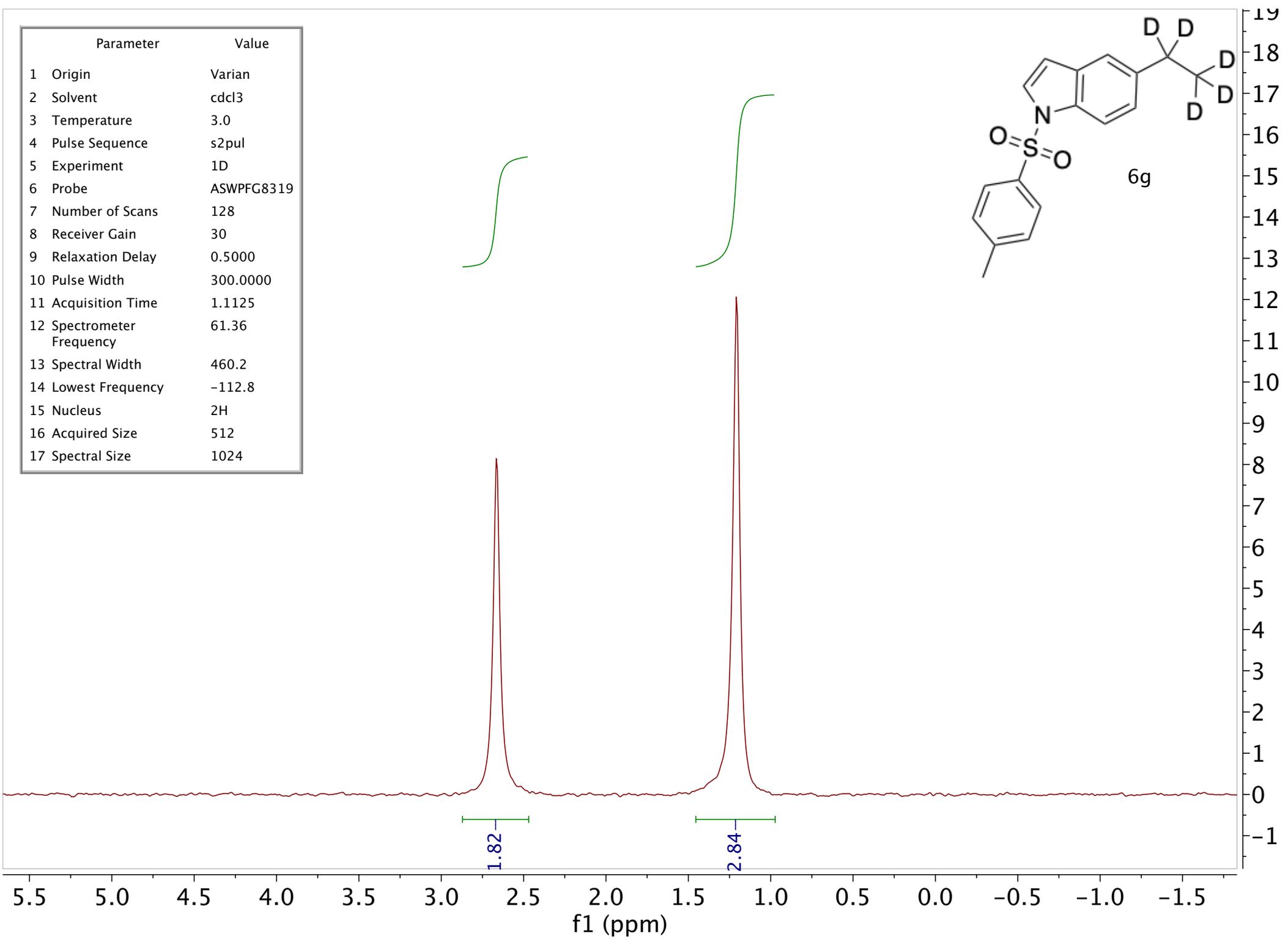
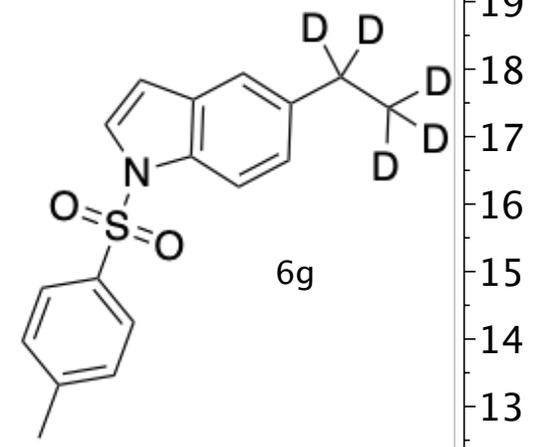
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1 Origin	Varian
2 Solvent	cdcl3
3 Temperature	20.0
4 Pulse Sequence	s2pul
5 Experiment	1D
6 Probe	ASWPFG8319
7 Number of Scans	1000
8 Receiver Gain	30
9 Relaxation Delay	5.0000
10 Pulse Width	5.7500
11 Acquisition Time	1.3107
12 Spectrometer Frequency	100.52
13 Spectral Width	25000.0
14 Lowest Frequency	-1437.9
15 Nucleus	13C
16 Acquired Size	32768
17 Spectral Size	65536



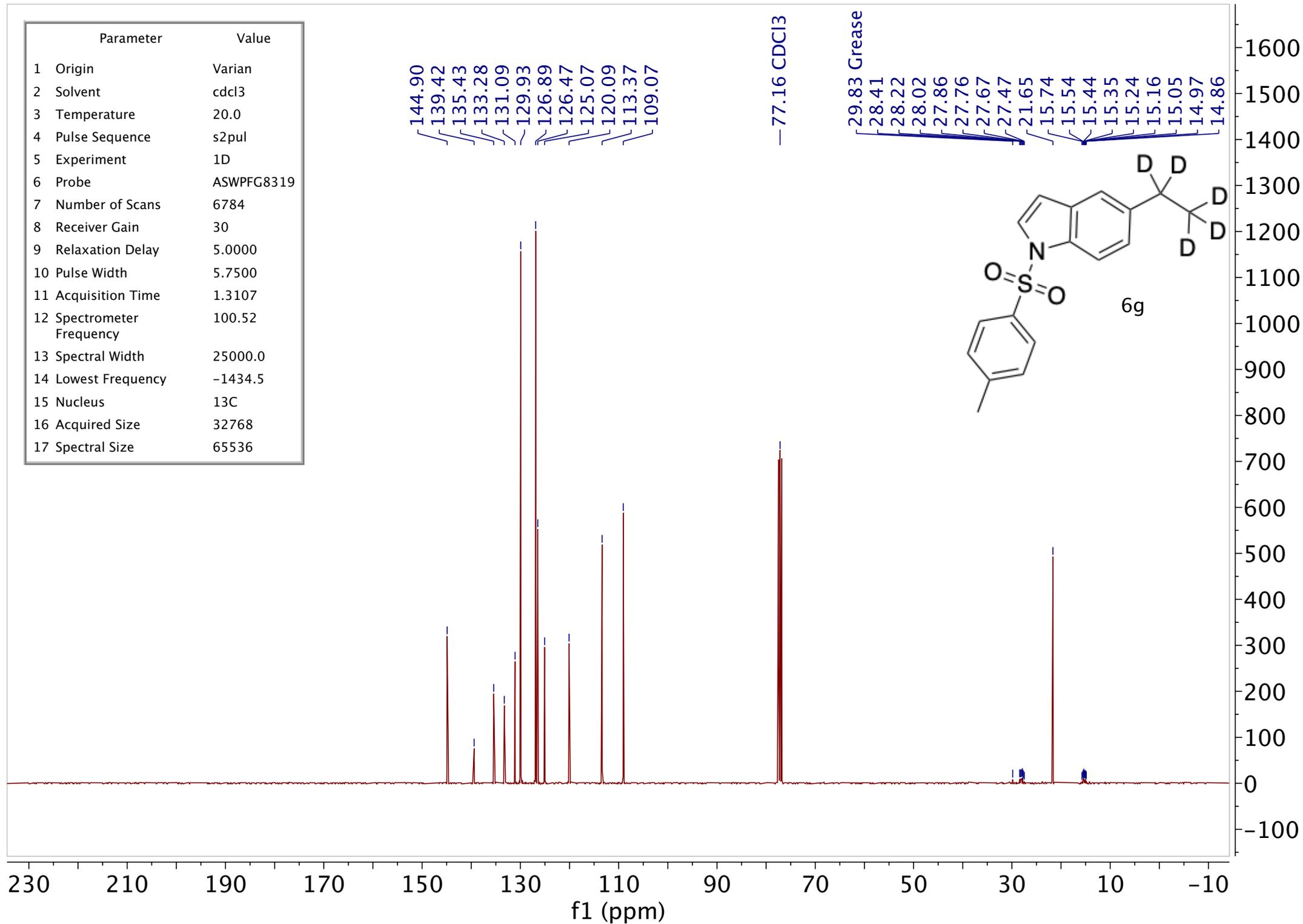
Parameter	Value
1 Origin	Varian
2 Solvent	cdcl3
3 Temperature	20.0
4 Pulse Sequence	s2pul
5 Experiment	1D
6 Probe	ASWPG8319
7 Number of Scans	16
8 Receiver Gain	40
9 Relaxation Delay	10.0000
10 Pulse Width	8.0000
11 Acquisition Time	2.5559
12 Spectrometer Frequency	399.73
13 Spectral Width	6410.3
14 Lowest Frequency	-806.7
15 Nucleus	1H
16 Acquired Size	16384
17 Spectral Size	65536



Parameter	Value
1 Origin	Varian
2 Solvent	cdcl3
3 Temperature	3.0
4 Pulse Sequence	s2pul
5 Experiment	1D
6 Probe	ASWPG8319
7 Number of Scans	128
8 Receiver Gain	30
9 Relaxation Delay	0.5000
10 Pulse Width	300.0000
11 Acquisition Time	1.1125
12 Spectrometer Frequency	61.36
13 Spectral Width	460.2
14 Lowest Frequency	-112.8
15 Nucleus	2H
16 Acquired Size	512
17 Spectral Size	1024



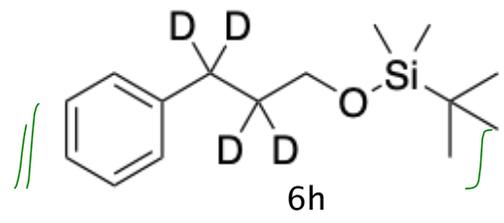
Parameter	Value
1 Origin	Varian
2 Solvent	cdcl3
3 Temperature	20.0
4 Pulse Sequence	s2pul
5 Experiment	1D
6 Probe	ASWPG8319
7 Number of Scans	6784
8 Receiver Gain	30
9 Relaxation Delay	5.0000
10 Pulse Width	5.7500
11 Acquisition Time	1.3107
12 Spectrometer Frequency	100.52
13 Spectral Width	25000.0
14 Lowest Frequency	-1434.5
15 Nucleus	<sup>13</sup> C
16 Acquired Size	32768
17 Spectral Size	65536



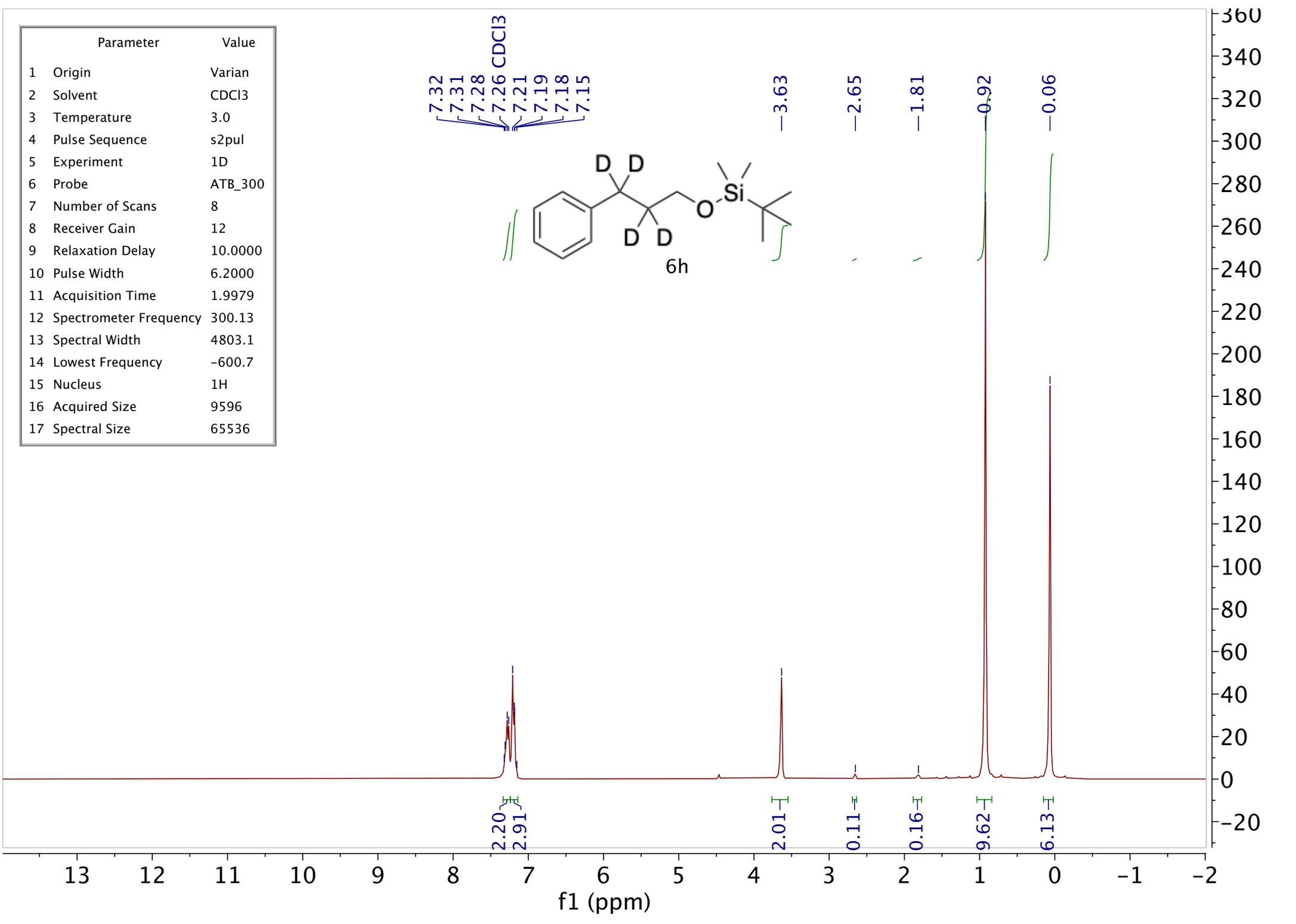
Parameter	Value
1 Origin	Varian
2 Solvent	CDCl3
3 Temperature	3.0
4 Pulse Sequence	s2pul
5 Experiment	1D
6 Probe	ATB_300
7 Number of Scans	8
8 Receiver Gain	12
9 Relaxation Delay	10.0000
10 Pulse Width	6.2000
11 Acquisition Time	1.9979
12 Spectrometer Frequency	300.13
13 Spectral Width	4803.1
14 Lowest Frequency	-600.7
15 Nucleus	1H
16 Acquired Size	9596
17 Spectral Size	65536

7.32  
7.31  
7.28  
7.26  
7.21  
7.19  
7.18  
7.15

CDCl3



3.63  
2.65  
1.81  
0.92  
0.06

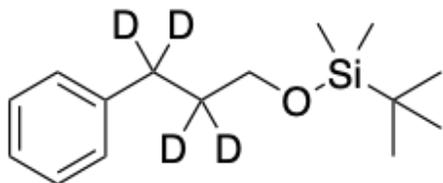


2.20  
2.91  
2.01  
0.11  
0.16  
9.62  
6.13

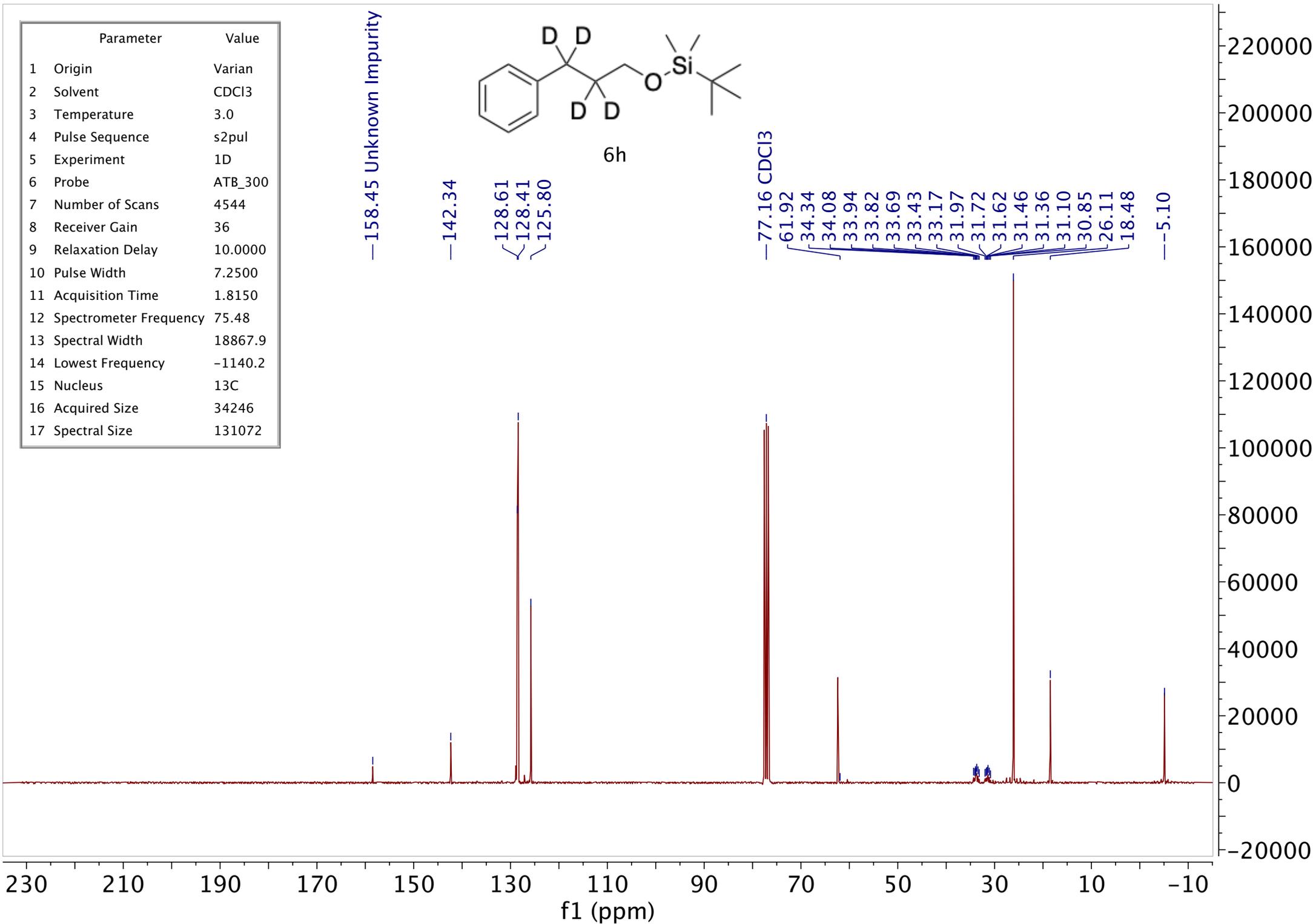
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f1 (ppm)

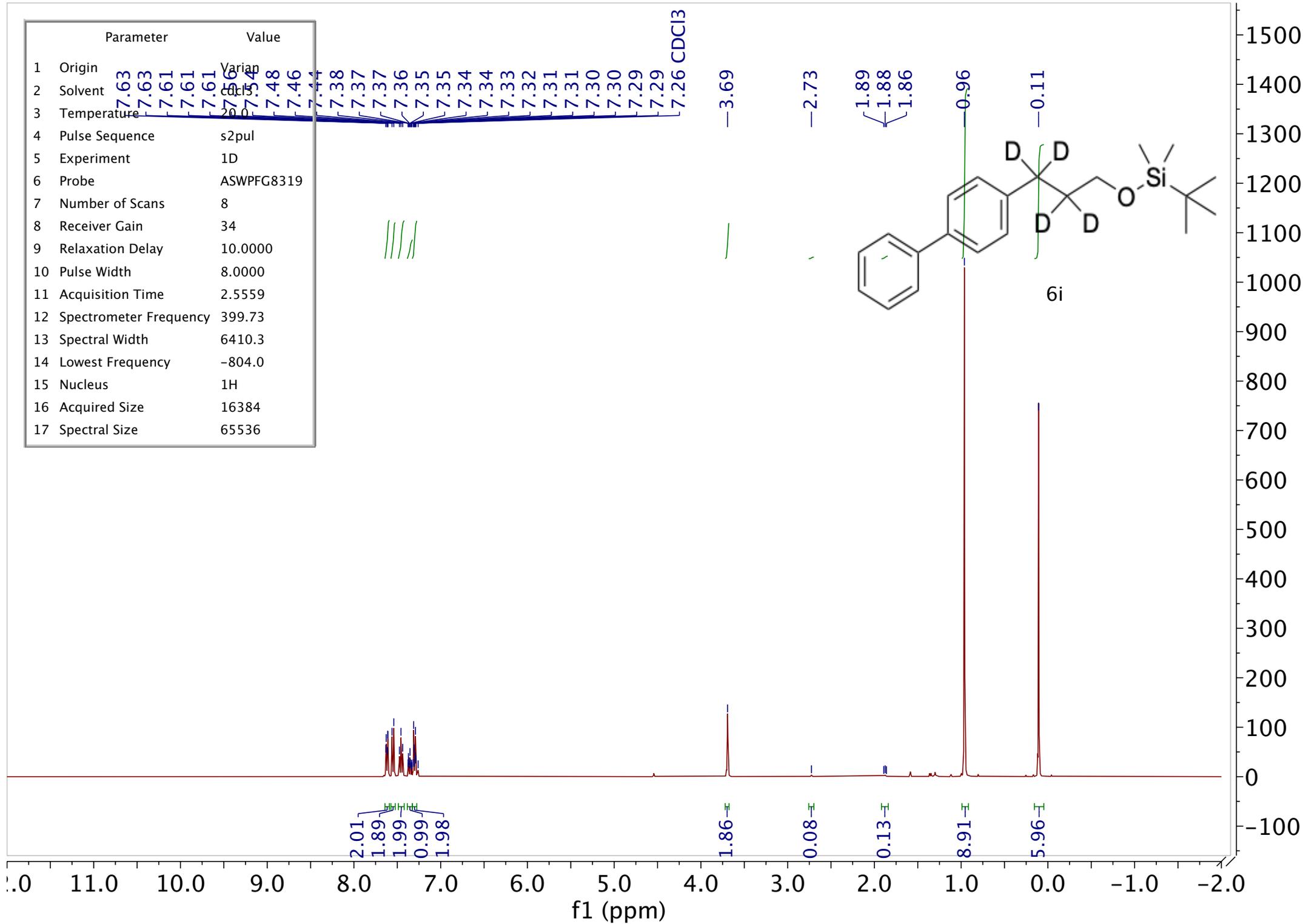
Parameter	Value
1 Origin	Varian
2 Solvent	CDCl3
3 Temperature	3.0
4 Pulse Sequence	s2pul
5 Experiment	1D
6 Probe	ATB_300
7 Number of Scans	4544
8 Receiver Gain	36
9 Relaxation Delay	10.0000
10 Pulse Width	7.2500
11 Acquisition Time	1.8150
12 Spectrometer Frequency	75.48
13 Spectral Width	18867.9
14 Lowest Frequency	-1140.2
15 Nucleus	13C
16 Acquired Size	34246
17 Spectral Size	131072



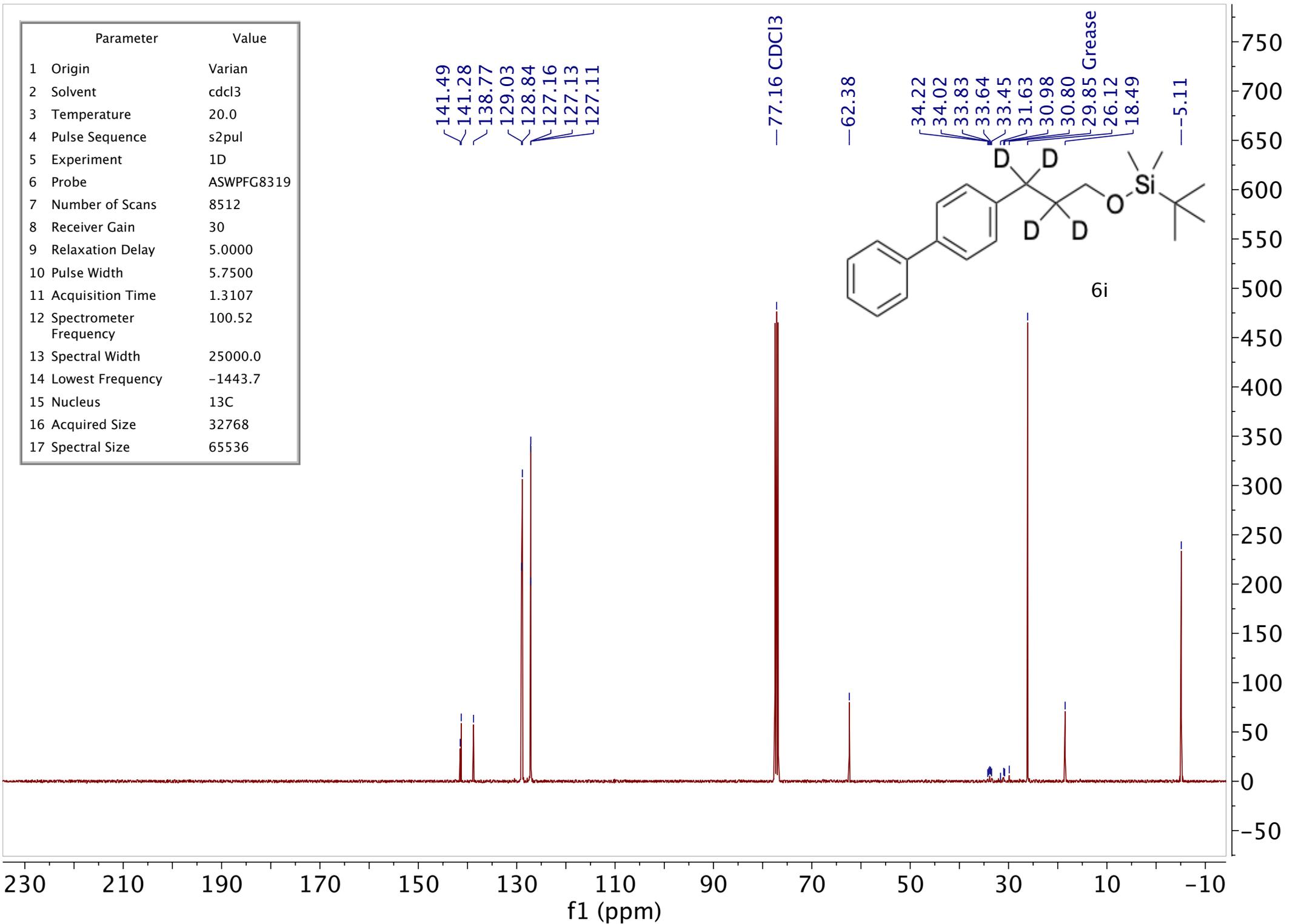
6h



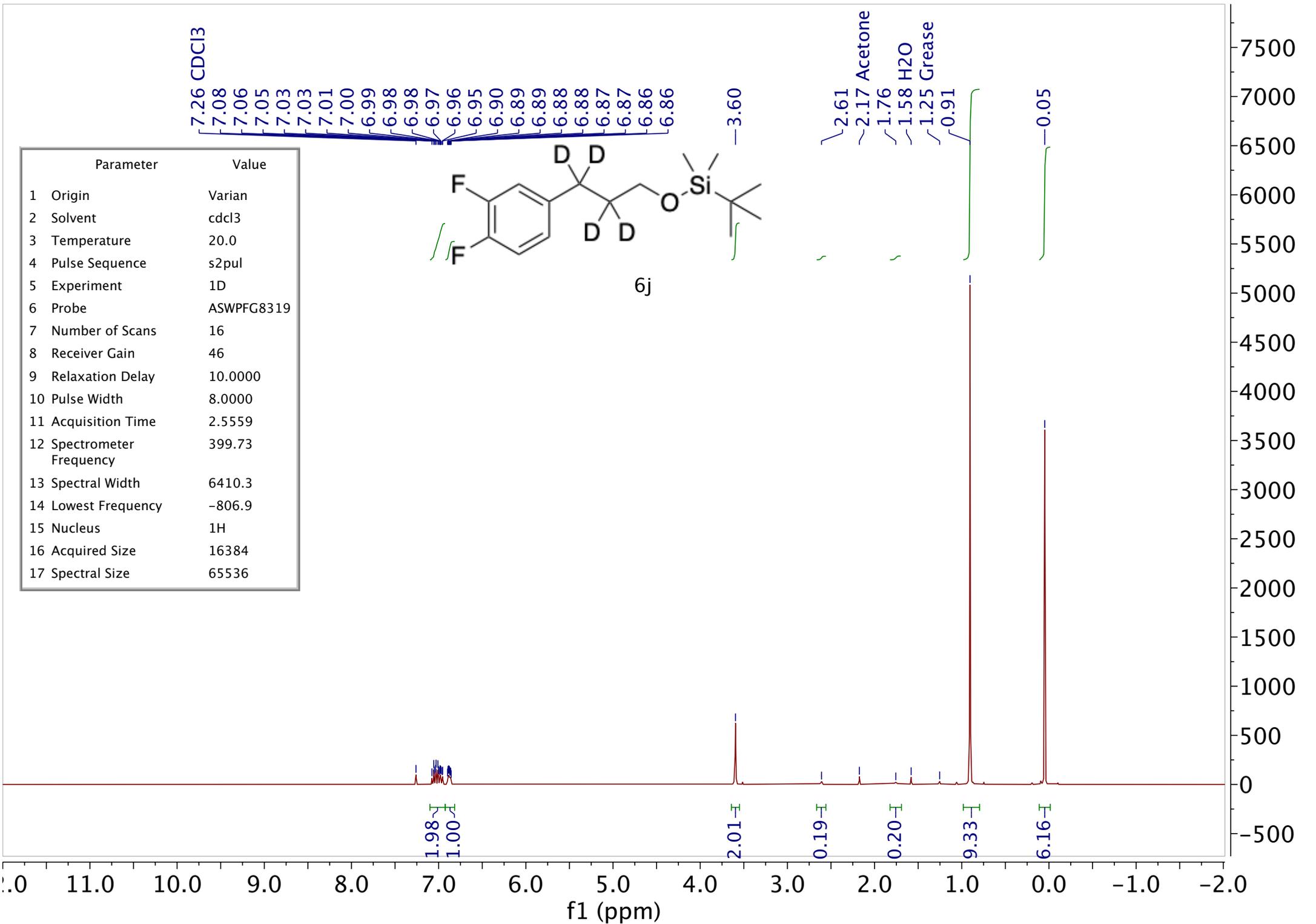
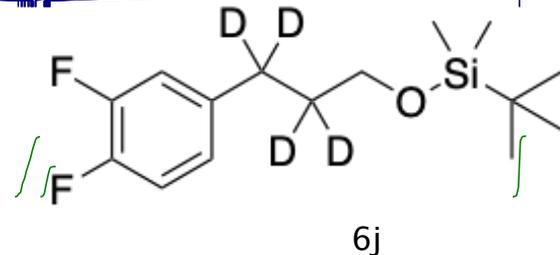
Parameter	Value
1 Origin	Varian
2 Solvent	CDCl3
3 Temperature	29.0
4 Pulse Sequence	s2pul
5 Experiment	1D
6 Probe	ASWPFG8319
7 Number of Scans	8
8 Receiver Gain	34
9 Relaxation Delay	10.0000
10 Pulse Width	8.0000
11 Acquisition Time	2.5559
12 Spectrometer Frequency	399.73
13 Spectral Width	6410.3
14 Lowest Frequency	-804.0
15 Nucleus	1H
16 Acquired Size	16384
17 Spectral Size	65536

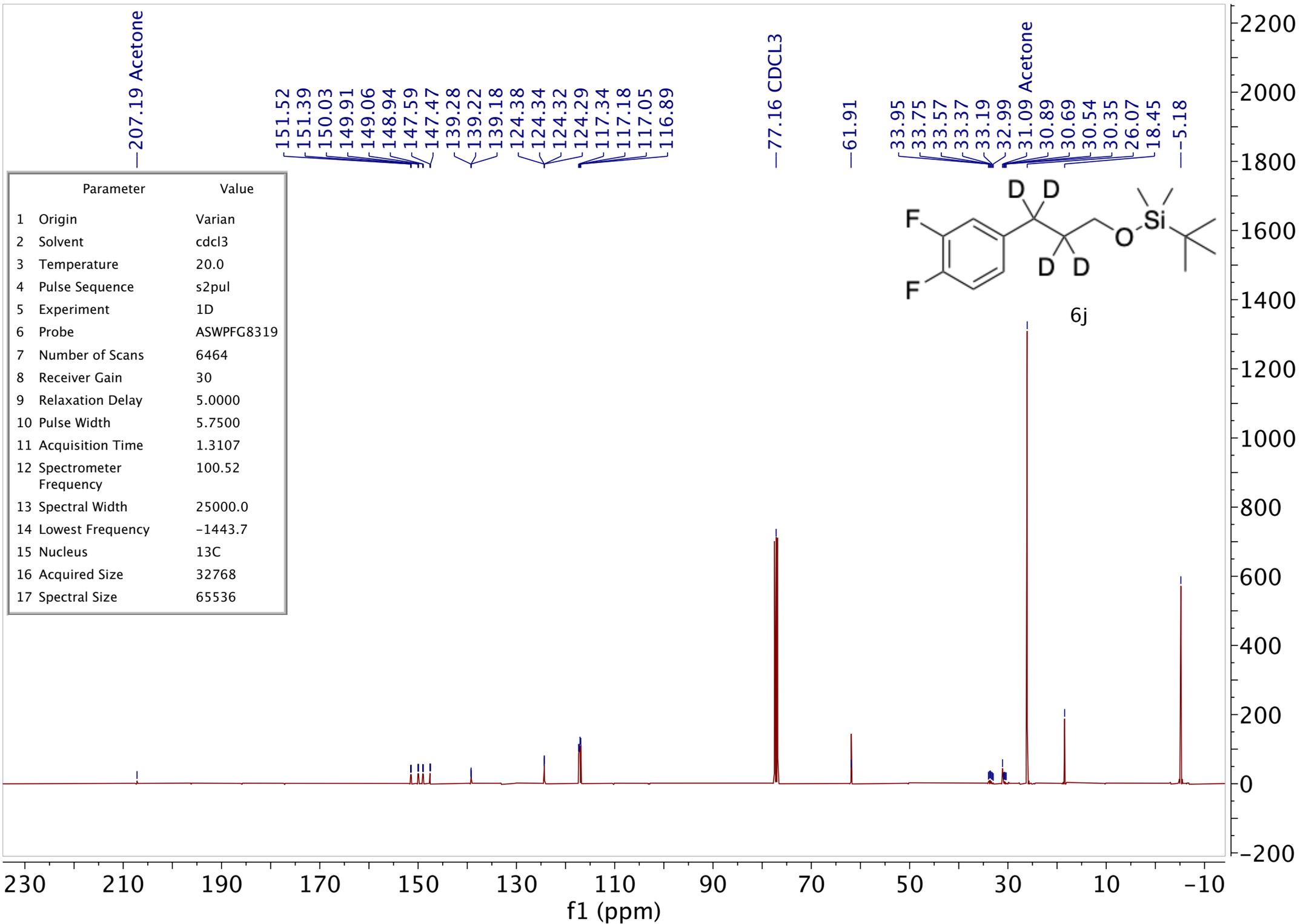


Parameter	Value
1 Origin	Varian
2 Solvent	cdcl3
3 Temperature	20.0
4 Pulse Sequence	s2pul
5 Experiment	1D
6 Probe	ASWPFG8319
7 Number of Scans	8512
8 Receiver Gain	30
9 Relaxation Delay	5.0000
10 Pulse Width	5.7500
11 Acquisition Time	1.3107
12 Spectrometer Frequency	100.52
13 Spectral Width	25000.0
14 Lowest Frequency	-1443.7
15 Nucleus	13C
16 Acquired Size	32768
17 Spectral Size	65536



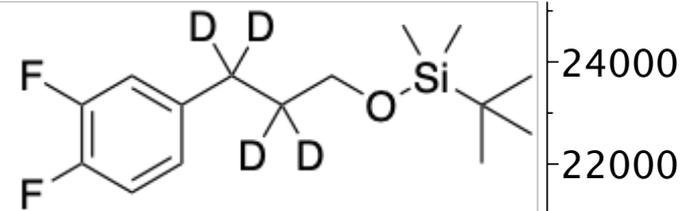
Parameter	Value
1 Origin	Varian
2 Solvent	cdcl3
3 Temperature	20.0
4 Pulse Sequence	s2pul
5 Experiment	1D
6 Probe	ASWPF8319
7 Number of Scans	16
8 Receiver Gain	46
9 Relaxation Delay	10.0000
10 Pulse Width	8.0000
11 Acquisition Time	2.5559
12 Spectrometer Frequency	399.73
13 Spectral Width	6410.3
14 Lowest Frequency	-806.9
15 Nucleus	1H
16 Acquired Size	16384
17 Spectral Size	65536



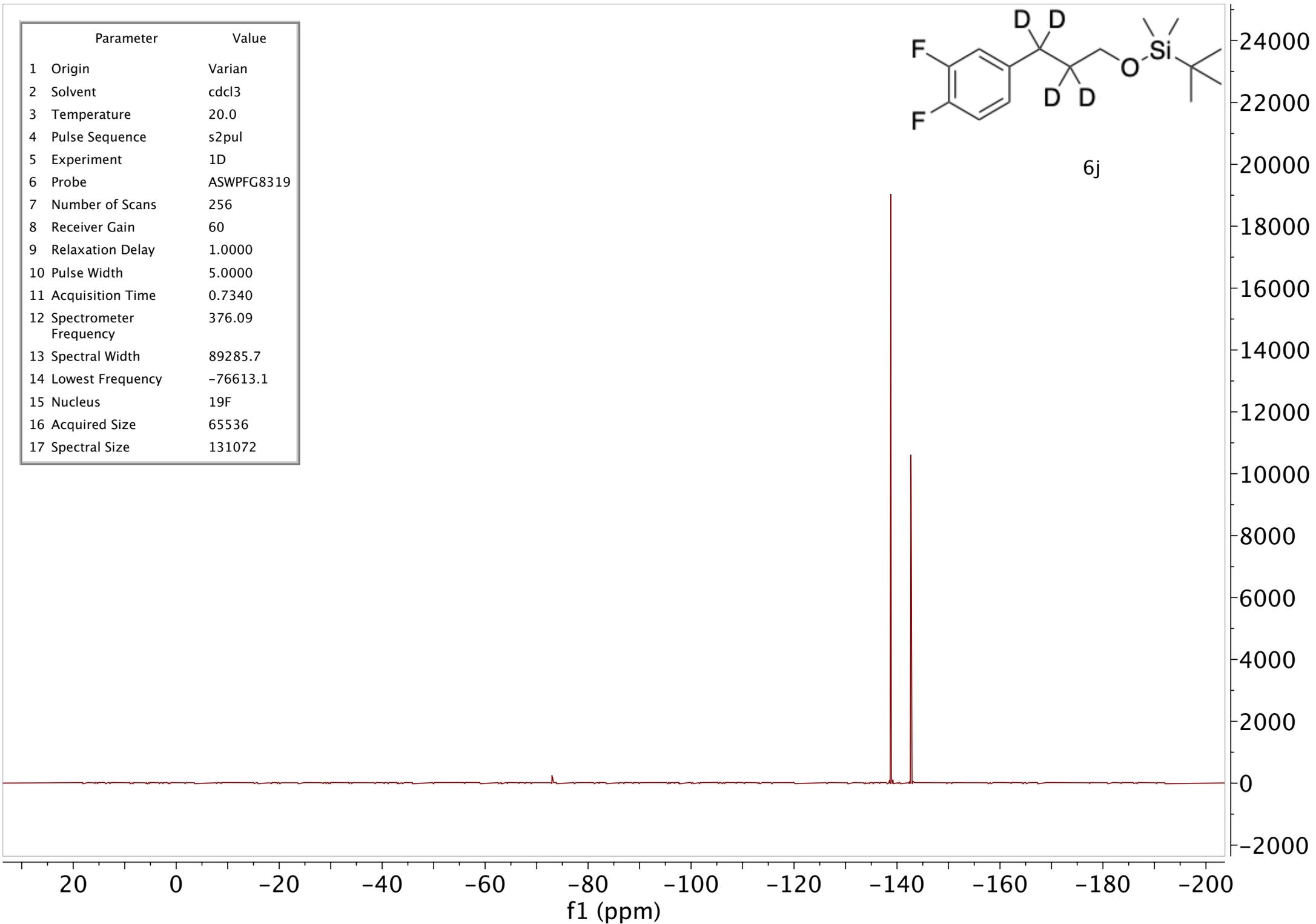


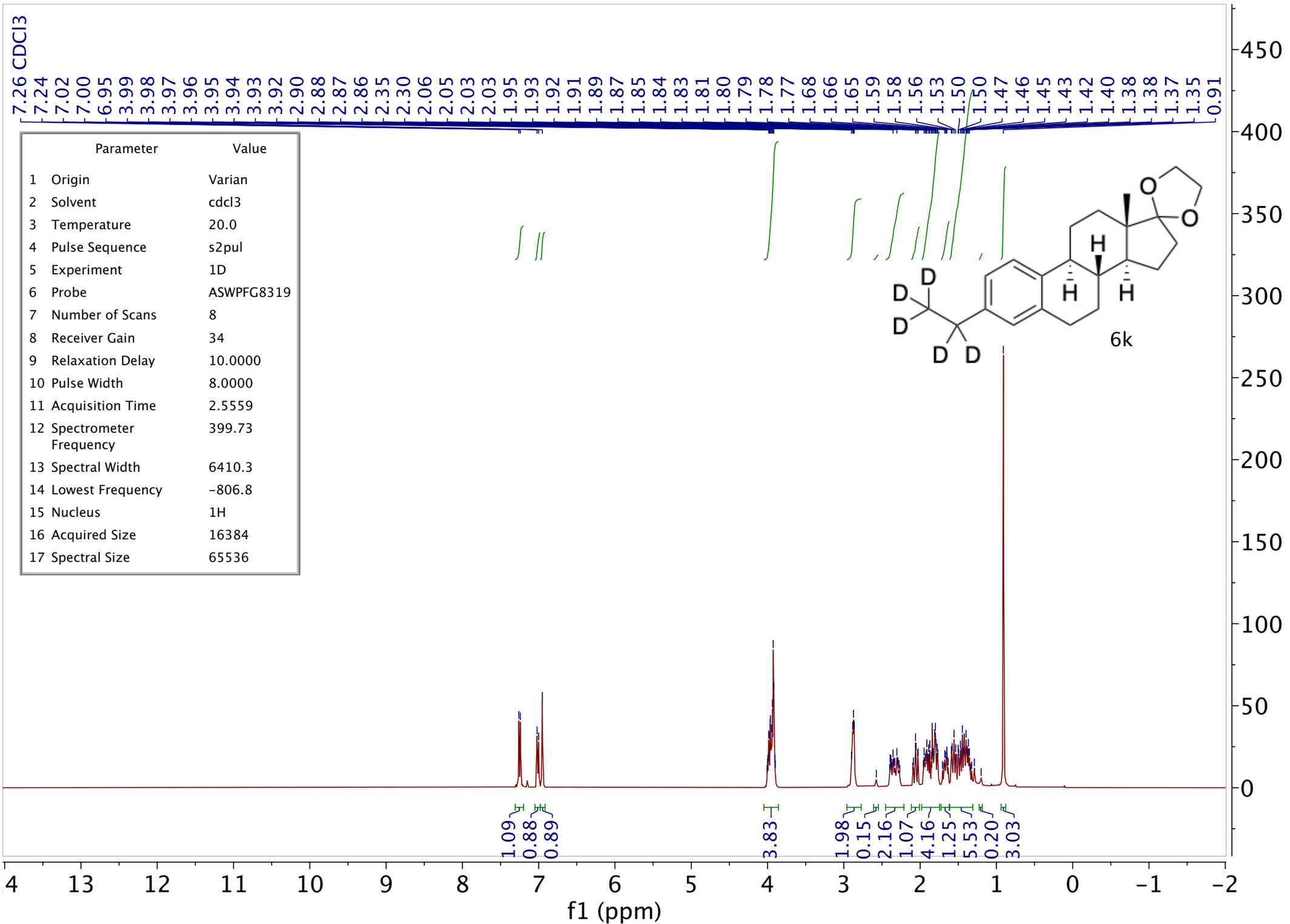
Parameter	Value
1 Origin	Varian
2 Solvent	cdcl3
3 Temperature	20.0
4 Pulse Sequence	s2pul
5 Experiment	1D
6 Probe	ASWPFG8319
7 Number of Scans	6464
8 Receiver Gain	30
9 Relaxation Delay	5.0000
10 Pulse Width	5.7500
11 Acquisition Time	1.3107
12 Spectrometer Frequency	100.52
13 Spectral Width	25000.0
14 Lowest Frequency	-1443.7
15 Nucleus	13C
16 Acquired Size	32768
17 Spectral Size	65536

Parameter	Value
1 Origin	Varian
2 Solvent	cdcl3
3 Temperature	20.0
4 Pulse Sequence	s2pul
5 Experiment	1D
6 Probe	ASWPG8319
7 Number of Scans	256
8 Receiver Gain	60
9 Relaxation Delay	1.0000
10 Pulse Width	5.0000
11 Acquisition Time	0.7340
12 Spectrometer Frequency	376.09
13 Spectral Width	89285.7
14 Lowest Frequency	-76613.1
15 Nucleus	19F
16 Acquired Size	65536
17 Spectral Size	131072

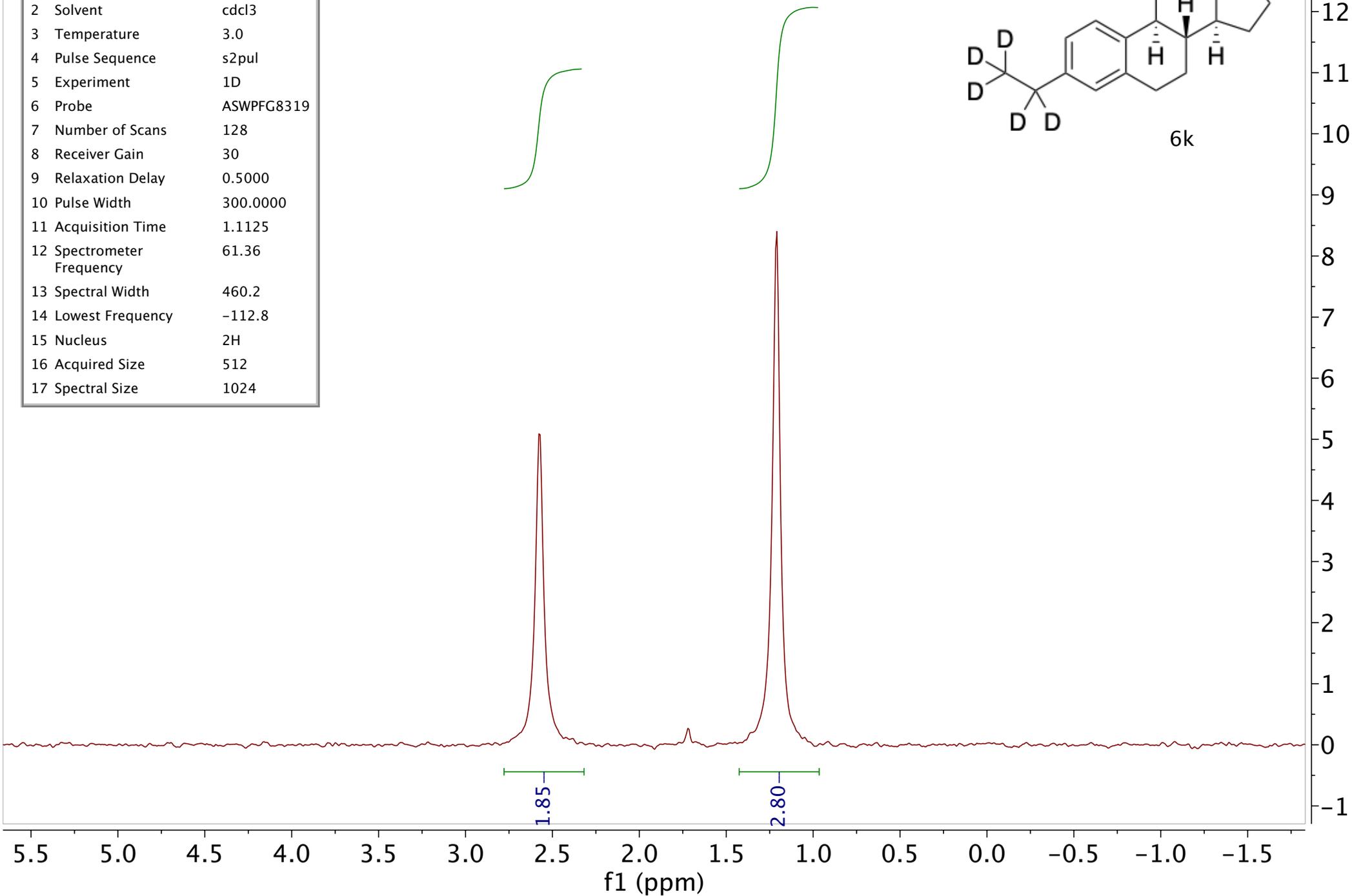
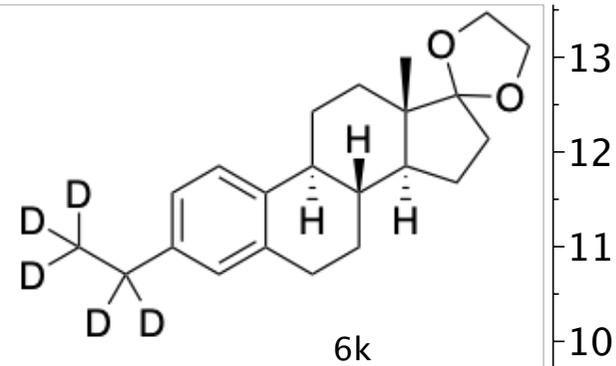


6j





Parameter	Value
1 Origin	Varian
2 Solvent	cdcl3
3 Temperature	3.0
4 Pulse Sequence	s2pul
5 Experiment	1D
6 Probe	ASWPG8319
7 Number of Scans	128
8 Receiver Gain	30
9 Relaxation Delay	0.5000
10 Pulse Width	300.0000
11 Acquisition Time	1.1125
12 Spectrometer Frequency	61.36
13 Spectral Width	460.2
14 Lowest Frequency	-112.8
15 Nucleus	2H
16 Acquired Size	512
17 Spectral Size	1024



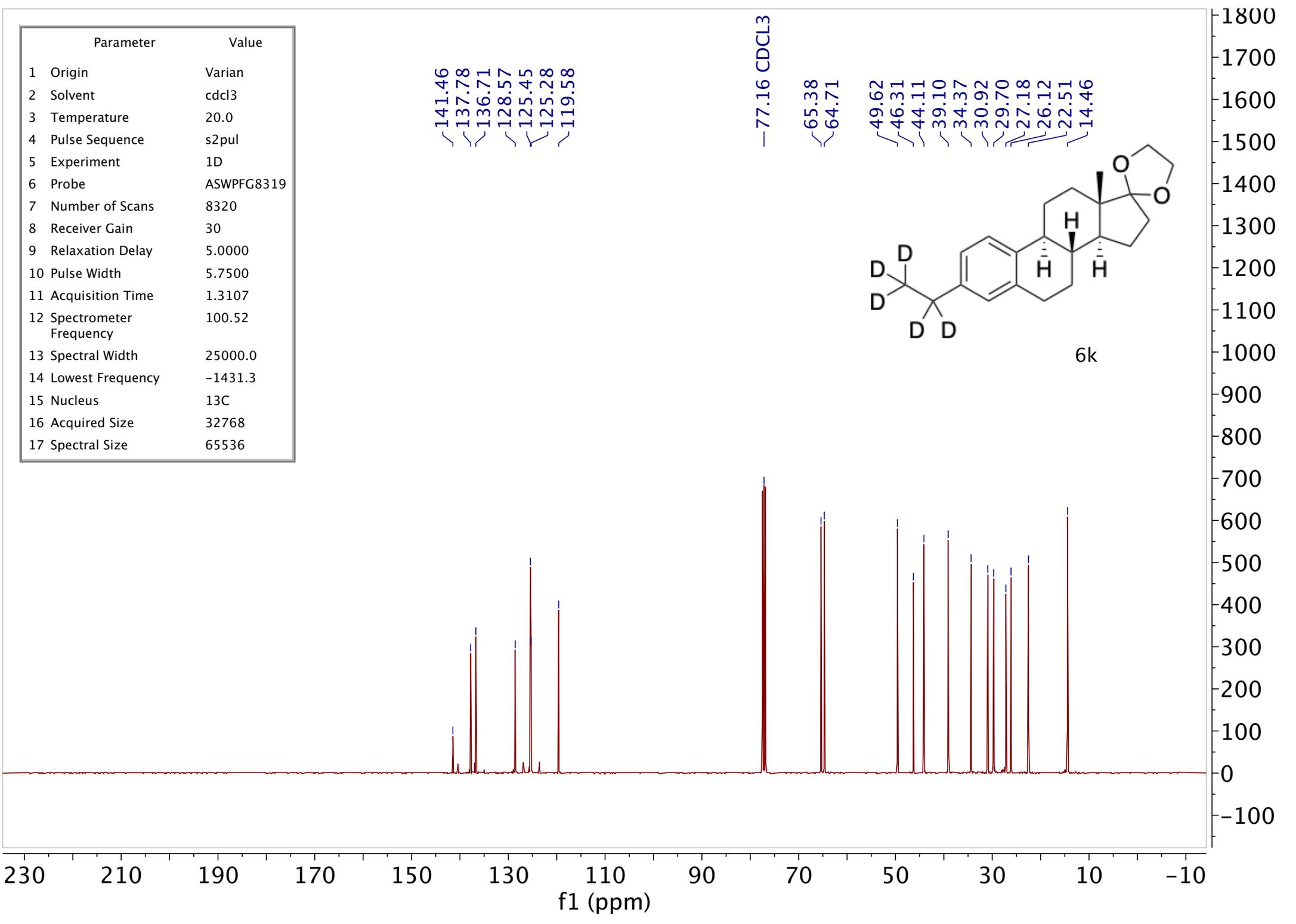
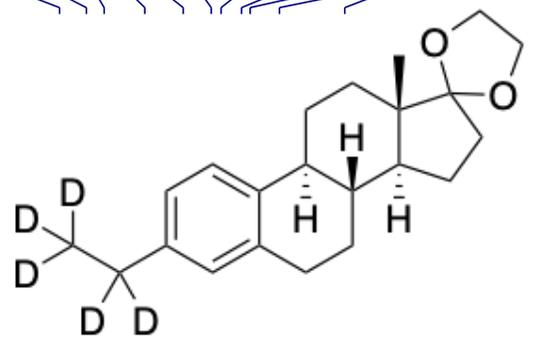
Parameter	Value
1 Origin	Varian
2 Solvent	cdcl3
3 Temperature	20.0
4 Pulse Sequence	s2pul
5 Experiment	1D
6 Probe	ASWPFG8319
7 Number of Scans	8320
8 Receiver Gain	30
9 Relaxation Delay	5.0000
10 Pulse Width	5.7500
11 Acquisition Time	1.3107
12 Spectrometer Frequency	100.52
13 Spectral Width	25000.0
14 Lowest Frequency	-1431.3
15 Nucleus	13C
16 Acquired Size	32768
17 Spectral Size	65536

141.46  
137.78  
136.71  
128.57  
125.45  
125.28  
119.58

77.16 CDCL3

65.38  
64.71

49.62  
46.31  
44.11  
39.10  
34.37  
30.92  
29.70  
27.18  
26.12  
22.51  
14.46



Parameter	Value
1 Origin	Varian
2 Solvent	cdcl3
3 Temperature	20.0
4 Pulse Sequence	s2pul
5 Experiment	1D
6 Probe	ASWPFG8319
7 Number of Scans	8
8 Receiver Gain	32
9 Relaxation Delay	1.0000
10 Pulse Width	8.0000
11 Acquisition Time	2.5559
12 Spectrometer Frequency	399.73
13 Spectral Width	6410.3
14 Lowest Frequency	-805.6
15 Nucleus	1H
16 Acquired Size	16384
17 Spectral Size	65536

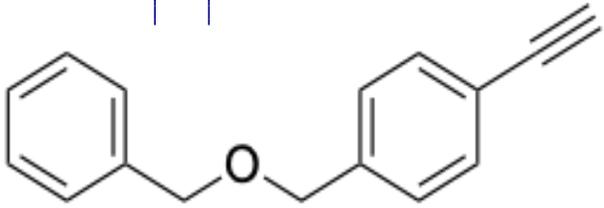
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7.34  
7.33  
7.32  
7.32  
7.32  
7.31  
7.30  
7.30  
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7.28  
7.26 CDCl3

4.56  
4.56

3.07

1.26 H Grease

0.89 H Grease

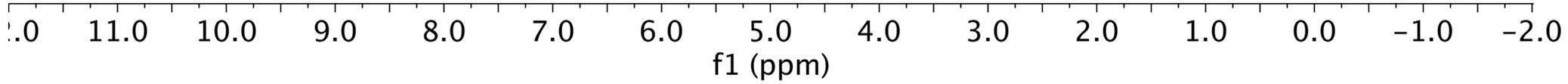


3g

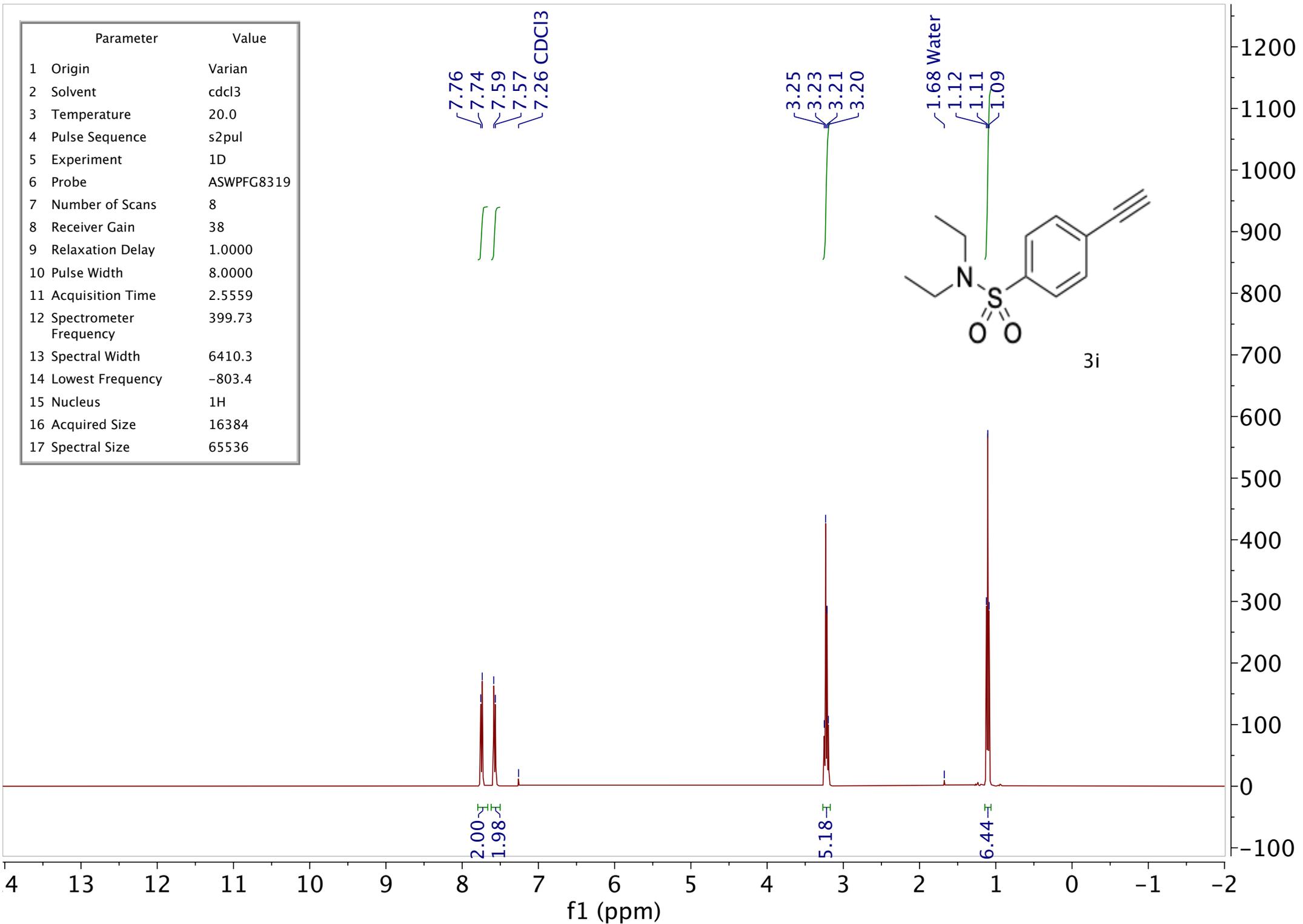
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4.02

0.87



Parameter	Value
1 Origin	Varian
2 Solvent	cdcl3
3 Temperature	20.0
4 Pulse Sequence	s2pul
5 Experiment	1D
6 Probe	ASWPG8319
7 Number of Scans	8
8 Receiver Gain	38
9 Relaxation Delay	1.0000
10 Pulse Width	8.0000
11 Acquisition Time	2.5559
12 Spectrometer Frequency	399.73
13 Spectral Width	6410.3
14 Lowest Frequency	-803.4
15 Nucleus	1H
16 Acquired Size	16384
17 Spectral Size	65536



Parameter	Value
1 Origin	Varian
2 Solvent	CDCl3
3 Temperature	3.0
4 Pulse Sequence	s2pul
5 Experiment	1D
6 Probe	ATB_300
7 Number of Scans	8
8 Receiver Gain	10
9 Relaxation Delay	1.0000
10 Pulse Width	6.2000
11 Acquisition Time	1.9979
12 Spectrometer Frequency	300.13
13 Spectral Width	4803.1
14 Lowest Frequency	-600.7
15 Nucleus	1H
16 Acquired Size	9596
17 Spectral Size	65536

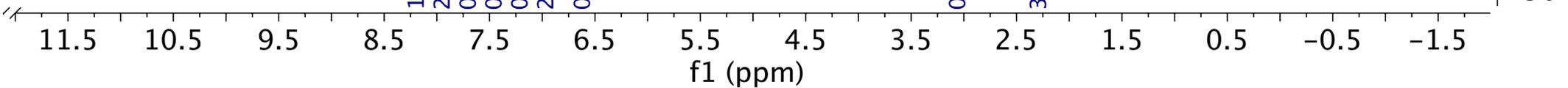
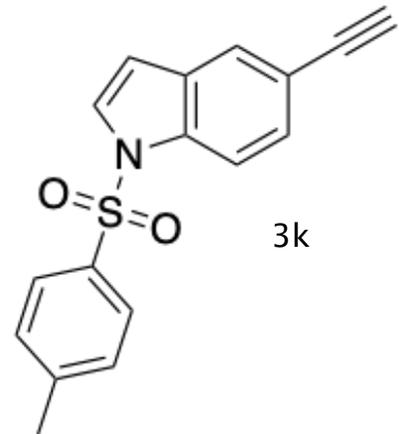
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7.60  
7.58  
7.46  
7.46  
7.43  
7.43  
7.26 CDCl3  
7.21  
7.18  
6.62  
6.61

1.04  
2.02  
0.92  
0.93  
0.98  
2.07  
0.98

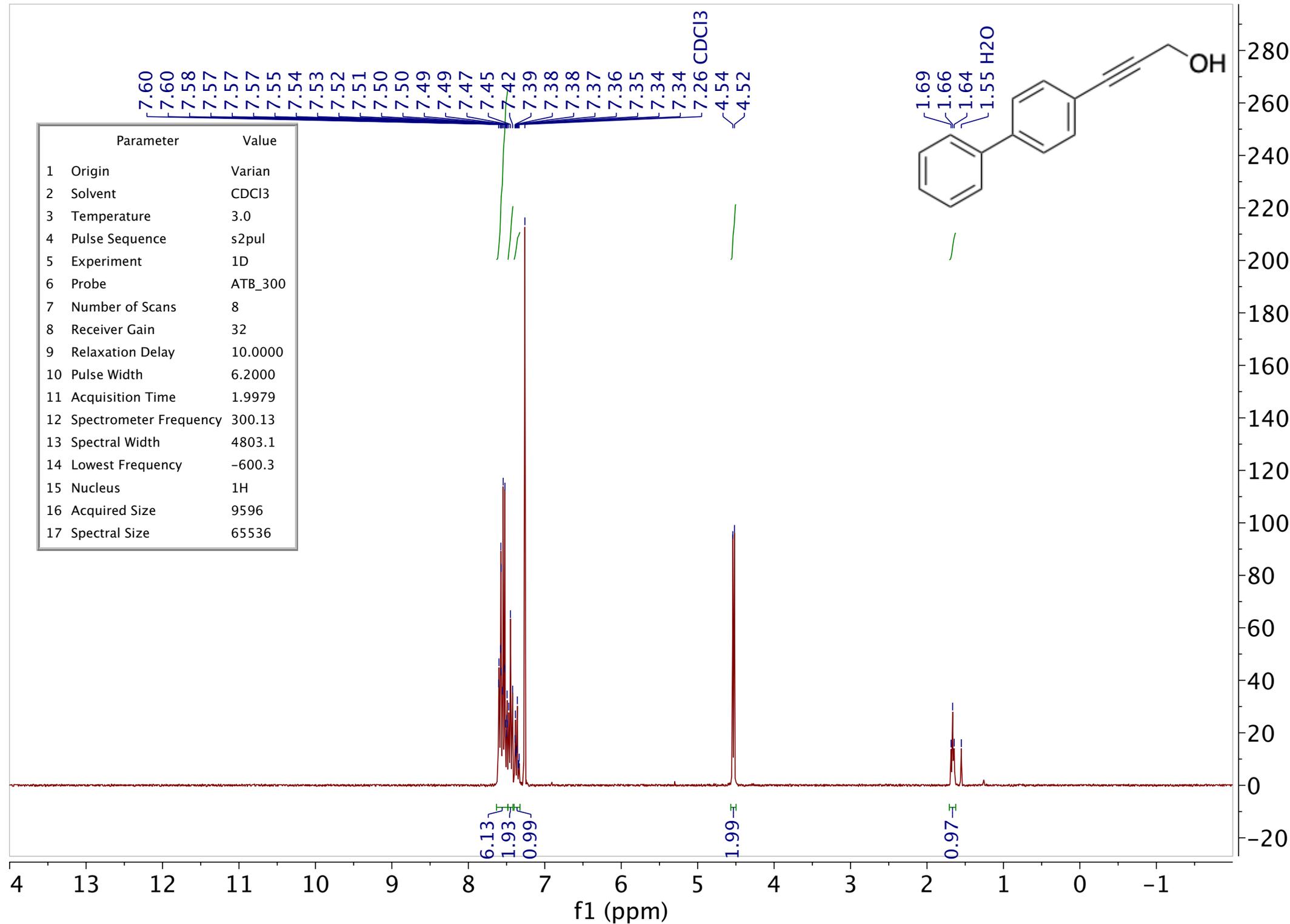
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3.38

3.06

2.30



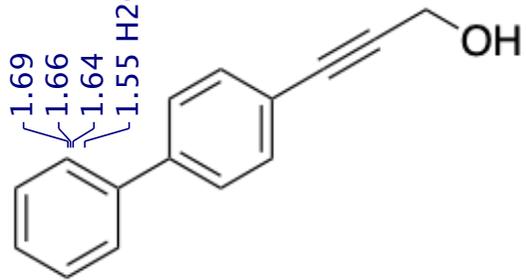
Parameter	Value
1 Origin	Varian
2 Solvent	CDCl3
3 Temperature	3.0
4 Pulse Sequence	s2pul
5 Experiment	1D
6 Probe	ATB_300
7 Number of Scans	8
8 Receiver Gain	32
9 Relaxation Delay	10.0000
10 Pulse Width	6.2000
11 Acquisition Time	1.9979
12 Spectrometer Frequency	300.13
13 Spectral Width	4803.1
14 Lowest Frequency	-600.3
15 Nucleus	1H
16 Acquired Size	9596
17 Spectral Size	65536



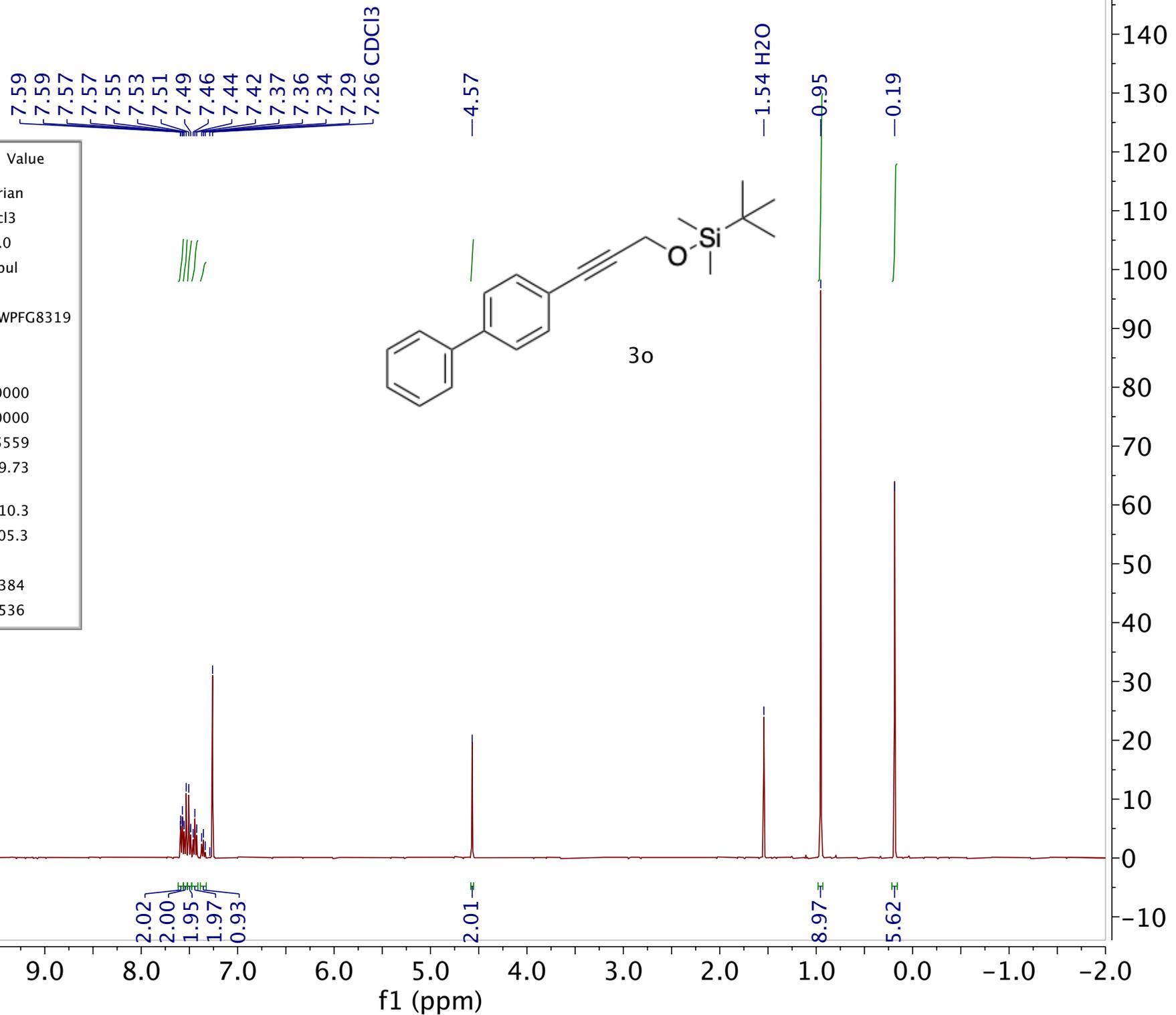
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7.53  
7.52  
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7.50  
7.50  
7.49  
7.49  
7.47  
7.45  
7.42  
7.39  
7.38  
7.38  
7.37  
7.36  
7.35  
7.34  
7.34  
7.26 CDCl3  
4.54  
4.52

6.13  
1.93  
0.99  
1.99  
0.97

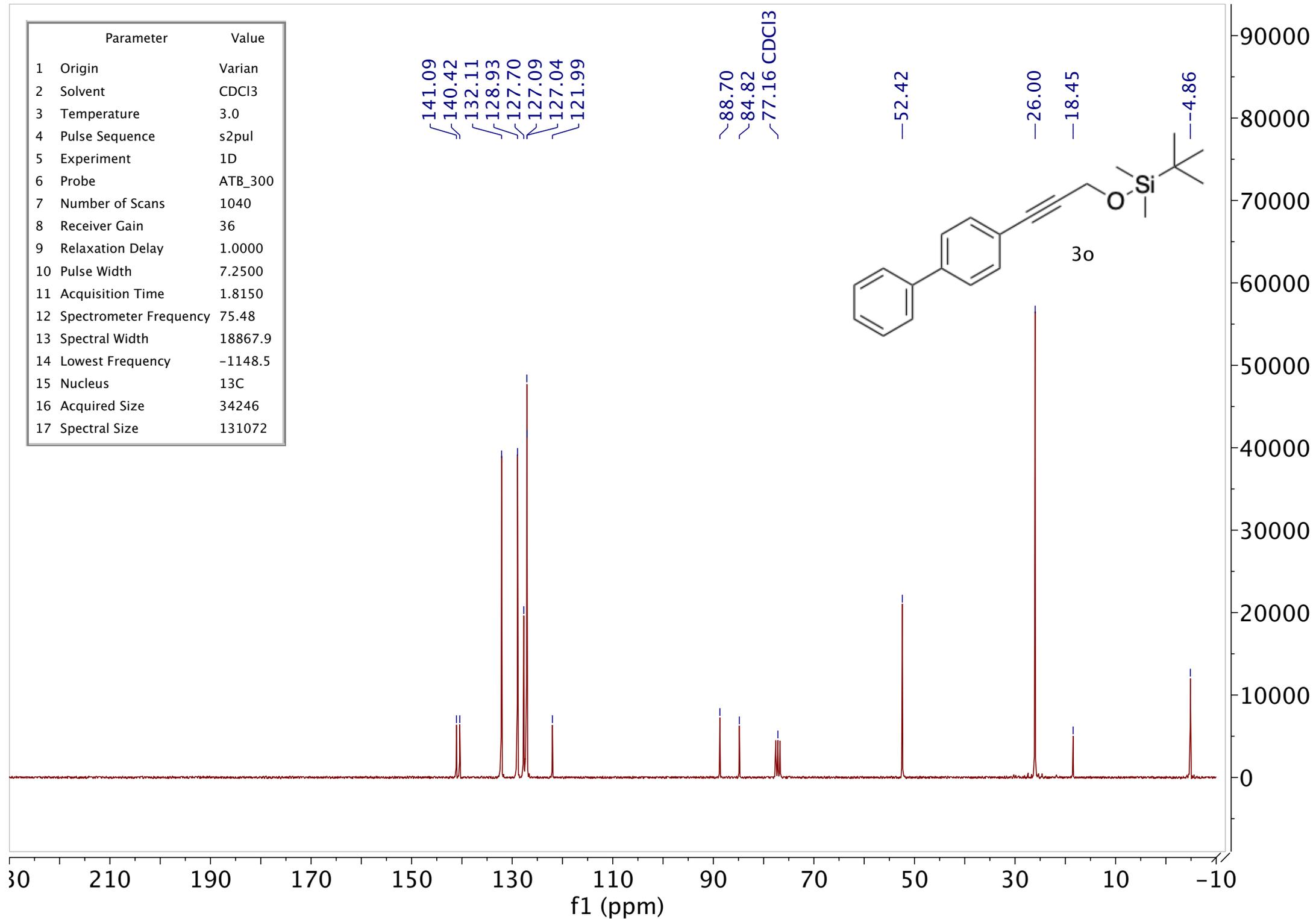
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1.55 H2O

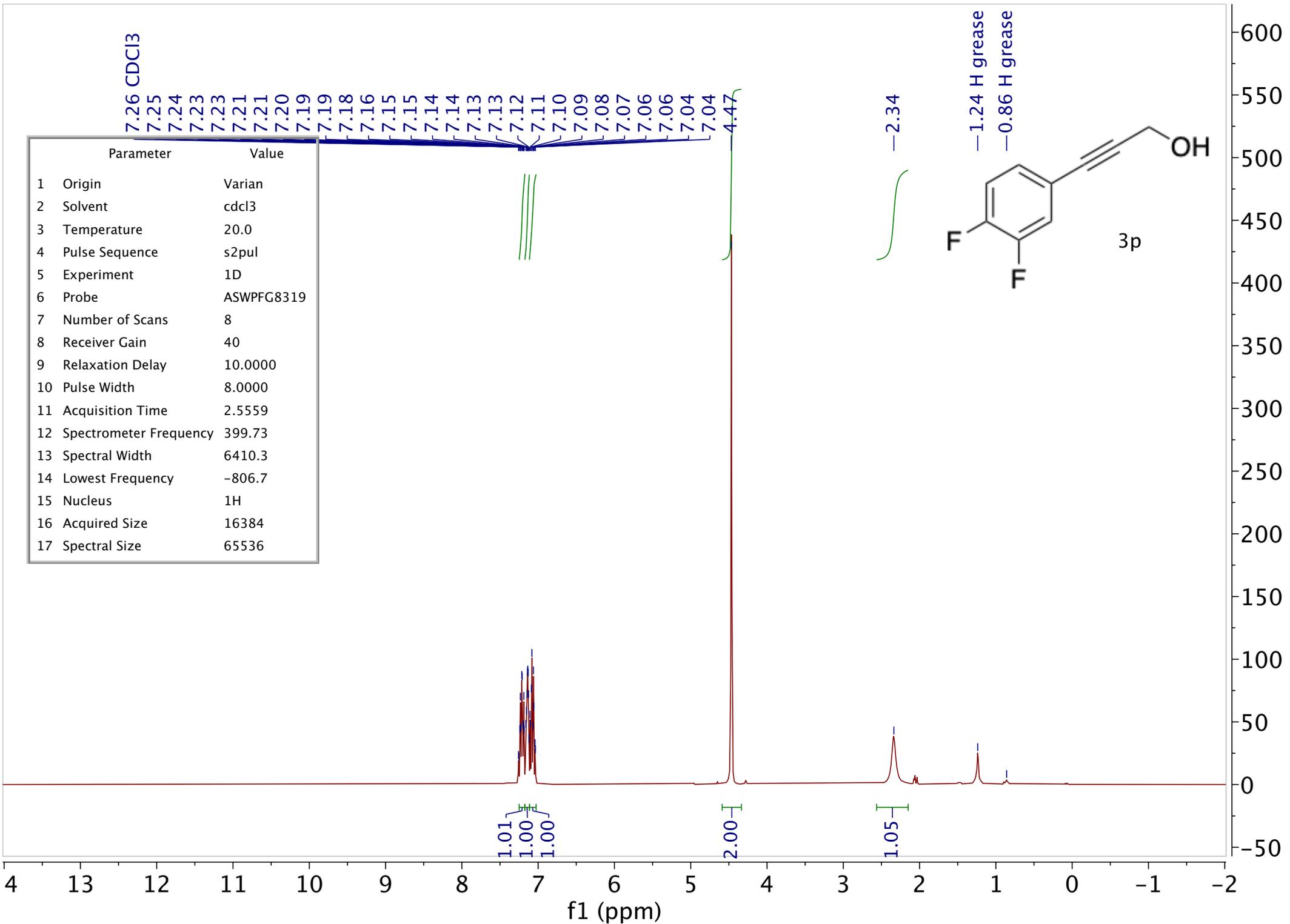


Parameter	Value
1 Origin	Varian
2 Solvent	cdcl3
3 Temperature	20.0
4 Pulse Sequence	s2pul
5 Experiment	1D
6 Probe	ASWPFG8319
7 Number of Scans	8
8 Receiver Gain	42
9 Relaxation Delay	1.0000
10 Pulse Width	8.0000
11 Acquisition Time	2.5559
12 Spectrometer Frequency	399.73
13 Spectral Width	6410.3
14 Lowest Frequency	-805.3
15 Nucleus	1H
16 Acquired Size	16384
17 Spectral Size	65536



Parameter	Value
1 Origin	Varian
2 Solvent	CDCl3
3 Temperature	3.0
4 Pulse Sequence	s2pul
5 Experiment	1D
6 Probe	ATB_300
7 Number of Scans	1040
8 Receiver Gain	36
9 Relaxation Delay	1.0000
10 Pulse Width	7.2500
11 Acquisition Time	1.8150
12 Spectrometer Frequency	75.48
13 Spectral Width	18867.9
14 Lowest Frequency	-1148.5
15 Nucleus	13C
16 Acquired Size	34246
17 Spectral Size	131072

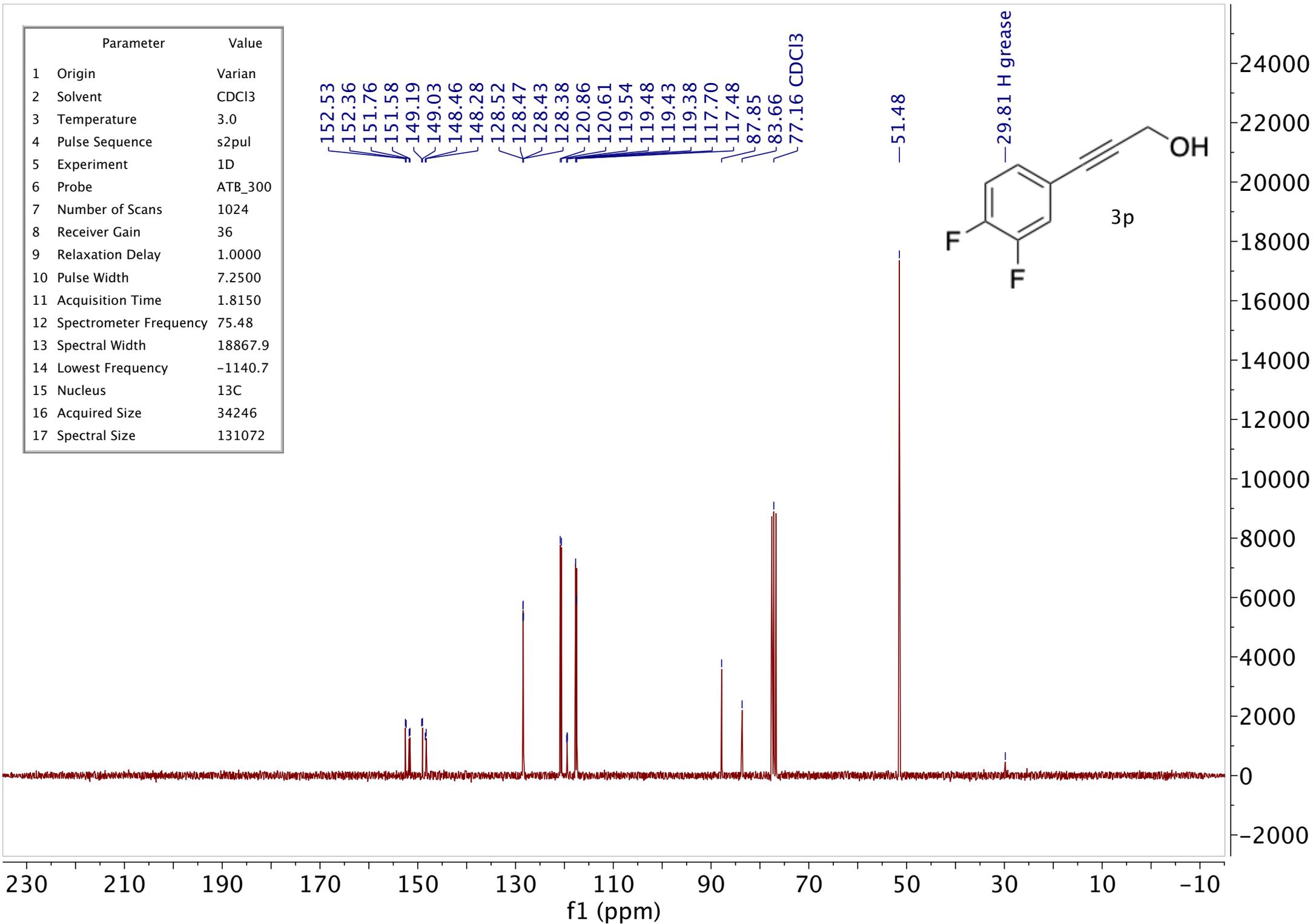
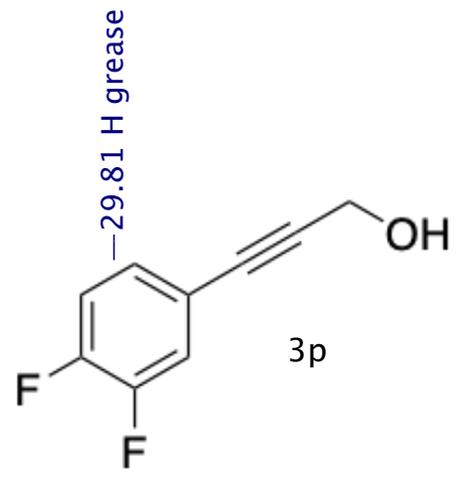




Parameter	Value
1 Origin	Varian
2 Solvent	CDCl3
3 Temperature	3.0
4 Pulse Sequence	s2pul
5 Experiment	1D
6 Probe	ATB_300
7 Number of Scans	1024
8 Receiver Gain	36
9 Relaxation Delay	1.0000
10 Pulse Width	7.2500
11 Acquisition Time	1.8150
12 Spectrometer Frequency	75.48
13 Spectral Width	18867.9
14 Lowest Frequency	-1140.7
15 Nucleus	13C
16 Acquired Size	34246
17 Spectral Size	131072

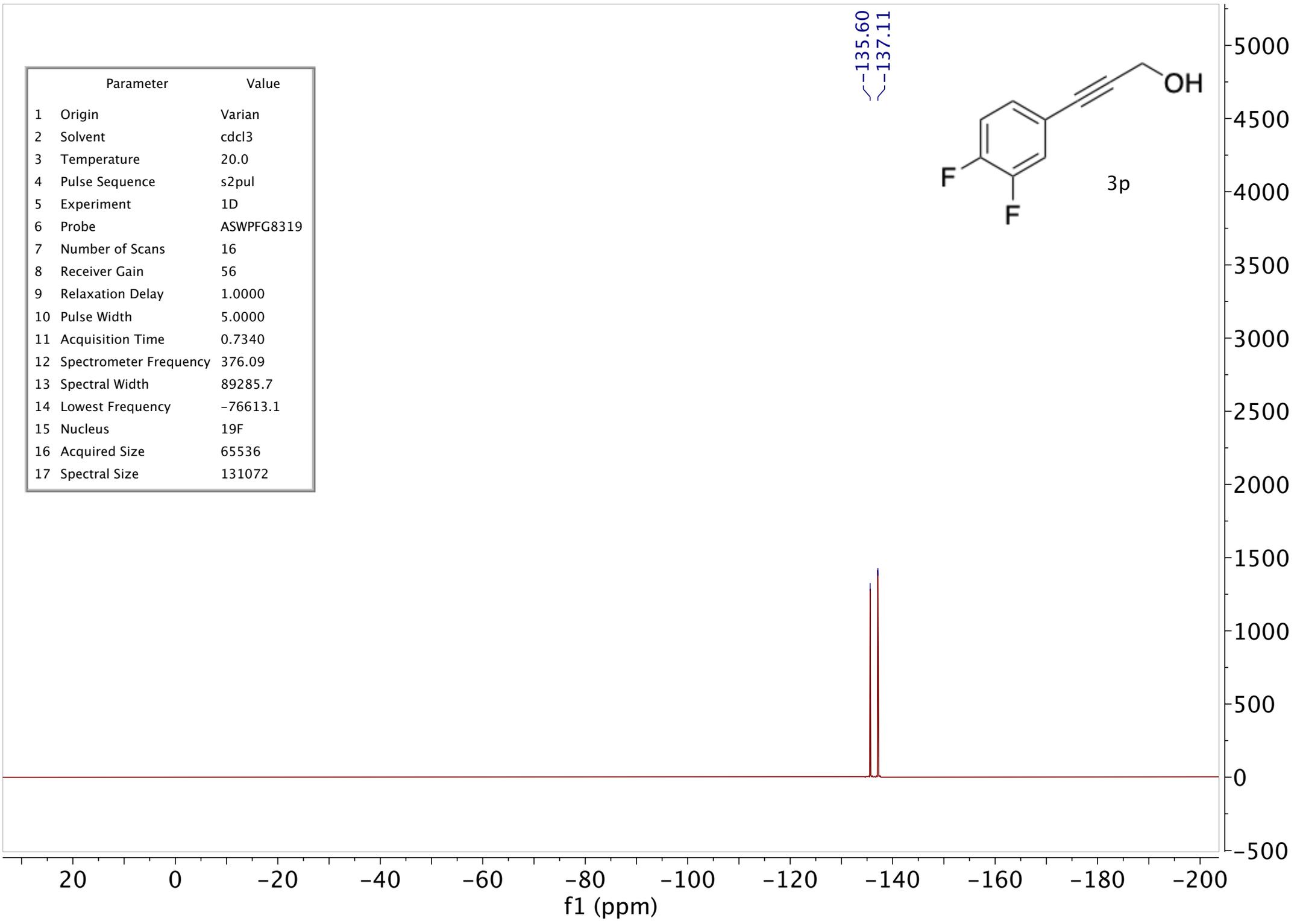
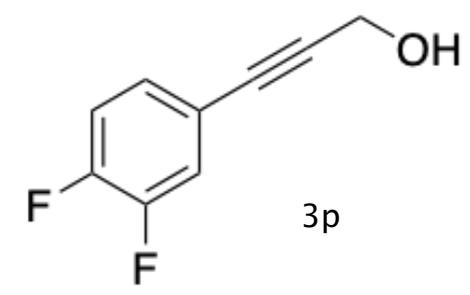
152.53  
152.36  
151.76  
151.58  
149.19  
149.03  
148.46  
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128.52  
128.47  
128.43  
128.38  
120.86  
120.61  
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119.38  
117.70  
117.48  
87.85  
83.66  
77.16 CDCl3

51.48



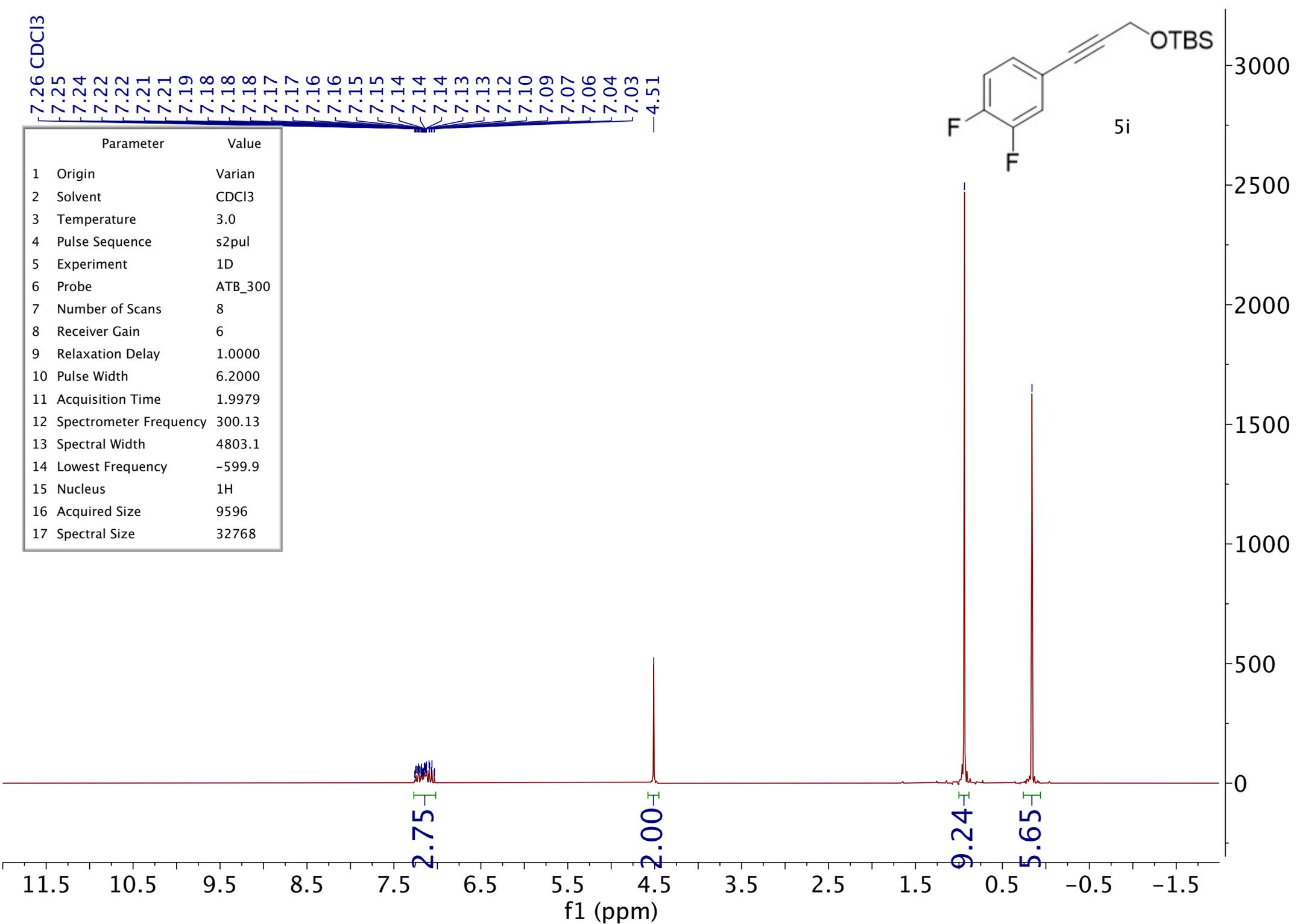
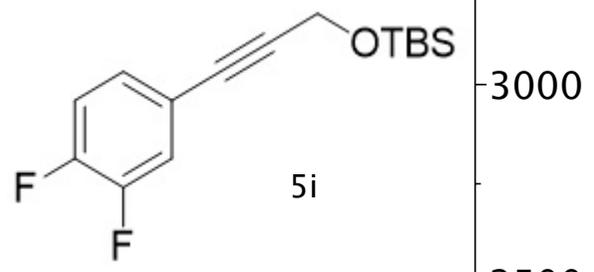
Parameter	Value
1 Origin	Varian
2 Solvent	cdcl3
3 Temperature	20.0
4 Pulse Sequence	s2pul
5 Experiment	1D
6 Probe	ASWPFG8319
7 Number of Scans	16
8 Receiver Gain	56
9 Relaxation Delay	1.0000
10 Pulse Width	5.0000
11 Acquisition Time	0.7340
12 Spectrometer Frequency	376.09
13 Spectral Width	89285.7
14 Lowest Frequency	-76613.1
15 Nucleus	19F
16 Acquired Size	65536
17 Spectral Size	131072

--135.60  
--137.11



7.26 CDCI3  
 7.25  
 7.24  
 7.22  
 7.22  
 7.21  
 7.21  
 7.19  
 7.18  
 7.18  
 7.18  
 7.17  
 7.17  
 7.16  
 7.16  
 7.15  
 7.15  
 7.14  
 7.14  
 7.14  
 7.13  
 7.13  
 7.12  
 7.10  
 7.09  
 7.07  
 7.06  
 7.04  
 7.03  
 4.51

Parameter	Value
1 Origin	Varian
2 Solvent	CDCl3
3 Temperature	3.0
4 Pulse Sequence	s2pul
5 Experiment	1D
6 Probe	ATB_300
7 Number of Scans	8
8 Receiver Gain	6
9 Relaxation Delay	1.0000
10 Pulse Width	6.2000
11 Acquisition Time	1.9979
12 Spectrometer Frequency	300.13
13 Spectral Width	4803.1
14 Lowest Frequency	-599.9
15 Nucleus	1H
16 Acquired Size	9596
17 Spectral Size	32768

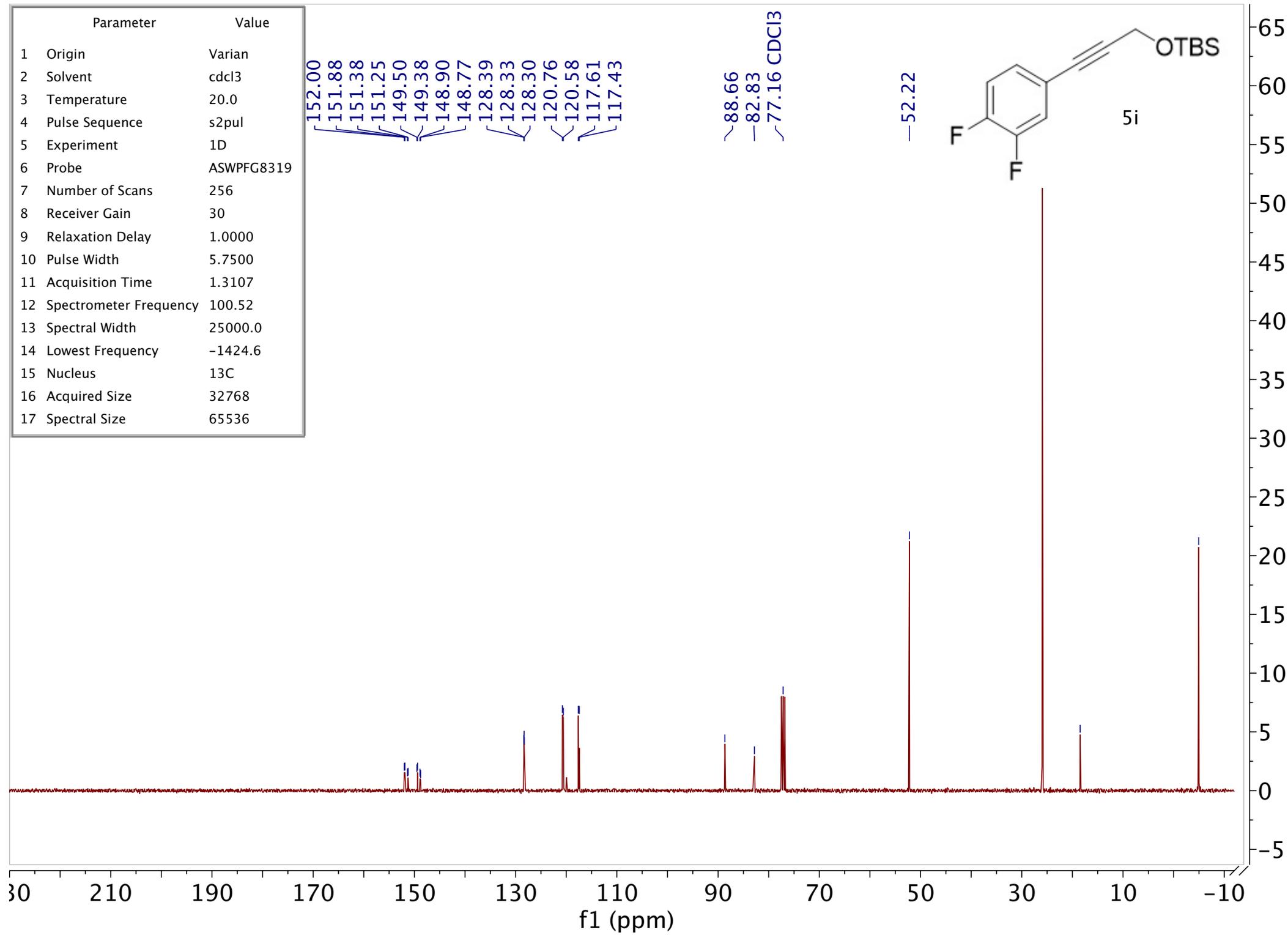
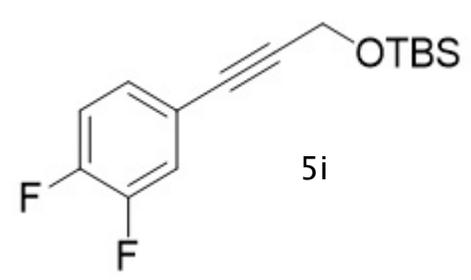


Parameter	Value
1 Origin	Varian
2 Solvent	cdcl3
3 Temperature	20.0
4 Pulse Sequence	s2pul
5 Experiment	1D
6 Probe	ASWPFG8319
7 Number of Scans	256
8 Receiver Gain	30
9 Relaxation Delay	1.0000
10 Pulse Width	5.7500
11 Acquisition Time	1.3107
12 Spectrometer Frequency	100.52
13 Spectral Width	25000.0
14 Lowest Frequency	-1424.6
15 Nucleus	13C
16 Acquired Size	32768
17 Spectral Size	65536

152.00  
151.88  
151.38  
151.25  
149.50  
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148.77  
128.39  
128.33  
128.30  
120.76  
120.58  
117.61  
117.43

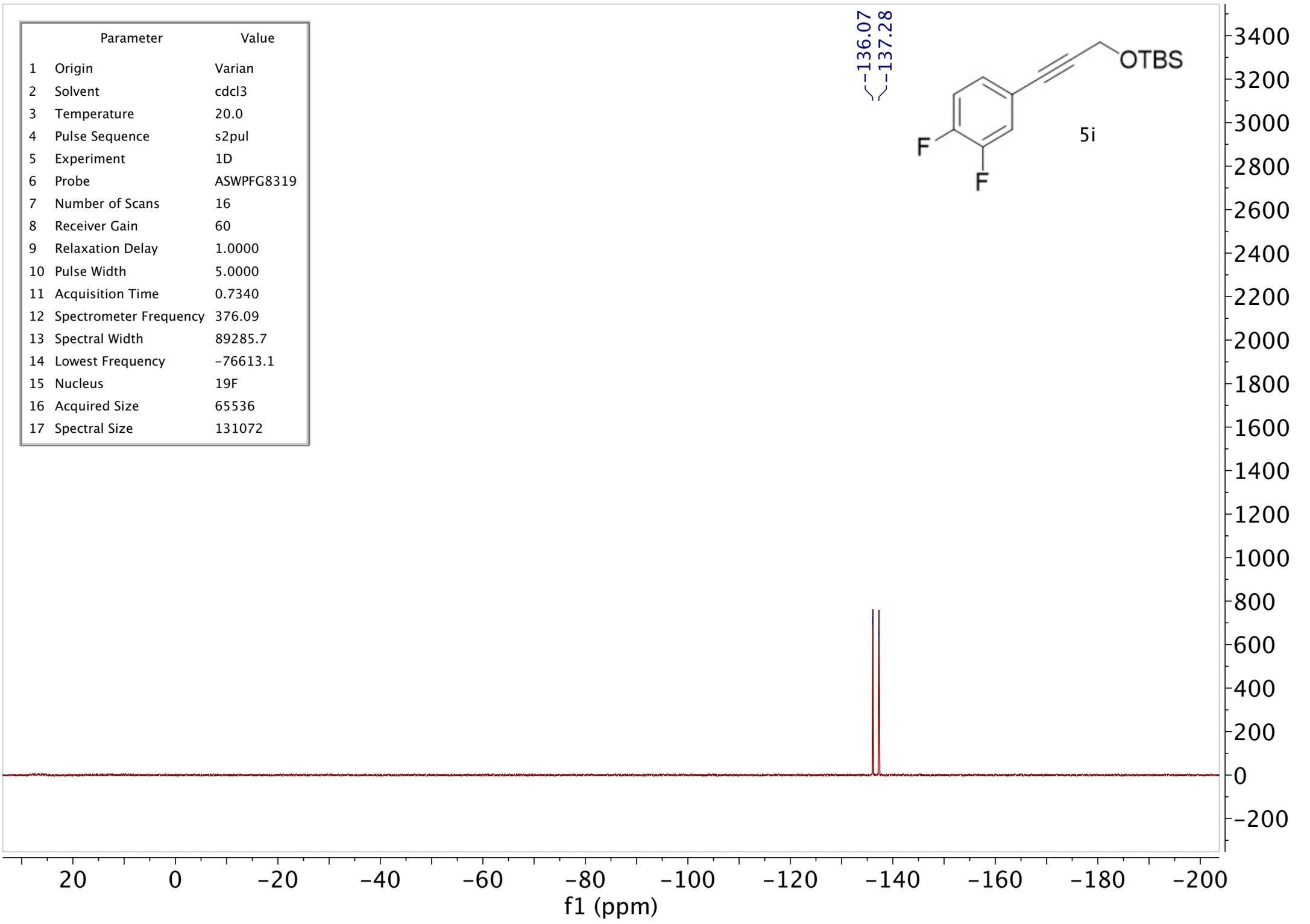
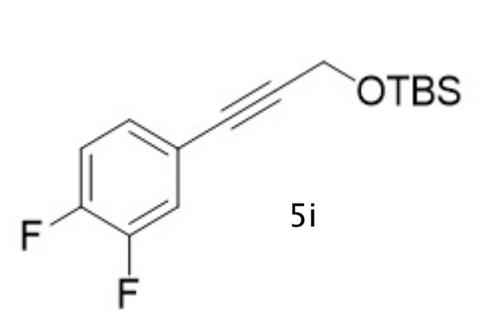
88.66  
82.83  
77.16 CDCl3

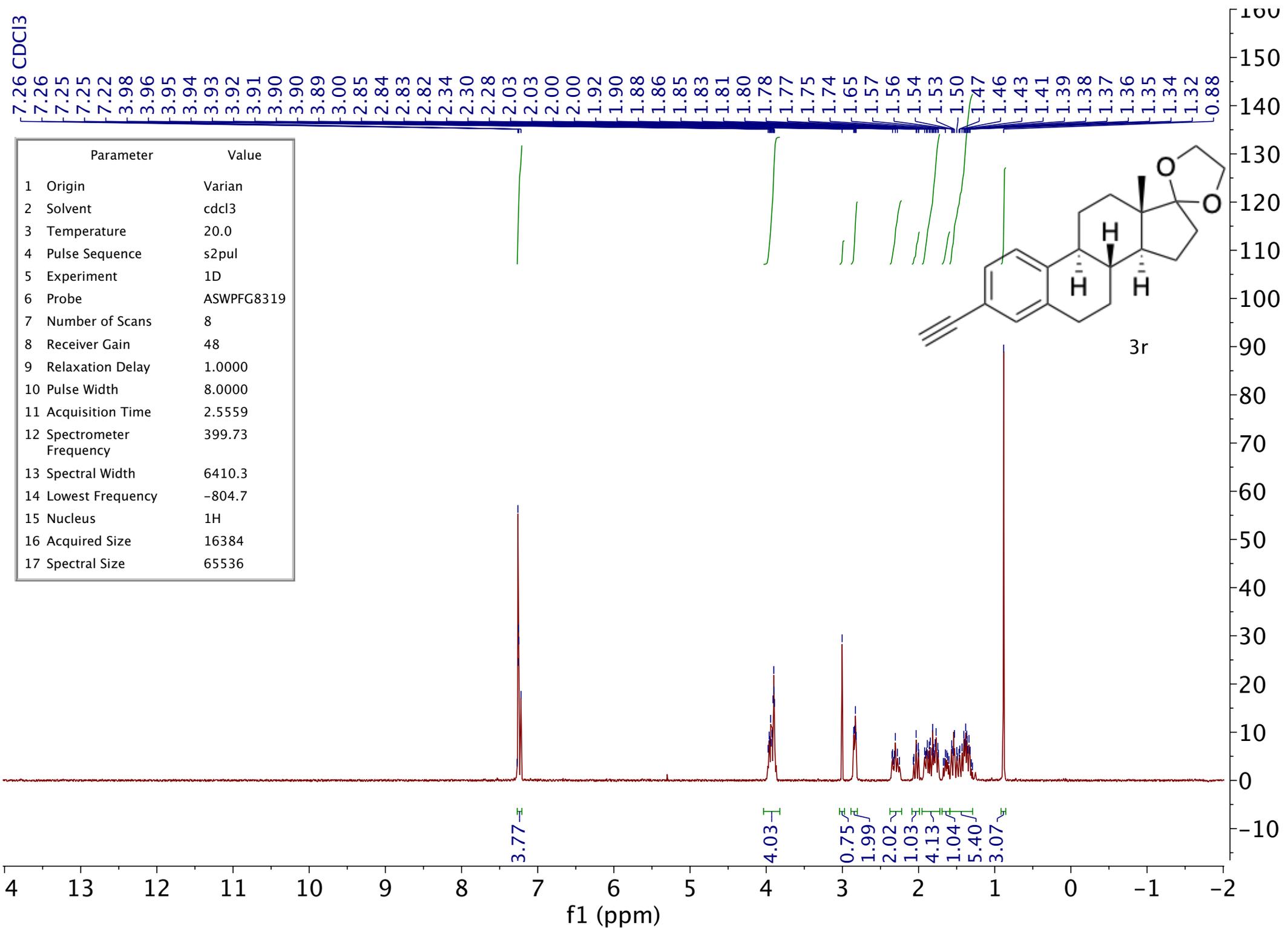
52.22



	Parameter	Value
1	Origin	Varian
2	Solvent	cdcl3
3	Temperature	20.0
4	Pulse Sequence	s2pul
5	Experiment	1D
6	Probe	ASWPFG8319
7	Number of Scans	16
8	Receiver Gain	60
9	Relaxation Delay	1.0000
10	Pulse Width	5.0000
11	Acquisition Time	0.7340
12	Spectrometer Frequency	376.09
13	Spectral Width	89285.7
14	Lowest Frequency	-76613.1
15	Nucleus	19F
16	Acquired Size	65536
17	Spectral Size	131072

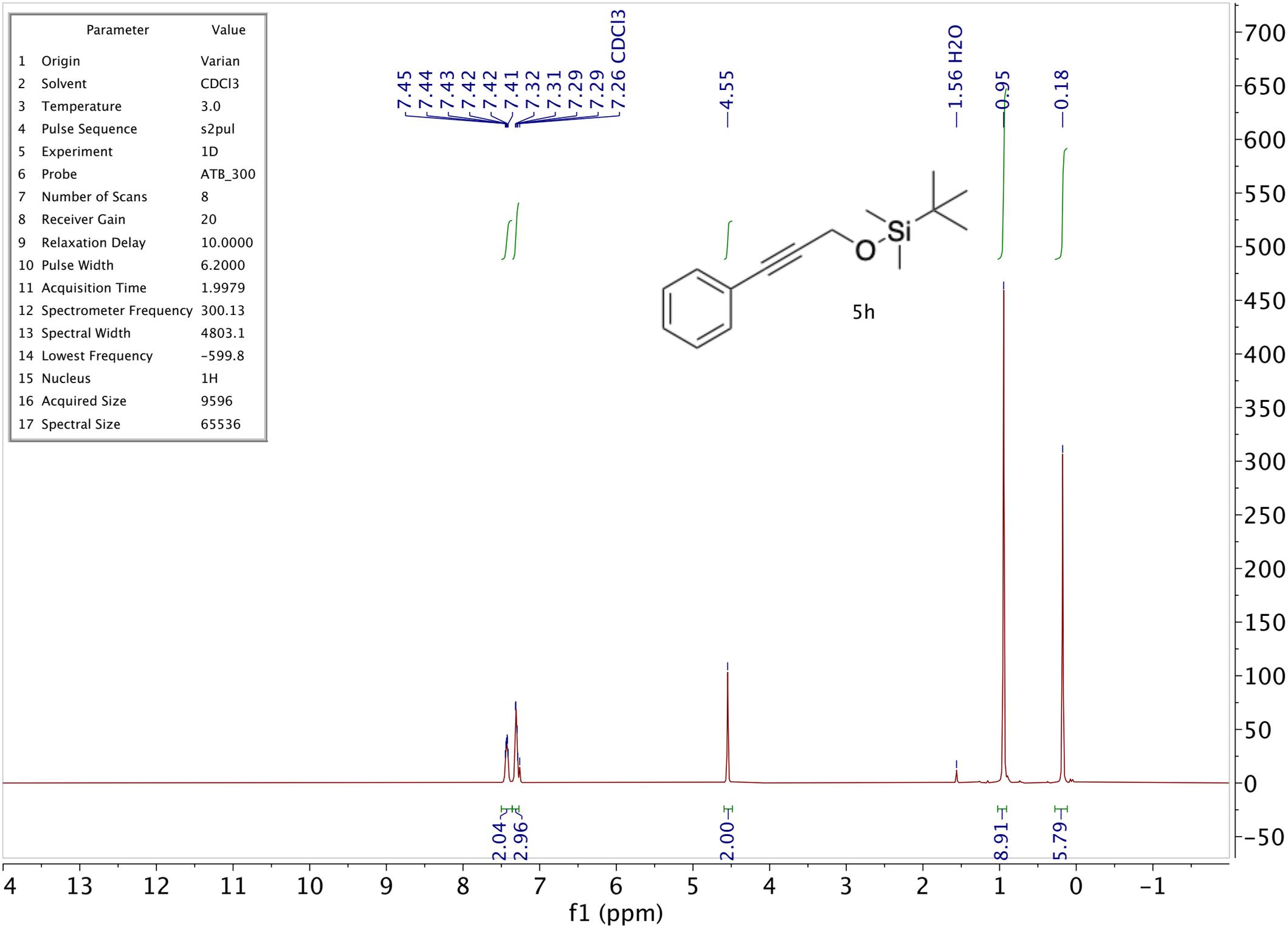
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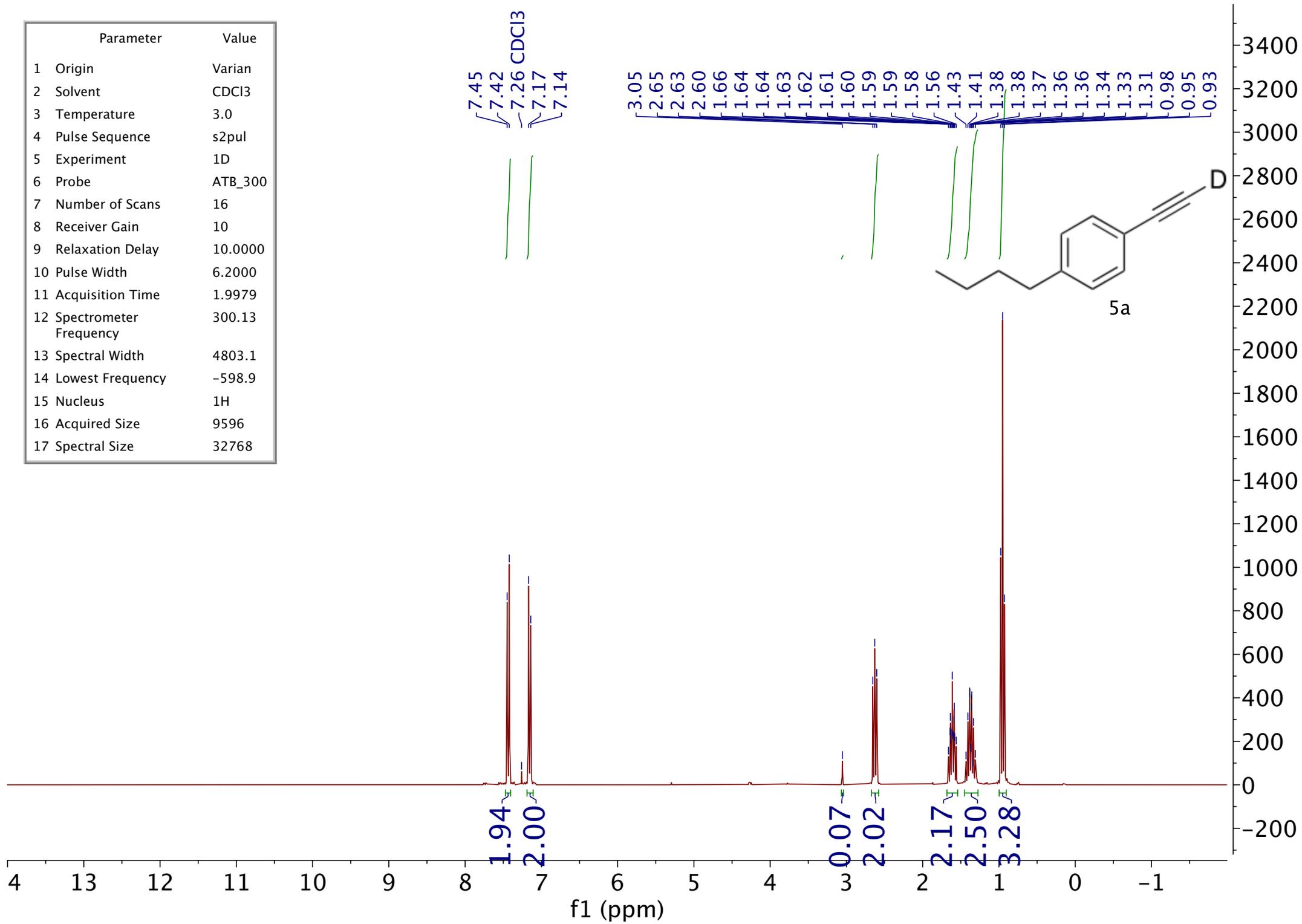




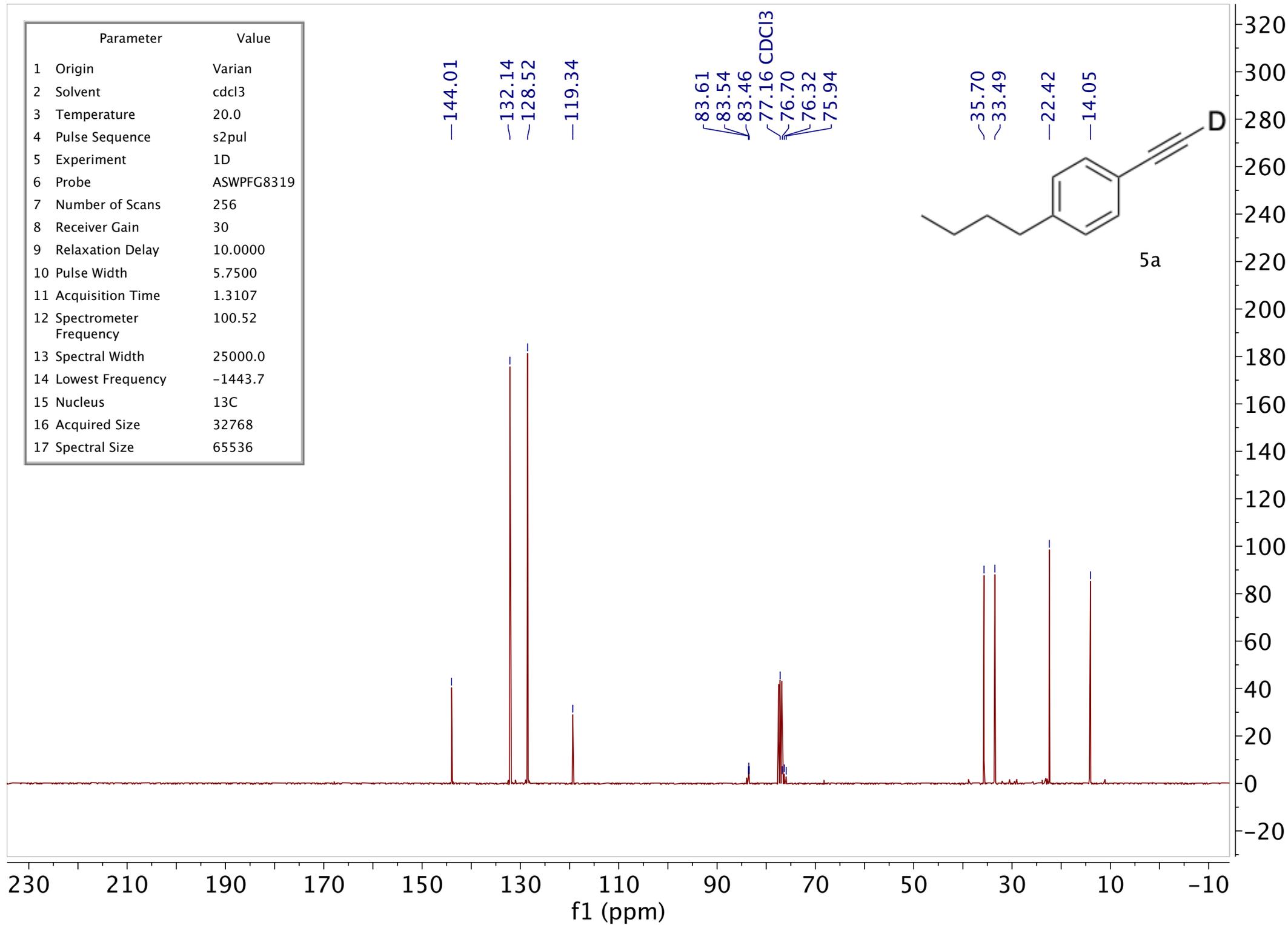
Parameter	Value
1 Origin	Varian
2 Solvent	CDCl3
3 Temperature	3.0
4 Pulse Sequence	s2pul
5 Experiment	1D
6 Probe	ATB_300
7 Number of Scans	8
8 Receiver Gain	20
9 Relaxation Delay	10.0000
10 Pulse Width	6.2000
11 Acquisition Time	1.9979
12 Spectrometer Frequency	300.13
13 Spectral Width	4803.1
14 Lowest Frequency	-599.8
15 Nucleus	1H
16 Acquired Size	9596
17 Spectral Size	65536



Parameter	Value
1 Origin	Varian
2 Solvent	CDCl3
3 Temperature	3.0
4 Pulse Sequence	s2pul
5 Experiment	1D
6 Probe	ATB_300
7 Number of Scans	16
8 Receiver Gain	10
9 Relaxation Delay	10.0000
10 Pulse Width	6.2000
11 Acquisition Time	1.9979
12 Spectrometer Frequency	300.13
13 Spectral Width	4803.1
14 Lowest Frequency	-598.9
15 Nucleus	1H
16 Acquired Size	9596
17 Spectral Size	32768



Parameter	Value
1 Origin	Varian
2 Solvent	cdcl3
3 Temperature	20.0
4 Pulse Sequence	s2pul
5 Experiment	1D
6 Probe	ASWPG8319
7 Number of Scans	256
8 Receiver Gain	30
9 Relaxation Delay	10.0000
10 Pulse Width	5.7500
11 Acquisition Time	1.3107
12 Spectrometer Frequency	100.52
13 Spectral Width	25000.0
14 Lowest Frequency	-1443.7
15 Nucleus	<sup>13</sup> C
16 Acquired Size	32768
17 Spectral Size	65536

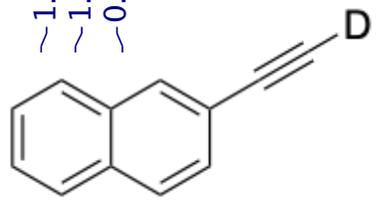


Parameter	Value
1 Origin	Varian
2 Solvent	cdcl3
3 Temperature	20.0
4 Pulse Sequence	s2pul
5 Experiment	1D
6 Probe	ASWPG8319
7 Number of Scans	8
8 Receiver Gain	52
9 Relaxation Delay	10.0000
10 Pulse Width	8.0000
11 Acquisition Time	2.5559
12 Spectrometer Frequency	399.73
13 Spectral Width	6410.3
14 Lowest Frequency	-804.0
15 Nucleus	1H
16 Acquired Size	16384
17 Spectral Size	65536

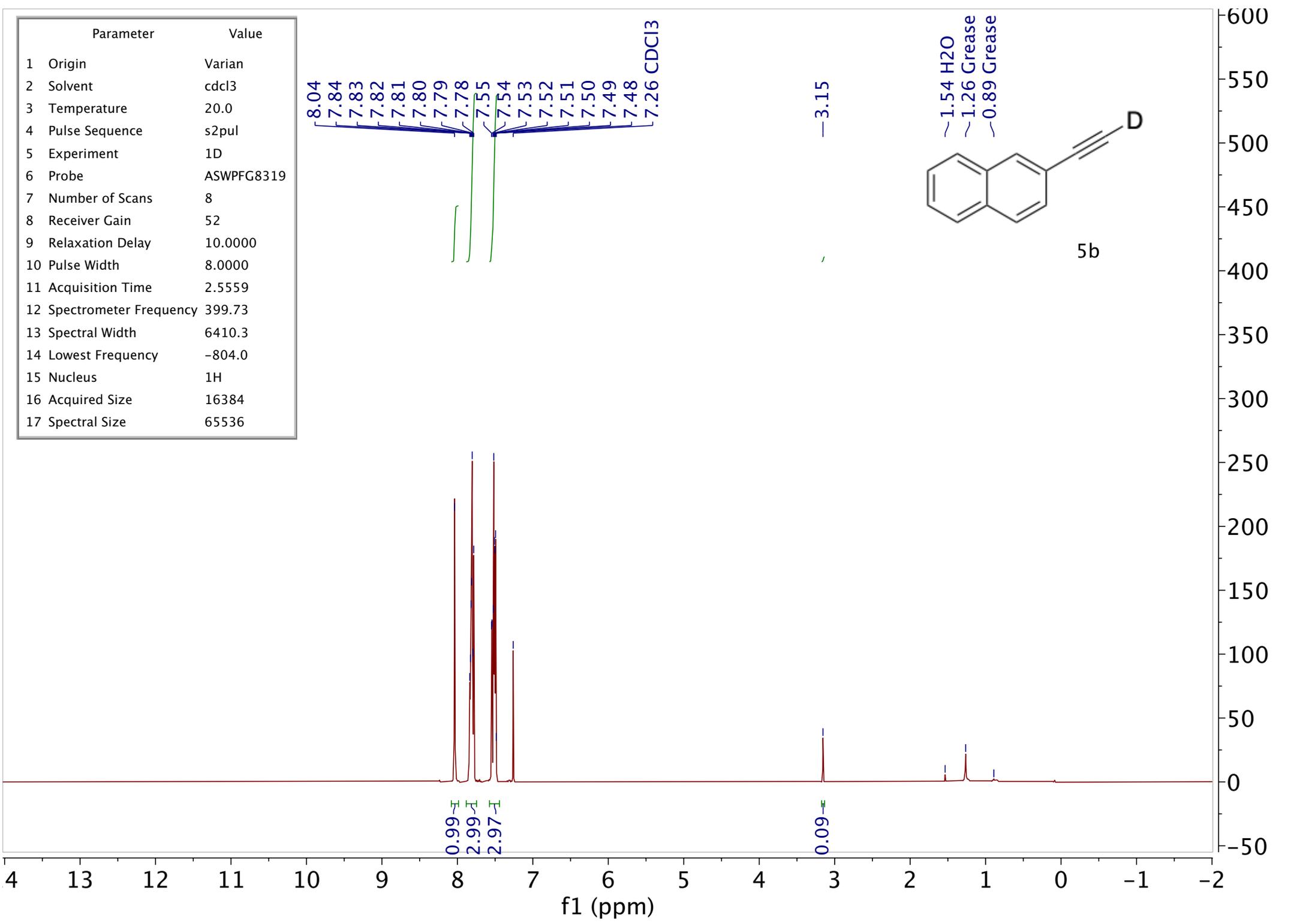
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7.83  
7.82  
7.81  
7.80  
7.79  
7.78  
7.55  
7.54  
7.53  
7.52  
7.51  
7.50  
7.49  
7.48  
7.26 CDCI3

-3.15

~1.54 H2O  
~1.26 Grease  
~0.89 Grease



5b

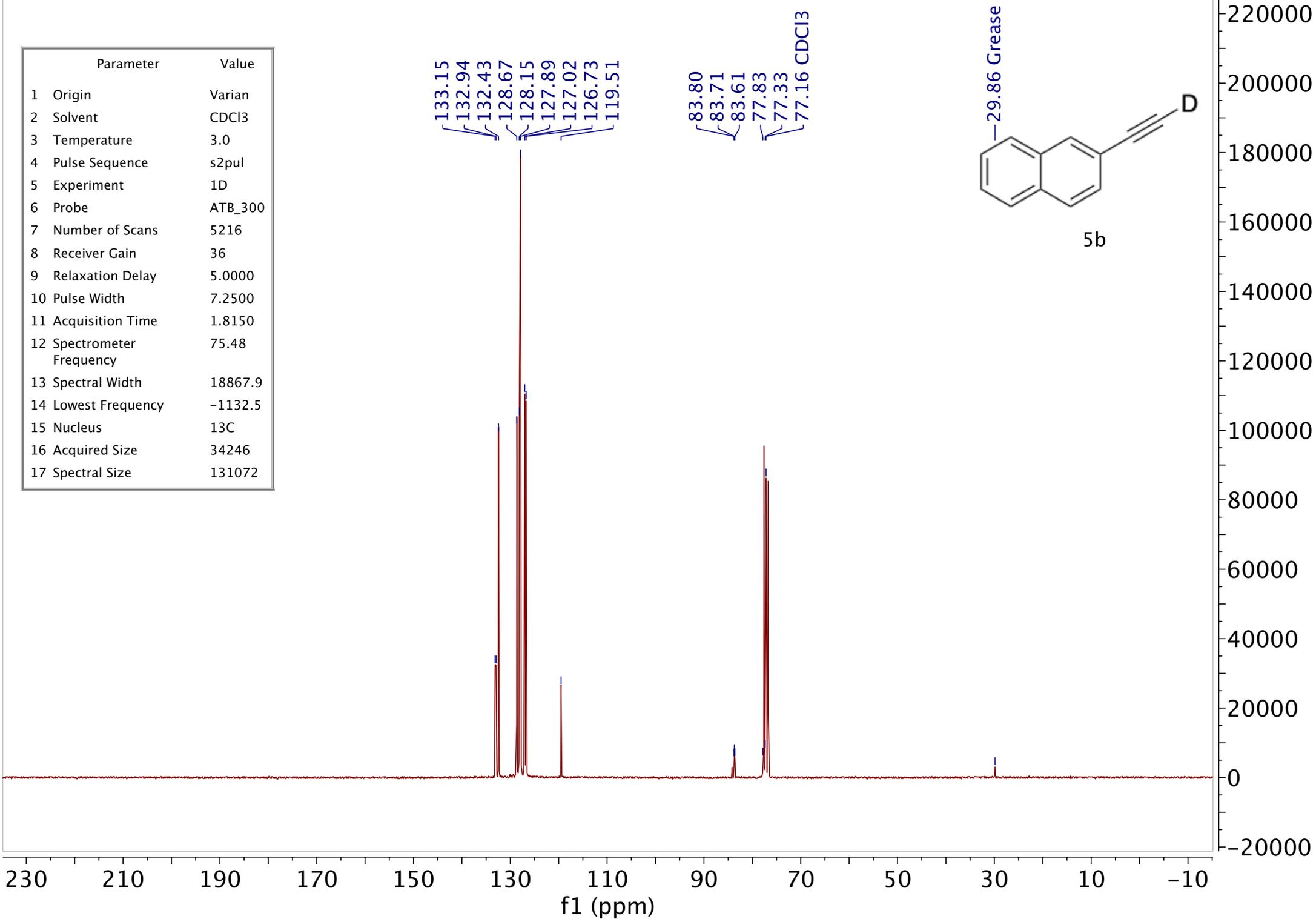


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2.99  
2.97

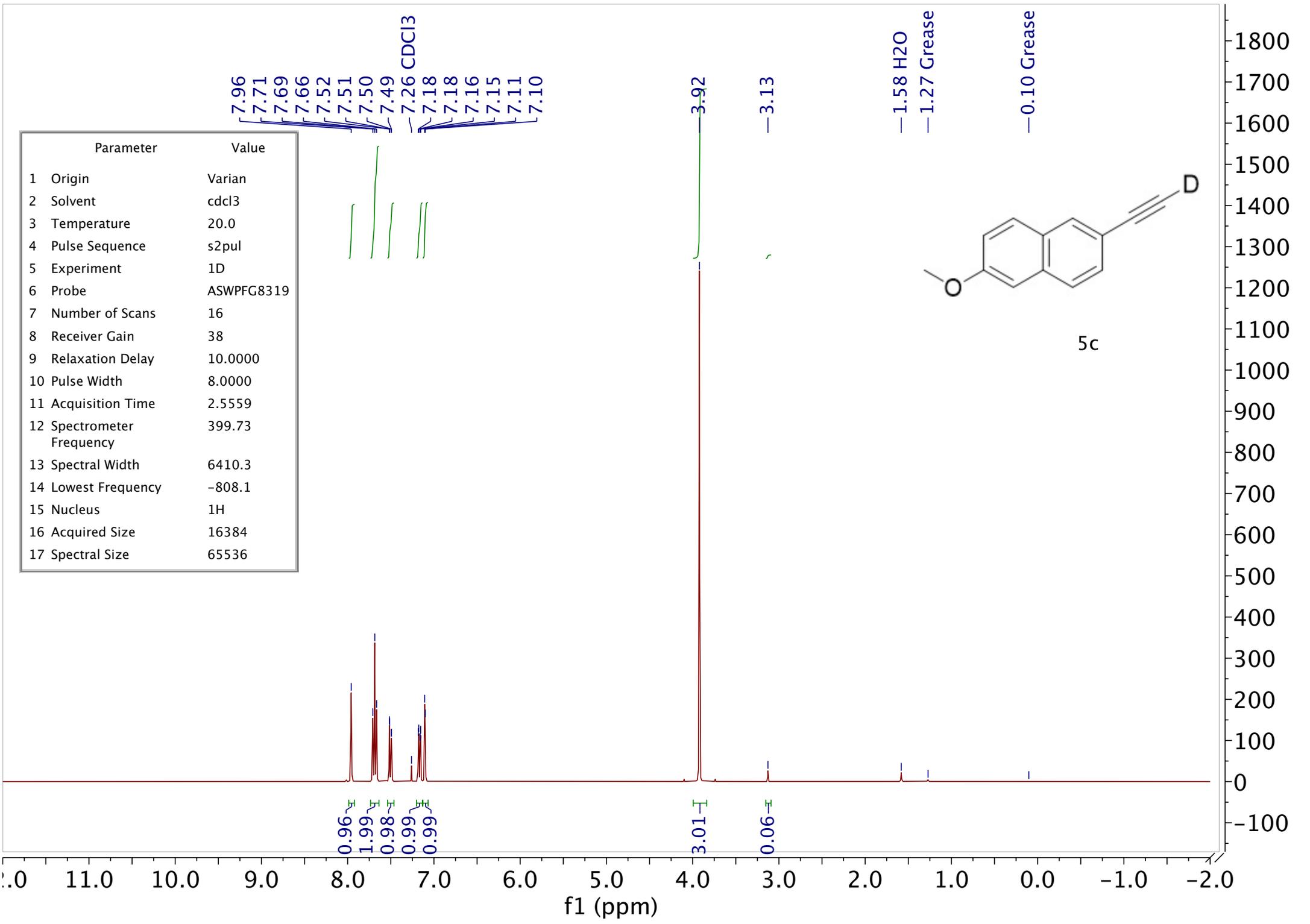
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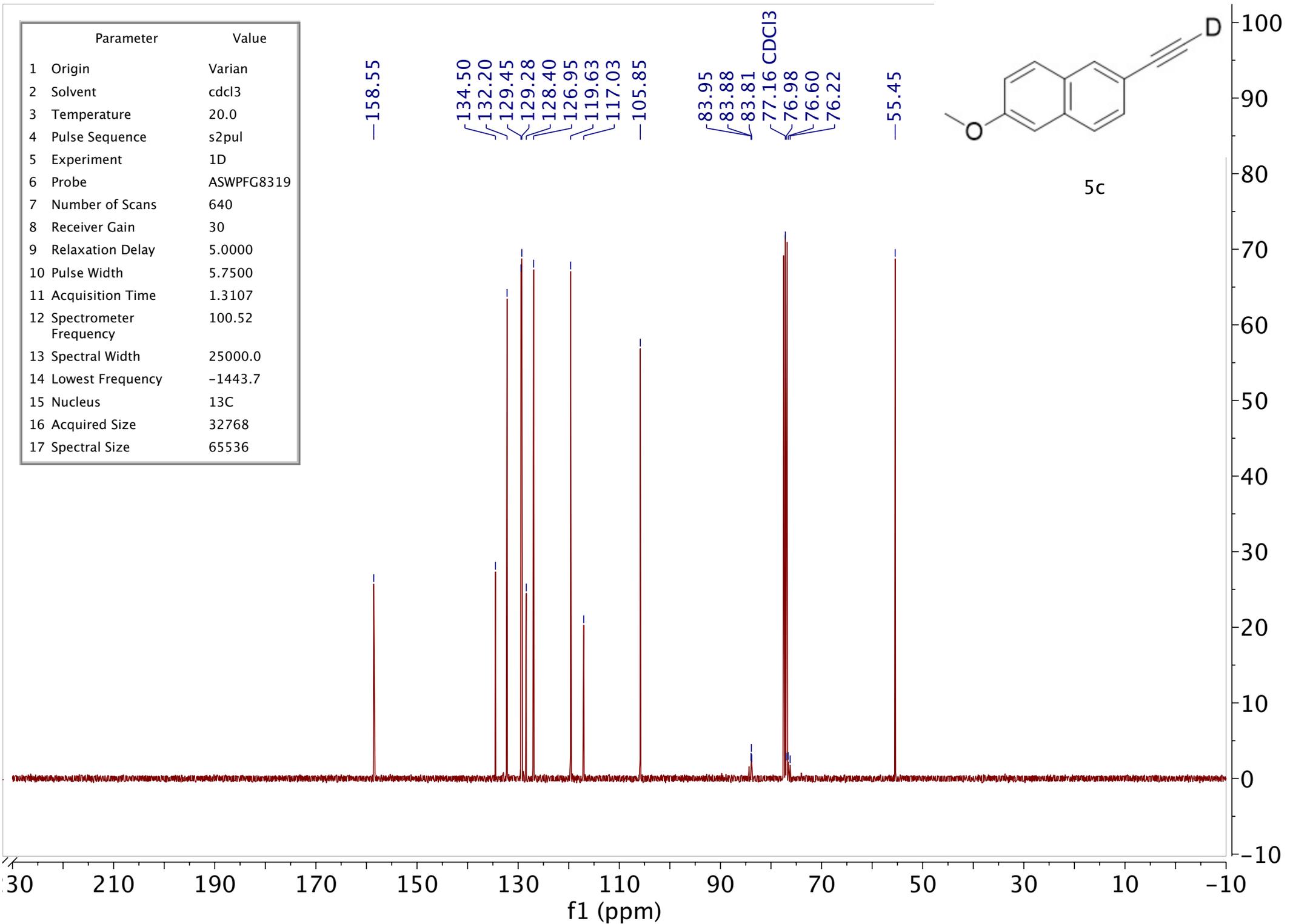
Parameter	Value
1 Origin	Varian
2 Solvent	CDCl3
3 Temperature	3.0
4 Pulse Sequence	s2pul
5 Experiment	1D
6 Probe	ATB_300
7 Number of Scans	5216
8 Receiver Gain	36
9 Relaxation Delay	5.0000
10 Pulse Width	7.2500
11 Acquisition Time	1.8150
12 Spectrometer Frequency	75.48
13 Spectral Width	18867.9
14 Lowest Frequency	-1132.5
15 Nucleus	13C
16 Acquired Size	34246
17 Spectral Size	131072



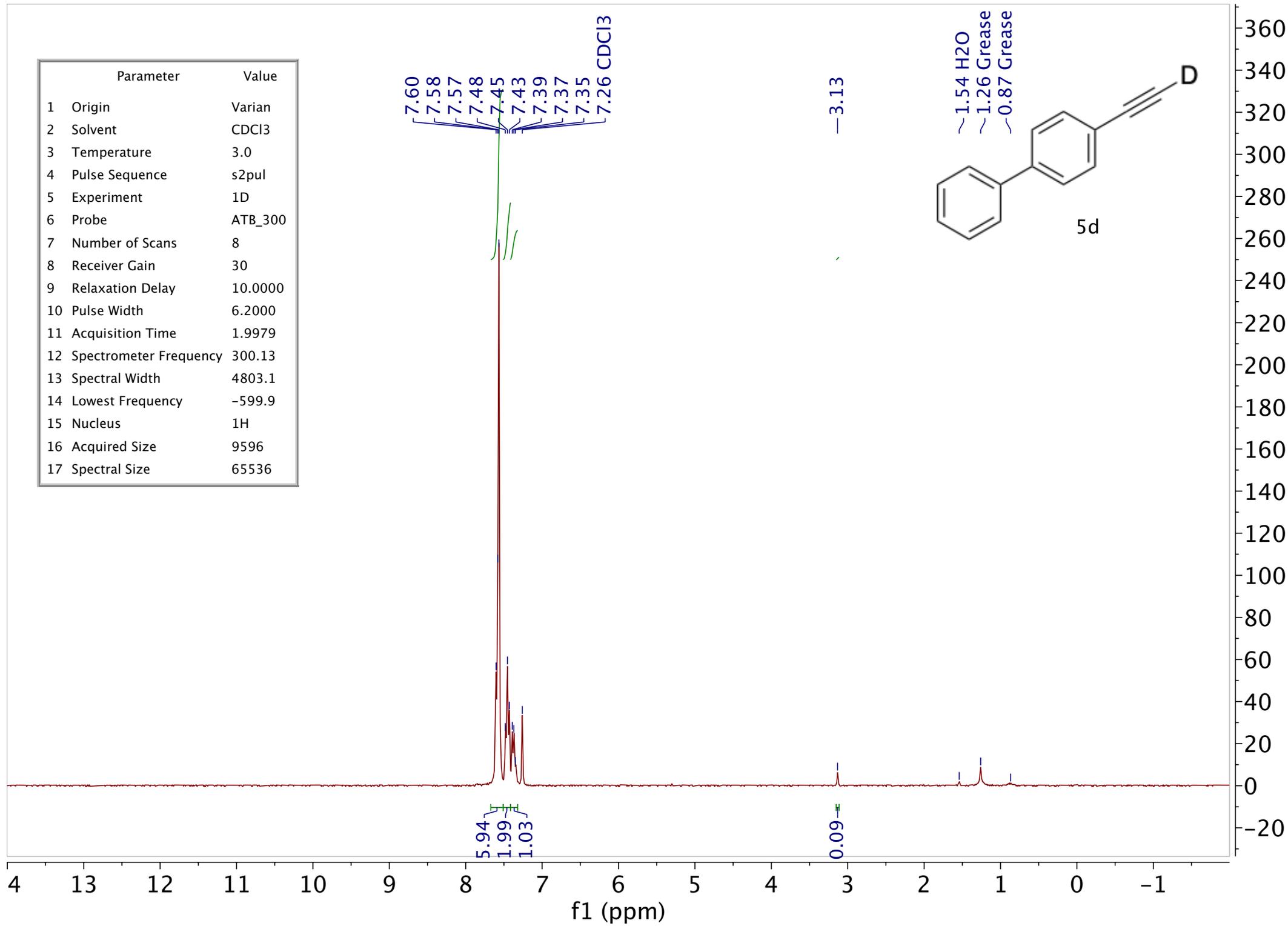
Parameter	Value
1 Origin	Varian
2 Solvent	cdcl3
3 Temperature	20.0
4 Pulse Sequence	s2pul
5 Experiment	1D
6 Probe	ASWPG8319
7 Number of Scans	16
8 Receiver Gain	38
9 Relaxation Delay	10.0000
10 Pulse Width	8.0000
11 Acquisition Time	2.5559
12 Spectrometer Frequency	399.73
13 Spectral Width	6410.3
14 Lowest Frequency	-808.1
15 Nucleus	1H
16 Acquired Size	16384
17 Spectral Size	65536



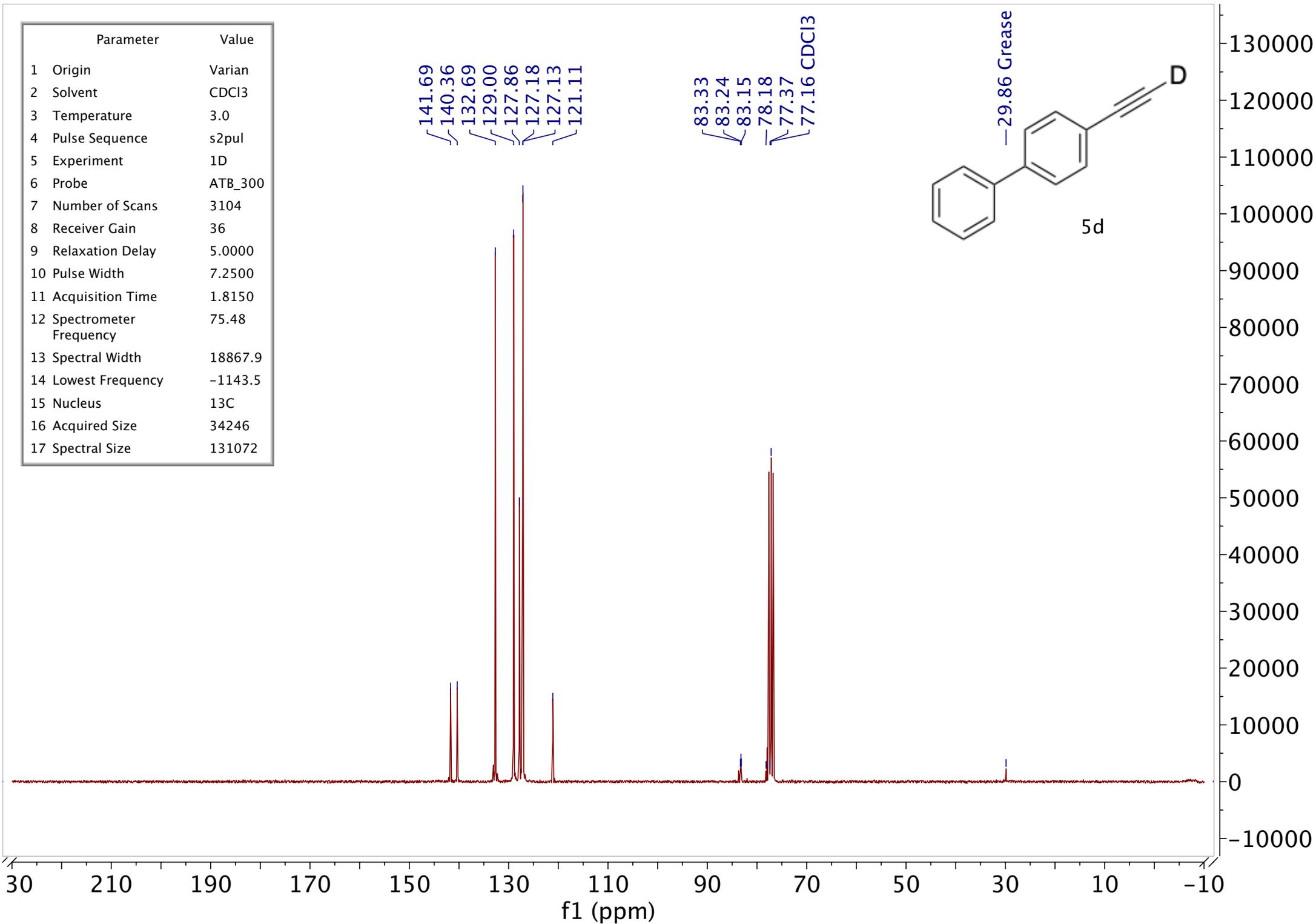
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1 Origin	Varian
2 Solvent	cdcl3
3 Temperature	20.0
4 Pulse Sequence	s2pul
5 Experiment	1D
6 Probe	ASWPG8319
7 Number of Scans	640
8 Receiver Gain	30
9 Relaxation Delay	5.0000
10 Pulse Width	5.7500
11 Acquisition Time	1.3107
12 Spectrometer Frequency	100.52
13 Spectral Width	25000.0
14 Lowest Frequency	-1443.7
15 Nucleus	<sup>13</sup> C
16 Acquired Size	32768
17 Spectral Size	65536



Parameter	Value
1 Origin	Varian
2 Solvent	CDCl3
3 Temperature	3.0
4 Pulse Sequence	s2pul
5 Experiment	1D
6 Probe	ATB_300
7 Number of Scans	8
8 Receiver Gain	30
9 Relaxation Delay	10.0000
10 Pulse Width	6.2000
11 Acquisition Time	1.9979
12 Spectrometer Frequency	300.13
13 Spectral Width	4803.1
14 Lowest Frequency	-599.9
15 Nucleus	1H
16 Acquired Size	9596
17 Spectral Size	65536



Parameter	Value
1 Origin	Varian
2 Solvent	CDCl3
3 Temperature	3.0
4 Pulse Sequence	s2pul
5 Experiment	1D
6 Probe	ATB_300
7 Number of Scans	3104
8 Receiver Gain	36
9 Relaxation Delay	5.0000
10 Pulse Width	7.2500
11 Acquisition Time	1.8150
12 Spectrometer Frequency	75.48
13 Spectral Width	18867.9
14 Lowest Frequency	-1143.5
15 Nucleus	13C
16 Acquired Size	34246
17 Spectral Size	131072

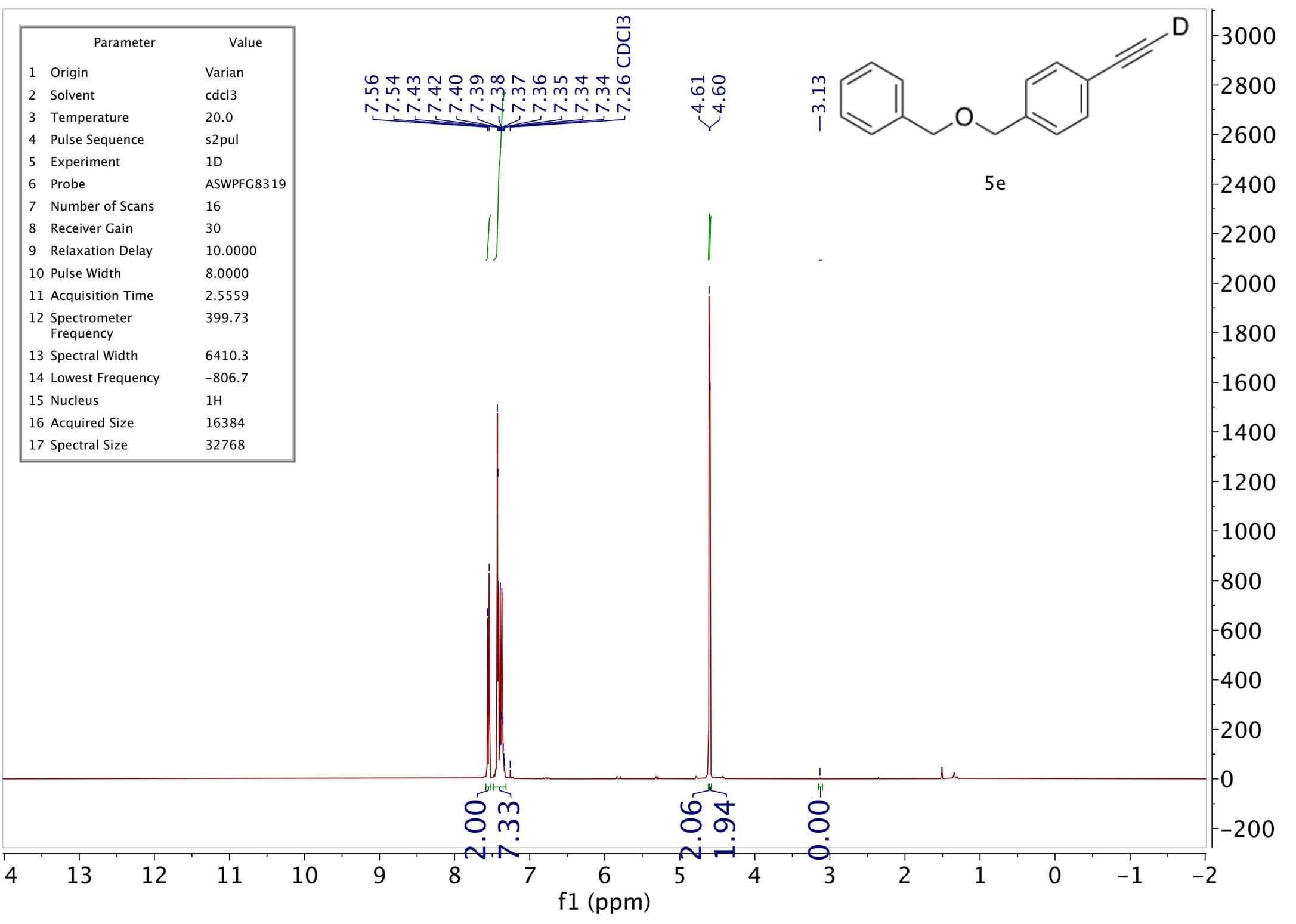
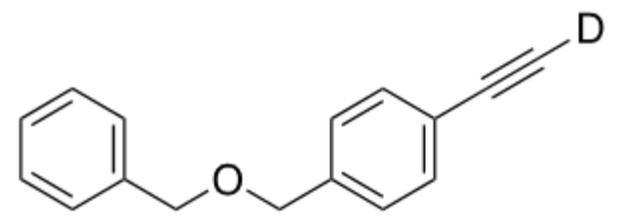


Parameter	Value
1 Origin	Varian
2 Solvent	cdcl3
3 Temperature	20.0
4 Pulse Sequence	s2pul
5 Experiment	1D
6 Probe	ASWPG8319
7 Number of Scans	16
8 Receiver Gain	30
9 Relaxation Delay	10.0000
10 Pulse Width	8.0000
11 Acquisition Time	2.5559
12 Spectrometer Frequency	399.73
13 Spectral Width	6410.3
14 Lowest Frequency	-806.7
15 Nucleus	1H
16 Acquired Size	16384
17 Spectral Size	32768

7.56  
7.54  
7.43  
7.42  
7.40  
7.39  
7.38  
7.37  
7.36  
7.35  
7.34  
7.34  
7.26 CDC13

4.61  
4.60

3.13



2.00  
7.33

2.06  
1.94

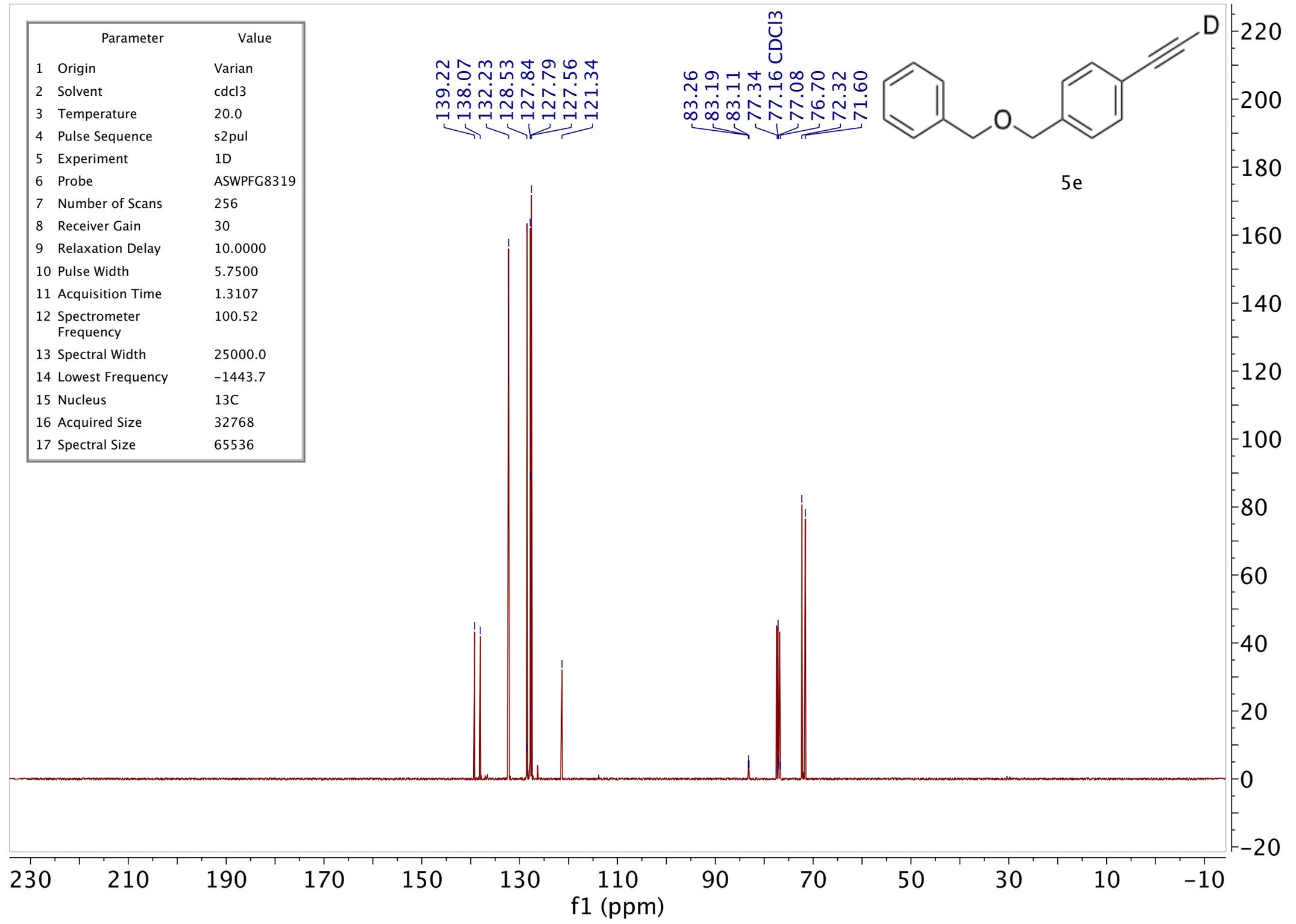
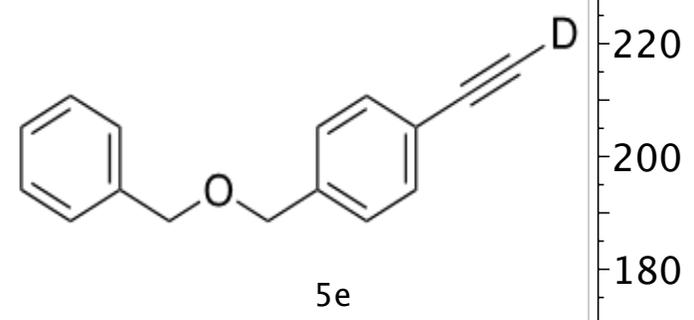
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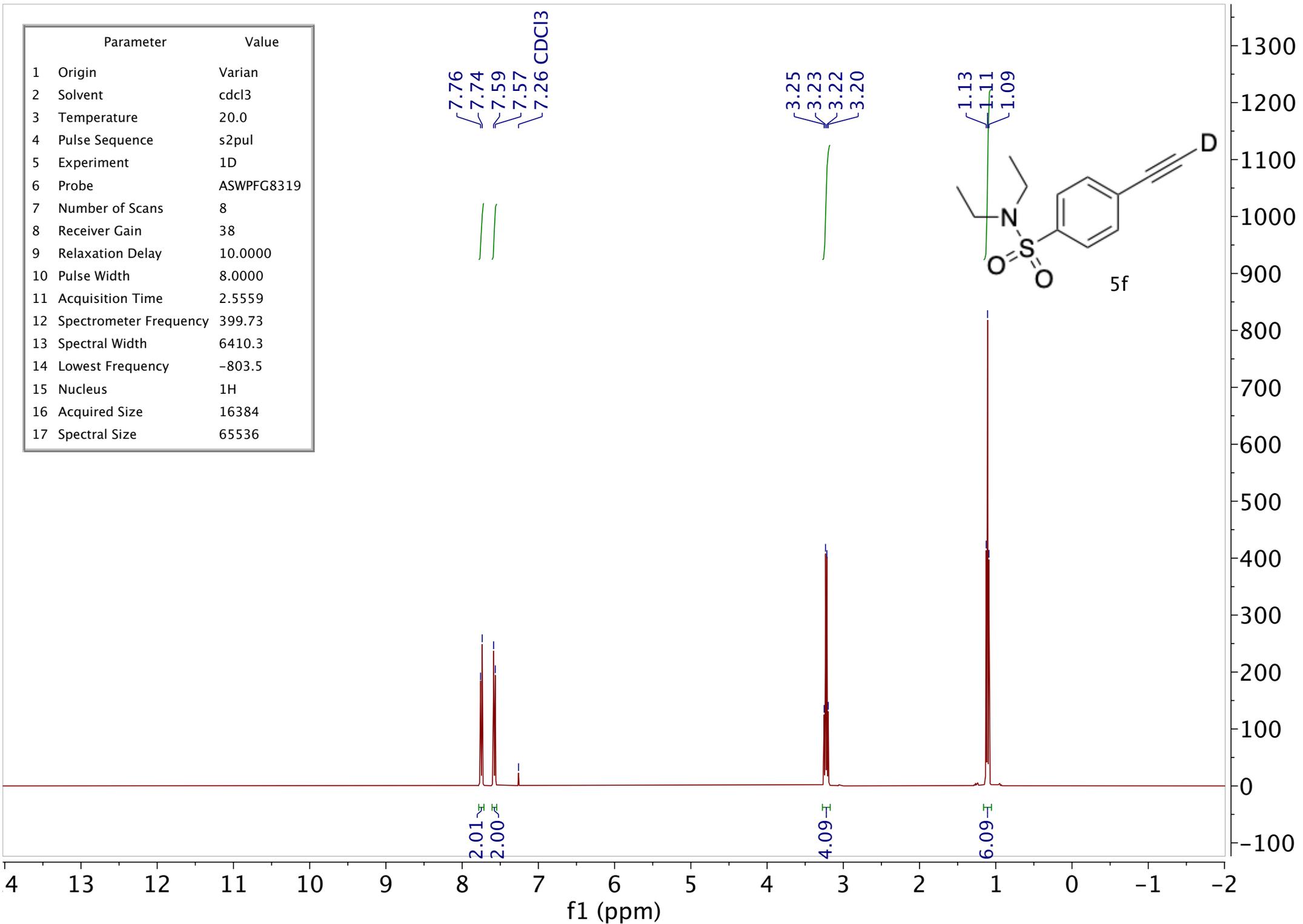
Parameter	Value
1 Origin	Varian
2 Solvent	cdcl3
3 Temperature	20.0
4 Pulse Sequence	s2pul
5 Experiment	1D
6 Probe	ASWPG8319
7 Number of Scans	256
8 Receiver Gain	30
9 Relaxation Delay	10.0000
10 Pulse Width	5.7500
11 Acquisition Time	1.3107
12 Spectrometer Frequency	100.52
13 Spectral Width	25000.0
14 Lowest Frequency	-1443.7
15 Nucleus	<sup>13</sup> C
16 Acquired Size	32768
17 Spectral Size	65536

139.22  
138.07  
132.23  
128.53  
127.84  
127.79  
127.56  
121.34

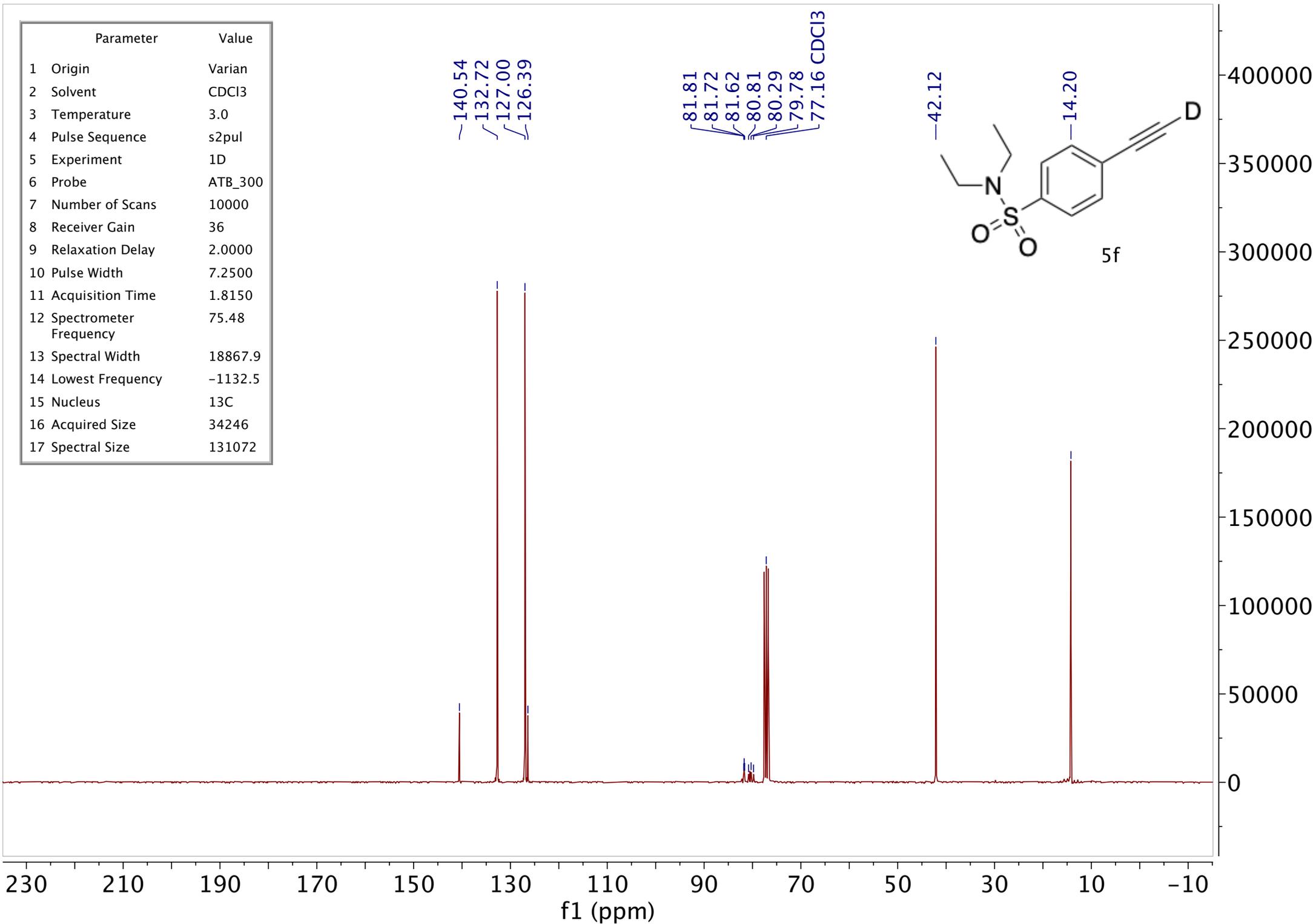
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83.11  
77.34  
77.16 CDCl<sub>3</sub>  
77.08  
76.70  
72.32  
71.60



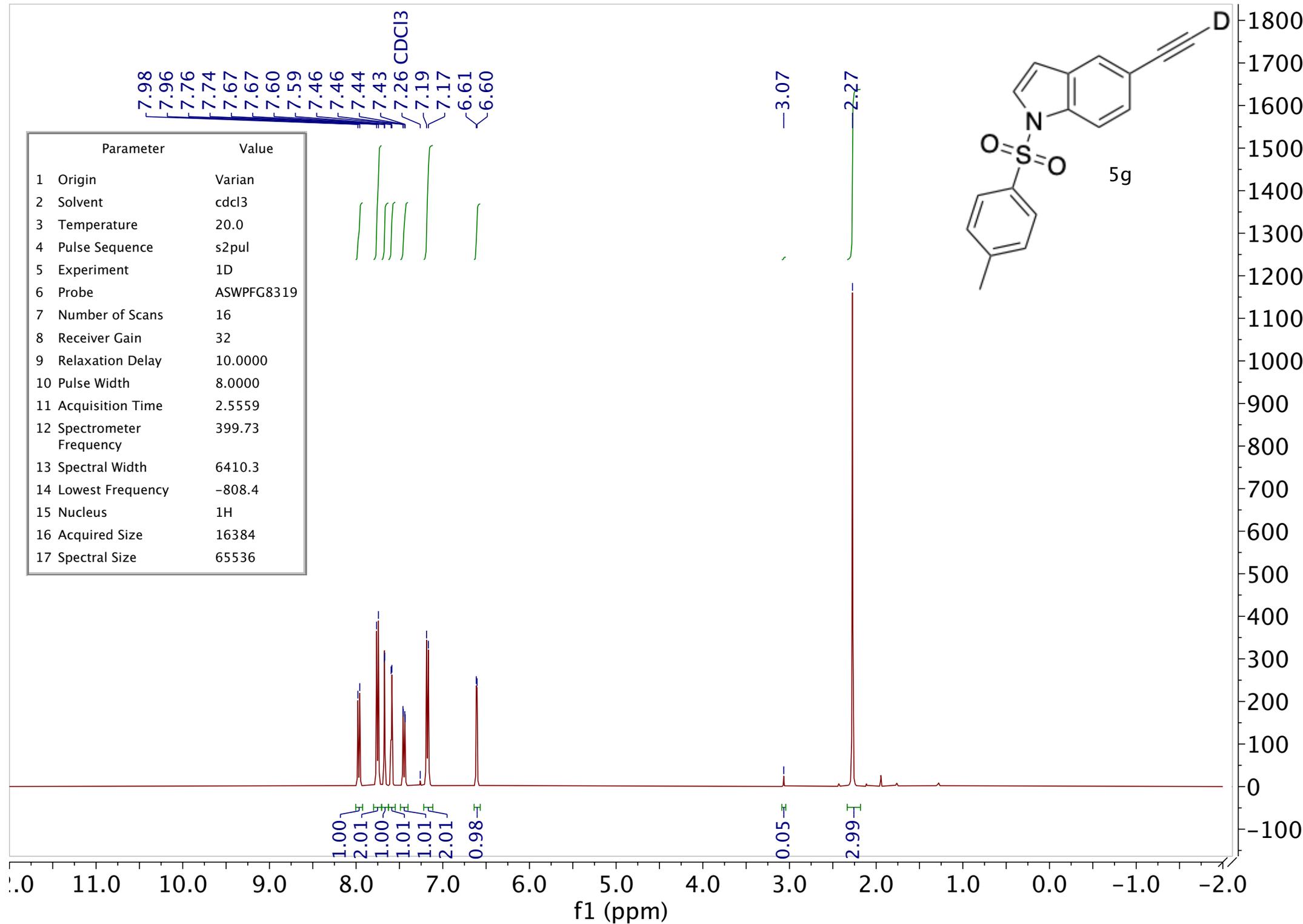
Parameter	Value
1 Origin	Varian
2 Solvent	cdcl3
3 Temperature	20.0
4 Pulse Sequence	s2pul
5 Experiment	1D
6 Probe	ASWPG8319
7 Number of Scans	8
8 Receiver Gain	38
9 Relaxation Delay	10.0000
10 Pulse Width	8.0000
11 Acquisition Time	2.5559
12 Spectrometer Frequency	399.73
13 Spectral Width	6410.3
14 Lowest Frequency	-803.5
15 Nucleus	1H
16 Acquired Size	16384
17 Spectral Size	65536



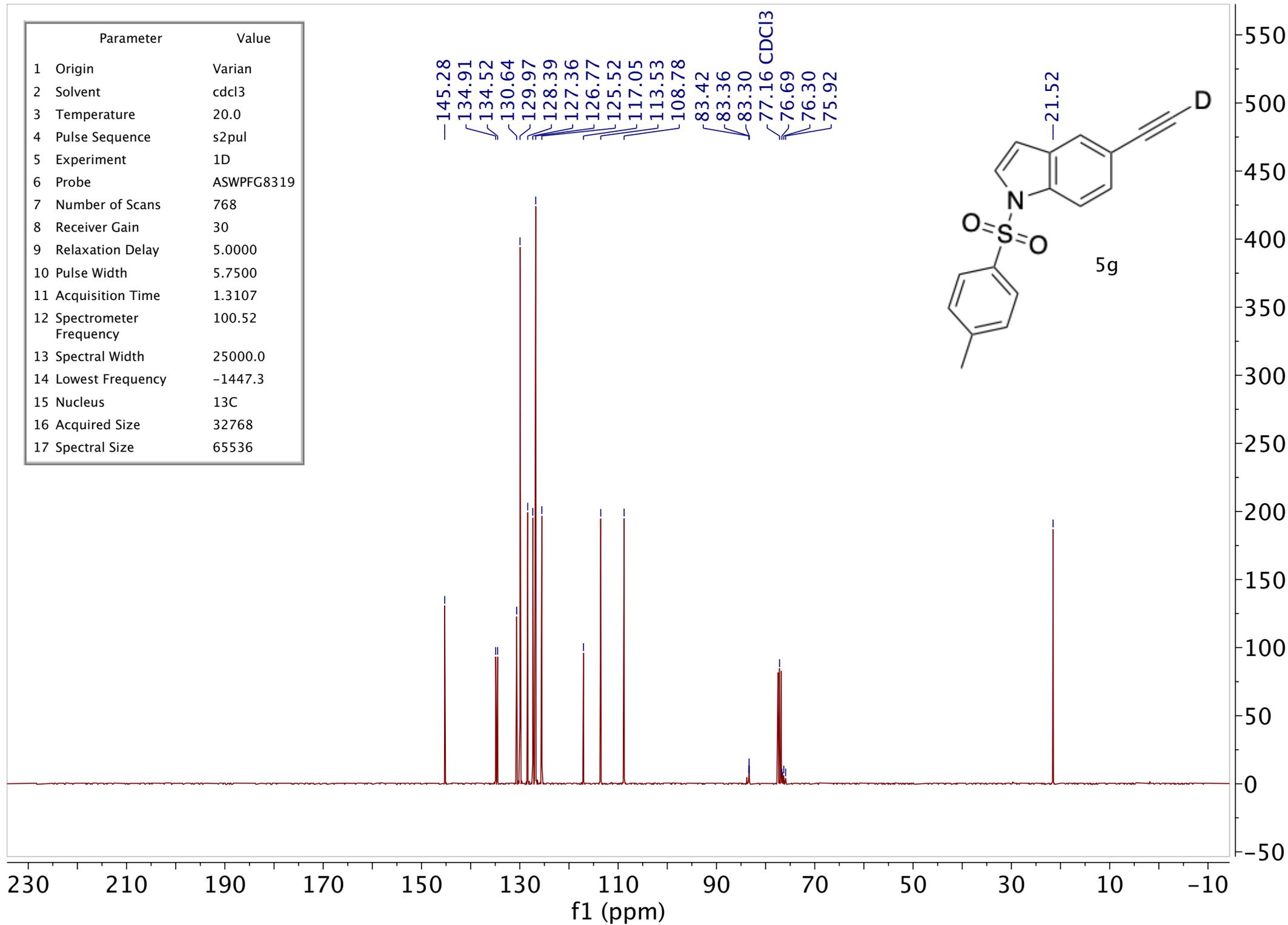
Parameter	Value
1 Origin	Varian
2 Solvent	CDCl3
3 Temperature	3.0
4 Pulse Sequence	s2pul
5 Experiment	1D
6 Probe	ATB_300
7 Number of Scans	10000
8 Receiver Gain	36
9 Relaxation Delay	2.0000
10 Pulse Width	7.2500
11 Acquisition Time	1.8150
12 Spectrometer Frequency	75.48
13 Spectral Width	18867.9
14 Lowest Frequency	-1132.5
15 Nucleus	13C
16 Acquired Size	34246
17 Spectral Size	131072

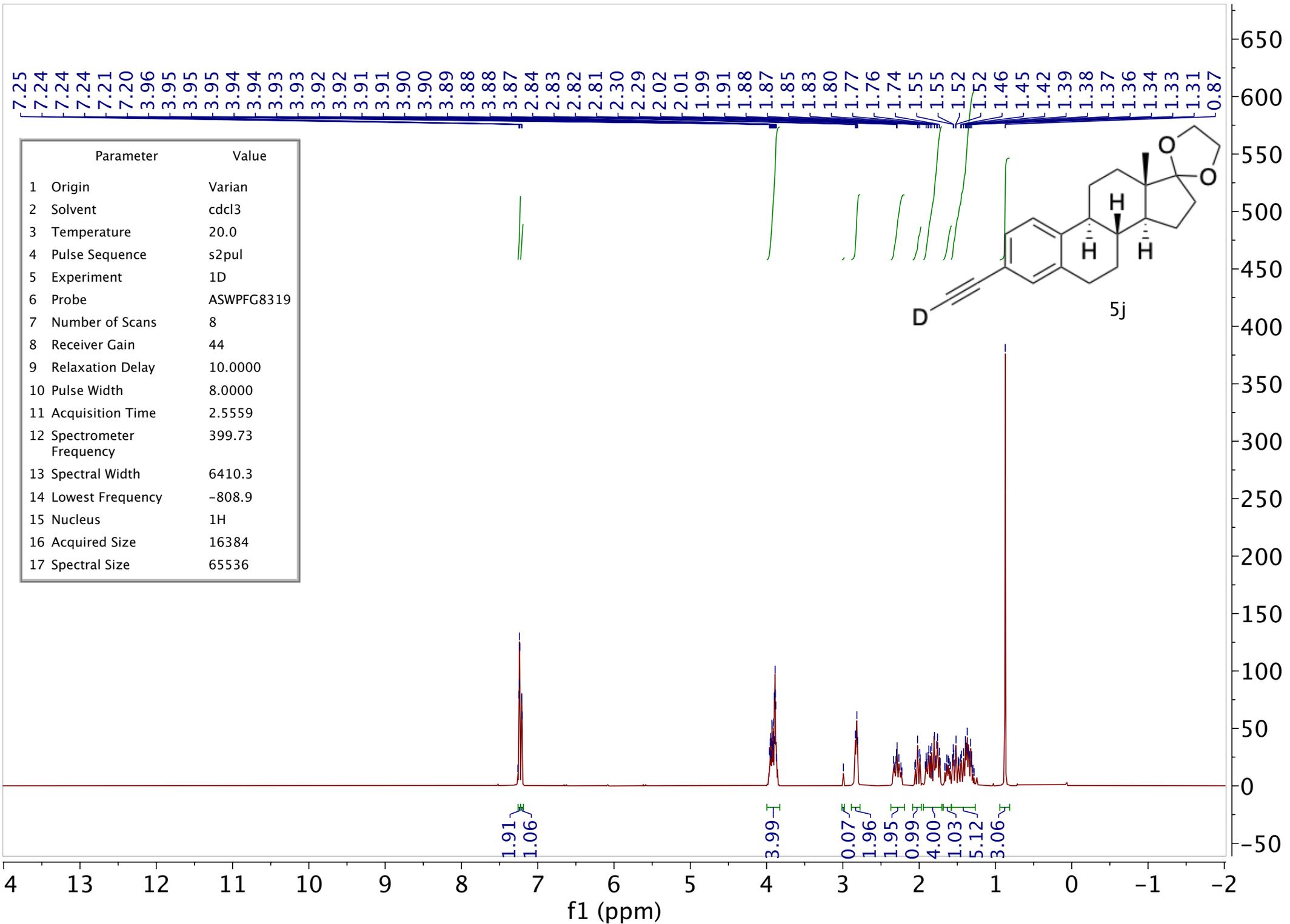


Parameter	Value
1 Origin	Varian
2 Solvent	cdcl3
3 Temperature	20.0
4 Pulse Sequence	s2pul
5 Experiment	1D
6 Probe	ASWPF8319
7 Number of Scans	16
8 Receiver Gain	32
9 Relaxation Delay	10.0000
10 Pulse Width	8.0000
11 Acquisition Time	2.5559
12 Spectrometer Frequency	399.73
13 Spectral Width	6410.3
14 Lowest Frequency	-808.4
15 Nucleus	1H
16 Acquired Size	16384
17 Spectral Size	65536



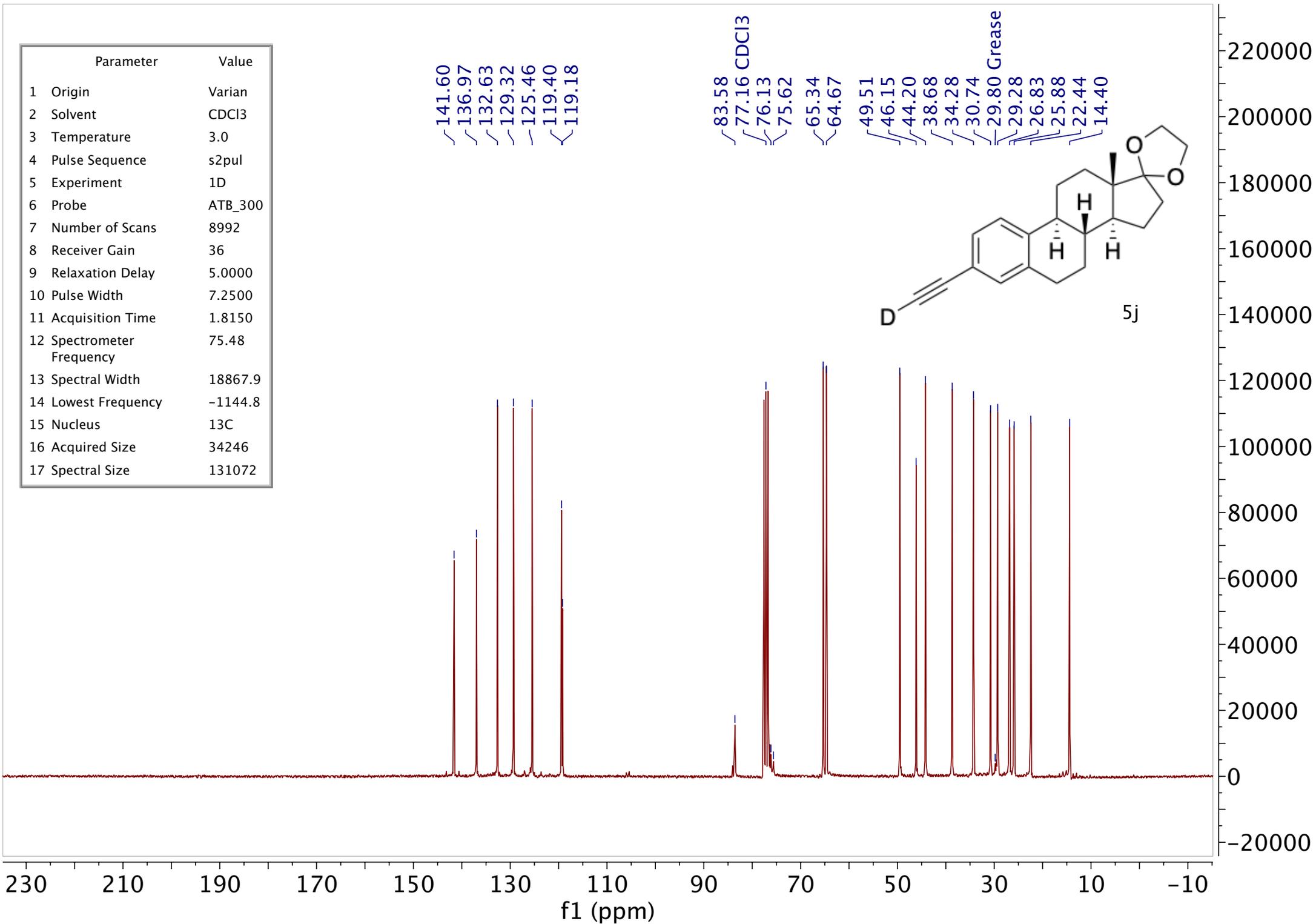
Parameter	Value
1 Origin	Varian
2 Solvent	cdcl3
3 Temperature	20.0
4 Pulse Sequence	s2pul
5 Experiment	1D
6 Probe	ASWPG8319
7 Number of Scans	768
8 Receiver Gain	30
9 Relaxation Delay	5.0000
10 Pulse Width	5.7500
11 Acquisition Time	1.3107
12 Spectrometer Frequency	100.52
13 Spectral Width	25000.0
14 Lowest Frequency	-1447.3
15 Nucleus	<sup>13</sup> C
16 Acquired Size	32768
17 Spectral Size	65536





Parameter	Value
1 Origin	Varian
2 Solvent	cdcl3
3 Temperature	20.0
4 Pulse Sequence	s2pul
5 Experiment	1D
6 Probe	ASWPG8319
7 Number of Scans	8
8 Receiver Gain	44
9 Relaxation Delay	10.0000
10 Pulse Width	8.0000
11 Acquisition Time	2.5559
12 Spectrometer Frequency	399.73
13 Spectral Width	6410.3
14 Lowest Frequency	-808.9
15 Nucleus	1H
16 Acquired Size	16384
17 Spectral Size	65536

Parameter	Value
1 Origin	Varian
2 Solvent	CDCl3
3 Temperature	3.0
4 Pulse Sequence	s2pul
5 Experiment	1D
6 Probe	ATB_300
7 Number of Scans	8992
8 Receiver Gain	36
9 Relaxation Delay	5.0000
10 Pulse Width	7.2500
11 Acquisition Time	1.8150
12 Spectrometer Frequency	75.48
13 Spectral Width	18867.9
14 Lowest Frequency	-1144.8
15 Nucleus	13C
16 Acquired Size	34246
17 Spectral Size	131072



141.60  
136.97  
132.63  
129.32  
125.46  
119.40  
119.18

83.58  
77.16 CDCl3  
76.13  
75.62  
65.34  
64.67

49.51  
46.15  
44.20  
38.68  
34.28  
30.74  
29.80 Grease  
29.28  
26.83  
25.88  
22.44  
14.40

5j

230 210 190 170 150 130 110 90 70 50 30 10 -10  
f1 (ppm)

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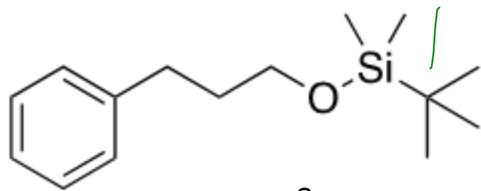
Parameter	Value
1 Origin	Varian
2 Solvent	cdcl3
3 Temperature	20.0
4 Pulse Sequence	s2pul
5 Experiment	1D
6 Probe	ASWPG8319
7 Number of Scans	8
8 Receiver Gain	38
9 Relaxation Delay	10.0000
10 Pulse Width	8.0000
11 Acquisition Time	2.5559
12 Spectrometer Frequency	399.73
13 Spectral Width	6410.3
14 Lowest Frequency	-806.7
15 Nucleus	1H
16 Acquired Size	16384
17 Spectral Size	65536

7.31  
7.29  
7.29  
7.28  
7.27  
7.26 CDCl3  
7.22  
7.21  
7.20  
7.20  
7.19  
7.17

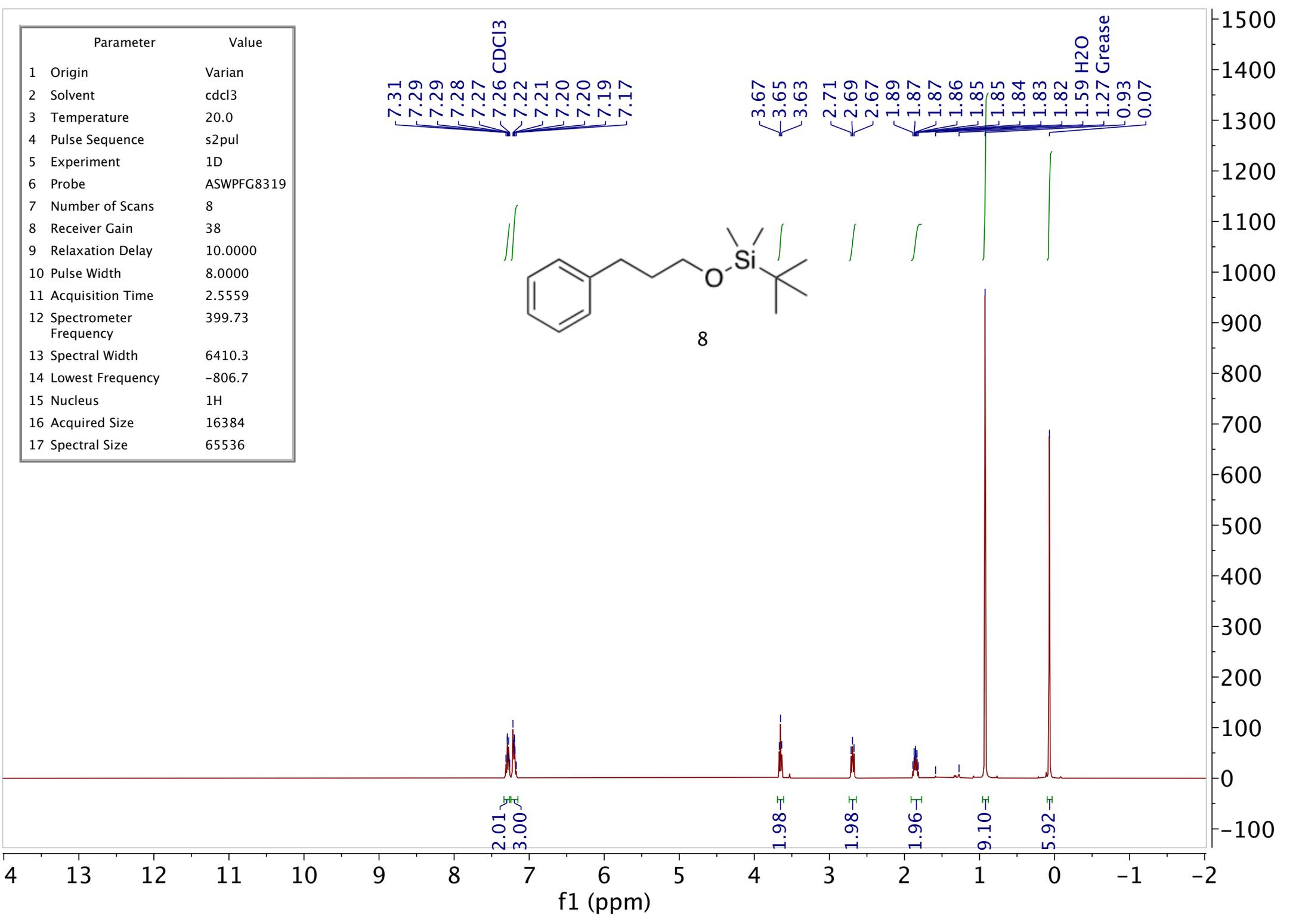
3.67  
3.65  
3.63

2.71  
2.69  
2.67

1.89  
1.87  
1.87  
1.86  
1.85  
1.85  
1.84  
1.83  
1.82  
1.59 H2O  
1.27 Grease  
0.93  
0.07

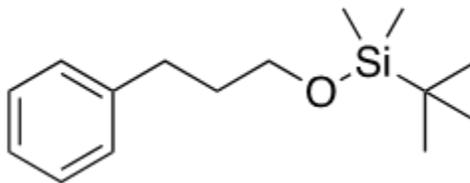


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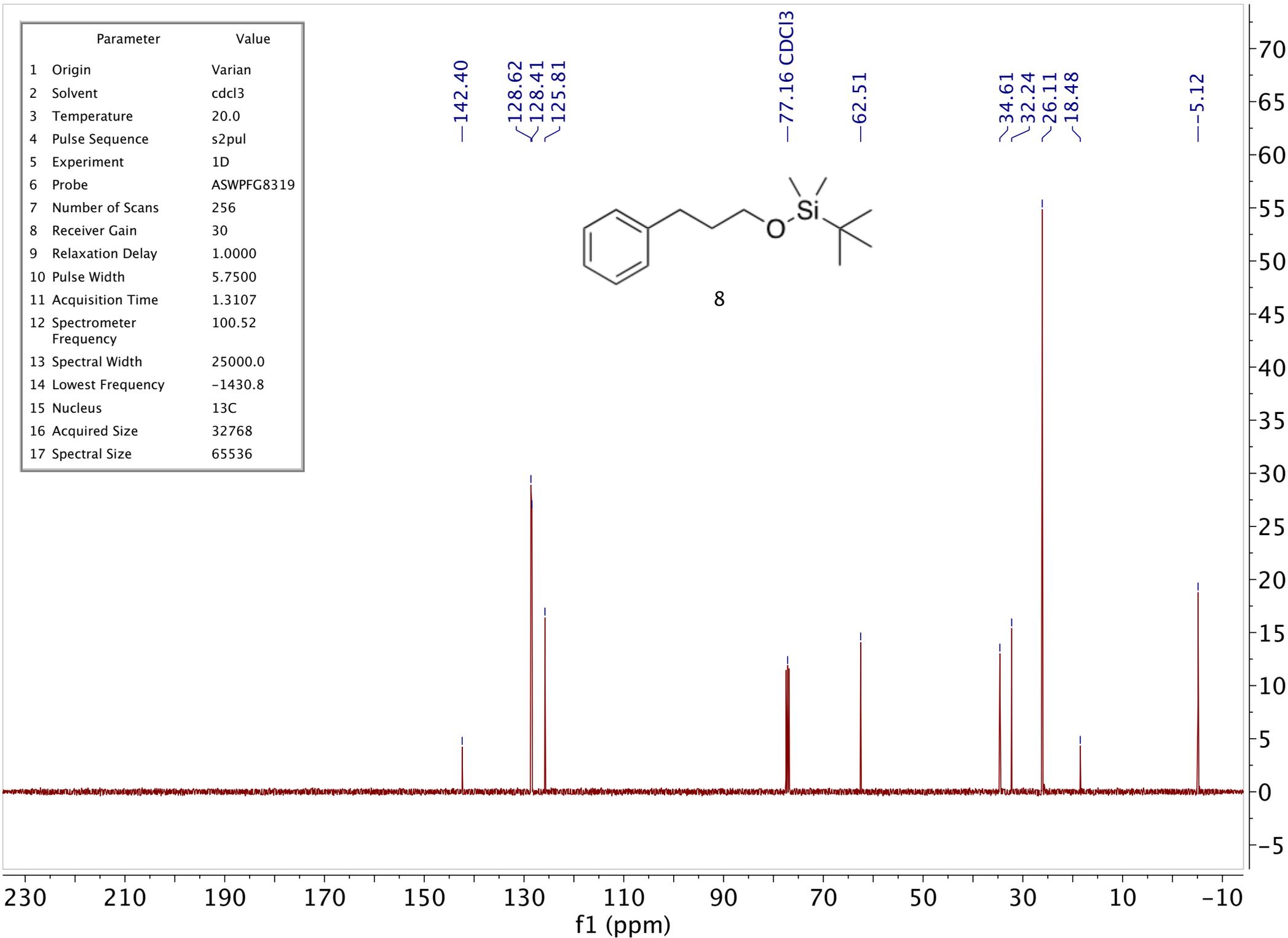


f1 (ppm)

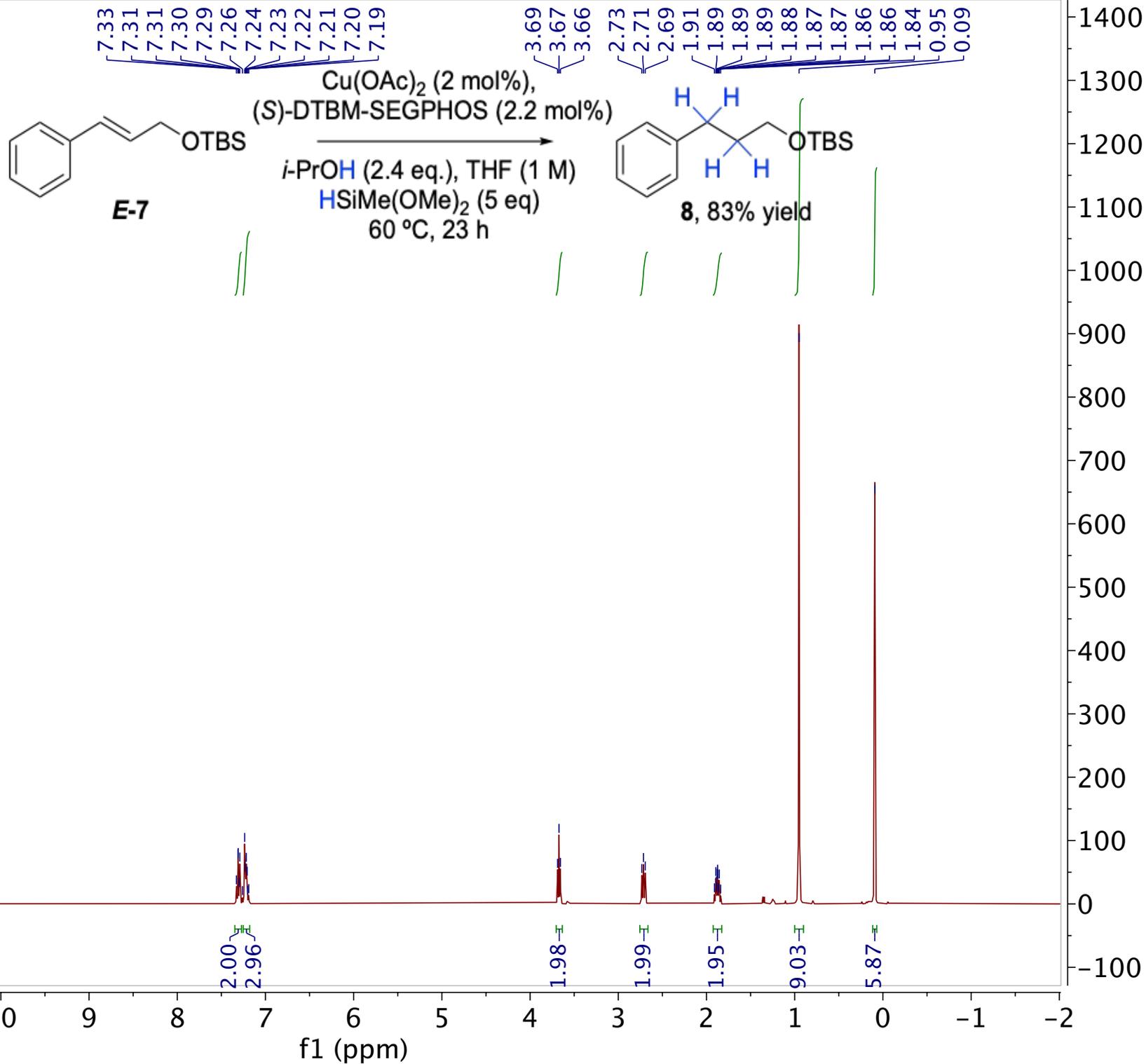
Parameter	Value
1 Origin	Varian
2 Solvent	cdcl3
3 Temperature	20.0
4 Pulse Sequence	s2pul
5 Experiment	1D
6 Probe	ASWPF8319
7 Number of Scans	256
8 Receiver Gain	30
9 Relaxation Delay	1.0000
10 Pulse Width	5.7500
11 Acquisition Time	1.3107
12 Spectrometer Frequency	100.52
13 Spectral Width	25000.0
14 Lowest Frequency	-1430.8
15 Nucleus	<sup>13</sup> C
16 Acquired Size	32768
17 Spectral Size	65536

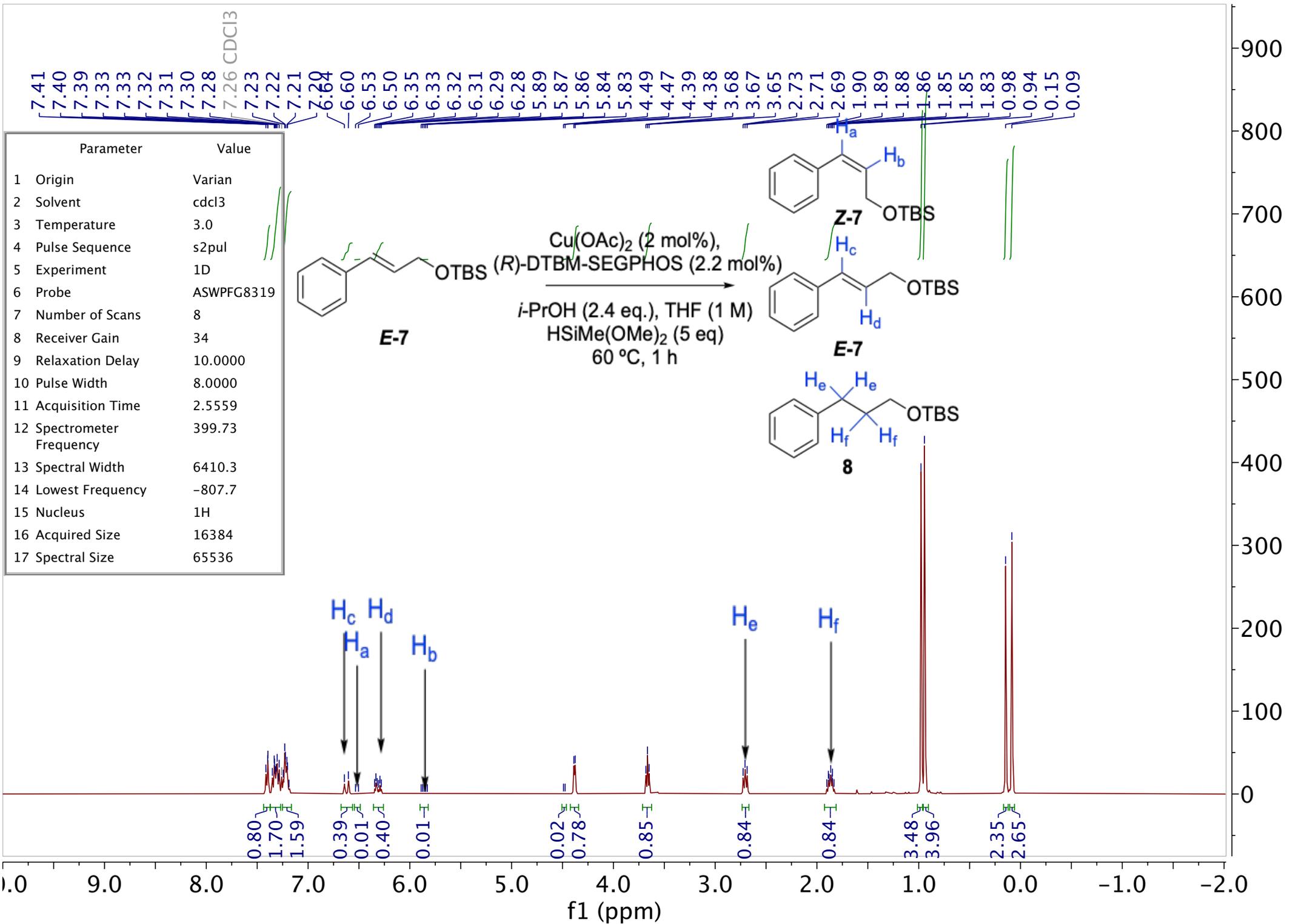


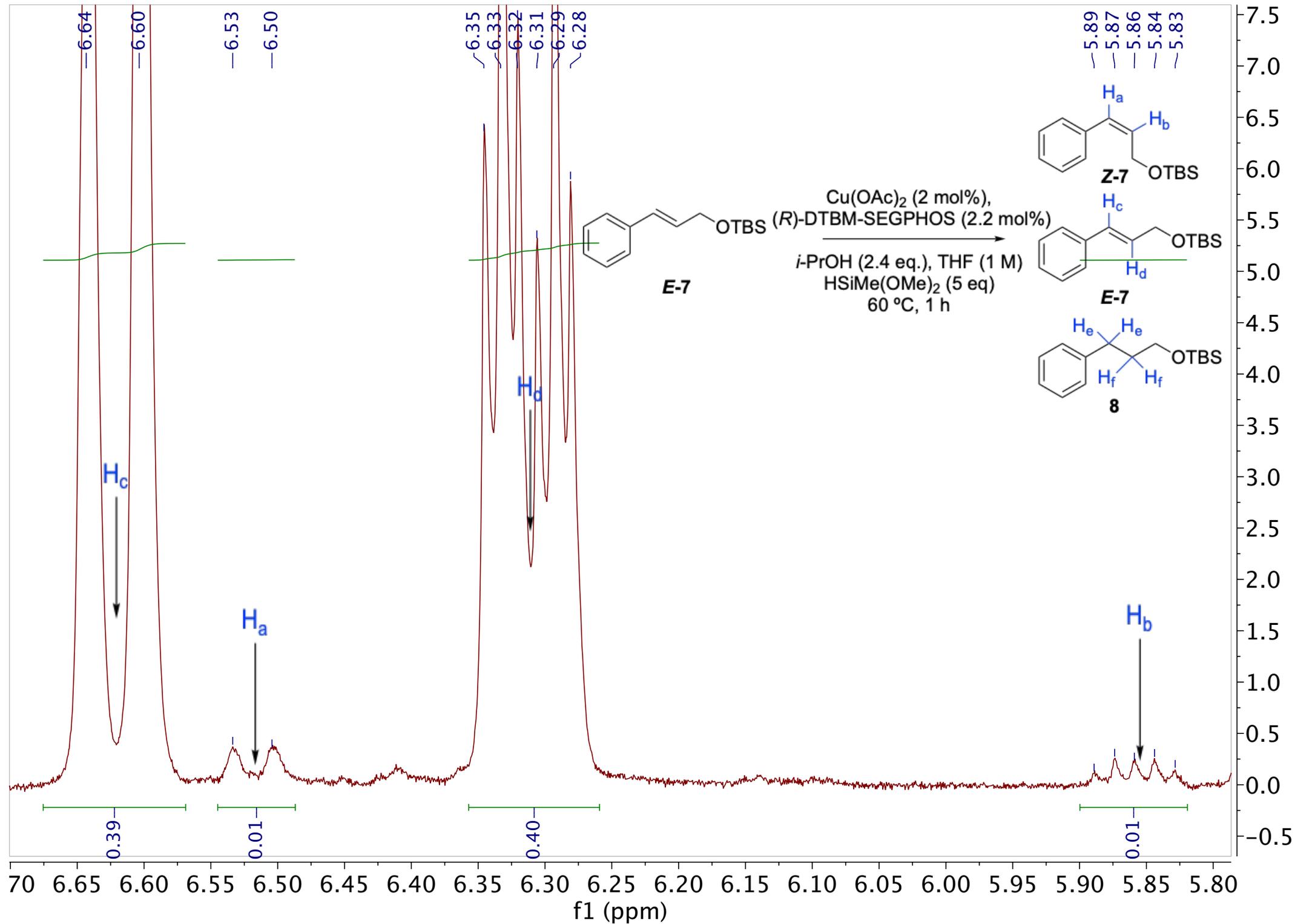
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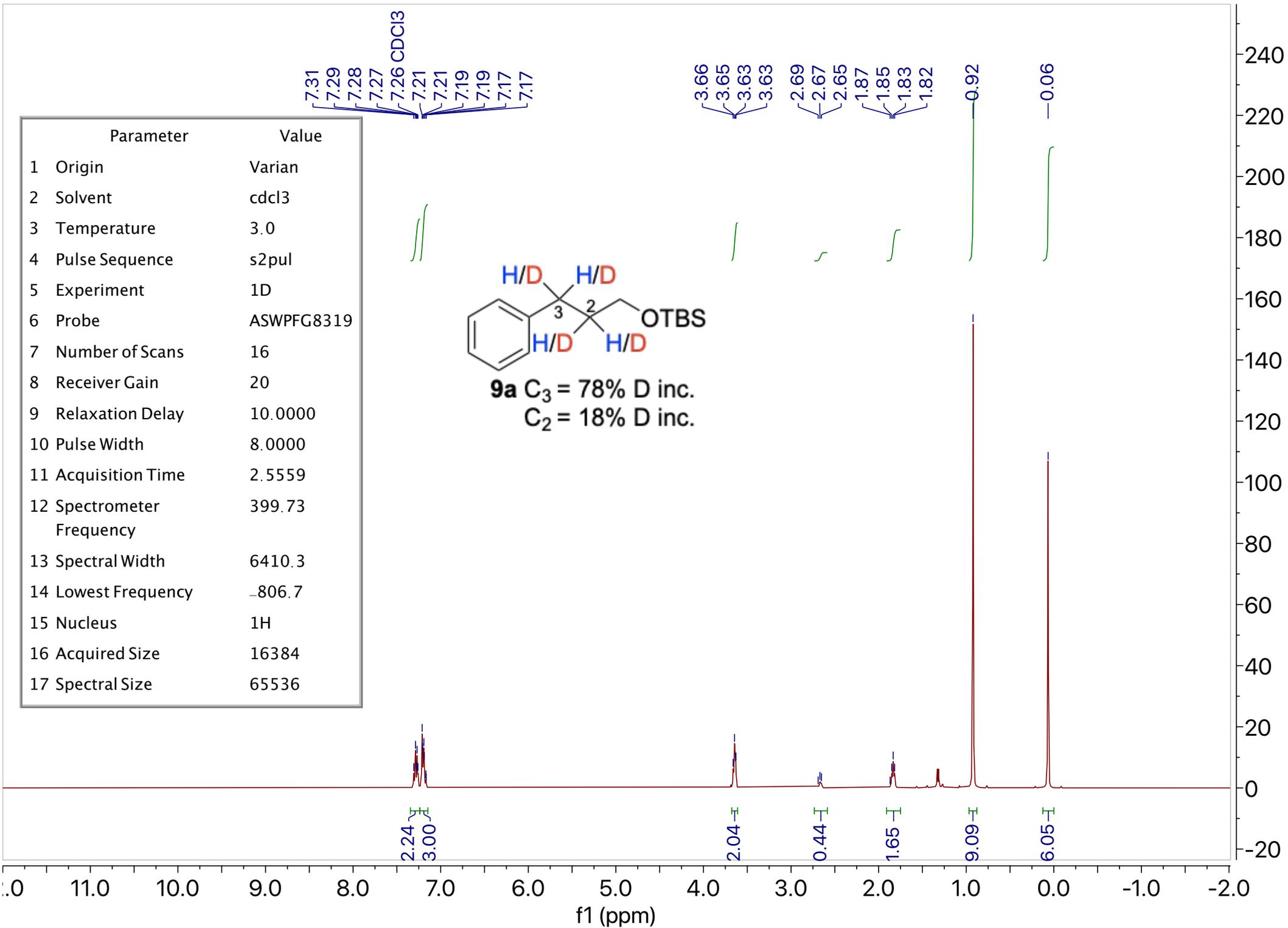
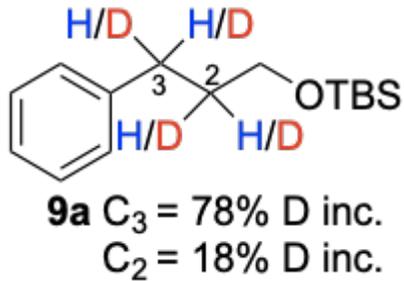
Parameter	Value
1 Origin	Varian
2 Solvent	cdcl3
3 Temperature	3.0
4 Pulse Sequence	s2pul
5 Experiment	1D
6 Probe	ASWPG8319
7 Number of Scans	8
8 Receiver Gain	32
9 Relaxation Delay	10.0000
10 Pulse Width	8.0000
11 Acquisition Time	2.5559
12 Spectrometer Frequency	399.73
13 Spectral Width	6410.3
14 Lowest Frequency	-806.7
15 Nucleus	1H
16 Acquired Size	16384
17 Spectral Size	65536



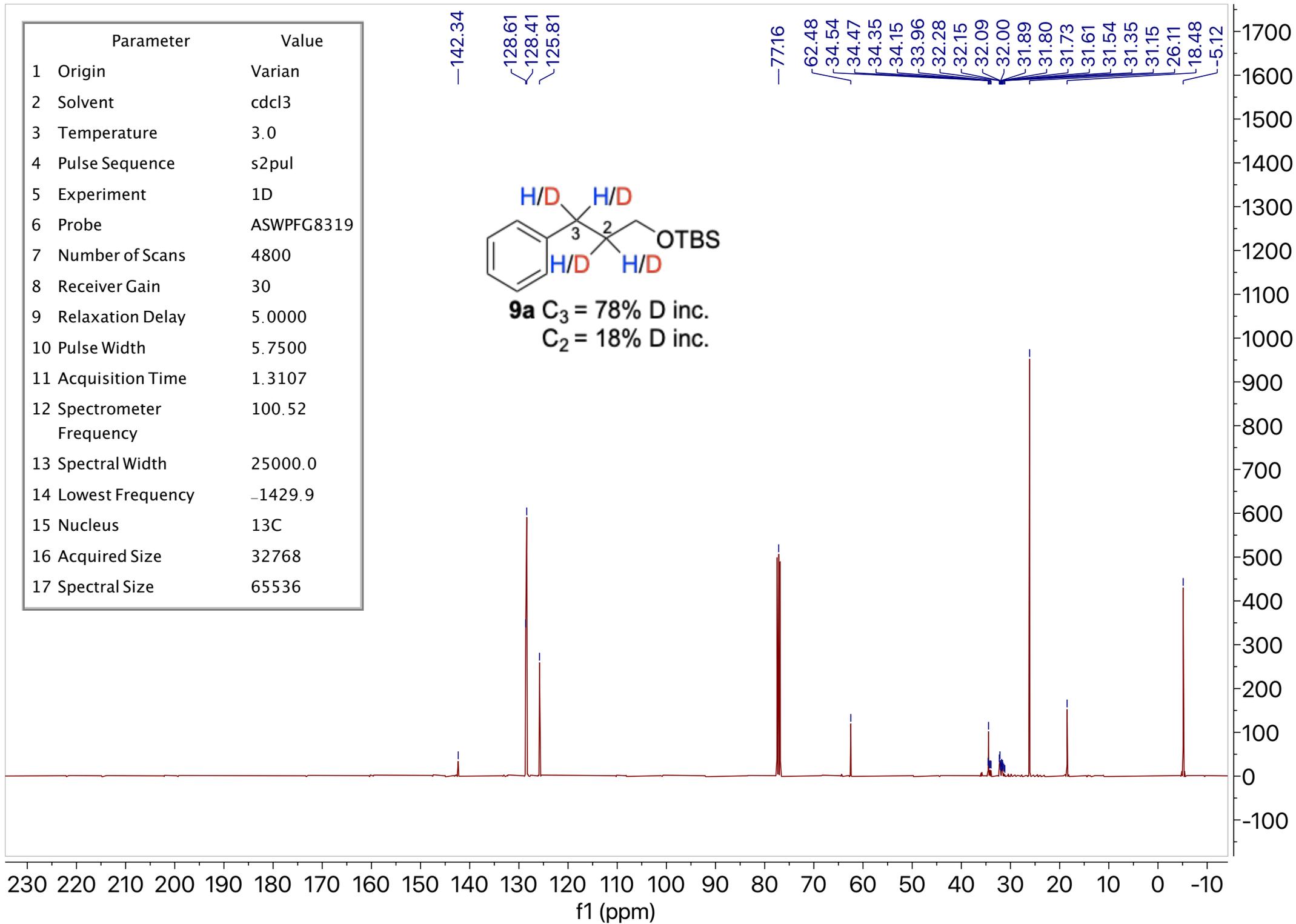
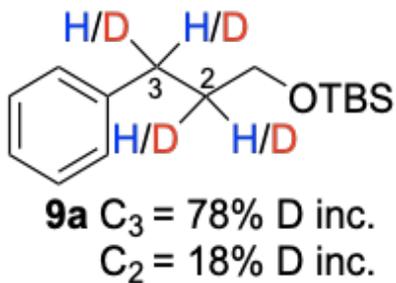


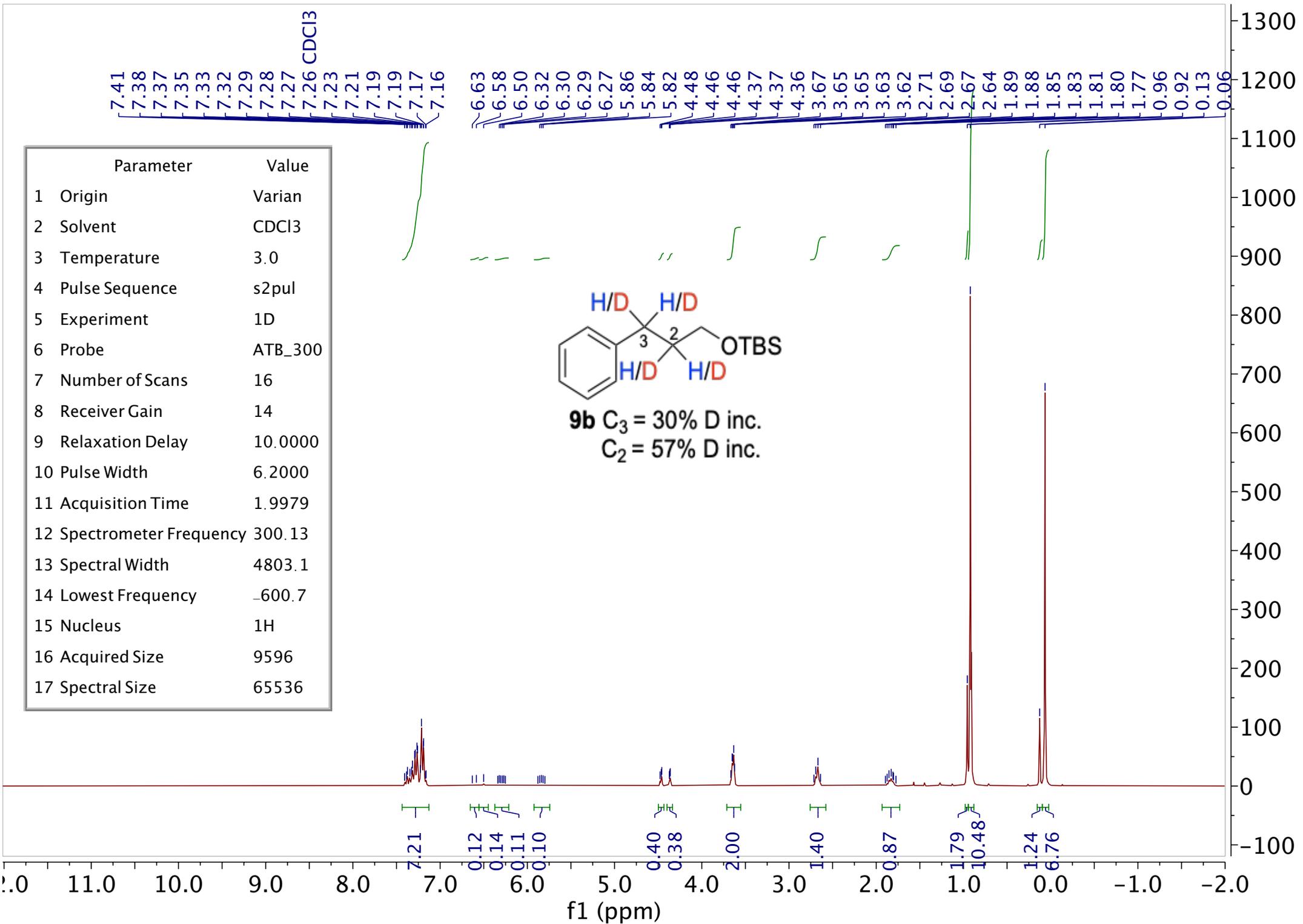


Parameter	Value
1 Origin	Varian
2 Solvent	cdcl3
3 Temperature	3.0
4 Pulse Sequence	s2pul
5 Experiment	1D
6 Probe	ASWPG8319
7 Number of Scans	16
8 Receiver Gain	20
9 Relaxation Delay	10.0000
10 Pulse Width	8.0000
11 Acquisition Time	2.5559
12 Spectrometer Frequency	399.73
13 Spectral Width	6410.3
14 Lowest Frequency	-806.7
15 Nucleus	1H
16 Acquired Size	16384
17 Spectral Size	65536

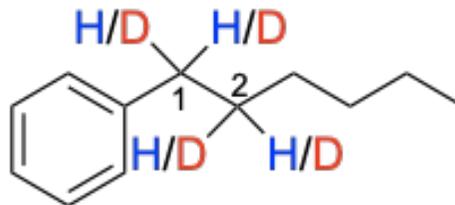


Parameter	Value
1 Origin	Varian
2 Solvent	cdcl3
3 Temperature	3.0
4 Pulse Sequence	s2pul
5 Experiment	1D
6 Probe	ASWPFG8319
7 Number of Scans	4800
8 Receiver Gain	30
9 Relaxation Delay	5.0000
10 Pulse Width	5.7500
11 Acquisition Time	1.3107
12 Spectrometer Frequency	100.52
13 Spectral Width	25000.0
14 Lowest Frequency	-1429.9
15 Nucleus	<sup>13</sup> C
16 Acquired Size	32768
17 Spectral Size	65536

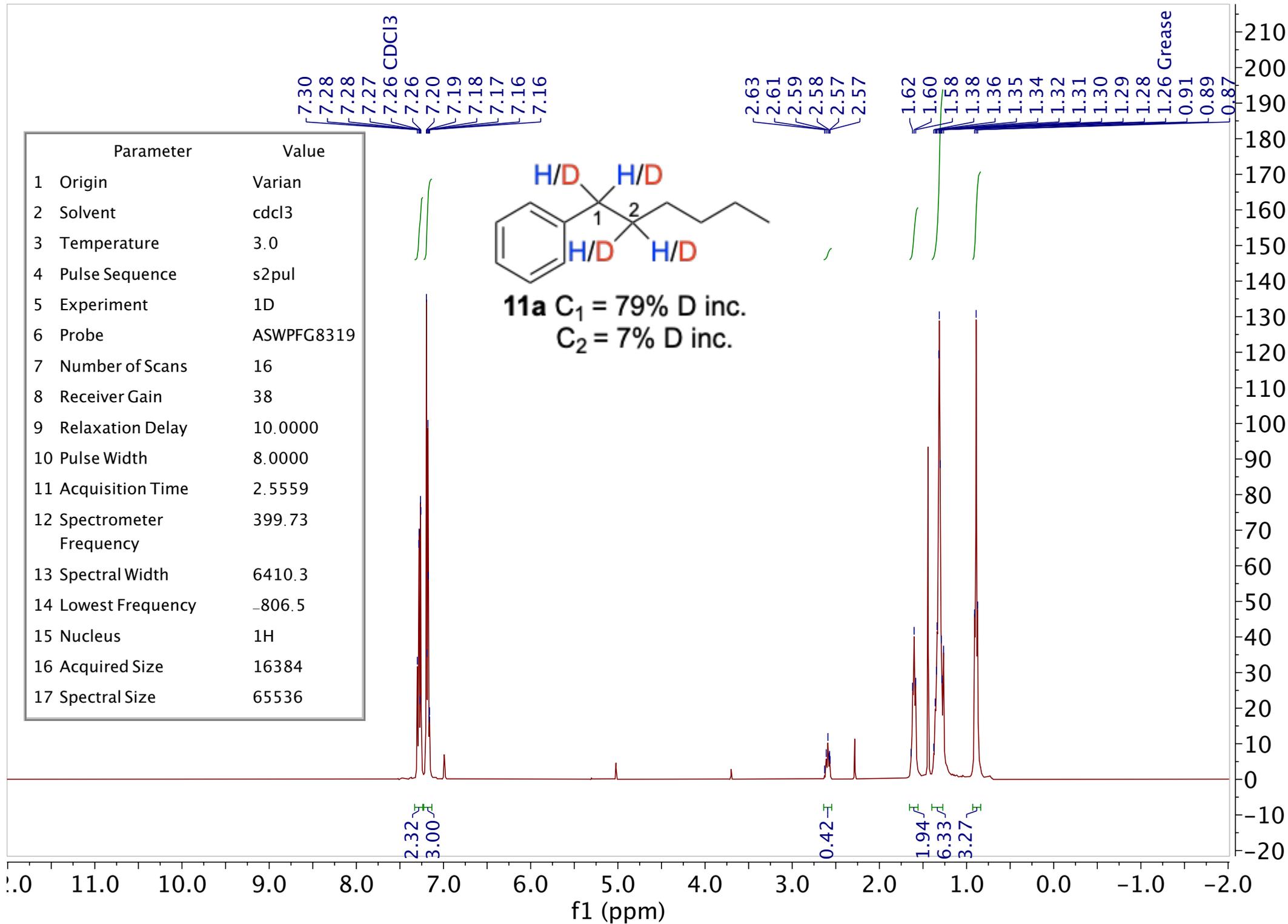




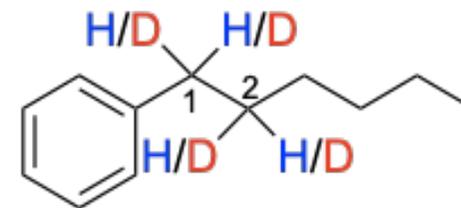
Parameter	Value
1 Origin	Varian
2 Solvent	cdcl3
3 Temperature	3.0
4 Pulse Sequence	s2pul
5 Experiment	1D
6 Probe	ASWPGF8319
7 Number of Scans	16
8 Receiver Gain	38
9 Relaxation Delay	10.0000
10 Pulse Width	8.0000
11 Acquisition Time	2.5559
12 Spectrometer	399.73
Frequency	
13 Spectral Width	6410.3
14 Lowest Frequency	-806.5
15 Nucleus	1H
16 Acquired Size	16384
17 Spectral Size	65536



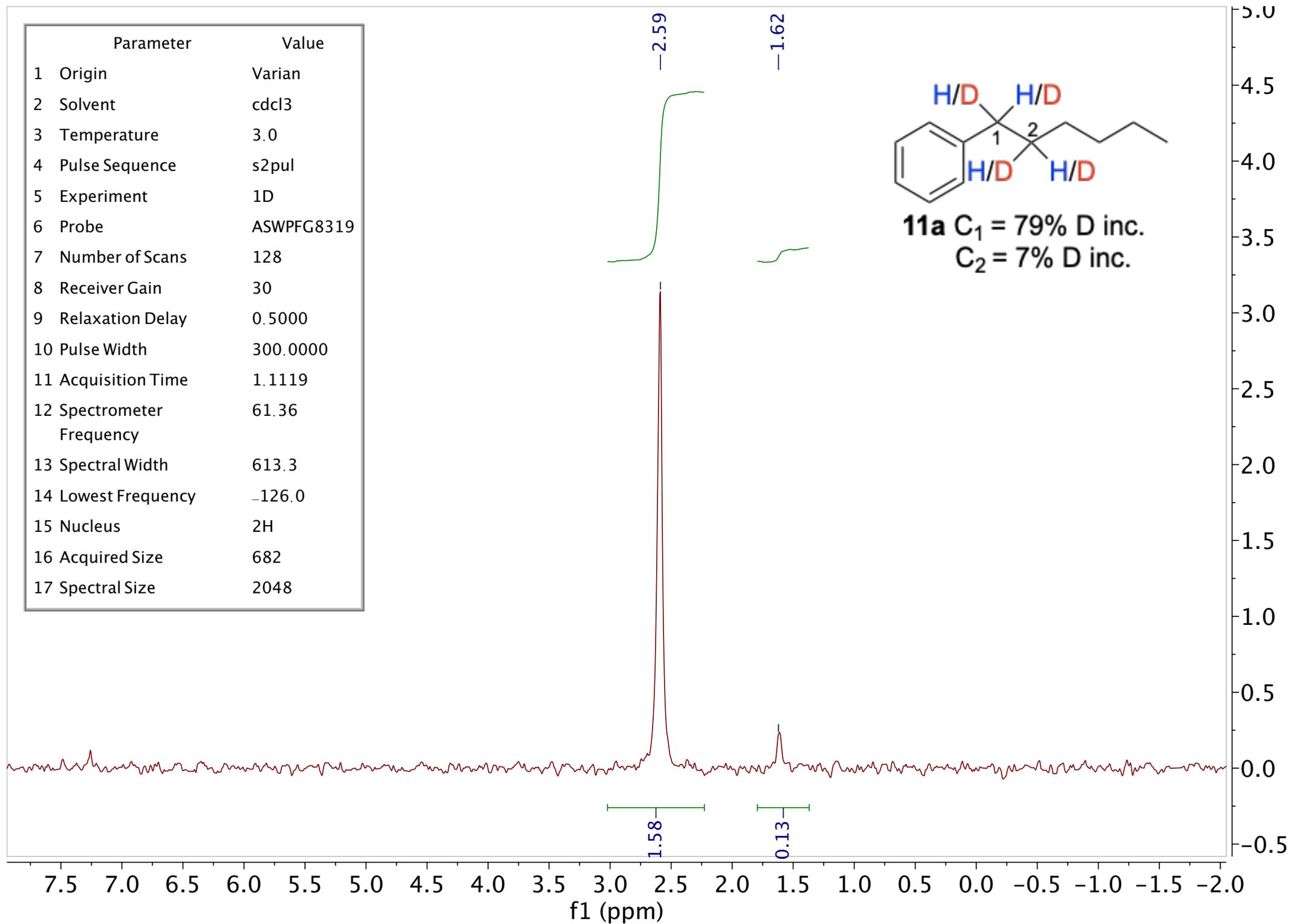
**11a** C<sub>1</sub> = 79% D inc.  
C<sub>2</sub> = 7% D inc.



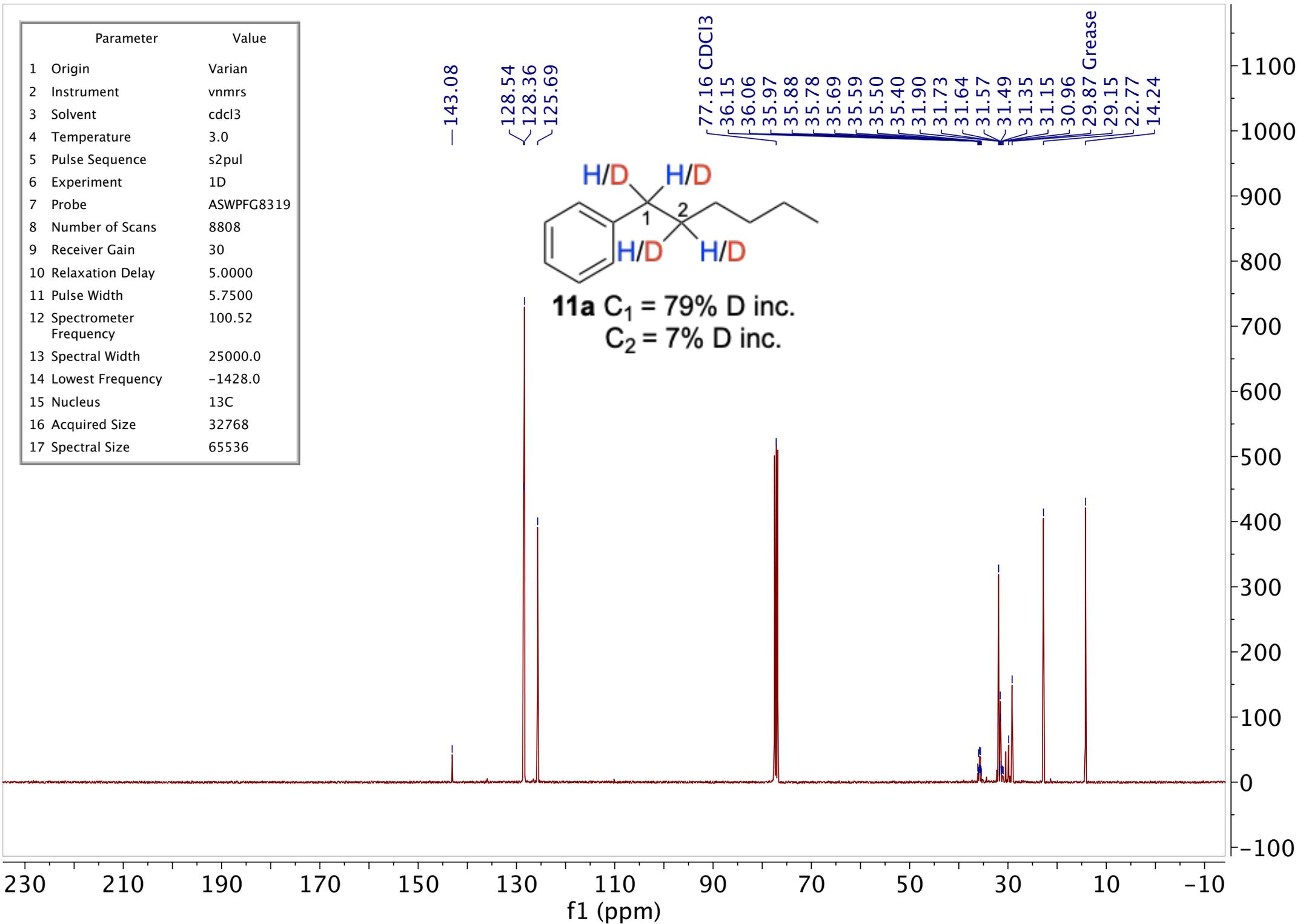
Parameter	Value
1 Origin	Varian
2 Solvent	cdcl3
3 Temperature	3.0
4 Pulse Sequence	s2pul
5 Experiment	1D
6 Probe	ASWPFG8319
7 Number of Scans	128
8 Receiver Gain	30
9 Relaxation Delay	0.5000
10 Pulse Width	300.0000
11 Acquisition Time	1.1119
12 Spectrometer Frequency	61.36
13 Spectral Width	613.3
14 Lowest Frequency	-126.0
15 Nucleus	2H
16 Acquired Size	682
17 Spectral Size	2048



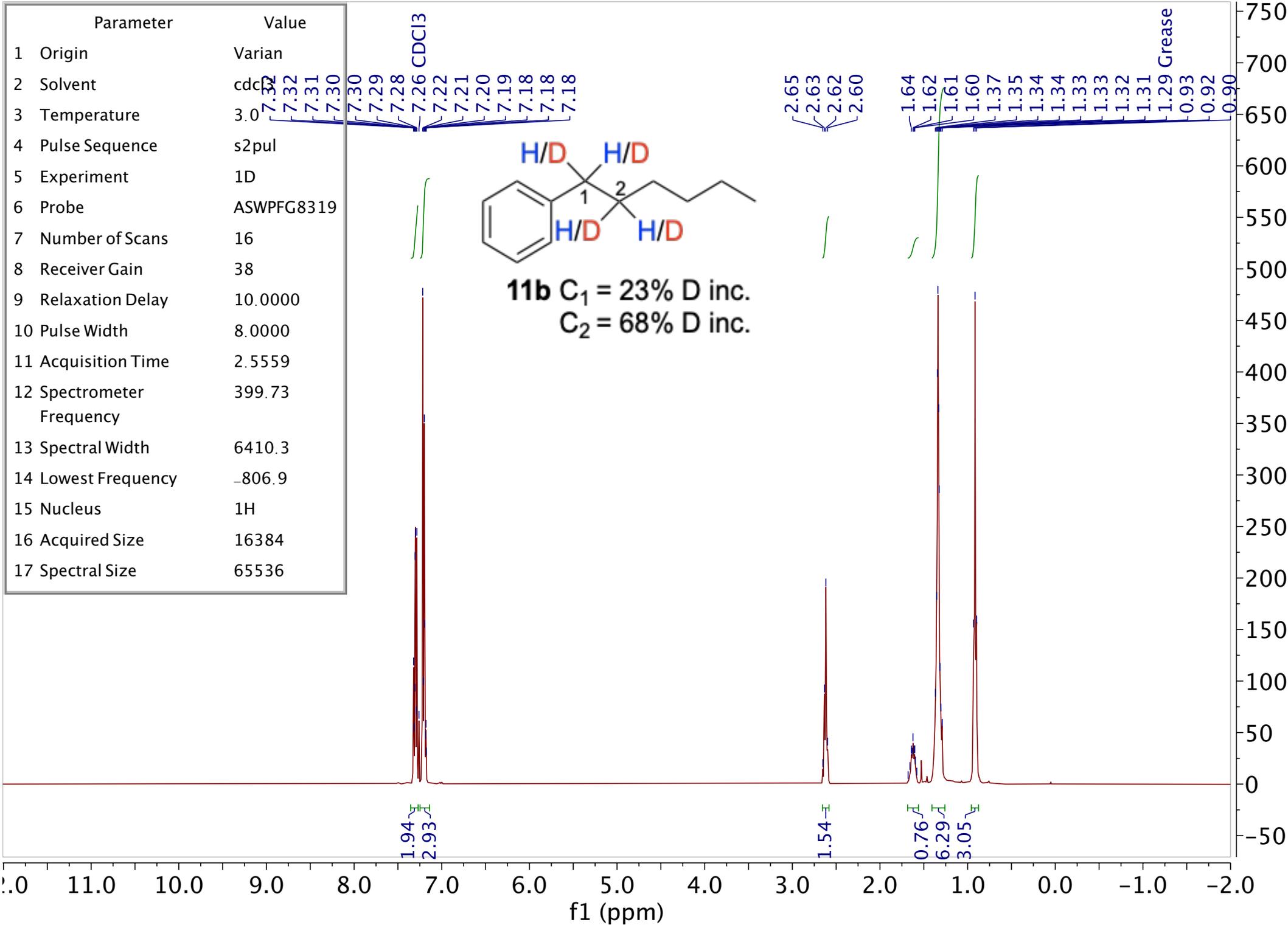
**11a** C<sub>1</sub> = 79% D inc.  
C<sub>2</sub> = 7% D inc.



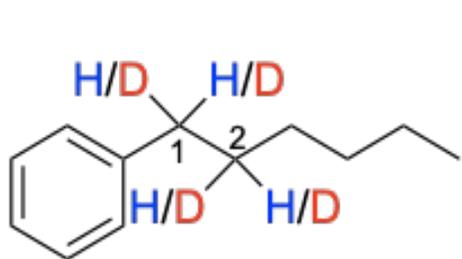
Parameter	Value
1 Origin	Varian
2 Instrument	vnmrs
3 Solvent	cdcl3
4 Temperature	3.0
5 Pulse Sequence	s2pul
6 Experiment	1D
7 Probe	ASWPG8319
8 Number of Scans	8808
9 Receiver Gain	30
10 Relaxation Delay	5.0000
11 Pulse Width	5.7500
12 Spectrometer Frequency	100.52
13 Spectral Width	25000.0
14 Lowest Frequency	-1428.0
15 Nucleus	13C
16 Acquired Size	32768
17 Spectral Size	65536



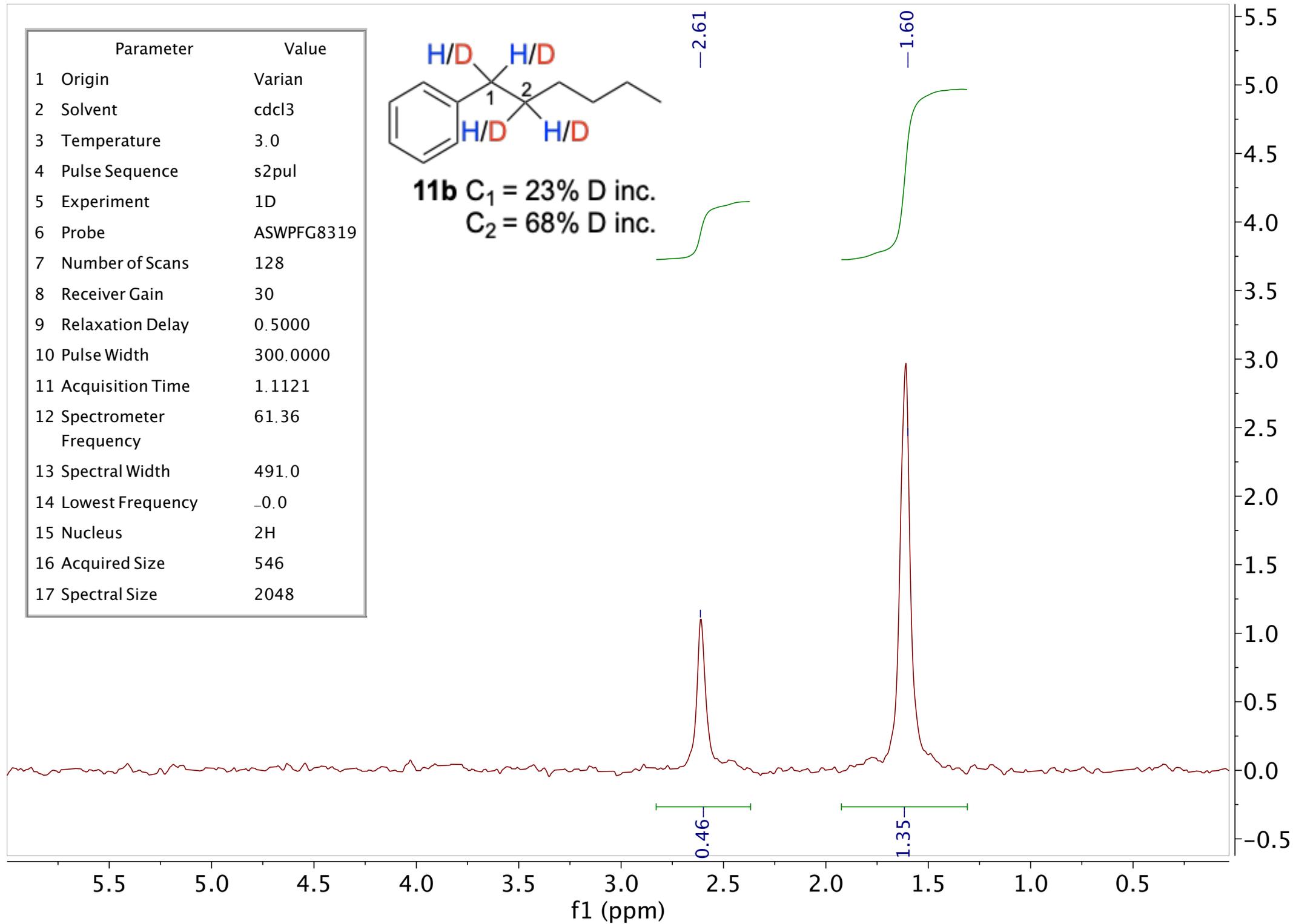
Parameter	Value
1 Origin	Varian
2 Solvent	cdcl3
3 Temperature	3.0
4 Pulse Sequence	s2pul
5 Experiment	1D
6 Probe	ASWPGF8319
7 Number of Scans	16
8 Receiver Gain	38
9 Relaxation Delay	10.0000
10 Pulse Width	8.0000
11 Acquisition Time	2.5559
12 Spectrometer	399.73
Frequency	
13 Spectral Width	6410.3
14 Lowest Frequency	-806.9
15 Nucleus	1H
16 Acquired Size	16384
17 Spectral Size	65536



Parameter	Value
1 Origin	Varian
2 Solvent	cdcl3
3 Temperature	3.0
4 Pulse Sequence	s2pul
5 Experiment	1D
6 Probe	ASWPF8319
7 Number of Scans	128
8 Receiver Gain	30
9 Relaxation Delay	0.5000
10 Pulse Width	300.0000
11 Acquisition Time	1.1121
12 Spectrometer Frequency	61.36
13 Spectral Width	491.0
14 Lowest Frequency	-0.0
15 Nucleus	2H
16 Acquired Size	546
17 Spectral Size	2048



**11b** C<sub>1</sub> = 23% D inc.  
C<sub>2</sub> = 68% D inc.



Parameter	Value
1 Origin	Varian
2 Solvent	cdcl3
3 Temperature	3.0
4 Pulse Sequence	s2pul
5 Experiment	1D
6 Probe	ASWPGF8319
7 Number of Scans	6720
8 Receiver Gain	30
9 Relaxation Delay	5.0000
10 Pulse Width	5.7500
11 Acquisition Time	1.3107
12 Spectrometer	100.52
Frequency	
13 Spectral Width	25000.0
14 Lowest Frequency	-1431.3
15 Nucleus	13C
16 Acquired Size	32768
17 Spectral Size	65536

