Chemoselective Tertiary C—H Hydroxylation for Late-Stage Functionalization with Mn(PDP)/Chloroacetic Acid Catalysis

Supplementary Information

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I. General Methods

All C—H oxidations were carried out under air with magnetic stirring, with no precautions to exclude oxygen or moisture. All other reactions were performed with oven dried or flame dried glassware under inert atmosphere of dry nitrogen or argon. Fe(PDP)[1], *cis*-[Ru(dtbpy)$_2$Cl$_2$][2], Mn(PDP)[3] and Mn(CF$_3$-PDP)[3] catalysts were synthesized according to literature procedures. All catalysts were stored at 0 ºC. The catalysts were warmed to room temperature prior to use and weighed out in air. Chloroacetic acid was purchased from Sigma-Aldrich and broken into small pieces before use. H_2O_2 (50% wt. aqueous solution) was purchased from Sigma-Aldrich and used as received. $AgSbF_6$ used for catalyst metathesis was purchased from Strem Chemicals and stored and weighed in an argon atmosphere glove box to avoid light. Solvents including THF, DCM, diethyl ether, DMF, toluene and benzene were dried by passing through a bed of activated alumina (Glass Contour, Laguna Beach, CA). Triethylamine and pyridine were distilled over calcium hydride prior to use. All other commercially available reagents were purchased from common sources (e.g. Sigma-Aldrich, Strem Chemicals, Oakwood, Alfa-Aesar, TCI America, etc.) and were used as received.

Thin-layer chromatography was conducted with E. Merck silica gel 60 F254 precoated plates (0.25 mm) and visualized with UV and/or staining including potassium permanganate, ceric ammonium molybdate, or phosphomolybdic acid/cerium sulfate. Flash column chromatography was performed as described by Still *et. al*[4] using EM reagent silica gel 60 (230-400 mesh).

^{1}H NMR were recorded using a Varian Unity-500 (500 MHz), Varian Unity Inova-500 (500 MHz) and Carver Bruker-500 (500 MHz) spectrometer, using solvent as internal standard ($CDCl_3$ at 7.26 ppm). Data are reported as: s=singlet, d=doublet, t=triplet, q=quartet, p=pentet, sxt=sextet, hept=heptet oct=octet, m=multiplet, br=broad, app=apparent; coupling constants in Hz; integration. Proton-decoupled ^{13}C NMR were recorded using a Varian Unity-500 (500 MHz) and Carver Bruker-500 (500 MHz) using solvent as internal standard ($CDCl_3$ at 77.16 ppm). ^{19}F NMR were recorded using a Varian Unity-500 (470 MHz) and Carver Bruker-500 (500 MHz) spectrometer, using external standard ($CFCl_3$ at 0 ppm). High resolution mass spectrometry (HRMS) was performed with a Waters Q-TOF Ultima spectrometer or Waters GCT Premier EI spectrometer. Optical rotations were obtained using a JASCO P2000 polarimeter (cell dimensions: 3.5 X 50 mm) and were reported as $[\alpha]_D^{T/^\circ C}$ concentration (c = g/100 mL, solvent).

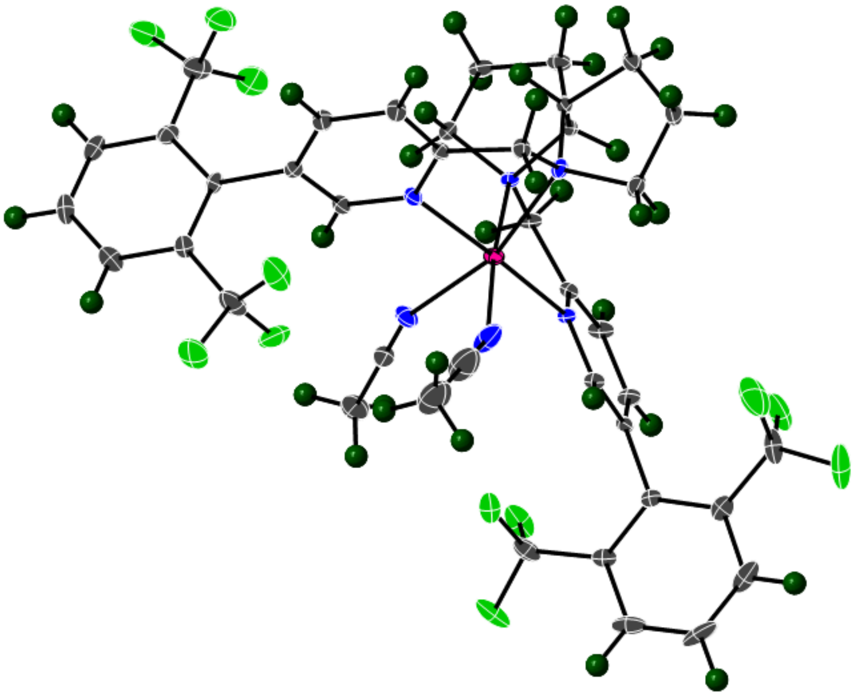
II. Characterization of Catalysts

Crystallographic data for **(*S,S*)-Mn(PDP)(MeCN)$_2$(SbF$_6$)$_2$ 3** can be obtained free of charge from www.ccdc.cam.ac.uk/structures/ with deposit number CCDC 1869257.

Crystal Structure of Mn(CF$_3$-PDP)(MeCN)$_2$(SbF$_6$)$_2$ 4

(*S,S*)-Mn(CF$_3$-PDP)(MeCN)$_2$(SbF$_6$)$_2$ **4**

A single crystal for X-ray crystallography was obtained by dissolving ~25 mg (*S,S*)-Mn(CF$_3$-PDP)(MeCN)$_2$(SbF$_6$)$_2$ **4** in 0.15 mL MeCN and 0.5 mL hexafluoroisopropanol, followed by diethyl ether diffuse into the catalyst solution at room temperature. The non-integer number of atoms is a result of partially occupied water, acetonitrile, and diethyl ether molecules in the unit cell (See table below).



Supplementary X-Ray Table 1. Crystal data and structure refinement for (*S,S*)-Mn(CF$_3$-PDP)(MeCN)$_2$(SbF$_6$)$_2$.

Empirical formula	C41.37 H42.17 F24 Mn N5.31 O1.37 Sb2
Formula weight	1390.19
Temperature	100(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	$P2_1$

Unit cell dimensions	a = 9.9977(2) Å	a= 90°.
	b = 15.1980(4) Å	b= 95.8246(6)°.
	c = 16.9784(4) Å	g = 90°.
Volume	2566.46(10) Å^3	
Z	2	
Density (calculated)	1.799 Mg/m^3	
Absorption coefficient	1.414 mm^{-1}	
F(000)	1363	
Crystal size	0.162 x 0.125 x 0.023 mm^3	
Theta range for data collection	2.268 to 25.380°.	
Index ranges	-12<=h<=12, -18<=k<=18, -20<=l<=20	
Reflections collected	74745	
Independent reflections	9411 [R(int) = 0.0392]	
Completeness to theta = 25.242°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7452 and 0.6915	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	9411 / 533 / 821	
Goodness-of-fit on F^2	1.046	
Final R indices [I>2sigma(I)]	R1 = 0.0269, wR2 = 0.0558	
R indices (all data)	R1 = 0.0296, wR2 = 0.0571	
Absolute structure parameter	-0.025(4)	
Extinction coefficient	0.00410(19)	
Largest diff. peak and hole	0.902 and -0.997 e.Å^{-3}	

Crystallographic data for *(S,S)*-Mn(CF$_3$-PDP)(MeCN)$_2$(SbF$_6$)$_2$ **4** can be obtained free of charge from www.ccdc.cam.ac.uk/structures/ with deposit number CCDC 1964541.

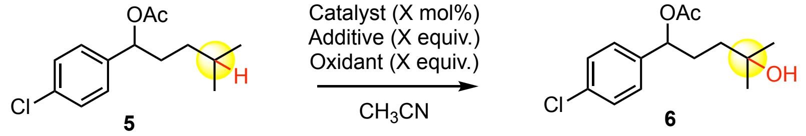
Author's response to Level B Warning:

PROBLEM: Poor Data / Parameter Ratio (Zmax > 18)   5.97 Note

RESPONSE: The collected data set is 99.8 % complete to 0.83 \%A resolution, which is the highest resolution that could be obtained with the 0.023 mm thick plate-shaped test crystal. There is a larger than average number of parameters in this refinement due to the large number of disordered atomic positions. If the 533 restraints that were used to model the disorder are treated as data, the data to parameter ratio is 6.62.

III. Supplementary Table 1A. Optimization of C—H oxidation protocol – Remote 3° Oxidation in the Presence of Aromatic Functionality

A. *Remote 3° C(sp^3)—H hydroxylation in aromatic molecules*



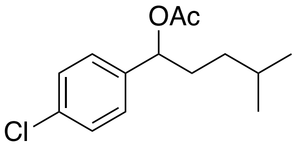
Entry	Catalyst (mol%)	Additive	Oxidant	Temperature (°C)	Yield (%)	Sel. (%)[a]
1	*cis*-[Ru(dtbpy)$_2$Cl$_2$] (5%)	–	H_5IO_6 (2 equiv.)	RT	38	54
2	Mn(OTf)$_2$ (0.1%) bipy (1%)	–	AcOOH (3 equiv.)	RT	40	48
3	Mn(CF$_3$-PDP) **4** (10%)	$ClCH_2COOH$ (15 equiv.)	H_2O_2 (5 equiv.)	0[b]	46	51
4	Fe(PDP) **1** (3x5%)	CH_3COOH (3x0.5 equiv.)	H_2O_2 (3x1.2 equiv.)	RT[c]	0	0
5	Mn(PDP) **3** (3x5%)	CH_3COOH (3x0.5 equiv.)	H_2O_2 (3x1.2 equiv.)	RT[c]	32	81
6	Mn(PDP) **3** (10%)	CH_3COOH (15 equiv.)	H_2O_2 (5 equiv.)	RT[d]	52	87
7	Mn(PDP) **3** (10%)	CH_3COOH (15 equiv.)	H_2O_2 (5 equiv.)	0[d]	58	76
8	Mn(PDP) **3** (0.1%)	CH_3COOH (14 equiv.)	H_2O_2 (2.5 equiv.)	0[e]	60	73
Condition A:						
9	Mn(PDP) **3** (0.1%)	CH_3COOH (14 equiv.)	H_2O_2 (2.5 equiv.)	0[f]	57	80
10	Mn(PDP) **3** (0.1%)	$ClCH_2COOH$ (14 equiv.)	H_2O_2 (2.5 equiv.)	0[f]	37	82

[a] Chemoselectivity (Sel.) = 3° C-H [O]/total conversion. [b] x mol% catalyst, x equiv. additive with slow addition of x equiv. H_2O_2 over 3 h. [c] Iterative addition of 5 mol% catalyst, 0.5 equiv. CH_3COOH, 1.2 equiv. H_2O_2 every 10-15 min. [d] x mol% catalyst, *x* equiv. additive with slow addition of *x* equiv. H_2O_2 over 1 h. [e] 0.1 mol% catalyst, 14 equiv. additive with slow addition of 2.5 equiv. H_2O_2 (in 0.3 mL MeCN) over 1 h and reaction mixture stirred for an additional 1 h. [f] 0.1 mol% catalyst, 14 equiv. additive with slow addition of 2.5 equiv. H_2O_2 (in 3.75 mL MeCN) over 1 h.

Chemoselectivity is defined as the yield of desired remote oxidation product over the conversion of starting material.

$$chemoselectivity = \frac{yield\ of\ remote\ oxidation\ product}{conversion\ of\ starting\ material}$$

Synthesis of **1-(4-chlorophenyl)-4-methylpentyl acetate [5]**



1-(4-chlorophenyl)-4-methylpentan-1-ol (638.2 mg, 3.0 mmol, 1.0 equiv.) was dissolved in 15 mL anhydrous pyridine. Acetic anhydride (1.42 mL, 15.0 mmol, 5.0 equiv.) was added dropwise at 0 ºC and the reaction was allowed to stir at room temperature overnight before being concentrated under reduced pressure. The residue was diluted with 30 mL DCM and washed with 30 mL 1M HCl solution twice followed by 20 mL brine. The organic layer was dried with $MgSO_4$, filtered, and concentrated. Flash column chromatography on silica (50 mm fritted glass column, 300 mL SiO_2) using 5% EtOAc/hexanes as eluent gave 1-(4-chlorophenyl)-4-methylpentyl acetate **(5)** as a colorless oil (735.6 mg, 2.89 mmol, 96% yield).

^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.31 (d, *J* = 8.5 Hz, 2H), 7.26 (d, *J* = 8.5 Hz, 2H), 5.65 (t, *J* = 7.0 Hz, 1H), 2.06 (s, 3H), 1.91 – 1.83 (m, 1H), 1.77 – 1.70 (m, 1H), 1.53 (app. hept, *J* = 6.7 Hz, 1H), 1.25 – 1.15 (m, 1H), 1.11 – 1.03 (m, 1H), 0.86 (d, *J* = 6.6 Hz, 3H), 0.85 (d, *J* = 6.6 Hz, 3H). ^{13}C-NMR (126 MHz, $CDCl_3$) δ 170.4, 139.5, 133.7, 128.7, 128.1, 75.8, 34.6, 34.2, 28.0, 22.6, 22.6, 21.4. HRMS (ESI+) *m/z* calculated for $C_{14}H_{19}O_2NaCl$ $[M+Na]^+$: 277.0971, found 277.0982.

Entry 1

The reaction was conducted according to the reported general procedure.[2] A 20 mL vial was charged with 1-(4-chlorophenyl)-4-methylpentyl acetate **5** (63.7 mg, 0.25 mmol, 1.0 equiv.), a magnetic stir bar and a solution of *cis*-Ru(dtbpy)$_2$Cl$_2$ (8.9 mg, 13 μmol, 0.05 equiv.) in 2.0 mL acetic acid. 2.0 mL water was added to the vial and the purple solution was stirred at room temperature for 2 min before a single portion of H_5IO_6 (114 mg, 0.50 mmol, 2.0 equiv.) was added. The reaction was wrapped with aluminum foil and stirred at room temperature for 4 hours. The reaction was transferred to a separatory funnel with 4 mL DCM and 30 mL water. The aqueous layer was extracted with 3 x 15 mL DCM and the combined organic layer was dried over Na_2SO_4. The crude reaction was purified by column chromatography on silica (15 mm fritted glass column, 30 mL SiO_2) using 10% acetone/hexanes → 20% acetone/hexanes → 30% acetone/hexanes as eluent to give both recovered starting material and product.

Run 1: (24.9 mg, 0.092 mmol, 36.8% yield), (16.7 mg, 0.066 mmol, 26.2% rsm). **Run 2:** (24.6 mg, 0.091 mmol, 36.3% yield), (16.1 mg, 0.063 mmol, 25.3% rsm). **Run 3:** (27.7 mg, 0.102 mmol, 40.9% yield), (22.6 mg, 0.089 mmol, 35.5% rsm). **Average: 38.0% yield ± 2.5%, 29.0% rsm ± 5.6%. Selectivity = 38.0/(100-29.0) = 54%.**

We also attempted to directly analyze the crude reaction *via* quantitative ^{1}H NMR analysis with nitrobenzene added as internal standard.

Run 1: 33.7% yield, 35.5% rsm. **Run 2:** 30.2% yield, 32.7% rsm. **Run 3:** 28.3% yield, 28.7% rsm. **Average: 30.7% yield ± 2.7%, 32.3% rsm ± 3.4%. Selectivity = 30.7/(100-32.3) = 45%.**

Entry 2

The reaction was conducted according to the reported general procedure.[5] A 20 mL vial was charged with 1-(4-chlorophenyl)-4-methylpentyl acetate **5** (63.7 mg, 0.25 mmol, 1.0 equiv.), AcOH (1.25 mL), Mn(OTf)$_2$ solution (20 μL, 12.5 mM solution in 9:1 AcOH/H_2O, 0.25 μmol, 0.001 equiv.) and bipyridine solution (100 μL, 0.025 M solution in AcOH, 2.5 μmmol, 0.01 equiv.). The mixture was stirred for 10 minutes at room temperature before a modified peracetic acid solution (220 μL, prepared by mixing 1.0 mL of commercial peracetic acid (35% Sigma-Aldrich) with 0.3 mL of 10% KOH solution, 0.75 mmol, 3.0 equiv.) was added dropwise over 30 seconds. The reaction was stirred for another 60 seconds and then diluted with 5 mL acetone. After stirring for 30 seconds, the mixture was filtered through Celite® and the filtrate was concentrated *in vacuo*. The crude mixture was analyzed by quantitative ^{1}H NMR analysis with nitrobenzene added as internal standard.

Run 1: 40.8% yield, 20.2% rsm. **Run 2:** 38.5% yield, 15.5% rsm. **Run 3:** 40.3% yield, 14.7% rsm. **Average: 39.9% yield ± 1.2%, 16.8% rsm ± 3.0%. Selectivity = 39.9/(100-16.8) = 48%.**

Entry 3

The reaction was conducted with Method B: single catalyst addition protocol (*vide infra*, Section V). A 40 mL vial was charged with 1-(4-chlorophenyl)-4-methylpentyl acetate **5** (76.4 mg, 0.30 mmol, 1.0 equiv), $ClCH_2COOH$ (425.3 mg, 4.5 mmol, 15.0 equiv.), (*R,R*)-Mn(CF_3-PDP) catalyst **4** (40.7 mg, 0.03 mmol, 0.10 equiv.) MeCN (0.6 mL) and a stir bar. A 10 mL syringe was charged with a solution of H_2O_2 (50% wt. in H_2O, 102 mg, 1.5 mmol, 5.0 equiv.) in MeCN (3.75 mL), fitted with a 25G needle and the solution was added dropwise *via* syringe pump over 3 hours (1.25 mL/hour) while the reaction vial was maintained at 0 ºC with an ice/water bath. Upon completion of addition, the reaction was concentrated *in vacuo* to a minimum amount of MeCN. The residue was dissolved in ~30 mL DCM and washed with 15 mL sat. $NaHCO_3$ solution (CAUTION: CO_2 was released) to remove $ClCH_2CO_2H$. The aqueous layer was extracted with ~15 mL DCM twice and the combined organic layer was dried with Na_2SO_4. After filtration, the reaction was purified by column chromatography on silica (15 mm fritted glass column, 30 mL SiO_2) using 10% acetone/hexanes → 20% acetone/hexanes → 30% acetone/hexanes as eluent to give both recovered starting material and product.

Run 1: (37.6 mg, 0.139 mmol, 46.3% product), <10% rsm. **Run 2:** (40.3 mg, 0.149 mmol, 49.6% product), <10% rsm. **Run 3:** (34.9 mg, 0.129 mmol, 43.0% yield), <10% rsm. **Average: 46.3% yield ± 3.3%, <10% rsm. Selectivity = 46.3/(100-10) = 51%.**

Entry 4

The reaction was conducted according to the iterative addition protocol.[1] A 40 mL vial was charged with 1-(4-chlorophenyl)-4-methylpentyl acetate **5** (76.4 mg, 0.30 mmol, 1.0 equiv.), (*R,R*)-Fe(PDP) catalyst **1** (14.0 mg, 0.015 mmol, 0.05 equiv.), CH_3COOH (9.0 mg, 0.15 mmol, 0.5 equiv.), MeCN (0.45 mL) and a stir bar. The vial was stirred vigorously and a solution of H_2O_2 (50% wt. in H_2O, 24.5 mg, 1.2 equiv.) in MeCN (3.75 mL) was added dropwise over 60-75 seconds. The reaction was allowed to stir for 10 minutes at room temperature before a second batch of catalyst (14.0 mg, 0.015 mmol, 0.05 equiv.) and AcOH (9.0 mg, 0.15 mmol, 0.5 equiv.) dissolved in 0.3 mL MeCN was added *via* pipette. This was followed by a solution of H_2O_2 (50 wt%, 24.5 mg, 1.2 equiv.) in MeCN (3.75 mL) over 60-75 seconds. After another 10 minutes a third batch of catalyst and H_2O_2 was added in the same manner. The third addition was allowed to stir for 10 minutes for a total reaction time of 30 minutes. **Significant decrease in yield was observed when the peroxide solution was added rapidly.**

Upon completion of the reaction, the mixture was concentrated *in vacuo* to a minimum amount of MeCN. Diethyl ether (20 mL) was added to precipitate the iron complex and the mixture was filtered *via* a Celite® plug. The filtrate was dried over Na_2SO_4, concentrated and analyzed by quantitative ^{1}H NMR analysis with nitrobenzene added as internal standard.

Run 1: 0 % product, (21.1 mg, 0.083 mmol, 27.6% rsm). **Run 2:** 0% product, (22.1 mg, 0.087 mmol, 28.9% rsm). **Run 3:** 0% product, (27.5 mg, 0.108 mmol, 36.0% rsm). **Average: 0% yield, 30.8% rsm ± 4.5%. Selectivity = 0/(100-30.8) = 0%.**

Entry 5

The reaction was conducted according to the iterative addition protocol.[1] A 40 mL vial was charged with 1-(4-chlorophenyl)-4-methylpentyl acetate **5** (76.4 mg, 0.30 mmol, 1.0 equiv.), (*R,R*)-Mn(PDP) catalyst **3** (14.0 mg, 0.015 mmol, 0.05 equiv.), CH_3COOH (9.0 mg, 0.15 mmol, 0.5 equiv.), MeCN (0.45 mL) and a stir bar. The vial was stirred vigorously and a solution of H_2O_2 (50% wt. in H_2O, 24.5 mg, 1.2 equiv.) in MeCN (3.75 mL) was added dropwise over 60-75 seconds. The reaction was allowed to stir for 10 minutes at room temperature before a second batch of catalyst (14.0 mg, 0.015 mmol, 0.05 equiv.) and AcOH (9.0 mg, 0.15 mmol, 0.5 equiv.) dissolved in 0.3 mL MeCN was added *via* pipette. This was followed by a solution of H_2O_2 (50 wt%, 24.5 mg, 1.2 equiv.) in MeCN (3.75 mL) over 60-75 seconds. After another 10 minutes a third batch of catalyst and H_2O_2 was added in the same manner. The third addition was allowed to stir for 10 minutes for a total reaction time of 30 minutes. **Significant decrease in yield was observed when the peroxide solution was added rapidly.**

Upon completion of the reaction, the mixture was concentrated *in vacuo* to a minimum amount of MeCN. Diethyl ether (20 mL) was added to precipitate the manganese complex and the mixture was filtered *via* a Celite® plug. The filtrate was dried over Na_2SO_4, concentrated and analyzed by quantitative ^{1}H NMR analysis with nitrobenzene added as internal standard.

Run 1: (25.8 mg, 0.095 mmol, 31.8% product), (46.2 mg, 0.181 mmol, 60.4% rsm). **Run 2:** (26.9 mg, 0.099 mmol, 33.1% product), (44.0 mg, 0.173 mmol, 57.6% rsm). **Run 3:** (26.0 mg, 0.096 mmol, 32.0% yield), (47.8 mg, 0.188 mmol, 62.7% rsm) **Average: 32.3% yield ± 0.7%, 60.2% rsm ± 2.6%. Selectivity = 32.3/(100-60.2) = 81%.**

Entry 6

The reaction was conducted with Method B: single catalyst addition protocol (*vide infra*, Section V). A 40 mL vial was charged with 1-(4-chlorophenyl)-4-methylpentyl acetate **5** (76.4 mg, 0.30 mmol, 1.0 equiv), CH_3COOH (270.2 mg, 4.5 mmol, 15.0 equiv.), (*R,R*)-Mn(PDP) catalyst **3** (27.9 mg, 0.03 mmol, 0.10 equiv.) MeCN (0.60 mL) and a stir bar. A 10 mL syringe was charged with a solution of H_2O_2 (50% wt. in H_2O, 102 mg, 1.5 mmol, 5.0 equiv.) in MeCN (3.75 mL), fitted with a 25G needle and the solution was added dropwise *via* syringe pump over 1 hour (3.75 mL/hour) at room temperature. Upon completion of addition, the reaction was concentrated *in vacuo* to a minimum amount of MeCN and purified by column chromatography on silica (15 mm fritted glass column, 30 mL SiO_2) using 10% acetone/hexanes → 20% acetone/hexanes → 30% acetone/hexanes as eluent to give both recovered starting material and product.

Run 1: (43.9 mg, 0.162 mmol, 54.0% yield), (27.9 mg, 0.110 mmol, 36.5% rsm). **Run 2:** (40.7 mg, 0.150 mmol, 50.1% yield), (31.3 mg, 0.122 mmol, 41.0% rsm) **Run 3:** (41.1 mg, 0.152 mmol, 50.6% yield), (34.4 mg, 0.135 mmol, 45.0% rsm). **Average: 51.6% yield ± 2.1%, 40.8% rsm ± 4.3%. Selectivity = 51.6/(100-40.8) = 87%.**

Entry 7

The reaction was conducted with Method B: single catalyst addition protocol (*vide infra*, Section V). A 40 mL vial was charged with 1-(4-chlorophenyl)-4-methylpentyl acetate **5** (76.4 mg, 0.30 mmol, 1.0 equiv), CH_3COOH (270.2 mg, 4.5 mmol, 15.0 equiv.), (*R,R*)-Mn(PDP) catalyst **3** (27.9 mg, 0.03 mmol, 0.10 equiv.) MeCN (0.60 mL) and a stir bar. A 10 mL syringe was charged with a solution of H_2O_2 (50% wt. in H_2O, 102 mg, 1.5 mmol, 5.0 equiv.) in MeCN (3.75 mL), fitted with a 25G needle and the solution was added dropwise *via* syringe pump over 1 hour (3.75 mL/hour) while the reaction vial was maintained at 0 ºC with an ice/water bath. Upon completion of addition, the reaction was concentrated *in vacuo* to a minimum amount of MeCN and purified by column chromatography on silica (15 mm fritted glass column, 30 mL SiO_2) using 10% acetone/hexanes → 20% acetone/hexanes → 30% acetone/hexanes as eluent to give both recovered starting material and product.

Run 1: (48.3 mg, 0.178 mmol, 59.5% yield), (15.5 mg, 0.061 mmol, 20.3% rsm). **Run 2:** (48.2 mg, 0.178 mmol, 59.3% yield), (21.5 mg, 0.084 mmol, 28.1% rsm). **Run 3:** (45.0 mg, 0.166 mmol, 55.4% yield), (17.8 mg, 0.070 mmol, 23.3% rsm). **Average: 58.1% yield ± 2.3%, 23.9% rsm ± 3.9%. Selectivity = 58.1/(100-23.9) = 76%.**

Entry 8

The reaction was conducted according to the "cyclohexane oxidation under practical conditions" procedure.[6] A 40 mL vial was charged with 1-(4-chlorophenyl)-4-methylpentyl acetate **5** (76.4 mg, 0.30 mmol, 1.0 equiv.), AcOH (0.24 mL, 4.2 mmol, 14 equiv.), (*R,R*)-Mn(PDP) catalyst **3** solution (60 μL, 5 mM solution in MeCN, 0.30 μmol, 0.001 equiv.) and MeCN (1.14 mL). A solution of H_2O_2 (50% wt. in H_2O, 51.0 mg, 0.75 mmol, 2.5 equiv.) in MeCN (0.3 mL) was added dropwise *via* syringe pump over 1 hour while the reaction vial was maintained at 0 ºC with an ice/water bath. The reaction was stirred for a further 1 hour at 0 ºC before being concentrated *in vacuo*. The residue was dissolved in ~30 mL DCM and washed with 15 mL sat. $NaHCO_3$ solution (CAUTION: CO_2 was released) to remove CH_3COOH. The aqueous layer was extracted with ~15 mL DCM twice and the combined organic layer was dried with Na_2SO_4. After filtration, the reaction was purified by column chromatography on silica (15 mm fritted glass column, 30 mL SiO_2) using 10% acetone/hexanes → 20% acetone/hexanes → 30% acetone/hexanes as eluent to give both recovered starting material and product.

Run 1: (46.0 mg, 0.170 mmol, 56.6% product), (11.9 mg, 0.047 mmol, 15.6% rsm). **Run 2:** (51.3 mg, 0.189 mmol, 63.2% product), (15.0 mg, 0.059 mmol, 19.6% rsm). **Average: 59.9% yield, 17.6% rsm. Selectivity = 59.9/(100-17.6) = 73%.**

Entry 9

The reaction was conducted with Method A: Low Catalyst Loading (0.1 mol%) Protocol (*vide infra*, Section V). A 40 mL vial was charged with 1-(4-chlorophenyl)-4-methylpentyl acetate **5** (76.4 mg, 0.30 mmol, 1.0 equiv), AcOH (0.24 mL, 4.2 mmol, 14.0 equiv.), (*R,R*)-Mn(PDP) catalyst **3** solution (60 μL, 5 mM solution in MeCN, 0.30 μmol, 0.001 equiv.) MeCN (0.60 mL) and a stir bar. A 10 mL syringe was charged with a solution of H_2O_2 (50% wt. in H_2O, 51.0 mg, 0.75 mmol, 2.5 equiv.) in MeCN (3.75 mL), fitted with a 25G needle and the solution was added dropwise *via* syringe pump over 1 hour (3.75 mL/hour) while the reaction vial was maintained at 0 ºC with an ice/water bath. Upon completion of addition, the reaction was concentrated *in vacuo* to a minimum amount of MeCN. The residue was dissolved in ~30 mL DCM and washed with 15 mL sat. $NaHCO_3$ solution (CAUTION: CO_2 was released) to remove CH_3COOH. The aqueous layer was extracted with ~15 mL DCM twice and the combined organic layer was dried with Na_2SO_4. After filtration, the reaction was purified by column chromatography on silica (15 mm fritted glass column, 30 mL SiO_2) using 10% acetone/hexanes → 20% acetone/hexanes → 30% acetone/hexanes as eluent to give both recovered starting material and product.

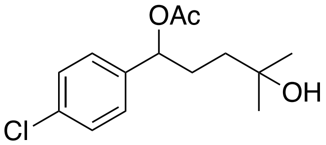
Run 1: (46.9 mg, 0.173 mmol, 57.7% yield), (22.9 mg, 0.090 mmol, 30.0% rsm). **Run 2:** (45.7 mg, 0.169 mmol, 56.3% yield), (20.6 mg, 0.081 mmol, 27.0% rsm). **Average: 57.0% yield, 28.5% rsm. Selectivity = 57.0/(100-28.5) = 80%.**

Entry 10

A 40 mL vial was charged with 1-(4-chlorophenyl)-4-methylpentyl acetate **5** (76.4 mg, 0.30 mmol, 1.0 equiv), $ClCH_2COOH$ (396.9 mg, 4.2 mmol, 14.0 equiv.), (*R,R*)-Mn(PDP) catalyst **3** solution (60 µL, 5 mM solution in MeCN, 0.30 µmol, 0.001 equiv.) MeCN (0.60 mL) and a stir bar. A 10 mL syringe was charged with a solution of H_2O_2 (50% wt. in H_2O, 51.0 mg, 0.75 mmol, 2.5 equiv.) in MeCN (3.75 mL), fitted with a 25G needle and the solution was added dropwise *via* syringe pump over 1 hour (3.75 mL/hour) while the reaction vial was maintained at 0 ºC with an ice/water bath. Upon completion of addition, the reaction was concentrated *in vacuo* to a minimum amount of MeCN. The residue was dissolved in ~30 mL DCM and washed with 15 mL sat. $NaHCO_3$ solution (CAUTION: CO_2 was released) to remove $ClCH_2COOH$. The aqueous layer was extracted with ~15 mL DCM twice and the combined organic layer was dried with Na_2SO_4. After filtration, the reaction was purified by column chromatography on silica (15 mm fritted glass column, 30 mL SiO_2) using 10% acetone/hexanes → 20% acetone/hexanes → 30% acetone/hexanes as eluent to give both recovered starting material and product.

Run 1: (30.1 mg, 0.111 mmol, 37.1% yield), (42.2 mg, 0.166 mmol, 55.2% rsm). **Run 2:** (29.6 mg, 0.109 mmol, 36.4% yield), (42.3 mg, 0.166 mmol, 55.3% rsm). **Average: 36.8% yield, 55.3% rsm. Selectivity = 36.8/(100-55.3) = 82%.**

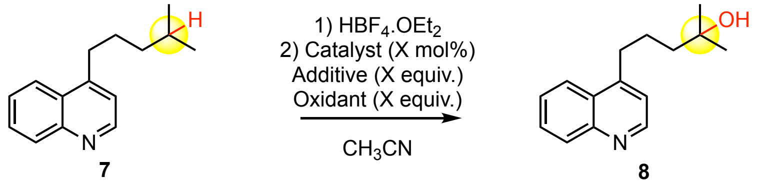
Characterization of **1-(4-chlorophenyl)-4-hydroxy-4-methylpentyl acetate [6]**



^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.32 (d, *J* = 8.5 Hz, 2H), 7.27 (d, *J* = 8.5 Hz, 2H), 5.68 (dd, *J* = 7.6, 6.3 Hz, 1H), 2.07 (s, 3H), 1.98 (dddd, *J* = 13.4, 12.3, 7.7, 4.7 Hz, 1H), 1.85 (dddd, *J* = 13.4, 11.9, 6.2, 4.6 Hz, 1H), 1.51 (ddd, *J* = 13.5, 12.2, 4.6 Hz, 1H), 1.39 (br. s, 1H), 1.39 – 1.31 (m, 1H), 1.20 (s, 6H). ^{13}C-NMR (126 MHz, $CDCl_3$) δ 170.4, 139.2, 133.8, 128.8, 128.1, 75.8, 70.6, 39.3, 31.2, 29.5, 29.4, 21.4. HRMS (ESI+) *m/z* calculated for $C_{14}H_{20}O_3Cl$ $[M+H]^+$: 271.1101, found 271.1107.

IV. Supplementary Table 1B. Optimization of C—H oxidation protocol – Remote 3° Oxidation in the Presence of Basic Nitrogen Functionality

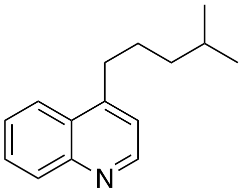
B. *Remote 3° C(sp^3)—H hydroxylation in basic heteroaromatic molecules*



Entry	Catalyst (mol%)	Additive	Oxidant	Temperature (°C)	Yield (%)	Sel. (%)^a
1	Mn(PDP)(OTf)$_2$ (0.1%)	CH$_3$COOH (14 equiv.)	H$_2$O$_2$ (2.5 equiv.)	0^e	0	0
2	Mn(PDP) **3** (0.1%)	CH$_3$COOH (14 equiv.)	H$_2$O$_2$ (2.5 equiv.)	0^f	0	0
3	Mn(PDP) **3** (10%)	CH$_3$COOH (14 equiv.)	H$_2$O$_2$ (2.5 equiv.)	0^d	33	92
4	Mn(PDP) **3** (10%)	CH$_3$COOH (14 equiv.)	H$_2$O$_2$ (5 equiv.)	0^d	59	85
5	Mn(PDP) **3** (10%)	ClCH$_2$COOH (15 equiv.)	H$_2$O$_2$ (5 equiv.)	0^b	73	85
Condition B:						
6	Mn(PDP) **3** (10%)	ClCH$_2$COOH (15 equiv.)	H$_2$O$_2$ (5 equiv.)	-36^b	70	94
7	Mn(PDP) **3** (5%)	ClCH$_2$COOH (15 equiv.)	H$_2$O$_2$ (5 equiv.)	-36^b	55	89
8	Mn(PDP) **3** (2.5%)	ClCH$_2$COOH (15 equiv.)	H$_2$O$_2$ (5 equiv.)	-36^b	41	95
9	Mn(PDP) **3** (0.1%)	ClCH$_2$COOH (15 equiv.)	H$_2$O$_2$ (5 equiv.)	-36^b	0	0

^{a}Chemoselectivity (Sel.) = 3° C-H [O]/total conversion. ^{b}x mol% catalyst, x equiv. additive with slow addition of x equiv. H$_2$O$_2$ over 3 h. ^{c}Iterative addition of 5 mol% catalyst, 0.5 equiv. CH$_3$COOH, 1.2 equiv. H$_2$O$_2$ every 10-15 min. ^{d}*x* mol% catalyst, *x* equiv. additive with slow addition of *x* equiv. H$_2$O$_2$ over 1 h. ^{e}0.1 mol% catalyst, 14 equiv. additive with slow addition of 2.5 equiv. H$_2$O$_2$ (in 0.3 mL MeCN) over 1 h and reaction mixture stirred for an additional 1 h. ^{f}0.1 mol% catalyst, 14 equiv. additive with slow addition of 2.5 equiv. H$_2$O$_2$ (in 3.75 mL MeCN) over 1 h.

4-(4-methylpentyl)quinoline [7]



To a 50 mL flame dried round bottom flask equipped with a magnetic stir bar, under N$_2$ atmosphere, was added diisopropylamine (2.0 mL, 14.2 mmol, 1.3 equiv.) in THF (12.0 mL, 1.2 M). The solution was cooled to -78 °C. *n*-Butyl lithium (1.6 M in hexane, 8.2 mL, 13.1 mmol, 1.2 equiv.) was added dropwise and the mixture was warmed to room temperature for 30 minutes. The mixture was cooled to -78 °C. In a 250 mL flame dried round bottom flask equipped with magnetic stir bar, under N$_2$ atmosphere, was added 4-methylquinoline (1.45 mL, 11.0 mmol, 1.0 equiv.) in THF (40 mL, 0.28 M) and the mixture was cooled to -78 °C. The LDA solution was added to the 4-methylquinoline solution via cannula at -78 °C. The mixture was stirred at -78 °C for 2.5 hours. 1-Bromo-3-methylbutane (1.7 mL, 14.2 mmol, 1.3 equiv.) was added dropwise and the reaction was stirred at -78 °C for a further 3 hours. The resulting mixture was allowed to warm to room temperature overnight (14 hours). The reaction was quenched with saturated aqueous NH_4Cl and the aqueous layer was extracted with EtOAc (3 x 50 mL). The combined organic layer was washed with H_2O (50 mL) and brine (50 mL), dried over Na_2SO_4, filtered and concentrated *in vacuo*. Flash chromatography on silica (35 mm fritted glass column, 150 mL SiO_2) using 100% hexanes → 20% EtOAc/hexanes as eluent afforded 4-(4-methylpentyl)quinoline (**7**) as a pale yellow oil (1.36 g, 6.38 mmol, 58% yield).

^{1}H-NMR (500 MHz, $CDCl_3$) δ 8.80 (d, *J* = 4.4 Hz, 1H), 8.15 – 8.08 (m, 1H), 8.04 (dd, *J* = 8.4, 1.4 Hz, 1H), 7.70 (ddd, *J* = 8.4, 6.8, 1.4 Hz, 1H), 7.56 (ddd, *J* = 8.3, 6.8, 1.4 Hz, 1H), 7.24 (d, *J* = 4.4 Hz, 1H), 3.05 (appt. t, *J* = 7.9 Hz, 2H), 1.83 – 1.71 (m, 2H), 1.61 (app. hept, *J* = 6.6 Hz, 1H), 1.40 – 1.27 (m, 2H), 0.89 (d, *J* = 6.6 Hz, 6H). ^{13}C-NMR (126 MHz, $CDCl_3$) δ 150.3, 148.9, 148.5, 130.4, 129.1, 127.8, 126.3, 123.7, 120.9, 39.1, 32.5, 28.1, 28.0, 22.7. HRMS (TOF ESI+) *m/z* calculated for $C_{15}H_{20}N$ $[M+H]^+$: 214.1596, found 214.1588.

General Procedure

According to the **general procedure for HBF_4•OEt_2 protection** (*vide infra*, Section V), 4-(4-methylpentyl)quinoline **7** (64.0 mg, 0.300 mmol, 1.0 equiv), was protected with HBF_4•OEt_2 (45.5 µL, 0.330 mmol, 54 wt.%, 1.1 equiv.) in CH_2Cl_2 (1.2 mL, 0.25 M).

Entry 1

The reaction was conducted according to the "cyclohexane oxidation under practical conditions" procedure.[6] $Mn(PDP)(OTf)_2$ was prepared by metathesis of $Mn(PDP)Cl_2$ with AgOTf according to a similar procedure as $Mn(PDP)(MeCN)_2(SbF_6)_2$.[3] A 20 mL vial was charged with the resultant **7•HBF_4** (0.30 mmol, 1.0 equiv.), CH_3COOH (0.24 mL, 4.2 mmol, 14 equiv.), $Mn(PDP)(OTf)_2$ solution (60 µL, 5 mM solution in MeCN, 0.30 µmol, 0.001 equiv.) and MeCN (1.14 mL). A solution of H_2O_2 (50% wt. in H_2O, 51.0 mg, 0.75 mmol, 2.5 equiv.) in MeCN (0.3 mL) was added dropwise *via* syringe pump over 1 hour while the reaction vial was maintained at 0 ºC with an ice/water bath. The reaction was stirred for a further 1 hour at 0 ºC before being concentrated *in vacuo*. The reaction was worked up according to the **General Procedure for HBF_4 Deprotection** (*vide infra*, Section V). The crude mixture was analyzed by quantitative ^{1}H NMR analysis with mesitylene added as internal standard.

Run 1: 0% product, 100% rsm. **Run 2:** 0% product, 100% rsm. **Average: 0% yield, 100% rsm. Selectivity = 0/(100-100) = 0%.**

Entry 2

The reaction was conducted with Method A: Low Catalyst Loading (0.1 mol%) Protocol (*vide infra*, Section V). A 40 mL vial was charged with the resultant **7•HBF$_4$** (0.30 mmol, 1.0 equiv.), CH_3COOH (0.24 mL, 4.2 mmol, 14.0 equiv.), (*R,R*)-Mn(PDP) catalyst **3** solution (60 µL, 5 mM solution in MeCN, 0.30 µmol, 0.001 equiv.) MeCN (0.60 mL) and a stir bar. A 10 mL syringe was charged with a solution of H_2O_2 (50% wt. in H_2O, 51.0 mg, 0.75 mmol, 2.5 equiv.) in MeCN (3.75 mL), fitted with a 25G needle and the solution was added dropwise *via* syringe pump over 1 hour (3.75 mL/hour) while the reaction vial was maintained at 0 ºC with an ice/water bath. Upon completion of addition, the reaction was concentrated *in vacuo* to a minimum amount of MeCN. The reaction was worked up according to the **General Procedure for HBF$_4$ Deprotection** (*vide infra*, Section V). The crude mixture was analyzed by quantitative ^{1}H NMR analysis with mesitylene added as internal standard.

Run 1: 0% product, 100% rsm. **Run 2:** 0% product, 100% rsm. **Average: 0% yield, 100% rsm. Selectivity = 0/(100-100) = 0%.**

Entry 3

The reaction was conducted with Method B: single catalyst addition protocol (*vide infra*, Section V). A 40 mL vial was charged with the resultant **7•HBF$_4$** (0.30 mmol, 1.0 equiv.), CH_3COOH (0.24 mL, 4.2 mmol, 14.0 equiv.), (*R,R*)-Mn(PDP) catalyst **3** (27.9 mg, 0.03 mmol, 0.10 equiv.) and MeCN (0.60 mL). A 10 mL syringe was charged with a solution of H_2O_2 (50% wt. in H_2O, 51 mg, 0.75 mmol, 2.5 equiv.) in MeCN (3.75 mL), fitted with a 25G needle and the solution was added dropwise *via* syringe pump over 1 hour (3.75 mL/hour) while the reaction vial was maintained at 0 ºC with an ice/water bath. Upon completion of addition, the reaction was concentrated *in vacuo* to a minimum amount of MeCN. The reaction was worked up according to the **General Procedure for HBF$_4$ Deprotection** (*vide infra*, Section V) and purified by column chromatography on silica (15 mm fritted glass column, 30 mL SiO_2) using 100% DCM → 5% MeOH/DCM as eluent to give both recovered starting material and product.

Run 1: (22.7 mg, 0.099 mmol, 33.0% yield), (41.7 mg, 0.195 mmol, 65.2% rsm). **Run 2:** (21.5 mg, 0.094 mmol, 31.3% yield), (42.3 mg, 0.198 mmol, 66.1% rsm). **Run 3:** (24.8 mg, 0.108 mmol, 36.0% yield), (38.0 mg, 0.178 mmol, 59.4% rsm). **Average: 33.4% yield ± 2.4%, 63.6% rsm ± 3.6%. Selectivity = 33.4/(100-63.5) = 92%.**

Entry 4

The reaction was conducted with Method B: single catalyst addition protocol (*vide infra*, Section V). A 40 mL vial was charged with the resultant **7•HBF$_4$** (0.30 mmol, 1.0 equiv.), CH_3COOH (0.24 mL, 4.2 mmol, 14.0 equiv.), (*R,R*)-Mn(PDP) catalyst **3** (27.9 mg, 0.03 mmol, 0.10 equiv.) and MeCN (0.60 mL).

A 10 mL syringe was charged with a solution of H_2O_2 (50% wt. in H_2O, 102 mg, 1.5 mmol, 5.0 equiv.) in MeCN (3.75 mL), fitted with a 25G needle and the solution was added dropwise *via* syringe pump over 1 hour (3.75 mL/hour) while the reaction vial was maintained at 0 ºC with an ice/water bath. Upon completion of addition, the reaction was concentrated *in vacuo* to a minimum amount of MeCN. The reaction was worked up according to the **General Procedure for HBF_4 Deprotection** (*vide infra*, Section V) and purified by column chromatography on silica (15 mm fritted glass column, 30 mL SiO_2) using 100% DCM → 5% MeOH/DCM as eluent to give both recovered starting material and product.

Run 1: (40.5 mg, 0.177 mmol, 58.9% yield), (18.9 mg, 0.089 mmol, 29.5% rsm). **Run 2:** (40.8 mg, 0.178 mmol, 59.3% yield), (20.5 mg, 0.096 mmol, 32.0% rsm). **Average: 59.1% yield, 30.8% rsm. Selectivity = 59.1/(100-30.8) = 85%.**

Entry 5

The reaction was conducted with Method B: single catalyst addition protocol (*vide infra*, Section V). A 40 mL vial was charged with the resultant **7•HBF$_4$** (0.30 mmol, 1.0 equiv.), $ClCH_2COOH$ (425.3 mg, 4.5 mmol, 15.0 equiv.), (*R,R*)-Mn(PDP) catalyst **3** (27.9 mg, 0.03 mmol, 0.10 equiv.) and MeCN (0.60 mL). A 10 mL syringe was charged with a solution of H_2O_2 (50% wt. in H_2O, 102 mg, 1.5 mmol, 5.0 equiv.) in MeCN (3.75 mL), fitted with a 25G needle and the solution was added dropwise *via* syringe pump over 3 hours (1.25 mL/hour) while the reaction vial was maintained at 0 ºC with an ice/water bath. Upon completion of addition, the reaction was concentrated *in vacuo* to a minimum amount of MeCN. The reaction was worked up according to the **General Procedure for HBF_4 Deprotection** (*vide infra*, Section V) and purified by column chromatography on silica (15 mm fritted glass column, 30 mL SiO_2) using 100% DCM → 5% MeOH/DCM as eluent to give both recovered starting material and product.

Run 1: (51.4 mg, 0.224 mmol, 74.7% yield), (9.0 mg, 0.042 mmol, 14.1% rsm). **Run 2:** (48.9 mg, 0.213 mmol, 71.1% yield), (9.6 mg, 0.045 mmol, 15.0% rsm). **Average: 72.9% yield, 14.6% rsm. Selectivity = 72.9/(100-14.6) = 85%.**

Entry 6

The reaction was conducted with Method B: single catalyst addition protocol (*vide infra*, Section V). A 40 mL vial was charged with the resultant **7•HBF$_4$** (0.30 mmol, 1.0 equiv.), $ClCH_2COOH$ (425.3 mg, 4.5 mmol, 15.0 equiv.), (*R,R*)-Mn(PDP) catalyst **3** (27.9 mg, 0.03 mmol, 0.10 equiv.) and MeCN (0.60 mL). A 10 mL syringe was charged with a solution of H_2O_2 (50% wt. in H_2O, 102 mg, 1.5 mmol, 5.0 equiv.) in MeCN (3.75 mL), fitted with a 25G needle and the solution was added dropwise *via* syringe pump over 3 hour (1.25 mL/hour) while the reaction vial was maintained at -36 ºC with a 1,2-dichloroethane/dry ice bath. Upon completion of addition, the reaction was concentrated *in vacuo* to a minimum amount of

MeCN. The reaction was worked up according to the **General Procedure for HBF_4 Deprotection** (*vide infra*, Section V) and purified by column chromatography on silica (15 mm fritted glass column, 30 mL SiO_2) using 100% DCM → 5% MeOH/DCM as eluent to give both recovered starting material and product.

Run 1: (46.9 mg, 0.205 mmol, 68.2% yield), (16.7 mg, 0.078 mmol, 26.1% rsm). **Run 2:** (48.7 mg, 0.212 mmol, 70.8% yield), (15.0 mg, 0.070 mmol, 23.4% rsm). **Run 3:** (49.6 mg, 0.216 mmol, 72.1% yield), (16.9 mg, 0.079 mmol, 26.4% rsm). **Average: 70.4% yield ± 2.0%, 25.3% rsm ± 1.7%. Selectivity = 70.4-(100-25.3) = 94%.**

Entry 7

The reaction was conducted with Method B: single catalyst addition protocol (*vide infra*, Section V). A 40 mL vial was charged with the resultant **7•HBF$_4$** (0.30 mmol, 1.0 equiv.), $ClCH_2COOH$ (425.3 mg, 4.5 mmol, 15.0 equiv.), (*R,R*)-Mn(PDP) catalyst **3** (14.0 mg, 0.015 mmol, 0.05 equiv.) and MeCN (0.60 mL). A 10 mL syringe was charged with a solution of H_2O_2 (50% wt. in H_2O, 102 mg, 1.5 mmol, 5.0 equiv.) in MeCN (3.75 mL), fitted with a 25G needle and the solution was added dropwise *via* syringe pump over 3 hour (1.25 mL/hour) while the reaction vial was maintained at -36 ºC with a 1,2-dichloroethane/dry ice bath. Upon completion of addition, the reaction was concentrated *in vacuo* to a minimum amount of MeCN. The reaction was worked up according to the **General Procedure for HBF_4 Deprotection** (*vide infra*, Section V) and purified by column chromatography on silica (15 mm fritted glass column, 30 mL SiO_2) using 100% DCM → 5% MeOH/DCM as eluent to give both recovered starting material and product.

Run 1: (38.0 mg, 0.166 mmol, 55.2% yield), (23.7 mg, 0.111 mmol, 37.0% rsm). **Run 2:** (37.7 mg, 0.164 mmol, 54.8% yield), (25.0 mg, 0.117 mmol, 39.1% rsm). **Average: 55.0% yield, 38.1% rsm. Selectivity = 55.0-(100-38.1) = 89%.**

Entry 8

The reaction was conducted with Method B: single catalyst addition protocol (*vide infra*, Section V). A 40 mL vial was charged with the resultant **7•HBF$_4$** (0.30 mmol, 1.0 equiv.), $ClCH_2COOH$ (425.3 mg, 4.5 mmol, 15.0 equiv.), (*R,R*)-Mn(PDP) catalyst **3** (7.0 mg, 0.0075 mmol, 0.025 equiv.) and MeCN (0.60 mL). A 10 mL syringe was charged with a solution of H_2O_2 (50% wt. in H_2O, 102 mg, 1.5 mmol, 5.0 equiv.) in MeCN (3.75 mL), fitted with a 25G needle and the solution was added dropwise *via* syringe pump over 3 hour (1.25 mL/hour) while the reaction vial was maintained at -36 ºC with a 1,2-dichloroethane/dry ice bath. Upon completion of addition, the reaction was concentrated *in vacuo* to a minimum amount of MeCN. The reaction was worked up according to the **General Procedure for HBF_4 Deprotection** (*vide* *infra*, Section V) and purified by column chromatography on silica (15 mm fritted glass column, 30 mL SiO_2) using 100% DCM → 5% MeOH/DCM as eluent to give both recovered starting material and product.

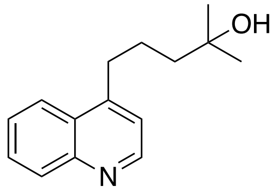
Run 1: (26.2 mg, 0.114 mmol, 38.1% yield), (38.3 mg, 0.180 mmol, 59.8% rsm). **Run 2:** (29.8 mg, 0.130 mmol, 43.3% yield), (34.6 mg, 0.162 mmol, 54.1% rsm). **Average: 40.7% yield, 57.0% rsm. Selectivity = 40.7-(100-57.0) = 95%.**

Entry 9

The reaction was conducted with Method B: single catalyst addition protocol (*vide infra*, Section V). A 40 mL vial was charged with the resultant **7•HBF$_4$** (0.30 mmol, 1.0 equiv.), $ClCH_2COOH$ (425.3 mg, 4.5 mmol, 15.0 equiv.), (*R,R*)-Mn(PDP) catalyst **3** solution (60 µL, 5 mM solution in MeCN, 0.30 µmol, 0.001 equiv.) and MeCN (0.60 mL). A 10 mL syringe was charged with a solution of H_2O_2 (50% wt. in H_2O, 102 mg, 1.5 mmol, 5.0 equiv.) in MeCN (3.75 mL), fitted with a 25G needle and the solution was added dropwise *via* syringe pump over 3 hour (1.25 mL/hour) while the reaction vial was maintained at -36 ºC with a 1,2-dichloroethane/dry ice bath. Upon completion of addition, the reaction was concentrated *in vacuo* to a minimum amount of MeCN. The reaction was worked up according to the **General Procedure for HBF$_4$ Deprotection** (*vide infra*, Section V) and purified by column chromatography on silica (15 mm fritted glass column, 30 mL SiO_2) using 100% DCM → 5% MeOH/DCM as eluent to give both recovered starting material and product.

Run 1: 0% yield, 100% rsm. **Run 2:** 0% yield, 100% rsm. **Average: 0% yield, 100% rsm. Selectivity = 0-(100-100) = 0%.**

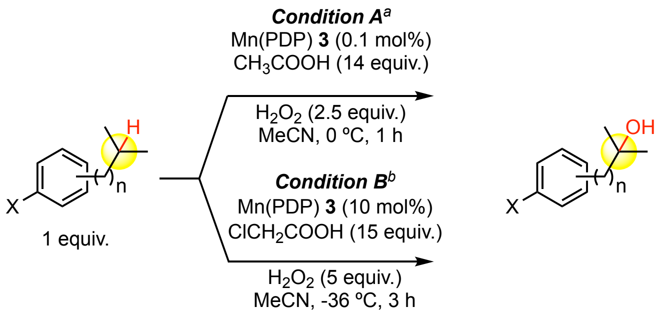
2-methyl-5-(quinolin-4-yl)pentan-2-ol [8]

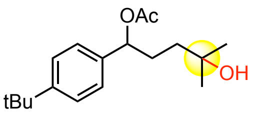


^{1}H-NMR (500 MHz, $CDCl_3$) δ 8.78 (d, *J* = 4.4 Hz, 1H), 8.11 (dd, *J* = 8.5, 1.2 Hz, 1H), 8.03 (dd, *J* = 8.4, 1.3 Hz, 1H), 7.69 (ddd, *J* = 8.4, 6.8, 1.4 Hz, 1H), 7.55 (ddd, *J* = 8.3, 6.8, 1.3 Hz, 1H), 7.23 (d, *J* = 4.4 Hz, 1H), 3.08 (t, *J* = 7.8 Hz, 2H), 1.93 (br. s, 1H), 1.91 – 1.81 (m, 2H), 1.67 – 1.57 (m, 2H), 1.22 (s, 6H). ^{13}C-NMR (126 MHz, $CDCl_3$) δ 150.1, 148.5, 148.3, 130.2, 129.1, 127.6, 126.4, 123.6, 120.8, 70.7, 43.7, 32.5, 29.5, 24.9. HRMS (TOF ESI+) *m/z* calculated for $C_{15}H_{20}NO$ $[M+H]^+$: 230.1545, found 230.1542.

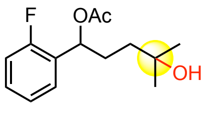
V. Supplementary Table 2. Chemoselective tertiary oxidation in aromatic substrates.

Preparation of Substrates and Compounds Characterization for Supplementary Table 2

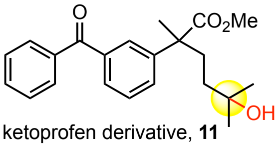




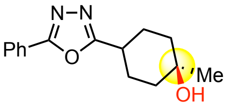
9
Cond. A: 54%
Cond. B: 60%



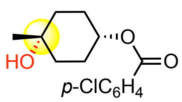
10
Cond. A: 35%
Cond. B: 43%



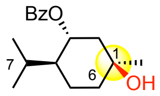
ketoprofen derivative, **11**
Cond. A: 53%
Cond. B: 71%



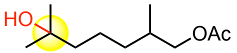
12
Cond. A: 36%[c]
Cond. B: 50%[c]



(±)-13
Cond. A: 44%, Cond. B: 58%
3:1 3º:2º, >20:1 d.r.
Electrochemical: 56%, 1:1 d.r.[19]



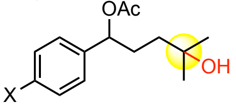
(−)-14[d]
Cond. A: 54%
Cond. B: 57%,
ca. 11:1 C1:C6



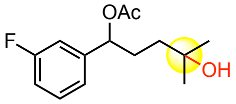
15

Cond. A: 51%
Cond. B: 62%
with Fe(PDP): 49%[2a]

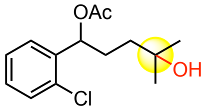
Condition B:
halogen-substituted aromatics:



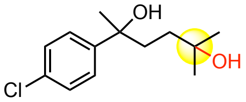
X = Cl, **6**, 69%
with 5 mol% **3**, **6**, 65%
Br, **16**, 67%
F, **17**, 66%



18, 56%

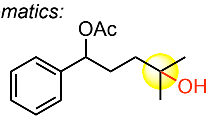


19, 56%



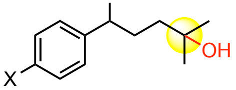
20, 69%

electron-neutral aromatics:



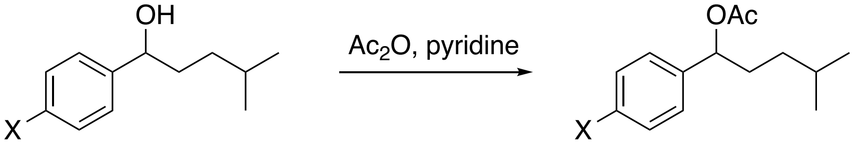
21, 35%

electron-withdrawn aromatics:

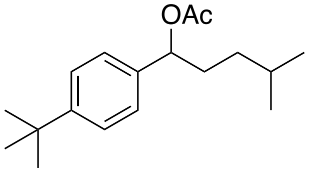


X = OCF_3, **22**, 73%
CO_2tBu, **23**, 73%
CN, **24**, 76%

(*R,R*)-Mn(PDP) and (*S,S*)-Mn(PDP) used interchangeably. Isolated yields based on the average of 2-3 reactions. [a]Substrate, 0.1 mol% Mn(PDP) **3**, 14 equiv. CH_3COOH additive with slow addition of 2.5 equiv. H_2O_2 (in MeCN, 0.2 M) over 1 h at 0 ºC. [b]Substrate, 5-10 mol% Mn(PDP) **3**, 15 equiv. $ClCH_2COOH$ additive with slow addition of 5.0 equiv. H_2O_2 (in MeCN, 0.4 M) over 3 h at -36 ºC. [c]Starting material recycled once. [d](*S,S*)-Mn(PDP) required for optimal yield.



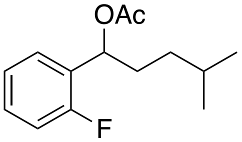
1-(4-*tert*-butyl)phenyl)-4-methylpentyl acetate [S1]



4-methyl-1-(4-*tert*-butyl)phenylpentan-1-ol (1.20 g, 5.12 mmol, 1.0 equiv.) was dissolved in CH_2Cl_2 (17 mL). Acetic anhydride (2.4 mL, 25.6 mmol, 5.0 equiv.) and pyridine (2.5 mL, 30.7 mmol, 6.0 equiv.) were added dropwise and the reaction was allowed to stir at room temperature overnight before being quenched with ~10 mL water. The layers were separated and the aqueous layer was extracted with CH_2Cl_2 (3 x 30 mL). The combined organic layers were dried with Na_2SO_4, filtered and concentrated *in vacuo*. The crude product was purified by flash column chromatography (35 mm fritted glass column, 150 mL SiO_2) using 5% EtOAc/hexanes → 10% EtOAc/hexanes → 15% EtOAc/hexanes → 20% EtOAc/hexanes as eluent gave 1-(4-*tert*-butyl)phenyl)-4-methylpentyl acetate **(S1)** as a colorless oil (1.16 g, 4.18 mmol, 81.6% yield).

^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.28 – 7.23 (m, 2H), 7.18 – 7.13 (m, 2H), 5.60 (dd, *J* = 7.9, 6.1 Hz, 1H), 1.96 (s, 3H), 1.86 – 1.75 (m, 1H), 1.71 – 1.63 (m, 1H), 1.45 (app. hept, *J* = 6.7 Hz, 1H), 1.22 (s, 9H), 1.19 – 1.07 (m, 1H), 1.06 – 0.98 (m, 1H), 0.78 (d, *J* = 6.7 Hz, 3H), 0.77 (d, *J* = 6.6 Hz, 3H). ^{13}C-NMR (126 MHz, $CDCl_3$) δ 170.6, 150.8, 137.9, 126.4, 125.4, 76.4, 34.8, 34.7, 34.3, 31.5, 28.0, 22.6, 21.5. HRMS (ESI+) *m/z* calculated for $C_{18}H_{28}O_2Na$ $[M+Na]^+$: 299.1987, found 299.1982.

1-(2-fluorophenyl)-4-methylpentyl acetate [S2]

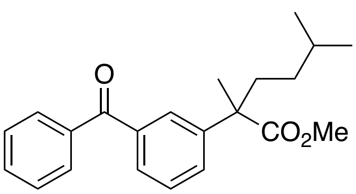


1-(2-fluorophenyl)-4-methylpentan-1-ol (785.1 mg, 4.0 mmol, 1.0 equiv.) was dissolved in 20 mL anhydrous pyridine. Acetic anhydride (1.9 mL, 20.0 mmol, 5.0 equiv.) was added dropwise at 0 ºC and the reaction was allowed to stir at room temperature overnight before being concentrated *in vacuo*. The residue was diluted with 30 mL DCM and washed with 30 mL 1M HCl solution twice followed by 20 mL brine. The organic layer was dried with $MgSO_4$, filtered, and concentrated. Flash column chromatography on silica (50 mm fritted glass column, 300 mL SiO_2) using 3% EtOAc/hexanes →5% EtOAc/hexanes as eluent gave 1-(2-fluorophenyl)-4-methylpentyl acetate (**S2)** as a colorless oil (852.9 mg, 3.58 mmol, 89% yield).

^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.37 – 7.32 (m, 1H), 7.28 – 7.23 (m, 1H), 7.15 – 7.10 (m, 1H), 7.06 – 7.00 (m, 1H), 6.00 (dd, *J* = 7.6, 6.2 Hz, 1H), 2.08 (s, 3H), 1.91 (dddd, *J* = 12.9, 11.1, 7.7, 5.0 Hz, 1H), 1.85 – 1.77 (m, 1H), 1.55 (app. hept, *J* = 6.7 Hz, 1H), 1.29 – 1.21 (m, 1H), 1.17 – 1.09 (m, 1H), 0.87 (d, *J* = 6.6 Hz, 6H). ^{13}C-NMR (126 MHz, $CDCl_3$) δ 170.3, 156.0 (d, *J* = 247.2 Hz), 129.3 (d, *J* = 8.2 Hz), 128.3 (d,

J = 13.5 Hz), 127.7 (d, J = 4.2 Hz), 124.3 (d, J = 3.5 Hz), 115.6 (d, J = 21.8 Hz), 70.6 (d, J = 2.3 Hz), 34.4, 33.5, 27.9, 22.6, 22.6, 21.3. ^{19}F-NMR (470 MHz, $CDCl_3$) δ -118.12. HRMS (TOF ESI+) *m/z* calculated for $C_{14}H_{19}O_2NaF$ $[M+Na]^+$: 261.1267, found 261.1267.

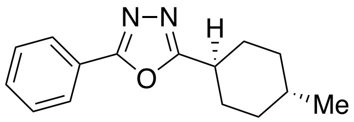
methyl 2-(3-benzoylphenyl)-2,5-dimethylhexanoate [S3]



In a flame dried 300 mL flask, methyl 2-(3-benzoylphenyl)propanoate (3.22 g, 12.0 mmol, 1.0 equiv.) was dissolved in 120 mL anhydrous THF and cooled to -78 ºC. Freshly made LDA solution (13.2 mmol, 1.1 equiv.) was added dropwise followed by HMPA (2.1 mL, 13.0 mmol, 1.0 equiv.). The reaction was maintained at -78 ºC for 5 minutes before addition of 1-bromo-3-methylbutane (4.3 mL, 36.0 mmol, 3.0 equiv.). The reaction was stirred at -78 ºC for an additional 30 minutes before warming to 0 ºC for 5 hours. The reaction was quenched with 30 mL saturated NH_4Cl solution and the aqueous layer was extracted with 60 mL diethyl ether. The combined organic layer was washed with 60 mL brine, dried with $MgSO_4$, filtered, and concentrated *in vacuo*. The crude reaction was purified on CombiFlash (40g silica column) using 0% → 10% ethyl acetate/hexanes as eluent to afford methyl 2-(3-benzoylphenyl)-2,5-dimethylhexanoate (**S3**) as a colorless oil (2.40 g, 7.09 mmol, 59% yield).

^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.82 – 7.78 (m, 2H), 7.76 (t, J = 1.9 Hz, 1H), 7.66 (d, J = 7.6 Hz, 1H), 7.61 – 7.57 (m, 1H), 7.55 – 7.52 (m, 1H), 7.48 (t, J = 7.7 Hz, 2H), 7.44 (t, J = 7.7 Hz, 1H), 3.66 (s, 3H), 2.09 – 2.01 (m, 1H), 1.98 – 1.90 (m, 1H), 1.57 (s, 3H), 1.51 (app. hept, J = 6.6 Hz, 1H), 1.09 – 1.03 (m, 2H), 0.88 (d, J = 6.6 Hz, 3H), 0.86 (d, J = 6.7 Hz, 3H). ^{13}C-NMR (126 MHz, $CDCl_3$) δ 196.8, 176.6, 144.5, 137.7, 137.7, 132.6, 130.5, 130.2, 128.7, 128.4 (2 carbons), 127.9, 52.3, 50.5, 37.1, 33.8, 28.6, 23.0, 22.7 (2 carbons). HRMS (ESI+) *m/z* calculated for $C_{22}H_{27}O_3$ $[M+H]^+$: 339.1960, found 339.1964.

2-(*trans*-4-methylcyclohexyl)-5-phenyl-1,3,4-oxadiazole [S4]

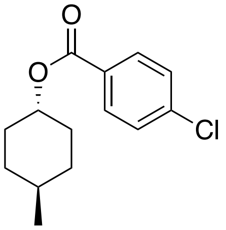


Prepared according to a reported procedure.[2] To a solution of benzoylhydrazine (1.36 g, 10.0 mmol, 1.0 equiv.) and *trans*-4-methyl-1-cyclohexanecarboxylic acid (1.42 g, 10.0 mmol, 1.0 equiv.) in 10 mL of toluene was slowly added $POCl_3$ (5 mL, 53.5 mmol, 5.3 equiv.). The mixture was stirred at 100 ºC for 2 h, following which time the solution was cooled to room temperature and cautiously poured into 50 mL of an ice water slurry. The mixture was transferred to a separatory funnel and the pH of the aqueous solution was adjusted to ∼10 with 100 mL of 2 M Na_2CO_3. The aqueous layer was extracted with EtOAc (3 x 40 mL). The combined organic extracts were dried over $NaSO_4$, filtered and concentrated *in vacuo* to afford a white solid. Recrystallization of this material using 5% EtOAc in cyclohexane solution afforded 2-((*trans*)-4-methylcyclohexyl)-5-phenyl-1,3,4-oxadiazole (**S4**) as a white solid, which was collected upon filtration and dried *in vacuo* (1.16 g, 4.78 mmol, 48% yield).

Spectral data in agreement with those previously reported in the literature.[2]

^{1}H-NMR (500 MHz, $CDCl_3$) δ 8.06 – 8.01 (m, 2H), 7.55 – 7.46 (m, 3H), 2.90 (tt, J = 12.2, 3.6 Hz, 1H), 2.24 – 2.15 (m, 2H), 1.91 – 1.82 (m, 2H), 1.68 (qd, J = 13.1, 3.5 Hz, 2H), 1.53 – 1.43 (m, 1H), 1.09 (qd, J = 13.3, 3.5 Hz, 2H), 0.96 (d, J = 6.5 Hz, 3H). ^{13}C-NMR (126 MHz, $CDCl_3$) δ 170.2, 164.5, 131.5, 129.1, 126.9, 124.4, 35.4, 34.4, 32.1, 30.4, 22.6. HRMS (TOF ESI+) *m/z* calculated for $C_{15}H_{19}N_2O$ $[M+H]^+$: 243.1497, found 243.1500.

trans-4-methylcyclohexyl 4-chlorobenzoate [S5]

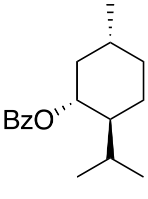


A flame dried 50 mL recovery flask was charged with *trans*-4-methylcyclohexanol (628.0 mg, 5.5 mmol, 1.1 equiv.) in 10 mL anhydrous CH_2Cl_2. The reaction was cooled to 0 °C and 4-chlorobenzoyl chloride (0.64 mL, 5 mmol, 1.0 equiv.) and triethylamine (1.05 mL, 7.5 mmol, 1.5 equiv.) were added sequentially. The reaction was warmed to room temperature and stirred overnight before being quenched with 30 mL water. The layers were separated and the aqueous layer was extracted with CH_2Cl_2 (2 x 30 mL). The combined organic layer was washed with brine, dried with Na_2SO_4, filtered and concentrated *in vacuo*. Flash column chromatography on silica (50 mm fritted glass column, 300 mL SiO_2) using 1% EtOAc/hexanes → 5% EtOAc/hexanes as eluent gave *trans*-4-methylcyclohexyl 4-chlorobenzoate **(S5)** as a white solid (1.05 g, 4.15 mmol, 83% yield).

Spectral data in agreement with those previously reported in the literature.[3]

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.98 – 7.94 (m, 2H), 7.42 – 7.37 (m, 2H), 4.90 (tt, J = 11.1, 4.4 Hz, 1H), 2.11 – 2.03 (m, 2H), 1.78 (dtt, J = 10.4, 4.2, 3.1, 1.4 Hz, 2H), 1.55 – 1.38 (m, 3H), 1.17 – 1.04 (m, 2H), 0.92 (d, J = 6.5 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.4, 139.2, 131.1, 129.5, 128.7, 74.5, 33.2, 31.9, 31.8, 22.0.

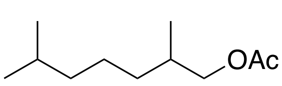
(1*R*,2*S*,5*R*)-2-isopropyl-5-methylcyclohexyl benzoate [S6]



(-)-menthol (1.56 g, 10.0 mmol, 1.0 equiv.) was dissolved in anhydrous CH_2Cl_2 (50 mL). Dimethylaminopyridine (0.24 g, 2.0 mmol, 0.2 equiv.) and triethylamine (2.09 mL, 15.0 mmol, 1.5 equiv.) were added and the mixture was cooled to 0 °C. Benzoyl chloride (1.39 mL, 12.0 mmol, 1.2 equiv.) was added dropwise and the reaction was allowed to stir at room temperature overnight before being quenched with 20 mL water. The layers were separated and the aqueous layer was extracted with CH_2Cl_2 (3 x 50 mL). The combined organic layers were dried with Na_2SO_4, filtered and concentrated *in vacuo*. The crude product was purified by flash column chromatography (35 mm fritted glass column, 150 mL SiO_2) using 100% hexanes → 3% acetone/hexanes as eluent gave (1*R*,2*S*,5*R*)-2-isopropyl-5-methylcyclohexyl benzoate **(S6)** as a white solid (2.28 g, 8.75 mmol, 88% yield).

^{1}H-NMR (500 MHz, $CDCl_3$) δ 8.07 – 8.03 (m, 2H), 7.58 – 7.52 (m, 1H), 7.47 – 7.41 (m, 2H), 4.94 (td, *J* = 10.9, 4.4 Hz, 1H), 2.13 (dtd, *J* = 12.0, 4.0, 1.7 Hz, 1H), 1.97 (heptd, *J* = 7.0, 2.8 Hz, 1H), 1.78 – 1.68 (m, 2H), 1.63 – 1.50 (m, 2H) 1.21 – 1.05 (m, 2H), 1.00 – 0.88 (m, 7H), 0.80 (d, *J* = 6.9 Hz, 3H). ^{13}C-NMR (126 MHz, $CDCl_3$) δ 166.2, 132.8, 131.0, 129.7, 128.4, 75.0, 47.4, 41.1, 34.5, 31.6, 26.6, 23.8, 22.2, 20.9, 16.7. $[\alpha]_D^{24}$ = –75.4 (c = 1.00, EtOH). HRMS (TOF ESI+) *m/z* calculated for $C_{17}H_{25}O_2$ $[M+H]^+$: 261.1855, found 261.1852.

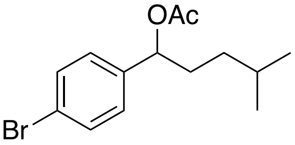
2,6-dimethylheptyl acetate [S7]



2,6-dimethylheptan-1-ol (0.72 g, 5.0 mmol, 1.0 equiv.) was dissolved in anhydrous CH_2Cl_2 (16 mL). Acetic anhydride (0.57 mL, 6.0 mmol, 1.2 equiv.) and pyridine (2.0 mL, 25.0 mmol, 5.0 equiv.) were added dropwise and the reaction was allowed to stir at room temperature overnight before being quenched with ~10 mL water. The layers were separated and the aqueous layer was extracted with CH_2Cl_2 (3 x 30 mL). The combined organic layers were dried with Na_2SO_4, filtered and concentrated *in vacuo*. The crude product was purified by flash column chromatography (35 mm fritted glass column, 150 mL SiO_2) using 100% hexanes → 10% EtOAc/hexanes as eluent gave 2,6-dimethylheptyl acetate **(S7)** as a colorless oil (559.8 mg, 3.00 mmol, 60.0% yield).

^{1}H-NMR (500 MHz, $CDCl_3$) δ 3.94 (dd, *J* = 10.7, 5.9 Hz, 1H), 3.84 (dd, *J* = 10.7, 6.9 Hz, 1H), 2.05 (s, 3H), 1.82 – 1.71 (m, 1H), 1.52 (dp, *J* = 13.3, 6.7 Hz, 1H), 1.39 – 1.08 (m, 6H), 0.92 (d, *J* = 6.7 Hz, 3H), 0.86 (d, *J* = 6.6 Hz, 6H). ^{13}C-NMR (126 MHz, $CDCl_3$) δ 171.4, 69.7, 39.3, 33.7, 32.7, 28.1, 24.7, 22.8, 22.7, 21.1, 17.0. HRMS (ESI+) *m/z* calculated for $C_{11}H_{22}O_2Na$ $[M+Na]^+$: 209.1517, found 209.1526.

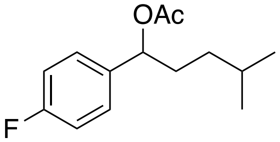
1-(4-bromophenyl)-4-methylpentyl acetate [S8]



1-(4-bromophenyl)-4-methylpentan-1-ol (771.5 mg, 3.0 mmol, 1.0 equiv.) was dissolved in 15 mL anhydrous pyridine. Acetic anhydride (1.42 mL, 15.0 mmol, 5.0 equiv.) was added dropwise at 0 ºC and the reaction was allowed to stir at room temperature overnight before being concentrated *in vacuo*. The residue was diluted with 30 mL DCM and washed with 1M HCl solution (2 x 30 mL) followed by 20 mL brine. The organic layer was dried with $MgSO_4$, filtered, and concentrated. Flash column chromatography on silica (50 mm fritted glass column, 300 mL SiO_2) using 3% EtOAc/hexanes →5% EtOAc/hexanes as eluent gave 1-(4-bromophenyl)-4-methylpentyl acetate **(S8)** as a colorless oil (827.6 mg, 2.77 mmol, 92% yield).

^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.48 – 7.44 (m, 2H), 7.22 – 7.17 (m, 2H), 5.63 (dd, *J* = 7.5, 6.4 Hz, 1H), 2.06 (s, 3H), 1.87 (dddd, *J* = 13.7, 11.3, 7.6, 5.0 Hz, 1H), 1.73 (dddd, *J* = 13.6, 11.4, 6.4, 5.1 Hz, 1H), 1.53 (hept, *J* = 6.7 Hz, 1H), 1.20 (dddd, *J* = 13.4, 11.5, 6.8, 5.0 Hz, 1H), 1.06 (dddd, *J* = 13.2, 11.5, 6.9, 5.1 Hz, 1H), 0.86 (d, *J* = 6.6 Hz, 3H), 0.85 (d, *J* = 6.6 Hz, 3H). ^{13}C-NMR (126 MHz, $CDCl_3$) δ 170.4, 140.0, 131.7, 128.4, 121.8, 75.9, 34.5, 34.2, 28.0, 22.6, 22.6, 21.4. HRMS (ESI+) *m/z* calculated for $C_{14}H_{19}O_2NaBr$ $[M+Na]^+$: 321.0466, found 321.0473.

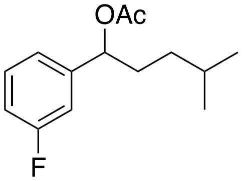
1-(4-fluorophenyl)-4-methylpentyl acetate [S9]



1-(4-fluorophenyl)-4-methylpentan-1-ol (981.3 mg, 5.0 mmol, 1.0 equiv.) was dissolved in 25 mL anhydrous pyridine. Acetic anhydride (2.4 mL, 25.0 mmol, 5.0 equiv.) was added dropwise at 0 ºC and the reaction was allowed to stir at room temperature overnight before being concentrated *in vacuo*. The residue was diluted with 30 mL DCM and washed with 1M HCl solution (2 x 30 mL) followed by 20 mL brine. The organic layer was dried with $MgSO_4$, filtered, and concentrated. Flash column chromatography on silica (50 mm fritted glass column, 300 mL SiO_2) using 3% EtOAc/hexanes →5% EtOAc/hexanes as eluent gave 1-(4-fluorophenyl)-4-methylpentyl acetate **(S9)** as a colorless oil (1.028 g, 4.31 mmol, 86% yield).

^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.33 – 7.27 (m, 2H), 7.05 – 6.99 (m, 2H), 5.66 (t, *J* = 7.0 Hz, 1H), 2.06 (s, 3H), 1.89 (dddd, *J* = 13.7, 11.4, 7.6, 5.0 Hz, 1H), 1.78 – 1.69 (m, 1H), 1.53 (app. hept, *J* = 6.7 Hz, 1H), 1.21 (dddd, *J* = 13.5, 11.6, 6.8, 5.0 Hz, 1H), 1.06 (dddd, *J* = 13.2, 11.5, 6.9, 5.0 Hz, 1H), 0.87 (d, *J* = 6.6 Hz, 3H), 0.85 (d, *J* = 6.6 Hz, 3H). ^{13}C-NMR (126 MHz, $CDCl_3$) δ 170.5, 162.4 (d, *J* = 245.9 Hz), 136.8 (d, *J* = 3.2 Hz), 128.5 (d, *J* = 8.0 Hz), 115.4 (d, *J* = 21.4 Hz), 75.9, 34.6, 34.3, 28.0, 22.6, 22.6, 21.4. ^{19}F-NMR (470 MHz, $CDCl_3$) δ -114.93. HRMS (TOF EI+) *m/z* calculated for $C_{14}H_{19}O_2F$ $[M]^+$: 238.13691, found 238.13661.

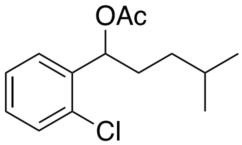
1-(3-fluorophenyl)-4-methylpentyl acetate [S10]



1-(3-fluorophenyl)-4-methylpentan-1-ol (785.1 mg, 4.0 mmol, 1.0 equiv.) was dissolved in 20 mL anhydrous pyridine. Acetic anhydride (1.9 mL, 20.0 mmol, 5.0 equiv.) was added dropwise at 0 ºC and the reaction was allowed to stir at room temperature overnight before being concentrated *in vacuo*. The residue was diluted with 30 mL DCM and washed with 1M HCl solution (2 x 30 mL) followed by 20 mL brine. The organic layer was dried with $MgSO_4$, filtered, and concentrated. Flash column chromatography on silica (50 mm fritted glass column, 300 mL SiO_2) using 3% EtOAc/hexanes →5% EtOAc/hexanes as eluent gave 1-(3-fluorophenyl)-4-methylpentyl acetate **(S10)** as a colorless oil (712.7 mg, 2.99 mmol, 75% yield).

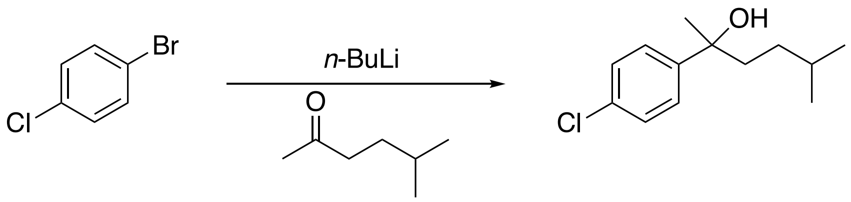
^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.35 (td, *J* = 7.5, 1.8 Hz, 1H), 7.29 – 7.23 (m, 1H), 7.13 (td, *J* = 7.5, 1.2 Hz, 1H), 7.03 (ddd, *J* = 10.4, 8.2, 1.2 Hz, 1H), 6.00 (dd, *J* = 7.7, 6.1 Hz, 1H), 2.08 (s, 3H), 1.90 (dddd, *J* = 13.0, 11.2, 7.7, 5.1 Hz, 1H), 1.85 – 1.77 (m, 1H), 1.55 (app. hept, *J* = 6.6 Hz, 1H), 1.25 (dddd, *J* = 13.4, 11.6, 6.9, 5.1 Hz, 1H), 1.13 (dddd, *J* = 13.2, 11.1, 6.8, 5.2 Hz, 1H), 0.87 (d, *J* = 6.6 Hz, 3H), 0.86 (d, *J* = 6.6 Hz, 3H). ^{13}C-NMR (126 MHz, CDCl$_3$) δ 170.3, 160.0 (d, *J* = 247.2 Hz), 129.3 (d, *J* = 8.3 Hz), 128.3 (d, *J* = 13.6 Hz), 127.7 (d, *J* = 4.3 Hz), 124.3 (d, *J* = 3.4 Hz), 115.6 (d, *J* = 21.9 Hz), 70.6 (d, *J* = 2.3 Hz), 34.4, 33.5, 27.9, 22.6, 22.6, 21.3. ^{19}F-NMR (470 MHz, CDCl$_3$) δ -118.61. HRMS (TOF ESI+) *m/z* calculated for $C_{14}H_{17}O_2NaF$ [M-2H+Na]$^+$: 259.1110, found 259.1114.

1-(2-chlorophenyl)-4-methylpentyl acetate [S11]

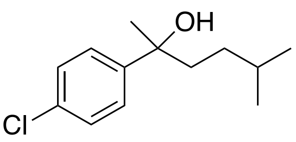


1-(2-chlorophenyl)-4-methylpentan-1-ol (1.017 g, 4.8 mmol, 1.0 equiv.) was dissolved in 25 mL anhydrous pyridine. Acetic anhydride (2.26 mL, 23.9 mmol, 5.0 equiv.) was added dropwise at 0 ºC and the reaction was allowed to stir at room temperature overnight before being concentrated *in vacuo*. The residue was diluted with 30 mL DCM and washed with 1M HCl solution (2 x 30 mL) followed by 20 mL brine. The organic layer was dried with MgSO$_4$, filtered, and concentrated. Flash column chromatography on silica (50 mm fritted glass column, 300 mL SiO$_2$) using 5% EtOAc/hexanes as eluent gave 1-(2-chlorophenyl)-4-methylpentyl acetate **(S11)** as a colorless oil (1.174 g, 4.61 mmol, 96% yield).

^{1}H-NMR (500 MHz, CDCl$_3$) δ 7.38 (dd, *J* = 7.8, 1.7 Hz, 1H), 7.34 (dd, *J* = 7.9, 1.4 Hz, 1H), 7.26 (td, *J* = 7.5, 1.4 Hz, 1H), 7.20 (td, *J* = 7.6, 1.8 Hz, 1H), 6.11 (t, *J* = 6.6 Hz, 1H), 2.10 (s, 3H), 1.85 – 1.79 (m, 2H), 1.56 (app. hept, *J* = 6.7 Hz, 1H), 1.33 – 1.16 (m, 2H), 0.88 (d, *J* = 6.4 Hz, 6H). ^{13}C-NMR (126 MHz, CDCl$_3$) δ 170.2, 139.1, 132.4, 129.7, 128.7, 127.1, 127.0, 73.0, 34.5, 33.5, 27.9, 22.7, 22.5, 21.3. HRMS (TOF ESI+) *m/z* calculated for $C_{14}H_{19}O_2NaCl$ [M+Na]$^+$: 277.0971, found 277.0964.



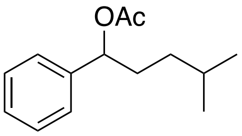
2-(4-chlorophenyl)-5-methylhexan-2-ol [S12]



In a flame dried 100 mL recovery flask, 1-bromo-4-chlorobenzene (2.872 g, 15.0 mmol, 1.0 equiv.) was dissolved in 40 mL anhydrous THF. *n*-BuLi (9.4 mL 1.6 M in hexanes, 1.0 equiv.) was added dropwise at -78 ºC and the reaction was allowed to stir at -78 ºC for 30 minutes. A solution of 5-methyl-2-hexanone (2.5 mL, 18.0 mmol, 1.2 equiv.) in 3 mL anhydrous THF was added dropwise at -78 ºC. The reaction was allowed to warm to room temperature and stirred overnight. The reaction was quenched with 10 mL saturated NH$_4$Cl solution and the aqueous layer was extracted with diethyl ether (2 x 30 mL). The combined organic layer was washed with 30 mL brine, dried with MgSO$_4$, filtered, and concentrated *in vacuo*. Flash column chromatography on silica (50 mm fritted glass column, 300 mL SiO_2) using 10% EtOAc/hexanes as eluent gave 2-(4-chlorophenyl)-5-methylhexan-2-ol (**S12**) as a colorless oil (1.287 g, 5.68 mmol, 38% yield).

^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.38 – 7.34 (m, 2H), 7.32 – 7.28 (m, 2H), 1.83 – 1.71 (m, 2H), 1.70 (br. s, 1H), 1.53 (s, 3H), 1.45 (app. hept, J = 6.6 Hz, 1H), 1.13 (dddd, J = 12.9, 11.8, 6.6, 5.1 Hz, 1H), 0.98 (dddd, J = 13.0, 11.8, 6.8, 5.1 Hz, 1H), 0.84 (d, J = 6.6 Hz, 3H), 0.83 (d, J = 6.6 Hz, 3H). ^{13}C-NMR (126 MHz, $CDCl_3$) δ 146.7, 132.4, 128.3, 126.5, 74.6, 42.1, 32.0, 30.4, 28.5, 22.7, 22.6. HRMS (TOF EI+) *m/z* calculated for $C_{13}H_{19}ONaCl$ $[M]^+$: 226.1124, found 226.1125.

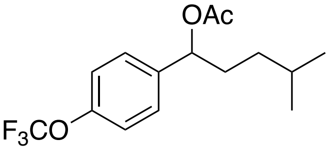
4-methyl-1-phenylpentyl acetate [S13]



4-methyl-1-phenylpentan-1-ol (766.6 mg, 4.3 mmol, 1.0 equiv.) was dissolved in 22 mL anhydrous pyridine. Acetic anhydride (2.0 mL, 21.5 mmol, 5.0 equiv.) was added dropwise at 0 ºC and the reaction was allowed to stir at room temperature overnight before being concentrated *in vacuo*. The residue was diluted with 30 mL DCM and washed with 1M HCl solution (2 x 30 mL) followed by 20 mL brine. The organic layer was dried with $MgSO_4$, filtered, and concentrated. Flash column chromatography on silica (50 mm fritted glass column, 300 mL SiO_2) using 3% EtOAc/hexanes →5% EtOAc/hexanes as eluent gave 4-methyl-1-phenylpentyl acetate **(S13)** as a colorless oil (871.6 mg, 3.96 mmol, 92% yield).

^{1}H-NMR (500 MHz, $CDCl_3$) 7.37 – 7.31 (m, 4H), 7.31 – 7.26 (m, 1H), 5.74 – 5.67 (m, 1H), 2.07 (s, 3H), 1.95 – 1.86 (m, 1H), 1.82 – 1.73 (m, 1H), 1.55 (app. hept, J = 6.7 Hz, 1H), 1.28 – 1.19 (m, 1H), 1.15 – 1.06 (m, 1H), 0.87 (d, J = 6.6 Hz, 3H), 0.86 (d, J = 6.6 Hz, 3H). ^{13}C-NMR (126 MHz, $CDCl_3$) δ 170.5, 141.0, 128.5, 127.9, 126.7, 76.5, 34.7, 34.4, 28.0, 22.6, 22.6, 21.4. HRMS (ESI+) *m/z* calculated for $C_{14}H_{20}O_2Na$ $[M+Na]^+$: 243.1361, found 243.1365.

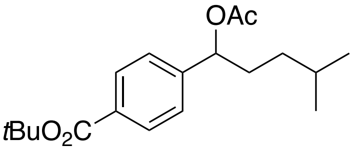
4-methyl-1-(4-(trifluoromethoxy)phenyl)pentyl acetate [S14]



4-methyl-1-(4-(trifluoromethoxy)phenyl)pentan-1-ol (1.2061 g, 4.6 mmol, 1.0 equiv.) was dissolved in 23 mL anhydrous pyridine. Acetic anhydride (2.20 mL, 23.0 mmol, 5.0 equiv.) was added dropwise at 0 ºC and the reaction was allowed to stir at room temperature overnight before being concentrated *in vacuo*. The residue was diluted with 30 mL DCM and washed with 1M HCl solution (2 x 30 mL) followed by 20 mL brine. The organic layer was dried with $MgSO_4$, filtered, and concentrated. Flash column chromatography on silica (50 mm fritted glass column, 300 mL SiO_2) using 3% EtOAc/hexanes →5% EtOAc/hexanes as eluent gave 4-methyl-1-(4-(trifluoromethoxy)phenyl)pentyl acetate **(S14)** as a colorless oil (1.22 g, 4.02 mmol, 87% yield).

^{1}H-NMR (500 MHz, CDCl$_3$) δ 7.38 – 7.33 (m, 2H), 7.21 – 7.15 (m, 2H), 5.69 (dd, *J* = 7.7, 6.2 Hz, 1H), 2.07 (s, 3H), 1.93 – 1.84 (m, 1H), 1.74 (dddd, *J* = 13.6, 11.3, 6.3, 5.1 Hz, 1H), 1.54 (app. hept, *J* = 6.7 Hz, 1H), 1.22 (dddd, *J* = 13.3, 11.5, 6.8, 4.9 Hz, 1H), 1.09 (dddd, *J* = 13.2, 11.6, 6.8, 5.1 Hz, 1H), 0.87 (d, *J* = 6.6 Hz, 3H), 0.86 (d, *J* = 6.6 Hz, 3H). ^{13}C-NMR (126 MHz, CDCl$_3$) δ 170.4, 148.8 (q, *J* = 2.1 Hz), 139.8, 128.1, 121.0, 120.6 (q, *J* = 257.1 Hz), 75.7, 34.6, 34.3, 28.0, 22.6 (2 carbons), 21.3. ^{19}F-NMR (470 MHz, CDCl$_3$) δ -58.34. HRMS (TOF ESI+) *m/z* calculated for $C_{15}H_{19}O_3F_3Na$ [M+Na]$^+$: 327.1184, found 327.1177.

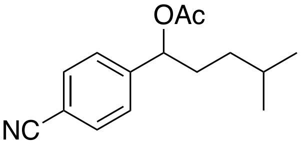
***tert*-butyl 4-(1-acetoxy-4-methylpentyl)benzoate [S15]**



tert-butyl 4-(1-hydroxy-4-methylpentyl)benzoate (738.3 mg, 2.65 mmol, 1.0 equiv.) and acetyl chloride (0.57 mL, 8.0 mmol, 3.0 equiv.) were dissolved in 13 mL anhydrous DCM. Triethylamine (1.85 mL, 13.3 mmol, 5.0 equiv.) was added dropwise at 0 ºC and the reaction was allowed to stir at room temperature overnight before being concentrated *in vacuo*. The residue was diluted with 20 mL DCM and washed with 1M HCl solution (2 x 20 mL) followed by 20 mL brine. The organic layer was dried with MgSO$_4$, filtered, and concentrated. Flash column chromatography on silica (50 mm fritted glass column, 300 mm SiO$_2$) using 3% EtOAc/hexanes →5% EtOAc/hexanes as eluent gave *tert*-butyl 4-(1-acetoxy-4-methylpentyl)benzoate (**S15**) as a colorless oil (392.5 mg, 1.22 mmol, 46% yield).

^{1}H-NMR (500 MHz, CDCl$_3$) δ 7.96 (d, *J* = 8.4 Hz, 2H), 7.36 (d, *J* = 8.3 Hz, 2H), 5.71 (dd, *J* = 7.5, 6.4 Hz, 1H), 2.07 (s, 3H), 1.92 – 1.84 (m, 1H), 1.76 (dddd, *J* = 13.6, 11.4, 6.3, 5.1 Hz, 1H), 1.58 (s, 9H), 1.52 (app. hept, *J* = 6.7 Hz, 1H), 1.21 (dddd, *J* = 13.3, 11.6, 6.8, 4.9 Hz, 1H), 1.12 – 1.04 (m, 1H), 0.86 (d, *J* = 6.6 Hz, 3H), 0.84 (d, *J* = 6.6 Hz, 3H). ^{13}C-NMR (126 MHz, CDCl$_3$) δ 170.4, 165.6, 145.5, 131.6, 129.7, 126.4, 81.1, 76.1, 34.5, 34.3, 28.3, 28.0, 22.6 (2 carbons), 21.4. HRMS (TOF ESI+) *m/z* calculated for $C_{19}H_{28}O_4Na$ [M+Na]$^+$: 343.1885, found 343.1884.

1-(4-cyanophenyl)-4-methylpentyl acetate [S16]



1-(4-cyanophenyl)-4-methylpentan-1-ol (226.5 mg, 1.11 mmol, 1.0 equiv.) was dissolved in 5.5 mL anhydrous DCM. Acetic anhydride (0.21 mL, 2.22 mmol, 2.0 equiv.), triethylamine (0.46 mL, 3.33 mmol, 3.0 equiv.) and 4-dimethylaminopyridine (13.4 mg, 0.11 mmol, 10 mol%) were added sequentially at 0 ºC and the reaction was allowed to stir at room temperature overnight before being concentrated *in vacuo*. The residue was diluted with 30 mL DCM and washed with water (2 x 30 mL) followed by 20 mL brine. The organic layer was dried with MgSO$_4$, filtered, and concentrated. Flash column chromatography on silica (35 mm fritted

glass column, 150 mm SiO_2) using 10% EtOAc/hexanes → 30% EtOAc/hexanes as eluent gave 1-(4-cyanophenyl)-4-methylpentyl acetate (**S16**) as a colorless oil (252.6 mg, 1.03 mmol, 93% yield).
^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.63 (d, *J* = 8.5 Hz, 2H), 7.42 (d, *J* = 8.2 Hz, 2H), 5.68 (dd, *J* = 7.7, 6.0 Hz, 1H), 2.09 (s, 3H), 1.87 (dddd, *J* = 13.8, 11.4, 7.8, 4.9 Hz, 1H), 1.74 (dddd, *J* = 13.8, 11.2, 6.0, 5.1 Hz, 1H), 1.53 (app. hept, *J* = 6.7 Hz, 1H), 1.21 (dddd, *J* = 13.4, 11.6, 6.9, 4.9 Hz, 1H), 1.08 (dddd, *J* = 13.2, 11.5, 6.8, 5.1 Hz, 1H), 0.86 (d, *J* = 6.6 Hz, 3H), 0.85 (d, *J* = 6.6 Hz, 3H). ^{13}C-NMR (126 MHz, $CDCl_3$) δ 170.3, 146.4, 132.5, 127.2, 118.8, 111.8, 75.7, 34.4, 34.3, 27.9, 22.6, 22.5, 21.3. HRMS (TOF ESI+) *m/z* calculated for $C_{15}H_{20}NO_2$ $[M+H]^+$: 246.1494, found 246.1490.

General Oxidation Procedures

Method A: Low Catalyst Loading (0.1 mol%) Protocol with Acetic Acid

A 40 mL vial was charged with the substrate (0.30 mmol, 1.0 equiv.), CH_3COOH (0.24 mL, 4.2 mmol, 14.0 equiv.), catalyst (60 µL, 5 mM solution in MeCN, 0.30 µmol, 0.001 equiv.), MeCN (0.60 mL, 0.5 M) and a stir bar and the vial was sealed with a screw cap fitted with a PTFE/Silicone septum. The vial was cooled to 0 ºC with an ice/water bath. A separate solution of H_2O_2 (51.0 mg, 0.75 mmol, 2.5 equiv., 50% wt. in H_2O, purchased from Sigma Aldrich) in MeCN (3.75 mL, 0.2 M) was loaded into a 10 mL syringe fitted with a 25G needle and was added dropwise *via* syringe pump over 1 hour (3.75 mL/hour) while the reaction vial was maintained at 0 ºC. Upon completion of addition, the reaction was concentrated *in vacuo* to a minimum amount of MeCN. The residue was dissolved in ~20 mL DCM and washed with 20 mL sat. $NaHCO_3$ solution. The aqueous layer was extracted with DCM (2 x 15 mL) and the combined organic layer was dried with Na_2SO_4. The filtrate was concentrated and purified by flash chromatography on silica gel.

Method B: Single Catalyst Addition Protocol with Chloroacetic Acid

A 40 mL vial was charged with substrate (0.3 mmol, 1.0 equiv.), catalyst (0.03 mmol, 10 mol%), $ClCH_2CO_2H$ (425 mg, 4.5 mmol, 15.0 equiv.) and a stir bar. MeCN (0.6 mL, 0.5 M) was added along the wall to ensure all compounds were washed beneath the solvent level and the vial was sealed with a screw cap fitted with a PTFE/Silicone septum. The vial was cooled to -36 ºC with 1,2-dichloroethane/dry ice bath or 0 ºC with an ice/water bath. A separate solution of H_2O_2 (102 mg, 1.5 mmol, 5.0 equiv., 50% wt. in H_2O, purchased from Sigma-Aldrich) in MeCN (3.75 mL, 0.4 M) was loaded into a 10 mL syringe fitted with a 25G needle and was added dropwise to the stirring reaction over 3 hours *via* a syringe pump (1.25 mL/h addition rate) while the reaction vial was maintained at the corresponding temperature. Upon completion, the reaction mixture was concentrated to a minimum amount of solvent. The residue was dissolved in ~20 mL DCM and washed with 20 mL sat. $NaHCO_3$ solution (CAUTION: CO_2 was released) to remove $ClCH_2CO_2H$. The aqueous layer was extracted with DCM (2 x 15 mL) and the combined organic layer was dried with Na_2SO_4. The filtrate was concentrated and purified by flash chromatography on silica gel.

Method C: Slow Catalyst Addition Protocol with Chloroacetic Acid

This protocol was used when Method B gave low conversion. A 40 mL vial was charged with substrate (0.3 mmol, 1.0 equiv.), $ClCH_2CO_2H$ (425 mg, 4.5 mmol, 15.0 equiv.) and a stir bar. MeCN (0.6 mL, 0.5

M) was added along the wall to ensure all compounds were washed beneath the solvent level and the vial was sealed with a screw cap fitted with a PTFE/Silicone septum. The vial was cooled to -36 ºC with 1,2-dichloroethane/dry ice bath or to 0 ºC with ice/water bath. A 1.0 mL syringe was filled with a solution of the catalyst (0.03 mmol, 10 mol%) in MeCN (0.375 mL, 0.083 M). A few drops of this solution was added to the reaction. A 10 mL syringe was filled with a solution of H_2O_2 (102 mg, 1.5 mmol, 5.0 equiv., 50% wt. in H_2O, purchased from Sigma-Aldrich) in MeCN (3.75 mL, 0.4 M). Both syringes were fitted with 25G needles and loaded in a syringe pump resulting in a simultaneous addition of catalyst and oxidant solutions over 3 hours while the reaction vial was maintained at the corresponding temperature (1.25 mL/h addition rate set for the H_2O_2 syringe; 0.125 mL/h for the catalyst syringe). Upon completion, the reaction mixture was concentrated to a minimum amount of solvent. The residue was dissolved in ~20 mL DCM and washed with 20 mL sat. $NaHCO_3$ solution (CAUTION: CO_2 was released) to remove $ClCH_2CO_2H$. The aqueous layer was extracted with DCM (2 x 15 mL) and the combined organic layer was dried with Na_2SO_4. The filtrate was concentrated and purified by flash chromatography on silica gel.

Method D: Iterative Catalyst Addition Protocol with Chloroacetic Acid

This protocol was used when Method B gave low conversion and method C gave low recovered starting material. A 40 mL vial was charged with substrate (0.3 mmol, 1.0 equiv.), catalyst (0.015 mmol, 5 mol%), $ClCH_2CO_2H$ (425 mg, 4.5 mmol, 15.0 equiv.) and a stir bar. MeCN (0.6 mL, 0.5 M) was added along the wall to ensure all compounds were washed beneath the solvent level and the vial was sealed with a screw cap fitted with a PTFE/Silicone septum. The vial was cooled to -36 ºC with dry ice/1,2-dichloroethane bath or 0 ºC with an ice/water bath. A separate solution of H_2O_2 (102 mg, 1.5 mmol, 5.0 equiv., 50% wt. in H_2O, purchased from Sigma-Aldrich) in MeCN (3.75 mL, 0.4 M) was loaded into a 10 mL syringe fitted with a 25G needle and was added dropwise to the stirring reaction over 3 hours *via* a syringe pump (1.25 mL/h addition rate) while the reaction vial was maintained at the corresponding temperature. At 1.5 hours, an additional 5 mol% catalyst (0.015 mmol in 0.1 mL MeCN) was added dropwise to the reaction. Upon completion, the reaction mixture was concentrated to a minimum amount of solvent. The residue was dissolved in ~20 mL DCM and washed with 20 mL sat. $NaHCO_3$ solution (CAUTION: CO_2 was released) to remove $ClCH_2CO_2H$. The aqueous layer was extracted with DCM (2 x 15 mL) and the combined organic layer was dried with Na_2SO_4. The filtrate was concentrated and purified by flash chromatography on silica gel.

General procedure for the $HBF_4•OEt_2$ protection[7]

To a flame dried 40 mL vial with a magnetic stir bar was added substrate (0.3 mmol, 1.0 equiv.) and anhydrous CH_2Cl_2 (1.2 mL, 0.25 M). The vial was flushed with a N_2 stream and then cooled to 0 ºC.

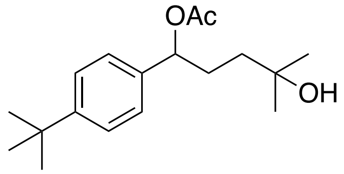
HBF_4•OEt_2 (45.5 µL, 1.1 equiv.) was added dropwise *via* syringe and the reaction was allowed to stir at 0 ºC for 30 minutes then warmed to room temperature and stirred for an additional 1 h. The reaction was concentrated *in vacuo* and left on high vacuum overnight (12-24 h). Resultant HBF_4 salt were used as substrates following the corresponding oxidation protocol described above.

General Procedure for HBF_4 Deprotection

Upon completion, the reaction was warmed to room temperature and concentrated *in vacuo* to a minimum amount of solvent. The reaction was diluted with DCM (10 mL), basified with 3 M NaOH (10 mL) and stirred vigorously for 20 minutes. The resulting solution was poured into 3 M NaOH (30 mL) and extracted with DCM (3 x 20 mL). The combined organic layer was washed with brine (1 x 60 mL) then dried with Na_2SO_4. The filtrate was concentrated and purified by flash column chromatography on silica gel.

C—H Oxidation of Substrates and Products Characterization for Supplementary Table 2

1-(4-(*tert*-butyl)phenyl)-4-hydroxy-4-methylpentyl acetate [9]



At 0.1 mol% catalyst: The reaction was run with **General Method A: Low Catalyst Loading (0.1 mol%) Protocol**: 1-(4-*tert*-butyl)phenyl)-4-methylpentyl acetate **S1** (82.9 mg, 0.300 mmol, 1.0 equiv), CH_3COOH (0.24 mL, 4.2 mmol, 14.0 equiv.), (*R,R*)-Mn(PDP) catalyst **3** solution (60 µL, 5 mM solution in MeCN, 0.30 µmol, 0.001 equiv.), H_2O_2 (50% wt. in H_2O, 51.0 mg, 0.75 mmol, 2.5 equiv.), MeCN (0.6 mL in 40 mL vial, 3.75 mL with oxidant). The reaction was run at 0 ºC with an ice/water bath. The reaction was worked up with 15 mL saturated $NaHCO_3$ and DCM as described in General Method A. Flash column chromatography on silica (15 mm fritted glass column, 30 mL SiO_2) using gradient 5% EtOAc/hexanes → 30% EtOAc/hexanes as eluent afforded product **9** as a pale yellow oil.

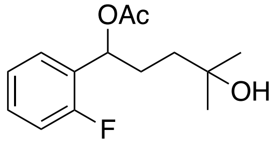
Run 1: (47.5 mg, 0.162 mmol, 54.1% yield), (16.8 mg, 0.061 mmol, 20.3% rsm). **Run 2:** (47.5 mg, 0.162 mmol, 54.1% yield), (18.3 mg, 0.066 mmol, 22.1% rsm). **Average: 54.1% yield, 21.2% rsm.**

At 10 mol% catalyst: The reaction was run with **General Method B: Single Catalyst Addition Protocol**: 1-(4-*tert*-butyl)phenyl)-4-methylpentyl acetate **S1** (82.9 mg, 0.300 mmol, 1.0 equiv), (*R,R*)-Mn(PDP) **3** (27.9 mg, 0.030 mmol, 10 mol%), $ClCH_2CO_2H$ (425.3 mg, 4.5 mmol, 15.0 equiv.), H_2O_2 (50% wt. in H_2O, 102 mg, 1.5 mmol, 5.0 equiv.), MeCN (0.6 mL in 40 mL vial, 3.75 mL with oxidant). The reaction was run at -36 ºC with 1,2-dichloroethane/dry ice bath. The reaction was worked up with 15 mL saturated $NaHCO_3$ and DCM as described in General Method B. Flash column chromatography on silica (15 mm fritted glass column, 30 mL SiO_2) using gradient 5% EtOAc/hexanes → 30% EtOAc/hexanes as eluent afforded product **9** as a pale yellow oil.

Run 1: (55.5 mg, 0.190 mmol, 63.3% yield), (10.5 mg, 0.038 mmol, 12.7% rsm). **Run 2:** (51.1 mg, 0.175 mmol, 58.2% yield), (6.8 mg, 0.025 mmol, 8.2% rsm). **Run 3:** (52.0 mg, 0.178 mmol, 59.3% yield), (10.5 mg, 0.038 mmol, 12.7% rsm). **Average: 60.3% yield ± 2.7%, 11.2% rsm ± 2.6%.**

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39 – 7.34 (m, 2H), 7.30 – 7.26 (m, 2H), 5.74 (dd, *J* = 7.7, 6.2 Hz, 1H), 2.07 (s, 3H), 2.06 – 1.96 (m, 1H), 1.89 (dddd, *J* = 13.3, 11.8, 6.1,4.6 Hz, 1H), 1.55 (ddd, *J* = 13.5, 12.2, 4.6 Hz, 1H), 1.46 – 1.29 (m, 2H), 1.32 (s, 9H), 1.21 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.6, 150.9, 137.5, 126.4, 125.5, 76.3, 70.7, 39.6, 34.6, 31.4, 31.3, 29.4, 29.4, 21.4. HRMS: (ESI+) *m/z* calculated for $C_{18}H_{28}O_3Na$ $[M+Na]^+$: 315.1936, found 315.1929.

1-(2-fluorophenyl)-4-hydroxy-4-methylpentyl acetate [10]



At 0.1 mol% catalyst: The reaction was run with **General Method A: Low Catalyst Loading (0.1 mol%) Protocol**: 1-(2-fluorophenyl)-4-methylpentyl acetate **S2** (71.5 mg, 0.300 mmol, 1.0 equiv), CH_3COOH (0.24 mL, 4.2 mmol,

14.0 equiv.), (*R,R*)-Mn(PDP) catalyst **3** solution (60 µL, 5 mM solution in MeCN, 0.30 µmol, 0.001 equiv.), H_2O_2 (50% wt. in H_2O, 51.0 mg, 0.75 mmol, 2.5 equiv.), MeCN (0.6 mL in 40 mL vial, 3.75 mL with oxidant). The reaction was run at 0 ºC with an ice/water bath. The reaction was worked up with 15 mL saturated $NaHCO_3$ and DCM as described in General Method A. Flash column chromatography on silica (15 mm fritted glass column, 30 mL SiO_2) using gradient using 10% acetone/hexanes → 20% acetone/hexanes as eluent afforded product **10** as a yellow oil.

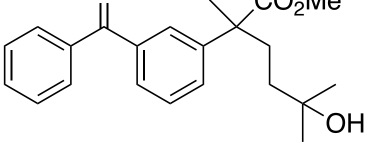
Run 1: (27.6 mg, 0.109 mmol, 36.2% yield), (35.2 mg, 0.148 mmol, 49.2% rsm). **Run 2:** (25.2 mg, 0.099 mmol, 33.0% yield), (39.3 mg, 0.165 mmol, 55.0% rsm). **Average: 34.6% yield, 52.1% rsm.**

At 10 mol% catalyst: The reaction was run with **General Method B: Single Catalyst Addition Protocol**: 1-(2-fluorophenyl)-4-methylpentyl acetate **S2** (119.2 mg, 0.500 mmol, 1.0 equiv), (*R,R*)-Mn(PDP) **3** (46.6 mg, 0.050 mmol, 10 mol%), $ClCH_2CO_2H$ (709 mg, 7.5 mmol, 15.0 equiv.), H_2O_2 (50% wt. in H_2O, 170 mg, 2.5 mmol, 5.0 equiv.), MeCN (1.0 mL in 40 mL vial, 6.25 mL with oxidant). The reaction was run at -36 ºC with 1,2-dicholoethane/ dry ice bath. The reaction was worked up with 15 mL saturated $NaHCO_3$ and DCM as described in General Method B. Flash column chromatography on silica (35 mm fritted glass column, 150 mL SiO_2) using 10% acetone/hexanes → 20% acetone/hexanes as eluent afforded product **10** as a yellow oil.

Run 1: (54.0 mg, 0.212 mmol, 42.4% yield), <10% rsm. **Run 2:** (53.5 mg, 0.210 mmol, 42.1% yield), <10% rsm. **Run 3:** (55.9 mg, 0.220 mmol, 44.0% yield), <10% rsm. **Average: 42.8% yield ± 1.0%, <10% rsm.**

^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.35 (td, *J* = 7.5, 1.7 Hz, 1H), 7.29 – 7.23 (m, 1H), 7.13 (td, *J* = 7.6, 1.1 Hz, 1H), 7.03 (ddd, *J* = 10.3, 8.2, 1.1 Hz, 1H), 6.02 (dd, *J* = 7.6, 6.1 Hz, 1H), 2.09 (s, 3H), 2.01 (tdd, *J* = 12.5, 7.7, 4.7 Hz, 1H), 1.92 (tdd, *J* = 13.2, 6.0, 4.8 Hz, 1H), 1.56 (ddd, *J* = 13.5, 12.1, 4.7 Hz, 1H), 1.40 (ddd, *J* = 13.5, 12.2, 4.7 Hz, 1H), 1.25 (br. s, 1H), 1.20 (s, 6H). ^{13}C-NMR (126 MHz, $CDCl_3$) δ 170.3, 156.0 (d, *J* = 247.1 Hz), 129.5 (d, *J* = 8.2 Hz), 128.0 (d, *J* = 13.4 Hz), 127.7 (d, *J* = 4.0 Hz), 124.4 (d, *J* = 3.6 Hz), 115.7 (d, *J* = 21.9 Hz), 70.7, 70.5 (d, *J* = 2.3 Hz), 39.2, 30.5, 29.5, 29.4, 21.3. ^{19}F NMR (471 MHz, $CDCl_3$) δ -118.01. HRMS (TOF ESI+) *m/z* calculated for $C_{14}H_{19}O_3FNa$ $[M+Na]^+$: 277.1216, found 277.1216.

methyl 2-(3-benzoylphenyl)-5-hydroxy-2,5-dimethylhexanoate [11]



At 0.1 mol% catalyst: The reaction was run with **General Method A: Low Catalyst Loading (0.1 mol%) Protocol**: methyl 2-(3-benzoylphenyl)-2,5-dimethylhexanoate **S3** (101.5 mg, 0.300 mmol, 1.0 equiv), CH_3COOH (0.24 mL, 4.2 mmol, 14.0 equiv.), (*R,R*)-Mn(PDP) catalyst **3** solution (60 µL, 5 mM solution in MeCN, 0.30 µmol, 0.001 equiv.), H_2O_2 (50% wt. in H_2O,

51.0 mg, 0.75 mmol, 2.5 equiv.), MeCN (0.6 mL in 40 mL vial, 3.75 mL with oxidant). The reaction was run at 0 ºC with an ice/water bath. The reaction was worked up with 15 mL saturated $NaHCO_3$ and DCM as described in General Method A. Flash column chromatography on silica (15 mm fritted glass column, 30 mL SiO_2) using gradient 10% acetone/hexanes → 25% acetone/hexanes as eluent afforded product **11** as a clear oil.

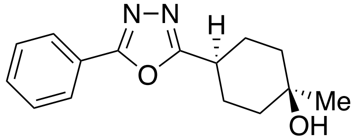
Run 1: (54.0 mg, 0.152 mmol, 50.8% yield), (32.4 mg, 0.096 mmol, 32.0% rsm). **Run 2:** (58.8 mg, 0.166 mmol, 55.3% yield), (32.1 mg, 0.095 mmol, 31.6% rsm). **Run 3:** (57.0 mg, 0.161 mmol, 53.6% yield), (36.5 mg, 0.108 mmol, 35.9% rsm). **Average: 53.2% yield ± 2.3%, 33.2% rsm ± 2.4%.**

At 10 mol% catalyst: The reaction was run with **General Method B: Single Catalyst Addition Protocol**: methyl 2-(3-benzoylphenyl)-2,5-dimethylhexanoate **S3** (101.5 mg, 0.300 mmol, 1.0 equiv), (*R,R*)-Mn(PDP) **3** (27.9 mg, 0.030 mmol, 10 mol%), $ClCH_2CO_2H$ (425 mg, 4.5 mmol, 15.0 equiv.), H_2O_2 (50% wt. in H_2O, 102 mg, 1.5 mmol, 5.0 equiv.), MeCN (0.6 mL in 40 mL vial, 3.75 mL with oxidant). The reaction was run at -36 ºC with 1,2-dichloroethane/dry ice bath. The reaction was worked up with 9 mL saturated $NaHCO_3$ and DCM as described in General Method B. Flash column chromatography on silica (35 mm fritted glass column, 150 mL SiO_2) using 20% acetone/hexanes → 30% acetone/hexanes as eluent afforded product **11** as a clear oil.

Run 1: (73.9 mg, 0.209 mmol, 69.5% yield), <10% rsm. **Run 2:** (77.2 mg, 0.218 mmol, 72.6% yield), <10% rsm. **Run 3:** (76.7 mg, 0.217 mmol, 72.2% yield), <10% rsm. **Average: 71.4% yield ± 1.7%, <10% rsm.**

^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.81 – 7.75 (m, 3H), 7.66 (dt, *J* = 7.5, 1.4 Hz, 1H), 7.61 – 7.57 (m, 1H), 7.56 – 7.53 (m, 1H), 7.51 – 7.42 (m, 3H), 3.67 (s, 3H), 2.13 (ddd, *J* = 13.4, 9.5, 7.3 Hz, 1H), 2.04 (ddd, *J* = 13.4, 9.6, 7.4 Hz, 1H), 1.59 (s, 3H), 1.42 – 1.30 (m, 3H), 1.20 (s, 6H). ^{13}C-NMR (126 MHz, $CDCl_3$) δ 196.7, 176.4, 144.1, 137.8, 137.7, 132.7, 130.4, 130.2, 128.8, 128.5, 128.4, 127.8, 70.8, 52.4, 50.3, 38.6, 34.0, 29.4, 29.3, 22.9. HRMS (TOF ESI+) *m/z* calculated for $C_{22}H_{27}O_4$ $[M+H]^+$: 335.1909, found 355.1901.

trans-1-methyl-4-(5-phenyl-1,3,4- oxadiazol-2-yl)cyclohexan-1-ol [12]



At 0.1 mol% catalyst: The reaction was run with **General Method A: Low Catalyst Loading (0.1 mol%) Protocol**: 2-(*trans*-4-methylcyclohexyl)-5-phenyl-1,3,4-oxadiazole **S4** (72.7 mg, 0.300 mmol, 1.0 equiv), CH_3COOH (0.24 mL, 4.2 mmol, 14.0 equiv.), (*R,R*)-Mn(PDP) catalyst **3** solution (60 μL, 5 mM solution in MeCN, 0.30 μmol, 0.001 equiv.), H_2O_2 (50% wt. in H_2O, 51.0 mg, 0.75 mmol, 2.5 equiv.), MeCN (0.6 mL in 40 mL vial, 3.75 mL with oxidant). The reaction was run at 0 ºC with an ice/water bath. The reaction was worked up with 15 mL saturated $NaHCO_3$ and DCM as described in General Method

A. Flash column chromatography on silica (15 mm fritted glass column, 30 mL SiO_2) using gradient 30% EtOAc/hexanes → 60% EtOAc/hexanes afforded product **12** as a white solid. Recovered starting material was recycled once.

Run 1: *Cycle 1* (16.8 mg, 0.065 mmol, 21.7% yield), (47.3 mg, 0.195 mmol, 65.0% rsm); *Cycle 2* (9.1 mg, 0.035 mmol, 18.1% yield), (28.2 mg, 0.116 mmol, 59.7% rsm); *Overall* (25.9 mg, 0.100 mmol, 33.4% yield), (28.2 mg, 0.116 mmol, 38.7% rsm). **Run 2:** *Cycle 1* (18.2 mg, 0.070 mmol, 23.5% yield), (43.1 mg, 0.178 mmol, 59.3% rsm); *Cycle 2* (11.5 mg, 0.045 mmol, 25.0% yield), (20.6 mg, 0.085 mmol, 47.8% rsm); *Overall* (29.7 mg, 0.115 mmol, 38.3% yield) (20.6 mg, 0.085 mmol, 28.3% rsm). **Average: 35.9% yield, 33.5% rsm.**

At 10 mol% catalyst: The reaction was run with **General Method B: Single Catalyst Addition Protocol**: 2-(*trans*-4-methylcyclohexyl)-5-phenyl-1,3,4-oxadiazole **S4** (72.7 mg, 0.300 mmol, 1.0 equiv), (*R,R*)-Mn(PDP) **3** (27.9 mg, 0.030 mmol, 10 mol%), $ClCH_2CO_2H$ (425.3 mg, 4.5 mmol, 15.0 equiv.), H_2O_2 (50% wt. in H_2O, 102 mg, 1.5 mmol, 5.0 equiv.), MeCN (0.6 mL in 40 mL vial, 3.75 mL with oxidant). The reaction was run at -36 ºC with 1,2-dichloroethane/dry ice bath. The reaction was worked up with 15 mL saturated $NaHCO_3$ and DCM as described in General Method B. Flash column chromatography on silica (15 mm fritted glass column, 30 mL SiO_2) using gradient 30% EtOAc/hexanes → 60% EtOAc/hexanes as eluent afforded product **12** as a white solid. Recovered starting material was recycled once.

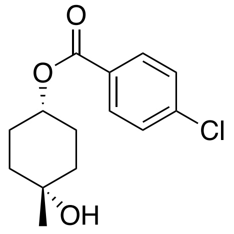
Run 1: *Cycle 1* (32.7 mg, 0.127 mmol, 42.2% yield), (37.9 mg, 0.156 mmol, 52.1% rsm); *Cycle 2* (6.6 mg, 0.026 mmol, 16.4% yield), (6.0 mg, 0.025 mmol, 16.0% rsm); *Overall* (39.3 mg, 0.152 mmol, 50.7% yield; 6.0 mg, 0.025 mmol, 8.3% rsm). **Run 2:** *Cycle 1* (29.1 mg, 0.113 mmol, 37.6% yield), (25.4 mg, 0.105 mmol, 34.9% rsm); *Cycle 2* (8.2 mg, 0.032 mmol, 30.2% yield), (6.6 mg, 0.027 mmol, 25.9% rsm); *Overall* (37.3 mg, 0.144 mmol, 48.1% yield; 6.6 mg, 0.027 mmol, 9.1% rsm). **Run 3 (0.5 mmol scale):** *Cycle 1* (48.0 mg, 0.186 mmol, 37.2% yield), (49.3 mg, 0.203 mmol, 40.7% rsm); *Cycle 2* (18.7 mg, 0.072 mmol, 35.7% yield), (12.8 mg, 0.053 mmol, 26.4% rsm); *Overall* (66.7 mg, 0.258 mmol, 51.6% yield; 12.8 mg, 0.053 mmol, 10.6% rsm). **Average: 50.1% yield ± 1.8% and 9.3% rsm ± 1.2%.**

Spectral data in agreement with those previously reported in the literature.[2]

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.08 – 7.98 (m, 2H), 7.55 – 7.44 (m, 3H), 2.93 (tt, *J* = 11.8, 3.9 Hz, 1H), 2.15 – 1.95 (m, 4H), 1.86 – 1.76 (m, 2H), 1.55 (td, *J* = 13.6, 4.3 Hz, 2H), 1.37 (br. s, 1H), 1.30 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 169.6, 164.5, 131.5, 129.0, 126.8, 124.1, 68.4, 37.8, 34.7, 31.3, 25.6.

***trans*-4-hydroxy-4-methylcyclohexyl 4-chlorobenzoate [13a]**



At 0.1 mol% catalyst: The reaction was run with **General Method A: Low Catalyst Loading (0.1 mol%) Protocol**: *trans*-4-hydroxy-4-methylcyclohexyl 4-chlorobenzoate **S5** (75.8 mg, 0.300 mmol, 1.0 equiv), CH_3COOH (0.24 mL, 4.2 mmol, 14.0 equiv.), (*R,R*)-Mn(PDP) catalyst **3** solution (60 μL, 5 mM solution in MeCN, 0.30 μmol, 0.001 equiv.), H_2O_2 (50% wt. in H_2O, 51.0 mg, 0.75 mmol, 2.5 equiv.), 4:1 MeCN:DCM (0.6 mL in 40 mL vial, 3.75 mL with oxidant). The reaction was run at 0 ºC with an ice/water bath. The reaction was worked up with 15 mL saturated $NaHCO_3$ and DCM as described in General Method A. Flash column chromatography on silica (15 mm fritted glass column, 30 mL SiO_2) using 10% EtOAc/hexanes →20% EtOAc/hexanes → 30% EtOAc/hexanes as eluent afforded (±)- *trans*-4-hydroxy-4-methylcyclohexyl 4-chlorobenzoate (δ-alcohol, **13a**) as a white solid and (±)-*trans*-4-methyl-3-oxocyclohexyl 4-chlorobenzoate (γ-ketone, **13b**) as a white solid.

Run 1: (27.1 mg, 0.101 mmol, 33.6% yield of δ-alcohol), (8.0 mg, 0.030 mmol, 10.0% yield of γ-ketone), (43.6% overall yield, 3.4:1 A:K ratio), (29.5 mg, 0.117 mmol, 38.9% rsm). **Run 2:** (26.6 mg, 0.099 mmol, 33.0% yield of δ-alcohol), (8.8 mg, 0.033 mmol, 11.0% yield of γ-ketone), (44.0% overall yield, 3.0:1 A:K ratio), (30.3 mg, 0.120 mmol, 40.0% rsm). **Average: 33.3% yield of δ- alcohol, 10.5% yield of γ-ketone, 43.8% overall yield with 3.2:1 A:K ratio, 39.5% rsm.**

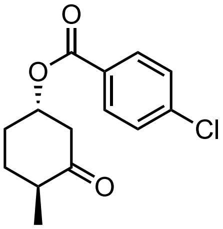
At 10 mol% catalyst: The reaction was run with **General Method C: Slow Catalyst Addition Protocol**: *trans*-4-hydroxy-4-methylcyclohexyl 4-chlorobenzoate **S5** (75.8 mg, 0.300 mmol, 1.0 equiv), (*R,R*)-Mn(PDP) **3** (27.9 mg, 0.030 mmol, 10 mol%), $ClCH_2CO_2H$ (425 mg, 4.5 mmol, 15.0 equiv.), H_2O_2 (50% wt. in H_2O, 102 mg, 1.5 mmol, 5.0 equiv.), 4:1 MeCN:DCM (0.6 mL in 40 mL vial, 3.75 mL with oxidant, 0.38 mL MeCN with catalyst). The reaction was run at -36 ºC with 1,2-dichloroethane/dry ice bath. The reaction was worked up with 9 mL saturated $NaHCO_3$ and DCM as described in General Method C. Flash column chromatography on silica (15 mm fritted glass column, 30 mL SiO_2) using 10% EtOAc/hexanes →20% EtOAc/hexanes → 30% EtOAc/hexanes as eluent afforded (±)- *trans*-4-hydroxy-4-methylcyclohexyl 4-chlorobenzoate (δ-alcohol, **13a**) as a white solid and (±)-*trans*-4-methyl-3-oxocyclohexyl 4-chlorobenzoate (γ-ketone, **13b**) as a white solid.

Run 1: (38.5 mg, 0.143 mmol, 47.8% yield of δ-alcohol), (11.3 mg, 0.042 mmol, 14.1% yield of γ-ketone), (61.9% overall yield, 3.4:1 A:K ratio), (23.0 mg, 0.091 mmol, 30.3% rsm). **Run 2:** (35.3 mg, 0.131 mmol, 43.8% yield of δ-alcohol), (10.6 mg, 0.040 mmol, 13.2% yield of γ-ketone), (57.0% overall yield, 3.4:1 A:K ratio), (18.0 mg, 0.071 mmol, 23.7% rsm). **Run 3:** (34.8 mg, 0.129 mmol, 43.2% yield of δ-alcohol), (9.8 mg, 0.037 mmol, 12.2% yield of γ-ketone), (55.4% overall yield, 3.5:1 A:K ratio), (23.5 mg, 0.093 mmol, 31.0% rsm). **Average: 44.9% yield ± 2.5% of δ- alcohol, 13.2% yield ± 1.0% of γ-ketone, 58.1% overall yield with 3.4:1 A:K ratio, 28.3% rsm ± 4.0%.**

Spectral data in agreement with those previously reported in the literature.[3]

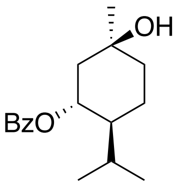
^{1}H NMR (500 MHz, CDCl$_3$) δ 7.97 (d, *J* = 8.5 Hz, 2H), 7.40 (d, *J* = 8.5 Hz, 2H), 4.97 (tt, *J* = 9.4, 4.7 Hz, 1H), 1.97 – 1.82 (m, 4H), 1.81 – 1.72 (m, 2H), 1.57 (ddd, *J* = 13.7, 11.4, 4.7 Hz, 2H), 1.28 (s, 3H). ^{13}C NMR (126 MHz, CDCl$_3$) δ 165.3, 139.3, 131.1, 129.3, 128.8, 73.0, 68.8, 36.7, 30.1, 27.4.

***trans*-4-methyl-3-oxocyclohexyl 4-chlorobenzoate [13b]**



^{1}H NMR (500 MHz, CDCl$_3$) δ 7.96 (d, *J* = 8.6 Hz, 2H), 7.42 (d, *J* = 8.5 Hz, 2H), 5.21 (tt, *J* = 10.2, 4.7 Hz, 1H), 2.92 (ddd, *J* = 13.6, 5.0, 2.0 Hz, 1H), 2.57 (ddd, *J* = 13.6, 10.7, 1.3 Hz, 1H), 2.46 – 2.30 (m, 2H), 2.18 – 2.09 (m, 1H), 1.91 (tdd, *J* = 12.7, 10.2, 4.0 Hz, 1H), 1.42 (dtd, *J* = 13.8, 12.0, 3.6 Hz, 1H), 1.10 (d, *J* = 6.6 Hz, 3H). ^{13}C NMR (126 MHz, CDCl$_3$) δ 208.9, 164.7, 139.7, 131.2, 128.9, 128.6, 72.6, 47.0, 44.4, 30.4, 29.2, 14.5.

(1*R*,2*S*,5*S*)-5-hydroxy-2-isopropyl-5-methylcyclohexyl benzoate [14]



At 0.1 mol% catalyst: The reaction was run with **General Method A: Low Catalyst Loading (0.1 mol%) Protocol**: (1*R*,2*S*,5*R*)-2-isopropyl-5-methylcyclohexyl benzoate **S6** (78.1 mg, 0.300 mmol, 1.0 equiv), CH$_3$COOH (0.24 mL, 4.2 mmol, 14.0 equiv.), (*S,S*)-Mn(PDP) catalyst **3** solution (60 µL, 5 mM solution in MeCN, 0.30 µmol, 0.001 equiv.), H$_2$O$_2$ (50% wt. in H$_2$O, 51.0 mg, 0.75 mmol, 2.5 equiv.), MeCN (0.6 mL in 40 mL vial, 3.75 mL with oxidant). The reaction was run at 0 ºC with an ice/water bath. The reaction was worked up with 15 mL saturated NaHCO$_3$ and DCM as described in General Method A. Flash column chromatography on silica (15 mm fritted glass column, 30 mL SiO$_2$) using gradient 100% hexanes → 20% EtOAc/hexanes as eluent afforded (1*R*,2*S*,5*S*)-5-hydroxy-2-isopropyl-5-methylcyclohexyl benzoate (alcohol, **14a**) as a white solid and (1*R*,2*S*,5*S*)-2-isopropyl-5-methyl-4-oxocyclohexyl benzoate (ketone, **14b**) as a white solid.

Run 1: (45.2 mg, 0.164 mmol, 54.5% yield), trace ketone, (13.6 mg, 0.052 mmol, 17.4% rsm). **Run 2:** (44.3 mg, 0.160 mmol, 53.4% yield), trace ketone, (12.4 mg, 0.048 mmol, 15.9% rsm). **Average: 54.0% yield, 16.7% rsm.**

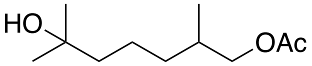
At 10 mol% catalyst: The reaction was run with **General Method B: Single Catalyst Addition Protocol**: (1*R*,2*S*,5*R*)-2-isopropyl-5-methylcyclohexyl benzoate **S6** (78.1 mg, 0.300 mmol, 1.0 equiv), (*S,S*)-Mn(PDP) **3** (27.9 mg, 0.030 mmol, 10 mol%), ClCH$_2$CO$_2$H (425.3 mg, 4.5 mmol, 15.0 equiv.), H$_2$O$_2$ (50% wt. in H$_2$O, 102 mg, 1.5 mmol, 5.0 equiv.), MeCN (0.6 mL in 40 mL vial, 3.75 mL with oxidant). The reaction was run at -36 ºC with 1,2-dichloroethane/dry ice bath. The reaction was worked up with 15 mL saturated NaHCO$_3$ and DCM as described in General Method B. Flash column chromatography on silica

(15 mm fritted glass column, 30 mL SiO_2) using gradient 100% hexanes → 20% EtOAc/hexanes as eluent afforded (1*R*,2*S*,5*S*)-5-hydroxy-2-isopropyl-5-methylcyclohexyl benzoate (alcohol, **14a**) as a white solid and (1*R*,2*S*,5*S*)-2-isopropyl-5-methyl-4-oxocyclohexyl benzoate (ketone, **14b**) as a white solid.

Run 1: (45.6 mg, 0.165 mmol, 55.0% yield), <5% ketone, (9.5 mg, 0.036 mmol, 12.2% rsm). **Run 2:** (48.4 mg, 0.175 mmol, 58.4% yield), <5% ketone, (12.6 mg, 0.048 mmol, 16.1% rsm). **Run 3:** (48.0 mg, 0.174 mmol, 57.9% yield), <5% ketone, (10.0 mg, 0.038 mmol, 12.8% rsm). **Average: 57.1% yield ± 1.8%, <5% ketone, ca. 11:1 A:K ratio, 13.7% rsm ± 2.1%.**

^{1}H-NMR (500 MHz, $CDCl_3$) δ 8.04 (d, *J* = 7.2 Hz, 2H), 7.58 – 7.51 (m, 1H), 7.43 (t, *J* = 7.8 Hz, 2H), 5.27 (td, *J* = 10.4, 4.6 Hz, 1H), 2.21 (ddd, *J* = 13.0, 4.5, 2.7 Hz, 1H), 2.08 – 2.04 (br s, 1H), 2.00 (pd, *J* = 7.0, 2.0 Hz, 1H), 1.75 (dq, *J* = 13.8, 2.9 Hz, 1H), 1.65 – 1.54 (m, 3H), 1.50 (dd, *J* = 12.9, 11.0 Hz, 1H), 1.42 – 1.32 (m, 1H), 1.28 (s, 3H), 0.95 (d, *J* = 7.1 Hz, 3H), 0.84 (d, *J* = 7.0 Hz, 3H). ^{13}C-NMR (126 MHz, $CDCl_3$) δ 166.2, 132.9, 130.8, 129.7, 128.4, 72.8, 71.2, 47.3, 44.8, 38.0, 31.5, 26.6, 20.9, 19.6, 16.8. $[\alpha]_D^{24}$ = –59.4 (c = 1.00, EtOH). HRMS (TOF ESI+) *m/z* calculated for $C_{17}H_{25}O_3$ $[M+H]^+$: 277.1804, found 277.1797.

6-hydroxy-2,6-dimethylheptyl acetate [15]



At 0.1 mol% catalyst: The reaction was run with **General Method A: Low Catalyst Loading (0.1 mol%) Protocol**: 2,6-dimethylheptyl acetate **S7** (55.9 mg, 0.300 mmol, 1.0 equiv), CH_3COOH (0.24 mL, 4.2 mmol, 14.0 equiv.), (*R,R*)-Mn(PDP) catalyst **3** solution (60 μL, 5 mM solution in MeCN, 0.30 μmol, 0.001 equiv.), H_2O_2 (50% wt. in H_2O, 51.0 mg, 0.75 mmol, 2.5 equiv.), MeCN (0.6 mL in 40 mL vial, 3.75 mL with oxidant). The reaction was run at 0 ºC with an ice/water bath. The reaction was worked up with 15 mL saturated $NaHCO_3$ and DCM as described in General Method A. Flash column chromatography on silica (15 mm fritted glass column, 30 mL SiO_2) using 25% ether/pentanes as eluent afforded 6-hydroxy-2,6-dimethylheptyl acetate **15** as a colorless oil.

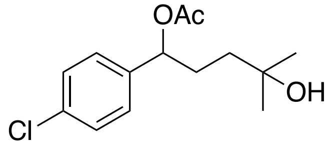
Run 1: (31.8 mg, 0.157 mmol, 52.4% yield), (13.7 mg, 0.074 mmol, 24.5% rsm). **Run 2:** (30.6 mg, 0.151 mmol, 50.4% yield), (7.8 mg, 0.042 mmol, 14.0% rsm). **Average: 51.4% yield, 19.3% rsm.**

At 10 mol% catalyst: The reaction was run with **General Method B: Single Catalyst Addition Protocol**: 2,6-dimethylheptyl acetate **S7** (55.9 mg, 0.300 mmol, 1.0 equiv), (*R,R*)-Mn(PDP) **3** (27.9 mg, 0.030 mmol, 10 mol%), $ClCH_2CO_2H$ (425 mg, 4.5 mmol, 15.0 equiv.), H_2O_2 (50% wt. in H_2O, 102 mg, 1.5 mmol, 5.0 equiv.), MeCN (0.6 mL in 40 mL vial, 3.75 mL with oxidant). The reaction was run at -36 ºC with 1,2-dichloroethane/dry ice bath. The reaction was worked up with 9 mL saturated $NaHCO_3$ and DCM as described in General Method B. Flash column chromatography on silica (35 mm fritted glass column, 150 mL SiO_2) using 25% ether/pentanes as eluent afforded 6-hydroxy-2,6-dimethylheptyl acetate **15** as a colorless oil.

Run 1: (36.9 mg, 0.182 mmol, 60.8% yield), 0% rsm. **Run 2:** (35.9 mg, 0.177 mmol, 59.2% yield), <10% rsm. **Run 3:** (40.1 mg, 0.198 mmol, 66.1% yield), 0% rsm. **Average: 62.0% yield ± 3.6%, 0% rsm.** Spectral data in agreement with those previously reported in the literature.[1]

^{1}H NMR (500 MHz, $CDCl_3$) δ 3.94 (dd, *J* = 10.7, 6.0 Hz, 1H), 3.84 (dd, *J* = 10.7, 6.8 Hz, 1H), 2.04 (s, 3H), 1.78 (dq, *J* = 12.9, 6.1 Hz, 1H), 1.48 – 1.26 (m, 7H), 1.20 (s, 6H), 0.92 (d, *J* = 6.7 Hz, 3H).

1-(4-chlorophenyl)-4-hydroxy-4-methylpentyl acetate [6]



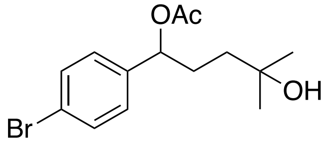
At 10 mol% catalyst: The reaction was run with **General Method B: Single Catalyst Addition Protocol**. 1-(4-chlorophenyl)-4-methylpentyl acetate **5** (127.4 mg, 0.500 mmol, 1.0 equiv), (*R,R*)-Mn(PDP) **3** (46.6 mg, 0.050 mmol, 10 mol%), $ClCH_2CO_2H$ (709 mg, 7.5 mmol, 15.0 equiv.), H_2O_2 (50% wt. in H_2O, 170 mg, 2.5 mmol, 5.0 equiv.), MeCN (1.0 mL in 40 mL vial, 6.25 mL with oxidant). The reaction was run at -36 ºC with a 1,2-dichloroethane/dry ice bath. The reaction was worked up with 15 mL saturated $NaHCO_3$ and DCM as described in the General Method B. Flash column chromatography on silica (35 mm fritted glass column, 150 mm SiO_2) using 10% acetone/hexanes → 20% acetone/hexanes → 30% acetone/hexanes as eluent afforded product **6** as a colorless oil.

Run 1: (96.7 mg, 0.357 mmol, 71.4% yield), (13.8 mg, 0.054 mmol, 10.8% rsm). **Run 2:** (94.0 mg, 0.347 mmol, 69.4% yield), (20.0 mg, 0.079 mmol, 15.7% rsm). **Run 3:** (90.5 mg, 0.334 mmol, 66.9% yield), (26.5 mg, 0.104 mmol, 20.8% rsm). **Average: 69.2% yield ± 2.3%, 15.8% rsm ± 5.0%.**

At 5 mol% catalyst: The reaction was run with **General Method B: Single Catalyst Addition Protocol**. 1-(4-chlorophenyl)-4-methylpentyl acetate **5** (76.4 mg, 0.300 mmol, 1.0 equiv), (*R,R*)-Mn(PDP) **3** (14.0 mg, 0.015 mmol, 5 mol%), $ClCH_2CO_2H$ (425 mg, 4.5 mmol, 15.0 equiv.), H_2O_2 (50% wt. in H_2O, 102 mg, 1.5 mmol, 5.0 equiv.), MeCN (0.6 mL in 40 mL vial, 3.75 mL with oxidant). The reaction was run at -36 ºC with a 1,2-dichloroethane/dry ice bath. The reaction was worked up with 15 mL saturated $NaHCO_3$ and DCM as described in the General Method B. Flash column chromatography on silica (35 mm fritted glass column, 150 mm SiO_2) using 10% acetone/hexanes → 20% acetone/hexanes → 30% acetone/hexanes as eluent afforded product **6** as a colorless oil.

Run 1: (54.0 mg, 0.199 mmol, 66.5% yield), <5% rsm. **Run 2:** (52.0 mg, 0.192 mmol, 64.0% yield), <5% rsm. **Average: 65.3% yield, <5% rsm.**

1-(4-bromophenyl)-4-hydroxy-4-methylpentyl acetate [16]

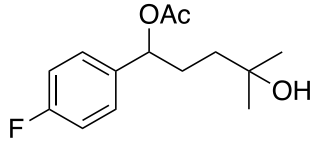


The reaction was run with **General Method B: Single Catalyst Addition Protocol**. 1-(4-bromophenyl)-4-methylpentyl acetate **S8** (89.8 mg, 0.300 mmol, 1.0 equiv), (*R,R*)-Mn(PDP) **3** (27.9 mg, 0.030 mmol, 10 mol%), $ClCH_2CO_2H$ (425 mg, 4.5 mmol, 15.0 equiv.), H_2O_2 (50% wt. in H_2O, 102 mg, 1.5 mmol, 5.0 equiv.), MeCN (0.6 mL in 40 mL vial, 3.75 mL with oxidant). The reaction was run at -36 ºC with 1,2-dichloroethane/dry ice bath. The reaction was worked up with 9 mL saturated $NaHCO_3$ and DCM as described in the General Method B. Flash column chromatography on silica (35 mm fritted glass column, 150 mm SiO_2) using 10% acetone/hexanes → 20% acetone/hexanes as eluent afforded product **16** as a colorless oil.

Run 1: (62.3 mg, 0.198 mmol, 65.9% yield), (15.8 mg, 0.053 mmol, 17.6% rsm). **Run 2:** (63.7 mg, 0.202 mmol, 67.4% yield), (11.7 mg, 0.039 mmol, 13.0% rsm). **Run 3:** (64.0 mg, 0.203 mmol, 67.7% yield), (12.9 mg, 0.043 mmol, 14.3% rsm). **Average: 67.0% yield ± 1.0%, 15.0% rsm ± 2.4%.**

^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.46 (d, *J* = 8.4 Hz, 2H), 7.20 (d, *J* = 8.4 Hz, 2H), 5.66 (dd, *J* = 7.6, 6.3 Hz, 1H), 2.06 (s, 3H), 2.00 – 1.92 (m, 1H), 1.84 (dddd, *J* = 13.6, 12.3, 6.2, 4.6 Hz, 1H), 1.50 (ddd, *J* = 13.6, 12.1, 4.6 Hz, 1H), 1.33 (ddd, *J* = 13.6, 12.2, 4.5 Hz, 1H), 1.18 (s, 6H). ^{13}C-NMR (126 MHz, $CDCl_3$) δ 170.4, 139.7, 131.7, 128.4, 121.9, 75.8, 70.6, 39.3, 31.1, 29.5, 29.4, 21.3. HRMS (ESI+) *m/z* calculated for $C_{14}H_{19}O_3NaBr$ $[M+Na]^+$: 337.0415, found 337.0402.

1-(4-fluorophenyl)-4-hydroxy-4-methylpentyl acetate [17]

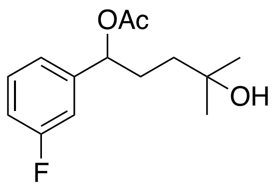


The reaction was run with **General Method B: Single Catalyst Addition Protocol**. 1-(4-fluorophenyl)-4-methylpentyl acetate **S9** (119.2 mg, 0.500 mmol, 1.0 equiv), (*R,R*)-Mn(PDP) **3** (46.6 mg, 0.050 mmol, 10 mol%), $ClCH_2CO_2H$ (709 mg, 7.5 mmol, 15.0 equiv.), H_2O_2 (50% wt. in H_2O, 140 mg, 2.5 mmol, 5.0 equiv.), MeCN (1.0 mL in 40 mL vial, 6.25 mL with oxidant). The reaction was run at -36 ºC with 1,2-dichloroethane/dry ice bath. The reaction was worked up with 15 mL saturated $NaHCO_3$ and DCM as described in the General Method B. Flash column chromatography on silica (35 mm fritted glass column, 150 mL SiO_2) using 10% acetone/hexanes → 20% acetone/hexanes as eluent afforded product **17** as a colorless oil.

Run 1: (84.3 mg, 0.331 mmol, 66.3% yield), (11.7 mg, 0.049 mmol, 9.8% rsm). **Run 2:** (84.6 mg, 0.333 mmol, 66.5% yield), (14.4 mg, 0.060 mmol, 12.1% rsm). **Run 3:** (81.8 mg, 0.322 mmol, 64.3% yield), (18.0 mg, 0.076 mmol, 15.1% rsm). **Average: 65.7 % yield ± 1.2%, 12.3% rsm ± 2.7%.**

^{1}H-NMR (500 MHz, $CDCl_3$) 7.33 – 7.28 (m, 2H), 7.05 – 7.00 (m, 2H), 5.69 (dd, *J* = 7.6, 6.3 Hz, 1H), 2.06 (s, 3H), 1.98 (dddd, *J* = 13.3, 12.2, 7.6, 4.6 Hz, 1H), 1.85 (dddd, *J* = 13.4, 12.1, 6.3, 4.6 Hz, 1H), 1.51 (ddd, *J* = 13.4, 12.2, 4.6 Hz, 1H), 1.37 (br. s, 1H), 1.36 – 1.29 (m, 1H), 1.19 (s, 6H). ^{13}C-NMR (126 MHz, $CDCl_3$) δ 170.5, 162.5 (d, *J* = 246.2 Hz), 136.5 (d, *J* = 3.2 Hz), 128.5 (d, *J* = 8.0 Hz), 115.5 (d, *J* = 21.4 Hz), 75.8, 70.6, 39.4, 31.3, 29.5, 29.4, 21.4. ^{19}F-NMR (470 MHz, $CDCl_3$) δ -114.72. HRMS (ESI+) *m/z* calculated for $C_{14}H_{19}O_3NaF$ $[M+Na]^+$: 277.1216, found 277.1219.

1-(3-fluorophenyl)-4-hydroxy-4-methylpentyl acetate [18]

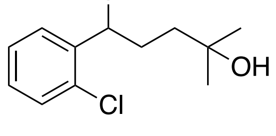


The reaction was run with **General Method B: Single Catalyst Addition Protocol**. 1-(3-fluorophenyl)-4-methylpentyl acetate **S10** (119.2 mg, 0.500 mmol, 1.0 equiv), (*R,R*)-Mn(PDP) **3** (46.6 mg, 0.050 mmol, 10 mol%), $ClCH_2CO_2H$ (709 mg, 7.5 mmol, 15.0 equiv.), H_2O_2 (50% wt. in H_2O, 140 mg, 2.5 mmol, 5.0 equiv.), MeCN (1.0 mL in 40 mL vial, 6.25 mL with oxidant). The reaction was run at -36 ºC with 1,2-dichloroethane/dry ice bath. The reaction was worked up with 15 mL saturated $NaHCO_3$ and DCM as described in the General Method B. Flash column chromatography on silica (35 mm fritted glass column, 150 mm SiO_2) using 10% acetone/hexanes → 20% acetone/hexanes as eluent afforded product **18** as a colorless oil.

Run 1: (71.2 mg, 0.280 mmol, 56.0% yield), (16.5 mg, 0.069 mmol, 13.8% rsm). **Run 2:** (72.4 mg, 0.285 mmol, 56.9% yield), (14.8 mg, 0.062 mmol, 12.4% rsm). **Run 3:** (70.4 mg, 0.277 mmol, 55.4% yield), (16.7 mg, 0.070 mmol, 14.0% rsm). **Average: 56.1% yield ± 0.8%, 13.4% rsm ± 0.9%.**

^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.35 (td, *J* = 7.5, 1.8 Hz, 1H), 7.29 – 7.22 (m, 1H), 7.13 (td, *J* = 7.5, 1.2 Hz, 1H), 7.03 (ddd, *J* = 10.5, 8.1, 1.2 Hz, 1H), 6.02 (dd, *J* = 7.6, 6.1 Hz, 1H), 2.09 (s, 3H), 2.04 – 1.87 (m, 2H), 1.55 (ddd, *J* = 13.4, 12.1, 4.7 Hz, 1H), 1.40 (ddd, *J* = 13.5, 12.2, 4.7 Hz, 1H), 1.40 (br. s, 1H), 1.19 (s, 6H). ^{13}C-NMR (126 MHz, $CDCl_3$) δ 170.3, 159.9 (d, *J* = 247.2 Hz), 129.5 (d, *J* = 8.3 Hz), 128.0 (d, *J* = 13.6 Hz), 127.7 (d, *J* = 4.1 Hz), 124.3 (d, *J* = 3.6 Hz), 115.7 (d, *J* = 21.7 Hz), 70.6, 70.5 (d, *J* = 2.3 Hz), 39.2, 30.4, 29.4, 29.4, 21.3. ^{19}F-NMR (470 MHz, $CDCl_3$) δ -118.48. HRMS (ESI) *m/z* calculated for $C_{14}H_{19}O_3NaF$ $[M+Na]^+$: 277.1216, found 277.1208.

1-(2-chlorophenyl)-4-hydroxy-4-methylpentyl acetate [19]



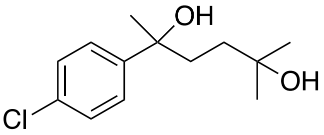
The reaction was run with **General Method B: Single Catalyst Addition Protocol**. 1-(2-chlorophenyl)-4-methylpentyl acetate **S11** (127.4 mg, 0.500 mmol, 1.0 equiv), (*R,R*)-Mn(PDP) **3** (46.6 mg, 0.050 mmol, 10 mol%), $ClCH_2CO_2H$ (709 mg, 7.5 mmol, 15.0 equiv.), H_2O_2 (50% wt. in H_2O, 170 mg, 2.5 mmol, 5.0 equiv.), MeCN (1.0 mL in 40 mL vial, 6.25 mL with oxidant). The reaction was run at -36 ºC with 1,2-dichloroethane/dry ice bath. The reaction was worked up with 15 mL saturated $NaHCO_3$ and DCM as described in the General Method B. Flash column chromatography on silica (35 mm fritted glass column, 150 mm SiO_2) using 10%

acetone/hexanes → 20% acetone/hexanes → 30% acetone/hexanes as eluent afforded product **19** as a colorless oil.

Run 1: (74.8 mg, 0.276 mmol, 55.2% yield), (29.1 mg, 0.114 mmol, 22.8% rsm). **Run 2:** (75.6 mg, 0.279 mmol, 55.8% yield), (23.3 mg, 0.091 mmol, 18.3% rsm). **Run 3:** (77.0 mg, 0.284 mmol, 56.9% yield), (21.8 mg, 0.086 mmol, 17.1% rsm). **Average: 56.0% yield ± 0.9%, 19.4% rsm ± 3.0%.**

^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.38 (d, *J* = 1.7 Hz, 1H), 7.33 (d, *J* = 7.9 Hz, 1H), 7.27 – 7.23 (m, 1H), 7.22 – 7.18 (m, 1H), 6.12 (t, *J* = 6.6 Hz, 1H), 2.09 (s, 3H), 1.96 – 1.88 (m, 2H), 1.58 (ddd, *J* = 13.5, 10.3, 6.5 Hz, 1H), 1.51 – 1.42 (m, 2H), 1.19 (s, 6H). ^{13}C-NMR (126 MHz, $CDCl_3$) 170.2, 138.7, 132.3, 129.7, 128.9, 127.1, 127.0, 72.9, 70.6, 39.2, 30.4, 29.4, 29.3, 21.2. HRMS (ESI+) *m/z* calculated for $C_{14}H_{19}O_3NaCl$ $[M+Na]^+$: 293.0920, found 293.0913.

2-(4-chlorophenyl)-5-methylhexane-2,5-diol [20]

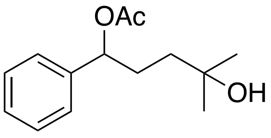


The reaction was run with **General Method B: Single Catalyst Addition Protocol**. 2-(4-chlorophenyl)-5-methylhexan-2-ol **S12** (113.4 mg, 0.500 mmol, 1.0 equiv), (*R,R*)-Mn(PDP) **3** (46.6 mg, 0.050 mmol, 10 mol%), $ClCH_2CO_2H$ (709 mg, 7.5 mmol, 15.0 equiv.), H_2O_2 (50% wt. in H_2O, 170 mg, 2.5 mmol, 5.0 equiv.), MeCN (1.0 mL in 40 mL vial, 6.25 mL with oxidant). The reaction was run at -36 ºC with 1,2-dichloroethane/dry ice bath. The reaction was worked up with 15 mL saturated $NaHCO_3$ and DCM as described in the General Method B. Flash column chromatography on silica (35 mm fritted glass column, 150 mm SiO_2) using 20% acetone/hexanes → 30% acetone/hexanes as eluent afforded product **20** as a slightly pink oil.

Run 1: (85.0 mg, 0.350 mmol, 70.0% yield), <10% rsm. **Run 2:** (84.3 mg, 0.347 mmol, 69.5% yield), <10% rsm. **Run 3:** (80.4 mg, 0.331 mmol, 66.3% yield), < 10% rsm. **Average: 68.6% yield ± 2.0%, <10% rsm.**

^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.38 – 7.35 (m, 2H), 7.31 – 7.28 (m, 2H), 2.07 (br. s, 2H), 1.99 – 1.87 (m, 2H), 1.54 (s, 3H), 1.47 – 1.40 (m, 1H), 1.36 – 1.29 (m, 1H), 1.20 (s, 3H), 1.17 (s, 3H). ^{13}C-NMR (126 MHz, $CDCl_3$) δ 146.7, 132.3, 128.4, 126.6, 74.2, 70.9, 38.4, 37.6, 31.1, 30.1, 29.2. HRMS (ESI+) *m/z* calculated for $C_{13}H_{19}O_2NaCl$ $[M+Na]^+$: 265.0971, found 265.0974.

4-hydroxy-4-methyl-1-phenylpentyl acetate [21]

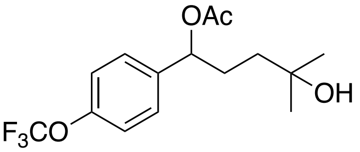


The reaction was run with **General Method B: Single Catalyst Addition Protocol**. 4-methyl-1-phenylpentyl acetate **S13** (110.2 mg, 0.500 mmol, 1.0 equiv), (*R,R*)-Mn(PDP) **3** (46.6 mg, 0.050 mmol, 10 mol%), $ClCH_2CO_2H$ (709 mg, 7.5 mmol, 15.0 equiv.), H_2O_2 (50% wt. in H_2O, 170 mg, 2.5 mmol, 5.0 equiv.), MeCN (1.0 mL in 40 mL vial, 6.25 mL with oxidant). The reaction was run at -36 ºC with 1,2-dichloroethane/dry ice bath. The reaction was worked up with 15 mL saturated $NaHCO_3$ and DCM as described in the General Method B. Flash column chromatography on silica (35 mm fritted glass column, 150 mL SiO_2) using 10% acetone/hexanes → 20% acetone/hexanes as eluent afforded product **21** as a slightly yellow oil.

Run 1: (40.7 mg, 0.172 mmol, 34.4% yield), <5% rsm. **Run 2:** (41.3 mg, 0.175 mmol, 35.0% yield), <5% rsm. **Run 3:** (41.8 mg, 0.177 mmol, 35.4% yield), <5% rsm. **Average: 34.9% yield ± 0.5%, <5% rsm.**

^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.36 – 7.27 (m, 5H), 5.73 (dd, *J* = 7.7, 6.2 Hz, 1H), 2.07 (s, 3H), 2.00 (dddd, *J* = 13.5, 12.2, 7.7, 4.6 Hz, 1H), 1.88 (dddd, *J* = 13.5, 12.1, 6.2, 4.6 Hz, 1H), 1.53 (ddd, *J* = 13.6, 12.1, 4.7 Hz, 1H), 1.37 (ddd, *J* = 13.6, 12.2, 4.6 Hz, 1H), 1.31 (br. s, 1H), 1.19 (s, 6H). ^{13}C-NMR (126 MHz, $CDCl_3$) δ 170.5, 140.7, 128.6, 128.0, 126.6, 76.5, 70.6, 39.4, 31.3, 29.4, 29.4, 21.4. HRMS (ESI+) *m/z* calculated for $C_{14}H_{20}O_3Na$ $[M+Na]^+$: 259.1310, found 259.1305.

4-hydroxy-4-methyl-1-(4-(trifluoromethoxy)phenyl)pentyl acetate [22]

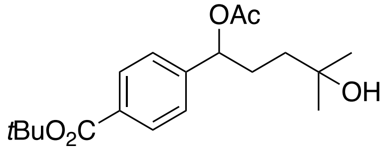


The reaction was run with **General Method B: Single Catalyst Addition Protocol**. 4-methyl-1-(4-(trifluoromethoxy)phenyl)pentyl acetate **S14** (91.3 mg, 0.300 mmol, 1.0 equiv), (*R,R*)-Mn(PDP) **3** (27.9 mg, 0.030 mmol, 10 mol%), $ClCH_2CO_2H$ (425 mg, 4.5 mmol, 15.0 equiv.), H_2O_2 (50% wt. in H_2O, 102 mg, 1.5 mmol, 5.0 equiv.), MeCN (0.6 mL in 40 mL vial, 3.75 mL with oxidant). The reaction was run at -36 ºC with 1,2-dichloroethane/dry ice bath. The reaction was worked up with 9 mL saturated $NaHCO_3$ and DCM as described in the General Method B. Flash column chromatography on silica (35 mm fritted glass column, 150 mm SiO_2) using 10% acetone/hexanes → 20% acetone/hexanes as eluent afforded product **22** as a colorless oil.

Run 1: (67.9 mg, 0.212 mmol, 70.7% yield), (13.7 mg, 0.045 mmol, 15.0% rsm). **Run 2:** (72.4 mg, 0.226 mmol, 75.3% yield), (11.5 mg, 0.038 mmol, 12.6% rsm). **Run 3:** (69.6 mg, 0.217 mmol, 72.4% yield), (15.7 mg, 0.052 mmol, 17.2% rsm). **Average: 72.8% yield ± 2.3%, 14.9% rsm ± 2.3%.**

^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.36 (d, *J* = 8.6 Hz, 2H), 7.18 (d, *J* = 7.9 Hz, 2H), 5.72 (dd, *J* = 7.8, 6.1 Hz, 1H), 2.07 (s, 3H), 1.98 (tdd, *J* = 12.5, 7.8, 4.6 Hz, 1H), 1.86 (tdd, *J* = 13.3, 6.0, 4.6 Hz, 1H), 1.52 (td, *J* = 12.8, 4.6 Hz, 1H), 1.39 – 1.33 (m, 1H), 1.33 (br. s, 1H), 1.20 (s, 6H). ^{13}C-NMR (126 MHz, $CDCl_3$) δ 170.4, 148.9 (q, *J* = 2.0 Hz), 139.4, 128.1, 121.1, 120.6 (q, *J* = 257.3 Hz), 75.6, 70.6, 39.3, 31.3, 29.5, 29.4, 21.3. ^{19}F-NMR (470 MHz, $CDCl_3$) δ -58.24. HRMS (ESI+) *m/z* calculated for $C_{15}H_{19}O_4F_3Na$ $[M+Na]^+$: 343.1133, found 343.1131.

tert-butyl 4-(1-acetoxy-4-hydroxy-4-methylpentyl)benzoate [23]

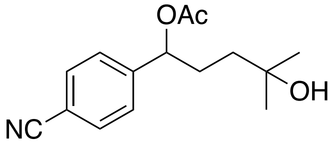


The reaction was run with **General Method B: Single Catalyst Addition Protocol**. *tert*-butyl 4-(1-acetoxy-4-methylpentyl)benzoate **S15** (96.1 mg, 0.300 mmol, 1.0 equiv), (*R,R*)-Mn(PDP) **3** (27.9 mg, 0.030 mmol, 10 mol%), $ClCH_2CO_2H$ (425 mg, 4.5 mmol, 15.0 equiv.), H_2O_2 (50% wt. in H_2O, 102 mg, 1.5 mmol, 5.0 equiv.), MeCN (0.6 mL in 40 mL vial, 3.75 mL with oxidant). The reaction was run at -36 ºC with 1,2-dichloroethane/dry ice bath. The reaction was worked up with 9 mL saturated $NaHCO_3$ and DCM as described in the General Method B. Flash column chromatography on silica (35 mm fritted glass column, 150 mm SiO_2) using 10% acetone/hexanes → 20% acetone/hexanes as eluent afforded product **23** as a colorless oil.

Run 1: (71.0 mg, 0.211 mmol, 70.3% yield), (18.4 mg, 0.057 mmol, 19.1% rsm). **Run 2:** (74.6 mg, 0.222 mmol, 73.9% yield), (13.4 mg, 0.042 mmol, 14.0% rsm). **Run 3:** (74.1 mg, 0.220 mmol, 73.4% yield), (15.2 mg, 0.047 mmol, 15.8% rsm). **Average: 72.5% yield ± 2.0%, 16.3% rsm ± 2.6%.**

^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.96 (d, *J* = 8.0 Hz, 2H), 7.36 (d, *J* = 8.1 Hz, 2H), 5.74 (t, *J* = 6.8 Hz, 1H), 2.08 (s, 3H), 2.02 – 1.94 (m, 1H), 1.92 – 1.84 (m, 1H), 1.58 (s, 9H), 1.54 – 1.47 (m, 1H), 1.39 (br. s, 1H), 1.38 – 1.32 (m, 1H), 1.18 (s, 6H). ^{13}C-NMR (126 MHz, $CDCl_3$) δ 170.4, 165.6, 145.2, 131.7, 129.8, 126.3, 81.2, 76.0, 70.6, 39.2, 31.2, 29.5, 29.4, 28.3, 21.3. HRMS (ESI+) *m/z* calculated for $C_{19}H_{28}O_5Na$ $[M+Na]^+$: 359.1834, found 359.1826.

1-(4-cyanophenyl)-4-hydroxy-4-methylpentyl acetate [24]



The reaction was run with **General Method B: Single Catalyst Addition Protocol**. 1-(4-cyanophenyl)-4-methylpentyl acetate **S16** (122.7 mg, 0.500 mmol, 1.0 equiv), (*R,R*)-Mn(PDP) **3** (46.6 mg, 0.050 mmol, 10 mol%), $ClCH_2CO_2H$ (709 mg, 7.5 mmol, 15.0 equiv.), H_2O_2 (50% wt. in H_2O, 170 mg, 2.5 mmol, 5.0 equiv.), MeCN (1.0 mL in 40 mL vial, 6.25 mL with oxidant). The reaction was run at -36 ºC with 1,2-dichloroethane/dry ice bath. The reaction was worked up with 15 mL saturated $NaHCO_3$ and DCM as described in the General Method B. Flash column chromatography on silica (35 mm fritted glass column, 150 mm SiO_2) using 10% acetone/hexanes → 25% acetone/hexanes → 40% acetone/hexanes as eluent afforded product **24** as a colorless oil.

Run 1: (97.0 mg, 0.371 mmol, 74.2% yield), (17.5 mg, 0.071 mmol, 14.3% rsm). **Run 2:** (101.3 mg, 0.388 mmol, 77.5% yield), (18.9 mg, 0.077 mmol, 15.4% rsm). **Run 3:** (99.5 mg, 0.381 mmol, 76.2% yield), (18.8 mg, 0.077 mmol, 15.3% rsm). **Average: 76.0% yield ± 1.7%, 15.0% rsm ± 0.6%.**

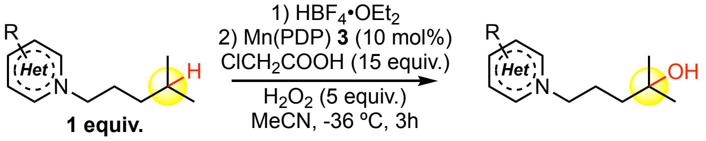
^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.64 (d, *J* = 8.3 Hz, 2H), 7.43 (d, *J* = 8.3 Hz, 2H), 5.73 (dd, *J* = 7.8, 5.8 Hz, 1H), 2.10 (s, 3H), 1.98 (dddd, *J* = 13.6, 12.3, 7.8, 4.7 Hz, 1H), 1.87 (dddd, *J* = 13.7, 12.0, 5.8, 4.6 Hz, 1H), 1.52 (ddd, *J* = 13.5, 12.0, 4.7 Hz, 1H), 1.37 (ddd, *J* = 13.6, 12.1, 4.6 Hz, 1H), 1.31 (br. s, 1H), 1.20 (s, 3H), 1.20 (s, 3H). ^{13}C-NMR (126 MHz, $CDCl_3$) δ 170.3, 146.1, 132.4, 127.1, 118.7, 111.7, 75.6, 70.4, 39.0, 31.1, 29.5, 29.3, 21.2. HRMS (ESI+) *m/z* calculated for $C_{15}H_{19}NO_3Na$ $[M+Na]^+$: 284.1263, found 284.1259.

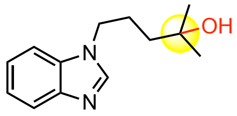
Condition with Fe(PDP): The reaction was conducted with iterative addition protocol previously described for Fe(PDP).[1] A 40 mL vial was charged with 1-(4-cyanophenyl)-4-methylpentyl acetate **S16** (73.6 mg, 0.300 mmol, 1.0 equiv), Fe(PDP) catalyst **1** (14.0 mg, 0.015 mmol, 0.05 equiv.), AcOH (9.0 mg, 0.15 mmol, 0.5 equiv.), MeCN (0.45 mL) and a stir bar. The vial was stirred vigorously and a solution of H_2O_2 (50% wt. in H_2O, 24.5 mg, 1.2 equiv.) in MeCN (3.75 mL) in a 10 mL syringe equipped with 25G needle was added dropwise over 60-75 seconds. The reaction was allowed to stir for 10 minutes at room temperature and a second batch of catalyst (14.0 mg, 0.015 mmol, 0.05 equiv.) and AcOH (9.0 mg, 0.15 mmol, 0.5 equiv.) dissolved in 0.3 mL MeCN was added *via* pipette. This was followed by a solution of H_2O_2 (50 wt%, 24.5 mg, 1.2 equiv.) in MeCN (3.75 mL) in a 10 mL syringe equipped with 25G needle dropwise over 60-75 seconds. After another 10 minutes a third batch of catalyst and H_2O_2 was added in the same manner. The third addition was allowed to stir for 10 minutes for a total reaction time of 30 minutes. **Significant decrease in yield was observed when the peroxide solution was added rapidly.** Upon completion of the reaction, the mixture was concentrated *in vacuo* to a minimum amount of MeCN. Flash column chromatography on silica (35 mm fritted glass column, 150 mm SiO_2) using 10% acetone/hexanes → 25% acetone/hexanes as eluent afforded product **24** as a clear oil.

Run 1: (33.6 mg, 0.129 mmol, 42.9% yield), (20.7 mg, 0.084 mmol, 28.1% rsm). **Run 2:** (35.6 mg, 0.136 mmol, 45.4% yield), (21.2 mg, 0.086 mmol, 28.8% rsm). **Average: 44.1% yield ± 1.8%, 28.5% rsm ± 0.5%. Selectivity = 44.1/(100-28.5) = 62%**

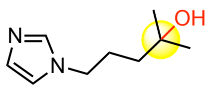
VI. Supplementary Table 3. Chemoselective tertiary oxidation in basic nitrogen containing substrates.

Table 3. Mn(PDP)-catalyzed 3° C(sp^3)—H hydroxylations in basic heteroaromatic compounds.

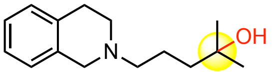




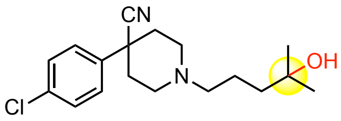
25, 52%
at 0 °C, 58%[a]
Cond. A: 0%[b]



26, 70%
at 0 °C, 54%[a]
Cond. A: 0%[b]



27, 27%
at 0 °C, 20%[a]
Cond. A: 0%[b]



28, 68%

[a]Reaction run at 0 °C instead of -36 °C. [b]0.1 mol% catalyst, 14 equiv. AcOH additive with slow addition of 2.5 equiv. H_2O_2 over 1 h at 0 °C.

Preparation of Substrates and Compound Characterization for Supplementary Table 3

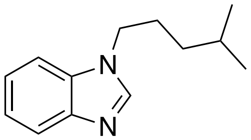
General Procedure A for N-Alkylation

To a flame-dried round bottom flask equipped with a magnetic stir bar, under N_2 atmosphere was added substrate (1.0 equiv.) and DMF (0.5 M). The solution was cooled to 0 ℃ and NaH (1.25 equiv.) was added in one portion. The solution was stirred at 0 ℃ for 15 minutes then 4-methylpentyl-4-methylbenzenesulfonate (1.1 equiv.) was added dropwise. The reaction was stirred overnight (16 h) at room temperature. The reaction was quenched by the addition of water and the aqueous layer was extracted with DCM (3 times). The combined organic layer was washed with H_2O (10 times), dried over Na_2SO_4, filtered and concentrated *in vacuo*. The crude material was purified by flash column chromatography.

General Procedure B for N-Alkylation via Reductive Amination

To a round bottom flask equipped with a magnetic stir bar, under N_2 atmosphere was added substrate (1.0 equiv.), 1,2-dichloroethane (0.1 M), aldehyde (1.1 equiv.) and acetic acid (1% v/v). The reaction was stirred for 30 minutes at room temperature. $NaBH(OAc)_3$ (1.2 equiv.) was added in one portion. The reaction was stirred at room temperature overnight (18 h). The reaction was quenched by the addition of saturated aqueous $NaHCO_3$ solution. The aqueous layer was extracted with DCM (2 times). The combined organic layer was dried with Na_2SO_4, filtered and concentrated *in vacuo*. The crude material was purified by flash column chromatography.

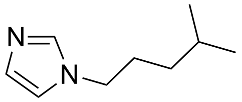
1-(4-methylpentyl)-1*H*-benzo[*d*]imidazole [S17]



According to general procedure A for N-alkylation, benzimidazole (500.0 mg, 4.23 mmol, 1.0 equiv.), NaH (121.8 mg, 5.08 mmol, 1.2 equiv.) and 4-methylpentyl-4-methylbenzenesulfonate (1.63 g, 6.35 mmol, 1.5 equiv.) were reacted. Flash column column chromatography (35 mm fritted glass column, 150 mL SiO_2, MeOH/DCM gradient) afforded 1-(4-methylpentyl)-1*H*-benzimidazole (**S17**) as a pale yellow oil (835 mg, 4.13 mmol, 98% yield).

^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.89 (s, 1H), 7.81 (dd, *J* = 6.8, 1.4 Hz, 1H), 7.40 (d, *J* = 7.2 Hz, 1H), 7.32 – 7.26 (m, 2H), 4.15 (appt. t, *J* = 7.2 Hz, 2H), 1.91 – 1.85 (m, 2H), 1.57 (app. hept, *J* = 6.7 Hz, 1H), 1.24 – 1.20 (m, 2H), 0.87 (d, *J* = 6.6 Hz, 6H). ^{13}C-NMR (126 MHz, $CDCl_3$) δ 144.0, 143.0, 134.0, 122.9, 122.1, 120.5, 109.8, 45.5, 36.0, 27.9, 27.8, 22.6. HRMS (TOF ESI+) *m/z* calculated for $C_{13}H_{19}N_2$ $[M+H]^+$: 203.1548, found 203.1546.

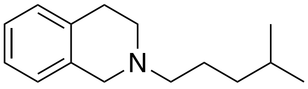
1-(4-methylpentyl)-1*H*-imidazole [S18]



According to general procedure A for N-alkylation, imidazole (500 mg, 7.3 mmol, 1.0 equiv.), NaH (220.8 mg, 9.2 mmol, 1.25 equiv.) and 4-methylpentyl-4-methylbenzenesulfonate (2.06 g, 8.0 mmol, 1.1 equiv.) were reacted. Flash column chromatography (35 mm fritted glass column, 150 mL SiO_2, MeOH/DCM gradient) afforded 1-(4-methylpentyl)-1*H*-imidazole (**S18**) as a pale yellow oil (996.8 mg, 6.55 mmol, 90% yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.44 (m, 1H), 7.04 (m, 1H), 6.89 (m, 1H), 3.89 (m, 2H), 1.82 – 1.71 (m, 2H), 1.54 (m, 1H), 1.16 (m, 2H), 0.87 (m, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 137.2, 129.5, 118.8, 47.4, 35.7, 29.1, 27.7, 22.5. HRMS: (TOF ESI+) *m/z*: calculated for $C_9H_{17}N_2$ $[M+H]^+$: 153.1392, found 153.1391.

2-(4-methylpentyl)-1,2,3,4-tetrahydroisoquinoline [S19]

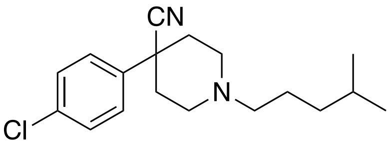


According to general procedure B for N-alkylation, 1,2,3,4-tetrahydroisoquinoline (1.25 mL, 1.33 g, 10.00 mmol, 1.0 equiv.), 4-methylpentanal (1.50 g, 15.0 mmol, 1.5 equiv.), acetic acid (1.0 mL) and $NaBH(OAc)_3$ (2.33 g, 11.0 mmol, 1.1 equiv.) were reacted. Flash column chromatography (35 mm fritted glass column, 150 mL SiO_2, 5→20%

EtOAc/hexanes) afforded 2-(4-methylpentyl)-1,2,3,4-tetrahydroisoquinoline (**S19**) as a pale yellow oil (1.59 g, 7.3 mmol, 73% yield).

^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.15 – 7.07 (m, 3H), 7.05 – 7.00 (m, 1H), 3.63 (s, 2H), 2.91 (t, *J* = 6.0 Hz, 2H), 2.73 (td, *J* = 6.0, 0.9 Hz, 2H), 2.51 – 2.45 (m, 2H), 1.65 – 1.53 (m, 3H), 1.27 – 1.20 (m, 2H), 0.91 (d, *J* = 6.6 Hz, 3H), 0.91 (d, *J* = 6.6 Hz, 3H). ^{13}C-NMR (126 MHz, $CDCl_3$) 135.1, 134.5, 128.8, 126.7, 126.2, 125.7, 59.1, 56.4, 51.2, 37.0, 29.3, 28.2, 25.3, 22.8. HRMS (TOF ESI+) *m/z* calculated for $C_{15}H_{24}N$ $[M+H]^+$: 218.1909, found 218.1902.

4-(4-chlorophenyl)-1-(4-methylpentyl)piperidine-4-carbonitrile [S20]

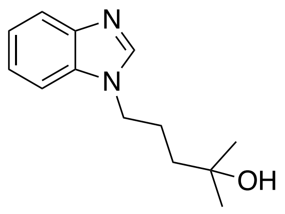


According to general procedure B for N-alkylation, 4-(4-chlorophenyl)piperidine-4-carbonitrile (1.10 g, 5.00 mmol, 1.0 equiv.), 4-methylpentanal (550.9 mg, 5.50 mmol, 1.1 equiv.), acetic acid (0.5 mL) and $NaBH(OAc)_3$ (1.17 g, 5.50 mmol, 1.1 equiv.) were reacted. Flash column chromatography (35 mm fritted glass column, 150 mL SiO_2, 5 → 30% EtOAc/hexanes) afforded 4-(4-chlorophenyl)-1-(4-methylpentyl)piperidine-4-carbonitrile (**S20**) as a white solid (877.6 mg, 2.88 mmol, 58% yield).

^{1}H-NMR (500 MHz, Methanol-*d$_4$*) δ 7.55 – 7.52 (m, 2H), 7.45 – 7.42 (m, 2H), 3.13 – 3.07 (m, 2H), 2.47 – 2.41 (m, 4H), 2.15 – 2.07 (m, 4H), 1.63 – 1.54 (m, 3H), 1.25 – 1.21 (m, 2H), 0.93 (d, *J* = 6.6 Hz, 6H). ^{13}C-NMR (126 MHz, Methanol-*d$_4$*) δ 140.4, 135.2, 130.2, 128.5, 122.7, 59.9, 51.8, 43.4, 37.9, 37.0, 29.1, 25.6, 23.0. HRMS (TOF ESI+) *m/z* calculated for $C_{18}H_{26}N_2Cl$ $[M+H]^+$: 305.1875, found 305.1775.

C—H Oxidation of Substrates and Product Characterization for Supplementary Table 3

1-(4-hydroxy-4-methylpentyl)benzimidazole [25]



At -36 ºC: According to the **general procedure for HBF_4•OEt_2 protection**, 1-(4-methylpentyl)-1*H*-benzimidazole **S17** (101.2 mg, 0.500 mmol, 1.0 equiv), was protected with HBF_4•OEt_2 (75.5 µL, 0.550 mmol, 54 wt.%, 1.1 equiv.) in CH_2Cl_2 (2.0 mL, 0.25 M). The oxidation was carried out according to **General Method D: Iterative Catalyst Addition Protocol**: the resultant **S17•HBF_4** (0.500 mmol, 1.0 equiv.), $ClCH_2CO_2H$ (708.7 mg, 7.5 mmol, 15.0 equiv.), (*S,S*)-Mn(PDP) catalyst **3** (23.3 mg, 0.025 mmol, 5 mol%), H_2O_2 (50% wt. in H_2O, 170 mg, 2.5 mmol, 5.0 equiv.), MeCN (1.0 mL in 40 mL vial, 6.25 mL with oxidant). The reaction was run at -36 ºC with a 1,2-dichloroethane/dry ice bath. A further addition of (*S,S*)-Mn(PDP) catalyst **3** (23.3 mg, 0.025 mmol, 5 mol%) in MeCN (0.2 mL) was added dropwise to the reaction at 1.5 hours. The reaction was worked up according to the **General Procedure for HBF_4 Deprotection**. Flash column chromatography on silica (15 mm fritted glass column, 30 mL SiO_2) using 2% MeOH/CH_2Cl_2 → 8% MeOH/CH_2Cl_2 as eluent afforded 1-(4-hydroxy-4-methylpentyl)benzimidazole **25** as a pale yellow oil.

Run 1: (57.6 mg, 0.264 mmol, 52.8% yield), (11.9 mg, 0.059 mmol, 11.8% rsm). **Run 2**: (56.8 mg, 0.260 mmol, 52.0% yield), (10.4 mg, 0.051 mmol, 10.3% rsm). **Run 3**: (56.5 mg, 0.259 mmol, 51.8% yield), (9.4 mg, 0.046 mmol, 9.3% rsm). **Average: 52.2% yield ± 0.5%, 10.5% rsm ± 1.3%.**

At 0 ºC: According to the **general procedure for HBF_4•OEt_2 protection**, 1-(4-methylpentyl)-1*H*-benzimidazole **S17** (60.7 mg, 0.300 mmol, 1.0 equiv), was protected with HBF_4•OEt_2 (45 µL, 0.33 mmol, 54 wt.%, 1.1 equiv.) in CH_2Cl_2 (1.2 mL, 0.25 M). The oxidation was carried out according to **General Method D: Iterative Catalyst Addition Protocol**: the resultant **S17•HBF_4** (0.300 mmol, 1.0 equiv.), $ClCH_2CO_2H$ (425.3 mg, 4.5 mmol, 15.0 equiv.), (*R,R*)-Mn(PDP) catalyst **3** (14.0 mg, 0.015 mmol, 5 mol%), H_2O_2 (50% wt. in H_2O, 102 mg, 1.5 mmol, 5.0 equiv.), MeCN (0.6 mL in 40 mL vial, 3.75 mL with oxidant). The reaction was run at 0 ºC with an ice/water bath. A further addition of (*R,R*)-Mn(PDP) catalyst **3** (14.0 mg, 0.015 mmol, 5 mol%) in MeCN (0.1 mL) was added dropwise to the reaction at 1.5 hours. The reaction was worked up according to the **General Procedure for HBF_4 Deprotection**. Flash column chromatography on silica (15 mm fritted glass column, 30 mL SiO_2) using 2% MeOH/CH_2Cl_2 → 8% MeOH/CH_2Cl_2 as eluent afforded 1-(4-hydroxy-4-methylpentyl)benzimidazole **25** as a pale yellow oil.

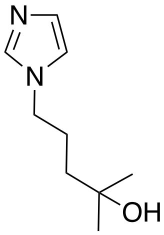
Run 1: (36.4 mg, 0.167 mmol, 55.6% yield), (15.1 mg, 0.075 mmol, 24.9% rsm). **Run 2**: (39.0 mg, 0.179 mmol, 59.6% yield), (14.0 mg, 0.069 mmol, 23.1% rsm). **Average: 57.6% yield, 24.0% rsm.**

At 0.1 mol% Mn(PDP) 3 loading: According to the **general procedure for HBF_4•OEt_2 protection**, 1-(4-methylpentyl)-1*H*-benzimidazole **S17** (60.7 mg, 0.300 mmol, 1.0 equiv), was protected with

HBF_4•OEt_2 (45 µL, 0.33 mmol, 54 wt.%, 1.1 equiv.) in CH_2Cl_2 (1.2 mL, 0.25 M). The oxidation was carried out according to **General Method A: Low Catalyst Loading (0.1 mol%) Protocol**: the resultant **S17•HBF_4** (0.300 mmol, 1.0 equiv.), CH_3COOH (0.24 mL, 4.2 mmol, 14.0 equiv.), (*R,R*)-Mn(PDP) catalyst **3** solution (60 µL, 5 mM solution in MeCN, 0.30 µmol, 0.001 equiv.), H_2O_2 (50% wt. in H_2O, 51.0 mg, 0.75 mmol, 2.5 equiv.), MeCN (0.6 mL in 40 mL vial, 3.75 mL with oxidant). The reaction was run at 0 ºC with an ice/water bath. The reaction was worked up according to the **General Procedure for HBF_4 Deprotection**. The crude mixture was analyzed by quantitative ^{1}H NMR analysis with mesitylene added as internal standard.

Run 1: (0% yield), (100% rsm). **Run 2**: (0% yield), (100% rsm). **Average: 0% yield, 100% rsm.**
^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.84 (s, 1H), 7.79 (dd, *J* = 6.6, 2.0 Hz, 1H), 7.39 (dd, *J* = 6.7, 2.0 Hz, 1H), 7.30 – 7.24 (m, 2H), 4.17 (t, *J* = 7.2 Hz, 2H), 2.20 (br. s, 1H), 2.02 – 1.96 (m, 2H), 1.49 – 1.46 (m, 2H), 1.19 (s, 6H). ^{13}C-NMR (126 MHz, $CDCl_3$) δ 143.8, 143.0, 133.8, 123.0, 122.2, 120.4, 109.8, 70.4, 45.6, 40.6, 29.5, 24.9. HRMS (TOF ESI+) *m/z* calculated for $C_{13}H_{19}N_2O$ $[M+H]^+$: 219.1497, found 219.1487.

5-(1*H*-imidazol-1-yl)-2-methylpentan-2-ol [26]



At -36 ºC: According to the **general procedure for HBF_4•OEt_2 protection**, 1-(4-methylpentyl)-1*H*-imidazole **S18** (45.7 mg, 0.300 mmol, 1.0 equiv.) was protected with HBF_4.OEt_2 (45 µL, 0.330 mmol, 1.1 equiv.) in CH_2Cl_2 (1.2 mL, 0.25 M). The oxidation was carried out according to **General Method C: Double Catalyst Addition Protocol**: the resultant **S18•HBF_4** (0.300 mmol, 1.0 equiv.), $ClCH_2CO_2H$ (425.3 mg, 4.5 mmol, 15.0 equiv.), (*S,S*)-Mn(PDP) catalyst **3** (27.9 mg, 0.03 mmol, 10 mol%), H_2O_2 (50% wt. in H_2O, 102.0 mg, 1.50 mmol, 5.0 equiv.), MeCN (0.6 mL in 40 mL vial, 3.75 mL with oxidant, 0.38 mL with catalyst). The reaction was run at -36 ºC with a 1,2-dichloroethane/dry ice bath. The reaction was worked up according to the **General Procedure for HBF_4 Deprotection**. Flash column chromatography on silica (15 mm fritted glass column, 30 mL SiO_2) using 5% MeOH/CH_2Cl_2 → 10% MeOH/CH_2Cl_2 as eluent afforded 5-(1*H*-imidazol-1-yl)-2-methylpentan-2-ol **26** as a pale yellow oil.

Run 1: (34.7 mg, 0.206 mmol, 68.8% yield), 0% rsm. **Run 2**: (35.0 mg, 0.208 mmol, 69.3% yield), 0% rsm. **Run 3**: (36.5 mg, 0.217 mmol, 72.3% yield), 0% rsm. **Average: 70.1% yield ± 1.9%, 0% rsm.**

At 0 ºC: According to the **general procedure for HBF_4•OEt_2 protection**, 1-(4-methylpentyl)-1*H*-imidazole **S18** (45.7 mg, 0.300 mmol, 1.0 equiv.) was protected with HBF_4.OEt_2 (45 µL, 0.330 mmol, 1.1 equiv.) in CH_2Cl_2 (1.2 mL, 0.25 M). The oxidation was carried out according to **General Method C: Double Catalyst Addition Protocol**: the resultant **S18•HBF_4** (0.300 mmol, 1.0 equiv.), $ClCH_2CO_2H$ (425.3 mg, 4.5 mmol, 15.0 equiv.), (*R,R*)-Mn(PDP) catalyst **3** (27.9 mg, 0.03 mmol, 10 mol%), H_2O_2 (50% wt. in H_2O, 102.0 mg, 1.50 mmol, 5.0 equiv.), MeCN (0.6 mL in 40 mL vial, 3.75 mL with oxidant, 0.38

mL with catalyst). The reaction was run at 0 ºC with an ice/water bath. The reaction was worked up according to the **General Procedure for HBF_4 Deprotection**. Flash column chromatography on silica (15 mm fritted glass column, 30 mL SiO_2) using 5% $MeOH/CH_2Cl_2$ → 10% $MeOH/CH_2Cl_2$ as eluent afforded 5-(1*H*-imidazol-1-yl)-2-methylpentan-2-ol **26** as a pale yellow oil.

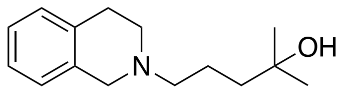
Run 1: (25.9 mg, 0.154 mmol, 51.3% yield), 0% rsm. **Run 2**: (28.5 mg, 0.169 mmol, 56.5% yield), 0% rsm. **Average: 53.9% yield, 0% rsm.**

At 0.1 mol%: According to the **general procedure for HBF_4•OEt_2 protection**, 1-(4-methylpentyl)-1*H*-imidazole **S18** (45.7 mg, 0.300 mmol, 1.0 equiv.) was protected with HBF_4•OEt_2 (45 µL, 0.33 mmol, 54 wt.%, 1.1 equiv.) in CH_2Cl_2 (1.2 mL, 0.25 M). The oxidation was carried out according to **General Method A: Low Catalyst Loading (0.1 mol%) Protocol**: the resultant **S18•HBF_4** (0.300 mmol, 1.0 equiv.), CH_3COOH (0.24 mL, 4.2 mmol, 14.0 equiv.), (*R,R*)-Mn(PDP) catalyst **3** solution (60 µL, 5 mM solution in MeCN, 0.30 µmol, 0.001 equiv.), H_2O_2 (50% wt. in H_2O, 51.0 mg, 0.75 mmol, 2.5 equiv.), MeCN (0.6 mL in 40 mL vial, 3.75 mL with oxidant). The reaction was run at 0 ºC with an ice/water bath. The reaction was worked up according to the **General Procedure for HBF_4 Deprotection**. The crude mixture was analyzed by quantitative ^{1}H NMR analysis with mesitylene added as internal standard.

Run 1: (0% yield), (100% rsm). **Run 2**: (0% yield), (100% rsm). **Average: 0% yield, 100% rsm.**

^{1}H-NMR (500 MHz, CD_3OD) δ 7.64 (br s, 1H), 7.13 (br s, 1H), 6.96 (br s, 1H), 4.03 (t, *J* = 7.1 Hz, 2H), 1.92 – 1.82 (m, 2H), 1.46 – 1.38 (m, 2H), 1.17 (s, 6H). ^{13}C-NMR (126 MHz, CD_3OD) δ 138.4, 128.9, 120.5, 70.9, 48.4, 41.2, 29.2, 27.2. HRMS (TOF ESI+) *m/z* calculated for $C_9H_{17}N_2O$ $[M+H]^+$: 169.1341, found 169.1333.

5-(3,4-dihydroisoquinolin-2(1*H*)-yl)-2-methylpentan-2-ol [27]



At -36 ºC: According to the **general procedure for HBF_4•OEt_2 protection**, 2-(4-methylpentyl)-1,2,3,4-tetrahydroisoquinoline **S19** (65.2 mg, 0.300 mmol, 1.0 equiv), was protected with HBF_4•OEt_2 (45 µL, 0.330 mmol, 54 wt.%, 1.1 equiv.) in CH_2Cl_2 (1.2 mL, 0.25 M). The oxidation was carried out according to **General Method B: Single Catalyst Addition Protocol**: the resultant **S19•HBF_4** (0.300 mmol, 1.0 equiv.), $ClCH_2CO_2H$ (425 mg, 4.5 mmol, 15.0 equiv.), (*R,R*)-Mn(PDP) catalyst **3** (27.9 mg, 0.030 mmol, 10 mol%), H_2O_2 (50% wt. in H_2O, 102 mg, 1.5 mmol, 5.0 equiv.), MeCN (0.6 mL in 40 mL vial, 3.75 mL with oxidant). The reaction was run at -36 ºC with a 1,2-dichloroethane/dry ice bath. The reaction was worked up according to the **General Procedure for HBF_4 Deprotection**. Flash column chromatography on silica (15 mm fritted glass column, 30 mL SiO_2) using 2% $MeOH/CH_2Cl_2$ → 8% $MeOH/CH_2Cl_2$ as eluent afforded product **27** as a pale yellow oil.

Run 1: (18.0 mg, 0.077 mmol, 25.7% yield), (18.8 mg, 0.086 mmol, 28.8% rsm). **Run 2:** (21.6 mg, 0.093

mmol, 30.9% yield), (22.5 mg, 0.104 mmol, 34.5% rsm). **Run 3:** (17.9 mg, 0.077 mmol, 25.6% yield), (16.4 mg, 0.075 mmol, 25.2% rsm). **Average: 27.4% yield ± 3.0%, 29.5% rsm ± 4.7%.**

At 0 ºC: According to the **general procedure for HBF_4•OEt_2 protection**, 2-(4-methylpentyl)-1,2,3,4-tetrahydroisoquinoline **S19** (65.2 mg, 0.300 mmol, 1.0 equiv) was protected with HBF_4•OEt_2 (45 µL, 0.330 mmol, 54 wt.%, 1.1 equiv.) in CH_2Cl_2 (1.2 mL, 0.25 M). The oxidation was carried out according to **General Method B: Single Catalyst Addition Protocol**: the resultant **S19•HBF_4** (0.300 mmol, 1.0 equiv.), $ClCH_2CO_2H$ (425 mg, 4.5 mmol, 15.0 equiv.), (*R,R*)-Mn(PDP) catalyst **3** (27.9 mg, 0.030 mmol, 10 mol%), H_2O_2 (50% wt. in H_2O, 102 mg, 1.5 mmol, 5.0 equiv.), MeCN (0.6 mL in 40 mL vial, 3.75 mL with oxidant). The reaction was run at 0 ºC with an ice/water bath. The reaction was worked up according to the **General Procedure for HBF_4 Deprotection**. Flash column chromatography on silica (15 mm fritted glass column, 30 mL SiO_2) using 2% MeOH/CH_2Cl_2 → 8% MeOH/CH_2Cl_2 as eluent afforded product **27** as a pale yellow oil.

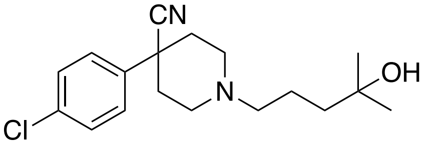
Run 1: (14.7 mg, 0.063 mmol, 21.0% yield), (24.3 mg, 0.112 mmol, 37.3% rsm). **Run 2:** (12.8 mg, 0.055 mmol, 18.3% yield), (27.4 mg, 0.126 mmol, 42.0% rsm). **Average: 19.7% yield, 39.7% rsm.**

At 0.1 mol%: According to the **general procedure for HBF_4•OEt_2 protection**, 2-(4-methylpentyl)-1,2,3,4-tetrahydroisoquinoline **S19** (65.2 mg, 0.300 mmol, 1.0 equiv) was protected with HBF_4•OEt_2 (45 µL, 0.33 mmol, 54 wt.%, 1.1 equiv.) in CH_2Cl_2 (1.2 mL, 0.25 M). The oxidation was carried out according to **General Method A: Low Catalyst Loading (0.1 mol%) Protocol**: the resultant **S19•HBF_4** (0.300 mmol, 1.0 equiv.), CH_3COOH (0.24 mL, 4.2 mmol, 14.0 equiv.), (*R,R*)-Mn(PDP) catalyst **3** solution (60 µL, 5 mM solution in MeCN, 0.30 µmol, 0.001 equiv.), H_2O_2 (50% wt. in H_2O, 51.0 mg, 0.75 mmol, 2.5 equiv.), MeCN (0.6 mL in 40 mL vial, 3.75 mL with oxidant). The reaction was run at 0 ºC with an ice/water bath. The reaction was worked up according to the **General Procedure for HBF_4 Deprotection**. The crude mixture was analyzed by quantitative ^{1}H NMR analysis with mesitylene added as internal standard.

Run 1: (0% yield), (100% rsm). **Run 2**: (0% yield), (100% rsm). **Average: 0% yield, 100% rsm.**

^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.14 – 7.04 (m, 3H), 7.00 (dd, *J* = 6.7, 2.0 Hz, 1H), 3.68 (s, 2H), 2.93 (t, *J* = 5.9 Hz, 2H), 2.79 (t, *J* = 6.0 Hz, 2H), 2.58 – 2.55 (m, 2H), 1.79 – 1.73 (m, 2H), 1.69 – 1.64 (m, 2H), 1.19 (s, 6H). ^{13}C-NMR (126 MHz, $CDCl_3$) δ 134.0, 133.9, 128.8, 126.7, 126.5, 125.9, 69.0, 58.9, 56.1, 50.6, 43.3, 29.8, 28.7, 21.9. HRMS (TOF ESI+) *m/z* calculated for $C_{15}H_{24}NO$ $[M+H]^+$: 234.1858, found 234.1855.

4-(4-chlorophenyl)-1-(4-hydroxy-4-methylpentyl)piperidine-4-carbonitrile [28]



At -36 ºC: According to the **general procedure for HBF_4•OEt_2 protection**, 4-(4-chlorophenyl)-1-(4-methylpentyl)piperidine-4-carbonitrile **S20** (91.5 mg, 0.300 mmol, 1.0 equiv), was protected with HBF_4•OEt_2 (45 µL, 0.330 mmol, 54 wt.%, 1.1 equiv.) in CH_2Cl_2 (1.2 mL, 0.25 M). The oxidation was carried out according to **General Method B: Single Catalyst Addition Protocol**: the resultant **S20•HBF_4** (0.300 mmol, 1.0 equiv.), $ClCH_2CO_2H$ (425.3 mg, 4.5 mmol, 15.0 equiv.), (*S,S*)-Mn(PDP) (27.9 mg, 0.030 mmol, 10 mol%), H_2O_2 (50% wt. in H_2O, 102 mg, 1.5 mmol, 5.0 equiv.), MeCN (0.6 mL in 40 mL vial, 3.75 mL with oxidant). The reaction was run at -36 ºC with 1,2-dichloroethane/dry ice bath. The reaction was worked up according to the **General Procedure for HBF_4 Deprotection**. Flash column chromatography on silica (15 mm fritted glass column, 30 mL SiO_2) using 2% MeOH/CH_2Cl_2 → 3% MeOH/CH_2Cl_2 as eluent afforded product **28** as a pale yellow oil.

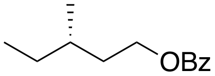
Run 1: (65.6 mg, 0.204 mmol, 68.1% yield), (15.7 mg. 0.051 mmol, 17.2% rsm). **Run 2:** (65.1 mg, 0.203 mmol, 67.6% yiel), (17.5 mg. 0.057 mmol, 19.1% rsm). **Run 3:** (64.7 mg, 0.202 mmol, 67.2% yield), (18.4 mg. 0.060 mmol, 20.1% rsm). **Average: 67.6% yield ± 0.5%, 18.8% rsm ± 1.5%.**

^{1}H NMR (500 MHz, CD_3OD) δ 7.55 – 7.51 (m, 2H), 7.45 – 7.41 (m, 2H), 3.17 – 3.04 (m, 2H), 2.52 – 2.39 (m, 4H), 2.19 – 2.03 (m, 4H), 1.73 – 1.61 (m, 2H), 1.55 – 1.47 (m, 2H), 1.20 (s, 6H). ^{13}C NMR (126 MHz, CD_3OD) δ 140.3, 135.1, 130.2, 128.5, 122.7, 70.9, 60.0, 51.7, 43.4, 42.7, 37.0, 29.4, 22.5. HRMS: (TOF ESI+) *m/z* calculated for $C_{18}H_{26}N_2OCl$ $[M+H]^+$: 321.1734, found 321.1727.

VII. Supplementary Figure 1. Stereoretention Study

Preparation of Substrates and Compounds Characterization for Supplementary Figure 1

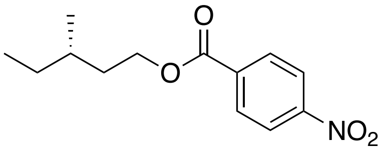
(*S*)-3-methylpentyl benzoate [29]



(*S*)-3-methylpentanol (510.9 mg, 0.62 mL, 5.0 mmol, 1.0 equiv.) was dissolved in 10 mL anhydrous DCM. Benzoyl chloride (1.41 g, 1.16 mL, 10.0 mmol, 2.0 equiv.) and triethylamine (1.52 g, 2.09 mL, 15.0 mmol, 3.0 equiv.) was added dropwise at 0 ºC. 4-Dimethylaminopyridine (61.1 mg, 0.5 mmol, 10 mol%) was added and the reaction was allowed to stir at room temperature overnight. The reaction was diluted with 20 mL DCM and washed with 40 mL 1M HCl solution, 40 mL saturated $NaHCO_3$ followed by 40 mL brine. The organic layer was dried with Na_2SO_4, filtered, and concentrated. Flash column chromatography on silica (50 mm fritted glass column, 200 mm SiO_2) using 5% EtOAc/hexanes as eluent gave (*S*)-3-methylpentyl benzoate (**29**) as a colorless oil (882.2 mg, 4.3 mmol, 86% yield).

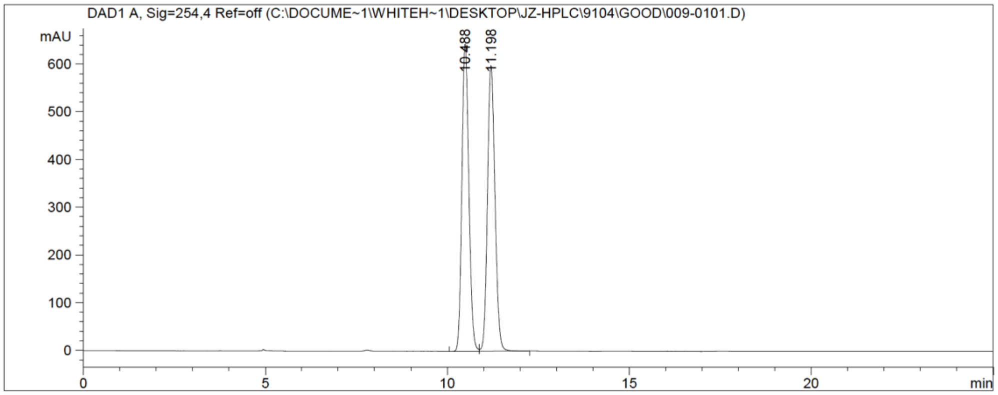
^{1}H-NMR (500 MHz, $CDCl_3$) δ 8.05 – 8.03 (m, 2H), 7.55 (td, *J* = 7.2, 1.3 Hz, 1H), 7.44 (t, *J* = 7.8 Hz, 2H), 4.40 – 4.32 (m, 2H), 1.86 – 1.77 (m, 1H), 1.61 – 1.54 (m, 2H), 1.42 (dqd, *J* = 12.6, 7.5, 5.0 Hz, 1H), 1.28 – 1.20 (m, 1H), 0.96 (d, *J* = 6.3 Hz, 3H), 0.91 (t, *J* = 7.4 Hz, 3H). ^{13}C-NMR (126 MHz, $CDCl_3$) δ 166.8, 132.9, 130.7, 129.7, 128.5, 63.7, 35.3, 31.7, 29.6, 19.2, 11.4. HRMS (ESI) *m/z* calculated for $C_{13}H_{19}O_2$ $[M+H]^+$: 207.1385, found 207.1376.

Determination of the enantiomeric excess of the substrate ***29****:*



The enantiomeric excess of substrate **29** was determined by synthesizing a *para*-nitro benzoate analogue **S21** using the same bottle of (*S*)-3-methylpentanol and *para*-nitrobenzoyl choride instead of benzoyl chloride with the same procedure. ^{1}H-NMR (500 MHz, $CDCl_3$) δ 8.30 – 8.28 (m, 2H), 8.22 – 8.20 (m, 2H), 4.46 – 4.37 (m, 2H), 1.87 – 1.80 (m, 1H), 1.64 – 1.53 (m, 2H), 1.47 – 1.38 (m, 1H), 1.30 – 1.21 (m, 1H), 0.97 (d, *J* = 6.5 Hz, 3H), 0.92 (t, *J* = 7.4 Hz, 3H). The enantiomeric excess was determined by using chiral HPLC with a Chiralcel OJ-H column, 30 ºC, 99:1 hexanes:isopropanol, 0.5 mL/min. t_R*(minor)* = 10.5 min, t_R*(major)* = 11.2 min. Enantiometric excess = 97%.

HPLC trace of the racemic standard (absorption at 254nm – time):



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=====================================================================
                         Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 A, Sig=254,4 Ref=off

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]        %
----|-------|----|-------|----------|----------|--------|
   1  10.488 BV    0.2050 8528.63770  644.33716  49.7987
   2  11.198 VV    0.2229 8597.57129  598.93005  50.2013

Totals :                  1.71262e4  1243.26721
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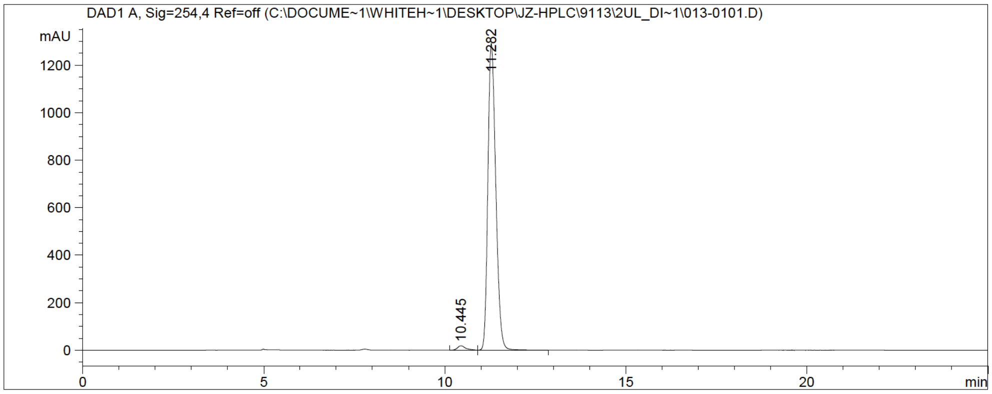
HPLC trace of **S21** (absorption at 254nm – time):



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=====================================================================
                         Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 A, Sig=254,4 Ref=off

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]        %
----|-------|----|-------|----------|----------|--------|
   1  10.445 BV    0.2349  295.06390   18.67324   1.4829
   2  11.282 VB    0.2354 1.96025e4  1291.01831  98.5171

Totals :                  1.98975e4  1309.69156
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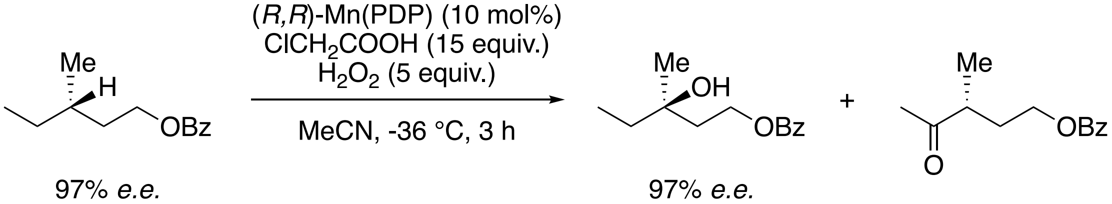
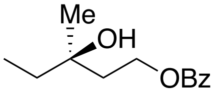
Oxidation of (S)-3-methylpentyl benzoate 29 under standard conditions



The reaction was run with **General Method B: Single Catalyst Addition Protocol**. (*S*)-3-methylpentyl benzoate **29** (103.1 mg, 0.500 mmol, 1.0 equiv), (*R,R*)-Mn(PDP) catalyst **3** (46.6 mg, 0.050 mmol, 10 mol%), $ClCH_2CO_2H$ (709 mg, 7.5 mmol, 15.0 equiv.), H_2O_2 (50% wt. in H_2O, 170 mg, 2.5 mmol, 5.00 equiv.), MeCN (1.0 mL in 40 mL vial, 6.25 mL with oxidant). The reaction was run at -36 ºC with a 1,2-dichloroethane/dry ice bath. The reaction was worked up with 15 mL saturated $NaHCO_3$ and DCM as described in General Method B. Flash column chromatography on silica (35 mm fritted glass column, 150 mm SiO_2) using 5% ethyl acetate/hexanes → 15% ethyl acetate/hexanes → 25% ethyl acetate/hexanes as eluent afforded tertiary alcohol **30a** and ketone **30b** oxidation products separately.

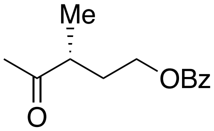
Run 1: (29.7 mg, 0.134 mmol, 26.7% alcohol yield), (18.7 mg, 0.085 mmol, 17.0% ketone yield), (41.0 mg, 0.199 mmol, 39.8% rsm). **Run 2:** (32.0 mg, 0.144 mmol, 28.8% alcohol yield), (18.5 mg, 0.084 mmol, 16.8% ketone yield), (46.0 mg, 0.223 mmol, 44.6% rsm). **Run 3:** (30.2 mg, 0.136 mmol, 27.2% alcohol yield), (14.9 mg, 0.068 mmol, 13.5% ketone yield), (54.8 mg, 0.266 mmol, 53.1% rsm). **Average: 27.6% alcohol yield ± 1.1%, 15.8% ketone yield ± 2.0%, 45.8% rsm ± 6.7%.**

(*R*)-3-hydroxy-3-methylpentyl benzoate 30a



^{1}H-NMR (500 MHz, $CDCl_3$) δ 8.03 (dd, *J* = 8.1, 1.5 Hz, 2H), 7.57 – 7.54 (m, 1H), 7.44 (t, *J* = 7.8 Hz, 2H), 4.50 (t, *J* = 6.9 Hz, 2H), 1.96 (td, *J* = 6.9, 4.1 Hz, 2H), 1.59 (dt, *J* = 15.1, 6.9 Hz, 3H), 1.26 (s, 3H), 0.95 (t, *J* = 7.5 Hz, 3H). ^{13}C-NMR (126 MHz, $CDCl_3$) δ 166.8, 133.1, 130.4, 129.6, 128.5, 72.3, 61.9, 39.5, 35.1, 26.7, 8.4. HRMS (ESI) *m/z* calculated for $C_{13}H_{19}O_3$ $[M+H]^+$: 223.1334, found 223.1324.

(*R*)-3-methyl-4-oxopentyl benzoate 30b



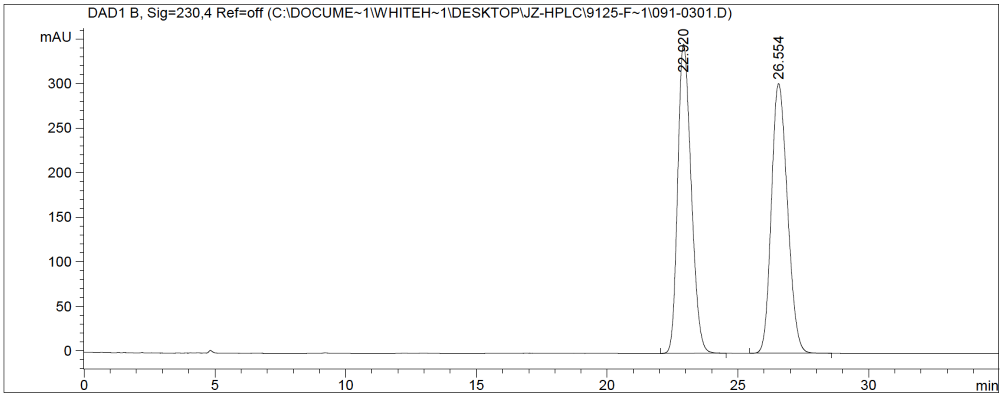
^{1}H-NMR (500 MHz, $CDCl_3$) δ 8.01 (d, *J* = 7.9 Hz, 2H), 7.58 – 7.54 (m, 1H), 7.44 (t, *J* = 7.7 Hz, 2H), 4.33 (t, *J* = 6.4 Hz, 2H), 2.73 (sxt, *J* = 7.0 Hz, 1H), 2.25 – 2.17 (m, 1H), 2.18 (s, 3H), 1.78 (dq, *J* = 14.2, 6.2 Hz, 1H), 1.19 (d, *J* = 7.0 Hz, 3H). ^{13}C-NMR (126 MHz, $CDCl_3$) δ 211.7, 166.7, 133.1, 130.3, 129.7, 128.5, 63.1, 44.1, 31.6, 28.5, 16.7. HRMS (ESI) *m/z* calculated for $C_{13}H_{17}O_3$ $[M+H]^+$: 221.1178, found 221.1168.

*Determination of the enantiomeric excess of the tertiary oxidation product **30a**:*

The enantiomeric excess was determined by using chiral HPLC with a Chiralcel AD-RH column, 30 ºC, 45:55 acetonitrile:water, 0.5 mL/min. $t_R(minor)$ = 22.9 min, $t_R(major)$ = 26.5 min. Enantiometric excess of 3 runs: **Run 1:** 97%. **Run 2:** 97%. **Run 3:** 97%. Average e.e. 97%.

HPLC trace of the racemic standard (absorption at 230 nm – time):

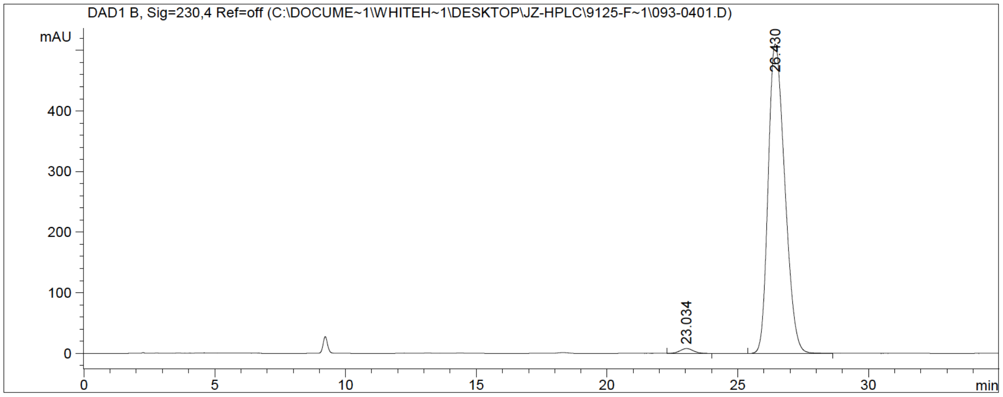
Standard Run



```
=====================================================================
                         Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 B, Sig=230,4 Ref=off

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]        %
----|-------|----|-------|----------|----------|--------|
   1  22.920 BB    0.5550 1.24447e4  347.12567  48.9925
   2  26.554 BB    0.6616 1.29566e4  302.89594  51.0075

Totals :                  2.54014e4  650.02161
```

HPLC trace of run 1 (absorption at 230 nm – time):

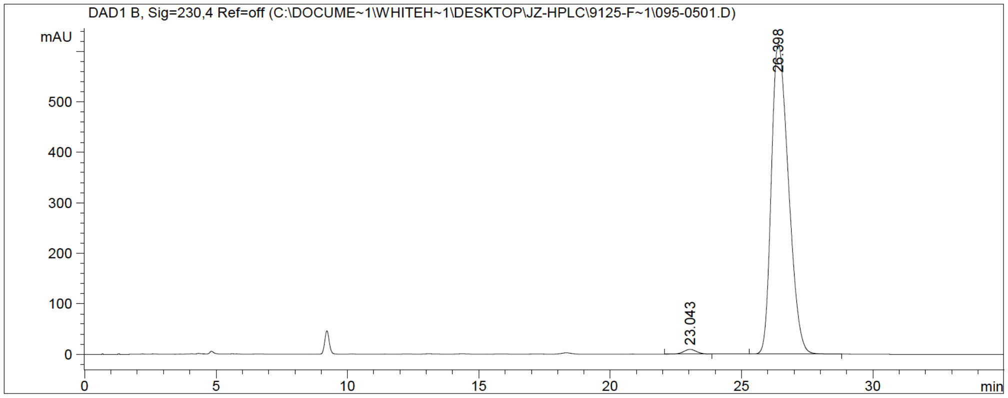
Standard Run



```
=====================================================================
                         Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 B, Sig=230,4 Ref=off

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]        %
----|-------|----|-------|----------|----------|--------|
   1  23.034 BV    0.4553  267.17834    7.82782   1.1732
   2  26.430 BB    0.6892 2.25066e4  510.53934  98.8268

Totals :                  2.27738e4  518.36715
```

HPLC trace of run 2 (absorption at 230 nm – time):

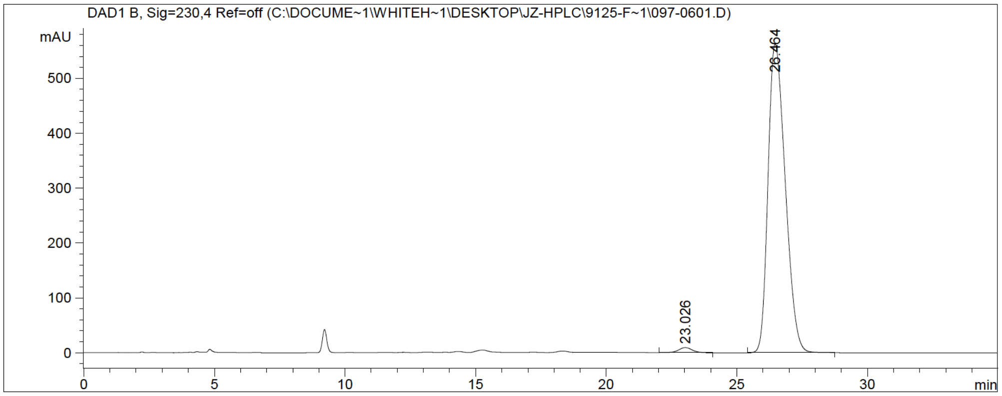
Standard Run



```
=====================================================================
                         Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 B, Sig=230,4 Ref=off

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]        %
----|-------|----|-------|----------|----------|--------|
   1  23.043 BV    0.4803  322.07516    9.31510   1.1423
   2  26.398 BB    0.7107 2.78737e4  614.36377  98.8577

Totals :                  2.81958e4  623.67887
```

HPLC trace of run 3 (absorption at 230 nm – time):

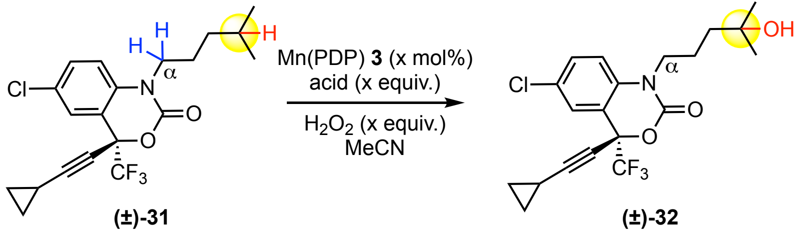
Standard Run



```
=====================================================================
                         Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 B, Sig=230,4 Ref=off

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]        %
----|-------|----|-------|----------|----------|--------|
   1  23.026 BB    0.4723  323.64169    9.16963   1.2425
   2  26.464 BB    0.7163 2.57239e4  562.57910  98.7575

Totals :                  2.60475e4  571.74873
```

VIII. Supplementary Figure 2. Late Stage Oxidation of Pharmaceutical Derivatives

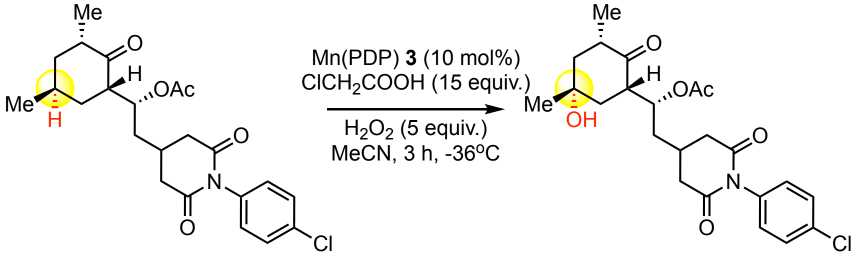
A. *Efavirenz derivative*



(±)-31 **(±)-32**

3 (mol %)	**Acid** (equiv.)	**H$_2$O$_2$** (equiv.)	**Temp.** (ºC)	**Yield** (%)
10	ClCH$_2$COOH (15)	5.0	-36	53
10	ClCH$_2$COOH (15)	5.0	0	43
0.1	AcOH (14)	2.5	0	46

B. *Cycloheximide derivative*

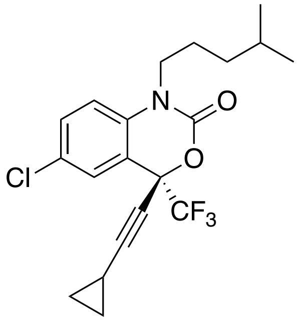


(+)-33 **(+)-34**, 63%[a]

Figure 2. Late stage C—H oxidation on pharmaceutical derivatives. [a]Starting material recycled once.

Preparation of Substrates and Compound Characterization for Supplementary Figure 2

(±)-6-chloro-4-(cyclopropylethynyl)-1-(4-methylpentyl)-4-(trifluoromethyl)-1,4-dihydro-2*H*-benzo[*d*][1,3]oxazin-2-one [31]

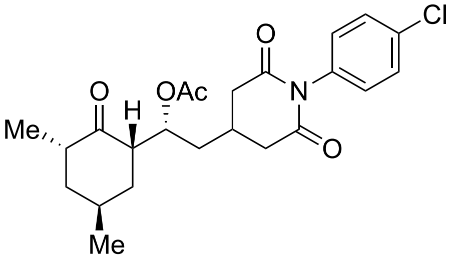


A flame-dried 50 mL recovery flask was charged with (±)-efavirenz (473.5 mg, 1.5 mmol, 1.0 equiv.) in anhydrous DMF (5 mL, 0.3 M). The reaction was cooled to 0 °C and NaH (43.2 mg, 1.8 mmol, 1.2 equiv.) was added in one portion. The reaction was allowed to stir and warmed from 0 °C to room temperature over 15 minutes. 4-Methylpentyl-4-methylbenzenesulfonate (461.4 mg, 1.8 mmol, 1.2 equiv.) and sodium iodide (269.8 mg, 1.8 mmol, 1.2 equiv.) were added and the reaction was heated to 80 °C for 24 hours. Upon completion, the reaction was cooled to room temperature, quenched with sat. aq. NH$_4$Cl and extracted with diethyl ether (3 times). The combined organic layer was washed with brine, dried with Na$_2$SO$_4$, filtered and concentrated *in vacuo*. Flash column chromatography on silica (35 mm fritted glass column, 150 mL SiO$_2$) using 100% hexanes

→ 20% EtOAc/hexanes as eluent afforded (±)-6-chloro-4-(cyclopropylethynyl)-1-(4-methylpentyl)-4-(trifluoromethyl)-1,4-dihydro-2*H*-benzo[*d*][1,3]oxazin-2-one (**31**) as a white solid (445.4 mg, 1.11 mmol, 74% yield).

^{1}H NMR (500 MHz, Methylene Chloride-d_2) δ 7.56 (d, *J* = 2.4 Hz, 1H), 7.44 (dd, *J* = 8.8, 2.4 Hz, 1H), 6.94 (d, *J* = 8.8 Hz, 1H), 3.89 (ddd, *J* = 14.5, 9.6, 6.3 Hz, 1H), 3.81 (ddd, *J* = 14.8, 9.5, 5.6 Hz, 1H), 1.74 – 1.52 (m, 3H), 1.41 (tt, *J* = 8.3, 5.0 Hz, 1H), 1.29 – 1.21 (m, 2H), 0.95 – 0.90 (m, 2H), 0.89 (d, *J* = 6.7 Hz, 3H), 0.89 (d, *J* = 6.7 Hz, 3H), 0.86 – 0.81 (m, 2H). ^{13}C NMR (126 MHz, Methylene Chloride-d_2) δ 146.9, 134.7, 130.8, 127.7, 127.3, 121.7 (q, *J* = 287.9 Hz), 116.8, 114.6, 94.8, 76.7 (q, *J* = 34.5 Hz), 65.6, 44.0, 34.8, 27.1, 23.8, 21.5, 21.5, 7.8, 7.8, -1.5. ^{19}F NMR (471 MHz, Methylene Chloride-d_2) δ -81.06. HRMS (TOF ESI+) *m/z* calculated for $C_{20}H_{22}NO_2F_3$ $[M+H]^+$: 400.1291, found 400.1287.

(*R*)-2-(1-4-chlorophenyl)-2,6-dioxopiperidine-4-yl)-1-((1*S*,3*S*,5*S*)-3,5-dimethyl-2-oxocyclohexyl)ethyl acetate [33]

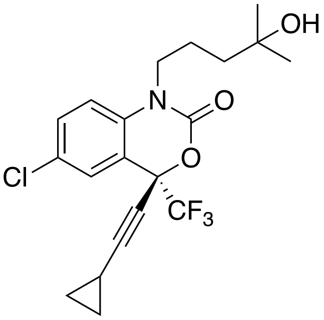


In a schlenk flask was added 4Å powdered molecular sieves (1 g) and a Teflon stir bar. The flask was sealed with a rubber septum, placed under vacuum, flame-dried to activate the molecular sieves and cooled under nitrogen. Once cooled, cycloheximide acetate (323.4 mg, 1.0 mmol, 1.0 equiv.), 4-chlorophenylboronic acid (470.0 mg, 3.0 mmol, 3.0 equiv.) and copper(II) acetate (544.9 mg, 3.0 mmol, 3.0 equiv.) were added. The flask was backfilled with nitrogen three times. Anhydrous CH_2Cl_2 (11.8 mL, 0.08 M) and anhydrous triethylamine (0.42 mL, 3.0 mmol, 3.0 equiv.) were added. The atmosphere was flushed with oxygen and the flask was sealed. The reaction was stirred at room temperature for 36 hours. Upon completion, the reaction was filtered through a short pad of silica using dichloromethane as eluent and concentrated *in vacuo*. Flash column chromatography on silica (35 mm fritted glass column, 150 mL SiO_2) using 100% hexanes → 60% EtOAc/hexanes as eluent gave (*R*)-2-(1-4-chlorophenyl)-2,6-dioxopiperidine-4-yl)-1-((1*S*,3*S*,5*S*)-3,5-dimethyl-2-oxocyclohexyl)ethyl acetate (**33**) as a white solid (387.6 mg, 0.89 mmol, 89% yield).

^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.41 (d, *J* = 8.5 Hz, 2H), 7.04 (d, *J* = 8.5 Hz, 2H), 5.63 (td, *J* = 7.9, 4.5 Hz, 1H), 3.14 (m, 1H), 2.85 (m, 1H), 2.75 – 2.56 (m, 3H), 2.50 (dd, *J* = 17.0, 10.5 Hz, 1H), 2.31 – 2.23 (m, 1H), 2.21 – 2.14 (m, 1H), 2.08 (s, 3H), 1.93 – 1.87 (m, 2H), 1.77 – 1.58 (m, 4H), 1.26 (d, *J* = 7.2 Hz, 3H), 1.00 (d, *J* = 6.4 Hz, 3H).^{13}C-NMR (126 MHz, $CDCl_3$) δ 212.4, 171.8, 171.6, 170.7, 134.6, 133.5, 130.0, 129.6, 69.8, 49.4, 42.9, 41.0, 39.7, 39.0, 38.3, 36.7, 27.0, 26.6, 21.2, 18.3, 14.4. $[\alpha]_D^{24}$ = +7.5 (c = 1.00, $CHCl_3$). HRMS (ESI+) *m/z* calculated for $C_{23}H_{29}NO_5Cl$ $[M+H]^+$: 434.1734, found 434.1747.

C—H Oxidation of Substrates and Product Characterization for Supplementary Figure 2

(±)-6-chloro-4-(cyclopropylethynyl)-1-(4-hydroxy-4-methylpentyl)-4-(trifluoromethyl)-1,4-dihydro-2*H*-benzo[*d*][1,3]oxazin-2-one [32]



At -36 °C: The reaction was run with **General Method B: Single Catalyst Addition Protocol**: (±)-6-chloro-4-(cyclopropylethynyl)-1-(4-methylpentyl)-4-(trifluoromethyl)-1,4-dihydro-2*H*-benzo[*d*][1,3]oxazin-2-one **31** (80.0 mg, 0.200 mmol, 1.0 equiv), (*R,R*)-Mn(PDP) catalyst **3** (18.6 mg, 0.020 mmol, 10 mol%), $ClCH_2CO_2H$ (283.5 mg, 3.0 mmol, 15.0 equiv.), H_2O_2 (50% wt. in H_2O, 68 mg, 1.0 mmol, 5.0 equiv.), MeCN (0.4 mL in 40 mL vial, 2.5 mL with oxidant). The reaction was run at -36 ºC with a 1,2-dichloroethane/dry ice bath. The reaction was worked up with 9 mL saturated $NaHCO_3$ and DCM as described in General Method B. Flash column chromatography on silica (15 mm fritted glass column, 30 mL SiO_2) using 100% hexanes → 50% EtOAc/hexanes as eluent afforded product **32** as an off white solid.

Run 1: (44.1 mg, 0.106 mmol, 53.0% yield), (6.7 mg, 0.017 mmol, 8.4% rsm). **Run 2:** (43.0 mg, 0.103 mmol, 51.7% yield), (6.2 mg, 0.016 mmol, 7.8% rsm). **Run 3:** (45.9 mg, 0.110 mmol, 55.2% yield), (5.8 mg, 0.015 mmol, 7.3% rsm). **Average: 53.3% yield ± 1.8%, 7.8% rsm ± 0.6%.**

At 0 °C: The reaction was run with **General Method B: Single Catalyst Addition Protocol**: (±)-6-chloro-4-(cyclopropylethynyl)-1-(4-methylpentyl)-4-(trifluoromethyl)-1,4-dihydro-2*H*-benzo[*d*][1,3]oxazin-2-one **31** (80.0 mg, 0.200 mmol, 1.0 equiv), (*R,R*)-Mn(PDP) catalyst **3** (18.6 mg, 0.020 mmol, 10 mol%), $ClCH_2CO_2H$ (283.5 mg, 3.0 mmol, 15.0 equiv.), H_2O_2 (50% wt. in H_2O, 68 mg, 1.0 mmol, 5.0 equiv.), MeCN (0.4 mL in 40 mL vial, 2.5 mL with oxidant). The reaction was run at 0 ºC with an ice/water bath. The reaction was worked up with 9 mL saturated $NaHCO_3$ and DCM as described in General Method B. Flash column chromatography on silica (15 mm fritted glass column, 30 mL SiO_2) using 100% hexanes → 50% EtOAc/hexanes as eluent afforded product **32** as an off white solid.

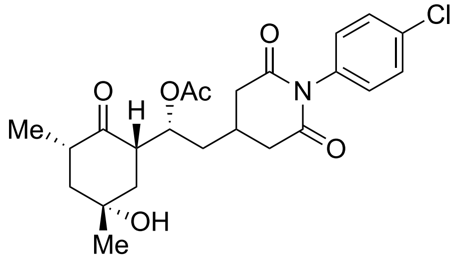
Run 1: (37.4 mg, 0.090 mmol, 45.0% yield), (4.6 mg, 0.012 mmol, 5.8% rsm). **Run 2:** (34.5 mg, 0.083 mmol, 41.5% yield), (5.6 mg, 0.014 mmol, 7.0% rsm). **Average: 43.3% yield, 6.4% rsm.**

At 0.1 mol% catalyst: The reaction was run with **General Method A: Low Catalyst Loading (0.1 mol%) Protocol**: (±)-6-chloro-4-(cyclopropylethynyl)-1-(4-methylpentyl)-4-(trifluoromethyl)-1,4-dihydro-2*H*-benzo[*d*][1,3]oxazin-2-one **31** (80.0 mg, 0.200 mmol, 1.0 equiv), CH_3COOH (0.16 mL, 2.8 mmol, 14.0 equiv.), Mn(PDP) catalyst **3** solution (40 µL, 5 mM solution in MeCN, 0.20 µmol, 0.001 equiv.), H_2O_2 (50% wt. in H_2O, 34.0 mg, 0.50 mmol, 2.5 equiv.), MeCN (0.4 mL in 40 mL vial, 2.5 mL with oxidant). The reaction was run at 0 ºC with an ice/water bath. The reaction was worked up with 15 mL saturated $NaHCO_3$ and DCM as described in General Method A. Flash column chromatography on silica (15 mm fritted glass column, 30 mL SiO_2) using gradient 100% hexanes → 20% EtOAc/hexanes afforded product **32** as a white solid.

Run 1: (38.3 mg, 0.092 mmol, 46.2% yield), (17.4 mg, 0.044 mmol, 21.8% rsm). **Run 2:** (37.8 mg, 0.091 mmol, 45.5% yield), (14.3 mg, 0.036 mmol, 17.9% rsm). **Average: 45.9% yield, 19.9% rsm.**

^{1}H NMR (500 MHz, Methylene Chloride-*d*$_2$) δ 7.56 (d, *J* = 2.3 Hz, 1H), 7.45 (dd, *J* = 8.9, 2.4 Hz, 1H), 6.99 (d, *J* = 8.8 Hz, 1H), 3.99 – 3.81 (m, 2H), 1.83 – 1.64 (m, 2H), 1.55 – 1.45 (m, 3H), 1.41 (tt, *J* = 8.3, 5.0 Hz, 1H), 1.19 (s, 3H), 1.18 (s, 3H), 0.96 – 0.90 (m, 2H), 0.86 – 0.80 (m, 2H). ^{13}C-NMR (126 MHz, Methylene Chloride-*d*$_2$) δ 146.9, 134.5, 130.8, 127.7, 127.3, 121.6 (q, *J* = 287.9 Hz), 116.7, 114.6, 94.8, 76.7 (q, *J* = 34.3 Hz), 69.5, 65.5, 44.2, 39.2, 28.4, 20.9, 7.8, 7.8, -1.6. ^{19}F NMR (471 MHz, Methylene Chloride-*d*$_2$) δ -81.08. HRMS (TOF ESI+) *m/z* calculated for $C_{20}H_{22}NO_3ClF_3$ $[M+H]^+$: 416.1240, found 416.1237.

(*R*)-2-(1-(4-chlorophenyl)-2,6-dioxopiperidin-4-yl)-1-((1*S*,3*S*,5*R*)-5-hydroxy-3,5-dimethyl-2-oxocyclohexyl)ethyl acetate [34]



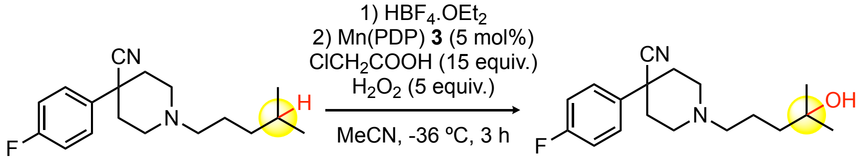
The reaction was run with **General Method C: Double Catalyst Addition Protocol**: (*R*)-2-(1-(4-chlorophenyl)-2,6-dioxopiperidin-4-yl)-1-((1*S*,3*S*,5*S*)-3,5-dimethyl-2-oxocyclohexyl)ethyl acetate **33** (173.6 mg, 0.400 mmol, 1.0 equiv), (*S,S*)-Mn(PDP) catalyst **3** (37.2 mg, 0.040 mmol, 10 mol%), $ClCH_2CO_2H$ (567 mg, 6.0 mmol, 15.0 equiv.), H_2O_2 (50% wt. in H_2O, 136 mg, 2.0 mmol, 5.0 equiv.), 4:1 MeCN:DCM (0.8 mL in 40 mL vial, 5.0 mL with oxidant, 0.5 mL with catalyst). The reaction was run at -36 ºC with a 1,2-dichloroethane/dry ice bath. The reaction was worked up with 9 mL saturated $NaHCO_3$ and DCM as described in General Method C. Flash column chromatography on silica (15 mm fritted glass column, 30 mL SiO_2) using 100% dichloromethane → 5% methanol/dichloromethane as eluent afforded product **34** as an off white solid. Recovered starting material was recycled once.

Run 1: *Cycle 1* (79.6 mg, 0.177 mmol, 44.2% yield; 84.2 mg, 0.194 mmol, 48.5% rsm); *Cycle 2* (40.3 mg, 0.090 mmol, 46.2% yield; 33.9 mg, 0.078 mmol, 40.3% rsm); *Overall* (119.9 mg, 0.266 mmol, 66.6% yield; 33.9 mg, 0.078 mmol, 19.5% rsm). **Run 2:** *Cycle 1* (64.0 mg, 0.142 mmol, 35.6% yield; 88.8 mg, 0.205 mmol, 51.2% rsm); *Cycle 2* (44.4 mg, 0.099 mmol, 48.2% yield; 36.5 mg, 0.084 mmol, 41.1% rsm); *Overall* (108.4 mg, 0.241 mmol, 60.2% yield; 36.5 mg, 0.084 mmol, 21.0% rsm). **Average: 63.4% yield and 20.3% rsm.**

^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.41 (d *J* = 8.7 Hz, 2H), 7.03 (d, *J* = 8.7 Hz, 2H), 5.36 (td, *J* = 7.8, 3.9 Hz, 1H), 3.13 (m, 1H), 2.85 (m, 1H), 2.67 – 2.42 (m, 4H), 2.31 – 2.20 (m, 1H) 2.08 (s, 3H), 2.08 – 2.01 (m, 2H), 1.77 – 1.68 (m, 3H), 1.66 – 1.55 (m, 2H), 1.58 (s, 3H), 1.02 (d, *J* = 6.4 Hz, 3H). ^{13}C-NMR (126 MHz, $CDCl_3$) δ 210.5, 171.7, 171.5, 170.7, 134.6, 133.4, 129.9, 129.6, 69.7, 69.2, 50.3, 49.2, 42.8, 42.2, 39.7, 39.0, 38.3, 26.6, 26.4, 21.2, 14.3. $[\alpha]_D^{24}$ = +8.6 (c = 1.00, $CHCl_3$). HRMS (TOF ESI+) *m/z* calculated for $C_{23}H_{29}NO_6Cl$ $[M+H]^+$: 450.1683, found 450.1688.

IX. Supplementary Figure 3. Scale Up C—H Oxidations

A. *Mn(PDP)-catalyzed 3° hydroxylation on 1.7 g (6.0 mmol) scale*

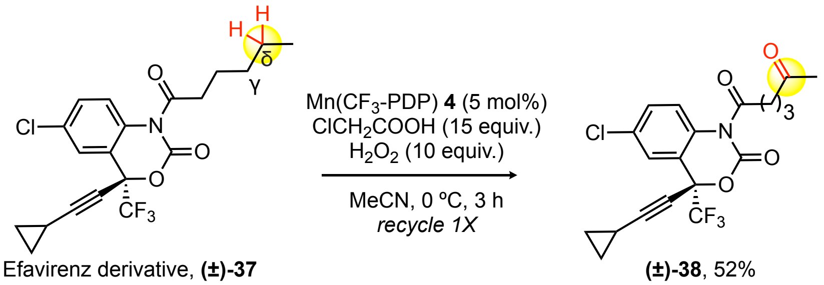


35
1.7 g (6 mmol)

36, 56%
1.0 g (3.4 mmol)

3 (mol %)	**Acid** (equiv.)	$\mathbf{H_2O_2}$ (equiv.)	**Temp.** (°C)	**Yield** (%)
10	$ClCH_2COOH$ (15)	5.0	-36	66
5	$ClCH_2COOH$ (15)	5.0	-36	60
2.5	$ClCH_2COOH$ (15)	5.0	-36	43
10	CH_3COOH (15)	5.0	-36	42[a]
0.1	CH_3COOH (14)	2.5	0	0[a]

B. *Mn(CF_3-PDP)-catalyzed 2° oxidation on 2.5g (6.0 mmol) scale*



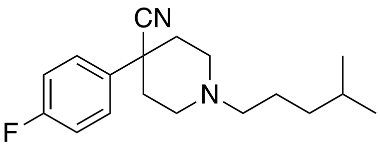
Efavirenz derivative, **(±)-37**
2.5 g (6 mmol)

(±)-38, 52%
4:1 δ:γ
1.3 g (3.1 mmol)

Figure 3. Scale-up C—H oxidations on bioactive molecules. [a]1 h addition of H_2O_2 (in MeCN) instead of 3 h addition.

Preparation of Substrates and Compound Characterization for Supplementary Figure 3

4-(4-fluorophenyl)-1-(4-methylpentyl)piperidine-4-carbonitrile [35]

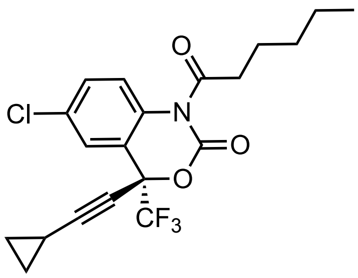


According to general procedure B for N-alkylation, 4-(4-fluorophenyl)piperidine-4-carbonitrile (1.02 g, 5.00 mmol, 1.0 equiv.), 4-methylpentanal (550.9 mg, 5.50 mmol, 1.1 equiv.), acetic acid (0.5 mL) and $NaBH(OAc)_3$ (1.17 g, 5.50 mmol, 1.1 equiv.) were reacted. Flash column chromatography (SiO_2, 5→30% EtOAc/hexanes) followed by recrystallization from ethanol afforded 4-(4-fluorophenyl)-1-(4-methylpentyl)piperidine-4-carbonitrile (**35**) as a white solid (720.0 mg, 2.50 mmol, 50% yield).

^{1}H-NMR (500 MHz, Methanol-*d₄*) δ 7.58 – 7.54 (m, 2H), 7.19 – 7.14 (m, 2H), 3.11 (dt, *J* = 13.2, 3.2 Hz, 2H), 2.47 – 2.42 (m, 4H), 2.16 – 2.07 (m, 4H), 1.63 – 1.54 (m, 3H), 1.26 – 1.21 (m, 2H), 0.93 (d, *J* = 6.6 Hz, 6H). ^{13}C-NMR (126 MHz, Methanol-d_4) δ 163.8 (d, *J* = 246.2 Hz), 137.6 (d, *J* = 3.2 Hz), 128.8 (d, *J* = 8.3 Hz), 122.9, 116.8 (d, *J* = 21.9 Hz), 59.9, 51.9, 43.2, 37.9, 37.2, 29.1, 25.6, 23.0. ^{19}F-NMR (471

MHz, Methanol-d_4) δ -114.14. HRMS (TOF ESI+) *m/z* calculated for $C_{18}H_{26}N_2F$ $[M+H]^+$: 289.2080, found 289.2085.

(±)-6-chloro-4-(cyclopropylethynyl)-1-hexanoyl-4-(trifluoromethyl)-1,4-dihydro-2*H*-benzo[*d*][1,3]oxazin-2-one [37]



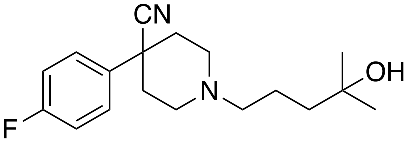
In a flame dried 50 mL recovery flask charged with (±)-efavirenz (1.263 g, 4.0 mmol, 1.0 equiv.) in anhydrous THF (8 mL, 0.5 M), NaH (95%, 121 mg. 4.8 mmol, 1.2 equiv.) was added at 0 ºC and the reaction was stirred at 0 ºC for 10 min. Hexanoyl chloride (531 µL, 3.8 mmol, 0.95 equiv.) was added and the reaction was stirred at room temperature overnight. The reaction was diluted with water and extracted with ethyl acetate. The organic layer was washed with 30 mL 1 M acetic acid solution, 30 mL sat. $NaHCO_3$ then brine. The combined organic layer was dried over Na_2SO_4 and concentrated. Purified by CombiFlash (40 g column) flushing with 100% hexanes → 100% ethyl acetate/hexanes afforded **37** as a white solid (567 mg, 1.37 mmol, 34% yield).

Spectral data in agreement with those previously reported in the literature.[3]

^{1}H-NMR (500 MHz, Methylene Chloride-d_2) 7.65 (d, J = 8.9 Hz, 1H), 7.61 (d, J = 2.4 Hz, 1H), 7.48 (dd, J = 8.9, 2.4 Hz, 1H), 3.04 – 2.98 (m, 1H), 2.90 (dt, J = 17.4, 7.4 Hz, 1H), 1.72 – 1.69 (m, 2H), 1.42 – 1.30 (m, 5H), 0.94 – 0.89 (m, 5H), 0.86 – 0.79 (m, 2H). ^{13}C-NMR (126 MHz, Methylene Chloride- d_2) δ 173.8, 148.4, 133.0, 132.3, 131.2, 126.9, 125.1, 123.4, 122.5 (q, J = 286.5 Hz), 97.4, 78.3 (q, J = 35.1 Hz), 65.6, 38.6, 31.7, 25.0, 23.0, 14.2, 9.3, 9.2, -0.3. ^{19}F-NMR (471 MHz, methylene chloride- d_2) δ -78.50.

C—H Oxidation of Substrates and Product Characterization for Supplementary Figure 3

4-(4-fluorophenyl)-1-(4-hydroxy-4-methylpentyl)piperidine-4-carbonitrile [36]



According to the **general procedure for HBF_4•OEt_2 protection**, 4-(4-fluorophenyl)-1-(4-methylpentyl)piperidine-4-carbonitrile **35** (86.5 mg, 0.300 mmol, 1.0 equiv), was protected with HBF_4•OEt_2 (45 µL, 0.330 mmol, 54 wt.%, 1.1 equiv.) in CH_2Cl_2 (1.2 mL, 0.25 M). The oxidation was carried out according to **General Method B: Single Catalyst Addition Protocol**: the resultant **35•HBF_4** (0.300 mmol, 1.0 equiv.), $ClCH_2CO_2H$ (425 mg, 4.5 mmol, 15.0 equiv.), (*S,S*)-Mn(PDP) catalyst **3** (27.9 mg, 0.030 mmol, 10 mol%), H_2O_2 (50% wt. in H_2O, 102 mg, 1.5 mmol, 5.0 equiv.), MeCN (0.6 mL in 40 mL vial, 3.75 mL with oxidant). The reaction was run at -36 ºC with a 1,2-dichloroethane/dry ice bath. The reaction was worked up according to the **General Procedure for HBF_4 Deprotection**. Flash column chromatography on silica gel (15 mm fritted glass column, 30 mL SiO_2) using 1% MeOH/CH_2Cl_2 → 4% MeOH/CH_2Cl_2 as eluent afforded product **36** as a colorless oil.

10 mol% catalyst:

Run 1: (62.1 mg, 0.204 mmol, 68.0% yield), (15.1 mg, 0.052 mmol, 17.5% rsm). **Run 2:** (60.4 mg, 0.198 mmol, 66.1% yield), (15.9 mg, 0.055 mmol, 18.4% rsm). **Run 3:** (59.4 mg, 0.195 mmol, 65.0% yield), (15.9 mg, 0.055 mmol, 18.4% rsm). **Average: 66.4% yield ± 1.5%, 18.1%± 0.5% rsm.**

5 mol% catalyst: (14.0 mg, 0.015 mmol, 5 mol%)

Run 1: (53.7 mg, 0.176 mmol, 58.8% yield), (29.0 mg, 0.101 mmol, 33.5% rsm). **Run 2:** (54.7 mg, 0.180 mmol, 59.9% yield), (26.2 mg, 0.091 mmol, 30.3% rsm). **Run 3:** (54.6 mg, 0.179 mmol, 59.8% yield), (26.2 mg, 0.091 mmol, 30.2% rsm). **Average: 59.5% yield ± 0.6%, 31.4%± 1.8% rsm.**

2.5 mol% catalyst: (7.0 mg, 0.008 mmol, 2.5 mol%)

Run 1: (40.6 mg, 0.133 mmol, 44.5% yield), (40.8 mg, 0.141 mmol, 47.2% rsm). **Run 2:** (37.7 mg, 0.124 mmol, 41.3% yield), (44.9 mg, 0.156 mmol, 51.9% rsm). **Run 3:** (38.2 mg, 0.125 mmol, 41.8% yield), (45.3 mg, 0.157 mmol, 52.3% rsm). **Average: 42.5% yield ± 1.7%, 50.5%± 2.8% rsm.**

10 mol% catalyst with AcOH: According to the **general procedure for HBF_4•OEt_2 protection**, 4-(4-fluorophenyl)-1-(4-methylpentyl)piperidine-4-carbonitrile **35** (86.5 mg, 0.300 mmol, 1.0 equiv), was protected with HBF_4•OEt_2 (45 µL, 0.330 mmol, 54 wt.%, 1.1 equiv.) in CH_2Cl_2 (1.2 mL, 0.25 M). The oxidation was carried out according to **a modified procedure of General Method B: Single Catalyst Addition Protocol**: the resultant **35•HBF_4** (0.300 mmol, 1.0 equiv.), (*R,R*)-Mn(PDP) catalyst **3** (27.9 mg, 0.030 mmol, 10 mol%), AcOH (270 mg, 4.5 mmol, 15.0 equiv.), H_2O_2 (50% wt. in H_2O, 102 mg, 1.5 mmol, 5.0 equiv.), MeCN (0.6 mL in 40 mL vial, 3.75 mL with oxidant). The reaction was run at -36 ºC with a 1,2-dichloroethane/dry ice bath with a 1 hour addition of H_2O_2 solution by syringe pump (3.75 mL/h). The reaction was worked up according to the **General Procedure for HBF_4 Deprotection**. Flash column chromatography on silica gel (15 mm fritted glass column, 30 mL SiO_2) using 1% MeOH/CH_2Cl_2 → 4% MeOH/CH_2Cl_2 as eluent afforded product **36** as a colorless oil.

Run 1: (37.6 mg, 0.124 mmol, 41.2% yield), (38.6 mg, 0.134 mmol, 44.6% rsm). **Run 2:** (38.5 mg, 0.126 mmol, 42.2% yield), (45.2 mg, 0.157 mmol, 52.2% rsm). **Run 3:** (39.8 mg, 0.131 mmol, 43.6% yield), (37.5 mg, 0.130 mmol, 43.3% rsm). **Average: 42.3% yield ± 1.2%, 46.7%± 4.8% rsm.**

At 0.1 mol% catalyst: According to the **general procedure for HBF_4•OEt_2 protection**, 4-(4-fluorophenyl)-1-(4-methylpentyl)piperidine-4-carbonitrile **35** (57.7 mg, 0.200 mmol, 1.0 equiv), was protected with HBF_4•OEt_2 (30 µL, 0.220 mmol, 54 wt.%, 1.1 equiv.) in CH_2Cl_2 (0.8 mL, 0.25 M). The reaction was run with **General Method A: Low Catalyst Loading (0.1 mol%) Protocol**: **35•HBF_4** (0.200 mmol, 1.0 equiv), CH_3COOH (0.16 mL, 2.8 mmol, 14.0 equiv.), (*R,R*)-Mn(PDP) catalyst **3** solution (40 µL, 5 mM solution in MeCN, 0.20 µmol, 0.001 equiv.), H_2O_2 (50% wt. in H_2O, 34.0 mg, 0.50 mmol, 2.5 equiv.), MeCN (0.4 mL in 40 mL vial, 2.5 mL with oxidant). The reaction was run at 0 °C with an ice/water bath. The reaction was worked up according to the **General Procedure for HBF_4 Deprotection**. The crude mixture was analyzed by quantitative ^{1}H NMR analysis with mesitylene added as internal standard.

Run 1: (0% yield), (100% rsm). **Run 2: (**0% yield), (100% rsm). **Average: 0% yield, 100% rsm.**

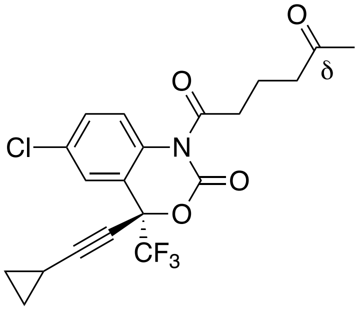
^{1}H-NMR (500 MHz, CD_3OD) δ 7.60 – 7.53 (m, 2H), 7.20 – 7.12 (m, 2H), 3.12 (dt, *J* = 13.4, 3.2 Hz, 2H), 2.51 – 2.40 (m, 4H), 2.21 – 2.04 (m, 4H), 1.73 – 1.62 (m, 2H), 1.57 – 1.47 (m, 2H), 1.21 (s, 6H). ^{13}C-NMR (126 MHz, CD_3OD) δ 163.7 (d, *J* = 246.2 Hz), 137.6 (d, *J* = 0.1 Hz), 128.8 (d, *J* = 8.3 Hz), 122.9, 116.8 (d, *J* = 21.8 Hz), 70.9, 60.1, 51.8, 43.2, 42.7, 37.2, 29.4, 22.5. ^{19}F NMR (471 MHz, CD_3OD) δ -114.14. HRMS (TOF ESI+) *m/z* calculated for $C_{18}H_{26}N_2OF$ $[M+H]^+$: 305.2029, found 305.2028.

Scale Up oxidation of 4-(4-fluorophenyl)-1-(4-methylpentyl)piperidine-4-carbonitrile [35] using 5 mol% Mn(PDP) 3

4-(4-fluorophenyl)-1-(4-methylpentyl)piperidine-4-carbonitrile **35** was recrystallized from ethanol a second time prior to scale up oxidation. According to the **general procedure for HBF_4•OEt_2 protection**, 4-(4-fluorophenyl)-1-(4-methylpentyl)piperidine-4-carbonitrile **35** (1.730 g, 6.0 mmol, 1.0 equiv), was protected with HBF_4•OEt_2 (0.9 mL, 6.60 mmol, 54 wt.%, 1.1 equiv.) in CH_2Cl_2 (24.0 mL, 0.25 M). The reaction was run with a modified **General Method B: Single Catalyst Addition Protocol**. the resultant **35•HBF_4** (6.0 mmol, 1.0 equiv), (*S,S*)-Mn(PDP) catalyst **3** (279.3 mg, 0.300 mmol, 5 mol%), $ClCH_2CO_2H$ (8.504 g, 90.0 mmol, 15.0 equiv.), H_2O_2 (50% wt. in H_2O, 2.041 g, 30.0 mmol, 5.0 equiv.), MeCN (12 mL in a 300 mL round bottom flask, 75 mL with oxidant, divided into three equal batches and loaded into 3 50 mL syringes). The reaction was run at -36 ºC with a 1,2-dichloroethane/dry ice bath. After each 1 hour of addition that depleted the syringe of oxidant solution, the next syringe with oxidant solution was loaded into the syringe pump and addition continued. Upon the completion of all oxidant addition, the reaction was worked up according to the **General Procedure for HBF_4 Deprotection**. Flash column chromatography on silica gel (35 mm fritted glass column, 150 mL SiO_2) using CH_2Cl_2 → 5% MeOH/CH_2Cl_2 as eluent afforded product **36** as a colorless oil.

Run 1: (1.0342 g, 3.397 mmol, 56.6% yield), (533.6 mg, 1.850 mmol, 30.8% rsm). **Run 2:** (1.0177 g, 3.343 mmol, 55.7% yield), (608.4 mg, 2.109 mmol, 35.2% rsm). **Average: 56.2% yield, 33.0% rsm.**

(±)-1-(6-chloro-4-(cyclopropylethynyl)-2-oxo-4-(trifluoromethyl)-2*H*-benzo[*d*][1,3]oxazin-1(4*H*)-yl)hexane-1,5-dione [38a]



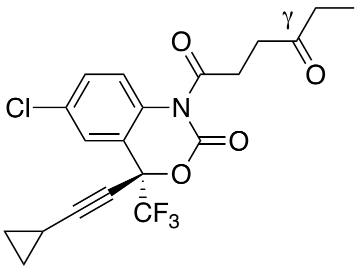
The reaction was run with a modified **General Method B: Single Catalyst Addition Protocol**. 6-chloro-4-(cyclopropylethynyl)-1-hexanoyl-4-(trifluoromethyl)-1,4-dihydro-2*H*-benzo[*d*][1,3]oxazin-2-one **37** (82.8 mg, 0.200 mmol, 1.0 equiv), (*R,R*)-Mn(CF_3-PDP) catalyst **4** (13.6 mg, 0.010 mmol, 5 mol%), $ClCH_2CO_2H$ (284 mg, 3.0 mmol, 15.0 equiv.), H_2O_2 (50% wt. in H_2O, 136 mg, 2.0 mmol, 10.0 equiv.), MeCN (0.4 mL in 40 mL vial, 2.5 mL with oxidant). The reaction was run at 0 ºC with an ice/water bath. The reaction was worked up with 9 mL saturated $NaHCO_3$ and DCM as described in the General Method B. Flash column chromatography on silica (35 mm fritted glass column, 150 mL SiO_2) using 10% ethyl acetate/hexanes → 25% ethyl acetate/hexanes → 50% ethyl acetate/hexanes as eluent afforded δ-ketone (**38a**) and γ–ketone (**38b**) products as white solid.

Run 1: (10.9 mg, 0.025 mmol, 12.7% yield of γ-ketone **38b**), (31.9 mg, 0.075 mmol, 37.3% yield of δ-ketone **38a**), (50.0% overall yield, 2.9:1 δ:γ ratio), (26.0 mg, 0.063 mmol, 31.4% rsm).

Spectral data in agreement with those previously reported in the literature.[3]

^{1}H NMR (500 MHz, Methylene Chloride-d_2) δ 7.66 (d, J = 8.9 Hz, 1H), 7.62 (d, J = 2.4 Hz, 1H), 7.48 (dd, J = 8.9, 2.4 Hz, 1H), 3.05 (ddd, J = 17.8, 7.7, 6.7 Hz, 1H), 2.91 (dt, J = 17.7, 7.3 Hz, 1H), 2.53 (t, J = 7.2 Hz, 2H), 2.11 (s, 3H), 1.95 (p, J = 7.2 Hz, 2H), 1.41 (tt, J = 8.3, 5.1 Hz, 1H), 0.96 – 0.91 (m, 2H), 0.83 (tdd, J = 6.2, 5.5, 3.2 Hz, 2H). ^{13}C NMR (126 MHz, Methylene Chloride-d_2) δ 208.0, 173.2, 148.4, 132.8, 132.5, 131.2, 127.0, 125.2, 123.6, 122.5 (q, J = 286.7 Hz), 97.6, 78.4 (q, J = 35.1 Hz), 65.5, 42.6, 37.6, 30.2, 19.3, 9.3, 9.2, -0.3. ^{19}F NMR (471 MHz, Methylene Chloride-d_2) δ -78.50.

(±)-1-(6-chloro-4-(cyclopropylethynyl)-2-oxo-4-(trifluoromethyl)-2*H*-benzo[*d*][1,3]oxazin-1(4*H*)-yl)hexane-1,4-dione [38b]



^{1}H NMR (500 MHz, Methylene Chloride-d_2) δ 7.61 (d, *J* = 2.5 Hz, 1H), 7.59 (d, *J* = 8.9 Hz, 1H), 7.46 (dd, *J* = 8.9, 2.4 Hz, 1H), 3.28 (ddd, *J* = 18.5, 7.5, 5.0 Hz, 1H), 3.14 (ddd, *J* = 18.5, 7.0, 4.7 Hz, 1H), 2.91 – 2.77 (m, 2H), 2.49 (q, *J* = 7.4 Hz, 2H), 1.43 (tt, *J* = 8.3, 5.0 Hz, 1H), 1.04 (t, *J* = 7.3 Hz, 3H), 0.96 – 0.91 (m, 2H), 0.87 – 0.82 (m, 2H). ^{13}C NMR (126 MHz, Methylene Chloride-d_2) δ 209.5, 173.6, 148.1, 133.0, 132.3, 131.3, 127.1, 125.0, 123.1, 122.5 (q, *J* = 286.8 Hz), 97.6, 78.5 (q, *J* = 35.2 Hz), 65.5, 37.2, 36.2, 33.2, 9.2, 9.2, 8.1, -0.2. ^{19}F NMR (471 MHz, Methylene Chloride-d_2) δ -78.72.

Scale up oxidation of efavirenz derivative 37 using 5 mol% Mn(CF$_3$-PDP):

The reaction was run with a modified **General Method B: Single Catalyst Addition Protocol**. 6-chloro-4-(cyclopropylethynyl)-1-hexanoyl-4-(trifluoromethyl)-1,4-dihydro-2*H*-benzo[*d*][1,3]oxazin-2-one **37** (2.4831 g, 6.0 mmol, 1.0 equiv), (*R,R*)-Mn(CF$_3$-PDP) catalyst **4** (406.6 mg, 0.300 mmol, 5 mol%), $ClCH_2CO_2H$ (8.504 g, 90.0 mmol, 15.0 equiv.), H_2O_2 (50% wt. in H_2O, 4.080 g, 60.0 mmol, 10.0 equiv.), MeCN (12 mL in a 300 mL round bottom flask to dissolve catalyst, substrate and chloroacetic acid) + MeCN (75 mL with oxidant, divided into two equal batches and loaded into 2 50 mL syringes). The reaction was run at 0 ºC with an ice/water bath. After 1.5 hours of addition that deplete the first syringe of oxidant solution, the second syringe with remaining half oxidant solution is loaded to syringe pump and continue addition. Upon the completion of all oxidant addition, the reaction was concentrated then worked up with a solution of 100 mL saturated $NaHCO_3$ and 100 mL water, 3 X 100 mL DCM was used to extract, and the organic layer is dried with Na_2SO_4. The crude reaction was loaded to Celite and purified directly on CombiFlash using a 40 g column flashing with 0% ethyl acetate/hexanes → 25% ethyl acetate/hexanes as eluent afforded δ-ketone (**38a**) and γ-ketone (**38b**) products as white solid. Recovered starting material **37** was collected and rotvaped into a 100 mL recovery flask and recycled 1X using the same oxidation protocol (equivalence of all reagents were calculated based on the amount of recovered **37** from the first oxidation).

Run 1: *cycle 1:* (210.0 mg, 0.491 mmol, 8.2% yield of γ-ketone **38b**), (882.7 mg, 2.06 mmol, 34.4% yield of δ-ketone **38a**), (604.4 mg, 1.46 mmol, 24.3% rsm). *cycle 2:* (47.8 mg, 0.117 mmol, 7.6% yield of γ-ketone **38b**), (208.1 mg, 0.486 mmol, 33.3% yield of δ-ketone **38a**), (151.5 mg, 0.366 mmol, 25.1% rsm). *Overall:* (257.8 mg, 0.603 mmol, 10.0% yield of γ-ketone **38b**), (1090.8 mg, 2.55 mmol, 42.5% yield of δ-ketone **38a**), (52.5% overall yield, 4.3:1 δ:γ ratio), (151.5 mg, 0.366 mmol, 6.1% rsm). **Run 2:** *cycle 1:* (187.4 mg, 0.438 mmol, 7.3% yield of γ-ketone **38b**), (826.4 mg, 1.93 mmol, 32.2% yield of δ-ketone **38a**), (738.1 mg, 1.78 mmol, 29.7% rsm). *cycle 2:* (55.4 mg, 0.129 mmol, 7.3% yield of γ-ketone **38b**), (267.4 mg, 0.625 mmol, 35.1% yield of δ-ketone **38a**), (189.0 mg, 0.457 mmol, 25.7% rsm). *Overall:* (242.8 mg, 0.568 mmol, 9.5% yield of γ-ketone **38b**), (1093.8 mg, 2.56 mmol, 42.6% yield of δ-ketone **38a**), (52.1% overall yield, 4.5:1 δ:γ ratio), (189.0 mg, 0.457 mmol, 7.6% rsm). **Average: 52.3% overall yield, 4:1 δ:γ., 6.9% rsm.**

X. References

1 M. S. Chen; M. C. White, *Science* **2007**, *318*, 783.

2 J. B. C. Mack.; J. D. Gipson; J. Du Bois; M. S. Sigman, *J. Am. Chem. Soc.* **2017**, *139*, 9503.

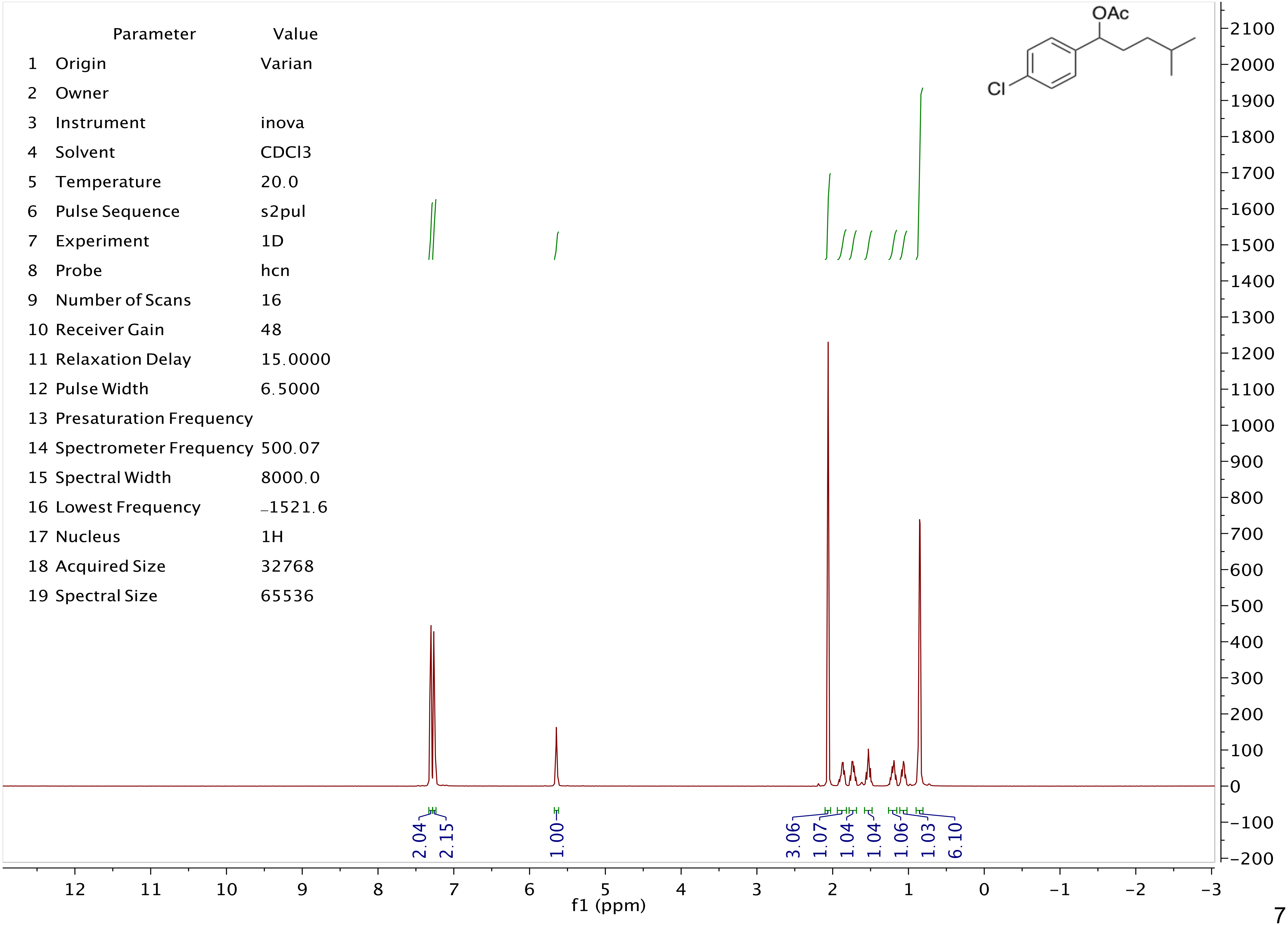
3 J. Zhao; T. Nanjo; E. de Lucca Jr.; M. C. White, *Nat. Chem.* **2019**, *11*, 213.

4 W. C. Still; M. Kahn; A. Mitra, *J. Org. Chem.* **1978**, *43*, 2923.

5 A. M. Adams; J. Du Bois; H. A. Malik, *Org. Lett.* **2015**, *17*, 6066.

6 R. V. Ottenbacher; D. G. Samsonenko; E. P. Talsi; K. P. Bryliakov, *Org. Lett.* **2012**, *14*, 4310.

7 J. M. Howell; K. Feng; J. R. Clark; L. J. Trezpkowski; M. C. White, *J. Am. Chem. Soc.* **2015**, *137*, 14590.



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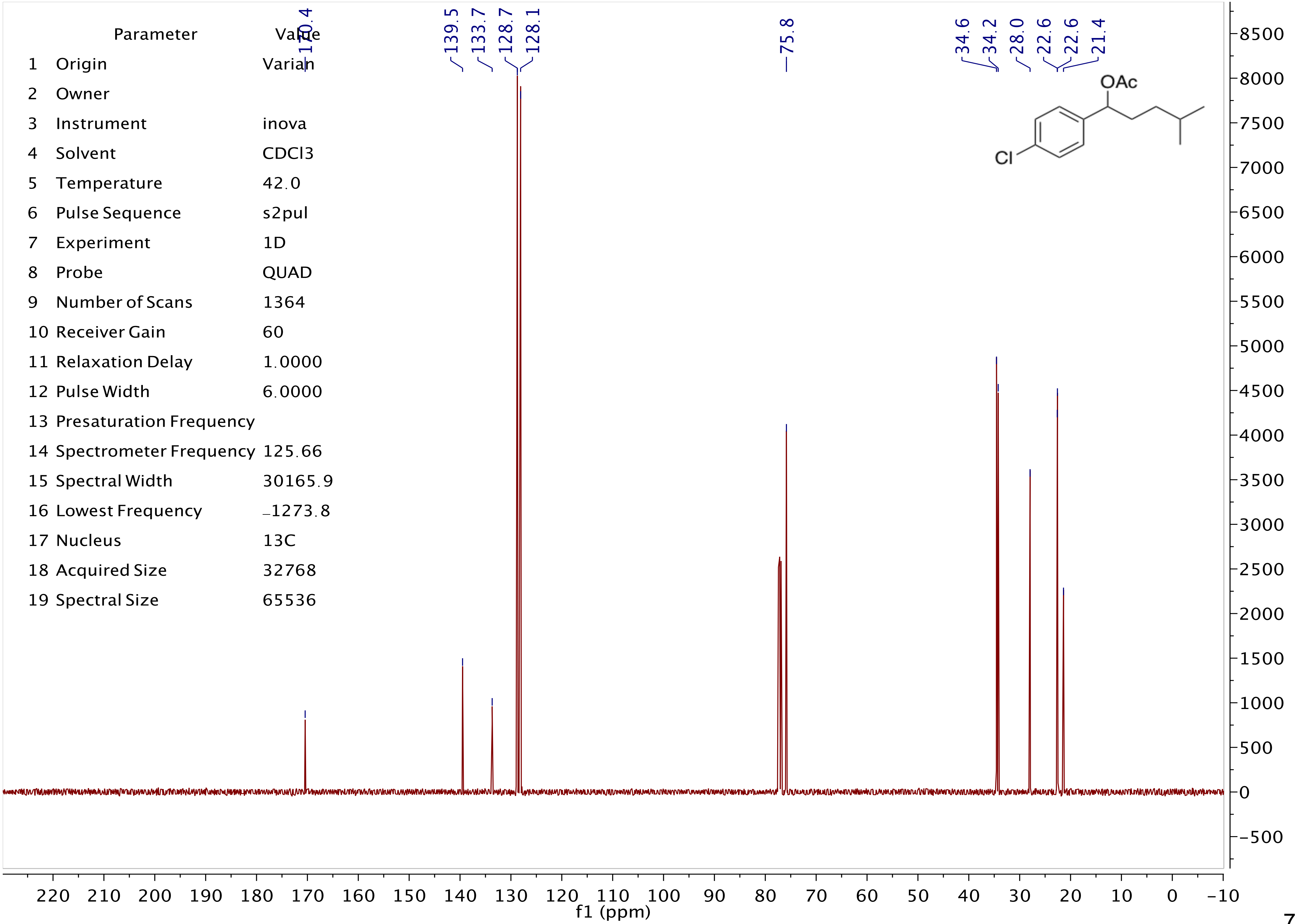

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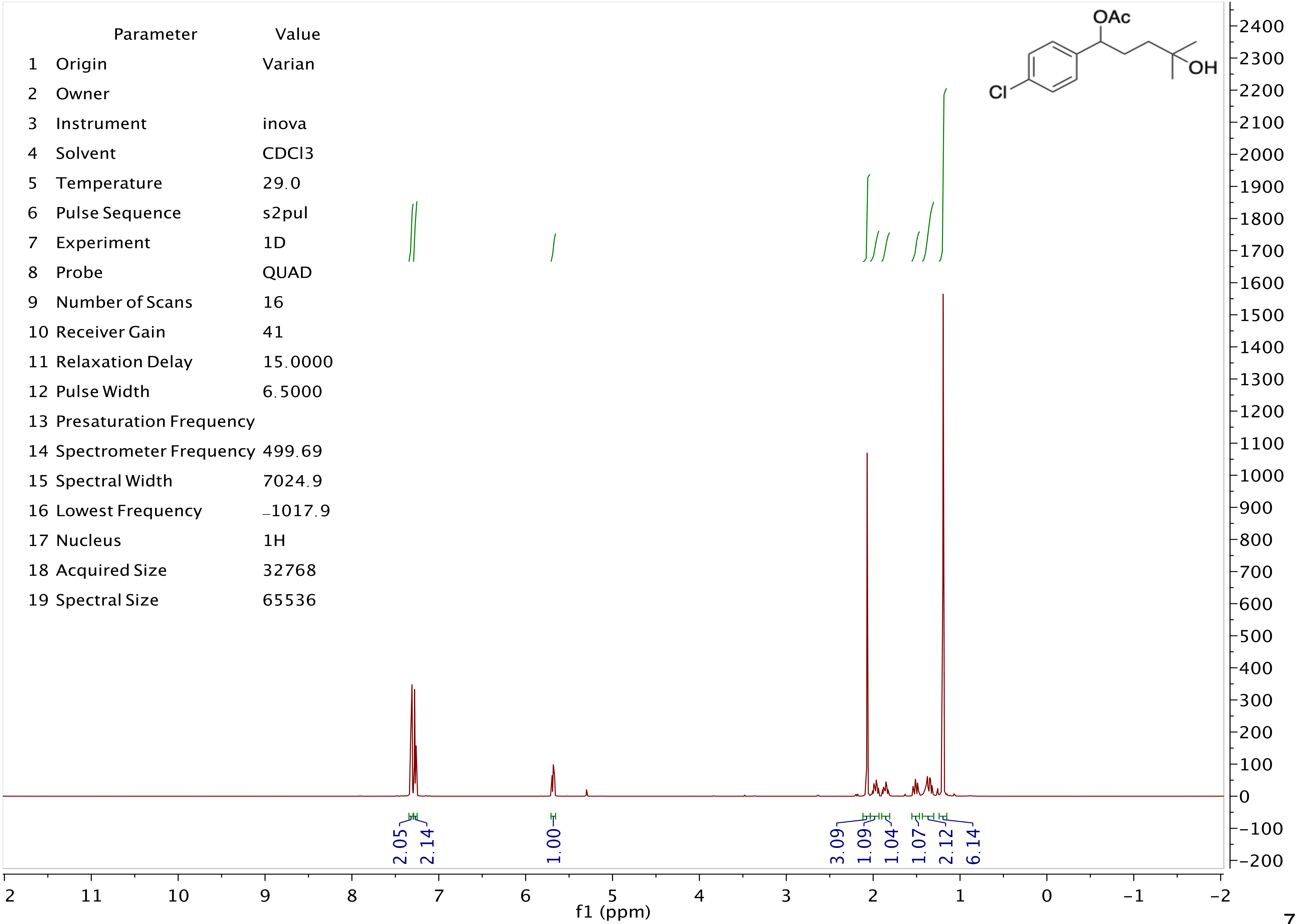

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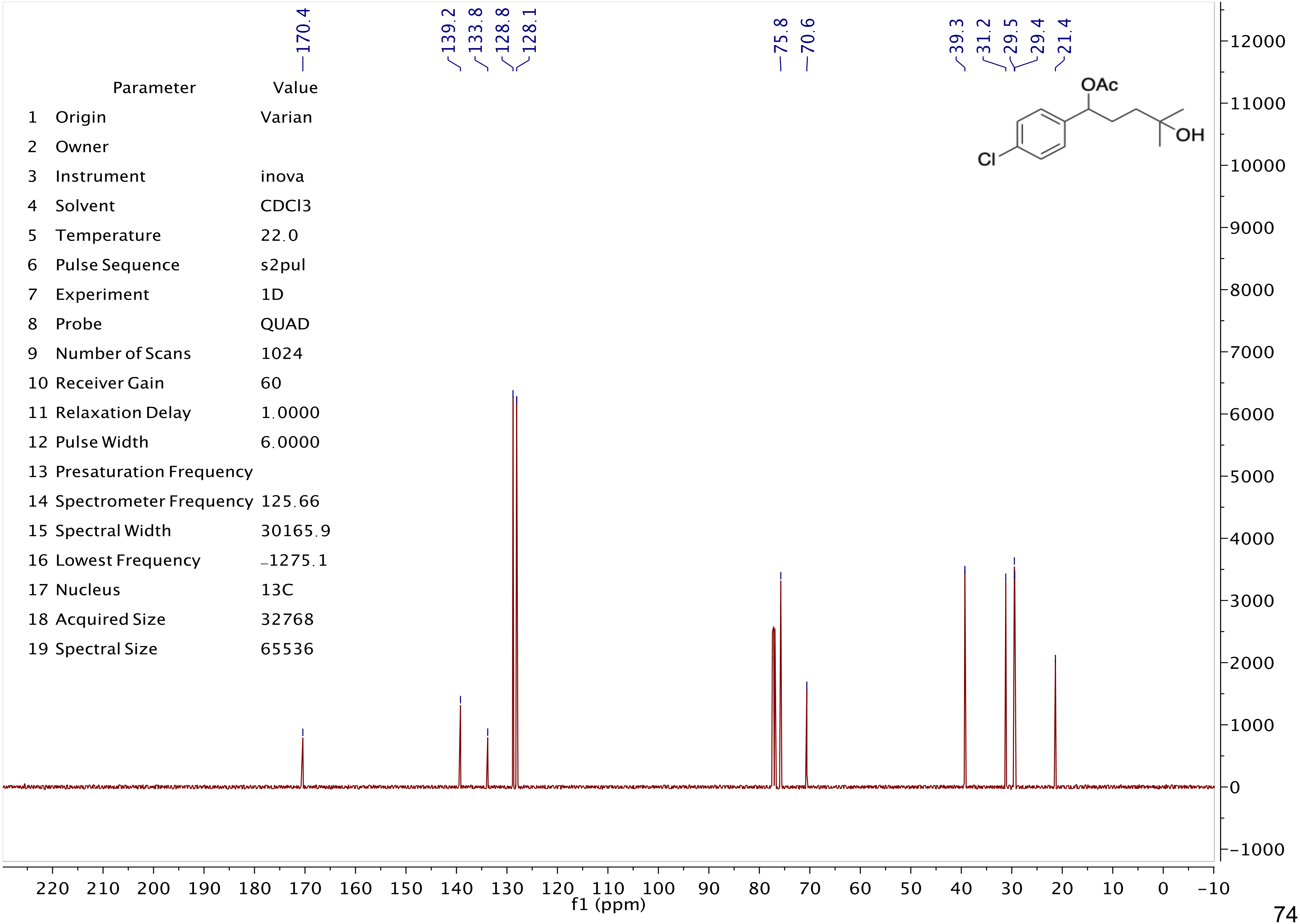

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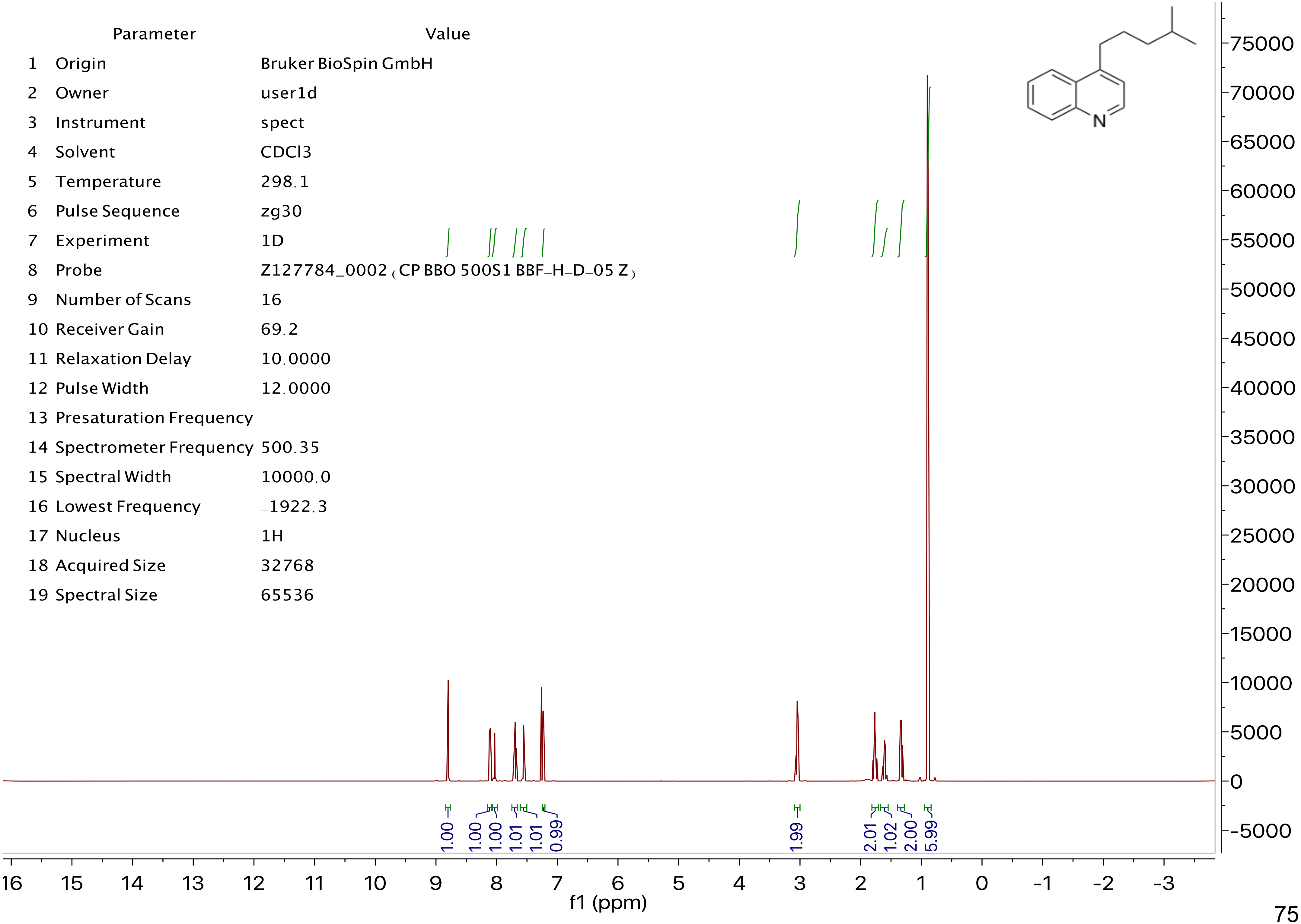

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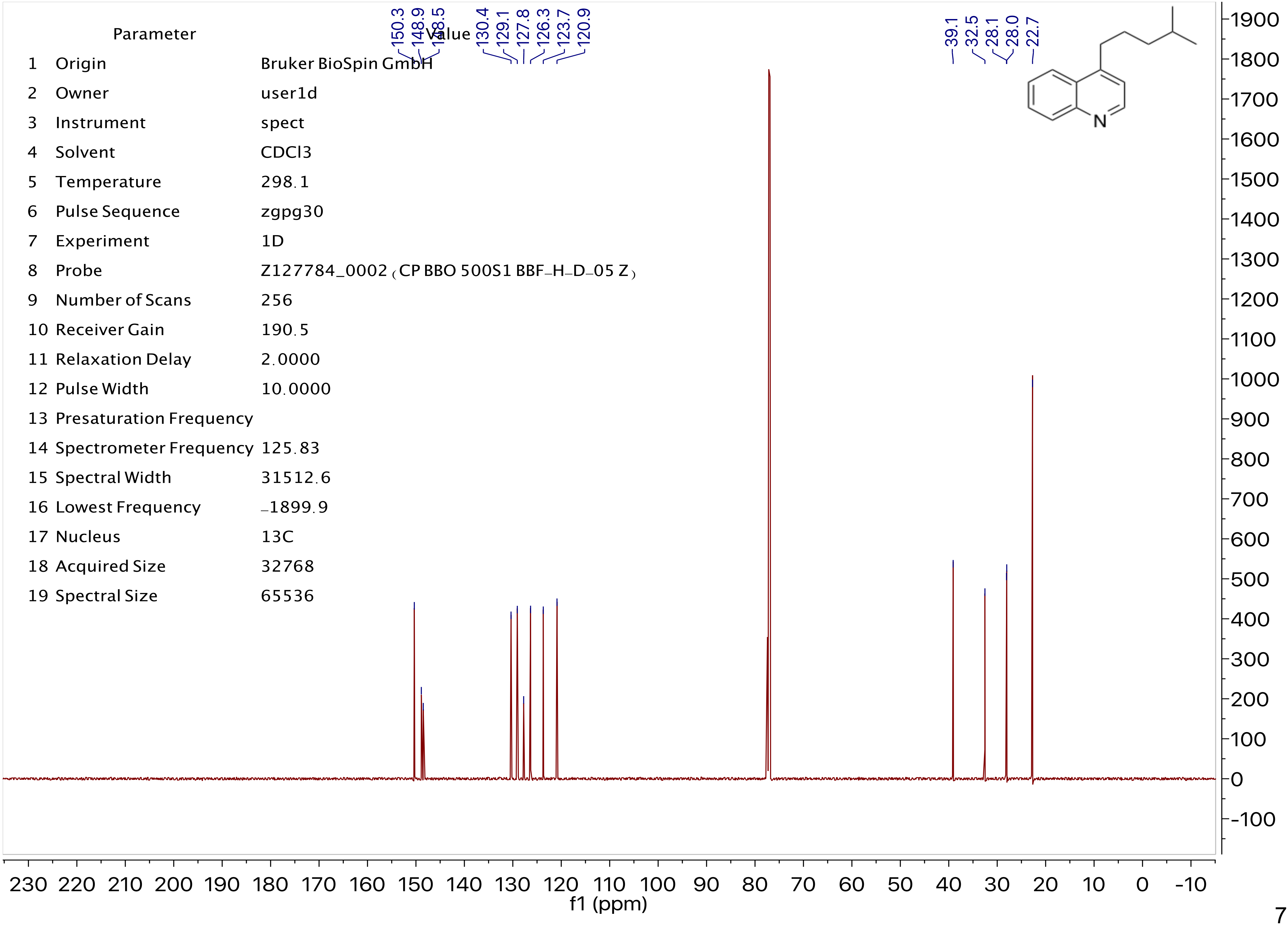

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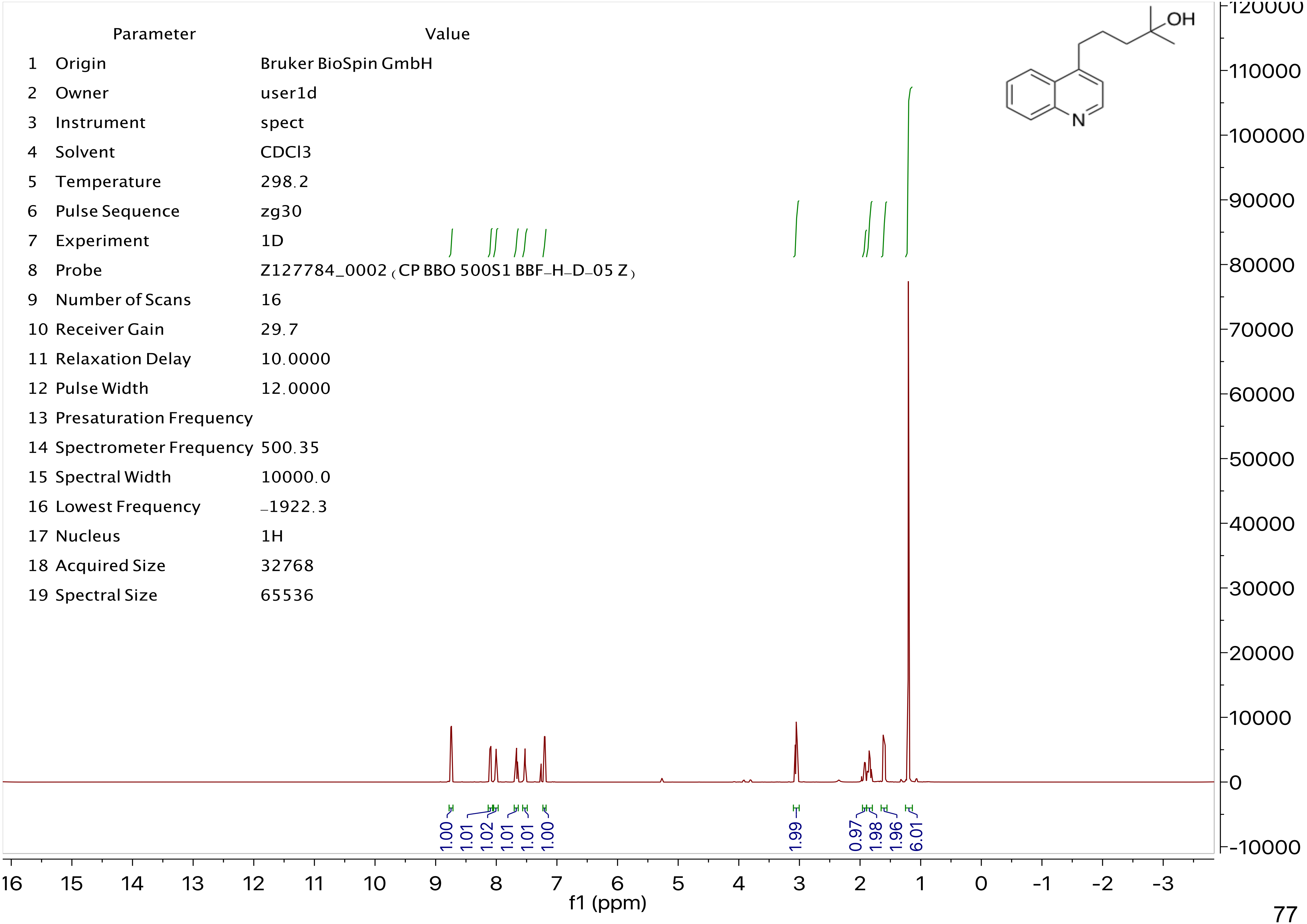
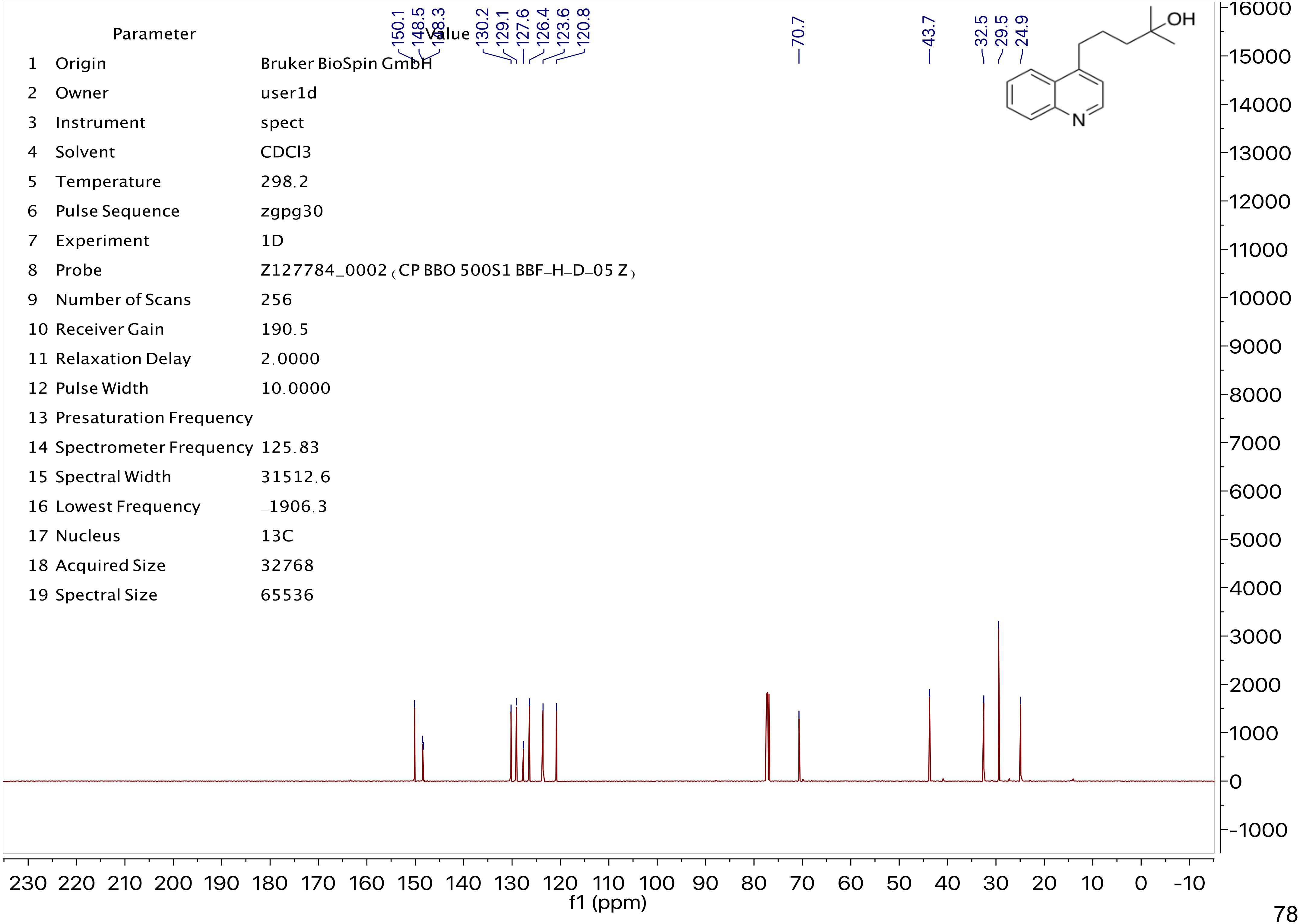
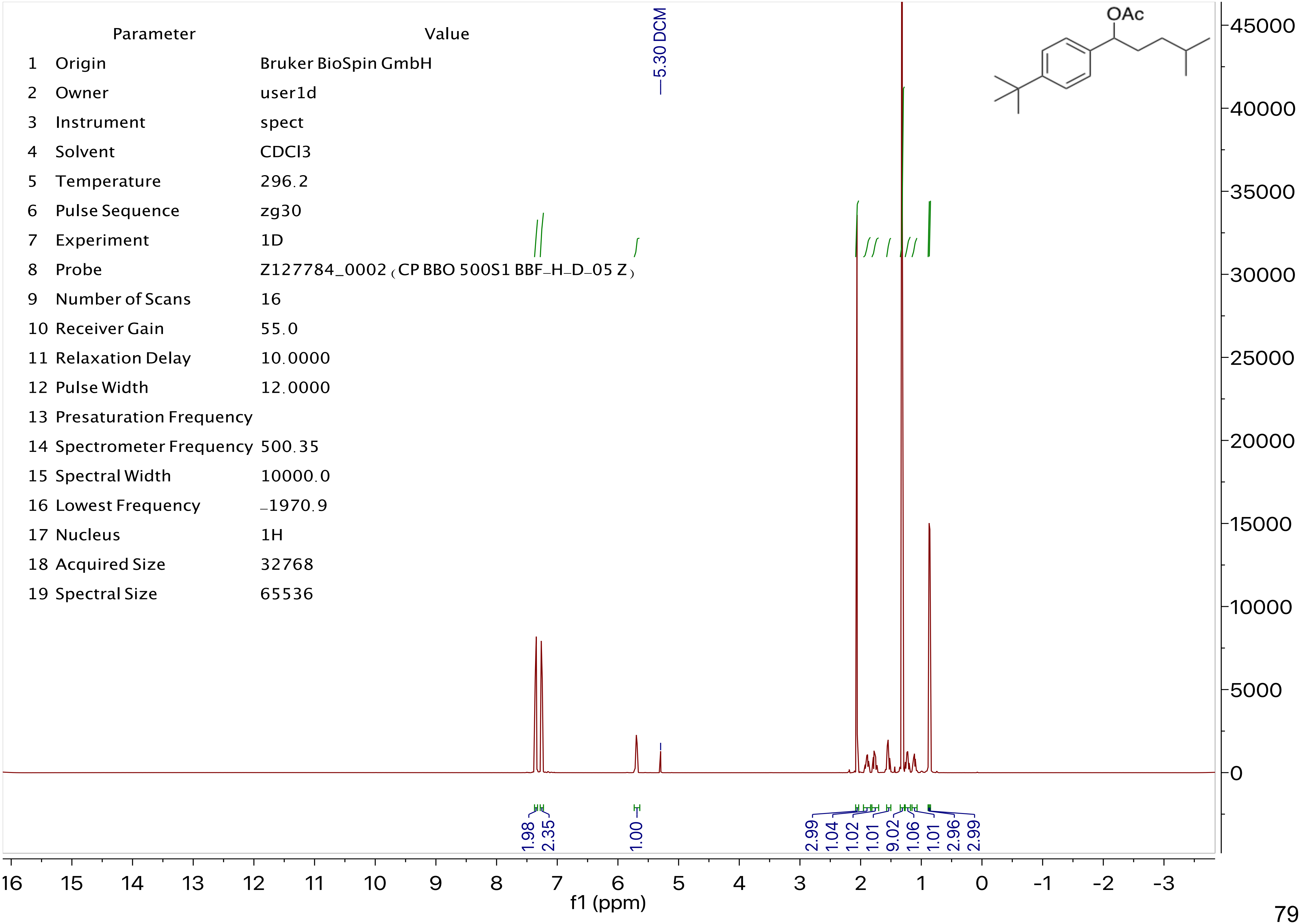
18	Acquired Size	32768
19	Spectral Size	65536



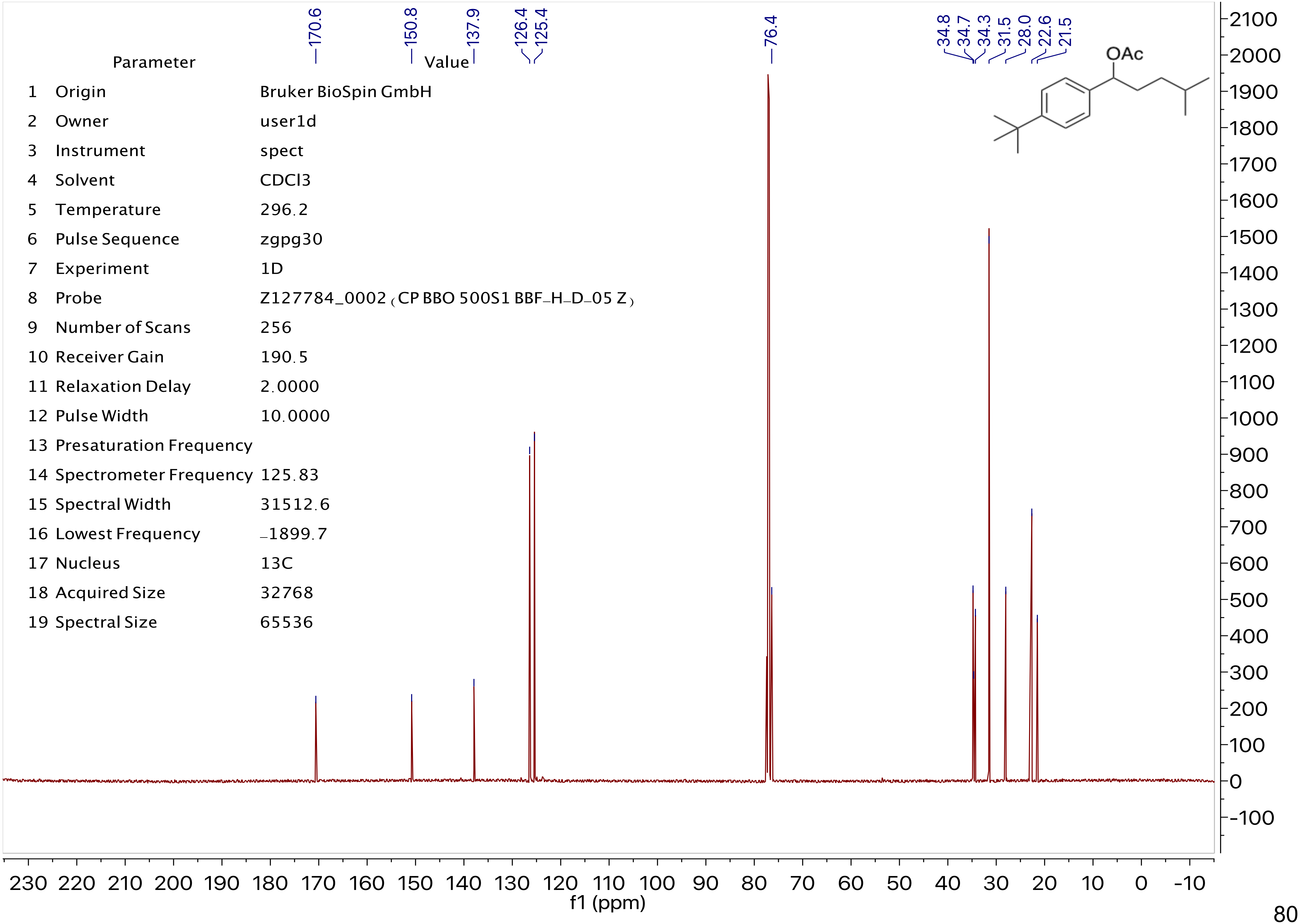
	Parameter	Value
1	Origin	Bruker BioSpin GmbH
2	Owner	user1d
3	Instrument	spect
4	Solvent	CDCl3
5	Temperature	298.2
6	Pulse Sequence	zg30
7	Experiment	1D
8	Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
9	Number of Scans	16
10	Receiver Gain	29.7
11	Relaxation Delay	10.0000
12	Pulse Width	12.0000
13	Presaturation Frequency	
14	Spectrometer Frequency	500.35
15	Spectral Width	10000.0
16	Lowest Frequency	-1922.3
17	Nucleus	1H
18	Acquired Size	32768
19	Spectral Size	65536



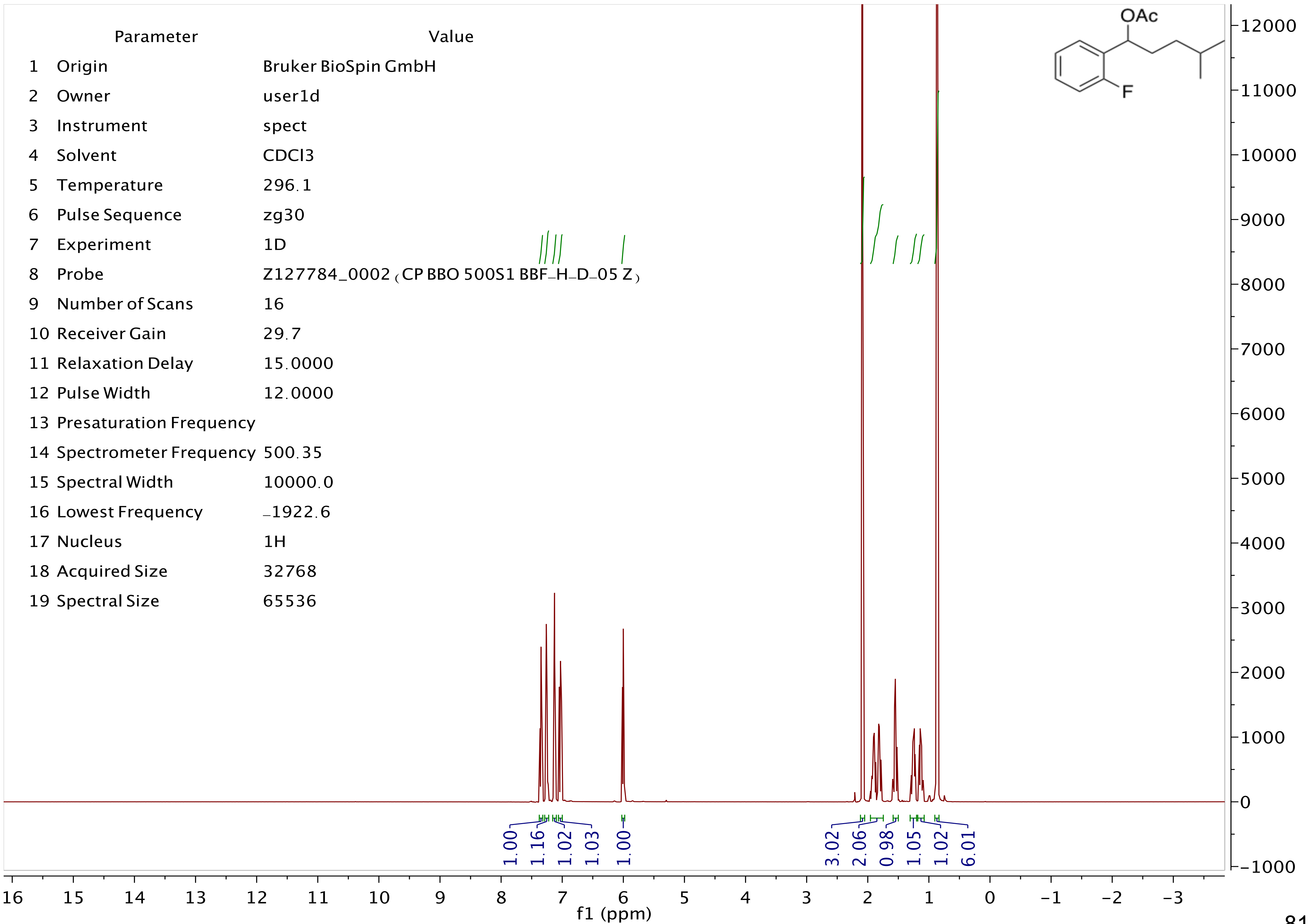
	Parameter	Value
1	Origin	Bruker BioSpin GmbH
2	Owner	user1d
3	Instrument	spect
4	Solvent	CDCl3
5	Temperature	298.2
6	Pulse Sequence	zgpg30
7	Experiment	1D
8	Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
9	Number of Scans	256
10	Receiver Gain	190.5
11	Relaxation Delay	2.0000
12	Pulse Width	10.0000
13	Presaturation Frequency	
14	Spectrometer Frequency	125.83
15	Spectral Width	31512.6
16	Lowest Frequency	-1906.3
17	Nucleus	13C
18	Acquired Size	32768
19	Spectral Size	65536



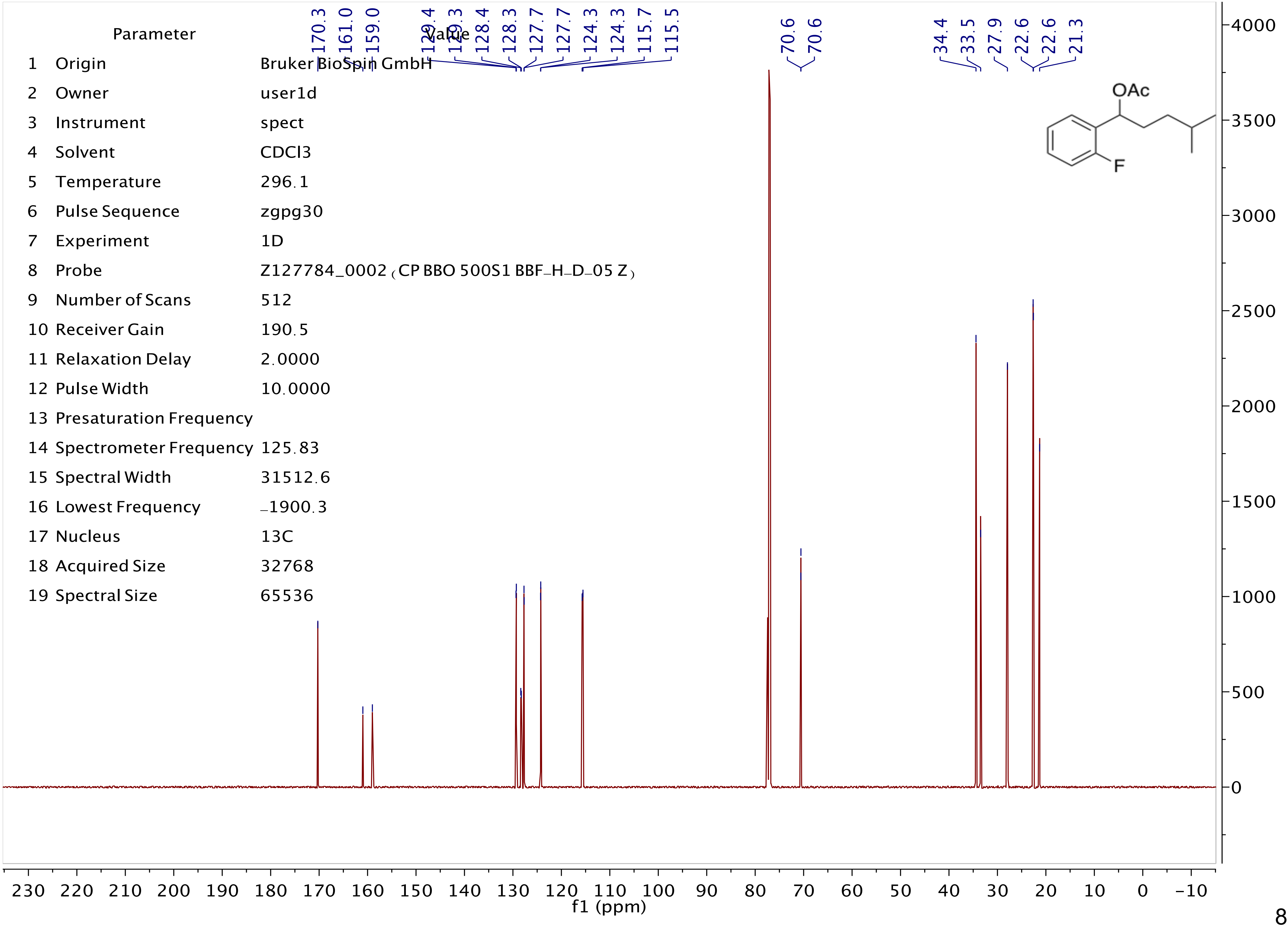
	Parameter	Value
1	Origin	Bruker BioSpin GmbH
2	Owner	user1d
3	Instrument	spect
4	Solvent	CDCl3
5	Temperature	296.2
6	Pulse Sequence	zg30
7	Experiment	1D
8	Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
9	Number of Scans	16
10	Receiver Gain	55.0
11	Relaxation Delay	10.0000
12	Pulse Width	12.0000
13	Presaturation Frequency	
14	Spectrometer Frequency	500.35
15	Spectral Width	10000.0
16	Lowest Frequency	-1970.9
17	Nucleus	1H
18	Acquired Size	32768
19	Spectral Size	65536



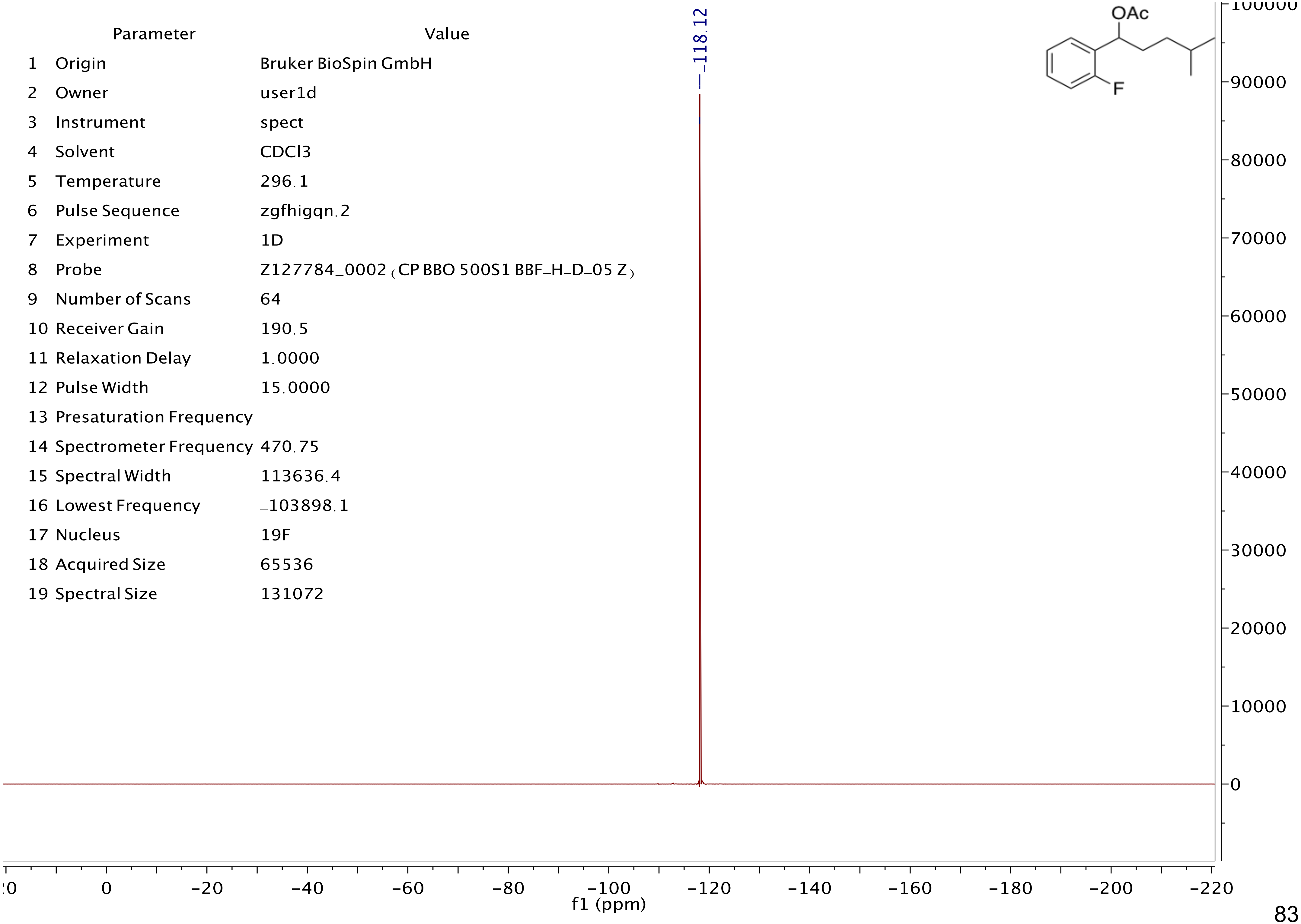
	Parameter	Value
1	Origin	Bruker BioSpin GmbH
2	Owner	user1d
3	Instrument	spect
4	Solvent	CDCl3
5	Temperature	296.2
6	Pulse Sequence	zgpg30
7	Experiment	1D
8	Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
9	Number of Scans	256
10	Receiver Gain	190.5
11	Relaxation Delay	2.0000
12	Pulse Width	10.0000
13	Presaturation Frequency	
14	Spectrometer Frequency	125.83
15	Spectral Width	31512.6
16	Lowest Frequency	-1899.7
17	Nucleus	13C
18	Acquired Size	32768
19	Spectral Size	65536



	Parameter	Value
1	Origin	Bruker BioSpin GmbH
2	Owner	user1d
3	Instrument	spect
4	Solvent	CDCl3
5	Temperature	296.1
6	Pulse Sequence	zg30
7	Experiment	1D
8	Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
9	Number of Scans	16
10	Receiver Gain	29.7
11	Relaxation Delay	15.0000
12	Pulse Width	12.0000
13	Presaturation Frequency	
14	Spectrometer Frequency	500.35
15	Spectral Width	10000.0
16	Lowest Frequency	-1922.6
17	Nucleus	1H
18	Acquired Size	32768
19	Spectral Size	65536

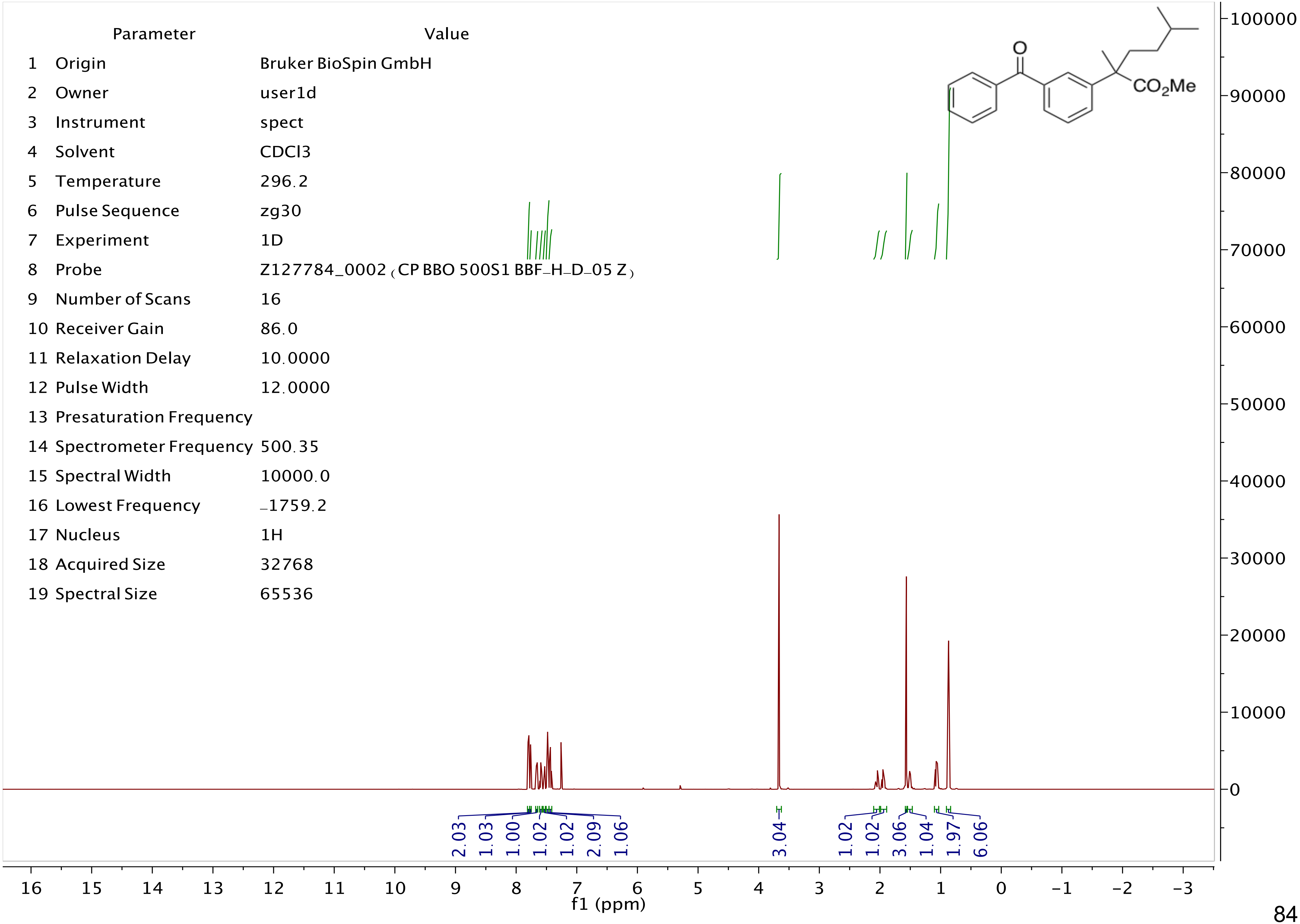


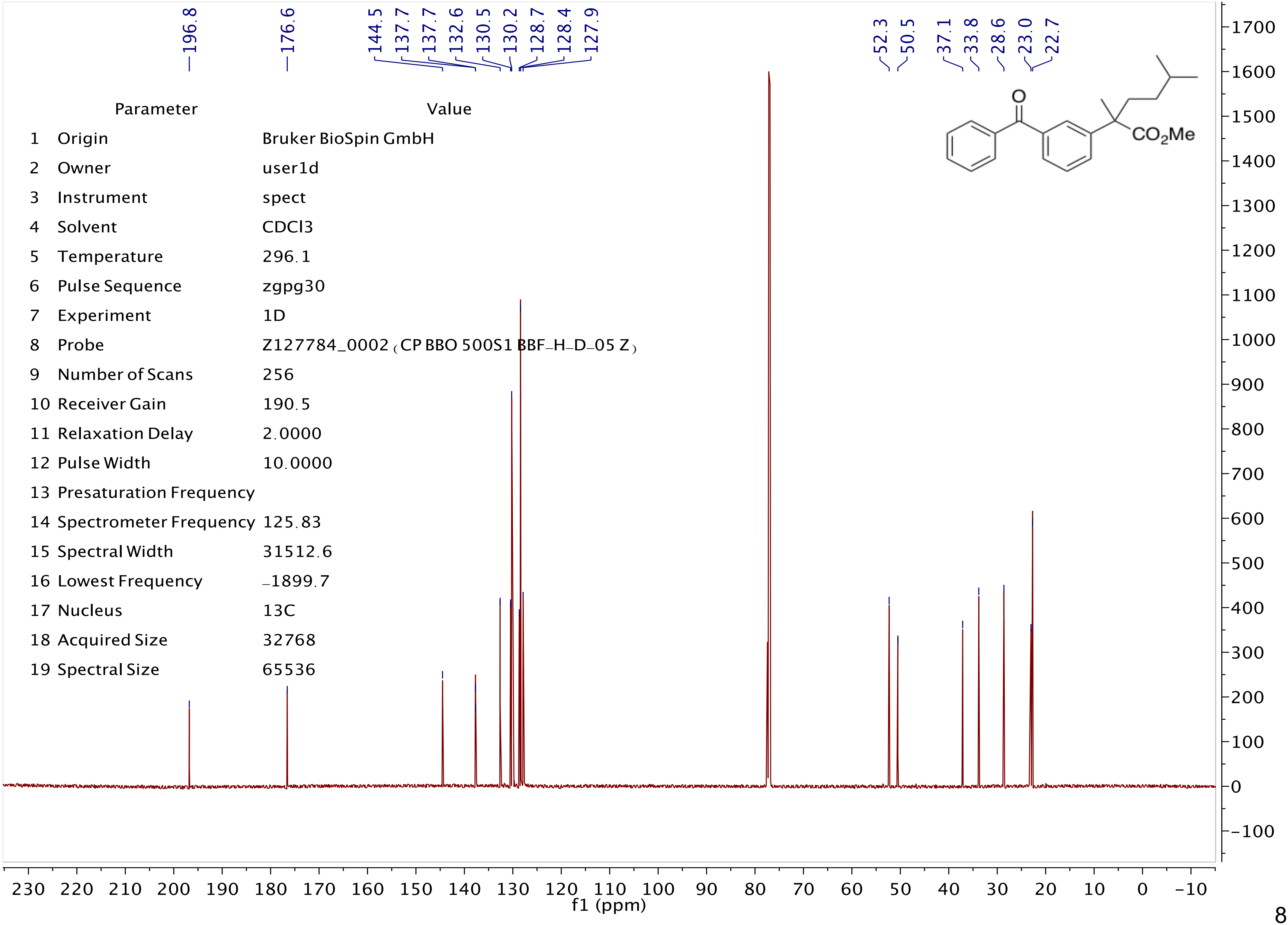
	Parameter	Value
1	Origin	Bruker BioSpin GmbH
2	Owner	user1d
3	Instrument	spect
4	Solvent	CDCl3
5	Temperature	296.1
6	Pulse Sequence	zgpg30
7	Experiment	1D
8	Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
9	Number of Scans	512
10	Receiver Gain	190.5
11	Relaxation Delay	2.0000
12	Pulse Width	10.0000
13	Presaturation Frequency	
14	Spectrometer Frequency	125.83
15	Spectral Width	31512.6
16	Lowest Frequency	-1900.3
17	Nucleus	13C
18	Acquired Size	32768
19	Spectral Size	65536



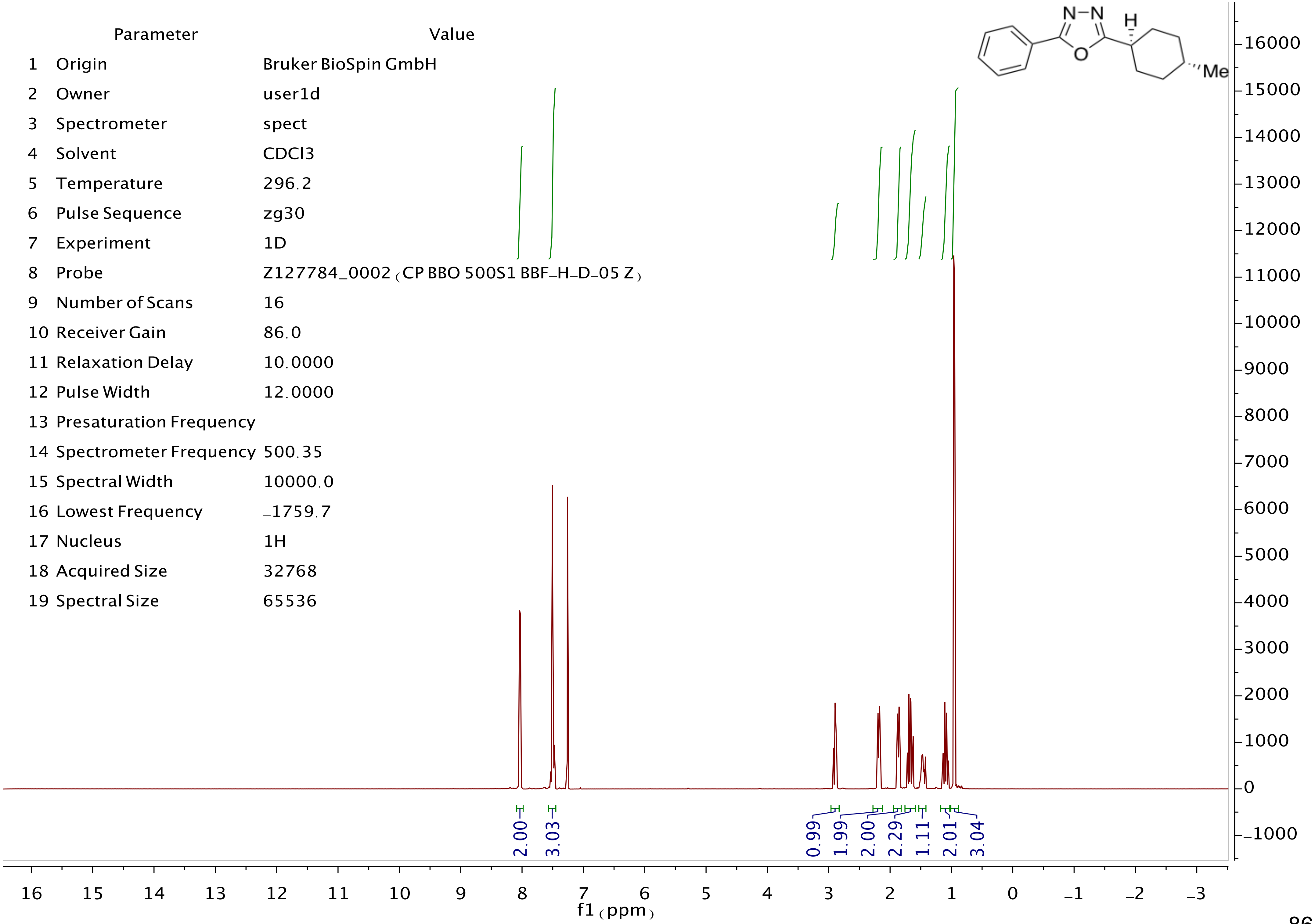
	Parameter	Value
1	Origin	Bruker BioSpin GmbH
2	Owner	user1d
3	Instrument	spect
4	Solvent	CDCl3
5	Temperature	296.1
6	Pulse Sequence	zgfhigqn.2
7	Experiment	1D
8	Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
9	Number of Scans	64
10	Receiver Gain	190.5
11	Relaxation Delay	1.0000
12	Pulse Width	15.0000
13	Presaturation Frequency	
14	Spectrometer Frequency	470.75
15	Spectral Width	113636.4
16	Lowest Frequency	-103898.1
17	Nucleus	19F
18	Acquired Size	65536
19	Spectral Size	131072

	Parameter	Value
1	Origin	Bruker BioSpin GmbH
2	Owner	user1d
3	Instrument	spect
4	Solvent	CDCl3
5	Temperature	296.2
6	Pulse Sequence	zg30
7	Experiment	1D
8	Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
9	Number of Scans	16
10	Receiver Gain	86.0
11	Relaxation Delay	10.0000
12	Pulse Width	12.0000
13	Presaturation Frequency	
14	Spectrometer Frequency	500.35
15	Spectral Width	10000.0
16	Lowest Frequency	-1759.2
17	Nucleus	1H
18	Acquired Size	32768
19	Spectral Size	65536

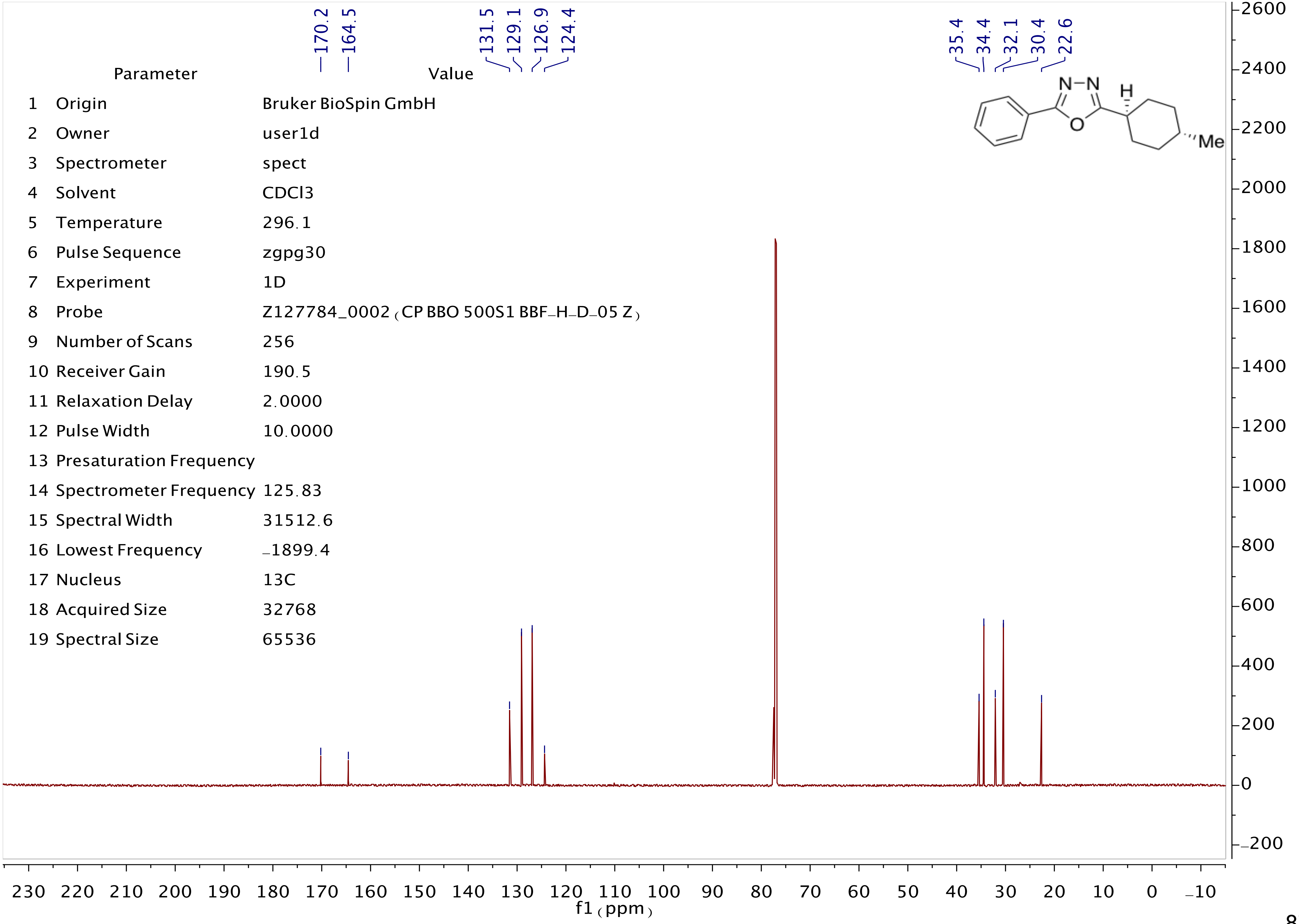




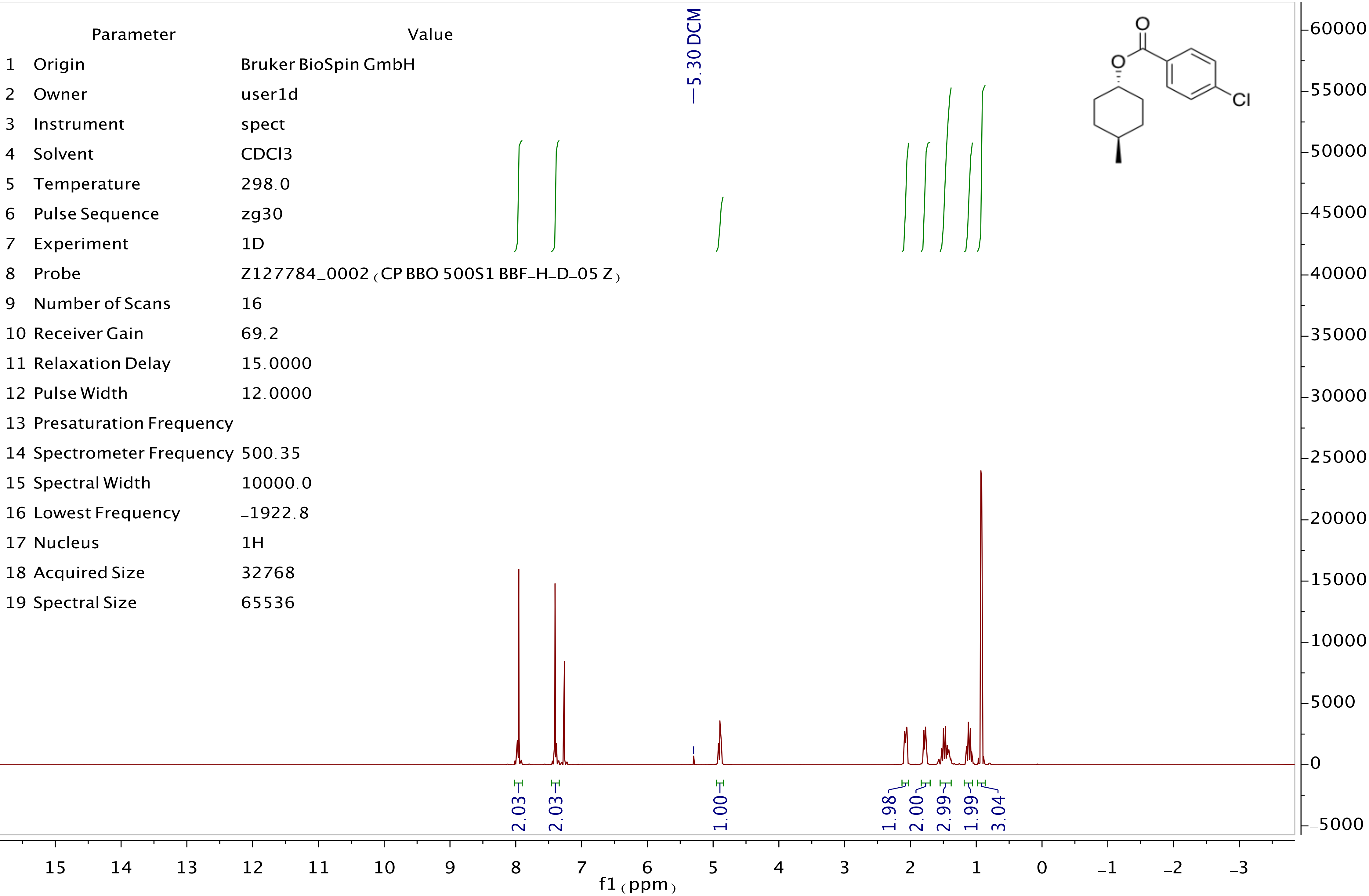
	Parameter	Value
1	Origin	Bruker BioSpin GmbH
2	Owner	user1d
3	Instrument	spect
4	Solvent	CDCl3
5	Temperature	296.1
6	Pulse Sequence	zgpg30
7	Experiment	1D
8	Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
9	Number of Scans	256
10	Receiver Gain	190.5
11	Relaxation Delay	2.0000
12	Pulse Width	10.0000
13	Presaturation Frequency	
14	Spectrometer Frequency	125.83
15	Spectral Width	31512.6
16	Lowest Frequency	-1899.7
17	Nucleus	13C
18	Acquired Size	32768
19	Spectral Size	65536



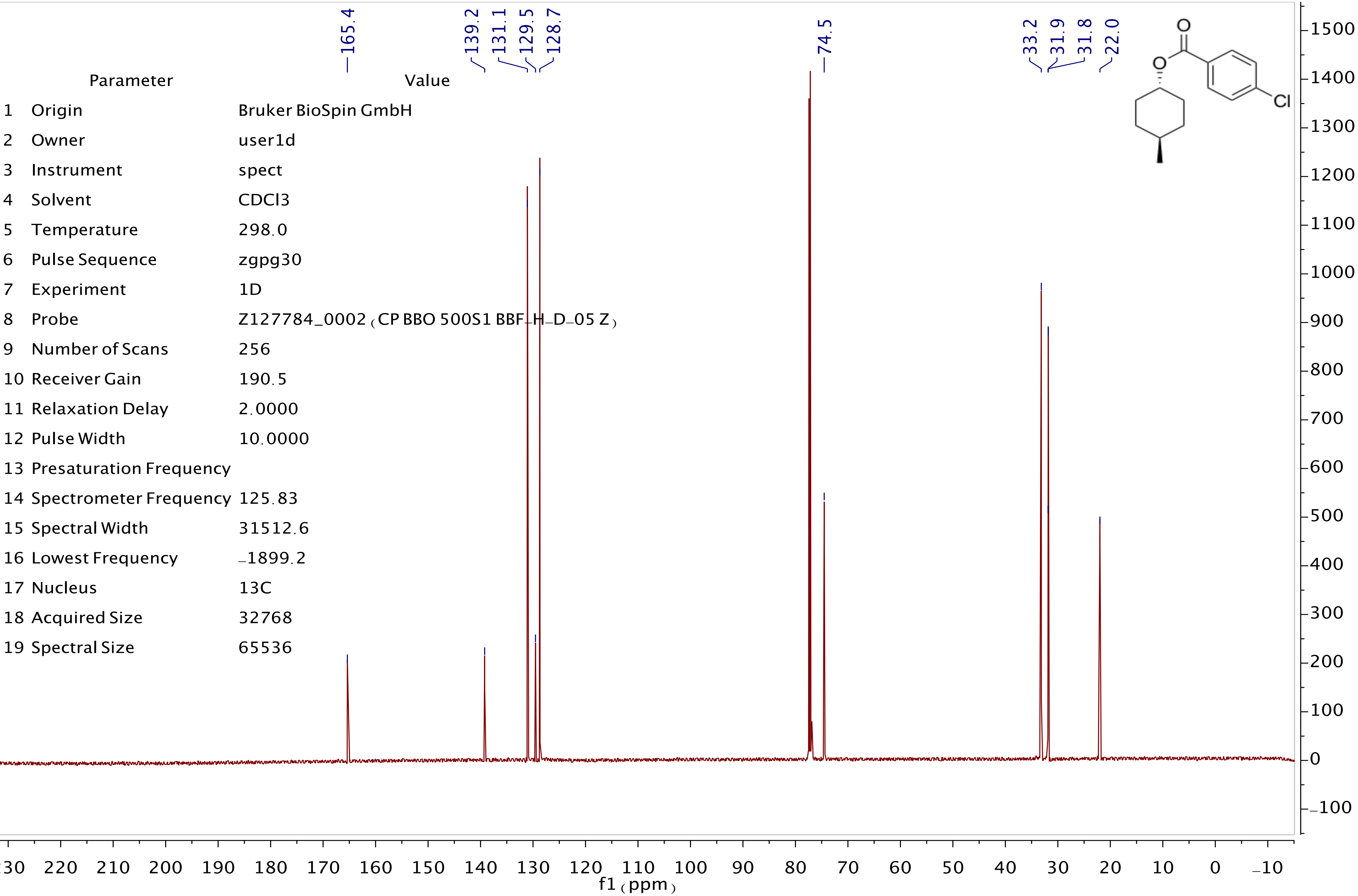
	Parameter	Value
1	Origin	Bruker BioSpin GmbH
2	Owner	user1d
3	Spectrometer	spect
4	Solvent	CDCl3
5	Temperature	296.2
6	Pulse Sequence	zg30
7	Experiment	1D
8	Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
9	Number of Scans	16
10	Receiver Gain	86.0
11	Relaxation Delay	10.0000
12	Pulse Width	12.0000
13	Presaturation Frequency	
14	Spectrometer Frequency	500.35
15	Spectral Width	10000.0
16	Lowest Frequency	-1759.7
17	Nucleus	1H
18	Acquired Size	32768
19	Spectral Size	65536



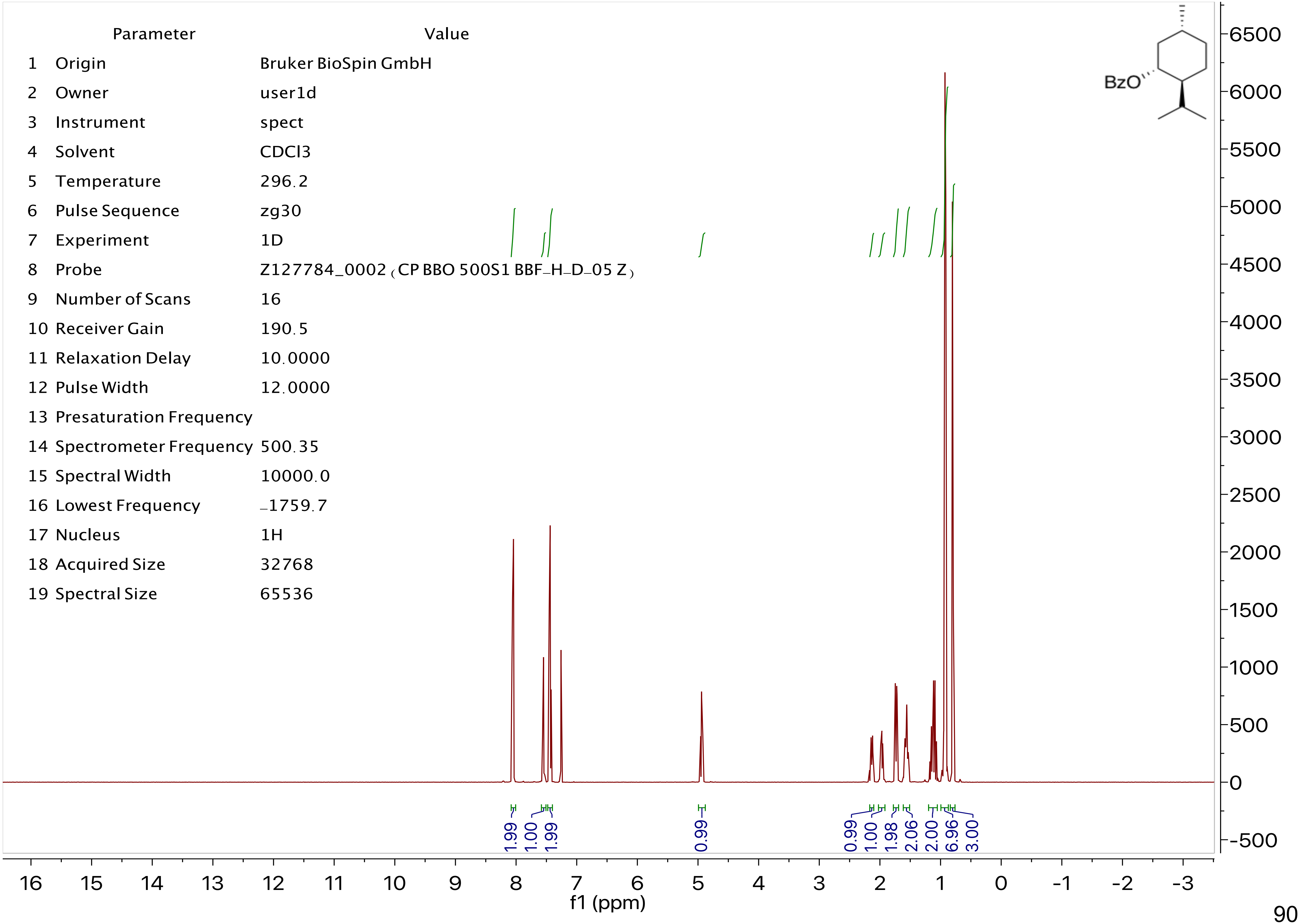
	Parameter	Value
1	Origin	Bruker BioSpin GmbH
2	Owner	user1d
3	Spectrometer	spect
4	Solvent	CDCl3
5	Temperature	296.1
6	Pulse Sequence	zgpg30
7	Experiment	1D
8	Probe	Z127784_0002 (CP BBO 500S1 BBF–H–D–05 Z)
9	Number of Scans	256
10	Receiver Gain	190.5
11	Relaxation Delay	2.0000
12	Pulse Width	10.0000
13	Presaturation Frequency	
14	Spectrometer Frequency	125.83
15	Spectral Width	31512.6
16	Lowest Frequency	–1899.4
17	Nucleus	13C
18	Acquired Size	32768
19	Spectral Size	65536



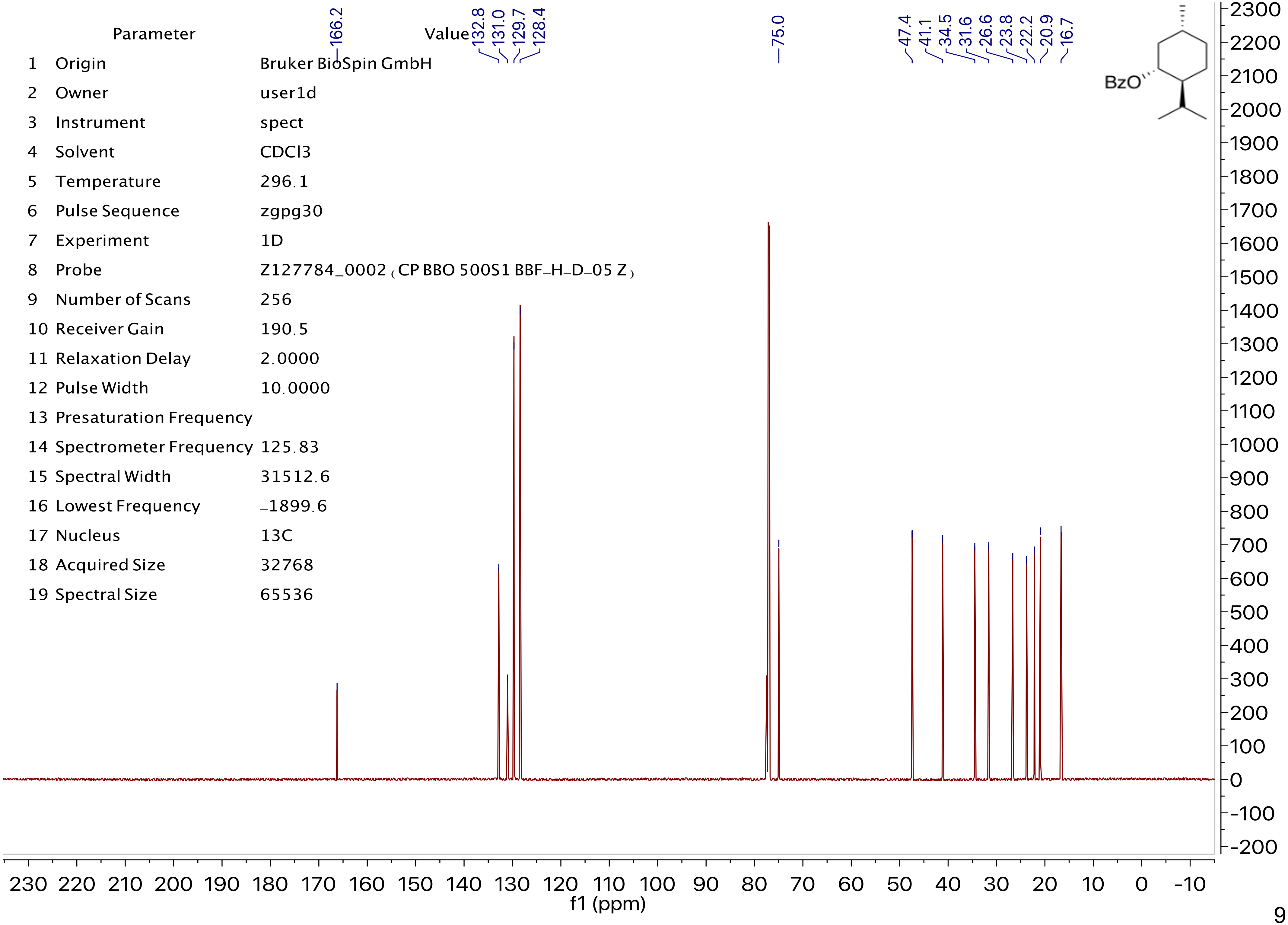
	Parameter	Value
1	Origin	Bruker BioSpin GmbH
2	Owner	user1d
3	Instrument	spect
4	Solvent	CDCl3
5	Temperature	298.0
6	Pulse Sequence	zg30
7	Experiment	1D
8	Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
9	Number of Scans	16
10	Receiver Gain	69.2
11	Relaxation Delay	15.0000
12	Pulse Width	12.0000
13	Presaturation Frequency	
14	Spectrometer Frequency	500.35
15	Spectral Width	10000.0
16	Lowest Frequency	-1922.8
17	Nucleus	1H
18	Acquired Size	32768
19	Spectral Size	65536



	Parameter	Value
1	Origin	Bruker BioSpin GmbH
2	Owner	user1d
3	Instrument	spect
4	Solvent	CDCl3
5	Temperature	298.0
6	Pulse Sequence	zgpg30
7	Experiment	1D
8	Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
9	Number of Scans	256
10	Receiver Gain	190.5
11	Relaxation Delay	2.0000
12	Pulse Width	10.0000
13	Presaturation Frequency	
14	Spectrometer Frequency	125.83
15	Spectral Width	31512.6
16	Lowest Frequency	-1899.2
17	Nucleus	13C
18	Acquired Size	32768
19	Spectral Size	65536

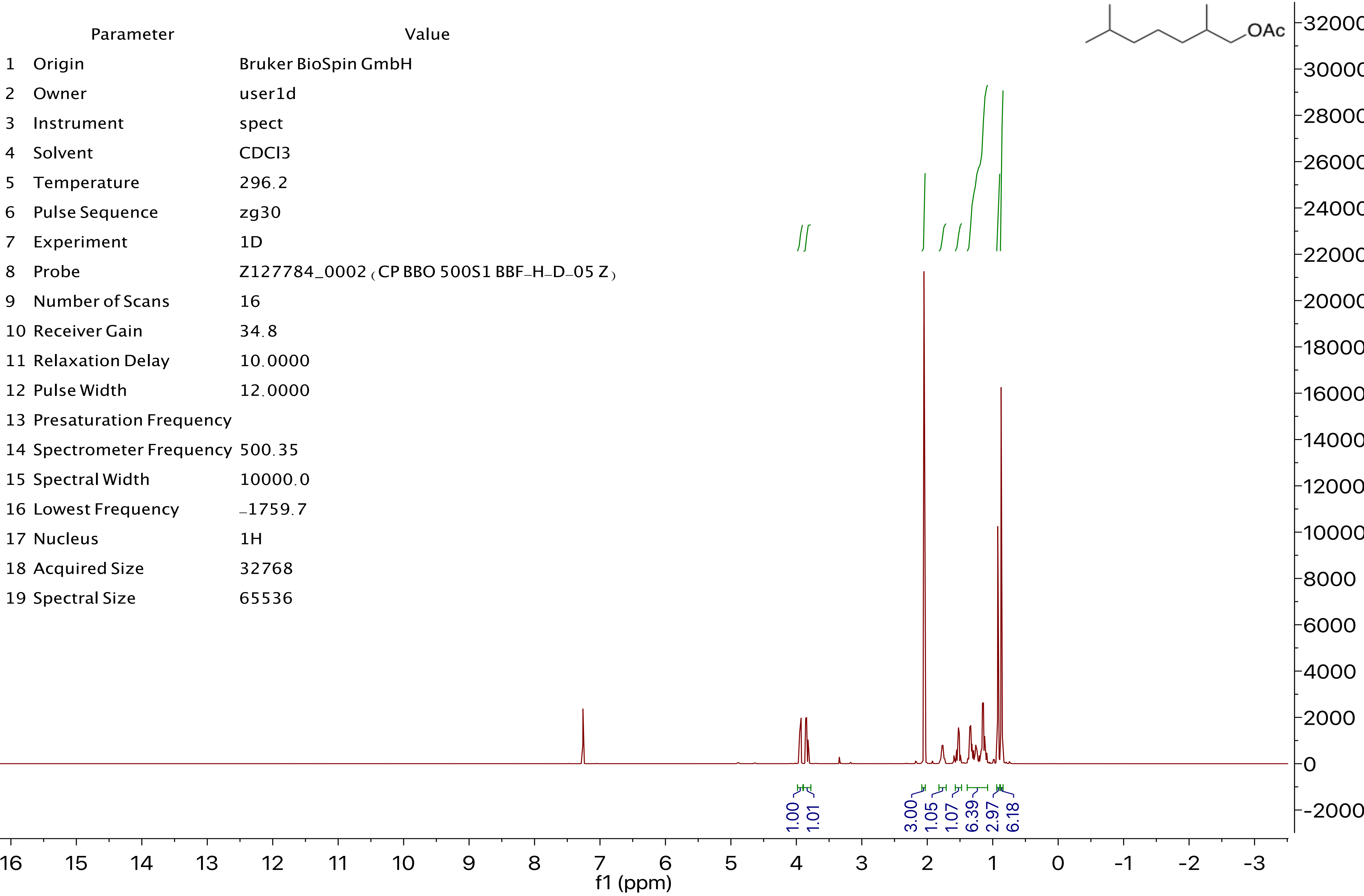


	Parameter	Value
1	Origin	Bruker BioSpin GmbH
2	Owner	user1d
3	Instrument	spect
4	Solvent	CDCl3
5	Temperature	296.2
6	Pulse Sequence	zg30
7	Experiment	1D
8	Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
9	Number of Scans	16
10	Receiver Gain	190.5
11	Relaxation Delay	10.0000
12	Pulse Width	12.0000
13	Presaturation Frequency	
14	Spectrometer Frequency	500.35
15	Spectral Width	10000.0
16	Lowest Frequency	-1759.7
17	Nucleus	1H
18	Acquired Size	32768
19	Spectral Size	65536

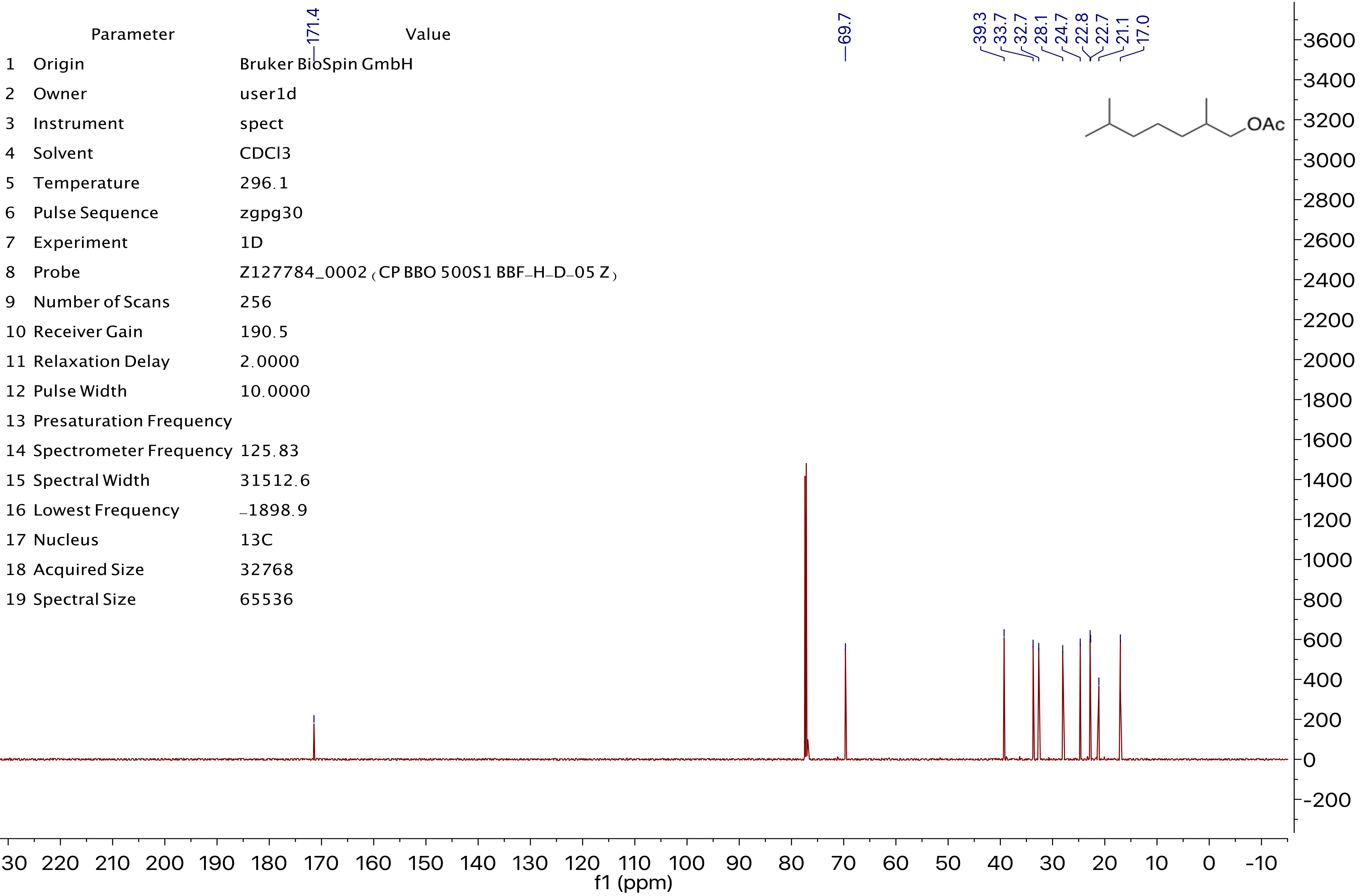


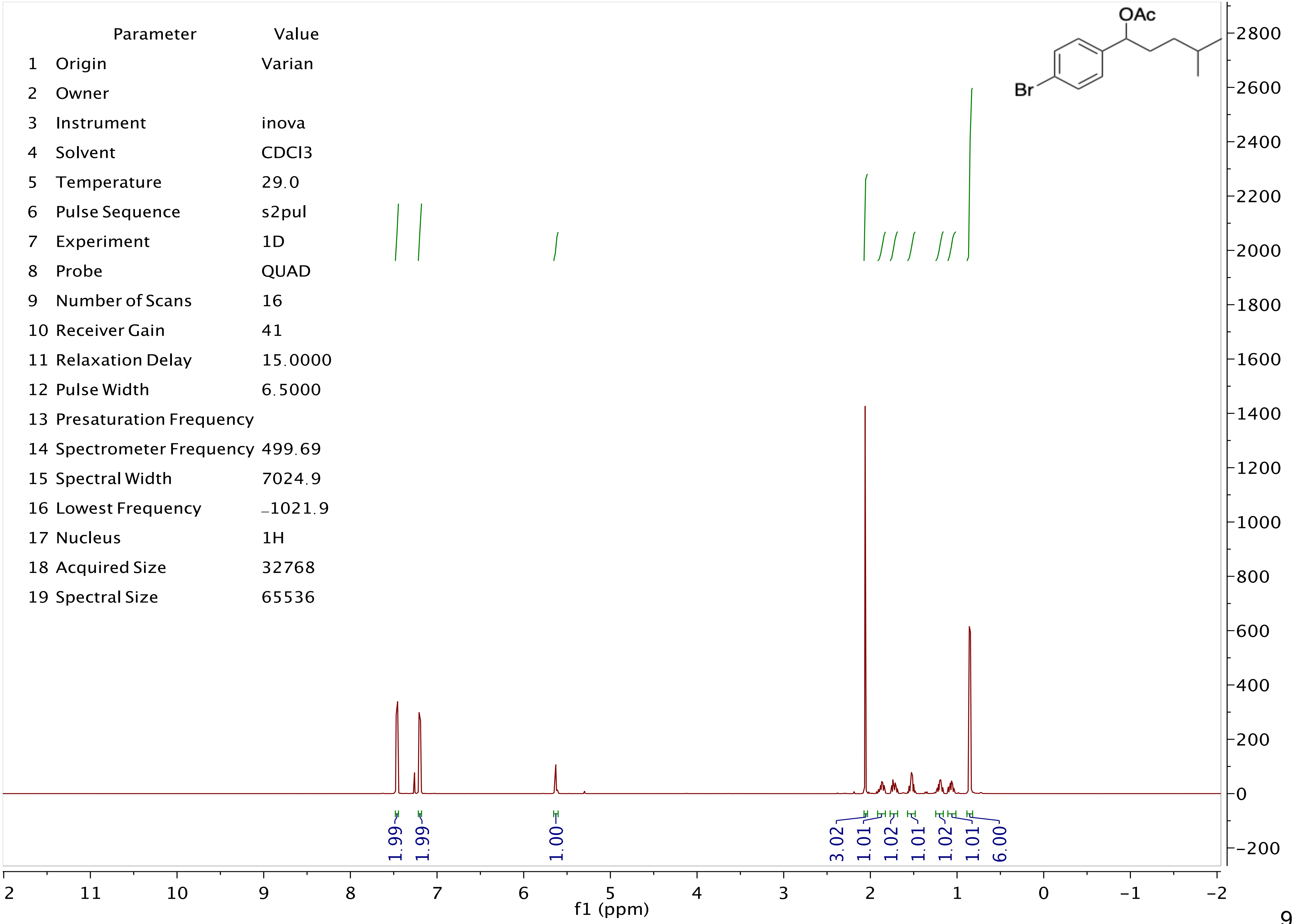
	Parameter	Value
1	Origin	Bruker BioSpin GmbH
2	Owner	user1d
3	Instrument	spect
4	Solvent	CDCl3
5	Temperature	296.1
6	Pulse Sequence	zgpg30
7	Experiment	1D
8	Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
9	Number of Scans	256
10	Receiver Gain	190.5
11	Relaxation Delay	2.0000
12	Pulse Width	10.0000
13	Presaturation Frequency	
14	Spectrometer Frequency	125.83
15	Spectral Width	31512.6
16	Lowest Frequency	-1899.6
17	Nucleus	13C
18	Acquired Size	32768
19	Spectral Size	65536

	Parameter	Value
1	Origin	Bruker BioSpin GmbH
2	Owner	user1d
3	Instrument	spect
4	Solvent	CDCl3
5	Temperature	296.2
6	Pulse Sequence	zg30
7	Experiment	1D
8	Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
9	Number of Scans	16
10	Receiver Gain	34.8
11	Relaxation Delay	10.0000
12	Pulse Width	12.0000
13	Presaturation Frequency	
14	Spectrometer Frequency	500.35
15	Spectral Width	10000.0
16	Lowest Frequency	-1759.7
17	Nucleus	1H
18	Acquired Size	32768
19	Spectral Size	65536

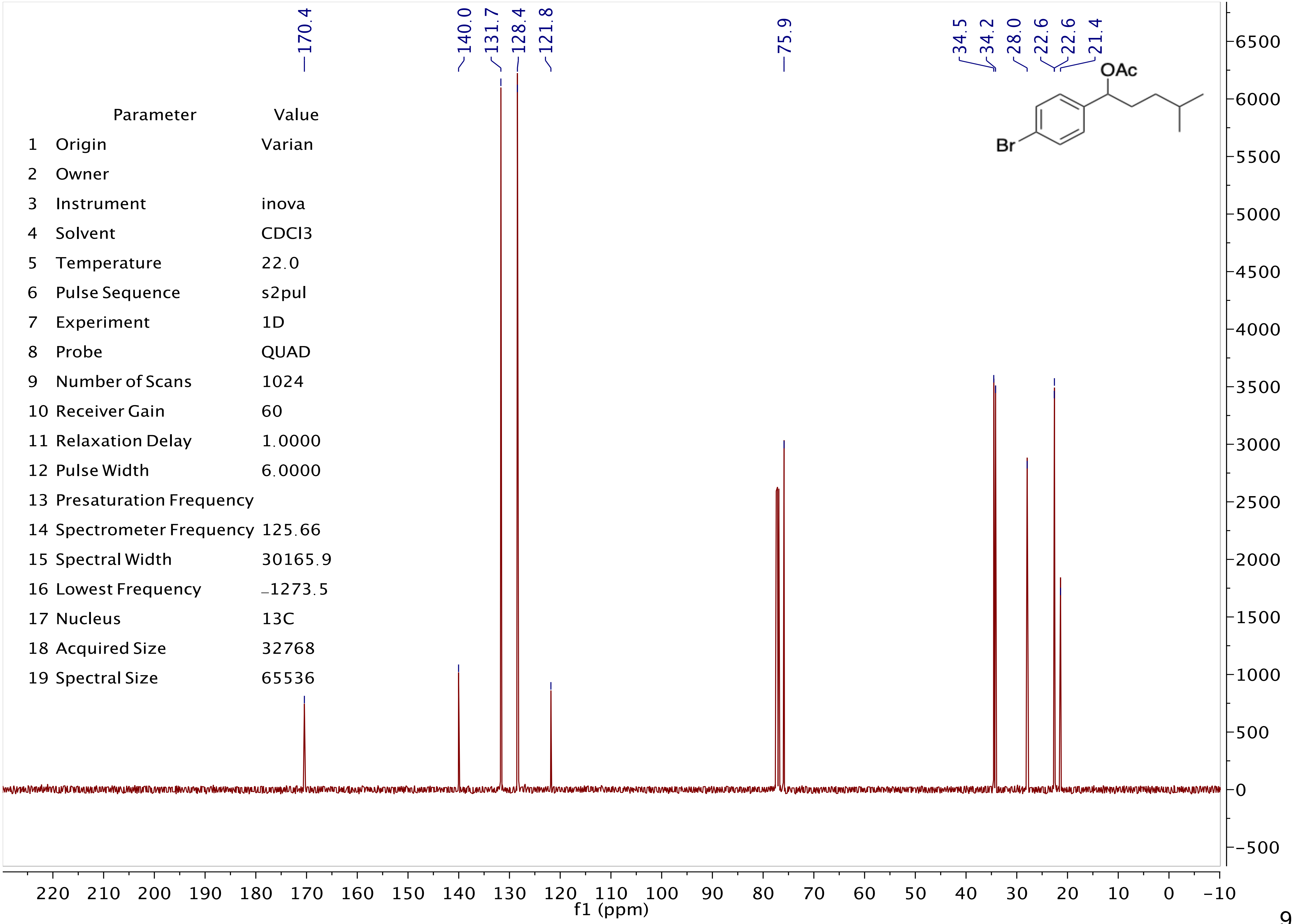


	Parameter	Value
1	Origin	Bruker BioSpin GmbH
2	Owner	user1d
3	Instrument	spect
4	Solvent	CDCl3
5	Temperature	296.1
6	Pulse Sequence	zgpg30
7	Experiment	1D
8	Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
9	Number of Scans	256
10	Receiver Gain	190.5
11	Relaxation Delay	2.0000
12	Pulse Width	10.0000
13	Presaturation Frequency	
14	Spectrometer Frequency	125.83
15	Spectral Width	31512.6
16	Lowest Frequency	-1898.9
17	Nucleus	13C
18	Acquired Size	32768
19	Spectral Size	65536

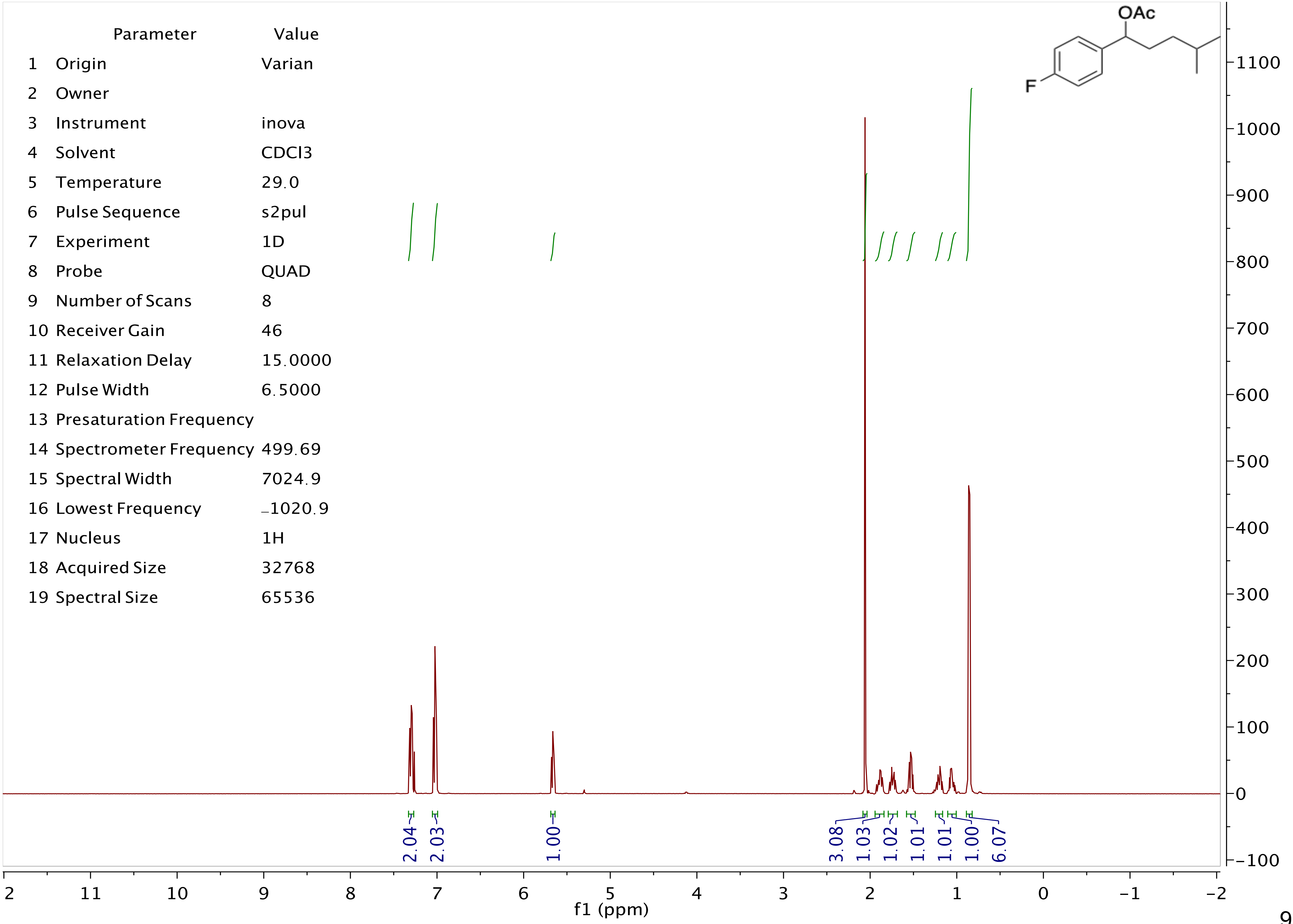




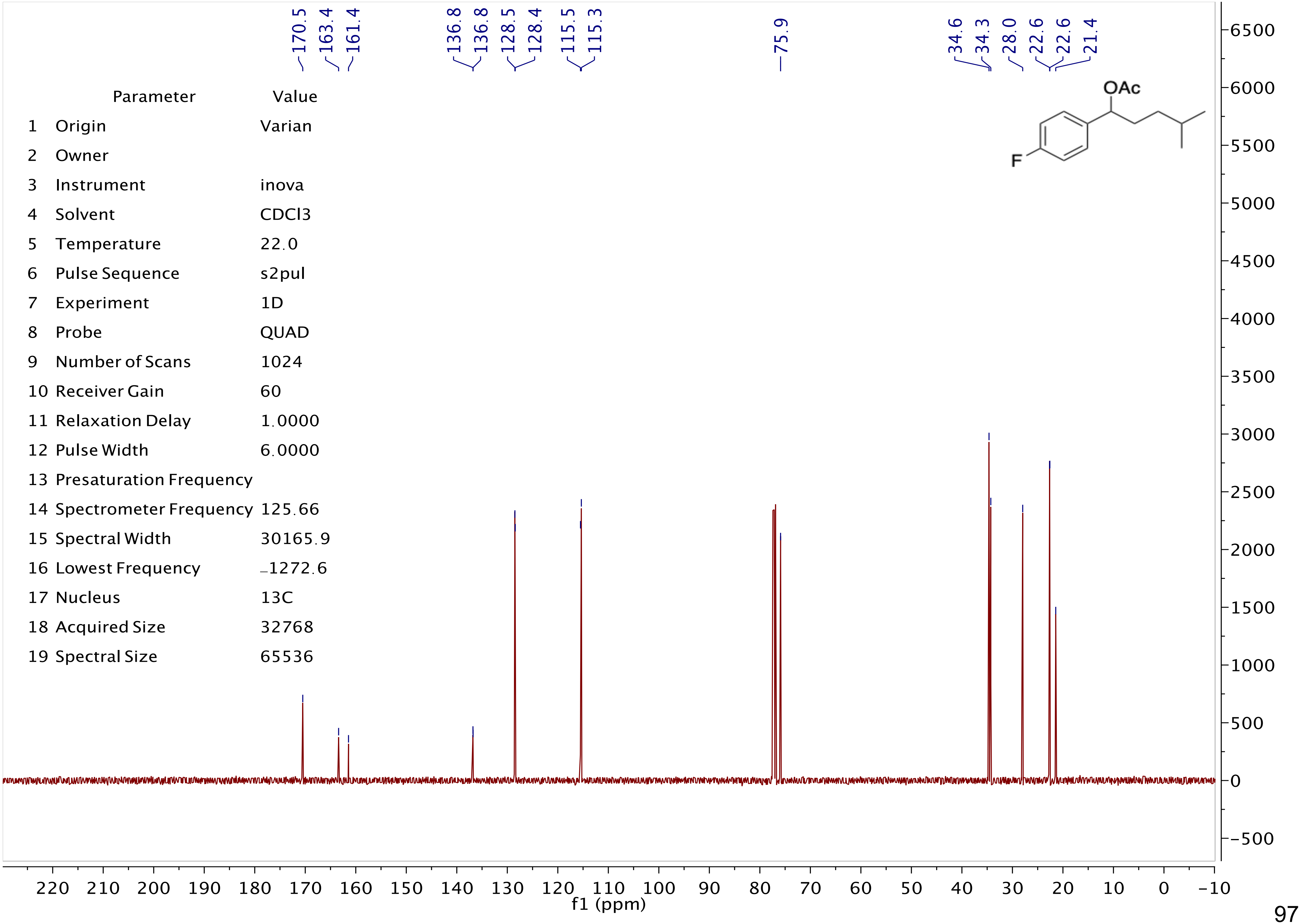
	Parameter	Value
1	Origin	Varian
2	Owner	
3	Instrument	inova
4	Solvent	CDCl3
5	Temperature	29.0
6	Pulse Sequence	s2pul
7	Experiment	1D
8	Probe	QUAD
9	Number of Scans	16
10	Receiver Gain	41
11	Relaxation Delay	15.0000
12	Pulse Width	6.5000
13	Presaturation Frequency	
14	Spectrometer Frequency	499.69
15	Spectral Width	7024.9
16	Lowest Frequency	-1021.9
17	Nucleus	1H
18	Acquired Size	32768
19	Spectral Size	65536



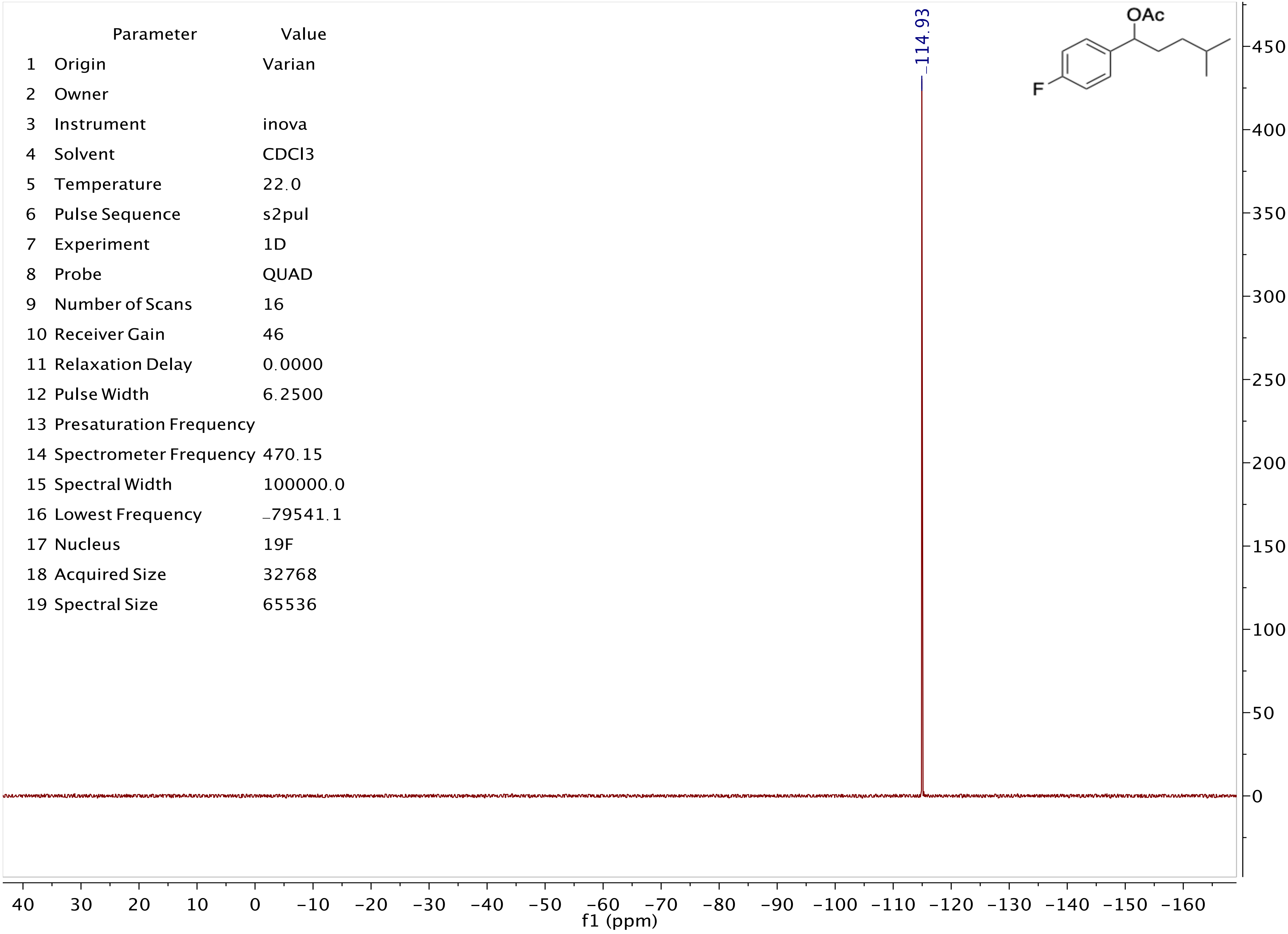
	Parameter	Value
1	Origin	Varian
2	Owner	
3	Instrument	inova
4	Solvent	CDCl3
5	Temperature	22.0
6	Pulse Sequence	s2pul
7	Experiment	1D
8	Probe	QUAD
9	Number of Scans	1024
10	Receiver Gain	60
11	Relaxation Delay	1.0000
12	Pulse Width	6.0000
13	Presaturation Frequency	
14	Spectrometer Frequency	125.66
15	Spectral Width	30165.9
16	Lowest Frequency	-1273.5
17	Nucleus	13C
18	Acquired Size	32768
19	Spectral Size	65536



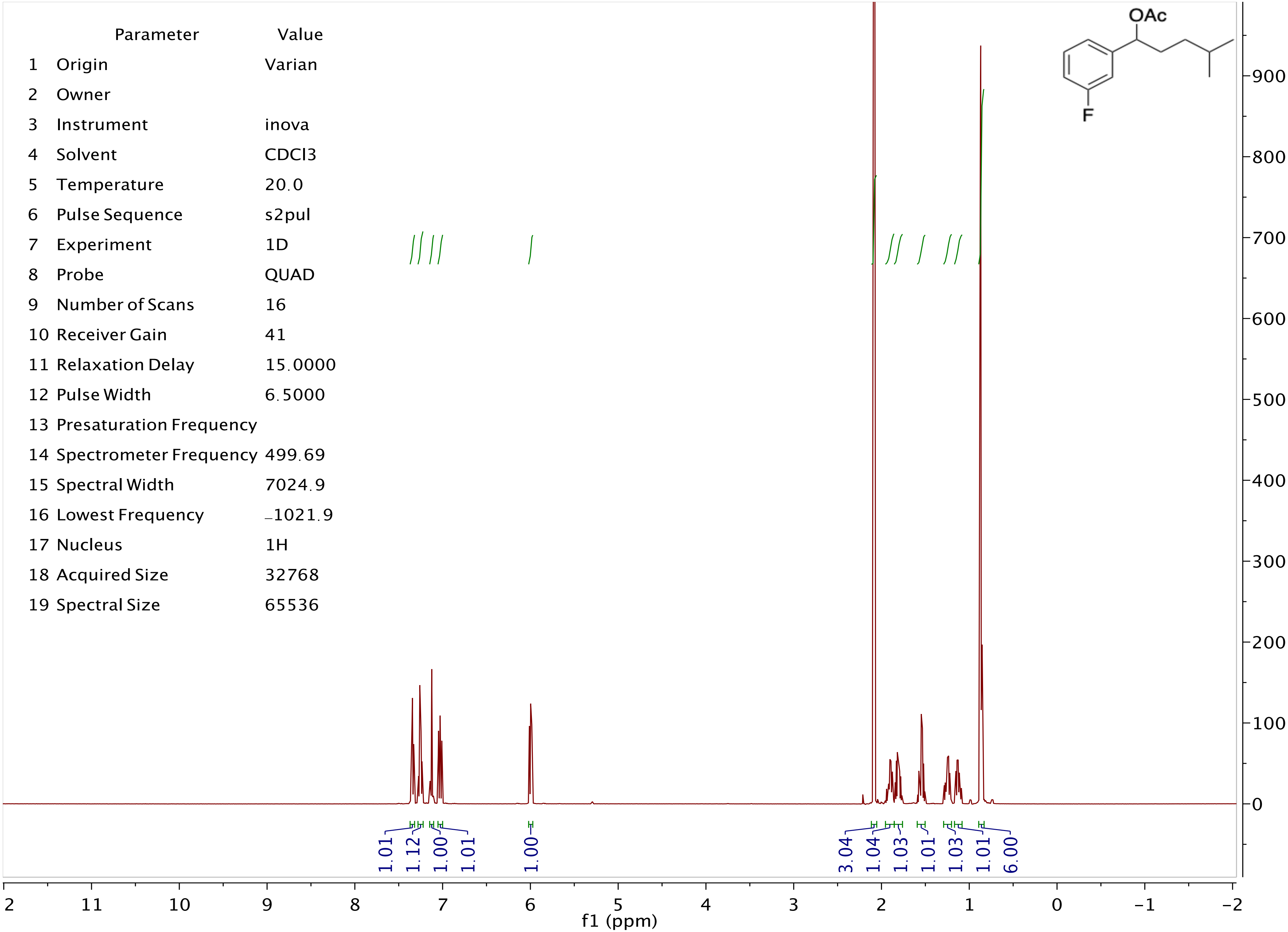
	Parameter	Value
1	Origin	Varian
2	Owner	
3	Instrument	inova
4	Solvent	CDCl3
5	Temperature	29.0
6	Pulse Sequence	s2pul
7	Experiment	1D
8	Probe	QUAD
9	Number of Scans	8
10	Receiver Gain	46
11	Relaxation Delay	15.0000
12	Pulse Width	6.5000
13	Presaturation Frequency	
14	Spectrometer Frequency	499.69
15	Spectral Width	7024.9
16	Lowest Frequency	–1020.9
17	Nucleus	1H
18	Acquired Size	32768
19	Spectral Size	65536



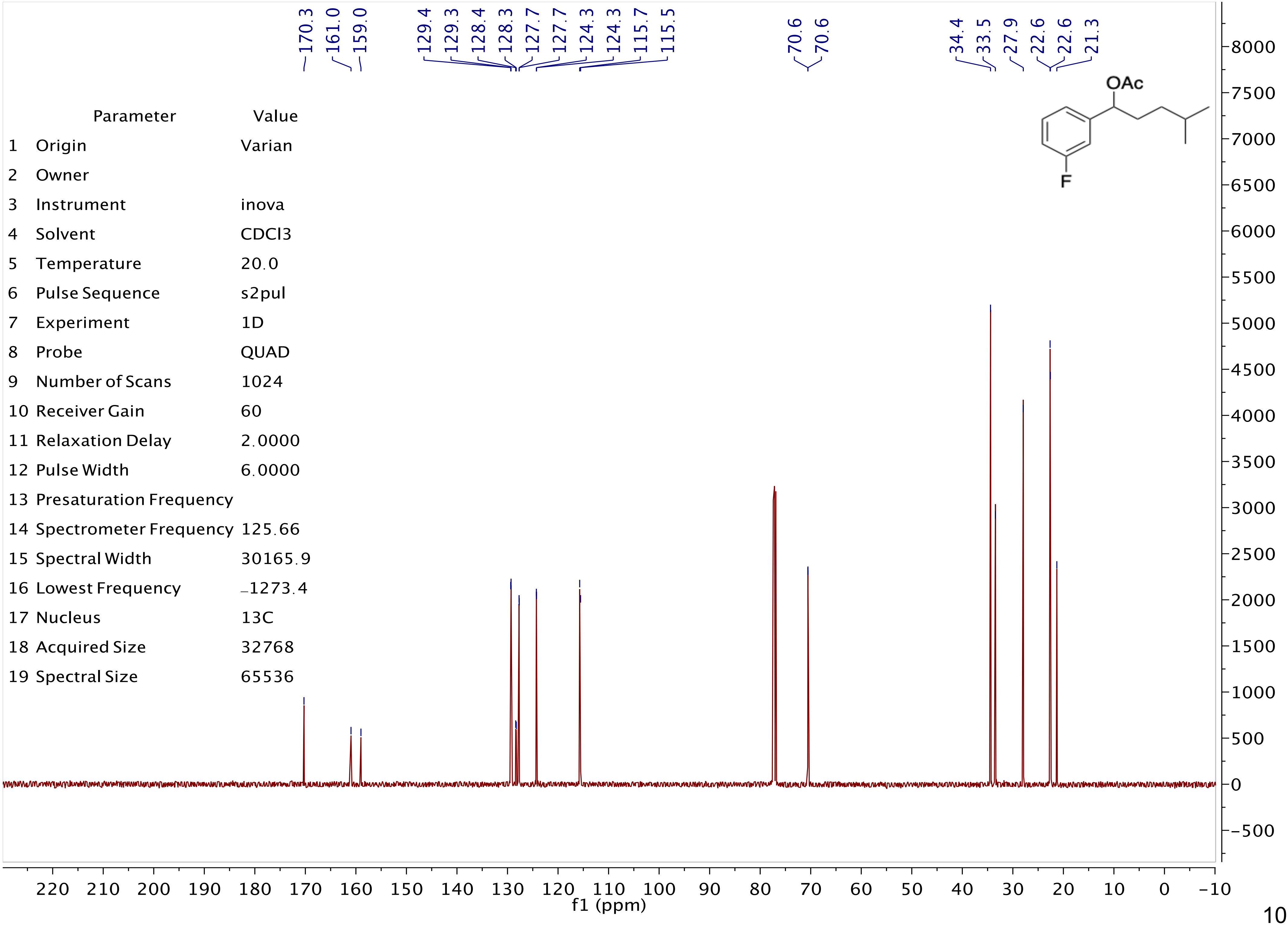
	Parameter	Value
1	Origin	Varian
2	Owner	
3	Instrument	inova
4	Solvent	CDCl3
5	Temperature	22.0
6	Pulse Sequence	s2pul
7	Experiment	1D
8	Probe	QUAD
9	Number of Scans	1024
10	Receiver Gain	60
11	Relaxation Delay	1.0000
12	Pulse Width	6.0000
13	Presaturation Frequency	
14	Spectrometer Frequency	125.66
15	Spectral Width	30165.9
16	Lowest Frequency	–1272.6
17	Nucleus	13C
18	Acquired Size	32768
19	Spectral Size	65536



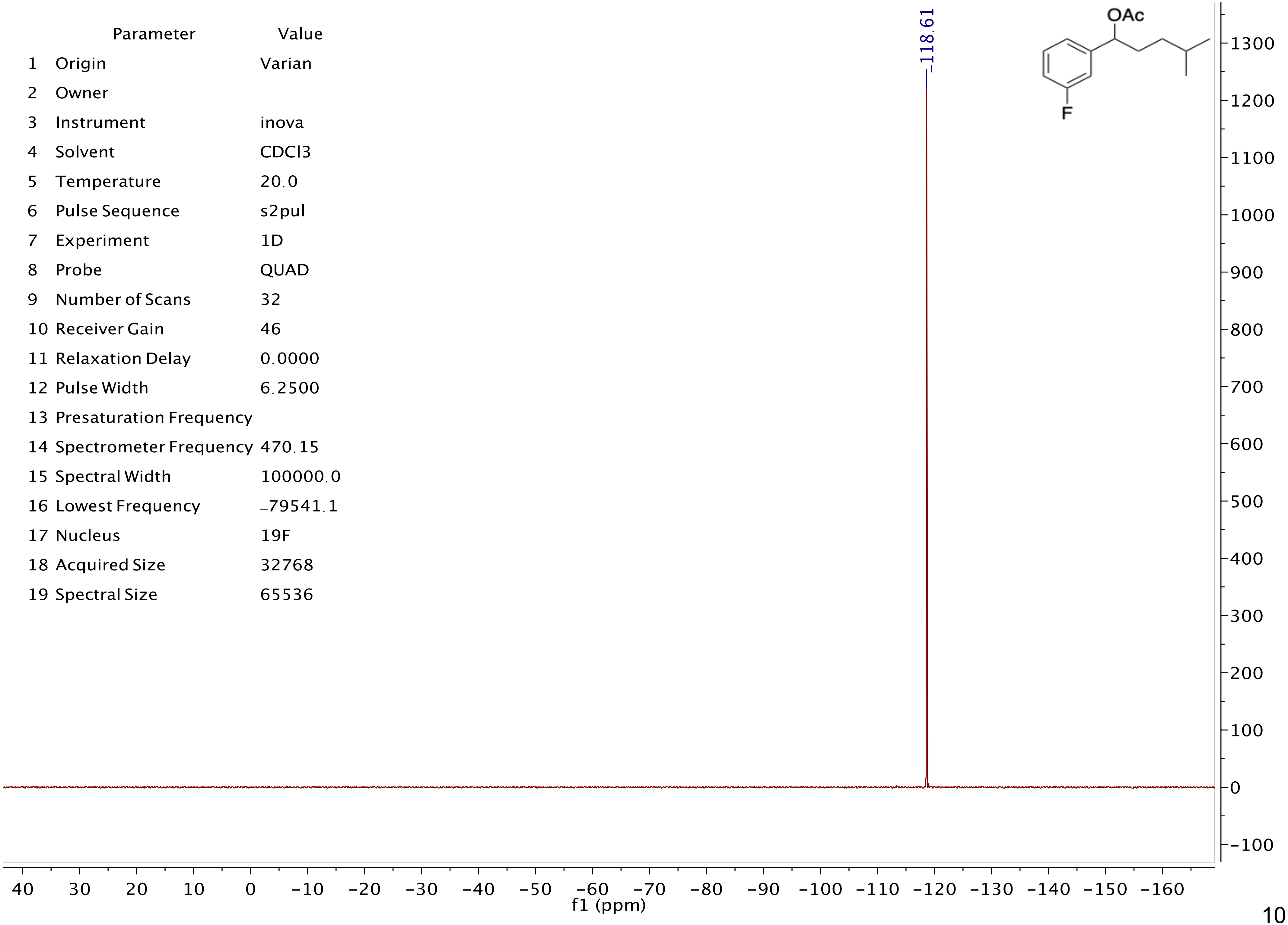
	Parameter	Value
1	Origin	Varian
2	Owner	
3	Instrument	inova
4	Solvent	CDCl3
5	Temperature	22.0
6	Pulse Sequence	s2pul
7	Experiment	1D
8	Probe	QUAD
9	Number of Scans	16
10	Receiver Gain	46
11	Relaxation Delay	0.0000
12	Pulse Width	6.2500
13	Presaturation Frequency	
14	Spectrometer Frequency	470.15
15	Spectral Width	100000.0
16	Lowest Frequency	-79541.1
17	Nucleus	19F
18	Acquired Size	32768
19	Spectral Size	65536



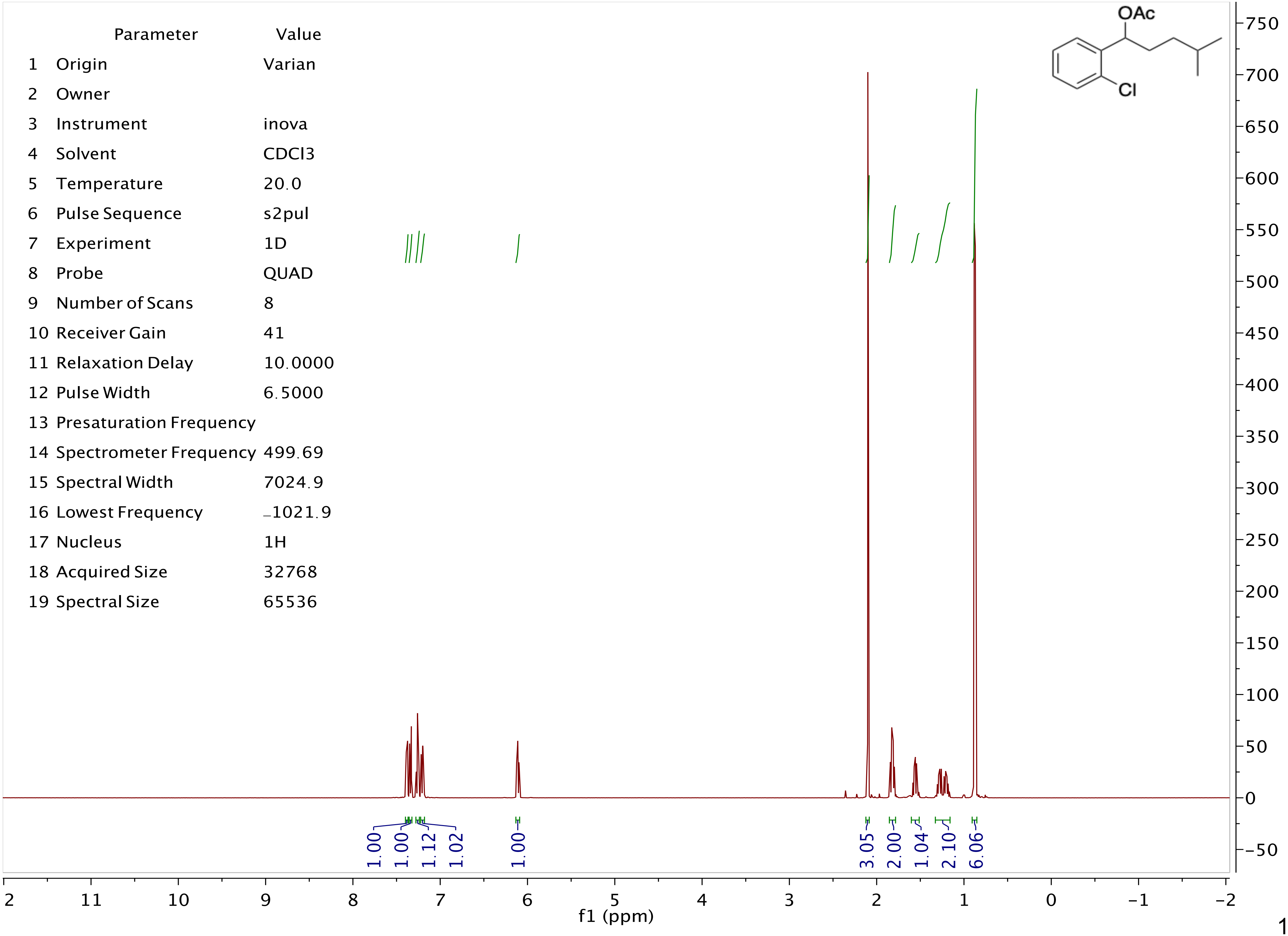
	Parameter	Value
1	Origin	Varian
2	Owner	
3	Instrument	inova
4	Solvent	CDCl3
5	Temperature	20.0
6	Pulse Sequence	s2pul
7	Experiment	1D
8	Probe	QUAD
9	Number of Scans	16
10	Receiver Gain	41
11	Relaxation Delay	15.0000
12	Pulse Width	6.5000
13	Presaturation Frequency	
14	Spectrometer Frequency	499.69
15	Spectral Width	7024.9
16	Lowest Frequency	-1021.9
17	Nucleus	1H
18	Acquired Size	32768
19	Spectral Size	65536



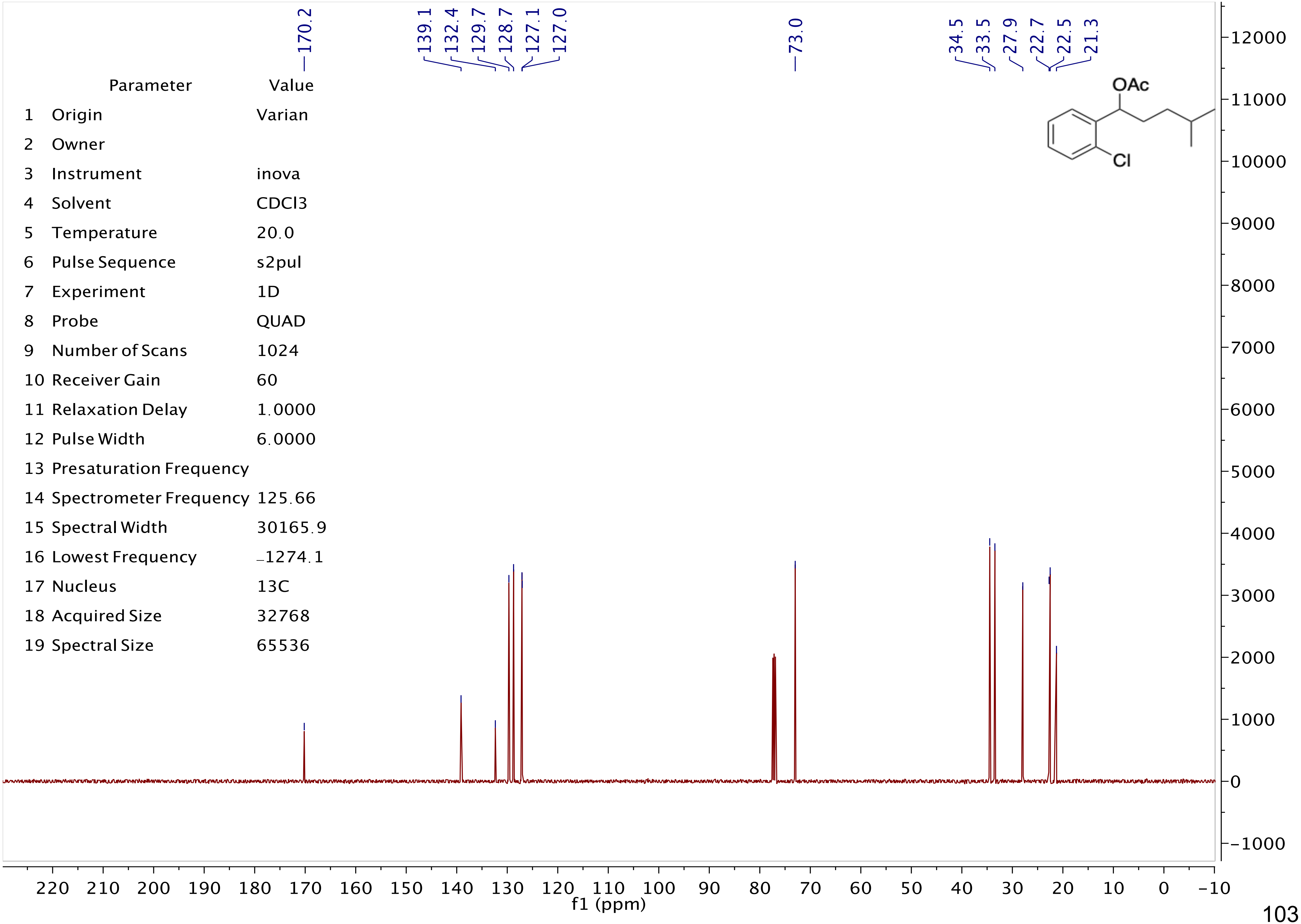
	Parameter	Value
1	Origin	Varian
2	Owner	
3	Instrument	inova
4	Solvent	CDCl3
5	Temperature	20.0
6	Pulse Sequence	s2pul
7	Experiment	1D
8	Probe	QUAD
9	Number of Scans	1024
10	Receiver Gain	60
11	Relaxation Delay	2.0000
12	Pulse Width	6.0000
13	Presaturation Frequency	
14	Spectrometer Frequency	125.66
15	Spectral Width	30165.9
16	Lowest Frequency	-1273.4
17	Nucleus	13C
18	Acquired Size	32768
19	Spectral Size	65536



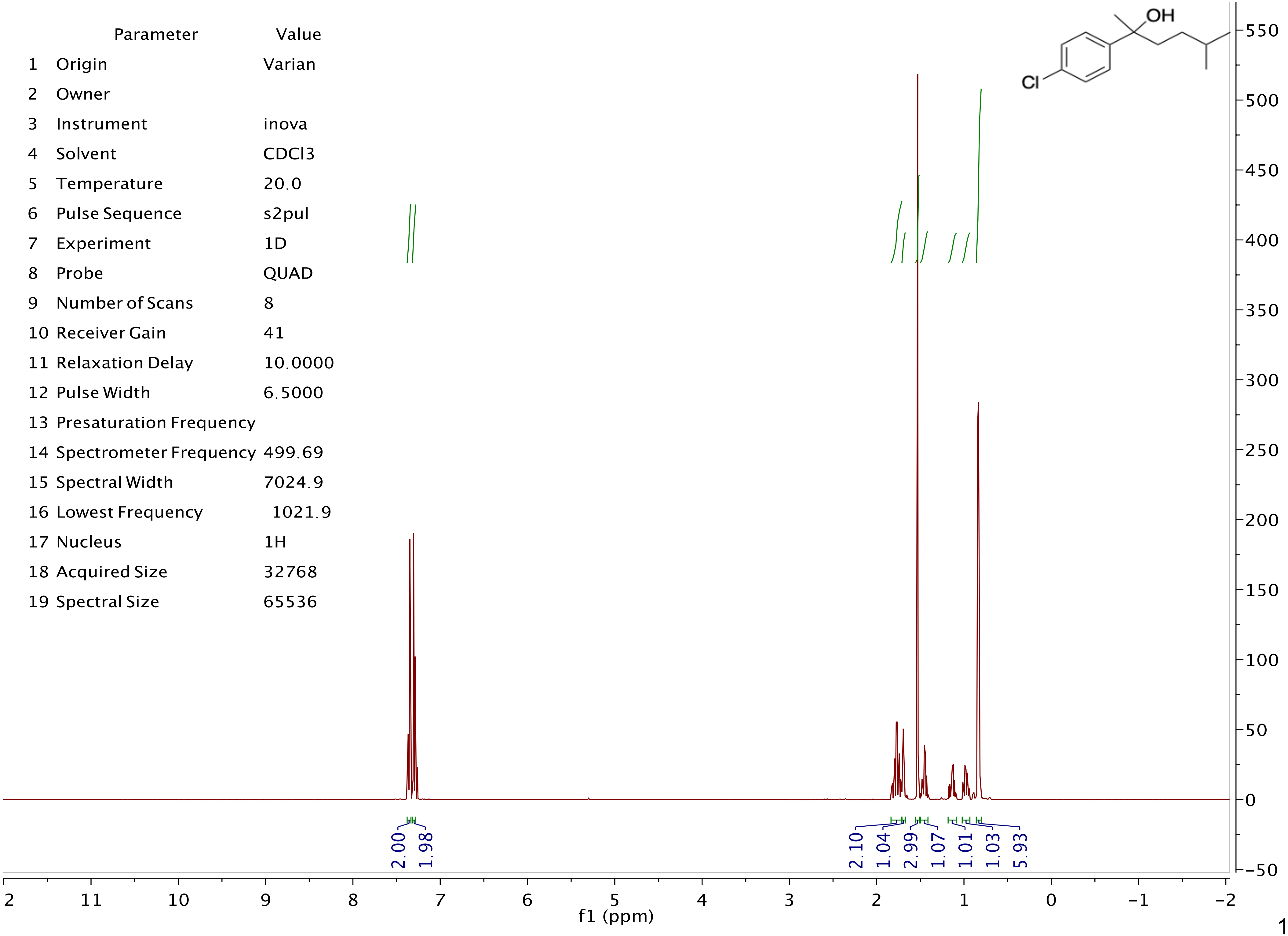
	Parameter	Value
1	Origin	Varian
2	Owner	
3	Instrument	inova
4	Solvent	CDCl3
5	Temperature	20.0
6	Pulse Sequence	s2pul
7	Experiment	1D
8	Probe	QUAD
9	Number of Scans	32
10	Receiver Gain	46
11	Relaxation Delay	0.0000
12	Pulse Width	6.2500
13	Presaturation Frequency	
14	Spectrometer Frequency	470.15
15	Spectral Width	100000.0
16	Lowest Frequency	-79541.1
17	Nucleus	19F
18	Acquired Size	32768
19	Spectral Size	65536



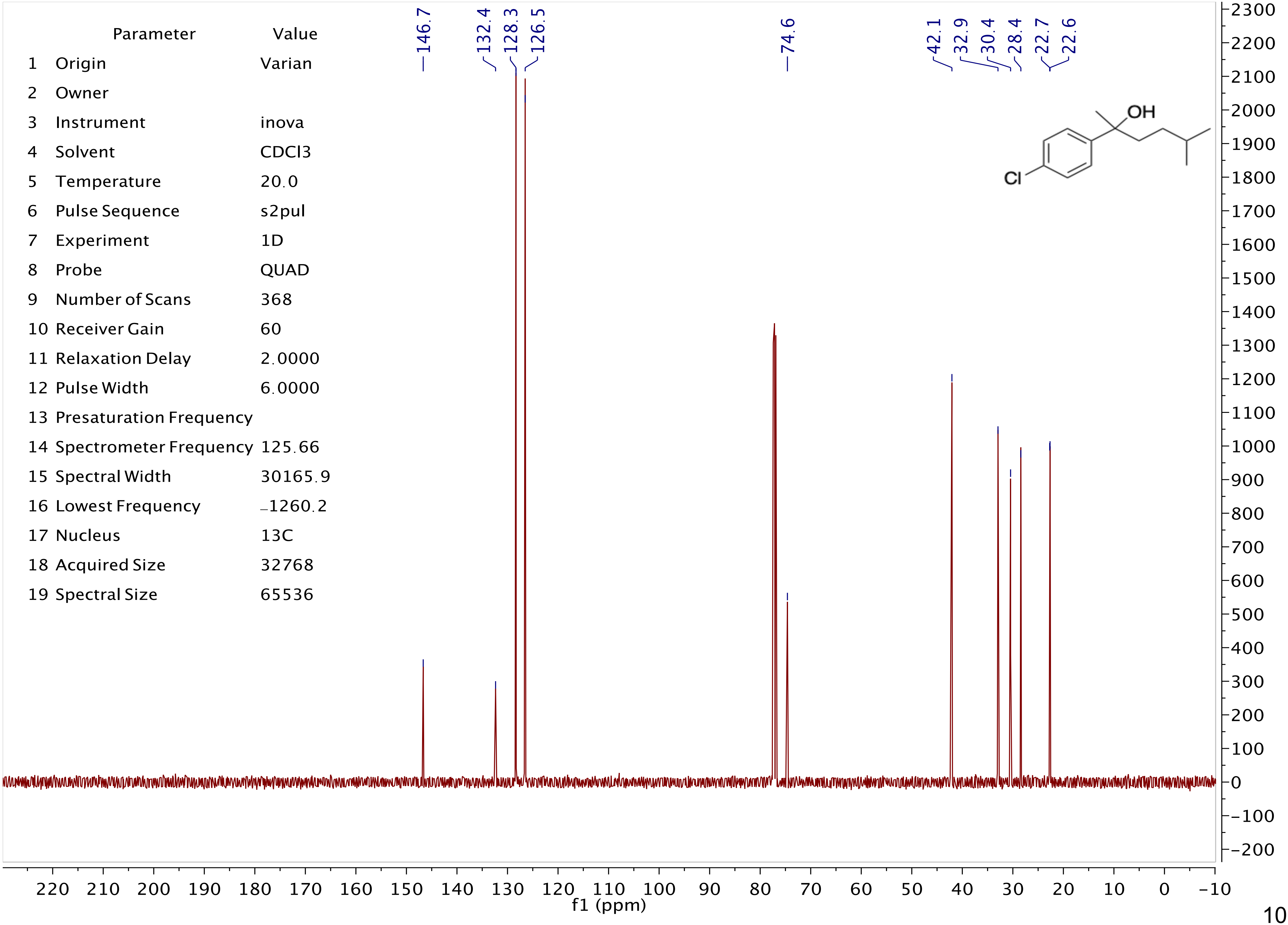
	Parameter	Value
1	Origin	Varian
2	Owner	
3	Instrument	inova
4	Solvent	CDCl3
5	Temperature	20.0
6	Pulse Sequence	s2pul
7	Experiment	1D
8	Probe	QUAD
9	Number of Scans	8
10	Receiver Gain	41
11	Relaxation Delay	10.0000
12	Pulse Width	6.5000
13	Presaturation Frequency	
14	Spectrometer Frequency	499.69
15	Spectral Width	7024.9
16	Lowest Frequency	-1021.9
17	Nucleus	1H
18	Acquired Size	32768
19	Spectral Size	65536



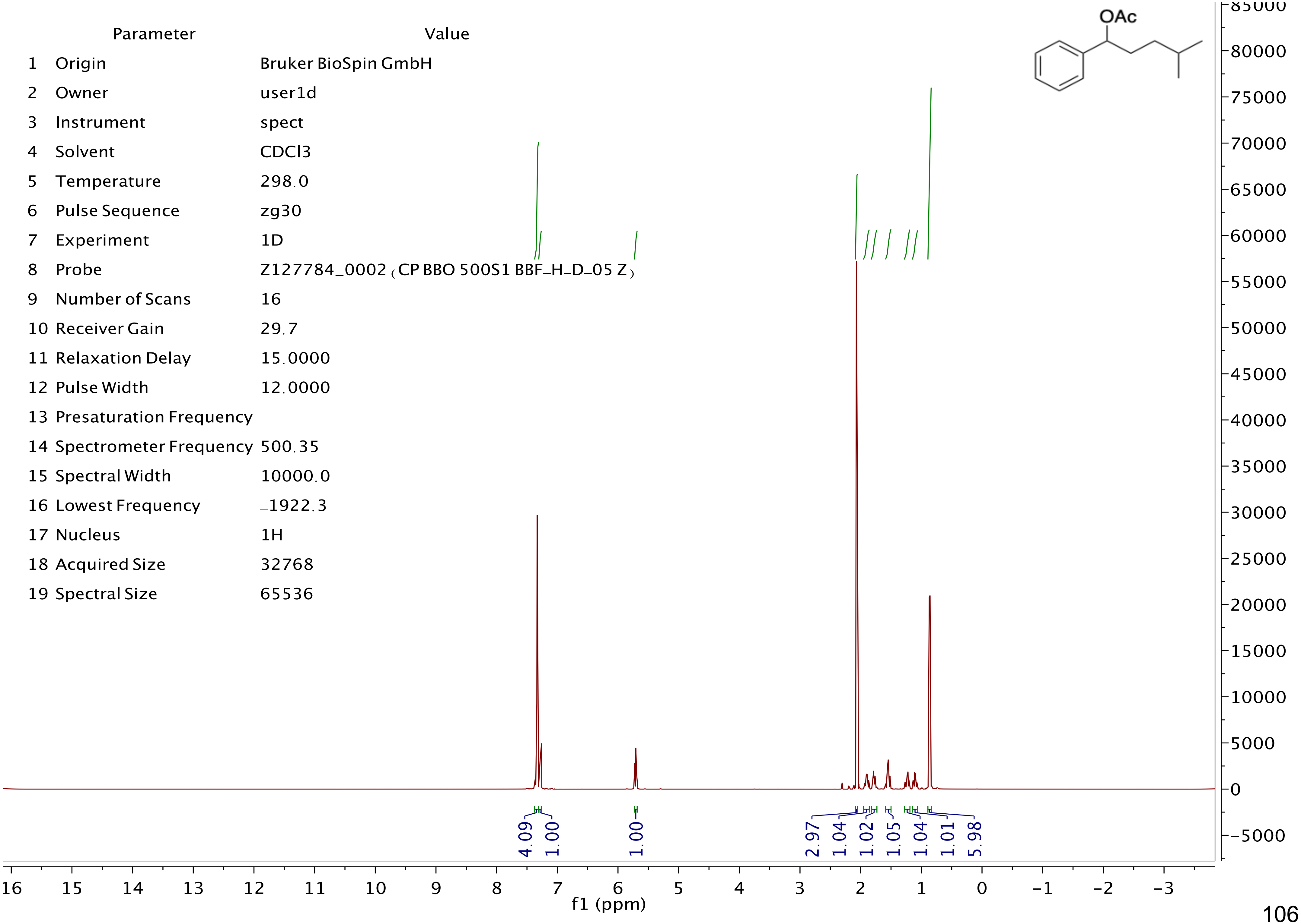
	Parameter	Value
1	Origin	Varian
2	Owner	
3	Instrument	inova
4	Solvent	CDCl3
5	Temperature	20.0
6	Pulse Sequence	s2pul
7	Experiment	1D
8	Probe	QUAD
9	Number of Scans	1024
10	Receiver Gain	60
11	Relaxation Delay	1.0000
12	Pulse Width	6.0000
13	Presaturation Frequency	
14	Spectrometer Frequency	125.66
15	Spectral Width	30165.9
16	Lowest Frequency	-1274.1
17	Nucleus	13C
18	Acquired Size	32768
19	Spectral Size	65536



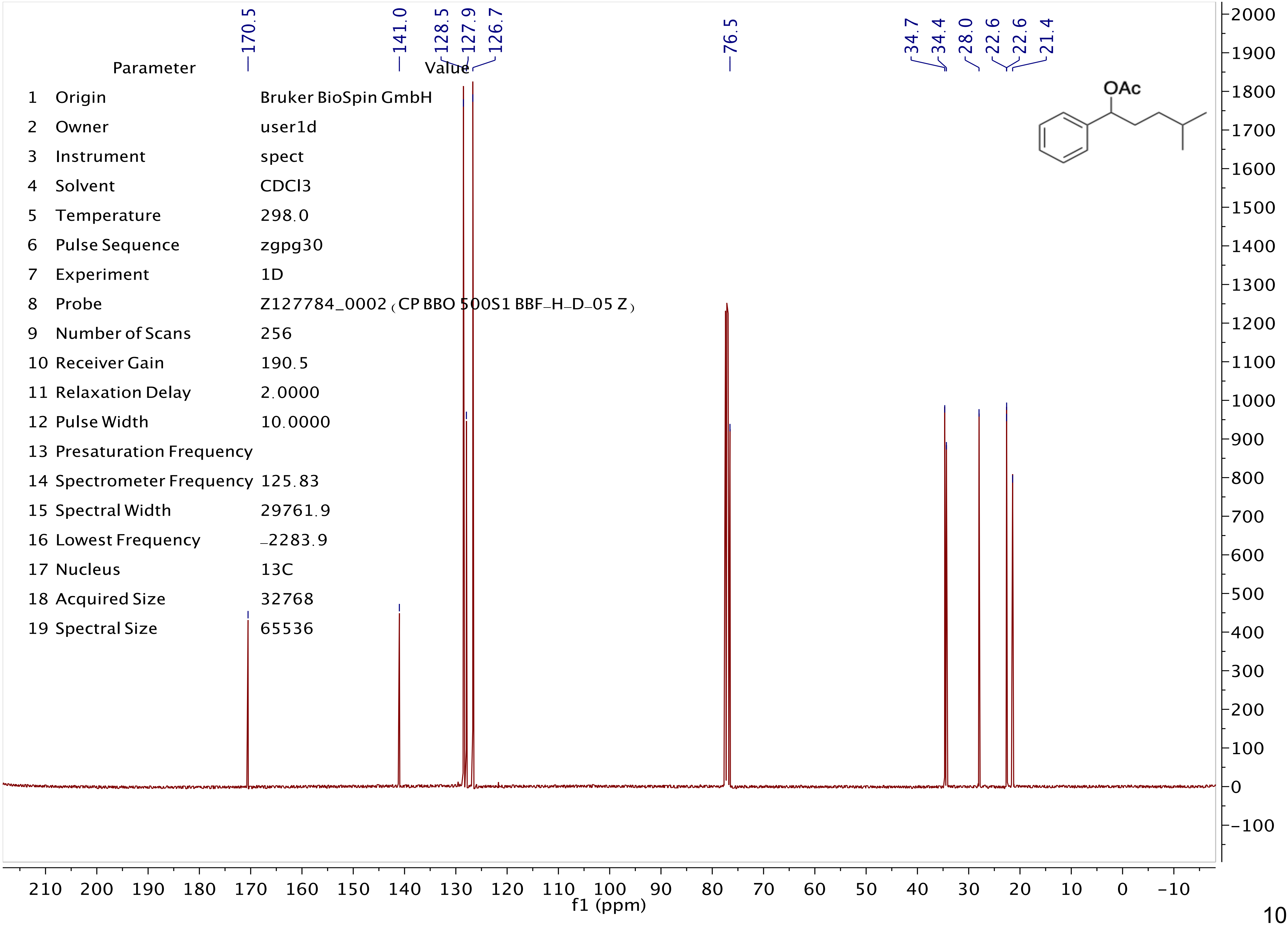
	Parameter	Value
1	Origin	Varian
2	Owner	
3	Instrument	inova
4	Solvent	CDCl3
5	Temperature	20.0
6	Pulse Sequence	s2pul
7	Experiment	1D
8	Probe	QUAD
9	Number of Scans	8
10	Receiver Gain	41
11	Relaxation Delay	10.0000
12	Pulse Width	6.5000
13	Presaturation Frequency	
14	Spectrometer Frequency	499.69
15	Spectral Width	7024.9
16	Lowest Frequency	–1021.9
17	Nucleus	1H
18	Acquired Size	32768
19	Spectral Size	65536



	Parameter	Value
1	Origin	Varian
2	Owner	
3	Instrument	inova
4	Solvent	CDCl3
5	Temperature	20.0
6	Pulse Sequence	s2pul
7	Experiment	1D
8	Probe	QUAD
9	Number of Scans	368
10	Receiver Gain	60
11	Relaxation Delay	2.0000
12	Pulse Width	6.0000
13	Presaturation Frequency	
14	Spectrometer Frequency	125.66
15	Spectral Width	30165.9
16	Lowest Frequency	-1260.2
17	Nucleus	13C
18	Acquired Size	32768
19	Spectral Size	65536

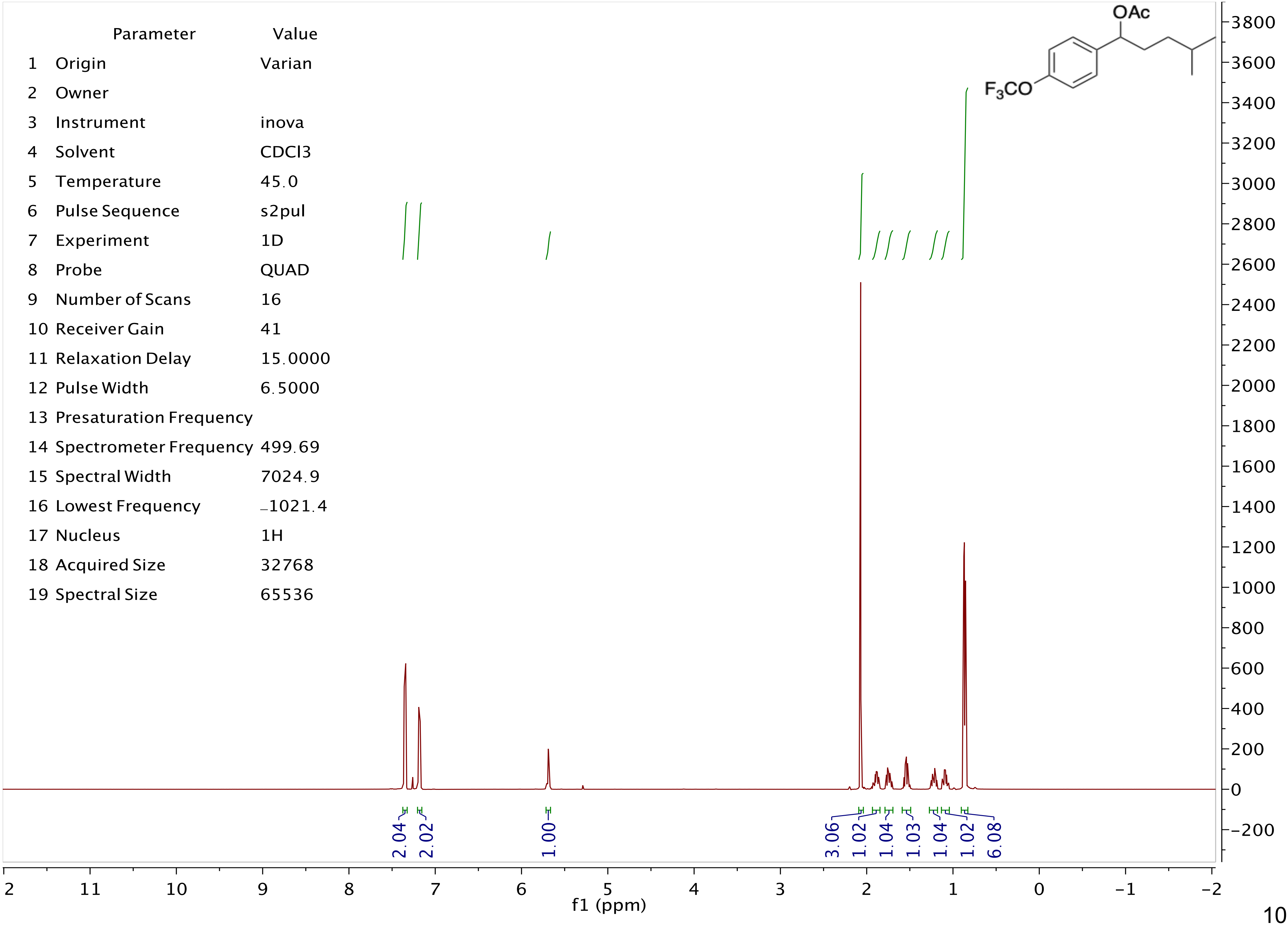


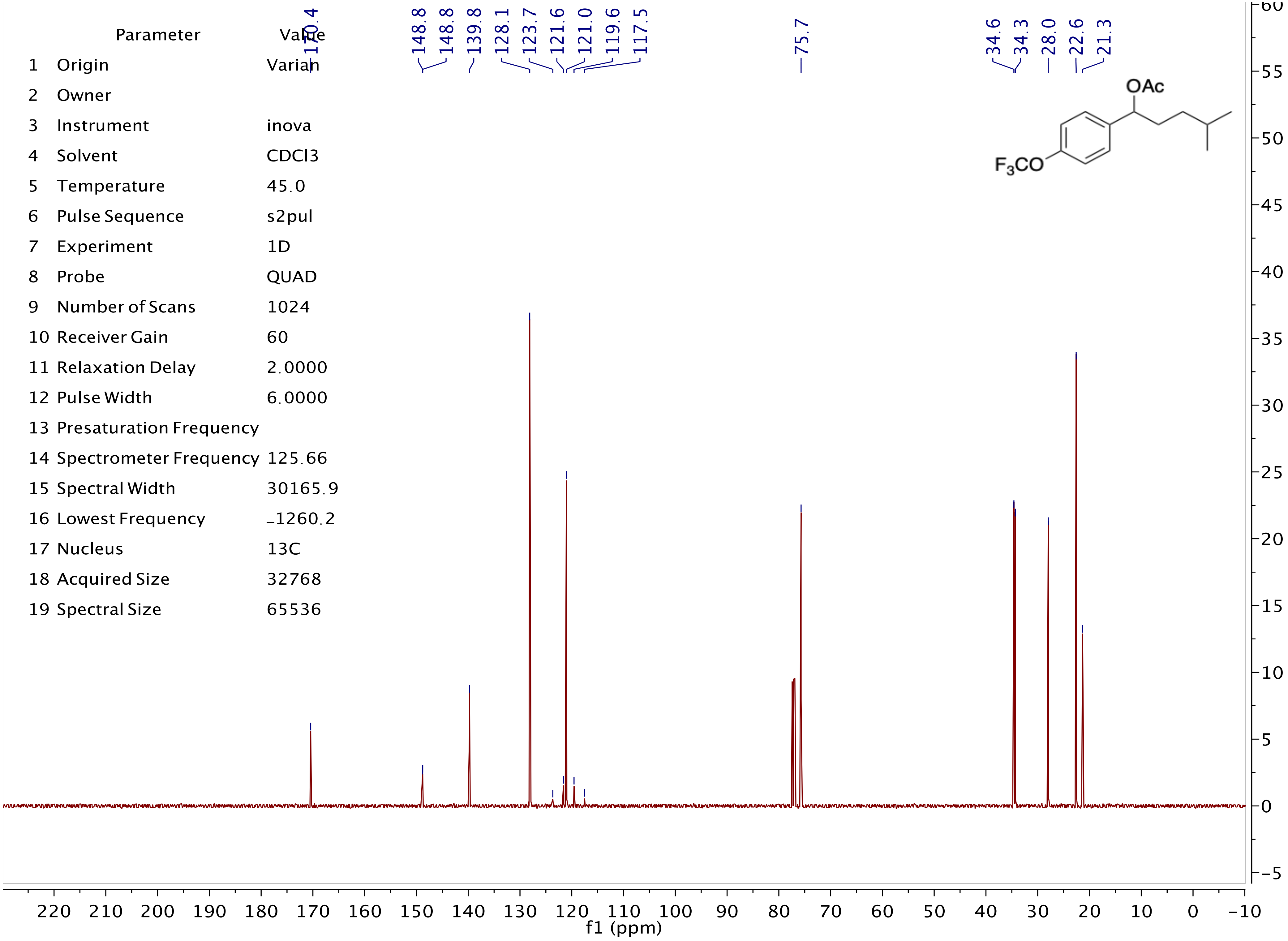
	Parameter	Value
1	Origin	Bruker BioSpin GmbH
2	Owner	user1d
3	Instrument	spect
4	Solvent	CDCl3
5	Temperature	298.0
6	Pulse Sequence	zg30
7	Experiment	1D
8	Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
9	Number of Scans	16
10	Receiver Gain	29.7
11	Relaxation Delay	15.0000
12	Pulse Width	12.0000
13	Presaturation Frequency	
14	Spectrometer Frequency	500.35
15	Spectral Width	10000.0
16	Lowest Frequency	-1922.3
17	Nucleus	1H
18	Acquired Size	32768
19	Spectral Size	65536



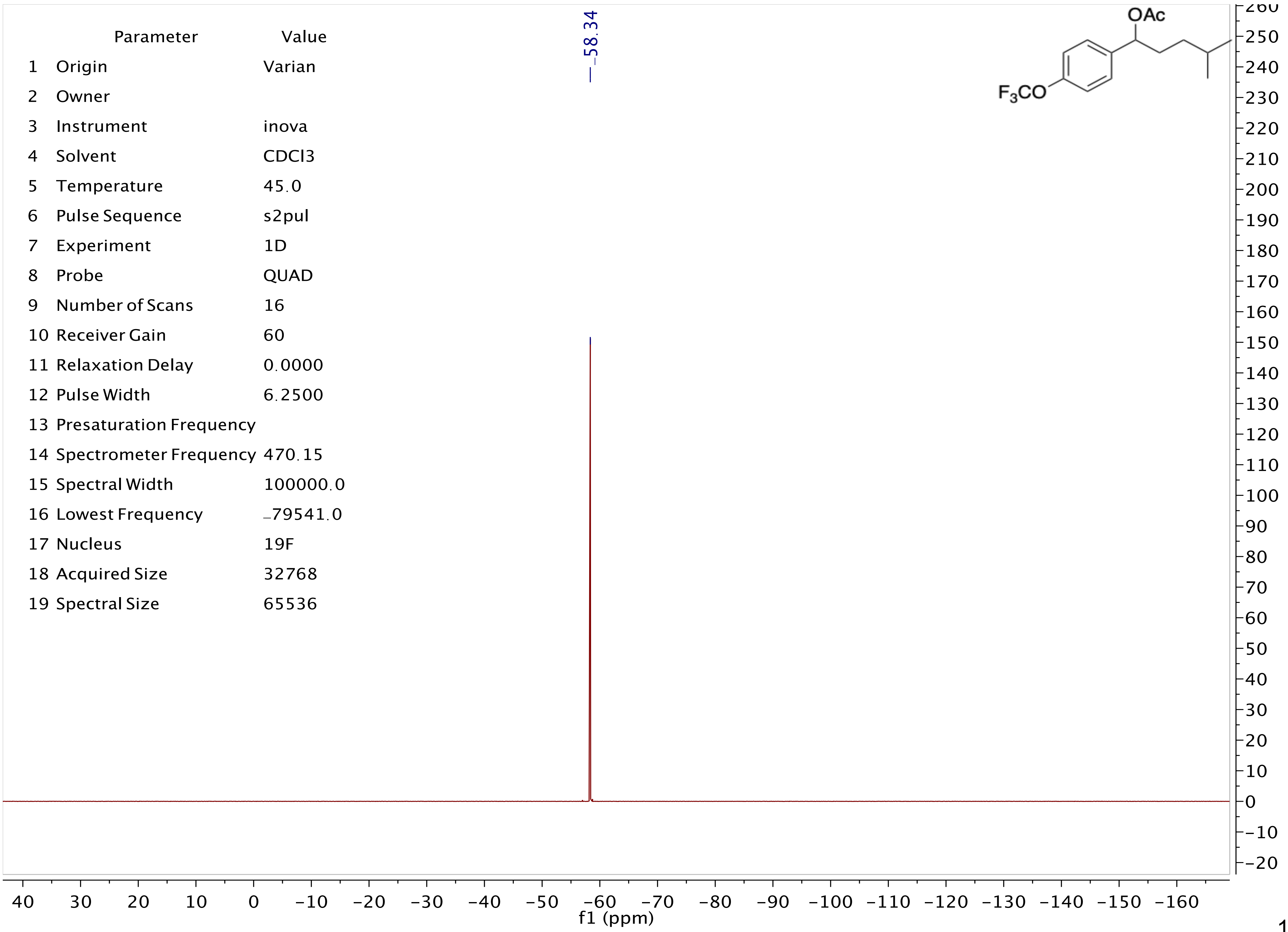
	Parameter	Value
1	Origin	Bruker BioSpin GmbH
2	Owner	user1d
3	Instrument	spect
4	Solvent	CDCl3
5	Temperature	298.0
6	Pulse Sequence	zgpg30
7	Experiment	1D
8	Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
9	Number of Scans	256
10	Receiver Gain	190.5
11	Relaxation Delay	2.0000
12	Pulse Width	10.0000
13	Presaturation Frequency	
14	Spectrometer Frequency	125.83
15	Spectral Width	29761.9
16	Lowest Frequency	-2283.9
17	Nucleus	13C
18	Acquired Size	32768
19	Spectral Size	65536

	Parameter	Value
1	Origin	Varian
2	Owner	
3	Instrument	inova
4	Solvent	CDCl3
5	Temperature	45.0
6	Pulse Sequence	s2pul
7	Experiment	1D
8	Probe	QUAD
9	Number of Scans	16
10	Receiver Gain	41
11	Relaxation Delay	15.0000
12	Pulse Width	6.5000
13	Presaturation Frequency	
14	Spectrometer Frequency	499.69
15	Spectral Width	7024.9
16	Lowest Frequency	-1021.4
17	Nucleus	1H
18	Acquired Size	32768
19	Spectral Size	65536

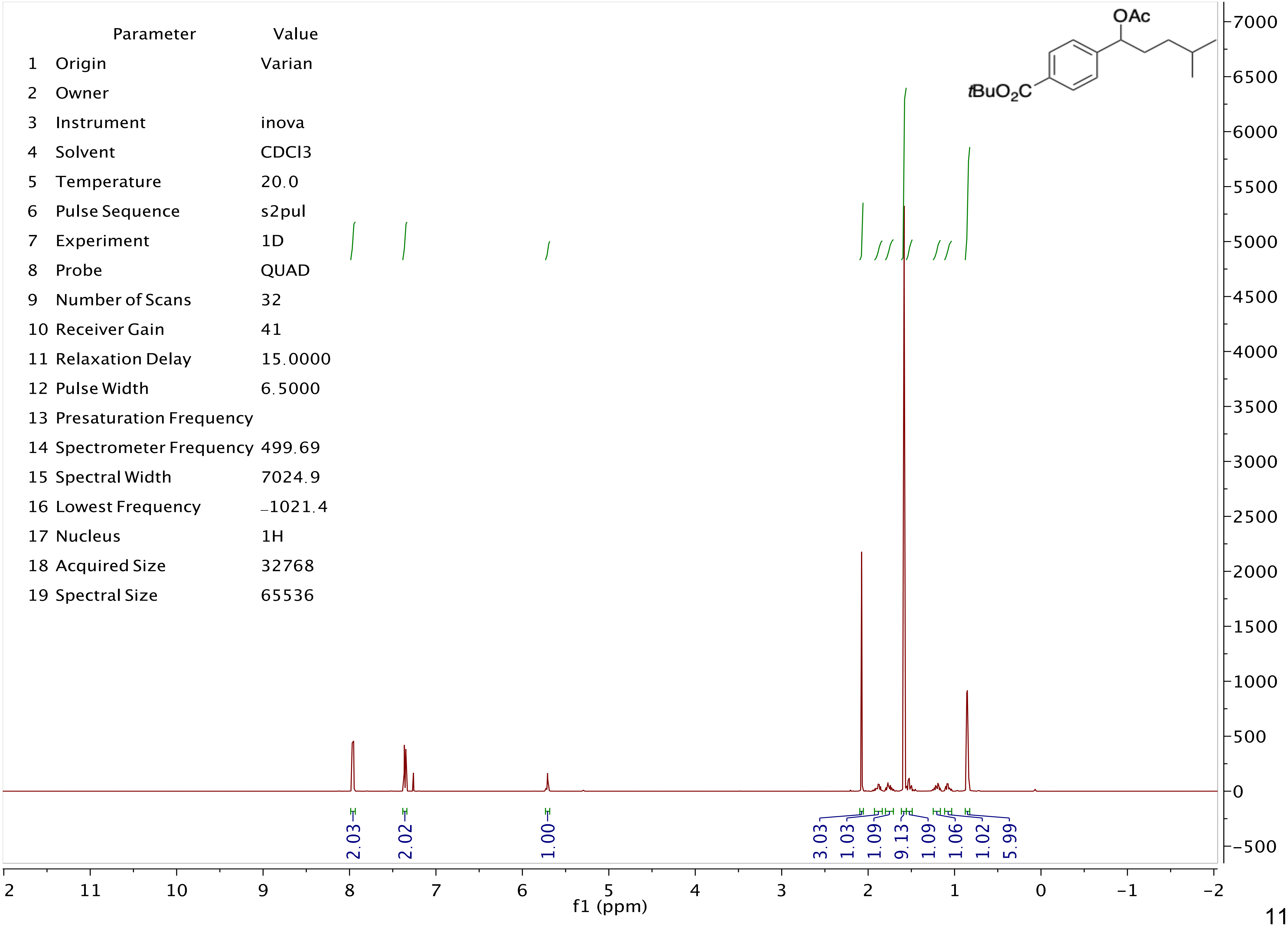




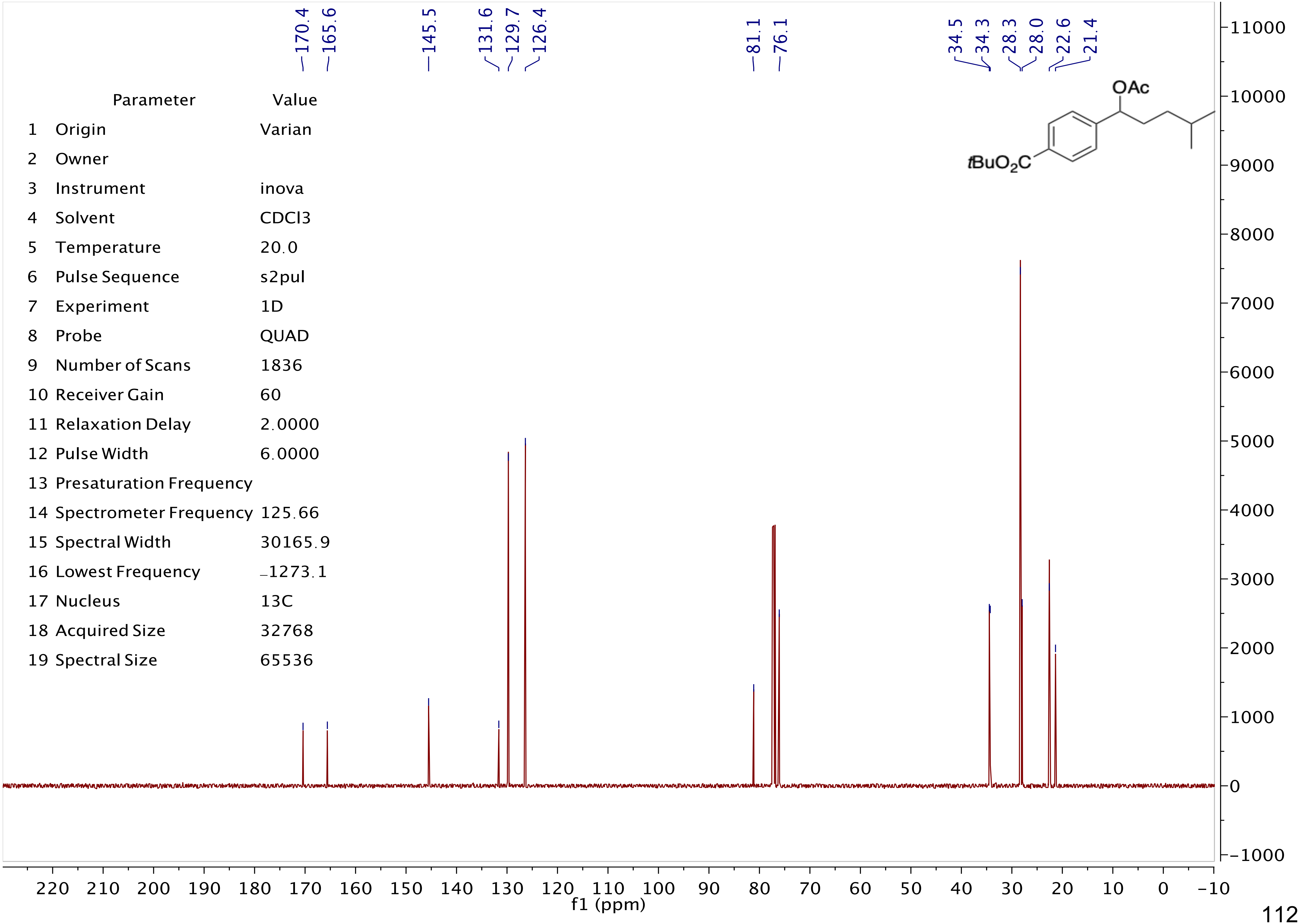
	Parameter	Value
1	Origin	Varian
2	Owner	
3	Instrument	inova
4	Solvent	CDCl3
5	Temperature	45.0
6	Pulse Sequence	s2pul
7	Experiment	1D
8	Probe	QUAD
9	Number of Scans	1024
10	Receiver Gain	60
11	Relaxation Delay	2.0000
12	Pulse Width	6.0000
13	Presaturation Frequency	
14	Spectrometer Frequency	125.66
15	Spectral Width	30165.9
16	Lowest Frequency	-1260.2
17	Nucleus	13C
18	Acquired Size	32768
19	Spectral Size	65536



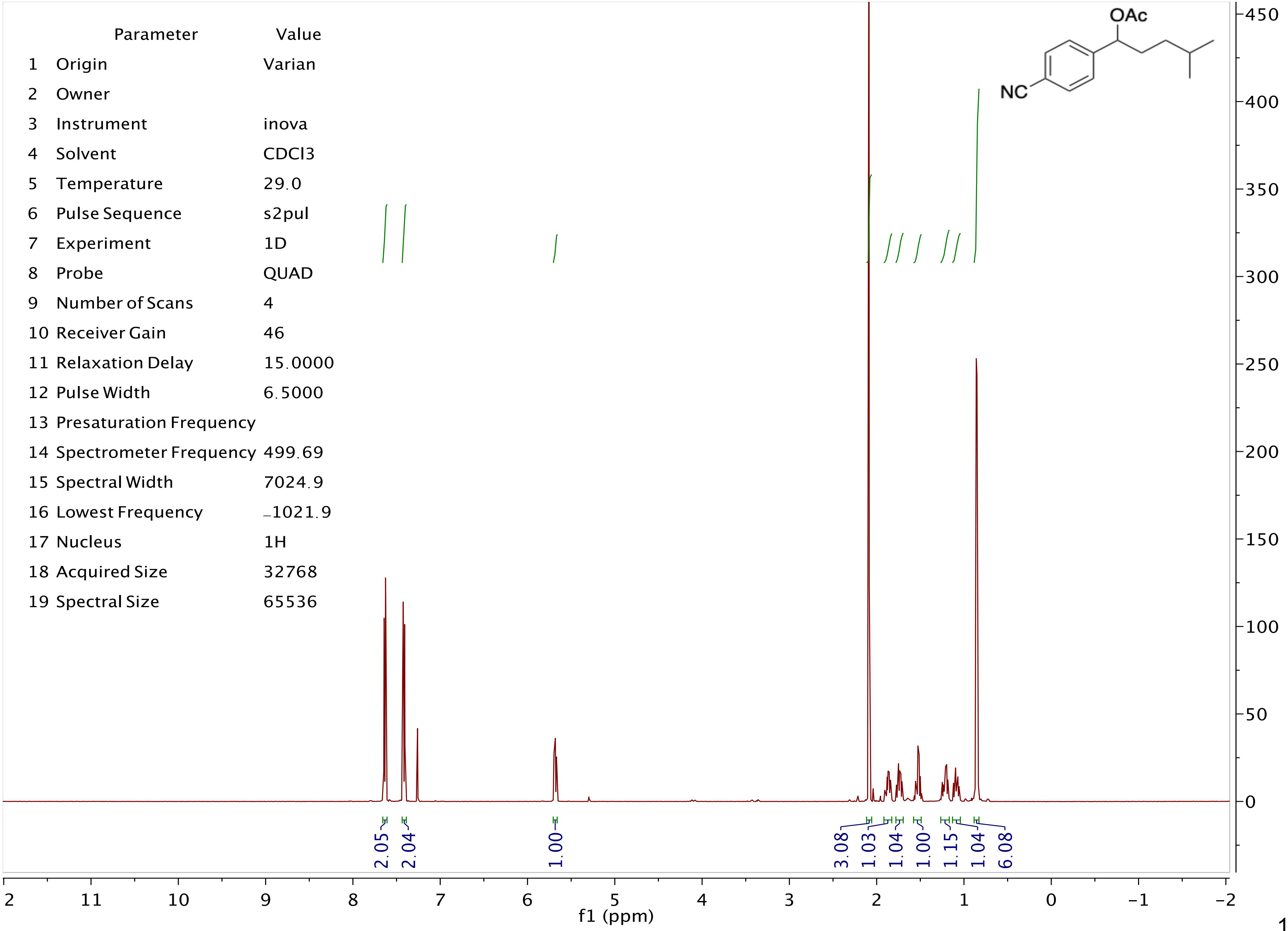
	Parameter	Value
1	Origin	Varian
2	Owner	
3	Instrument	inova
4	Solvent	CDCl3
5	Temperature	45.0
6	Pulse Sequence	s2pul
7	Experiment	1D
8	Probe	QUAD
9	Number of Scans	16
10	Receiver Gain	60
11	Relaxation Delay	0.0000
12	Pulse Width	6.2500
13	Presaturation Frequency	
14	Spectrometer Frequency	470.15
15	Spectral Width	100000.0
16	Lowest Frequency	-79541.0
17	Nucleus	19F
18	Acquired Size	32768
19	Spectral Size	65536



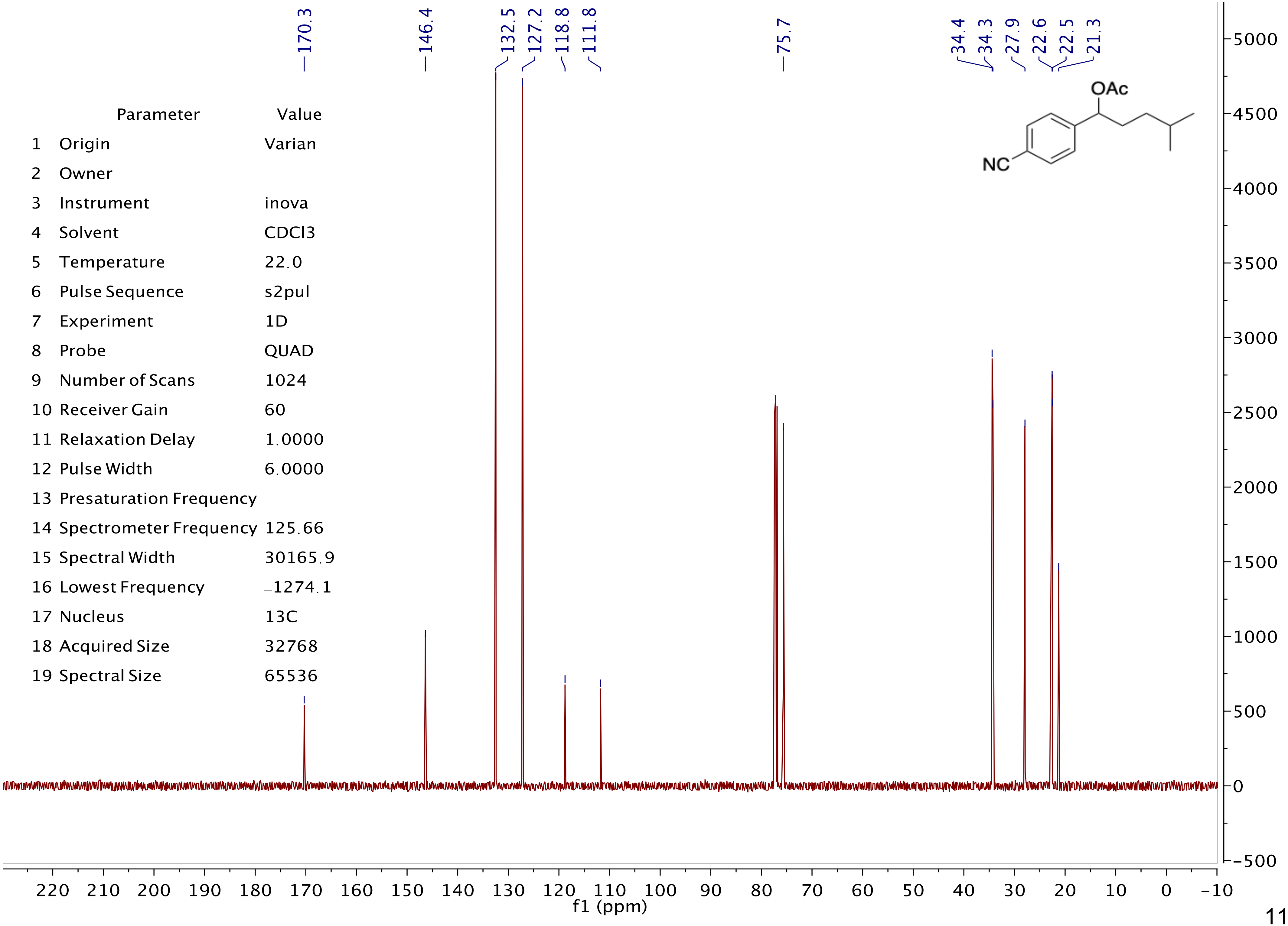
	Parameter	Value
1	Origin	Varian
2	Owner	
3	Instrument	inova
4	Solvent	CDCl3
5	Temperature	20.0
6	Pulse Sequence	s2pul
7	Experiment	1D
8	Probe	QUAD
9	Number of Scans	32
10	Receiver Gain	41
11	Relaxation Delay	15.0000
12	Pulse Width	6.5000
13	Presaturation Frequency	
14	Spectrometer Frequency	499.69
15	Spectral Width	7024.9
16	Lowest Frequency	-1021.4
17	Nucleus	1H
18	Acquired Size	32768
19	Spectral Size	65536



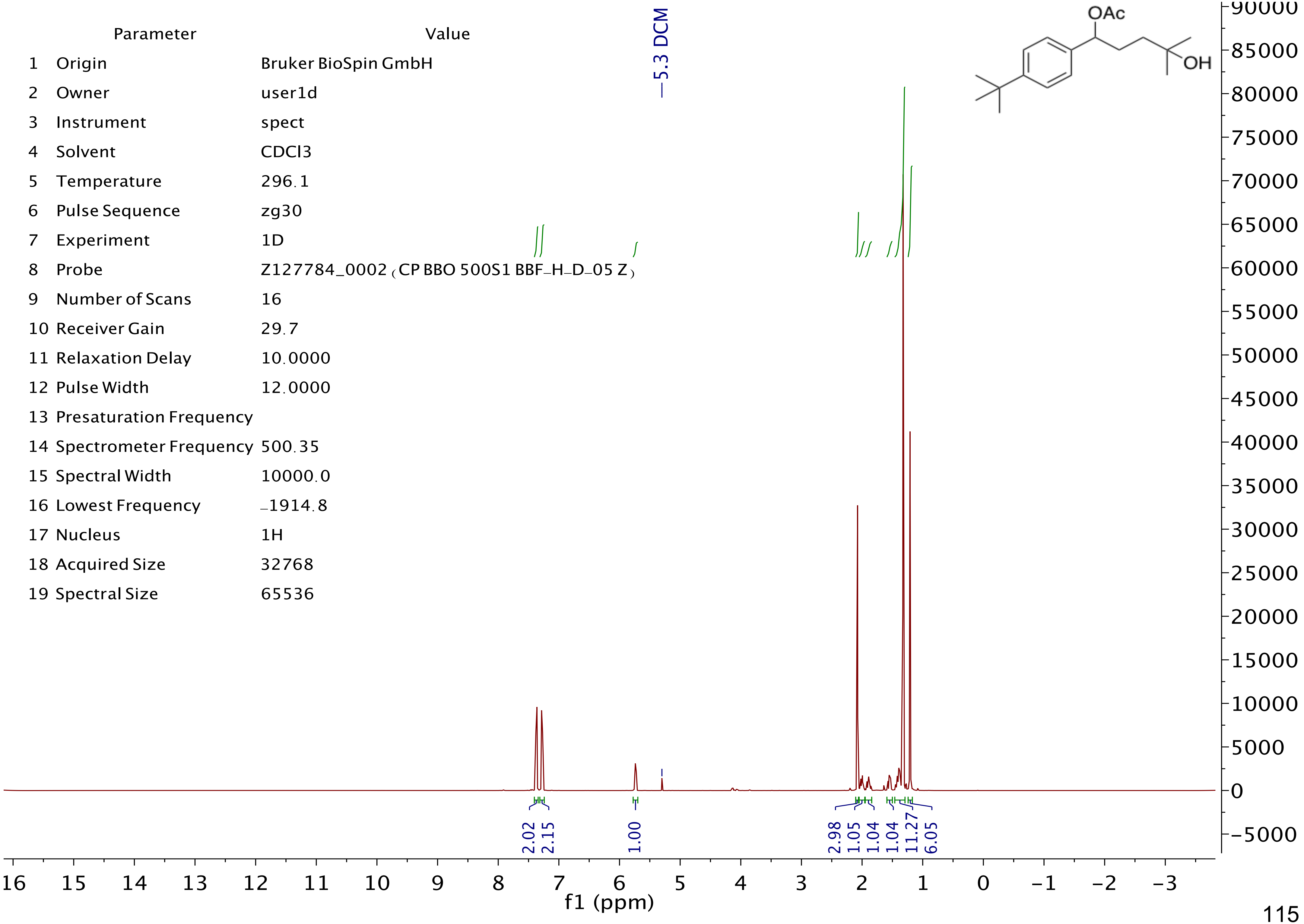
	Parameter	Value
1	Origin	Varian
2	Owner	
3	Instrument	inova
4	Solvent	CDCl3
5	Temperature	20.0
6	Pulse Sequence	s2pul
7	Experiment	1D
8	Probe	QUAD
9	Number of Scans	1836
10	Receiver Gain	60
11	Relaxation Delay	2.0000
12	Pulse Width	6.0000
13	Presaturation Frequency	
14	Spectrometer Frequency	125.66
15	Spectral Width	30165.9
16	Lowest Frequency	-1273.1
17	Nucleus	13C
18	Acquired Size	32768
19	Spectral Size	65536



	Parameter	Value
1	Origin	Varian
2	Owner	
3	Instrument	inova
4	Solvent	CDCl3
5	Temperature	29.0
6	Pulse Sequence	s2pul
7	Experiment	1D
8	Probe	QUAD
9	Number of Scans	4
10	Receiver Gain	46
11	Relaxation Delay	15.0000
12	Pulse Width	6.5000
13	Presaturation Frequency	
14	Spectrometer Frequency	499.69
15	Spectral Width	7024.9
16	Lowest Frequency	-1021.9
17	Nucleus	1H
18	Acquired Size	32768
19	Spectral Size	65536

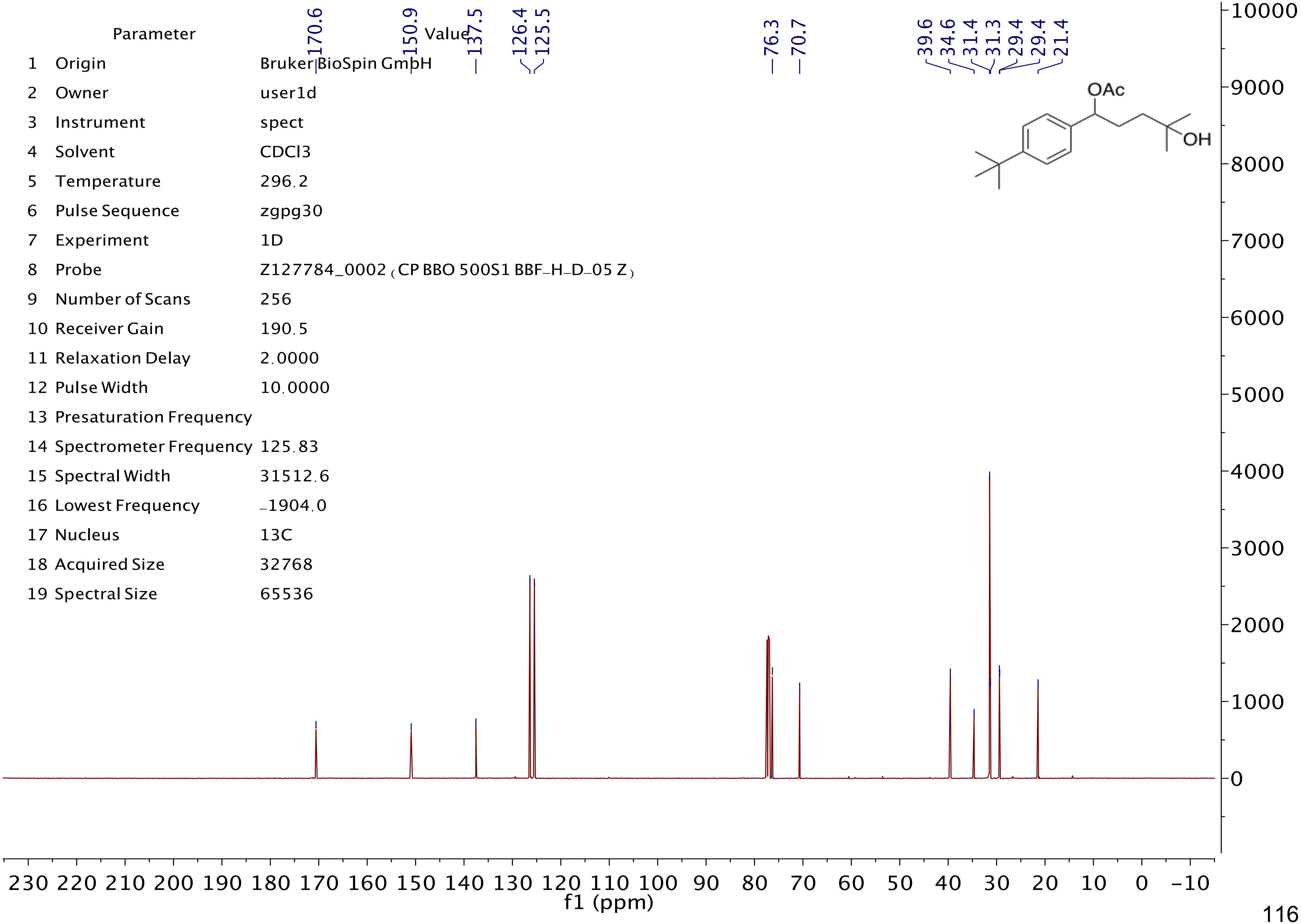


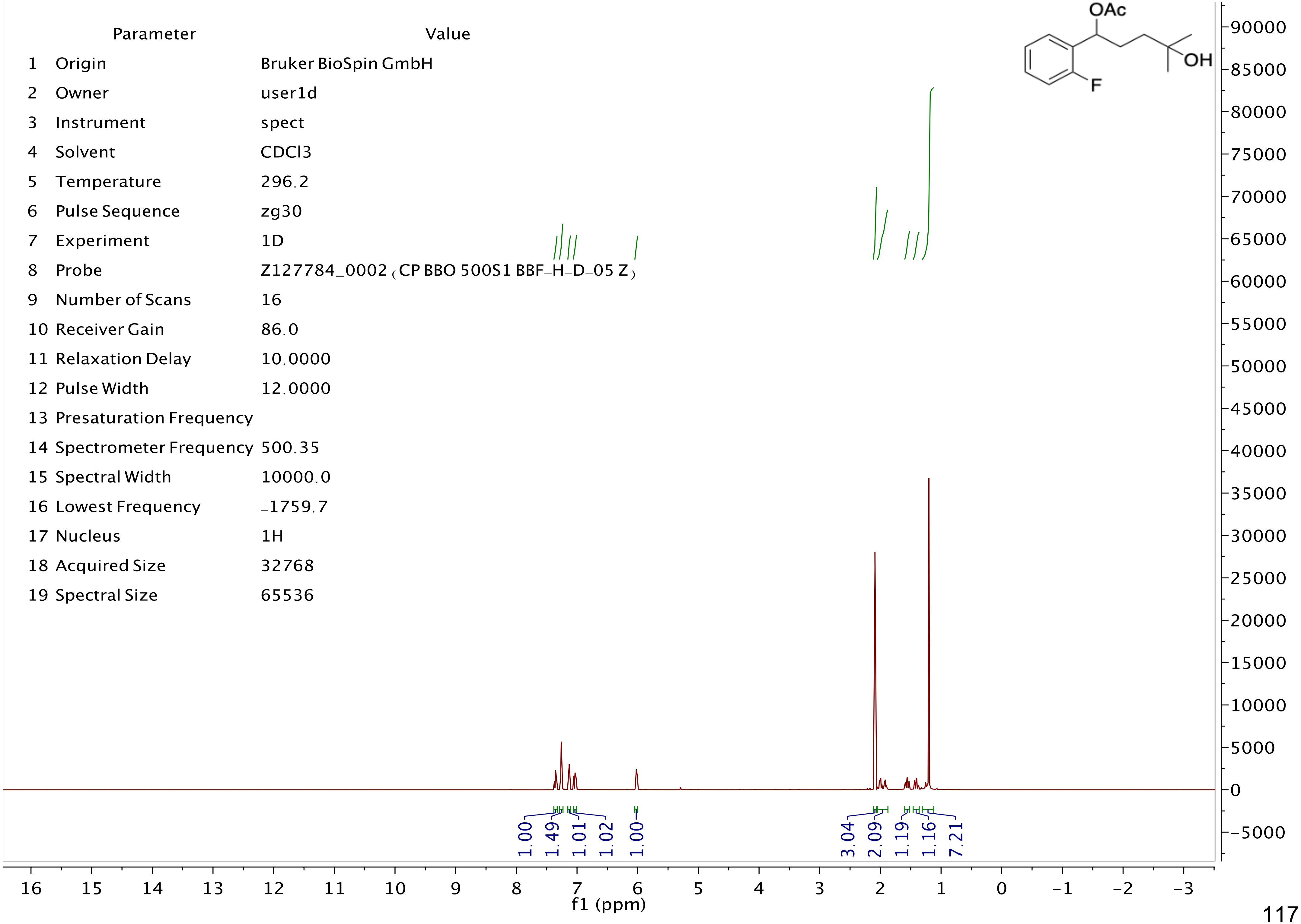
	Parameter	Value
1	Origin	Varian
2	Owner	
3	Instrument	inova
4	Solvent	CDCl3
5	Temperature	22.0
6	Pulse Sequence	s2pul
7	Experiment	1D
8	Probe	QUAD
9	Number of Scans	1024
10	Receiver Gain	60
11	Relaxation Delay	1.0000
12	Pulse Width	6.0000
13	Presaturation Frequency	
14	Spectrometer Frequency	125.66
15	Spectral Width	30165.9
16	Lowest Frequency	-1274.1
17	Nucleus	13C
18	Acquired Size	32768
19	Spectral Size	65536



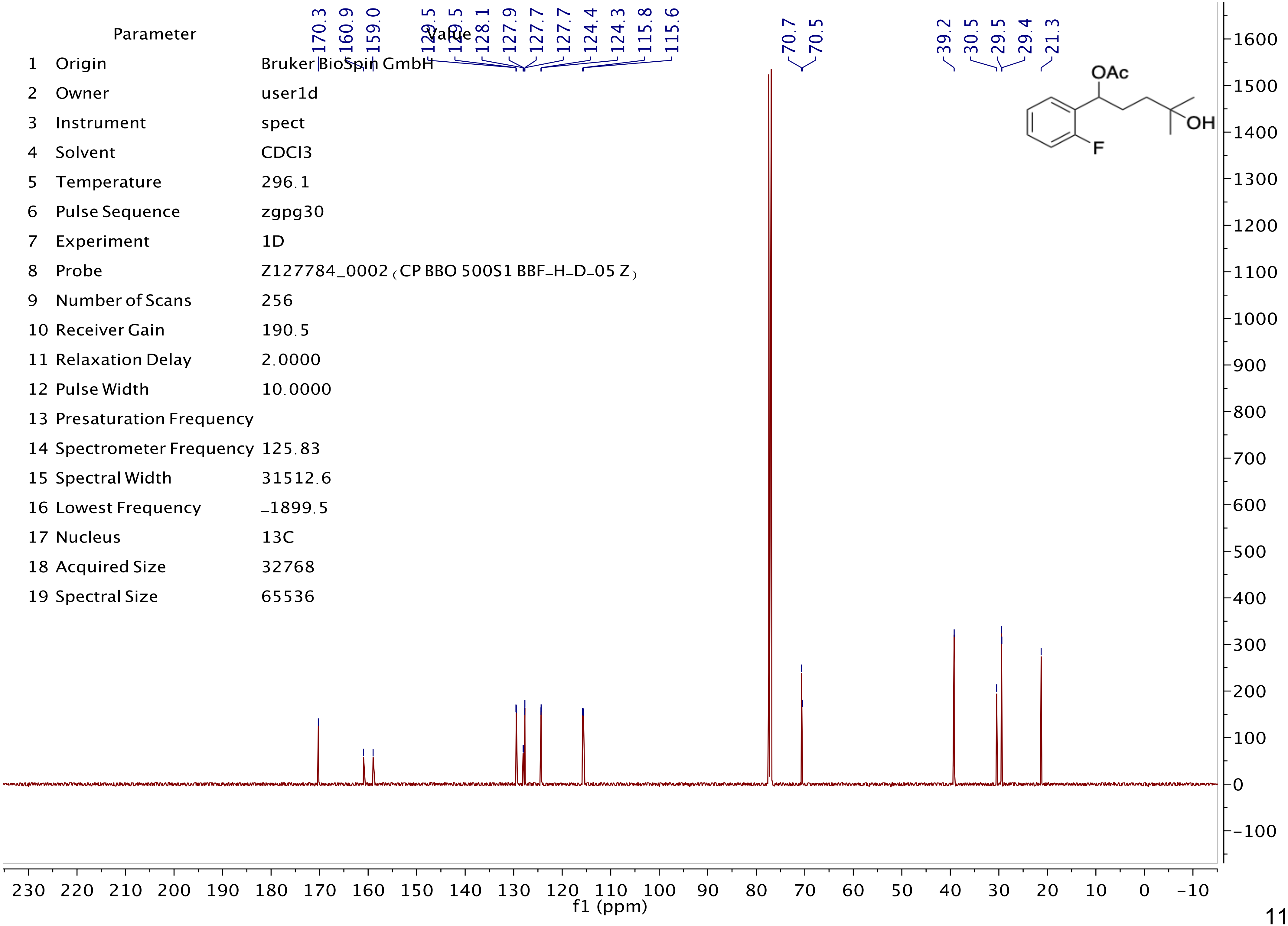
	Parameter	Value
1	Origin	Bruker BioSpin GmbH
2	Owner	user1d
3	Instrument	spect
4	Solvent	CDCl3
5	Temperature	296.1
6	Pulse Sequence	zg30
7	Experiment	1D
8	Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
9	Number of Scans	16
10	Receiver Gain	29.7
11	Relaxation Delay	10.0000
12	Pulse Width	12.0000
13	Presaturation Frequency	
14	Spectrometer Frequency	500.35
15	Spectral Width	10000.0
16	Lowest Frequency	-1914.8
17	Nucleus	1H
18	Acquired Size	32768
19	Spectral Size	65536

	Parameter	Value
1	Origin	Bruker BioSpin GmbH
2	Owner	user1d
3	Instrument	spect
4	Solvent	CDCl3
5	Temperature	296.2
6	Pulse Sequence	zgpg30
7	Experiment	1D
8	Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
9	Number of Scans	256
10	Receiver Gain	190.5
11	Relaxation Delay	2.0000
12	Pulse Width	10.0000
13	Presaturation Frequency	
14	Spectrometer Frequency	125.83
15	Spectral Width	31512.6
16	Lowest Frequency	-1904.0
17	Nucleus	13C
18	Acquired Size	32768
19	Spectral Size	65536



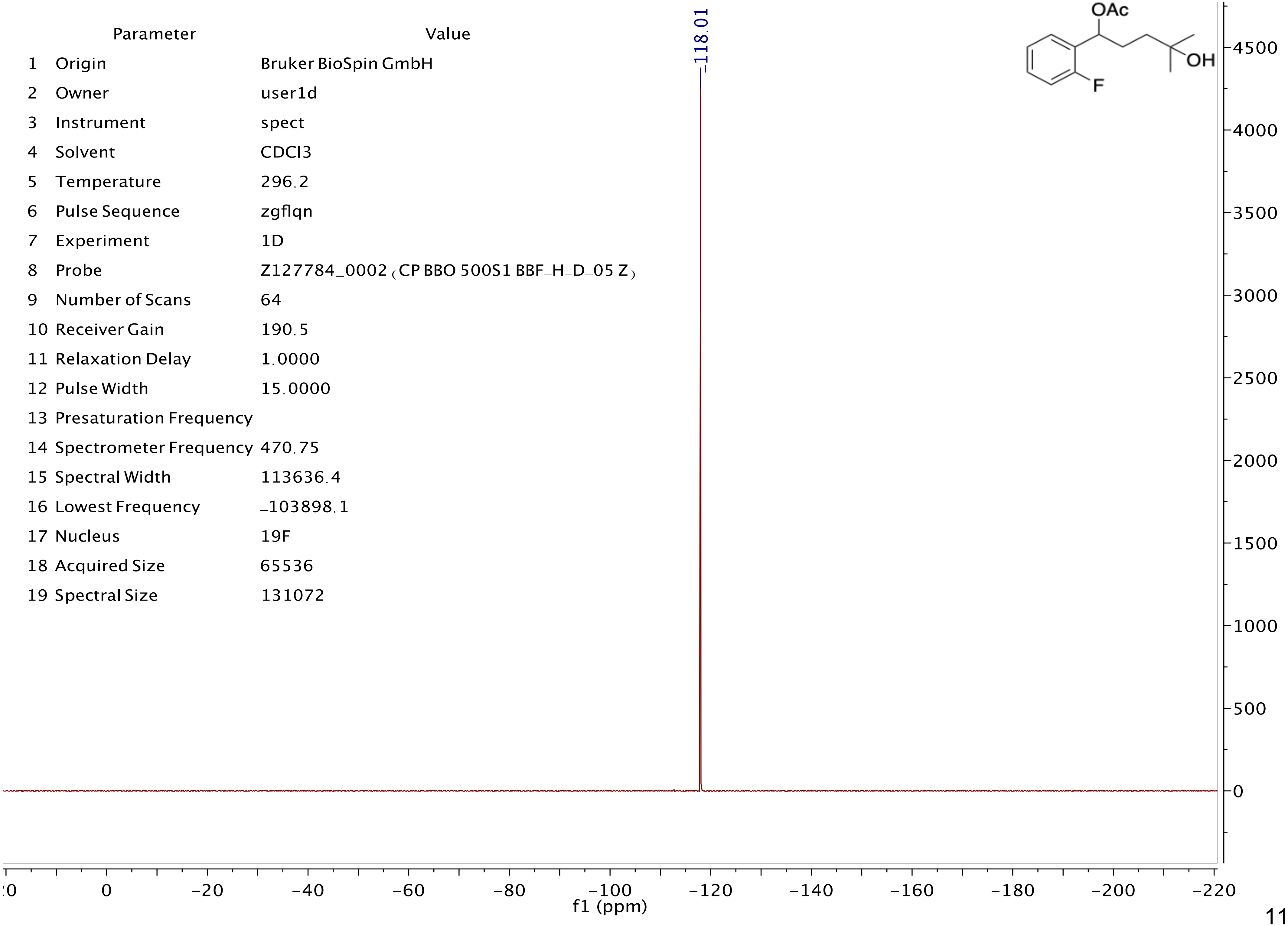


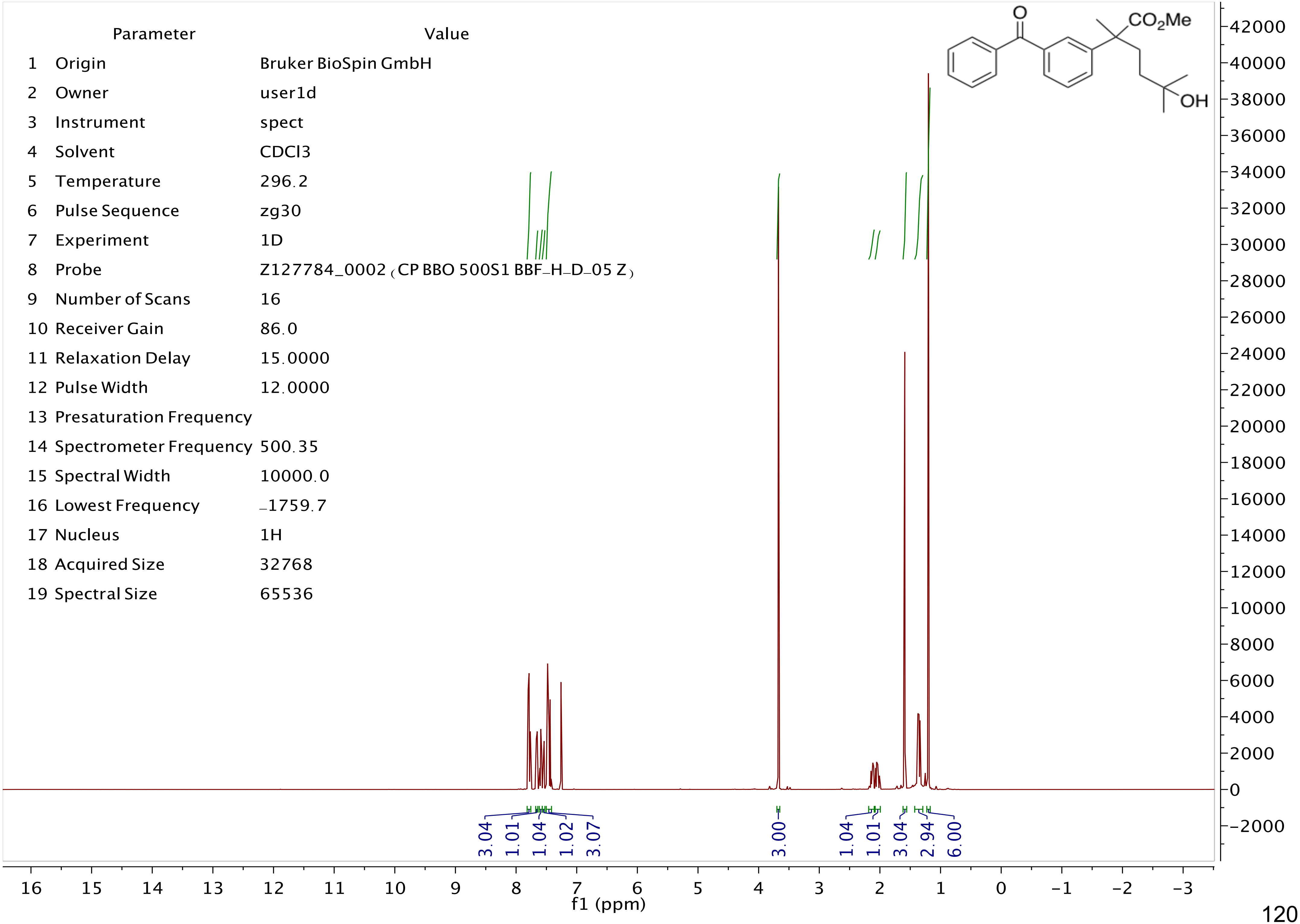
	Parameter	Value
1	Origin	Bruker BioSpin GmbH
2	Owner	user1d
3	Instrument	spect
4	Solvent	CDCl3
5	Temperature	296.2
6	Pulse Sequence	zg30
7	Experiment	1D
8	Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
9	Number of Scans	16
10	Receiver Gain	86.0
11	Relaxation Delay	10.0000
12	Pulse Width	12.0000
13	Presaturation Frequency	
14	Spectrometer Frequency	500.35
15	Spectral Width	10000.0
16	Lowest Frequency	-1759.7
17	Nucleus	1H
18	Acquired Size	32768
19	Spectral Size	65536



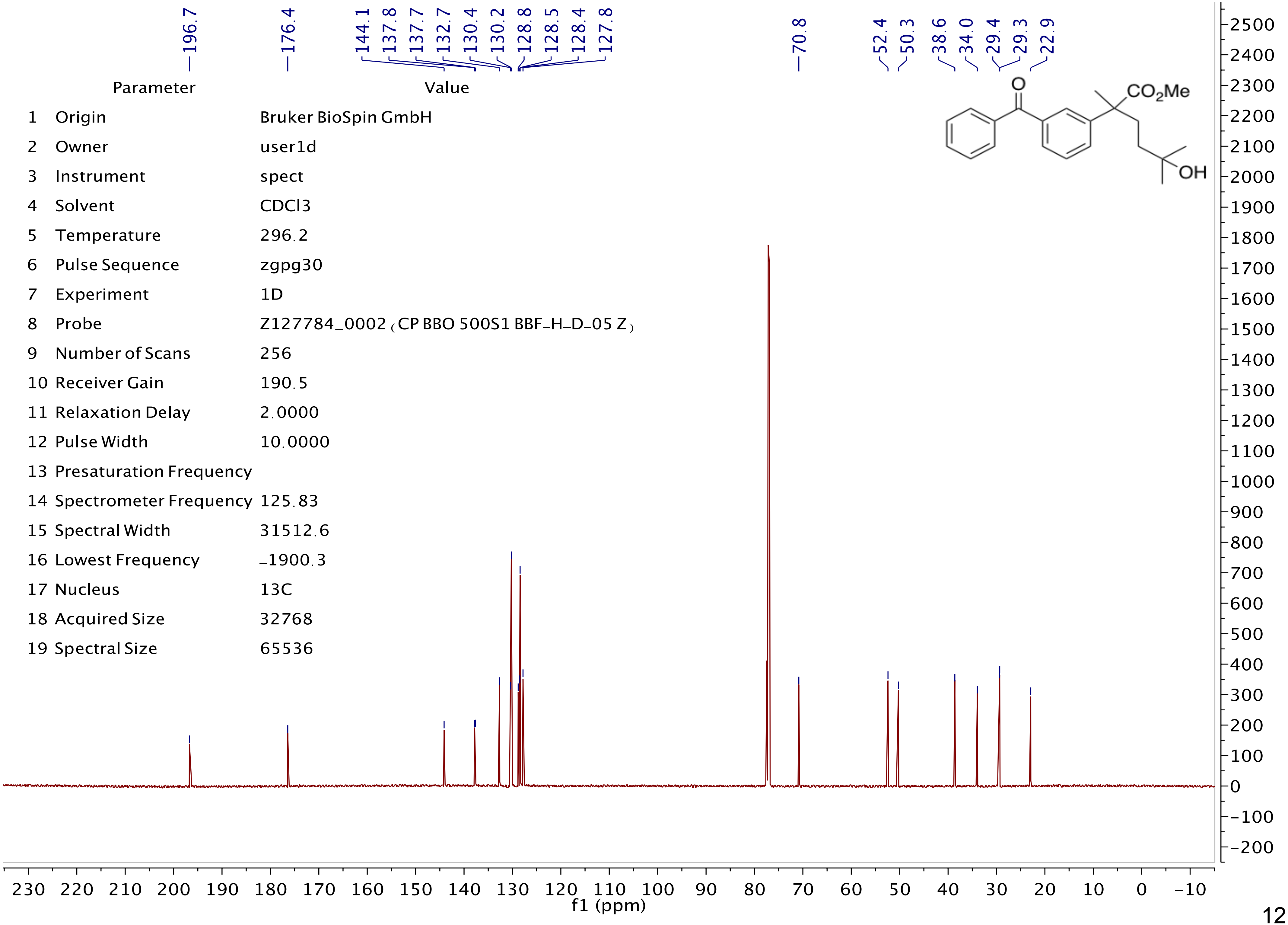
	Parameter	Value
1	Origin	Bruker BioSpin GmbH
2	Owner	user1d
3	Instrument	spect
4	Solvent	CDCl3
5	Temperature	296.1
6	Pulse Sequence	zgpg30
7	Experiment	1D
8	Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
9	Number of Scans	256
10	Receiver Gain	190.5
11	Relaxation Delay	2.0000
12	Pulse Width	10.0000
13	Presaturation Frequency	
14	Spectrometer Frequency	125.83
15	Spectral Width	31512.6
16	Lowest Frequency	-1899.5
17	Nucleus	13C
18	Acquired Size	32768
19	Spectral Size	65536

	Parameter	Value
1	Origin	Bruker BioSpin GmbH
2	Owner	user1d
3	Instrument	spect
4	Solvent	CDCl3
5	Temperature	296.2
6	Pulse Sequence	zgflqn
7	Experiment	1D
8	Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
9	Number of Scans	64
10	Receiver Gain	190.5
11	Relaxation Delay	1.0000
12	Pulse Width	15.0000
13	Presaturation Frequency	
14	Spectrometer Frequency	470.75
15	Spectral Width	113636.4
16	Lowest Frequency	-103898.1
17	Nucleus	19F
18	Acquired Size	65536
19	Spectral Size	131072



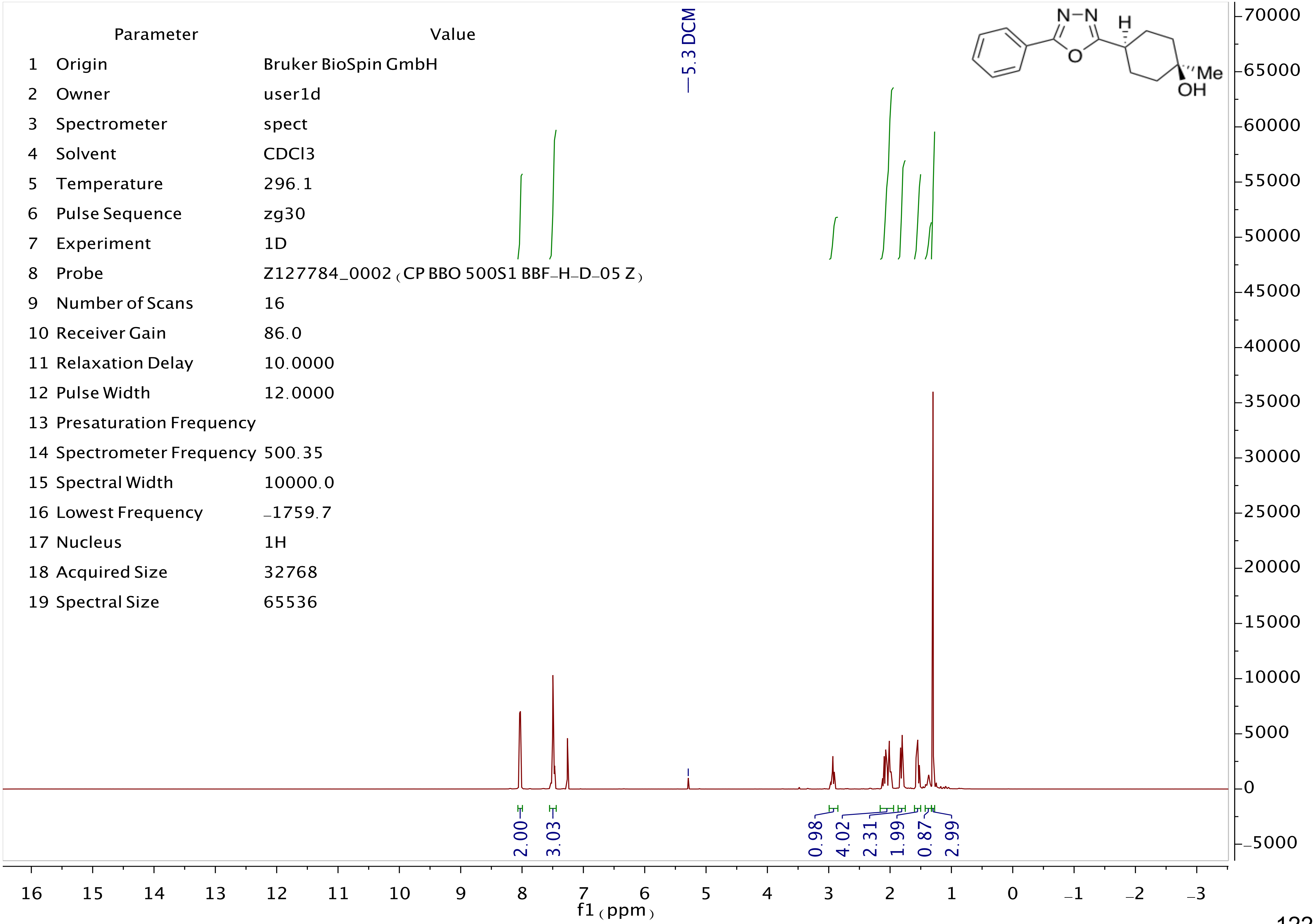


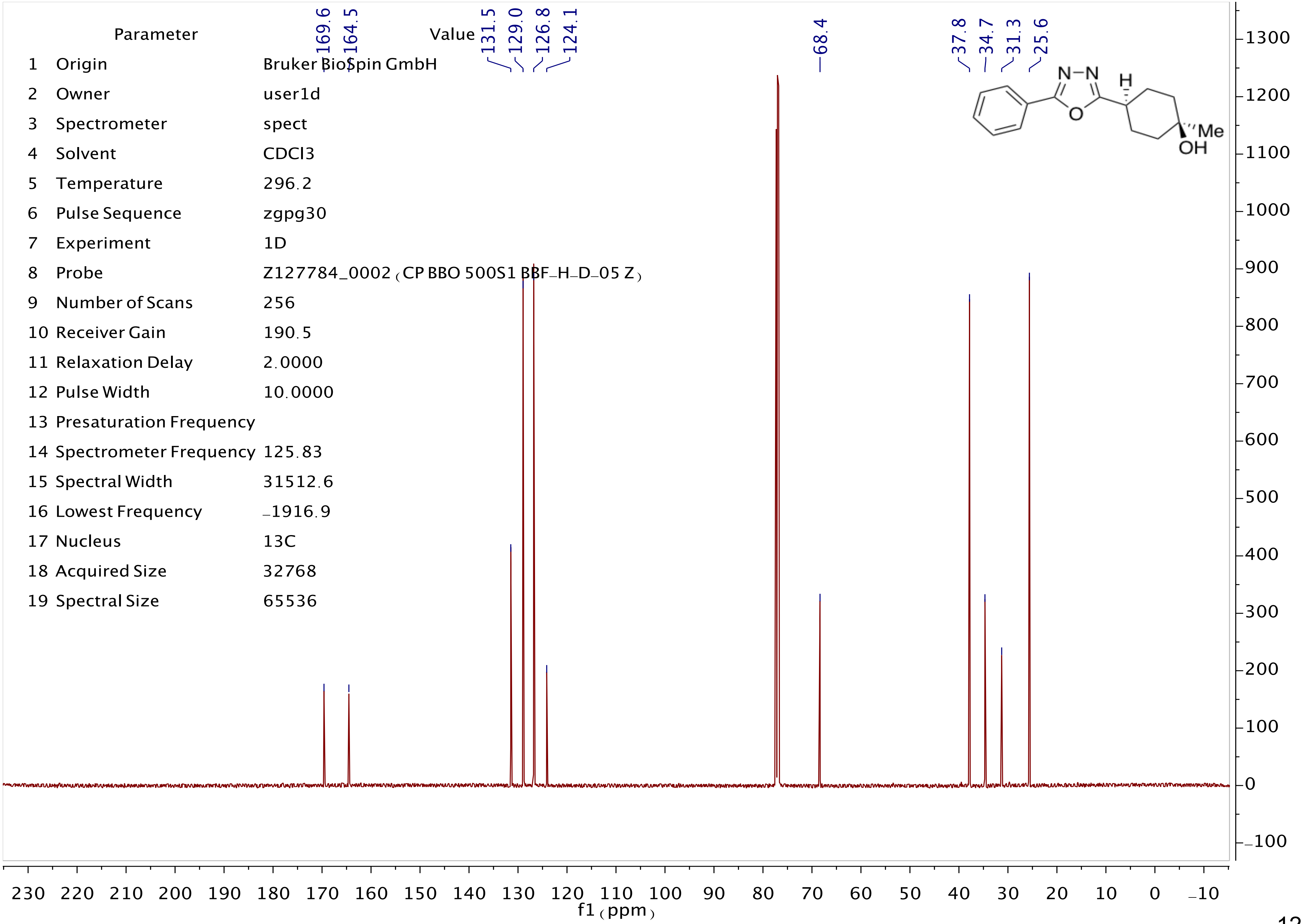
	Parameter	Value
1	Origin	Bruker BioSpin GmbH
2	Owner	user1d
3	Instrument	spect
4	Solvent	CDCl3
5	Temperature	296.2
6	Pulse Sequence	zg30
7	Experiment	1D
8	Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
9	Number of Scans	16
10	Receiver Gain	86.0
11	Relaxation Delay	15.0000
12	Pulse Width	12.0000
13	Presaturation Frequency	
14	Spectrometer Frequency	500.35
15	Spectral Width	10000.0
16	Lowest Frequency	-1759.7
17	Nucleus	1H
18	Acquired Size	32768
19	Spectral Size	65536



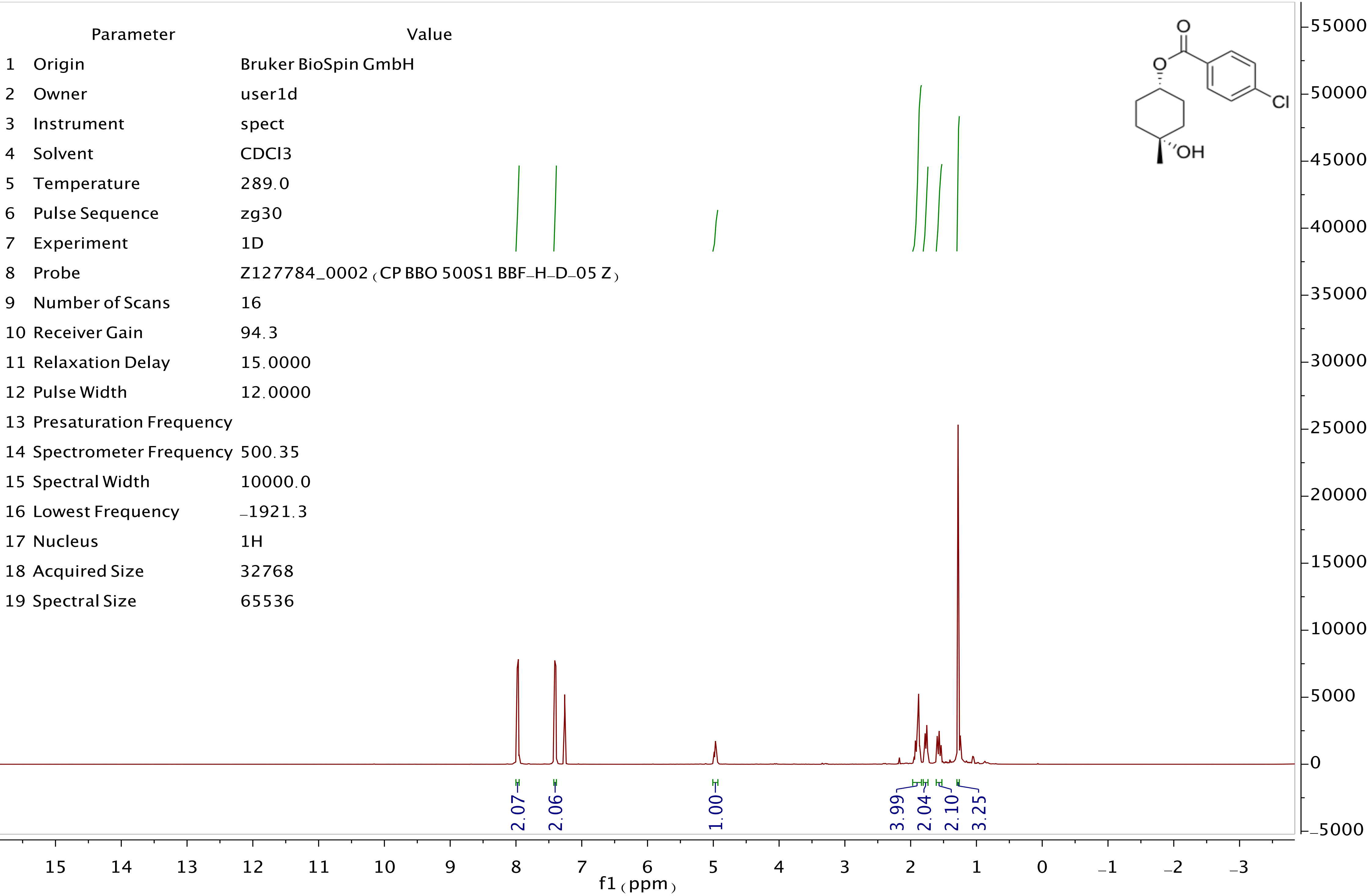
	Parameter	Value
1	Origin	Bruker BioSpin GmbH
2	Owner	user1d
3	Instrument	spect
4	Solvent	CDCl3
5	Temperature	296.2
6	Pulse Sequence	zgpg30
7	Experiment	1D
8	Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
9	Number of Scans	256
10	Receiver Gain	190.5
11	Relaxation Delay	2.0000
12	Pulse Width	10.0000
13	Presaturation Frequency	
14	Spectrometer Frequency	125.83
15	Spectral Width	31512.6
16	Lowest Frequency	-1900.3
17	Nucleus	13C
18	Acquired Size	32768
19	Spectral Size	65536

	Parameter	Value
1	Origin	Bruker BioSpin GmbH
2	Owner	user1d
3	Spectrometer	spect
4	Solvent	CDCl3
5	Temperature	296.1
6	Pulse Sequence	zg30
7	Experiment	1D
8	Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
9	Number of Scans	16
10	Receiver Gain	86.0
11	Relaxation Delay	10.0000
12	Pulse Width	12.0000
13	Presaturation Frequency	
14	Spectrometer Frequency	500.35
15	Spectral Width	10000.0
16	Lowest Frequency	-1759.7
17	Nucleus	1H
18	Acquired Size	32768
19	Spectral Size	65536

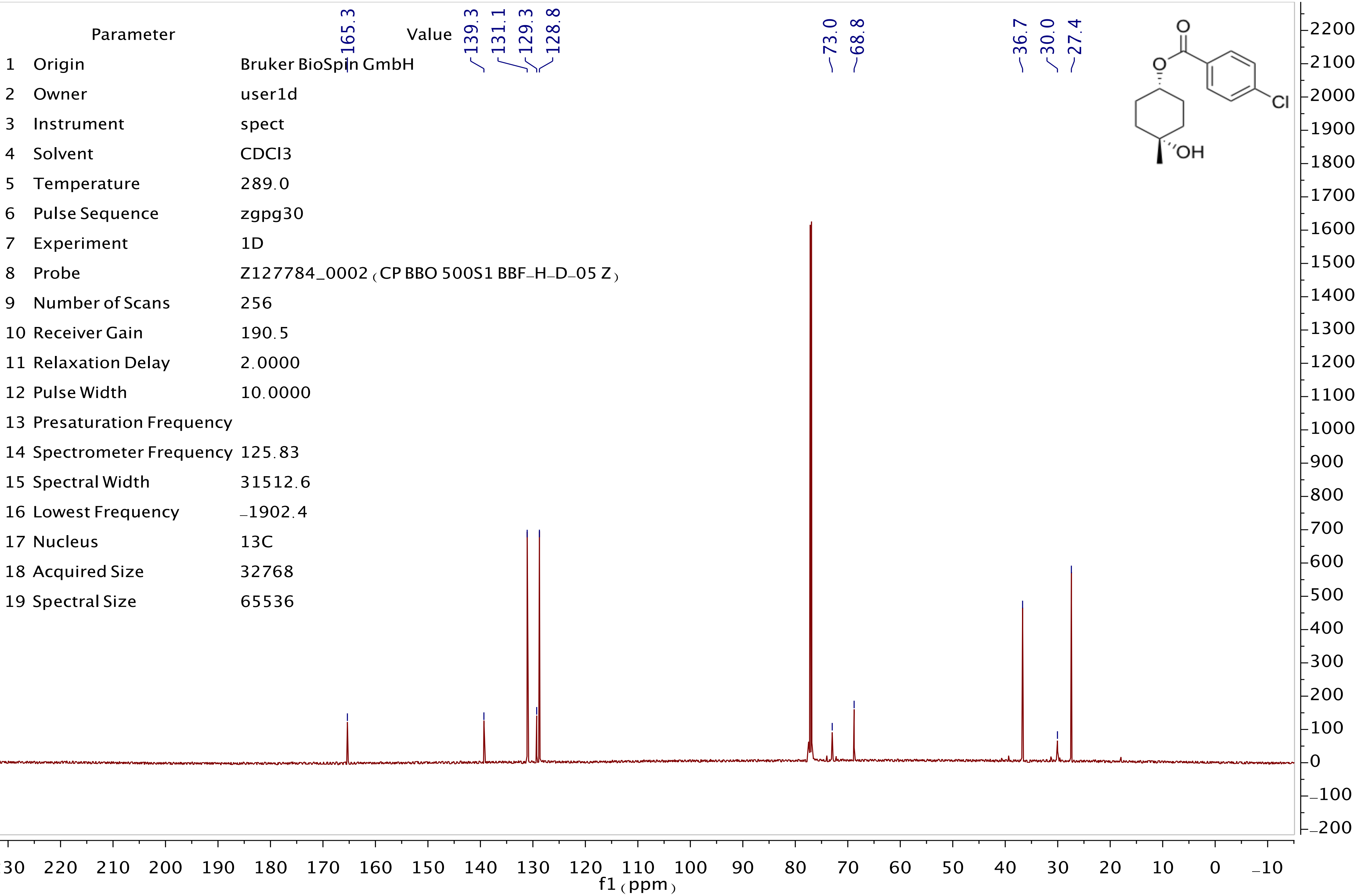




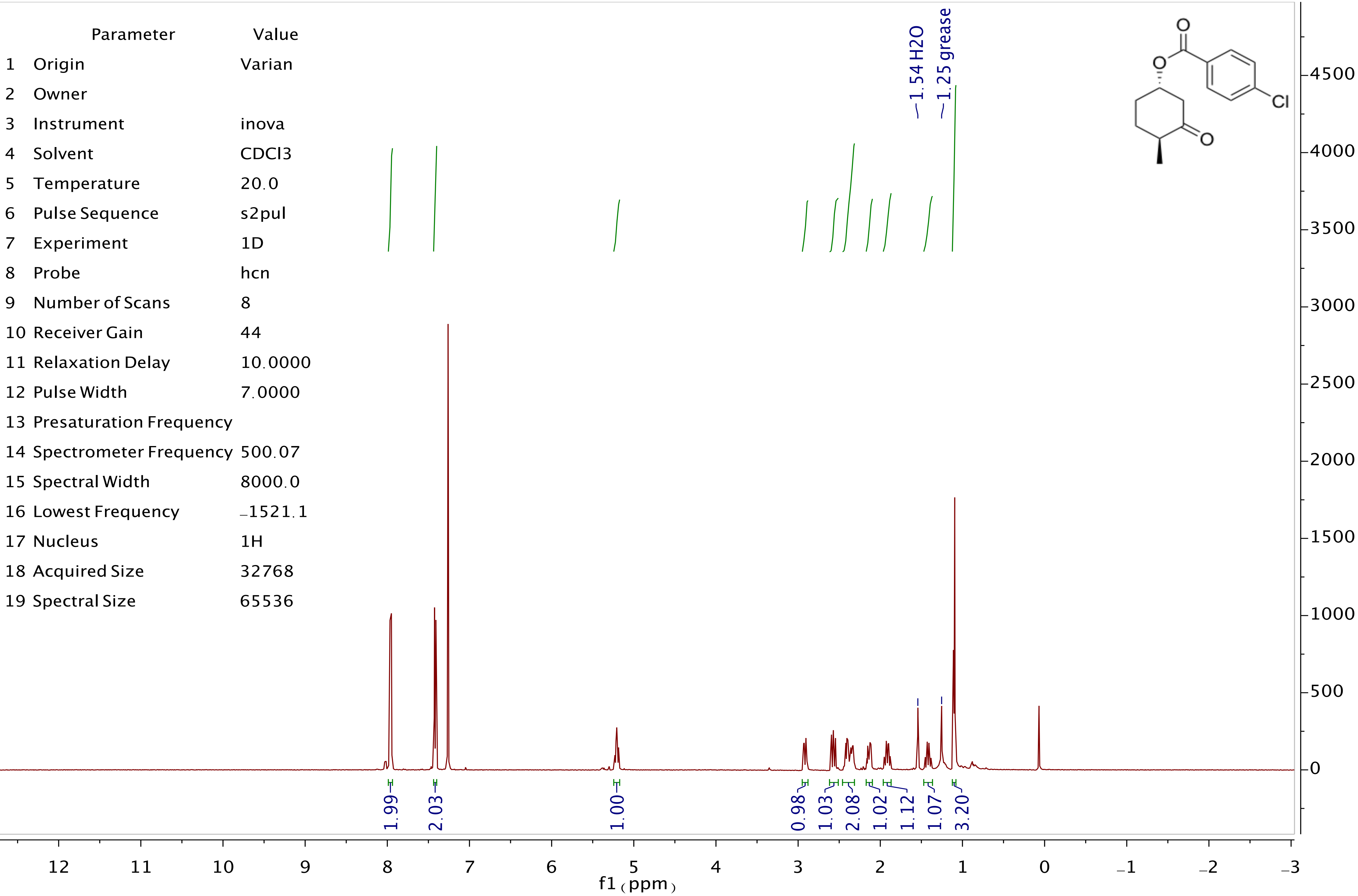
	Parameter	Value
1	Origin	Bruker BioSpin GmbH
2	Owner	user1d
3	Spectrometer	spect
4	Solvent	CDCl3
5	Temperature	296.2
6	Pulse Sequence	zgpg30
7	Experiment	1D
8	Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
9	Number of Scans	256
10	Receiver Gain	190.5
11	Relaxation Delay	2.0000
12	Pulse Width	10.0000
13	Presaturation Frequency	
14	Spectrometer Frequency	125.83
15	Spectral Width	31512.6
16	Lowest Frequency	-1916.9
17	Nucleus	13C
18	Acquired Size	32768
19	Spectral Size	65536



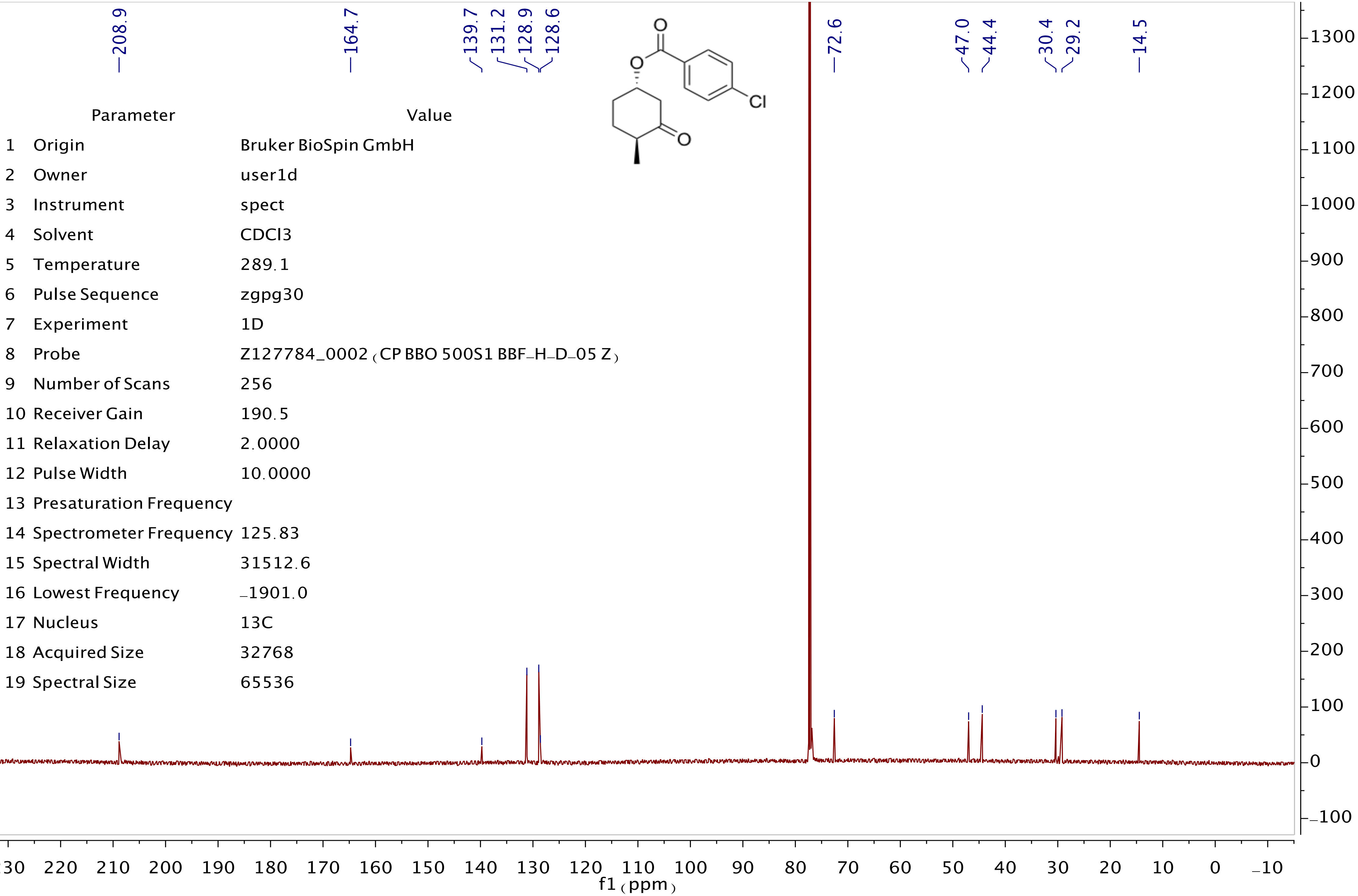
	Parameter	Value
1	Origin	Bruker BioSpin GmbH
2	Owner	user1d
3	Instrument	spect
4	Solvent	CDCl3
5	Temperature	289.0
6	Pulse Sequence	zg30
7	Experiment	1D
8	Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
9	Number of Scans	16
10	Receiver Gain	94.3
11	Relaxation Delay	15.0000
12	Pulse Width	12.0000
13	Presaturation Frequency	
14	Spectrometer Frequency	500.35
15	Spectral Width	10000.0
16	Lowest Frequency	-1921.3
17	Nucleus	1H
18	Acquired Size	32768
19	Spectral Size	65536



	Parameter	Value
1	Origin	Bruker BioSpin GmbH
2	Owner	user1d
3	Instrument	spect
4	Solvent	CDCl3
5	Temperature	289.0
6	Pulse Sequence	zgpg30
7	Experiment	1D
8	Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
9	Number of Scans	256
10	Receiver Gain	190.5
11	Relaxation Delay	2.0000
12	Pulse Width	10.0000
13	Presaturation Frequency	
14	Spectrometer Frequency	125.83
15	Spectral Width	31512.6
16	Lowest Frequency	-1902.4
17	Nucleus	13C
18	Acquired Size	32768
19	Spectral Size	65536

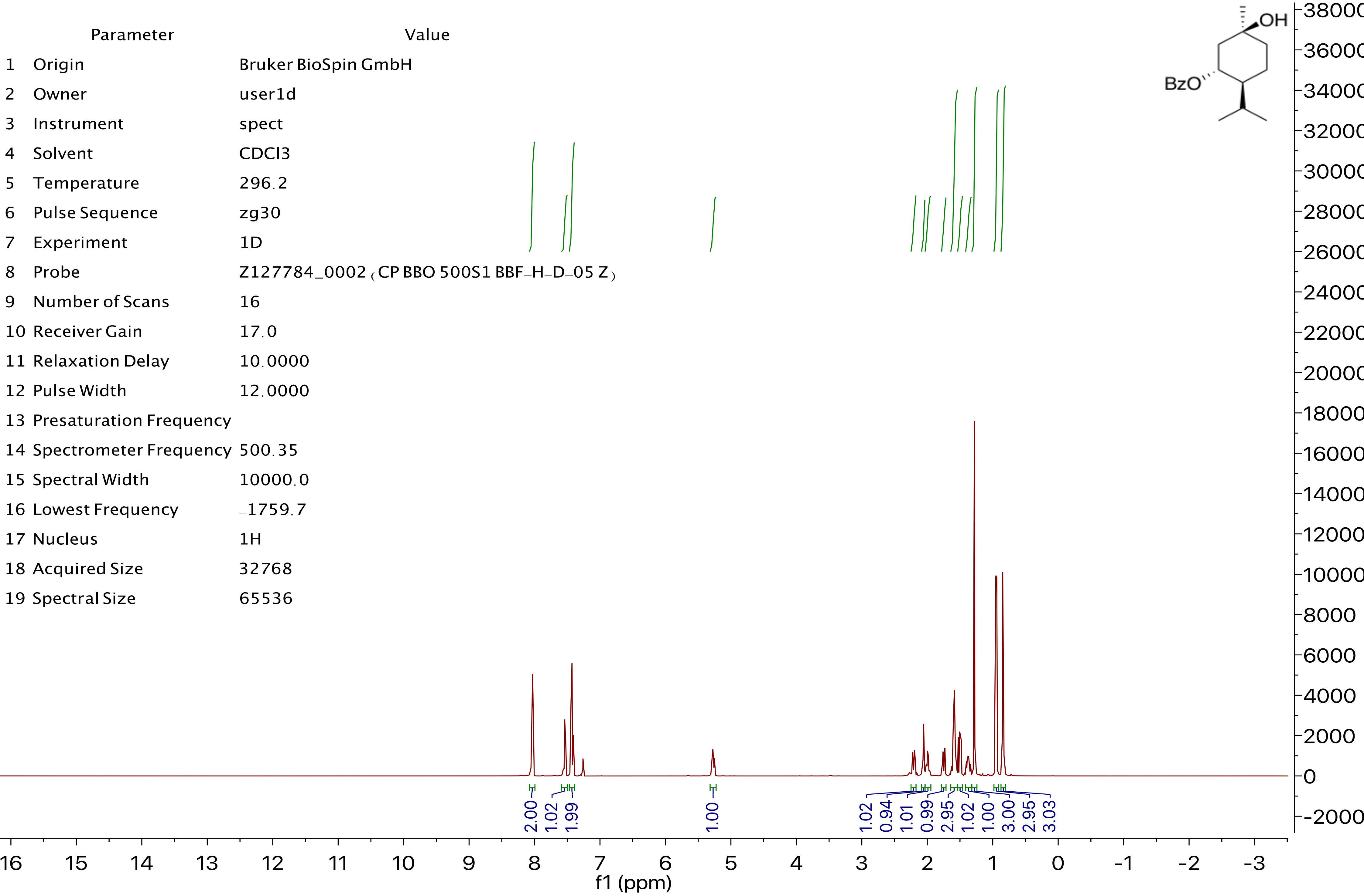


	Parameter	Value
1	Origin	Varian
2	Owner	
3	Instrument	inova
4	Solvent	CDCl3
5	Temperature	20.0
6	Pulse Sequence	s2pul
7	Experiment	1D
8	Probe	hcn
9	Number of Scans	8
10	Receiver Gain	44
11	Relaxation Delay	10.0000
12	Pulse Width	7.0000
13	Presaturation Frequency	
14	Spectrometer Frequency	500.07
15	Spectral Width	8000.0
16	Lowest Frequency	-1521.1
17	Nucleus	1H
18	Acquired Size	32768
19	Spectral Size	65536

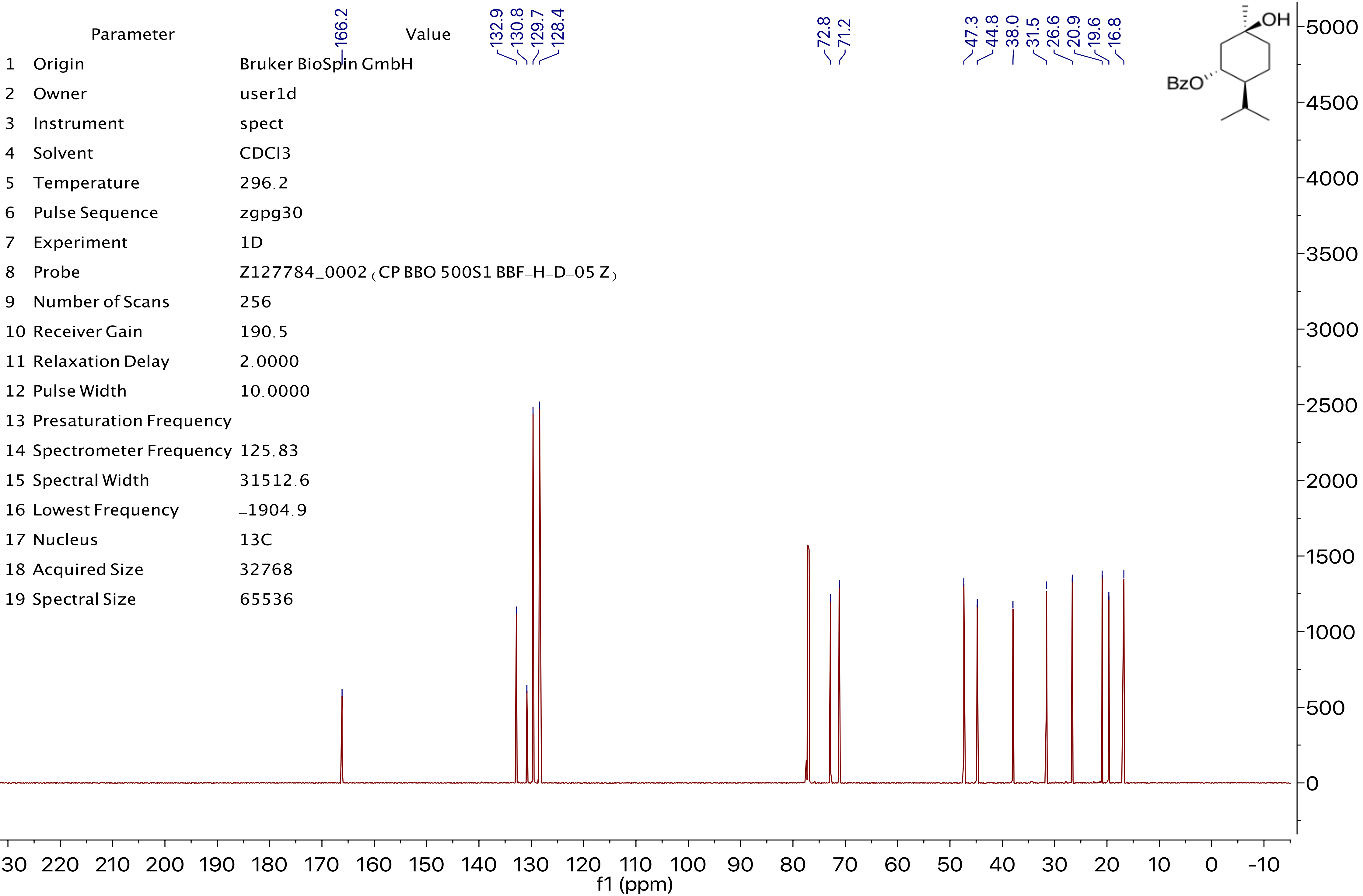


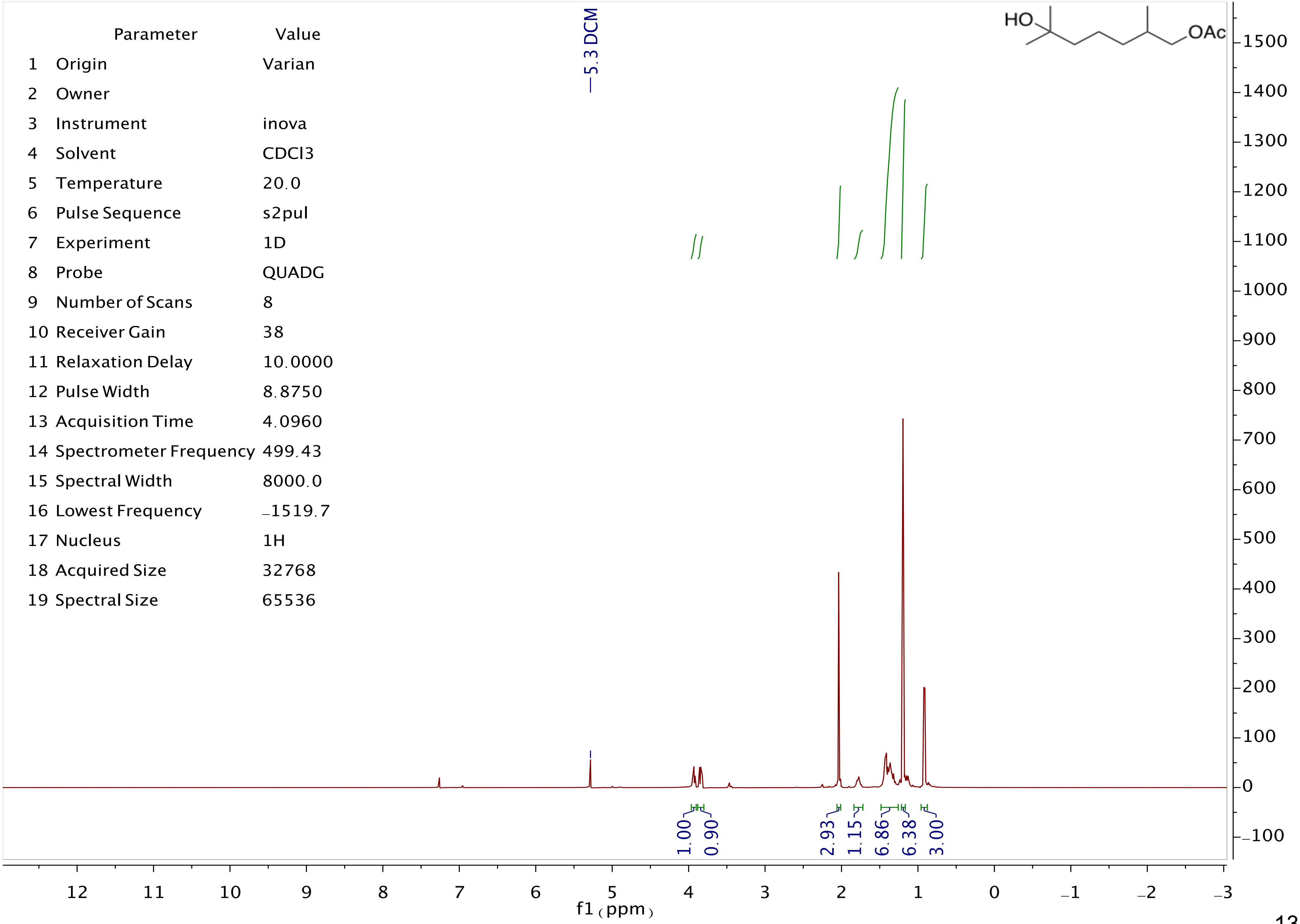
	Parameter	Value
1	Origin	Bruker BioSpin GmbH
2	Owner	user1d
3	Instrument	spect
4	Solvent	CDCl3
5	Temperature	289.1
6	Pulse Sequence	zgpg30
7	Experiment	1D
8	Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
9	Number of Scans	256
10	Receiver Gain	190.5
11	Relaxation Delay	2.0000
12	Pulse Width	10.0000
13	Presaturation Frequency	
14	Spectrometer Frequency	125.83
15	Spectral Width	31512.6
16	Lowest Frequency	-1901.0
17	Nucleus	13C
18	Acquired Size	32768
19	Spectral Size	65536

	Parameter	Value
1	Origin	Bruker BioSpin GmbH
2	Owner	user1d
3	Instrument	spect
4	Solvent	CDCl3
5	Temperature	296.2
6	Pulse Sequence	zg30
7	Experiment	1D
8	Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
9	Number of Scans	16
10	Receiver Gain	17.0
11	Relaxation Delay	10.0000
12	Pulse Width	12.0000
13	Presaturation Frequency	
14	Spectrometer Frequency	500.35
15	Spectral Width	10000.0
16	Lowest Frequency	-1759.7
17	Nucleus	1H
18	Acquired Size	32768
19	Spectral Size	65536

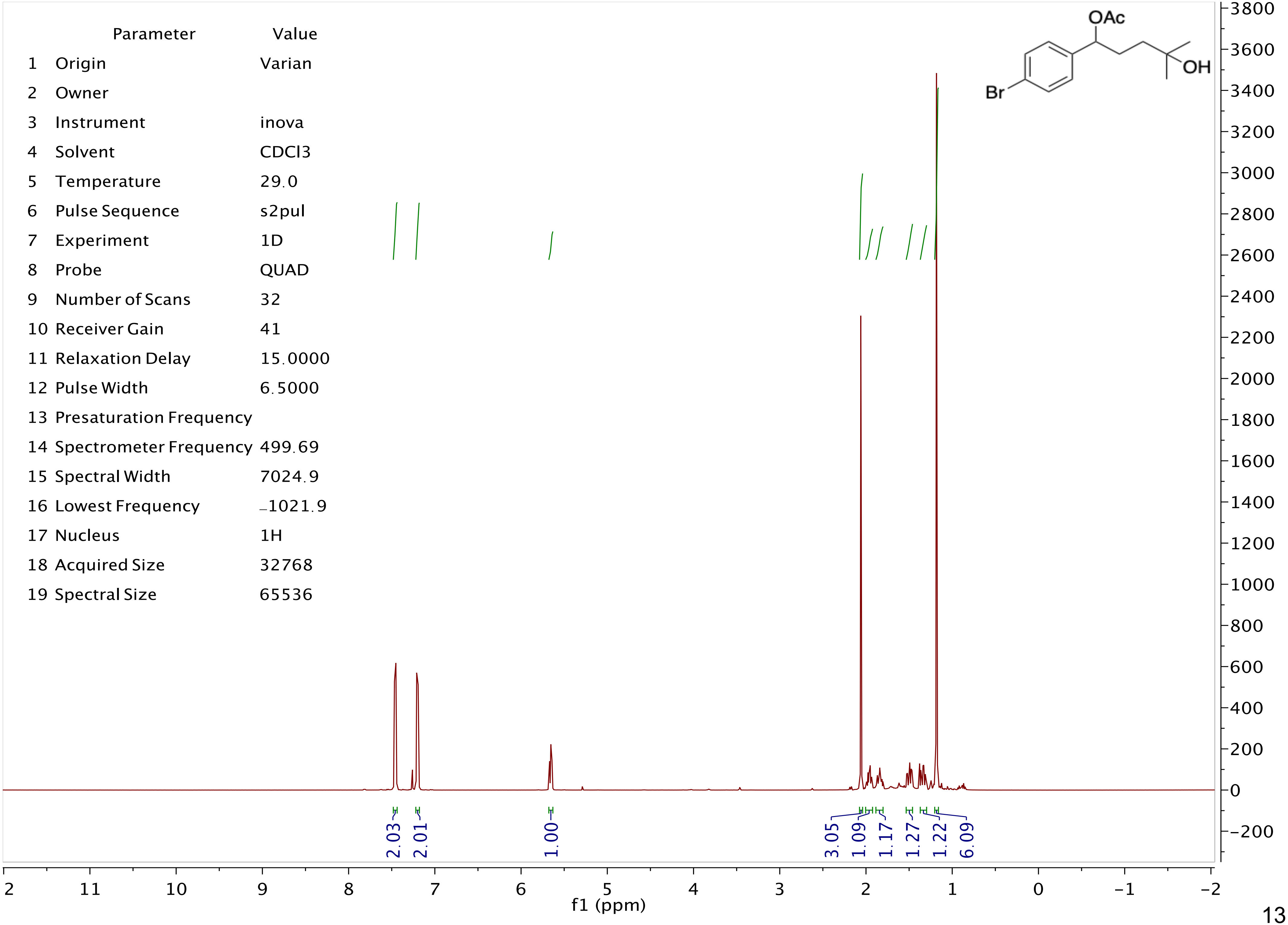


	Parameter	Value
1	Origin	Bruker BioSpin GmbH
2	Owner	user1d
3	Instrument	spect
4	Solvent	CDCl3
5	Temperature	296.2
6	Pulse Sequence	zgpg30
7	Experiment	1D
8	Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
9	Number of Scans	256
10	Receiver Gain	190.5
11	Relaxation Delay	2.0000
12	Pulse Width	10.0000
13	Presaturation Frequency	
14	Spectrometer Frequency	125.83
15	Spectral Width	31512.6
16	Lowest Frequency	-1904.9
17	Nucleus	13C
18	Acquired Size	32768
19	Spectral Size	65536

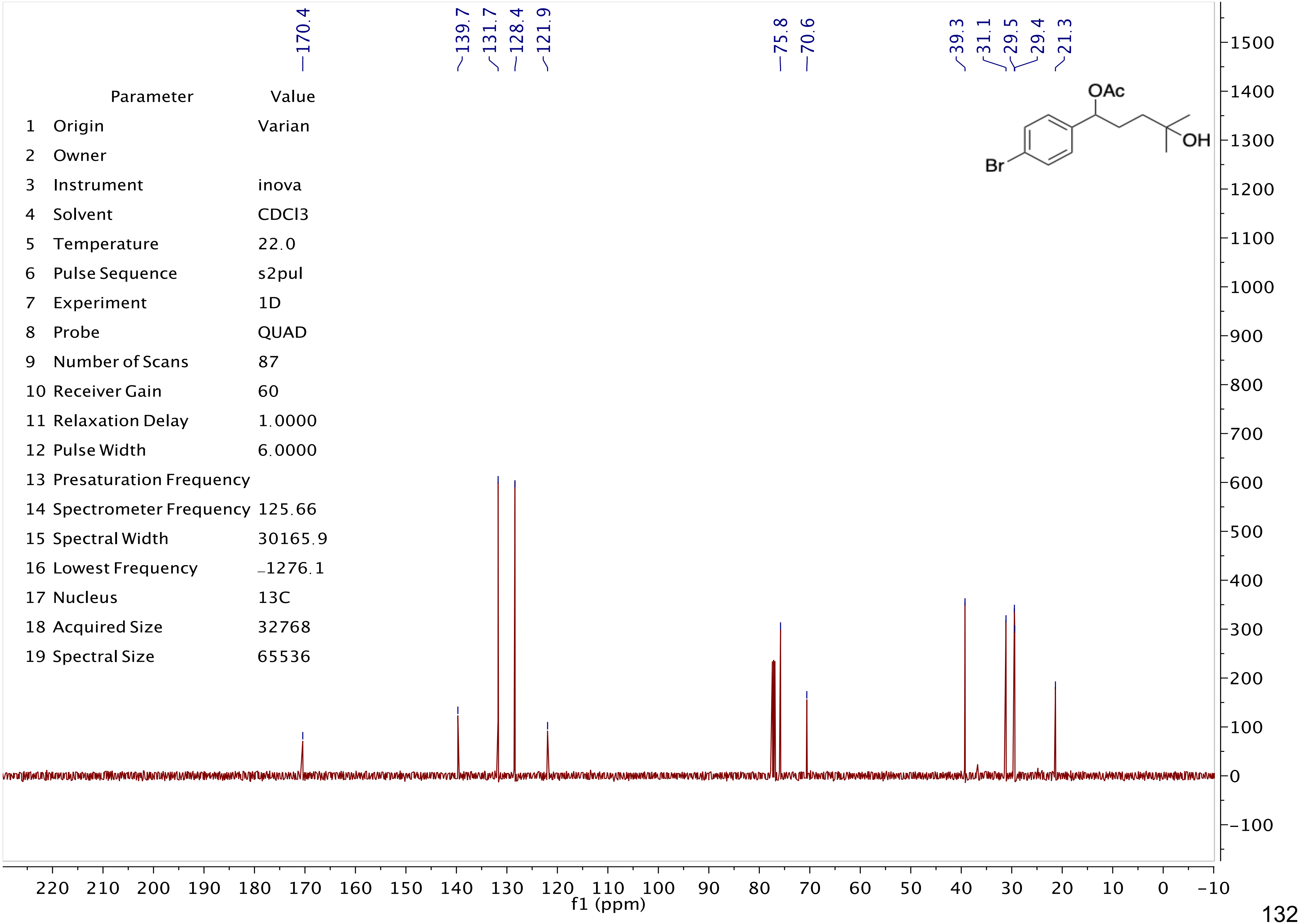




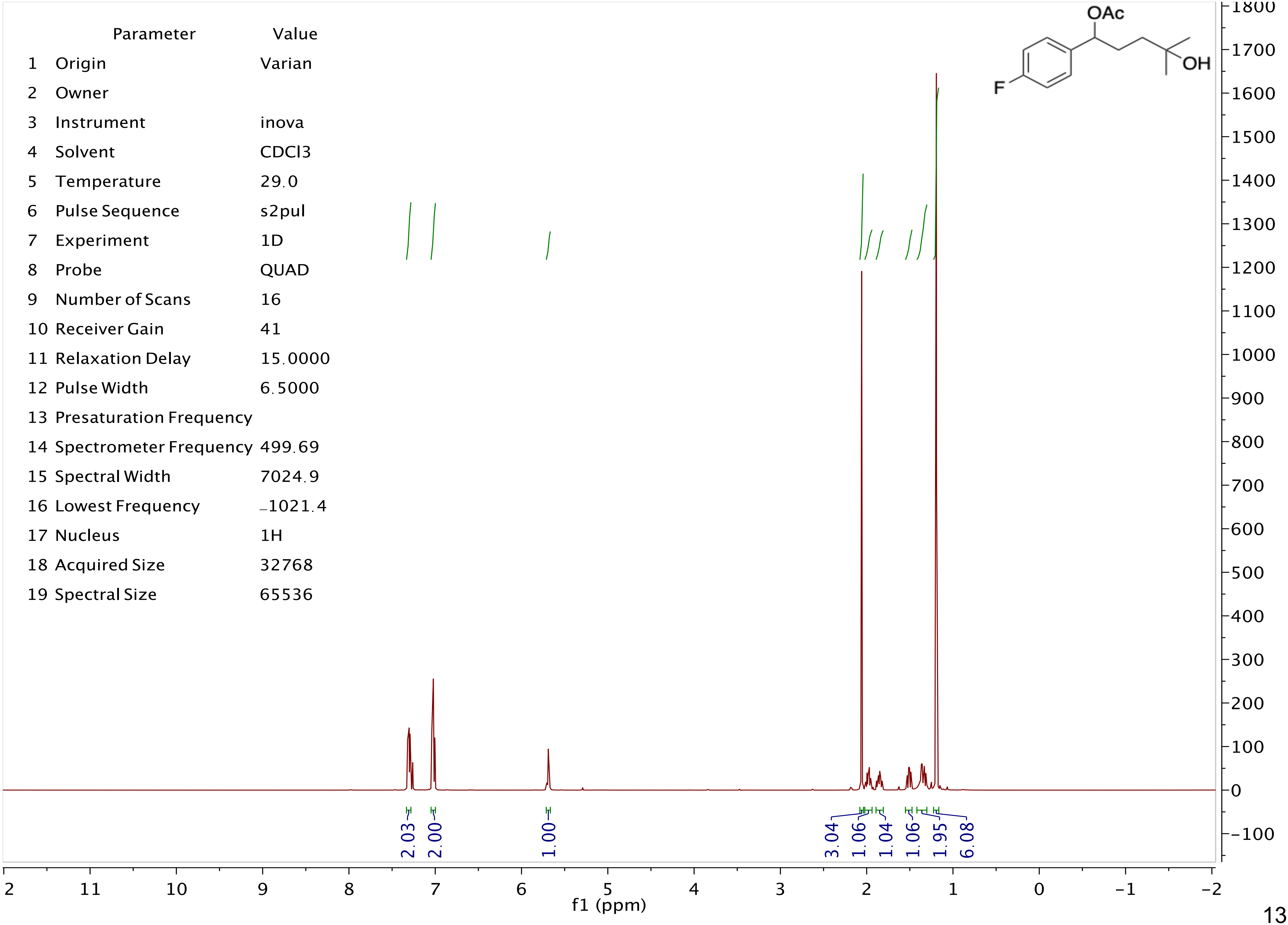
	Parameter	Value
1	Origin	Varian
2	Owner	
3	Instrument	inova
4	Solvent	CDCl3
5	Temperature	20.0
6	Pulse Sequence	s2pul
7	Experiment	1D
8	Probe	QUADG
9	Number of Scans	8
10	Receiver Gain	38
11	Relaxation Delay	10.0000
12	Pulse Width	8.8750
13	Acquisition Time	4.0960
14	Spectrometer Frequency	499.43
15	Spectral Width	8000.0
16	Lowest Frequency	–1519.7
17	Nucleus	1H
18	Acquired Size	32768
19	Spectral Size	65536



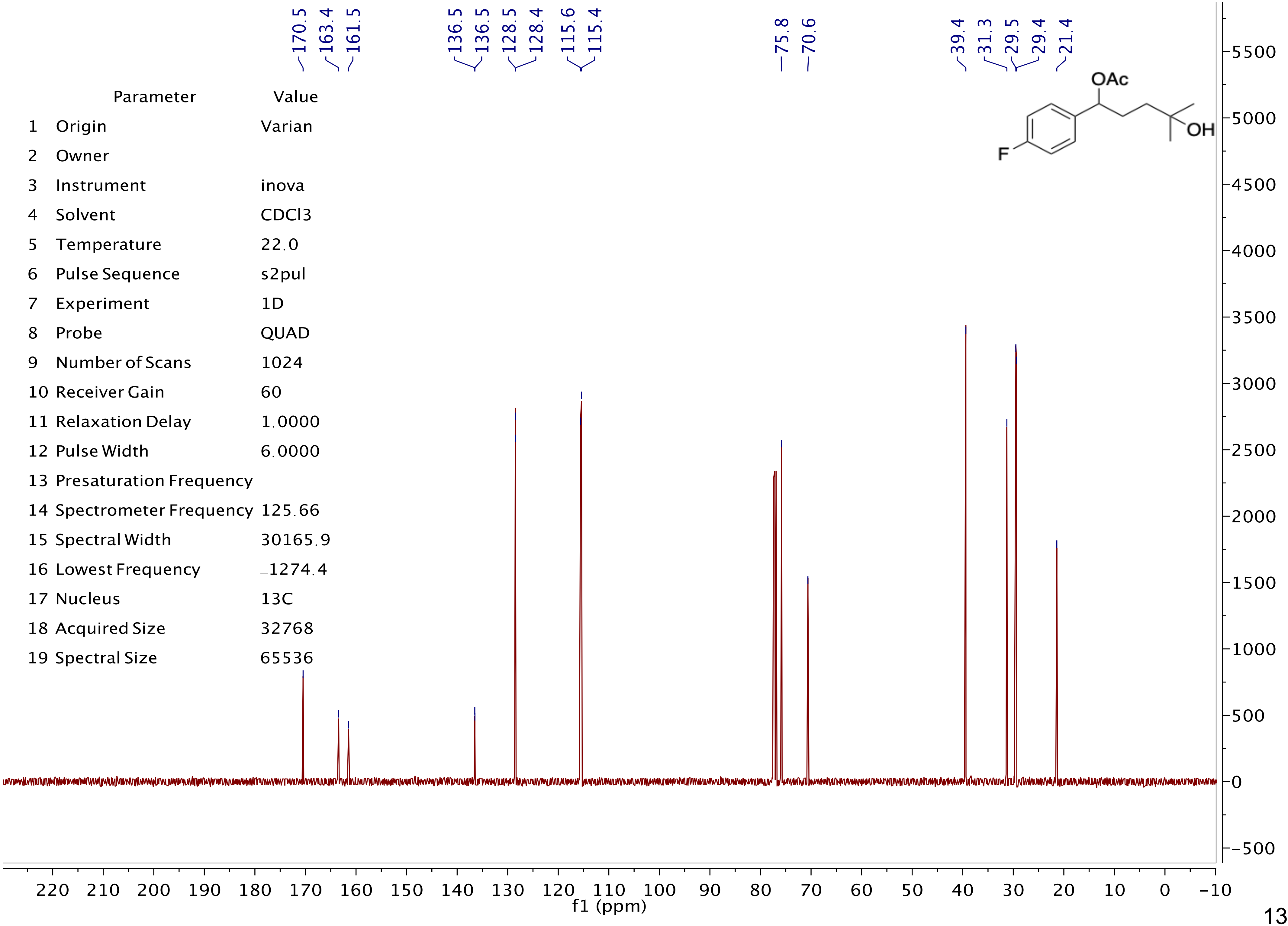
	Parameter	Value
1	Origin	Varian
2	Owner	
3	Instrument	inova
4	Solvent	CDCl3
5	Temperature	29.0
6	Pulse Sequence	s2pul
7	Experiment	1D
8	Probe	QUAD
9	Number of Scans	32
10	Receiver Gain	41
11	Relaxation Delay	15.0000
12	Pulse Width	6.5000
13	Presaturation Frequency	
14	Spectrometer Frequency	499.69
15	Spectral Width	7024.9
16	Lowest Frequency	-1021.9
17	Nucleus	1H
18	Acquired Size	32768
19	Spectral Size	65536



	Parameter	Value
1	Origin	Varian
2	Owner	
3	Instrument	inova
4	Solvent	CDCl3
5	Temperature	22.0
6	Pulse Sequence	s2pul
7	Experiment	1D
8	Probe	QUAD
9	Number of Scans	87
10	Receiver Gain	60
11	Relaxation Delay	1.0000
12	Pulse Width	6.0000
13	Presaturation Frequency	
14	Spectrometer Frequency	125.66
15	Spectral Width	30165.9
16	Lowest Frequency	-1276.1
17	Nucleus	13C
18	Acquired Size	32768
19	Spectral Size	65536

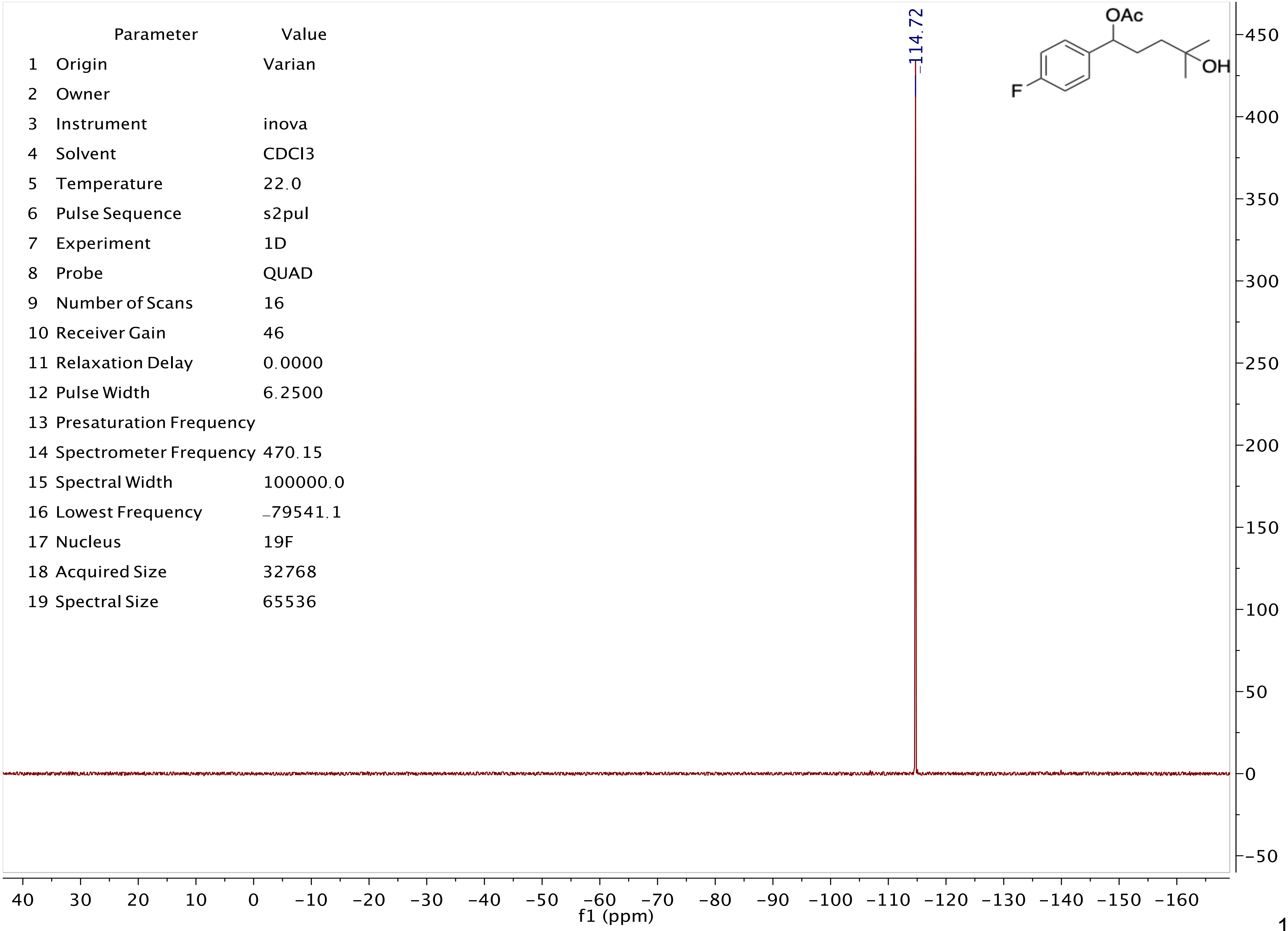


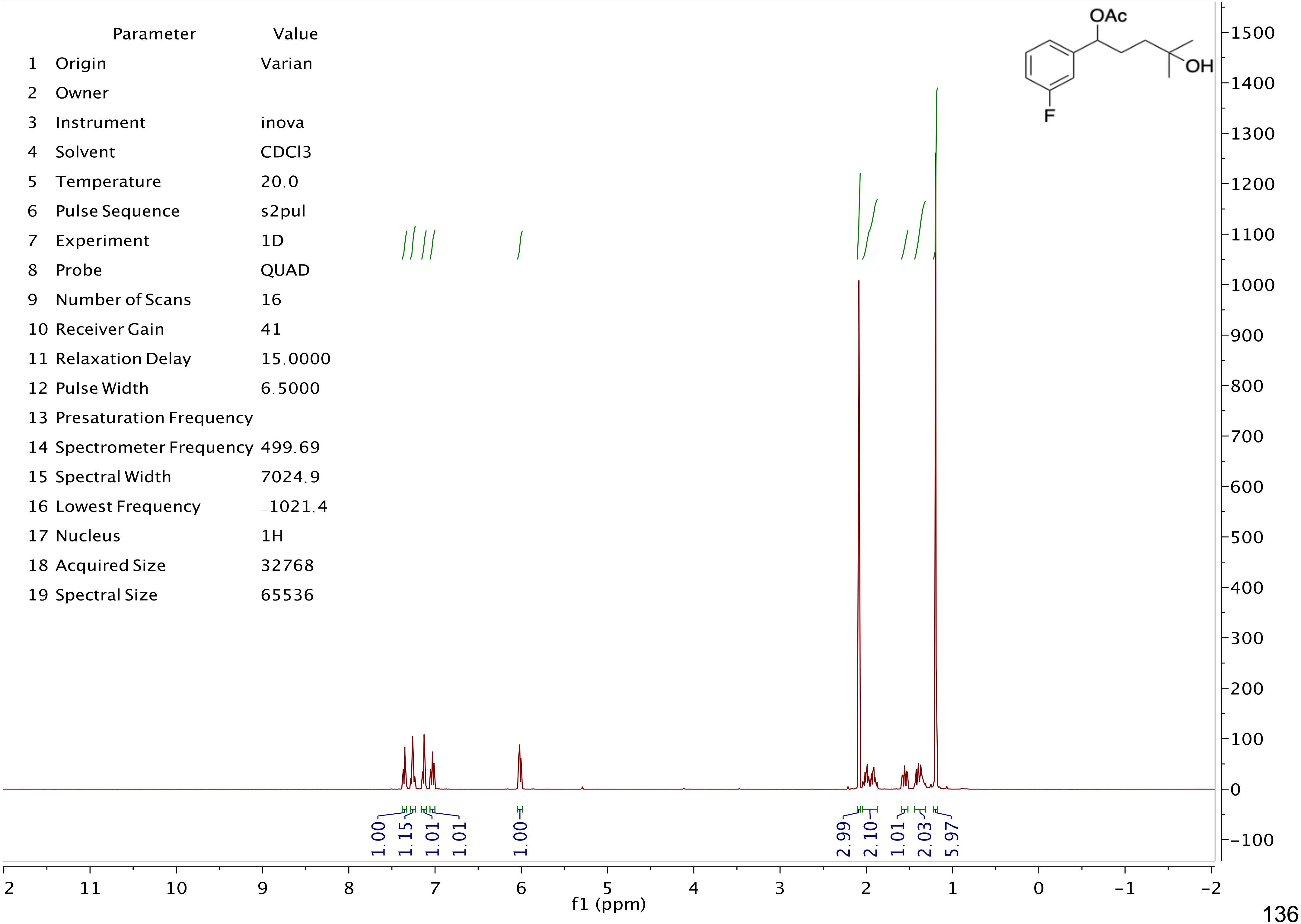
	Parameter	Value
1	Origin	Varian
2	Owner	
3	Instrument	inova
4	Solvent	CDCl3
5	Temperature	29.0
6	Pulse Sequence	s2pul
7	Experiment	1D
8	Probe	QUAD
9	Number of Scans	16
10	Receiver Gain	41
11	Relaxation Delay	15.0000
12	Pulse Width	6.5000
13	Presaturation Frequency	
14	Spectrometer Frequency	499.69
15	Spectral Width	7024.9
16	Lowest Frequency	-1021.4
17	Nucleus	1H
18	Acquired Size	32768
19	Spectral Size	65536



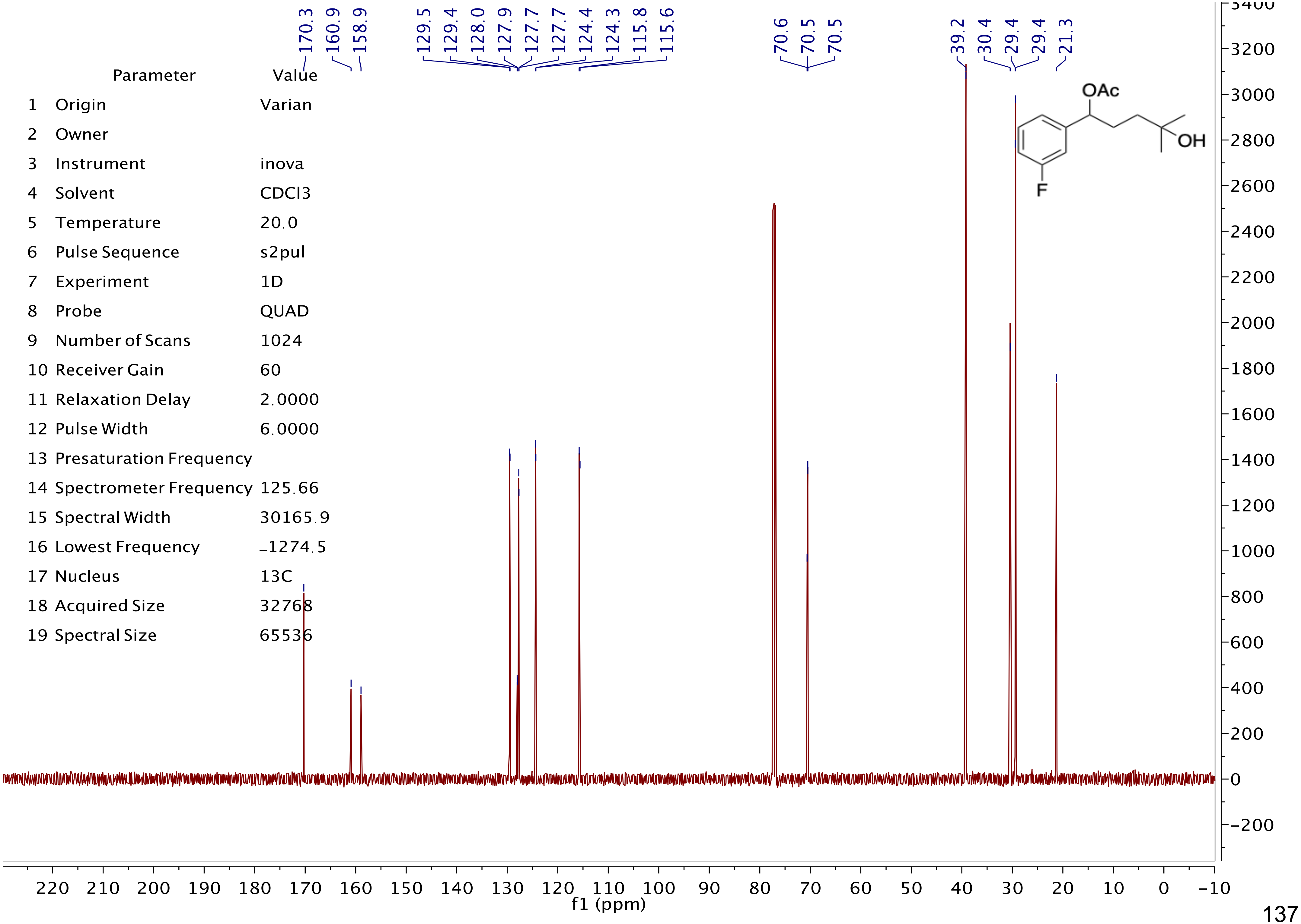
	Parameter	Value
1	Origin	Varian
2	Owner	
3	Instrument	inova
4	Solvent	CDCl3
5	Temperature	22.0
6	Pulse Sequence	s2pul
7	Experiment	1D
8	Probe	QUAD
9	Number of Scans	1024
10	Receiver Gain	60
11	Relaxation Delay	1.0000
12	Pulse Width	6.0000
13	Presaturation Frequency	
14	Spectrometer Frequency	125.66
15	Spectral Width	30165.9
16	Lowest Frequency	-1274.4
17	Nucleus	13C
18	Acquired Size	32768
19	Spectral Size	65536

	Parameter	Value
1	Origin	Varian
2	Owner	
3	Instrument	inova
4	Solvent	CDCl3
5	Temperature	22.0
6	Pulse Sequence	s2pul
7	Experiment	1D
8	Probe	QUAD
9	Number of Scans	16
10	Receiver Gain	46
11	Relaxation Delay	0.0000
12	Pulse Width	6.2500
13	Presaturation Frequency	
14	Spectrometer Frequency	470.15
15	Spectral Width	100000.0
16	Lowest Frequency	-79541.1
17	Nucleus	19F
18	Acquired Size	32768
19	Spectral Size	65536

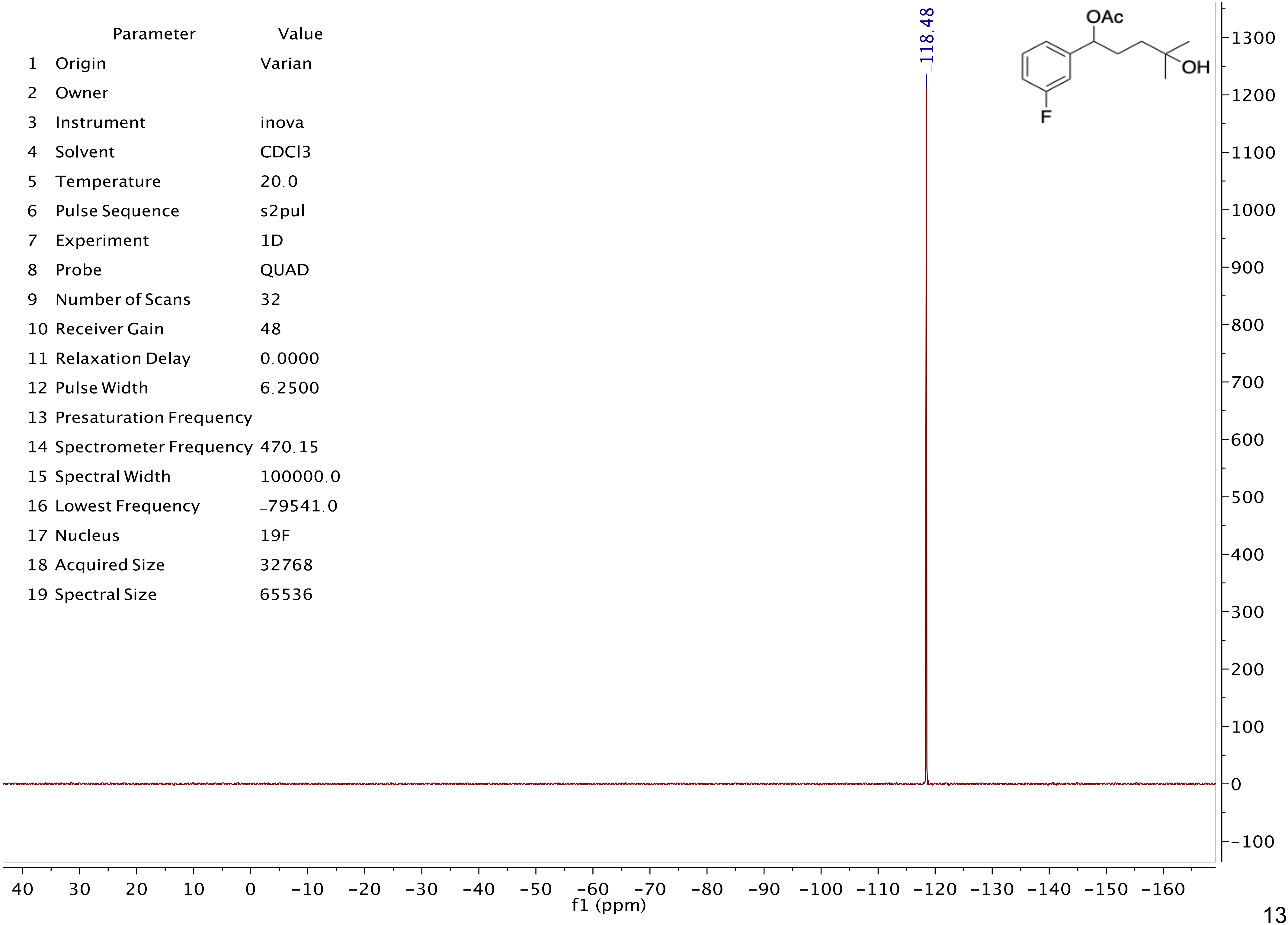




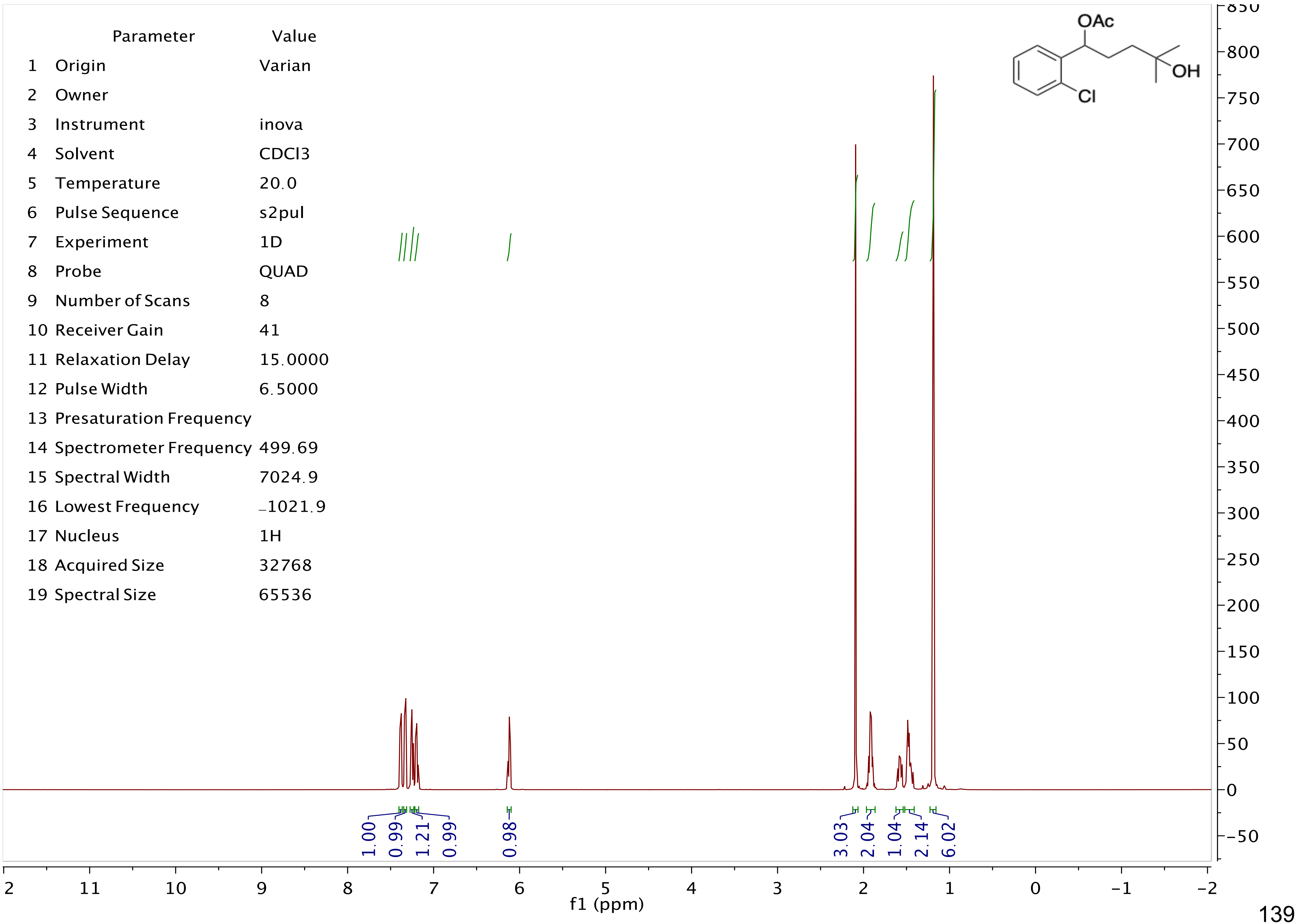
	Parameter	Value
1	Origin	Varian
2	Owner	
3	Instrument	inova
4	Solvent	CDCl3
5	Temperature	20.0
6	Pulse Sequence	s2pul
7	Experiment	1D
8	Probe	QUAD
9	Number of Scans	16
10	Receiver Gain	41
11	Relaxation Delay	15.0000
12	Pulse Width	6.5000
13	Presaturation Frequency	
14	Spectrometer Frequency	499.69
15	Spectral Width	7024.9
16	Lowest Frequency	-1021.4
17	Nucleus	1H
18	Acquired Size	32768
19	Spectral Size	65536



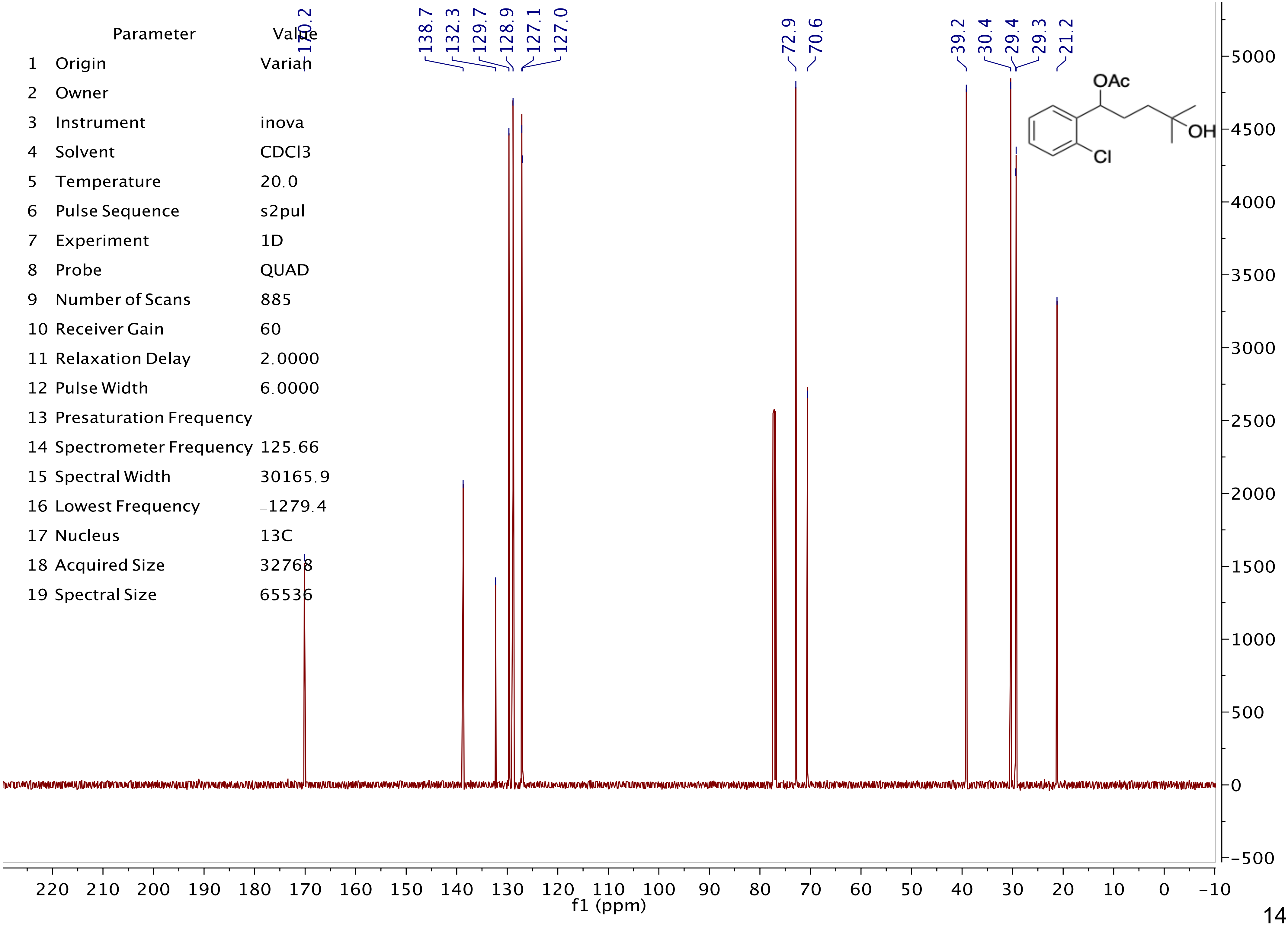
	Parameter	Value
1	Origin	Varian
2	Owner	
3	Instrument	inova
4	Solvent	CDCl3
5	Temperature	20.0
6	Pulse Sequence	s2pul
7	Experiment	1D
8	Probe	QUAD
9	Number of Scans	1024
10	Receiver Gain	60
11	Relaxation Delay	2.0000
12	Pulse Width	6.0000
13	Presaturation Frequency	
14	Spectrometer Frequency	125.66
15	Spectral Width	30165.9
16	Lowest Frequency	-1274.5
17	Nucleus	13C
18	Acquired Size	32768
19	Spectral Size	65536



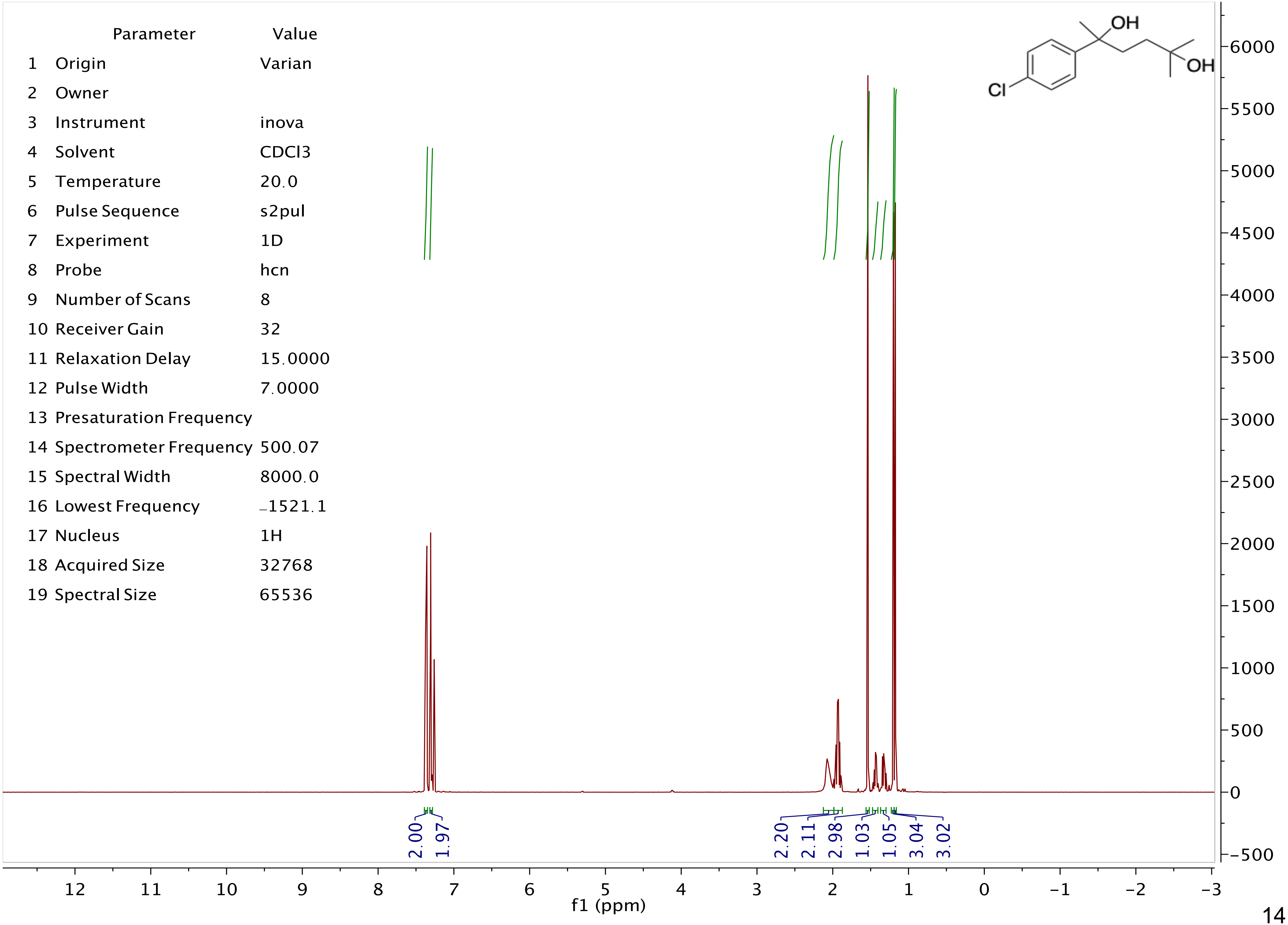
	Parameter	Value
1	Origin	Varian
2	Owner	
3	Instrument	inova
4	Solvent	CDCl3
5	Temperature	20.0
6	Pulse Sequence	s2pul
7	Experiment	1D
8	Probe	QUAD
9	Number of Scans	32
10	Receiver Gain	48
11	Relaxation Delay	0.0000
12	Pulse Width	6.2500
13	Presaturation Frequency	
14	Spectrometer Frequency	470.15
15	Spectral Width	100000.0
16	Lowest Frequency	-79541.0
17	Nucleus	19F
18	Acquired Size	32768
19	Spectral Size	65536



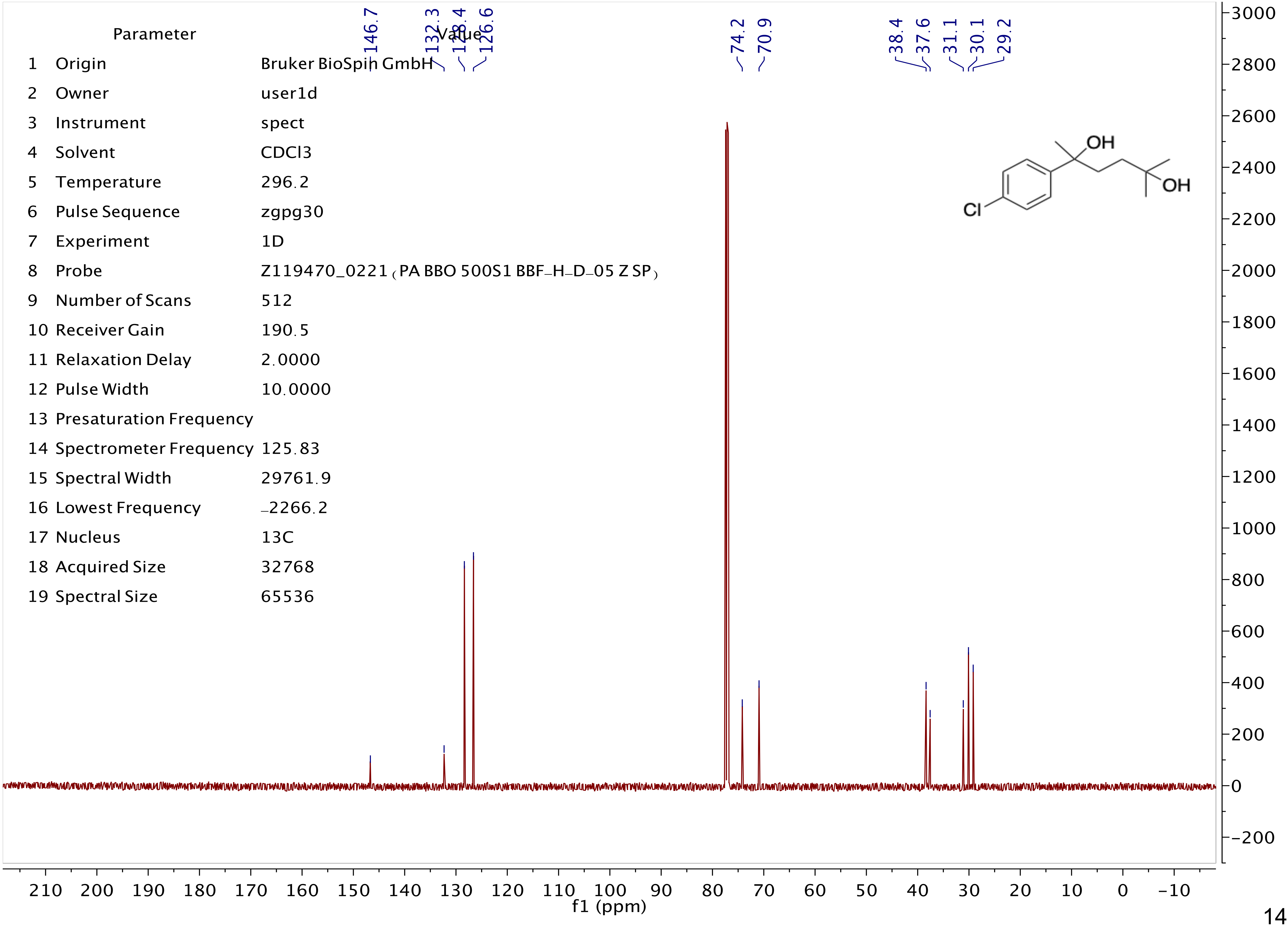
	Parameter	Value
1	Origin	Varian
2	Owner	
3	Instrument	inova
4	Solvent	CDCl3
5	Temperature	20.0
6	Pulse Sequence	s2pul
7	Experiment	1D
8	Probe	QUAD
9	Number of Scans	8
10	Receiver Gain	41
11	Relaxation Delay	15.0000
12	Pulse Width	6.5000
13	Presaturation Frequency	
14	Spectrometer Frequency	499.69
15	Spectral Width	7024.9
16	Lowest Frequency	-1021.9
17	Nucleus	1H
18	Acquired Size	32768
19	Spectral Size	65536



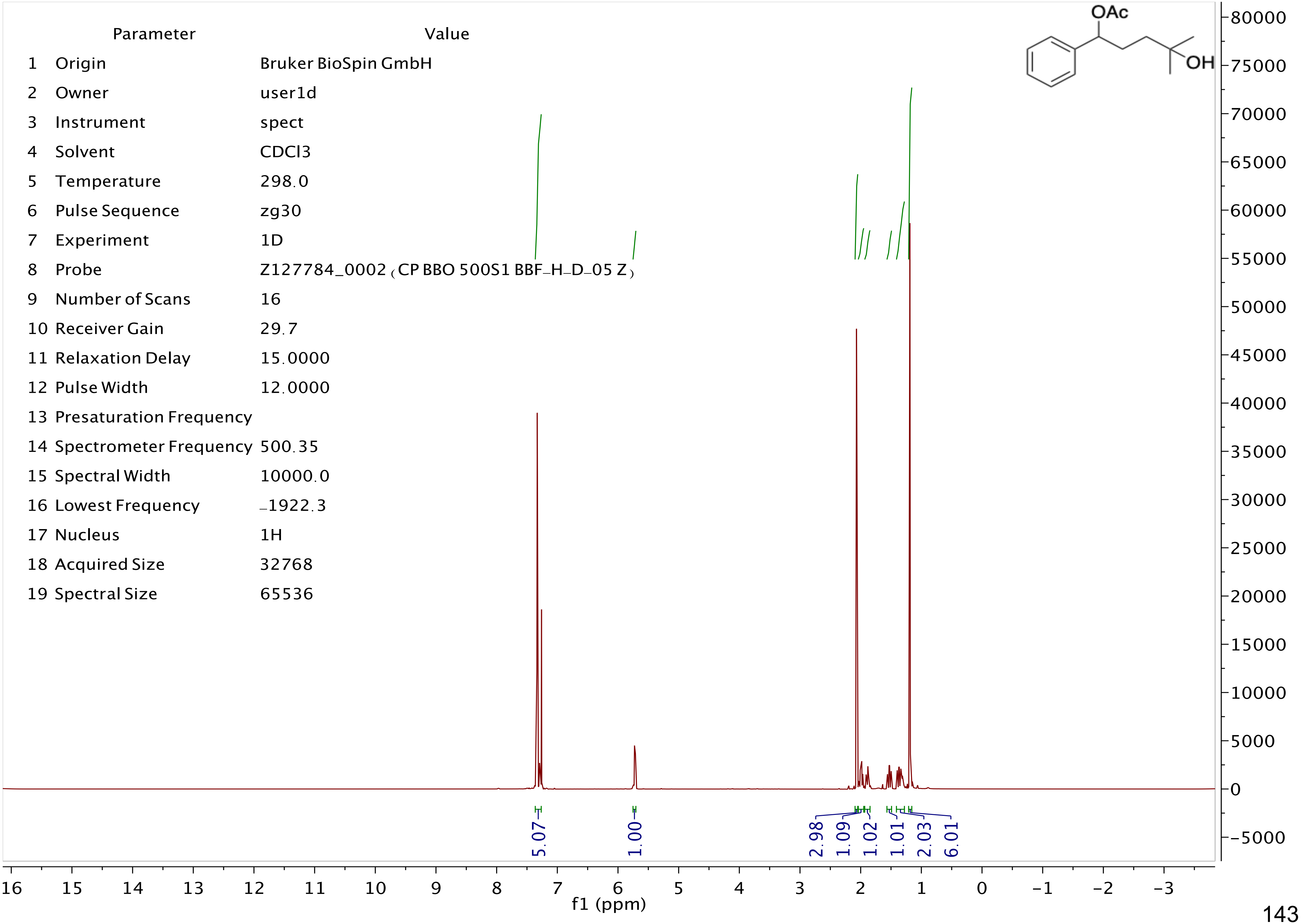
	Parameter	Value
1	Origin	Varian
2	Owner	
3	Instrument	inova
4	Solvent	CDCl3
5	Temperature	20.0
6	Pulse Sequence	s2pul
7	Experiment	1D
8	Probe	QUAD
9	Number of Scans	885
10	Receiver Gain	60
11	Relaxation Delay	2.0000
12	Pulse Width	6.0000
13	Presaturation Frequency	
14	Spectrometer Frequency	125.66
15	Spectral Width	30165.9
16	Lowest Frequency	-1279.4
17	Nucleus	13C
18	Acquired Size	32768
19	Spectral Size	65536



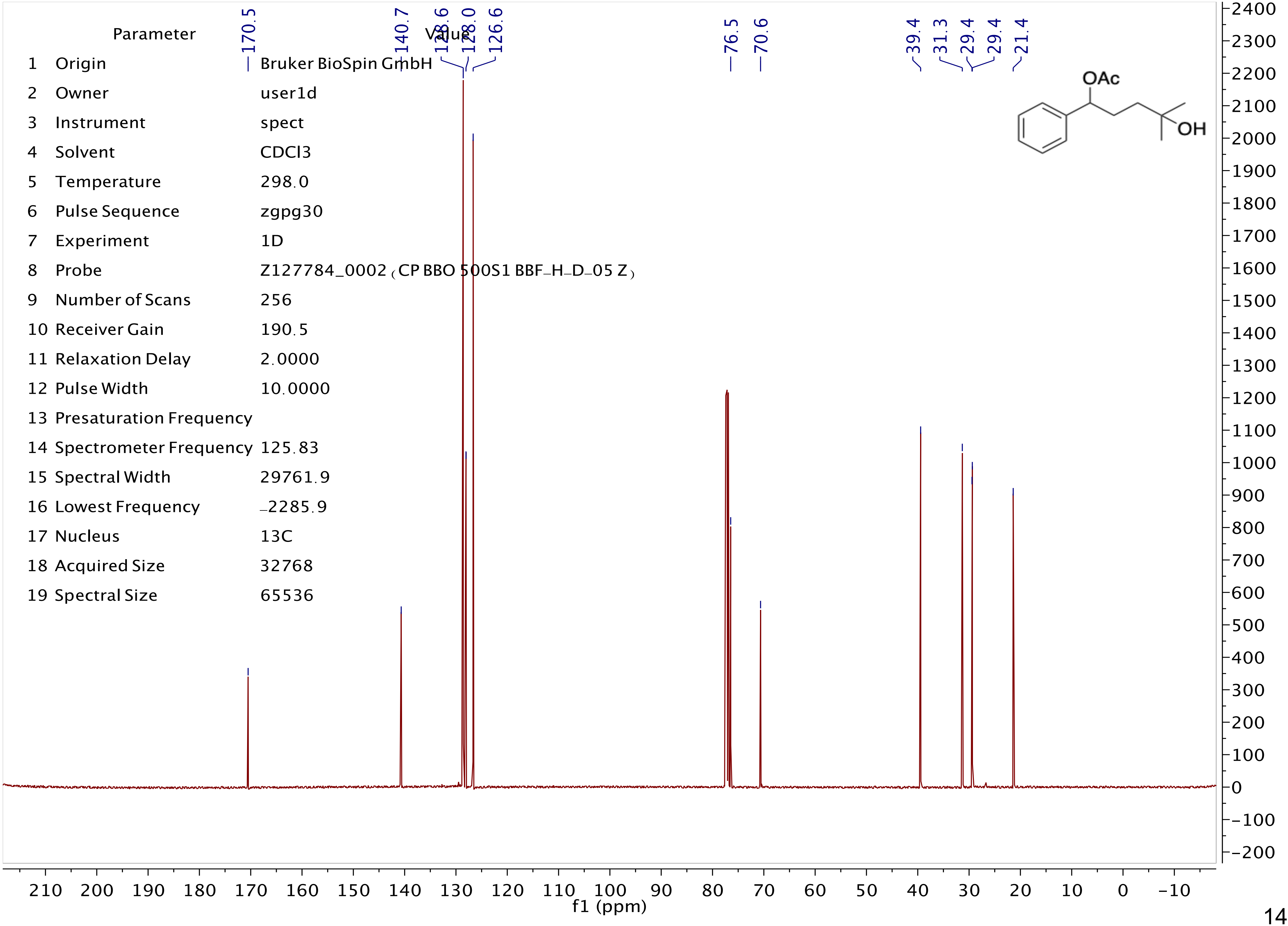
	Parameter	Value
1	Origin	Varian
2	Owner	
3	Instrument	inova
4	Solvent	CDCl3
5	Temperature	20.0
6	Pulse Sequence	s2pul
7	Experiment	1D
8	Probe	hcn
9	Number of Scans	8
10	Receiver Gain	32
11	Relaxation Delay	15.0000
12	Pulse Width	7.0000
13	Presaturation Frequency	
14	Spectrometer Frequency	500.07
15	Spectral Width	8000.0
16	Lowest Frequency	-1521.1
17	Nucleus	1H
18	Acquired Size	32768
19	Spectral Size	65536



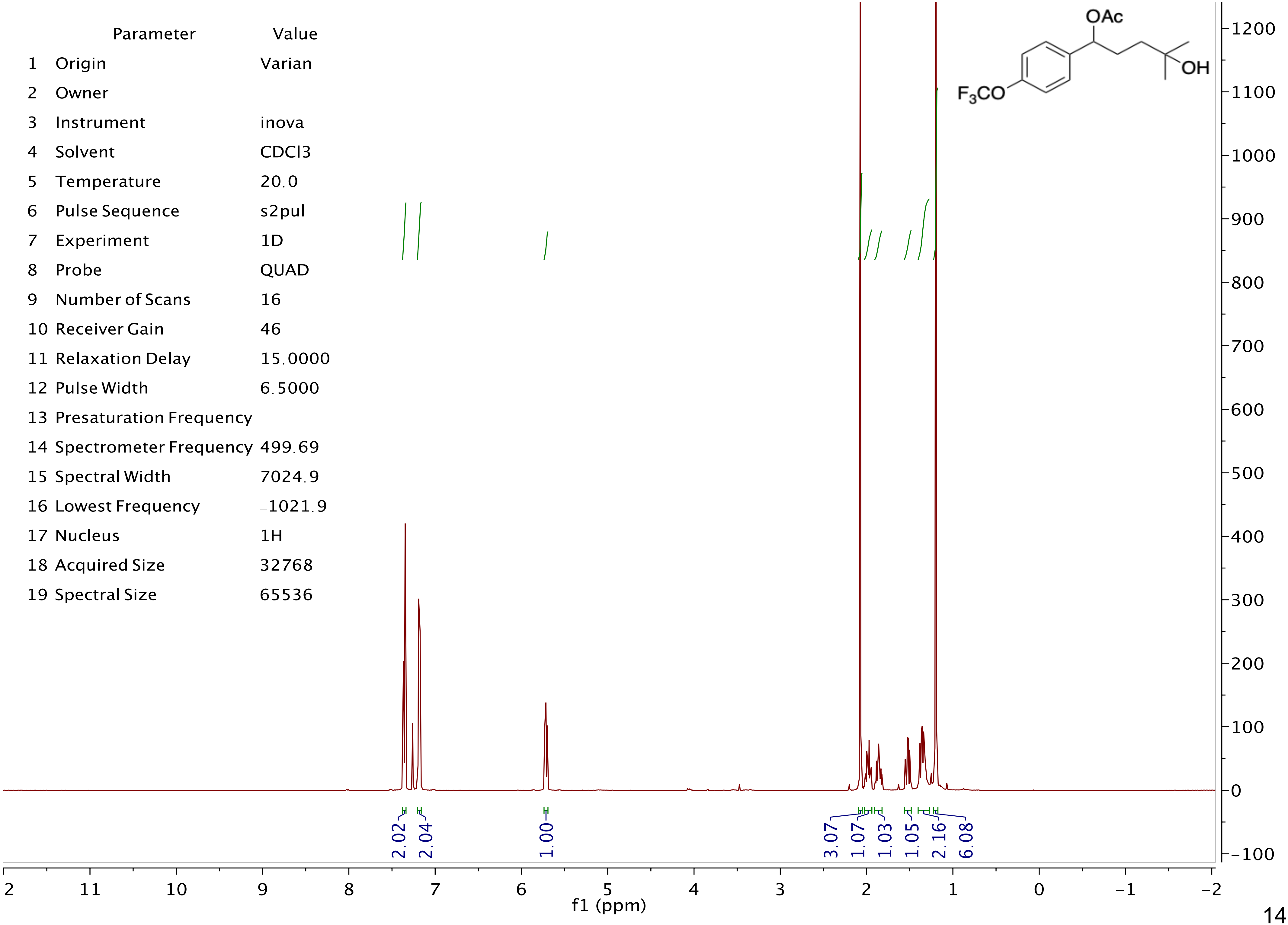
	Parameter	Value
1	Origin	Bruker BioSpin GmbH
2	Owner	user1d
3	Instrument	spect
4	Solvent	CDCl3
5	Temperature	296.2
6	Pulse Sequence	zgpg30
7	Experiment	1D
8	Probe	Z119470_0221 (PA BBO 500S1 BBF-H-D-05 Z SP)
9	Number of Scans	512
10	Receiver Gain	190.5
11	Relaxation Delay	2.0000
12	Pulse Width	10.0000
13	Presaturation Frequency	
14	Spectrometer Frequency	125.83
15	Spectral Width	29761.9
16	Lowest Frequency	-2266.2
17	Nucleus	13C
18	Acquired Size	32768
19	Spectral Size	65536



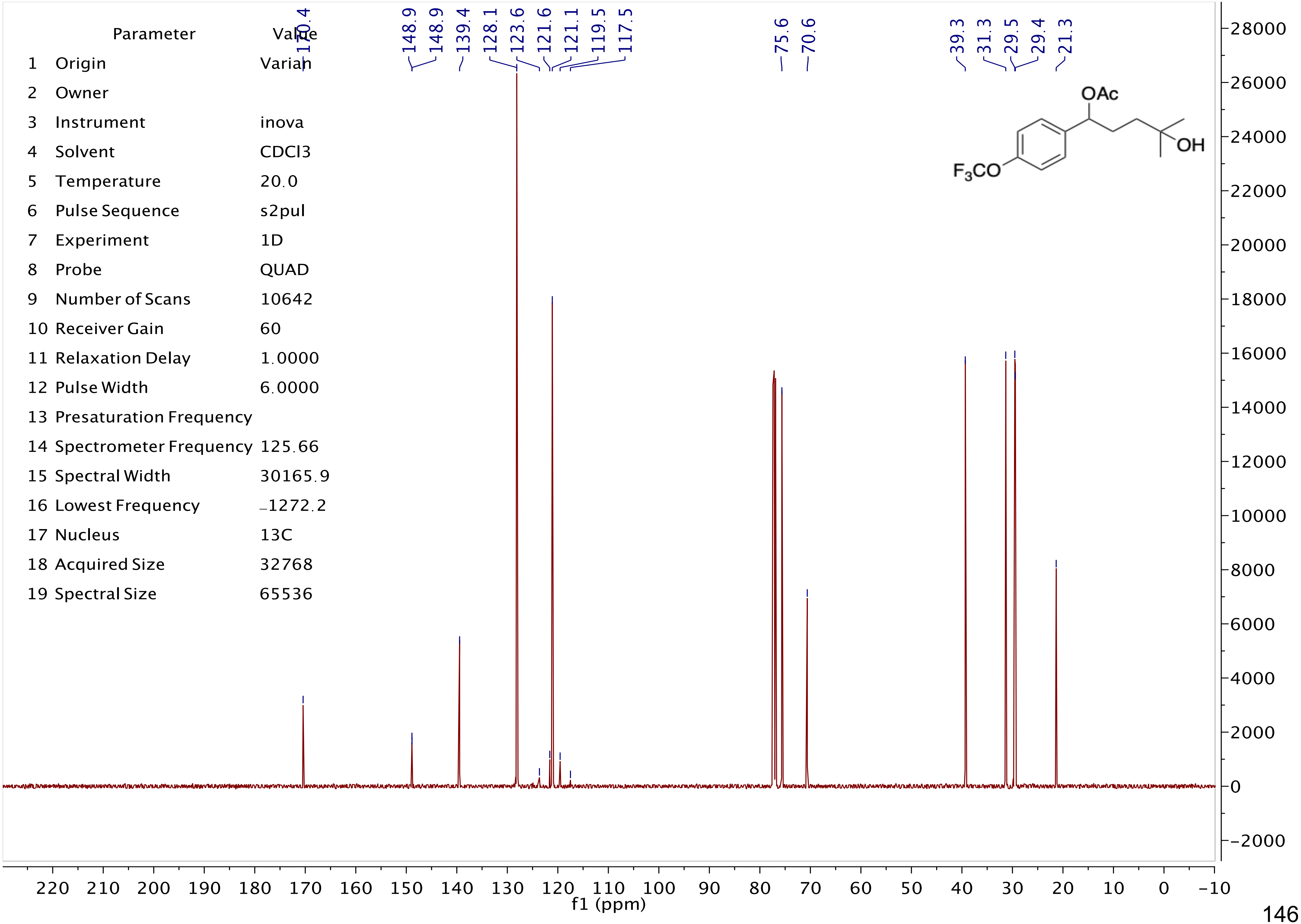
	Parameter	Value
1	Origin	Bruker BioSpin GmbH
2	Owner	user1d
3	Instrument	spect
4	Solvent	CDCl3
5	Temperature	298.0
6	Pulse Sequence	zg30
7	Experiment	1D
8	Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
9	Number of Scans	16
10	Receiver Gain	29.7
11	Relaxation Delay	15.0000
12	Pulse Width	12.0000
13	Presaturation Frequency	
14	Spectrometer Frequency	500.35
15	Spectral Width	10000.0
16	Lowest Frequency	-1922.3
17	Nucleus	1H
18	Acquired Size	32768
19	Spectral Size	65536



	Parameter	Value
1	Origin	Bruker BioSpin GmbH
2	Owner	user1d
3	Instrument	spect
4	Solvent	CDCl3
5	Temperature	298.0
6	Pulse Sequence	zgpg30
7	Experiment	1D
8	Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
9	Number of Scans	256
10	Receiver Gain	190.5
11	Relaxation Delay	2.0000
12	Pulse Width	10.0000
13	Presaturation Frequency	
14	Spectrometer Frequency	125.83
15	Spectral Width	29761.9
16	Lowest Frequency	-2285.9
17	Nucleus	13C
18	Acquired Size	32768
19	Spectral Size	65536

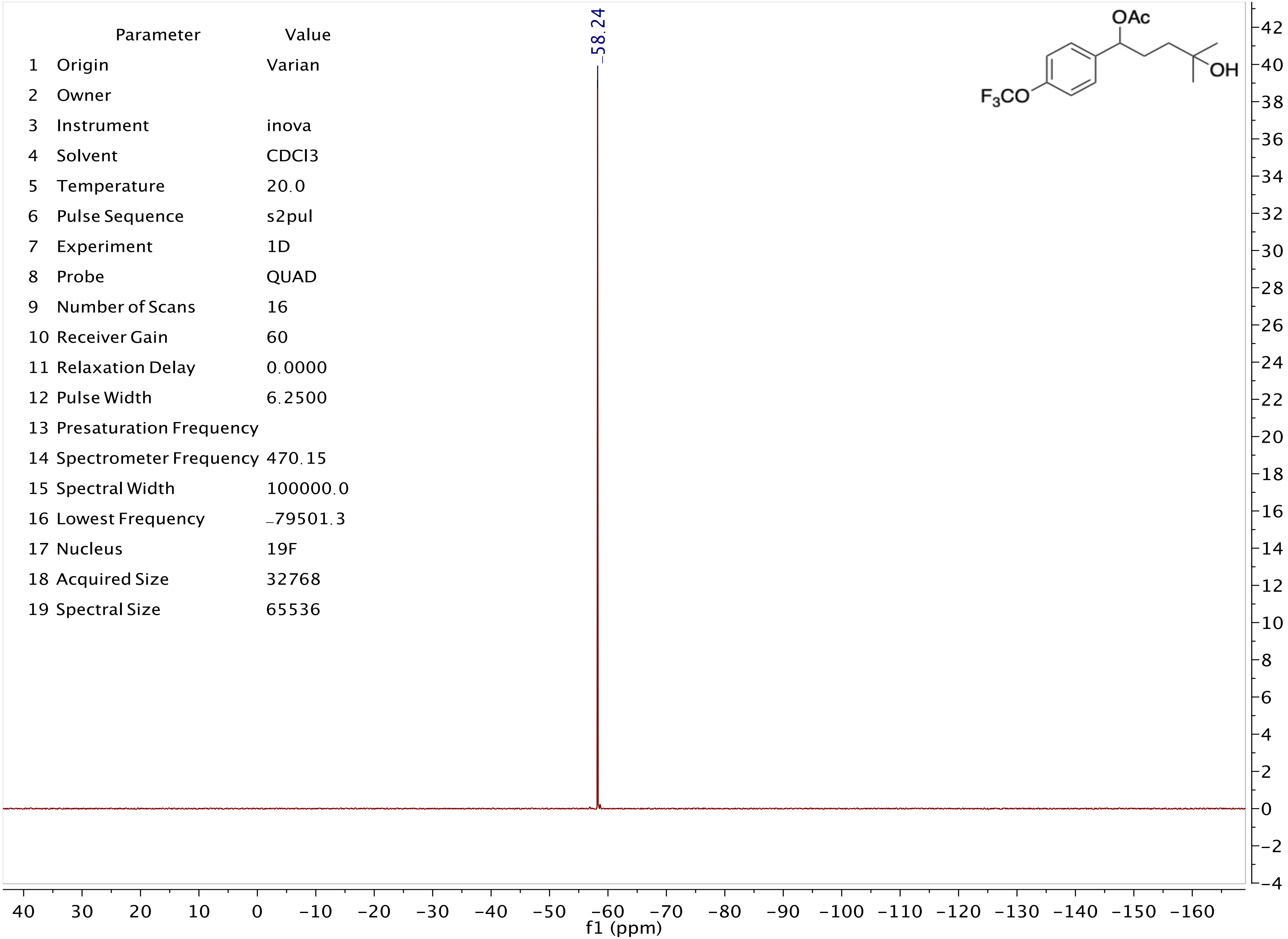


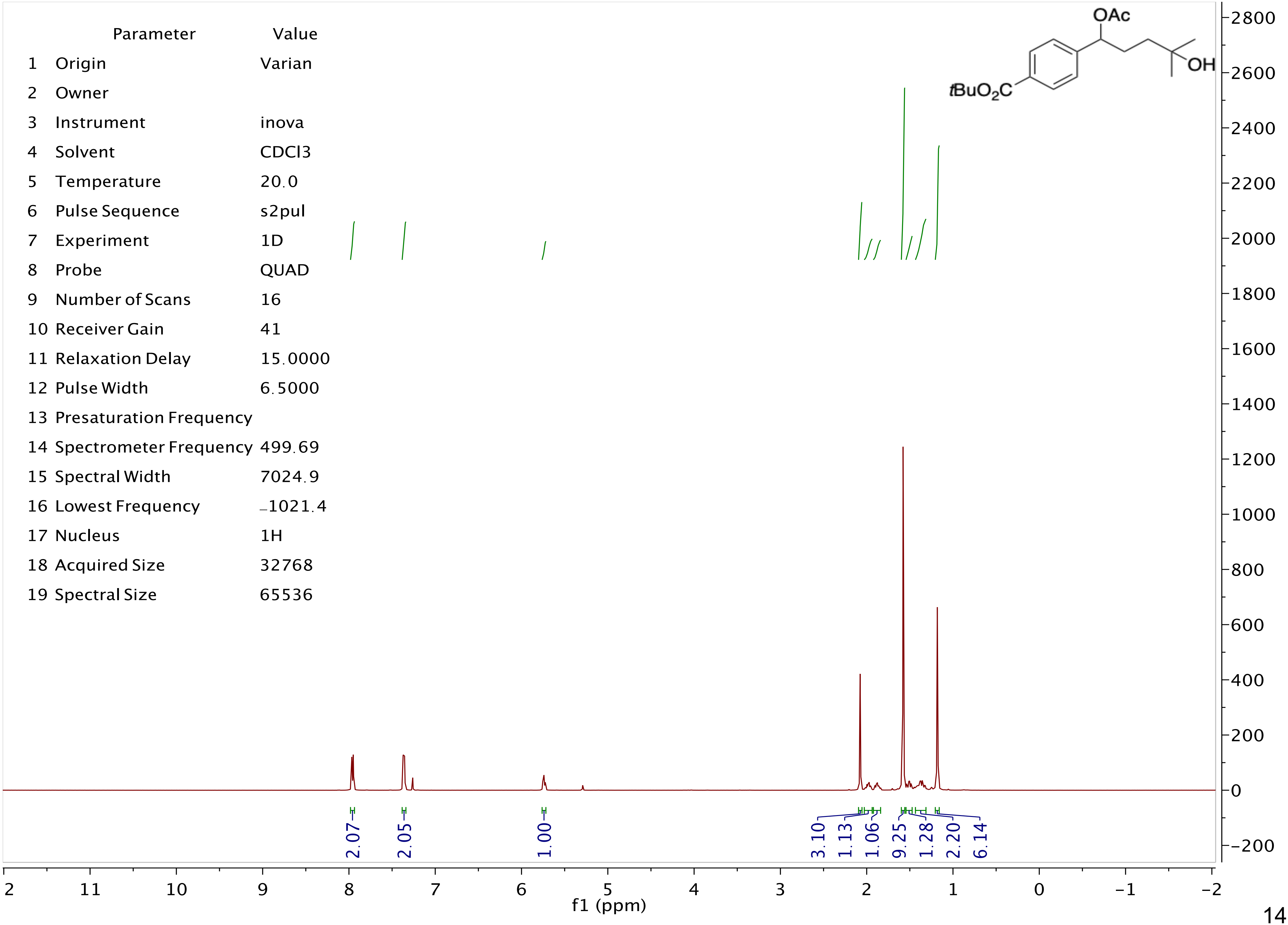
	Parameter	Value
1	Origin	Varian
2	Owner	
3	Instrument	inova
4	Solvent	CDCl3
5	Temperature	20.0
6	Pulse Sequence	s2pul
7	Experiment	1D
8	Probe	QUAD
9	Number of Scans	16
10	Receiver Gain	46
11	Relaxation Delay	15.0000
12	Pulse Width	6.5000
13	Presaturation Frequency	
14	Spectrometer Frequency	499.69
15	Spectral Width	7024.9
16	Lowest Frequency	-1021.9
17	Nucleus	1H
18	Acquired Size	32768
19	Spectral Size	65536



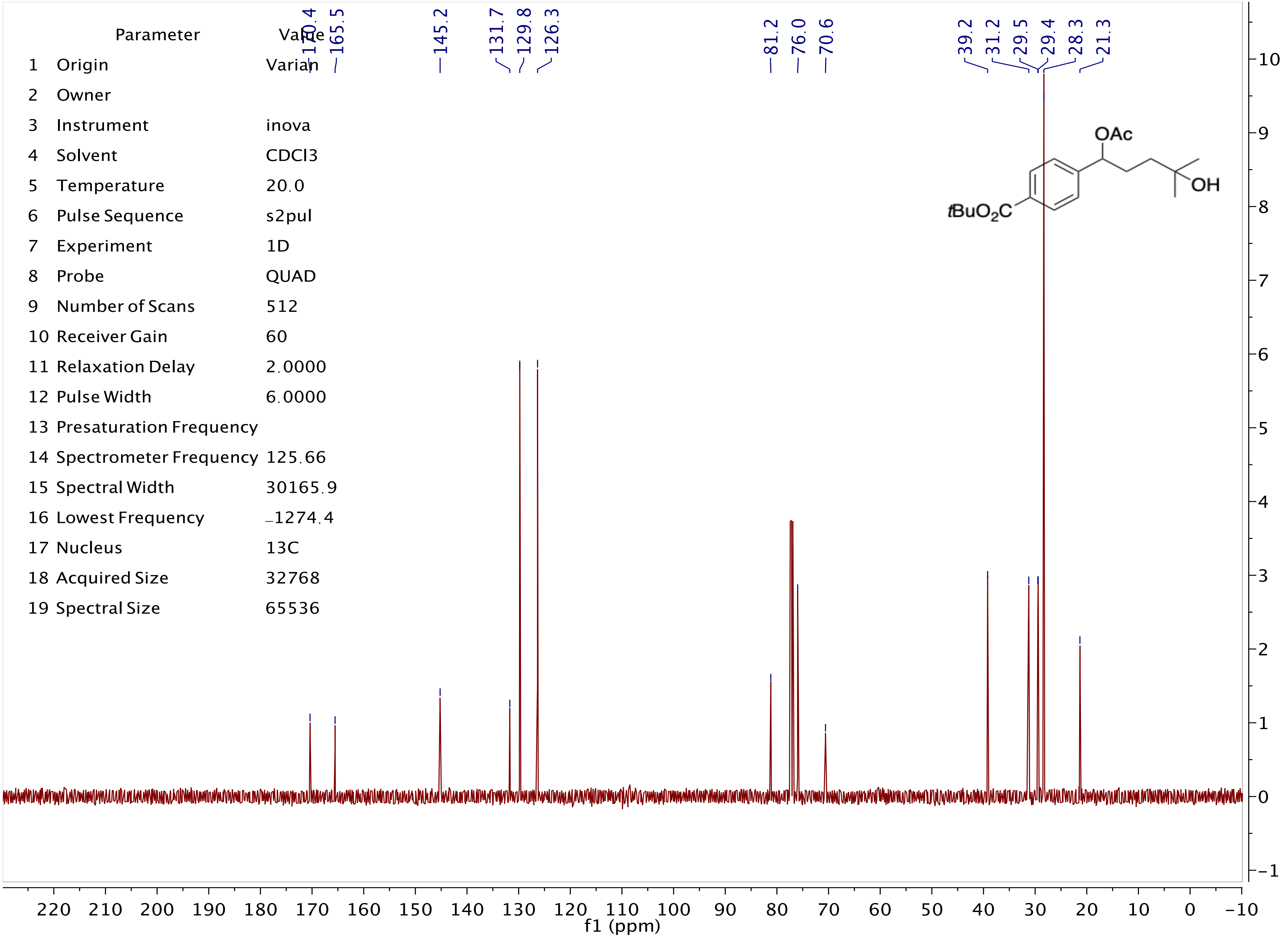
Parameter		Value
1	Origin	Varian
2	Owner	
3	Instrument	inova
4	Solvent	CDCl3
5	Temperature	20.0
6	Pulse Sequence	s2pul
7	Experiment	1D
8	Probe	QUAD
9	Number of Scans	10642
10	Receiver Gain	60
11	Relaxation Delay	1.0000
12	Pulse Width	6.0000
13	Presaturation Frequency	
14	Spectrometer Frequency	125.66
15	Spectral Width	30165.9
16	Lowest Frequency	-1272.2
17	Nucleus	13C
18	Acquired Size	32768
19	Spectral Size	65536

	Parameter	Value
1	Origin	Varian
2	Owner	
3	Instrument	inova
4	Solvent	CDCl3
5	Temperature	20.0
6	Pulse Sequence	s2pul
7	Experiment	1D
8	Probe	QUAD
9	Number of Scans	16
10	Receiver Gain	60
11	Relaxation Delay	0.0000
12	Pulse Width	6.2500
13	Presaturation Frequency	
14	Spectrometer Frequency	470.15
15	Spectral Width	100000.0
16	Lowest Frequency	-79501.3
17	Nucleus	19F
18	Acquired Size	32768
19	Spectral Size	65536

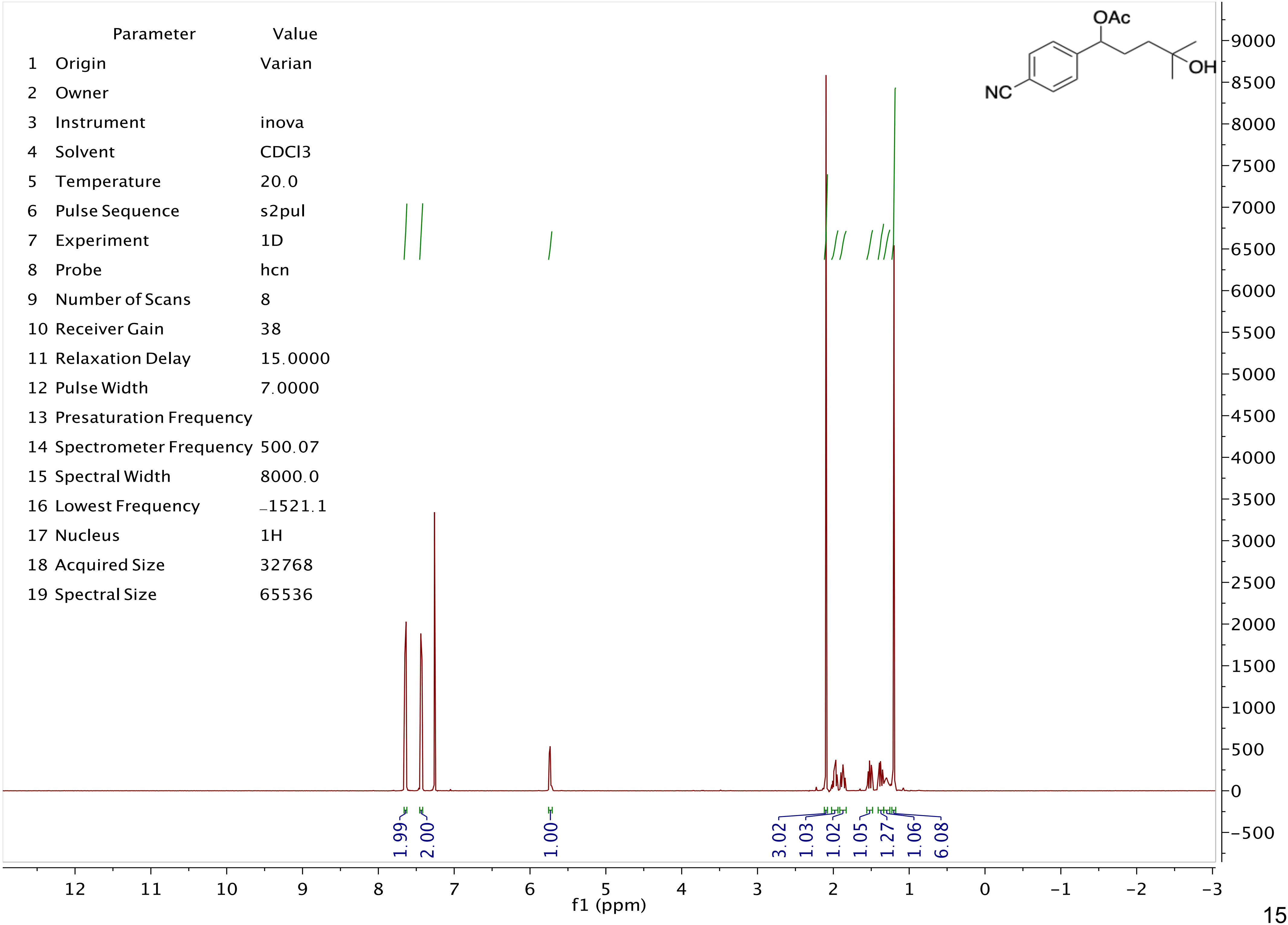




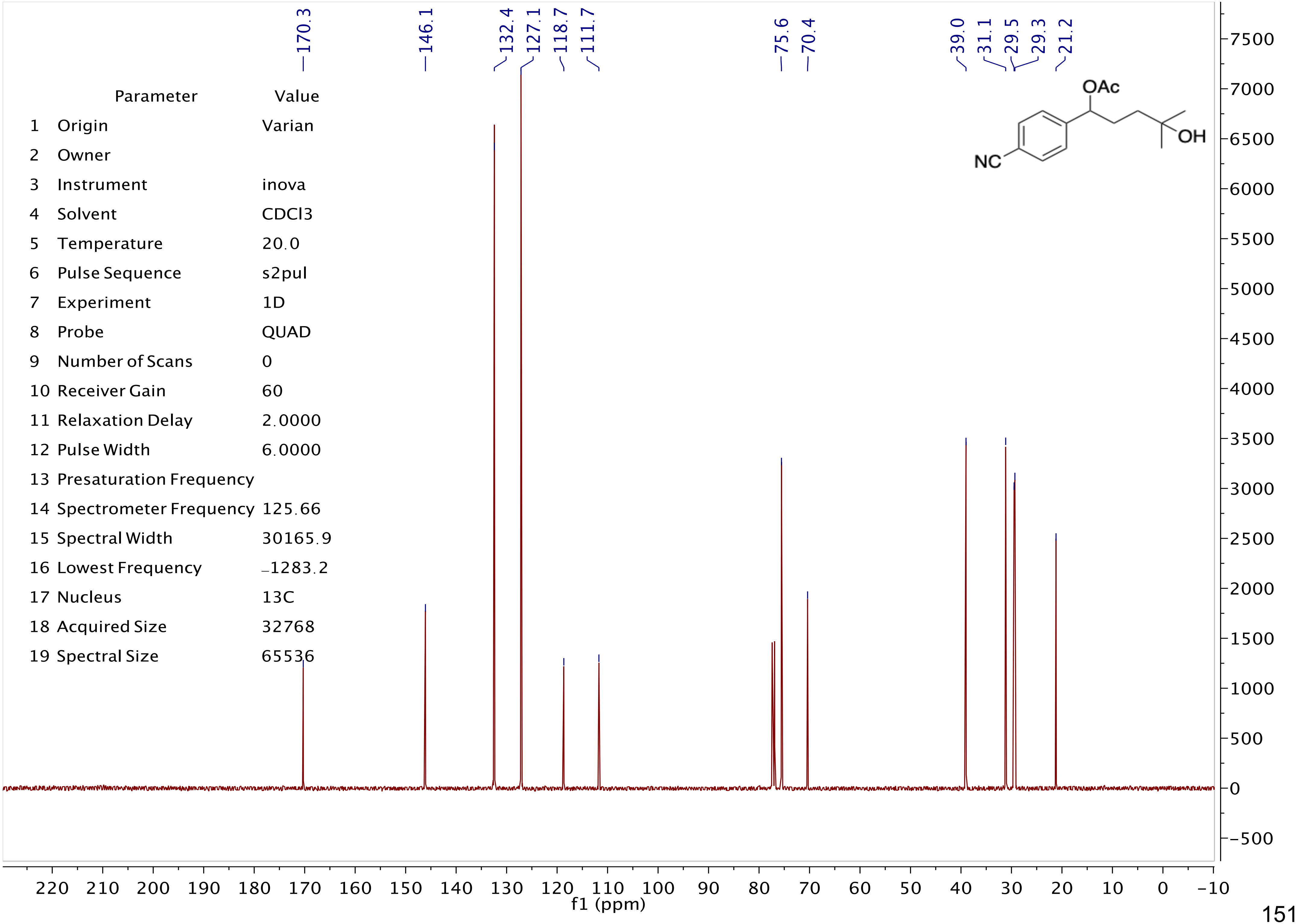
	Parameter	Value
1	Origin	Varian
2	Owner	
3	Instrument	inova
4	Solvent	CDCl3
5	Temperature	20.0
6	Pulse Sequence	s2pul
7	Experiment	1D
8	Probe	QUAD
9	Number of Scans	16
10	Receiver Gain	41
11	Relaxation Delay	15.0000
12	Pulse Width	6.5000
13	Presaturation Frequency	
14	Spectrometer Frequency	499.69
15	Spectral Width	7024.9
16	Lowest Frequency	-1021.4
17	Nucleus	1H
18	Acquired Size	32768
19	Spectral Size	65536



	Parameter	Value
1	Origin	Varian
2	Owner	
3	Instrument	inova
4	Solvent	CDCl3
5	Temperature	20.0
6	Pulse Sequence	s2pul
7	Experiment	1D
8	Probe	QUAD
9	Number of Scans	512
10	Receiver Gain	60
11	Relaxation Delay	2.0000
12	Pulse Width	6.0000
13	Presaturation Frequency	
14	Spectrometer Frequency	125.66
15	Spectral Width	30165.9
16	Lowest Frequency	-1274.4
17	Nucleus	13C
18	Acquired Size	32768
19	Spectral Size	65536

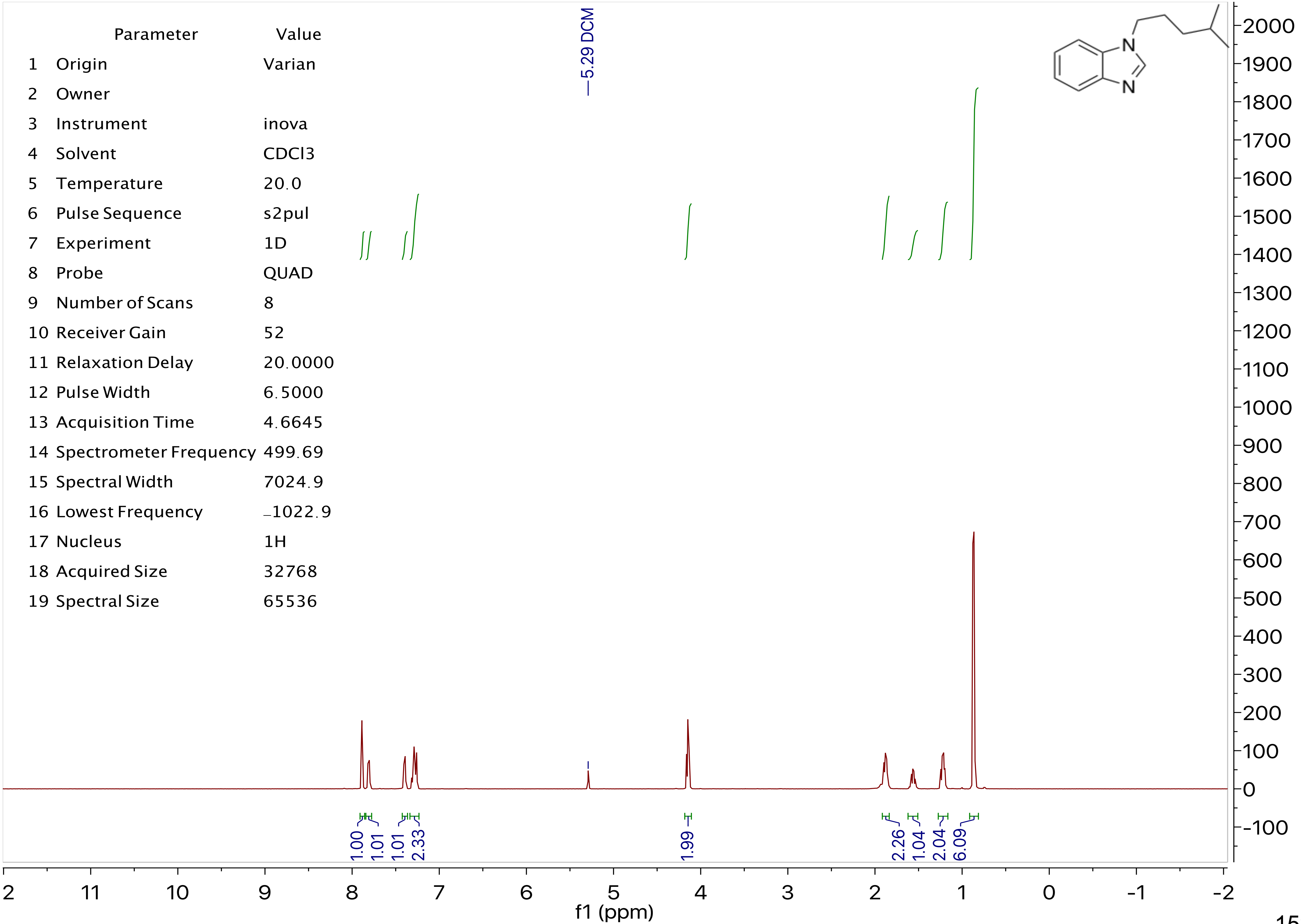


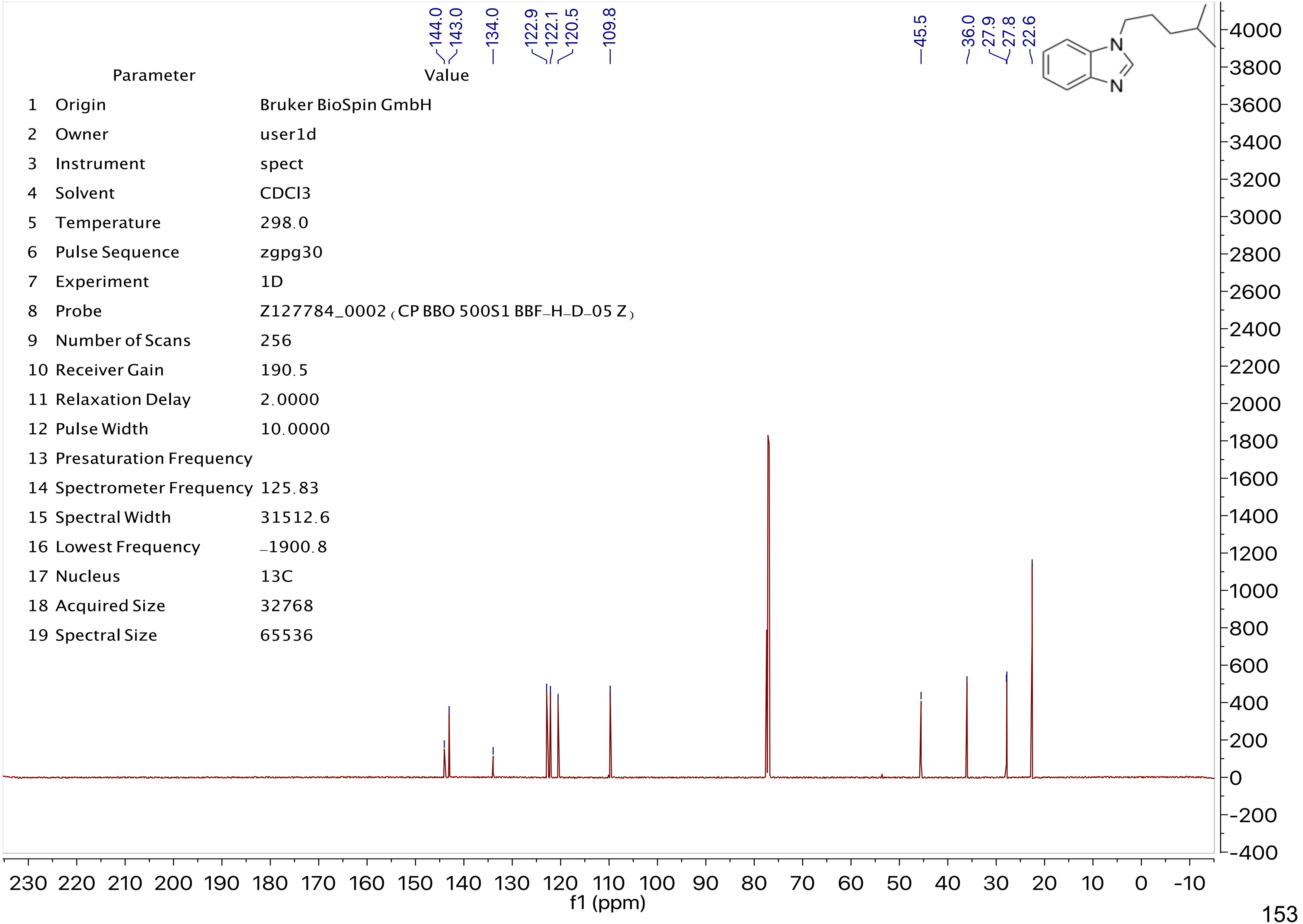
	Parameter	Value
1	Origin	Varian
2	Owner	
3	Instrument	inova
4	Solvent	CDCl3
5	Temperature	20.0
6	Pulse Sequence	s2pul
7	Experiment	1D
8	Probe	hcn
9	Number of Scans	8
10	Receiver Gain	38
11	Relaxation Delay	15.0000
12	Pulse Width	7.0000
13	Presaturation Frequency	
14	Spectrometer Frequency	500.07
15	Spectral Width	8000.0
16	Lowest Frequency	-1521.1
17	Nucleus	1H
18	Acquired Size	32768
19	Spectral Size	65536



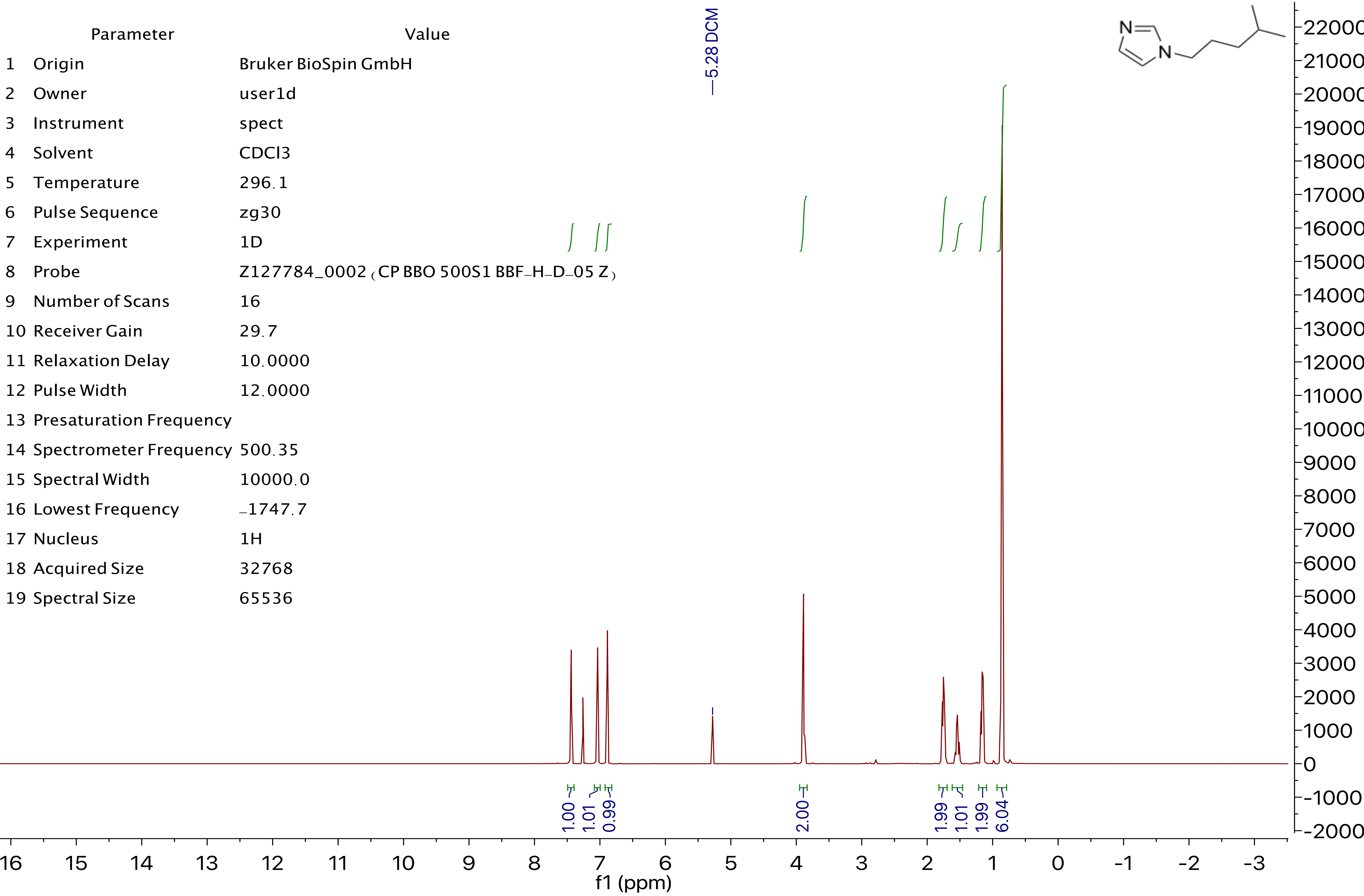
	Parameter	Value
1	Origin	Varian
2	Owner	
3	Instrument	inova
4	Solvent	CDCl3
5	Temperature	20.0
6	Pulse Sequence	s2pul
7	Experiment	1D
8	Probe	QUAD
9	Number of Scans	0
10	Receiver Gain	60
11	Relaxation Delay	2.0000
12	Pulse Width	6.0000
13	Presaturation Frequency	
14	Spectrometer Frequency	125.66
15	Spectral Width	30165.9
16	Lowest Frequency	-1283.2
17	Nucleus	13C
18	Acquired Size	32768
19	Spectral Size	65536

	Parameter	Value
1	Origin	Varian
2	Owner	
3	Instrument	inova
4	Solvent	CDCl3
5	Temperature	20.0
6	Pulse Sequence	s2pul
7	Experiment	1D
8	Probe	QUAD
9	Number of Scans	8
10	Receiver Gain	52
11	Relaxation Delay	20.0000
12	Pulse Width	6.5000
13	Acquisition Time	4.6645
14	Spectrometer Frequency	499.69
15	Spectral Width	7024.9
16	Lowest Frequency	-1022.9
17	Nucleus	1H
18	Acquired Size	32768
19	Spectral Size	65536



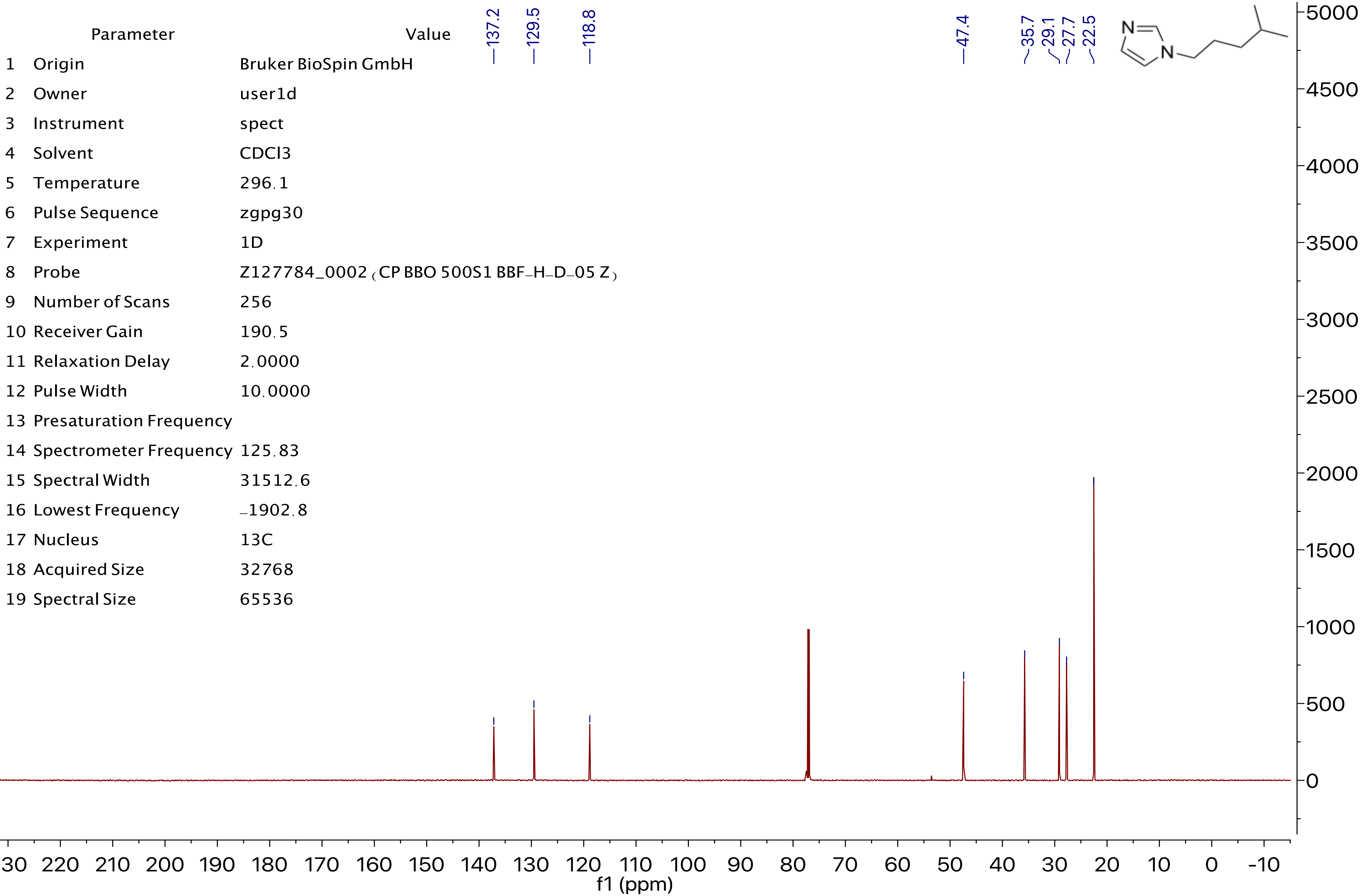


	Parameter	Value
1	Origin	Bruker BioSpin GmbH
2	Owner	user1d
3	Instrument	spect
4	Solvent	CDCl3
5	Temperature	298.0
6	Pulse Sequence	zgpg30
7	Experiment	1D
8	Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
9	Number of Scans	256
10	Receiver Gain	190.5
11	Relaxation Delay	2.0000
12	Pulse Width	10.0000
13	Presaturation Frequency	
14	Spectrometer Frequency	125.83
15	Spectral Width	31512.6
16	Lowest Frequency	-1900.8
17	Nucleus	13C
18	Acquired Size	32768
19	Spectral Size	65536

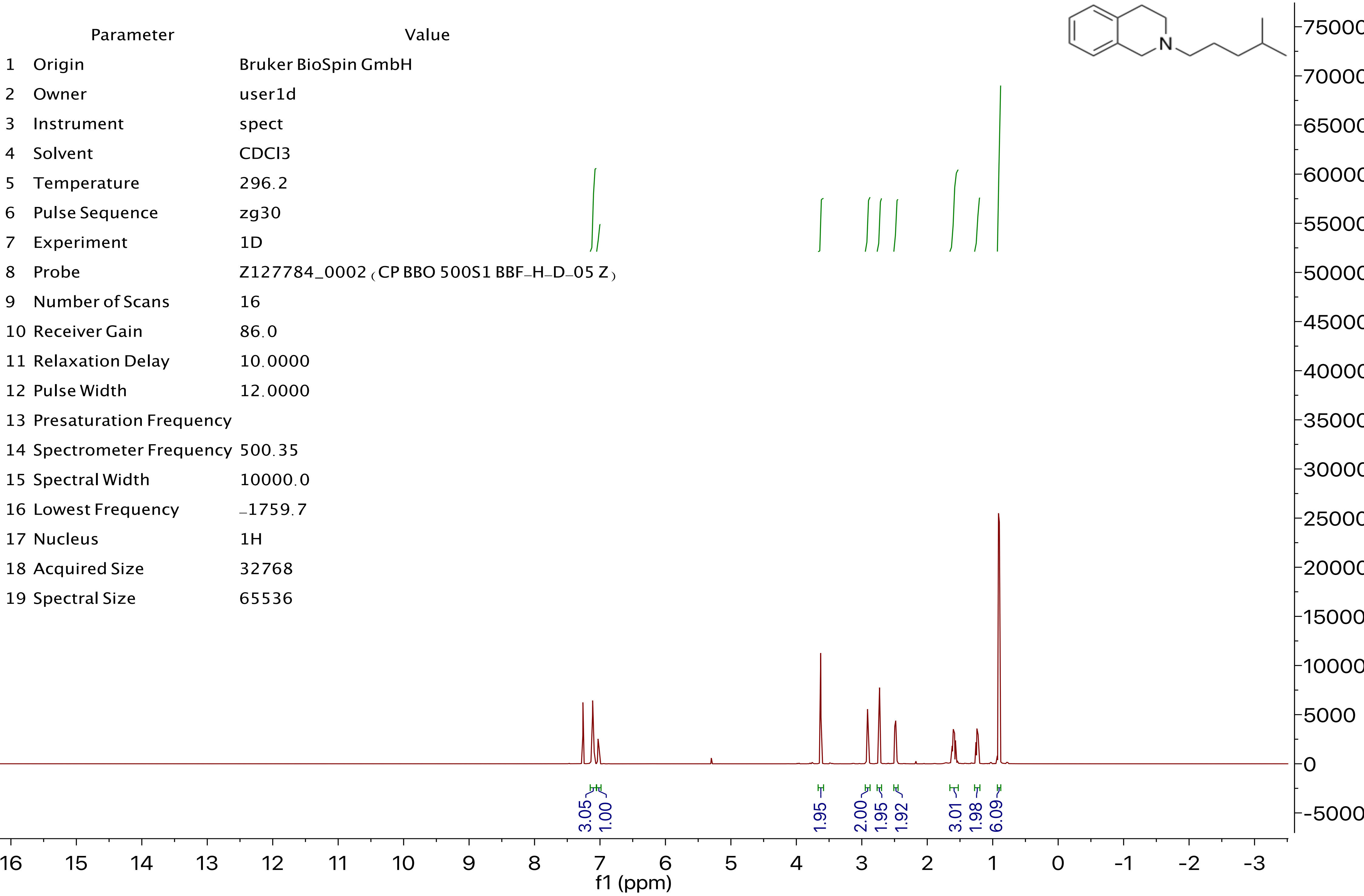


	Parameter	Value
1	Origin	Bruker BioSpin GmbH
2	Owner	user1d
3	Instrument	spect
4	Solvent	CDCl3
5	Temperature	296.1
6	Pulse Sequence	zg30
7	Experiment	1D
8	Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
9	Number of Scans	16
10	Receiver Gain	29.7
11	Relaxation Delay	10.0000
12	Pulse Width	12.0000
13	Presaturation Frequency	
14	Spectrometer Frequency	500.35
15	Spectral Width	10000.0
16	Lowest Frequency	-1747.7
17	Nucleus	1H
18	Acquired Size	32768
19	Spectral Size	65536

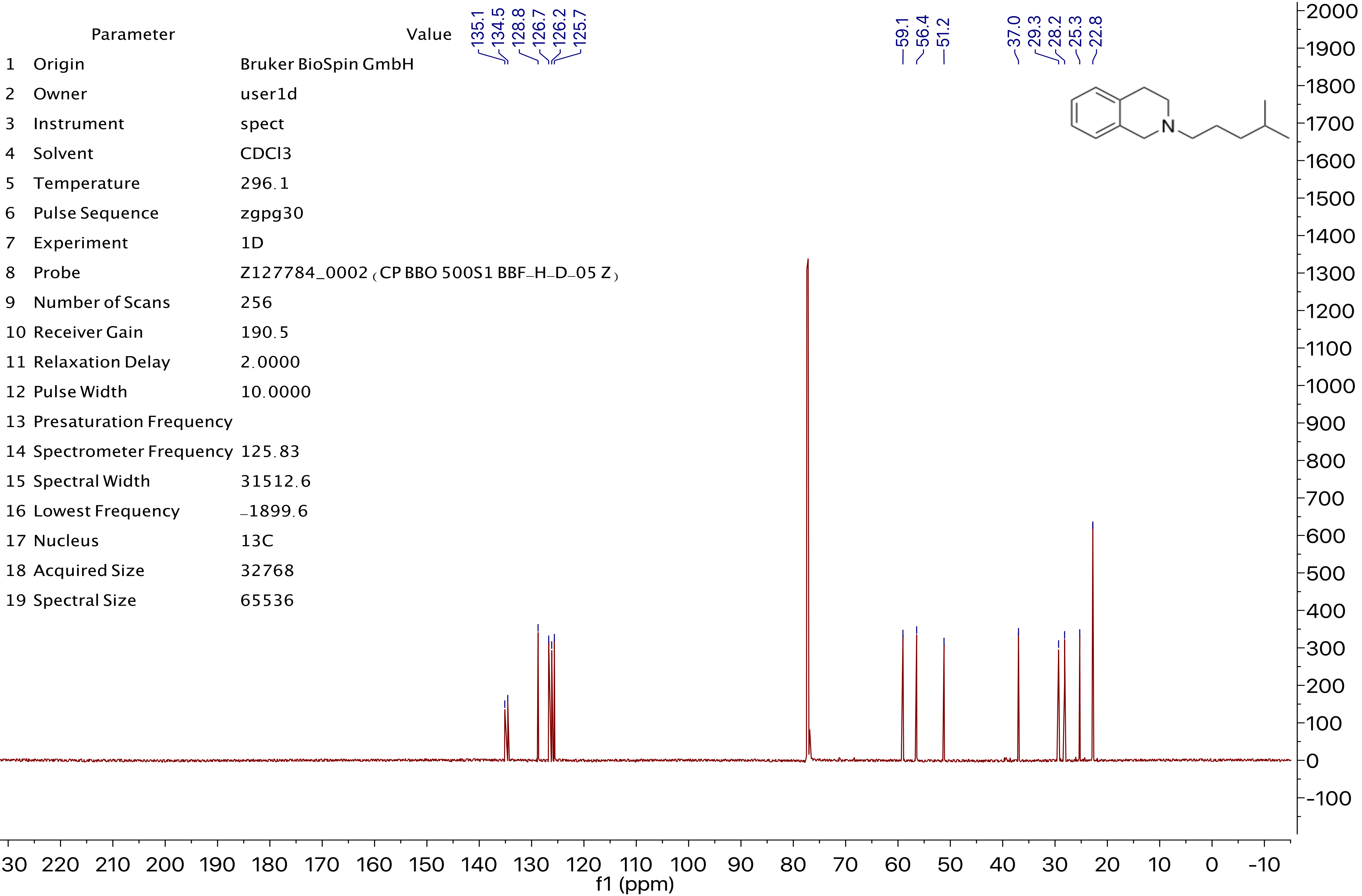
	Parameter	Value
1	Origin	Bruker BioSpin GmbH
2	Owner	user1d
3	Instrument	spect
4	Solvent	CDCl3
5	Temperature	296.1
6	Pulse Sequence	zgpg30
7	Experiment	1D
8	Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
9	Number of Scans	256
10	Receiver Gain	190.5
11	Relaxation Delay	2.0000
12	Pulse Width	10.0000
13	Presaturation Frequency	
14	Spectrometer Frequency	125.83
15	Spectral Width	31512.6
16	Lowest Frequency	-1902.8
17	Nucleus	13C
18	Acquired Size	32768
19	Spectral Size	65536

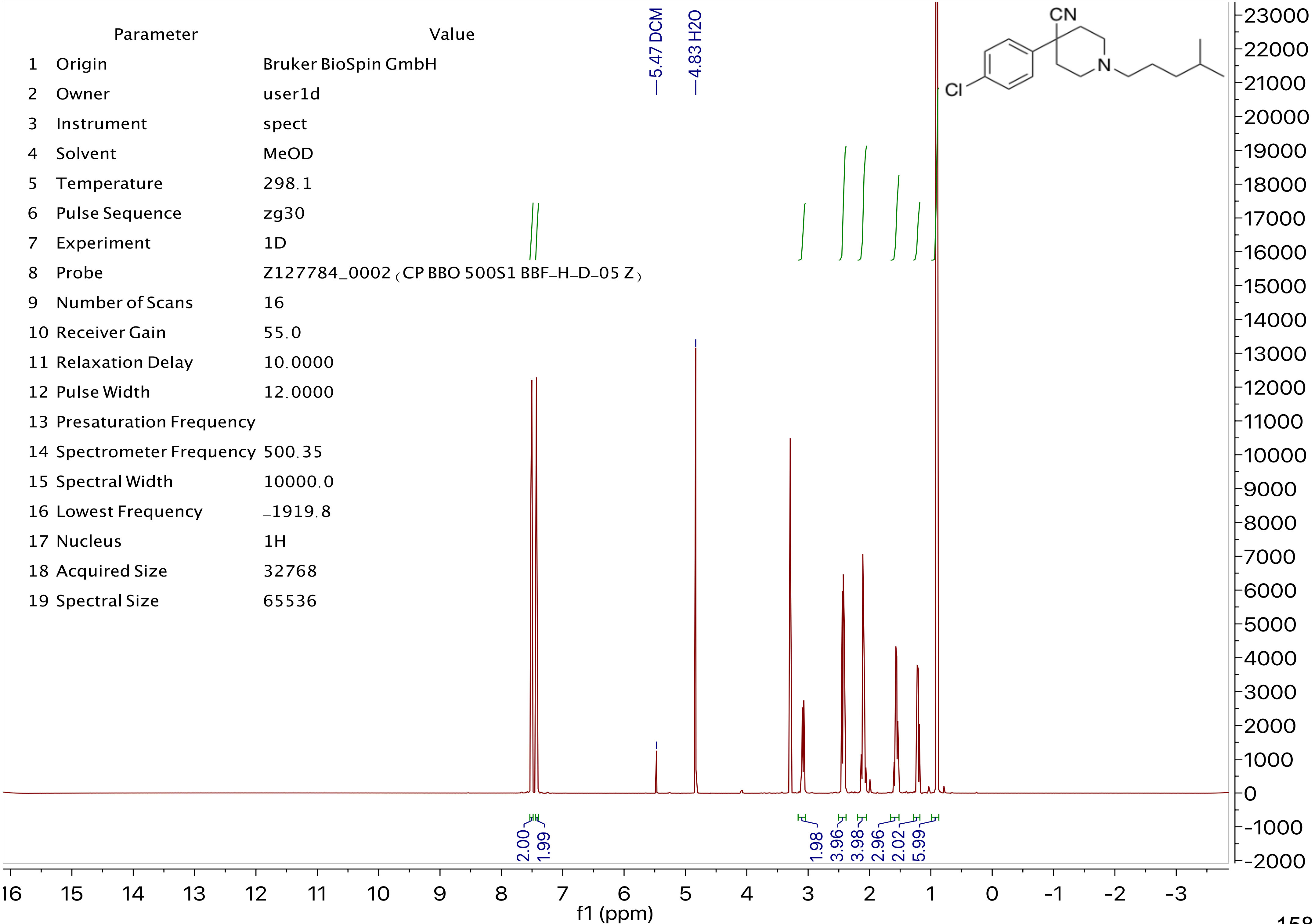


	Parameter	Value
1	Origin	Bruker BioSpin GmbH
2	Owner	user1d
3	Instrument	spect
4	Solvent	CDCl3
5	Temperature	296.2
6	Pulse Sequence	zg30
7	Experiment	1D
8	Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
9	Number of Scans	16
10	Receiver Gain	86.0
11	Relaxation Delay	10.0000
12	Pulse Width	12.0000
13	Presaturation Frequency	
14	Spectrometer Frequency	500.35
15	Spectral Width	10000.0
16	Lowest Frequency	-1759.7
17	Nucleus	1H
18	Acquired Size	32768
19	Spectral Size	65536

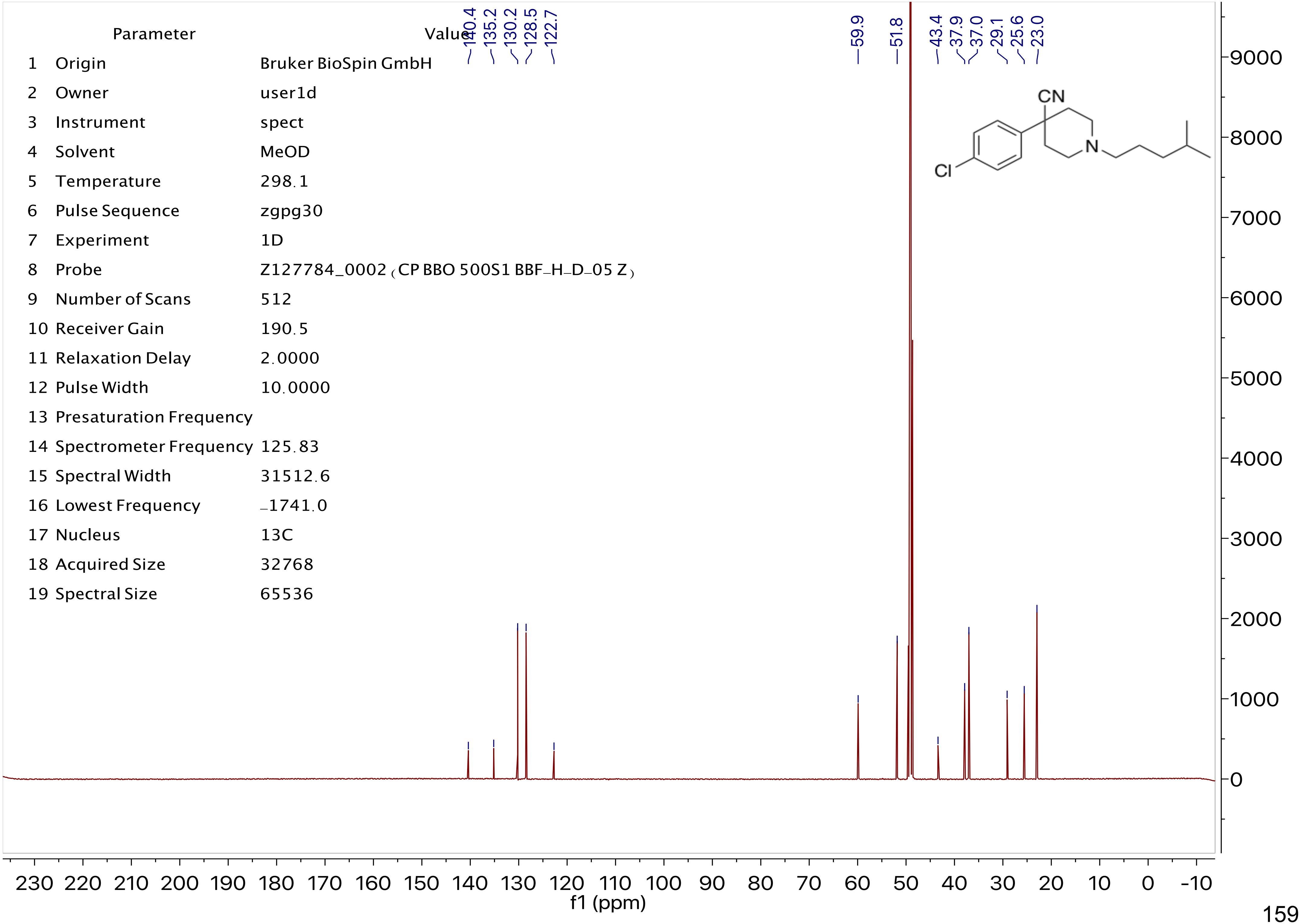


	Parameter	Value
1	Origin	Bruker BioSpin GmbH
2	Owner	user1d
3	Instrument	spect
4	Solvent	CDCl3
5	Temperature	296.1
6	Pulse Sequence	zgpg30
7	Experiment	1D
8	Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
9	Number of Scans	256
10	Receiver Gain	190.5
11	Relaxation Delay	2.0000
12	Pulse Width	10.0000
13	Presaturation Frequency	
14	Spectrometer Frequency	125.83
15	Spectral Width	31512.6
16	Lowest Frequency	-1899.6
17	Nucleus	13C
18	Acquired Size	32768
19	Spectral Size	65536

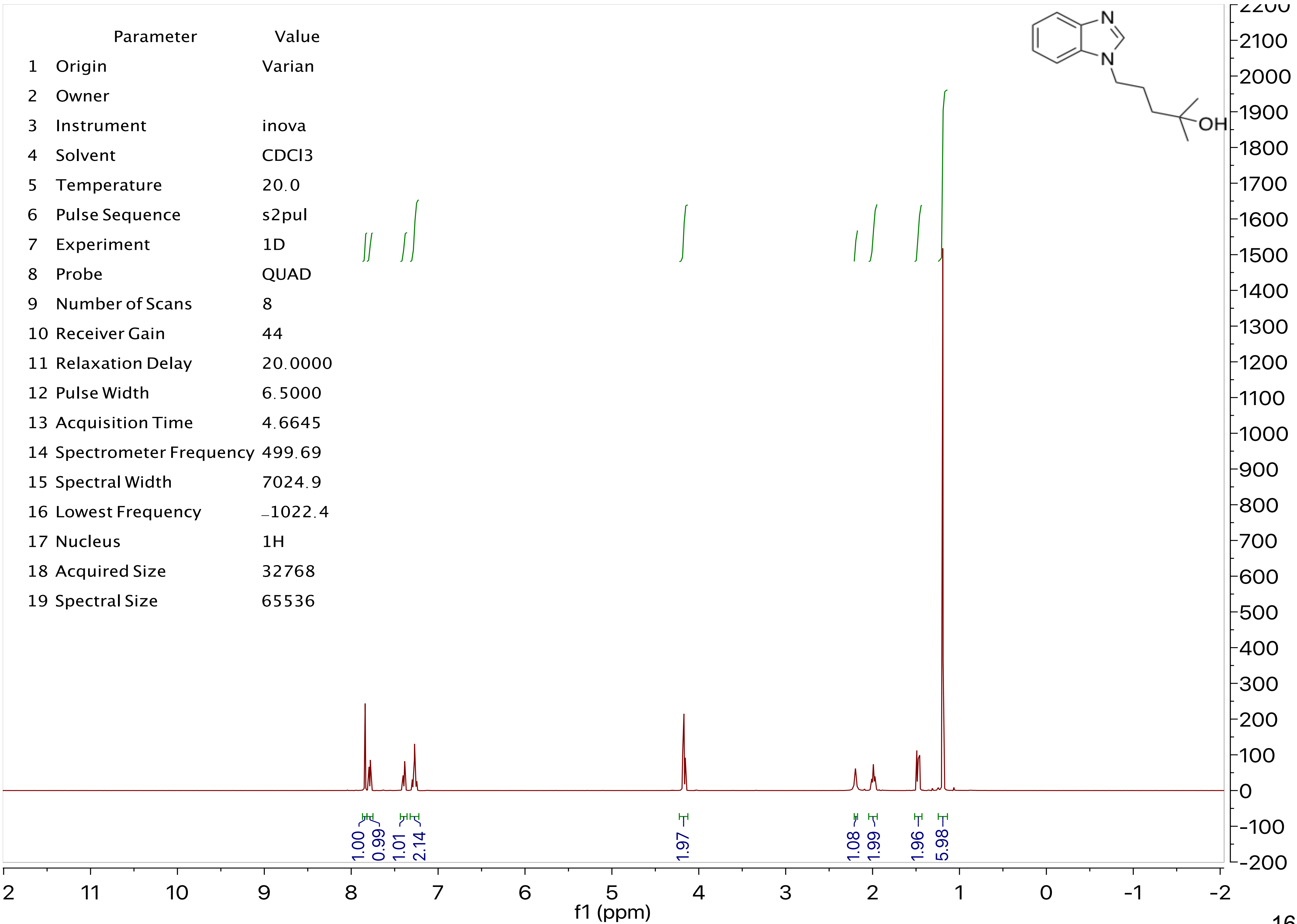




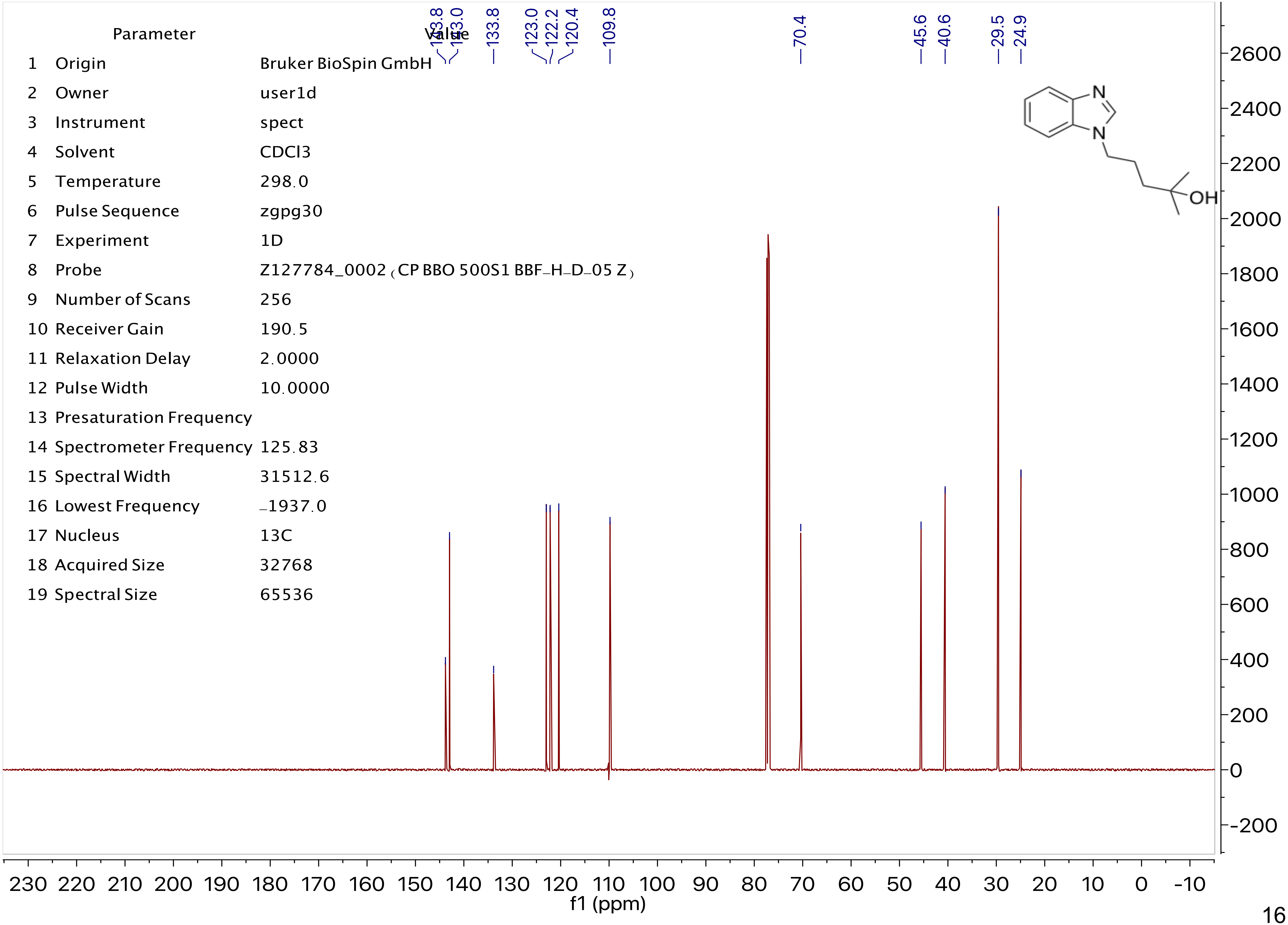
	Parameter	Value
1	Origin	Bruker BioSpin GmbH
2	Owner	user1d
3	Instrument	spect
4	Solvent	MeOD
5	Temperature	298.1
6	Pulse Sequence	zg30
7	Experiment	1D
8	Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
9	Number of Scans	16
10	Receiver Gain	55.0
11	Relaxation Delay	10.0000
12	Pulse Width	12.0000
13	Presaturation Frequency	
14	Spectrometer Frequency	500.35
15	Spectral Width	10000.0
16	Lowest Frequency	-1919.8
17	Nucleus	1H
18	Acquired Size	32768
19	Spectral Size	65536



	Parameter	Value
1	Origin	Bruker BioSpin GmbH
2	Owner	user1d
3	Instrument	spect
4	Solvent	MeOD
5	Temperature	298.1
6	Pulse Sequence	zgpg30
7	Experiment	1D
8	Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
9	Number of Scans	512
10	Receiver Gain	190.5
11	Relaxation Delay	2.0000
12	Pulse Width	10.0000
13	Presaturation Frequency	
14	Spectrometer Frequency	125.83
15	Spectral Width	31512.6
16	Lowest Frequency	-1741.0
17	Nucleus	13C
18	Acquired Size	32768
19	Spectral Size	65536

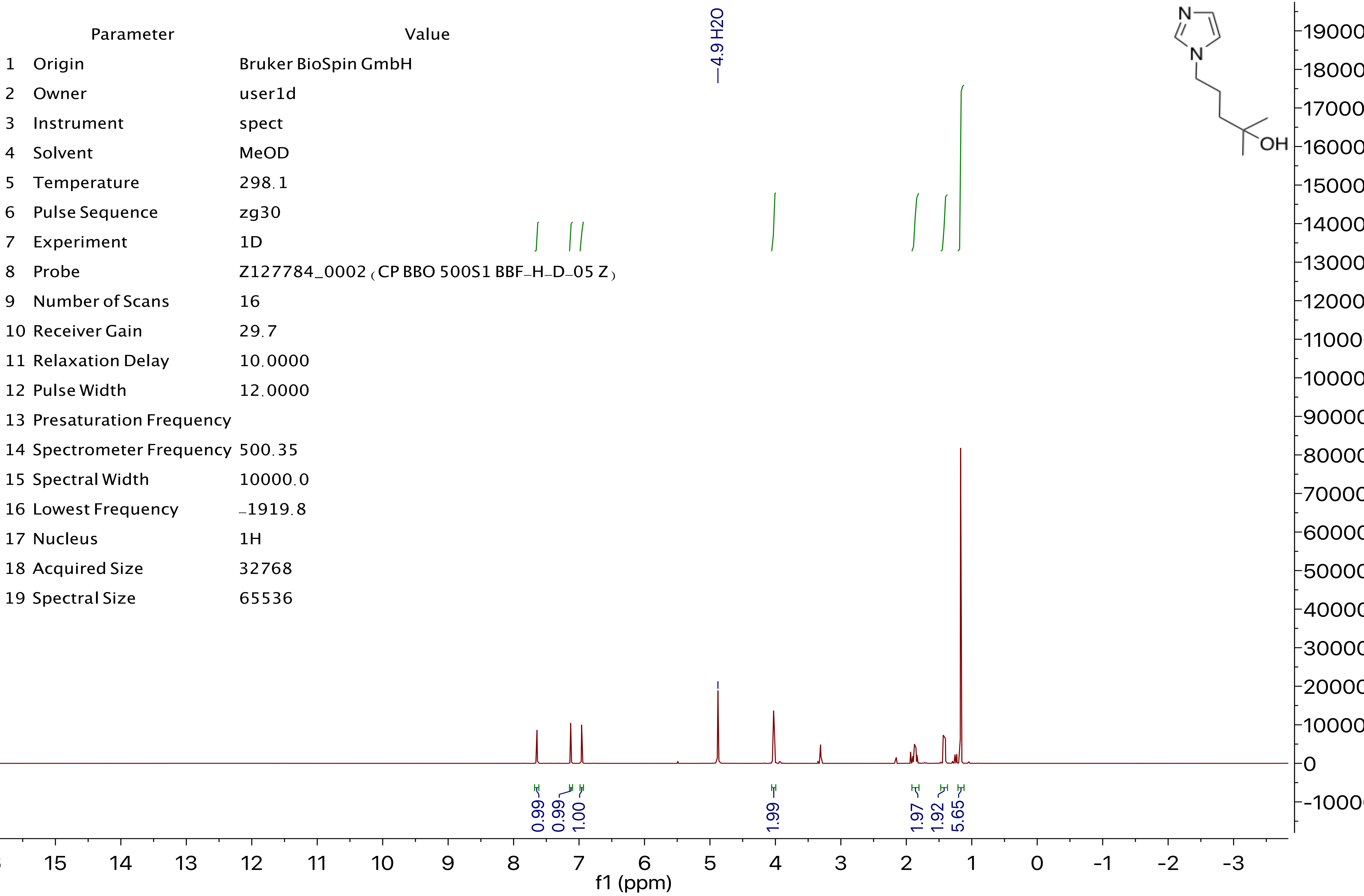


	Parameter	Value
1	Origin	Varian
2	Owner	
3	Instrument	inova
4	Solvent	CDCl3
5	Temperature	20.0
6	Pulse Sequence	s2pul
7	Experiment	1D
8	Probe	QUAD
9	Number of Scans	8
10	Receiver Gain	44
11	Relaxation Delay	20.0000
12	Pulse Width	6.5000
13	Acquisition Time	4.6645
14	Spectrometer Frequency	499.69
15	Spectral Width	7024.9
16	Lowest Frequency	–1022.4
17	Nucleus	1H
18	Acquired Size	32768
19	Spectral Size	65536

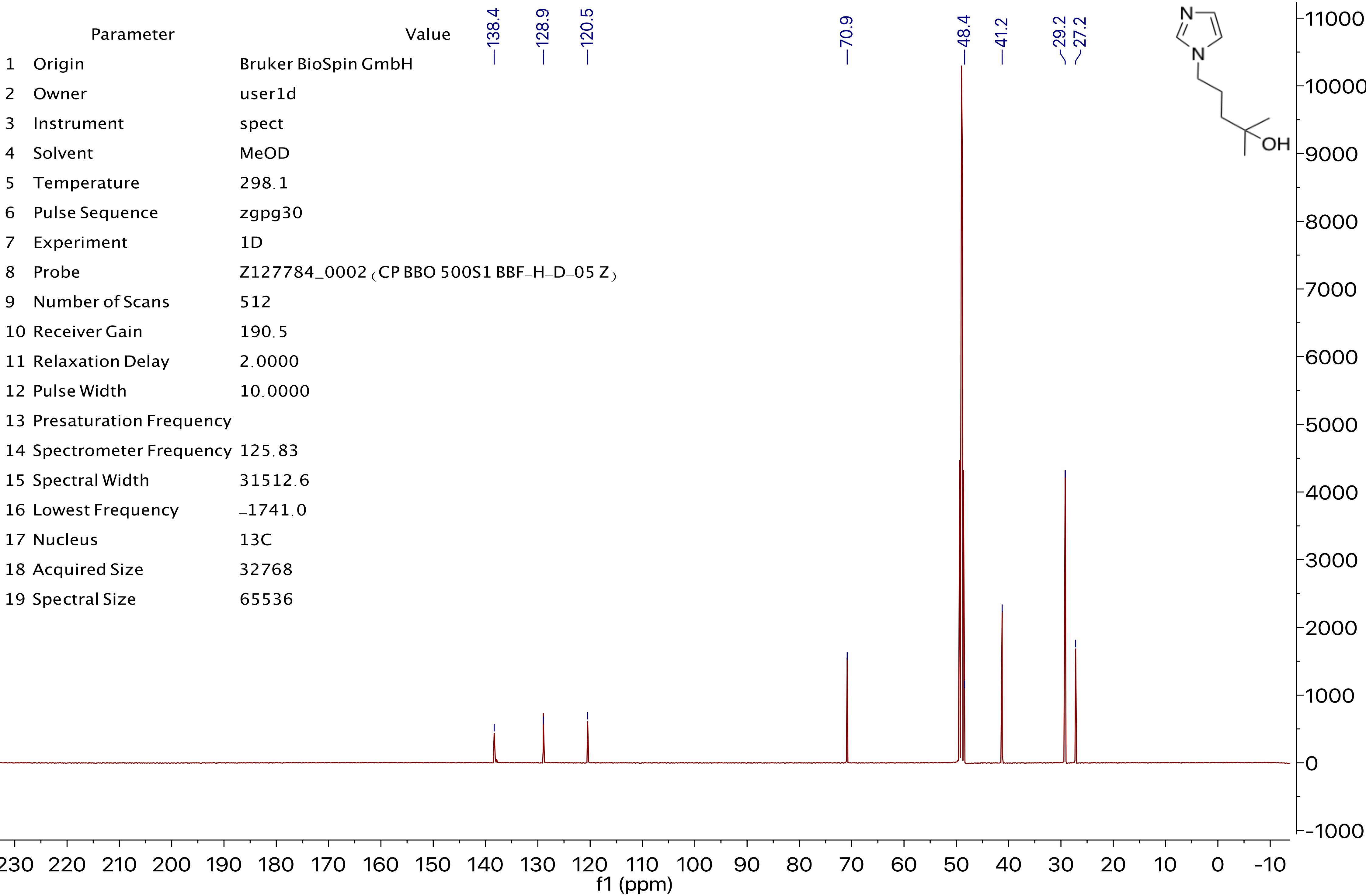


	Parameter	Value
1	Origin	Bruker BioSpin GmbH
2	Owner	user1d
3	Instrument	spect
4	Solvent	CDCl3
5	Temperature	298.0
6	Pulse Sequence	zgpg30
7	Experiment	1D
8	Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
9	Number of Scans	256
10	Receiver Gain	190.5
11	Relaxation Delay	2.0000
12	Pulse Width	10.0000
13	Presaturation Frequency	
14	Spectrometer Frequency	125.83
15	Spectral Width	31512.6
16	Lowest Frequency	-1937.0
17	Nucleus	13C
18	Acquired Size	32768
19	Spectral Size	65536

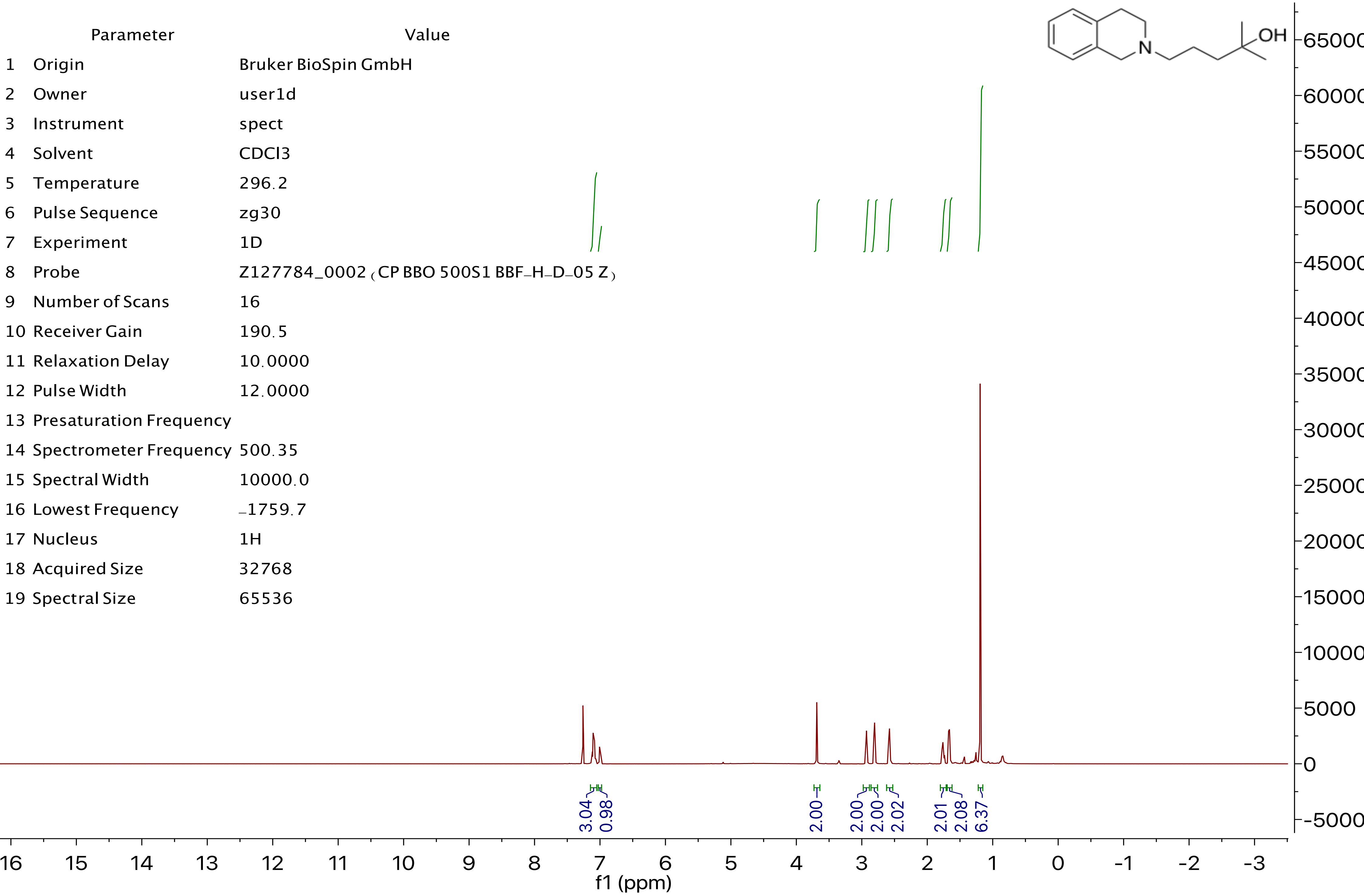
	Parameter	Value
1	Origin	Bruker BioSpin GmbH
2	Owner	user1d
3	Instrument	spect
4	Solvent	MeOD
5	Temperature	298.1
6	Pulse Sequence	zg30
7	Experiment	1D
8	Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
9	Number of Scans	16
10	Receiver Gain	29.7
11	Relaxation Delay	10.0000
12	Pulse Width	12.0000
13	Presaturation Frequency	
14	Spectrometer Frequency	500.35
15	Spectral Width	10000.0
16	Lowest Frequency	-1919.8
17	Nucleus	1H
18	Acquired Size	32768
19	Spectral Size	65536

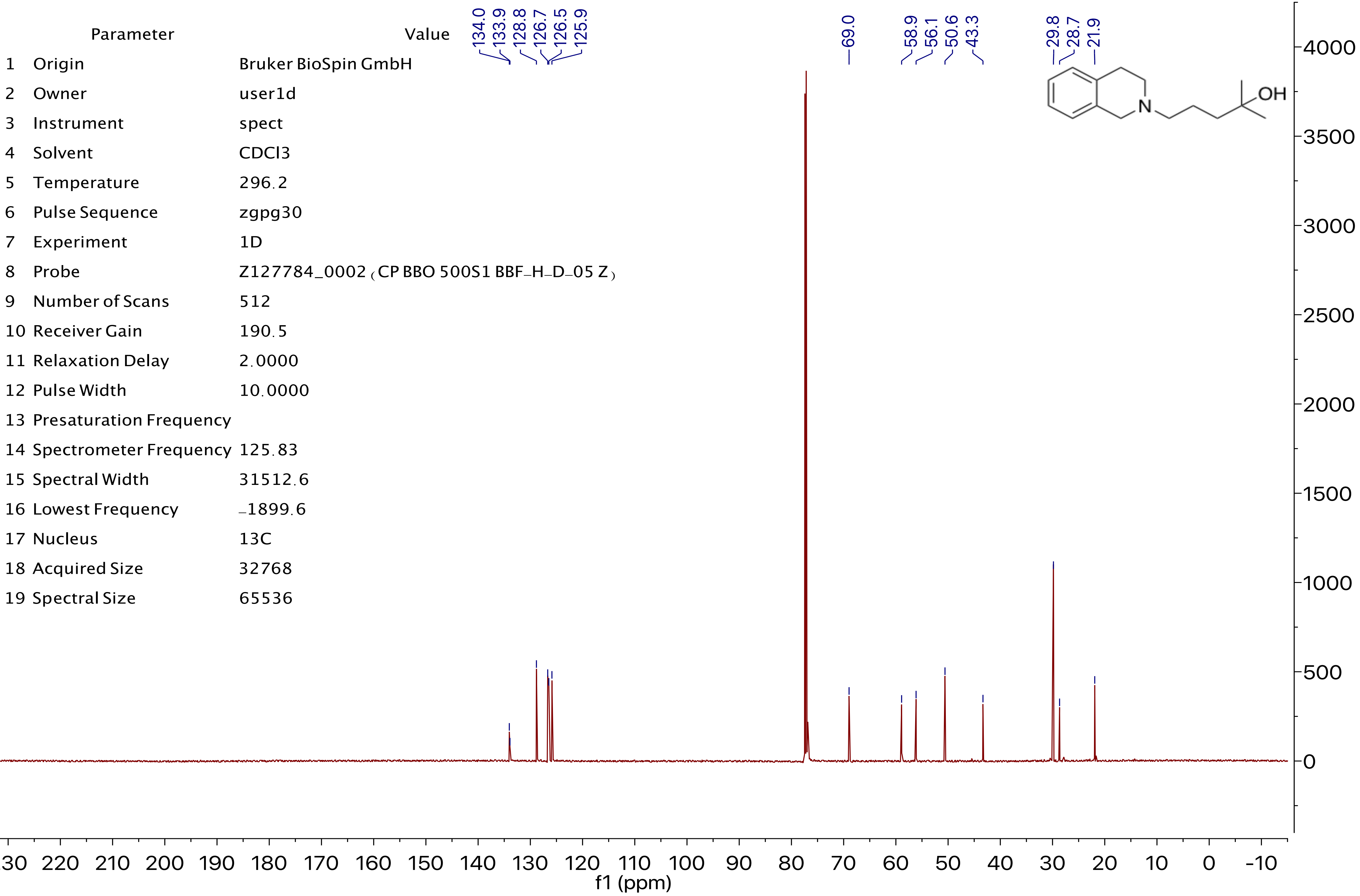


	Parameter	Value
1	Origin	Bruker BioSpin GmbH
2	Owner	user1d
3	Instrument	spect
4	Solvent	MeOD
5	Temperature	298.1
6	Pulse Sequence	zgpg30
7	Experiment	1D
8	Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
9	Number of Scans	512
10	Receiver Gain	190.5
11	Relaxation Delay	2.0000
12	Pulse Width	10.0000
13	Presaturation Frequency	
14	Spectrometer Frequency	125.83
15	Spectral Width	31512.6
16	Lowest Frequency	-1741.0
17	Nucleus	13C
18	Acquired Size	32768
19	Spectral Size	65536

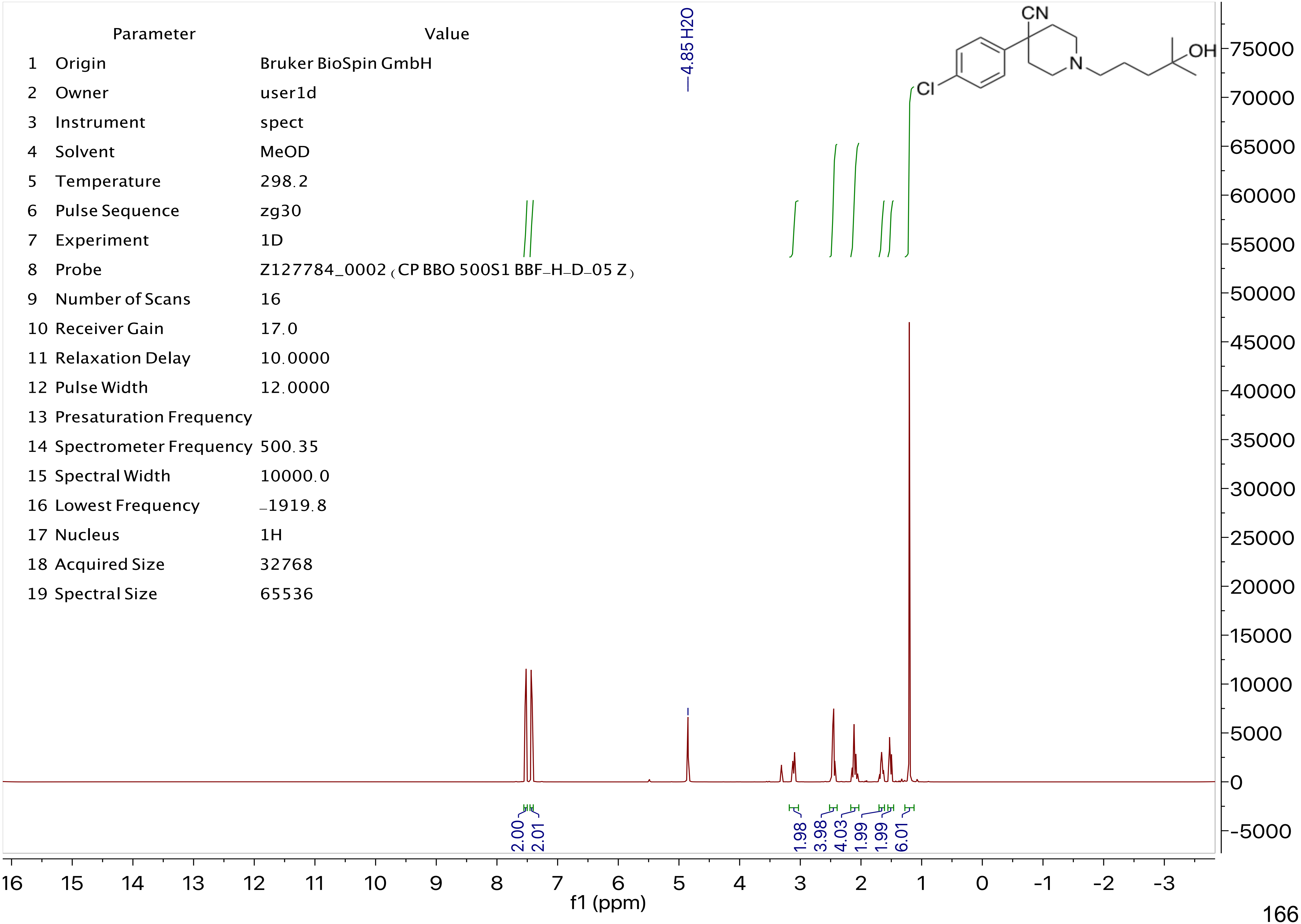


	Parameter	Value
1	Origin	Bruker BioSpin GmbH
2	Owner	user1d
3	Instrument	spect
4	Solvent	CDCl3
5	Temperature	296.2
6	Pulse Sequence	zg30
7	Experiment	1D
8	Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
9	Number of Scans	16
10	Receiver Gain	190.5
11	Relaxation Delay	10.0000
12	Pulse Width	12.0000
13	Presaturation Frequency	
14	Spectrometer Frequency	500.35
15	Spectral Width	10000.0
16	Lowest Frequency	-1759.7
17	Nucleus	1H
18	Acquired Size	32768
19	Spectral Size	65536

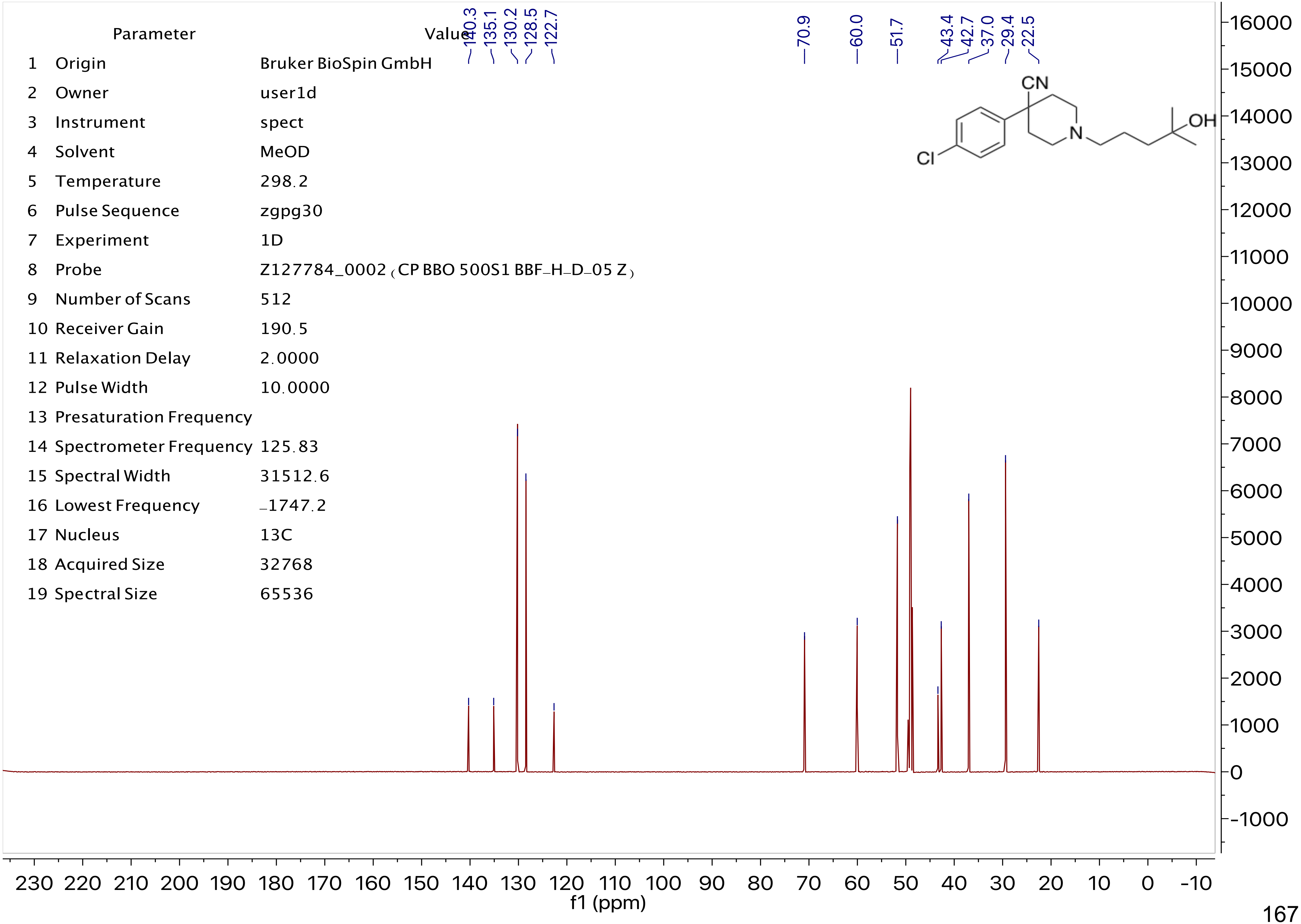




	Parameter	Value
1	Origin	Bruker BioSpin GmbH
2	Owner	user1d
3	Instrument	spect
4	Solvent	CDCl3
5	Temperature	296.2
6	Pulse Sequence	zgpg30
7	Experiment	1D
8	Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
9	Number of Scans	512
10	Receiver Gain	190.5
11	Relaxation Delay	2.0000
12	Pulse Width	10.0000
13	Presaturation Frequency	
14	Spectrometer Frequency	125.83
15	Spectral Width	31512.6
16	Lowest Frequency	-1899.6
17	Nucleus	13C
18	Acquired Size	32768
19	Spectral Size	65536

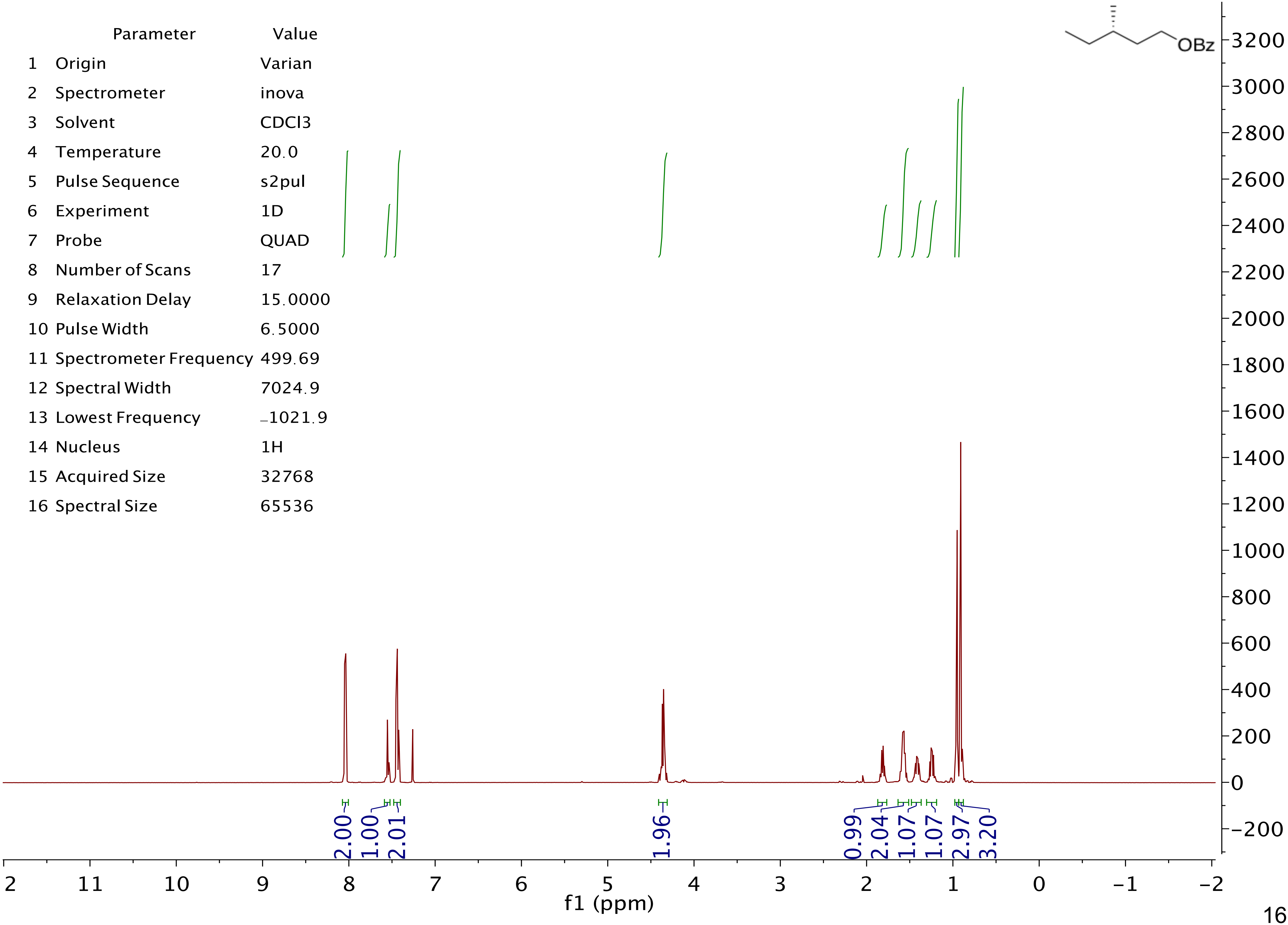


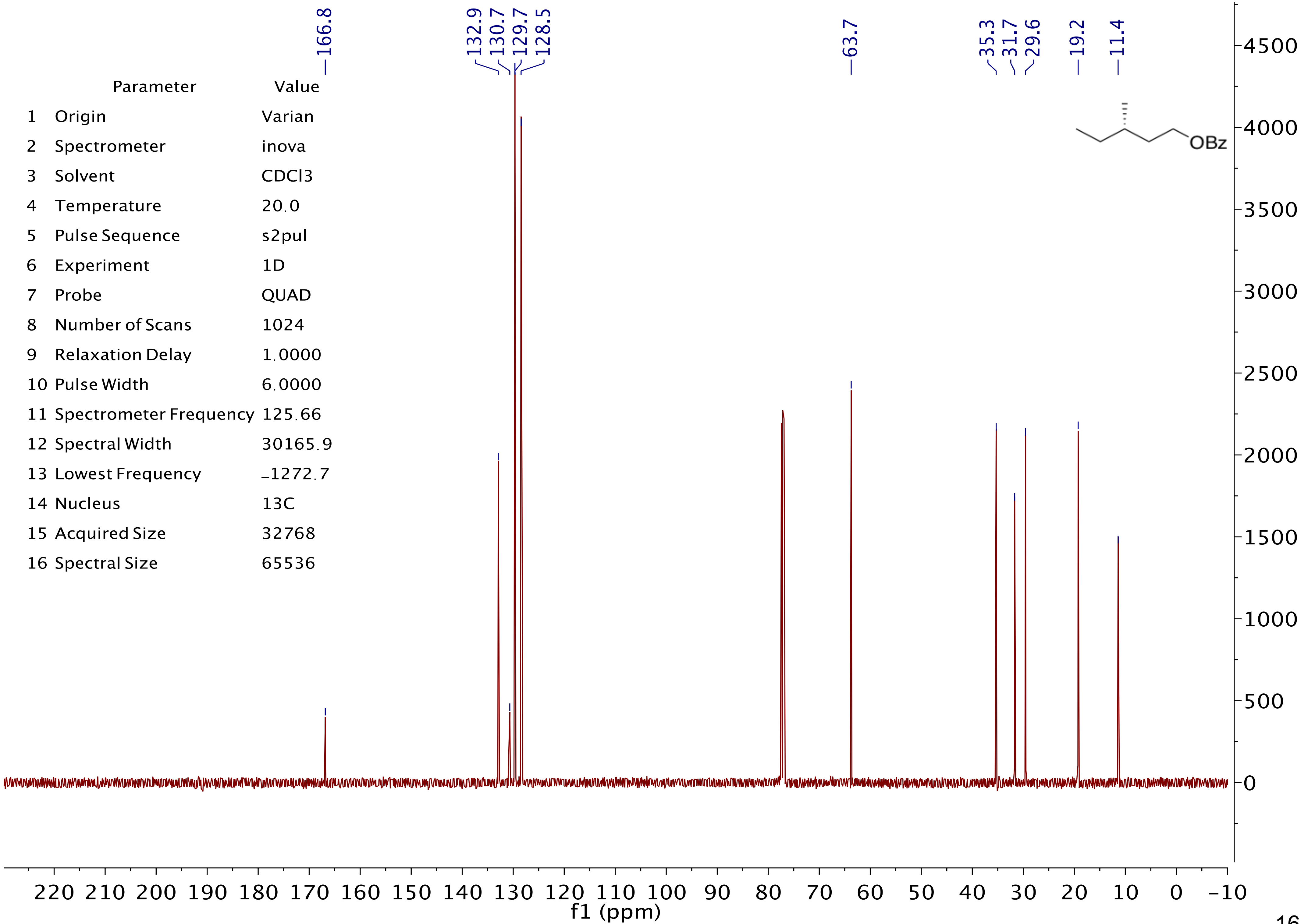
	Parameter	Value
1	Origin	Bruker BioSpin GmbH
2	Owner	user1d
3	Instrument	spect
4	Solvent	MeOD
5	Temperature	298.2
6	Pulse Sequence	zg30
7	Experiment	1D
8	Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
9	Number of Scans	16
10	Receiver Gain	17.0
11	Relaxation Delay	10.0000
12	Pulse Width	12.0000
13	Presaturation Frequency	
14	Spectrometer Frequency	500.35
15	Spectral Width	10000.0
16	Lowest Frequency	-1919.8
17	Nucleus	1H
18	Acquired Size	32768
19	Spectral Size	65536



	Parameter	Value
1	Origin	Bruker BioSpin GmbH
2	Owner	user1d
3	Instrument	spect
4	Solvent	MeOD
5	Temperature	298.2
6	Pulse Sequence	zgpg30
7	Experiment	1D
8	Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
9	Number of Scans	512
10	Receiver Gain	190.5
11	Relaxation Delay	2.0000
12	Pulse Width	10.0000
13	Presaturation Frequency	
14	Spectrometer Frequency	125.83
15	Spectral Width	31512.6
16	Lowest Frequency	-1747.2
17	Nucleus	13C
18	Acquired Size	32768
19	Spectral Size	65536

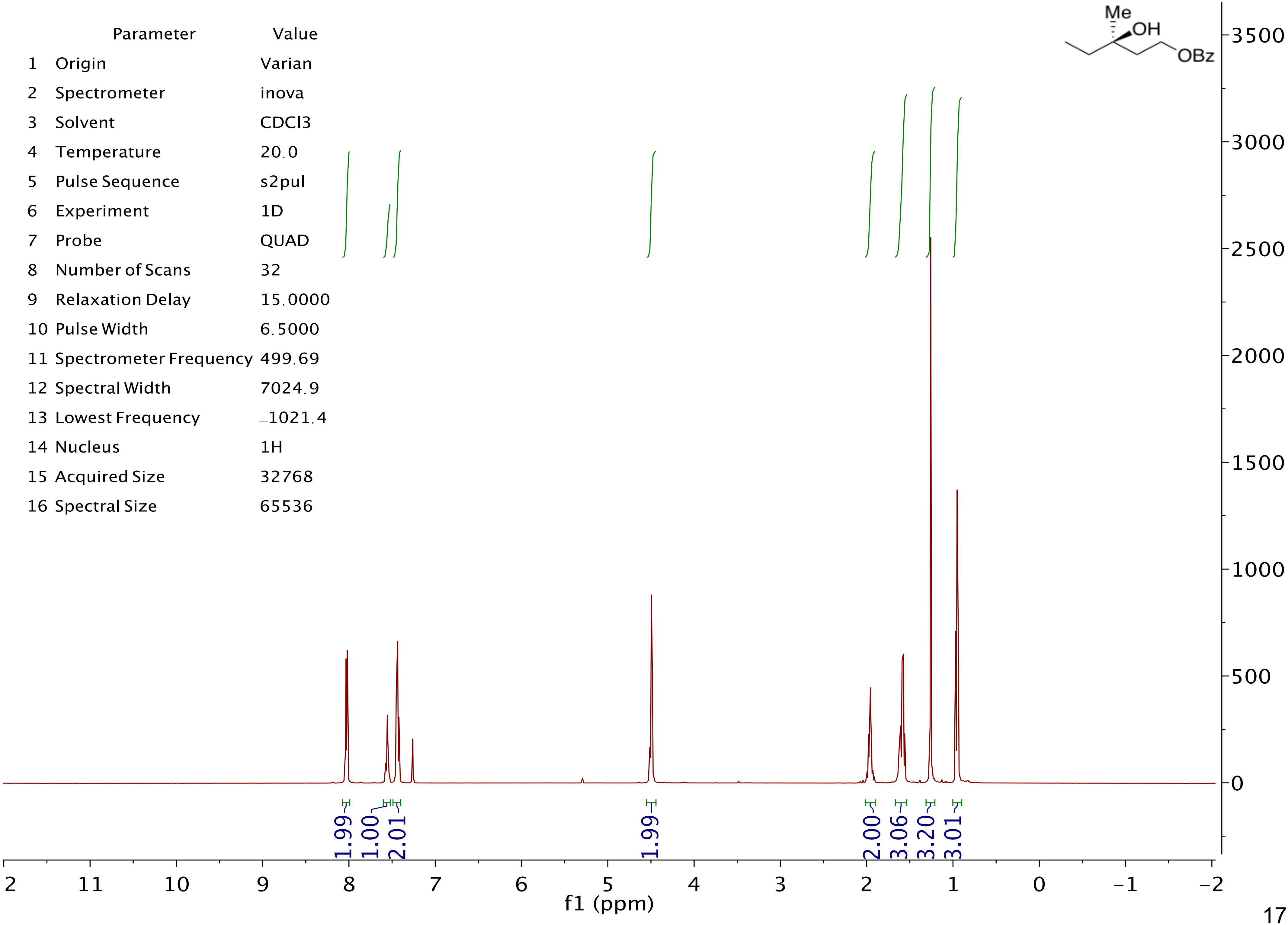
	Parameter	Value
1	Origin	Varian
2	Spectrometer	inova
3	Solvent	CDCl3
4	Temperature	20.0
5	Pulse Sequence	s2pul
6	Experiment	1D
7	Probe	QUAD
8	Number of Scans	17
9	Relaxation Delay	15.0000
10	Pulse Width	6.5000
11	Spectrometer Frequency	499.69
12	Spectral Width	7024.9
13	Lowest Frequency	-1021.9
14	Nucleus	1H
15	Acquired Size	32768
16	Spectral Size	65536

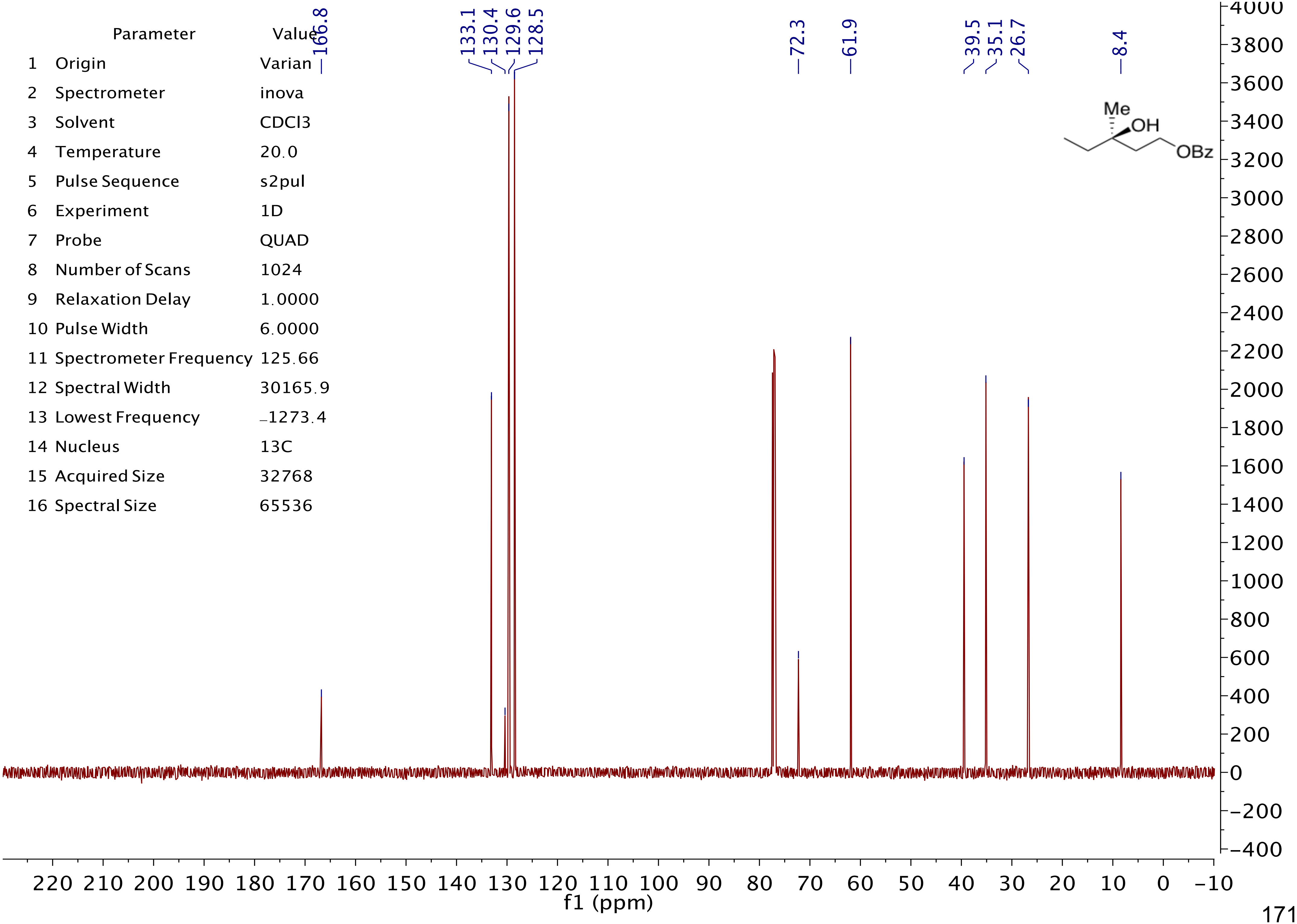




	Parameter	Value
1	Origin	Varian
2	Spectrometer	inova
3	Solvent	CDCl3
4	Temperature	20.0
5	Pulse Sequence	s2pul
6	Experiment	1D
7	Probe	QUAD
8	Number of Scans	1024
9	Relaxation Delay	1.0000
10	Pulse Width	6.0000
11	Spectrometer Frequency	125.66
12	Spectral Width	30165.9
13	Lowest Frequency	-1272.7
14	Nucleus	13C
15	Acquired Size	32768
16	Spectral Size	65536

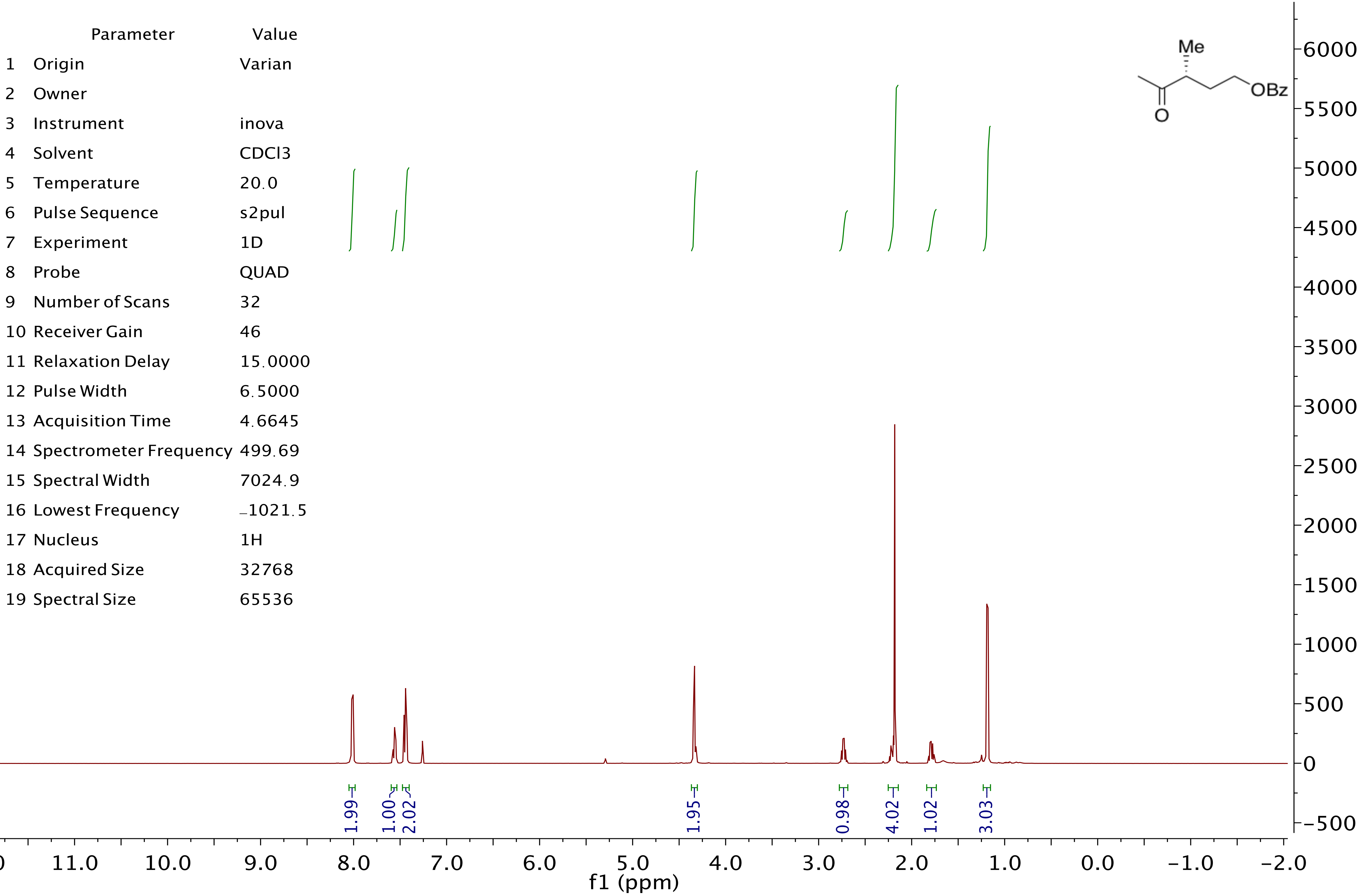
	Parameter	Value
1	Origin	Varian
2	Spectrometer	inova
3	Solvent	CDCl3
4	Temperature	20.0
5	Pulse Sequence	s2pul
6	Experiment	1D
7	Probe	QUAD
8	Number of Scans	32
9	Relaxation Delay	15.0000
10	Pulse Width	6.5000
11	Spectrometer Frequency	499.69
12	Spectral Width	7024.9
13	Lowest Frequency	–1021.4
14	Nucleus	1H
15	Acquired Size	32768
16	Spectral Size	65536

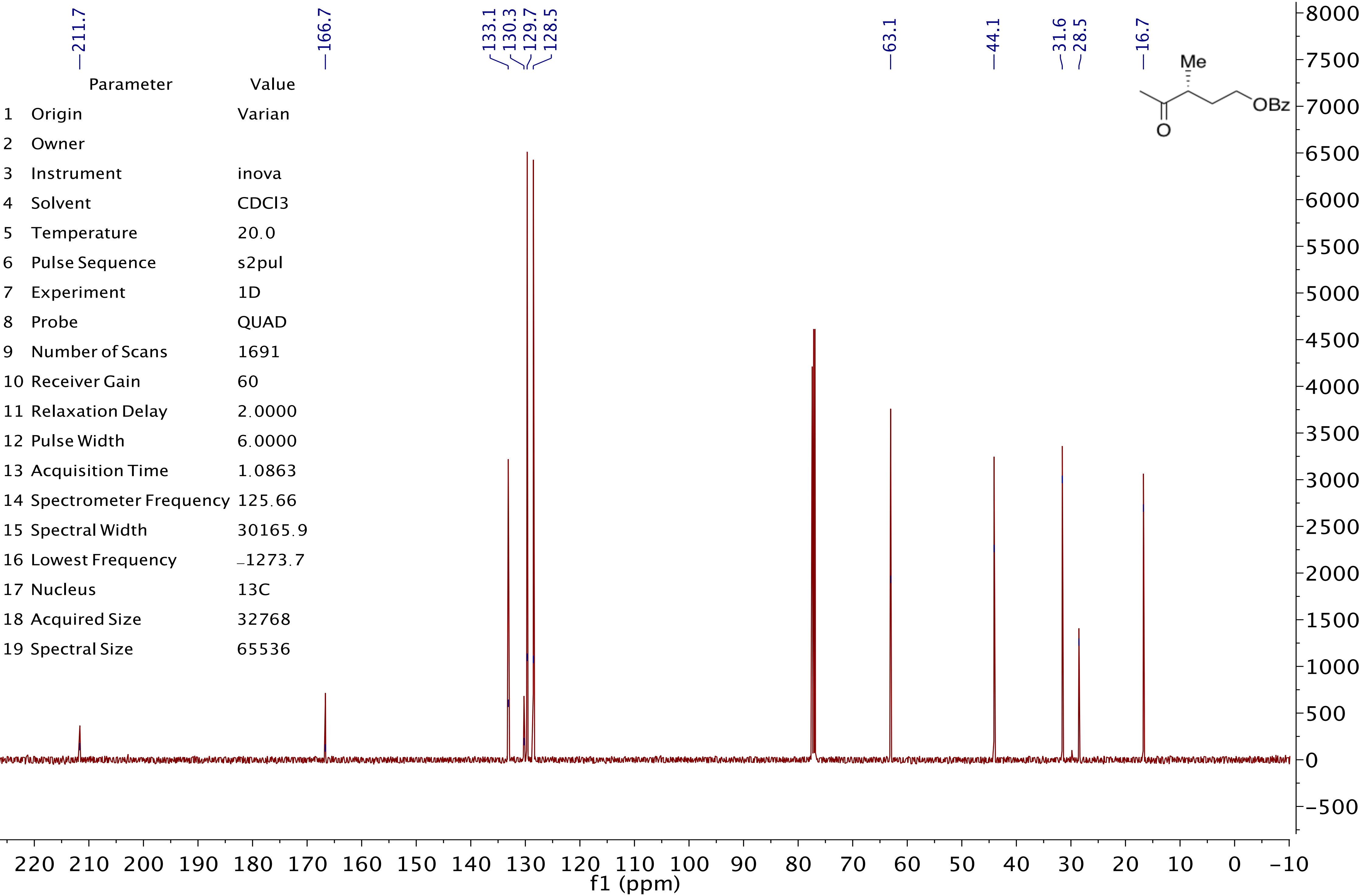




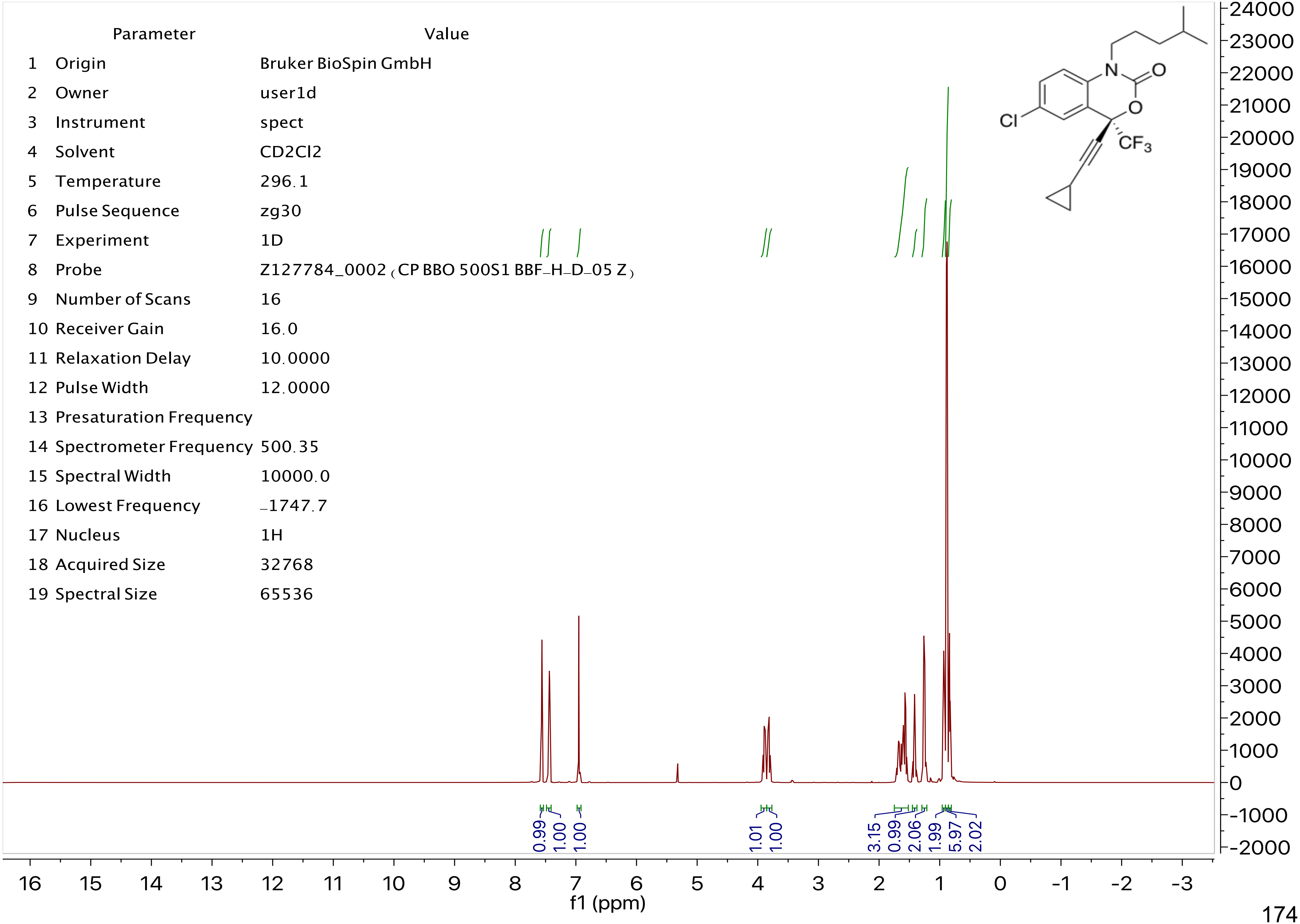
	Parameter	Value
1	Origin	Varian
2	Spectrometer	inova
3	Solvent	CDCl3
4	Temperature	20.0
5	Pulse Sequence	s2pul
6	Experiment	1D
7	Probe	QUAD
8	Number of Scans	1024
9	Relaxation Delay	1.0000
10	Pulse Width	6.0000
11	Spectrometer Frequency	125.66
12	Spectral Width	30165.9
13	Lowest Frequency	–1273.4
14	Nucleus	13C
15	Acquired Size	32768
16	Spectral Size	65536

	Parameter	Value
1	Origin	Varian
2	Owner	
3	Instrument	inova
4	Solvent	CDCl3
5	Temperature	20.0
6	Pulse Sequence	s2pul
7	Experiment	1D
8	Probe	QUAD
9	Number of Scans	32
10	Receiver Gain	46
11	Relaxation Delay	15.0000
12	Pulse Width	6.5000
13	Acquisition Time	4.6645
14	Spectrometer Frequency	499.69
15	Spectral Width	7024.9
16	Lowest Frequency	-1021.5
17	Nucleus	1H
18	Acquired Size	32768
19	Spectral Size	65536

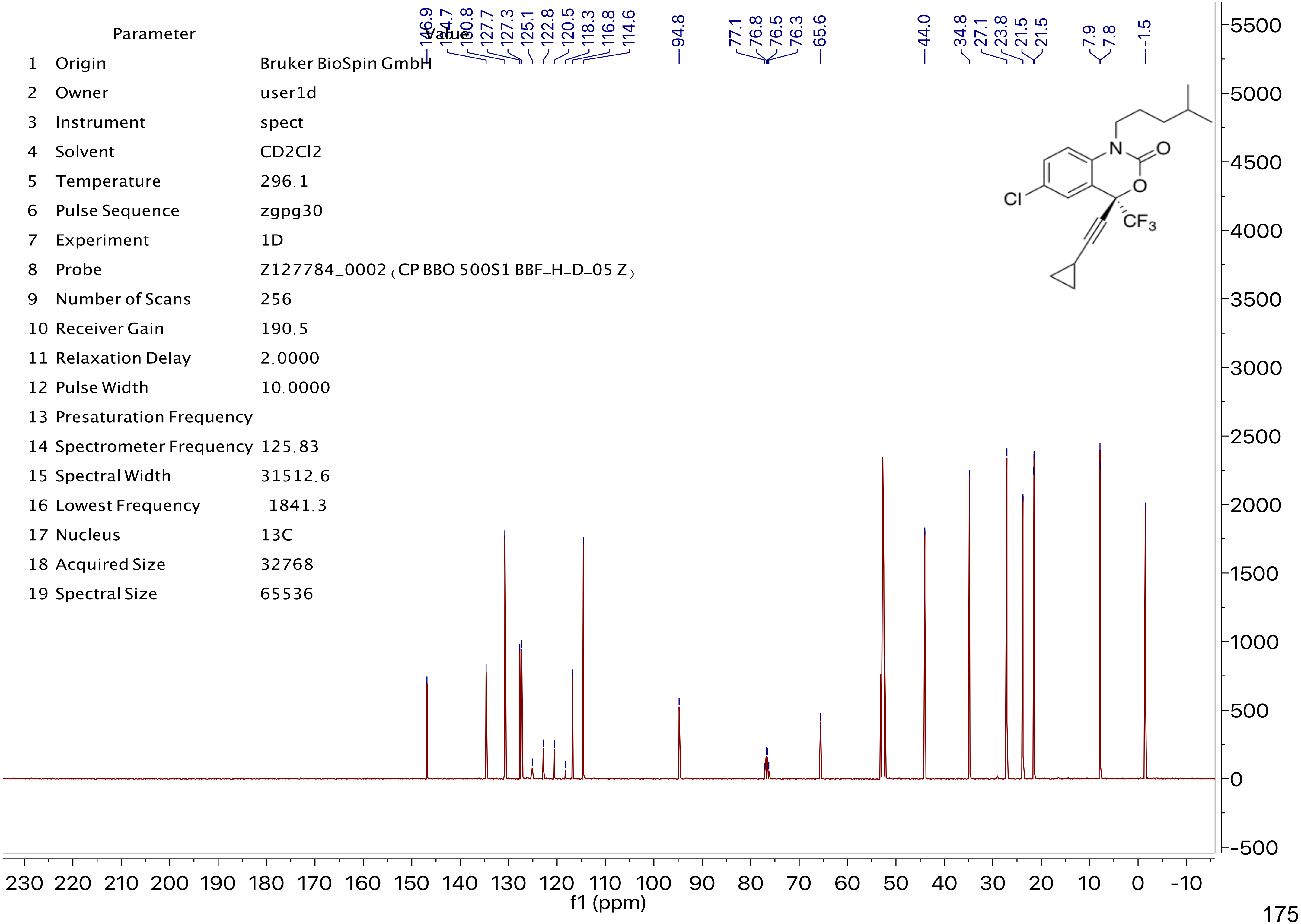




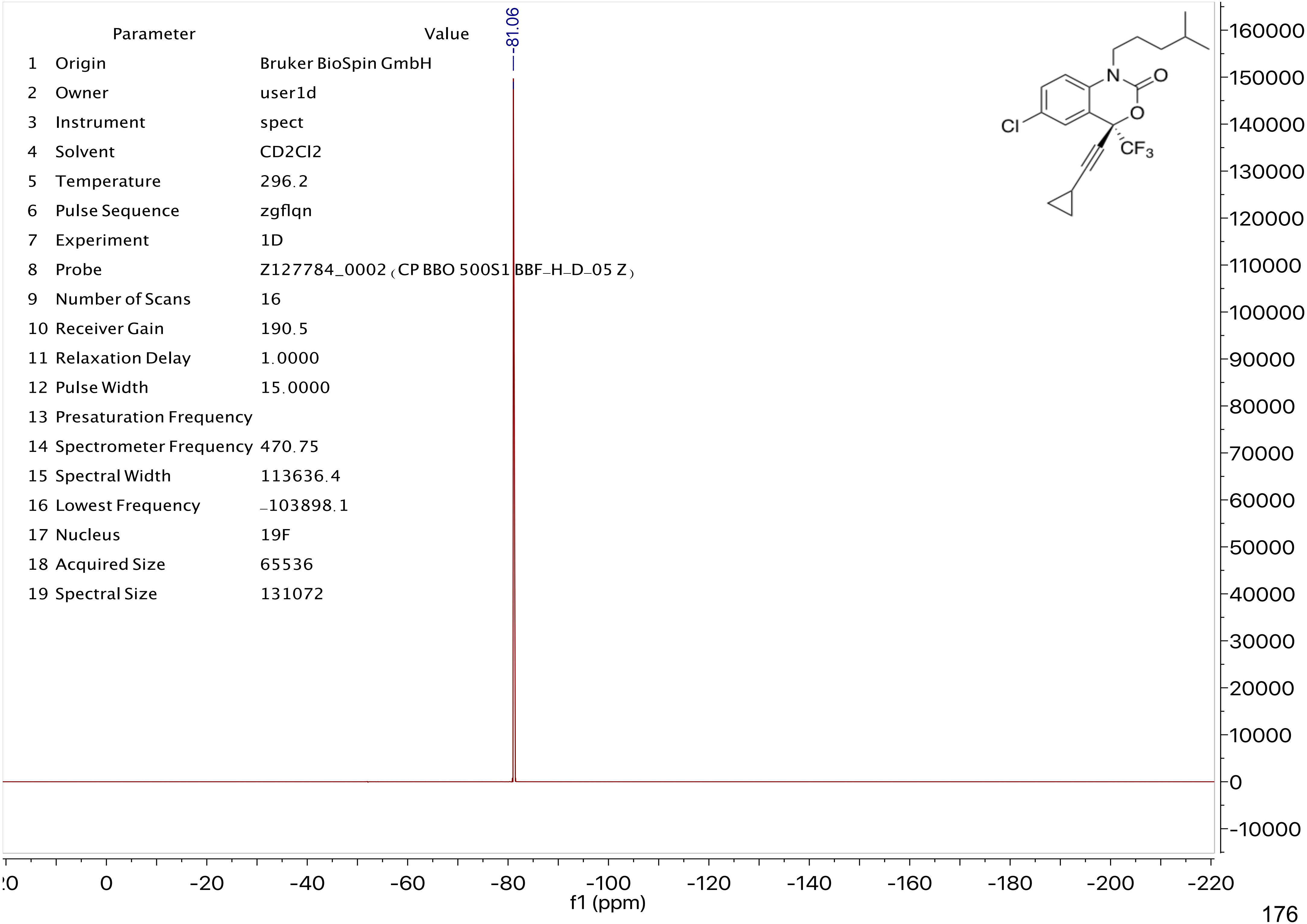
	Parameter	Value
1	Origin	Varian
2	Owner	
3	Instrument	inova
4	Solvent	CDCl3
5	Temperature	20.0
6	Pulse Sequence	s2pul
7	Experiment	1D
8	Probe	QUAD
9	Number of Scans	1691
10	Receiver Gain	60
11	Relaxation Delay	2.0000
12	Pulse Width	6.0000
13	Acquisition Time	1.0863
14	Spectrometer Frequency	125.66
15	Spectral Width	30165.9
16	Lowest Frequency	-1273.7
17	Nucleus	13C
18	Acquired Size	32768
19	Spectral Size	65536



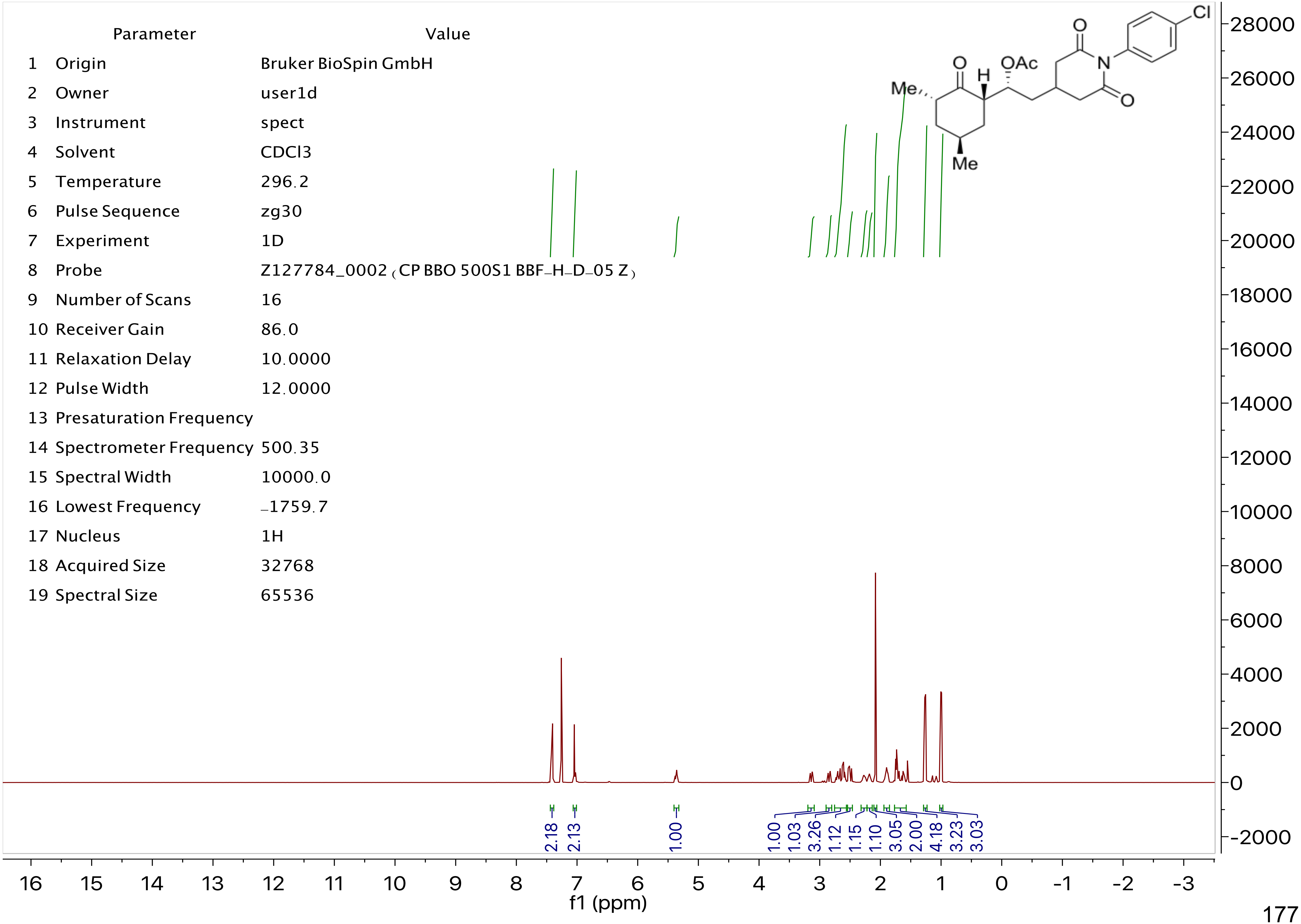
	Parameter	Value
1	Origin	Bruker BioSpin GmbH
2	Owner	user1d
3	Instrument	spect
4	Solvent	CD2Cl2
5	Temperature	296.1
6	Pulse Sequence	zg30
7	Experiment	1D
8	Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
9	Number of Scans	16
10	Receiver Gain	16.0
11	Relaxation Delay	10.0000
12	Pulse Width	12.0000
13	Presaturation Frequency	
14	Spectrometer Frequency	500.35
15	Spectral Width	10000.0
16	Lowest Frequency	-1747.7
17	Nucleus	1H
18	Acquired Size	32768
19	Spectral Size	65536



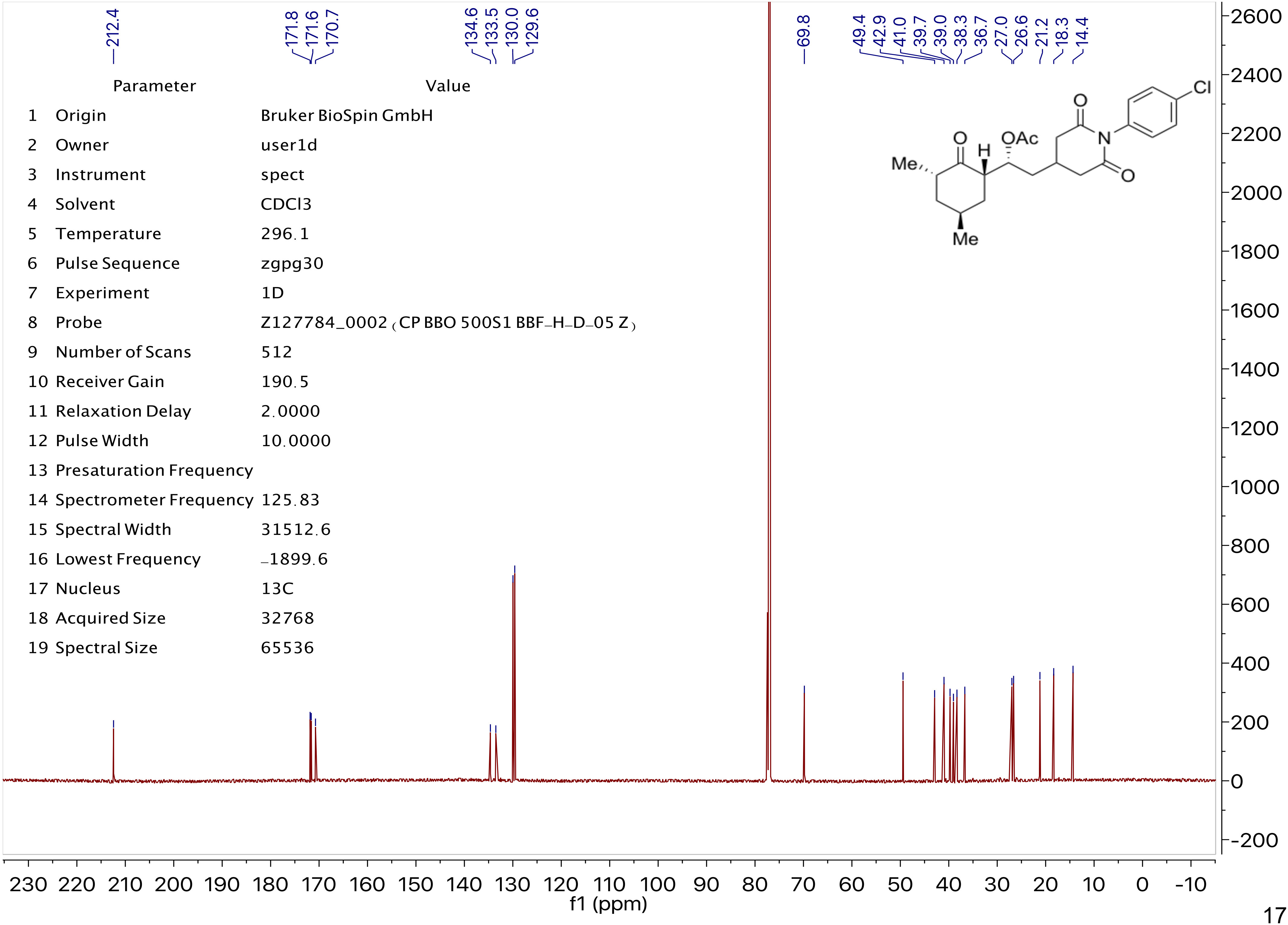
	Parameter	Value
1	Origin	Bruker BioSpin GmbH
2	Owner	user1d
3	Instrument	spect
4	Solvent	CD2Cl2
5	Temperature	296.1
6	Pulse Sequence	zgpg30
7	Experiment	1D
8	Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
9	Number of Scans	256
10	Receiver Gain	190.5
11	Relaxation Delay	2.0000
12	Pulse Width	10.0000
13	Presaturation Frequency	
14	Spectrometer Frequency	125.83
15	Spectral Width	31512.6
16	Lowest Frequency	-1841.3
17	Nucleus	13C
18	Acquired Size	32768
19	Spectral Size	65536



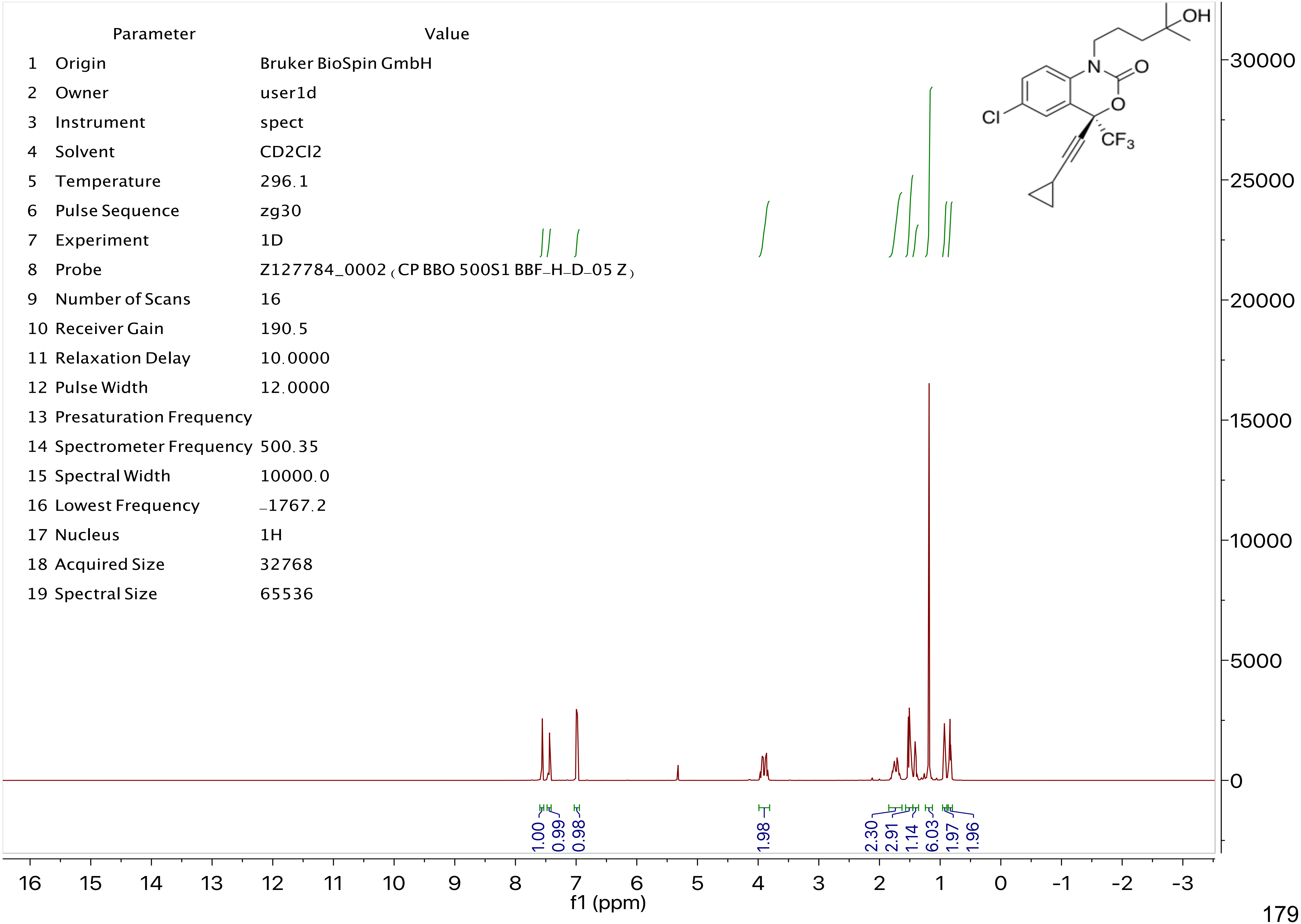
	Parameter	Value
1	Origin	Bruker BioSpin GmbH
2	Owner	user1d
3	Instrument	spect
4	Solvent	CD2Cl2
5	Temperature	296.2
6	Pulse Sequence	zgflqn
7	Experiment	1D
8	Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
9	Number of Scans	16
10	Receiver Gain	190.5
11	Relaxation Delay	1.0000
12	Pulse Width	15.0000
13	Presaturation Frequency	
14	Spectrometer Frequency	470.75
15	Spectral Width	113636.4
16	Lowest Frequency	-103898.1
17	Nucleus	19F
18	Acquired Size	65536
19	Spectral Size	131072



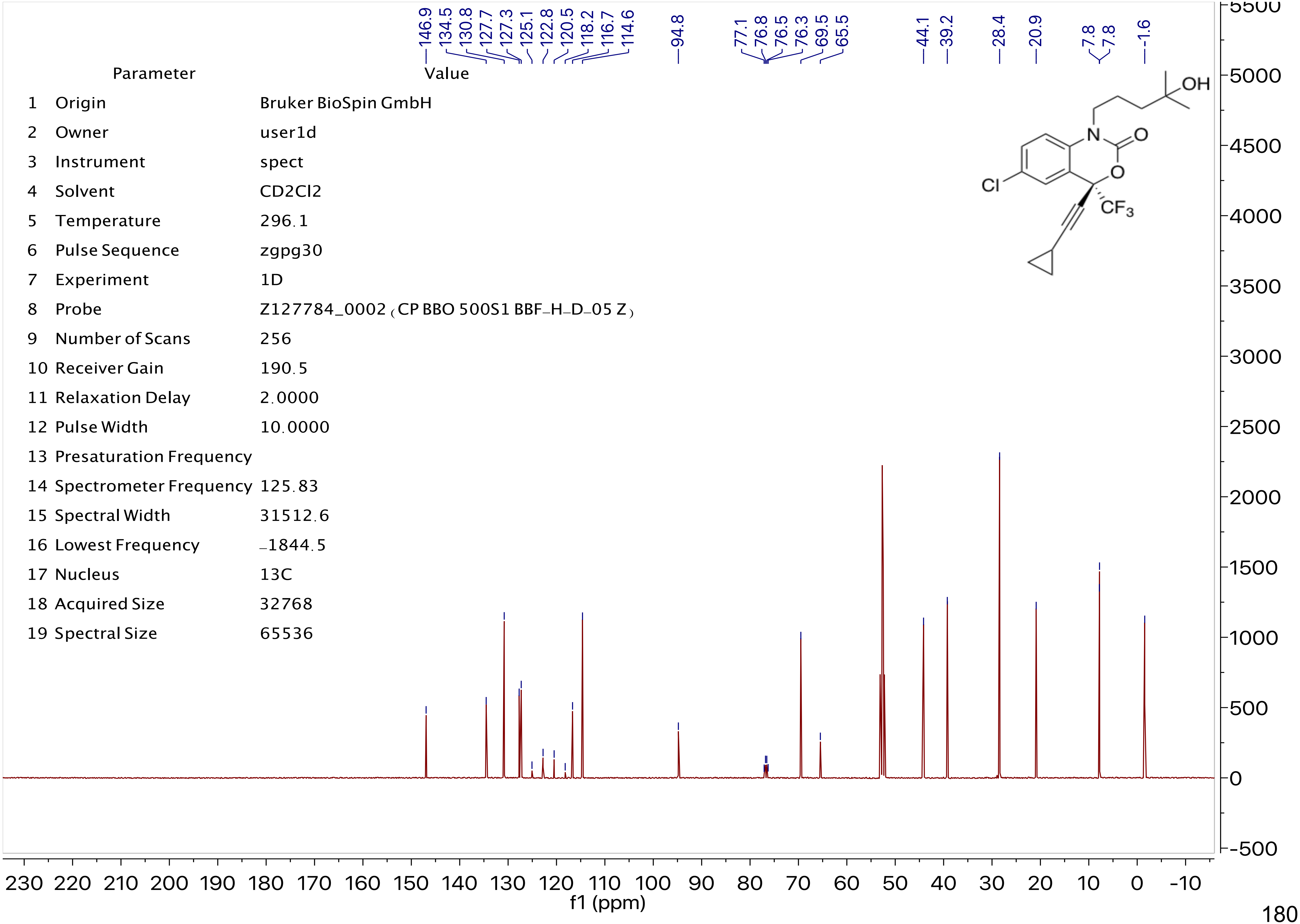
	Parameter	Value
1	Origin	Bruker BioSpin GmbH
2	Owner	user1d
3	Instrument	spect
4	Solvent	CDCl3
5	Temperature	296.2
6	Pulse Sequence	zg30
7	Experiment	1D
8	Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
9	Number of Scans	16
10	Receiver Gain	86.0
11	Relaxation Delay	10.0000
12	Pulse Width	12.0000
13	Presaturation Frequency	
14	Spectrometer Frequency	500.35
15	Spectral Width	10000.0
16	Lowest Frequency	-1759.7
17	Nucleus	1H
18	Acquired Size	32768
19	Spectral Size	65536



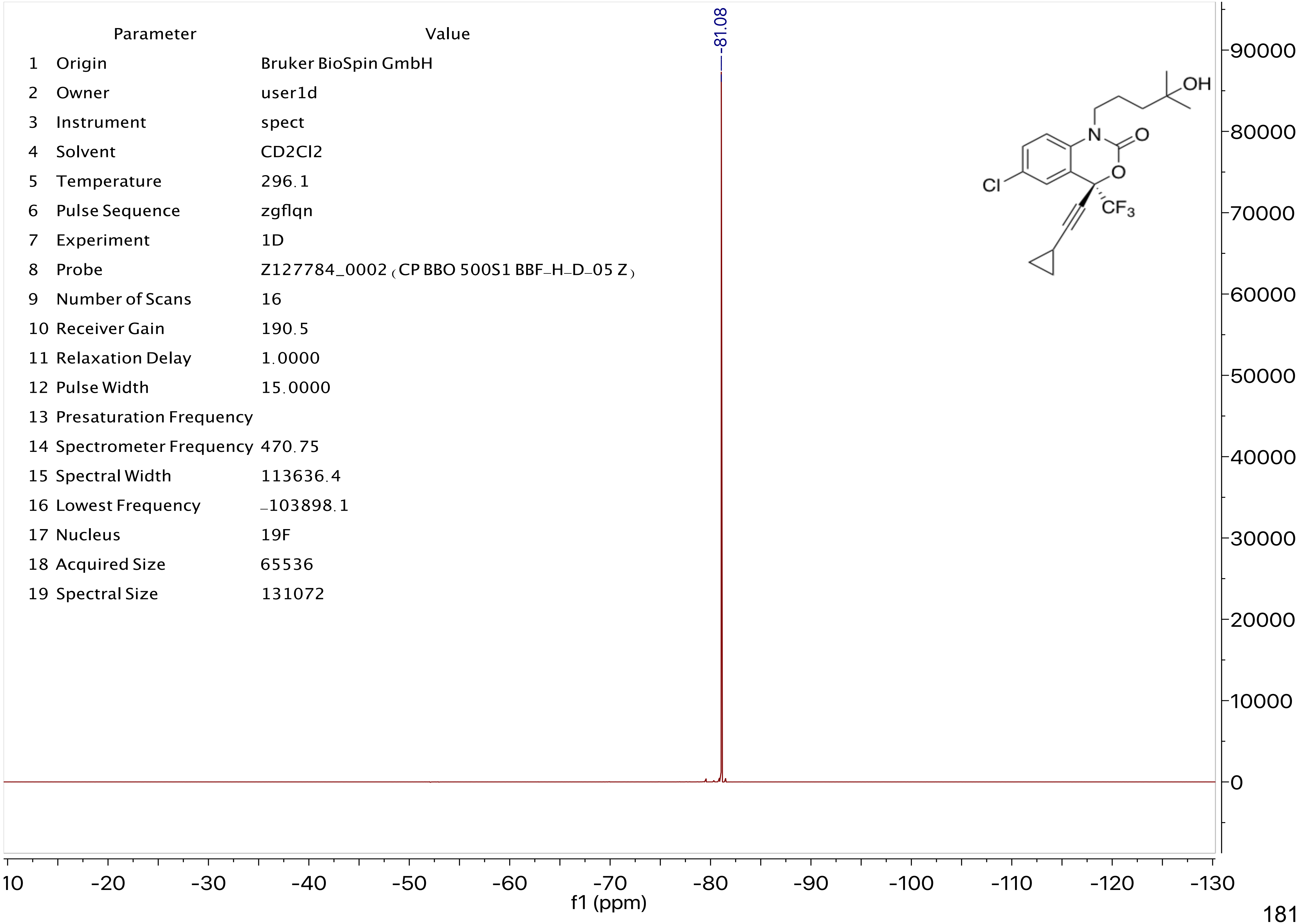
	Parameter	Value
1	Origin	Bruker BioSpin GmbH
2	Owner	user1d
3	Instrument	spect
4	Solvent	CDCl3
5	Temperature	296.1
6	Pulse Sequence	zgpg30
7	Experiment	1D
8	Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
9	Number of Scans	512
10	Receiver Gain	190.5
11	Relaxation Delay	2.0000
12	Pulse Width	10.0000
13	Presaturation Frequency	
14	Spectrometer Frequency	125.83
15	Spectral Width	31512.6
16	Lowest Frequency	-1899.6
17	Nucleus	13C
18	Acquired Size	32768
19	Spectral Size	65536



	Parameter	Value
1	Origin	Bruker BioSpin GmbH
2	Owner	user1d
3	Instrument	spect
4	Solvent	CD2Cl2
5	Temperature	296.1
6	Pulse Sequence	zg30
7	Experiment	1D
8	Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
9	Number of Scans	16
10	Receiver Gain	190.5
11	Relaxation Delay	10.0000
12	Pulse Width	12.0000
13	Presaturation Frequency	
14	Spectrometer Frequency	500.35
15	Spectral Width	10000.0
16	Lowest Frequency	-1767.2
17	Nucleus	1H
18	Acquired Size	32768
19	Spectral Size	65536

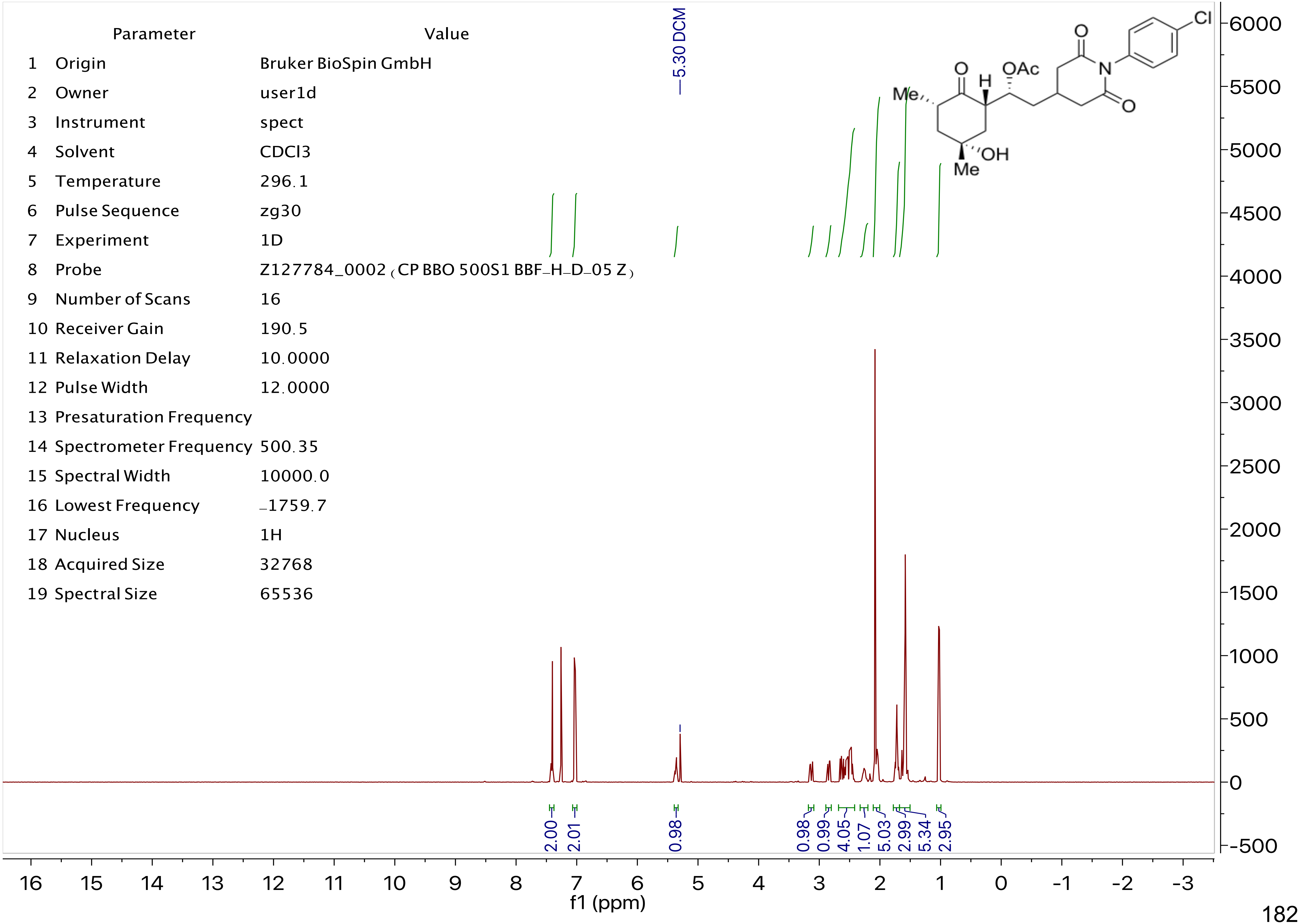


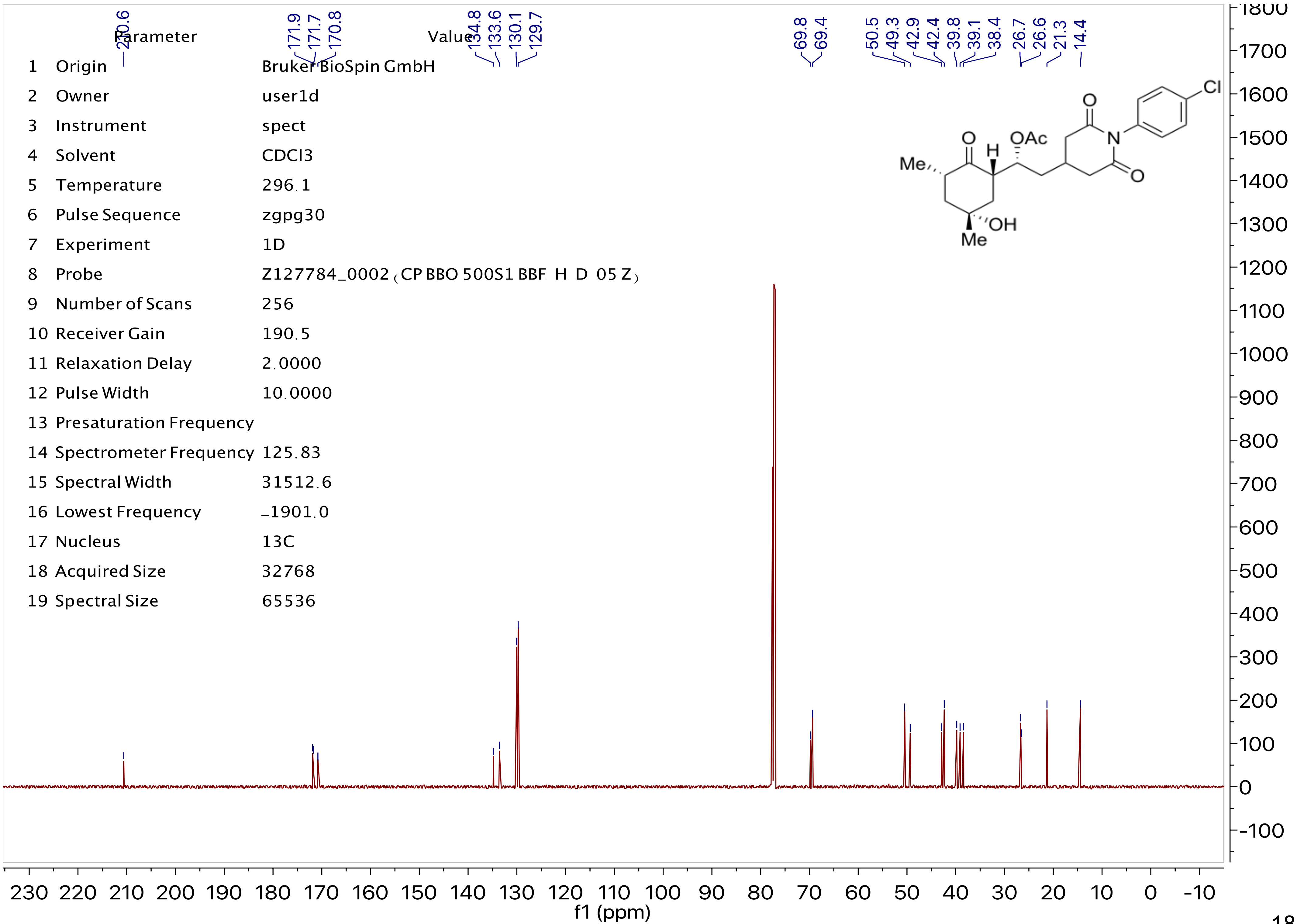
	Parameter	Value
1	Origin	Bruker BioSpin GmbH
2	Owner	user1d
3	Instrument	spect
4	Solvent	CD2Cl2
5	Temperature	296.1
6	Pulse Sequence	zgpg30
7	Experiment	1D
8	Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
9	Number of Scans	256
10	Receiver Gain	190.5
11	Relaxation Delay	2.0000
12	Pulse Width	10.0000
13	Presaturation Frequency	
14	Spectrometer Frequency	125.83
15	Spectral Width	31512.6
16	Lowest Frequency	-1844.5
17	Nucleus	13C
18	Acquired Size	32768
19	Spectral Size	65536



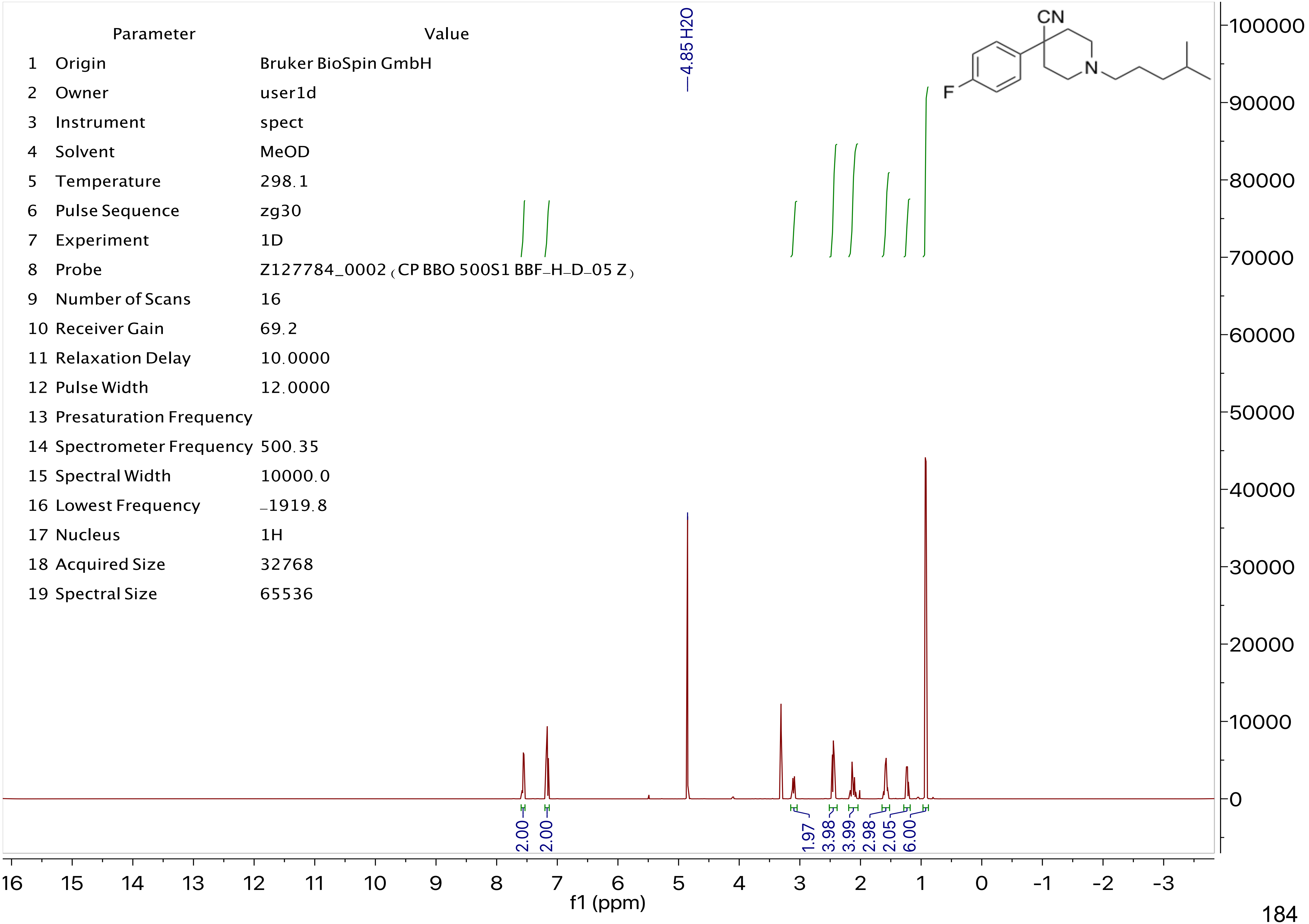
	Parameter	Value
1	Origin	Bruker BioSpin GmbH
2	Owner	user1d
3	Instrument	spect
4	Solvent	CD2Cl2
5	Temperature	296.1
6	Pulse Sequence	zgflqn
7	Experiment	1D
8	Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
9	Number of Scans	16
10	Receiver Gain	190.5
11	Relaxation Delay	1.0000
12	Pulse Width	15.0000
13	Presaturation Frequency	
14	Spectrometer Frequency	470.75
15	Spectral Width	113636.4
16	Lowest Frequency	-103898.1
17	Nucleus	19F
18	Acquired Size	65536
19	Spectral Size	131072

	Parameter	Value
1	Origin	Bruker BioSpin GmbH
2	Owner	user1d
3	Instrument	spect
4	Solvent	CDCl3
5	Temperature	296.1
6	Pulse Sequence	zg30
7	Experiment	1D
8	Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
9	Number of Scans	16
10	Receiver Gain	190.5
11	Relaxation Delay	10.0000
12	Pulse Width	12.0000
13	Presaturation Frequency	
14	Spectrometer Frequency	500.35
15	Spectral Width	10000.0
16	Lowest Frequency	-1759.7
17	Nucleus	1H
18	Acquired Size	32768
19	Spectral Size	65536

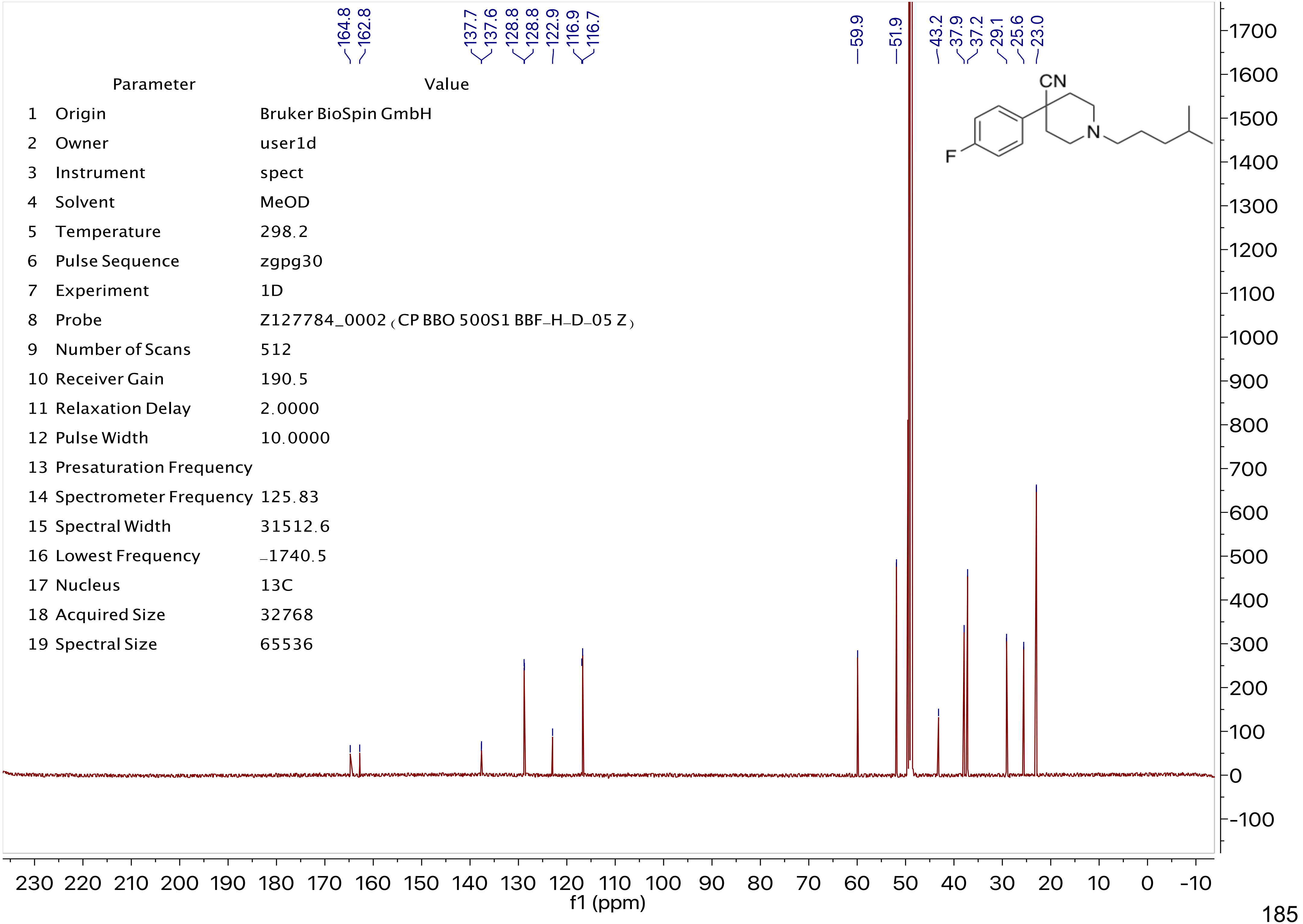




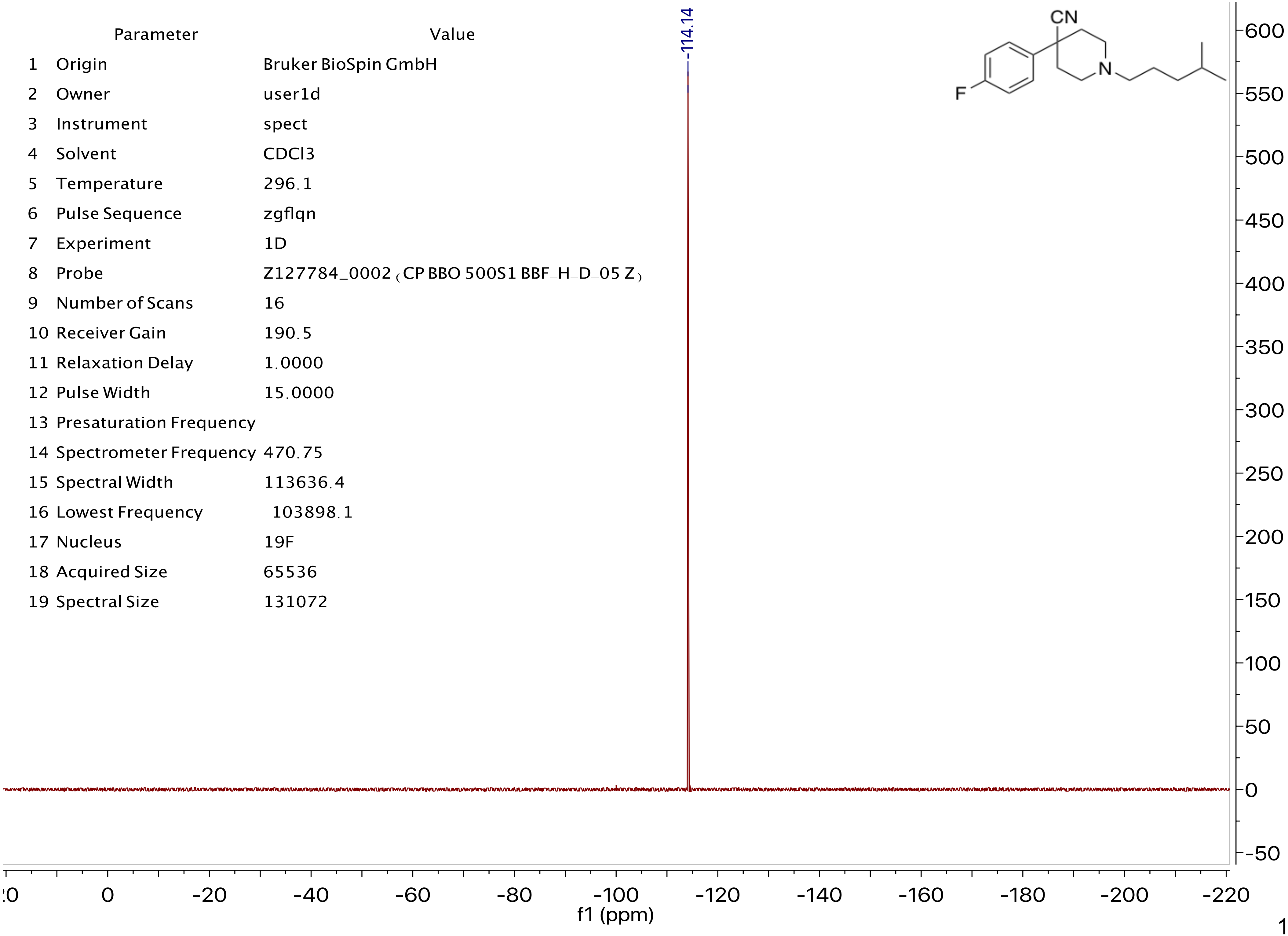
	Parameter	Value
1	Origin	Bruker BioSpin GmbH
2	Owner	user1d
3	Instrument	spect
4	Solvent	CDCl3
5	Temperature	296.1
6	Pulse Sequence	zgpg30
7	Experiment	1D
8	Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
9	Number of Scans	256
10	Receiver Gain	190.5
11	Relaxation Delay	2.0000
12	Pulse Width	10.0000
13	Presaturation Frequency	
14	Spectrometer Frequency	125.83
15	Spectral Width	31512.6
16	Lowest Frequency	-1901.0
17	Nucleus	13C
18	Acquired Size	32768
19	Spectral Size	65536



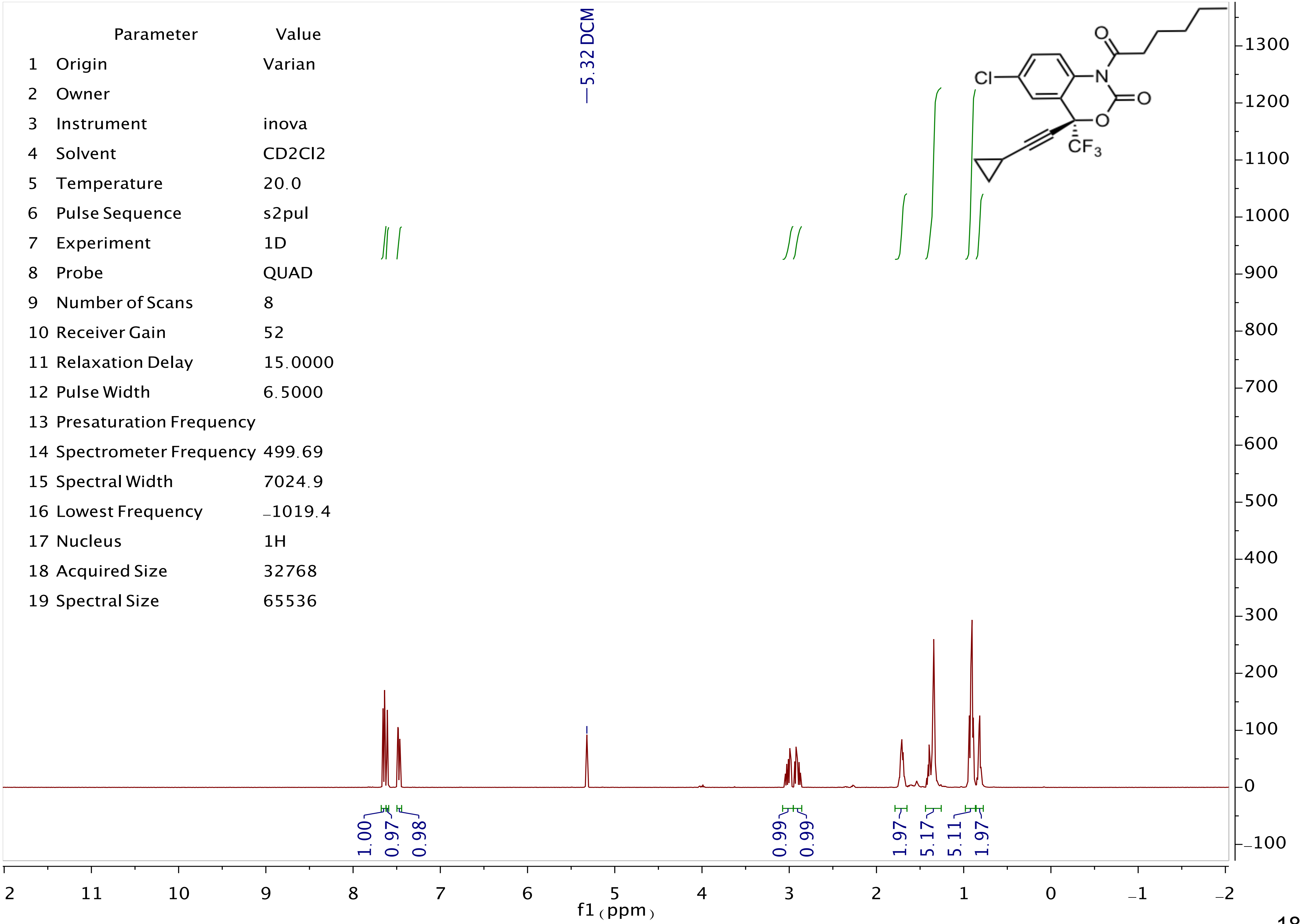
	Parameter	Value
1	Origin	Bruker BioSpin GmbH
2	Owner	user1d
3	Instrument	spect
4	Solvent	MeOD
5	Temperature	298.1
6	Pulse Sequence	zg30
7	Experiment	1D
8	Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
9	Number of Scans	16
10	Receiver Gain	69.2
11	Relaxation Delay	10.0000
12	Pulse Width	12.0000
13	Presaturation Frequency	
14	Spectrometer Frequency	500.35
15	Spectral Width	10000.0
16	Lowest Frequency	-1919.8
17	Nucleus	1H
18	Acquired Size	32768
19	Spectral Size	65536



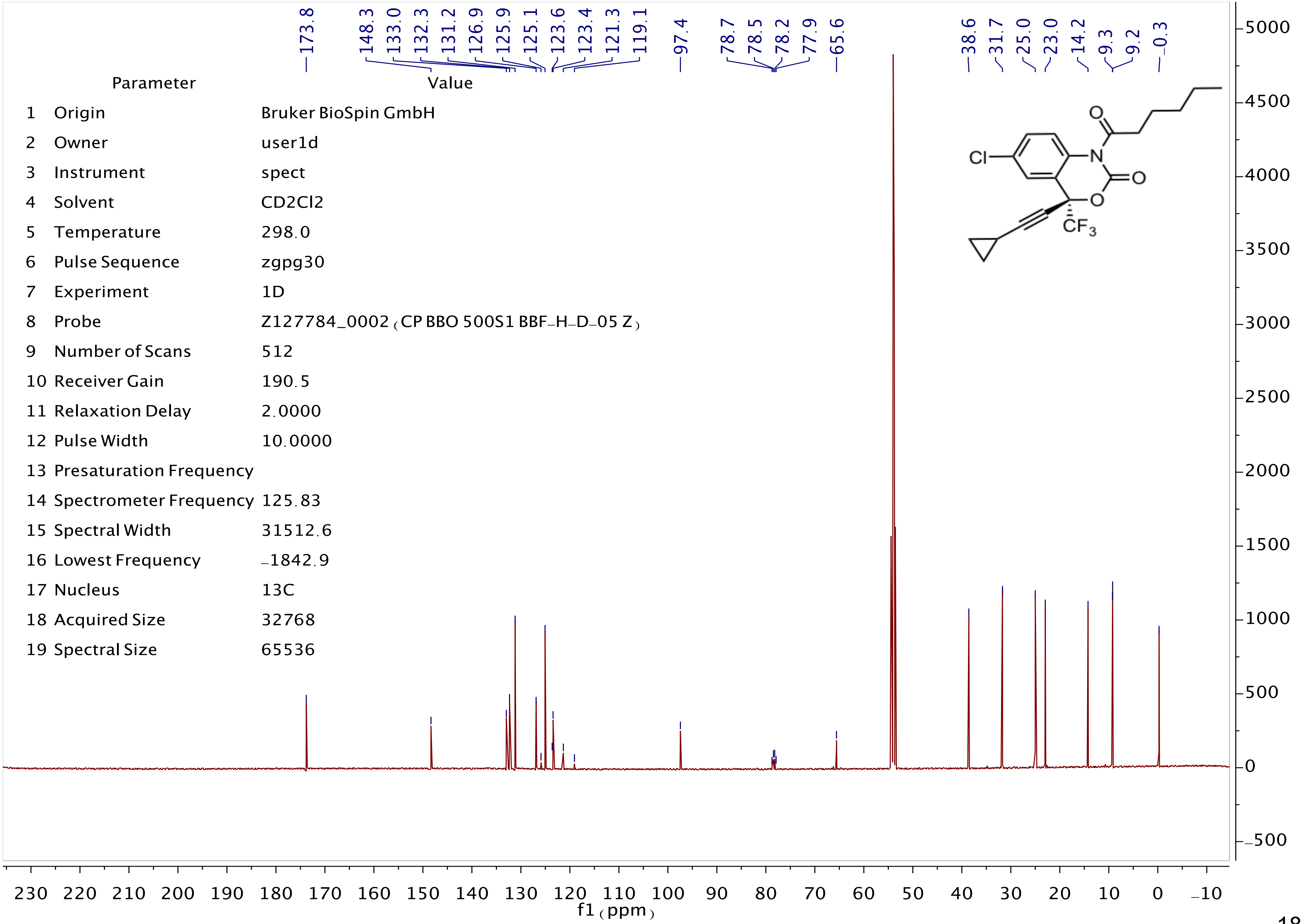
	Parameter	Value
1	Origin	Bruker BioSpin GmbH
2	Owner	user1d
3	Instrument	spect
4	Solvent	MeOD
5	Temperature	298.2
6	Pulse Sequence	zgpg30
7	Experiment	1D
8	Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
9	Number of Scans	512
10	Receiver Gain	190.5
11	Relaxation Delay	2.0000
12	Pulse Width	10.0000
13	Presaturation Frequency	
14	Spectrometer Frequency	125.83
15	Spectral Width	31512.6
16	Lowest Frequency	-1740.5
17	Nucleus	13C
18	Acquired Size	32768
19	Spectral Size	65536



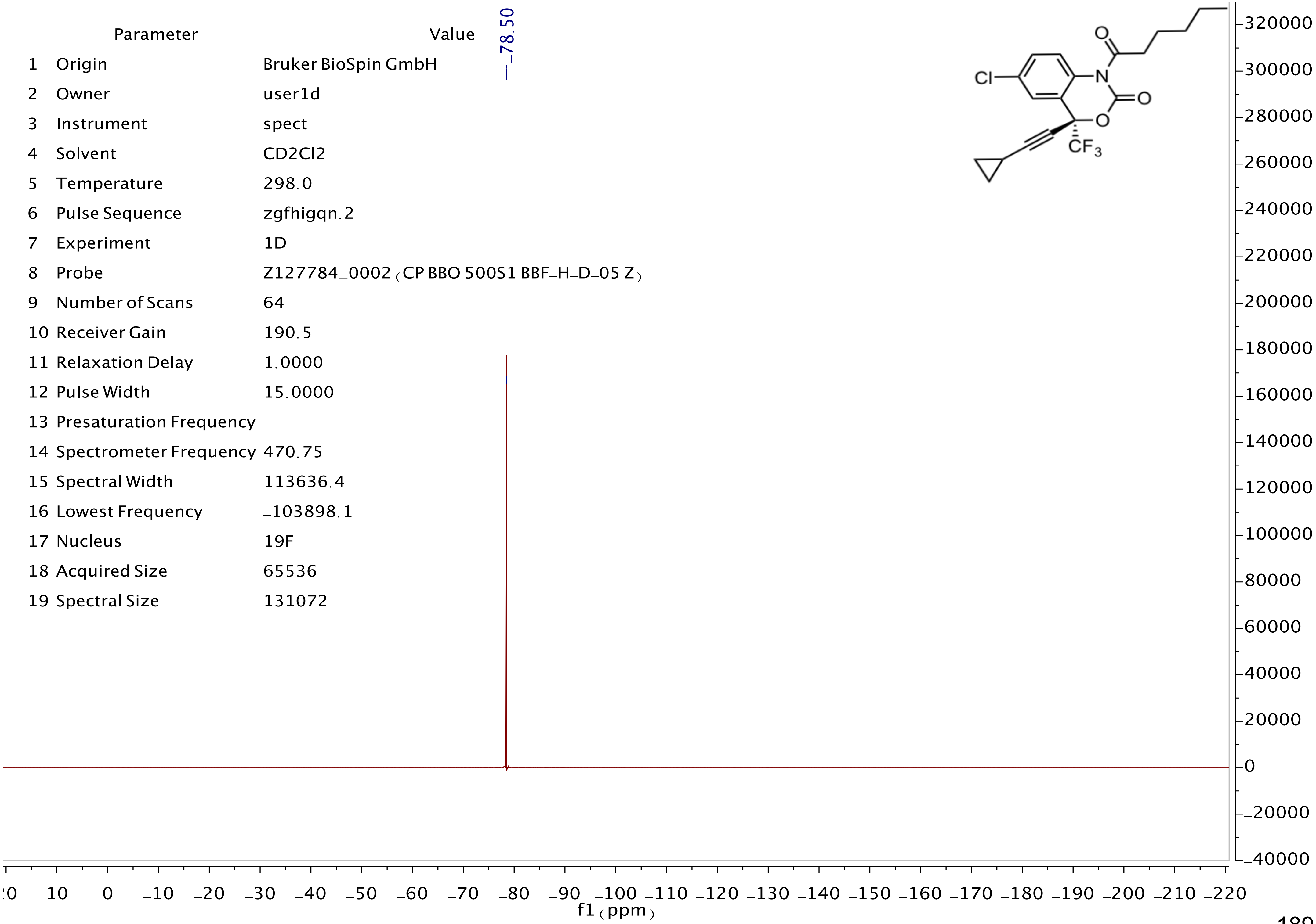
	Parameter	Value
1	Origin	Bruker BioSpin GmbH
2	Owner	user1d
3	Instrument	spect
4	Solvent	CDCl3
5	Temperature	296.1
6	Pulse Sequence	zgflqn
7	Experiment	1D
8	Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
9	Number of Scans	16
10	Receiver Gain	190.5
11	Relaxation Delay	1.0000
12	Pulse Width	15.0000
13	Presaturation Frequency	
14	Spectrometer Frequency	470.75
15	Spectral Width	113636.4
16	Lowest Frequency	-103898.1
17	Nucleus	19F
18	Acquired Size	65536
19	Spectral Size	131072



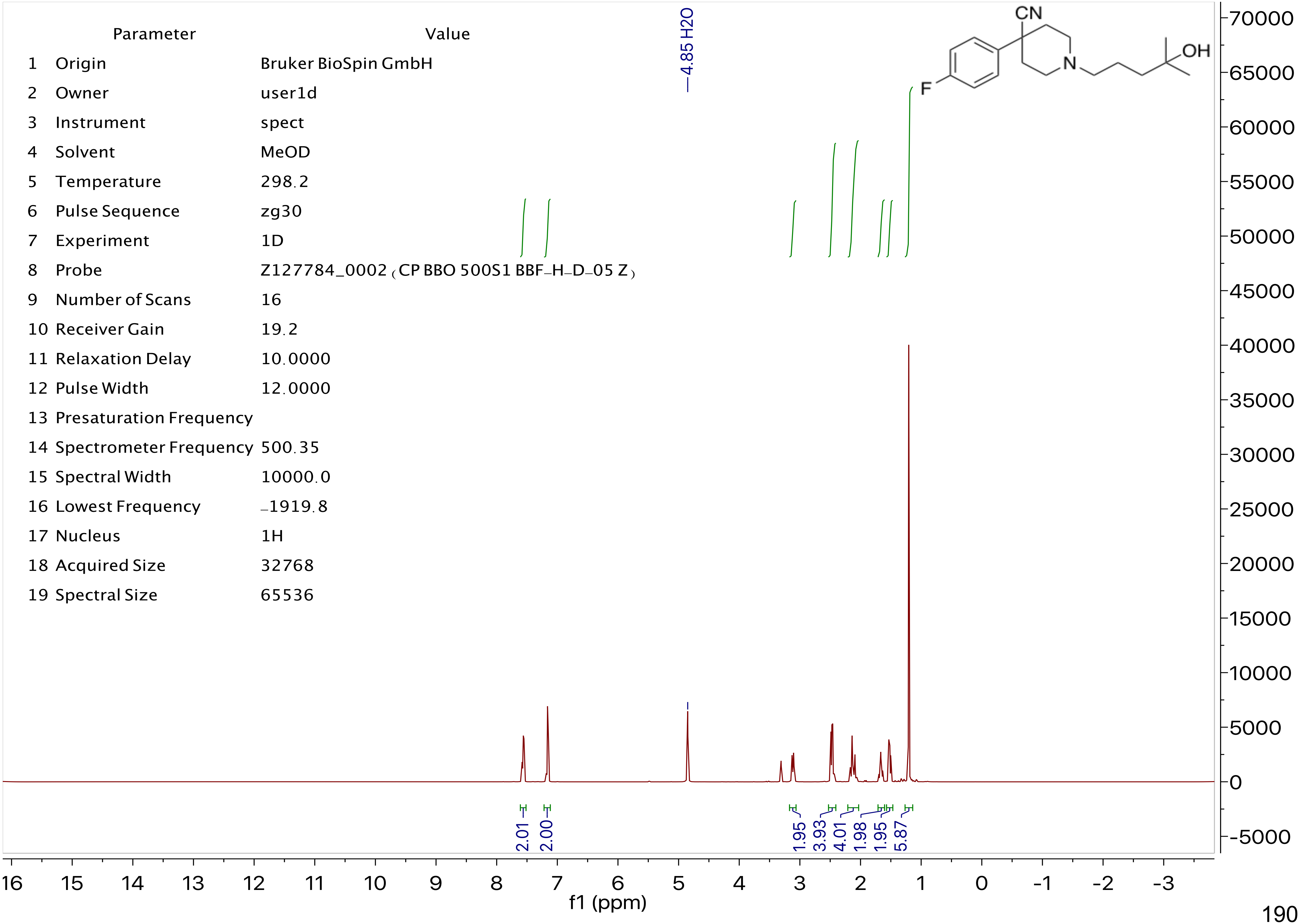
	Parameter	Value
1	Origin	Varian
2	Owner	
3	Instrument	inova
4	Solvent	CD2Cl2
5	Temperature	20.0
6	Pulse Sequence	s2pul
7	Experiment	1D
8	Probe	QUAD
9	Number of Scans	8
10	Receiver Gain	52
11	Relaxation Delay	15.0000
12	Pulse Width	6.5000
13	Presaturation Frequency	
14	Spectrometer Frequency	499.69
15	Spectral Width	7024.9
16	Lowest Frequency	-1019.4
17	Nucleus	1H
18	Acquired Size	32768
19	Spectral Size	65536



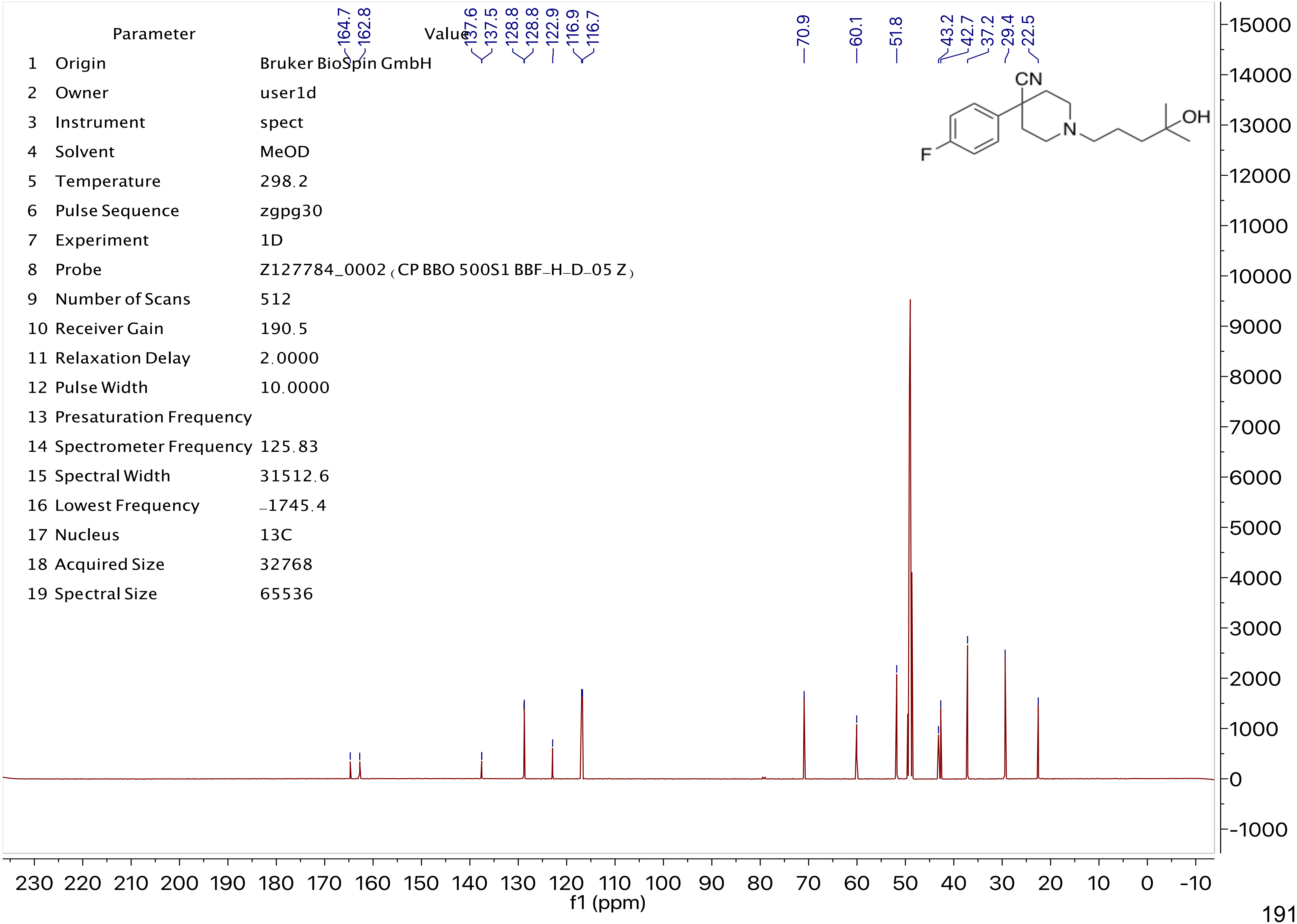
	Parameter	Value
1	Origin	Bruker BioSpin GmbH
2	Owner	user1d
3	Instrument	spect
4	Solvent	CD2Cl2
5	Temperature	298.0
6	Pulse Sequence	zgpg30
7	Experiment	1D
8	Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
9	Number of Scans	512
10	Receiver Gain	190.5
11	Relaxation Delay	2.0000
12	Pulse Width	10.0000
13	Presaturation Frequency	
14	Spectrometer Frequency	125.83
15	Spectral Width	31512.6
16	Lowest Frequency	-1842.9
17	Nucleus	13C
18	Acquired Size	32768
19	Spectral Size	65536



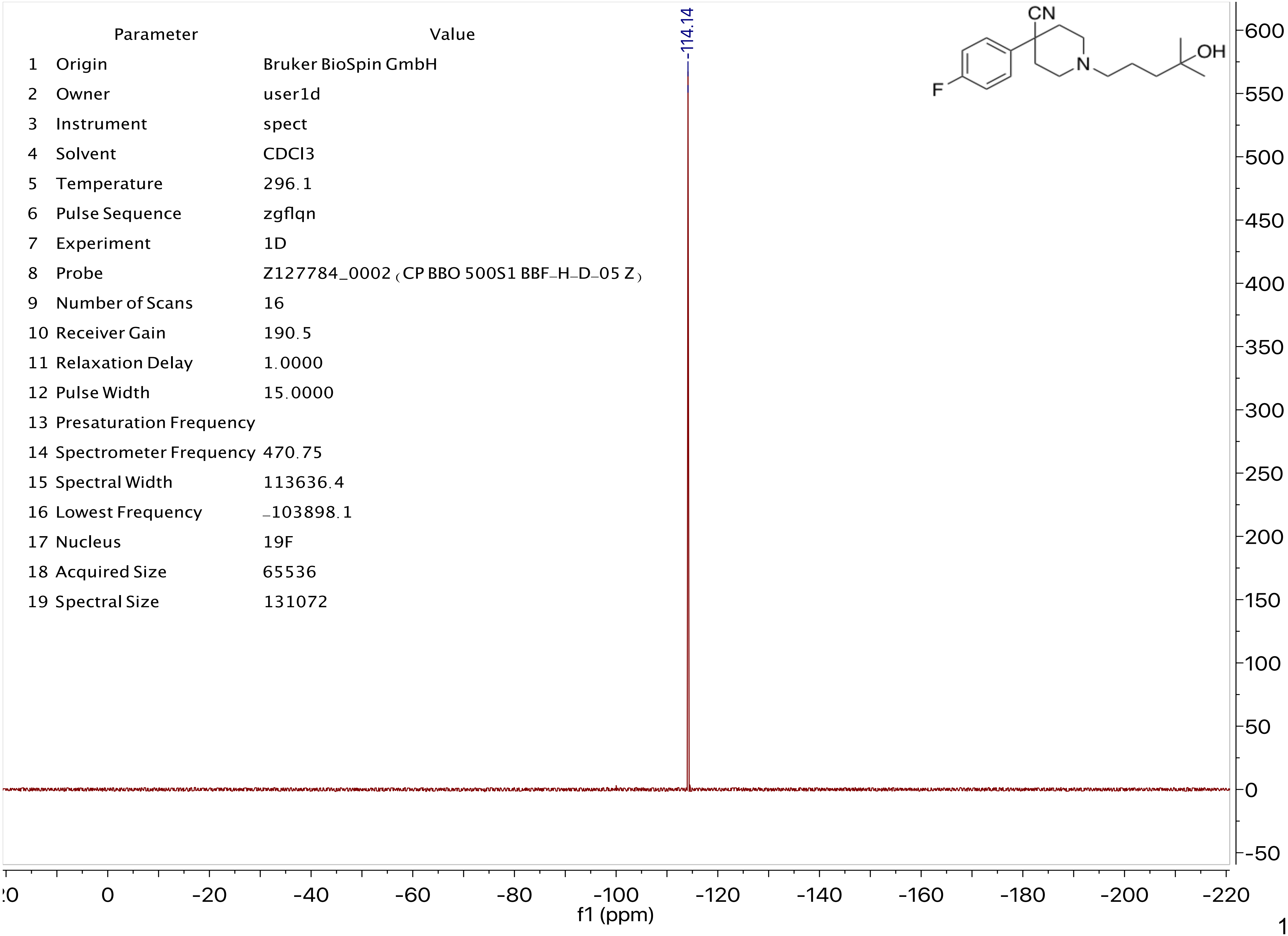
	Parameter	Value
1	Origin	Bruker BioSpin GmbH
2	Owner	user1d
3	Instrument	spect
4	Solvent	CD2Cl2
5	Temperature	298.0
6	Pulse Sequence	zgfhigqn.2
7	Experiment	1D
8	Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
9	Number of Scans	64
10	Receiver Gain	190.5
11	Relaxation Delay	1.0000
12	Pulse Width	15.0000
13	Presaturation Frequency	
14	Spectrometer Frequency	470.75
15	Spectral Width	113636.4
16	Lowest Frequency	-103898.1
17	Nucleus	19F
18	Acquired Size	65536
19	Spectral Size	131072



	Parameter	Value
1	Origin	Bruker BioSpin GmbH
2	Owner	user1d
3	Instrument	spect
4	Solvent	MeOD
5	Temperature	298.2
6	Pulse Sequence	zg30
7	Experiment	1D
8	Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
9	Number of Scans	16
10	Receiver Gain	19.2
11	Relaxation Delay	10.0000
12	Pulse Width	12.0000
13	Presaturation Frequency	
14	Spectrometer Frequency	500.35
15	Spectral Width	10000.0
16	Lowest Frequency	-1919.8
17	Nucleus	1H
18	Acquired Size	32768
19	Spectral Size	65536

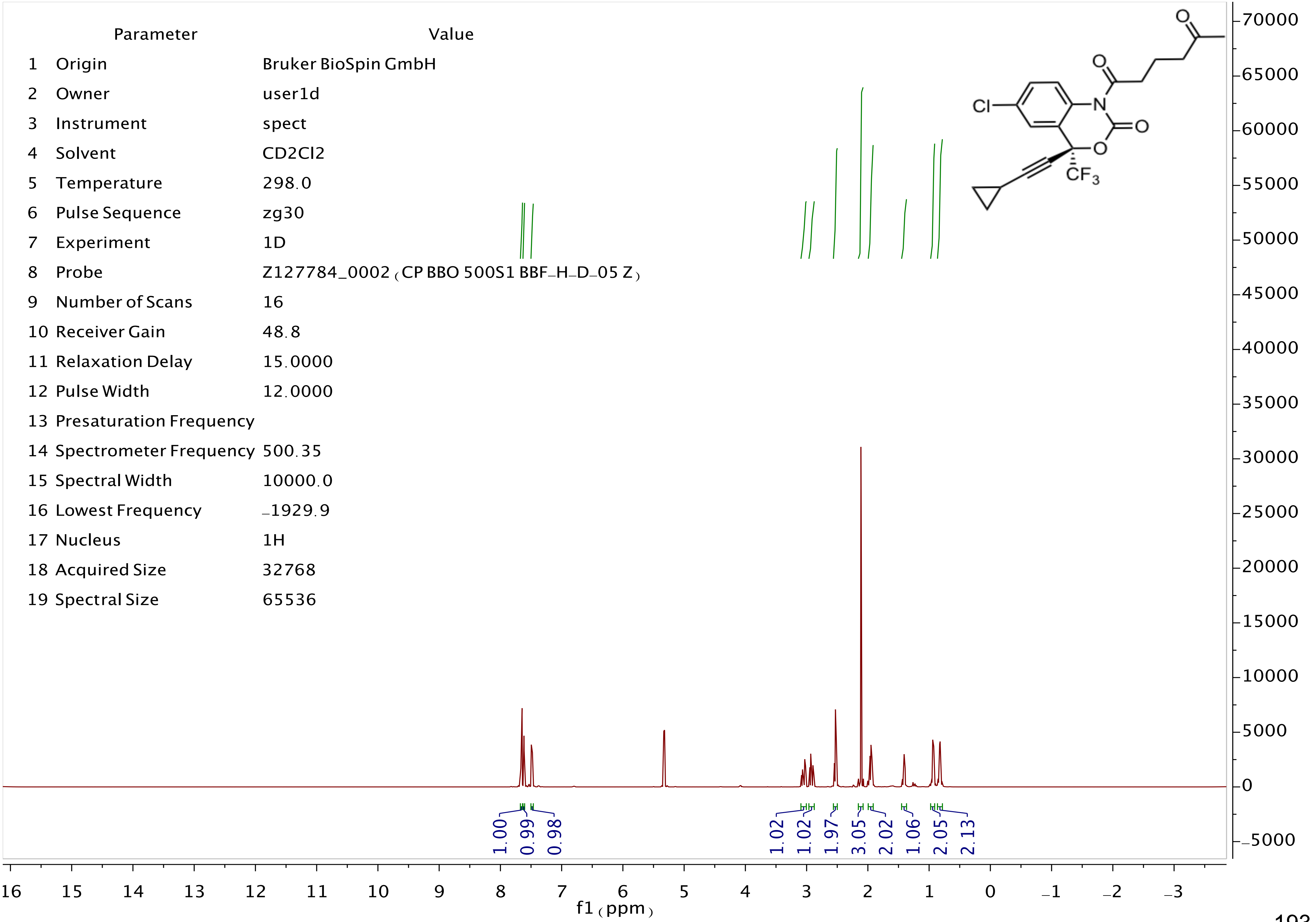


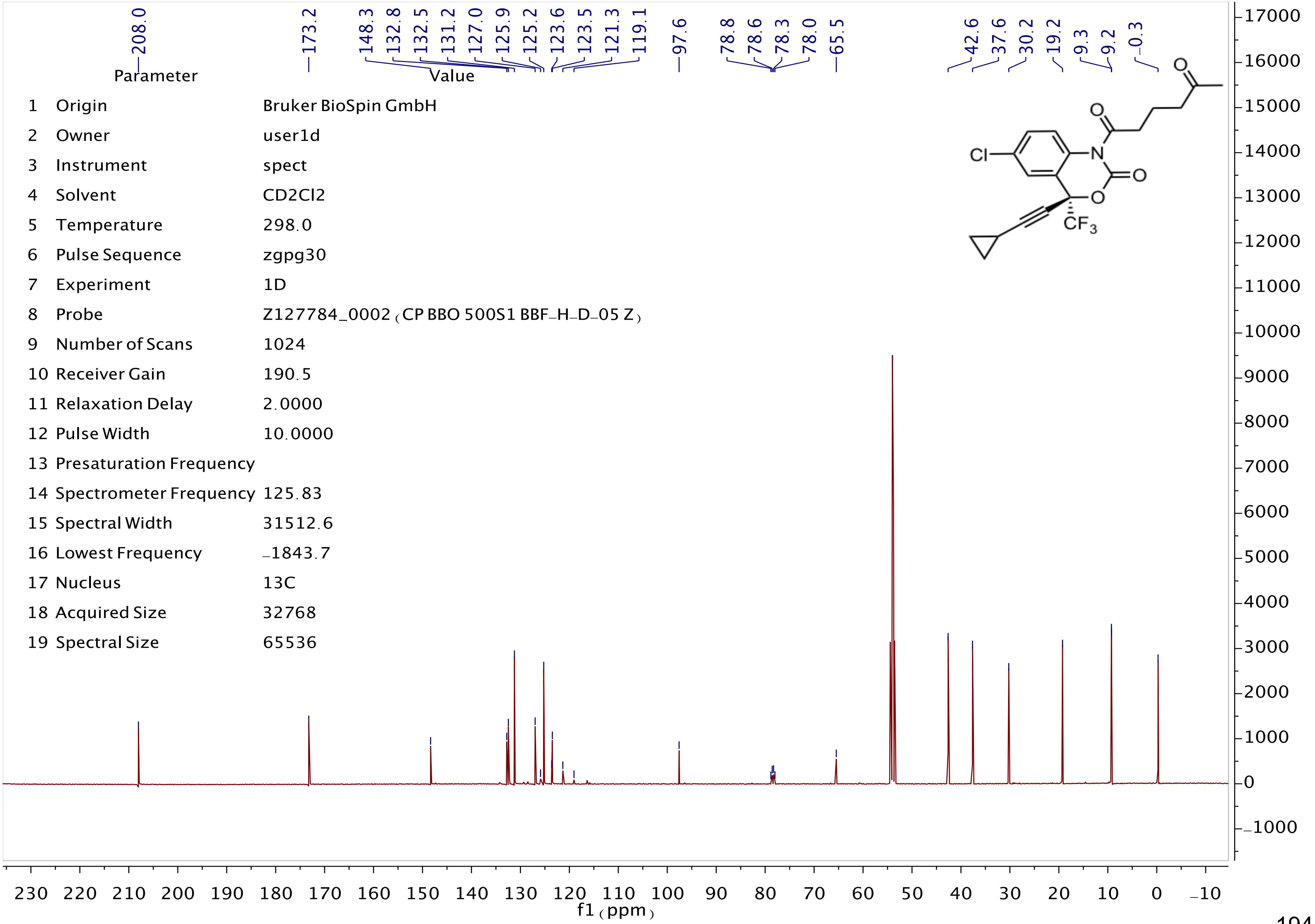
	Parameter	Value
1	Origin	Bruker BioSpin GmbH
2	Owner	user1d
3	Instrument	spect
4	Solvent	MeOD
5	Temperature	298.2
6	Pulse Sequence	zgpg30
7	Experiment	1D
8	Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
9	Number of Scans	512
10	Receiver Gain	190.5
11	Relaxation Delay	2.0000
12	Pulse Width	10.0000
13	Presaturation Frequency	
14	Spectrometer Frequency	125.83
15	Spectral Width	31512.6
16	Lowest Frequency	-1745.4
17	Nucleus	13C
18	Acquired Size	32768
19	Spectral Size	65536



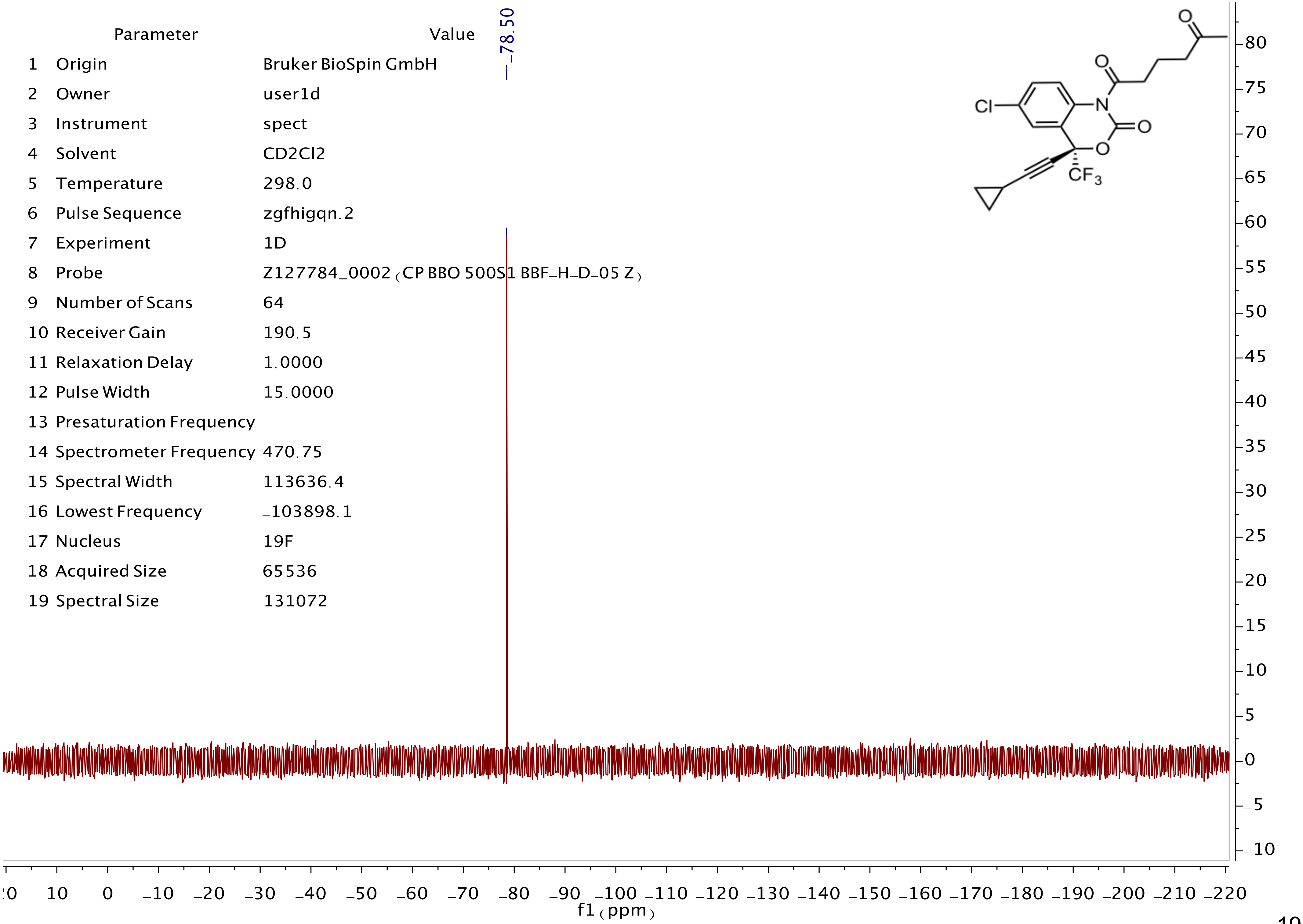
	Parameter	Value
1	Origin	Bruker BioSpin GmbH
2	Owner	user1d
3	Instrument	spect
4	Solvent	CDCl3
5	Temperature	296.1
6	Pulse Sequence	zgflqn
7	Experiment	1D
8	Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
9	Number of Scans	16
10	Receiver Gain	190.5
11	Relaxation Delay	1.0000
12	Pulse Width	15.0000
13	Presaturation Frequency	
14	Spectrometer Frequency	470.75
15	Spectral Width	113636.4
16	Lowest Frequency	-103898.1
17	Nucleus	19F
18	Acquired Size	65536
19	Spectral Size	131072

	Parameter	Value
1	Origin	Bruker BioSpin GmbH
2	Owner	user1d
3	Instrument	spect
4	Solvent	CD2Cl2
5	Temperature	298.0
6	Pulse Sequence	zg30
7	Experiment	1D
8	Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
9	Number of Scans	16
10	Receiver Gain	48.8
11	Relaxation Delay	15.0000
12	Pulse Width	12.0000
13	Presaturation Frequency	
14	Spectrometer Frequency	500.35
15	Spectral Width	10000.0
16	Lowest Frequency	-1929.9
17	Nucleus	1H
18	Acquired Size	32768
19	Spectral Size	65536

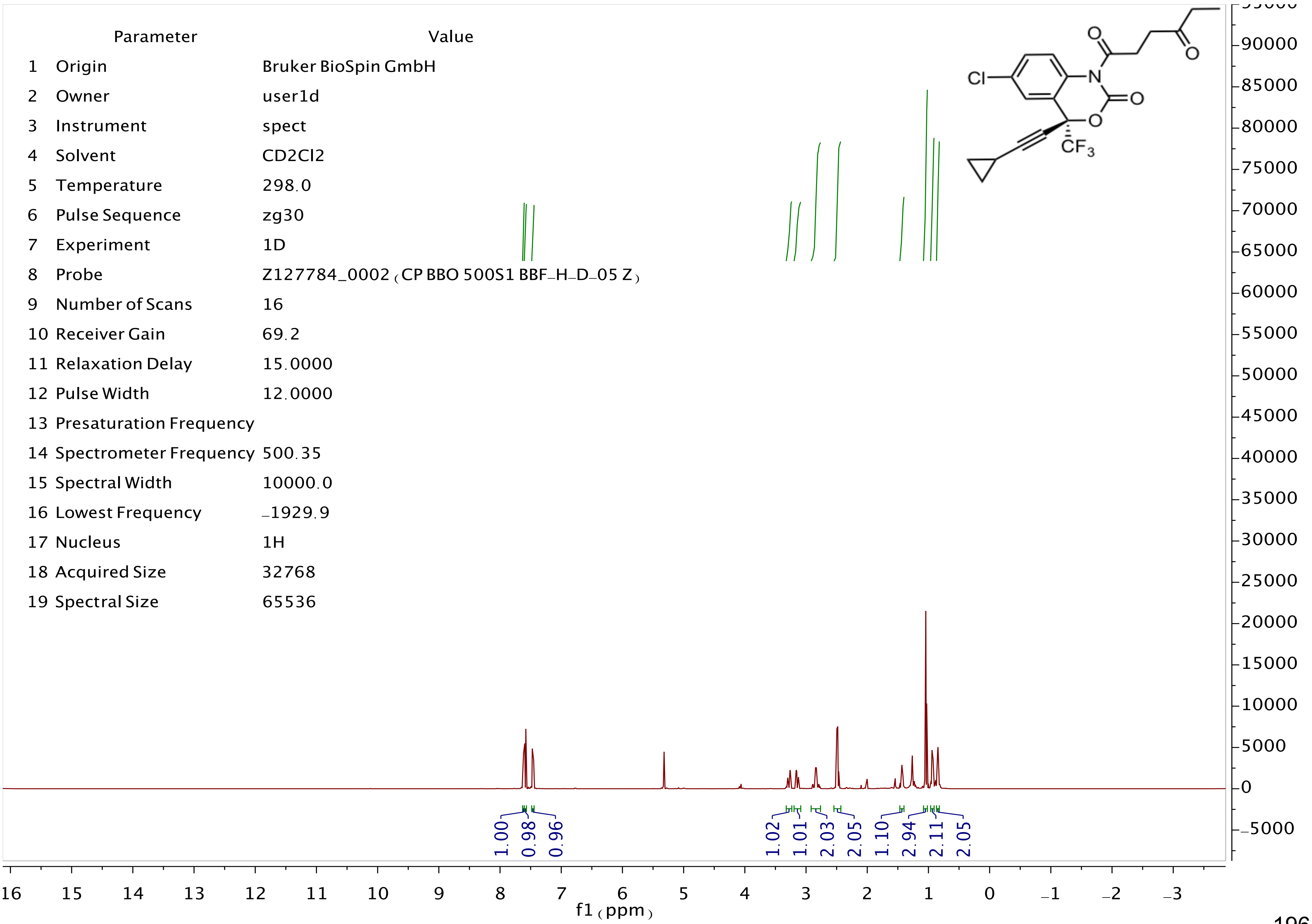




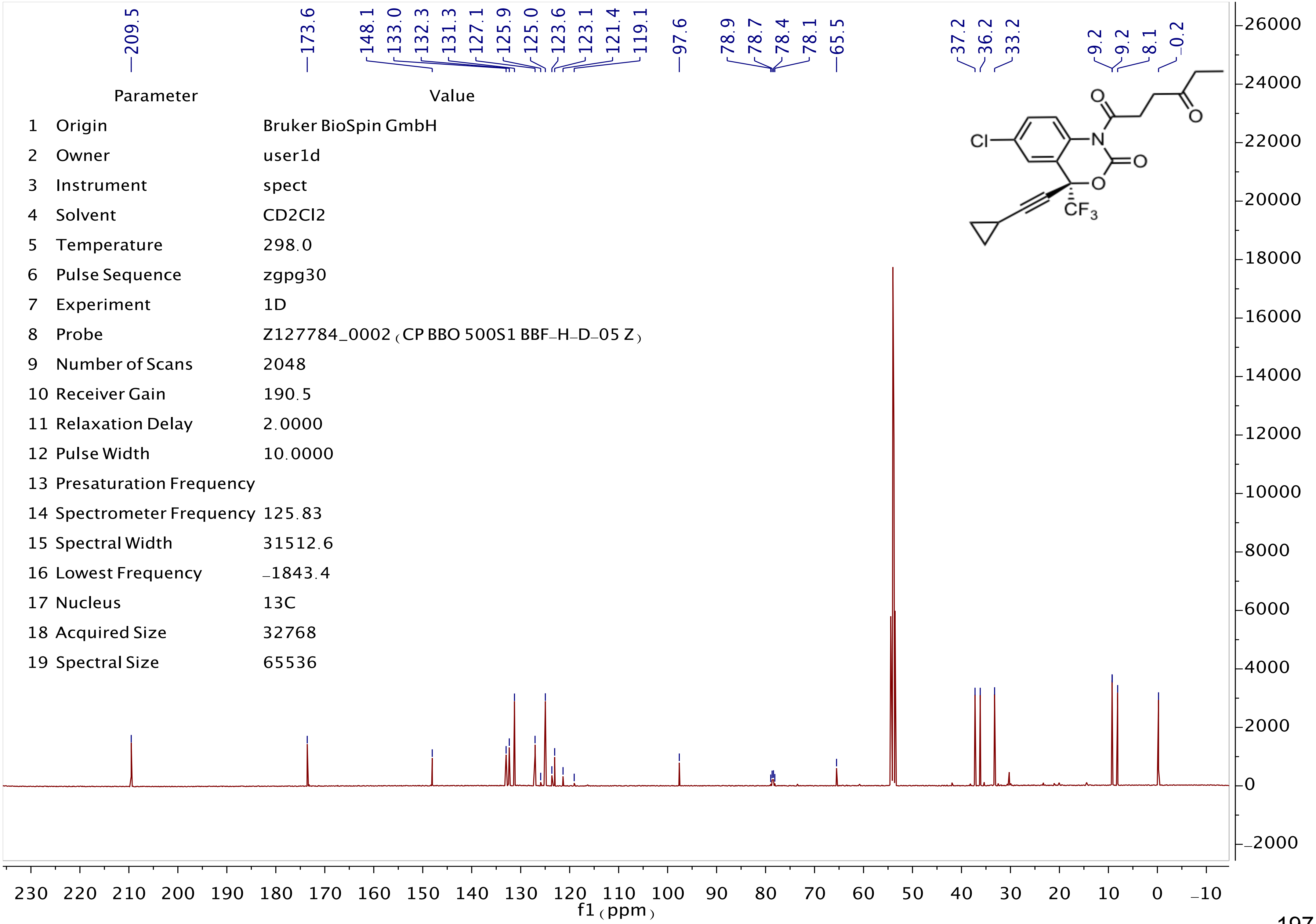
	Parameter	Value
1	Origin	Bruker BioSpin GmbH
2	Owner	user1d
3	Instrument	spect
4	Solvent	CD2Cl2
5	Temperature	298.0
6	Pulse Sequence	zgpg30
7	Experiment	1D
8	Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
9	Number of Scans	1024
10	Receiver Gain	190.5
11	Relaxation Delay	2.0000
12	Pulse Width	10.0000
13	Presaturation Frequency	
14	Spectrometer Frequency	125.83
15	Spectral Width	31512.6
16	Lowest Frequency	-1843.7
17	Nucleus	13C
18	Acquired Size	32768
19	Spectral Size	65536



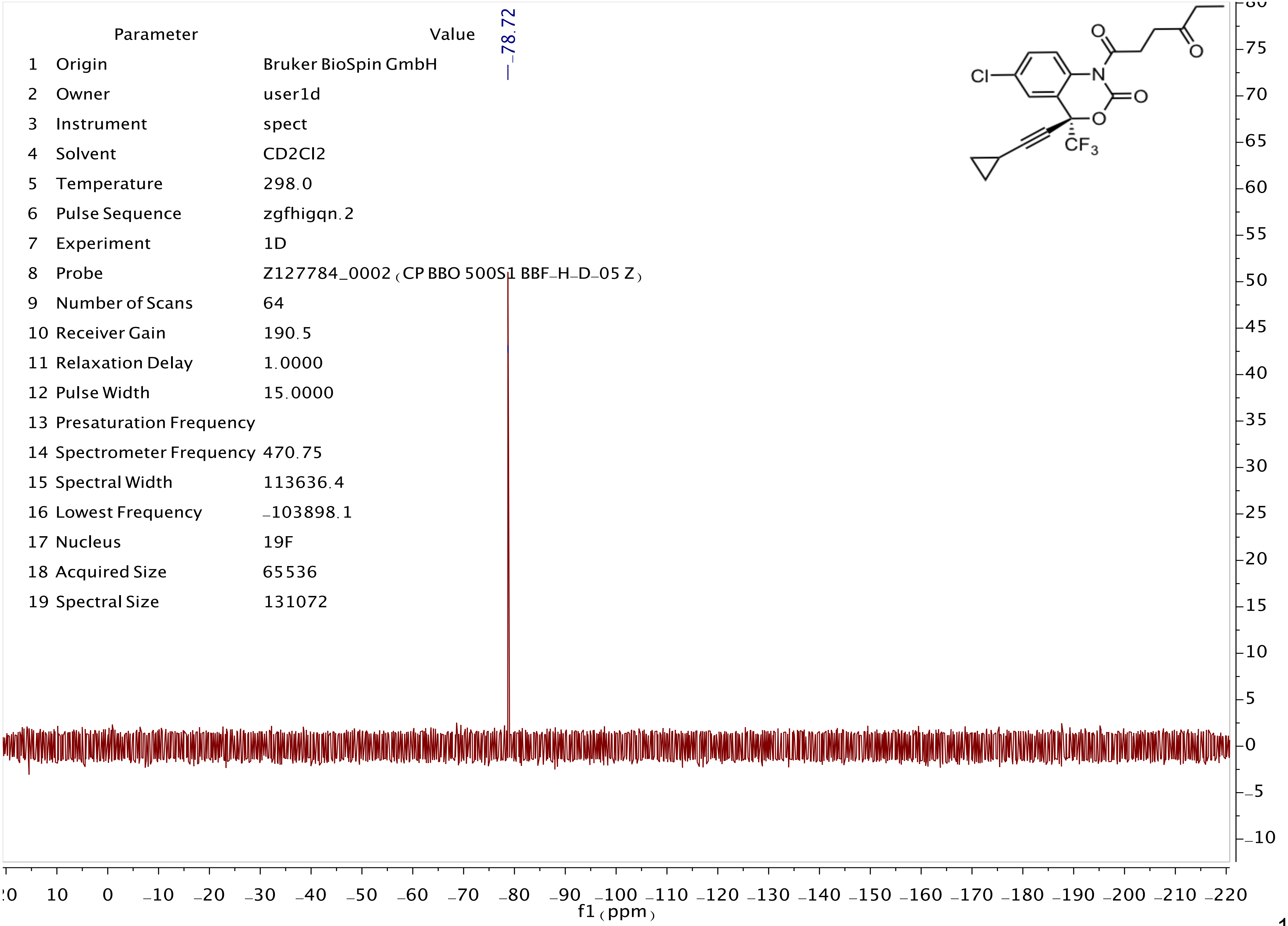
	Parameter	Value
1	Origin	Bruker BioSpin GmbH
2	Owner	user1d
3	Instrument	spect
4	Solvent	CD2Cl2
5	Temperature	298.0
6	Pulse Sequence	zgfhigqn.2
7	Experiment	1D
8	Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
9	Number of Scans	64
10	Receiver Gain	190.5
11	Relaxation Delay	1.0000
12	Pulse Width	15.0000
13	Presaturation Frequency	
14	Spectrometer Frequency	470.75
15	Spectral Width	113636.4
16	Lowest Frequency	-103898.1
17	Nucleus	19F
18	Acquired Size	65536
19	Spectral Size	131072



	Parameter	Value
1	Origin	Bruker BioSpin GmbH
2	Owner	user1d
3	Instrument	spect
4	Solvent	CD2Cl2
5	Temperature	298.0
6	Pulse Sequence	zg30
7	Experiment	1D
8	Probe	Z127784_0002 (CP BBO 500S1 BBF–H–D–05 Z)
9	Number of Scans	16
10	Receiver Gain	69.2
11	Relaxation Delay	15.0000
12	Pulse Width	12.0000
13	Presaturation Frequency	
14	Spectrometer Frequency	500.35
15	Spectral Width	10000.0
16	Lowest Frequency	–1929.9
17	Nucleus	1H
18	Acquired Size	32768
19	Spectral Size	65536



	Parameter	Value
1	Origin	Bruker BioSpin GmbH
2	Owner	user1d
3	Instrument	spect
4	Solvent	CD2Cl2
5	Temperature	298.0
6	Pulse Sequence	zgpg30
7	Experiment	1D
8	Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
9	Number of Scans	2048
10	Receiver Gain	190.5
11	Relaxation Delay	2.0000
12	Pulse Width	10.0000
13	Presaturation Frequency	
14	Spectrometer Frequency	125.83
15	Spectral Width	31512.6
16	Lowest Frequency	-1843.4
17	Nucleus	13C
18	Acquired Size	32768
19	Spectral Size	65536



	Parameter	Value
1	Origin	Bruker BioSpin GmbH
2	Owner	user1d
3	Instrument	spect
4	Solvent	CD2Cl2
5	Temperature	298.0
6	Pulse Sequence	zgfhigqn.2
7	Experiment	1D
8	Probe	Z127784_0002 (CP BBO 500S1 BBF-H-D-05 Z)
9	Number of Scans	64
10	Receiver Gain	190.5
11	Relaxation Delay	1.0000
12	Pulse Width	15.0000
13	Presaturation Frequency	
14	Spectrometer Frequency	470.75
15	Spectral Width	113636.4
16	Lowest Frequency	-103898.1
17	Nucleus	19F
18	Acquired Size	65536
19	Spectral Size	131072