

## **Total Synthesis of (+)-Pleuromutilin**

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## 1. General Procedures

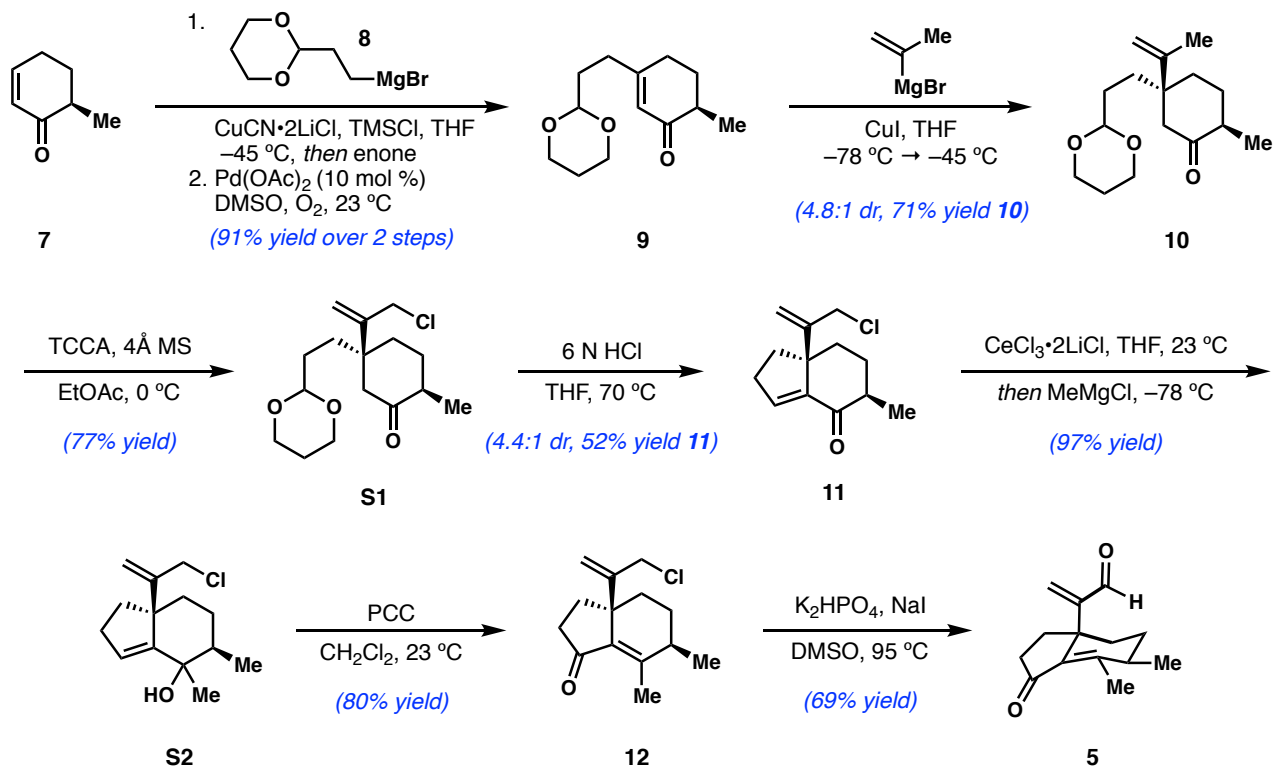
Unless otherwise stated, reactions were performed under an inert atmosphere (Ar) with freshly dried solvents utilizing standard Schlenk techniques. Glassware was oven-dried at 120 °C for a minimum of four hours, or flame-dried utilizing a Bunsen burner under high vacuum. Tetrahydrofuran (THF), methylene chloride (CH<sub>2</sub>Cl<sub>2</sub>), diethyl ether (Et<sub>2</sub>O), benzene (PhH), and toluene (PhMe) were dried by passing through activated alumina columns. Absolute ethanol (200 Proof) was purchased from Koptec. Methanol (HPLC grade) was purchased from Fisher Scientific. Anhydrous ammonia (NH<sub>3</sub>) was purchased from Matheson Tri-Gas. *N,N*-diisopropylethylamine (*i*Pr<sub>2</sub>NEt), triethylamine (Et<sub>3</sub>N), methanol (MeOH), isopropanol (*i*PrOH), *tert*-butanol (*t*BuOH), and trimethylsilyl chloride (TMSCl) were distilled over calcium hydride prior to use. Unless otherwise stated, chemicals and reagents were used as received. All reactions were monitored by thin-layer chromatography using EMD/Merck silica gel 60 F254 pre-coated plates (0.25 mm) and were visualized by UV (254 nm), *p*-anisaldehyde, and/or KMnO<sub>4</sub> staining. Flash column chromatography was performed using silica gel (SiliaFlash® P60, particle size 40-63 microns [230 to 400 mesh]) purchased from Silicycle. <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on a Bruker Avance III HD with Prodigy Cryoprobe (at 400 MHz and 101 MHz, respectively) or a Varian Inova 500 (at 500 MHz and 101 MHz respectively) and are reported relative to internal CHCl<sub>3</sub> (<sup>1</sup>H, δ = 7.26) and CDCl<sub>3</sub> (<sup>13</sup>C, δ = 77.0). Data for <sup>1</sup>H NMR spectra are reported as follows: chemical shift (δ ppm) (multiplicity, coupling constant (Hz), integration). Multiplicity and qualifier abbreviations are as follows: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad, app = apparent. IR spectra were recorded on a Perkin Elmer Paragon 1000 spectrometer and are reported in frequency of absorption (cm<sup>-1</sup>). HRMS were acquired from the Caltech Mass Spectral Facility using fast-atom bombardment (FAB), electrospray ionization (ES+-TOF) or electron impact (EI). Optical rotations were measured on a Jasco P-2000 polarimeter using a 100 mm path-length cell at 589 nm.

Reagents were purchased from commercial vendors as follows: 2-(2-bromoethyl)-1,3-dioxane was purchased from TCI America. Palladium(II) acetate (Pd(OAc)<sub>2</sub>, >99%), copper(I) iodide (CuI, 99.999%) and tetrakis(acetonitrile)palladium(II) tetrafluoroborate (Pd(CH<sub>3</sub>CN)<sub>4</sub>(BF<sub>4</sub>)<sub>2</sub>, >98%) were purchased from Strem Chemicals and stored in a nitrogen-filled glovebox. Tetrahydroxydiboron (B<sub>2</sub>(OH)<sub>2</sub>, 95%) and copper(I) cyanide (CuCN, 99.98%) were purchased from Sigma-Aldrich and stored in a nitrogen-filled glovebox. Samarium ingot (99.9% trace rare earth metals basis), tris(2,2,6,6-tetramethyl-3,5-heptanedionato)manganese(III) (Mn(dpm)<sub>3</sub>, 97%), phenylsilane (PhSiH<sub>3</sub>, 97%), lithium (wire stored in mineral oil, 99.9% trace metal basis), and *tert*-butyl hydroperoxide (TBHP, 5.5 M in decane over 4 Å MS) were purchased from Sigma-Aldrich.

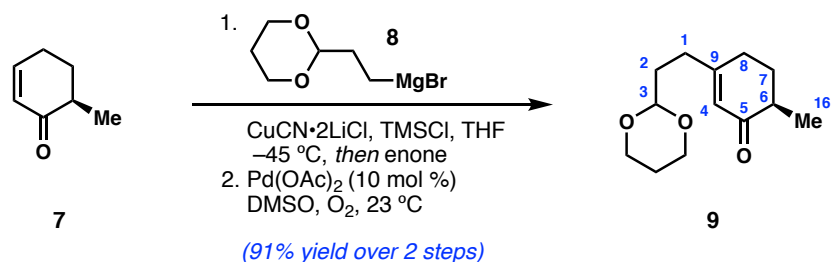
## 2. Synthetic Procedures

### i. Synthesis of hydrindanone enal (5)

#### Scheme S1. Complete Route Towards Enal (5)



#### Preparation of trisubstituted enone (9):



A flame-dried, 1 L, 3-necked round bottom flask equipped with a stir bar, reflux condenser, addition funnel, and glass stopper was charged with activated magnesium turnings (8.02 g, 330.0 mmol, 3 equiv). The atmosphere was exchanged three times with argon before addition of THF (40 mL). To the rapidly stirred suspension was added 1,2-dibromoethane (3.10 g, 16.5 mmol, 0.15 equiv) dropwise. An exothermic reaction was observed, and the suspension became grey. The reaction was cooled to ambient temperature, and subsequently, a solution of 2-(2-bromoethyl)-1,3-dioxane (42.9 g, 219.9 mmol, 2 equiv) in THF (170 mL, 0.64 M) was added dropwise via an addition funnel over 1 h. Upon completion of addition, the reaction was stirred for an additional 30 min. The resulting suspension was filtered via cannula into a flame-dried, 2 L, 2-necked round bottom flask equipped with a

large stir bar under an atmosphere of argon, and the Grignard reagent **8** was diluted with THF (170 mL, 0.64 M). Titration against salicylaldehyde phenylhydrazone yielded the concentration of Grignard reagent **8** as 0.38 M.

The Grignard solution was cooled to  $-45\text{ }^{\circ}\text{C}$ . Subsequently, a freshly prepared solution of  $\text{CuCN}\cdot 2\text{LiCl}$  in THF was added via cannula over 20 min.  $\text{CuCN}\cdot 2\text{LiCl}$  was prepared by dissolving CuCN (9.85 g, 110.0 mmol, 1 equiv) and LiCl (9.32 g, 220.0 mmol, 2 equiv) in THF (110 mL, 1.0 M w.r.t. CuCN) and vigorously stirring at ambient temperature for 1 h. After an additional 20 min, freshly distilled TMSCl (14.3 g, 132.0 mmol, 1.2 equiv) was added. The reaction became heterogeneous, and stirring was difficult. After 10 min, a solution of (*R*)-enone **7** (12.1 g, 110.0 mmol, 1 equiv) in THF (183 mL, 0.6 M) was added via cannula over 30 min. The reaction was stirred for 1 h and then quenched with sat. aq.  $\text{NaHCO}_3$  (10 mL) at  $-45\text{ }^{\circ}\text{C}$ . After warming to ambient temperature, pentane (600 mL) was added, and the suspension was filtered through Celite. The volatiles were concentrated under reduced pressure, additional pentane (500 mL) was added and the slurry was filtered through Celite. This process was repeated an additional time to afford 38.2 g of a clear oil.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ) shows desired silyl enol ether along with 2-(2-cyanoethyl)-1,3-dioxane. The silyl enol ether was used immediately without further purification.

To a 1 L round bottom flask equipped with a stir bar was added the silyl enol ether, anhydrous DMSO (550 mL, 0.2 M) and  $\text{Pd}(\text{OAc})_2$  (2.47 g, 11.0 mmol, 10 mol %). The mixture was sparged with  $\text{O}_2$  for 2 h then stirred at ambient temperature for 36 h. At this time,  $^1\text{H}$  NMR analysis showed the ratio of product to remaining silyl enol ether was 11:1. Water (700 mL) was added, and the product was extracted into  $\text{Et}_2\text{O}$  (4 x 400 mL). The combined organic layers were washed with brine (1 x 50 mL), dried over  $\text{Na}_2\text{SO}_4$ , and concentrated under reduced pressure to afford 38.1 g of a viscous, yellow oil.

Purification was achieved via flash column chromatography on  $\text{SiO}_2$  [750 g  $\text{SiO}_2$ , 60 mL fractions,  $\text{Et}_2\text{O}$ /hexanes = 40% (1.5 L), 45% (500 mL), 50% (500 mL), 55% (500 mL), 65% (500 mL), 80% (500 mL)] to afford trisubstituted enone **9** (20.3 g, 90.5 mmol, 91% yield over 2 steps) as a viscous, clear oil.

**TLC (25% EtOAc/hexanes):**  $R_f = 0.23$  (UV, *p*-anisaldehyde).

**$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):**  $\delta$  5.84 (s, 1H,  $\text{C}_4$ ), 4.53 (t,  $J = 5.0$  Hz, 1H,  $\text{C}_3$ ), 4.09 (ddt,  $J = 10.7, 5.1, 1.3$  Hz, 2H,  $\text{OCH}_2\text{CH}_2\text{CH}_2\text{O}$ ), 3.75 (m, 2H,  $\text{OCH}_2\text{CH}_2\text{CH}_2\text{O}$ ), 2.31 (m, 5H,  $\text{C}_1, \text{C}_2, \text{C}_6, \text{C}_8$ ), 2.05 (m, 2H,  $\text{OCH}_2\text{CH}_2$ ,  $\text{C}_7$ ), 1.78 (m, 2H,  $\text{C}_1, \text{C}_2$ ), 1.68 (m, 1H,  $\text{C}_7$ ), (d sept,  $J = 13.5, 1.4$  Hz, 1H,  $\text{OCH}_2\text{CH}_2$ ), 1.12 (d,  $J = 6.9$  Hz, 3H,  $\text{C}_{16}$ ).

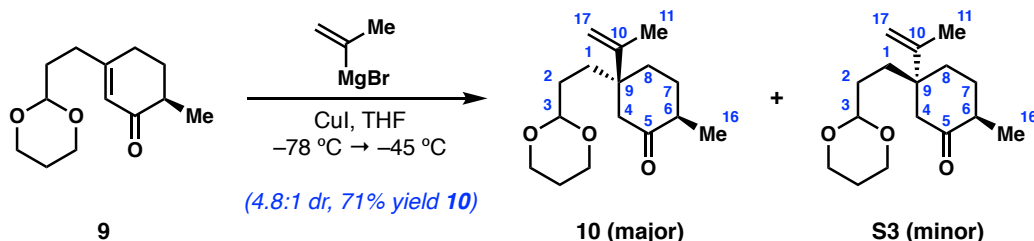
**$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ):**  $\delta$  202.3 ( $\text{C}_5=\text{O}$ ), 164.5 ( $\text{C}_9$ ), 125.1 ( $\text{C}_4$ ), 101.2 ( $\text{C}_3$ ), 66.9 ( $\text{OCH}_2\text{CH}_2$ ), 40.8 ( $\text{C}_6$ ), 32.3 ( $\text{C}_1$ ), 31.9 ( $\text{C}_2$ ), 30.8 ( $\text{C}_7$ ), 29.3 ( $\text{C}_8$ ), 25.7 ( $\text{OCH}_2\text{CH}_2$ ), 15.1 ( $\text{C}_{16}$ ).

**FTIR (AT-IR):** 2857, 2249, 1662, 1375, 1211, 1146, 1079, 1046, 907, 647  $\text{cm}^{-1}$ .

**HRMS (FAB+,  $m/z$ ):** calc'd for  $\text{C}_{13}\text{H}_{21}\text{O}_3$  [ $\text{M}+\text{H}$ ] $^+$  225.1491, found: 225.1502.

**$[\alpha]_D^{23}$ :**  $+65^{\circ}$  ( $c = 1.055$ ,  $\text{CHCl}_3$ ).

#### Preparation of isopropenyl cyclohexanone (**10**):



A flame-dried, 3 L, 2-necked round bottom flask equipped with a stir bar was evacuated and backfilled with argon three times. The flask was charged with CuI (17.6 g, 92.6 mmol, 1.5 equiv) and THF (617 mL). The suspension was cooled to  $-78\text{ }^{\circ}\text{C}$  and stirred for 15 min. Isopropenylmagnesium bromide (0.5 M in THF (Aldrich), 371 mL, 185 mmol, 3 equiv) was added dropwise via cannula transfer and the solution was stirred for 5 min. The

reaction was warmed to  $-25\text{ }^{\circ}\text{C}$  and stirred for 10 min. Thereafter, the mixture was cooled back down to  $-78\text{ }^{\circ}\text{C}$  and stirred for 15 min. Trisubstituted enone **9** (13.9 g, 61.8 mmol, 1 equiv) was dissolved in THF (617 mL) and added dropwise via cannula transfer. The solution was warmed to  $-50\text{ }^{\circ}\text{C}$  and stirred for 25 min or until complete by TLC analysis. The reaction mixture was quenched with sat. aq.  $\text{NH}_4\text{Cl}$  (400 mL) at  $-50\text{ }^{\circ}\text{C}$  and the biphasic solution was warmed to ambient temperature. The layers were separated and the aqueous phase was extracted with  $\text{Et}_2\text{O}$  (3 x 350 mL). The combined organic layers were washed with brine (100 mL), dried over  $\text{MgSO}_4$  and concentrated under reduced pressure to afford 18.4 g of a viscous oil.

Purification was achieved via flash column chromatography on  $\text{SiO}_2$  [1400 g  $\text{SiO}_2$ , 20%  $\text{EtOAc}$ /hexanes] to afford isopropenyl cyclohexenone **10** (11.64 g, 43.7 mmol, 71% yield) as a white solid.

### Major Diastereomer (**10**)

**TLC (20%  $\text{EtOAc}$ /hexanes):**  $R_f = 0.16$  (*p*-anisaldehyde).

**$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):**  $\delta$  4.93 (br s, 1H,  $\text{C}_{17}$ ), 4.69 (s, 1H,  $\text{C}_{17}$ ), 4.45 (t,  $J = 4.7$  Hz, 1H,  $\text{C}_3$ ), 4.07 (m, 2H,  $\text{OCH}_2\text{CH}_2$ ), 3.72 (m, 2H,  $\text{OCH}_2\text{CH}_2$ ), 2.73 (dd,  $J = 14.2, 3.0$  Hz, 1H,  $\text{C}_4$ ), 2.20 (app d of septets,  $J = 6.7, 1.2$  Hz, 1H,  $\text{C}_6$ ), 2.07 (dd,  $J = 14.2, 1.0$  Hz, 1H,  $\text{C}_4$ ), 2.04 (m, 1H,  $\text{OCH}_2\text{CH}_2$ ), 1.96 (dq,  $J = 13.8, 3.2$  Hz, 1H,  $\text{C}_8$ ), 1.83 (m, 1H,  $\text{C}_7$ ), 1.65 (m, 1H,  $\text{C}_2$ ), 1.61 (dd,  $J = 1.2, 0.5$  Hz, 3H,  $\text{C}_{11}$ ), 1.59 (m, 1H,  $\text{C}_8$ ), 1.46 (m, 1H,  $\text{C}_1$ ), 1.41 (m, 1H,  $\text{C}_1$ ), 1.37 (m, 1H,  $\text{C}_2$ ), 1.36 (m, 1H,  $\text{C}_7$ ), 1.32 (m, 1H,  $\text{OCH}_2\text{CH}_2$ ), 0.97 (d,  $J = 6.5$  Hz, 3H,  $\text{C}_{16}$ ).

**$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ):**  $\delta$  212.2 ( $\text{C}_5=\text{O}$ ), 145.7 ( $\text{C}_{10}$ ), 116.0 ( $\text{C}_{17}$ ), 102.3 ( $\text{C}_3$ ), 66.9 ( $\text{OCH}_2\text{CH}_2$ ), 49.8 ( $\text{C}_4$ ), 47.7 ( $\text{C}_9$ ), 44.8 ( $\text{C}_6$ ), 34.8 ( $\text{C}_8$ ), 34.5 ( $\text{C}_2$ ), 30.4 ( $\text{C}_7$ ), 29.5 ( $\text{C}_1$ ), 25.7 ( $\text{OCH}_2\text{CH}_2$ ), 18.9 ( $\text{C}_{11}$ ), 14.5 ( $\text{C}_{16}$ ).

**FTIR (AT-IR):** 2960, 2929, 2853, 1706, 1454, 1239, 1144, 994, 880  $\text{cm}^{-1}$ .

**HRMS (FAB+,  $m/z$ ):** calc'd for  $\text{C}_{16}\text{H}_{27}\text{O}_3$  [ $\text{M}+\text{H}$ ] $^+$  267.1960, found: 267.1966.

**$[\alpha]_D^{23}$ :**  $+42^{\circ}$  ( $c = 1.16$ ,  $\text{CHCl}_3$ ).

### Minor Diastereomer (**S3**)

**TLC (20%  $\text{EtOAc}$ /hexanes):**  $R_f = 0.27$  (*p*-anisaldehyde).

**$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):**  $\delta$  4.86 (pent,  $J = 1.2$  Hz, 1H,  $\text{C}_{17}$ ), 4.70 (m, 1H,  $\text{C}_{17}$ ), 4.42 (m, 1H,  $\text{C}_3$ ), 4.06 (ddt,  $J = 10.5, 5.0, 1.2$  Hz, 2H,  $\text{OCH}_2\text{CH}_2$ ), 3.72 (m, 2H,  $\text{OCH}_2\text{CH}_2$ ), 2.40 (dd,  $J = 13.3, 2.0$  Hz, 1H,  $\text{C}_4$ ), 2.35 (m, 1H,  $\text{C}_6$ ), 2.32 (m, 1H,  $\text{C}_4$ ), 2.07 (tt,  $J = 13.3, 5.2$  Hz, 1H,  $\text{OCH}_2\text{CH}_2$ ), 1.98 (m, 1H,  $\text{C}_7$ ), 1.88 (m, 1H,  $\text{C}_1$ ), 1.76 (td,  $J = 11.5, 4.1$  Hz, 1H,  $\text{C}_1$ ), 1.68 (dd,  $J = 1.3, 0.8$  Hz, 3H,  $\text{C}_{11}$ ), 1.50 (m, 1H,  $\text{C}_7$ ), 1.40 (m, 1H,  $\text{C}_2$ ), 1.39 (m, 1H,  $\text{C}_2$ ), 1.37 (m, 1H,  $\text{C}_8$ ), 1.35 (m, 1H,  $\text{C}_8$ ), 1.30 (m, 1H,  $\text{OCH}_2\text{CH}_2$ ), 1.05 (d,  $J = 6.7$  Hz, 3H,  $\text{C}_{16}$ ).

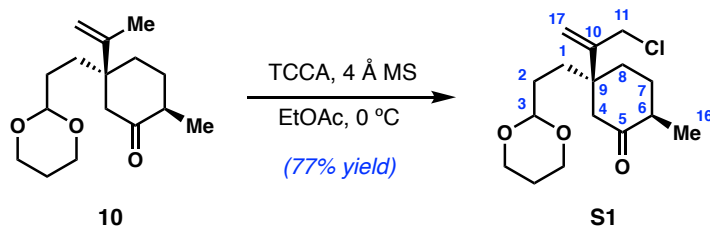
**$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ):**  $\delta$  213.3 ( $\text{C}_5=\text{O}$ ), 148.8 ( $\text{C}_{10}$ ), 111.9 ( $\text{C}_{17}$ ), 102.3 ( $\text{C}_3$ ), 66.9 ( $\text{OCH}_2\text{CH}_2$ ), 66.8 ( $\text{OCH}_2\text{CH}_2$ ), 50.0 ( $\text{C}_4$ ), 46.7 ( $\text{C}_9$ ), 44.3 ( $\text{C}_6$ ), 31.9 ( $\text{C}_1$ ), 30.2 ( $\text{C}_7$ ), 29.5 ( $\text{C}_8$ ), 28.2 ( $\text{C}_2$ ), 25.7 ( $\text{OCH}_2\text{CH}_2$ ), 19.0 ( $\text{C}_{11}$ ), 14.9 ( $\text{C}_{16}$ ).

**FTIR (AT-IR):** 2961, 2930, 2850, 1708, 1635, 1452, 1377, 1143, 994, 880  $\text{cm}^{-1}$ .

**HRMS (FAB+,  $m/z$ ):** calc'd for  $\text{C}_{16}\text{H}_{27}\text{O}_3$  [ $\text{M}+\text{H}$ ] $^+$  267.1960, found: 267.1949.

**$[\alpha]_D^{23}$ :**  $+1.9^{\circ}$  ( $c = 0.91$ ,  $\text{CHCl}_3$ ).

### Preparation of allylic chloride (S1):



This procedure was adapted from the work of Kumar and coworkers.<sup>2</sup> A flame-dried, 2 L, 2-neck round bottom flask equipped with a stir bar was charged with activated 4 Å mol sieves and cyclohexanone **10** (12.06 g, 45.28 mmol, 1 equiv). The atmosphere was exchanged three times with argon before adding EtOAc (916 mL, 0.05 M) that had been degassed with argon. The resulting colorless solution was cooled to 0 °C and stirred for an additional 10 min. Subsequently, finely ground trichloroisocyanuric acid (TCCA) (10.52 g, 45.28 mmol, 1 equiv) was added in one portion. The reaction was stirred (900 rpm) for 10 min or until complete by TLC analysis. The reaction mixture was quenched at 0 °C with sat. aq. Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> (150 mL). The biphasic solution was warmed to ambient temperature and filtered. The aqueous layer was extracted with EtOAc (4 x 100 mL). The combined organic layers were washed with H<sub>2</sub>O (100 mL), dried over MgSO<sub>4</sub>, filtered, and concentrated under reduced pressure to afford a yellow oil.

Purification was achieved via flash column chromatography on SiO<sub>2</sub> [1400 g SiO<sub>2</sub>, 15% EtOAc/hexanes → 30%] to afford allylic chloride **S1** (10.52 g, 39.5 mmol, 77% yield) as a white solid.

**TLC (50% EtOAc/hexanes):** R<sub>f</sub> = 0.5 (*p*-anisaldehyde).

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):** δ 5.54 (s, 1H, C<sub>17</sub>), 5.15 (s, 1H, C<sub>17</sub>), 4.46 (t, *J* = 4.8 Hz, 1H, C<sub>3</sub>), 4.12 – 4.03 (m, 2H, OCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>O), 4.01 (d, *J* = 1.0 Hz, 2H, C<sub>11</sub>), 3.73 (td, *J* = 12.2, 2.4 Hz, 2H, OCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>O), 2.76 (dd, *J* = 14.2, 3.0 Hz, 1H, C<sub>4</sub>), 2.34 – 2.20 (m, 1H, C<sub>6</sub>), 2.14 (dd, *J* = 14.2, 1.1 Hz, 1H, C<sub>2</sub>), 2.04 (tdd, *J* = 17.5, 8.7, 4.2 Hz, 2H, C<sub>1</sub>), 1.89 (ddt, *J* = 13.3, 6.6, 3.5 Hz, 1H, C<sub>7</sub>), 1.80 – 1.65 (m, 2H, C<sub>8</sub>), 1.55 – 1.28 (m, 4H, C<sub>1</sub>, C<sub>7</sub>, C<sub>2</sub>, OCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>O), 0.99 (d, 3H, C<sub>16</sub>).

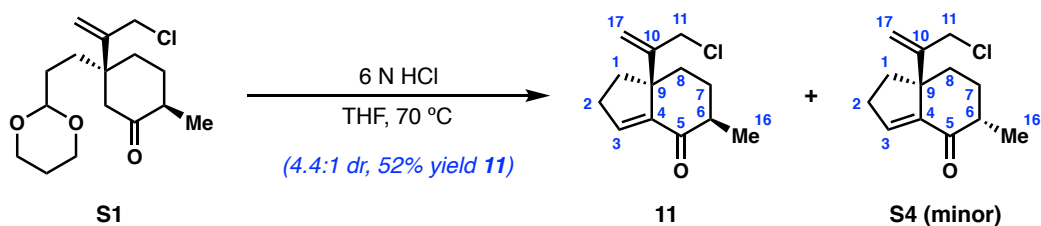
**<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>):** δ 211.7 (C<sub>5</sub>=O), 145.0 (C<sub>10</sub>), 121.0 (C<sub>17</sub>), 101.9 (C<sub>3</sub>), 66.9 (OCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>O), 50.2 (C<sub>4</sub>), 48.1 (C<sub>9</sub>), 44.9 (C<sub>6</sub>), 44.0 (C<sub>11</sub>), 35.0 (C<sub>8</sub>), 35.0 (C<sub>1</sub>), 30.6 (C<sub>7</sub>), 29.5 (C<sub>2</sub>), 25.7 (OCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>O), 14.4 (C<sub>16</sub>).

**FTIR (AT-IR):** 2929, 2359, 1707, 1377, 1214, 1143, 1079, 880, 730, 668 cm<sup>-1</sup>.

**HRMS (FAB+, *m/z*):** calc'd for C<sub>16</sub>H<sub>26</sub>O<sub>3</sub>Cl [M+H]<sup>+</sup> 301.1571, found: 301.1564.

[α]<sub>D</sub><sup>23</sup>: +49° (*c* = 0.495, CHCl<sub>3</sub>).

### Preparation of enone (11):



A 250 mL round bottom flask equipped with a stir bar and reflux condenser was charged with allylic chloride **S1** (10.8 g, 35.9 mmol, 1 equiv) and THF (125 mL). The homogeneous solution was vigorously stirred (960 rpm) and 6 N HCl (17.96 mL, 108 mmol, 3 equiv) was added dropwise. The reaction was heated to 70 °C and stirred for 4 h. The reaction was quenched with sat. aq. NaHCO<sub>3</sub> (45 mL). The layers were separated and the aqueous

layer was extracted with Et<sub>2</sub>O (3 x 75 mL). The combined organic layers were washed with brine (25 mL) and dried over MgSO<sub>4</sub>. The suspension was filtered, and concentrated under reduced pressure to afford 10.4 g of a viscous yellow oil.

Purification was achieved via flash column chromatography on SiO<sub>2</sub> [1400 g SiO<sub>2</sub>, 5% Et<sub>2</sub>O/hexanes → 10%] to afford enone **11** (4.15 g, 18.5 mmol, 52% yield) as a colorless solid.

### Major Diastereomer (**11**)

**TLC (50% Et<sub>2</sub>O/hexanes):**  $R_f = 0.75$  (UV, *p*-anisaldehyde).

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):**  $\delta$  6.55 (t,  $J = 2.7$  Hz, 1H, C<sub>3</sub>), 5.39 (s, 1H, C<sub>17</sub>), 4.96 (s, 1H, C<sub>17</sub>), 4.16 – 4.05 (m, 2H, C<sub>11</sub>), 2.39 – 2.32 (m, 3H, C<sub>1</sub>, C<sub>2</sub>), 2.29 – 2.18 (m, 2H, C<sub>6</sub>, C<sub>8</sub>), 1.95 – 1.84 (m, 2H, C<sub>7</sub>, C<sub>8</sub>), 1.73 – 1.45 (m, 2H, C<sub>1</sub>, C<sub>7</sub>), 1.09 (d,  $J = 6.7$  Hz, 2H, C<sub>6</sub>).

**<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>):**  $\delta$  202.1 (C<sub>5</sub>=O), 146.8 (C<sub>4</sub>), 146.4 (C<sub>10</sub>), 137.6 (C<sub>3</sub>), 119.0 (C<sub>17</sub>), 57.9 (C<sub>9</sub>), 45.2 (C<sub>6</sub>), 44.7 (C<sub>11</sub>), 39.4 (C<sub>8</sub>), 35.3 (C<sub>1</sub>), 30.5 (C<sub>7</sub>), 30.1 (C<sub>2</sub>), 14.9 (C<sub>16</sub>).

**FTIR (AT-IR):** 2929, 2860, 1682, 1622, 1454, 1312, 1232, 1012, 927, 757, cm<sup>-1</sup>.

**HRMS (FAB+, m/z):** calc'd for C<sub>13</sub>H<sub>18</sub>ClO [M+H]<sup>+</sup> 225.1046, found: 225.1061.

**$[\alpha]_D^{23}$ :** +58.4° ( $c = 0.715$ , CHCl<sub>3</sub>).

### Minor Diastereomer (**S3**)

**TLC (50% Et<sub>2</sub>O/hexanes):**  $R_f = 0.75$  (UV, *p*-anisaldehyde)

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):**  $\delta$  6.70 (t,  $J = 2.7$  Hz, 1H, C<sub>3</sub>), 5.3 (s, 1H, C<sub>17</sub>), 5.00 (s, 1H, C<sub>17</sub>), 4.21 – 4.01 (m, 2H, C<sub>11</sub>), 2.55 – 2.44 (m, 1H, C<sub>6</sub>), 2.42 – 2.32 (m, 2H, C<sub>2</sub>), 2.28 (ddt,  $J = 12.6, 5.4, 2.7$  Hz, 1H, C<sub>1</sub>), 2.16 (dt,  $J = 13.8, 4.0$  Hz, 1H, C<sub>8</sub>), 2.04 – 1.83 (m, 2H, C<sub>1</sub>, C<sub>7</sub>), 1.74 (td,  $J = 13.4, 3.9$  Hz, 1H, C<sub>8</sub>), 1.54 (dq,  $J = 13.9, 3.9$  Hz, 1H, C<sub>7</sub>), 1.12 (d,  $J = 7.4$  Hz, 3H, C<sub>16</sub>).

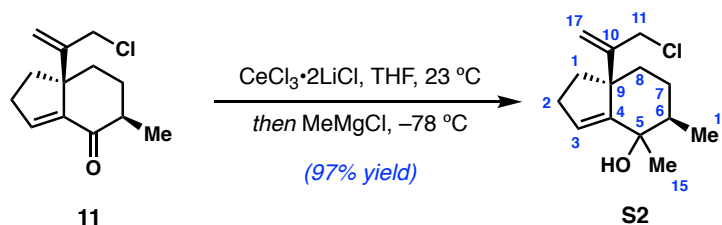
**<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>):**  $\delta$  203.4 (C<sub>5</sub>=O), 146.7 (C<sub>4</sub>), 145.3 (C<sub>10</sub>), 140.1 (C<sub>3</sub>), 118.2 (C<sub>17</sub>), 56.7 (C<sub>9</sub>), 44.8 (C<sub>11</sub>), 41.9 (C<sub>6</sub>), 39.8 (C<sub>12</sub>), 30.7 (C<sub>8</sub>), 30.0 (C<sub>2</sub>), 28.0 (C<sub>7</sub>), 17.8 (C<sub>16</sub>).

**FTIR (AT-IR):** 2925, 2855, 1687, 1620, 1456, 1376, 1262, 1175, 1098, 924 cm<sup>-1</sup>.

**HRMS (EI+, m/z):** calc'd for C<sub>13</sub>H<sub>17</sub>ClO [M]<sup>+</sup> 224.0968, found: 224.0940.

**$[\alpha]_D^{23}$ :** 46.8° ( $c = 0.115$ , CHCl<sub>3</sub>).

### Preparation of allylic alcohol (**S2**):



A flame-dried, 50 mL round bottom flask equipped with a stir bar was charged with enone **11** (1.101 g, 4.9 mmol, 1 equiv). The atmosphere was exchanged with argon three times before adding a solution of CeCl<sub>3</sub>·2LiCl<sup>3</sup> (0.3 M in THF, 16.3 mL, 1 equiv). Upon addition of CeCl<sub>3</sub>·2LiCl, a bright yellow solution was obtained and stirred for 1 h at ambient temperature. The reaction mixture was then cooled to -78 °C and stirred for 15 min. The solution then became pale yellow slurry and stirring became difficult. A solution of methylmagnesium chloride (3.0 M in THF (Aldrich), 3.3 mL, 9.8 mmol, 2 equiv) was added dropwise over 30 min. The slurry was perturbed by hand until magnetic stirring resumed. The reaction was stirred at -78 °C until TLC analysis indicated complete consumption of starting material (about 15 min).



The gray solution was quenched at  $-78\text{ }^{\circ}\text{C}$  via slow addition of 1 M HCl (15 mL) using a vent needle to relieve excess pressure. Thereafter, the solution was warmed to ambient temperature while the slurry slowly quenched. The mixture was then transferred to a separatory funnel and diluted with  $\text{H}_2\text{O}$  (20 mL) and  $\text{Et}_2\text{O}$  (50 mL). The layers separated, and the aqueous layer was extracted with  $\text{Et}_2\text{O}$  (3 x 20 mL). The combined organic layers was washed with brine (40 mL) and dried over  $\text{MgSO}_4$ . The suspension was filtered and concentrated under reduced pressure to afford a yellow oil.

Purification was achieved via flash column chromatography on  $\text{SiO}_2$  [100 g  $\text{SiO}_2$ , 45 mL fractions, 200 mL forerun,  $\text{Et}_2\text{O}$ /hexanes = 15% (1.2 L), 30% (250 mL), 40% (1 L)] to afford the less polar diastereomer (fractions 3–10) followed by the more polar diastereomer (fractions 17–33). The volatiles were concentrated under reduced pressure to afford an inconsequential mixture of diastereomers **S2** (1.15 g, 4.78 mmol, 97% combined yield). An analytically pure sample of the less polar diastereomer was obtained and a representative spectrum of the mixture as used in the next step is also provided.

**TLC (20%  $\text{Et}_2\text{O}$ /hexanes):**  $R_f = 0.46$  and  $0.09$  (*p*-anisaldehyde).

**$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):**  $\delta$  5.79 (t,  $J = 2.4$  Hz, 1H,  $\text{C}_3$ ), 5.44 – 5.41 (m, 1H,  $\text{C}_{17}$ ), 5.27 (s, 1H,  $\text{C}_{17}$ ), 4.24 (dd,  $J = 13.1, 0.6$  Hz, 1H,  $\text{C}_{11}$ ), 4.08 (dd,  $J = 13.1, 1.0$  Hz, 1H,  $\text{C}_{11}$ ), 2.46 – 2.33 (m, 3H,  $\text{C}_2, \text{C}_8$ ), 2.05 (ddd,  $J = 13.4, 7.9, 3.4$  Hz, 1H,  $\text{C}_1$ ), 1.76 (dt,  $J = 13.3, 9.0$  Hz, 1H,  $\text{C}_1$ ), 1.57 (s, 1H, OH), 1.46 – 1.38 (m, 3H,  $\text{C}_6, \text{C}_7, \text{C}_8$ ), 1.37 (s, 3H,  $\text{C}_{15}$ ), 0.92 (d,  $J = 6.4$  Hz, 3H,  $\text{C}_{16}$ ).

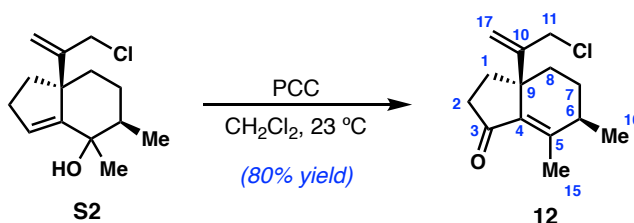
**$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ):**  $\delta$  150.1 ( $\text{C}_4$ ), 149.7 ( $\text{C}_{10}$ ), 126.5 ( $\text{C}_3$ ), 113.8 ( $\text{C}_{17}$ ), 72.1 ( $\text{C}_5$ ), 54.5 ( $\text{C}_9$ ), 45.7 ( $\text{C}_{11}$ ), 43.1 ( $\text{C}_6$ ), 41.4 ( $\text{C}_1$ ), 38.2 ( $\text{C}_8$ ), 30.3 ( $\text{C}_2$ ), 28.3 ( $\text{C}_7$ ), 24.4 ( $\text{C}_{15}$ ), 14.8 ( $\text{C}_{16}$ ).

**FTIR (AT-IR):** 3315, 2872, 2360, 1596, 1489, 1275, 1031, 1001, 899, 697  $\text{cm}^{-1}$ .

**HRMS (FAB+,  $m/z$ ):** calc'd for  $\text{C}_{14}\text{H}_{20}\text{ClO}$  [ $\text{M}+\text{H}$ ] $^+$ – $\text{H}_2$  239.1203, found: 239.1176.

**$[\alpha]_D^{23}$ :**  $+27.0^\circ$  ( $c = 0.210$ ,  $\text{CHCl}_3$ ).

### Preparation of hydrindenone (**12**):



This procedure was adapted from the work of Dauben and coworkers.<sup>4</sup> To a 100 mL round bottom flask equipped with a stir bar was added allylic alcohol **S2** (1.15 g, 4.78 mmol, 1 equiv) and  $\text{CH}_2\text{Cl}_2$  (32 mL). Pyridinium chlorochromate (3.09 g, 14.24 mmol, 3 equiv) was added in one portion and the reaction was stirred at ambient temperature for 12 h or until complete by aliquot NMR.

Upon complete consumption of starting material, the reaction mixture was transferred to a 500 mL separatory funnel. In the reaction flask remained a black resin, which was diluted with 20 mL  $\text{Et}_2\text{O}$  and 60 mL of 5% NaOH. The biphasic mixture was stirred until all the black resin had gone into solution, where it was then transferred into the separatory funnel. The organic layer was separated, and the aqueous layer was extracted with  $\text{Et}_2\text{O}$  (3 x 20 mL). The combined organic layers were then washed with 1 M HCl (2 x 15 mL) which gave a pale yellow organic layer. The phases were again separated, and washed with sat. aq.  $\text{NaHCO}_3$ . The combined organic layers were dried over  $\text{MgSO}_4$ , filtered, and concentrated under reduced pressure.

Purification was achieved via flash column chromatography with  $\text{SiO}_2$  [50 g  $\text{SiO}_2$ , 10%  $\text{Et}_2\text{O}$ /hexanes] to afford enone **12** (902 mg, 3.78 mmol, 80% yield) as viscous, clear oil.

**TLC (20% Et<sub>2</sub>O/hexanes):** R<sub>f</sub> = 0.24 (UV, *p*-anisaldehyde).

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):** δ 5.49 (s, 1H, C<sub>17</sub>), 4.93 (d, *J* = 0.8 Hz, 1H, C<sub>17</sub>), 4.10 (d, *J* = 0.9 Hz, 2H, C<sub>11</sub>), 2.34 – 2.04 (m, 5H, C<sub>1</sub>, C<sub>2</sub>, C<sub>6</sub>, C<sub>8</sub>, C<sub>15</sub>), 1.75 – 1.66 (m, 1H, C<sub>7</sub>), 1.63 – 1.54 (m, 1H, C<sub>1</sub>), 1.39 – 1.15 (m, 2H, C<sub>7</sub>, C<sub>8</sub>), 1.06 (d, *J* = 7.1 Hz, 3H, C<sub>16</sub>).

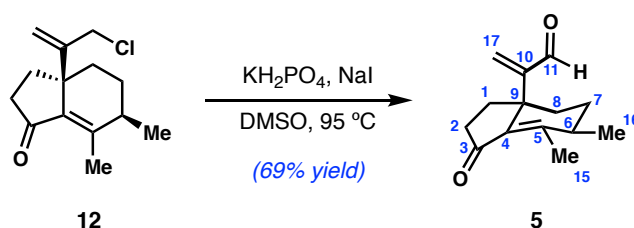
**<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>):** δ 207.4 (C<sub>3</sub>=O), 152.3 (C<sub>4</sub>), 147.4 (C<sub>5</sub>), 135.6 (C<sub>10</sub>), 121.8 (C<sub>17</sub>), 50.6 (C<sub>9</sub>), 43.9 (C<sub>11</sub>), 37.7 (C<sub>6</sub>), 35.6 (C<sub>2</sub>), 33.2 (C<sub>8</sub>), 32.5 (C<sub>1</sub>), 28.2 (C<sub>7</sub>), 19.1 (C<sub>16</sub>), 16.9 (C<sub>15</sub>).

**FTIR (AT-IR):** 2932, 1707, 1630, 1444, 1267, 1211, 1077, 926, 801, 754, 622 cm<sup>-1</sup>.

**HRMS (TOF, ES<sup>+</sup>):** calc'd for C<sub>14</sub>H<sub>19</sub>ClO<sub>2</sub>[M+Na]<sup>+</sup> 261.1022, found 261.1006.

**[α]<sub>D</sub><sup>23</sup>:** –252.8° (*c* = 0.66, CHCl<sub>3</sub>).

### Preparation of enal (5):



This procedure was adapted from the work of Kumar and coworkers.<sup>2</sup> A 20 mL scintillation vial equipped with a stir bar was charged with hydrindenone **12** (250 mg, 1.047 mmol, 1 equiv), K<sub>2</sub>HPO<sub>4</sub>•3H<sub>2</sub>O (595 mg, 2.62 mmol, 2.5 equiv), NaI (65 mg, 0.419 mmol, 0.4 equiv) and DMSO (10 mL). The vial was sealed with a teflon cap and the heterogeneous mixture was heated to 95 °C with vigorous stirring (1000 rpm). After 7.5 h, aliquot NMR analysis indicated complete consumption of starting material. The heterogeneous mixture was allowed to cool to ambient temperature and sat. aq. NaHCO<sub>3</sub> (5 mL) was added. The layers were separated and the aqueous layer was extracted with Et<sub>2</sub>O (4 x 15 mL). The combined organic layers were washed with H<sub>2</sub>O (10 mL), and dried over MgSO<sub>4</sub>. The suspension was filtered and concentrated under reduced pressure to afford a yellow oil.

Purification was achieved via flash column chromatography on SiO<sub>2</sub> [75 g SiO<sub>2</sub>, Et<sub>2</sub>O/hexanes = 20%] to afford enal **5** (157 mg, 0.719 mmol, 69% yield) as a white solid.

**TLC (30% Et<sub>2</sub>O/hexanes):** R<sub>f</sub> = 0.30 (UV, *p*-anisaldehyde).

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):** δ 9.57 (s, 3H, C<sub>11</sub>), 6.17 (s, 1H, C<sub>17</sub>), 6.06 (s, 1H, C<sub>17</sub>), 2.58 (ddd, *J* = 12.9, 7.9, 1.2 Hz, 1H, C<sub>2</sub>), 2.48 (dt, *J* = 13.1, 3.4 Hz, 1H, C<sub>8</sub>), 2.17 (m, 1H, C<sub>6</sub>), 2.16 (s, 3H, C<sub>15</sub>), 2.12 (ddd, *J* = 18.5, 8.6, 1.1 Hz, 1H, C<sub>1</sub>), 2.06 (ddd, *J* = 18.5, 12.6, 7.9 Hz, 1H, C<sub>1</sub>), 1.70 (m, 1H, C<sub>7</sub>), 1.64 (dd, *J* = 12.6, 8.7, Hz, 1H, C<sub>2</sub>), 1.34 (td, *J* = 14.0, 2.7 Hz, 1H, C<sub>8</sub>), 1.04 (s, 3H, C<sub>16</sub>), 0.97 (m, 1H, C<sub>7</sub>).

**<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>):** δ 207.9 (C<sub>3</sub>=O), 193.8 (C<sub>11</sub>=O), 153.5 (C<sub>5</sub>), 152.8 (C<sub>10</sub>), 140.5 (C<sub>17</sub>), 135.1 (C<sub>4</sub>), 48.1 (C<sub>9</sub>), 37.5 (C<sub>6</sub>), 35.9 (C<sub>1</sub>), 32.3 (C<sub>8</sub>), 31.8 (C<sub>2</sub>), 28.5 (C<sub>7</sub>), 19.3 (C<sub>16</sub>), 17.0 (C<sub>15</sub>).

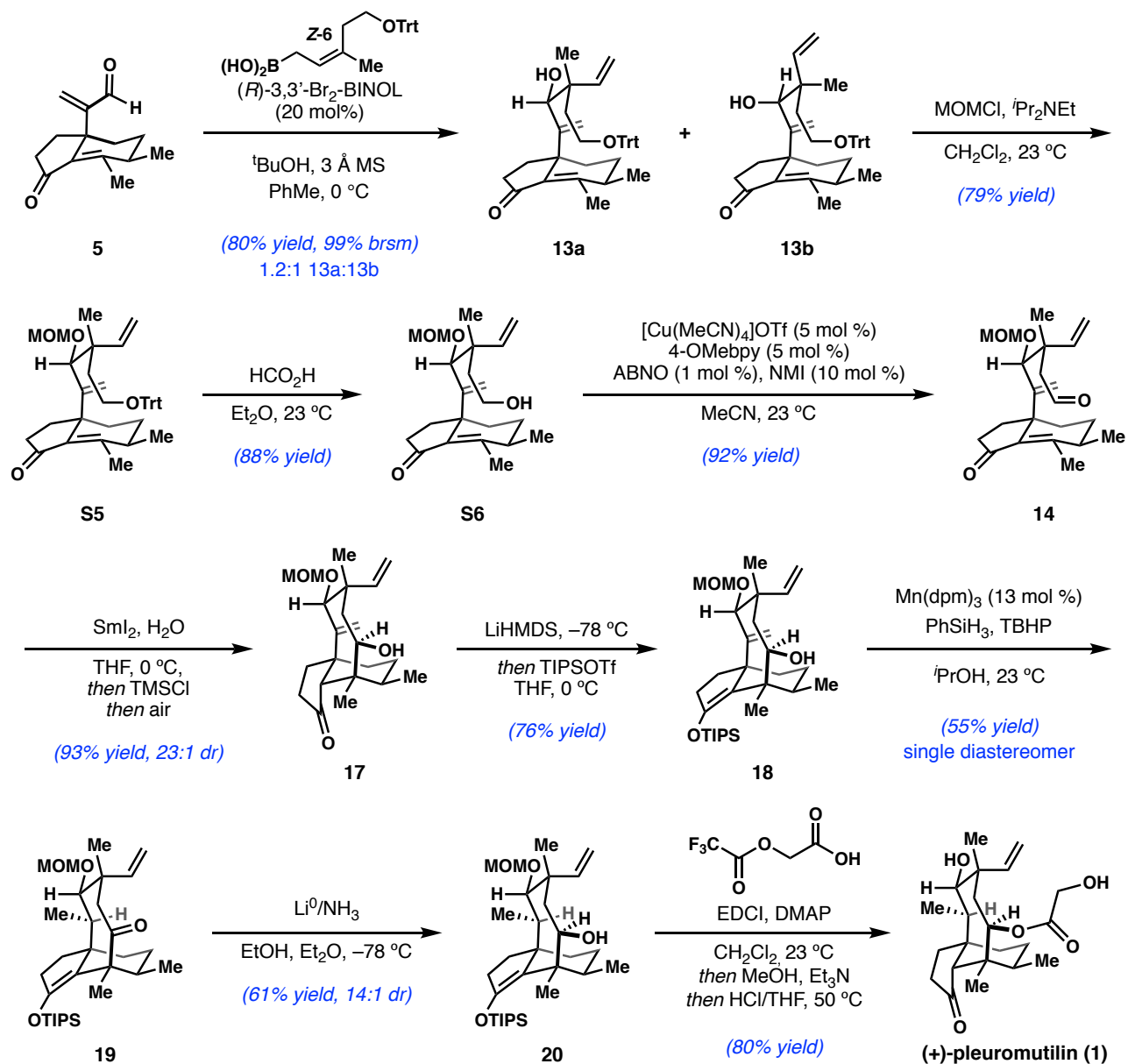
**FTIR (AT-IR):** 2950, 2931, 1705, 1629, 1080, 907, 878, 764, 702, 647 cm<sup>-1</sup>.

**HRMS (FAB<sup>+</sup>, *m/z*):** calc'd for C<sub>14</sub>H<sub>19</sub>O<sub>2</sub> [M+H]<sup>+</sup> 219.1385, found 219.1387.

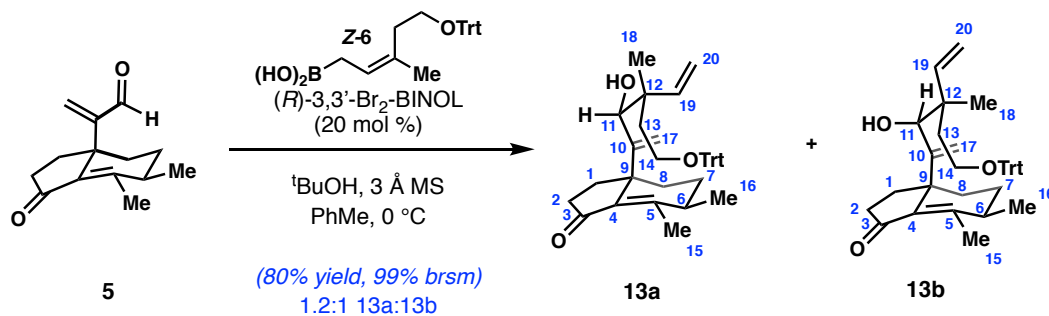
**[α]<sub>D</sub><sup>23</sup>:** –215° (*c* = 1.01, CHCl<sub>3</sub>).

## ii. Synthesis of (+)-pleuromutilin (1)

### Scheme S2. Completion of pleuromutilin (1)



## Preparation of crotylation adducts (13a) and (13b):



This procedure was adapted from the work of Szabó and coworkers.<sup>5</sup> In a nitrogen-filled glovebox, a flame-dried, 100 mL Schlenk flask equipped with a stir bar was charged with freshly activated 3 Å molecular sieves (pellets) (1.79 g), allylboronic acid **Z-6** (25.3 mL of a 0.18 M solution, 4.47 mmol, 1 equiv, see page S36),  $(R)$ -3,3'-Br<sub>2</sub>-BINOL (397 mg, 0.894 mmol, 20 mol %), freshly distilled *t*BuOH (1.28 mL, 13.4 mmol, 3 equiv), and a solution of the enal hydrindanone **5** (976 mg, 4.47 mmol, 1 equiv) in dry, degassed PhMe (4.5 mL). The resulting heterogeneous mixture was sealed, removed from the glovebox, cooled to -30 °C for 5 min, then placed in a pre-equilibrated 0 °C bath and stirred.

After 40 h, the reaction was quenched with MeOH (5 mL), stirred for 5 min, filtered, and concentrated under reduced pressure to afford a viscous residue. Purification was achieved via flash column chromatography on SiO<sub>2</sub> [100 g SiO<sub>2</sub>, Acetone/hexanes = 4%→15%] to afford remaining enal (fractions 22–31), the desired diastereomer **13a** (fractions 37–70), and **13b** and residual  $(R)$ -3,3'-Br<sub>2</sub>-BINOL (fractions 71–85). The volatiles were concentrated under reduced pressure to afford remaining enal (237 mg, 1.09 mmol, 24% recovered contaminated with ~5% protodeboronated nucleophile), the desired diastereomer **13a** (1.03 g, 1.84 mmol, 41% yield), and the more polar diastereomer **13b**/BINOL mixture respectively.

The **13b**/BINOL mixture was subjected to flash column chromatography on SiO<sub>2</sub> [100 g SiO<sub>2</sub>, Et<sub>2</sub>O/hexanes = 40%] to afford  $(R)$ -3,3'-Br<sub>2</sub>-BINOL (fractions 1–3) and the more polar diastereomer **13b** (fractions 23–38). Obtained  $(R)$ -3,3'-Br<sub>2</sub>-BINOL (343 mg, 0.772 mmol, 86% recovered) and the more polar diastereomer **13b** (972 mg, 1.73 mmol, 39% yield). Both diastereomers were isolated as puffy white foams.

**Experimental Note:** It is critical that all operations be carried out in a rigorously oxygen-free environment. Failure to do so will result in rapid decomposition of the allylboronic acid.

### Desired Diastereomer (13a)

**TLC (desired diastereomer) (20% Acetone/hexanes):**  $R_f$  = 0.38 (UV, *p*-anisaldehyde).

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):** δ 7.46–7.38 (m, 6H, **Ph<sub>3</sub>CO**), 7.34–7.19 (m, 9H, **Ph<sub>3</sub>CO**), 5.81 (dd,  $J$  = 17.6, 10.9 Hz, 1H, C<sub>19</sub>), 5.41 (s, 1H, C<sub>17</sub>), 5.00 (dd,  $J$  = 10.9, 1.2 Hz, 1H, C<sub>20</sub>), 4.95 (dd,  $J$  = 17.7, 1.2 Hz, 1H, C<sub>20</sub>), 4.81 (d,  $J$  = 1.1 Hz, 1H, C<sub>17</sub>), 3.89 (d,  $J$  = 8.3 Hz, 1H, C<sub>11</sub>), 3.20 (t,  $J$  = 6.7 Hz, 2H, C<sub>14</sub>), 2.34 (d,  $J$  = 8.3 Hz, 1H, **OH**), 2.22 (app dt,  $J$  = 10.0, 1.6 Hz, 1H, C<sub>8</sub>), 2.17 (m, 1H, C<sub>6</sub>), 2.17 (m, 1H, C<sub>2</sub>), 2.16 (s, 3H, C<sub>15</sub>), 2.09 (m, 1H, C<sub>1</sub>), 2.05 (m, 1H, C<sub>2</sub>), 1.86 (dt,  $J$  = 13.5, 6.5 Hz, 1H, C<sub>13</sub>), 1.30 (td,  $J$  = 13.5, 1.9 Hz, 1H, C<sub>7</sub>), 1.63 (m, 1H, C<sub>13</sub>), 1.54 (m, 1H, C<sub>1</sub>), 1.30 (td,  $J$  = 13.5, 1.9 Hz, 1H, C<sub>7</sub>), (1.22, m, 1H, C<sub>8</sub>), 1.07 (s, 3H, C<sub>18</sub>), 1.05 (d,  $J$  = 7.0 Hz, 3H, C<sub>16</sub>).

**<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>):** δ 208.1 (C<sub>3</sub>=O), 153.4 (C<sub>10</sub>), 152.4 (C<sub>5</sub>), 144.0 (**Ph<sub>3</sub>CO**), 142.8 (C<sub>19</sub>), 135.7 (C<sub>4</sub>) 128.6 (**Ph<sub>3</sub>CO**), 127.8 (**Ph<sub>3</sub>CO**), 127.0 (**Ph<sub>3</sub>CO**), 118.4 (C<sub>17</sub>), 114.7 (C<sub>20</sub>), 87.4 (**Ph<sub>3</sub>CO**), 74.6 (C<sub>11</sub>), 60.8 (C<sub>14</sub>), 52.0 (C<sub>9</sub>), 44.6 (C<sub>12</sub>), 38.8 (C<sub>13</sub>), 38.0 (C<sub>6</sub>), 35.6 (C<sub>2</sub>), 33.2 (C<sub>8</sub>), 32.3 (C<sub>1</sub>), 28.2 (C<sub>7</sub>), 20.5 (C<sub>18</sub>), 19.1 (C<sub>16</sub>), 17.0 (C<sub>15</sub>).

**FTIR (AT-IR):** 3540, 2901, 2380, 2365, 1699, 1627, 1448, 1274, 1064, 1031, 749 cm<sup>-1</sup>.

**HRMS (TOF, ES+):** calc'd for C<sub>39</sub>H<sub>44</sub>O<sub>3</sub>Na [M+Na]<sup>+</sup> 583.3188, found 583.3198.

$[\alpha]_D^{23}$ :  $-104^\circ$  ( $c = 0.326$ ,  $\text{CHCl}_3$ ).

**Melting point:**  $57.3\text{--}58.7^\circ\text{C}$

**11,12-bis-*epi* crotylation adduct (13b)**

**TLC (13b) (20% Acetone/hexanes):**  $R_f = 0.30$  (UV, *p*-anisaldehyde).

**$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):**  $\delta$  7.44–7.38 (m, 6H,  $\text{Ph}_3\text{CO}$ ), 7.34–7.19 (m, 9H,  $\text{Ph}_3\text{CO}$ ), 5.86 (dd,  $J = 17.6, 10.9$  Hz, 1H,  $\text{C}_{19}$ ), 5.48 (s, 1H,  $\text{C}_{17}$ ), 5.02 (dd,  $J = 10.9, 1.2$  Hz, 1H,  $\text{C}_{20}$ ), 4.96 (dd,  $J = 17.7, 1.2$  Hz, 1H,  $\text{C}_{20}$ ), 4.86 (d,  $J = 1.1$  Hz, 1H,  $\text{C}_{17}$ ), 3.82 (d,  $J = 9.4$  Hz, 1H,  $\text{C}_{11}$ ), 3.19 (m, 2H,  $\text{C}_{14}$ ), 2.50 (dd,  $J = 12.3, 7.9$  Hz, 1H,  $\text{C}_2$ ), 2.39 (d,  $J = 8.3$  Hz, 1H,  $\text{OH}$ ), 2.28 (ddd,  $J = 18.4, 12.8, 8.0$  Hz, 1H,  $\text{C}_1$ ), 2.17 (m, 1H,  $\text{C}_6$ ), 2.16 (s, 3H,  $\text{C}_{15}$ ), 2.08 (d,  $J = 7.9$  Hz, 1H,  $\text{C}_1$ ), 2.01 (dd,  $J = 16.5, 7.0$  Hz, 1H,  $\text{C}_{13}$ ), 1.97 (dd,  $J = 14.0, 6.8$  Hz,  $\text{C}_8$ ), 1.63 (m, 1H,  $\text{C}_7$ ), 1.58 (q,  $J = 6.6$  Hz,  $\text{C}_{13}$ ), 1.46 (m, 1H,  $\text{C}_2$ ), 1.29 (m, 1H,  $\text{C}_8$ ), 1.26 (m, 1H,  $\text{C}_7$ ), 1.10 (d,  $J = 7.0$  Hz, 3H,  $\text{C}_{16}$ ), 1.06 (s, 3H,  $\text{C}_{18}$ ).

**$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ):**  $\delta$  208.4 ( $\text{C}_3=\text{O}$ ), 153.2 ( $\text{C}_{10}$ ), 151.1 ( $\text{C}_5$ ), 144.0 ( $\text{Ph}_3\text{CO}$ ), 143.1 ( $\text{C}_{19}$ ), 136.4 ( $\text{C}_4$ ), 128.6 ( $\text{Ph}_3\text{CO}$ ), 127.8 ( $\text{Ph}_3\text{CO}$ ), 127.0 ( $\text{Ph}_3\text{CO}$ ), 118.6 ( $\text{C}_{17}$ ), 114.6 ( $\text{C}_{20}$ ), 87.3 ( $\text{Ph}_3\text{CO}$ ), 75.2 ( $\text{C}_{11}$ ), 60.9 ( $\text{C}_{14}$ ), 52.1 ( $\text{C}_9$ ), 44.3 ( $\text{C}_{12}$ ), 38.7 ( $\text{C}_{13}$ ), 37.8 ( $\text{C}_6$ ), 35.7 ( $\text{C}_1$ ), 32.7 ( $\text{C}_8$ ), 32.5 ( $\text{C}_2$ ), 28.3 ( $\text{C}_7$ ), 21.3 ( $\text{C}_{18}$ ), 19.2 ( $\text{C}_{16}$ ), 16.8 ( $\text{C}_{15}$ ).

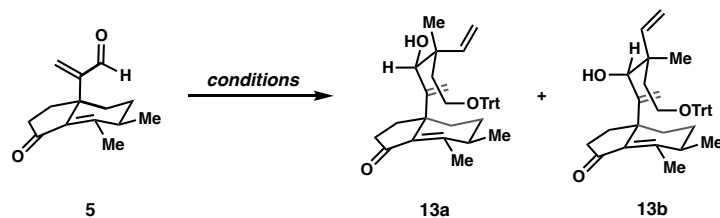
**FTIR (AT-IR):** 3409, 2930, 2359, 2246, 1700, 1628, 1490, 1448, 1271, 1030, 759  $\text{cm}^{-1}$ .

**HRMS (TOF, ES+):** calc'd for  $\text{C}_{39}\text{H}_{44}\text{O}_3\text{Na}$   $[\text{M}+\text{Na}]^+$  583.3188, found 583.3184.

$[\alpha]_D^{25}$ :  $-55^\circ$  ( $c = 1.04$ ,  $\text{CHCl}_3$ ).

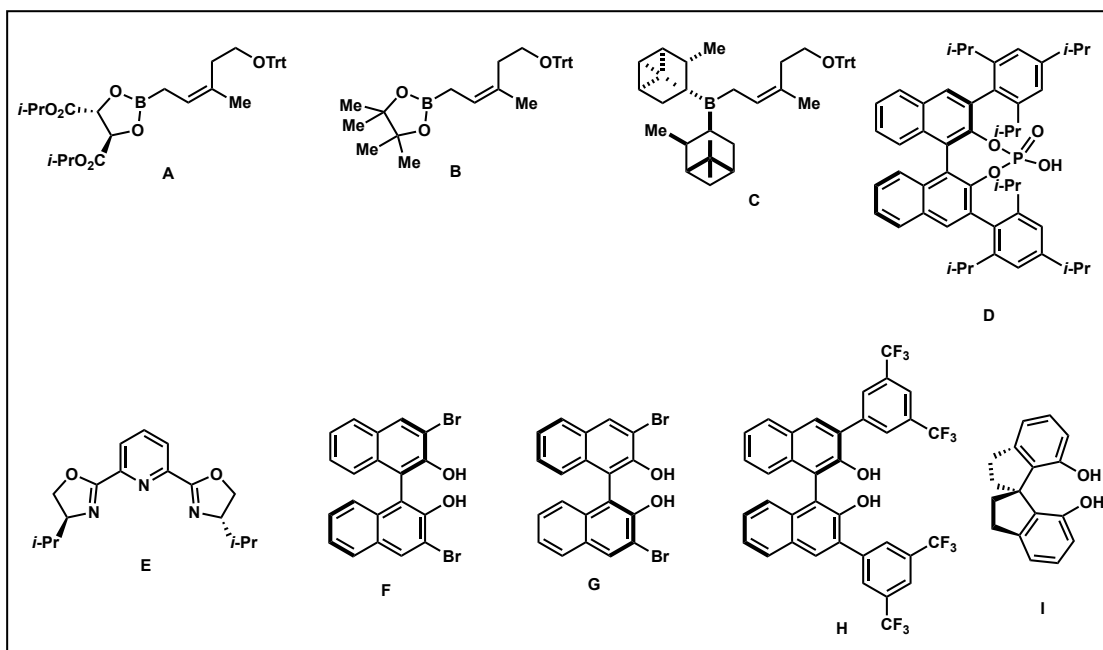
**Melting point:**  $66.5\text{--}68.4^\circ\text{C}$

Table S1. Other tested crotylation conditions

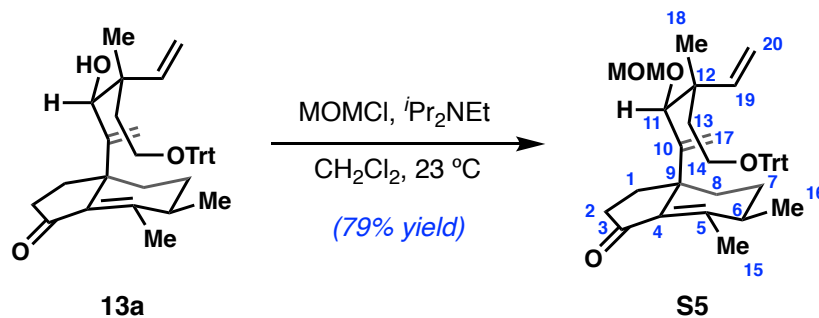


Entry	nucleophile	catalyst	additive	solvent	conc.	T	t	conv.	Yield (13a)	Yield (13b)
1	A (2 equiv)	–	4Å MS	PhMe	0.08 M	–78 °C → 0 °C	6 h	10%	–	–
2	A (2 equiv)	–	4Å MS	PhMe	0.3 M	0 °C	18 h	43%	–	–
3	B (2 equiv)	–	4Å MS	PhMe	0.3 M	0 °C	18 h	26%	–	–
4 <sup>†</sup>	C (1 equiv)	–	–	THF/hexanes	0.5 M	–78 °C → 23 °C	3 h	ND	–	–
5	B (2 equiv)	D (1 mol %)	–	PhMe	0.13 M	0 °C	18 h	22%	–	–
6	B (2 equiv)	–	Sc(OTf) <sub>3</sub> (10 mol %)	PhMe	0.15 M	0 °C	18 h	47%	–	–
7	B (2 equiv)	E	Sc(OTf) <sub>3</sub> (10 mol %)	PhMe	0.15 M	0 °C	18 h	29%	–	–
8	Z-6 (1 equiv)	F (20 mol %)	4Å MS	PhMe	0.08 M	0 °C	40 h	77%	38%	36%
9	Z-6 (1 equiv)	G (20 mol %)	4Å MS	PhMe	0.08 M	0 °C	40 h	66%	28%	38%
10	Z-6 (1 equiv)	H (20 mol %)	4Å MS	PhMe	0.08 M	0 °C	40 h	100%	25%	24%
11	Z-6 (1 equiv)	I (20 mol %)	4Å MS	PhMe	0.08 M	0 °C	40 h	68%	12%	10%

<sup>†</sup>The lpc-borane (C) used in this reaction was not of high purity due to synthetic challenges



### Preparation of MOM protected crotylation adduct (S5):



A flame-dried, 25 mL round bottom flask equipped with a stir bar was charged with alcohol **13a** (300 mg, 0.535 mmol, 1 equiv),  $\text{CH}_2\text{Cl}_2$  (8.7 mL), and freshly distilled  $i\text{Pr}_2\text{NEt}$  (2.42 mL, 13.9 mmol, 26 equiv). To the homogeneous solution was added chloromethyl methyl ether (1.02 mL, 7.80 mmol, 25 equiv) dropwise over 10 min, taking care to vent HCl fumes formed via the use of a needle. The reaction was stirred at ambient temperature for 36 h. The resulting viscous, orange mixture was quenched via addition of sat. aq.  $\text{NaHCO}_3$  (20 mL) and stirred at ambient temperature for 30 min. The aqueous layer was extracted with  $\text{CH}_2\text{Cl}_2$  (3 x 10 mL). The combined organic layers were washed with  $\text{H}_2\text{O}$  (1 x 10 mL), brine (1 x 10 mL), dried over  $\text{Na}_2\text{SO}_4$ , and concentrated via distillation to afford a viscous, dark orange residue.

Purification was achieved via flash column chromatography on  $\text{SiO}_2$  [35 g  $\text{SiO}_2$ ,  $\text{Et}_2\text{O}$ /hexanes = 16%→35%] to afford MOM ether **S5** (281 mg, 0.465 mmol, 79% yield) as a puffy white solid. Starting material **13a** was also isolated (38.0 mg, 0.0678 mmol, 13% recovered).

**TLC (40%  $\text{Et}_2\text{O}$ /hexanes):**  $R_f = 0.71$  (UV, *p*-anisaldehyde).

**$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):**  $\delta$  7.46–7.38 (m, 6H,  $\text{Ph}_3\text{CO}$ ), 7.32–7.19 (m, 9H,  $\text{Ph}_3\text{CO}$ ), 5.77 (dd,  $J = 16.9, 9.9$  Hz, 1H, C<sub>19</sub>), 5.42 (d,  $J = 1.1$  Hz, 1H, C<sub>17</sub>), 4.93 (br m, 1H, C<sub>17</sub>), 4.84 (dd,  $J = 9.9, 2.4$  Hz, 1H, C<sub>20</sub>), 4.80 (dd,  $J = 16.9, 2.4$  Hz, 1H, C<sub>20</sub>), 4.52 (d,  $J = 6.7$  Hz, 1H,  $\text{OCH}_2\text{OMe}$ ), 4.46 (d,  $J = 6.7$  Hz, 1H,  $\text{OCH}_2\text{OMe}$ ), 3.87 (br s, 1H, C<sub>11</sub>), 3.37 (s, 3H,  $\text{OCH}_2\text{OCH}_3$ ), 3.10 (m, m, 2H, C<sub>14</sub>), 2.17 (app dt,  $J = 12.0, 7.9$  Hz, 1H, C<sub>2</sub>), 2.15 (m 1H, C<sub>1</sub>), 2.11 (m, 1H, C<sub>6</sub>), 2.10 (s, 3H, C<sub>15</sub>), 2.08 (m, 1H, C<sub>8</sub>), 1.98 (m, 1H, C<sub>13</sub>), 1.93 (m, 1H, C<sub>2</sub>), 1.86 (m, 1H, C<sub>13</sub>), 1.62 (m, 1H, C<sub>7</sub>), 1.44 (m, 1H, C<sub>1</sub>), 1.25 (m, 1H, C<sub>7</sub>), 1.23 (m, 1H, C<sub>8</sub>), 1.05 (d,  $J = 7.0$  Hz, 3H, C<sub>16</sub>), 0.99 (s, 3H, C<sub>18</sub>).

**$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ):**  $\delta$  208.4 (C<sub>3</sub>=O), 151.1 (C<sub>5</sub>), 149.7 (C<sub>10</sub>), 144.4 ( $\text{Ph}_3\text{CO}$ ), 142.6 (C<sub>19</sub>), 136.4 (C<sub>4</sub>), 128.7 ( $\text{Ph}_3\text{CO}$ ), 127.7 ( $\text{Ph}_3\text{CO}$ ), 126.8 ( $\text{Ph}_3\text{CO}$ ), 122.3 (C<sub>17</sub>), 113.9 (C<sub>20</sub>), 95.1 ( $\text{OCH}_2\text{OCH}_3$ ), 86.7 ( $\text{Ph}_3\text{CO}$ ), 80.2 (C<sub>11</sub>), 60.7 (C<sub>14</sub>), 56.4 ( $\text{OCH}_2\text{OCH}_3$ ), 50.8 (C<sub>9</sub>), 45.2 (C<sub>12</sub>), 38.3 (C<sub>13</sub>), 37.5 (C<sub>6</sub>), 35.9 (C<sub>2</sub>), 33.2 (C<sub>8</sub>), 32.7 (C<sub>1</sub>), 28.2 (C<sub>7</sub>), 19.1 (C<sub>16</sub>), 17.9 (C<sub>18</sub>), 17.0 (C<sub>15</sub>).

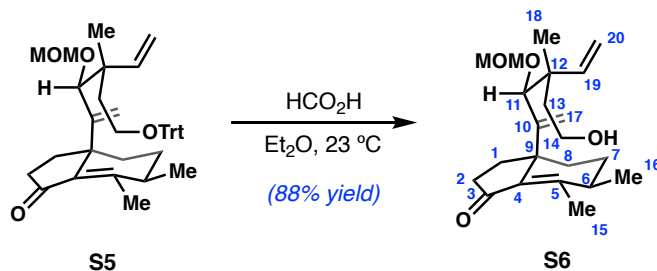
**FTIR (AT-IR):** 2930, 1703, 1627, 1448, 1213, 1034, 919, 735  $\text{cm}^{-1}$ .

**HRMS (TOF, ES<sup>+</sup>):** calc'd for  $\text{C}_{41}\text{H}_{48}\text{O}_4\text{Na}$  [ $\text{M}+\text{Na}$ ]<sup>+</sup> 627.3450, found 627.3419.

**$[\alpha]_D^{23}$ :**  $-39^\circ$  ( $c = 1.06$ ,  $\text{CHCl}_3$ ).

**Melting point:** 62.0–63.3  $^\circ\text{C}$

## Preparation of alcohol (S6):



A flame-dried, 250 mL round bottom flask equipped with a stir bar was charged with MOM ether **S5** (431 mg, 0.713 mmol, 1 equiv). Thereafter, a freshly prepared solution of formic acid (98%, 4.8 mL) and Et<sub>2</sub>O (4.8 mL) was rapidly added, and within 5 min, the reaction was judged to be complete by TLC analysis. We found it critical to stop this reaction immediately after full conversion was achieved. Prolonged times afforded copious quantities of formate ester product. The reaction was diluted with Et<sub>2</sub>O (10 mL) and quenched via slow addition of NaHCO<sub>3</sub> (100 mL). The aqueous layer was extracted with Et<sub>2</sub>O (4 x 25 mL) and washed with H<sub>2</sub>O (1 x 10 mL). The combined organic layers were washed with brine (1 x 5 mL), dried over Na<sub>2</sub>SO<sub>4</sub>, and concentrated under reduced pressure to afford a viscous yellow residue.

Purification was achieved via flash column chromatography on SiO<sub>2</sub> [15 g SiO<sub>2</sub>, Et<sub>2</sub>O/hexanes = 70%] to afford alcohol **S6** (225 mg, 0.621 mmol, 88% yield) as a viscous, colorless oil.

**TLC (70% Et<sub>2</sub>O/hexanes):**  $R_f = 0.20$  (UV, *p*-anisaldehyde).

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):**  $\delta$  5.99 (dd,  $J = 16.9, 9.9$  Hz, 1H, C<sub>19</sub>), 5.49 (d,  $J = 1.1$  Hz, 1H, C<sub>17</sub>), 5.05 (dd,  $J = 9.9, 2.4$  Hz, 1H, C<sub>20</sub>), 5.01 (br m, 1H, C<sub>17</sub>), 4.99 (dd,  $J = 16.9, 2.4$  Hz, 1H, C<sub>20</sub>), 4.58 (d,  $J = 6.7$  Hz, 1H, OCH<sub>2</sub>OMe), 4.50 (d,  $J = 6.7$  Hz, 1H, OCH<sub>2</sub>OMe), 4.01 (br s, 1H, C<sub>11</sub>), 3.66 (m, 2H, C<sub>14</sub>), 3.41 (s, 3H, OCH<sub>2</sub>OCH<sub>3</sub>), 2.24 (m, 1H, C<sub>2</sub>), 2.22 (m, 1H, C<sub>1</sub>), 2.13 (m, 1H, C<sub>6</sub>), 2.11 (m, 1H, C<sub>8</sub>), 2.10 (s, 3H, C<sub>15</sub>), 1.99 (m, 1H, C<sub>2</sub>), 1.95 (m, 1H, C<sub>13</sub>), 1.88 (m, 1H, C<sub>13</sub>), 1.63 (m, 1H, C<sub>7</sub>), 1.50 (m, 1H, C<sub>1</sub>), 1.27 (m, 1H, C<sub>8</sub>), 1.25 (m, 1H, C<sub>7</sub>), 1.12 (s, 3H, C<sub>18</sub>), 1.05 (d,  $J = 7.0$  Hz, 3H, C<sub>16</sub>).

**<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>):**  $\delta$  208.3 (C<sub>3</sub>=O), 151.2 (C<sub>5</sub>), 149.7 (C<sub>10</sub>), 143.1 (C<sub>19</sub>), 136.4 (C<sub>4</sub>), 122.5 (C<sub>17</sub>), 114.1 (C<sub>20</sub>), 95.0 (OCH<sub>2</sub>OCH<sub>3</sub>), 80.0 (C<sub>11</sub>), 59.8 (C<sub>14</sub>), 56.4 (OCH<sub>2</sub>OCH<sub>3</sub>), 50.7 (C<sub>9</sub>), 45.3 (C<sub>12</sub>), 41.5 (C<sub>13</sub>), 37.5 (C<sub>6</sub>), 35.9 (C<sub>2</sub>), 33.2 (C<sub>8</sub>), 32.8 (C<sub>1</sub>), 28.2 (C<sub>7</sub>), 19.1 (C<sub>16</sub>), 17.7 (C<sub>18</sub>), 17.0 (C<sub>15</sub>).

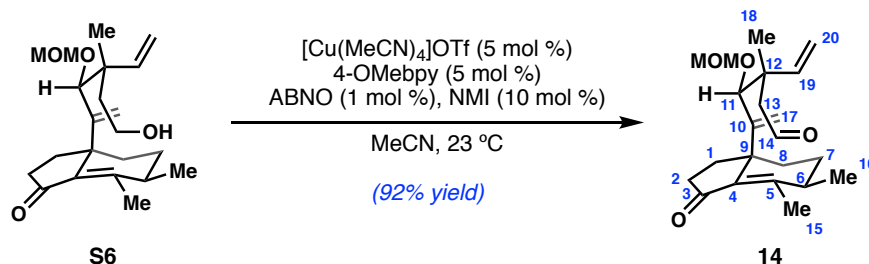
**FTIR (AT-IR):** 3397, 2930, 1701, 1625, 1456, 1371, 1212, 1145, 1035, 917, 734 cm<sup>-1</sup>.

**HRMS (TOF, ES<sup>+</sup>):** calc'd for C<sub>22</sub>H<sub>34</sub>O<sub>4</sub>Na [M+Na]<sup>+</sup> 385.2355, found 385.2371.

**$[\alpha]_D^{23}$ :**  $-53^\circ$  ( $c = 0.475$ , CHCl<sub>3</sub>).



## Preparation of aldehyde (14):



## Stahl Oxidation:<sup>6</sup>

A flame-dried, 2 dram vial equipped with a stir bar was charged with alcohol **S6** (165 mg, 0.455 mmol, 1 equiv) and MeCN (2.0 mL). Thereafter, added 860  $\mu\text{L}$  of the [Cu]/bpy stock solution, 860  $\mu\text{L}$  of the NMI stock solution, and 860  $\mu\text{L}$  of the ABNO stock solution, in that order. The orange reaction was stirred at 960 rpm open to the atmosphere for 90 min. Subsequently, the resulting light blue solution was diluted with Et<sub>2</sub>O (10 mL), passed through a short pad of SiO<sub>2</sub> using Et<sub>2</sub>O as the eluent and concentrated under reduced pressure to afford a pale yellow oil.

Purification was achieved via flash column chromatography on SiO<sub>2</sub> [8 g SiO<sub>2</sub>, Et<sub>2</sub>O/hexanes = 30%→60%] to afford aldehyde **14** (151 mg, 0.419 mmol, 92% yield) as a viscous, colorless oil that solidified to a white solid upon standing in the freezer.

**Preparation of stock solutions:** [Cu(MeCN)<sub>4</sub>]OTf (30.0 mg) and 4,4'-dimethoxy-2,2'-bipyridyl (4-OMebpy) (17.0 mg) were suspended in MeCN (3.0 mL) and stirred for 5 min resulting in a homogeneous, green solution. ABNO (2.5 mg) was dissolved in MeCN (3.0 mL). *N*-methylimidazole (13.4 mg) was dissolved in MeCN (3.0 mL).

**TLC (80% Et<sub>2</sub>O/hexanes):**  $R_f$  = 0.65 (UV, *p*-anisaldehyde).

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):**  $\delta$  9.74 (t,  $J$  = 2.8 Hz, 1H, C<sub>14</sub>), 6.07 (dd,  $J$  = 16.9, 9.9 Hz, 1H, C<sub>19</sub>), 5.48 (d,  $J$  = 0.7 Hz, 1H, C<sub>17</sub>), 5.13 (dd,  $J$  = 9.9, 2.4 Hz, 1H, C<sub>20</sub>), 5.09 (dd,  $J$  = 16.9, 2.4 Hz, 1H, C<sub>20</sub>), 5.05 (br m, 1H, C<sub>17</sub>), 4.54 (d,  $J$  = 6.7 Hz, 1H, OCH<sub>2</sub>OMe), 4.42 (d,  $J$  = 6.7 Hz, 1H, OCH<sub>2</sub>OMe), 4.12 (br s, 1H, C<sub>11</sub>), 3.36 (s, 3H, OCH<sub>2</sub>OCH<sub>3</sub>), 2.56 (m, 2H, C<sub>13</sub>), 2.26 (m, 1H, C<sub>1</sub>), 2.19 (m, 1H, C<sub>8</sub>), 2.17 (m, 1H, C<sub>2</sub>), 2.14 (m 1H, C<sub>6</sub>), 2.11 (s, 3H, C<sub>15</sub>), 2.00 (dd,  $J$  = 17.0, 7.6 Hz, 1H, C<sub>2</sub>), 1.65 (m, 1H, C<sub>7</sub>), 1.52 (m, 1H, C<sub>1</sub>), 1.27 (s, 3H, C<sub>18</sub>), 1.25 (m, 1H, C<sub>8</sub>), 1.23 (m, 1H, C<sub>7</sub>), 1.07 (d,  $J$  = 7.0 Hz, 3H, C<sub>16</sub>).

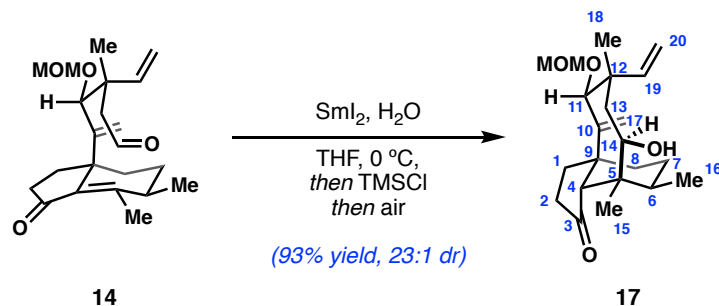
**<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>):**  $\delta$  208.1 (C<sub>3</sub>=O), 202.2 (C<sub>14</sub>=O), 151.4 (C<sub>5</sub>), 149.0 (C<sub>10</sub>), 142.4 (C<sub>19</sub>), 136.2 (C<sub>4</sub>), 122.7 (C<sub>17</sub>), 114.5 (C<sub>20</sub>), 94.2 (OCH<sub>2</sub>OCH<sub>3</sub>), 78.2 (C<sub>11</sub>), 56.6 (OCH<sub>2</sub>OCH<sub>3</sub>), 52.4 (C<sub>13</sub>), 50.5 (C<sub>9</sub>), 45.5 (C<sub>12</sub>), 37.4 (C<sub>6</sub>), 35.9 (C<sub>2</sub>), 33.1 (C<sub>8</sub>), 32.7 (C<sub>1</sub>), 28.2 (C<sub>7</sub>), 19.1 (C<sub>16</sub>), 18.9 (C<sub>18</sub>), 17.0 (C<sub>15</sub>).

**FTIR (AT-IR):** 2931, 1704, 1627, 1456, 1212, 1146, 1032, 919, 708 cm<sup>-1</sup>.

**HRMS (TOF, ES<sup>+</sup>):** calc'd for C<sub>22</sub>H<sub>32</sub>O<sub>4</sub>[M+Na]<sup>+</sup> 383.2198, found 383.2189.

**$[\alpha]_D^{23}$ :** -56° ( $c$  = 0.475, CHCl<sub>3</sub>).

### Preparation of tricycle (17):



A 100 mL Schlenk flask equipped with a stir bar was charged with aldehyde **14** (108 mg, 0.300 mmol, 1 equiv), deionized H<sub>2</sub>O (32  $\mu$ L, 1.80 mmol, 6 equiv), and THF (15.0 mL) and submitted to five freeze-pump-thaw cycles. The solution was cooled to 0 °C and stirred at this temperature for 15 min. Thereafter, SmI<sub>2</sub>/THF (9.0 mL, 0.900 mmol, 3 equiv) was added dropwise over 8 min. The deep blue color of SmI<sub>2</sub> was immediately quenched upon addition of each drop. The first drop afforded a yellow solution, fading to pale yellow and almost clear by the time 1.6 equiv SmI<sub>2</sub> had been added. When 2.2 equiv SmI<sub>2</sub> had been added, the blue color became increasingly persistent and upon addition of 2.6 equiv SmI<sub>2</sub>, the reaction was dark blue/green. After stirring an additional 10 min at 0 °C, TMSCl/THF (1.5 mL, 1.50 mmol, 5 equiv TMSCl) was added dropwise over 2 min, and the reaction was stirred an additional 10 min. Throughout this time, the deep blue color was quenched to yellow. Thereafter, the reaction was removed from the ice bath and stirred open to the atmosphere for 5 min.

The resulting pale yellow solution was diluted with Et<sub>2</sub>O (75 mL), and washed with H<sub>2</sub>O (2 x 15 mL). The aqueous layer was back-extracted with Et<sub>2</sub>O (2 x 15 mL), and the combined organic layers were dried over Na<sub>2</sub>SO<sub>4</sub>, filtered, and concentrated under reduced pressure to afford a dark orange oil.

Purification was achieved via flash column chromatography on SiO<sub>2</sub> [12 g SiO<sub>2</sub>, Et<sub>2</sub>O/hexanes = 30%] to afford tricycle **17** (100 mg, 0.276 mmol, 92% yield) as a crystalline white solid.

**Preparation of SmI<sub>2</sub>:** A 100 mL Schlenk flask containing a stir bar was charged with freshly filed Sm metal (650 mg). The system was flame-dried under high vacuum then cooled to ambient temperature before adding freshly purified 1,2-diiodoethane (700 mg). 1,2-diiodoethane (1.6 g) was dissolved in Et<sub>2</sub>O (50 mL) and washed with sat. aq. Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> (3 x 10 mL) and deionized water (2 x 10 mL), dried over Na<sub>2</sub>SO<sub>4</sub>, filtered, and dried to 1.41 g of a white solid. The atmosphere was exchanged three times for argon. Subsequently, the flask was charged with anhydrous THF (25 mL) that had been submitted to five freeze-pump-thaw cycles. Note: The THF used for the synthesis of SmI<sub>2</sub> must contain <50 ppm H<sub>2</sub>O; THF containing greater quantities of water resulted in excessive induction times for the synthesis of SmI<sub>2</sub>. Further, residual oxygen results in formation of oxidative fragmentation products in the radical cyclization. The suspension was stirred for 2 min and the flask was cautiously and briefly (5 s) placed under partial high vacuum, then purged with argon. This process was repeated two additional times to remove ethylene gas formed from insertion of Sm metal into 1,2-diiodoethane. The resulting heterogeneous suspension was rapidly (930 rpm) stirred; after 5 min, the reaction turned dark green, and within 10 min, a dark blue color was observed. After stirring under argon for 3 h at ambient temperature, the system was cautiously and briefly placed under high vacuum, then purged with argon. This process was repeated two additional times, then stirring was halted. The mixture was allowed to settle for 15 min prior to use.

**Stock solution of TMSCl:** TMSCl was freshly distilled from CaH<sub>2</sub> (5% w/w) under argon, collecting a 15% forerun then taking the middle fraction. A solution of TMSCl (350  $\mu$ L) in THF (5.0 mL) was submitted to five freeze-pump-thaw cycles.

**TLC (50% Et<sub>2</sub>O/hexanes):**  $R_f = 0.55$  (*p*-anisaldehyde).

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):**  $\delta$  6.35 (dd,  $J = 17.8, 11.3$  Hz, 1H, C<sub>19</sub>), 5.33 (dd,  $J = 17.8, 1.4$  Hz, 1H, C<sub>20</sub>), 5.34 (s, 1H, C<sub>17</sub>), 5.28 (s, 1H, C<sub>17</sub>), 5.19 (dd,  $J = 11.2, 1.4$  Hz, 1H, C<sub>20</sub>), 4.54 (d,  $J = 7.1$  Hz, 1H, OCH<sub>2</sub>OMe), 4.40 (d,  $J = 6.7$  Hz, 1H, OCH<sub>2</sub>OMe), 4.13 (d,  $J = 5.9$  Hz, 1H, C<sub>14</sub>), 3.95 (s, 1H, C<sub>11</sub>), 3.38 (s, 3H, OCH<sub>2</sub>OCH<sub>3</sub>), 2.33 (m, 1H, C<sub>2</sub>), 2.29 (m, 1H, C<sub>2</sub>), 2.24 (m, 1H, C<sub>4</sub>), 2.06 (m, 1H, C<sub>1</sub>), 2.03 (m, 1H, C<sub>8</sub>), 1.92 (dd,  $J = 16.1, 6.5$  Hz, 1H, C<sub>13</sub>), 1.70 (m, 1H, C<sub>6</sub>), 1.60 (dt,  $J = 13.3, 3.4$  Hz, 1H, C<sub>7</sub>), 1.50 (dd,  $J = 16.1, 0.9$  Hz, 1H, C<sub>13</sub>), 1.39 (ddt,  $J = 13.3, 6.5, 3.4$  Hz, 1H, C<sub>7</sub>), 1.33 (m, 1H, C<sub>1</sub>), 1.30 (s, 3H, C<sub>15</sub>), 1.28 (m, 1H, C<sub>8</sub>), 1.24 (s, 3H, C<sub>18</sub>), 0.96 (d,  $J = 7.0$  Hz, 3H, C<sub>16</sub>).

**<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>):**  $\delta$  216.8 (C<sub>3</sub>=O), 148.3 (C<sub>10</sub>), 139.9 (C<sub>19</sub>), 114.2 (C<sub>20</sub>), 112.2 (C<sub>17</sub>), 92.1 (OCH<sub>2</sub>OCH<sub>3</sub>), 77.2 (C<sub>11</sub>), 67.2 (C<sub>14</sub>), 59.6 (C<sub>4</sub>), 56.0 (OCH<sub>2</sub>OCH<sub>3</sub>), 46.5 (C<sub>9</sub>), 45.2 (C<sub>13</sub>), 44.7 (C<sub>12</sub>), 42.1 (C<sub>5</sub>), 37.3 (C<sub>6</sub>), 34.9 (C<sub>2</sub>), 31.0 (C<sub>8</sub>), 29.7 (C<sub>1</sub>), 28.8 (C<sub>18</sub>), 26.8 (C<sub>7</sub>), 18.2 (C<sub>16</sub>), 13.4 (C<sub>15</sub>).

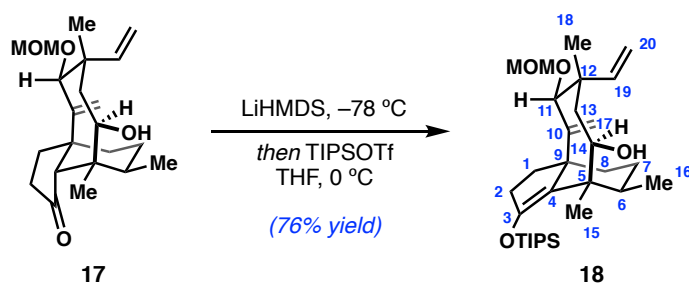
**FTIR (AT-IR):** 3508 (br), 2926, 1735, 1628, 1458, 1264, 1144, 1093, 1024, 907, 738 cm<sup>-1</sup>.

**HRMS (TOF, ES<sup>+</sup>):** calc'd for C<sub>22</sub>H<sub>35</sub>O<sub>4</sub> [M+H]<sup>+</sup> 363.2535, found 363.2536.

**$[\alpha]_D^{23}$ :** +155° ( $c = 0.330$ , CHCl<sub>3</sub>).

**Melting point:** 142.0–143.4 °C

### Preparation of silyl enol ether (**18**):



A flame-dried 25 mL round bottom flask equipped with a stir bar was charged with tricycle **17** (129 mg, 0.356 mmol, 1 equiv) and anhydrous THF (7.1 mL) under an atmosphere of argon. The mixture was cooled to -78 °C and stirred for 5 min prior to dropwise addition of LiHMDS in THF (1.07 mL of a 1.0 M solution, 1.07 mmol, 3 equiv) over 5 min. The resulting yellow solution was stirred at -78 °C for 5 min and was then placed in an ice bath and stirred for 5 min. Subsequently, TIPSOTf (191  $\mu$ L, 0.712 mmol, 2 equiv) was added rapidly. After 3 min, the reaction was quenched at 0 °C via rapid addition of sat. aq. NaHCO<sub>3</sub> (3 mL) and vigorously stirred at 0 °C for 10 min. Thereafter, the mixture was extracted into Et<sub>2</sub>O (3 x 20 mL) and the combined organic layers were washed with sat. aq. NaHCO<sub>3</sub> (3 x 10 mL) (note: failure to quench residual TIPSOTf in this manner resulted in extensive decomposition of product upon concentration). The combined organic layers were dried over Na<sub>2</sub>SO<sub>4</sub>, filtered, and concentrated under reduced pressure to afford a pale yellow oil.

Purification was achieved via flash column chromatography on SiO<sub>2</sub> [15 g SiO<sub>2</sub>, Et<sub>2</sub>O/hexanes = 8%] to afford silyl enol ether **18** (141 mg, 0.272 mmol, 76% yield) as a puffy, viscous, colorless oil that formed a white solid upon standing in the freezer overnight.

**TLC (15% Et<sub>2</sub>O/hexanes):**  $R_f = 0.48$  (*p*-anisaldehyde).

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):**  $\delta$  6.39 (dd,  $J = 17.8, 11.3$  Hz, 1H, C<sub>19</sub>), 5.28 (dd,  $J = 17.8, 1.4$  Hz, 1H, C<sub>20</sub>), 5.17 (dd,  $J = 11.2, 1.4$  Hz, 1H, C<sub>20</sub>), 5.13 (s, 1H, C<sub>17</sub>), 5.05 (s, 1H, C<sub>17</sub>), 4.68 (d,  $J = 7.1$  Hz, 1H, OCH<sub>2</sub>OMe), 4.40 (d,  $J = 6.7$  Hz, 1H, OCH<sub>2</sub>OMe), 4.06 (m, 1H, C<sub>14</sub>), 3.64 (s, 1H, C<sub>11</sub>), 3.34 (s, 3H, OCH<sub>2</sub>OCH<sub>3</sub>), 2.53 (ddd,  $J = 15.6, 10.2, 7.5$  Hz, 1H, C<sub>2</sub>), 2.37 (dd,  $J = 15.6, 11.0, 3.8$  Hz, 1H, C<sub>2</sub>), 2.32 (dd,  $J = 10.9, 3.6$  Hz, 1H, C<sub>8</sub>), 2.11 (dd,  $J = 15.0, 6.0$  Hz, 1H, C<sub>13</sub>), 1.78 (ddd,  $J = 13.9, 10.2, 3.8$  Hz, 1H, C<sub>1</sub>), 1.64 (m, 1H, C<sub>7</sub>), 1.51 (m, 1H, C<sub>6</sub>), 1.46 (ddd,  $J = 13.9,$

6.3, 3.8 Hz, 1H, C<sub>1</sub>), 1.41 (m, 1H, C<sub>13</sub>), 1.40 (m, 1H, C<sub>7</sub>), 1.39 (m, 1H, C<sub>8</sub>), (s, 3H, C<sub>15</sub>), 1.17 (s, 3H, C<sub>18</sub>), 1.15 (m, 3H, OSi(CH(CH<sub>3</sub>)<sub>2</sub>)<sub>3</sub>), 1.12 (m, 18H, OSi(CH(CH<sub>3</sub>)<sub>2</sub>)<sub>3</sub>), 0.97 (d, *J* = 7.0 Hz, 3H, C<sub>16</sub>).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>): δ 151.8 (C<sub>10</sub>), 147.8 (C<sub>3</sub>), 140.7 (C<sub>19</sub>), 119.2 (C<sub>4</sub>), 113.9 (C<sub>20</sub>), 108.9 (C<sub>17</sub>), 92.2 (OCH<sub>2</sub>OCH<sub>3</sub>), 79.0 (C<sub>11</sub>), 67.6 (C<sub>14</sub>), 55.6 (OCH<sub>2</sub>OCH<sub>3</sub>), 51.5 (C<sub>9</sub>), 46.9 (C<sub>13</sub>), 46.6 (C<sub>5</sub>), 44.8 (C<sub>12</sub>), 44.1 (C<sub>6</sub>), 38.8 (C<sub>8</sub>), 34.9 (C<sub>1</sub>), 34.4 (C<sub>2</sub>), 28.9 (C<sub>18</sub>), 28.7 (C<sub>7</sub>), 18.19 (OSi(CH(CH<sub>3</sub>)<sub>2</sub>)<sub>3</sub>), 18.15 (OSi(CH(CH<sub>3</sub>)<sub>2</sub>)<sub>3</sub>), 18.1 (C<sub>16</sub>), 16.4 (C<sub>15</sub>), 13.6 (OSi(CH(CH<sub>3</sub>)<sub>2</sub>)<sub>3</sub>).

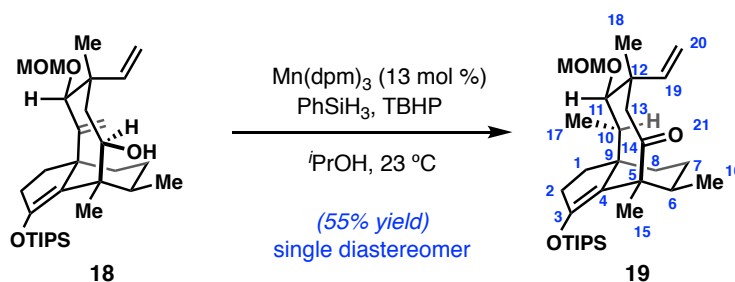
FTIR (AT-IR): 3495 (br), 2941, 2866, 2359, 2323, 1627, 1462, 1327, 1040, 1002, 882 cm<sup>-1</sup>.

HRMS (TOF, ES<sup>+</sup>): calc'd for C<sub>31</sub>H<sub>54</sub>O<sub>4</sub>SiNa [M+Na]<sup>+</sup> 541.3689, found 541.3711.

[α]<sub>D</sub><sup>23</sup>: +42.2° (*c* = 0.490, CHCl<sub>3</sub>).

Melting point: 99.8–101.1°C

### Preparation of ketone (19):



This procedure was adapted from the work of Shenvi and coworkers.<sup>7</sup> A flame-dried 25 mL Schlenk tube was charged with silyl enol ether **18** (116 mg, 0.224 mmol, 1 equiv) and adventitious water was removed via azeotropic drying with PhH (3 x 1 mL) under high vacuum. An oven-dried stir bar was added, and the atmosphere was exchanged three times for argon. Thereafter, <sup>i</sup>PrOH (3.4 mL), PhSiH<sub>3</sub> (36.3 mg, 0.336 mmol, 41.4 μL, 1.5 equiv), and *tert*-butyl hydroperoxide (89.5 μL of a 5.0 M solution in nonane, 0.448 mmol, 2 equiv) were added. The mixture was subjected to three freeze-pump-thaw cycles. Another Schlenk tube was charged with tris(2,2,6,6-tetramethyl-3,5-heptanedionato)manganese(III) (17.5 mg), and the atmosphere was exchanged three times for argon before adding <sup>i</sup>PrOH (1.4 mL). This solution was subjected to three freeze-pump-thaw cycles then purged with argon. A portion of this stock solution (1.1 mL, equating to 13.5 mg Mn(dpm)<sub>3</sub>, 0.0224 mmol, 10 mol %) was added to the substrate solution, and the reaction was stirred at ambient temperature. The reaction began as a dark orange solution but became light yellow within 10 min. After 30 min, an additional portion (300 μL) of the Mn(dpm)<sub>3</sub> stock solution was added.

After 1 h, the reaction was passed through a plug of SiO<sub>2</sub> (eluting with Et<sub>2</sub>O/hexanes = 10%), and concentrated under reduced pressure to afford a dark orange oil that was immediately purified via flash column chromatography on SiO<sub>2</sub> [15 g SiO<sub>2</sub>, Et<sub>2</sub>O/hexanes = 7%→11%] to afford ketone **19** (63.9 mg, 0.123 mmol, 55% yield) as a viscous, colorless oil.

In addition, the following were isolated: C19–C20 reduced product (9.9 mg, 0.0190 mmol, 8% yield) (15% Et<sub>2</sub>O/hexanes, R<sub>f</sub> = 0.70 [*p*-anisaldehyde, stains green]), fully reduced product (4.4 mg, 0.00842 mmol, 4% yield, 1:1 dr) (15% Et<sub>2</sub>O/hexanes, R<sub>f</sub> = 0.53 [*p*-anisaldehyde, stains dark blue]), and remaining starting material (26.6 mg, 0.0513 mmol, 23% recovered).

**Experimental Notes:** This reaction exhibits a pronounced sensitivity to both residual oxygen and water. In addition, we found it critical to perform this reaction at 23 °C, as higher temperatures promoted over-reduction and lower temperatures slowed catalysis. <sup>i</sup>PrOH was stored over activated 4 Å molecular sieves (pellets) overnight then was distilled from CaH<sub>2</sub> (10% w/v) in a flame-dried, argon-filled apparatus immediately prior to use.

**TLC (15% Et<sub>2</sub>O/hexanes):** R<sub>f</sub> = 0.60 (*p*-anisaldehyde).

**<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):** δ 6.15 (dd, *J* = 17.6, 11.1 Hz, 1H, C<sub>19</sub>), 5.28 (dd, *J* = 17.6, 1.6 Hz, 1H, C<sub>20</sub>), 5.23 (dd, *J* = 11.1, 1.6 Hz, 1H, C<sub>20</sub>), 4.69 (d, *J* = 7.0 Hz, 1H, OCH<sub>2</sub>OMe), 4.62 (d, *J* = 7.0 Hz, 1H, OCH<sub>2</sub>OMe), 3.40 (s, 3H, OCH<sub>2</sub>OCH<sub>3</sub>), 3.29 (d, *J* = 4.6 Hz, 1H, C<sub>11</sub>), 2.80 (d, *J* = 11.4 Hz, 1H, C<sub>13</sub>), 2.47 (m, 2H, C<sub>2</sub>), 2.04 (ddd, *J* = 13.8, 10.2, 5.1 Hz, 1H, C<sub>1</sub>), 1.98 (dt, *J* = 13.1, 3.0 Hz, 1H, C<sub>8</sub>), 1.95 (d, *J* = 11.4 Hz, 1H, C<sub>13</sub>), 1.91 (dq, *J* = 7.1, 4.6 Hz, 1H, C<sub>10</sub>), 1.65 (qd, *J* = 13.8, 3.4 Hz, 1H, C<sub>7</sub>), 1.57 (s, 3H, C<sub>15</sub>), 1.43 (m, 1H, C<sub>6</sub>), 1.34 (m, 1H, C<sub>7</sub>), 1.31 (m, 1H, C<sub>1</sub>), 1.26 (m, 1H, C<sub>8</sub>), 1.24 (d, *J* = 7.0 Hz, 3H, C<sub>16</sub>), 1.18 (m, 3H, OSi(CH(CH<sub>3</sub>)<sub>2</sub>)<sub>3</sub>), 1.13 (m, 18H, OSi(CH(CH<sub>3</sub>)<sub>2</sub>)<sub>3</sub>), 1.10 (s, 3H, C<sub>18</sub>), 0.83 (d, *J* = 7.1 Hz, 3H, C<sub>17</sub>).

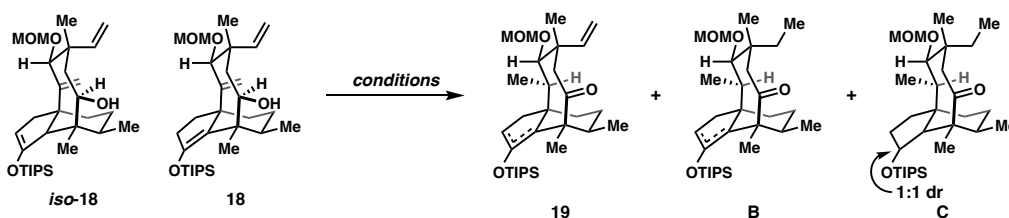
**<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):** δ 215.1 (C<sub>14</sub>=O), 148.2 (C<sub>3</sub>), 139.0 (C<sub>19</sub>), 117.8 (C<sub>4</sub>), 115.5 (C<sub>20</sub>), 99.3 (OCH<sub>2</sub>OCH<sub>3</sub>), 85.2 (C<sub>11</sub>), 56.4 (OCH<sub>2</sub>OCH<sub>3</sub>), 54.8 (C<sub>5</sub>), 51.5 (C<sub>9</sub>), 49.3 (C<sub>13</sub>), 48.3 (C<sub>12</sub>), 43.8 (C<sub>6</sub>), 39.4 (C<sub>8</sub>), 37.1 (C<sub>10</sub>), 34.0 (C<sub>2</sub>), 27.8 (C<sub>7</sub>), 27.5 (C<sub>1</sub>), 27.3 (C<sub>18</sub>), 22.2 (C<sub>15</sub>), 18.15 (OSi(CH(CH<sub>3</sub>)<sub>2</sub>)<sub>3</sub>), 18.11 (OSi(CH(CH<sub>3</sub>)<sub>2</sub>)<sub>3</sub>), 16.5 (C<sub>16</sub>), 13.6 (OSi(CH(CH<sub>3</sub>)<sub>2</sub>)<sub>3</sub>), 11.5 (C<sub>17</sub>).

**FTIR (AT-IR):** 2944, 2867, 1698, 1650, 1463, 1331, 1206, 1038, 1004 cm<sup>-1</sup>.

**HRMS (TOF, ES<sup>+</sup>):** calc'd for C<sub>31</sub>H<sub>54</sub>O<sub>4</sub>SiNa [M+Na]<sup>+</sup> 541.3689, found 541.3701.

**[α]<sub>D</sub><sup>23</sup>:** -204.8° (*c* = 1.48, CHCl<sub>3</sub>).

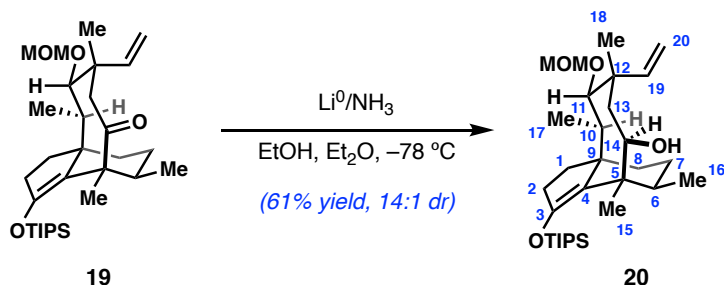
**Table S2. Radical 1,5-HAT conditions**



Entry	Substrate	[M]	[H <sup>•</sup> ]	TBHP <sup>a</sup>	solvent	conc.	T	<i>t</i>	conv.	Yield (19)	Yield (B)	Yield (C)
1	<i>iso</i> -18	Mn(dpm) <sub>3</sub> (10 mol % x 2)	Ph(O <sup>i</sup> Pr)SiH <sub>2</sub> (1 equiv)	Yes	hexanes	0.2 M	23 °C	5 min	80%	36%	22%	22%
2	<i>iso</i> -18	Mn(dpm) <sub>3</sub> (10 mol % x 2)	PhSiH <sub>3</sub> (1.5 equiv)	Yes	<sup>i</sup> PrOH	0.2 M	23 °C	1 h	69%	38%	5%	–
3	<i>iso</i> -18	Mn(dpm) <sub>3</sub> (10 mol % x 2)	PhSiH <sub>3</sub> (1.5 equiv)	Yes	<sup>i</sup> PrOH	0.04 M	23 °C	1 h	66%	50%	6%	–
4	<i>iso</i> -18	Mn(dpm) <sub>3</sub> (10 mol %)	PhSiH <sub>3</sub> (1.5 equiv)	Yes	<sup>i</sup> PrOH	0.04 M	23 °C	1 h	88%	66%	6%	–
5 <sup>b</sup>	18	Mn(dpm) <sub>3</sub> (10 mol %)	PhSiH <sub>3</sub> (1.5 equiv)	Yes	<sup>i</sup> PrOH	0.04 M	23 °C	1 h	82%	58%	8%	4%
6 <sup>b,c</sup>	18	Mn(dpm) <sub>3</sub> (10 mol % + 3 mol %)	PhSiH <sub>3</sub> (1.5 equiv)	Yes	<sup>i</sup> PrOH	0.04 M	23 °C	1 h	77%	55%	8%	4%
7	18	Mn(dpm) <sub>3</sub> (10 mol % x 2)	Ph(O <sup>i</sup> Pr)SiH <sub>2</sub> (1 equiv)	Yes	hexanes	0.2 M	23 °C	5 min	ND	30%	ND	ND
8	18	Mn(dpm) <sub>3</sub> (10 mol % x 2)	Ph(O <sup>i</sup> Pr) <sub>2</sub> SiH (1 equiv)	Yes	hexanes	0.2 M	23 °C	5 min	14%	14%	ND	ND
9	18	Co(Salen) <sup>tBu</sup> <sub>2</sub> Cl (3 mol % x 2)	PhSiH <sub>3</sub> (6 mol %)	No	PhH	0.05 M	23 °C	30 min	10%	<5%	–	–
10	18	Co(Salen) <sup>tBu</sup> <sub>2</sub> Cl (3 mol % x 2)	PhSiH <sub>3</sub> (6 mol %)	No	PhH	0.05 M	60 °C	30 min	10%	<5%	–	–
11	18	Co(Salen) <sup>tBu</sup> <sub>2</sub> Cl (10 mol %)	PhSiH <sub>3</sub> (6 mol %)	No	PhH	0.05 M	23 °C	30 min	ND	10%	–	7%

<sup>a</sup>1.5 equiv. <sup>b</sup>Under rigorously degassed conditions using freshly-distilled anhydrous <sup>i</sup>PrOH. <sup>c</sup>Reaction conducted on 0.224 mmol scale.

## Preparation of alcohol (20):



A 250 mL 3-necked flask equipped with a stir bar was equipped with a cold finger connected to a two-way valve, and the entire apparatus was flame-dried under high vacuum. After cooling to ambient temperature, the atmosphere was exchanged three times for argon, and anhydrous EtOH (13.3 mL) and Et<sub>2</sub>O (7.3 mL) were added. The mixture was cooled to -78 °C, and ammonia (53 mL) was condensed into the vessel. Subsequently, a solution of ketone **19** (41.4 mg, 0.0798 mmol, 1 equiv) in Et<sub>2</sub>O (8.3 mL) was added. After allowing the system to equilibrate for 5 min, Li<sup>0</sup> wire (124 mg, 17.9 mmol, 224 equiv) that had been freshly washed with hexanes and cut into ~5 mg pieces was added. Within 3 min, a deep blue color developed, and after 30 min, the reaction was colorless.

The apparatus was removed from the cooling bath, and ammonia was boiled off over 2 h. The resulting slurry was extracted into Et<sub>2</sub>O (100 mL), washed with sat. aq. NaHCO<sub>3</sub> (1 x 15 mL), dried over Na<sub>2</sub>SO<sub>4</sub>, filtered, and concentrated under reduced pressure to afford an oil. Purification was achieved via flash column chromatography on SiO<sub>2</sub> [3 g SiO<sub>2</sub>, Et<sub>2</sub>O/hexanes = 7%] to afford alcohol **20** (25.2 mg, 0.0487 mmol, 61% yield) as a viscous, colorless oil.

**TLC (15% Et<sub>2</sub>O/hexanes):** R<sub>f</sub> = 0.41 (*p*-anisaldehyde).

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):** δ 6.07 (ddd, *J* = 17.9, 11.2 Hz, 0.7 Hz, 1H, C<sub>19</sub>), 5.28 (dd, *J* = 17.9, 1.6 Hz, 1H, C<sub>20</sub>), 5.23 (dd, *J* = 11.2, 1.6 Hz, 1H, C<sub>20</sub>), 4.64 (d, *J* = 6.7 Hz, 1H, OCH<sub>2</sub>OMe), 4.62 (d, *J* = 6.7 Hz, 1H, OCH<sub>2</sub>OMe), 4.16 (dd, *J* = 7.1, 2.6 Hz, 1H, C<sub>14</sub>), 3.40 (s, 3H, OCH<sub>2</sub>OCH<sub>3</sub>), 3.01 (d, *J* = 5.6 Hz, 1H, C<sub>11</sub>), 2.46–2.34 (m, 2H, C<sub>2</sub>), 2.04 (ddd, *J* = 14.9, 7.8, 0.8 Hz, 1H, C<sub>13</sub>), 1.99 (m, 1H, C<sub>10</sub>), 1.96 (dt, *J* = 9.4, 3.4 Hz, 1H, C<sub>1</sub>), 1.60 (d, *J* = 14.9 Hz, 1H, C<sub>13</sub>), 1.46 (m, 1H, C<sub>7</sub>), 1.41 (m, 1H, C<sub>6</sub>), 1.40 (s, 3H, C<sub>15</sub>), 1.35 (m, 1H, C<sub>7</sub>), 1.23 (m, 1H, C<sub>8</sub>), 1.21 (m, 1H, C<sub>8</sub>), 1.17 (m, 1H, C<sub>1</sub>), 1.15 (m, 3H, OSi(CH(CH<sub>3</sub>)<sub>2</sub>)<sub>3</sub>), 1.13 (m, 18H, OSi(CH(CH<sub>3</sub>)<sub>2</sub>)<sub>3</sub>), 1.01 (s, 3H, C<sub>18</sub>), 0.99 (d, *J* = 6.3 Hz, 3H, C<sub>16</sub>), 0.85 (d, *J* = 7.1 Hz, 3H, C<sub>17</sub>).

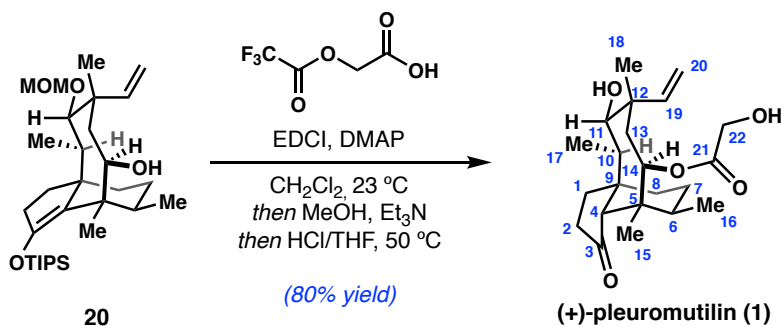
**<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>):** δ 147.0 (C<sub>3</sub>=O), 141.3 (C<sub>19</sub>), 120.5 (C<sub>4</sub>), 114.4 (C<sub>20</sub>), 99.2 (OCH<sub>2</sub>OCH<sub>3</sub>), 84.6 (C<sub>11</sub>), 68.6 (C<sub>14</sub>), 56.5 (OCH<sub>2</sub>OCH<sub>3</sub>), 50.7 (C<sub>9</sub>), 46.5 (C<sub>12</sub>), 46.1 (C<sub>13</sub>), 46.0 (C<sub>5</sub>), 43.3 (C<sub>6</sub>), 39.3 (C<sub>1</sub>), 38.2 (C<sub>10</sub>), 34.3 (C<sub>2</sub>), 30.0 (C<sub>18</sub>), 28.5 (C<sub>8</sub>), 28.3 (C<sub>7</sub>), 18.3 (C<sub>15</sub>), 18.24 (OSi(CH(CH<sub>3</sub>)<sub>2</sub>)<sub>3</sub>), 18.18 (OSi(CH(CH<sub>3</sub>)<sub>2</sub>)<sub>3</sub>), 17.8 (C<sub>16</sub>), 13.8 (OSi(CH(CH<sub>3</sub>)<sub>2</sub>)<sub>3</sub>), 11.8 (C<sub>17</sub>).

**FTIR (AT-IR):** 3493 (br), 2944, 2866, 2359, 2341, 1637, 1461, 1218, 1038, 1002 cm<sup>-1</sup>.

**HRMS (TOF, ES<sup>+</sup>):** calc'd for C<sub>31</sub>H<sub>55</sub>O<sub>4</sub>Si [(M+H)–H<sub>2</sub>]<sup>+</sup> 519.3870, found 519.3873.

**[α]<sub>D</sub><sup>23</sup>:** -52.3° (*c* = 0.342, CHCl<sub>3</sub>).

## Preparation of (+)-pleuromutilin (1):



This procedure was adapted from the work of Procter and coworkers.<sup>8</sup> A flame-dried 2 dram vial equipped with a stir bar was charged with alcohol **20** (20.2 mg, 0.0388 mmol, 1 equiv), EDCI·HCl (44.6 mg, 0.233 mmol, 6 equiv), and DMAP (28.4 mg, 0.233 mmol, 6 equiv), and the atmosphere was exchanged three times for argon. Subsequently, the vessel was charged with anhydrous CH<sub>2</sub>Cl<sub>2</sub> (1.9 mL) and 2-(2,2,2-trifluoroacetoxy)acetic acid (40.0 mg, 0.230 mmol, 6 equiv), and the reaction was stirred at ambient temperature. After 10 min, a light yellow color developed, and after 30 min, the reaction was complete by TLC analysis (30% Et<sub>2</sub>O/hexanes, R<sub>f</sub> = 0.77 [*p*-anisaldehyde, stains dark blue/purple], R<sub>f</sub>(starting material) = 0.70). Thereafter, a solution of anhydrous MeOH (31 μL, 0.776 mmol, 20 equiv) in freshly distilled Et<sub>3</sub>N (107 μL, 0.768 mmol, 20 equiv) was added, and the reaction immediately turned bright yellow. After 5 min, the reaction was judged complete by TLC analysis (30% Et<sub>2</sub>O/hexanes, R<sub>f</sub> = 0.35 [*p*-anisaldehyde, stains dark blue/purple]). A solution of HCl in THF (1.16 mL of a 2.0 M solution, 1.92 mmol) was added, and the reaction was heated to 50 °C. After 30 min, an additional portion of HCl in THF (500 μL) was added. At this time, hydrolysis of the methoxymethyl group was judged complete by TLC analysis (70% Et<sub>2</sub>O/hexanes, R<sub>f</sub> = 0.42 [*p*-anisaldehyde, stains dark blue/black]), and after 2 h global hydrolysis was complete.

The reaction was cooled to 0 °C and was cautiously quenched with sat. aq. NaHCO<sub>3</sub> (3 mL). After warming to ambient temperature, the crude mixture was extracted into Et<sub>2</sub>O (3 x 5 mL), dried over Na<sub>2</sub>SO<sub>4</sub>, filtered, and concentrated under reduced pressure to afford an orange oil. Purification was achieved via flash column chromatography on SiO<sub>2</sub> [1.5 g SiO<sub>2</sub>, Et<sub>2</sub>O/hexanes = 50%→70%] to afford (+)-pleuromutilin **1** (11.8 mg, 0.0312 mmol, 80% yield) as a white solid.

**TLC (70% Et<sub>2</sub>O/hexanes):** R<sub>f</sub> = 0.22 (*p*-anisaldehyde).

**<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):** δ 6.50 (dd, *J* = 17.4, 11.0 Hz, 1H, C<sub>19</sub>), 5.85 (d, *J* = 8.6 Hz, 1H, C<sub>14</sub>), 5.37 (dd, *J* = 11.0, 1.3 Hz, 1H, C<sub>20</sub>), 5.22 (dd, *J* = 17.4, 1.4 Hz, 1H, C<sub>20</sub>), 4.05 (qd, *J* = 17.1, 5.4 Hz, 2H, C<sub>22</sub>), 3.34 (dd, *J* = 10.8, 6.6 Hz, 1H, C<sub>11</sub>), 2.35 (t, *J* = 5.5 Hz, 1H, C<sub>22</sub>-OH), 2.33 (m, 1H, C<sub>10</sub>), 2.25 (m, 1H, C<sub>2</sub>), 2.22 (m, 1H, C<sub>2</sub>), 2.11 (br s, 1H, C<sub>4</sub>), 2.10 (dd, *J* = 16.0, 8.7 Hz, 1H, C<sub>13</sub>), 1.79 (dq, *J* = 14.5, 3.1 Hz, 1H, C<sub>8</sub>), 1.68 (m, 1H, C<sub>6</sub>), 1.66 (m, 1H, C<sub>1</sub>), 1.55 (dd, *J* = 13.8, 2.7 Hz, 1H, C<sub>7</sub>), 1.51 (m, 1H, C<sub>1</sub>), 1.46 (br m, 1H, C<sub>12</sub>-OH), 1.44 (s, 3H, C<sub>15</sub>), 1.40 (ddd, *J* = 13.8, 6.0, 2.7 Hz, 1H, C<sub>7</sub>), 1.33 (d, *J* = 16.0 Hz, 1H, C<sub>13</sub>), 1.19 (s, 3H, C<sub>18</sub>), 1.15 (td, *J* = 14.3, 4.4 Hz, 1H, C<sub>8</sub>), 0.91 (d, *J* = 7.1 Hz, 3H, C<sub>17</sub>), 0.72 (d, *J* = 7.1 Hz, 3H, C<sub>16</sub>).

**<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>):** δ 216.8 (C<sub>3</sub>=O), 172.1 (C<sub>21</sub>=O), 138.8 (C<sub>19</sub>), 117.4 (C<sub>20</sub>), 74.5 (C<sub>11</sub>), 69.8 (C<sub>14</sub>), 61.3 (C<sub>22</sub>), 58.0 (C<sub>4</sub>), 45.4 (C<sub>9</sub>), 44.7 (C<sub>13</sub>), 44.0 (C<sub>12</sub>), 41.8 (C<sub>5</sub>), 36.6 (C<sub>6</sub>), 36.0 (C<sub>10</sub>), 34.4 (C<sub>2</sub>), 30.4 (C<sub>8</sub>), 26.8 (C<sub>7</sub>), 26.3 (C<sub>18</sub>), 24.8 (C<sub>1</sub>), 16.6 (C<sub>16</sub>), 14.7 (C<sub>15</sub>), 11.5 (C<sub>17</sub>).

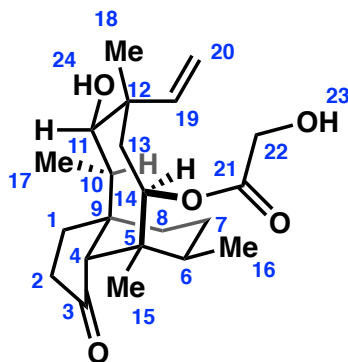
**FTIR (AT-IR):** 3437 (br), 2931, 1728, 1454, 1374, 1267, 1215, 1153, 1094, 1015, 915, 858, 734 cm<sup>-1</sup>.

**HRMS (TOF, ES<sup>+</sup>):** calc'd for C<sub>22</sub>H<sub>34</sub>O<sub>5</sub>Na [M+Na]<sup>+</sup> 401.2304, found 401.2296.

**[α]<sub>D</sub><sup>23</sup>:** +33.4° (*c* = 0.252, CHCl<sub>3</sub>).

**[α]<sub>D</sub><sup>23</sup>:** +33° (*c* = 0.25, CHCl<sub>3</sub>).<sup>9</sup>

**Table S3. Comparison of <sup>1</sup>H NMR data for (+)-pleuromutilin (1)**



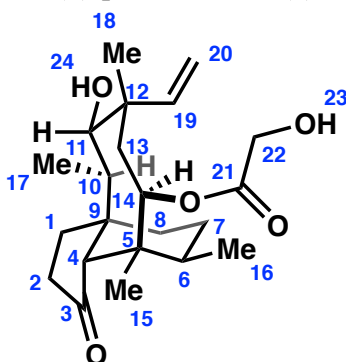
Proton Number	Natural (+)-Pleuromutilin <sup>§</sup> <sup>1</sup> H NMR, 500 MHz, CDCl <sub>3</sub> <sup>1</sup> H [δ, multi, <i>J</i> (Hz)]	This Work, Synthetic (+)-Pleuromutilin <sup>1</sup> H NMR, 500 MHz, CDCl <sub>3</sub> <sup>1</sup> H [δ, multi, <i>J</i> (Hz)]
1 $\alpha$	1.41–1.53 (m)	1.41–1.52 (m)
1 $\beta$	1.61–1.73 (m)	1.61–1.73 (m)
2 $\alpha$	2.16–2.30 (m)	2.16–2.30 (m)
2 $\beta$	2.16–2.30 (m)	2.16–2.30 (m)
3		
4	2.11 (s)	2.11 (s)
5		
6	1.61–1.73 (m)	1.61–1.73 (m)
7 $\alpha$	1.55 (dd, <i>J</i> = 13.8, 2.7 Hz)	1.55 (dd, <i>J</i> = 13.8, 2.7 Hz)
7 $\beta$	1.40 (ddd, <i>J</i> = 13.8, 6.0, 2.7 Hz)	1.40 (ddd, <i>J</i> = 13.8, 6.0, 2.7 Hz)
8 $\alpha$	1.79 (dq, <i>J</i> = 14.5, 3.1 Hz)	1.79 (dq, <i>J</i> = 14.5, 3.1 Hz)
8 $\beta$	1.15 (td, <i>J</i> = 14.3, 4.4 Hz)	1.15 (td, <i>J</i> = 14.3, 4.4 Hz)
9		
10	2.29–2.40 (m)	2.29–2.40 (m)
11	3.34 (dd, <i>J</i> = 10.8, 6.6 Hz)	3.34 (dd, <i>J</i> = 10.8, 6.6 Hz)
12		
13 $\alpha$	2.10 (dd, <i>J</i> = 16.0, 8.7 Hz)	2.10 (dd, <i>J</i> = 16.0, 8.7 Hz)
13 $\beta$	1.33 (d, <i>J</i> = 16.0 Hz)	1.33 (d, <i>J</i> = 16.0 Hz)
14	5.85 (d, <i>J</i> = 8.6 Hz)	5.85 (d, <i>J</i> = 8.6 Hz)
15	1.44 (s)	1.44 (s)
16	0.71 (d, <i>J</i> = 7.1 Hz)	0.71 (d, <i>J</i> = 7.1 Hz)
17	0.90 (d, <i>J</i> = 7.1 Hz)	0.90 (d, <i>J</i> = 7.1 Hz)
18	1.18 (s)	1.18 (s)
19	6.50 (dd, <i>J</i> = 17.4, 11.0 Hz)	6.50 (dd, <i>J</i> = 17.4, 11.0 Hz)
20 $\alpha$	5.37 (dd, <i>J</i> = 11.0, 1.4 Hz)	5.37 (dd, <i>J</i> = 11.0, 1.3 Hz)
20 $\beta$	5.22 (dd, <i>J</i> = 17.4, 1.4 Hz)	5.22 (dd, <i>J</i> = 17.4, 1.4 Hz)
21		
22	4.05 (qd, <i>J</i> = 17.1, 5.4 Hz)	4.05 (qd, <i>J</i> = 17.1, 5.4 Hz)
23	2.30–2.40 (br)*	2.30–2.40 (br)*
24	1.44–1.52 (br)*	1.44–1.52 (br)*



\*Signals disappeared upon D<sub>2</sub>O quench

§Spectrum acquired using a sample of natural (+)-pleuromutilin purchased from Sigma-Aldrich (SML0285-5MG, Lot# 032M4709V)

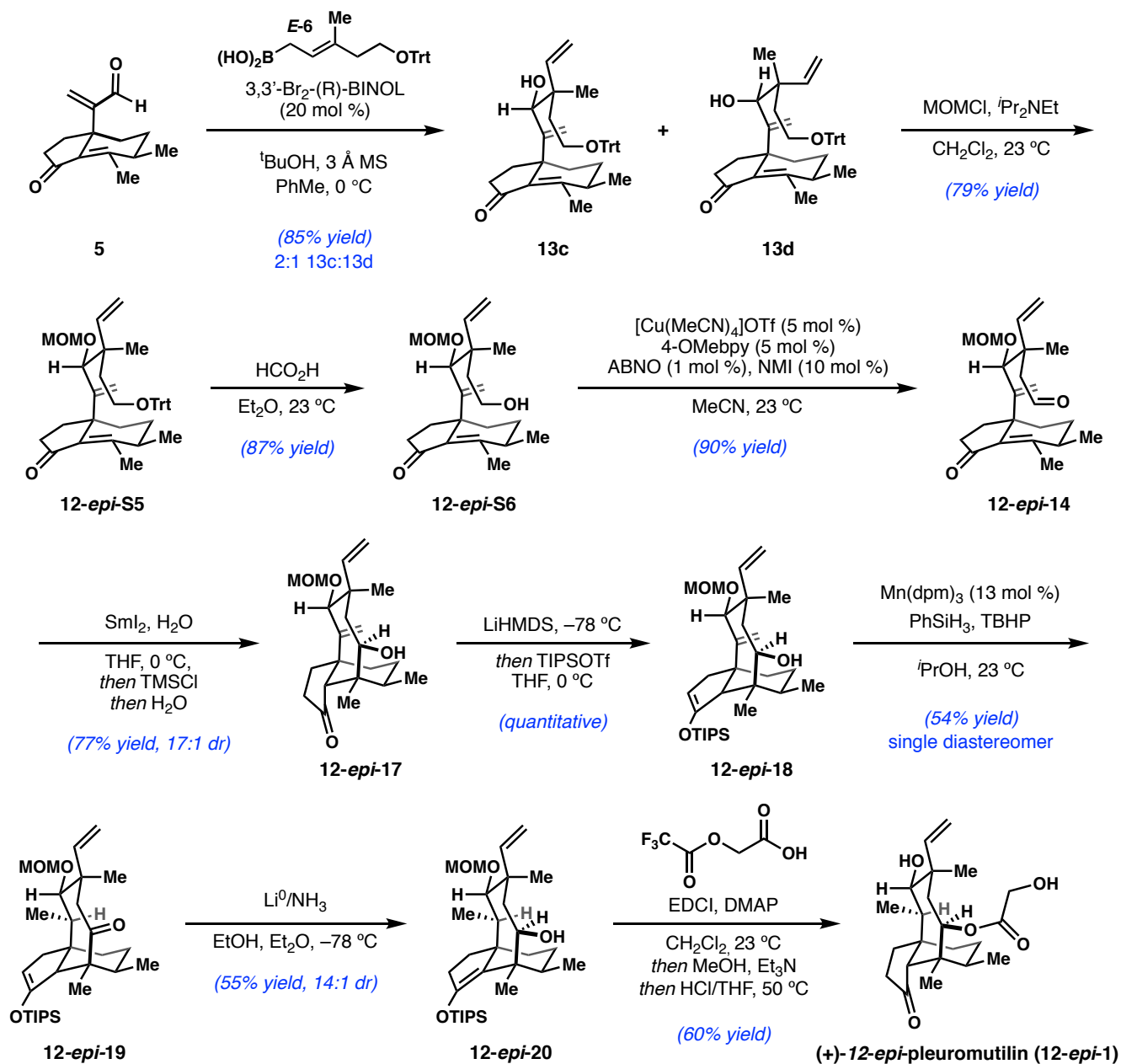
**Table S4. Comparison of <sup>13</sup>C NMR data for (+)-pleuromutilin (1)**



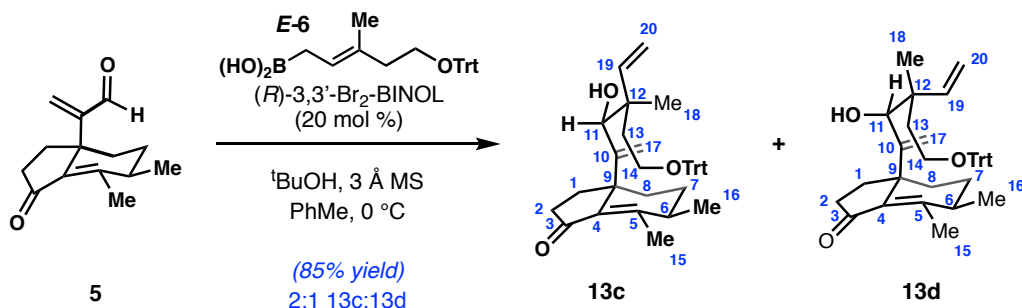
Carbon Number	Schulz and Berner Report <sup>10</sup> , Natural (+)-Pleuromutilin <sup>13</sup> C NMR, 90 MHz, CDCl <sub>3</sub> <sup>13</sup> C (δ) ppm	This Work, Synthetic (+)-Pleuromutilin <sup>13</sup> C NMR, 126 MHz, CDCl <sub>3</sub> <sup>13</sup> C (δ) ppm	Chemical Shift Difference
1	24.9	24.8	0.1
2	34.5	34.4	0.1
3	216.8	216.8	0
4	58.2	58.0	0.2
5	41.9	41.8	0.1
6	36.7	36.6	0.1
7	26.9	26.8	0.1
8	30.4	30.4	0
9	45.5	45.4	0.1
10	36.1	36.0	0.1
11	74.7	74.5	0.2
12	44.1	44.0	0.1
13	44.9	44.7	0.2
14	69.9	69.8	0.1
15	14.8	14.7	0
16	16.6	16.6	0
17	11.5	11.5	0
18	26.5	26.3	0.2
19	138.9	138.8	0.1
20	117.3	117.4	0.1
21	172.2	172.1	0.1
22	61.4	61.3	0.1

### iii. Synthesis of (+)-12-*epi*-pleuromutilin

Scheme S3. Enal (5) to (+)-12-*epi*-pleuromutilin (12-*epi*-1).



## Preparation of 12-*epi* (13c) and 11-*epi* (13d) crotylation adducts:



This procedure was adapted from the work of Szabó and coworkers.<sup>5</sup> In a nitrogen-filled glovebox, a flame-dried, 50 mL Schlenk flask equipped with a stir bar was charged with freshly activated 3 Å molecular sieves (pellets) (613 mg), allylboronic acid *E*-6 (11.5 mL of a 0.15 M solution, 1.68 mmol, 1 equiv, see S40), (*R*)-3,3'-Br<sub>2</sub>-BINOL (149 mg, 0.336 mmol, 20 mol %), freshly distilled <sup>t</sup>BuOH (483 μL, 5.09 mmol, 3 equiv), and a solution of the enal hydrindanone **5** (367 mg, 1.68 mmol, 1 equiv) in dry, degassed PhMe (1.68 mL). The resulting heterogeneous mixture was sealed, removed from the glovebox, then placed in a pre-equilibrated 0 °C bath and stirred.

After 40 h, the reaction was quenched with MeOH (5 mL), stirred for 5 min, filtered, and concentrated under reduced pressure to afford a viscous residue. Purification was achieved via flash column chromatography on SiO<sub>2</sub> [100 g SiO<sub>2</sub>, Acetone/hexanes = 4%→15%] to afford **13c** and a mixture of **13d** and residual (*R*)-3,3'-Br<sub>2</sub>-BINOL (fractions 71–85). The volatiles were concentrated under reduced pressure to afford **13c** (566 mg, 1.01 mmol, 60% yield) as a puffy white solid and the **13d**/BINOL mixture, respectively.

The **13d**/BINOL mixture was subjected to flash column chromatography on SiO<sub>2</sub> [100 g SiO<sub>2</sub>, Et<sub>2</sub>O/hexanes = 40%] to afford (*R*)-3,3'-Br<sub>2</sub>-BINOL and **13d** (237 mg, 0.423 mmol, 25% yield) as a puffy white solid.

**Experimental Note:** It is critical that all operations be carried out in a rigorously oxygen-free environment. Failure to do so will result in rapid decomposition of the allylboronic acid.

### 12-*epi* crotylation adduct (**13c**)

**TLC (20% acetone/hexanes):** *R*<sub>f</sub> = 0.54 (UV, *p*-anisaldehyde).

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):** δ 7.43 (dd, *J* = 8.4, 1.3 Hz, 6H, O*CPh*<sub>3</sub>), 7.34 – 7.19 (m, 9H, O*CPh*<sub>3</sub>), 6.15 (dd, *J* = 17.8, 10.9 Hz, 1H, C<sub>19</sub>), 5.59 (s, 1H, C<sub>17</sub>), 5.04 (dd, *J* = 10.9, 1.2 Hz, 1H, C<sub>20</sub>), 4.92 (dd, *J* = 17.8, 1.3 Hz, 1H, C<sub>20</sub>), 4.76 (s, 1H, C<sub>17</sub>), 4.01 (d, *J* = 6.7 Hz, 1H, C<sub>11</sub>), 3.21 (dt, *J* = 10.0, 6.3 Hz, 1H, C<sub>14</sub>), 3.11 (ddd, *J* = 9.9, 7.4, 5.4 Hz, 1H, C<sub>14</sub>), 2.54 (d, *J* = 7.0 Hz, 1H, OH), 2.22 – 2.05 (m, 8H, C<sub>1</sub>, C<sub>2</sub>, C<sub>6</sub>, C<sub>8</sub>), 1.92 (dd, *J* = 13.5, 6.2 Hz, 1H, C<sub>13</sub>), 1.80 (dd, *J* = 12.9, 6.9 Hz, 1H, C<sub>13</sub>), 1.64 (dtd, *J* = 15.5, 6.1, 5.1, 3.5 Hz, 1H, C<sub>7</sub>), 1.57 – 1.46 (m, 1H, C<sub>1</sub>), 1.36 – 1.13 (m, 3H, C<sub>7</sub>, C<sub>8</sub>), 1.05 (d, *J* = 7.1 Hz, 3H, C<sub>16</sub>), 0.88 (s, 3H, C<sub>18</sub>).

**<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>):** δ 208.0 (C<sub>3</sub>=O), 152.8 (C<sub>10</sub>), 152.5 (C<sub>5</sub>), 143.9 (O*CPh*<sub>3</sub>), 142.8 (C<sub>19</sub>), 135.7 (C<sub>4</sub>), 128.6 (O*CPh*<sub>3</sub>), 127.8 (O*CPh*<sub>3</sub>), 127.0 (O*CPh*<sub>3</sub>), 118.4 (C<sub>17</sub>), 113.9 (C<sub>20</sub>), 87.4 (O*CPh*<sub>3</sub>), 74.4 (C<sub>11</sub>), 60.7 (C<sub>14</sub>), 52.0 (C<sub>9</sub>), 44.5 (C<sub>12</sub>), 40.0 (C<sub>13</sub>), 38.0 (C<sub>6</sub>), 35.5 (C<sub>2</sub>), 33.2 (C<sub>8</sub>), 32.4 (C<sub>1</sub>), 28.4 (C<sub>7</sub>), 19.9 (C<sub>18</sub>), 19.1 (C<sub>16</sub>), 17.0 (C<sub>15</sub>).

**FTIR (thin film, NaCl):** 3416, 2930, 1702, 1627, 1448, 1213, 1032, 758, 632 cm<sup>-1</sup>.

**HRMS (TOF, ES<sup>+</sup>):** calc'd for C<sub>39</sub>H<sub>44</sub>O<sub>3</sub>Na [M+Na]<sup>+</sup> 583.3188, found 583.3174.

[α]<sub>D</sub><sup>23</sup>: -72.0° (*c* = 0.41, CHCl<sub>3</sub>).

### 11-*epi* crotylation adduct (**13d**)

**TLC (40% Et<sub>2</sub>O/hexanes):** *R*<sub>f</sub> = 0.14 (UV, *p*-anisaldehyde).

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):** δ 7.46 – 7.39 (m, 6H, OCP<sub>h</sub><sub>3</sub>), 7.33 – 7.20 (m, 9H, OCP<sub>h</sub><sub>3</sub>), 6.15 (dd, *J* = 17.8, 10.9 Hz, 1H, C<sub>19</sub>), 5.62 (s, 1H, C<sub>17</sub>), 5.04 (dd, *J* = 10.9, 1.3 Hz, 1H, C<sub>20</sub>), 4.95 (dd, *J* = 17.8, 1.4 Hz, 1H, C<sub>20</sub>), 4.77 (s, 1H, C<sub>17</sub>), 3.95 (d, *J* = 7.3 Hz, 1H, C<sub>11</sub>), 3.26 – 3.16 (m, 1H, C<sub>14</sub>), 3.15 – 3.05 (m, 1H, C<sub>14</sub>), 2.62 (d, *J* = 7.4 Hz, 1H, OH), 2.47 (dd, *J* = 12.2, 7.9 Hz, 1H, C<sub>2</sub>), 2.32 – 2.17 (m, 1H, C<sub>8</sub>), 2.15 (d, *J* = 5.9 Hz, 1H, C<sub>6</sub>), 2.12 (s, 3H, C<sub>15</sub>), 2.04 (dd, *J* = 18.4, 7.6 Hz, 1H, C<sub>8</sub>), 1.95 (dd, *J* = 12.5, 7.2 Hz, 1H, C<sub>13</sub>), 1.89 (d, *J* = 13.2 Hz, 1H, C<sub>1</sub>), 1.85 – 1.76 (m, 1H, C<sub>13</sub>), 1.65 – 1.56 (m, 1H, C<sub>7</sub>), 1.42 (td, *J* = 12.5, 7.9 Hz, 1H, C<sub>2</sub>), 1.33 – 1.11 (m, 3H, C<sub>1</sub>, C<sub>7</sub>), 1.06 (d, *J* = 7.1 Hz, 3H, C<sub>16</sub>), 0.89 (s, 3H, C<sub>18</sub>).

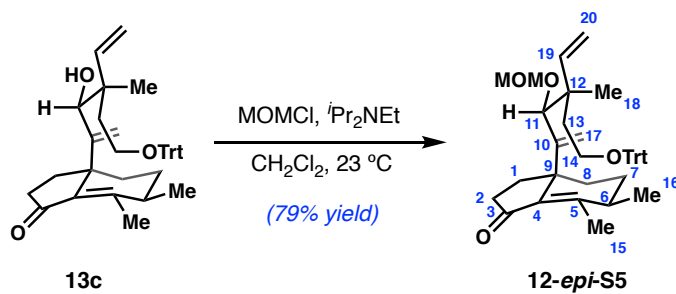
**<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>):** δ 208.4 (C<sub>3</sub>=O), 152.2 (C<sub>10</sub>), 151.0 (C<sub>5</sub>), 143.9 (OCPh<sub>3</sub>), 142.9 (C<sub>19</sub>), 136.3 (C<sub>4</sub>), 128.6 (OCPh<sub>3</sub>), 127.8 (OCPh<sub>3</sub>), 127.0 (OCPh<sub>3</sub>), 118.7 (C<sub>17</sub>), 113.9 (C<sub>20</sub>), 87.5 (OCPh<sub>3</sub>), 74.7 (C<sub>11</sub>), 60.7 (C<sub>14</sub>), 52.0 (C<sub>9</sub>), 44.3 (C<sub>12</sub>), 40.2 (C<sub>13</sub>), 37.5 (C<sub>6</sub>), 35.8 (C<sub>8</sub>), 32.7 (C<sub>1</sub>), 32.5 (C<sub>2</sub>), 28.2 (C<sub>7</sub>), 20.4 (C<sub>18</sub>), 19.2 (C<sub>16</sub>), 16.8 (C<sub>15</sub>).

**FTIR (thin film, NaCl):** 3451, 2930, 1702, 1630, 1449, 1214, 1066, 923, 759, 705 cm<sup>-1</sup>.

**HRMS (TOF, ES+):** calc'd for C<sub>39</sub>H<sub>44</sub>O<sub>3</sub>Na [M+Na]<sup>+</sup> 583.3188, found 583.3178.

**[α]<sub>D</sub><sup>23</sup>:** –53.4° (*c* = 0.585, CHCl<sub>3</sub>).

### Preparation of MOM protected crotylation adduct (12-*epi*-S5):



A flame-dried, 50 mL round bottom flask equipped with a stir bar was charged with alcohol **13c** (535 mg, 0.954 mmol, 1 equiv), CH<sub>2</sub>Cl<sub>2</sub> (4.8 mL), and freshly distilled <sup>*i*</sup>Pr<sub>2</sub>NEt (4.3 mL, 24.7 mmol, 26 equiv). To the homogeneous solution was added chloromethyl methyl ether (1.8 mL, 23.8 mmol, 25 equiv) dropwise over 10 min, taking care to vent HCl fumes formed via the use of a needle. The reaction was stirred at ambient temperature for 20 h. The resulting viscous, orange mixture was quenched via addition of sat. aq. NaHCO<sub>3</sub> (20 mL) and stirred at ambient temperature for 30 min. The aqueous layer was extracted with CH<sub>2</sub>Cl<sub>2</sub> (3 x 10 mL) and washed with H<sub>2</sub>O (1 x 10 mL). The combined organic layers were washed with brine (1 x 10 mL), dried over Na<sub>2</sub>SO<sub>4</sub>, and concentrated via distillation to afford a viscous, dark orange residue.

Purification was achieved via flash column chromatography on SiO<sub>2</sub> [50 g SiO<sub>2</sub>, Et<sub>2</sub>O/hexanes = 20%] to afford MOM ether **12-*epi*-S5** (455 mg, 0.75 mmol, 79% yield) as a puffy white solid.

**TLC (40% Et<sub>2</sub>O/hexanes):** R<sub>f</sub> = 0.56 (UV, *p*-anisaldehyde).

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):** δ 7.42 (m, 6H, OCP<sub>h</sub><sub>3</sub>), 7.32 – 7.17 (m, 9H, OCP<sub>h</sub><sub>3</sub>), 5.88 (dd, *J* = 17.7, 10.9 Hz, 1H, C<sub>19</sub>), 5.49 (s, 1H, C<sub>17</sub>), 4.93 (dd, *J* = 10.9, 1.2 Hz, 1H, C<sub>20</sub>), 4.86 (s, 1H, C<sub>17</sub>), 4.79 (dd, *J* = 17.7, 1.2 Hz, 1H, C<sub>20</sub>), 4.59 (d, *J* = 6.7 Hz, 1H, OCH<sub>2</sub>OCH<sub>3</sub>), 4.55 (d, *J* = 6.7 Hz, 1H, OCH<sub>2</sub>OCH<sub>3</sub>), 3.84 (s, 1H, C<sub>11</sub>), 3.38 (s, 3H, OCH<sub>2</sub>OCH<sub>3</sub>), 3.14 – 3.00 (m, 2H, C<sub>14</sub>), 2.22 – 2.04 (m, 8H, C<sub>1</sub>, C<sub>2</sub>, C<sub>6</sub>, C<sub>7</sub>, C<sub>15</sub>), 1.98 – 1.81 (m, 2H, C<sub>13</sub>), 1.67 – 1.57 (m, 1H, C<sub>8</sub>), 1.56 – 1.40 (m, 1H, C<sub>1</sub>), 1.28 – 1.20 (m, 2H, C<sub>7</sub>, C<sub>8</sub>), 1.06 (d, *J* = 7.1 Hz, 3H, C<sub>16</sub>), 0.93 (s, 3H, C<sub>18</sub>).

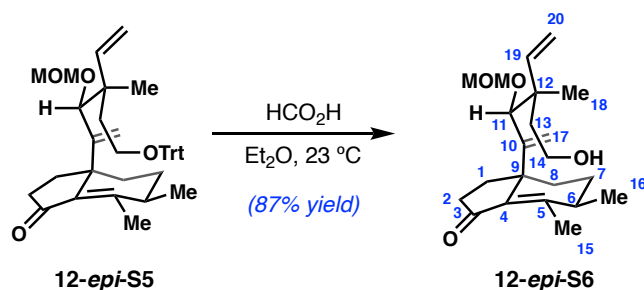
**<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>):** δ 208.1 (C<sub>3</sub>=O), 151.8 (C<sub>5</sub>), 149.8 (C<sub>10</sub>), 144.4 (OCPh<sub>3</sub>), 143.2 (C<sub>19</sub>), 136.2 (C<sub>4</sub>), 128.7 (OCPh<sub>3</sub>), 127.7 (OCPh<sub>3</sub>), 126.8 (OCPh<sub>3</sub>), 121.4 (C<sub>17</sub>), 113.8 (C<sub>20</sub>), 96.4 (OCH<sub>2</sub>OCH<sub>3</sub>), 86.8 (OCPh<sub>3</sub>), 82.1 (C<sub>11</sub>), 60.7 (C<sub>14</sub>), 56.4 (OCH<sub>2</sub>OCH<sub>3</sub>), 51.0 (C<sub>9</sub>), 45.3 (C<sub>12</sub>), 37.7 (C<sub>6</sub>), 36.9 (C<sub>13</sub>), 35.9 (C<sub>2</sub>), 33.4 (C<sub>7</sub>), 32.5 (C<sub>1</sub>), 28.2 (C<sub>8</sub>), 19.7 (C<sub>19</sub>), 19.1 (C<sub>16</sub>), 17.1 (C<sub>15</sub>).

**FTIR (thin film, NaCl):** 3418, 2931, 2071, 1704, 1628, 1449, 1214, 1036, 920, 760  $\text{cm}^{-1}$ .

**HRMS (TOF, ES+):** calc'd for  $\text{C}_{41}\text{H}_{48}\text{O}_4\text{Na}$   $[\text{M}+\text{Na}]^+$  627.3450, found 627.3444.

$[\alpha]_D^{23}$ :  $-52.6^\circ$  ( $c = 0.965$ ,  $\text{CHCl}_3$ ).

### Preparation of alcohol (**12-*epi*-S6**)



A flame-dried, 250 mL round bottom flask equipped with a stir bar was charged with MOM ether **12-*epi*-S5** (332 mg, 0.549 mmol, 1 equiv). Thereafter, a freshly prepared solution of formic acid (98%, 3.4 mL) and  $\text{Et}_2\text{O}$  (3.4 mL) was rapidly added, and within 5 min, the reaction was judged to be complete by TLC analysis. We found it critical to stop this reaction immediately after full conversion was achieved. Prolonged times afforded copious quantities of formate ester product. The reaction was diluted with  $\text{Et}_2\text{O}$  (15 mL) and quenched via slow addition of  $\text{NaHCO}_3$  (100 mL). The aqueous layer was extracted with  $\text{Et}_2\text{O}$  (4 x 25 mL) and washed with  $\text{H}_2\text{O}$  (1 x 10 mL). The combined organic layers were washed with brine (1 x 25 mL), dried over  $\text{Na}_2\text{SO}_4$ , and concentrated under reduced pressure to afford a viscous yellow residue.

Purification was achieved via flash column chromatography on  $\text{SiO}_2$  [7 g  $\text{SiO}_2$ ,  $\text{Et}_2\text{O}$ /hexanes = 70%] to afford alcohol **12-*epi*-S6** (173 mg, 0.477 mmol, 87% yield) as a viscous, colorless oil.

**TLC (40%  $\text{Et}_2\text{O}$ /hexanes):**  $R_f = 0.13$  (UV, *p*-anisaldehyde).

**$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):**  $\delta$  6.07 (dd,  $J = 17.8, 10.9$  Hz, 1H,  $\text{C}_{19}$ ), 5.58 (s, 1H,  $\text{C}_{17}$ ), 5.11 (dd,  $J = 10.9, 1.1$  Hz, 1H,  $\text{C}_{20}$ ), 5.03 (dd,  $J = 17.8, 1.2$  Hz, 1H,  $\text{C}_{20}$ ), 4.92 (s, 1H,  $\text{C}_{17}$ ), 4.65 (d,  $J = 6.8$  Hz, 1H,  $\text{OCH}_2\text{OCH}_3$ ), 4.59 (d,  $J = 6.8$  Hz, 1H,  $\text{OCH}_2\text{OCH}_3$ ), 3.94 (s, 1H,  $\text{C}_{11}$ ), 3.66 (td,  $J = 6.9, 3.0$  Hz, 2H,  $\text{C}_{14}$ ), 3.42 (s, 3H,  $\text{OCH}_2\text{OCH}_3$ ), 2.30 – 2.11 (m, 8H,  $\text{C}_1, \text{C}_2, \text{C}_6, \text{C}_8, \text{C}_{15}$ ), 1.89 (td,  $J = 6.8, 4.1$  Hz, 2H,  $\text{C}_{13}$ ), 1.66 – 1.54 (m, 2H,  $\text{C}_1, \text{C}_7$ ), 1.31 – 1.23 (m, 2H,  $\text{C}_7, \text{C}_8$ ), 1.11 (s, 3H), 1.07 (d,  $J = 7.0$  Hz, 3H).

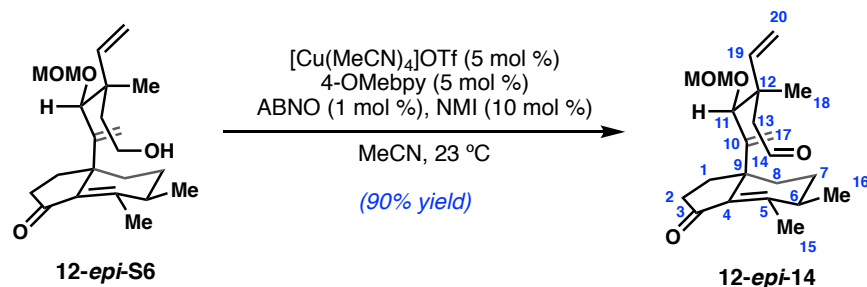
**$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ):**  $\delta$  207.9 ( $\text{C}_3=\text{O}$ ), 151.9 ( $\text{C}_5$ ), 149.8 ( $\text{C}_{10}$ ), 143.7 ( $\text{C}_{19}$ ), 136.1 ( $\text{C}_4$ ), 121.7 ( $\text{C}_{17}$ ), 114.0 ( $\text{C}_{20}$ ), 96.2 ( $\text{OCH}_2\text{OCH}_3$ ), 82.1 ( $\text{C}_{11}$ ), 59.7 ( $\text{C}_{14}$ ), 56.4 ( $\text{OCH}_2\text{OCH}_3$ ), 50.9 ( $\text{C}_9$ ), 45.4 ( $\text{C}_{12}$ ), 39.9 ( $\text{C}_{13}$ ), 37.7 ( $\text{C}_7$ ), 35.8 ( $\text{C}_2$ ), 33.4 ( $\text{C}_8$ ), 32.5 ( $\text{C}_1$ ), 28.1 ( $\text{C}_7$ ), 19.8 ( $\text{C}_{18}$ ), 19.0 ( $\text{C}_{16}$ ), 17.0 ( $\text{C}_{15}$ ).

**FTIR (thin film, NaCl):** 3417, 2931, 1704, 1627, 1455, 1212, 1152, 1036, 918, 731  $\text{cm}^{-1}$ .

**HRMS (TOF, ES+):** calc'd for  $\text{C}_{22}\text{H}_{34}\text{O}_4\text{Na}$   $[\text{M}+\text{Na}]^+$  385.2355, found 385.2344.

$[\alpha]_D^{23}$ :  $-43.8^\circ$  ( $c = 0.230$ ,  $\text{CHCl}_3$ ).

### Preparation of aldehyde (**12-*epi*-14**):



### Stahl Oxidation:<sup>6</sup>

A flame-dried, 2 dram vial equipped with a stir bar was charged with alcohol **12-*epi*-S6** (164 mg, 0.452 mmol, 1 equiv) and MeCN (2.0 mL). Thereafter, added 860  $\mu$ L of the [Cu]/bpy stock solution, 860  $\mu$ L of the NMI stock solution, and 860  $\mu$ L of the ABNO stock solution, in that order. The orange reaction was stirred at 960 rpm open to the atmosphere for 90 min. Subsequently, the resulting light blue solution was diluted with Et<sub>2</sub>O (3 mL), passed through a short pad of SiO<sub>2</sub> using Et<sub>2</sub>O as the eluent, and concentrated under reduced pressure to afford a pale yellow oil.

Purification was achieved via flash column chromatography on SiO<sub>2</sub> [8 g SiO<sub>2</sub>, Et<sub>2</sub>O/hexanes = 30%→60%] to afford aldehyde **12-*epi*-14** (148 mg, 0.411 mmol, 90% yield) as a viscous, colorless oil that solidified to a white solid upon standing in the freezer.

**Preparation of stock solutions:** See page S15.

**TLC (70% Et<sub>2</sub>O/hexanes):**  $R_f = 0.57$  (UV, *p*-anisaldehyde).

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):**  $\delta$  9.73 (dd,  $J = 4.1, 1.8$  Hz, 1H, C<sub>14</sub>), 6.08 (dd,  $J = 17.7, 10.9$  Hz, 1H, C<sub>19</sub>), 5.51 (s, 1H, C<sub>17</sub>), 5.16 (dd,  $J = 10.9, 0.7$  Hz, 1H, C<sub>20</sub>), 5.10 (dd,  $J = 17.7, 0.7$  Hz, 1H, C<sub>20</sub>), 4.99 – 4.97 (m, 1H, C<sub>17</sub>), 4.58 (d,  $J = 6.9$  Hz, 1H, OCH<sub>2</sub>OCH<sub>3</sub>), 4.51 (d,  $J = 6.9$  Hz, 1H, OCH<sub>2</sub>OCH<sub>3</sub>), 4.00 (d,  $J = 1.2$  Hz, 1H, C<sub>11</sub>), 3.40 (s, 3H, OCH<sub>2</sub>OCH<sub>3</sub>), 2.66 (dd,  $J = 15.1, 4.1$  Hz, 1H, C<sub>13</sub>), 2.49 (dd,  $J = 15.1, 1.7$  Hz, 1H, C<sub>13</sub>), 2.29 – 2.05 (m, 8H, C<sub>1</sub>, C<sub>2</sub>, C<sub>6</sub>, C<sub>8</sub>, C<sub>15</sub>), 1.68 – 1.49 (m, 2H, C<sub>1</sub>, C<sub>7</sub>), 1.32 (s, 3H, C<sub>18</sub>), 1.30 – 1.21 (m, 2H, C<sub>7</sub>, C<sub>8</sub>), 1.06 (d,  $J = 7.1$  Hz, 3H, C<sub>16</sub>).

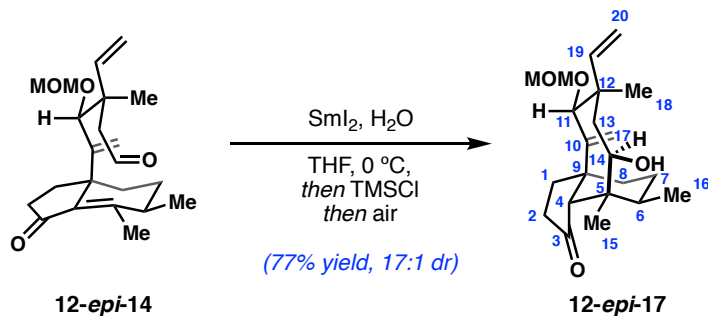
**<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>):**  $\delta$  207.8 (C<sub>14</sub>=O), 202.6 (C<sub>3</sub>=O), 141.8 (C<sub>5</sub>), 122.0 (C<sub>10</sub>), 114.8 (C<sub>19</sub>), 95.3 (OCH<sub>2</sub>OCH<sub>3</sub>), 80.4 (C<sub>11</sub>), 56.5 (OCH<sub>2</sub>OCH<sub>3</sub>), 50.7 (C<sub>9</sub>), 50.2 (C<sub>13</sub>), 45.7 (C<sub>12</sub>), 37.6 (C<sub>6</sub>), 35.9 (C<sub>2</sub>), 33.4 (C<sub>8</sub>), 32.5 (C<sub>1</sub>), 28.1 (C<sub>7</sub>), 21.8 (C<sub>18</sub>), 19.1 (C<sub>16</sub>), 17.1 (C<sub>15</sub>).

**FTIR (thin film, NaCl):** 2932, 1714, 1628, 1456, 1413, 1373, 1212, 1151, 1035, 921 cm<sup>-1</sup>.

**HRMS (TOF, ES<sup>+</sup>):** calc'd for C<sub>22</sub>H<sub>32</sub>O<sub>4</sub>Na [M+Na]<sup>+</sup> 383.2198, found 383.2182.

**$[\alpha]_D^{23}$ :** -67.3° ( $c = 0.095$ , CHCl<sub>3</sub>).

## Preparation of tricycle (12-*epi*-17)



A 25 mL Schlenk tube equipped with a stir bar was charged with a solution of aldehyde **12-*epi*-14** (75 mg, 0.208 mmol, 1 equiv) in 10.3 mL of THF that had been submitted to five freeze-pump-thaw cycles and H<sub>2</sub>O/THF (1.88 mL). The solution was cooled to 0 °C and stirred at this temperature for 5 min. Thereafter, SmI<sub>2</sub>/THF (6.3 mL, 0.63 mmol, 3 equiv) was added dropwise over 8 min. The deep blue color of SmI<sub>2</sub> was immediately quenched upon addition of each drop. The first drop afforded a yellow solution, fading to a pale yellow and almost clear by the time 1.6 equiv SmI<sub>2</sub> had been added. When 2.2 equiv SmI<sub>2</sub> had been added, the blue color became increasingly persistent and upon addition of 2.6 equiv SmI<sub>2</sub>, the reaction was dark blue/green. After stirring an additional 10 min at 0 °C, TMSCl/THF (1.9 mL, 1.05 mmol, 5 equiv TMSCl) was added dropwise over 2 min, and the reaction was stirred an additional 10 min. Throughout this time, the deep blue color was quenched to yellow. Thereafter, the reaction was removed from the ice bath and stirred open to the atmosphere for 5 min.

The resulting pale yellow solution was diluted with Et<sub>2</sub>O (50 mL), and washed with H<sub>2</sub>O (2 x 10 mL). The aqueous layer was back-extracted with Et<sub>2</sub>O (2 x 10 mL), and the combined organic layers were dried over Na<sub>2</sub>SO<sub>4</sub>, filtered, and concentrated under reduced pressure to afford a dark orange oil. Purification was achieved via flash column chromatography on SiO<sub>2</sub> [10 g SiO<sub>2</sub>, Et<sub>2</sub>O/hexanes = 30%] to afford tricycle **12-*epi*-17** (62 mg, 0.172 mmol, 77% yield) as a white solid.

**Preparation of SmI<sub>2</sub>:** See page S16.

**Stock solution of TMSCl:** See page S16.

**Stock solution of H<sub>2</sub>O/THF:** A solution of H<sub>2</sub>O (60 μL) in THF (5.0 mL) was submitted to five freeze-pump-thaw cycles.

**TLC (50% Et<sub>2</sub>O/hexanes):** R<sub>f</sub> = 0.50 (*p*-anisaldehyde).

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):** δ 5.98 (dd, *J* = 17.5, 10.8 Hz, 1H, C<sub>19</sub>), 5.42 (d, *J* = 0.9 Hz, 1H, C<sub>17</sub>), 5.32 (t, *J* = 0.7 Hz, 1H, C<sub>17</sub>), 5.09 (dd, *J* = 17.5, 1.0 Hz, 1H, C<sub>20</sub>), 5.03 (dd, *J* = 10.8, 1.0 Hz, 1H, C<sub>20</sub>), 4.54 (d, *J* = 7.1 Hz, 1H, OCH<sub>2</sub>OCH<sub>3</sub>), 4.34 (dd, *J* = 7.1, 0.5 Hz, 1H, OCH<sub>2</sub>OCH<sub>3</sub>), 4.12 (d, *J* = 6.2 Hz, 1H, C<sub>14</sub>), 4.00 (s, 1H, C<sub>11</sub>), 3.34 (s, 3H, OCH<sub>2</sub>OCH<sub>3</sub>), 2.39 – 2.16 (m, 3H, C<sub>2</sub>, C<sub>4</sub>), 2.13 – 1.96 (m, 3H, C<sub>1</sub>, C<sub>8</sub>, C<sub>13</sub>), 1.72 (dtt, *J* = 15.9, 6.2, 2.9 Hz, 1H, C<sub>6</sub>), 1.63 (dd, *J* = 13.1, 3.3 Hz, 1H, C<sub>7</sub>), 1.46 – 1.37 (m, 1H, C<sub>7</sub>), 1.29 (s, 4H, C<sub>1</sub>, C<sub>15</sub>), 1.24 (d, *J* = 0.8 Hz, 3H, C<sub>18</sub>), 1.08 (dd, *J* = 15.8, 1.2 Hz, 1H, C<sub>8</sub>), 0.98 (d, *J* = 6.8 Hz, 3H, C<sub>16</sub>).

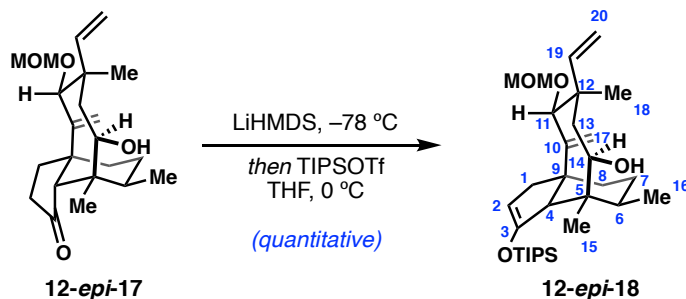
**<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>):** δ 216.6 (C<sub>3</sub>=O), 148.1 (C<sub>19</sub>), 147.9 (C<sub>10</sub>), 112.8 (C<sub>17</sub>), 111.3 (C<sub>20</sub>), 92.3 (OCH<sub>2</sub>OCH<sub>3</sub>), 76.2 (C<sub>11</sub>), 67.0 (C<sub>14</sub>), 59.5 (C<sub>4</sub>), 55.9 (OCH<sub>2</sub>OCH<sub>3</sub>), 46.5 (C<sub>9</sub>), 45.7 (C<sub>8</sub>), 43.6 (C<sub>12</sub>), 42.1 (C<sub>5</sub>), 37.4 (C<sub>6</sub>), 34.9 (C<sub>2</sub>), 31.2 (C<sub>13</sub>), 29.8 (C<sub>1</sub>), 26.8 (C<sub>7</sub>), 18.2 (C<sub>16</sub>), 15.1 (C<sub>18</sub>), 13.4 (C<sub>15</sub>).

**FTIR (thin film, NaCl):** 3521, 2937, 1738, 1456, 1376, 1147, 1095, 1032, 967 cm<sup>-1</sup>.

**HRMS (FAB+)** calc'd for C<sub>22</sub>H<sub>35</sub>O<sub>4</sub> [M+H]<sup>+</sup> 363.2535, found 363.2556.

[ $\alpha$ ]<sub>D</sub><sup>23</sup>: +161.6° (*c* = 0.09, CHCl<sub>3</sub>).

**Preparation of silyl enol ether (12-*epi*-18):**



A flame-dried 1 dram vial equipped with a stir bar was charged with tricyclic **12-*epi*-17** (13.1 mg, 0.036 mmol, 1 equiv) and anhydrous THF (720  $\mu$ L) under an atmosphere of argon. The mixture was cooled to -78 °C and stirred for 5 min prior to dropwise addition of LiHMDS in THF (108  $\mu$ L of a 1.0 M solution, 0.108 mmol, 3 equiv) over 5 min. The resulting yellow solution was stirred at -78 °C for 5 min and was then placed in an ice bath and stirred for 5 min. Subsequently, TIPSOTf (22  $\mu$ L, 0.072 mmol, 2 equiv) was added rapidly. After 3 min, the reaction was quenched at 0 °C via rapid addition of sat. aq. NaHCO<sub>3</sub> (1 mL) and vigorously stirred at 0 °C for 10 min. Thereafter, the mixture was extracted into Et<sub>2</sub>O (3 x 1 mL) and the combined organic layers were washed with sat. aq. NaHCO<sub>3</sub> (3 x 1 mL) (note: failure to quench residual TIPSOTf in this manner resulted in extensive decomposition of product upon concentration). The combined organic layers were dried over Na<sub>2</sub>SO<sub>4</sub>, filtered, and concentrated under reduced pressure to afford a pale yellow oil.

Purification was achieved via flash column chromatography on SiO<sub>2</sub> [3 g SiO<sub>2</sub>, Et<sub>2</sub>O/hexanes = 8%] to afford silyl enol ether **12-*epi*-18** (19.1 mg, 0.036 mmol, quantitative yield) as a puffy, viscous, colorless oil that formed a white solid upon standing in the freezer overnight.

**TLC (30% Et<sub>2</sub>O/hexanes):** R<sub>f</sub> = 0.56 (*p*-anisaldehyde).

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):**  $\delta$  6.02 (dd, *J* = 17.5, 10.8 Hz, 1H, C<sub>19</sub>), 5.39 (s, 1H, C<sub>17</sub>), 5.23 (s, 1H, C<sub>17</sub>), 5.09 (dd, *J* = 17.5, 1.1 Hz, 1H, C<sub>20</sub>), 5.01 (dd, *J* = 10.8, 1.1 Hz, 1H, C<sub>20</sub>), 4.50 (d, *J* = 6.9 Hz, 1H, OCH<sub>2</sub>OCH<sub>3</sub>), 4.42 (q, *J* = 2.8 Hz, 2H, C<sub>2</sub>), 4.33 (d, *J* = 6.9 Hz, 1H, OCH<sub>2</sub>OCH<sub>3</sub>), 4.24 – 4.15 (m, 2H, C<sub>11</sub>, C<sub>14</sub>), 3.33 (s, 3H, OCH<sub>2</sub>OCH<sub>3</sub>), 2.81 (s, 1H, C<sub>4</sub>), 2.33 (ddd, *J* = 14.2, 3.2, 1.7 Hz, 1H, C<sub>1</sub>), 2.21 – 1.95 (m, 3H, C<sub>8</sub>, C<sub>13</sub>), 1.77 (ddq, *J* = 14.3, 7.1, 3.8 Hz, 1H, C<sub>6</sub>), 1.65 – 1.53 (m, 1H, C<sub>7</sub>), 1.45 – 1.32 (m, 2H, C<sub>1</sub>, C<sub>7</sub>), 1.32 – 1.18 (m, 6H, C<sub>18</sub>, OSi(CH(CH<sub>3</sub>)<sub>2</sub>)<sub>3</sub>), 1.15 (s, 3H, C<sub>15</sub>), 1.12 (dd, *J* = 7.2, 5.1 Hz, 18H, OSi(CH(CH<sub>3</sub>)<sub>2</sub>)<sub>3</sub>), 1.04 – 0.95 (m, 4H, C<sub>13</sub>, C<sub>16</sub>).

**<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)**  $\delta$  157.5 (C<sub>3</sub>), 149.5 (C<sub>10</sub>), 148.6 (C<sub>19</sub>), 112.0 (C<sub>17</sub>), 110.9 (C<sub>20</sub>), 98.6 (C<sub>2</sub>), 92.7 (OCH<sub>2</sub>OCH<sub>3</sub>), 77.2 (C<sub>11</sub>), 67.7 (C<sub>14</sub>), 55.9 (OCH<sub>2</sub>OCH<sub>3</sub>), 53.2 (C<sub>4</sub>), 48.9 (C<sub>9</sub>), 46.3 (C<sub>13</sub>), 43.8 (C<sub>12</sub>), 41.3 (C<sub>5</sub>), 40.9 (C<sub>1</sub>), 38.4 (C<sub>6</sub>), 30.1 (C<sub>8</sub>), 27.2 (C<sub>7</sub>), 18.3 (C<sub>16</sub>), 18.1 (OSi(CH(CH<sub>3</sub>)<sub>2</sub>)<sub>3</sub>), 17.7 (OSi(CH(CH<sub>3</sub>)<sub>2</sub>)<sub>3</sub>), 15.6 (C<sub>18</sub>), 15.3 (C<sub>15</sub>), 12.9 (OSi(CH(CH<sub>3</sub>)<sub>2</sub>)<sub>3</sub>).

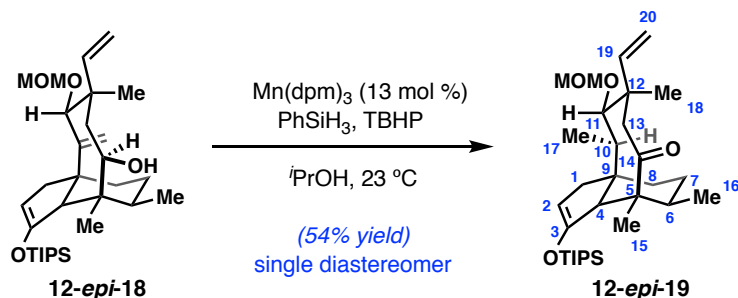
**FTIR (thin film, NaCl):** 2928, 1636, 1465, 1298, 1140, 1026, 906, 689 cm<sup>-1</sup>.

**HRMS (FAB+)** calc'd for C<sub>31</sub>H<sub>54</sub>O<sub>4</sub>Si [M+H]<sup>+</sup> 518.3791, found 518.3798.

[ $\alpha$ ]<sub>D</sub><sup>23</sup>: +31.1° (*c* = 0.15, CHCl<sub>3</sub>).



### Preparation of ketone (**12-*epi*-19**):



This procedure was adapted from the work of Shenvi and coworkers.<sup>7</sup> To a 1 dram vial was added TIPS enol ether **12-*epi*-18** (25.6 mg, 0.049 mmol, 1 equiv) and adventitious water was removed via azeotropic drying with PhH (3 x 1 mL) under high vacuum (70 mTorr). An oven dried stir bar was added, and the atmosphere was exchanged three times with argon. Thereafter, 775  $\mu\text{L}$  of a stock solution containing  $\text{PhSiH}_3$  (9.3  $\mu\text{L}$ , 0.075 mmol, 1.5 equiv) and TBHP (20  $\mu\text{L}$ , 0.100 mmol, 2 equiv) in  $i\text{PrOH}$  was added, followed by 175  $\mu\text{L}$  of a stock solution containing  $\text{Mn(dpm)}_3$  (3.0 mg, 0.00506 mmol, 0.1 equiv) in  $i\text{PrOH}$ . The reaction was stirred for 30 min at ambient temperature and another 50  $\mu\text{L}$  of the  $\text{Mn(dpm)}_3$  (0.9 mg, 0.00144 mmol, 0.03 equiv) was added. After 1 h, the reaction was passed through a plug of  $\text{SiO}_2$  (eluting with  $\text{Et}_2\text{O}$ /hexanes = 10%), and concentrated under reduced pressure to afford a dark orange oil.

Purification was achieved via flash column chromatography on  $\text{SiO}_2$  [3 g  $\text{SiO}_2$ ,  $\text{Et}_2\text{O}$ /hexanes = 7% $\rightarrow$ 11%] to afford ketone **12-*epi*-19** (13.7 mg, 0.0251 mmol, 54% yield) as a viscous, colorless oil.

**Experimental Notes:** This reaction exhibits a pronounced sensitivity to both residual oxygen and water. In addition, we found it critical to perform this reaction at 23 °C, as higher temperatures promoted over-reduction and lower temperatures slowed catalysis.  $i\text{PrOH}$  was stored over activated 4 Å molecular sieves (pellets) overnight then was distilled from  $\text{CaH}_2$  (10% w/v) in a flame-dried, argon-filled apparatus immediately prior to use.

**Preparation of stock solutions:**  $\text{PhSiH}_3$  (30  $\mu\text{L}$ ) and *tert*-butyl hydroperoxide (65  $\mu\text{L}$  of a 5.0 M solution in nonane) were dissolved in  $i\text{PrOH}$  (2.5 mL) and the homogeneous solution was submitted to three freeze-pump-thaw cycles.  $\text{Mn(dpm)}_3$  (17.3 mg) was dissolved in 1 mL  $i\text{PrOH}$  and the dark brown homogeneous solution was submitted to three freeze-pump-thaw cycles.

**TLC (30%  $\text{Et}_2\text{O}$ /hexanes):**  $R_f$  = 0.72 (*p*-anisaldehyde).

**$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ):**  $\delta$  5.96 (dd,  $J$  = 17.4, 10.7 Hz, 1H, C<sub>19</sub>), 5.09 – 4.97 (m, 2H, C<sub>20</sub>), 4.55 (d,  $J$  = 7.0 Hz, 1H,  $\text{OCH}_2\text{OCH}_3$ ), 4.53 (d,  $J$  = 7.0 Hz, 1H,  $\text{OCH}_2\text{OCH}_3$ ), 4.44 (s, 1H, C<sub>2</sub>), 3.81 (d,  $J$  = 5.8 Hz, 1H, C<sub>11</sub>), 3.37 (s, 3H,  $\text{OCH}_2\text{OCH}_3$ ), 3.22 (s, 1H, C<sub>4</sub>), 2.92 (d,  $J$  = 12.0 Hz, 1H, C<sub>13</sub>), 2.15 (ddd,  $J$  = 14.1, 3.2, 1.6 Hz, 1H, C<sub>1</sub>), 1.95 – 1.66 (m, 4H, C<sub>7</sub>, C<sub>8</sub>, C<sub>10</sub>, C<sub>13</sub>), 1.66 – 1.50 (m, 3H, C<sub>1</sub>, C<sub>6</sub>, C<sub>7</sub>), 1.34 (s, 3H, C<sub>15</sub>), 1.27 – 1.22 (m, 4H, C<sub>8</sub>,  $\text{OSi}(\text{CH}(\text{CH}_3)_2)_3$ ), 1.19 (s, 3H, C<sub>18</sub>), 1.17 (d,  $J$  = 7.0 Hz, 3H, C<sub>16</sub>), 1.13 (d,  $J$  = 2.9 Hz, 9H,  $\text{OSi}(\text{CH}(\text{CH}_3)_2)_3$ ), 1.11 (d,  $J$  = 2.9 Hz, 9H,  $\text{OSi}(\text{CH}(\text{CH}_3)_2)_3$ ).

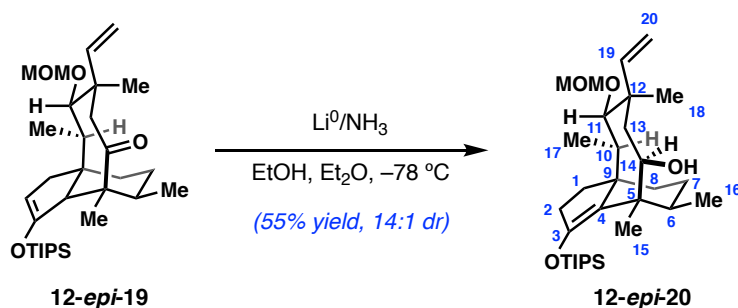
**$^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ ):**  $\delta$  214.4 (C<sub>14</sub>=O), 156.8 (C<sub>3</sub>), 147.7 (C<sub>19</sub>), 111.4 (C<sub>20</sub>), 98.6 (C<sub>2</sub>), 98.1 ( $\text{OCH}_2\text{OCH}_3$ ), 81.5 (C<sub>11</sub>), 56.6 ( $\text{OCH}_2\text{OCH}_3$ ), 51.5 (C<sub>4</sub>), 50.6 (C<sub>5</sub>), 48.1 (C<sub>9</sub>), 47.9 (C<sub>12</sub>), 46.6 (C<sub>13</sub>), 37.2 (C<sub>6</sub>), 34.5 (C<sub>1</sub>), 34.4 (C<sub>10</sub>), 32.0 (C<sub>7</sub>), 26.7 (C<sub>8</sub>), 23.2 (C<sub>15</sub>), 18.1 ( $\text{OSi}(\text{CH}(\text{CH}_3)_2)_3$ ), 16.2 (C<sub>16</sub>), 15.0 (C<sub>18</sub>), 12.9 ( $\text{OSi}(\text{CH}(\text{CH}_3)_2)_3$ ), 12.0 (C<sub>17</sub>).

**FTIR (thin film, NaCl):** 2946, 2868, 1698, 1634, 1463, 1300, 1129, 1086, 882, 692  $\text{cm}^{-1}$ .

**HRMS (FAB+):** calc'd for  $\text{C}_{31}\text{H}_{54}\text{O}_4\text{Si}$  [M]<sup>+</sup> 518.3791, found 518.3797.

**$[\alpha]_D^{23}$ :**  $-18.5^\circ$  ( $c$  = 0.195,  $\text{CHCl}_3$ ).

## Preparation of alcohol (12-*epi*-20)



A 100 mL 3-necked flask equipped with a stir bar was equipped with a cold finger connected to a two-way valve, and the entire apparatus was flame-dried under high vacuum. After cooling to ambient temperature, the atmosphere was exchanged three times for argon, and anhydrous EtOH (7.3 mL) and Et<sub>2</sub>O (4 mL) were added. The mixture was cooled to -78 °C, and ammonia (30 mL) was condensed into the vessel. Subsequently, a solution of ketone **12-*epi*-19** (23 mg, 0.0443 mmol, 1 equiv) in Et<sub>2</sub>O (5.3 mL) was added. After allowing the system to equilibrate for 5 min, Li<sup>0</sup> wire (69 mg, 9.9 mmol, 223 equiv) that had been freshly washed with hexanes and cut into ~10 mg pieces was added. Within 3 min, a deep blue color developed, and after 30 min, the reaction was colorless.

The apparatus was removed from the cooling bath, and ammonia was boiled off over 1 h. The resulting slurry was extracted into Et<sub>2</sub>O (50 mL), washed with sat. aq. NaHCO<sub>3</sub> (10 mL), dried over Na<sub>2</sub>SO<sub>4</sub>, filtered, and concentrated under reduced pressure to afford an oil.

Purification was achieved via flash column chromatography on SiO<sub>2</sub> [3 g SiO<sub>2</sub>, Et<sub>2</sub>O/hexanes = 7%] to afford alcohol **12-*epi*-20** (12.7 mg, 0.0244 mmol, 55% yield) as a viscous, colorless oil.

**TLC (15% Et<sub>2</sub>O/hexanes):** R<sub>f</sub> = 0.36 (*p*-anisaldehyde).

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):** δ 5.76 (dd, *J* = 17.6, 10.8 Hz, 1H, C<sub>19</sub>), 4.97 (dd, *J* = 17.6, 1.2 Hz, 1H, C<sub>20</sub>), 4.90 (dd, *J* = 10.8, 1.2 Hz, 1H, C<sub>20</sub>), 4.50 (d, *J* = 6.9 Hz, 1H, OCH<sub>2</sub>OCH<sub>3</sub>), 4.47 (d, *J* = 6.8 Hz, 1H, OCH<sub>2</sub>OCH<sub>3</sub>), 4.20 (t, *J* = 7.5, 6.7 Hz, 1H, C<sub>14</sub>), 3.35 (s, 3H, OCH<sub>2</sub>OCH<sub>3</sub>), 3.08 (d, *J* = 5.6 Hz, 1H, C<sub>11</sub>), 2.47 – 2.28 (m, 2H, C<sub>2</sub>), 2.22 – 2.07 (m, 2H, C<sub>10</sub>, C<sub>13</sub>), 1.98 (d, *J* = 15.3 Hz, 2H, C<sub>1</sub>, C<sub>7</sub>), 1.40 (m, 5H, C<sub>6</sub>, C<sub>7</sub>, C<sub>15</sub>), 1.26 – 1.08 (m, 27H, C<sub>1</sub>, C<sub>8</sub>, C<sub>13</sub>, C<sub>18</sub>, OSi(CH(CH<sub>3</sub>)<sub>2</sub>)<sub>3</sub>), 1.01 (d, *J* = 6.6 Hz, 3H, C<sub>16</sub>), 0.84 (d, *J* = 7.2 Hz, 3H, C<sub>17</sub>).

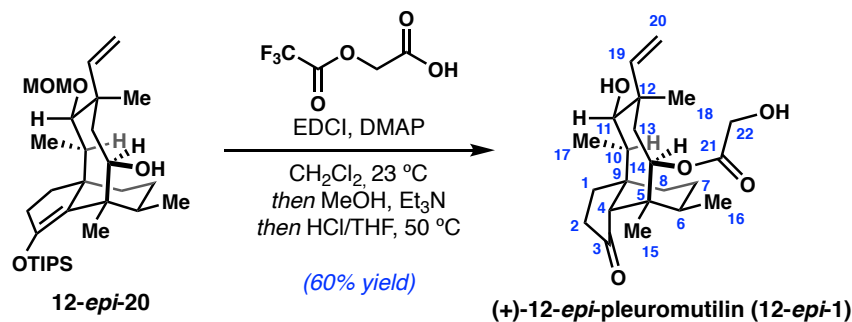
**<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>):** δ 149.1 (C<sub>19</sub>), 147.2 (C<sub>3</sub>), 120.3 (C<sub>4</sub>), 110.5 (C<sub>20</sub>), 99.0 (OCH<sub>2</sub>OCH<sub>3</sub>), 83.5 (C<sub>11</sub>), 68.2 (C<sub>14</sub>), 56.5 (OCH<sub>2</sub>OCH<sub>3</sub>), 50.6 (C<sub>9</sub>), 47.1 (C<sub>13</sub>), 46.2 (C<sub>5</sub>), 44.9 (C<sub>12</sub>), 43.2 (C<sub>6</sub>), 39.4 (C<sub>1</sub>), 36.3 (C<sub>10</sub>), 34.4 (C<sub>2</sub>), 28.4 (C<sub>7</sub>), 28.3 (C<sub>8</sub>), 18.33 (C<sub>15</sub>), 18.26 (OSi(CH(CH<sub>3</sub>)<sub>2</sub>)<sub>3</sub>), 18.2 (OSi(CH(CH<sub>3</sub>)<sub>2</sub>)<sub>3</sub>), 17.8 (C<sub>16</sub>), 14.4 (C<sub>18</sub>), 13.8 (OSi(CH(CH<sub>3</sub>)<sub>2</sub>)<sub>3</sub>), 11.4 (C<sub>17</sub>).

**FTIR (thin film, NaCl):** 2921, 2866, 1635, 1463, 1328, 1218, 1030, 1002, 913, 797 cm<sup>-1</sup>.

**HRMS (FAB+):** calc'd for C<sub>31</sub>H<sub>56</sub>O<sub>4</sub>Si [M]<sup>+</sup> 520.3948, found 520.3932.

**[α]<sub>D</sub><sup>23</sup>:** -46.3° (*c* = 0.14, CHCl<sub>3</sub>).

### Preparation of (+)-12-*epi*-pleuromutilin (12-*epi*-1):



This procedure was adapted from the work of Procter and coworkers.<sup>8</sup> A flame-dried 2 dram vial equipped with a stir bar was charged with alcohol **12-*epi*-20** (12.7 mg, 0.0244 mmol, 1 equiv), EDCI•HCl (28.0 mg, 0.146 mmol, 6 equiv), and DMAP (17.8 mg, 0.146 mmol, 6 equiv), and the atmosphere was exchanged three times for argon. Subsequently, the vessel was charged with anhydrous CH<sub>2</sub>Cl<sub>2</sub> (1.2 mL) and 2-(2,2,2-trifluoroacetoxy)acetic acid (25.0 mg, 0.146 mmol, 6 equiv), and the reaction was stirred at ambient temperature. After 10 min, a light yellow color developed, and after 30 min, the reaction was complete by TLC analysis (30% Et<sub>2</sub>O/hexanes, R<sub>f</sub> = 0.77 [*p*-anisaldehyde], R<sub>f</sub> (starting material) = 0.70). Thereafter, a solution of anhydrous MeOH (19 μL, 0.480 mmol, 20 equiv) in freshly distilled Et<sub>3</sub>N (67 μL, 0.480 mmol, 20 equiv) was added, and the reaction immediately turned bright yellow. After 5 min, the reaction was judged complete by TLC analysis (30% Et<sub>2</sub>O/hexanes, R<sub>f</sub> = 0.35 [*p*-anisaldehyde]). A solution of HCl in THF (600 μL of a 2.0 M solution, 1.2 mmol) was added, and the reaction was heated to 50 °C. After 30 min, an additional portion of HCl in THF (260 μL) was added. At this time, hydrolysis of the methoxymethyl group was judged complete by TLC analysis (70% Et<sub>2</sub>O/hexanes, R<sub>f</sub> = 0.42 [*p*-anisaldehyde]), and after 2 h global hydrolysis was complete.

The reaction was cooled to 0 °C and was cautiously quenched with sat. aq. NaHCO<sub>3</sub> (3 mL). After warming to ambient temperature, the crude mixture was extracted into Et<sub>2</sub>O (3 x 5 mL), dried over Na<sub>2</sub>SO<sub>4</sub>, filtered, and concentrated under reduced pressure to afford an orange oil.

Purification was achieved via flash column chromatography on SiO<sub>2</sub> [1.5 g SiO<sub>2</sub>, Et<sub>2</sub>O/hexanes = 50%→70%] to afford (+)-12-*epi*-pleuromutilin **12-*epi*-1** (5.4 mg, 0.0143 mmol, 60% yield) as a white solid.

**TLC (70% Et<sub>2</sub>O/hexanes):** R<sub>f</sub> = 0.26 (*p*-anisaldehyde).

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):** δ 5.81 – 5.65 (m, 2H, C<sub>14</sub>, C<sub>19</sub>), 5.27 – 5.17 (m, 2H, C<sub>20</sub>), 4.07 (dd, *J* = 17.1, 5.6 Hz, 1H, C<sub>22</sub>), 4.01 (dd, *J* = 17.1, 5.2 Hz, 1H, C<sub>22</sub>), 3.45 (d, *J* = 6.4 Hz, 1H, C<sub>11</sub>), 2.45 – 2.00 (m, 6H, C<sub>2</sub>, C<sub>4</sub>, C<sub>10</sub>, C<sub>13</sub>, C<sub>22</sub>OH), 1.81 (dq, *J* = 13.9, 2.7 Hz, 1H, C<sub>8</sub>), 1.73 – 1.58 (m, 2H, C<sub>1</sub>, C<sub>6</sub>), 1.58 – 1.45 (m, 3H, C<sub>1</sub>, C<sub>7</sub>, C<sub>11</sub>OH), 1.44 (s, 3H, C<sub>15</sub>), 1.42 – 1.36 (m, 1H, C<sub>7</sub>), 1.25 (s, 3H, C<sub>18</sub>), 1.18 – 1.04 (m, 2H, C<sub>8</sub>, C<sub>13</sub>), 0.97 (d, *J* = 7.1 Hz, 3H, C<sub>17</sub>), 0.70 (d, *J* = 7.0 Hz, 3H, C<sub>16</sub>).

**<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>):** δ 217.0 (C<sub>3</sub>=O), 172.1 (C<sub>21</sub>), 146.8 (C<sub>19</sub>), 115.4 (C<sub>20</sub>), 71.9 (C<sub>11</sub>), 70.1 (C<sub>14</sub>), 61.3 (C<sub>22</sub>), 58.2 (C<sub>4</sub>), 45.4 (C<sub>9</sub>), 45.3 (C<sub>12</sub>), 43.6 (C<sub>13</sub>), 41.8 (C<sub>5</sub>), 36.6 (C<sub>6</sub>), 34.5 (C<sub>2</sub>), 34.4 (C<sub>10</sub>), 30.1 (C<sub>8</sub>), 26.9 (C<sub>7</sub>), 25.0 (C<sub>1</sub>), 16.7 (C<sub>16</sub>), 14.8 (C<sub>15</sub>), 14.1 (C<sub>18</sub>), 10.8 (C<sub>17</sub>).

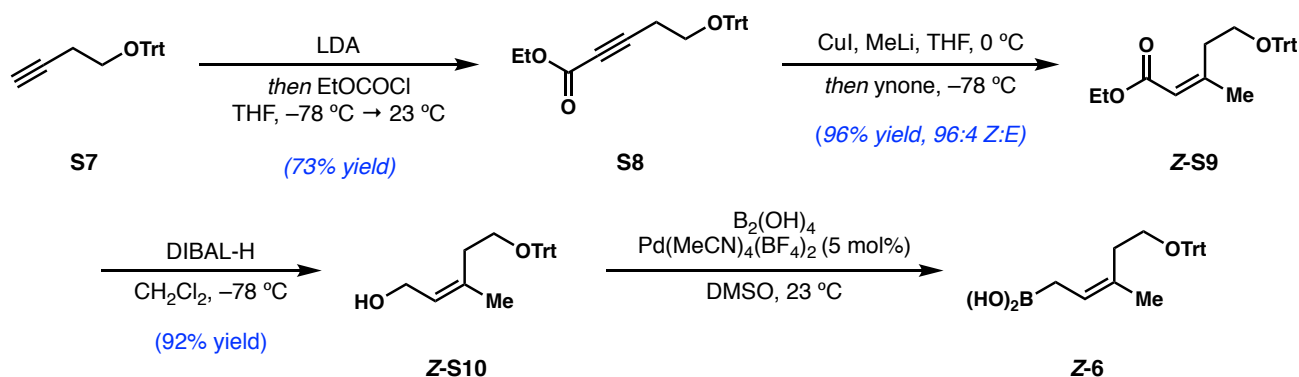
**FTIR (thin film, NaCl):** 3437, 2927, 1728, 1603, 1444, 1382, 1232, 1098, 1011, 755 cm<sup>-1</sup>.

**HRMS (FAB+):** calc'd for C<sub>22</sub>H<sub>33</sub>O<sub>5</sub> [M+H]<sup>+</sup>–H<sub>2</sub> 377.2328, found 377.2329

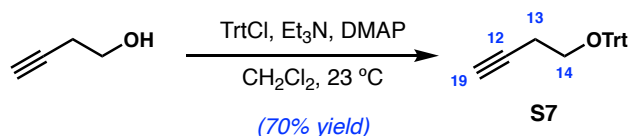
**[α]<sub>D</sub><sup>23</sup>:** +9.12° (*c* = 0.125, CHCl<sub>3</sub>).

#### iv. Synthesis of allylboronic acid (Z-6)

##### Scheme S4. Synthesis of allylboronic acid (Z-6)



##### Preparation of trityl protected alcohol (S7):

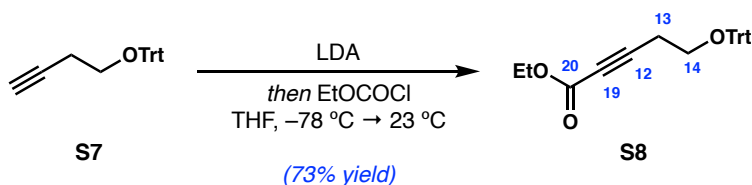


A flame-dried, 250 mL round bottom flask equipped with a stir bar was charged with 3-butyn-1-ol (7.01 g, 100.0 mmol, 7.57 mL, 1 equiv),  $\text{CH}_2\text{Cl}_2$  (150 mL, 0.67 M), and DMAP (2.44 g, 20.0 mmol, 20 mol %). To the homogeneous solution was added  $\text{Et}_3\text{N}$  (20.2 g, 200.0 mmol, 27.9 mL, 2 equiv) and trityl chloride (27.8 g, 100.0 mmol, 1 equiv). The reaction was stirred at ambient temperature for 18 h. Subsequently, added  $\text{H}_2\text{O}$  (225 mL) and extracted into  $\text{Et}_2\text{O}$  (3 x 200 mL). The combined organic layers were washed with brine (2 x 50 mL), dried over  $\text{Na}_2\text{SO}_4$ , and concentrated under reduced pressure to afford a white solid.

The solid was dissolved in a minimal volume of  $\text{CH}_2\text{Cl}_2$  (30 mL) and purified via flash column chromatography on  $\text{SiO}_2$  (300 g  $\text{SiO}_2$ ,  $\text{Et}_2\text{O}$ /hexanes = 5%) to afford product S7 (21.9 g, 70.1 mmol, 70% yield) as a white solid. Spectral data were in complete agreement with literature values.<sup>11</sup>

**TLC (20%  $\text{Et}_2\text{O}$ /hexanes):**  $R_f = 0.73$  (UV,  $\text{KMnO}_4$ ).

##### Preparation of ynoate (S8):



The atmosphere of a flame-dried, 1 L round bottom flask equipped with a stir bar was exchanged three times for nitrogen then charged with anhydrous THF (180 mL) and freshly distilled diisopropylamine (9.58 g, 94.6 mmol, 13.3 mL, 1.35 equiv). The mixture was cooled to  $-78\text{ }^\circ\text{C}$  and  $n\text{-BuLi}$  (35.9 mL of a 2.46 M solution, 88.3 mmol, 1.26 equiv) was added slowly over 15 min. The solution was stirred at

–78 °C for 5 min, warmed to 0 °C, stirred 10 min, then cooled back to –78 °C. Thereafter, a solution of the trityl-protected substrate **S7** (21.9 g, 70.1 mmol, 1 equiv) in anhydrous THF (70 mL) was added dropwise over 30 min, and the reaction was stirred for an additional 15 min. Ethyl chloroformate (22.8 g, 210.3 mmol, 20.1 mL, 3 equiv) was then added over 15 min, and the reaction was stirred for an additional 10 min before being warmed to ambient temperature and stirred for 3 h.

The reaction was quenched via addition of saturated aq. NH<sub>4</sub>Cl (150 mL) and stirred for 10 min. Thereafter, H<sub>2</sub>O (150 mL) was added, the reaction was extracted into Et<sub>2</sub>O (2 x 150 mL), the combined organic layers were dried over Na<sub>2</sub>SO<sub>4</sub>, and concentrated under reduced pressure to afford a pale yellow solid. The crude residue was suspended in hexanes (80 mL), heated to a boil, additional hexanes (100 mL) was added, and the heterogeneous suspension was filtered while hot to remove residual ammonium salts. The mixture was re-heated and slowly cooled overnight to afford product **S8** (19.6 g, 51.0 mmol, 73% yield) as white crystals.

**TLC (20% Et<sub>2</sub>O/hexanes):** R<sub>f</sub> = 0.52 (UV).

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):** δ 7.52–7.42 (m, 6H, Ph<sub>3</sub>CO), 7.34–7.20 (m, 9H, Ph<sub>3</sub>CO), 4.25 (q, *J* = 7.2 Hz, 2H, OCH<sub>2</sub>CH<sub>3</sub>), 3.31 (t, *J* = 6.9 Hz, 2H, C<sub>14</sub>), 2.63 (t, *J* = 6.9 Hz, 2H, C<sub>13</sub>), 1.34 (t, *J* = 7.1 Hz, 3H, OCH<sub>2</sub>CH<sub>3</sub>).

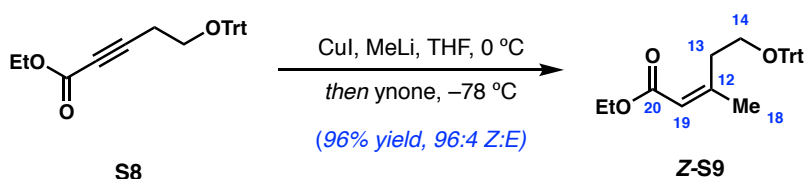
**<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>):** δ 153.7 (C<sub>20</sub>=O), 143.7 (Ph<sub>3</sub>CO), 128.6 (Ph<sub>3</sub>CO), 127.9 (Ph<sub>3</sub>CO), 127.1 (Ph<sub>3</sub>CO), 86.9 (Ph<sub>3</sub>CO), 86.5 (C<sub>12</sub>), 74.0 (C<sub>19</sub>), 61.9 (OCH<sub>2</sub>CH<sub>3</sub>), 61.1 (C<sub>14</sub>), 20.3 (C<sub>13</sub>), 14.1 (OCH<sub>2</sub>CH<sub>3</sub>).

**FTIR (AT-IR):** 2937, 2882, 2243, 1713, 1471, 1377, 1018 cm<sup>-1</sup>.

**HRMS (FAB+, *m/z*):** calc'd for C<sub>26</sub>H<sub>24</sub>O<sub>3</sub> [M]<sup>+</sup> 384.1726, found 384.1739.

**Melting point:** 89.4–90.0 °C

#### Preparation of acrylate (**Z-S9**):



In a nitrogen-filled glovebox, a flame-dried 2 L flask equipped with a large stir bar was charged with CuI (9.68 g, 50.9 mmol, 1 equiv). Anhydrous THF (390 mL) was transferred to the flask via cannula, and the heterogeneous suspension was stirred at 0 °C for 20 min. Thereafter, MeLi (64.8 mL of a 1.57 M solution in Et<sub>2</sub>O, 101.7 mmol, 2 equiv) was added dropwise over 25 min during which time the reaction went from a heterogeneous brown suspension to a nearly colorless, homogeneous solution. After an additional 5 min of stirring, the mixture was cooled to –78 °C and stirred for 20 min prior to dropwise addition of alkynoate ester **S8** (19.6 g, 50.9 mmol, 1 equiv) in anhydrous THF (130 mL) via cannula over 20 min. The reaction was stirred at –78 °C for 2 h then quenched with H<sub>2</sub>O (25 mL) at –78 °C.

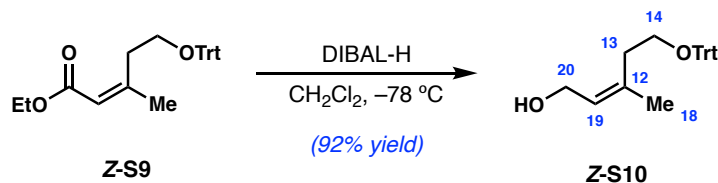
After 10 min, the solution was warmed to ambient temperature, filtered through a pad of Celite, and the Celite was rinsed with Et<sub>2</sub>O (3 x 75 mL). The combined organic layers were washed with H<sub>2</sub>O (2 x 50 mL) and brine (1 x 50 mL), dried over Na<sub>2</sub>SO<sub>4</sub>, and concentrated under reduced pressure to afford acrylate **Z-S9** (19.5 g, 48.7 mmol, 96% yield, 96:4 *Z:E*) as a viscous, yellow oil.

**TLC (10% Et<sub>2</sub>O/hexanes):** R<sub>f</sub> = 0.55 (UV).

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):** δ 7.48–7.41 (m, 6H, Ph<sub>3</sub>CO), 7.32–7.19 (m, 9H, Ph<sub>3</sub>CO), 5.74 (d, *J* = 1.4 Hz, 1H, C<sub>19</sub>), 4.13 (q, *J* = 7.1 Hz, 2H, OCH<sub>2</sub>CH<sub>3</sub>), 3.26 (t, *J* = 6.4 Hz, 2H, C<sub>14</sub>), 2.97 (t, *J* = 6.4 Hz, 2H, C<sub>13</sub>), 1.90 (d, *J* = 1.4 Hz, 3H, C<sub>18</sub>), 1.26 (t, *J* = 7.1 Hz, 3H, OCH<sub>2</sub>CH<sub>3</sub>).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>): δ 166.2 (C<sub>20</sub>=O), 157.9 (C<sub>12</sub>), 144.2 (Ph<sub>3</sub>CO), 128.7 (Ph<sub>3</sub>CO), 127.7 (Ph<sub>3</sub>CO), 126.8 (Ph<sub>3</sub>CO), 117.5 (C<sub>19</sub>), 86.6 (Ph<sub>3</sub>CO), 62.4 (C<sub>14</sub>), 59.5 (OCH<sub>2</sub>CH<sub>3</sub>), 33.7 (C<sub>13</sub>), 26.1 (C<sub>18</sub>), 14.3 (OCH<sub>2</sub>CH<sub>3</sub>).  
 FTIR (AT-IR): 2982, 2915, 2873, 1709, 1652, 1489, 1447, 1265, 1194, 1146, 779 cm<sup>-1</sup>.  
 HRMS (FAB+, m/z): calc'd for C<sub>17</sub>H<sub>27</sub>O<sub>3</sub>[(M+H)-H<sub>2</sub>]<sup>+</sup> 399.1960, found 399.1958.

#### Preparation of (Z)-3-methyl-5-(trityloxy)pent-2-en-1-ol (Z-S10):



The atmosphere of a flame-dried, 1 L round bottom flask equipped with a stir bar was exchanged three times for argon then charged with acrylate **Z-S9** (19.5 g, 48.7 mmol, 1 equiv) and anhydrous CH<sub>2</sub>Cl<sub>2</sub> (162 mL) and cooled to -78 °C. Subsequently, a freshly-prepared solution of DIBAL-H (20.8 g, 146.2 mmol, 26.1 mL) in anhydrous hexanes (122 mL) was added via cannula over 25 min. The resulting light yellow reaction was stirred at -78 °C for 2 h.

The reaction was quenched at -78 °C via slow addition of H<sub>2</sub>O (30 mL) followed by 2 M NaOH (30 mL), stirred 10 min at -78 °C, and warmed to 0 °C. Additional H<sub>2</sub>O (30 mL) was added, and the suspension was transferred to a 1 L Erlenmeyer flask containing a large stir bar and cooled to 0 °C. Subsequently, anhydrous MgSO<sub>4</sub> (100 g) was added slowly, and a strongly exothermic reaction was observed. After stirring vigorously for 20 min, the slurry was filtered through Celite, the Celite was washed with Et<sub>2</sub>O (3 x 100 mL), and concentrated under reduced pressure to afford a viscous, pale yellow oil.

Purification was achieved via flash column chromatography on SiO<sub>2</sub> [300 g SiO<sub>2</sub>, Et<sub>2</sub>O/hexanes = 30% → 50%] to afford allylic alcohol **Z-S10** (16.2 g, 45.2 mmol, 92% yield) as a viscous, colorless oil.

**TLC (30% Et<sub>2</sub>O/hexanes):** R<sub>f</sub> = 0.30 (KMnO<sub>4</sub>).

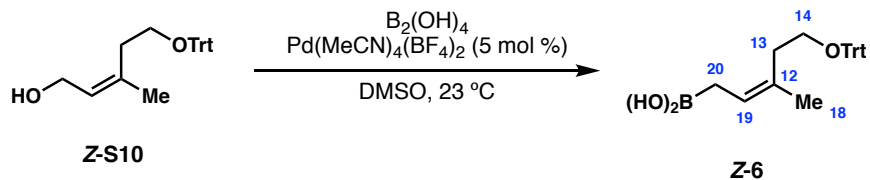
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.48–7.41 (m, 6H, Ph<sub>3</sub>CO), 7.32–7.19 (m, 9H, Ph<sub>3</sub>CO), 5.59 (t, *J* = 7.1 Hz, 1H, C<sub>19</sub>), 4.14 (d, *J* = 7.1 Hz, 2H, C<sub>20</sub>), 3.20 (t, *J* = 6.4 Hz, 2H, C<sub>14</sub>), 2.37 (t, *J* = 6.4 Hz, 2H, C<sub>13</sub>), 1.66 (s, 3H, C<sub>18</sub>), 1.50 (br m, 1H, OH).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>): δ 144.0 (Ph<sub>3</sub>CO), 137.5 (C<sub>12</sub>), 128.7 (Ph<sub>3</sub>CO), 127.8 (Ph<sub>3</sub>CO), 127.0 (Ph<sub>3</sub>CO), 126.1 (C<sub>19</sub>), 87.0 (Ph<sub>3</sub>CO), 61.8 (C<sub>14</sub>), 58.9 (C<sub>20</sub>), 32.6 (C<sub>13</sub>), 23.7 (C<sub>18</sub>).

FTIR (AT-IR): 3361 (br), 3057, 2915, 2875, 1596, 1490, 1448, 1265, 1061, 1001 cm<sup>-1</sup>.

HRMS (TOF, ES+): calc'd for C<sub>25</sub>H<sub>26</sub>O<sub>2</sub>Na [M+Na]<sup>+</sup> 381.1831, found 381.1843.

#### Preparation of trityl-protected (Z)-allylboronic acid (Z-6):

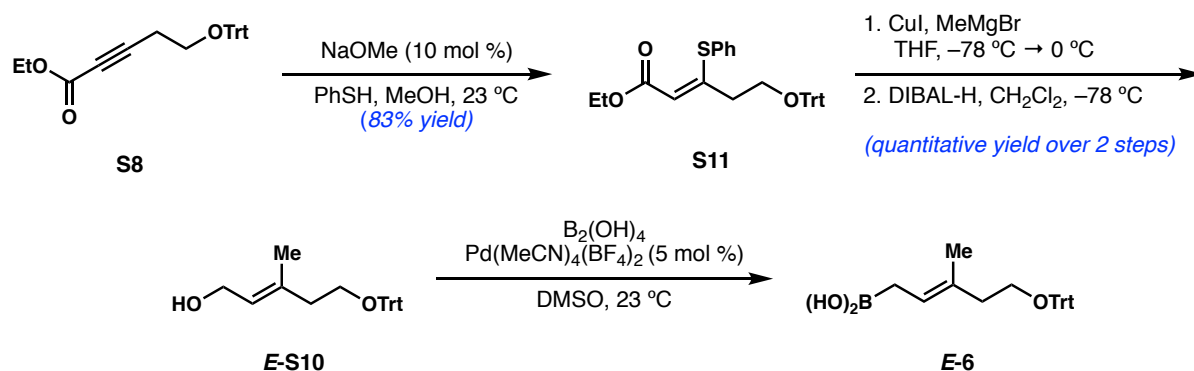


This procedure was adapted from the work of Szabó and coworkers.<sup>5</sup> In a nitrogen-filled glovebox, a flame-dried, 100 mL round bottom flask equipped with a stir bar was charged with allylic alcohol **Z-S10** (2.67 g, 7.45 mmol, 1 equiv) and anhydrous, degassed DMSO (18.6 mL, 0.4 M). The mixture was stirred until the viscous allylic

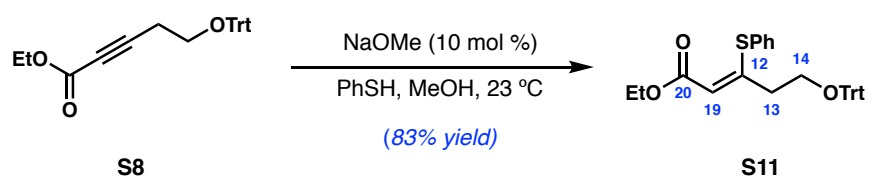
alcohol dissolved, at which time Pd(MeCN)<sub>4</sub>(BF<sub>4</sub>)<sub>2</sub> (165 mg, 0.373 mmol, 5 mol %) was added followed by tetrahydroxydiboron (801 mg, 8.94 mmol, 1.2 equiv). The reaction was vigorously stirred and transformed from a dark orange/red solution to dark green to black within 2 min. After stirring for 90 min at ambient temperature, the black mixture was transferred via cannula to a 100 mL Schlenk flask, the atmosphere of which had been exchanged with argon three times. Degassed PhMe (37.0 mL) was added to the black mixture followed by degassed 16% aq. NaCl (15 mL). The system was sealed off, shaken, and the layers were separated. The organic layer was washed with additional degassed 16% aq. NaCl (3 x 15 mL) to afford an organic solution with a black particulate suspension. The suspension was allowed to stand for 30 min, during which time the particulates settled. The top solution was transferred via cannula to a 100 mL Schlenk tube, the atmosphere of which had been exchanged with argon three times, and the tube was pumped into the glovebox where naphthalene was added as an internal standard. A <sup>1</sup>H NMR sample was prepared in the glovebox using dry, degassed CDCl<sub>3</sub>, and it was determined that [allylboronic acid] = 0.18 M. Allylboronic acid **Z-6** was immediately used in the next reaction.

## v. Synthesis of allylboronic acid (*E*-6)

### Scheme S5. Synthesis of allylboronic acid (*E*-6)



### Preparation of thiol acrylate (**S11**):



A flame-dried, 250 mL round bottom flask equipped with a stir bar was charged with alkynoate ester **S8** (7.79 g, 20.2 mmol, 1 equiv) and freshly distilled MeOH (100 mL). Thereafter, thiophenol (2.3 mL, 22.2 mmol, 1.1 equiv) and a freshly prepared solution of NaOMe (0.1 M, 2.02 mL, 2.02 mmol, 0.1 equiv) were added. The solution was stirred under argon for 12 h or until TLC analysis indicated complete consumption of starting material. The reaction mixture was filtered over a pad of SiO<sub>2</sub> and concentrated under reduced pressure to afford a yellow oil.

Purification was achieved via flash column chromatography on SiO<sub>2</sub> [500 g SiO<sub>2</sub>, Et<sub>2</sub>O/hexanes = 7% Et<sub>2</sub>O/hexanes → 10%] to afford thiol acrylate **S11** (8.3 g, 16.8 mmol, 83% yield) as a white foamy solid.

**TLC (40% Et<sub>2</sub>O/hexanes):** *R<sub>f</sub>* = 0.56 (UV, *p*-anisaldehyde).

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):** δ 7.39 – 7.18 (m, 15H, OCP<sub>h3</sub>, SPh), 5.90 (d, *J* = 0.8 Hz, 1H, C<sub>19</sub>), 4.21 (q, *J* = 7.1 Hz, 2H, OCH<sub>2</sub>CH<sub>3</sub>), 3.00 (t, *J* = 6.7 Hz, 2H, C<sub>14</sub>), 2.42 (t, *J* = 6.7 Hz, 2H, C<sub>13</sub>), 1.31 (t, *J* = 7.1 Hz, 3H, OCH<sub>2</sub>CH<sub>3</sub>).

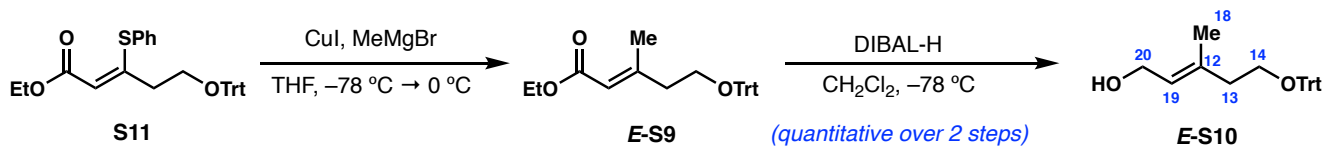
**<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>):** δ 166.1 (C<sub>20</sub>=O), 157.8 (C<sub>12</sub>), 143.8 (OCP<sub>h3</sub>), 135.7 (SPh), 130.5 (SPh), 129.2 (SPh), 129.1 (SPh), 128.6 (OCP<sub>h3</sub>), 127.8 (OCP<sub>h3</sub>), 126.9 (OCP<sub>h3</sub>), 113.7 (C<sub>19</sub>), 86.5 (OCP<sub>h3</sub>), 62.1 (C<sub>14</sub>), 60.0 (OCH<sub>2</sub>CH<sub>3</sub>), 36.9 (C<sub>13</sub>), 14.4 (OCH<sub>2</sub>CH<sub>3</sub>).

**FTIR (AT-IR):** 3057, 2975, 2871, 1699, 1590, 1448, 1209, 1115, 1059, 1031 cm<sup>-1</sup>.

**HRMS (TOF, ES<sup>+</sup>):** calc'd for C<sub>32</sub>H<sub>30</sub>O<sub>3</sub>NaS [M+Na]<sup>+</sup> 517.1813, found 517.1819.



### Preparation of (*E*)-3-methyl-5-(trityloxy)pent-2-en-1-ol (*E*-S10):



In a nitrogen-filled glovebox, a flame-dried, 500 mL round bottom flask equipped with a stir bar was charged with CuI (4.2 g, 21.8 mmol, 1.3 equiv). Anhydrous THF (168 mL) was added and the heterogeneous suspension was stirred at  $-78\text{ }^\circ\text{C}$  for 10 min. Thereafter, MeMgBr (6.7 mL of a 3.0 M solution in Et<sub>2</sub>O, 20.2 mmol, 1.2 equiv) was added dropwise. The reaction was warmed to  $0\text{ }^\circ\text{C}$  and stirred for 30 min. The solution was cooled back down to  $-78\text{ }^\circ\text{C}$ , where thiol acrylate **S11** (8.3 g, 16.8 mmol) was added via cannula transfer in anhydrous THF (30 mL). The reaction was stirred for 1 h or until complete by TLC analysis. Upon completion, the reaction was quenched with H<sub>2</sub>O (25 mL) at  $-78\text{ }^\circ\text{C}$  and warmed to ambient temperature, and filtered through a pad of Celite. The Celite was rinsed with Et<sub>2</sub>O until TLC analysis indicated there was no product remaining. The combined organic layers were washed with H<sub>2</sub>O (2 x 50 mL) and brine (1 x 50 mL), dried over MgSO<sub>4</sub>, and concentrated under reduced pressure to afford product as a viscous, yellow oil. The crude material was subjected to the next reaction without further purification. A representative spectrum of the crude mixture as used in the next step is provided.

**TLC (20% Et<sub>2</sub>O/hexanes):**  $R_f = 0.60$  (UV, *p*-anisaldehyde).

A flame-dried, 250 mL round bottom flask equipped with a stir bar was charged with crude acrylate **E-S9** (16.8 mmol, 1 equiv). Thereafter, anhydrous CH<sub>2</sub>Cl<sub>2</sub> (56 mL) was added and the solution was cooled to  $-78\text{ }^\circ\text{C}$ . A freshly prepared solution of DIBAL-H in hexanes (12 mL of a 1.2 M solution in hexanes, 67.2 mmol, 4 equiv) was added via cannula transfer. The reaction was stirred at  $-78\text{ }^\circ\text{C}$  for 40 min.

The solution was slowly quenched with sat. aq. Rochelle's salt (50 mL) and stirred overnight or until two clear layers formed. The aqueous layer was extracted with CH<sub>2</sub>Cl<sub>2</sub> (3 x 30 mL). The combined organic layers were washed with brine (50 mL) and dried over MgSO<sub>4</sub>. The suspension was filtered and concentrated under reduced pressure to afford a pale yellow oil.

Purification was achieved via flash column chromatography on SiO<sub>2</sub> [125 g SiO<sub>2</sub>, 30% Et<sub>2</sub>O/hexanes  $\rightarrow$  60%] to afford allylic alcohol **E-S10** (6.02 g, 16.8 mmol, quantitative yield over 2 steps) as a clear viscous oil.

**TLC (60% Et<sub>2</sub>O/hexanes):**  $R_f = 0.42$  (UV, *p*-anisaldehyde).

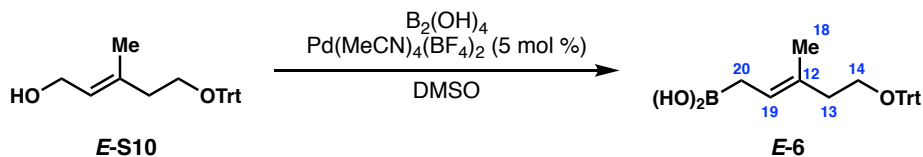
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):**  $\delta$  7.40 (dt,  $J = 8.6, 1.9$  Hz, 6H, OCP<sub>h</sub>), 7.31 – 7.09 (m, 9H, OCP<sub>h</sub>), 5.41 (td,  $J = 6.9, 1.3$  Hz, 1H, C<sub>19</sub>), 4.10 (d,  $J = 7.0$  Hz, 2H, C<sub>20</sub>), 3.13 (t,  $J = 6.8$  Hz, 2H, C<sub>14</sub>), 2.30 (t,  $J = 6.8$  Hz, 2H, C<sub>13</sub>), 1.59 (s, 3H), 1.16 (s, 1H, OH).

**<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>):**  $\delta$  144.3 (OCPh<sub>3</sub>), 137.1 (C<sub>12</sub>), 128.6 (OCPh<sub>3</sub>), 127.7 (OCPh<sub>3</sub>), 126.9 (OCPh<sub>3</sub>), 125.1 (C<sub>19</sub>), 86.5 (OCPh<sub>3</sub>), 62.3 (C<sub>14</sub>), 59.3 (C<sub>20</sub>), 39.9 (C<sub>13</sub>), 16.6 (C<sub>18</sub>).

**FTIR (AT-IR):** 3321, 3057, 2871, 1596, 1448, 1218, 1061, 1031, 1001, 704 cm<sup>-1</sup>

**HRMS (TOF, ES+):** calc'd for C<sub>25</sub>H<sub>26</sub>O<sub>2</sub>Na [M+Na]<sup>+</sup> 381.1831, found 381.1826.

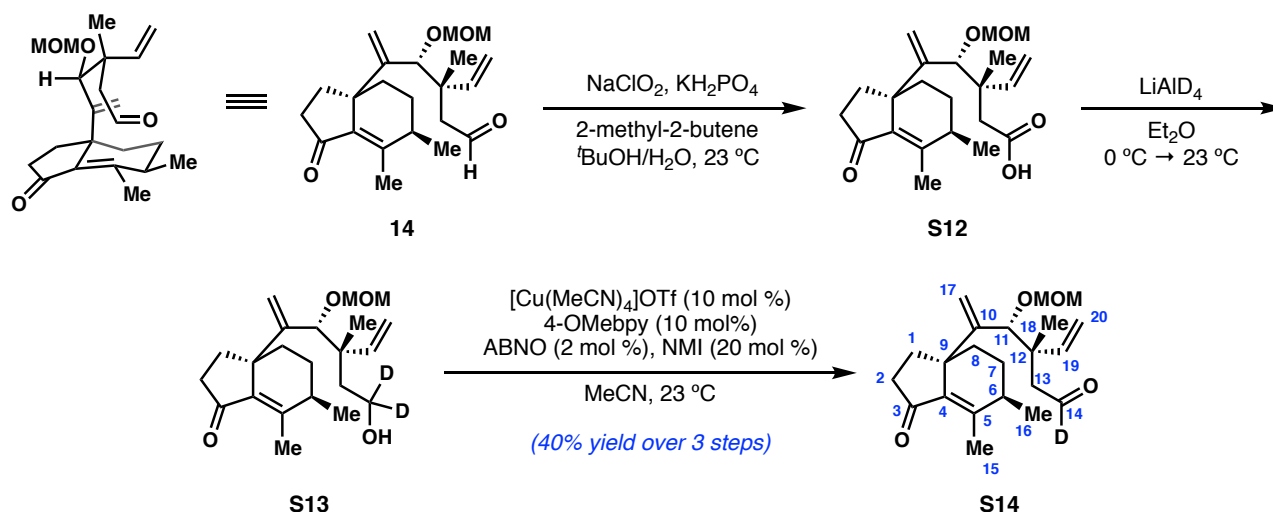
### Preparation of trityl-protected (*E*)-allylboronic acid (*E*-6):



This procedure was adapted from the work of Szabó and coworkers.<sup>5</sup> In a nitrogen-filled glovebox, a flame-dried, 25 mL round bottom flask equipped with a stir bar was charged with allylic alcohol **E-S10** (896 mg, 2.5 mmol, 1 equiv) and anhydrous, degassed DMSO (6.25 mL). The mixture was stirred until the viscous allyl alcohol dissolved, at which time  $\text{Pd}(\text{MeCN})_4(\text{BF}_4)_2$  (55.5 mg, 0.125 mmol, 5 mol %) was added followed by tetrahydroxydiboron (269 mg, 3.00 mmol, 1.2 equiv). The reaction was vigorously stirred and transformed from a dark orange/red solution to dark green to black within 2 min. After stirring for 90 min at ambient temperature, the black mixture was transferred via cannula to a 25 mL Schlenk flask, the atmosphere of which had been exchanged with argon three times. Degassed PhMe (12.3 mL) was added to the black mixture followed by degassed 16% aq. NaCl (5 mL). The system was sealed off, shaken, and the layers were separated. The organic layer was washed with additional degassed 16% aq. NaCl (3 x 5 mL) to afford an organic solution with a black particulate suspension. The suspension was allowed to stand for 30 min, during which time the particulates settled. The top solution was transferred via cannula to a 50 mL Schlenk tube, the atmosphere of which had been exchanged with argon three times, and the tube was pumped into the glovebox where naphthalene was added as an internal standard. A  $^1\text{H}$  NMR sample was prepared in the glovebox using dry, degassed  $\text{CDCl}_3$ , and it was determined that [allylboronic acid] = 0.15 M. Allylboronic acid **E-6** was immediately used in the next reaction.

## vi. Transannular [1,5]-HAT deuterium-labeling studies

### Scheme S6. Synthesis of deuterium-labeled aldehyde (S14).



A 25 mL round bottom flask equipped with a stir bar was charged with aldehyde **14** (32.2 mg, 0.0894 mmol, 1 equiv) and <sup>t</sup>BuOH (4.5 mL) followed by deionized water (3.2 mL) and 2-methyl-2-butene (163 mg, 2.32 mmol, 246  $\mu$ L, 26 equiv). Thereafter, a solution of KH<sub>2</sub>PO<sub>4</sub> (42.6 mg, 0.313 mmol, 3.5 equiv) in H<sub>2</sub>O (650  $\mu$ L) was added followed by a solution of NaClO<sub>2</sub> (8.9 mg, 0.0983 mmol, 1.1 equiv) in H<sub>2</sub>O (650  $\mu$ L). The mixture was rapidly stirred at ambient temperature for 6 h, at which time the reaction was extracted into Et<sub>2</sub>O (4 x 2 mL). The combined organic layers were dried over Na<sub>2</sub>SO<sub>4</sub>, filtered, and concentrated under reduced pressure to afford 25.8 mg of a clear oil that was used in the next step without further purification.

A flame-dried 2 dram vial equipped with a stir bar was charged with LiAlD<sub>4</sub> (11.5 mg, 0.274 mmol, 4 equiv) and the atmosphere was exchanged three times for argon. Subsequently, anhydrous Et<sub>2</sub>O (1.7 mL) was added followed by dropwise addition of carboxylic acid **S12** in Et<sub>2</sub>O (1.7 mL) over 5 min. The resulting light grey suspension was rapidly stirred at ambient temperature for 45 min, at which time H<sub>2</sub>O (1 mL) was cautiously added, using a vent needle to aid in expulsion of gas. The slurry was extracted into Et<sub>2</sub>O (4 x 2 mL), the combined organic layers were dried over Na<sub>2</sub>SO<sub>4</sub>, and concentrated under reduced pressure to afford 14.1 mg of a viscous oil that was used in the next step without further purification.

#### Stahl Oxidation:<sup>6</sup>

A flame-dried, 2 dram vial equipped with a stir bar was charged with alcohol **S13** and MeCN (100  $\mu$ L). Thereafter, added 140  $\mu$ L of the [Cu]/bpy stock solution, 140  $\mu$ L of the NMI stock solution, and 140  $\mu$ L of the ABNO stock solution, in that order. The orange reaction was stirred at 960 rpm open to the atmosphere. Within 15 min, TLC analysis (Et<sub>2</sub>O/hexanes = 70%, UV and anisaldehyde) indicated complete conversion to aldehyde **S14** (R<sub>f</sub> = 0.57, stains deep blue), and after 2 h, complete conversion to the desired enone-aldehyde product (R<sub>f</sub> = 0.66, stains brown) was observed. Subsequently, the resulting light blue solution was diluted with Et<sub>2</sub>O (2 mL), passed through a short pad of SiO<sub>2</sub> using Et<sub>2</sub>O as the eluent, and concentrated under reduced pressure to afford a pale yellow oil.

Purification was achieved via flash column chromatography on SiO<sub>2</sub> [1.5 g SiO<sub>2</sub>, Et<sub>2</sub>O/hexanes = 30%→45%] to afford deuterated aldehyde **S14** (9.8 mg, 0.027 mmol, 40% yield over 3 steps) as a viscous, colorless

oil. It should be noted that this compound was isolated as a 9:1 mixture of C<sub>6</sub>-epimers, separable after the reductive radical cyclization. <sup>1</sup>H NMR indicates 94% deuterium incorporation at C<sub>14</sub>.

**Preparation of stock solutions:** See page S15.

**TLC (80% Et<sub>2</sub>O/hexanes):** R<sub>f</sub> = 0.65 (UV).

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):** δ 6.07 (dd, *J* = 16.9, 9.9 Hz, 1H, C<sub>19</sub>), 5.48 (d, *J* = 0.7 Hz, 1H, C<sub>17</sub>), 5.13 (dd, *J* = 9.9, 2.4 Hz, 1H, C<sub>20</sub>), 5.09 (dd, *J* = 16.9, 2.4 Hz, 1H, C<sub>20</sub>), 5.05 (br m, 1H, C<sub>17</sub>), 4.54 (d, *J* = 6.7 Hz, 1H, OCH<sub>2</sub>OMe), 4.42 (d, *J* = 6.7 Hz, 1H, OCH<sub>2</sub>OMe), 4.12 (br s, 1H, C<sub>11</sub>), 3.36 (s, 3H, OCH<sub>2</sub>OCH<sub>3</sub>), 2.56 (m, 2H, C<sub>13</sub>), 2.26 (m, 1H, C<sub>1</sub>), 2.19 (m, 1H, C<sub>8</sub>), 2.17 (m, 1H, C<sub>2</sub>), 2.14 (m, 1H, C<sub>6</sub>), 2.11 (s, 3H, C<sub>15</sub>), 2.00 (dd, *J* = 17.0, 7.6 Hz, 1H, C<sub>2</sub>), 1.65 (m, 1H, C<sub>7</sub>), 1.52 (m, 1H, C<sub>1</sub>), 1.27 (s, 3H, C<sub>18</sub>), 1.25 (m, 1H, C<sub>8</sub>), 1.23 (m, 1H, C<sub>7</sub>), 1.07 (d, *J* = 7.0 Hz, 3H, C<sub>16</sub>).

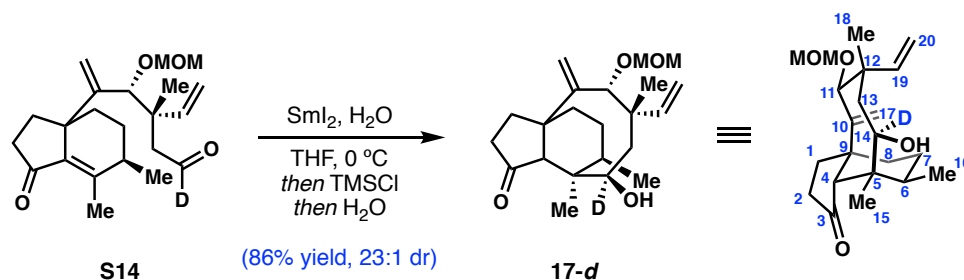
**<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>):** δ 208.1 (C<sub>3</sub>=O), 202.2 (C<sub>14</sub>=O) (1:1:1 triplet) (coupling of *I* = ½ <sup>13</sup>C nucleus to quadrupolar <sup>2</sup>H nucleus also causes T<sub>2</sub> broadening), 151.4 (C<sub>5</sub>), 149.0 (C<sub>10</sub>), 142.4 (C<sub>19</sub>), 136.2 (C<sub>4</sub>), 122.7 (C<sub>17</sub>), 114.5 (C<sub>20</sub>), 94.2 (OCH<sub>2</sub>OCH<sub>3</sub>), 78.2 (C<sub>11</sub>), 56.6 (OCH<sub>2</sub>OCH<sub>3</sub>), 52.4 (C<sub>13</sub>) (reduced intensity due to <sup>2</sup>H coupling), 50.5 (C<sub>9</sub>), 45.5 (C<sub>12</sub>), 37.4 (C<sub>6</sub>), 35.9 (C<sub>2</sub>), 33.1 (C<sub>8</sub>), 32.7 (C<sub>1</sub>), 28.2 (C<sub>7</sub>), 19.1 (C<sub>16</sub>), 18.9 (C<sub>18</sub>), 17.0 (C<sub>15</sub>).

**FTIR (AT-IR):** 2931, 2359, 2323, 1704, 1628, 1456, 1212, 1148, 1036, 919 cm<sup>-1</sup>.

**HRMS (TOF, ES+):** calc'd for C<sub>22</sub>H<sub>31</sub>DO<sub>4</sub>Na [M+Na]<sup>+</sup> 384.2261, found 384.2270.

**[α]<sub>D</sub><sup>23</sup>:** -43.2° (*c* = 0.455, CHCl<sub>3</sub>).

**Preparation of deuterium-labeled tricycle (17-d):**



A 25 mL Schlenk flask equipped with a stir bar was charged with deuterated aldehyde **S14** (7.3 mg, 0.0202 mmol, 1 equiv), THF (1.0 mL), and a solution of deionized H<sub>2</sub>O (2.2 μL, 0.121 mmol, 6 equiv) in THF (184 μL) and submitted to five freeze-pump-thaw cycles. The solution was cooled to 0 °C and stirred at this temperature for 15 min. Thereafter, SmI<sub>2</sub>/THF (606 μL, 0.0606 mmol, 3 equiv) was added dropwise over 8 min. After stirring an additional 10 min at 0 °C, TMSCl/THF (195 μL, 0.101 mmol, 5 equiv TMSCl) was added dropwise over 2 min, and the reaction was stirred an additional 10 min. Throughout this time, the deep blue color was quenched to yellow. Thereafter, the reaction was removed from the ice bath and stirred open to the atmosphere for 5 min. The resulting pale yellow solution was diluted with Et<sub>2</sub>O (5 mL), and washed with H<sub>2</sub>O (2 x 2 mL). The aqueous layer was back-extracted with Et<sub>2</sub>O (2 x 2 mL), and the combined organic layers were dried over Na<sub>2</sub>SO<sub>4</sub>, filtered, and concentrated under reduced pressure to afford a dark orange oil.

Purification was achieved via flash column chromatography on SiO<sub>2</sub> [1.5 g SiO<sub>2</sub>, Et<sub>2</sub>O/hexanes = 30%→40%] to afford deuterated tricycle **17-d** (6.3 mg, 0.017 mmol, 84% yield) as a clear residue.

**Preparation of SmI<sub>2</sub>:** See page S16.

**Stock solution of TMSCl:** See page S16.

**TLC (50% Et<sub>2</sub>O/hexanes):**  $R_f = 0.55$  (*p*-anisaldehyde, KMnO<sub>4</sub>).

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):**  $\delta$  6.35 (dd,  $J = 17.8, 11.3$  Hz, 1H, C<sub>19</sub>), 5.33 (dd,  $J = 17.8, 1.4$  Hz, 1H, C<sub>20</sub>), 5.34 (s, 1H, C<sub>17</sub>), 5.28 (s, 1H, C<sub>17</sub>), 5.19 (dd,  $J = 11.2, 1.4$  Hz, 1H, C<sub>20</sub>), 4.54 (d,  $J = 7.1$  Hz, 1H, OCH<sub>2</sub>OMe), 4.40 (d,  $J = 6.7$  Hz, 1H, OCH<sub>2</sub>OMe), 3.95 (s, 1H, C<sub>11</sub>), 3.38 (s, 3H, OCH<sub>2</sub>OCH<sub>3</sub>), 2.33 (m, 1H, C<sub>2</sub>), 2.29 (m, 1H, C<sub>2</sub>), 2.24 (m, 1H, C<sub>4</sub>), 2.06 (m, 1H, C<sub>1</sub>), 2.03 (m, 1H, C<sub>8</sub>), 1.92 (dd,  $J = 16.1, 6.5$  Hz, 1H, C<sub>13</sub>), 1.70 (m, 1H, C<sub>6</sub>), 1.60 (dt,  $J = 13.3, 3.4$  Hz, 1H, C<sub>7</sub>), 1.50 (dd,  $J = 16.1, 0.9$  Hz, 1H, C<sub>13</sub>), 1.39 (ddt,  $J = 13.3, 6.5, 3.4$  Hz, 1H, C<sub>7</sub>), 1.33 (m, 1H, C<sub>1</sub>), 1.30 (s, 3H, C<sub>15</sub>), 1.28 (m, 1H, C<sub>8</sub>), 1.24 (s, 3H, C<sub>18</sub>), 0.96 (d,  $J = 7.0$  Hz, 3H, C<sub>16</sub>).

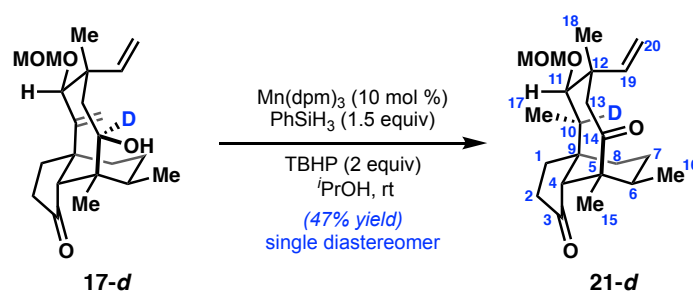
**<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>):**  $\delta$  216.8 (C<sub>3</sub>=O), 148.3 (C<sub>10</sub>), 139.9 (C<sub>19</sub>), 114.2 (C<sub>20</sub>), 112.2 (C<sub>17</sub>), 92.1 (OCH<sub>2</sub>OCH<sub>3</sub>), 77.2 (C<sub>11</sub>), 67.2 (C<sub>14</sub>) (1:1:1 triplet) (coupling of  $I = \frac{1}{2}$  <sup>13</sup>C nucleus to quadrupolar <sup>2</sup>H nucleus also causes T<sub>2</sub> broadening), 59.6 (C<sub>4</sub>), 56.0 (OCH<sub>2</sub>OCH<sub>3</sub>), 46.5 (C<sub>9</sub>), 45.2 (C<sub>13</sub>) (reduced intensity due to <sup>2</sup>H coupling), 44.7 (C<sub>12</sub>), 42.1 (C<sub>5</sub>), 37.3 (C<sub>6</sub>), 34.9 (C<sub>2</sub>), 31.0 (C<sub>8</sub>), 29.7 (C<sub>1</sub>), 28.8 (C<sub>18</sub>), 26.8 (C<sub>7</sub>), 18.2 (C<sub>16</sub>), 13.4 (C<sub>15</sub>).

**FTIR (AT-IR):** 3508, 2926, 1735, 1628, 1458, 1264, 1144, 1093, 1024, 907, 738 cm<sup>-1</sup>.

**HRMS (TOF, ES<sup>+</sup>):** calc'd for C<sub>22</sub>H<sub>34</sub>DO<sub>4</sub> [M+H]<sup>+</sup> 364.2598, found 364.2595.

**$[\alpha]_D^{23}$ :** +123.5° ( $c = 0.235$ , CHCl<sub>3</sub>).

### Redox relay by transannular 1,5-HAT is confirmed by deuterium-labeling:



This procedure was adapted from work by Shenvi and coworkers.<sup>7</sup> A flame-dried 0.5 dram vial was charged with deuterated tricyclic **17-d** (3.0 mg, 0.00825 mmol, 1 equiv) and adventitious water was removed via azeotropic drying with PhMe (3 x 200  $\mu$ L) under high vacuum. An oven-dried stir bar was added, and the atmosphere was exchanged three times for argon. Thereafter, a stock solution of PhSiH<sub>3</sub> (0.89 mg, 0.00825 mmol, 1.0  $\mu$ L, 1.5 equiv) and *tert*-butyl hydroperoxide (2.5  $\mu$ L of a 5.0 M solution in nonane, 0.0124 mmol, 2 equiv) in <sup>i</sup>PrOH (96  $\mu$ L) were added. Additional <sup>i</sup>PrOH (100  $\mu$ L) was added, and the mixture was sparged with argon for 10 min. Subsequently, tris(2,2,6,6-tetramethyl-3,5-heptanedionato)manganese(III) (0.50 mg, 0.000825 mmol, 10 mol %) was added as a solid, sparging was continued for an additional 20 sec, and the reaction was stirred at ambient temperature. After 10 min, the reaction was diluted with Et<sub>2</sub>O/hexanes = 50%, passed through a plug of SiO<sub>2</sub> (eluting with Et<sub>2</sub>O/hexanes = 50%), and concentrated under reduced pressure to afford a dark orange oil.

Purification was achieved via flash column chromatography on SiO<sub>2</sub> [750 mg SiO<sub>2</sub>, Et<sub>2</sub>O/hexanes = 20%→30%] to afford ketone **21-d** (1.4 mg, 0.00385 mmol, 47%) as a clear residue. Isolated starting material (1.4 mg, 0.00385 mmol, 47%).

**Experimental Notes:** This reaction exhibits a pronounced sensitivity to both residual oxygen and water. In addition, we found it critical to perform this reaction at 23 °C, as higher temperatures promoted over-reduction and lower temperatures slowed catalysis. <sup>i</sup>PrOH was stored over activated 4 Å molecular sieves (pellets) overnight then was distilled from CaH<sub>2</sub> (10% w/v) in a flame-dried, argon-filled apparatus immediately prior to use.

**Preparation of Stock Solutions:** A stock solution of PhSiH<sub>3</sub> (20 μL) and *tert*-butyl hydroperoxide (50 μL of a 5.0 M solution in nonane) in <sup>i</sup>PrOH (1.6 mL) was prepared under an atmosphere of argon, and 100 μL of this stock solution was added to substrate, as described below.

**TLC (40% Et<sub>2</sub>O/hexanes):** R<sub>f</sub> = 0.24 (*p*-anisaldehyde).

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):** δ 6.18 (dd, *J* = 17.8, 11.3 Hz, 1H, C<sub>19</sub>), 5.36 (dd, *J* = 17.8, 1.5 Hz, 1H, C<sub>20</sub>), 5.27 (dd, *J* = 11.2, 1.5 Hz, 1H, C<sub>20</sub>), 4.67 (ABq, *J* = 6.8 Hz, 2H, OCH<sub>2</sub>OMe), 3.54 (d, *J* = 5.2 Hz, 1H, C<sub>11</sub>), 3.42 (s, 3H, OCH<sub>2</sub>OCH<sub>3</sub>), 2.70 (d, *J* = 12.4 Hz, 1H, C<sub>13</sub>), 2.57 (d, *J* = 2.3 Hz, 1H, C<sub>4</sub>), 2.27 (m, 2H, C<sub>2</sub>), 2.07 (d, *J* = 12.4 Hz, 1H, C<sub>13</sub>), [1.99 (C<sub>10</sub>) (dq signal absent)], 1.83 (dd, *J* = 12.9, 9.6 Hz, 1H, C<sub>1</sub>), 1.74 (dq, *J* = 14.3, 2.9 Hz, C<sub>8</sub>), 1.63 (dt, *J* = 12.9, 3.3 Hz, 1H, C<sub>7</sub>), 1.56 (m, 1H, C<sub>6</sub>), 1.53 (m, 1H, C<sub>1</sub>), 1.46 (s, 3H, C<sub>15</sub>), 1.29 (m, 1H, C<sub>7</sub>), 1.21 (s, 3H, C<sub>18</sub>), 1.18 (d, *J* = 6.8 Hz, 3H, C<sub>16</sub>), 1.17 (m, 1H, C<sub>8</sub>), 0.89 (d, *J* = 7.2 Hz, 3H, C<sub>17</sub>).

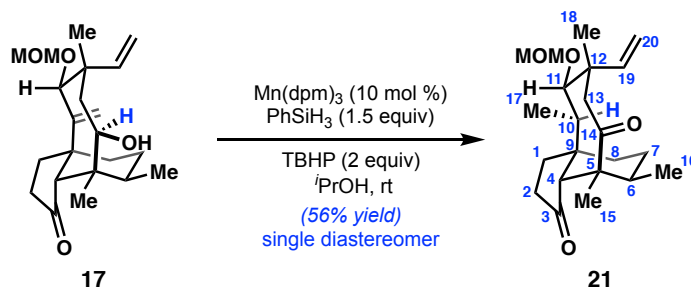
**<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>):** δ 216.9 (C<sub>3</sub>=O), 212.5 (C<sub>14</sub>=O), 138.5 (C<sub>19</sub>), 116.1 (C<sub>20</sub>), 98.1 (OCH<sub>2</sub>OCH<sub>3</sub>), 81.9 (C<sub>11</sub>) (reduced intensity due to <sup>2</sup>H coupling), 57.9 (C<sub>4</sub>), 56.8 (OCH<sub>2</sub>OCH<sub>3</sub>), 50.6 (C<sub>5</sub>), 48.1 (C<sub>12</sub>), 47.5 (C<sub>13</sub>), 45.6 (C<sub>9</sub>), 36.5 (C<sub>6</sub>), 35.5 (C<sub>10</sub>) (signal absent), 34.6 (C<sub>2</sub>), 31.0 (C<sub>8</sub>), 27.9 (C<sub>18</sub>), 26.1 (C<sub>7</sub>), 24.7 (C<sub>1</sub>), 21.0 (C<sub>15</sub>), 16.2 (C<sub>16</sub>), 11.1 (C<sub>17</sub>).

**FTIR (AT-IR):** 2930, 1733, 1698, 1455, 1089, 1035 cm<sup>-1</sup>.

**HRMS (TOF, ES+):** calc'd for C<sub>22</sub>H<sub>34</sub>DO<sub>4</sub> [M+H]<sup>+</sup> 364.2598, found 364.2600.

[α]<sub>D</sub><sup>23</sup>: +24.3° (*c* = 0.065, CHCl<sub>3</sub>).

#### Redox relay by transannular 1,5-HAT without deuterium-labeling:



This procedure was adapted from work by Shenvi and coworkers.<sup>7</sup> A flame-dried 1 dram vial was charged with tricycle **17** (30.0 mg, 0.0828 mmol, 1 equiv) and adventitious water was removed via azeotropic drying with PhMe (3 x 400 μL) under high vacuum. An oven-dried stir bar was added, and the atmosphere was exchanged three times for argon. Thereafter, <sup>i</sup>PrOH (830 μL), PhSiH<sub>3</sub> (13.4 mg, 0.124 mmol, 15.2 μL, 1.5 equiv), and *tert*-butyl hydroperoxide (33.1 μL of a 5.0 M solution in nonane, 0.166 mmol, 2 equiv) were added. The heterogeneous mixture was sparged with argon for 10 min. Subsequently, tris(2,2,6,6-tetramethyl-3,5-heptanedionato)manganese(III) (5.0 mg, 0.00828 mmol, 10 mol %) was added as a solid, sparging was continued for an additional 20 sec, and the reaction was stirred at ambient temperature. After 10 min, the reaction was diluted with Et<sub>2</sub>O/hexanes = 50%, passed through a plug of SiO<sub>2</sub> (eluting with Et<sub>2</sub>O/hexanes = 50%), and concentrated under reduced pressure to afford a dark orange oil.

Purification was achieved via flash column chromatography on SiO<sub>2</sub> [15 g SiO<sub>2</sub>, Et<sub>2</sub>O/hexanes = 20%→35%] to afford ketone **21** (16.9 mg, 0.047 mmol, 56% yield) as a clear residue. Isolated starting material (12.1 mg, 0.033 mmol, 40%).

**Experimental Notes:** This reaction exhibits a pronounced sensitivity to both residual oxygen and water. In addition, we found it critical to perform this reaction at 23 °C, as higher temperatures promoted over-reduction and lower

temperatures slowed catalysis. <sup>i</sup>PrOH was stored over activated 4 Å molecular sieves (pellets) overnight then was distilled from CaH<sub>2</sub> (10% w/v) in a flame-dried, argon-filled apparatus immediately prior to use.

**TLC (40% Et<sub>2</sub>O/hexanes):** R<sub>f</sub> = 0.24 (*p*-anisaldehyde).

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):** δ 6.18 (dd, *J* = 17.8, 11.3 Hz, 1H, C<sub>19</sub>), 5.36 (dd, *J* = 17.8, 1.5 Hz, 1H, C<sub>20</sub>), 5.27 (dd, *J* = 11.2, 1.5 Hz, 1H, C<sub>20</sub>), 4.67 (ABq, *J* = 6.8 Hz, 2H, OCH<sub>2</sub>OMe), 3.54 (d, *J* = 5.2 Hz, 1H, C<sub>11</sub>), 3.42 (s, 3H, OCH<sub>2</sub>OCH<sub>3</sub>), 2.70 (d, *J* = 12.4 Hz, 1H, C<sub>13</sub>), 2.57 (d, *J* = 2.3 Hz, 1H, C<sub>4</sub>), 2.27 (m, 2H, C<sub>2</sub>), 2.07 (d, *J* = 12.4 Hz, 1H, C<sub>13</sub>), 1.99 (dq, *J* = 7.2, 5.2 Hz, 1H, C<sub>10</sub>), 1.83 (dd, *J* = 12.9, 9.6 Hz, 1H, C<sub>1</sub>), 1.74 (dq, *J* = 14.3, 2.9 Hz, C<sub>8</sub>), 1.63 (dt, *J* = 12.9, 3.3 Hz, 1H, C<sub>7</sub>), 1.56 (m, 1H, C<sub>6</sub>), 1.53 (m, 1H, C<sub>1</sub>), 1.46 (s, 3H, C<sub>15</sub>), 1.29 (m, 1H, C<sub>7</sub>), 1.21 (s, 3H, C<sub>18</sub>), 1.18 (d, *J* = 6.8 Hz, 3H, C<sub>16</sub>), 1.17 (m, 1H, C<sub>8</sub>), 0.89 (d, *J* = 7.2 Hz, 3H, C<sub>17</sub>).

**<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>):** δ 216.9 (C<sub>3</sub>=O), 212.5 (C<sub>14</sub>=O), 138.5 (C<sub>19</sub>), 116.1 (C<sub>20</sub>), 98.1 (OCH<sub>2</sub>OCH<sub>3</sub>), 81.9 (C<sub>11</sub>), 57.9 (C<sub>4</sub>), 56.8 (OCH<sub>2</sub>OCH<sub>3</sub>), 50.6 (C<sub>5</sub>), 48.1 (C<sub>12</sub>), 47.5 (C<sub>13</sub>), 45.6 (C<sub>9</sub>), 36.5 (C<sub>6</sub>), 35.5 (C<sub>10</sub>), 34.6 (C<sub>2</sub>), 31.0 (C<sub>8</sub>), 27.9 (C<sub>18</sub>), 26.1 (C<sub>7</sub>), 24.7 (C<sub>1</sub>), 21.0 (C<sub>15</sub>), 16.2 (C<sub>16</sub>), 11.1 (C<sub>17</sub>).

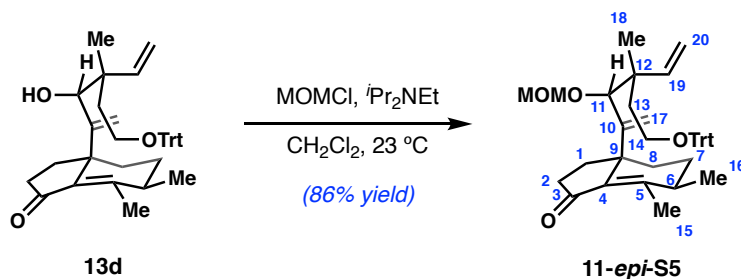
**FTIR (AT-IR):** 2957, 1734, 1698, 1455, 1089, 1035, 916 cm<sup>-1</sup>.

**HRMS (TOF, ES+):** calc'd C<sub>22</sub>H<sub>34</sub>O<sub>4</sub> [(M+H)-H<sub>2</sub>]<sup>+</sup> 361.2379, found 361.2396.

**[α]<sub>D</sub><sup>23</sup>:** +34.0° (*c* = 0.951, CHCl<sub>3</sub>).

vii. Synthesis of 11-*epi* and 11,12-bis-*epi* Dowd-Beckwith rearrangement tricycles (11-*epi*-26) and (26)

Preparation of MOM protected 11-*epi* crotylation adduct (11-*epi*-S5):



A flame-dried, 25 mL round bottom flask equipped with a stir bar was charged with alcohol **13d** (200 mg, 0.360 mmol, 1 equiv), CH<sub>2</sub>Cl<sub>2</sub> (1.8 mL), and freshly distilled *i*Pr<sub>2</sub>NEt (1.63 mL, 9.36 mmol, 26 equiv). To the homogeneous solution was added chloromethyl methyl ether (677 μL, 8.92 mmol, 25 equiv) dropwise over 10 min, taking care to vent HCl fumes formed via the use of a needle. The reaction was stirred at ambient temperature for 20 h. The resulting viscous, orange mixture was quenched via addition of sat. aq. NaHCO<sub>3</sub> (10 mL) and stirred at ambient temperature for 30 min. The aqueous layer was extracted with CH<sub>2</sub>Cl<sub>2</sub> (3 x 10 mL) and washed with H<sub>2</sub>O (10 mL). The combined organic layers were washed with brine (10 mL), dried over Na<sub>2</sub>SO<sub>4</sub>, and concentrated via distillation to afford a viscous, dark orange residue.

Purification was achieved via flash column chromatography on SiO<sub>2</sub> [4 g SiO<sub>2</sub>, Et<sub>2</sub>O/hexanes = 16%→35%] to afford MOM ether **11-*epi*-S5** (187 mg, 0.031 mmol, 86% yield) as a puffy white solid.

**TLC (40% Et<sub>2</sub>O/hexanes):** *R*<sub>f</sub> = 0.4 (UV, *p*-anisaldehyde).

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):** δ 7.49 – 7.36 (m, 6H, O*CPh*<sub>3</sub>), 7.35 – 7.17 (m, 9H, O*CPh*<sub>3</sub>), 5.85 (dd, *J* = 17.7, 10.8 Hz, 1H, C<sub>19</sub>), 5.46 (s, 1H, C<sub>17</sub>), 4.96 – 4.90 (m, 2H, C<sub>17</sub>, C<sub>20</sub>), 4.82 (dd, *J* = 17.7, 1.3 Hz, 1H, C<sub>20</sub>), 4.57 (d, *J* = 6.9 Hz, 1H, O*CH*<sub>2</sub>O*CH*<sub>3</sub>), 4.51 (d, *J* = 6.9 Hz, 1H, O*CH*<sub>2</sub>O*CH*<sub>3</sub>), 3.86 (s, 1H, C<sub>11</sub>), 3.34 (s, 3H, O*CH*<sub>2</sub>O*CH*<sub>3</sub>), 3.08 (t, *J* = 7.2 Hz, 2H, C<sub>14</sub>), 2.41 (dd, *J* = 12.8, 7.8 Hz, 1H, C<sub>2</sub>), 2.29 – 2.10 (m, 6H, C<sub>1</sub>, C<sub>6</sub>, C<sub>15</sub>), 2.07 – 2.02 (m, 1H, C<sub>8</sub>), 1.89 (dt, *J* = 10.9, 7.3 Hz, 2H, C<sub>13</sub>), 1.63 – 1.41 (m, 2H, C<sub>2</sub>, C<sub>7</sub>), 1.26 – 1.15 (m, 2H, C<sub>7</sub>, C<sub>8</sub>), 1.09 (d, *J* = 7.0 Hz, 3H, C<sub>16</sub>), 0.95 (s, 3H, C<sub>18</sub>).

**<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>):** δ 208.5 (C<sub>3</sub>=O), 150.8 (C<sub>5</sub>), 149.3 (C<sub>10</sub>), 144.4 (O*CPh*<sub>3</sub>), 143.6 (C<sub>19</sub>), 137.2 (C<sub>4</sub>), 128.6 (O*CPh*<sub>3</sub>), 127.6 (O*CPh*<sub>3</sub>), 126.7 (O*CPh*<sub>3</sub>), 122.4 (C<sub>17</sub>), 113.6 (C<sub>20</sub>), 95.8 (O*CH*<sub>2</sub>O*CH*<sub>3</sub>), 86.8 (O*CPh*<sub>3</sub>), 82.2 (C<sub>11</sub>), 60.7 (C<sub>14</sub>), 56.2 (O*CH*<sub>2</sub>O*CH*<sub>3</sub>), 51.3 (C<sub>9</sub>), 45.1 (C<sub>12</sub>), 37.5 (C<sub>6</sub>), 37.0 (C<sub>13</sub>), 35.7 (C<sub>1</sub>), 33.3 (C<sub>8</sub>), 32.3 (C<sub>2</sub>), 28.7 (C<sub>7</sub>), 20.1 (C<sub>18</sub>), 19.2 (C<sub>16</sub>), 17.0 (C<sub>15</sub>).

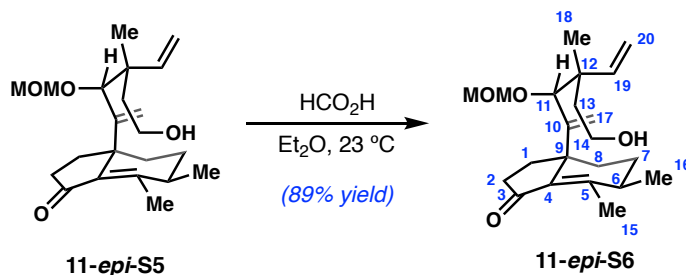
**FTIR (thin film, NaCl):** 2928, 1707, 1631, 1448, 1212, 1151, 1033, 917, 705 cm<sup>-1</sup>.

**HRMS (TOF, ES<sup>+</sup>):** calc'd for C<sub>41</sub>H<sub>48</sub>O<sub>4</sub>Na [M+Na]<sup>+</sup> 627.3450, found 627.3453.

**[α]<sub>D</sub><sup>23</sup>:** -60.1° (*c* = 0.355, CHCl<sub>3</sub>).



### Preparation of alcohol (**11-*epi*-S6**):



A 100 mL round bottom flask equipped with a stir bar was charged with MOM ether **11-*epi*-S5** (150 mg, 0.248 mmol, 1 equiv). Thereafter, a freshly prepared solution of formic acid (98%, 1.56 mL) and Et<sub>2</sub>O (1.56 mL) was rapidly added, and within 5 min, the reaction was judged to be complete by TLC analysis. We found it critical to stop this reaction immediately after full conversion was achieved. Prolonged times afforded copious quantities of formate ester product. The reaction was diluted with Et<sub>2</sub>O (5 mL) and quenched via slow addition of NaHCO<sub>3</sub> (25 mL). The aqueous layer was extracted with Et<sub>2</sub>O (4 x 10 mL) and washed with H<sub>2</sub>O (10 mL). The combined organic layers were washed with brine (10 mL), dried over Na<sub>2</sub>SO<sub>4</sub>, and concentrated under reduced pressure to afford a viscous yellow residue.

Purification was achieved via flash column chromatography on SiO<sub>2</sub> [Et<sub>2</sub>O/hexanes = 70%→90%] to afford alcohol **11-*epi*-S6** (80.0 mg, 0.221 mmol, 89% yield) as a viscous, colorless oil.

**TLC (40% Et<sub>2</sub>O/hexanes):** R<sub>f</sub> = 0.09 (UV, *p*-anisaldehyde).

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):** δ 6.05 (dd, *J* = 17.7, 10.9 Hz, 1H, C<sub>19</sub>), 5.54 (s, 1H, C<sub>17</sub>), 5.11 (dd, *J* = 10.9, 1.2 Hz, 1H, C<sub>20</sub>), 5.04 (dd, *J* = 17.7, 1.2 Hz, 1H, C<sub>20</sub>), 4.98 (s, 1H, C<sub>17</sub>), 4.63 (d, *J* = 7.0 Hz, 1H, OCH<sub>2</sub>OCH<sub>3</sub>), 4.55 (d, *J* = 7.0 Hz, 1H, OCH<sub>2</sub>OCH<sub>3</sub>), 3.94 (s, 1H, C<sub>11</sub>), 3.67 (tt, *J* = 7.2, 3.8 Hz, 2H, C<sub>14</sub>), 3.39 (s, 3H, OCH<sub>2</sub>OCH<sub>3</sub>), 2.44 (dd, *J* = 13.0, 7.7 Hz, 1H, C<sub>2</sub>), 2.28 – 2.05 (m, 7H, C<sub>1</sub>, C<sub>6</sub>, C<sub>8</sub>, C<sub>15</sub>), 1.88 (t, *J* = 7.0 Hz, 2H, C<sub>13</sub>), 1.60 – 1.45 (m, 2H, C<sub>2</sub>, C<sub>7</sub>), 1.28 – 1.18 (m, 2H, C<sub>7</sub>, C<sub>8</sub>), 1.12 (s, 3H, C<sub>18</sub>), 1.08 (d, *J* = 7.0 Hz, 3H, C<sub>16</sub>).

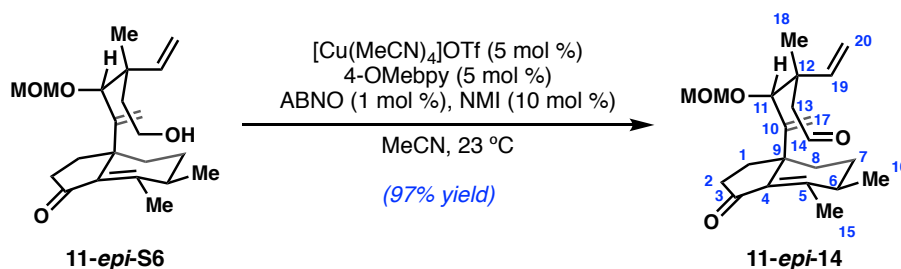
**<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>):** δ 208.4 (C<sub>3</sub>=O), 151.0 (C<sub>5</sub>), 149.2 (C<sub>10</sub>), 144.1 (C<sub>19</sub>), 137.1 (C<sub>4</sub>), 122.8 (C<sub>17</sub>), 114.0 (C<sub>20</sub>), 95.6 (OCH<sub>2</sub>OCH<sub>3</sub>), 82.2 (C<sub>11</sub>), 59.8 (C<sub>14</sub>), 56.3 (OCH<sub>2</sub>OCH<sub>3</sub>), 51.3 (C<sub>9</sub>), 45.2 (C<sub>12</sub>), 39.9 (C<sub>13</sub>), 37.5 (C<sub>6</sub>), 35.6 (C<sub>1</sub>), 33.3 (C<sub>8</sub>), 32.3 (C<sub>2</sub>), 28.7 (C<sub>7</sub>), 20.1 (C<sub>18</sub>), 19.2 (C<sub>16</sub>), 17.0 (C<sub>15</sub>).

**FTIR (thin film, NaCl):** 3424, 2932, 1707, 1629, 1460, 1212, 1145, 1038, 916, 730 cm<sup>-1</sup>.

**HRMS (TOF, ES<sup>+</sup>):** calc'd for C<sub>22</sub>H<sub>34</sub>O<sub>4</sub>Na [M+Na]<sup>+</sup> 385.2355, found 385.2347.

**[α]<sub>D</sub><sup>23</sup>:** -138.9° (*c* = 0.29, CHCl<sub>3</sub>).

### Preparation of aldehyde (11-*epi*-14):



### Stahl Oxidation:<sup>6</sup>

A flame-dried, 2 dram vial equipped with a stir bar was charged with alcohol **11-*epi*-S6** (69.0 mg, 0.190 mmol, 1 equiv) and MeCN (1.9 mL). Thereafter, added 377  $\mu$ L of the [Cu]/bpy stock solution, 377  $\mu$ L of the NMI stock solution, and 377  $\mu$ L of the ABNO stock solution, in that order. The orange reaction was stirred at 960 rpm open to the atmosphere for 90 min. Subsequently, the resulting light blue solution was diluted with Et<sub>2</sub>O (1 mL), passed through a short pad of SiO<sub>2</sub> using Et<sub>2</sub>O as the eluent, and concentrated under reduced pressure to afford a pale yellow oil.

Purification was achieved via flash column chromatography on SiO<sub>2</sub> [10 g SiO<sub>2</sub>, Et<sub>2</sub>O/hexanes = 30%→60%] to afford aldehyde **11-*epi*-14** (66.4 mg, 0.184 mmol, 97% yield) as a viscous, colorless oil that solidified to a white solid upon standing in the freezer.

**Preparation of stock solutions:** See page S15.

**TLC (40% Et<sub>2</sub>O/hexanes):** R<sub>f</sub> = 0.59 (UV, *p*-anisaldehyde).

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):**  $\delta$  9.75 (dd, *J* = 3.7, 2.3 Hz, 1H, C<sub>14</sub>), 6.11 (dd, *J* = 17.6, 10.9 Hz, 1H, C<sub>19</sub>), 5.46 (s, 1H, C<sub>17</sub>), 5.17 (dd, *J* = 10.9, 0.8 Hz, 1H, C<sub>20</sub>), 5.10 (dd, *J* = 17.7, 0.8 Hz, 1H, C<sub>20</sub>), 5.03 (s, 1H, C<sub>17</sub>), 4.57 (d, *J* = 7.1 Hz, 1H, OCH<sub>2</sub>OCH<sub>3</sub>), 4.47 (d, *J* = 7.1 Hz, 1H, OCH<sub>2</sub>OCH<sub>3</sub>), 4.03 (s, 1H, C<sub>11</sub>), 3.37 (s, 3H, OCH<sub>2</sub>OCH<sub>3</sub>), 2.61 (dd, *J* = 15.0, 3.7 Hz, 1H, C<sub>13</sub>), 2.55 (dd, *J* = 15.0, 2.3 Hz, 1H, C<sub>13</sub>), 2.43 (dd, *J* = 13.0, 6.5 Hz, 1H, C<sub>2</sub>), 2.26 – 2.03 (m, 7H, C<sub>1</sub>, C<sub>6</sub>, C<sub>8</sub>, C<sub>15</sub>), 1.64 – 1.46 (m, 3H, C<sub>2</sub>, C<sub>7</sub>), 1.31 (s, 3H, C<sub>18</sub>), 1.27 – 1.12 (m, 2H, C<sub>7</sub>, C<sub>8</sub>), 1.08 (d, *J* = 7.0 Hz, 3H, C<sub>16</sub>).

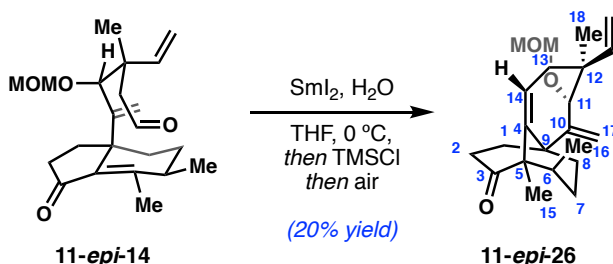
**<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>):**  $\delta$  208.2 (C<sub>3</sub>=O), 202.9 (C<sub>14</sub>=O), 151.2 (C<sub>5</sub>), 148.8 (C<sub>10</sub>), 141.9 (C<sub>19</sub>), 136.9 (C<sub>4</sub>), 123.3 (C<sub>17</sub>), 114.8 (C<sub>20</sub>), 94.7 (OCH<sub>2</sub>OCH<sub>3</sub>), 80.6 (C<sub>11</sub>), 56.3 (OCH<sub>2</sub>OCH<sub>3</sub>), 51.2 (C<sub>9</sub>), 50.5 (C<sub>13</sub>), 45.5 (C<sub>12</sub>), 37.5 (C<sub>6</sub>), 35.6 (C<sub>1</sub>), 33.2 (C<sub>8</sub>), 32.2 (C<sub>2</sub>), 28.8 (C<sub>7</sub>), 22.1 (C<sub>18</sub>), 19.2 (C<sub>16</sub>), 17.0 (C<sub>20</sub>).

**FTIR (thin film, NaCl):** 2931, 1706, 1628, 1457, 1268, 1210, 1144, 1095, 1030, 917 cm<sup>-1</sup>.

**HRMS (TOF, ES+):** calc'd for C<sub>22</sub>H<sub>32</sub>O<sub>4</sub>Na [M+Na]<sup>+</sup> 383.2198, found 383.2202.

**[ $\alpha$ ]<sub>D</sub><sup>23</sup>:** -108.9° (*c* = 0.05, CHCl<sub>3</sub>).

### Preparation of 11-*epi* Dowd-Beckwith rearrangement tricycle (11-*epi*-26):



A 2 dram vial equipped with a stir bar was charged with a solution of aldehyde **11-*epi*-14** (30 mg, 0.083 mmol, 1 equiv) in 4.1 mL of THF that had been submitted to five freeze-pump-thaw cycles and H<sub>2</sub>O/THF (2.3 mL). The solution was cooled to 0 °C and stirred at this temperature for 5 min. Thereafter, SmI<sub>2</sub>/THF (2.52 mL, 0.252 mmol, 3 equiv) was added dropwise over 8 min. The deep blue color of SmI<sub>2</sub> was immediately quenched upon addition of each drop. The first drop afforded a yellow solution, fading to a pale yellow and almost clear by the time 1.6 equiv SmI<sub>2</sub> had been added. When 2.2 equiv SmI<sub>2</sub> had been added, the blue color became increasingly persistent and upon addition of 2.6 equiv SmI<sub>2</sub>, the reaction was dark blue/green. After stirring an additional 10 min at 0 °C, TMSCl/THF (762 μL, 0.415 mmol, 5 equiv TMSCl) was added dropwise over 2 min, and the reaction was stirred an additional 10 min. Throughout this time, the deep blue color was quenched to yellow. Thereafter, the reaction was removed from the ice bath and stirred open to the atmosphere for 5 min.

The resulting pale yellow solution was diluted with Et<sub>2</sub>O (2 mL), and washed with H<sub>2</sub>O (2 x 1 mL). The aqueous layer was back-extracted with Et<sub>2</sub>O (2 x 1 mL), and the combined organic layers were dried over Na<sub>2</sub>SO<sub>4</sub>, filtered, and concentrated under reduced pressure to afford a dark orange oil.

Purification was achieved via flash column chromatography on SiO<sub>2</sub> [3 g SiO<sub>2</sub>, Et<sub>2</sub>O/hexanes = 20%] to afford tricycle **11-*epi*-26** (5.8 mg, 0.0169 mmol, 20 % yield) as a white solid.

**Preparation of SmI<sub>2</sub>:** See page S16.

**Stock solution of TMSCl:** See page S16.

**Stock solution of H<sub>2</sub>O/THF:** See page S29.

**TLC (50% Et<sub>2</sub>O/hexanes):** R<sub>f</sub> = 0.77 (*p*-anisaldehyde).

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):** 6.06 (dd, *J* = 17.5, 10.7 Hz, 1H, C<sub>19</sub>), 5.49 (dd, *J* = 9.0, 5.7 Hz, 1H, C<sub>14</sub>), 5.13 (s, 1H, C<sub>17</sub>), 5.12 (dd, *J* = 17.5, 1.3 Hz, 1H, C<sub>20</sub>), 5.06 (s, 1H, C<sub>17</sub>), 5.02 (dd, *J* = 10.7, 1.3 Hz, 1H, C<sub>20</sub>), 4.61 (d, *J* = 6.7 Hz, 1H, OCH<sub>2</sub>OCH<sub>3</sub>), 4.46 (d, *J* = 6.7 Hz, 1H, OCH<sub>2</sub>OCH<sub>3</sub>), 4.34 (s, 1H, C<sub>11</sub>), 3.33 (s, 3H, OCH<sub>2</sub>OCH<sub>3</sub>), 2.51 – 2.35 (m, 3H, C<sub>1</sub>, C<sub>2</sub>), 2.26 (td, *J* = 14.0, 13.6, 5.4 Hz, 1H, C<sub>8</sub>), 2.15 (dd, *J* = 13.7, 5.7 Hz, 1H, C<sub>13</sub>), 2.07 – 1.97 (m, 1H, C<sub>6</sub>), 1.99 – 1.88 (m, 1H, C<sub>1</sub>), 1.79 (dd, *J* = 13.8, 9.0 Hz, 1H, C<sub>13</sub>), 1.77 – 1.66 (dq, *J* = 14.1, 4.7 Hz, 1H, C<sub>7</sub>), 1.43 – 1.35 (m, 1H, C<sub>7</sub>), 1.08 (s, 4H, C<sub>8</sub>, C<sub>15</sub>), 1.02 (s, 3H, C<sub>18</sub>), 0.90 (d, *J* = 7.0 Hz, 3H, C<sub>16</sub>).

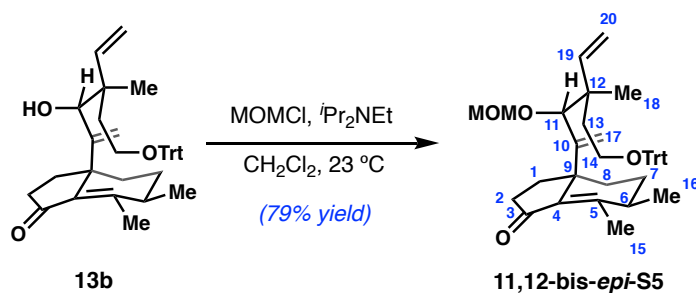
**<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>):** δ 219.2 (C<sub>3</sub>), 155.2 (C<sub>10</sub>), 145.6 (C<sub>19</sub>), 141.6 (C<sub>4</sub>), 120.0 (C<sub>14</sub>), 111.6 (C<sub>20</sub>), 107.2 (C<sub>17</sub>), 93.3 (OCH<sub>2</sub>OCH<sub>3</sub>), 77.7 (C<sub>11</sub>), 56.9 (C<sub>5</sub>), 55.4 (OCH<sub>2</sub>OCH<sub>3</sub>), 45.6 (C<sub>9</sub>), 44.9 (C<sub>12</sub>), 38.8 (C<sub>6</sub>), 38.5 (C<sub>2</sub>), 37.3 (C<sub>8</sub>), 36.5 (C<sub>13</sub>), 29.7 (C<sub>1</sub>), 27.9 (C<sub>7</sub>), 19.8 (C<sub>15</sub>), 18.3 (C<sub>18</sub>), 13.7 (C<sub>16</sub>).

**FTIR (thin film, NaCl):** 2930, 1712, 1632, 1454, 1369, 1213, 1147, 1101, 1042, 908 cm<sup>-1</sup>.

**HRMS (FAB+):** calc'd for C<sub>22</sub>H<sub>32</sub>O<sub>3</sub> [M]<sup>+</sup> 344.2352, found 344.2381.

**[α]<sub>D</sub><sup>23</sup>:** -276.7° (*c* = 0.27, CHCl<sub>3</sub>).

**Preparation of MOM protected 11,12-bis-*epi* crotylation adduct (11,12-bis-*epi*-S5):**



A flame-dried, 25 mL round bottom flask equipped with a stir bar was charged with alcohol **13b** (20 mg, 0.036 mmol, 1 equiv), CH<sub>2</sub>Cl<sub>2</sub> (594 μL), and freshly distilled *i*Pr<sub>2</sub>NEt (163 μL, 0.936 mmol, 26 equiv). To the homogeneous solution was added chloromethyl methyl ether (68 μL, 0.900 mmol, 25 equiv) dropwise over 10 min, taking care to vent HCl fumes formed via the use of a needle. The reaction was stirred at ambient temperature for 36 h. The resulting viscous, orange mixture was quenched via addition of sat. aq. NaHCO<sub>3</sub> (2 mL) and stirred at ambient temperature for 30 min. The aqueous layer was extracted with CH<sub>2</sub>Cl<sub>2</sub> (3 x 1 mL). The combined organic layers were washed with H<sub>2</sub>O (1 mL), brine (1 mL), dried over Na<sub>2</sub>SO<sub>4</sub>, and concentrated via distillation to afford a viscous, dark orange residue.

Purification was achieved via flash column chromatography on SiO<sub>2</sub> [5 g SiO<sub>2</sub>, Et<sub>2</sub>O/hexanes = 16%→35%] to afford MOM ether **11,12-bis-*epi*-S5** (12 mg, 0.020 mmol, 79% yield) as a puffy white solid.

**TLC (40% Et<sub>2</sub>O/hexanes):** R<sub>f</sub> = 0.44 (UV, *p*-anisaldehyde).

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):** δ 7.47 – 7.38 (m, 6H, Ph<sub>3</sub>CO), 7.33 – 7.18 (m, 9H, Ph<sub>3</sub>CO), 5.74 (dd, *J* = 17.5, 10.8 Hz, 1H, C<sub>19</sub>), 5.41 (s, 1H, C<sub>17</sub>), 4.98 (s, 1H, C<sub>17</sub>), 4.84 (d, *J* = 10.8 Hz, 1H, C<sub>20</sub>), 4.80 (d, *J* = 17.6 Hz, 1H, C<sub>20</sub>), 4.50 (d, *J* = 6.9 Hz, 1H, OCH<sub>2</sub>OCH<sub>3</sub>), 4.40 (d, *J* = 7.0 Hz, 1H, OCH<sub>2</sub>OCH<sub>3</sub>), 3.92 (s, 1H, C<sub>11</sub>), 3.32 (s, 3H, OCH<sub>2</sub>OCH<sub>3</sub>), 3.08 (d, *J* = 22.2 Hz, 2H, C<sub>13</sub>), 2.38 (s, 1H, C<sub>2</sub>), 2.11 (d, *J* = 9.5 Hz, 8H, C<sub>1</sub>, C<sub>2</sub>, C<sub>6</sub>, C<sub>8</sub>, C<sub>13</sub>, C<sub>15</sub>), 1.85 (s, 1H, C<sub>13</sub>), 1.47 (m, 2H, C<sub>2</sub>, C<sub>7</sub>), 1.11 (m, 2H, C<sub>7</sub>, C<sub>8</sub>), 1.06 (d, *J* = 7.1 Hz, 3H, C<sub>16</sub>), 0.97 (s, 3H, C<sub>18</sub>).

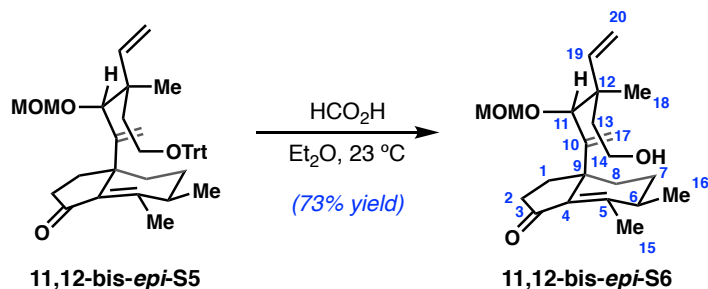
**<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>):** δ 208.5 (C<sub>3</sub>=O), 150.98 (C<sub>5</sub>), 149.2 (C<sub>10</sub>), 144.4 (OCPh<sub>3</sub>), 143.1 (C<sub>19</sub>), 137.3 (C<sub>4</sub>), 128.6 (OCPh<sub>3</sub>), 127.6 (OCPh<sub>3</sub>), 126.8 (OCPh<sub>3</sub>), 123.2 (C<sub>17</sub>), 113.4 (C<sub>20</sub>), 94.6 (OCH<sub>2</sub>OCH<sub>3</sub>), 86.6 (OCPh<sub>3</sub>), 80.3 (C<sub>11</sub>), 60.7 (C<sub>14</sub>), 56.3 (OCH<sub>2</sub>OCH<sub>3</sub>), 51.0 (C<sub>9</sub>), 44.8 (C<sub>12</sub>), 38.1 (C<sub>13</sub>), 37.4 (C<sub>6</sub>), 35.6 (C<sub>1</sub>), 33.2 (C<sub>8</sub>), 32.1 (C<sub>2</sub>), 28.6 (C<sub>7</sub>), 19.1 (C<sub>16</sub>), 18.0 (C<sub>18</sub>), 17.0 (C<sub>15</sub>).

**FTIR (thin film, NaCl):** 2928, 1708, 1630, 1448, 1211, 1146, 1040, 916 cm<sup>-1</sup>.

**HRMS (TOF, ES<sup>+</sup>):** calc'd for C<sub>41</sub>H<sub>48</sub>O<sub>4</sub>Na [M+Na]<sup>+</sup> 627.3450, found 627.3445.

**[α]<sub>D</sub><sup>23</sup>:** -86.2° (*c* = 0.43, CHCl<sub>3</sub>).

### Preparation of alcohol (11,12-bis-*epi*-S6):



A 2 dram vial equipped with a stir bar was charged with MOM ether **11,12-bis-*epi*-S5** (12 mg, 0.020 mmol, 1 equiv). Thereafter, a freshly prepared solution of formic acid (98%, 125  $\mu\text{L}$ ) and  $\text{Et}_2\text{O}$  (125  $\mu\text{L}$ ) was rapidly added, and within 5 min, the reaction was judged to be complete by TLC analysis. We found it critical to stop this reaction immediately after full conversion was achieved. Prolonged times afforded copious quantities of formate ester product. The reaction was diluted with  $\text{Et}_2\text{O}$  (1 mL) and quenched via slow addition of  $\text{NaHCO}_3$  (4 mL). The aqueous layer was extracted with  $\text{Et}_2\text{O}$  (4 x 1 mL). The combined organic layers were washed with  $\text{H}_2\text{O}$  (1 mL), brine (1 mL), dried over  $\text{Na}_2\text{SO}_4$ , and concentrated under reduced pressure to afford a viscous yellow residue.

Purification was achieved via flash column chromatography on  $\text{SiO}_2$  [ $\text{Et}_2\text{O}/\text{hexanes} = 70\% \rightarrow 90\%$ ] to afford alcohol **11,12-bis-*epi*-S6** (5.3 mg, 0.015 mmol, 73% yield) as a viscous, colorless oil.

**TLC (70%  $\text{Et}_2\text{O}/\text{hexanes}$ ):**  $R_f = 0.13$  (UV, *p*-anisaldehyde).

**$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):**  $\delta$  5.97 (dd,  $J = 17.5, 10.9$  Hz, 1H,  $\text{C}_{19}$ ), 5.48 (s, 1H,  $\text{C}_{17}$ ), 5.07 – 4.99 (m, 3H,  $\text{C}_{17}, \text{C}_{20}$ ), 4.56 (d,  $J = 7.0$  Hz, 1H, ( $\text{OCH}_2\text{OCH}_3$ )), 4.45 (d,  $J = 7.0$  Hz, 1H, ( $\text{OCH}_2\text{OCH}_3$ )), 4.07 (s, 1H,  $\text{C}_{11}$ ), 3.67 (qdd,  $J = 10.9, 7.7, 6.4$  Hz, 2H,  $\text{C}_{14}$ ), 3.38 (s, 3H, ( $\text{OCH}_2\text{OCH}_3$ )), 2.47 (dd,  $J = 13.0, 7.0$  Hz, 1H,  $\text{C}_2$ ), 2.27 – 2.11 (m, 4H,  $\text{C}_1, \text{C}_6, \text{C}_8$ ), 2.11 (s, 3H,  $\text{C}_{15}$ ), 1.96 (ddd,  $J = 13.6, 7.6, 6.0$  Hz, 1H,  $\text{C}_{13}$ ), 1.86 (dt,  $J = 13.7, 7.2$  Hz, 1H,  $\text{C}_{13}$ ), 1.56 – 1.40 (m, 2H,  $\text{C}_2, \text{C}_7$ ), 1.19 – 1.11 (m, 2H,  $\text{C}_7, \text{C}_8$ ), 1.11 (s, 3H,  $\text{C}_{18}$ ), 1.07 (d,  $J = 7.1$  Hz, 3H,  $\text{C}_{16}$ ).

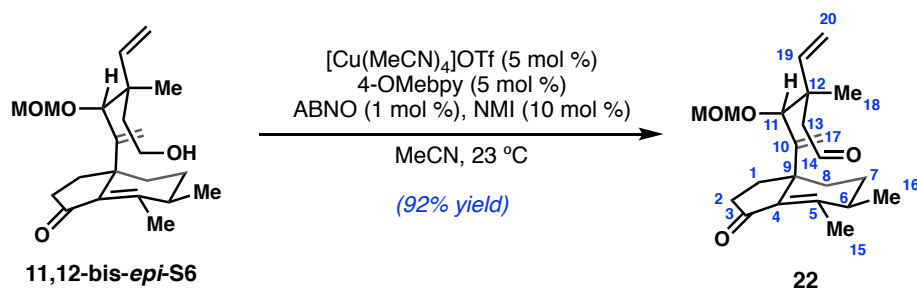
**$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ):**  $\delta$  208.4 ( $\text{C}_3=\text{O}$ ), 151.1 ( $\text{C}_5$ ), 149.2 ( $\text{C}_{19}$ ), 143.7 ( $\text{C}_4$ ), 137.3 ( $\text{C}_4$ ), 123.5 ( $\text{C}_{17}$ ), 113.8 ( $\text{C}_{20}$ ), 94.4 ( $\text{OCH}_2\text{OCH}_3$ ), 80.2 ( $\text{C}_{11}$ ), 60.0 ( $\text{C}_{14}$ ), 56.3 ( $\text{OCH}_2\text{OCH}_3$ ), 51.1 ( $\text{C}_9$ ), 45.0 ( $\text{C}_{12}$ ), 41.4 ( $\text{C}_{13}$ ), 37.5 ( $\text{C}_6$ ), 35.7 ( $\text{C}_1$ ), 33.3 ( $\text{C}_8$ ), 32.1 ( $\text{C}_2$ ), 28.6 ( $\text{C}_7$ ), 19.1 ( $\text{C}_{16}$ ), 17.5 ( $\text{C}_{18}$ ), 17.1 ( $\text{C}_{15}$ ).

**FTIR (thin film, NaCl):** 3407, 2931, 1706, 1628, 1442, 1211, 1146, 1034, 915  $\text{cm}^{-1}$ .

**HRMS (TOF, ES+):** calc'd for  $\text{C}_{22}\text{H}_{34}\text{O}_4\text{Na}$  [ $\text{M}+\text{Na}$ ] $^+$  385.2355, found 385.2353.

**$[\alpha]_D^{23}$ :**  $-177.9^\circ$  ( $c = 0.135, \text{CHCl}_3$ ).

## Preparation of aldehyde (22):



### Stahl Oxidation:<sup>6</sup>

A flame-dried, 2 dram vial equipped with a stir bar was charged with alcohol **11,12-bis-*epi*-S6** (210 mg, 0.580 mmol, 1 equiv) and MeCN (1.5 mL). Thereafter, added 1.1 mL of the [Cu]/bpy stock solution, 1.1 mL of the NMI stock solution, and 1.1 mL of the ABNO stock solution, in that order. The orange reaction was stirred at 960 rpm open to the atmosphere for 90 min. Subsequently, the resulting light blue solution was diluted with Et<sub>2</sub>O (5 mL), passed through a short pad of SiO<sub>2</sub> using Et<sub>2</sub>O as the eluent, and concentrated under reduced pressure to afford a pale yellow oil.

Purification was achieved via flash column chromatography on SiO<sub>2</sub> [10 g SiO<sub>2</sub>, Et<sub>2</sub>O/hexanes = 30%→60%] to afford aldehyde **22** (196 mg, 0.544 mmol, 92% yield) as a viscous, colorless oil that solidified to a white solid upon standing in the freezer.

**Preparation of stock solutions:** See page S15.

**TLC (40% Et<sub>2</sub>O/hexanes):** R<sub>f</sub> = 0.59 (UV, *p*-anisaldehyde).

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):** δ 9.74 (dd, *J* = 3.5, 2.2 Hz, 1H, C<sub>14</sub>), 6.02 (dd, *J* = 17.7, 10.7 Hz, 1H, C<sub>19</sub>), 5.45 (d, *J* = 1.2 Hz, 1H, C<sub>17</sub>), 5.15 – 5.02 (m, 3H, C<sub>17</sub>, C<sub>20</sub>), 4.52 (d, *J* = 7.1 Hz, 1H, OCH<sub>2</sub>OCH<sub>3</sub>), 4.37 (d, *J* = 7.1 Hz, 1H, OCH<sub>2</sub>OCH<sub>3</sub>), 4.16 (d, *J* = 1.1 Hz, 1H, C<sub>11</sub>), 3.33 (s, 3H, OCH<sub>2</sub>OCH<sub>3</sub>), 2.57 (dd, *J* = 15.6, 3.5 Hz, 1H, C<sub>2</sub>, C<sub>13</sub>), 2.53 – 2.41 (m, 2H, C<sub>2</sub>, C<sub>13</sub>), 2.28 – 2.11 (m, 4H, C<sub>1</sub>, C<sub>6</sub>, C<sub>8</sub>), 2.11 (s, 3H, C<sub>15</sub>), 1.59 – 1.50 (m, 1H, C<sub>2</sub>), 1.50 – 1.42 (m, 1H, C<sub>7</sub>), 1.28 (s, 3H, C<sub>18</sub>), 1.22 – 1.08 (m, 2H, C<sub>7</sub>, C<sub>8</sub>), 1.07 (d, *J* = 7.1 Hz, 3H, C<sub>16</sub>).

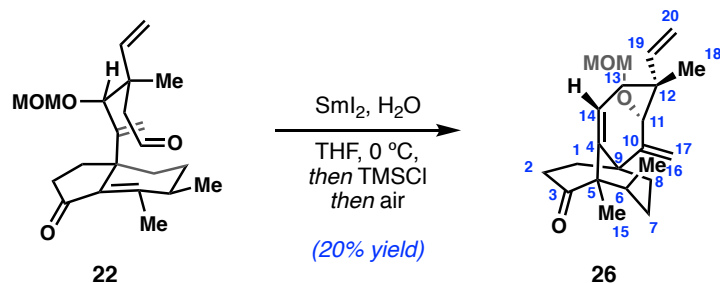
**<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>):** δ 208.3 (C<sub>3</sub>=O), 202.2 (C<sub>14</sub>=O), 151.3 (C<sub>5</sub>), 148.6 (C<sub>10</sub>), 142.9 (C<sub>19</sub>), 137.1 (C<sub>4</sub>), 123.7 (C<sub>17</sub>), 114.3 (C<sub>20</sub>), 93.8 (OCH<sub>2</sub>OCH<sub>3</sub>), 78.7 (C<sub>11</sub>), 56.5 (OCH<sub>2</sub>OCH<sub>3</sub>), 52.6 (C<sub>13</sub>), 51.0 (C<sub>9</sub>), 45.2 (C<sub>12</sub>), 37.5 (C<sub>6</sub>), 35.6 (C<sub>1</sub>), 33.2 (C<sub>8</sub>), 32.0 (C<sub>2</sub>), 19.2 (C<sub>16</sub>), 18.7 (C<sub>18</sub>), 17.1 (C<sub>15</sub>).

**FTIR (thin film, NaCl):** 2930, 1709, 1629, 1443, 1372, 1211, 1147, 1096, 1038, 917 cm<sup>-1</sup>.

**HRMS (TOF, ES<sup>+</sup>):** calc'd for C<sub>22</sub>H<sub>32</sub>O<sub>4</sub>Na [M+Na]<sup>+</sup> 383.2198, found 383.2190.

**[α]<sub>D</sub><sup>23</sup>:** -164.5° (*c* = 0.393, CHCl<sub>3</sub>).

## Preparation of 11,12-bis-*epi* Dowd-Beckwith rearrangement tricycle (**26**)



A 2 dram vial equipped with a stir bar was charged with a solution of aldehyde **22** (35 mg, 0.097 mmol, 1 equiv) in 4.8 mL of THF that had been submitted to five freeze-pump-thaw cycles and H<sub>2</sub>O/THF (2.7 mL). The solution was cooled to 0 °C and stirred at this temperature for 5 min. Thereafter, SmI<sub>2</sub>/THF (2.9 mL, 0.294 mmol, 3 equiv) was added dropwise over 8 min. The deep blue color of SmI<sub>2</sub> was immediately quenched upon addition of each drop. The first drop afforded a yellow solution, fading to a pale yellow and almost clear by the time 1.6 equiv SmI<sub>2</sub> had been added. When 2.2 equiv SmI<sub>2</sub> had been added, the blue color became increasingly persistent and upon addition of 2.6 equiv SmI<sub>2</sub>, the reaction was dark blue/green. After stirring an additional 10 min at 0 °C, TMSCl/THF (889 μL, 0.490 mmol, 5 equiv TMSCl) was added dropwise over 2 min, and the reaction was stirred an additional 10 min. Throughout this time, the deep blue color was quenched to yellow. Thereafter, the reaction was removed from the ice bath and stirred open to the atmosphere for 5 min.

The resulting pale yellow solution was diluted with Et<sub>2</sub>O (2 mL), and washed with H<sub>2</sub>O (2 x 1 mL). The aqueous layer was back-extracted with Et<sub>2</sub>O (2 x 1 mL), and the combined organic layers were dried over Na<sub>2</sub>SO<sub>4</sub>, filtered, and concentrated under reduced pressure to afford a dark orange oil.

Purification was achieved via flash column chromatography on SiO<sub>2</sub> [3 g SiO<sub>2</sub>, Et<sub>2</sub>O/hexanes = 20%] to afford tricycle **26** (7 mg, 0.020 mmol, 21% yield) as a white solid.

**Preparation of SmI<sub>2</sub>:** See page S16.

**Stock solution of TMSCl:** See page S16.

**Stock solution of H<sub>2</sub>O/THF:** See page S29.

**TLC (30% Et<sub>2</sub>O/hexanes):** R<sub>f</sub> = 0.33 (*p*-anisaldehyde).

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):** δ 6.11 (dd, *J* = 17.6, 10.9 Hz, 1H, C<sub>19</sub>), 5.53 (dd, *J* = 9.0, 5.5 Hz, 1H, C<sub>14</sub>), 5.10 (dd, *J* = 11.0, 1.4 Hz, 1H, C<sub>20</sub>), 5.07 (d, *J* = 0.8 Hz, 1H, C<sub>17</sub>), 5.03 (d, *J* = 0.8 Hz, 1H, C<sub>17</sub>), 5.00 (dd, *J* = 17.7, 1.5 Hz, 1H, C<sub>20</sub>), 4.63 (d, *J* = 6.8 Hz, 1H, OCH<sub>2</sub>OCH<sub>3</sub>), 4.49 (d, *J* = 6.7 Hz, 1H, OCH<sub>2</sub>OCH<sub>3</sub>), 4.21 (s, 1H, C<sub>11</sub>), 3.38 (s, 3H, OCH<sub>2</sub>OCH<sub>3</sub>), 2.49 – 2.36 (m, 3H, C<sub>1</sub>, C<sub>2</sub>), 2.35 – 2.18 (m, 2H, C<sub>8</sub>, C<sub>13</sub>), 2.02 (tq, *J* = 9.4, 3.6, 2.4 Hz, 1H, C<sub>6</sub>), 1.92 (ddd, *J* = 11.7, 9.0, 6.1 Hz, 1H, C<sub>2</sub>), 1.81 – 1.65 (m, 1H, C<sub>7</sub>), 1.61 (dd, *J* = 13.6, 9.0 Hz, 1H, C<sub>13</sub>), 1.45 – 1.36 (m, 1H, C<sub>7</sub>), 1.26 (d, *J* = 0.9 Hz, 3H, C<sub>18</sub>), 1.10 (s, 3H, C<sub>15</sub>), 1.10 – 1.01 (m, 1H, C<sub>8</sub>), 0.92 (d, *J* = 7.0 Hz, 3H, C<sub>16</sub>).

**<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>):** δ 219.1 (C<sub>3</sub>=O), 155.2 (C<sub>10</sub>), 142.3 (C<sub>19</sub>), 141.8 (C<sub>10</sub>), 119.8 (C<sub>17</sub>), 112.3 (C<sub>20</sub>), 106.7 (C<sub>14</sub>), 93.1 (OCH<sub>2</sub>OCH<sub>3</sub>), 79.9 (C<sub>11</sub>), 56.9 (C<sub>5</sub>), 55.4 (OCH<sub>2</sub>OCH<sub>3</sub>), 45.1 (C<sub>9</sub>), 45.0 (C<sub>12</sub>), 38.7 (C<sub>6</sub>), 38.5 (C<sub>1</sub>), 37.1 (C<sub>8</sub>), 35.6 (C<sub>13</sub>), 29.6 (C<sub>2</sub>), 27.8 (C<sub>7</sub>), 23.1 (C<sub>18</sub>), 19.8 (C<sub>15</sub>), 13.7 (C<sub>16</sub>).

**FTIR (thin film, NaCl):** 2923, 2853, 1711, 1461, 1378, 1261, 1142, 1101, 1040 cm<sup>-1</sup>.

**HRMS (TOF, ES<sup>+</sup>):** calc'd for C<sub>22</sub>H<sub>33</sub>O<sub>3</sub> [M+H]<sup>+</sup> 345.2430, found 345.2409.

[α]<sub>D</sub><sup>23</sup>: -78.7° (*c* = 0.045, CHCl<sub>3</sub>).

### 3. Single Crystal X-ray Diffraction Data

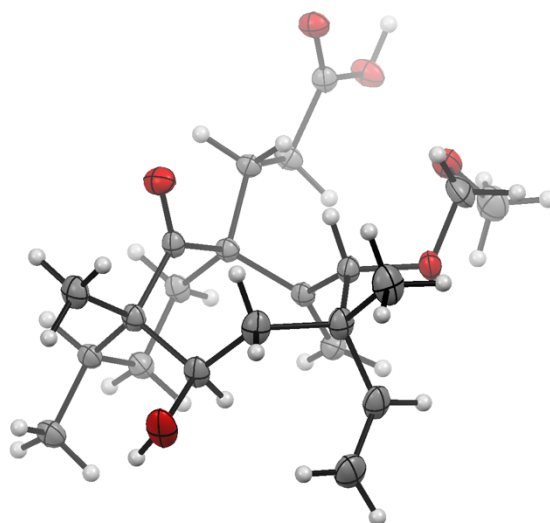
Low-temperature diffraction data ( $\varphi$ - and  $\omega$ -scans) were collected on a Bruker AXS D8 VENTURE KAPPA diffractometer coupled to a PHOTON 100 CMOS detector with Cu-K $\alpha$  radiation ( $\lambda = 1.54178 \text{ \AA}$ ) from a I $\mu$ S HB micro-focus sealed X-ray tube. All diffractometer manipulations, including data collection, integration, and scaling were carried out using the Bruker APEXII software.<sup>12</sup> Absorption corrections were applied using SADABS.<sup>13</sup> The structure was solved by intrinsic phasing using SHELXT<sup>14</sup> and refined against  $F^2$  on all data by full-matrix least squares with SHELXL-2014<sup>15</sup> using established refinement techniques.<sup>16</sup> All non-hydrogen atoms were refined anisotropically. Unless otherwise noted, all hydrogen atoms were included into the model at geometrically calculated positions and refined using a riding model. The isotropic displacement parameters of all hydrogen atoms were fixed to 1.2 times the  $U$  value of the atoms they are linked to (1.5 times for methyl and hydroxyl groups). Crystallographic data for **16**, **17**, and **26** can be obtained free of charge from The Cambridge Crystallographic Data Centre (CCDC) via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif) under CCDC deposition numbers 1589653-1589655. Graphical representation of the structure with 50% probability thermal ellipsoids was generated using Mercury visualization software.<sup>17</sup>

**Table S5: Crystal and refinement data for compounds 16, 17, and 26.**

	<b>16</b>	<b>17</b>	<b>26</b>
CCDC Number	1589655	1589654	1589653
Empirical formula	C <sub>22</sub> H <sub>34</sub> O <sub>6</sub>	C <sub>22</sub> H <sub>34</sub> O <sub>4</sub>	C <sub>22</sub> H <sub>32</sub> O <sub>3</sub>
Formula weight	394.49	362.49	344.47
T (K)	100	100	100
Crystal system	Orthorhombic	Orthorhombic	Orthorhombic
Space group	P2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub>	P2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub>	P2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub>
a, $\text{\AA}$	7.2336(4)	8.8601(3)	7.4344(9)
b, $\text{\AA}$	16.5583(8)	11.6560(4)	11.7916(15)
c, $\text{\AA}$	34.6198(18)	37.8871(14)	21.810(3)
$\alpha$ , $^\circ$	90	90	90
$\beta$ , $^\circ$	90	90	90
$\gamma$ , $^\circ$	90	90	90
Volume, $\text{\AA}^3$	4146.6(4)	3912.7(2)	1912.0(4)
Z	8	8	4
$d_{\text{calc}}$ , g/cm <sup>3</sup>	1.264	1.231	1.197
Abs. coeff. (mm <sup>-1</sup> )	0.738	0.658	0.609
$\theta$ range, $^\circ$	2.552 to 79.430	3.968 to 79.461	4.054 to 78.898
Abs. correction	Semi-empirical	Semi-empirical	Semi-empirical
GOF	1.066	1.097	1.064
$R_1$ , <sup>a</sup> $wR_2$ , <sup>b</sup> [ $I > 2\sigma(I)$ ]	0.0345, 0.0897	0.0339, 0.0877	0.0291, 0.0764
Flack parameter	0.04(3)	0.06(2)	0.00(4)
Extinction coefficient	n/a	0.00096(12)	0.0103(7)

$$^a R_1 = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}, \quad ^b wR_2 = \frac{[\sum [w(F_o^2 - F_c^2)^2]]}{\sum [w(F_o^2)^2]}^{1/2}.$$

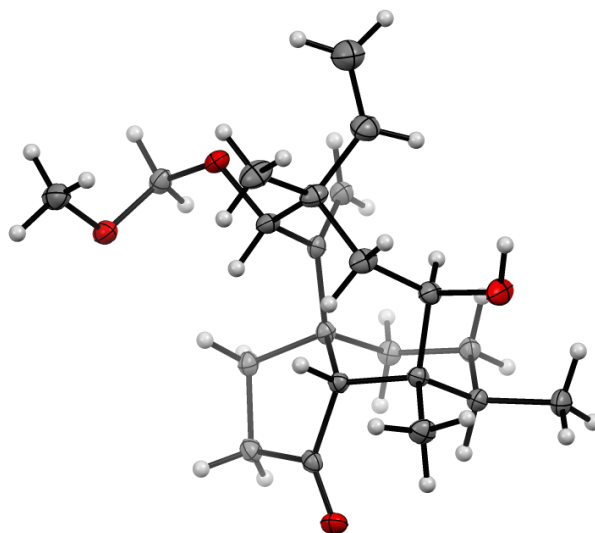




**Figure S1:** Structure of **16** with 50% probability anisotropic displacement ellipsoids. The second molecule of **16** is omitted for clarity.

#### **Special Refinement Details for 16**

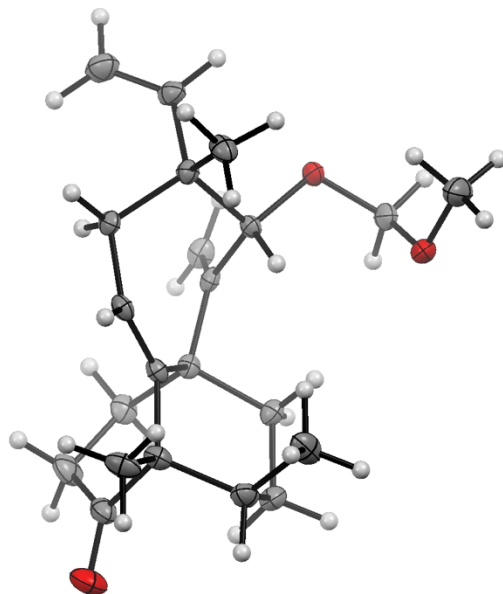
Compound **16** crystallizes in the orthorhombic space group  $P2_12_12_1$  with two molecules in the asymmetric unit. The coordinates for the hydrogen atoms bound to O2A, O4A, O2B, and O4B were located in the difference Fourier synthesis and refined using a riding model. No hydrogen bond acceptor was found for O2B. Absolute configuration was determined by anomalous dispersion (Flack = 0.04(3)).<sup>16</sup>



**Figure S2:** Structure of **17** with 50% probability anisotropic displacement ellipsoids. The second molecule of **17** is omitted for clarity.

#### **Special Refinement Details for 17**

Compound **17** crystallizes in the orthorhombic space group  $P2_12_12_1$  with two molecules in the asymmetric unit. The coordinates for the hydrogen atoms bound to O2A and O2B were located in the difference Fourier synthesis and refined using a riding model. Absolute configuration was determined by anomalous dispersion (Flack = 0.06(2)).<sup>16</sup>



**Figure S3:** Structure of **26** with 50% probability anisotropic displacement ellipsoids.

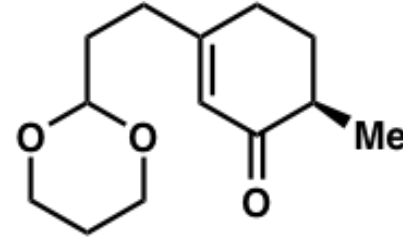
**Special Refinement Details for 26**

Compound **26** crystallizes in the orthorhombic space group  $P2_12_12_1$  with one molecule in the asymmetric unit. Absolute configuration was determined by anomalous dispersion ( $\text{Flack} = 0.00(4)$ ).<sup>16</sup>

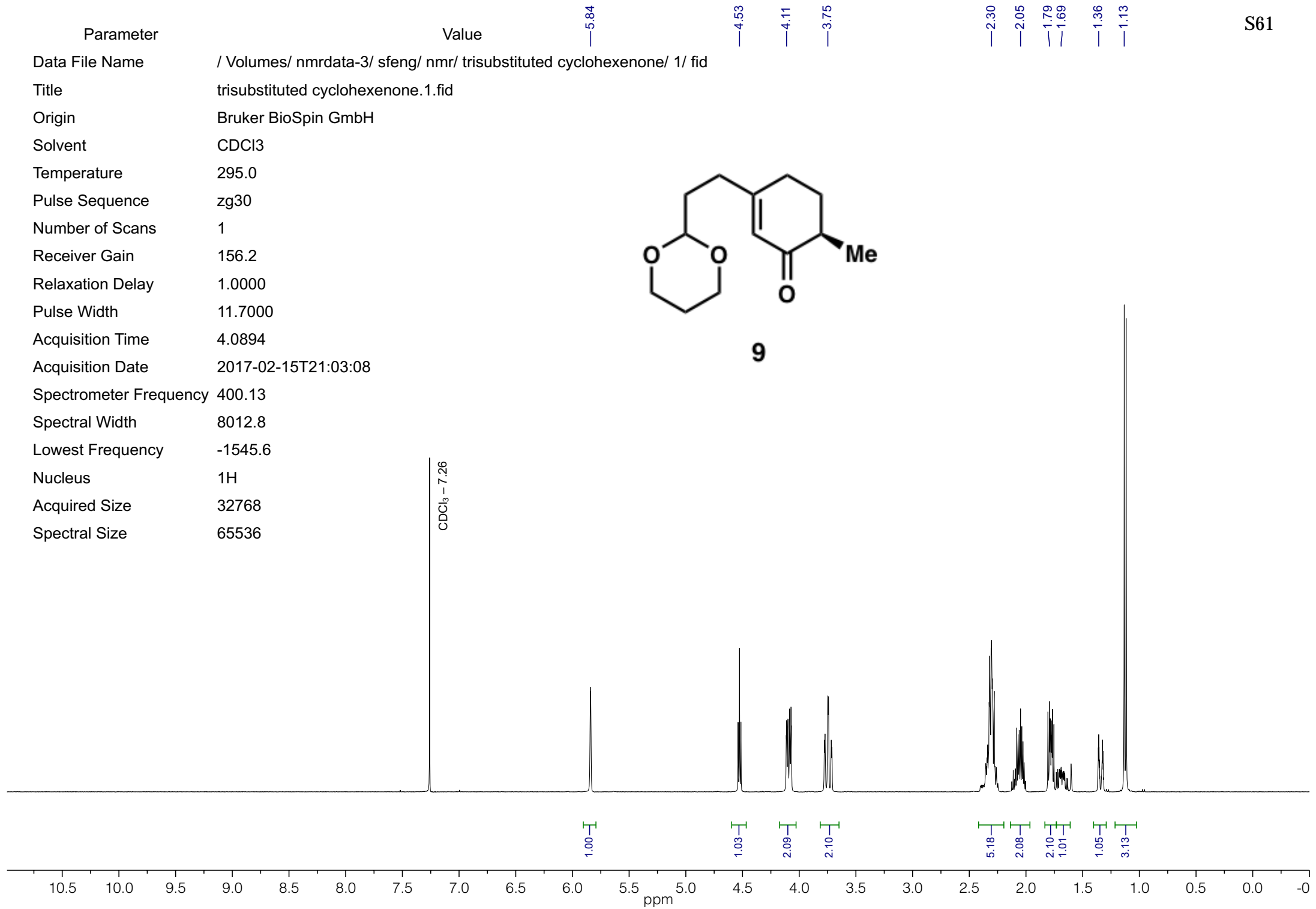
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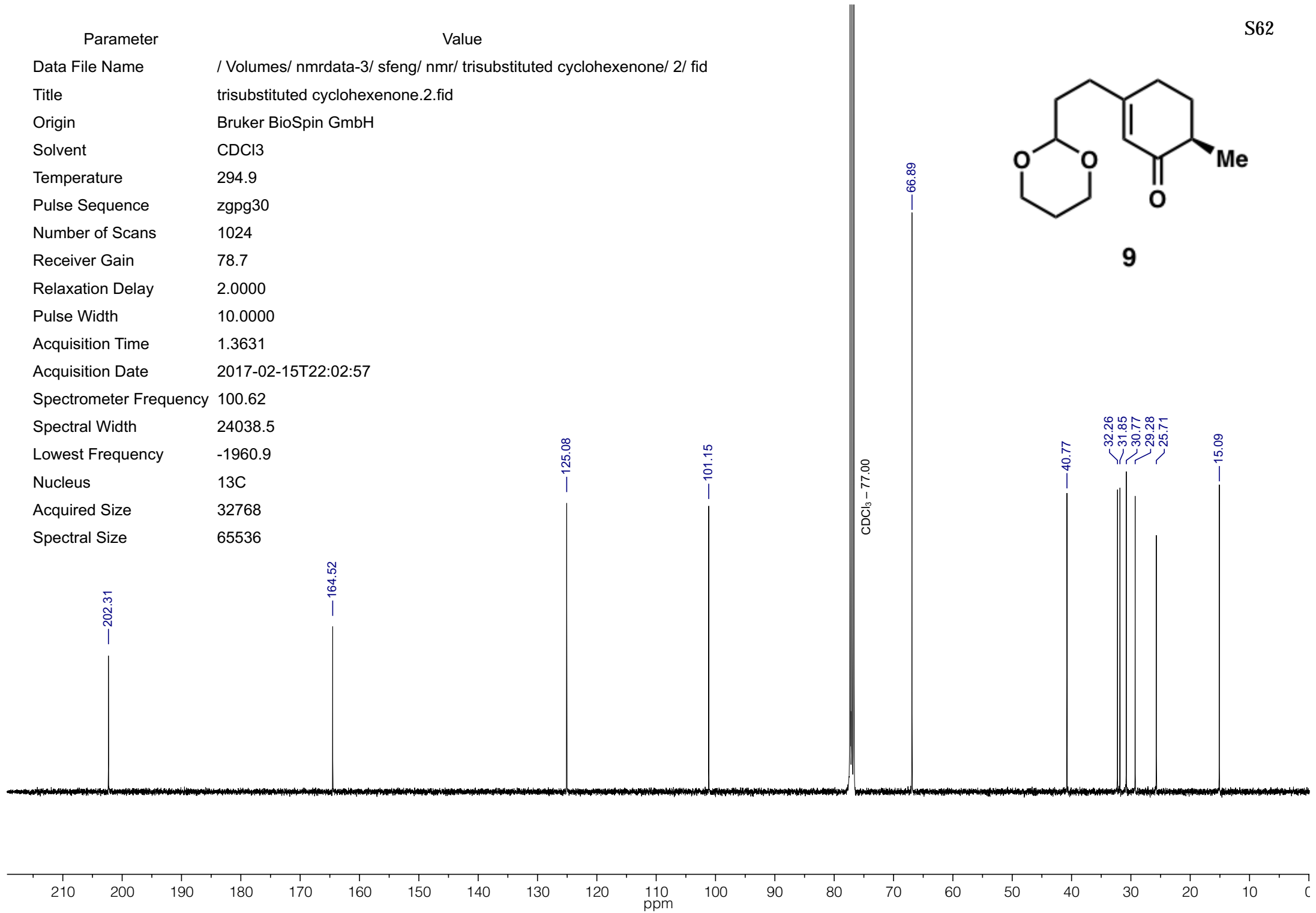
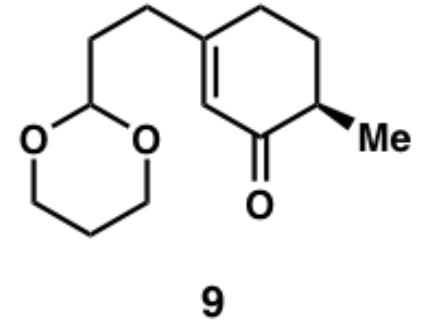
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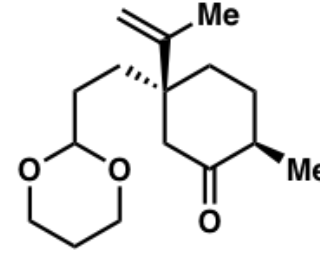
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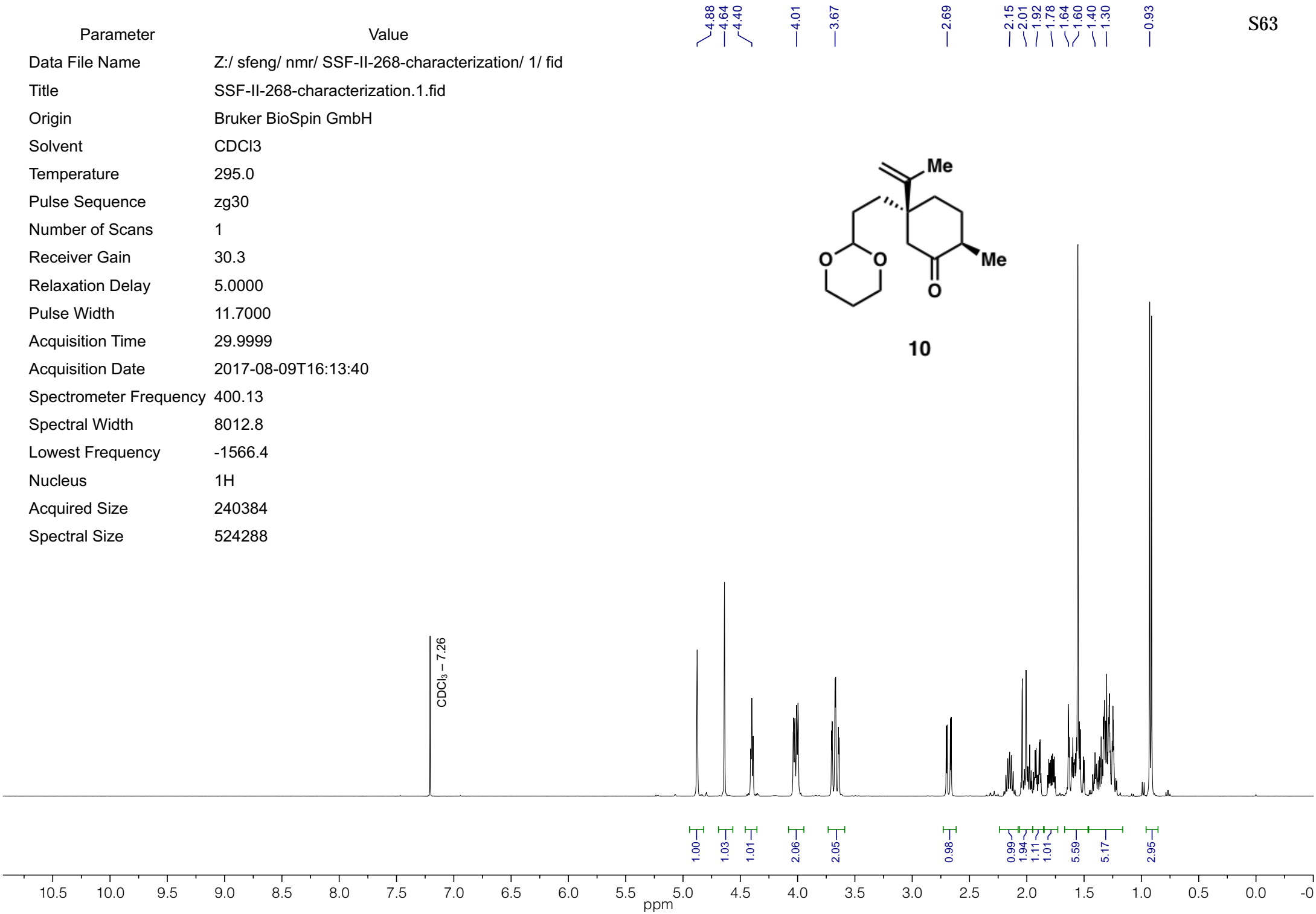
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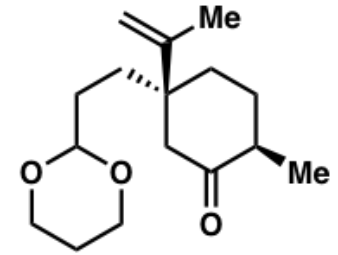
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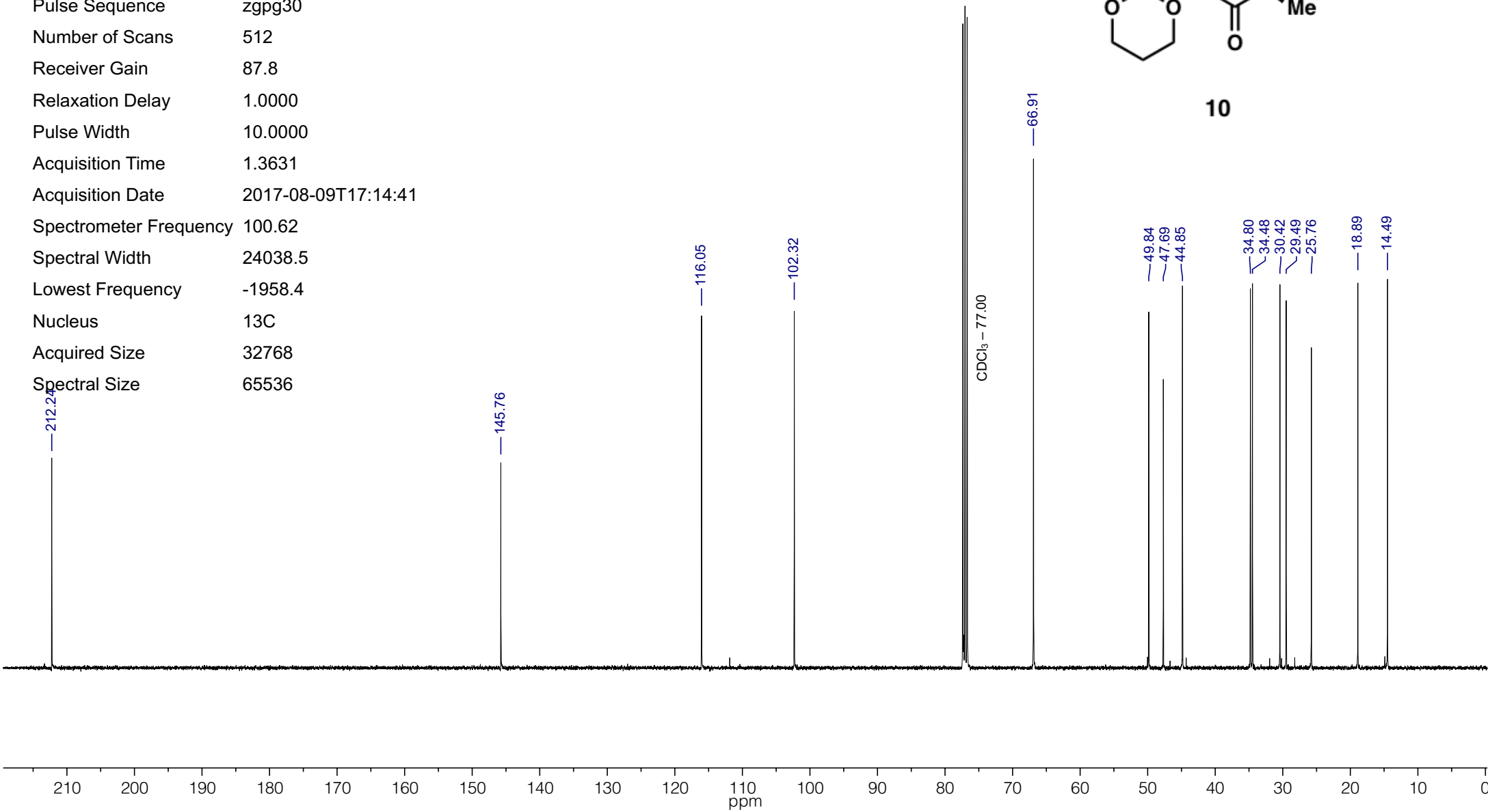
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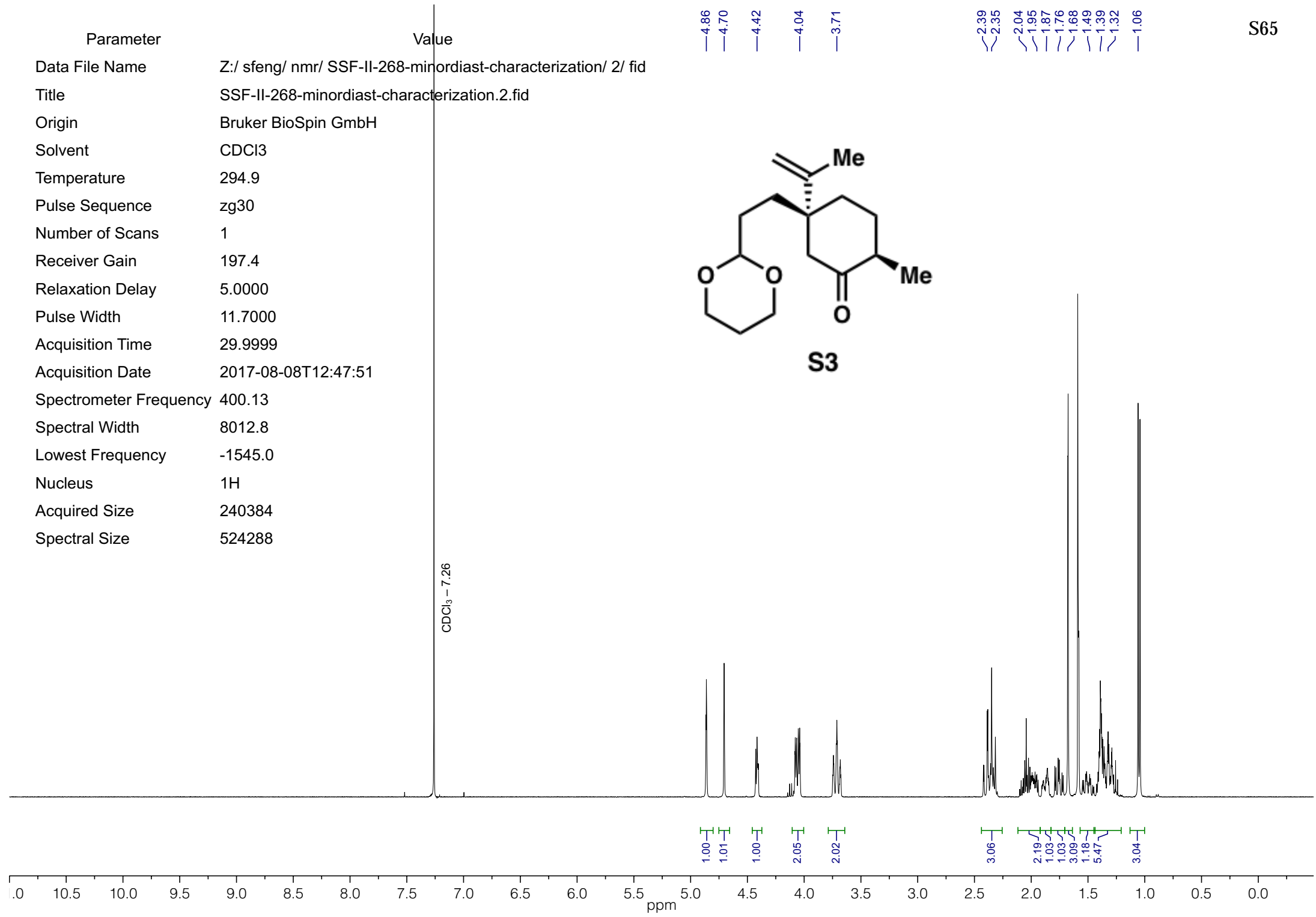
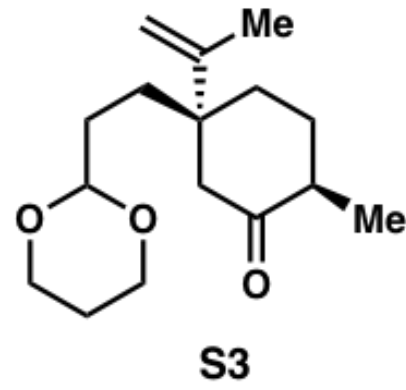


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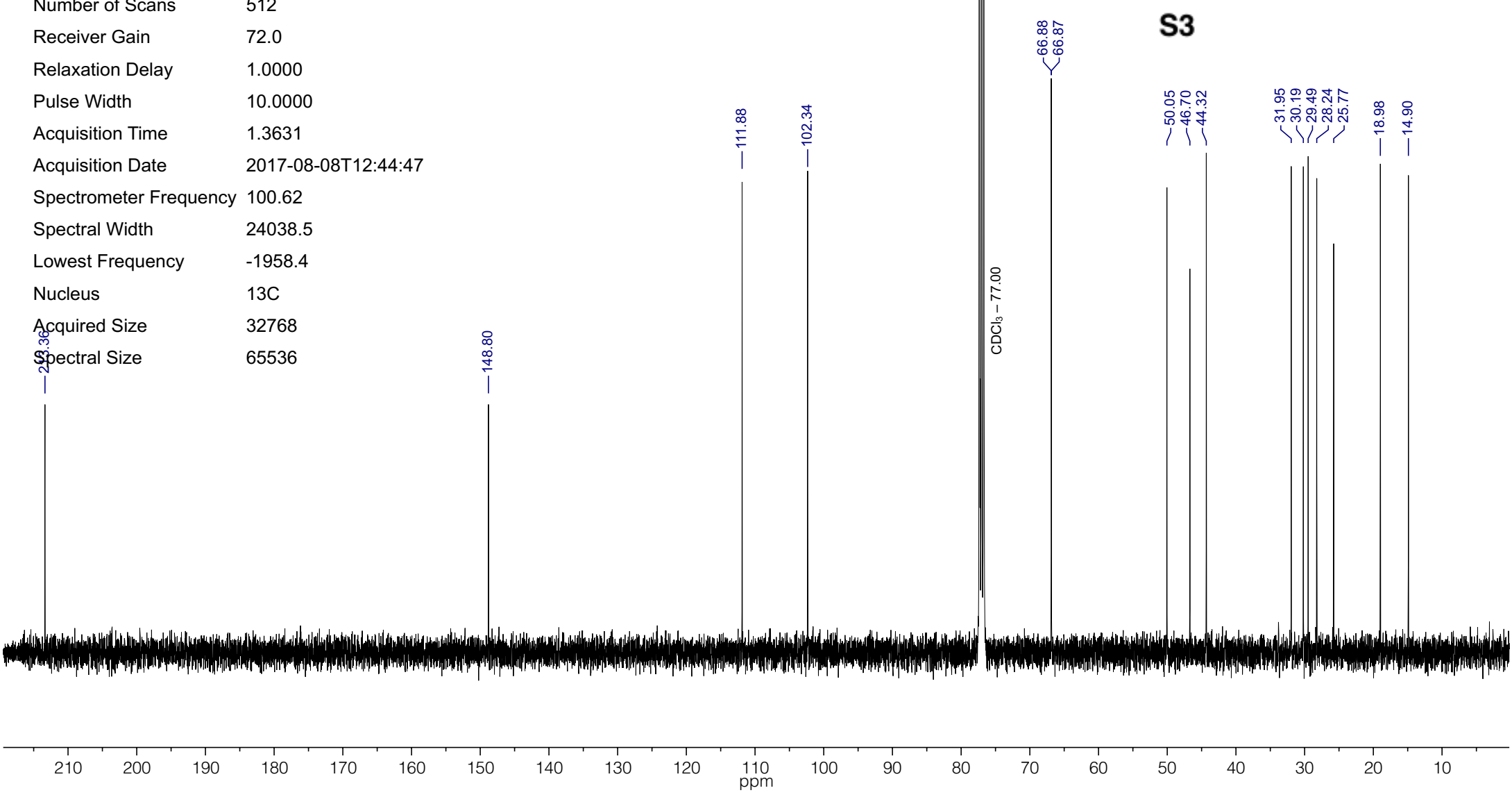
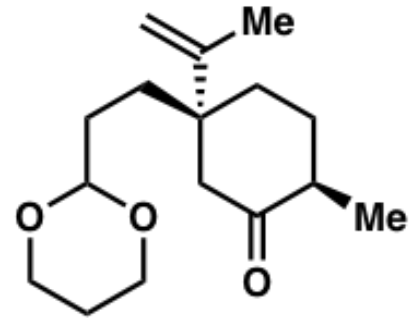




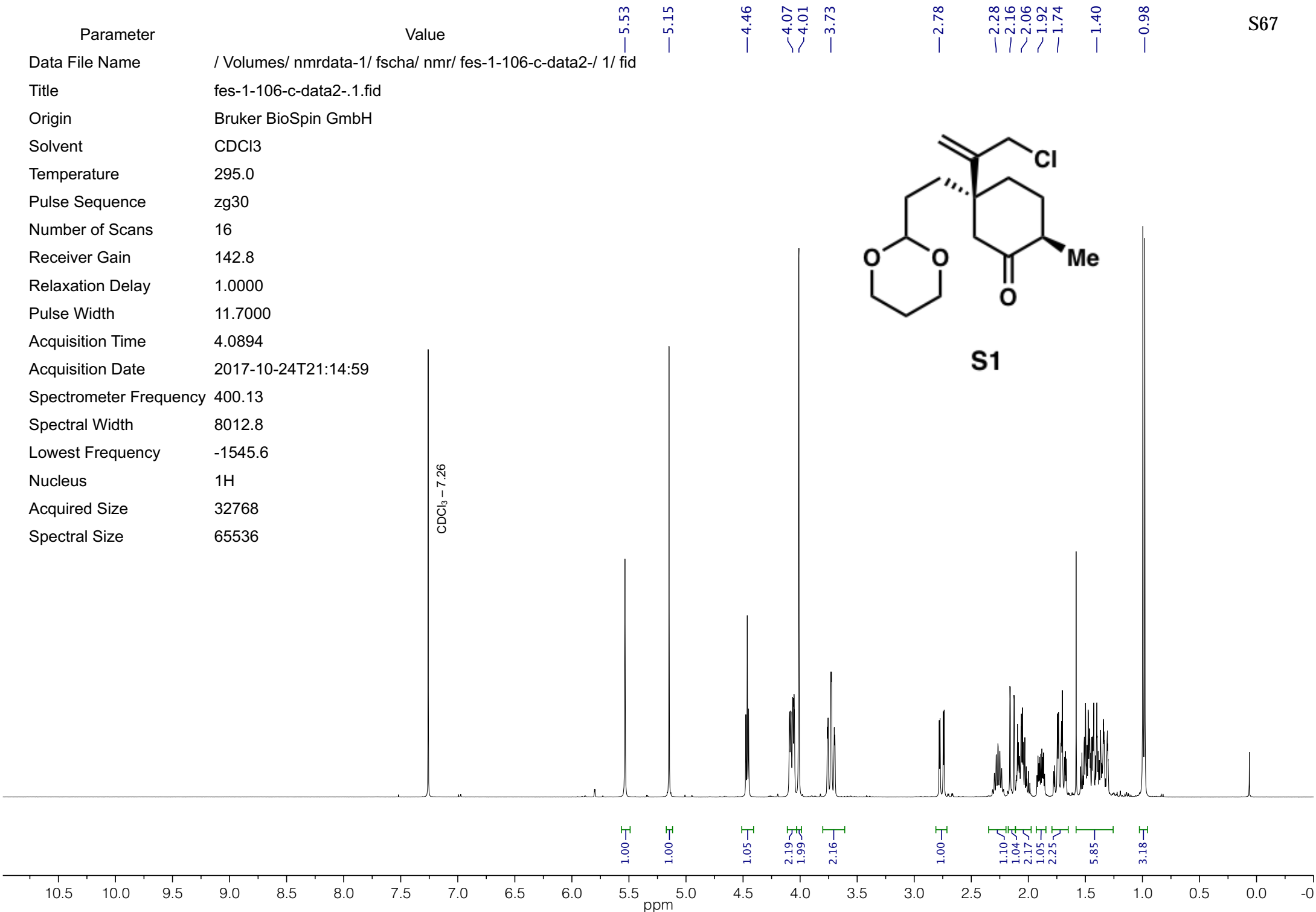
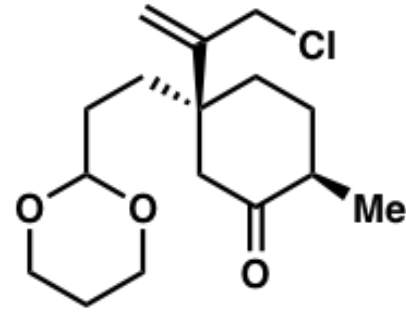
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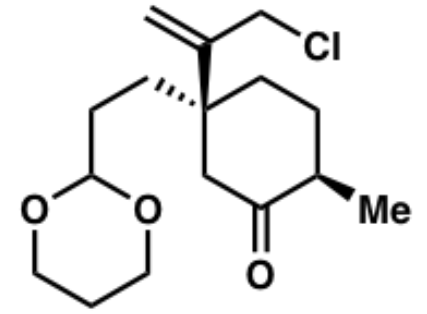
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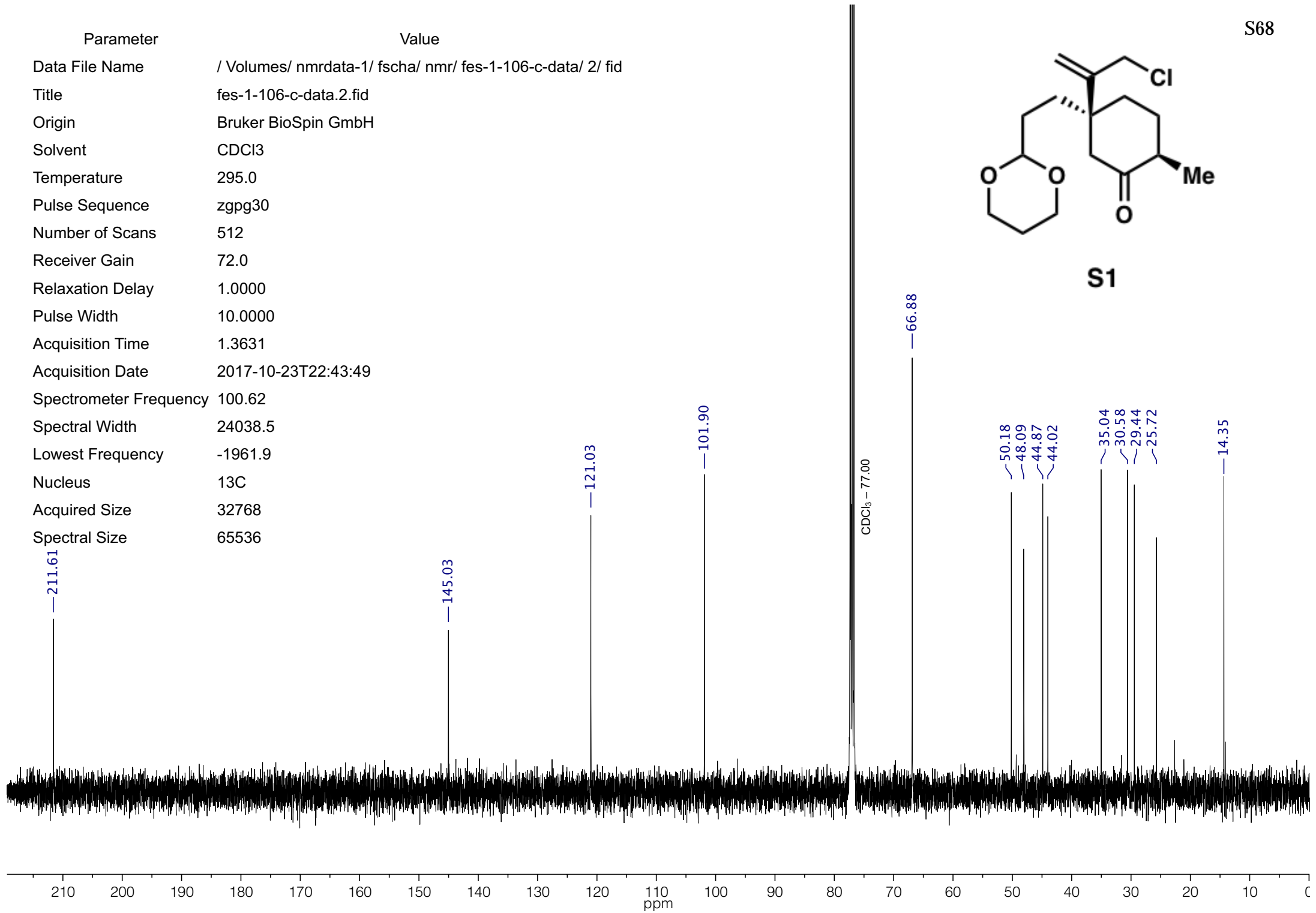
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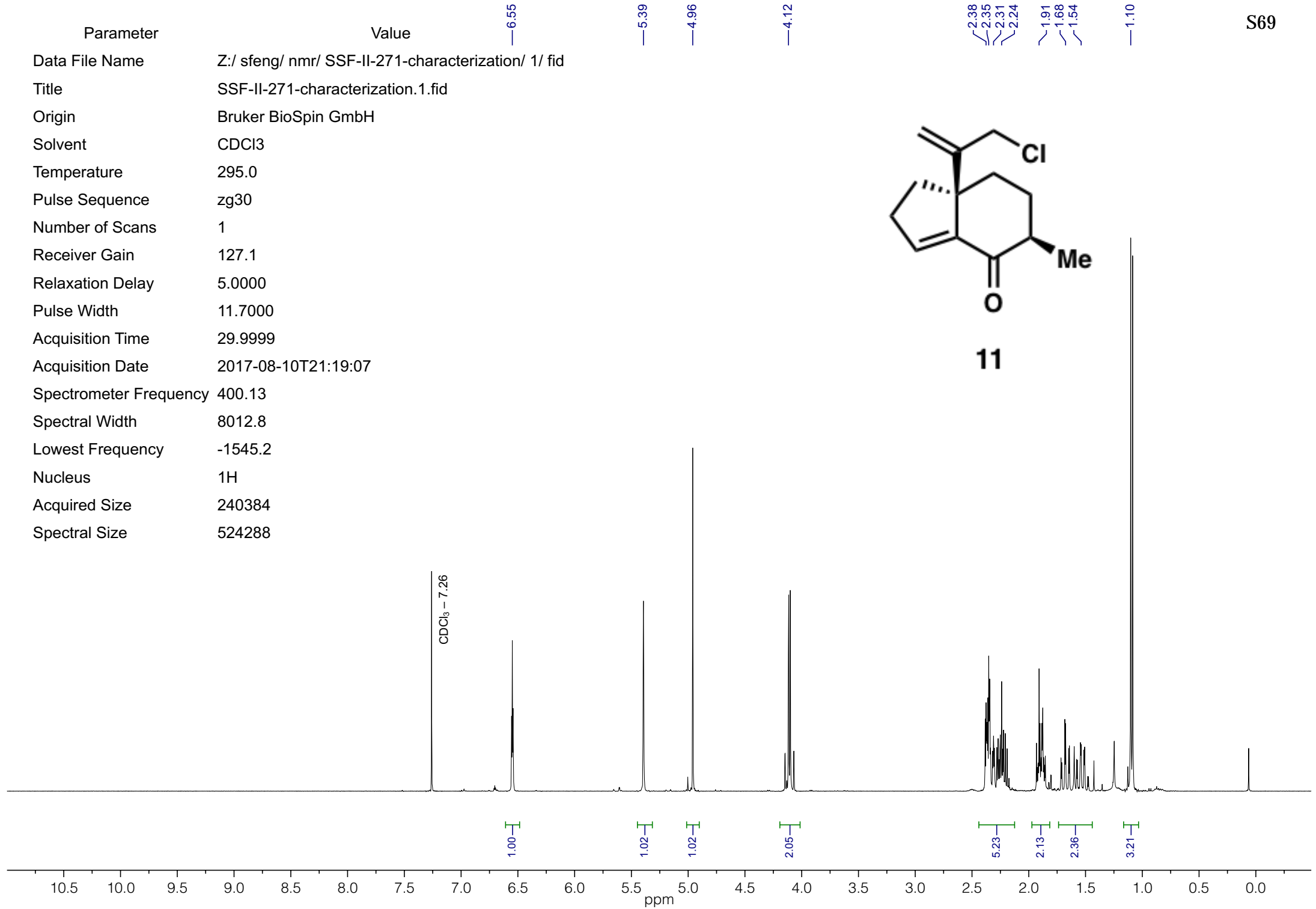
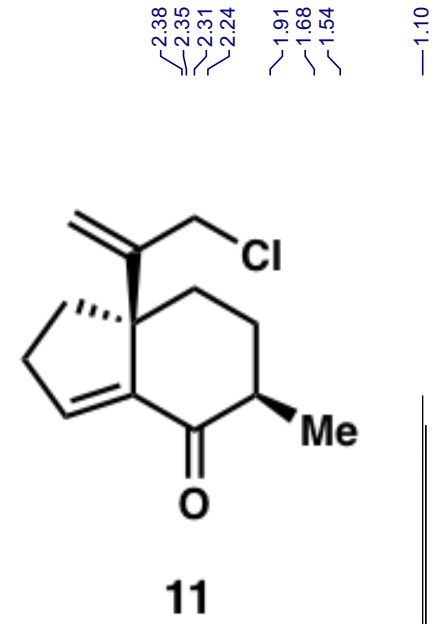
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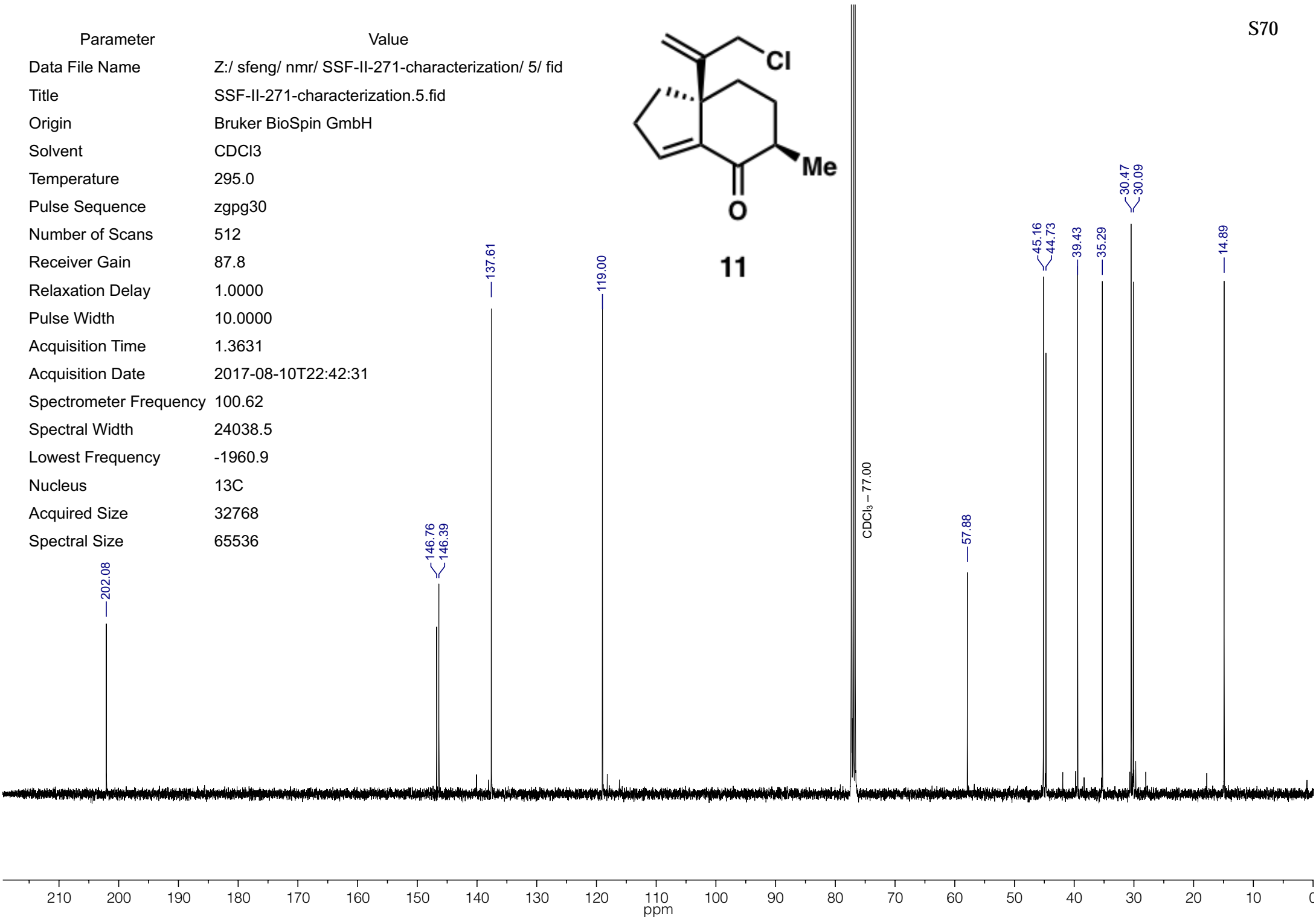
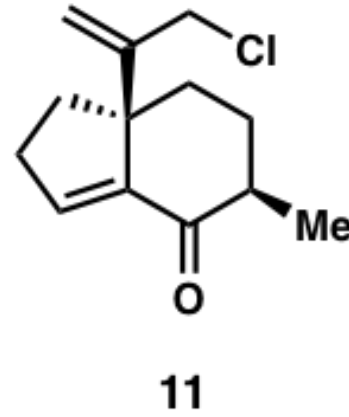
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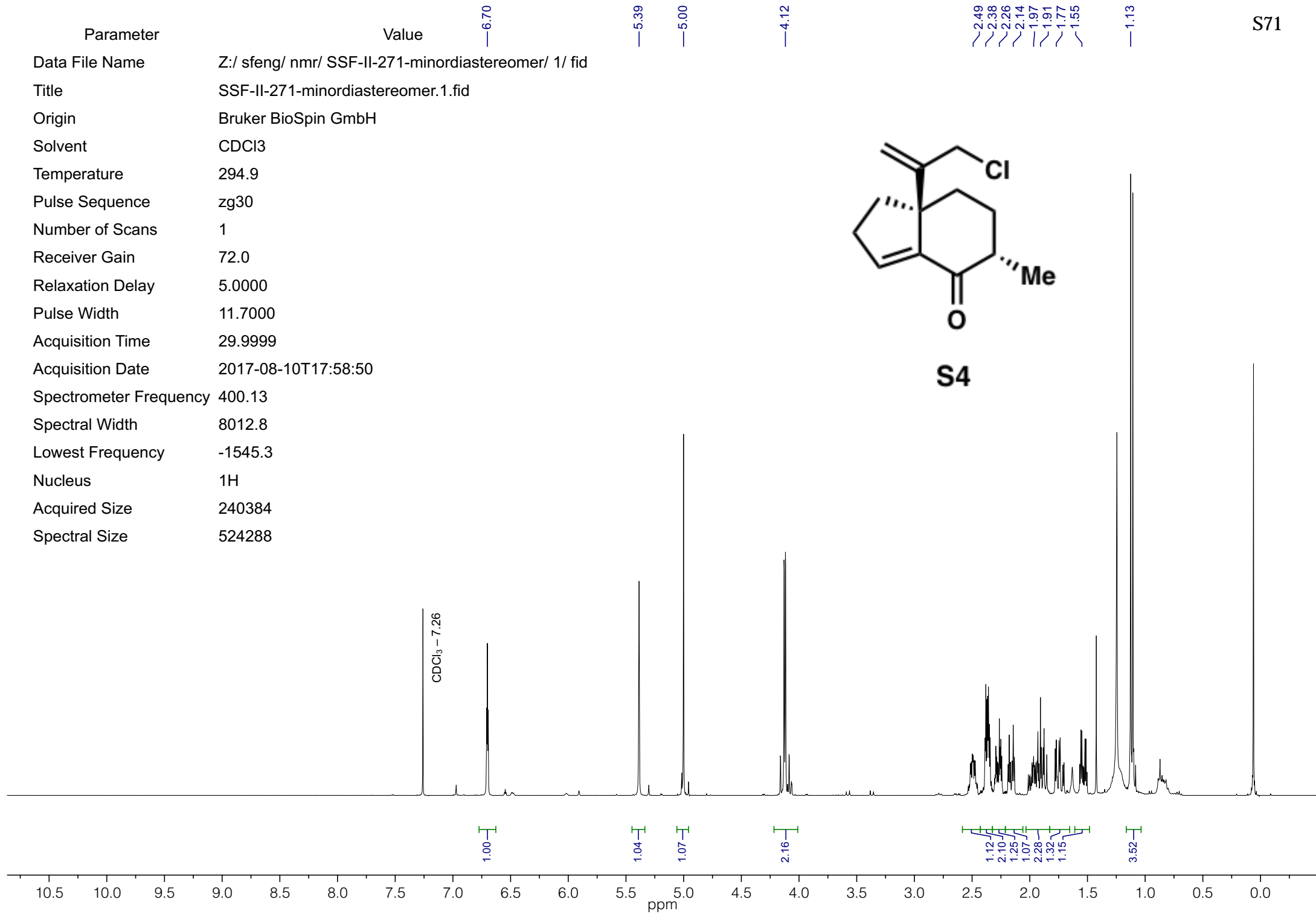
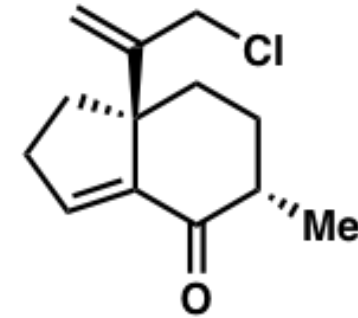
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Acquired Size	240384
Spectral Size	524288



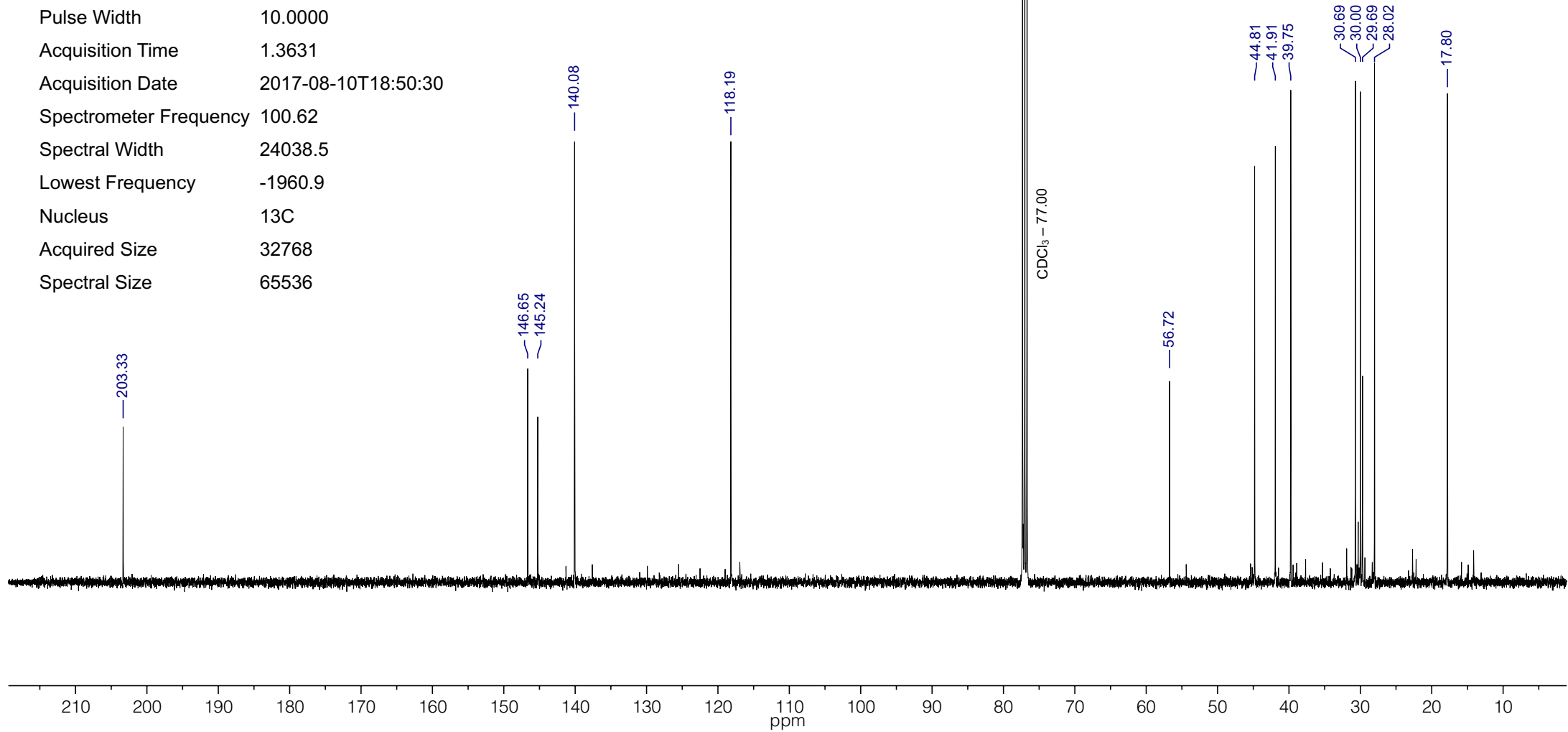
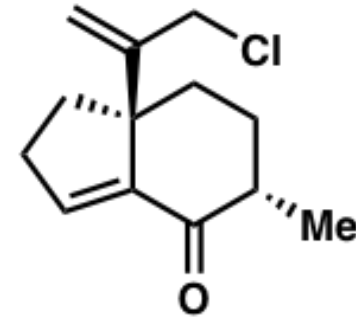
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Data File Name	Z:/ sfeng/ nmr/ SSF-II-271-characterization/ 5/ fid
Title	SSF-II-271-characterization.5.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	295.0
Pulse Sequence	zgpg30
Number of Scans	512
Receiver Gain	87.8
Relaxation Delay	1.0000
Pulse Width	10.0000
Acquisition Time	1.3631
Acquisition Date	2017-08-10T22:42:31
Spectrometer Frequency	100.62
Spectral Width	24038.5
Lowest Frequency	-1960.9
Nucleus	13C
Acquired Size	32768
Spectral Size	65536



Parameter	Value
Data File Name	Z:/ sfeng/ nmr/ SSF-II-271-minordiastereomer/ 1/ fid
Title	SSF-II-271-minordiastereomer.1.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl <sub>3</sub>
Temperature	294.9
Pulse Sequence	zg30
Number of Scans	1
Receiver Gain	72.0
Relaxation Delay	5.0000
Pulse Width	11.7000
Acquisition Time	29.9999
Acquisition Date	2017-08-10T17:58:50
Spectrometer Frequency	400.13
Spectral Width	8012.8
Lowest Frequency	-1545.3
Nucleus	<sup>1</sup> H
Acquired Size	240384
Spectral Size	524288



Parameter	Value
Data File Name	Z:/ sfeng/ nmr/ SSF-II-271-minordiastereomer/ 5/ fid
Title	SSF-II-271-minordiastereomer.5.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl <sub>3</sub>
Temperature	295.0
Pulse Sequence	zgpg30
Number of Scans	256
Receiver Gain	87.8
Relaxation Delay	1.0000
Pulse Width	10.0000
Acquisition Time	1.3631
Acquisition Date	2017-08-10T18:50:30
Spectrometer Frequency	100.62
Spectral Width	24038.5
Lowest Frequency	-1960.9
Nucleus	<sup>13</sup> C
Acquired Size	32768
Spectral Size	65536





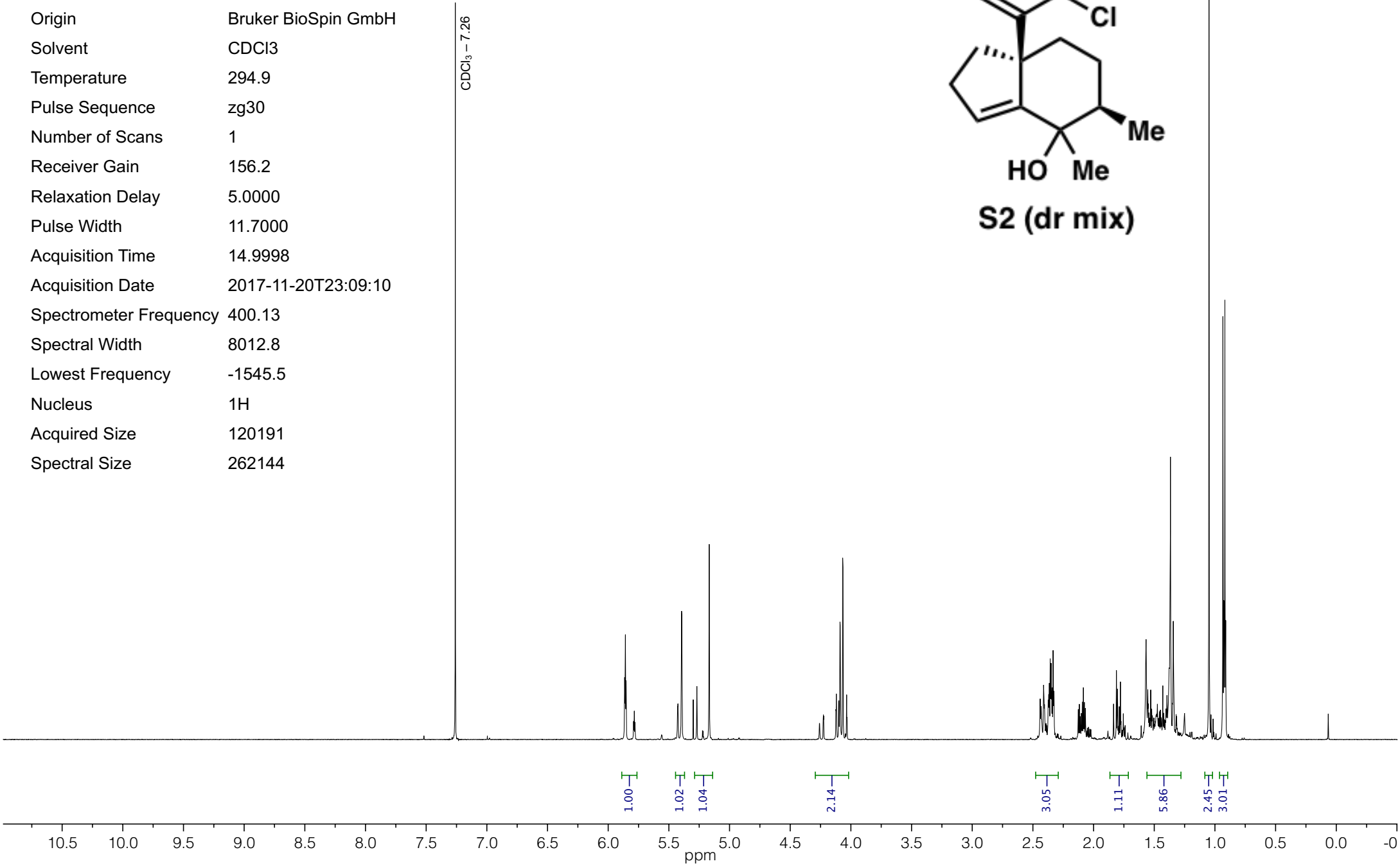
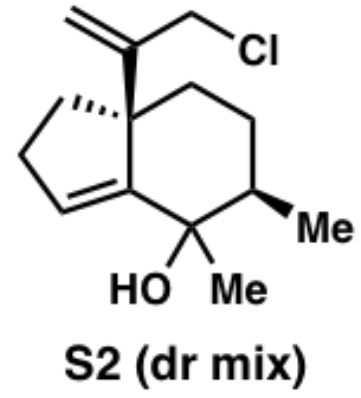
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Data File Name / Volumes/ nmrdata-1/ sfeng/ nmr/ SSF-III-67-flashed/ 1/ fid  
Title SSF-III-67-flashed.1.fid  
Origin Bruker BioSpin GmbH  
Solvent CDCl<sub>3</sub>  
Temperature 294.9  
Pulse Sequence zg30  
Number of Scans 1  
Receiver Gain 156.2  
Relaxation Delay 5.0000  
Pulse Width 11.7000  
Acquisition Time 14.9998  
Acquisition Date 2017-11-20T23:09:10  
Spectrometer Frequency 400.13  
Spectral Width 8012.8  
Lowest Frequency -1545.5  
Nucleus <sup>1</sup>H  
Acquired Size 120191  
Spectral Size 262144

CDCl<sub>3</sub> - 7.26

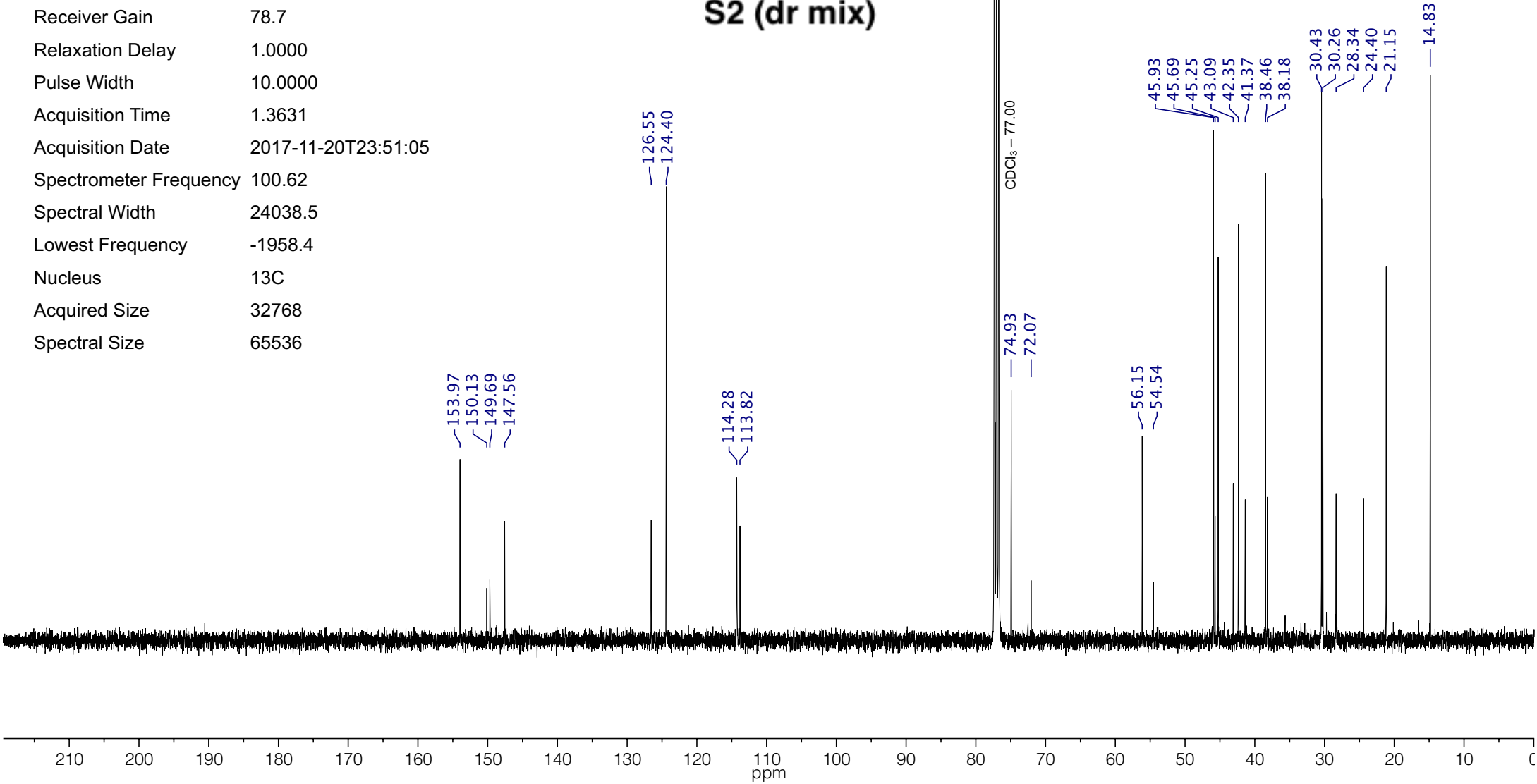
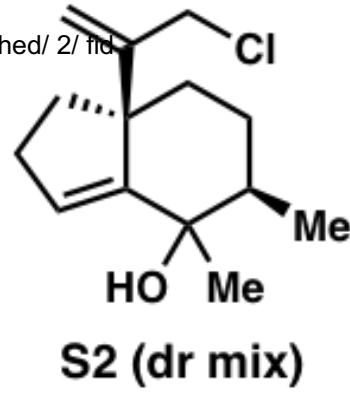
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5.27  
5.17

4.07

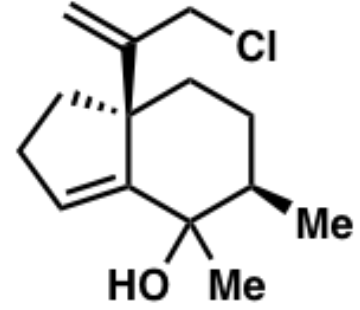
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1.57  
1.52  
1.37  
1.05  
0.93  
0.91



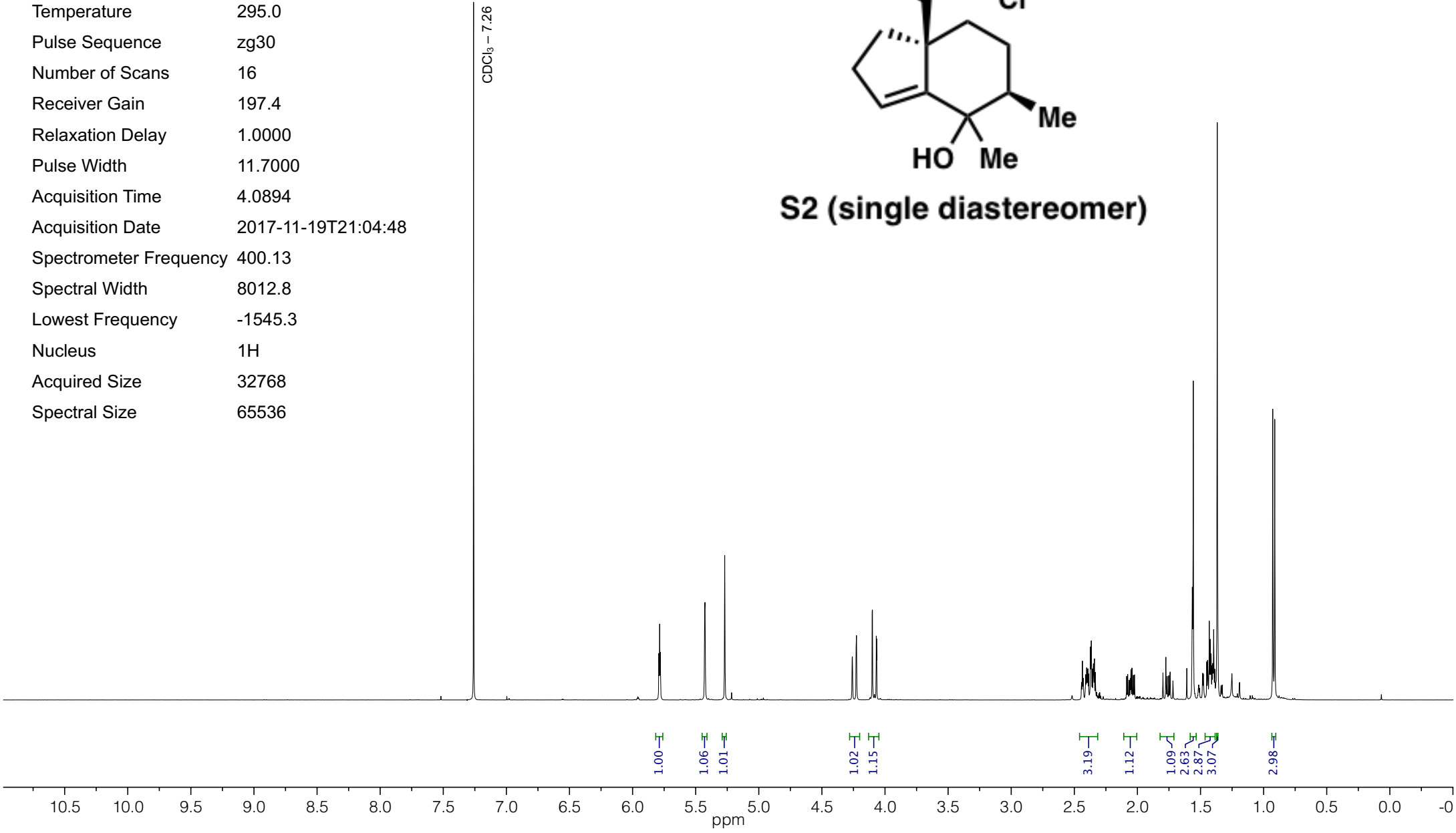
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Title	SSF-III-67-flashed.2.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	294.9
Pulse Sequence	zgpg30
Number of Scans	1024
Receiver Gain	78.7
Relaxation Delay	1.0000
Pulse Width	10.0000
Acquisition Time	1.3631
Acquisition Date	2017-11-20T23:51:05
Spectrometer Frequency	100.62
Spectral Width	24038.5
Lowest Frequency	-1958.4
Nucleus	13C
Acquired Size	32768
Spectral Size	65536



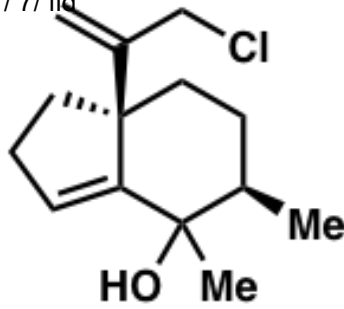
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Data File Name	/ Volumes/ nmrdata-1/ sfeng/ nmr/ SSF-III-60-F1/ 2/ fid
Title	SSF-III-60-F1.2.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	295.0
Pulse Sequence	zg30
Number of Scans	16
Receiver Gain	197.4
Relaxation Delay	1.0000
Pulse Width	11.7000
Acquisition Time	4.0894
Acquisition Date	2017-11-19T21:04:48
Spectrometer Frequency	400.13
Spectral Width	8012.8
Lowest Frequency	-1545.3
Nucleus	1H
Acquired Size	32768
Spectral Size	65536



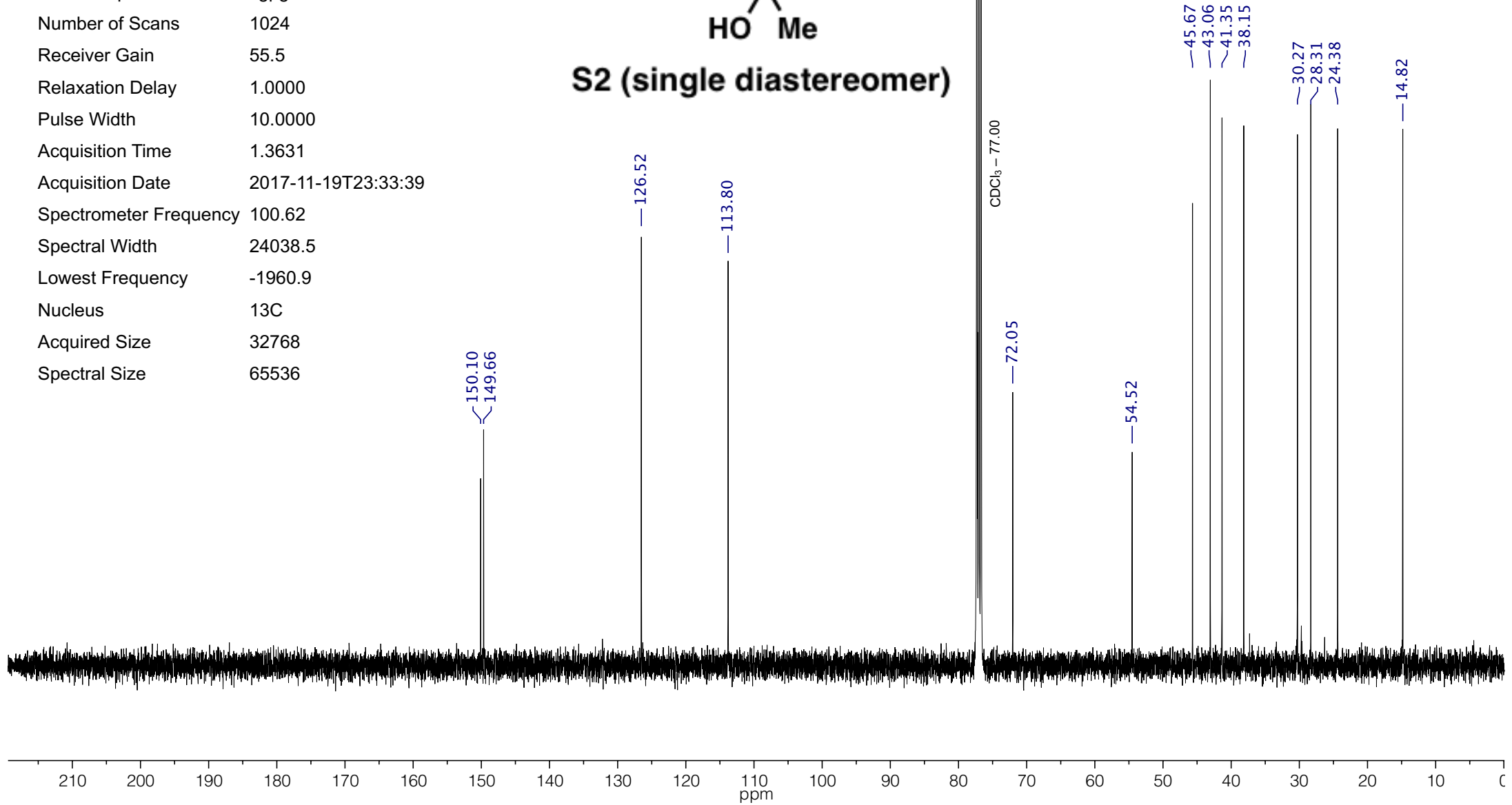
S2 (single diastereomer)



Parameter	Value
Data File Name	/ Volumes/ nmrdata-1/ sfeng/ nmr/ SSF-III-60-F1/ 7/ fid
Title	SSF-III-60-F1.7.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	295.0
Pulse Sequence	zgpg30
Number of Scans	1024
Receiver Gain	55.5
Relaxation Delay	1.0000
Pulse Width	10.0000
Acquisition Time	1.3631
Acquisition Date	2017-11-19T23:33:39
Spectrometer Frequency	100.62
Spectral Width	24038.5
Lowest Frequency	-1960.9
Nucleus	13C
Acquired Size	32768
Spectral Size	65536

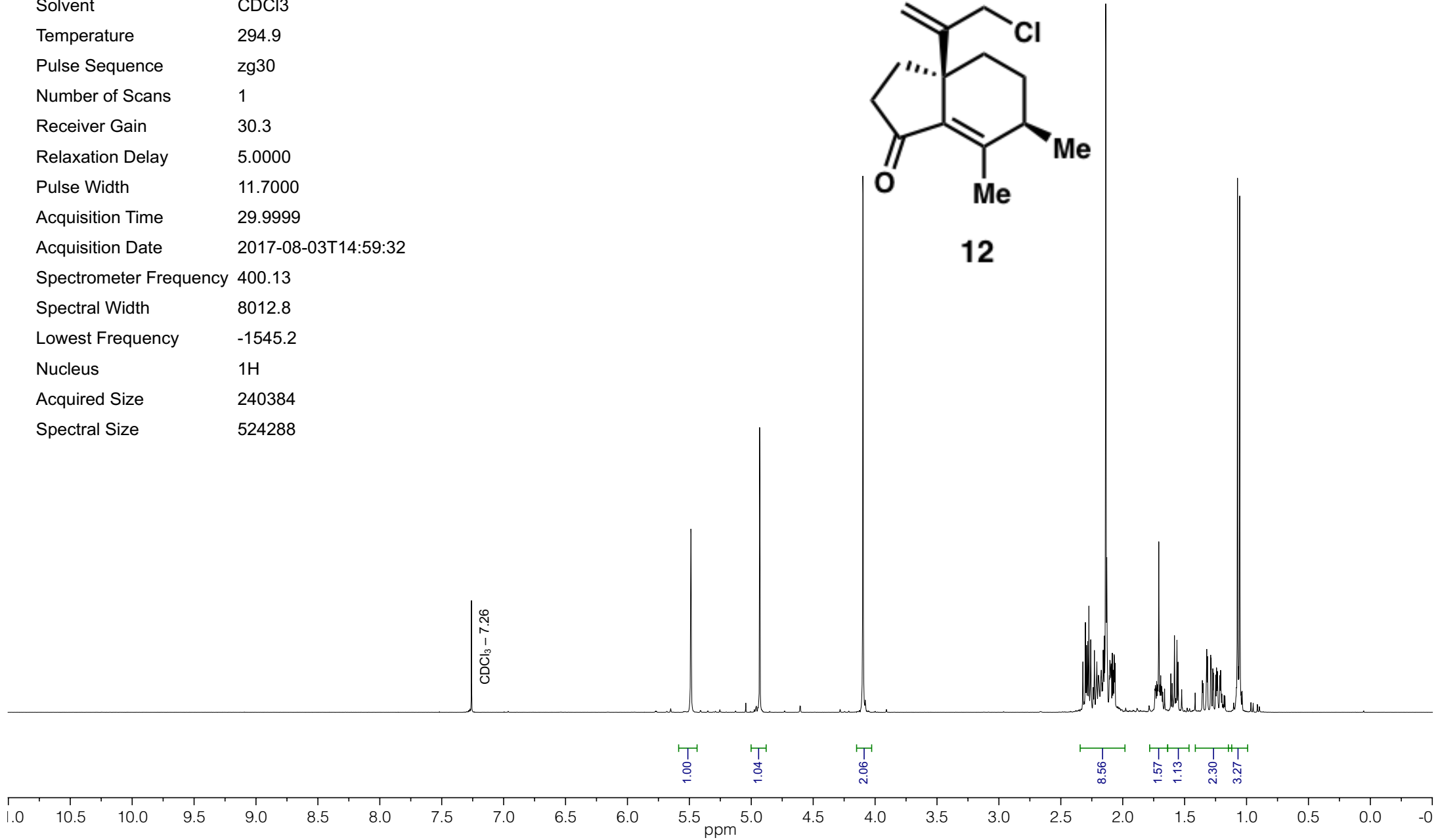
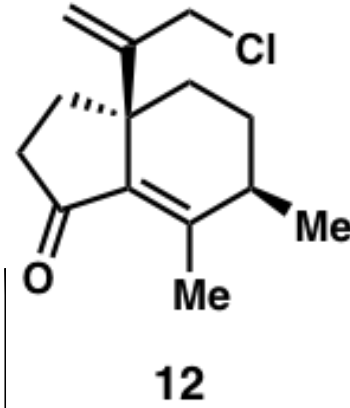


S2 (single diastereomer)

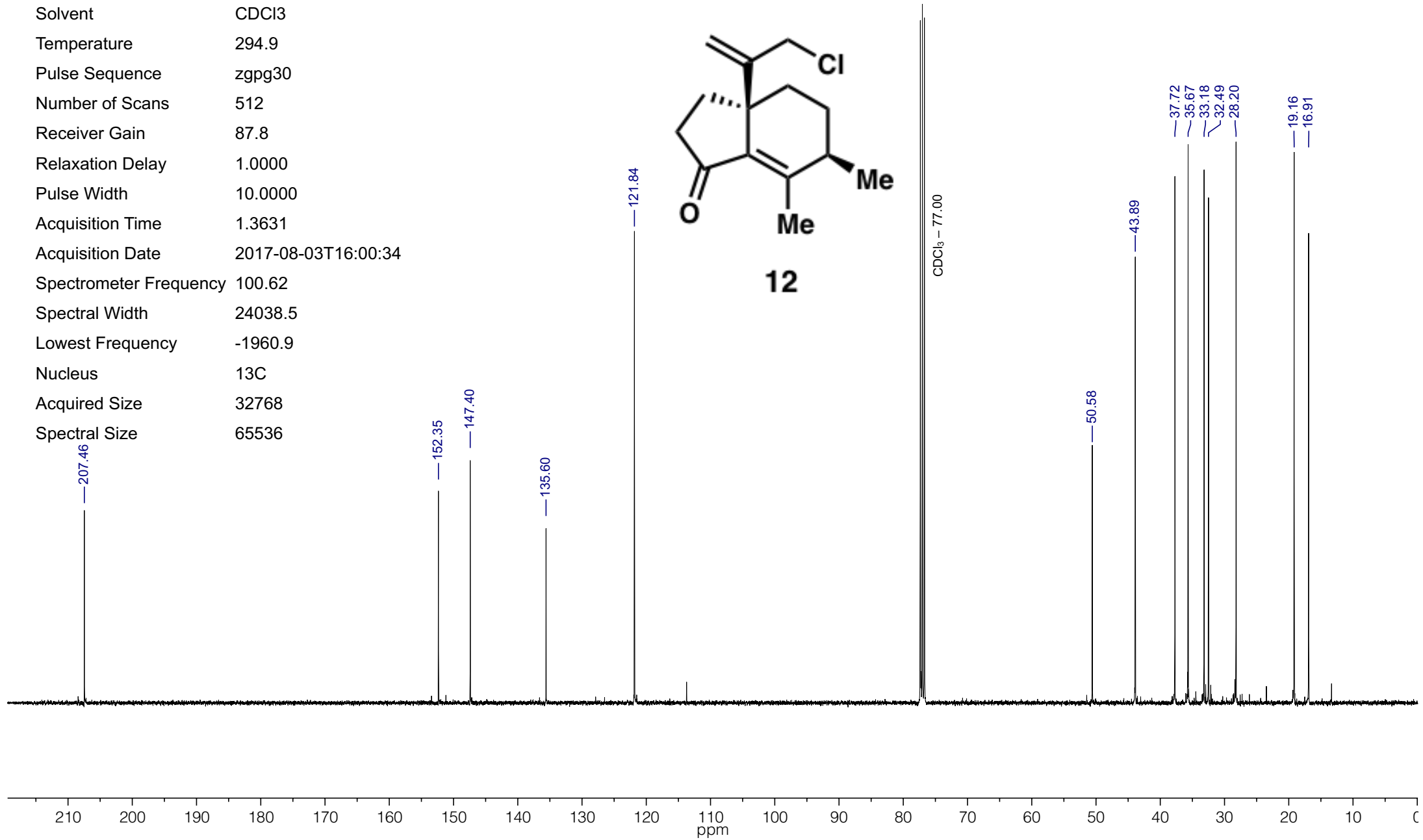
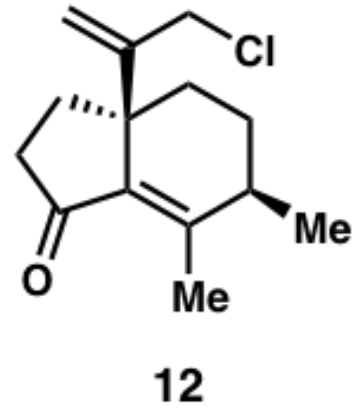


Parameter	Value
Data File Name	Z:/ sfeng/ nmr/ SSF-II-265-characterization/ 1/ fid
Title	SSF-II-265-characterization.1.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	294.9
Pulse Sequence	zg30
Number of Scans	1
Receiver Gain	30.3
Relaxation Delay	5.0000
Pulse Width	11.7000
Acquisition Time	29.9999
Acquisition Date	2017-08-03T14:59:32
Spectrometer Frequency	400.13
Spectral Width	8012.8
Lowest Frequency	-1545.2
Nucleus	1H
Acquired Size	240384
Spectral Size	524288

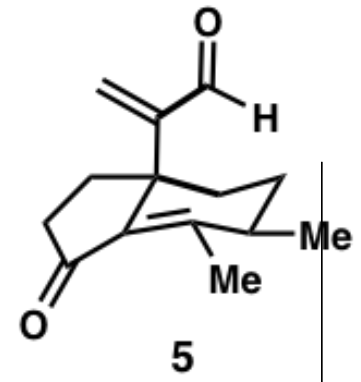
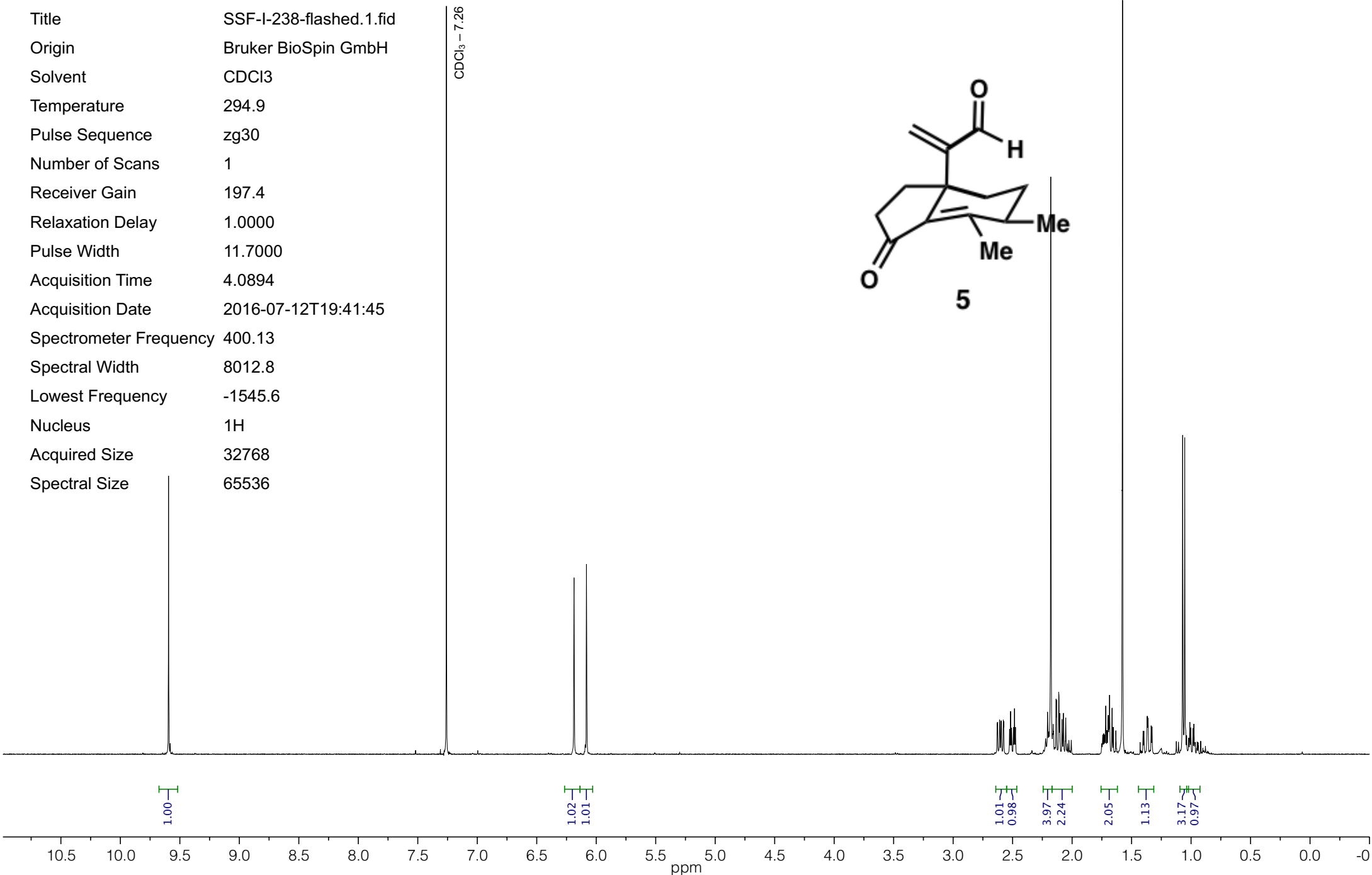
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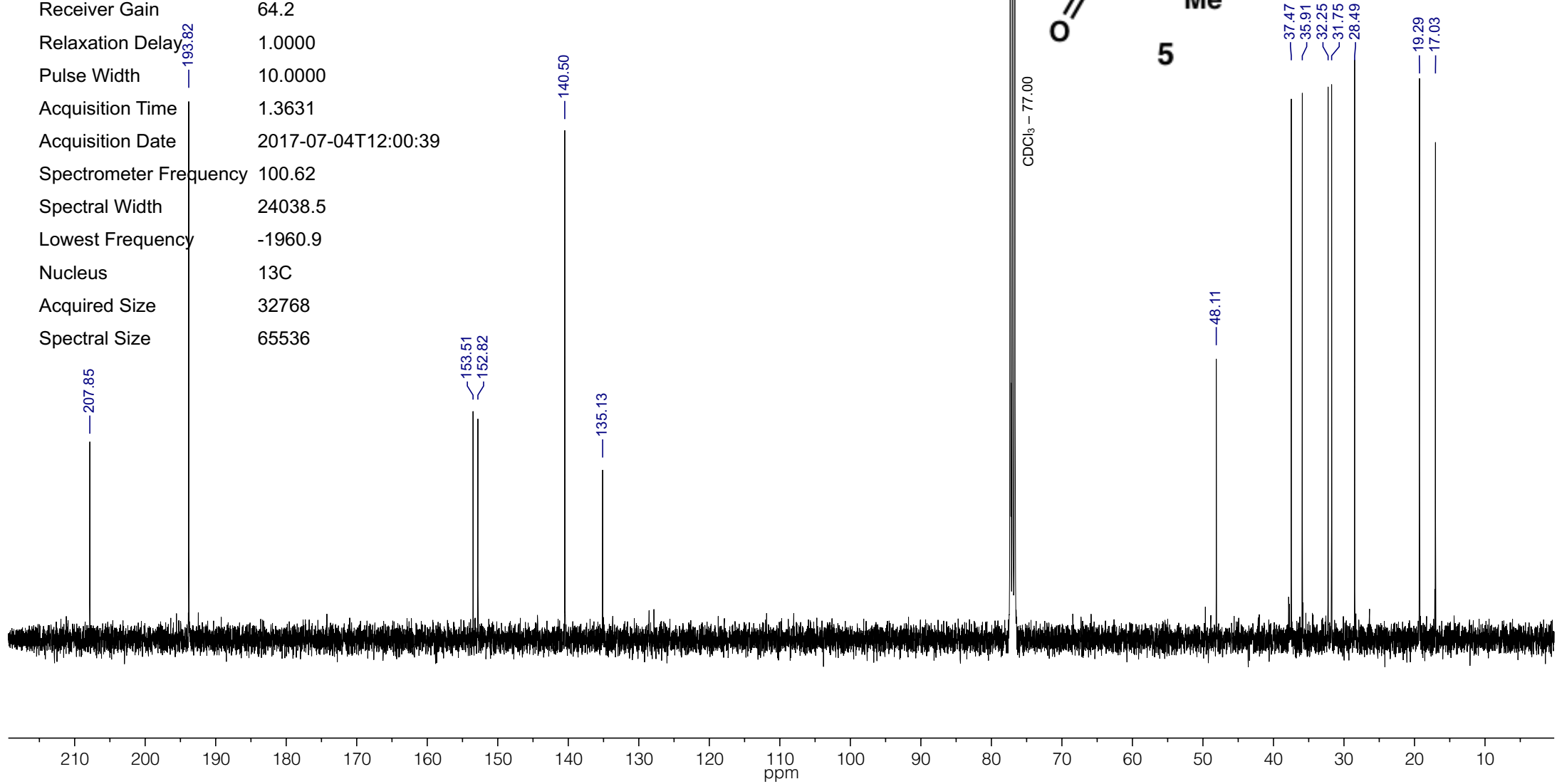
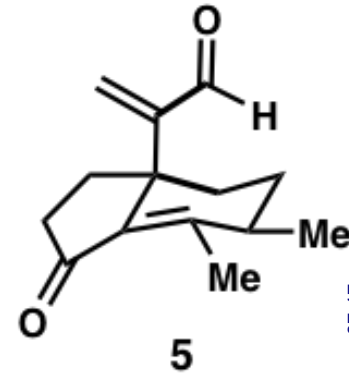
Parameter	Value
Data File Name	Z:/ sfeng/ nmr/ SSF-II-265-characterization/ 5/ fid
Title	SSF-II-265-characterization.5.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl <sub>3</sub>
Temperature	294.9
Pulse Sequence	zgpg30
Number of Scans	512
Receiver Gain	87.8
Relaxation Delay	1.0000
Pulse Width	10.0000
Acquisition Time	1.3631
Acquisition Date	2017-08-03T16:00:34
Spectrometer Frequency	100.62
Spectral Width	24038.5
Lowest Frequency	-1960.9
Nucleus	<sup>13</sup> C
Acquired Size	32768
Spectral Size	65536



Parameter	Value
Data File Name	Z:/ sfeng/ nmr/ SSF-I-238-flashed/ 1/ fid
Title	SSF-I-238-flashed.1.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	294.9
Pulse Sequence	zg30
Number of Scans	1
Receiver Gain	197.4
Relaxation Delay	1.0000
Pulse Width	11.7000
Acquisition Time	4.0894
Acquisition Date	2016-07-12T19:41:45
Spectrometer Frequency	400.13
Spectral Width	8012.8
Lowest Frequency	-1545.6
Nucleus	1H
Acquired Size	32768
Spectral Size	65536



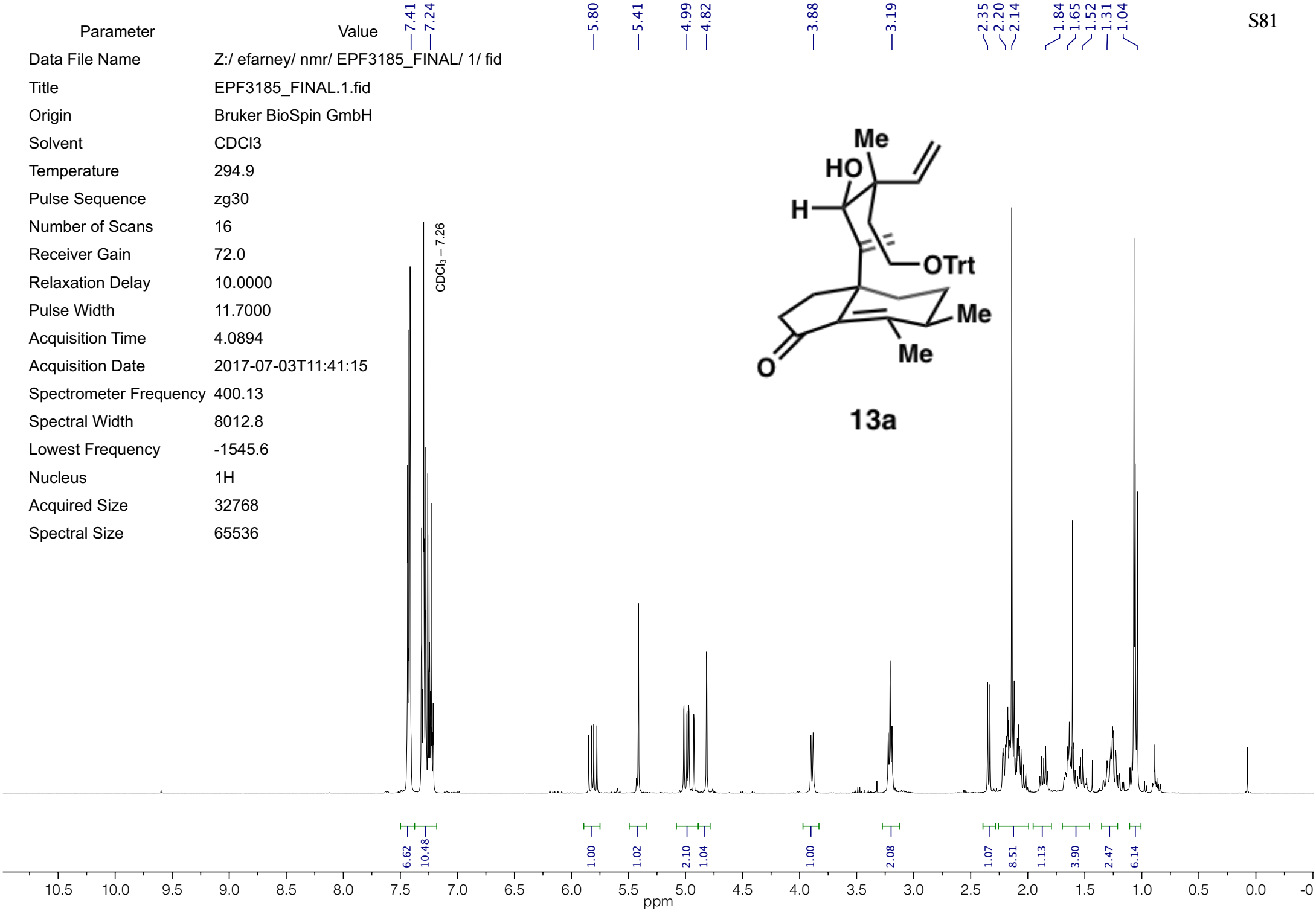
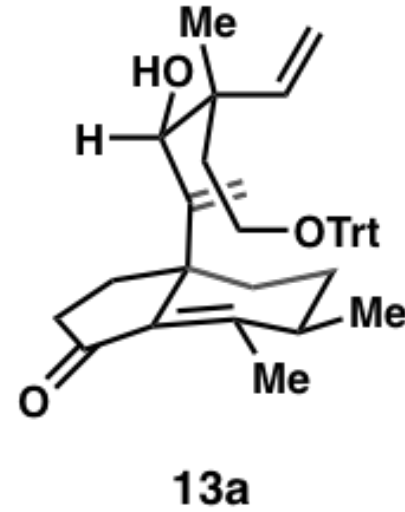
Parameter	Value
Data File Name	Z:/ efarney/ nmr/ EPF3187_PTLC_Top/ 2/ fid
Title	EPF3187_PTLC_Top.2.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	295.0
Pulse Sequence	zgpg30
Number of Scans	512
Receiver Gain	64.2
Relaxation Delay	1.0000
Pulse Width	10.0000
Acquisition Time	1.3631
Acquisition Date	2017-07-04T12:00:39
Spectrometer Frequency	100.62
Spectral Width	24038.5
Lowest Frequency	-1960.9
Nucleus	13C
Acquired Size	32768
Spectral Size	65536



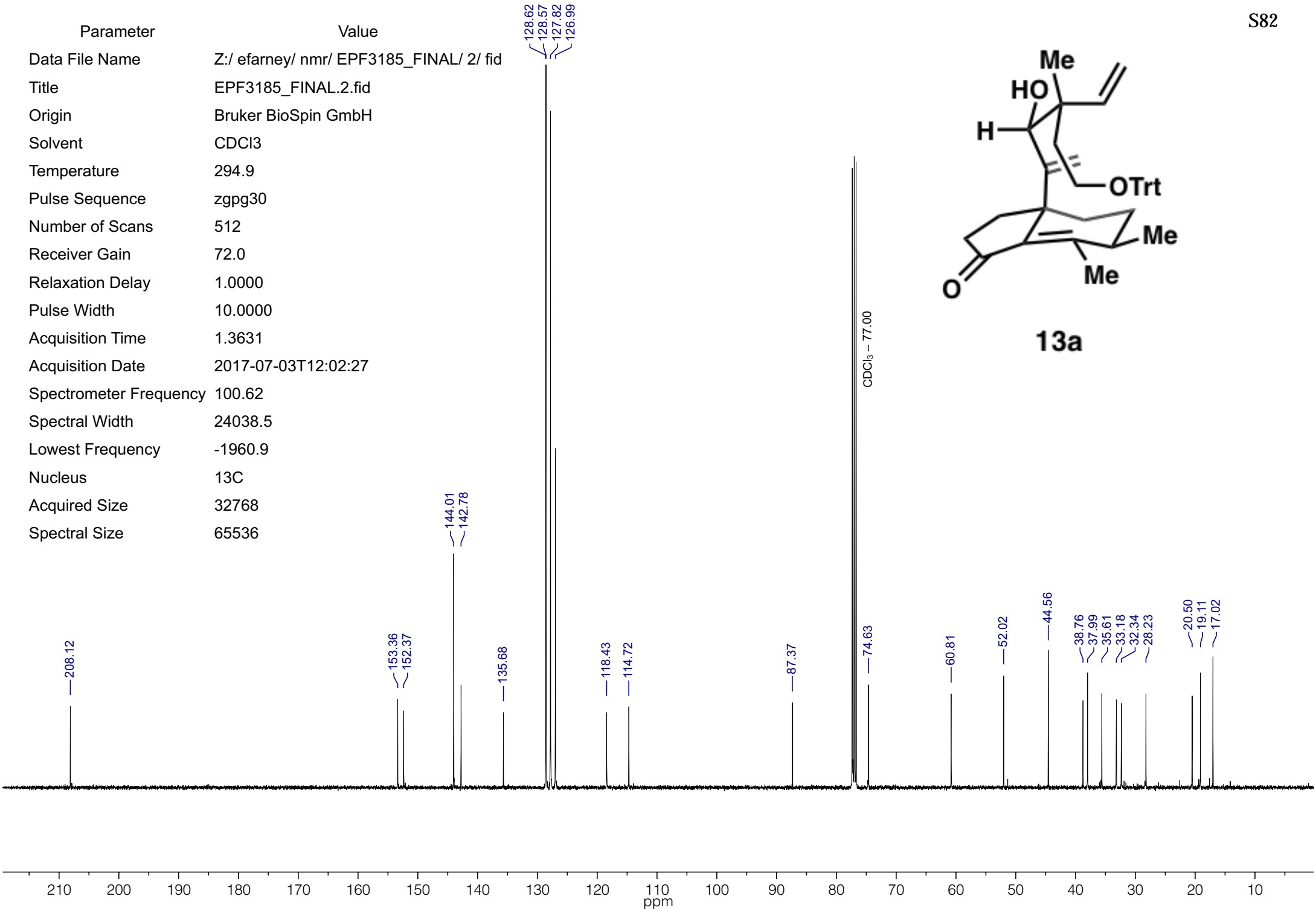


Parameter	Value
Data File Name	Z:/ efarney/ nmr/ EPF3185_FINAL/ 1/ fid
Title	EPF3185_FINAL.1.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	294.9
Pulse Sequence	zg30
Number of Scans	16
Receiver Gain	72.0
Relaxation Delay	10.0000
Pulse Width	11.7000
Acquisition Time	4.0894
Acquisition Date	2017-07-03T11:41:15
Spectrometer Frequency	400.13
Spectral Width	8012.8
Lowest Frequency	-1545.6
Nucleus	1H
Acquired Size	32768
Spectral Size	65536

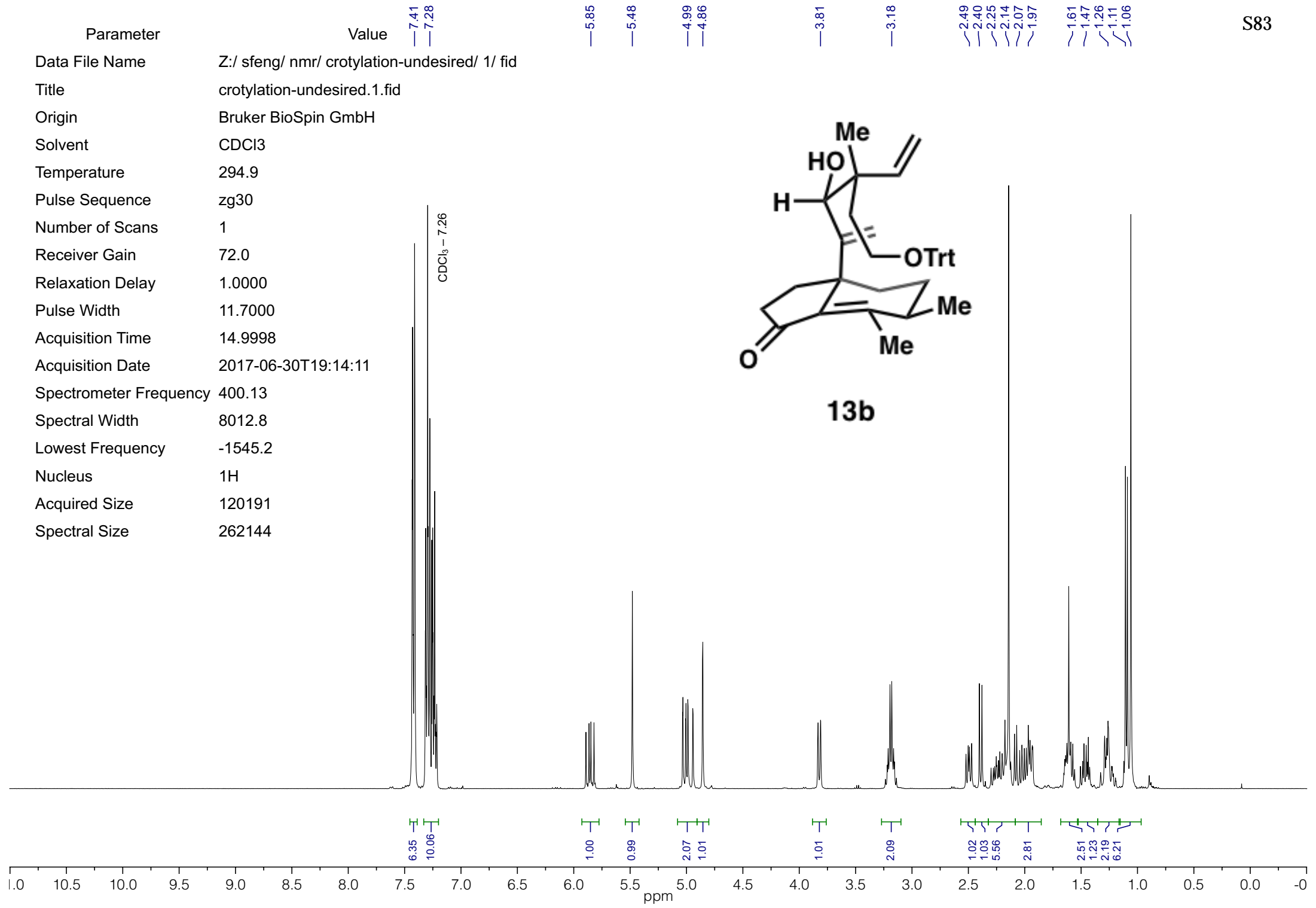
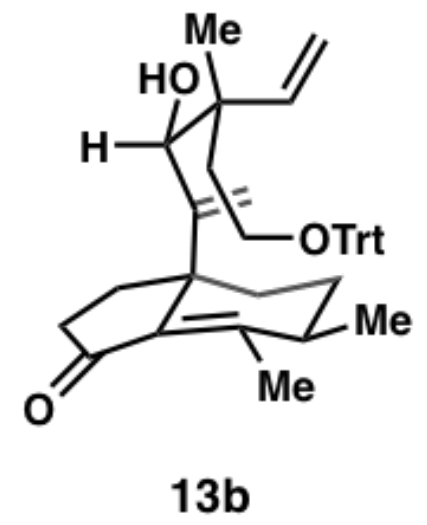
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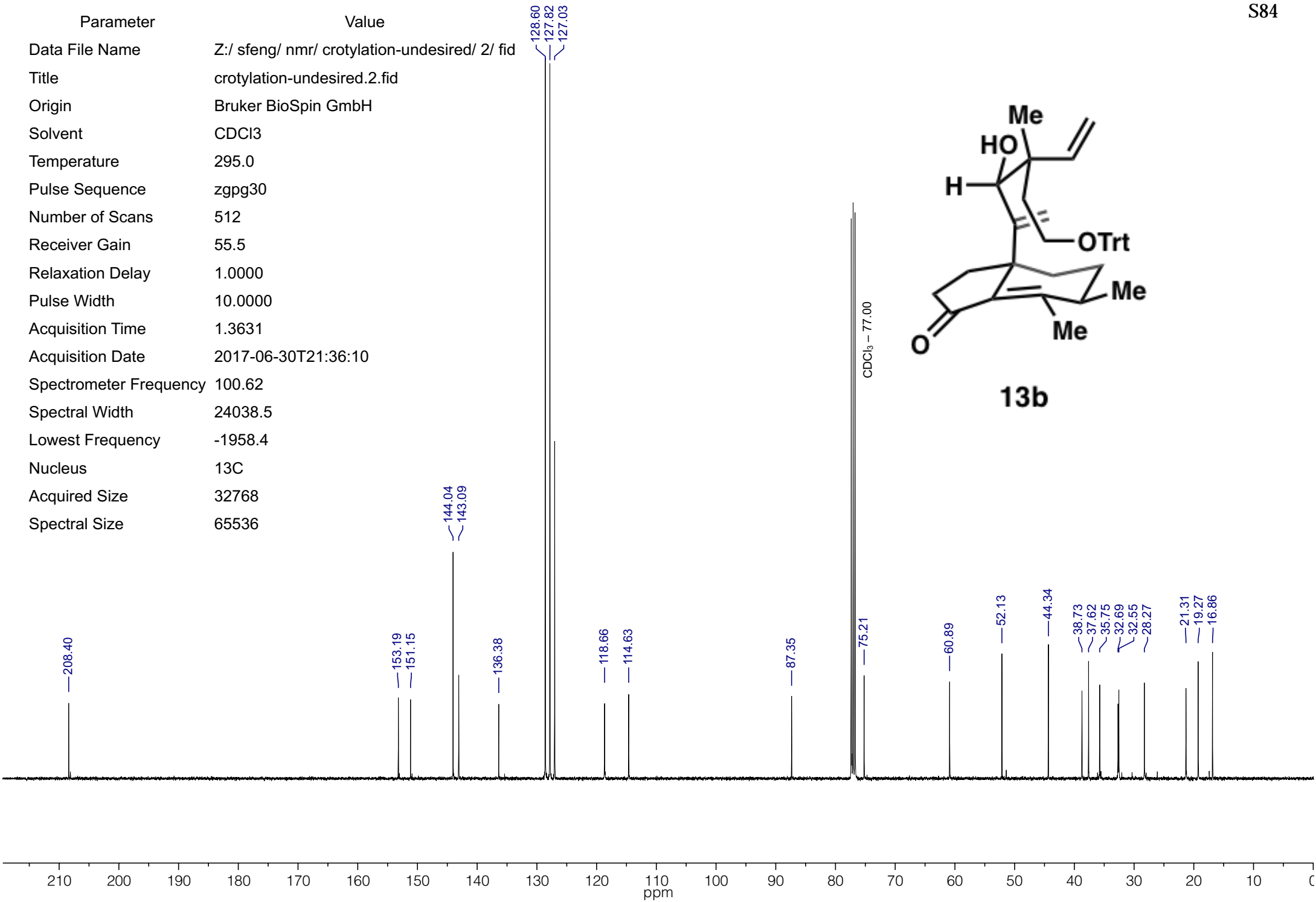
Parameter	Value
Data File Name	Z:/ efarney/ nmr/ EPF3185_FINAL/ 2/ fid
Title	EPF3185_FINAL.2.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	294.9
Pulse Sequence	zgpg30
Number of Scans	512
Receiver Gain	72.0
Relaxation Delay	1.0000
Pulse Width	10.0000
Acquisition Time	1.3631
Acquisition Date	2017-07-03T12:02:27
Spectrometer Frequency	100.62
Spectral Width	24038.5
Lowest Frequency	-1960.9
Nucleus	13C
Acquired Size	32768
Spectral Size	65536



Parameter	Value
Data File Name	Z:/ sfeng/ nmr/ crotylation-undesired/ 1/ fid
Title	crotylation-undesired.1.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	294.9
Pulse Sequence	zg30
Number of Scans	1
Receiver Gain	72.0
Relaxation Delay	1.0000
Pulse Width	11.7000
Acquisition Time	14.9998
Acquisition Date	2017-06-30T19:14:11
Spectrometer Frequency	400.13
Spectral Width	8012.8
Lowest Frequency	-1545.2
Nucleus	1H
Acquired Size	120191
Spectral Size	262144

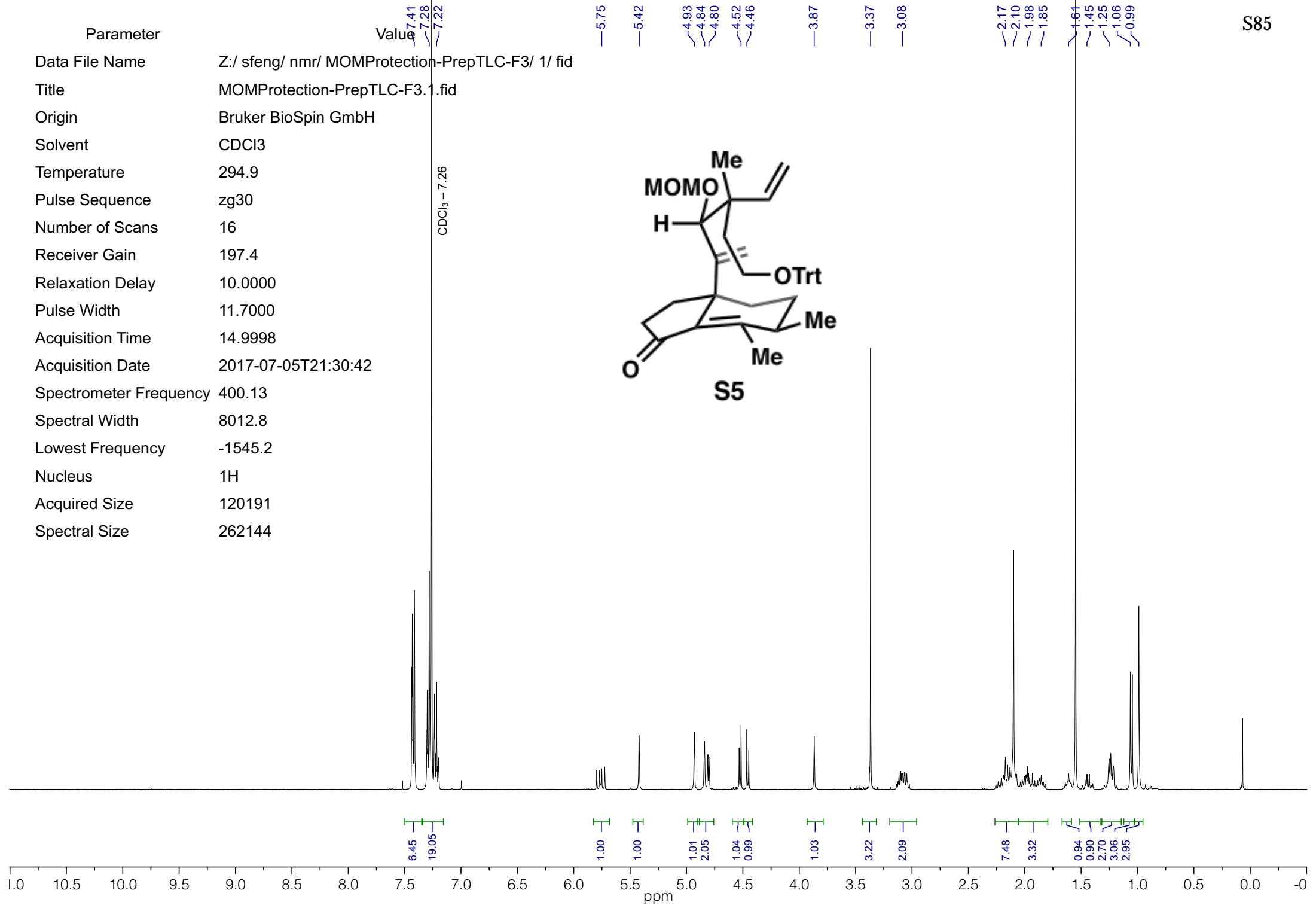
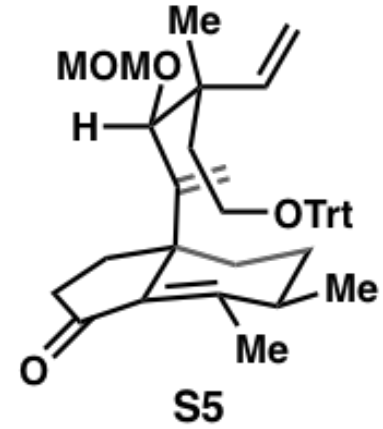


Parameter	Value
Data File Name	Z:/ sfeng/ nmr/ crotylation-undesired/ 2/ fid
Title	crotylation-undesired.2.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	295.0
Pulse Sequence	zgpg30
Number of Scans	512
Receiver Gain	55.5
Relaxation Delay	1.0000
Pulse Width	10.0000
Acquisition Time	1.3631
Acquisition Date	2017-06-30T21:36:10
Spectrometer Frequency	100.62
Spectral Width	24038.5
Lowest Frequency	-1958.4
Nucleus	13C
Acquired Size	32768
Spectral Size	65536

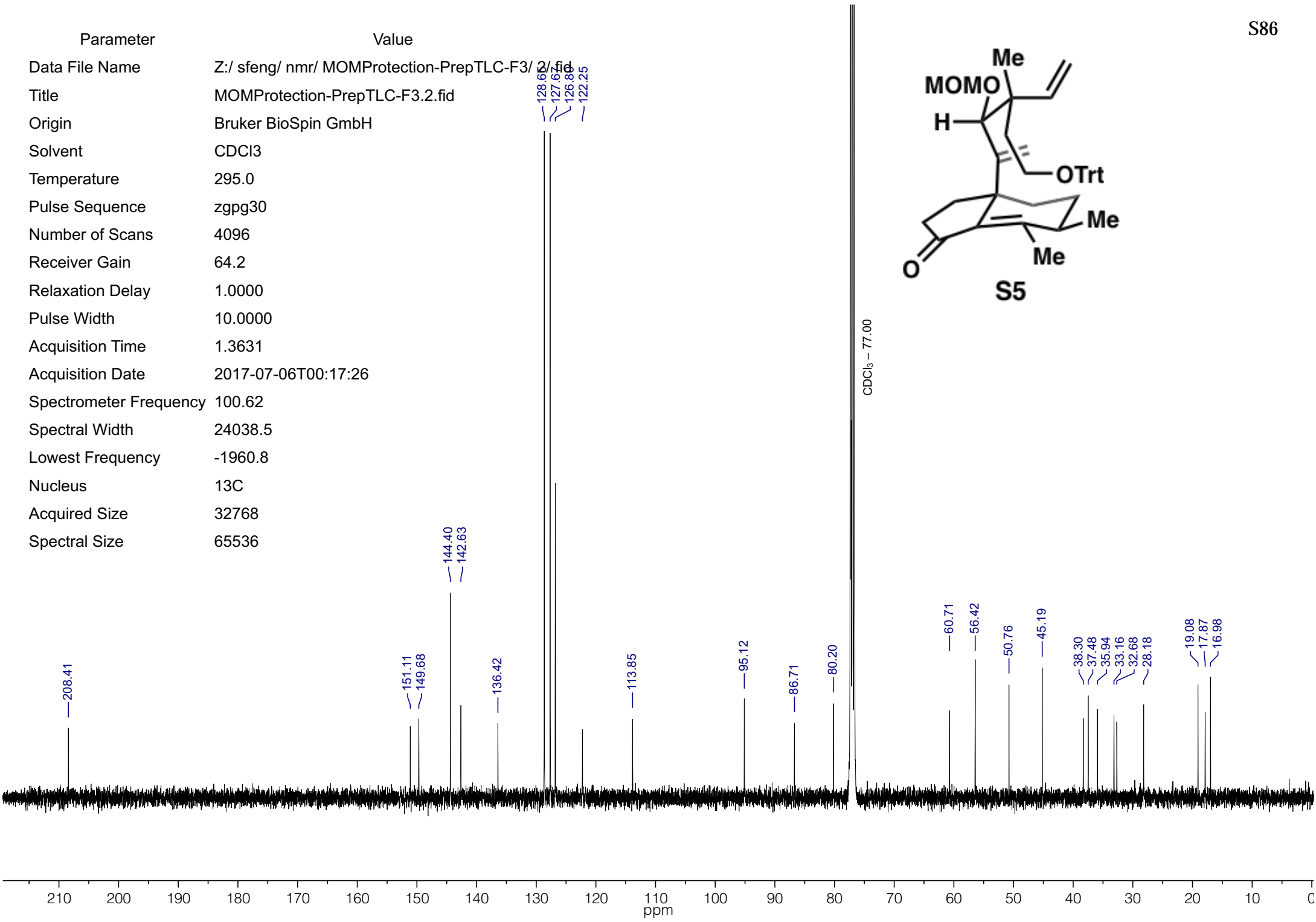
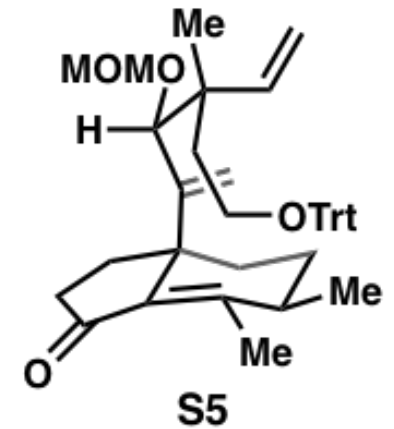


Parameter Value  
Data File Name Z:/ sfeng/ nmr/ MOMProtection-PrepTLC-F3/ 1/ fid  
Title MOMProtection-PrepTLC-F3.1.fid  
Origin Bruker BioSpin GmbH  
Solvent CDCl3  
Temperature 294.9  
Pulse Sequence zg30  
Number of Scans 16  
Receiver Gain 197.4  
Relaxation Delay 10.0000  
Pulse Width 11.7000  
Acquisition Time 14.9998  
Acquisition Date 2017-07-05T21:30:42  
Spectrometer Frequency 400.13  
Spectral Width 8012.8  
Lowest Frequency -1545.2  
Nucleus 1H  
Acquired Size 120191  
Spectral Size 262144

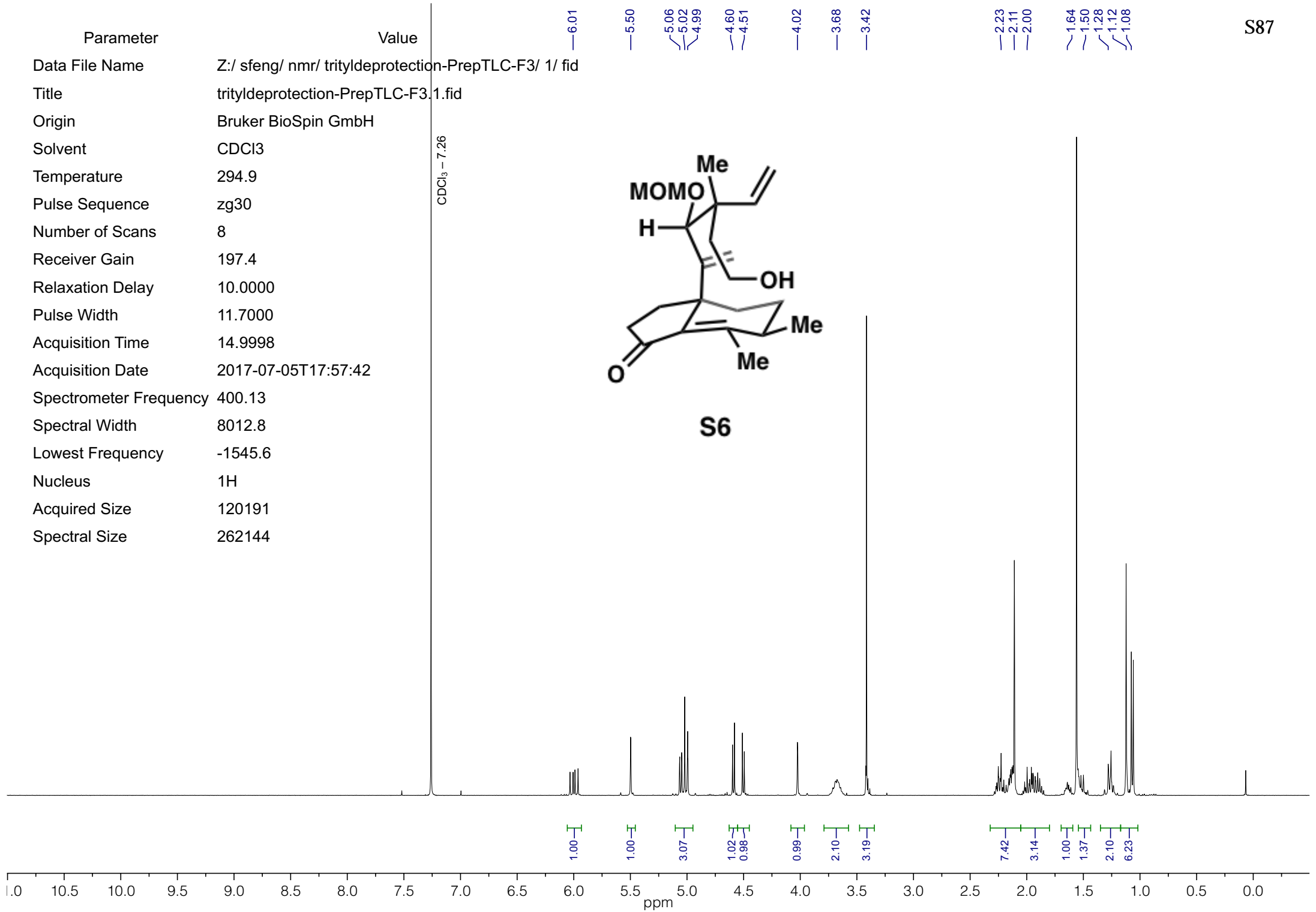
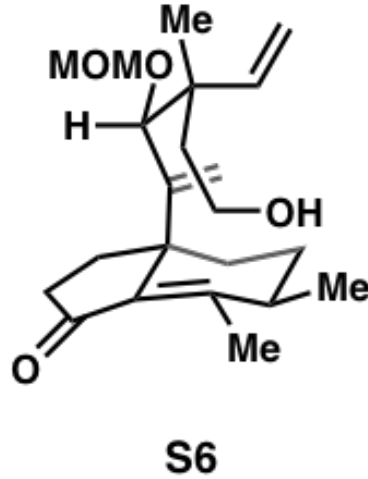
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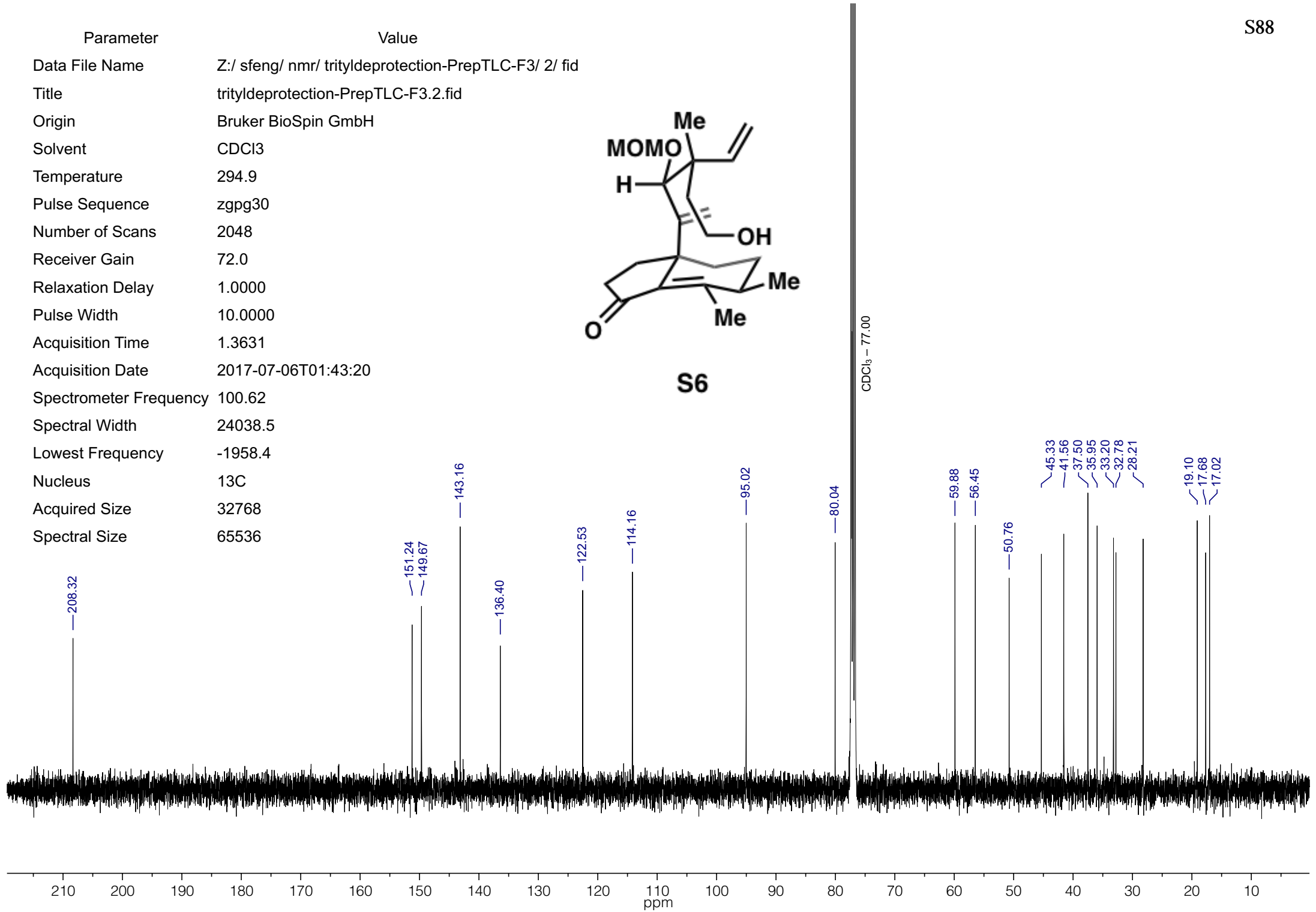
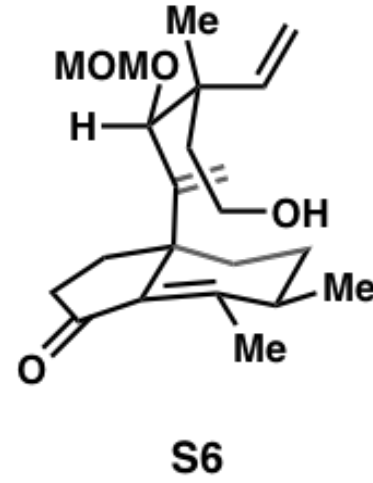
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Data File Name	Z:/ sfeng/ nmr/ MOMProtection-PrepTLC-F3/ 2/ fid
Title	MOMProtection-PrepTLC-F3.2.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	295.0
Pulse Sequence	zgpg30
Number of Scans	4096
Receiver Gain	64.2
Relaxation Delay	1.0000
Pulse Width	10.0000
Acquisition Time	1.3631
Acquisition Date	2017-07-06T00:17:26
Spectrometer Frequency	100.62
Spectral Width	24038.5
Lowest Frequency	-1960.8
Nucleus	13C
Acquired Size	32768
Spectral Size	65536



Parameter	Value
Data File Name	Z:/ sfeng/ nmr/ trityldeprotection-PrepTLC-F3/ 1/ fid
Title	trityldeprotection-PrepTLC-F3.1.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl <sub>3</sub>
Temperature	294.9
Pulse Sequence	zg30
Number of Scans	8
Receiver Gain	197.4
Relaxation Delay	10.0000
Pulse Width	11.7000
Acquisition Time	14.9998
Acquisition Date	2017-07-05T17:57:42
Spectrometer Frequency	400.13
Spectral Width	8012.8
Lowest Frequency	-1545.6
Nucleus	<sup>1</sup> H
Acquired Size	120191
Spectral Size	262144



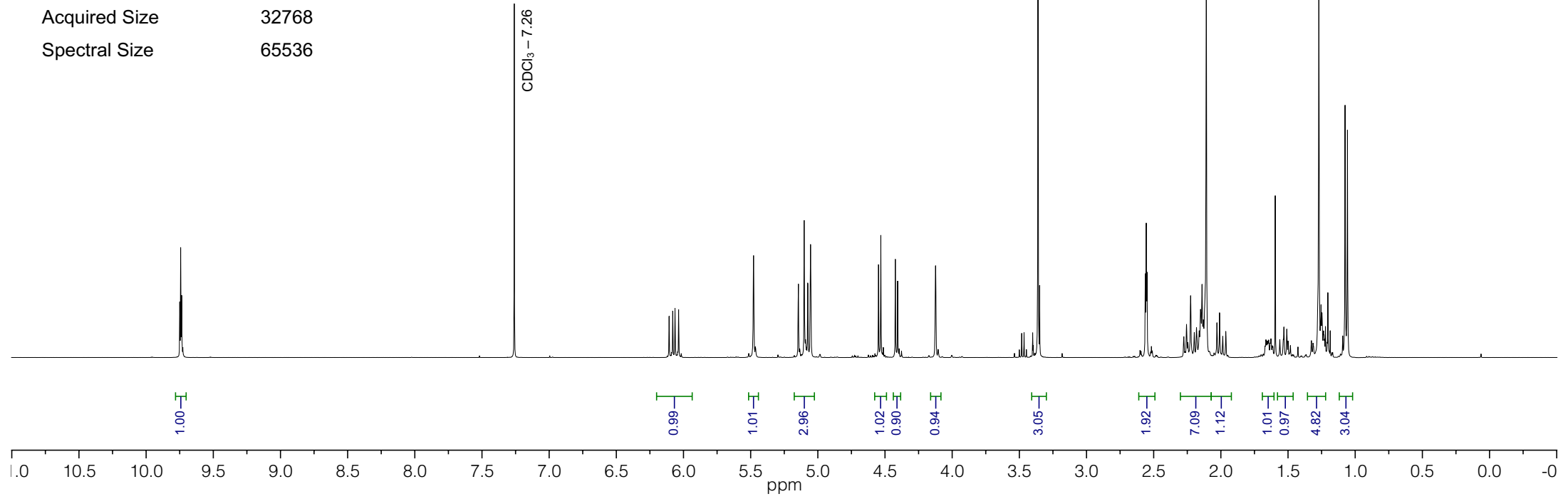
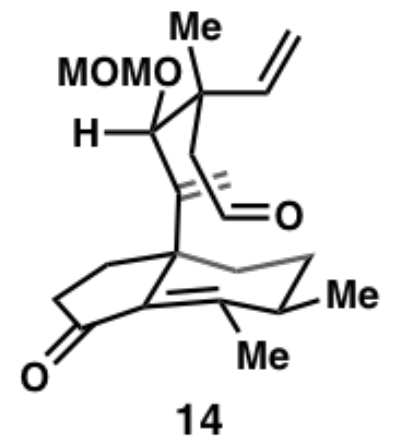
Parameter	Value
Data File Name	Z:/ sfeng/ nmr/ trityldeprotection-PrepTLC-F3/ 2/ fid
Title	trityldeprotection-PrepTLC-F3.2.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	294.9
Pulse Sequence	zgpg30
Number of Scans	2048
Receiver Gain	72.0
Relaxation Delay	1.0000
Pulse Width	10.0000
Acquisition Time	1.3631
Acquisition Date	2017-07-06T01:43:20
Spectrometer Frequency	100.62
Spectral Width	24038.5
Lowest Frequency	-1958.4
Nucleus	13C
Acquired Size	32768
Spectral Size	65536



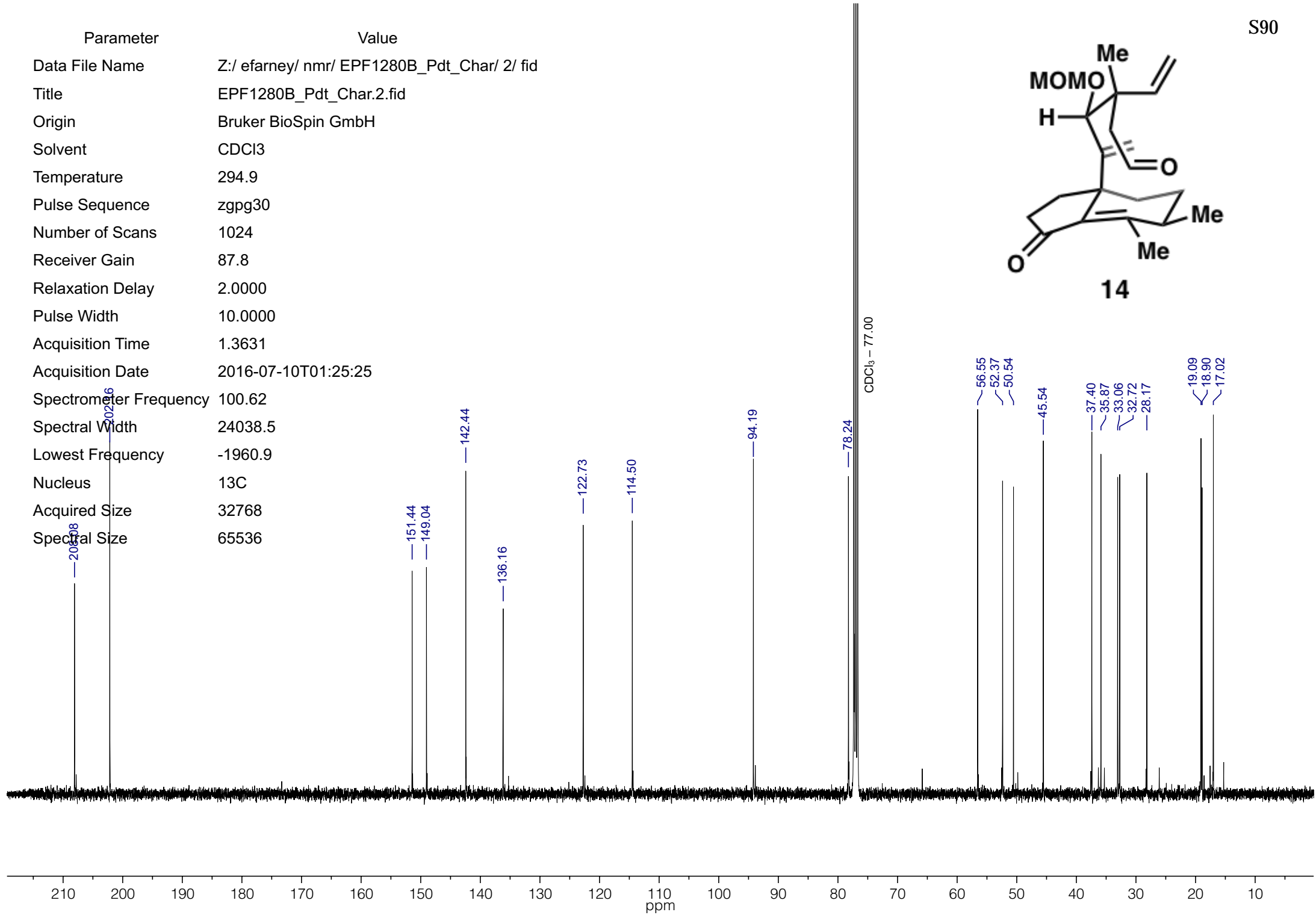
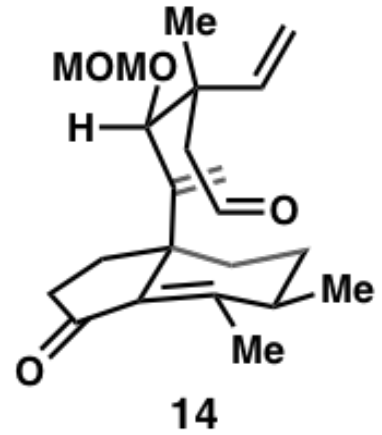


Parameter	Value
Data File Name	Z:/ efarney/ nmr/ EPF1280B_Pdt_Char/ 1/ fid
Title	EPF1280B_Pdt_Char.1.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	294.9
Pulse Sequence	zg30
Number of Scans	16
Receiver Gain	142.8
Relaxation Delay	10.0000
Pulse Width	11.7000
Acquisition Time	4.0894
Acquisition Date	2016-07-10T00:26:18
Spectrometer Frequency	400.13
Spectral Width	8012.8
Lowest Frequency	-1545.6
Nucleus	1H
Acquired Size	32768
Spectral Size	65536

9.74  
6.06  
5.48  
5.14  
5.10  
5.08  
5.05  
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1.08

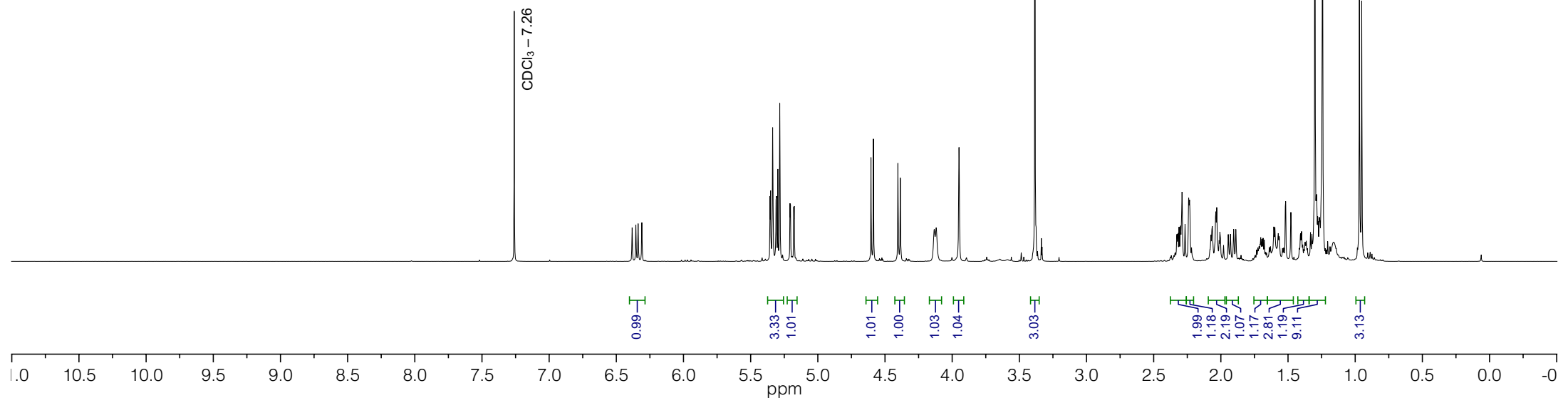
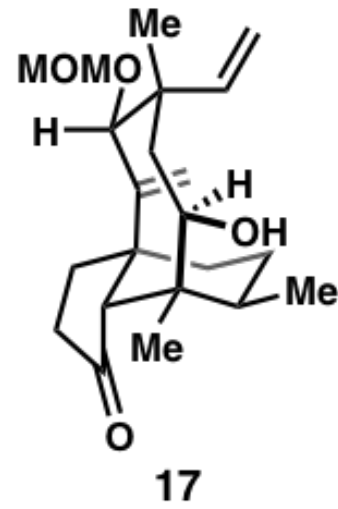


Parameter	Value
Data File Name	Z:/ efarney/ nmr/ EPF1280B_Pdt_Char/ 2/ fid
Title	EPF1280B_Pdt_Char.2.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	294.9
Pulse Sequence	zgpg30
Number of Scans	1024
Receiver Gain	87.8
Relaxation Delay	2.0000
Pulse Width	10.0000
Acquisition Time	1.3631
Acquisition Date	2016-07-10T01:25:25
Spectrometer Frequency	100.62
Spectral Width	24038.5
Lowest Frequency	-1960.9
Nucleus	13C
Acquired Size	32768
Spectral Size	65536

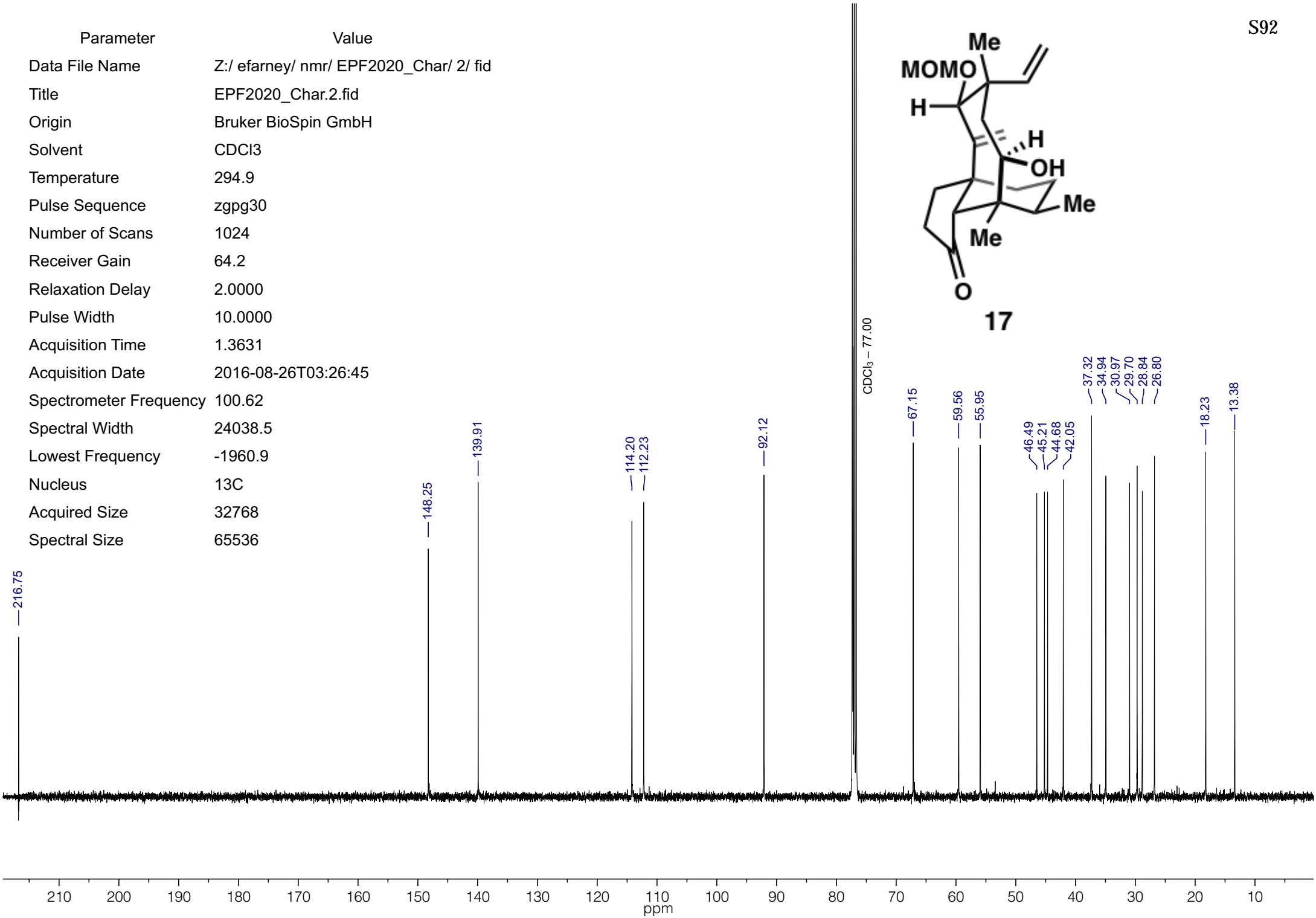
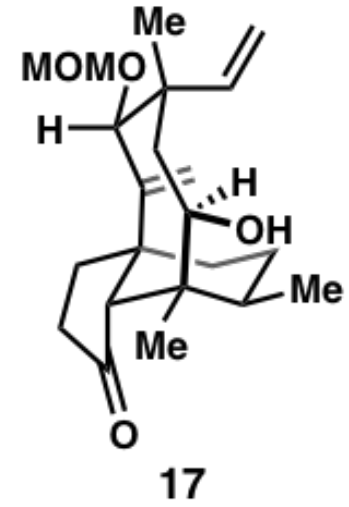


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Data File Name Z:/ efarney/ nmr/ EPF2020\_Char/ 1/ fid  
Title EPF2020\_Char.1.fid  
Origin Bruker BioSpin GmbH  
Solvent CDCl3  
Temperature 295.0  
Pulse Sequence zg30  
Number of Scans 16  
Receiver Gain 98.9  
Relaxation Delay 10.0000  
Pulse Width 11.7000  
Acquisition Time 4.0894  
Acquisition Date 2016-08-26T02:27:38  
Spectrometer Frequency 400.13  
Spectral Width 8012.8  
Lowest Frequency -1545.6  
Nucleus 1H  
Acquired Size 32768  
Spectral Size 65536

6.34 5.36 5.30 5.28 5.21 4.60 4.40 4.13 3.95 3.38 2.29 2.24 2.04 1.90 1.70 1.61 1.52 1.41 1.30 1.24 0.97

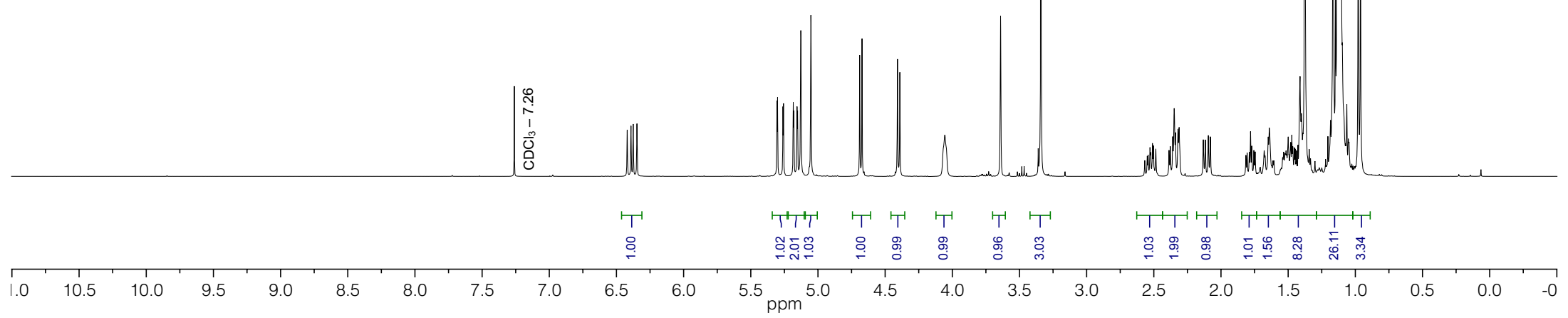
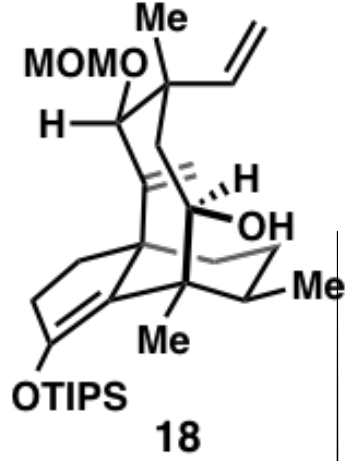


Parameter	Value
Data File Name	Z:/ efarney/ nmr/ EPF2020_Char/ 2/ fid
Title	EPF2020_Char.2.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	294.9
Pulse Sequence	zgpg30
Number of Scans	1024
Receiver Gain	64.2
Relaxation Delay	2.0000
Pulse Width	10.0000
Acquisition Time	1.3631
Acquisition Date	2016-08-26T03:26:45
Spectrometer Frequency	100.62
Spectral Width	24038.5
Lowest Frequency	-1960.9
Nucleus	13C
Acquired Size	32768
Spectral Size	65536

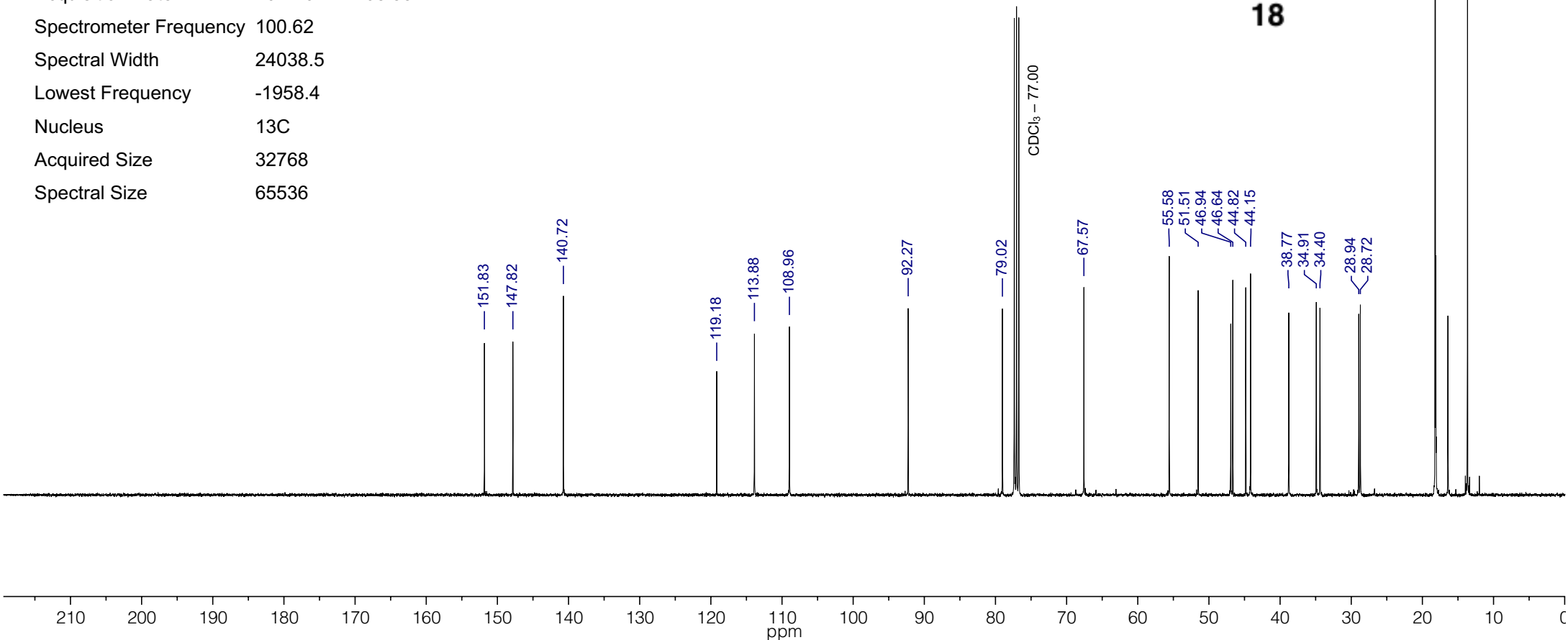
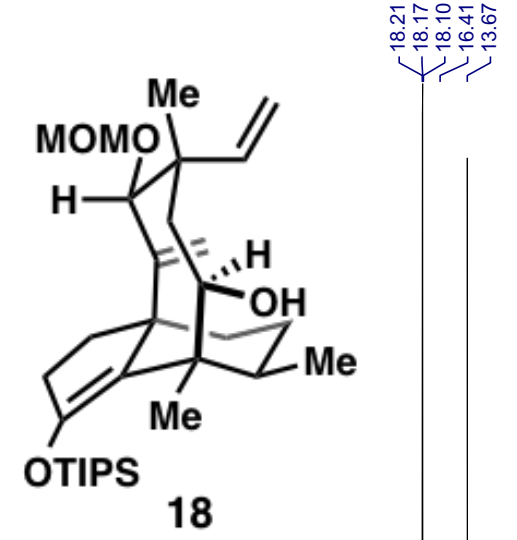


Parameter Value  
Data File Name Z:/ efarney/ nmr/ EPF3216\_Frac\_13\_21\_Char/ 1/ fid  
Title EPF3216\_Frac\_13\_21\_Char.1.fid  
Origin Bruker BioSpin GmbH  
Solvent CDCl3  
Temperature 294.9  
Pulse Sequence zg30  
Number of Scans 16  
Receiver Gain 30.3  
Relaxation Delay 10.0000  
Pulse Width 11.7000  
Acquisition Time 4.0894  
Acquisition Date 2017-07-22T08:34:15  
Spectrometer Frequency 400.13  
Spectral Width 8012.8  
Lowest Frequency -1545.2  
Nucleus 1H  
Acquired Size 32768  
Spectral Size 65536

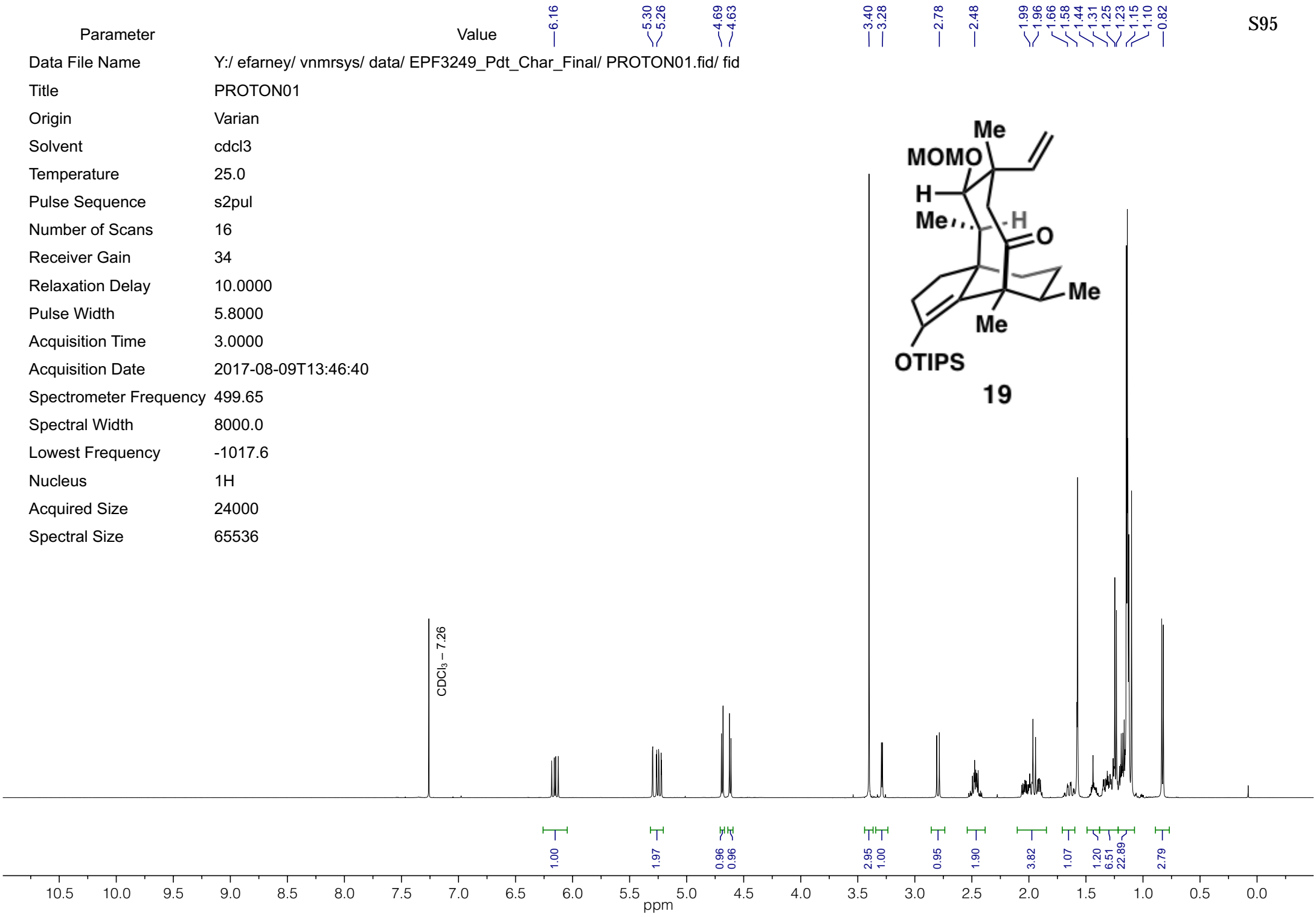
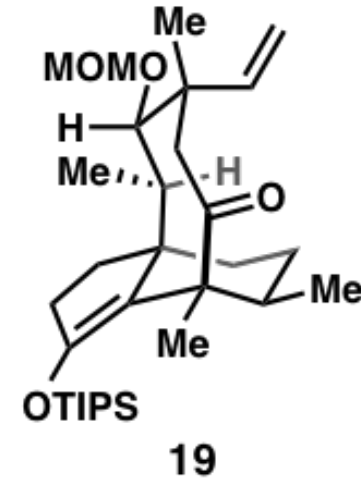
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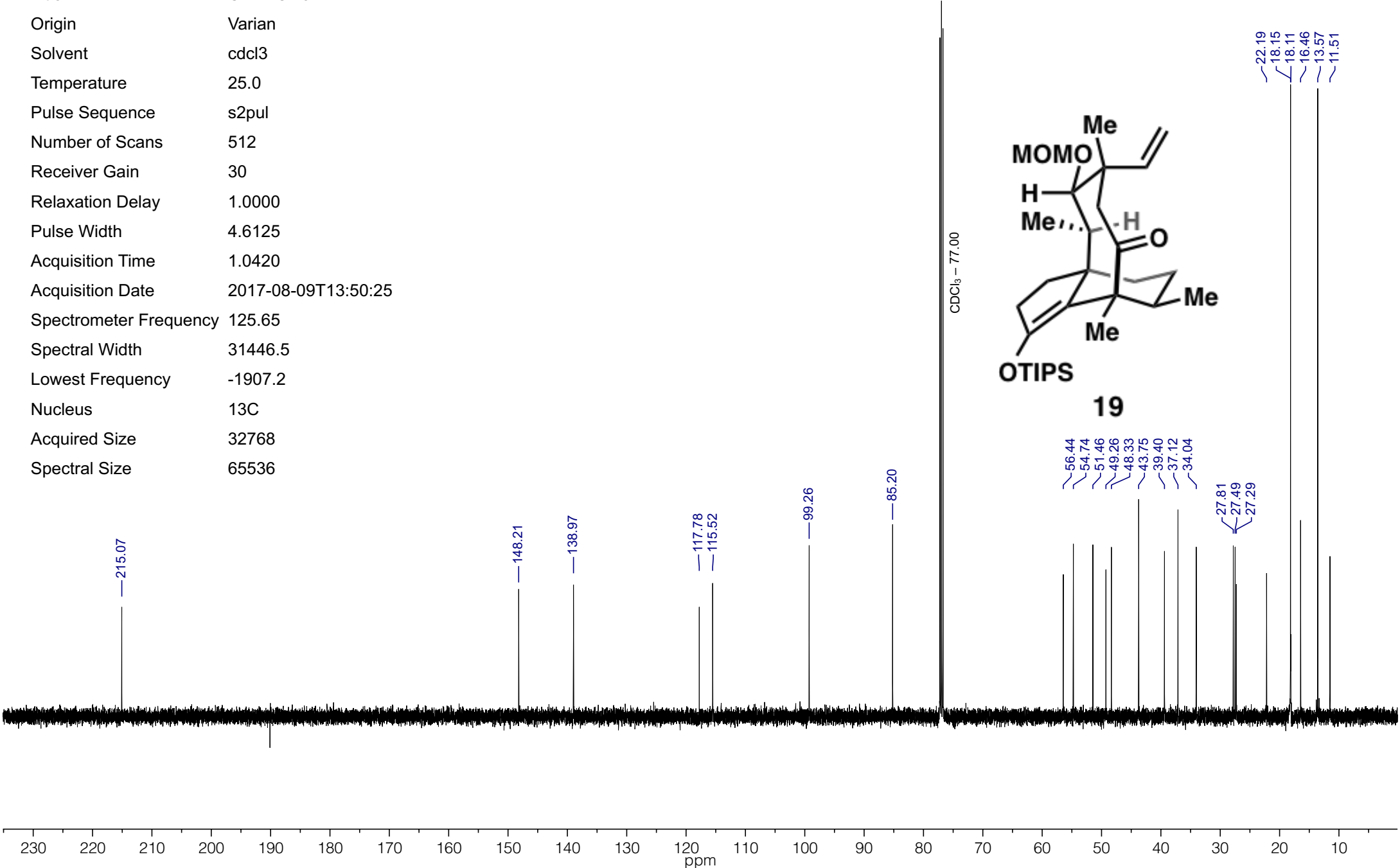
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Data File Name	Z:/ efarney/ nmr/ EPF3216_Frac_13_21_Char/ 2/ fid
Title	EPF3216_Frac_13_21_Char.2.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	295.0
Pulse Sequence	zgpg30
Number of Scans	512
Receiver Gain	72.0
Relaxation Delay	1.0000
Pulse Width	10.0000
Acquisition Time	1.3631
Acquisition Date	2017-07-22T08:55:27
Spectrometer Frequency	100.62
Spectral Width	24038.5
Lowest Frequency	-1958.4
Nucleus	13C
Acquired Size	32768
Spectral Size	65536



Parameter	Value
Data File Name	Y:/ efarney/ vnmrsys/ data/ EPF3249_Pdt_Char_Final/ PROTON01.fid/ fid
Title	PROTON01
Origin	Varian
Solvent	cdcl3
Temperature	25.0
Pulse Sequence	s2pul
Number of Scans	16
Receiver Gain	34
Relaxation Delay	10.0000
Pulse Width	5.8000
Acquisition Time	3.0000
Acquisition Date	2017-08-09T13:46:40
Spectrometer Frequency	499.65
Spectral Width	8000.0
Lowest Frequency	-1017.6
Nucleus	1H
Acquired Size	24000
Spectral Size	65536



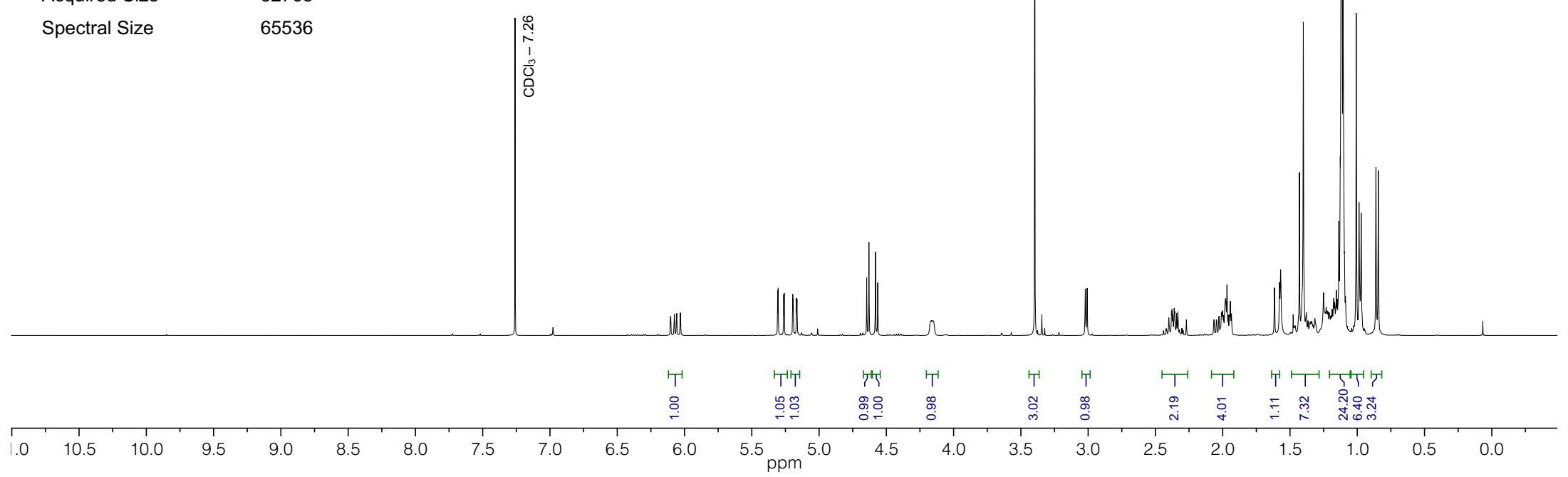
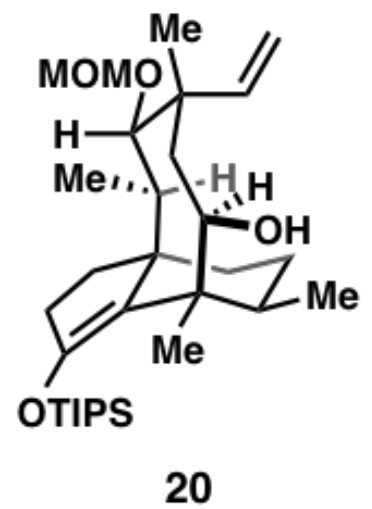
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Data File Name	Y:/ efarney/ vnmrsys/ data/ EPF3249_Pdt_Char_Final/ CARBON01.fid/ fid
Title	CARBON01
Origin	Varian
Solvent	cdcl3
Temperature	25.0
Pulse Sequence	s2pul
Number of Scans	512
Receiver Gain	30
Relaxation Delay	1.0000
Pulse Width	4.6125
Acquisition Time	1.0420
Acquisition Date	2017-08-09T13:50:25
Spectrometer Frequency	125.65
Spectral Width	31446.5
Lowest Frequency	-1907.2
Nucleus	13C
Acquired Size	32768
Spectral Size	65536



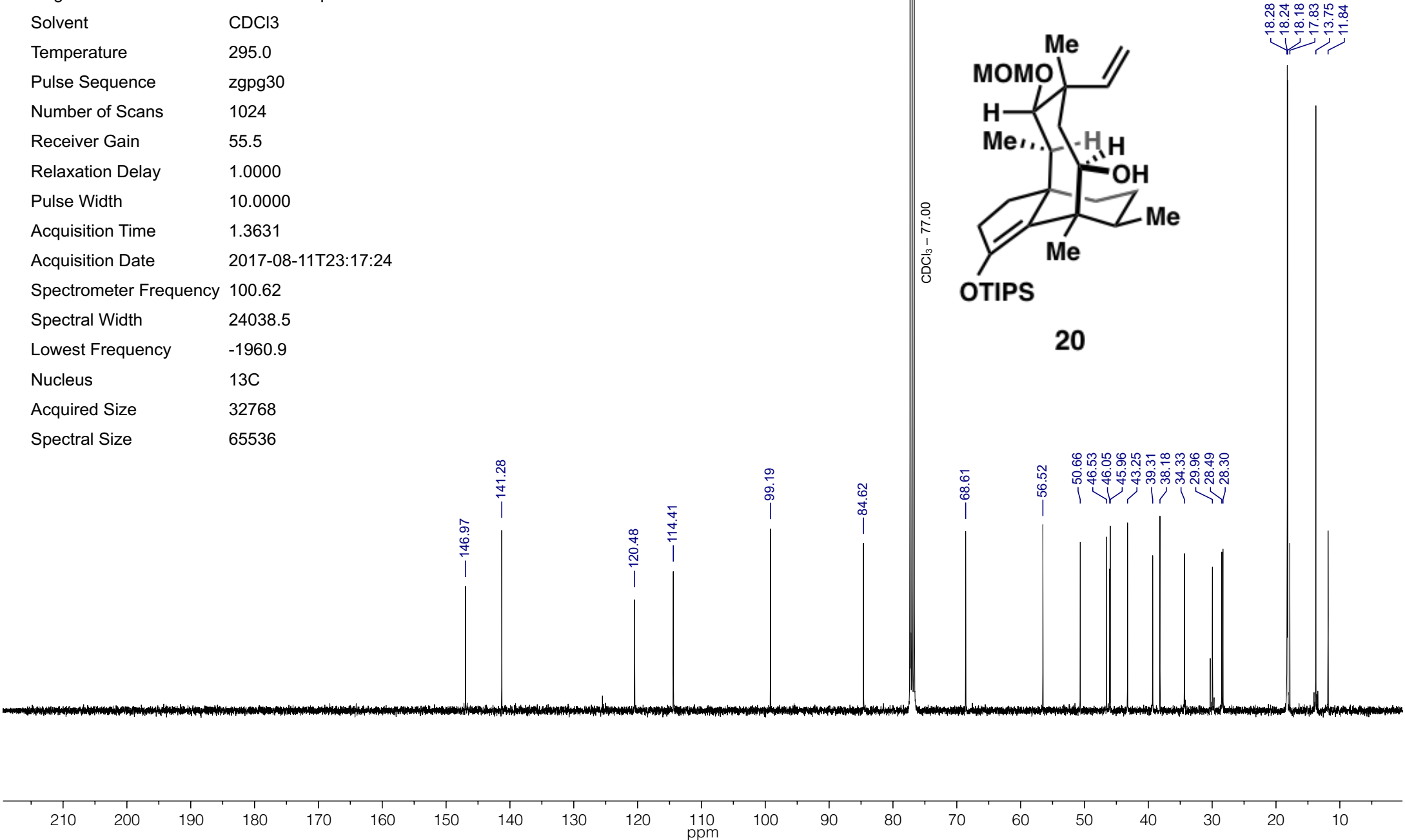


Parameter	Value
Data File Name	Z:/ efarney/ nmr/ EPF3250_Frac_35_67_Char/ 1/ fid
Title	EPF3250_Frac_35_67_Char.1.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	294.9
Pulse Sequence	zg30
Number of Scans	16
Receiver Gain	112.8
Relaxation Delay	10.0000
Pulse Width	11.7000
Acquisition Time	4.0894
Acquisition Date	2017-08-11T22:35:29
Spectrometer Frequency	400.13
Spectral Width	8012.8
Lowest Frequency	-1545.6
Nucleus	1H
Acquired Size	32768
Spectral Size	65536

6.08  
5.30  
5.20  
4.63  
4.58  
4.15  
3.40  
3.01  
2.36  
2.03  
1.97  
1.62  
1.40  
1.20  
1.11  
1.01  
0.99  
0.86

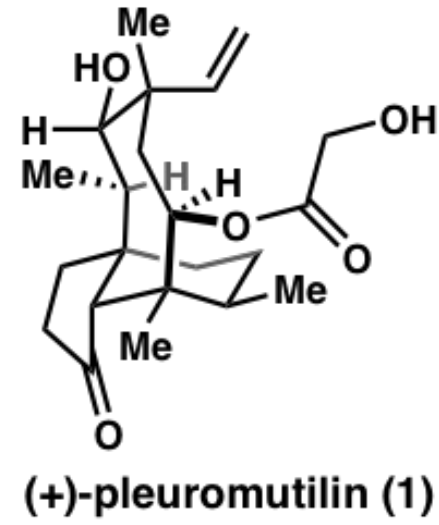


Parameter	Value
Data File Name	Z:/ efarney/ nmr/ EPF3250_Frac_35_67_Char/ 2/ fid
Title	EPF3250_Frac_35_67_Char.2.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	295.0
Pulse Sequence	zgpg30
Number of Scans	1024
Receiver Gain	55.5
Relaxation Delay	1.0000
Pulse Width	10.0000
Acquisition Time	1.3631
Acquisition Date	2017-08-11T23:17:24
Spectrometer Frequency	100.62
Spectral Width	24038.5
Lowest Frequency	-1960.9
Nucleus	13C
Acquired Size	32768
Spectral Size	65536

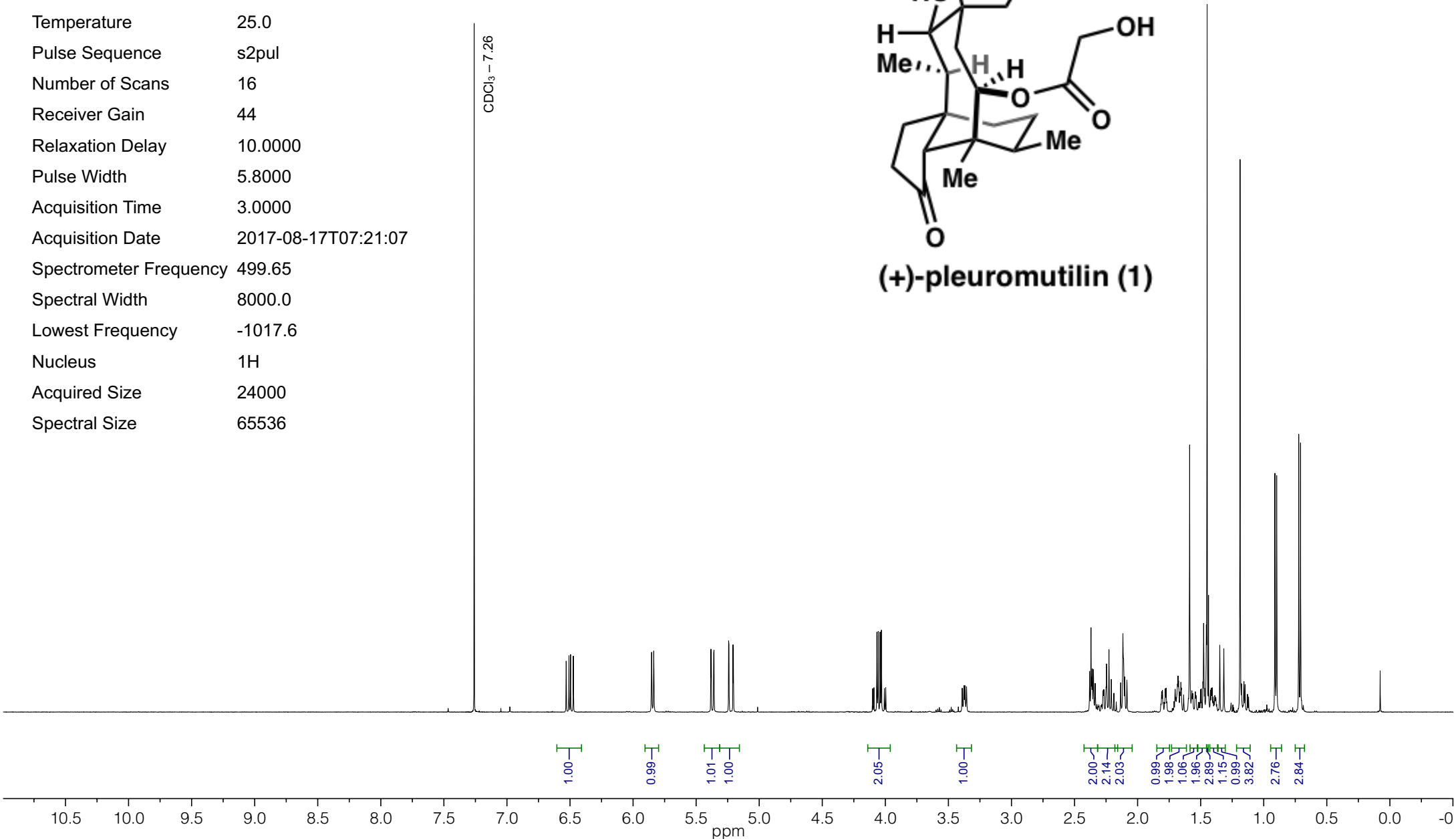


Parameter Value  
Data File Name Y:/ efarney/ vnmrsys/ data/ EPF3256\_Pdt\_FINAL/ PROTON01.fid/ fid  
Title PROTON01  
Origin Varian  
Solvent cdcl3  
Temperature 25.0  
Pulse Sequence s2pul  
Number of Scans 16  
Receiver Gain 44  
Relaxation Delay 10.0000  
Pulse Width 5.8000  
Acquisition Time 3.0000  
Acquisition Date 2017-08-17T07:21:07  
Spectrometer Frequency 499.65  
Spectral Width 8000.0  
Lowest Frequency -1017.6  
Nucleus 1H  
Acquired Size 24000  
Spectral Size 65536

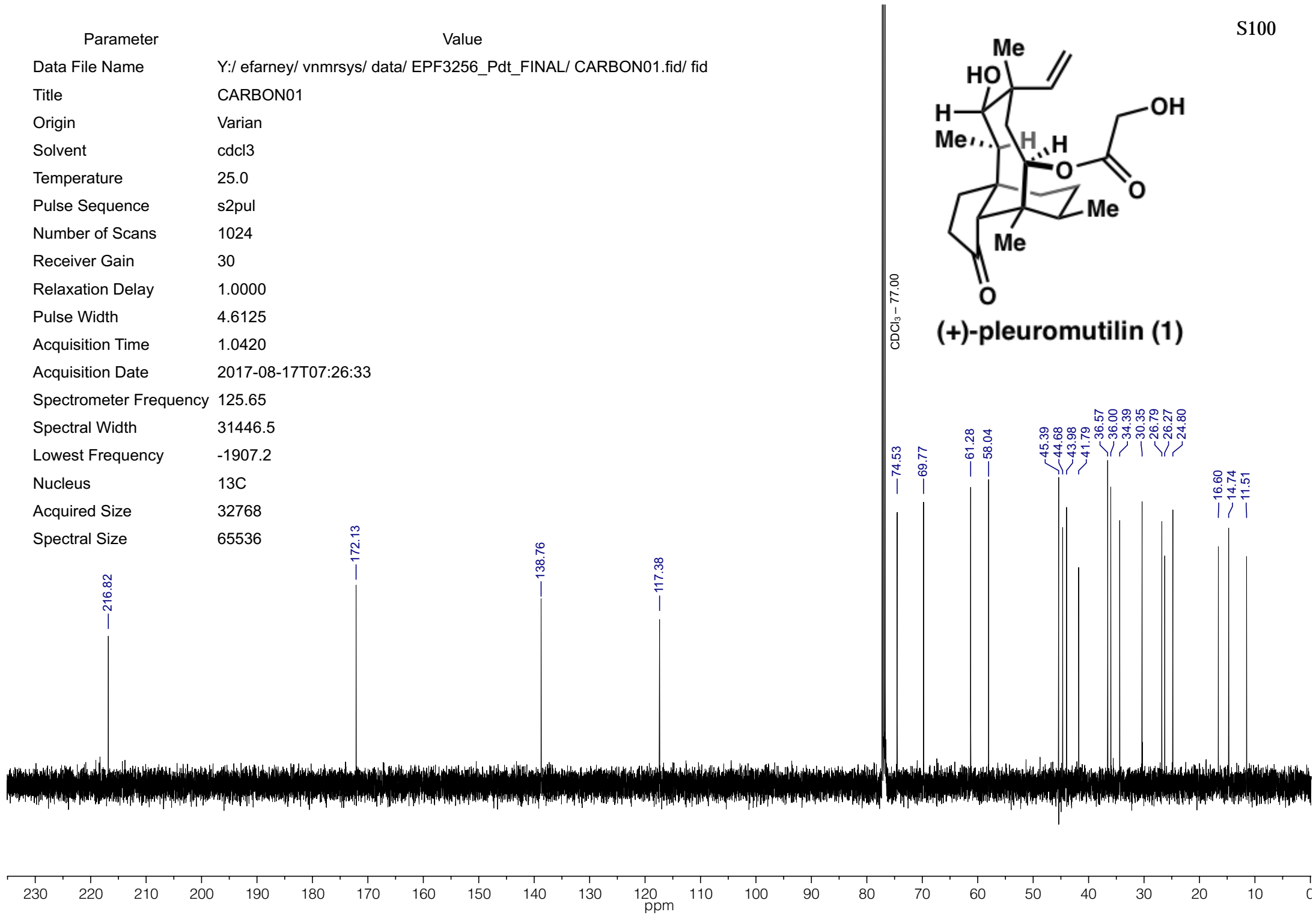
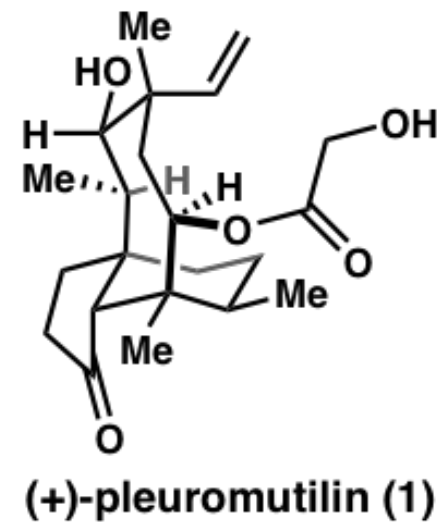
CDCl<sub>3</sub> - 7.26



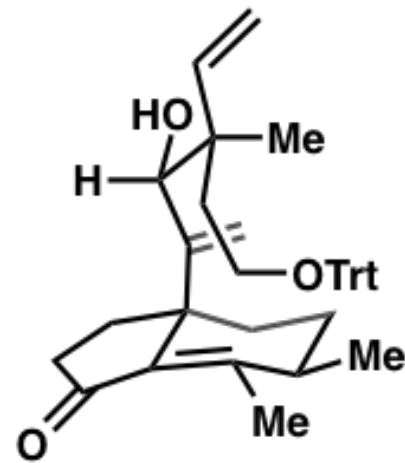
6.51 5.85 5.38 5.24 4.06 3.38 2.37 2.23 2.12 1.80 1.68 1.56 1.45 1.35 1.19 1.15 0.91 0.72



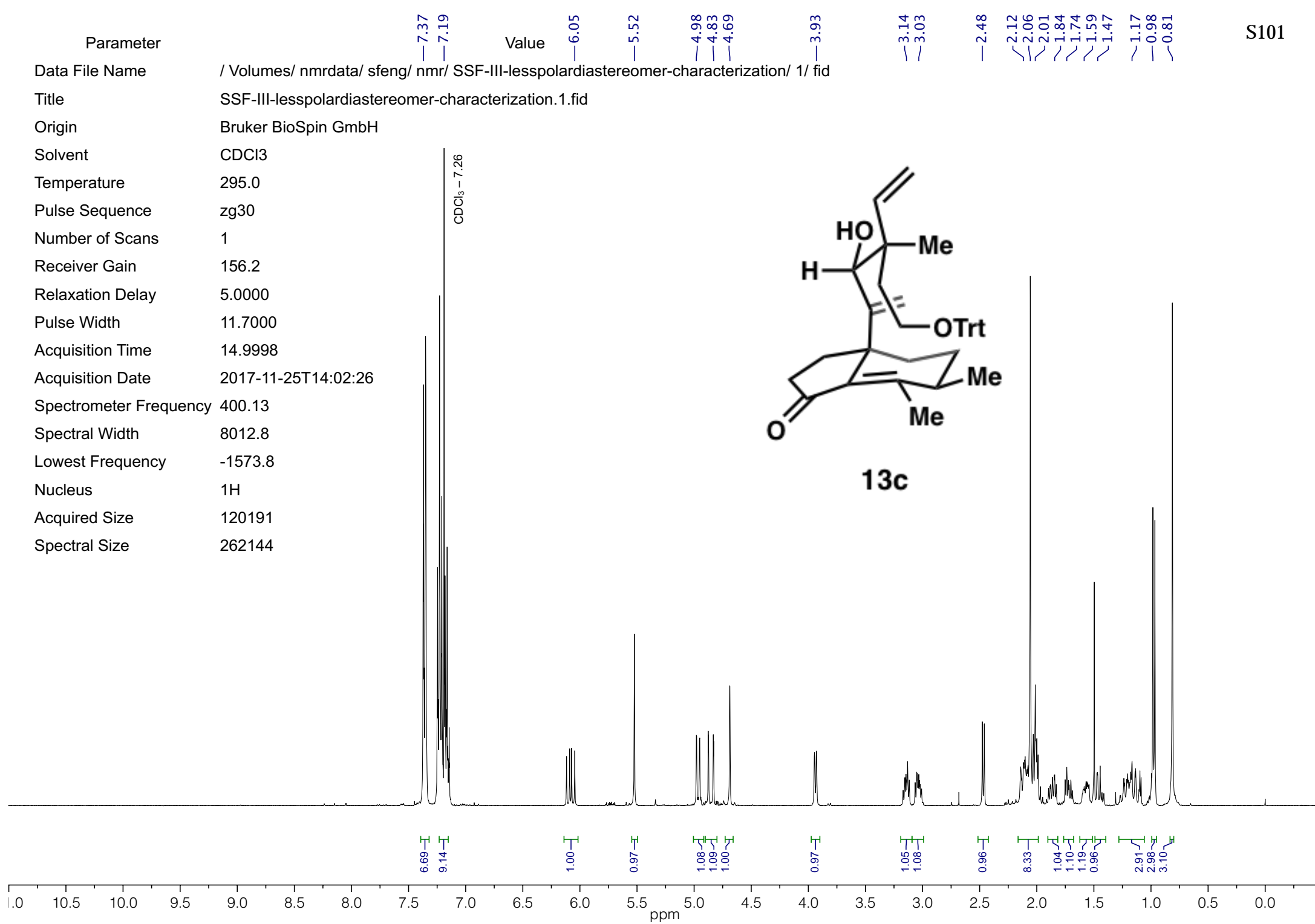
Parameter	Value
Data File Name	Y:/ efarney/ vnmrsys/ data/ EPF3256_Pdt_FINAL/ CARBON01.fid/ fid
Title	CARBON01
Origin	Varian
Solvent	cdcl3
Temperature	25.0
Pulse Sequence	s2pul
Number of Scans	1024
Receiver Gain	30
Relaxation Delay	1.0000
Pulse Width	4.6125
Acquisition Time	1.0420
Acquisition Date	2017-08-17T07:26:33
Spectrometer Frequency	125.65
Spectral Width	31446.5
Lowest Frequency	-1907.2
Nucleus	13C
Acquired Size	32768
Spectral Size	65536



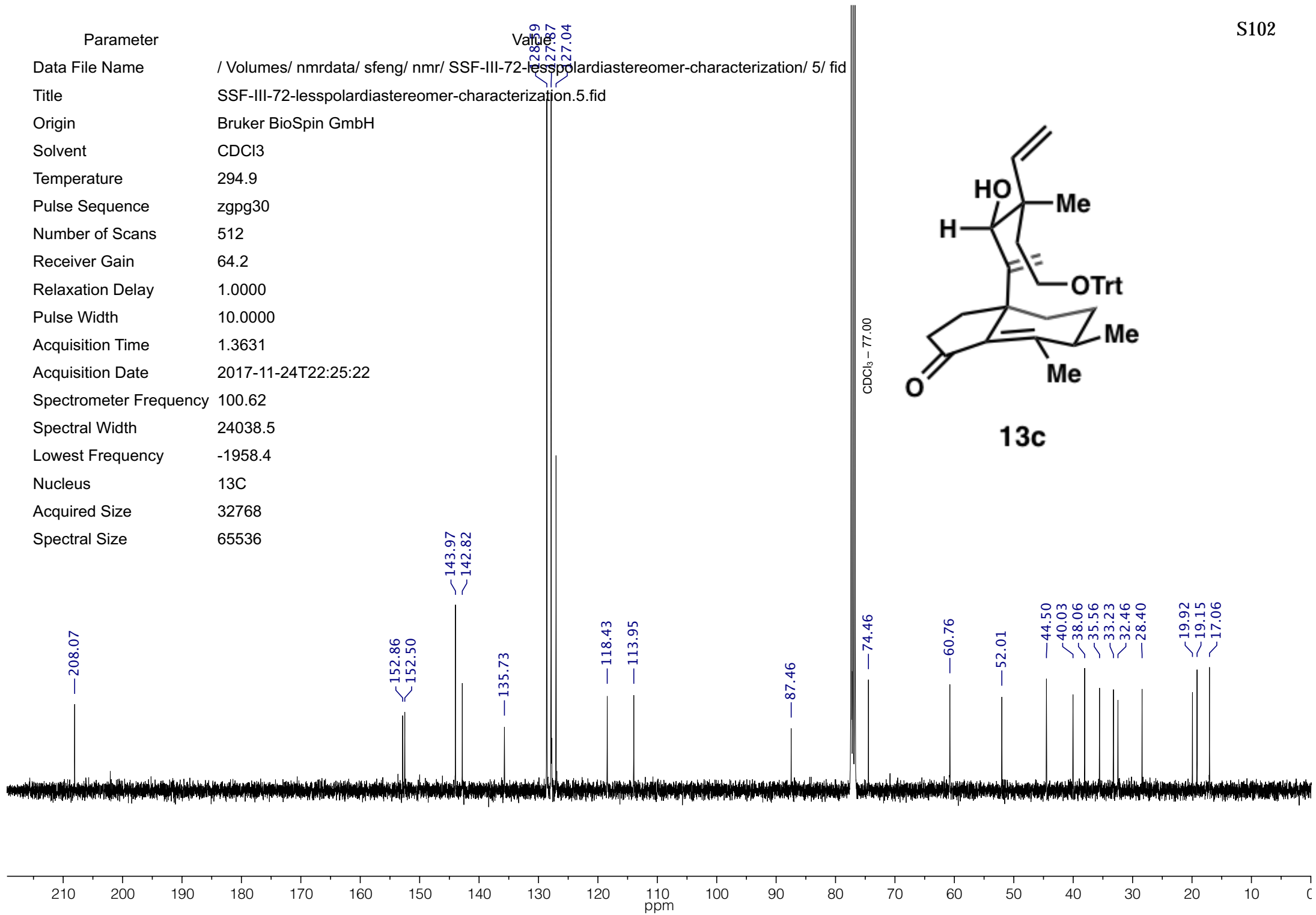
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Data File Name	/Volumes/nmrdata/sfeng/nmr/SSF-III-lesspolardiastereomer-characterization/1/fid
Title	SSF-III-lesspolardiastereomer-characterization.1.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl <sub>3</sub>
Temperature	295.0
Pulse Sequence	zg30
Number of Scans	1
Receiver Gain	156.2
Relaxation Delay	5.0000
Pulse Width	11.7000
Acquisition Time	14.9998
Acquisition Date	2017-11-25T14:02:26
Spectrometer Frequency	400.13
Spectral Width	8012.8
Lowest Frequency	-1573.8
Nucleus	<sup>1</sup> H
Acquired Size	120191
Spectral Size	262144

CDCl<sub>3</sub> - 7.26

13c

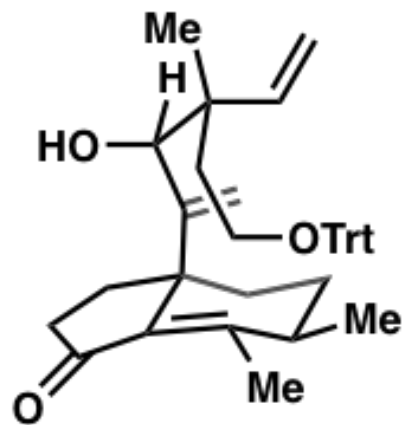


Parameter	Value
Data File Name	/ Volumes/ nmrdata/ sfeng/ nmr/ SSF-III-72-lesspolardiastereomer-characterization/ 5/ fid
Title	SSF-III-72-lesspolardiastereomer-characterization.5.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl <sub>3</sub>
Temperature	294.9
Pulse Sequence	zgpg30
Number of Scans	512
Receiver Gain	64.2
Relaxation Delay	1.0000
Pulse Width	10.0000
Acquisition Time	1.3631
Acquisition Date	2017-11-24T22:25:22
Spectrometer Frequency	100.62
Spectral Width	24038.5
Lowest Frequency	-1958.4
Nucleus	<sup>13</sup> C
Acquired Size	32768
Spectral Size	65536

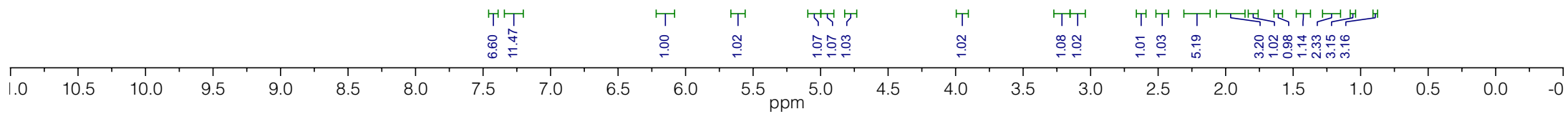


Parameter	Value
Data File Name	/ Volumes/ nmrdata-4/ sfeng/ nmr/ SSF-III-72-morepolardiastereomer-characterization/ 6/ fid
Title	SSF-III-72-morepolardiastereomer-characterization.6.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl <sub>3</sub>
Temperature	294.9
Pulse Sequence	zg30
Number of Scans	1
Receiver Gain	156.2
Relaxation Delay	5.0000
Pulse Width	11.7000
Acquisition Time	14.9998
Acquisition Date	2017-11-25T13:57:25
Spectrometer Frequency	400.13
Spectral Width	8012.8
Lowest Frequency	-1545.3
Nucleus	<sup>1</sup> H
Acquired Size	120191
Spectral Size	262144

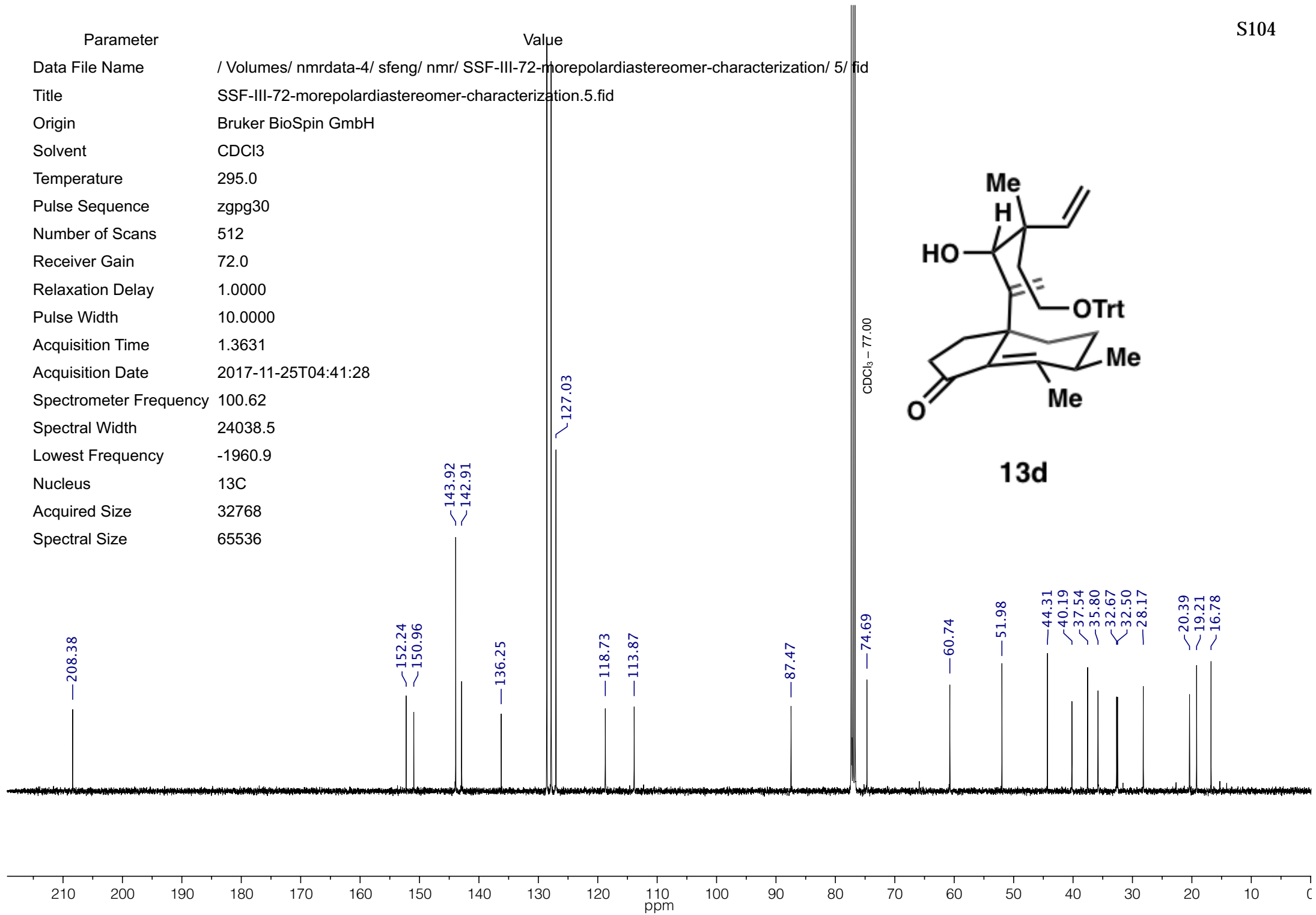
CDCl<sub>3</sub> - 7.26



**13d**

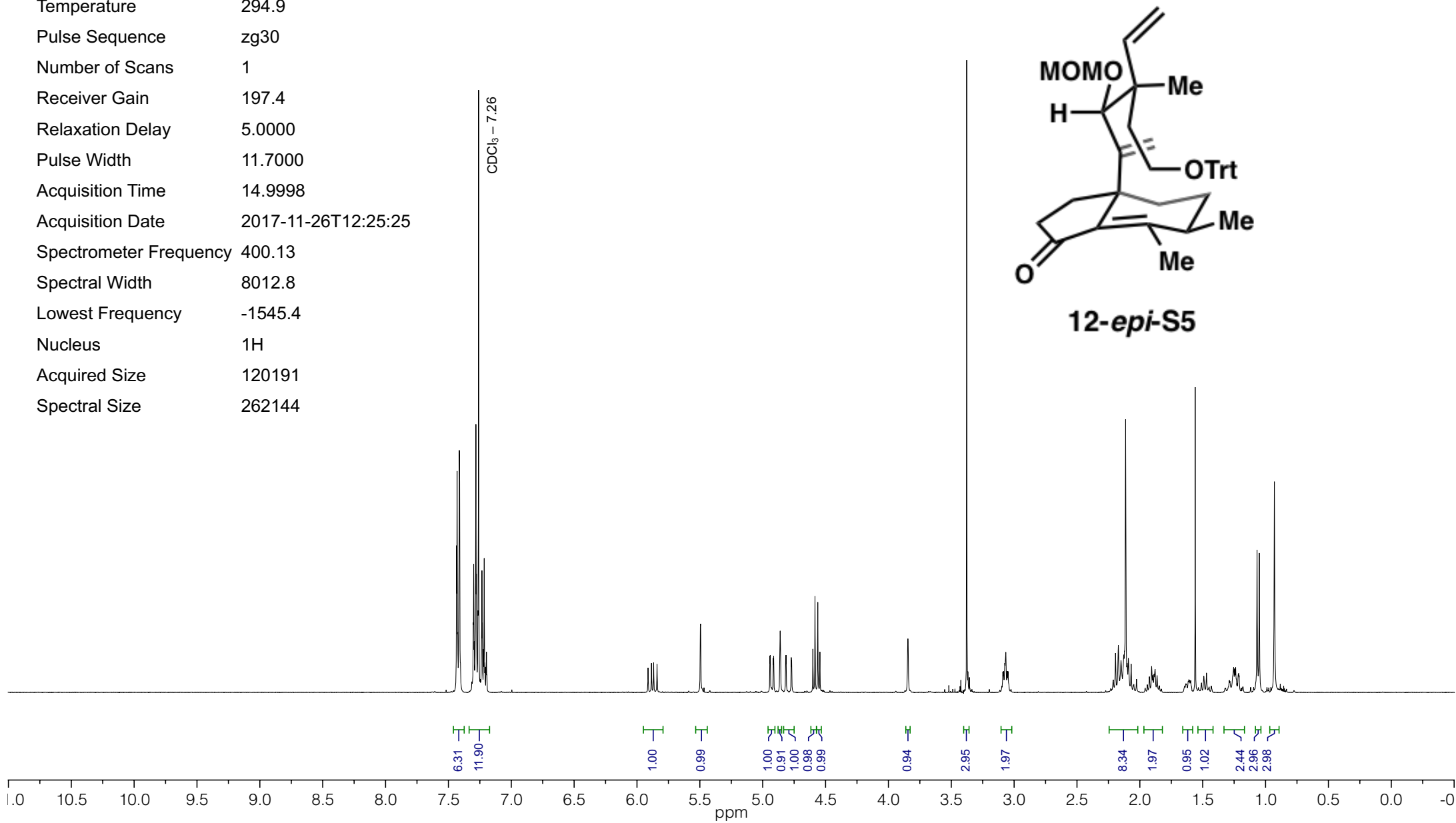


Parameter	Value
Data File Name	/ Volumes/ nmrdata-4/ sfeng/ nmr/ SSF-III-72-morepolardiastereomer-characterization/ 5/ fid
Title	SSF-III-72-morepolardiastereomer-characterization.5.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl <sub>3</sub>
Temperature	295.0
Pulse Sequence	zgpg30
Number of Scans	512
Receiver Gain	72.0
Relaxation Delay	1.0000
Pulse Width	10.0000
Acquisition Time	1.3631
Acquisition Date	2017-11-25T04:41:28
Spectrometer Frequency	100.62
Spectral Width	24038.5
Lowest Frequency	-1960.9
Nucleus	<sup>13</sup> C
Acquired Size	32768
Spectral Size	65536

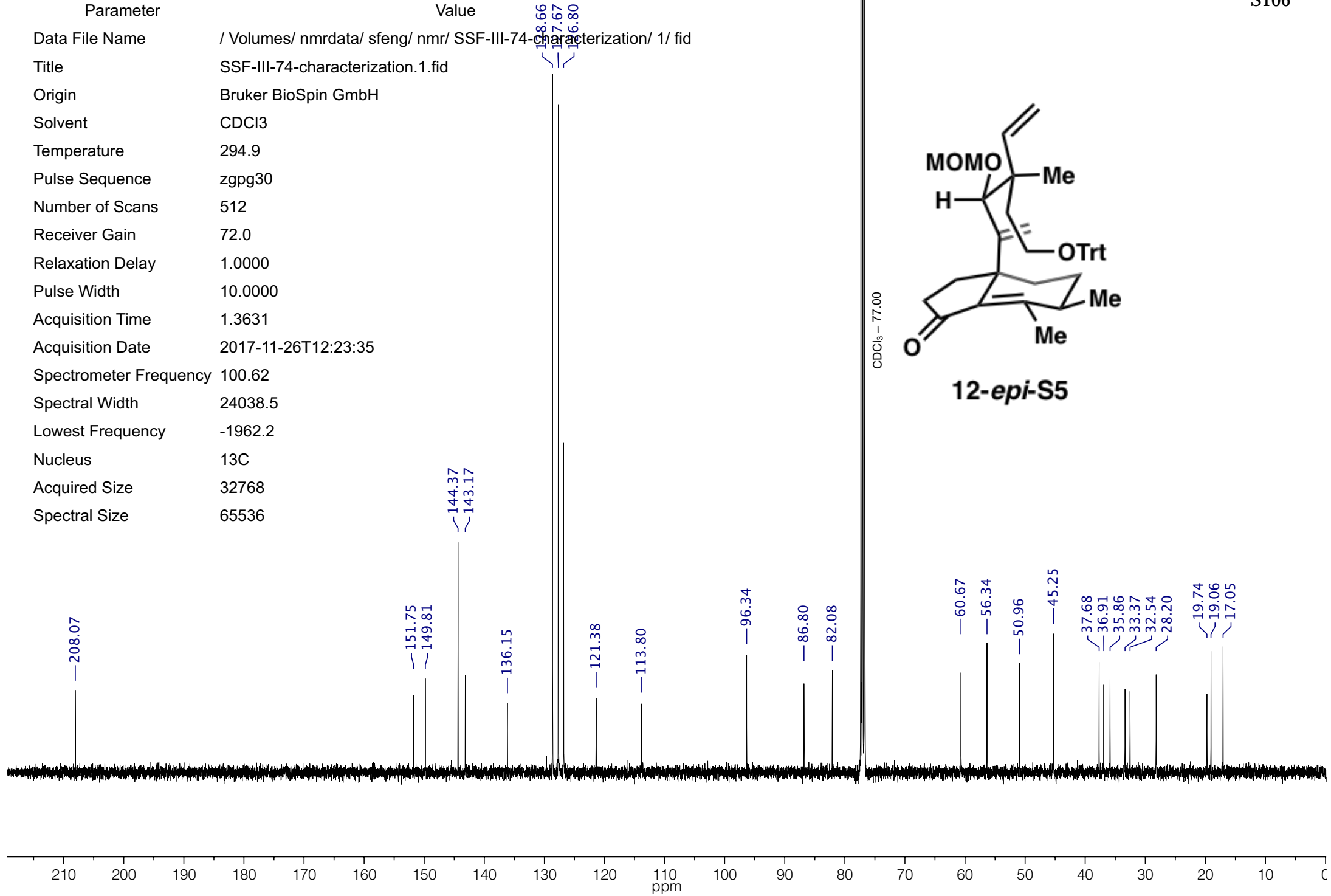




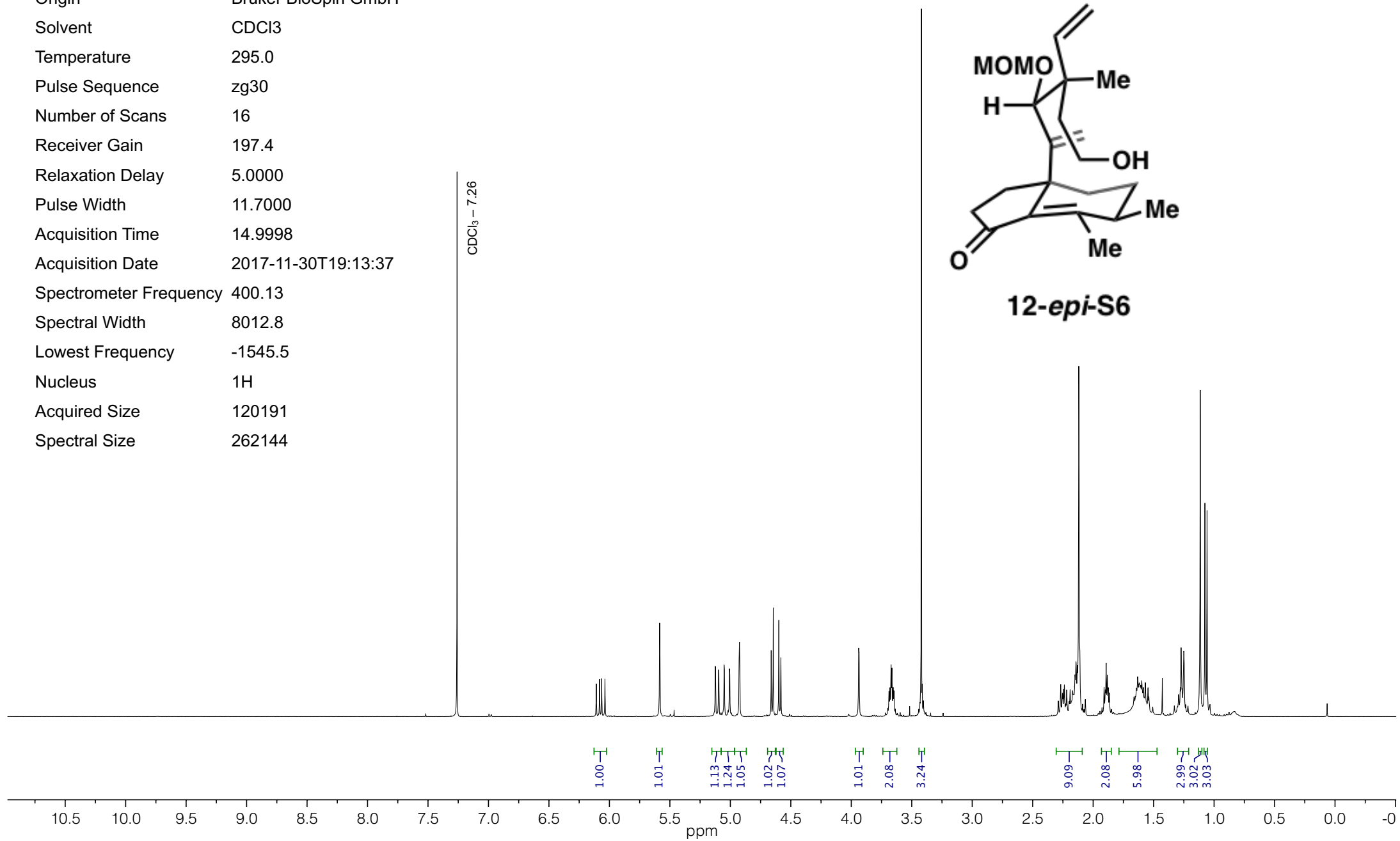
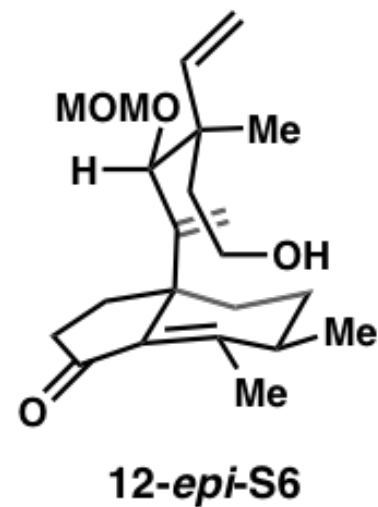
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Data File Name	/ Volumes/ nmrdata/ sfeng/ nmr/ SSF-III-74-characterization/ 2/ fid
Title	SSF-III-74-characterization.2.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl <sub>3</sub>
Temperature	294.9
Pulse Sequence	zg30
Number of Scans	1
Receiver Gain	197.4
Relaxation Delay	5.0000
Pulse Width	11.7000
Acquisition Time	14.9998
Acquisition Date	2017-11-26T12:25:25
Spectrometer Frequency	400.13
Spectral Width	8012.8
Lowest Frequency	-1545.4
Nucleus	<sup>1</sup> H
Acquired Size	120191
Spectral Size	262144



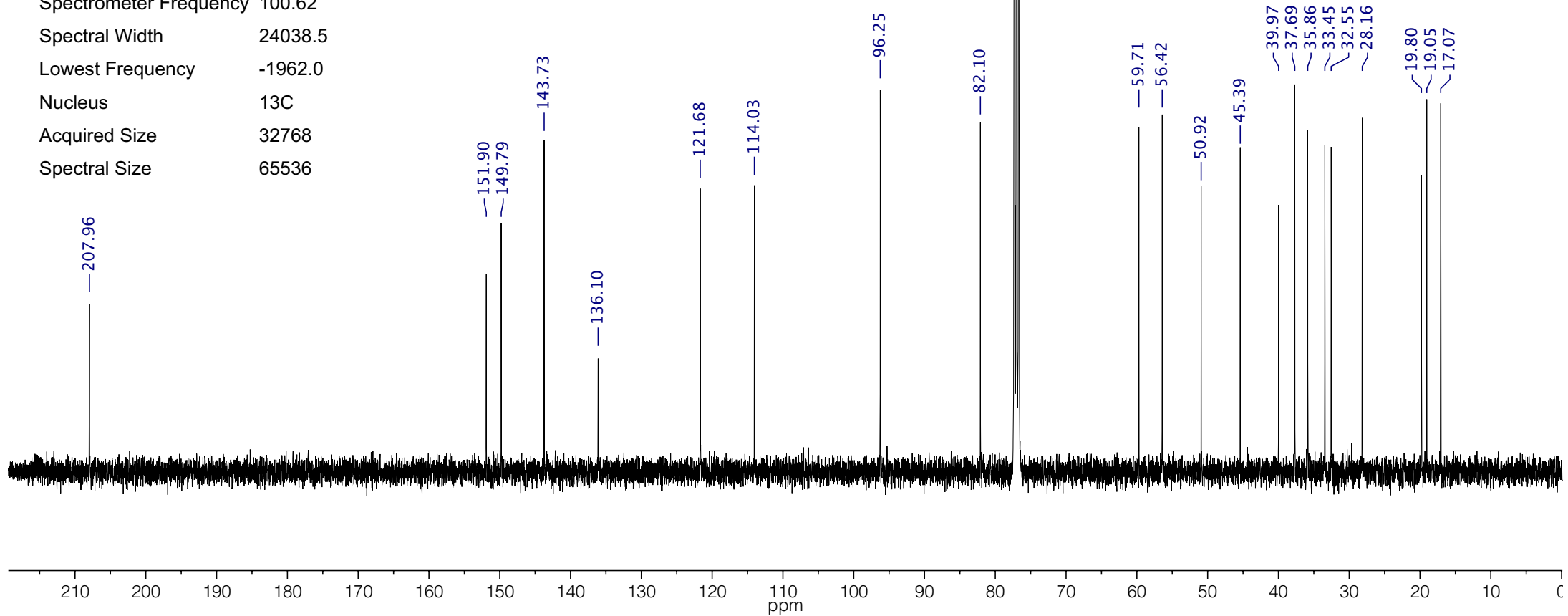
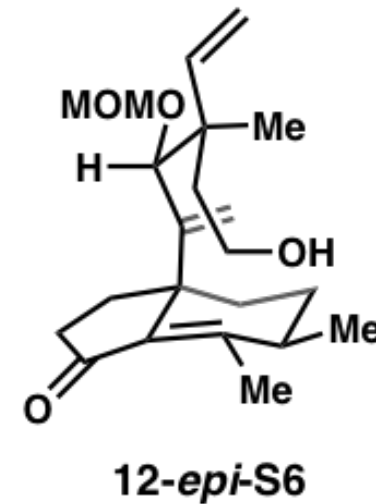
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Data File Name	/ Volumes/ nmrdata/ sfeng/ nmr/ SSF-III-74-characterization/ 1/ fid
Title	SSF-III-74-characterization.1.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl <sub>3</sub>
Temperature	294.9
Pulse Sequence	zgpg30
Number of Scans	512
Receiver Gain	72.0
Relaxation Delay	1.0000
Pulse Width	10.0000
Acquisition Time	1.3631
Acquisition Date	2017-11-26T12:23:35
Spectrometer Frequency	100.62
Spectral Width	24038.5
Lowest Frequency	-1962.2
Nucleus	<sup>13</sup> C
Acquired Size	32768
Spectral Size	65536



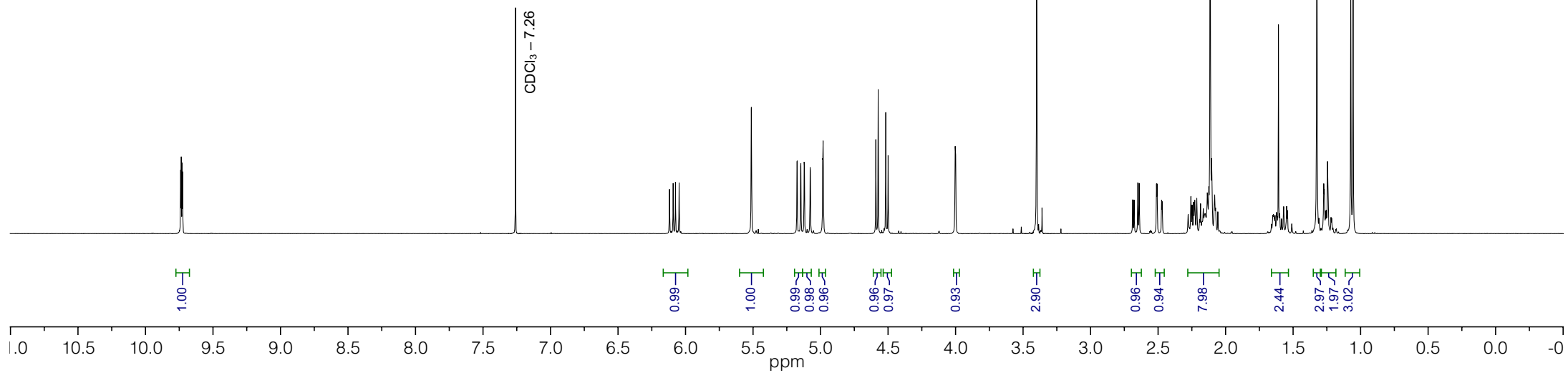
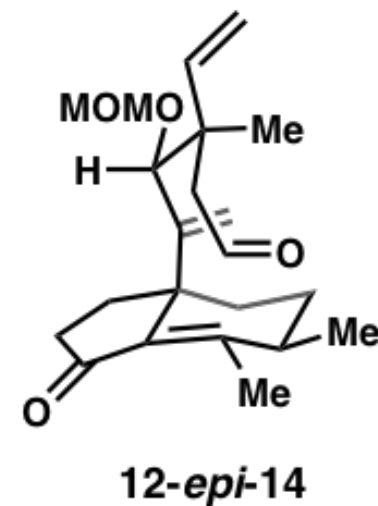
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Data File Name	/ Volumes/ nmrdata-1/ sfeng/ nmr/ SSF-III-77-characterization2/ 1/ fid
Title	SSF-III-77-characterization2.1.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl <sub>3</sub>
Temperature	295.0
Pulse Sequence	zg30
Number of Scans	16
Receiver Gain	197.4
Relaxation Delay	5.0000
Pulse Width	11.7000
Acquisition Time	14.9998
Acquisition Date	2017-11-30T19:13:37
Spectrometer Frequency	400.13
Spectral Width	8012.8
Lowest Frequency	-1545.5
Nucleus	<sup>1</sup> H
Acquired Size	120191
Spectral Size	262144

CDCl<sub>3</sub> - 7.26

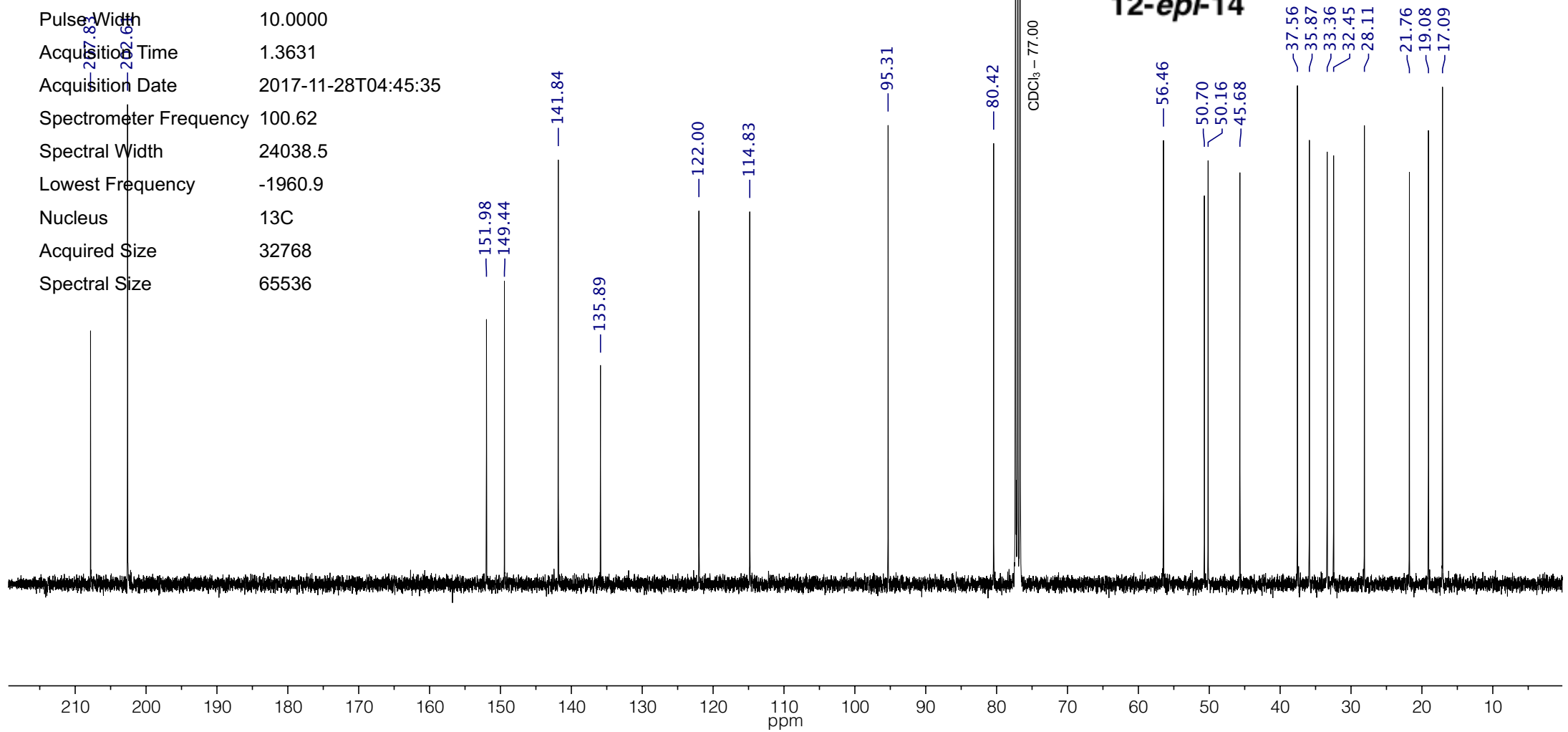
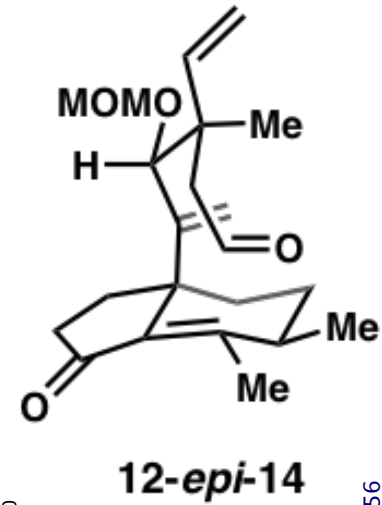
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Data File Name	/ Volumes/ nmrdata-1/ sfeng/ nmr/ SSF-III-77-characterization2/ 2/ fid
Title	SSF-III-77-characterization2.2.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl <sub>3</sub>
Temperature	294.9
Pulse Sequence	zgpg30
Number of Scans	1024
Receiver Gain	64.2
Relaxation Delay	1.0000
Pulse Width	10.0000
Acquisition Time	1.3631
Acquisition Date	2017-11-30T19:55:32
Spectrometer Frequency	100.62
Spectral Width	24038.5
Lowest Frequency	-1962.0
Nucleus	<sup>13</sup> C
Acquired Size	32768
Spectral Size	65536



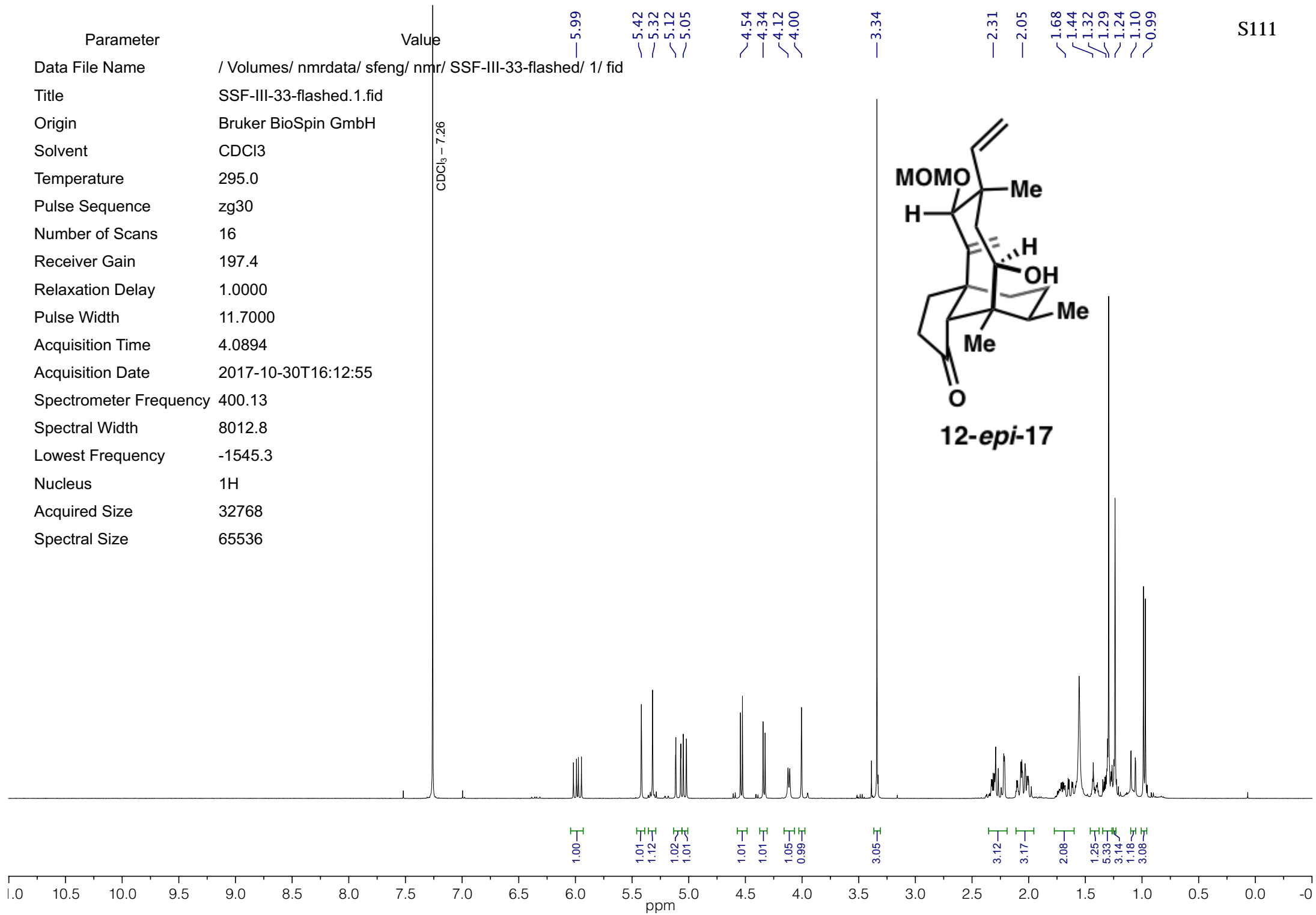
Parameter	Value
Data File Name	/ Volumes/ nmrdata/ sfeng/ nmr/ SSF-III-78-characterization/ 2/ fid
Title	SSF-III-78-characterization.2.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl <sub>3</sub>
Temperature	295.0
Pulse Sequence	zg30
Number of Scans	1
Receiver Gain	112.8
Relaxation Delay	5.0000
Pulse Width	11.7000
Acquisition Time	14.9998
Acquisition Date	2017-11-28T04:47:25
Spectrometer Frequency	400.13
Spectral Width	8012.8
Lowest Frequency	-1545.4
Nucleus	<sup>1</sup> H
Acquired Size	120191
Spectral Size	262144



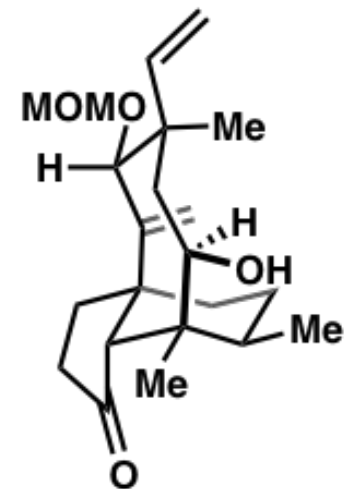
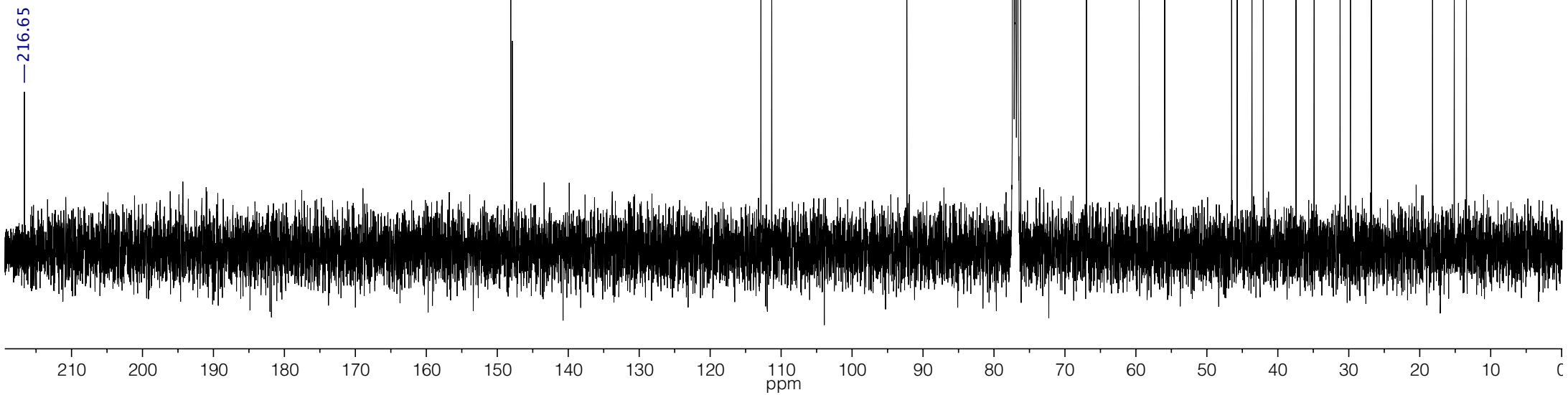
Parameter	Value
Data File Name	/ Volumes/ nmrdata/ sfeng/ nmr/ SSF-III-78-characterization/ 1/ fid
Title	SSF-III-78-characterization.1.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	295.0
Pulse Sequence	zgpg30
Number of Scans	512
Receiver Gain	72.0
Relaxation Delay	1.0000
Pulse Width	10.0000
Acquisition Time	1.3631
Acquisition Date	2017-11-28T04:45:35
Spectrometer Frequency	100.62
Spectral Width	24038.5
Lowest Frequency	-1960.9
Nucleus	13C
Acquired Size	32768
Spectral Size	65536



Parameter	Value
Data File Name	/ Volumes/ nmrdata/ sfeng/ nmr/ SSF-III-33-flashed/ 1/ fid
Title	SSF-III-33-flashed.1.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl <sub>3</sub>
Temperature	295.0
Pulse Sequence	zg30
Number of Scans	16
Receiver Gain	197.4
Relaxation Delay	1.0000
Pulse Width	11.7000
Acquisition Time	4.0894
Acquisition Date	2017-10-30T16:12:55
Spectrometer Frequency	400.13
Spectral Width	8012.8
Lowest Frequency	-1545.3
Nucleus	<sup>1</sup> H
Acquired Size	32768
Spectral Size	65536



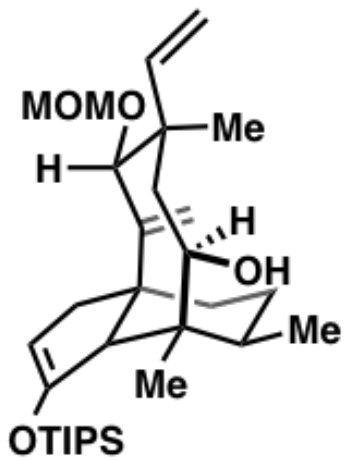
Parameter	Value
Data File Name	/ Volumes/ nmrdata/ sfeng/ nmr/ SSF-III-33-flashed/ 5/ fid
Title	SSF-III-33-flashed.5.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl <sub>3</sub>
Temperature	294.9
Pulse Sequence	zgpg30
Number of Scans	512
Receiver Gain	87.8
Relaxation Delay	1.0000
Pulse Width	10.0000
Acquisition Time	1.3631
Acquisition Date	2017-10-30T17:14:01
Spectrometer Frequency	100.62
Spectral Width	24038.5
Lowest Frequency	-1961.0
Nucleus	<sup>13</sup> C
Acquired Size	32768
Spectral Size	65536



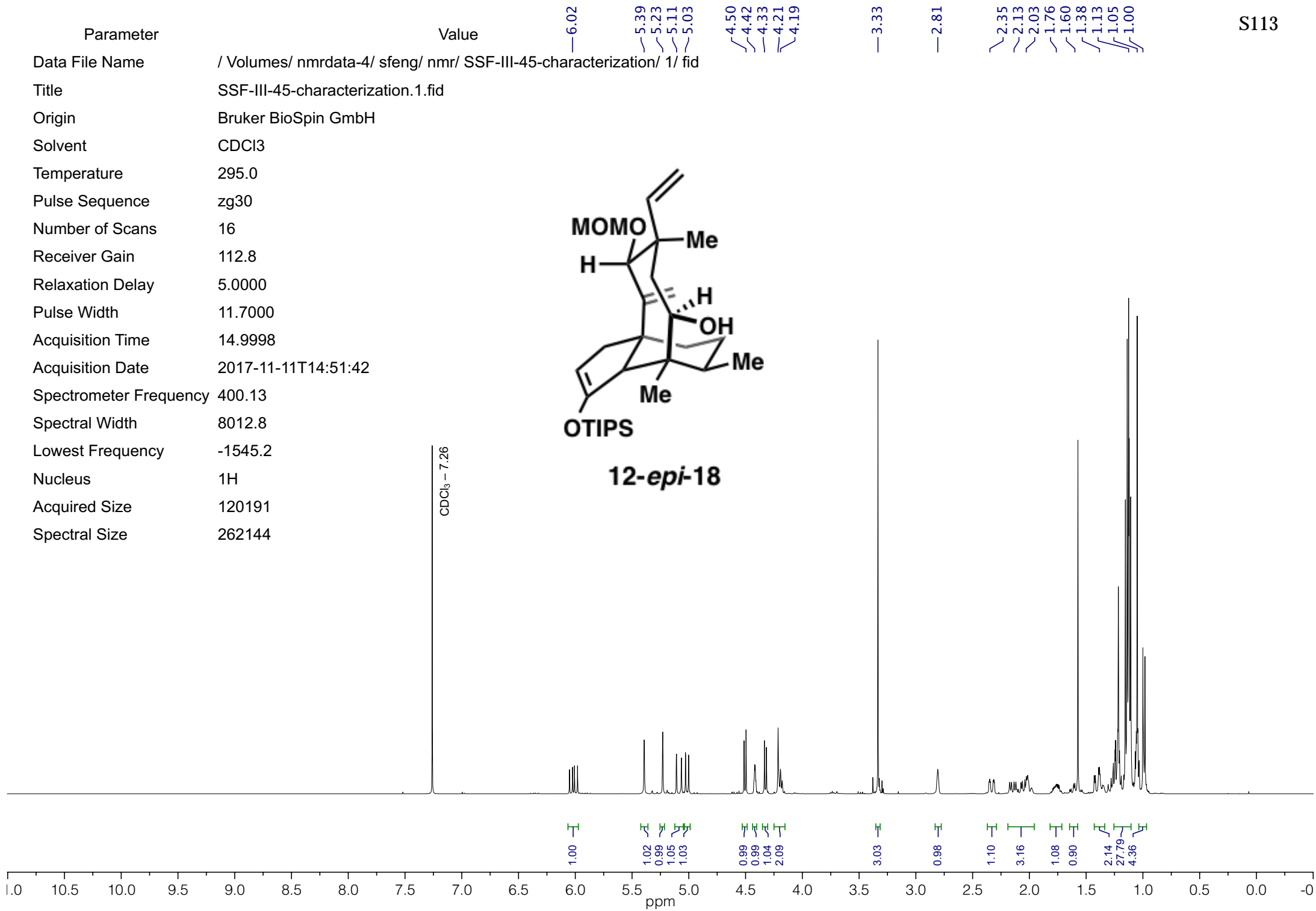
**12-epi-17**



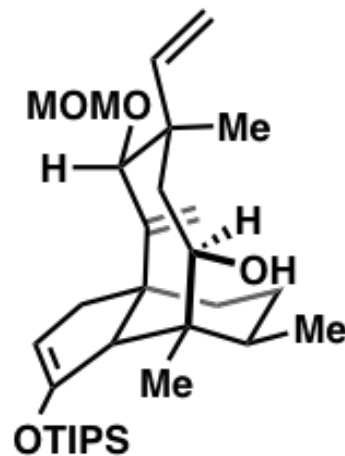
Parameter	Value
Data File Name	/ Volumes/ nmrdata-4/ sfeng/ nmr/ SSF-III-45-characterization/ 1/ fid
Title	SSF-III-45-characterization.1.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	295.0
Pulse Sequence	zg30
Number of Scans	16
Receiver Gain	112.8
Relaxation Delay	5.0000
Pulse Width	11.7000
Acquisition Time	14.9998
Acquisition Date	2017-11-11T14:51:42
Spectrometer Frequency	400.13
Spectral Width	8012.8
Lowest Frequency	-1545.2
Nucleus	1H
Acquired Size	120191
Spectral Size	262144



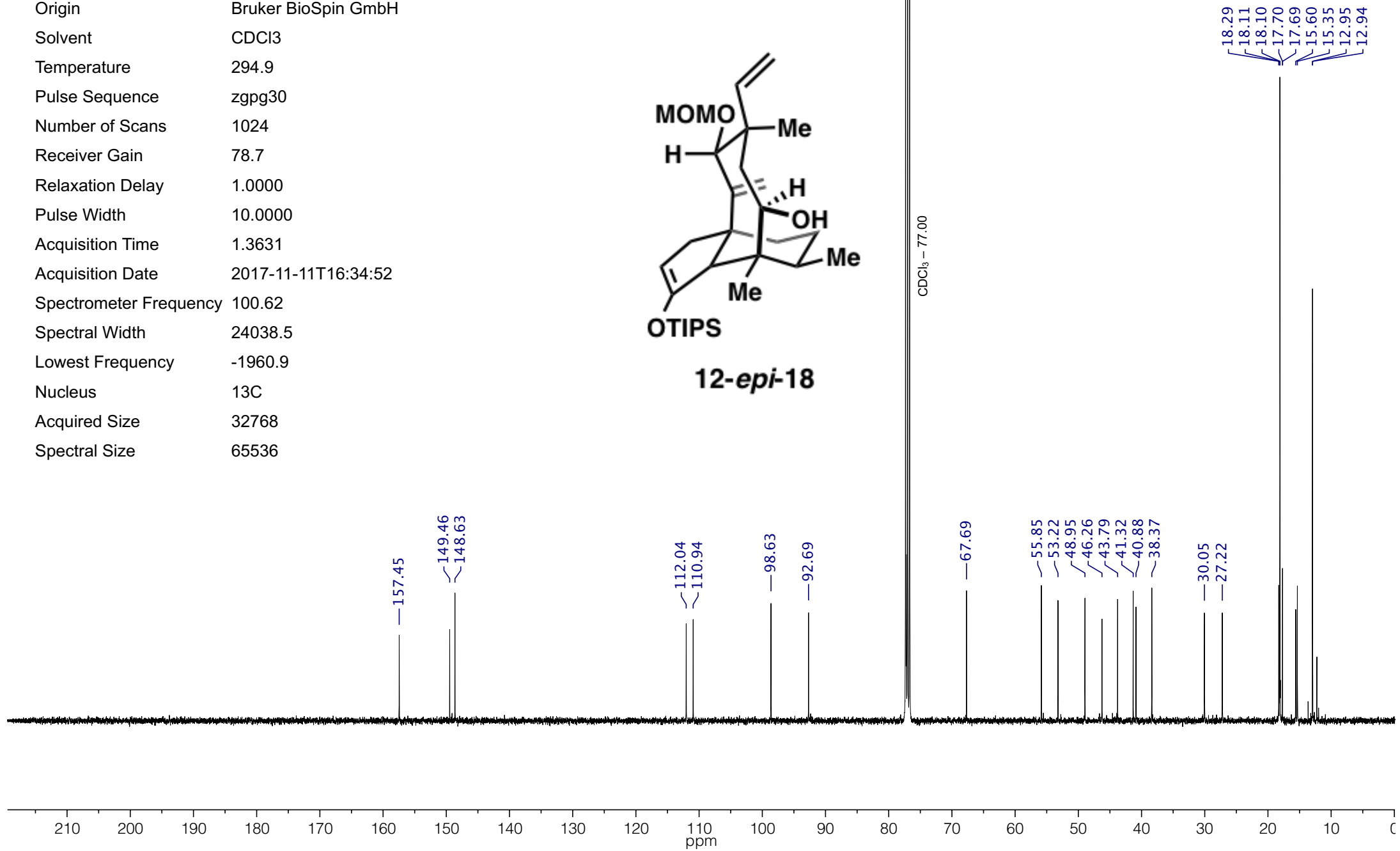
**12-*epi*-18**



Parameter	Value
Data File Name	/ Volumes/ nmrdata-4/ sfeng/ nmr/ SSF-III-45-characterization/ 5/ fid
Title	SSF-III-45-characterization.5.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCI3
Temperature	294.9
Pulse Sequence	zgpg30
Number of Scans	1024
Receiver Gain	78.7
Relaxation Delay	1.0000
Pulse Width	10.0000
Acquisition Time	1.3631
Acquisition Date	2017-11-11T16:34:52
Spectrometer Frequency	100.62
Spectral Width	24038.5
Lowest Frequency	-1960.9
Nucleus	13C
Acquired Size	32768
Spectral Size	65536



12-epi-18



Parameter	Value
Data File Name	/ Volumes/ nmrdata-4/ sfeng/ nmr/ SSF-III-46-characterization/ 1/ fid
Title	SSF-III-46-characterization.1.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl <sub>3</sub>
Temperature	295.0
Pulse Sequence	zg30
Number of Scans	16
Receiver Gain	197.4
Relaxation Delay	5.0000
Pulse Width	11.7000
Acquisition Time	14.9998
Acquisition Date	2017-11-14T11:33:23
Spectrometer Frequency	400.13
Spectral Width	8012.8
Lowest Frequency	-1545.4
Nucleus	<sup>1</sup> H
Acquired Size	120191
Spectral Size	262144

Value

5.97

5.06

5.02

4.54

4.44

3.82

3.37

3.22

2.93

2.17

1.85

1.70

1.59

1.34

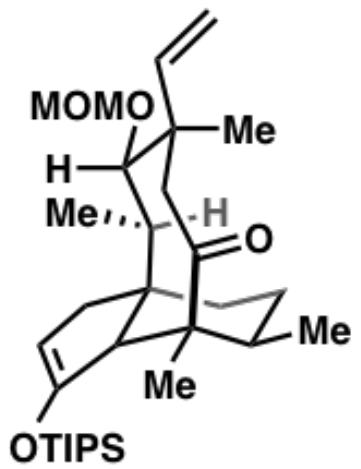
1.26

1.19

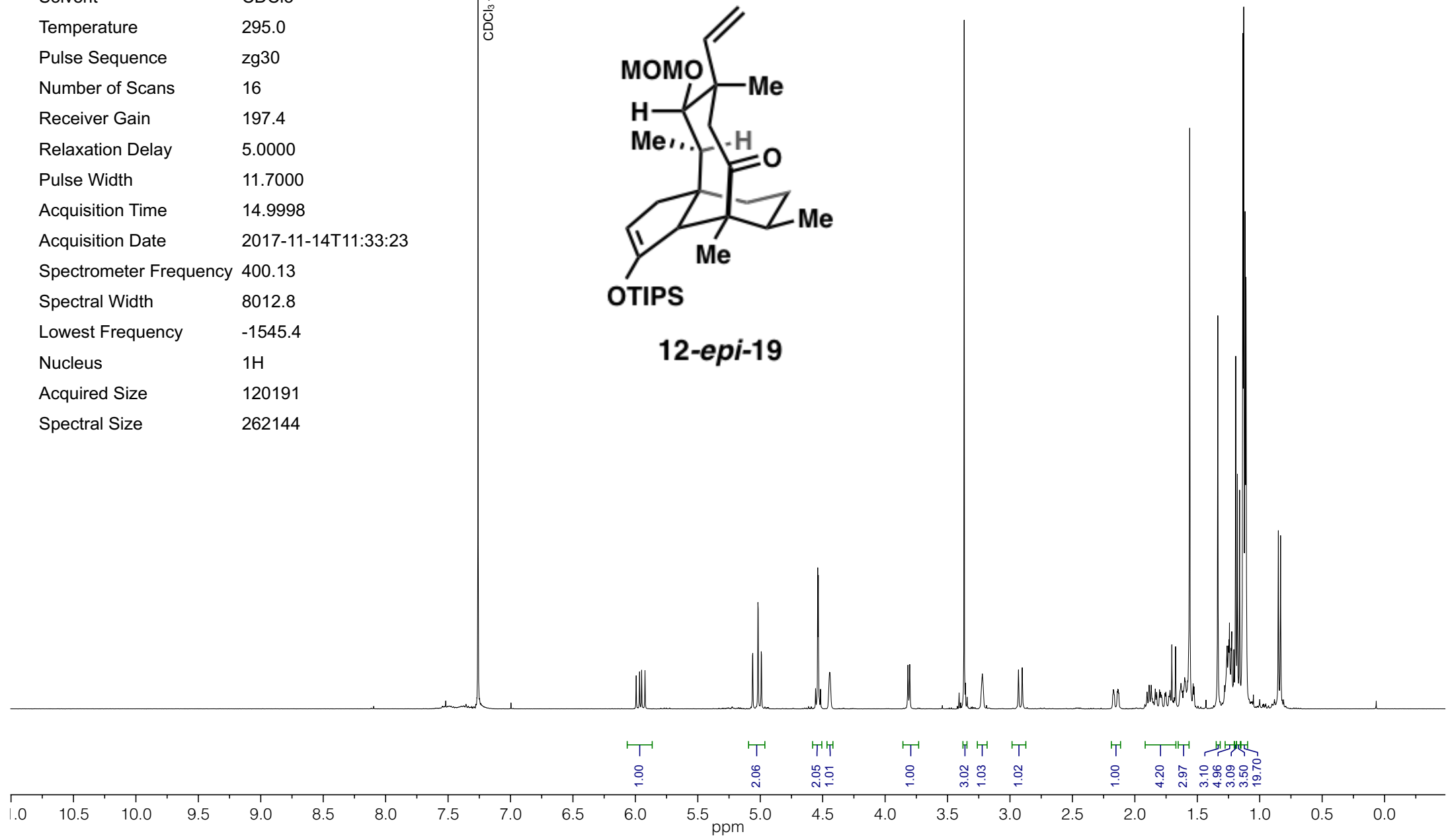
1.16

1.12

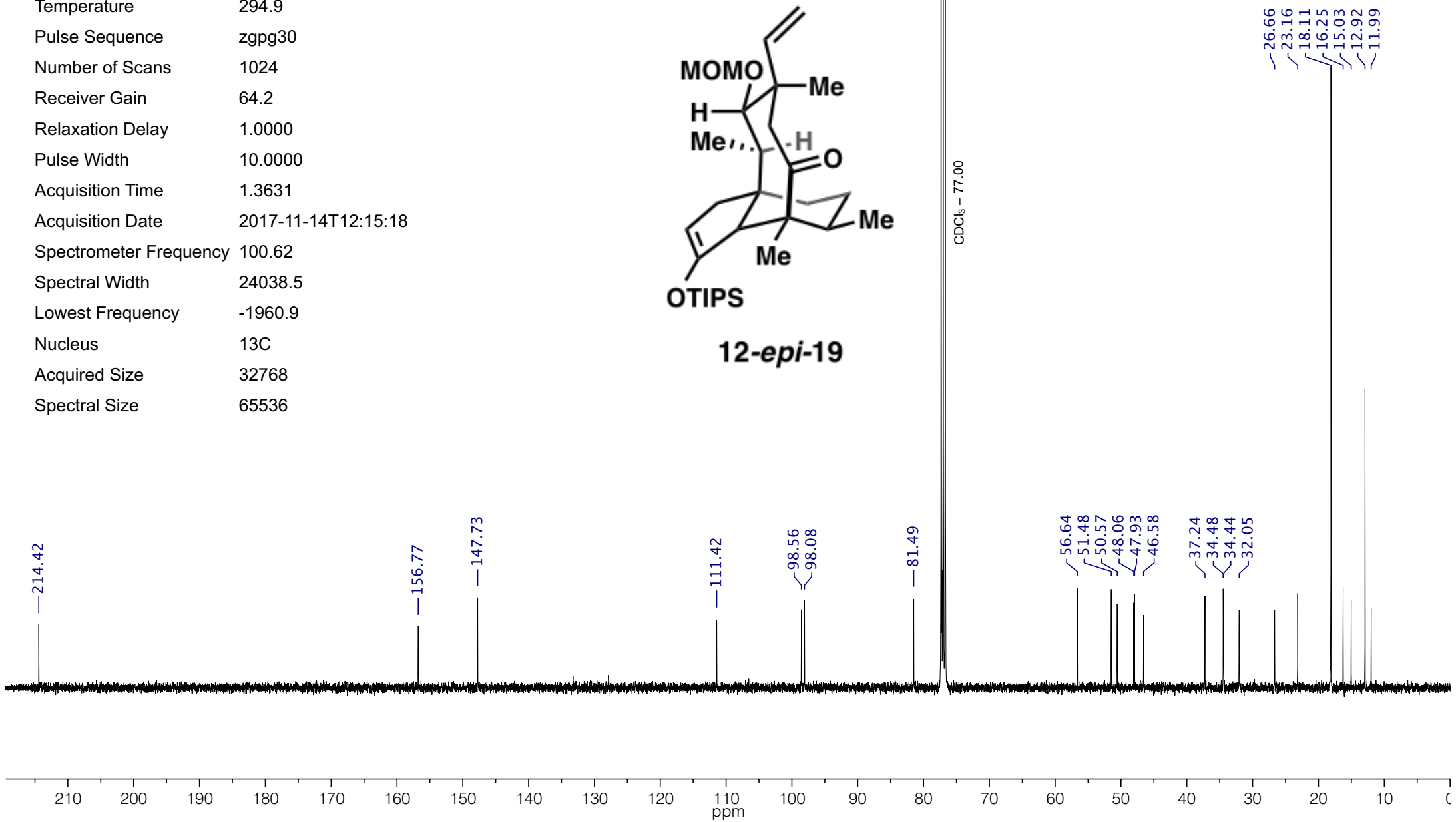
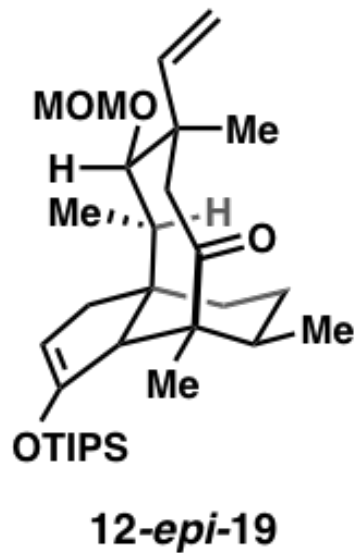
CDCl<sub>3</sub> - 7.26



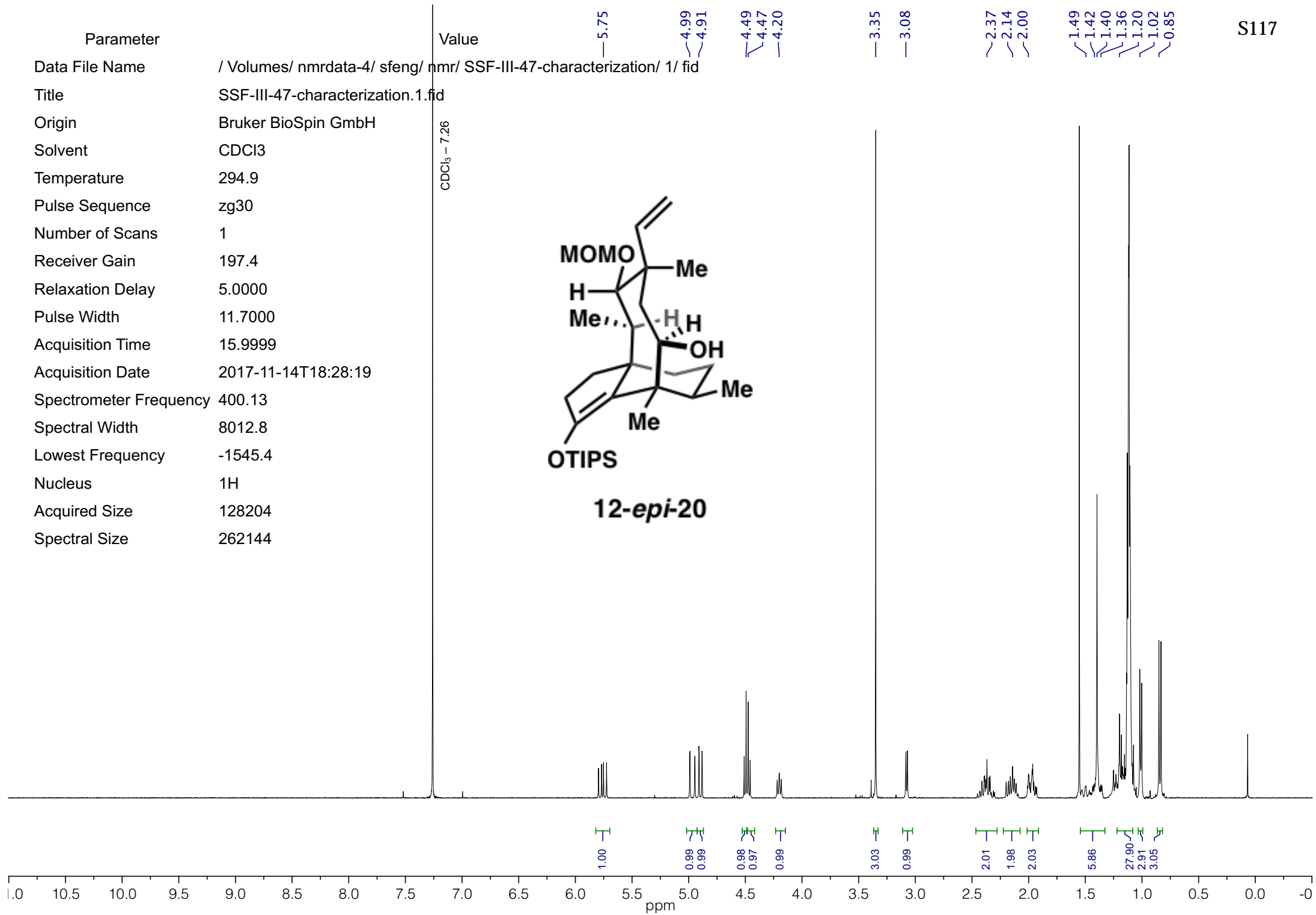
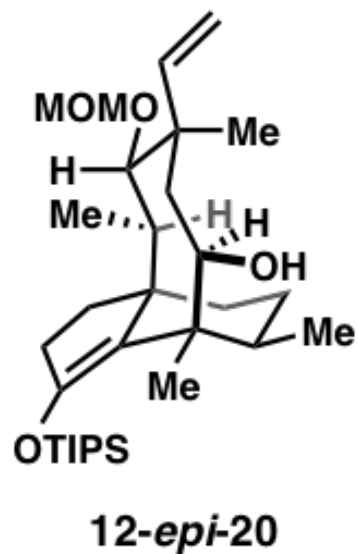
**12-epi-19**



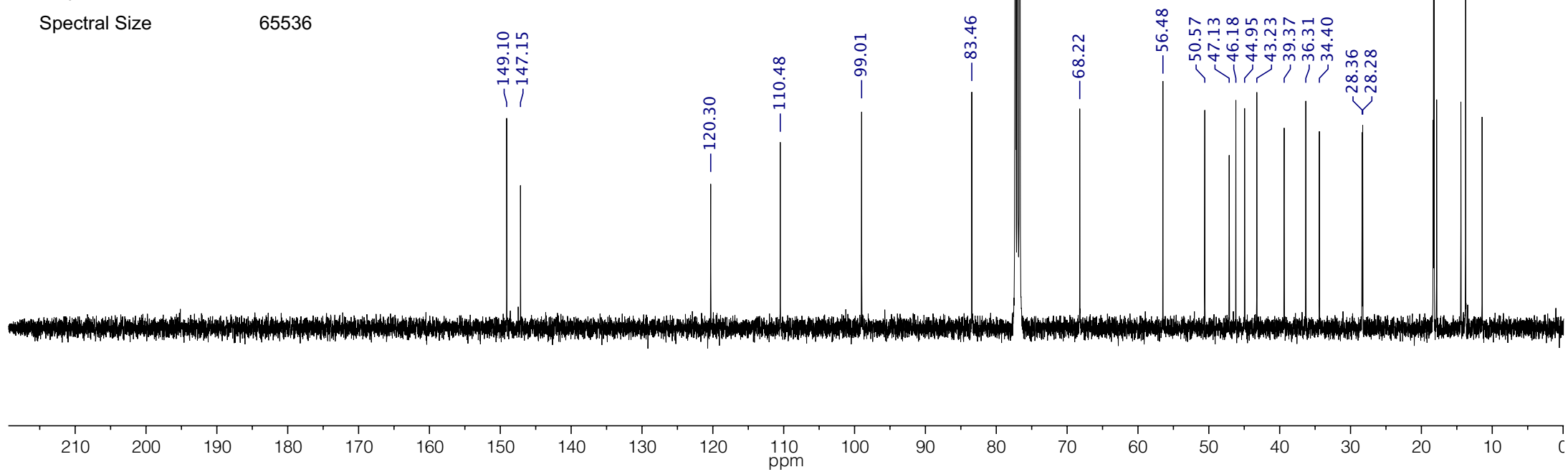
Parameter	Value
Data File Name	/ Volumes/ nmrdata-4/ sfeng/ nmr/ SSF-III-46-characterization/ 2/ fid
Title	SSF-III-46-characterization.2.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl <sub>3</sub>
Temperature	294.9
Pulse Sequence	zgpg30
Number of Scans	1024
Receiver Gain	64.2
Relaxation Delay	1.0000
Pulse Width	10.0000
Acquisition Time	1.3631
Acquisition Date	2017-11-14T12:15:18
Spectrometer Frequency	100.62
Spectral Width	24038.5
Lowest Frequency	-1960.9
Nucleus	<sup>13</sup> C
Acquired Size	32768
Spectral Size	65536



Parameter	Value
Data File Name	/ Volumes/ nmrdata-4/ sfeng/ nmr/ SSF-III-47-characterization/ 1/ fid
Title	SSF-III-47-characterization.1.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl <sub>3</sub>
Temperature	294.9
Pulse Sequence	zg30
Number of Scans	1
Receiver Gain	197.4
Relaxation Delay	5.0000
Pulse Width	11.7000
Acquisition Time	15.9999
Acquisition Date	2017-11-14T18:28:19
Spectrometer Frequency	400.13
Spectral Width	8012.8
Lowest Frequency	-1545.4
Nucleus	<sup>1</sup> H
Acquired Size	128204
Spectral Size	262144

CDCl<sub>3</sub> - 7.26

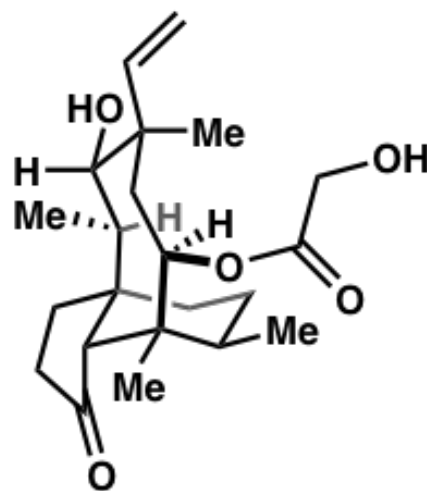
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Data File Name	/ Volumes/ nmrdata-4/ sfeng/ nmr/ SSF-III-47-F/ 1/ fid
Title	SSF-III-47-F.1.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl <sub>3</sub>
Temperature	294.9
Pulse Sequence	zgpg30
Number of Scans	2048
Receiver Gain	78.7
Relaxation Delay	1.0000
Pulse Width	10.0000
Acquisition Time	1.3631
Acquisition Date	2017-11-15T00:48:23
Spectrometer Frequency	100.62
Spectral Width	24038.5
Lowest Frequency	-1960.9
Nucleus	<sup>13</sup> C
Acquired Size	32768
Spectral Size	65536



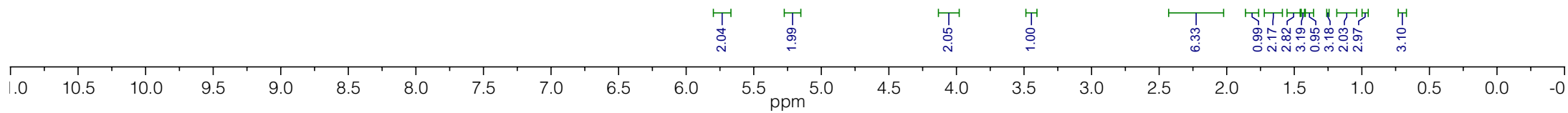
Parameter	Value
Data File Name	/Volumes/nmrdata/sfeng/nmr/SSF-III-52-characterization/1/fid
Title	SSF-III-52-characterization.1.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl <sub>3</sub>
Temperature	294.9
Pulse Sequence	zg30
Number of Scans	1
Receiver Gain	197.4
Relaxation Delay	5.0000
Pulse Width	11.7000
Acquisition Time	14.9998
Acquisition Date	2017-11-18T14:59:57
Spectrometer Frequency	400.13
Spectral Width	8012.8
Lowest Frequency	-1545.4
Nucleus	<sup>1</sup> H
Acquired Size	120191
Spectral Size	262144

CDCl<sub>3</sub> - 7.26

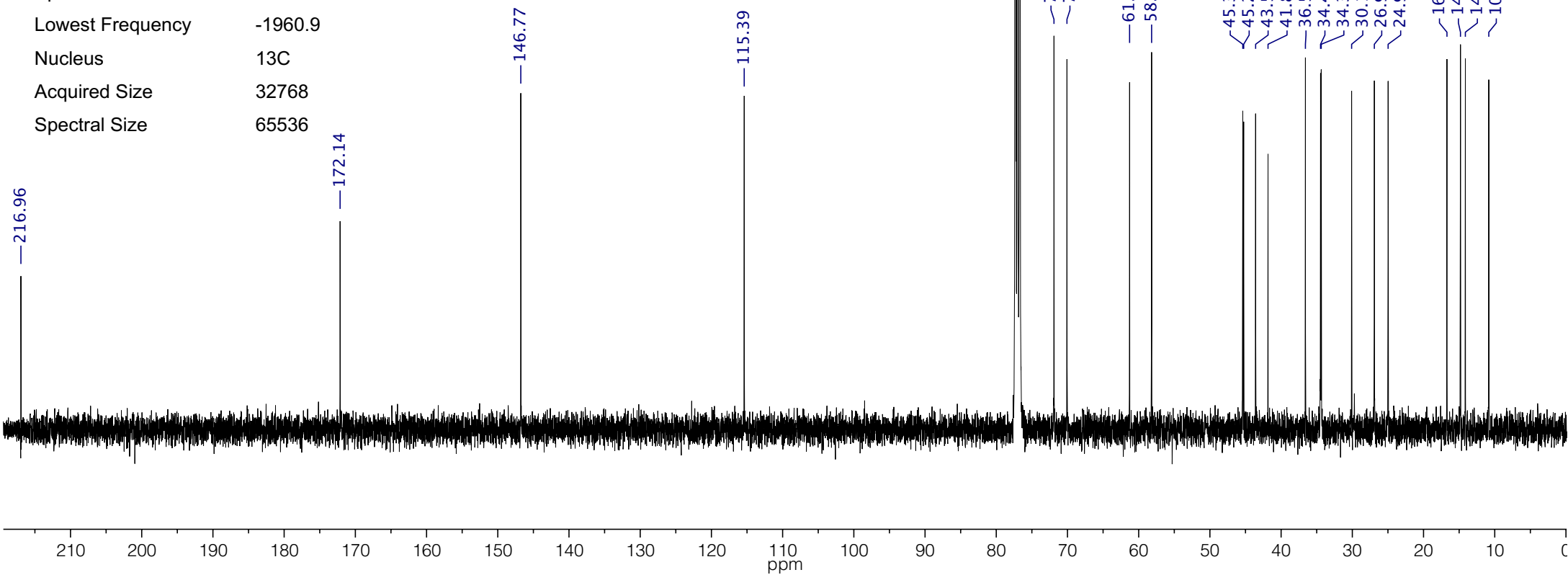
5.77  
5.72  
5.24  
5.21  
4.06  
4.02  
3.45  
2.36  
2.23  
2.11  
2.05  
1.80  
1.66  
1.53  
1.44  
1.39  
1.25  
1.13  
0.98  
0.71



**(+)-12-epi-pleuromutilin (12-epi-1)**

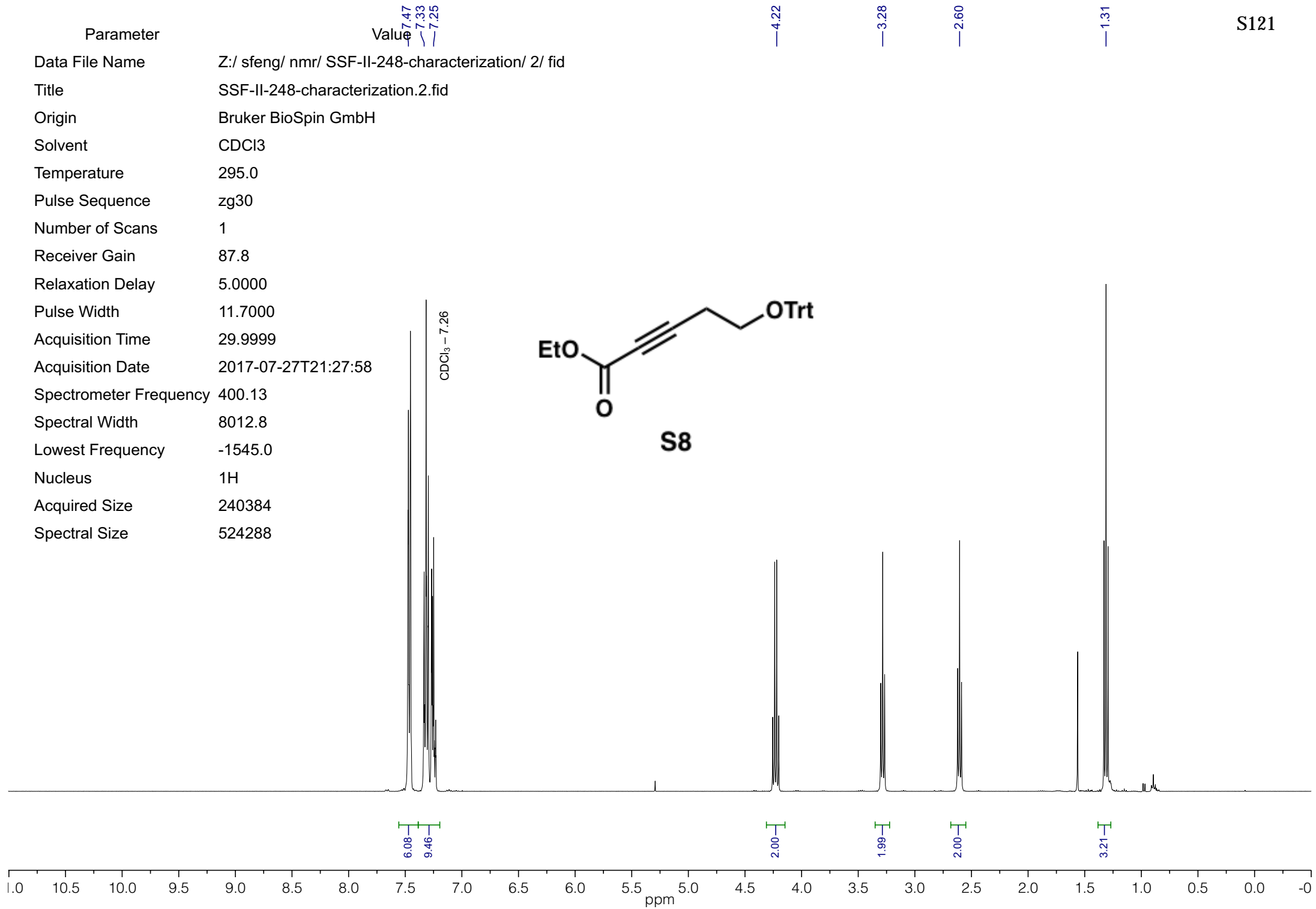


Parameter	Value
Data File Name	/ Volumes/ nmrdata/ sfeng/ nmr/ SSF-III-52-characterization/ 2/ fid
Title	SSF-III-52-characterization.2.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl <sub>3</sub>
Temperature	295.0
Pulse Sequence	zgpg30
Number of Scans	2048
Receiver Gain	87.8
Relaxation Delay	1.0000
Pulse Width	10.0000
Acquisition Time	1.3631
Acquisition Date	2017-11-19T00:01:06
Spectrometer Frequency	100.62
Spectral Width	24038.5
Lowest Frequency	-1960.9
Nucleus	<sup>13</sup> C
Acquired Size	32768
Spectral Size	65536

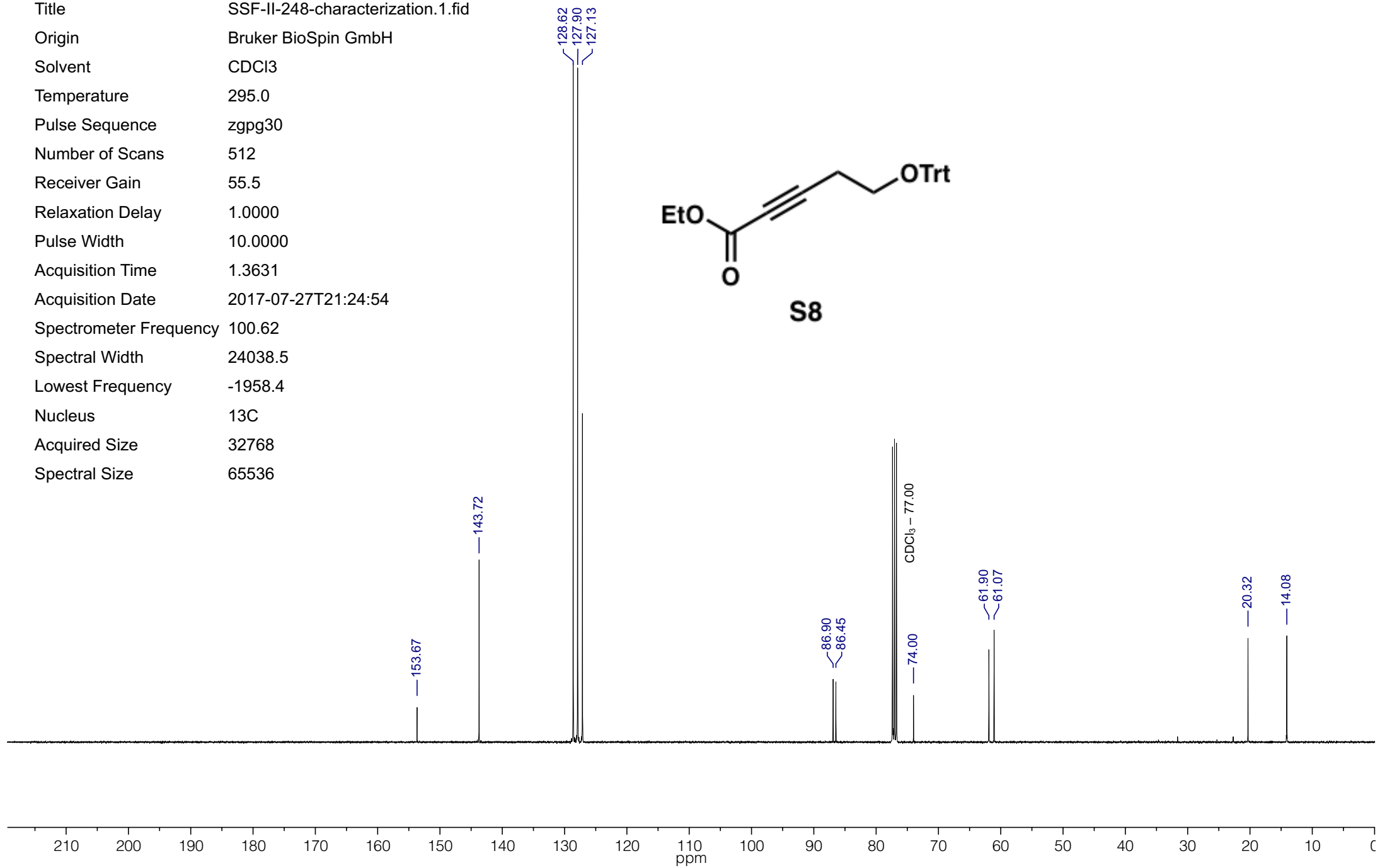
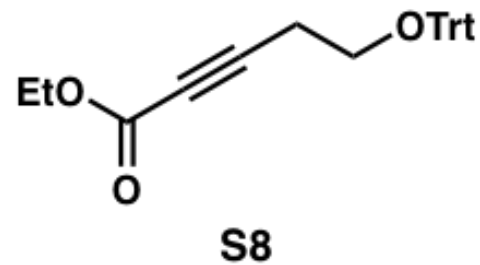




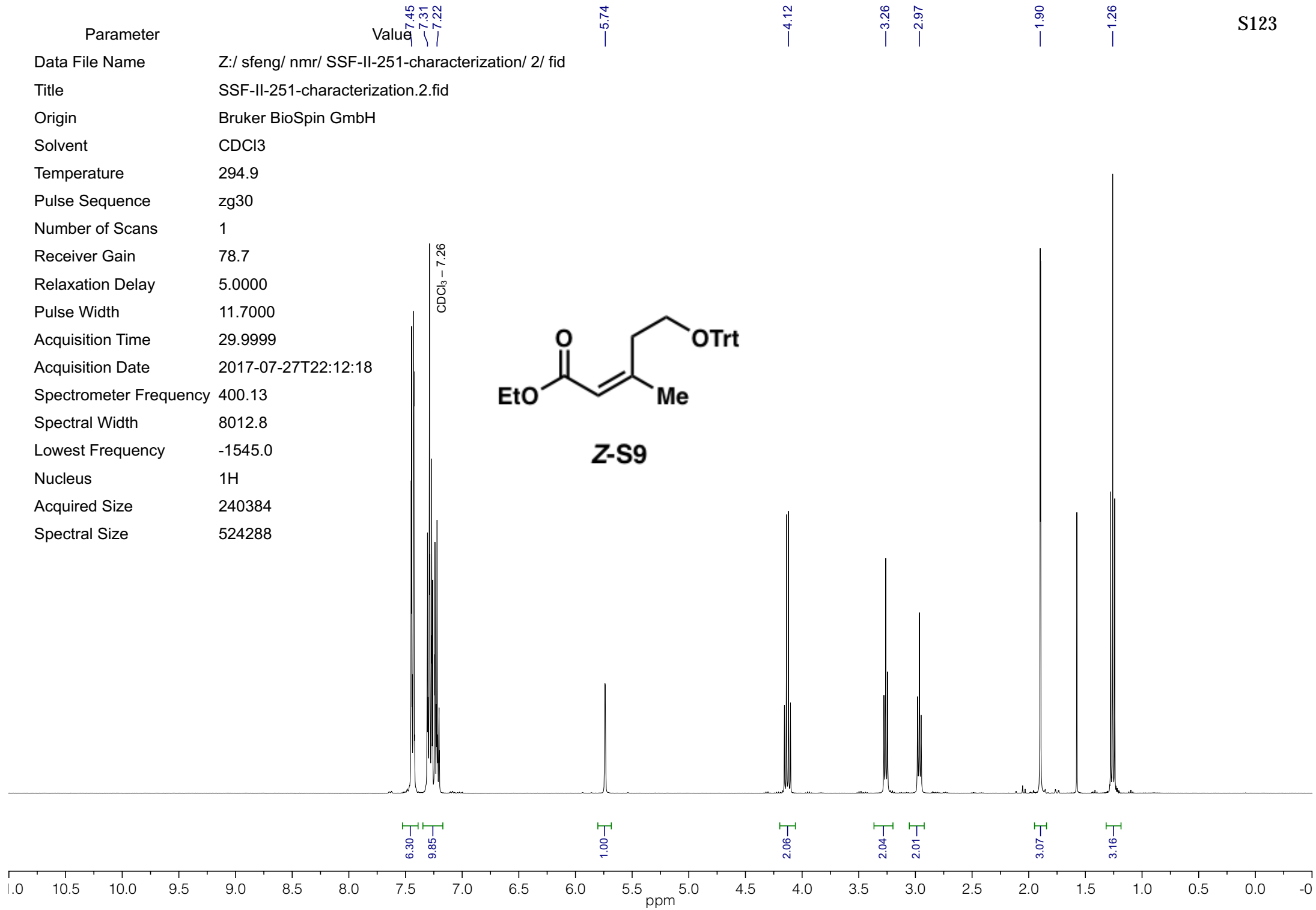
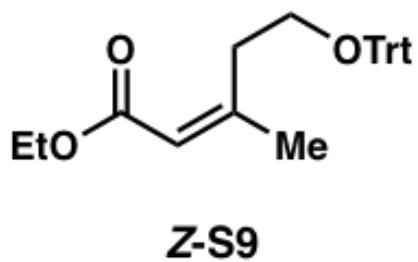
Parameter	Value
Data File Name	Z:/ sfeng/ nmr/ SSF-II-248-characterization/ 2/ fid
Title	SSF-II-248-characterization.2.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl <sub>3</sub>
Temperature	295.0
Pulse Sequence	zg30
Number of Scans	1
Receiver Gain	87.8
Relaxation Delay	5.0000
Pulse Width	11.7000
Acquisition Time	29.9999
Acquisition Date	2017-07-27T21:27:58
Spectrometer Frequency	400.13
Spectral Width	8012.8
Lowest Frequency	-1545.0
Nucleus	<sup>1</sup> H
Acquired Size	240384
Spectral Size	524288



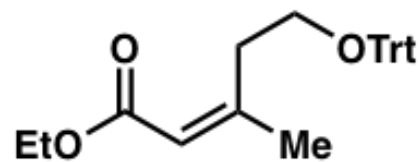
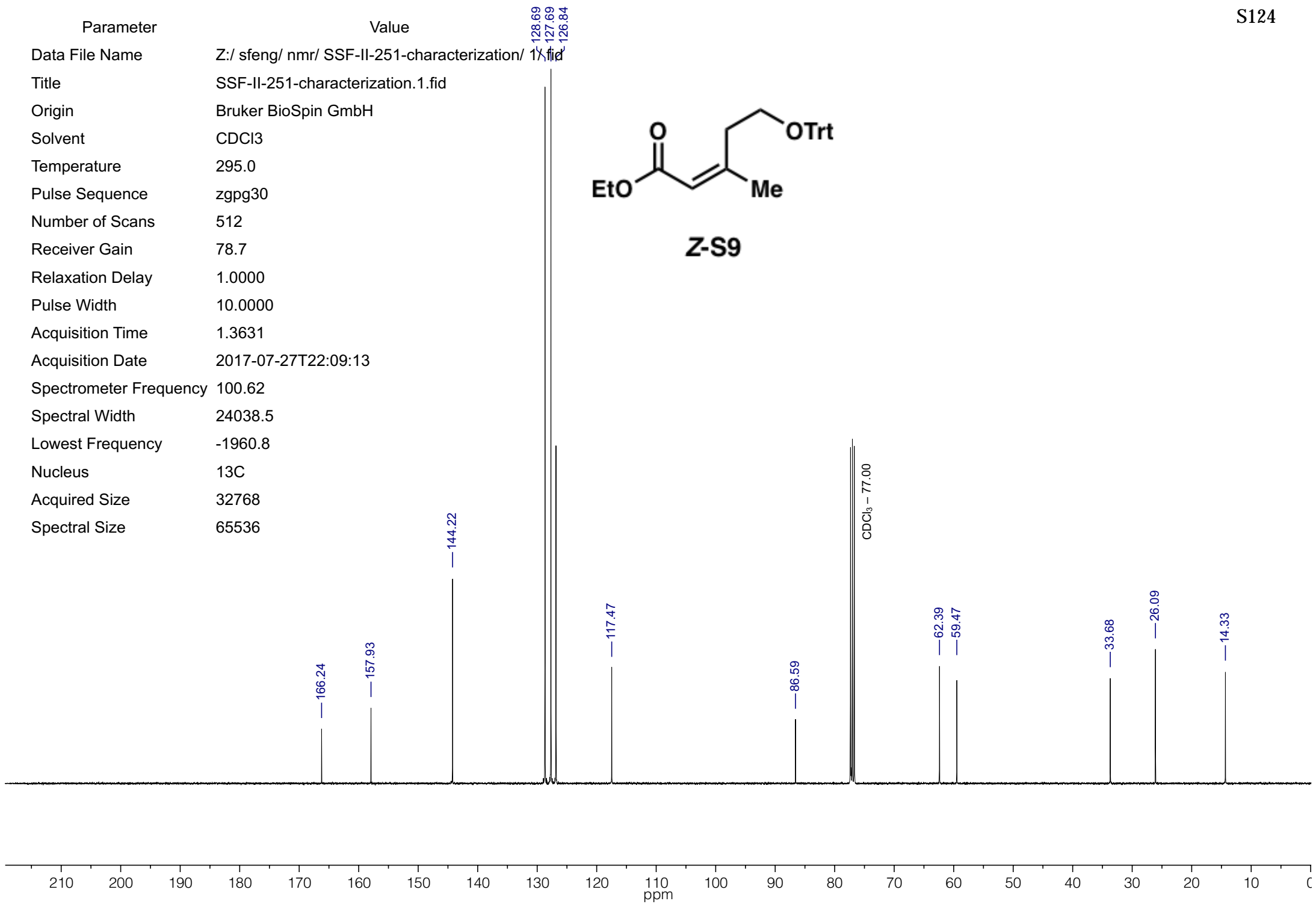
Parameter	Value
Data File Name	Z:/ sfeng/ nmr/ SSF-II-248-characterization/ 1/ fid
Title	SSF-II-248-characterization.1.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	295.0
Pulse Sequence	zgpg30
Number of Scans	512
Receiver Gain	55.5
Relaxation Delay	1.0000
Pulse Width	10.0000
Acquisition Time	1.3631
Acquisition Date	2017-07-27T21:24:54
Spectrometer Frequency	100.62
Spectral Width	24038.5
Lowest Frequency	-1958.4
Nucleus	<sup>13</sup> C
Acquired Size	32768
Spectral Size	65536



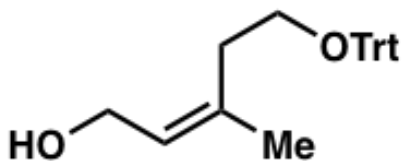
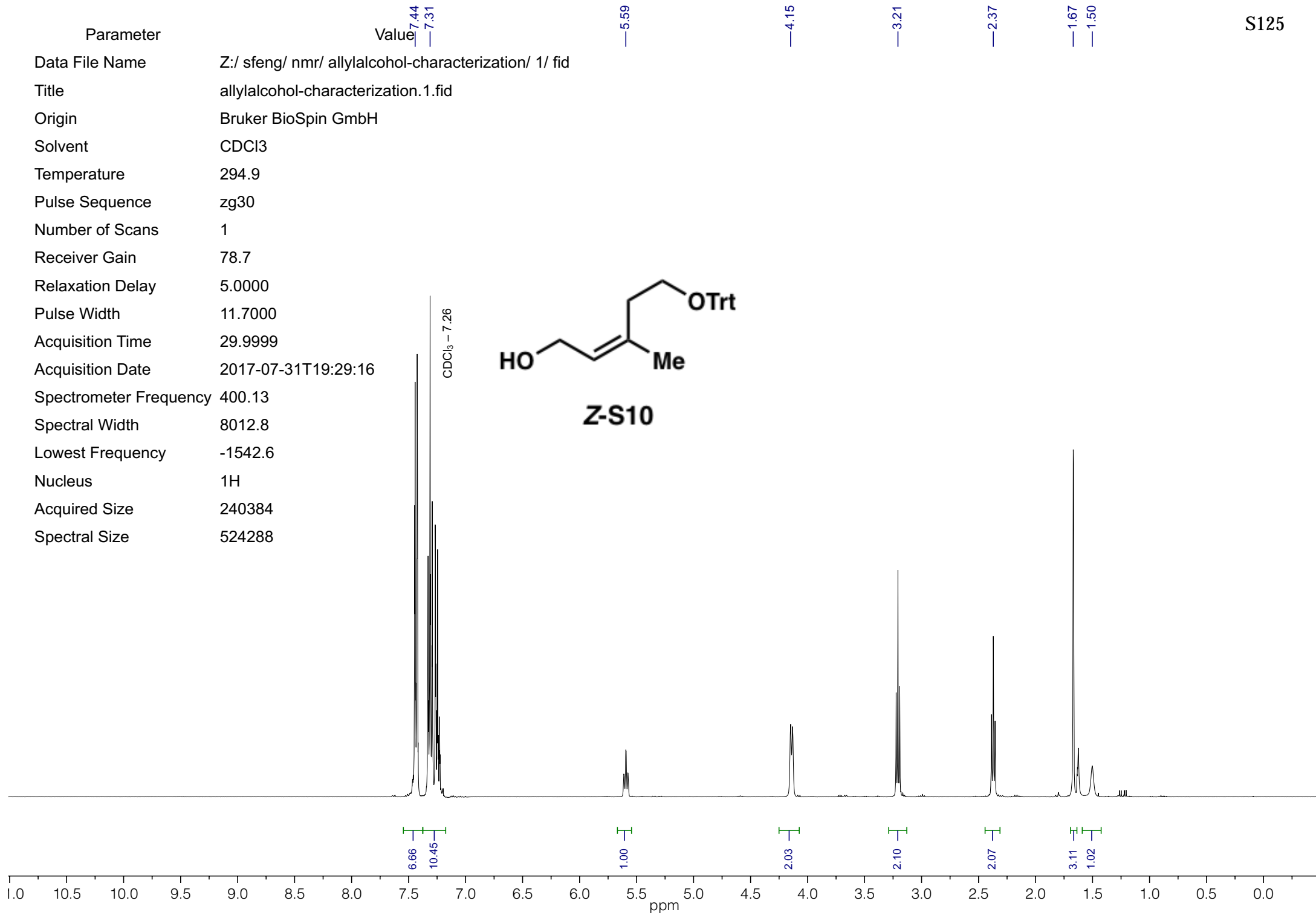
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Data File Name	Z:/ sfeng/ nmr/ SSF-II-251-characterization/ 2/ fid
Title	SSF-II-251-characterization.2.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl <sub>3</sub>
Temperature	294.9
Pulse Sequence	zg30
Number of Scans	1
Receiver Gain	78.7
Relaxation Delay	5.0000
Pulse Width	11.7000
Acquisition Time	29.9999
Acquisition Date	2017-07-27T22:12:18
Spectrometer Frequency	400.13
Spectral Width	8012.8
Lowest Frequency	-1545.0
Nucleus	<sup>1</sup> H
Acquired Size	240384
Spectral Size	524288



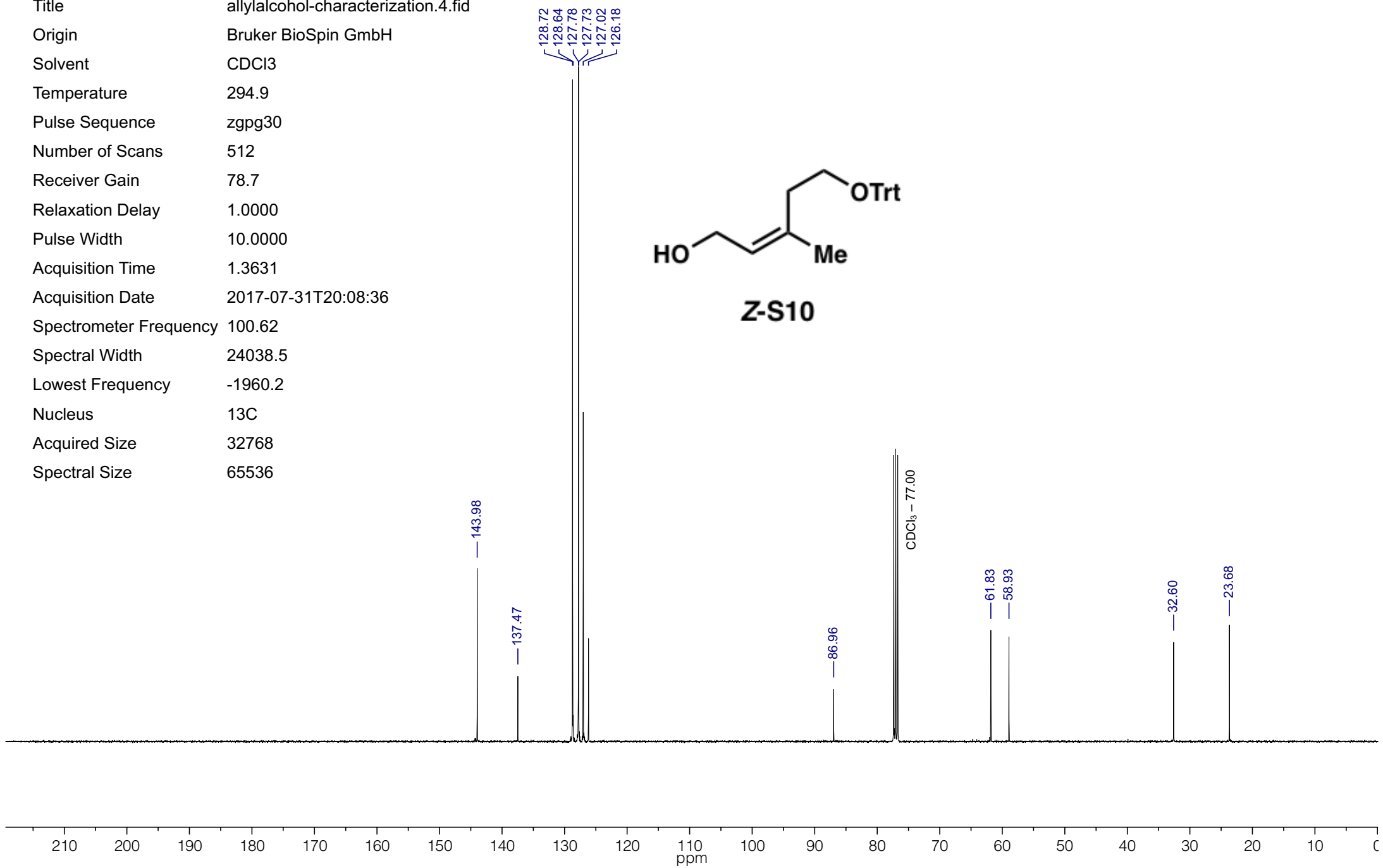
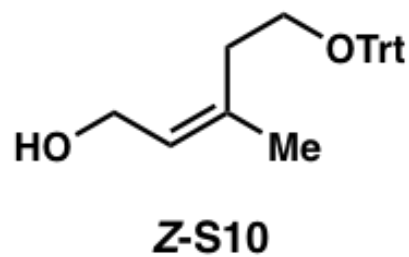
Parameter	Value
Data File Name	Z:/ sfeng/ nmr/ SSF-II-251-characterization/ 17.fid
Title	SSF-II-251-characterization.1.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	295.0
Pulse Sequence	zgpg30
Number of Scans	512
Receiver Gain	78.7
Relaxation Delay	1.0000
Pulse Width	10.0000
Acquisition Time	1.3631
Acquisition Date	2017-07-27T22:09:13
Spectrometer Frequency	100.62
Spectral Width	24038.5
Lowest Frequency	-1960.8
Nucleus	13C
Acquired Size	32768
Spectral Size	65536

**Z-S9**

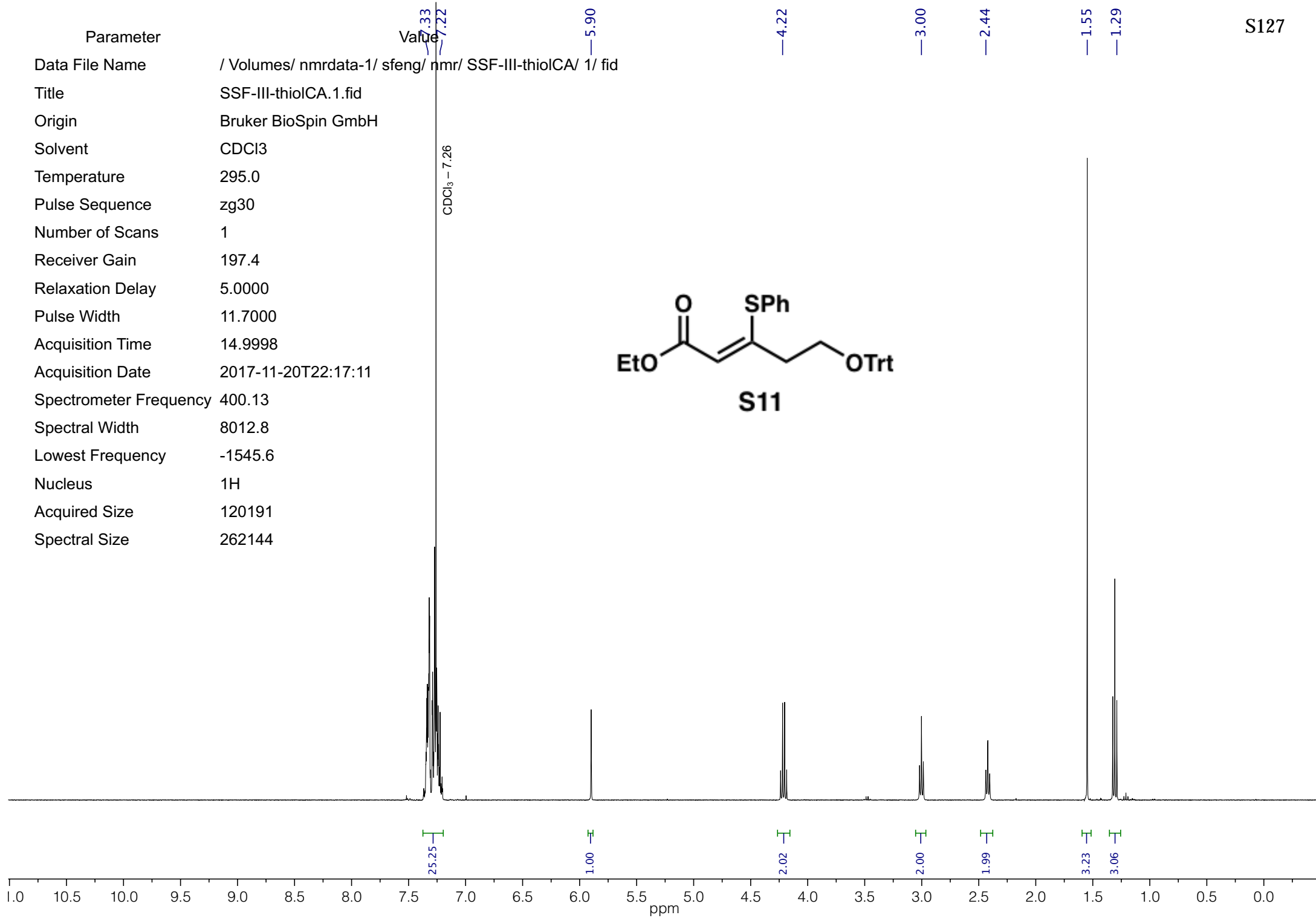
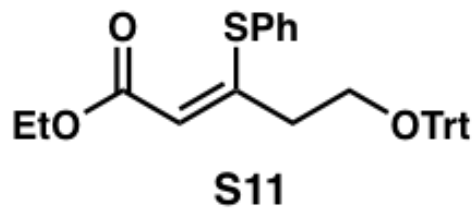
Parameter	Value
Data File Name	Z:/ sfeng/ nmr/ allylalcohol-characterization/ 1/ fid
Title	allylalcohol-characterization.1.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl <sub>3</sub>
Temperature	294.9
Pulse Sequence	zg30
Number of Scans	1
Receiver Gain	78.7
Relaxation Delay	5.0000
Pulse Width	11.7000
Acquisition Time	29.9999
Acquisition Date	2017-07-31T19:29:16
Spectrometer Frequency	400.13
Spectral Width	8012.8
Lowest Frequency	-1542.6
Nucleus	<sup>1</sup> H
Acquired Size	240384
Spectral Size	524288

**Z-S10**

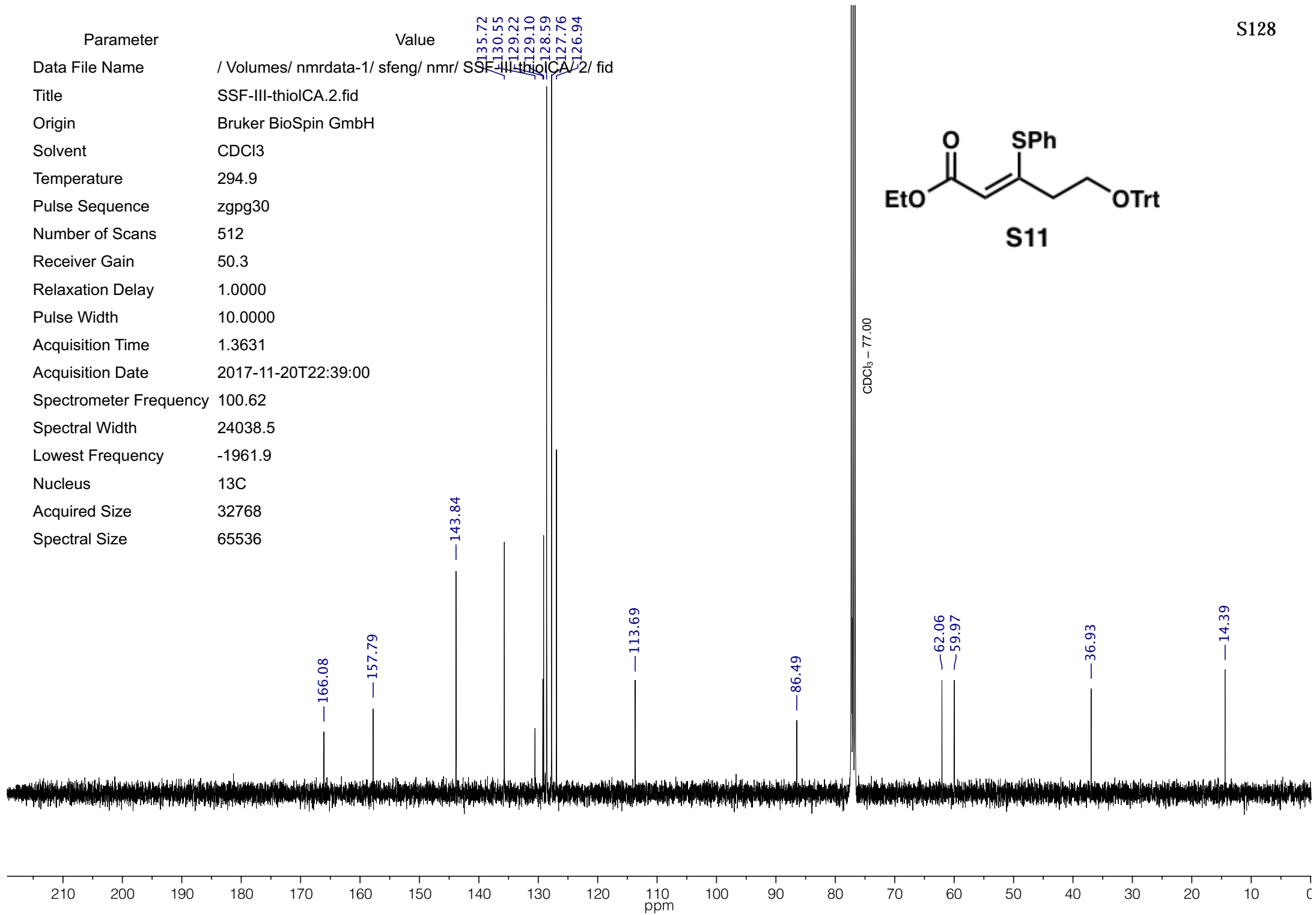
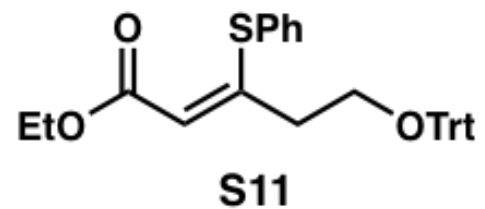
Parameter	Value
Data File Name	Z:/ sfeng/ nmr/ allyl alcohol-characterization/ 4/ fid
Title	allyl alcohol-characterization.4.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl <sub>3</sub>
Temperature	294.9
Pulse Sequence	zgpg30
Number of Scans	512
Receiver Gain	78.7
Relaxation Delay	1.0000
Pulse Width	10.0000
Acquisition Time	1.3631
Acquisition Date	2017-07-31T20:08:36
Spectrometer Frequency	100.62
Spectral Width	24038.5
Lowest Frequency	-1960.2
Nucleus	<sup>13</sup> C
Acquired Size	32768
Spectral Size	65536



Parameter	Value
Data File Name	/Volumes/nmrdata-1/sfeng/nmr/SSF-III-thiolCA/1/ fid
Title	SSF-III-thiolCA.1.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl <sub>3</sub>
Temperature	295.0
Pulse Sequence	zg30
Number of Scans	1
Receiver Gain	197.4
Relaxation Delay	5.0000
Pulse Width	11.7000
Acquisition Time	14.9998
Acquisition Date	2017-11-20T22:17:11
Spectrometer Frequency	400.13
Spectral Width	8012.8
Lowest Frequency	-1545.6
Nucleus	<sup>1</sup> H
Acquired Size	120191
Spectral Size	262144

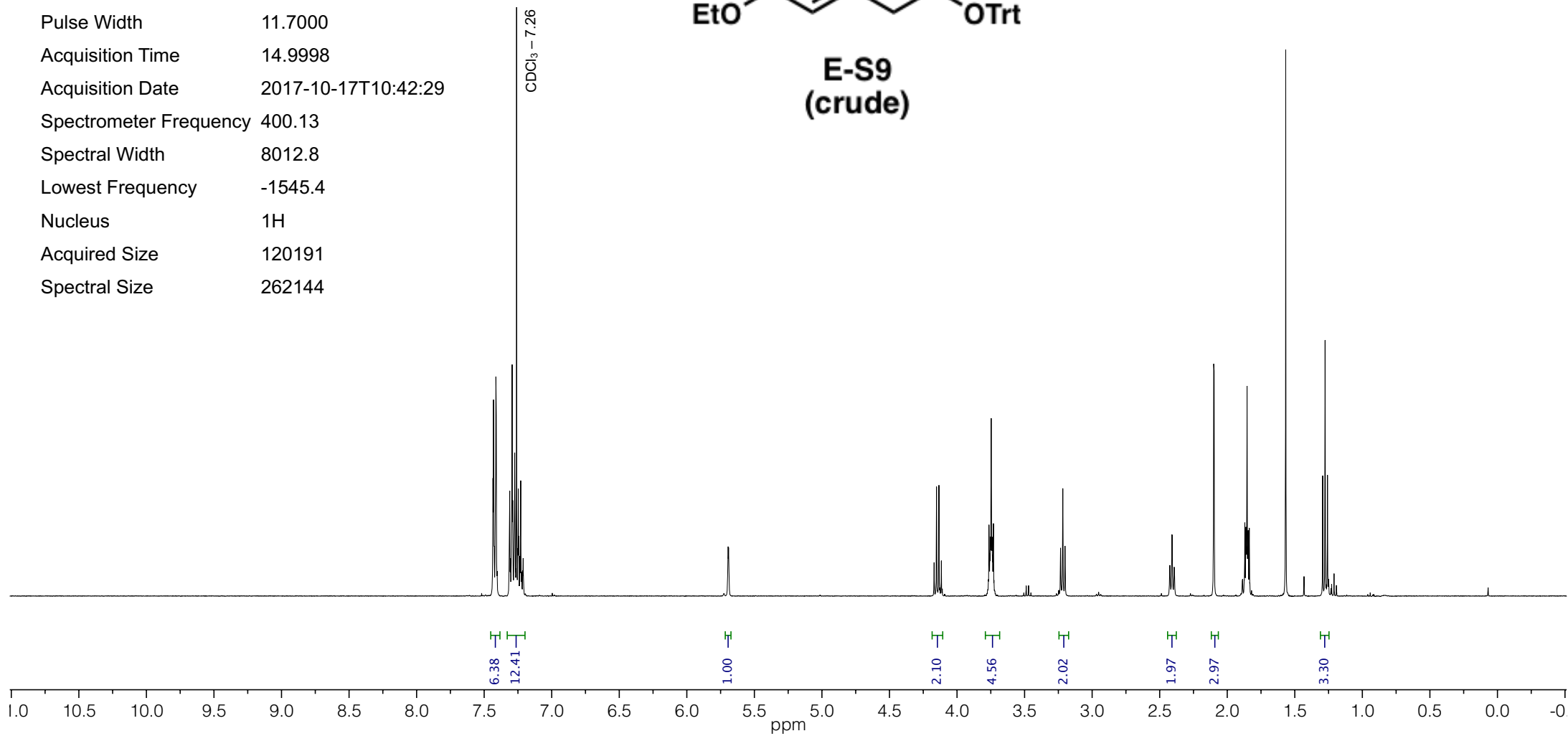
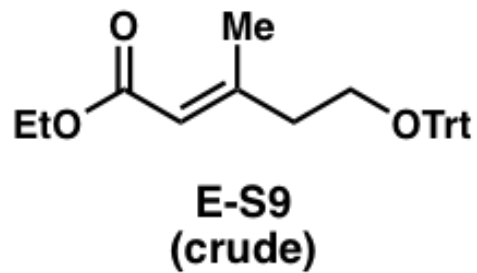


Parameter	Value
Data File Name	/Volumes/nmrdata-1/sfeng/nmr/SSF-III-thiolCA/2/fid
Title	SSF-III-thiolCA.2.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl <sub>3</sub>
Temperature	294.9
Pulse Sequence	zgpg30
Number of Scans	512
Receiver Gain	50.3
Relaxation Delay	1.0000
Pulse Width	10.0000
Acquisition Time	1.3631
Acquisition Date	2017-11-20T22:39:00
Spectrometer Frequency	100.62
Spectral Width	24038.5
Lowest Frequency	-1961.9
Nucleus	<sup>13</sup> C
Acquired Size	32768
Spectral Size	65536

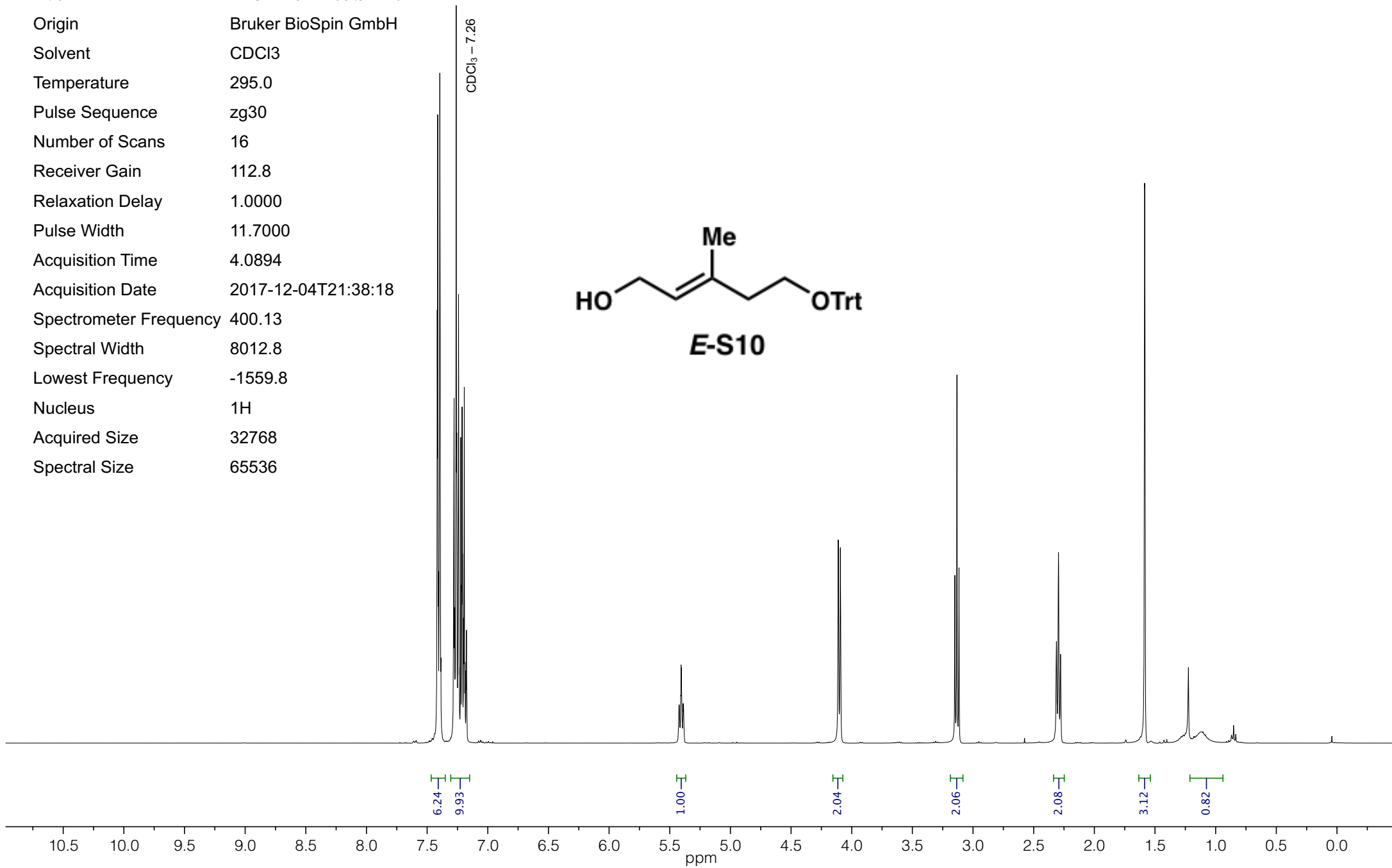
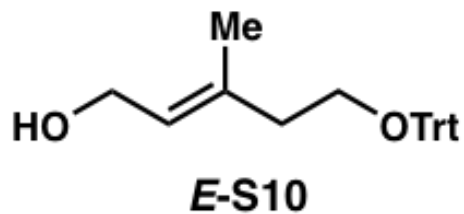




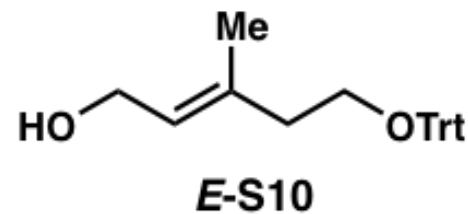
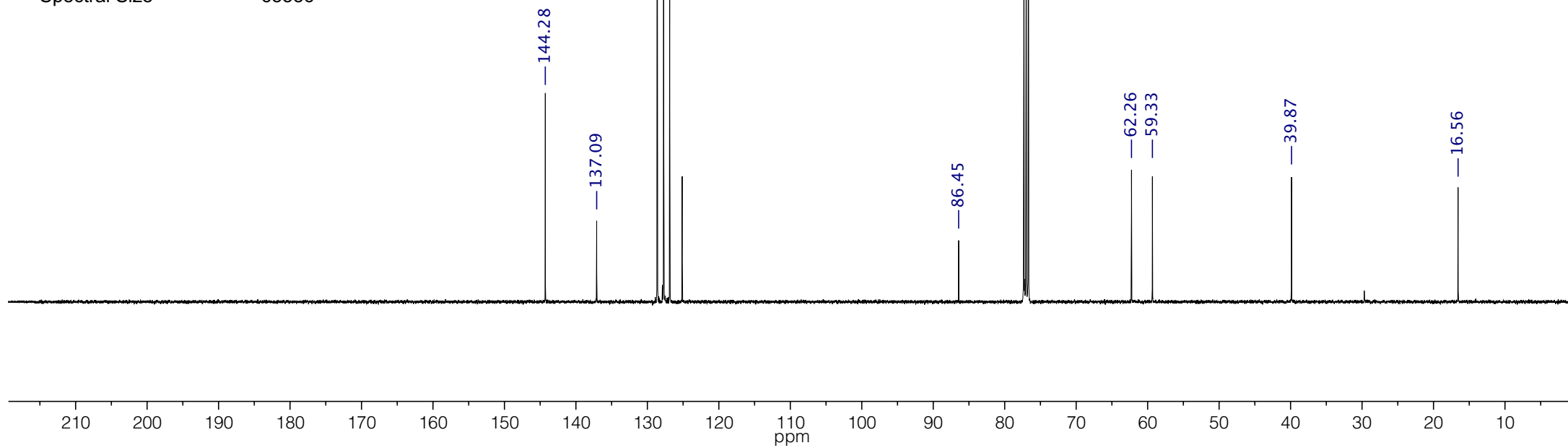
Parameter	Value
Data File Name	/ Volumes/ nmrdata-1/ sfeng/ nmr/ SSF-III-14-crude/ 1/ fid
Title	SSF-III-14-crude.1.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl <sub>3</sub>
Temperature	294.9
Pulse Sequence	zg30
Number of Scans	1
Receiver Gain	197.4
Relaxation Delay	5.0000
Pulse Width	11.7000
Acquisition Time	14.9998
Acquisition Date	2017-10-17T10:42:29
Spectrometer Frequency	400.13
Spectral Width	8012.8
Lowest Frequency	-1545.4
Nucleus	<sup>1</sup> H
Acquired Size	120191
Spectral Size	262144



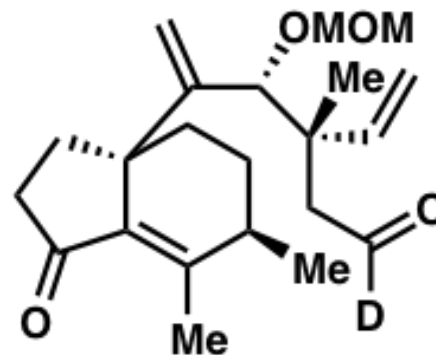
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Data File Name	/ Volumes/ nmrdata-1/ fscha/ nmr/ FES-1-152-2-data/ 2/ fid
Title	FES-1-152-2-data.2.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl <sub>3</sub>
Temperature	295.0
Pulse Sequence	zg30
Number of Scans	16
Receiver Gain	112.8
Relaxation Delay	1.0000
Pulse Width	11.7000
Acquisition Time	4.0894
Acquisition Date	2017-12-04T21:38:18
Spectrometer Frequency	400.13
Spectral Width	8012.8
Lowest Frequency	-1559.8
Nucleus	<sup>1</sup> H
Acquired Size	32768
Spectral Size	65536



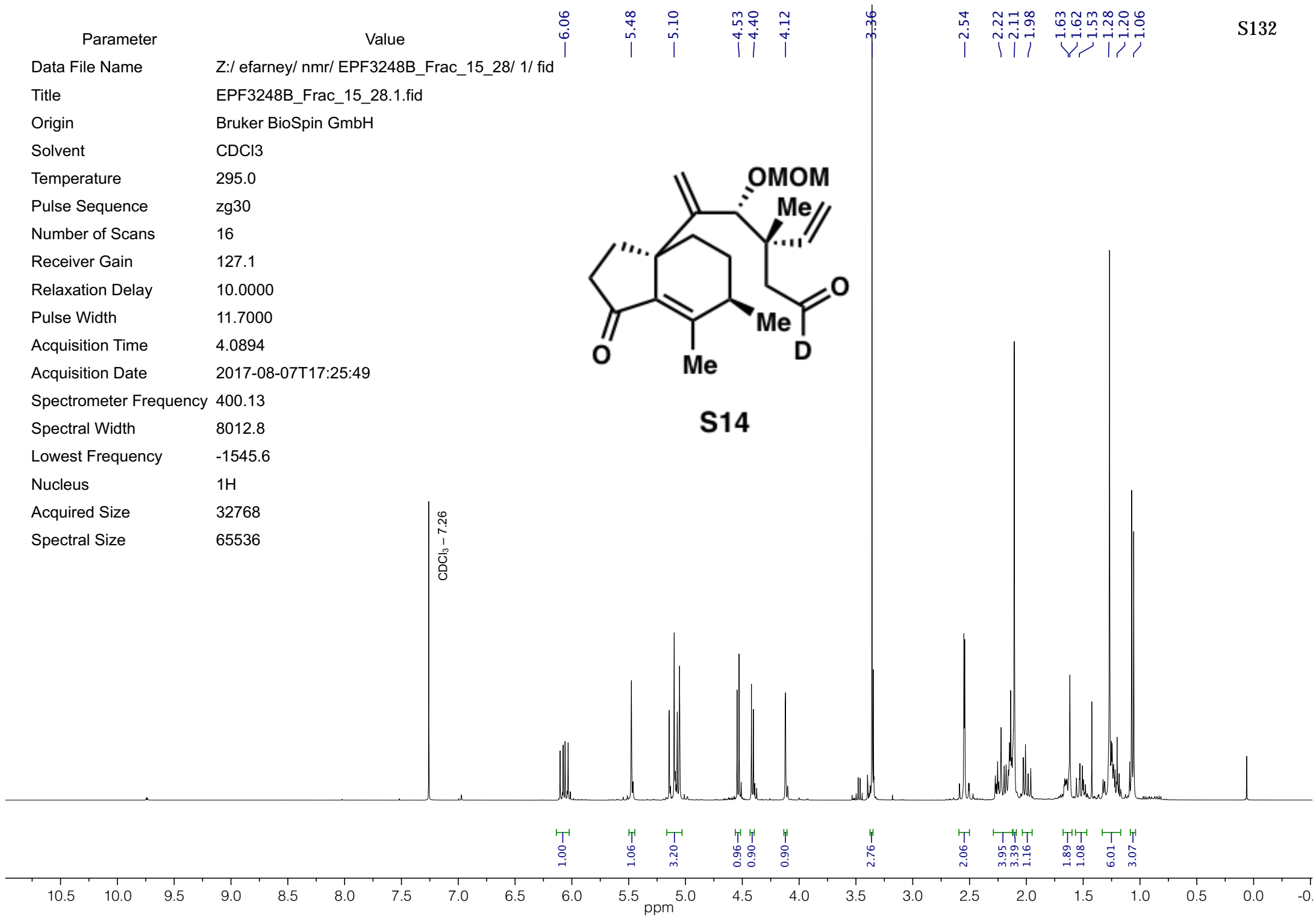
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Data File Name	/ Volumes/ nmrdata-1/ fscha/ nmr/ FES-1-152-2-data/ 1/ fid
Title	FES-1-152-2-data.1.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl <sub>3</sub>
Temperature	294.9
Pulse Sequence	zgpg30
Number of Scans	512
Receiver Gain	78.7
Relaxation Delay	1.0000
Pulse Width	10.0000
Acquisition Time	1.3631
Acquisition Date	2017-12-04T21:36:26
Spectrometer Frequency	100.62
Spectral Width	24038.5
Lowest Frequency	-1963.5
Nucleus	<sup>13</sup> C
Acquired Size	32768
Spectral Size	65536



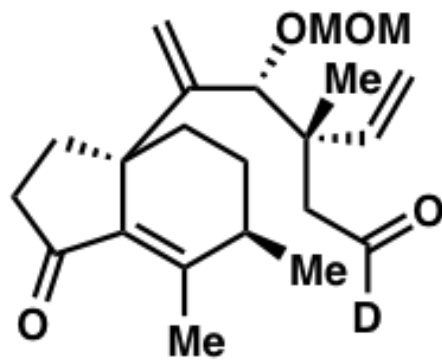
Parameter	Value
Data File Name	Z:/ efarney/ nmr/ EPF3248B_Frac_15_28/ 1/ fid
Title	EPF3248B_Frac_15_28.1.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl <sub>3</sub>
Temperature	295.0
Pulse Sequence	zg30
Number of Scans	16
Receiver Gain	127.1
Relaxation Delay	10.0000
Pulse Width	11.7000
Acquisition Time	4.0894
Acquisition Date	2017-08-07T17:25:49
Spectrometer Frequency	400.13
Spectral Width	8012.8
Lowest Frequency	-1545.6
Nucleus	<sup>1</sup> H
Acquired Size	32768
Spectral Size	65536



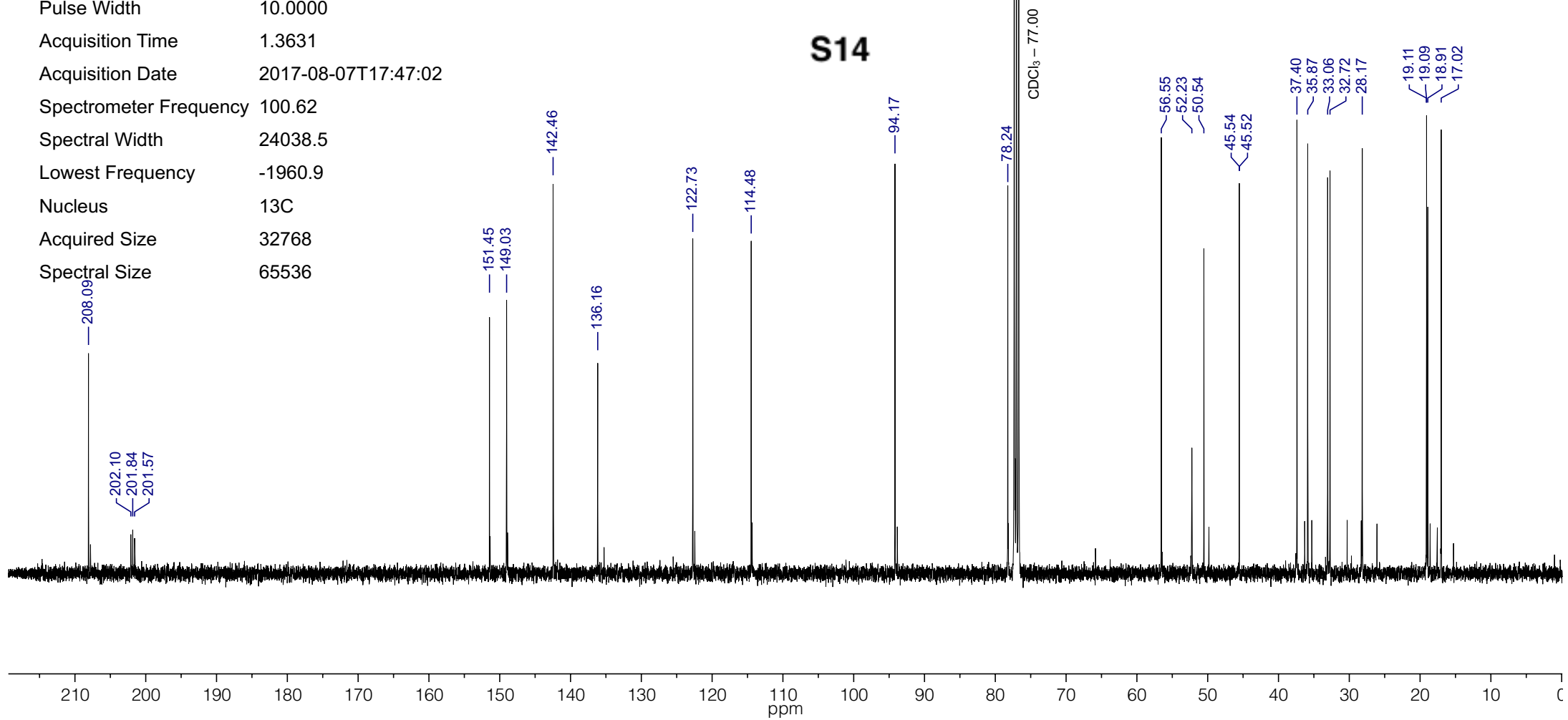
S14



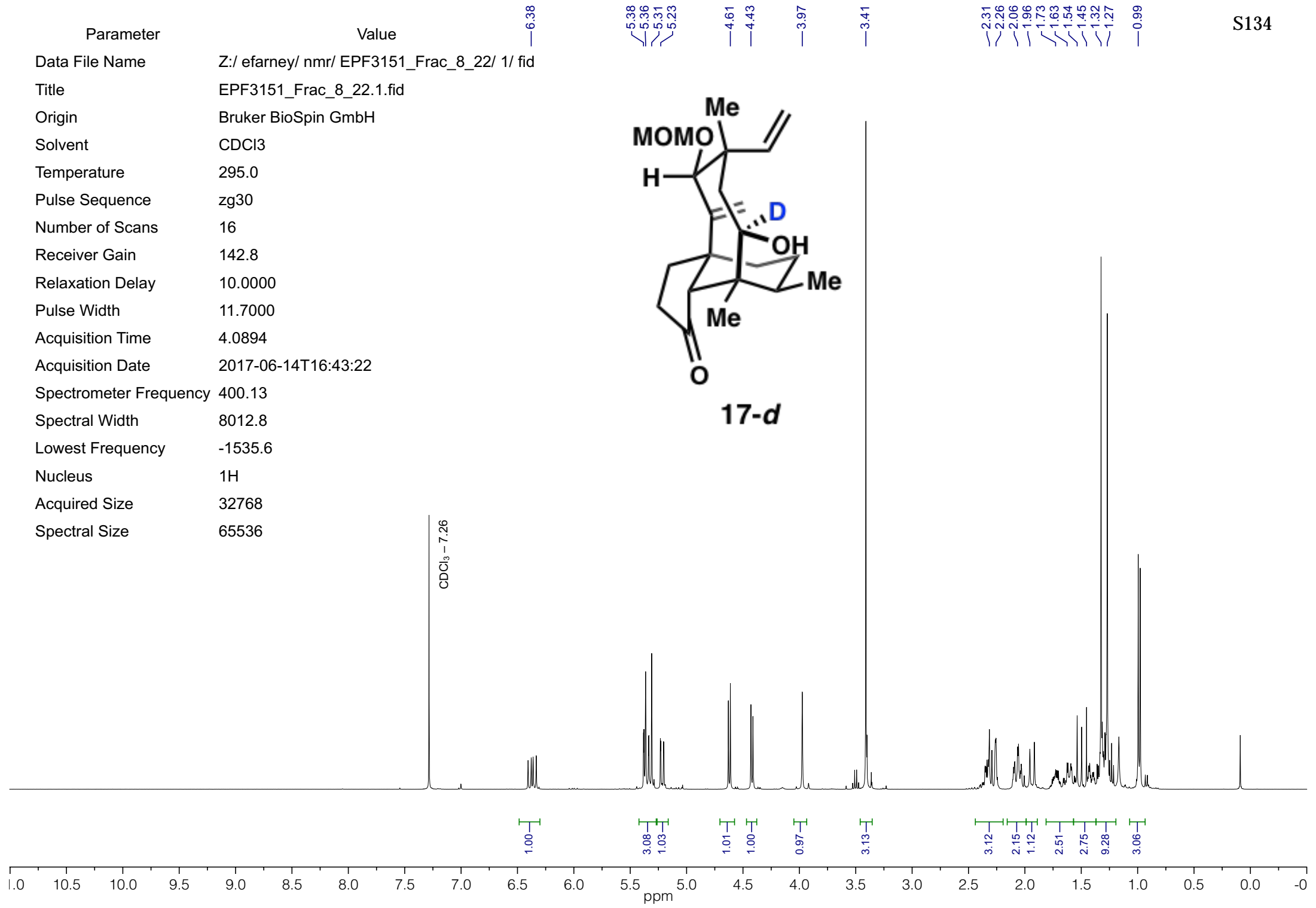
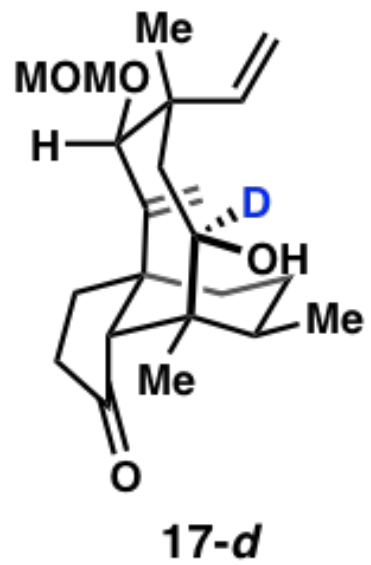
Parameter	Value
Data File Name	Z:/ efarney/ nmr/ EPF3248B_Frac_15_28/ 2/ fid
Title	EPF3248B_Frac_15_28.2.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl <sub>3</sub>
Temperature	295.0
Pulse Sequence	zgpg30
Number of Scans	512
Receiver Gain	64.2
Relaxation Delay	1.0000
Pulse Width	10.0000
Acquisition Time	1.3631
Acquisition Date	2017-08-07T17:47:02
Spectrometer Frequency	100.62
Spectral Width	24038.5
Lowest Frequency	-1960.9
Nucleus	<sup>13</sup> C
Acquired Size	32768
Spectral Size	65536



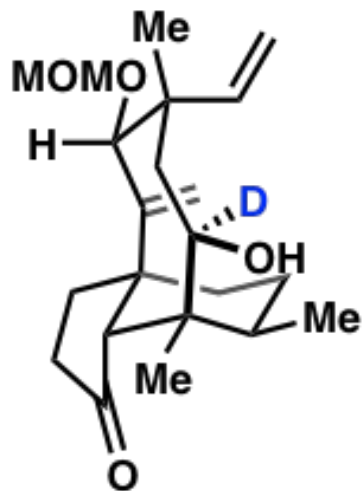
S14



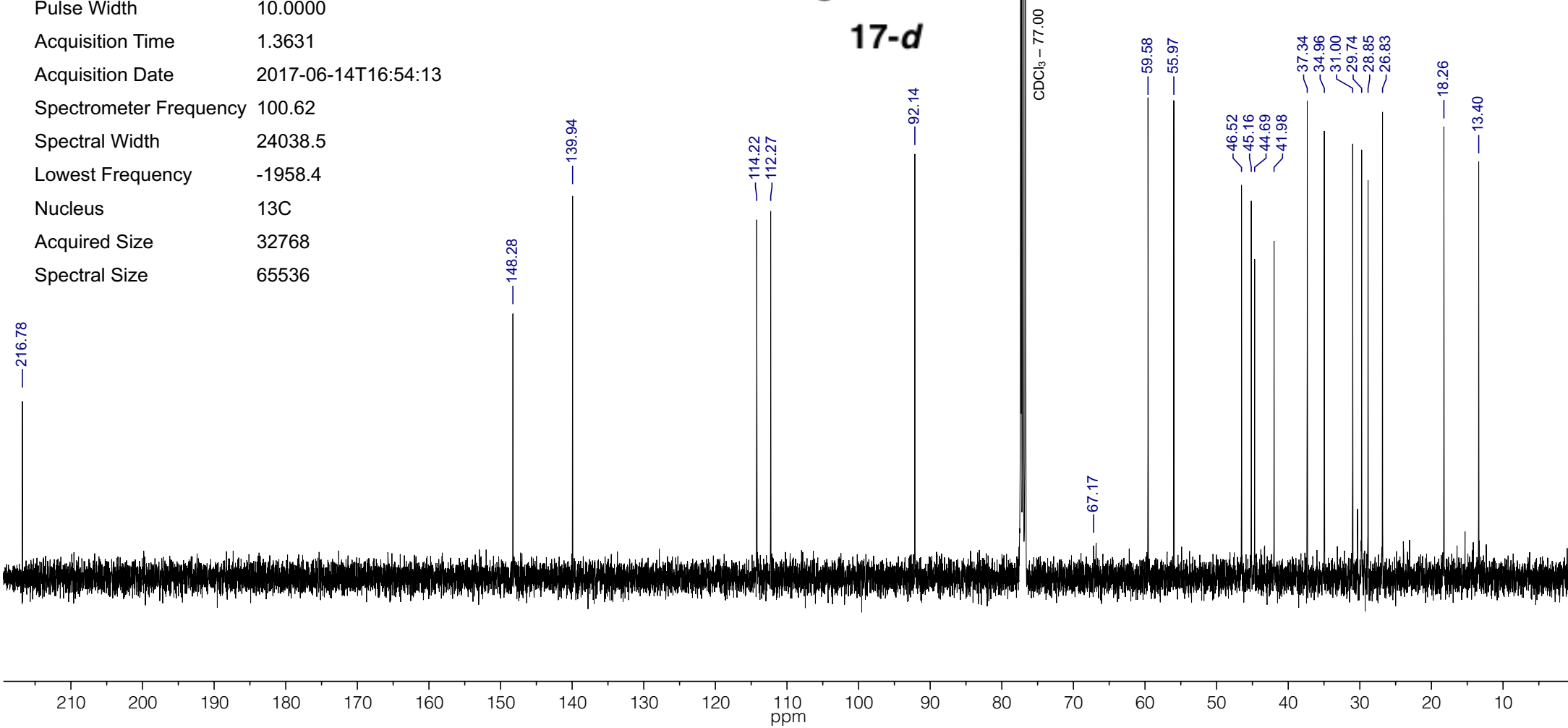
Parameter	Value
Data File Name	Z:/ efarney/ nmr/ EPF3151_Frac_8_22/ 1/ fid
Title	EPF3151_Frac_8_22.1.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	295.0
Pulse Sequence	zg30
Number of Scans	16
Receiver Gain	142.8
Relaxation Delay	10.0000
Pulse Width	11.7000
Acquisition Time	4.0894
Acquisition Date	2017-06-14T16:43:22
Spectrometer Frequency	400.13
Spectral Width	8012.8
Lowest Frequency	-1535.6
Nucleus	1H
Acquired Size	32768
Spectral Size	65536



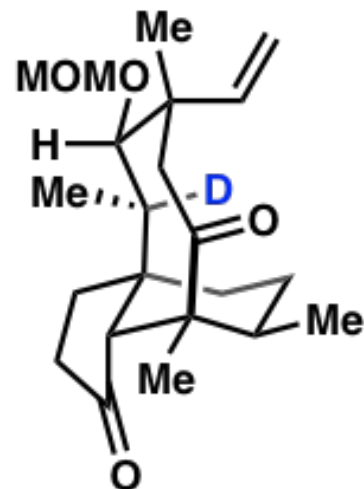
Parameter	Value
Data File Name	Z:/ efarney/ nmr/ EPF3151_Frac_8_22/ 2/ fid
Title	EPF3151_Frac_8_22.2.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl <sub>3</sub>
Temperature	294.9
Pulse Sequence	zgpg30
Number of Scans	256
Receiver Gain	64.2
Relaxation Delay	1.0000
Pulse Width	10.0000
Acquisition Time	1.3631
Acquisition Date	2017-06-14T16:54:13
Spectrometer Frequency	100.62
Spectral Width	24038.5
Lowest Frequency	-1958.4
Nucleus	<sup>13</sup> C
Acquired Size	32768
Spectral Size	65536



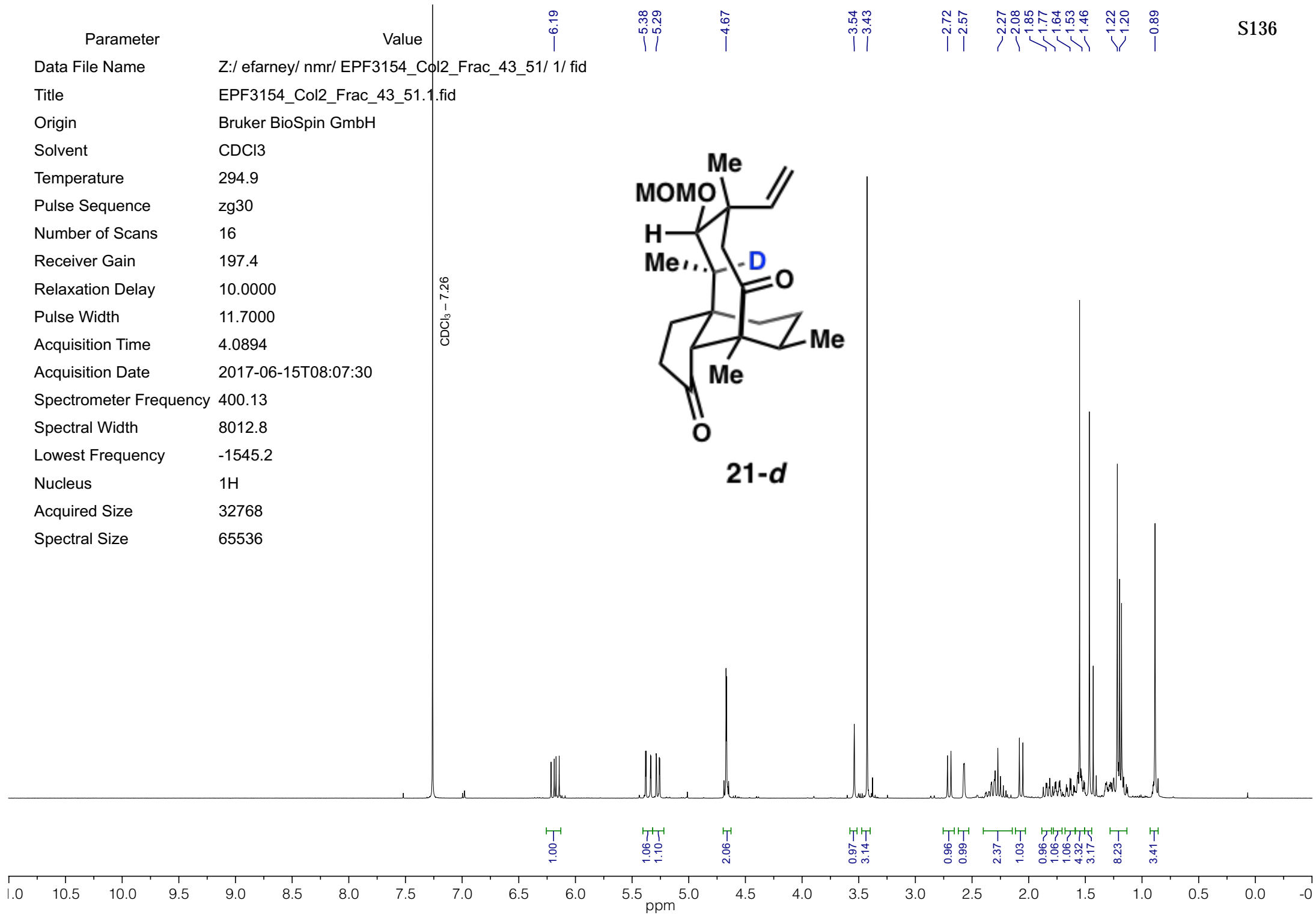
17-d



Parameter	Value
Data File Name	Z:/ efarney/ nmr/ EPF3154_Col2_Frac_43_51/ 1/ fid
Title	EPF3154_Col2_Frac_43_51.1.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl <sub>3</sub>
Temperature	294.9
Pulse Sequence	zg30
Number of Scans	16
Receiver Gain	197.4
Relaxation Delay	10.0000
Pulse Width	11.7000
Acquisition Time	4.0894
Acquisition Date	2017-06-15T08:07:30
Spectrometer Frequency	400.13
Spectral Width	8012.8
Lowest Frequency	-1545.2
Nucleus	<sup>1</sup> H
Acquired Size	32768
Spectral Size	65536

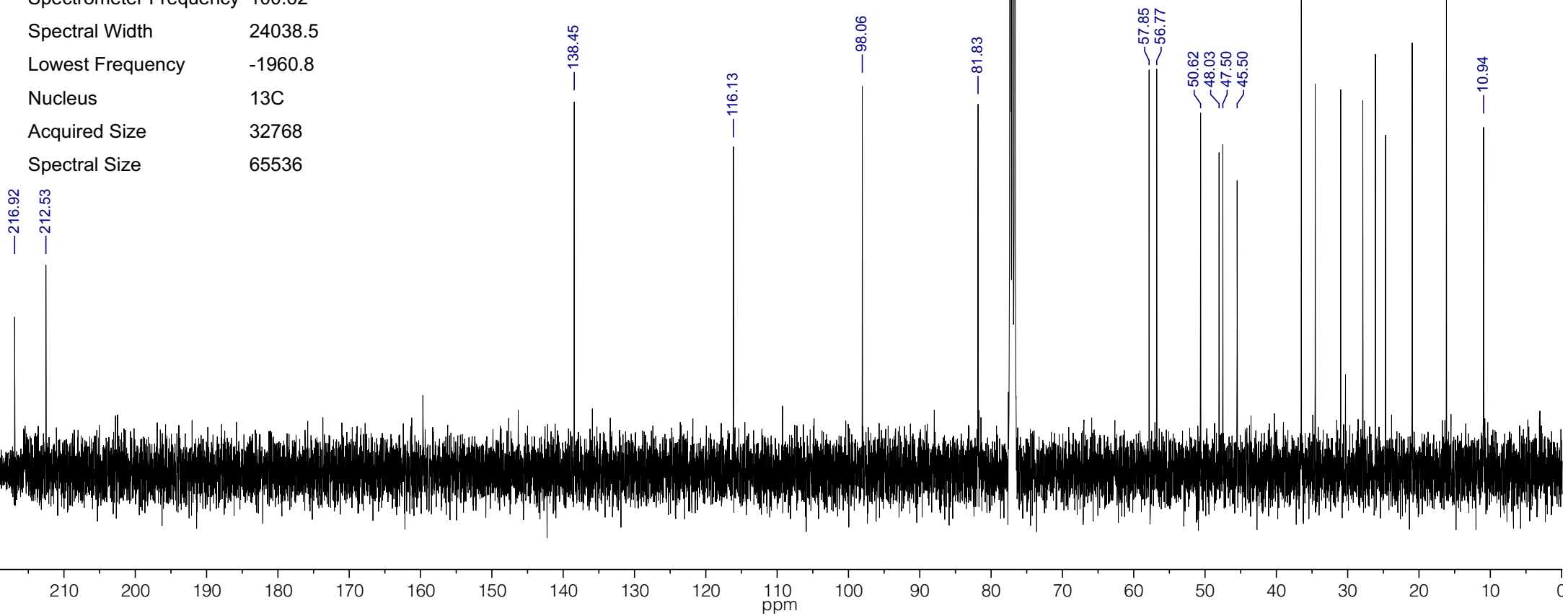
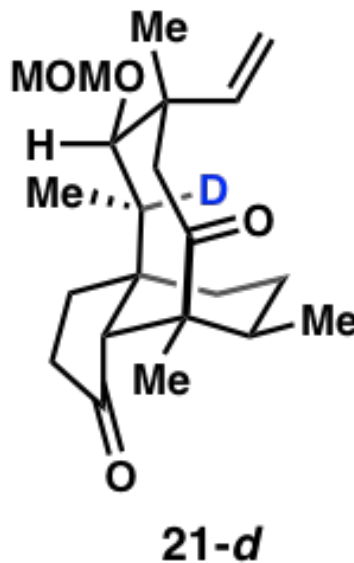
CDCl<sub>3</sub> - 7.26

21-d





Parameter	Value
Data File Name	Z:/ efarney/ nmr/ EPF3154_Col2_Frac_43_51/ 2/ fid
Title	EPF3154_Col2_Frac_43_51.2.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	294.9
Pulse Sequence	zgpg30
Number of Scans	822
Receiver Gain	72.0
Relaxation Delay	1.0000
Pulse Width	10.0000
Acquisition Time	1.3631
Acquisition Date	2017-06-15T08:41:14
Spectrometer Frequency	100.62
Spectral Width	24038.5
Lowest Frequency	-1960.8
Nucleus	13C
Acquired Size	32768
Spectral Size	65536



Parameter Value

Data File Name Z:/ efarney/ nmr/ EPF3070\_Col2\_Frac\_39\_50\_Char/ 1/ fid

Title EPF3070\_Col2\_Frac\_39\_50\_Char.1.fid

Origin Bruker BioSpin GmbH

Solvent CDCl3

Temperature 294.9

Pulse Sequence zg30

Number of Scans 16

Receiver Gain 197.4

Relaxation Delay 10.0000

Pulse Width 11.7000

Acquisition Time 4.0894

Acquisition Date 2017-04-26T21:13:58

Spectrometer Frequency 400.13

Spectral Width 8012.8

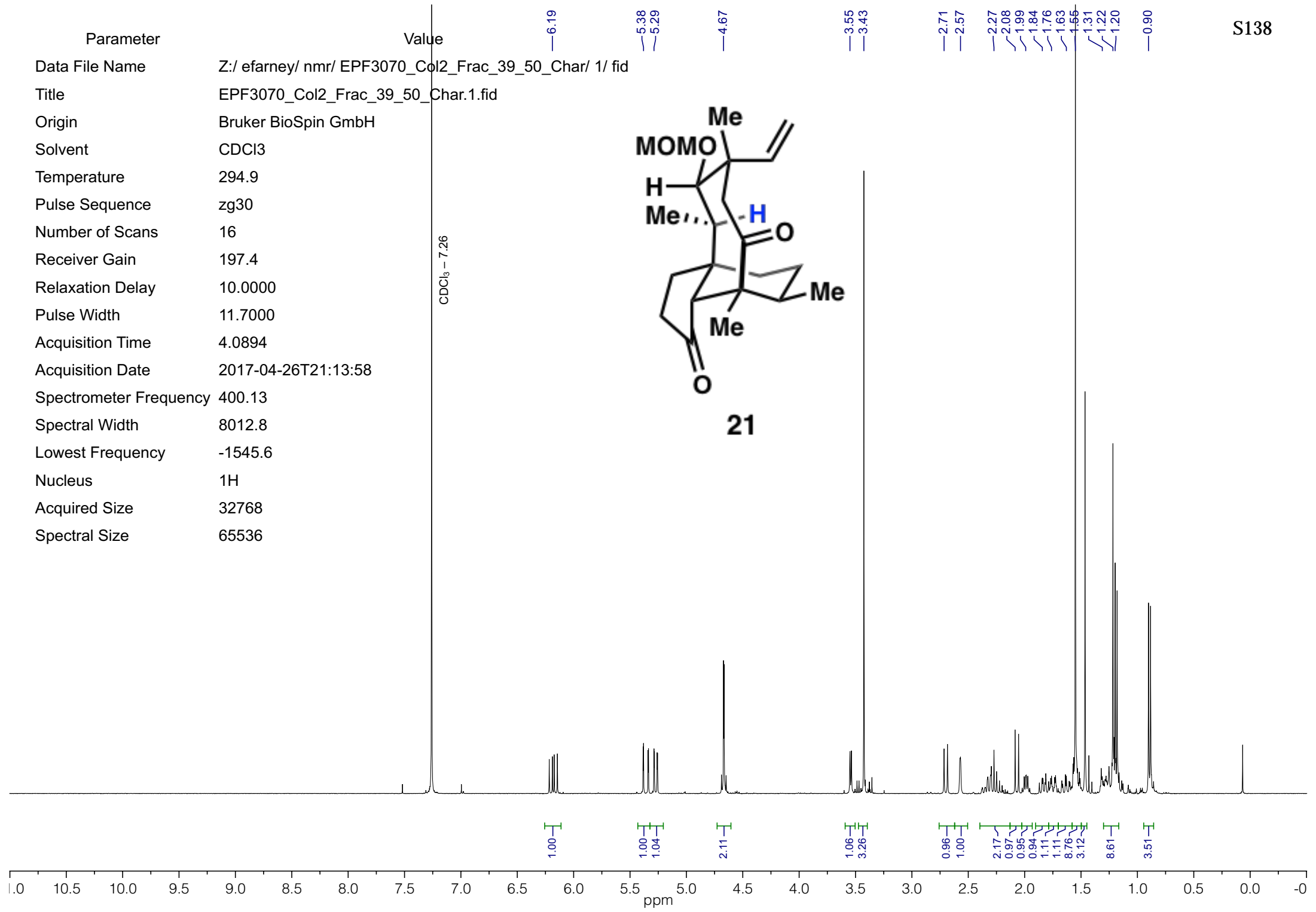
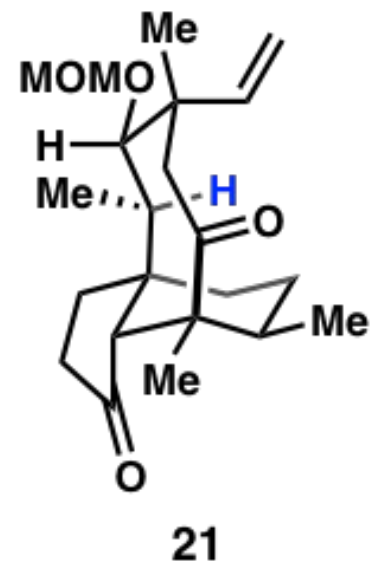
Lowest Frequency -1545.6

Nucleus 1H

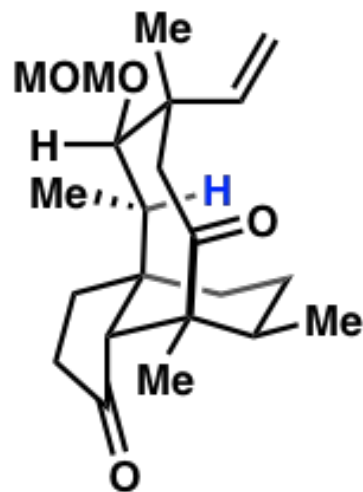
Acquired Size 32768

Spectral Size 65536

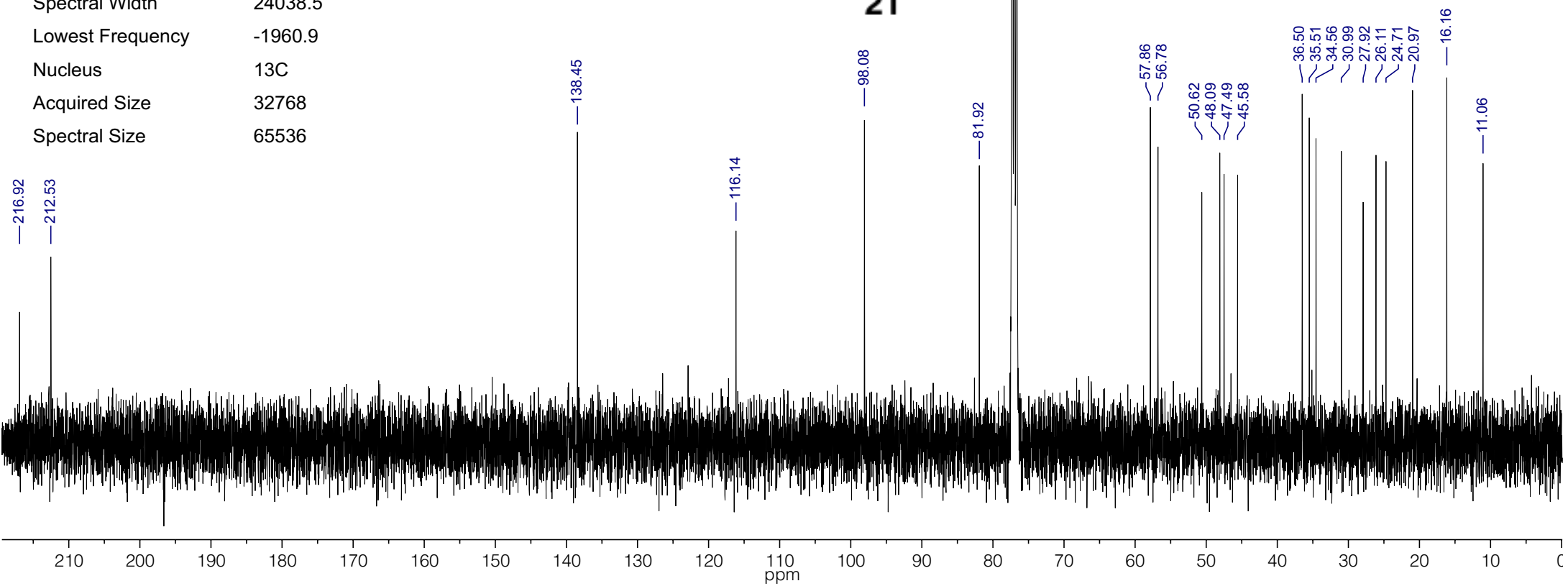
CDCl<sub>3</sub> - 7.26

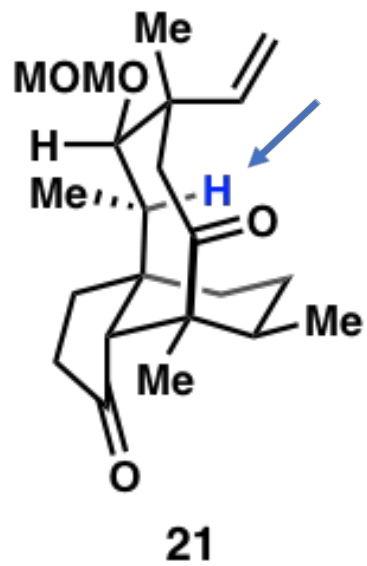


Parameter	Value
Data File Name	Z:/ efarney/ nmr/ EPF3070_Col2_Frac_39_50_Char/ 2/ fid
Title	EPF3070_Col2_Frac_39_50_Char.2.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl <sub>3</sub>
Temperature	295.0
Pulse Sequence	zgpg30
Number of Scans	1024
Receiver Gain	72.0
Relaxation Delay	2.0000
Pulse Width	10.0000
Acquisition Time	1.3631
Acquisition Date	2017-04-26T22:13:04
Spectrometer Frequency	100.62
Spectral Width	24038.5
Lowest Frequency	-1960.9
Nucleus	<sup>13</sup> C
Acquired Size	32768
Spectral Size	65536

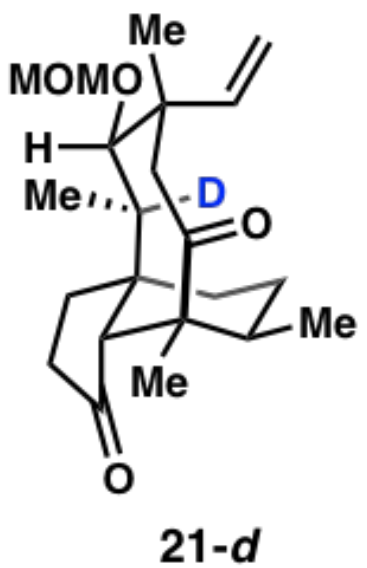


21

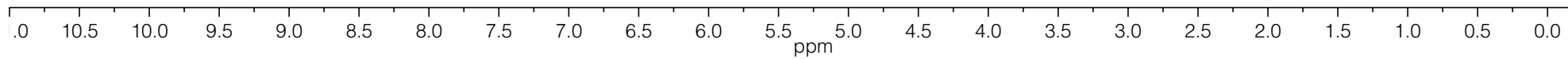
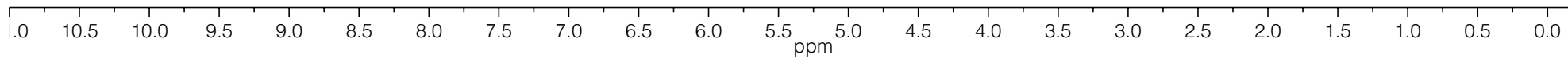


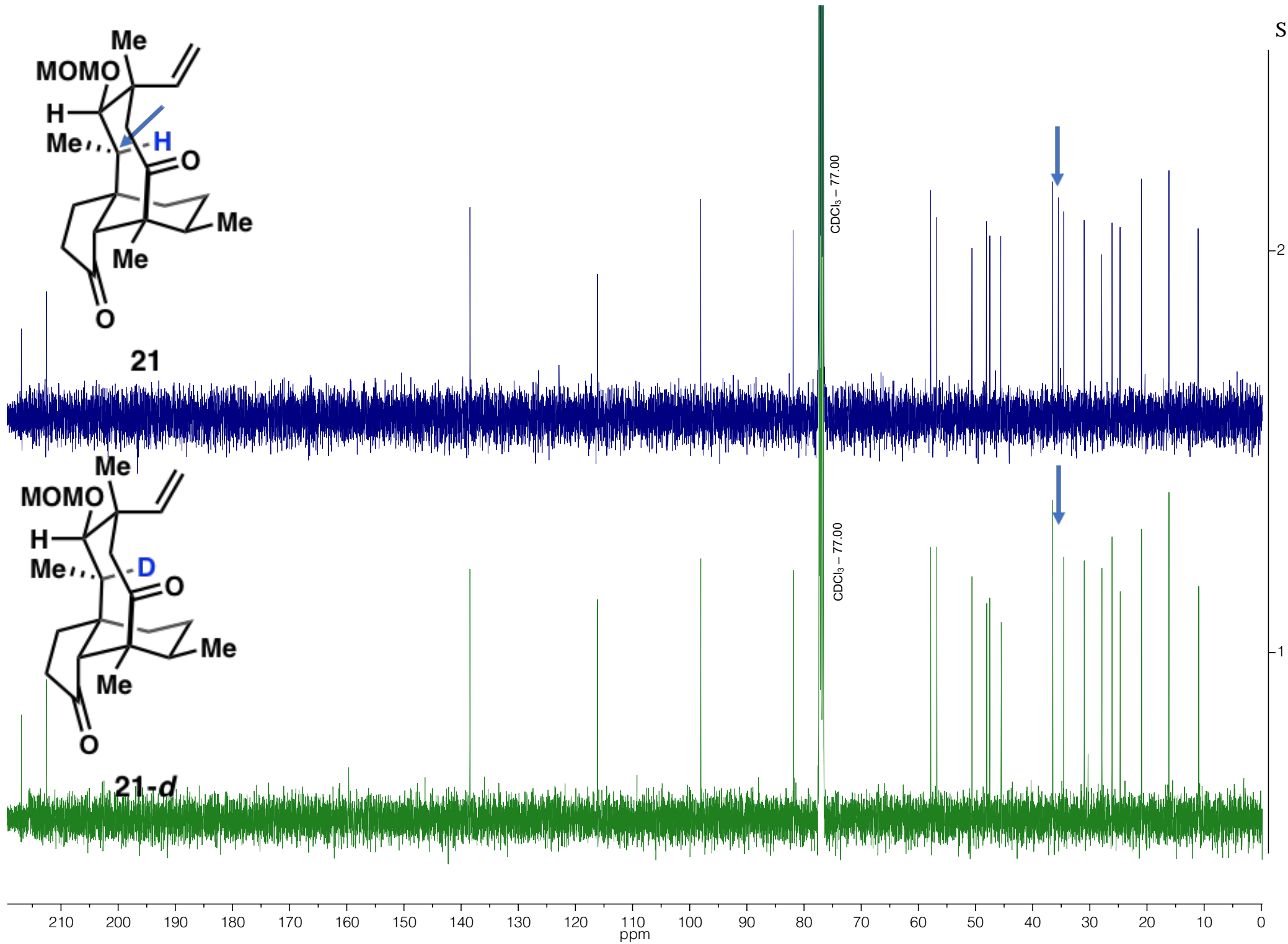
CDCl<sub>3</sub> - 7.26

-2

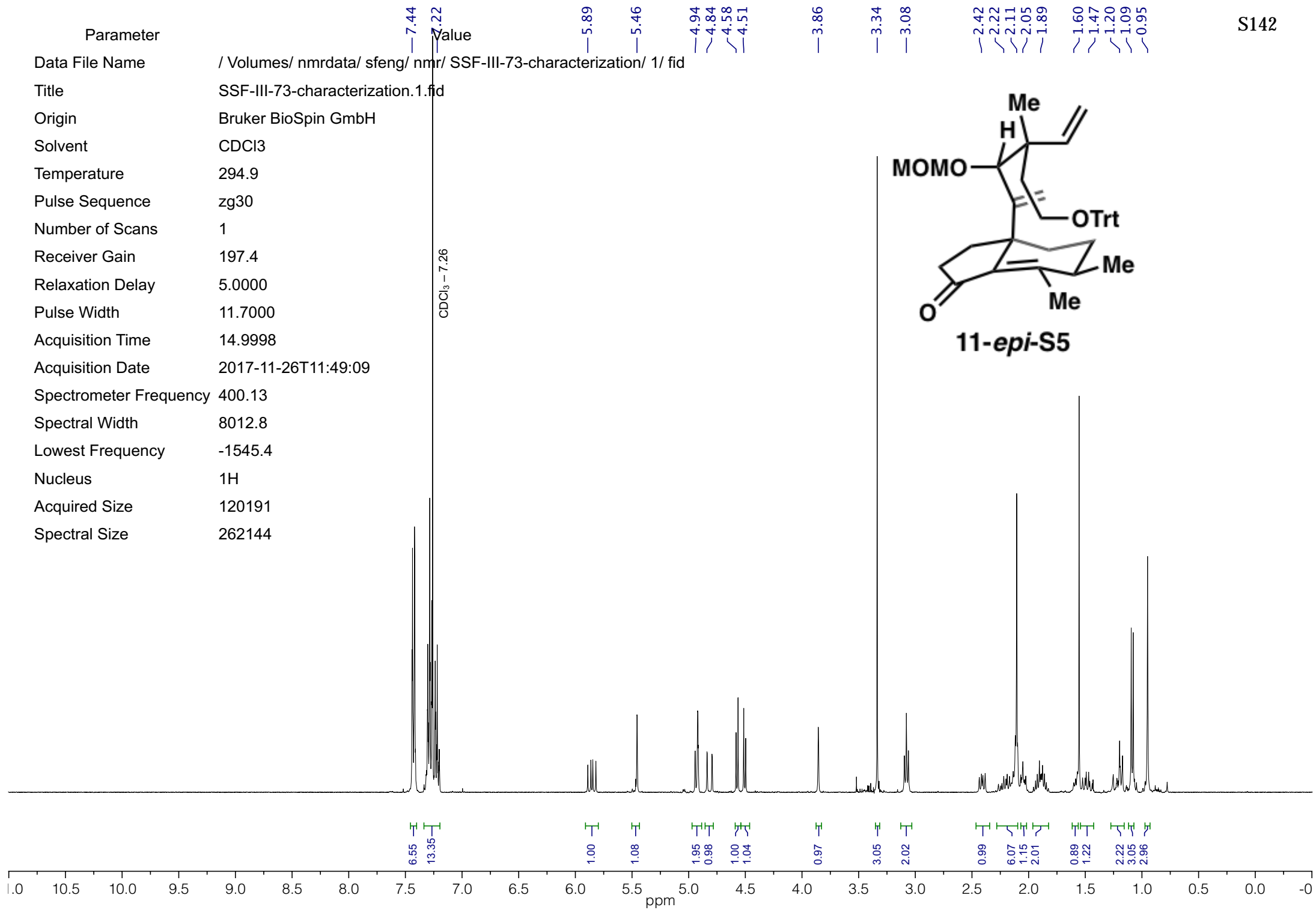
CDCl<sub>3</sub> - 7.26

-1

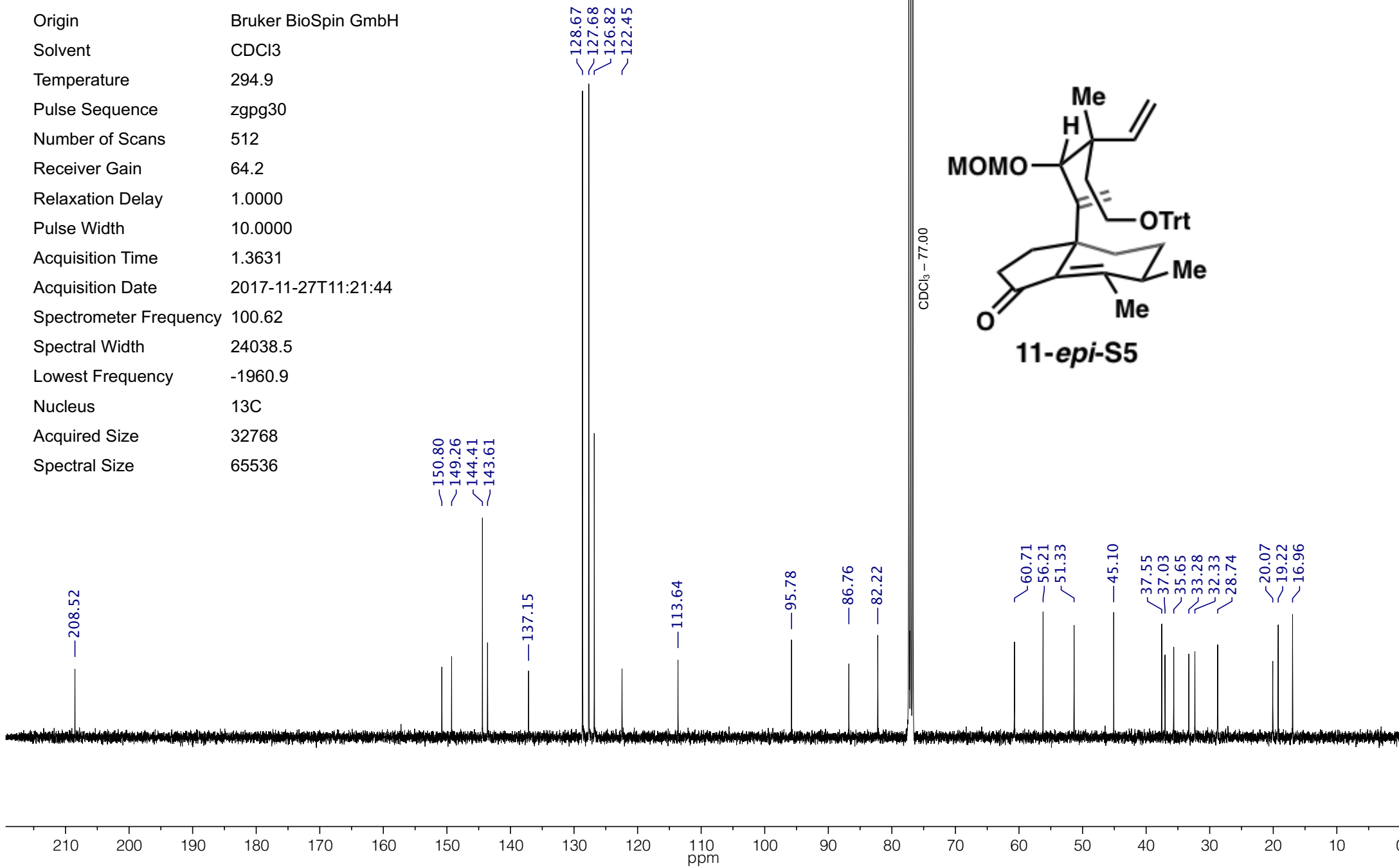




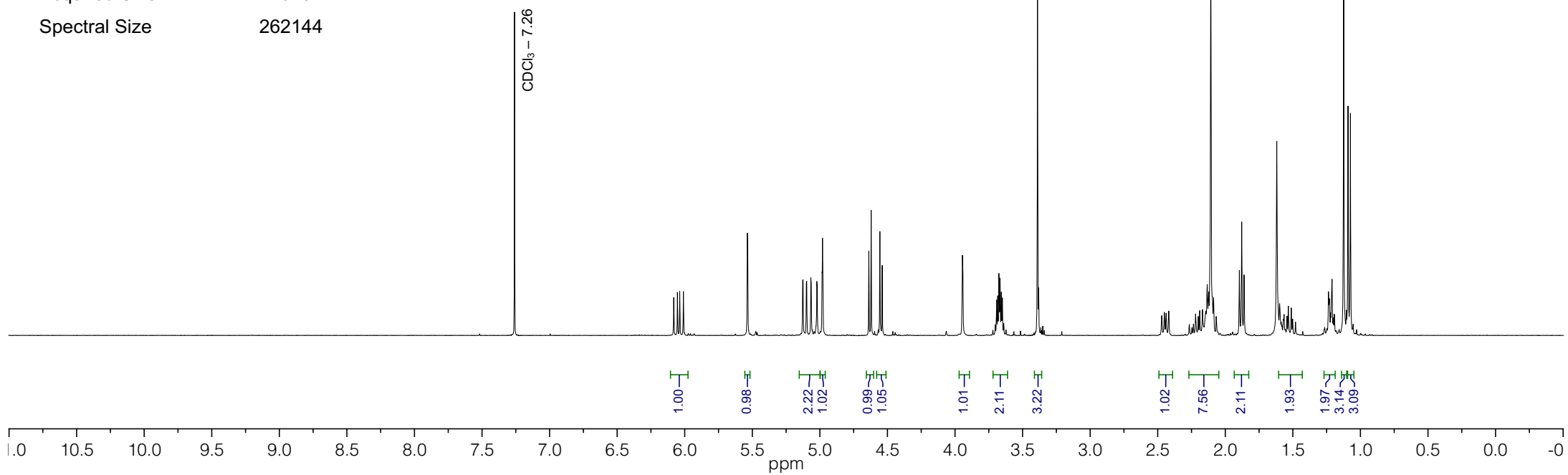
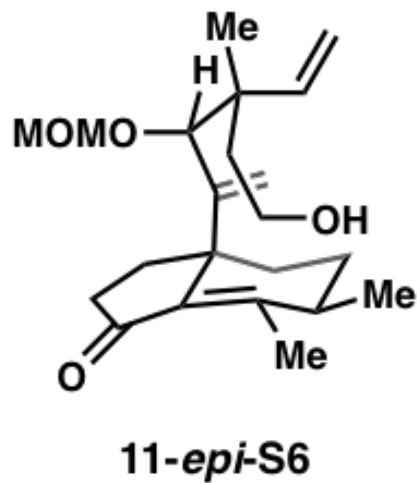
Parameter	Value
Data File Name	/Volumes/nmrdata/sfeng/nmr/SSF-III-73-characterization/1/fid
Title	SSF-III-73-characterization.1.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl <sub>3</sub>
Temperature	294.9
Pulse Sequence	zg30
Number of Scans	1
Receiver Gain	197.4
Relaxation Delay	5.0000
Pulse Width	11.7000
Acquisition Time	14.9998
Acquisition Date	2017-11-26T11:49:09
Spectrometer Frequency	400.13
Spectral Width	8012.8
Lowest Frequency	-1545.4
Nucleus	<sup>1</sup> H
Acquired Size	120191
Spectral Size	262144



Parameter	Value
Data File Name	/ Volumes/ nmrdata/ sfeng/ nmr/ SSF-III-73-characterization2/ 6/ fid
Title	SSF-III-73-characterization2.6.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCI3
Temperature	294.9
Pulse Sequence	zgpg30
Number of Scans	512
Receiver Gain	64.2
Relaxation Delay	1.0000
Pulse Width	10.0000
Acquisition Time	1.3631
Acquisition Date	2017-11-27T11:21:44
Spectrometer Frequency	100.62
Spectral Width	24038.5
Lowest Frequency	-1960.9
Nucleus	13C
Acquired Size	32768
Spectral Size	65536

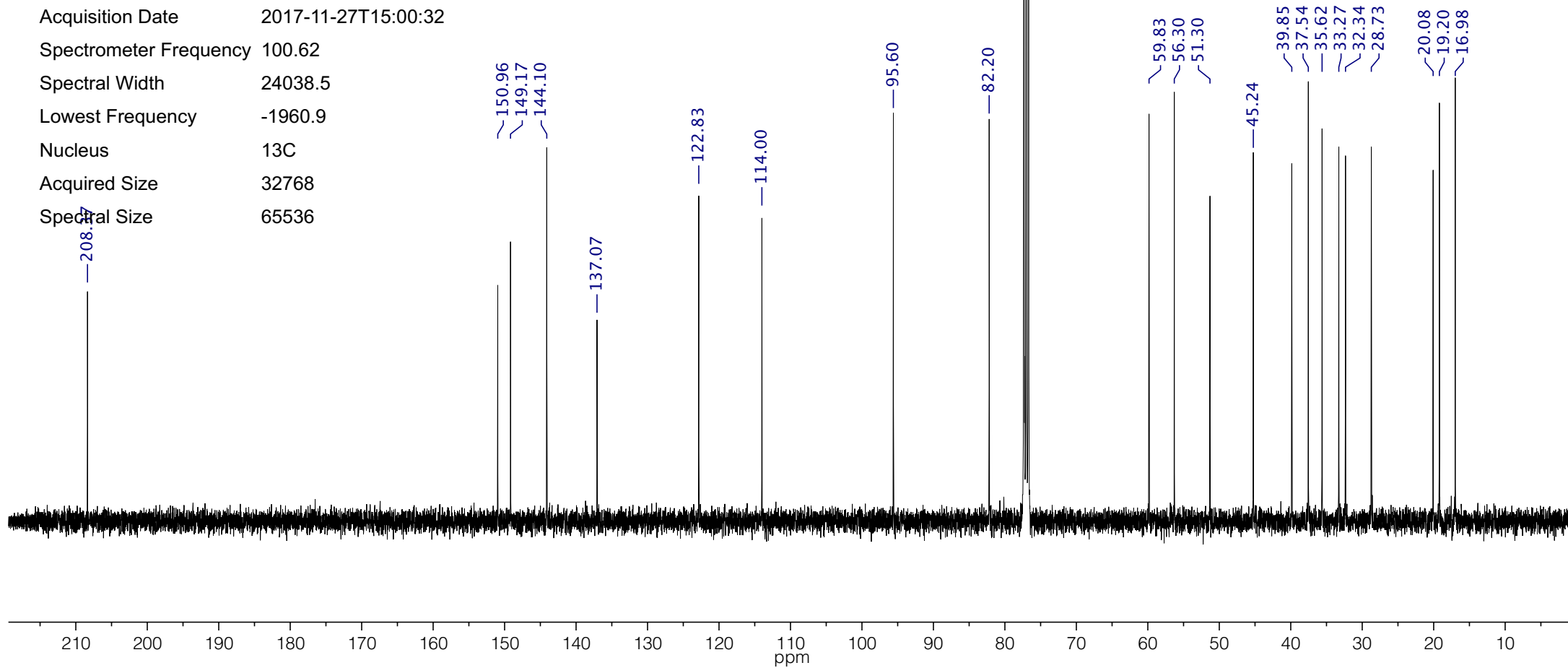
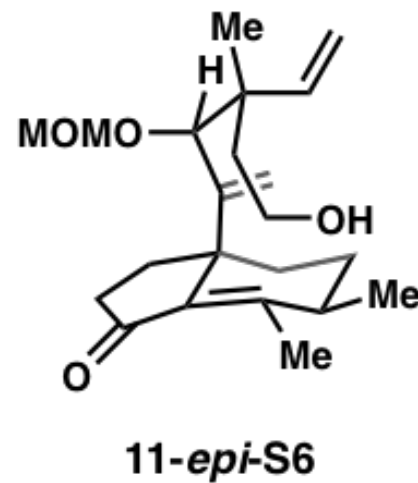


Parameter	Value
Data File Name	/ Volumes/ nmrdata/ sfeng/ nmr/ SSF-III-76-characterization/ 2/ fid
Title	SSF-III-76-characterization.2.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl <sub>3</sub>
Temperature	295.0
Pulse Sequence	zg30
Number of Scans	1
Receiver Gain	156.2
Relaxation Delay	5.0000
Pulse Width	11.7000
Acquisition Time	14.9998
Acquisition Date	2017-11-27T15:02:22
Spectrometer Frequency	400.13
Spectral Width	8012.8
Lowest Frequency	-1545.4
Nucleus	<sup>1</sup> H
Acquired Size	120191
Spectral Size	262144

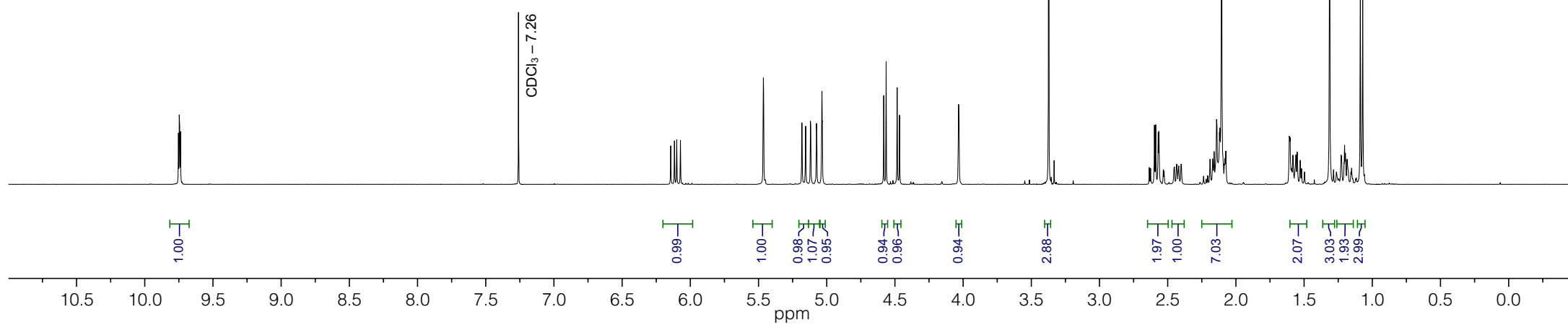
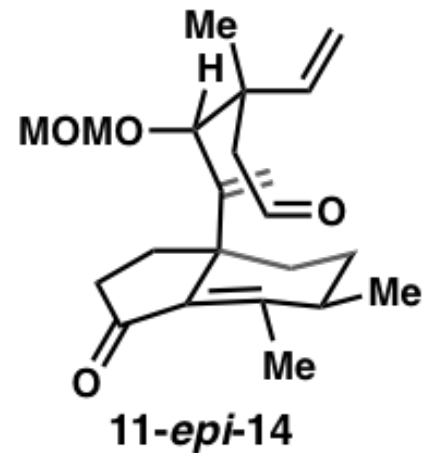




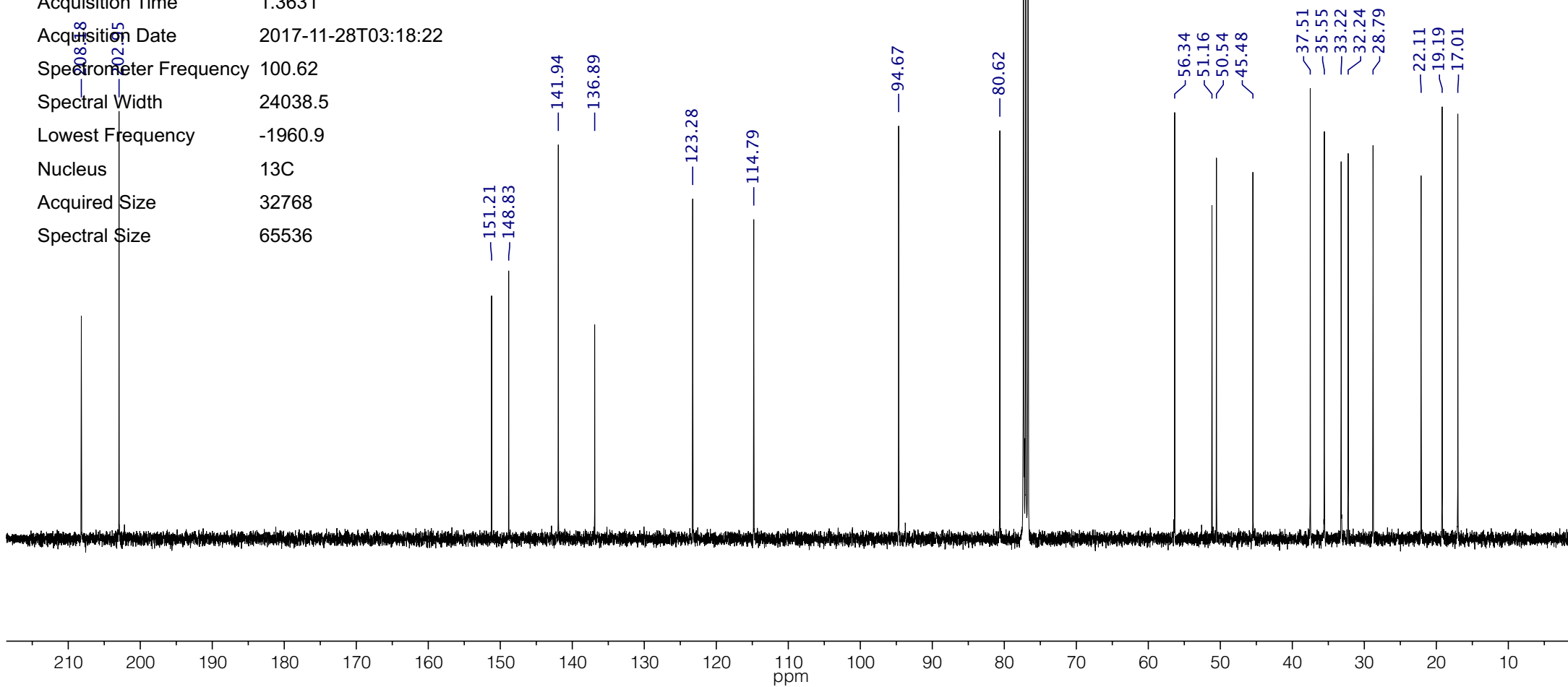
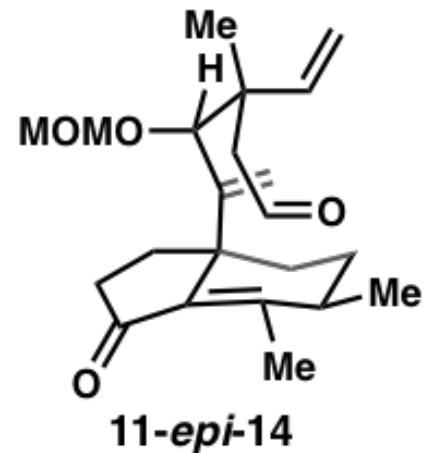
Parameter	Value
Data File Name	/ Volumes/ nmrdata/ sfeng/ nmr/ SSF-III-76-characterization/ 1/ fid
Title	SSF-III-76-characterization.1.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl <sub>3</sub>
Temperature	294.9
Pulse Sequence	zgpg30
Number of Scans	512
Receiver Gain	72.0
Relaxation Delay	1.0000
Pulse Width	10.0000
Acquisition Time	1.3631
Acquisition Date	2017-11-27T15:00:32
Spectrometer Frequency	100.62
Spectral Width	24038.5
Lowest Frequency	-1960.9
Nucleus	<sup>13</sup> C
Acquired Size	32768
Spectral Size	65536



Parameter	Value
Data File Name	/Volumes/nmrdata/sfeng/nmr/SSF-III-79-characterization/2/fid
Title	SSF-III-79-characterization.2.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl <sub>3</sub>
Temperature	294.9
Pulse Sequence	zg30
Number of Scans	1
Receiver Gain	112.8
Relaxation Delay	5.0000
Pulse Width	11.7000
Acquisition Time	14.9998
Acquisition Date	2017-11-28T03:20:12
Spectrometer Frequency	400.13
Spectral Width	8012.8
Lowest Frequency	-1545.3
Nucleus	<sup>1</sup> H
Acquired Size	120191
Spectral Size	262144

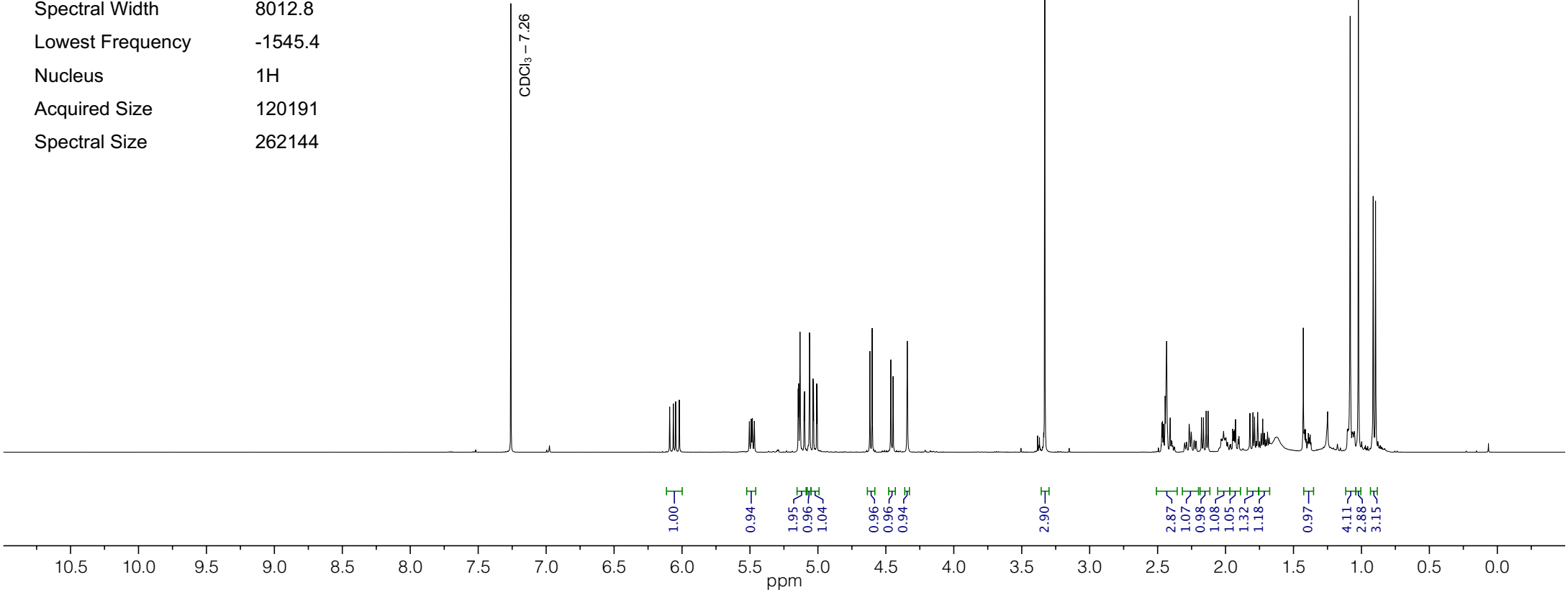
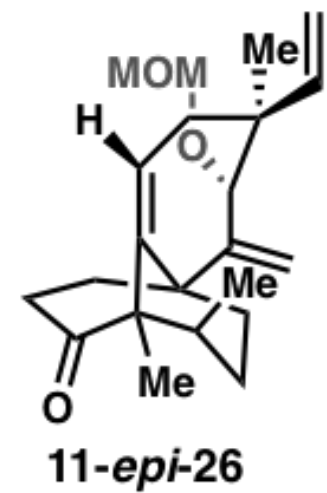


Parameter	Value
Data File Name	/ Volumes/ nmrdata/ sfeng/ nmr/ SSF-III-79-characterization/ 1/ fid
Title	SSF-III-79-characterization.1.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl <sub>3</sub>
Temperature	295.0
Pulse Sequence	zgpg30
Number of Scans	512
Receiver Gain	87.8
Relaxation Delay	1.0000
Pulse Width	10.0000
Acquisition Time	1.3631
Acquisition Date	2017-11-28T03:18:22
Spectrometer Frequency	100.62
Spectral Width	24038.5
Lowest Frequency	-1960.9
Nucleus	<sup>13</sup> C
Acquired Size	32768
Spectral Size	65536

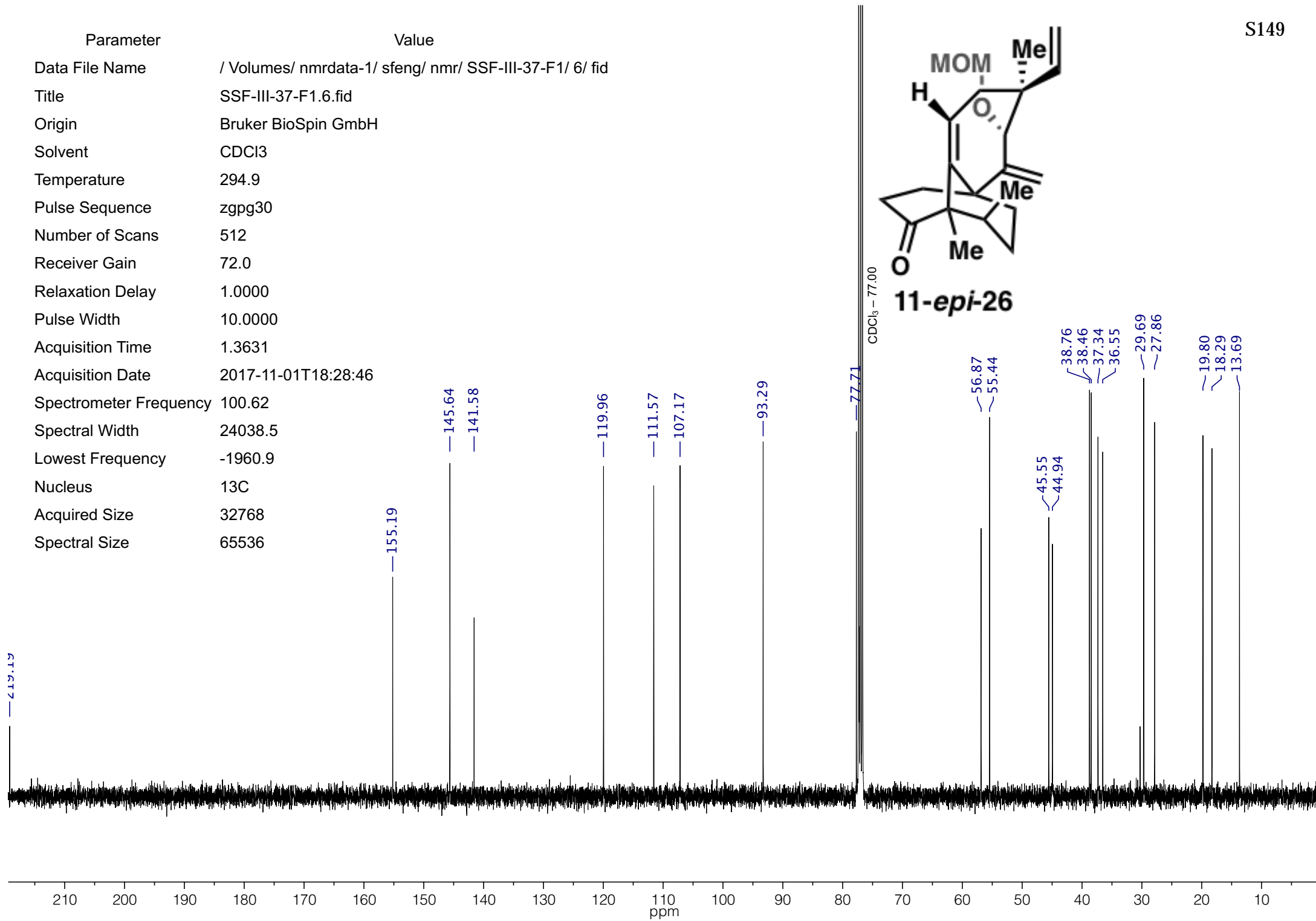
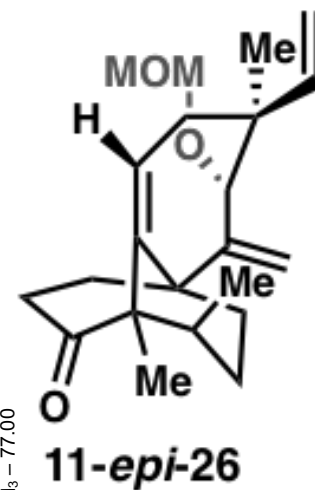


Parameter	Value
Data File Name	/ Volumes/ nmrdata-1/ sfeng/ nmr/ SSF-III-37-F1/ 1/ fid
Title	SSF-III-37-F1.1.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl <sub>3</sub>
Temperature	294.9
Pulse Sequence	zg30
Number of Scans	16
Receiver Gain	142.8
Relaxation Delay	5.0000
Pulse Width	11.7000
Acquisition Time	14.9998
Acquisition Date	2017-10-31T22:42:24
Spectrometer Frequency	400.13
Spectral Width	8012.8
Lowest Frequency	-1545.4
Nucleus	<sup>1</sup> H
Acquired Size	120191
Spectral Size	262144

6.06  
5.49  
5.13  
5.10  
5.06  
5.03  
4.60  
4.46  
4.34  
3.33  
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2.16  
2.01  
1.93  
1.40  
1.08  
1.07  
1.02  
0.91

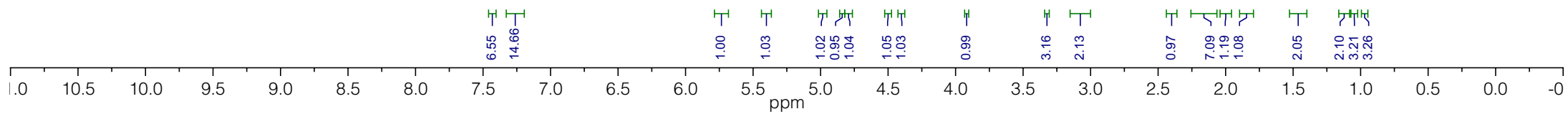
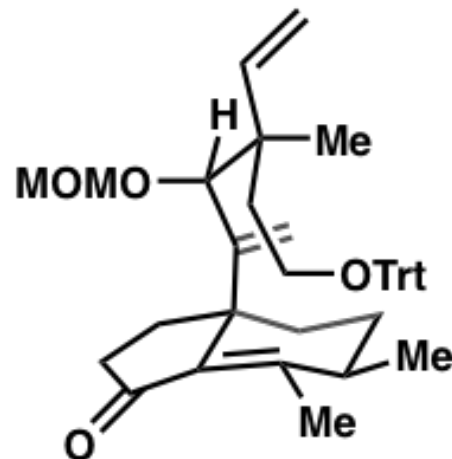


Parameter	Value
Data File Name	/ Volumes/ nmrdata-1/ sfeng/ nmr/ SSF-III-37-F1/ 6/ fid
Title	SSF-III-37-F1.6.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl <sub>3</sub>
Temperature	294.9
Pulse Sequence	zgpg30
Number of Scans	512
Receiver Gain	72.0
Relaxation Delay	1.0000
Pulse Width	10.0000
Acquisition Time	1.3631
Acquisition Date	2017-11-01T18:28:46
Spectrometer Frequency	100.62
Spectral Width	24038.5
Lowest Frequency	-1960.9
Nucleus	<sup>13</sup> C
Acquired Size	32768
Spectral Size	65536

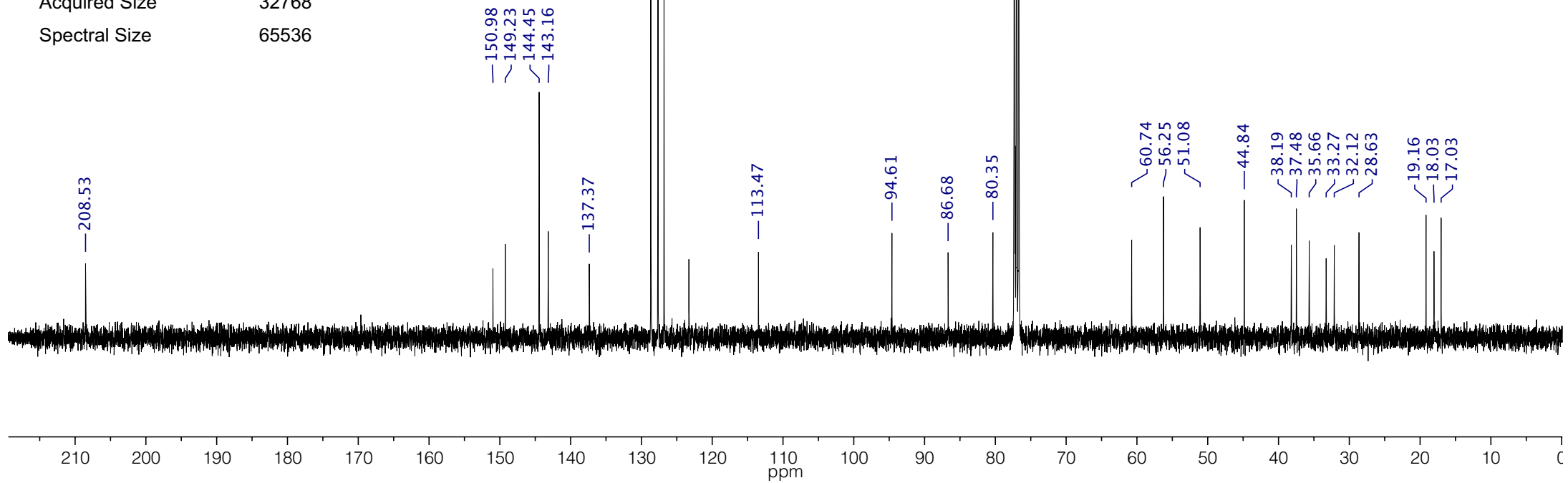


Parameter	Value
Data File Name	/ Volumes/ nmrdata-4/ sfeng/ nmr/ SSF-III-67-flashed-characterization/ 1/ fid
Title	SSF-III-67-flashed-characterization.1.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl <sub>3</sub>
Temperature	294.9
Pulse Sequence	zg30
Number of Scans	1
Receiver Gain	197.4
Relaxation Delay	5.0000
Pulse Width	11.7000
Acquisition Time	14.9998
Acquisition Date	2017-11-25T13:45:37
Spectrometer Frequency	400.13
Spectral Width	8012.8
Lowest Frequency	-1545.4
Nucleus	<sup>1</sup> H
Acquired Size	120191
Spectral Size	262144

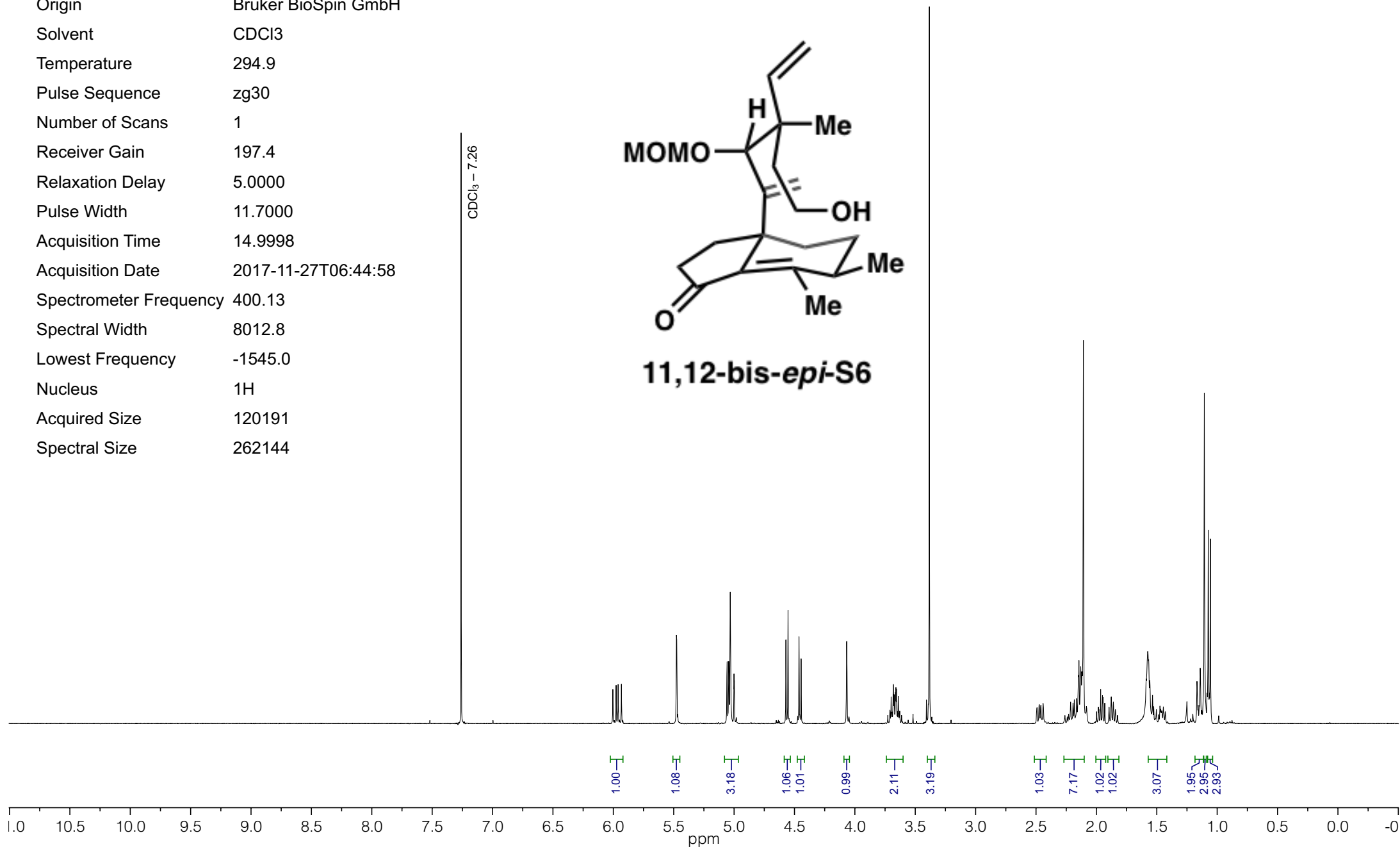
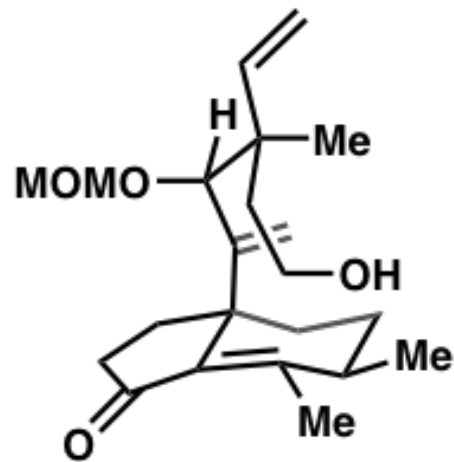
7.42 7.24 5.73 5.41 4.98 4.85 4.77 4.51 4.41 3.92 3.32 3.08 2.39 2.18 2.10 2.00 1.85 1.48 1.12 1.07 0.97

CDCl<sub>3</sub> - 7.26

Parameter	Value
Data File Name	/ Volumes/ nmrdata-4/ sfeng/ nmr/ SSF-III-67-flashed/ 8/ fid
Title	SSF-III-67-flashed.8.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl <sub>3</sub>
Temperature	295.0
Pulse Sequence	zgpg30
Number of Scans	512
Receiver Gain	72.0
Relaxation Delay	1.0000
Pulse Width	10.0000
Acquisition Time	1.3631
Acquisition Date	2017-11-23T15:01:09
Spectrometer Frequency	100.62
Spectral Width	24038.5
Lowest Frequency	-1960.9
Nucleus	<sup>13</sup> C
Acquired Size	32768
Spectral Size	65536

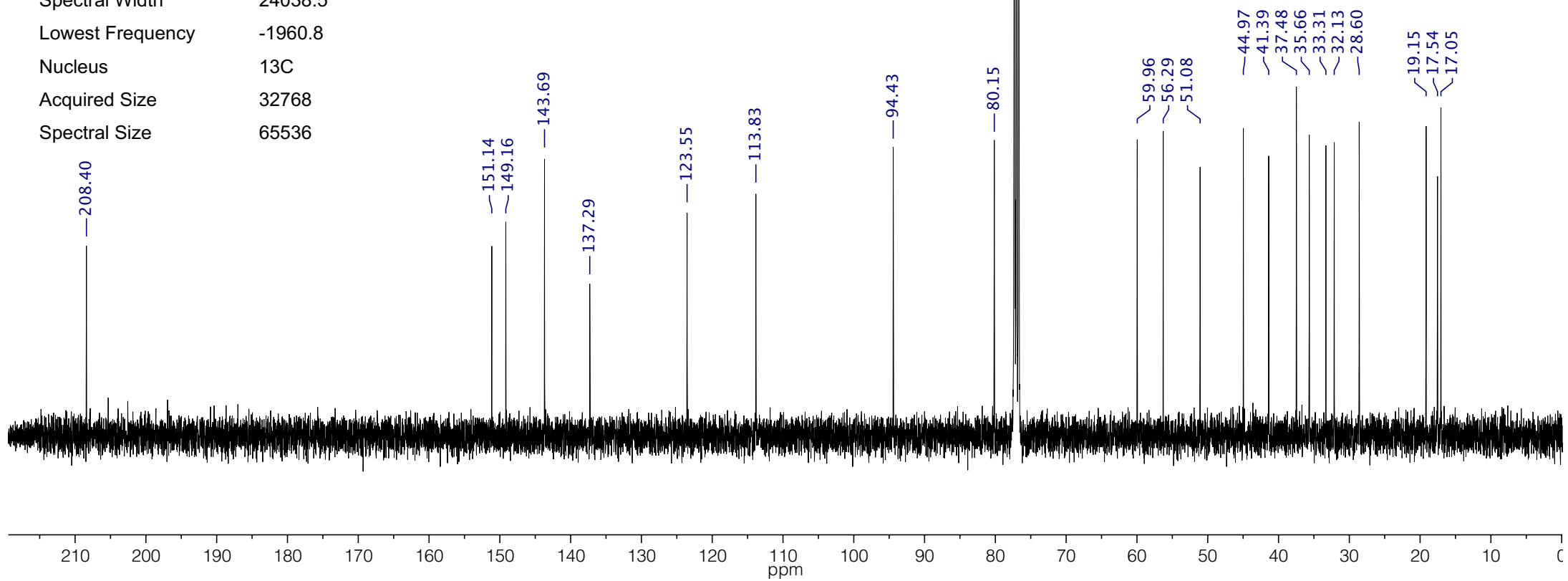
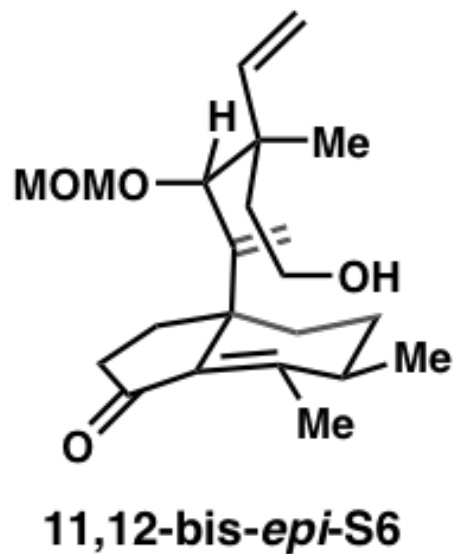


Parameter	Value
Data File Name	/ Volumes/ nmrdata/ sfeng/ nmr/ SSF-III-75-characterization/ 2/ fid
Title	SSF-III-75-characterization.2.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl <sub>3</sub>
Temperature	294.9
Pulse Sequence	zg30
Number of Scans	1
Receiver Gain	197.4
Relaxation Delay	5.0000
Pulse Width	11.7000
Acquisition Time	14.9998
Acquisition Date	2017-11-27T06:44:58
Spectrometer Frequency	400.13
Spectral Width	8012.8
Lowest Frequency	-1545.0
Nucleus	<sup>1</sup> H
Acquired Size	120191
Spectral Size	262144

CDCl<sub>3</sub> - 7.26



Parameter	Value
Data File Name	/ Volumes/ nmrdata/ sfeng/ nmr/ SSF-III-75-characterization/ 1/ fid
Title	SSF-III-75-characterization.1.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl <sub>3</sub>
Temperature	295.0
Pulse Sequence	zgpg30
Number of Scans	512
Receiver Gain	72.0
Relaxation Delay	1.0000
Pulse Width	10.0000
Acquisition Time	1.3631
Acquisition Date	2017-11-27T06:43:09
Spectrometer Frequency	100.62
Spectral Width	24038.5
Lowest Frequency	-1960.8
Nucleus	<sup>13</sup> C
Acquired Size	32768
Spectral Size	65536



Parameter Value

Data File Name / Volumes/ nmrdata/ sfeng/ nmr/ SSF-III-27-characterization/ 1/ fid

Title SSF-III-27-characterization.1.fid

Origin Bruker BioSpin GmbH

Solvent CDCl3

Temperature 294.9

Pulse Sequence zg30

Number of Scans 1

Receiver Gain 127.1

Relaxation Delay 5.0000

Pulse Width 11.7000

Acquisition Time 14.9998

Acquisition Date 2017-11-26T11:58:08

Spectrometer Frequency 400.13

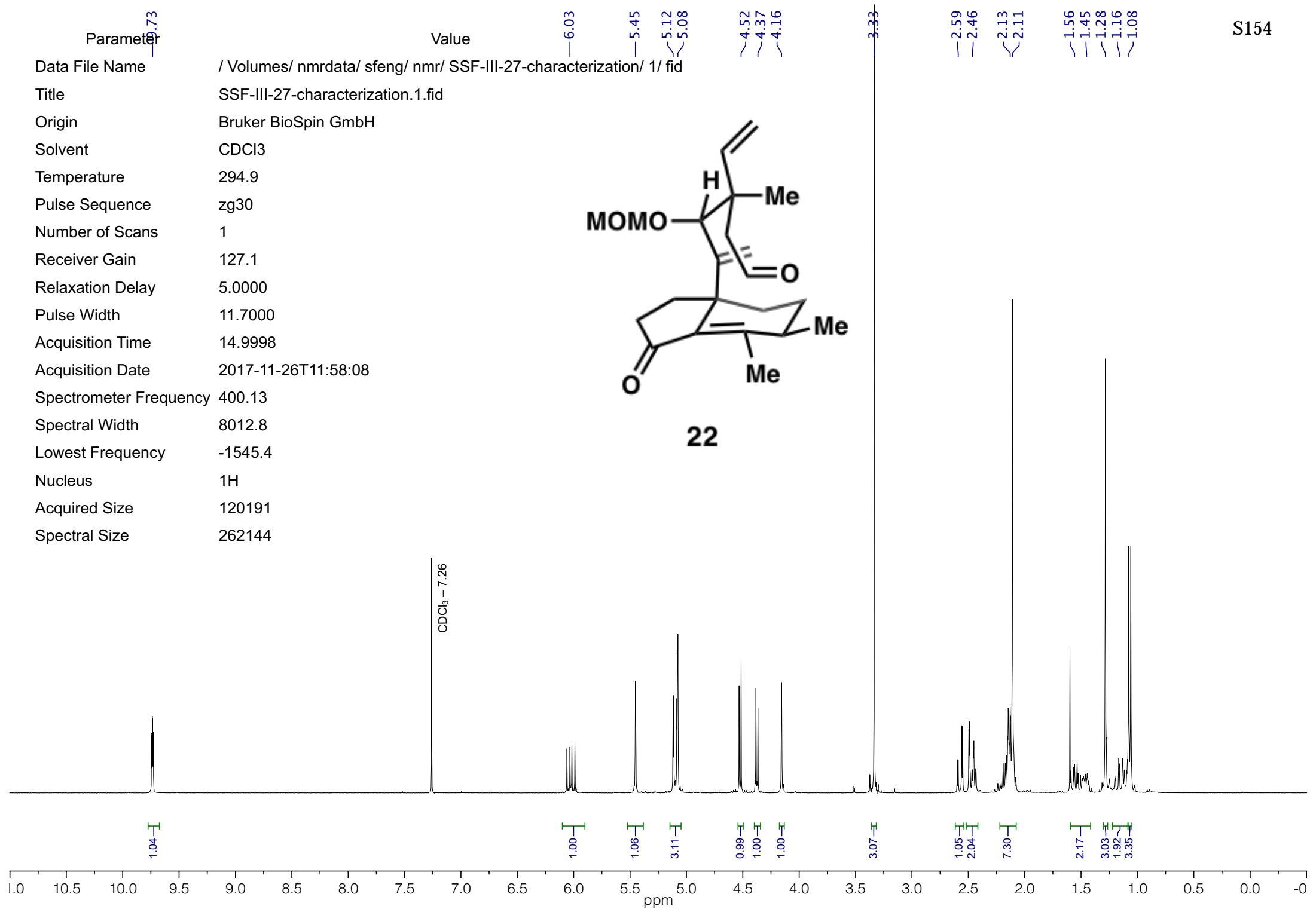
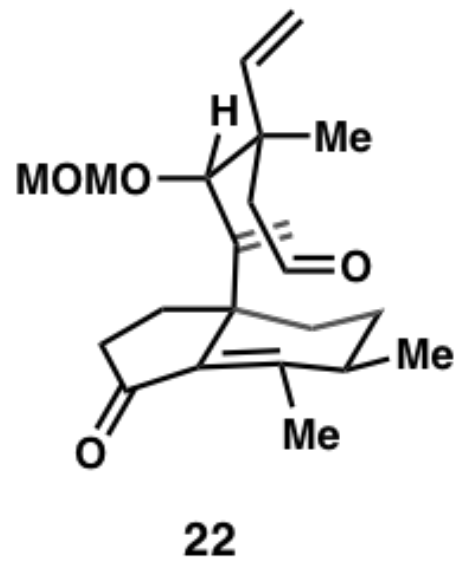
Spectral Width 8012.8

Lowest Frequency -1545.4

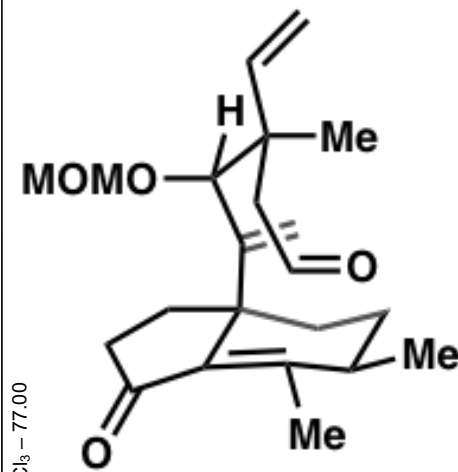
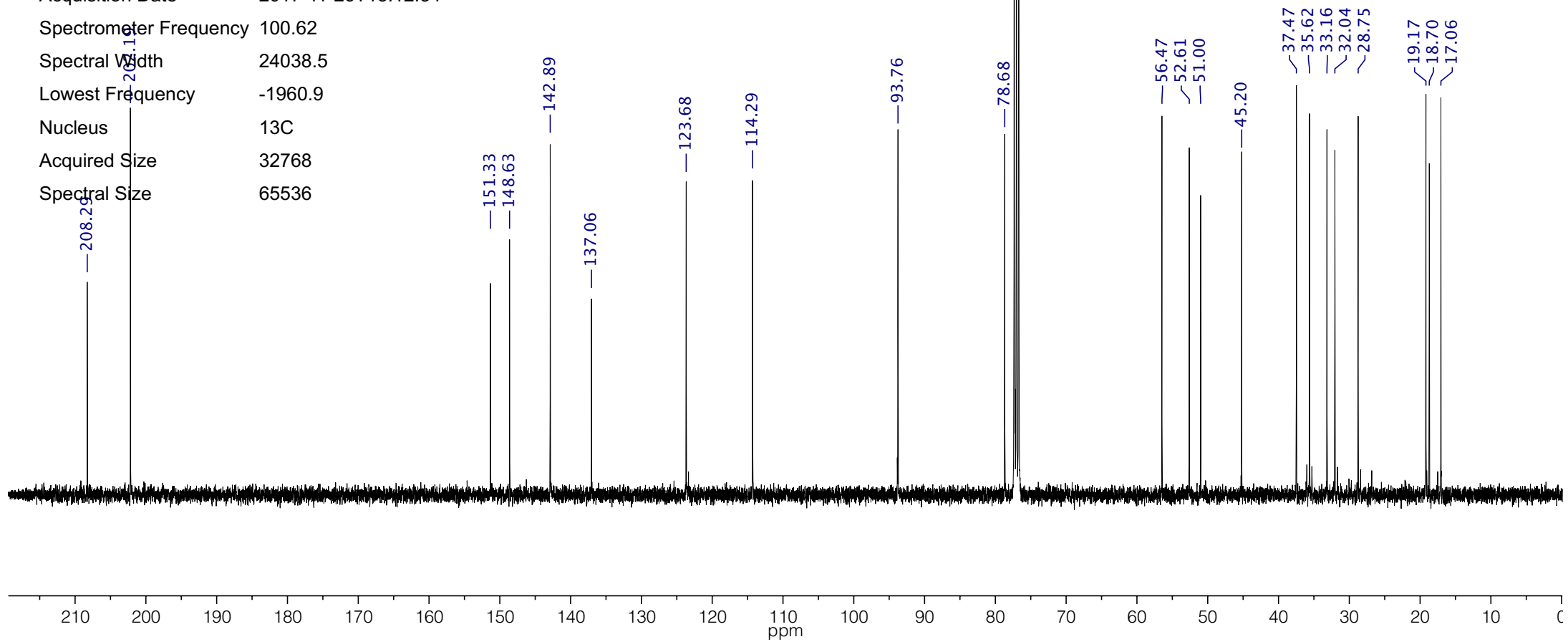
Nucleus 1H

Acquired Size 120191

Spectral Size 262144



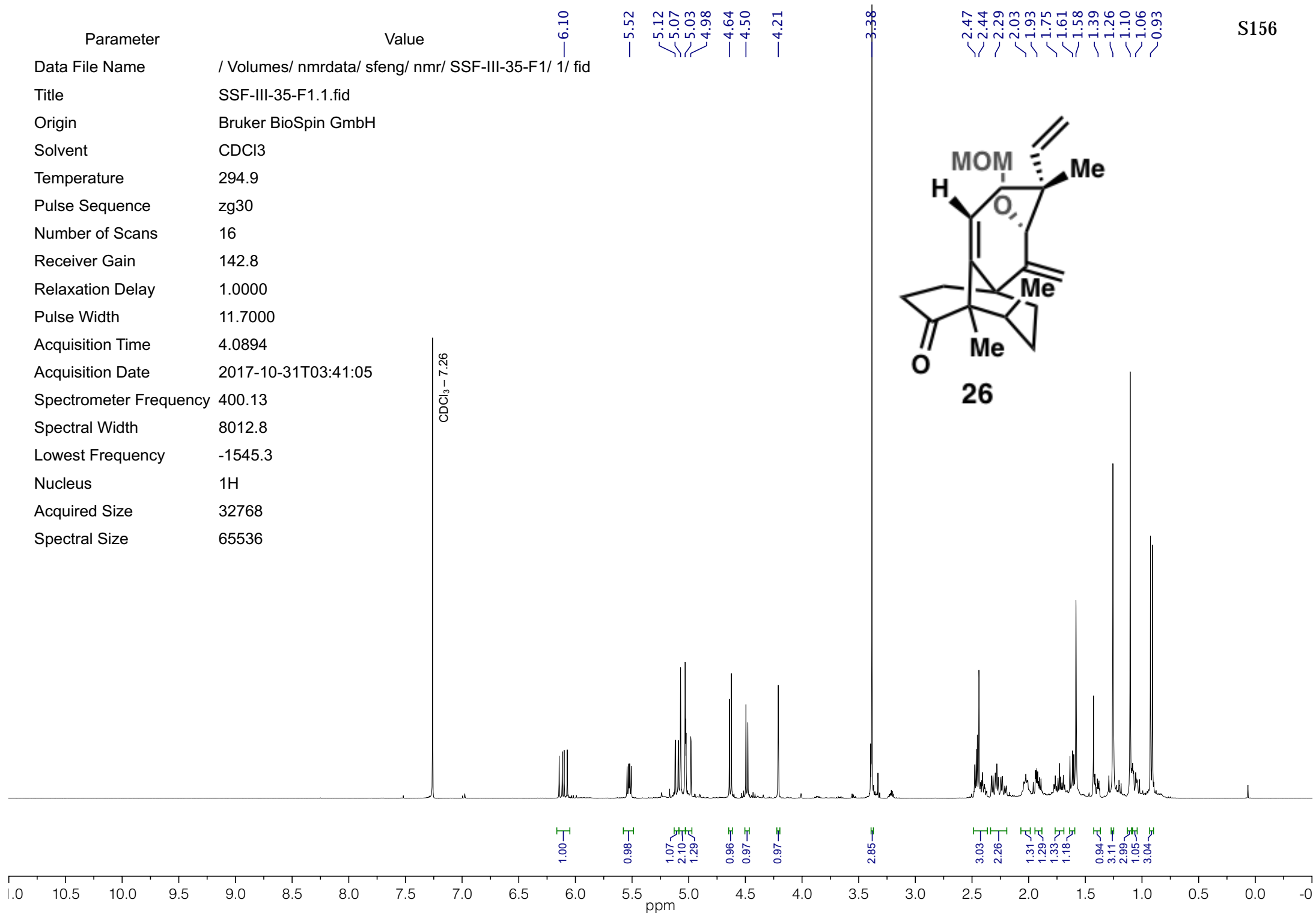
Parameter	Value
Data File Name	/ Volumes/ nmrdata/ sfeng/ nmr/ SSF-III-27-characterization/ 5/ fid
Title	SSF-III-27-characterization.5.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl <sub>3</sub>
Temperature	294.9
Pulse Sequence	zgpg30
Number of Scans	500
Receiver Gain	64.2
Relaxation Delay	1.0000
Pulse Width	10.0000
Acquisition Time	1.3631
Acquisition Date	2017-11-26T13:12:34
Spectrometer Frequency	100.62
Spectral Width	24038.5
Lowest Frequency	-1960.9
Nucleus	<sup>13</sup> C
Acquired Size	32768
Spectral Size	65536



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CDCl<sub>3</sub> - 77.00

Parameter	Value
Data File Name	/ Volumes/ nmrdata/ sfeng/ nmr/ SSF-III-35-F1/ 1/ fid
Title	SSF-III-35-F1.1.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl <sub>3</sub>
Temperature	294.9
Pulse Sequence	zg30
Number of Scans	16
Receiver Gain	142.8
Relaxation Delay	1.0000
Pulse Width	11.7000
Acquisition Time	4.0894
Acquisition Date	2017-10-31T03:41:05
Spectrometer Frequency	400.13
Spectral Width	8012.8
Lowest Frequency	-1545.3
Nucleus	<sup>1</sup> H
Acquired Size	32768
Spectral Size	65536



Parameter	Value
Data File Name	/ Volumes/ nmrdata/ sfeng/ nmr/ SSF-III-35-F1/ 5/ fid
Title	SSF-III-35-F1.5.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl <sub>3</sub>
Temperature	295.0
Pulse Sequence	zgpg30
Number of Scans	512
Receiver Gain	78.7
Relaxation Delay	1.0000
Pulse Width	10.0000
Acquisition Time	1.3631
Acquisition Date	2017-10-31T05:03:34
Spectrometer Frequency	100.62
Spectral Width	24038.5
Lowest Frequency	-1960.9
Nucleus	<sup>13</sup> C
Acquired Size	32768
Spectral Size	65536

