

## Synthesis of the C19–C30 Bis-THF Fragment of Iriomoteolide-13a via Stepwise S<sub>N</sub>2 Cyclization and Intramolecular *syn*-Oxypalladation

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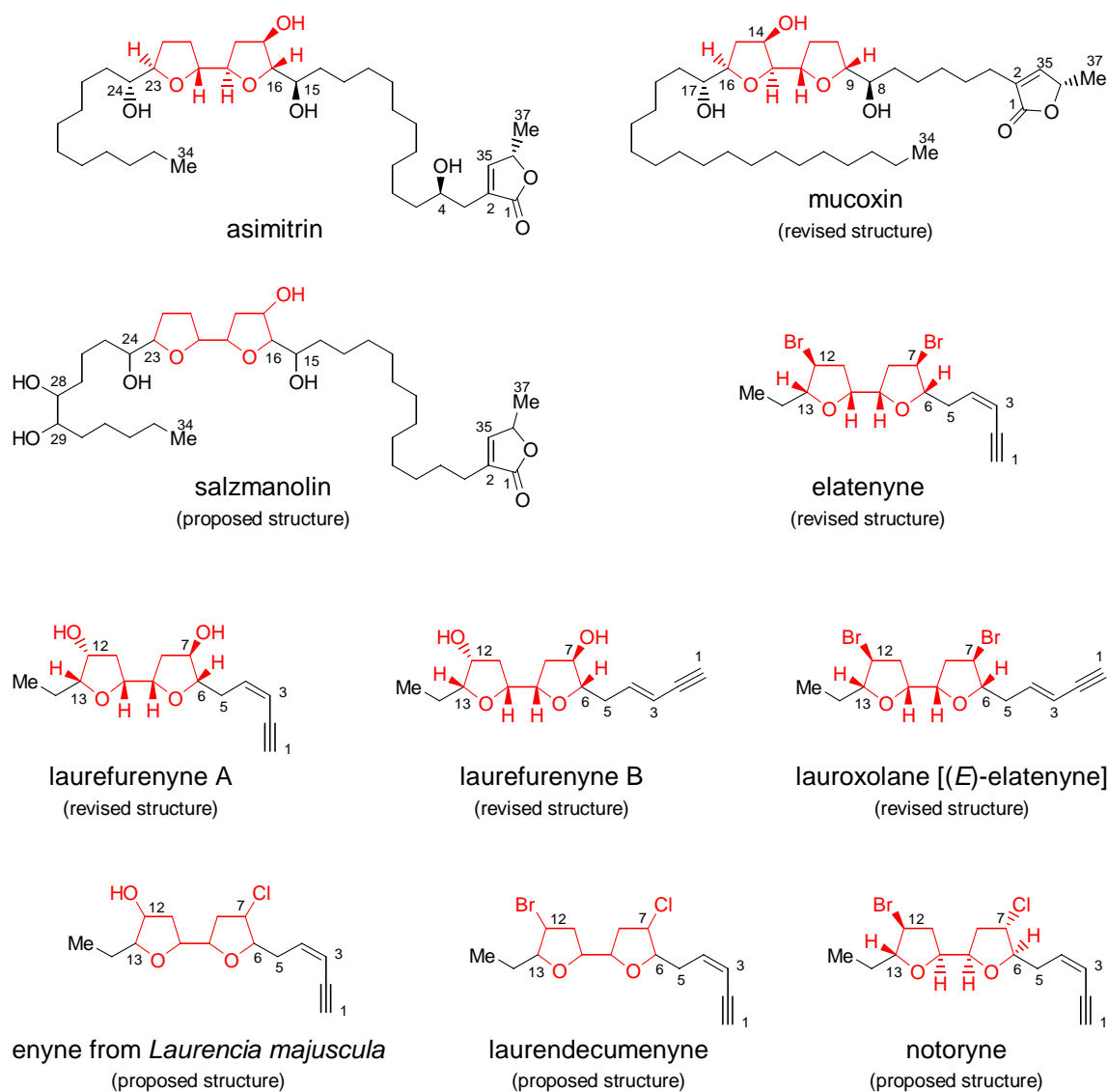
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**References:** [For asinitrin, see:](#) (a) Kim, E. J.; Suh, K. M.; Kim, D. H.; Jung, E. J.; Seo, C. S.; Son, J. K.; Woo, M. H.; McLaughlin, J. L. *J. Nat. Prod.* **2005**, *68*, 194–197. [For mucoxin, see:](#) (b) Yan, J.; Garzan, A.; Narayan, R. S.; Vasileiou, C.; Borhan, B. *Chem. Eur. J.* **2010**, *16*, 13749–13756. [For salzmanolin, see:](#) (c) Queiroz, E. F.; Roblot, F.; Lapr votte, O.; Paulo, M. de Q.; Hocquemiller, R. *J. Nat. Prod.* **2003**, *66*, 755–758. [For elatenyne, see:](#) (d) Urban, S.; Brklja a, R.; Hoshino, M.; Lee, S.; Fujita, M. *Angew. Chem. Int. Ed.* **2016**, *55*, 2678–2682. [For lauroxolane, see:](#) (e) Kim, K.; Brennan, M. R.; Erickson, K. L. *Tetrahedron Lett.* **1989**, *30*, 1757–1760. [For laurefurenynes A and B, see:](#) (f) Shepherd, D. J.; Broadwith, P. A.; Dyson, B. S.; Paton, R. S.; Burton, J. W. *Chem. Eur. J.* **2013**, *19*, 12644–12648. (g) Holmes, M. T.; Britton, R. *Chem. Eur. J.* **2013**, *19*, 12649–12652. [For notoryne, see:](#) (h) Kikuchi, H.; Suzuki, T.; Kurosawa, E.; Suzuki, M. *Bull. Chem. Soc. Jpn.* **1991**, *64*, 1763–1775. [For laurendecumenyne, see:](#) (i) Ji, N.-Y.; Li, X.-M.; Li, K.; Wang, B.-G. *J. Nat. Prod.* **2007**, *70*, 1499–1502. Correction: Ji, N.-Y.; Li, X.-M.; Li, K.; Wang, B.-G. *J. Nat. Prod.* **2010**, *73*, 1192. [For a bis-THF-containing enyne for \*Laurencia majuscula\*, see:](#) (j) Wright, A. D.; K nig, G. M.; Nys, R.; Sticher, O. *J. Nat. Prod.* **1993**, *56*, 394–401.

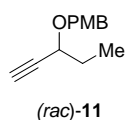
**Fig. S1.** Structures of some known naturally occurring bis-THF compounds possessing additional substituents (OH/Br/Cl) on the THF ring(s).

## Experimental Procedures

**General Methods.**  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded in  $\text{CDCl}_3$  (400 MHz for  $^1\text{H}$  and 100 MHz for  $^{13}\text{C}$ , respectively). Residual solvent peaks (7.26 and 77.16 ppm for  $\text{CDCl}_3$ ) are used as the internal references for  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra. Optical rotation data were recorded using quartz cells and sodium D line at the specific temperature and the reported rotation data are the average of three measurements for each sample. IR spectra were taken on an FT-IR spectrophotometer. High resolution mass spectra (HRMS) were measured by TOF MS under the +ESI, +CI, or –CI conditions. Silica gel plates pre-coated on glass were used for thin-layer chromatography using UV light, or 7% ethanolic phosphomolybdic acid and heating as the visualizing methods. Silica gel was used for flash column chromatography with mixed ethyl acetate (EtOAc) and hexane as the eluting solvents. Yields refer to chromatographically and spectroscopically ( $^1\text{H}$  NMR) homogeneous materials. All reactions were performed under an oxygen-free atmosphere of nitrogen or argon unless otherwise stated. Air- and moisture-sensitive liquids were transferred via a syringe. Reagents were obtained commercially and used as received unless otherwise mentioned. Anhydrous THF,  $\text{Et}_2\text{O}$  and PhMe were freshly distilled from sodium and benzophenone ketyl and anhydrous  $\text{Et}_3\text{N}$ ,  $\text{CH}_2\text{Cl}_2$ , and HMPA were freshly distilled over  $\text{CaH}_2$ , respectively, under a  $\text{N}_2$  atmosphere. Anhydrous MeOH was freshly distilled from iodine-activated magnesium turnings. It is mentioned here that due to separation of the stereogenic propargylic carbon from other stereogenic centers in the same molecules, the inseparable diastereoisomeric mixtures such as **12** and the related compounds show very similar  $^1\text{H}$  and/or  $^{13}\text{C}$  NMR spectra. In the cases of **12** and **12a**, optical rotation data were taken to differentiate each other.

### A. Synthesis of Alkyne (*rac*)-11.

#### (*rac*)-3-(4'-Methoxybenzyloxy)pent-1-yne (*rac*)-11.



*Preparation of 4-methoxybenzyl 2,2,2-trichloroacetimidate:*<sup>1</sup> To a solution of 4-methoxybenzyl alcohol (12.5 mL, 100 mmol) in anhydrous  $\text{Et}_2\text{O}$  (100 mL) cooled in an ice–water bath (0 °C) was added NaH (60% in mineral oil, 400.0 mg, 10.0 mmol) followed by stirring at the same temperature for 30 min. To the above mixture was slowly added  $\text{Cl}_3\text{CCN}$  (10.0 mL, 100 mmol). The resultant mixture was slowly warmed to room temperature and stirred for 1.5 h. The reaction was quenched by saturated aqueous solution of  $\text{NaHCO}_3$  (100 mL) and the reaction mixture was extracted with  $\text{Et}_2\text{O}$  (100 mL  $\times$  3). The combined organic layer was washed with brine, dried over anhydrous  $\text{Na}_2\text{SO}_4$ , filtered, and concentrated under reduced pressure to give the crude 4-methoxybenzyltrichloroacetimidate (25.1 g, 89.3 mmol) as a pale-yellow oil, which was used directly in the next step.

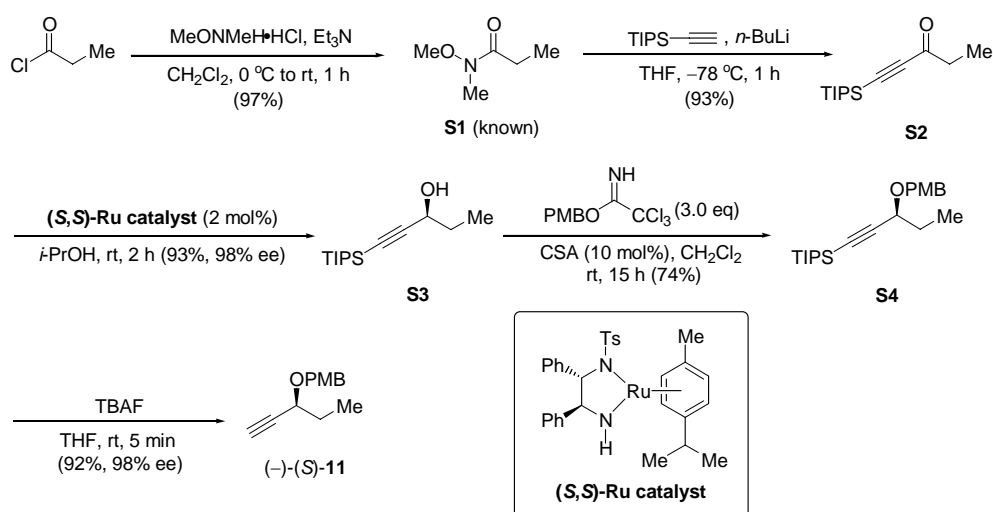
To a solution of the commercially available ( $\pm$ )-pent-1-yn-3-ol (2.50 g, 29.7 mmol) and 4-methoxybenzyl

<sup>1</sup> Burova, S. A.; McDonald, F. E. *J. Am. Chem. Soc.* **2004**, *126*, 2495–2500.

2,2,2-trichloroacetimidate (25.10 g, 89.3 mmol) in anhydrous CH<sub>2</sub>Cl<sub>2</sub> (100 mL) cooled in an ice–water bath (0 °C) was added (±)-camphorsulfonic acid (690.0 mg, 2.97 mmol) followed by stirring 15 h at room temperature. The reaction was quenched by saturated aqueous solution of NaHCO<sub>3</sub> (100 mL). The reaction mixture was extracted with CH<sub>2</sub>Cl<sub>2</sub> (50 mL × 3) and the combined organic layer was washed with brine (50 mL × 3), dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered, and concentrated under reduced pressure. The residue was purified by flash column chromatography (silica gel, eluting with 10% EtOAc in hexane) to give (*rac*)-**11** (4.24 g, 70%) as a pale-yellow oil. *R*<sub>f</sub> = 0.63 (25% EtOAc in hexane); IR (film) 3289 (br), 2967, 2936, 2837, 1613, 1514, 1248, 1035 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.32–7.28 (m, 2H), 6.91–6.80 (m, 2H), 4.74 and 4.45 (ABq, *J* = 11.6 Hz, 2H), 3.99 (td, *J* = 6.8, 2.9 Hz, 1H), 3.81 (s, 3H), 2.46 (d, *J* = 2.0 Hz, 1H), 1.82–1.70 (m, 2H), 1.01 (t, *J* = 7.6 Hz, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 159.4, 130.1, 129.8 (×2), 113.9 (×2), 83.0, 73.9, 70.3, 69.5, 55.4, 28.9, 9.8; HRMS (–CI) calcd for C<sub>13</sub>H<sub>15</sub>O<sub>2</sub> (M–H<sup>+</sup>) 203.1072, found 203.1082.

## B. Synthesis of Alkyne (–)-(*S*)-**11**.

### (–)-(*S*)-3-(4'-Methoxybenzyloxy)pent-1-yne (–)-(*S*)-**11**.



*N*-Methoxy-*N*-methylpropionamide (**S1**).<sup>2</sup> To a suspension of *N*-methoxymethylamine hydrochloride salt (5.27 g, 54.0 mmol) in anhydrous CH<sub>2</sub>Cl<sub>2</sub> (150 mL) cooled in an ice–water bath (0 °C) was slowly added Et<sub>3</sub>N (15.0 mL, 108.0 mmol) followed by adding propionyl chloride (4.7 mL, 54.0 mmol) dropwise to maintain the internal temperature of the mixture below 4 °C. The resultant mixture was then allowed to warm to room temperature and followed by stirring for 1 h at room temperature. The reaction was quenched by saturated aqueous solution of NaHCO<sub>3</sub> (50 mL) and the reaction mixture was extracted with CH<sub>2</sub>Cl<sub>2</sub> (50 mL × 3). The combined organic layer was washed with 1M aqueous solution of HCl (20 mL) and brine (20 mL), dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtrated, and concentrated under reduced pressure. The residue was further dried under vacuum to give the known product **S1** (6.13 g, 97%) as a colorless oil.<sup>2</sup> *R*<sub>f</sub> = 0.42 (9% EtOAc in hexane); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, a mixture of two major conformers) δ 3.64 and

<sup>2</sup> Kerr, W. J.; Morrison, A. J.; Pazicky, M.; Weber, T. *Org. Lett.* **2012**, *14*, 2250–2253.

3.63 (s, 3H), 3.13 (s, 3H), 2.40 (q,  $J = 7.6$  Hz, 2H), 1.11–1.06 (m, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  175.5 (br), 61.2, 32.3 (br), 25.2, 8.8.

**Addition of TIPS-C $\equiv$ C-Li to the Weinreb Amide S1.**<sup>3a</sup> **1-(Triisopropylsilyl)pent-1-yn-3-one (S2).**<sup>3b</sup> To a solution of TIPS-C $\equiv$ C-H (14.5 mL, 65.0 mmol) in anhydrous THF (50 mL) cooled in a dry ice–acetone bath at  $-78$  °C was added *n*-BuLi (2.5 M in hexanes, 26 mL, 65.0 mmol) followed by stirring at the same temperature for 5 min. The resultant solution of the acetylide was transferred via a cannula to a solution of *N*-methoxy-*N*-methylpropionamide (S1) (6.13 g, 52.0 mmol) in THF (20 mL) cooled at  $-78$  °C. After stirring at the same temperature for 1 h, the reaction was quenched by saturated aqueous solution of  $\text{NH}_4\text{Cl}$ . The reaction mixture was extracted with EtOAc (20 mL  $\times$  3) and the combined organic layer was washed with brine, dried over anhydrous  $\text{Na}_2\text{SO}_4$ , filtered, and concentrated under reduced pressure. The residue was purified by flash column chromatography (silica gel, eluting with hexane) to yield the ketone S2<sup>3b</sup> (16.9 g, 93%) as a pale yellow oil.  $R_f = 0.75$  (9% EtOAc in hexane);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  2.59 (q,  $J = 7.6$  Hz, 2H), 1.16 (t,  $J = 7.6$  Hz, 3H), 1.14–1.05 (m, 21H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  188.5, 104.2, 95.6, 39.1, 18.6 ( $\times 6$ ), 11.1 ( $\times 3$ ), 8.3.

**(–)-(S)-1-(Triisopropylsilyl)pent-1-yn-3-ol (S3).**<sup>4,5</sup> A flame-dried 100-mL round-bottom flask equipped with a magnetic stirring bar was charged with degassed *i*-PrOH (50 mL) and 1-(triisopropylsilyl)pent-1-yn-3-one (S2) (1.90 g, 5.5 mmol) under Ar atmosphere. A solution of the (S,S)-Ru catalyst (67.0 mg,  $1.1 \times 10^{-1}$  mmol) in anhydrous  $\text{CH}_2\text{Cl}_2$  (5 mL) was added to the above flask in one portion. The resultant mixture was stirred at room temperature for 1.5 h and then concentrated under reduced pressure. The residue was purified by flash column chromatography (silica gel, eluting with 5% EtOAc in hexane) to give (S)-1-(triisopropylsilyl)pent-1-yn-3-ol (S3) (1.79 g, 93%) as a colorless oil.  $R_f = 0.53$  (9% EtOAc in hexane);  $[\alpha]_{\text{D}}^{20} -3.7$  (*c* 1.0,  $\text{CHCl}_3$ ) {Lit.<sup>5</sup> (R)-S3  $[\alpha]_{\text{D}}^{25} +4.13$  (*c* 2.3,  $\text{CHCl}_3$ ), 92% ee}; IR (film) 3330 (br), 2961, 2943, 2866, 2169, 1463, 1016  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  4.34 (td,  $J = 6.0, 6.0$  Hz, 1H), 1.82 (d,  $J = 5.6$  Hz, 1H, OH), 1.80–1.69 (m, 2H), 1.08–1.05 (m, 21H), 1.02 (t,  $J = 7.6$  Hz, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  108.8, 85.6, 64.4, 31.2, 18.7 ( $\times 6$ ), 11.3 ( $\times 3$ ), 9.5.

**(S)-Triisopropyl[3-(4'-methoxybenzyloxy)pent-1-ynyl]silane (S4).** To a solution of 4-methoxybenzyl 2,2,2-trichloroacetimidate (12.7 g, 45.0 mmol) and (S)-1-(triisopropylsilyl)pent-1-yn-3-ol (S3) (5.3 g, 15.0 mmol) in anhydrous  $\text{CH}_2\text{Cl}_2$  (100 mL) cooled in an ice–water bath (0 °C) was added ( $\pm$ )-camphorsulfonic acid (348.0 mg, 1.5 mmol) followed by stirring at room temperature for overnight. The reaction was quenched by saturated aqueous solution of  $\text{NaHCO}_3$  (100 mL). The reaction mixture was extracted with  $\text{CH}_2\text{Cl}_2$  (50 mL  $\times$  3) and the combined organic layer was washed with brine (50 mL  $\times$  3), dried over

<sup>3</sup> (a) For a similar reaction of TIPS-C $\equiv$ C-Li with Weinreb amides, see: Son, S. U.; Yoon, Y. A.; Choi, D. S.; Park, J. K.; Kim, B. M.; Chung, Y. K. *Org. Lett.* **2001**, *3*, 1065–1067. (b) Wang, P.-F.; Feng, Y.-S.; Cheng, Z.-F.; Wu, Q.-M.; Wang, G.-Y.; Liu, L.-L.; Dai, J.-J.; Xu, J.; Xu, H.-J. *J. Org. Chem.* **2015**, *80*, 9314–9320.

<sup>4</sup> For a similar procedure for reduction of 4-(triisopropylsilyl)but-3-yn-2-one, see: (a) Marshall, J. A.; Eidam, P.; Eidam, H. S. *J. Org. Chem.* **2006**, *71*, 4840–4844. For reduction of 1-(trimethylsilyl)pent-1-yn-3-one, see: (b) Krishnamurthy, V. R.; Dougherty, A.; Haller, C. A.; Chaikof, E. L. *J. Org. Chem.* **2011**, *76*, 5433–5437.

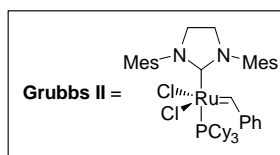
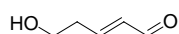
<sup>5</sup> For (+)-(R)-1-(triisopropylsilyl)pent-1-yn-3-ol, see: Ko, D.-H.; Kim, K. H.; Ha, D.-C. *Org. Lett.* **2002**, *4*, 3759–3762.

anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered, and concentrated under reduced pressure. The residue was purified by flash column chromatography (silica gel, eluting with 5% EtOAc in hexane) to give the PMB ether **S4** (5.2 g, 74%) as a yellow oil.  $R_f$  = 0.80 (9% EtOAc in hexane); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.31–7.28 (m, 2H), 6.90–6.86 (m, 2H), 4.76 and 4.48 (ABq,  $J$  = 11.2 Hz, 2H), 4.02 (t,  $J$  = 6.4 Hz, 1H), 3.81 (s, 3H), 1.87–1.63 (m, 2H), 1.08–1.05 (m, 21H), 1.02 (t,  $J$  = 7.6 Hz, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 159.4, 130.4, 129.9 (×2), 113.9 (×2), 106.9, 86.7, 70.2, 70.1, 55.4, 29.1, 18.8 (×6), 11.3 (×3), 9.9.

(–)-(S)-3-(4'-Methoxybenzyloxy)pent-1-yne (–)-(S)-**11**. To a solution of the silylated compound **S4** (5.2 g, 11.0 mmol) in THF (20 mL) cooled in an ice–water bath (0 °C) was added TBAF solution (1 M in THF, 11.0 mL, 11.0 mmol) followed by stirring at room temperature for 5 min. The reaction was quenched by saturated aqueous solution of NH<sub>4</sub>Cl and the reaction mixture was extracted with EtOAc (30 mL × 3). The combined organic layer was washed with brine, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered, and concentrated under reduced pressure. The residue was purified by flash column chromatography (silica gel, eluting with 5% EtOAc in hexane) to give the alkyne (–)-(S)-**11** (2.1 g, 92%) as a pale-yellow oil.  $R_f$  = 0.73 (9% EtOAc in hexane);  $[\alpha]_D^{20}$  –137.2 ( $c$  1.0, CHCl<sub>3</sub>), 98% ee by HPLC [analysis conditions: Daicel CHIRALPAK AD-H column, eluting with 3% *i*-PrOH in hexane at 1.0 mL/min;  $R_t$ : 4.8 min (major) and 5.1 min (minor)]. Other spectroscopic data are the same as those for (*rac*)-**11**.

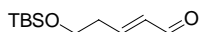
### C. Synthesis of Aldehyde 7.

#### (E)-5-Hydroxypent-2-enal.



To a solution of 3-butene-1-ol (7.21 g, 8.6 mL, 100.0 mmol) and acrolein (16.8 g, 20.0 mL, 300.0 mmol) in degassed anhydrous CH<sub>2</sub>Cl<sub>2</sub> (50 mL) under a nitrogen atmosphere and cooled in an ice–water bath (0 °C) was added a solution of **Grubbs II** (170.0 mg, 0.2 mmol) in degassed anhydrous CH<sub>2</sub>Cl<sub>2</sub> (5 mL) via a syringe. The cooling bath was then removed and the mixture was heated under refluxing for 24 h. The reaction was cooled down to room temperature and the solvent and the volatile materials were removed under reduced pressure. The residue was purified by flash column chromatography (silica gel, eluted with 50% EtOAc in hexane) to give (*E*)-5-hydroxypent-2-enal (8.51 g, 85%) as a colorless oil.  $R_f$  = 0.24 (50% EtOAc in hexane); IR (film) 3403 (br), 2944, 2886, 2838, 1684, 1637, 1402, 1140, 1047, 975 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 9.42 (d,  $J$  = 8.0 Hz, 1H), 6.87 (dt,  $J$  = 15.6, 6.8 Hz, 1H), 6.12 (dd,  $J$  = 15.6, 8.0 Hz, 1H), 3.76 (t,  $J$  = 6.4 Hz, 2H), 3.00 (br s, 1H, OH), 2.55–2.50 (m, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 194.4, 155.7, 134.2, 60.3, 35.7; HRMS (+CI) calcd for C<sub>5</sub>H<sub>9</sub>O<sub>2</sub> (M+H<sup>+</sup>) 101.0603, found 101.0602; and calcd for C<sub>5</sub>H<sub>9</sub>O<sub>2</sub> (M<sup>+</sup>–H) 99.0446, found 99.0442.

#### (E)-5-[(*tert*-Butyldimethylsilyl)oxy]pent-2-enal (**7**).

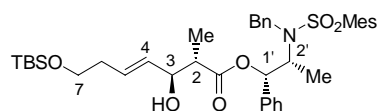


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To a solution of (*E*)-5-hydroxypent-2-enal (10.91 g, 109.0 mmol) and imidazole (11.16 g, 164.0 mmol) in anhydrous CH<sub>2</sub>Cl<sub>2</sub> (200 mL) cooled in an ice–water bath (0 °C) was added TBSCl (19.74 g, 131.0 mmol) followed by stirring at room temperature for 2 h. The reaction was quenched by saturated aqueous solution of NH<sub>4</sub>Cl, and the reaction mixture was extracted with CH<sub>2</sub>Cl<sub>2</sub> (150 mL × 3). The combined organic layer was washed with brine, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtrated, and concentrated under reduced pressure. The residue was purified by flash column chromatography (silica gel, eluted with 9% EtOAc in hexane) to afford the silylated aldehyde **7** (20.56 g, 88%) as a colorless oil. *R*<sub>f</sub> = 0.43 (9% EtOAc in hexane); IR (film) 2956, 2930, 2858, 1697, 1637, 1256, 1103 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 9.53 (d, *J* = 8.0 Hz, 1H), 6.89 (dt, *J* = 15.6, 6.8 Hz, 1H), 6.18 (dd, *J* = 15.6, 7.6 Hz, 1H), 3.80 (t, *J* = 6.0 Hz, 2H), 2.56 (dt, *J* = 6.4, 6.4 Hz, 2H), 0.90 (s, 9H), 0.07 (s, 6H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 193.5, 155.3, 134.2, 61.0, 35.9, 25.7 (×3), 18.1, -5.5 (×2); HRMS (+CI) calcd for C<sub>11</sub>H<sub>23</sub>O<sub>2</sub>Si (M+H<sup>+</sup>) 215.1467, found 215.1461.

#### D. Synthesis of Alkyl Triflate **10**.

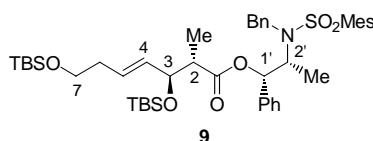
**(1'S,2S,2'R,3S,E)-2'-(*N*-Benzyl-*N*-mesitylenesulfonyl)amino-1'-phenyl-1'-propyl 7-[(*tert*-Butyl-dimethylsilyl)oxy]-3-hydroxy-2-methylhept-4-enoate.**



A solution of the chiral ester **8** (19.19 g, 40.0 mmol) in anhydrous CH<sub>2</sub>Cl<sub>2</sub> (80 mL) charged in an oven-dried 250-mL round-bottom flask under a nitrogen atmosphere was cooled in dry ice–acetone bath (–78 °C). To the solution was added Et<sub>3</sub>N (15.0 mL, 108.0 mmol) via a syringe followed by stirring at –78 °C for 5 min. A solution of dicyclohexylboron triflate (1.0 M in hexane, 92.4 mL, 92.4 mmol) was added dropwise over 50 min. The resultant mixture was stirred at –78 °C for 2 h followed by adding a solution of the aldehyde **7** (6.60 g, 30.8 mmol) in anhydrous CH<sub>2</sub>Cl<sub>2</sub> (5 mL) dropwise. The resultant mixture was stirred for 5 h from –78 °C to room temperature, and then the reaction was quenched by a buffer solution (pH = 7, 50 mL). The reaction mixture was diluted with MeOH (100 mL) and 30% H<sub>2</sub>O<sub>2</sub> (60 mL) and stirred vigorously for overnight. The mixture was concentrated under reduced pressure. The residue was partitioned between H<sub>2</sub>O and CH<sub>2</sub>Cl<sub>2</sub>. The aqueous layer was extracted with CH<sub>2</sub>Cl<sub>2</sub> (100 mL × 3), and the combined organic layer was washed with brine, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered, and concentrated under reduced pressure. The residue was purified by flash column chromatography (silica gel, eluted with 9% EtOAc in hexane) to give the *anti*-aldol product (17.52 g, 82% with 95:5 dr) as a light yellow viscous oil. *R*<sub>f</sub> = 0.39 (17% EtOAc in hexane); [α]<sub>D</sub><sup>22</sup> –48.8 (*c* 0.24, CHCl<sub>3</sub>); IR (film) 3500 (br), 2927, 2857, 1736, 1457, 1378, 1320, 1253, 1153, 1095, 1015 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.33–7.29 (m, 2H), 7.27–7.15 (m, 6H), 6.88 (s, 2H), 6.86–6.83 (m, 2H), 5.82 (d, *J* = 4.0 Hz, 1H), 5.70 (dt, *J* = 15.2, 6.8 Hz, 1H), 5.46 (dd, *J* = 15.6, 7.6 Hz, 1H), 4.79 and 4.57 (ABq, *J* = 16.8 Hz, 2H), 4.14–4.05 (m, 2H), 3.63 (t, *J* = 6.4

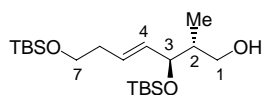
Hz, 2H), 2.51–2.45 (m, 1H), 2.50 (s, 6H), 2.28 (s, 3H), 2.28–2.22 (m, 2H), 1.16 (d,  $J = 6.8$  Hz, 3H), 1.06 (d,  $J = 7.2$  Hz, 3H), 0.88 (s, 9H), 0.04 (s, 6H) (the signal for *OH* not observed);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  174.5, 142.7, 140.4 ( $\times 2$ ), 138.8, 138.4, 133.6, 132.3 ( $\times 2$ ), 131.7, 131.4, 128.6 ( $\times 2$ ), 128.5 ( $\times 2$ ), 128.1, 127.8 ( $\times 2$ ), 127.3, 126.0 ( $\times 2$ ), 78.4, 75.0, 62.7, 57.0, 48.4, 45.9, 36.0, 26.1 ( $\times 3$ ), 23.1 ( $\times 2$ ), 21.0, 18.5, 14.2, 13.5,  $-5.1$  ( $\times 2$ ); HRMS (+ESI) calcd for  $\text{C}_{39}\text{H}_{55}\text{NO}_6\text{SSiNa}$  ( $\text{M}+\text{Na}^+$ ) 716.3417, found 716.3416.

**(1'S,2S,2'R,3S,E)-2'-(*N*-Benzyl-*N*-mesitylenesulfonyl)amino-1'-phenyl-1'-propyl 3,7-[Bis(*tert*-butyldimethylsilyl)oxy]-3-hydroxy-2-methylhept-4-enoate (9).**



To a solution of the *anti*-aldol compound (20.82 g, 30.0 mmol) and 2,6-lutidine (5.2 mL, 45.0 mmol) in anhydrous  $\text{CH}_2\text{Cl}_2$  (100 mL) cooled in a dry ice–acetone bath ( $-78$  °C) was added TBSOTf (8.3 mL, 36.0 mmol) via a syringe follow by stirring at the same temperature for 1 h. The reaction was quenched by saturated aqueous solution of  $\text{NaHCO}_3$ , and the reaction mixture was extracted with  $\text{CH}_2\text{Cl}_2$  (100 mL  $\times$  3). The combined organic layer was washed with brine, dried over anhydrous  $\text{Na}_2\text{SO}_4$ , filtered, and concentrated under reduced pressure. The residue was purified by flash column chromatography (silica gel, eluted with 9% EtOAc in hexane) to provide the bis-silyl ether **9** as a light yellow oil (22.3 g, 92%).  $R_f = 0.71$  (25% EtOAc in hexane);  $[\alpha]_D^{22} -35.4$  ( $c$  1.0,  $\text{CHCl}_3$ ); IR (film) 2936, 2858, 1742, 1459, 1376, 1323, 1251, 1154, 1097, 1049  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.37 (br d,  $J = 7.2$  Hz, 2H), 7.30–7.15 (m, 4H), 7.10 (br dd,  $J = 7.6, 7.2$  Hz, 2H), 6.87 (s, 2H), 6.76 (br d,  $J = 7.2$  Hz, 2H), 5.71 (d,  $J = 5.2$  Hz, 1H), 5.55 (dt,  $J = 15.6, 6.8$  Hz, 1H), 5.28 (dd,  $J = 15.6, 7.6$  Hz, 1H), 4.83 and 4.46 (ABq,  $J = 16.4$  Hz, 2H), 4.24 (dd,  $J = 7.2, 7.2$  Hz, 1H), 4.04 (qd,  $J = 6.8, 5.2$  Hz, 1H), 3.58 (t,  $J = 6.8$  Hz, 2H), 2.48 (dq,  $J = 7.2, 7.2$  Hz, 1H), 2.43 (s, 6H), 2.30 (s, 3H), 2.19 (dt,  $J = 6.8, 6.8$  Hz, 2H), 1.15 (d,  $J = 7.2$  Hz, 3H), 0.92 (d,  $J = 7.2$  Hz, 3H), 0.87 (s, 9H), 0.83 (s, 9H), 0.03 (s, 6H),  $-0.01$  (s, 3H),  $-0.01$  (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  173.1, 142.6, 140.5 ( $\times 2$ ), 138.7, 138.5, 133.3, 132.3 ( $\times 2$ ), 132.0, 130.0, 128.5 ( $\times 2$ ), 128.4 ( $\times 2$ ), 128.2 ( $\times 2$ ), 127.9, 127.4, 126.5 ( $\times 2$ ), 77.9, 75.2, 62.9, 56.9, 48.3, 47.0, 36.0, 26.1 ( $\times 6$ ), 23.1 ( $\times 2$ ), 21.0, 18.5, 18.3, 14.5, 12.9,  $-4.1$ ,  $-4.6$ ,  $-5.2$  ( $\times 2$ ); HRMS (+ESI) calcd for  $\text{C}_{45}\text{H}_{69}\text{NO}_6\text{SSi}_2\text{Na}$  ( $\text{M}+\text{Na}^+$ ) 830.4282, found 830.4285.

**(2R,3S,E)-3,7-Bis-[(*tert*-butyldimethylsilyl)oxy]-2-methylhept-4-en-1-ol.**

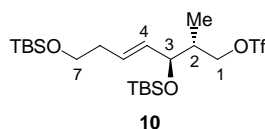


To a solution of the ester **9** (21.00 g, 26.0 mmol) in anhydrous  $\text{CH}_2\text{Cl}_2$  (90 mL) cooled in a dry ice–acetone bath ( $-78$  °C) was added DIBAL-H (1.0 M in hexane, 65 mL, 65 mmol) dropwise followed by stirring at the same temperature for 1 h. The reaction was allowed to warm to  $0$  °C and quenched by carefully adding



MeOH (100 mL) at 0 °C. Saturated aqueous solution of potassium sodium tartrate was added to the reaction mixture followed by stirring at room temperature for overnight. The resultant mixture was extracted with CH<sub>2</sub>Cl<sub>2</sub> (100 mL × 3), the combined organic layer was washed with brine, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered, and concentrated under reduced pressure. The residue was purified by flash column chromatography (silica gel, eluted with 9% EtOAc in hexane) to provide the alcohol (9.1 g, 90%) as a colorless oil (The chiral auxiliary was recovered from the silica gel column by eluting with 25% EtOAc in hexane). *R*<sub>f</sub> = 0.40 (9% EtOAc in hexane); [α]<sub>D</sub><sup>22</sup> +8.4 (*c* 2.0, CHCl<sub>3</sub>); IR (film) 3450 (br), 2956, 2930, 2888, 2858, 1472, 1255, 1100 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 5.58 (dt, *J* = 15.6, 6.8 Hz, 1H), 5.49 (dd, *J* = 15.6, 6.8 Hz, 1H), 4.00 (t, *J* = 6.8 Hz, 1H), 3.71 (ABqd, *J* = 10.8, 3.2 Hz, 1H), 3.64 (t, *J* = 6.4 Hz, 2H), 3.56 (ABqd, *J* = 10.8, 6.4 Hz, 1H), 2.26 (dt, *J* = 6.4, 6.4 Hz, 2H), 1.74–1.60 (m, 1H), 0.90 (d, *J* = 6.4 Hz, 3H), 0.89 (s, 18H), 0.08 (s, 3H), 0.05 (s, 6H), 0.03 (s, 3H) (the signal for OH not observed); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 134.1, 128.9, 79.8, 66.4, 62.9, 41.1, 36.0, 26.1 (×3), 26.0 (×3), 18.5, 18.2, 14.3, -3.6, -4.7, -5.2 (×2); HRMS (-CI) calcd for C<sub>20</sub>H<sub>43</sub>O<sub>3</sub>Si<sub>2</sub> (M-H<sup>+</sup>) 387.2751, found 387.2755.

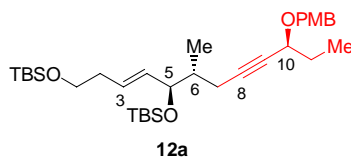
**(2*R*,3*S*,*E*)-3,7-Bis-[(*tert*-butyldimethylsilyl)oxy]-2-methylhept-4-en-1-yl Trifluoromethanesulfonate (10).**



To a solution of the primary alcohol (894.0 mg, 2.3 mmol) in anhydrous CH<sub>2</sub>Cl<sub>2</sub> (10 mL) cooled in a dry ice-acetone bath (-78 °C) were added dropwise 2,6-lutidine (0.41 mL, 3.5 mmol) and Tf<sub>2</sub>O (1.0 M in CH<sub>2</sub>Cl<sub>2</sub>, 2.8 mL, 2.8 mmol). The resulted mixture was stirred at the same temperature for 1 h. The reaction was quenched by saturated aqueous solution of NaHCO<sub>3</sub> and the reaction mixture was extracted with CH<sub>2</sub>Cl<sub>2</sub> (10 mL × 3). The combined organic layer was washed with brine, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered, and concentrated under reduced pressure. The residue was purified by filtering through a short pad of Celite and anhydrous Na<sub>2</sub>SO<sub>4</sub> with eluting with 10% EtOAc in hexanes. The combined filtrate was concentrated under reduced pressure and the residue was further dried under vacuum to give the triflate **10** (1.0 g, 85%) as a colorless oil. *R*<sub>f</sub> = 0.80 (9% EtOAc in hexane); [α]<sub>D</sub><sup>22</sup> +4.8 (*c* 1.0, CHCl<sub>3</sub>); IR (film) 2956, 2932, 2889, 2859, 1415, 1248, 1218, 1148 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 5.62 (dt, *J* = 15.2, 6.8 Hz, 1H), 5.40 (ddt, *J* = 15.6, 7.6, 1.2 Hz, 1H), 4.61 (ABqd, *J* = 9.6, 4.4 Hz, 1H), 4.50 (ABqd, *J* = 9.6, 6.4 Hz, 1H), 3.94 (dd, *J* = 7.2, 7.2 Hz, 1H), 3.67–3.61 (m, 2H), 2.26 (dtd, *J* = 6.8, 6.8, 1.2 Hz, 2H), 2.02–1.92 (m, 1H), 0.98 (d, *J* = 6.8 Hz, 3H), 0.89 (s, 9H), 0.88 (s, 9H), 0.05 (s, 6H), 0.04 (s, 3H), 0.01 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 132.6, 130.3, 118.8 (q, *J*<sub>C-F</sub> = 319.6 Hz), 79.6, 74.9, 62.8, 40.2, 36.0, 26.1 (×3), 25.9 (×3), 18.5, 18.2, 13.3, -3.7, -4.9, -5.2 (×2); HRMS (+CI) calcd for C<sub>21</sub>H<sub>44</sub>F<sub>3</sub>O<sub>5</sub>SSi<sub>2</sub> (M+H<sup>+</sup>) 521.2400, found 521.2416.

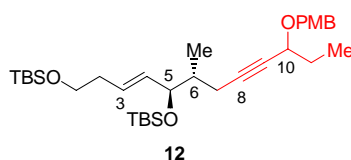
**E. Alkynylation of Alkyl Triflate 10.**

**(5*R*,6*R*,10*S*,*E*)-1,5-Bis-[(*tert*-Butyldimethylsilyl)oxy]-10-[(4'-methoxybenzyl)oxy]-6-methyldodec-3-en-8-yne (**12a**).**



To a solution of the alkyne (*S*)-**11** (70.0 mg,  $3.4 \times 10^{-1}$  mmol, 1.7 equiv) in anhydrous THF (3 mL) cooled in a dry ice–acetone bath at  $-78$  °C was added *n*-BuLi (2.0 M in cyclohexane, 0.15 mL, 0.3 mmol, 1.5 equiv) followed by stirring at the same temperature for 2 h. HMPA (0.14 mL, 0.8 mmol, 4.0 equiv) was added to the above solution and the resultant mixture was stirred at  $-78$  °C for 1 h to form the lithium acetylide. Then, a solution of the triflate **10** (100.0 mg, 0.2 mmol, 1.0 equiv) in anhydrous THF (2 mL) was added very slowly via a syringe to the lithium acetylide solution cooled at  $-78$  °C followed by stirring at the same temperature for 2 h. The reaction was then allowed to warm to room temperature within 1 h and was quenched by saturated aqueous solution of  $\text{NH}_4\text{Cl}$ . The reaction mixture was extracted with EtOAc (20 mL  $\times$  3) and the combined organic layer was washed with brine, dried over anhydrous  $\text{Na}_2\text{SO}_4$ , filtered, and concentrated under reduced pressure. The residue was purified by flash column chromatography (silica gel, eluting with 9% EtOAc in hexane) to afford **12a** (108.0 mg, 95%) as a pale-yellow oil.  $R_f = 0.85$  (9% EtOAc in hexane);  $[\alpha]_D^{20} -63.6$  (*c* 1.0,  $\text{CHCl}_3$ ); IR (film) 2956, 2930, 2857, 1514, 1463, 1250, 1099, 1062  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.33–7.28 (m, 2H), 6.91–6.87 (m, 2H), 5.57 (td,  $J = 15.6, 6.8$  Hz, 1H), 5.42 (dd,  $J = 15.6, 7.6$  Hz, 1H), 4.73 and 4.44 (d,  $J = 11.6$  Hz, 2H), 4.02–3.94 (m, 2H), 3.81 (s, 3H), 3.65 (td,  $J = 6.7, 1.6$  Hz, 2H), 2.36 (ABqdd,  $J = 16.4, 5.2, 2.0$  Hz, 1H), 2.29–2.21 (m, 3H), 1.80–1.68 (m, 3H), 1.00 (t,  $J = 7.2$  Hz, 3H), 0.96 (d,  $J = 6.8$  Hz, 3H), 0.90 (s, 9H), 0.90 (s, 9H), 0.06 (s, 9H), 0.02 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  159.3, 133.5, 130.6, 129.7 ( $\times 2$ ), 128.7, 113.9 ( $\times 2$ ), 85.4, 80.2, 76.8, 70.1, 70.0, 63.1, 55.4, 39.4, 36.1, 29.4, 26.1 ( $\times 3$ ), 26.1 ( $\times 3$ ), 22.0, 18.5, 18.3, 15.6, 10.0,  $-3.8, -4.7, -5.2$  ( $\times 2$ ); HRMS (+CI) calcd for  $\text{C}_{33}\text{H}_{62}\text{NO}_4\text{Si}_2$  ( $\text{M}+\text{NH}_4^+$ ) 592.4217, found 592.4220.

**Synthesis of **12**.**

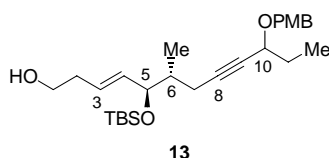


When (*rac*)-**11** was used instead of (*S*)-**11** in the alkylation of the triflate **10**, a 1:1 mixture of the two C10-epimers **12** was obtained as a pale-yellow oil.  $R_f = 0.85$  (9% EtOAc in hexane);  $[\alpha]_D^{22} +1.6$  (*c* 1.0,  $\text{CHCl}_3$ );  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  159.3, 133.5/133.5 (two epimers), 130.6, 129.7 ( $\times 2$ ), 128.7, 113.9 ( $\times 2$ ), 85.4, 80.2, 76.8 (overlapped with solvent residue peak), 70.1/70.1 (two epimers), 70.0/70.0 (two epimers), 63.1, 55.4, 39.4, 36.1, 29.4/29.4 (two epimers), 26.1 ( $\times 3$ ), 26.1 ( $\times 3$ ), 22.0, 18.5, 18.3, 15.7, 10.0,  $-3.8, -4.7, -5.1$  ( $\times 2$ ). IR,  $^1\text{H}$  NMR, and HRMS data of **12** are identical to those of **12a**.

**Alternative Procedure for Synthesis of 12.** An alternative procedure using a different addition order was tried but it gave a lower yield of the product. To a solution of the alkyne (*rac*)-**11** (388.0 mg, 1.9 mmol) in anhydrous THF (2 mL) cooled in a dry ice–acetone bath at  $-78\text{ }^{\circ}\text{C}$  was added *n*-BuLi (2.0 M in cyclohexane, 0.9 mL, 1.7 mmol) followed by stirring at the same temperature for 1 h, and then, allowing warm to room temperature to form the lithium acetylide. A separate flask was charged with the triflate **10** (500.0 mg,  $9.6 \times 10^{-1}$  mmol) and HMPA (0.7 mL, 3.8 mmol) in anhydrous THF (5 mL) and cooled in a dry ice–acetone bath at  $-78\text{ }^{\circ}\text{C}$ . To the mixture was added the above prepared lithium acetylide dropwise via a syringe followed by stirring at the same temperature for 2 h. The reaction was allowed to warm to room temperature within 1 h and quenched by saturated aqueous solution of  $\text{NH}_4\text{Cl}$ . The reaction mixture was extracted with EtOAc (30 mL  $\times$  3) and the combined organic layer was washed with brine, dried over anhydrous  $\text{Na}_2\text{SO}_4$ , filtered, and concentrated under reduced pressure. The residue was purified by flash column chromatography (silica gel, eluting with 5% EtOAc in hexane) to give a 50:50 mixture of the two C10-epimers **12** (286.0 mg, 52%) as a colorless oil.

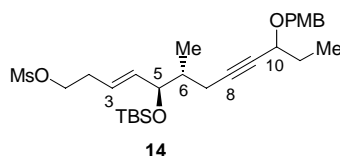
#### F. Synthesis of Bis-THF Compounds **23a** and **23b** (Method A).

**(5*R*,6*R*,10*R*,*E*)- and (5*R*,6*R*,10*S*,*E*)-5-[(*tert*-Butyldimethylsilyl)oxy]-10-[(4'-methoxybenzyl)oxy]-6-methyldodec-3-en-8-yn-1-ol (**13**).**



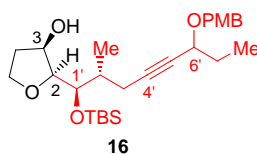
To a solution of the bis-TBS ether **12** (1.35 g, 2.3 mmol) in THF (10 mL) cooled in an ice–water bath at  $0\text{ }^{\circ}\text{C}$  was added a mixture of TBAF (1.0 M in THF, 7.0 mL, 7.0 mmol) and AcOH (0.4 mL, 7.0 mmol). The resultant mixture was then stirred at room temperature for 5 h. The reaction was quenched by saturated aqueous solution of  $\text{NaHCO}_3$  and the reaction mixture was extracted with  $\text{Et}_2\text{O}$  (20 mL  $\times$  3). The combined organic layer was washed with brine, dried over anhydrous  $\text{Na}_2\text{SO}_4$ , filtered, and concentrated under reduced pressure. The residue was purified by flash column chromatography (silica gel, eluting with 25% EtOAc in hexane) to give the primary alcohol **13** (1.01 g, 93%; a 50:50 mixture of two C10-epimers) as a colorless oil.  $R_f = 0.55$  (25% EtOAc in hexane);  $[\alpha]_D^{22} -6.8$  ( $c$  1.0,  $\text{CHCl}_3$ ); IR (film) 3421 (br), 2957, 2931, 2857, 1613, 1514, 1463, 1250, 1058  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.30–7.27 (m, 2H), 6.88–6.85 (m, 2H), 5.60–5.45 (m, 2H), 4.71 and 4.43 (ABq,  $J = 11.6$  Hz, 2H), 4.02–3.95 (m, 2H), 3.80 (s, 3H), 3.65 (t,  $J = 6.4$  Hz, 2H), 2.37–2.18 (m, 4H), 1.80–1.67 (m, 3H), 0.99 (t,  $J = 7.6$  Hz, 3H), 0.96 (d,  $J = 6.8$  Hz, 3H), 0.89 (s, 9H), 0.06 (s, 3H), 0.01 (s, 3H) (the signal for OH not observed);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  159.3, 134.7, 130.6, 129.7 ( $\times 2$ ), 127.9, 113.9 ( $\times 2$ ), 85.1, 80.4, 76.5, 70.1, 70.0, 62.2, 55.4, 39.3, 35.8, 29.3, 26.0 ( $\times 3$ ), 22.0, 18.3, 15.6, 10.0,  $-3.9$ ,  $-4.7$ ; HRMS ( $-\text{CI}$ ) calcd for  $\text{C}_{27}\text{H}_{44}\text{O}_4\text{Si}$  ( $M^-$ ) 460.3009, found 460.3013.

**(5*R*,6*R*,10*R*,*E*)- and (5*R*,6*R*,10*S*,*E*)-5-[(*tert*-Butyldimethylsilyl)oxy]-10-[(4'-methoxybenzyl)oxy]-6-methyldodec-3-en-8-ynyl Methanesulfonate (**14**).**



To a solution of the primary alcohol **13** (152.0 mg,  $3.3 \times 10^{-1}$  mmol) in anhydrous  $\text{CH}_2\text{Cl}_2$  (4 mL) cooled in an ice–water bath at 0 °C were added  $\text{Et}_3\text{N}$  (0.1 mL,  $6.6 \times 10^{-1}$  mmol) and  $\text{MsCl}$  (39  $\mu\text{L}$ ,  $5.0 \times 10^{-1}$  mmol) followed by stirring at the same temperature for 1 h. The reaction was quenched by saturated aqueous solution of  $\text{NaHCO}_3$  and the reaction mixture was extracted with  $\text{CH}_2\text{Cl}_2$  (10 mL  $\times$  3). The combined organic layer was washed with brine, dried over anhydrous  $\text{Na}_2\text{SO}_4$ , filtered, and concentrated under reduced pressure. The residue was purified by flash column chromatography (silica gel, eluting with 25%  $\text{EtOAc}$  in hexane) to give the mesylate **14** (165.0 mg, 92%; a 50:50 mixture of two C10-epimers) as a pale-yellow oil.  $R_f = 0.55$  (25%  $\text{EtOAc}$  in hexane); IR (film) 2957, 2932, 2857, 1613, 1514, 1463, 1359, 1249, 1176, 1061  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.30–7.26 (m, 2H), 6.90–6.86 (m, 2H), 5.60–5.45 (m, 2H), 4.71 and 4.43 (ABq,  $J = 11.2$  Hz, 2H), 4.23 (t,  $J = 6.4$  Hz, 2H), 4.04–3.95 (m, 2H), 3.80 (s, 3H), 2.99 (s, 3H), 2.50 (td,  $J = 6.0, 5.2$  Hz, 2H), 2.32 (ABqd,  $J = 16.4, 4.0$  Hz, 1H), 2.23 (ABqd,  $J = 16.8, 5.6$  Hz, 1H), 1.79–1.65 (m, 3H), 0.99 (t,  $J = 7.6$  Hz, 3H), 0.95 (d,  $J = 7.2$  Hz, 3H), 0.89 (s, 9H), 0.06 (s, 3H), 0.01 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  159.3, 135.7, 130.6, 129.7 ( $\times 2$ ), 125.4, 113.9 ( $\times 2$ ), 85.0, 80.5, 76.1, 70.1, 70.0, 68.8, 55.4, 39.3, 37.6, 32.2, 29.4, 26.0 ( $\times 3$ ), 22.0, 18.3, 15.6, 10.0, –3.9, –4.7; HRMS (–CI) calcd for  $\text{C}_{28}\text{H}_{46}\text{O}_6\text{SSi}$  ( $M^-$ ) 538.2784, found 538.2798.

**(1'*R*,2*S*,2'*R*,3*R*,6'*R*)- and (1'*R*,2*S*,2'*R*,3*R*,6'*S*)-2-{1'-[(*tert*-Butyldimethylsilyl)oxy]-6'-[(4''-methoxybenzyl)oxy]-2'-methyloct-4'-ynyl}tetrahydrofuran-3-ol (**16**).**

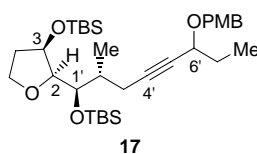


To a solution of the mesylate **14** (165.0 mg,  $3.0 \times 10^{-1}$  mmol) in *t*-BuOH and  $\text{H}_2\text{O}$  (v/v = 1:1, 3 mL) cooled in an ice–water bath at 0 °C were added  $\text{MeSO}_2\text{NH}_2$  (58.0 mg,  $6.0 \times 10^{-1}$  mmol) and  $(\text{DHQD})_2\text{PHAL}$  (38.0 mg,  $4.9 \times 10^{-2}$  mmol). Then,  $\text{K}_2\text{CO}_3$  (125.0 mg,  $9.0 \times 10^{-1}$  mmol),  $\text{K}_3\text{Fe}(\text{CN})_6$  (297.0 mg,  $9.0 \times 10^{-1}$  mmol) and  $\text{K}_2\text{OsO}_4 \cdot 2\text{H}_2\text{O}$  (4.5 mg,  $1.2 \times 10^{-2}$  mmol) were sequentially added. The resulted mixture was stirred at 0 °C for 18 h and then the reaction was quenched by  $\text{H}_2\text{O}$ . The reaction mixture was extracted with  $\text{EtOAc}$  (10 mL  $\times$  3) and the combined organic layer was washed with brine, dried over anhydrous  $\text{Na}_2\text{SO}_4$ , filtered, and concentrated under reduced pressure. The residue was passed through a short silica gel plug eluting with 50%  $\text{EtOAc}$  in hexane and the filtrate was concentrated under reduced pressure to give the crude diol

**15** (161.0 mg), which was used for the next step without further purification.

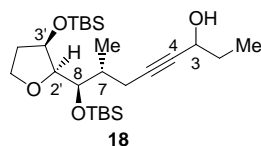
A solution of the above crude diol **15** (161.0 mg) in pyridine (3 mL) was heated at 90 °C for 4 h. After cooling to room temperature, pyridine in the reaction mixture was removed under vacuum pump pressure and the residue was purified by flash column chromatography (silica gel, eluting with 25% EtOAc in hexane) to give the THF product **16** (112.0 mg, 77% yield for two steps; a 50:50 mixture of two C6'-epimers) as a pale-yellow oil.  $R_f$  = 0.64 (25% EtOAc in hexane); IR (film) 3463 (br), 2956, 2933, 2857, 1613, 1514, 1463, 1249, 1069  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.30–7.26 (m, 2H), 6.90–6.85 (m, 2H), 4.71 and 4.42 (ABq,  $J$  = 11.2 Hz, 2H), 4.51–4.46 (m, 1H), 4.40 (d,  $J$  = 3.2 Hz, 1H, OH), 4.15–4.10 (m, 1H), 4.06 (ddd,  $J$  = 8.4, 8.0, 8.0 Hz, 1H), 3.99 (t,  $J$  = 6.4 Hz, 1H), 3.83 (ddd,  $J$  = 12.4, 8.4, 4.0 Hz, 1H), 3.80 (s, 3H), 3.66 (br s, 1H), 2.48 (ABqdd,  $J$  = 12.0, 4.8, 2.0 Hz, 1H), 2.40 (ABqd,  $J$  = 12.0, 6.0 Hz, 1H), 2.15–1.94 (m, 3H), 1.75–1.66 (m, 2H), 1.12 (d,  $J$  = 6.8 Hz, 3H), 0.99 (t,  $J$  = 7.6 Hz, 3H), 0.92 (s, 9H), 0.18 (s, 3H), 0.17 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  159.3, 130.5, 129.6 ( $\times 2$ ), 113.9 ( $\times 2$ ), 84.2, 81.3, 80.9, 76.1, 72.8, 70.1, 70.0/70.0 (two epimers), 66.0, 55.4, 36.8, 36.4, 29.3, 26.1 ( $\times 3$ ), 23.0, 18.4, 16.3, 10.0, –4.3, –4.8; HRMS (+CI) calcd for  $\text{C}_{27}\text{H}_{45}\text{O}_5\text{Si}$  ( $\text{M}+\text{H}^+$ ) 477.3036, found 477.3016.

**(1'R,2S,2'R,3R,6'R)- and (1'R,2S,2'R,3R,6'S)-3-[(tert-Butyldimethylsilyl)oxy]-2-{1'-[(tert-butylidimethylsilyl)oxy]-6'-[(4''-methoxybenzyl)oxy]-2'-methyloct-4'-ynyl}tetrahydrofuran (**17**).**



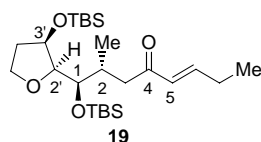
To a solution of the alcohol **16** (362.3 mg,  $7.6 \times 10^{-1}$  mmol) in anhydrous  $\text{CH}_2\text{Cl}_2$  (7 mL) cooled in a dry ice–acetone bath at  $-78$  °C was added 2,6-lutidine (177.0  $\mu\text{L}$ , 1.5 mmol) and TBSOTf (261.8  $\mu\text{L}$ , 1.1 mmol) followed by stirring at same temperature for 2 h. The reaction was quenched by saturated aqueous solution of  $\text{NaHCO}_3$  (5 mL) and the reaction mixture was extracted by  $\text{CH}_2\text{Cl}_2$  (10 mL  $\times 3$ ). The combined organic layer was washed with brine, dried over anhydrous  $\text{Na}_2\text{SO}_4$ , filtered, and concentrated under reduced pressure. The residue was purified by flash column chromatography (silica gel, eluting with 9% EtOAc in hexane) to give the bis-TBS ether **17** (426.7 mg, 95%; a 50:50 mixture of two C6'-epimers) as a pale-yellow oil.  $R_f$  = 0.88 (25% EtOAc in hexane); IR (film) 2956, 2931, 2857, 1513, 1250, 1074, 1040  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.32–7.28 (m, 2H), 6.89–6.86 (m, 2H), 4.73 and 4.45 (ABq,  $J$  = 11.6 Hz, 2H), 4.41–4.37 (m, 1H), 4.03–3.93 (m, 3H), 3.80 (s, 3H), 3.77 (ddd,  $J$  = 12.4, 8.4, 4.0 Hz, 1H), 3.58 (dd,  $J$  = 4.8, 4.0 Hz, 1H), 2.66 (ABq,  $J$  = 16.4 Hz, 1H), 2.24 (ABqd,  $J$  = 16.4, 10.4 Hz, 1H), 2.19–1.73 (m, 5H), 1.12 (d,  $J$  = 6.8 Hz, 3H), 0.99 (t,  $J$  = 7.6 Hz, 3H), 0.92 (s, 9H), 0.91 (s, 9H), 0.12 (s, 6H), 0.10 (s, 3H), 0.08 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  159.2, 130.8, 129.7 ( $\times 2$ ), 113.8 ( $\times 2$ ), 87.2/87.2 (two epimers), 86.5, 79.2/79.2 (two epimers), 73.1, 72.9, 70.1, 69.8, 65.8, 55.3, 37.0/36.9 (two epimers), 35.6, 29.4, 26.2 ( $\times 3$ ), 26.1 ( $\times 3$ ), 21.2, 18.4, 18.3, 17.1/17.1 (two epimers), 10.0, –3.7, –3.7, –4.3, –4.3; HRMS (+CI) calcd for  $\text{C}_{33}\text{H}_{62}\text{NO}_5\text{Si}_2$  ( $\text{M}+\text{NH}_4^+$ ) 608.4167, found 608.4144.

**(2'S,3R,3'R,7R,8R)- and (2'S,3S,3'R,7R,8R)-8-[(*tert*-Butyldimethylsilyl)oxy]-8-{3'-[(*tert*-butyldimethylsilyl)oxy]tetrahydrofuran-2-yl}-7-methyloct-4-yn-3-ol (**18**).**



To a solution of the PMB ether **17** (426.7 mg,  $7.2 \times 10^{-1}$  mmol) in  $\text{CH}_2\text{Cl}_2$  (7 mL) cooled in an ice–water bath at 0 °C were added pH 7.0 buffer (7 mL) and DDQ (326.9 mg,  $14.4 \times 10^{-1}$  mmol). The resultant mixture was stirred at the same temperature for 2 h and the reaction was quenched by saturated aqueous solution of  $\text{NaHCO}_3$ . The reaction mixture was extracted with  $\text{CH}_2\text{Cl}_2$  (20 mL  $\times$  3) and the combined organic layer was washed with brine, dried over anhydrous  $\text{Na}_2\text{SO}_4$ , filtered, and concentrated under reduced pressure. The residue was purified by flash column chromatography (silica gel, eluting with 10% EtOAc in hexane) to give the alcohol **18** (308.5 mg, 91%; a 50:50 mixture of two C3 epimers) as a pale-yellow oil.  $R_f$  = 0.76 (25% EtOAc in hexane); IR (film) 3377 (br), 2957, 2931, 2858, 1463, 1255, 1190, 1137, 1078  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  4.38–4.34 (m, 1H), 4.32–4.25 (m, 1H), 3.97 (dd,  $J$  = 4.8, 2.0 Hz, 1H), 3.93 (ddd,  $J$  = 8.4, 8.4, 7.2 Hz, 1H), 3.75 (ddd,  $J$  = 12.4, 8.4, 4.4 Hz, 1H), 3.54 (dd,  $J$  = 5.2, 3.6 Hz, 1H), 2.60 (ddd,  $J$  = 16.8, 4.4, 2.0 Hz, 1H), 2.17 (ddd,  $J$  = 16.8, 9.6, 1.6 Hz, 1H), 2.10–1.85 (m, 3H), 1.74 (dd,  $J$  = 5.2, 2.4 Hz, 1H), 1.70 (d,  $J$  = 2.4 Hz, 1H, OH), 1.67 (dd,  $J$  = 8.8, 2.4 Hz, 1H), 1.05 (d,  $J$  = 7.6 Hz, 3H), 0.99 (t,  $J$  = 7.6 Hz, 3H), 0.90 (s, 9H), 0.87 (s, 9H), 0.10 (s, 6H), 0.07 (s, 3H), 0.05 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  86.5, 86.3, 81.3/81.3 (two epimers), 72.9, 72.8, 65.8, 64.2, 36.9/36.9 (two epimers), 35.5, 31.4, 26.1 ( $\times$ 3), 26.1 ( $\times$ 3), 21.1/21.1 (two epimers), 18.4, 18.3, 16.9/16.9 (two epimers), 9.6, –3.6, –3.7, –4.2, –4.3; HRMS (+CI) calcd for  $\text{C}_{25}\text{H}_{51}\text{O}_4\text{Si}_2$  ( $\text{M}+\text{H}^+$ ) 471.3326, found 471.3307.

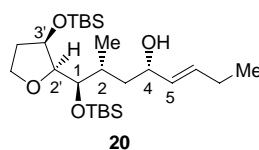
**(1R,2R,2'S,3'R,E)-1-[(*tert*-Butyldimethylsilyl)oxy]-1-{3'-[(*tert*-butyldimethylsilyl)-oxy]tetrahydrofuran-2'-yl]-2-methyloct-5-en-4-one (**19**).**



To a solution of the propargyl alcohol **18** (308.5 mg,  $6.6 \times 10^{-1}$  mmol) in degassed anhydrous PhMe (4 mL) at room temperature, was added a solution of  $(\text{Ph}_3\text{PAuNTf}_2)_2 \cdot \text{PhMe}$  (10.4 mg,  $6.6 \times 10^{-3}$  mmol, 2.0 mol% Au) in degassed anhydrous PhMe (2.5 mL) via a syringe, followed by the addition of anhydrous MeOH (19.5  $\mu\text{L}$ ,  $6.6 \times 10^{-1}$  mmol). The resultant mixture was stirred at room temperature for 12 h and the reaction mixture was concentrated under reduced pressure. The residue was purified by flash column chromatography (silica gel, eluting with 9% EtOAc in hexane) to give the enone **19** (236.2 mg, 76%) as a pale-yellow oil.  $R_f$  = 0.58 (9% EtOAc in hexane);  $[\alpha]_D^{22}$  –22.7 ( $c$  1.0,  $\text{CHCl}_3$ ); IR (film) 2957, 2930, 2857,

1675, 1629, 1472, 1462, 1255, 1078  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  6.92 (dt,  $J = 16.0, 6.4$  Hz, 1H), 6.09 (dt,  $J = 16.0, 1.6$  Hz, 1H), 4.38–4.35 (m, 1H), 3.96–3.88 (m, 2H), 3.76 (ddd,  $J = 12.8, 8.4, 4.4$  Hz, 1H), 3.61 (dd,  $J = 4.4, 4.0$  Hz, 1H), 3.08 (ABqd,  $J = 15.6, 3.6$  Hz, 1H), 2.50–2.41 (m, 1H), 2.33 (ABqd,  $J = 15.6, 9.6$  Hz, 1H), 2.26–2.18 (m, 2H), 2.05–1.86 (m, 2H), 1.07 (t,  $J = 7.2$  Hz, 3H), 0.94 (d,  $J = 6.8$  Hz, 3H), 0.90 (s, 9H), 0.89 (s, 9H), 0.10 (s, 3H), 0.09 (s, 3H), 0.09 (s, 3H), 0.07 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  202.1, 148.2, 130.2, 87.0, 73.8, 73.0, 65.9, 43.0, 35.5, 33.2, 26.2 ( $\times 3$ ), 26.1 ( $\times 3$ ), 25.6, 18.4, 18.2, 17.6, 12.5, -3.8, -3.9, -4.2, -4.3; HRMS ( $-\text{CI}$ ) calcd for  $\text{C}_{25}\text{H}_{49}\text{O}_4\text{Si}_2$  ( $\text{M}-\text{H}^+$ ) 469.3169, found 469.3157.

**(1*R*,2*R*,2'*S*,3'*R*,4*S*,*E*)-1-[(*tert*-Butyldimethylsilyl)oxy]-1-{3'-[(*tert*-butyldimethylsilyl)oxy]tetrahydrofuran-2'-yl]-2-methyloct-5-en-4-ol (20).**

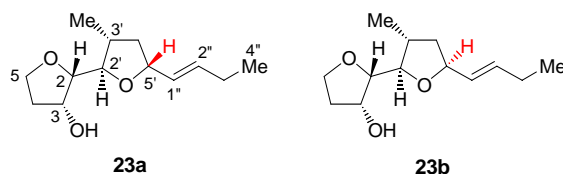


(*R*)-2-Methyl-CBS-oxazaborolidine (138.9 mg,  $5.0 \times 10^{-1}$  mmol) was charged into to a flame-dried flask in a glove box under a nitrogen atmosphere and the loaded flask was sealed with a silicon septum. The sealed flask was relocated to a fumehood and anhydrous THF (3 mL) was added in via a syringe at room temperature to dissolve the solid. The resultant solution was then cooled in an ice-salt water bath ( $-10$   $^{\circ}\text{C}$ ) followed by slowly adding a solution of the enone **19** (236.2 mg,  $5.0 \times 10^{-1}$  mmol) in anhydrous THF (2 mL) via a syringe. To the above mixture was then added  $\text{BH}_3 \cdot \text{THF}$  (1.0 M in THF, 0.6 mL,  $6.0 \times 10^{-1}$  mmol) dropwise followed by stirring at the same temperature for 1 h. The reaction was quenched by addition of MeOH (2 mL) and the reaction mixture was concentrated under reduced pressure. The residue was purified by flash column chromatography (silica gel, eluting with 10% EtOAc in hexane) to give the allylic alcohol **20** (212.8 mg, 90%; as an 87:13 mixture of C4-epimers) as a pale-yellow oil.  $R_f = 0.79$  (25% EtOAc in hexane);  $[\alpha]_D^{22} -29.8$  ( $c$  1.0,  $\text{CHCl}_3$ ); IR (film) 3449 (br), 2958, 2930, 2857, 1632, 1462, 1255, 1076  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  5.68 (dt,  $J = 15.2, 6.4$  Hz, 1H), 5.45 (dd,  $J = 15.2, 6.8$  Hz, 1H), 4.35 (br s, 1H), 4.23–4.16 (m, 1H), 4.01 (d,  $J = 6.0$  Hz, 1H), 3.94 (ddd,  $J = 8.8, 7.6, 7.6$  Hz, 1H), 3.81 (ddd,  $J = 12.0, 8.8, 4.0$  Hz, 1H), 3.58 (dd,  $J = 6.0, 2.8$  Hz, 1H), 3.19 (br s, 0.87H, OH for the major epimer), 3.10 (br s, 0.13H, OH for minor epimer), 2.08–1.80 (m, 6H), 1.48–1.40 (m, 1H), 1.01–0.96 (m, 6H), 0.90 (s, 9H), 0.88 (s, 9H), 0.10 (s, 6H), 0.07–0.05 (m, 6H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  132.5, 132.4, 87.4, 73.5, 72.5, 71.1, 65.7, 40.1, 35.3, 32.2, 26.1 ( $\times 6$ ), 25.4, 19.3, 18.4, 18.3, 13.6, -3.5, -3.8, -4.1 ( $\times 2$ ); HRMS ( $-\text{CI}$ ) calcd for  $\text{C}_{25}\text{H}_{51}\text{O}_4\text{Si}_2$  ( $\text{M}-\text{H}^+$ ) 471.3326, found 471.3308.

## **$\text{S}_{\text{N}}2$ Cyclization of the Enantiomerically Pure Allylic Mesylate **21**.**

**(2*S*,2'*R*,3*R*,3'*R*,5'*R*,*E*)-5'-(But-1''-enyl)-3'-methyloctahydro[2,2']bifuran-3-ol (23a) and**

**(2*S*,2'*R*,3*R*,3'*R*,5'*S*,*E*)-5'-(But-1''-enyl)-3'-methyloctahydro[2,2']bifuran-3-ol (23b).**

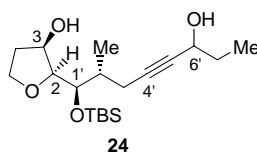


To a solution of the allylic alcohol **20** (47.3 mg,  $1.0 \times 10^{-1}$  mmol) in anhydrous  $\text{CH}_2\text{Cl}_2$  (1 mL) cooled in an ice–water bath ( $0^\circ\text{C}$ ) was added (*i*-Pr) $_2\text{NEt}$  (41.3  $\mu\text{L}$ ,  $2.5 \times 10^{-1}$  mmol) and  $\text{MsCl}$  (15.5  $\mu\text{L}$ ,  $2.0 \times 10^{-1}$  mmol) followed by stirring at the same temperature for 4 h. The reaction was quenched by adding saturated aqueous  $\text{NaHCO}_3$  (10 mL) and the reaction mixture was extracted with  $\text{CH}_2\text{Cl}_2$  (10 mL  $\times$  3). The combined organic layer was washed with brine, dried over anhydrous  $\text{Na}_2\text{SO}_4$ , filtered, and concentrated under reduced pressure. The residue (crude allylic mesylate **21**) was used directly for the next step without column chromatographic purification.

To a solution of the crude allylic mesylate **21** obtained above in THF (0.5 mL) cooled in an ice–water bath ( $0^\circ\text{C}$ ) was added HF·pyridine complex (0.72 mL, 80.0 mmol) followed by stirring at room temperature for 10 h. The reaction was quenched by saturated aqueous  $\text{NaHCO}_3$  (5 mL) and the reaction mixture was extracted by  $\text{Et}_2\text{O}$  (10 mL  $\times$  3). The combined organic layer was washed with brine, dried over anhydrous  $\text{Na}_2\text{SO}_4$ , filtered, and concentration under reduced pressure. The residue was purified by flash column chromatography (silica gel, eluting with 25%  $\text{EtOAc}$  in hexane) to give an inseparable mixture of the two epimeric bis-THF products **23a** and **23b** (12.7 mg, 56% for 2 steps; a 40:60 mixture of **23a** and **23b**) as a colorless oil.  $R_f = 0.38$  (25%  $\text{EtOAc}$  in hexane);  $[\alpha]_D^{22} -17.3$  ( $c$  0.7,  $\text{CHCl}_3$ ); IR (film) 3442 (br), 2960, 2928, 2875, 1460, 1376, 1068  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ; a 40:60 mixture of **23a** and **23b**)  $\delta$  5.73–5.63 (m, 1H), 5.43 (dd,  $J = 15.2, 7.6$  Hz, 0.4H for **23a**), 5.39 (dd,  $J = 15.2, 7.2$  Hz, 0.6H for **23b**), 4.52–4.47 (m, 1H), 4.41–4.33 (m, 1H), 4.07 (ddd,  $J = 8.4, 8.4, 7.2$  Hz, 1H), 3.90–3.80 (m, 1H), 3.78 (dd,  $J = 7.2, 7.2$  Hz, 0.4H for **23a**), 3.70 (dd,  $J = 7.2, 6.0$  Hz, 0.6H for **23b**), 3.63 (dd,  $J = 7.2, 3.6$  Hz, 0.4H for **23a**), 3.60 (dd,  $J = 7.6, 4.0$  Hz, 0.6H for **23b**), 2.32–2.20 (m, 2H), 2.14–1.94 (m, 4.6H), 1.45–1.35 (m, 0.4H for **23a**), 1.14 (d,  $J = 7.6$  Hz, 1.2H for **23a**), 1.12 (d,  $J = 6.8$  Hz, 1.8H for **23b**), 0.98 (t,  $J = 7.2$  Hz, 3H) (the signal for *OH* not observed);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ; a 40:60 mixture of **23a** and **23b**)  $\delta$  the signals assigned for the minor epimer **23a**: 134.8, 129.9, 84.6, 83.6, 80.4, 72.9, 67.1, 42.4, 39.9, 35.1, 25.3, 17.5, 13.4; the signals assigned for the major epimer **23b**: 134.9, 129.7, 84.7 ( $\times 2$ ), 79.6, 72.9, 67.2, 40.4, 37.7, 35.1, 25.3, 18.7, 13.5; HRMS (+CI) calcd for  $\text{C}_{13}\text{H}_{23}\text{O}_3$  ( $\text{M}+\text{H}^+$ ) 227.1647, found 227.1639.

### G. Synthesis of Bis-THF Compounds **23a** and **23b** (Method B).

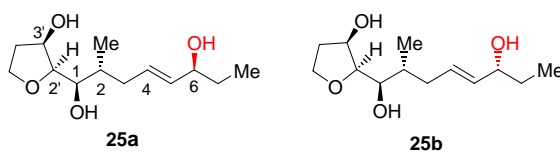
(1'*R*,2*S*,2'*R*,3*R*,6'*R*)- and (1'*R*,2*S*,2'*R*,3*R*,6'*S*)-2-{1'-[(*tert*-Butyldimethylsilyloxy)]-6'-hydroxy-2'-methyloct-4'-ynyl}tetrahydrofuran-3-ol (**24**).





To a solution of the PMB ether **16** (112.0 mg,  $2.4 \times 10^{-1}$  mmol) in  $\text{CH}_2\text{Cl}_2$  (2 mL) cooled in an ice–water bath at 0 °C were added pH 7.0 buffer (2 mL) and DDQ (107.0 mg,  $4.7 \times 10^{-1}$  mmol). The resultant mixture was stirred at the same temperature for 2 h and the reaction was quenched by saturated aqueous solution of  $\text{NaHCO}_3$ . The reaction mixture was extracted with  $\text{CH}_2\text{Cl}_2$  (5 mL  $\times$  3) and the combined organic layer was washed with brine, dried over anhydrous  $\text{Na}_2\text{SO}_4$ , filtered, and concentrated under reduced pressure. The residue was purified by flash column chromatography (silica gel, eluting with 10% EtOAc in hexane) to give the diol **24** (74.0 mg, 88%; a 50:50 mixture of two C6' epimers) as a colorless oil.  $R_f = 0.31$  (25% EtOAc in hexane);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ; a 50:50 mixture of two C6' epimers)  $\delta$  4.50–4.45 (m, 1H), 4.40 (d,  $J = 3.2$  Hz, 1H, OH), 4.33–4.27 (m, 1H), 4.09 (dd,  $J = 7.2, 3.2$  Hz, 1H), 4.04 (ddd,  $J = 8.8, 8.0, 8.0$  Hz, 1H), 3.84 (ddd,  $J = 12.4, 8.4, 4.0$  Hz, 1H), 3.64 (dd,  $J = 3.2, 3.2$  Hz, 1H), 2.43 (ABqdd,  $J = 16.4, 5.2, 2.0$  Hz, 1H), 2.31 (ABqdd,  $J = 16.8, 7.2, 1.6$  Hz, 1H), 2.12–1.97 (m, 3H), 1.94–1.87 (m, 1H, OH), 1.74–1.63 (m, 2H), 1.08 (d,  $J = 6.8$  Hz, 3H), 1.00 (t,  $J = 7.6$  Hz, 3H), 0.90 (s, 9H), 0.17 (s, 3H), 0.14 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ; a 50:50 mixture of two C6' epimers)  $\delta$  83.5, 83.3, 80.9, 76.1, 72.8, 66.0, 64.1, 36.8, 36.4, 31.3, 26.1 ( $\times 3$ ), 23.0, 18.4, 16.3, 9.7, –4.2, –4.9. The IR and HRMS data of **24** (a 50:50 mixture of two C6' epimers) are identical to those of **24a** given below.

**(1R,2R,2'S,3'R,6S,E)- and (1R,2R,2'S,3'R,6R,E)-1-(3'-Hydroxytetrahydrofuran-2'-yl)-2-methyloct-4-ene-1,6-diol (25a and 25b).**

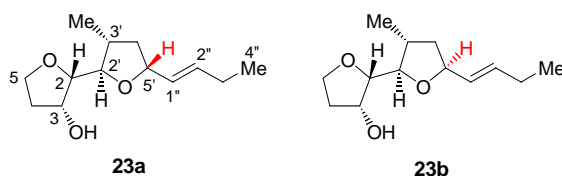


To a solution of the propargyl alcohol **24** (28.0 mg,  $7.9 \times 10^{-2}$  mmol) in anhydrous THF (4 mL) cooled in an ice–water bath at 0 °C was added slowly Red-Al (3.5 M in toluene, 0.1 mL,  $3.2 \times 10^{-1}$  mmol). The resultant mixture was heated at 40 °C for 3 h and then stirred at room temperature for 15 h. The reaction was quenched by slowly adding saturated aqueous solution of potassium sodium tartrate followed by stirring for 10 min. The reaction mixture was extracted with EtOAc (10 mL  $\times$  3) and the combined organic layer was washed with brine, dried over anhydrous  $\text{Na}_2\text{SO}_4$ , filtrated, and concentrated under reduced pressure. The residue was purified by flash column chromatography (silica gel, eluting with 10% MeOH in  $\text{CH}_2\text{Cl}_2$ ) to give the triols **25a** and **25b** (17.0 mg, 90%; a 50:50 mixture of two C6 epimers) as a colorless oil.  $R_f = 0.37$  (9% MeOH in  $\text{CH}_2\text{Cl}_2$ );  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ; a 50:50 mixture of two C6 epimers)  $\delta$  5.72–5.61 (m, 1H), 5.57–5.47 (m, 1H), 4.52 (br s, 1H), 4.11 (td,  $J = 8.0, 7.6$  Hz, 1H), 4.00 (ddd,  $J = 6.8, 6.4, 6.4$  Hz, 1H), 3.90 (ddd,  $J = 12.0, 8.4, 3.6$  Hz, 1H), 3.81 (dd,  $J = 6.4, 5.6$  Hz, 1H), 3.72 (dd,  $J = 4.8, 3.2$  Hz, 1H), 3.64 (br s, 1H, OH), 2.70 (br s, 1H, OH), 2.52–2.40 (m, 1H), 2.15–1.93 (m, 4H), 1.63–1.45 (m, 2H), 0.97 (d,  $J = 6.4$  Hz, 1.5H for **25b**), 0.96 (d,  $J = 6.8$  Hz, 1.5H for **25a**), 0.91 (t,  $J = 7.6$  Hz, 3H) (the signal for one OH not observed);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ; a 50:50 mixture of two C6 epimers)  $\delta$  135.2, 130.0, 81.8, 75.2, 74.6, 72.8, 66.8, 36.1, 35.7, 35.3, 30.3, 15.9, 9.9. The IR and HRMS data of a 50:50 mixture of two C6' epimers **25a** and **25b** are identical to those of **25a** given below.

### Intramolecular *syn*-Oxypalladation of Allylic Alcohols **25a** and **25b**.

(2*S*,2'*R*,3*R*,3'*R*,5'*R*,*E*)-5'-(But-1''-enyl)-3'-methyloctahydro[2,2']bifuran-3-ol (**23a**) and

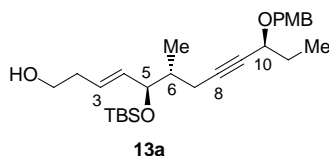
(2*S*,2'*R*,3*R*,3'*R*,5'*S*,*E*)-5'-(But-1''-enyl)-3'-methyloctahydro[2,2']bifuran-3-ol (**23b**).



A solution of the 50:50 epimeric mixture of the allylic alcohols **25a** and **25b** (10.0 mg,  $4.1 \times 10^{-2}$  mmol) and  $\text{PdCl}_2(\text{PhCN})_2$  (1.5 mg,  $4.0 \times 10^{-3}$  mmol) in anhydrous THF (0.5 mL) cooled in an ice–water bath at 0 °C was stirred for 2 h. The reaction mixture was diluted with hexane (5 mL) and filtered through a short pad of Celite with washing by EtOAc. The combined filtrate was concentrated under reduced pressure and the residue was purified by flash column chromatography (silica gel, eluting with 25% EtOAc in hexane) to give an inseparable mixture of the two epimeric bis-THF products **23a** and **23b** (8.0 mg, 86%; a 60:40 mixture of **23a** and **23b**) as a colorless oil.  $R_f = 0.38$  (25% EtOAc in hexane);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ; a 60:40 mixture of **23a** and **23b**)  $\delta$  5.73–5.63 (m, 1H), 5.43 (dd,  $J = 15.2, 7.6$  Hz, 0.6H for **23a**), 5.40 (dd,  $J = 15.2, 7.2$  Hz, 0.4H for **23b**), 4.53–4.47 (m, 1H), 4.42–4.34 (m, 1H), 4.07 (ddd,  $J = 8.0, 8.0, 7.6$  Hz, 1H), 3.90–3.80 (m, 1H), 3.78 (dd,  $J = 7.2, 7.2$  Hz, 0.6H for **23a**), 3.71 (dd,  $J = 7.6, 6.0$  Hz, 0.4H for **23b**), 3.63 (dd,  $J = 7.2, 3.6$  Hz, 0.6H for **23a**), 3.60 (dd,  $J = 7.6, 3.6$  Hz, 0.4H for **23b**), 3.26 (br s, 0.6H for **23a**, OH), 3.13 (br s, 0.4H for **23b**, OH), 2.32–2.20 (m, 2H), 2.14–1.94 (m, 4.4H), 1.45–1.35 (m, 0.6H for **23a**), 1.14 (d,  $J = 6.0$  Hz, 1.8H for **23a**), 1.13 (d,  $J = 7.2$  Hz, 1.2H for **23b**), 0.98 (t,  $J = 7.6$  Hz, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ; a 60:40 mixture of **23a** and **23b**)  $\delta$  the signals observed for the major epimer **23a**: 134.8, 129.9, 84.6, 83.6, 80.4, 73.0, 67.1, 42.4, 39.9, 35.1, 25.3, 17.5, 13.4; the signals assigned for the minor epimer **23b**: 134.9, 129.7, 84.7 ( $\times 2$ ), 79.6, 72.9, 67.2, 40.5, 37.7, 35.1, 25.3, 18.7, 13.5. The IR and HRMS data of a 60:40 mixture of **23a** and **23b** are identical to the sample obtained by Method A as described above.

### H. Synthesis of Bis-THF Compounds **23a** (Method C).

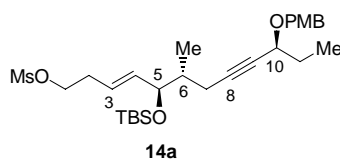
(5*R*,6*R*,10*S*,*E*)-5-[(*tert*-Butyldimethylsilyl)oxy]-10-[(4'-methoxybenzyl)oxy]-6-methyldodec-3-en-8-yn-1-ol (**13a**).



To a solution of the bis-TBS ether **12a** (2.70 g, 4.7 mmol) in THF (20 mL) cooled in an ice–water bath at 0 °C was added a mixture of TBAF (1.0 M in THF, 14.1 mL, 14.1 mmol) and AcOH (0.8 mL, 14.1 mmol).

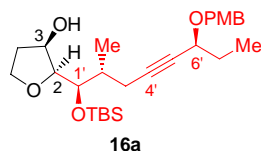
The resultant mixture was then stirred at room temperature for 6 h. The reaction was quenched by saturated aqueous solution of NaHCO<sub>3</sub> and the reaction mixture was extracted with Et<sub>2</sub>O (40 mL × 3). The combined organic layer was washed with brine, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered, and concentrated under reduced pressure. The residue was purified by flash column chromatography (silica gel, eluting with 25% EtOAc in hexane) to give the primary alcohol **13a** (1.75 g, 81%) as a colorless oil. *R<sub>f</sub>* = 0.55 (25% EtOAc in hexane); [α]<sub>D</sub><sup>22</sup> -77.1 (*c* 1.0, CHCl<sub>3</sub>); IR (film) 3416 (br), 2957, 2931, 2857, 1613, 1514, 1463, 1250, 1058 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.30–7.27 (m, 2H), 6.88–6.86 (m, 2H), 5.59–5.46 (m, 2H), 4.71 and 4.43 (ABq, *J* = 11.2 Hz, 2H), 4.01–3.96 (m, 2H), 3.80 (s, 3H), 3.66 (dt, *J* = 6.4, 6.0 Hz, 2H), 2.37–2.20 (m, 4H), 1.80–1.67 (m, 3H), 1.38 (t, *J* = 6.0 Hz, 1H, OH), 0.99 (t, *J* = 7.6 Hz, 3H), 0.96 (d, *J* = 6.8 Hz, 3H), 0.89 (s, 9H), 0.06 (s, 3H), 0.01 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 159.3, 134.8, 130.6, 129.7 (×2), 127.9, 113.9 (×2), 85.2, 80.4, 76.5, 70.1, 70.0, 62.2, 55.4, 39.3, 35.8, 29.4, 26.0 (×3), 22.0, 18.3, 15.6, 10.0, -3.9, -4.7; HRMS data of **13a** are identical to those of **13**.

**(5*R*,6*R*,10*S*,*E*)-5-[(*tert*-Butyldimethylsilyl)oxy]-10-[(4'-methoxybenzyl)oxy]-6-methyldodec-3-en-8-ynyl Methanesulfonate (**14a**).**



To a solution of the primary alcohol **13a** (304.0 mg, 6.6 × 10<sup>-1</sup> mmol) in anhydrous CH<sub>2</sub>Cl<sub>2</sub> (7 mL) cooled in an ice–water bath at 0 °C were added Et<sub>3</sub>N (0.18 mL, 13.2 × 10<sup>-1</sup> mmol) and MsCl (77 μL, 9.9 × 10<sup>-1</sup> mmol) followed by stirring at the same temperature for 2 h. The reaction was quenched by saturated aqueous solution of NaHCO<sub>3</sub> and the reaction mixture was extracted with CH<sub>2</sub>Cl<sub>2</sub> (20 mL × 3). The combined organic layer was washed with brine, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered, and concentrated under reduced pressure. The residue was purified by flash column chromatography (silica gel, eluting with 25% EtOAc in hexane) to give the mesylate **14a** (331.0 mg, 93%) as a pale-yellow oil. *R<sub>f</sub>* = 0.55 (25% EtOAc in hexane); [α]<sub>D</sub><sup>20</sup> -79.9 (*c* 1.0, CHCl<sub>3</sub>); IR (film) 2958, 2933, 2857, 1613, 1514, 1464, 1359, 1250, 1176, 1063 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.30–7.26 (m, 2H), 6.89–6.86 (m, 2H), 5.55–5.29 (m, 2H), 4.71 and 4.43 (ABq, *J* = 11.2 Hz, 2H), 4.23 (t, *J* = 6.4 Hz, 2H), 4.02–3.97 (m, 2H), 3.80 (s, 3H), 2.99 (s, 3H), 2.50 (td, *J* = 6.4, 5.2 Hz, 2H), 2.32 (ABqdd, *J* = 16.8, 5.6, 2.0 Hz, 1H), 2.24 (ABqdd, *J* = 16.8, 7.2, 1.2 Hz, 1H), 1.79–1.66 (m, 3H), 0.99 (t, *J* = 7.2 Hz, 3H), 0.95 (d, *J* = 7.2 Hz, 3H), 0.89 (s, 9H), 0.06 (s, 3H), 0.00 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 159.3, 135.7, 130.5, 129.6 (×2), 125.3, 113.8 (×2), 85.0, 80.4, 76.1, 70.0, 70.0, 68.8, 55.4, 39.3, 37.6, 32.2, 29.3, 26.0 (×3), 21.9, 18.3, 15.5, 10.0, -3.9, -4.7; HRMS data of **14a** are identical to those of **14**.

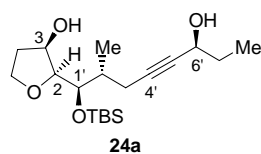
**(1'*R*,2*S*,2'*R*,3*R*,6'*S*)-2-{1'-[(*tert*-Butyldimethylsilyl)oxy]-6'-[(4''-methoxybenzyl)oxy]-2'-methyloct-4'-ynyl}tetrahydrofuran-3-ol (**16a**).**



To a solution of the mesylate **14a** (330.0 mg,  $6.1 \times 10^{-1}$  mmol) in *t*-BuOH and H<sub>2</sub>O (v/v = 1:1, 6 mL) cooled in an ice–water bath at 0 °C were added MeSO<sub>2</sub>NH<sub>2</sub> (116.0 mg,  $12.0 \times 10^{-1}$  mmol) and (DHQD)<sub>2</sub>PHAL (76.0 mg,  $9.8 \times 10^{-2}$  mmol). Then, K<sub>2</sub>CO<sub>3</sub> (249.0 mg,  $18.0 \times 10^{-1}$  mmol), K<sub>3</sub>Fe(CN)<sub>6</sub> (593.0 mg,  $18.0 \times 10^{-1}$  mmol) and K<sub>2</sub>OsO<sub>4</sub>·2H<sub>2</sub>O (9.0 mg,  $2.4 \times 10^{-2}$  mmol) were sequentially added. The resulted mixture was stirred at 0 °C for 18 h and then the reaction was quenched by H<sub>2</sub>O. The reaction mixture was extracted with EtOAc (10 mL × 3) and the combined organic layer was washed with brine, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered, and concentrated under reduced pressure. The residue was passed through a short silica gel plug eluting with 50% EtOAc in hexane and the filtrate was concentrated under reduced pressure to give the crude diol **15a** (321.0 mg), which was used for the next step without further purification.

A solution of the above crude diol **15a** (321.0 mg) in pyridine (3 mL) was heated at 90 °C for 4 h. After cooling to room temperature, pyridine in the reaction mixture was removed under vacuum pump pressure and the residue was purified by flash column chromatography (silica gel, eluting with 25% EtOAc in hexane) to give the THF product **16a** (224.0 mg, 77% yield for two steps) as a pale-yellow oil.  $R_f$  = 0.64 (25% EtOAc in hexane);  $[\alpha]_D^{20}$  –80.4 (*c* 1.0, CHCl<sub>3</sub>); IR (film) 3465 (br), 2956, 2933, 2857, 1613, 1514, 1463, 1249, 1069 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.30–7.26 (m, 2H), 6.89–6.86 (m, 2H), 4.71 and 4.42 (ABq, *J* = 11.6 Hz, 2H), 4.50–4.48 (m, 1H), 4.44 (d, *J* = 4.0 Hz, 1H, OH), 4.13 (dd, *J* = 7.6, 3.2 Hz, 1H), 4.06 (dd, *J* = 8.4, 8.0, 8.0 Hz, 1H), 3.98 (t, *J* = 6.8 Hz, 1H), 3.84 (ddd, *J* = 12.0, 8.4, 4.0 Hz, 1H), 3.80 (s, 3H), 3.67 (dd, *J* = 3.2, 2.8 Hz, 1H), 2.47 (ABqdd, *J* = 16.8, 5.2, 2.0 Hz, 1H), 2.39 (ABqd, *J* = 16.8, 6.0 Hz, 1H), 2.15–1.95 (m, 3H), 1.80–1.70 (m, 2H), 1.11 (d, *J* = 6.8 Hz, 3H), 0.98 (t, *J* = 7.6 Hz, 3H), 0.91 (s, 9H), 0.18 (s, 3H), 0.16 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 159.3, 130.5, 129.7 (×2), 113.9 (×2), 84.1, 81.4, 80.9, 76.1, 72.8, 70.1, 70.0, 66.0, 55.4, 36.8, 36.5, 29.3, 26.2 (×3), 23.1, 18.4, 16.3, 10.0, –4.2, –4.8; HRMS data of **16a** are identical to those of **16**.

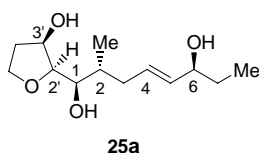
**(1'*R*,2*S*,2'*R*,3*R*,6'*S*)-2-{1'-[(*tert*-Butyldimethylsilyl)oxy]-6'-hydroxy-2'-methyl-oct-4'-ynyl}tetrahydrofuran-3-ol (24a).**



To a solution of the PMB ether **16a** (224.0 mg,  $4.7 \times 10^{-1}$  mmol) in CH<sub>2</sub>Cl<sub>2</sub> (4 mL) cooled in an ice–water bath at 0 °C were added pH 7.0 buffer (4 mL) and DDQ (213.0 mg,  $9.4 \times 10^{-1}$  mmol). The resultant

mixture was stirred at the same temperature for 2 h and the reaction was quenched by saturated aqueous solution of NaHCO<sub>3</sub>. The reaction mixture was extracted with CH<sub>2</sub>Cl<sub>2</sub> (10 mL × 3) and the combined organic layer was washed with brine, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered, and concentrated under reduced pressure. The residue was purified by flash column chromatography (silica gel, eluting with 10% EtOAc in hexane) to give the diol **24a** (147.0 mg, 88%) as a colorless oil. *R*<sub>f</sub> = 0.31 (25% EtOAc in hexane); [α]<sub>D</sub><sup>20</sup> -10.8 (*c* 1.0, CHCl<sub>3</sub>); IR (film) 3395 (br), 2958, 2932, 2883, 2858, 1463, 1252, 1089, 1034 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 4.47 (br s, 1H), 4.39 (br s, 1H, OH), 4.30 (t, *J* = 6.4 Hz, 1H), 4.09 (dd, *J* = 7.2, 3.2 Hz, 1H), 4.05 (ddd, *J* = 8.4, 8.0, 8.0 Hz, 1H), 3.84 (ddd, *J* = 12.4, 8.4, 4.0 Hz, 1H), 3.64 (dd, *J* = 3.2, 3.2 Hz, 1H), 2.43 (ABqdd, *J* = 16.4, 4.8, 1.6 Hz, 1H), 2.32 (ABqdd, *J* = 16.8, 7.2, 1.6 Hz, 1H), 2.12–1.96 (m, 3H), 1.85 (br s, 1H, OH), 1.74–1.64 (m, 2H), 1.08 (d, *J* = 6.8 Hz, 3H), 1.00 (t, *J* = 7.6 Hz, 3H), 0.90 (s, 9H), 0.17 (s, 3H), 0.14 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 83.5, 83.3, 80.9, 76.1, 72.8, 66.0, 64.1, 36.8, 36.4, 31.3, 26.1 (×3), 23.0, 18.4, 16.3, 9.7, -4.2, -4.9; HRMS (+CI) calcd for C<sub>19</sub>H<sub>37</sub>O<sub>4</sub>Si (M+H<sup>+</sup>) 357.2461, found 357.2459.

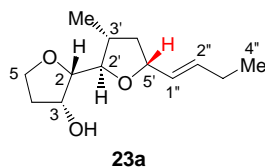
**(1*R*,2*R*,2'*S*,3'*R*,6*R*,*E*)-1-(3'-Hydroxytetrahydrofuran-2'-yl)-2-methyloct-4-ene-1,6-diol (25a).**



To a solution of the propargyl alcohol **24a** (113.0 mg, 3.2 × 10<sup>-1</sup> mmol) in anhydrous THF (4 mL) cooled in an ice–water bath at 0 °C was added slowly Red-Al (3.5 M in toluene, 0.4 mL, 12.8 × 10<sup>-1</sup> mmol). The resultant mixture was heated at 40 °C for 3 h and then stirred at room temperature for 15 h. The reaction was quenched by slowly adding saturated aqueous solution of potassium sodium tartrate followed by stirring for 10 min. The reaction mixture was extracted with EtOAc (20 mL × 3) and the combined organic layer was washed with brine, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtrated, and concentrated under reduced pressure. The residue was purified by flash column chromatography (silica gel, eluting with 10% MeOH in CH<sub>2</sub>Cl<sub>2</sub>) to give the triol **25a** (70.0 mg, 90%) as a colorless oil. *R*<sub>f</sub> = 0.37 (9% MeOH in CH<sub>2</sub>Cl<sub>2</sub>); [α]<sub>D</sub><sup>20</sup> -24.0 (*c* 0.8, CHCl<sub>3</sub>); IR (film) 3384 (br), 2962, 2929, 2877, 1456, 1057 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 5.66 (dt, *J* = 15.2, 7.6 Hz, 1H), 5.50 (dd, *J* = 15.2, 7.2 Hz, 1H), 4.51 (dd, *J* = 3.6, 3.2 Hz, 1H), 4.10 (td, *J* = 8.0, 7.6 Hz, 1H), 3.99 (ddd, *J* = 6.8, 6.4, 6.4 Hz, 1H), 3.89 (ddd, *J* = 12.0, 8.4, 3.6 Hz, 1H), 3.80 (dd, *J* = 6.8, 5.6 Hz, 1H), 3.71 (dd, *J* = 5.2, 3.6 Hz, 1H), 2.48–2.43 (m, 1H), 2.15–1.93 (m, 4H), 1.63–1.45 (m, 2H), 0.95 (d, *J* = 6.8 Hz, 3H), 0.90 (t, *J* = 7.6 Hz, 3H) (the signals for three OH not observed); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 135.1, 130.1, 81.8, 75.1, 74.6, 72.7, 66.8, 36.0, 35.7, 35.3, 30.3, 15.9, 9.9; HRMS (+CI) calcd for C<sub>13</sub>H<sub>23</sub>O<sub>4</sub> (M<sup>+</sup>-H) 243.1596, found 243.1594.

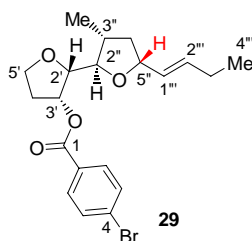
**Intramolecular *syn*-Oxypalladation of Allylic Alcohol 25a.**

**(2*S*,2'*R*,3*R*,3'*R*,5'*R*,*E*)-5'-(But-1''-enyl)-3'-methyloctahydro[2,2']bifuran-3-ol (23a).**



A solution of the allylic alcohols **23a** (9.8 mg,  $4.0 \times 10^{-2}$  mmol) and  $\text{PdCl}_2(\text{PhCN})_2$  (1.5 mg,  $4.0 \times 10^{-3}$  mmol) in anhydrous THF (0.5 mL) cooled in an ice–water bath at 0 °C was stirred for 2 h. The reaction mixture was diluted with hexane (5 mL) and filtered through a short pad of Celite with washing by EtOAc. The combined filtrate was concentrated under reduced pressure and the residue was purified by flash column chromatography (silica gel, eluting with 25% EtOAc in hexane) to give an inseparable mixture of the two epimeric bis-THF products **23a** and **23b** (7.9 mg, 87%; an 88:12 mixture of **23a** and **23b**) as a colorless oil.  $R_f = 0.38$  (25% EtOAc in hexane);  $[\alpha]_D^{20} -3.7$  ( $c$  1.0,  $\text{CHCl}_3$ ); IR (film) 3443 (br), 2961, 2930, 2875, 1460, 1383, 1068, 1030  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ; an 88:12 mixture of **23a** and **23b**)  $\delta$  the signals observed for the major epimer **23a**: 5.67 (dt,  $J = 15.2, 6.4$  Hz, 1H), 5.42 (ddt,  $J = 15.2, 7.6, 1.6$  Hz, 1H), 4.49 (ddd,  $J = 5.6, 4.0, 2.0$  Hz, 1H), 4.36 (ddd,  $J = 10.0, 7.6, 5.6$  Hz, 1H), 4.06 (ddd,  $J = 8.4, 8.4, 6.8$  Hz, 1H), 3.82 (ddd,  $J = 8.4, 8.4, 4.4$  Hz, 1H), 3.77 (dd,  $J = 7.2, 7.2$  Hz, 1H), 3.62 (dd,  $J = 7.2, 3.6$  Hz, 1H), 3.50–2.75 (br s, 1H, OH), 2.29–2.17 (m, 2H), 2.12–1.93 (m, 4H), 1.44–1.35 (m, 1H), 1.13 (d,  $J = 6.0$  Hz, 3H), 0.97 (t,  $J = 7.6$  Hz, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ; an 88:12 mixture of **23a** and **23b**)  $\delta$  the signals observed for the major epimer **23a**: 134.9, 129.8, 84.6, 83.6, 80.4, 72.8, 67.1, 42.3, 39.8, 35.1, 25.2, 17.5, 13.3; HRMS (+CI) calcd for  $\text{C}_{13}\text{H}_{23}\text{O}_3$  ( $\text{M}+\text{H}^+$ ) 227.1647, found, 227.1632.

#### Synthesis of Ester **29**. (2'S,2''R,3'R,3''R,5''R,E)-5''-(But-1''-enyl)-3''-methyloctahydro[2,2'']bifuran-3-yl 4-Bromobenzoate (**29**).



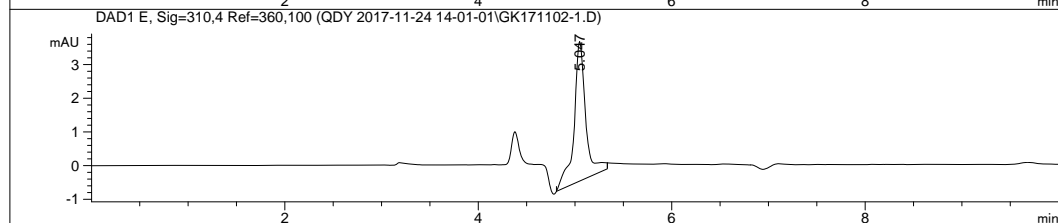
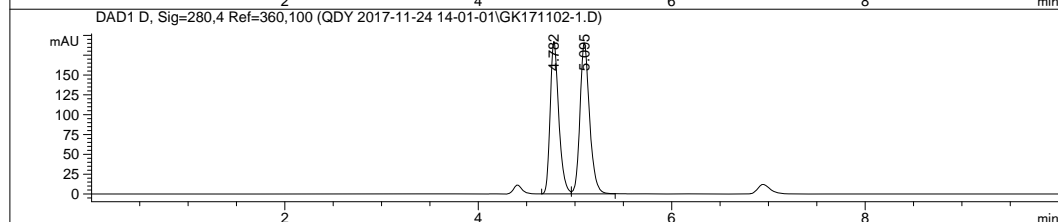
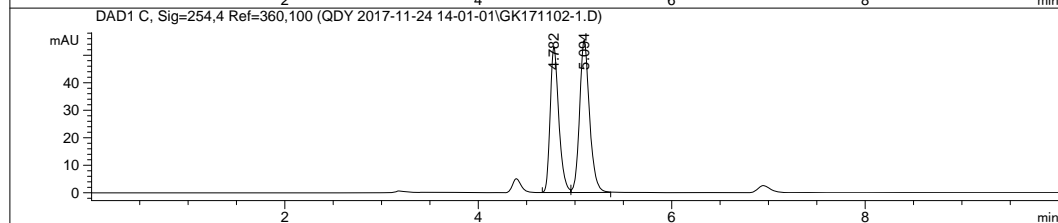
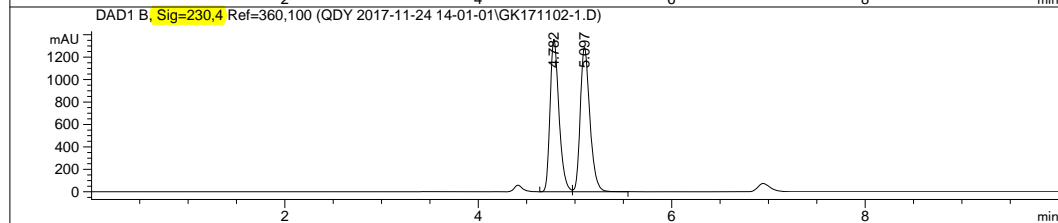
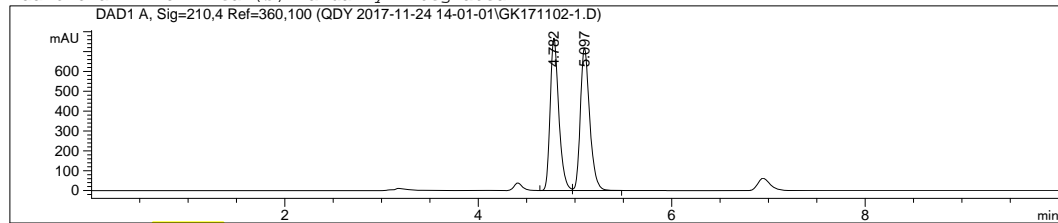
To a solution of bis-THF alcohol **23a** (7.0 mg, an 88:12 mixture of **23a** and **23b**,  $3.1 \times 10^{-2}$  mmol) in anhydrous  $\text{CH}_2\text{Cl}_2$  (1 mL) cooled in an ice–water bath at 0 °C was added  $\text{Et}_3\text{N}$  (9  $\mu\text{L}$ ,  $6.2 \times 10^{-2}$  mmol), DMAP (1.0 mg,  $0.8 \times 10^{-2}$  mmol) and 4-bromobenzoyl chloride (8.0 mg,  $3.4 \times 10^{-2}$  mmol) followed by stirring at room temperature for 24 h. The reaction was quenched by  $\text{H}_2\text{O}$  and the reaction mixture was extracted with  $\text{CH}_2\text{Cl}_2$  (10 mL  $\times$  3). The combined organic layer was washed with brine, dried over anhydrous  $\text{Na}_2\text{SO}_4$ , filtered, and concentrated under reduced pressure. The residue was purified by flash column chromatography (silica gel, eluting with 20% EtOAc in hexanes) to give the 4-bromobenzoate **29** (9.0 mg, 71%) as a white foam.  $R_f = 0.45$  (16.7% EtOAc in hexane);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.92–7.88 (m, 2H), 7.60–7.56 (m, 2H), 5.63 (ddd,  $J = 4.8, 3.2, 1.6$  Hz, 1H), 5.53 (dt,  $J = 15.2, 6.8$  Hz, 1H), 5.28

(ddt,  $J = 15.2, 7.2, 1.6$  Hz, 1H), 4.30 (ddd,  $J = 9.2, 6.4, 6.4$  Hz, 1H), 4.07 (ddd,  $J = 8.0, 8.0, 8.0$  Hz, 1H), 3.91 (ddd,  $J = 8.8, 8.8, 4.4$  Hz, 1H), 3.79 (dd,  $J = 8.4, 8.4$  Hz, 1H), 3.76 (dd,  $J = 8.4, 3.6$  Hz, 1H), 2.40–2.12 (m, 4H), 1.94–1.87 (m, 2H), 1.34 (ddd,  $J = 12.0, 10.0, 9.2$  Hz, 1H), 1.19 (d,  $J = 6.4$  Hz, 3H), 0.87 (t,  $J = 7.6$  Hz, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  165.3, 133.9, 131.8 ( $\times 2$ ), 131.3 ( $\times 2$ ), 129.9, 129.7, 128.1, 84.7, 81.9, 80.0, 75.4, 66.9, 42.5, 39.9, 33.5, 25.2, 18.4, 13.3.

Sample Name:

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Last changed   : 8/16/2017 10:08:17 PM
Additional Info: Peak(s) manually integrated
    
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Sample Name:

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Area Percent Report
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Use Multiplier & Dilution Factor with ISTDs
    
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Signal 1: DAD1 A, Sig=210,4 Ref=360,100

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1	4.782	VV	0.0942	4750.67725	767.92322	49.7663
2	5.097	VB	0.1018	4795.30078	718.90100	50.2337

Totals : 9545.97803 1486.82422

Signal 2: DAD1 B, Sig=230,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.782	VV	0.0966	8693.07129	1359.77454	49.5675
2	5.097	VB	0.1042	8844.77148	1287.18469	50.4325

Totals : 1.75378e4 2646.95923

Signal 3: DAD1 C, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.782	BV	0.0943	327.51840	52.82029	45.4124
2	5.094	VB	0.1070	393.69037	55.30482	54.5876

Totals : 721.20877 108.12511

Signal 4: DAD1 D, Sig=280,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.782	BV	0.0938	1182.85852	192.21938	47.4749
2	5.095	VB	0.1022	1308.68811	190.38620	52.5251

Totals : 2491.54663 382.60558

Signal 5: DAD1 E, Sig=310,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
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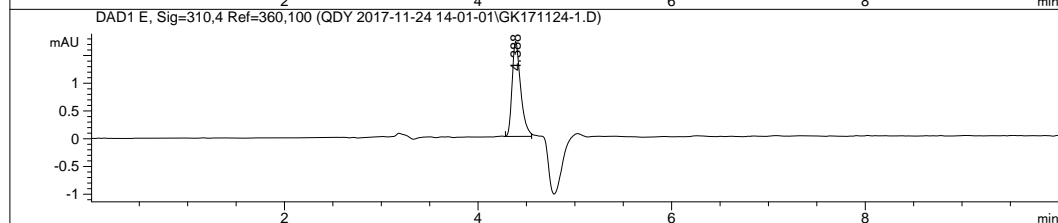
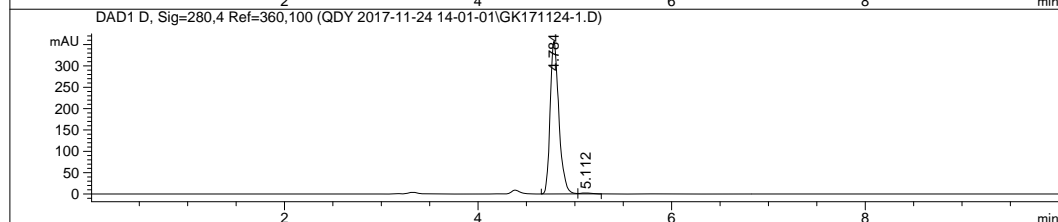
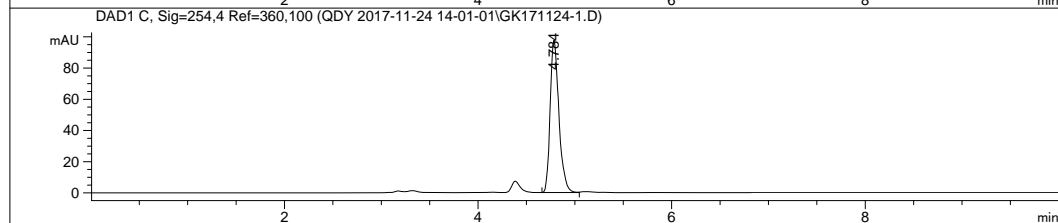
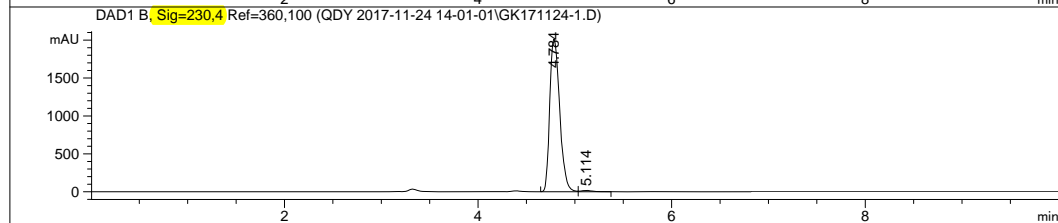
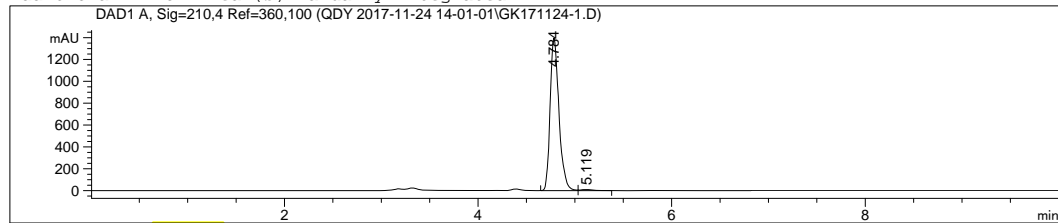
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Sample Name:

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Additional Info : Peak(s) manually integrated
    
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Sample Name:

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Dilution      :      1.0000
Use Multiplier & Dilution Factor with ISTDs
    
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Signal 1: DAD1 A, Sig=210,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.784	BV	0.0975	8814.12402	1398.78845	98.9848
2	5.119	VB	0.1280	90.39679	10.54381	1.0152

Totals : 8904.52081 1409.33226

Signal 2: DAD1 B, Sig=230,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.784	BV	0.1129	1.42999e4	2013.46533	99.0419
2	5.114	VB	0.1159	138.33916	17.56370	0.9581

Totals : 1.44383e4 2031.02904

Signal 3: DAD1 C, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.784	BB	0.0949	611.02850	97.75879	100.0000

Totals : 611.02850 97.75879

Signal 4: DAD1 D, Sig=280,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.784	BV	0.0925	2224.98706	357.84753	99.1730
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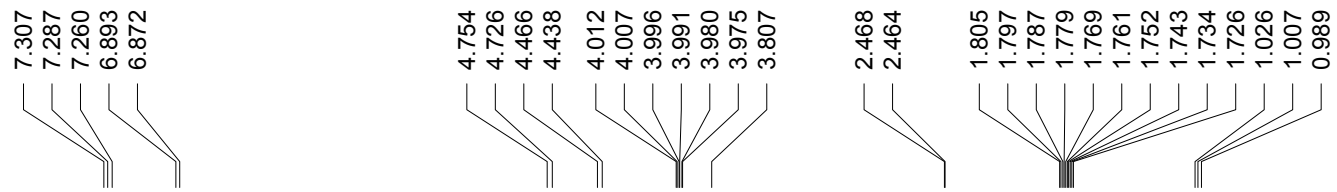
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Signal 5: DAD1 E, Sig=310,4 Ref=360,100

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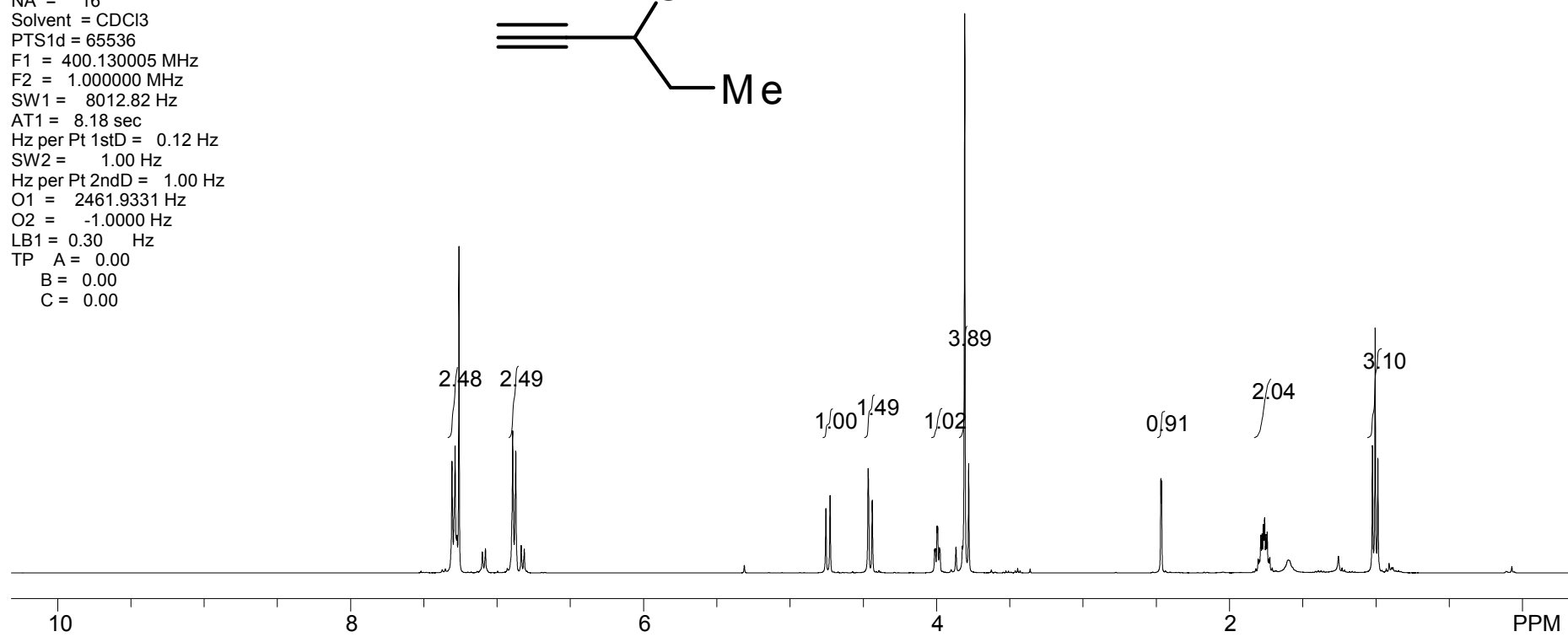
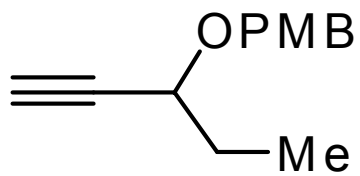
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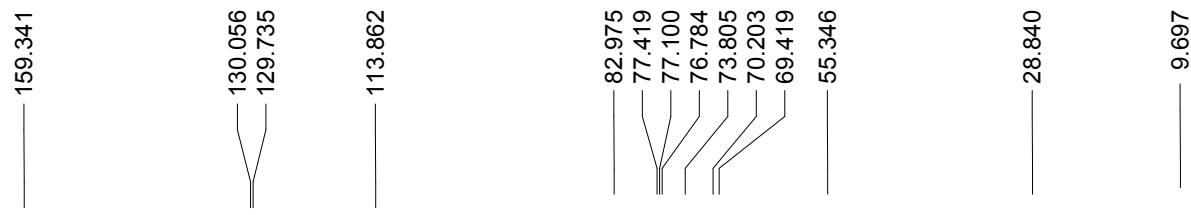
S25



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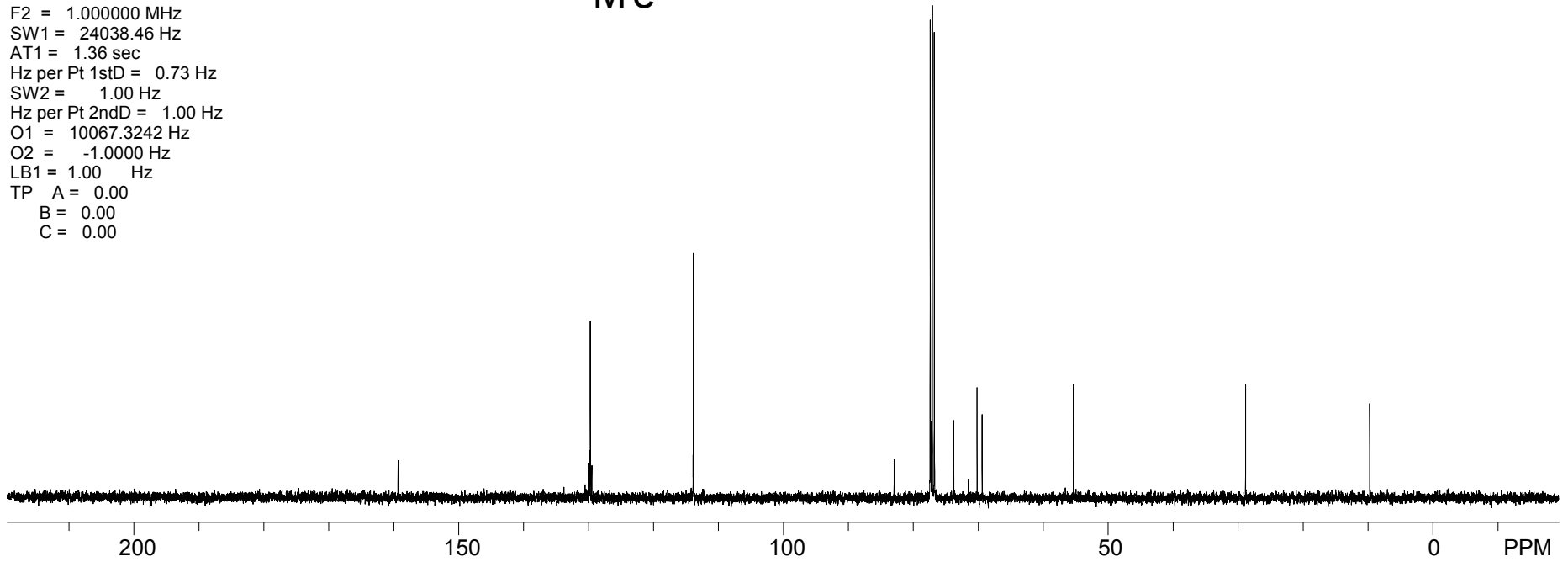
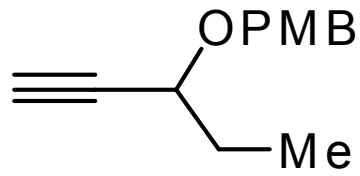
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 SW1 = 8012.82 Hz  
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 Hz per Pt 2ndD = 1.00 Hz  
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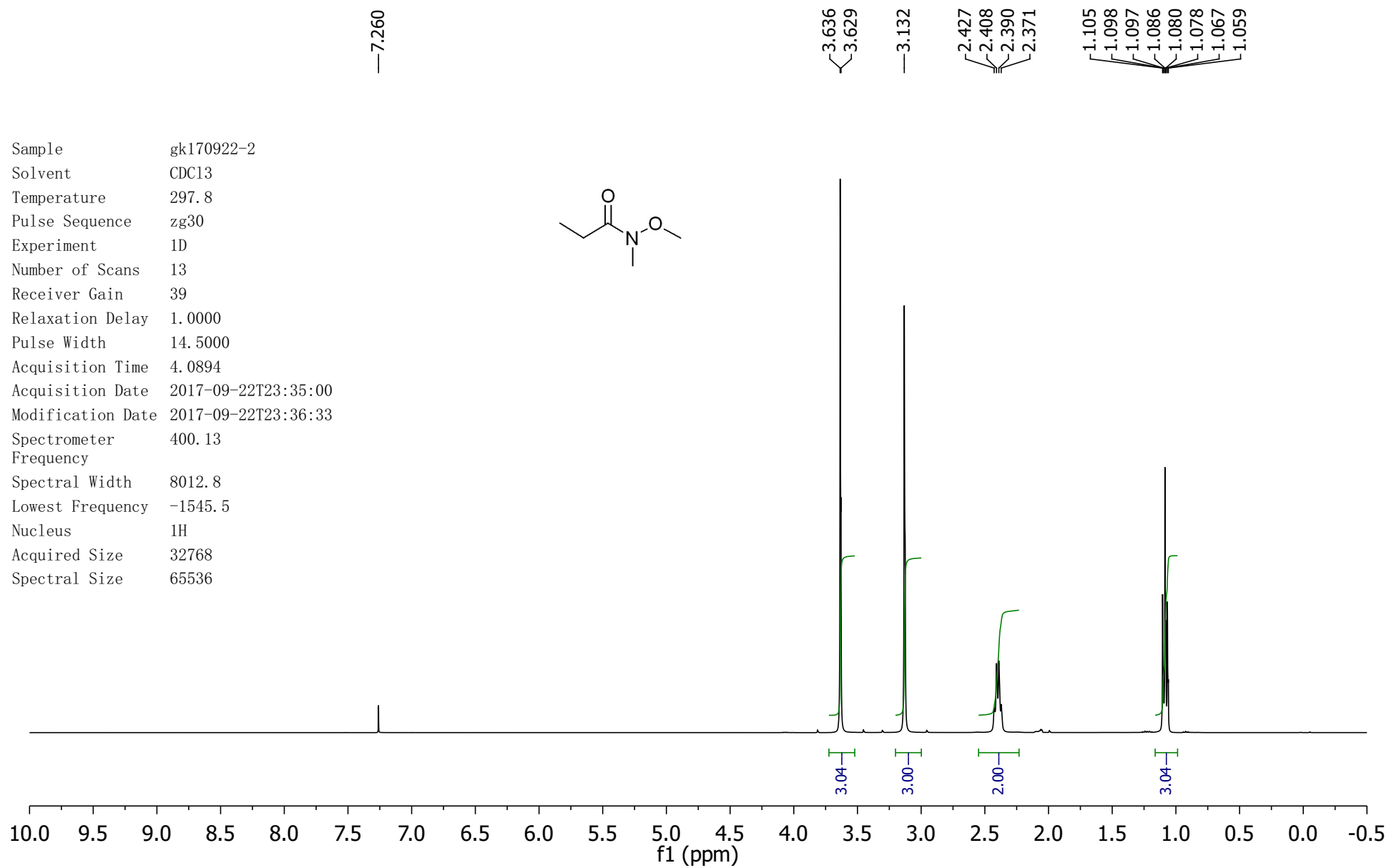




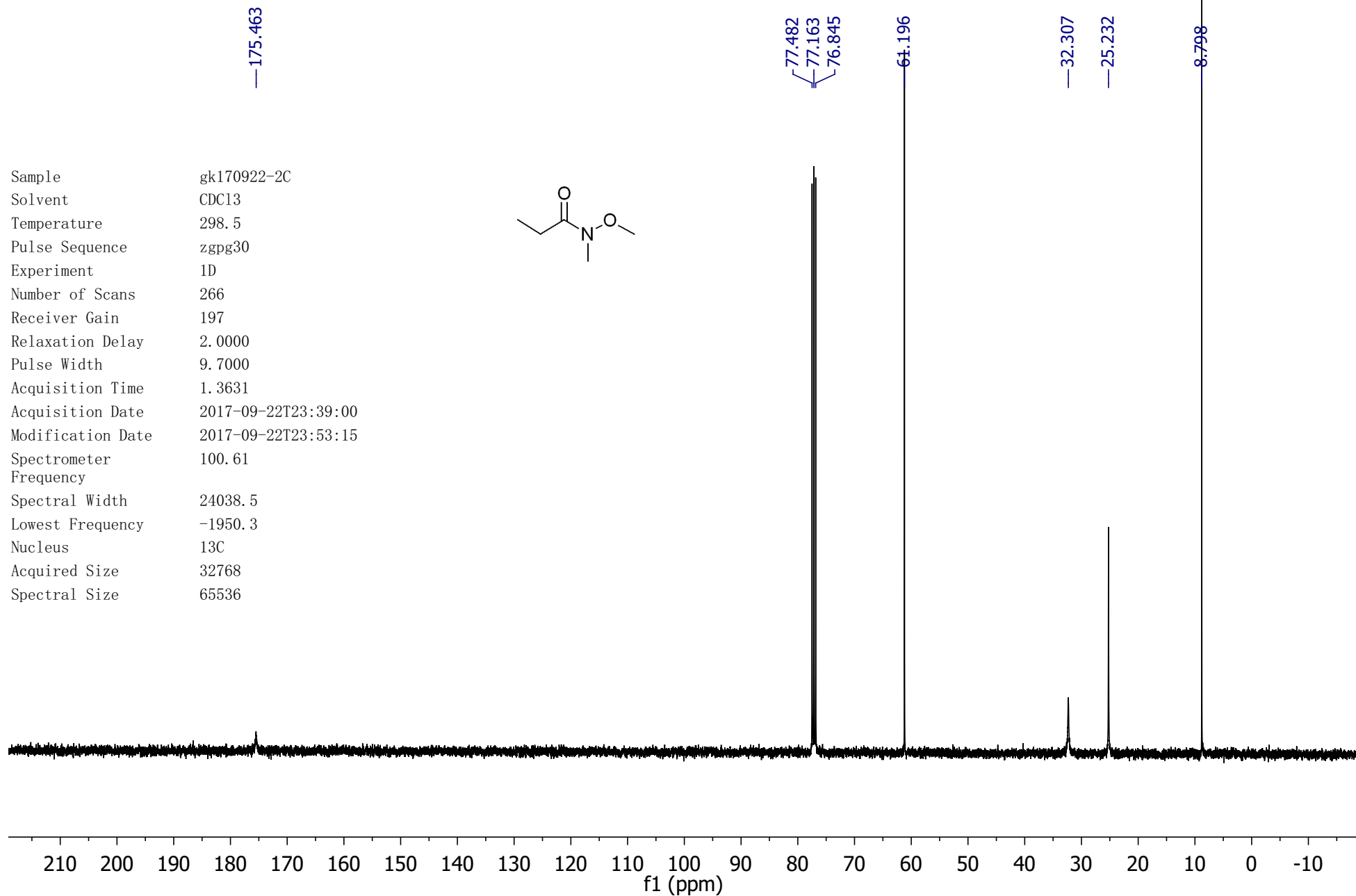
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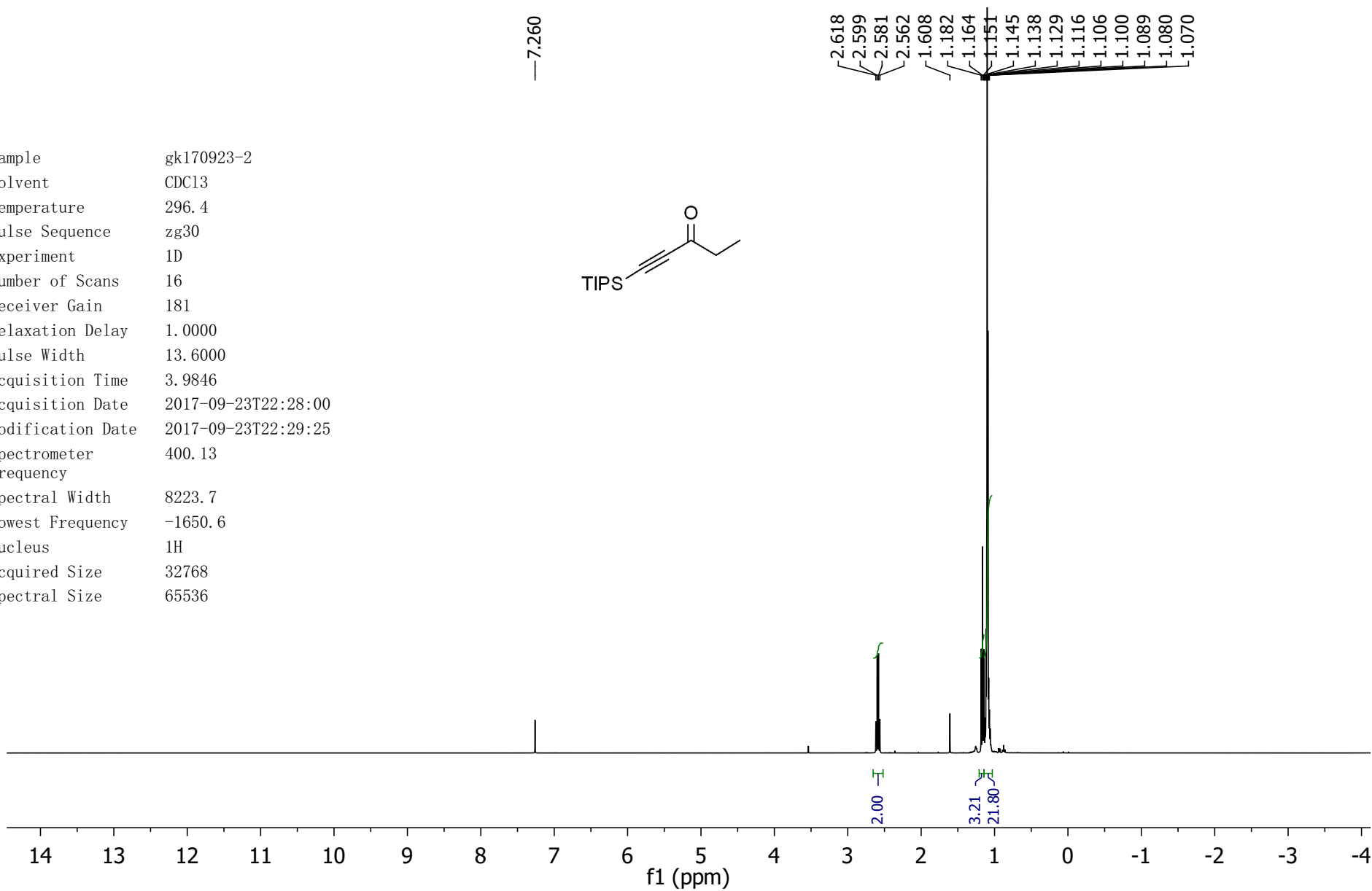
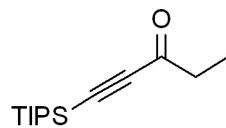




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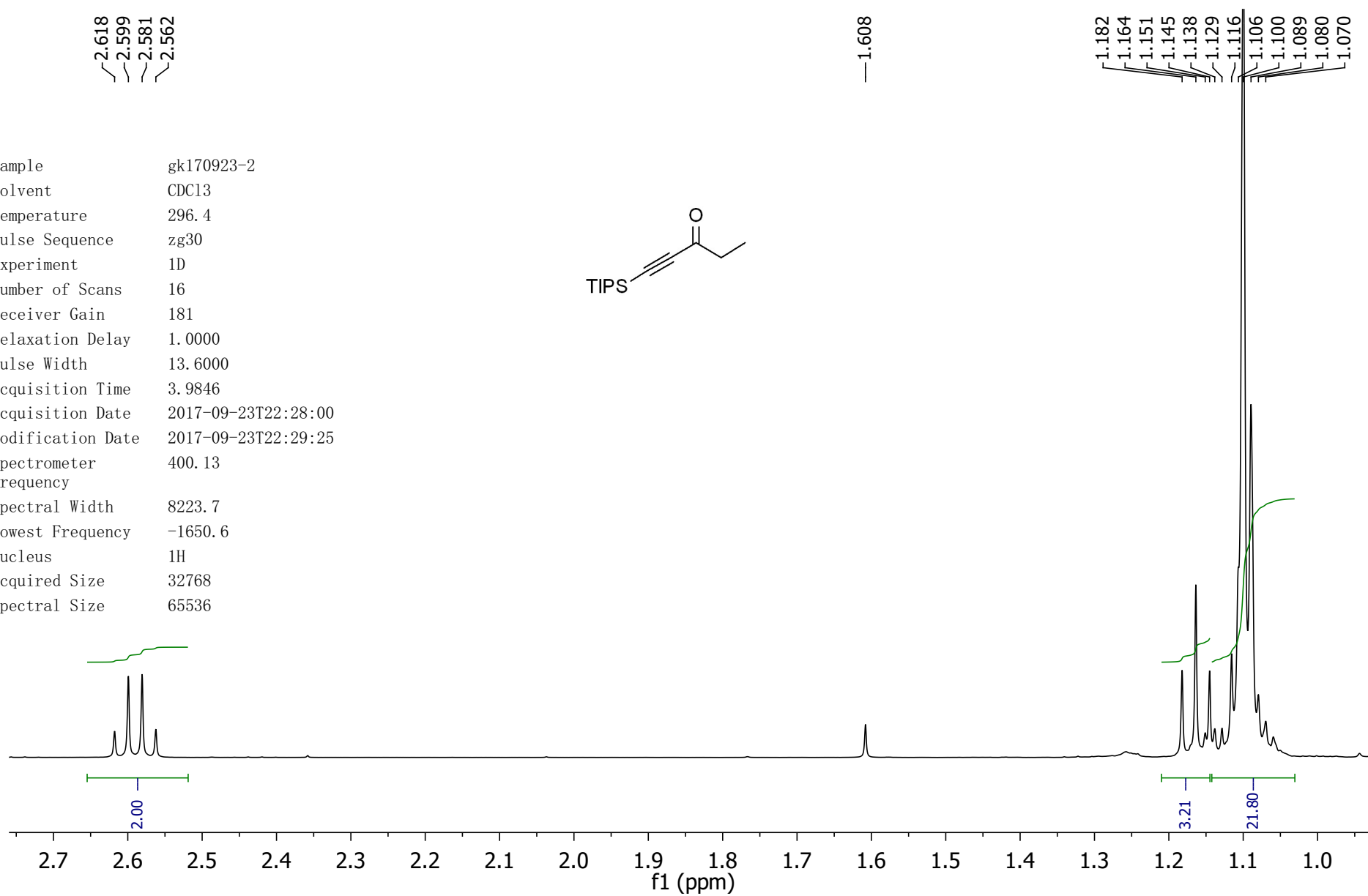
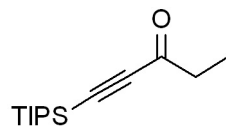


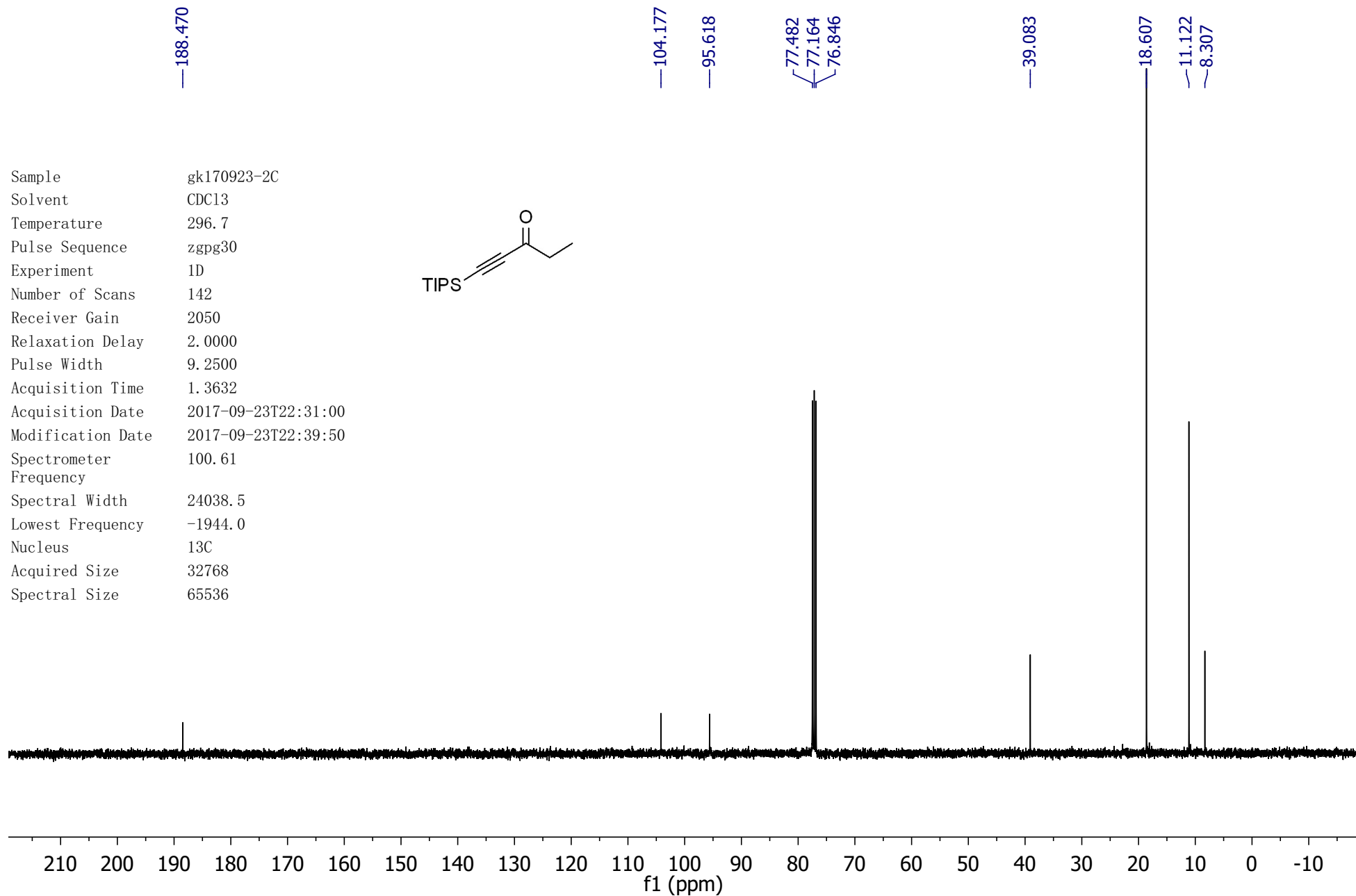
2.618  
2.599  
2.581  
2.562

1.608

1.182  
1.164  
1.151  
1.145  
1.138  
1.129  
1.116  
1.106  
1.100  
1.089  
1.080  
1.070

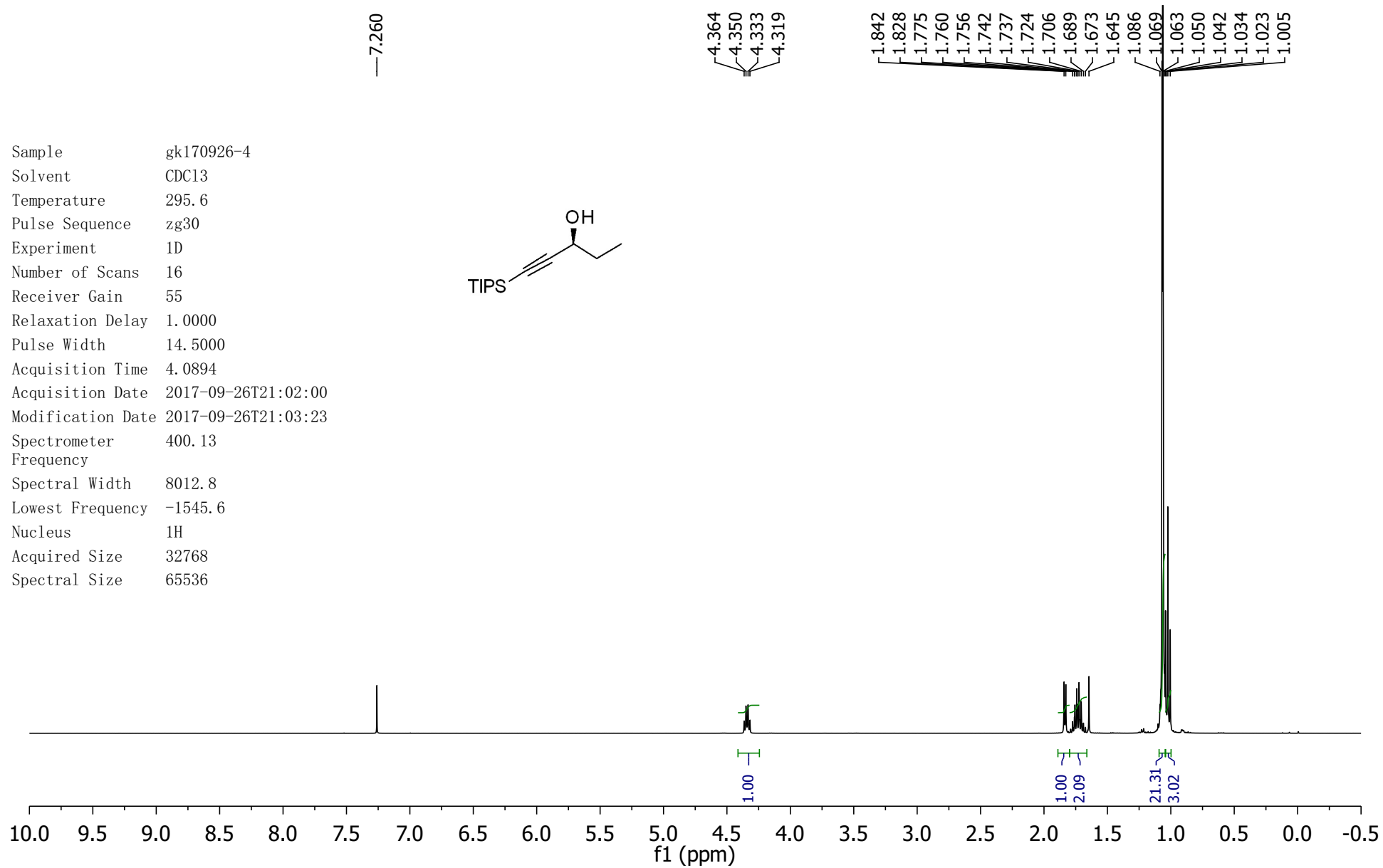
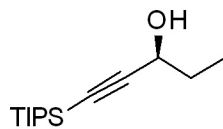
Sample gk170923-2  
Solvent CDCl3  
Temperature 296.4  
Pulse Sequence zg30  
Experiment 1D  
Number of Scans 16  
Receiver Gain 181  
Relaxation Delay 1.0000  
Pulse Width 13.6000  
Acquisition Time 3.9846  
Acquisition Date 2017-09-23T22:28:00  
Modification Date 2017-09-23T22:29:25  
Spectrometer 400.13  
Frequency  
Spectral Width 8223.7  
Lowest Frequency -1650.6  
Nucleus 1H  
Acquired Size 32768  
Spectral Size 65536



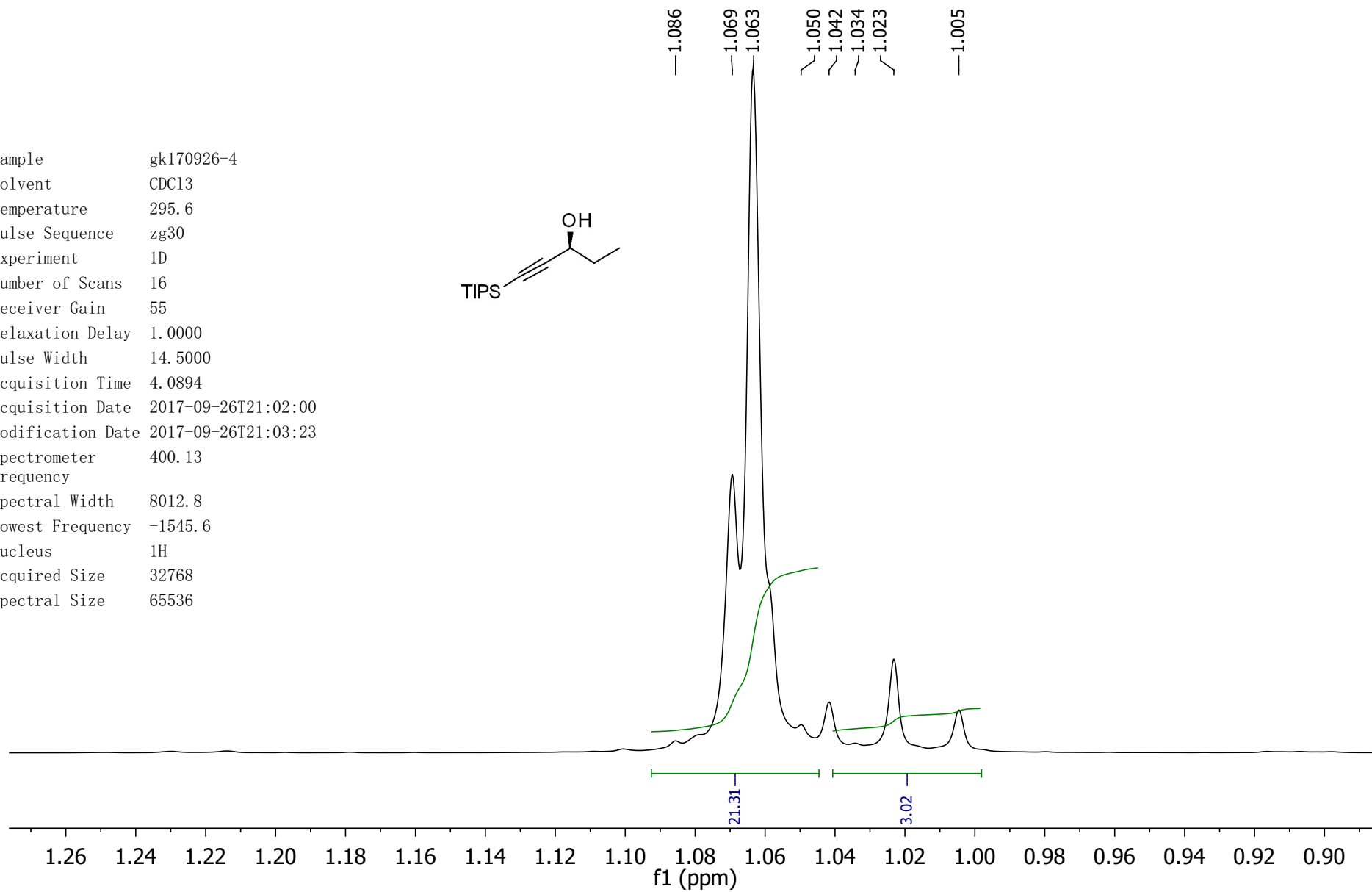
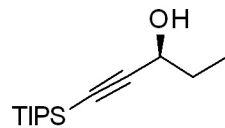




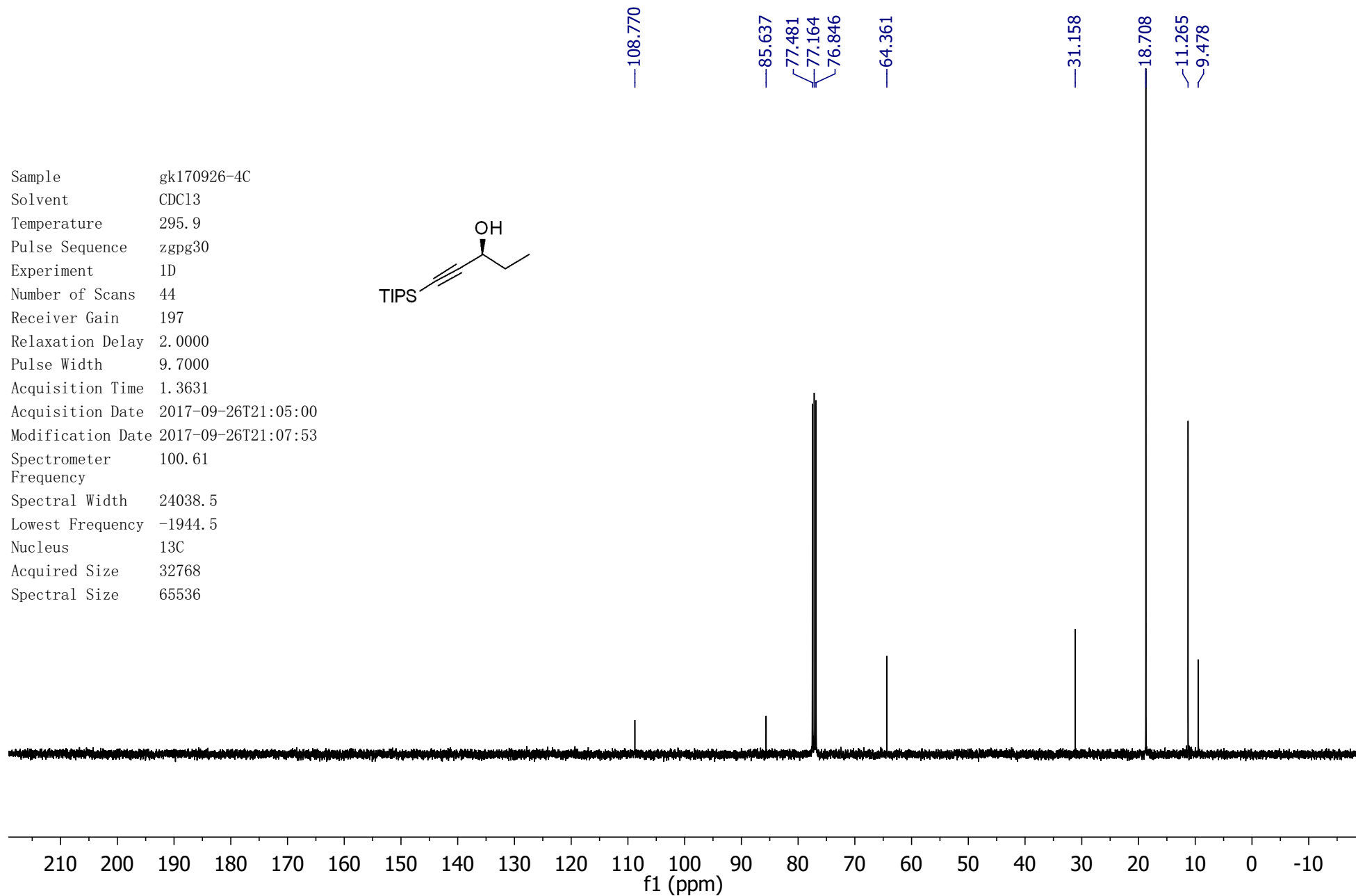
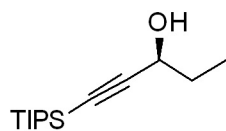
Sample gk170926-4  
 Solvent CDC13  
 Temperature 295.6  
 Pulse Sequence zg30  
 Experiment 1D  
 Number of Scans 16  
 Receiver Gain 55  
 Relaxation Delay 1.0000  
 Pulse Width 14.5000  
 Acquisition Time 4.0894  
 Acquisition Date 2017-09-26T21:02:00  
 Modification Date 2017-09-26T21:03:23  
 Spectrometer 400.13  
 Frequency  
 Spectral Width 8012.8  
 Lowest Frequency -1545.6  
 Nucleus 1H  
 Acquired Size 32768  
 Spectral Size 65536



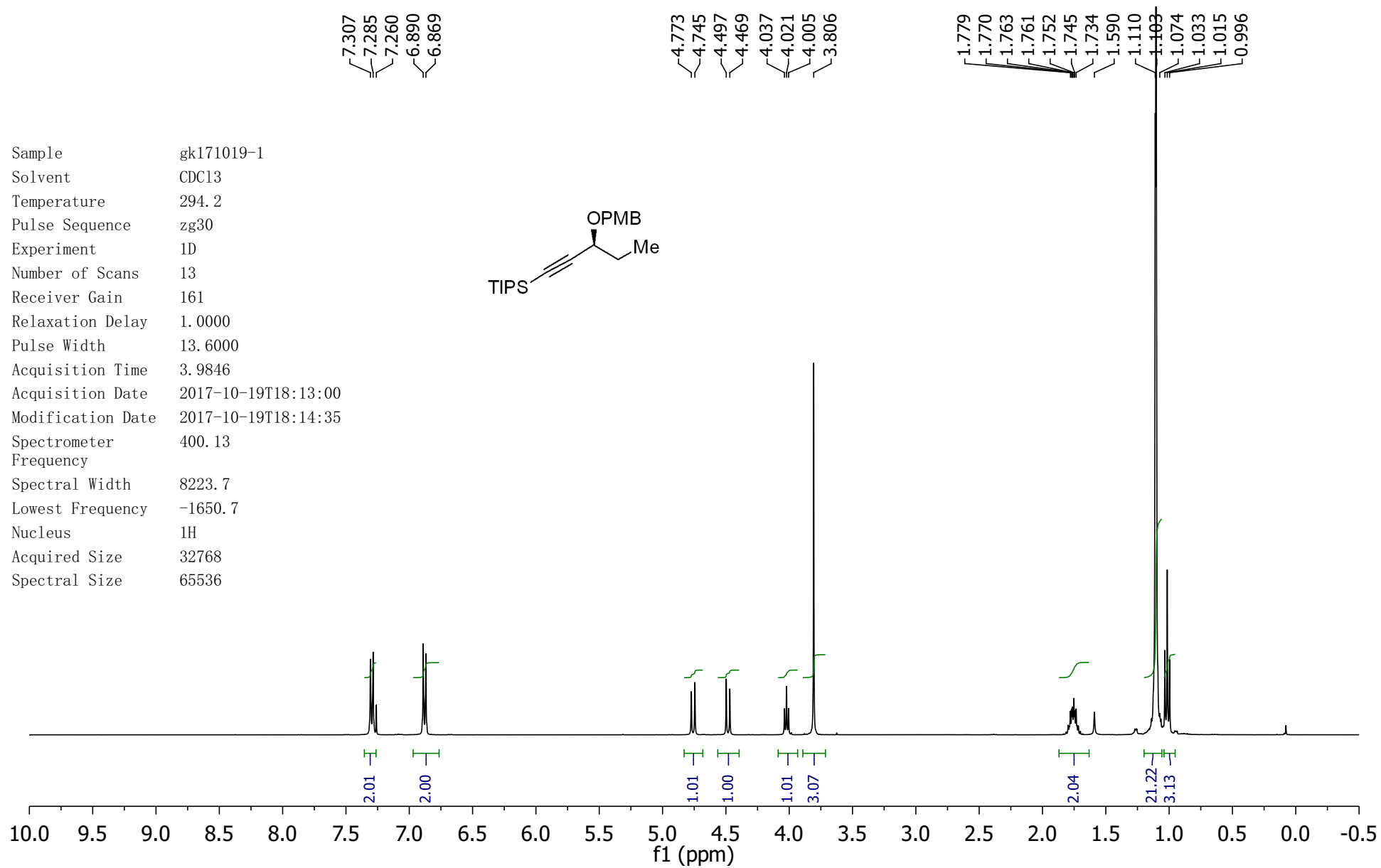
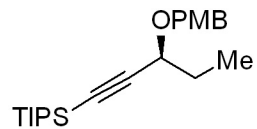
Sample gk170926-4  
Solvent CDC13  
Temperature 295.6  
Pulse Sequence zg30  
Experiment 1D  
Number of Scans 16  
Receiver Gain 55  
Relaxation Delay 1.0000  
Pulse Width 14.5000  
Acquisition Time 4.0894  
Acquisition Date 2017-09-26T21:02:00  
Modification Date 2017-09-26T21:03:23  
Spectrometer 400.13  
Frequency  
Spectral Width 8012.8  
Lowest Frequency -1545.6  
Nucleus 1H  
Acquired Size 32768  
Spectral Size 65536



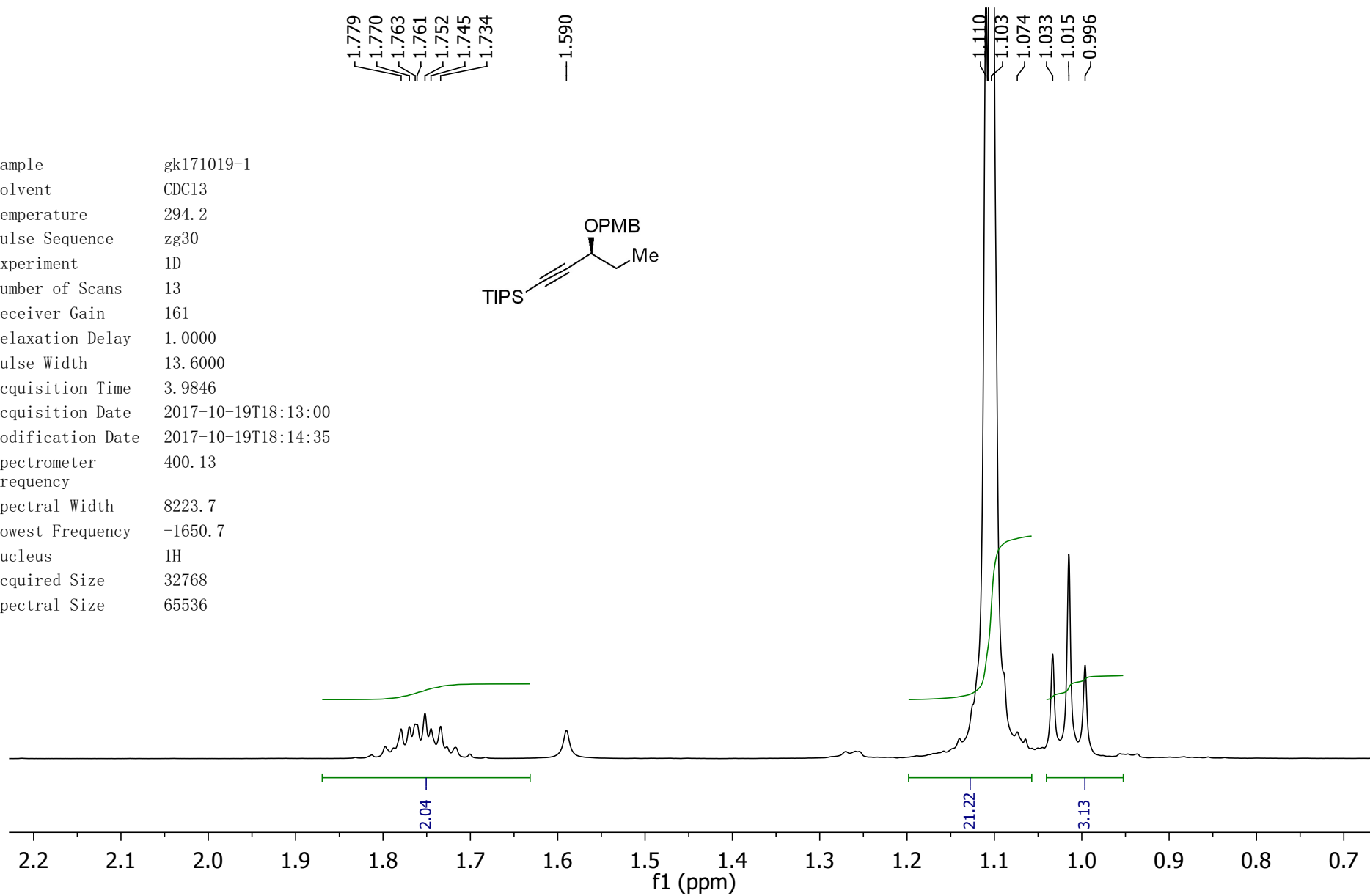
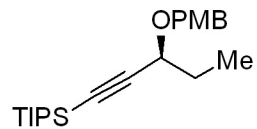
Sample gk170926-4C  
Solvent CDC13  
Temperature 295.9  
Pulse Sequence zgpg30  
Experiment 1D  
Number of Scans 44  
Receiver Gain 197  
Relaxation Delay 2.0000  
Pulse Width 9.7000  
Acquisition Time 1.3631  
Acquisition Date 2017-09-26T21:05:00  
Modification Date 2017-09-26T21:07:53  
Spectrometer 100.61  
Frequency  
Spectral Width 24038.5  
Lowest Frequency -1944.5  
Nucleus 13C  
Acquired Size 32768  
Spectral Size 65536



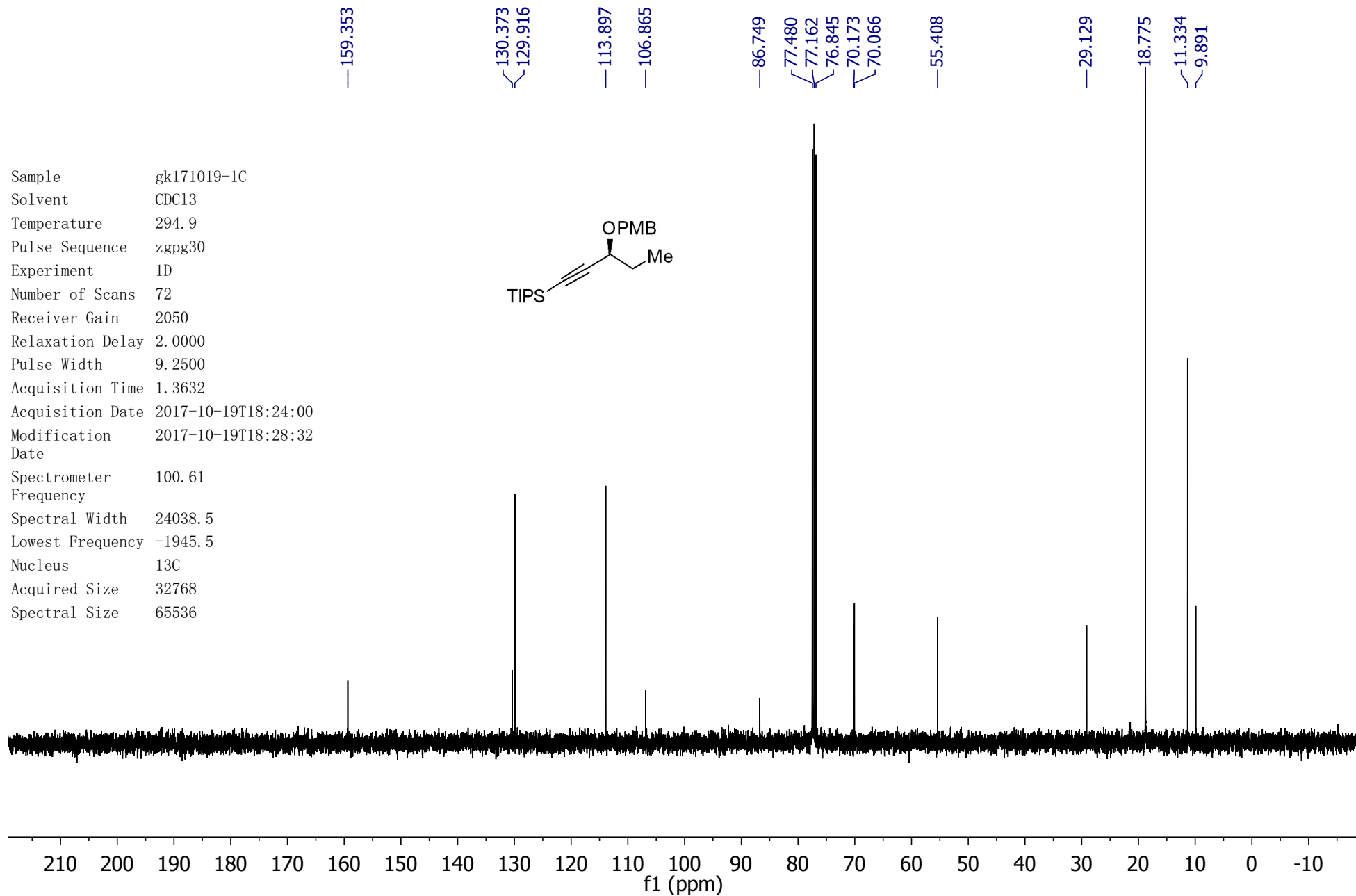
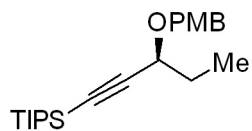
Sample gk171019-1  
 Solvent CDC13  
 Temperature 294.2  
 Pulse Sequence zg30  
 Experiment 1D  
 Number of Scans 13  
 Receiver Gain 161  
 Relaxation Delay 1.0000  
 Pulse Width 13.6000  
 Acquisition Time 3.9846  
 Acquisition Date 2017-10-19T18:13:00  
 Modification Date 2017-10-19T18:14:35  
 Spectrometer 400.13  
 Frequency  
 Spectral Width 8223.7  
 Lowest Frequency -1650.7  
 Nucleus 1H  
 Acquired Size 32768  
 Spectral Size 65536



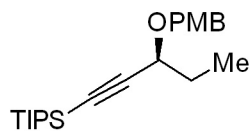
Sample gk171019-1  
 Solvent CDC13  
 Temperature 294.2  
 Pulse Sequence zg30  
 Experiment 1D  
 Number of Scans 13  
 Receiver Gain 161  
 Relaxation Delay 1.0000  
 Pulse Width 13.6000  
 Acquisition Time 3.9846  
 Acquisition Date 2017-10-19T18:13:00  
 Modification Date 2017-10-19T18:14:35  
 Spectrometer 400.13  
 Frequency  
 Spectral Width 8223.7  
 Lowest Frequency -1650.7  
 Nucleus 1H  
 Acquired Size 32768  
 Spectral Size 65536



Sample gk171019-1C  
Solvent CDCl3  
Temperature 294.9  
Pulse Sequence zgpg30  
Experiment 1D  
Number of Scans 72  
Receiver Gain 2050  
Relaxation Delay 2.0000  
Pulse Width 9.2500  
Acquisition Time 1.3632  
Acquisition Date 2017-10-19T18:24:00  
Modification Date 2017-10-19T18:28:32  
Spectrometer 100.61  
Frequency  
Spectral Width 24038.5  
Lowest Frequency -1945.5  
Nucleus 13C  
Acquired Size 32768  
Spectral Size 65536



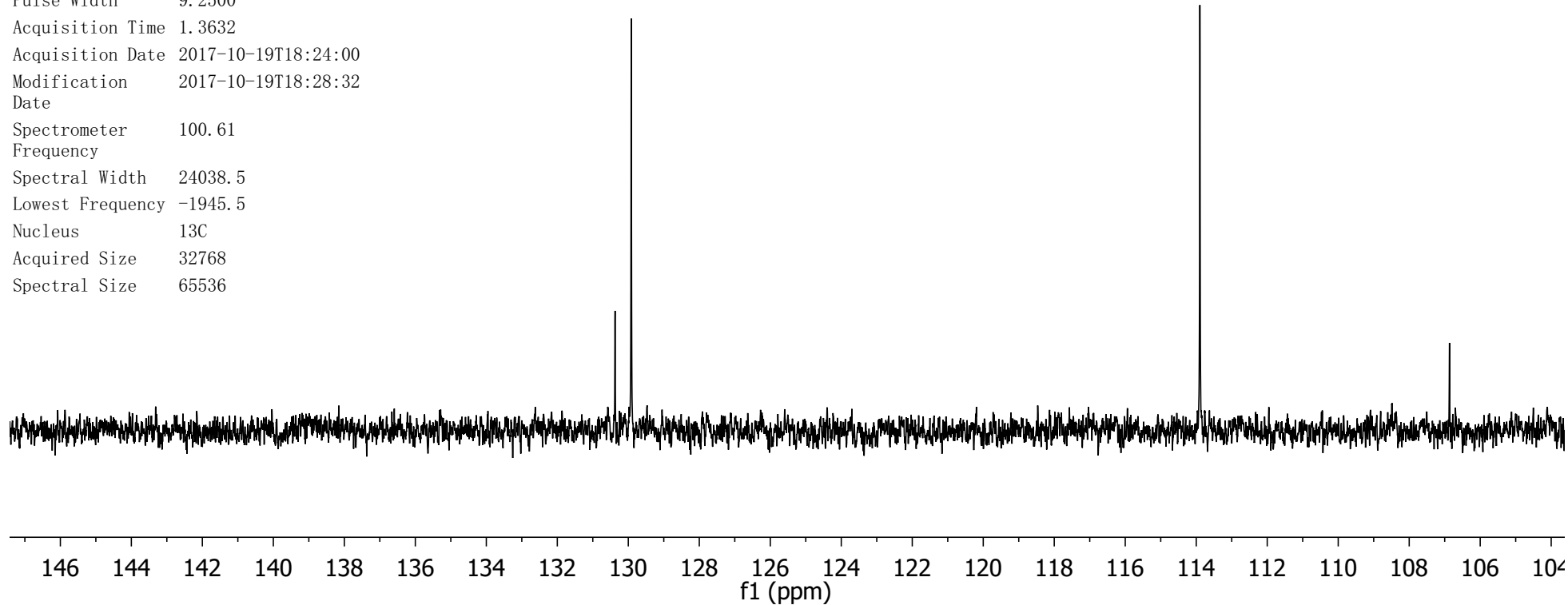
Sample gk171019-2C  
Solvent CDCl3  
Temperature 294.9  
Pulse Sequence zgpg30  
Experiment 1D  
Number of Scans 72  
Receiver Gain 2050  
Relaxation Delay 2.0000  
Pulse Width 9.2500  
Acquisition Time 1.3632  
Acquisition Date 2017-10-19T18:24:00  
Modification Date 2017-10-19T18:28:32  
Spectrometer 100.61  
Frequency  
Spectral Width 24038.5  
Lowest Frequency -1945.5  
Nucleus 13C  
Acquired Size 32768  
Spectral Size 65536



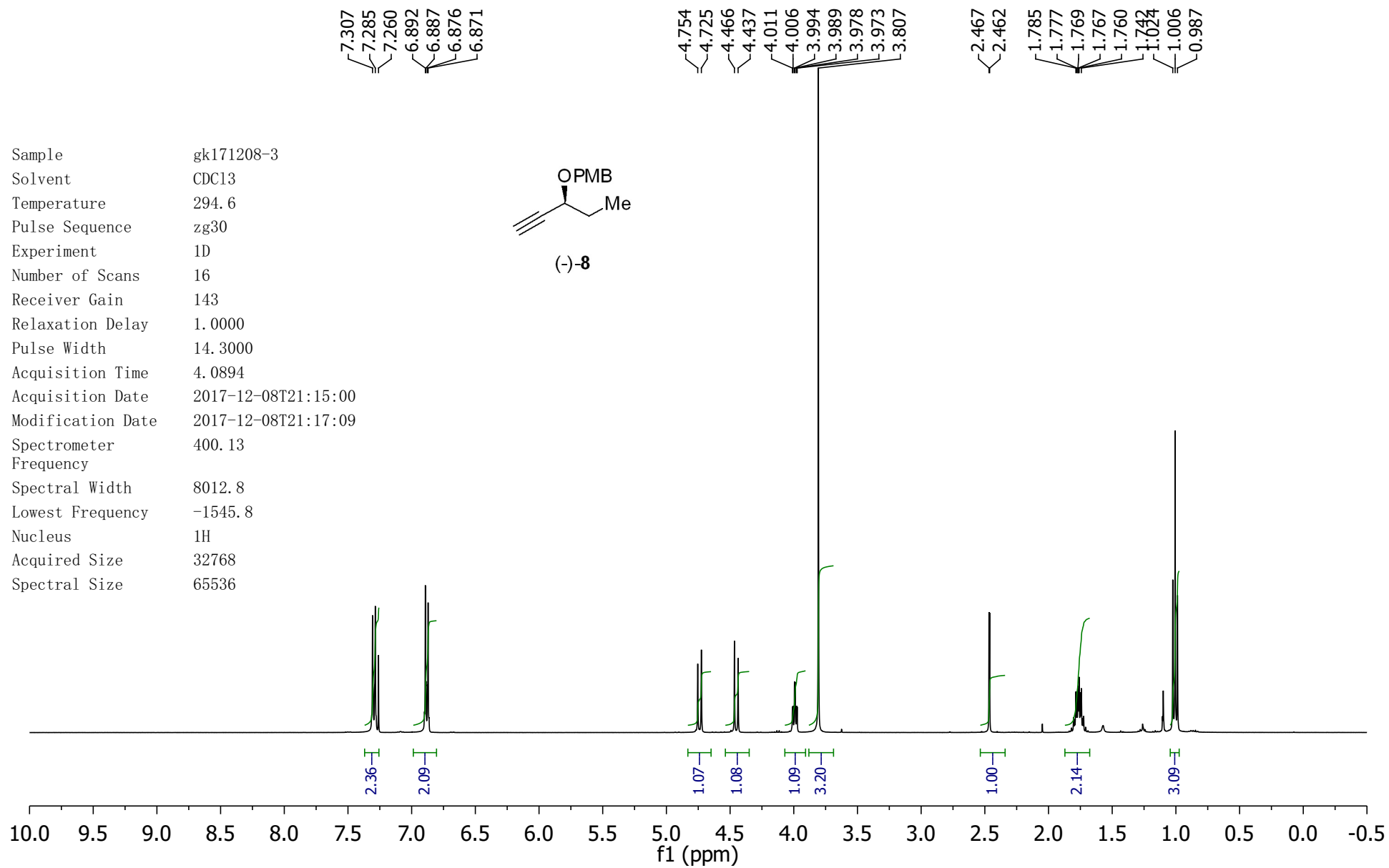
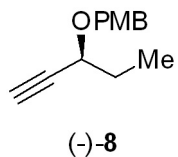
130.373  
129.916

113.897

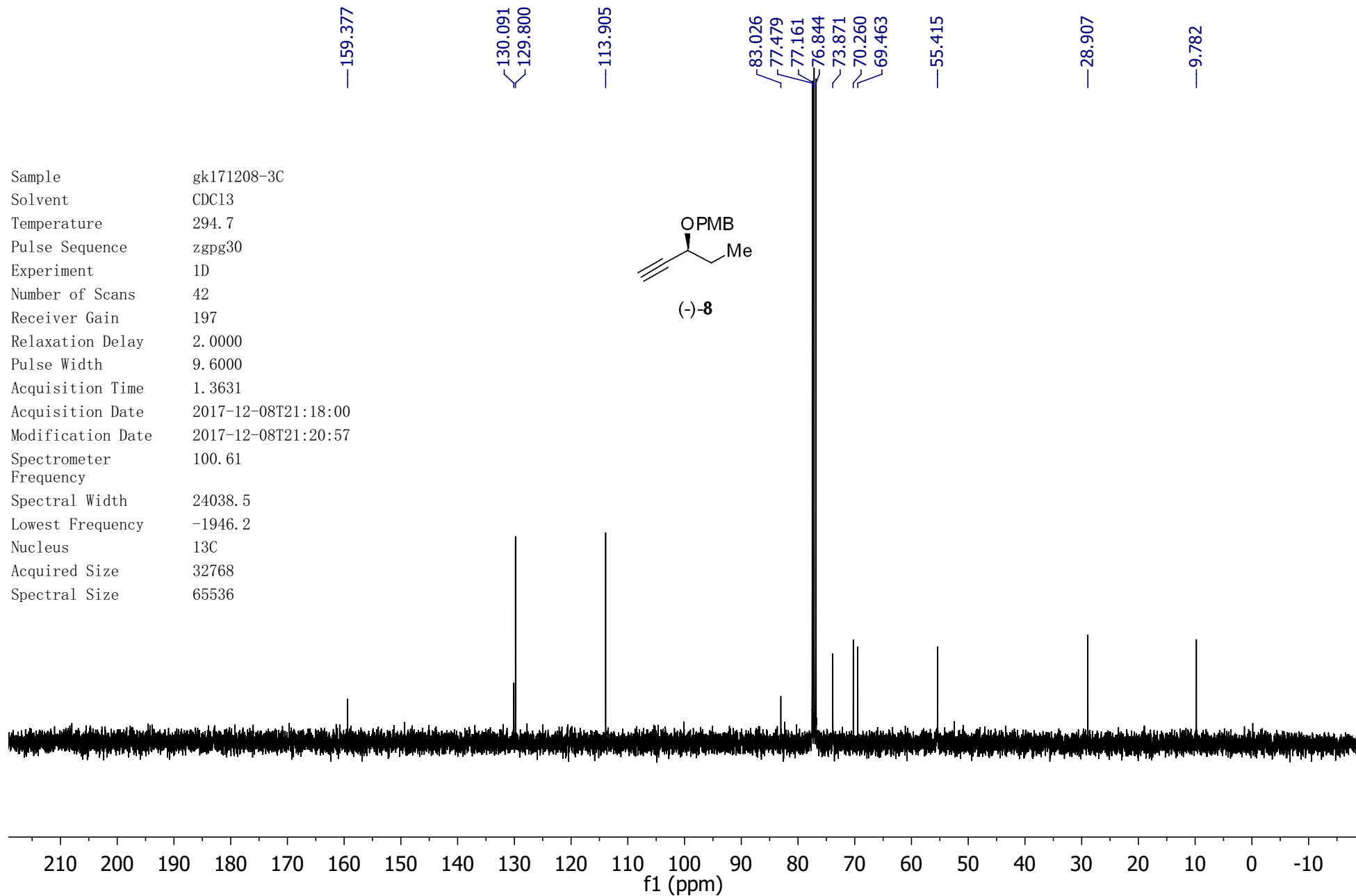
106.865



Sample gk171208-3  
 Solvent CDC13  
 Temperature 294.6  
 Pulse Sequence zg30  
 Experiment 1D  
 Number of Scans 16  
 Receiver Gain 143  
 Relaxation Delay 1.0000  
 Pulse Width 14.3000  
 Acquisition Time 4.0894  
 Acquisition Date 2017-12-08T21:15:00  
 Modification Date 2017-12-08T21:17:09  
 Spectrometer 400.13  
 Frequency  
 Spectral Width 8012.8  
 Lowest Frequency -1545.8  
 Nucleus 1H  
 Acquired Size 32768  
 Spectral Size 65536







Sample gk171208-3C  
 Solvent CDC13  
 Temperature 294.7  
 Pulse Sequence zgpg30  
 Experiment 1D  
 Number of Scans 42  
 Receiver Gain 197  
 Relaxation Delay 2.0000  
 Pulse Width 9.6000  
 Acquisition Time 1.3631  
 Acquisition Date 2017-12-08T21:18:00  
 Modification Date 2017-12-08T21:20:57  
 Spectrometer 100.61  
 Frequency  
 Spectral Width 24038.5  
 Lowest Frequency -1946.2  
 Nucleus 13C  
 Acquired Size 32768  
 Spectral Size 65536

9.427  
9.407

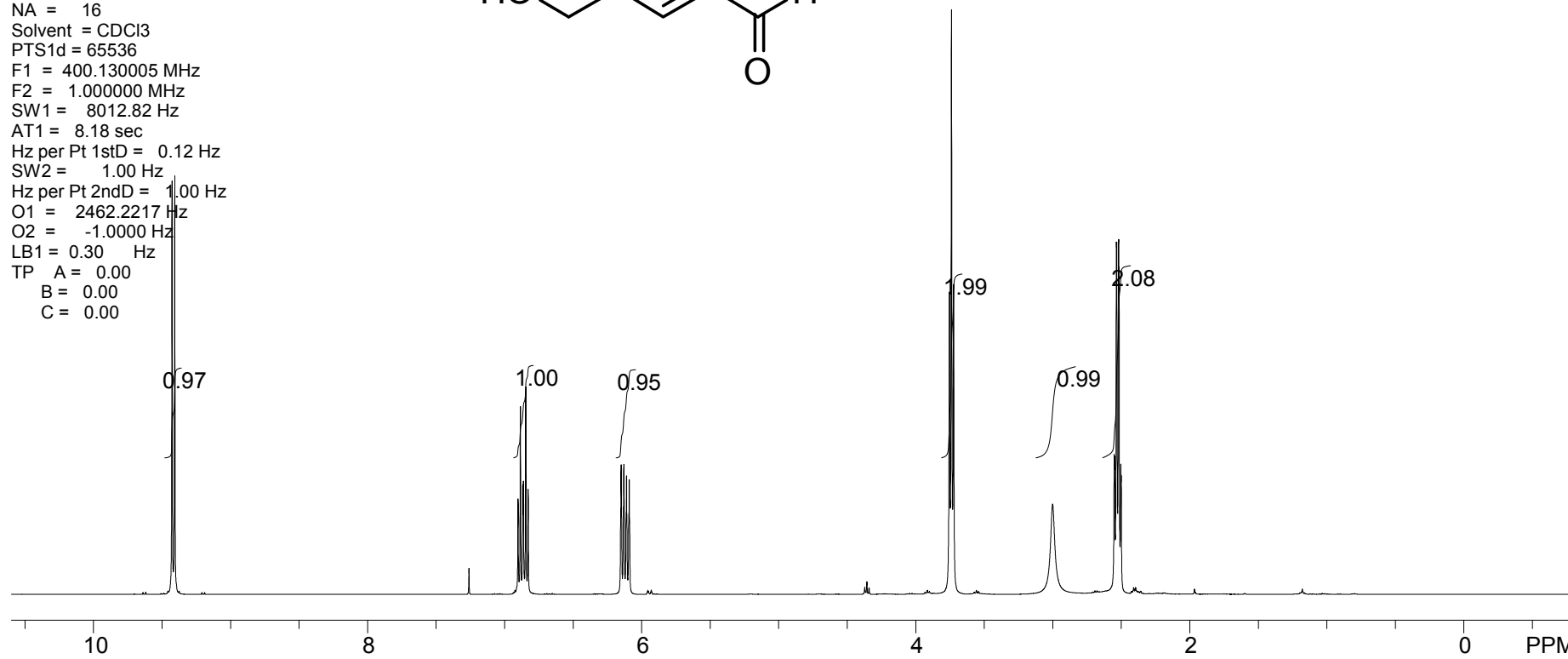
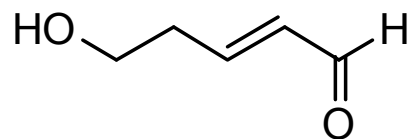
7.260  
6.902  
6.885  
6.868  
6.863  
6.846  
6.829  
6.150  
6.130  
6.111  
6.091

3.756  
3.740  
3.724

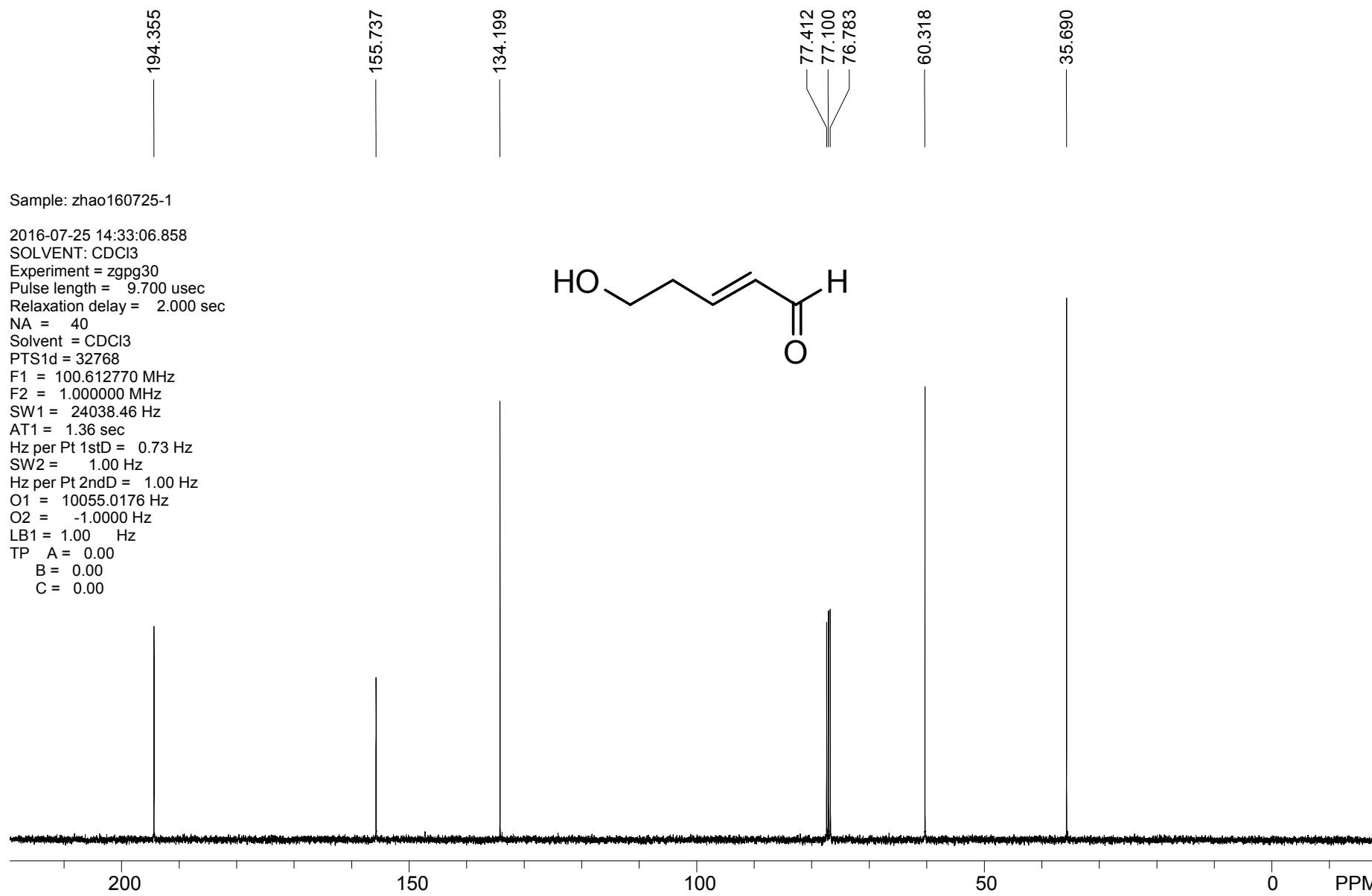
3.002  
2.553  
2.550  
2.537  
2.535  
2.521  
2.505  
2.502

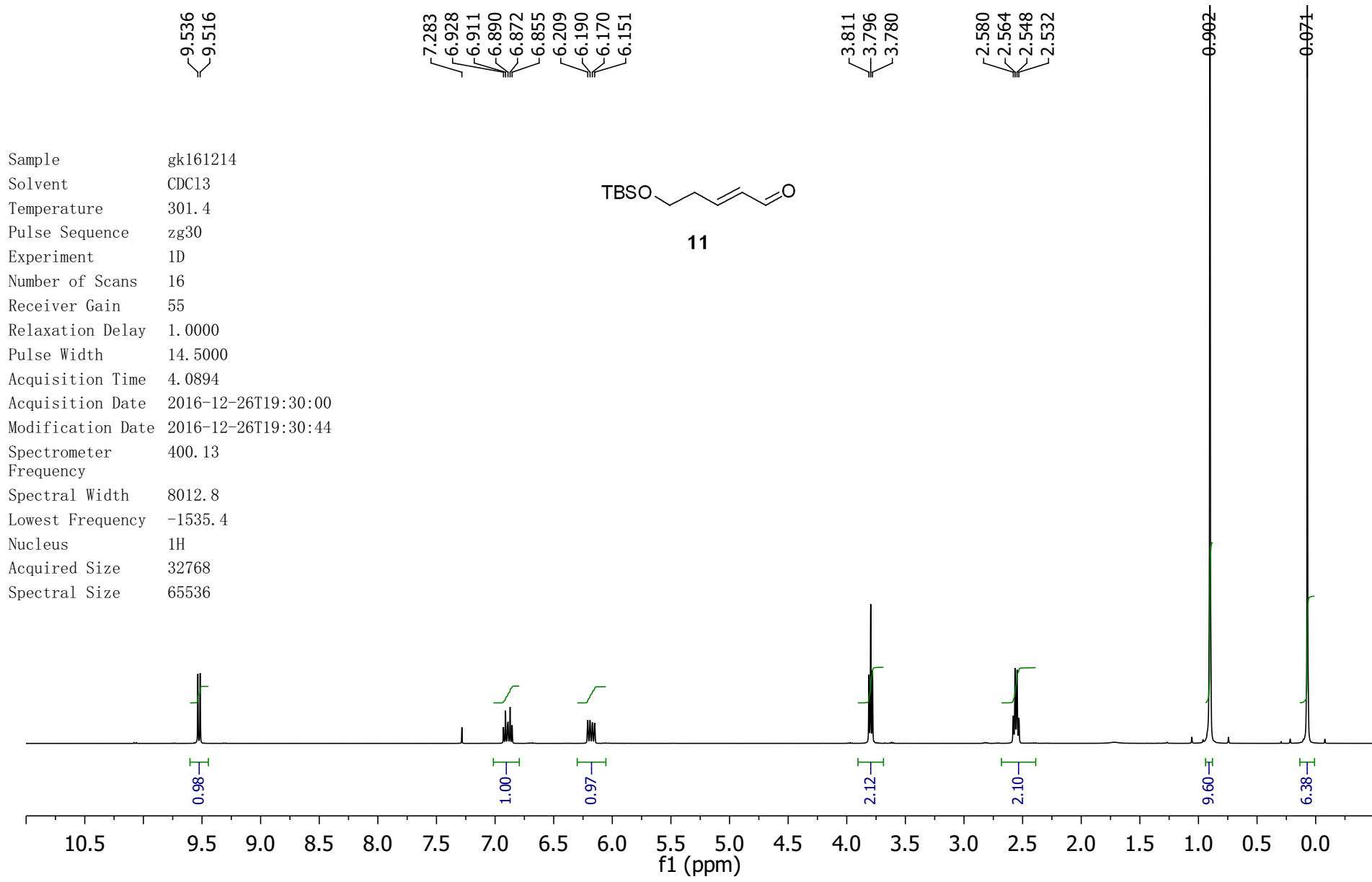
Sample: zhao160725-1

2016-07-25 14:30:04.938  
SOLVENT: CDCl3  
Experiment = zg30  
Pulse length = 14.500 usec  
Relaxation delay = 1.000 sec  
NA = 16  
Solvent = CDCl3  
PTS1d = 65536  
F1 = 400.130005 MHz  
F2 = 1.000000 MHz  
SW1 = 8012.82 Hz  
AT1 = 8.18 sec  
Hz per Pt 1stD = 0.12 Hz  
SW2 = 1.00 Hz  
Hz per Pt 2ndD = 1.00 Hz  
O1 = 2462.2217 Hz  
O2 = -1.0000 Hz  
LB1 = 0.30 Hz  
TP A = 0.00  
B = 0.00  
C = 0.00

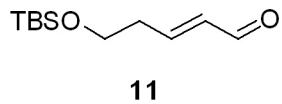


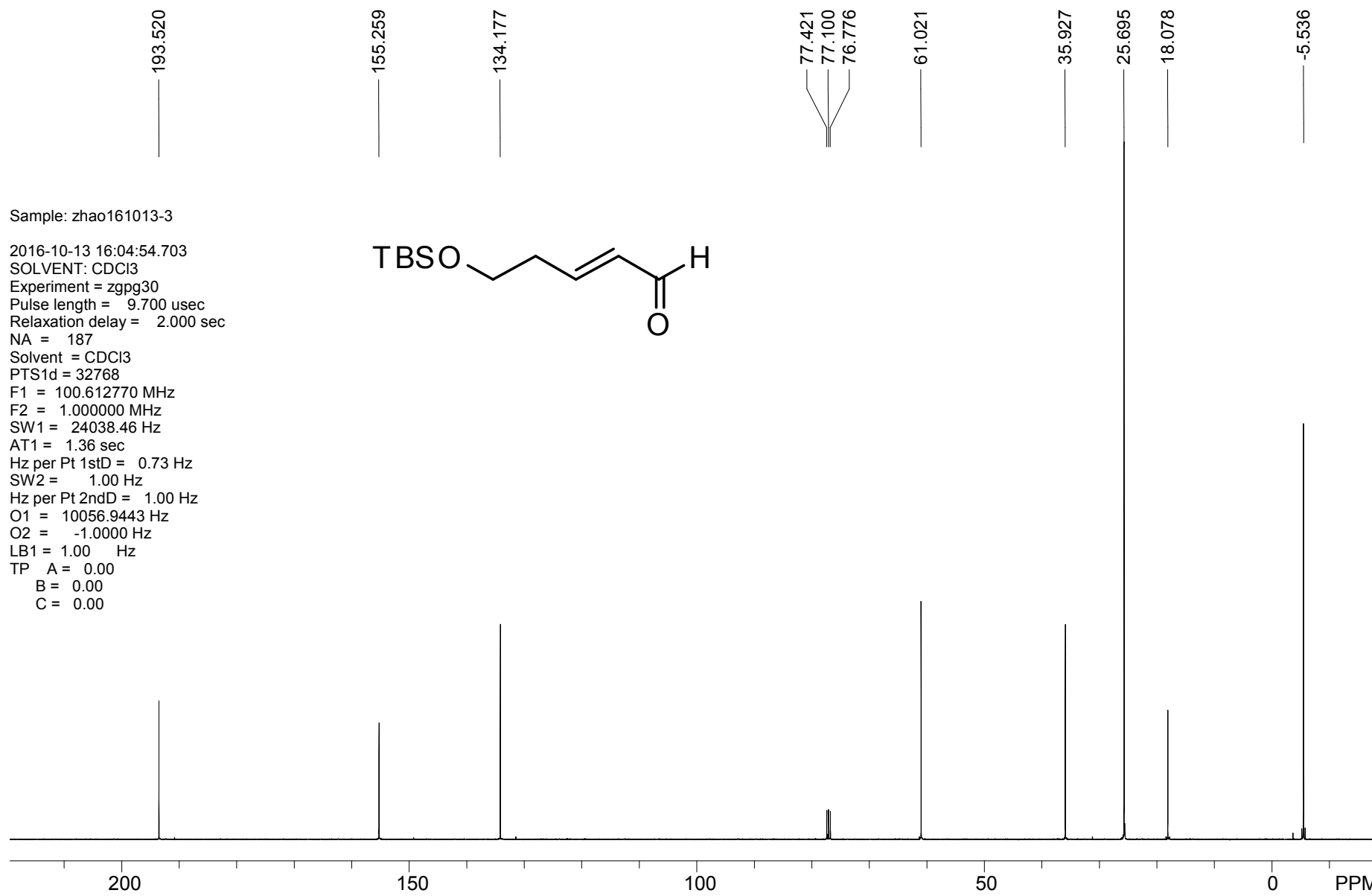
S42





Sample gk161214  
 Solvent CDC13  
 Temperature 301.4  
 Pulse Sequence zg30  
 Experiment 1D  
 Number of Scans 16  
 Receiver Gain 55  
 Relaxation Delay 1.0000  
 Pulse Width 14.5000  
 Acquisition Time 4.0894  
 Acquisition Date 2016-12-26T19:30:00  
 Modification Date 2016-12-26T19:30:44  
 Spectrometer 400.13  
 Frequency  
 Spectral Width 8012.8  
 Lowest Frequency -1535.4  
 Nucleus 1H  
 Acquired Size 32768  
 Spectral Size 65536

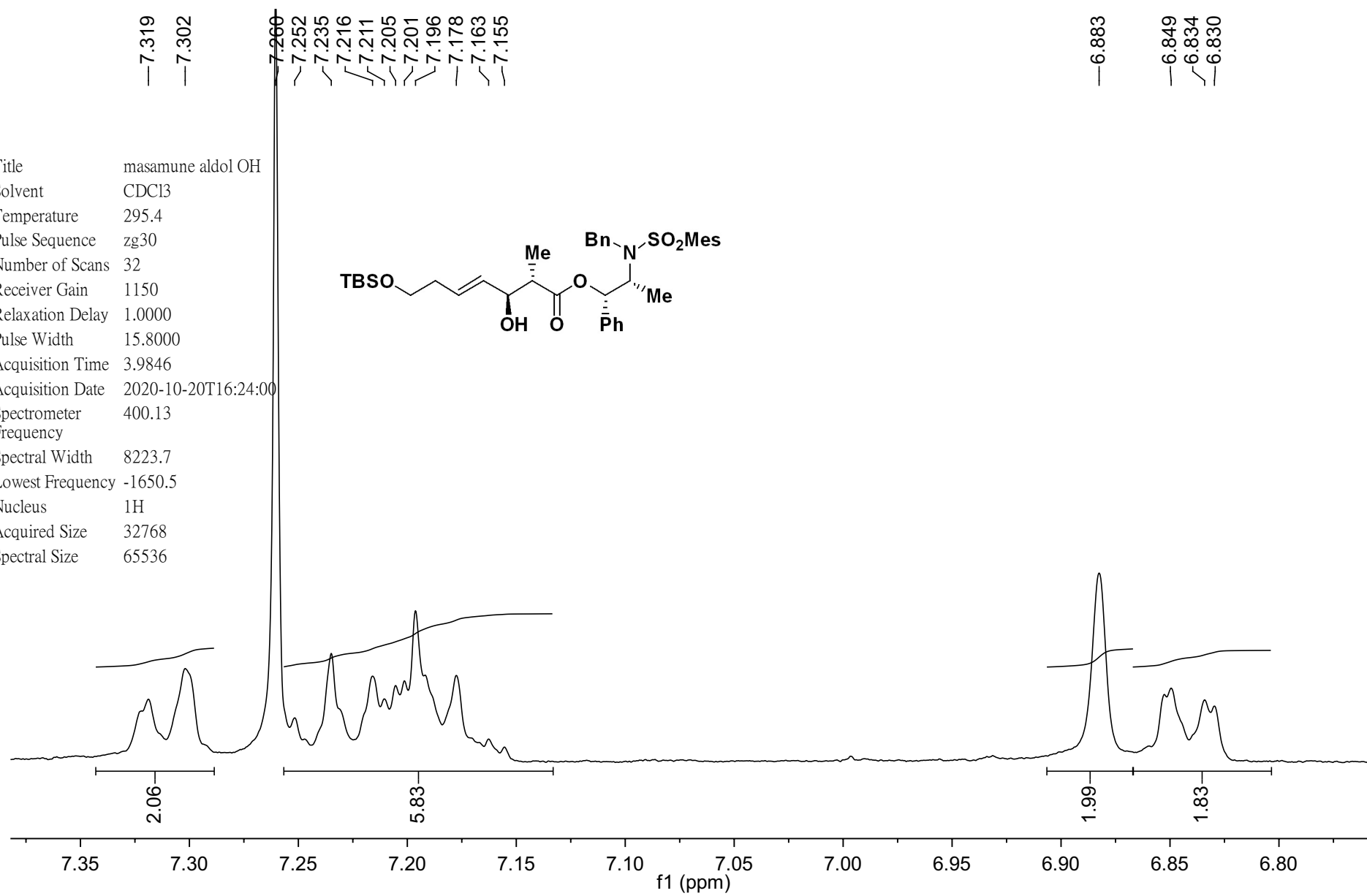
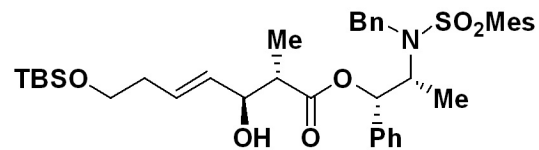




S45



Title masamune aldol OH  
Solvent CDCl3  
Temperature 295.4  
Pulse Sequence zg30  
Number of Scans 32  
Receiver Gain 1150  
Relaxation Delay 1.0000  
Pulse Width 15.8000  
Acquisition Time 3.9846  
Acquisition Date 2020-10-20T16:24:00  
Spectrometer 400.13  
Frequency  
Spectral Width 8223.7  
Lowest Frequency -1650.5  
Nucleus 1H  
Acquired Size 32768  
Spectral Size 65536



5.824  
5.814  
5.741  
5.724  
5.704  
5.686  
5.668  
5.489  
5.470  
5.450  
5.431

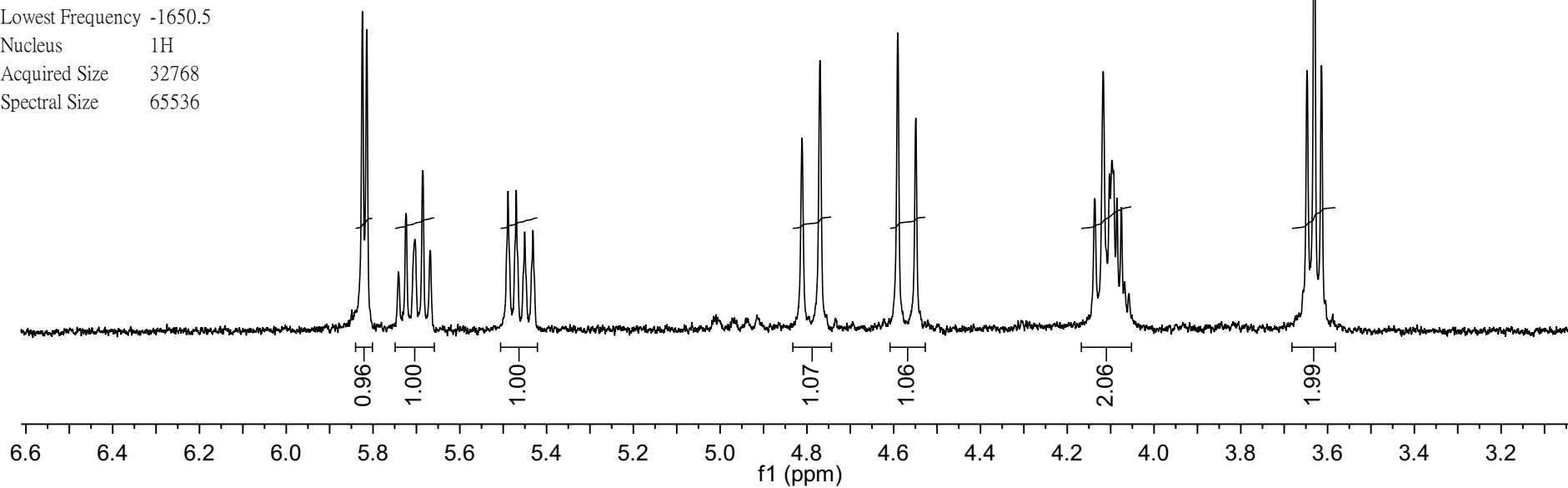
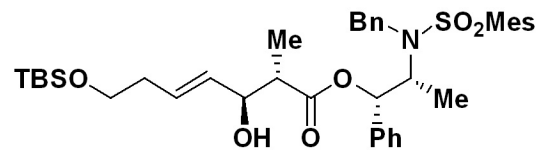
4.811  
4.770

4.591  
4.549

4.137  
4.117  
4.103  
4.097  
4.085  
4.075  
4.058

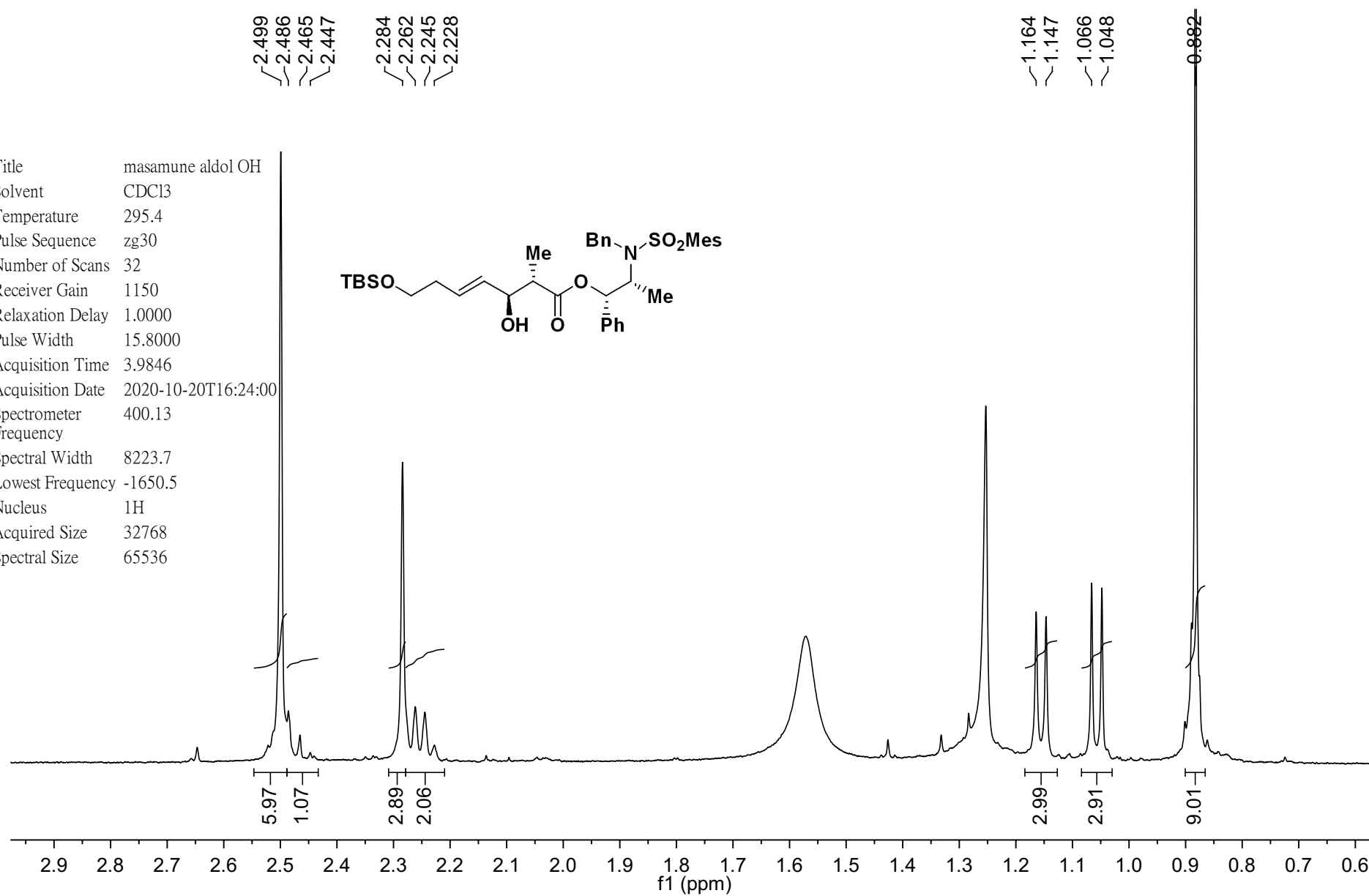
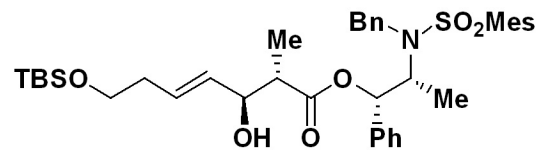
3.647  
3.631  
3.614

Title masamune aldol OH  
Solvent CDCl3  
Temperature 295.4  
Pulse Sequence zg30  
Number of Scans 32  
Receiver Gain 1150  
Relaxation Delay 1.0000  
Pulse Width 15.8000  
Acquisition Time 3.9846  
Acquisition Date 2020-10-20T16:24:00  
Spectrometer 400.13  
Frequency  
Spectral Width 8223.7  
Lowest Frequency -1650.5  
Nucleus 1H  
Acquired Size 32768  
Spectral Size 65536

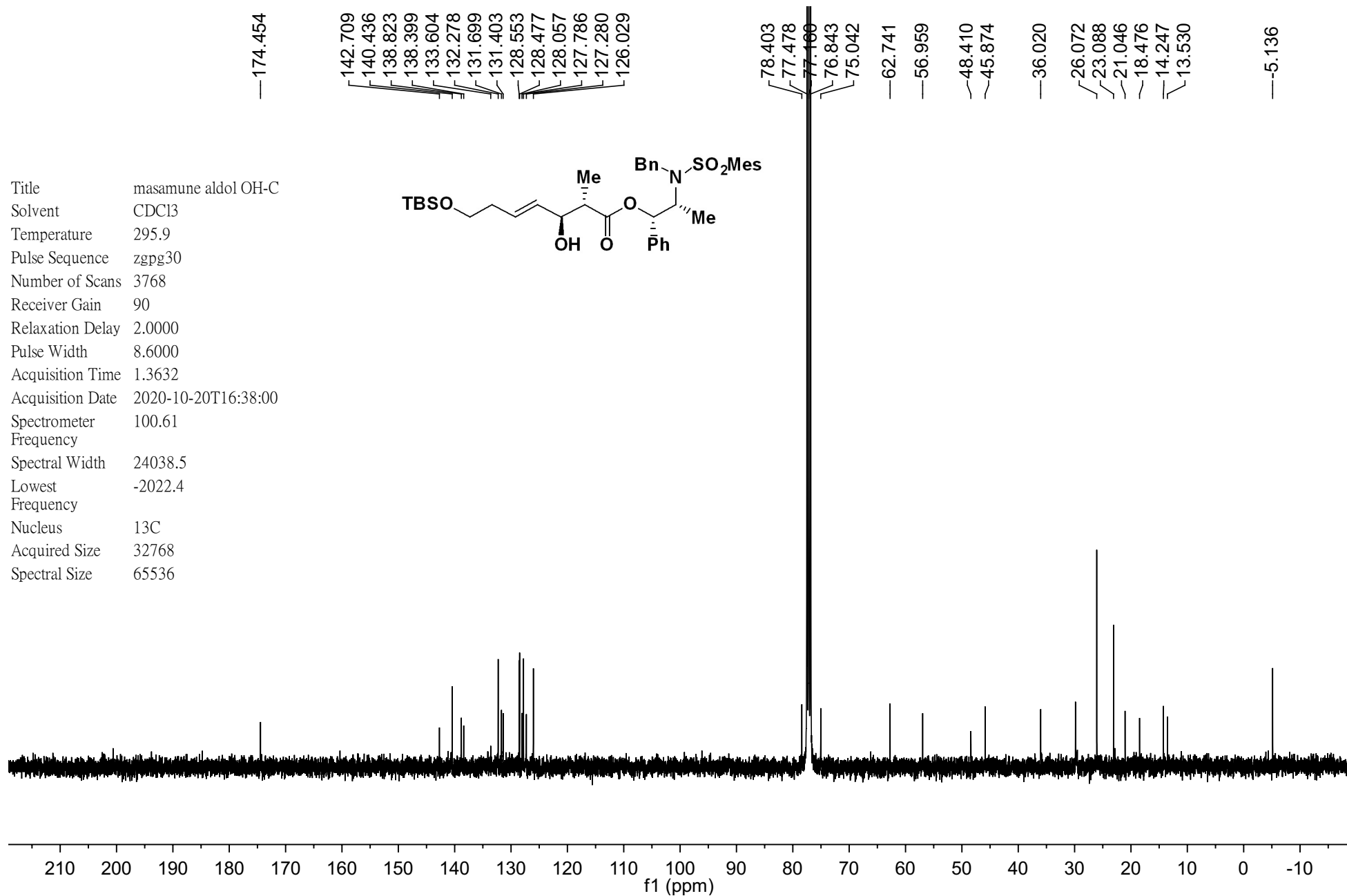
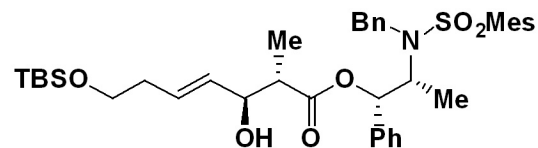




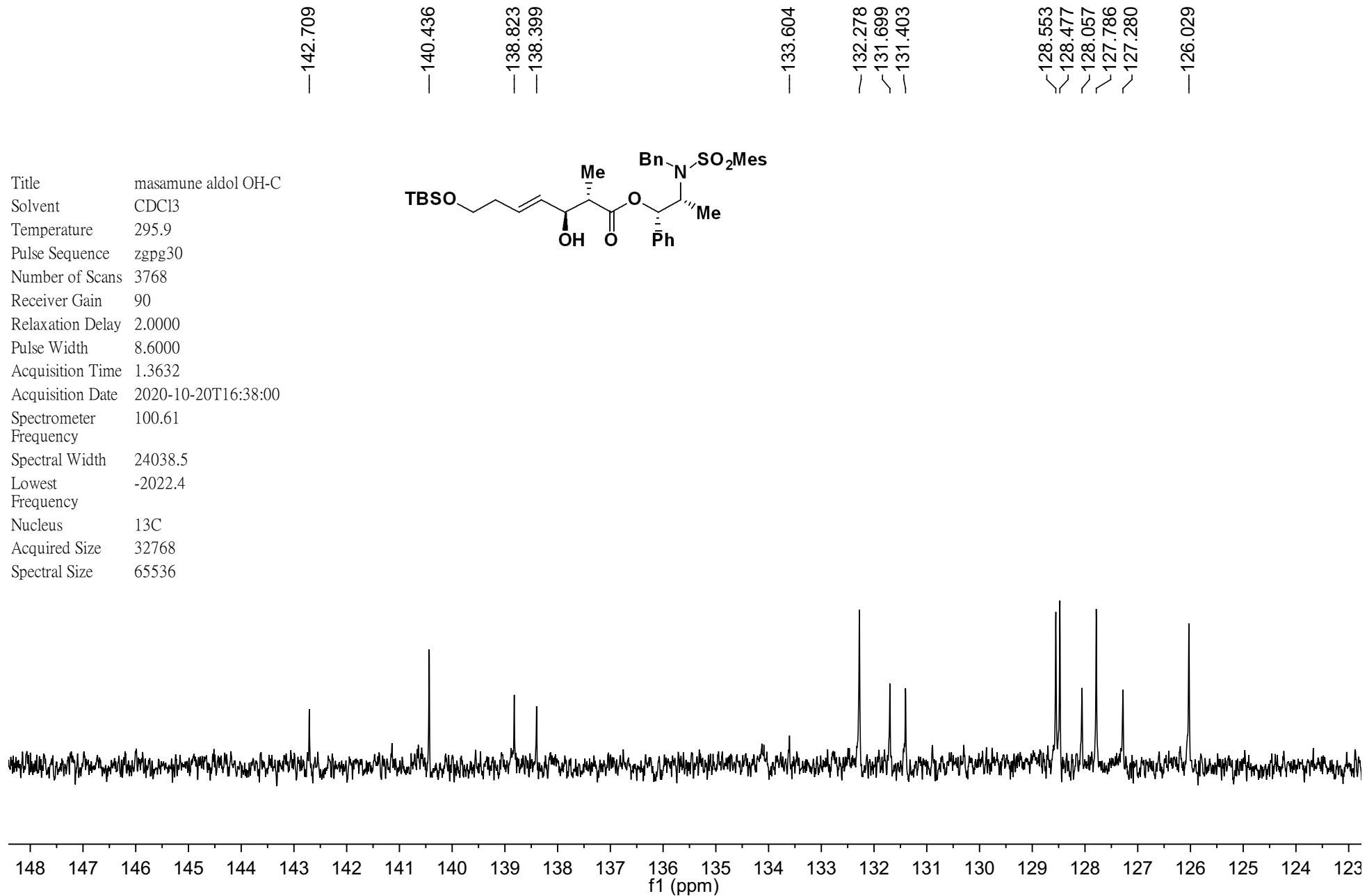
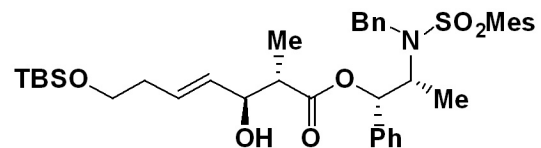
Title masamune aldol OH  
 Solvent CDCl3  
 Temperature 295.4  
 Pulse Sequence zg30  
 Number of Scans 32  
 Receiver Gain 1150  
 Relaxation Delay 1.0000  
 Pulse Width 15.8000  
 Acquisition Time 3.9846  
 Acquisition Date 2020-10-20T16:24:00  
 Spectrometer 400.13  
 Frequency  
 Spectral Width 8223.7  
 Lowest Frequency -1650.5  
 Nucleus 1H  
 Acquired Size 32768  
 Spectral Size 65536



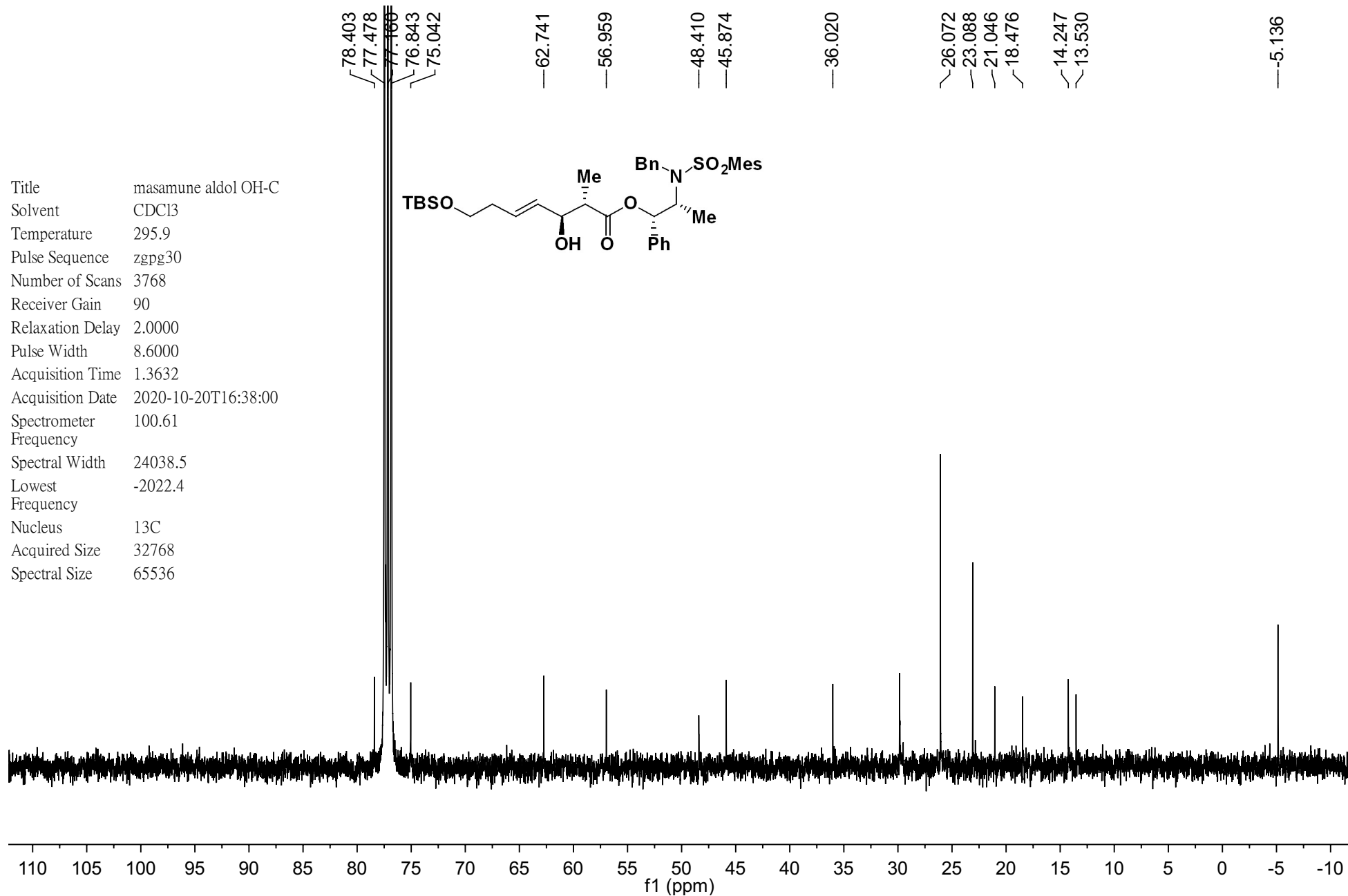
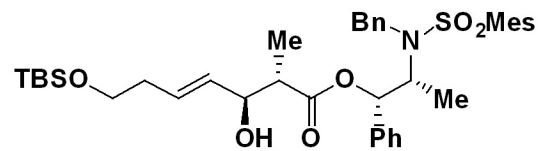
Title masamune aldol OH-C  
 Solvent CDCl3  
 Temperature 295.9  
 Pulse Sequence zgpg30  
 Number of Scans 3768  
 Receiver Gain 90  
 Relaxation Delay 2.0000  
 Pulse Width 8.6000  
 Acquisition Time 1.3632  
 Acquisition Date 2020-10-20T16:38:00  
 Spectrometer 100.61  
 Frequency  
 Spectral Width 24038.5  
 Lowest -2022.4  
 Frequency  
 Nucleus 13C  
 Acquired Size 32768  
 Spectral Size 65536

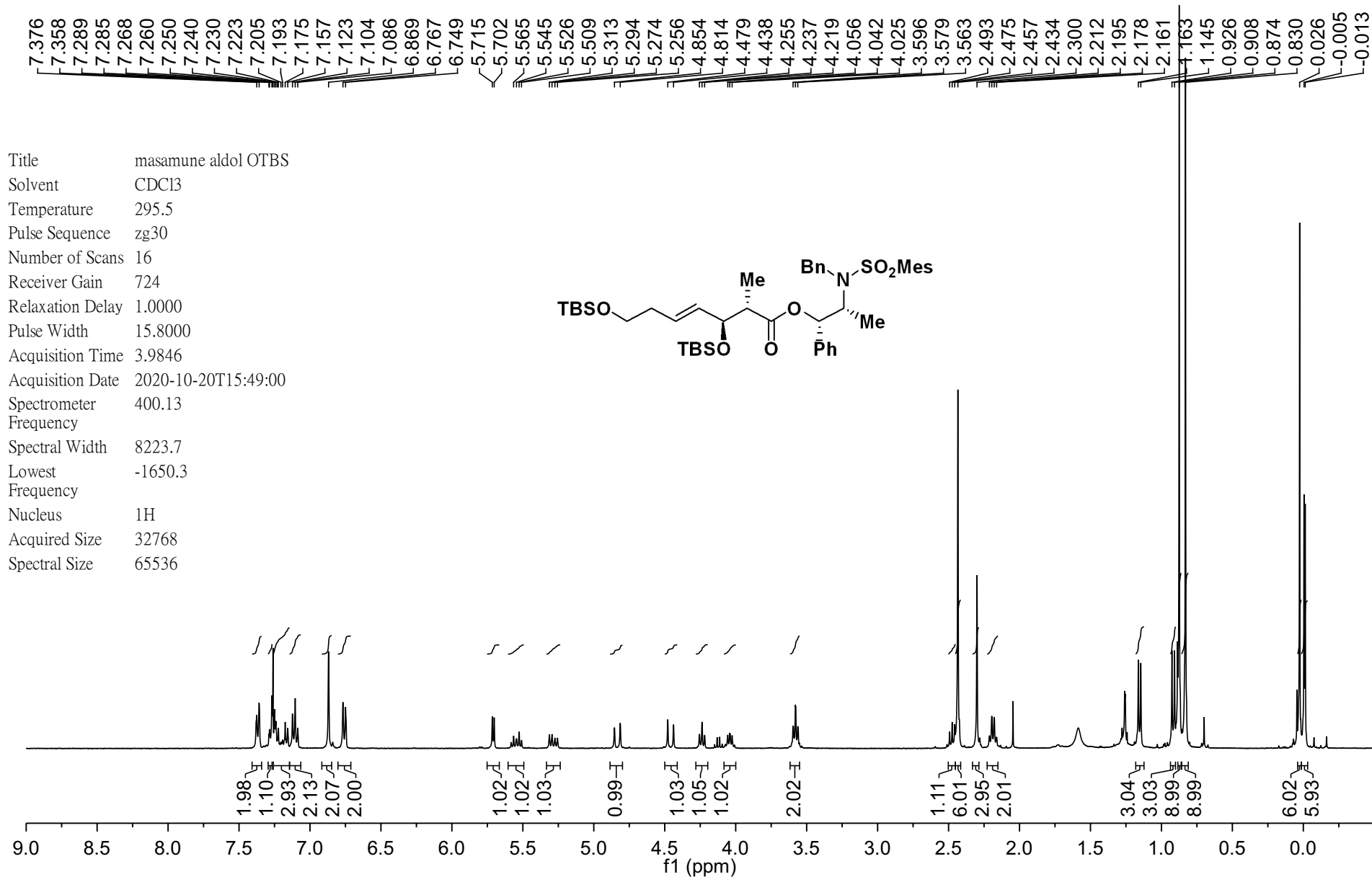


Title masamune aldol OH-C  
 Solvent CDCl3  
 Temperature 295.9  
 Pulse Sequence zgpg30  
 Number of Scans 3768  
 Receiver Gain 90  
 Relaxation Delay 2.0000  
 Pulse Width 8.6000  
 Acquisition Time 1.3632  
 Acquisition Date 2020-10-20T16:38:00  
 Spectrometer 100.61  
 Frequency  
 Spectral Width 24038.5  
 Lowest Frequency -2022.4  
 Nucleus 13C  
 Acquired Size 32768  
 Spectral Size 65536



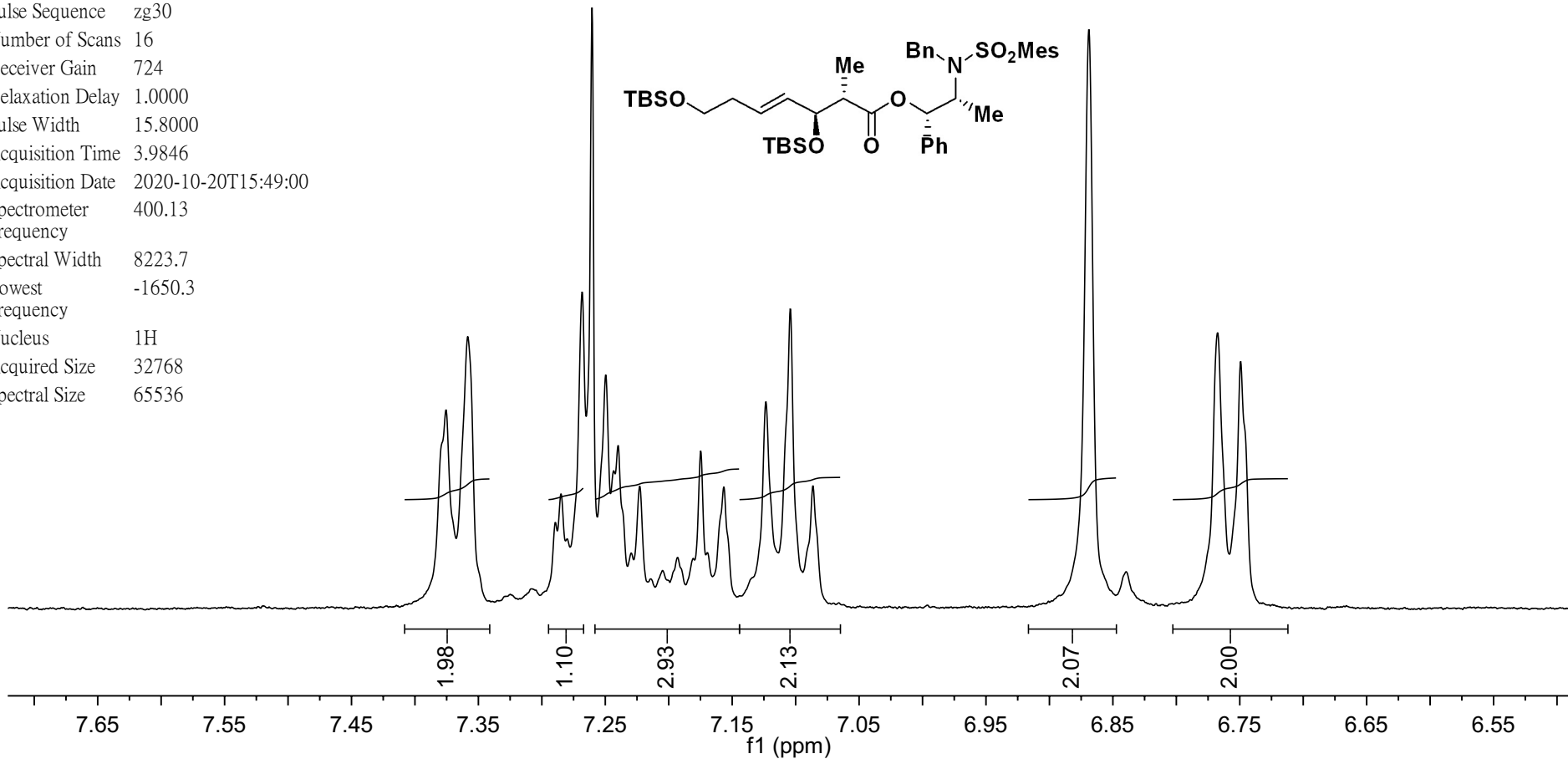
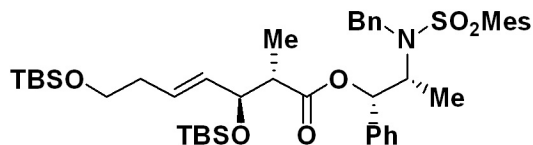
Title masamune aldol OH-C  
 Solvent CDCl3  
 Temperature 295.9  
 Pulse Sequence zgpg30  
 Number of Scans 3768  
 Receiver Gain 90  
 Relaxation Delay 2.0000  
 Pulse Width 8.6000  
 Acquisition Time 1.3632  
 Acquisition Date 2020-10-20T16:38:00  
 Spectrometer 100.61  
 Frequency  
 Spectral Width 24038.5  
 Lowest -2022.4  
 Frequency  
 Nucleus 13C  
 Acquired Size 32768  
 Spectral Size 65536





Title masamune aldol OTBS  
 Solvent CDCl3  
 Temperature 295.5  
 Pulse Sequence zg30  
 Number of Scans 16  
 Receiver Gain 724  
 Relaxation Delay 1.0000  
 Pulse Width 15.8000  
 Acquisition Time 3.9846  
 Acquisition Date 2020-10-20T15:49:00  
 Spectrometer 400.13  
 Frequency  
 Spectral Width 8223.7  
 Lowest Frequency -1650.3  
 Nucleus 1H  
 Acquired Size 32768  
 Spectral Size 65536

7.376  
 7.358  
 7.289  
 7.285  
 7.268  
 7.260  
 7.250  
 7.240  
 7.230  
 7.223  
 7.205  
 7.193  
 7.175  
 7.157  
 7.123  
 7.104  
 7.086  
 6.869  
 6.767  
 6.749



5.715  
5.702  
5.582  
5.565  
5.545  
5.526  
5.509

5.313  
5.294  
5.274  
5.256

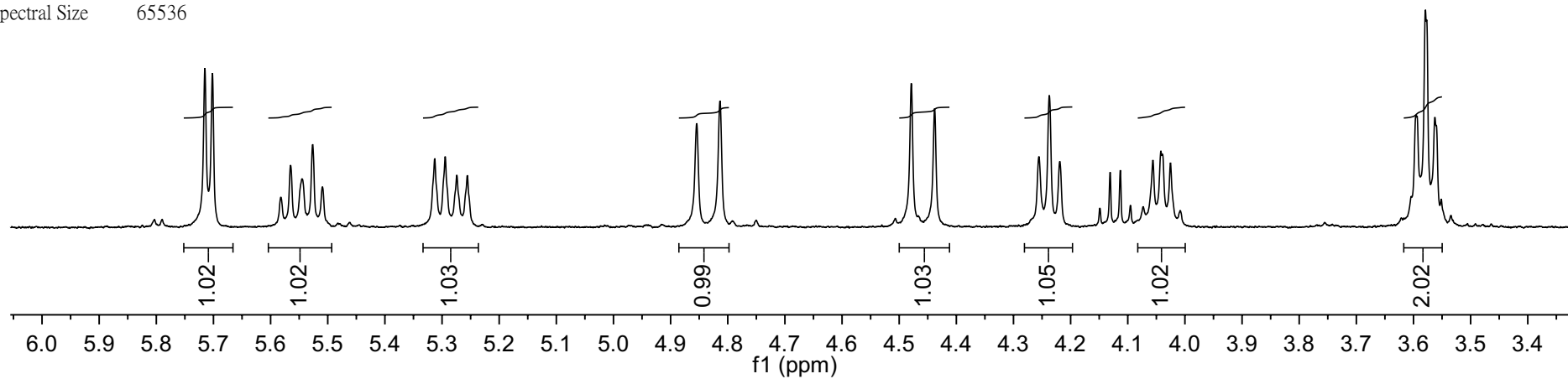
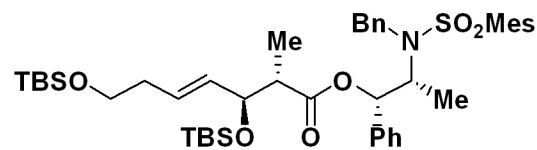
4.854  
4.814

4.479  
4.438

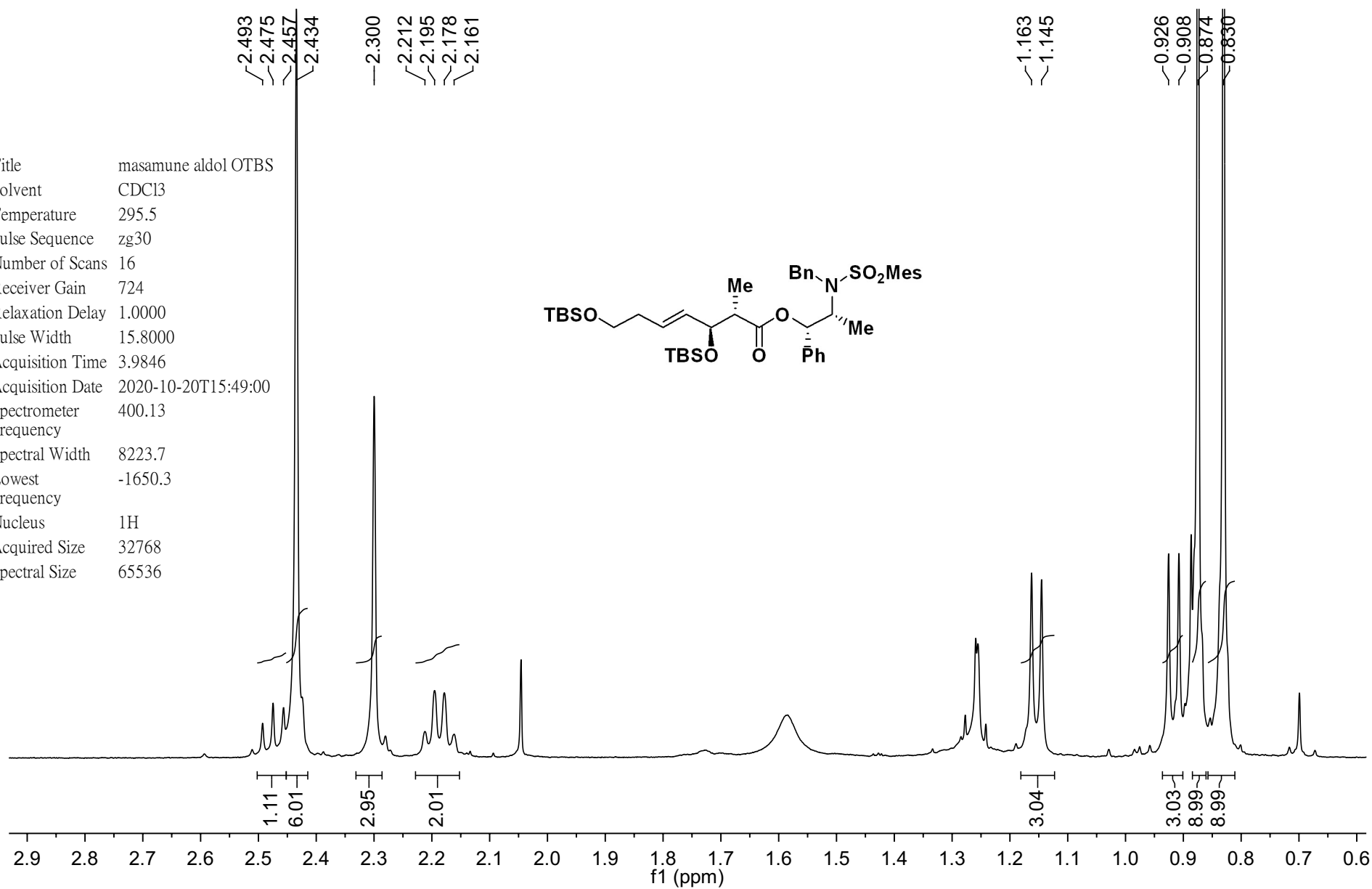
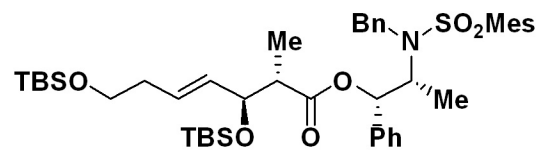
4.255  
4.237  
4.219  
4.073  
4.056  
4.042  
4.025  
4.008

3.596  
3.579  
3.563

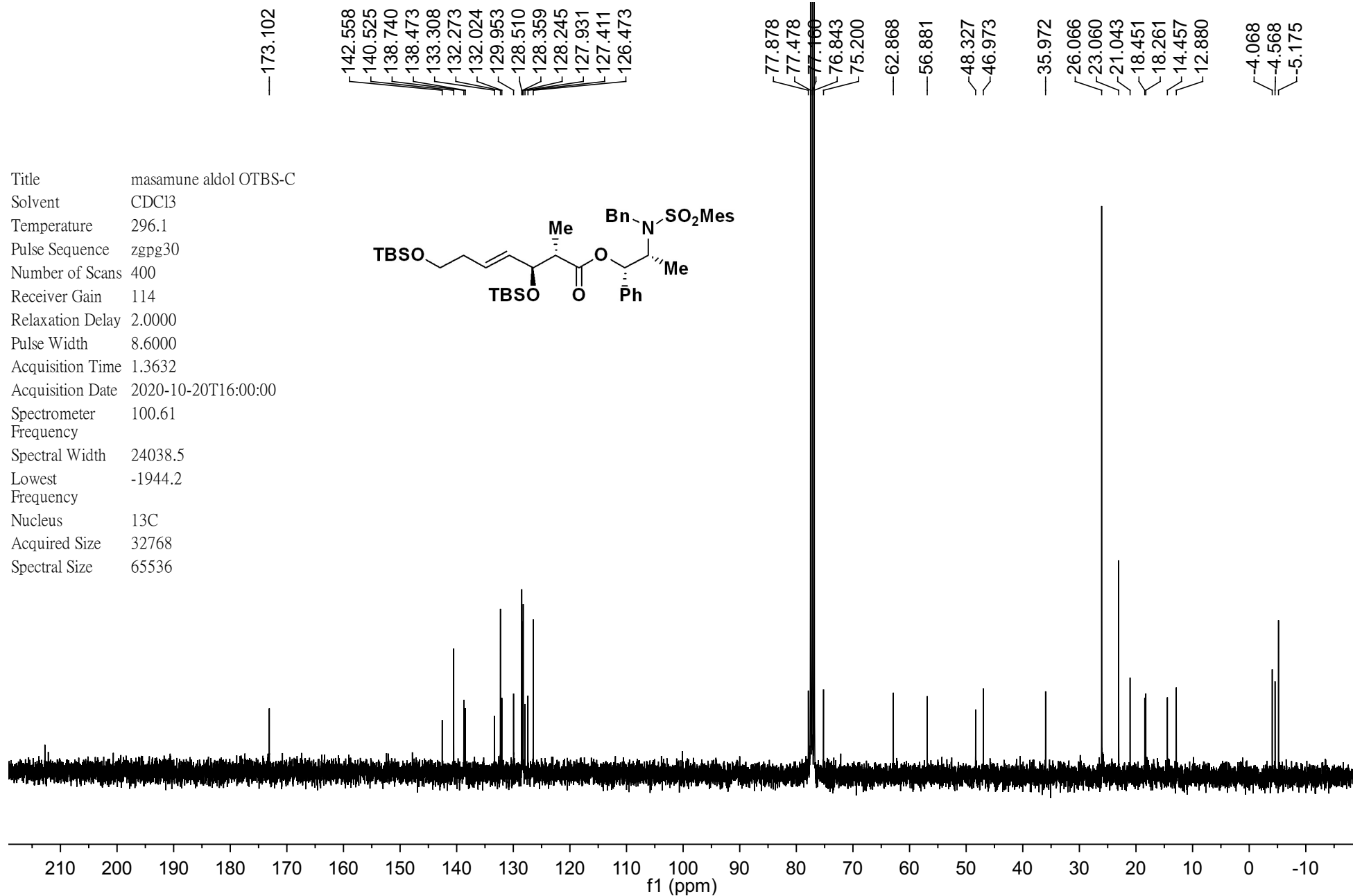
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Solvent CDCl3  
Temperature 295.5  
Pulse Sequence zg30  
Number of Scans 16  
Receiver Gain 724  
Relaxation Delay 1.0000  
Pulse Width 15.8000  
Acquisition Time 3.9846  
Acquisition Date 2020-10-20T15:49:00  
Spectrometer 400.13  
Frequency  
Spectral Width 8223.7  
Lowest -1650.3  
Frequency  
Nucleus 1H  
Acquired Size 32768  
Spectral Size 65536



Title masamune aldol OTBS  
 Solvent CDCl3  
 Temperature 295.5  
 Pulse Sequence zg30  
 Number of Scans 16  
 Receiver Gain 724  
 Relaxation Delay 1.0000  
 Pulse Width 15.8000  
 Acquisition Time 3.9846  
 Acquisition Date 2020-10-20T15:49:00  
 Spectrometer 400.13  
 Frequency  
 Spectral Width 8223.7  
 Lowest Frequency -1650.3  
 Nucleus 1H  
 Acquired Size 32768  
 Spectral Size 65536

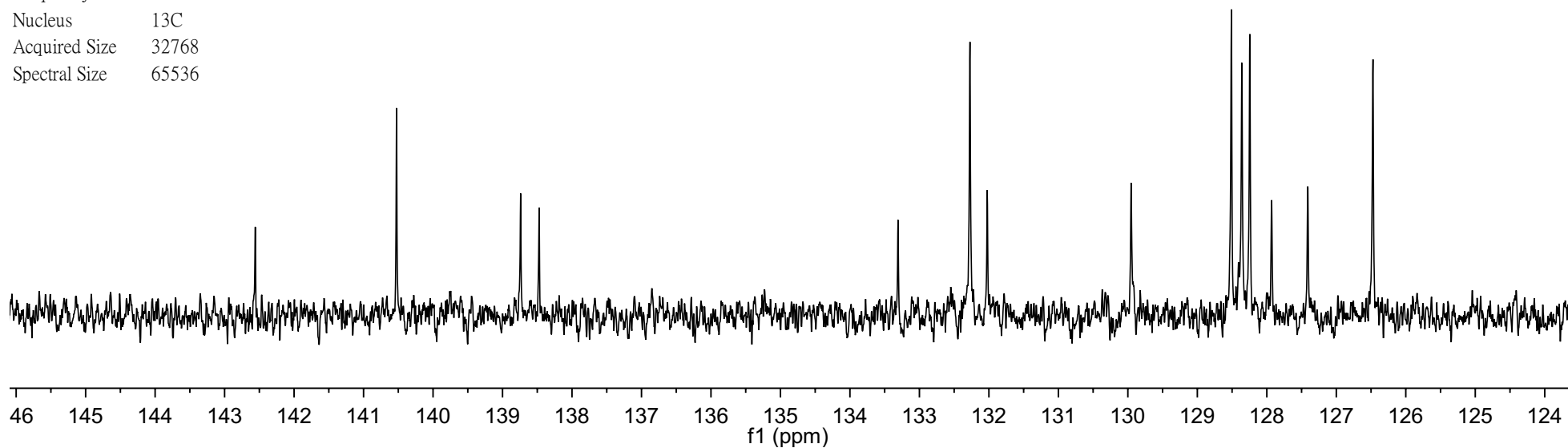
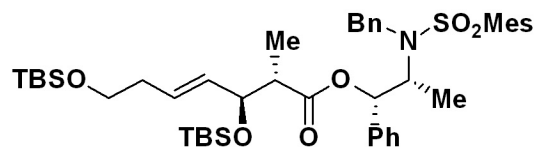


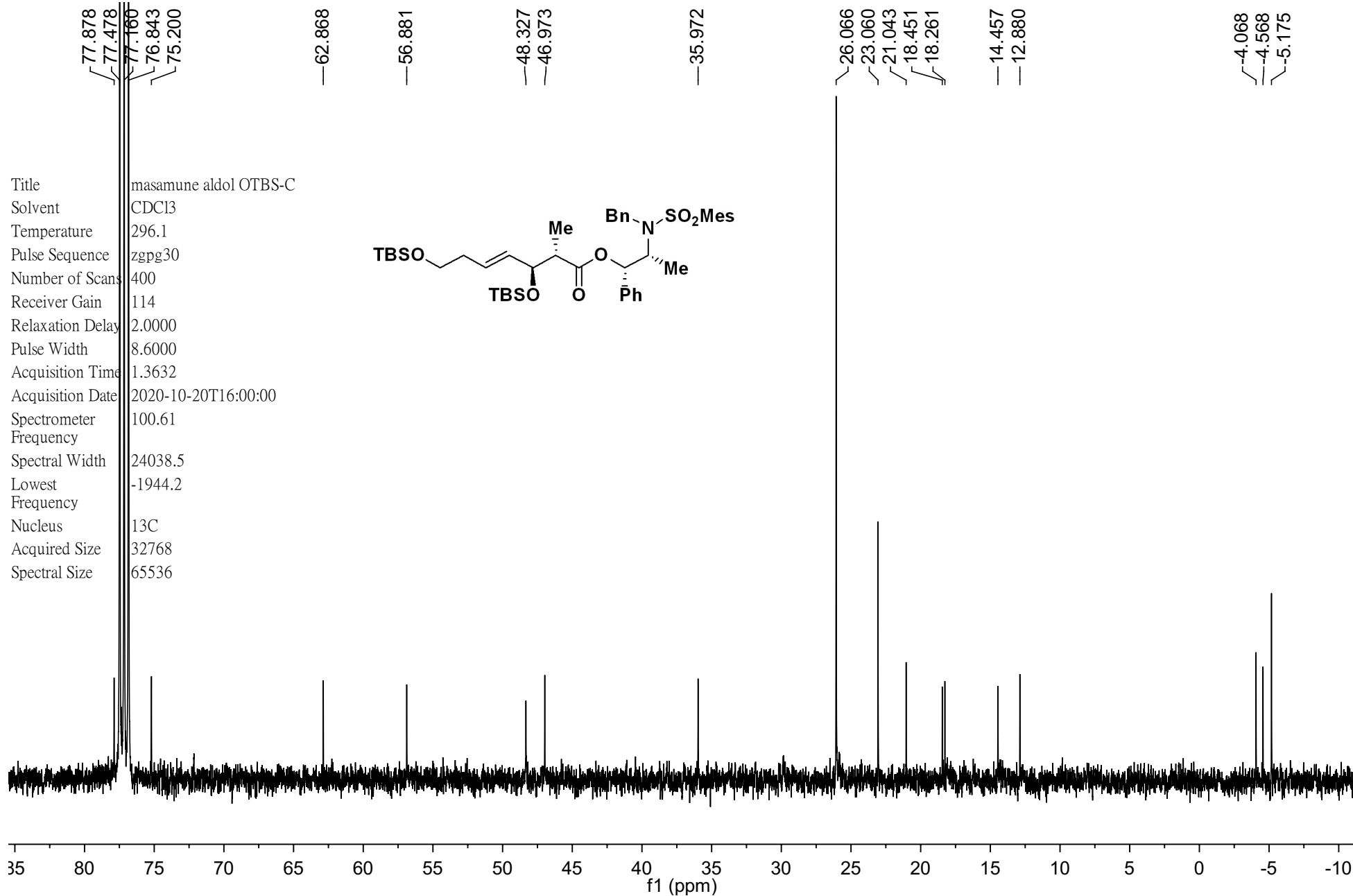




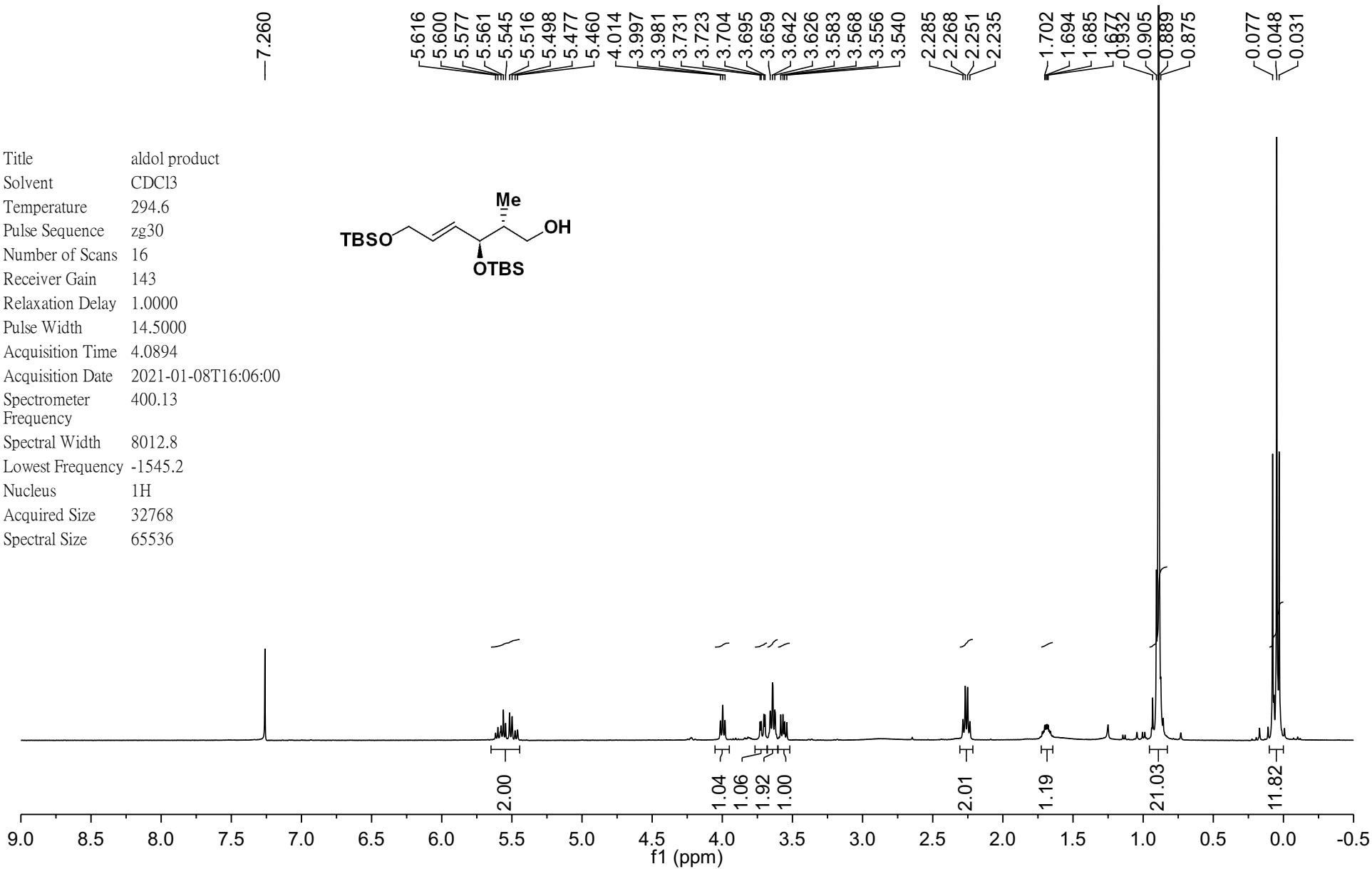
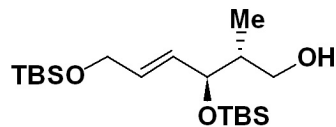
— 142.558  
 — 140.525  
 ~ 138.740  
 ~ 138.473  
 — 133.308  
 ~ 132.273  
 ~ 132.024  
 — 129.953  
 ~ 128.510  
 ~ 128.359  
 ~ 128.245  
 ~ 127.931  
 ~ 127.411  
 — 126.473

Title masamune aldol OTBS-C  
 Solvent CDCl3  
 Temperature 296.1  
 Pulse Sequence zgpg30  
 Number of Scans 400  
 Receiver Gain 114  
 Relaxation Delay 2.0000  
 Pulse Width 8.6000  
 Acquisition Time 1.3632  
 Acquisition Date 2020-10-20T16:00:00  
 Spectrometer 100.61  
 Frequency  
 Spectral Width 24038.5  
 Lowest Frequency -1944.2  
 Nucleus 13C  
 Acquired Size 32768  
 Spectral Size 65536





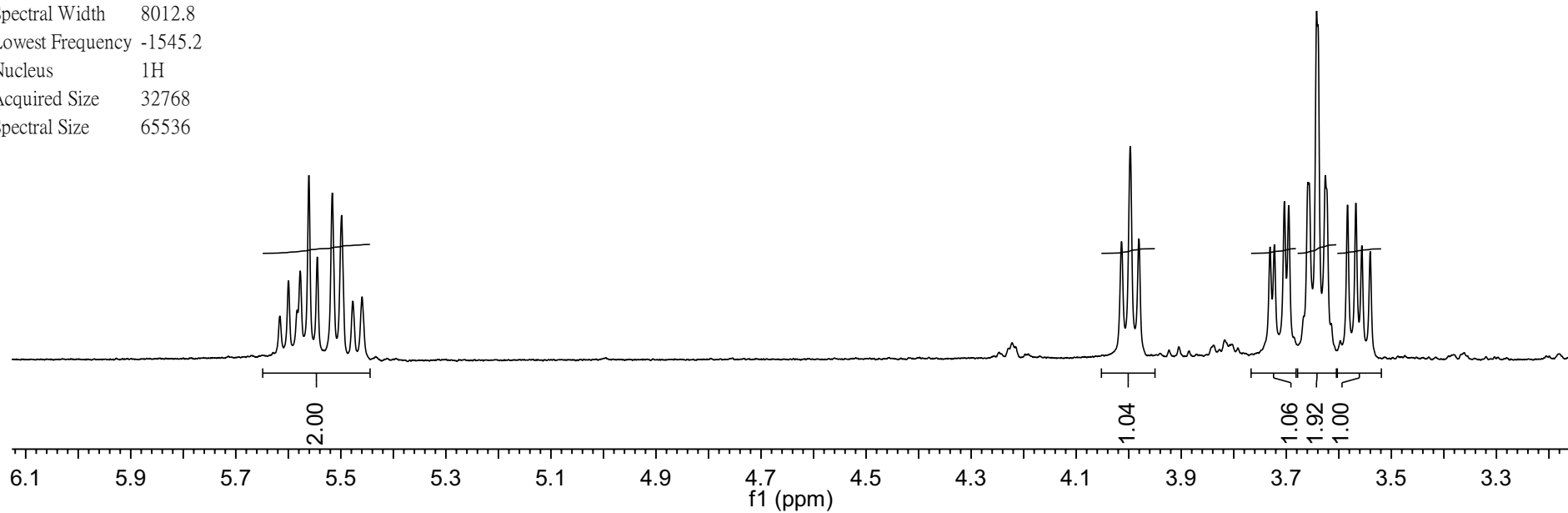
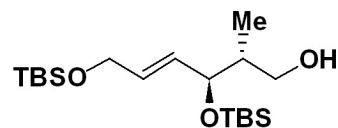
Title aldol product  
 Solvent CDCl3  
 Temperature 294.6  
 Pulse Sequence zg30  
 Number of Scans 16  
 Receiver Gain 143  
 Relaxation Delay 1.0000  
 Pulse Width 14.5000  
 Acquisition Time 4.0894  
 Acquisition Date 2021-01-08T16:06:00  
 Spectrometer 400.13  
 Frequency  
 Spectral Width 8012.8  
 Lowest Frequency -1545.2  
 Nucleus 1H  
 Acquired Size 32768  
 Spectral Size 65536



5.616  
5.600  
5.577  
5.561  
5.545  
5.516  
5.498  
5.477  
5.460

4.014  
3.997  
3.981  
3.731  
3.723  
3.704  
3.695  
3.659  
3.642  
3.626  
3.583  
3.568  
3.556  
3.540

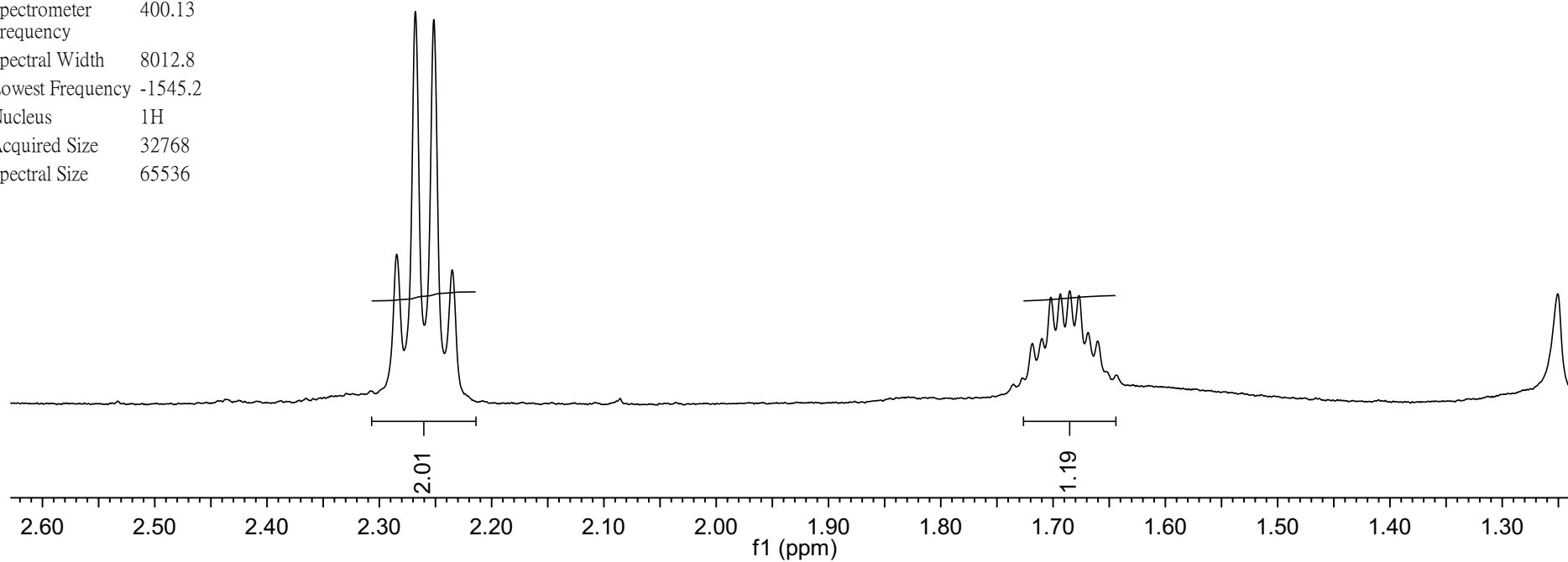
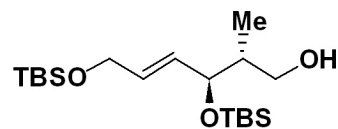
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Solvent CDCl3  
Temperature 294.6  
Pulse Sequence zg30  
Number of Scans 16  
Receiver Gain 143  
Relaxation Delay 1.0000  
Pulse Width 14.5000  
Acquisition Time 4.0894  
Acquisition Date 2021-01-08T16:06:00  
Spectrometer 400.13  
Frequency  
Spectral Width 8012.8  
Lowest Frequency -1545.2  
Nucleus 1H  
Acquired Size 32768  
Spectral Size 65536



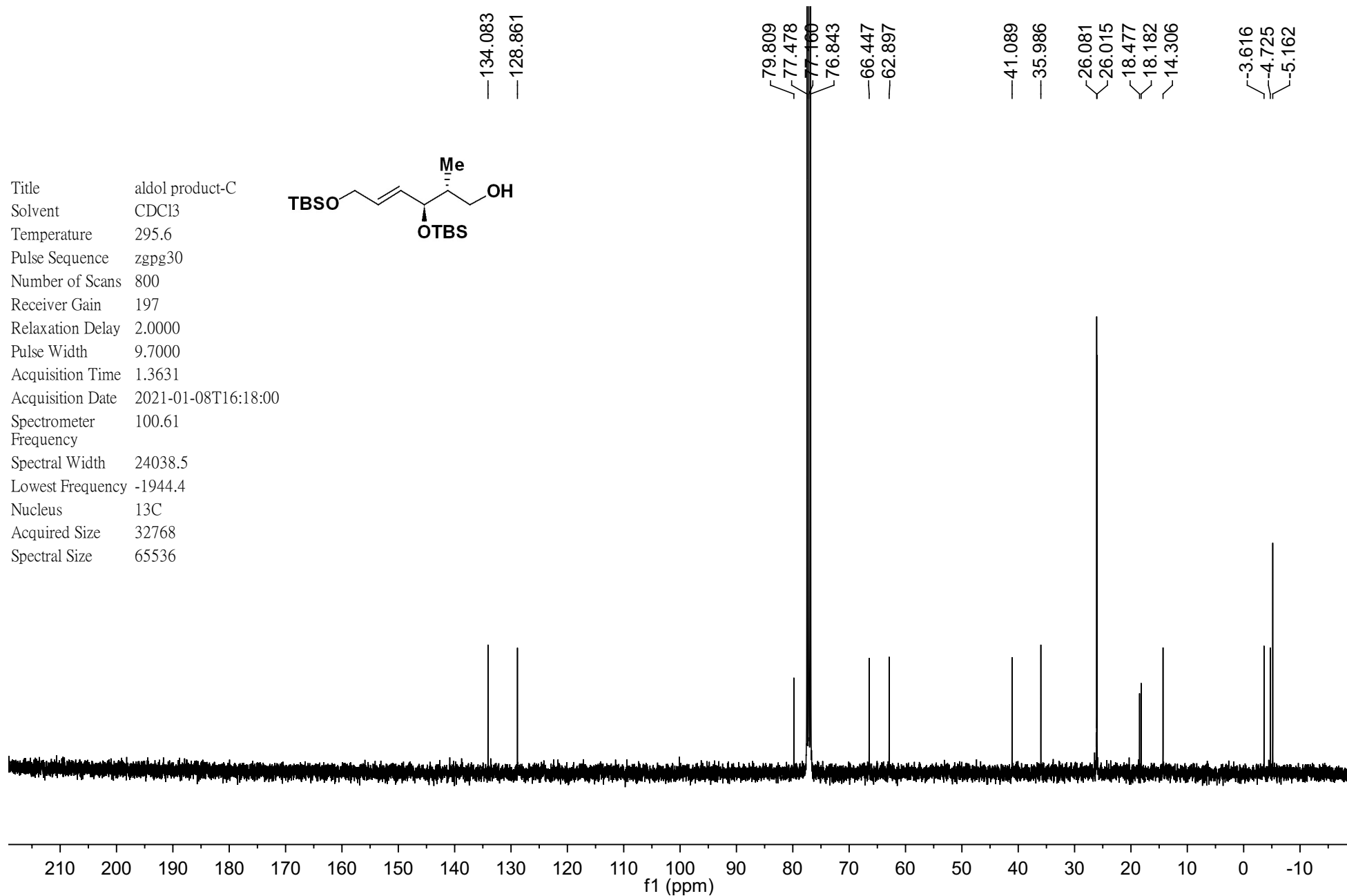
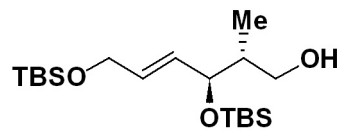
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Solvent CDCl3  
Temperature 294.6  
Pulse Sequence zg30  
Number of Scans 16  
Receiver Gain 143  
Relaxation Delay 1.0000  
Pulse Width 14.5000  
Acquisition Time 4.0894  
Acquisition Date 2021-01-08T16:06:00  
Spectrometer 400.13  
Frequency  
Spectral Width 8012.8  
Lowest Frequency -1545.2  
Nucleus 1H  
Acquired Size 32768  
Spectral Size 65536

2.285  
2.268  
2.251  
2.235

1.718  
1.710  
1.702  
1.694  
1.685  
1.677  
1.669  
1.660

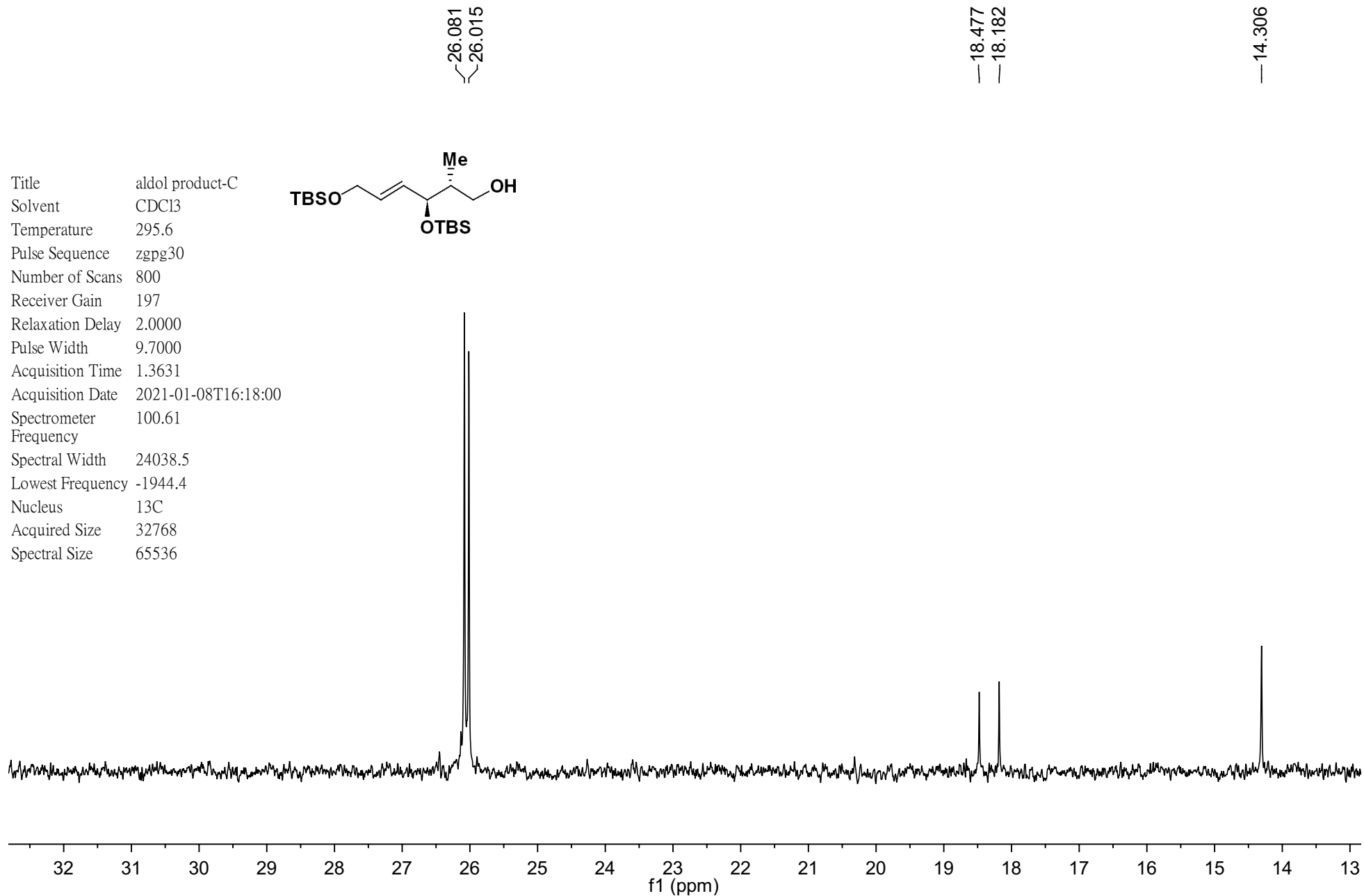
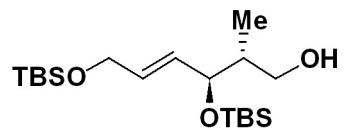


Title aldol product-C  
Solvent CDCl3  
Temperature 295.6  
Pulse Sequence zgpg30  
Number of Scans 800  
Receiver Gain 197  
Relaxation Delay 2.0000  
Pulse Width 9.7000  
Acquisition Time 1.3631  
Acquisition Date 2021-01-08T16:18:00  
Spectrometer 100.61  
Frequency  
Spectral Width 24038.5  
Lowest Frequency -1944.4  
Nucleus 13C  
Acquired Size 32768  
Spectral Size 65536



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Title aldol product-C  
Solvent CDCl3  
Temperature 295.6  
Pulse Sequence zgpg30  
Number of Scans 800  
Receiver Gain 197  
Relaxation Delay 2.0000  
Pulse Width 9.7000  
Acquisition Time 1.3631  
Acquisition Date 2021-01-08T16:18:00  
Spectrometer 100.61  
Frequency  
Spectral Width 24038.5  
Lowest Frequency -1944.4  
Nucleus 13C  
Acquired Size 32768  
Spectral Size 65536



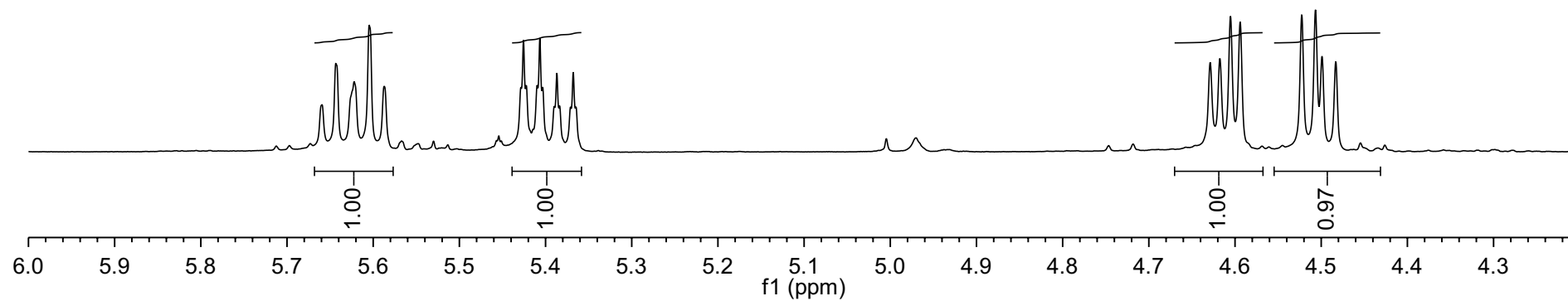
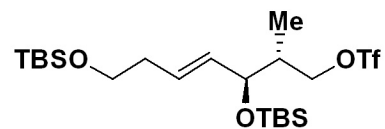




5.659  
5.643  
5.622  
5.605  
5.587  
5.429  
5.426  
5.422  
5.410  
5.407  
5.403  
5.390  
5.387  
5.384  
5.371  
5.368  
5.365

4.629  
4.618  
4.605  
4.594  
4.523  
4.507  
4.499  
4.483

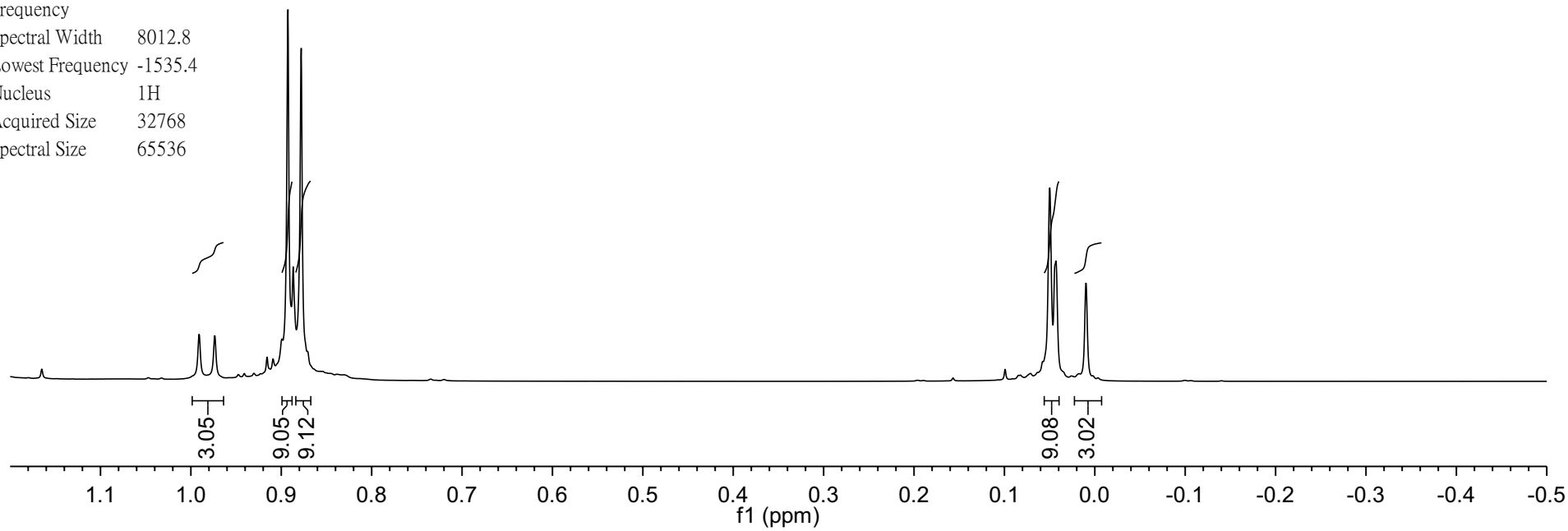
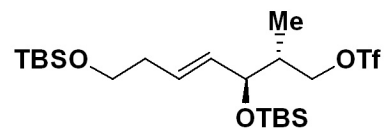
Title zhao160802-1  
Solvent CDCl3  
Temperature 298.8  
Pulse Sequence zg30  
Number of Scans 16  
Receiver Gain 46  
Relaxation Delay 1.0000  
Pulse Width 14.5000  
Acquisition Time 4.0894  
Acquisition Date 2016-08-02T14:08:00  
Spectrometer 400.13  
Frequency  
Spectral Width 8012.8  
Lowest Frequency -1535.4  
Nucleus 1H  
Acquired Size 32768  
Spectral Size 65536



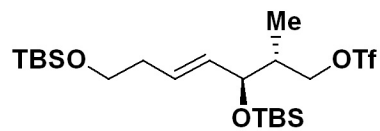
0.991  
0.974  
0.893  
0.878

0.050  
0.043  
0.010

Title zha0160802-1  
Solvent CDCl3  
Temperature 298.8  
Pulse Sequence zg30  
Number of Scans 16  
Receiver Gain 46  
Relaxation Delay 1.0000  
Pulse Width 14.5000  
Acquisition Time 4.0894  
Acquisition Date 2016-08-02T14:08:00  
Spectrometer 400.13  
Frequency  
Spectral Width 8012.8  
Lowest Frequency -1535.4  
Nucleus 1H  
Acquired Size 32768  
Spectral Size 65536



Title zhao160802-1C  
 Solvent CDCl3  
 Temperature 299.9  
 Pulse Sequence zgpg30  
 Number of Scans 100  
 Receiver Gain 197  
 Relaxation Delay 2.0000  
 Pulse Width 9.7000  
 Acquisition Time 1.3631  
 Acquisition Date 2016-08-02T14:16:00  
 Spectrometer 100.61  
 Frequency  
 Spectral Width 24038.5  
 Lowest Frequency -1958.4  
 Nucleus 13C  
 Acquired Size 32768  
 Spectral Size 65536

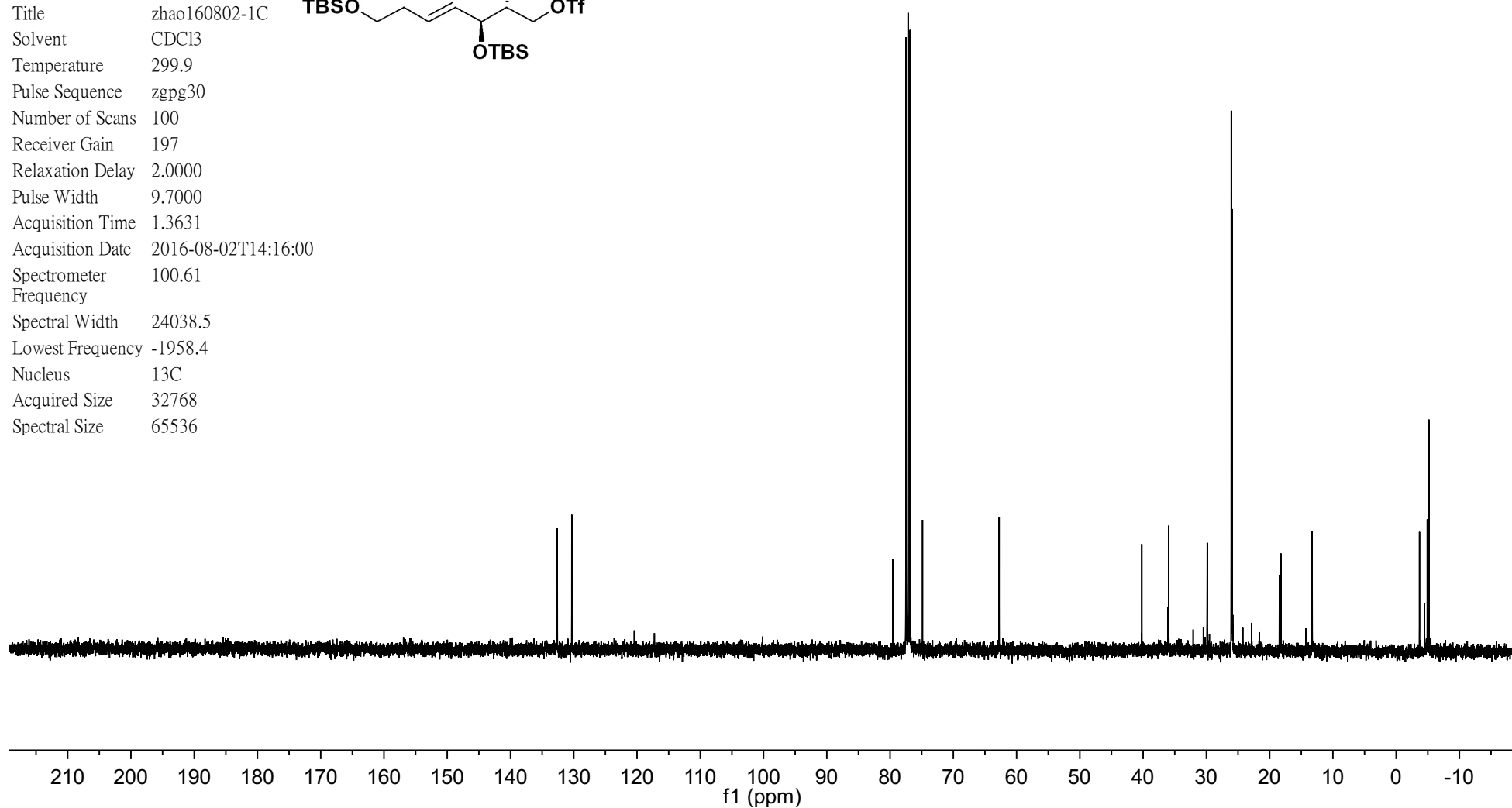


~132.602  
 ~130.315  
 ~120.430  
 ~117.253

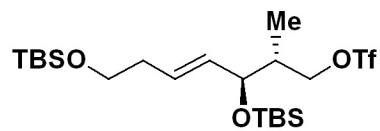
{79.559  
 {77.477  
 {77.160  
 {76.842  
 {74.865  
 —62.752

~40.202  
 ~35.962  
 {29.864  
 {26.070  
 {25.936  
 {18.461  
 {18.206  
 ~13.277

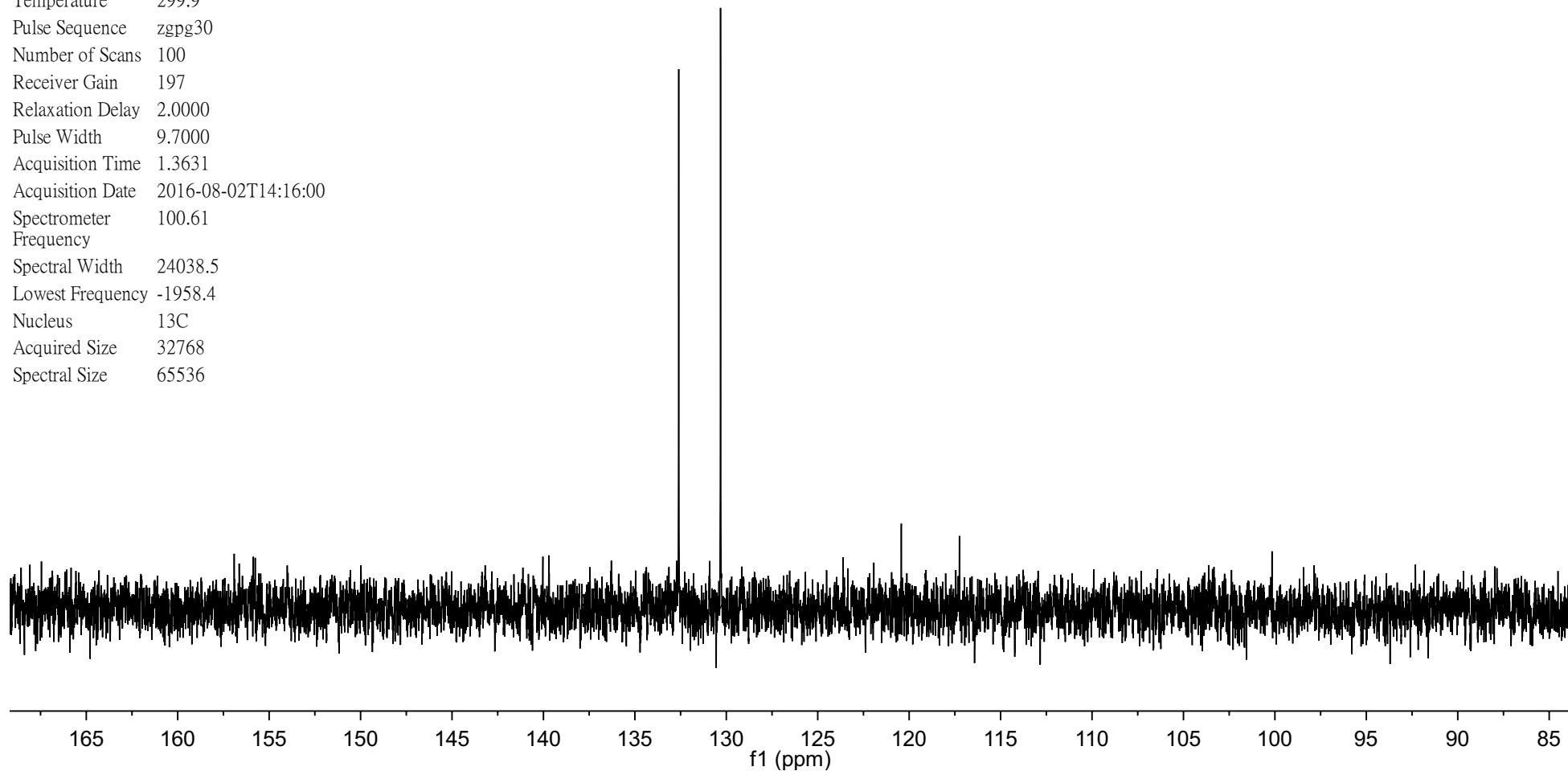
{~3.686  
 {~4.482  
 {~4.921  
 {~5.189

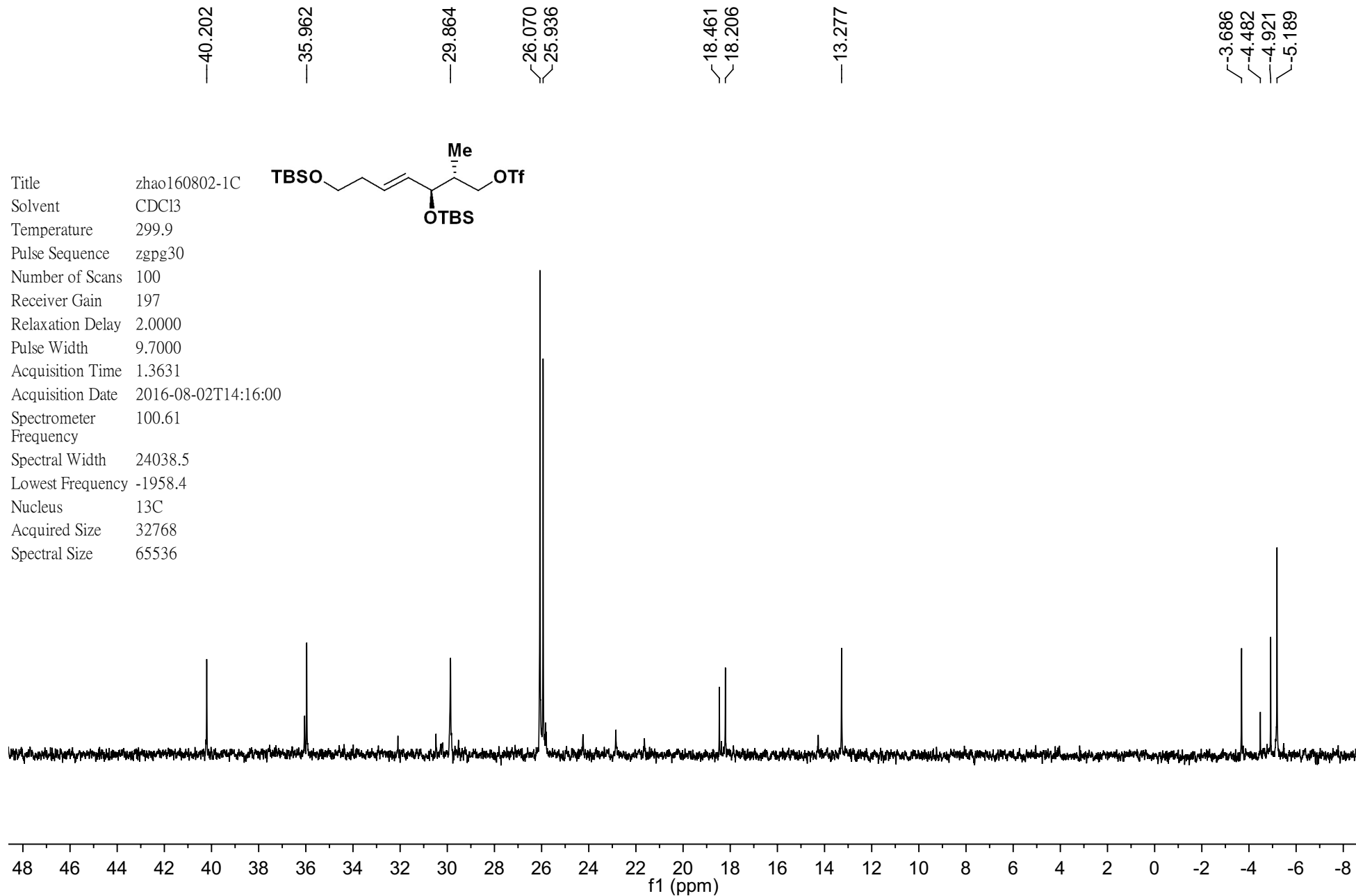


Title zhao160802-1C  
Solvent CDCl3  
Temperature 299.9  
Pulse Sequence zgpg30  
Number of Scans 100  
Receiver Gain 197  
Relaxation Delay 2.0000  
Pulse Width 9.7000  
Acquisition Time 1.3631  
Acquisition Date 2016-08-02T14:16:00  
Spectrometer 100.61  
Frequency  
Spectral Width 24038.5  
Lowest Frequency -1958.4  
Nucleus 13C  
Acquired Size 32768  
Spectral Size 65536

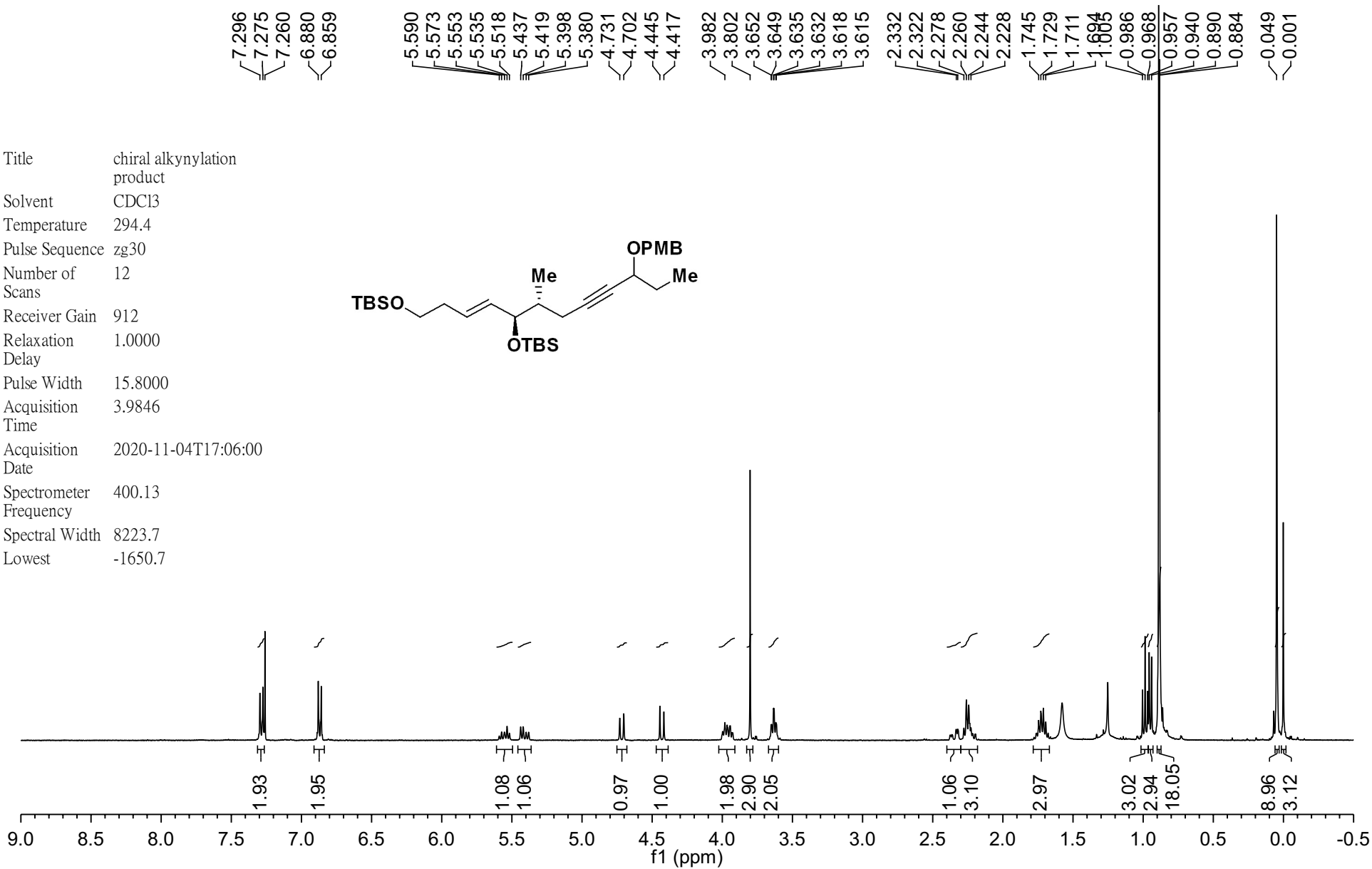
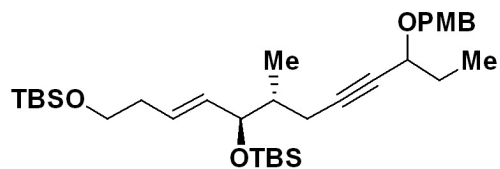


—132.602  
—130.315  
—120.430  
—117.253

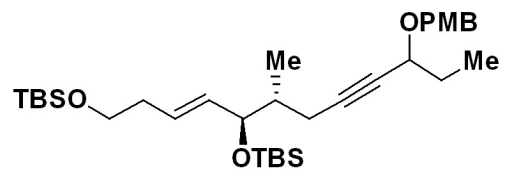




Title chiral alkynylation product  
 Solvent CDCl3  
 Temperature 294.4  
 Pulse Sequence zg30  
 Number of Scans 12  
 Receiver Gain 912  
 Relaxation Delay 1.0000  
 Pulse Width 15.8000  
 Acquisition Time 3.9846  
 Acquisition Date 2020-11-04T17:06:00  
 Spectrometer Frequency 400.13  
 Spectral Width 8223.7  
 Lowest -1650.7



Title chiral alkynylation product  
 Solvent CDCl3  
 Temperature 294.4  
 Pulse Sequence zg30  
 Number of Scans 12  
 Receiver Gain 912  
 Relaxation Delay 1.0000  
 Pulse Width 15.8000  
 Acquisition Time 3.9846  
 Acquisition Date 2020-11-04T17:06:00  
 Spectrometer Frequency 400.13  
 Spectral Width 8223.7  
 Lowest -1650.7



5.590  
 5.573  
 5.553  
 5.535  
 5.518  
 5.437  
 5.419  
 5.398  
 5.380

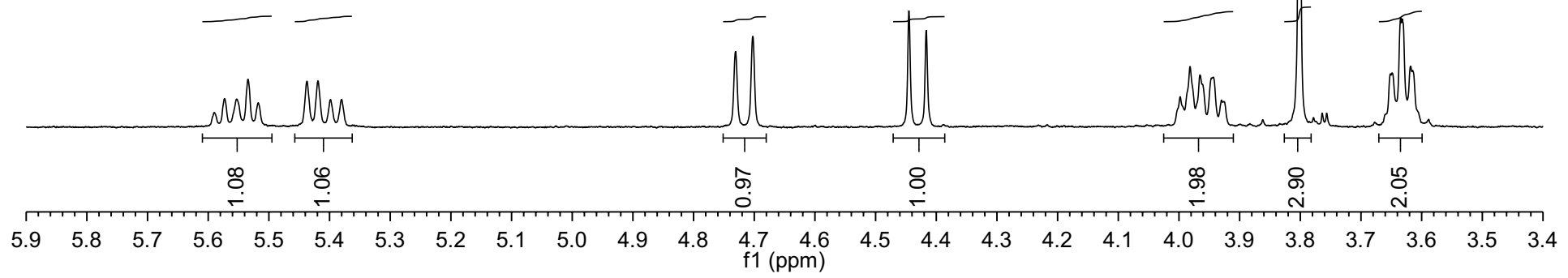
4.731  
 4.702

4.445  
 4.417

3.998  
 3.982  
 3.965  
 3.943  
 3.930

3.802

3.652  
 3.649  
 3.635  
 3.632  
 3.618  
 3.615

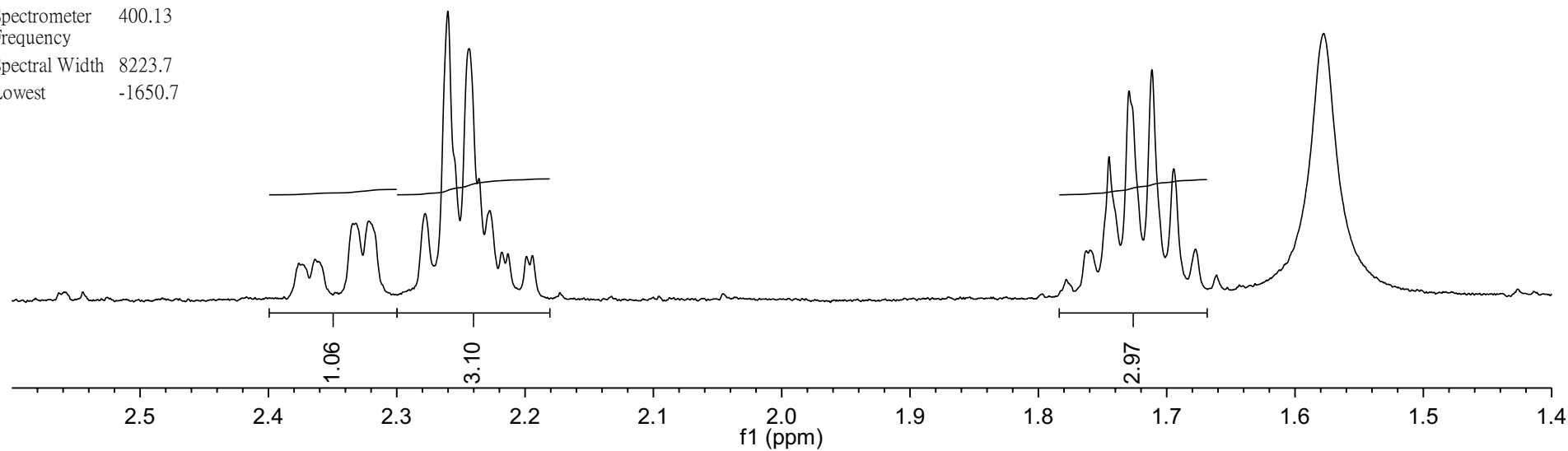
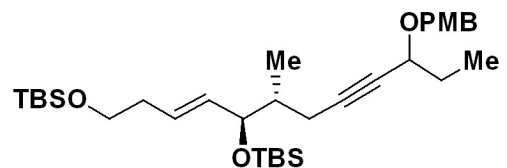




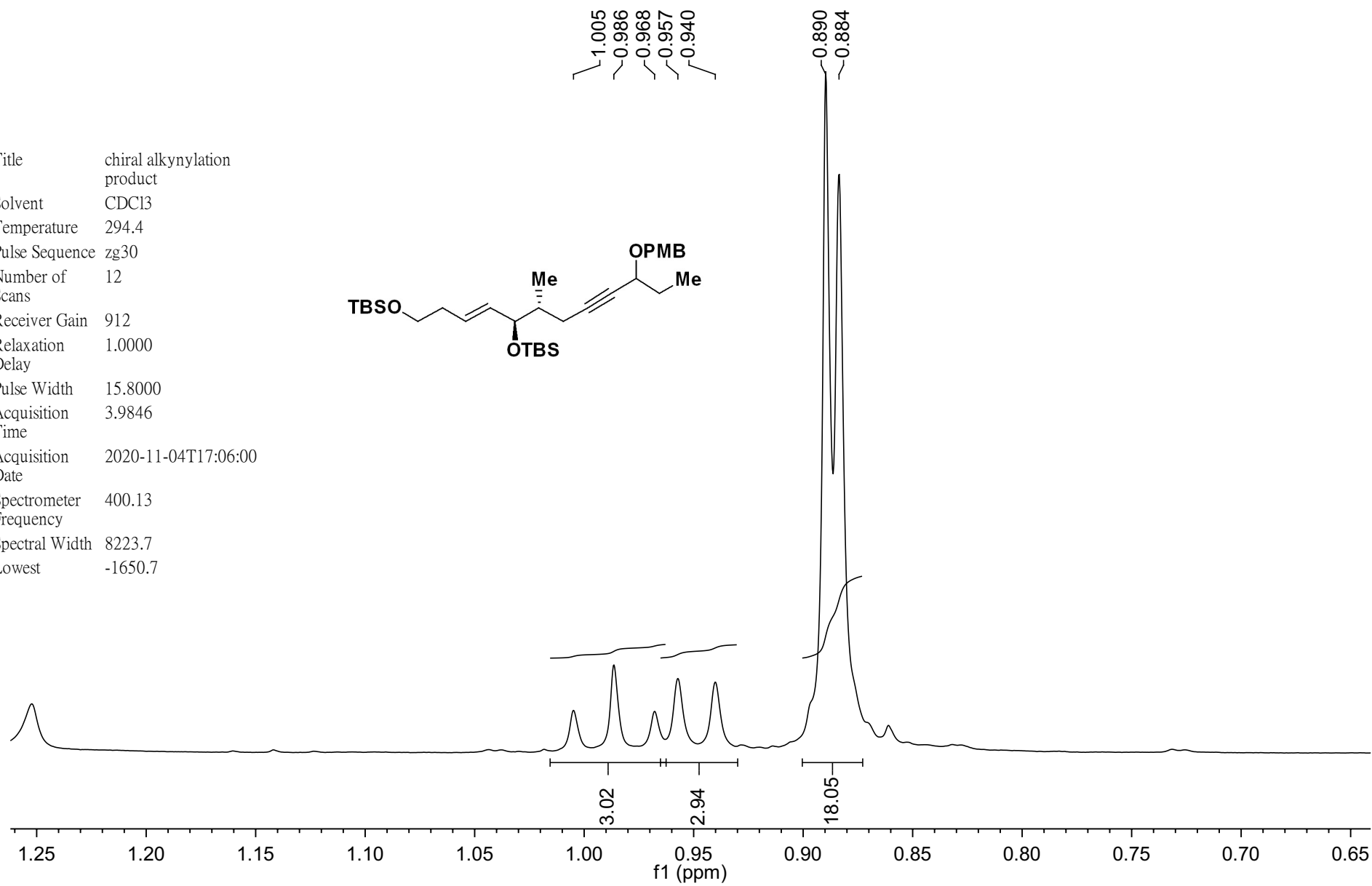
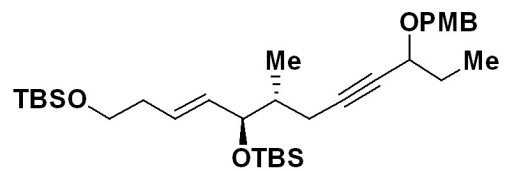
2.376  
2.364  
2.332  
2.322  
2.278  
2.260  
2.244  
2.236  
2.228  
2.218  
2.213  
2.199  
2.194

1.778  
1.760  
1.745  
1.729  
1.711  
1.694  
1.678

Title chiral alkynylation product  
 Solvent CDCl3  
 Temperature 294.4  
 Pulse Sequence zg30  
 Number of Scans 12  
 Receiver Gain 912  
 Relaxation Delay 1.0000  
 Pulse Width 15.8000  
 Acquisition Time 3.9846  
 Acquisition Date 2020-11-04T17:06:00  
 Spectrometer Frequency 400.13  
 Spectral Width 8223.7  
 Lowest -1650.7



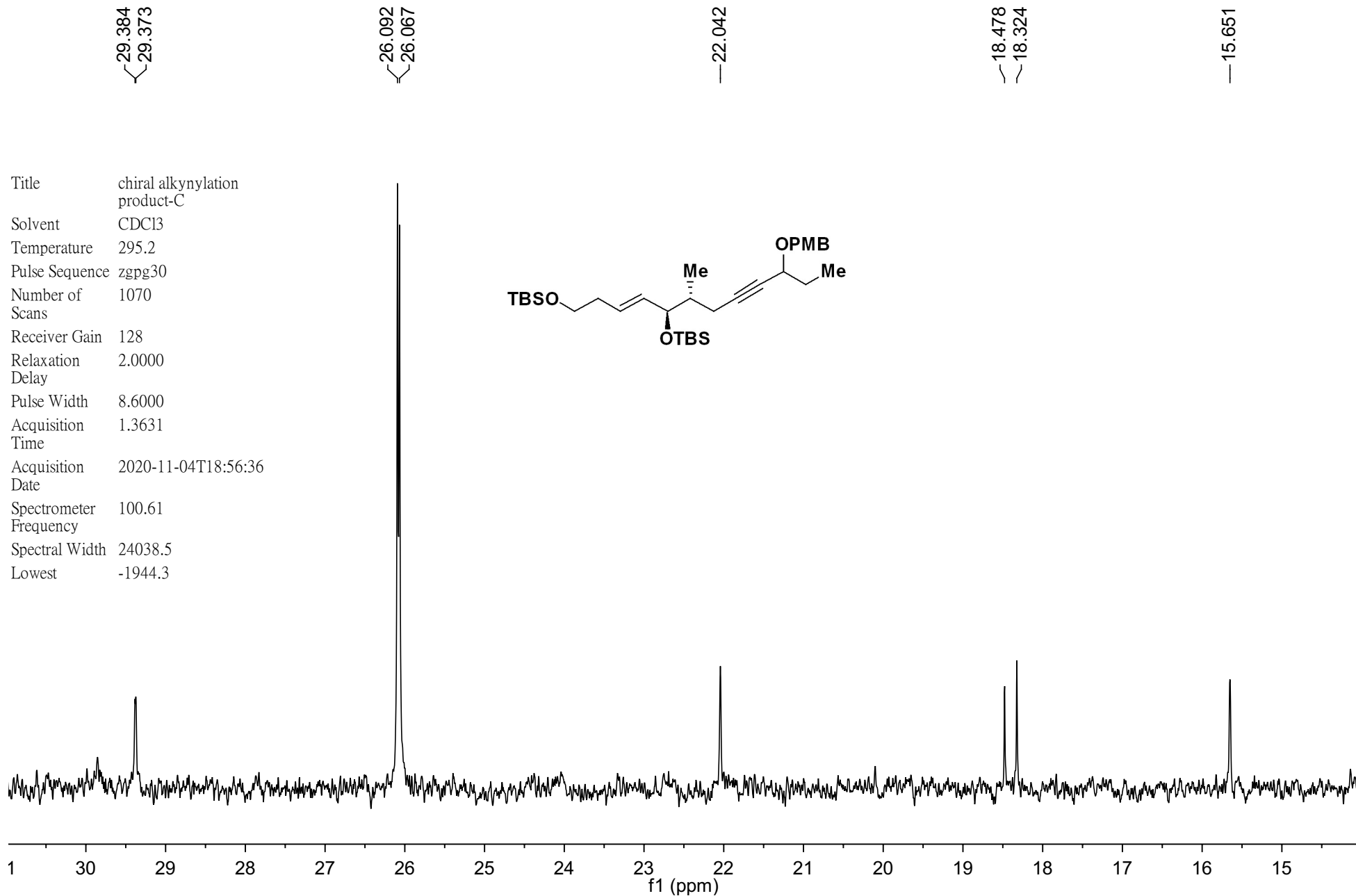
Title chiral alkynylation product  
Solvent CDCl3  
Temperature 294.4  
Pulse Sequence zg30  
Number of Scans 12  
Receiver Gain 912  
Relaxation Delay 1.0000  
Pulse Width 15.8000  
Acquisition Time 3.9846  
Acquisition Date 2020-11-04T17:06:00  
Spectrometer Frequency 400.13  
Spectral Width 8223.7  
Lowest -1650.7

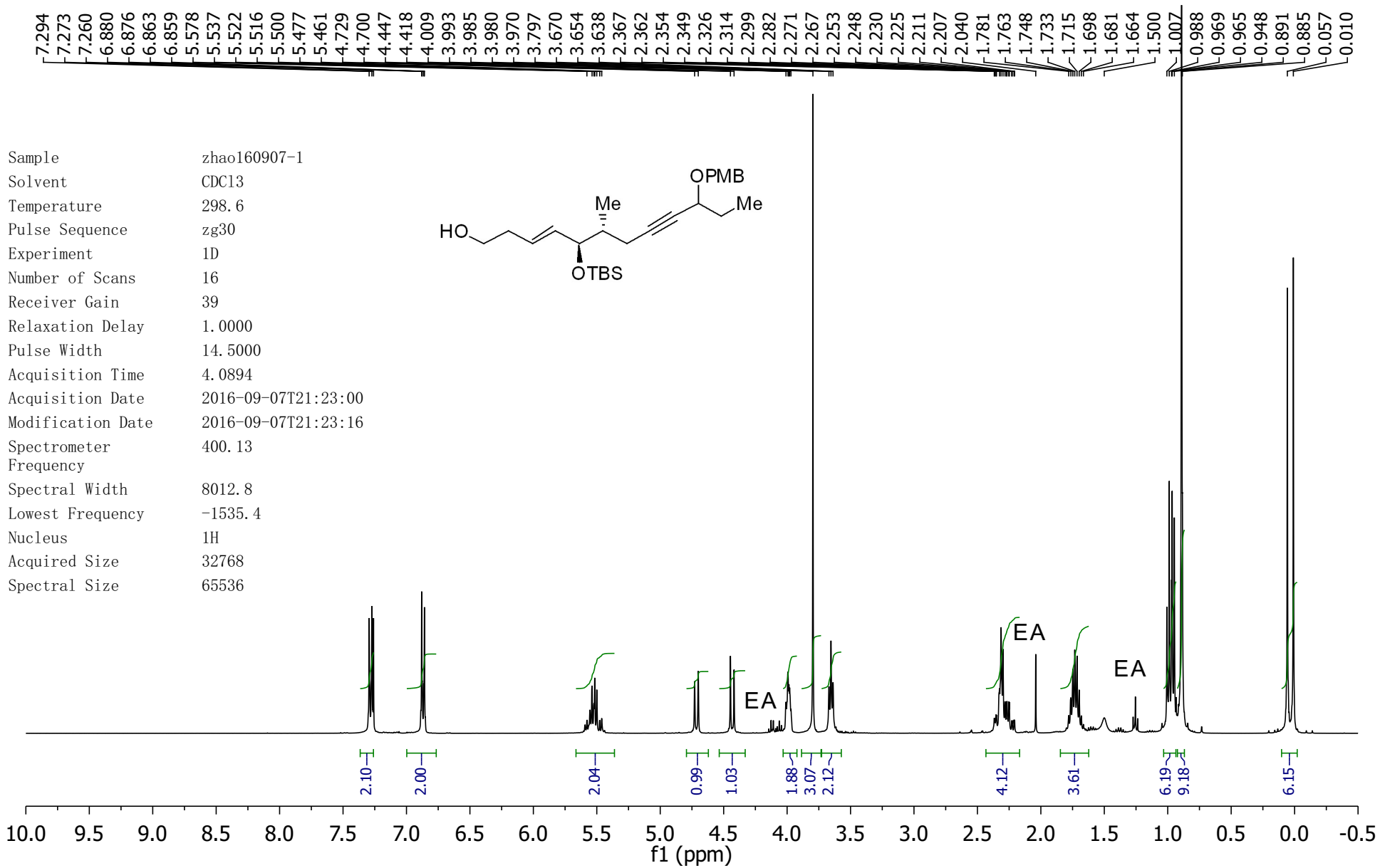










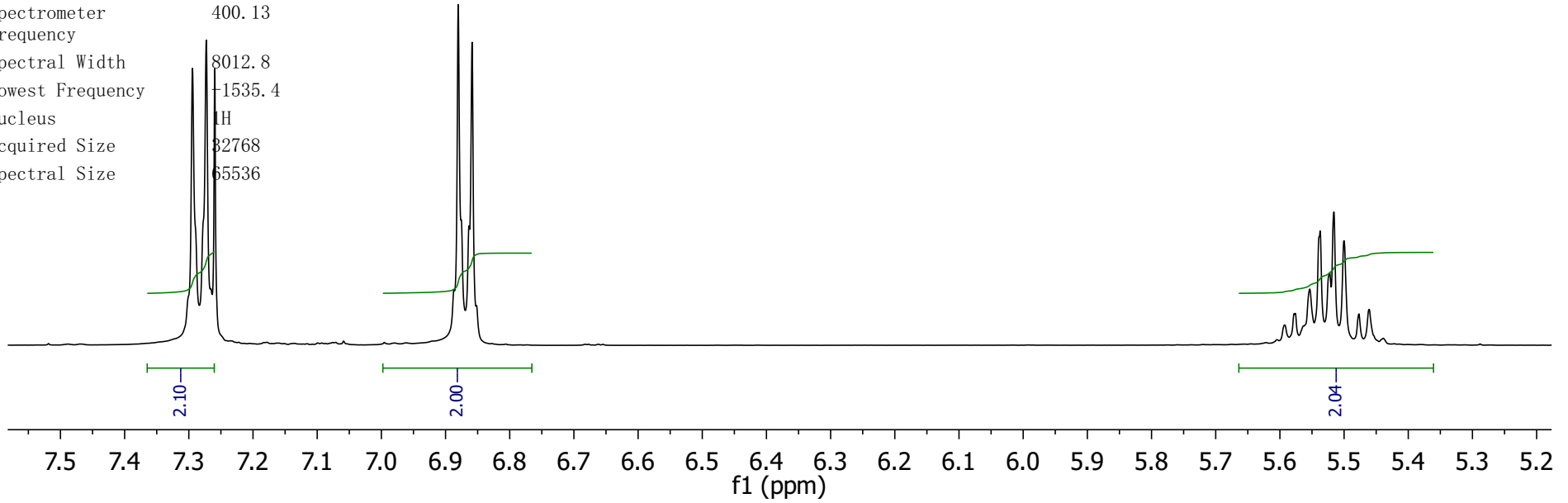
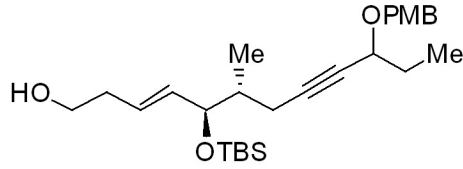


7.294  
7.273  
7.260

6.880  
6.876  
6.863  
6.859

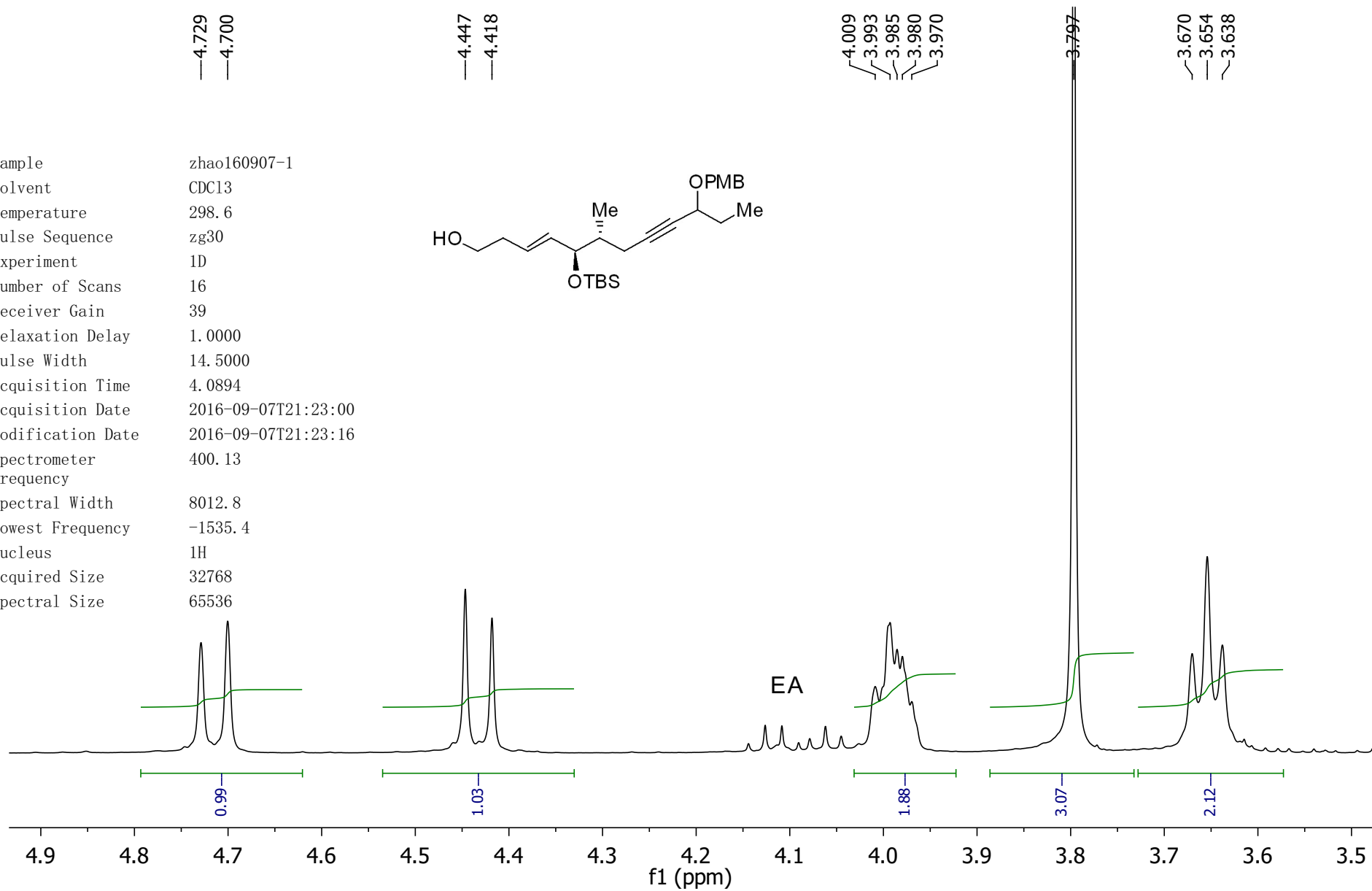
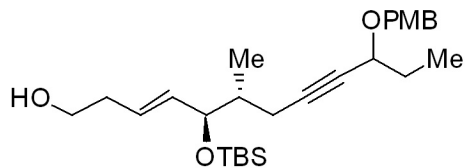
5.592  
5.578  
5.537  
5.522  
5.516  
5.500  
5.477  
5.461

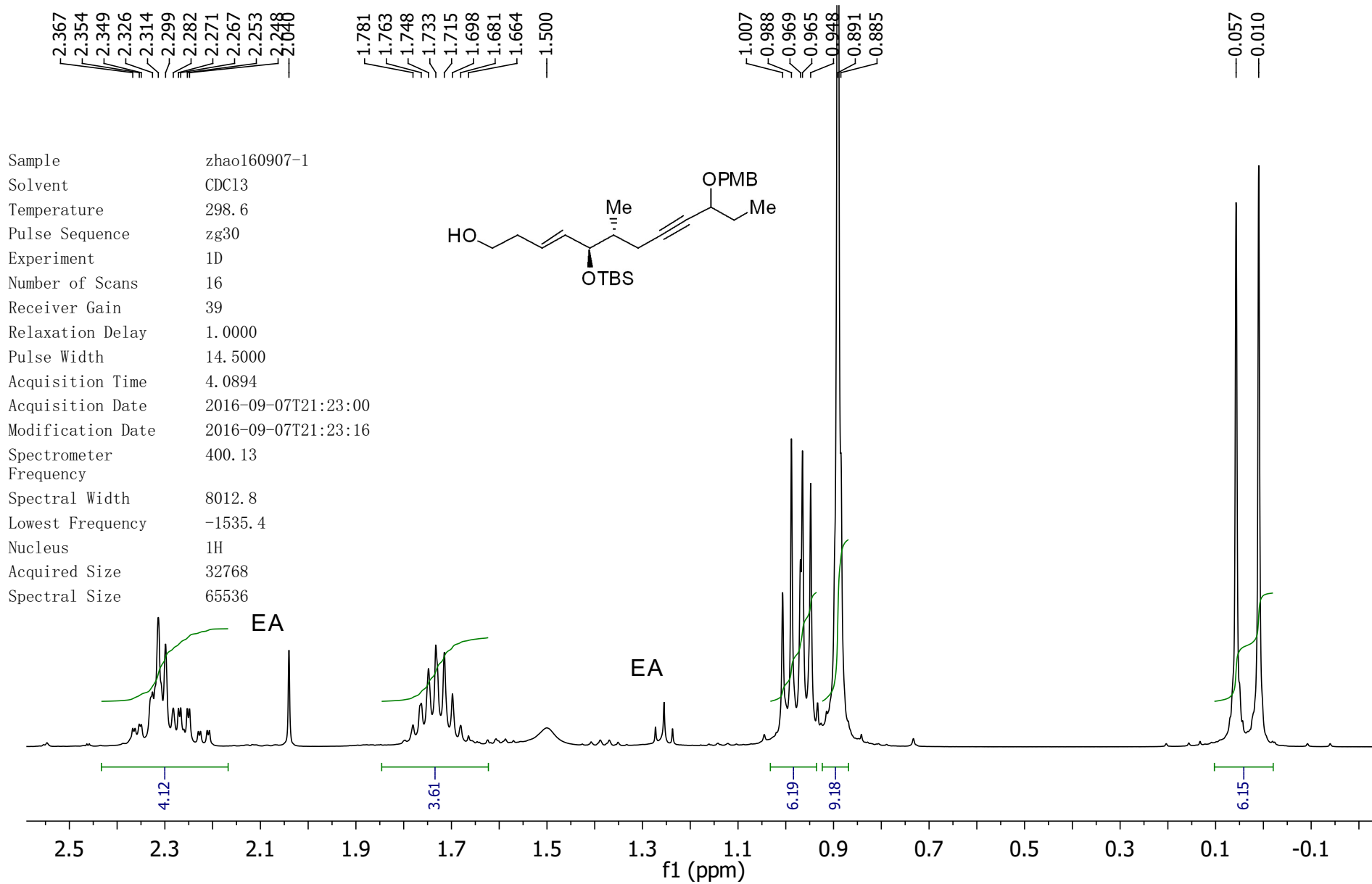
Sample zhaol60907-1  
Solvent CDCl3  
Temperature 298.6  
Pulse Sequence zg30  
Experiment 1D  
Number of Scans 16  
Receiver Gain 39  
Relaxation Delay 1.0000  
Pulse Width 14.5000  
Acquisition Time 4.0894  
Acquisition Date 2016-09-07T21:23:00  
Modification Date 2016-09-07T21:23:16  
Spectrometer 400.13  
Frequency  
Spectral Width 8012.8  
Lowest Frequency -1535.4  
Nucleus 1H  
Acquired Size 32768  
Spectral Size 65536



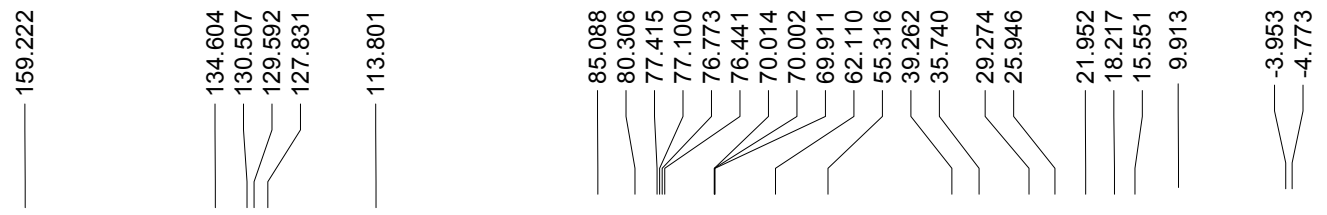


Sample zhao160907-1  
 Solvent CDCl3  
 Temperature 298.6  
 Pulse Sequence zg30  
 Experiment 1D  
 Number of Scans 16  
 Receiver Gain 39  
 Relaxation Delay 1.0000  
 Pulse Width 14.5000  
 Acquisition Time 4.0894  
 Acquisition Date 2016-09-07T21:23:00  
 Modification Date 2016-09-07T21:23:16  
 Spectrometer 400.13  
 Frequency  
 Spectral Width 8012.8  
 Lowest Frequency -1535.4  
 Nucleus 1H  
 Acquired Size 32768  
 Spectral Size 65536



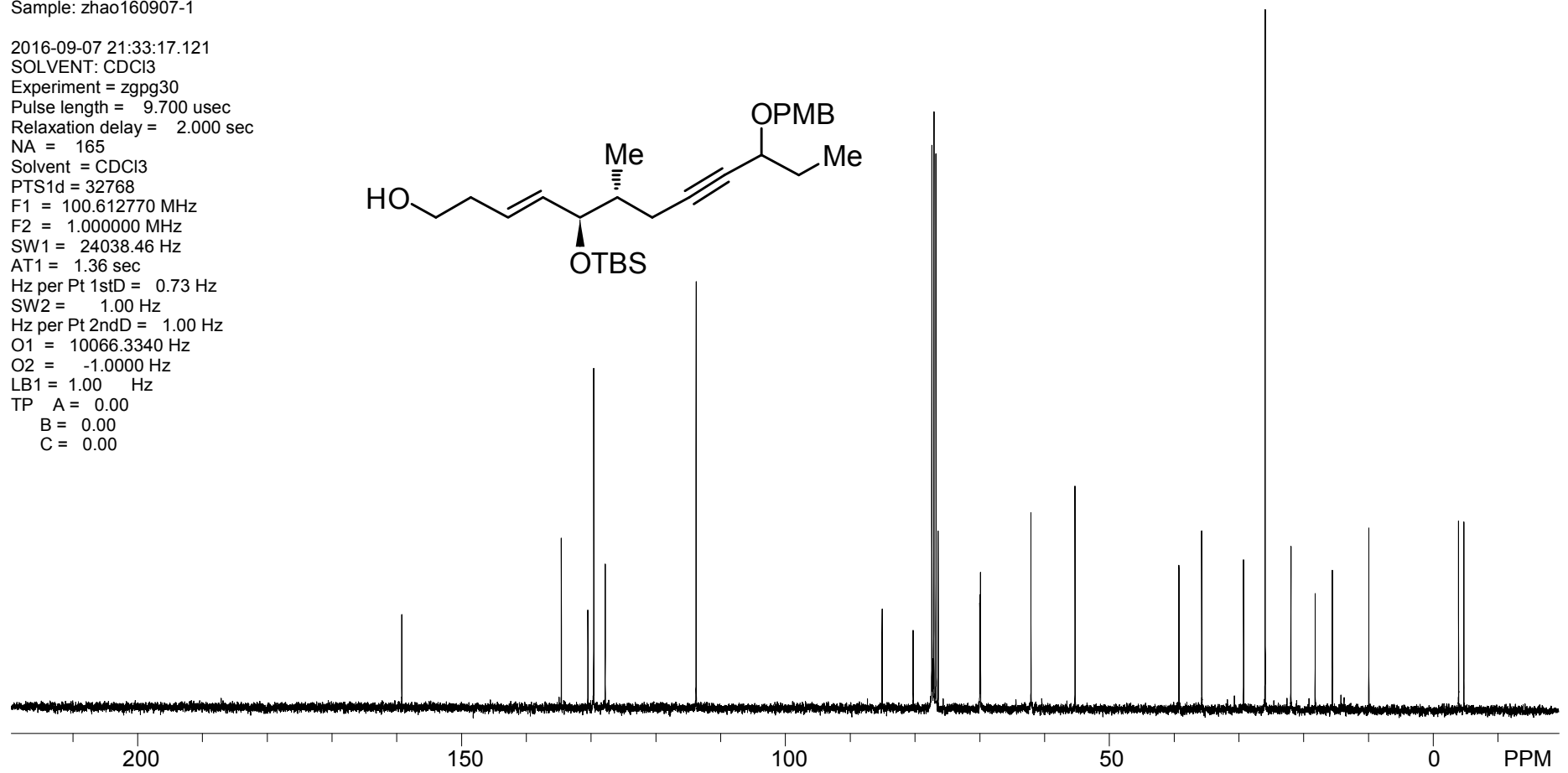
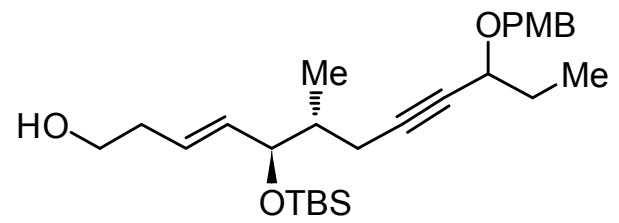


Sample zhao160907-1  
 Solvent CDCl3  
 Temperature 298.6  
 Pulse Sequence zg30  
 Experiment 1D  
 Number of Scans 16  
 Receiver Gain 39  
 Relaxation Delay 1.0000  
 Pulse Width 14.5000  
 Acquisition Time 4.0894  
 Acquisition Date 2016-09-07T21:23:00  
 Modification Date 2016-09-07T21:23:16  
 Spectrometer 400.13  
 Frequency  
 Spectral Width 8012.8  
 Lowest Frequency -1535.4  
 Nucleus 1H  
 Acquired Size 32768  
 Spectral Size 65536

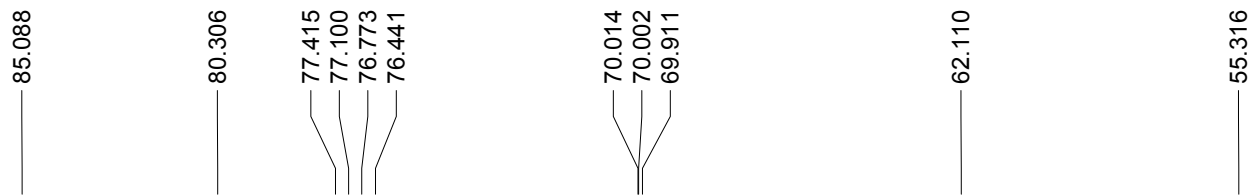


Sample: zhao160907-1

2016-09-07 21:33:17.121  
 SOLVENT: CDCl3  
 Experiment = zgpg30  
 Pulse length = 9.700 usec  
 Relaxation delay = 2.000 sec  
 NA = 165  
 Solvent = CDCl3  
 PTS1d = 32768  
 F1 = 100.612770 MHz  
 F2 = 1.000000 MHz  
 SW1 = 24038.46 Hz  
 AT1 = 1.36 sec  
 Hz per Pt 1stD = 0.73 Hz  
 SW2 = 1.00 Hz  
 Hz per Pt 2ndD = 1.00 Hz  
 O1 = 10066.3340 Hz  
 O2 = -1.0000 Hz  
 LB1 = 1.00 Hz  
 TP A = 0.00  
 B = 0.00  
 C = 0.00

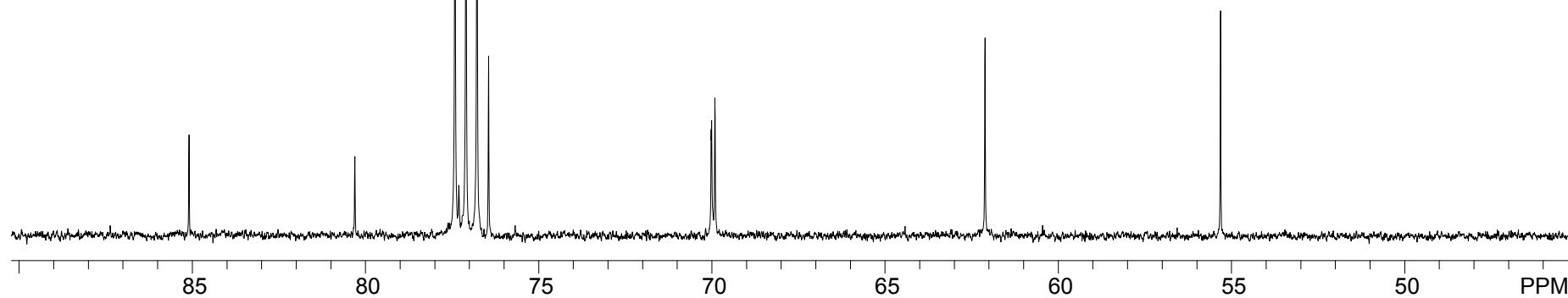
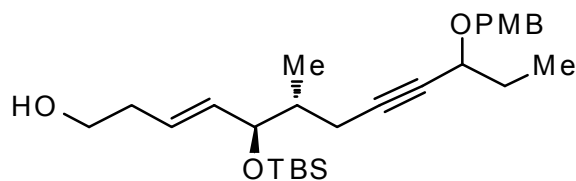


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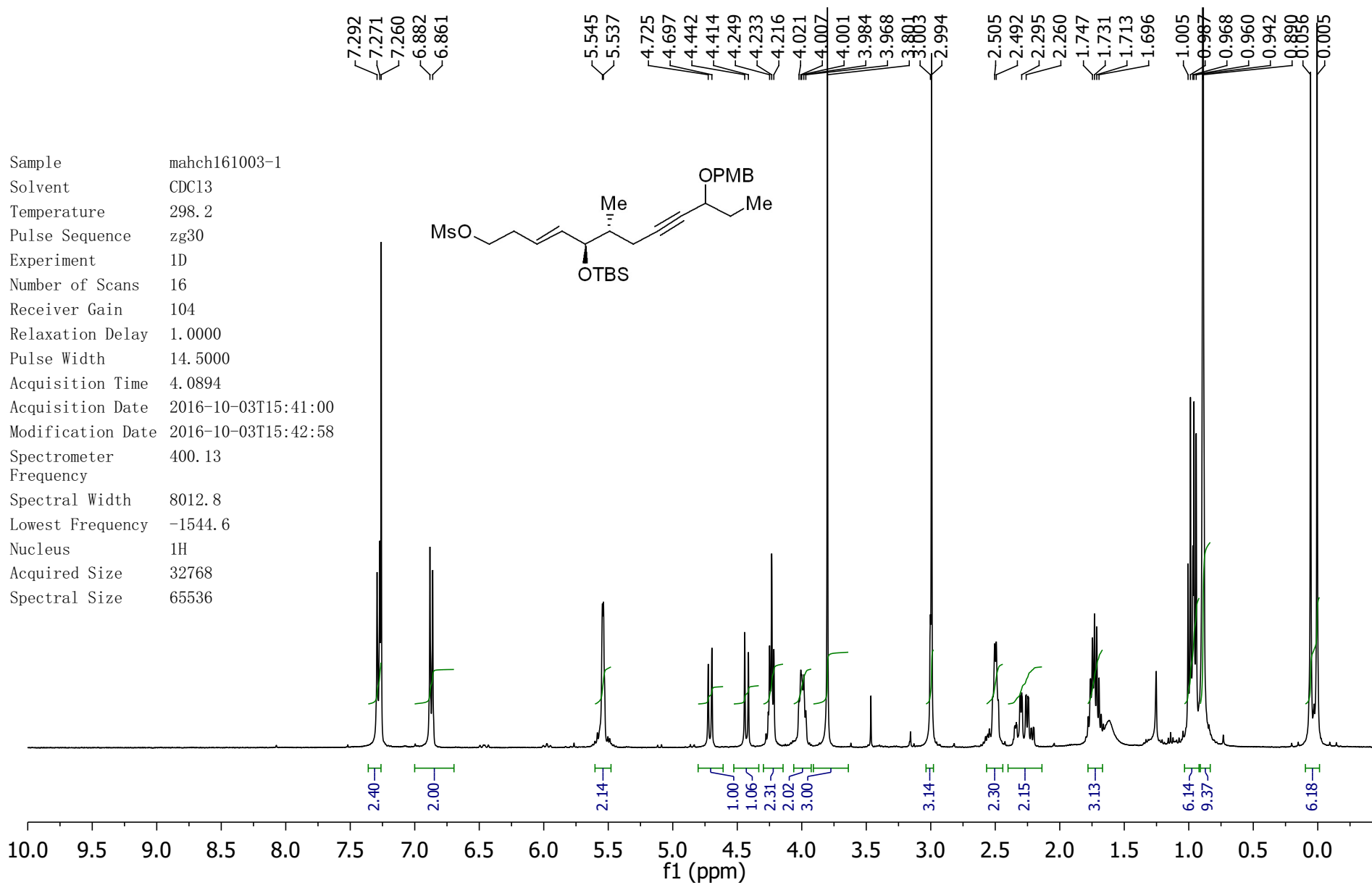


Sample: zhao160907-1

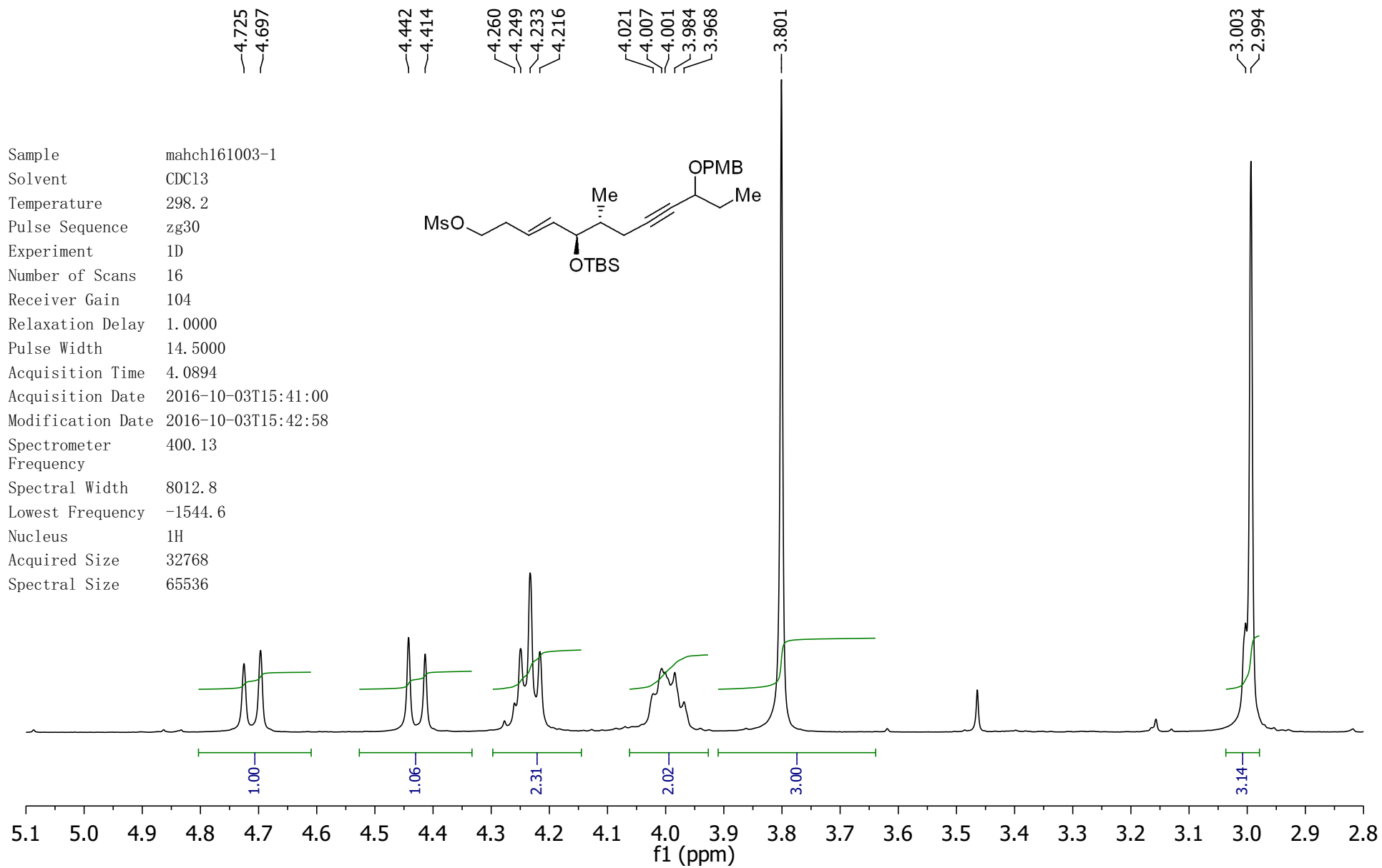
2016-09-07 21:33:17.121  
 SOLVENT: CDCl3  
 Experiment = zgpg30  
 Pulse length = 9.700 usec  
 Relaxation delay = 2.000 sec  
 NA = 165  
 Solvent = CDCl3  
 PTS1d = 32768  
 F1 = 100.612770 MHz  
 F2 = 1.000000 MHz  
 SW1 = 24038.46 Hz  
 AT1 = 1.36 sec  
 Hz per Pt 1stD = 0.73 Hz  
 SW2 = 1.00 Hz  
 Hz per Pt 2ndD = 1.00 Hz  
 O1 = 10066.3340 Hz  
 O2 = -1.0000 Hz  
 LB1 = 1.00 Hz  
 TP A = 0.00  
 B = 0.00  
 C = 0.00



Sample mahch161003-1  
 Solvent CDC13  
 Temperature 298.2  
 Pulse Sequence zg30  
 Experiment 1D  
 Number of Scans 16  
 Receiver Gain 104  
 Relaxation Delay 1.0000  
 Pulse Width 14.5000  
 Acquisition Time 4.0894  
 Acquisition Date 2016-10-03T15:41:00  
 Modification Date 2016-10-03T15:42:58  
 Spectrometer 400.13  
 Frequency  
 Spectral Width 8012.8  
 Lowest Frequency -1544.6  
 Nucleus 1H  
 Acquired Size 32768  
 Spectral Size 65536



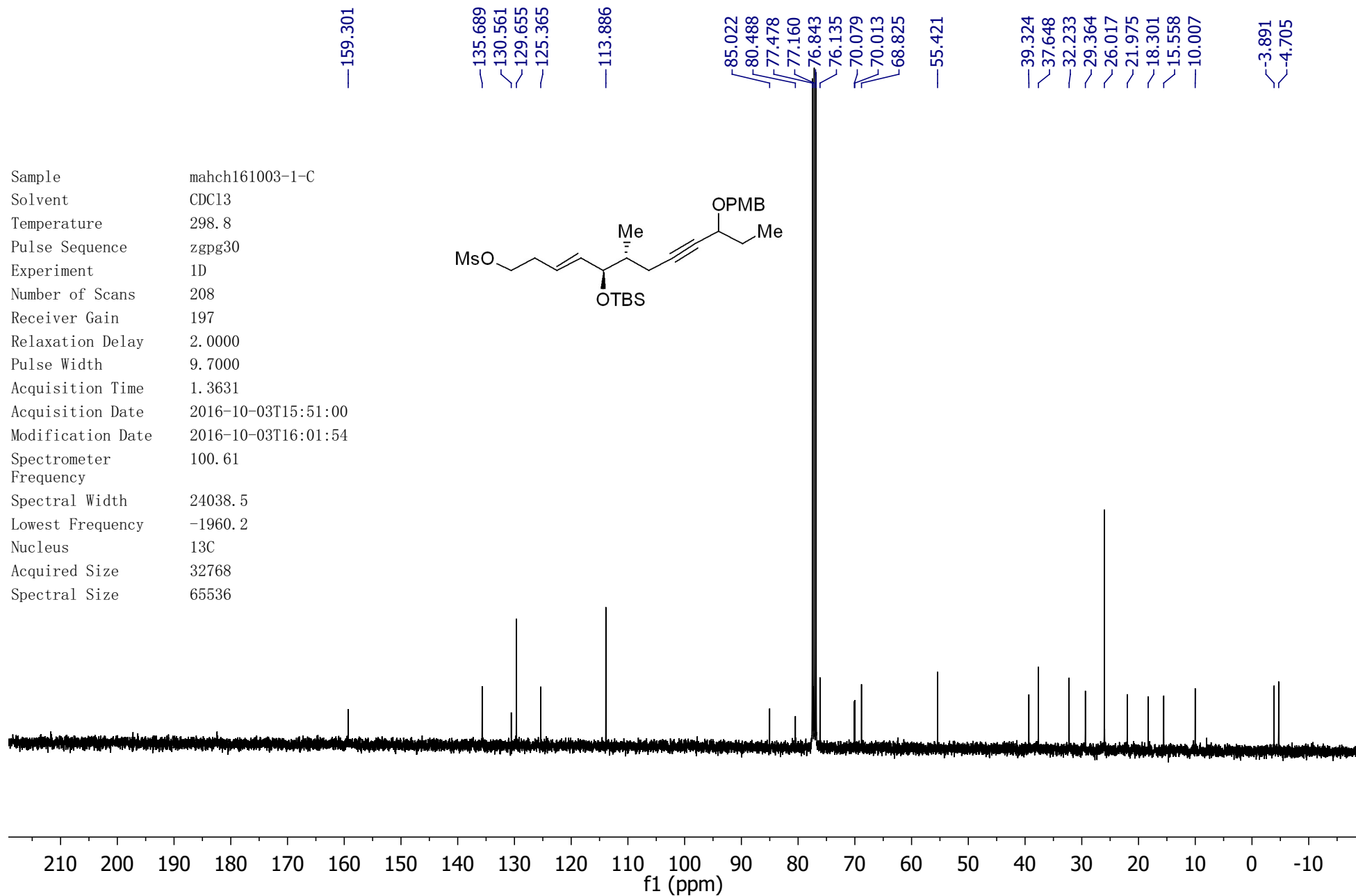
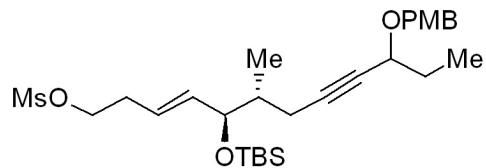


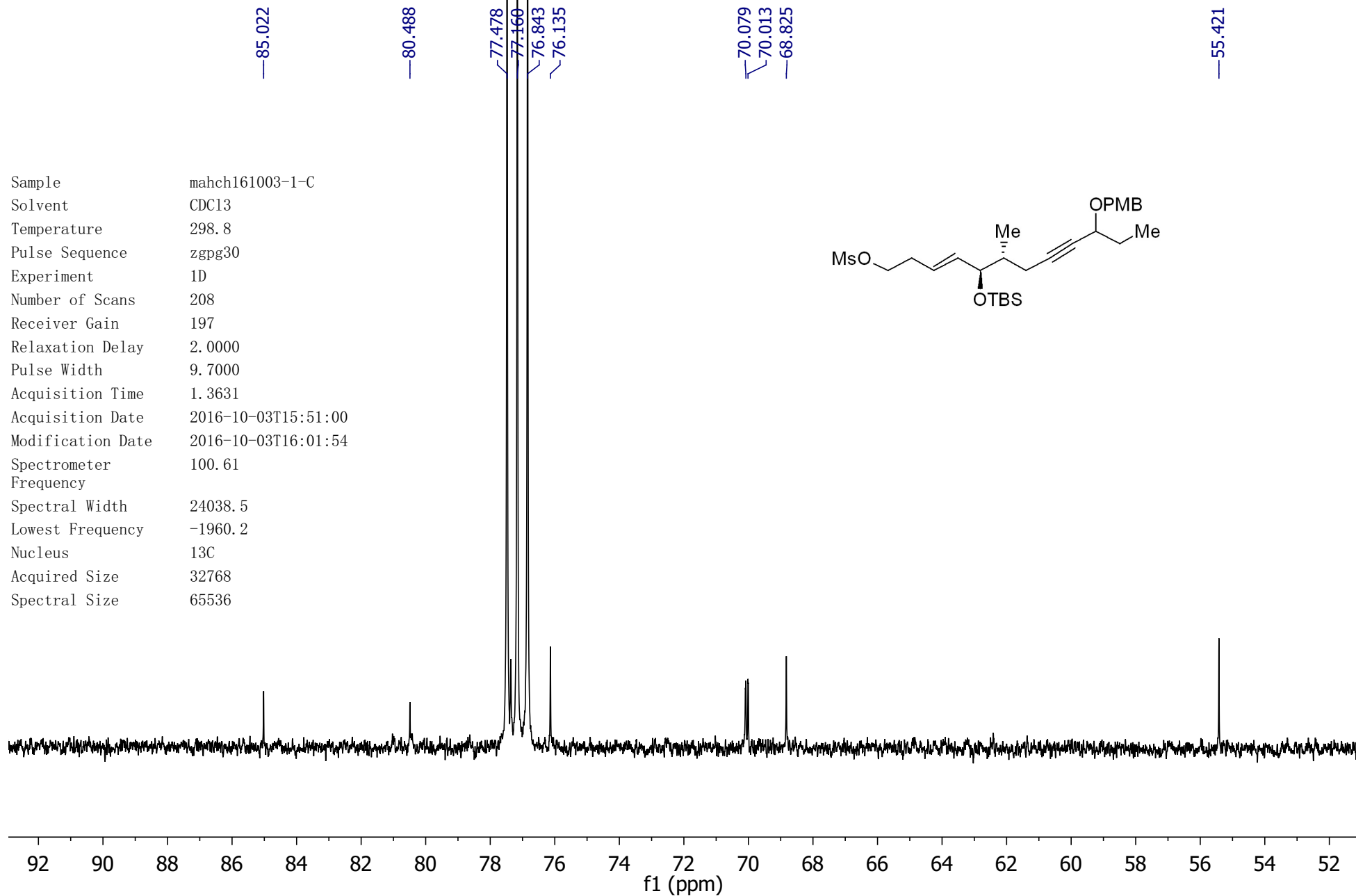




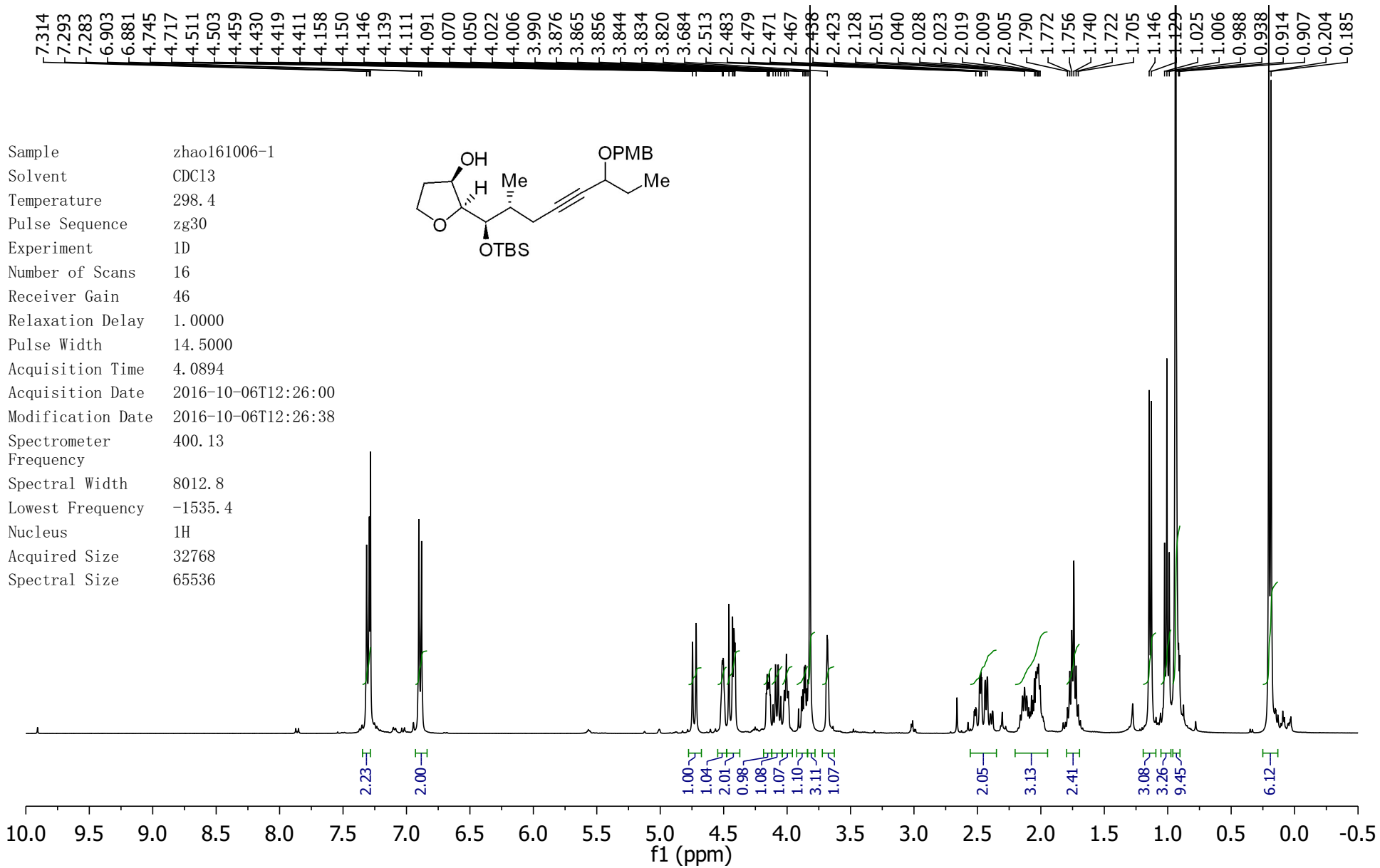


Sample mahch161003-1-C  
 Solvent CDC13  
 Temperature 298.8  
 Pulse Sequence zgpg30  
 Experiment 1D  
 Number of Scans 208  
 Receiver Gain 197  
 Relaxation Delay 2.0000  
 Pulse Width 9.7000  
 Acquisition Time 1.3631  
 Acquisition Date 2016-10-03T15:51:00  
 Modification Date 2016-10-03T16:01:54  
 Spectrometer 100.61  
 Frequency  
 Spectral Width 24038.5  
 Lowest Frequency -1960.2  
 Nucleus 13C  
 Acquired Size 32768  
 Spectral Size 65536

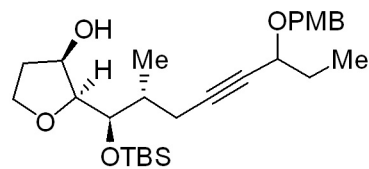




S90

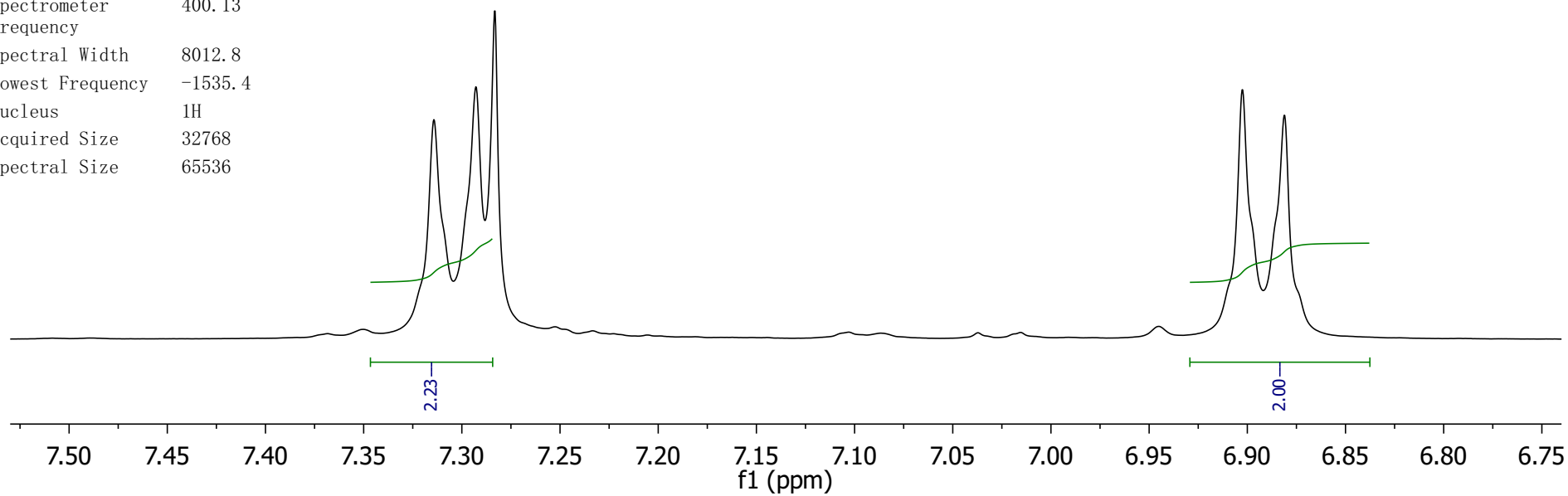


Sample zhaol61006-1  
Solvent CDCl3  
Temperature 298.4  
Pulse Sequence zg30  
Experiment 1D  
Number of Scans 16  
Receiver Gain 46  
Relaxation Delay 1.0000  
Pulse Width 14.5000  
Acquisition Time 4.0894  
Acquisition Date 2016-10-06T12:26:00  
Modification Date 2016-10-06T12:26:38  
Spectrometer 400.13  
Frequency  
Spectral Width 8012.8  
Lowest Frequency -1535.4  
Nucleus 1H  
Acquired Size 32768  
Spectral Size 65536



~7.314  
~7.293  
~7.283

—6.903  
—6.881



—4.745  
—4.717

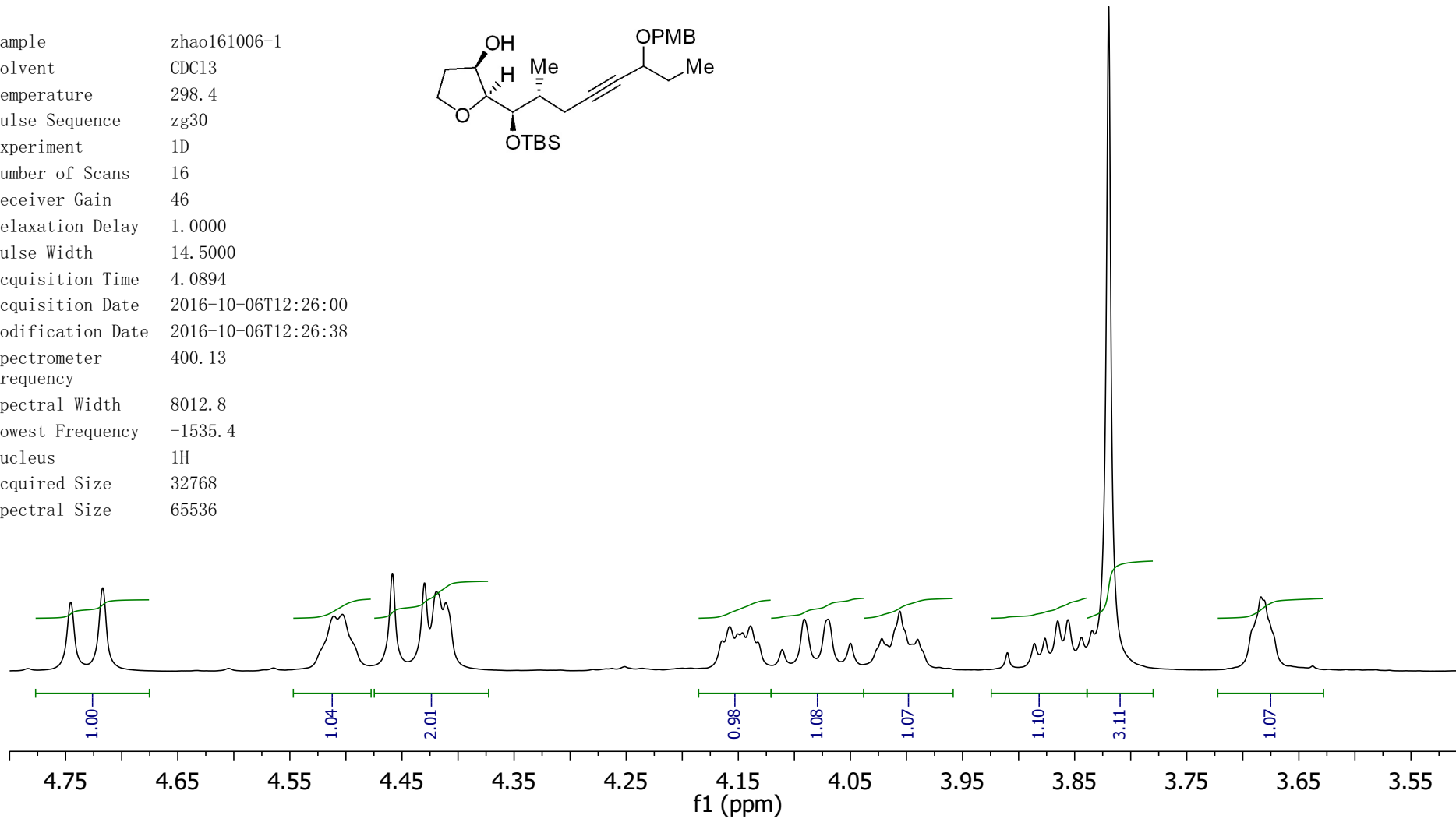
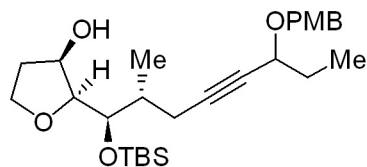
4.511  
4.503  
4.459  
4.430  
4.419  
4.411

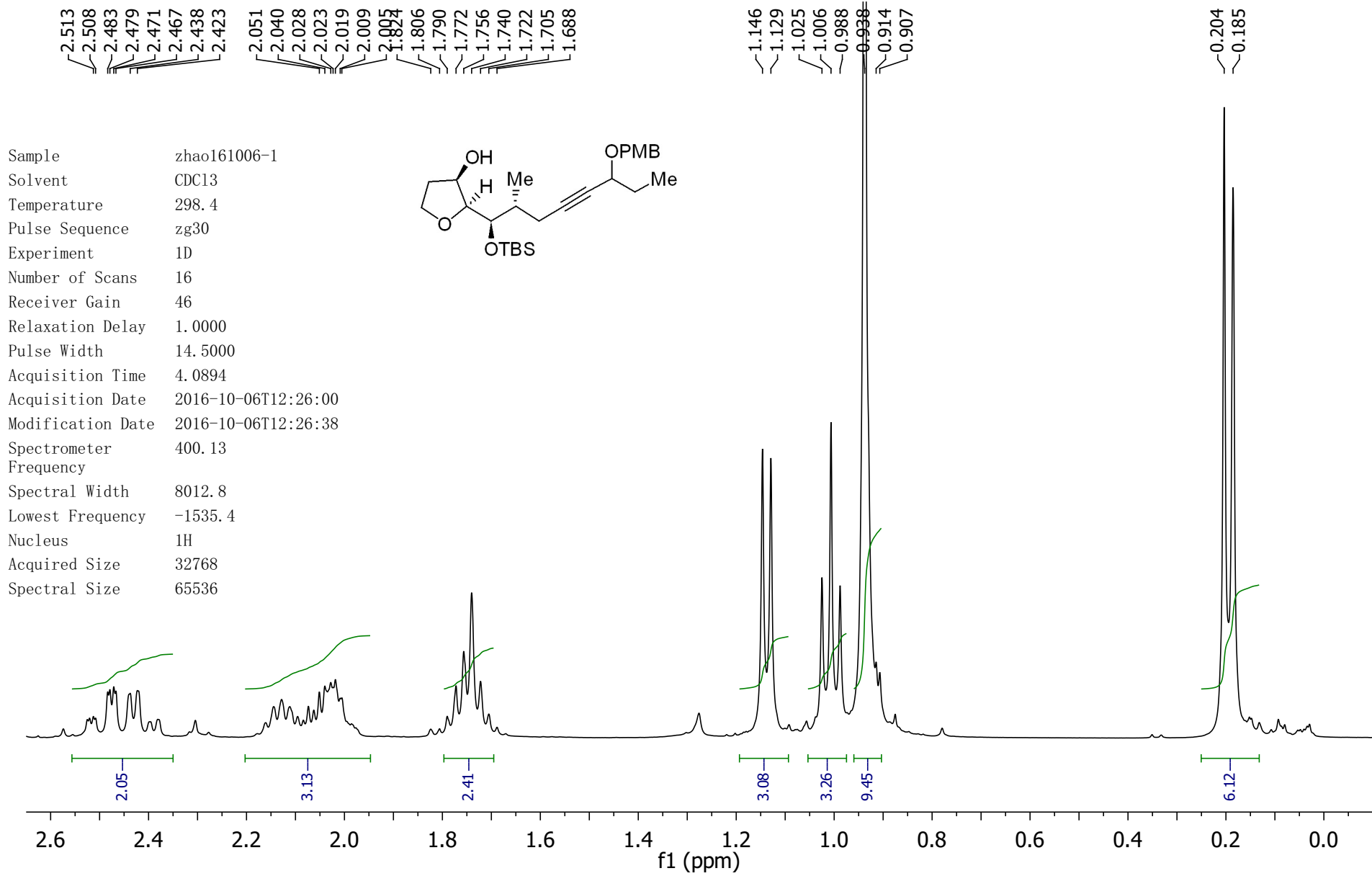
4.158  
4.150  
4.146  
4.139  
4.111  
4.091  
4.070  
4.050  
4.022  
4.006  
3.990

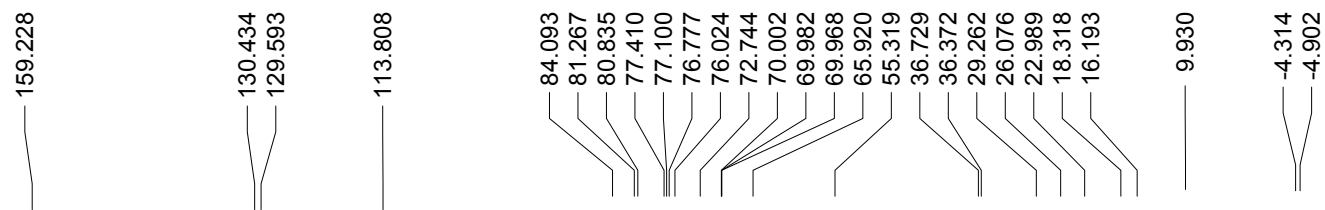
3.876  
3.865  
3.856  
3.844  
3.834  
3.820

—3.684

Sample zhaol61006-1  
Solvent CDCl3  
Temperature 298.4  
Pulse Sequence zg30  
Experiment 1D  
Number of Scans 16  
Receiver Gain 46  
Relaxation Delay 1.0000  
Pulse Width 14.5000  
Acquisition Time 4.0894  
Acquisition Date 2016-10-06T12:26:00  
Modification Date 2016-10-06T12:26:38  
Spectrometer 400.13  
Frequency  
Spectral Width 8012.8  
Lowest Frequency -1535.4  
Nucleus 1H  
Acquired Size 32768  
Spectral Size 65536

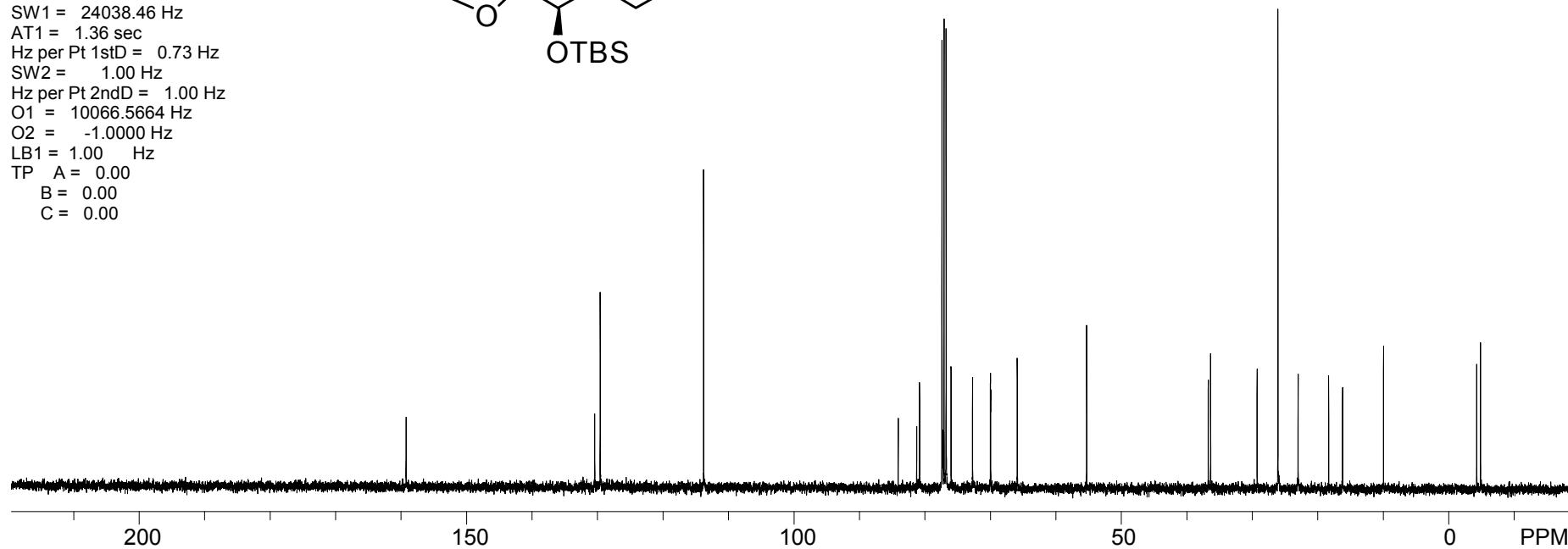
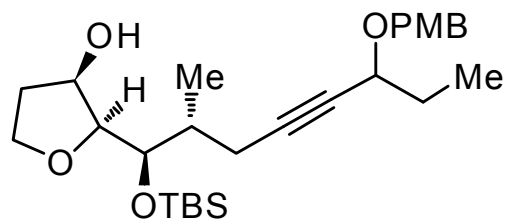




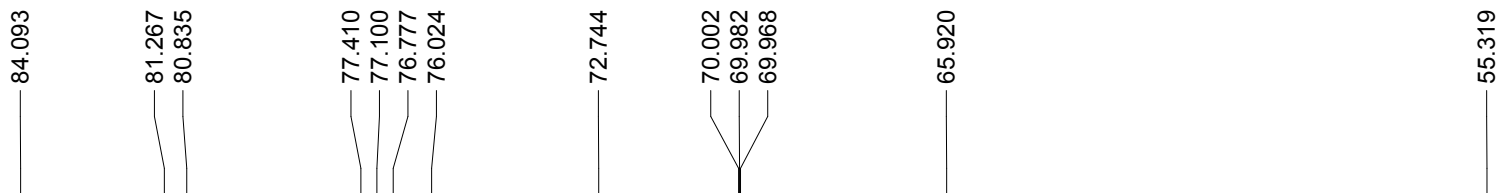


Sample: zhao161006-1

2016-10-06 12:34:11.760  
 SOLVENT: CDCl3  
 Experiment = zgpg30  
 Pulse length = 9.700 usec  
 Relaxation delay = 2.000 sec  
 NA = 122  
 Solvent = CDCl3  
 PTS1d = 32768  
 F1 = 100.612770 MHz  
 F2 = 1.000000 MHz  
 SW1 = 24038.46 Hz  
 AT1 = 1.36 sec  
 Hz per Pt 1stD = 0.73 Hz  
 SW2 = 1.00 Hz  
 Hz per Pt 2ndD = 1.00 Hz  
 O1 = 10066.5664 Hz  
 O2 = -1.0000 Hz  
 LB1 = 1.00 Hz  
 TP A = 0.00  
 B = 0.00  
 C = 0.00

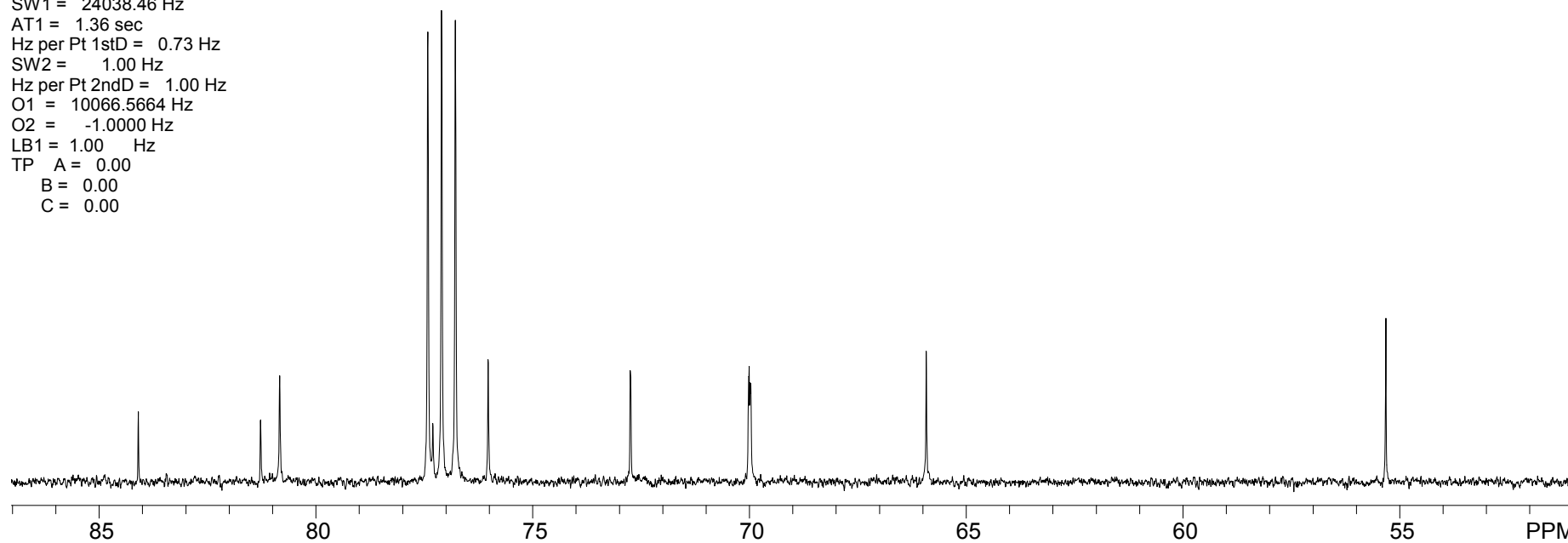
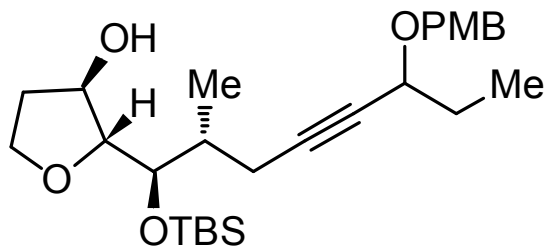


S95

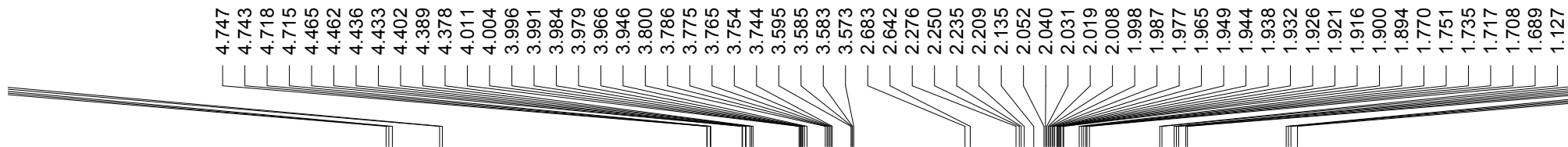


Sample: zhao161006-1

2016-10-06 12:34:11.760  
 SOLVENT: CDCl3  
 Experiment = zgpg30  
 Pulse length = 9.700 usec  
 Relaxation delay = 2.000 sec  
 NA = 122  
 Solvent = CDCl3  
 PTS1d = 32768  
 F1 = 100.612770 MHz  
 F2 = 1.000000 MHz  
 SW1 = 24038.46 Hz  
 AT1 = 1.36 sec  
 Hz per Pt 1stD = 0.73 Hz  
 SW2 = 1.00 Hz  
 Hz per Pt 2ndD = 1.00 Hz  
 O1 = 10066.5664 Hz  
 O2 = -1.0000 Hz  
 LB1 = 1.00 Hz  
 TP A = 0.00  
 B = 0.00  
 C = 0.00

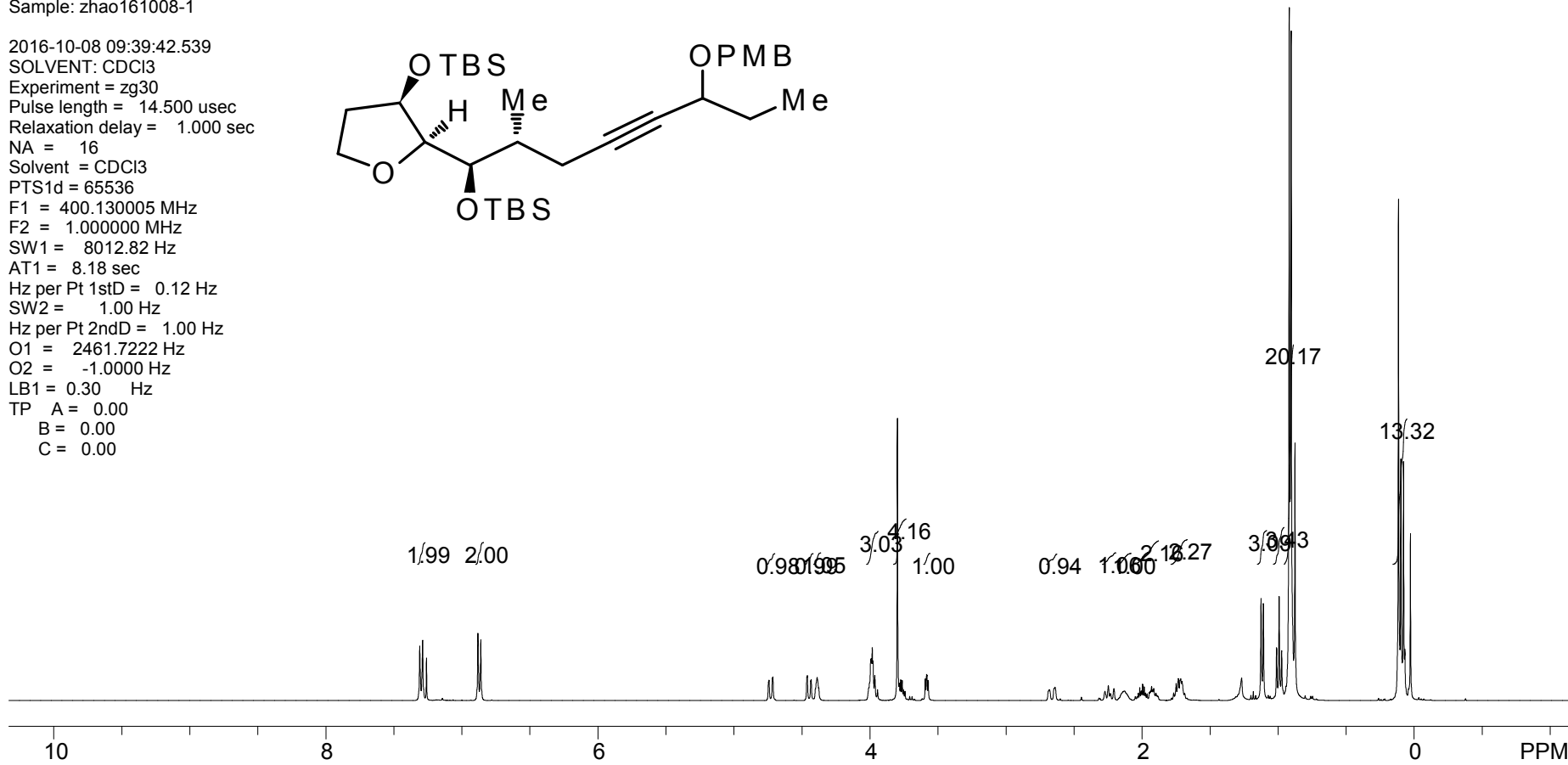
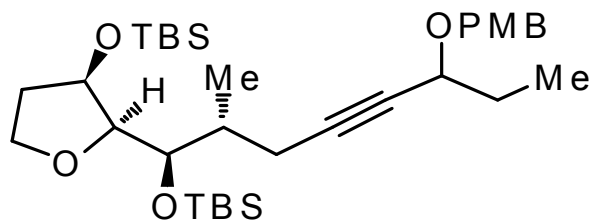




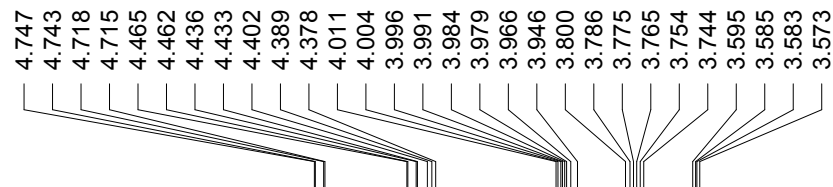
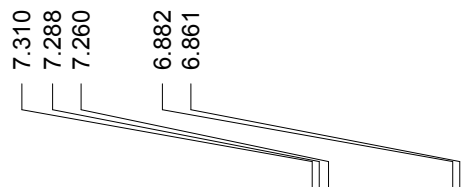


Sample: zhao161008-1

2016-10-08 09:39:42.539  
 SOLVENT: CDCl3  
 Experiment = zg30  
 Pulse length = 14.500 usec  
 Relaxation delay = 1.000 sec  
 NA = 16  
 Solvent = CDCl3  
 PTS1d = 65536  
 F1 = 400.130005 MHz  
 F2 = 1.000000 MHz  
 SW1 = 8012.82 Hz  
 AT1 = 8.18 sec  
 Hz per Pt 1stD = 0.12 Hz  
 SW2 = 1.00 Hz  
 Hz per Pt 2ndD = 1.00 Hz  
 O1 = 2461.7222 Hz  
 O2 = -1.0000 Hz  
 LB1 = 0.30 Hz  
 TP A = 0.00  
 B = 0.00  
 C = 0.00

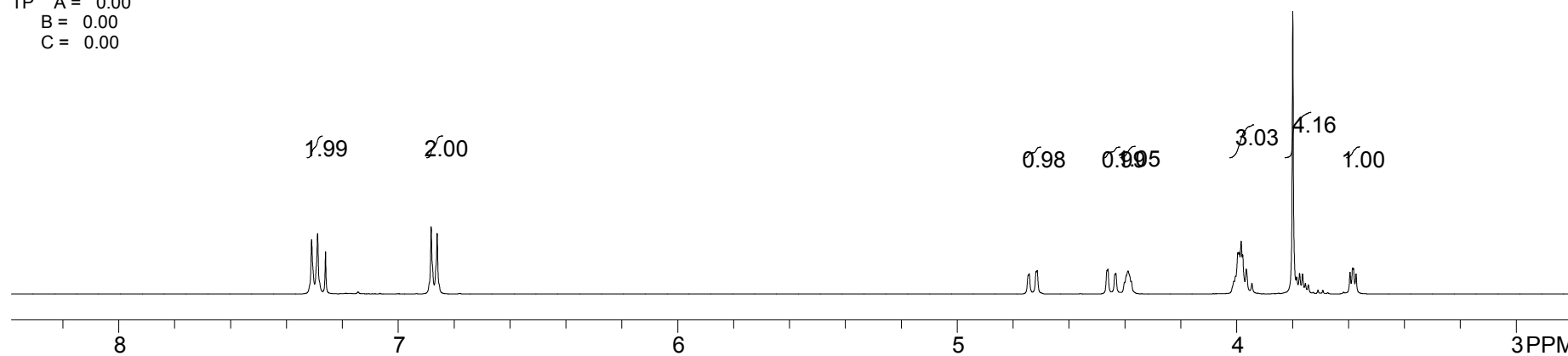
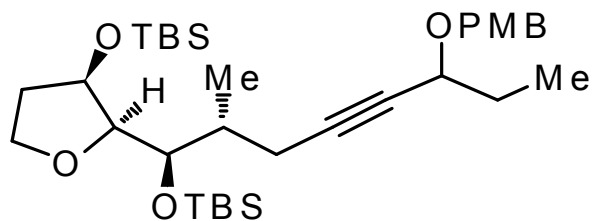


S97

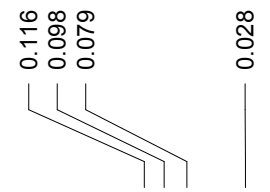
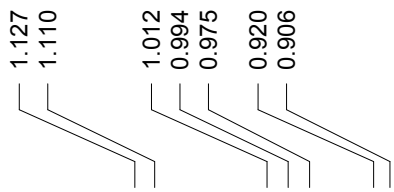


Sample: zhao161008-1

2016-10-08 09:39:42.539  
 SOLVENT: CDCl3  
 Experiment = zg30  
 Pulse length = 14.500 usec  
 Relaxation delay = 1.000 sec  
 NA = 16  
 Solvent = CDCl3  
 PTS1d = 65536  
 F1 = 400.130005 MHz  
 F2 = 1.000000 MHz  
 SW1 = 8012.82 Hz  
 AT1 = 8.18 sec  
 Hz per Pt 1stD = 0.12 Hz  
 SW2 = 1.00 Hz  
 Hz per Pt 2ndD = 1.00 Hz  
 O1 = 2461.7222 Hz  
 O2 = -1.0000 Hz  
 LB1 = 0.30 Hz  
 TP A = 0.00  
 B = 0.00  
 C = 0.00

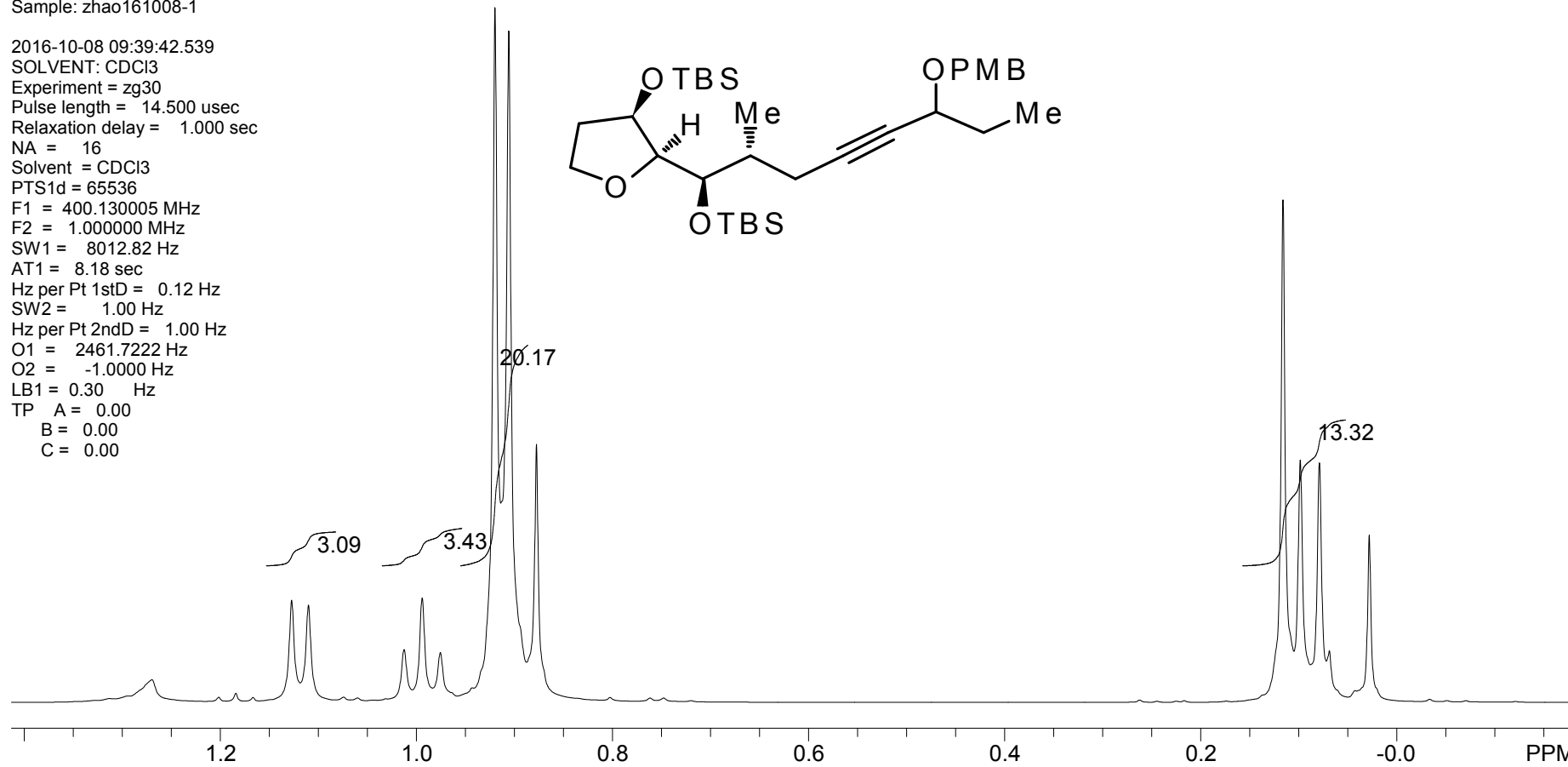
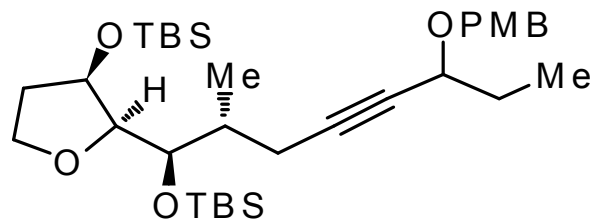




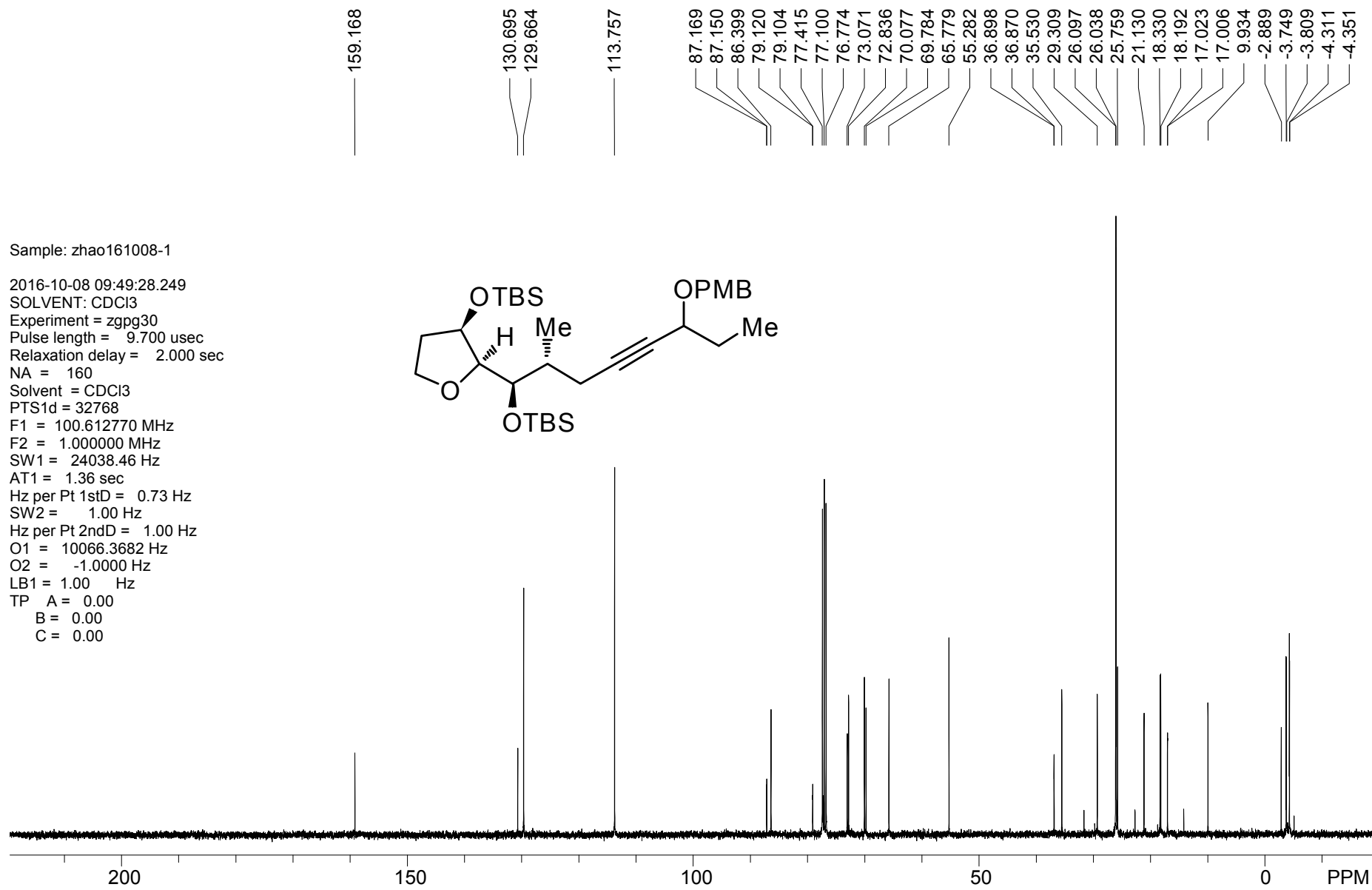


Sample: zhao161008-1

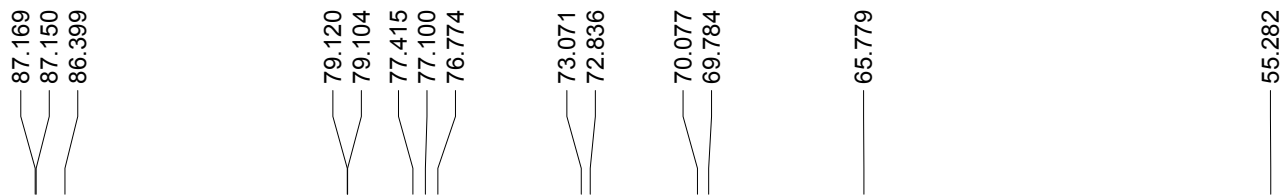
2016-10-08 09:39:42.539  
 SOLVENT: CDCl3  
 Experiment = zg30  
 Pulse length = 14.500 usec  
 Relaxation delay = 1.000 sec  
 NA = 16  
 Solvent = CDCl3  
 PTS1d = 65536  
 F1 = 400.130005 MHz  
 F2 = 1.000000 MHz  
 SW1 = 8012.82 Hz  
 AT1 = 8.18 sec  
 Hz per Pt 1stD = 0.12 Hz  
 SW2 = 1.00 Hz  
 Hz per Pt 2ndD = 1.00 Hz  
 O1 = 2461.7222 Hz  
 O2 = -1.0000 Hz  
 LB1 = 0.30 Hz  
 TP A = 0.00  
 B = 0.00  
 C = 0.00



S100

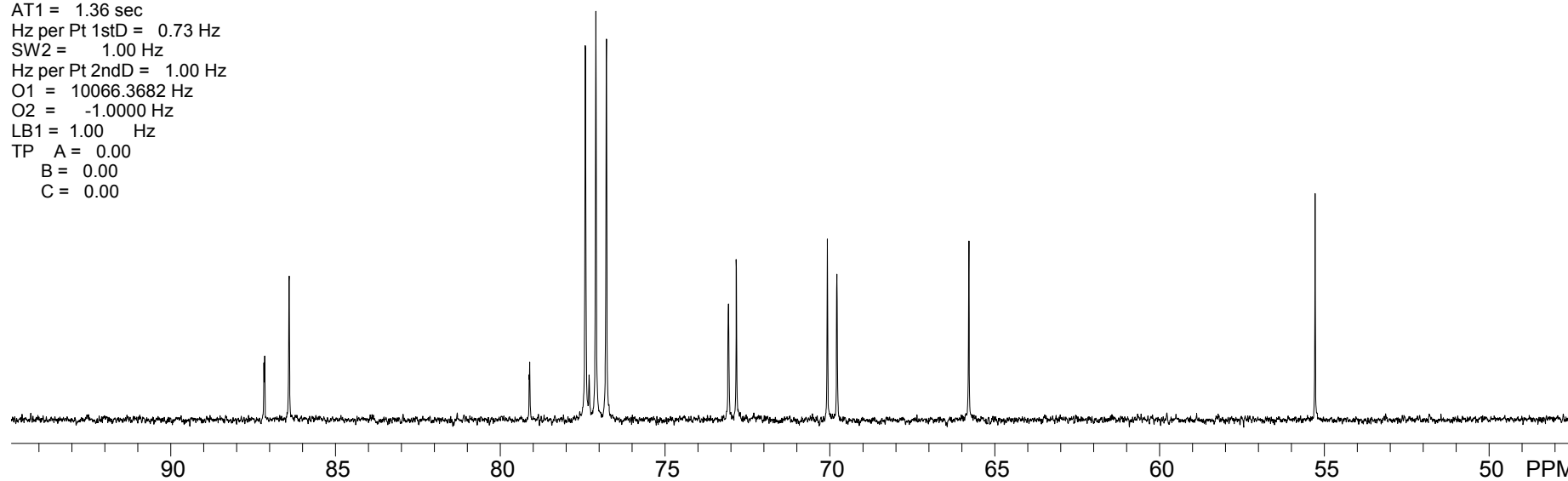
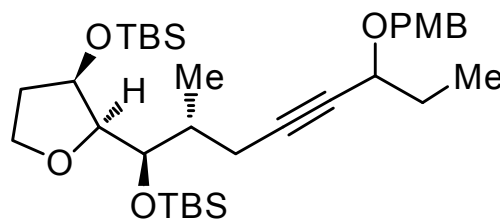


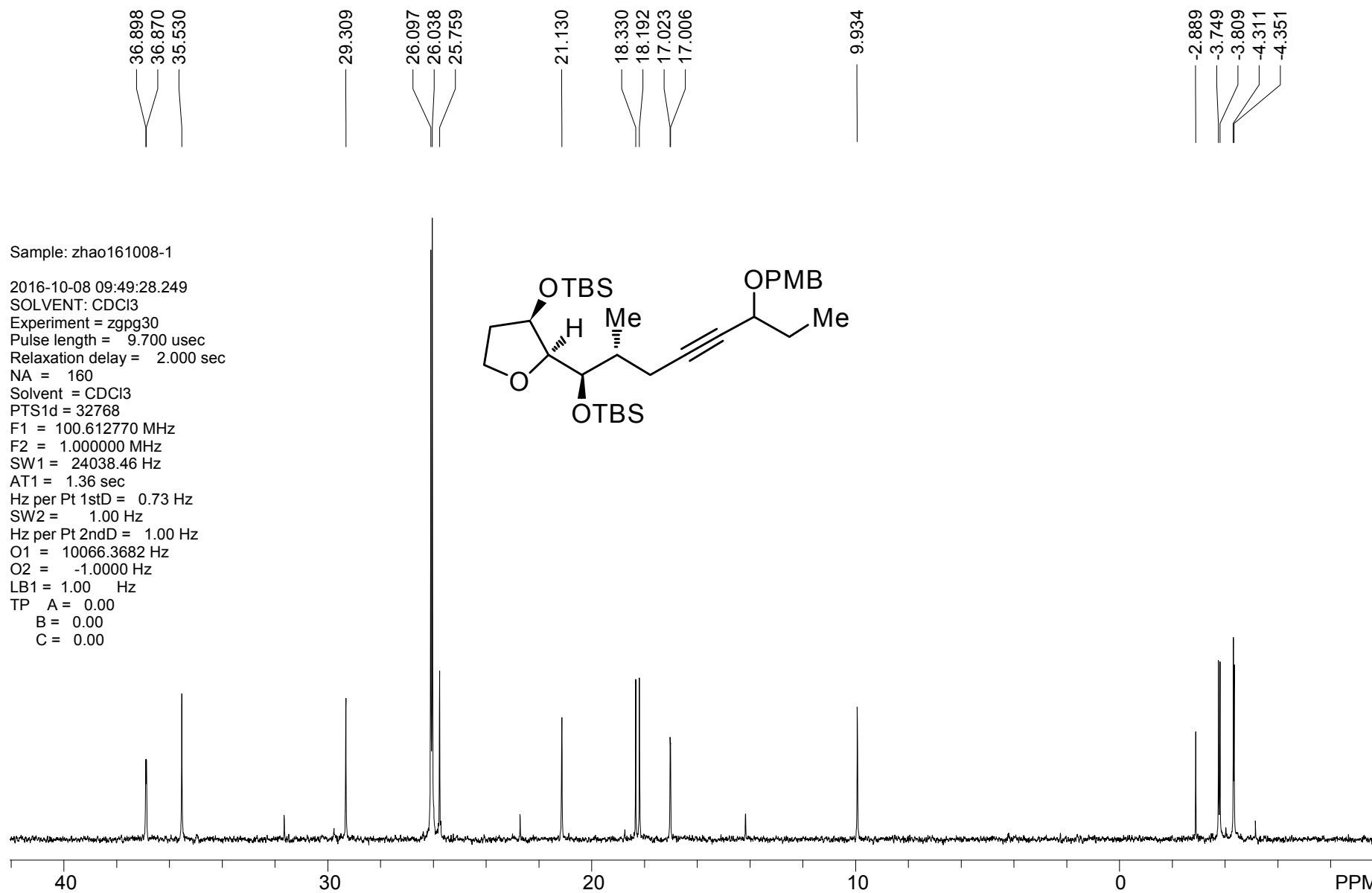
S101

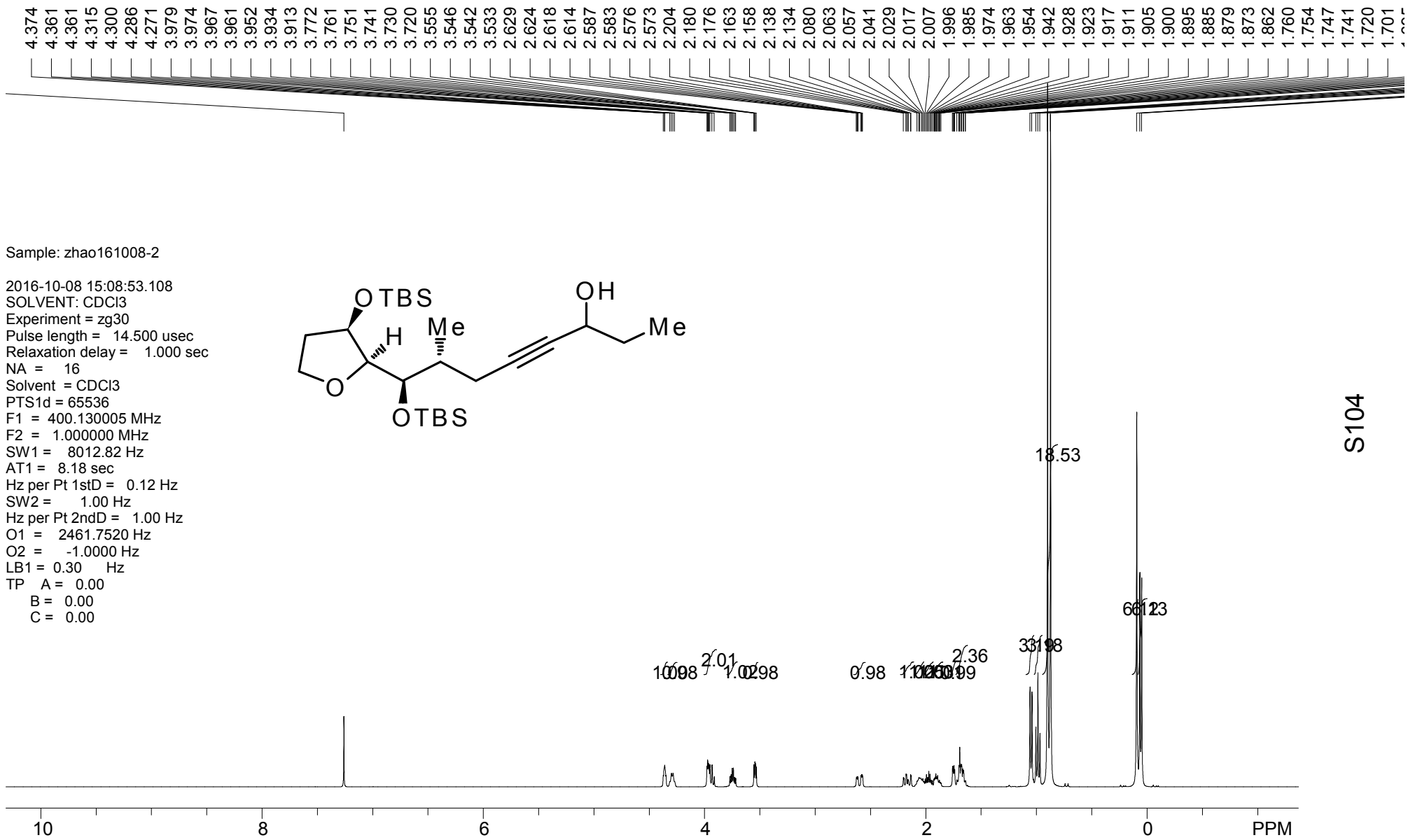


Sample: zhao161008-1

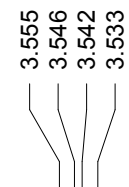
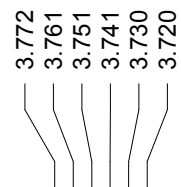
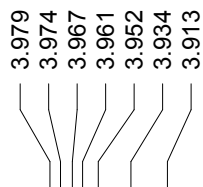
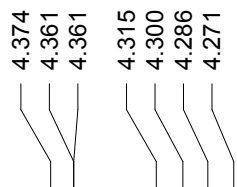
2016-10-08 09:49:28.249  
 SOLVENT: CDCl3  
 Experiment = zgpg30  
 Pulse length = 9.700 usec  
 Relaxation delay = 2.000 sec  
 NA = 160  
 Solvent = CDCl3  
 PTS1d = 32768  
 F1 = 100.612770 MHz  
 F2 = 1.000000 MHz  
 SW1 = 24038.46 Hz  
 AT1 = 1.36 sec  
 Hz per Pt 1stD = 0.73 Hz  
 SW2 = 1.00 Hz  
 Hz per Pt 2ndD = 1.00 Hz  
 O1 = 10066.3682 Hz  
 O2 = -1.0000 Hz  
 LB1 = 1.00 Hz  
 TP A = 0.00  
 B = 0.00  
 C = 0.00





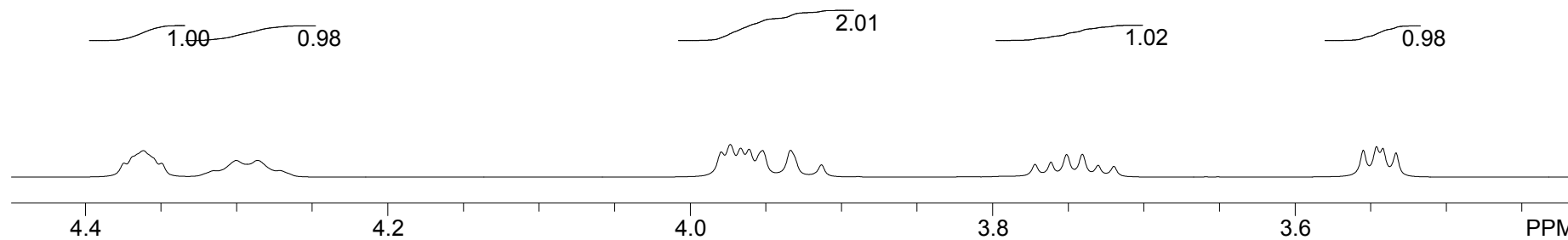
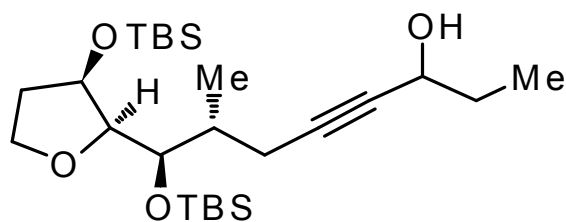


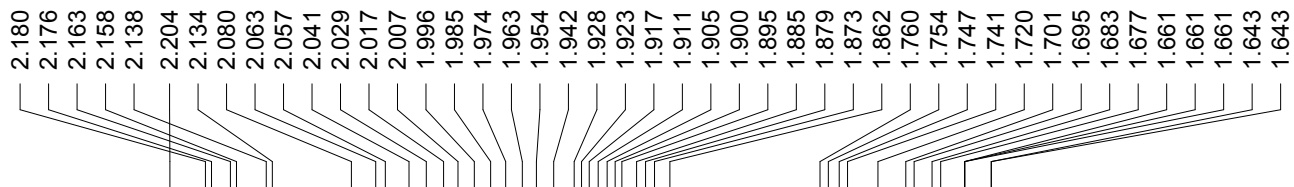
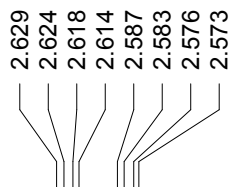




Sample: zhao161008-2

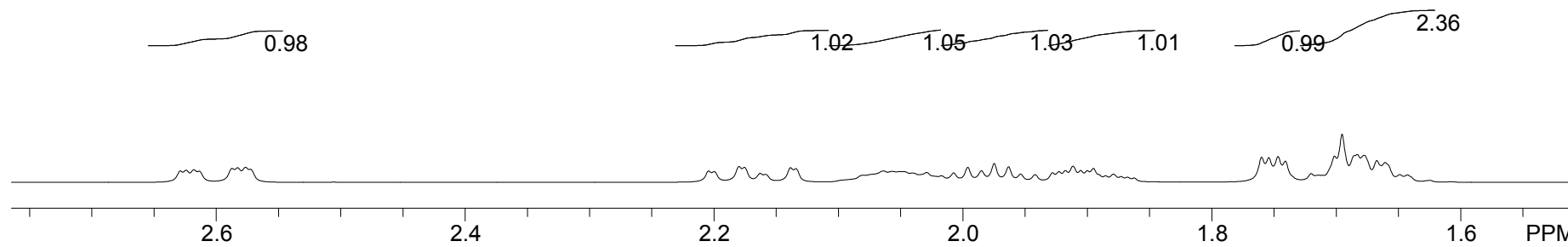
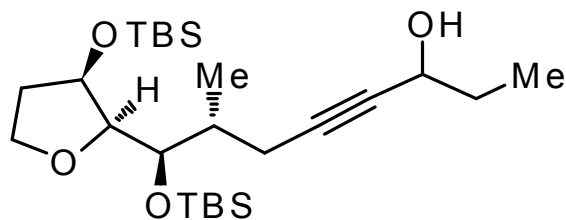
2016-10-08 15:08:53.108  
SOLVENT: CDCl3  
Experiment = zg30  
Pulse length = 14.500 usec  
Relaxation delay = 1.000 sec  
NA = 16  
Solvent = CDCl3  
PTS1d = 65536  
F1 = 400.130005 MHz  
F2 = 1.000000 MHz  
SW1 = 8012.82 Hz  
AT1 = 8.18 sec  
Hz per Pt 1stD = 0.12 Hz  
SW2 = 1.00 Hz  
Hz per Pt 2ndD = 1.00 Hz  
O1 = 2461.7520 Hz  
O2 = -1.0000 Hz  
LB1 = 0.30 Hz  
TP A = 0.00  
B = 0.00  
C = 0.00



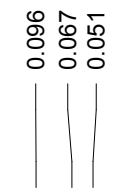
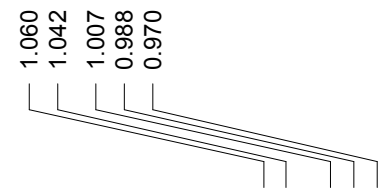


Sample: zhao161008-2

2016-10-08 15:08:53.108  
 SOLVENT: CDCl3  
 Experiment = zg30  
 Pulse length = 14.500 usec  
 Relaxation delay = 1.000 sec  
 NA = 16  
 Solvent = CDCl3  
 PTS1d = 65536  
 F1 = 400.130005 MHz  
 F2 = 1.000000 MHz  
 SW1 = 8012.82 Hz  
 AT1 = 8.18 sec  
 Hz per Pt 1stD = 0.12 Hz  
 SW2 = 1.00 Hz  
 Hz per Pt 2ndD = 1.00 Hz  
 O1 = 2461.7520 Hz  
 O2 = -1.0000 Hz  
 LB1 = 0.30 Hz  
 TP A = 0.00  
 B = 0.00  
 C = 0.00

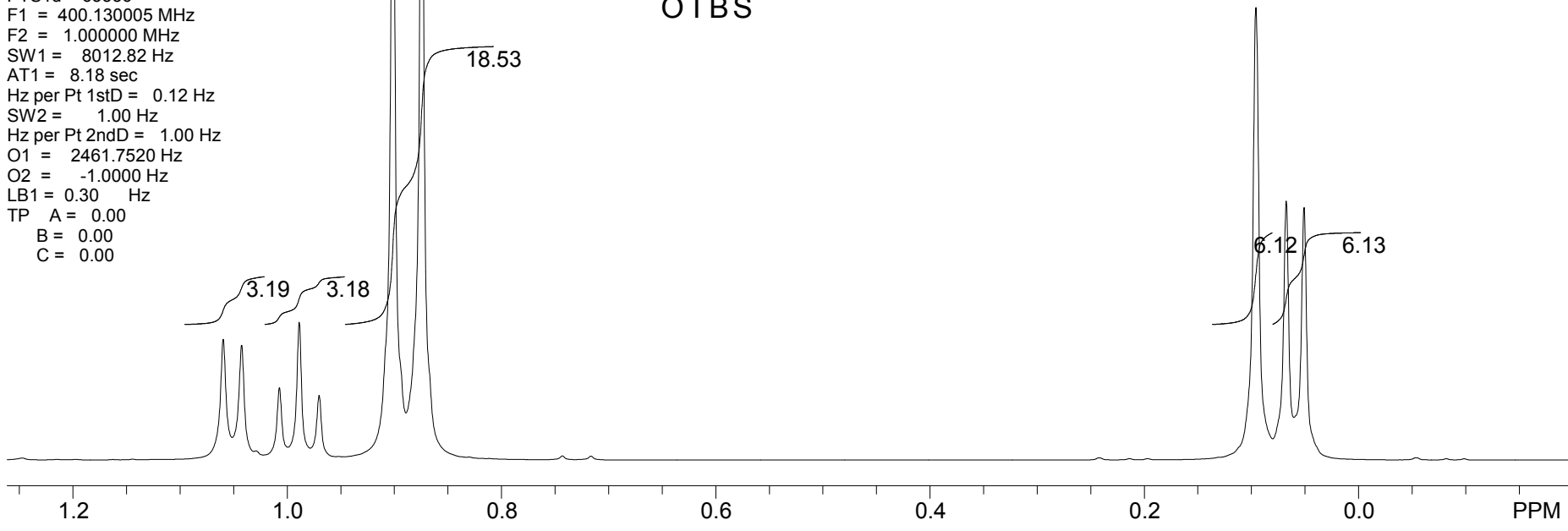
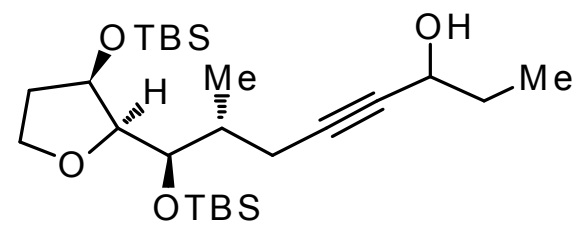


S106



Sample: zhao161008-2

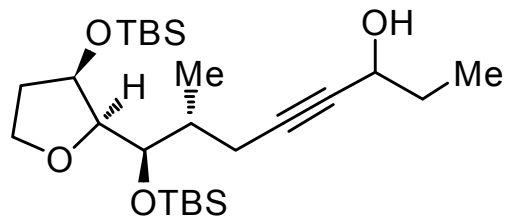
2016-10-08 15:08:53.108  
SOLVENT: CDCl3  
Experiment = zg30  
Pulse length = 14.500 usec  
Relaxation delay = 1.000 sec  
NA = 16  
Solvent = CDCl3  
PTS1d = 65536  
F1 = 400.130005 MHz  
F2 = 1.000000 MHz  
SW1 = 8012.82 Hz  
AT1 = 8.18 sec  
Hz per Pt 1stD = 0.12 Hz  
SW2 = 1.00 Hz  
Hz per Pt 2ndD = 1.00 Hz  
O1 = 2461.7520 Hz  
O2 = -1.0000 Hz  
LB1 = 0.30 Hz  
TP A = 0.00  
B = 0.00  
C = 0.00



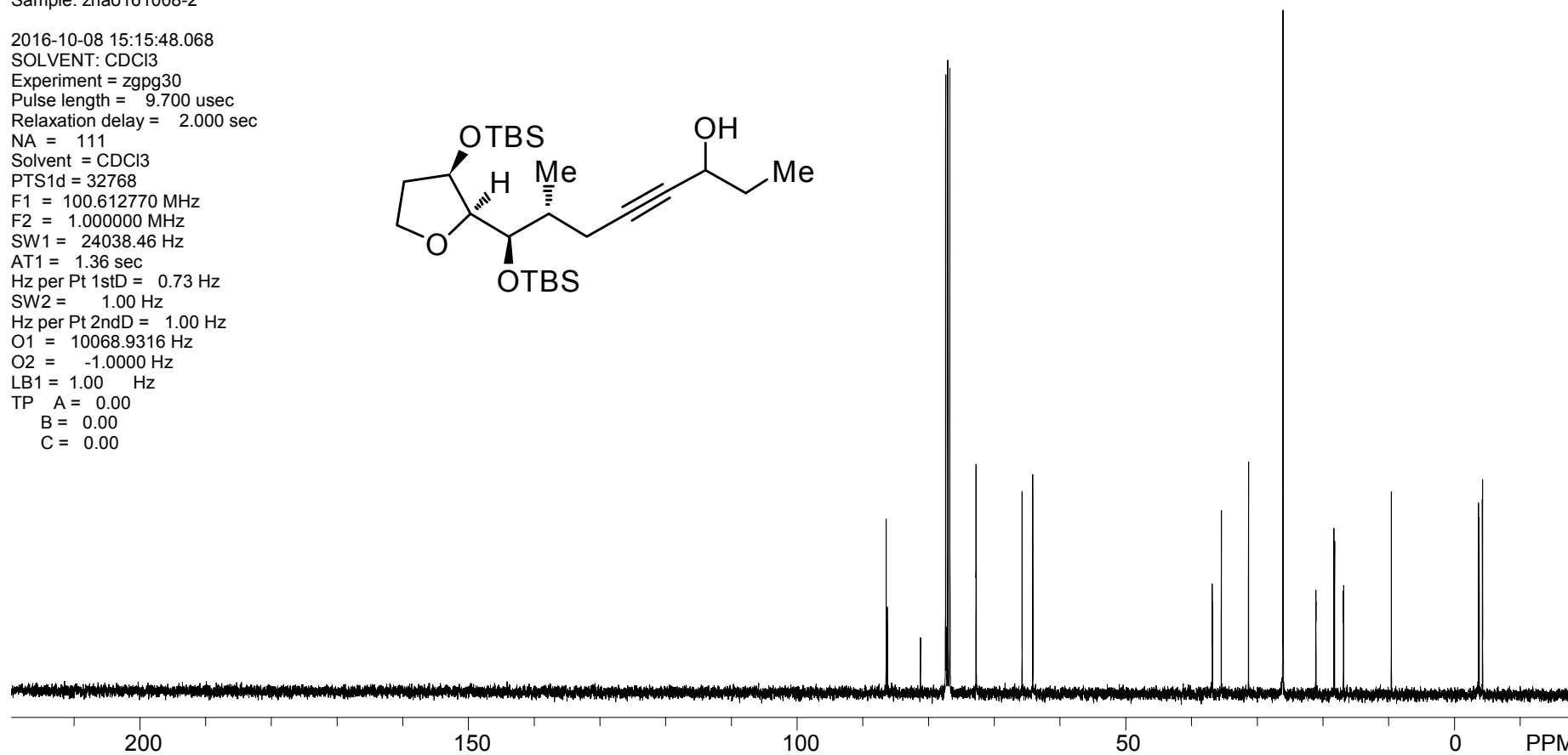
S107

Sample: zhao161008-2

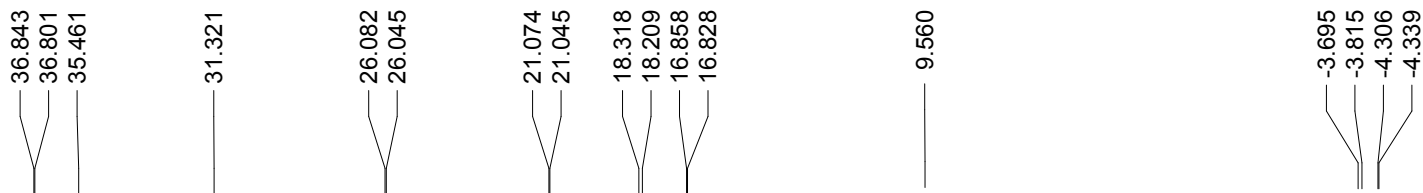
2016-10-08 15:15:48.068  
SOLVENT: CDCl3  
Experiment = zgpg30  
Pulse length = 9.700 usec  
Relaxation delay = 2.000 sec  
NA = 111  
Solvent = CDCl3  
PTS1d = 32768  
F1 = 100.612770 MHz  
F2 = 1.000000 MHz  
SW1 = 24038.46 Hz  
AT1 = 1.36 sec  
Hz per Pt 1stD = 0.73 Hz  
SW2 = 1.00 Hz  
Hz per Pt 2ndD = 1.00 Hz  
O1 = 10068.9316 Hz  
O2 = -1.0000 Hz  
LB1 = 1.00 Hz  
TP A = 0.00  
B = 0.00  
C = 0.00



86.462 86.279 81.257 81.243 77.413 77.100 76.780 72.804 72.768 65.791 64.164  
36.843 36.801 35.461 31.321 26.082 26.045 21.074 21.045 18.318 18.209 16.858 16.828 9.560 -3.695 -3.815 -4.306 -4.339

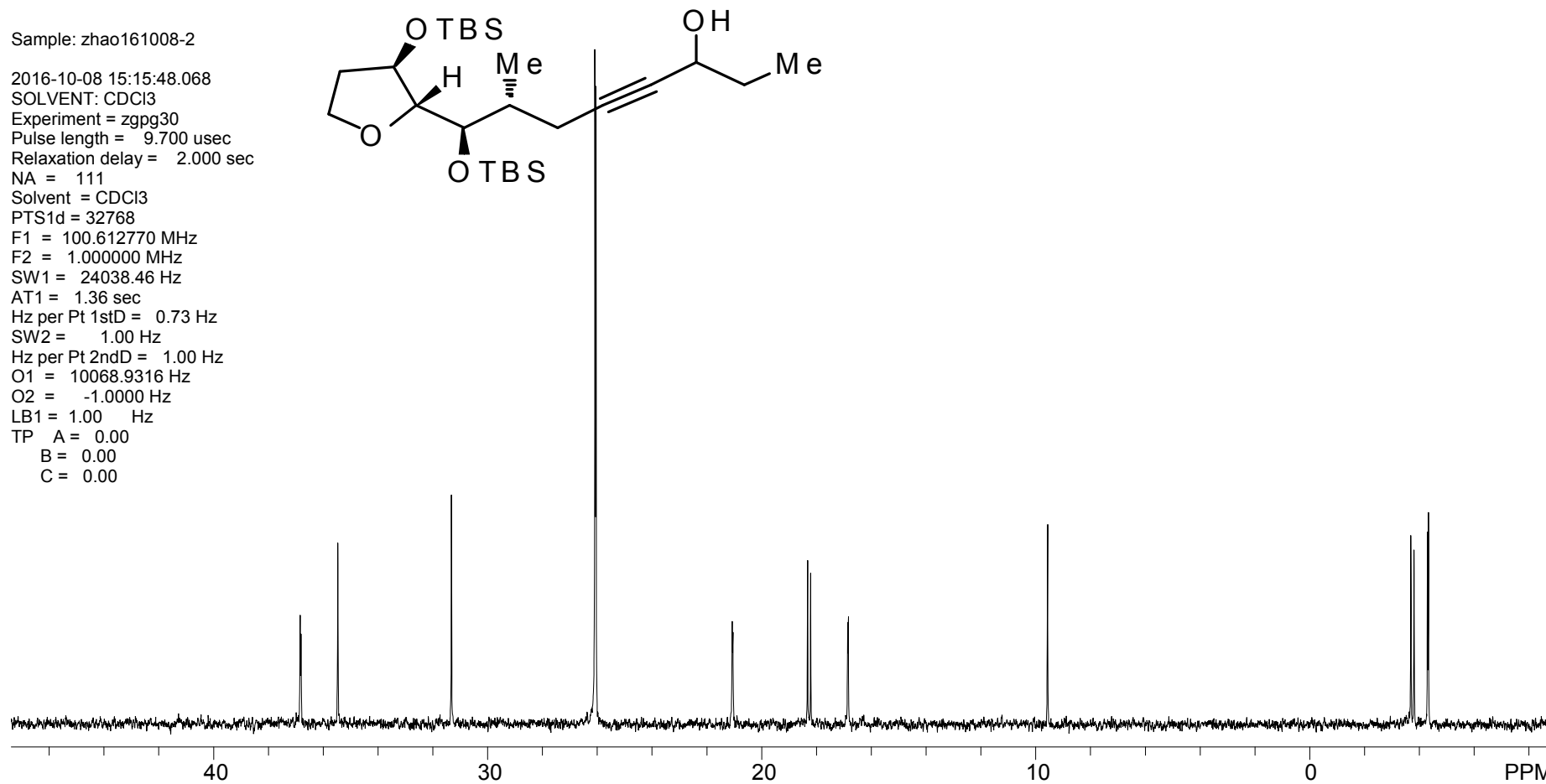
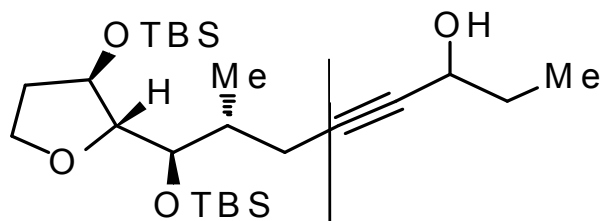


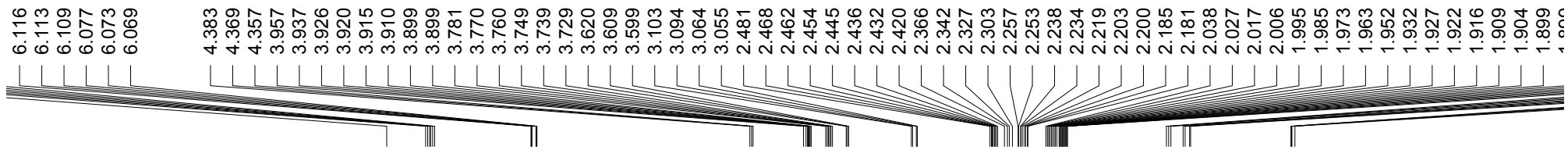
S108



Sample: zhao161008-2

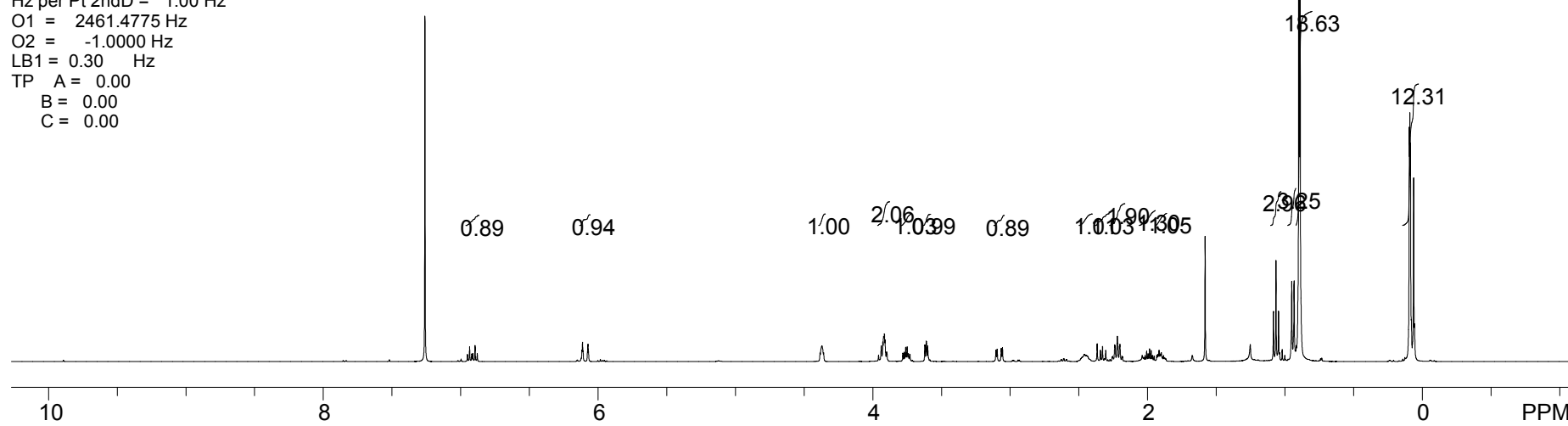
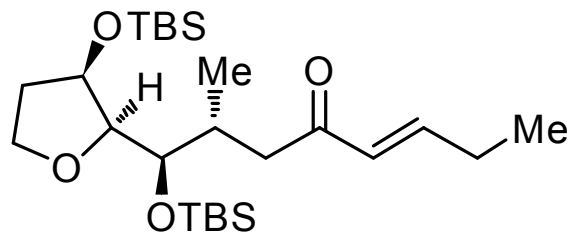
2016-10-08 15:15:48.068  
 SOLVENT: CDCl3  
 Experiment = zgpg30  
 Pulse length = 9.700 usec  
 Relaxation delay = 2.000 sec  
 NA = 111  
 Solvent = CDCl3  
 PTS1d = 32768  
 F1 = 100.612770 MHz  
 F2 = 1.000000 MHz  
 SW1 = 24038.46 Hz  
 AT1 = 1.36 sec  
 Hz per Pt 1stD = 0.73 Hz  
 SW2 = 1.00 Hz  
 Hz per Pt 2ndD = 1.00 Hz  
 O1 = 10068.9316 Hz  
 O2 = -1.0000 Hz  
 LB1 = 1.00 Hz  
 TP A = 0.00  
 B = 0.00  
 C = 0.00





Sample: zhao161008-3

2016-10-08 23:46:27.435  
 SOLVENT: CDCl3  
 Experiment = zg30  
 Pulse length = 14.500 usec  
 Relaxation delay = 1.000 sec  
 NA = 16  
 Solvent = CDCl3  
 PTS1d = 65536  
 F1 = 400.130005 MHz  
 F2 = 1.000000 MHz  
 SW1 = 8012.82 Hz  
 AT1 = 8.18 sec  
 Hz per Pt 1stD = 0.12 Hz  
 SW2 = 1.00 Hz  
 Hz per Pt 2ndD = 1.00 Hz  
 O1 = 2461.4775 Hz  
 O2 = -1.0000 Hz  
 LB1 = 0.30 Hz  
 TP A = 0.00  
 B = 0.00  
 C = 0.00



S110

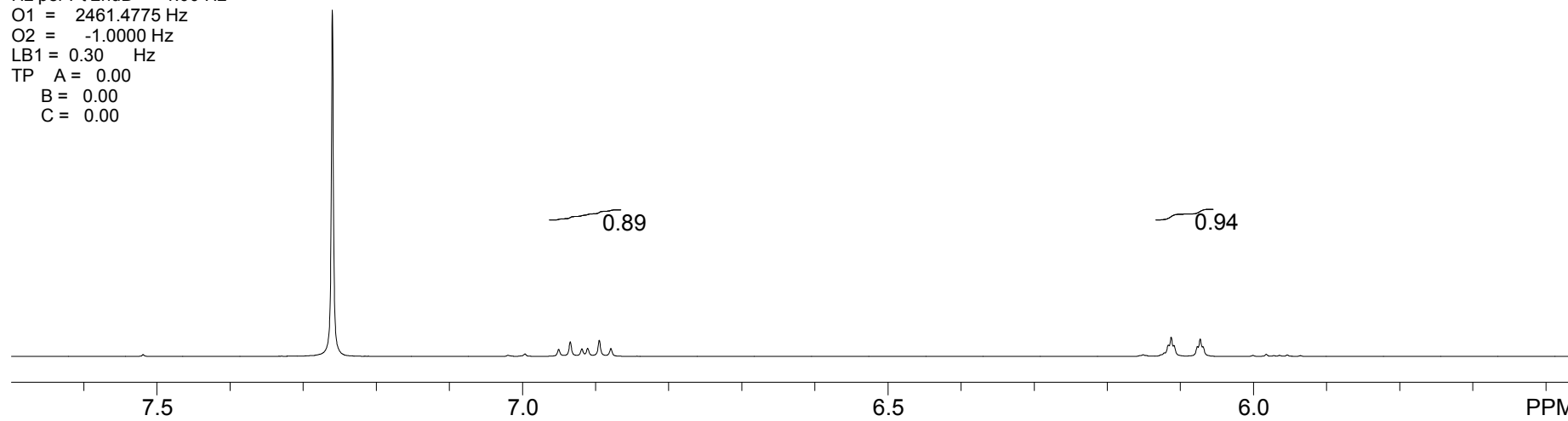
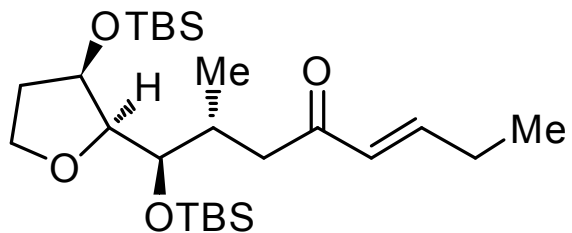
7.260

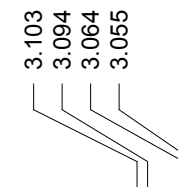
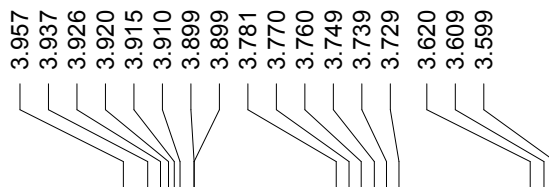
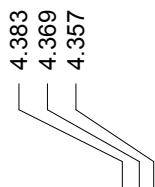
6.950  
6.935  
6.919  
6.911  
6.895  
6.879

6.116  
6.113  
6.109  
6.077  
6.073  
6.069

Sample: zhao161008-3

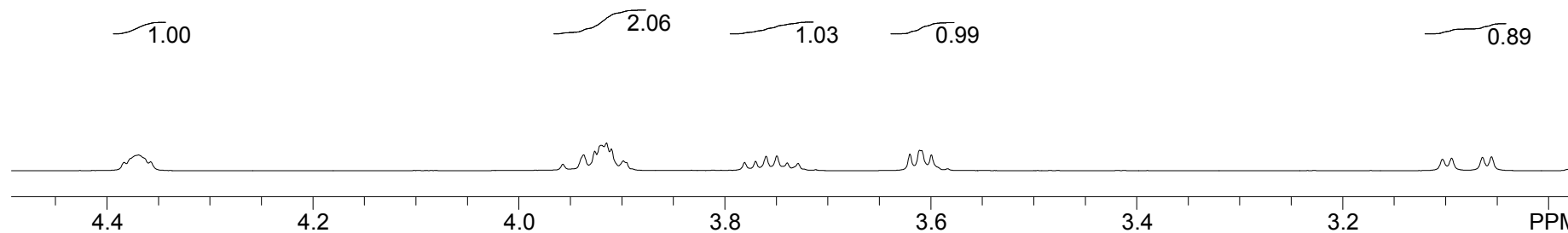
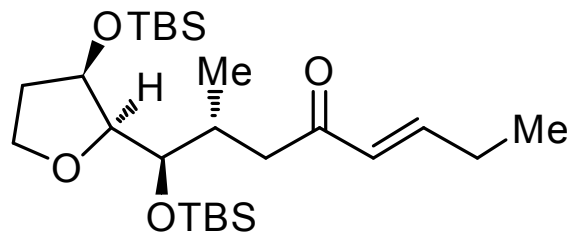
2016-10-08 23:46:27.435  
SOLVENT: CDCl3  
Experiment = zg30  
Pulse length = 14.500 usec  
Relaxation delay = 1.000 sec  
NA = 16  
Solvent = CDCl3  
PTS1d = 65536  
F1 = 400.130005 MHz  
F2 = 1.000000 MHz  
SW1 = 8012.82 Hz  
AT1 = 8.18 sec  
Hz per Pt 1stD = 0.12 Hz  
SW2 = 1.00 Hz  
Hz per Pt 2ndD = 1.00 Hz  
O1 = 2461.4775 Hz  
O2 = -1.0000 Hz  
LB1 = 0.30 Hz  
TP A = 0.00  
B = 0.00  
C = 0.00



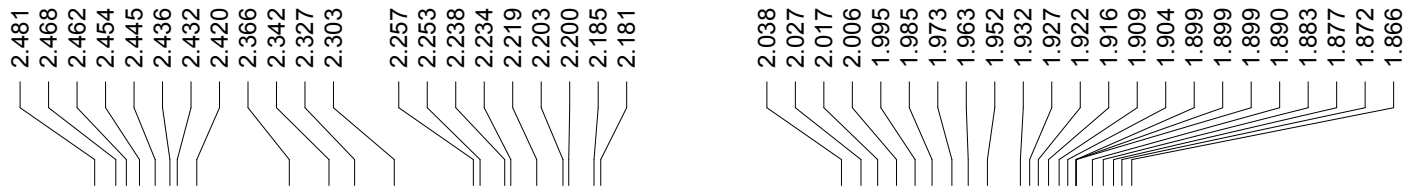


Sample: zhao161008-3

2016-10-08 23:46:27.435  
 SOLVENT: CDCl3  
 Experiment = zg30  
 Pulse length = 14.500 usec  
 Relaxation delay = 1.000 sec  
 NA = 16  
 Solvent = CDCl3  
 PTS1d = 65536  
 F1 = 400.130005 MHz  
 F2 = 1.000000 MHz  
 SW1 = 8012.82 Hz  
 AT1 = 8.18 sec  
 Hz per Pt 1stD = 0.12 Hz  
 SW2 = 1.00 Hz  
 Hz per Pt 2ndD = 1.00 Hz  
 O1 = 2461.4775 Hz  
 O2 = -1.0000 Hz  
 LB1 = 0.30 Hz  
 TP A = 0.00  
 B = 0.00  
 C = 0.00

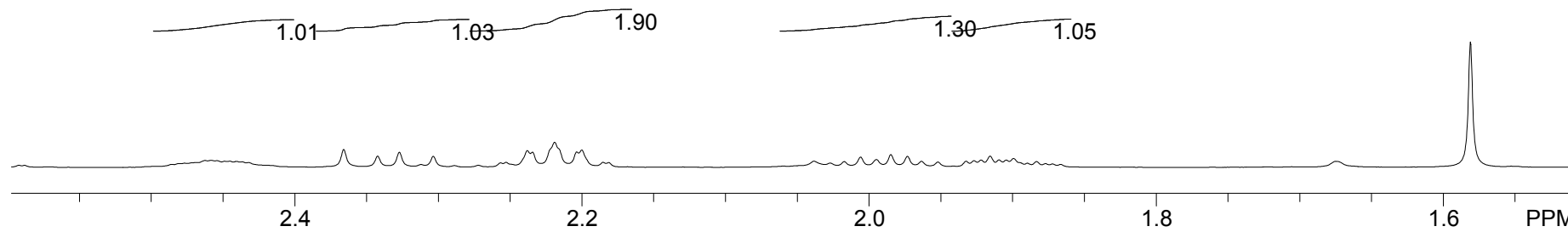
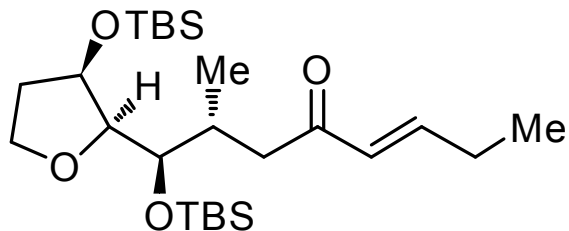






Sample: zhao161008-3

2016-10-08 23:46:27.435  
 SOLVENT: CDCl3  
 Experiment = zg30  
 Pulse length = 14.500 usec  
 Relaxation delay = 1.000 sec  
 NA = 16  
 Solvent = CDCl3  
 PTS1d = 65536  
 F1 = 400.130005 MHz  
 F2 = 1.000000 MHz  
 SW1 = 8012.82 Hz  
 AT1 = 8.18 sec  
 Hz per Pt 1stD = 0.12 Hz  
 SW2 = 1.00 Hz  
 Hz per Pt 2ndD = 1.00 Hz  
 O1 = 2461.4775 Hz  
 O2 = -1.0000 Hz  
 LB1 = 0.30 Hz  
 TP A = 0.00  
 B = 0.00  
 C = 0.00



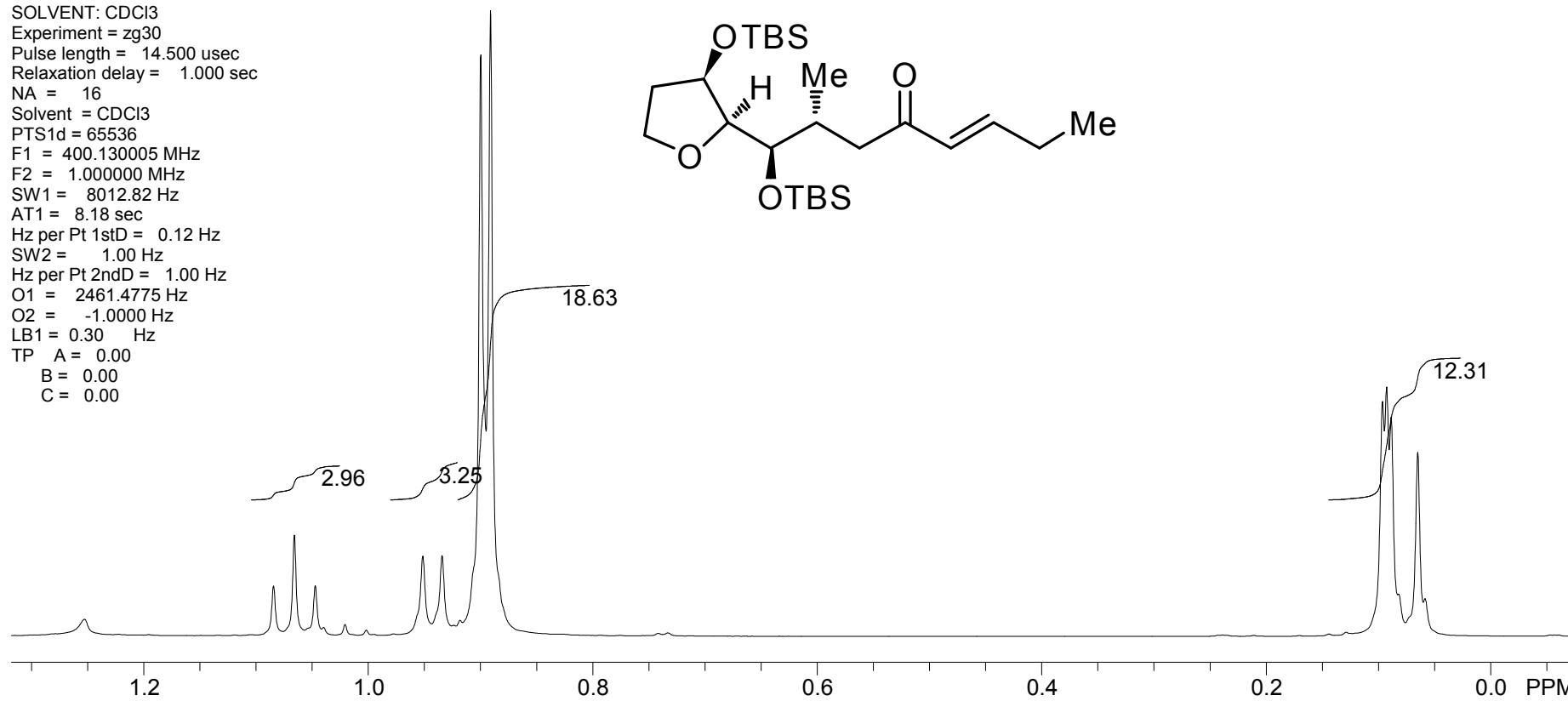
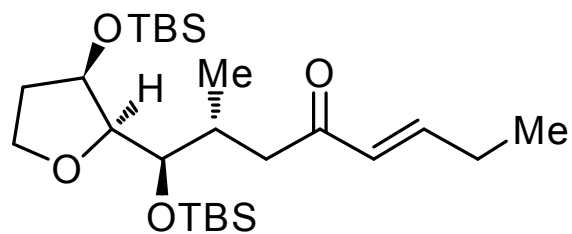
1.084  
1.066  
1.047

0.951  
0.934  
0.899  
0.891

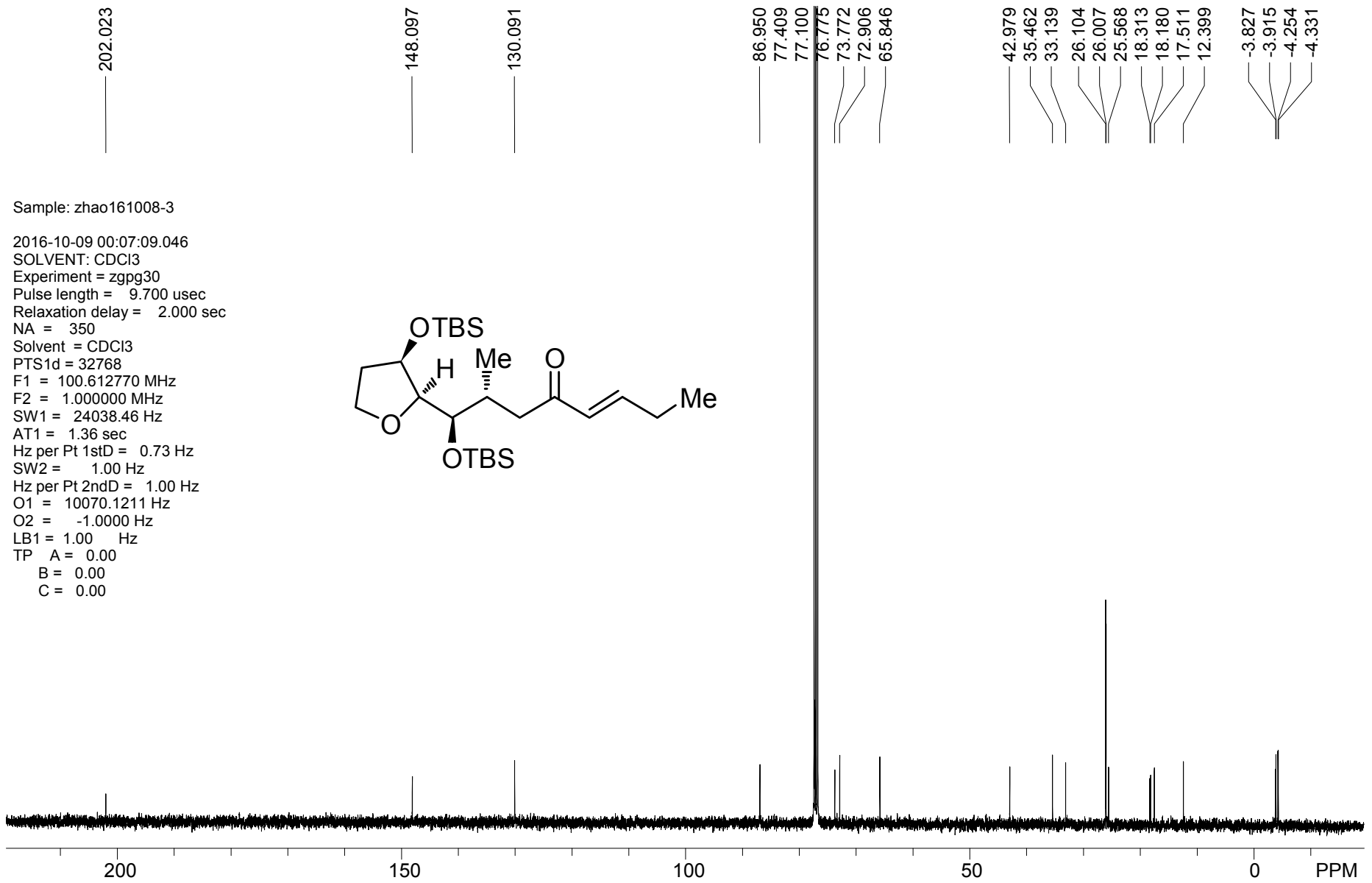
0.096  
0.093  
0.089  
0.065

Sample: zhao161008-3

2016-10-08 23:46:27.435  
SOLVENT: CDCl3  
Experiment = zg30  
Pulse length = 14.500 usec  
Relaxation delay = 1.000 sec  
NA = 16  
Solvent = CDCl3  
PTS1d = 65536  
F1 = 400.130005 MHz  
F2 = 1.000000 MHz  
SW1 = 8012.82 Hz  
AT1 = 8.18 sec  
Hz per Pt 1stD = 0.12 Hz  
SW2 = 1.00 Hz  
Hz per Pt 2ndD = 1.00 Hz  
O1 = 2461.4775 Hz  
O2 = -1.0000 Hz  
LB1 = 0.30 Hz  
TP A = 0.00  
B = 0.00  
C = 0.00

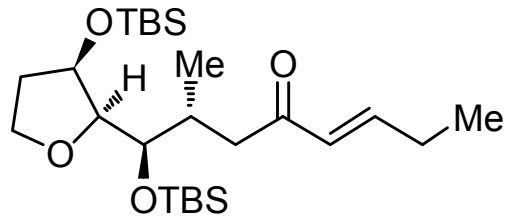


S114

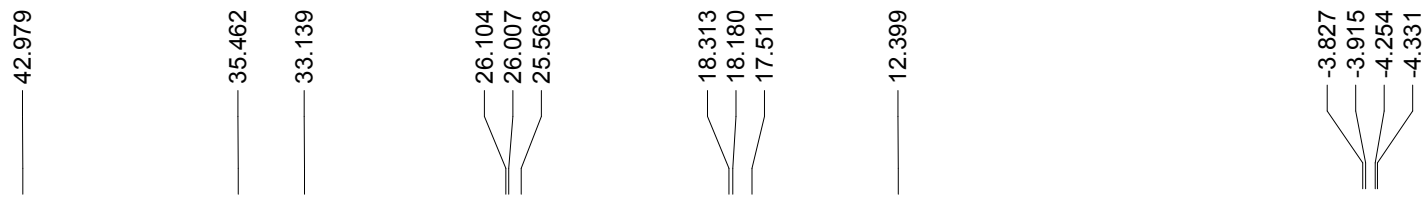


Sample: zhao161008-3

2016-10-09 00:07:09.046  
 SOLVENT: CDCl3  
 Experiment = zgpg30  
 Pulse length = 9.700 usec  
 Relaxation delay = 2.000 sec  
 NA = 350  
 Solvent = CDCl3  
 PTS1d = 32768  
 F1 = 100.612770 MHz  
 F2 = 1.000000 MHz  
 SW1 = 24038.46 Hz  
 AT1 = 1.36 sec  
 Hz per Pt 1stD = 0.73 Hz  
 SW2 = 1.00 Hz  
 Hz per Pt 2ndD = 1.00 Hz  
 O1 = 10070.1211 Hz  
 O2 = -1.0000 Hz  
 LB1 = 1.00 Hz  
 TP A = 0.00  
 B = 0.00  
 C = 0.00

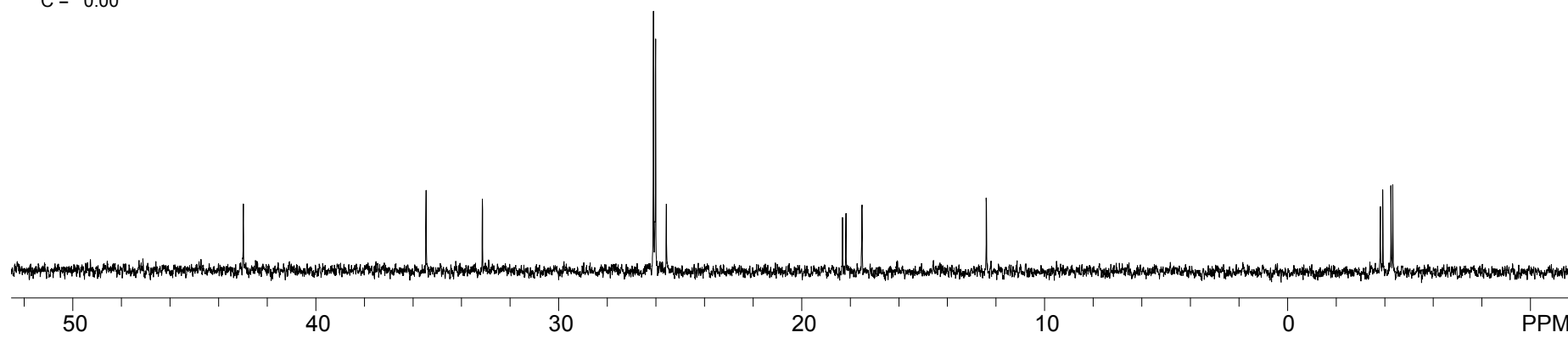
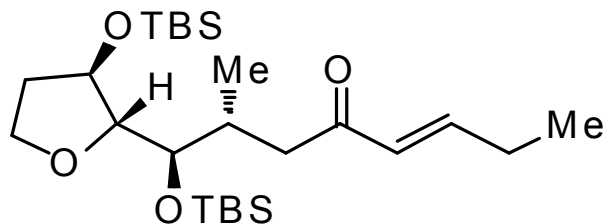


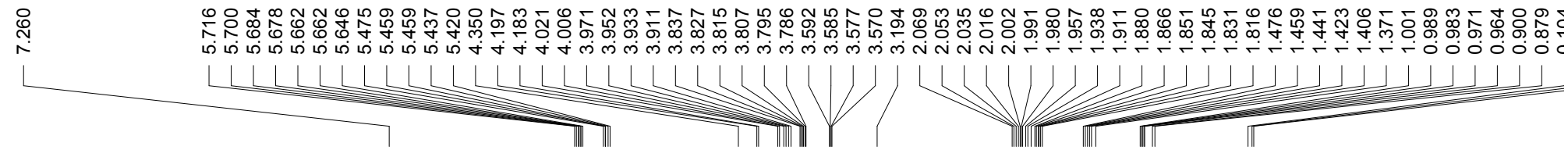
S115



Sample: zhao161008-3

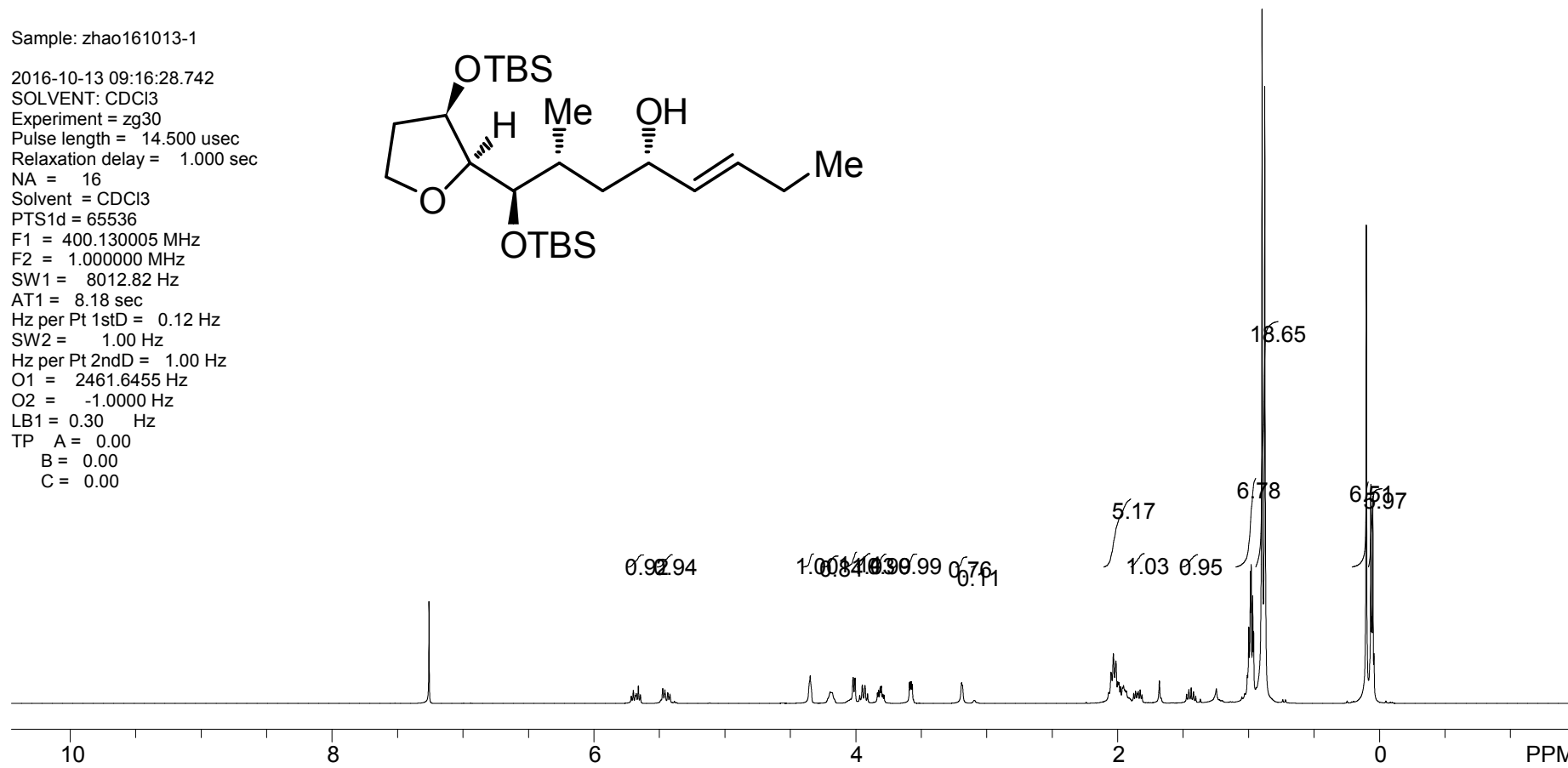
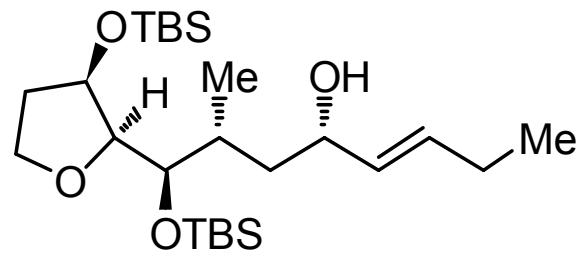
2016-10-09 00:07:09.046  
 SOLVENT: CDCl3  
 Experiment = zgpg30  
 Pulse length = 9.700 usec  
 Relaxation delay = 2.000 sec  
 NA = 350  
 Solvent = CDCl3  
 PTS1d = 32768  
 F1 = 100.612770 MHz  
 F2 = 1.000000 MHz  
 SW1 = 24038.46 Hz  
 AT1 = 1.36 sec  
 Hz per Pt 1stD = 0.73 Hz  
 SW2 = 1.00 Hz  
 Hz per Pt 2ndD = 1.00 Hz  
 O1 = 10070.1211 Hz  
 O2 = -1.0000 Hz  
 LB1 = 1.00 Hz  
 TP A = 0.00  
 B = 0.00  
 C = 0.00



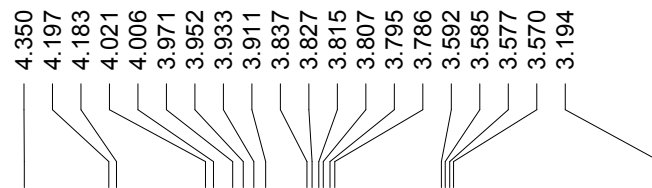
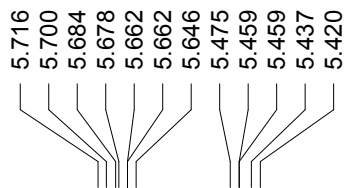


Sample: zhao161013-1

2016-10-13 09:16:28.742  
 SOLVENT: CDCl3  
 Experiment = zg30  
 Pulse length = 14.500 usec  
 Relaxation delay = 1.000 sec  
 NA = 16  
 Solvent = CDCl3  
 PTS1d = 65536  
 F1 = 400.130005 MHz  
 F2 = 1.000000 MHz  
 SW1 = 8012.82 Hz  
 AT1 = 8.18 sec  
 Hz per Pt 1stD = 0.12 Hz  
 SW2 = 1.00 Hz  
 Hz per Pt 2ndD = 1.00 Hz  
 O1 = 2461.6455 Hz  
 O2 = -1.0000 Hz  
 LB1 = 0.30 Hz  
 TP A = 0.00  
 B = 0.00  
 C = 0.00

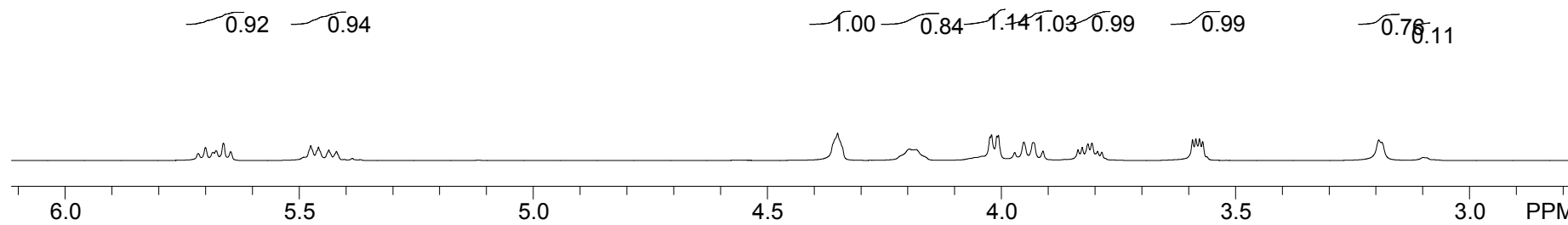
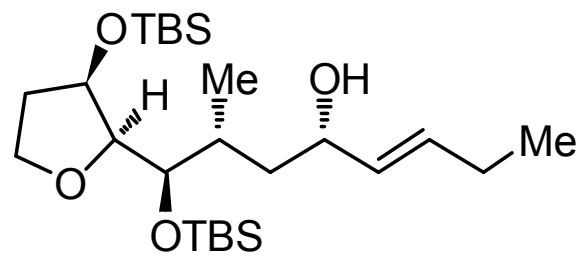


S117



Sample: zhao161013-1

2016-10-13 09:16:28.742  
 SOLVENT: CDCl3  
 Experiment = zg30  
 Pulse length = 14.500 usec  
 Relaxation delay = 1.000 sec  
 NA = 16  
 Solvent = CDCl3  
 PTS1d = 65536  
 F1 = 400.130005 MHz  
 F2 = 1.000000 MHz  
 SW1 = 8012.82 Hz  
 AT1 = 8.18 sec  
 Hz per Pt 1stD = 0.12 Hz  
 SW2 = 1.00 Hz  
 Hz per Pt 2ndD = 1.00 Hz  
 O1 = 2461.6455 Hz  
 O2 = -1.0000 Hz  
 LB1 = 0.30 Hz  
 TP A = 0.00  
 B = 0.00  
 C = 0.00



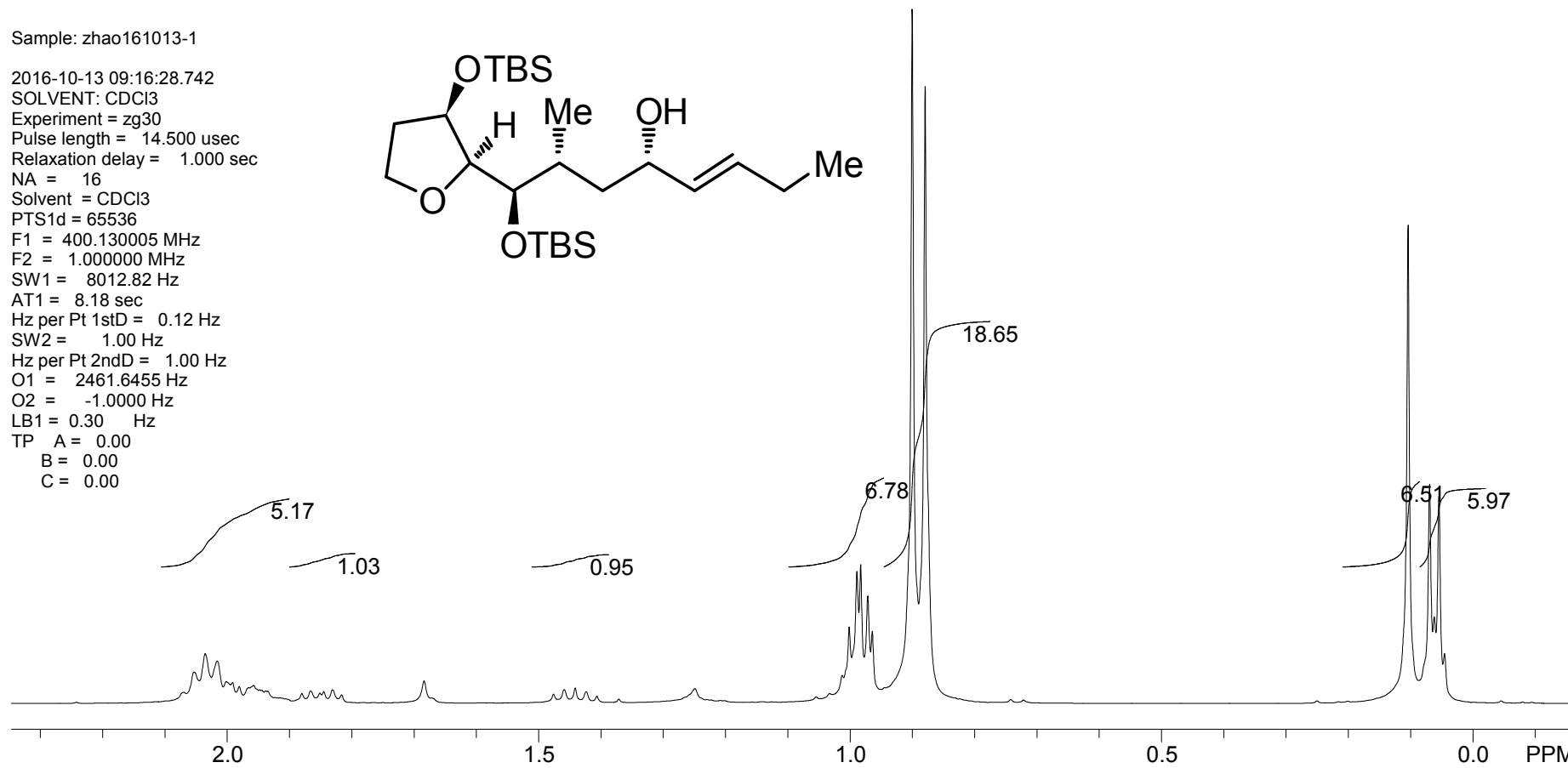
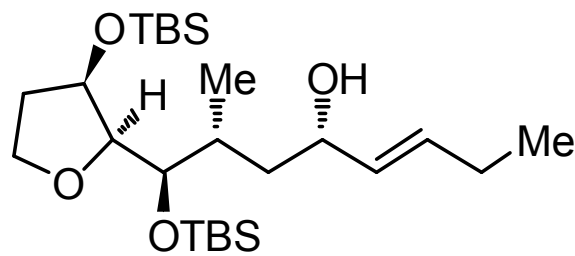
2.069  
2.053  
2.035  
2.016  
2.002  
1.991  
1.980  
1.957  
1.938  
1.911  
1.880  
1.866  
1.851  
1.845  
1.831  
1.816  
1.476  
1.459  
1.441  
1.423  
1.406  
1.371

1.001  
0.989  
0.983  
0.971  
0.964  
0.900  
0.879

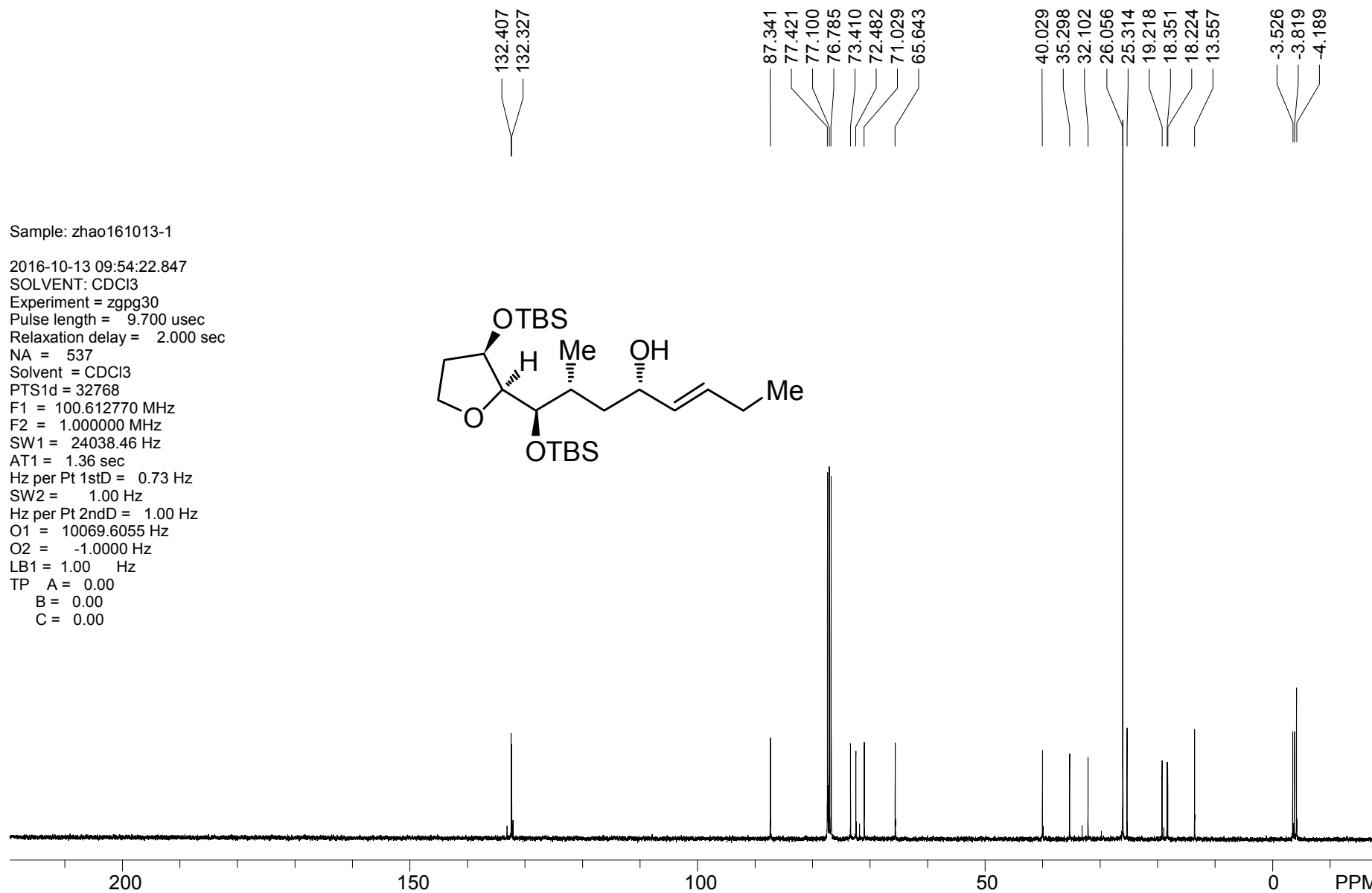
0.104  
0.069  
0.055

Sample: zhao161013-1

2016-10-13 09:16:28.742  
SOLVENT: CDCl3  
Experiment = zg30  
Pulse length = 14.500 usec  
Relaxation delay = 1.000 sec  
NA = 16  
Solvent = CDCl3  
PTS1d = 65536  
F1 = 400.130005 MHz  
F2 = 1.000000 MHz  
SW1 = 8012.82 Hz  
AT1 = 8.18 sec  
Hz per Pt 1stD = 0.12 Hz  
SW2 = 1.00 Hz  
Hz per Pt 2ndD = 1.00 Hz  
O1 = 2461.6455 Hz  
O2 = -1.0000 Hz  
LB1 = 0.30 Hz  
TP A = 0.00  
B = 0.00  
C = 0.00



S119





132.407  
132.327

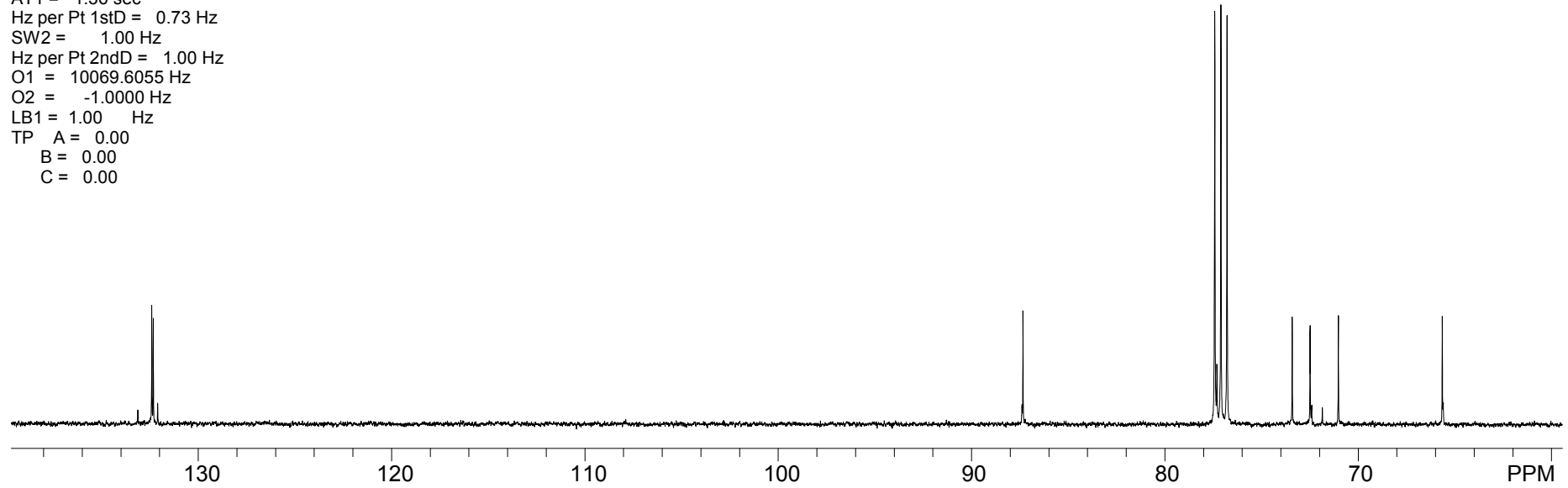
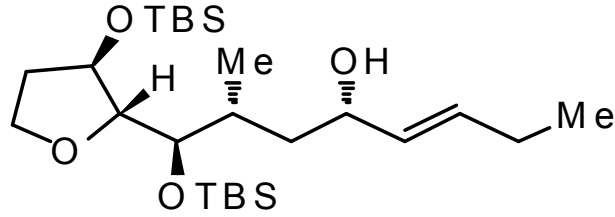
87.341

77.421  
77.100  
76.785  
73.410  
72.482  
71.029

65.643

Sample: zhao161013-1

2016-10-13 09:54:22.847  
SOLVENT: CDCl3  
Experiment = zgpg30  
Pulse length = 9.700 usec  
Relaxation delay = 2.000 sec  
NA = 537  
Solvent = CDCl3  
PTS1d = 32768  
F1 = 100.612770 MHz  
F2 = 1.000000 MHz  
SW1 = 24038.46 Hz  
AT1 = 1.36 sec  
Hz per Pt 1stD = 0.73 Hz  
SW2 = 1.00 Hz  
Hz per Pt 2ndD = 1.00 Hz  
O1 = 10069.6055 Hz  
O2 = -1.0000 Hz  
LB1 = 1.00 Hz  
TP A = 0.00  
B = 0.00  
C = 0.00



S121

Sample: zhao161013-1

2016-10-13 09:54:22.847

SOLVENT: CDCl3

Experiment = zgpg30

Pulse length = 9.700 usec

Relaxation delay = 2.000 sec

NA = 537

Solvent = CDCl3

PTS1d = 32768

F1 = 100.612770 MHz

F2 = 1.000000 MHz

SW1 = 24038.46 Hz

AT1 = 1.36 sec

Hz per Pt 1stD = 0.73 Hz

SW2 = 1.00 Hz

Hz per Pt 2ndD = 1.00 Hz

O1 = 10069.6055 Hz

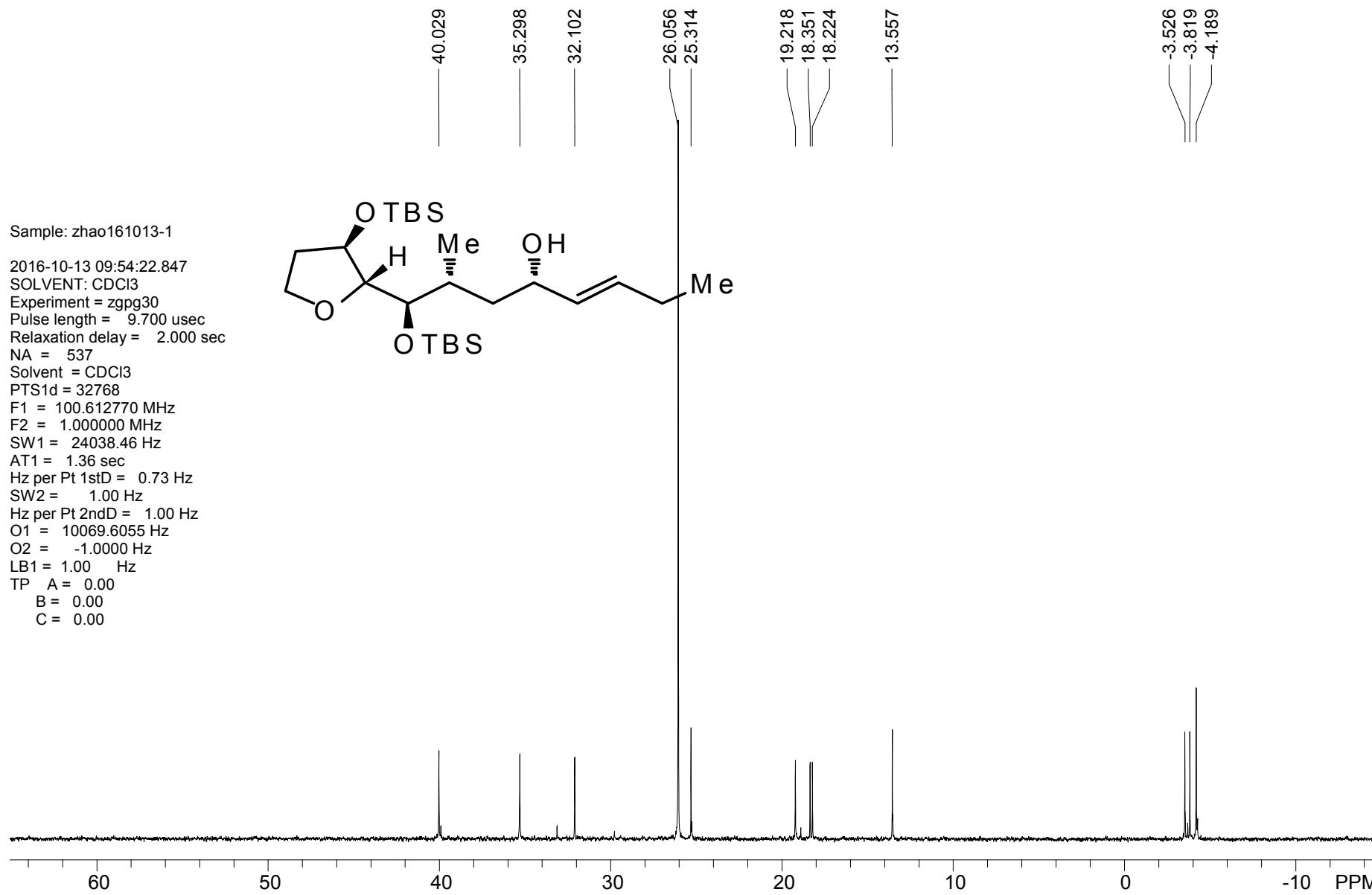
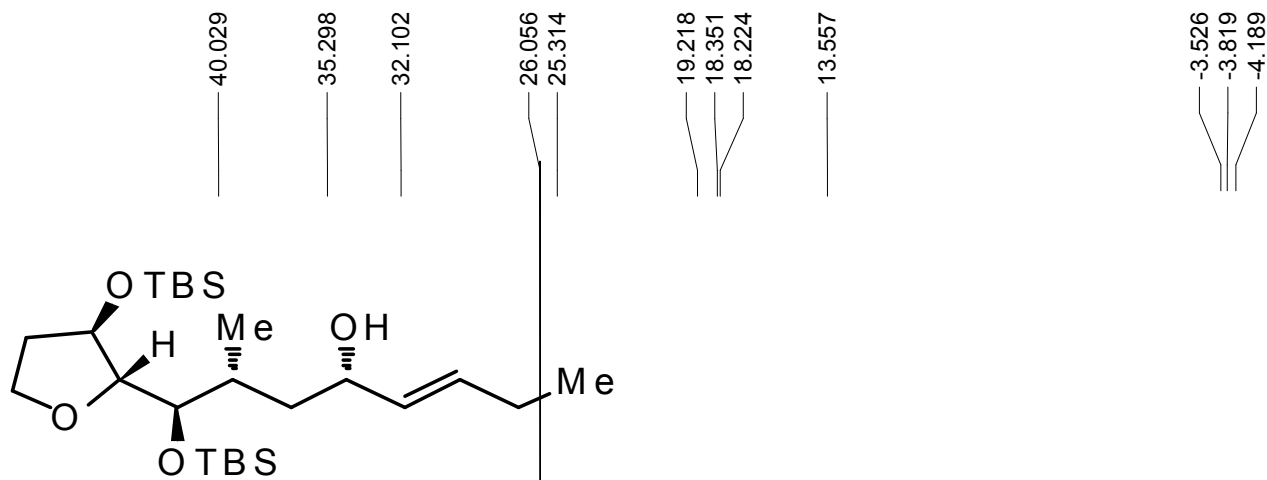
O2 = -1.0000 Hz

LB1 = 1.00 Hz

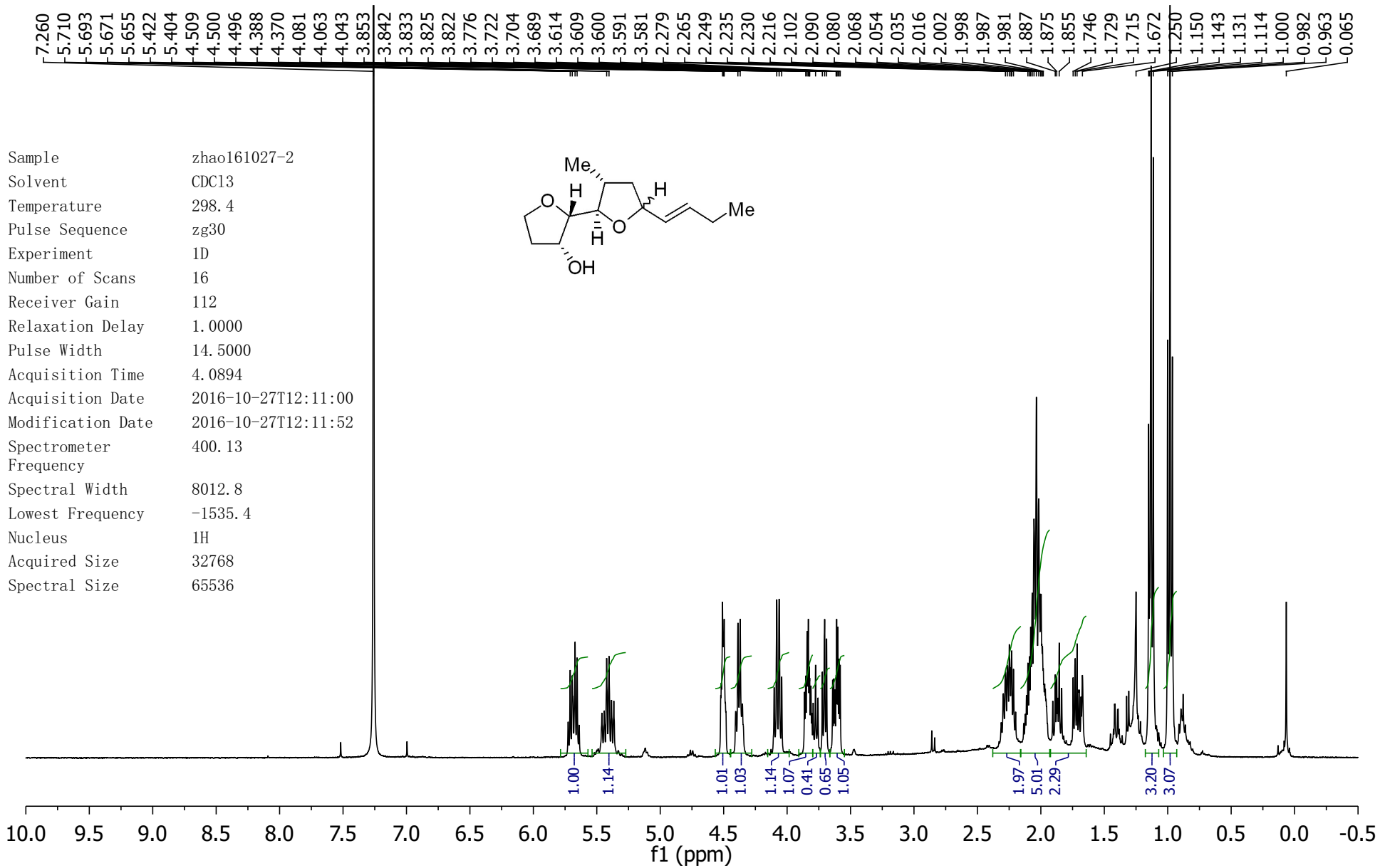
TP A = 0.00

B = 0.00

C = 0.00



S122



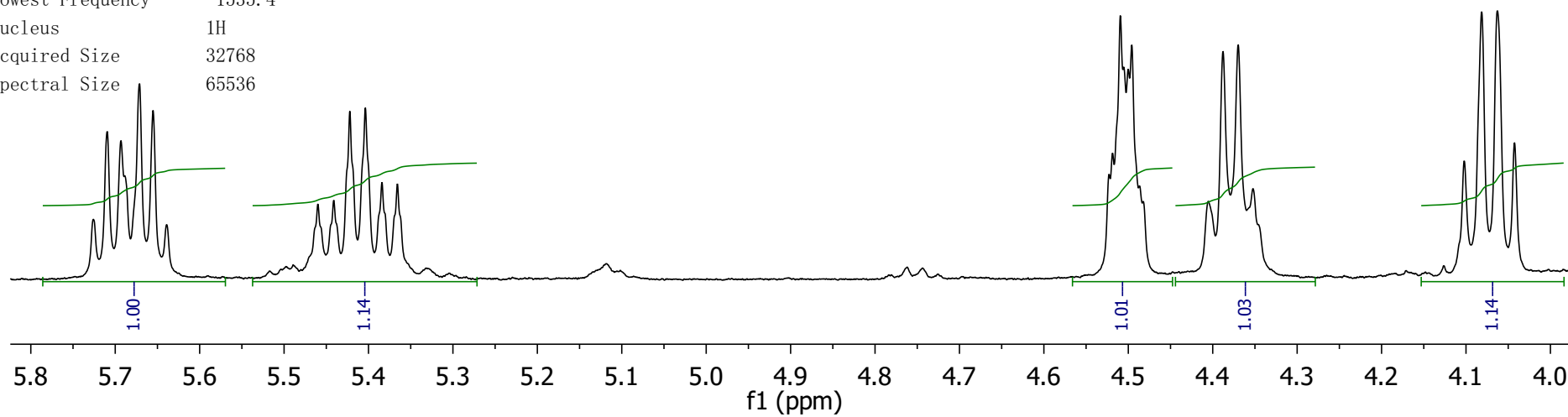
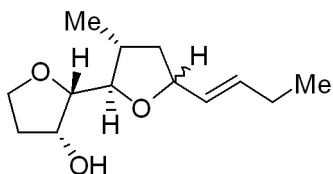
5.726  
5.710  
5.693  
5.671  
5.655  
5.639

5.460  
5.441  
5.422  
5.404  
5.384  
5.366

4.523  
4.519  
4.509  
4.500  
4.496  
4.405  
4.388  
4.370  
4.352

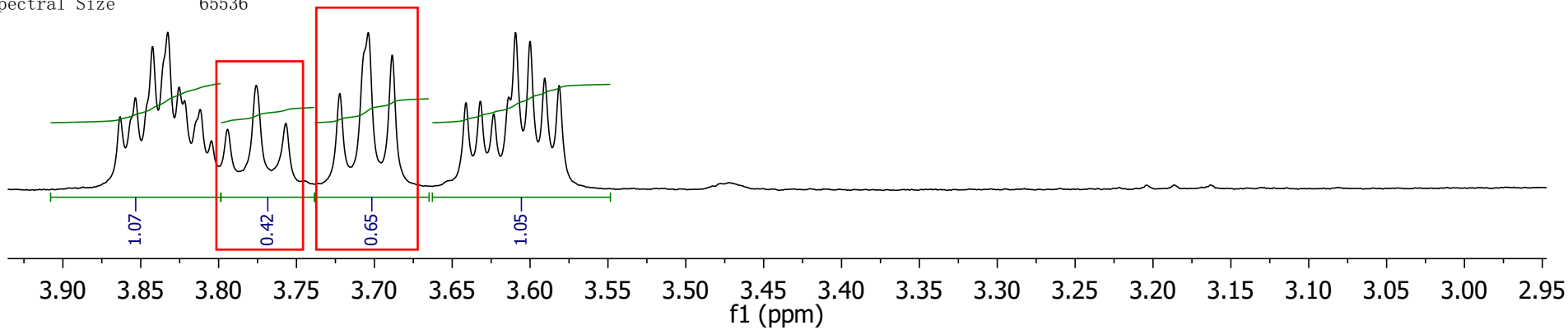
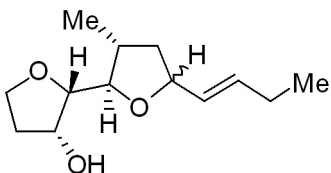
4.102  
4.081  
4.063  
4.043

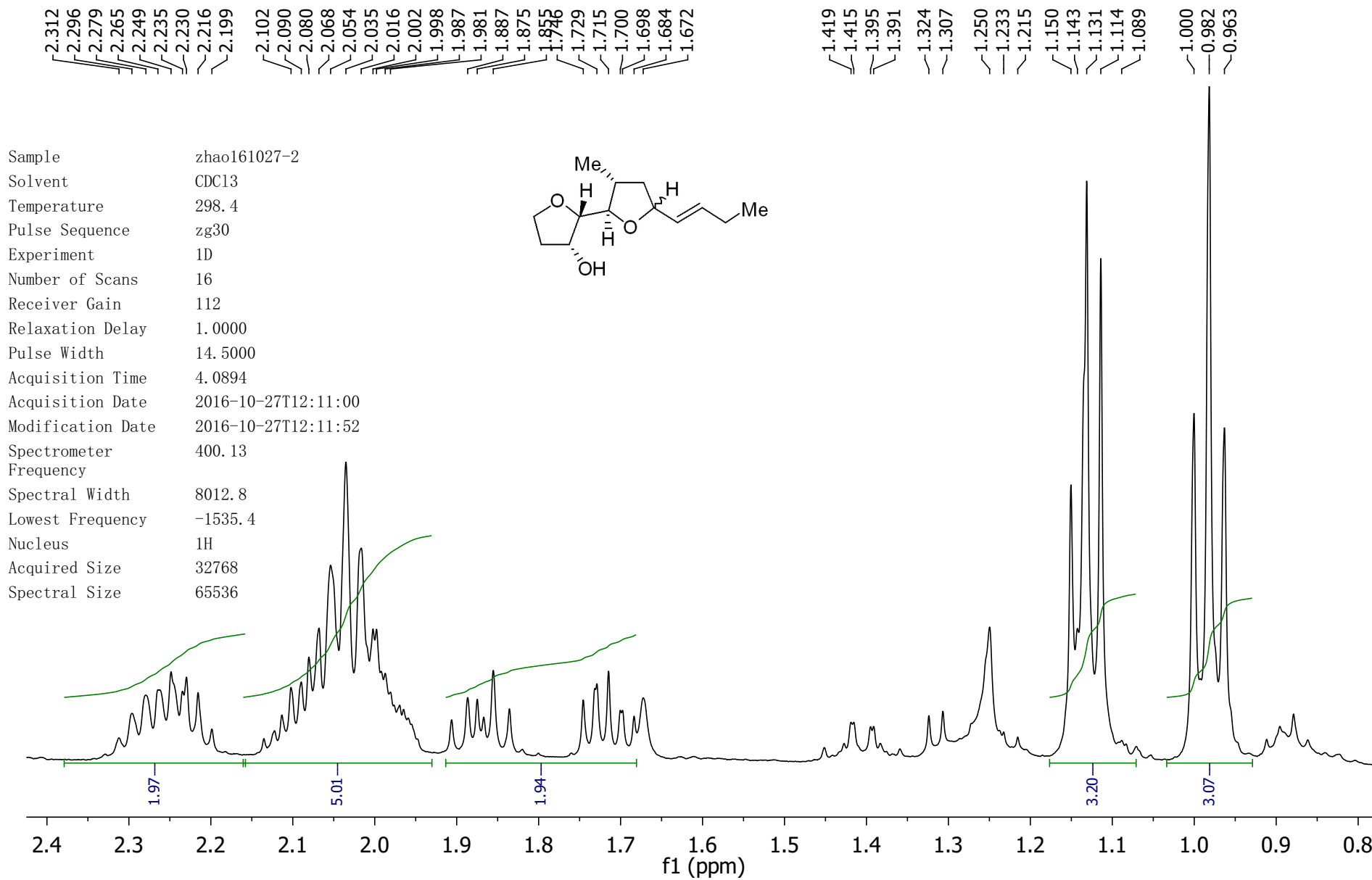
Sample zha0161027-2  
Solvent CDCl3  
Temperature 298.4  
Pulse Sequence zg30  
Experiment 1D  
Number of Scans 16  
Receiver Gain 112  
Relaxation Delay 1.0000  
Pulse Width 14.5000  
Acquisition Time 4.0894  
Acquisition Date 2016-10-27T12:11:00  
Modification Date 2016-10-27T12:11:52  
Spectrometer 400.13  
Frequency  
Spectral Width 8012.8  
Lowest Frequency -1535.4  
Nucleus 1H  
Acquired Size 32768  
Spectral Size 65536



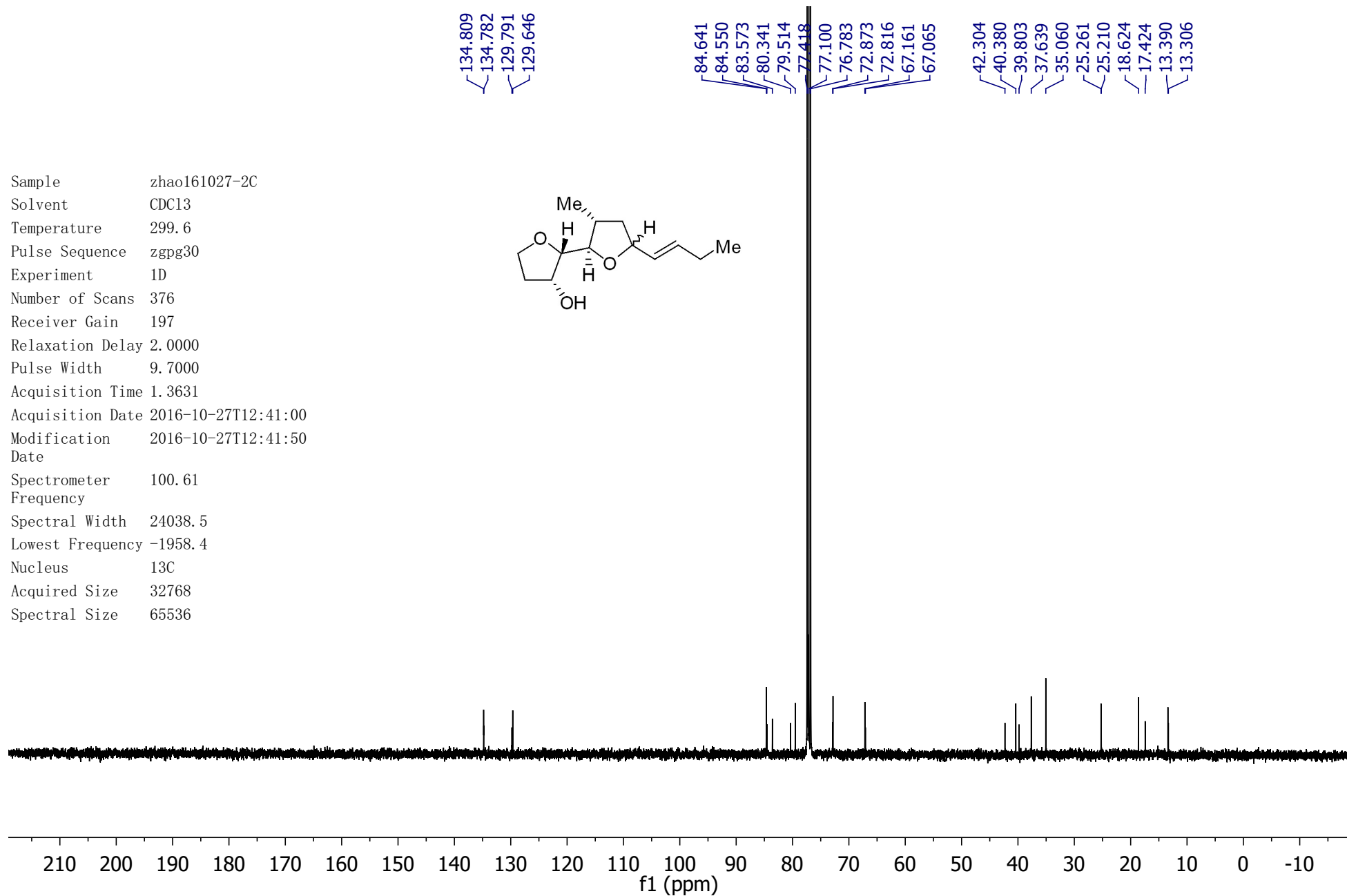
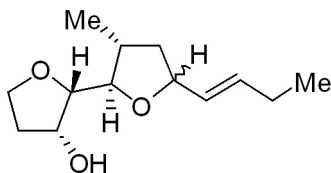
3.863  
3.853  
3.842  
3.833  
3.825  
3.822  
3.812  
3.805  
3.794  
3.776  
3.757  
3.722  
3.704  
3.689  
3.641  
3.632  
3.623  
3.614  
3.609  
3.600  
3.591  
3.581

Sample zhao161027-2  
Solvent CDCl3  
Temperature 298.4  
Pulse Sequence zg30  
Experiment 1D  
Number of Scans 16  
Receiver Gain 112  
Relaxation Delay 1.0000  
Pulse Width 14.5000  
Acquisition Time 4.0894  
Acquisition Date 2016-10-27T12:11:00  
Modification Date 2016-10-27T12:11:52  
Spectrometer 400.13  
Frequency  
Spectral Width 8012.8  
Lowest Frequency -1535.4  
Nucleus 1H  
Acquired Size 32768  
Spectral Size 65536

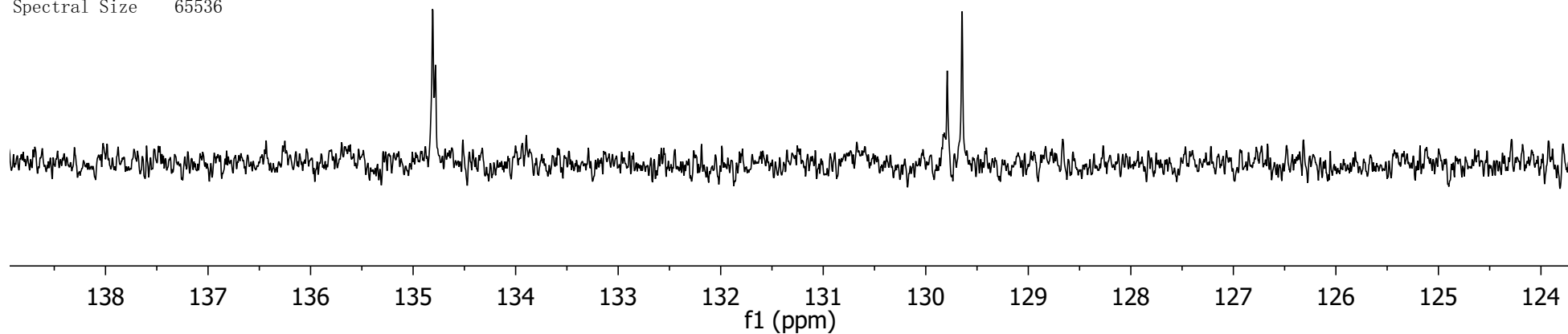
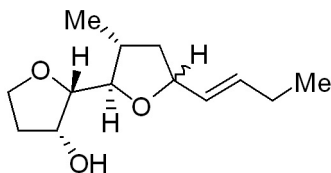




Sample zhao161027-2C  
Solvent CDCl3  
Temperature 299.6  
Pulse Sequence zgpg30  
Experiment 1D  
Number of Scans 376  
Receiver Gain 197  
Relaxation Delay 2.0000  
Pulse Width 9.7000  
Acquisition Time 1.3631  
Acquisition Date 2016-10-27T12:41:00  
Modification Date 2016-10-27T12:41:50  
Spectrometer 100.61  
Frequency  
Spectral Width 24038.5  
Lowest Frequency -1958.4  
Nucleus 13C  
Acquired Size 32768  
Spectral Size 65536



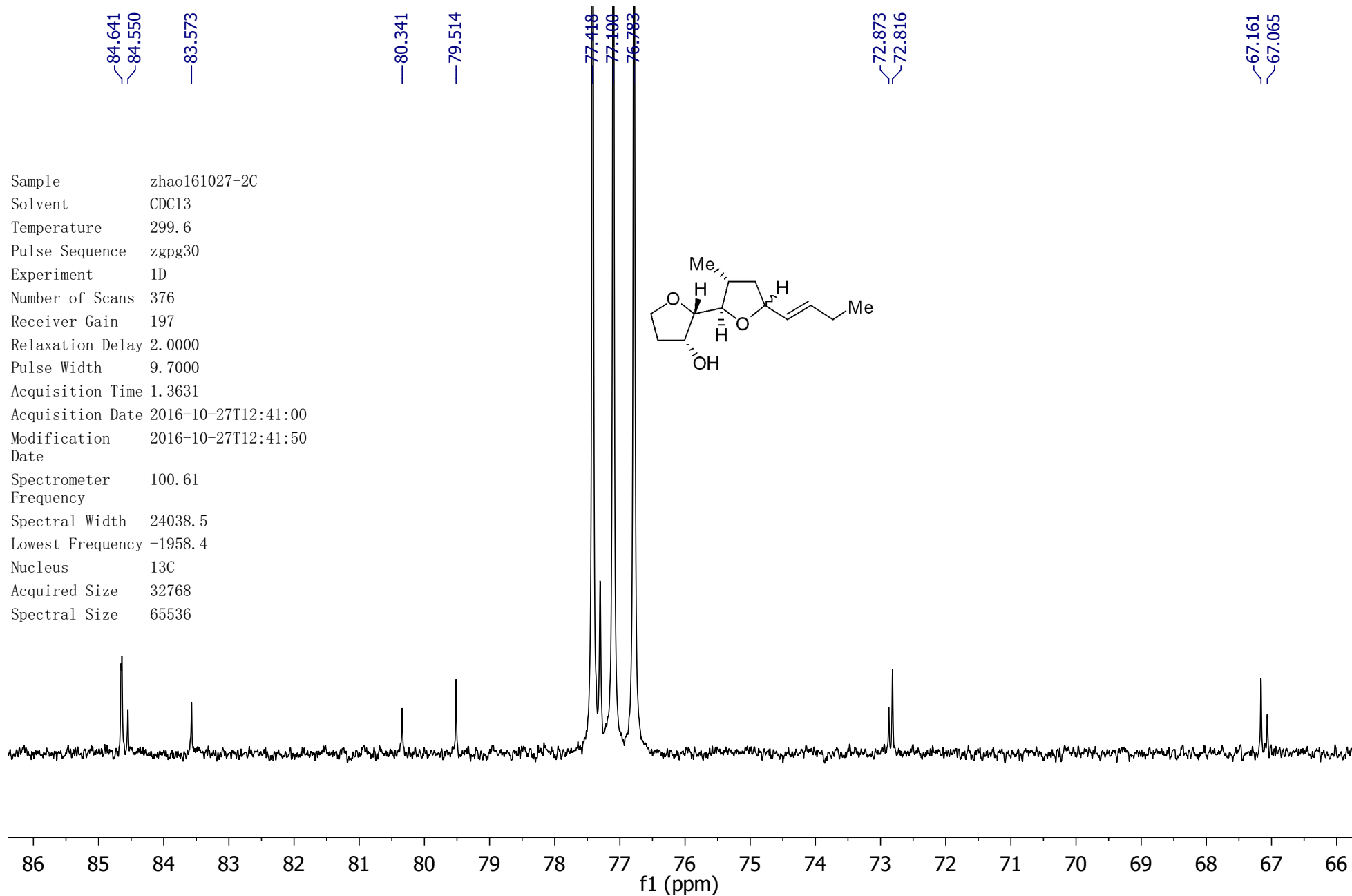
Sample zhao161027-2C  
Solvent CDCl3  
Temperature 299.6  
Pulse Sequence zgpg30  
Experiment 1D  
Number of Scans 376  
Receiver Gain 197  
Relaxation Delay 2.0000  
Pulse Width 9.7000  
Acquisition Time 1.3631  
Acquisition Date 2016-10-27T12:41:00  
Modification 2016-10-27T12:41:50  
Date  
Spectrometer 100.61  
Frequency  
Spectral Width 24038.5  
Lowest Frequency -1958.4  
Nucleus 13C  
Acquired Size 32768  
Spectral Size 65536



134.809  
134.782

129.791  
129.646





—42.304

—40.380  
—39.803

—37.639

—35.060

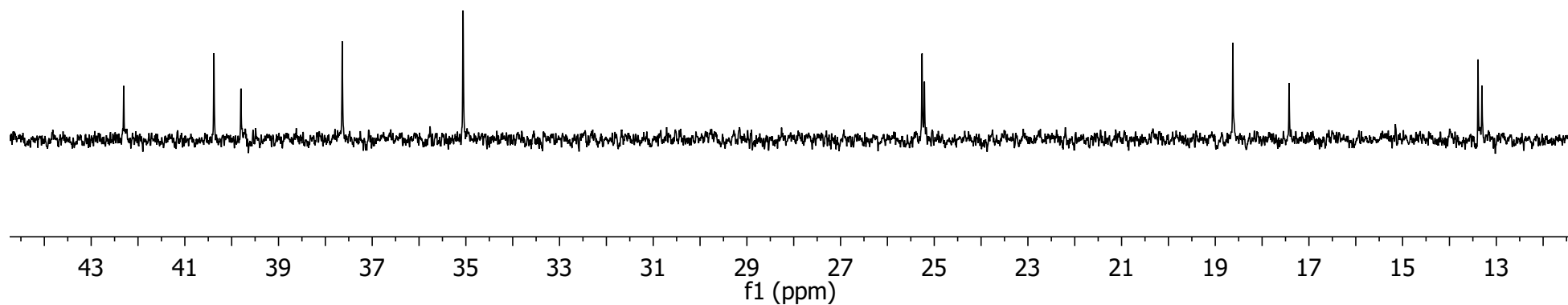
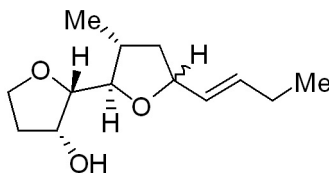
—25.261  
—25.210

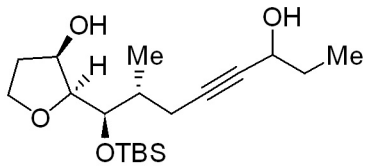
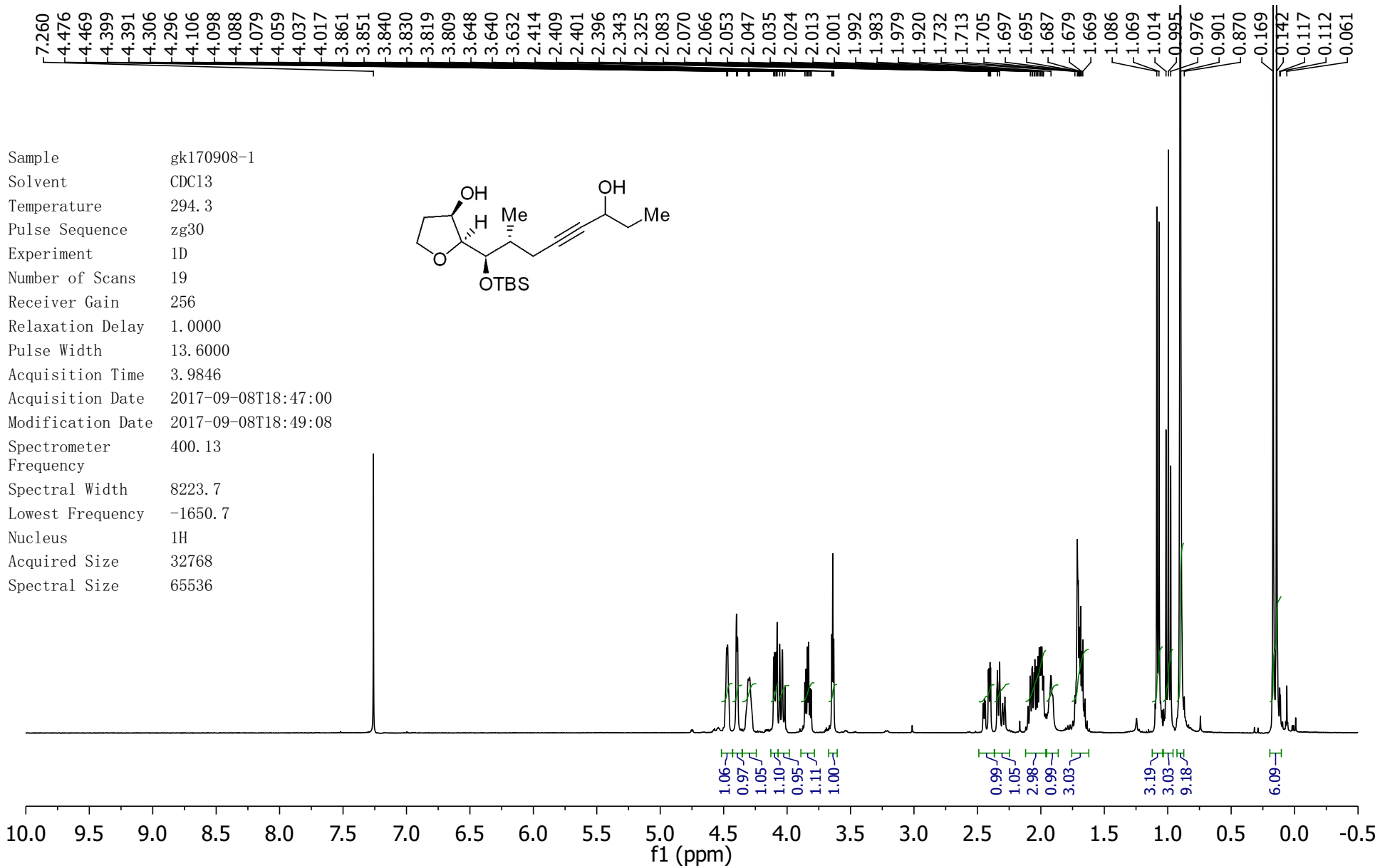
—18.624

—17.424

—13.390  
—13.306

Sample zhao161027-2C  
Solvent CDCl3  
Temperature 299.6  
Pulse Sequence zgpg30  
Experiment 1D  
Number of Scans 376  
Receiver Gain 197  
Relaxation Delay 2.0000  
Pulse Width 9.7000  
Acquisition Time 1.3631  
Acquisition Date 2016-10-27T12:41:00  
Modification 2016-10-27T12:41:50  
Date  
Spectrometer 100.61  
Frequency  
Spectral Width 24038.5  
Lowest Frequency -1958.4  
Nucleus 13C  
Acquired Size 32768  
Spectral Size 65536





S131

4.476  
4.469

4.399  
4.391

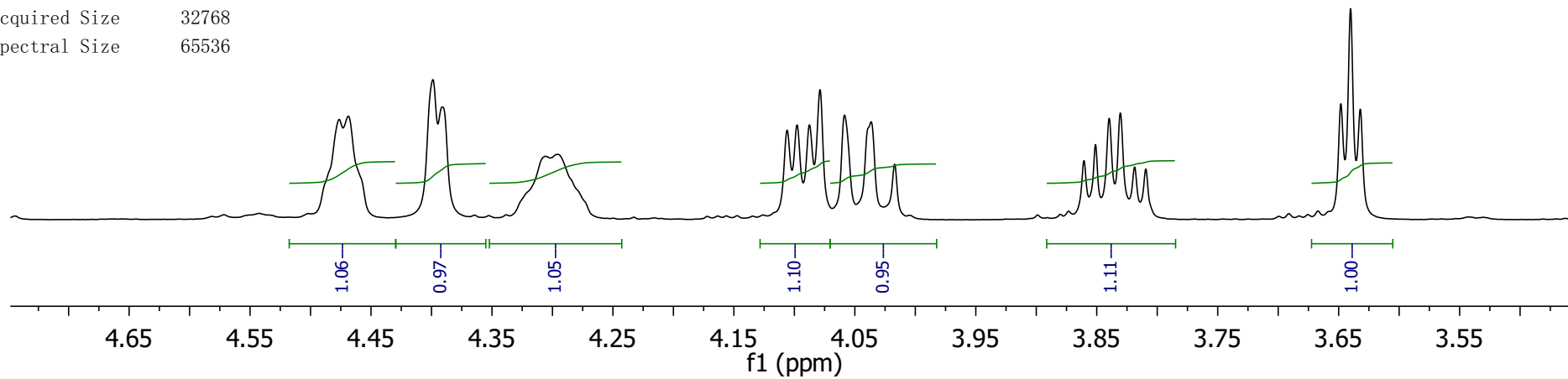
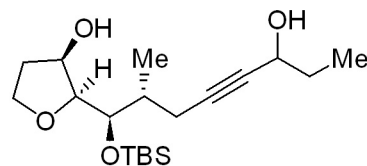
4.306  
4.296

4.106  
4.098  
4.088  
4.079  
4.059  
4.037  
4.017

3.861  
3.851  
3.840  
3.830  
3.819  
3.809

3.648  
3.640  
3.632

Sample gk170908-1  
Solvent CDCl3  
Temperature 294.3  
Pulse Sequence zg30  
Experiment 1D  
Number of Scans 19  
Receiver Gain 256  
Relaxation Delay 1.0000  
Pulse Width 13.6000  
Acquisition Time 3.9846  
Acquisition Date 2017-09-08T18:47:00  
Modification Date 2017-09-08T18:49:08  
Spectrometer 400.13  
Frequency  
Spectral Width 8223.7  
Lowest Frequency -1650.7  
Nucleus 1H  
Acquired Size 32768  
Spectral Size 65536

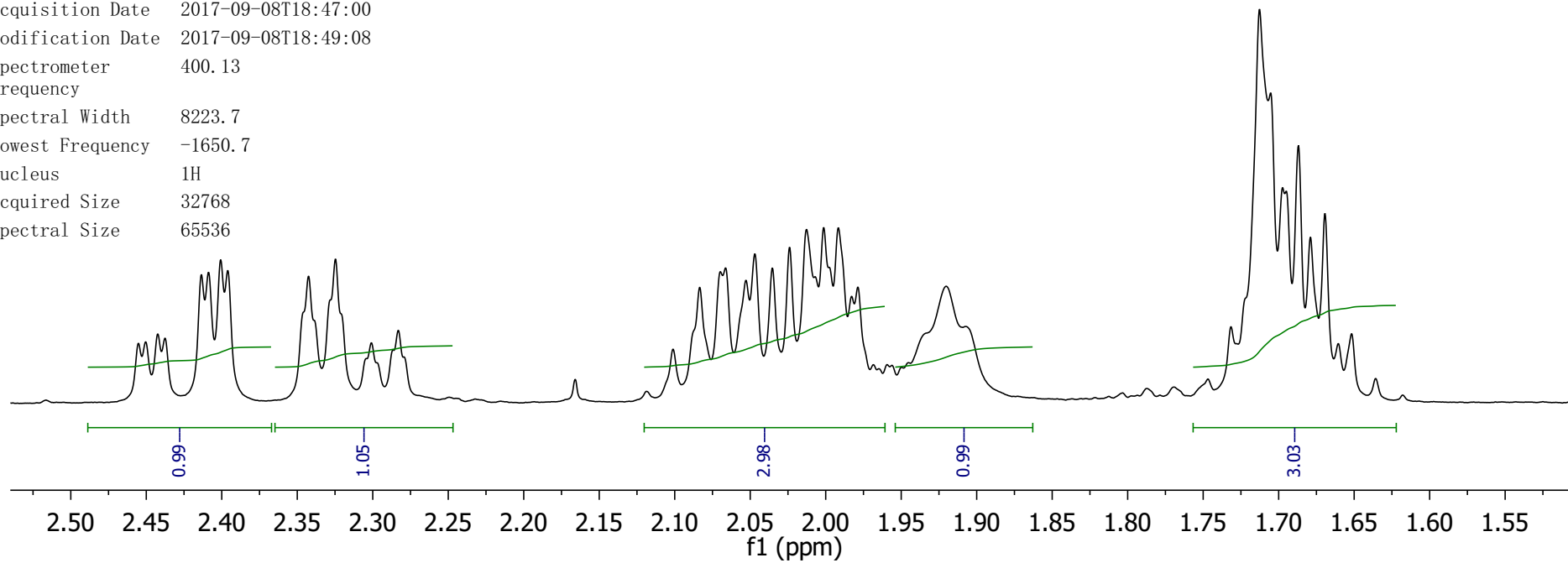
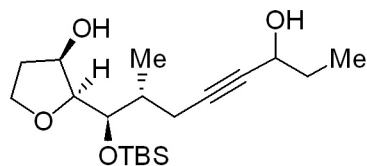


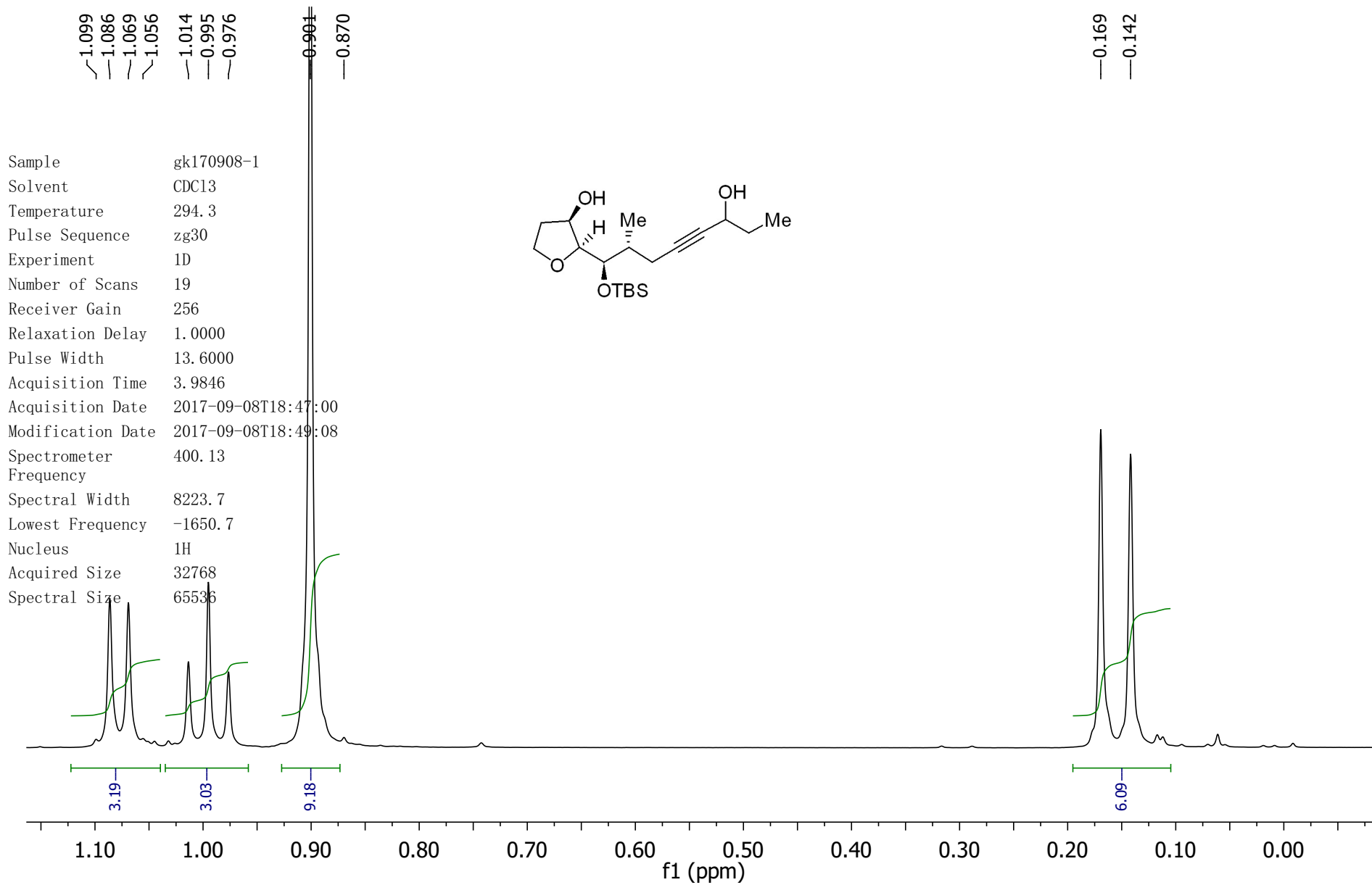
2.455  
2.450  
2.442  
2.438  
2.414  
2.409  
2.401  
2.396  
2.343  
2.325  
2.301  
2.283

2.101  
2.083  
2.070  
2.066  
2.053  
2.047  
2.035  
2.024  
2.013  
2.001  
1.992  
1.983  
1.979  
1.920

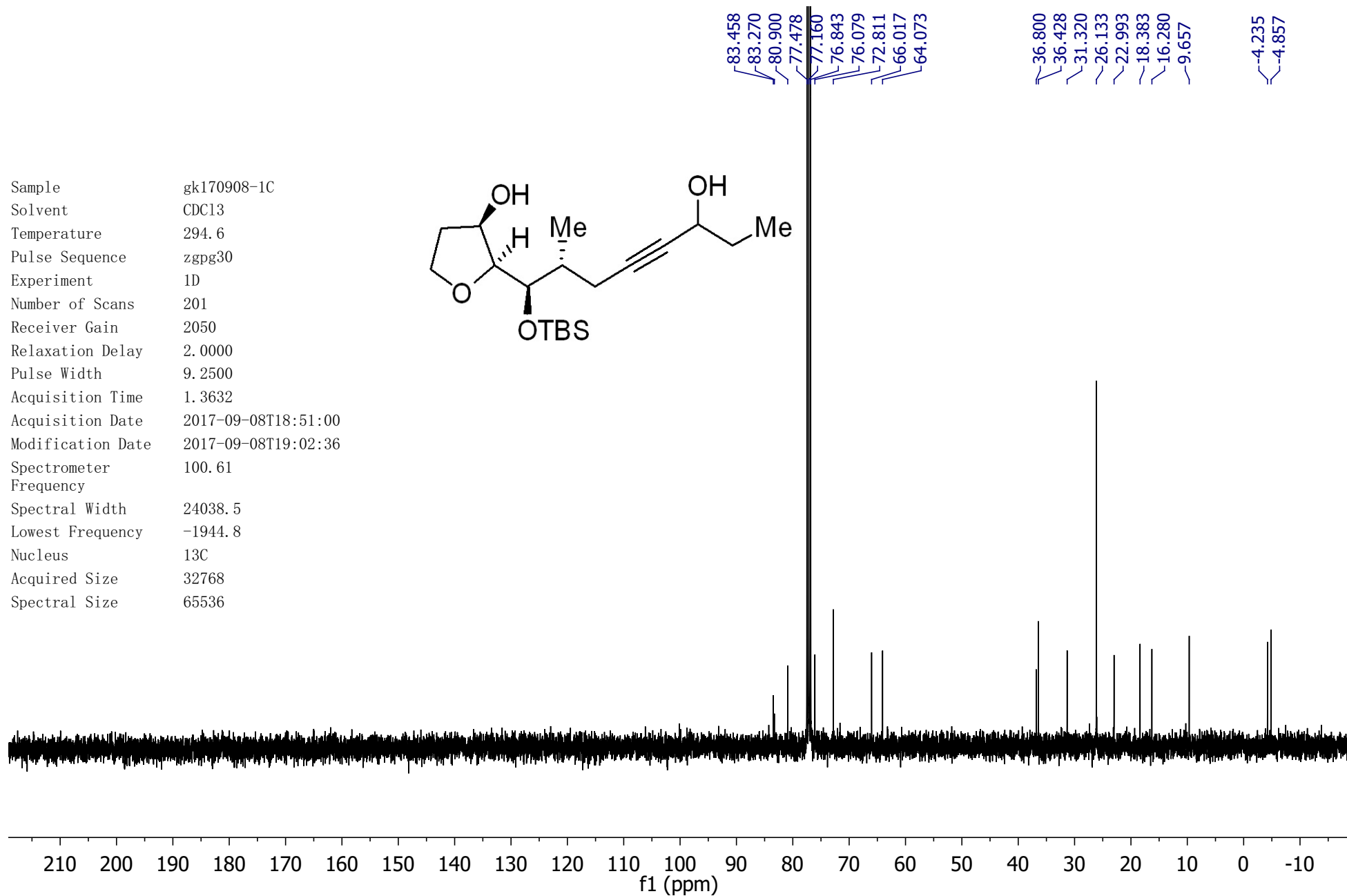
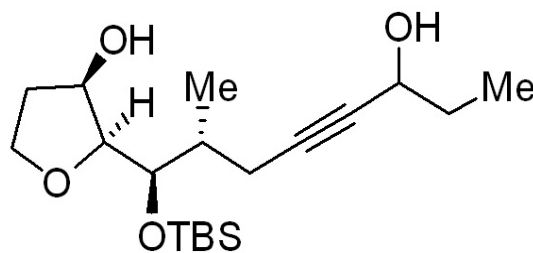
1.732  
1.713  
1.705  
1.697  
1.695  
1.687  
1.679  
1.669  
1.661  
1.652

Sample gk170908-1  
Solvent CDCl3  
Temperature 294.3  
Pulse Sequence zg30  
Experiment 1D  
Number of Scans 19  
Receiver Gain 256  
Relaxation Delay 1.0000  
Pulse Width 13.6000  
Acquisition Time 3.9846  
Acquisition Date 2017-09-08T18:47:00  
Modification Date 2017-09-08T18:49:08  
Spectrometer 400.13  
Frequency  
Spectral Width 8223.7  
Lowest Frequency -1650.7  
Nucleus 1H  
Acquired Size 32768  
Spectral Size 65536

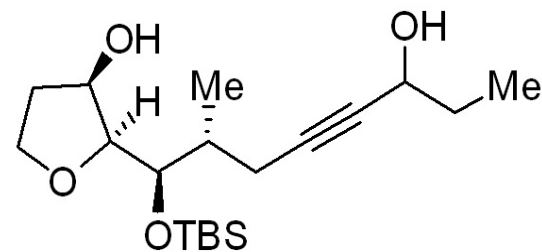
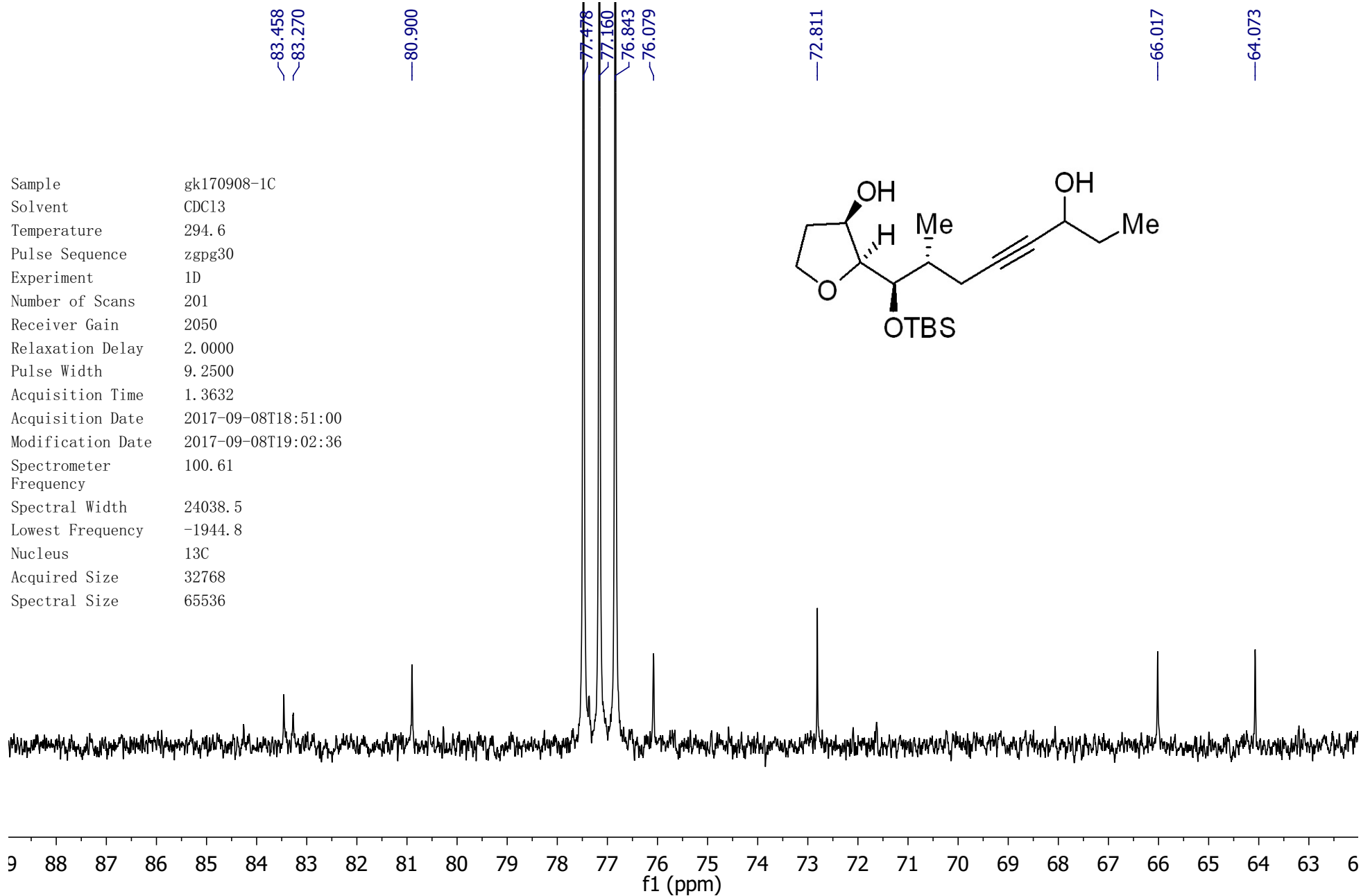




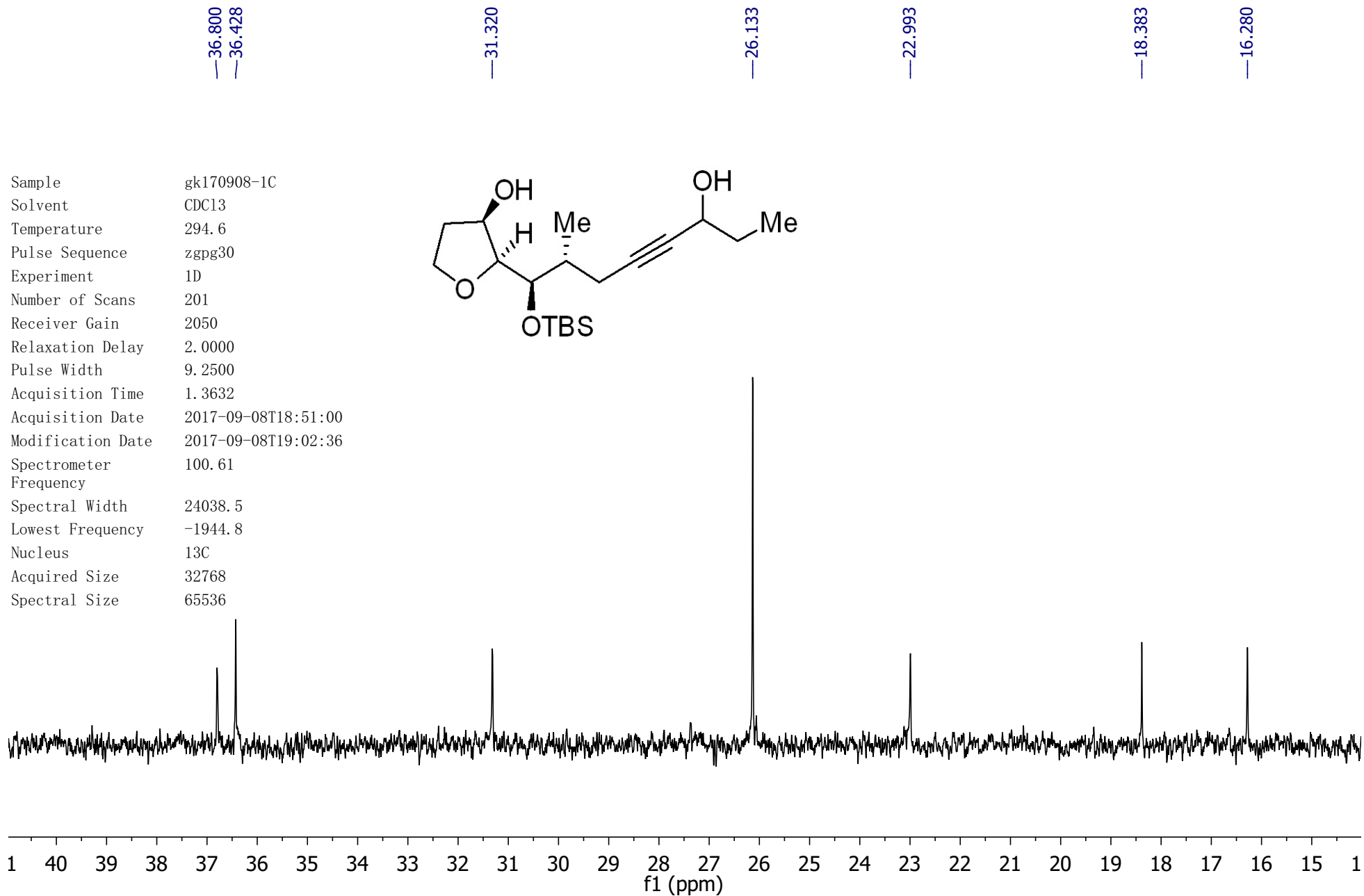
Sample gk170908-1C  
Solvent CDCl3  
Temperature 294.6  
Pulse Sequence zgpg30  
Experiment 1D  
Number of Scans 201  
Receiver Gain 2050  
Relaxation Delay 2.0000  
Pulse Width 9.2500  
Acquisition Time 1.3632  
Acquisition Date 2017-09-08T18:51:00  
Modification Date 2017-09-08T19:02:36  
Spectrometer 100.61  
Frequency  
Spectral Width 24038.5  
Lowest Frequency -1944.8  
Nucleus 13C  
Acquired Size 32768  
Spectral Size 65536

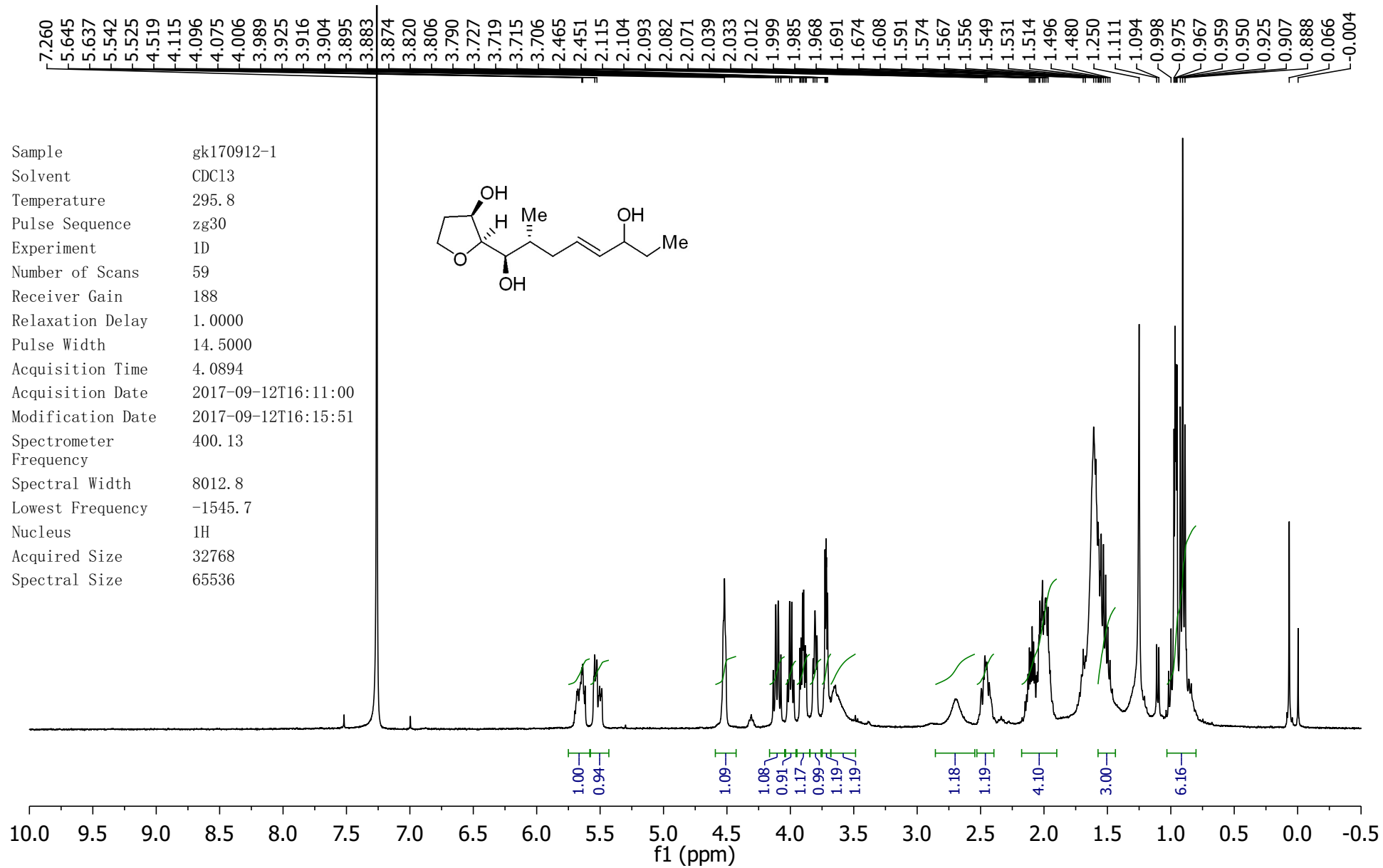


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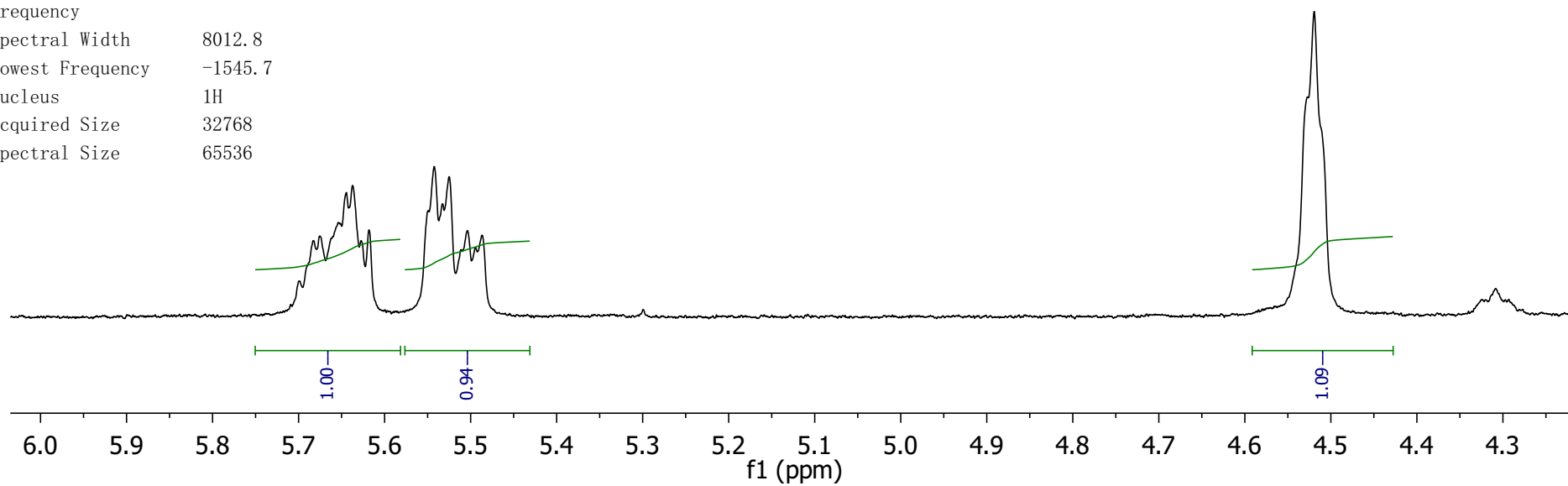
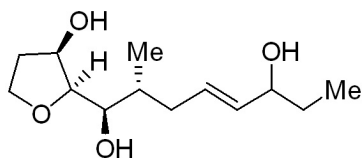




5.699  
5.683  
5.675  
5.645  
5.637  
5.627  
5.618  
5.542  
5.525  
5.504  
5.486

—4.519

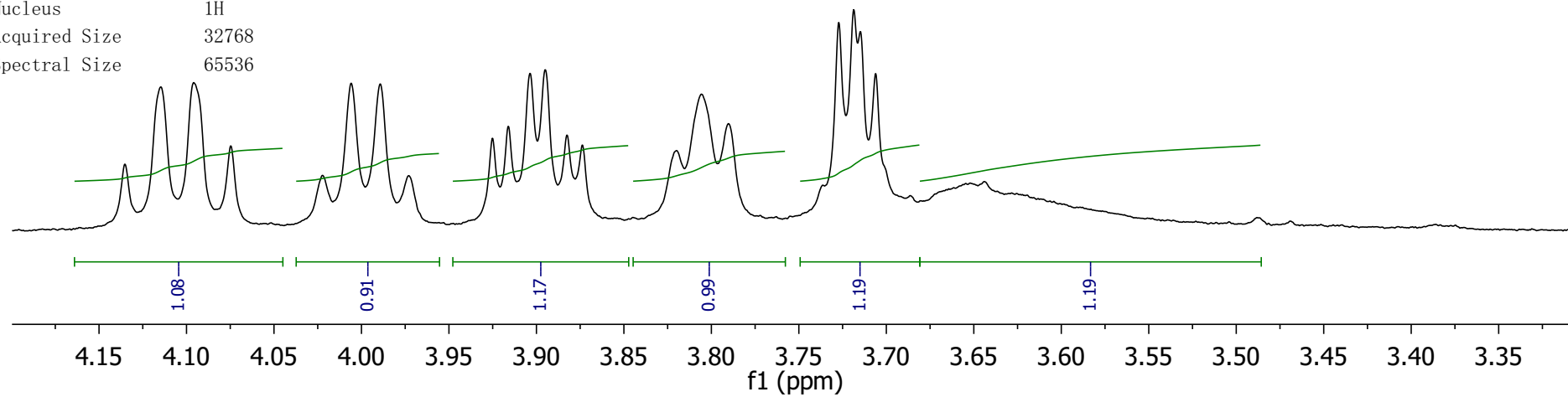
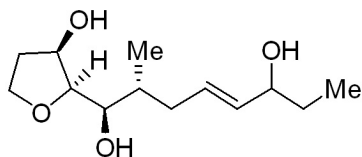
Sample gk170912-1  
Solvent CDCl3  
Temperature 295.8  
Pulse Sequence zg30  
Experiment 1D  
Number of Scans 59  
Receiver Gain 188  
Relaxation Delay 1.0000  
Pulse Width 14.5000  
Acquisition Time 4.0894  
Acquisition Date 2017-09-12T16:11:00  
Modification Date 2017-09-12T16:15:51  
Spectrometer 400.13  
Frequency  
Spectral Width 8012.8  
Lowest Frequency -1545.7  
Nucleus 1H  
Acquired Size 32768  
Spectral Size 65536

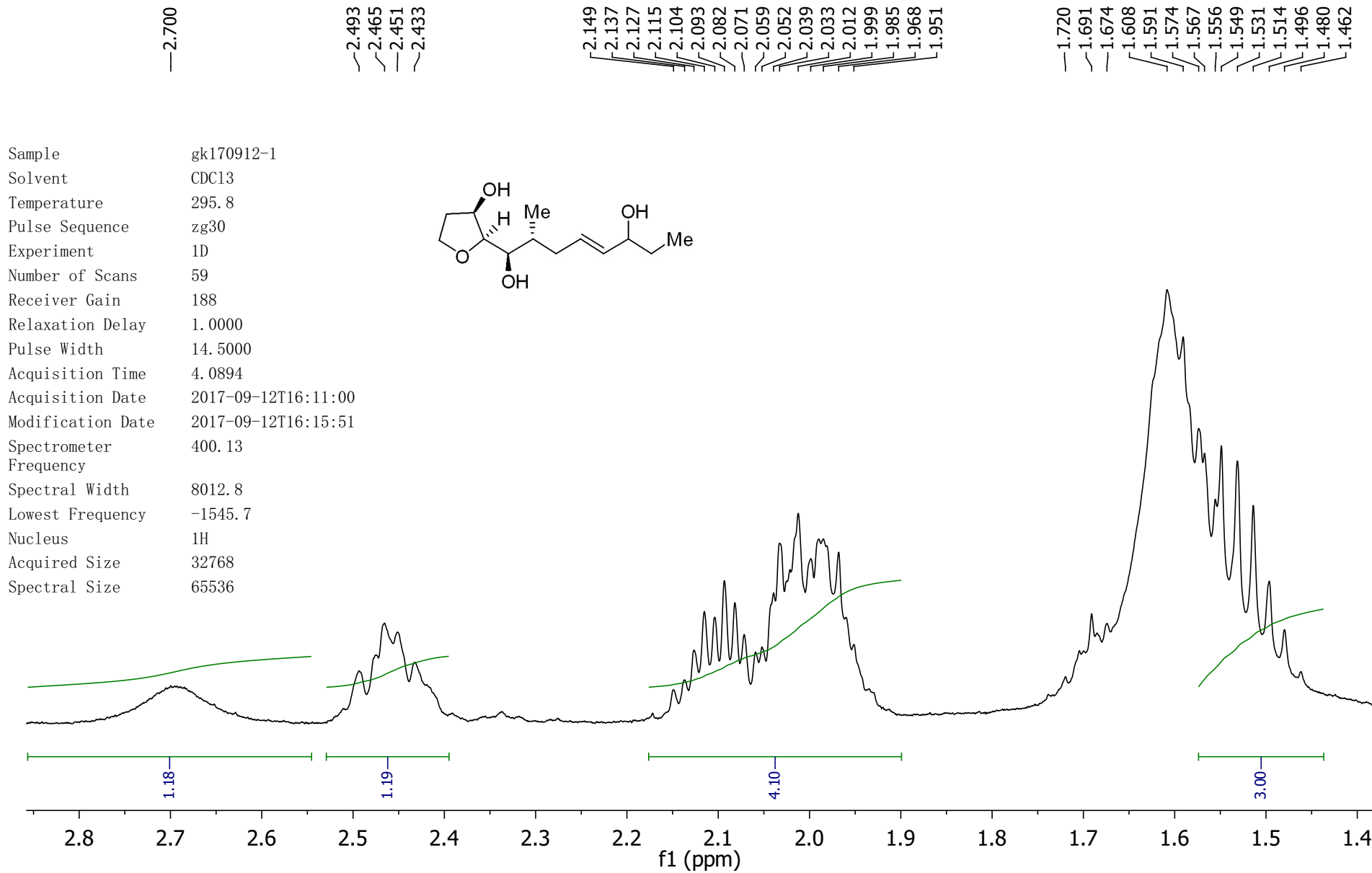


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4.135  
 4.115  
 4.096  
 4.075  
 4.022  
 4.006  
 3.989  
 3.973  
 3.925  
 3.916  
 3.904  
 3.895  
 3.883  
 3.874  
 3.820  
 3.806  
 3.790  
 3.727  
 3.719  
 3.715  
 3.706  
 3.644

Sample gk170912-1  
 Solvent CDC13  
 Temperature 295.8  
 Pulse Sequence zg30  
 Experiment 1D  
 Number of Scans 59  
 Receiver Gain 188  
 Relaxation Delay 1.0000  
 Pulse Width 14.5000  
 Acquisition Time 4.0894  
 Acquisition Date 2017-09-12T16:11:00  
 Modification Date 2017-09-12T16:15:51  
 Spectrometer 400.13  
 Frequency  
 Spectral Width 8012.8  
 Lowest Frequency -1545.7  
 Nucleus 1H  
 Acquired Size 32768  
 Spectral Size 65536

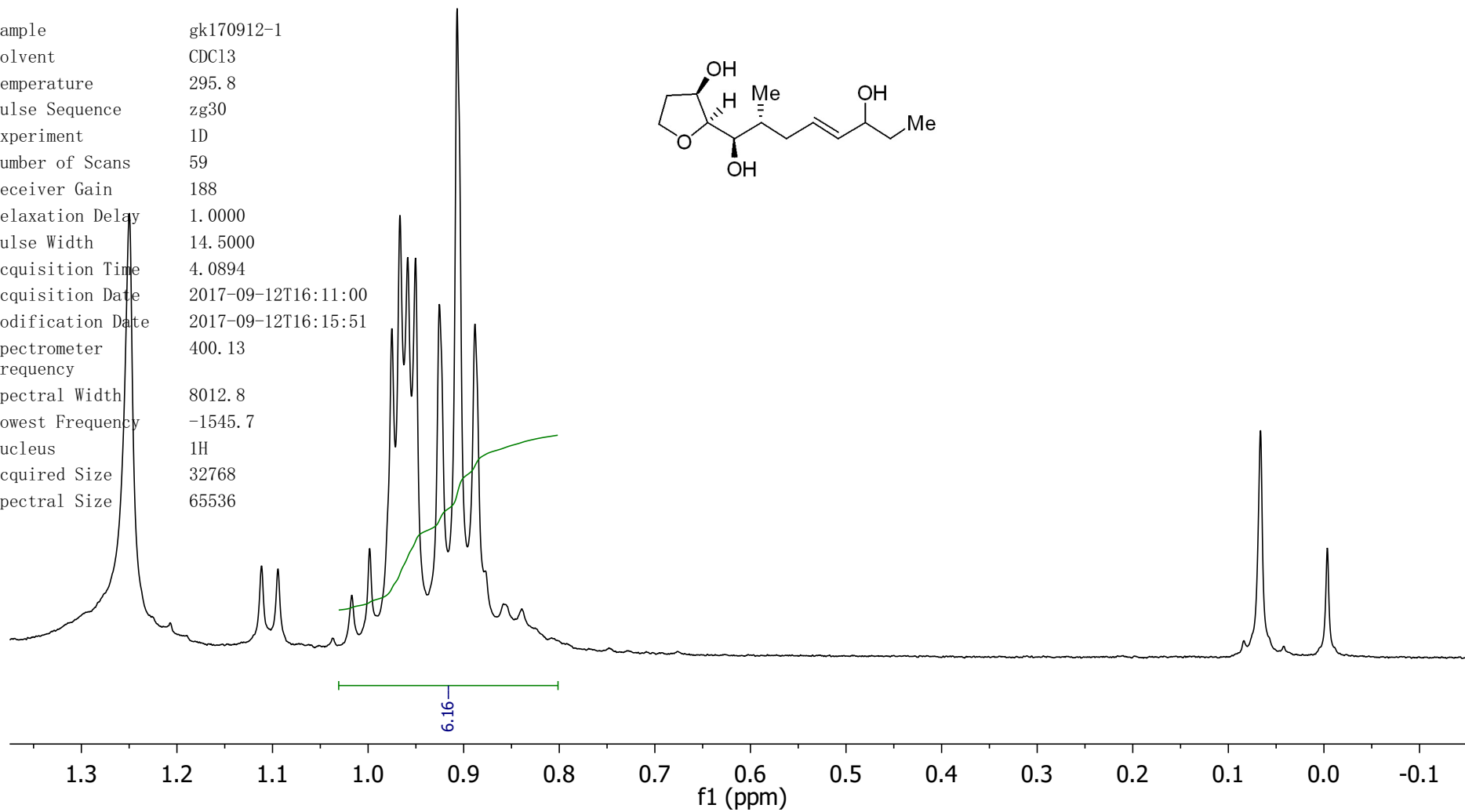
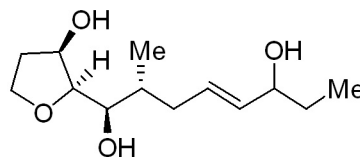




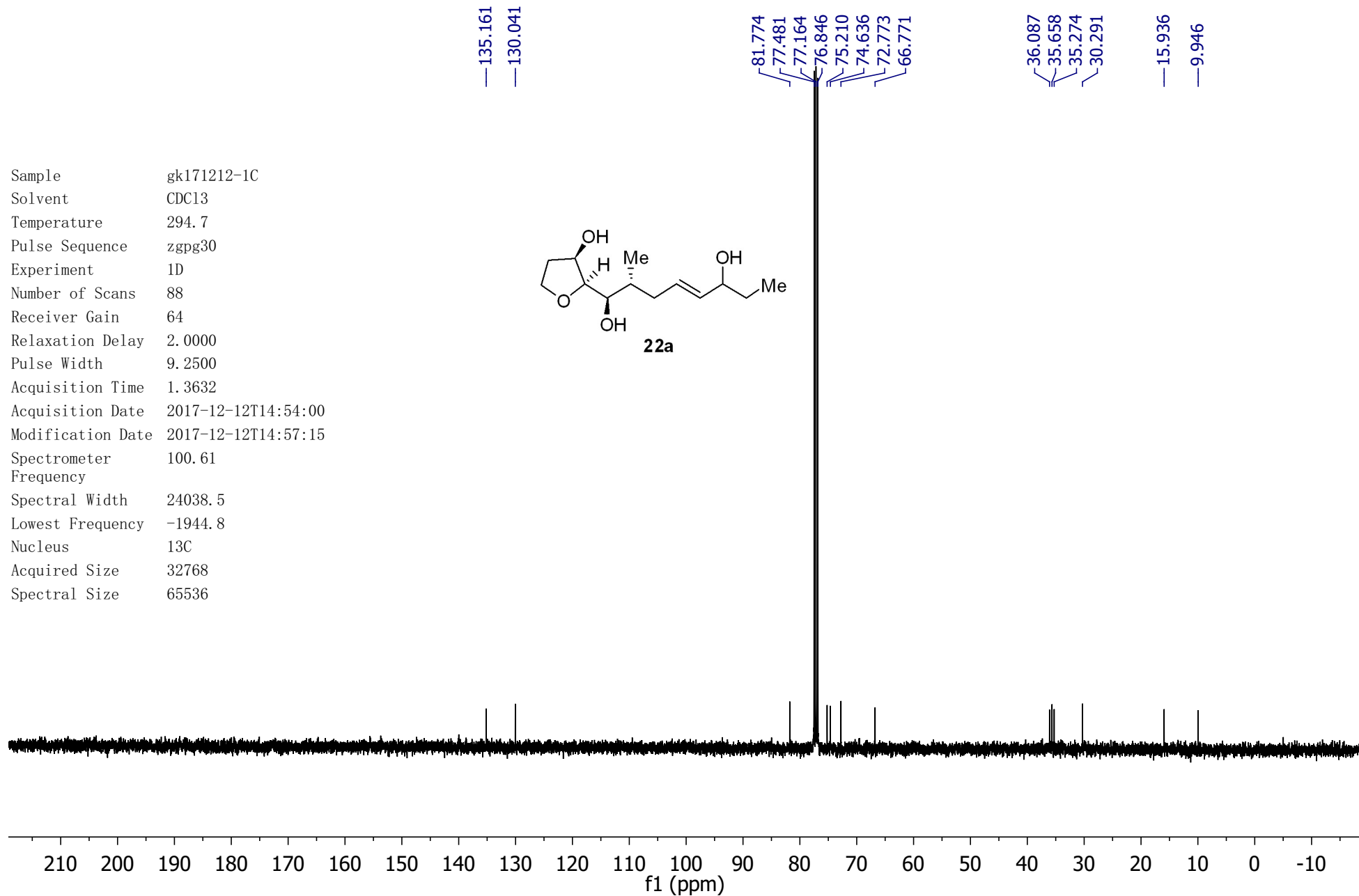
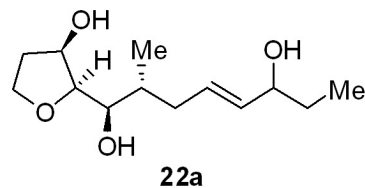
— 1.250  
 — 1.207  
 — 1.111  
 — 1.094  
 — 1.017  
 — 0.998  
 — 0.975  
 — 0.967  
 — 0.959  
 — 0.950  
 — 0.925  
 — 0.907  
 — 0.888  
 — 0.858  
 — 0.839

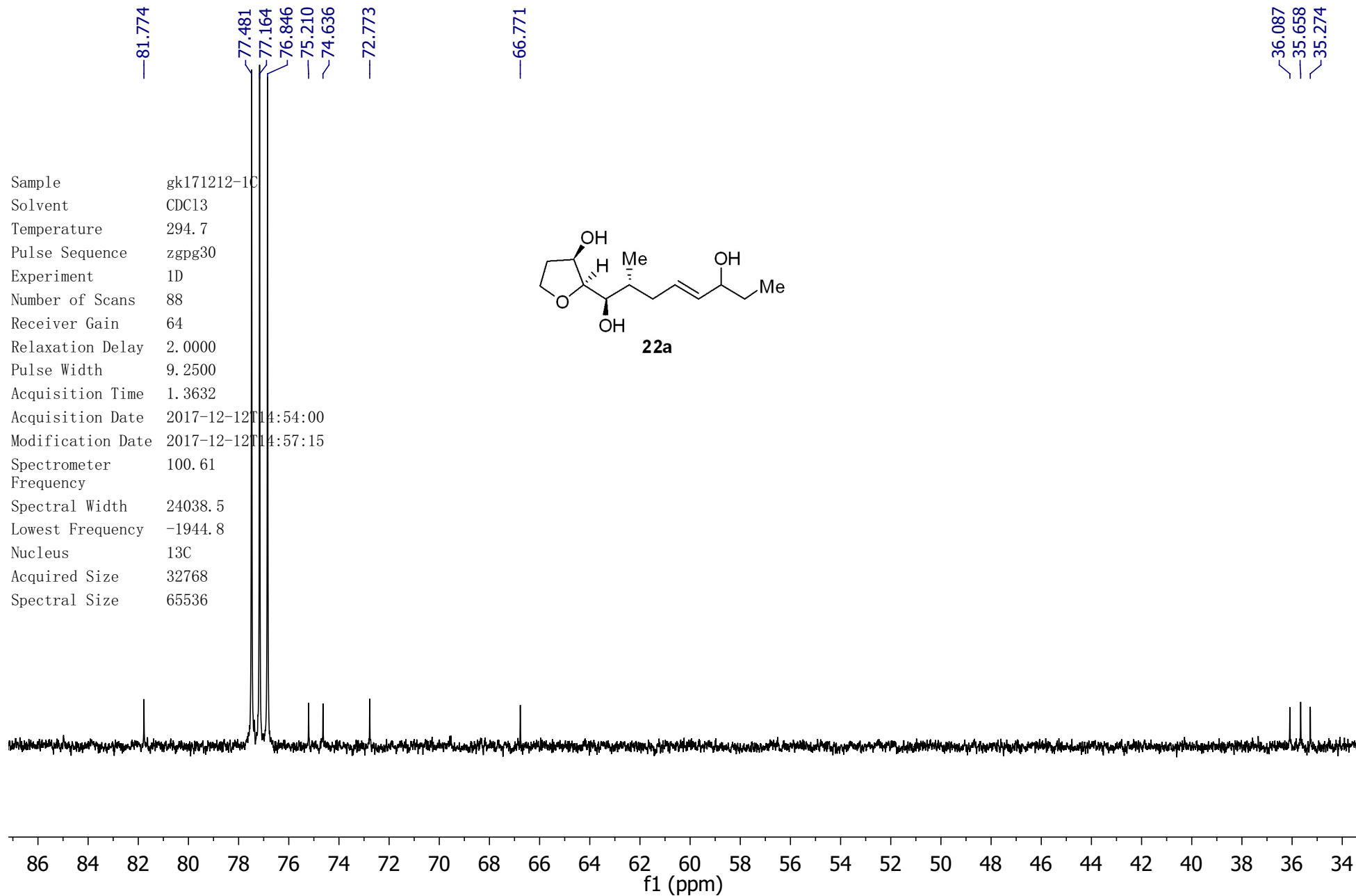
— 0.066  
 — 0.004

Sample gk170912-1  
 Solvent CDC13  
 Temperature 295.8  
 Pulse Sequence zg30  
 Experiment 1D  
 Number of Scans 59  
 Receiver Gain 188  
 Relaxation Delay 1.0000  
 Pulse Width 14.5000  
 Acquisition Time 4.0894  
 Acquisition Date 2017-09-12T16:11:00  
 Modification Date 2017-09-12T16:15:51  
 Spectrometer 400.13  
 Frequency  
 Spectral Width 8012.8  
 Lowest Frequency -1545.7  
 Nucleus 1H  
 Acquired Size 32768  
 Spectral Size 65536



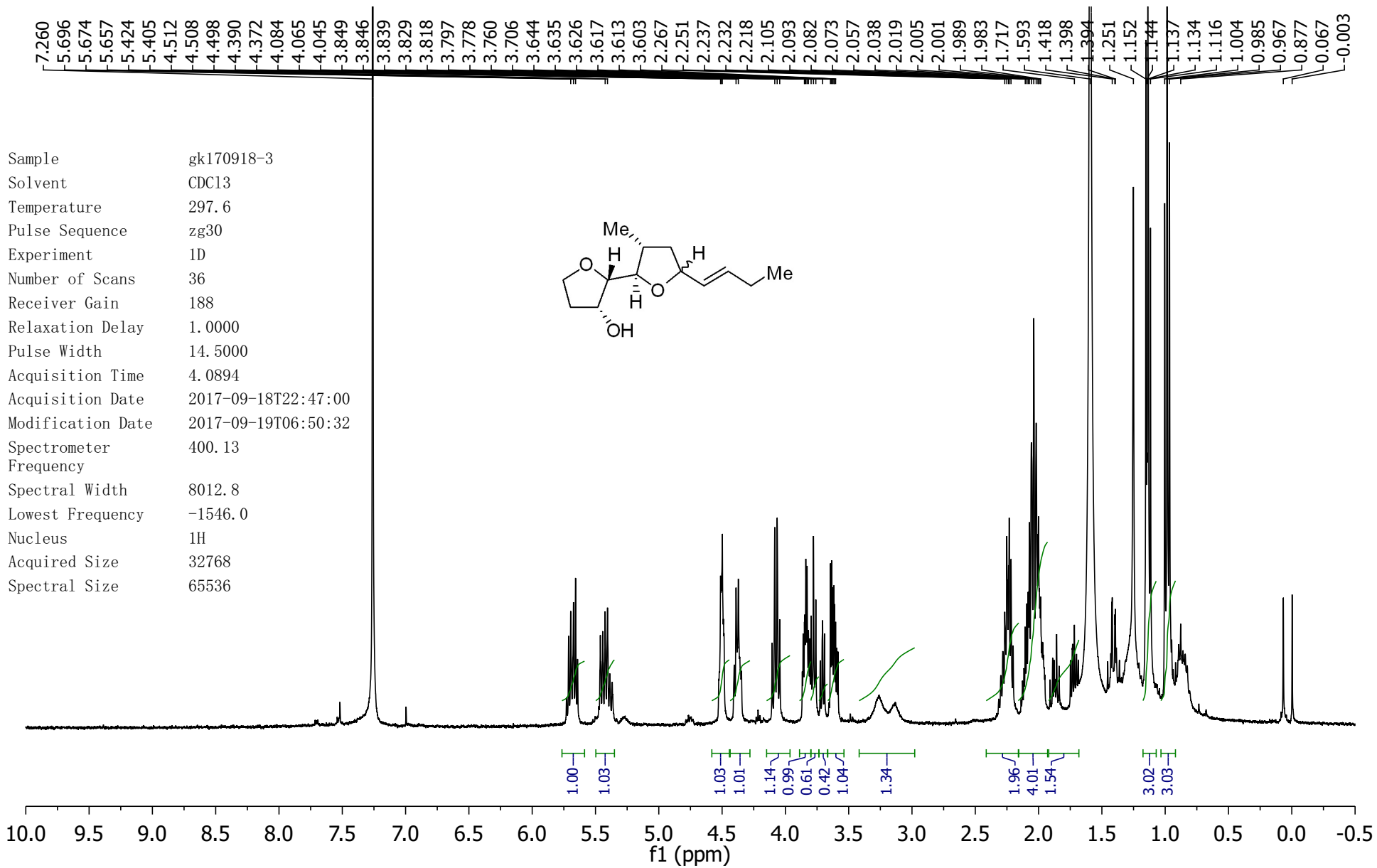
Sample gk171212-1C  
Solvent CDCl3  
Temperature 294.7  
Pulse Sequence zgpg30  
Experiment 1D  
Number of Scans 88  
Receiver Gain 64  
Relaxation Delay 2.0000  
Pulse Width 9.2500  
Acquisition Time 1.3632  
Acquisition Date 2017-12-12T14:54:00  
Modification Date 2017-12-12T14:57:15  
Spectrometer 100.61  
Frequency  
Spectral Width 24038.5  
Lowest Frequency -1944.8  
Nucleus 13C  
Acquired Size 32768  
Spectral Size 65536





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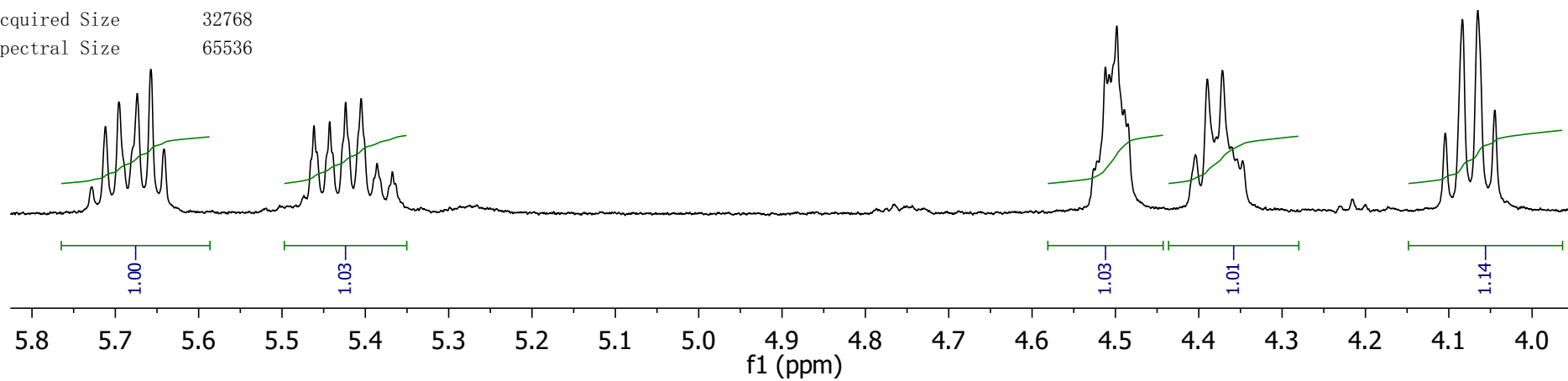
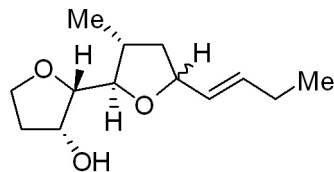
5.728  
5.712  
5.696  
5.674  
5.657  
5.641

5.462  
5.443  
5.424  
5.405  
5.386  
5.368

4.522  
4.512  
4.508  
4.498  
4.489  
4.404  
4.390  
4.372  
4.360  
4.354  
4.347

4.104  
4.084  
4.065  
4.045

Sample gk170918-3  
Solvent CDCl3  
Temperature 297.6  
Pulse Sequence zg30  
Experiment 1D  
Number of Scans 36  
Receiver Gain 188  
Relaxation Delay 1.0000  
Pulse Width 14.5000  
Acquisition Time 4.0894  
Acquisition Date 2017-09-18T22:47:00  
Modification Date 2017-09-19T06:50:32  
Spectrometer 400.13  
Frequency  
Spectral Width 8012.8  
Lowest Frequency -1546.0  
Nucleus 1H  
Acquired Size 32768  
Spectral Size 65536

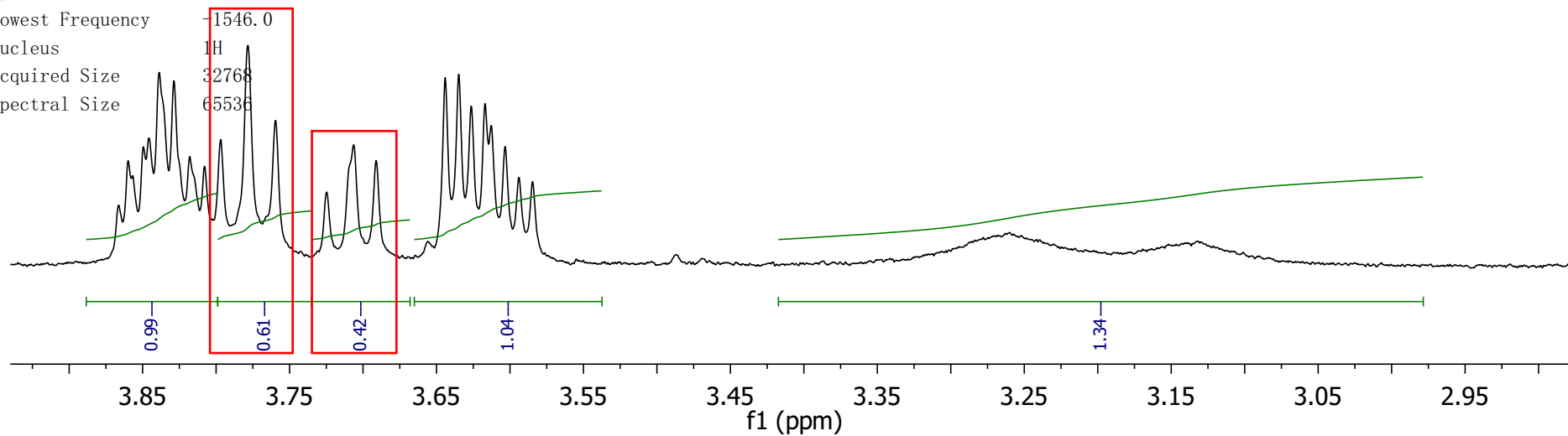
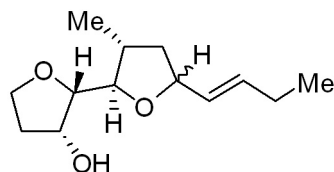


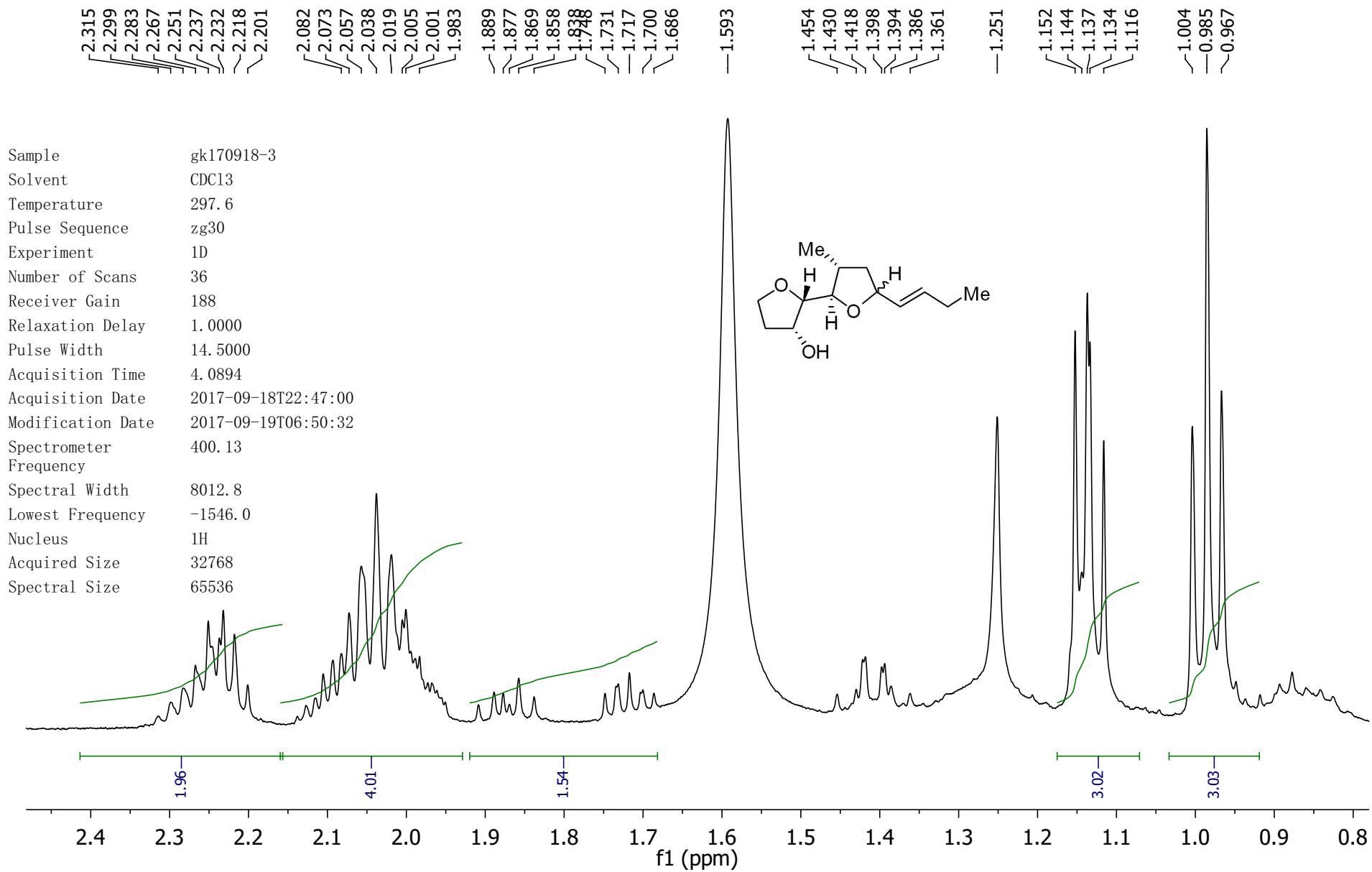
3.866  
3.860  
3.849  
3.846  
3.839  
3.829  
3.818  
3.808  
3.797  
3.778  
3.760  
3.725  
3.706  
3.691  
3.644  
3.635  
3.626  
3.617  
3.613  
3.603  
3.594  
3.585

—3.260

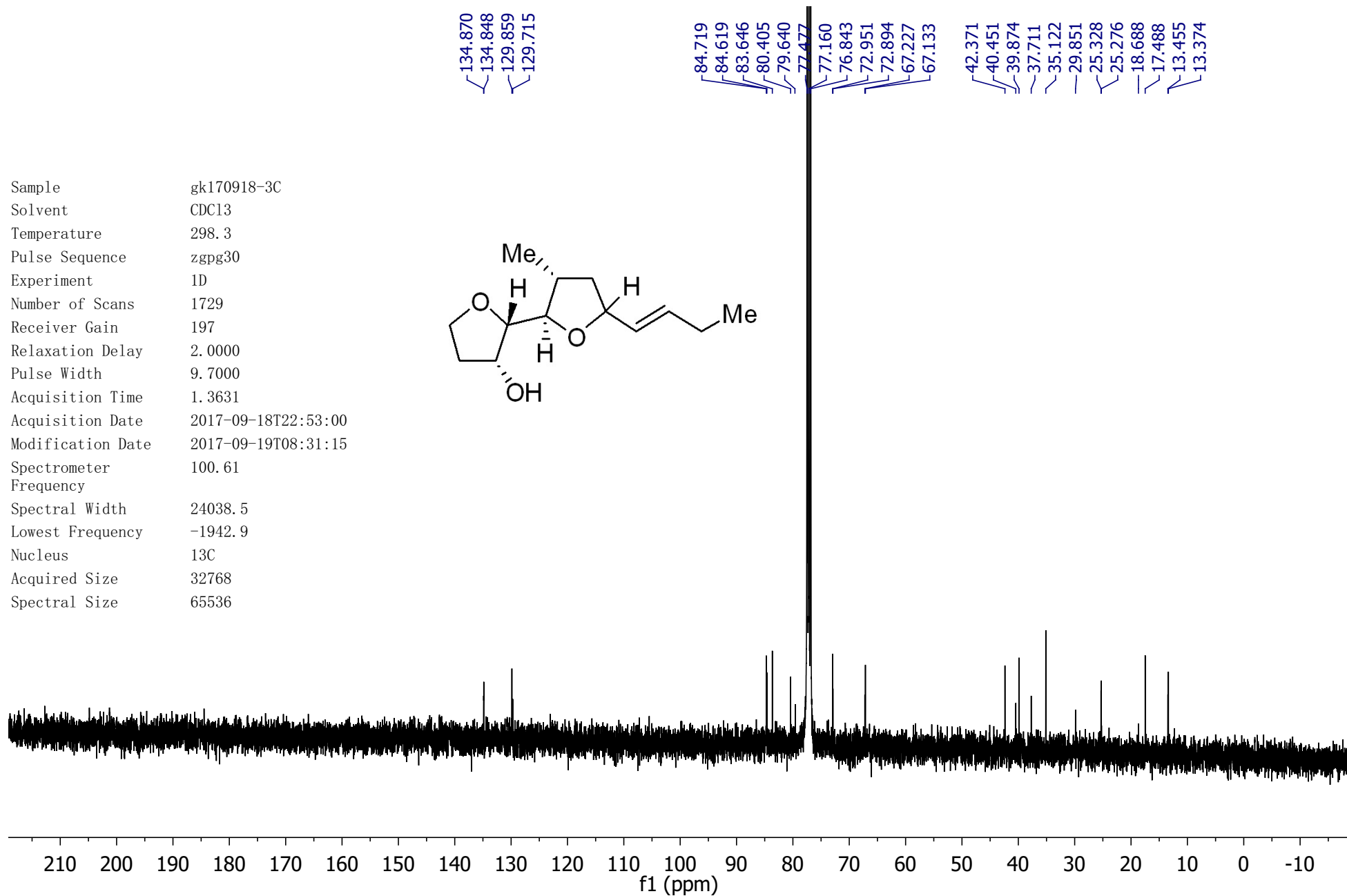
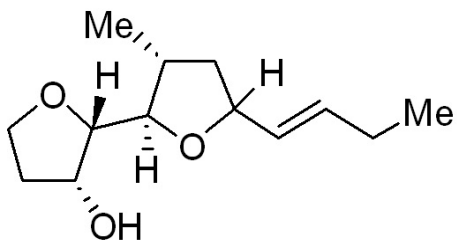
—3.132

Sample gk170918-3  
Solvent CDCl3  
Temperature 297.6  
Pulse Sequence zg30  
Experiment 1D  
Number of Scans 36  
Receiver Gain 188  
Relaxation Delay 1.0000  
Pulse Width 14.5000  
Acquisition Time 4.0894  
Acquisition Date 2017-09-18T22:47:00  
Modification Date 2017-09-19T06:50:32  
Spectrometer 400.13  
Frequency  
Spectral Width 8012.8  
Lowest Frequency 1546.0  
Nucleus 1H  
Acquired Size 32768  
Spectral Size 65536

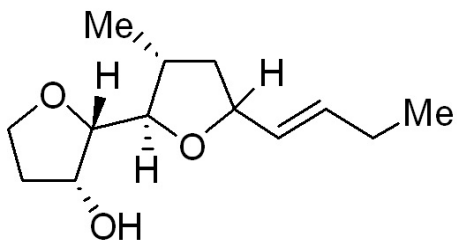




Sample gk170918-3C  
Solvent CDC13  
Temperature 298.3  
Pulse Sequence zgpg30  
Experiment 1D  
Number of Scans 1729  
Receiver Gain 197  
Relaxation Delay 2.0000  
Pulse Width 9.7000  
Acquisition Time 1.3631  
Acquisition Date 2017-09-18T22:53:00  
Modification Date 2017-09-19T08:31:15  
Spectrometer 100.61  
Frequency  
Spectral Width 24038.5  
Lowest Frequency -1942.9  
Nucleus 13C  
Acquired Size 32768  
Spectral Size 65536

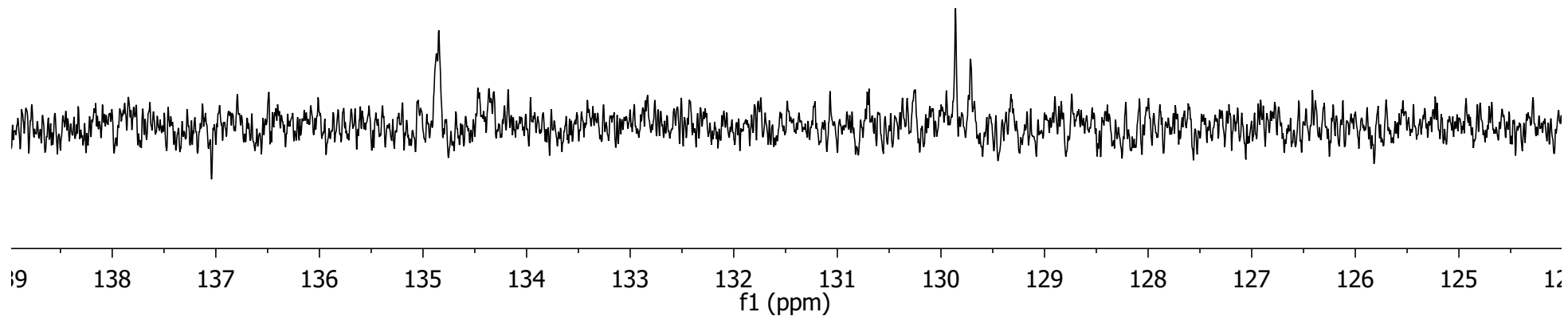


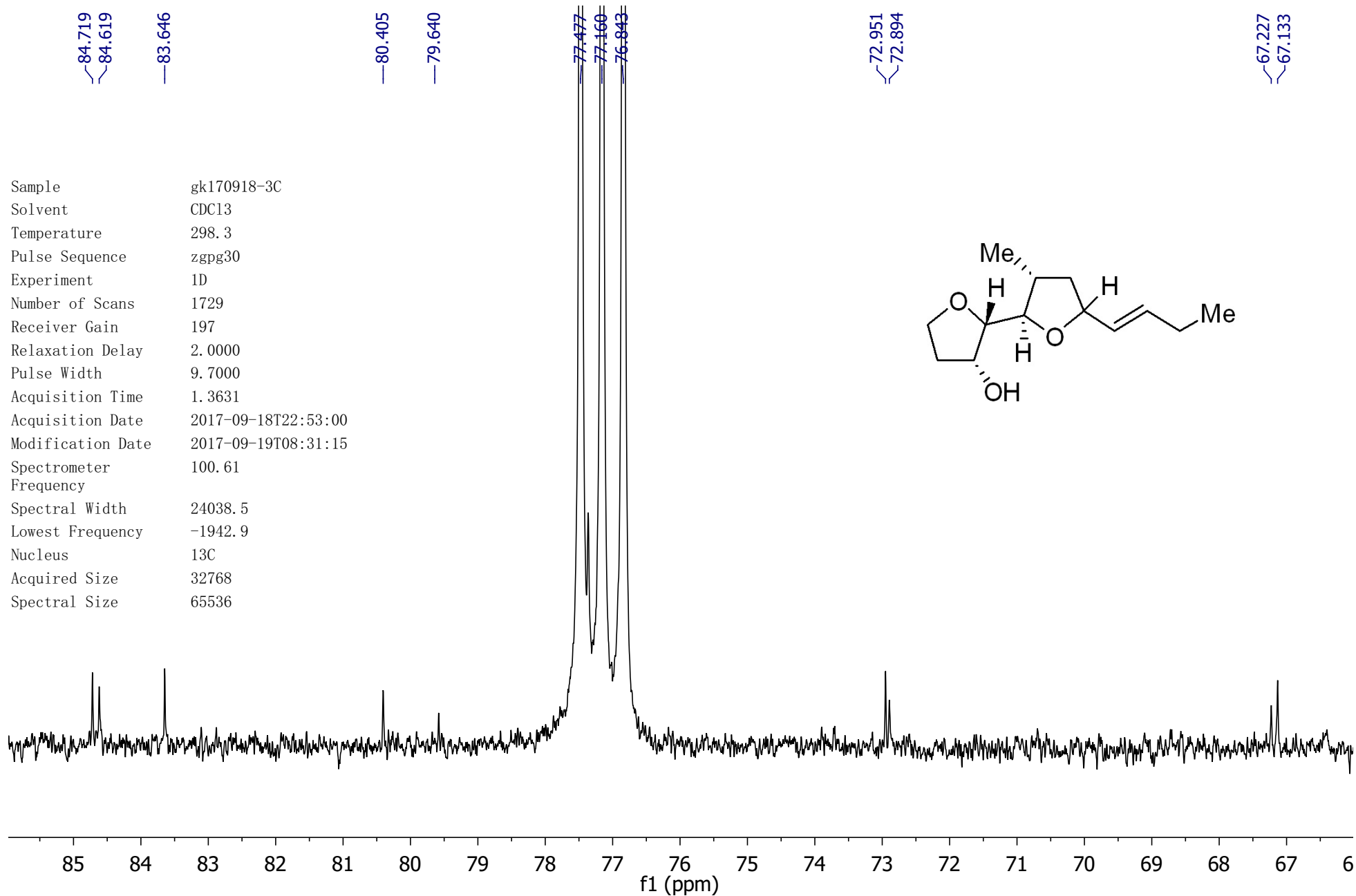
Sample gk170918-3C  
Solvent CDC13  
Temperature 298.3  
Pulse Sequence zgpg30  
Experiment 1D  
Number of Scans 1729  
Receiver Gain 197  
Relaxation Delay 2.0000  
Pulse Width 9.7000  
Acquisition Time 1.3631  
Acquisition Date 2017-09-18T22:53:00  
Modification Date 2017-09-19T08:31:15  
Spectrometer 100.61  
Frequency  
Spectral Width 24038.5  
Lowest Frequency -1942.9  
Nucleus 13C  
Acquired Size 32768  
Spectral Size 65536



134.870  
134.848

129.859  
129.715





—42.371

—40.451  
—39.874

—37.711

—35.122

—29.851

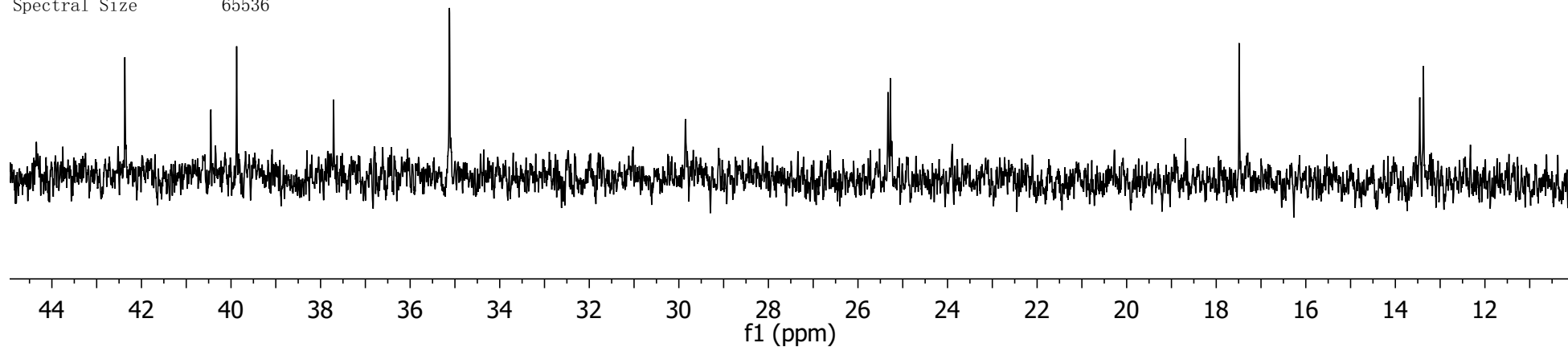
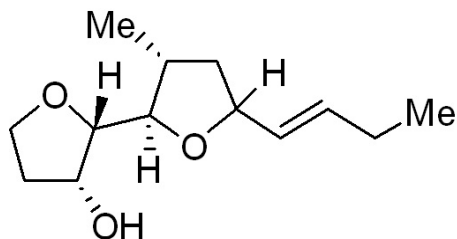
—25.328  
—25.276

—18.688

—17.488

—13.455  
—13.374

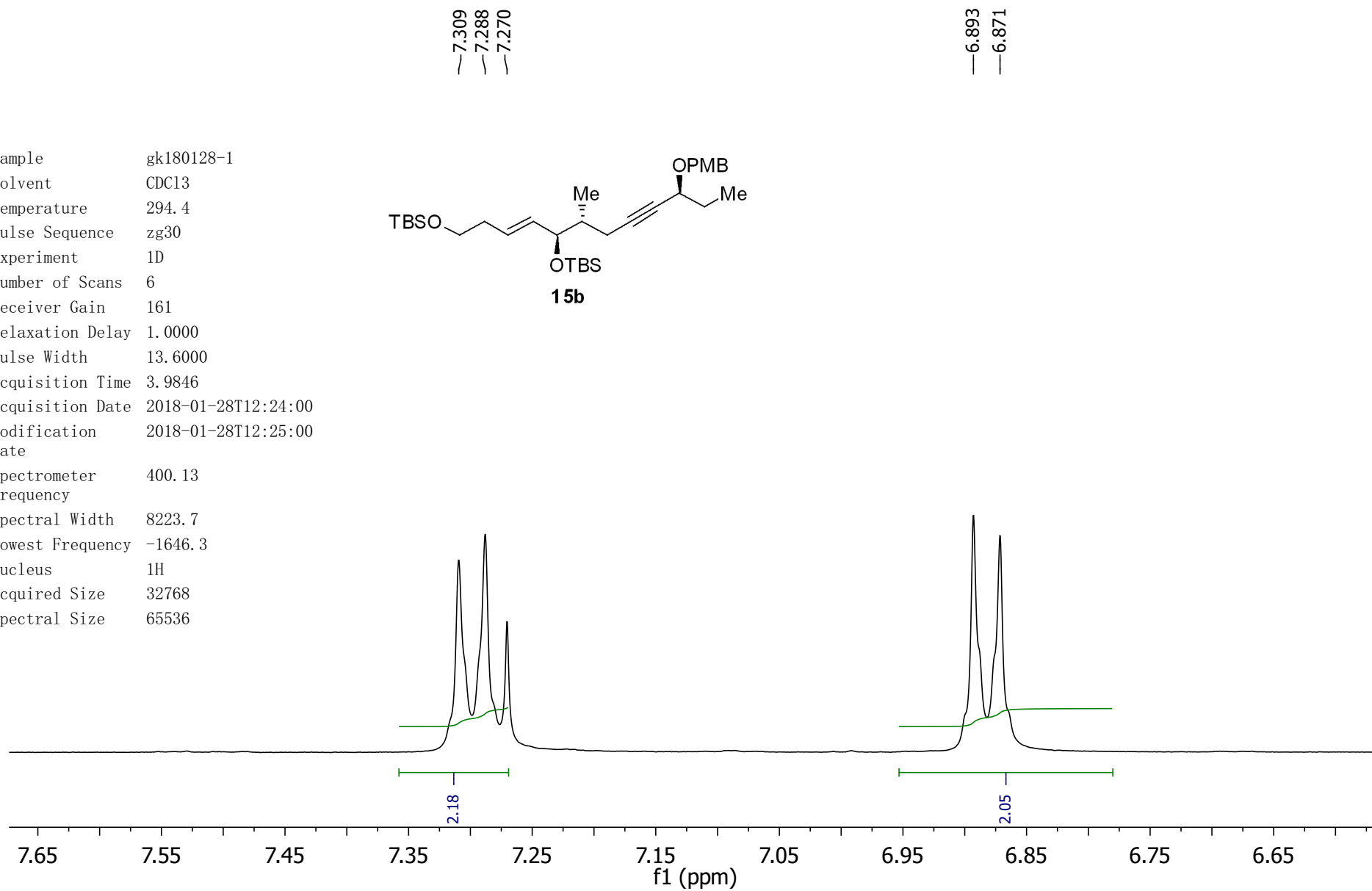
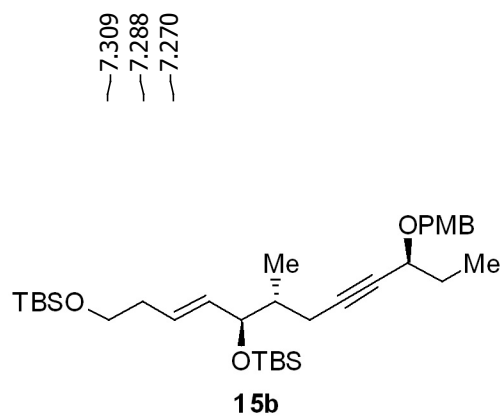
Sample gk170918-3C  
Solvent CDC13  
Temperature 298.3  
Pulse Sequence zgpg30  
Experiment 1D  
Number of Scans 1729  
Receiver Gain 197  
Relaxation Delay 2.0000  
Pulse Width 9.7000  
Acquisition Time 1.3631  
Acquisition Date 2017-09-18T22:53:00  
Modification Date 2017-09-19T08:31:15  
Spectrometer 100.61  
Frequency  
Spectral Width 24038.5  
Lowest Frequency -1942.9  
Nucleus 13C  
Acquired Size 32768  
Spectral Size 65536



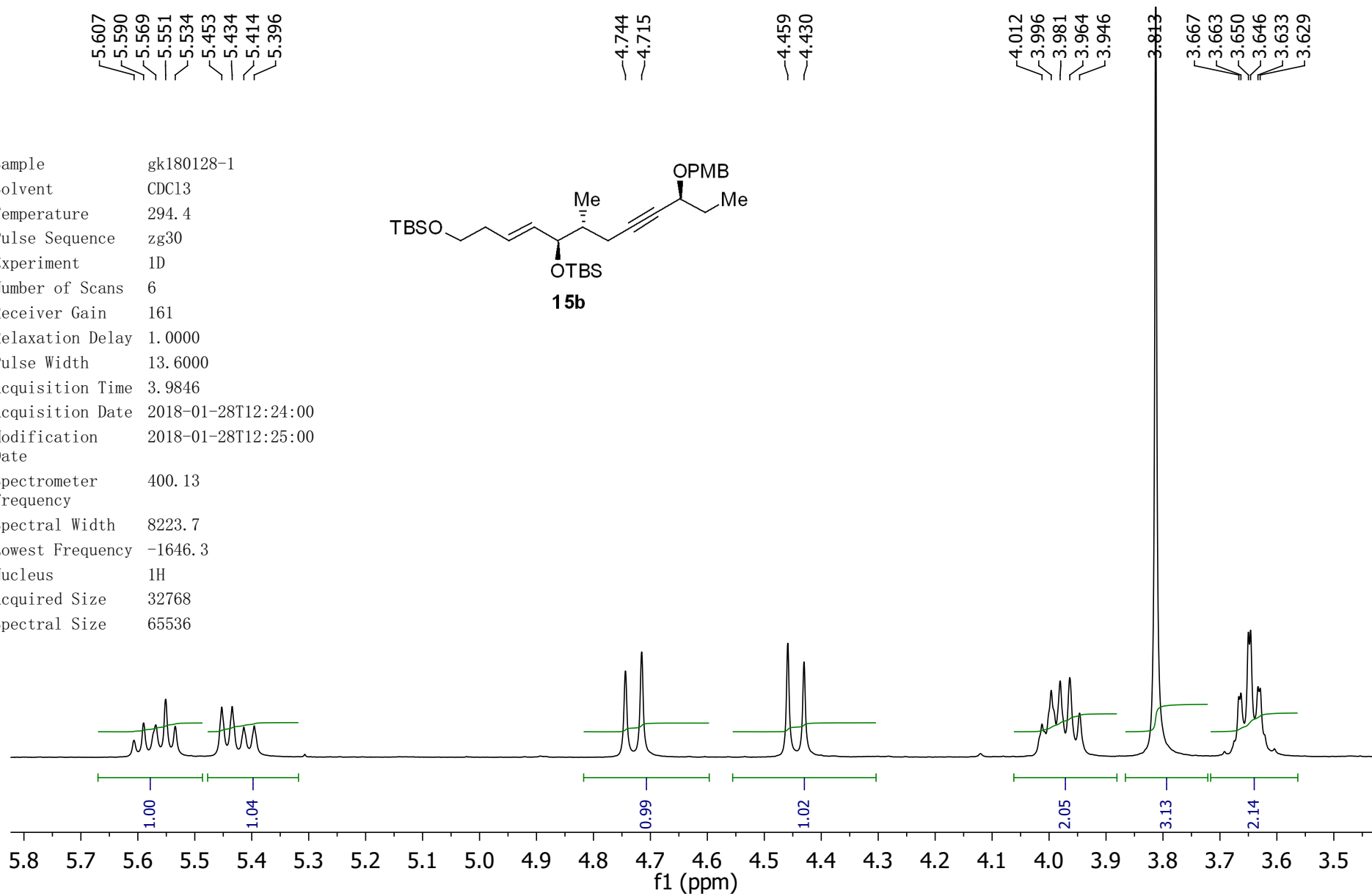
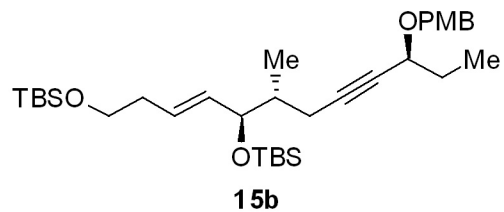




Sample gk180128-1  
Solvent CDCl3  
Temperature 294.4  
Pulse Sequence zg30  
Experiment 1D  
Number of Scans 6  
Receiver Gain 161  
Relaxation Delay 1.0000  
Pulse Width 13.6000  
Acquisition Time 3.9846  
Acquisition Date 2018-01-28T12:24:00  
Modification 2018-01-28T12:25:00  
Date  
Spectrometer 400.13  
Frequency  
Spectral Width 8223.7  
Lowest Frequency -1646.3  
Nucleus 1H  
Acquired Size 32768  
Spectral Size 65536



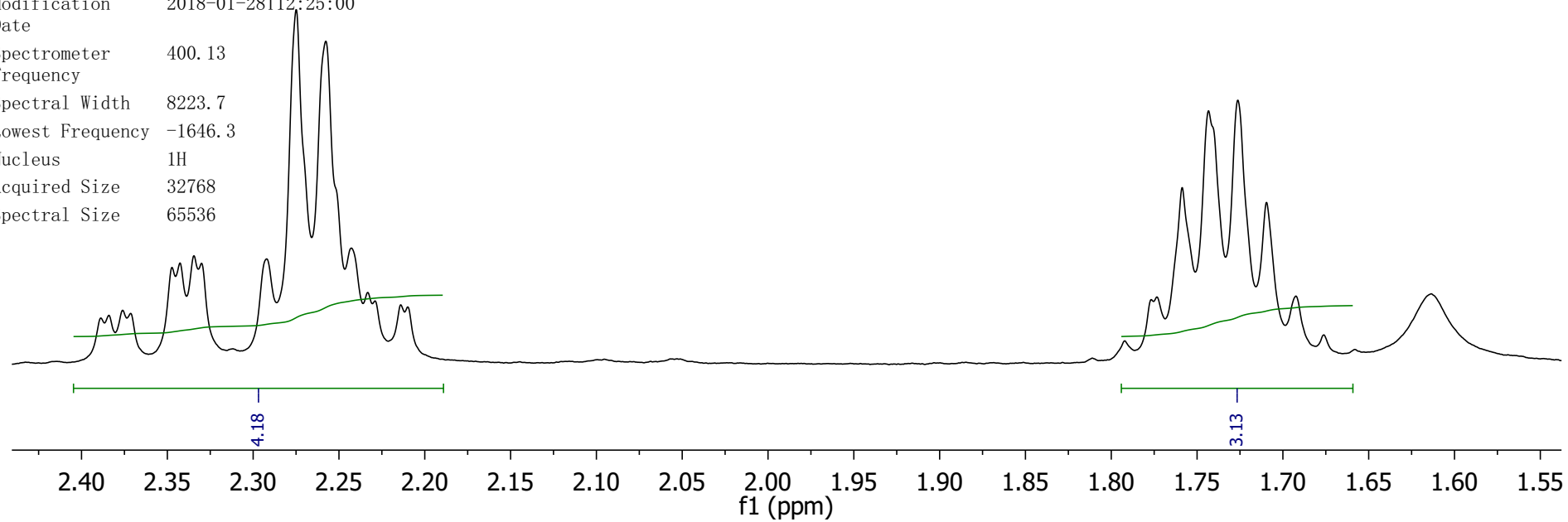
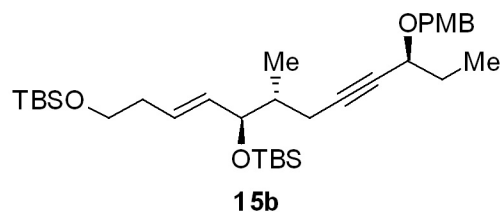
Sample gk180128-1  
 Solvent CDCl3  
 Temperature 294.4  
 Pulse Sequence zg30  
 Experiment 1D  
 Number of Scans 6  
 Receiver Gain 161  
 Relaxation Delay 1.0000  
 Pulse Width 13.6000  
 Acquisition Time 3.9846  
 Acquisition Date 2018-01-28T12:24:00  
 Modification 2018-01-28T12:25:00  
 Date  
 Spectrometer 400.13  
 Frequency  
 Spectral Width 8223.7  
 Lowest Frequency -1646.3  
 Nucleus 1H  
 Acquired Size 32768  
 Spectral Size 65536



2.389  
2.384  
2.376  
2.371  
2.347  
2.343  
2.335  
2.330  
2.292  
2.275  
2.258  
2.243  
2.233  
2.229  
2.214  
2.210

1.777  
1.773  
1.759  
1.743  
1.726  
1.710  
1.692  
1.614

Sample gk180128-1  
Solvent CDCl3  
Temperature 294.4  
Pulse Sequence zg30  
Experiment 1D  
Number of Scans 6  
Receiver Gain 161  
Relaxation Delay 1.0000  
Pulse Width 13.6000  
Acquisition Time 3.9846  
Acquisition Date 2018-01-28T12:24:00  
Modification 2018-01-28T12:25:00  
Date  
Spectrometer 400.13  
Frequency  
Spectral Width 8223.7  
Lowest Frequency -1646.3  
Nucleus 1H  
Acquired Size 32768  
Spectral Size 65536



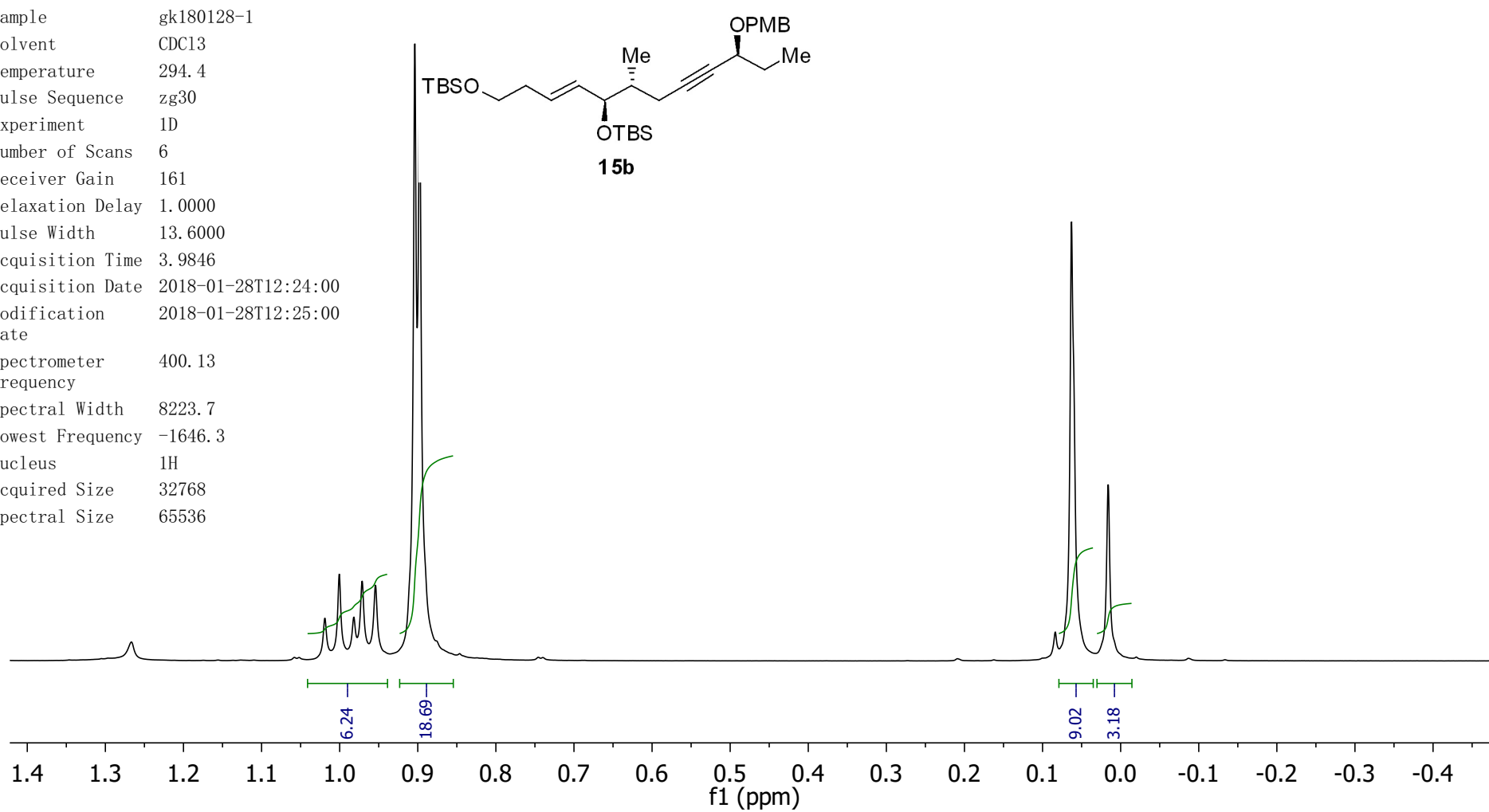
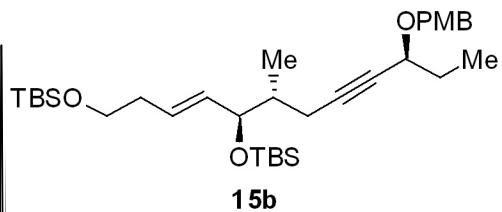
—1.267

1.019  
1.001  
0.982  
0.971  
0.954  
0.904  
0.898

—0.063

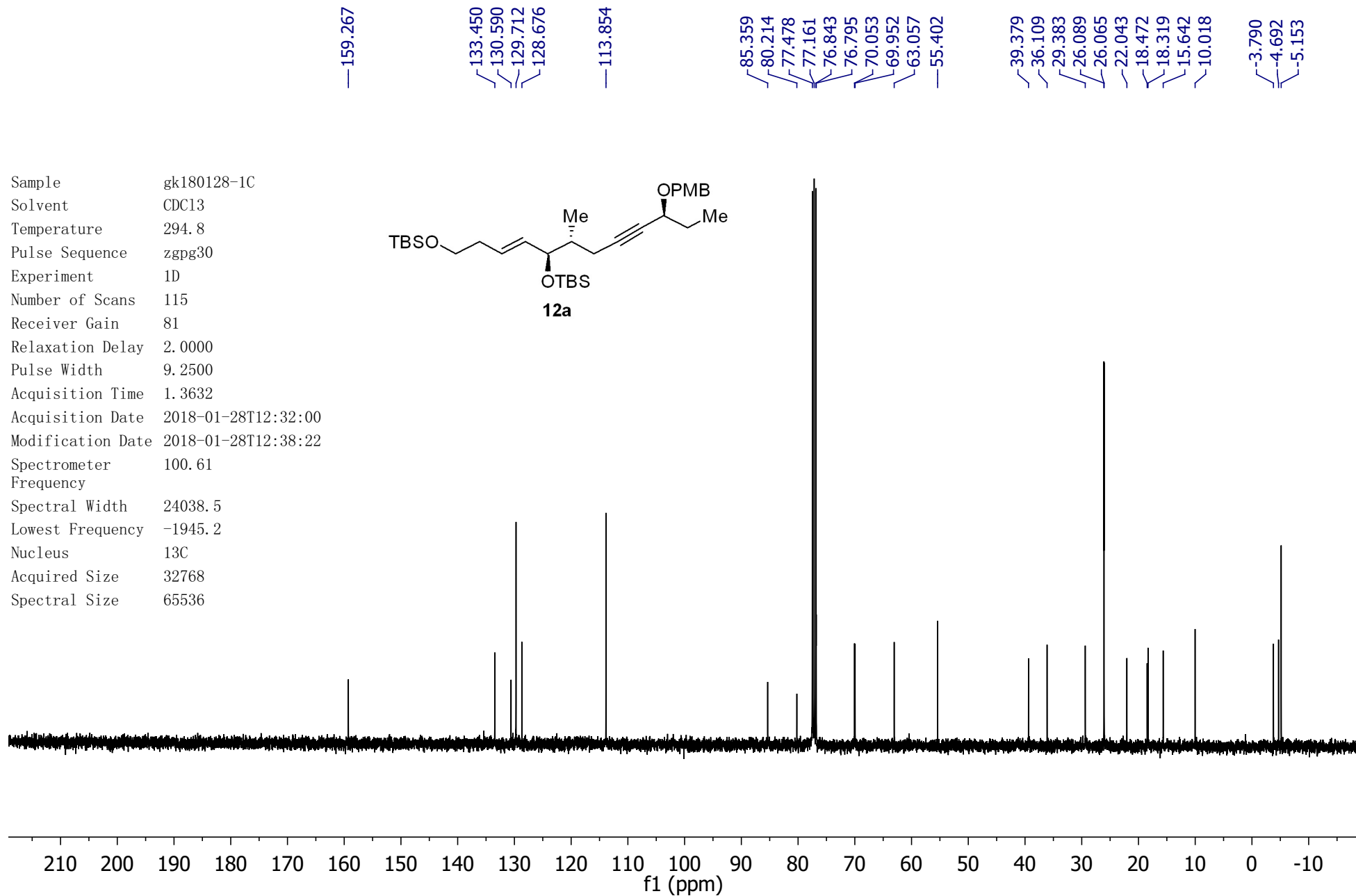
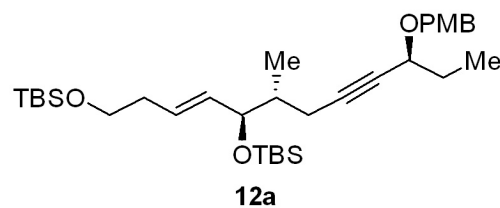
—0.016

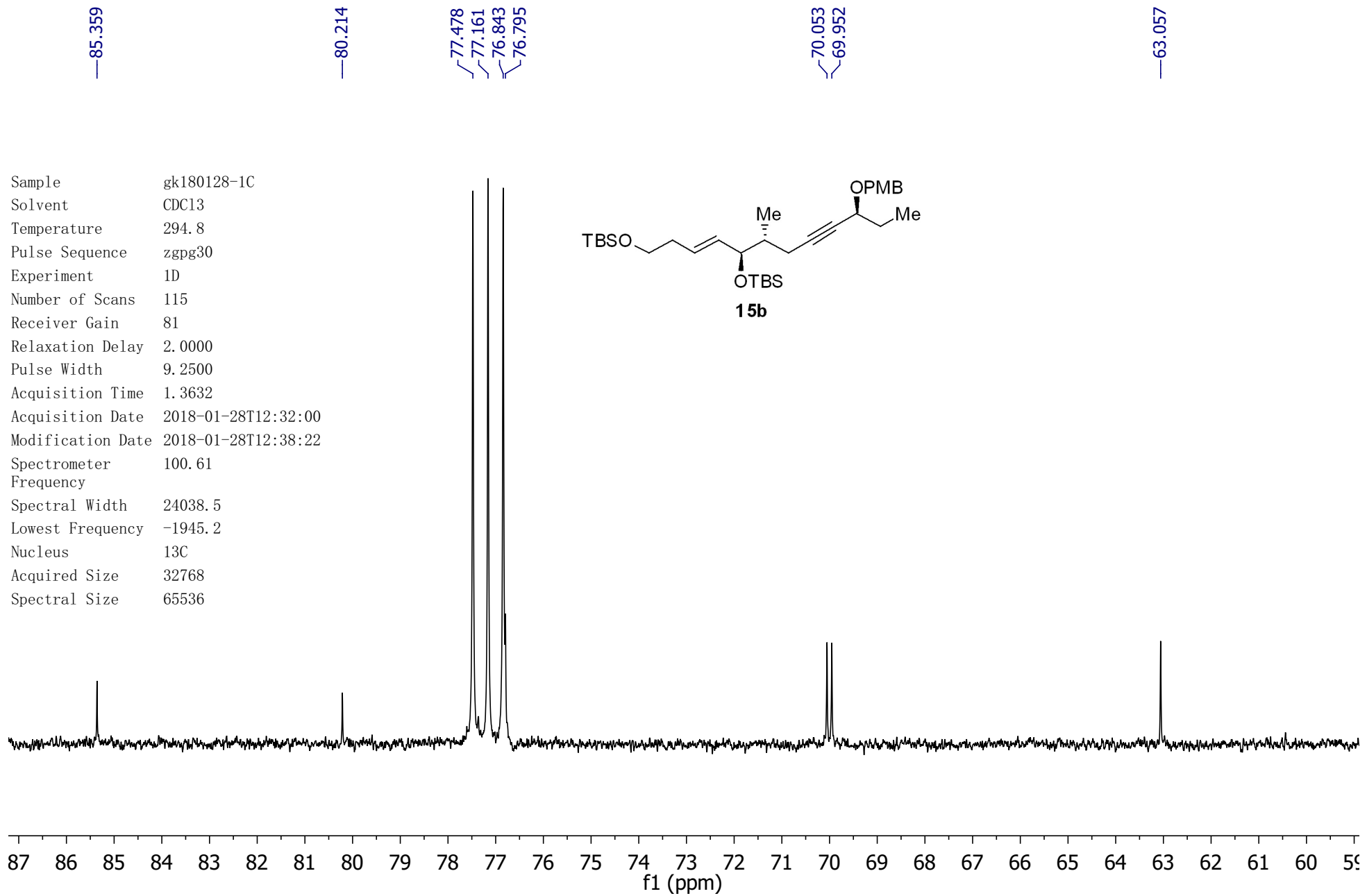
Sample gk180128-1  
Solvent CDC13  
Temperature 294.4  
Pulse Sequence zg30  
Experiment 1D  
Number of Scans 6  
Receiver Gain 161  
Relaxation Delay 1.0000  
Pulse Width 13.6000  
Acquisition Time 3.9846  
Acquisition Date 2018-01-28T12:24:00  
Modification 2018-01-28T12:25:00  
Date  
Spectrometer 400.13  
Frequency  
Spectral Width 8223.7  
Lowest Frequency -1646.3  
Nucleus 1H  
Acquired Size 32768  
Spectral Size 65536



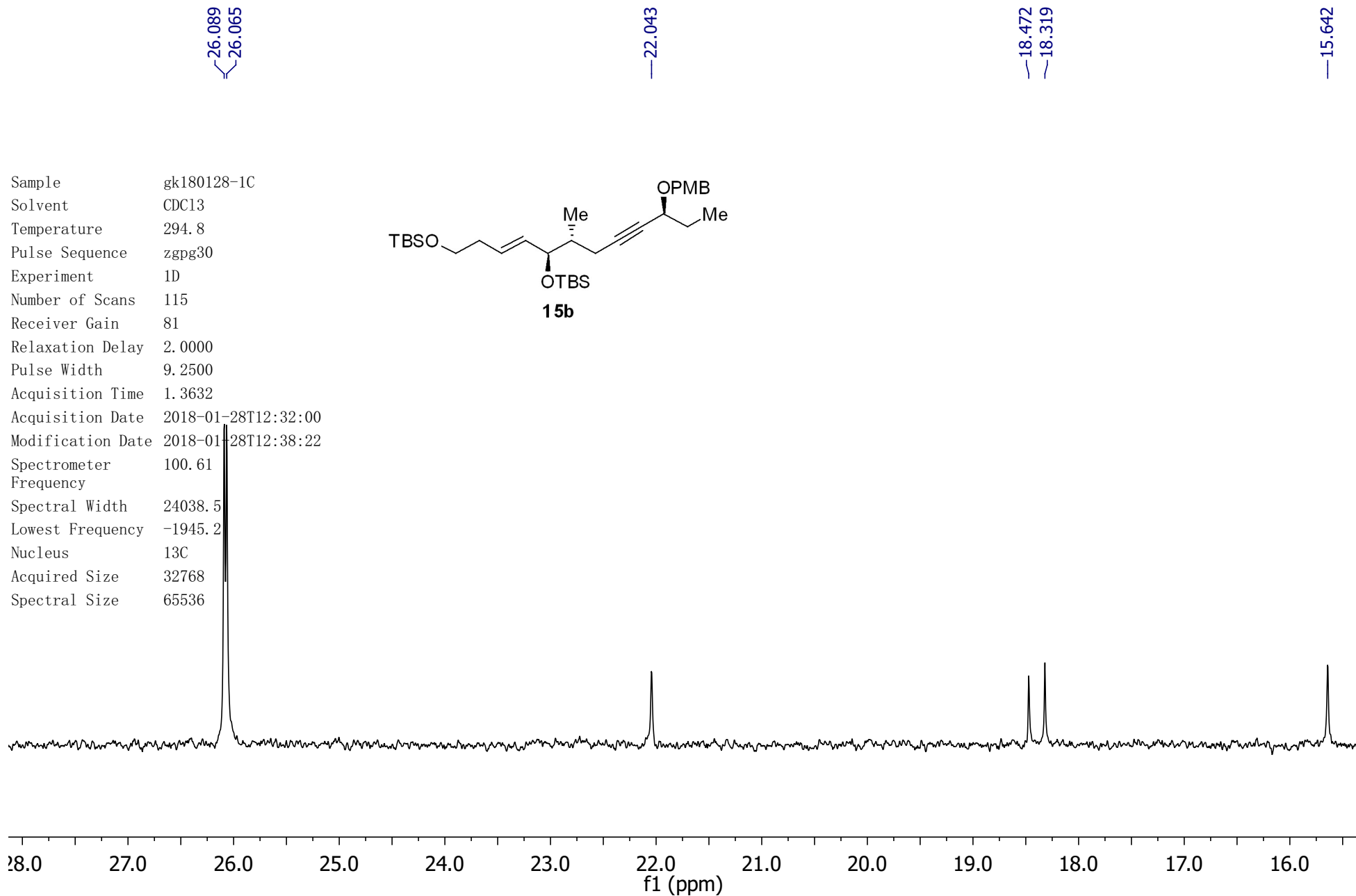
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Sample gk180128-1C  
 Solvent CDC13  
 Temperature 294.8  
 Pulse Sequence zgpg30  
 Experiment 1D  
 Number of Scans 115  
 Receiver Gain 81  
 Relaxation Delay 2.0000  
 Pulse Width 9.2500  
 Acquisition Time 1.3632  
 Acquisition Date 2018-01-28T12:32:00  
 Modification Date 2018-01-28T12:38:22  
 Spectrometer 100.61  
 Frequency  
 Spectral Width 24038.5  
 Lowest Frequency -1945.2  
 Nucleus 13C  
 Acquired Size 32768  
 Spectral Size 65536





Sample gk180128-1C  
 Solvent CDC13  
 Temperature 294.8  
 Pulse Sequence zgpg30  
 Experiment 1D  
 Number of Scans 115  
 Receiver Gain 81  
 Relaxation Delay 2.0000  
 Pulse Width 9.2500  
 Acquisition Time 1.3632  
 Acquisition Date 2018-01-28T12:32:00  
 Modification Date 2018-01-28T12:38:22  
 Spectrometer 100.61  
 Frequency  
 Spectral Width 24038.5  
 Lowest Frequency -1945.2  
 Nucleus 13C  
 Acquired Size 32768  
 Spectral Size 65536



S160



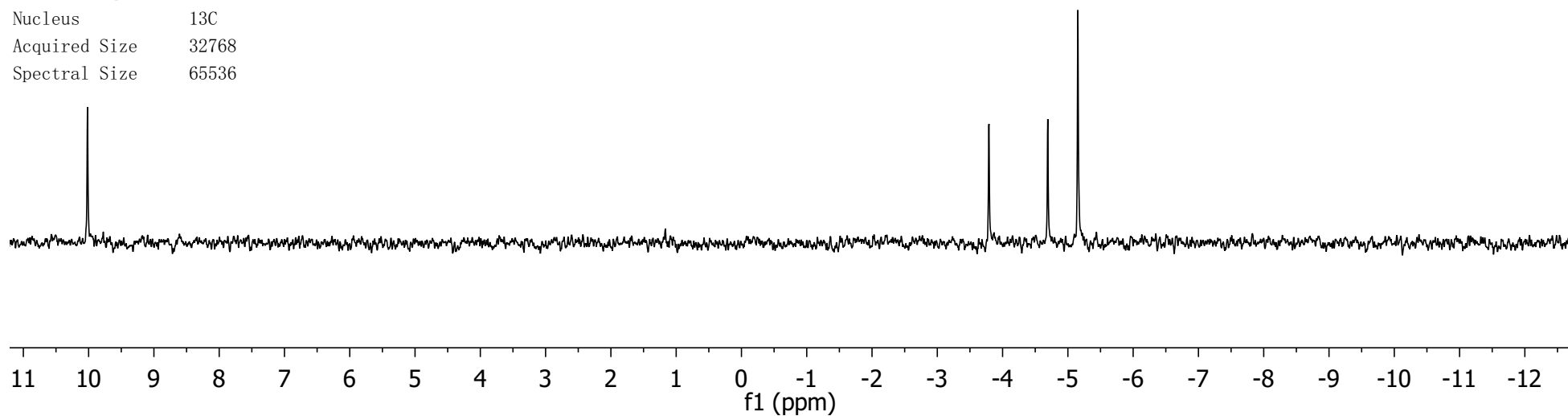
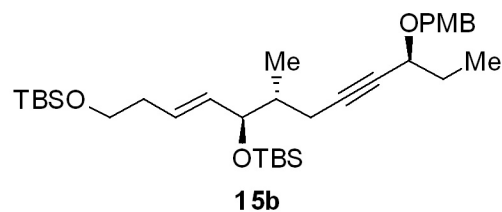
—10.018

—3.790

—4.692

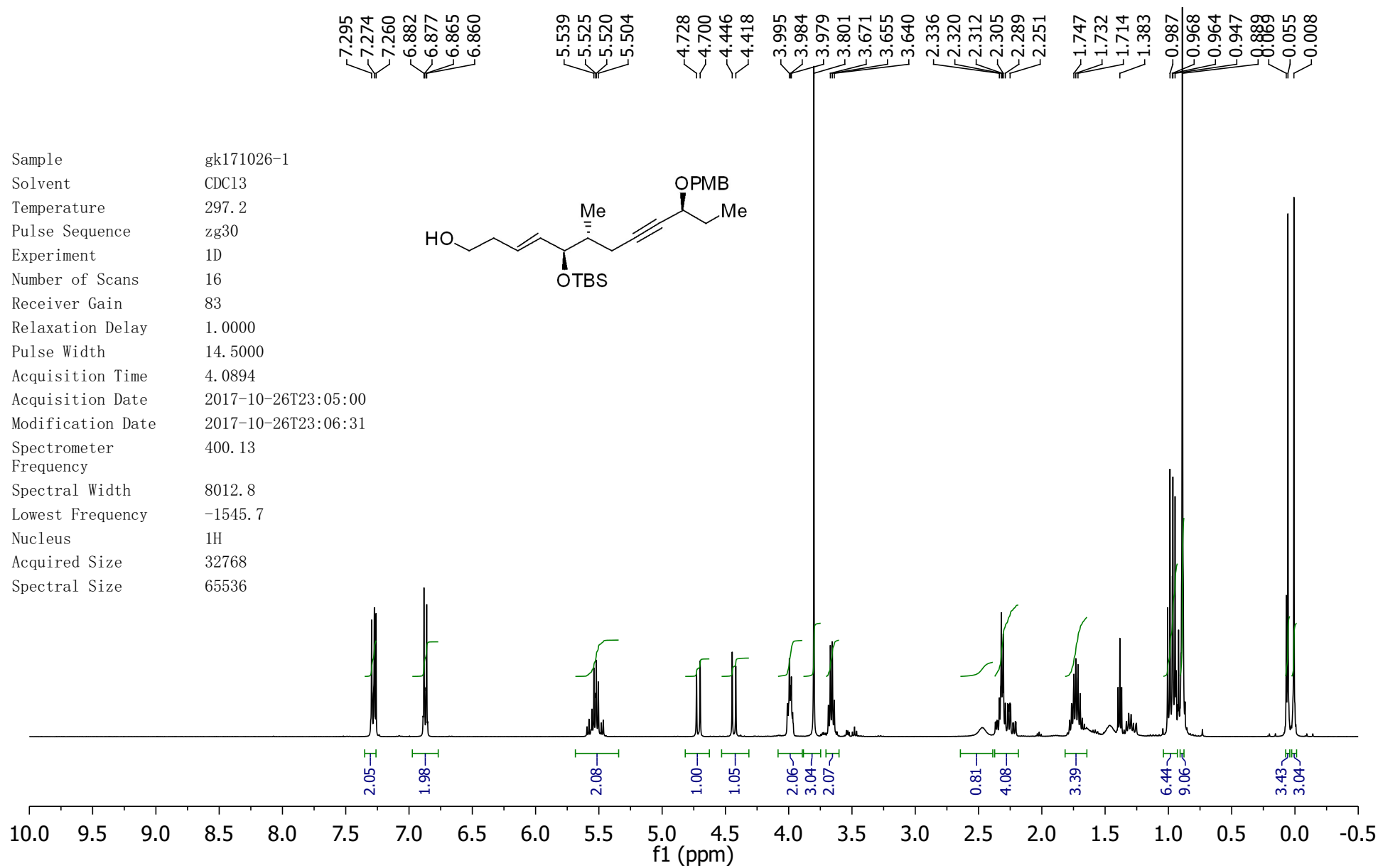
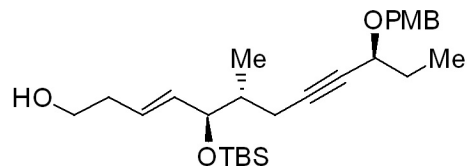
—5.153

Sample gk180128-1C  
Solvent CDC13  
Temperature 294.8  
Pulse Sequence zgpg30  
Experiment 1D  
Number of Scans 115  
Receiver Gain 81  
Relaxation Delay 2.0000  
Pulse Width 9.2500  
Acquisition Time 1.3632  
Acquisition Date 2018-01-28T12:32:00  
Modification Date 2018-01-28T12:38:22  
Spectrometer 100.61  
Frequency  
Spectral Width 24038.5  
Lowest Frequency -1945.2  
Nucleus 13C  
Acquired Size 32768  
Spectral Size 65536

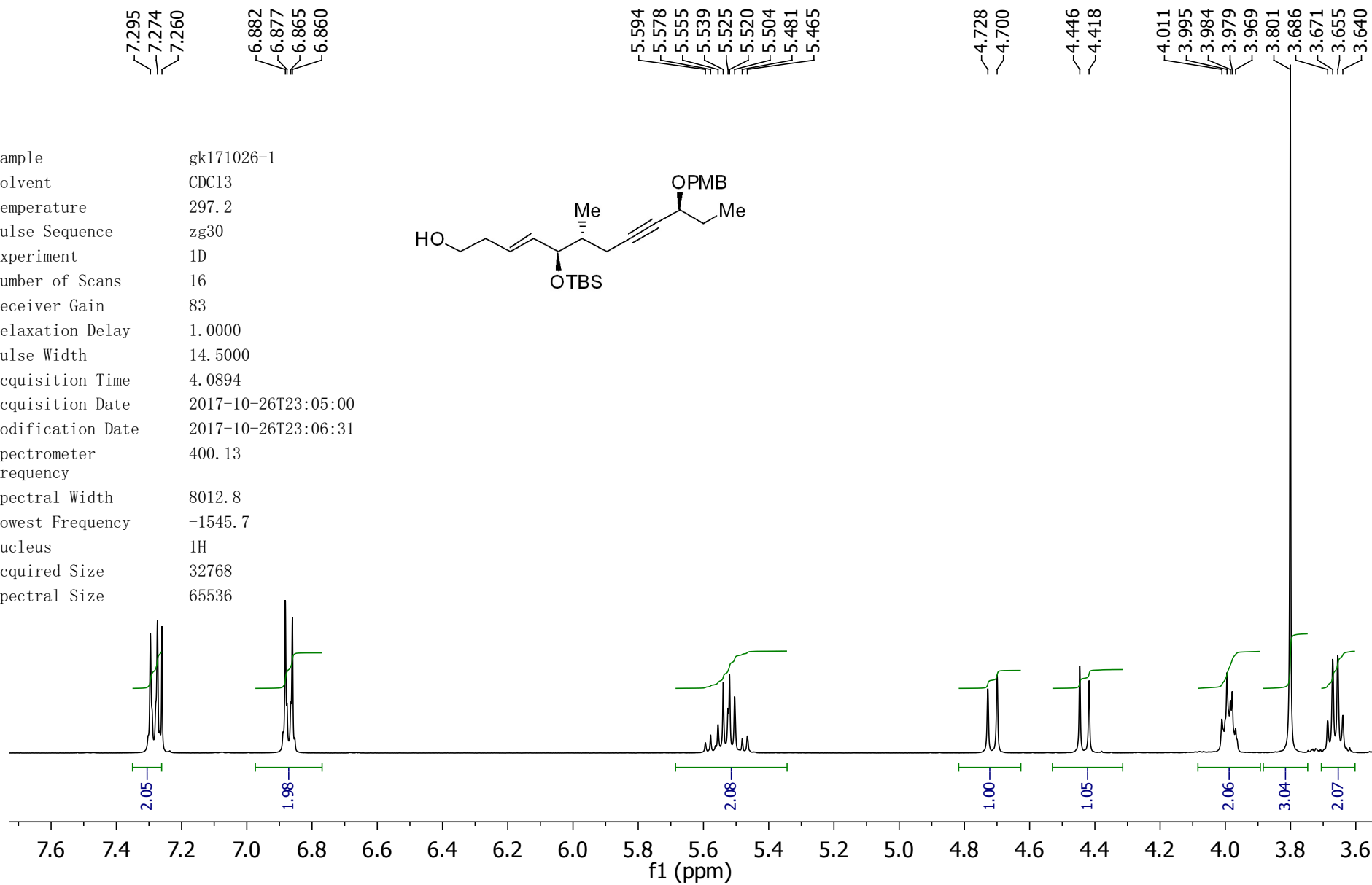
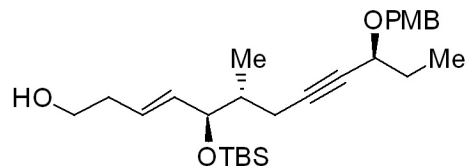


S161

Sample gk171026-1  
 Solvent CDCl3  
 Temperature 297.2  
 Pulse Sequence zg30  
 Experiment 1D  
 Number of Scans 16  
 Receiver Gain 83  
 Relaxation Delay 1.0000  
 Pulse Width 14.5000  
 Acquisition Time 4.0894  
 Acquisition Date 2017-10-26T23:05:00  
 Modification Date 2017-10-26T23:06:31  
 Spectrometer 400.13  
 Frequency  
 Spectral Width 8012.8  
 Lowest Frequency -1545.7  
 Nucleus 1H  
 Acquired Size 32768  
 Spectral Size 65536



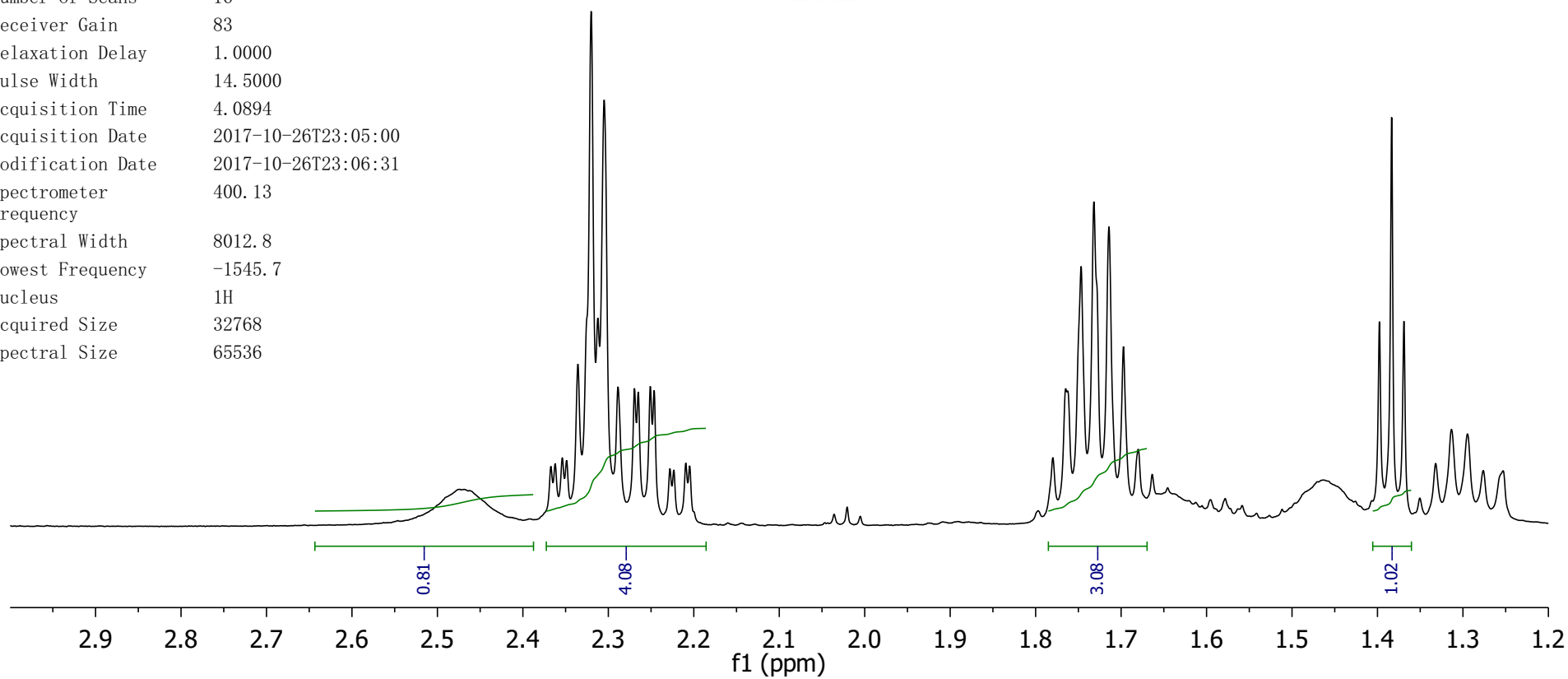
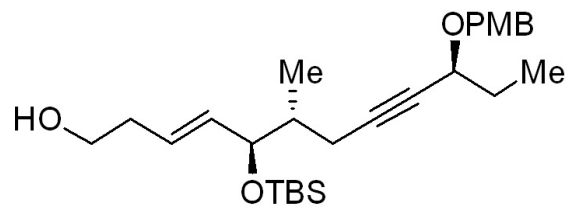
Sample gk171026-1  
 Solvent CDCl3  
 Temperature 297.2  
 Pulse Sequence zg30  
 Experiment 1D  
 Number of Scans 16  
 Receiver Gain 83  
 Relaxation Delay 1.0000  
 Pulse Width 14.5000  
 Acquisition Time 4.0894  
 Acquisition Date 2017-10-26T23:05:00  
 Modification Date 2017-10-26T23:06:31  
 Spectrometer 400.13  
 Frequency  
 Spectral Width 8012.8  
 Lowest Frequency -1545.7  
 Nucleus 1H  
 Acquired Size 32768  
 Spectral Size 65536



S163

Sample gk171026-1  
 Solvent CDCl3  
 Temperature 297.2  
 Pulse Sequence zg30  
 Experiment 1D  
 Number of Scans 16  
 Receiver Gain 83  
 Relaxation Delay 1.0000  
 Pulse Width 14.5000  
 Acquisition Time 4.0894  
 Acquisition Date 2017-10-26T23:05:00  
 Modification Date 2017-10-26T23:06:31  
 Spectrometer 400.13  
 Frequency  
 Spectral Width 8012.8  
 Lowest Frequency -1545.7  
 Nucleus 1H  
 Acquired Size 32768  
 Spectral Size 65536

2.462 2.367 2.362 2.354 2.349 2.336 2.320 2.312 2.305 2.289 2.269 2.265 2.251 2.246 2.228 2.223 2.209 2.205  
 1.780 1.765 1.747 1.732 1.714 1.697 1.680 1.664  
 1.398 1.383 1.369

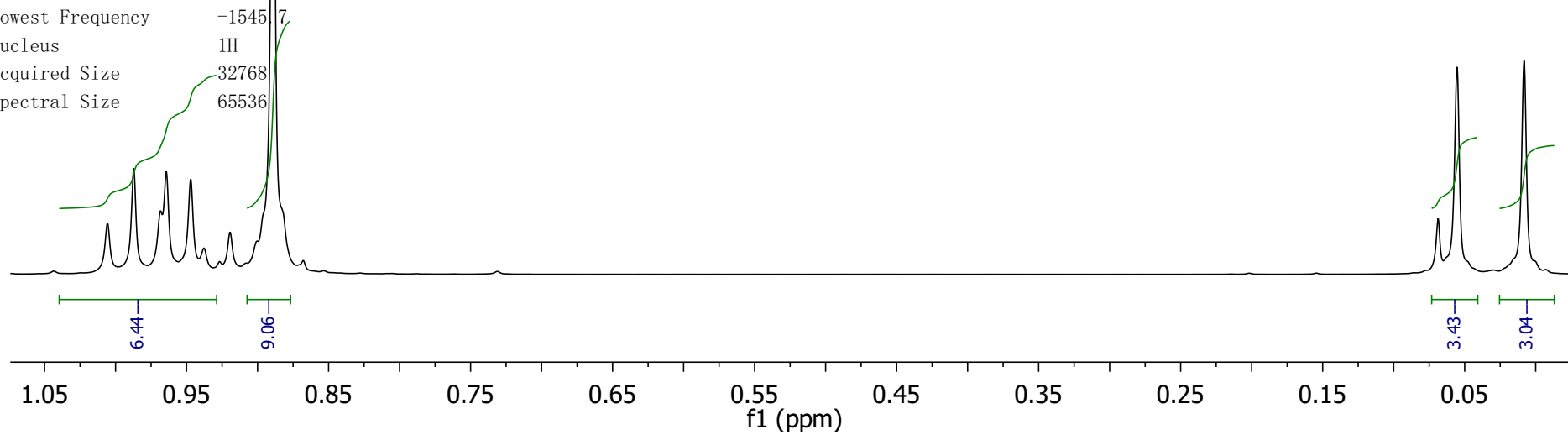
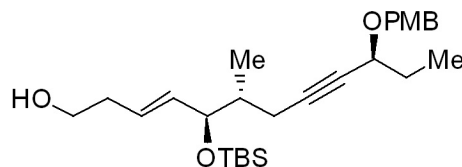


S164

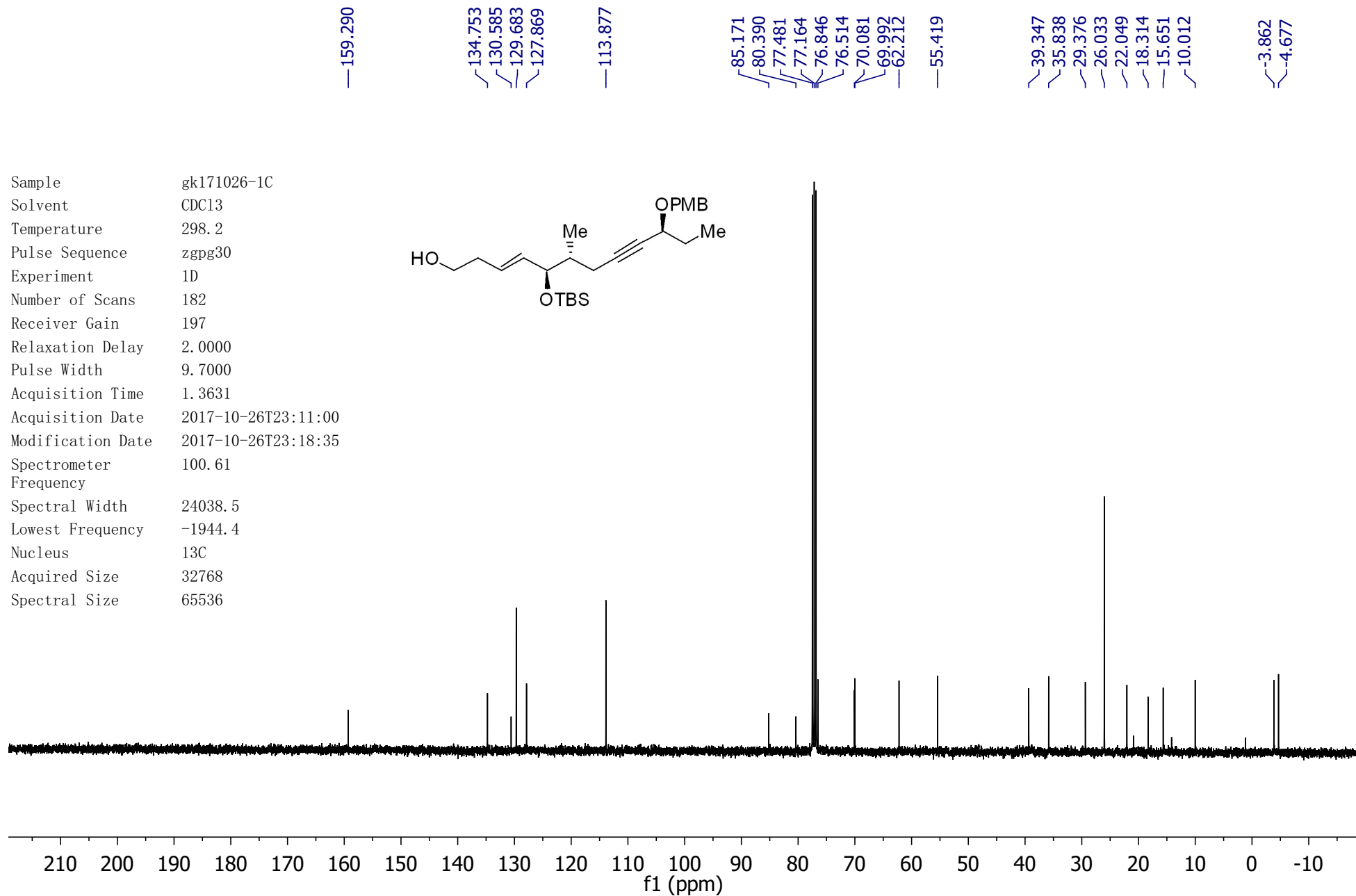
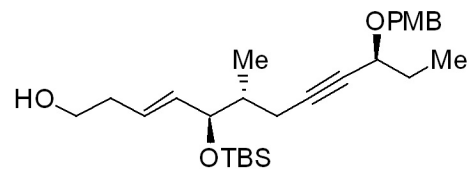
1.006  
0.987  
0.968  
0.964  
0.947  
0.938  
0.927  
0.919  
0.889

0.069  
0.055  
0.008

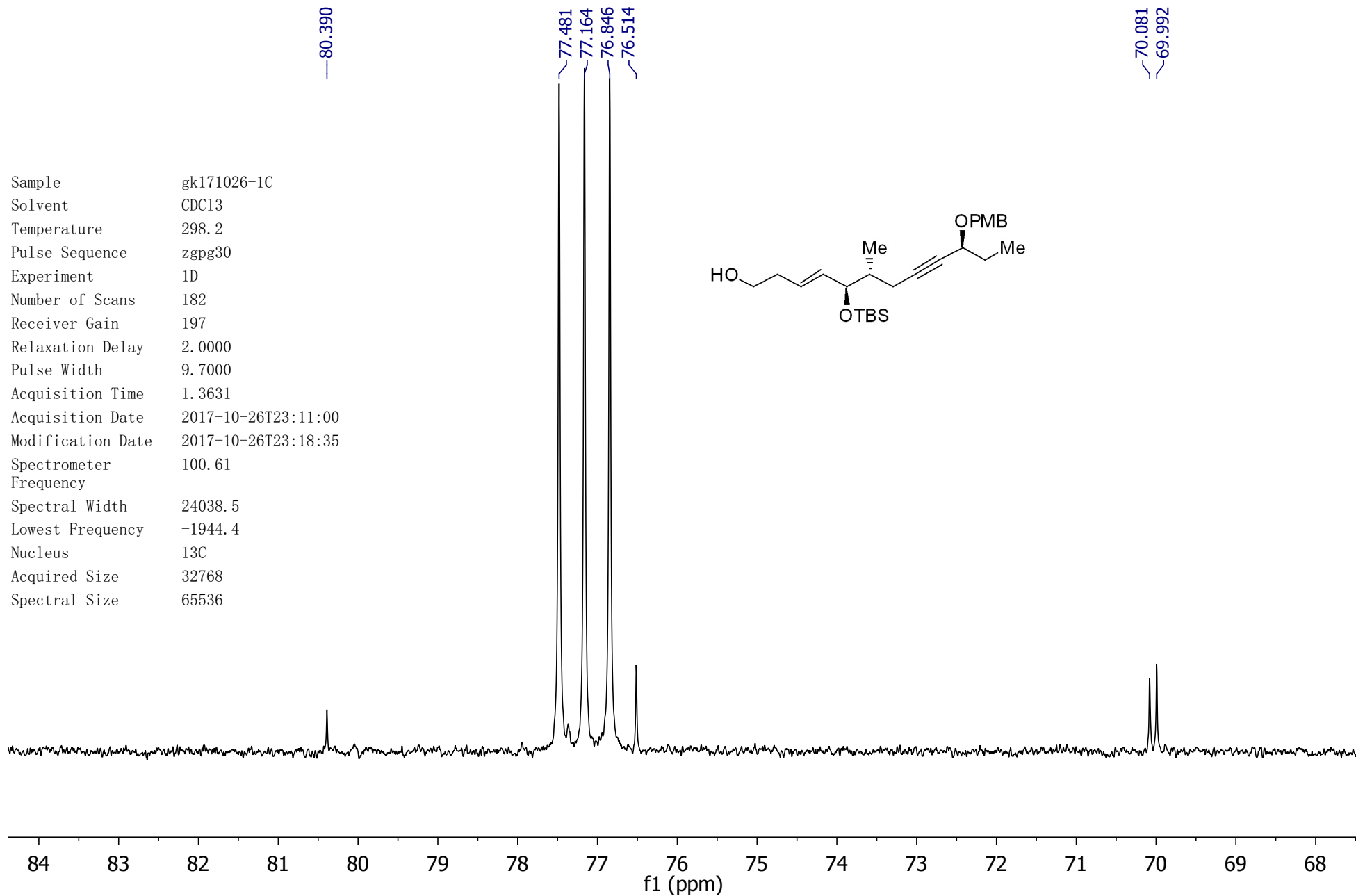
Sample gk171026-1  
Solvent CDCl3  
Temperature 297.2  
Pulse Sequence zg30  
Experiment 1D  
Number of Scans 16  
Receiver Gain 83  
Relaxation Delay 1.0000  
Pulse Width 14.5000  
Acquisition Time 4.0894  
Acquisition Date 2017-10-26T23:05:00  
Modification Date 2017-10-26T23:06:31  
Spectrometer 400.13  
Frequency  
Spectral Width 8012.8  
Lowest Frequency -1545.7  
Nucleus 1H  
Acquired Size 32768  
Spectral Size 65536



Sample gk171026-1C  
 Solvent CDC13  
 Temperature 298.2  
 Pulse Sequence zgpg30  
 Experiment 1D  
 Number of Scans 182  
 Receiver Gain 197  
 Relaxation Delay 2.0000  
 Pulse Width 9.7000  
 Acquisition Time 1.3631  
 Acquisition Date 2017-10-26T23:11:00  
 Modification Date 2017-10-26T23:18:35  
 Spectrometer 100.61  
 Frequency  
 Spectral Width 24038.5  
 Lowest Frequency -1944.4  
 Nucleus <sup>13</sup>C  
 Acquired Size 32768  
 Spectral Size 65536

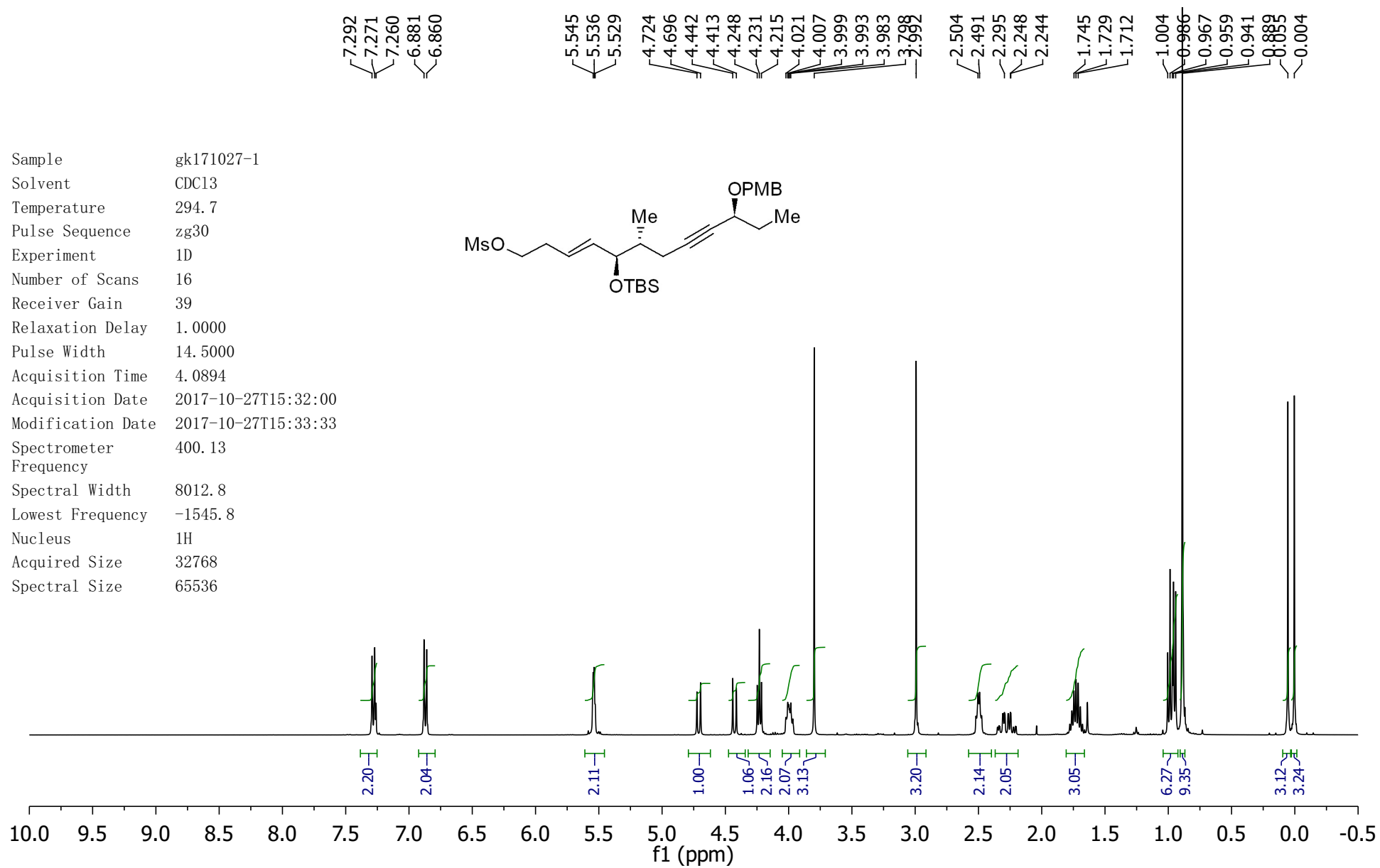
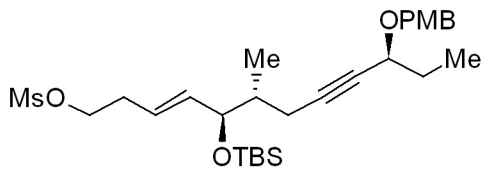


Sample gk171026-1C  
Solvent CDC13  
Temperature 298.2  
Pulse Sequence zgpg30  
Experiment 1D  
Number of Scans 182  
Receiver Gain 197  
Relaxation Delay 2.0000  
Pulse Width 9.7000  
Acquisition Time 1.3631  
Acquisition Date 2017-10-26T23:11:00  
Modification Date 2017-10-26T23:18:35  
Spectrometer 100.61  
Frequency  
Spectral Width 24038.5  
Lowest Frequency -1944.4  
Nucleus 13C  
Acquired Size 32768  
Spectral Size 65536



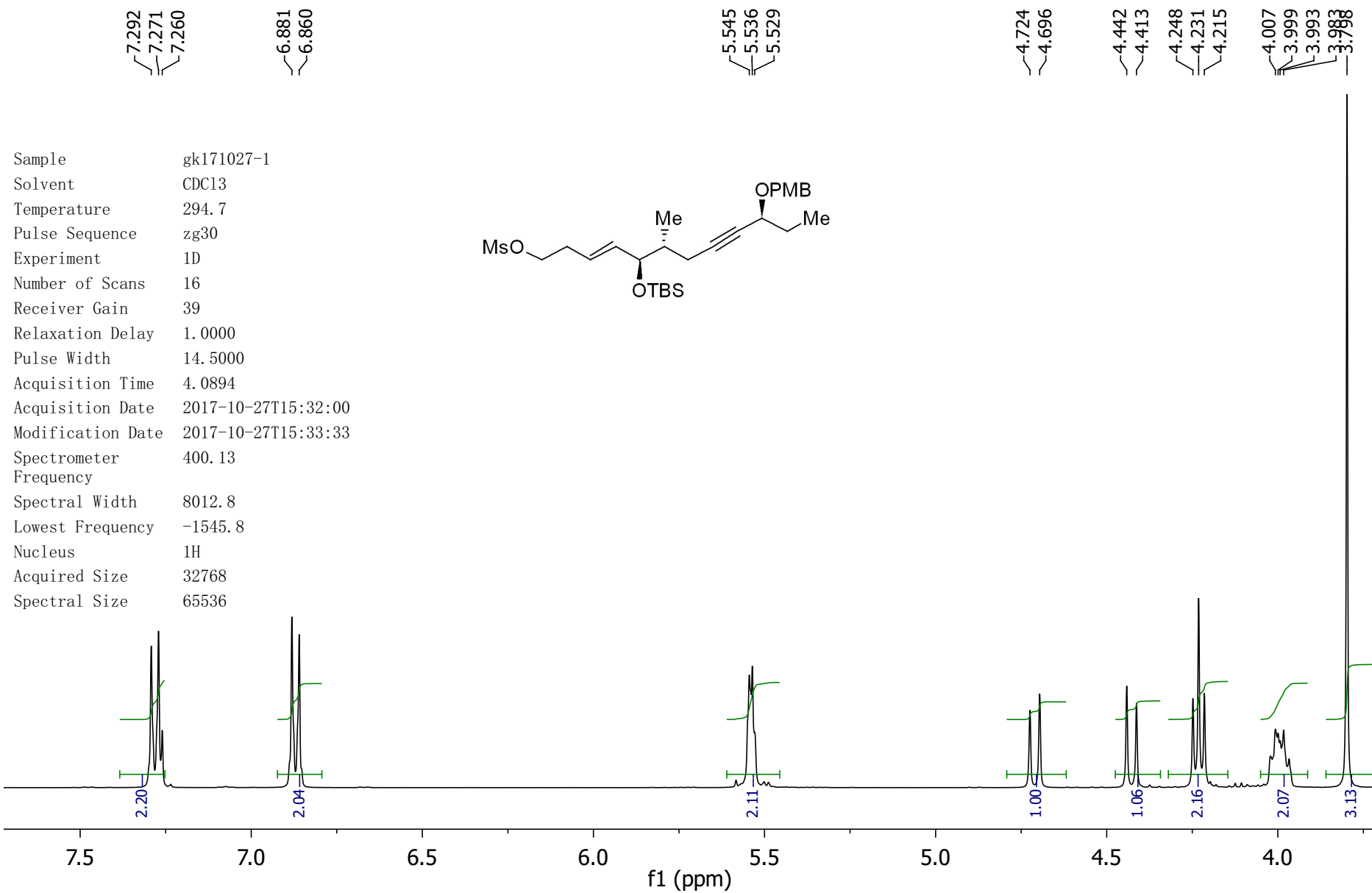
S167

Sample gk171027-1  
 Solvent CDCl3  
 Temperature 294.7  
 Pulse Sequence zg30  
 Experiment 1D  
 Number of Scans 16  
 Receiver Gain 39  
 Relaxation Delay 1.0000  
 Pulse Width 14.5000  
 Acquisition Time 4.0894  
 Acquisition Date 2017-10-27T15:32:00  
 Modification Date 2017-10-27T15:33:33  
 Spectrometer 400.13  
 Frequency  
 Spectral Width 8012.8  
 Lowest Frequency -1545.8  
 Nucleus 1H  
 Acquired Size 32768  
 Spectral Size 65536



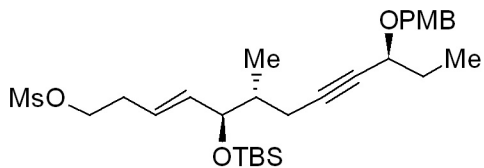
S168





Sample gk171027-1  
 Solvent CDCl3  
 Temperature 294.7  
 Pulse Sequence zg30  
 Experiment 1D  
 Number of Scans 16  
 Receiver Gain 39  
 Relaxation Delay 1.0000  
 Pulse Width 14.5000  
 Acquisition Time 4.0894  
 Acquisition Date 2017-10-27T15:32:00  
 Modification Date 2017-10-27T15:33:33  
 Spectrometer 400.13  
 Frequency  
 Spectral Width 8012.8  
 Lowest Frequency -1545.8  
 Nucleus 1H  
 Acquired Size 32768  
 Spectral Size 65536

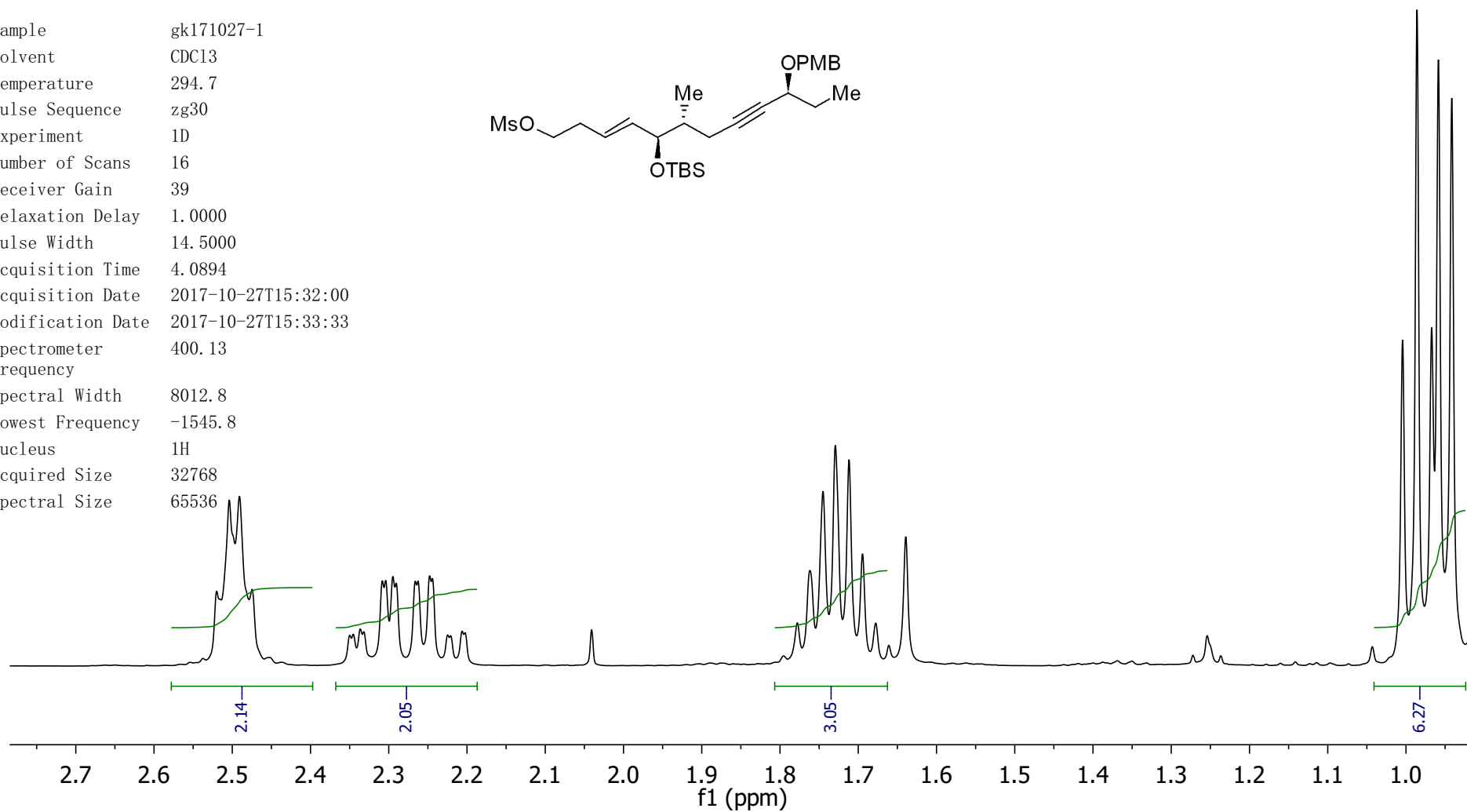
Sample gk171027-1  
 Solvent CDCl3  
 Temperature 294.7  
 Pulse Sequence zg30  
 Experiment 1D  
 Number of Scans 16  
 Receiver Gain 39  
 Relaxation Delay 1.0000  
 Pulse Width 14.5000  
 Acquisition Time 4.0894  
 Acquisition Date 2017-10-27T15:32:00  
 Modification Date 2017-10-27T15:33:33  
 Spectrometer 400.13  
 Frequency  
 Spectral Width 8012.8  
 Lowest Frequency -1545.8  
 Nucleus 1H  
 Acquired Size 32768  
 Spectral Size 65536



2.520  
 2.504  
 2.491  
 2.475  
 2.350  
 2.345  
 2.336  
 2.308  
 2.304  
 2.295  
 2.290  
 2.266  
 2.263  
 2.248  
 2.244  
 2.225  
 2.206

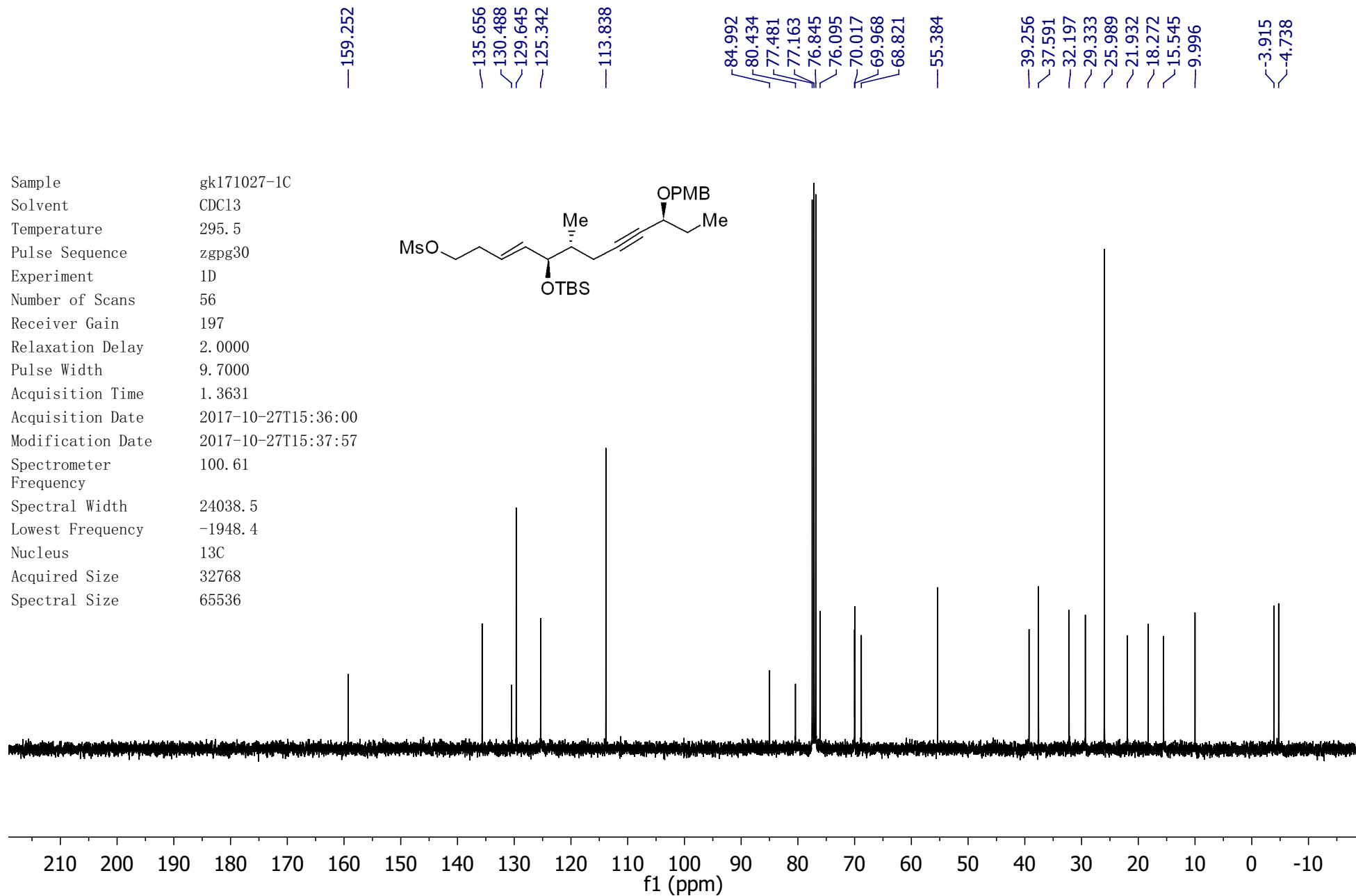
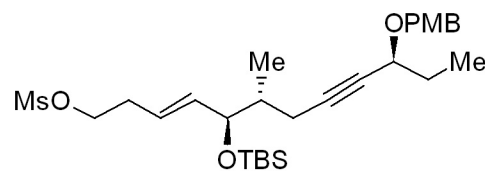
1.778  
 1.762  
 1.745  
 1.729  
 1.712  
 1.695  
 1.678  
 1.661  
 1.639

1.004  
 0.986  
 0.967  
 0.959  
 0.941

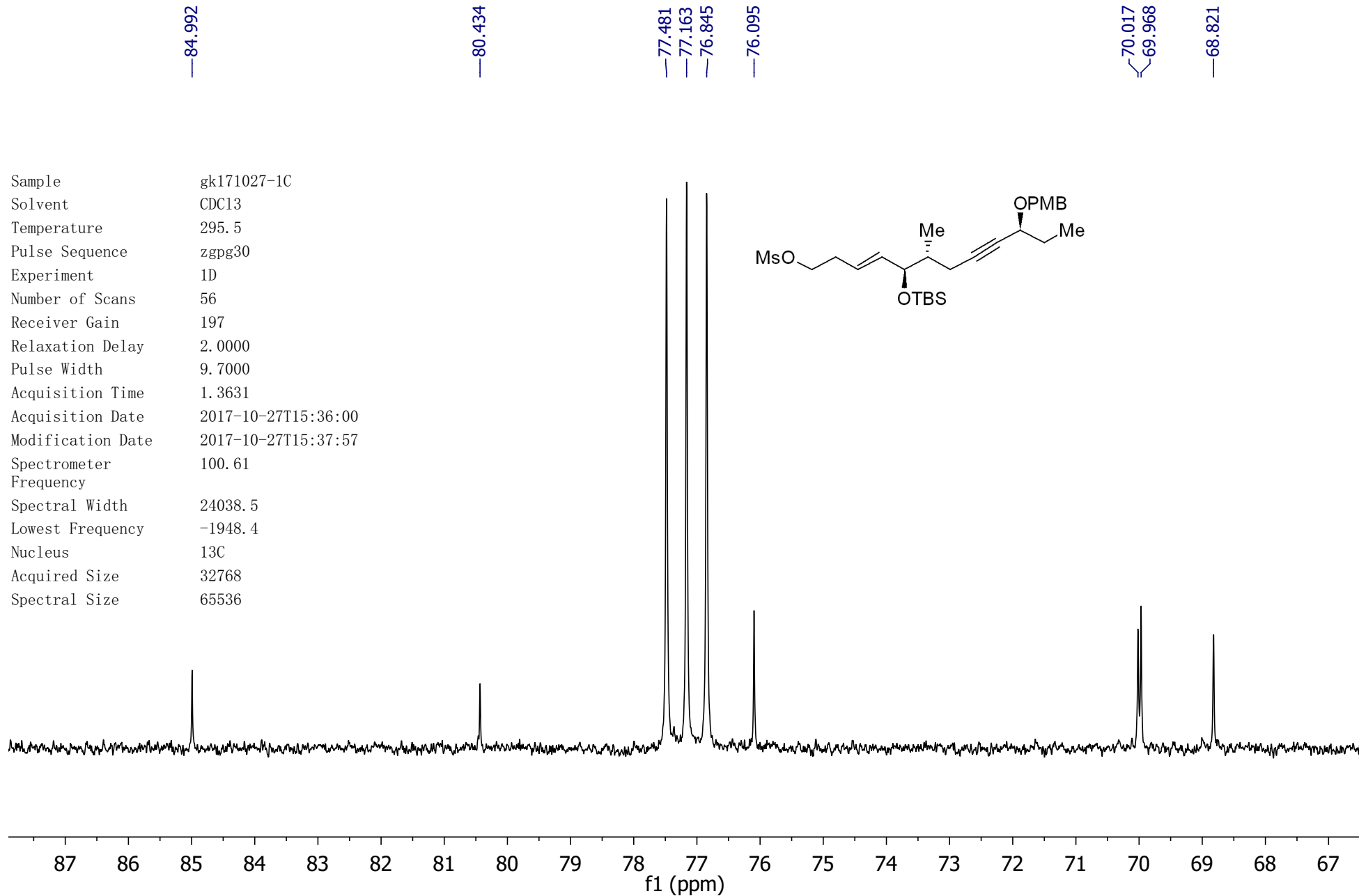


S170

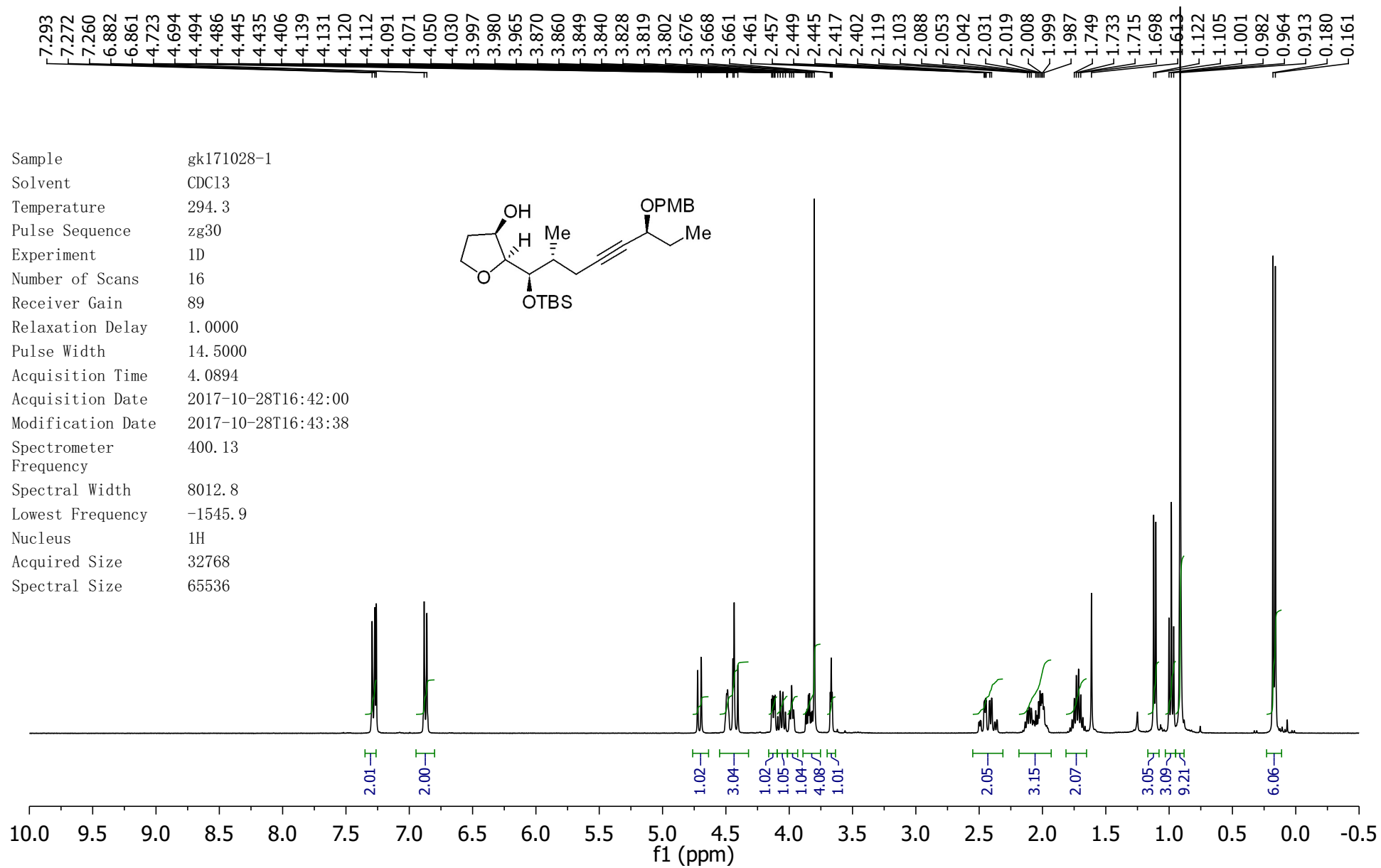
Sample gk171027-1C  
 Solvent CDC13  
 Temperature 295.5  
 Pulse Sequence zgpg30  
 Experiment 1D  
 Number of Scans 56  
 Receiver Gain 197  
 Relaxation Delay 2.0000  
 Pulse Width 9.7000  
 Acquisition Time 1.3631  
 Acquisition Date 2017-10-27T15:36:00  
 Modification Date 2017-10-27T15:37:57  
 Spectrometer 100.61  
 Frequency  
 Spectral Width 24038.5  
 Lowest Frequency -1948.4  
 Nucleus 13C  
 Acquired Size 32768  
 Spectral Size 65536



S171



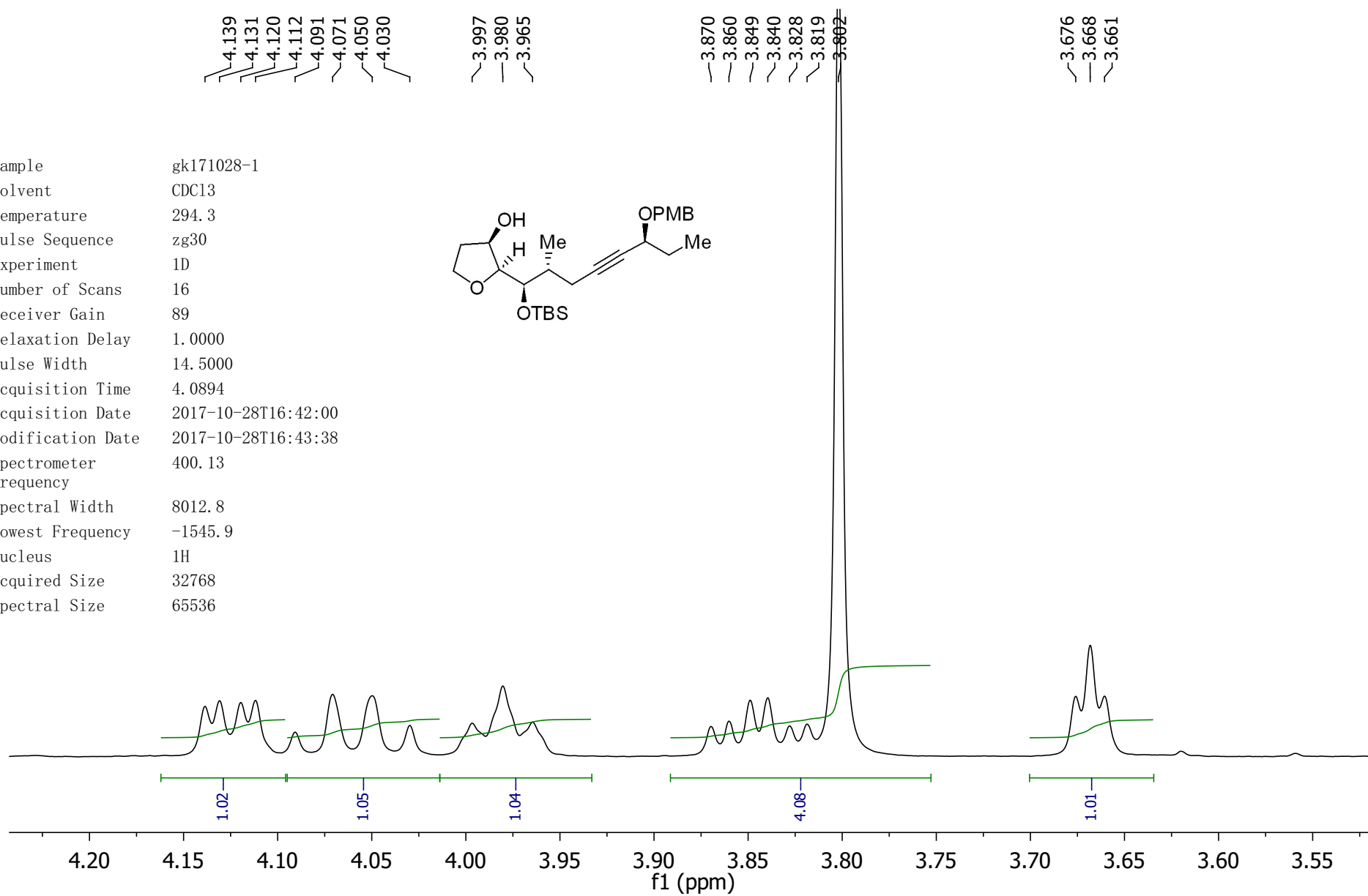
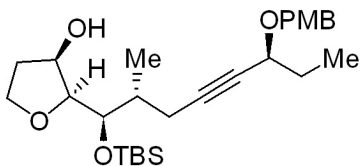
S172



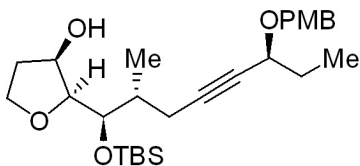
S173



Sample gk171028-1  
 Solvent CDC13  
 Temperature 294.3  
 Pulse Sequence zg30  
 Experiment 1D  
 Number of Scans 16  
 Receiver Gain 89  
 Relaxation Delay 1.0000  
 Pulse Width 14.5000  
 Acquisition Time 4.0894  
 Acquisition Date 2017-10-28T16:42:00  
 Modification Date 2017-10-28T16:43:38  
 Spectrometer 400.13  
 Frequency  
 Spectral Width 8012.8  
 Lowest Frequency -1545.9  
 Nucleus 1H  
 Acquired Size 32768  
 Spectral Size 65536



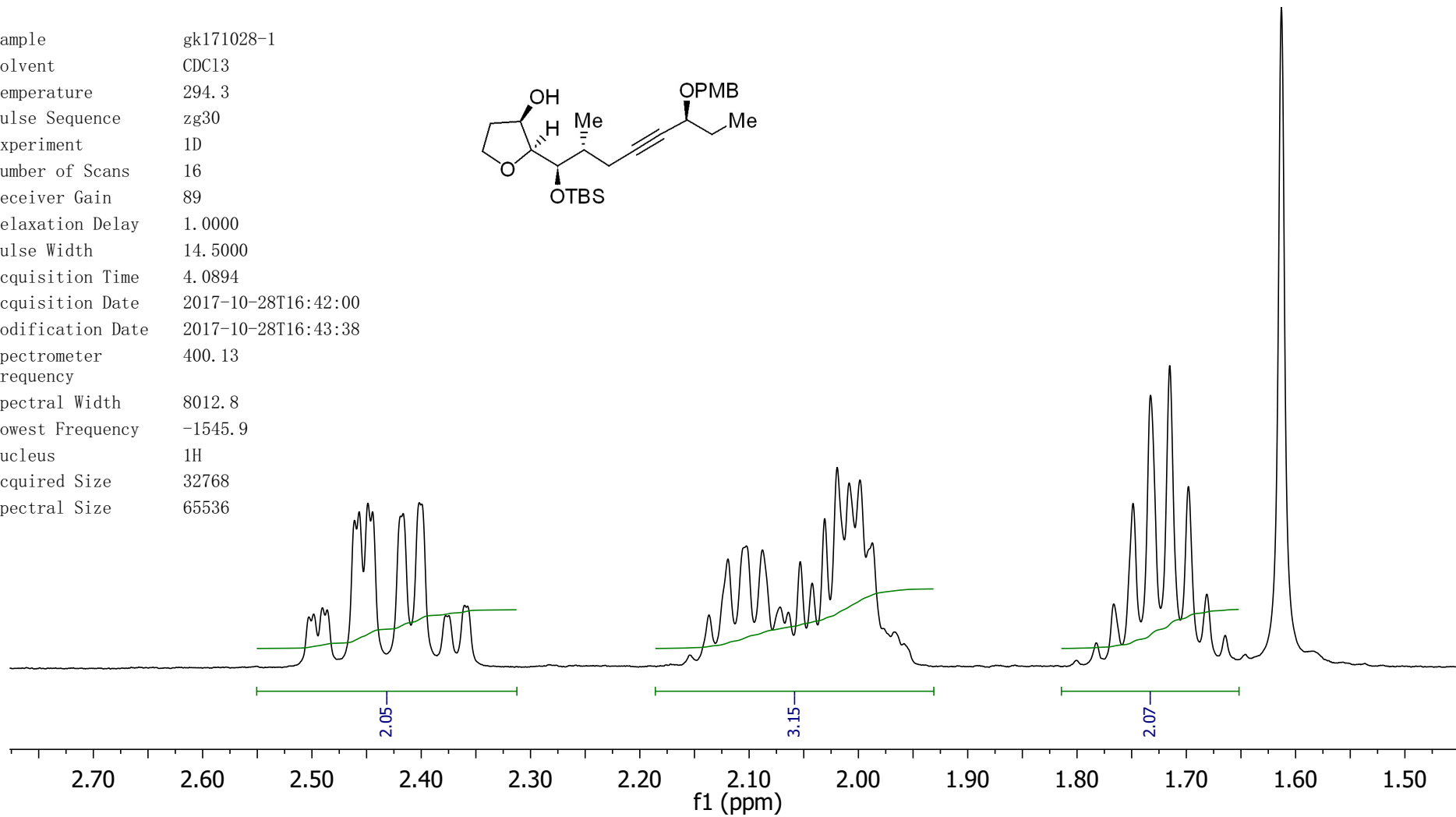
Sample gk171028-1  
 Solvent CDC13  
 Temperature 294.3  
 Pulse Sequence zg30  
 Experiment 1D  
 Number of Scans 16  
 Receiver Gain 89  
 Relaxation Delay 1.0000  
 Pulse Width 14.5000  
 Acquisition Time 4.0894  
 Acquisition Date 2017-10-28T16:42:00  
 Modification Date 2017-10-28T16:43:38  
 Spectrometer 400.13  
 Frequency  
 Spectral Width 8012.8  
 Lowest Frequency -1545.9  
 Nucleus 1H  
 Acquired Size 32768  
 Spectral Size 65536



2.503  
 2.498  
 2.490  
 2.486  
 2.461  
 2.457  
 2.449  
 2.445  
 2.417  
 2.402  
 2.375  
 2.360

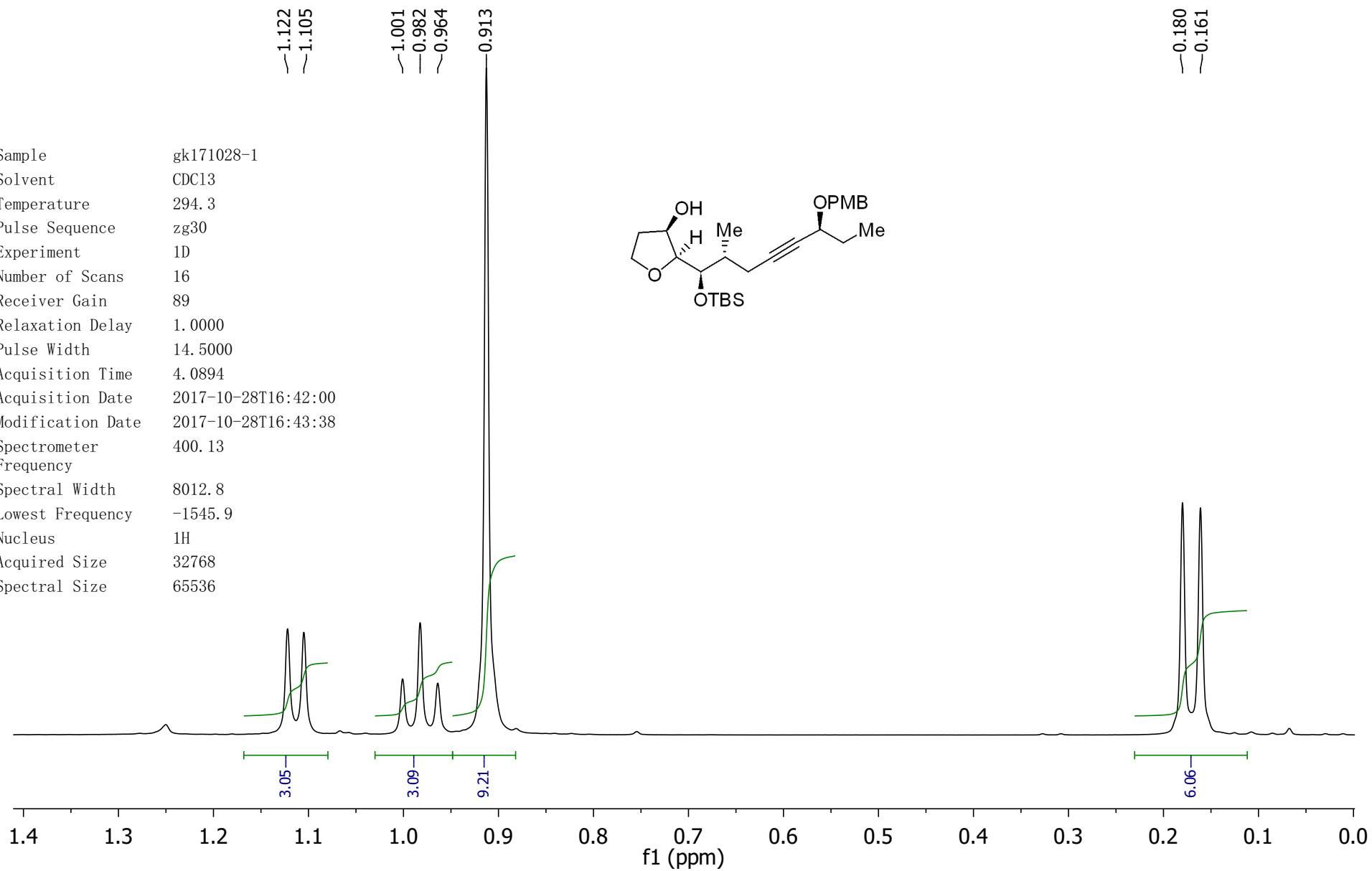
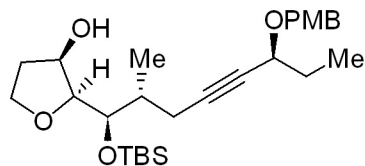
2.137  
 2.119  
 2.103  
 2.088  
 2.072  
 2.064  
 2.053  
 2.042  
 2.031  
 2.019  
 2.008  
 1.999  
 1.987

1.782  
 1.766  
 1.749  
 1.733  
 1.715  
 1.698  
 1.681  
 1.664  
 1.613

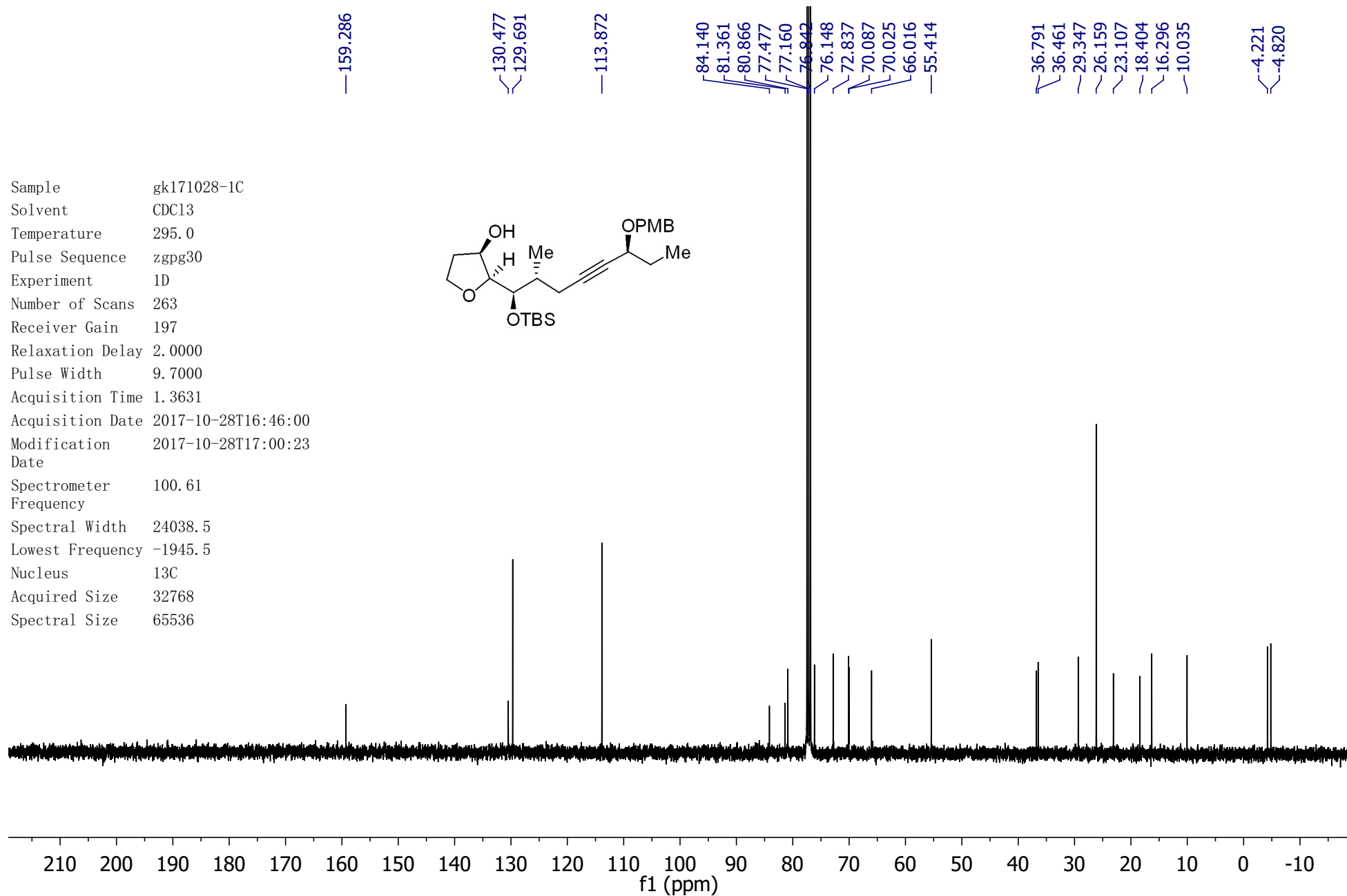
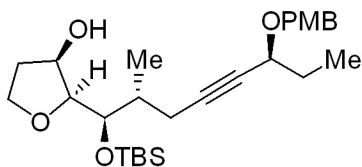




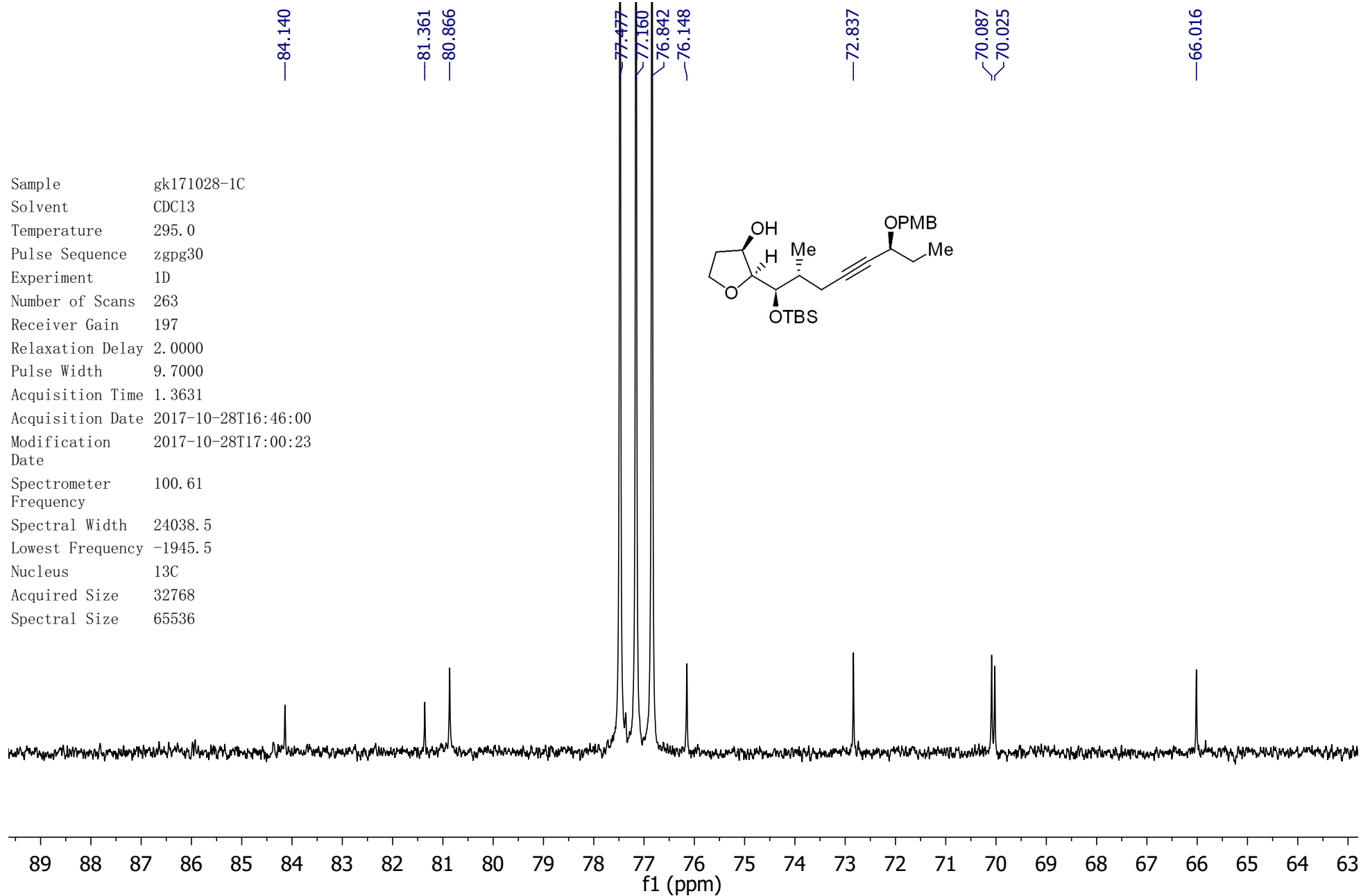
Sample gk171028-1  
Solvent CDC13  
Temperature 294.3  
Pulse Sequence zg30  
Experiment 1D  
Number of Scans 16  
Receiver Gain 89  
Relaxation Delay 1.0000  
Pulse Width 14.5000  
Acquisition Time 4.0894  
Acquisition Date 2017-10-28T16:42:00  
Modification Date 2017-10-28T16:43:38  
Spectrometer 400.13  
Frequency  
Spectral Width 8012.8  
Lowest Frequency -1545.9  
Nucleus 1H  
Acquired Size 32768  
Spectral Size 65536



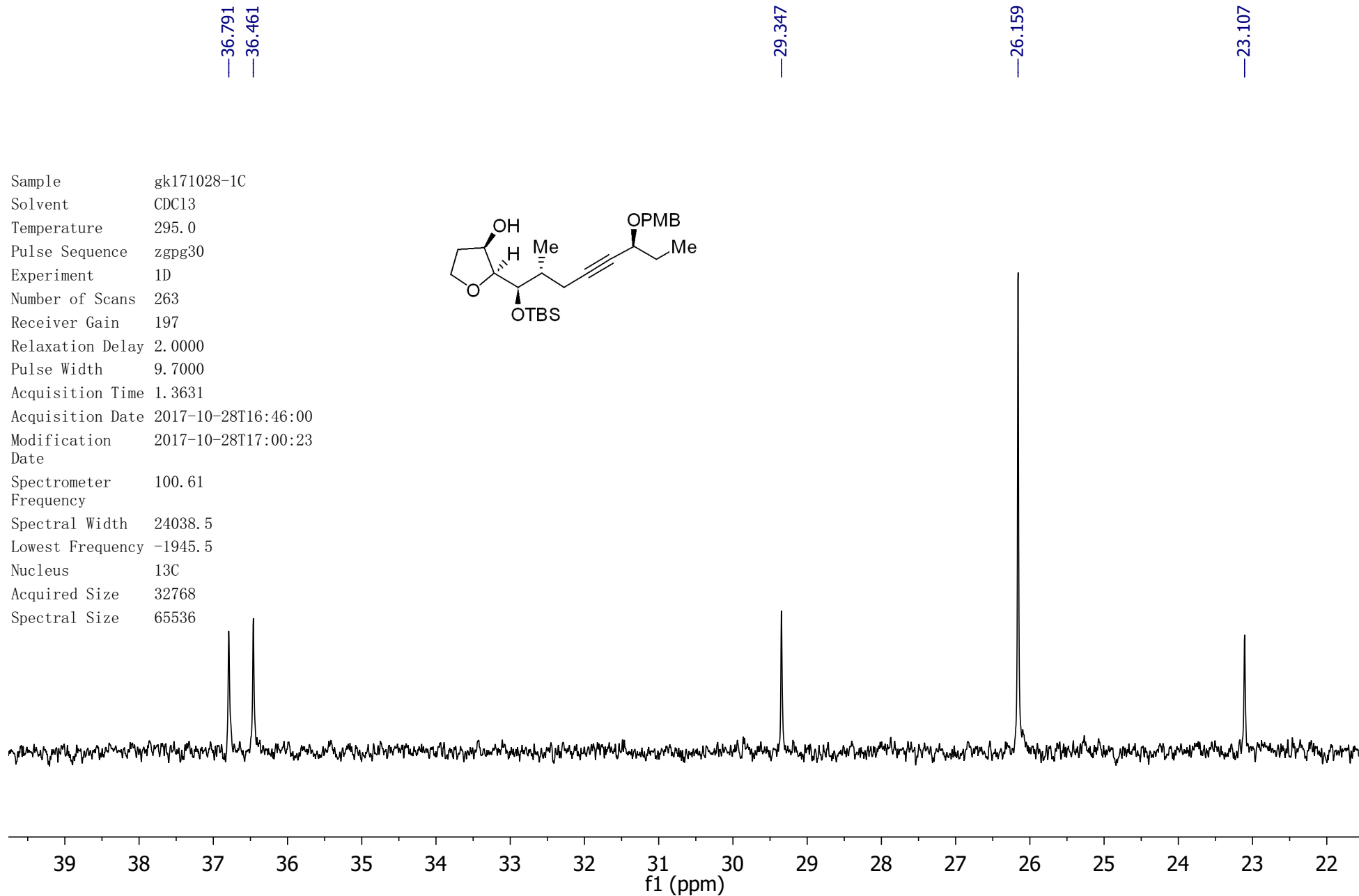
Sample gk171028-1C  
 Solvent CDC13  
 Temperature 295.0  
 Pulse Sequence zgpg30  
 Experiment 1D  
 Number of Scans 263  
 Receiver Gain 197  
 Relaxation Delay 2.0000  
 Pulse Width 9.7000  
 Acquisition Time 1.3631  
 Acquisition Date 2017-10-28T16:46:00  
 Modification Date 2017-10-28T17:00:23  
 Spectrometer 100.61  
 Frequency  
 Spectral Width 24038.5  
 Lowest Frequency -1945.5  
 Nucleus 13C  
 Acquired Size 32768  
 Spectral Size 65536

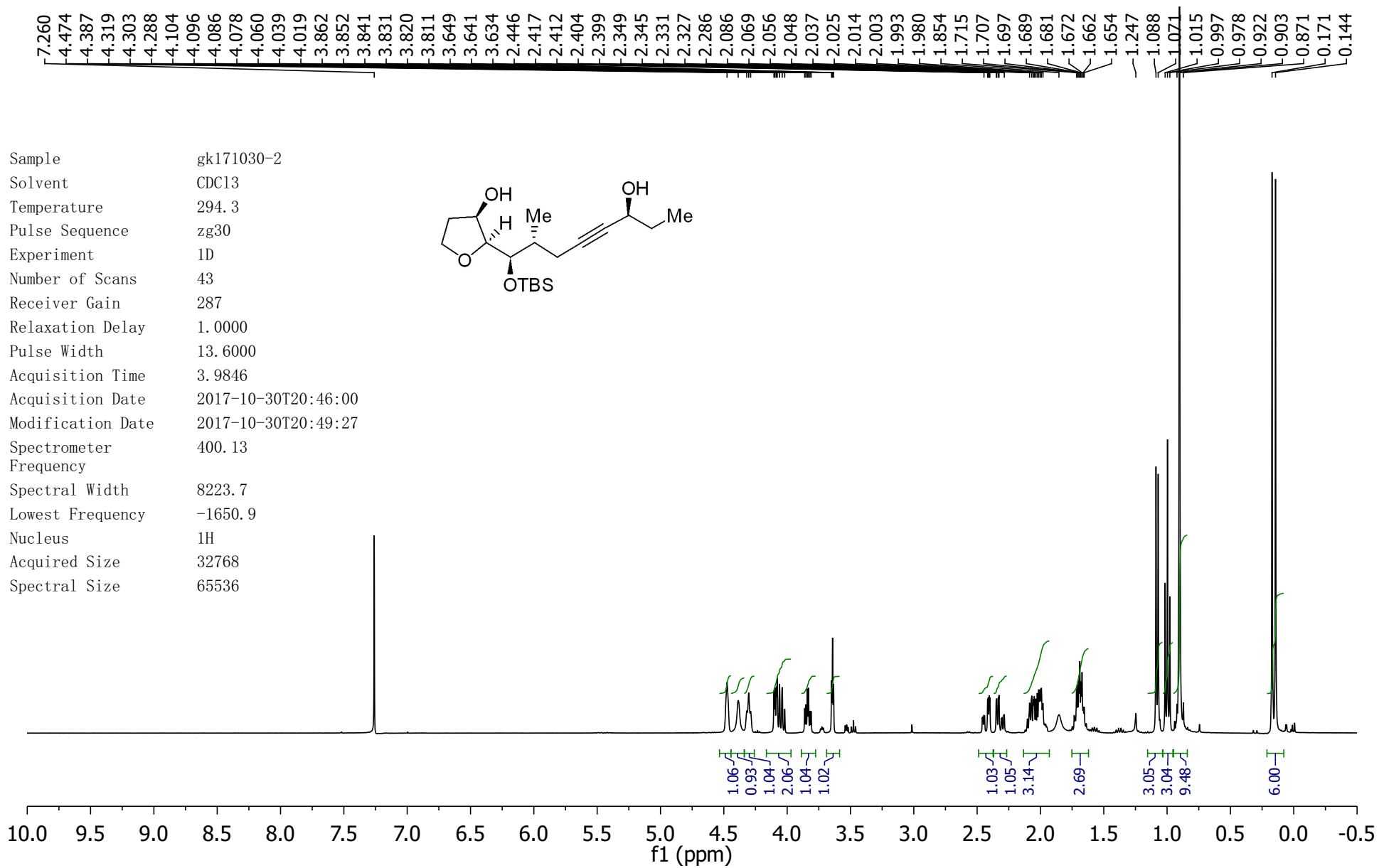


S178



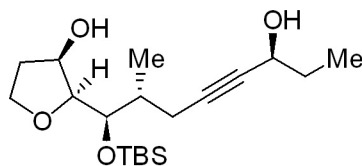
Sample gk171028-1C  
 Solvent CDC13  
 Temperature 295.0  
 Pulse Sequence zgpg30  
 Experiment 1D  
 Number of Scans 263  
 Receiver Gain 197  
 Relaxation Delay 2.0000  
 Pulse Width 9.7000  
 Acquisition Time 1.3631  
 Acquisition Date 2017-10-28T16:46:00  
 Modification 2017-10-28T17:00:23  
 Date  
 Spectrometer 100.61  
 Frequency  
 Spectral Width 24038.5  
 Lowest Frequency -1945.5  
 Nucleus 13C  
 Acquired Size 32768  
 Spectral Size 65536



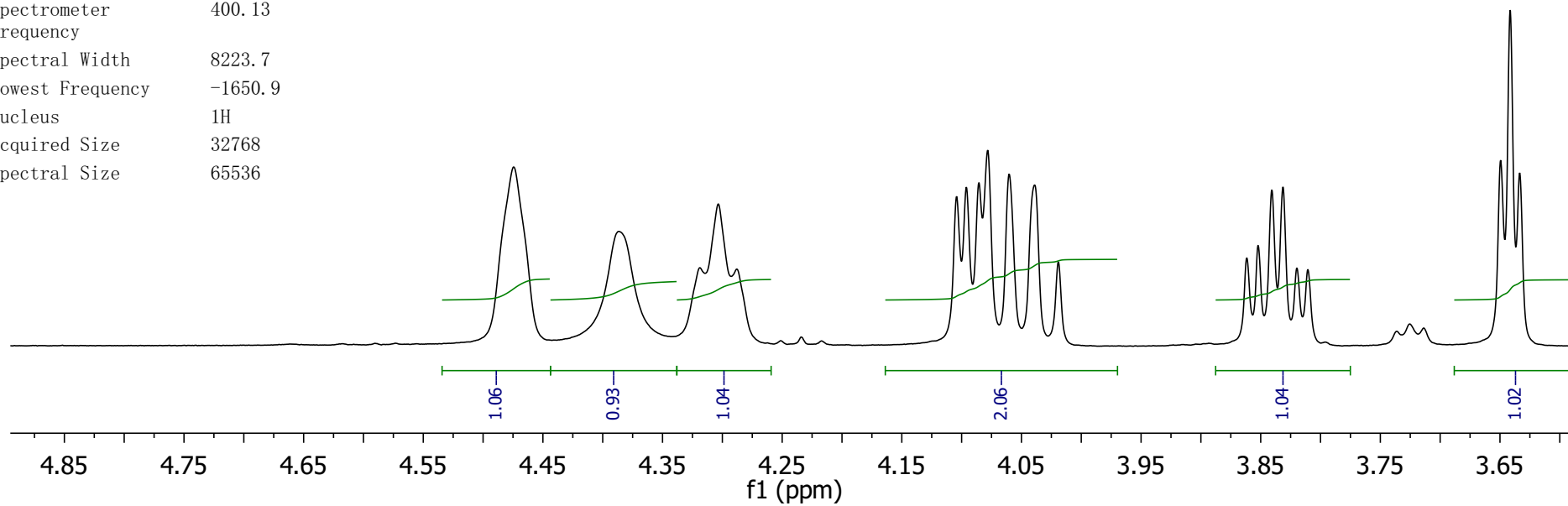


S181

Sample gk171030-2  
 Solvent CDCl3  
 Temperature 294.3  
 Pulse Sequence zg30  
 Experiment 1D  
 Number of Scans 43  
 Receiver Gain 287  
 Relaxation Delay 1.0000  
 Pulse Width 13.6000  
 Acquisition Time 3.9846  
 Acquisition Date 2017-10-30T20:46:00  
 Modification Date 2017-10-30T20:49:27  
 Spectrometer 400.13  
 Frequency  
 Spectral Width 8223.7  
 Lowest Frequency -1650.9  
 Nucleus 1H  
 Acquired Size 32768  
 Spectral Size 65536



—4.474      —4.387      —4.319  
 —4.303      —4.288      —4.104  
 —4.096      —4.086      —4.078  
 —4.060      —4.039      —4.019      —3.862  
 —3.852      —3.841      —3.831      —3.820  
 —3.811      —3.649      —3.641      —3.634



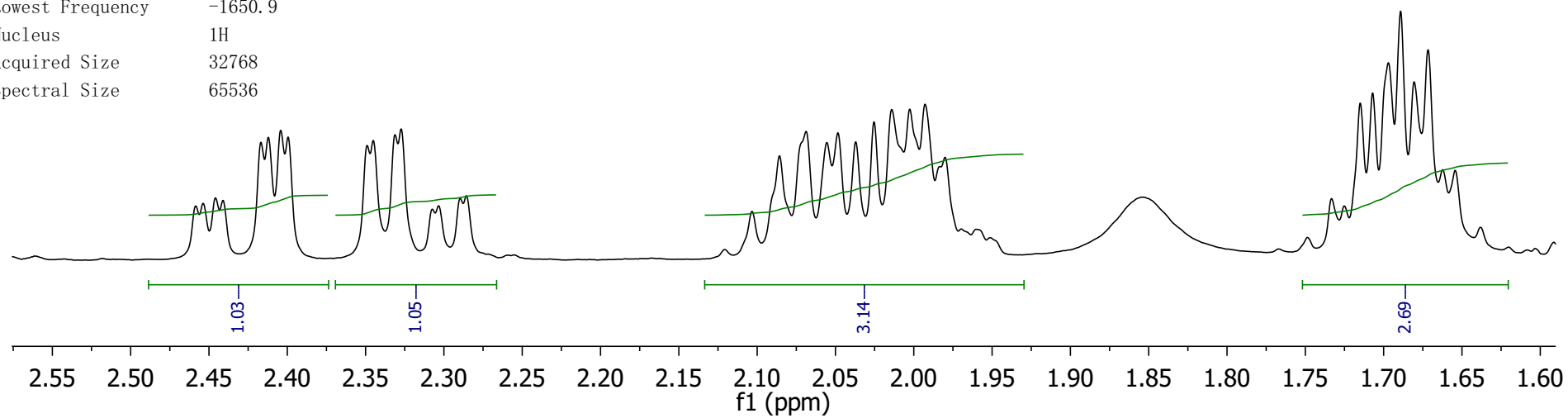
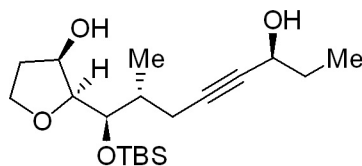
2.458  
2.454  
2.446  
2.441  
2.417  
2.412  
2.404  
2.399  
2.349  
2.345  
2.331  
2.327  
2.307  
2.303  
2.290  
2.286

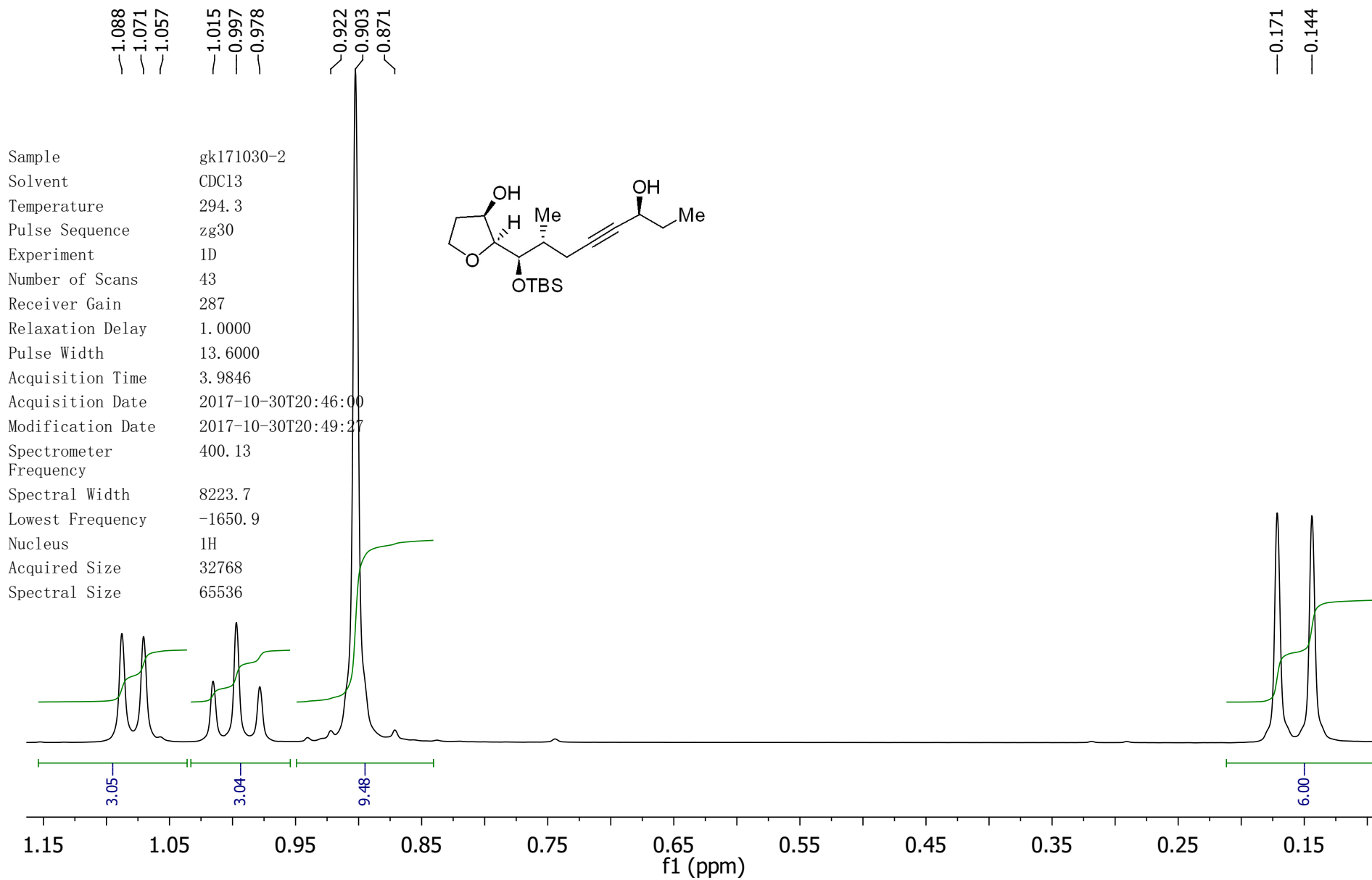
2.103  
2.086  
2.069  
2.056  
2.048  
2.037  
2.025  
2.014  
2.003  
1.993  
1.980

1.854

1.733  
1.725  
1.715  
1.707  
1.697  
1.689  
1.681  
1.672  
1.662  
1.654

Sample gk171030-2  
Solvent CDCl3  
Temperature 294.3  
Pulse Sequence zg30  
Experiment 1D  
Number of Scans 43  
Receiver Gain 287  
Relaxation Delay 1.0000  
Pulse Width 13.6000  
Acquisition Time 3.9846  
Acquisition Date 2017-10-30T20:46:00  
Modification Date 2017-10-30T20:49:27  
Spectrometer 400.13  
Frequency  
Spectral Width 8223.7  
Lowest Frequency -1650.9  
Nucleus 1H  
Acquired Size 32768  
Spectral Size 65536

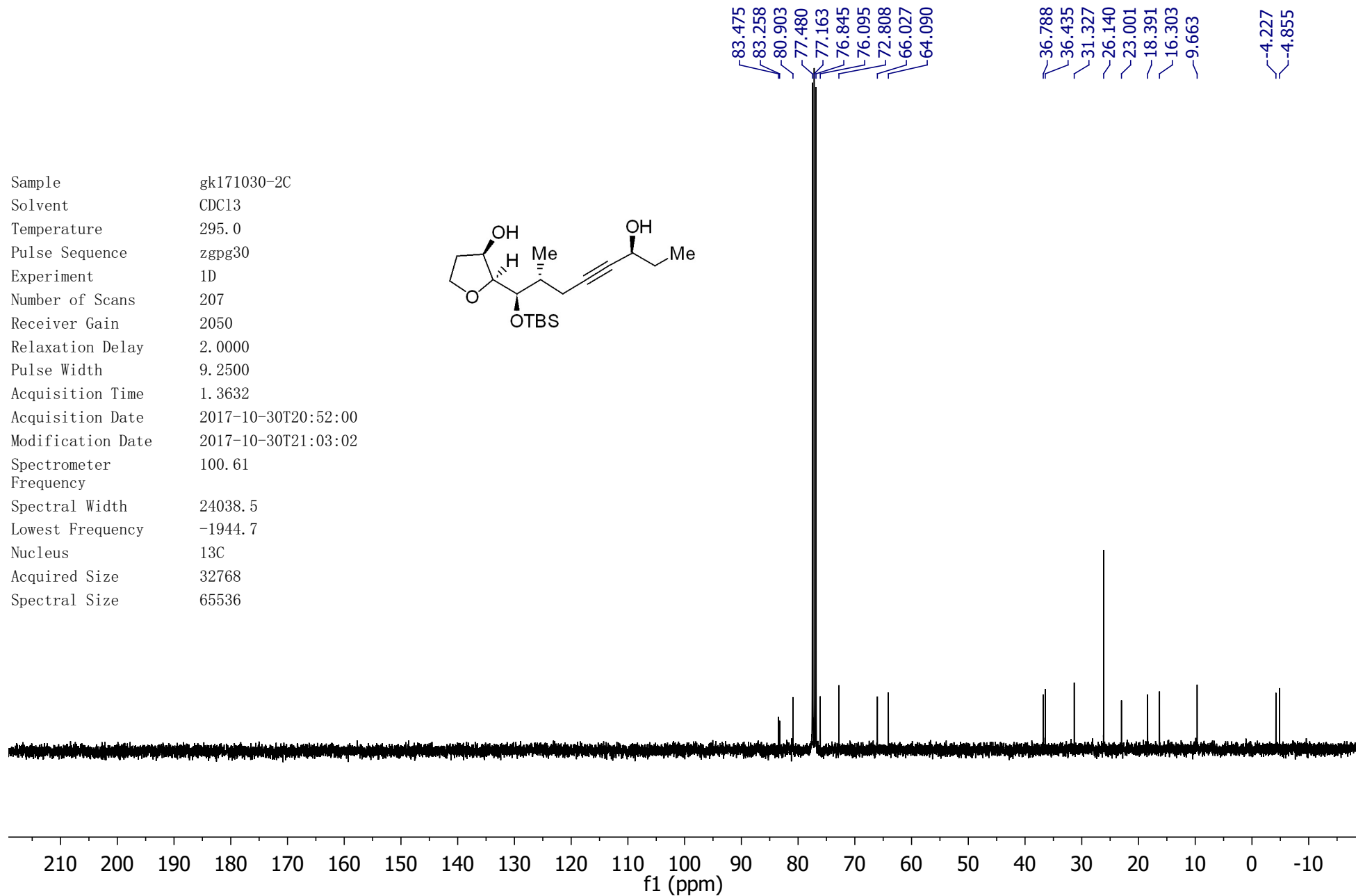
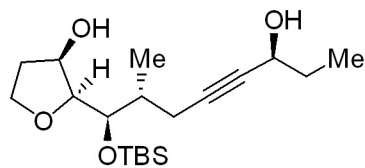




S184

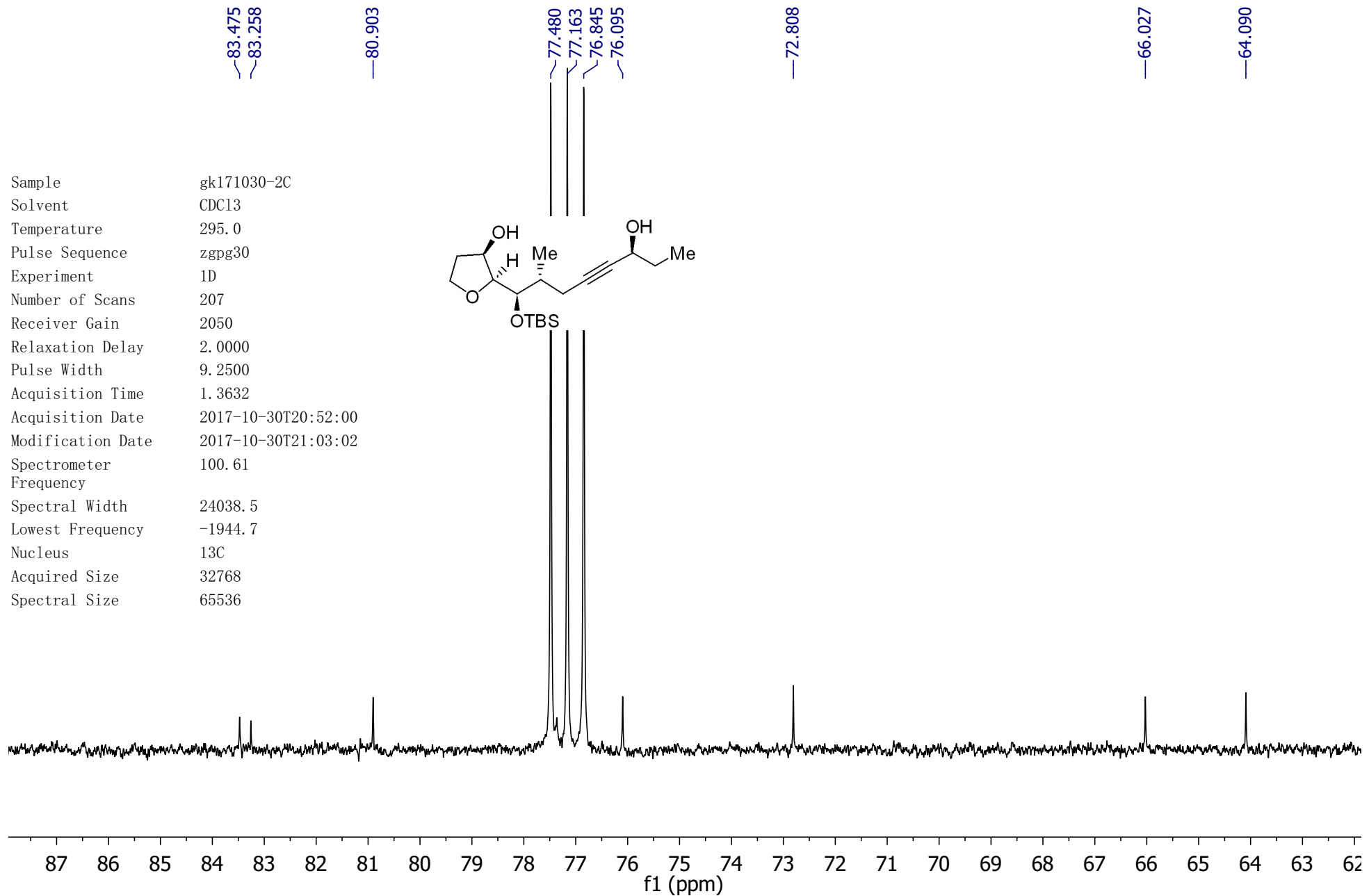
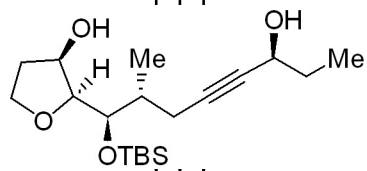


Sample gk171030-2C  
Solvent CDCl3  
Temperature 295.0  
Pulse Sequence zgpg30  
Experiment 1D  
Number of Scans 207  
Receiver Gain 2050  
Relaxation Delay 2.0000  
Pulse Width 9.2500  
Acquisition Time 1.3632  
Acquisition Date 2017-10-30T20:52:00  
Modification Date 2017-10-30T21:03:02  
Spectrometer 100.61  
Frequency  
Spectral Width 24038.5  
Lowest Frequency -1944.7  
Nucleus 13C  
Acquired Size 32768  
Spectral Size 65536

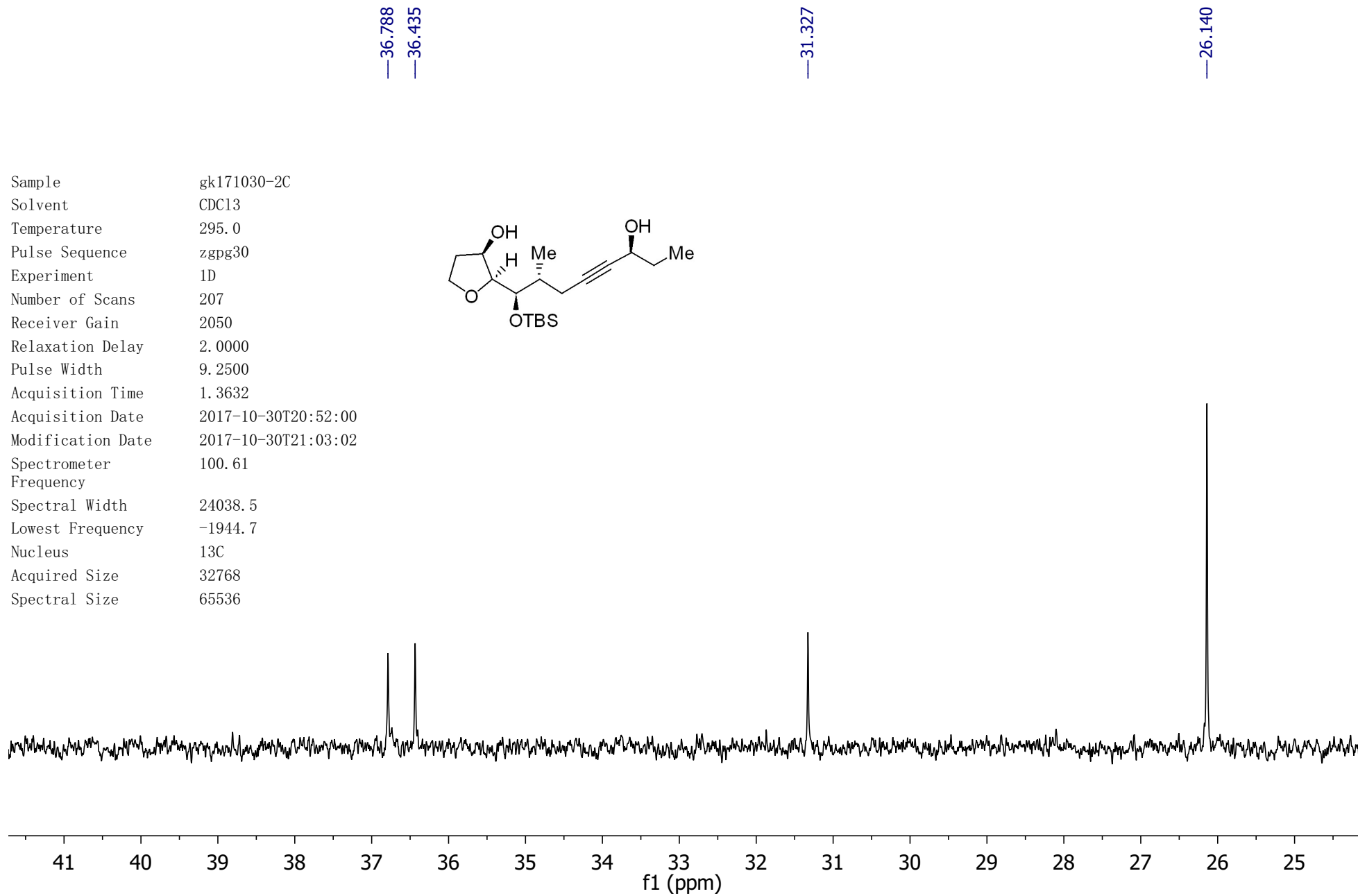
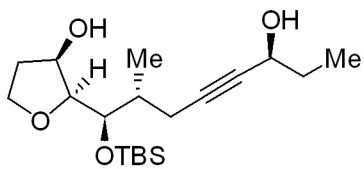


S185

Sample gk171030-2C  
Solvent CDC13  
Temperature 295.0  
Pulse Sequence zgpg30  
Experiment 1D  
Number of Scans 207  
Receiver Gain 2050  
Relaxation Delay 2.0000  
Pulse Width 9.2500  
Acquisition Time 1.3632  
Acquisition Date 2017-10-30T20:52:00  
Modification Date 2017-10-30T21:03:02  
Spectrometer 100.61  
Frequency  
Spectral Width 24038.5  
Lowest Frequency -1944.7  
Nucleus 13C  
Acquired Size 32768  
Spectral Size 65536

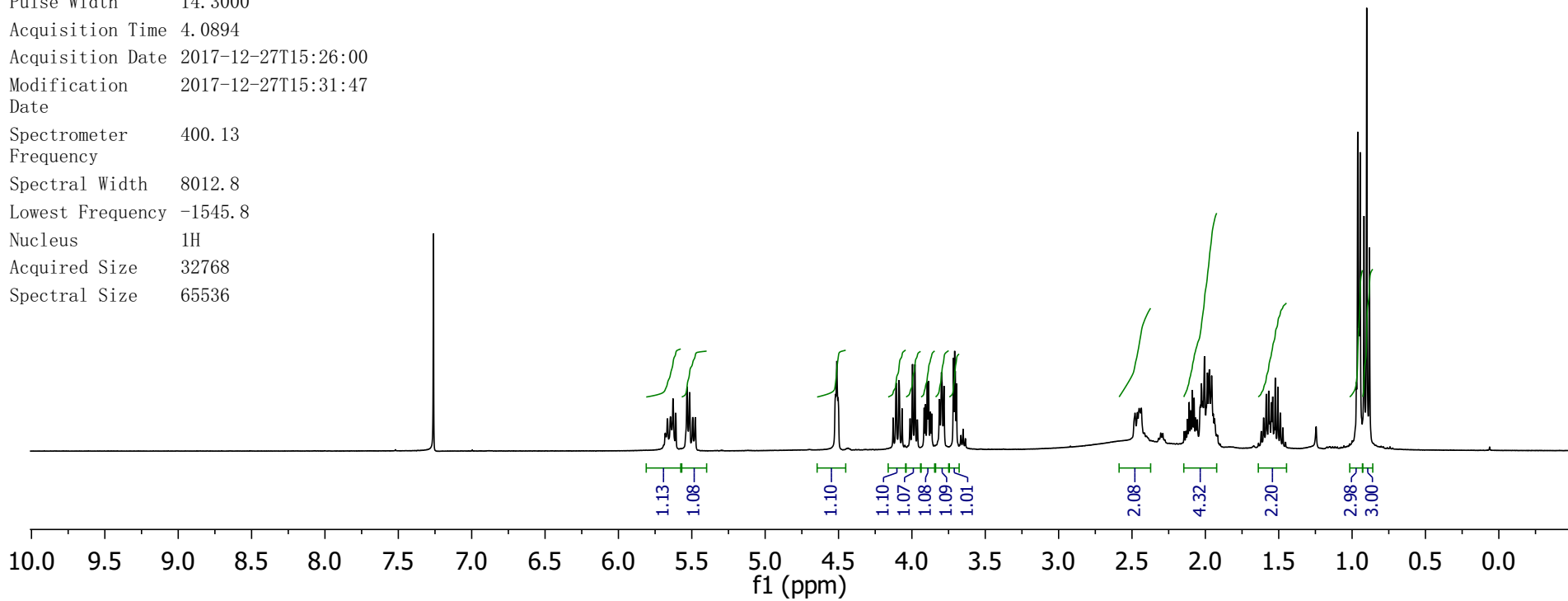
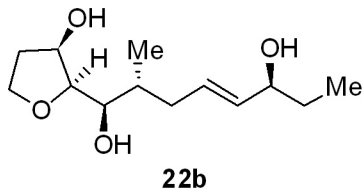


Sample gk171030-2C  
Solvent CDCl3  
Temperature 295.0  
Pulse Sequence zgpg30  
Experiment 1D  
Number of Scans 207  
Receiver Gain 2050  
Relaxation Delay 2.0000  
Pulse Width 9.2500  
Acquisition Time 1.3632  
Acquisition Date 2017-10-30T20:52:00  
Modification Date 2017-10-30T21:03:02  
Spectrometer 100.61  
Frequency  
Spectral Width 24038.5  
Lowest Frequency -1944.7  
Nucleus 13C  
Acquired Size 32768  
Spectral Size 65536



7.260  
5.645  
5.628  
5.609  
5.532  
5.515  
5.494  
5.476  
4.520  
4.512  
4.503  
4.107  
4.088  
4.067  
3.996  
3.979  
3.916  
3.907  
3.895  
3.886  
3.874  
3.865  
3.812  
3.798  
3.781  
3.717  
3.708  
3.704  
3.696  
2.479  
2.463  
2.451  
2.437  
2.111  
2.099  
2.088  
2.077  
2.066  
2.036  
2.033  
2.027  
2.019  
2.016  
2.006  
1.986  
1.973  
1.957  
1.946  
1.585  
1.568  
1.550  
1.541  
1.523  
1.506  
1.489  
0.970  
0.962  
0.954  
0.945  
0.919  
0.900  
0.882

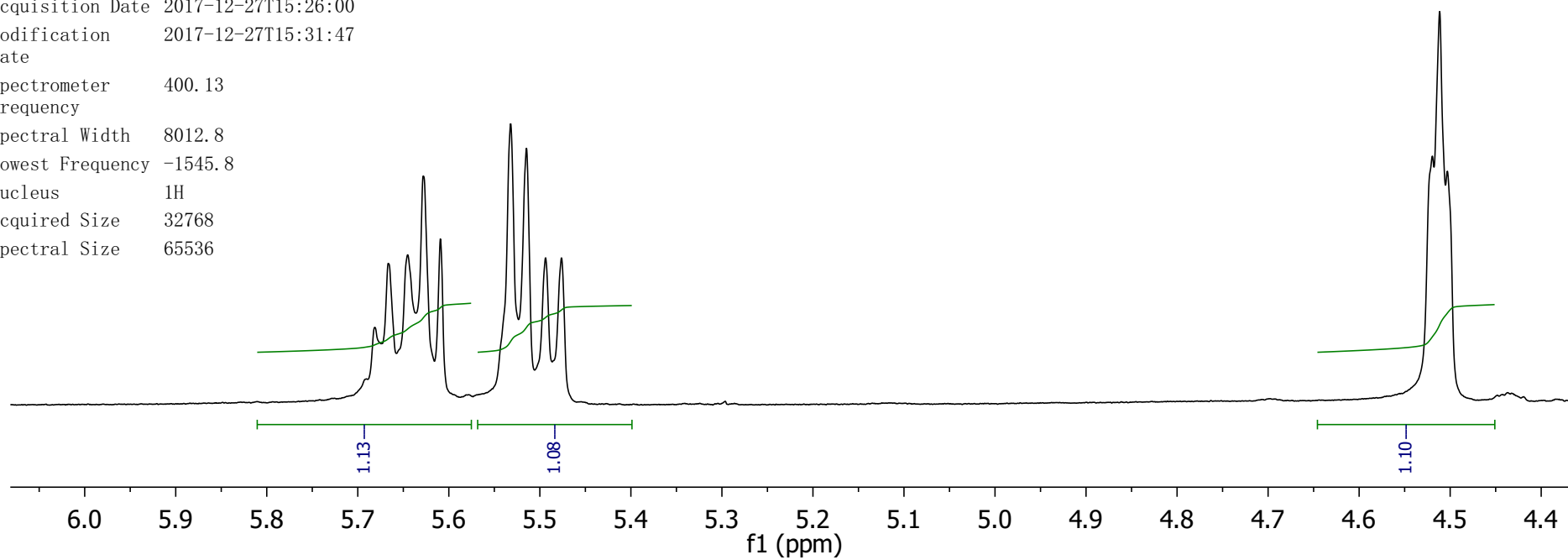
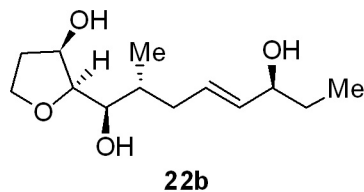
Sample gk171227-1  
 Solvent CDCl3  
 Temperature 294.3  
 Pulse Sequence zg30  
 Experiment 1D  
 Number of Scans 67  
 Receiver Gain 143  
 Relaxation Delay 1.0000  
 Pulse Width 14.3000  
 Acquisition Time 4.0894  
 Acquisition Date 2017-12-27T15:26:00  
 Modification 2017-12-27T15:31:47  
 Date  
 Spectrometer 400.13  
 Frequency  
 Spectral Width 8012.8  
 Lowest Frequency -1545.8  
 Nucleus 1H  
 Acquired Size 32768  
 Spectral Size 65536



5.681  
5.666  
5.645  
5.628  
5.609  
5.532  
5.515  
5.494  
5.476

4.520  
4.512  
4.503

Sample gk171227-1  
Solvent CDCl3  
Temperature 294.3  
Pulse Sequence zg30  
Experiment 1D  
Number of Scans 67  
Receiver Gain 143  
Relaxation Delay 1.0000  
Pulse Width 14.3000  
Acquisition Time 4.0894  
Acquisition Date 2017-12-27T15:26:00  
Modification 2017-12-27T15:31:47  
Date  
Spectrometer 400.13  
Frequency  
Spectral Width 8012.8  
Lowest Frequency -1545.8  
Nucleus 1H  
Acquired Size 32768  
Spectral Size 65536



4.127  
4.107  
4.088  
4.067

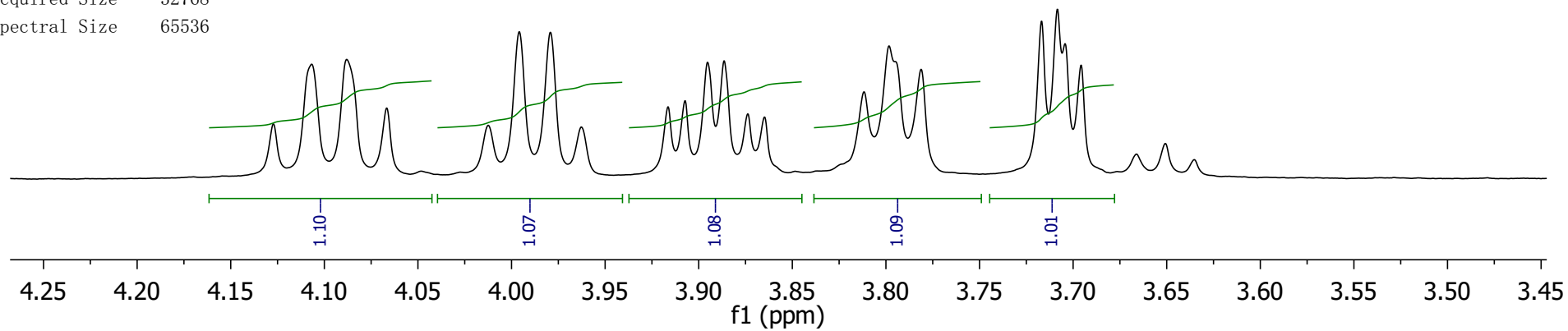
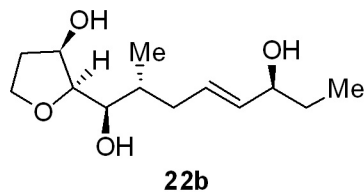
4.012  
3.996  
3.979  
3.963

3.916  
3.907  
3.895  
3.886  
3.874  
3.865

3.812  
3.798  
3.781

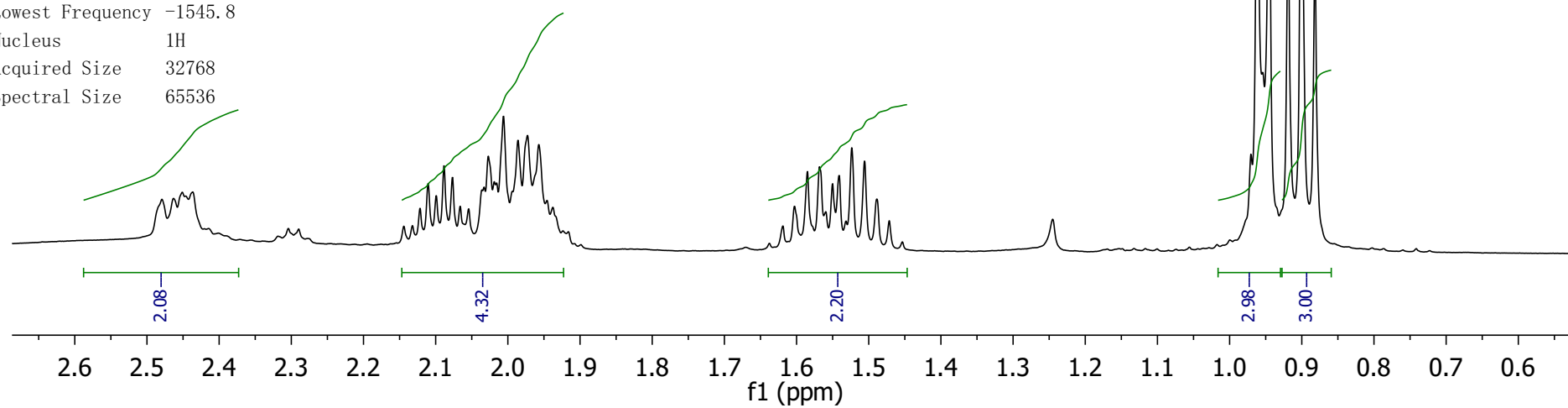
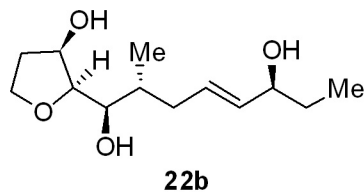
3.717  
3.708  
3.704  
3.696

Sample gk171227-1  
Solvent CDCl3  
Temperature 294.3  
Pulse Sequence zg30  
Experiment 1D  
Number of Scans 67  
Receiver Gain 143  
Relaxation Delay 1.0000  
Pulse Width 14.3000  
Acquisition Time 4.0894  
Acquisition Date 2017-12-27T15:26:00  
Modification 2017-12-27T15:31:47  
Date  
Spectrometer 400.13  
Frequency  
Spectral Width 8012.8  
Lowest Frequency -1545.8  
Nucleus 1H  
Acquired Size 32768  
Spectral Size 65536

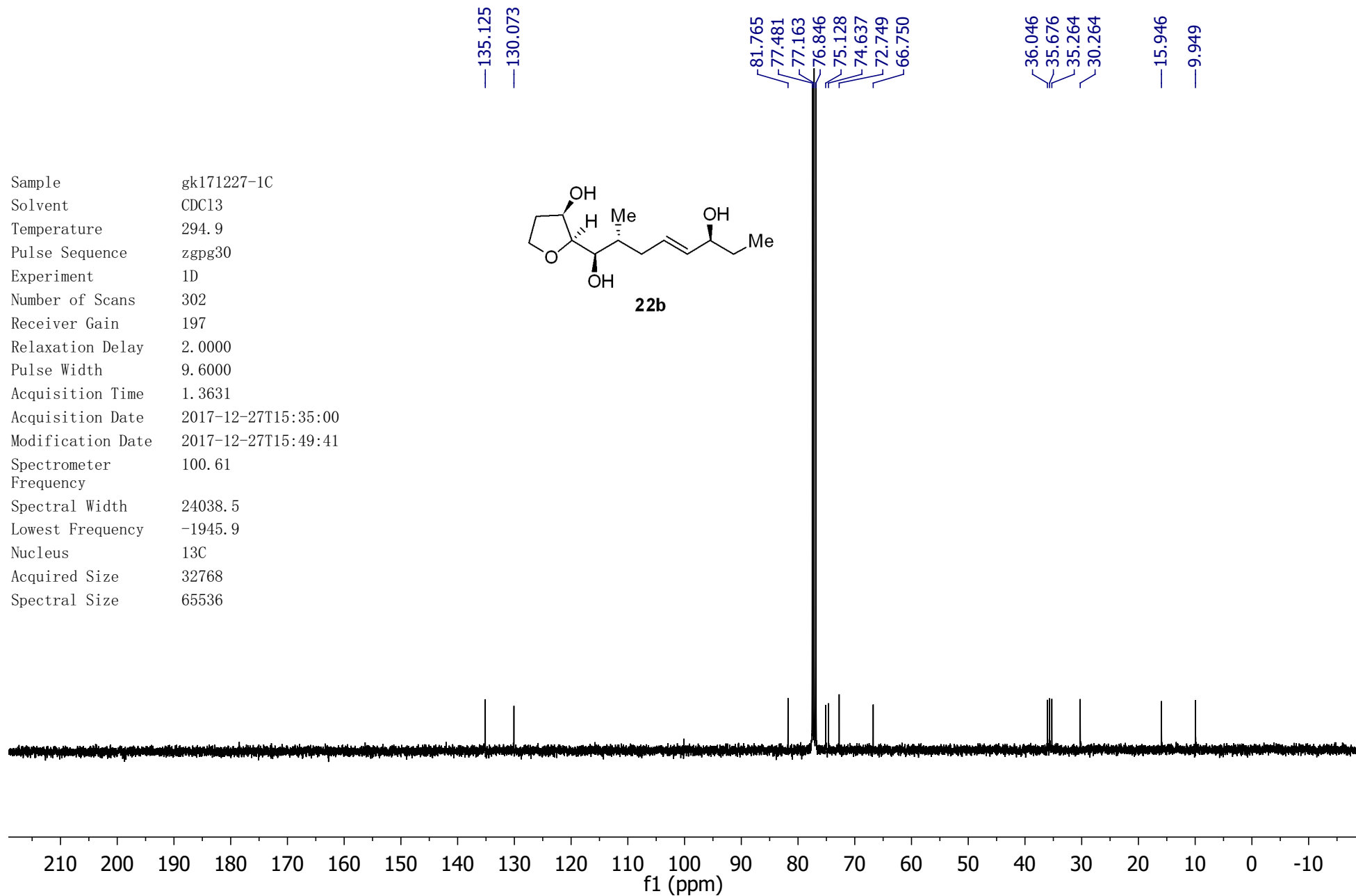
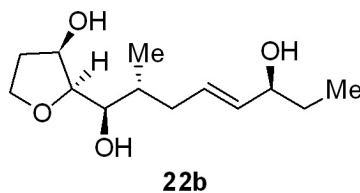


2.479  
2.463  
2.451  
2.437  
2.122  
2.111  
2.099  
2.088  
2.077  
2.066  
2.054  
2.036  
2.033  
2.027  
2.019  
2.016  
2.006  
1.986  
1.973  
1.957  
1.946  
1.938  
1.903  
1.585  
1.568  
1.560  
1.550  
1.541  
1.532  
1.523  
1.506  
1.489  
1.472  
—1.245  
0.962  
0.945  
0.919  
0.900  
0.882

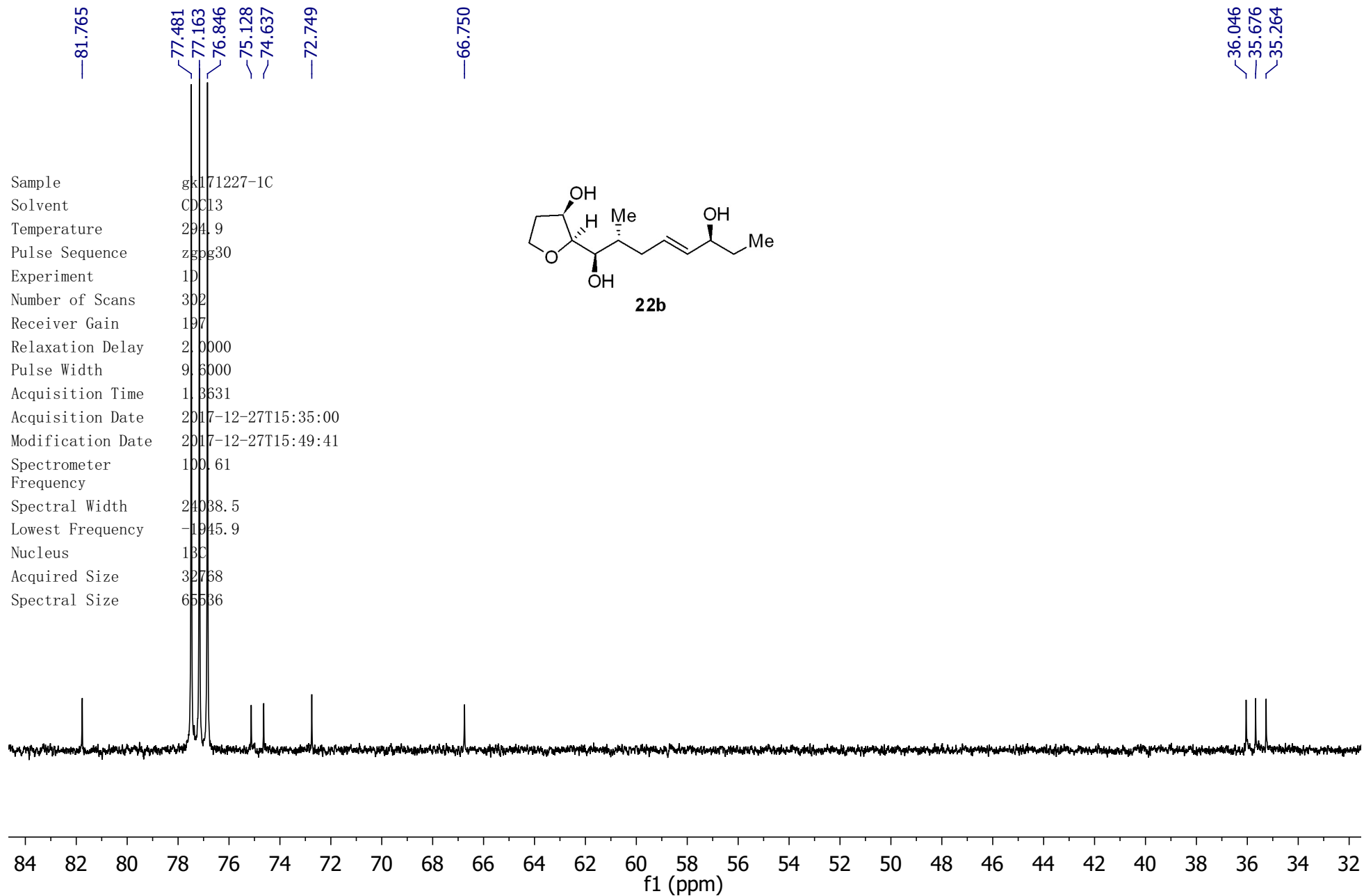
Sample gk171227-1  
Solvent CDCl3  
Temperature 294.3  
Pulse Sequence zg30  
Experiment 1D  
Number of Scans 67  
Receiver Gain 143  
Relaxation Delay 1.0000  
Pulse Width 14.3000  
Acquisition Time 4.0894  
Acquisition Date 2017-12-27T15:26:00  
Modification 2017-12-27T15:31:47  
Date  
Spectrometer 400.13  
Frequency  
Spectral Width 8012.8  
Lowest Frequency -1545.8  
Nucleus 1H  
Acquired Size 32768  
Spectral Size 65536

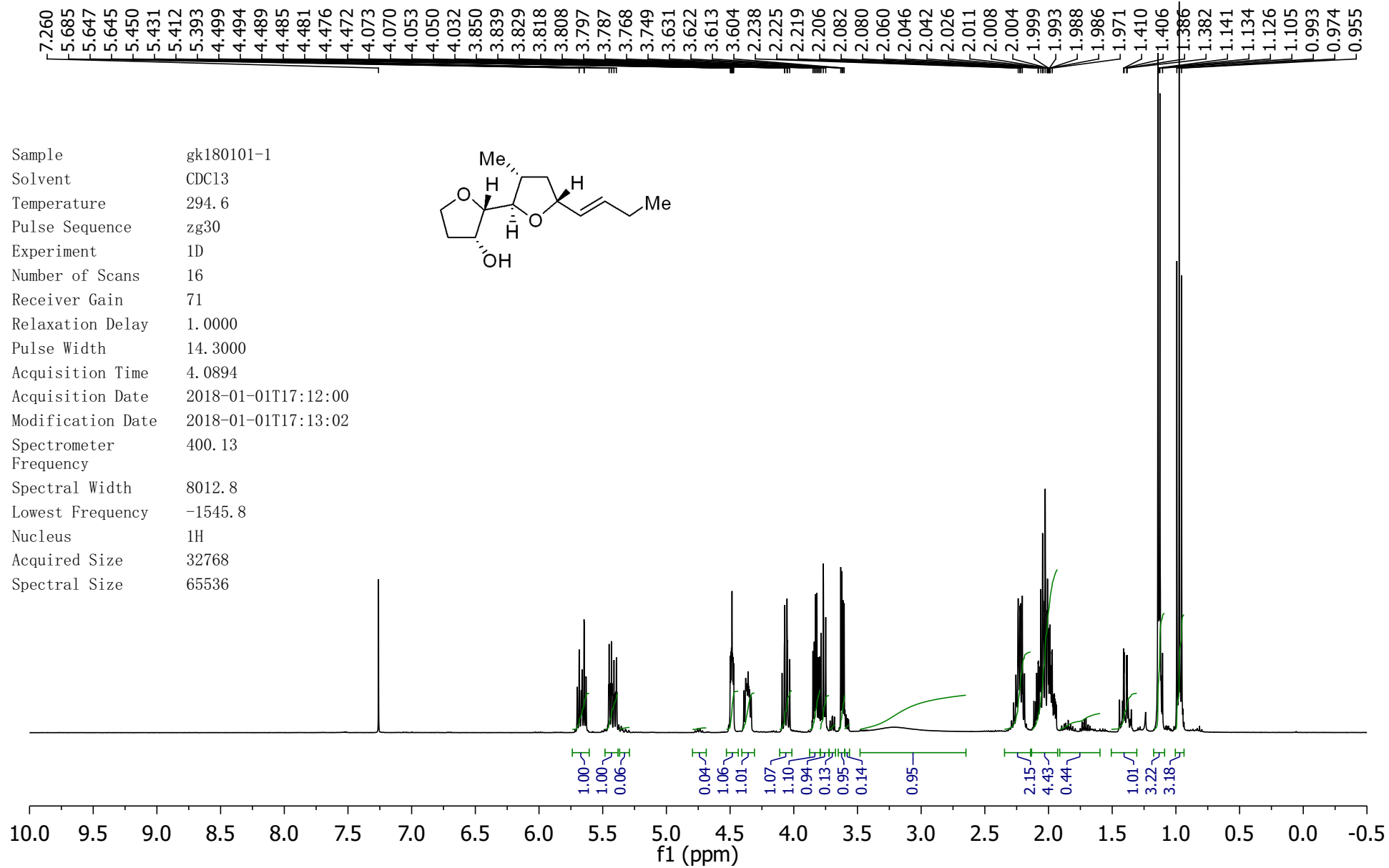


Sample gk171227-1C  
 Solvent CDC13  
 Temperature 294.9  
 Pulse Sequence zgpg30  
 Experiment 1D  
 Number of Scans 302  
 Receiver Gain 197  
 Relaxation Delay 2.0000  
 Pulse Width 9.6000  
 Acquisition Time 1.3631  
 Acquisition Date 2017-12-27T15:35:00  
 Modification Date 2017-12-27T15:49:41  
 Spectrometer 100.61  
 Frequency  
 Spectral Width 24038.5  
 Lowest Frequency -1945.9  
 Nucleus <sup>13</sup>C  
 Acquired Size 32768  
 Spectral Size 65536





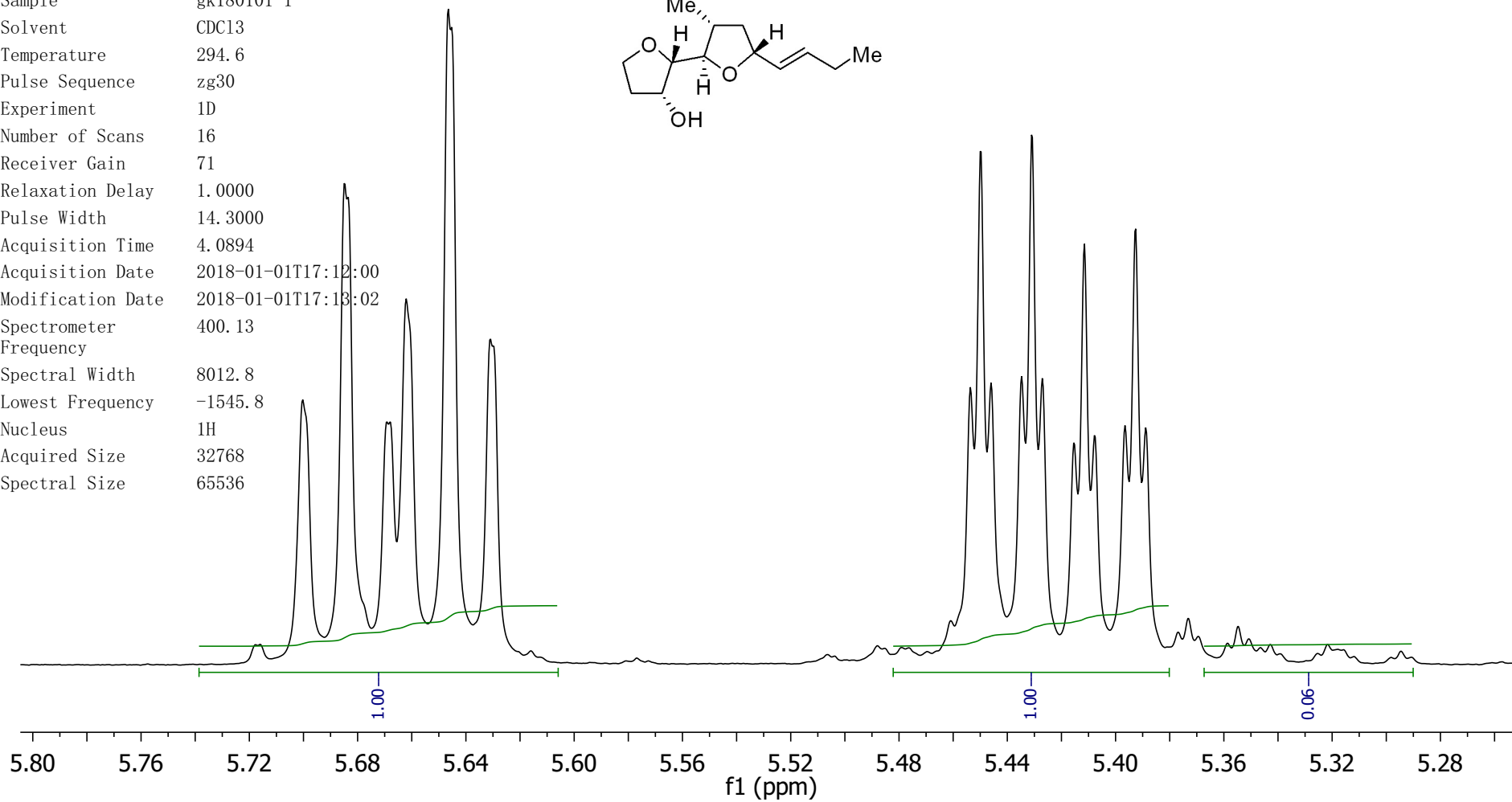
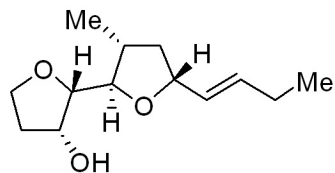




5.700  
5.685  
5.684  
5.669  
5.668  
5.662  
5.647  
5.645  
5.631  
5.630

5.454  
5.450  
5.446  
5.435  
5.431  
5.427  
5.415  
5.412  
5.408  
5.397  
5.393  
5.389

Sample gk180101-1  
Solvent CDC13  
Temperature 294.6  
Pulse Sequence zg30  
Experiment 1D  
Number of Scans 16  
Receiver Gain 71  
Relaxation Delay 1.0000  
Pulse Width 14.3000  
Acquisition Time 4.0894  
Acquisition Date 2018-01-01T17:12:00  
Modification Date 2018-01-01T17:13:02  
Spectrometer 400.13  
Frequency  
Spectral Width 8012.8  
Lowest Frequency -1545.8  
Nucleus 1H  
Acquired Size 32768  
Spectral Size 65536

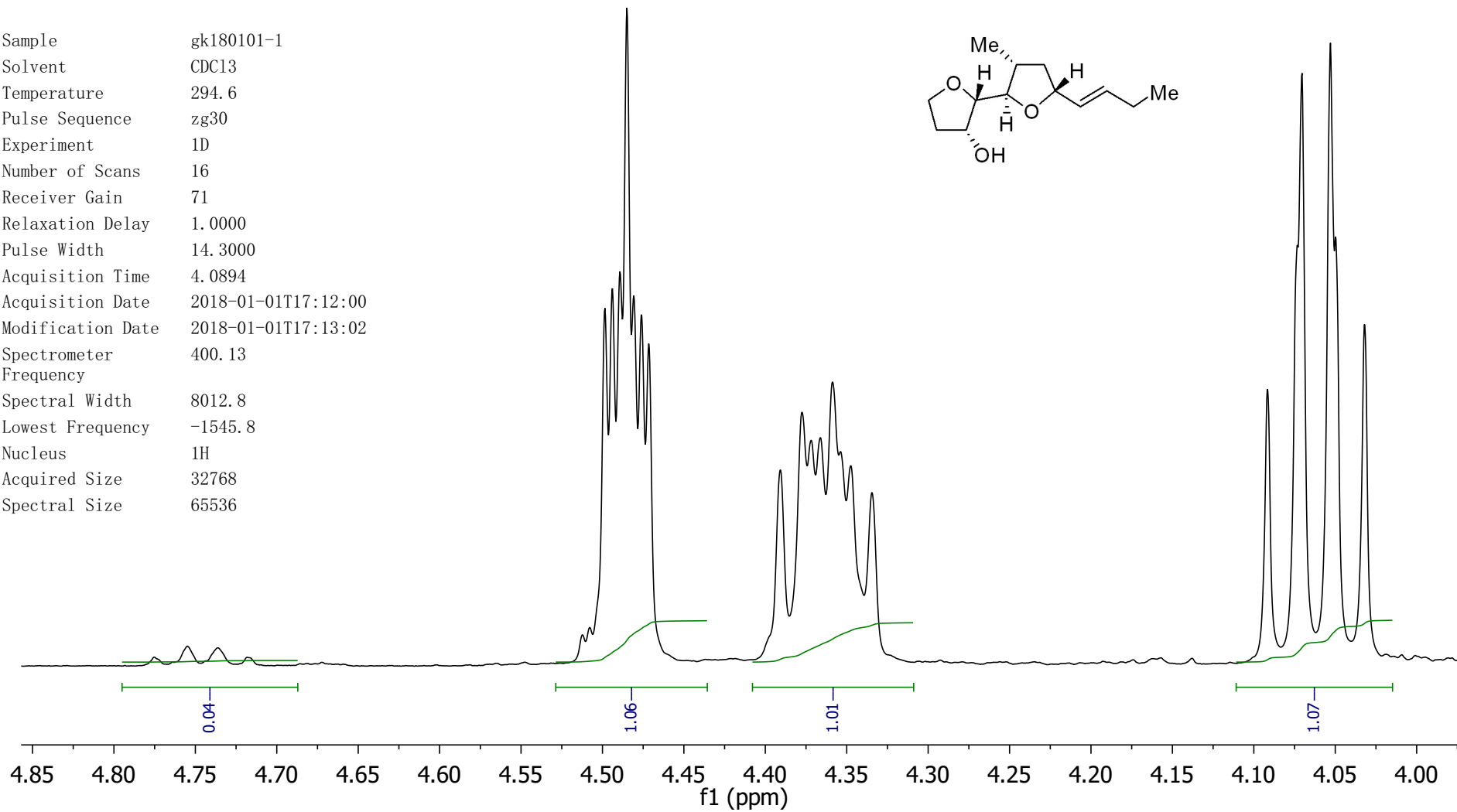
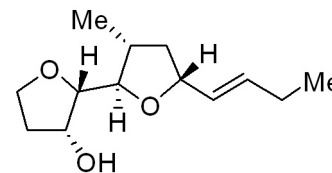


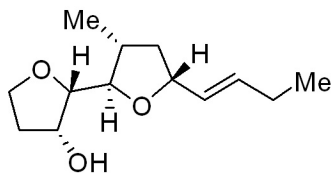
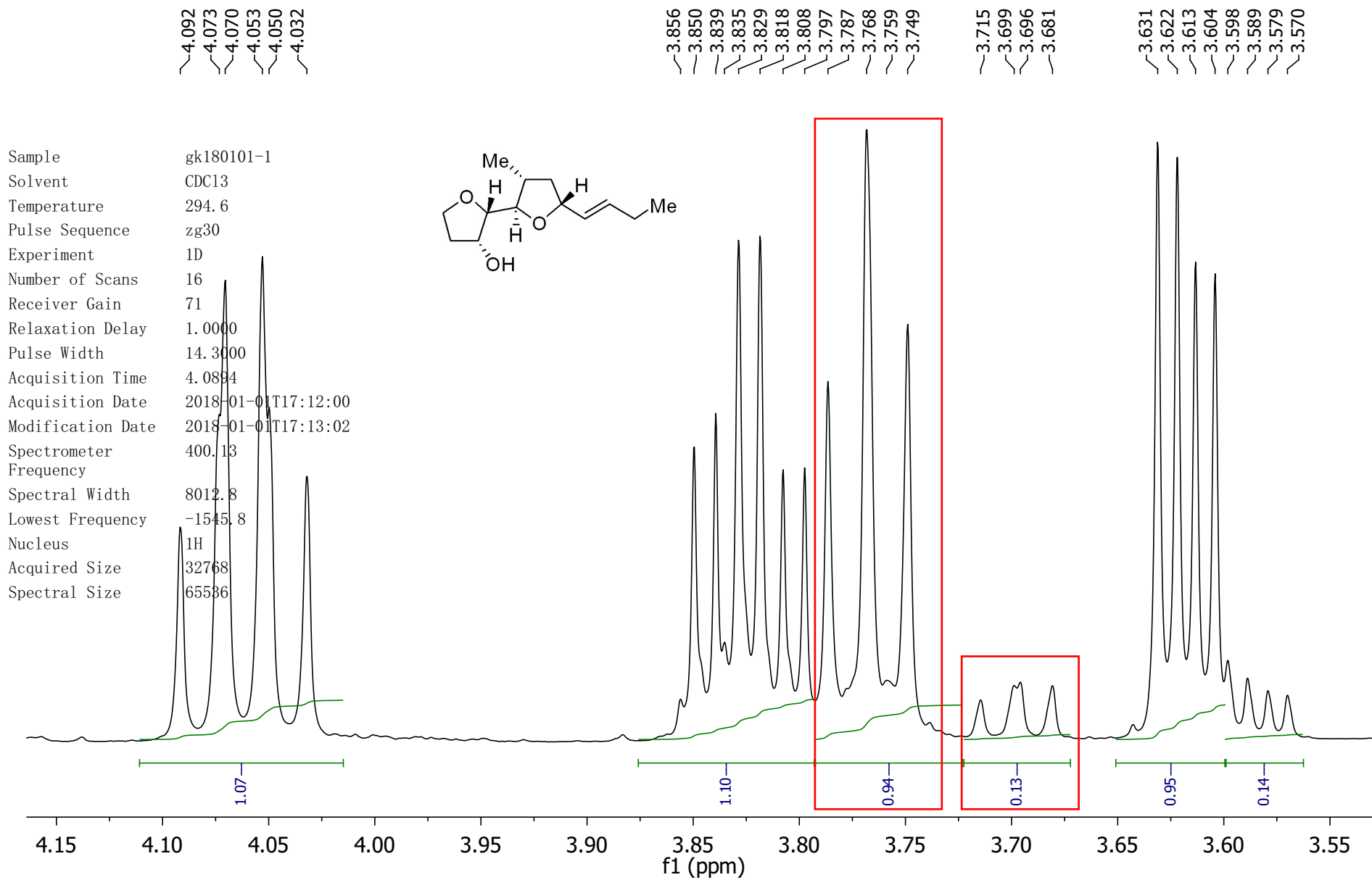
4.775  
4.755  
4.736  
4.718

4.499  
4.494  
4.489  
4.485  
4.481  
4.476  
4.472  
4.391  
4.377  
4.372  
4.366  
4.359  
4.354  
4.348  
4.335

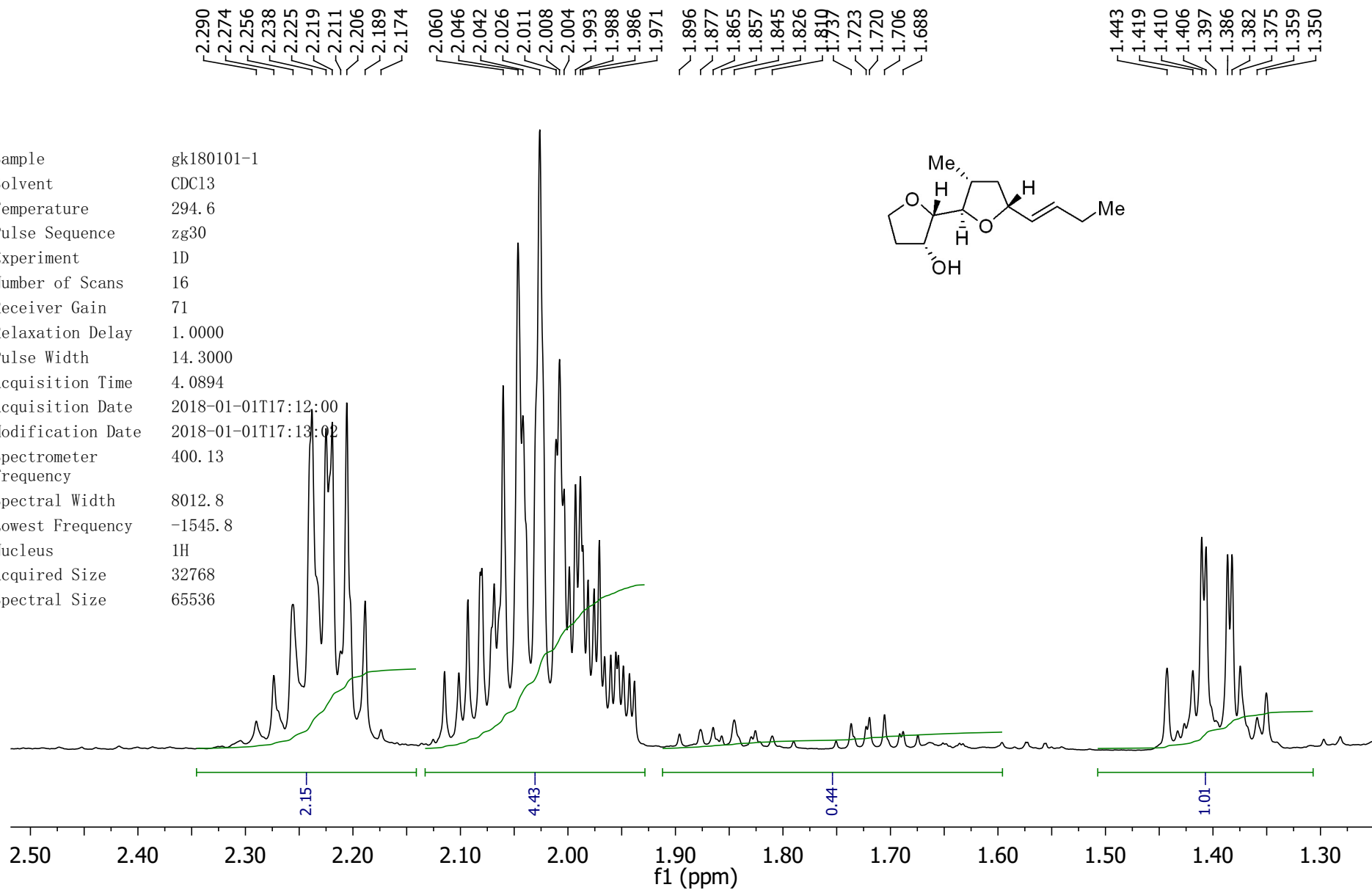
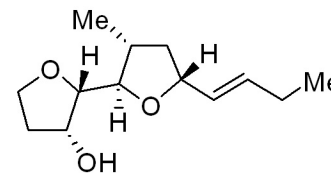
4.092  
4.073  
4.070  
4.053  
4.050  
4.032

Sample gk180101-1  
Solvent CDCl3  
Temperature 294.6  
Pulse Sequence zg30  
Experiment 1D  
Number of Scans 16  
Receiver Gain 71  
Relaxation Delay 1.0000  
Pulse Width 14.3000  
Acquisition Time 4.0894  
Acquisition Date 2018-01-01T17:12:00  
Modification Date 2018-01-01T17:13:02  
Spectrometer 400.13  
Frequency  
Spectral Width 8012.8  
Lowest Frequency -1545.8  
Nucleus 1H  
Acquired Size 32768  
Spectral Size 65536

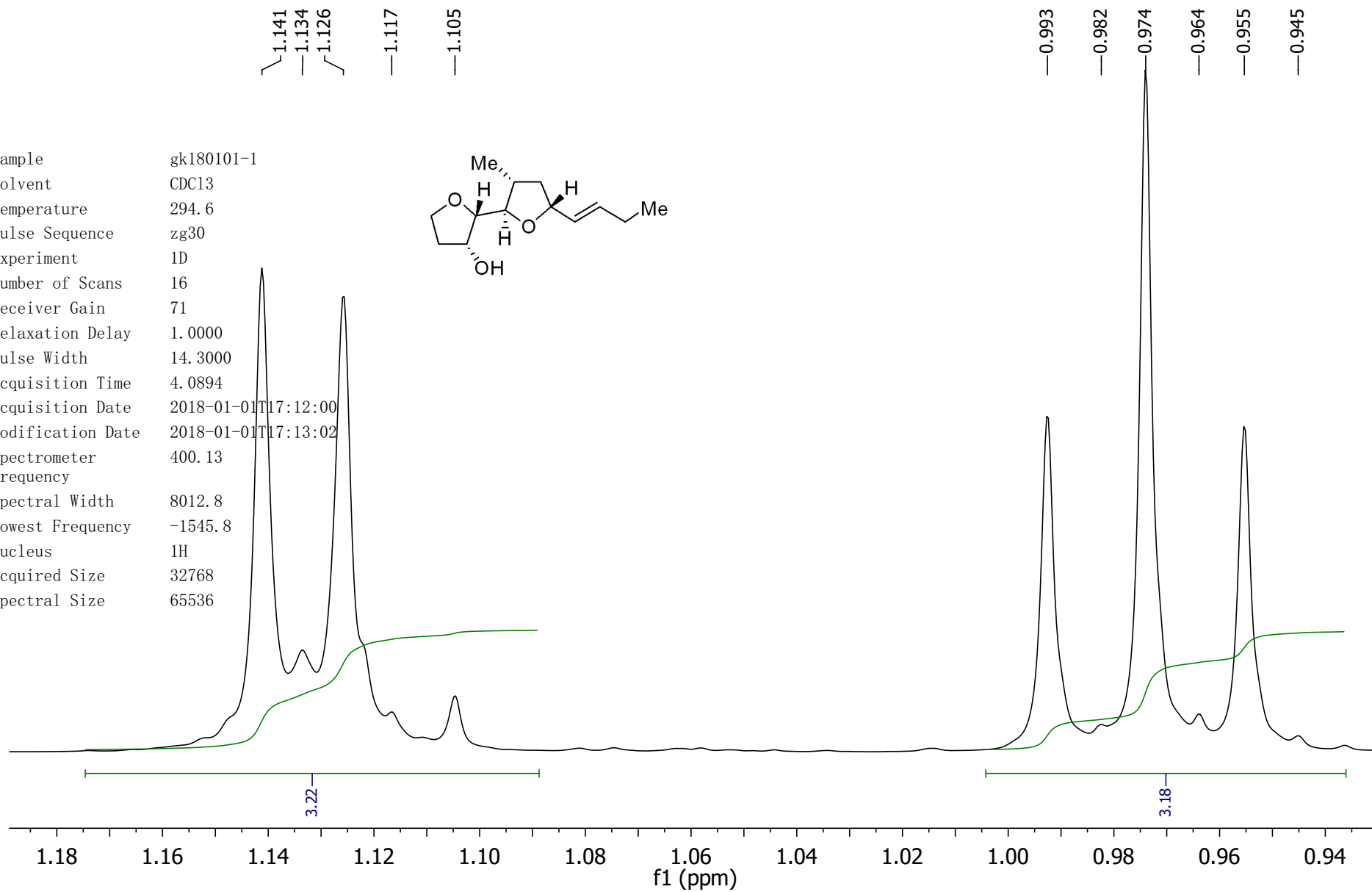
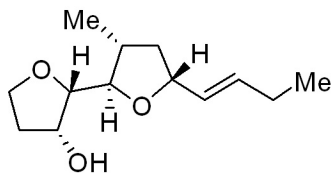




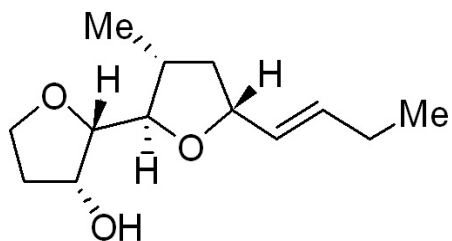
Sample gk180101-1  
 Solvent CDC13  
 Temperature 294.6  
 Pulse Sequence zg30  
 Experiment 1D  
 Number of Scans 16  
 Receiver Gain 71  
 Relaxation Delay 1.0000  
 Pulse Width 14.3000  
 Acquisition Time 4.0894  
 Acquisition Date 2018-01-01T17:12:00  
 Modification Date 2018-01-01T17:13:02  
 Spectrometer 400.13  
 Frequency  
 Spectral Width 8012.8  
 Lowest Frequency -1545.8  
 Nucleus 1H  
 Acquired Size 32768  
 Spectral Size 65536



Sample gk180101-1  
 Solvent CDC13  
 Temperature 294.6  
 Pulse Sequence zg30  
 Experiment 1D  
 Number of Scans 16  
 Receiver Gain 71  
 Relaxation Delay 1.0000  
 Pulse Width 14.3000  
 Acquisition Time 4.0894  
 Acquisition Date 2018-01-01T17:12:00  
 Modification Date 2018-01-01T17:13:02  
 Spectrometer 400.13  
 Frequency  
 Spectral Width 8012.8  
 Lowest Frequency -1545.8  
 Nucleus 1H  
 Acquired Size 32768  
 Spectral Size 65536



Sample gk180101-1C  
Solvent CDC13  
Temperature 295.2  
Pulse Sequence zgpg30  
Experiment 1D  
Number of Scans 103  
Receiver Gain 197  
Relaxation Delay 2.0000  
Pulse Width 9.6000  
Acquisition Time 1.3631  
Acquisition Date 2018-01-01T17:17:00  
Modification Date 2018-01-01T17:19:50  
Spectrometer 100.61  
Frequency  
Spectral Width 24038.5  
Lowest Frequency -1947.0  
Nucleus 13C  
Acquired Size 32768  
Spectral Size 65536

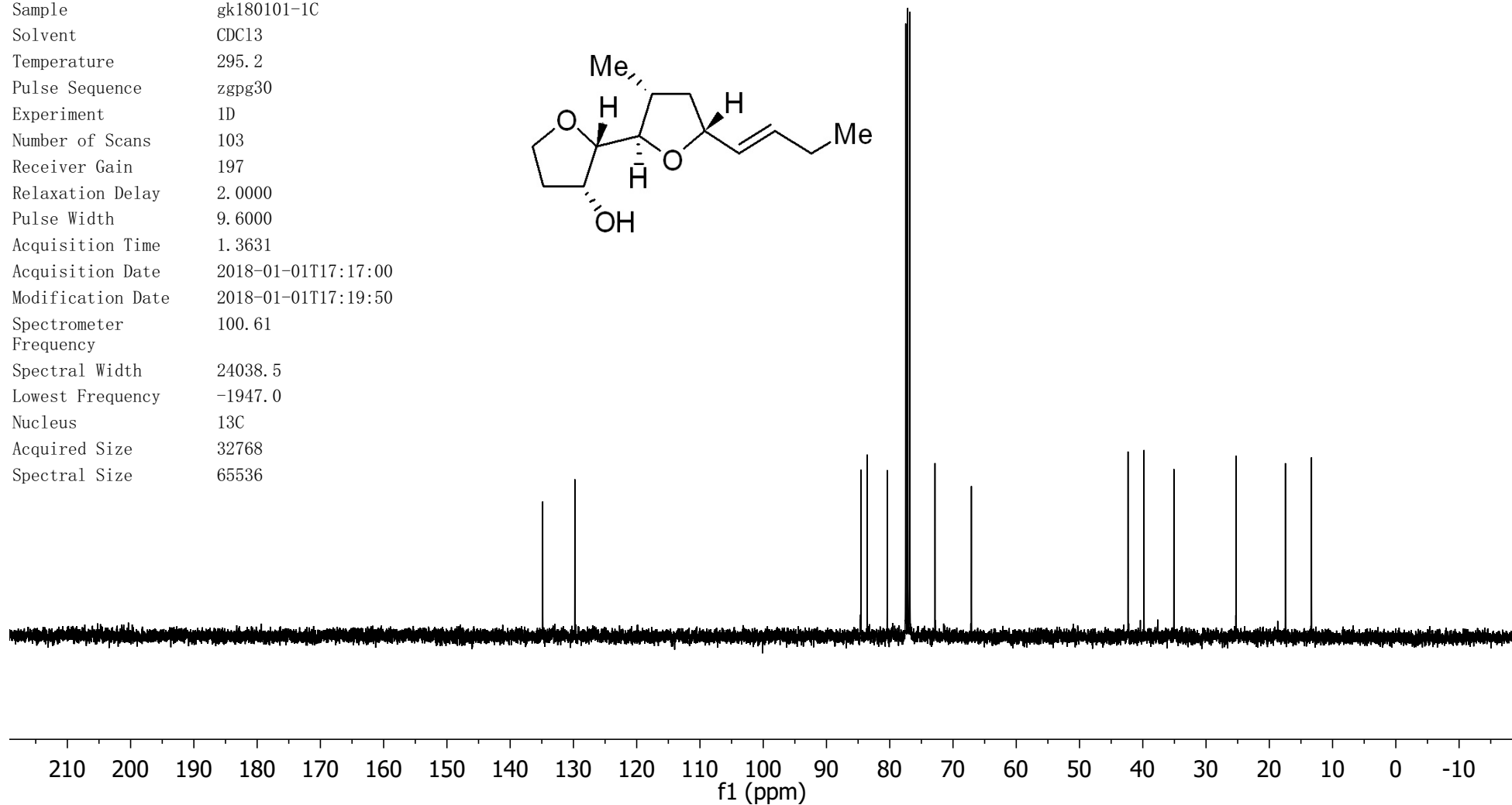


—134.861  
—129.777

84.557  
83.559  
80.391  
77.477  
77.160  
76.842  
72.847  
67.092

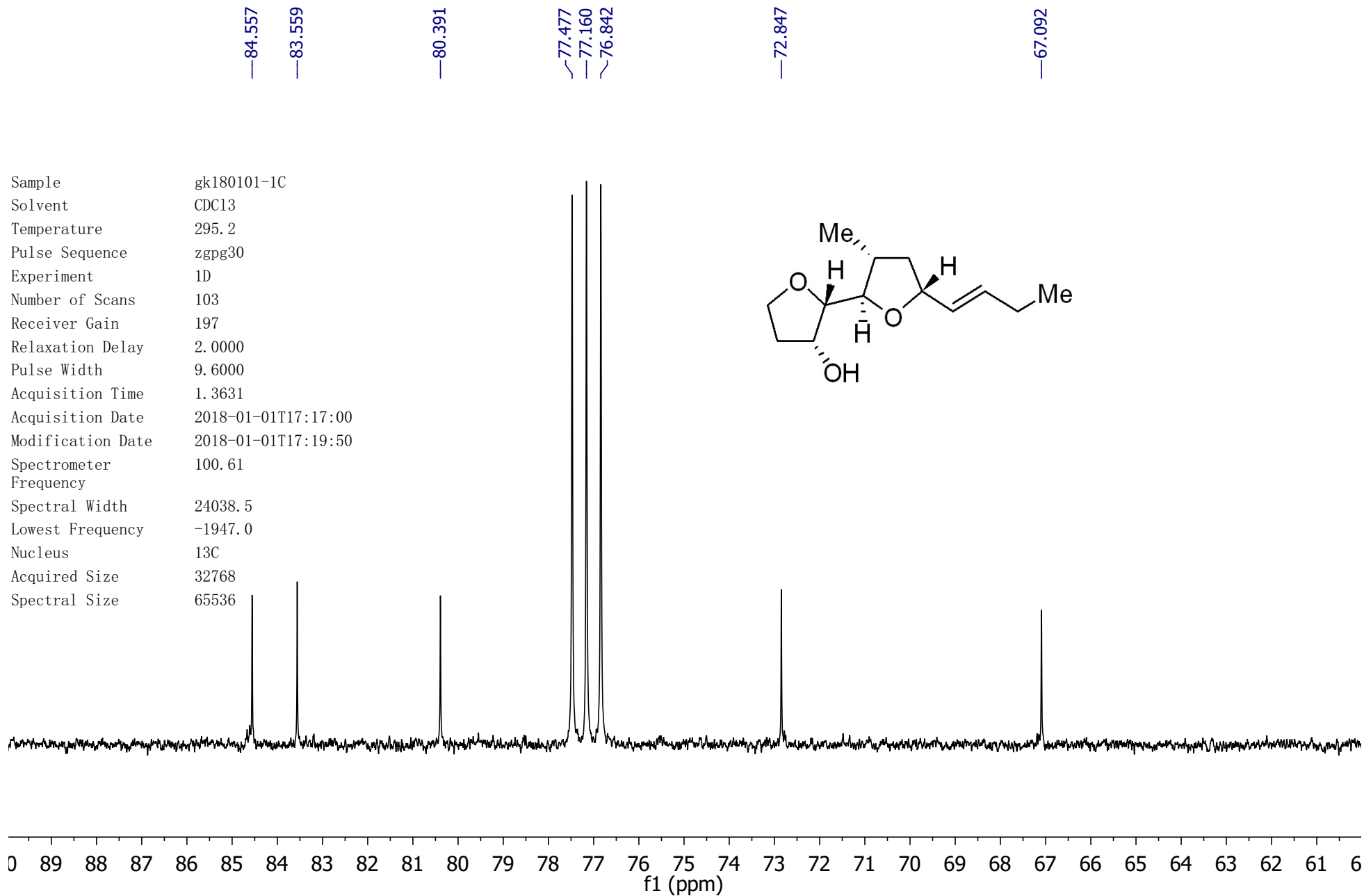
—42.327  
—39.807  
—35.081

—25.244  
—17.454  
—13.333



S200



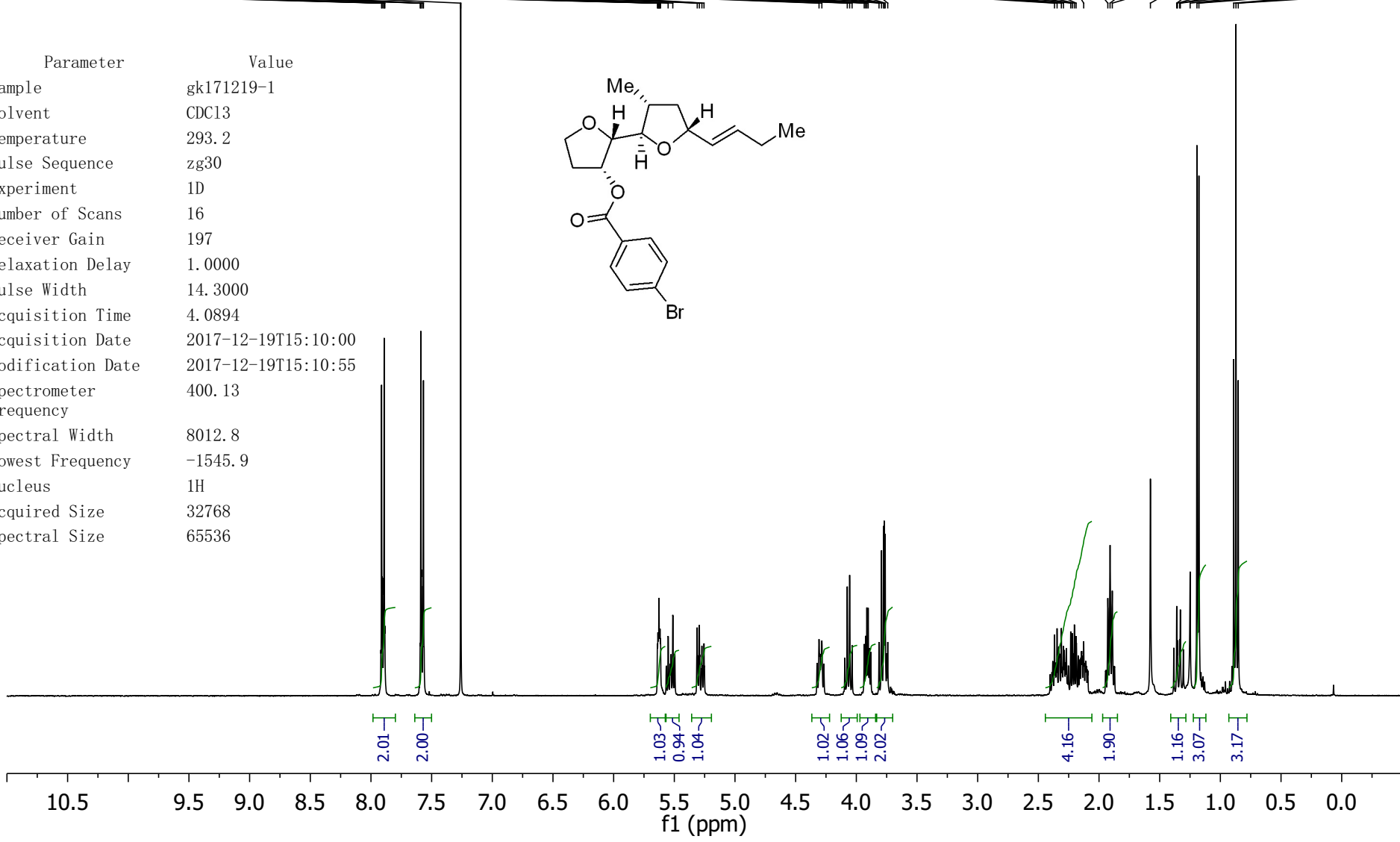
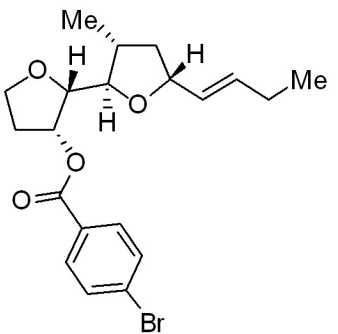


Sample gk180101-1C  
 Solvent CDC13  
 Temperature 295.2  
 Pulse Sequence zgpg30  
 Experiment 1D  
 Number of Scans 103  
 Receiver Gain 197  
 Relaxation Delay 2.0000  
 Pulse Width 9.6000  
 Acquisition Time 1.3631  
 Acquisition Date 2018-01-01T17:17:00  
 Modification Date 2018-01-01T17:19:50  
 Spectrometer 100.61  
 Frequency  
 Spectral Width 24038.5  
 Lowest Frequency -1947.0  
 Nucleus <sup>13</sup>C  
 Acquired Size 32768  
 Spectral Size 65536

S201

7.913  
7.908  
7.896  
7.891  
7.886  
7.594  
7.589  
7.584  
7.572  
7.567  
7.260  
5.639  
5.635  
5.631  
5.627  
5.622  
5.618  
5.614  
5.551  
5.513  
5.311  
5.294  
5.273  
5.255  
5.255  
4.307  
4.284  
4.075  
4.055  
4.035  
3.935  
3.924  
3.913  
3.902  
3.813  
3.792  
3.775  
3.770  
3.762  
3.741  
3.367  
2.367  
2.346  
2.310  
2.293  
2.293  
2.233  
2.219  
2.203  
2.189  
2.126  
1.927  
1.909  
1.890  
1.576  
1.360  
1.354  
1.335  
1.330  
1.249  
1.193  
1.177  
0.890  
0.871  
0.853

Parameter	Value
Sample	gk171219-1
Solvent	CDC13
Temperature	293.2
Pulse Sequence	zg30
Experiment	1D
Number of Scans	16
Receiver Gain	197
Relaxation Delay	1.0000
Pulse Width	14.3000
Acquisition Time	4.0894
Acquisition Date	2017-12-19T15:10:00
Modification Date	2017-12-19T15:10:55
Spectrometer	400.13
Frequency	
Spectral Width	8012.8
Lowest Frequency	-1545.9
Nucleus	1H
Acquired Size	32768
Spectral Size	65536

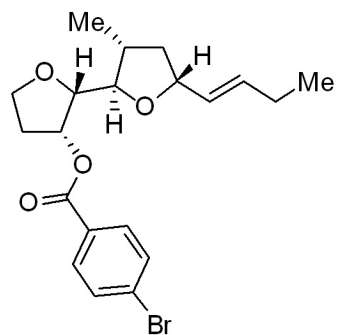


S202

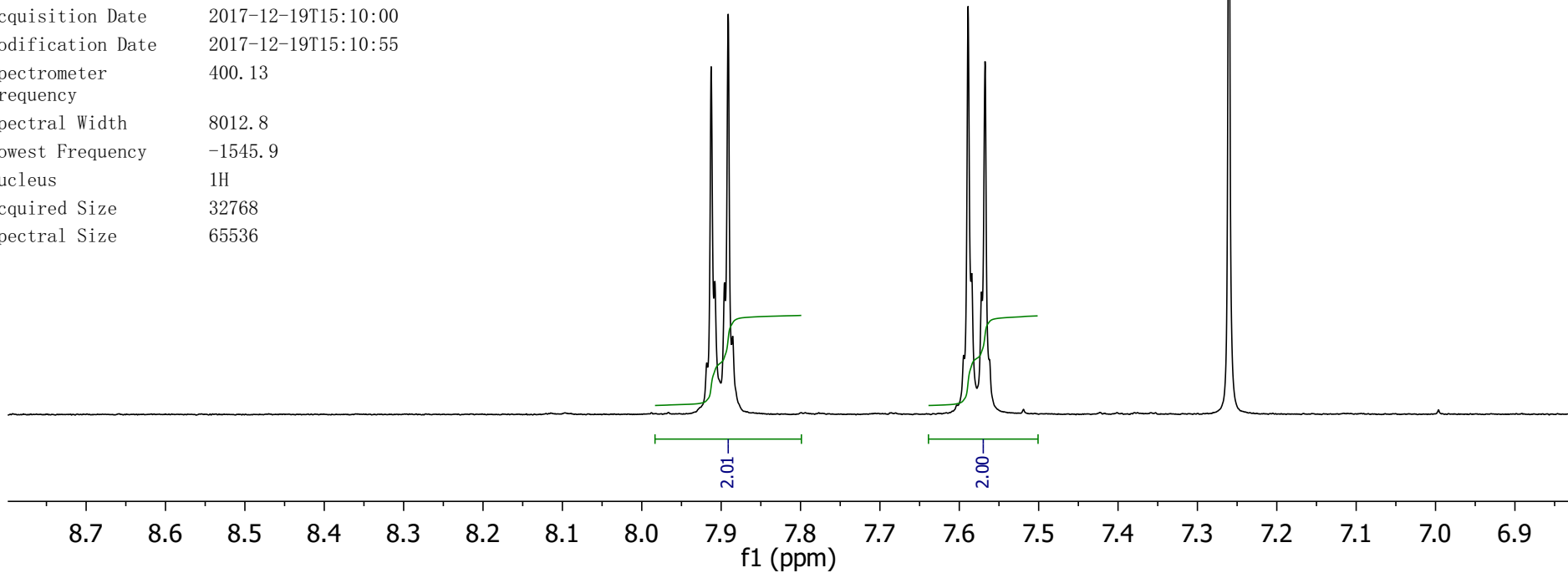
Parameter	Value
Sample	gk171219-1
Solvent	CDC13
Temperature	293.2
Pulse Sequence	zg30
Experiment	1D
Number of Scans	16
Receiver Gain	197
Relaxation Delay	1.0000
Pulse Width	14.3000
Acquisition Time	4.0894
Acquisition Date	2017-12-19T15:10:00
Modification Date	2017-12-19T15:10:55
Spectrometer	400.13
Frequency	
Spectral Width	8012.8
Lowest Frequency	-1545.9
Nucleus	<sup>1</sup> H
Acquired Size	32768
Spectral Size	65536

7.918  
7.913  
7.908  
7.896  
7.891  
7.886

7.594  
7.589  
7.584  
7.572  
7.567



7.260



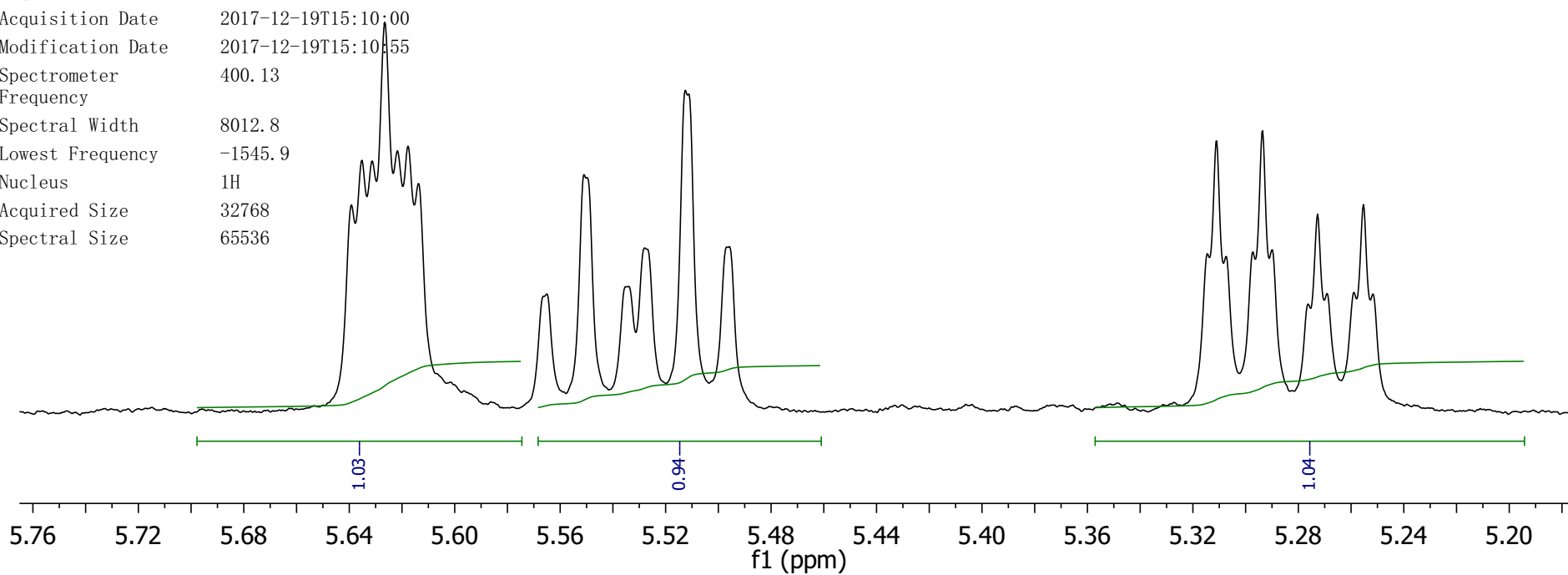
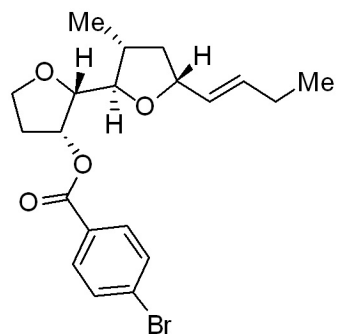
S203

5.639  
5.635  
5.631  
5.627  
5.622  
5.618  
5.614

5.565  
5.551  
5.534  
5.528  
5.513  
5.496

5.315  
5.311  
5.307  
5.297  
5.294  
5.290  
5.276  
5.273  
5.269  
5.259  
5.255  
5.252

Parameter	Value
Sample	gk171219-1
Solvent	CDC13
Temperature	293.2
Pulse Sequence	zg30
Experiment	1D
Number of Scans	16
Receiver Gain	197
Relaxation Delay	1.0000
Pulse Width	14.3000
Acquisition Time	4.0894
Acquisition Date	2017-12-19T15:10:00
Modification Date	2017-12-19T15:10:55
Spectrometer	400.13
Frequency	
Spectral Width	8012.8
Lowest Frequency	-1545.9
Nucleus	1H
Acquired Size	32768
Spectral Size	65536



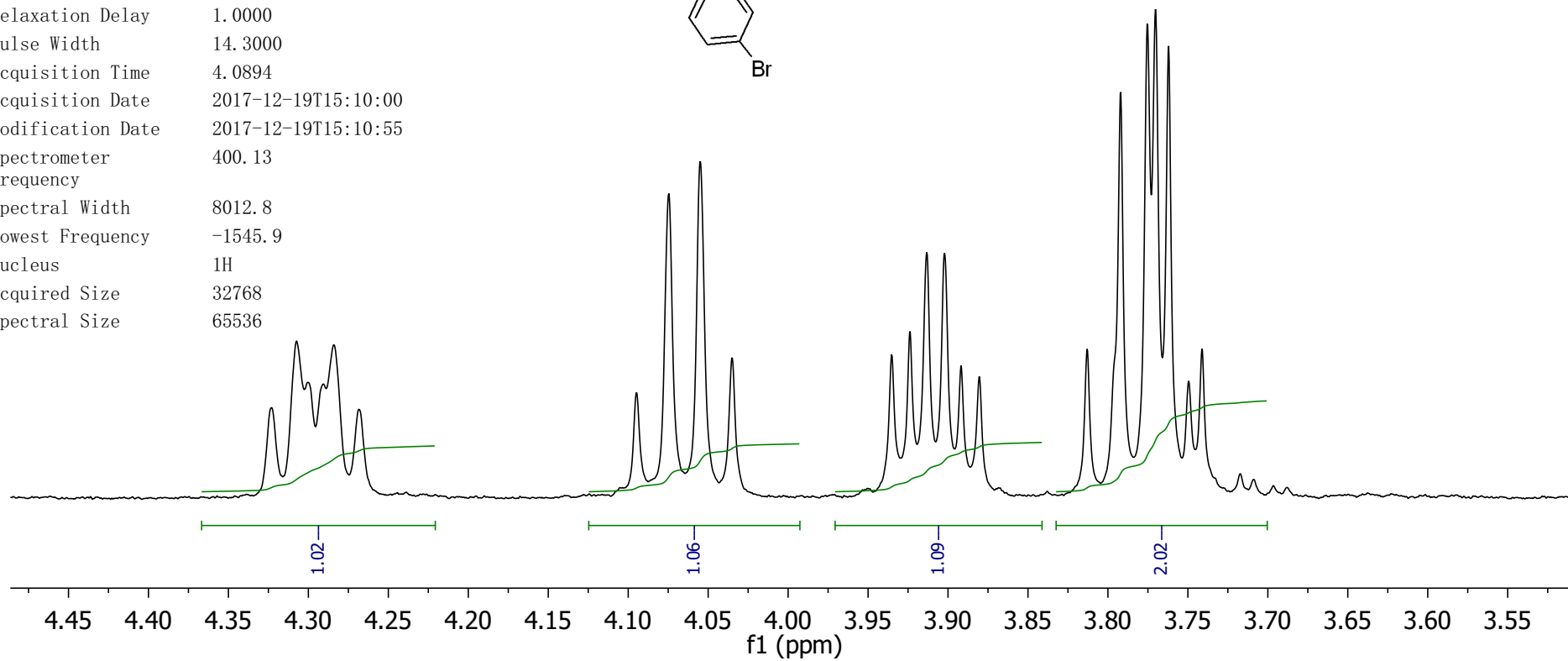
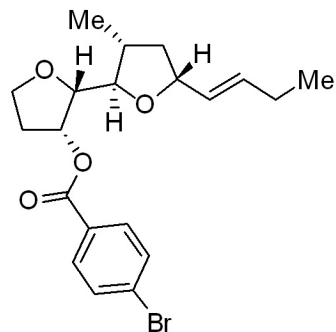
4.323  
4.307  
4.300  
4.291  
4.284  
4.268

4.095  
4.075  
4.055  
4.035

3.935  
3.924  
3.913  
3.902  
3.892  
3.880

3.813  
3.792  
3.775  
3.770  
3.762  
3.750  
3.741

Parameter	Value
Sample	gk171219-1
Solvent	CDC13
Temperature	293.2
Pulse Sequence	zg30
Experiment	1D
Number of Scans	16
Receiver Gain	197
Relaxation Delay	1.0000
Pulse Width	14.3000
Acquisition Time	4.0894
Acquisition Date	2017-12-19T15:10:00
Modification Date	2017-12-19T15:10:55
Spectrometer	400.13
Frequency	
Spectral Width	8012.8
Lowest Frequency	-1545.9
Nucleus	1H
Acquired Size	32768
Spectral Size	65536



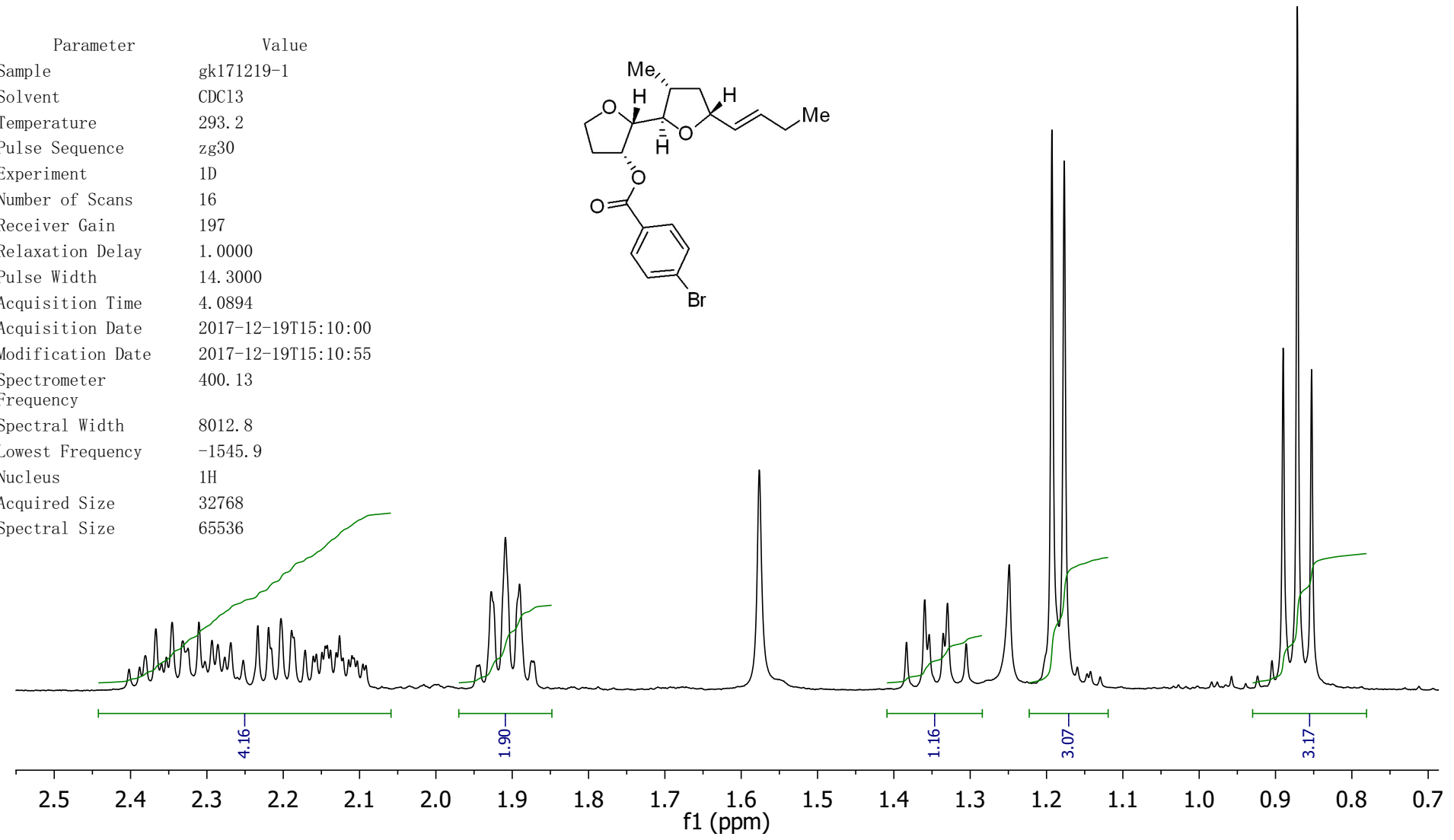
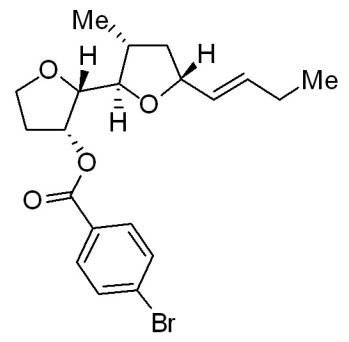
2.367  
2.346  
2.332  
2.325  
2.310  
2.293  
2.286  
2.269  
2.233  
2.219  
2.203  
2.189  
2.171  
2.149  
2.145  
2.142  
2.138  
2.126  
1.945  
1.927  
1.909  
1.890  
1.875

1.576

1.383  
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1.335  
1.330  
1.305  
1.249  
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1.177  
1.160

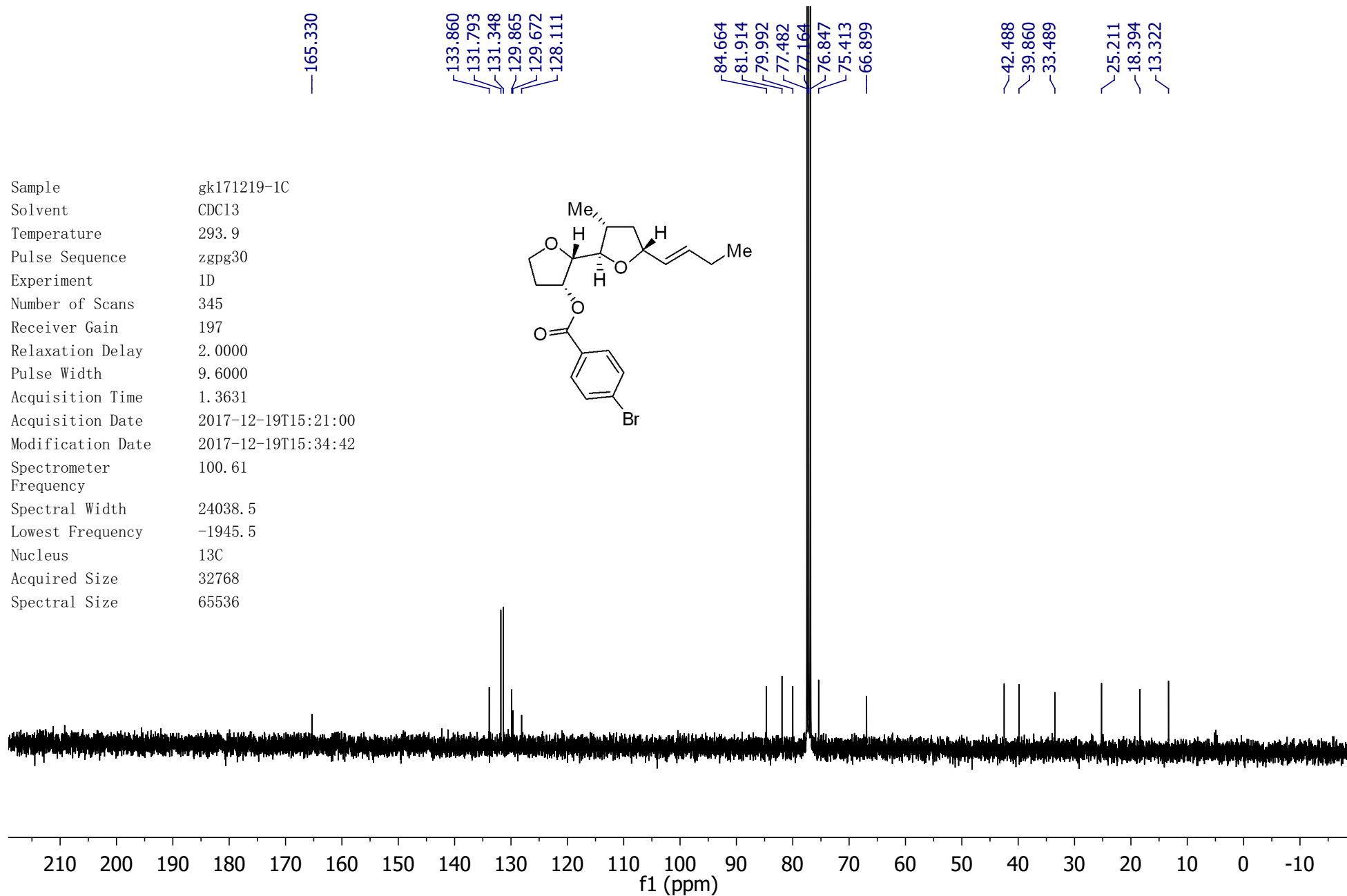
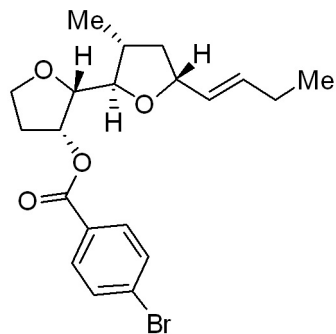
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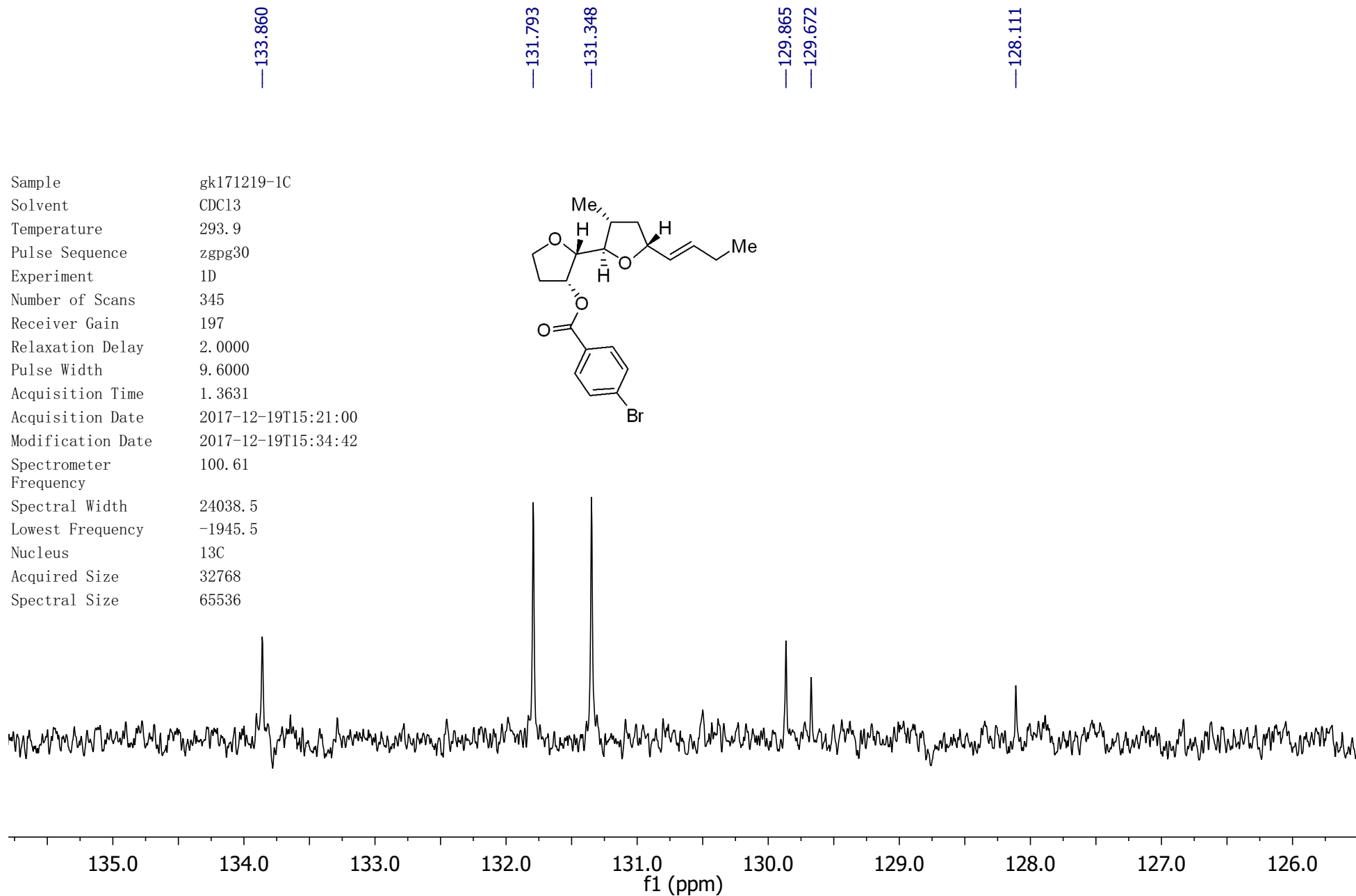
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Sample	gk171219-1
Solvent	CDC13
Temperature	293.2
Pulse Sequence	zg30
Experiment	1D
Number of Scans	16
Receiver Gain	197
Relaxation Delay	1.0000
Pulse Width	14.3000
Acquisition Time	4.0894
Acquisition Date	2017-12-19T15:10:00
Modification Date	2017-12-19T15:10:55
Spectrometer	400.13
Frequency	
Spectral Width	8012.8
Lowest Frequency	-1545.9
Nucleus	1H
Acquired Size	32768
Spectral Size	65536



S206

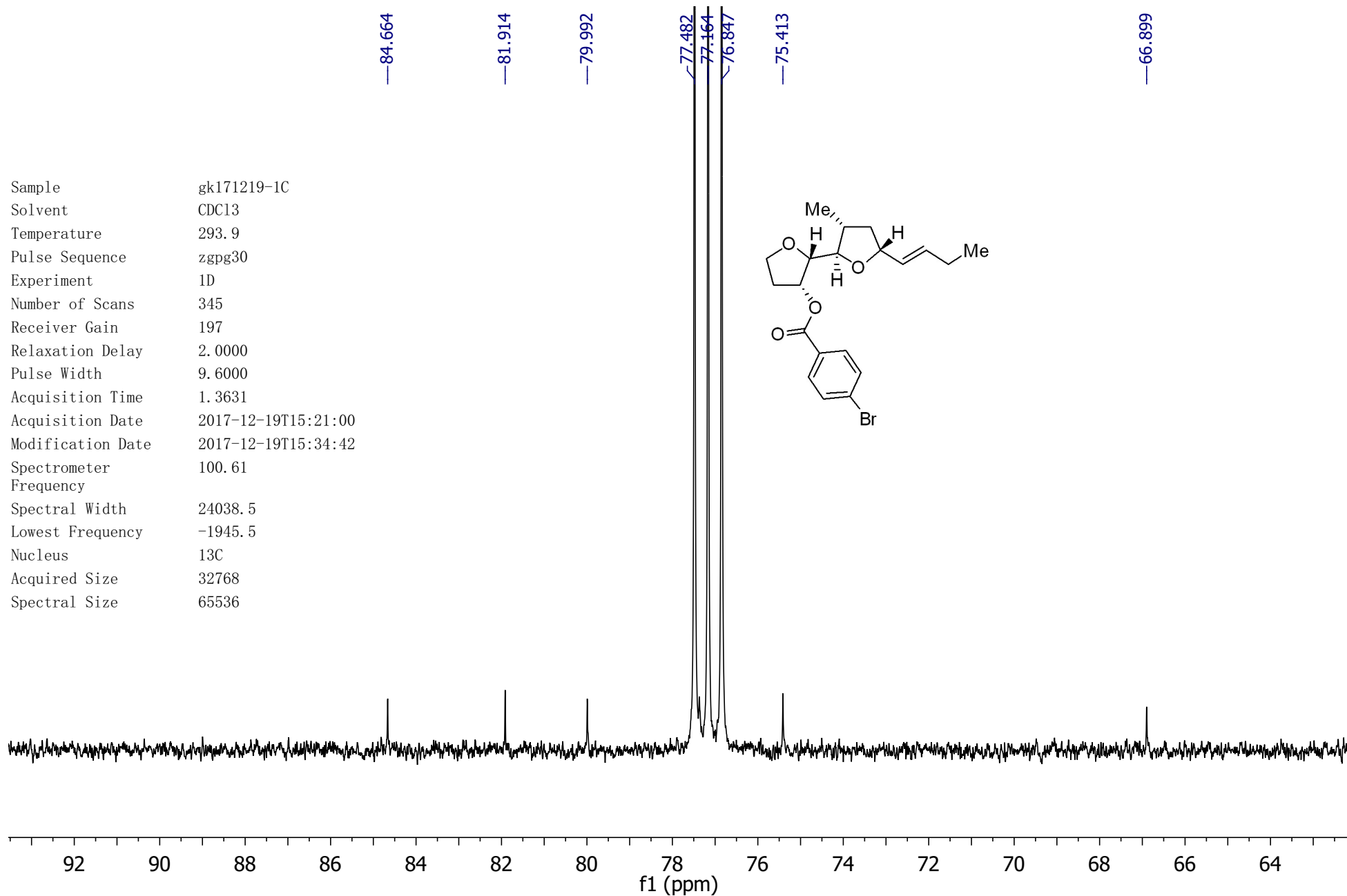
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Solvent CDC13  
Temperature 293.9  
Pulse Sequence zgpg30  
Experiment 1D  
Number of Scans 345  
Receiver Gain 197  
Relaxation Delay 2.0000  
Pulse Width 9.6000  
Acquisition Time 1.3631  
Acquisition Date 2017-12-19T15:21:00  
Modification Date 2017-12-19T15:34:42  
Spectrometer 100.61  
Frequency  
Spectral Width 24038.5  
Lowest Frequency -1945.5  
Nucleus 13C  
Acquired Size 32768  
Spectral Size 65536

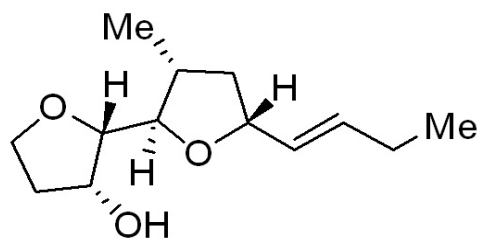






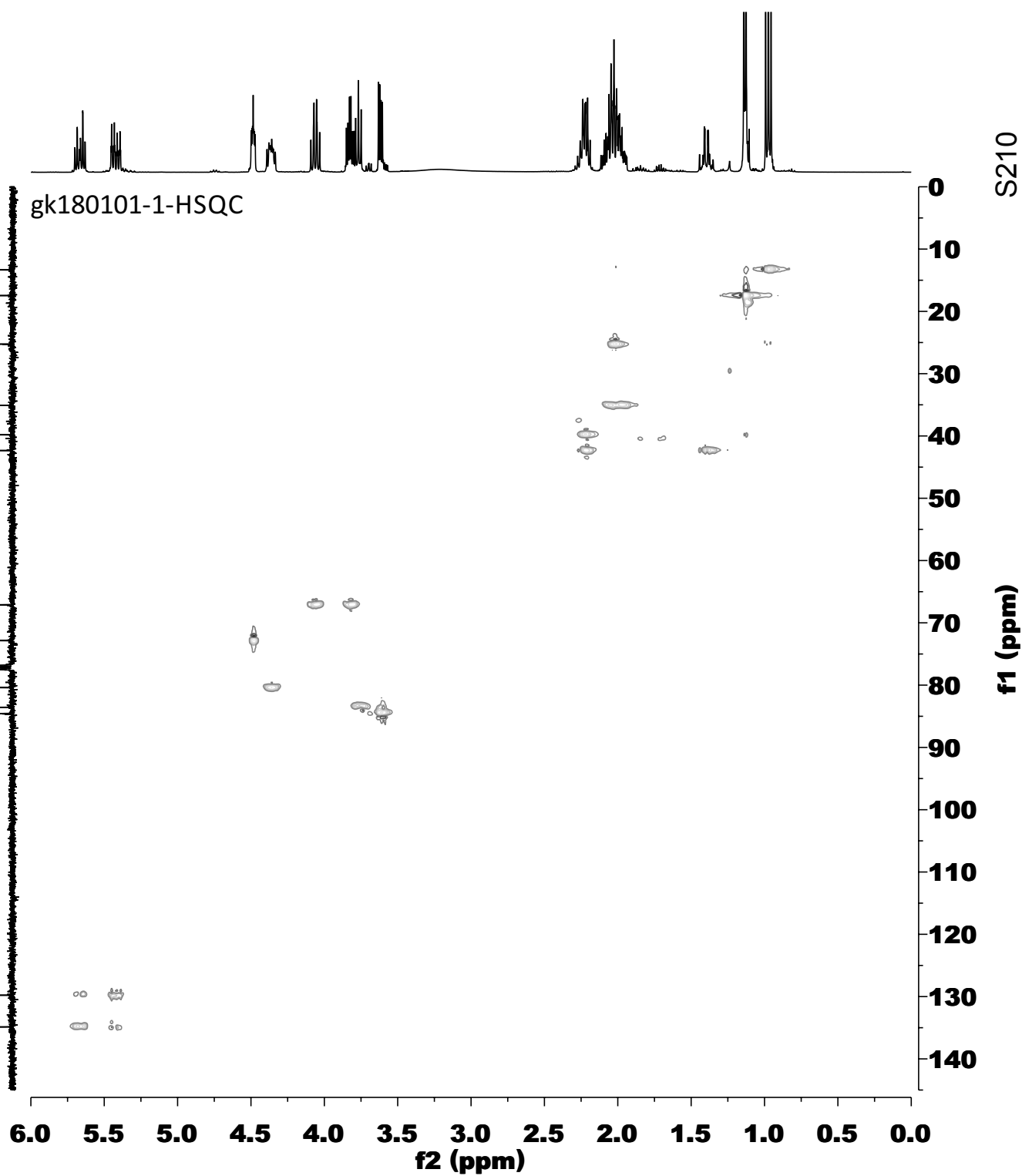
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Pulse Width 9.6000  
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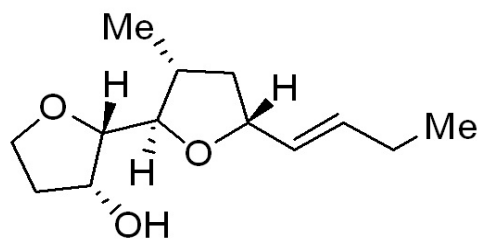




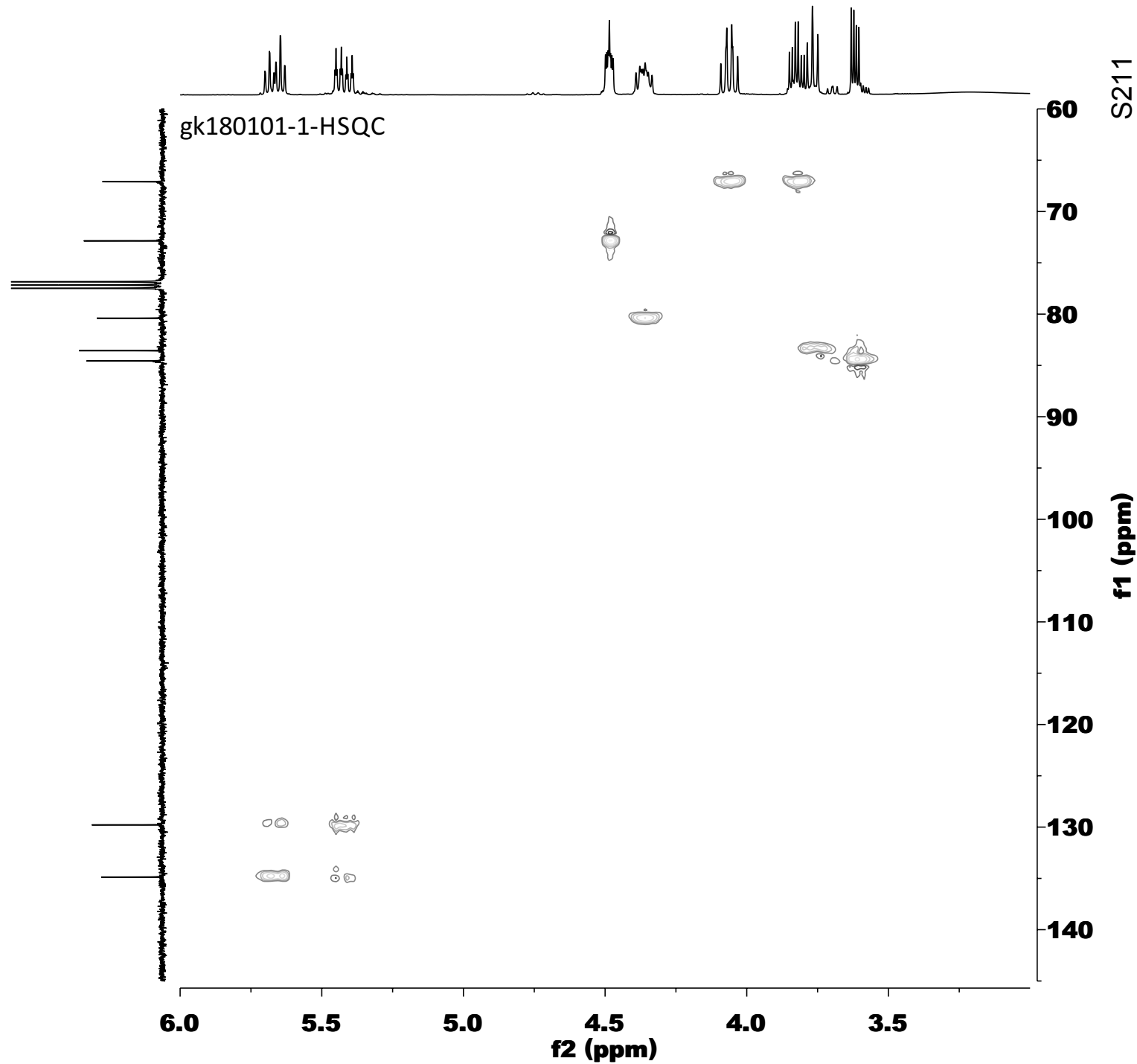
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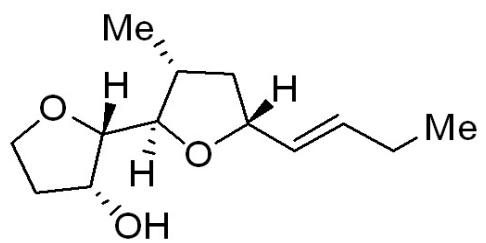
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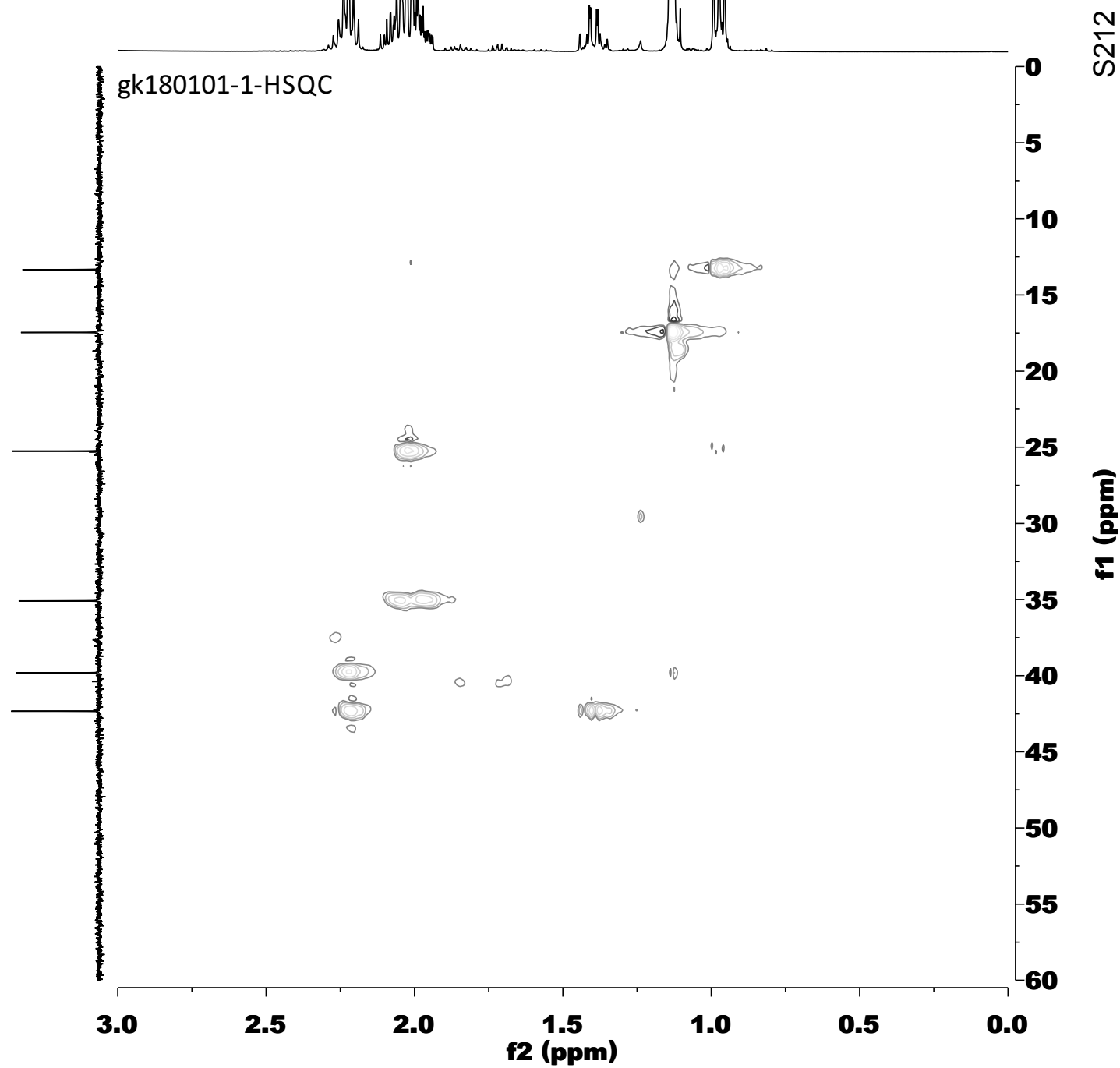


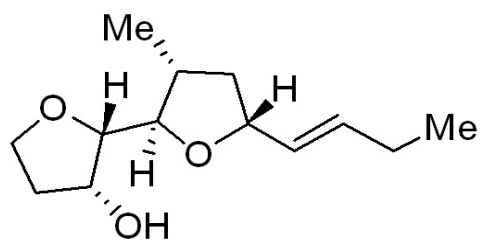
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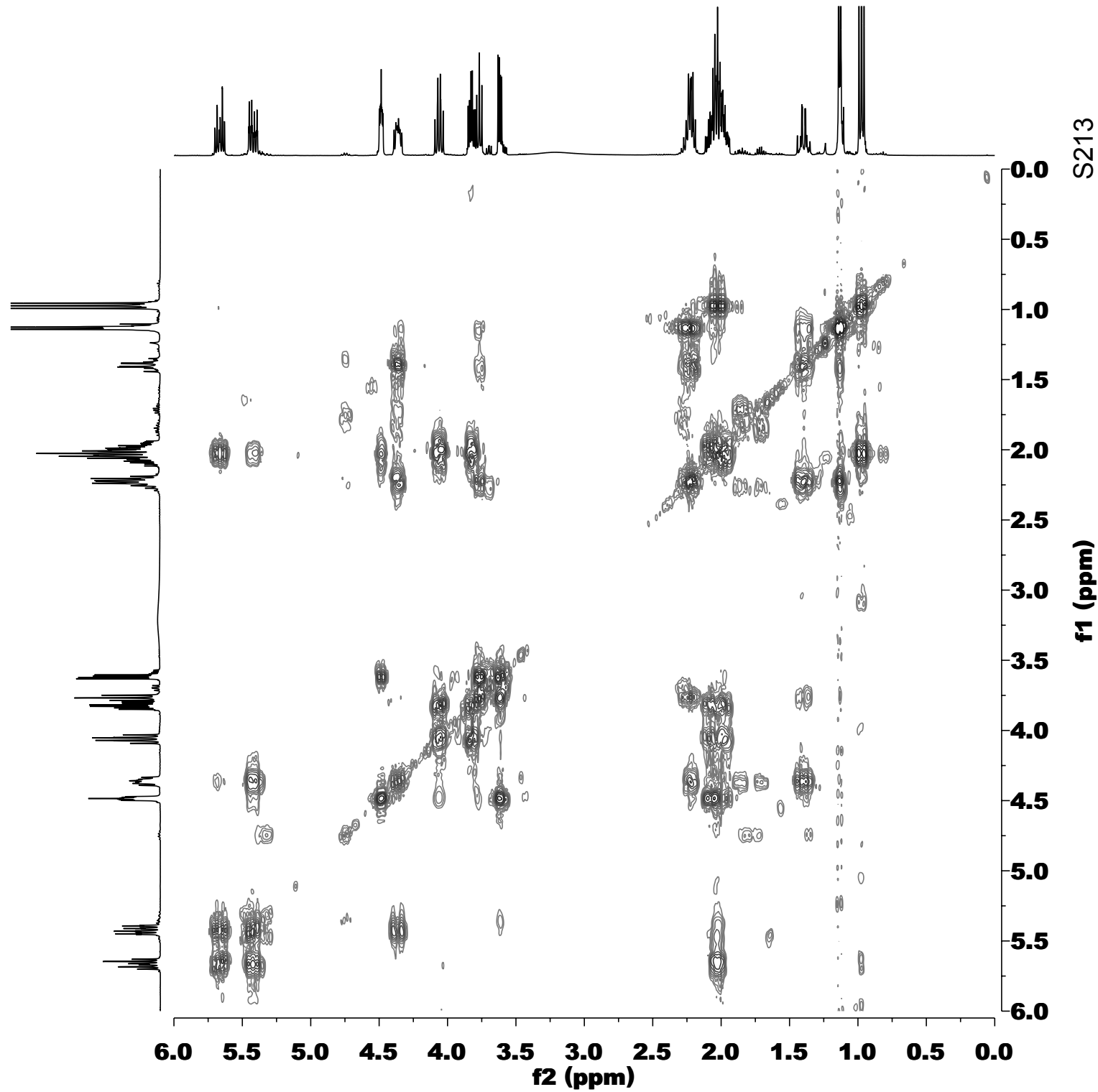


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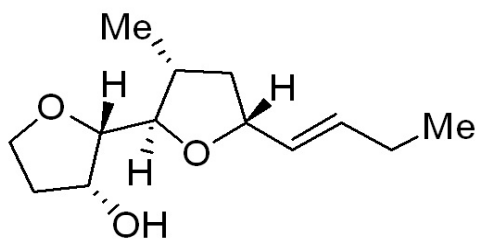


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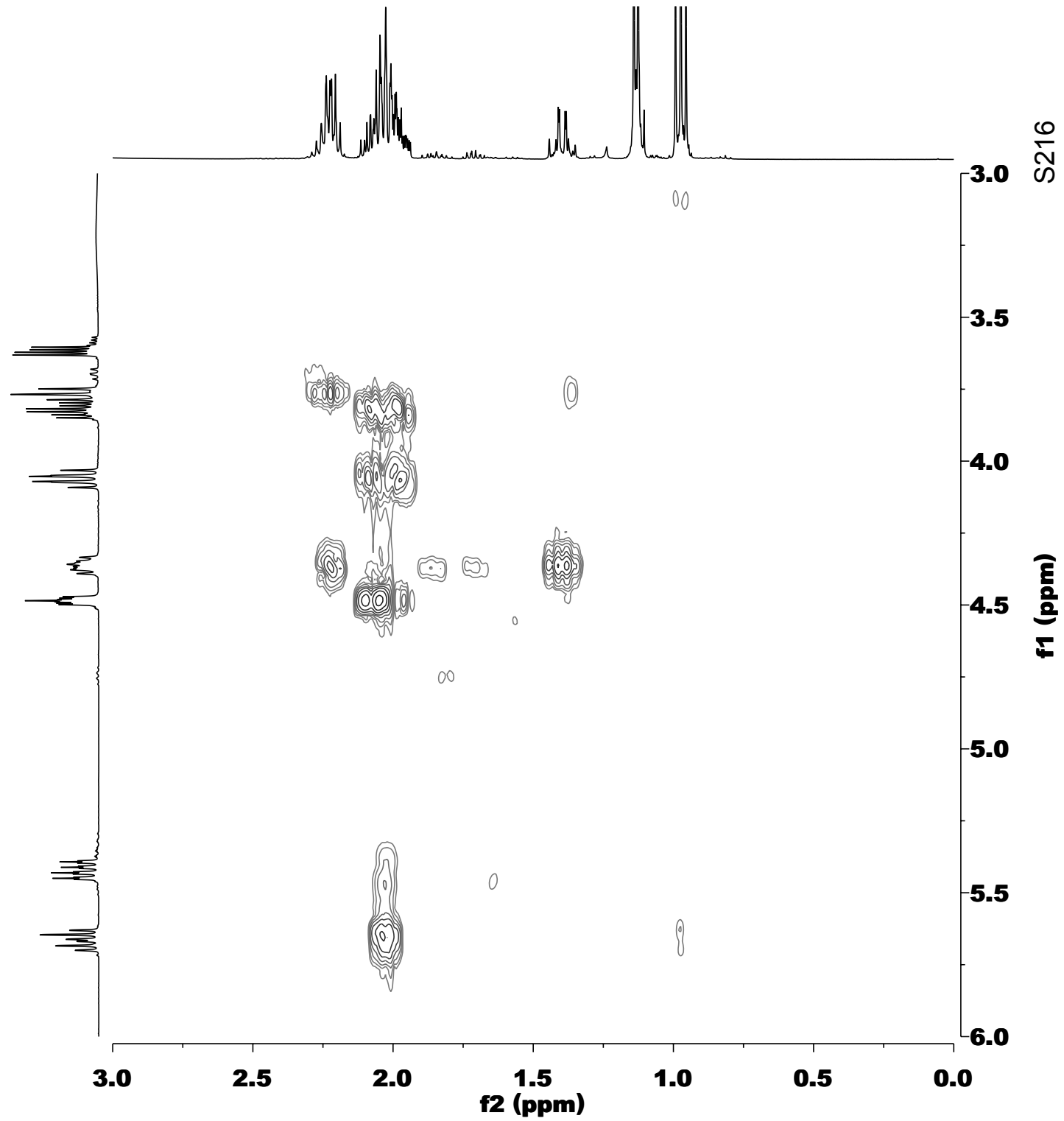




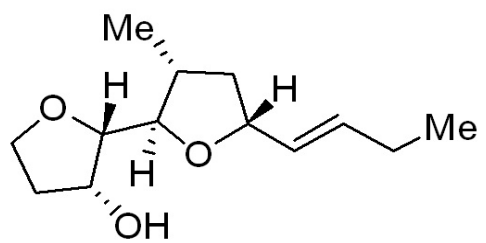




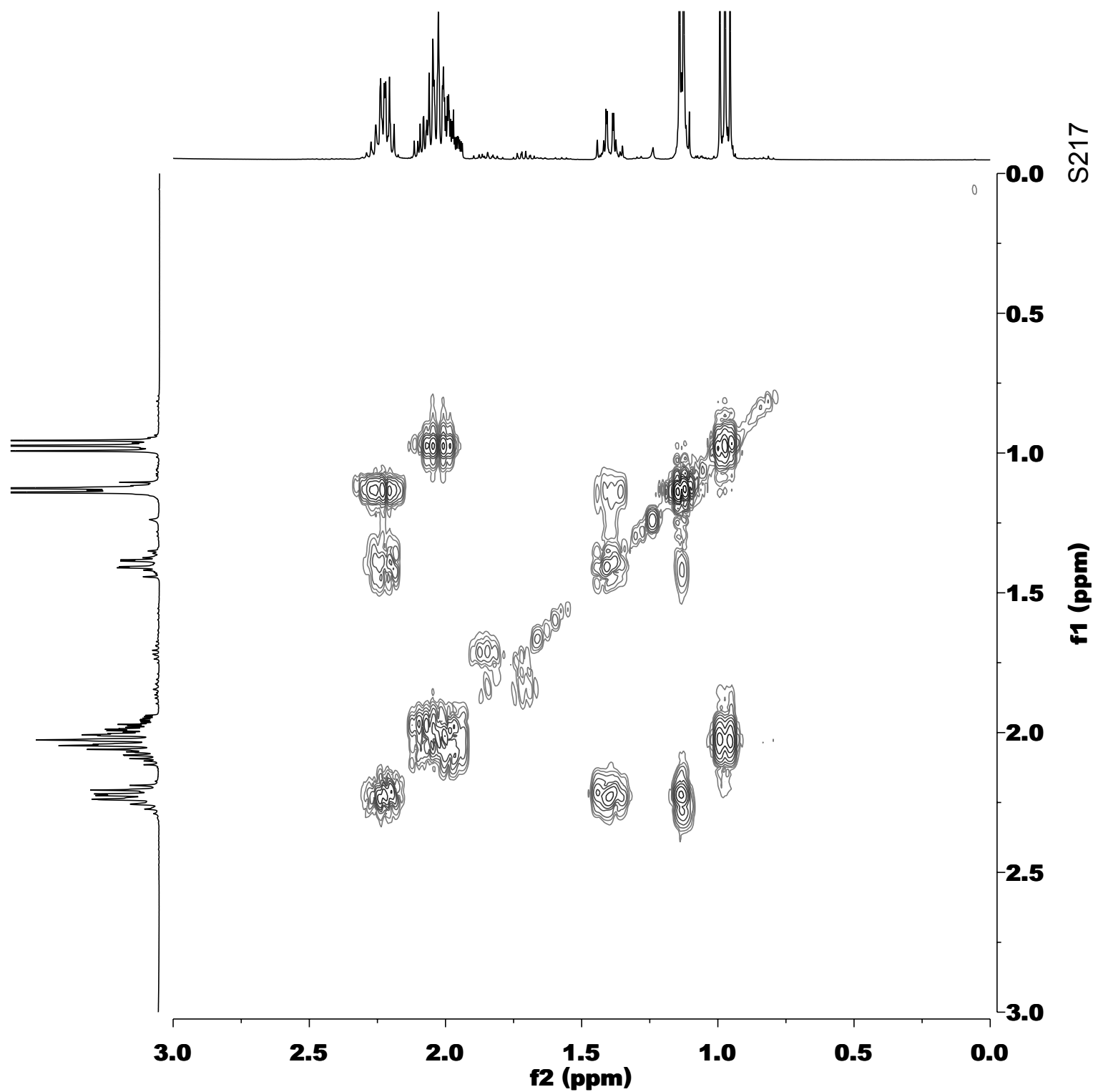
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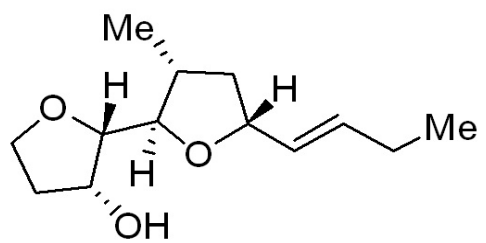




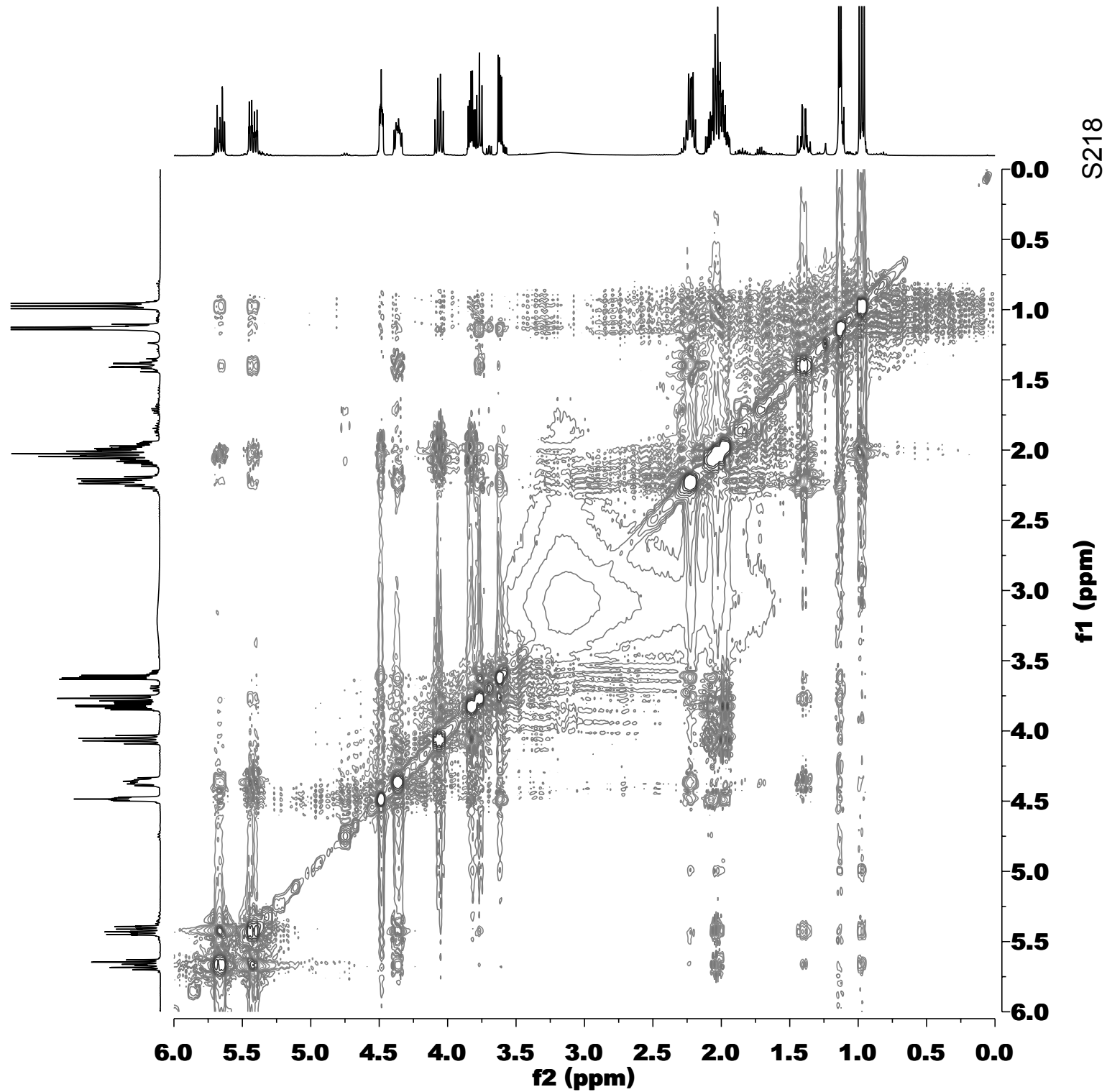


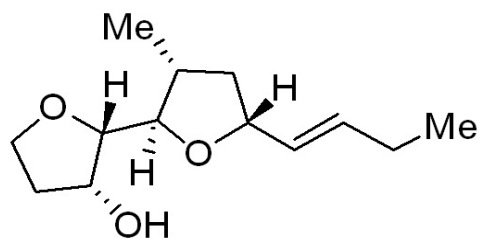
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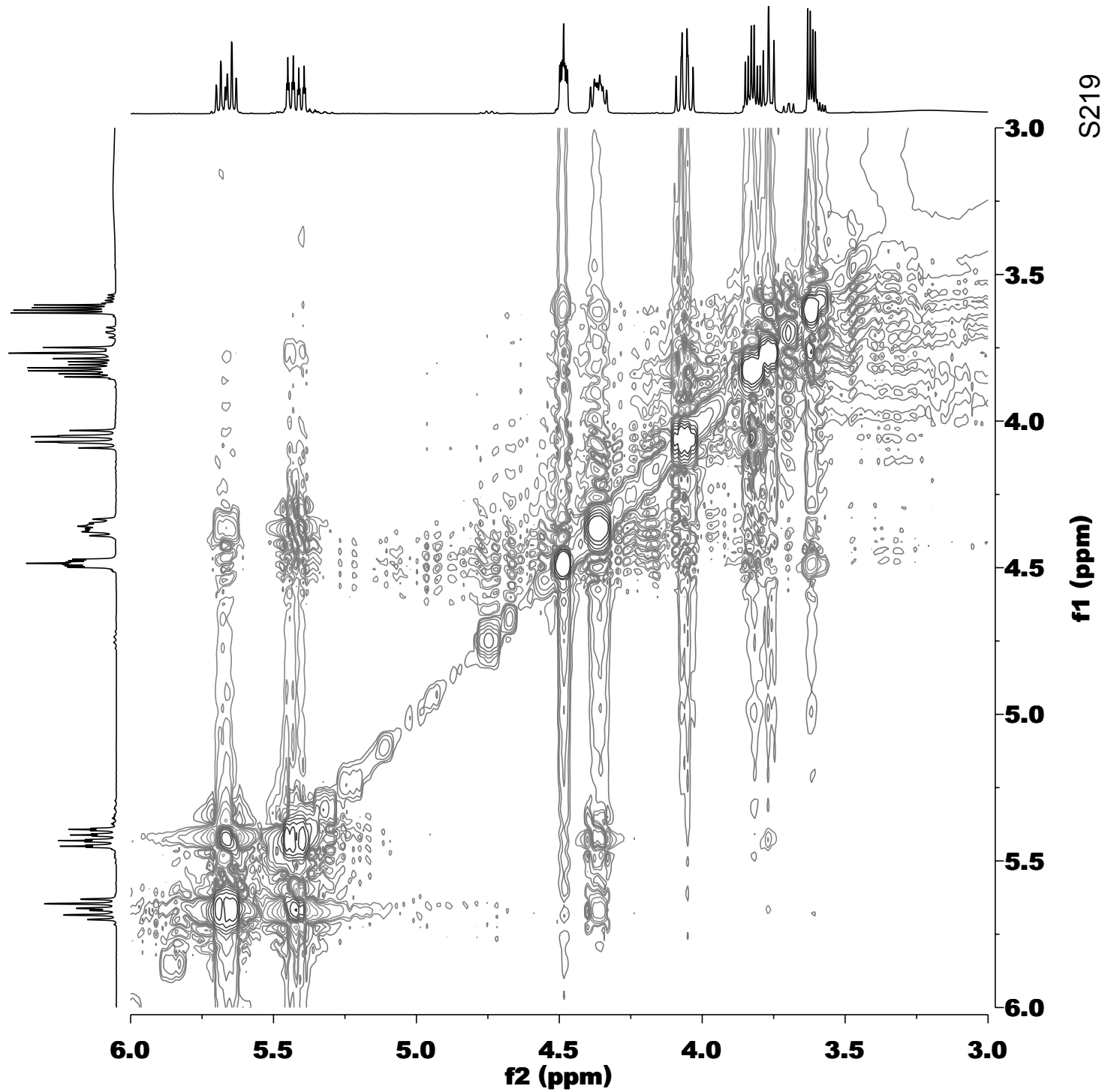


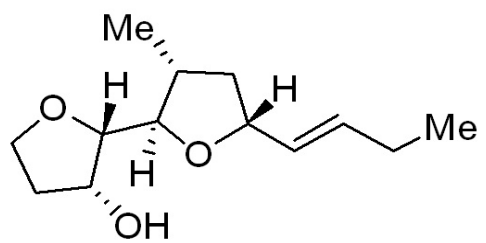
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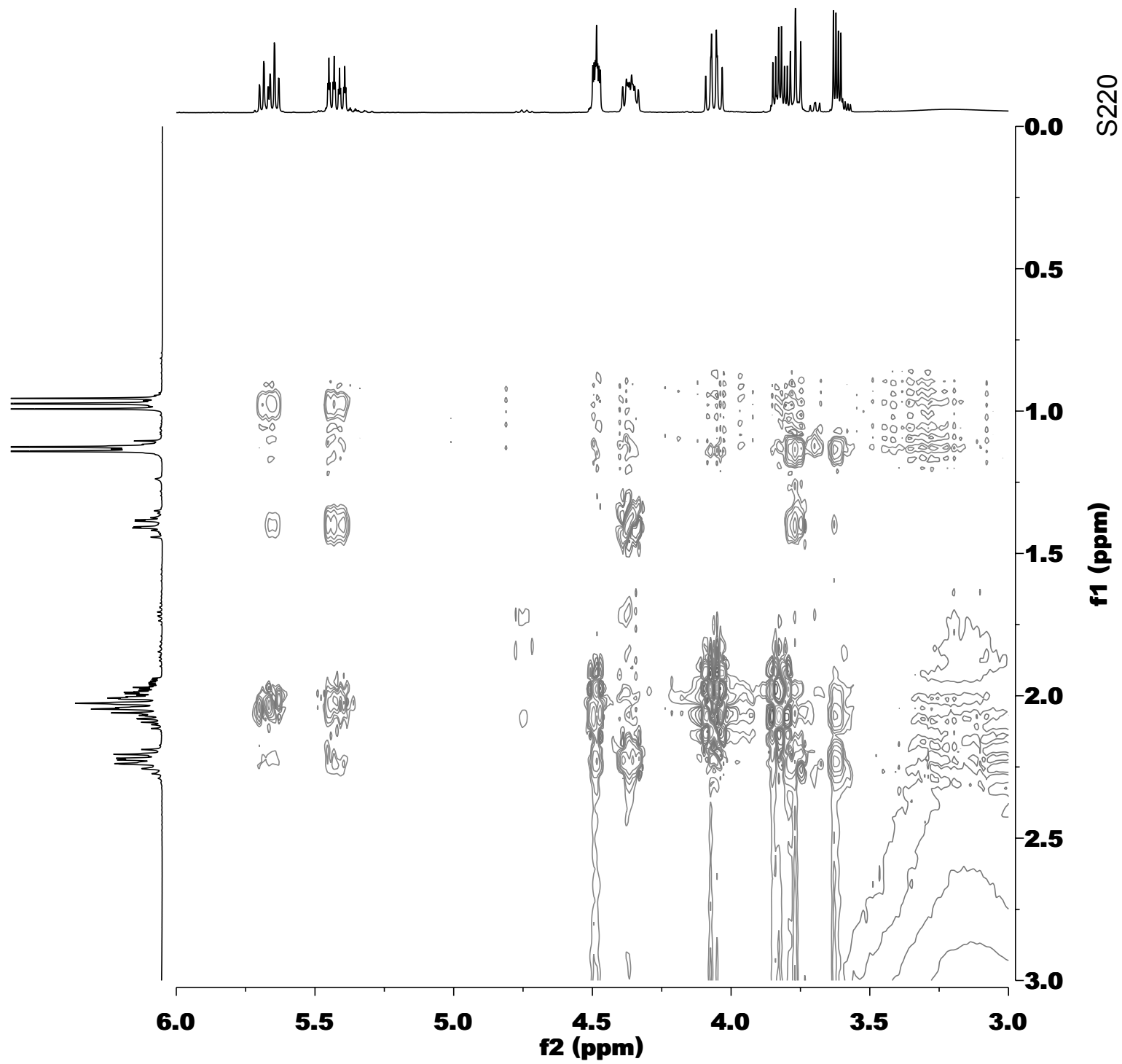


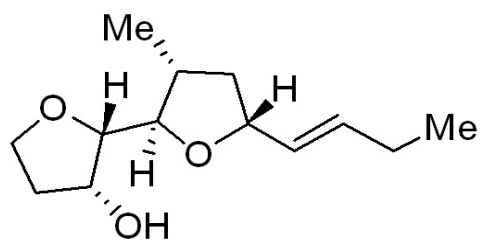
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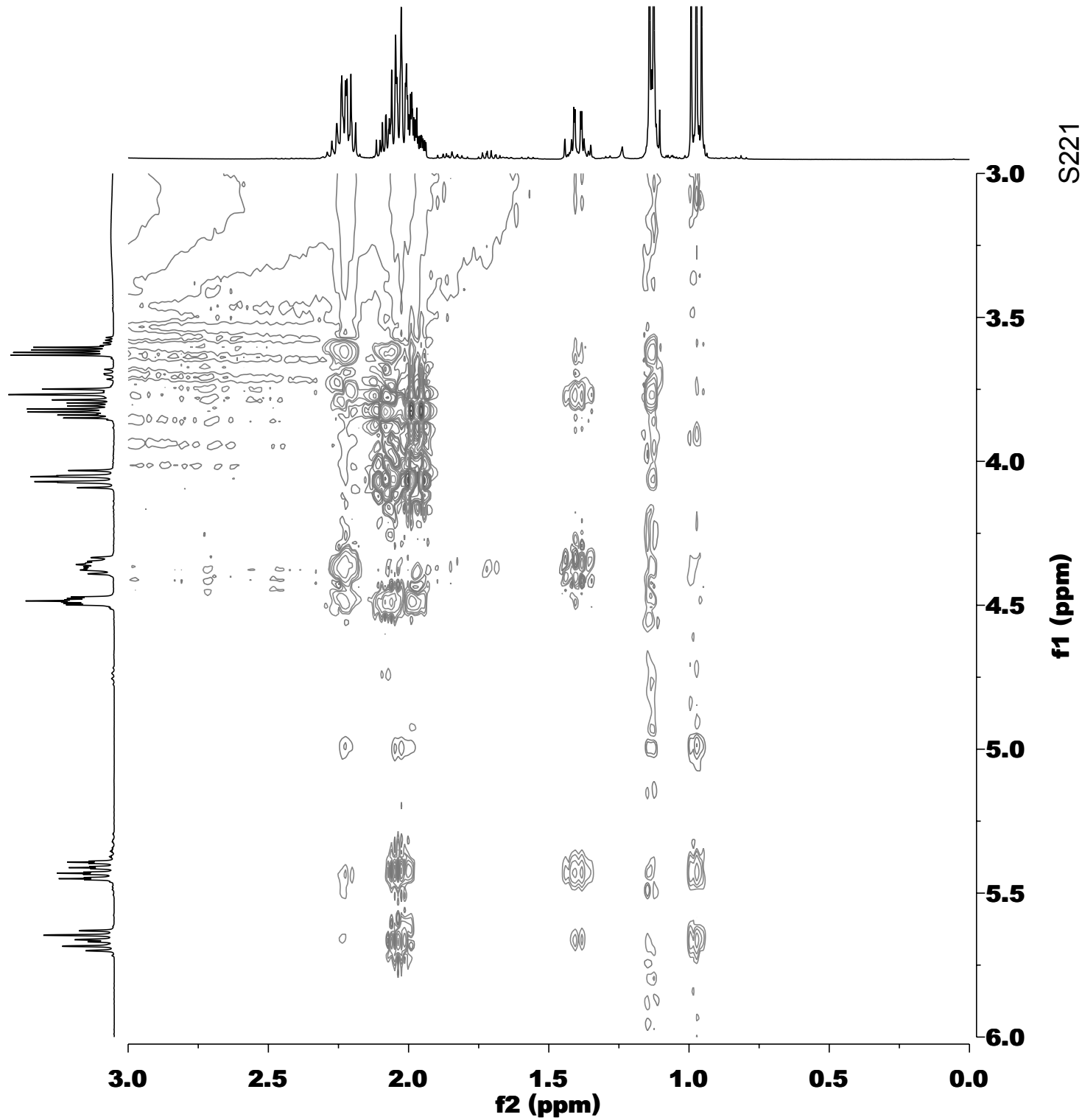


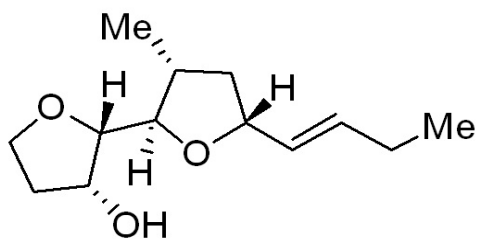
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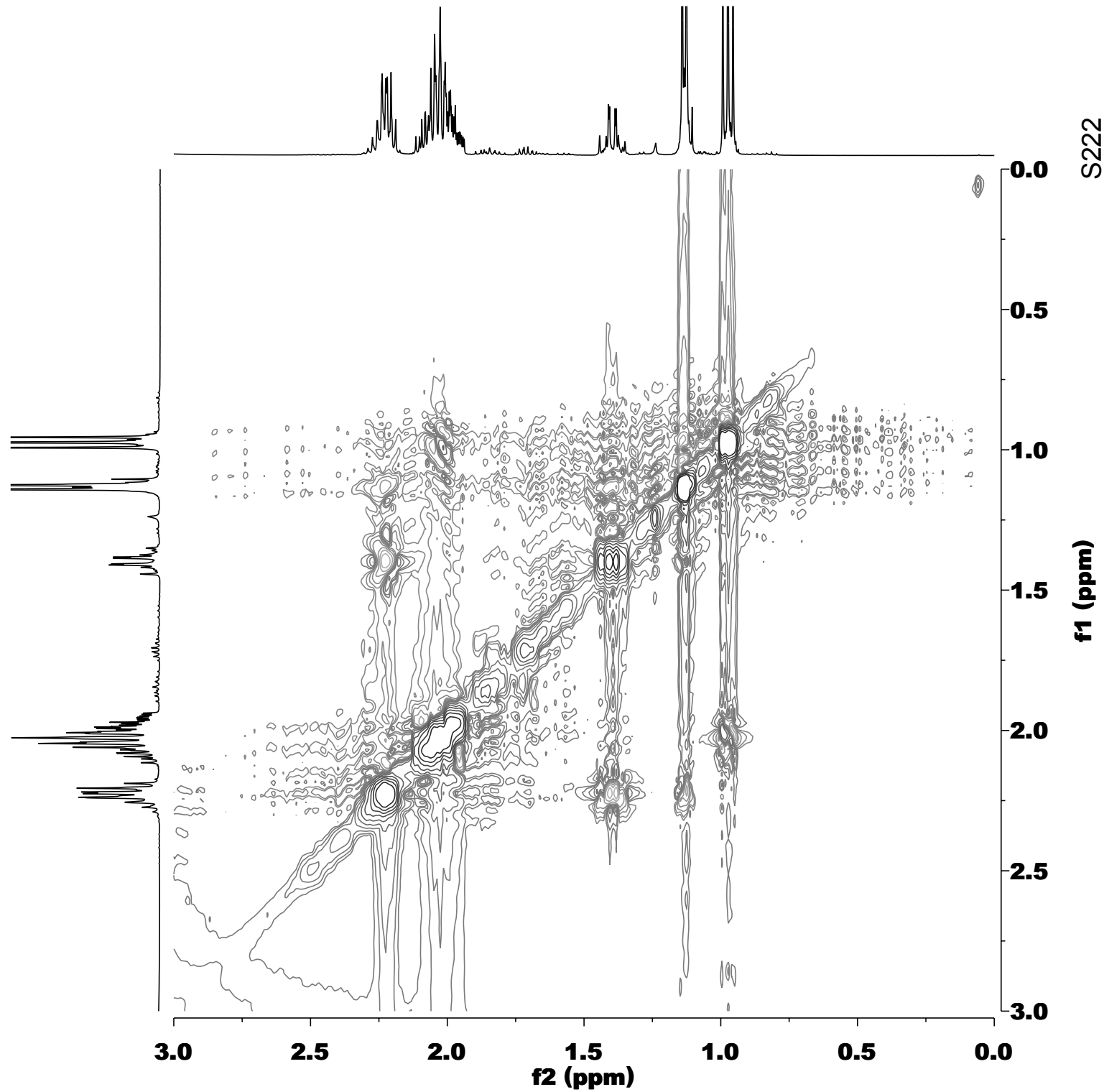


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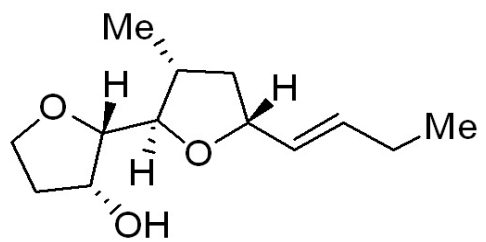




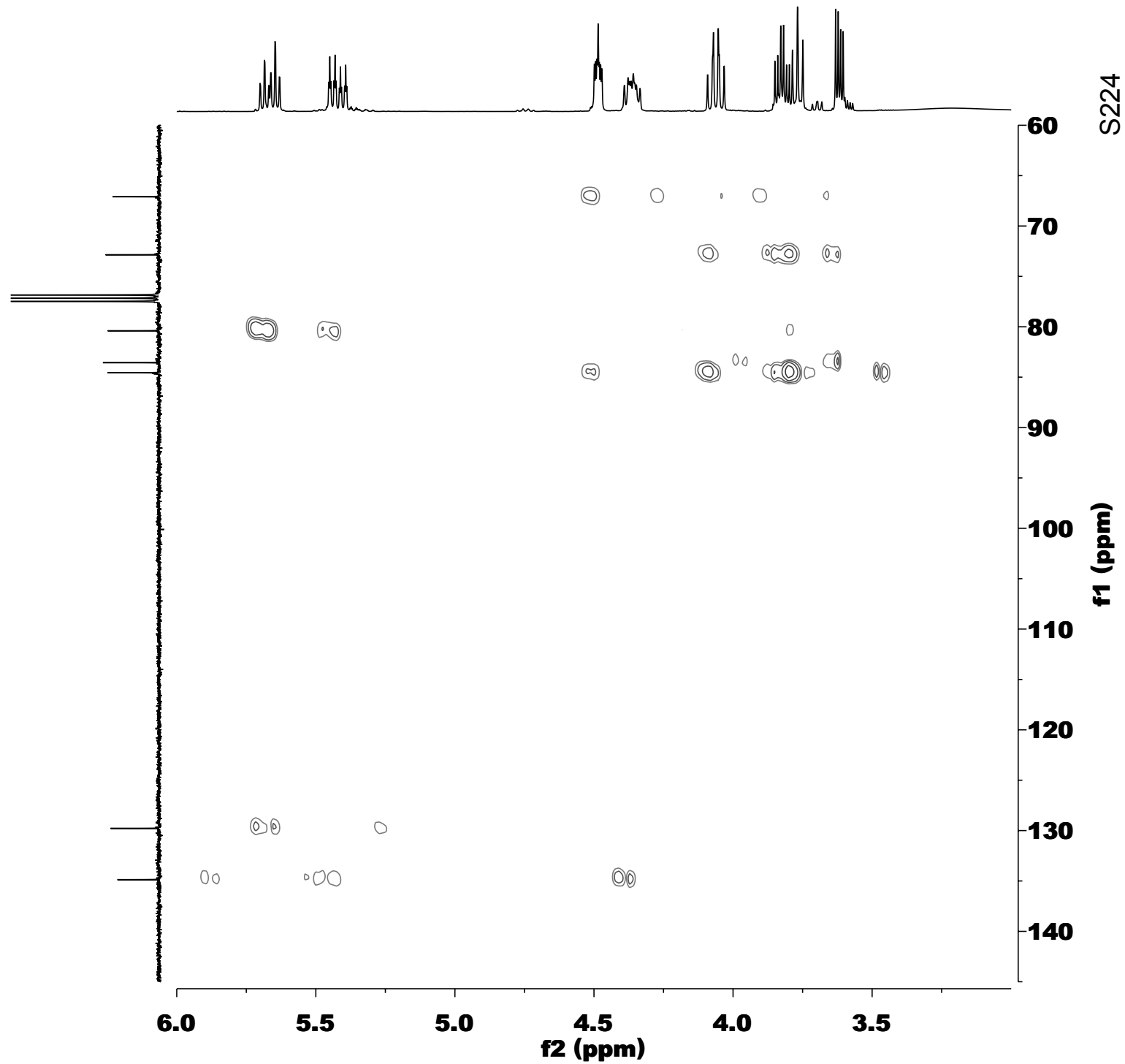
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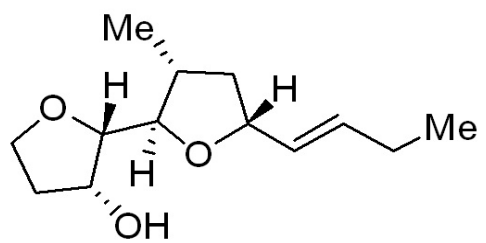




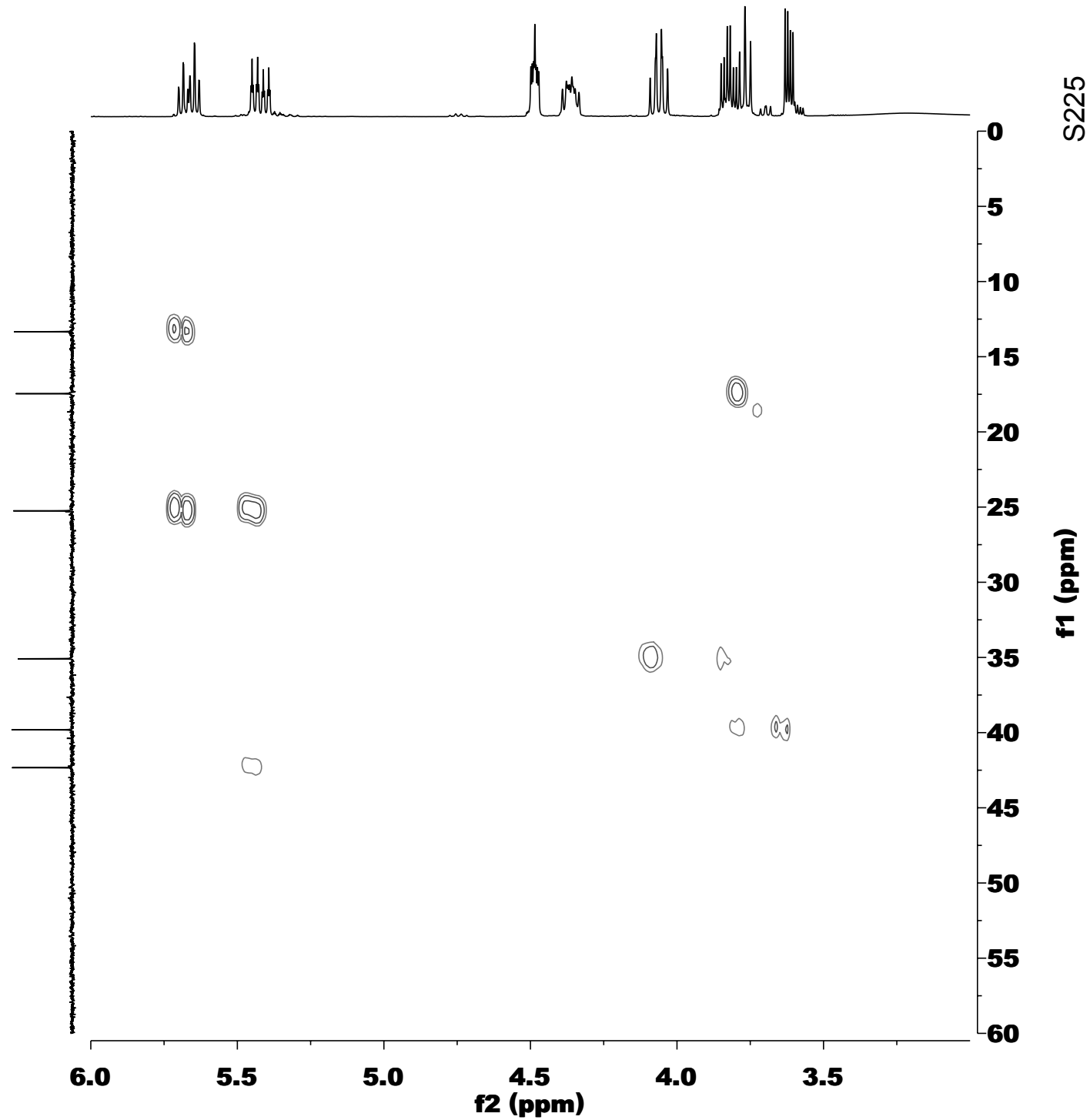
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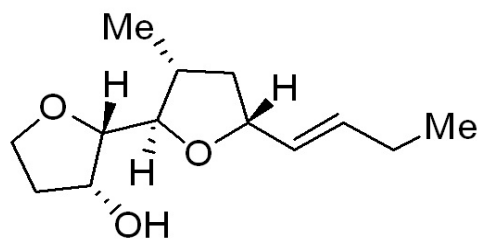




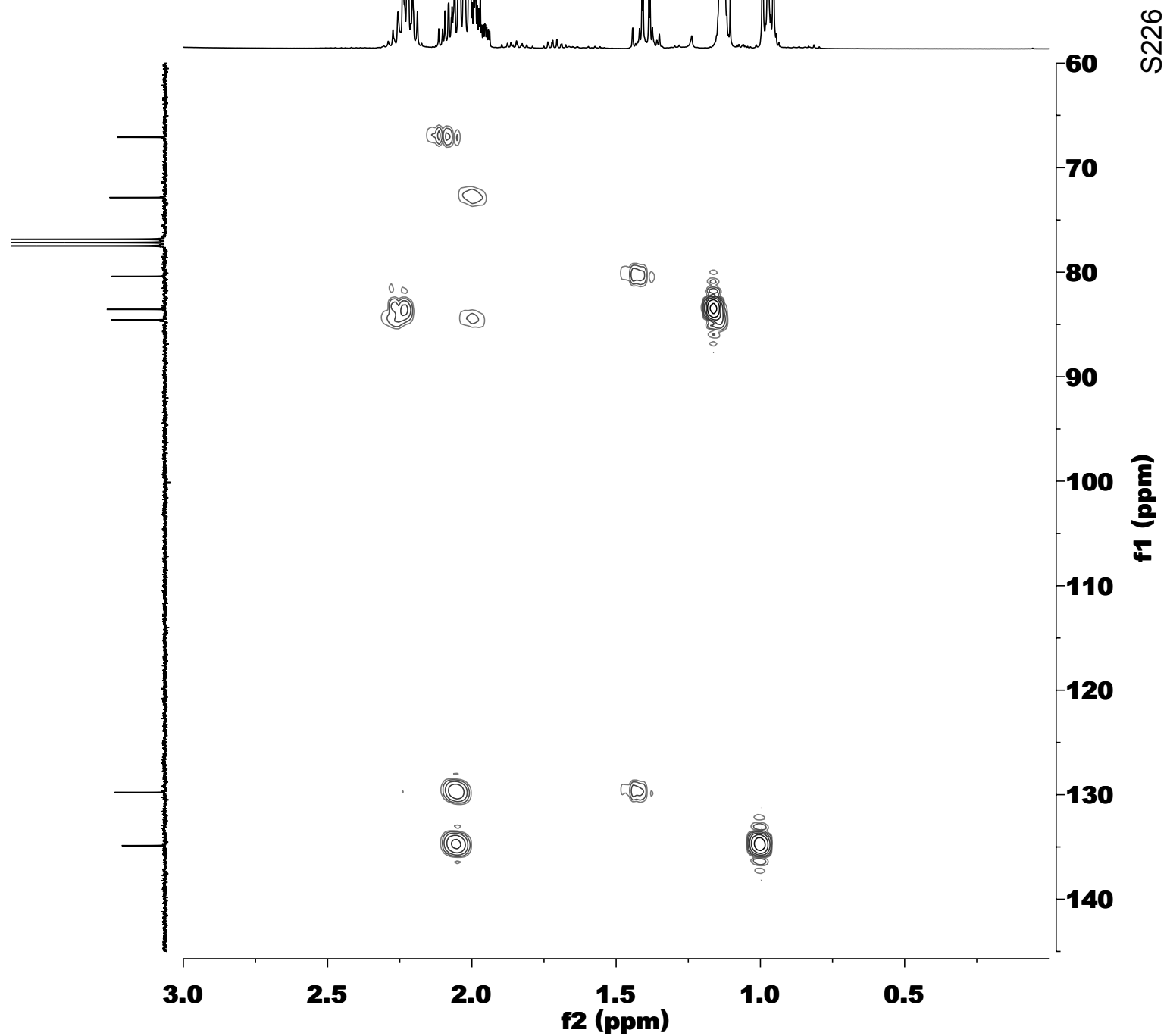


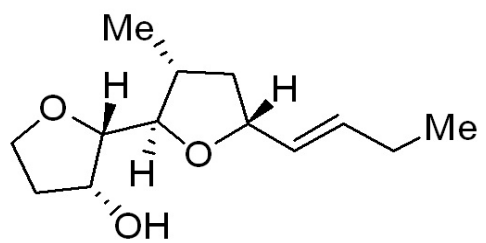
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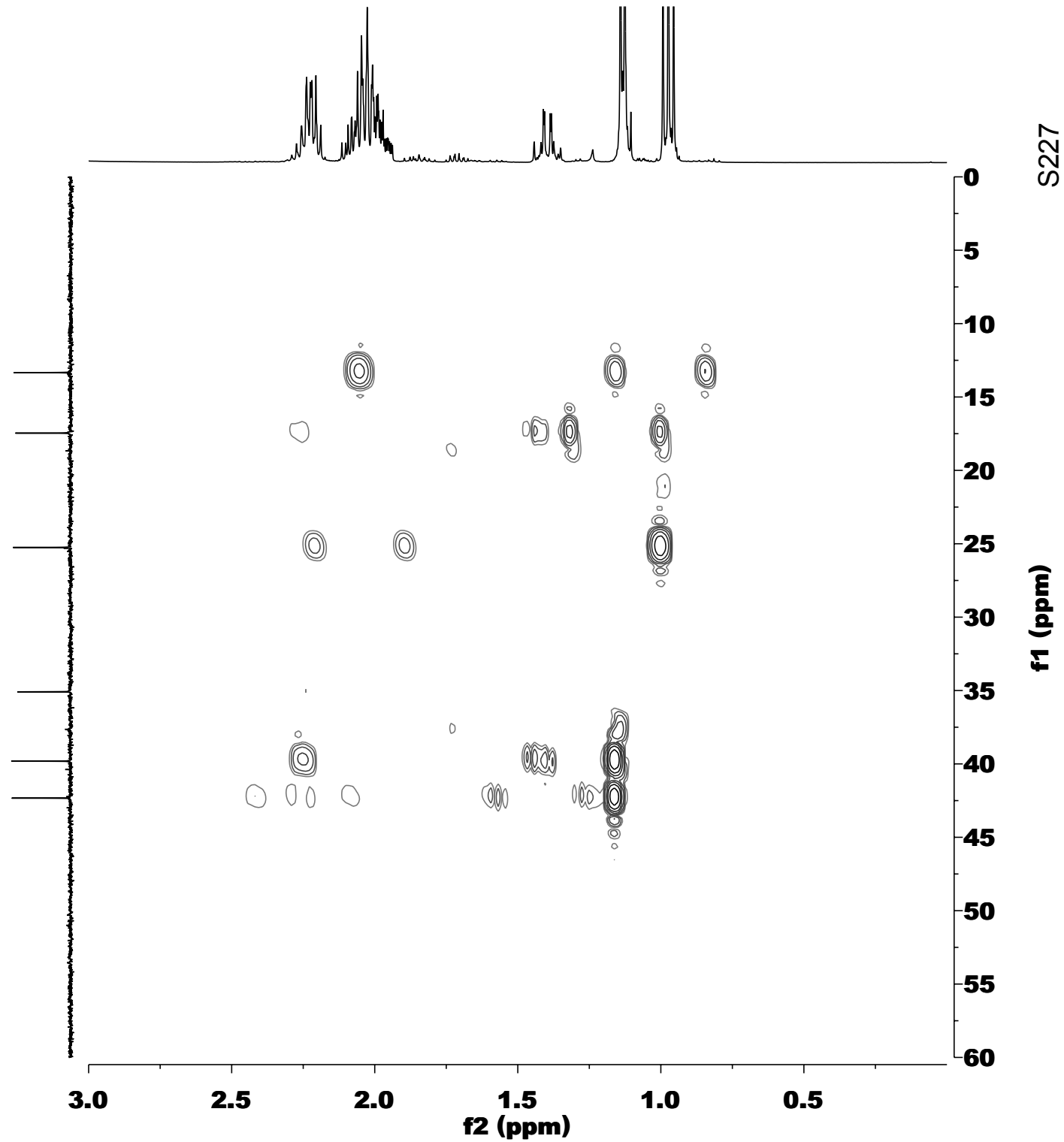


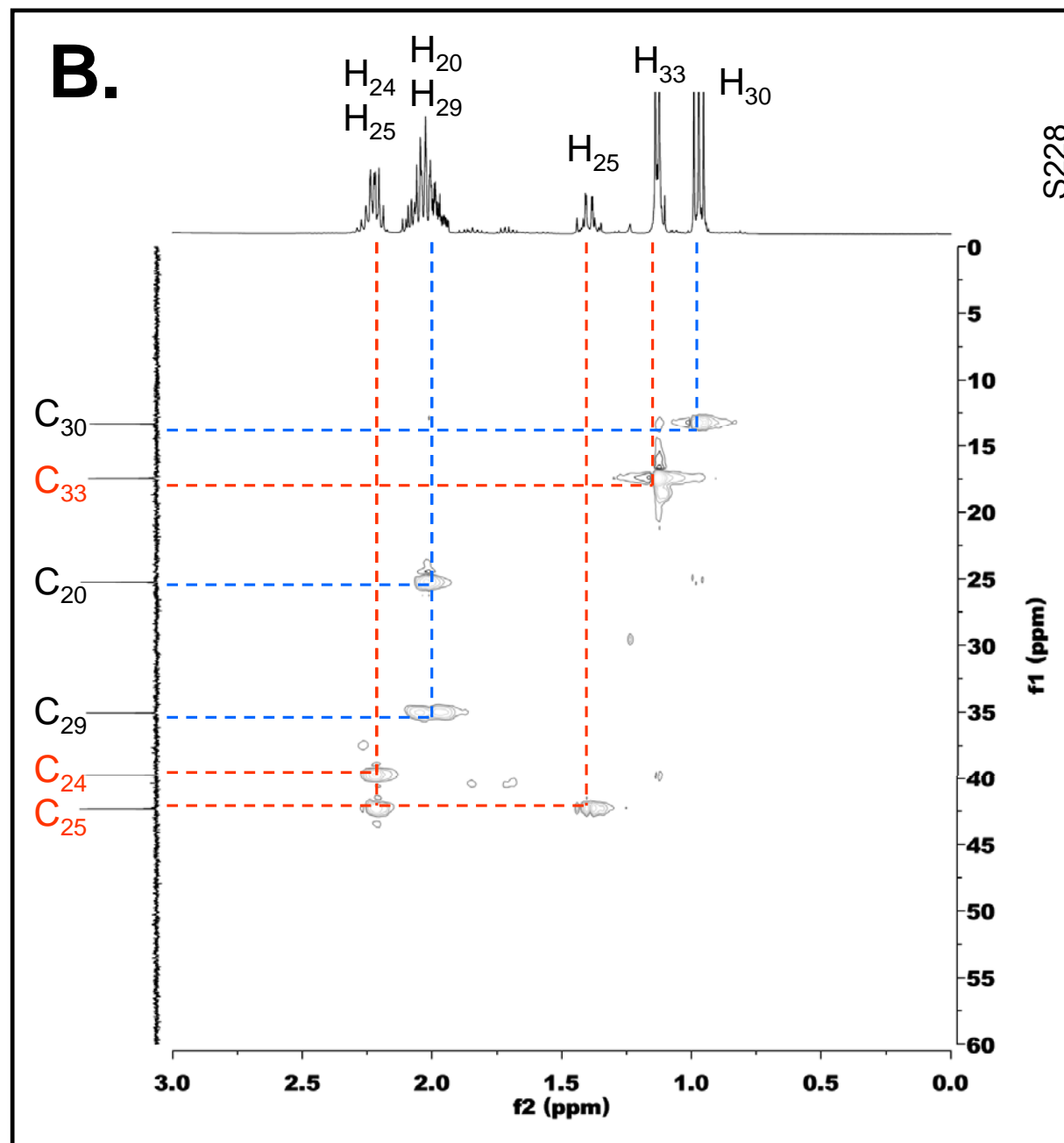
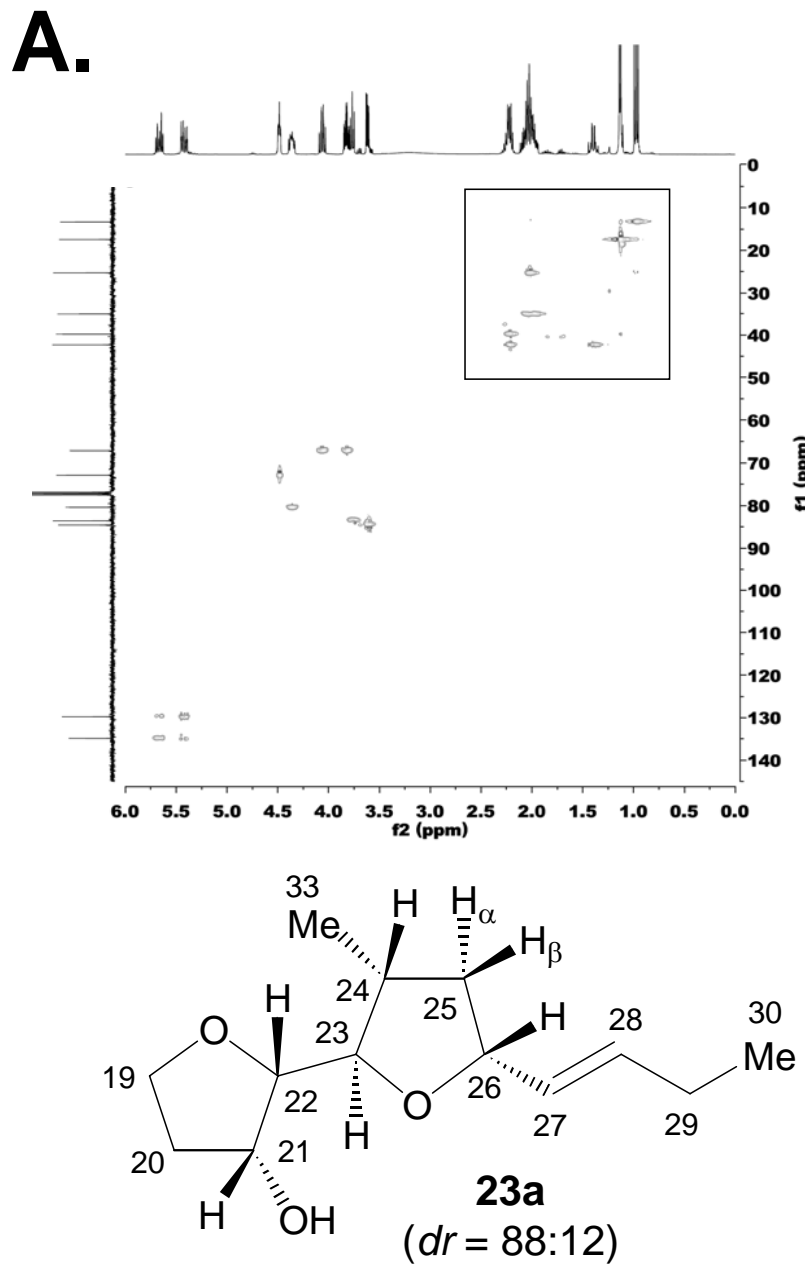
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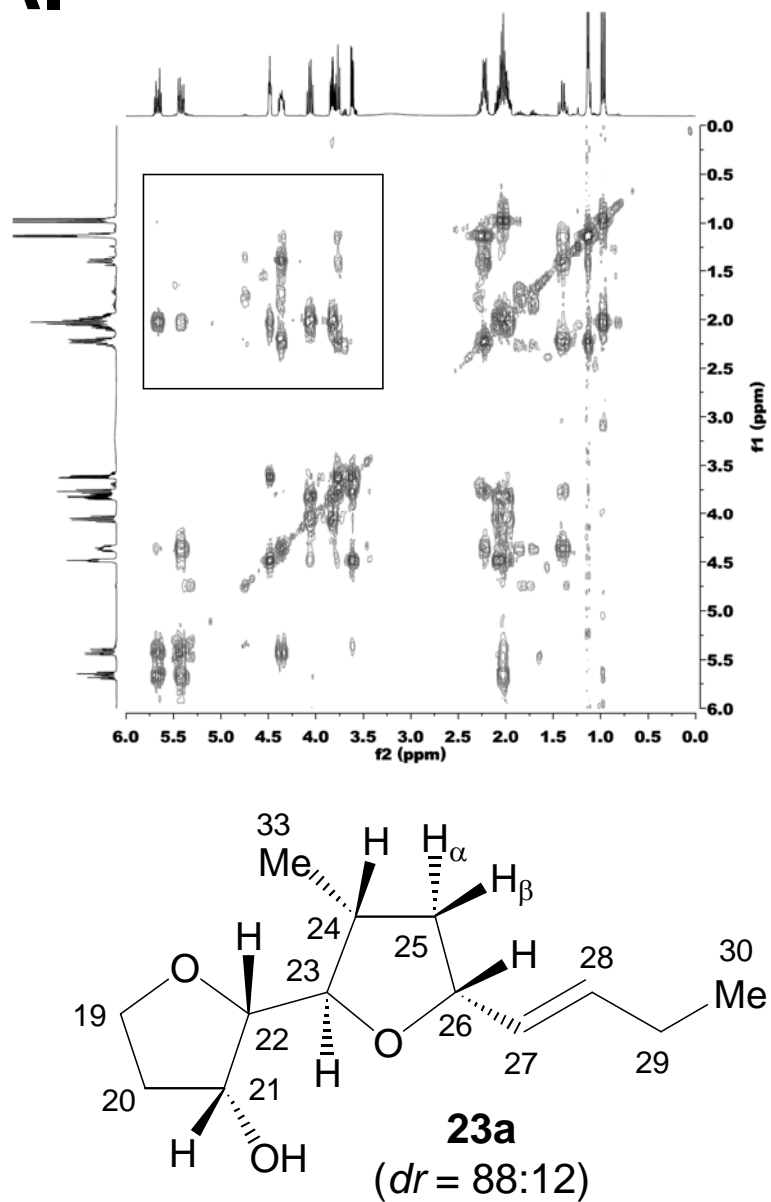
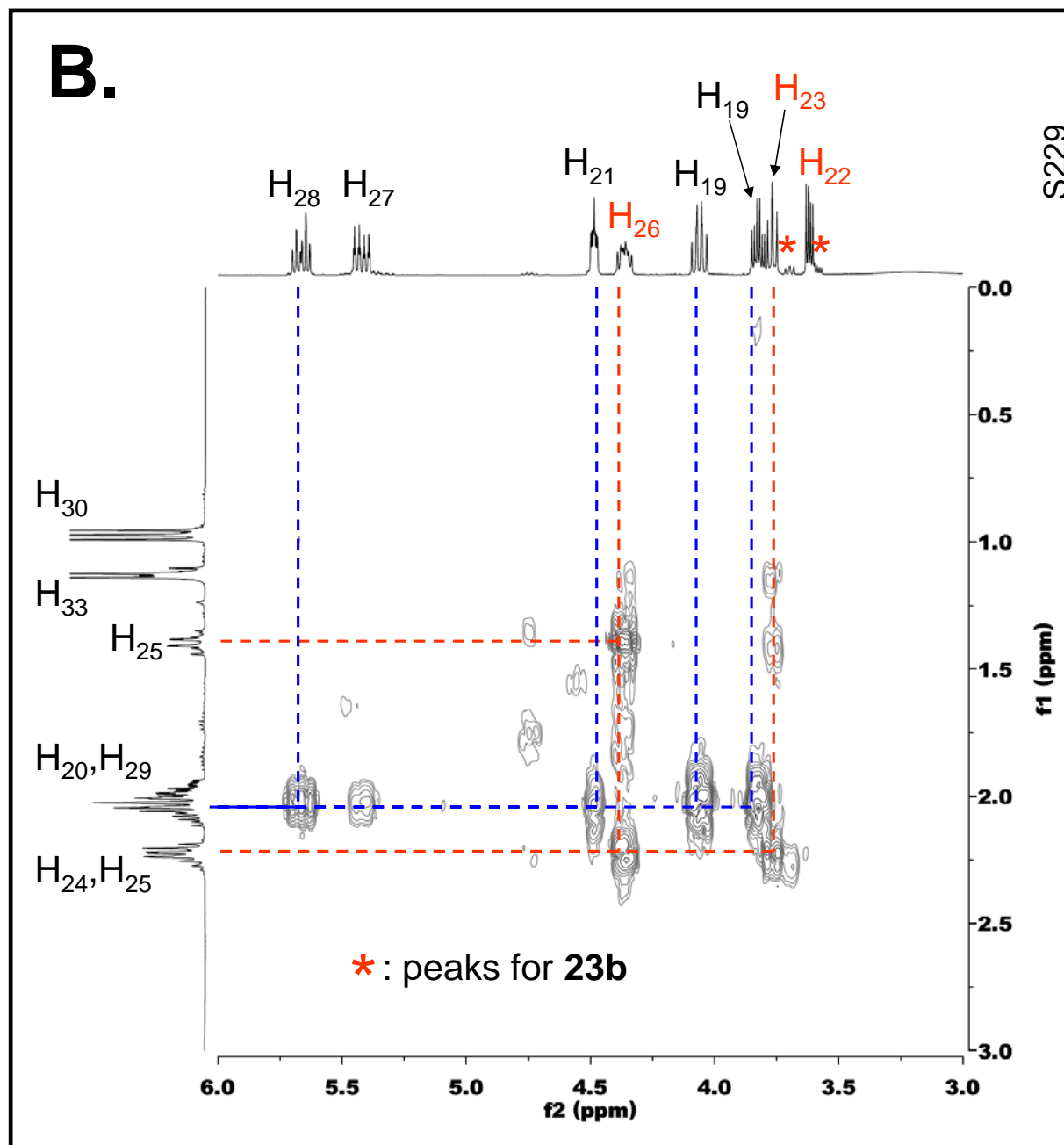


**gk180101-1\_HMBC**





**Fig. S2.** Analysis of HSQC spectrum of **23a**. **A:** The whole HSQC spectrum. **B:** Expansion of the box in **A**.

**A.****B.**

**Fig. S3.** Analysis of COSY spectrum of **23a**. **A:** The whole COSY spectrum. **B:** Expansion of the box in **A**.