An Oxidative Dearomatization Approach to Prepare the Pentacyclic Core of Ryanodol

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Supporting Information:

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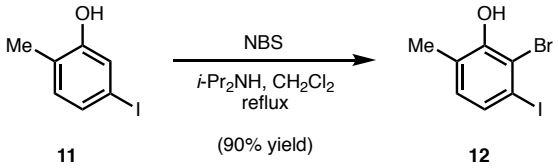
1. General Procedures

Unless otherwise stated, reactions were performed under an inert atmosphere (dry N_2 or Ar) with freshly dried solvents utilizing standard Schlenk techniques. Glassware was oven-dried at 120 °C for a minimum of four hours, or flame-dried utilizing a Bunsen burner under high vacuum. Tetrahydrofuran (THF), methylene chloride (CH_2Cl_2), acetonitrile (CH_3CN), 1,4-dioxane, benzene (PhH), and toluene (PhMe) were dried by passing through activated alumina columns. Methanol (HPLC grade) was purchased from Fisher Scientific. Triethylamine (Et_3N), diisopropylamine (*i*-Pr_2NH), diisopropylethylamine (*i*-Pr_2EtN), pyridine (Pyr), and 2,6-lutidine were distilled from calcium hydride prior to use and stored under N_2 or Ar. Commercial reagents were used directly as supplied from commercial sources and without further purification unless otherwise specified. All reactions were monitored by thin-layer chromatography using EMD/Merck silica gel 60 F254 pre-coated plates (0.25 mm) and were visualized by UV (254 nm) and $KMnO_4$, *p*-anisaldehyde, or CAM staining. Flash column chromatography was performed using silica gel (SiliaFlash® P60, particle size 40-63 microns [230 to 400 mesh]) purchased from Silicycle. ^1H and ^{13}C NMR spectra were recorded on a Bruker Avance III HD with Prodigy Cryoprobe (at 400 MHz and 101 MHz, respectively) or Varian Inova 500 (at 500 MHz and 126 MHz, respectively) and are reported relative to internal $CHCl_3$ (^1H, δ = 7.26) or CD_2HOD (^1H, δ = 3.31) and $CDCl_3$ (^{13}C, δ = 77.0) or CD_3OD (^{13}C, δ = 49.0). Data for ^1H NMR spectra are reported as follows: chemical shift (δ ppm) (multiplicity, coupling constant (Hz), integration). Multiplicity and qualifier abbreviations are as follows: s = singlet, d = doublet, t = triplet, q = quartet, p = pentet, m = multiplet, br = broad, app = apparent. IR spectra were recorded on a Perkin Elmer Paragon 1000 spectrometer and are reported in frequency of absorption (cm^{-1}). HRMS were acquired using an Agilent 6200 Series TOF with an Agilent G1978A Multimode source in electrospray ionization (ESI), atmospheric pressure chemical ionization (APCI), or mixed (MM) ionization mode.

2. Synthetic Procedures

Preparation of iodobromophenol 12:

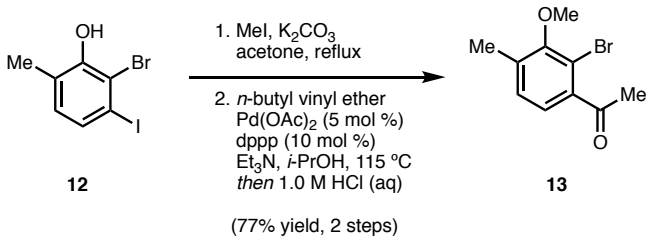


11 **12**

A flame-dried, 1 L flask was equipped with a Soxhlet apparatus and flushed with Ar prior to the addition of iodoarene **11** (18.9 g, 81.0 mmol, 1.0 equiv), anhydrous *i*-$PrNH_2$ (2.8 mL, 20.3 mmol, 0.25 equiv), and anhydrous CH_2Cl_2 (405 mL). The thimble was filled with NBS (14.4 g, 81.0 mmol, 1.0 equiv) and the system was then heated to reflux for 20 h. During this time, the NBS was slowly consumed. After cooling to ambient temperature, the reaction mixture was treated with aqueous H_2SO_4 (2.0 M, 100 mL). The organic layer was separated, washed with sat. aq. $NaHCO_3$ (100 mL) and brine (100 mL), dried over $MgSO_4$, filtered, and concentrated *in vacuo*. Purification by SiO_2 flash chromatography (5% EtOAc/hexanes) afforded the desired product **12** as a white solid (22.7 g, 72.5 mmol, 90% yield).

TLC (5% EtOAc/hexanes): R_f 0.55 (UV, $KMnO_4$).
^{1}H NMR (400 MHz, $CDCl_3$): 7.31 (d, J = 8.0 Hz, 1H), 6.84 (d, J = 8.0 Hz, 1H), 5.65 (s, 1H), 2.25 (d, J = 0.8 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$): δ 151.0, 131.4, 131.2, 125.5, 117.7, 96.1, 16.5.
FTIR (NaCl, thin film): 3396, 1582, 1215, 795 cm^{-1}.
HRMS (MM:ESI–APCI): calc'd for $[M–H]^-$ 310.8574, found 310.8579.

Preparation of methyl ketone 13:



12 **13**

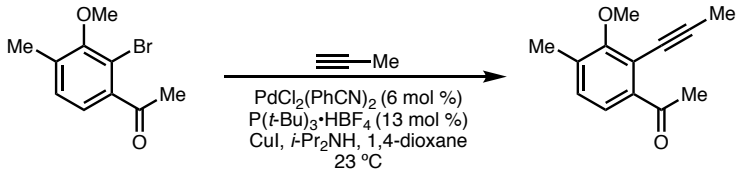
A 1 L round-bottomed flask was charged with **12** (22.7 g, 72.5 mmol, 1.0 equiv), K_2CO_3 (30 g, 218.0 mmol, 3.0 equiv), MeI (12.4 g, 87.0 mmol, 1.2 equiv) and acetone (290 mL). After stirring at 70 ºC for 5 h, the reaction mixture was cooled to room temperature, diluted with hexanes (300 mL), filtered through SiO_2 (50 g), and concentrated *in vacuo* to afford a thick oil. The crude product was used in the next step without further purification.

A flame-dried, 500 mL Schlenk tube was charged with crude methyl ether, $Pd(OAc)_2$ (763 mg, 3.4 mmol, 0.05 equiv), 1,3-bis(diphenylphosphino)propane (2.9 g, 6.9 mmol, 0.1 equiv), *n*-butyl vinyl ether (26.5 mL, 204.0 mmol, 3.0 equiv), anhydrous Et_3N (23.4 mL, 150 mmol, 2.5 equiv), and distilled *i*-PrOH (100 mL). The solution was degassed with N_2 for 10 min. The Schlenk tube was sealed and then placed in a preheated oil bath at 115 ºC. After stirring at this temperature for 20 h, the reaction mixture was cooled to ambient temperature, diluted with EtOAc (300 mL), and poured into a 1 L Erlenmeyer flask equipped with a stir bar. Aqueous HCl (1.0 M, 300 mL) was added to the reaction mixture. After stirring for 10 min, the organic layer was separated, washed with sat. aq. $NaHCO_3$ (2 × 150 mL) and brine (100 mL), dried over $MgSO_4$, filtered, and concentrated *in vacuo*. Purification by

SiO_2 flash chromatography (10% EtOAc/hexanes) afforded the desired product **13** as a thick oil (13.6 g, 56.0 mmol, 77% yield).

TLC (10% EtOAc/hexanes): R_f 0.40 (UV, $KMnO_4$).
^{1}H NMR (400 MHz, $CDCl_3$): 7.17 (dd, J = 7.8, 0.7 Hz, 1H), 7.11 (d, J = 7.8 Hz, 1H), 3.81 (s, 3H), 2.60 (s, 3H), 2.36 (d, J = 0.7 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$): δ 201.2, 155.8, 141.2, 135.7, 130.2, 123.9, 114.5, 60.2, 30.4, 16.7.
FTIR (NaCl, thin film): 2939, 1700, 1375, 1282, 1016, 815 cm^{-1}.
HRMS (ESI) calc'd for $[M]^+$ 241.9942, found 241.9938.

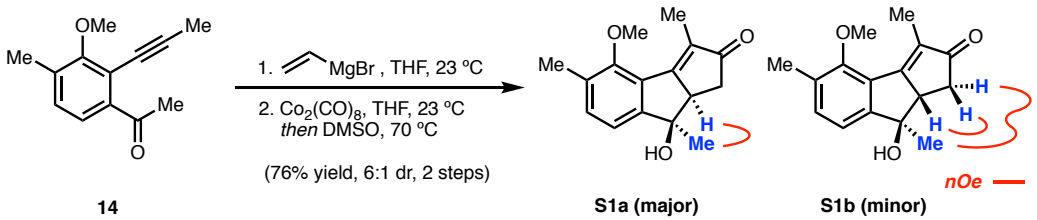
Preparation of alkyne 14:



To an oven-dried, 500 mL Schlenk tube was added bromoarene **13** (9.7g, 40.0 mmol, 1.0 equiv), $PdCl_2(PhCN)_2$ (922 mg, 2.4 mmol, 0.06 equiv), P(*t*-Bu)$_3$•HBF_4 (1.5g, 5.2 mmol, 0.13 equiv), CuI (305 mg, 1.6 mmol, 0.04 equiv), and anhydrous 1,4-dioxane (40 mL). The solution was degassed with N_2 for 10 min, then anhydrous *i*-Pr_2NH (14.0 mL, 100.0 mmol, 2.5 equiv) was added, prior to degassing for another 10 min. The resulting solution was cooled to –78 ºC via a dry ice/acetone bath and propyne (*g*) (approx. 30 mL) was condensed over the reaction mixture. [Caution! All manipulations involving propyne (*g*) were performed behind a blast shield as a safety precaution.] The Schlenk tube was then sealed and warmed to ambient temperature. After stirring for 22 h, the reaction mixture turned brown and was again cooled to –78 ºC. The Schlenk tube was vented carefully and then slowly warmed to ambient temperature. During this process, excess propyne gas was evaporated. After all the propyne gas was evacuated, the reaction mixture was diluted with EtOAc (30 mL). The solution was filtered through a pad of SiO_2 (100 g), which was then washed with additional EtOAc (400 mL), and the combined filtrate was concentrated *in vacuo* to afford a black oil. Purification by SiO_2 flash chromatography (5 to 10% EtOAc/hexanes) afforded the desired product **14** as a light yellow oil (6.2 g, 30.6 mmol, 77 % yield).

TLC (10% EtOAc/hexanes): R_f 0.45 (UV, *p*-anisaldehyde).
^{1}H NMR (400 MHz, $CDCl_3$): 7.32 (d, J = 7.9 Hz, 1H), 7.13 (dd, J = 7.9, 0.7 Hz, 1H), 3.87 (s, 3H), 2.66 (s, 3H), 2.29 (d, J = 0.7 Hz, 3H), 2.15 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$): δ 200.5, 160.3, 141.0, 135.2, 130.0, 123.7, 116.2, 96.4, 74.5, 60.3, 29.9, 16.3, 4.9.
FTIR (NaCl, thin film): 2927, 1688, 1265, 1018 cm^{-1}.
HRMS (MM:ESI–APCI): calc'd for $[M+H]^+$ 203.1073, found 203.1088.

Preparation of Pauson-Khand cycloadduct S1:



14 **S1a (major)** **S1b (minor)**

A flame-dried, 1 L round-bottomed flask was charged with vinylmagnesium bromide (1.0 M in THF, 50.0 mL, 50.0 mmol, 2.0 equiv) and anhydrous THF (50 mL). A separate flask was then charged with ketone **14** (5.05 g, 25.0 mmol, 1.0 equiv) and anhydrous THF (200 mL). The resulting solution of **14** in THF was added dropwise to the 1 L flask containing the Grignard reagent via cannula over 2 h. Upon complete addition, the reaction mixture was quenched with sat. aq. NH_4Cl (100 mL). The organic layer was separated and the aqueous layer was extracted with Et_2O (2 × 150 mL). The combined organic layers were dried over $MgSO_4$, filtered through a plug of Celite, and concentrated *in vacuo* to afford a crude mixture of the desired 1,2-addition product, which was azeotroped with PhH (3 × 100 mL) and dried under high vacuum for 30 min.

This crude mixture was dissolved in anhydrous THF (250 mL), and $Co_2(CO)_8$ (10.3 g, 30.0 mmol, 1.2 equiv) was next added in one portion. The reaction mixture was stirred for 1 h with a vent needle under N_2 at ambient temperature [Note: The complexation evolves CO and so the reaction should be run in a well-ventilated fume hood with a vent needle]. Anhydrous DMSO (17.8 mL, 250 mmol, 10 equiv) was then added dropwise via syringe. The reaction mixture was next placed in a preheated oil bath at 70 ºC. After continued stirring at this temperature for 13 h, the reaction was cooled to ambient temperature and diluted with EtOAc (100 mL). Celite (100 g) was added and the reaction mixture stirred for another 2 h, prior to filtering over a pad of SiO_2 (50 g) and washing the pad with additional EtOAc (300 mL). ^{1}H NMR analysis of the crude mixture shows a 6:1 diastereomeric mixture. Purification by SiO_2 flash chromatography (30 to 50 to 75% EtOAc/hexanes) afforded a mixture of the diastereomers **S1** as a white solid (6.2 g, 30.6 mmol, 76% yield). A small sample was purified by a second round of SiO_2 flash chromatography (40 to 50 to 70% EtOAc/hexanes) to separate the major and minor diastereomer for characterization purpose. The *relative* stereochemistry of the cycloadducts were confirmed by nOe analysis.

Major Diastereomer:

TLC (50% EtOAc/Hexanes): R_f 0.40 (UV, *p*-anisaldehyde).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.32 (dd, *J* = 7.7, 0.8 Hz, 1H), 7.19 (d, *J* = 7.7 Hz, 1H), 3.77 (s, 3H), 3.20 (ddq, *J* = 6.7, 4.5, 2.2 Hz, 1H), 2.63 (dd, *J* = 17.8, 4.5 Hz, 1H), 2.55 (dd, *J* = 17.8, 6.6 Hz, 1H), 2.34 (d, *J* = 0.7 Hz, 3H), 2.08 (d, *J* = 2.2 Hz, 3H), 1.69 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 210.3, 168.8, 155.1, 152.0, 134.7, 133.8, 132.3, 128.1, 118.8, 75.6, 60.8, 55.7, 35.2, 24.6, 15.9, 9.9.

FTIR (NaCl, thin film): 3389, 2963, 2919, 1690, 1639, 1320, 1227, 1091, 1018, 921 cm^{-1}.

HRMS (MM:ESI–APCI): calc'd for $[M+Na]^+$ 259.1334, found 259.1347.

Minor Diastereomer:

TLC (10% EtOAc/hexanes): R_f 0.25 (UV, *p*-anisaldehyde).

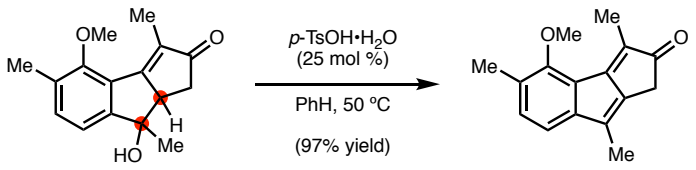
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.34 (dd, *J* = 7.6, 0.8 Hz, 1H), 7.22 (d, *J* = 7.7 Hz, 1H), 3.76 (s, 3H), 3.44 (ddd, *J* = 6.6, 4.1, 2.2 Hz, 1H), 2.67 (dd, *J* = 18.3, 6.8 Hz, 1H), 2.45 (dd, *J* = 18.3, 4.0 Hz, 1H), 2.34 (d, *J* = 0.7 Hz, 3H), 2.07 (d, *J* = 2.3 Hz, 3H), 1.23 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 209.7, 167.5, 154.6, 153.8, 135.0, 132.4, 131.4, 126.6, 118.7, 78.6, 60.9, 58.8, 36.0, 24.4, 15.8, 9.7.

FTIR (NaCl, thin film): 3404, 2966, 2927, 1700, 1639, 1324, 1247, 1020, 732 cm^{-1}.

HRMS (MM:ESI–APCI): calc'd for $[M+Na]^+$ 259.1334, found 259.1333.

Preparation of tricycle 15:

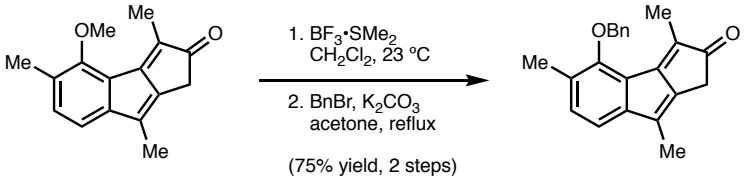


S1 **15**

A 250 mL round-bottomed flask was charged with **S1** (4.9 g, 18.9 mmol, 1.0 equiv) and anhydrous PhH (95 mL). *p*-TsOH•H_2O (897 mg, 4.7 mmol, 0.25 equiv) was next added in one portion. The reaction mixture was placed in a preheated oil bath at 50 ºC and stirred for 40 min. Upon cooling to ambient temperature, the reaction mixture was diluted with EtOAc (100 mL) and carefully quenched with the addition of sat. aq. $NaHCO_3$ (50 mL). The organic layer was separated and washed with sat. aq. $NaHCO_3$ (3 × 100 mL). The aqueous layers were then back extracted with EtOAc (75 mL). The combined organic layers were dried over $MgSO_4$, filtered, and concentrated *in vacuo* to afford tricycle **15** as a bright orange solid (4.4 g, 18.3 mmol, 97% yield).

TLC (10% EtOAc/hexanes): R_f 0.50 (UV, $KMnO_4$).
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.18 (dd, *J* = 7.4, 0.9 Hz, 1H), 6.84 (d, *J* = 7.4 Hz, 1H), 3.78 (s, 3H), 3.14 (d, *J* = 1.1 Hz, 2H), 2.33 (dd, *J* = 5.3, 0.8 Hz, 6H), 2.06 (d, *J* = 1.2 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$): δ 207.9, 163.0, 155.9, 149.0, 136.7, 135.6, 134.2, 129.3, 128.7, 123.3, 115.2, 61.5, 33.8, 15.9, 11.4, 10.4.
FTIR (NaCl, thin film): 1694, 1294, 1018 cm^{-1}.
HRMS (MM:ESI–APCI): calc'd for $[M+H]^+$ 241.1220, found 241.1229.

Preparation of benzyl-protected tricycle 16:



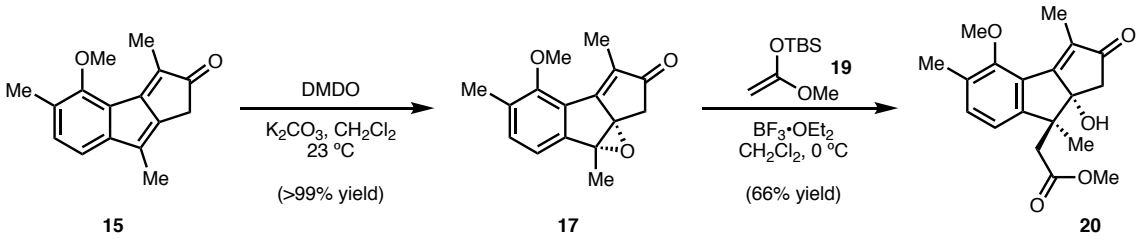
15 **16**

To an oven-dried, 250 mL round-bottomed flask was added **15** (5.0 g, 20.8 mmol, 1.0 equiv) and anhydrous CH_2Cl_2 (60 mL). The solution was cooled to 0 ºC via an ice/water bath prior to the dropwise addition of BF_3•SMe_2 (95%, 21.9 mL, 208 mmol, 10 equiv) via syringe. After complete addition, the solution was warmed to 23 ºC and stirred for 12 h. The reaction was quenched by the careful addition of aqueous NaOH (1.0 M, 250 mL), thereby rendering the free phenol alkaline. The aqueous layer was separated and extracted with Et_2O (3 x 100 mL) to remove unreacted starting material and dimethyl sulfide. The aqueous layer was next acidified in an ice/water bath with aqueous HCl (6.0 N) until a pH = 2 was achieved, and the aqueous layer was then extracted with EtOAc (3 × 100 mL). The combined EtOAc layers were washed with brine (100 mL), dried over $MgSO_4$, filtered, and concentrated *in vacuo* to afford an orange solid, which was used in the next step without further purification.

A 1 L round-bottomed flask was charged with the crude phenol, K_2CO_3 (8.7 g, 62.9 mmol, 3.0 equiv), BnBr (7.2 g, 42.1 mmol, 2.0 equiv), and acetone (210 mL). After stirring at 70 ºC for 24 h, the reaction mixture was cooled to ambient temperature, diluted with hexanes (300 mL), filtered through SiO_2 (50 g), and concentrated *in vacuo*. Purification by SiO_2 flash chromatography (5 to 10% EtOAc/hexanes) afforded benzyl ether **16** as an orange solid (5.0 g, 15.8 mmol, 75% yield).

TLC (10% EtOAc/hexanes): R_f 0.50 (UV, $KMnO_4$).
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.47 – 7.30 (m, 5H), 7.20 (dd, *J* = 7.3, 0.9 Hz, 1H), 6.87 (d, *J* = 7.4 Hz, 1H), 4.91 (s, 2H), 3.15 (d, *J* = 1.1 Hz, 2H), 2.29 (d, *J* = 0.8 Hz, 3H), 2.20 (d, *J* = 0.8 Hz, 3H), 2.08 (q, *J* = 0.8 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$): δ 207.9, 163.1, 154.7, 149.1, 136.9, 136.7, 135.6, 134.2, 129.3, 129.1, 128.5, 128.1, 127.5, 123.7, 115.3, 75.9, 33.8, 16.3, 11.4, 11.0.
FTIR (NaCl, thin film): 1702, 1294, 1215, 1018 cm^{-1}.
HRMS (MM:ESI–APCI): calc'd for $[M+H]^+$ 317.1542, found 317.1546.

Preparation of methyl ester 20:

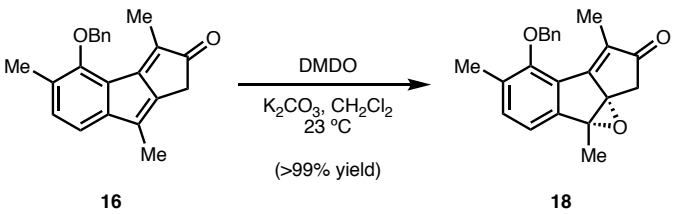


An oven-dried, 100 mL round-bottomed flask was charged with tricycle **15** (500 mg, 2.08 mmol, 1.0 equiv), K_2CO_3 (2.59 g, 18.7 mmol, 9.0 equiv), and anhydrous CH_2Cl_2 (10 mL). Freshly prepared DMDO[1] (0.06 M in acetone, 49 mL, 2.91 mmol, 1.4 equiv) was next added. The resulting reaction mixture was stirred for 10 min at ambient temperature at which point TLC analysis indicated the complete consumption of starting material. The reaction mixture was next filtered over a pad of Celite and concentrated *in vacuo* to afford epoxide **17** as a pale yellow-orange solid (535 mg, 2.09 mmol, >99% yield) [Note: epoxide **17** is not stable and should be used immediately in the next step without purification].

To an oven-dried, 50 mL round-bottomed flask was added crude epoxide **17** (535 mg, 2.09 mmol, 1.0 equiv) and anhydrous CH_2Cl_2 (10 mL). The stirred solution was treated with silyl ketene acetal **19** (0.46 mL, 2.09 mmol, 1.0 equiv) prior to cooling to 0 ºC via an ice/water bath. After 15 min of continued stirring, BF_3•OEt_2 (0.26 mL, 2.09 mmol, 1.0 equiv) was rapidly added as a single portion via syringe. The resulting reaction mixture was vigorously stirred (1000 rpm) for 3 min at 0 ºC, and then immediately quenched with the addition of sat. aq. $NaHCO_3$ (20 mL). The quenched solution was stirred for another 25 min at 0 ºC and then diluted with CH_2Cl_2 (30 mL). The layers were separated and the aqueous layer was extracted with CH_2Cl_2 (3 × 40 mL), then the combined organic layers were washed with brine (40 mL), dried over Na_2SO_4, filtered, and concentrated *in vacuo* to afford a deep orange foam. Purification by SiO_2 flash chromatography (30 to 50% EtOAc/hexanes) afforded the methyl ester **20** as an orange foam (453 mg, 1.37 mmol, 66% yield).

TLC (50% EtOAc/hexanes): R_f 0.33 (UV, CAM).
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.28 (d, *J* = 7.7 Hz, 1H), 7.01 (d, *J* = 7.7 Hz, 1H), 3.76 (s, 3H), 3.48 (s, 3H), 2.66 (d, *J* = 18.1 Hz, 1H), 2.52 (d, *J* = 18.1 Hz, 1H), 2.36 (d, *J* = 13.4 Hz, 1H), 2.33 (s, 3H), 2.12 (s, 3H), 2.11 (s, 1H, OH), 2.08 (d, *J* = 13.5 Hz, 1H), 1.65 (s, 3H).
^{13}C NMR (126 MHz, $CDCl_3$): δ 208.0, 170.8, 168.3, 156.5, 151.8, 134.9, 133.6, 131.2, 125.7, 120.9, 89.1, 61.0, 51.4, 49.4, 43.7, 42.9, 17.7, 15.8, 9.8.
FTIR (NaCl, thin film): 3448, 2950, 1734, 1700, 1652, 1319, 1228, 1018 cm^{-1}.
HRMS (ESI): calc'd for $[M+H]^+$ 331.1540, found 331.1554.

Preparation of epoxide 18:

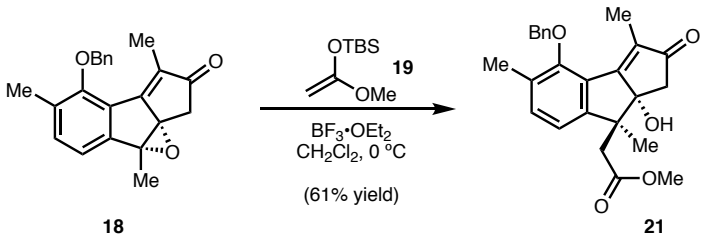


16 **18**

A flame-dried, 250 mL round-bottomed flask was charged with tricycle **16** (1.58 g, 5.0 mmol, 1.0 equiv), K_2CO_3 (6.32 g, 45.7 mmol, 9.1 equiv) and anhydrous CH_2Cl_2 (25 mL). Freshly prepared DMDO[1] (0.09 M in acetone, 83 mL, 7.5 mmol, 1.5 equiv) was next added. The resulting reaction mixture was stirred for 10 min at 23 ºC at which point TLC analysis indicated the complete consumption of starting material. The reaction mixture was next filtered over a pad of Celite and concentrated *in vacuo* to afford epoxide **18** as a light orange solid (1.65 g, 5.0 mmol, 100% yield).

TLC (25% EtOAc/hexanes): R_f 0.30 (UV, $KMnO_4$).
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.40 – 7.30 (m, 5H), 7.25 (d, *J* = 5.7 Hz, 1H), 7.20 (d, *J* = 7.5 Hz, 1H), 4.99 (d, *J* = 11.4 Hz, 1H), 4.81 (d, *J* = 11.4 Hz, 1H), 2.85 (s, 2H), 2.25 (d, *J* = 0.7 Hz, 3H), 2.11 (s, 3H), 1.89 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$): δ 206.4, 161.6, 156.1, 147.4, 137.7, 136.2, 133.9, 133.2, 128.5, 128.3, 128.1, 126.5, 119.6, 76.0, 71.5, 65.5, 34.4, 16.4, 12.5, 10.7.
FTIR (NaCl, thin film): 1706, 1645, 1296 cm^{-1}.
HRMS (MM:ESI–APCI): calc'd for $[M+H]^+$ 333.1491, found 333.1487.

Preparation of methyl ester 21:



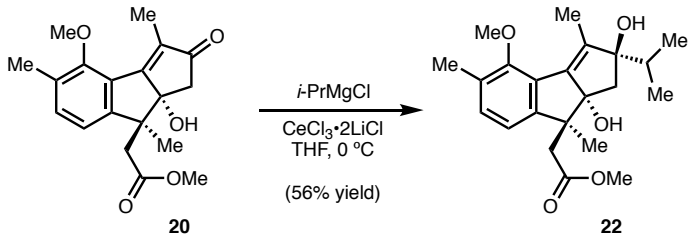
18 **21**

To a flame-dried, 100 mL round-bottomed flask was added crude epoxide **18** (1.65 g, 5.0 mmol, 1.0 equiv) and anhydrous CH_2Cl_2 (25 mL). The stirred solution was treated with silyl ketene acetal **19** (1.1 mL, 5.0 mmol, 1.0 equiv) prior to cooling to 0 ºC via an ice/water bath. After 15 min of continued stirring, BF_3•OEt_2 (0.62 mL, 5.0 mmol, 1.0 equiv) was rapidly added as a single portion via syringe. The resulting reaction mixture was vigorously stirred (1500 rpm) for 3 min at 0 ºC, and then immediately quenched with the addition of sat. aq. $NaHCO_3$ (60 mL). The quenched solution was stirred for another 25 min at 0 ºC and then diluted with CH_2Cl_2 (150 mL). The layers were separated and the organic layer was washed with sat. aq. $NaHCO_3$ (2 × 100 mL). The combined aqueous layers were extracted with CH_2Cl_2 (50 mL), then the combined organic layers were dried over Na_2SO_4, filtered, and concentrated *in vacuo* to afford a deep orange foam. Purification by SiO_2 flash chromatography (35 to 50% EtOAc/hexanes) afforded the methyl ester **21** as a light orange foam (1.23 g, 3.1 mmol, 61% yield).

TLC (50% EtOAc/hexanes): R_f 0.48 (UV, CAM).
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.33 (s, 5H), 7.29 (dd, *J* = 7.7, 0.8 Hz, 1H), 7.02 (d, *J* = 7.7 Hz, 1H), 4.95 (d, *J* = 11.3 Hz, 1H), 4.87 (d, *J* = 11.3 Hz, 1H), 3.47 (s, 3H), 2.65 (d, *J* = 18.2 Hz, 1H), 2.50 (d, *J* = 18.3 Hz, 1H), 2.34 (d, *J* = 13.5 Hz, 1H), 2.31 (s, 3H), 2.06 (d, *J* = 13.4 Hz, 1H), 2.04 (s, 3H), 1.75 (s, 1H, O*H*), 1.64 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 207.9, 170.8, 168.3, 154.7, 151.5, 136.3, 134.9, 134.0, 131.6, 128.4, 128.4, 128.4, 126.6, 121.1, 89.0, 75.4, 51.4, 49.5, 43.6, 42.9, 17.8, 16.2, 10.3.
FTIR (NaCl, thin film): 3447, 2949, 1734, 1700, 1652, 1318, 1216, 1012 cm^{-1}.
HRMS (ESI): calc'd for $[M+H]^+$ 407.1853, found 407.1850.

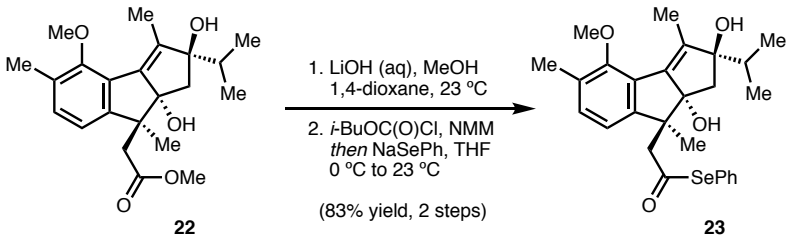
Preparation of diol 22:



An oven-dried, 100 mL round-bottomed flask was charged with enone **20** (453 mg, 1.37 mmol, 1.0 equiv) and anhydrous THF (27 mL). To the resulting solution was added a solution of $CeCl_3$•2LiCl[2] (0.3 M in THF, 9.1 mL, 2.74 mmol, 2.0 equiv) at ambient temperature via syringe and stirring was continued for an additional 1 h before cooling the bright orange solution to 0 ºC via an ice/water bath. After 15 min, isopropylmagnesium chloride (2.0 M in THF, 1.0 mL, 2.06 mmol, 1.5 equiv) was added dropwise over 10 min via syringe. Upon complete addition, the reaction was allowed 30 min at 0 ºC before an additional portion of isopropylmagnesium chloride (2.0 M in THF, 0.5 mL, 1.03 mmol, 0.75 equiv) was added dropwise via syringe. After another 30 min of stirring, the reaction mixture was quenched with the addition of sat. aq. NH_4Cl (10 mL). The quenched reaction was diluted with Et_2O (20 mL) and then filtered through a pre-equilibrated SiO_2 pad layered with Celite, washing with 75% EtOAc/hexanes. The filtrate was concentrated *in vacuo* and the crude residue was purified via SiO_2 flash chromatography (20 to 30 to 40% EtOAc/hexanes) to afford 1,2-addition product **22** as an orange foam (287 mg, 0.77 mmol, 56% yield).

TLC (50% EtOAc/hexanes): R_f 0.57 (UV, *p*-anisaldehyde).
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.09 (dd, *J* = 7.6, 0.8 Hz, 1H), 6.90 (d, *J* = 7.6 Hz, 1H), 3.71 (s, 3H), 3.33 (s, 3H), 2.76 (s, 1H, OH), 2.47 (d, *J* = 12.9 Hz, 1H), 2.40 (d, *J* = 12.9 Hz, 1H), 2.28 (s, 3H), 2.26 (d, *J* = 15.4 Hz, 1H), 2.11 (d, *J* = 15.4 Hz, 1H), 2.03 (p, *J* = 6.9 Hz, 1H), 1.97 (s, 3H), 1.66 (s, 1H, OH), 1.48 (s, 3H), 1.09 (d, *J* = 7.0 Hz, 3H), 0.94 (d, *J* = 7.0 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$): δ 172.6, 154.6, 151.7, 141.0, 139.3, 131.3, 130.3, 126.1, 120.0, 94.9, 94.6, 59.6, 51.5, 49.5, 45.2, 40.2, 33.8, 19.1, 18.4, 17.0, 15.8, 10.5.
FTIR (NaCl, thin film): 3492, 2958, 2876, 1722, 1441, 1252, 1069, 1024 cm^{-1}.
HRMS (ESI): calc'd for $[M–OH]^+$ 357.2060, found 357.2063.

Preparation of acyl selenide 23:



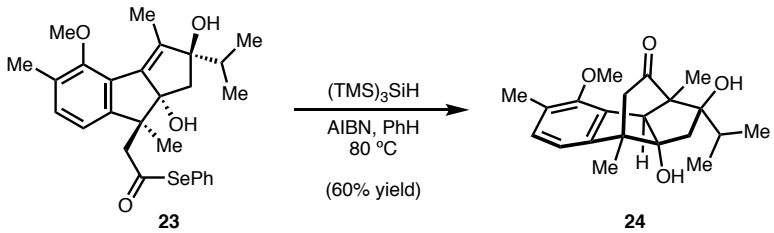
A 50 mL round-bottomed flask was charged with **22** (242 mg, 0.65 mmol, 1.0 eqiuv), LiOH (773 mg, 32.3 mmol, 50.0 equiv), 1,4-dioxane (9.0 mL), MeOH (9.0 mL), and H_2O (3.0 mL). The reaction mixture was stirred at

ambient temperature for 36 h, at which point TLC showed complete consumption of the starting material. The reaction mixture was diluted with EtOAc (10 mL) and acidified with the addition of a pH = 2.5 phosphate buffer solution (prepared by dissolving 100 g of NaH_2PO_4 and 32 g of $KHSO_4$ in 1 L H_2O, 65 mL). The layers were separated and the aqueous layer then extracted with EtOAc (3 × 40 mL). The combined organic layers were dried over Na_2SO_4, filtered, and concentrated *in vacuo* to afford a yellow-orange foam. The crude carboxylic acid was dried under high vacuum for 1 h before used in the next step.

An oven-dried, 50 mL round-bottomed flask was charged with the carboxylic acid (233 mg, 0.65 mmol, 1.0 equiv) and anhydrous THF (13 mL), and the resulting solution was cooled to 0 ºC via an ice/water bath. *N*-methylmorpholine (142 µL, 1.29 mmol, 2.0 equiv) and isobutyl chloroformate (109 µL, 0.84 mmol, 1.3 equiv) were subsequently added via microsyringe. The reaction mixture was continued at 0 ºC for 30 min. Next, a THF solution of NaSePh–freshly prepared by stirring PhSeH (172 µL, 1.62 mmol, 2.5 equiv) and NaH (95%, 41 mg, 1.62 mmol, 2.5 equiv) in THF (3 mL) at 0 ºC for 1 h–was added dropwise via syringe. Upon complete addition, the reaction mixture was stirred at 0 ºC for 15 min and an additional 15 min at ambient temperature, before quenching the reaction with the slow addition of sat. aq. NH_4Cl (5 mL). The mixture was next diluted with EtOAc (5 mL) and the layers separated. The aqueous layer was extracted with EtOAc (3 × 10 mL) and the combined organic layers were washed with brine (10 mL), dried over Na_2SO_4, filtered, and concentrated *in vacuo*. Purification by SiO_2 flash chromatography (20 to 30% EtOAc/hexanes) afforded acyl selenide **23** as an off-white foam (268 mg, 0.54 mmol, 83% yield).

TLC (30% EtOAc/hexanes): R_f 0.41 (UV, *p*-anisaldehyde).
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35 – 7.28 (m, 3H), 7.27 – 7.23 (m, 2H), 7.14 (dd, *J* = 7.6, 0.8 Hz, 1H), 6.95 (d, *J* = 7.6 Hz, 1H), 3.72 (s, 3H), 2.80 (s, *J* = 13.7 Hz, 1H), 2.72 (d, *J* = 13.7 Hz, 1H), 2.31 (s, 3H), 2.22 (d, *J* = 15.3 Hz, 1H), 2.18 (s, 1H, OH), 2.01 (p, *J* = 7.0 Hz, 1H), 1.99 (d, *J* = 15.3 Hz, 1H), 1.95 (s, 3H), 1.66 (s, 1H, OH), 1.51 (s, 3H), 1.07 (d, *J* = 6.7 Hz, 3H), 0.94 (d, *J* = 7.0 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$): δ 200.3, 154.9, 150.8, 141.0, 139.3, 135.6, 131.5, 130.8, 129.2, 128.9, 126.9, 126.3, 120.9, 94.9, 94.8, 59.7, 56.0, 50.3, 40.3, 34.1, 18.9, 18.5, 17.0, 15.9, 10.6.
FTIR (NaCl, thin film): 3450, 2960, 2360, 1699, 1558, 1457, 1066 cm^{-1}.
HRMS (ESI): calc'd for $[M–OH]^+$ 477.1433, found 477.1458.

Preparation of tetracycle 24:

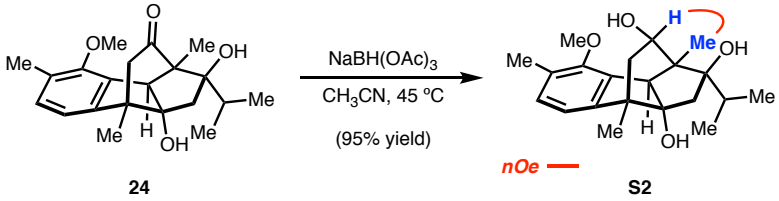


An oven-dried, 100 mL Schlenk tube was charged with acyl selenide **23** (235 mg, 0.47 mmol, 1.0 equiv) and anhydrous PhH (24 mL). The Schlenk tube was evacuated/refilled three times with Ar before being placed in a preheated oil bath at 80 ºC. A solution of azobisisobutyronitrile (0.2 M in PhMe, 2.4 mL, 0.47 mmol, 1.0 equiv) and $(TMS)_3SiH$ (0.36 mL, 1.18 mmol, 2.5 equiv) in anhydrous PhH (3 mL) was next added dropwise via syringe pump over 30 min at 80 ºC. Upon complete addition, the Schlenk tube was sealed and the reaction was stirred for 1 h before an additional portion of azobisisobutyronitrile (0.2 M in PhMe, 1.2 mL, 0.24 mmol, 0.5 equiv) and $(TMS)_3SiH$ (0.15 mL, 0.47 mmol, 1.0 equiv) in anhydrous PhH (1.5 mL) was added dropwise via syringe. After an additional 1 h at 80 ºC, the reaction mixture was removed from the oil bath and cooled to ambient temperature. The solution was diluted with EtOAc (20 mL), transferred to a 100 mL round-bottomed flask, and concentrated *in vacuo*

to afford a white solid [Note: tetracycle **24** is sparingly soluble in EtOAc/hexanes mixtures–CH_2Cl_2 was used to redissolve the crude residue for purification]. Purification by SiO_2 flash chromatography (30 to 50 to 70% EtOAc/hexanes) afforded tetracycle **24** as a white solid (97.1 mg, 0.28 mmol, 60% yield).

TLC (40% EtOAc/hexanes): R_f 0.22 (UV, *p*-anisaldehyde).
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.04 (dd, *J* = 7.5, 0.8 Hz, 1H), 6.80 (d, *J* = 7.5 Hz, 1H), 3.75 (s, 3H), 3.64 (s, 1H), 2.94 (d, *J* = 16.1 Hz, 1H). 2.37 (d, *J* = 15.4 Hz, 1H), 2.25 (d, *J* = 15.4 Hz, 1H), 2.23 (s, 3H), 2.21 (d, *J* = 16.0 Hz, 1H), 1.94 (p, *J* = 6.7 Hz, 1H), 1.79 (s, 1H), 1.34 (s, 3H), 1.33 (s, 1H), 1.24 (d, *J* = 6.7 Hz, 3H), 1.18 (s, 3H), 1.04 (d, *J* = 6.7 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$): δ 208.7, 156.6, 148.8, 131.8, 130.1, 130.0, 118.0, 91.7, 84.0, 66.3, 60.5, 60.3, 53.7, 52.3, 37.8, 36.5, 19.6, 17.2, 16.2, 15.2, 12.1.
FTIR (NaCl, thin film): 3501, 3429, 2955, 1698, 1477, 1278, 1137, 1007 cm^{-1}.
HRMS (ESI): calc'd for $[M–OH]^+$ 327.1955, found 327.1949.

Preparation of triol S2:

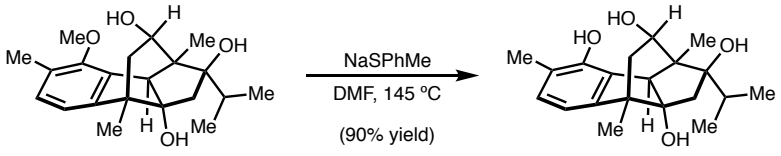


24 **S2**

An oven-dried, 40 mL scintillation vial was charged with ketoalcohol **24** (112 mg, 0.33 mmol, 1.0 equiv) and anhydrous CH_3CN (11 mL). The solution was next treated with $NaBH(OAc)_3$ (1.38 g, 6.50 mmol, 20 equiv) as a single portion [Note: $NaBH(OAc)_3$ was stored in a nitrogen-filled glovebox to maintain the integrity of the reagent]. The scintillation vial was then capped with a Teflon-lined cap and the reaction mixture was placed in a preheated heating block at 45 ºC. Stirring was continued at 45 ºC until complete consumption of starting material was observed by TLC and LCMS (*ca.* 24 h). The reaction mixture was next diluted with EtOAc (10 mL) and carefully quenched with the addition of sat. aq. NH_4Cl (15 mL). The layers were separated and the aqueous layer was extracted with EtOAc (3 × 15 mL). The combined organic layers were washed with brine (15 mL), dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The crude residue was purified via SiO_2 flash chromatography (50 to 65 to 80% EtOAc/hexanes) to afford triol **S2** as a pale-yellow solid (107 mg, 0.31 mmol, 95% yield). The stereochemistry of the triol was confirmed by nOe analysis.

TLC (50% EtOAc/hexanes): R_f 0.28 (UV, *p*-anisaldehyde).
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.09 (dd, *J* = 7.5, 0.8 Hz, 1H), 6.86 (d, *J* = 7.5 Hz, 1H), 3.80 (s, 3H), 3.77 (m, 1H), 3.43 (s, 1H, OH), 2.29 (dd, *J* = 14.8 Hz, 6.0 Hz, 1H), 2.27 (s, 3H), 2.12 (d, *J* = 15.1 Hz, 1H), 2.02 (p, *J* = 6.6 Hz, 1H), 1.85 (d, *J* = 15.1 Hz, 1H), 1.74 (s, 1H, OH), 1.72 (dd, *J* = 14.8, 1.0 Hz, 1H), 1.22 (s, 3H), 1.22 (s, 3H), 1.22 (d, *J* = 6.6 Hz, 1H), 1.05 (d, *J* = 6.6 Hz, 3H), 0.17 (d, *J* = 11.8 Hz, 1H, OH).
^{13}C NMR (101 MHz, $CDCl_3$): δ 156.3, 149.9, 132.1, 131.5, 130.2, 118.8, 92.5, 84.4, 72.9, 60.5, 58.2, 54.9, 50.7, 44.8, 37.8, 37.1, 20.3, 17.9, 16.2, 15.9, 15.0.
FTIR (NaCl, thin film): 3564, 3425, 2958, 1476, 1014, 736 cm^{-1}.
HRMS (ESI): calc'd for $[M–OH]^+$ 329.2111, found 329.2112.

Preparation of phenol 25:

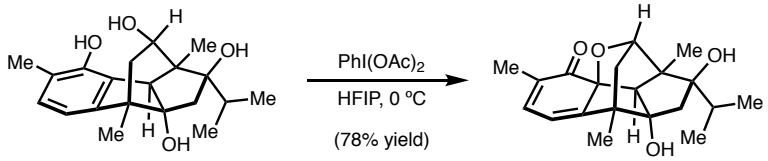


S2 **25**

In a nitrogen-filled glovebox, an oven-dried, 20 mL scintillation vial was charged with triol **S2** (58.1 mg, 0.17 mmol, 1.0 equiv) and anhydrous DMF (5.6 mL). The solution was treated with NaSPhMe (368 mg, 2.51 mmol, 15 equiv). The scintillation vial was then capped with a Teflon-lined cap, removed from the glovebox, and placed in a preheated heating block at 145 ºC. The reaction mixture was stirred at 145 ºC until complete consumption of starting material was observed by TLC analysis (*ca.* 18 h) and then cooled to ambient temperature. EtOAc (5 mL) was added prior to the careful addition of sat. aq. NH_4Cl (5 mL). The layers were separated and the aqueous layer was extracted with EtOAc (3 × 5 mL). The combined organic layers were washed with H_2O (5 mL) and then brine (5 mL) before drying over Na_2SO_4, filtering, and concentrating *in vacuo.* The crude residue was purified via SiO_2 flash chromatography (40 to 55 to 70% EtOAc/hexanes) to afford triol **25** as a sparingly-soluble tan solid (50.1 mg, 0.15 mmol, 90% yield) [Note: acetone was used for all flask-to-flask transfers].

TLC (60% EtOAc/hexanes): R_f 0.32 (UV, *p*-anisaldehyde).
^{1}H NMR (500 MHz, CD_3OD): δ 6.99 (d, *J* = 7.4 Hz, 1H), 6.63 (d, *J* = 7.4 Hz, 1H), 3.73 (d, *J* = 5.8 Hz, 1H), 3.49 (s, 1H), 2.27 (dd, *J* = 14.6, 5.9 Hz, 1H), 2.20 (s, 3H), 2.06 (p, *J* = 6.6 Hz, 1H), 2.04 (d, *J* = 15.0 Hz, 1H), 1.82 (d, *J* = 15.0 Hz, 1H), 1.61 (d, *J* = 14.6 Hz, 1H), 1.24 (d, *J* = 6.7 Hz, 3H), 1.21 (s, 3H), 1.19 (s, 3H), 1.03 (d, *J* = 6.6 Hz, 3H).
^{13}C NMR (126 MHz, CD_3OD): δ 153.5, 151.5, 131.4, 128.0, 125.2, 115.4, 92.9, 85.3, 74.9, 58.4, 55.7, 51.9, 45.8, 39.3, 37.5, 20.3, 18.7, 16.5, 16.2, 15.5.
FTIR (NaCl, thin film): 3551, 3443, 2940, 1577, 1022 cm^{-1}.
HRMS (ESI): calc'd for $[M–OH]^+$ 315.1955, found 315.1941.

Preparation of pentacycle 26:

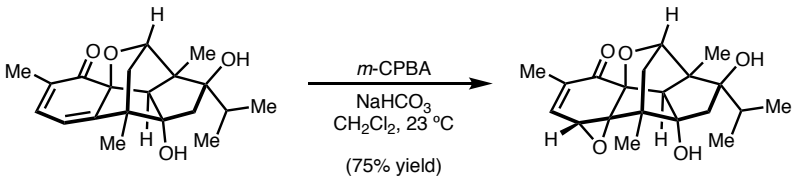


25 **26**

An oven-dried, 25 mL round-bottomed flask was charged with phenol **25** (111 mg, 0.34 mmol, 1.0 equiv) and HFIP (6.7 mL) and the mixture was allowed to stir at ambient temperature until complete dissolution was observed. The resulting solution was cooled to 0 ºC via an ice/water bath before adding $PhI(OAc)_2$ (140 mg, 0.43 mmol, 1.3 equiv) as a single portion. Vigorous stirring was continued at 0 ºC until TLC analysis indicated the complete consumption of the starting material (*ca.* 5 min) before diluting the bright yellow reaction mixture with CH_2Cl_2 (10 mL) and filtering the ice-cold solution over a pre-equilibrated SiO_2 pad, washing with 80% EtOAc/hexanes. The filtrate was concentrated *in vacuo* and the crude residue was purified via SiO_2 flash chromatography (40 to 50 to 60% EtOAc/hexanes) to afford pentacycle **26** (86.4 mg, 0.36 mmol, 78% yield) as a bright-yellow solid.

TLC (60% EtOAc/hexanes): R_f 0.35 (UV, *p*-anisaldehyde).
^{1}H NMR (400 MHz, $CDCl_3$): δ 6.79 (dq, *J* = 5.9, 1.5 Hz, 1H), 5.80 (d, *J* = 5.9 Hz, 1H), 4.03 – 3.96 (m, 1H), 2.50 (d, *J* = 1.4 Hz, 1H), 2.42 (dd, *J* = 13.5, 1.4 Hz, 1H), 2.05 (d, *J* = 15.2 Hz, 1H), 2.03 (p, *J* = 6.7 Hz, 1H), 1.94 (dd, *J* = 13.5, 3.4 Hz, 1H), 1.90 (d, *J* = 15.6 Hz, 1H), 1.86 (d, *J* = 1.5 Hz, 3H), 1.38 (s, 1H), 1.38 (s, 3H), 1.35 (s, 1H), 1.05 (s, 3H), 1.03 (d, *J* = 6.7 Hz, 3H), 0.97 (d, *J* = 6.7 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$): δ 198.6, 160.9, 138.1, 131.0, 109.9, 85.7, 85.2, 82.7, 82.1, 65.4, 64.5, 50.3, 43.2, 39.3, 36.3, 18.9, 16.4, 15.8, 15.1, 12.4.
FTIR (NaCl, thin film): 3475, 2959, 1677, 1652, 1386, 1063, 981 cm^{-1}.
HRMS (ESI): calc'd for $[M+H]^+$ 331.1904, found 331.1924.

Preparation of epoxide S3:

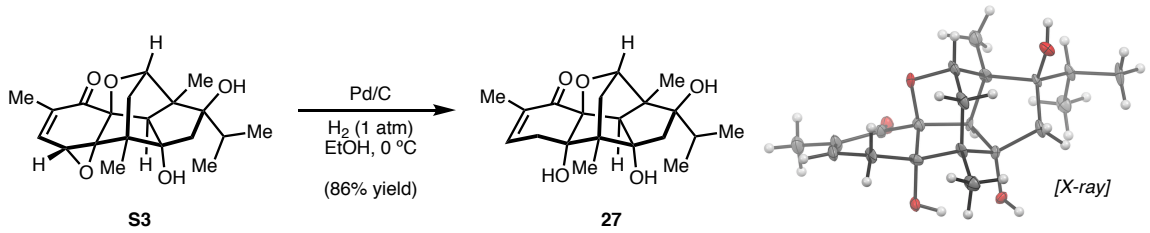


26 **S3**

An oven-dried, 1 dram vial was charged with enone **26** (11.7 mg, 35.4 μmol, 1.0 equiv) and anhydrous CH_2Cl_2 (0.9 mL). The solution was treated with $NaHCO_3$ (17.8 mg, 212 μmol, 6.0 equiv) and then *m*-CPBA (99%,[3] 12.2 mg, 70.8 μmol, 2.0 equiv). The bright yellow suspension was vigorously stirred at ambient temperature for 2 h before an additional portion of *m*-CPBA (99%, 6.1 mg, 35.4 μmol, 1.0 equiv) was added. The reaction was continued at ambient temperature until TLC and LCMS analysis indicated the complete consumption of starting material (*ca.* 2 h). The resulting colorless reaction mixture was quenched with the addition of sat. aq. $NaHCO_3$ (1 mL) and sat. aq. $Na_2S_2O_3$ (0.5 mL), diluted with CH_2Cl_2 (1 mL), and the layers were separated. The aqueous layer was extracted with EtOAc (3 × 1 mL) and the combined organic layers were washed with sat. aq. $NaHCO_3$ (1 mL), dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The crude residue was purified via preparative TLC (65% EtOAc/hexanes) affording epoxide **S3** as a white solid (9.2 mg, 26.6 μmol, 75% yield).

TLC (60% EtOAc/hexanes): R_f 0.31 (UV, *p*-anisaldehyde).
^{1}H NMR (400 MHz, $CDCl_3$): δ 6.89 (dq, *J* = 4.1, 1.6 Hz, 1H), 3.86 (dt, *J* = 3.5, 1.4 Hz, 1H), 3.63 (d, *J* = 4.1 Hz, 1H), 2.98 (d, *J* = 1.4 Hz, 1H), 2.43 (dd, *J* = 13.8, 1.4 Hz, 1H), 2.27 (s, 1H), 2.13 (d, *J* = 15.3 Hz, 1H), 2.01 (p, *J* = 6.7 Hz, 1H), 1.97 (dd, *J* = 13.8, 3.4 Hz, 1H), 1.91 (d, *J* = 1.6 Hz, 3H), 1.91 (d, *J* = 15.3 Hz, 1H), 1.37 (s, 1H), 1.17 (s, 3H), 1.12 (s, *J* = 6.7 Hz, 3H), 0.98 (d, *J* = 6.6 Hz, 3H), 0.86 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$): δ 192.1, 140.9, 138.1, 89.3, 86.3, 84.9, 82.7, 73.8, 64.2, 59.7, 49.2, 45.2, 39.8, 39.7, 36.3, 18.9, 16.3, 16.2, 15.7, 10.1.
FTIR (NaCl, thin film): 3502, 2960, 2927, 1734, 1699, 1456, 1376, 1291, 1072 cm^{-1}.
HRMS (ESI): calc'd for $[M+H]^+$ 347.1853, found 347.1853.

Preparation of enone 27:



S3 27

An oven-dried, 1 dram vial was charged with epoxide **S3** (4.0 mg, 11.5 μmol, 1.0 equiv) and EtOH (1.0 mL). The solution was cooled to 0 ºC via an ice/water bath prior to the addition of Pd/C (10% w/w on activated carbon, 4.0 mg). The vial was capped with a rubber septum and the reaction mixture was vigorously stirred (≥750 rpm) at 0 ºC while flushing the headspace with H_2 for 3 min via a double-walled balloon. Stirring was stopped and the ice-cold reaction mixture was immediately diluted with CH_2Cl_2 (2 mL), filtered through a short pad of Celite, and concentrated *in vacuo*. Purification of the crude residue by preparative TLC (70% EtOAc/hexanes) afforded **27** as a white solid (3.5 mg, 10.0 μmol, 86% yield). The stereochemistry of the triol was confirmed by nOe and X-ray analysis.

TLC (60% EtOAc/hexanes): R_f 0.24 (UV, *p*-anisaldehyde).
^{1}H NMR (400 MHz, $CDCl_3$): δ 6.65 (ddq, *J* = 5.2, 2.8, 1.4 Hz, 1H), 3.76 (dt, *J* = 3.6, 1.4 Hz, 1H), 3.55 (s, 1H, OH), 3.43 (s, 1H, OH), 3.08 (dt, *J* = 18.3, 2.6 Hz, 1H), 3.03 (d, *J* = 1.4 Hz, 1H), 2.29 (ddq, *J* = 18.3, 5.4, 1.4 Hz, 1H), 2.19 (dd, *J* = 14.5, 1.3 Hz, 1H), 1.98 (p, *J* = 6.6 Hz, 1H), 1.98 (s, 2H), 1.93 (dd, *J* = 14.5, 3.6 Hz, 1H), 1.89 (dt, *J* = 2.8, 1.4 Hz, 3H), 1.28 (s, 1H, OH), 1.12 (s, 3H), 1.10 (d, *J* = 6.6 Hz, 3H), 0.98 (s, 3H), 0.96 (d, *J* = 6.6 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$): δ 194.2, 141.1, 135.1, 91.3, 89.0, 86.9, 83.6, 82.8, 64.5, 59.1, 50.5, 41.7, 37.2, 36.2, 33.5, 18.9, 16.3, 15.9, 15.5, 10.2.
FTIR (NaCl, thin film): 3369, 2958, 2926, 1682, 1454, 1375, 1296, 1061 cm^{-1}.
HRMS (ESI): calc'd for $[M+H]^+$ 349.2010, found 349.2014.

Preparation of diketone 28:

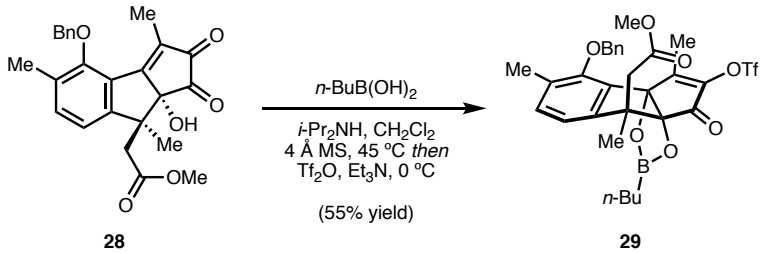
21 28

A flame-dried, 20 mL microwave tube equipped with a rubber septum was charged with **21** (407 mg, 1.0 mmol, 1.0 equiv), SeO_2 (1.1 g, 10.0 mmol, 10 equiv), H_2O (1.0 mL), and anhydrous 1,4-dioxane (10 mL). The solution was degassed with Ar for 10 min, then AcOH (21 μL, 0.5 mmol, 0.5 equiv) was added to the mixture. The septum was quickly exchanged with a microwave cap under Ar and the microwave tube was next sealed closed. After microwave irradiation for 2 h at 130 ºC, the reaction mixture was cooled to ambient temperature, diluted with EtOAc, and washed with sat. aq. $NaHCO_3$ (2 × 20 mL). The organic layer was dried over Na_2SO_4, filtered, and concentrated *in vacuo* to afford a dark orange foam. Crude ^{1}H NMR analysis shows partial hydrolysis of the methyl ester. As such, a 50-mL round-bottomed flask charged with the crude orange foam was treated with anhydrous MeOH (4 mL) and PhH (16 mL). $TMSCHN_2$ (2.0 M in hexanes, 0.5 mL, 1.0 mmol, 1.0 equiv) was added via

syringe as a single portion. The resulting reaction mixture was stirred for 10 min at ambient temperature and then concentrated *in vacuo*. Purification by SiO_2 flash chromatography (20% EtOAc/hexanes) afforded diketone **28** as a light orange foam (277.5 mg, 0.66 mmol, 66 % yield) [Note: The diketone **28** slowly decomposes on SiO_2 and even when stored at 0 ºC–we recommend using the diketone immediately upon purification]. A small sample was further purified by preparative HPLC for characterization purposes.

TLC (20% EtOAc/hexanes): R_f 0.55 (UV, $KMnO_4$).
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.40 (dd, *J* = 7.7, 0.8 Hz, 1H), 7.35-7.31 (m, 5H), 7.05 (d, *J* = 7.7 Hz, 1H), 4.96 (s, 2H), 3.39 (s, 3H), 2.50 (d, *J* = 13.8 Hz, 1H), 2.32 (s, 3H), 2.31 (d, *J* = 13.8 Hz, 1H), 2.22 (s, 3H), 2.01 (s, 1H), 1.73 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$): δ 195.1, 191.0, 170.1, 166.6, 155.3, 149.4, 142.5, 137.1, 136.0, 132.3, 128.7, 128.6, 128.5, 128.4, 128.4, 126.7, 120.6, 82.0, 76.2, 51.4, 48.7, 42.3, 18.8, 16.2, 11.6.
FTIR (NaCl, thin film): 3420, 2931, 1708, 1211, 1018 cm^{-1}.
HRMS (MM:ESI–APCI): calc'd for $[M+H]^+$ 421.1651, found 421.1637.

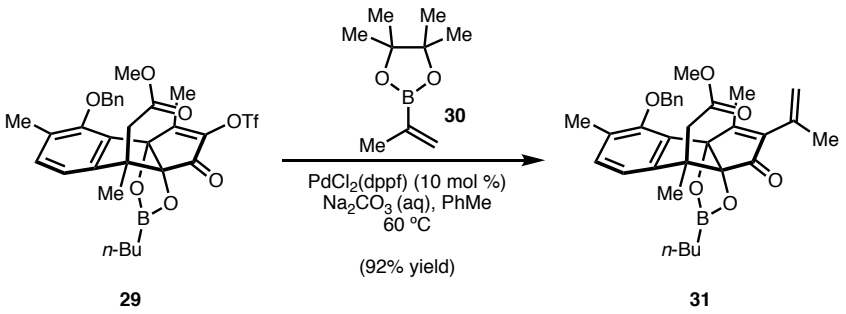
Preparation of triflate 29:



An oven-dried, 60 mL pressure flask equipped with a magnetic stirbar was charged with diketone **28** (841 mg, 2.0 mmol, 1.0 equiv), *n*-$BuB(OH)_2$ (810 mg, 8.0 mmol, 4.0 equiv), and freshly activated 4 Å molecular sieves (2.7 g) in a nitrogen-filled glovebox. Anhydrous CH_2Cl_2 (20 mL) and *i*-Pr_2NH (0.56 mL, 4.0 mmol, 2.0 equiv) were then added and the vessel was next tightly sealed with a Teflon-lined cap, removed from the glovebox, and placed in a preheated oil bath at 45 ºC. After 24 h of stirring at this temperature, the flask was allowed to cool to ambient temperature and the cap was quickly exchanged with a rubber septum under Ar. The reaction mixture was then cooled to 0 ºC via an ice/water bath. Anhydrous Et_3N (0.56 mL, 4.0 mmol, 2.0 equiv) and Tf_2O (0.41 mL, 2.4 mmol, 1.2 equiv) were subsequently added and the resulting reaction mixture was allowed to stir at 0 ºC for 30 min, before carefully adding sat. aq. $NaHCO_3$. The layers were separated and the organic layer was washed with sat. aq. $NaHCO_3$ (2 × 10 mL), brine (10 mL), dried over Na_2SO_4, filtered and concentrated *in vacuo*. Purification by SiO_2 flash chromatography (5 to 10% EtOAc/hexanes) afforded triflate **29** as a light orange oil (700 mg, 1.1 mmol, 55% yield).

TLC (10% EtOAc/hexanes): R_f 0.45 (UV, $KMnO_4$)
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.59 – 7.53 (m, 2H), 7.47 – 7.36 (m, 3H), 7.29 (dd, *J* = 7.8, 0.9 Hz, 1H), 6.84 (d, *J* = 7.8 Hz, 1H), 5.21 (d, *J* = 10.4 Hz, 1H), 4.87 (d, *J* = 10.4 Hz, 1H), 3.44 (s, 3H), 3.18 (d, *J* = 17.1 Hz, 1H), 2.83 (d, *J* = 17.0 Hz, 1H), 2.36 (d, *J* = 0.8 Hz, 6H), 1.44 (s, 3H), 1.43 – 1.37 (m, 2H), 1.35 – 1.22 (m, 2H), 0.91 (t, *J* = 7.7 Hz, 2H), 0.84 (t, *J* = 7.3 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$): δ 190.1, 171.2, 161.0, 154.9, 149.1, 144.9, 137.2, 135.0, 131.9, 129.2, 128.6, 128.2, 118.9, 118.4 (q, $J_{C\text{-}F}$ = 321 Hz, SO_2CF_3), 95.1, 92.2, 76.1, 51.5, 48.0, 42.0, 26.5, 25.8, 25.1, 16.0, 13.8, 13.6, 10.5.
FTIR (NaCl, thin film): 2927, 1744, 1430, 1209 cm^{-1}.
HRMS (MM:ESI–APCI): calc'd for $[M+H]^+$ 637.1890, found 637.1876.

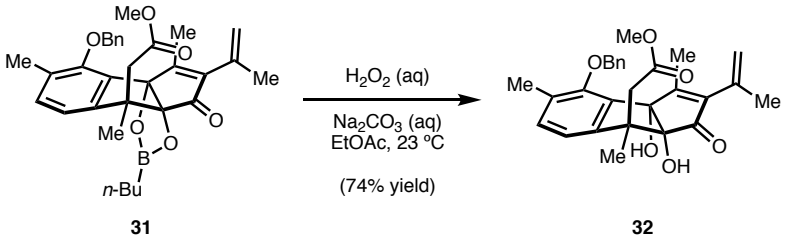
Preparation of diene 31:



A 20 mL scintillation vial equipped with a septum and magnetic stirbar was charged with **29** (260 mg, 0.41 mmol, 1.0 equiv), $PdCl_2(dppf)•CH_2Cl_2$ (33 mg, 0.041mmol, 0.1 equiv), and PhMe (6.2 mL). The solution was degassed with Ar for 5 min. Isopropenylboronic acid pinacol ester **30** (0.49 mL, 4.1 mmol, 10.0 equiv) was next added, followed by a degassed, aqueous solution of Na_2CO_3 (1.0 M, 2.1 mL, 2.1 mmol, 5.0 equiv). The scintillation vial was then sealed and placed in a preheated oil bath at 60 ºC. After 1 h, the reaction mixture was cooled to ambient temperature, diluted with EtOAc (10 mL), and washed with sat. aq. NH_4Cl (10 mL) and brine (10 mL). The organic layer was dried over $MgSO_4$, filtered, and concentrated *in vacuo*. Purification by SiO_2 flash chromatography (10% EtOAc/hexanes) afforded the cross-coupled product **31** as a thick oil (200 mg, 0.38 mmol, 92% yield).

TLC (10% EtOAc/hexanes): R_f 0.55 (UV, *p*-anisaldehyde).
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.62 – 7.55 (m, 2H), 7.46 – 7.33 (m, 3H), 7.25 (d, *J* = 7.8 Hz, 1H), 6.82 (d, *J* = 7.8 Hz, 1H), 5.30 (d, *J* = 10.4 Hz, 1H), 5.22 (p, *J* = 1.6 Hz, 1H), 4.83 (dd, *J* = 2.0, 1.0 Hz, 1H), 4.82 (d, *J* = 10.4 Hz, 1H), 3.45 (s, 3H), 3.11 (d, *J* = 16.7 Hz, 1H), 2.80 (d, *J* = 16.7 Hz, 1H), 2.35 (s, 3H), 2.32 (s, 3H), 1.85 (t, *J* = 1.3 Hz, 3H), 1.45 (s, 3H), 1.44 – 1.36 (m, 2H), 1.33 – 1.22 (m, 2H), 0.89 (t, *J* = 7.7 Hz, 2H), 0.83 (t, *J* = 7.3 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$): δ 199.8, 171.3, 167.0, 154.9, 149.4, 143.5, 137.6, 136.2, 134.1, 131.6, 130.5, 128.5, 128.3, 128.0, 118.8, 117.8, 98.1, 94.0, 76.0, 51.3, 47.7, 42.1, 26.5, 26.0, 25.2, 21.7, 16.0, 15.6, 13.8, 10.8.
FTIR (NaCl, thin film): 2959, 2923, 1746, 1716, 1373, 1195, 1178, 1032, 1012 cm^{-1}.
HRMS (MM:ESI–APCI): calc'd for $[M+H]^+$ 529.2761, found 529.2758.

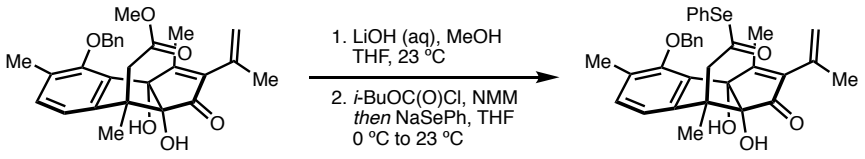
Preparation of diol 32:



A 100 mL round-bottomed flask was charged with **31** (200 mg, 0.38 mmol, 1.0 equiv) and EtOAc (21 mL) before adding aqueous H_2O_2 (30% w/w, 2.1 mL) and sat. aq. Na_2CO_3 (21 mL). The reaction mixture was stirred at ambient temperature for 15 min, before quenching with a 5:1 v/v mixture of sat. aq. $NaHCO_3$ and sat. aq. $Na_2S_2O_3$ solution (60 mL). After continued stirring for 10 min, the mixture was saturated with solid NaCl and extracted with EtOAc (2 × 100 mL). The combined organic extracts were dried over Na_2SO_4, filtered, and concentrated *in vacuo*. Purification by SiO_2 flash chromatography (20% EtOAc/hexanes) afforded diol **32** as a white solid (131 mg, 0.28 mmol, 74% yield).

TLC (20% EtOAc/hexanes): R_f 0.40 (UV, *p*-anisaldehyde).
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.60 – 7.49 (m, 2H), 7.44 – 7.29 (m, 3H), 7.18 (dd, *J* = 7.7, 0.8 Hz, 1H), 6.77 (d, *J* = 7.7 Hz, 1H), 5.84 (s, 1H), 5.41 (d, *J* = 11.0 Hz, 1H), 5.16 (p, *J* = 1.6 Hz, 1H), 4.85 (d, *J* = 11.0 Hz, 1H), 4.77 (dq, *J* = 1.9, 1.0 Hz, 1H), 3.81 (s, 3H), 3.46 (s, 1H), 3.12 (d, *J* = 17.9 Hz, 1H), 2.90 (d, *J* = 17.9 Hz, 1H), 2.37 (s, 3H), 2.27 (m, 3H), 1.82 (dd, *J* = 1.6, 1.0 Hz, 3H), 1.48 (d, *J* = 0.9 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$): δ 202.2, 175.7, 172.0, 155.1, 148.0, 141.5, 137.7, 136.3, 134.3, 132.9, 131.6, 128.4, 128.1, 127.9, 118.3, 117.8, 86.3, 83.1, 77.2 (derived from HSQC), 52.2, 45.5, 40.9, 29.7, 27.9, 21.7, 16.2, 15.1.
FTIR (NaCl, thin film): 2919, 1700, 1209 cm^{-1}.
HRMS (MM:ESI–APCI): calc'd for $[M+H]^+$ 463.2121, found 463.2141.

Preparation of acyl selenide 33:



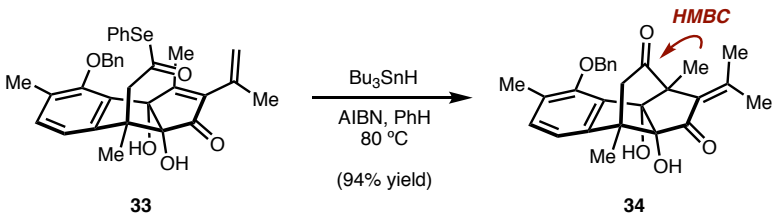
32 **33**

A 50 mL round-bottomed flask was charged with **32** (587 mg, 1.27 mmol, 1.0 eqiuv), LiOH (1.5 g, 63.5 mmol, 50.0 equiv), THF (7.6 mL), MeOH (7.6 mL), and H_2O (2.5 mL). The reaction mixture was stirred at ambient temperature under N_2 for 48 h, at which point TLC showed complete consumption of the starting material. The reaction mixture was diluted with EtOAc (10 mL), washed with pH = 2.5 phosphate buffer solution (3 × 25 mL), and brine (20 mL). The organic layer was dried over Na_2SO_4, filtered, and concentrated *in vacuo* to afford a white solid. The crude carboxylic acid was dried under high vacuum for 1 h before used in the next step.

A flame-dried, 100 mL round-bottomed flask was charged with the carboxylic acid (570 mg, 1.27 mmol, 1.0 equiv) and anhydrous THF (25 mL), and the resulting solution was cooled to 0 ºC via an ice/water bath. *N*-methylmorpholine (0.28 mL, 2.54 mmol, 2.0 equiv) and isobutyl chloroformate (0.22 mL, 1.65 mmol, 1.3 equiv) were subsequently added. The reaction mixture was continued at 0 ºC for 15 min before warming to ambient temperature and stirring for an additional 15 min. Upon recooling to 0 ºC, a THF solution of NaSePh–freshly prepared by stirring PhSeH (0.17 mL, 1.52 mmol, 1.2 equiv) and NaH (95%, 42 mg, 1.65 mmol, 1.3 equiv) in THF (25 mL) at 0 ºC for 1 h–was added dropwise via cannula. Upon complete addition, the reaction mixture was stirred at 0 ºC for 20 min and then warmed to ambient temperature and allowed another 30 min, before quenching the reaction with the slowing addition of sat. aq. NH_4Cl (20 mL). The mixture was next diluted with EtOAc (50 mL), the layers separated, and the organic layer further washed with sat. aq. NH_4Cl (2 × 20 mL) and brine (30 mL). The organic layer was dried over Na_2SO_4, filtered, and concentrated *in vacuo*. Purification by SiO_2 flash chromatography (10 to 20% EtOAc/hexanes) afforded acyl selenide **33** as a white solid (587 mg, 0.99 mmol, 79% yield).

TLC (20% EtOAc/hexanes): R_f 0.33 (UV, *p*-anisaldehyde).
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.64 – 7.59 (m, 2H), 7.57 – 7.51 (m, 2H), 7.45 – 7.31 (m, 6H), 7.18 (dd, *J* = 7.7, 0.7 Hz, 1H), 6.78 (d, *J* = 7.7 Hz, 1H), 5.39 (d, *J* = 11.0 Hz, 1H), 5.17 (p, *J* = 1.6 Hz, 1H), 4.92 (s, 1H, OH), 4.84 (d, *J* = 11.0 Hz, 1H), 4.77 (dd, *J* = 2.0, 1.0 Hz, 1H), 3.57 (d, *J* = 18.1 Hz, 1H), 3.41 (d, *J* = 18.1 Hz, 1H), 3.39 (s, 1H, OH), 2.34 (s, 3H), 2.28 (s, 3H), 1.82 (dd, *J* = 1.6, 0.9 Hz, 3H), 1.43 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$): δ 203.5, 201.6, 171.6, 155.2, 147.3, 141.5, 137.6, 136.3, 136.1, 134.2, 132.9, 131.8, 129.4, 129.1, 128.4, 128.0, 127.9, 126.2, 118.3, 117.9, 86.4, 83.0, 76.4, 53.7, 47.1, 27.4, 21.8, 16.2, 15.0.
FTIR (NaCl, thin film): 3437, 2925, 1703, 1376, 1209, 983, 738 cm^{-1}.
HRMS (ESI): calc'd for $[M–OH]^+$ 571.1415, found 571.1410.

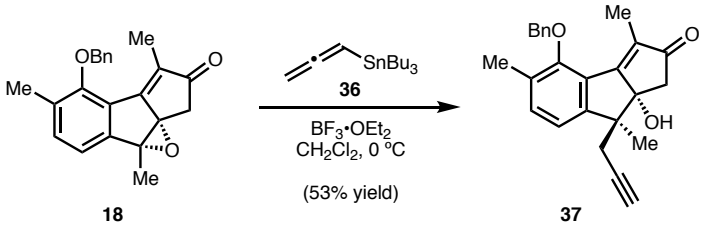
Preparation of tetracycle 34:



An oven-dried, 25 mL Schlenk tube was charged with acyl selenide **33** (95 mg, 0.16 mmol, 1.0 equiv) and anhydrous PhH (3.2 mL). The Schlenk tube was evacuated/refilled three times with Ar before being placed in a preheated oil bath at 80 ºC. A solution of azobisisobutyronitrile (0.2 M in toluene, 2.0 mL, 0.4 mmol, 2.5 equiv) and *n*-Bu_3SnH (97 µL, 0.4 mmol, 2.5 equiv) in anhydrous PhH (3.2 mL) was next added dropwise via cannula at 80 ºC. Upon complete addition, the Schlenk tube was sealed and the reaction was stirred for 3 h before cooling the reaction mixture to ambient temperature. The whole solution was transferred to a 50 mL, round-bottomed flask and concentrated *in vacuo* to afford a thick oil. Purification by SiO_2 flash chromatography (30% EtOAc/hexanes) afforded tetracycle **34** as a white solid (65 mg, 0.15 mmol, 94% yield).

TLC (25% EtOAc/hexanes): R_f 0.17 (UV, *p*-anisaldehyde).
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.51 – 7.46 (m, 2H), 7.42 – 7.34 (m, 3H), 7.15 (dd, *J* = 7.6, 0.8 Hz, 1H), 6.82 (d, *J* = 7.6 Hz, 1H), 5.01 (d, *J* = 10.8 Hz, 1H), 4.95 (d, *J* = 10.8 Hz, 1H), 3.42 (s, 1H, OH), 3.29 (s, 1H, OH), 2.73 (d, *J* = 16.0 Hz, 1H), 2.37 (s, 3H), 2.33 (s, 3H), 2.20 (d, *J* = 16.0 Hz, 1H), 1.89 (s, 3H), 1.69 (s, 3H), 1.41 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$): δ 202.7, 201.9, 158.6, 155.1, 147.0, 137.0, 133.4, 132.1, 131.2, 129.6, 128.6, 128.2, 127.7, 117.3, 95.3, 89.9, 75.8, 65.4, 50.6, 48.0, 24.2, 23.8, 16.6, 15.7, 13.2.
FTIR (NaCl, thin film): 3468, 2928, 1716, 1612, 1378, 1248, 1053 cm^{-1}.
HRMS (ESI): calc'd for $[M+H]^+$ 433.2010, found 433.2007.

Preparation of alkyne 37:

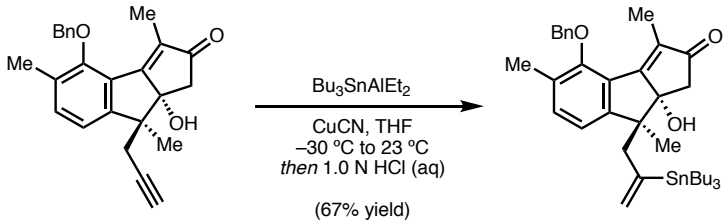


A flame-dried, 10 mL round-bottomed flask was treated with epoxide **18** (300 mg, 0.90 mmol, 1.0 equiv), anhydrous CH_2Cl_2 (1.86 mL) then allenyltributyltin **36** (0.28 mL, 0.90 mmol, 1.0 equiv). The mixture was cooled to 0 ºC via an ice/water bath and vigorously stirred for an additional 15 min before adding BF_3•Et_2O (114 µL, 0.90 mmol, 1.0 equiv) rapidly as a single portion via syringe. The solution was stirred at 1500 rpm for 3 min at 0 ºC, and then immediately quenched with the addition of sat. aq. $NaHCO_3$ (3 mL). The quenched solution was stirred for another 25 min at 0 ºC and then diluted with CH_2Cl_2 (3 mL), the layers separated, and the organic layer was further washed with sat. aq. $NaHCO_3$ (2 × 5 mL). The combined aqueous washings were extracted with CH_2Cl_2 (10 mL), then the combined organic layers were dried over $MgSO_4$, filtered, and concentrated *in vacuo* to afford a deep orange foam. Purification by SiO_2 flash chromatography (30% EtOAc/hexanes) afforded alkyne **37** as a light orange foam (178 mg, 0.48 mmol, 53 % yield).

TLC (30% EtOAc/hexanes): R_f 0.30 (UV, $KMnO_4$).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36 (s, 5H), 7.35 (d, *J* = 7.6 Hz, 1H), 7.15 (d, *J* = 7.6 Hz, 1H), 4.99 (d, *J* = 11.3 Hz, 1H), 4.90 (d, *J* = 11.3 Hz, 1H), 2.87 (d, *J* = 18.3 Hz, 1H), 2.53 (d, *J* = 18.2 Hz, 1H), 2.35 (d, *J* = 0.7 Hz, 3H), 2.24 (dd, *J* = 16.5, 2.7 Hz, 1H), 2.05 (s, 3H), 2.05 (dd, *J* = 16.5, 2.7 Hz, 1H), 2.01 (t, *J* = 2.7 Hz, 1H), 1.73 (s, 1H), 1.59 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$): δ 208.2, 168.6, 154.6, 152.0, 136.3, 134.9, 133.8, 131.5, 128.4, 128.4, 128.4, 126.6, 120.9, 88.5, 80.2, 75.5, 71.7, 49.7, 43.2, 30.0, 17.9, 16.2, 10.3.
FTIR (NaCl, thin film): 3424, 1702, 1645, 1322, 1219, 1014 cm^{-1}.
HRMS (MM:ESI–APCI): calc'd for $[M+H]^+$ 373.1804, found 373.1809.

Preparation of the vinyltributylstannane S4:



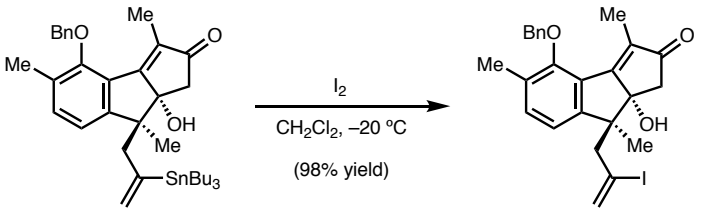
37 **S4**

Preparation of $Bu_3SnAlEt_2$:[4] *n*-BuLi (2.5 M in hexane, 4.0 mL, 10.0 mmol) was added to a solution of freshly distilled *i*-Pr_2NH (1.5 mL, 10.7 mmol) and anhydrous THF (21.3 mL). After 30 min, the freshly prepared THF solution of LDA was cooled to –30 ºC and treated dropwise with *n*-Bu_3SnH (2.7 mL, 10.0 mmol, 1.0 equiv) via syringe. After 1 h of continued stirring, Et_2AlCl (0.9 M in PhMe, 11.1 mL, 10.0 mmol, 1.0 equiv) was added dropwise via syringe. The reaction was stirred for another 1.5 h at –30 ºC and used as $Bu_3SnAlEt_2$ (0.246 M, 40.6 mL) immediately.

A flame-dried, 25 mL round-bottomed flask was charged with alkyne **37** (180 mg, 0.48 mmol, 1.0 equiv) and anhydrous THF (4.8 mL), and the resulting solution was cooled to –30 ºC via a dry ice/acetone bath. After 15 min of continued stirring, freshly prepared $Bu_3SnAlEt_2$ (0.246 M, 1.45 mmol, 3.0 equiv) was added dropwise via syringe, then CuCN (43.3 mg, 0.48 mmol, 1.0 equiv) was quickly added as a single portion. After 1 h of stirring at –30 ºC, another portion of $Bu_3SnAlEt_2$ (0.25 M, 2 mL, 1.0 equiv) was added. The reaction mixture was then warmed to ambient temperature and stirred for an additional 3 min before adding sat. aq. NH_4Cl (10 mL). After an additional 30 min of stirring, the organic layer was separated and washed with aqueous HCl (1.0 M, 3 × 10 mL). The combined aqueous layers were extracted with EtOAc (20 mL), and the combined organic layers were then washed with sat. aq. $NaHCO_3$ (10 mL), brine (10 mL), dried over Na_2SO_4, filtered, and concentrated *in vacuo*. Purification by SiO_2 flash chromatography (20% EtOAc/hexanes) afforded vinyl stannane **S4** as a colorless oil (215 mg, 0.32 mmol, 67 % yield, ~95% pure, contaminated by ~5% Bu_3Sn based impurity).

TLC (25% EtOAc/hexanes): R_f 0.50 (UV, $KMnO_4$).
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36-7.31 (m, 5H), 7.21 (dd, *J* = 7.6, 0.8 Hz, 1H), 6.78 (d, *J* = 7.6 Hz, 1H), 5.51 (d, *J* = 2.5 Hz, $^3J_{Sn\text{-}H}$ = 134.4Hz, 1H), 5.30 (d, *J* = 2.6 Hz, $^3J_{Sn\text{-}H}$ = 60.0 Hz, 1H), 5.23 (dd, *J* = 2.6, 1.4 Hz, 0H), 4.97 (d, *J* = 11.4 Hz, 1H), 4.86 (d, *J* = 11.4 Hz, 1H), 2.71 (d, *J* = 18.3 Hz, 1H), 2.46 (d, *J* = 18.2 Hz, 1H), 2.30 (s, 3H), 2.24 (d, *J* = 12.1 Hz, 1H), 2.04 (s, 3H), 1.87 (d, *J* = 12.0 Hz, 1H), 1.40 (s, 3H), 1.39 – 1.14 (m, 12H), 0.85 (t, *J* = 7.2 Hz, 9H), 0.63 – 0.40 (m, 6H).
^{13}C NMR (101 MHz, $CDCl_3$): δ 208.6, 169.4, 155.0, 152.1, 150.2, 136.5, 134.2, 133.5, 132.1 ($J_{Sn\text{-}C}$ = 24.9 Hz), 130.9, 128.4, 128.2, 126.7, 122.4, 89.9, 75.3, 51.0, 47.4, 42.7, 28.9 ($J_{Sn\text{-}C}$ = 19.3 Hz), 27.4 ($J_{Sn\text{-}C}$ = 58.2 Hz), 17.7, 17.5, 16.1, 13.6, 10.2, 10.0 ($J_{Sn\text{-}C}$ = 323 Hz).
FTIR (NaCl, thin film): 3424, 2955, 2919, 1692, 1651, 1377, 1322, 1219 cm^{-1}.
HRMS (FAB): calc'd for $[M+H]^+$ 665.3017, found 665.2997.

Preparation of vinyl iodide 38:

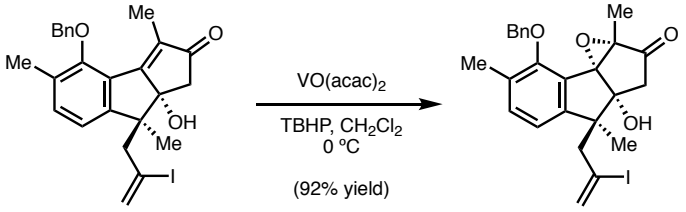


S4 **38**

A flame-dried, 50 mL round-bottomed flask was charged with stannane **S4** (412 mg, 0.62 mmol, 1.0 equiv) and anhydrous CH_2Cl_2 (6.2 mL). The resulting solution was cooled to –20 ºC prior to the addition of a freshly prepared solution of I_2 (0.1 M in CH_2Cl_2, 12.4 mL, 1.24 mmol, 2.0 equiv) at –20 ºC. The resulting reaction mixture was stirred vigorously at this temperature until TLC showed complete consumption of the starting material. Next, sat. aq. $NaHCO_3$ (10 mL) was added to the reaction mixture before warming the reaction mixture to ambient temperature. The aqueous layer was extracted with CH_2Cl_2 (10 mL), then the combined organic layers were dried over $MgSO_4$, filtered, and concentrated *in vacuo*. Purification by SiO_2 flash chromatography (25% EtOAc/hexanes) afforded vinyl iodide **38** as a white foam (305 mg, 0.61 mmol, 98 % yield).

TLC (25% EtOAc/hexanes): R_f 0.27 (UV, $KMnO_4$).
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.37 – 7.32 (m, 5H), 7.30 (dd, *J* = 7.7, 0.8 Hz, 1H), 7.05 (d, *J* = 7.6 Hz, 1H), 5.75 (d, *J* = 1.5 Hz, 1H), 5.46 (q, *J* = 1.0 Hz, 1H), 4.95 (d, *J* = 11.3 Hz, 1H), 4.87 (d, *J* = 11.3 Hz, 1H), 2.59 (d, *J* = 18.4 Hz, 1H), 2.59 (d, *J* = 13.6 Hz, 1H), 2.47 (d, *J* = 18.4 Hz, 1H), 2.34 (d, *J* = 0.7 Hz, 3H), 2.21 (d, *J* = 13.6 Hz, 1H), 2.04 (s, 3H), 1.76 (s, 1H), 1.61 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$): δ 207.9, 168.7, 154.9, 150.5, 136.3, 134.5, 134.1, 131.5, 131.4, 128.4, 128.4, 128.3, 126.7, 122.9, 101.3, 89.6, 75.4, 52.5, 51.6, 42.4, 17.9, 16.3, 10.3.
FTIR (NaCl, thin film): 3416, 2923, 1698, 1645, 1322, 1217, 1008 cm^{-1}.
HRMS (MM:ESI–APCI): calc'd for $[M+H]^+$ 501.0927, found 501.0938.

Preparation of epoxide 39:



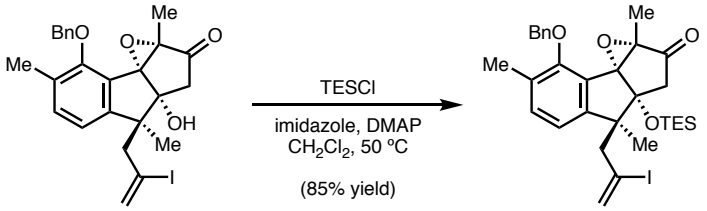
38 **39**

An oven-dried, 50 mL round-bottomed flask was charged with enone **38** (305 mg, 0.61 mmol, 1.0 equiv), $VO(acac)_2$ (81 mg, 0.31 mmol, 0.5 equiv) and anhydrous CH_2Cl_2 (12.2 mL). The resulting green solution was cooled to 0 ºC via an ice/water bath prior to the dropwise addition of TBHP (5.5 M in decane, 0.4 mL, 1.83 mmol, 3.0 equiv). The resulting dark-brown solution was stirred for 2.5 h at 0 ºC before additional TBHP (5.5 M in decane, 50 μL) was added to the reaction mixture. Stirring was continued for 0.5 h until TLC analysis indicated complete consumption of the starting material. The mixture was next diluted with EtOAc (20 mL) and quenched with the careful addition of sat. aq. $Na_2S_2O_3$ (12 mL). The two layers were separated, and the organic layer was washed with sat. aq. $Na_2S_2O_3$ (2 × 12 mL) and sat. aq. $NaHCO_3$ (2 × 12 mL). The combined aqueous layers were extracted with EtOAc (2 × 10 mL), and the combined organic layers were washed with brine (20 mL), dried over Na_2SO_4, filtered,

and concentrated *in vacuo*. The crude residue was purified by SiO_2 flash chromatography (20% EtOAc/hexanes) to afford epoxide **39** (271 mg, 0.52 mmol, 92% yield).

TLC (25% EtOAc/hexanes): R_f 0.35 (UV).
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.56 – 7.46 (m, 2H), 7.45 – 7.32 (m, 3H), 7.27 (d, *J* = 7.7 Hz, 1H), 7.05 (d, *J* = 7.7 Hz, 1H), 5.80 (d, *J* = 1.6 Hz, 1H), 5.57 (dd, *J* = 1.7, 0.8 Hz, 1H), 5.08 (d, *J* = 10.1 Hz, 1H), 4.72 (d, *J* = 10.1 Hz, 1H), 2.74 (d, *J* = 19.6 Hz, 1H), 2.62 (dd, *J* = 13.8, 1.0 Hz, 1H), 2.46 (d, *J* = 19.6 Hz, 1H), 2.33 (d, *J* = 0.7 Hz, 3H), 2.21 (s, 1H), 2.10 (d, *J* = 13.7 Hz, 1H), 1.66 (s, 3H), 1.60 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$): δ 206.1, 154.4, 148.7, 137.1, 132.6, 132.1, 131.9, 128.5, 128.1, 123.3, 122.4, 100.6, 84.2, 81.5, 76.5, 72.2, 52.7, 51.3, 42.3, 17.7, 15.8, 9.1.
FTIR (NaCl, thin film): 2927, 1738, 1225, 1081, 1002 cm^{-1}.
HRMS (MM:ESI–APCI): calc'd for $[M+H]^+$ 517.0876, found 517.0867.

Preparation of TES ether 40:

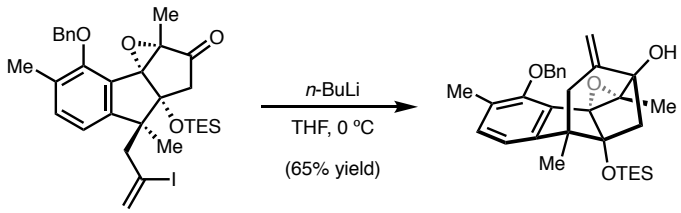


39 **40**

A flame-dried, 20 mL scintillation vial was charged with alcohol **39** (270 mg, 0.52 mmol, 1.0 equiv) and anhydrous CH_2Cl_2 (10 mL) prior to the addition of imidazole (178 mg, 2.61 mmol, 5.0 equiv), 4-dimethylaminopyridine (32 mg, 0.26 mmol, 0.5 equiv), then chlorotriethylsilane (0.22 mL, 1.3 mmol, 2.5 equiv). The scintillation vial was sealed with a Teflon-lined cap and placed in a preheated heating block at 50 ºC. After stirring at this temperature for 5 h, the reaction mixture was cooled to ambient temperature, diluted with EtOAc (20 mL), washed with sat. aq. $NaHCO_3$ (20 mL) and brine (20 mL). The organic layer was dried over anhydrous $MgSO_4$, filtered, and concentrated *in vacuo*. Purification by SiO_2 flash chromatography (10% EtOAc/hexanes) afforded TES ether **40** as a thick oil (278 mg, 0.44 mmol, 85% yield).

TLC (10% EtOAc/hexanes): R_f 0.70 (UV, $KMnO_4$).
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.54 – 7.49 (m, 2H), 7.44 – 7.31 (m, 3H), 7.18 (dd, *J* = 7.6, 0.9 Hz, 1H), 6.97 (d, *J* = 7.6 Hz, 1H), 5.77 (d, *J* = 1.6 Hz, 1H), 5.47 (t, *J* = 1.2 Hz, 1H), 5.17 (d, *J* = 10.2 Hz, 1H), 4.71 (d, *J* = 10.2 Hz, 1H), 2.63 (d, *J* = 19.2 Hz, 1H), 2.53 (d, *J* = 13.4 Hz, 1H), 2.50 (d, *J* = 19.2 Hz, 1H), 2.28 (d, *J* = 0.7 Hz, 3H), 1.95 (d, *J* = 13.4 Hz, 1H), 1.61 (s, 3H), 1.53 (s, 3H), 0.84 – 0.77 (m, 9H), 0.67 – 0.47 (m, 6H).
^{13}C NMR (101 MHz, $CDCl_3$): δ 206.6, 153.7, 149.0, 137.4, 131.8, 131.5, 131.2, 128.5, 128.1, 123.7, 122.0, 101.1, 86.9, 80.9, 75.8, 70.9, 52.9, 52.1, 42.1, 17.6, 16.0, 9.0, 6.8, 6.3.
FTIR (NaCl, thin film): 2951, 2872, 1742, 1002 cm^{-1}.
HRMS (MM:ESI–APCI): calc'd for $[M+H]^+$ 631.1741, found 631.1761.

Preparation of tetracycle 41:

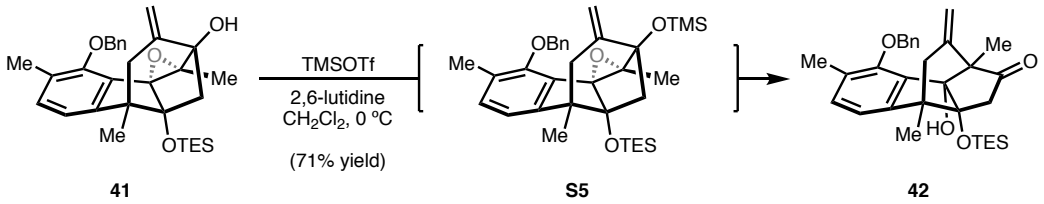


40 **41**

A flame-dried, 10 mL round-bottomed flask was charged with anhydrous THF (1.9 mL) and cooled to 0 ºC via an ice/water bath. A solution of *n*-BuLi (2.5 M in hexanes, 0.36 mL, 0.90 mmol, 3.5 equiv) was added, immediately followed by the dropwise addition of a solution of vinyl iodide **40** (163 mg, 0.26 mmol, 1.0 equiv) in anhydrous THF (1.9 mL) via syringe over 5 min [Note: **40** was azeotroped with PhH three times prior to use]. Upon complete addition, the solution was stirred for another 20 min at 0 ºC, at which point TLC analysis indicated the complete consumption of starting material. The reaction mixture was quenched with the addition of H_2O (3 mL), diluted with EtOAc (5 mL), and the layers separated. The organic layer was washed with brine (2 × 5 mL) then back extracted with EtOAc (5 mL). The combined organic layers were dried over $MgSO_4$, filtered, and concentrated *in vacuo*. Purification by SiO_2 flash chromatography (10% EtOAc/hexanes) afforded 1,2-addition product **41** as a clear oil (85 mg, 0.17 mmol, 65% yield).

TLC (10% EtOAc/hexanes): R_f 0.25 (UV, $KMnO_4$).
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.52 – 7.47 (m, 2H), 7.40 – 7.32 (m, 3H), 7.03 (dd, *J* = 7.5, 0.8 Hz, 1H), 6.86 (d, *J* = 7.5 Hz, 1H), 5.28 (d, *J* = 10.6 Hz, 1H), 5.09 (td, *J* = 1.9, 0.9 Hz, 1H), 4.80 (d, *J* = 10.6 Hz, 1H), 4.76 (q, *J* = 1.7 Hz, 1H), 2.62 (dt, *J* = 17.3, 1.8 Hz, 1H), 2.22 (dt, *J* = 17.3, 2.0 Hz, 1H), 2.16 (s, 3H), 1.99 (s, 1H, OH), 1.98 (d, *J* = 11.0 Hz, 1H), 1.91 (d, *J* = 11.0 Hz, 1H), 1.36 (s, 3H), 1.23 (s, 3H), 0.86 (t, *J* = 7.8 Hz, 9H), 0.63 – 0.56 (m, 6H).
^{13}C NMR (101 MHz, $CDCl_3$): δ 153.2, 152.4, 149.1, 137.7, 130.3, 129.6, 128.6, 128.4, 127.9, 123.8, 117.1, 107.7, 88.5, 80.5, 76.3, 75.1, 68.0, 47.4, 44.5, 38.1, 19.9, 16.2, 10.0, 6.9, 6.4.
FTIR (NaCl, thin film): 3441, 2954, 2875, 1454, 1264, 1005 cm^{-1}.
HRMS (ESI): calc'd for $[M+H]^+$ 505.2769, found 505.2787.

Semipinacol rearrangement of 41:



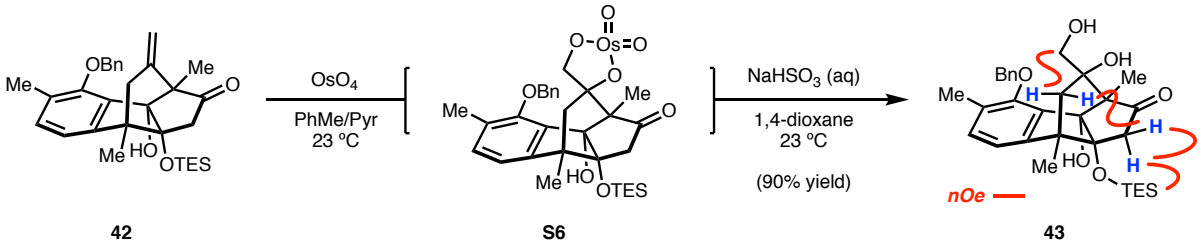
41 **S5** **42**

An oven-dried, 2-dram vial was charged with epoxyalcohol **41** (20.1 mg, 39.8 μmol, 1.0 equiv) and anhydrous CH_2Cl_2 (0.85 mL) [Note: **41** was azeotroped with PhH three times prior to use]. The solution was cooled to 0 ºC via an ice/water bath prior to the addition of freshly distilled 2,6-lutidine (19 μL, 159 μmol, 4.0 equiv). After continued stirring at 0 ºC for 15 min, a freshly prepared stock solution of TMSOTf in anhydrous CH_2Cl_2 (1.0 M, 80 μL, 79.6 μmol, 2.0 equiv) was added via microsyringe. After TLC analysis indicated the complete conversion of the alcohol to the silyl ether **S5** (*ca.* 1 h), an additional portion of the TMSOTf stock solution (1.0 M in CH_2Cl_2, 80 μL, 79.6 μmol, 2.0 equiv) was added and the reaction continued at 0 ºC. After TLC indicated the complete consumption of silyl ether **S5**, sat. aq. $NaHCO_3$ (1 mL) was added [Note: Allowing the reaction to run too long results in TES deprotection, so the reaction must be carefully monitored by TLC.]. The quenched mixture was

allowed to warm to ambient temperature, diluted with CH_2Cl_2 (1 mL), and the layers were separated. Next, the aqueous layer was extracted with CH_2Cl_2 (3 × 2 mL). The combined organic layers were dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The crude residue was purified via SiO_2 flash chromatography (5 to 8% EtOAc/hexanes) to afford semipinacol product **42** as clear oil (14.3 mg, 28.3 μmol, 71% yield).

TLC (10% EtOAc/hexanes): R_f 0.50 (UV, *p*-anisaldehyde).
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.53 – 7.48 (m, 2H), 7.45 – 7.40 (m, 2H), 7.39-7.34 (m, 1H), 7.08 (dd, *J* = 7.5, 0.8 Hz, 1H), 6.80 (d, *J* = 7.5 Hz, 1H), 4.97 (s, 2H), 4.63 (d, *J* = 1.9 Hz, 1H), 4.47 (d, *J* = 2.2 Hz, 1H), 3.46 (s, 1H, OH), 2.70 (d, *J* = 19.1 Hz, 1H), 2.55 (d, *J* = 19.1 Hz, 1H), 2.34 (dt, *J* = 15.4, 2.4 Hz, 1H), 2.33 (s, 3H), 2.05 (d, *J* = 15.4 Hz, 1H), 1.35 (s, 3H), 1.33 (s, 3H), 0.77 (t, *J* = 7.8 Hz, 9H), 0.60 – 0.49 (m, 6H).
^{13}C NMR (101 MHz, $CDCl_3$): δ 213.8, 154.6, 148.2, 142.4, 137.2, 131.6, 131.0, 129.2, 128.7, 128.2, 127.6, 117.1, 111.5, 92.2, 91.5, 75.5, 66.3, 51.0, 44.7, 42.6, 16.8, 16.6, 10.7, 6.9, 6.5.
FTIR (NaCl, thin film): 3546, 2953, 2874, 1750, 1456, 1010 cm^{-1}.
HRMS (ESI): calc'd for $[M+H]^+$ 505.2769, found 505.2781.

Preparation of diol 43:



42 **S6** **43**

An oven-dried, 1-dram vial was charged with alkene **42** (5.7 mg, 11.3 μmol, 1.0 equiv) and freshly distilled pyridine (0.27 mL). The solution was next treated with OsO_4 (0.05 M in PhMe, 0.29 mL, 14.7 μmol, 1.3 equiv) via syringe. The reaction was stirred at ambient temperature for 3 h and then concentrated *in vacuo*. The crude osmate ester **S6** was redissolved in wet 1,4-dioxane (0.35 mL) and then treated with sat. aq. $NaHSO_3$ (0.35 mL). The biphasic mixture was vigorously stirred for 12 h and then diluted with H_2O (0.1 mL) and EtOAc (0.5 mL). The layers were separated and the aqueous layer was then extracted with EtOAc (4 × 1 mL). The combined organic layers were dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The crude residue was purified via preparative TLC (55% EtOAc/hexanes) to afford a single diastereomer of diol **43** as a clear oil (5.5 mg, 10.1 μmol, 90% yield). The stereochemistry of the diol was confirmed by nOe analysis.

TLC (40% EtOAc/hexanes): R_f 0.20 (UV, *p*-anisaldehyde).
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.52 – 7.48 (m, 2H), 7.45- 7.33 (m, 3H), 7.16 (dd, *J* = 7.5, 0.8 Hz, 1H), 6.87 (d, *J* = 7.5 Hz, 1H), 4.99 (d, *J* = 10.7 Hz, 1H), 4.95 (d, *J* = 10.7 Hz, 1H), 3.32 (s, 1H, OH), 2.91 (d, *J* = 9.8 Hz, 1H), 2.71 (d, *J* = 19.2 Hz, 1H), 2.51 (d, *J* = 19.2 Hz, 1H), 2.36 (s, 3H), 2.35 (d, *J* = 8.2 Hz, 1H, OH), 2.12 (d, *J* = 14.5 Hz, 1H), 1.61 (dd, *J* = 9.8, 8.2 Hz, 1H), 1.55 (m, 1H, OH), 1.43 (dd, *J* = 14.4, 1.5 Hz, 1H), 1.32 (s, 3H), 1.21 (s, 3H), 0.78 (t, *J* = 7.9 Hz, 9H), 0.57 – 0.50 (m, 6H).
^{13}C NMR (101 MHz, $CDCl_3$): δ 214.9, 155.1, 147.5, 136.9, 132.6, 131.5, 130.3, 128.7, 128.3, 127.8, 118.1, 92.1, 89.5, 75.8, 73.7, 65.3, 64.3, 50.1, 43.9, 42.3, 17.6, 16.6, 8.7, 6.9, 6.5.
FTIR (NaCl, thin film): 3483, 2953, 2875, 1747, 1456, 1151, 1050, 1010, 737 cm^{-1}.
HRMS (ESI): calc'd for $[M+NH_4]^+$ 556.3089, found 556.3112.

3. Single Crystal X-ray Diffraction Data

Low-temperature diffraction data (φ- and ω-scans) were collected on a Bruker AXS D8 VENTURE KAPPA diffractometer coupled to a PHOTON 100 CMOS detector with Cu-K_α radiation (λ = 1.54178 Å) from a $I_\mu S$ HB micro-focus sealed X-ray tube. All diffractometer manipulations, including data collection, integration, and scaling were carried out using the Bruker APEXII software.[5] Absorption corrections were applied using SADABS.[6] The structure was solved by intrinsic phasing using SHELXT[7] and refined against F^2 on all data by full-matrix least squares with SHELXL-2014[7] using established refinement techniques.[8] All non-hydrogen atoms were refined anisotropically. With the exception of hydroxyl hydrogen atoms (which were located in the difference Fourier synthesis), all hydrogen atoms were included into the model at geometrically calculated positions and refined using a riding model. The isotropic displacement parameters of all hydrogen atoms were fixed to 1.2 times the *U* value of the atoms they are linked to (1.5 times for methyl groups and hydroxyl groups). Crystallographic data for **27** can be obtained free of charge from The Cambridge Crystallographic Data Centre (CCDC) via www.ccdc.cam.ac.uk/data_request/cif under CCDC deposition number 1840855. Graphical representation of **27** with 50% probability thermal ellipsoids was generated using Mercury visualization software.

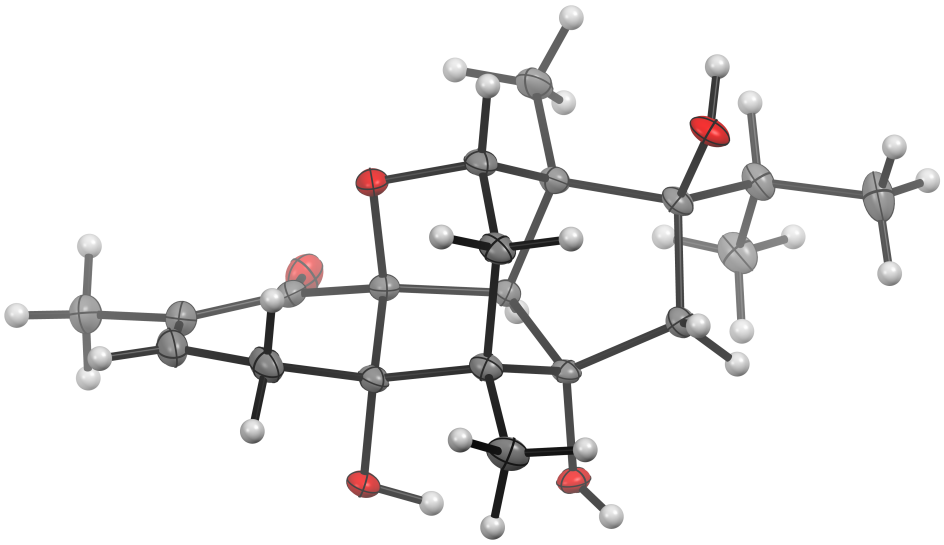


Figure S1. Structure of **27** with 50% probability anisotropic displacement ellipsoids.

Table S1. Crystal data and structure refinement for **27**.

Identification code	**27**	
Empirical formula	$C_{20}H_{28}O_5$	
Formula weight	348.42	
Temperature	100.03 K	
Wavelength	1.54178 Å	
Crystal system	Monoclinic	
Space group	P 1 21/n 1	
Unit cell dimensions	a = 10.7374(4) Å	α= 90°.
	b = 12.7029(5) Å	β= 92.435(2)°.
	c = 12.8377(5) Å	γ = 90°.
Volume	1749.43(12) $Å^3$	
Z	4	
Density (calculated)	1.323 Mg/m^3	
Absorption coefficient	0.763 mm^{-1}	
F(000)	752	
Crystal size	0.26 x 0.06 x 0.05 mm^3	
Theta range for data collection	4.900 to 79.664°.	
Index ranges	-13<=h<=13, -16<=k<=15, -16<=l<=16	
Reflections collected	33519	
Independent reflections	3669 [R(int) = 0.0623]	
Completeness to theta = 67.679°	98.7 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7543 and 0.6505	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3669 / 0 / 243	
Goodness-of-fit on F^2	1.074	
Final R indices [I>2sigma(I)]	R1 = 0.0502, wR2 = 0.1160	
R indices (all data)	R1 = 0.0613, wR2 = 0.1231	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.542 and -0.324 $e.Å^{-3}$	

4. References

1. Murray, R. W.; Singh, M. *Org. Synth.* **1997**, *74*, 91.
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3. Aggarwal, V. K.; Gultekin, Z.; Grainger, R. S.; Adams, H.; Spargo, P. L. *J. Chem. Soc., Perkin Trans. 1* **1998**, 2771.
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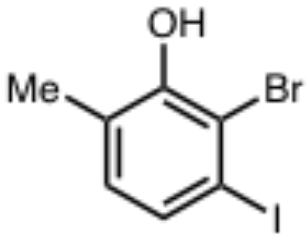
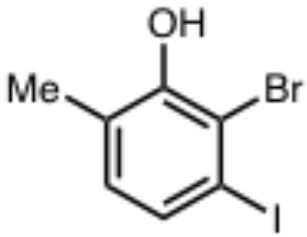
5. ^{1}H and ^{13}C NMR Spectral Data

Data File Name	/ Volumes/ nmrdata-1/ chenxu91/ nmr/ xuchen-160831-10-87/ 1/ fid
Title	xuchen-160831-10-87.1.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	294.9
Pulse Sequence	zg30
Number of Scans	16
Receiver Gain	197.4
Relaxation Delay	1.0000
Pulse Width	11.7000
Acquisition Time	4.0894
Acquisition Date	2016-08-31T22:13:52
Spectrometer Frequency	400.13
Spectral Width	8012.8
Lowest Frequency	-1545.6
Nucleus	1H
Acquired Size	32768
Spectral Size	65536



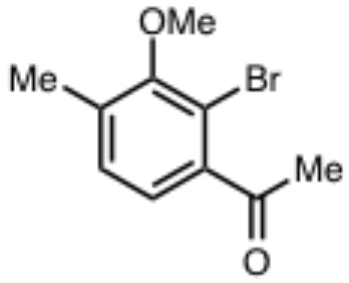
12

Parameter	Value
Data File Name	/ Volumes/ nmrdata-1/ chenxu91/ nmr/ xuchen-160831-10-87/ 2/ fid
Title	xuchen-160831-10-87.2.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	295.0
Pulse Sequence	zgpg30
Number of Scans	512
Receiver Gain	78.7
Relaxation Delay	2.0000
Pulse Width	10.0000
Acquisition Time	1.3631
Acquisition Date	2016-08-31T22:43:44
Spectrometer Frequency	100.62
Spectral Width	24038.5
Lowest Frequency	-1961.9
Nucleus	13C
Acquired Size	32768
Spectral Size	65536



12

Parameter	Value
Data File Name	/ Volumes/ nmrdata-1/ chenxu91/ nmr/ xuchen-160909-10-91/ 1/ fid
Title	xuchen-160909-10-91.1.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	294.9
Pulse Sequence	zg30
Number of Scans	16
Receiver Gain	98.9
Relaxation Delay	1.0000
Pulse Width	11.7000
Acquisition Time	4.0894
Acquisition Date	2016-09-09T09:54:10
Spectrometer Frequency	400.13
Spectral Width	8012.8
Lowest Frequency	-1545.6
Nucleus	1H
Acquired Size	32768
Spectral Size	65536



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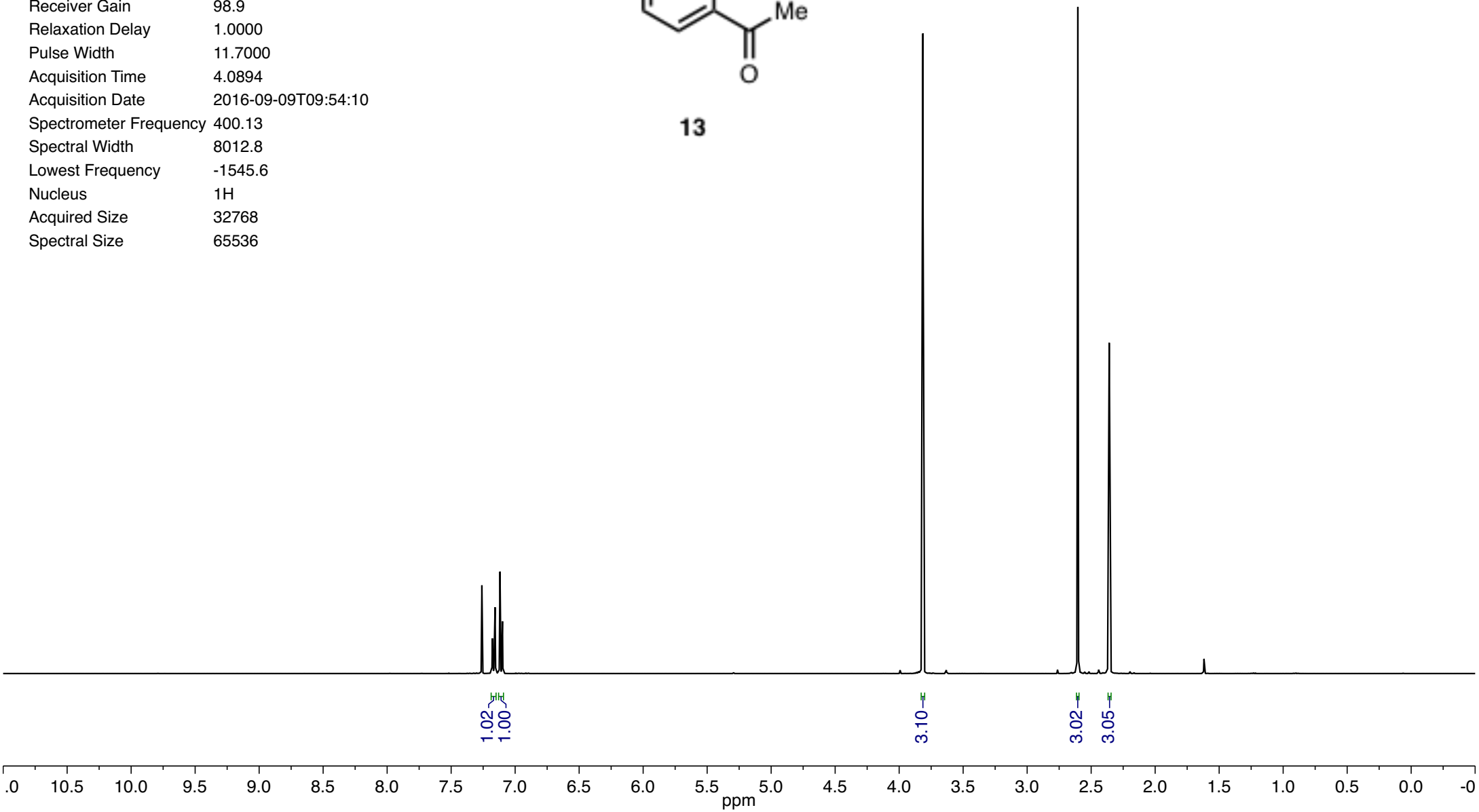
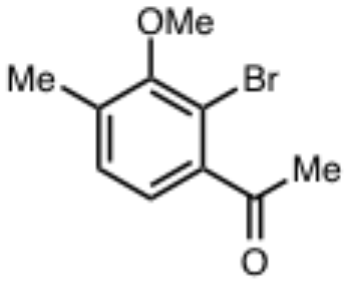
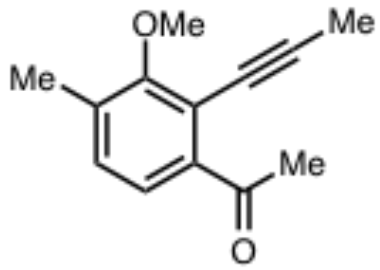


Parameter	Value
Data File Name	/ Volumes/ nmrdata-1/ chenxu91/ nmr/ xuchen-160909-10-91/ 2/ fid
Title	xuchen-160909-10-91.2.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	295.0
Pulse Sequence	zgpg30
Number of Scans	512
Receiver Gain	38.0
Relaxation Delay	2.0000
Pulse Width	10.0000
Acquisition Time	1.3631
Acquisition Date	2016-09-09T10:30:43
Spectrometer Frequency	100.62
Spectral Width	24038.5
Lowest Frequency	-1963.3
Nucleus	13C
Acquired Size	32768
Spectral Size	65536

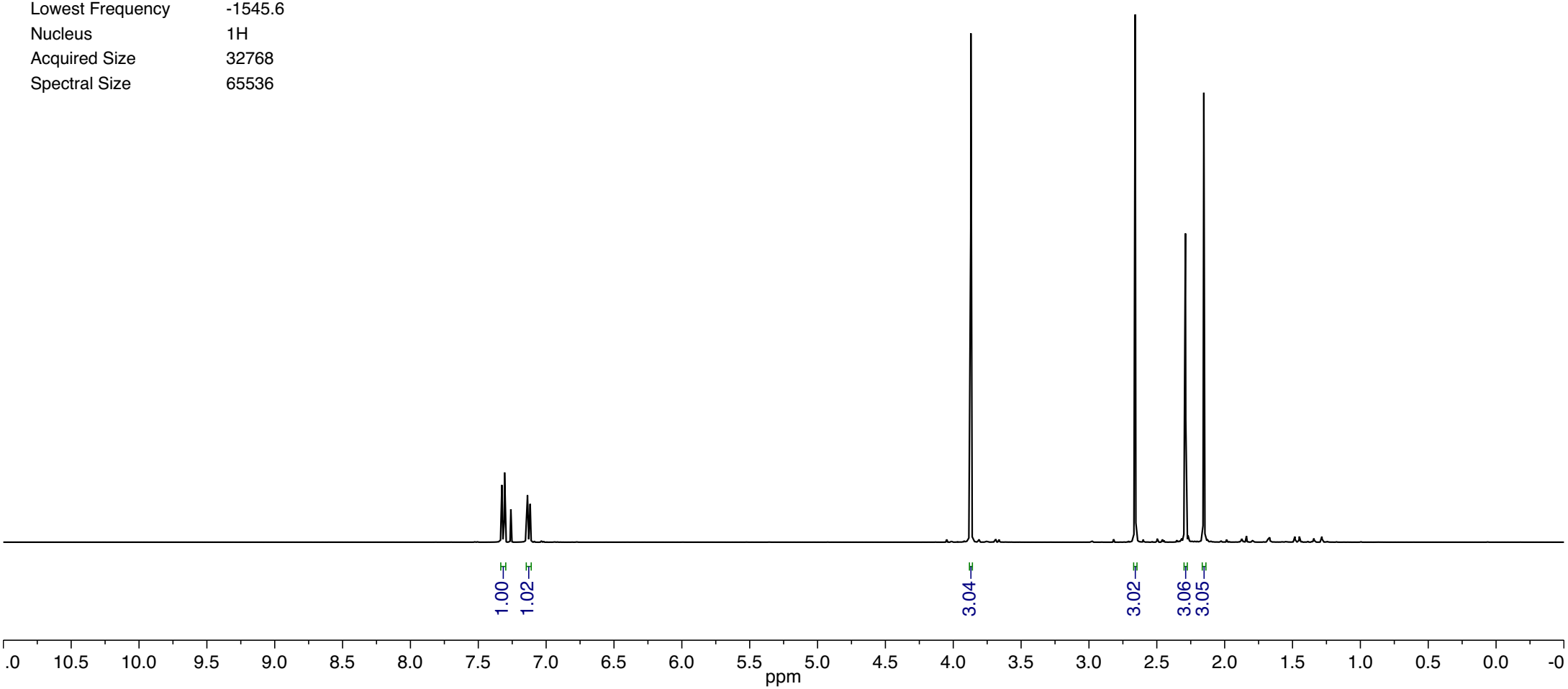


13

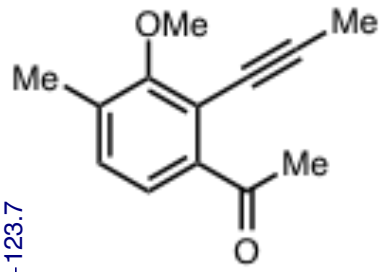
Parameter	Value
Data File Name	/ Volumes/ nmrdata-1/ chenxu91/ nmr/ xuchen-160919-10-103/ 1/ fid
Title	xuchen-160919-10-103.1.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	294.9
Pulse Sequence	zg30
Number of Scans	16
Receiver Gain	87.8
Relaxation Delay	1.0000
Pulse Width	11.7000
Acquisition Time	4.0894
Acquisition Date	2016-09-19T09:46:01
Spectrometer Frequency	400.13
Spectral Width	8012.8
Lowest Frequency	-1545.6
Nucleus	1H
Acquired Size	32768
Spectral Size	65536



14

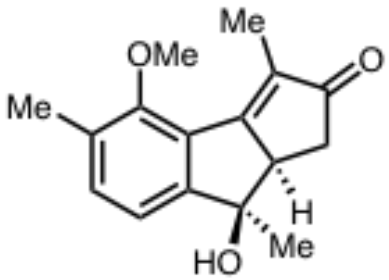


Parameter	Value
Data File Name	/ Volumes/ nmrdata-1/ chenxu91/ nmr/ xuchen-160919-10-103/ 2/ fid
Title	xuchen-160919-10-103.2.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	294.9
Pulse Sequence	zgpg30
Number of Scans	300
Receiver Gain	64.2
Relaxation Delay	2.0000
Pulse Width	10.0000
Acquisition Time	1.3631
Acquisition Date	2016-09-19T10:03:47
Spectrometer Frequency	100.62
Spectral Width	24038.5
Lowest Frequency	-1964.0
Nucleus	13C
Acquired Size	32768
Spectral Size	65536

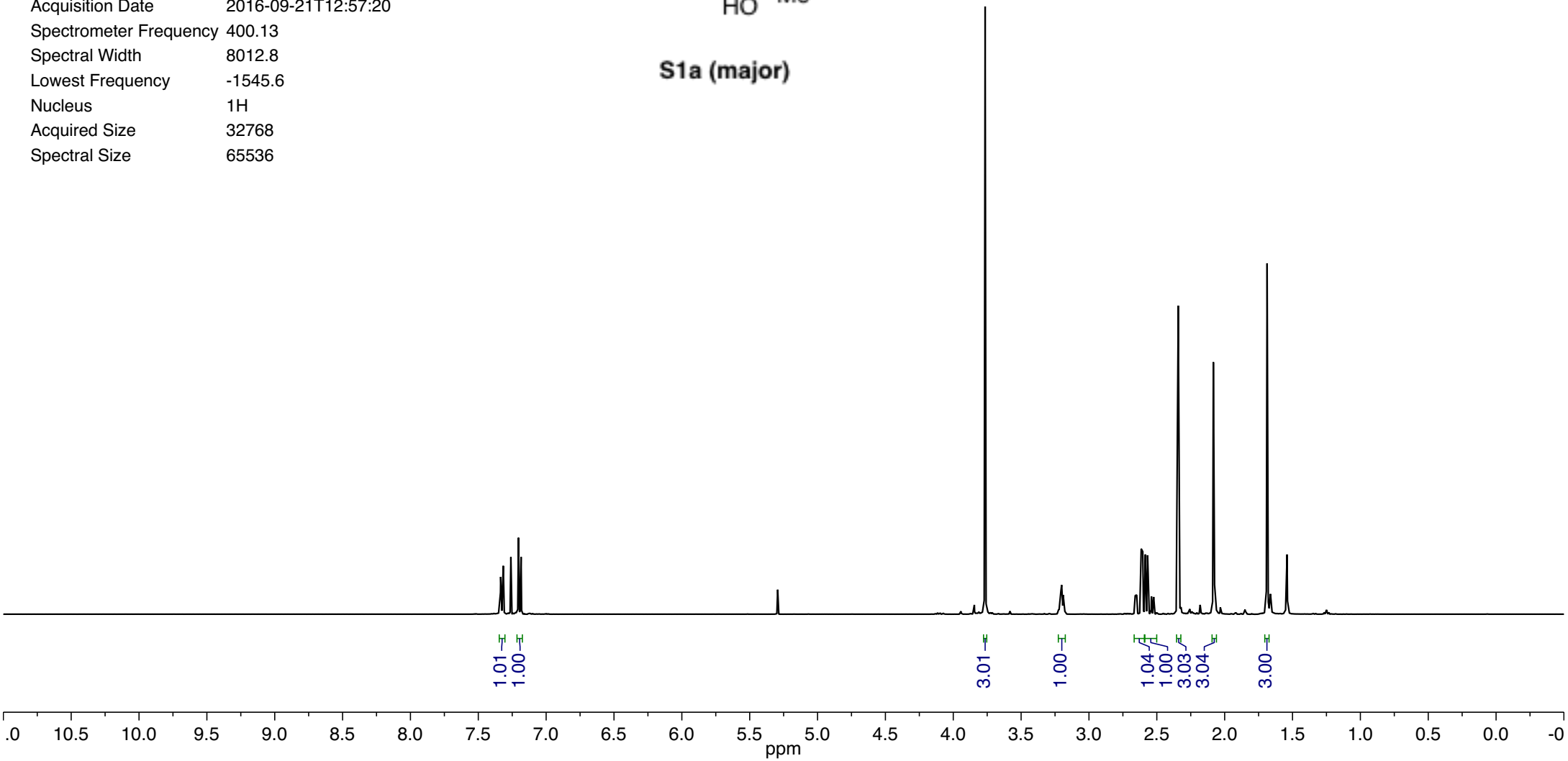


14

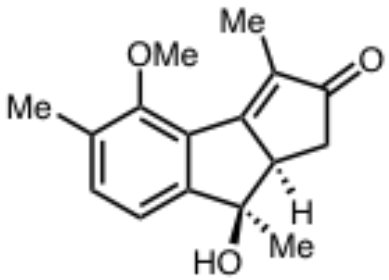
Parameter	Value
Data File Name	/ Volumes/ nmrdata-1/ chenxu91/ nmr/ xuchen-160921-10-105-major diasteromer/ 1/ fid
Title	xuchen-160921-10-105-major diasteromer.1.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	294.9
Pulse Sequence	zg30
Number of Scans	16
Receiver Gain	127.1
Relaxation Delay	1.0000
Pulse Width	11.7000
Acquisition Time	4.0894
Acquisition Date	2016-09-21T12:57:20
Spectrometer Frequency	400.13
Spectral Width	8012.8
Lowest Frequency	-1545.6
Nucleus	1H
Acquired Size	32768
Spectral Size	65536



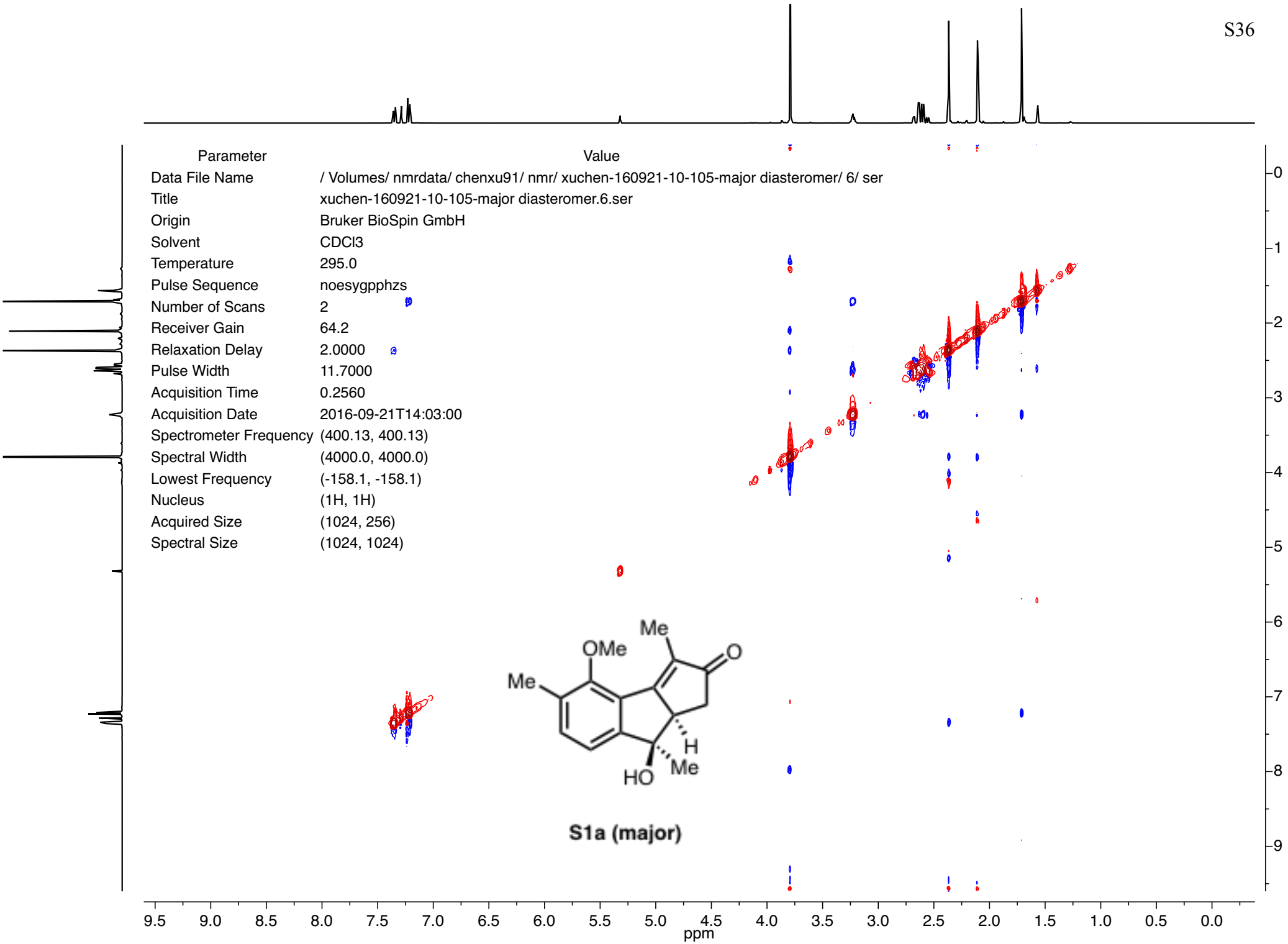
S1a (major)



Parameter	Value
Data File Name	/ Volumes/ nmrdata-1/ chenxu91/ nmr/ xuchen-160921-10-105-major diasteromer/ 2/ fid
Title	xuchen-160921-10-105-major diasteromer.2.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	294.9
Pulse Sequence	zgpg30
Number of Scans	400
Receiver Gain	98.9
Relaxation Delay	2.0000
Pulse Width	10.0000
Acquisition Time	1.3631
Acquisition Date	2016-09-21T13:20:49
Spectrometer Frequency	100.62
Spectral Width	24038.5
Lowest Frequency	-1963.0
Nucleus	13C
Acquired Size	32768
Spectral Size	65536



S1a (major)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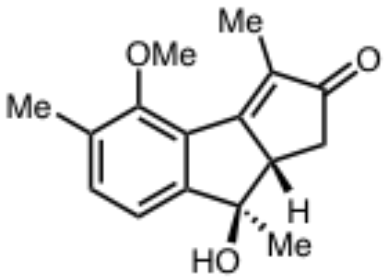
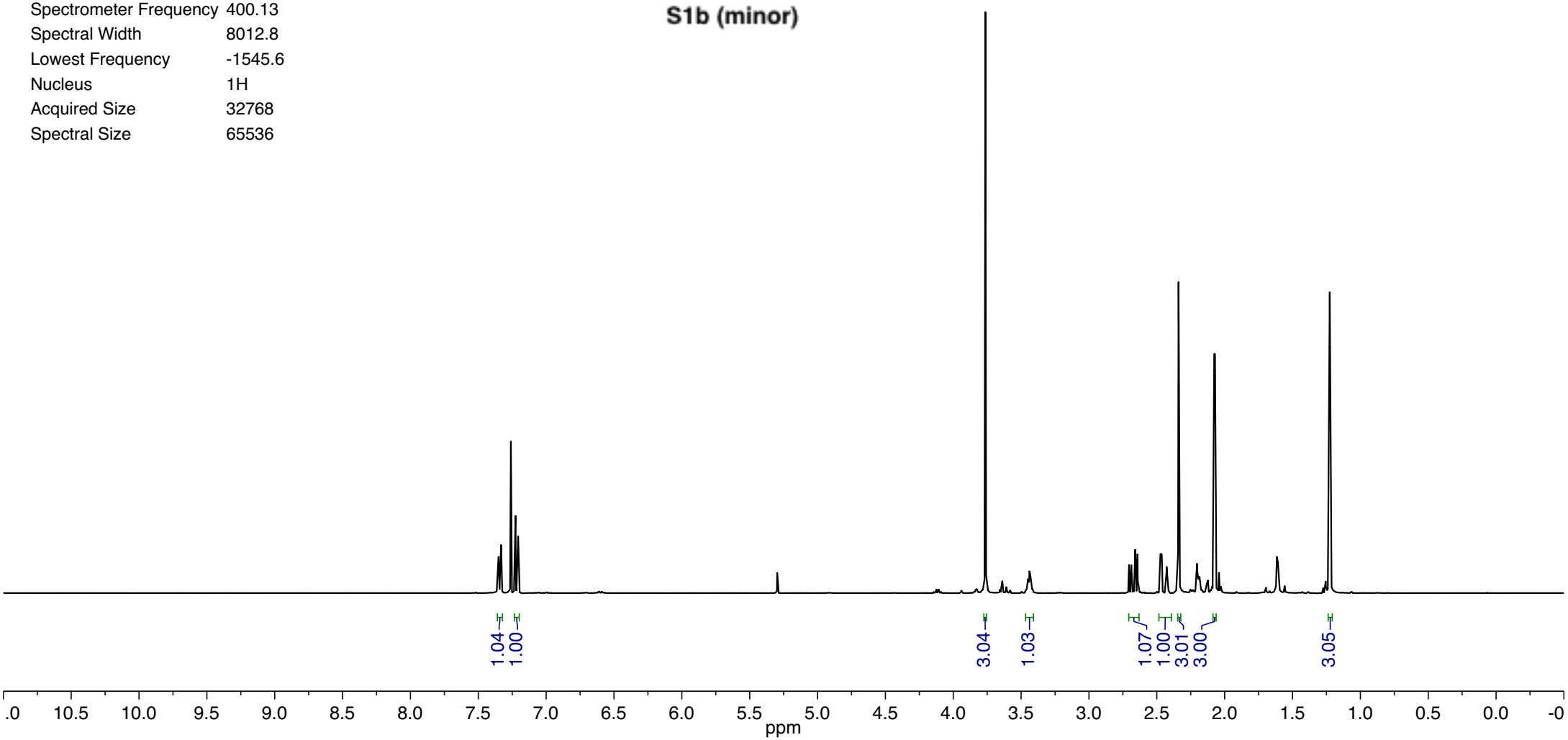
Title xuchen-160921-10-105-major diasteromer.6.ser
Origin Bruker BioSpin GmbH
Solvent CDCl3
Temperature 295.0
Pulse Sequence noesygpphzs
Number of Scans 2
Receiver Gain 64.2
Relaxation Delay 2.0000
Pulse Width 11.7000
Acquisition Time 0.2560
Acquisition Date 2016-09-21T14:03:00
Spectrometer Frequency (400.13, 400.13)
Spectral Width (4000.0, 4000.0)
Lowest Frequency (-158.1, -158.1)
Nucleus (1H, 1H)
Acquired Size (1024, 256)
Spectral Size (1024, 1024)
Me
OMe
O
Me
H
HO
Me
S1a (major)
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
ppm
0 1 2 3 4 5 6 7 8 9

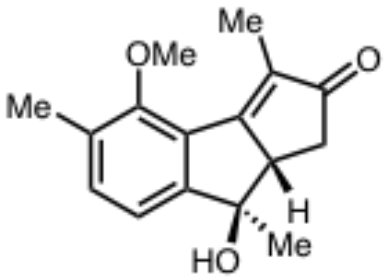
Parameter	Value
Data File Name	/ Volumes/ nmrdata-1/ chenxu91/ nmr/ xuchen-160921-10-105-minor/ 1/ fid
Title	xuchen-160921-10-105-minor.1.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	294.9
Pulse Sequence	zg30
Number of Scans	16
Receiver Gain	197.4
Relaxation Delay	1.0000
Pulse Width	11.7000
Acquisition Time	4.0894
Acquisition Date	2016-09-22T01:06:26
Spectrometer Frequency	400.13
Spectral Width	8012.8
Lowest Frequency	-1545.6
Nucleus	1H
Acquired Size	32768
Spectral Size	65536



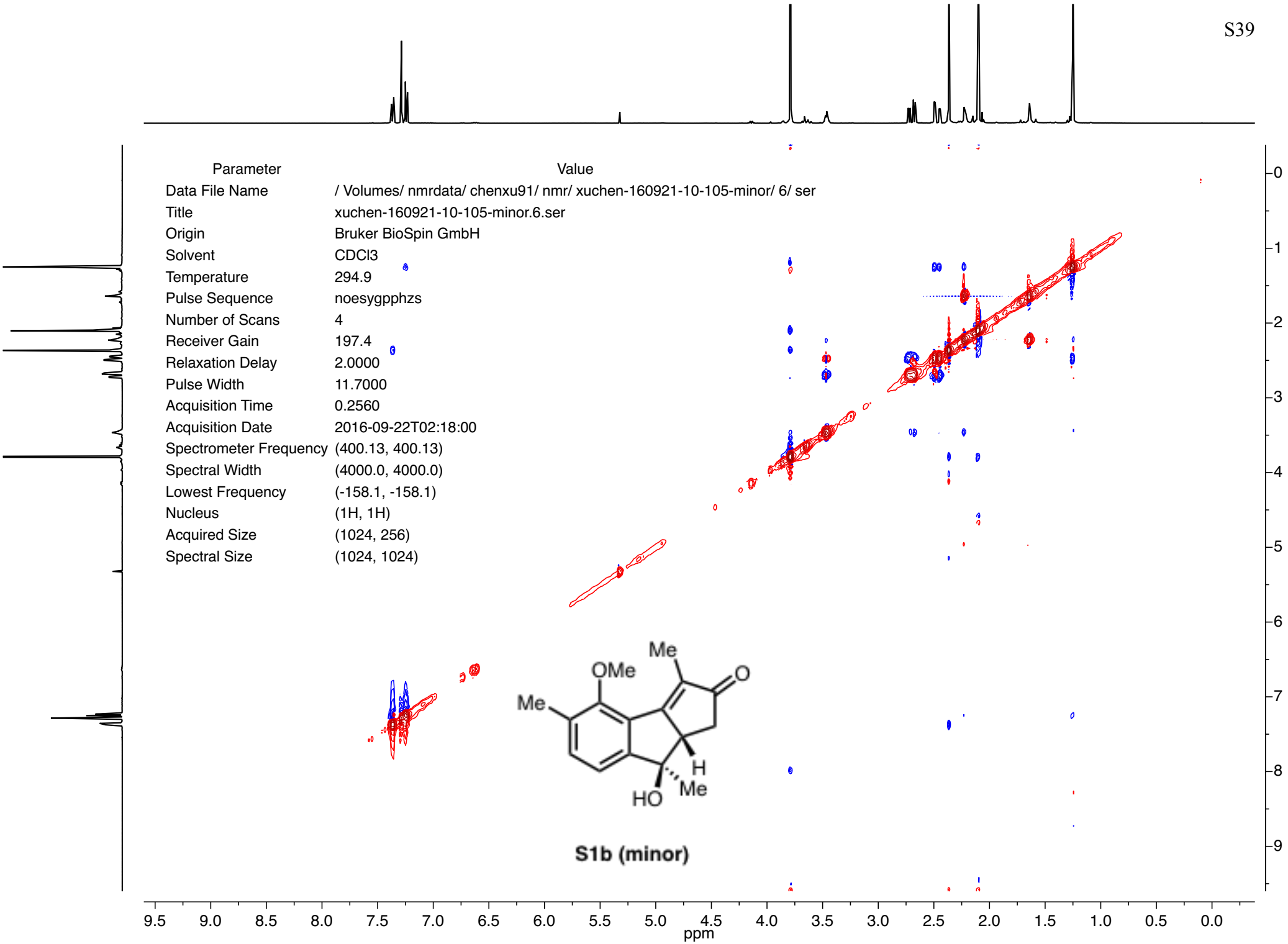
S1b (minor)



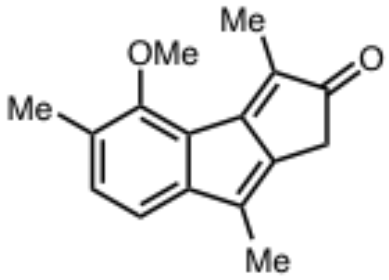
Parameter	Value
Data File Name	/ Volumes/ nmrdata-1/ chenxu91/ nmr/ xuchen-160921-10-105-minor/ 2/ fid
Title	xuchen-160921-10-105-minor.2.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	294.9
Pulse Sequence	zgpg30
Number of Scans	500
Receiver Gain	87.8
Relaxation Delay	2.0000
Pulse Width	10.0000
Acquisition Time	1.3631
Acquisition Date	2016-09-22T01:35:37
Spectrometer Frequency	100.62
Spectral Width	24038.5
Lowest Frequency	-1961.7
Nucleus	13C
Acquired Size	32768
Spectral Size	65536



S1b (minor)

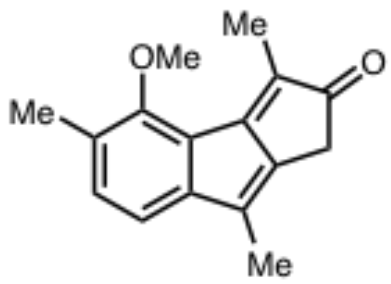

Parameter Value
Data File Name / Volumes/ nmrdata/ chenxu91/ nmr/ xuchen-160921-10-105-minor/ 6/ ser
Title xuchen-160921-10-105-minor.6.ser
Origin Bruker BioSpin GmbH
Solvent CDCl3
Temperature 294.9
Pulse Sequence noesygpphzs
Number of Scans 4
Receiver Gain 197.4
Relaxation Delay 2.0000
Pulse Width 11.7000
Acquisition Time 0.2560
Acquisition Date 2016-09-22T02:18:00
Spectrometer Frequency (400.13, 400.13)
Spectral Width (4000.0, 4000.0)
Lowest Frequency (-158.1, -158.1)
Nucleus (1H, 1H)
Acquired Size (1024, 256)
Spectral Size (1024, 1024)
Me
OMe
O
Me
H
HO
Me
S1b (minor)
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
ppm
0 1 2 3 4 5 6 7 8 9

Parameter	Value
Data File Name	/ Volumes/ nmrdata-1/ chenxu91/ nmr/ xuchen-160923-10-109/ 1/ fid
Title	xuchen-160923-10-109.1.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	294.9
Pulse Sequence	zg30
Number of Scans	16
Receiver Gain	142.8
Relaxation Delay	1.0000
Pulse Width	11.7000
Acquisition Time	4.0894
Acquisition Date	2016-09-23T12:41:40
Spectrometer Frequency	400.13
Spectral Width	8012.8
Lowest Frequency	-1545.6
Nucleus	1H
Acquired Size	32768
Spectral Size	65536



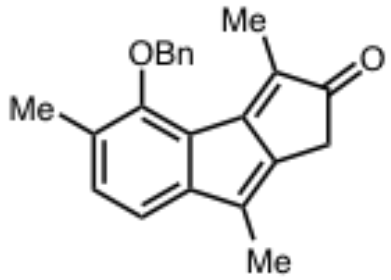
15

Parameter	Value
Data File Name	/ Volumes/ nmrdata-1/ chenxu91/ nmr/ xuchen-160923-10-109/ 2/ fid
Title	xuchen-160923-10-109.2.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	295.0
Pulse Sequence	zgpg30
Number of Scans	512
Receiver Gain	72.0
Relaxation Delay	2.0000
Pulse Width	10.0000
Acquisition Time	1.3631
Acquisition Date	2016-09-23T13:18:08
Spectrometer Frequency	100.62
Spectral Width	24038.5
Lowest Frequency	-1962.3
Nucleus	13C
Acquired Size	32768
Spectral Size	65536

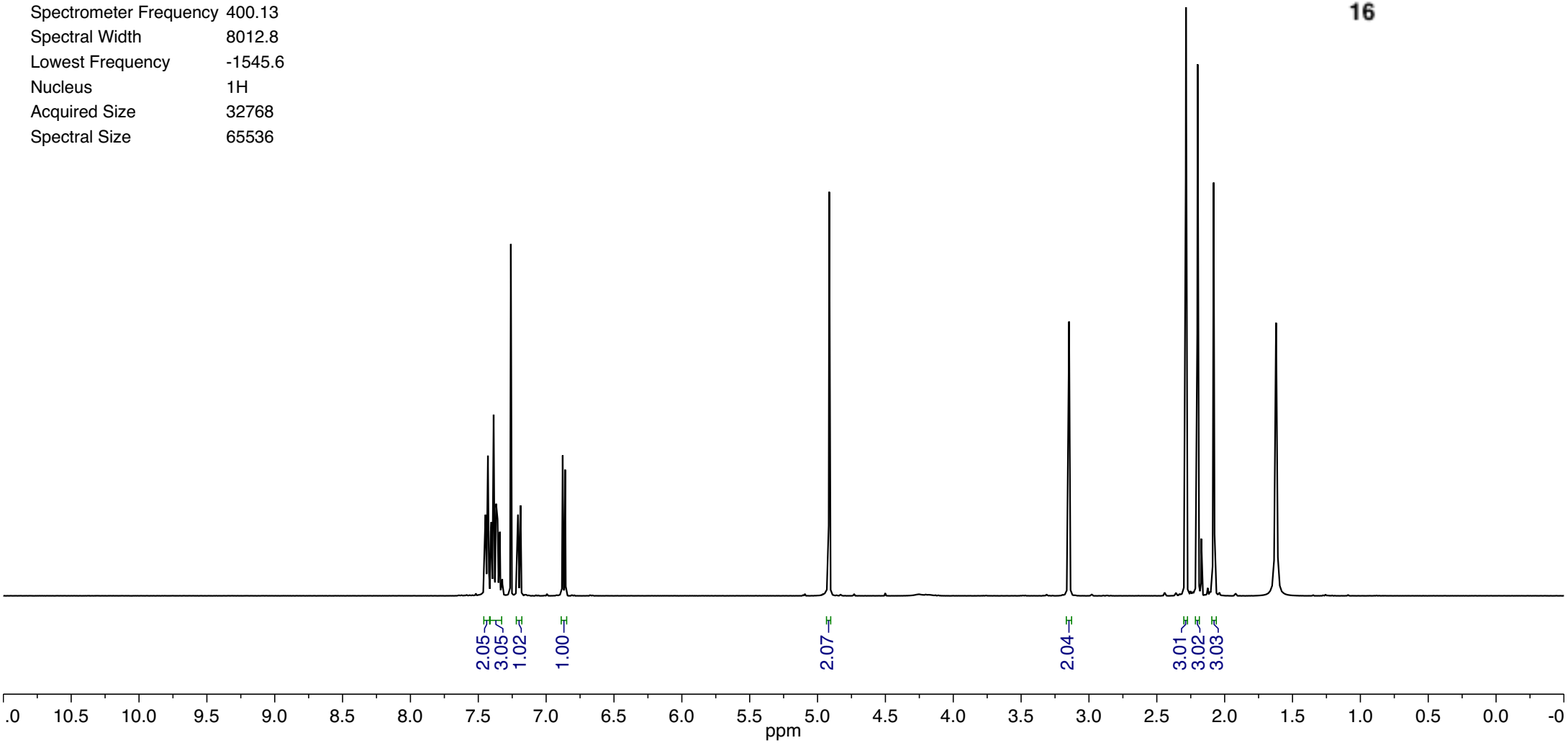


15

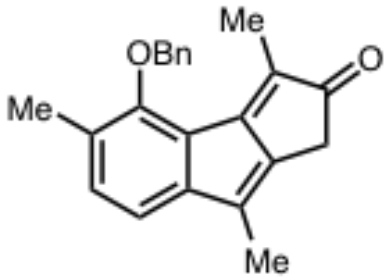
Parameter	Value
Data File Name	/ Volumes/ nmrdata-1/ chenxu91/ nmr/ xuchen-160822-Bn-ortho-tricycle/ 1/ fid
Title	xuchen-160822-Bn-ortho-tricycle.1.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	294.9
Pulse Sequence	zg30
Number of Scans	16
Receiver Gain	176.8
Relaxation Delay	1.0000
Pulse Width	11.7000
Acquisition Time	4.0894
Acquisition Date	2016-08-22T19:29:21
Spectrometer Frequency	400.13
Spectral Width	8012.8
Lowest Frequency	-1545.6
Nucleus	1H
Acquired Size	32768
Spectral Size	65536



16

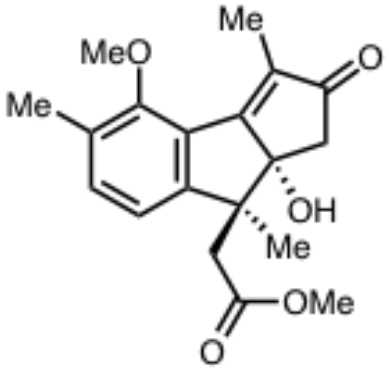


Parameter	Value
Data File Name	/ Volumes/ nmrdata-1/ chenxu91/ nmr/ xuchen-160822-Bn-ortho-tricycle/ 2/ fid
Title	xuchen-160822-Bn-ortho-tricycle.2.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	295.0
Pulse Sequence	zgpg30
Number of Scans	512
Receiver Gain	38.0
Relaxation Delay	2.0000
Pulse Width	10.0000
Acquisition Time	1.3631
Acquisition Date	2016-08-22T19:59:47
Spectrometer Frequency	100.62
Spectral Width	24038.5
Lowest Frequency	-1962.2
Nucleus	13C
Acquired Size	32768
Spectral Size	65536



16

Parameter	Value
Data File Name	/ Volumes/ nmrdata/ ahan/ vnmrsys/ data/ 8-AH-039-CH/ PROTON01.fid/ fid
Title	PROTON01
Origin	Varian
Solvent	cdcl3
Temperature	25.0
Pulse Sequence	s2pul
Number of Scans	8
Receiver Gain	32
Relaxation Delay	5.0000
Pulse Width	5.8000
Acquisition Time	3.0000
Acquisition Date	2017-09-03T12:56:51
Spectrometer Frequency	499.64
Spectral Width	8000.0
Lowest Frequency	-1017.7
Nucleus	1H
Acquired Size	24000
Spectral Size	65536



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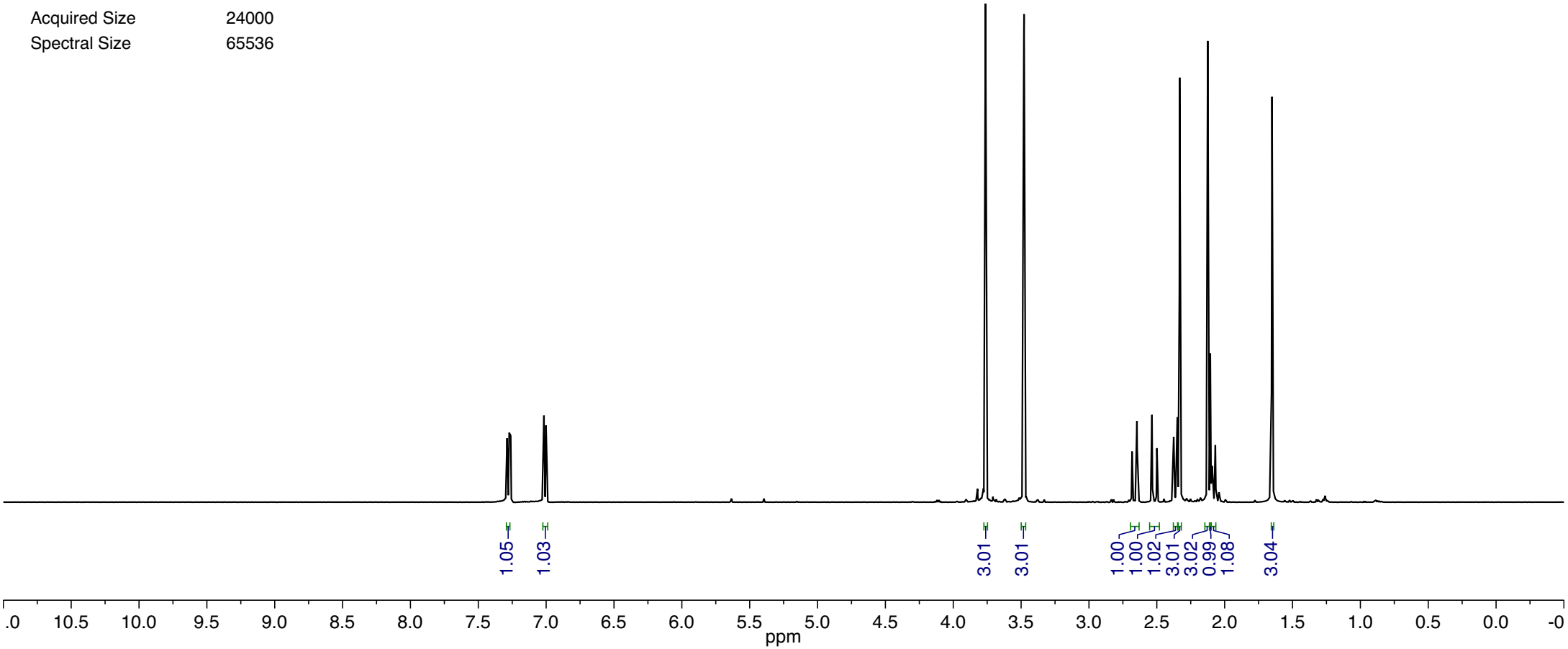
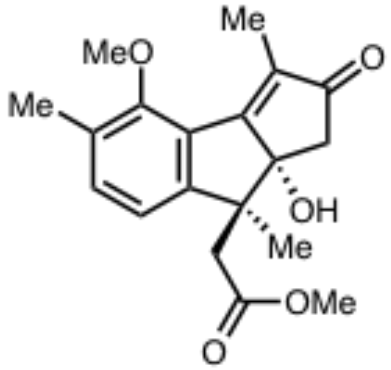
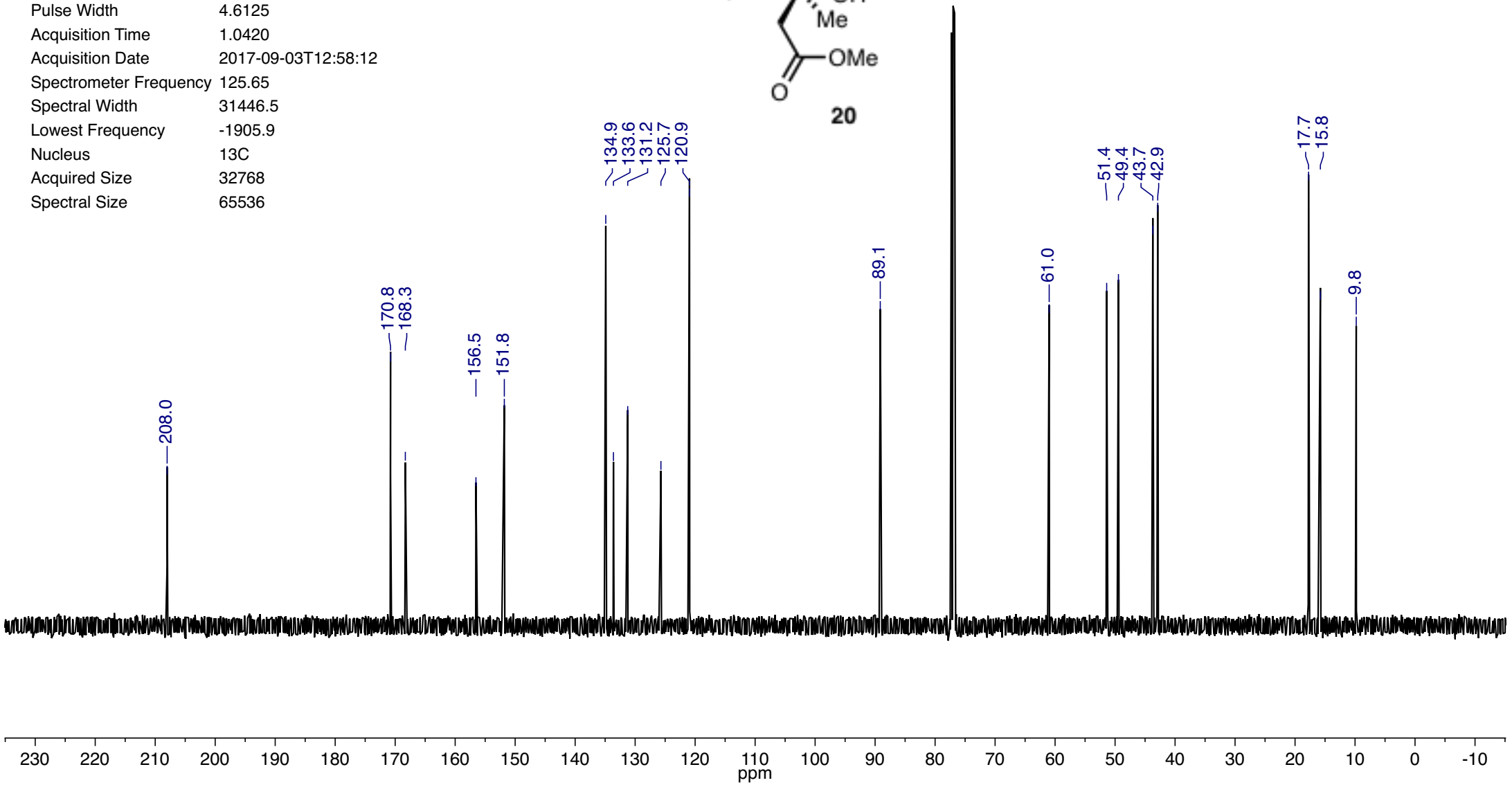


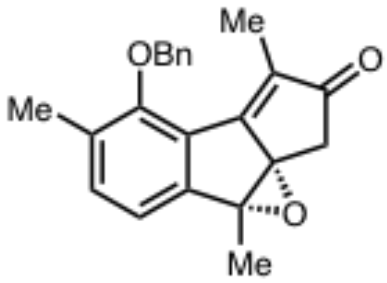
Parameter	Value
Data File Name	/ Volumes/ nmrdata/ ahan/ vnmrsys/ data/ 8-AH-039-CH/ CARBON01.fid/ fid
Title	CARBON01
Origin	Varian
Solvent	cdcl3
Temperature	25.0
Pulse Sequence	s2pul
Number of Scans	1000
Receiver Gain	30
Relaxation Delay	1.0000
Pulse Width	4.6125
Acquisition Time	1.0420
Acquisition Date	2017-09-03T12:58:12
Spectrometer Frequency	125.65
Spectral Width	31446.5
Lowest Frequency	-1905.9
Nucleus	13C
Acquired Size	32768
Spectral Size	65536



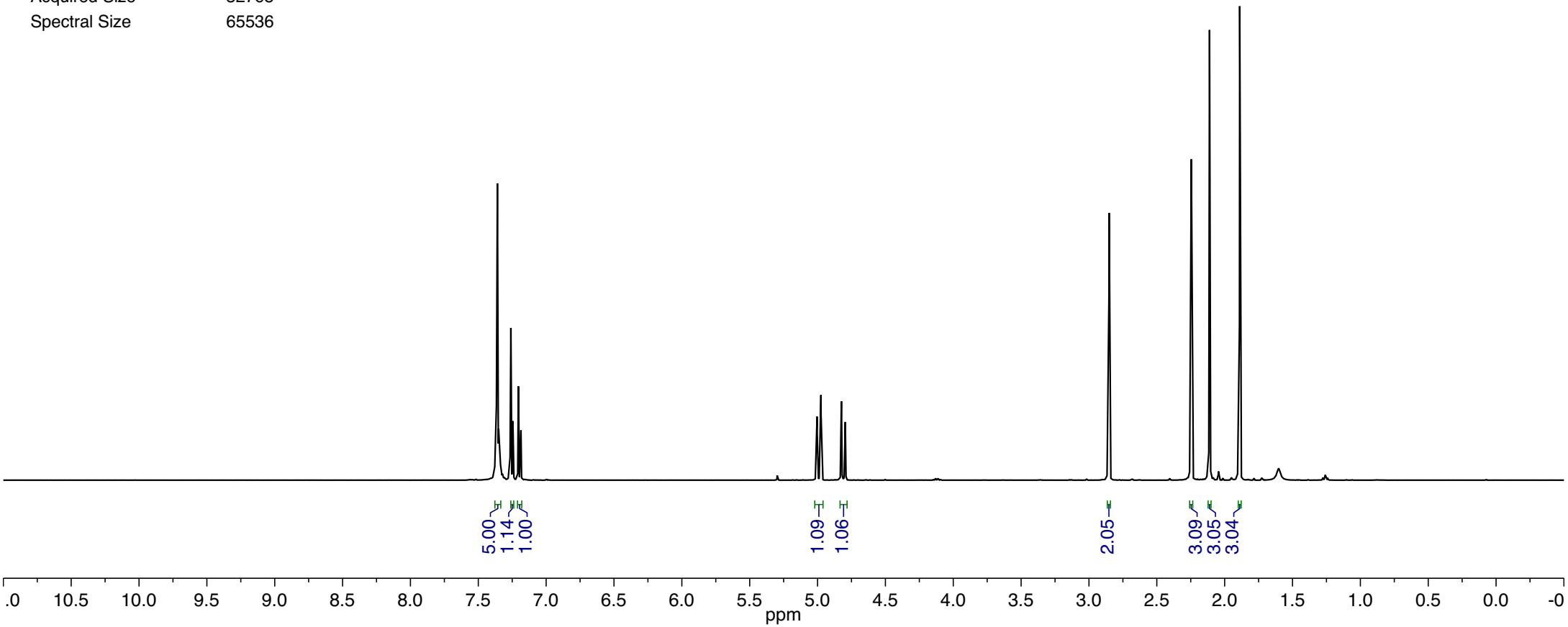
20



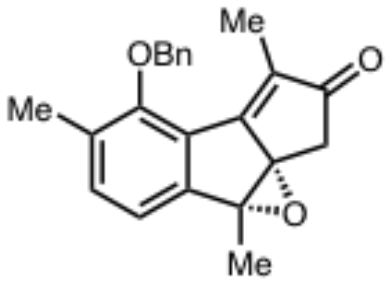
Parameter	Value
Data File Name	/ Volumes/ nmrdata-1/ chenxu91/ nmr/ xuchen-160823-10-80-crude/ 1/ fid
Title	xuchen-160823-10-80-crude.1.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	294.9
Pulse Sequence	zg30
Number of Scans	16
Receiver Gain	156.2
Relaxation Delay	1.0000
Pulse Width	11.7000
Acquisition Time	4.0894
Acquisition Date	2016-08-23T18:11:26
Spectrometer Frequency	400.13
Spectral Width	8012.8
Lowest Frequency	-1545.6
Nucleus	1H
Acquired Size	32768
Spectral Size	65536



18

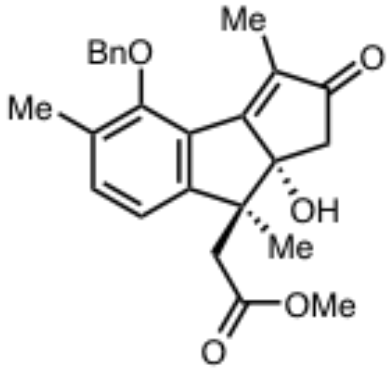


Parameter	Value
Data File Name	/ Volumes/ nmrdata-1/ chenxu91/ nmr/ xuchen-160823-10-80-crude/ 3/ fid
Title	xuchen-160823-10-80-crude.3.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	294.9
Pulse Sequence	zgpg30
Number of Scans	600
Receiver Gain	78.7
Relaxation Delay	2.0000
Pulse Width	10.0000
Acquisition Time	1.3631
Acquisition Date	2016-08-23T18:57:57
Spectrometer Frequency	100.62
Spectral Width	24038.5
Lowest Frequency	-1962.3
Nucleus	13C
Acquired Size	32768
Spectral Size	65536

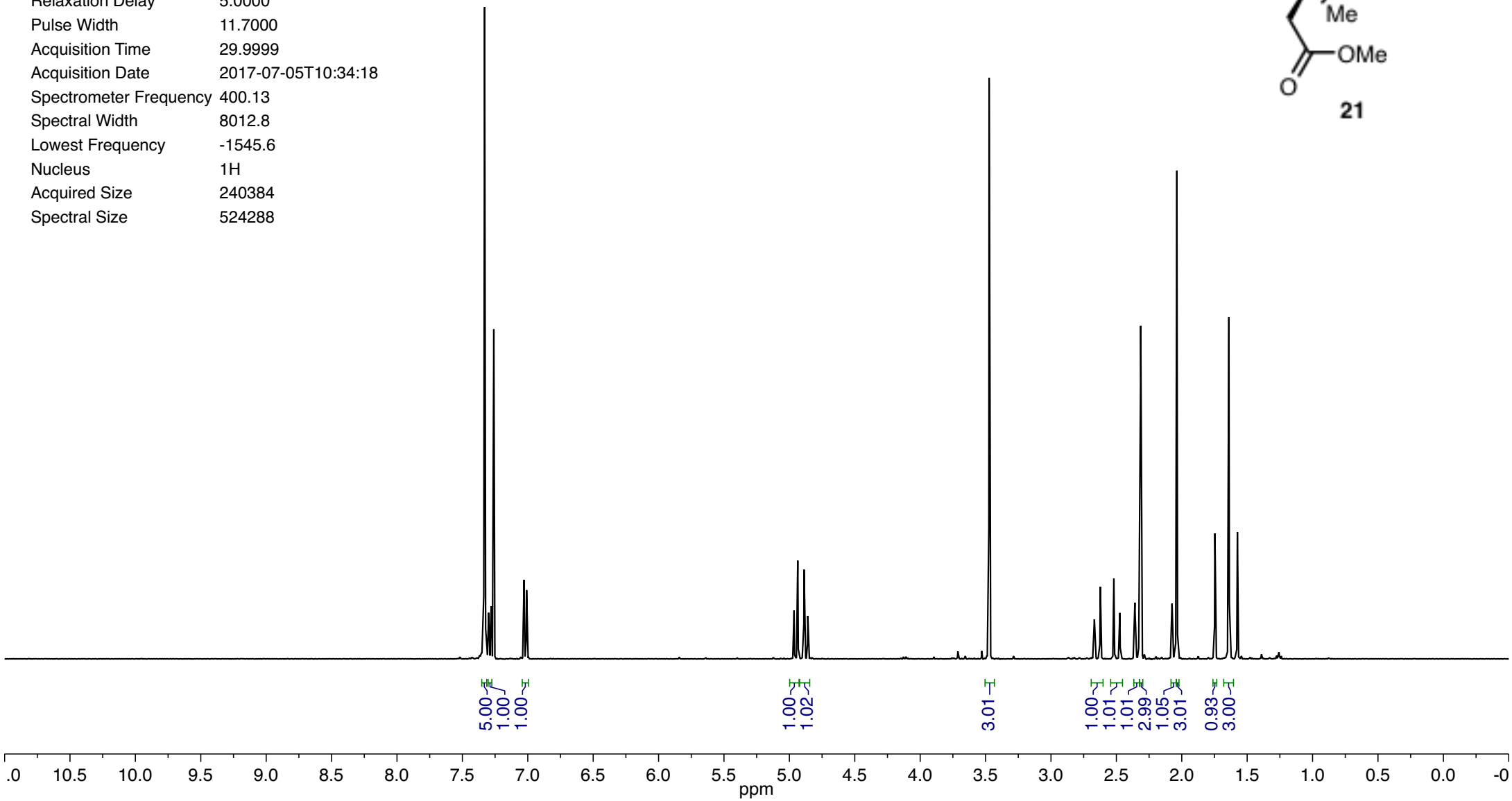


18

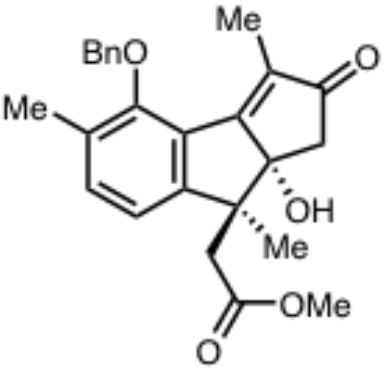
Parameter	Value
Data File Name	/ Volumes/ nmrdata/ ahan/ nmr/ 7-AH-285-P/ 4/ fid
Title	7-AH-285-P.4.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	294.9
Pulse Sequence	zg30
Number of Scans	1
Receiver Gain	197.4
Relaxation Delay	5.0000
Pulse Width	11.7000
Acquisition Time	29.9999
Acquisition Date	2017-07-05T10:34:18
Spectrometer Frequency	400.13
Spectral Width	8012.8
Lowest Frequency	-1545.6
Nucleus	1H
Acquired Size	240384
Spectral Size	524288



21

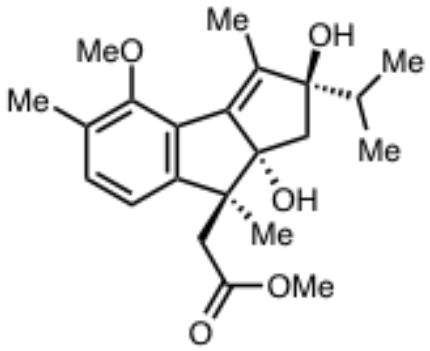


Parameter	Value
Data File Name	/ Volumes/ nmrdata/ ahan/ nmr/ 7-AH-285-P/ 3/ fid
Title	7-AH-285-P.3.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	295.0
Pulse Sequence	zgpg30
Number of Scans	400
Receiver Gain	72.0
Relaxation Delay	1.0000
Pulse Width	10.0000
Acquisition Time	1.3631
Acquisition Date	2017-07-05T10:31:13
Spectrometer Frequency	100.62
Spectral Width	24038.5
Lowest Frequency	-1961.7
Nucleus	13C
Acquired Size	32768
Spectral Size	65536

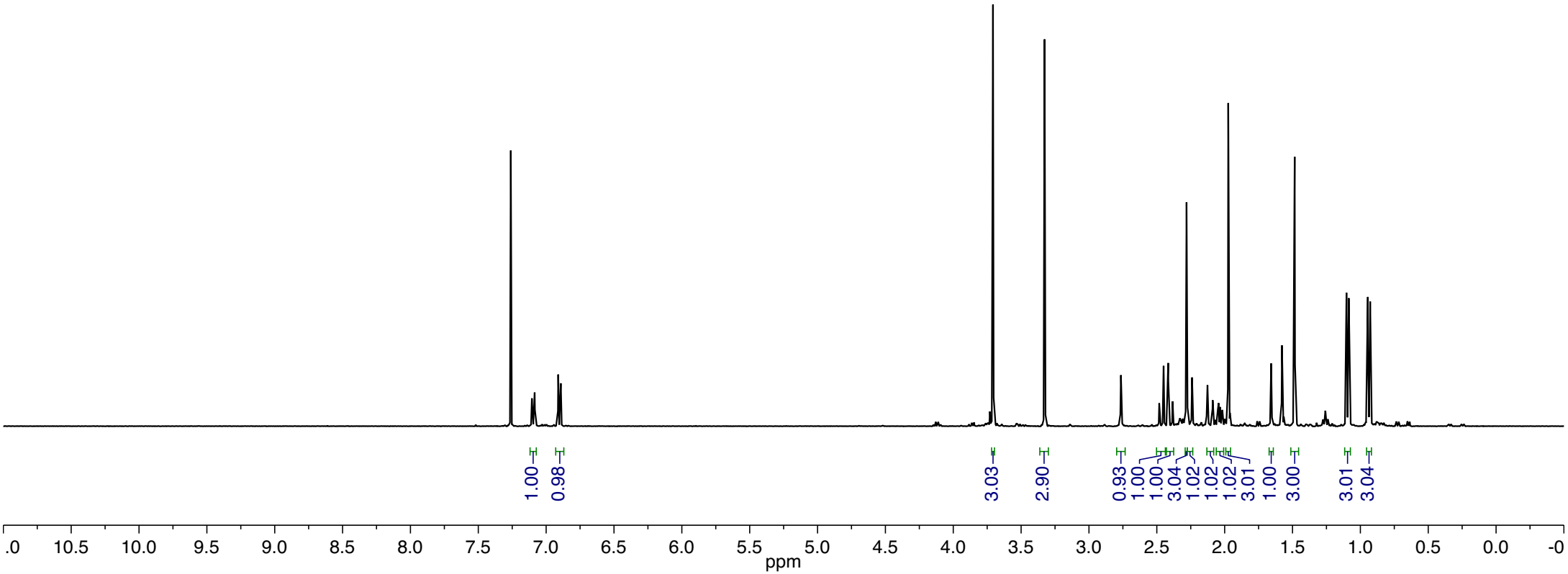


21

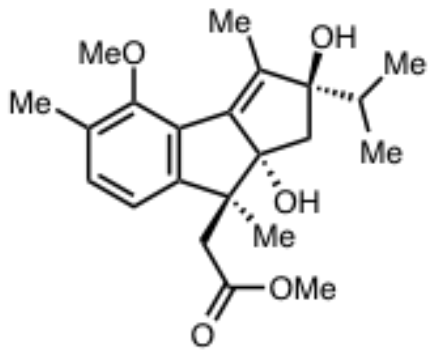
Parameter	Value
Data File Name	/ Volumes/ nmrdata/ ahan/ nmr/ 8-AH-040-CH/ 1/ fid
Title	8-AH-040-CH.1.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	295.0
Pulse Sequence	zg30
Number of Scans	1
Receiver Gain	176.8
Relaxation Delay	5.0000
Pulse Width	11.7000
Acquisition Time	29.9999
Acquisition Date	2017-08-23T15:34:54
Spectrometer Frequency	400.13
Spectral Width	8012.8
Lowest Frequency	-1545.2
Nucleus	1H
Acquired Size	240384
Spectral Size	524288



22

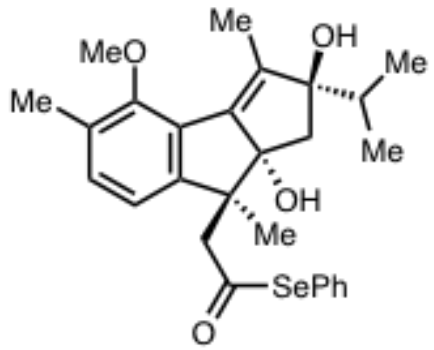


Parameter	Value
Data File Name	/ Volumes/ nmrdata/ ahan/ nmr/ 8-AH-040-CH/ 2/ fid
Title	8-AH-040-CH.2.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	294.9
Pulse Sequence	zgpg30
Number of Scans	691
Receiver Gain	72.0
Relaxation Delay	1.0000
Pulse Width	10.0000
Acquisition Time	1.3631
Acquisition Date	2017-08-23T16:03:22
Spectrometer Frequency	100.62
Spectral Width	24038.5
Lowest Frequency	-1961.3
Nucleus	13C
Acquired Size	32768
Spectral Size	65536

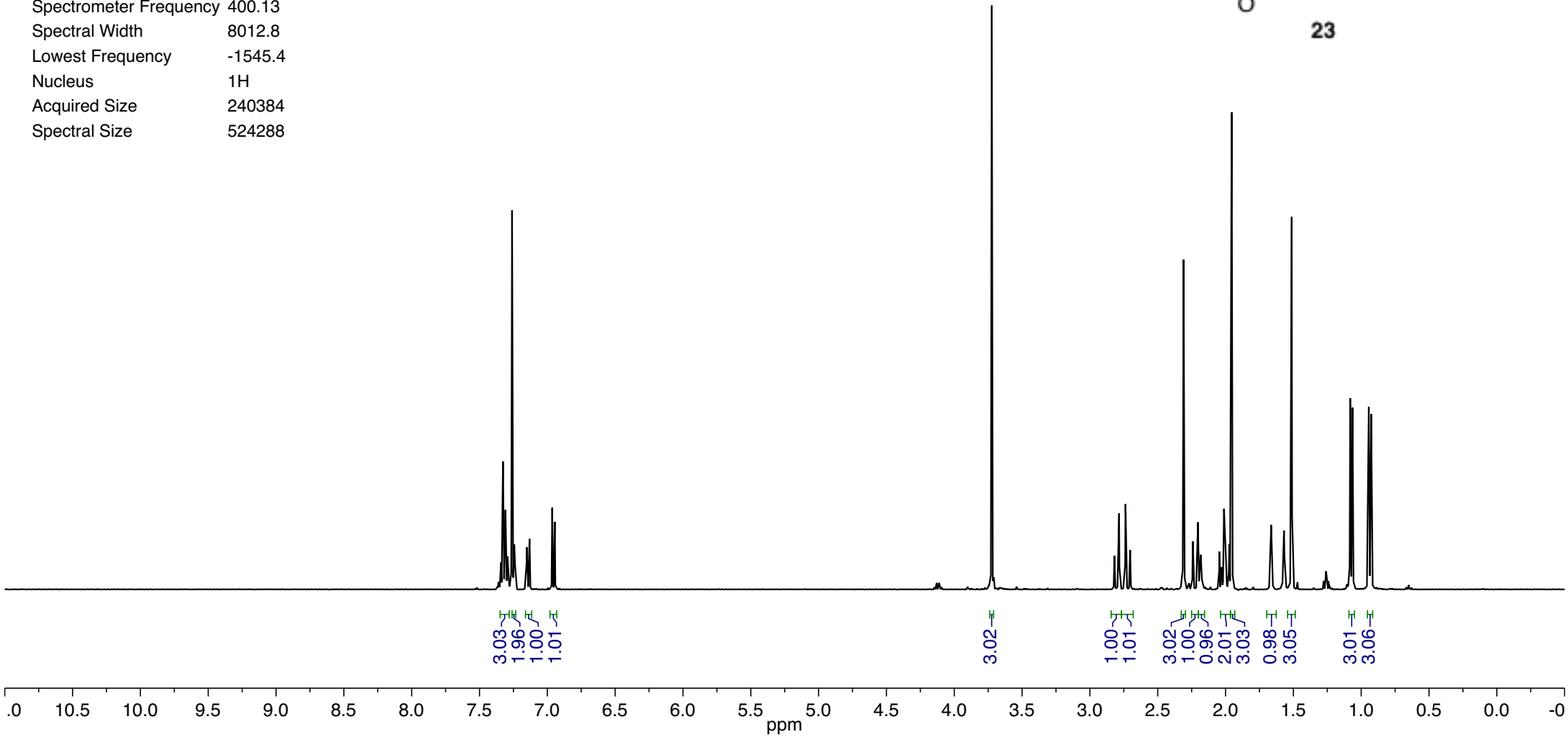


22

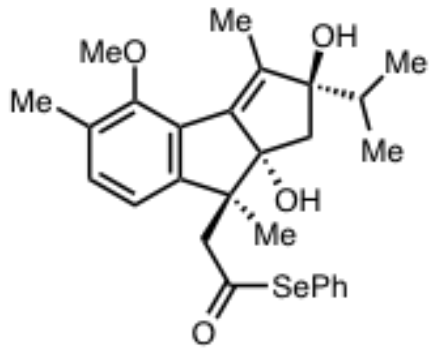
Parameter	Value
Data File Name	/ Volumes/ nmrdata/ ahan/ nmr/ 8-AH-042-1-CH/ 1/ fid
Title	8-AH-042-1-CH.1.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	294.9
Pulse Sequence	zg30
Number of Scans	1
Receiver Gain	176.8
Relaxation Delay	5.0000
Pulse Width	11.7000
Acquisition Time	29.9999
Acquisition Date	2017-08-26T13:11:08
Spectrometer Frequency	400.13
Spectral Width	8012.8
Lowest Frequency	-1545.4
Nucleus	1H
Acquired Size	240384
Spectral Size	524288



23

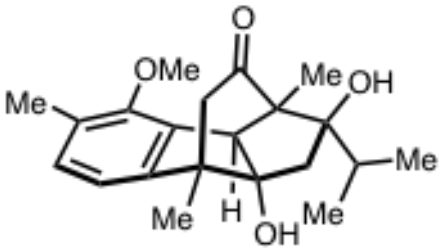


Parameter	Value
Data File Name	/ Volumes/ nmrdata/ ahan/ nmr/ 8-AH-042-1-CH/ 2/ fid
Title	8-AH-042-1-CH.2.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	294.9
Pulse Sequence	zgpg30
Number of Scans	750
Receiver Gain	64.2
Relaxation Delay	1.0000
Pulse Width	10.0000
Acquisition Time	1.3631
Acquisition Date	2017-08-26T13:42:41
Spectrometer Frequency	100.62
Spectral Width	24038.5
Lowest Frequency	-1961.6
Nucleus	13C
Acquired Size	32768
Spectral Size	65536

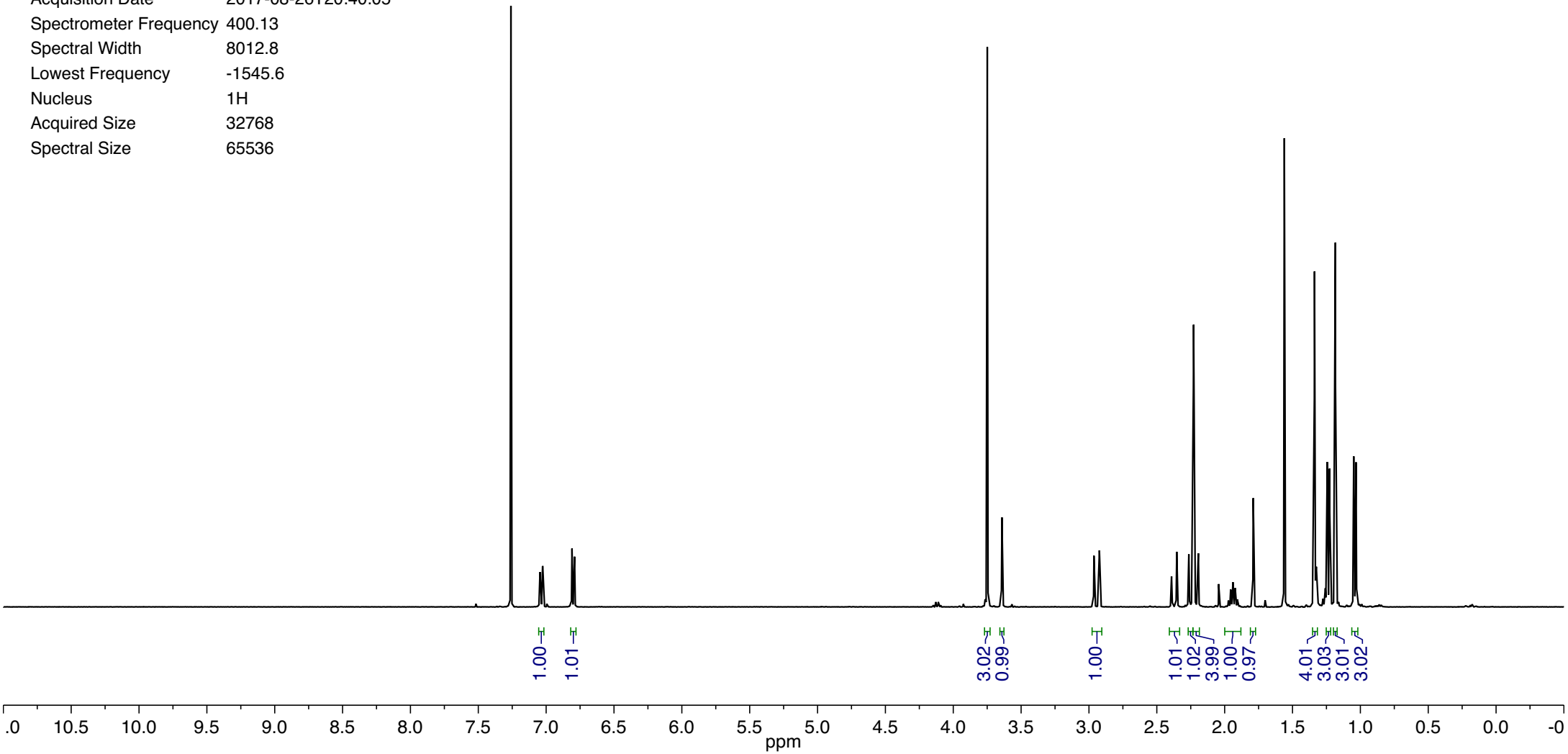


23

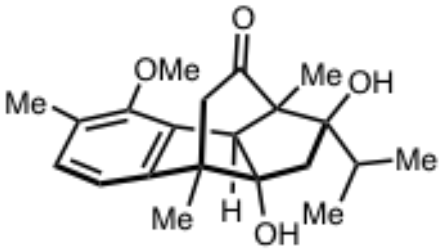
Parameter	Value
Data File Name	/ Volumes/ nmrdata/ ahan/ nmr/ 8-AH-043-CH/ 1/ fid
Title	8-AH-043-CH.1.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	294.9
Pulse Sequence	zg30
Number of Scans	8
Receiver Gain	197.4
Relaxation Delay	5.0000
Pulse Width	11.7000
Acquisition Time	4.0894
Acquisition Date	2017-08-26T20:40:05
Spectrometer Frequency	400.13
Spectral Width	8012.8
Lowest Frequency	-1545.6
Nucleus	1H
Acquired Size	32768
Spectral Size	65536



24

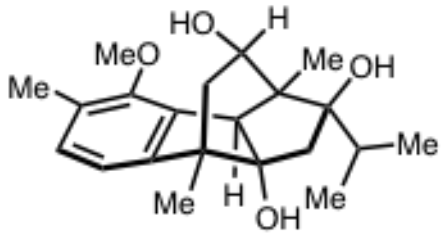


Parameter	Value
Data File Name	/ Volumes/ nmrdata/ ahan/ nmr/ 8-AH-043-CH/ 2/ fid
Title	8-AH-043-CH.2.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	295.0
Pulse Sequence	zgpg30
Number of Scans	1000
Receiver Gain	72.0
Relaxation Delay	1.0000
Pulse Width	10.0000
Acquisition Time	1.3631
Acquisition Date	2017-08-26T21:21:02
Spectrometer Frequency	100.62
Spectral Width	24038.5
Lowest Frequency	-1961.1
Nucleus	13C
Acquired Size	32768
Spectral Size	65536

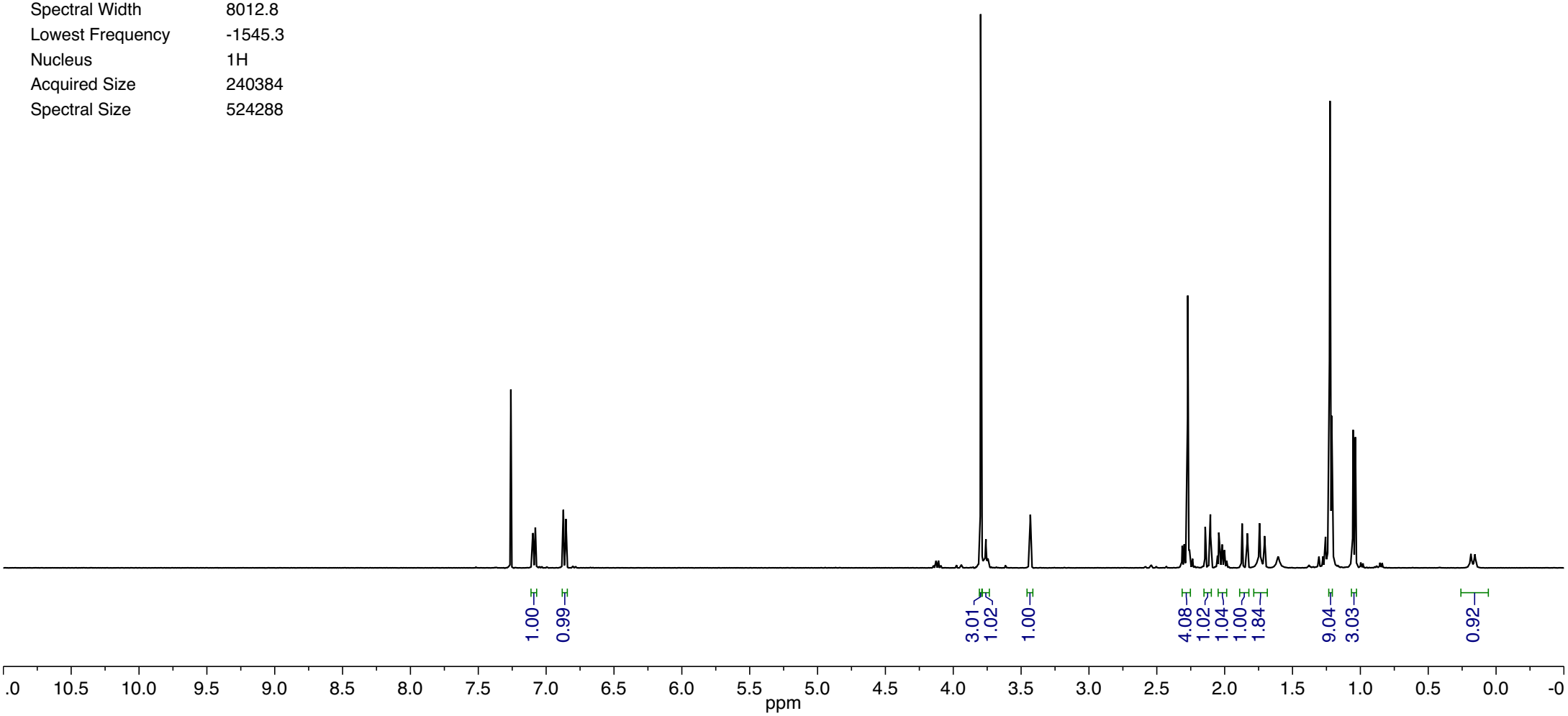


24

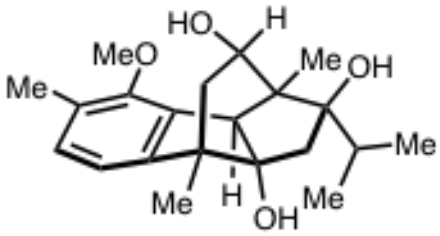
Parameter	Value
Data File Name	/ Volumes/ nmrdata/ ahan/ nmr/ 8-AH-044-CH/ 1/ fid
Title	8-AH-044-CH.1.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	295.0
Pulse Sequence	zg30
Number of Scans	1
Receiver Gain	127.1
Relaxation Delay	5.0000
Pulse Width	11.7000
Acquisition Time	29.9999
Acquisition Date	2017-08-29T07:47:19
Spectrometer Frequency	400.13
Spectral Width	8012.8
Lowest Frequency	-1545.3
Nucleus	1H
Acquired Size	240384
Spectral Size	524288



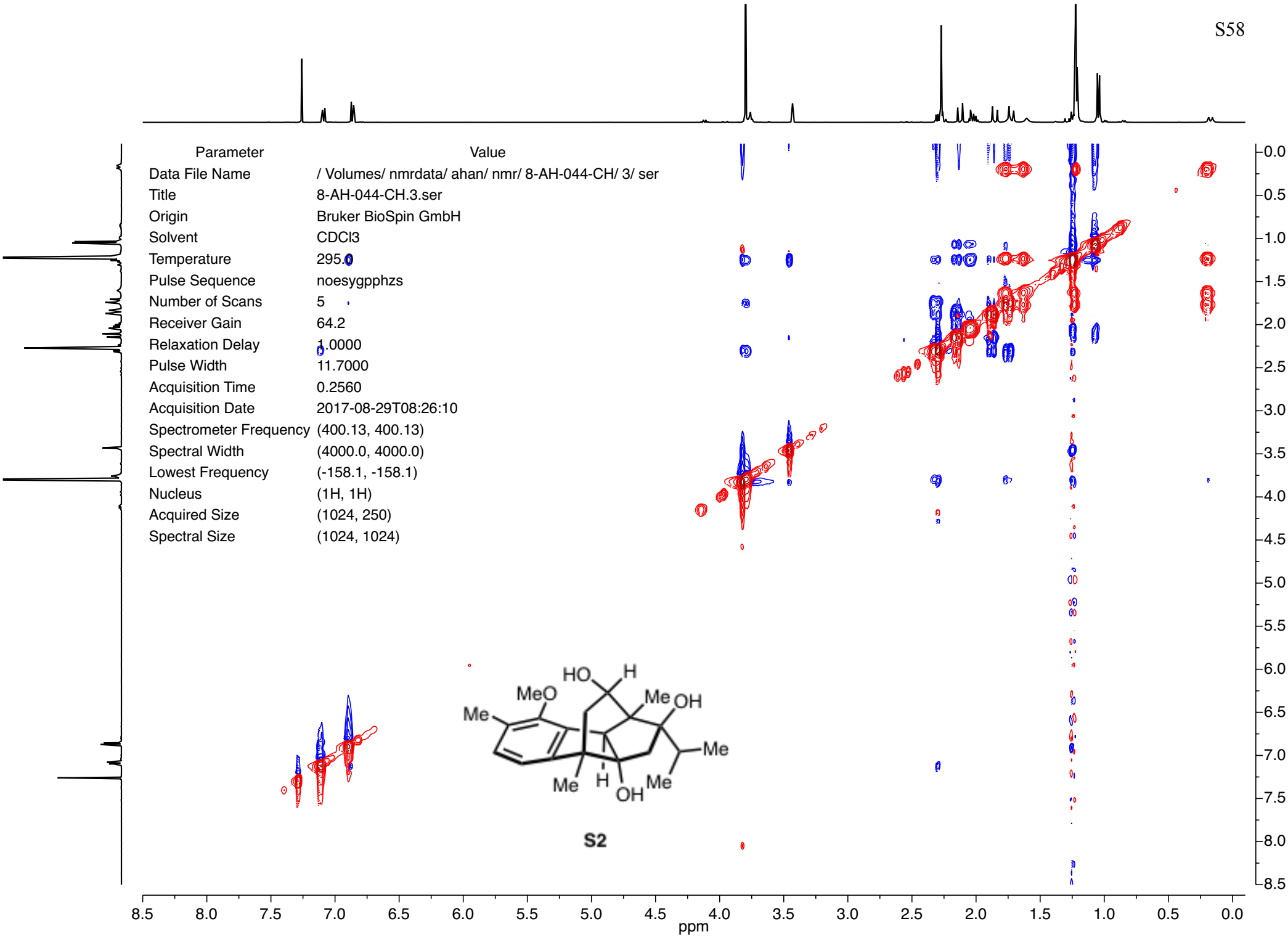
S2



Parameter	Value
Data File Name	/ Volumes/ nmrdata/ ahan/ nmr/ 8-AH-044-CH/ 2/ fid
Title	8-AH-044-CH.2.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	295.0
Pulse Sequence	zgpg30
Number of Scans	900
Receiver Gain	72.0
Relaxation Delay	1.0000
Pulse Width	10.0000
Acquisition Time	1.3631
Acquisition Date	2017-08-29T08:24:48
Spectrometer Frequency	100.62
Spectral Width	24038.5
Lowest Frequency	-1961.8
Nucleus	13C
Acquired Size	32768
Spectral Size	65536



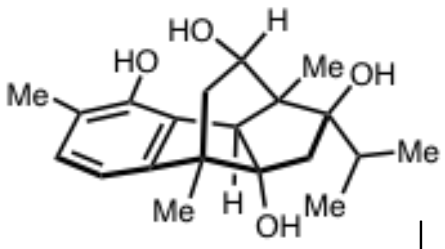
S2



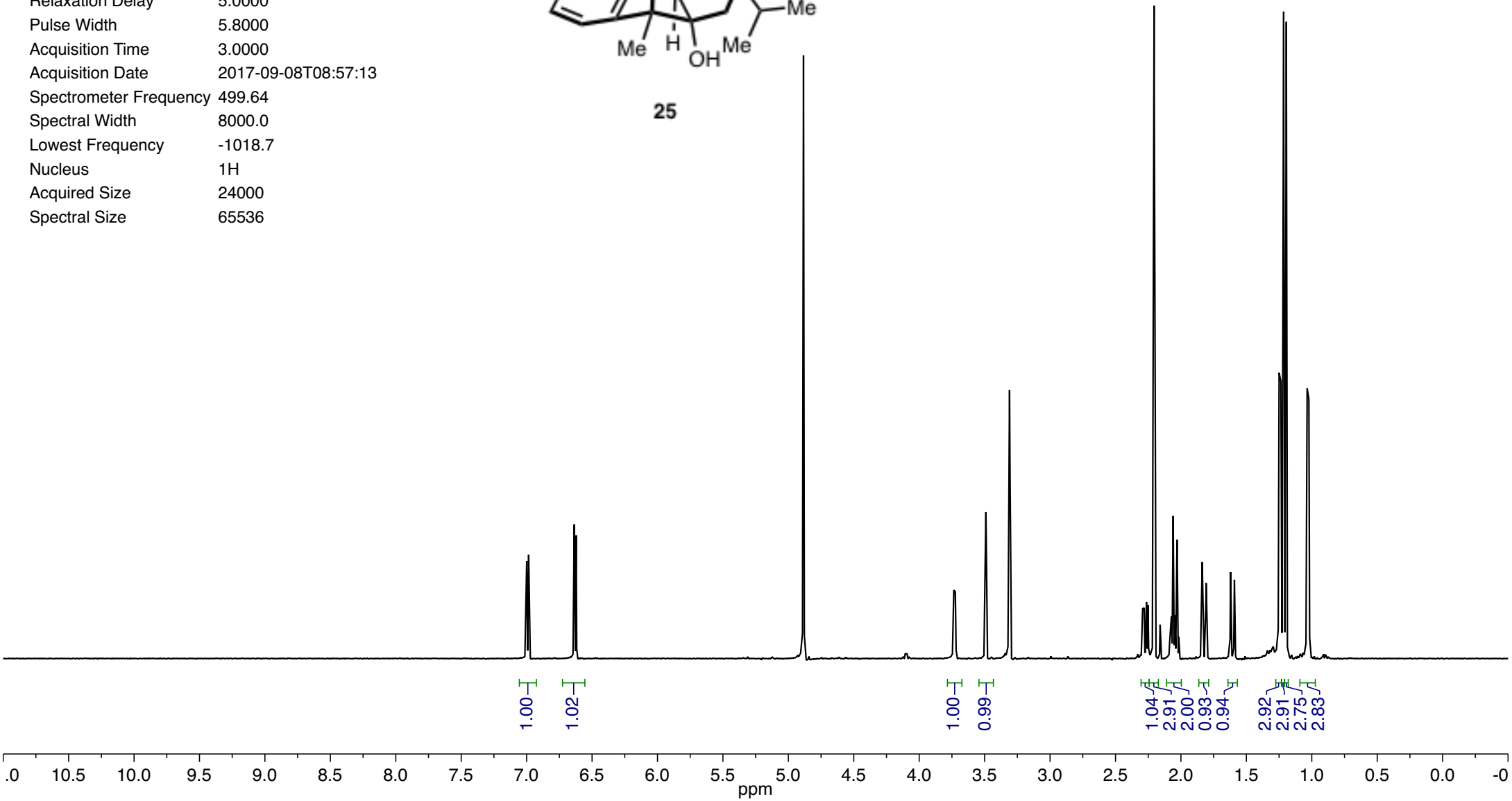
Parameter	Value
Data File Name	/ Volumes/ nmrdata/ ahan/ nmr/ 8-AH-044-CH/ 3/ ser
Title	8-AH-044-CH.3.ser
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	295.0
Pulse Sequence	noesygpphzs
Number of Scans	5
Receiver Gain	64.2
Relaxation Delay	1.0000
Pulse Width	11.7000
Acquisition Time	0.2560
Acquisition Date	2017-08-29T08:26:10
Spectrometer Frequency	(400.13, 400.13)
Spectral Width	(4000.0, 4000.0)
Lowest Frequency	(-158.1, -158.1)
Nucleus	(1H, 1H)
Acquired Size	(1024, 250)
Spectral Size	(1024, 1024)

S2

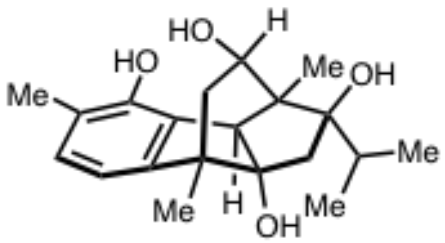
Parameter	Value
Data File Name	/ Volumes/ nmrdata/ ahan/ vnmrsys/ data/ 8-AH-045-1-CH/ PROTON01.fid/ fid
Title	PROTON01
Origin	Varian
Solvent	cd3od
Temperature	25.0
Pulse Sequence	s2pul
Number of Scans	4
Receiver Gain	34
Relaxation Delay	5.0000
Pulse Width	5.8000
Acquisition Time	3.0000
Acquisition Date	2017-09-08T08:57:13
Spectrometer Frequency	499.64
Spectral Width	8000.0
Lowest Frequency	-1018.7
Nucleus	1H
Acquired Size	24000
Spectral Size	65536



25

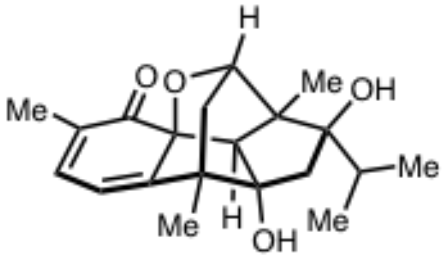


Parameter	Value
Data File Name	/ Volumes/ nmrdata/ ahan/ vnmrsys/ data/ 8-AH-045-1-CH/ CARBON01.fid/ fid
Title	CARBON01
Origin	Varian
Solvent	cd3od
Temperature	25.0
Pulse Sequence	s2pul
Number of Scans	1000
Receiver Gain	30
Relaxation Delay	1.0000
Pulse Width	4.6125
Acquisition Time	1.0420
Acquisition Date	2017-09-08T08:58:05
Spectrometer Frequency	125.65
Spectral Width	31446.5
Lowest Frequency	-1724.2
Nucleus	13C
Acquired Size	32768
Spectral Size	65536



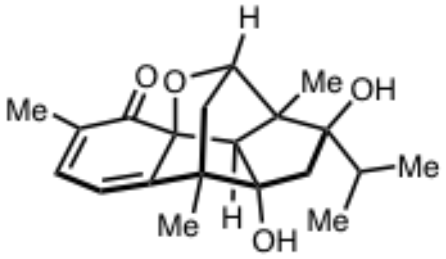
25

Parameter	Value
Data File Name	/ Volumes/ nmrdata/ ahan/ nmr/ 8-AH-046-CH/ 4/ fid
Title	8-AH-046-CH.4.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	294.9
Pulse Sequence	zg30
Number of Scans	1
Receiver Gain	197.4
Relaxation Delay	5.0000
Pulse Width	11.7000
Acquisition Time	29.9999
Acquisition Date	2017-08-31T10:20:30
Spectrometer Frequency	400.13
Spectral Width	8012.8
Lowest Frequency	-1545.6
Nucleus	1H
Acquired Size	240384
Spectral Size	524288



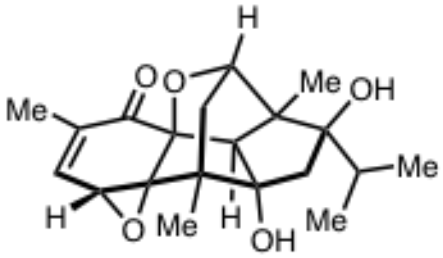
26

Parameter	Value
Data File Name	/ Volumes/ nmrdata/ ahan/ nmr/ 8-AH-046-CH/ 2/ fid
Title	8-AH-046-CH.2.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	295.0
Pulse Sequence	zgpg30
Number of Scans	900
Receiver Gain	78.7
Relaxation Delay	1.0000
Pulse Width	10.0000
Acquisition Time	1.3631
Acquisition Date	2017-08-29T13:34:24
Spectrometer Frequency	100.62
Spectral Width	24038.5
Lowest Frequency	-1961.5
Nucleus	13C
Acquired Size	32768
Spectral Size	65536

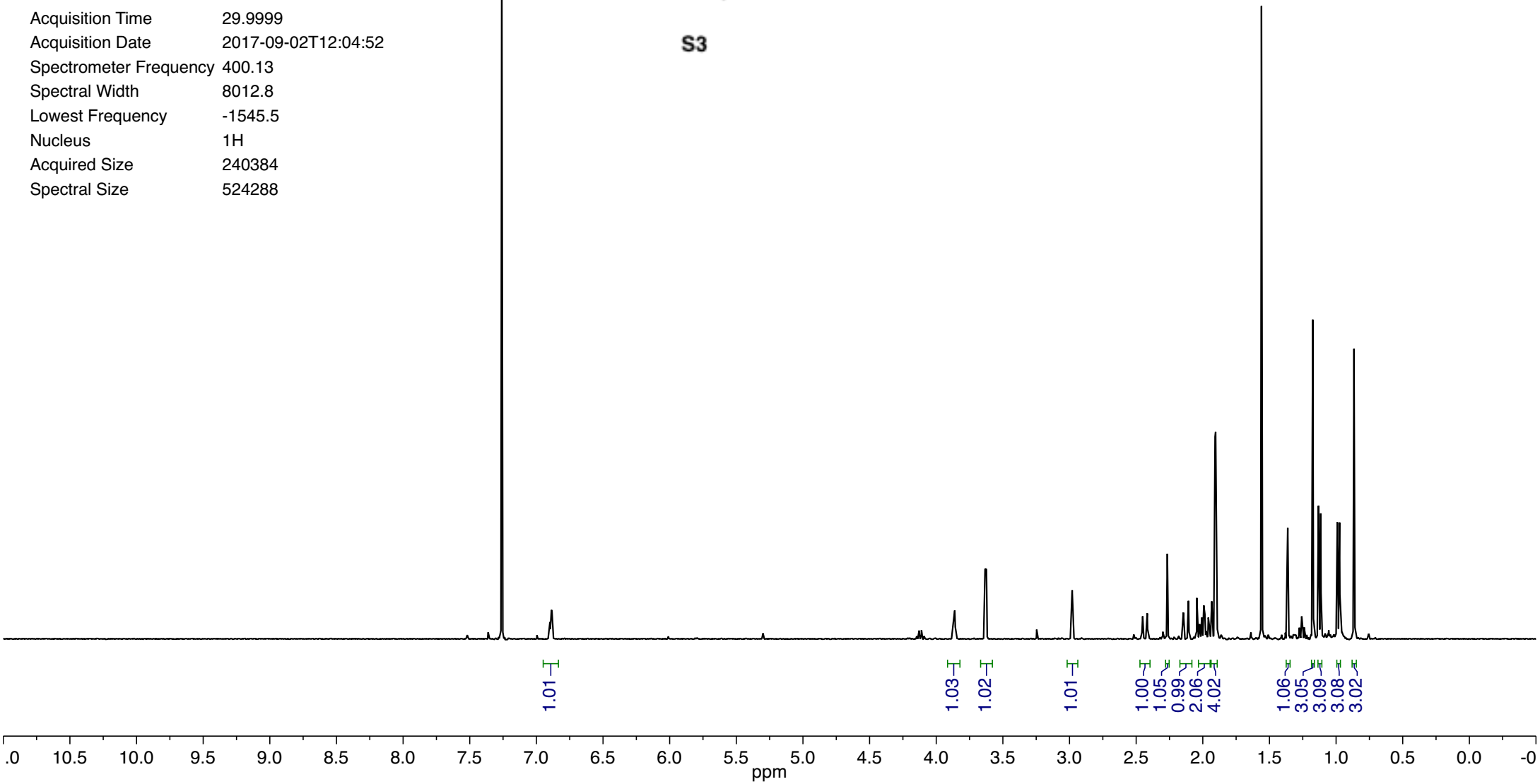


26

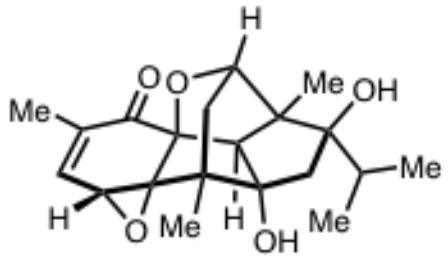
Parameter	Value
Data File Name	/ Volumes/ nmrdata/ ahan/ nmr/ 8-AH-047-CH/ 1/ fid
Title	8-AH-047-CH.1.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	294.9
Pulse Sequence	zg30
Number of Scans	1
Receiver Gain	197.4
Relaxation Delay	5.0000
Pulse Width	11.7000
Acquisition Time	29.9999
Acquisition Date	2017-09-02T12:04:52
Spectrometer Frequency	400.13
Spectral Width	8012.8
Lowest Frequency	-1545.5
Nucleus	1H
Acquired Size	240384
Spectral Size	524288



S3

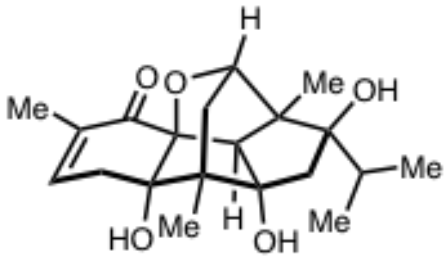


Parameter	Value
Data File Name	/ Volumes/ nmrdata/ ahan/ nmr/ 8-AH-047-CH/ 2/ fid
Title	8-AH-047-CH.2.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	294.9
Pulse Sequence	zgpg30
Number of Scans	1000
Receiver Gain	50.3
Relaxation Delay	1.0000
Pulse Width	10.0000
Acquisition Time	1.3631
Acquisition Date	2017-09-02T12:46:48
Spectrometer Frequency	100.62
Spectral Width	24038.5
Lowest Frequency	-1961.1
Nucleus	13C
Acquired Size	32768
Spectral Size	65536



S3

Parameter	Value
Data File Name	/ Volumes/ nmrdata/ ahan/ nmr/ 8-AH-055-C/ 1/ fid
Title	8-AH-055-C.1.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	295.0
Pulse Sequence	zg30
Number of Scans	8
Receiver Gain	197.4
Relaxation Delay	5.0000
Pulse Width	11.7000
Acquisition Time	4.0894
Acquisition Date	2017-09-09T15:21:00
Spectrometer Frequency	400.13
Spectral Width	8012.8
Lowest Frequency	-1545.8
Nucleus	1H
Acquired Size	32768
Spectral Size	65536



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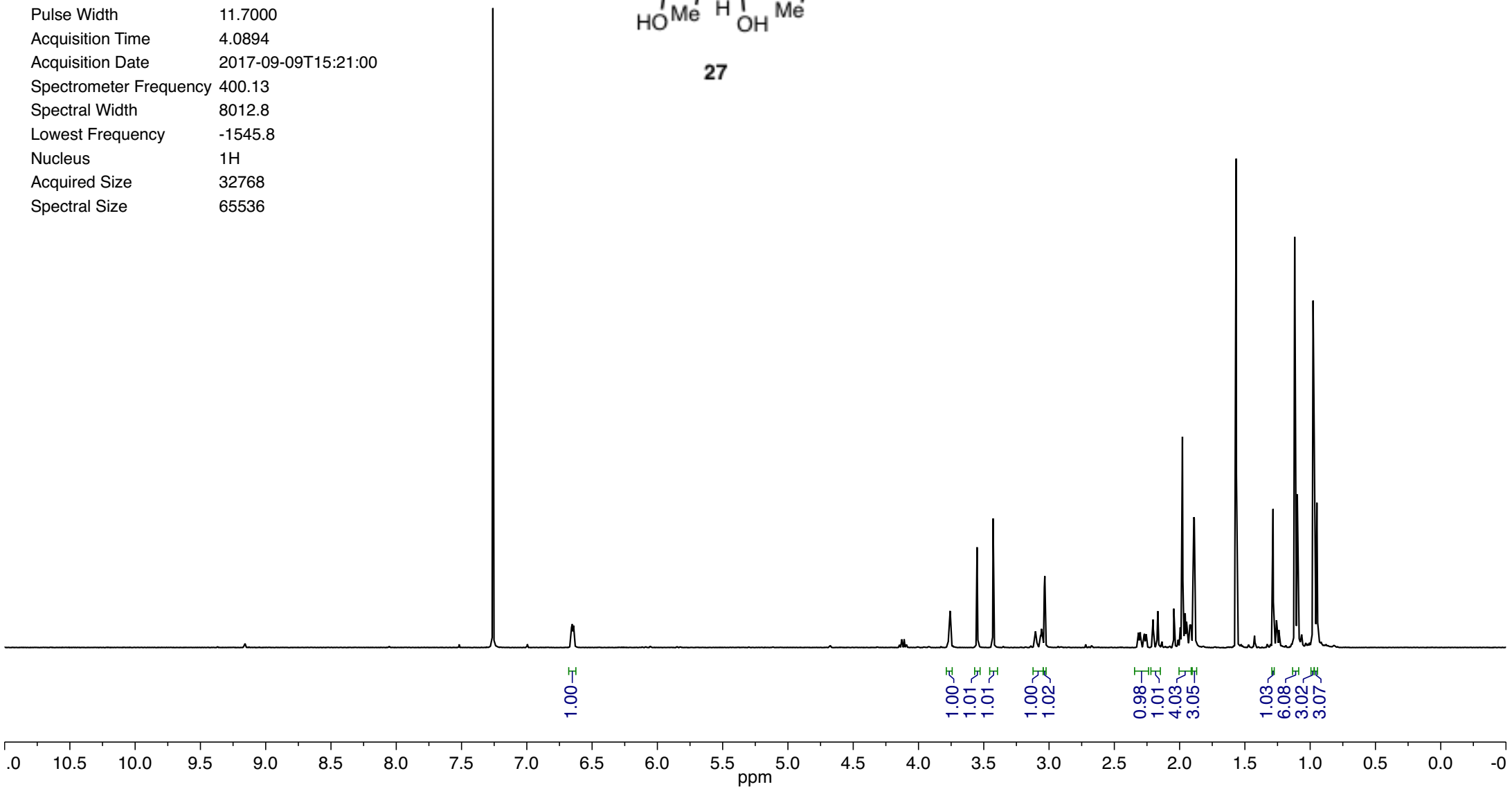
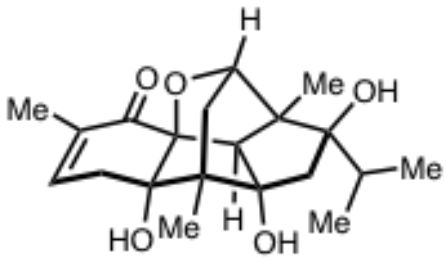


Parameter	Value
Data File Name	/ Volumes/ nmrdata/ ahan/ nmr/ 8-AH-055-CH/ 2/ fid
Title	8-AH-055-CH.2.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	294.9
Pulse Sequence	zgpg30
Number of Scans	2200
Receiver Gain	78.7
Relaxation Delay	1.0000
Pulse Width	10.0000
Acquisition Time	1.3631
Acquisition Date	2017-09-09T22:37:39
Spectrometer Frequency	100.62
Spectral Width	24038.5
Lowest Frequency	-1961.1
Nucleus	13C
Acquired Size	32768
Spectral Size	65536



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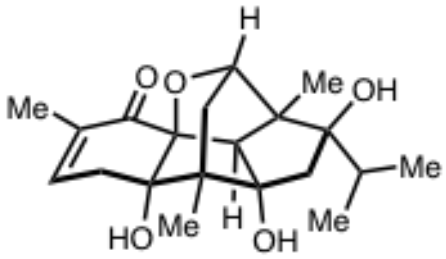
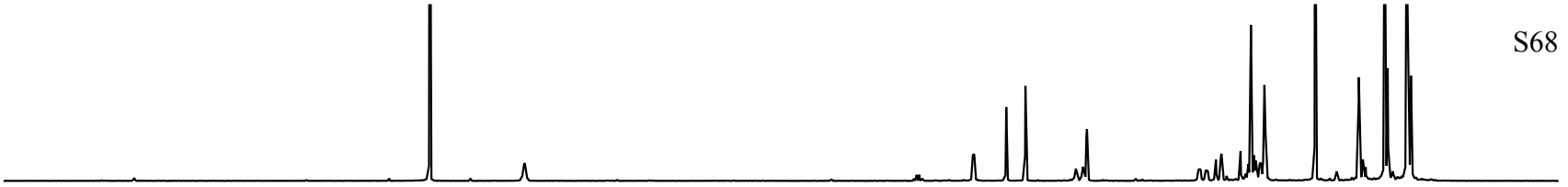
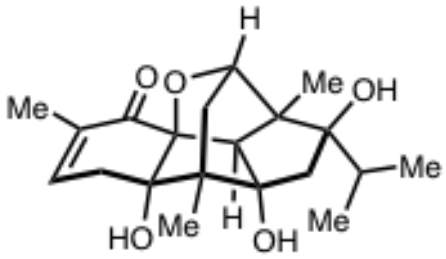
Parameter	Value
Data File Name	/ Volumes/ nmrdata/ ahan/ nmr/ 8-AH-055-CH/ 4/ ser
Title	8-AH-055-CH.4.ser
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	295.0
Pulse Sequence	hsqcedetgpsisp2.4
Number of Scans	8
Receiver Gain	197.4
Relaxation Delay	1.0000
Pulse Width	11.7000
Acquisition Time	0.2135
Acquisition Date	2017-09-09T22:40:45
Spectrometer Frequency	(400.13, 100.62)
Spectral Width	(4795.4, 16611.3)
Lowest Frequency	(-527.3, -1265.3)
Nucleus	(1H, 13C)
Acquired Size	(1024, 180)
Spectral Size	(1024, 1024)



27

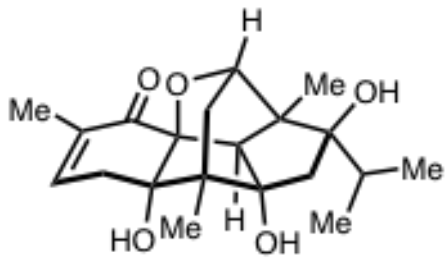


Parameter	Value
Data File Name	/ Volumes/ nmrdata/ ahan/ nmr/ 8-AH-055-CH/ 5/ ser
Title	8-AH-055-CH.5.ser
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	294.9
Pulse Sequence	hmbcetgpl3nd
Number of Scans	7
Receiver Gain	197.4
Relaxation Delay	1.0000
Pulse Width	11.7000
Acquisition Time	0.4260
Acquisition Date	2017-09-09T23:11:22
Spectrometer Frequency	(400.13, 100.62)
Spectral Width	(4807.7, 22321.4)
Lowest Frequency	(-173.3, -1119.0)
Nucleus	(1H, 13C)
Acquired Size	(2048, 256)
Spectral Size	(2048, 1024)



27

Parameter	Value
Data File Name	/ Volumes/ nmrdata/ ahan/ nmr/ 8-AH-055-CH/ 6/ ser
Title	8-AH-055-CH.6.ser
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	294.9
Pulse Sequence	noesygpphzs
Number of Scans	11
Receiver Gain	197.4
Relaxation Delay	1.0000
Pulse Width	11.7000
Acquisition Time	0.2560
Acquisition Date	2017-09-09T23:57:47
Spectrometer Frequency	(400.13, 400.13)
Spectral Width	(4000.0, 4000.0)
Lowest Frequency	(-168.3, -168.3)
Nucleus	(1H, 1H)
Acquired Size	(1024, 256)
Spectral Size	(1024, 1024)



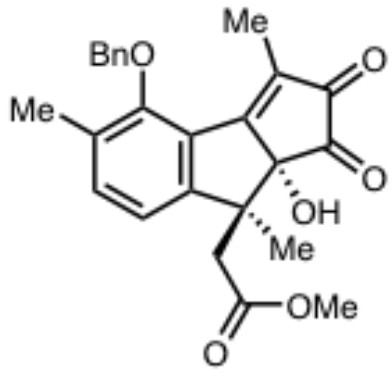
27

9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

ppm

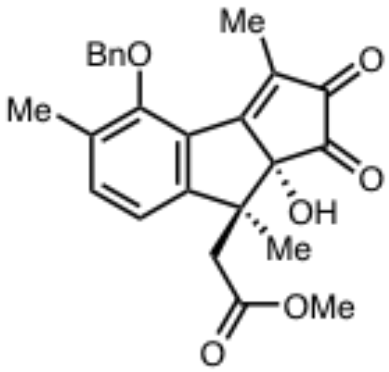
0 1 2 3 4 5 6 7 8 9

Parameter	Value
Data File Name	/ Volumes/ nmrdata-1/ chenxu91/ nmr/ xuchen-160906-10-diketone/ 1/ fid
Title	xuchen-160906-10-diketone.1.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	295.0
Pulse Sequence	zg30
Number of Scans	16
Receiver Gain	197.4
Relaxation Delay	1.0000
Pulse Width	11.7000
Acquisition Time	4.0894
Acquisition Date	2016-09-06T17:08:17
Spectrometer Frequency	400.13
Spectral Width	8012.8
Lowest Frequency	-1545.6
Nucleus	1H
Acquired Size	32768
Spectral Size	65536



28

Parameter	Value
Data File Name	/ Volumes/ nmrdata-1/ chenxu91/ nmr/ xuchen-160904-diketone/ 1/ fid
Title	xuchen-160904-diketone.1.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	295.0
Pulse Sequence	zgpg30
Number of Scans	512
Receiver Gain	38.0
Relaxation Delay	2.0000
Pulse Width	10.0000
Acquisition Time	1.3631
Acquisition Date	2016-09-04T18:51:59
Spectrometer Frequency	100.62
Spectral Width	24038.5
Lowest Frequency	-1961.3
Nucleus	13C
Acquired Size	32768
Spectral Size	65536



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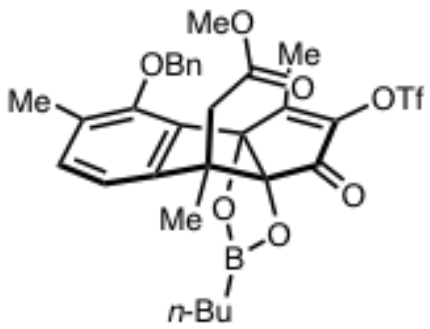
Parameter	Value
Data File Name	/ Volumes/ nmrdata-1/ chenxu91/ nmr/ xuchen-160906-10-92/ 1/ fid
Title	xuchen-160906-10-92.1.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	295.0
Pulse Sequence	zg30
Number of Scans	16
Receiver Gain	142.8
Relaxation Delay	1.0000
Pulse Width	11.7000
Acquisition Time	4.0894
Acquisition Date	2016-09-07T05:35:07
Spectrometer Frequency	400.13
Spectral Width	8012.8
Lowest Frequency	-1545.6
Nucleus	1H
Acquired Size	32768
Spectral Size	65536



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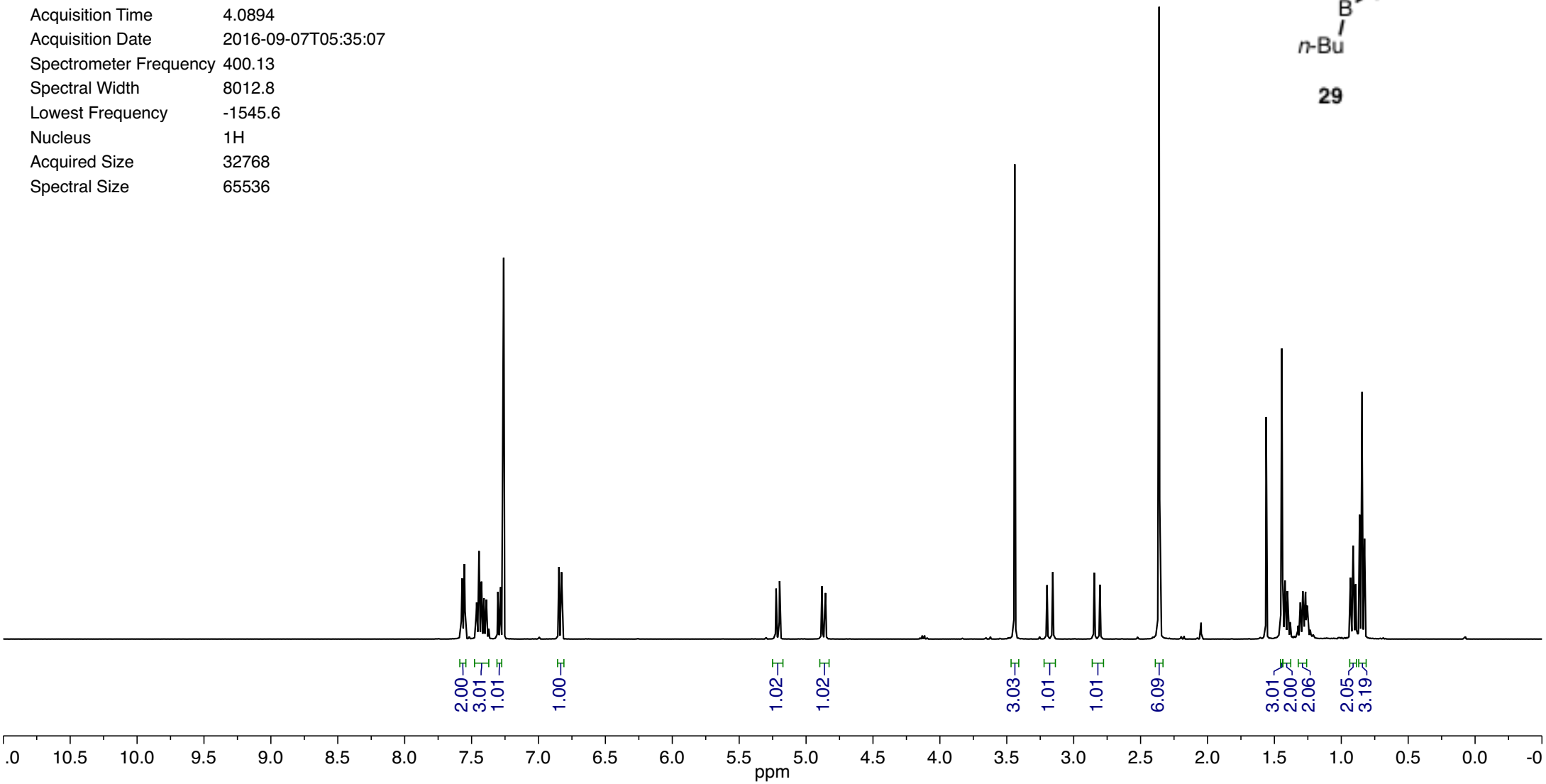
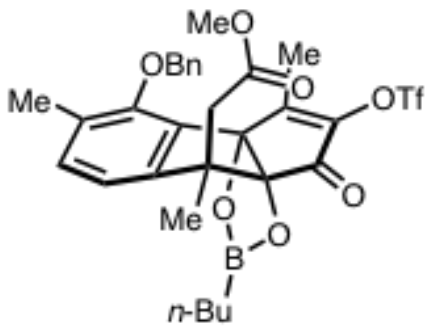
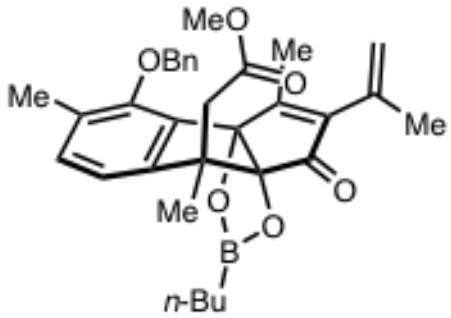


Parameter	Value
Data File Name	/ Volumes/ nmrdata-1/ chenxu91/ nmr/ xuchen-160906-10-92/ 2/ fid
Title	xuchen-160906-10-92.2.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	295.0
Pulse Sequence	zgpg30
Number of Scans	1024
Receiver Gain	64.2
Relaxation Delay	2.0000
Pulse Width	10.0000
Acquisition Time	1.3631
Acquisition Date	2016-09-07T06:34:15
Spectrometer Frequency	100.62
Spectral Width	24038.5
Lowest Frequency	-1961.4
Nucleus	13C
Acquired Size	32768
Spectral Size	65536



29

Parameter	Value
Data File Name	/ Volumes/ nmrdata-1/ chenxu91/ nmr/ xuchen-160909-10-93-1/ 1/ fid
Title	xuchen-160909-10-93-1.1.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	295.0
Pulse Sequence	zg30
Number of Scans	16
Receiver Gain	142.8
Relaxation Delay	1.0000
Pulse Width	11.7000
Acquisition Time	4.0894
Acquisition Date	2016-09-09T19:38:58
Spectrometer Frequency	400.13
Spectral Width	8012.8
Lowest Frequency	-1545.6
Nucleus	1H
Acquired Size	32768
Spectral Size	65536



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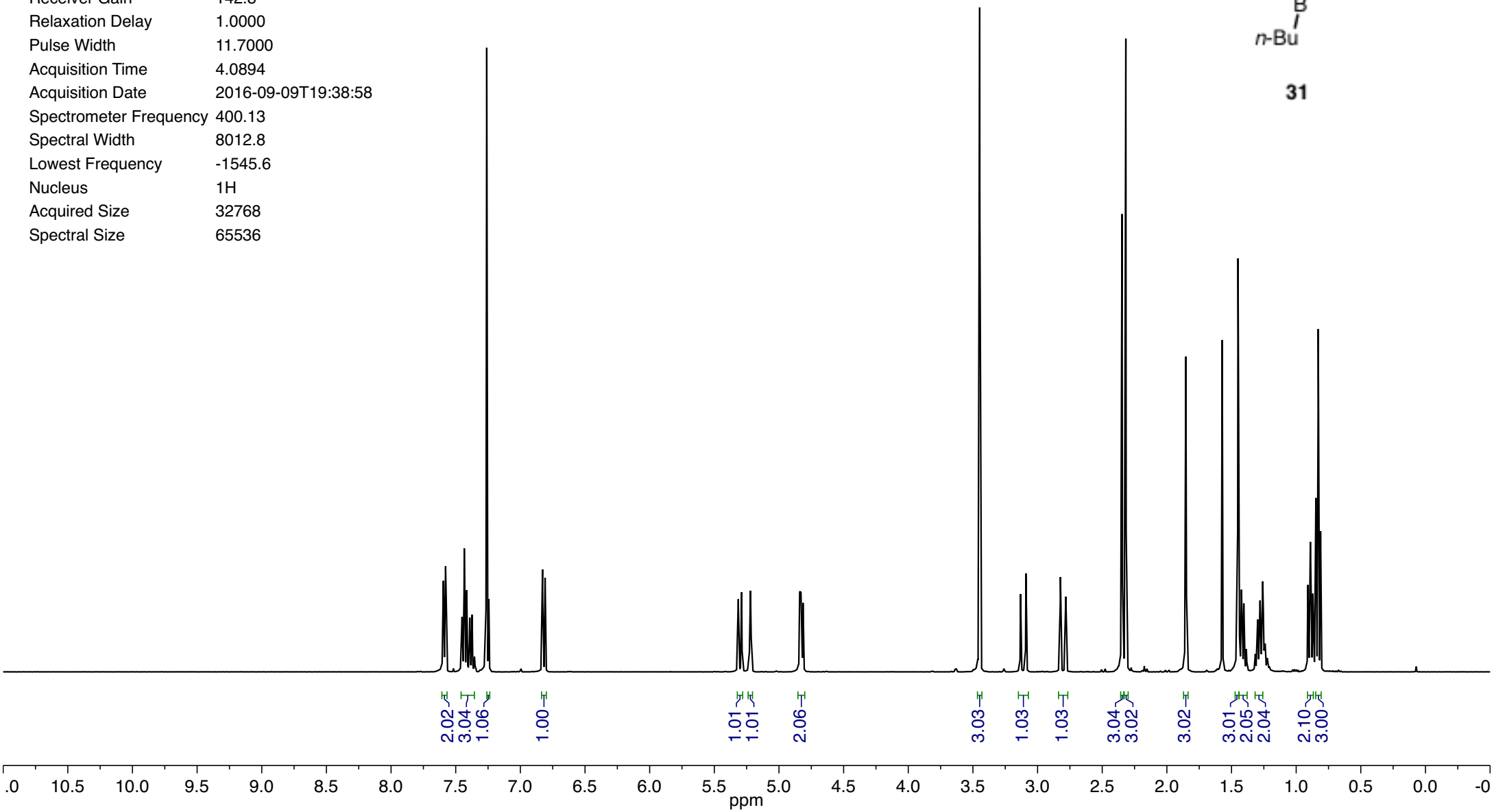
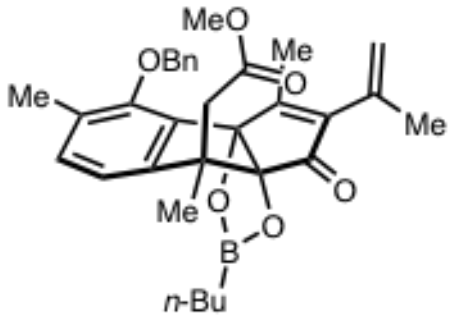
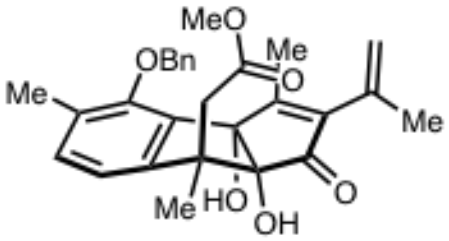


Parameter	Value
Data File Name	/ Volumes/ nmrdata-1/ chenxu91/ nmr/ xuchen-160909-10-93-1/ 2/ fid
Title	xuchen-160909-10-93-1.2.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	294.9
Pulse Sequence	zgpg30
Number of Scans	1024
Receiver Gain	72.0
Relaxation Delay	2.0000
Pulse Width	10.0000
Acquisition Time	1.3631
Acquisition Date	2016-09-09T20:38:06
Spectrometer Frequency	100.62
Spectral Width	24038.5
Lowest Frequency	-1961.7
Nucleus	13C
Acquired Size	32768
Spectral Size	65536



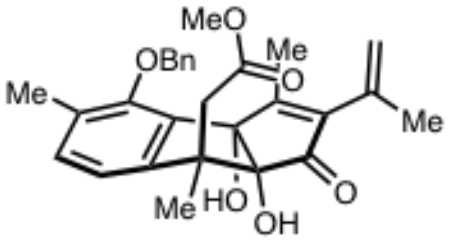
31

Parameter	Value
Data File Name	/ Volumes/ nmrdata-1/ chenxu91/ nmr/ xuchen-160910-10-93-2/ 1/ fid
Title	xuchen-160910-10-93-2.1.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	294.9
Pulse Sequence	zg30
Number of Scans	16
Receiver Gain	197.4
Relaxation Delay	1.0000
Pulse Width	11.7000
Acquisition Time	4.0894
Acquisition Date	2016-09-10T10:38:50
Spectrometer Frequency	400.13
Spectral Width	8012.8
Lowest Frequency	-1545.6
Nucleus	1H
Acquired Size	32768
Spectral Size	65536



32

Parameter	Value
Data File Name	/ Volumes/ nmrdata-1/ chenxu91/ nmr/ xuchen-160910-10-93-2-2/ 1/ fid
Title	xuchen-160910-10-93-2-2.1.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	294.9
Pulse Sequence	zgpg30
Number of Scans	10000
Receiver Gain	78.7
Relaxation Delay	2.0000
Pulse Width	10.0000
Acquisition Time	1.3631
Acquisition Date	2016-09-11T06:44:47
Spectrometer Frequency	100.62
Spectral Width	24038.5
Lowest Frequency	-1961.0
Nucleus	13C
Acquired Size	32768
Spectral Size	65536



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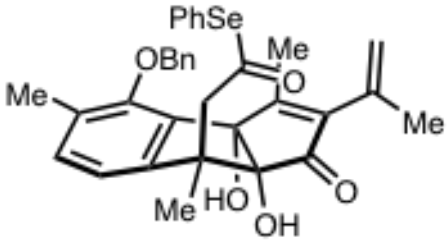
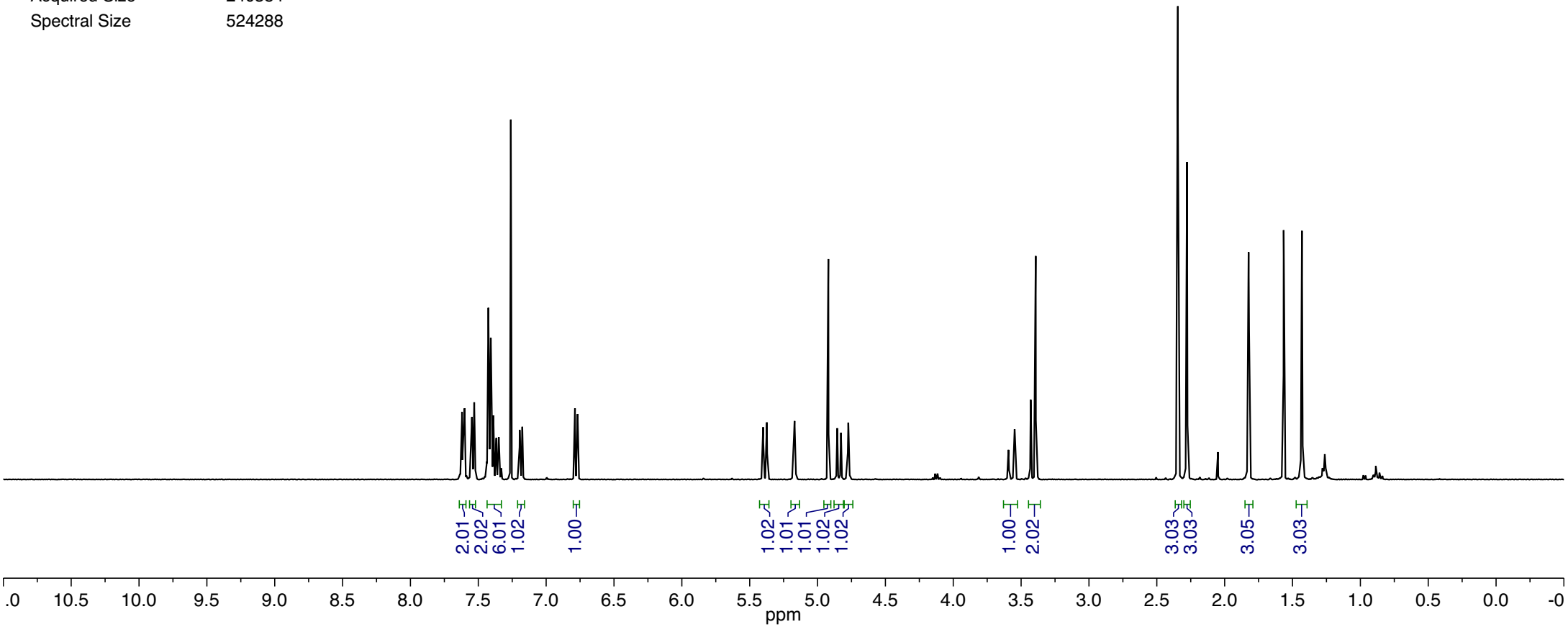
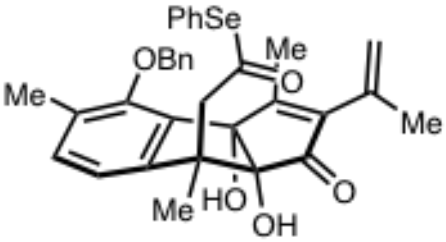
Parameter	Value
Data File Name	/ Volumes/ nmrdata/ ahan/ nmr/ 8-AH-049-CH/ 1/ fid
Title	8-AH-049-CH.1.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	294.9
Pulse Sequence	zg30
Number of Scans	1
Receiver Gain	176.8
Relaxation Delay	5.0000
Pulse Width	11.7000
Acquisition Time	29.9999
Acquisition Date	2017-08-30T20:09:09
Spectrometer Frequency	400.13
Spectral Width	8012.8
Lowest Frequency	-1545.2
Nucleus	1H
Acquired Size	240384
Spectral Size	524288



33

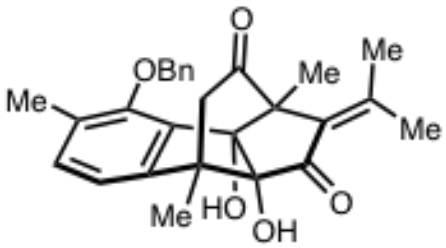


Parameter	Value
Data File Name	/ Volumes/ nmrdata/ ahan/ nmr/ 8-AH-049-CH/ 2/ fid
Title	8-AH-049-CH.2.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	295.0
Pulse Sequence	zgpg30
Number of Scans	800
Receiver Gain	72.0
Relaxation Delay	1.0000
Pulse Width	10.0000
Acquisition Time	1.3631
Acquisition Date	2017-08-30T20:43:04
Spectrometer Frequency	100.62
Spectral Width	24038.5
Lowest Frequency	-1961.9
Nucleus	13C
Acquired Size	32768
Spectral Size	65536



33

Parameter	Value
Data File Name	/ Volumes/ nmrdata/ ahan/ nmr/ 8-AH-027-CH/ 1/ fid
Title	8-AH-027-CH.1.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	295.0
Pulse Sequence	zg30
Number of Scans	1
Receiver Gain	197.4
Relaxation Delay	5.0000
Pulse Width	11.7000
Acquisition Time	29.9999
Acquisition Date	2017-08-02T16:32:40
Spectrometer Frequency	400.13
Spectral Width	8012.8
Lowest Frequency	-1545.4
Nucleus	1H
Acquired Size	240384
Spectral Size	524288



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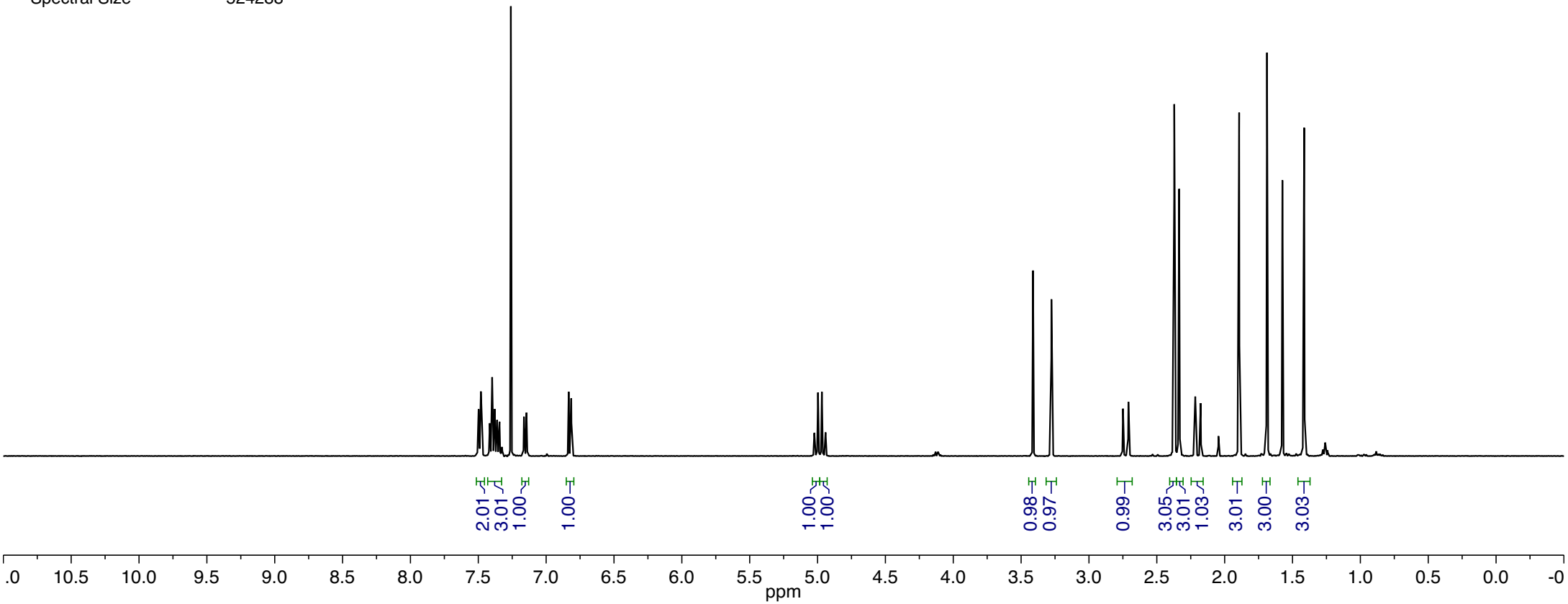
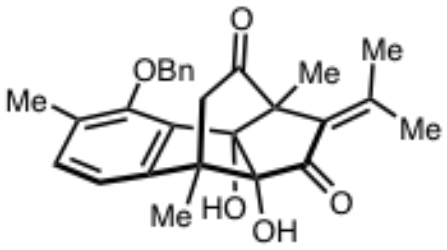
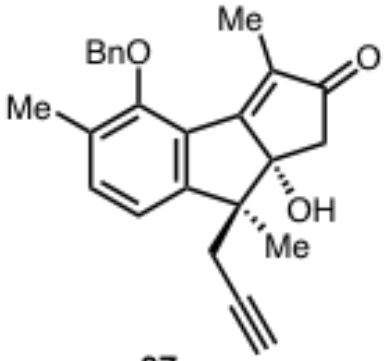


Parameter	Value
Data File Name	/ Volumes/ nmrdata/ ahan/ nmr/ 8-AH-027-CH/ 2/ fid
Title	8-AH-027-CH.2.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	294.9
Pulse Sequence	zgpg30
Number of Scans	750
Receiver Gain	78.7
Relaxation Delay	1.0000
Pulse Width	10.0000
Acquisition Time	1.3631
Acquisition Date	2017-08-02T17:03:30
Spectrometer Frequency	100.62
Spectral Width	24038.5
Lowest Frequency	-1961.7
Nucleus	13C
Acquired Size	32768
Spectral Size	65536



34

Parameter	Value
Data File Name	/ Volumes/ nmrdata-1/ chenxu91/ nmr/ xuchen-160824-10-81-flashed/ 1/ fid
Title	xuchen-160824-10-81-flashed.1.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	294.9
Pulse Sequence	zg30
Number of Scans	32
Receiver Gain	197.4
Relaxation Delay	2.0000
Pulse Width	11.7000
Acquisition Time	4.0894
Acquisition Date	2016-08-24T11:22:54
Spectrometer Frequency	400.13
Spectral Width	8012.8
Lowest Frequency	-1545.6
Nucleus	1H
Acquired Size	32768
Spectral Size	65536



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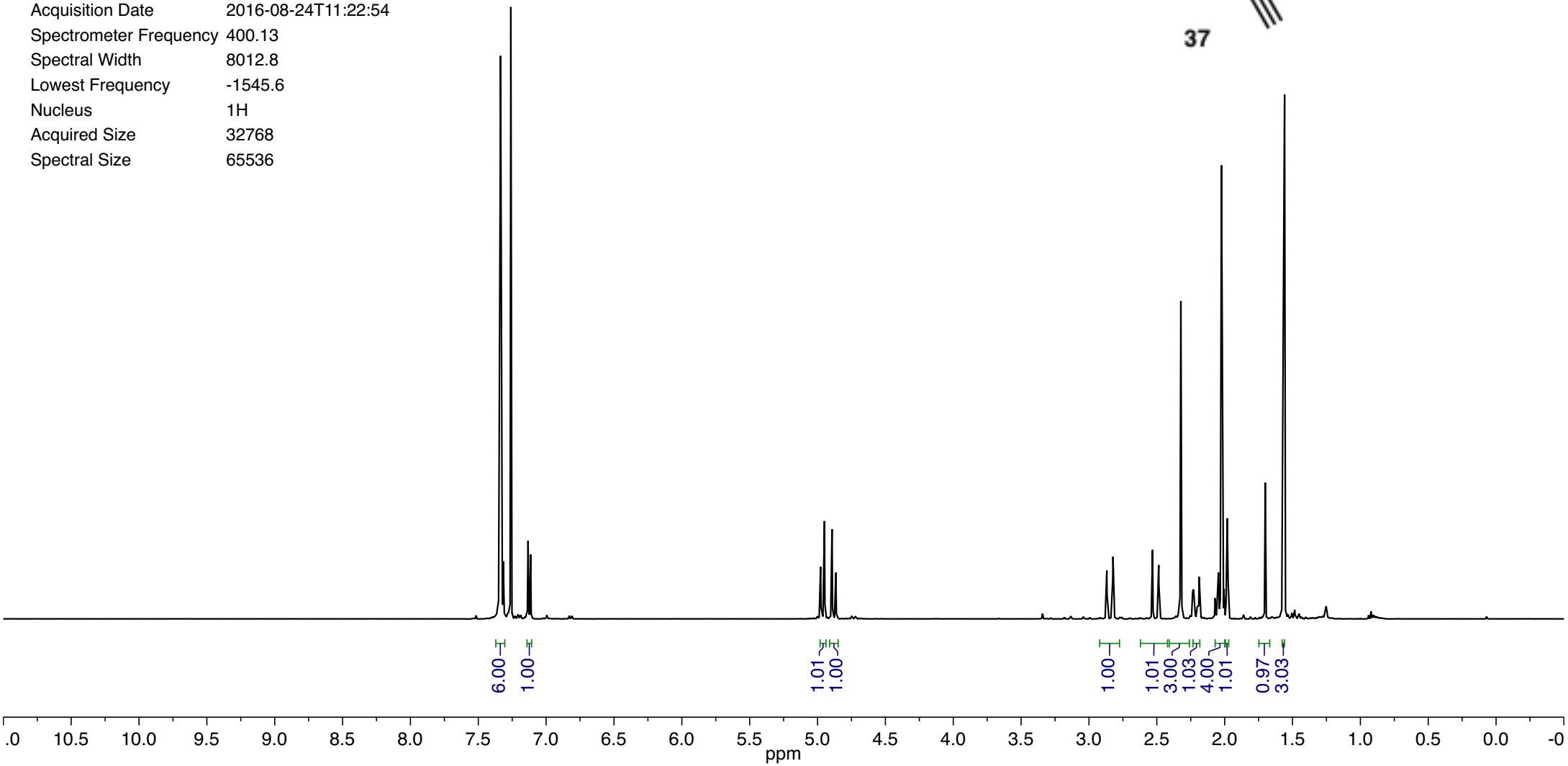
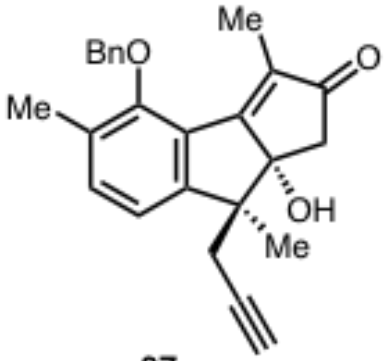
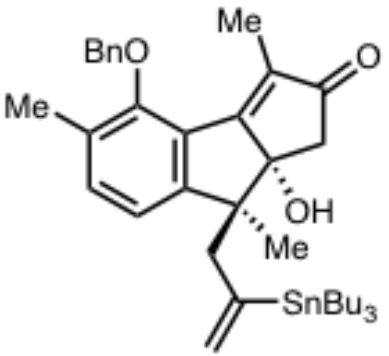


Parameter	Value
Data File Name	/ Volumes/ nmrdata-1/ chenxu91/ nmr/ xuchen-160824-10-81-flashed/ 2/ fid
Title	xuchen-160824-10-81-flashed.2.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	294.9
Pulse Sequence	zgpg30
Number of Scans	1024
Receiver Gain	64.2
Relaxation Delay	2.0000
Pulse Width	10.0000
Acquisition Time	1.3631
Acquisition Date	2016-08-24T12:22:01
Spectrometer Frequency	100.62
Spectral Width	24038.5
Lowest Frequency	-1961.2
Nucleus	13C
Acquired Size	32768
Spectral Size	65536

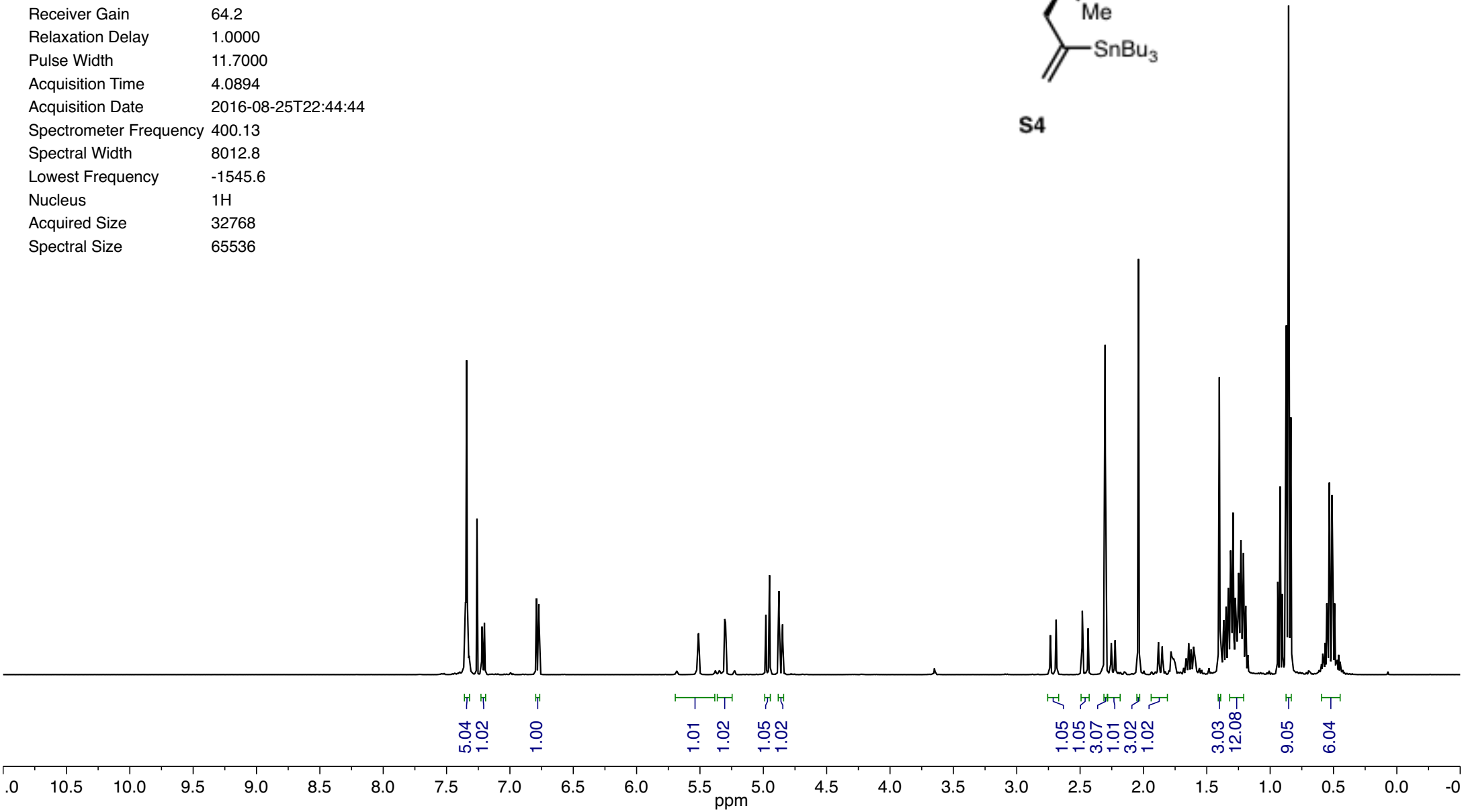


37

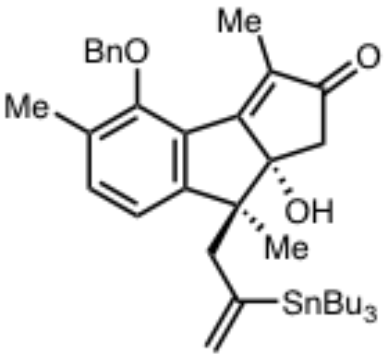
Parameter	Value
Data File Name	/ Volumes/ nmrdata-1/ chenxu91/ nmr/ xuchen-160825-10-82-flashed/ 1/ fid
Title	xuchen-160825-10-82-flashed.1.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	295.0
Pulse Sequence	zg30
Number of Scans	16
Receiver Gain	64.2
Relaxation Delay	1.0000
Pulse Width	11.7000
Acquisition Time	4.0894
Acquisition Date	2016-08-25T22:44:44
Spectrometer Frequency	400.13
Spectral Width	8012.8
Lowest Frequency	-1545.6
Nucleus	1H
Acquired Size	32768
Spectral Size	65536



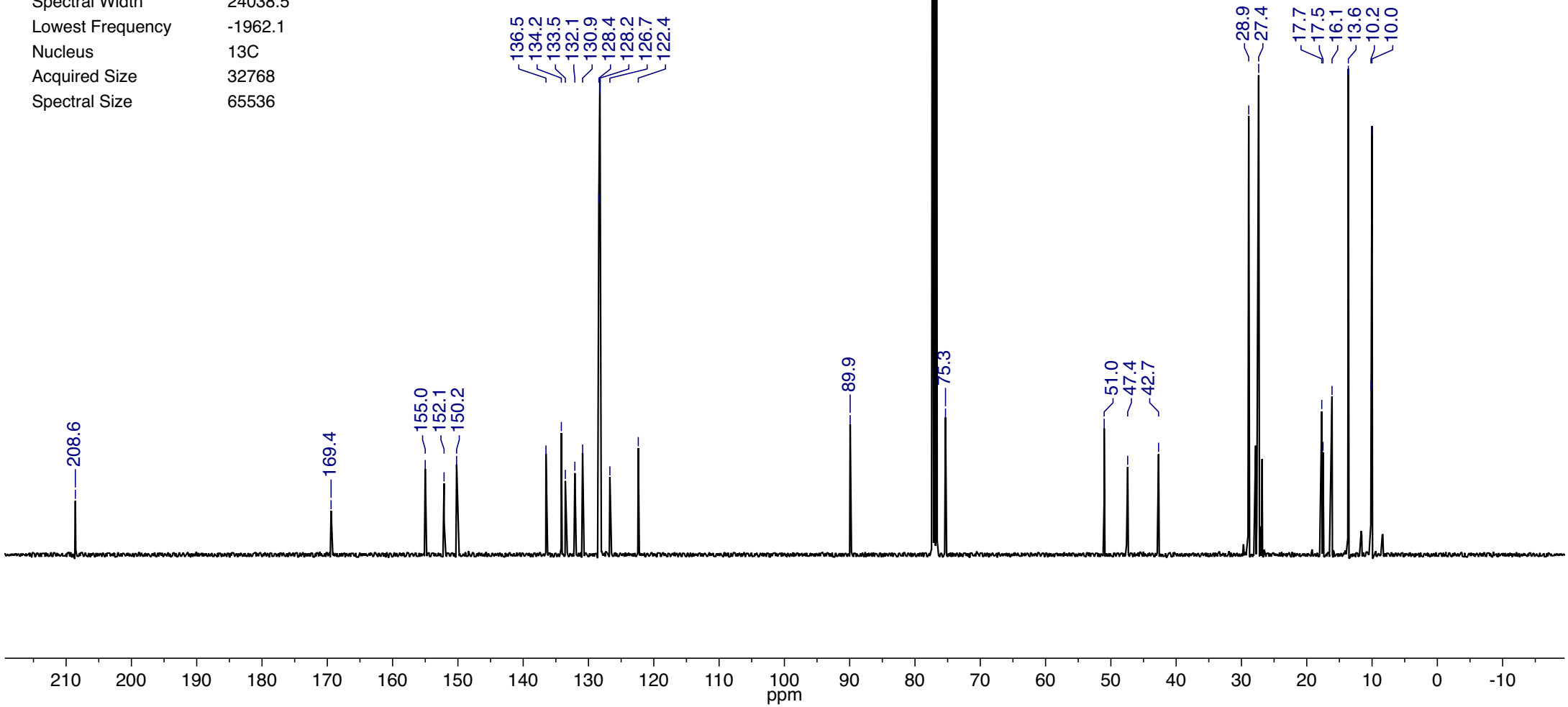
S4



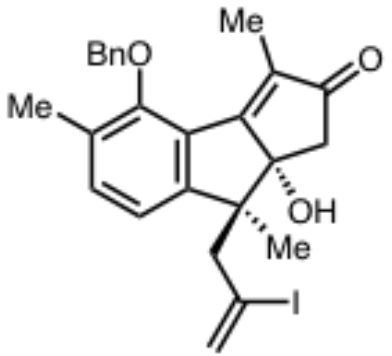
Parameter	Value
Data File Name	/ Volumes/ nmrdata-1/ chenxu91/ nmr/ xuchen-160825-10-82-flashed/ 2/ fid
Title	xuchen-160825-10-82-flashed.2.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	295.0
Pulse Sequence	zgpg30
Number of Scans	1024
Receiver Gain	72.0
Relaxation Delay	2.0000
Pulse Width	10.0000
Acquisition Time	1.3631
Acquisition Date	2016-08-25T23:43:51
Spectrometer Frequency	100.62
Spectral Width	24038.5
Lowest Frequency	-1962.1
Nucleus	13C
Acquired Size	32768
Spectral Size	65536



S4



Parameter	Value
Data File Name	/ Volumes/ nmrdata-1/ chenxu91/ nmr/ xuchen-160828-10-84-flashed/ 1/ fid
Title	xuchen-160828-10-84-flashed.1.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	294.9
Pulse Sequence	zg30
Number of Scans	16
Receiver Gain	176.8
Relaxation Delay	1.0000
Pulse Width	11.7000
Acquisition Time	4.0894
Acquisition Date	2016-08-28T20:02:49
Spectrometer Frequency	400.13
Spectral Width	8012.8
Lowest Frequency	-1545.6
Nucleus	1H
Acquired Size	32768
Spectral Size	65536



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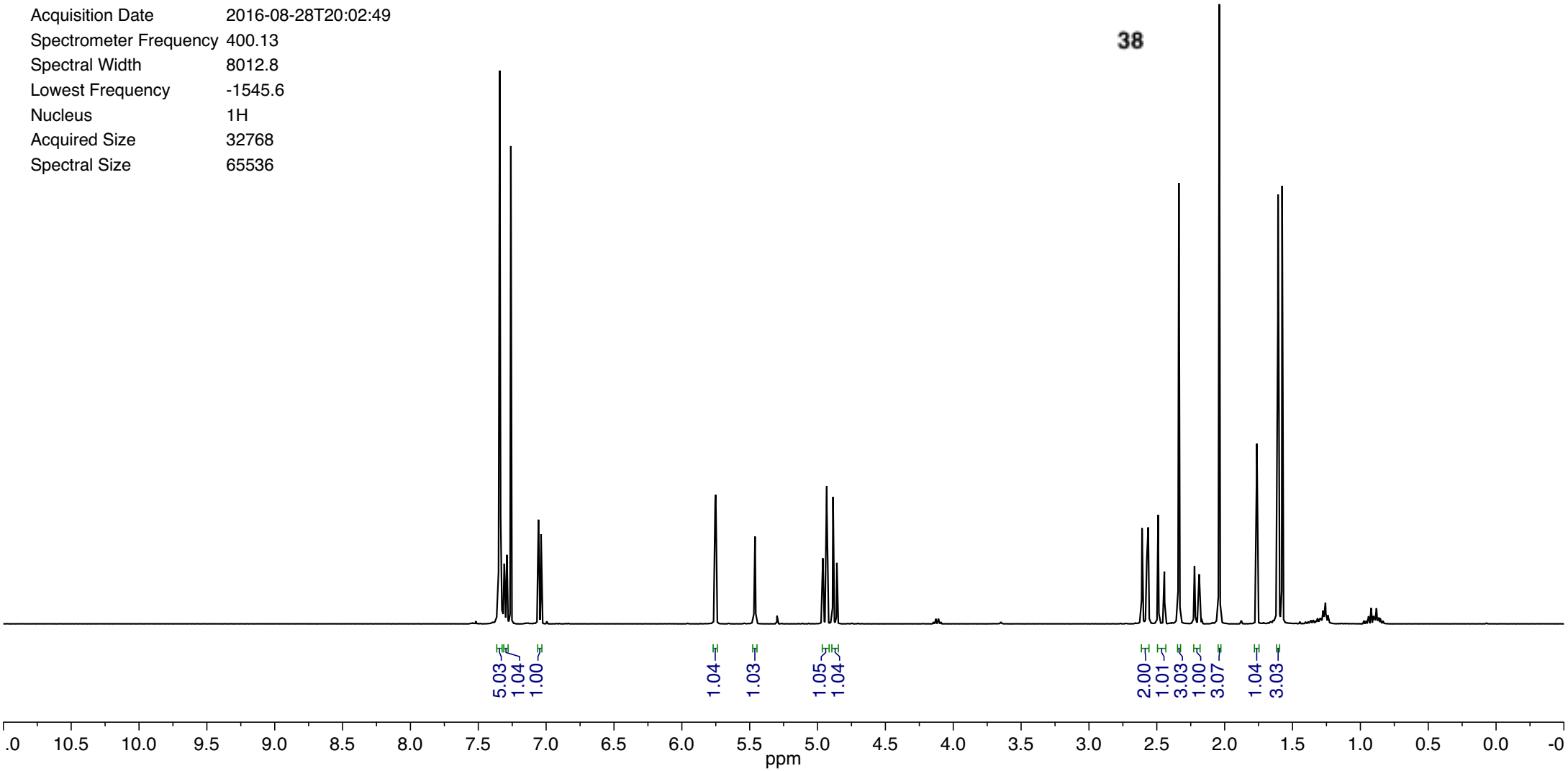
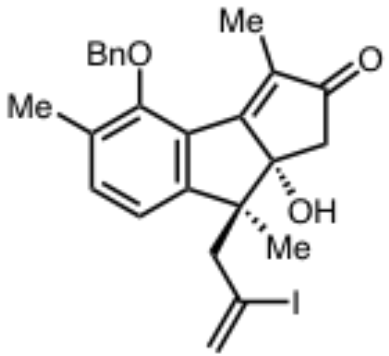
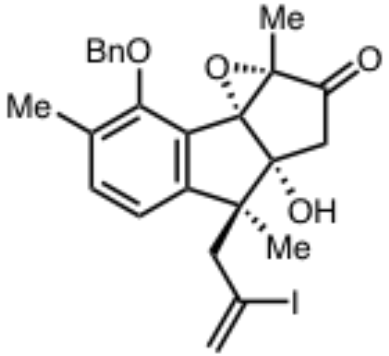


Parameter	Value
Data File Name	/ Volumes/ nmrdata-1/ chenxu91/ nmr/ xuchen-160828-10-84-flashed/ 2/ fid
Title	xuchen-160828-10-84-flashed.2.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	294.9
Pulse Sequence	zgpg30
Number of Scans	1024
Receiver Gain	55.5
Relaxation Delay	2.0000
Pulse Width	10.0000
Acquisition Time	1.3631
Acquisition Date	2016-08-28T21:01:57
Spectrometer Frequency	100.62
Spectral Width	24038.5
Lowest Frequency	-1961.7
Nucleus	13C
Acquired Size	32768
Spectral Size	65536

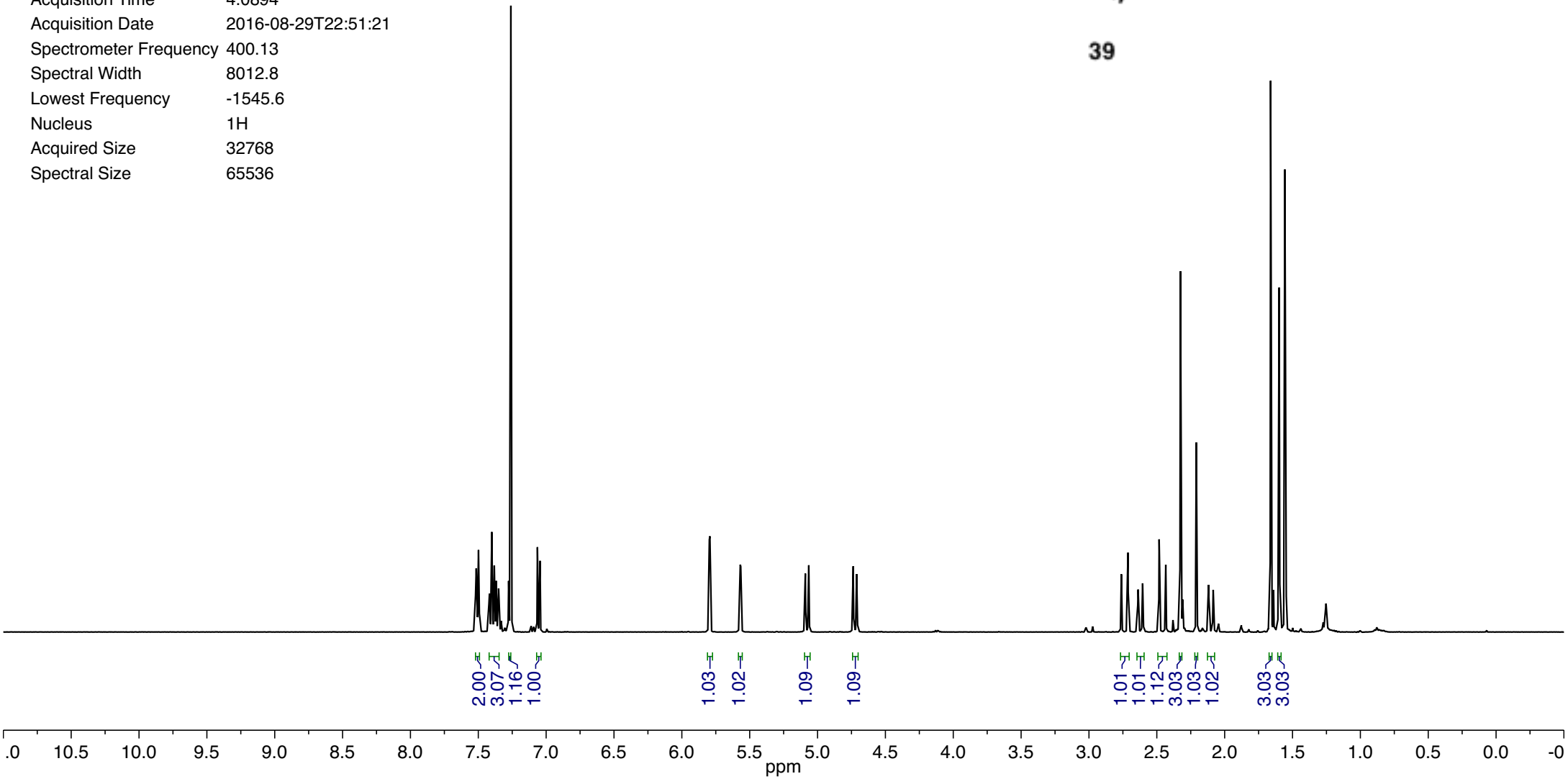


38

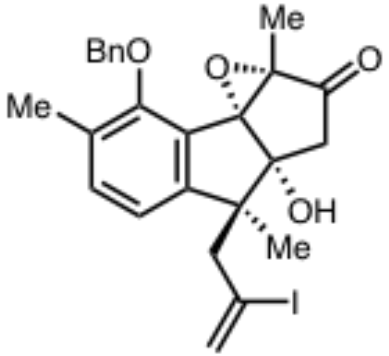
Parameter	Value
Data File Name	/ Volumes/ nmrdata-1/ chenxu91/ nmr/ xuchen-160829-10-85/ 1/ fid
Title	xuchen-160829-10-85.1.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	295.0
Pulse Sequence	zg30
Number of Scans	16
Receiver Gain	197.4
Relaxation Delay	1.0000
Pulse Width	11.7000
Acquisition Time	4.0894
Acquisition Date	2016-08-29T22:51:21
Spectrometer Frequency	400.13
Spectral Width	8012.8
Lowest Frequency	-1545.6
Nucleus	1H
Acquired Size	32768
Spectral Size	65536



39

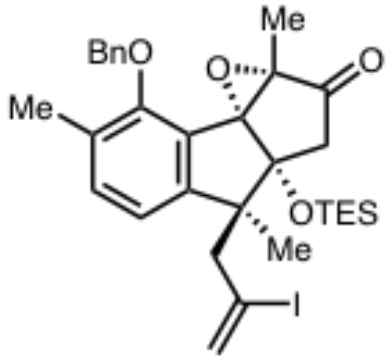


Parameter	Value
Data File Name	/ Volumes/ nmrdata-1/ chenxu91/ nmr/ xuchen-160829-10-85/ 2/ fid
Title	xuchen-160829-10-85.2.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	294.9
Pulse Sequence	zgpg30
Number of Scans	1024
Receiver Gain	38.0
Relaxation Delay	2.0000
Pulse Width	10.0000
Acquisition Time	1.3631
Acquisition Date	2016-08-29T23:51:55
Spectrometer Frequency	100.62
Spectral Width	24038.5
Lowest Frequency	-1961.3
Nucleus	13C
Acquired Size	32768
Spectral Size	65536

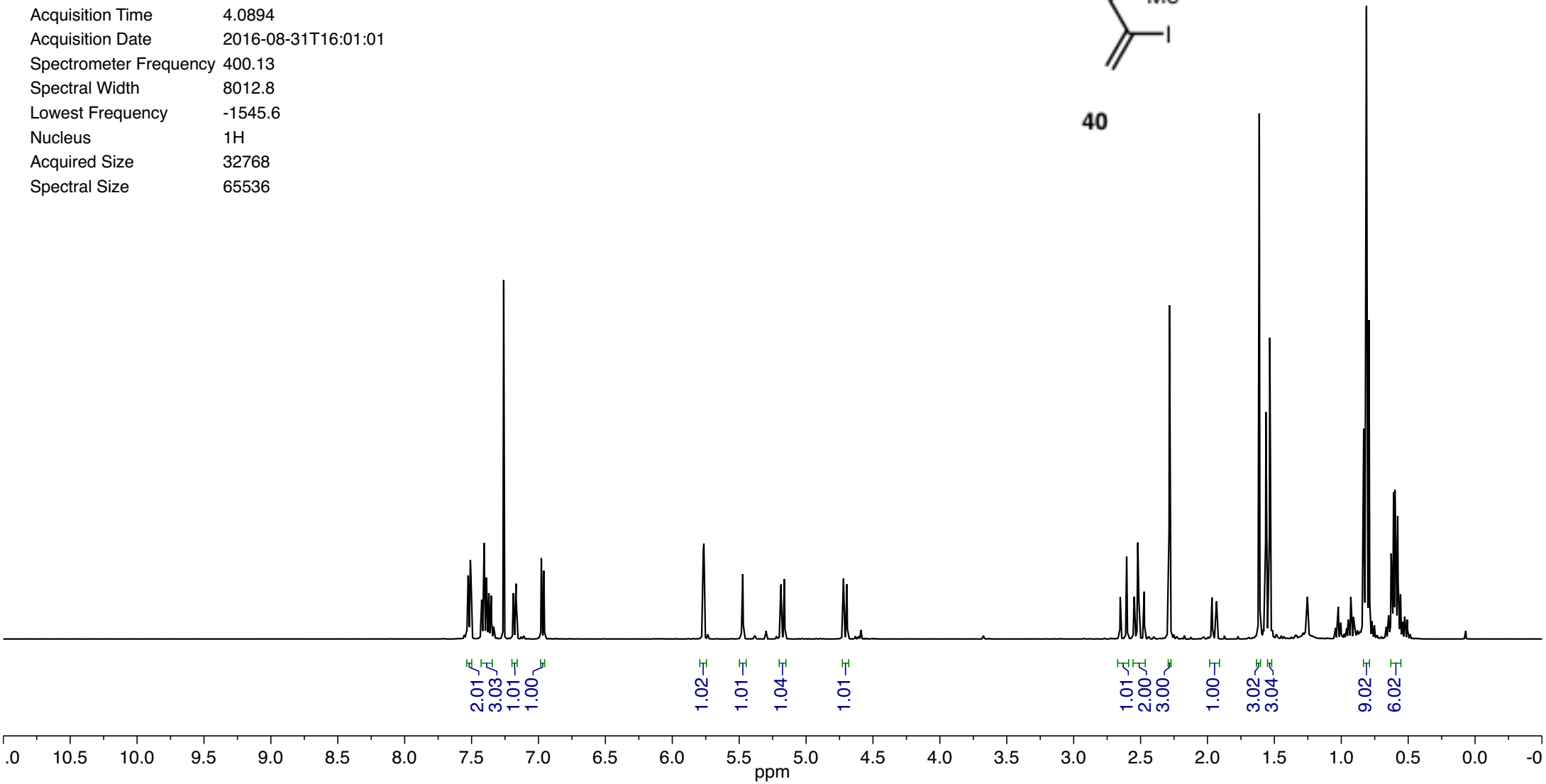


39

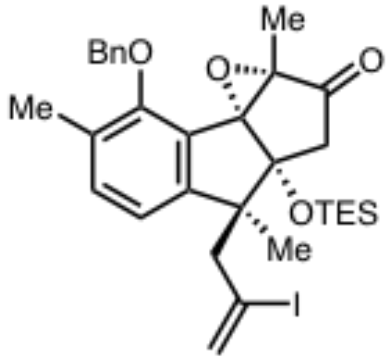
Parameter	Value
Data File Name	/ Volumes/ nmrdata-1/ chenxu91/ nmr/ xuchen-160831-10-88/ 1/ fid
Title	xuchen-160831-10-88.1.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	295.0
Pulse Sequence	zg30
Number of Scans	16
Receiver Gain	142.8
Relaxation Delay	1.0000
Pulse Width	11.7000
Acquisition Time	4.0894
Acquisition Date	2016-08-31T16:01:01
Spectrometer Frequency	400.13
Spectral Width	8012.8
Lowest Frequency	-1545.6
Nucleus	1H
Acquired Size	32768
Spectral Size	65536



40

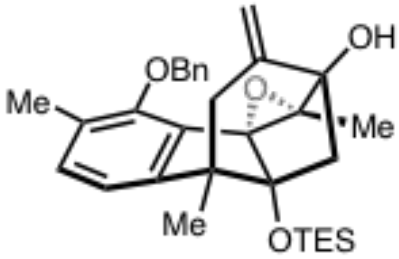


Parameter	Value
Data File Name	/ Volumes/ nmrdata-1/ chenxu91/ nmr/ xuchen-160831-10-88/ 2/ fid
Title	xuchen-160831-10-88.2.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	295.0
Pulse Sequence	zgpg30
Number of Scans	1024
Receiver Gain	72.0
Relaxation Delay	2.0000
Pulse Width	10.0000
Acquisition Time	1.3631
Acquisition Date	2016-08-31T17:00:09
Spectrometer Frequency	100.62
Spectral Width	24038.5
Lowest Frequency	-1961.4
Nucleus	13C
Acquired Size	32768
Spectral Size	65536

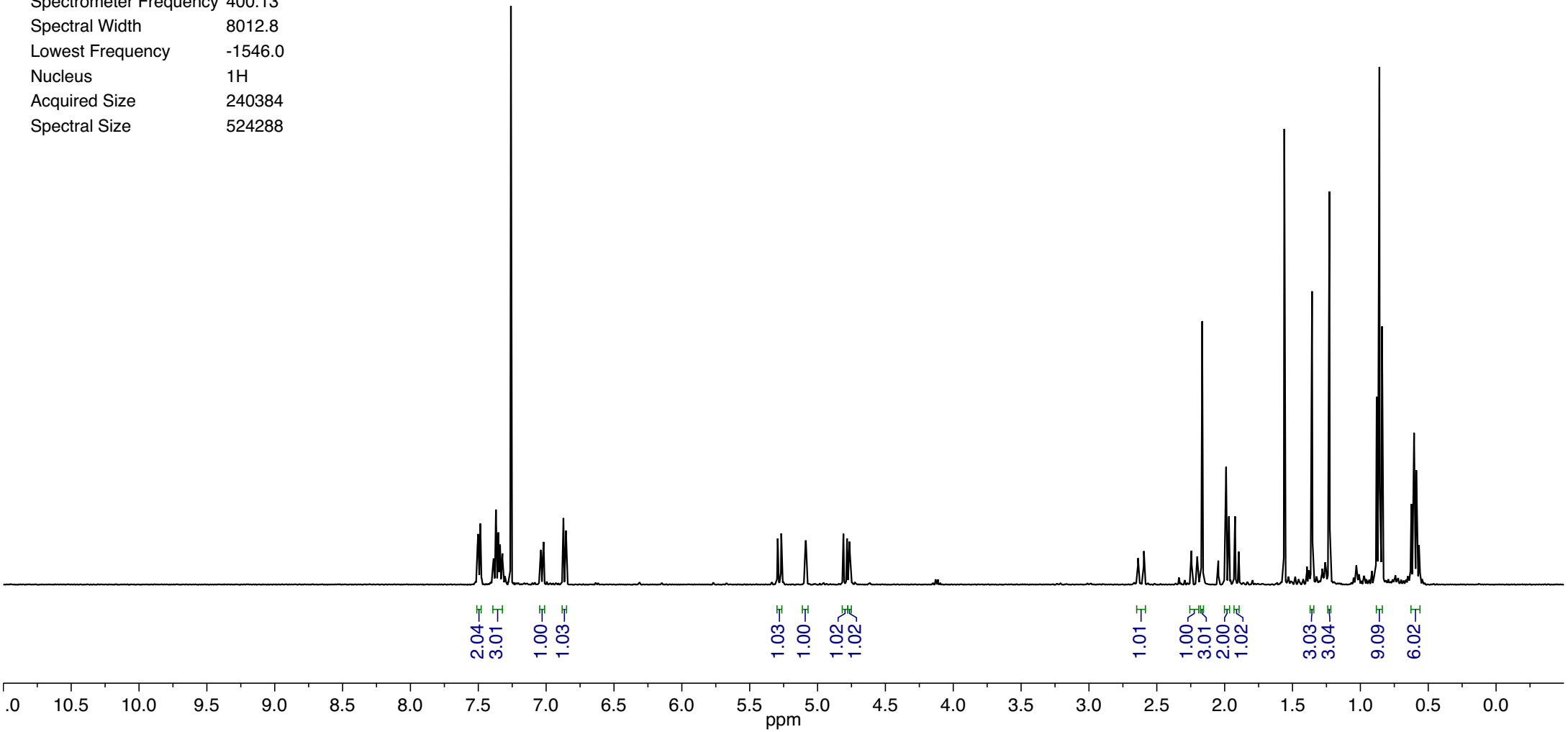


40

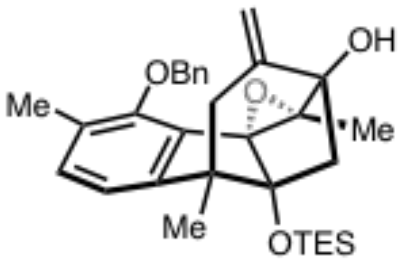
Parameter	Value
Data File Name	/ Volumes/ nmrdata-1/ ahan/ nmr/ 7-AH-288-CH/ 1/ fid
Title	7-AH-288-CH.1.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	294.9
Pulse Sequence	zg30
Number of Scans	1
Receiver Gain	197.4
Relaxation Delay	5.0000
Pulse Width	11.7000
Acquisition Time	29.9999
Acquisition Date	2017-07-14T15:29:05
Spectrometer Frequency	400.13
Spectral Width	8012.8
Lowest Frequency	-1546.0
Nucleus	1H
Acquired Size	240384
Spectral Size	524288



41

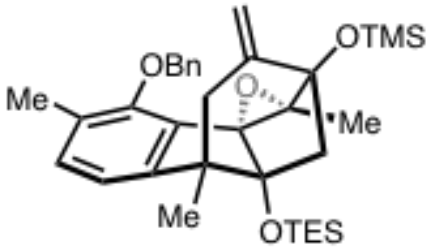


Parameter	Value
Data File Name	/ Volumes/ nmrdata-1/ ahan/ nmr/ 7-AH-288-CH/ 2/ fid
Title	7-AH-288-CH.2.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	295.0
Pulse Sequence	zgpg30
Number of Scans	1105
Receiver Gain	72.0
Relaxation Delay	1.0000
Pulse Width	10.0000
Acquisition Time	1.3631
Acquisition Date	2017-07-14T16:14:51
Spectrometer Frequency	100.62
Spectral Width	24038.5
Lowest Frequency	-1961.1
Nucleus	13C
Acquired Size	32768
Spectral Size	65536

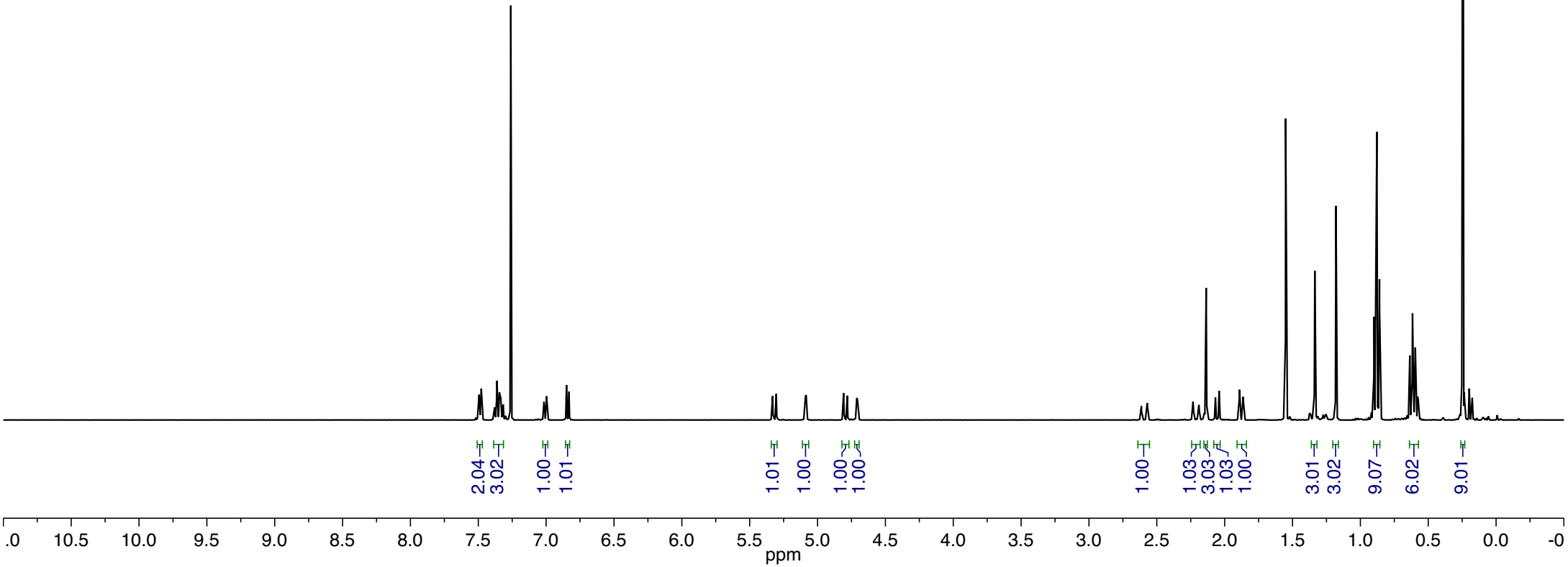


41

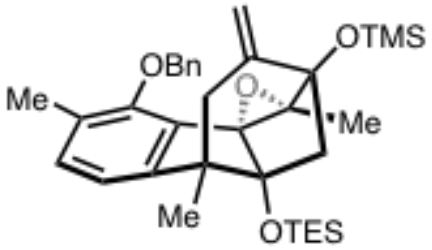
Parameter	Value
Data File Name	/ Volumes/ nmrdata/ ahan/ nmr/ 7-AH-297-P/ 3/ fid
Title	7-AH-297-P.3.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	294.9
Pulse Sequence	zg30
Number of Scans	8
Receiver Gain	197.4
Relaxation Delay	5.0000
Pulse Width	11.7000
Acquisition Time	4.0894
Acquisition Date	2017-07-16T12:21:55
Spectrometer Frequency	400.13
Spectral Width	8012.8
Lowest Frequency	-1545.4
Nucleus	1H
Acquired Size	32768
Spectral Size	65536



S5

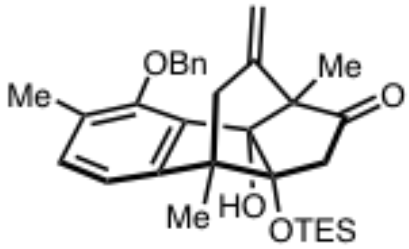


Parameter	Value
Data File Name	/ Volumes/ nmrdata/ ahan/ nmr/ 7-AH-297-P/ 6/ fid
Title	7-AH-297-P.6.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	295.0
Pulse Sequence	zgpg30
Number of Scans	1100
Receiver Gain	78.7
Relaxation Delay	1.0000
Pulse Width	10.0000
Acquisition Time	1.3631
Acquisition Date	2017-07-16T14:13:34
Spectrometer Frequency	100.62
Spectral Width	24038.5
Lowest Frequency	-1961.2
Nucleus	13C
Acquired Size	32768
Spectral Size	65536



S5

Parameter	Value
Data File Name	/ Volumes/ nmrdata/ ahan/ nmr/ 7-AH-297-CH/ 1/ fid
Title	7-AH-297-CH.1.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	294.9
Pulse Sequence	zg30
Number of Scans	1
Receiver Gain	197.4
Relaxation Delay	5.0000
Pulse Width	11.7000
Acquisition Time	29.9999
Acquisition Date	2017-07-18T13:41:41
Spectrometer Frequency	400.13
Spectral Width	8012.8
Lowest Frequency	-1545.6
Nucleus	1H
Acquired Size	240384
Spectral Size	524288



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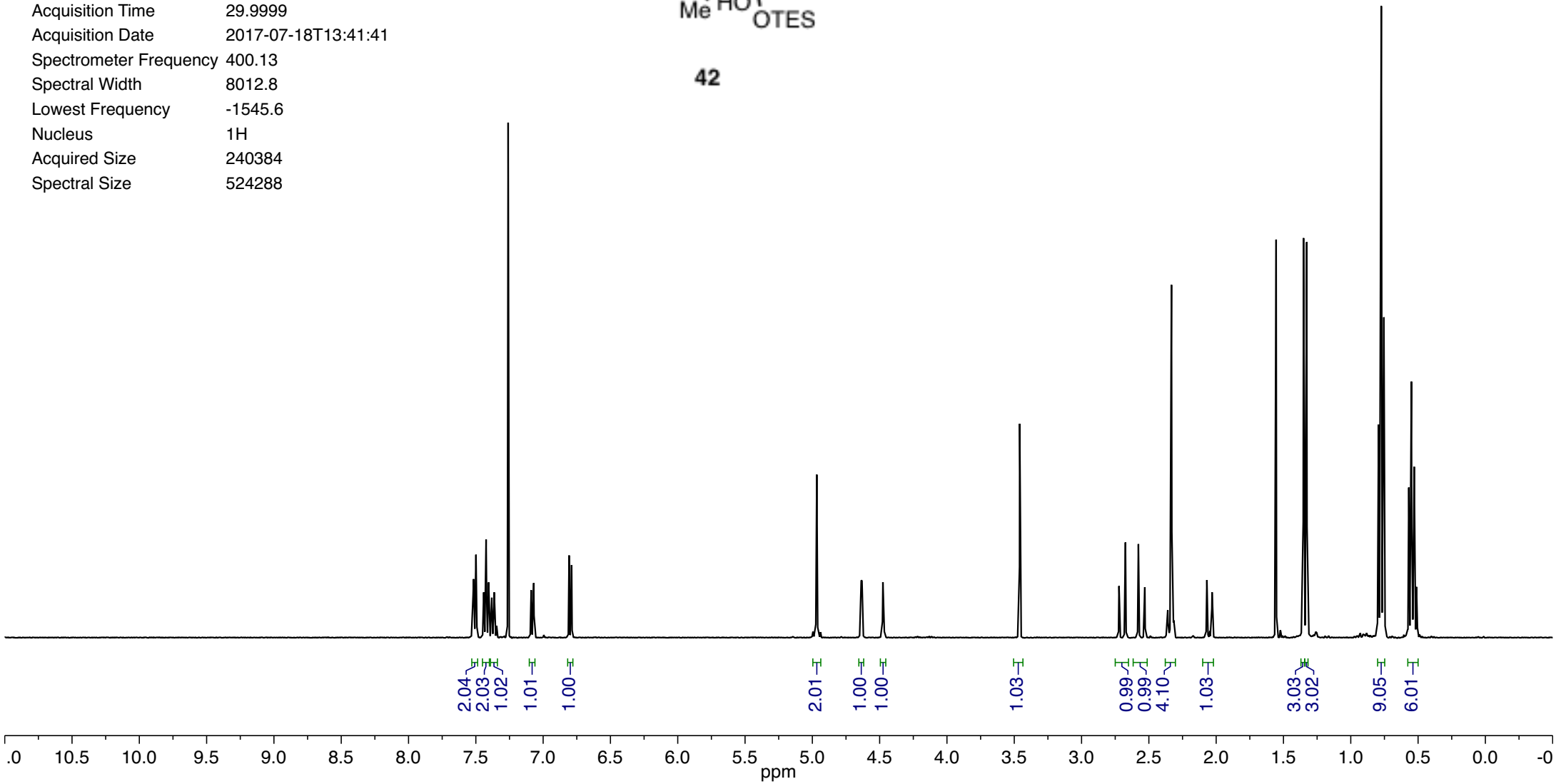
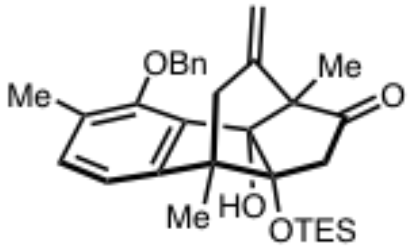
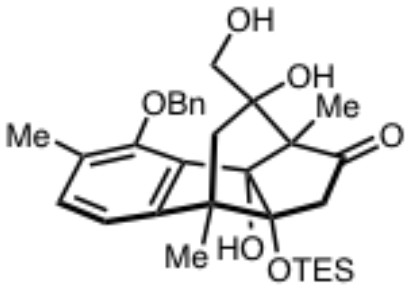


Parameter	Value
Data File Name	/ Volumes/ nmrdata/ ahan/ nmr/ 7-AH-297-CH/ 5/ fid
Title	7-AH-297-CH.5.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	295.0
Pulse Sequence	zgpg30
Number of Scans	801
Receiver Gain	64.2
Relaxation Delay	1.0000
Pulse Width	10.0000
Acquisition Time	1.3631
Acquisition Date	2017-07-18T15:16:43
Spectrometer Frequency	100.62
Spectral Width	24038.5
Lowest Frequency	-1961.3
Nucleus	13C
Acquired Size	32768
Spectral Size	65536



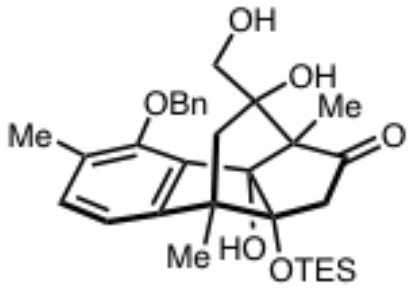
42

Parameter	Value
Data File Name	/ Volumes/ nmrdata/ ahan/ nmr/ 7-AH-298-CH/ 1/ fid
Title	7-AH-298-CH.1.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	295.0
Pulse Sequence	zg30
Number of Scans	1
Receiver Gain	197.4
Relaxation Delay	5.0000
Pulse Width	11.7000
Acquisition Time	29.9999
Acquisition Date	2017-07-19T08:24:20
Spectrometer Frequency	400.13
Spectral Width	8012.8
Lowest Frequency	-1545.4
Nucleus	1H
Acquired Size	240384
Spectral Size	524288

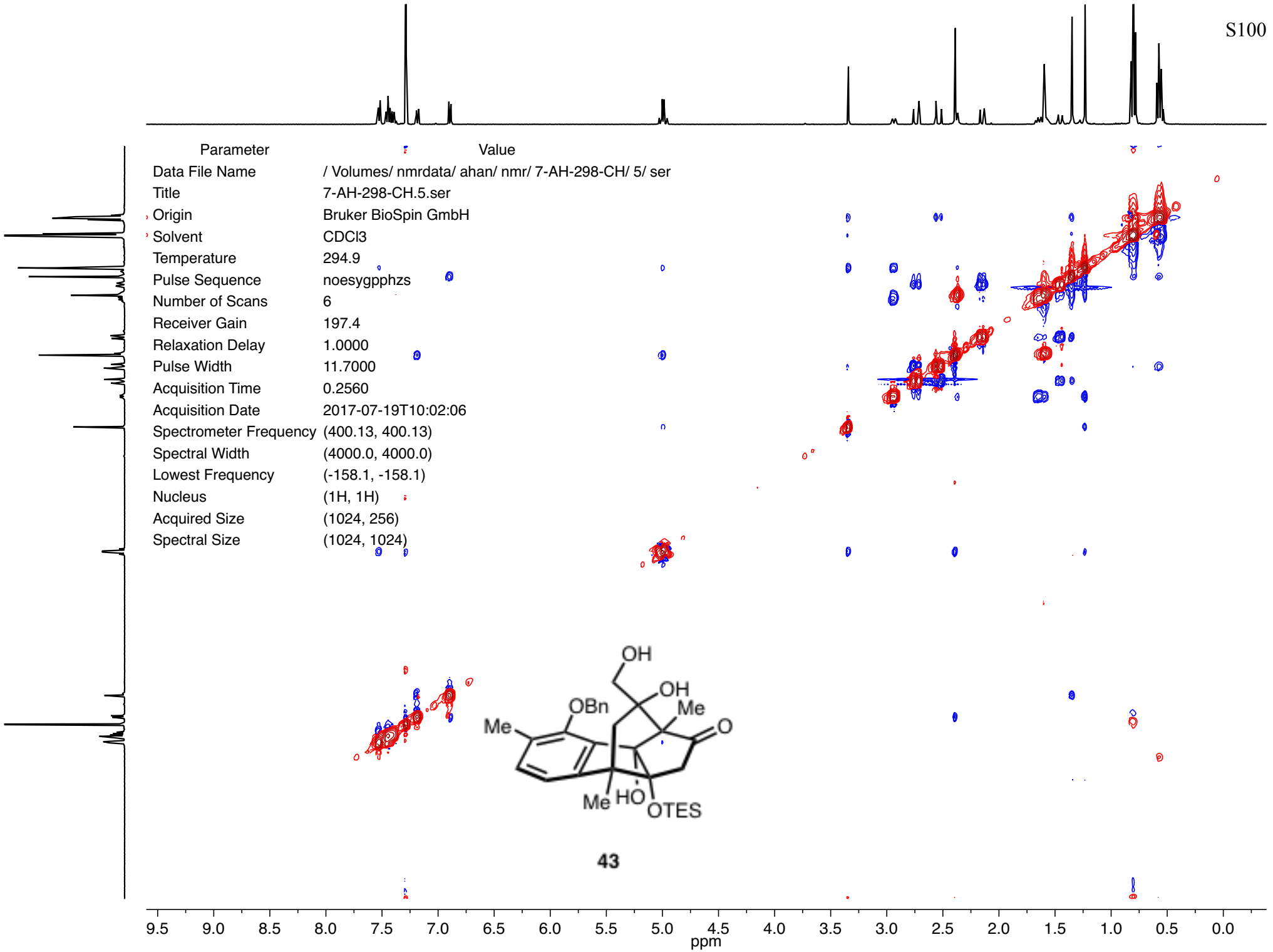


43

Parameter	Value
Data File Name	/ Volumes/ nmrdata/ ahan/ nmr/ 7-AH-298-CH/ 4/ fid
Title	7-AH-298-CH.4.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	294.9
Pulse Sequence	zgpg30
Number of Scans	1100
Receiver Gain	64.2
Relaxation Delay	1.0000
Pulse Width	10.0000
Acquisition Time	1.3631
Acquisition Date	2017-07-19T10:00:43
Spectrometer Frequency	100.62
Spectral Width	24038.5
Lowest Frequency	-1961.2
Nucleus	13C
Acquired Size	32768
Spectral Size	65536



43


Parameter Value
Data File Name / Volumes/ nmrdata/ ahan/ nmr/ 7-AH-298-CH/ 5/ ser
Title 7-AH-298-CH.5.ser
Origin Bruker BioSpin GmbH
Solvent CDCl3
Temperature 294.9
Pulse Sequence noesygpphzs
Number of Scans 6
Receiver Gain 197.4
Relaxation Delay 1.0000
Pulse Width 11.7000
Acquisition Time 0.2560
Acquisition Date 2017-07-19T10:02:06
Spectrometer Frequency (400.13, 400.13)
Spectral Width (4000.0, 4000.0)
Lowest Frequency (-158.1, -158.1)
Nucleus (1H, 1H)
Acquired Size (1024, 256)
Spectral Size (1024, 1024)
OH
OH
OBn
Me
Me
O
Me
HO
OTES
43
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
ppm
0 1 2 3 4 5 6 7 8 9