SeO_2-Mediated Oxidative Transposition of Pauson–Khand Products

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Supporting Information

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1. General Information

Abbreviations Used

DCE – dichloroethane; DCM – dichloromethane; DIPEA – diisopropylethylamine; DMF – dimethylformamide; dr – diasteromeric ratio; ee – enantiomeric excess; Et_2O – diethyl ether; EtOAc – ethyl acetate; FTIR – Fourier transform infrared; HPLC – high-performance liquid chromatography; IPA – isopropyl alcohol; LCMS – liquid chromatography mass spectrometry; MeCN – acetonitrile; MeOH – methanol; NaH – sodium hydride; NMR – nuclear magnetic resonance; PhH – benzene; PhMe – toluene; Pyr – pyridine; SFC – supercritical fluid chromatography; tBuOH – *tert*-butanol; THF – tetrahydrofuran; TLC – thin layer chromatography; UV – ultraviolet

Materials and Methods

Unless otherwise stated, reactions were performed 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. THF, DCM, MeCN, PhH, and PhMe were dried by passing through activated alumina columns. MeOH (HPLC grade) was purchased from Fisher Scientific. 1,4-dioxane, anhydrous ≥99.9%, was purchased from Millipore Sigma. DCE, Et_3N, *i*-Pr_2NH, DIPEA, 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, iodine, or CAM staining. Flash column chromatography was performed as described by Still et al.[1] 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 Advance 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 $CDCl_3$ (^1H, δ = 7.26), CD_3OD (^1H, δ = 3.31), 1,4-dioxane-d_8 (^1H, δ = 3.53), $(CH_3)_2SO$ (^1H, δ = 2.50), or pyridine-d_4 (^1H, δ = 8.74) and $CDCl_3$ (^{13}C, δ = 77.16), CD_3OD (^{13}C, δ = 49.0), 1,4-dioxane-d_8 (^{13}C, δ = 66.66), $(CH_3)_2SO$ (^{13}C, δ = 39.51), or pyridine-d_4 (^{13}C, δ = 150.35). 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, hept = heptet, m = multiplet. IR spectra were recorded on a Perkin Elmer Paragon 1000 spectrometer and are reported in frequency of absorption (cm^{-1}). Analytical chiral SFC was performed with a Mettler SFC supercritical CO_2 analytical chromatography system (CO_2 = 1450 psi, column temperature = 40 °C) with a Chiralcel OD-H column (4.6 mm x 25 cm). Preparative and analytical chiral HPLC was performed with an

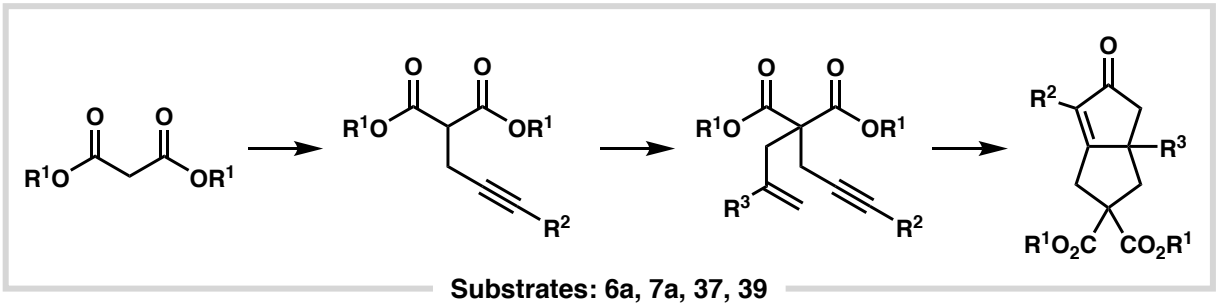
Agilent 1100 Series HPLC with a Chiralpak IH column (4.6 mm x 25 cm, Daicel Chemical Industries, Ltd.). HRMS were acquired using an Agilent 6200 Series TOF with an Agilent G1978A Multimode source in electrospray ionization (ESI) mode. Molecular formulas of the compounds [M] are given, with the observed ion fragment in brackets, e.g. $[M+H]^+$.

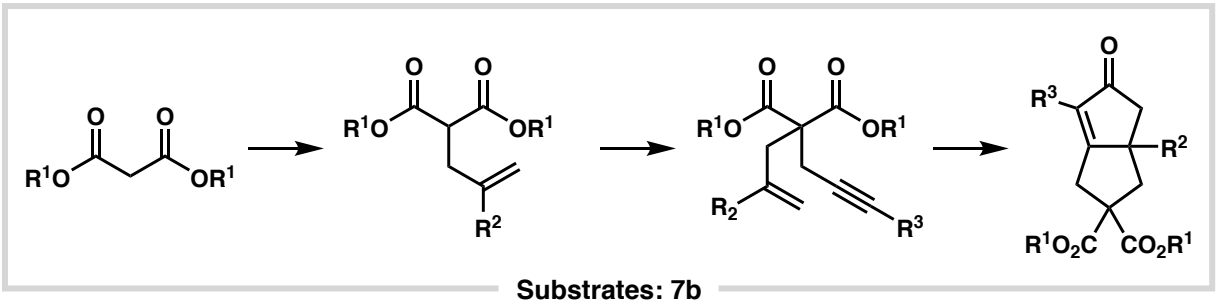
X-Ray Structure Determination

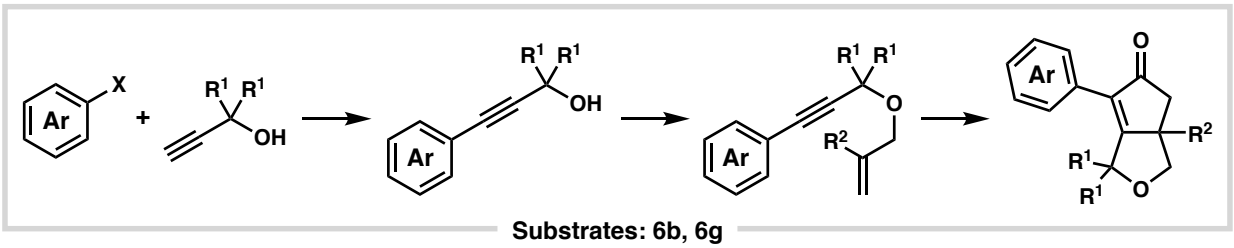
Low-temperature diffraction data (φ- and ω-scans) were collected on a Bruker AXS D8 VENTURE KAPPA diffractometer coupled to a PHOTON II CPAD detector with Mo-K_α radiation (λ = 0.71073 Å) from a $I_\mu S$ HB micro-focus sealed X-ray tube. All diffractometer manipulations, including data collection, integration, and scaling were carried out using the Bruker APEXII software.[2] Absorption corrections were applied using SADABS.[3] The structure was solved by intrinsic phasing using SHELXT[4] and refined against F^2 on all data by full-matrix least squares with SHELXL-2014[3] using established refinement techniques.[5] All non-hydrogen atoms were refined anisotropically. Unless otherwise noted, all hydrogen atoms were included into the model at geometrically calculated positions and refined using a riding model. The isotropic displacement parameters of all hydrogen atoms were fixed to 1.2 times the *U* value of the atoms they are linked to (1.5 times for methyl groups and hydroxyl groups). Crystallographic data for **15e** 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 numbers **1970101**. Graphical representation of the structures with 50% probability thermal ellipsoids was generated using Mercury visualization software.

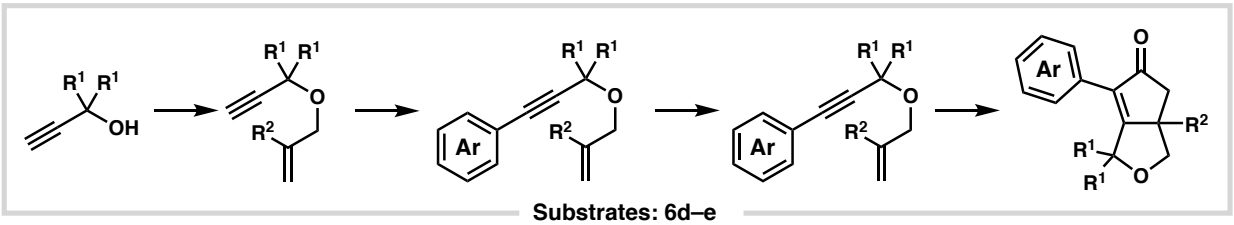
2. Substrate Preparation

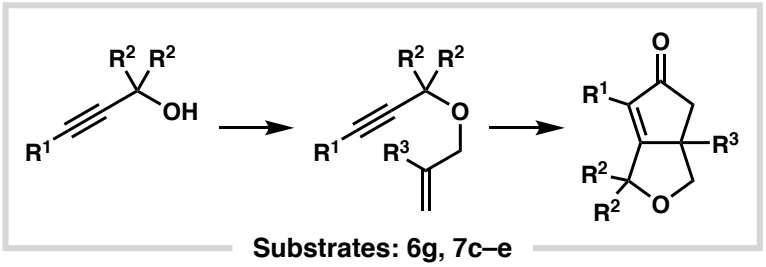
General Synthetic Schemes

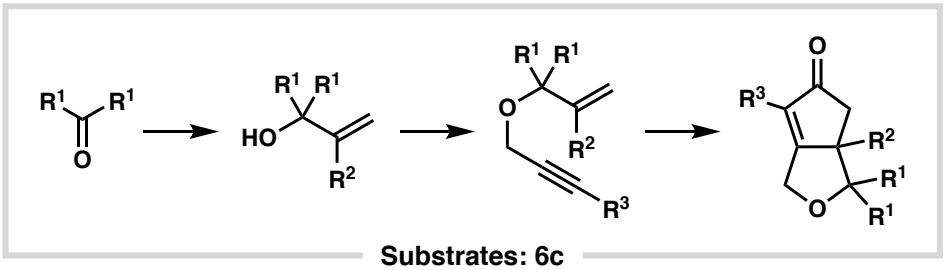




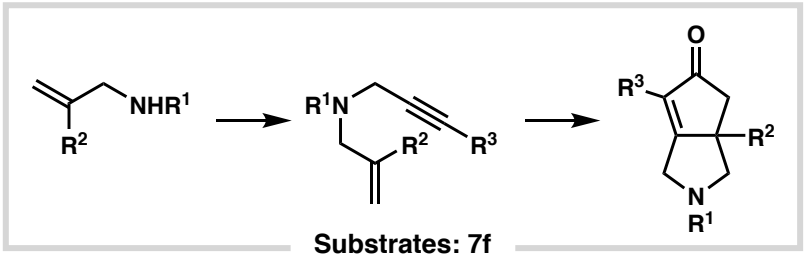




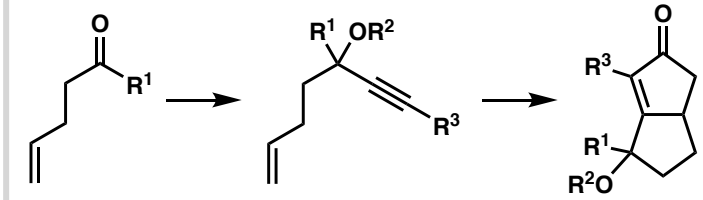




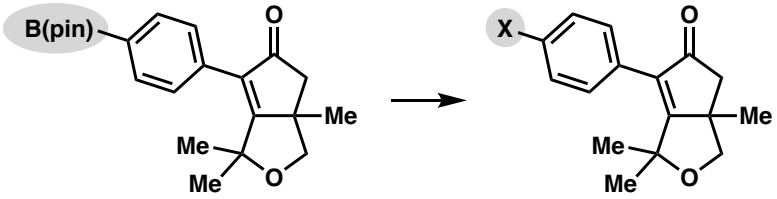
Substrates: 6c



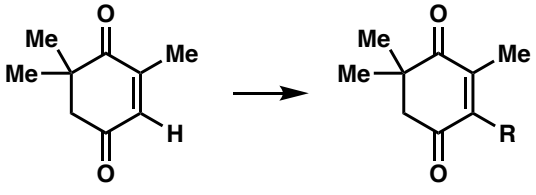
Substrates: 7f



Substrates: 7g–h



Substrates: 6f, 6h–i



ketoisophorone

Substrates: 40

General Procedures

Enyne Preparation: General Procedure A

To a dry round-bottomed flask with a Teflon-coated stir bar was added NaH in a glovebox. The flask was sealed with a rubber septum, removed from the glovebox, and placed under an atmosphere of dry N_2. Dry THF or DMF was then added and the mixture stirred. The resulting slurry was cooled to 0 °C in an ice water bath. The substrate was then added dropwise via syringe, with a vent needle in place to ensure efficient release of hydrogen gas into a well-ventilated fume hood. The resulting mixture was removed from the ice bath and allowed to stir at room temperature for 30 minutes or until hydrogen evolution ceased. At this time, the reaction was returned to the ice bath, and the alkyl bromide was added dropwise. The resulting mixture was allowed to reach room temperature while stirring and monitored by TLC. Upon completion, the reaction was quenched by dropwise addition of sat. aq. NH_4Cl, being careful not to cause vigorous hydrogen gas evolution or exotherm. The reaction was then diluted with water and Et_2O. The layers were separated and the aqueous layer extracted twice with Et_2O. Combined organics were washed with water and brine, dried over Na_2SO_4, filtered, and concentrated. The crude residue was purified by column chromatography to afford the desired product.

Enyne Preparation: General Procedure B

To a dry round-bottomed flask with a Teflon-coated stir bar was added $Pd(PPh_3)_2Cl_2$ and CuI in a glovebox. The flask was sealed with a rubber septum, removed from the glovebox, and placed under an atmosphere of dry N_2. The alkyne and aryl halide were then added. The combined solids were taken up in freshly distilled amine and dry solvent then stirred. The resulting yellow solution was stirred at various temperatures and monitored by TLC. Upon complete consumption of the aryl halide (typically accompanied by rapid gelation of the reaction mixture), the reaction was allowed to reach to room temperature then diluted with EtOAc and water. The layers were separated and the aqueous layer extracted twice with EtOAc. Combined organics were washed with water and brine, dried over Na_2SO_4, filtered, and concentrated. The crude residue was purified by column chromatography to afford the desired product.

PKR: General Procedure C[6]

To a dry round-bottomed flask with a Teflon-coated stir bar was added the enyne and placed under an atmosphere of dry N_2. Anhydrous solvent was added and the solution stirred at room temperature. $Co_2(CO)_8$ was added in one portion, and the reaction mixture was stirred for 1 h with a vent needle to allow efficient release of CO. CAUTION: all manipulations with CO should be performed in a well-ventilated fume hood. Upon complete consumption of the enyne as judged by TLC, anhydrous DMSO was added dropwise via

syringe. The reaction mixture was then placed in a preheated oil bath and monitored by TLC. Upon complete consumption of the intermediate Co-alkyne complex, the reaction was allowed to reach room temperature then diluted with EtOAc. Celite was added and the reaction mixture stirred overnight open to the air to sequester any Co species. The slurry was filtered over a pad of silica gel, washing with additional EtOAc. The filtrate was concentrated, and the crude residue was purified by column chromatography to afford the desired product. Note: initial elution with nonpolar solvent system is particularly important, as it washes away any remaining Co impurities that otherwise hamper purification.

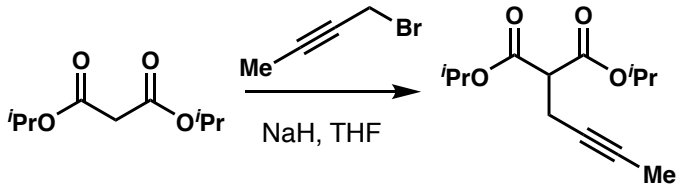
PKR: General Procedure D[7]

To a dry round-bottomed flask with a Teflon-coated stir bar was added $[Rh(CO)_2Cl]_2$ in a glovebox. The flask was sealed with a rubber septum, removed from the glovebox, and placed under an atmosphere of dry N_2. The solid was taken up in *m*-xylene or PhMe and stirred, and the enyne was added via syringe. The resulting solution was stirred at room temperature, sparged with dry N_2 then dry CO successively for five minutes each, and was then kept under an atmosphere of CO via balloon. CAUTION: all manipulations with CO should be performed in a well-ventilated fume hood. At this time, the reaction was placed in a preheated oil bath at 120 °C and was stirred and monitored by TLC. Upon completion, the reaction was allowed to reach room temperature, and the CO was cautiously released into the fume hood. The solvent was evaporated, and the crude residue was purified by column chromatography to afford the desired product. Note: additional chromatography may be required to remove trace rhodium (i.e. passing a concentrated solution of the desired product in DCM through a pre-packed plug of SiliCycle® thiol-functionalized silica gel).

PKR: General Procedure E[8]

To a dry round-bottomed flask with a Teflon-coated stir bar was added $Mo(CO)_3(DMF)_3$ in a glovebox. The flask was sealed with a rubber septum, removed from the glovebox, and placed under an atmosphere of dry N_2. The enyne was added as a solution in DCM, and the reaction was stirred at room temperature with a vent needle to allow efficient release of CO. Note: in the event of solvent evaporation, fresh DCM was added periodically. CAUTION: all manipulations with CO should be performed in a well-ventilated fume hood. Upon completion as judged by TLC, the reaction mixture was filtered over a pad of silica gel and celite, eluting with DCM. The filtrate was concentrated, and the crude residue was purified by column chromatography to afford the desired product.

diisopropyl 2-(but-2-yn-1-yl)malonate (16)



Prepared from diisopropyl malonate (11.4 mL, 60.0 mmol, 3.0 equiv), 1-bromobut-2-yne (1.75 mL, 20.0 mmol, 1.0 equiv), NaH (95%, 720 mg, 30.0 mmol, 1.5 equiv), and THF (60 mL, 0.33 M) following General Procedure A. The crude residue was purified by column chromatography (silica, 8 to 15% Et_2O/hexanes) to afford **16** (2.99 g, 63% yield) as a colorless oil.

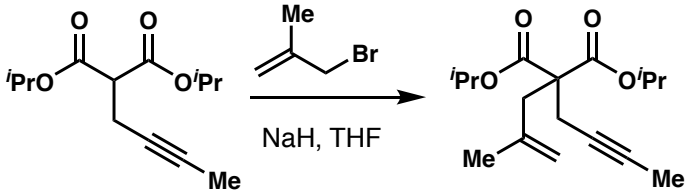
^{1}H NMR (500 MHz, CD_3Cl) δ 5.08 (hept, *J* = 6.2 Hz, 2H), 3.44 (t, *J* = 7.8 Hz, 1H), 2.69 (dq, *J* = 7.7, 2.5 Hz, 2H), 1.75 (t, *J* = 2.5 Hz, 3H), 1.26 (dd, *J* = 6.3, 4.3 Hz, 12H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 167.98, 77.77, 74.96, 69.20, 52.15, 21.79, 21.69, 18.80, 3.60.

FTIR (NaCl, thin film, cm^{-1}): 3055, 2978, 2850, 1706, 1655, 1301, 1120, 1026, 907, 766, 696.

HRMS (TOF-ESI, m/z): calc'd for $C_{13}H_{20}O_4$: 241.1434 $[M+H]^+$; found: 241.1439.

diisopropyl 2-(but-2-yn-1-yl)-2-(2-methylallyl)malonate (17)



Prepared from **16** (721 mg, 3.0 mmol, 1.0 equiv), methallyl bromide (0.34 mL, 3.3 mmol, 1.1 equiv), NaH (95%, 84.0 mg, 3.3 mmol, 1.1 equiv), and THF (6 mL, 0.50 M) following General Procedure A. The crude, clear colorless oil of **17** was used without further purification (821 mg, 93% yield).

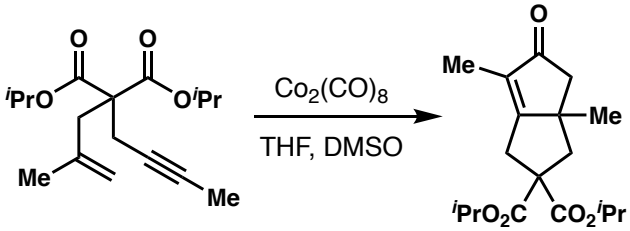
^{1}H NMR (500 MHz, $CDCl_3$) δ 5.05 (hept, *J* = 6.3 Hz, 2H), 4.88 (dt, *J* = 2.0, 1.5 Hz, 1H), 4.84 (dq, *J* = 1.8, 0.9 Hz, 1H), 2.79 (d, *J* = 0.9 Hz, 2H), 2.74 (q, *J* = 2.5 Hz, 2H), 1.78 – 1.72 (m, 3H), 1.69 (dd, *J* = 1.5, 0.8 Hz, 3H), 1.24 (dd, *J* = 6.3, 1.4 Hz, 12H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 170.17, 140.58, 115.99, 78.87, 74.05, 69.06, 56.67, 39.39, 23.57, 23.03, 21.68, 3.59.

FTIR (NaCl, thin film, cm^{-1}): 3465, 3080, 2980, 2938, 1732, 1645, 1456, 1374, 1277.

HRMS (TOF-ESI, m/z): calc'd for $C_{17}H_{26}O_4$: 295.1904 $[M+H]^+$; found: 295.1904.

diisopropyl 3a,6-dimethyl-5-oxo-3,3a,4,5-tetrahydropentalene-2,2(1H)-dicarboxylate (6a)



Prepared from **17** (2.95 g, 10.0 mmol, 1.0 equiv), $Co_2(CO)_8$ (3.77 g, 11.0 mmol, 1.1 equiv), DMSO (7.1 mL, 100.0 mmol, 10.0 equiv), and THF (100 mL, 0.10 M) following General Procedure C. The crude residue was purified by column chromatography (silica, 40 to 50% Et_2O/hexanes) to afford **6a** (3.06 g, 95% yield) as a white, glassy solid.

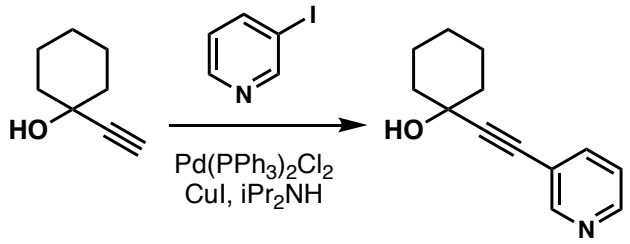
^{1}H NMR (500 MHz, $CDCl_3$) δ 5.10 (hept, *J* = 6.3 Hz, 1H), 5.00 (hept, *J* = 6.3 Hz, 1H), 3.34 (dq, *J* = 17.4, 1.9 Hz, 1H), 3.12 (d, *J* = 17.4 Hz, 1H), 2.55 (d, *J* = 13.6 Hz, 1H), 2.40 (d, *J* = 17.5 Hz, 1H), 2.34 (d, *J* = 17.5 Hz, 1H), 2.11 (d, *J* = 13.5 Hz, 1H), 1.70 (d, *J* = 1.7 Hz, 3H), 1.30 – 1.19 (m, 12H), 1.12 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 209.55, 181.23, 171.41, 171.17, 131.63, 69.72, 69.68, 60.51, 51.23, 47.67, 44.74, 33.14, 26.76, 21.66, 21.64, 21.60, 21.57, 8.63.

FTIR (NaCl, thin film, cm^{-1}): 2981, 2934, 2874, 1727, 1714, 1677, 1375, 1262, 1183, 1104, 1064, 912.

HRMS (TOF-ESI, m/z): calc'd for $C_{18}H_{26}O_5$: 323.1853 $[M+H]^+$; found: 323.1858.

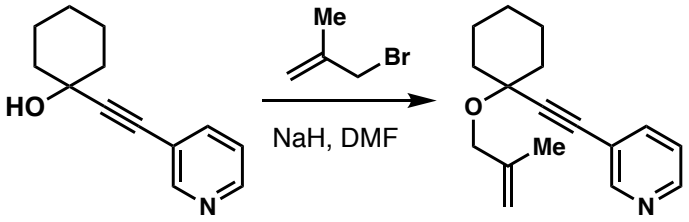
3-((1-((2-methylallyl)oxy)cyclohexyl)ethynyl)pyridine (18)



Prepared from 1-ethynylcyclohexan-1-ol (1.49 g, 12.0 mmol, 1.2 equiv), 3-iodopyridine (2.05 g, 10.0 mmol, 1.0 equiv), $Pd(PPh_3)_2Cl_2$ (211 mg, 0.3 mmol, 0.03 equiv), CuI (58 mg, 0.30 mmol, 0.03 equiv), and *i*Pr_2NH (20 mL, 0.50 M) at 80 ºC following General Procedure B. The crude residue was purified by column chromatography (silica, 55 to 65% EtOAc/hexanes) to afford **18** (2.00 g, >99% yield) as a tan, amorphous solid.

Spectral data matched those reported in the literature.[9]

3-((1-((2-methylallyl)oxy)cyclohexyl)ethynyl)pyridine (19)



Prepared from **18** (1.01 g, 5.0 mmol, 1.0 equiv), methallyl bromide (0.56 mL, 5.5 mmol, 1.1 equiv), NaH (95%, 140 mg, 5.5 mmol, 1.1 equiv), and DMF (20 mL, 0.25 M) following General Procedure A. The crude, clear amber oil of **19** was used without further purification (1.23 g, 97% yield).

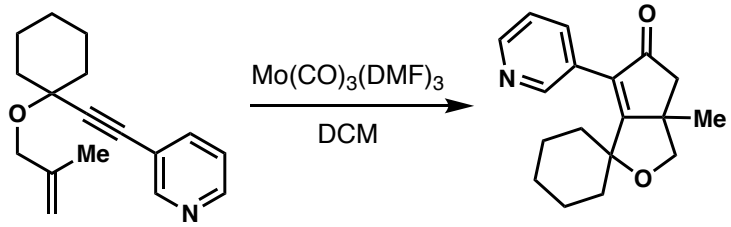
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.61 (d, *J* = 55.6 Hz, 2H), 7.71 (dt, *J* = 7.9, 1.8 Hz, 1H), 7.24 (d, *J* = 7.9 Hz, 1H), 5.04 (dp, *J* = 1.9, 1.0 Hz, 1H), 4.88 (dp, *J* = 2.4, 1.1 Hz, 1H), 4.07 (d, *J* = 1.1 Hz, 2H), 2.00 (ddd, *J* = 12.0, 7.2, 4.5 Hz, 2H), 1.79 (t, *J* = 1.2 Hz, 3H), 1.72 (qt, *J* = 9.5, 2.5 Hz, 3H), 1.57 (dddt, *J* = 17.8, 11.5, 8.6, 3.5 Hz, 3H), 1.45 – 1.30 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 152.51, 148.66, 143.07, 138.68, 123.11, 111.66, 94.60, 82.66, 74.23, 67.62, 37.28, 25.57, 22.96, 20.02.

FTIR (NaCl, thin film, cm^{-1}): 3077, 3029, 2935, 2857, 1656, 1560, 1475, 1448, 1406, 1086.

HRMS (TOF-ESI, m/z): calc'd for $C_{17}H_{21}NO$: 256.1696 $[M+H]^+$; found: 256.1697.

3a'-methyl-6'-(pyridin-3-yl)-3a',4'-dihydrospiro[cyclohexane-1,1'-cyclopenta[*c*]furan]-5'(3'*H*)-one (6b)



Prepared from **19** (1.22 g, 4.8 mmol, 1.0 equiv) and $Mo(CO)_3(DMF)_3$ (2.10 g, 5.3 mmol, 1.1 equiv) following General Procedure E. The crude residue was purified by column chromatography (silica, 30 to 50% EtOAc/hexanes) to afford **6b** (241 mg, 18% yield) as a tan, amorphous solid.

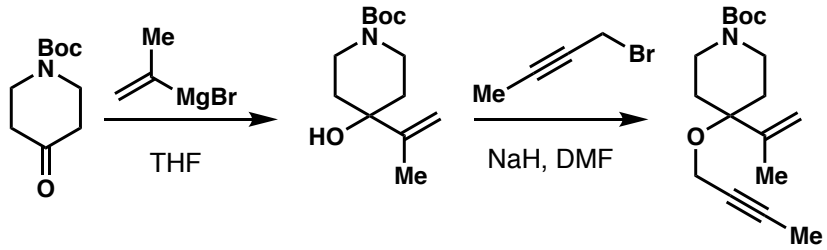
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.53 (dd, *J* = 4.9, 1.7 Hz, 1H), 8.45 (dd, *J* = 2.3, 0.9 Hz, 1H), 7.56 (dt, *J* = 7.8, 2.0 Hz, 1H), 7.28 (ddd, *J* = 7.8, 4.9, 0.9 Hz, 1H), 3.96 (d, *J* = 8.5 Hz, 1H), 3.48 (dd, *J* = 8.5, 0.9 Hz, 1H), 2.46 (d, *J* = 1.4 Hz, 2H), 2.17 (dp, *J* = 14.2, 2.7 Hz, 1H), 1.79 (td, *J* = 12.9, 4.8 Hz, 1H), 1.71 – 1.45 (m, 4H), 1.41 (s, 3H), 1.40 – 1.25 (m, 2H), 1.07 – 0.90 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 207.28, 191.05, 149.86, 149.59, 136.91, 131.83, 127.70, 123.46, 81.04, 74.72, 50.50, 48.92, 38.56, 32.03, 26.20, 24.90, 22.02, 21.79.

FTIR (NaCl, thin film, cm^{-1}): 2934, 2855, 1710, 1652, 1447, 1411, 1117, 1015, 919, 734, 713.

HRMS (TOF-ESI, m/z): calc'd for $C_{18}H_{21}NO_2$: 284.1645 $[M+H]^+$; found: 284.1642.

***tert*-butyl 4-(but-2-yn-1-yloxy)-4-(prop-1-en-2-yl)piperidine-1-carboxylate (20)**



To a dry round-bottomed flask with a Teflon-coated stir bar was added isopropenylmagnesium bromide (0.5 M in THF, 40.0 mL, 20.0 mmol, 2.0 equiv) and stirred at room temperature under an atmosphere of dry N_2. *N*-boc-piperidone (2.00 g, 10.0 mmol, 1.0 equiv) was then added as a solution in THF (27 mL, 0.15 M final), and the solution was stirred at room temperature and monitored by TLC. Upon complete consumption of the ketone, the reaction was quenched by slow dropwise addition of sat. aq. NH_4Cl, being careful not to cause vigorous propene gas evolution or exotherm. When propene evolution ceased, the reaction was diluted with water and EtOAc. The layers were separated and the aqueous extracted twice with EtOAc. Combined organics were washed with water and brine, dried over Na_2SO_4, filtered, and concentrated. The crude oil (10.0 mmol, 1.0 equiv) was used directly in the next step, following General Procedure A with 1-bromobut-2-yne (1.1 mL, 12.5 mmol, 1.25 equiv), NaH (95%, 316 mg, 12.5 mmol, 1.25 equiv), and DMF (40 mL, 0.25 M). The crude oil was purified by column chromatography (silica, 15 to 25% Et_2O/hexanes) to afford **20** (1.64 g, 56% yield over 2 steps) as a colorless oil.

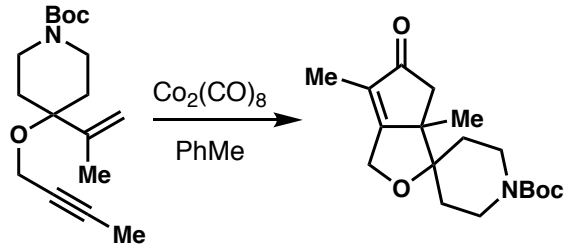
^{1}H NMR (500 MHz, $CDCl_3$) δ 5.04 (p, *J* = 1.4 Hz, 1H), 4.91 (t, *J* = 1.0 Hz, 1H), 3.99 – 3.72 (m, 4H), 3.18 (s, 2H), 1.93 – 1.84 (m, 2H), 1.84 (t, *J* = 2.4 Hz, 3H), 1.74 (dd, *J* = 1.4, 0.7 Hz, 3H), 1.63 – 1.53 (m, 2H), 1.45 (s, 9H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 154.99, 146.69, 114.02, 81.64, 79.44, 77.03, 76.03, 50.94, 28.59, 18.23, 3.89.

FTIR (NaCl, thin film, cm^{-1}): 3495, 3364, 3091, 2927, 2318, 2241, 1958, 1822, 1689, 1454.

HRMS (TOF-ESI, m/z): calc'd for $C_{17}H_{27}NO_3$: 294.2064 $[M+H]^+$; found: 294.2078.

***tert*-butyl 4,6a-dimethyl-5-oxo-3,5,6,6a-tetrahydrospiro[cyclopenta[*c*]furan-1,4'-piperidine]-1'-carboxylate (6c)**



Prepared from **20** (733 mg, 2.5 mmol, 1.0 equiv), $Co_2(CO)_8$ (941 mg, 2.75 mmol, 1.1 equiv), and PhMe (25 mL, 0.10 M) following modified General Procedure C without addition of DMSO. Upon complete conversion of the enyne to the Co-alkyne complex, the reaction was placed in a preheated oil bath at 110 °C. Upon complete consumption of the Co-alkyne complex, the reaction was allowed to reach room temperature, filtered over a pad of SiO_2 and Celite, and the filtrate concentrated. The crude residue was purified by column chromatography (silica, 5 to 40% EtOAc/hexanes) to afford **6c** (494 mg, 62% yield) as an off-white, amorphous solid.

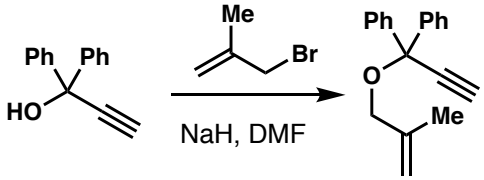
^{1}H NMR (400 MHz, $CDCl_3$) δ 4.64 (dq, *J* = 16.0, 1.7 Hz, 1H), 4.43 (d, *J* = 16.0 Hz, 1H), 4.14 – 3.82 (m, 2H), 3.01 (s, 2H), 2.34 (d, *J* = 17.7 Hz, 1H), 2.18 (d, *J* = 17.7 Hz, 1H), 1.85 – 1.74 (m, 1H), 1.70 (dd, *J* = 1.6, 1.0 Hz, 3H), 1.54 (td, *J* = 13.2, 5.3 Hz, 1H), 1.44 (s, 9H), 1.36 (dd, *J* = 12.7, 4.5 Hz, 1H), 1.29 – 1.19 (m, 1H), 1.18 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 209.39, 180.68, 154.83, 130.62, 81.26, 79.66, 62.56, 52.62, 45.28, 31.68, 29.78, 28.56, 22.72, 8.74.

FTIR (NaCl, thin film, cm^{-1}): 3415, 2974, 2935, 1769, 1715, 1693, 1427, 1366, 1247, 1163, 1052, 737.

HRMS (TOF-ESI, m/z): calc'd for $C_{18}H_{27}NO_4$: 322.2013 $[M+H]^+$; found: 322.2000.

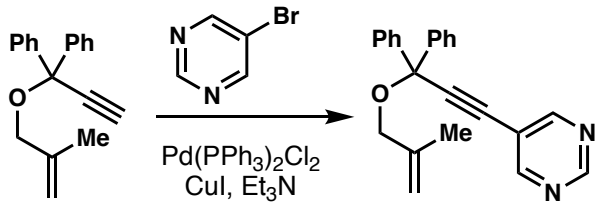
(1-((2-methylallyl)oxy)prop-2-yne-1,1-diyl)dibenzene (21)



Prepared from 1,1-diphenylprop-2-yn-1-ol (4.17 g, 20.0 mmol, 1.0 equiv), methallyl bromide (2.22 mL, 22.0 mmol, 1.1 equiv), NaH (95%, 556 mg, 22.0 mmol, 1.1 equiv), and DMF (80 mL, 0.25 M) following General Procedure A. The crude oil was purified by column chromatography (silica, 1 to 3% Et_2O/hexanes) to afford **21** (4.69 g, 90% yield) as a yellow oil.

Spectral data matched those reported in the literature.[10]

5-(3-((2-methylallyl)oxy)-3,3-diphenylprop-1-yn-1-yl)pyrimidine (22)



Prepared from **21** (374 mg, 1.42 mmol, 1.0 equiv), 5-bromopyrimidine (240 mg, 1.5 mmol, 1.05 equiv), $Pd(PPh_3)_2Cl_2$ (43 mg, 0.06 mmol, 0.04 equiv), CuI (11.5 mg, 0.06 mmol, 0.04 equiv), and Et_3N (6 mL, 0.25 M) at 50 ºC following General Procedure B. The crude residue was purified by column chromatography (silica, 25 to 30% Et_2O/hexanes) to afford **22** (365 mg, 75% yield) as a yellow, amorphous solid.

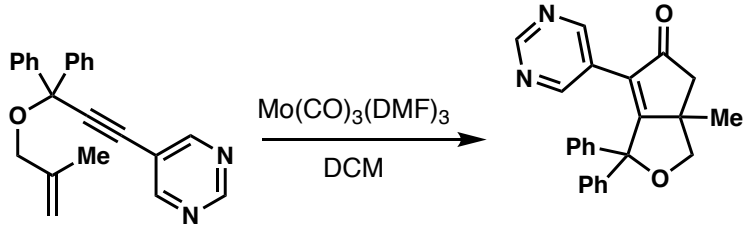
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.17 (s, 1H), 8.85 (s, 2H), 7.64 – 7.56 (m, 4H), 7.40 – 7.32 (m, 4H), 7.34 – 7.25 (m, 2H), 5.12 (tp, *J* = 1.9, 0.9 Hz, 1H), 4.93 (dh, *J* = 2.6, 1.3 Hz, 1H), 3.97 (d, *J* = 1.5 Hz, 2H), 1.81 (dd, *J* = 1.5, 0.8 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 159.05, 157.30, 143.00, 142.24, 128.52, 128.13, 126.72, 119.29, 111.65, 96.49, 82.48, 80.69, 68.99, 20.13.

FTIR (NaCl, thin film, cm^{-1}): 3356, 3312, 2953, 2922, 2851, 2352, 2333, 1633, 1540, 1447, 1415, 1267.

HRMS (TOF-ESI, m/z): calc'd for $C_{23}H_{20}N_2O$: 341.1648 $[M+H]^+$; found: 341.1653.

3a-methyl-1,1-diphenyl-6-(pyrimidin-5-yl)-3a,4-dihydro-1*H*-cyclopenta[*c*]furan-5(3*H*)-one (6d)



Prepared from **22** (340 mg, 1.0 mmol, 1.0 equiv) and $Mo(CO)_3(DMF)_3$ (401 mg, 1.0 mmol, 1.0 equiv) following General Procedure E. The crude residue was purified by column chromatography (silica, 30 to 60% EtOAc/hexanes) to afford **6d** (101 mg, 28% yield) as a light yellow, amorphous solid.

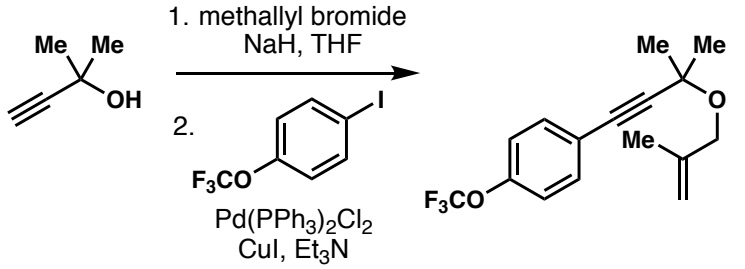
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.92 (s, 1H), 8.22 (s, 2H), 7.50 – 7.37 (m, 5H), 7.07 – 6.93 (m, 3H), 6.84 – 6.76 (m, 2H), 4.39 (d, *J* = 8.2 Hz, 1H), 4.20 (dd, *J* = 8.1, 0.8 Hz, 1H), 2.81 (d, *J* = 17.7 Hz, 1H), 2.71 (d, *J* = 17.7 Hz, 1H), 1.31 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 206.12, 187.62, 157.69, 156.30, 142.88, 141.70, 133.17, 128.77, 128.70, 128.27, 127.92, 127.76, 127.56, 124.55, 87.88, 78.83, 50.50, 49.64, 27.33.

FTIR (NaCl, thin film, cm^{-1}): 3055, 2969, 2926, 2858, 2362, 1715, 1548, 1447, 1413.

HRMS (TOF-ESI, m/z): calc'd for $C_{24}H_{20}N_2O_2$: 369.1598 $[M+H]^+$; found: 369.1612.

1-(3-methyl-3-((2-methylallyl)oxy)but-1-yn-1-yl)-4-(trifluoromethoxy)benzene (23)



Prepared in two steps. Intermediate prepared from 2-methyl-3-butyn-2-ol (1.94 mL, 20.0 mmol, 1.0 equiv), methallyl bromide (2.22 mL, 22.0 mmol, 1.1 equiv), NaH (95%, 555 mg, 22.0 mmol, 1.1 equiv), and THF (80 mL, 0.25 M) following General Procedure A. The crude residue was purified by column chromatography (silica, 2 to 4% Et_2O/hexanes) to afford the desired intermediate as a clear colorless oil, which was left as a solution in hexanes to avoid product evaporation upon concentration. The intermediate (~690 mg in hexanes, ~5.0 mmol, 1.0 equiv) was then used directly in the next step, following General Procedure B with *p*-trifluoromethoxy-iodobenzene (0.79 mL, 5.0 mmol, 1.0 equiv), $Pd(PPh_3)_2Cl_2$ (141 mg, 0.2 mmol, 0.04 equiv), CuI (38.1 mg, 0.2 mmol, 0.04 equiv), and Et_3N (20 mL, 0.25 M). The crude oil was purified by column chromatography (silica, 2 to 3% Et_2O/hexanes) to afford **23** (799 mg, 54% yield over 2 steps) as a colorless oil.

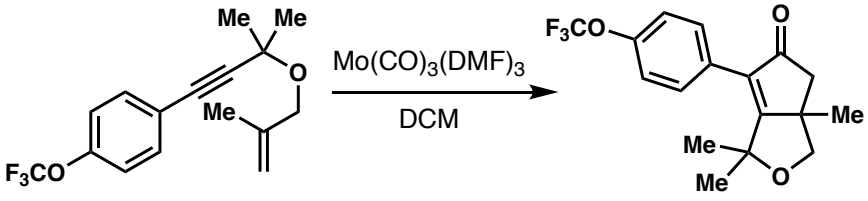
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 – 7.40 (m, 2H), 7.15 (ddt, J = 7.7, 2.0, 1.0 Hz, 2H), 5.03 (dh, J = 2.2, 1.1 Hz, 1H), 4.88 (dqd, J = 2.4, 1.5, 0.8 Hz, 1H), 4.08 – 4.03 (m, 2H), 1.81 – 1.74 (m, 3H), 1.57 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 148.98, 148.96, 143.00, 133.31, 120.50 (q, $^1J_{CF}$ = 160 Hz), 121.87, 120.96, 111.74, 92.63, 82.78, 70.90, 68.60, 28.96, 19.92.

FTIR (NaCl, thin film, cm^{-1}): 3437, 2984, 2935, 1726, 1608, 1507, 1264, 1219, 1162.

HRMS (TOF-ESI, m/z): calc'd for $C_{12}H_{11}F_3O_2$: 227.0678 $[M–C_4H_7O+H]^+$; found: 227.0688.

1,1,3a-trimethyl-6-(4-(trifluoromethoxy)phenyl)-3a,4-dihydro-1*H*-cyclopenta[*c*]furan-5(3*H*)-one (6e)



Prepared from **23** (745 mg, 2.5 mmol, 1.0 equiv) and $Mo(CO)_3(DMF)_3$ (1.00 g, 2.5 mmol, 1.0 equiv) following General Procedure E. The crude residue was purified by column chromatography (silica, 30 to 35% EtOAc/hexanes). To remove residual [Mo] byproducts, the sample was taken up in 5 mL DCM, then 450 mg (~0.2 mmol) TAAcONa capped silica gel (SiliCycle®) was added and the mixture stirred overnight.

The mixture was then filtered and concentrated to afford **6e** (330 mg, 41% yield) as an off-white amorphous solid.

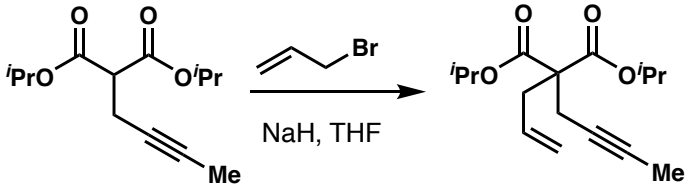
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 – 7.23 (m, 2H), 7.23 – 7.15 (m, 2H), 3.95 (d, *J* = 8.4 Hz, 1H), 3.51 (dd, *J* = 8.5, 0.9 Hz, 1H), 2.48 (d, *J* = 1.0 Hz, 2H), 1.67 (s, 3H), 1.44 (s, 3H), 1.02 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ ^{13}C NMR (101 MHz, $CDCl_3$) δ 207.17, 189.24, 149.40, 149.38, 149.36, 133.97, 130.81, 129.80, 120.54 (q, $^1J_{CF}$ = 258 Hz), 120.99, 79.23, 75.06, 50.63, 49.04, 29.60, 26.04, 25.13.

FTIR (NaCl, thin film, cm^{-1}): 2977, 2933, 2848, 1712, 1652, 1507, 1263, 1224, 1162, 1019.

HRMS (TOF-ESI, m/z): calc'd for $C_{17}H_{17}F_3O_3$: 327.1203 $[M+H]^+$; found: 327.1203.

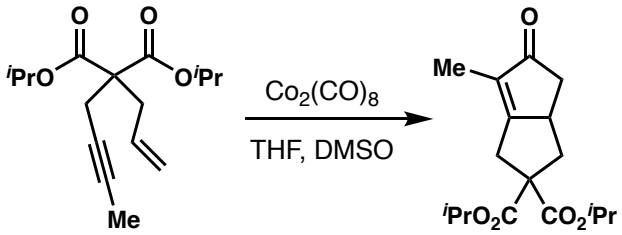
diisopropyl 2-allyl-2-(but-2-yn-1-yl)malonate (24)



Prepared from **16** (1.44 g, 6.0 mmol, 1.0 equiv), allyl bromide (0.55 mL, 6.3 mmol, 1.05 equiv), NaH (95%, 173 mg, 7.2 mmol, 1.2 equiv), and THF (15 mL, 0.40 M) following General Procedure A. The crude oil was purified by column chromatography (silica, 7 to 10% Et_2O/hexanes) to afford **24** (1.63 g, 97% yield) as a colorless oil.

Spectral data matched those reported in the literature.[11]

Diisopropyl 6-methyl-5-oxo-3,3a,4,5-tetrahydropentalene-2,2(1H)-dicarboxylate (7a)



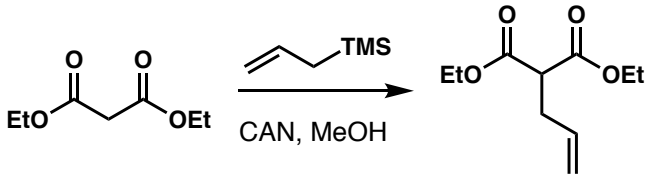
Prepared from **24** (1.40 g, 5.0 mmol, 1.0 equiv), $Co_2(CO)_8$ (2.06 g, 6.0 mmol, 1.2 equiv), and THF (50 mL, 0.10 M) following General Procedure C. The crude residue was purified by column chromatography (silica, 10 to 60% Et_2O/hexanes) to afford **7a** (1.30 g, 85% yield) as a white powder.

^{1}H NMR (400 MHz, CD_3OD) δ 5.04 (dhept, *J* = 20.8, 6.3 Hz, 2H), 3.19 (dt, *J* = 2.5, 1.5 Hz, 2H), 3.05 – 2.95 (m, 1H), 2.72 (dd, *J* = 12.7, 7.6 Hz, 1H), 2.61 (dd, *J* = 18.0, 6.2 Hz, 1H), 2.16 – 2.06 (m, 1H), 1.69 (dt, *J* = 2.5, 1.3 Hz, 3H), 1.64 (t, *J* = 12.5 Hz, 1H), 1.27 (d, *J* = 6.3 Hz, 6H), 1.24 (dd, *J* = 6.3, 3.7 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 209.80, 178.32, 171.41, 170.79, 133.14, 69.77, 69.68, 61.28, 42.90, 41.66, 39.32, 34.19, 21.77, 8.81.

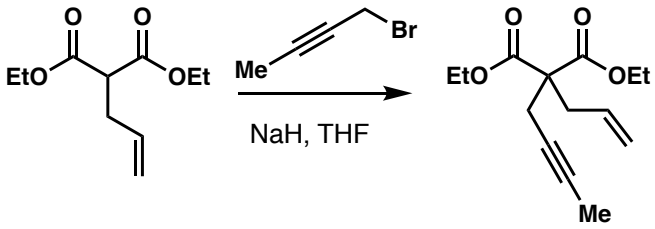
FTIR (NaCl, thin film, cm^{-1}): 2981, 2924, 1728, 1714, 1678, 1455, 1375, 1271, 1192, 1102, 911.
HRMS (TOF-ESI, m/z): calc'd for $C_{17}H_{24}O_5$: 309.1697 $[M+H]^+$; found: 309.1684.

diethyl 2-allylmalonate (25)



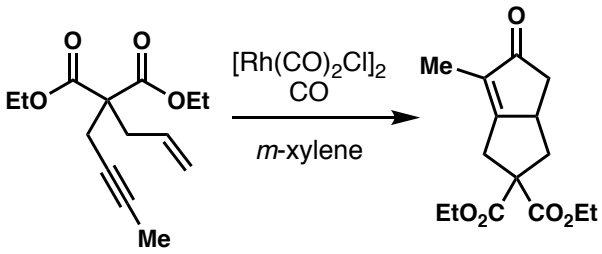
Prepared from diethylmalonate (2.29 mL, 15.0 mmol, 1.0 equiv) following a procedure by Shiao and coworkers.[12] The crude oil was purified by column chromatography (silica, 15% Et_2O/hexanes) to afford **25** (1.70 g, 57% yield) as a colorless oil.
Spectral data matched those reported in the literature.[12]

diethyl 2-allyl-2-(but-2-yn-1-yl)malonate (26)



Prepared from **25** (1.00 g, 5.0 mmol, 1.0 equiv), 1-bromobut-2-yne (0.44 mL, 5.0 mmol, 1.0 equiv), NaH (60% in mineral oil, 240 mg, 6.0 mmol, 1.2 equiv), and THF (10 mL, 0.50 M) following General Procedure A. The crude residue was purified by column chromatography (12% Et_2O/hexanes) to afford **26** (1.12 g, 89% yield) as a colorless oil.
Spectral data matched those reported in the literature.[13]

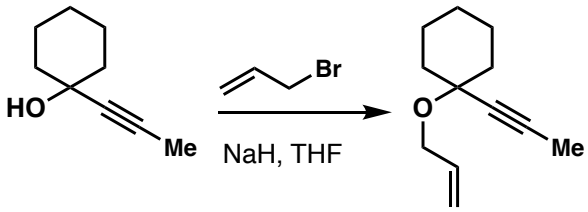
diethyl 6-methyl-5-oxo-3,3a,4,5-tetrahydropentalene-2,2(1*H*)-dicarboxylate (7b)



Prepared from **26** (504 mg, 2.0 mmol, 1.0 equiv), $[Rh(CO)_2Cl]_2$ (78.0 mg, 0.2 mmol, 0.1 equiv), and *m*-xylene (20 mL, 0.10 M) following General Procedure D. The crude residue was purified by column chromatography (silica, 30% EtOAc/hexanes) to afford **7b** (438 mg, 79% yield) as an off-white powder.

Spectral data matched those reported in the literature.[14]

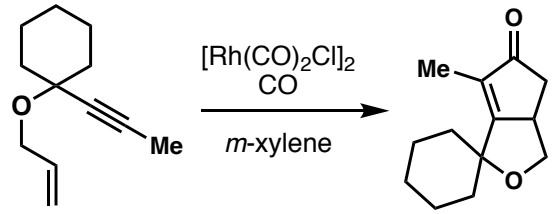
1-(allyloxy)-1-(prop-1-yn-1-yl)cyclohexane (27)



Prepared from 1-(prop-1-yn-1-yl)cyclohexan-1-ol (1.39 g, 10.0 mmol, 1.0 equiv), allyl bromide (1.73 mL, 20.0 mmol, 2.0 equiv), NaH (95%, 360 mg, 15.0 mmol, 1.5 equiv), and THF (20 mL, 0.50 M) following General Procedure A. The crude oil was purified by column chromatography (silica, 2 to 5% Et_2O/hexanes) to afford **27** (914 mg, 52% yield) as a colorless oil.

Spectral data matched those reported in the literature.[15]

6'-methyl-3a',4'-dihydrospiro[cyclohexane-1,1'-cyclopenta[*c*]furan]-5'(3'*H*)-one (7c)



Prepared from **27** (446 mg, 2.5 mmol, 1.0 equiv), $[Rh(CO)_2Cl]_2$ (73 mg, 0.19 mmol, 0.75 equiv), and *m*-xylene (12.5 mL, 0.20 M) following General Procedure D. The crude oil was purified by column chromatography (silica, 20 to 30% EtOAc/hexanes) to afford **7c** (27 mg, 68% yield) as a clear yellow oil.

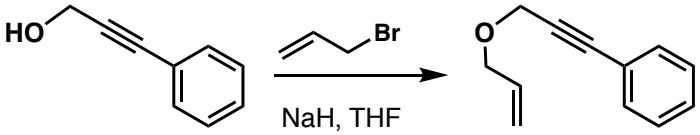
^{1}H NMR (500 MHz, $CDCl_3$) δ 4.29 – 4.17 (m, 1H), 3.28 – 3.17 (m, 3H), 2.58 (dd, *J* = 17.6, 5.9 Hz, 1H), 2.09 (dd, *J* = 17.5, 3.5 Hz, 1H), 1.79 (d, *J* = 2.2 Hz, 4H), 1.76 (ddt, *J* = 11.5, 6.5, 2.5 Hz, 2H), 1.72 – 1.59 (m, 6H), 1.33 – 1.19 (m, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 210.00, 182.70, 130.57, 79.72, 69.77, 44.10, 38.61, 35.28, 32.22, 25.40, 22.19, 21.58, 8.36.

FTIR (NaCl, thin film, cm^{-1}): 3412, 2924, 2856, 1698, 1682, 1446, 1269, 1058, 1024, 917, 840, 738, 665.

HRMS (TOF-ESI, m/z): calc'd for $C_{13}H_{18}O_2$: 207.1380 $[M+H]^+$; found: 207.1376.

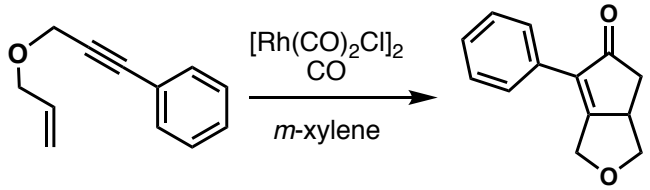
(3-(allyloxy)prop-1-yn-1-yl)benzene (28)



Prepared from 3-phenylprop-2-yn-1-ol (1.25 mL, 10.0 mmol, 1.0 equiv), allyl bromide (1.73 mL, 20.0 mmol, 2.0 equiv), NaH (95%, 300 mg, 12.5 mmol, 1.25 equiv), and THF (20 mL, 0.50 M) following General Procedure A. The resulting crude, colorless oil of **28** (1.68 g, 98% yield) was used without further purification.

Spectral data matched those reported in the literature.[16]

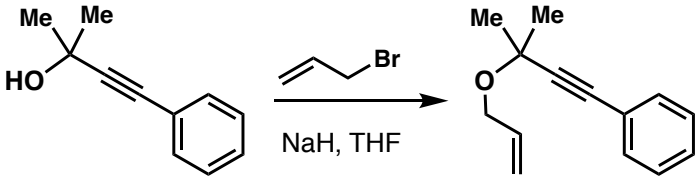
6-phenyl-3a,4-dihydro-1*H*-cyclopenta[*c*]furan-5(3*H*)-one (7d)



Prepared from **28** (345 mg, 2.0 mmol, 1.0 equiv), $[Rh(CO)_2Cl]_2$ (59 mg, 0.15 mmol, 0.75 equiv), and *m*-xylene (20 mL, 0.10 M) following General Procedure D. The crude residue was purified by column chromatography (silica, 30 to 40% EtOAc/hexanes) to afford **7d** (336 mg, 84% yield) as a white powder.

Spectral data matched those reported in the literature.[17]

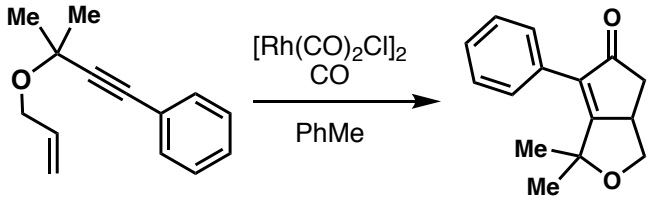
(3-(allyloxy)-3-methylbut-1-yn-1-yl)benzene (29)



Prepared from 2-methyl-4-phenylbut-3-yn-2-ol (801 mg, 5.0 mmol, 1.0 equiv), allyl bromide (0.87 mL, 10.0 mmol, 2.0 equiv), NaH (95%, 158 mg, 6.25 mmol, 1.25 equiv), and THF (10 mL, 0.50 M) following General Procedure A. The resulting yellow oil of **29** (283 mg, 48% yield) was used without further purification.

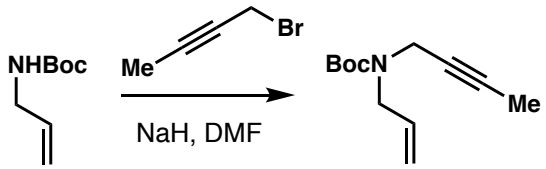
Spectral data matched those reported in the literature.[18]

1,1-dimethyl-6-phenyl-3a,4-dihydro-1*H*-cyclopenta[*c*]furan-5(3*H*)-one (7e)



Prepared from **29** (20.0 mg, 0.1 mmol, 1.0 equiv), $[Rh(CO)_2Cl]_2$ (2.9 mg, 0.0075 mmol, 0.075 equiv), and PhMe (1 mL, 0.10 M) following General Procedure D. The crude residue was purified by column chromatography (silica, 15 to 25% EtOAc/hexanes) to yield **7e** (15.5 mg, 68% yield) as a white powder. Spectral data matched those reported in the literature.[18]

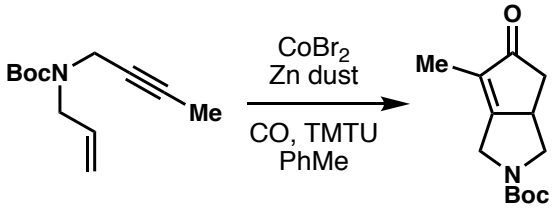
***tert*-butyl allyl(but-2-yn-1-yl)carbamate (30)**



Prepared from *tert*-butyl allylcarbamate (786 mg, 5.0 mmol, 1.0 equiv), 1-bromobut-2-yne (0.44 mL, 5.0 mmol, 1.0 equiv), NaH (95%, 168 mg, 7.0 mmol, 1.4 equiv), and DMF (20 mL, 0.25 M) following General Procedure A. The crude residue of **30** was used in the next step without further purification (881 mg, 85% yield).

Spectral data matched those reported in the literature.[17]

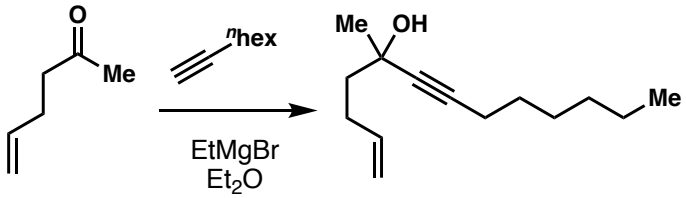
***tert*-butyl 6-methyl-5-oxo-3,3a,4,5-tetrahydrocyclopenta[*c*]pyrrole-2(1*H*)-carboxylate (7f)**



To a dry vial with a Teflon-coated stir bar was added $CoBr_2$ (22 mg, 0.1 mmol, 0.1 equiv) in a glovebox. The flask was sealed with a rubber septum, removed from the glovebox, and placed under an atmosphere of dry CO via balloon. CAUTION: all manipulations with CO should be performed in a well-ventilated fume hood. Zinc dust (131 mg, 2.0 mmol, 2.0 equiv) and tetramethyltiourea (80 mg, 0.6 mmol, 0.6 equiv) were then added and the solids taken up in PhMe (20 mL, 0.50 M) and stirred. The solution was degassed with CO for 5 min and the reaction kept under an atmosphere of CO following addition of **30** (295 mg, 1.0 mmol, 1.0 equiv). The reaction was brought to 70 °C in a preheated oil bath and monitored by TLC. Upon

complete consumption of the enyne (typically indicated by a color change from deep green to light turquoise green or colorless), the reaction mixture was filtered over a pad of silica gel and celite, eluting with EtOAc. The filtrate was concentrated, and the crude residue was purified by column chromatography (silica, 30 to 40% EtOAc/hexanes) to afford **7f** (165 mg, 70% yield) as an off-white, amorphous solid.
Spectral data matched those reported in the literature.[17]

5-methyltridec-1-en-6-yn-5-ol (31)



To a dry round-bottom flask with a Teflon-coated stir bar was added oct-1-yne (8.9 mL, 60.0 mmol, 3.0 equiv) and Et_2O (100 mL, 0.1 M). 3 M EtMgBr in Et_2O (20.0 mL, 60.0 mmol, 3.0 equiv) was then added dropwise. The solution was then heated to 30 ºC for 1 h then allowed to reach room temperature. To a separate dry round-bottom flask with a Teflon-coated stir bar was added hex-5-en-2-one (2.3 mL, 20.0 mmol, 1.0 equiv) and Et_2O (80 mL). This solution was added to the first solution slowly via canula. The reaction was allowed to stir at room temperature and monitored by TLC. Upon completion, the reaction was quenched by dropwise addition of sat. aq. NH_4Cl. The resulting mixture was diluted with Et_2O and water and the layers separated. The aqueous layer was extracted twice with Et_2O. Combined organics were washed with water and brine, dried over Na_2SO_4, filtered, and concentrated. The crude residue was purified by column chromatography (silica, 15 to 20% Et_2O/hexanes) to afford **31** (2.89 g, 70% yield) as a colorless oil.

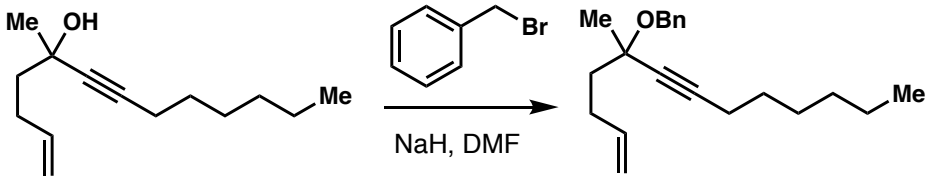
^{1}H NMR (500 MHz, $CDCl_3$) δ 5.88 (ddt, *J* = 16.9, 10.1, 6.6 Hz, 1H), 5.07 (dq, *J* = 17.1, 1.7 Hz, 1H), 4.98 (ddt, *J* = 10.2, 1.8, 1.3 Hz, 1H), 2.37 – 2.22 (m, 2H), 2.19 (t, *J* = 7.1 Hz, 2H), 1.96 – 1.91 (m, 1H), 1.80 – 1.66 (m, 2H), 1.55 – 1.48 (m, 2H), 1.47 (s, 3H), 1.43 – 1.35 (m, 2H), 1.35 – 1.24 (m, 3H), 0.90 (t, *J* = 7.0 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 138.74, 114.81, 84.41, 83.80, 68.39, 43.03, 31.44, 30.46, 29.53, 28.81, 28.64, 22.69, 18.73, 14.18.

FTIR (NaCl, thin film, cm^{-1}): 3364, 3078, 2930, 2859, 2239, 1642, 1455, 1371, 1127.

HRMS (TOF-ESI, m/z): calc'd for $C_{14}H_{24}O$: 191.1800 $[M–H_2O+H]^+$; found: 191.1794.

(((5-methyltridec-1-en-6-yn-5-yl)oxy)methyl)benzene (32)



Prepared from **31** (1.04 g, 5.0 mmol, 1.0 equiv), benzyl bromide (0.66 mL, 5.5 mmol, 1.1 equiv), NaH (95%, 139 mg, 5.5 mmol, 1.1 equiv), and DMF (20 mL, 0.25 M) following General Procedure A. The resulting crude residue of **32** was used in the next step without further purification (1.46 g, 98% yield).

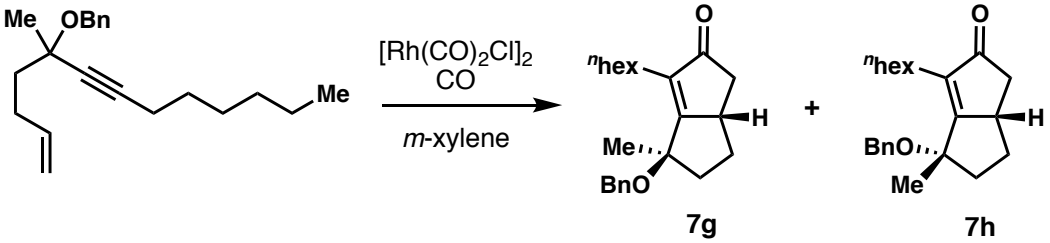
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.33 (m, 3H), 7.35 – 7.21 (m, 2H), 5.87 (ddt, *J* = 16.8, 10.2, 6.5 Hz, 1H), 5.04 (dq, *J* = 17.2, 1.7 Hz, 1H), 4.95 (ddt, *J* = 10.2, 2.3, 1.3 Hz, 1H), 4.67 (d, *J* = 11.2 Hz, 1H), 4.57 (d, *J* = 11.2 Hz, 1H), 2.42 – 2.25 (m, 1H), 2.23 (t, *J* = 7.0 Hz, 2H), 1.92 – 1.71 (m, 2H), 1.60 – 1.48 (m, 2H), 1.48 (s, 3H), 1.45 – 1.35 (m, 2H), 1.29 (ddtt, *J* = 10.0, 7.1, 5.1, 2.5 Hz, 3H), 0.96 – 0.82 (m, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 139.64, 138.90, 128.37, 127.73, 127.32, 114.37, 86.46, 81.41, 73.80, 66.17, 41.38, 31.45, 29.08, 28.91, 28.64, 26.97, 22.71, 18.79, 14.19.

FTIR (NaCl, thin film, cm^{-1}): 2931, 2860, 2237, 1455, 1088, 1062, 911, 731, 697.

HRMS (TOF-ESI, m/z): calc'd for $C_{21}H_{30}O$: 299.2369 $[M+H]^+$; found: 299.2378.

(4*R*,6a*S*)-4-(benzyloxy)-3-hexyl-4-methyl-4,5,6,6a-tetrahydropentalen-2(1*H*)-one (7g) and **(4*S*,6a*S*)-4-(benzyloxy)-3-hexyl-4-methyl-4,5,6,6a-tetrahydropentalen-2(1*H*)-one (7h)**



Prepared from **32** (1.19 g, 4.0 mmol, 1.0 equiv), $[Rh(CO)_2Cl]_2$ (77.7 mg, 0.2 mmol, 0.05 equiv), and *m*-xylene (40 mL, 0.10 M) following General Procedure D. The crude residue was purified by column chromatography (silica, 15 to 30% EtOAc/hexanes) to afford **7g** (693 mg, 53% yield) and **7h** (312 mg, 24% yield) as off-white oils.

(7g):

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37 – 7.25 (m, 5H), 4.45 (d, *J* = 10.8 Hz, 1H), 4.36 (d, *J* = 10.7 Hz, 1H), 3.11 (d, *J* = 8.8 Hz, 1H), 2.68 (dd, *J* = 17.9, 6.4 Hz, 1H), 2.42 – 2.26 (m, 3H), 2.22 (dtd, *J* = 12.3, 8.1, 2.8 Hz, 1H), 2.08 (dd, *J* = 17.9, 3.3 Hz, 1H), 1.99 (ddd, *J* = 13.6, 8.9, 2.8 Hz, 1H), 1.66 (s, 3H), 1.56 (d, *J* = 1.1 Hz, 1H), 1.58 – 1.15 (m, 9H), 0.92 – 0.85 (m, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 211.84, 179.39, 139.80, 139.20, 129.01, 128.16, 128.07, 81.63, 66.98,

43.78, 43.18, 42.03, 32.21, 30.37, 29.45, 28.99, 24.37, 23.20, 23.13, 14.68.

FTIR (NaCl, thin film, cm^{-1}): 2930, 1713, 1652, 1462, 1086, 736, 697.

HRMS (TOF-ESI, m/z): calc'd for $C_{22}H_{30}O_2$: 327.2319 $[M+H]^+$; found: 327.2326.

(7h):

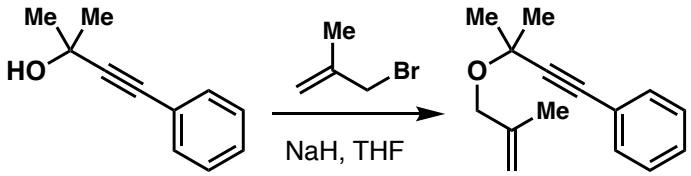
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.30 (m, 4H), 7.32 – 7.19 (m, 1H), 4.45 (d, *J* = 10.9 Hz, 1H), 4.26 (d, *J* = 11.2 Hz, 1H), 2.93 – 2.81 (m, 1H), 2.65 (dd, *J* = 17.9, 6.4 Hz, 1H), 2.47 – 2.39 (m, 1H), 2.39 – 2.25 (m, 2H), 2.19 – 2.09 (m, 3H), 1.95 (ddd, *J* = 14.5, 12.0, 7.4 Hz, 1H), 1.62 (s, 3H), 1.49 – 1.13 (m, 12H), 0.89 – 0.80 (m, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 210.71, 181.73, 138.82, 138.11, 128.50, 127.55, 127.34, 81.23, 65.78, 42.91, 42.04, 38.46, 31.80, 31.20, 29.82, 28.79, 27.48, 23.53, 23.37, 22.74, 14.23.

FTIR (NaCl, thin film, cm^{-1}): 2928, 2858, 1698, 1660, 1455, 1062, 733, 696.

HRMS (TOF-ESI, m/z): calc'd for $C_{22}H_{30}O_2$: 327.2319 $[M+H]^+$; found: 327.2314.

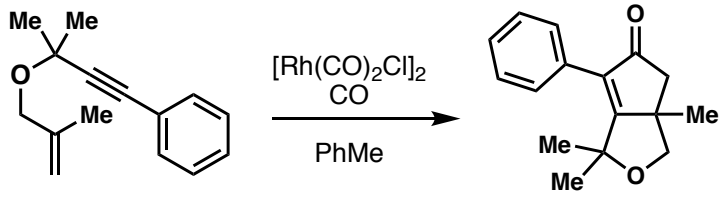
(3-methyl-3-((2-methylallyl)oxy)but-1-yn-1-yl)benzene (33)



Prepared from 2-methyl-4-phenylbut-3yn-2-ol (270 mg, 1.7 mmol, 1.0 equiv), methallyl bromide (0.3 mL, 3.4 mmol, 2.0 equiv), NaH (95%, 53.2 mg, 2.1 mmol, 1.25 equiv), and THF (3.4 mL, 0.50 M) following General Procedure A. The crude residue was purified by column chromatography (silica, 0 to 10% EtOAc/hexanes) to afford **33** (127 mg, 35% yield) as a white powder.

Spectral data matched those reported in the literature.[19]

1,1,3a-trimethyl-6-phenyl-3a,4-dihydro-1*H*-cyclopenta[*c*]furan-5(3*H*)-one (6f)



Prepared from **33** (60 mg, 0.28 mmol, 1.0 equiv), $[Rh(CO)_2Cl]_2$ (10.9 mg, 0.03 mmol, 0.1 equiv), and PhMe (1.4 mL, 0.20 M) following General Procedure D. The crude residue was purified by column chromatography (silica, 7% EtOAc/hexanes) to afford **6f** (21.7 mg, 32% yield) as a white powder.

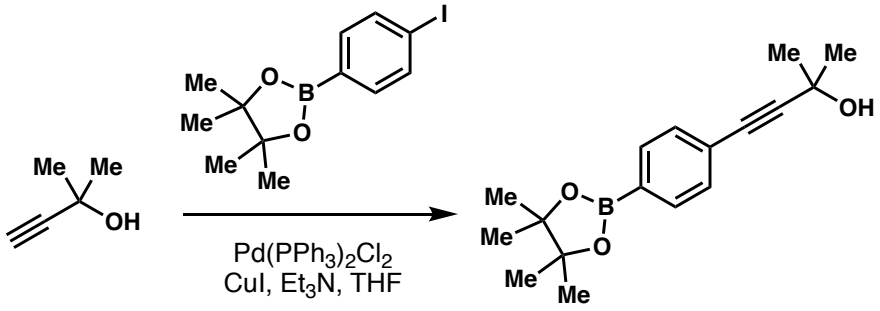
^{1}H NMR (400 MHz, 1,4-dioxane-*d*$_8$) δ 7.23 – 7.00 (m, 5H), 3.66 (d, *J* = 8.3 Hz, 1H), 3.25 (d, *J* = 8.3 Hz, 1H), 2.23 (q, *J* = 16.9 Hz, 2H), 1.46 (s, 3H), 1.21 (s, 3H), 0.77 (s, 3H).

^{13}C NMR (101 MHz, 1,4-dioxane-d_8) δ 206.54, 188.15, 135.69, 132.59, 130.11, 129.02, 128.94, 79.53, 75.42, 50.96, 49.25, 29.93, 26.00, 25.20.

FTIR (NaCl, thin film, cm^{-1}): 2974, 2928, 2852, 1713, 1652, 1235, 1137, 1018, 699.

HRMS (TOF-ESI, m/z): calc'd for $C_{16}H_{18}O_2$: 243.1380 $[M+H]^+$; found: 243.1385.

2-methyl-4-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)but-3-yn-2-ol (34)



Prepared from 2-methylbut-3-yn-2-ol (0.12 mL, 1.2 mmol, 1.0 equiv), 4-iodophenylboronic acid pinacol ester (450 mg, 1.4 mmol, 1.1 equiv), $Pd(PPh_3)_2Cl_2$ (8.7 mg, 0.012 mmol, 0.01 equiv), CuI (4.7 mg, 0.025 mmol, 0.02 equiv), and Et_3N (0.52 mL, 3.7 mmol, 3.0 equiv), and THF (1.2 mL, 1.00 M) following General Procedure B. The crude residue was purified by column chromatography (silica, 0 to 20% Et_2O/hexanes) to afford **34** (355 mg, 73% yield) as a pale yellow powder.

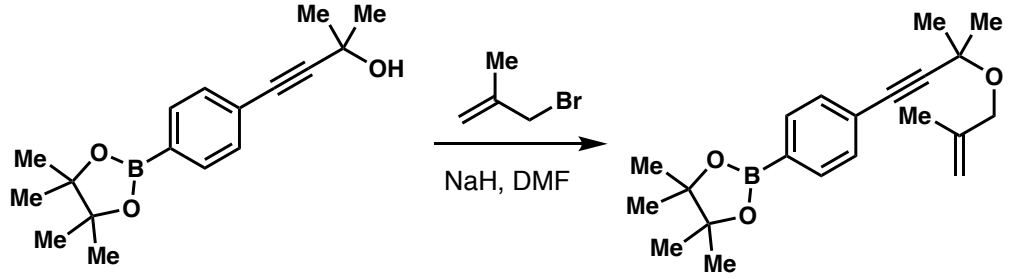
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 – 7.70 (m, 2H), 7.44 – 7.37 (m, 2H), 1.62 (s, 6H), 1.34 (s, 12H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 134.64, 130.96, 125.54, 114.80, 95.13, 84.11, 82.45, 65.81, 31.60, 25.03.

FTIR (NaCl, thin film, cm^{-1}): 3390, 2981, 2933, 1608, 1393, 1364, 1146, 1088, 963, 858, 658.

HRMS (TOF-ESI, m/z): calc'd for $C_{17}H_{23}BO_3$: 268.1744 $[M–H_2O+H]^+$; found: 268.1743.

4,4,5,5-tetramethyl-2-(4-(3-methyl-3-((2-methylallyl)oxy)but-1-yn-1-yl)phenyl)-1,3,2-dioxaborolane (35)



Prepared **34** (242 mg, 0.7 mmol, 1.0 equiv), methallyl bromide (0.7 mL, 1.7 mmol, 2.5 equiv), NaH (95%, 32 mg, 1.3 mmol, 1.9 equiv), and DMF (3.4 mL, 0.20 M) following General Procedure A. The crude residue was purified by column chromatography (silica, 0 to 20% EtOAc/hexanes) to afford **35** (75 mg, 33% yield) as a yellow powder.

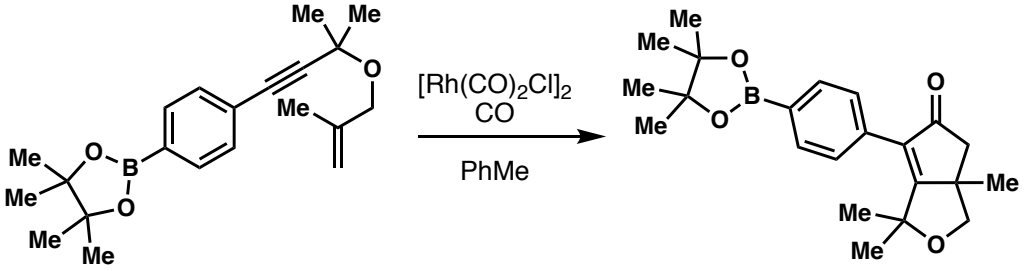
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 – 7.70 (m, 2H), 7.44 – 7.37 (m, 2H), 5.05 – 5.00 (m, 1H), 4.90 – 4.84 (m, 1H), 4.07 (s, 2H), 1.81 – 1.76 (m, 3H), 1.57 (s, 6H), 1.34 (s, 12H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 143.14, 134.65, 130.96, 125.77, 111.72, 93.02, 84.34, 84.10, 70.98, 68.61, 29.02, 25.02, 19.94.

FTIR (NaCl, thin film, cm^{-1}): 2981, 2931, 2856, 1608, 1398, 1360, 1323, 1144, 1089.

HRMS (TOF-ESI, m/z): calc'd for $C_{21}H_{29}BO_3$: 268.1744 $[M–C_4H_7O+H]^+$; found: 268.1741.

1,1,3a-trimethyl-6-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)-3a,4-dihydro-1*H*-cyclopenta[*c*]furan-5(3*H*)-one (6g)



Prepared from **35** (75.4 mg, 0.22 mmol), $[Rh(CO)_2Cl]_2$ (8.6 mg, 0.022 mmol, 0.1 equiv), and PhMe (1.1 mL, 0.20 M), following General Procedure D. The crude residue was purified by column chromatography (silica, 7% EtOAc/hexanes) to yield **6g** (25.1 mg, 31% yield) as an off-white powder.

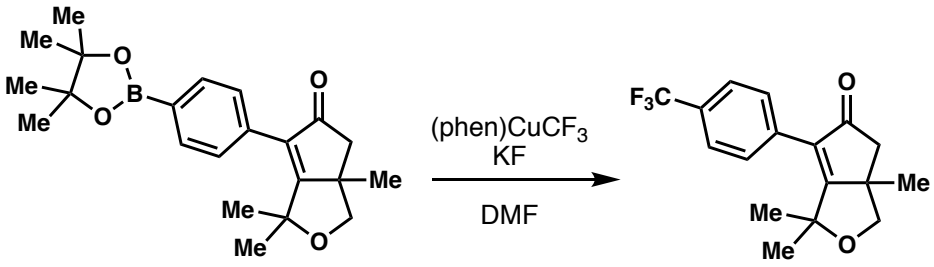
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 – 7.77 (m, 2H), 7.28 – 7.22 (m, 2H), 3.97 (d, J = 8.4 Hz, 1H), 3.53 (d, J = 8.4 Hz, 1H), 2.50 (s, 2H), 1.69 (s, 3H), 1.46 (s, 3H), 1.32 (s, 12H), 1.01 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 207.10, 188.65, 135.30, 134.74, 133.86, 128.44, 83.93, 79.26, 75.01, 50.40, 49.09, 29.47, 25.90, 24.99, 24.93, 24.88, 24.84, 14.22 (C_{Ar}–B not observed).

FTIR (NaCl, thin film, cm^{-1}): 2978, 2927, 2850, 1711, 1610, 1399, 1360, 1144, 1088, 1021.

HRMS (TOF-ESI, m/z): calc'd for $C_{22}H_{29}BO_4$: 368.2268 $[M+H]^+$; found: 368.2278.

1,1,3a-trimethyl-6-(4-(trifluoromethyl)phenyl)-3a,4-dihydro-1*H*-cyclopenta[*c*]furan-5(3*H*)-one (6h)



Prepared from **6g** (60.0 mg, 0.16 mmol, 1.0 equiv), $(phen)CuCF_3$ (61.1 mg, 0.2 mmol, 1.25 equiv), KF (9.46 mg, 0.16 mmol, 1.0 equiv), and DMF (1.63 mL, 0.10 M) at 100 ºC following a literature procedure.[20] The crude residue was purified by column chromatography (silica, 0 to 20% EtOAc/hex) to yield **6h** (24.5

mg, 48% yield) as an off-white powder.

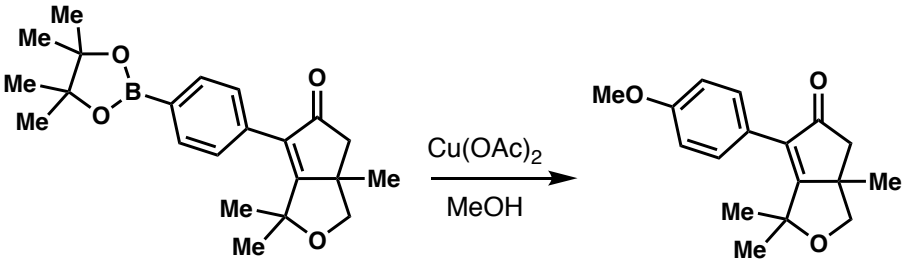
^{1}H NMR (400 MHz, 1,4-dioxane-*d*$_8$) δ 7.50 (d, *J* = 8.1 Hz, 2H), 7.24 (d, *J* = 8.1 Hz, 2H), 3.69 (d, *J* = 8.3 Hz, 1H), 3.28 (d, *J* = 8.4 Hz, 1H), 2.26 (q, *J* = 17.0 Hz, 2H), 1.47 (s, 3H), 1.22 (s, 3H), 0.78 (s, 3H).

^{13}C NMR (101 MHz, 1,4-dioxane-*d*$_8$) δ 206.01, 190.02, 136.45, 134.54, 130.69 (q, $^2J_{CF}$ = 32 Hz), 130.58, 126.05 (q, $^3J_{CF}$ = 4 Hz), 125.24 (q, $^1J_{CF}$ = 272 Hz), 79.53, 75.32, 51.30, 49.20, 29.75, 25.92, 25.36.

FTIR (NaCl, thin film, cm^{-1}): 2977, 2933, 2851, 1712, 1325, 1163, 1127, 1067, 1018.

HRMS (TOF-ESI, m/z): calc'd for $C_{17}H_{18}F_3O_2$: 311.1253 $[M+H]^+$; found: 311.1258.

6-(4-methoxyphenyl)-1,1,3a-trimethyl-3a,4-dihydro-1*H*-cyclopenta[*c*]furan-5(3*H*)-one (6i)



Prepared from **6g** (60 mg, 0.16 mmol, 1.0 equiv), $Cu(OAc)_2$ (3.0 mg, 0.016 mmol, 0.1 equiv), MeOH (0.8 mL, 0.20 M), and a balloon of O_2 following a literature procedure.[21] The crude residue was purified by column chromatography (silica, 0 to 20% EtOAc/hexanes) to yield **6i** (17 mg, 39% yield) as an off-white powder.

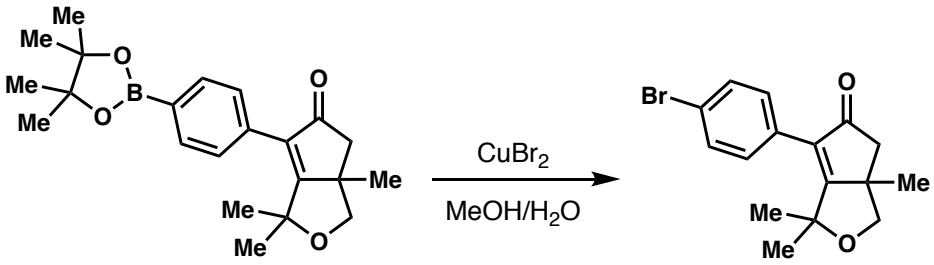
^{1}H NMR (400 MHz, 1,4-dioxane-*d*$_8$) δ 7.05 – 6.97 (m, 2H), 6.75 – 6.66 (m, 2H), 3.65 (d, *J* = 8.2 Hz, 1H), 3.23 (d, *J* = 8.1 Hz, 1H), 2.24 – 2.11 (m, 2H), 1.46 (s, 3H), 1.19 (s, 3H), 0.80 (s, 3H).

^{13}C NMR (101 MHz, 1,4-dioxane-*d*$_8$) δ 207.02, 186.72, 160.67, 135.20, 131.32, 124.68, 114.38, 79.53, 75.48, 55.34, 50.79, 49.16, 29.97, 26.03, 25.04.

FTIR (NaCl, thin film, cm^{-1}): 2974, 2934, 2852, 2342, 1706, 1512, 1249, 1018, 1031.

HRMS (TOF-ESI, m/z): calc'd for $C_{17}H_{20}O_3$: 273.1485 $[M+H]^+$; found: 273.1498.

6-(4-bromophenyl)-1,1,3a-trimethyl-3a,4-dihydro-1*H*-cyclopenta[*c*]furan-5(3*H*)-one (6j)



Prepared from **6g** (54 mg, 0.15 mmol, 1.0 equiv), $CuBr_2$ (32.7 mg, 0.15 mmol, 1.0 equiv), MeOH (1.8 mL, 0.04 M), and H_2O (1.8 mL, 0.04 M) at 100 ºC following a literature procedure.[22] The crude residue was

purified by column chromatography (silica, 0 to 20% EtOAc/hexanes) to yield **6j** (26.8 mg, 57% yield) as an off-white powder.

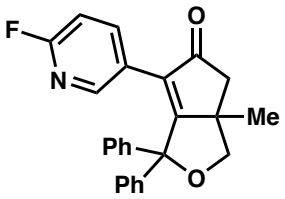
^{1}H NMR (400 MHz, 1,4-dioxane-*d*$_8$) δ 7.40 – 7.30 (m, 2H), 7.05 – 6.95 (m, 2H), 3.67 (d, *J* = 8.3 Hz, 1H), 3.25 (d, *J* = 8.3 Hz, 1H), 2.30 – 2.14 (m, 2H), 1.45 (s, 3H), 1.20 (s, 3H), 0.79 (s, 3H).

^{13}C NMR (101 MHz, 1,4-dioxane-*d*$_8$) δ 206.21, 188.84, 134.61, 132.28, 131.83, 131.52, 123.11, 79.52, 75.35, 51.12, 49.15, 29.82, 25.93, 25.22.

FTIR (NaCl, thin film, cm^{-1}): 2974, 2928, 2849, 1708, 1487, 1234, 1013.

HRMS (TOF-ESI, m/z): calc'd for $C_{16}H_{17}BrO_2$: 321.0485 $[M+H]^+$; found: 321.0475.

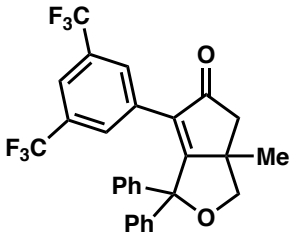
6-(6-fluoropyridin-3-yl)-3a-methyl-1,1-diphenyl-3a,4-dihydro-1*H*-cyclopenta[*c*]furan-5(3*H*)-one (6k)



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (dt, *J* = 2.5, 0.8 Hz, 1H), 7.46 – 7.35 (m, 5H), 7.17 (ddd, *J* = 8.5, 7.6, 2.5 Hz, 1H), 7.06 – 6.93 (m, 3H), 6.84 – 6.76 (m, 2H), 6.59 (ddd, *J* = 8.4, 3.0, 0.7 Hz, 1H), 4.37 (d, *J* = 8.1 Hz, 1H), 4.17 (dd, *J* = 8.2, 0.8 Hz, 1H), 2.77 (d, *J* = 17.7 Hz, 1H), 2.68 (d, *J* = 17.6 Hz, 1H), 1.31 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 206.84, 186.03, 164.27, 161.87, 147.82, 147.67, 143.10, 142.03, 141.57, 141.49, 135.07, 128.66, 128.57, 127.93, 127.80, 127.71, 127.68, 124.09, 124.04, 108.79, 108.42, 87.95, 78.79, 50.28, 49.55, 27.34.

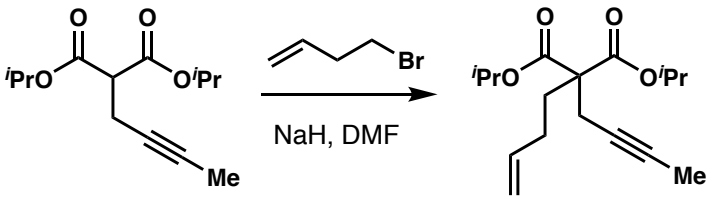
6-(3,5-bis(trifluoromethyl)phenyl)-3a-methyl-1,1-diphenyl-3a,4-dihydro-1*H*-cyclopenta[*c*]furan-5(3*H*)-one (6l)



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (tt, *J* = 1.6, 0.8 Hz, 1H), 7.50 – 7.37 (m, 5H), 7.30 (d, *J* = 1.8 Hz, 2H), 7.00 – 6.93 (m, 1H), 6.93 – 6.84 (m, 2H), 6.75 – 6.67 (m, 2H), 4.39 (d, *J* = 8.2 Hz, 1H), 4.23 – 4.16 (m, 1H), 2.81 (d, *J* = 17.6 Hz, 1H), 2.71 (d, *J* = 17.7 Hz, 1H), 1.32 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 206.16, 186.80, 142.83, 141.75, 136.76, 132.24, 131.50, 131.17, 130.84, 129.29, 128.66, 128.08, 127.68, 127.60, 127.52, 124.44, 121.90, 121.72, 87.88, 78.76, 50.27, 49.67, 27.29.

diisopropyl 2-(but-2-yn-1-yl)-2-(but-3-en-1-yl)malonate (36)

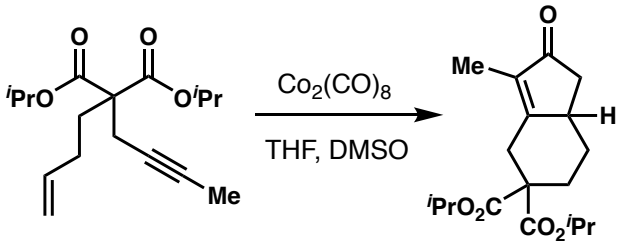


Prepared from **16** (361 mg, 1.5 mmol, 1.0 equiv), homoallyl bromide (0.23 mL, 2.25 mmol, 1.5 equiv), NaH (95%, 57.0 mg, 2.25 mmol, 1.5 equiv), and DMF (3 mL, 0.50 M) following General Procedure A. The crude, clear colorless oil of **36** was used without further purification (417 mg, 93% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.81 (ddt, *J* = 16.7, 10.2, 6.4 Hz, 1H), 5.11 – 5.00 (m, 3H), 4.97 (dq, *J* = 10.1, 1.3 Hz, 1H), 2.73 (q, *J* = 2.6 Hz, 2H), 2.14 – 2.05 (m, 2H), 2.01 – 1.91 (m, 2H), 1.74 (t, *J* = 2.6 Hz, 3H), 1.22 (dd, *J* = 6.3, 1.7 Hz, 13H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.15, 137.89, 115.10, 78.60, 77.48, 77.16, 76.84, 73.63, 68.92, 56.91, 31.19, 28.48, 23.14, 21.71, 21.67, 3.61.

diisopropyl 3-methyl-2-oxo-1,2,4,6,7,7a-hexahydro-5*H*-indene-5,5-dicarboxylate (37)



Prepared from **36** (368 mg, 1.25 mmol, 1.0 equiv), $Co_2(CO)_8$ (513 mg, 1.5 mmol, 1.2 equiv), DMSO (0.89 mL, 12.5 mmol, 10.0 equiv), and THF (12.5 mL, 0.10 M) following General Procedure C. The crude residue was purified by column chromatography (silica, 55 to 65% Et_2O/hexanes) to afford **37** (165 mg, 41% yield) as a white, amorphous solid.

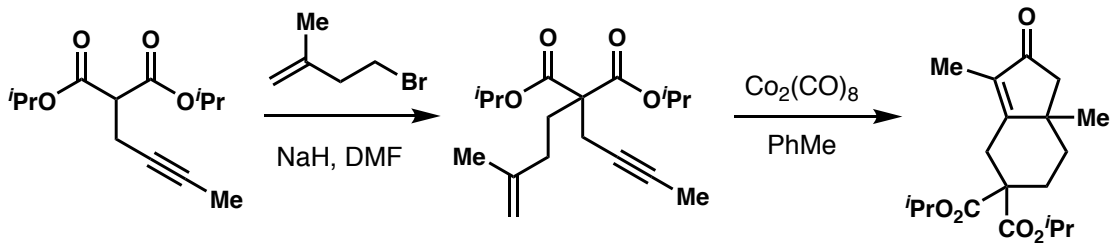
^{1}H NMR (400 MHz, $CDCl_3$) δ 5.04 (dhept, *J* = 22.4, 6.3 Hz, 2H), 3.49 (dd, *J* = 14.0, 2.3 Hz, 1H), 2.64 – 2.42 (m, 4H), 2.12 (ddt, *J* = 13.5, 5.4, 3.4 Hz, 1H), 1.99 – 1.87 (m, 2H), 1.75 (t, *J* = 1.6 Hz, 3H), 1.29 – 1.17 (m, 13H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 208.62, 170.97, 170.32, 169.41, 136.06, 77.48, 77.16, 76.84, 69.63, 69.18, 56.46, 41.00, 39.31, 33.25, 31.00, 30.70, 21.71, 21.70, 21.69, 21.67, 8.00.

FTIR (NaCl, thin film, cm^{-1}): 3446, 2980, 2932, 2873, 1723, 1714, 1696, 1453, 1373, 1254, 1107.

HRMS (GC-EI+, m/z): calc'd for $C_{18}H_{26}O_5$: 322.1780 $[M]^+$; found: 322.1782.

diisopropyl 3,7a-dimethyl-2-oxo-1,2,4,6,7,7a-hexahydro-5*H*-indene-5,5-dicarboxylate (38)



Prepared in two steps. Intermediate prepared from **16** (800 mg, 3.3 mmol, 1.0 equiv), 4-bromo-2-methylbut-

1-ene (0.44 mL, 3.6 mmol, 1.1 equiv), NaH (95%, 151 mg, 6.0 mmol, 1.8 equiv), and DMF (4.15 mL, 0.80 M) following General Procedure A. The crude residue was purified by column chromatography (silica, 2% EtOAc/hexanes) to afford the crude intermediate (433 mg, 42% yield) as a colorless oil. The intermediate (308 mg, 1.0 mmol, 1.0 equiv) was then used directly in the next step with $Co_2(CO)_8$ (410 mg, 1.2 mmol, 1.2 equiv) and PhMe (10 mL, 0.10 M), following modified General Procedure C without addition of DMSO. Upon complete conversion of the enyne to the Co-alkyne complex, the reaction was placed in a preheated oil bath at 110 °C. Upon complete consumption of the Co-alkyne complex, the reaction was allowed to reach room temperature, filtered over a pad of SiO_2 and Celite, and the filtrate concentrated. The crude residue was purified by column chromatography (silica, 10 to 20 to 35% EtOAc/hexanes) to afford **38** (134 mg, 40% yield) as a clear oil.

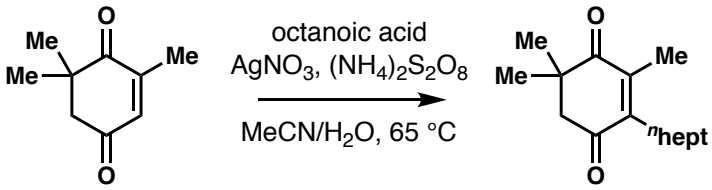
^{1}H NMR (400 MHz, $CDCl_3$) δ 5.03 (dp, *J* = 26.7, 6.3 Hz, 2H), 3.35 (dd, *J* = 14.0, 2.3 Hz, 1H), 2.67 (dd, *J* = 14.0, 1.7 Hz, 1H), 2.39 – 2.31 (m, 1H), 2.31 – 2.12 (m, 2H), 2.06 (td, *J* = 14.1, 4.0 Hz, 1H), 1.87 (ddd, *J* = 13.6, 3.9, 2.8 Hz, 1H), 1.72 (d, *J* = 1.4 Hz, 3H), 1.51 (td, *J* = 13.8, 4.0 Hz, 1H), 1.29 – 1.17 (m, 16H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 207.88, 173.62, 170.97, 169.30, 135.44, 77.48, 77.16, 76.84, 69.63, 69.21, 56.86, 51.02, 40.64, 36.46, 29.74, 27.66, 24.56, 21.71, 21.68, 8.16.

FTIR (NaCl, thin film, cm^{-1}): 3456, 3394, 2980, 2924, 2870, 2049, 2021, 1731, 1704, 1659, 1456.

HRMS (GC-EI+, m/z): calc'd for $C_{19}H_{28}O_5$: 336.1937 $[M]^+$; found: 336.1919.

2-heptyl-3,5,5-trimethylcyclohex-2-ene-1,4-dione (39)



To a dry round-bottomed flask with a Teflon-coated stir bar was added ketoisophorone (0.74 mL, 5.0 mmol, 1.0 equiv), MeCN (15 mL), and H_2O (3 mL). Octanoic acid (1.98 mL, 12.5 mmol, 2.5 equiv) was added, and the mixture was stirred placed in a preheated oil bath at 65 °C. Silver nitrate (170 mg, 1.00 mmol, 0.20 equiv) was added in a single portion, and the flask was sealed with a rubber septum and flushed with N_2. Ammonium persulfate (1.49 g, 6.50 mmol, 1.3 equiv) was added as a solution in MeCN (15 mL) and H_2O (12 mL) (0.1 M final concentration) over 1.5 h via syringe pump. Upon complete consumption of the ketoisophorone as judged by TLC, the reaction was allowed to reach room temperature and concentrated to approximately ½ volume. The resulting liquid was extracted three times with EtOAc. Combined organics were washed with sat. aq. $NaHCO_3$ and brine, dried over Na_2SO_4, filtered, and concentrated. The crude residue was purified by column chromatography (silica, 5 to 10% Et_2O/hexanes) to afford **39** (380 mg, 31% yield) as a clear oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 2.70 (s, 2H), 2.41 (dd, *J* = 8.3, 6.4 Hz, 2H), 1.99 (s, 3H), 1.39 – 1.24 (m, 10H), 1.21 (s, 6H), 0.90 – 0.84 (m, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 203.74, 197.83, 149.20, 143.45, 77.48, 77.16, 76.84, 52.01, 45.23, 31.87, 30.01, 29.22, 28.46, 27.05, 26.38, 22.76, 14.22, 13.19.

FTIR (NaCl, thin film, cm^{-1}): 3340, 2957, 2923, 2856, 1682, 1614, 1469, 1378, 1276.

HRMS (GC-FAB+, m/z): calc'd for $C_{16}H_{27}O_2$: 251.2011 $[M+H]^+$; found: 251.2001.

3. SeO_2-Mediated Oxidative Transpositions

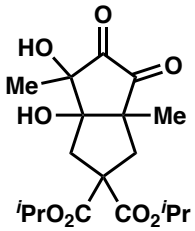
Reaction Optimization: General Procedure F

To a flame-dried vial with a Teflon-coated stir bar was added **6a** or **7a** (1.0 equiv), SeO_2, and 4 Å molecular sieves (activated by flame-drying under high vacuum for 10 minutes), if applicable. To this mixture was added 1,4-dioxane (0.05 M) then H_2O, if applicable. The reaction was capped and sealed with Teflon tape, stirred, and brought to 100 °C in a preheated aluminum reaction block. The reaction was monitored by LCMS. When the reaction was judged to be complete, it was allowed to reach room temperature then concentrated. To the crude residue was added pyrazine as an internal standard, then the mixture was taken up in CD_3OD and filtered over a cotton plug into an NMR tube. Yield determined by ^{1}H NMR versus the internal standard.

Note: *The reactions were judged to be complete when the greatest amount of starting material had been consumed and the least amount of the desired product was degraded by further oxidation. This is particularly important for the trioxidation; usually, after two-thirds of the starting material converted, rapid degradation of the desired product was observed.*

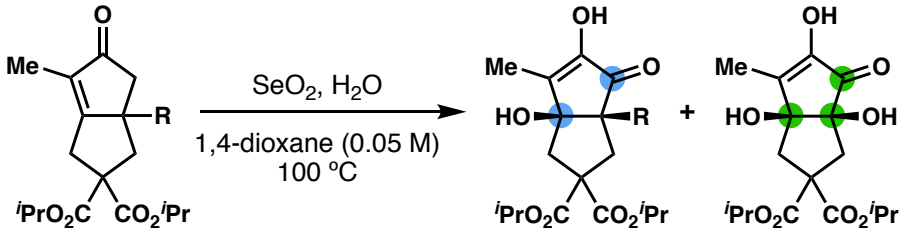
diisopropyl 3a,4-dihydroxy-4,6a-dimethyl-5,6-dioxohexahydropentalene-2,2(1*H*)-dicarboxylate (41)

Observed to be a major byproduct during optimization of **6a** subjected to dioxidation conditions, generally in 10–30% yield (by ^{1}H NMR versus an internal standard).



^{1}H NMR (400 MHz, CD_3OD) δ 5.08 (dp, *J* = 12.5, 6.2 Hz, 1H), 4.87 (p, *J* = 6.3 Hz, 1H), 3.01 (dd, *J* = 15.6, 1.2 Hz, 1H), 2.78 – 2.69 (m, 1H), 2.67 – 2.55 (m, 2H), 1.97 (s, 3H), 1.29 – 1.20 (m, 9H), 1.15 (dd, *J* = 7.2, 6.3 Hz, 5H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 202.54, 190.10, 173.51, 168.62, 102.83, 86.53, 77.36, 71.47, 69.94, 57.86, 55.94, 45.12, 42.98, 21.69, 21.53, 21.40, 18.75, 14.34.



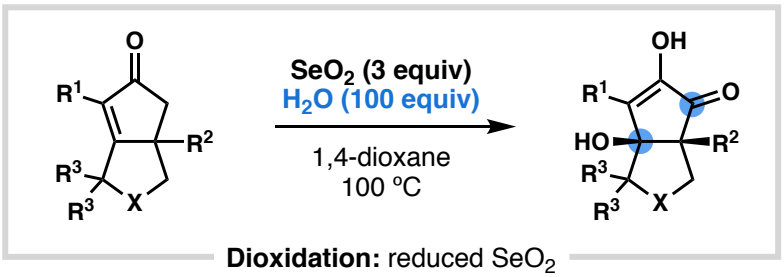
6a, R = Me
7a, R = H

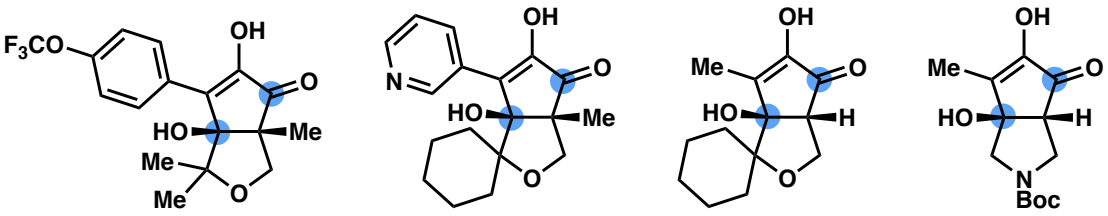
8a, R = Me
9a, R = H

10a

Entry	R	SeO_2 (equiv)	H_2O (equiv)	Time (h)	8a *or* 9a (%)[a]	10a (%)[a]	RSM (%)[a]	Scale (mmol)
1	Me	10	0	3	11	—	39	0.10
2[b]	Me	10	0	35	0	—	100	0.05
3	Me	10	10	24	13	—	2	0.03
4	Me	10	100	38	71[c]	—	0	1.00
5	Me	3	30	12	58	—	28	0.03
6	Me	3	30	24	32	—	0	0.03
7	Me	3	60	24	54	—	20	0.03
8	Me	3	100	48	62	—	24	0.03
9	Me	3	100	120	52	—	0	0.03
10	Me	1.5	15	24	29	—	25	0.03
11	Me	1.5	100	48	37	—	51	0.03
12	Me	1.5	100	120	42	—	39	0.03
13	H	10	0	2	0	21[c]	ND	0.02
14	H	10	10	1	0	15	ND	0.02
15	H	10	100	4	64[c]	0	ND	0.03
16	H	10	100	46	0	14	ND	0.07
17	H	3	0	3	0	10	ND	0.05
18	H	3	30	6	18	17	ND	0.02
19	H	3	100	14	7	15	ND	0.02

Table S1. Optimization of the di- and trioxidation reactions. [a]Yield determined by ^{1}H NMR versus an internal standard. [b]Reaction performed with 4 Å molecular sieves. [c]Isolated yield.



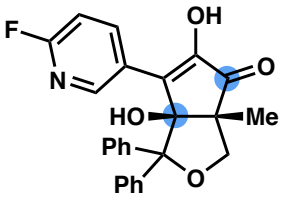


8e, 96% yield (76%)

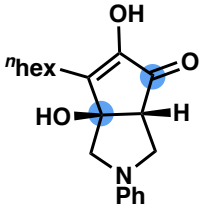
8b, 38% yield (64%)

9c, 2% yield (74%)

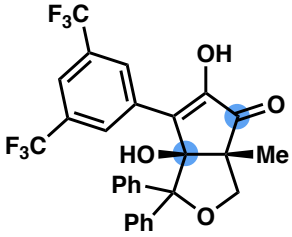
9f, 14% yield (57%)



8k, 0% yield (0%)
54% yield[a]

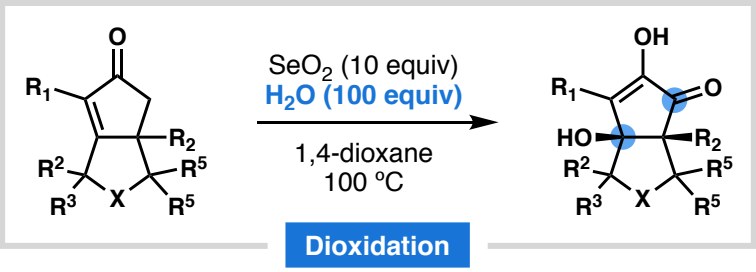


0% yield (0%)



8l, 15% yield (0%)
79% yield[a]

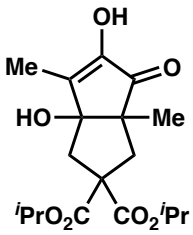
Table S2. Exploration of the generality of the dioxidation with reduced SeO_2 (3.0 equiv). Yields determined by ^1H NMR versus an internal standard. Yield in parentheses obtained under standard dioxidation conditions (SeO_2, 10.0 equiv). [a]Yield obtained under alternative dioxidation protocol conditions: SeO_2 (1.5 equiv), 1,4-dioxane (0.05 M), 100 ºC, 18 h; *then* H_2O (100.0 equiv), 0.5–3 h.



Dioxidation: General Procedure G

To a round-bottomed flask with a Teflon-coated stir bar was added the enone (**6a–e** or **7a–g**) (1.0 equiv), SeO_2 (10.0 equiv), 1,4-dioxane (0.05 M), and water (100.0 equiv). The reaction was sealed with a rubber septum, stirred, and brought to 100 °C in a preheated oil bath and monitored by TLC and/or LCMS. After the reaction was judged to be complete, typically 24–48 h (see note in General Procedure F), the reaction was allowed to reach room temperature and filtered over a pad of celite, washing with EtOAc. The filtrate was washed with sat. aq. $NaHCO_3$ twice then with water. The combined aqueous washings were extracted with EtOAc. The combined organics were dried over Na_2SO_4, filtered, and concentrated. The crude residue was purified by column chromatography to afford the desired product. Alternatively, some compounds could be purified by trituration.

diisopropyl 5,6a-dihydroxy-3a,6-dimethyl-4-oxo-3,3a,4,6a-tetrahydropentalene-2,2(1*H*)-dicarboxylate (8a)



Prepared from **6a** (323 mg, 1.0 mmol) following General Procedure G. The crude residue was purified by column chromatography (silica, 30 to 35% EtOAc/hexanes) to yield **8a** (251 mg, 71% yield) as an off-white powder.

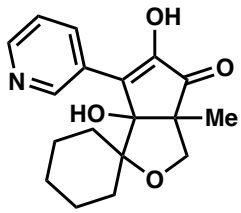
^{1}H NMR (400 MHz, CD_3OD) δ 5.08 (hept, J = 6.3 Hz, 1H), 4.97 (hept, J = 6.3 Hz, 1H), 3.36 (dq, J = 17.6, 1.9 Hz, 1H), 3.17 (d, J = 17.5 Hz, 1H), 2.55 (d, J = 13.6 Hz, 1H), 2.37 (s, 2H), 2.13 (d, J = 13.7 Hz, 1H), 1.67 (d, J = 1.7 Hz, 3H), 1.28 (dd, J = 6.2, 1.9 Hz, 6H), 1.21 (dd, J = 6.2, 2.9 Hz, 6H), 1.12 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 203.71, 171.01, 169.52, 148.40, 141.75, 85.25, 69.93, 69.61, 58.23, 53.88, 42.74, 42.42, 21.61, 21.60, 21.57, 21.47, 19.31, 9.09.

FTIR (NaCl, thin film, cm^{-1}): 3444, 2981, 2937, 1731, 1455, 1372, 1266, 1106, 912, 823.

HRMS (TOF-ESI, m/z): calc'd for $C_{18}H_{26}O_7$: 337.1646 $[M–H_2O+H]^+$; found: 337.1658.

5',6a'-dihydroxy-3a'-methyl-6'-(pyridin-3-yl)-3a',6a'-dihydrospiro[cyclohexane-1,1'-cyclopenta[*c*]furan]-4'(3'*H*)-one (8b)



Prepared from **6b** (14.4 mg, 0.05 mmol) following General Procedure G. The crude residue was purified by column chromatography (silica, 5% MeOH/DCM) to yield **8b** (10 mg, 64% yield) as an off-white powder.

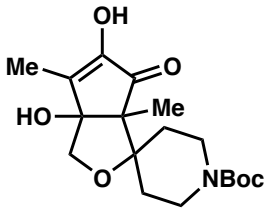
^{1}H NMR (400 MHz, pyridine-d_5) δ 10.25 (dd, *J* = 2.3, 0.9 Hz, 1H), 9.11 (dt, *J* = 8.1, 1.9 Hz, 1H), 8.70 (dd, *J* = 4.7, 1.7 Hz, 1H), 7.47 (s, 1H), 7.37 (ddd, *J* = 8.2, 4.7, 0.9 Hz, 1H), 3.76 (d, *J* = 9.4 Hz, 1H), 2.44 – 2.34 (m, 1H), 1.95 (td, *J* = 13.8, 4.1 Hz, 1H), 1.79 – 1.52 (m, 5H), 1.48 (s, 3H), 1.08 (qt, *J* = 13.1, 4.1 Hz, 1H).

^{13}C NMR (101 MHz, pyridine-d_5) δ 206.56, 153.09, 151.95, 150.63, 149.38, 137.32, 136.22, 135.72, 135.47, 133.14, 124.21, 123.72, 89.73, 86.24, 72.20, 58.90, 36.94, 29.16, 26.38, 23.93, 22.64, 17.80.

FTIR (NaCl, thin film, cm^{-1}): 3335, 2911, 2851, 2639, 2544, 2355, 2336, 2004, 1664, 1539.

HRMS (TOF-ESI, m/z): calc'd for $C_{18}H_{21}NO_4$: 316.1543 $[M+H]^+$; found: 316.1552.

***tert*-butyl 3a,5-dihydroxy-4,6a-dimethyl-6-oxo-3,3a,6,6a-tetrahydrospiro[cyclopenta[*c*]furan-1,4'-piperidine]-1'-carboxylate (8c)**



Prepared from **6c** (161 mg, 0.5 mmol) following General Procedure G. The crude residue was purified by column chromatography (silica, 5 to 7% MeOH/DCM) to yield **8c** (94 mg, 53% yield) as off-white powder.

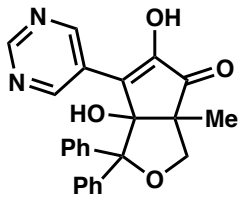
^{1}H NMR (400 MHz, $CDCl_3$) δ 3.95 (d, *J* = 10.0 Hz, 1H), 3.64 (d, *J* = 10.1 Hz, 1H), 2.94 (s, 2H), 1.99 (s, 3H), 1.92 – 1.74 (m, 2H), 1.74 – 1.58 (m, 2H), 1.45 (s, 10H), 1.38 – 1.27 (m, 1H), 1.02 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 200.79, 153.90, 147.50, 139.31, 85.58, 85.35, 81.65, 78.73, 69.57, 58.29, 32.10, 28.84, 27.58, 27.15, 13.06, 8.20.

FTIR (NaCl, thin film, cm^{-1}): 3367, 2975, 2933, 2874, 1682, 1428, 1367, 1289, 1251.

HRMS (TOF-ESI, m/z): calc'd for $C_{18}H_{27}NO_6$: 354.1911 $[M+H]^+$; found: 354.1926.

5,6a-dihydroxy-3a-methyl-1,1-diphenyl-6-(pyrimidin-5-yl)-1,3,3a,6a-tetrahydro-4*H*-cyclopenta[*c*]furan-4-one (8d)



Prepared from **6d** (18.4 mg, 0.05 mmol) following General Procedure G. The crude residue was purified by trituration from DCM and pentanes to yield **8d** (7 mg, 35% yield) as an off-white powder.

^{1}H NMR (400 MHz, pyridine-d_4) δ 9.12 (s, 1H), 8.54 (s, 2H), 7.78 (dd, *J* = 6.7, 3.0 Hz, 2H), 7.57 – 7.50 (m, 2H), 7.39 – 7.30 (m, 3H), 7.30 – 7.23 (m, 3H), 4.48 (d, *J* = 8.8 Hz, 1H), 3.87 (d,

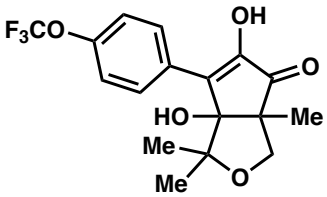
J = 8.8 Hz, 1H), 2.25 (s, 3H).

^{13}C NMR (101 MHz, pyridine-d_4) δ 202.69, 195.78, 186.85, 183.09, 182.92, 176.74, 176.47, 176.20, 169.54, 169.07, 162.36, 162.12, 161.87, 159.35, 157.26, 156.51, 155.15, 154.99, 154.86, 154.46, 154.26, 149.86, 121.19, 103.12, 83.26, 49.23, 26.56.

FTIR (NaCl, thin film, cm^{-1}): 3062, 2924, 2870, 2537, 2249, 1714, 1562, 1446, 1413, 1230, 1060.

HRMS (TOF-ESI, m/z): calc'd for $C_{24}H_{20}N_2O_4$: 401.1496 $[M+H]^+$; found: 401.1503.

5,6a-dihydroxy-1,1,3a-trimethyl-6-(4-(trifluoromethoxy)phenyl)-1,3,3a,6a-tetrahydro-4*H*-cyclopenta[*c*]furan-4-one (8e)



Prepared from **6e** (164 mg, 0.5 mmol) following General Procedure G. The crude residue was purified by trituration from DCM and pentanes to yield **8e** (135 mg, 76% yield) as an off-white powder.

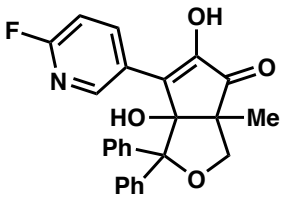
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.27 (d, *J* = 9.2 Hz, 10H), 6.25 (dt, *J* = 8.1, 1.0 Hz, 2H), 5.53 (s, 1H), 3.06 (d, *J* = 9.7 Hz, 1H), 2.71 – 2.62 (m, 1H), 1.39 (s, 1H), 0.39 (s, 3H), 0.23 (s, 3H), 0.02 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 204.08, 155.58, 149.35, 148.19, 135.62, 131.93, 131.67, 120.43, 89.18, 84.53, 71.45, 58.21, 26.87, 21.58, 16.51.

FTIR (NaCl, thin film, cm^{-1}): 3310, 2979, 2371, 2348, 1719, 1701, 1388, 1260, 1198.

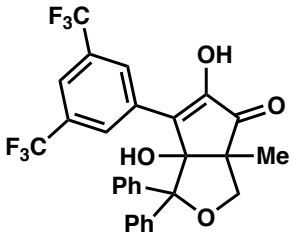
HRMS (TOF-ESI, m/z): calc'd for $C_{17}H_{17}F_3O_5$: 359.1101 $[M+H]^+$; found: 359.1114.

6-(6-fluoropyridin-3-yl)-5,6a-dihydroxy-3a-methyl-1,1-diphenyl-1,3,3a,6a-tetrahydro-4*H*-cyclopenta[*c*]furan-4-one (8k)



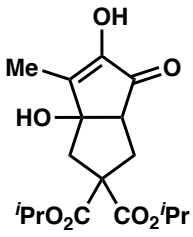
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 – 7.92 (m, 1H), 7.58 – 7.50 (m, 4H), 7.52 – 7.45 (m, 1H), 7.40 – 7.32 (m, 1H), 7.03 – 6.87 (m, 3H), 6.81 – 6.74 (m, 2H), 6.61 (dd, *J* = 8.5, 3.0 Hz, 1H), 4.41 (d, *J* = 9.1 Hz, 1H), 4.05 (d, *J* = 9.1 Hz, 1H), 1.35 (s, 3H).

6-(3,5-bis(trifluoromethyl)phenyl)-5,6a-dihydroxy-3a-methyl-1,1-diphenyl-1,3,3a,6a-tetrahydro-4*H*-cyclopenta[*c*]furan-4-one (8l)



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 (s, 1H), 7.27 (d, *J* = 4.5 Hz, 4H), 7.25 – 7.18 (m, 1H), 7.17 – 7.11 (m, 3H), 6.65 – 6.51 (m, 2H), 6.47 – 6.39 (m, 2H), 4.13 (d, *J* = 9.1 Hz, 1H), 3.77 (d, *J* = 9.1 Hz, 1H), 1.07 (s, 3H).

Diisopropyl 5,6a-dihydroxy-6-methyl-4-oxo-3,3a,4,6a-tetrahydropentalene-2,2(1*H*)-dicarboxylate (9a)



Prepared from **7a** (154.1 mg, 0.5 mmol) following General Procedure G. The crude residue was purified by column chromatography (silica, 60% EtOAc/hexanes) to yield **9a** (132 mg, 78% yield) as an off-white powder.

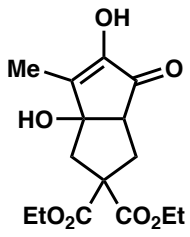
^{1}H NMR (400 MHz, CD_3OD) δ 4.98 (p, *J* = 6.3 Hz, 1H), 4.83 (dt, *J* = 12.6, 6.3 Hz, 1H), 2.72 (dd, *J* = 13.6, 1.6 Hz, 1H), 2.56 – 2.39 (m, 3H), 2.31 (d, *J* = 13.5 Hz, 1H), 1.88 (d, *J* = 0.6 Hz, 3H), 1.27 – 1.11 (m, 12H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 200.52, 171.93, 169.63, 147.90, 141.77, 85.26, 70.26, 69.70, 61.98, 55.66, 43.27, 34.53, 21.74, 21.73, 21.69, 21.63, 9.29.

FTIR (NaCl, thin film, cm^{-1}): 3431, 2988, 2936, 2742, 1732, 1455, 1377, 1168, 1022, 985, 901, 832, 758.

HRMS (TOF-ESI, m/z): calc'd for $C_{17}H_{24}O_7$: 323.1489 $[M–H_2O+H]^+$; found: 323.1480.

diethyl 5,6a-dihydroxy-6-methyl-4-oxo-3,3a,4,6a-tetrahydropentalene-2,2(1*H*)-dicarboxylate (9b)



Prepared from **7b** (14.1 mg, 0.05 mmol) following General Procedure G. The crude residue was purified by column chromatography (silica, 60% EtOAc/hexanes) to yield **9b** (12.7 mg, 82% yield) as an off-white powder.

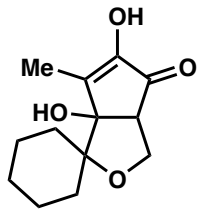
^{1}H NMR (500 MHz, CD_3OD) δ 5.73 (s, 1H), 4.25 (qd, *J* = 7.1, 2.6 Hz, 2H), 4.13 (q, *J* = 7.1 Hz, 2H), 2.98 (s, 1H), 2.79 (dd, *J* = 10.5, 5.3 Hz, 1H), 2.64 (ddd, *J* = 13.7, 10.4, 0.9 Hz, 1H), 2.61 – 2.50 (m, 2H), 2.43 (ddd, *J* = 13.8, 5.3, 0.8 Hz, 1H), 2.01 (d, *J* = 0.6 Hz, 3H), 1.30 (t, *J* = 7.1 Hz, 4H), 1.24 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, CD_3OD) δ 202.81, 171.92, 171.73, 151.49, 144.09, 84.55, 63.03, 62.97, 61.63, 55.97, 43.22, 35.59, 14.27, 14.22, 8.93.

FTIR (NaCl, thin film, cm^{-1}): 3381, 2984, 2940, 1727, 1714, 1672, 1437, 1405, 1370, 1262.

HRMS (TOF-ESI, m/z): calc'd for $C_{15}H_{20}O_7$: 311.1136 $[M–H]^-$; found: 311.1122.

5',6a'-dihydroxy-6'-methyl-3a',6a'-dihydrospiro[cyclohexane-1,1'-cyclopenta[*c*]furan]-4'(3'*H*)-one (9c)



Prepared from **7c** (104 mg, 0.5 mmol) following General Procedure G. The crude residue was purified by column chromatography (silica, 50% EtOAc/hexanes) to yield **9c** (87 mg, 74% yield) as an off-white powder.

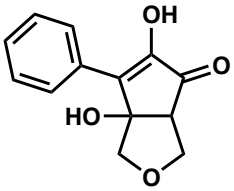
^{1}H NMR (400 MHz, $CDCl_3$) δ 4.00 (dd, *J* = 9.8, 8.6 Hz, 1H), 3.79 (dd, *J* = 9.8, 3.9 Hz, 1H), 2.89 – 2.81 (m, 1H), 2.07 – 1.94 (m, 4H), 1.73 – 1.60 (m, 2H), 1.60 – 1.38 (m, 4H), 1.34 – 1.09 (m, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 199.38, 148.53, 140.21, 87.16, 82.89, 62.25, 58.42, 31.52, 28.00, 24.58, 21.43, 20.97, 9.74.

FTIR (NaCl, thin film, cm^{-1}): 3342, 2928, 2858, 1713, 1698, 1668, 1402, 1361, 1133. 1060, 1022.

HRMS (TOF-ESI, m/z): calc'd for $C_{13}H_{18}O_4$: 239.1278 $[M+H]^+$; found: 239.1282.

5,6a-dihydroxy-6-phenyl-1,3,3a,6a-tetrahydro-4*H*-cyclopenta[*c*]furan-4-one (9d)



Prepared from **7d** (500 mg, 2.5 mmol) following General Procedure G. The crude residue was purified by trituration from DCM and pentanes to yield **9d** (397.2 mg, 73% yield) as an off-white powder.

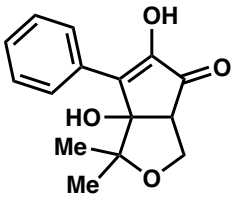
^{1}H NMR (400 MHz, CD_3OD) δ 8.18 – 8.11 (m, 2H), 7.46 – 7.38 (m, 2H), 7.38 – 7.30 (m, 1H), 4.12 (d, *J* = 9.2 Hz, 1H), 4.00 – 3.90 (m, 2H), 3.75 (d, *J* = 9.2 Hz, 1H), 2.74 (dd, *J* = 5.6, 3.5 Hz, 1H).

^{13}C NMR (101 MHz, CD_3OD) δ 202.00, 151.69, 139.33, 133.66, 130.60, 129.82, 129.29, 85.13, 76.95, 69.52, 58.97.

FTIR (NaCl, thin film, cm^{-1}): 3339, 2880, 2753, 1680, 1501, 1369, 1268, 1016, 698.

HRMS (TOF-ESI, m/z): calc'd for $C_{13}H_{12}O_4$: 233.0808 $[M+H]^+$; found: 233.0802.

5,6a-dihydroxy-1,1-dimethyl-6-phenyl-1,3,3a,6a-tetrahydro-4*H*-cyclopenta[*c*]furan-4-one (9e)



Prepared from **7e** (22.8 mg, 0.11 mmol) following General Procedure G. The crude residue was purified by column chromatography (silica, 20% EtOAc/hexanes) to yield **9e** (8.0 mg, 32% yield) as an off-white powder.

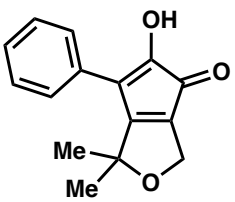
^{1}H NMR (400 MHz, CD_3OD) δ 8.27 – 8.19 (m, 2H), 7.45 – 7.35 (m, 2H), 4.17 – 4.08 (m, 1H), 3.82 (dd, *J* = 9.4, 3.6 Hz, 1H), 2.94 (dd, *J* = 8.2, 3.6 Hz, 1H), 1.40 (d, *J* = 4.0 Hz, 3H), 0.92 (s, 5H).

^{13}C NMR (101 MHz, CD_3OD) δ 202.61, 150.95, 139.36, 135.53, 130.86, 129.53, 128.92, 88.78, 85.74, 64.87, 61.51, 26.00, 22.64.

FTIR (NaCl, thin film, cm^{-1}): 3388, 2925, 2855, 1694, 1385, 1204, 1062.

HRMS (TOF-ESI, m/z): calc'd for $C_{15}H_{16}O_4$: 261.1121 $[M+H]^+$; found: 261.1122.

5-hydroxy-1,1-dimethyl-6-phenyl-1,3-dihydro-4*H*-cyclopenta[*c*]furan-4-one (40)

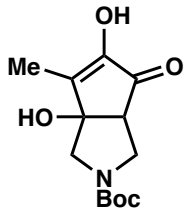


Prepared from **7e** (30.6 mg, 0.1 mmol) following General Procedure G. The crude residue was purified by column chromatography (silica, 30% EtOAc/hexanes) then preparative thin layer chromatography (silica, 10% MeOH/DCM) to yield **40** (7.5 mg, 30% yield) as an off-white powder.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 – 7.86 (m, 2H), 7.60 (ddt, *J* = 7.9, 6.9, 1.3 Hz, 1H), 7.57 – 7.42 (m, 2H), 4.89 (s, 2H), 1.40 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ ^{13}C NMR (101 MHz, $CDCl_3$) δ 193.41, 165.32, 157.15, 135.83, 134.29, 129.33, 128.91, 128.47, 91.27, 71.82, 29.86, 26.75.

tert-butyl 5,6a-dihydroxy-6-methyl-4-oxo-3,3a,4,6a-tetrahydrocyclopenta[_c_]pyrrole-2(1_H_)-carboxylate (9f)



Prepared from **7f** (24 mg, 0.1 mmol) following General Procedure G. The crude residue was purified by column chromatography (silica, 75% EtOAc/hexanes) to yield **9f** (15 mg, 57% yield) as an off-white powder.

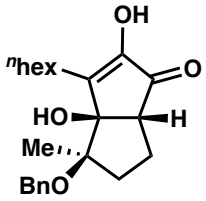
^{1}H NMR (400 MHz, CD_3OD) δ 3.81 (d, *J* = 11.9 Hz, 1H), 3.73 (dd, *J* = 11.7, 1.9 Hz, 1H), 3.49 (t, *J* = 10.2 Hz, 1H), 3.16 (d, *J* = 11.9 Hz, 1H), 2.55 (dd, *J* = 8.5, 1.9 Hz, 1H), 1.98 – 1.93 (m, 3H), 1.41 (s, 9H).

^{13}C NMR (101 MHz, CD_3OD, asterisk denotes minor rotamer) δ 201.58, 156.39, 151.57, 144.65*, 144.40*, 83.96*, 83.31*, 81.61, 56.88*, 56.22*, 55.31*, 54.75*, 47.87*, 47.42*, 28.65, 9.22*.

FTIR (NaCl, thin film, cm^{-1}): 3446, 2862, 2352, 1698, 1668, 1660, 1634, 1436, 1224.

HRMS (TOF-ESI, m/z): calc'd for $C_{13}H_{19}O_5$: 270.1336 $[M+H]^+$; found: 270.1341.

(3a_R_,4_R_,6a_R_)-4-(benzyloxy)-3-hexyl-2,3a-dihydroxy-4-methyl-4,5,6,6a-tetrahydropentalen-1(3a_H_)-one (9g)



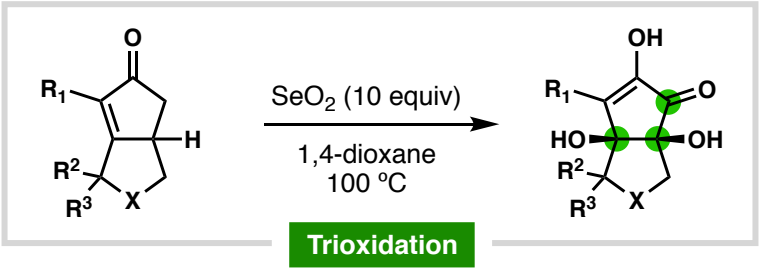
Prepared from **7g** (6.5 mg, 0.02 mmol) following General Procedure G. The crude residue was purified by preparative thin layer chromatography (silica, 40% EtOAc/hexanes) to yield **9g** (1.7 mg, 24% yield) as a white amorphous solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 – 7.28 (m, 5H), 5.63 (s, 1H), 4.56 (d, *J* = 10.9 Hz, 1H), 4.44 (d, *J* = 10.9 Hz, 1H), 4.23 (d, *J* = 0.8 Hz, 1H), 2.76 – 2.68 (m, 1H), 2.52 – 2.38 (m, 1H), 2.38 – 2.23 (m, 1H), 2.23 – 2.11 (m, 1H), 2.11 – 1.98 (m, 1H), 1.77 – 1.59 (m, 5H), 1.42 – 1.25 (m, 5H), 1.24 (s, 3H), 0.93 – 0.81 (m, 4H).

^{13}C NMR (101 MHz, $CDCl_3$) δ ^{13}C NMR (101 MHz, $CDCl_3$) δ 202.81, 149.56, 145.27, 138.17, 128.69, 127.98, 127.70, 87.38, 84.14, 65.43, 56.15, 35.06, 31.73, 30.07, 27.66, 26.78, 22.75, 22.69, 19.59, 14.25.

FTIR (NaCl, thin film, cm^{-1}): 3388, 2925, 2855, 1694, 1385, 104, 1062.

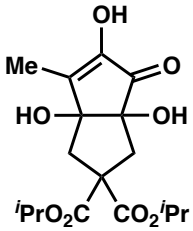
HRMS (TOF-ESI, m/z): calc'd for $C_{22}H_{30}O_4$: 359.2217 $[M+H]^+$; found: 359.2205.



Trioxidation: General Procedure H

To a flame-dried vial with a Teflon-coated stir bar was added the enone (**7a–h**) (1.0 equiv), SeO_2 (10.0 equiv), and 1,4-dioxane (0.05 M). The reaction was capped and sealed with Teflon tape, stirred, and brought to 100 °C in a preheated aluminum reaction block and monitored by TLC and/or LCMS. After the reaction was judged to be complete, typically 1–4 h (see note in General Procedure F), the reaction was allowed to reach room temperature then concentrated. The crude residue was purified by chromatography to afford the desired product.

Diisopropyl 3a,5,6a-trihydroxy-6-methyl-4-oxo-3,3a,4,6a-tetrahydropentalene-2,2(1*H*)-dicarboxylate (10a)



Prepared from **7a** (7.0 mg, 0.02 mmol) following General Procedure H. The crude residue was purified by preparative thin layer chromatography (silica, 70% EtOAc/hexanes) to yield **10a** (1.7 mg, 21% yield) as a white amorphous solid.

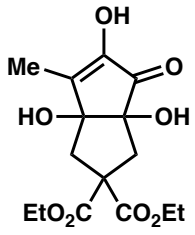
^{1}H NMR (400 MHz, CD_3OD) δ 4.97 (hept, *J* = 6.3 Hz, 1H), 4.87 – 4.78 (m, 1H), 2.86 (dd, *J* = 13.8, 1.9 Hz, 1H), 2.80 (dd, *J* = 13.3, 1.9 Hz, 1H), 2.33 (d, *J* = 13.4 Hz, 1H), 2.14 (d, *J* = 13.7 Hz, 1H), 1.86 (s, 3H), 1.30 – 1.11 (m, 12H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 198.08, 172.12, 169.27, 147.56, 142.77, 83.23, 79.99, 70.64, 69.95, 59.43, 42.99, 42.03, 21.74, 21.68, 9.58.

FTIR (NaCl, thin film, cm^{-1}): 3438, 2984, 2931, 1727, 1714, 1660, 1263, 1100, 902.

HRMS (TOF-ESI, m/z): calc'd for $C_{17}H_{24}O_8$: 374.1809 $[M+NH_4]^+$; found: 374.1813.

diethyl 3a,5,6a-trihydroxy-6-methyl-4-oxo-3,3a,4,6a-tetrahydropentalene-2,2(1*H*)-dicarboxylate (10b)



Prepared from **7b** (14.1 mg, 0.05 mmol) following General Procedure H. The crude residue was purified by column chromatography (silica, 5% MeOH/DCM) to yield **10b** (5.1 mg, 31% yield) as a white amorphous solid.

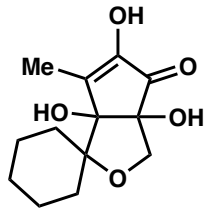
^{1}H NMR (400 MHz, CD_3OD) δ 4.15 (qd, *J* = 7.1, 1.3 Hz, 2H), 4.03 (qd, *J* = 7.2, 2.2 Hz, 2H), 2.86 (ddd, *J* = 20.9, 13.5, 2.0 Hz, 2H), 2.35 (d, *J* = 13.3 Hz, 1H), 2.17 (d, *J* = 13.7 Hz, 1H), 1.87 (s, 3H), 1.21 (dt, *J* = 8.2, 7.1 Hz, 6H).

^{13}C NMR (101 MHz, CD_3OD) δ 201.23, 171.88, 171.37, 152.07, 143.21, 82.47, 79.98, 63.17, 63.08, 57.10, 43.88, 41.87, 14.25, 14.22, 9.06.

FTIR (NaCl, thin film, cm^{-1}): 3402, 2984, 2940, 2852, 1728, 1667, 1404, 1366, 1252.

HRMS (TOF-ESI, m/z): calc'd for $C_{15}H_{20}O_8$: 327.1085 $[M–H]^-$; found: 327.1077.

3a',5',6a'-trihydroxy-6'-methyl-3a',6a'-dihydrospiro[cyclohexane-1,1'-cyclopenta[*c*]furan]-4'(3'*H*)-one (10c)



Prepared from **7c** (20.6 mg, 0.1 mmol) following General Procedure H. The crude residue was purified by column chromatography (silica, 40 to 50% EtOAc/hexanes) to yield **10c** (6.2 mg, 23% yield) as a white amorphous solid.

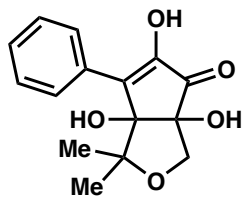
^{1}H NMR (400 MHz, CD_3OD) δ 5.49 (s, 1H), 3.89 (d, *J* = 10.0 Hz, 1H), 3.55 (d, *J* = 10.1 Hz, 1H), 1.97 (s, 3H), 1.77 – 1.35 (m, 8H), 1.35 – 1.12 (m, 2H).

^{13}C NMR (101 MHz, CD_3OD) δ 201.20, 152.33, 145.38, 85.90, 85.24, 81.39, 70.51, 54.81, 35.25, 30.76, 28.45, 26.69, 23.64, 22.39, 12.11.

FTIR (NaCl, thin film, cm^{-1}): 3394, 2925, 2855, 1714, 1650, 1460, 1361, 1109, 1072.

HRMS (TOF-ESI, m/z): calc'd for $C_{13}H_{18}O_5$: 237.1121 $[M–H_2O+H]^+$; found: 237.1111.

3a,5,6a-trihydroxy-1,1-dimethyl-6-phenyl-1,3,3a,6a-tetrahydro-4*H*-cyclopenta[*c*]furan-4-one (10e)



Prepared from **7e** (15.0 mg, 0.07 mmol) following General Procedure H. The crude residue was purified by preparative thin layer chromatography (silica, 40 to 55% EtOAc/hexanes then 10% MeOH/DCM) to yield **10e** (3.0 mg, 17% yield) as a white amorphous solid.

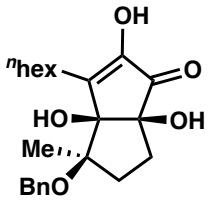
^{1}H NMR (400 MHz, CD_3OD) δ 8.24 – 8.17 (m, 2H), 7.43 – 7.28 (m, 3H), 3.98 (d, *J* = 10.1 Hz, 1H), 3.71 (d, *J* = 10.1 Hz, 1H), 1.35 (s, 3H), 0.90 (s, 3H).

^{13}C NMR (101 MHz, $(CD_3)_2SO$) δ 201.01, 150.42, 138.58, 135.22, 129.95, 128.81, 128.28, 84.91, 84.44, 80.63, 69.83, 27.14, 22.36.

FTIR (NaCl, thin film, cm^{-1}): 3341, 2920, 1694, 1463, 1393, 1049, 730.

HRMS (TOF-ESI, m/z): calc'd for $C_{15}H_{16}O_5$: 259.0965 $[M–H_2O+H]^+$; found: 259.0963.

(3a*S*,4*R*,6a*S*)-4-(benzyloxy)-3-hexyl-2,3a,6a-trihydroxy-4-methyl-4,5,6,6a-tetrahydropentalen-1(3a*H*)-one (10g)



Prepared from **7g** (32.6 mg, 0.1 mmol) following General Procedure H. The crude residue was purified by column chromatography (silica, 20% EtOAc/hexanes then 2% MeOH/DCM) to yield **10g** (9 mg, 24% yield) as a pale orange amorphous solid.

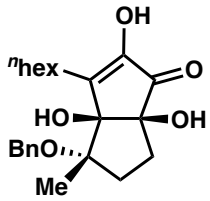
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 – 7.30 (m, 5H), 4.55 – 4.43 (m, 2H), 4.41 (s, 1H), 3.32 (s, 1H), 2.51 (ddd, *J* = 13.9, 9.3, 6.7 Hz, 1H), 2.32 (ddd, *J* = 13.9, 9.1, 7.2 Hz, 1H), 2.13 – 2.02 (m, 2H), 1.94 – 1.80 (m, 1H), 1.77 – 1.60 (m, 1H), 1.39 (s, 3H), 1.37 – 1.18 (m, 6H), 0.92 – 0.83 (m, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 200.48, 150.53, 144.83, 137.59, 128.78, 128.14, 127.78, 85.29, 83.68, 79.42, 64.78, 31.69, 30.50, 30.26, 29.93, 27.83, 27.48, 22.73, 19.88, 14.23.

FTIR (NaCl, thin film, cm^{-1}): 3444, 2926, 2856, 1714, 1660, 1393, 1104, 1040, 738.

HRMS (TOF-ESI, m/z): calc'd for $C_{22}H_{30}O_5$: 375.2166 $[M+H]^+$; found: 375.2174.

(3a*S*,4*S*,6a*S*)-4-(benzyloxy)-3-hexyl-2,3a,6a-trihydroxy-4-methyl-4,5,6,6a-tetrahydropentalen-1(3a*H*)-one (10h)



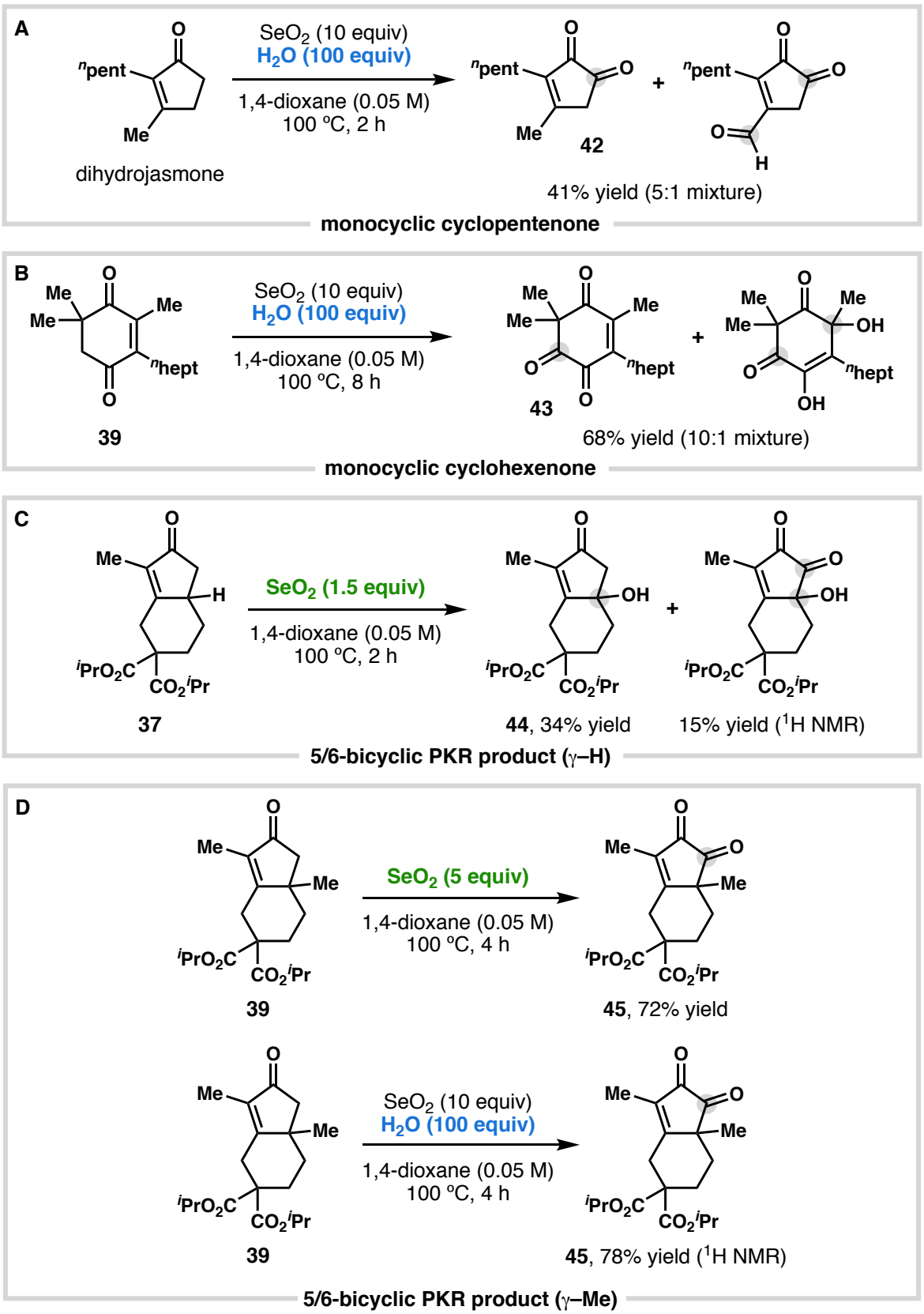
Prepared from **7h** (32.6 mg, 0.1 mmol) following General Procedure H. The crude residue was purified by column chromatography (silica, 20% EtOAc/hexanes) to yield **10h** (7.7 mg, 21% yield) as a pale orange amorphous solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.17 (m, 5H), 5.44 (s, 1H), 4.50 (d, *J* = 11.4 Hz, 1H), 4.33 (d, *J* = 11.4 Hz, 1H), 3.21 (s, 1H), 2.98 (s, 1H), 2.54 (ddd, *J* = 14.3, 10.4, 5.8 Hz, 1H), 2.41 (ddd, *J* = 14.3, 10.4, 6.0 Hz, 2H), 2.08 – 1.90 (m, 2H), 1.83 (q, *J* = 6.4, 5.8 Hz, 1H), 1.77 – 1.67 (m, 1H), 1.68 – 1.51 (m, 1H), 1.49 (s, 3H), 1.37 – 1.11 (m, 6H), 0.84 (t, *J* = 7.0 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ δ 199.61, 149.37, 148.48, 138.98, 128.37, 127.31, 126.98, 86.24, 85.37, 80.20, 64.78, 33.08, 31.74, 31.59, 30.04, 27.67, 27.42, 22.75, 18.07, 14.24.

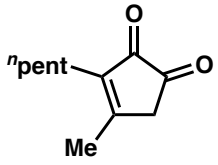
FTIR (NaCl, thin film, cm^{-1}): 3388, 2927, 2855, 1698, 1651, 1454, 1394, 1106, 1052, 734.

HRMS (TOF-ESI, m/z): calc'd for $C_{22}H_{30}O_5$: 375.2166 $[M+H]^+$; found: 375.2164.



Scheme S1. Investigation of oxidative transformations in other ring systems.

4-methyl-3-pentylcyclopent-3-ene-1,2-dione (42)



See Scheme S1a. Prepared from dihydrojasmone (41.6 mg, 0.25 mmol) following General Procedure G. The crude residue was purified by column chromatography (silica, 50% EtOAc/hexanes) to yield **42** as a 5:1 mixture with an aldehyde byproduct (17.9 mg, 41% combined) as a pale yellow oil.

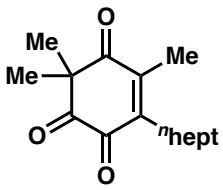
^{1}H NMR (400 MHz, $CDCl_3$) δ 2.94 (h, *J* = 1.2 Hz, 2H), 2.37 (t, *J* = 7.7 Hz, 2H), 2.23 (d, *J* = 1.2 Hz, 3H), 1.47 – 1.43 (m, 2H), 1.36 – 1.28 (m, 6H), 0.90 – 0.86 (m, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 198.55, 188.85, 166.73, 146.73, 77.48, 77.16, 76.84, 40.04, 31.84, 27.83, 23.45, 22.56, 17.82, 14.12.

FTIR (NaCl, thin film, cm^{-1}) of mixture: 3387, 2952, 2924, 2855, 1714, 1455, 1385, 1261, 1094.

HRMS (GC-EI+, m/z): calc'd for $C_{11}H_{16}O_2$: 180.1150 $[M]^+$; found: 180.1141.

6-heptyl-3,3,5-trimethylcyclohex-5-ene-1,2,4-trione (43)



See Scheme S1b. Prepared from **39** (47.3 mg, 0.20 mmol) following General Procedure G. The crude residue was purified by column chromatography (silica, 20% EtOAc/hexanes) to yield **43** as a 10:1 mixture with a byproduct of oxy-Michael addition (35.6 mg, 68% yield combined) as a pale yellow oil.

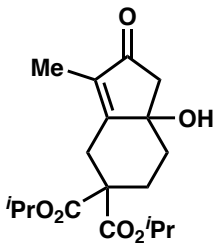
^{1}H NMR (400 MHz, $CDCl_3$) δ 2.62 – 2.55 (m, 2H), 2.15 (s, 3H), 1.42 (s, 6H), 1.30 (m, 10H), 0.90 – 0.85 (m, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 197.37, 194.47, 184.30, 150.74, 148.59, 77.48, 77.16, 76.84, 61.84, 31.79, 29.96, 29.11, 28.20, 26.91, 22.73, 21.88, 14.45, 14.20.

FTIR (NaCl, thin film, cm^{-1}) of mixture: 3442, 2953, 2924, 2854, 1728, 1667, 1463, 1380, 1312, 1156, 1034.

HRMS (GC-EI+, m/z): calc'd for $C_{16}H_{24}O_3$: 264.1726 $[M]^+$; found: 264.1749.

diisopropyl 7a-hydroxy-3-methyl-2-oxo-1,2,4,6,7,7a-hexahydro-5*H*-indene-5,5-dicarboxylate (44)



See Scheme S1c. Prepared from **37** (16.1 mg, 0.05 mmol) following General Procedure H with SeO_2 (8.3 mg, 0.075 mmol, 1.5 equiv). The crude residue was purified by column chromatography (silica, 45% EtOAc/hexanes) to yield **44** (5.7 mg, 34% yield) as a pale yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.03 (dp, *J* = 29.1, 6.3 Hz, 2H), 3.31 (dd, *J* = 13.9, 1.5 Hz, 1H), 2.89 (dq, *J* = 13.8, 1.6 Hz, 1H), 2.55 – 2.40 (m, 2H), 2.35 – 2.28 (m, 2H), 2.19 (dt, *J* = 14.3, 3.3 Hz, 1H), 1.75 (d, *J* = 1.5 Hz, 3H), 1.73 – 1.71 (m, 1H), 1.69 – 1.61 (m, 1H), 1.25 (dd, *J* = 6.3, 1.7 Hz, 7H),

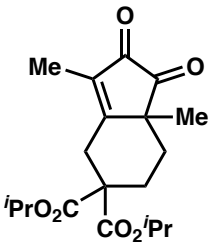
1.20 (dd, *J* = 6.3, 4.0 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 205.34, 170.48, 169.23, 167.35, 137.18, 77.35, 77.03, 76.71, 73.98, 69.55, 69.16, 56.23, 49.77, 35.64, 29.27, 26.74, 21.58, 21.55, 7.90.

FTIR (NaCl, thin film, cm^{-1}): 3443, 2981, 2856, 1810, 1714, 1667, 1454, 1376, 1303, 1251, 1104.

HRMS (GC-FAB+, m/z): calc'd for $C_{18}H_{27}O_6$: 339.1808 $[M+H]^+$; found: 339.1797.

diisopropyl 3,7a-dimethyl-1,2-dioxo-1,2,4,6,7,7a-hexahydro-5*H*-indene-5,5-dicarboxylate (45)



See Scheme S1d. Prepared from **39** (16.8 mg, 0.05 mmol) following General Procedure H with SeO_2 (27.7 mg, 0.25 mmol, 5.0 equiv). The crude residue was purified by column chromatography (silica, 25% EtOAc/hexanes) to yield **45** (12.6 mg, 72% yield) as a pale yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.08 (hept, *J* = 6.3 Hz, 1H), 4.98 (hept, *J* = 6.3 Hz, 1H), 3.49 (dd, *J* = 14.1, 2.1 Hz, 1H), 2.74 (dq, *J* = 14.1, 1.4 Hz, 1H), 2.42 (ddt, *J* = 14.4, 4.1, 2.6 Hz, 1H), 2.15 (td, *J* = 14.2, 4.0 Hz, 1H), 1.95 (d, *J* = 1.3 Hz, 3H), 1.89 (ddd, *J* = 13.9, 4.0, 2.8 Hz, 1H), 1.51 (td, *J* = 13.9, 4.1 Hz, 1H), 1.31 (s, 3H), 1.26 (dd, *J* = 6.3, 3.5 Hz, 7H), 1.19 (dd, *J* = 6.3, 1.5 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 202.05, 188.28, 172.37, 170.29, 168.81, 140.59, 77.48, 77.16, 76.84, 70.09, 69.70, 56.53, 43.83, 29.93, 29.27, 26.38, 21.68, 21.66, 19.94, 8.55.

FTIR (NaCl, thin film, cm^{-1}): 3505, 3408, 2980, 2939, 2872, 1732, 1633, 1456, 1386.

HRMS (TOF-ES+, m/z): calc'd for $C_{19}H_{27}O_6$: 351.1808 $[M+H]^+$; found: 351.1784.

4. Stereochemical Analysis

Stereochemical Analysis: General Procedure I

To a flame-dried vial with a Teflon-coated stir bar was added the substrate (1.0 equiv), SeO_2 (10.0 equiv), 1,4-dioxane (0.05 M), and water (100.0 equiv). The reaction was capped and sealed with Teflon tape, stirred, and brought to 100 °C in a preheated aluminum reaction block and monitored by TLC and/or LCMS. At specified time points, the reaction was allowed to reach room temperature and an aliquot was removed and concentrated. To the residue was added an internal standard (pyrazine, ~1.0 equiv), then the mixture was taken up in CD_3OD and filtered over a cotton plug into an NMR tube. Yield determined by ^1H NMR versus the internal standard. Alternatively, isolated yields were determined by concentration of the entire reaction and purification of the crude residue by chromatography to afford the desired product. Enantiomeric excess was determined by analytical chiral SFC or HPLC.

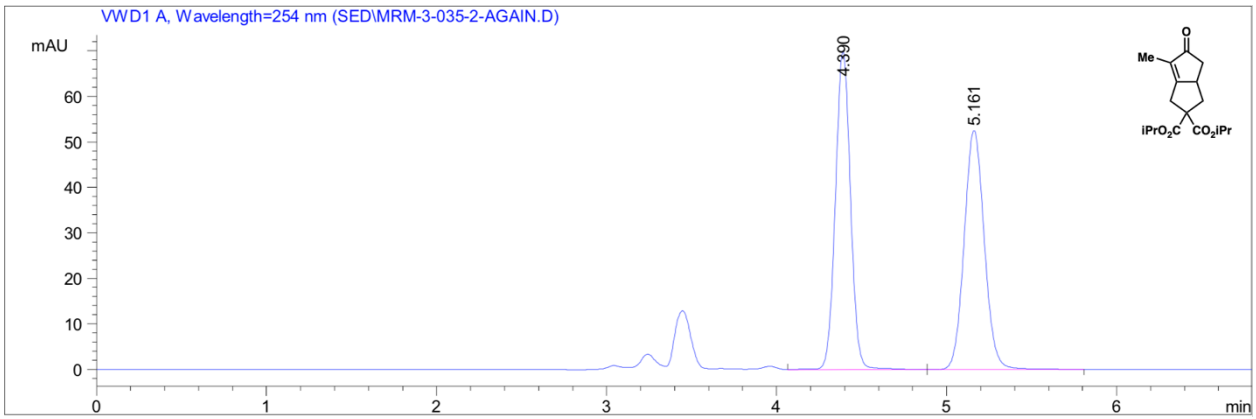
Stereochemical Analysis: General Procedure J

General Procedure I was followed except that the addition of water to the reaction mixture was omitted.

Diisopropyl 6-methyl-5-oxo-3,3a,4,5-tetrahydropentalene-2,2(1H)-dicarboxylate (7a)

Chiral HPLC: (IH, 1.0 mL/min, 10% IPA/hexanes, λ = 254 nm): t_R = 4.4 min, t_R = 5.2 min.

7a: racemic

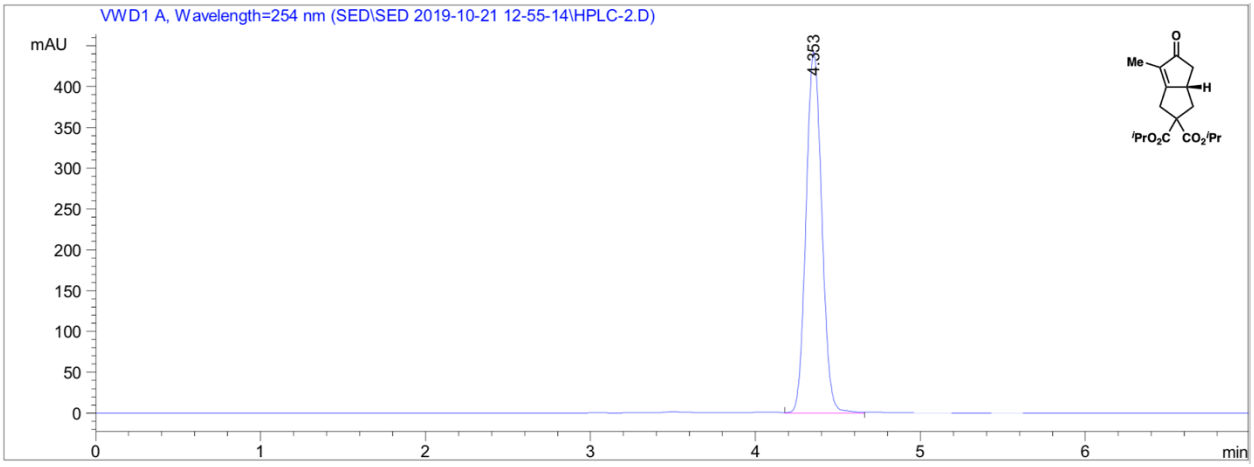


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	4.390	VV	0.0954	433.76349	70.21899	50.0120
2	5.161	VV	0.1281	433.55533	52.62845	49.9880

Prepared by purification of **7a** by chiral HPLC (IH, 1.0 mL/min, 10% IPA/hexanes, λ = 254 nm) to yield **(+)-7a*** as a single enantiomer.

$[\alpha]_D^{22} =$ +126 (c = 0.2, $CHCl_3$).

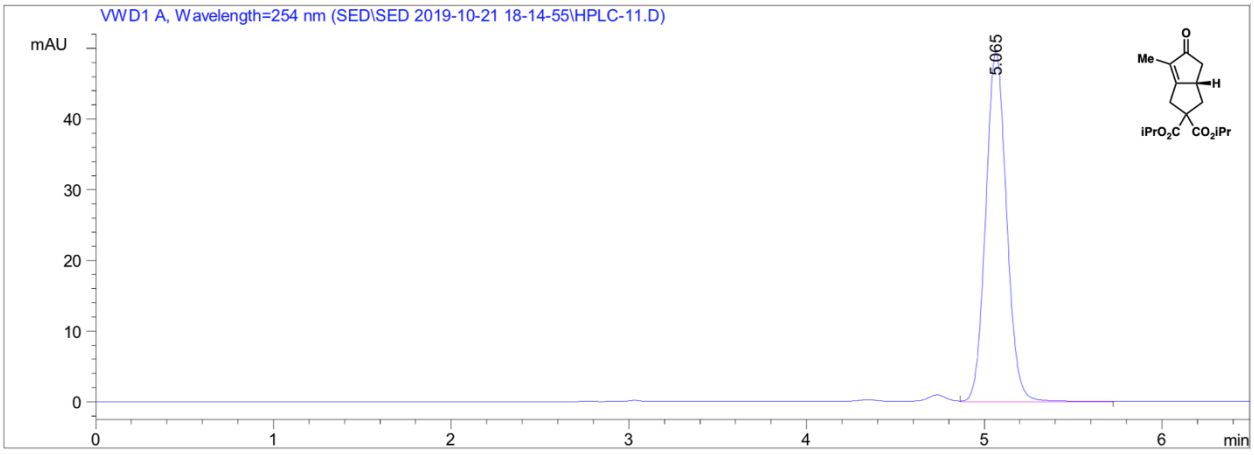
(+)-7a*: enantioenriched, >99% ee



Prepared by purification of **7a** by chiral HPLC (IH, 1.0 mL/min, 10% IPA/hexanes, λ = 254 nm) to yield **(–)-7a*** as a single enantiomer.

$[\alpha]_D^{22} =$ –95 (c = 0.3, $CHCl_3$).

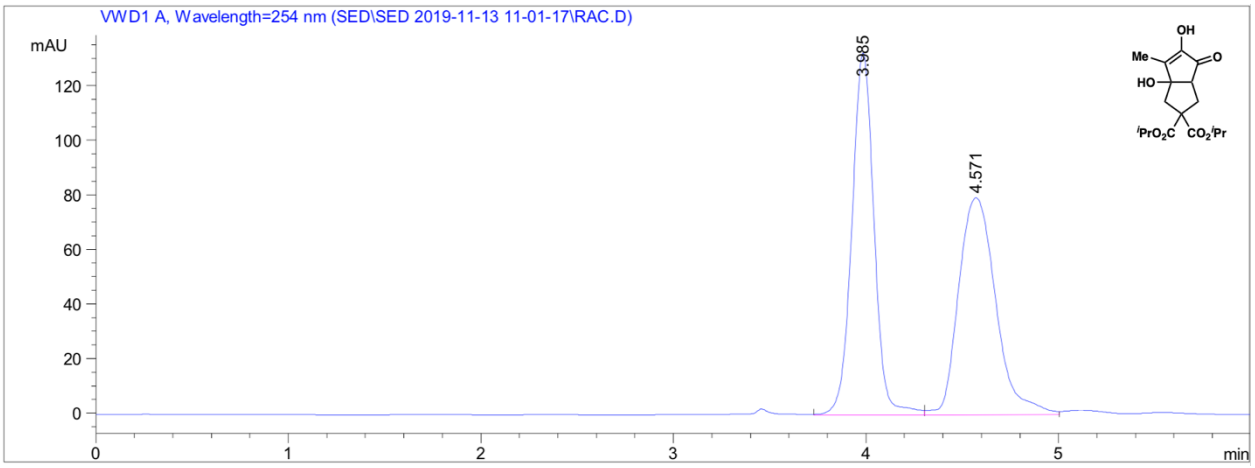
(–)-7a*: enantioenriched, >99% ee



Diisopropyl 5,6a-dihydroxy-6-methyl-4-oxo-3,3a,4,6a-tetrahydropentalene-2,2(1*H*)-dicarboxylate (9a)

Chiral HPLC: (IH, 1.0 mL/min, 65% IPA/hexanes, λ = 254 nm): t_R = 3.9 min, t_R = 4.6 min.

9a: racemic

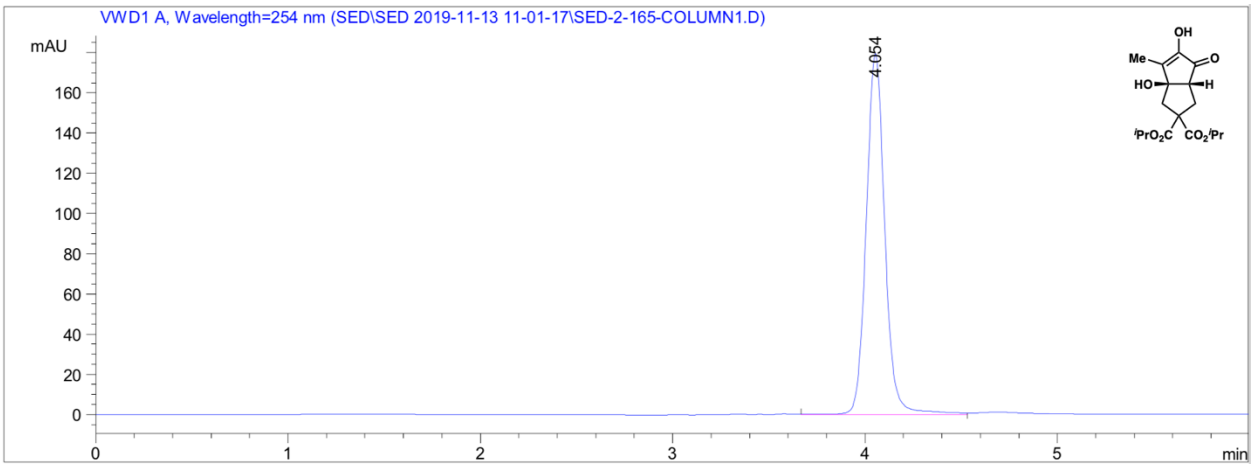


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	3.985	BV	0.1241	1063.69312	132.66316	49.8308
2	4.571	VV	0.2153	1070.91724	79.57430	50.1692

Prepared from **(–)-7a*** (176 mg, 0.57 mmol, >99% ee) following General Procedure I. The crude residue was purified by column chromatography (silica, 0 to 40% EtOAc/hexanes) to yield **(–)-9a*** (114 mg, 59% yield) in >99% ee.

$[\alpha]_D^{22} =$ –67 (c = 0.5, $CHCl_3$).

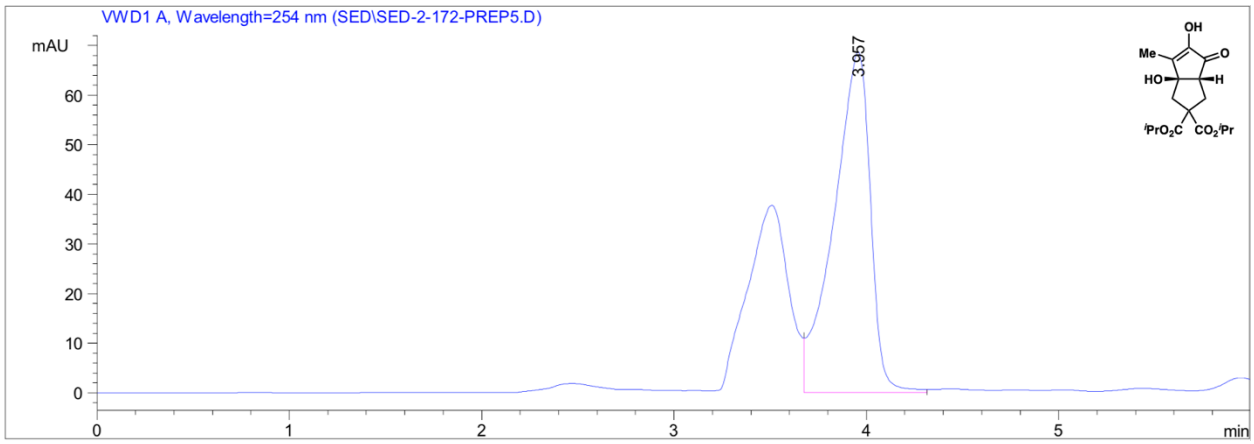
(–)-9a*: enantioenriched, >99% ee



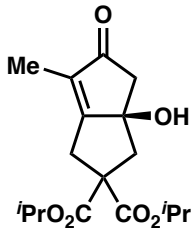
Prepared from **(–)-7a*** (22 mg, 0.07 mmol, >99% ee) following General Procedure J. The crude residue was purified by preparative thin layer chromatography (silica, 7% MeOH/DCM) to yield **(–)-9a*** (1.0 mg, 4% yield) in >99% ee.

$[\alpha]_D^{22} = -15$ (c = 0.1, $CHCl_3$).

(–)-9a*: enantioenriched, >99% ee



Diisopropyl 3a-hydroxy-6-methyl-5-oxo-3,3a,4,5-tetrahydropentalene-2,2(1*H*)-dicarboxylate (11a)



^{1}H NMR (500 MHz, $CDCl_3$) δ 5.09 (dp, *J* = 37.2, 6.2 Hz, 2H), 3.33 (dd, *J* = 18.5, 2.0 Hz, 1H), 3.26 (d, *J* = 18.5 Hz, 1H), 3.00 (s, 1H), 2.89 (d, *J* = 14.3 Hz, 1H), 2.63 (d, *J* = 17.9 Hz, 1H), 2.51 (d, *J* = 18.0 Hz, 1H), 2.11 (d, *J* = 14.4 Hz, 1H), 1.74 (dd, *J* = 1.9, 1.0 Hz, 3H), 1.37 – 1.14 (m, 12H).

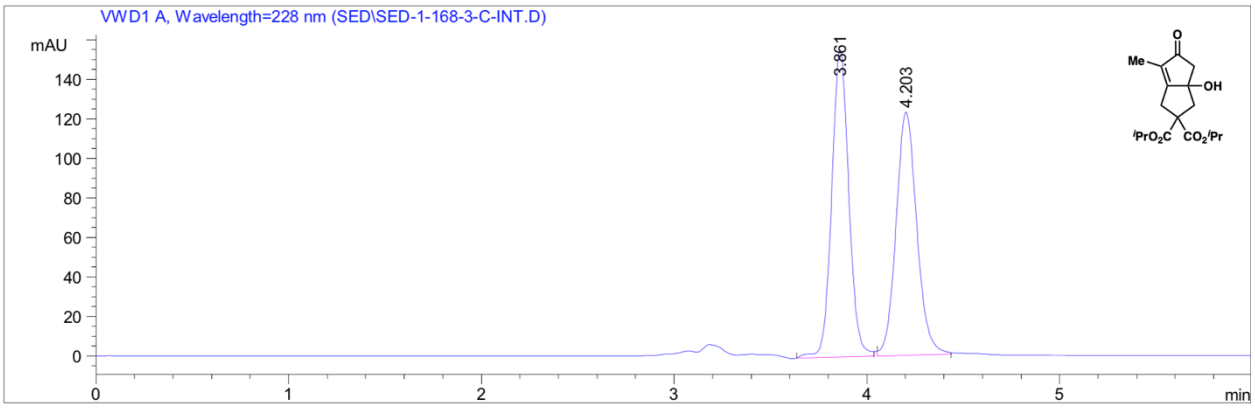
^{13}C NMR (101 MHz, $CDCl_3$) δ 207.52, 174.39, 173.24, 170.51, 134.39, 82.47, 70.68, 70.01, 61.00, 48.11, 45.22, 32.91, 21.74, 21.70, 8.78.

FTIR (NaCl, thin film, cm^{-1}): 3472, 2927, 2855, 1716, 1682, 1456, 1375, 1267, 1188, 1109, 1027, 913.

HRMS (TOF-ESI, m/z): calc'd for $C_{17}H_{24}O_6$: 307.1540 $[M–H_2O+H]^+$; found: 307.1549.

Chiral HPLC: (IH, 1.0 mL/min, 60% IPA/hexanes, λ = 228 nm): t_R = 3.9 min, t_R = 4.2 min.

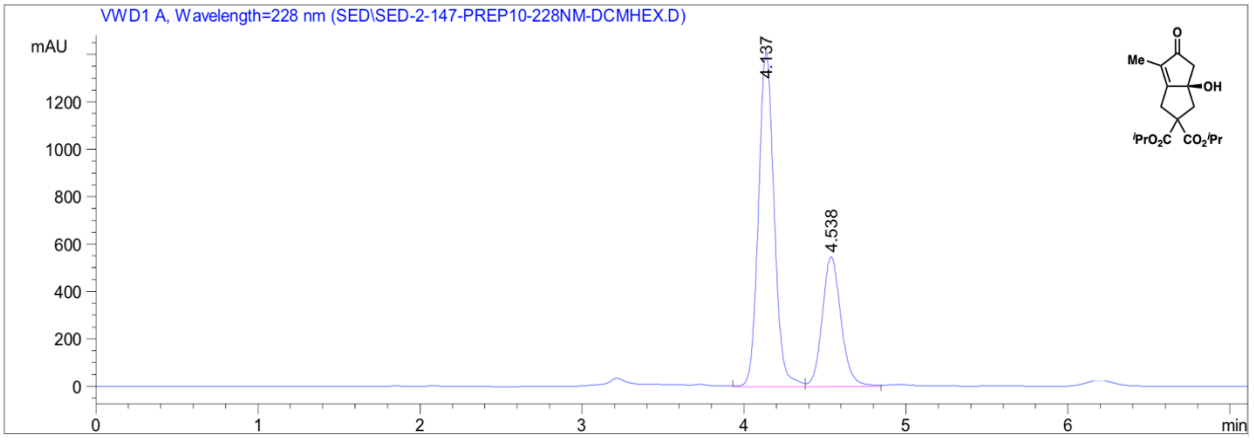
11a: racemic



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	3.861	BB	0.0953	958.98309	155.45844	51.0419
2	4.203	BB	0.1149	919.83228	123.07118	48.9581

Prepared from **(+)-7a*** (200 mg, 0.65 mmol, >99% ee) following General Procedure I. The crude residue was purified by column chromatography (silica, 0 to 30% EtOAc/hexanes) followed by preparative thin layer chromatography (silica, 30 to 50% EtOAc/hexanes) to yield **(+)-11a*** (3.5 mg, 2% yield) in 36% ee. $[\alpha]_D^{22} =$ +6 (c = 0.2, $CHCl_3$).

(+)-11a*: enantioenriched, 36% ee

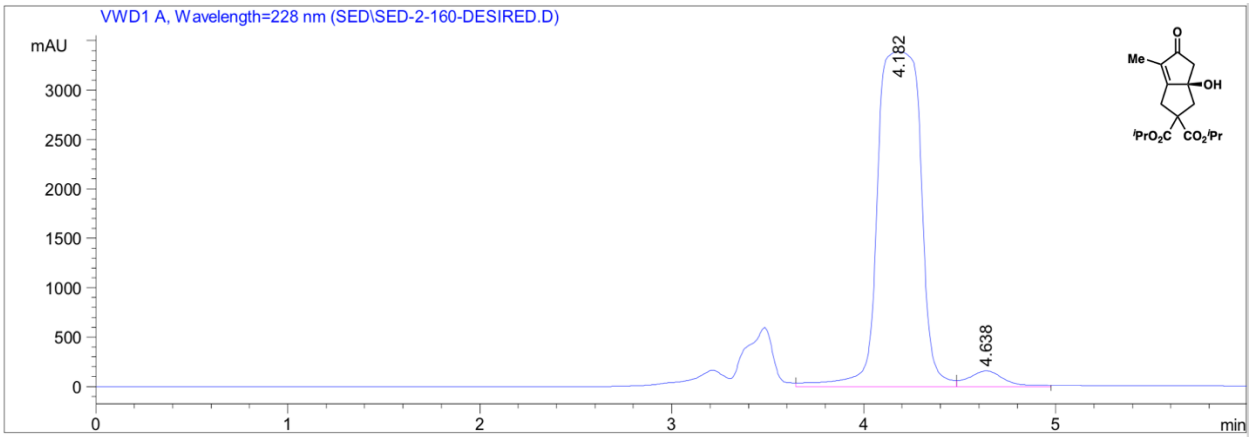


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	4.137	VV	0.1047	9508.88184	1414.22021	68.1725
2	4.538	VV	0.1250	4439.37842	548.41638	31.8275

Prepared from **(+)-7a*** (150 mg, 0.49 mmol) following General Procedure J. The crude residue was purified by column chromatography (silica, 0 to 30% EtOAc/hexanes). This procedure was repeated seven times, and the combined material yielded yield **(+)-11a*** (41 mg, 26% yield) in 92% ee.

$[\alpha]_D^{22} =$ +12 (c = 1.0, $CHCl_3$).

(+)-11a*: enantioenriched, 92% ee

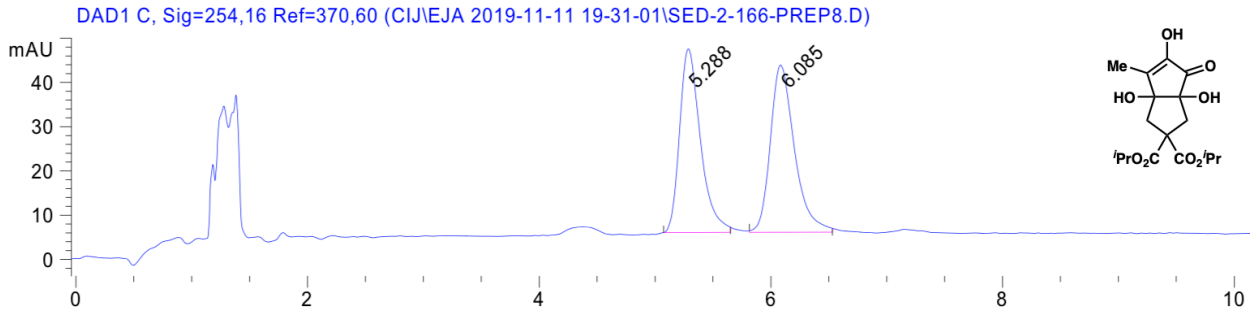


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	4.182	VV	0.2509	5.25926e4	3389.88306	96.1357
2	4.638	VV	0.1925	2114.04004	160.96941	3.8643

Diisopropyl 3a,5,6a-trihydroxy-6-methyl-4-oxo-3,3a,4,6a-tetrahydropentalene-2,2(1*H*)-dicarboxylate (10a)

Chiral SFC: (OD-H, 1.0 mL/min, 15% IPA in CO_2, λ = 254 nm): t_R = 5.3 min, t_R = 6.0 min.

10a: racemic

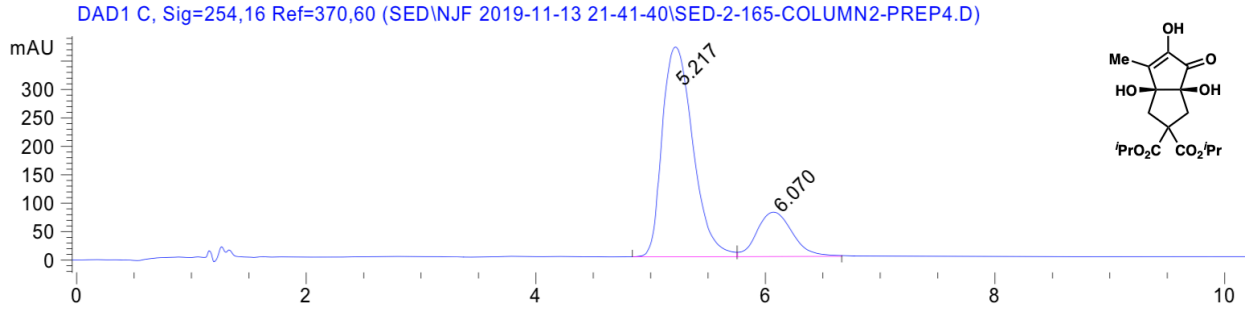


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.288	BB	0.1903	519.55811	41.44424	48.6659
2	6.085	BB	0.2214	548.04315	37.73867	51.3341

Prepared from **(–)-7a*** (176 mg, 0.57 mmol, >99% ee) following General Procedure I. The crude residue was purified by column chromatography (silica, 0 to 40% EtOAc/hexanes) followed by preparative thin layer chromatography (7% MeOH/DCM) to yield **(–)-10a*** (6.9 mg, 3% yield) in 60% ee.

$[\alpha]_D^{22} =$ –49 (c = 0.5, $CHCl_3$).

(–)-10a*: enantioenriched, 60% ee

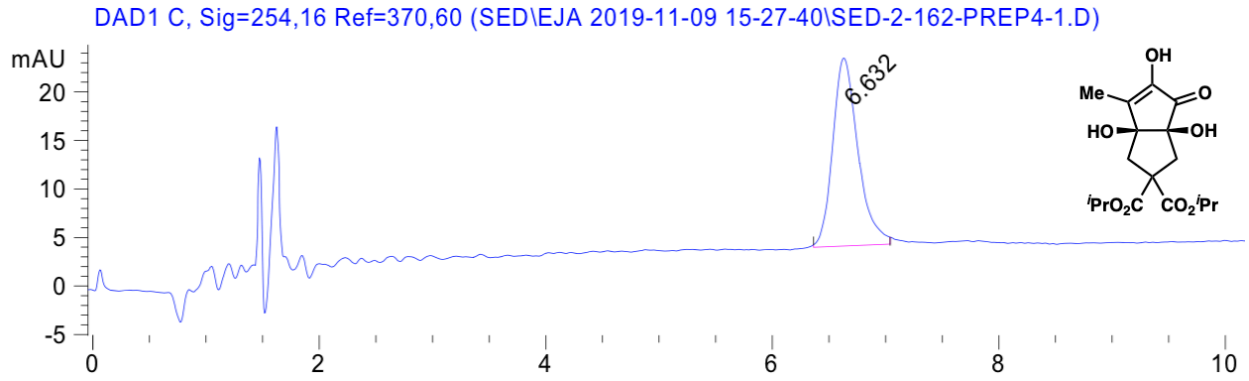


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.217	BV	0.2970	6858.47607	368.79010	80.3824
2	6.070	VB	0.3388	1673.83008	77.87675	19.6176

Prepared from **(–)-7a*** (31 mg, 0.1 mmol, >99% ee) following General Procedure J. The crude residue was purified by preparative thin layer chromatography (silica, 70% EtOAc/hexanes then 7% MeOH/DCM) to yield **(–)-10a*** (5.2 mg, 15% yield) in >99% ee.

$[\alpha]_D^{22} =$ –59 (c = 0.3, $CHCl_3$).

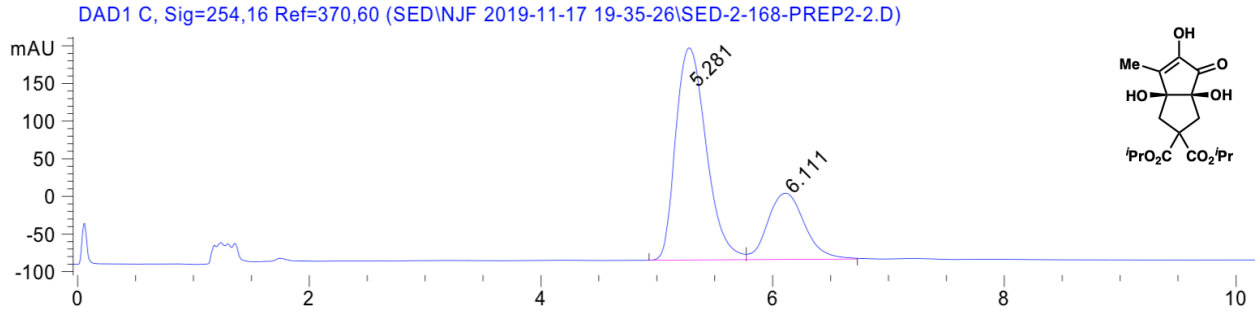
(–)-10a*: enantioenriched, >99% ee



Prepared from **(–)-9a*** (60 mg, 0.18 mmol, >99% ee) following General Procedure I. The crude residue was purified by preparative thin layer chromatography (silica, 10% MeOH/DCM) to yield **(–)-10a*** (7.5 mg, 12% yield) in 46% ee.

$[\alpha]_D^{22} =$ –29 (c = 0.3, $CHCl_3$).

(–)-10a*: enantioenriched, 46% ee

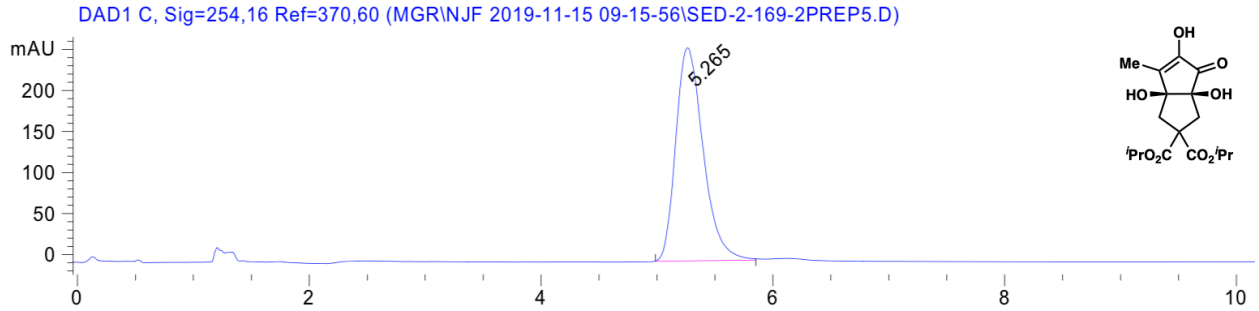


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.281	BV	0.2901	5172.07080	281.81711	72.6377
2	6.111	VB	0.3501	1948.29785	88.05092	27.3623

Prepared from **(–)-9a*** (40 mg, 0.12 mmol, >99% ee) following General Procedure J. The crude residue was purified by preparative thin layer chromatography (silica, 10% MeOH/DCM) to yield **(–)-10a*** (10.1 mg, 24% yield) in >99% ee.

$[\alpha]_D^{22} =$ –90 (c = 0.7, $CHCl_3$).

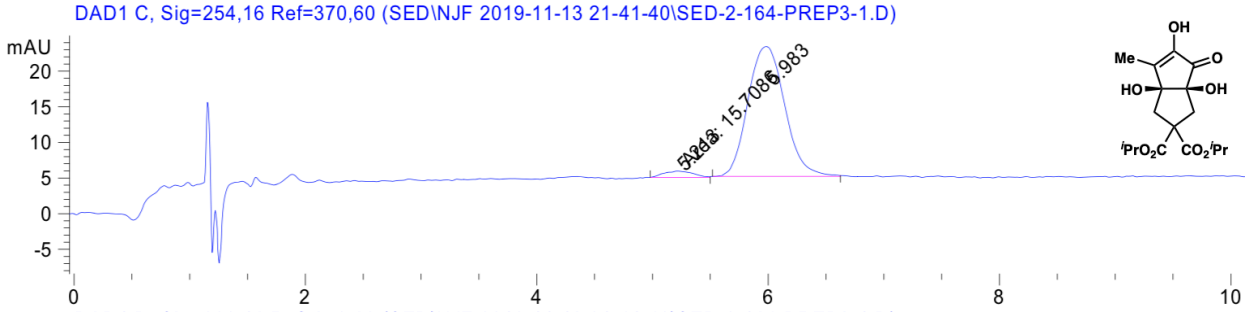
(–)-10a*: enantioenriched, >99% ee



Prepared from **(+)-11a*** (20 mg, 0.06 mmol, 92% ee) following General Procedure I. The crude residue was purified by column chromatography (silica, 7% MeOH/DCM) to yield **(+)-10a*** (1.1 mg, 5% yield) in 92% ee.

$[\alpha]_D^{22} =$ +14 (c = 0.1, $CHCl_3$).

(+)-10a*: enantioenriched, 92% ee

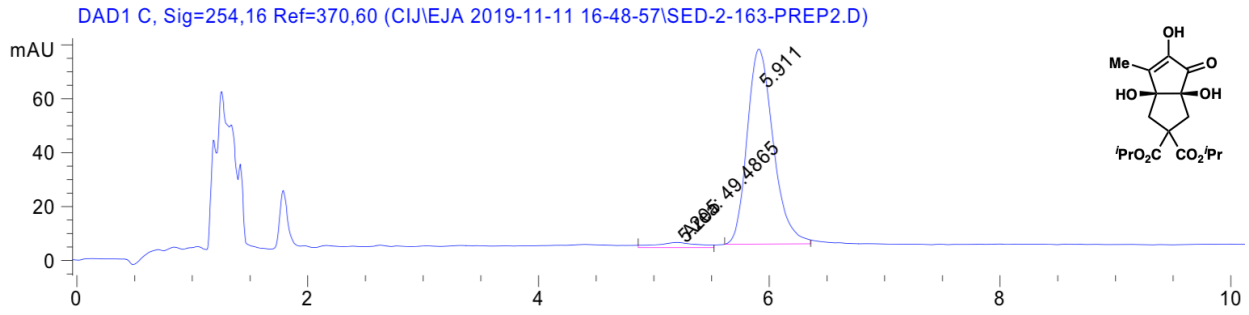


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.213	MM	0.2931	15.70860	8.93133e-1	3.7445
2	5.983	BB	0.3545	403.80246	18.22254	96.2555

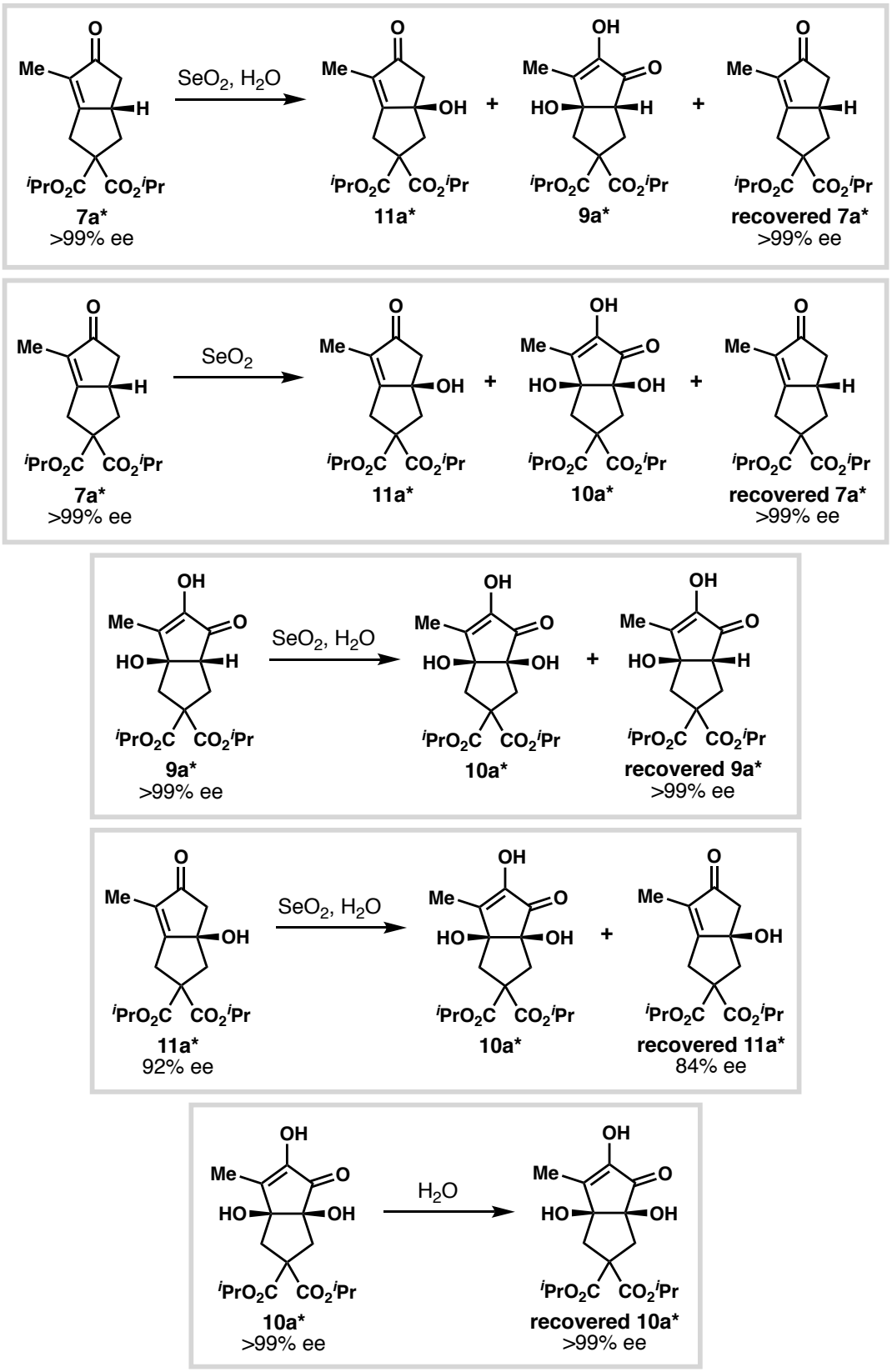
Prepared from **(+)-11a*** (20 mg, 0.06 mmol, 92% ee) following General Procedure J. The crude residue was purified by column chromatography (silica, 7% MeOH/DCM) to yield **(+)-10a*** (0.2 mg, 1% yield) in 92% ee.

$[\alpha]_D^{22} =$ +1 (c = 0.1, $CHCl_3$).

(+)-10a*: enantioenriched, 92% ee



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.205	MM	0.4254	49.48651	1.93883	4.1664
2	5.911	BB	0.2437	1138.27368	72.27718	95.8336

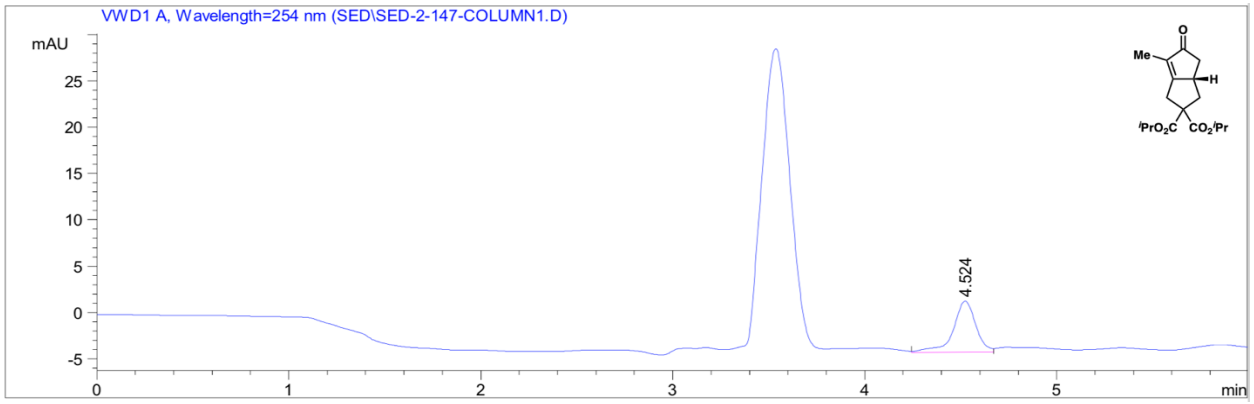


Scheme S2. Control experiments.

Recovered from **(+)-7a*** (200 mg, 0.65 mmol, >99% ee) following General Procedure I. The crude residue was purified by column chromatography (silica, 0 to 30% EtOAc/hexanes) to yield **(+)-7a*** (150 mg, 75% recovery) in >99% ee.

$[\alpha]_D^{22} =$ +126 (c = 0.2, $CHCl_3$).

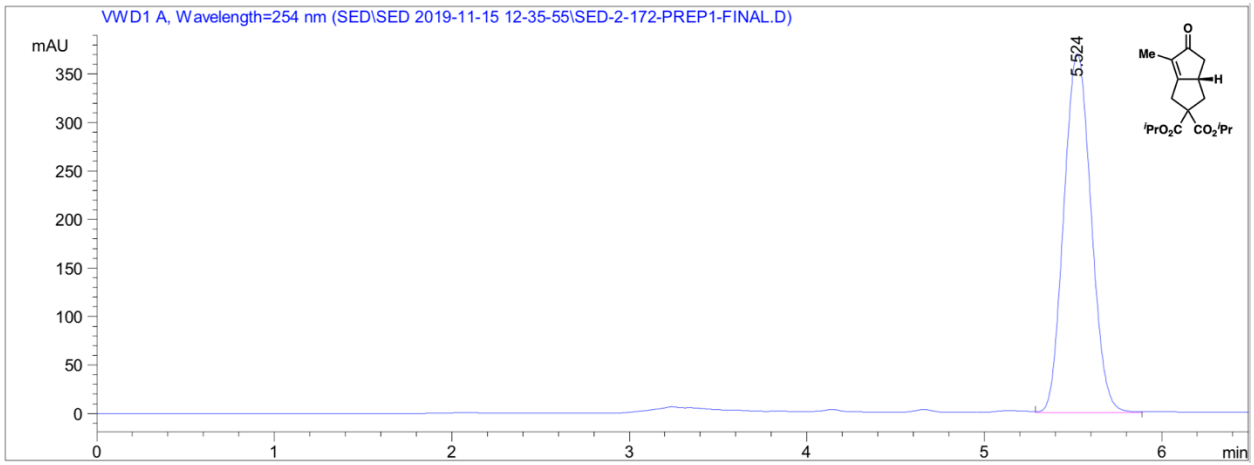
(+)-7a*: enantioenriched, >99% ee



Recovered from **(–)-7a*** (22 mg, 0.07 mmol, >99% ee) following General Procedure J. The crude residue was purified by preparative thin layer chromatography (silica, 7% MeOH/DCM) to yield **(–)-7a*** (1 mg, 4% recovery) in >99% ee.

$[\alpha]_D^{22} =$ –94 (c = 0.7, $CHCl_3$).

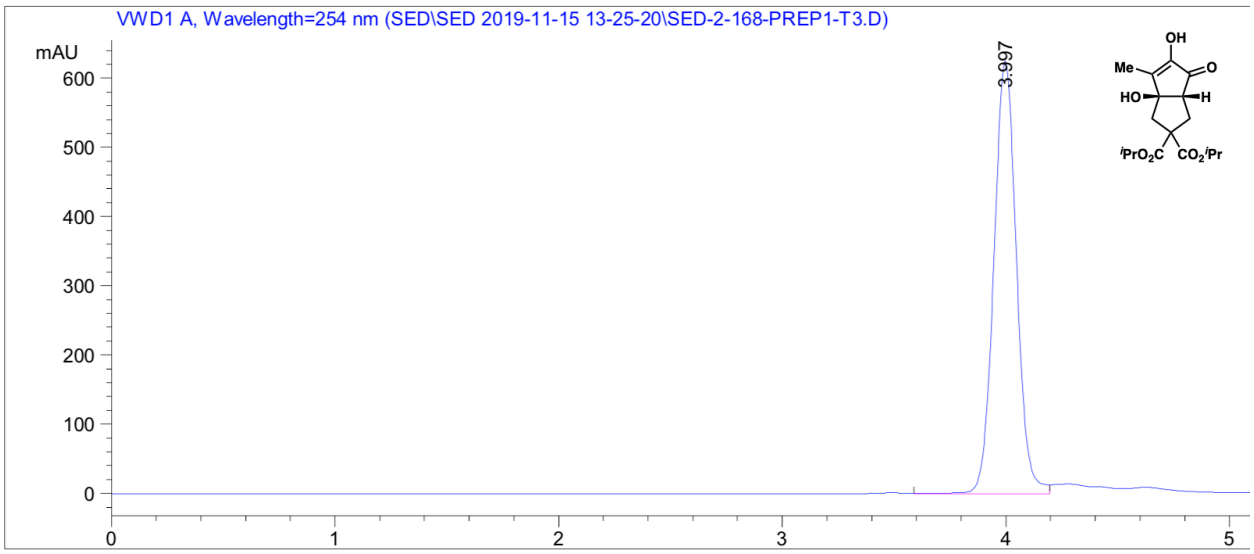
(–)-7a*: enantioenriched, >99% ee



Recovered from **(–)-9a*** (60 mg, 0.18 mmol, >99% ee) following General Procedure I. The crude residue was purified by preparative thin layer chromatography (silica, 10% MeOH/DCM) to yield **(–)-9a*** (2.2 mg, 4% recovery) in >99% ee.

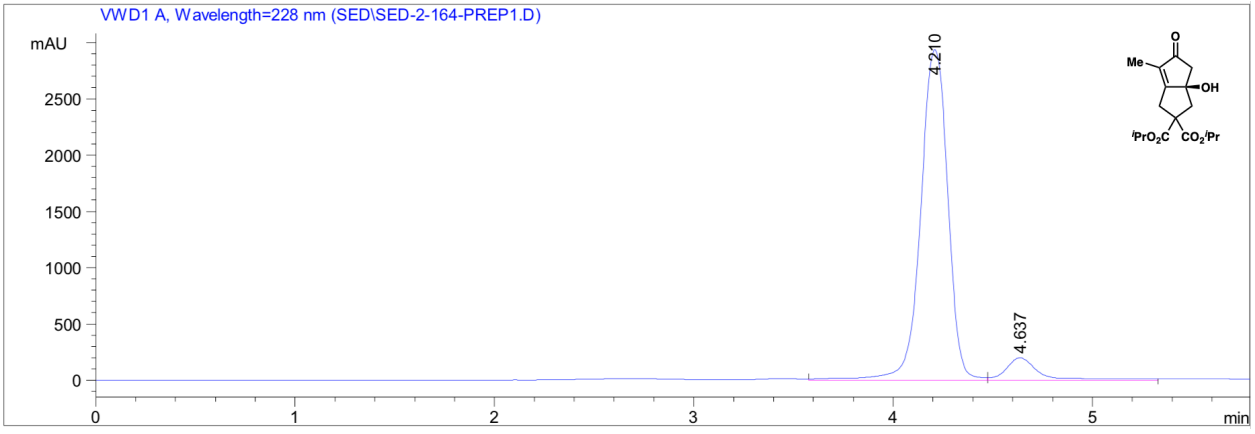
$[\alpha]_D^{22} =$ –36 (c = 0.1, $CHCl_3$).

(–)-9a*: enantioenriched, >99% ee



Recovered from **(+)-11a*** (20 mg, 0.65 mmol, 92% ee) following General Procedure I. The crude residue was purified by column chromatography (silica, 0 to 30% EtOAc/hexanes) followed by preparative thin layer chromatography (silica, 7% MeOH/DCM) to yield **(+)-11a*** (2.2 mg, 11% recovery) in 84% ee. $[\alpha]_D^{22} =$ +30 (c = 0.1, $CHCl_3$).

(+)-11a*: enantioenriched, 84% ee

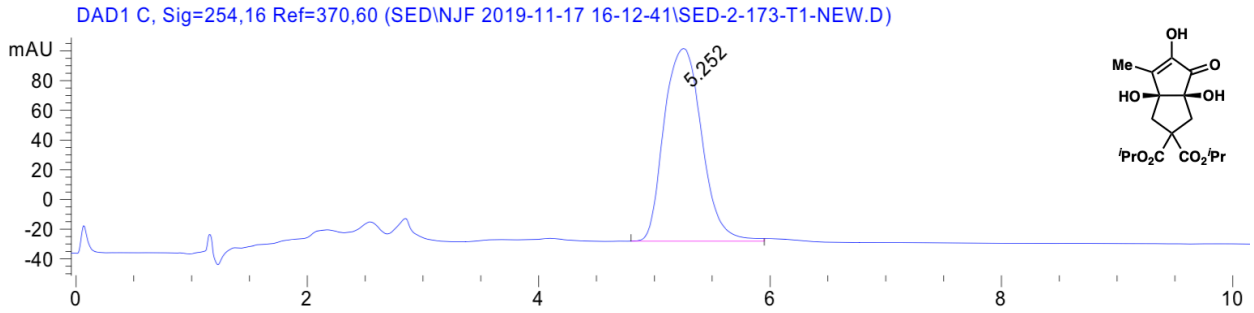


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	4.210	VV	0.1488	2.79395e4	2938.34180	92.1256
2	4.637	VB	0.1743	2388.11646	199.86485	7.8744

Recovered from **(–)-10a*** (10 mg, 0.03 mmol, >99% ee) following General Procedure I except that the addition of SeO_2 to the reaction mixture was omitted. The crude residue afforded **(–)-10a*** (10 mg, 99% recovery) in >99% ee.

$[\alpha]_D^{22} =$ –90 (c = 0.7, $CHCl_3$).

(–)-10a*: enantioenriched, >99% ee

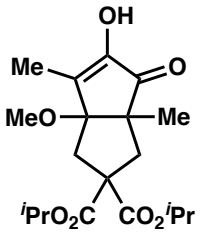


5. Mechanistic Investigation

Mechanistic Investigation: General Procedure K

All synthetic manipulations were performed in a glovebox. To a flame-dried vial with a Teflon-coated stir bar was added the enone (**6a** or **6e–i**) (0.1 mmol, 1.0 equiv), SeO_2 (111 mg, 1.0 mmol, 10.0 equiv), internal standard 1,2,4,5-tetrachloro-3-nitrobenzene (26 mg, 0.1 mmol, 1.0 equiv), and 1,4-dioxane-d_8 (0.8 mL, 0.125 M). The reaction was capped and sealed with Teflon tape, stirred, and brought to 100 °C in a preheated aluminum reaction block. A t specified time points, the reaction was allowed to reach room temperature and an aliquot (0.1–0.2 mL) was removed and filtered over a cotton plug directly into a dry NMR tube, washing with additional 1,4-dioxane-d_8 (0.3–0.4 mL). The tube was sealed and analyzed by NMR. If applicable, D_2O (180 µL, 10.0 mmol, 100.0 equiv) or CD_3OD (406 µL, 10.0 mmol, 100.0 equiv) was added to the appropriate aliquot, which was then brought to 100 ºC in a preheated oil bath (outside of the glovebox); at specified time points, the aliquots were allowed to reach room temperature, analyzed by NMR, then returned to the heat. Yield determined by ^{1}H NMR versus the internal standard.

diisopropyl 5-hydroxy-6a-methoxy-3a,6-dimethyl-4-oxo-3,3a,4,6a-tetrahydropentalene-2,2(1*H*)-dicarboxylate (13)



^{1}H NMR (400 MHz, $CDCl_3$) δ 4.98 (hept, *J* = 6.2 Hz, 1H), 4.85 (hept, *J* = 6.3 Hz, 1H), 3.15 (s, 3H), 2.78 (ddd, *J* = 13.8, 5.8, 2.2 Hz, 2H), 2.43 (d, *J* = 13.7 Hz, 1H), 1.97 (d, *J* = 13.9 Hz, 1H), 1.92 (s, 3H), 1.24 – 1.12 (m, 16H).

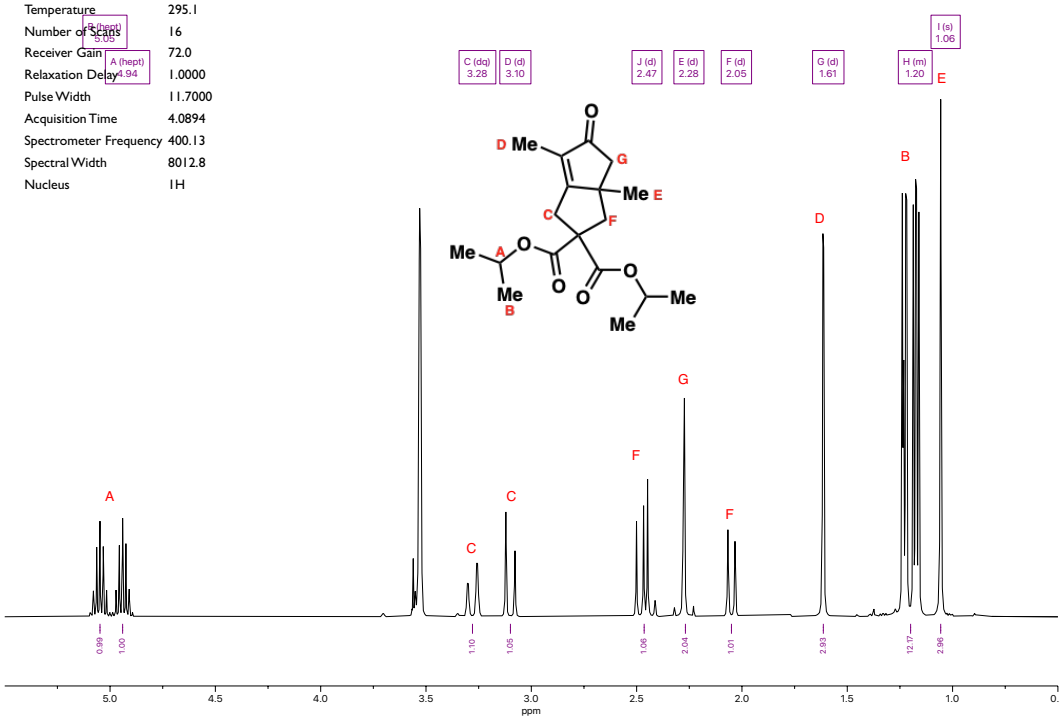
^{13}C NMR (101 MHz, $CDCl_3$) δ 203.53, 170.29, 169.71, 150.71, 138.57, 90.56, 77.36, 69.72, 69.64, 57.48, 53.05, 52.79, 44.42, 40.52, 29.86, 21.66, 21.64, 21.62, 21.53, 18.34, 10.29.

FTIR (NaCl, thin film, cm^{-1}): 3453, 2919, 2851, 1731, 1282, 1076.

HRMS (TOF-ESI, m/z): calc'd for $C_{19}H_{28}O_7$: 337.1646 $[M–CH_3OH+H]^+$; found: 337.1653.

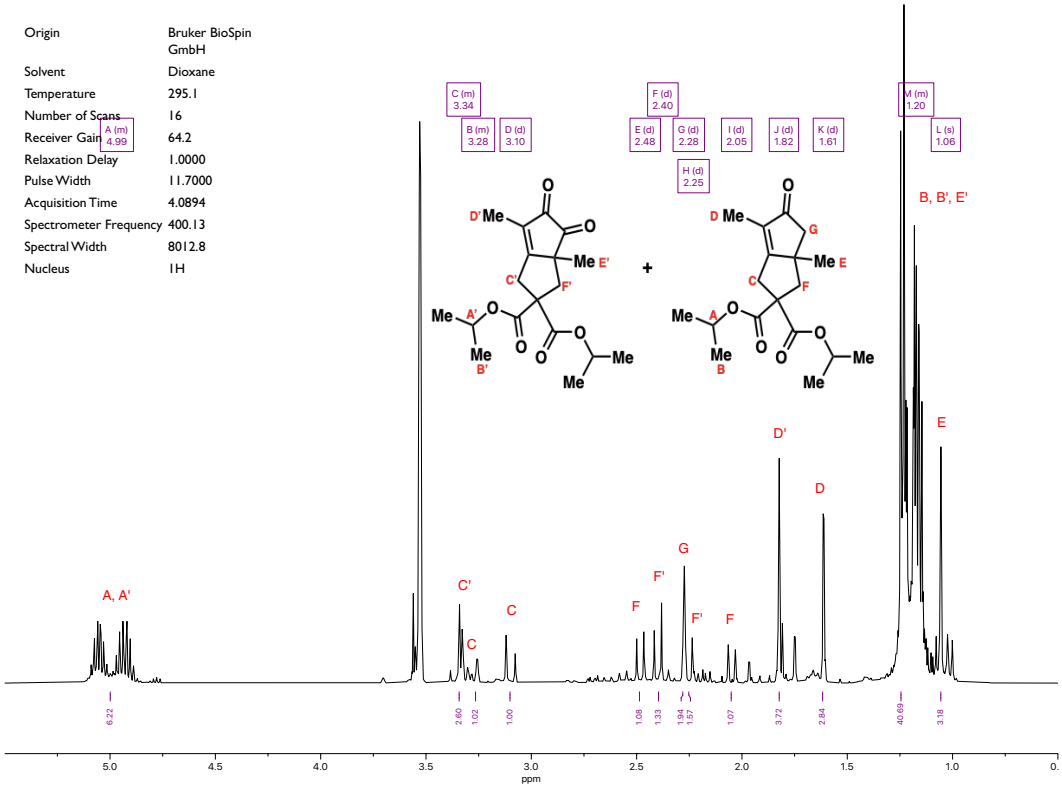
A

Origin	Bruker BioSpin GmbH
Solvent	Dioxane
Temperature	295.1
Number of Scans	16
Receiver Gain	72.0
Relaxation Delay	1.0000
Pulse Width	11.7000
Acquisition Time	4.0894
Spectrometer Frequency	400.13
Spectral Width	8012.8
Nucleus	1H



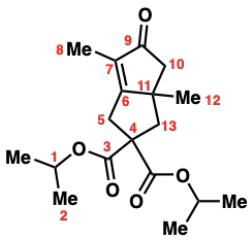
B

Origin	Bruker BioSpin GmbH
Solvent	Dioxane
Temperature	295.1
Number of Scans	16
Receiver Gain	64.2
Relaxation Delay	1.0000
Pulse Width	11.7000
Acquisition Time	4.0894
Spectrometer Frequency	400.13
Spectral Width	8012.8
Nucleus	1H



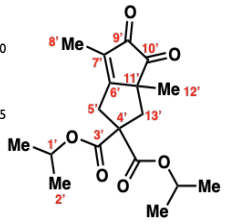
C

Origin	Bruker BioSpin GmbH
Solvent	Dioxane
Temperature	295.1
Number of Scans	256
Receiver Gain	64.2
Relaxation Delay	1.0000
Pulse Width	10.0000
Acquisition Time	1.3631
Spectrometer Frequency	100.62
Spectral Width	24038.5
Nucleus	13C



D

Origin	Bruker BioSpin GmbH
Solvent	Dioxane
Temperature	295.2
Number of Scans	256
Receiver Gain	64.2
Relaxation Delay	1.0000
Pulse Width	10.0000
Acquisition Time	1.3631
Spectrometer Frequency	100.62
Spectral Width	24038.5
Nucleus	13C



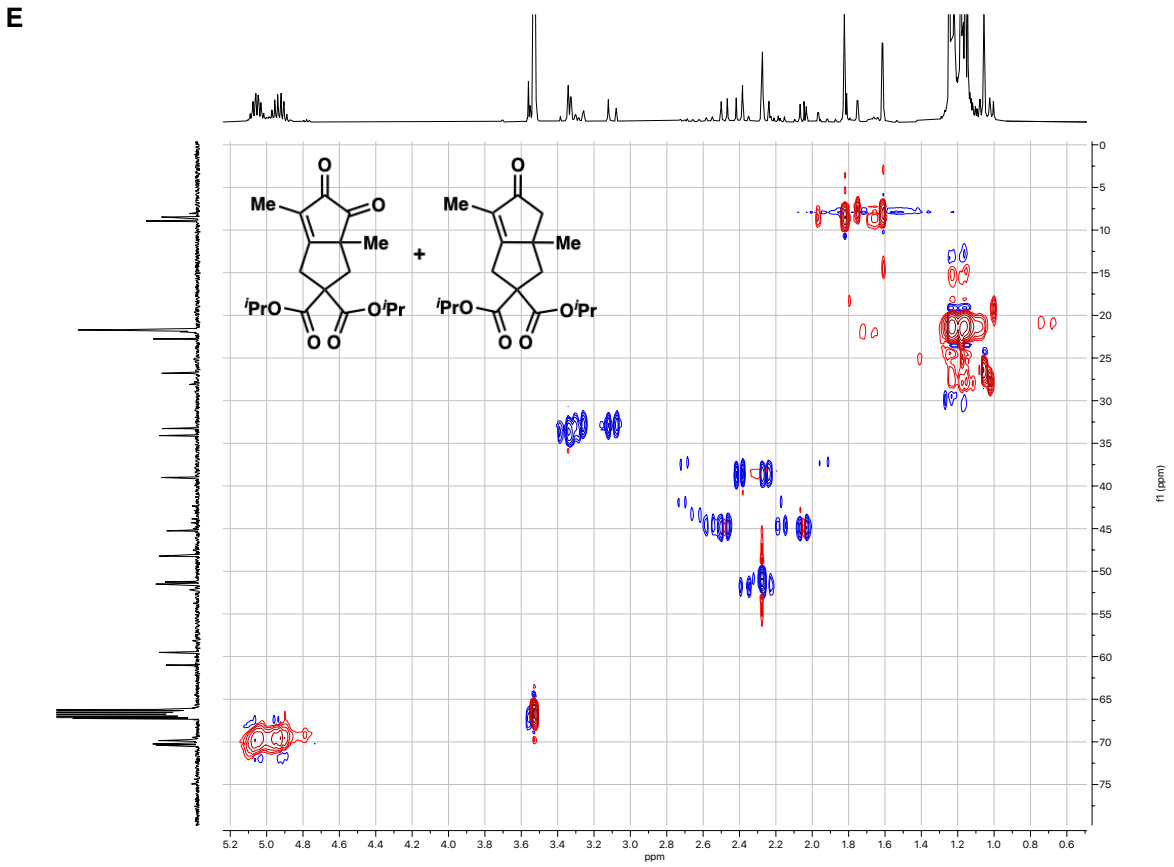


Figure S1. Structural assignment of **12a** based on ^{1}H (b), ^{13}C (d), and HSQC (e) NMR spectra of reaction of **6a** (a,c) under anhydrous conditions [SeO_2 (10.0 equiv), 1,4-dioxane-d_8 (0.125 M), 100 °C] after 6 hours.

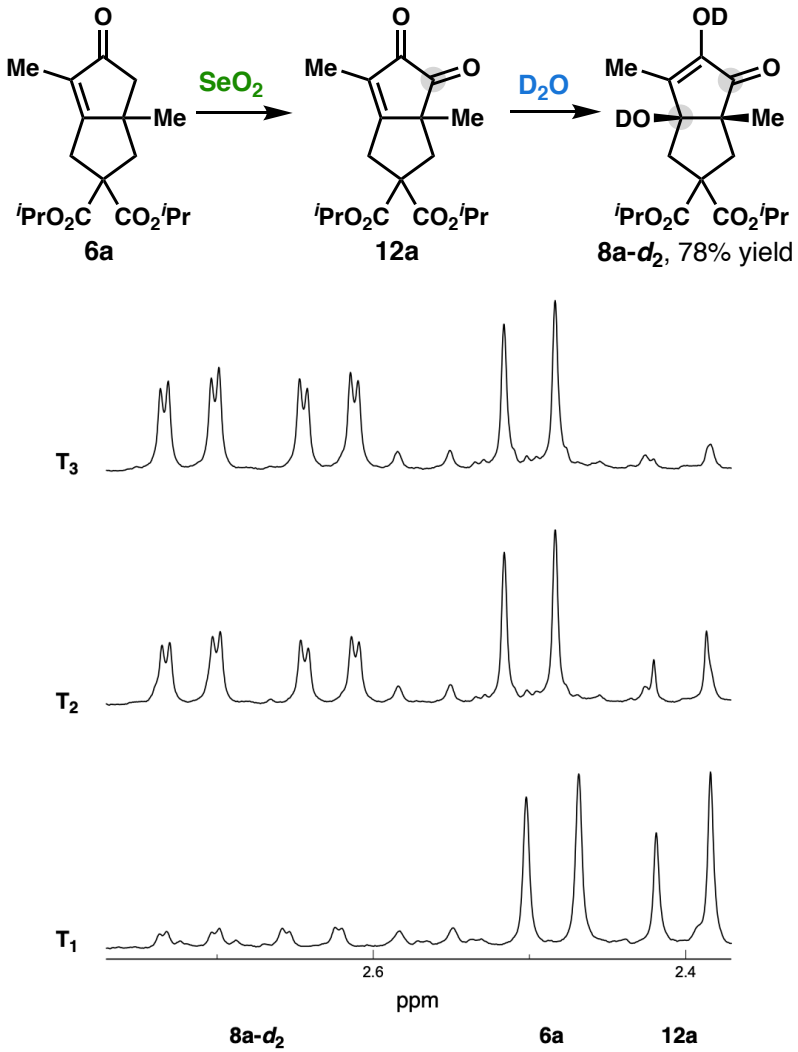


Figure S2. Section of ^{1}H NMR spectra highlighting *in situ* formation of **12a** from reaction of **6a** under anhydrous conditions [SeO_2 (10.0 equiv), 1,4-dioxane-d_8 (0.125 M), 100 °C] after 3 hours (T_1) followed by *in situ* formation of **8a-*d*$_2$** from addition of D_2O (100.0 equiv) at 1 h (T_2) and 3 h (T_3).

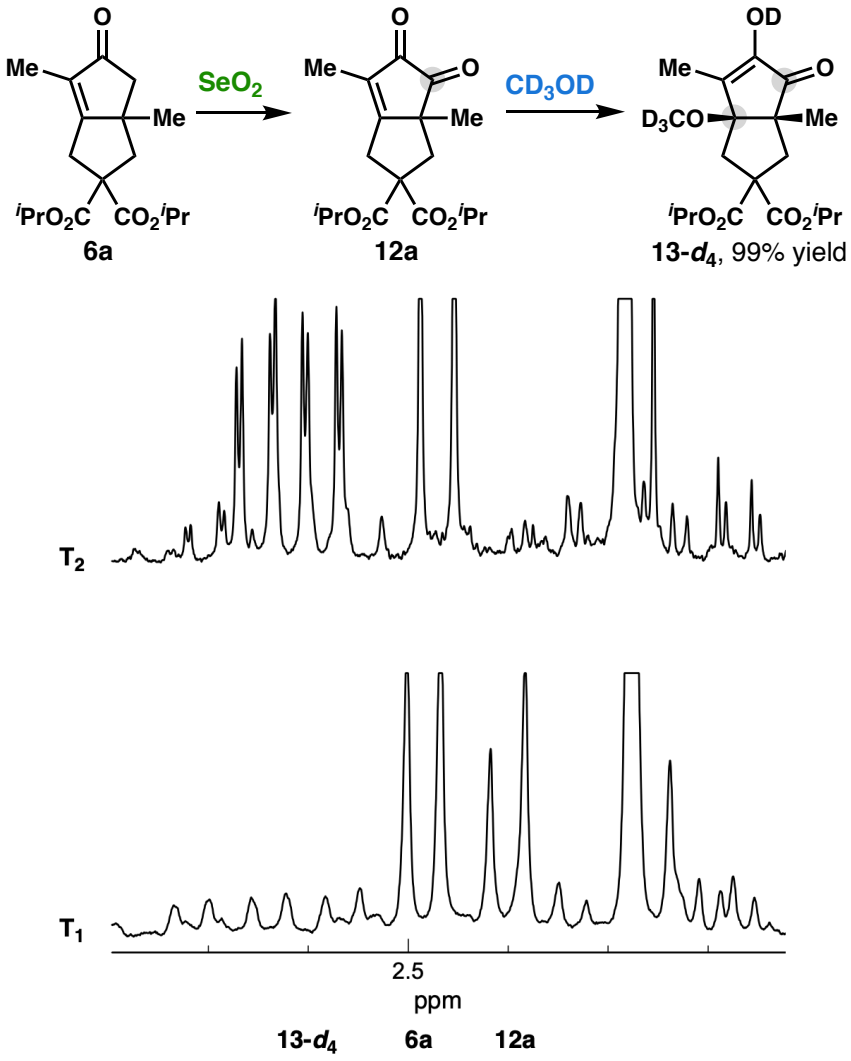
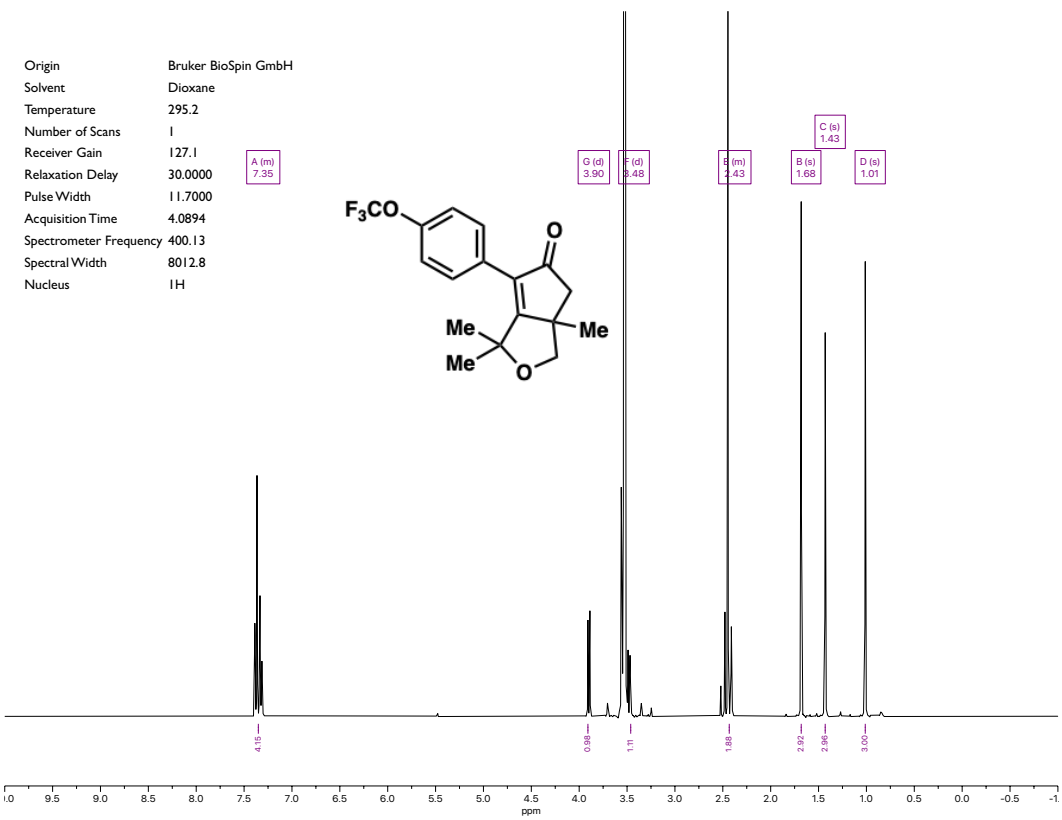
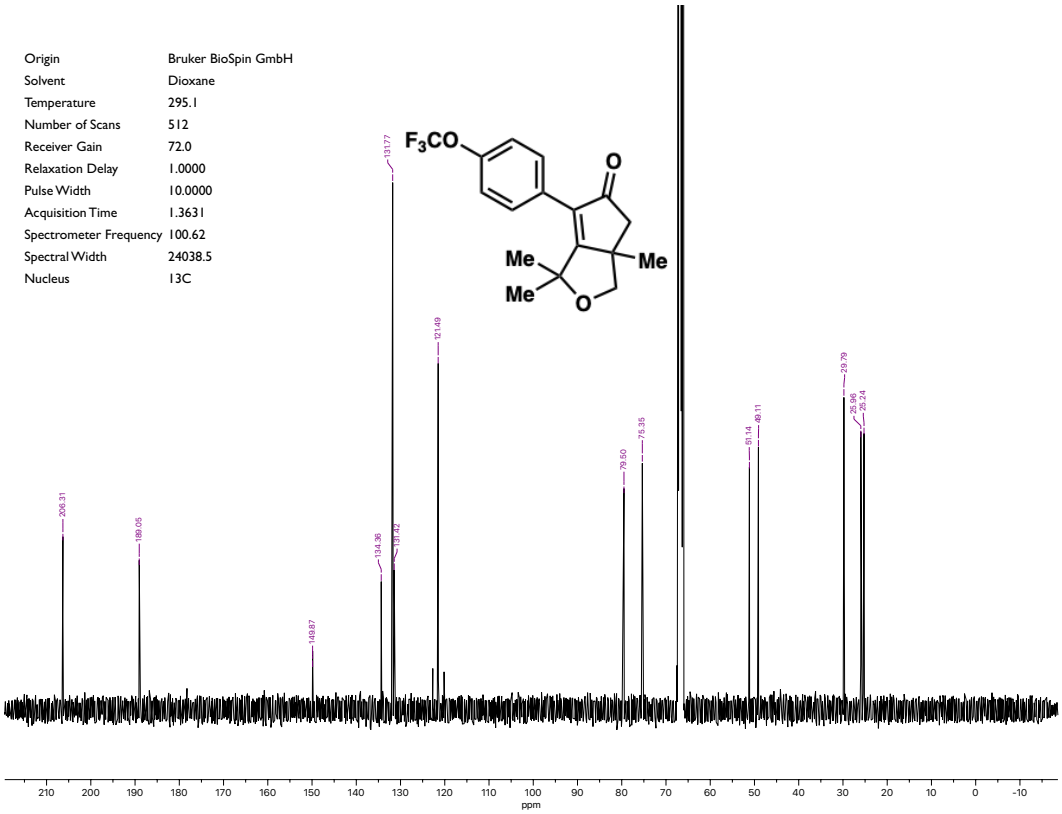


Figure S3. Section of ^{1}H NMR spectra highlighting *in situ* formation of **12a** from reaction of **6a** under anhydrous conditions [SeO_2 (10.0 equiv), 1,4-dioxane-d_8 (0.125 M), 100 °C] after 3 hours (T_1) followed by *in situ* formation of **13-*d*$_4$** from addition of CD_3OD (100.0 equiv) at 25 h (T_2).

A


Origin Bruker BioSpin GmbH
Solvent Dioxane
Temperature 295.2
Number of Scans 1
Receiver Gain 127.1
Relaxation Delay 30.0000
Pulse Width 11.7000
Acquisition Time 4.0894
Spectrometer Frequency 400.13
Spectral Width 8012.8
Nucleus 1H
A (m) 7.35
G (d) 3.90
F (d) 3.48
E (m) 2.43
C (s) 1.43
B (s) 1.68
D (s) 1.01
F3CO
O
Me
Me
Me
O
4.15
0.98
1.11
1.88
2.92
2.96
3.00
ppm

B


Origin Bruker BioSpin GmbH
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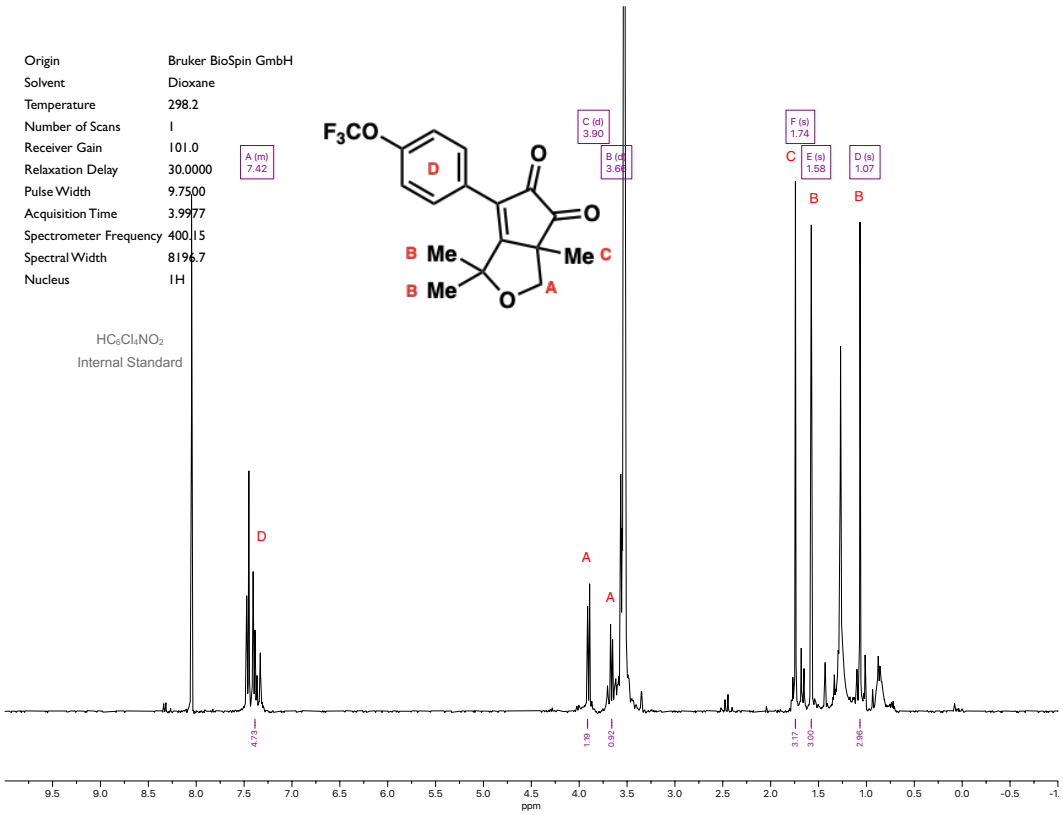
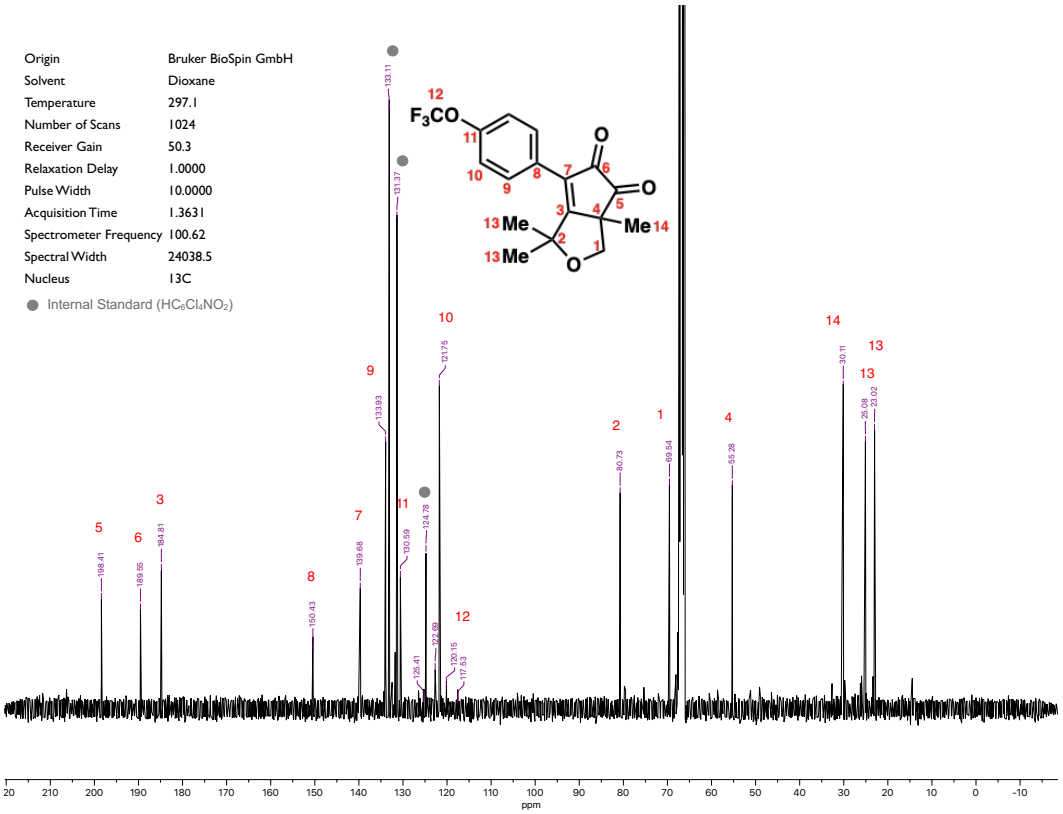
Receiver Gain 72.0
Relaxation Delay 1.0000
Pulse Width 10.0000
Acquisition Time 1.3631
Spectrometer Frequency 100.62
Spectral Width 24038.5
Nucleus 13C
F3CO
O
Me
Me
Me
O
206.31
189.05
149.87
134.36
131.42
131.77
121.49
79.50
75.35
51.14
49.11
29.79
25.96
25.24
ppm

C


Origin Bruker BioSpin GmbH
Solvent Dioxane
Temperature 298.2
Number of Scans 1
Receiver Gain 101.0
Relaxation Delay 30.0000
Pulse Width 9.7500
Acquisition Time 3.9977
Spectrometer Frequency 400.15
Spectral Width 8196.7
Nucleus 1H
HC6Cl4NO2
Internal Standard
A (m) 7.42
C (d) 3.90
B (d) 3.66
F (s) 1.74
E (s) 1.58
D (s) 1.07
F3CO
Me
Me
ppm

D


Origin Bruker BioSpin GmbH
Solvent Dioxane
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Number of Scans 1024
Receiver Gain 50.3
Relaxation Delay 1.0000
Pulse Width 10.0000
Acquisition Time 1.3631
Spectrometer Frequency 100.62
Spectral Width 24038.5
Nucleus 13C
Internal Standard (HC6Cl4NO2)
F3CO
Me
Me
ppm

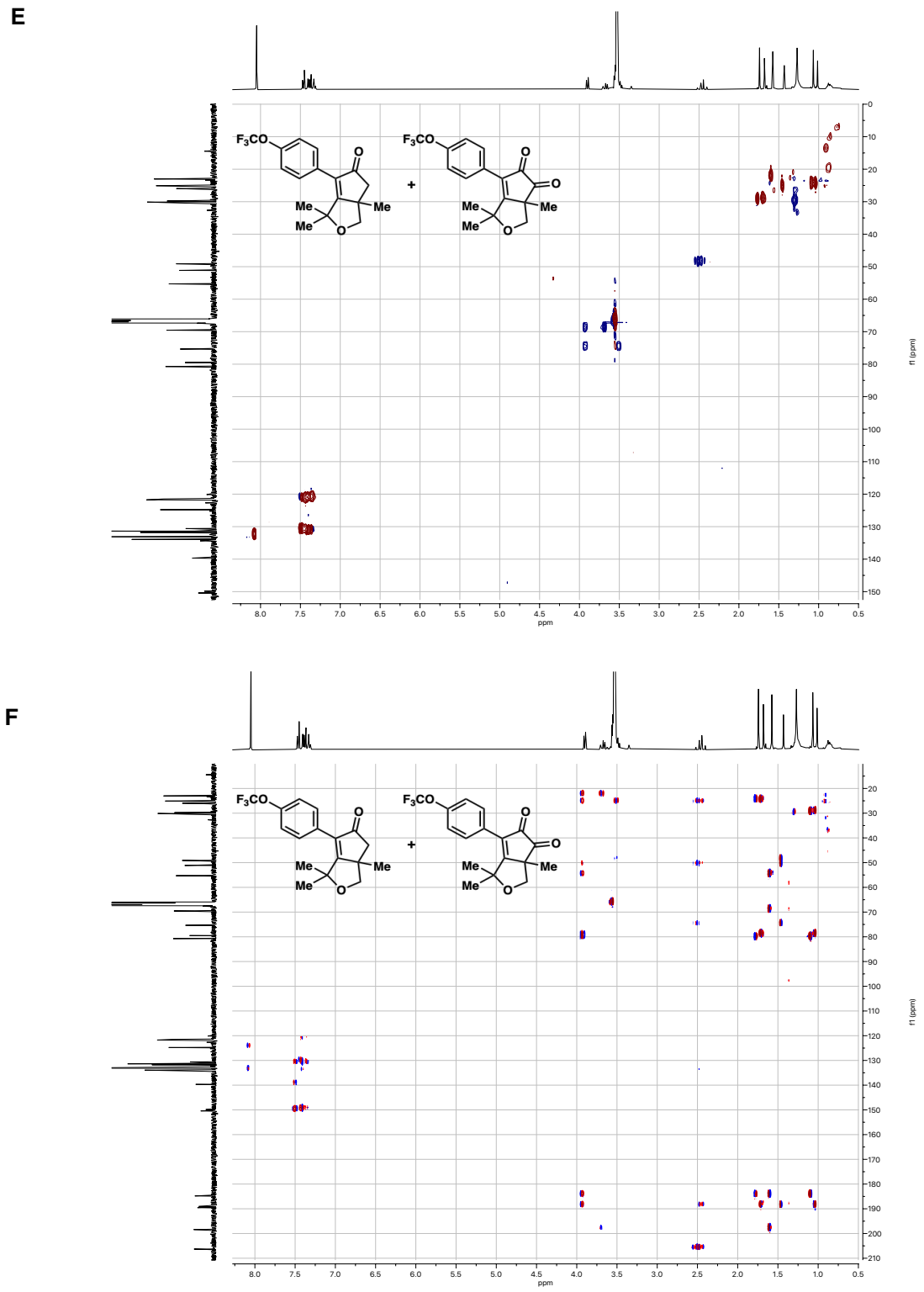
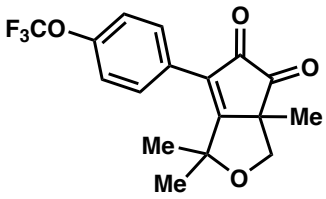


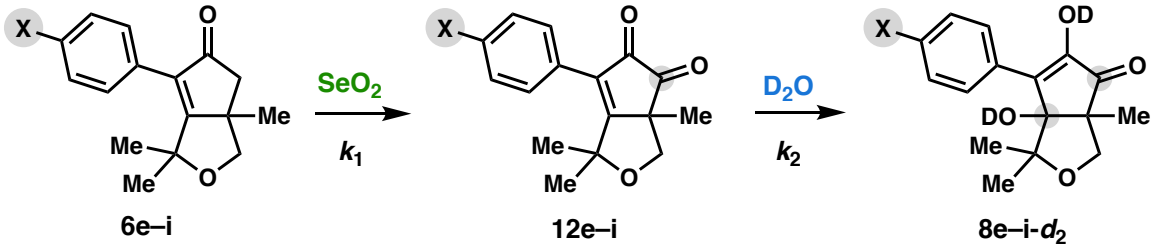
Figure S4. Structural assignment of **12e** based on ^{1}H (c), ^{13}C (d), HSQC (e), and HMBC (f) NMR spectra of reaction of **6e** (a,b) under anhydrous conditions [SeO_2 (10.0 equiv), 1,4-dioxane-d_8 (0.125 M), 100 °C] after 4 hours (e,f) and 8 hours (c,d). Structural assignments of ene-diketones **12f–i** made by analogy to **12e**.

diisopropyl 5-hydroxy-6a-methoxy-3a,6-dimethyl-4-oxo-3,3a,4,6a-tetrahydropentalene-2,2(1*H*)-dicarboxylate (12e)



^{1}H NMR (400 MHz, 1,4-dioxane-d_8) δ 7.51 – 7.36 (m, 4H), 3.90 (d, J = 8.5 Hz, 1H), 3.66 (d, J = 8.5 Hz, 1H), 1.74 (s, 3H), 1.58 (s, 3H), 1.07 (s, 3H).

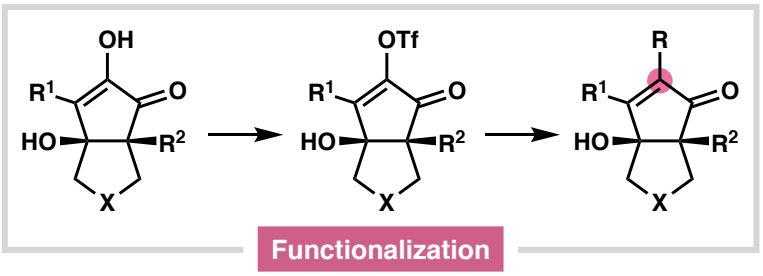
^{13}C NMR (101 MHz, 1,4-dioxane-d_8) δ 198.41, 189.55, 184.81, 150.43, 139.68, 133.93, 131.77, 131.50, 130.59, 122.69, 121.75, 121.61, 121.48, 80.73, 69.54, 55.28, 30.41, 30.11, 25.96, 23.02.



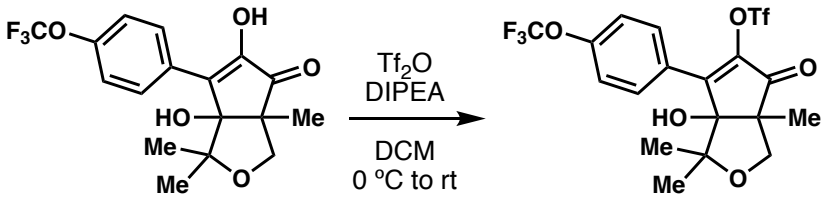
X	σ_p	k_1 (Ms^{-1})	$\log(k_X/k_H)$	k_2 (Ms^{-1})	$\log(k_X/k_H)$
OMe	–0.27	6.5 x10^{-6}	0.042	2.4 x10^{-6}	–0.267
H	0	5.9 x10^{-6}	0	4.4 x10^{-6}	0
Br	0.23	5.5 x10^{-6}	–0.029	6.1 x10^{-6}	0.141
OCF_3	0.35	5.1 x10^{-6}	–0.061	1.1 x10^{-5}	0.415
CF_3	0.54	5.0 x10^{-6}	–0.072	1.0 x10^{-5}	0.357
		ρ	–0.15	**ρ**	0.84
		R^2	0.98	**R^2**	0.91

Table S3. Tabulated Hammett parameters[23] and rate constants. Initial rates measured for the *in situ* formation of **12e–i** from **6e–i** under anhydrous conditions [SeO_2 (10.0 equiv), 1,4-dioxane-d_8 (0.125 M), 100 ºC] (k_1) and for the *in situ* formation of **8e–i** from **12e–i** [D_2O (100.0 equiv), 1,4-dioxane-d_8 (0.125 M), 100 ºC] (k_2). Structural assignments of dioxidation products **8f–i-d_2** made by analogy to ^{1}H and ^{13}C NMR spectra of **8e-d_2**.

6. Functionalization of Dioxidation Product



6a-hydroxy-1,1,3a-trimethyl-4-oxo-6-(4-(trifluoromethoxy)phenyl)-3,3a,4,6a-tetrahydro-1*H*-cyclopenta[*c*]furan-5-yl trifluoromethanesulfonate (15e)



To a dry 1-dram vial with a Teflon-coated stir bar was added **8e** (65 mg, 0.2 mmol, 1.0 equiv). The vial was sealed with a rubber septum and placed under an atmosphere of dry N_2. The solid was taken up in DCM (1 mL, 0.20 M) and stirred, iPr_2NEt (53 µL, 0.3 mmol, 1.5 equiv) added, and the solution cooled to 0 °C in an ice water bath. Trifluoromethanesulfonic anhydride (34 µL, 0.2 mmol, 1.0 equiv) was then added dropwise via syringe, with a vent needle to release any triflic acid generated. The resulting mixture was allowed to reach room temperature and monitored by TLC. Upon completion, the reaction was quenched by dropwise addition of water then diluted with water and DCM. The layers were separated, and the aqueous layer was extracted twice with DCM. Combined organics were washed with water and brine, dried over Na_2SO_4, filtered, and concentrated. The crude residue was purified by trituration from DCM and pentanes (1:4) to yield **15e** (88 mg, 0.20 mmol, 99% yield) as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 – 7.92 (m, 2H), 7.32 (ddt, *J* = 8.0, 2.2, 1.1 Hz, 2H), 4.13 (d, *J* = 9.9 Hz, 1H), 3.68 (d, *J* = 9.9 Hz, 1H), 1.31 (d, *J* = 3.0 Hz, 6H), 0.96 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 197.78, 154.23, 150.22, 142.15, 130.58, 127.74, 120.74, 119.77, 118.92, 118.16, 115.73, 87.96, 83.57, 70.39, 57.68, 28.85, 24.99, 20.77, 15.62.

FTIR (NaCl, thin film, cm^{-1}): 3446, 2994, 29256, 2854, 2355, 1738, 1732, 1715, 1632, 1506, 1434, 1212.

HRMS (TOF-ESI, m/z): calc'd for $C_{18}H_{16}F_6O_7S$: 491.0594 $[M+H]^+$; found: 491.0603.

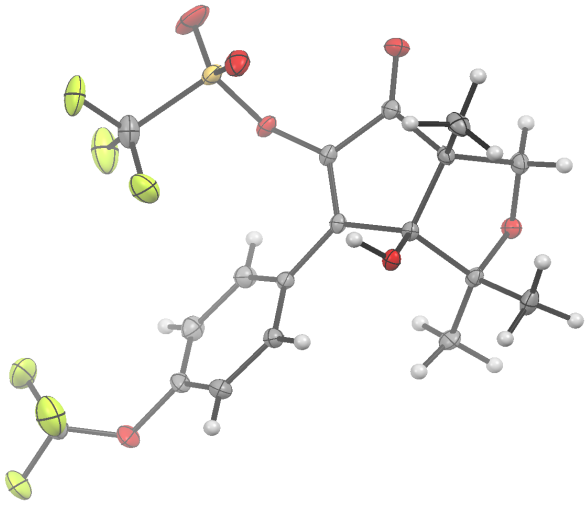


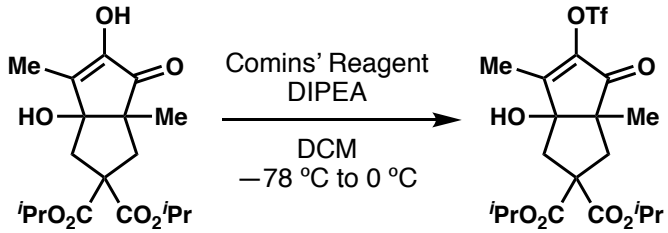
Figure S5. Structure of **15e** with 50% probability anisotropic displacement ellipsoids. Compound **15e** crystallizes in the monoclinic space group $P12_1/c1$ with one molecule in the asymmetric unit. The coordinates for the hydrogen atom bound to O3 was located in the difference Fourier synthesis and refined using a riding model.

Table S4. Crystal data and structure refinement for v18444_a.

Identification code	v18444_a	
Empirical formula	C18 H16 F6 O7 S	
Formula weight	490.37	
Temperature	99.99 K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 1 21/c 1	
Unit cell dimensions	a = 6.0928(3) Å	α= 90°.
	b = 9.2223(5) Å	β= 91.673(2)°.
	c = 35.161(2) Å	γ = 90°.
Volume	1974.84(18) $Å^3$	
Z	4	
Density (calculated)	1.649 Mg/m^3	
Absorption coefficient	0.260 mm^{-1}	
F(000)	1000	
Crystal size	0.26 x 0.23 x 0.15 mm^3	
Theta range for data collection	2.494 to 27.518°.	
Index ranges	-7<=h<=7, -11<=k<=11, -45<=l<=45	
Reflections collected	59485	

Independent reflections	4529 [R(int) = 0.0412]
Completeness to theta = 26.000°	99.9 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7456 and 0.7195
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4529 / 0 / 295
Goodness-of-fit on F^2	1.090
Final R indices [I>2sigma(I)]	R1 = 0.0326, wR2 = 0.0807
R indices (all data)	R1 = 0.0357, wR2 = 0.0820
Extinction coefficient	n/a
Largest diff. peak and hole	0.442 and -0.399 e.Å^{-3}

diisopropyl 6a-hydroxy-3a,6-dimethyl-4-oxo-5-(((trifluoromethyl)sulfonyl)oxy)-3,3a,4,6a-tetrahydropentalene-2,2(1*H*)-dicarboxylate (15a)



To a dry round bottom flask with a Teflon-coated stir bar was added **8a** (648 mg, 1.8 mmol, 1.0 equiv). The vial was sealed with a rubber septum and placed under an atmosphere of dry N_2. The solid was taken up in DCM (37 mL, 0.05 M) and stirred, DIPEA (1.6 mL, 1.25 mmol, 5.0 equiv) added, and the solution cooled to –78 °C in a dry ice/acetone bath. Comins' Reagent (719 mg, 0.25 mmol, 1.0 equiv) was then added in one portion. The resulting mixture was allowed to reach 0 ºC following transfer to an ice water bath and monitored by TLC. Upon completion, the reaction was directly purified by column chromatography (silica, 20% EtOAc/hexanes) to afford **15a** (797 mg, 90% yield) as an orange oil.

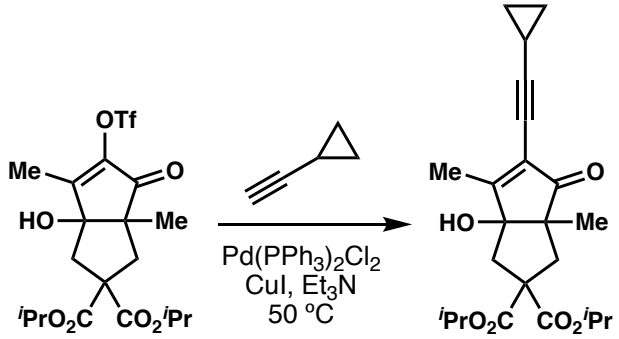
^{1}H NMR (400 MHz, $CDCl_3$) δ 5.06 (heptd, *J* = 6.3, 0.9 Hz, 1H), 4.93 (pd, *J* = 6.3, 0.8 Hz, 1H), 2.72 (d, *J* = 14.5 Hz, 1H), 2.52 (s, 2H), 2.24 (d, *J* = 14.5 Hz, 1H), 2.18 (s, 3H), 1.24 (dd, *J* = 6.3, 3.0 Hz, 6H), 1.21 – 1.09 (m, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 198.44, 171.95, 169.21, 162.78, 142.51, 120.15, 116.96, 85.09, 70.56, 70.02, 59.41, 55.72, 44.20, 41.99, 21.57, 21.55, 21.35, 19.30, 10.82.

FTIR (NaCl, thin film, cm^{-1}): 3477, 2982, 2939, 1738, 1732, 1715, 1428, 1219, 1099, 987, 896.

HRMS (TOF-ESI, m/z): calc'd for $C_{19}H_{25}F_3O_9S$: 504.1510 $[M+NH_4]^+$; found: 504.1521.

diisopropyl 5-(cyclopropylethynyl)-6a-hydroxy-3a,6-dimethyl-4-oxo-3,3a,4,6a-tetrahydropentalene-2,2(1*H*)-dicarboxylate (14a)



Prepared from **15a** (24.4 mg, 0.05 mmol, 1.0 equiv), cyclopropyl acetylene (22 L, 0.25 mmol, 5.0 equiv), $Pd(PPh_3)_2Cl_2$ (3.5 mg, 0.005 mmol, 0.1 equiv), CuI (1.91 mg, 0.01 mmol, 0.2 equiv), Et_3N (0.20 mL, 0.25 M) at 50 ºC following General Procedure B. The resulting crude residue was purified by column chromatography (silica, 30% EtOAc/hexanes) to afford **14a** (10.1 mg, 51% yield) as a brown oil.

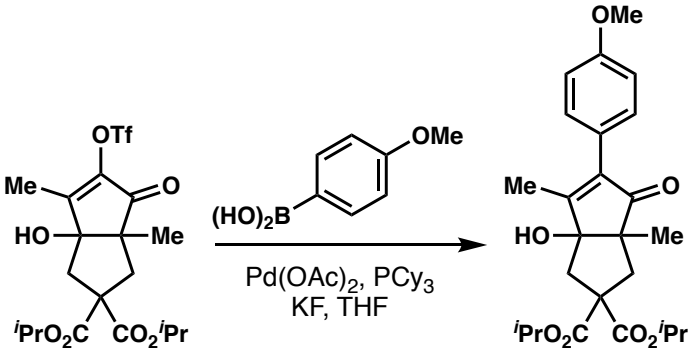
^{1}H NMR (400 MHz, $CDCl_3$) δ 5.02 (hept, *J* = 6.3 Hz, 1H), 4.89 (hept, *J* = 6.3 Hz, 1H), 2.73 (dd, *J* = 14.2, 1.3 Hz, 1H), 2.58 (dd, *J* = 13.9, 1.2 Hz, 1H), 2.56 (s, 1H), 2.44 (dd, *J* = 13.9, 0.8 Hz, 1H), 2.16 (s, 3H), 2.12 (dd, *J* = 14.1, 0.8 Hz, 1H), 1.44 (tt, *J* = 8.2, 5.0 Hz, 1H), 1.22 (dd, *J* = 6.3, 2.2 Hz, 6H), 1.18 (t, *J* = 6.0 Hz, 6H), 1.12 (s, 3H), 0.93 – 0.80 (m, 2H), 0.81 – 0.75 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 206.20, 175.31, 171.87, 169.34, 125.41, 103.47, 87.80, 70.10, 69.76, 65.93, 59.21, 56.14, 44.03, 42.93, 30.10, 29.84, 22.84, 21.58, 21.57, 21.45, 19.47, 13.57, 9.21, 1.16.

FTIR (NaCl, thin film, cm^{-1}): 3480, 2927, 2870, 2231, 1716, 1627, 1456, 1386, 1259, 1098.

HRMS (TOF-ESI, m/z): calc'd for $C_{23}H_{30}O_6$: 403.2155 $[M+H]^+$; found: 403.2135.

diisopropyl 6a-hydroxy-5-(4-methoxyphenyl)-3a,6-dimethyl-4-oxo-3,3a,4,6a-tetrahydropentalene-2,2(1*H*)-dicarboxylate (14b)



Prepared from **15a** (43 mg, 0.09 mmol, 1.0 equiv), (*p*-methoxyphenyl boronic acid (41 mg, 0.27 mmol, 3.0 equiv), potassium fluoride (30.8 mg, 0.53 mmol, 6.0 equiv), THF (5 mL), and catalyst stock solution (0.9 mL, 0.10 M, 0.04 equiv [Pd], 0.05 equiv PCy_3), prepared from $Pd(OAc)_2$ (4.5 mg, 0.02 mmol) and

tricyclohexyl phosphine (7.1 mg, 0.025 mmol), at 60 ºC following a literature procedure.[24] The crude residue was purified by column chromatography (silica, 30 to 40% EtOAc/hexanes) to afford **14b** (36.4 mg, 92% yield) as a white amorphous solid.

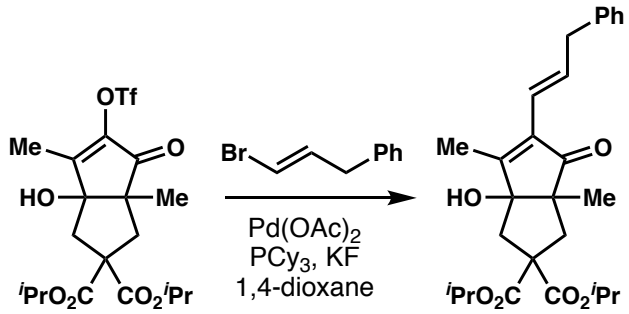
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 – 7.22 (m, 2H), 6.96 – 6.88 (m, 2H), 5.04 (hept, *J* = 6.3 Hz, 1H), 4.79 (hept, *J* = 6.3 Hz, 1H), 3.82 (s, 3H), 2.78 (ddd, *J* = 17.5, 13.9, 1.5 Hz, 2H), 2.48 (d, *J* = 12.4 Hz, 1H), 2.19 (d, *J* = 14.0 Hz, 1H), 2.18 (s, 3H), 1.22 (dd, *J* = 6.3, 1.2 Hz, 6H), 1.09 (d, *J* = 6.3 Hz, 3H), 0.99 (d, *J* = 6.3 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 207.85, 171.68, 169.63, 168.08, 159.46, 138.41, 130.55, 123.30, 113.76, 87.60, 69.99, 69.52, 58.88, 55.67, 55.39, 43.87, 43.14, 21.62, 21.53, 21.23, 19.59, 12.84.

FTIR (NaCl, thin film, cm^{-1}): 3471, 3047, 2843, 2549, 2248, 2056, 1713, 1454, 1249.

HRMS (TOF-ESI, m/z): calc'd for $C_{25}H_{32}O_7$: 445.2221$[M+H]^+$; found: 445.2242.

diisopropyl (*E*)-6a-hydroxy-3a,6-dimethyl-4-oxo-5-(3-phenylprop-1-en-1-yl)-3,3a,4,6a-tetrahydropentalene-2,2(1*H*)-dicarboxylate (14c)



Prepared from **15a** (49 mg, 0.1 mmol, 1.0 equiv), (E)-(3-bromoallyl)benzene (49 mg, 0.3 mmol, 3.0 equiv), potassium fluoride (35 mg, 0.6 mmol, 6.0 equiv), 1,4-dioxane (1 mL), and catalyst stock solution (0.5 mL, 0.10 M, 0.04 equiv [Pd], 0.05 equiv PCy_3), prepared from $Pd(OAc)_2$ (1.8 mg, 0.008 mmol) and tricyclohexyl phosphine (2.8 mg, 0.01 mmol), at 60 ºC following a literature procedure.[24] The crude residue was purified by column chromatography (silica, 30% (Et_2O/EtOAc, 1:1)/hexanes) to afford **14c** (35.3 mg, 78% yield) as a white amorphous solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 – 7.23 (m, 2H), 7.19 (tt, *J* = 6.4, 1.2 Hz, 3H), 6.94 (dt, *J* = 15.8, 7.1 Hz, 1H), 6.03 (dt, *J* = 15.8, 1.6 Hz, 1H), 5.01 (hept, *J* = 6.2 Hz, 1H), 4.74 (pd, *J* = 6.3, 1.0 Hz, 1H), 3.51 – 3.44 (m, 2H), 2.74 (dd, *J* = 13.9, 1.4 Hz, 1H), 2.65 (dt, *J* = 13.7, 1.2 Hz, 1H), 2.40 (d, *J* = 13.7 Hz, 1H), 2.12 (d, *J* = 14.2 Hz, 1H), 2.10 (s, 3H), 1.21 (dd, *J* = 6.3, 1.5 Hz, 6H), 1.11 (t, *J* = 3.1 Hz, 6H), 1.05 (d, *J* = 6.3 Hz, 3H).

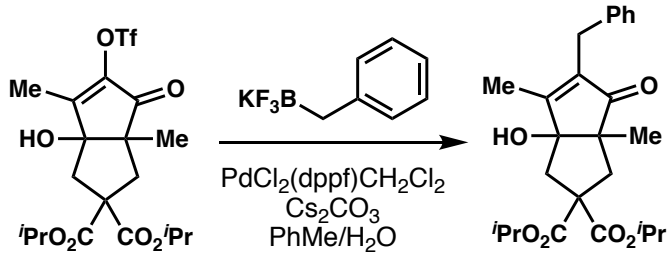
^{13}C NMR (101 MHz, $CDCl_3$) δ 13C NMR (101 MHz, CDCl3) δ 208.26, 171.72, 169.43, 167.36, 139.74, 136.99, 133.88, 128.78, 128.59, 126.29, 119.62, 87.37, 69.95, 69.56, 58.88, 55.87, 43.83, 43.07, 40.51,

21.59, 21.48, 21.37, 19.59, 12.03.

FTIR (NaCl, thin film, cm^{-1}): 3470, 2981, 2929, 1728, 1715, 1454, 1375, 1258, 1258, 1100.

HRMS (TOF-ESI, m/z): calc'd for $C_{27}H_{34}O_6$: 437.2323 $[M–H_2O+H]^+$; found: 437.2320.

diisopropyl 5-benzyl-6a-hydroxy-3a,6-dimethyl-4-oxo-3,3a,4,6a-tetrahydropentalene-2,2(1*H*)-dicarboxylate (14d)



Prepared from **15a** (36.8 mg, 0.08 mmol, 1.0 equiv), $BnBF_3K$ (41.9 mg, 0.23 mmol, 3.01 equiv), Cs_2CO_3 (70.7 mg, 0.22 mmol, 2.9 equiv), $PdCl_2(dppf)CH_2Cl_2$ (5.9 mg, 0.007 mmol, 0.1 equiv), and PhMe (0.43 mL) and water (0.14 mL, 0.125 M total (PhMe/H_2O, 3:1)) at 80 ºC following a literature procedure.[25] The crude residue was purified by column chromatography (silica, 10 to 20% EtOAc/hexanes) to afford **14d** (27.9 mg, 86% yield) as a yellow gel.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.29 (m, 2H), 7.29 – 7.21 (m, 3H), 5.13 (hept, *J* = 6.2 Hz, 1H), 4.81 (heptd, *J* = 6.3, 1.3 Hz, 1H), 3.63 (d, *J* = 14.5 Hz, 1H), 3.47 (d, *J* = 14.5 Hz, 1H), 2.80 (dd, *J* = 14.2, 1.1 Hz, 1H), 2.68 (s, 1H), 2.65 (dd, *J* = 14.0, 1.1 Hz, 1H), 2.53 (d, *J* = 14.0 Hz, 1H), 2.26 (d, *J* = 14.1 Hz, 1H), 2.16 (s, 3H), 1.32 (dd, *J* = 6.3, 2.8 Hz, 6H), 1.23 (dd, *J* = 6.2, 1.5 Hz, 6H), 1.20 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 208.88, 172.03, 169.47, 169.14, 138.67, 138.36, 128.67, 128.61, 126.25, 88.15, 70.00, 69.35, 59.31, 59.29, 55.95, 43.92, 42.41, 29.14, 21.58, 21.55, 21.45, 19.58, 12.18.

FTIR (NaCl, thin film, cm^{-1}): 3460, 2981, 2933, 1728, 1645, 1376, 1259, 1098.

HRMS (TOF-ESI, m/z): calc'd for $C_{25}H_{32}O_6$: 429.2272 $[M+H]^+$; found: 429.2289.

7. References

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6a

Origin	Varian
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Acquisition Time	3.0000
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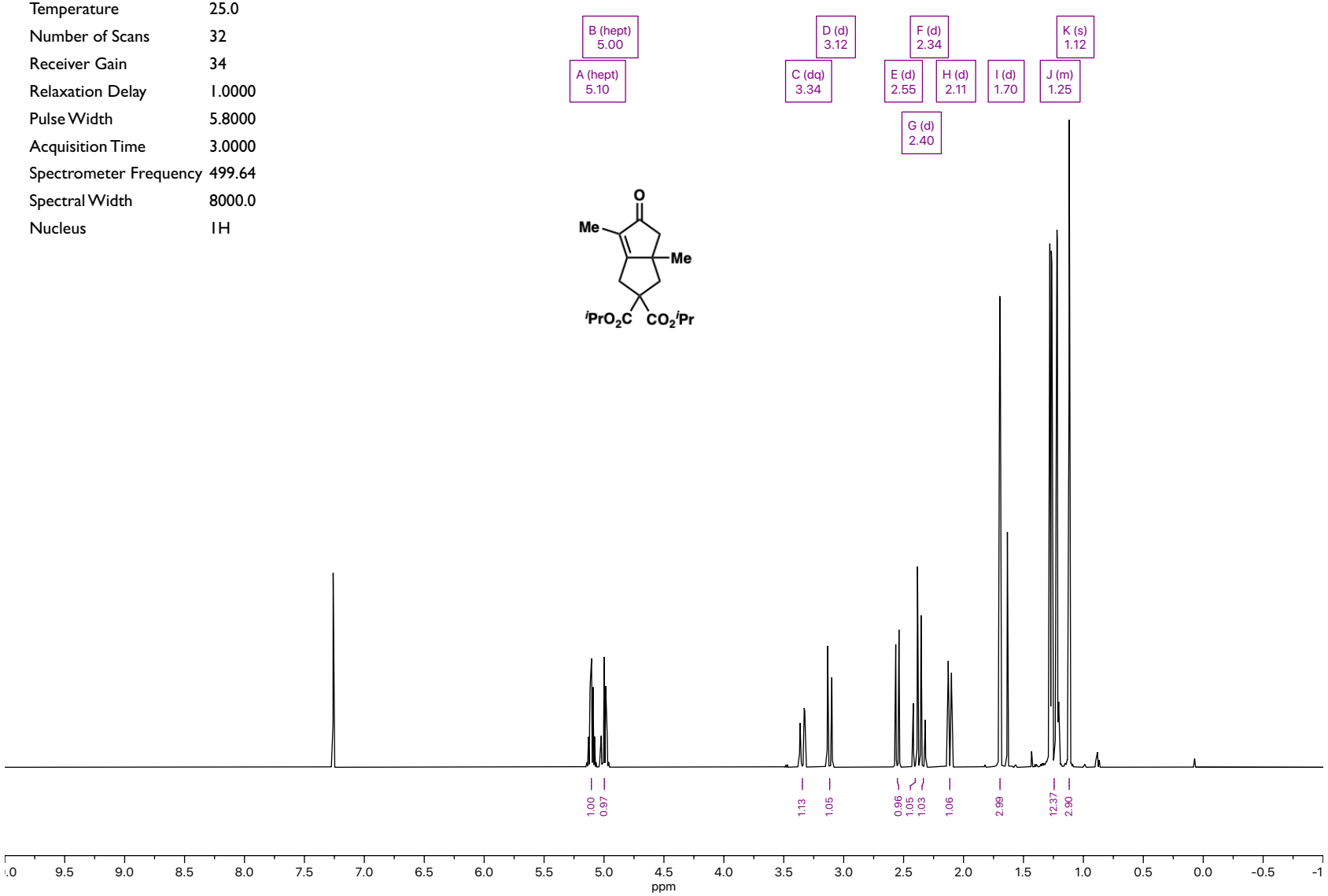
Spectral Width	8000.0
Nucleus	1H



6a

Origin	Varian
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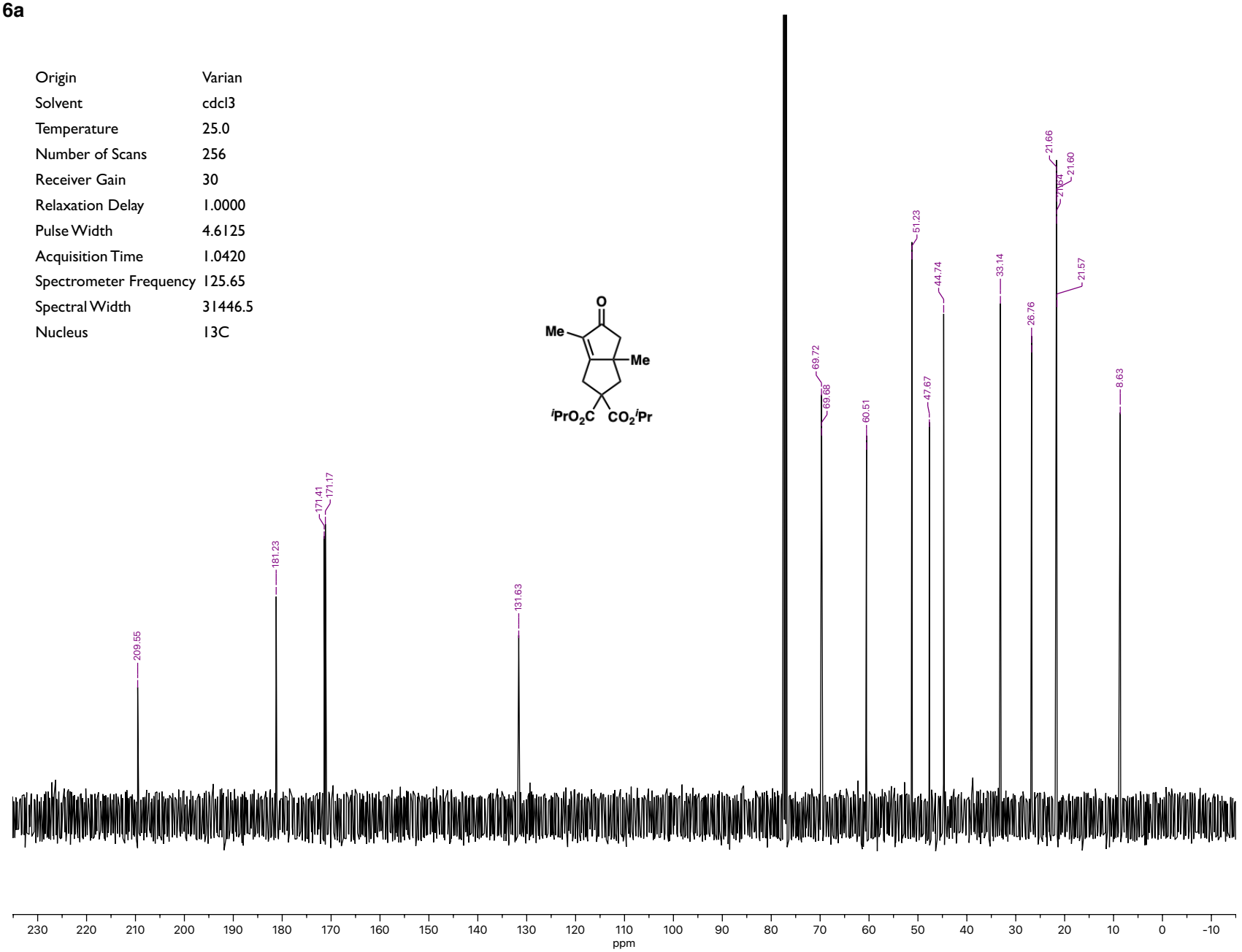
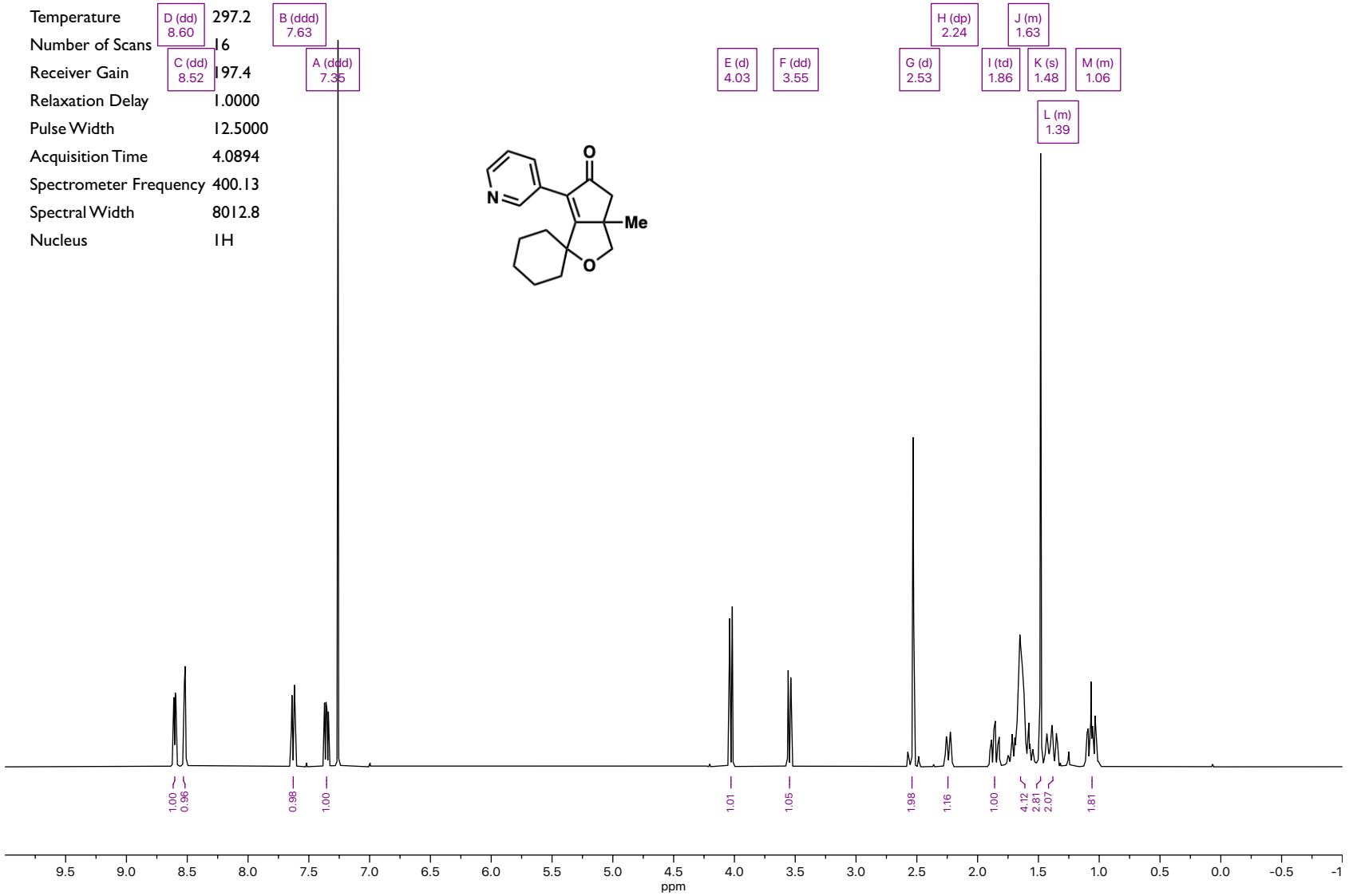
Number of Scans	256
Receiver Gain	30
Relaxation Delay	1.0000
Pulse Width	4.6125
Acquisition Time	1.0420
Spectrometer Frequency	125.65
Spectral Width	31446.5
Nucleus	13C



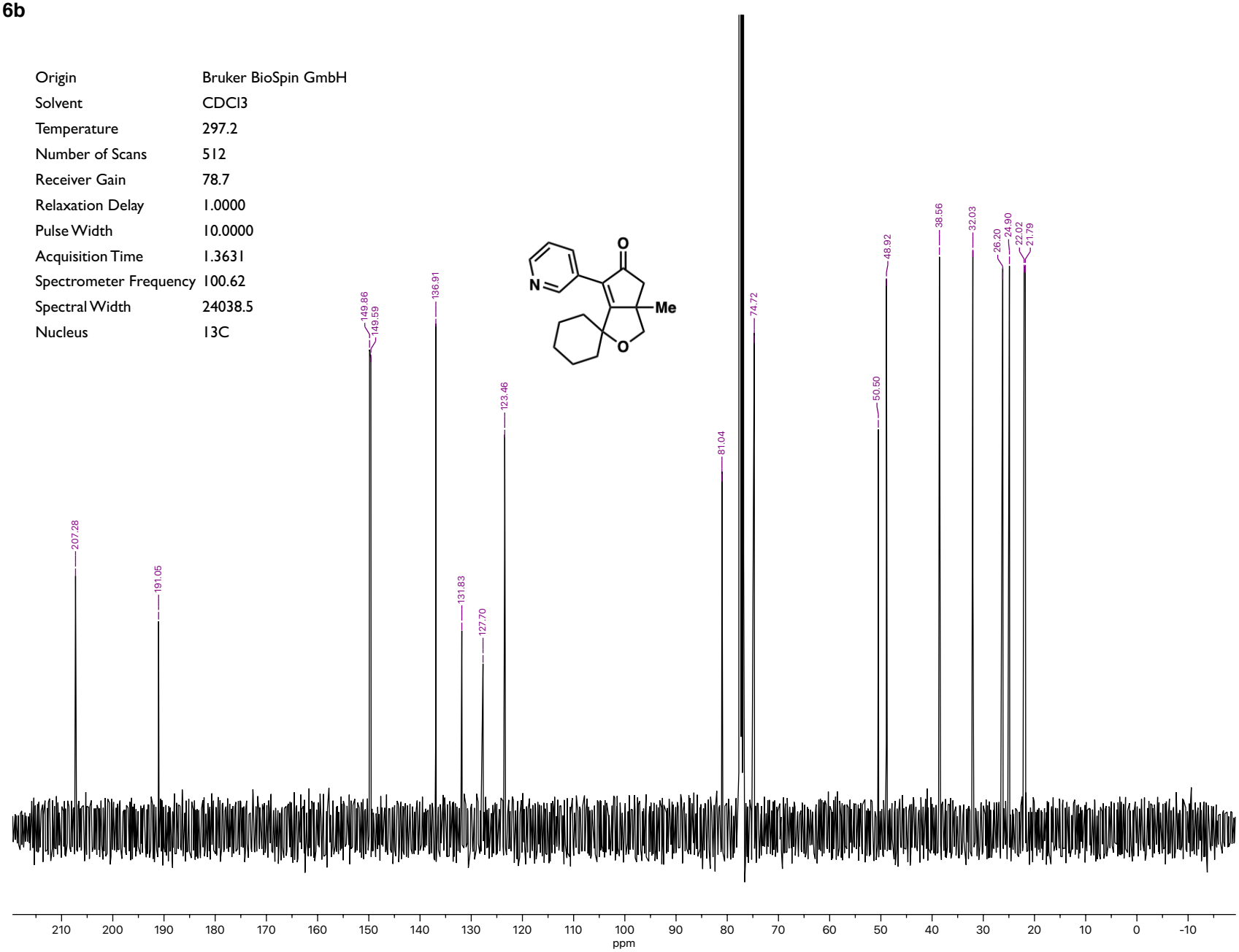
6b

Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	297.2
Number of Scans	16
Receiver Gain	197.4
Relaxation Delay	1.0000
Pulse Width	12.5000
Acquisition Time	4.0894
Spectrometer Frequency	400.13
Spectral Width	8012.8
Nucleus	1H



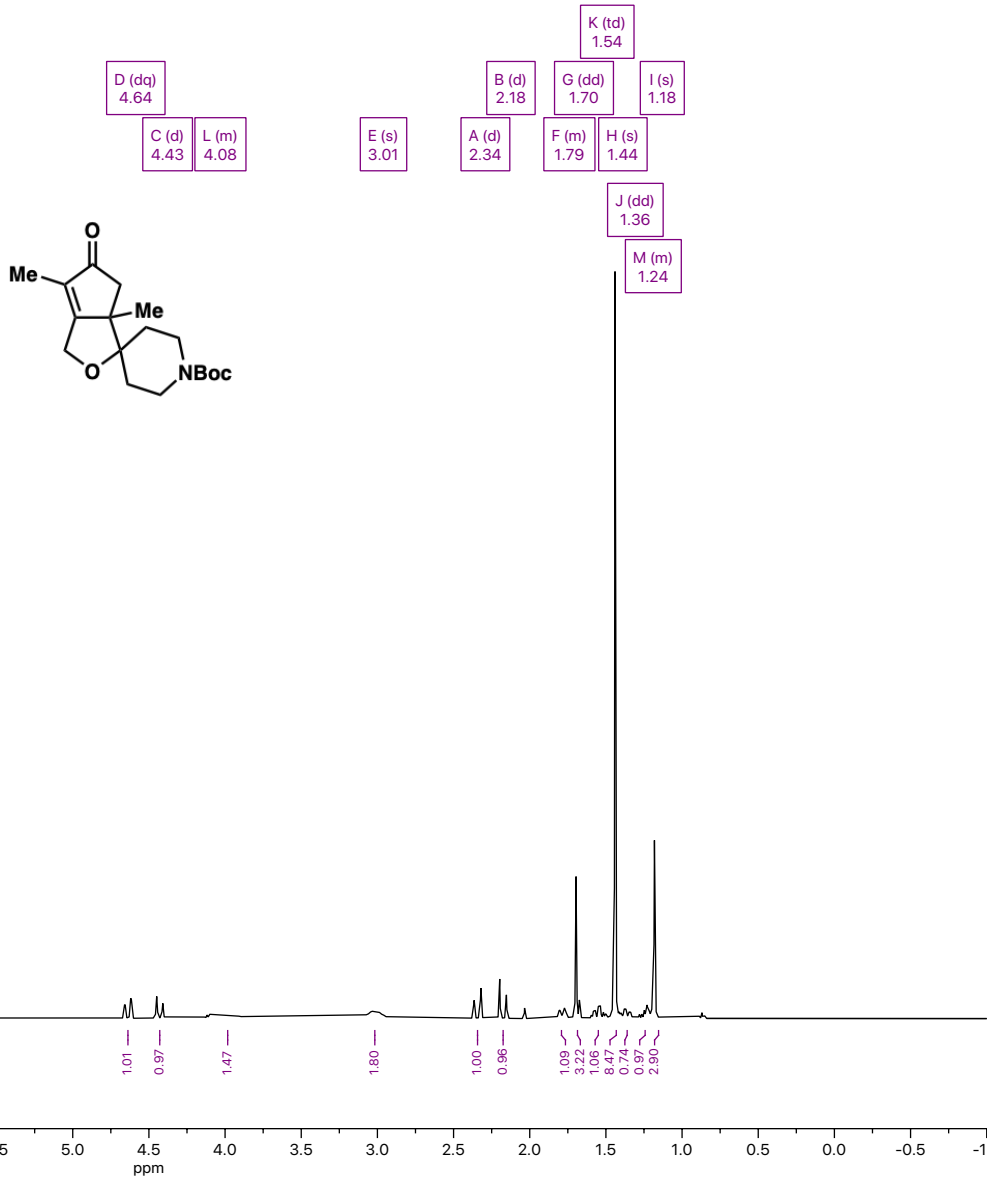
6b

Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	297.2
Number of Scans	512
Receiver Gain	78.7
Relaxation Delay	1.0000
Pulse Width	10.0000
Acquisition Time	1.3631
Spectrometer Frequency	100.62
Spectral Width	24038.5
Nucleus	13C



6c

Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	295.2
Number of Scans	16
Receiver Gain	78.7
Relaxation Delay	1.0000
Pulse Width	11.7000
Acquisition Time	4.0894
Spectrometer Frequency	400.13
Spectral Width	8012.8
Nucleus	1H



6c

Origin	Bruker BioSpin GmbH
Solvent	CDCl3
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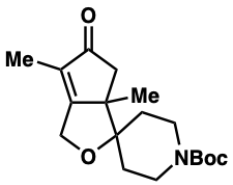
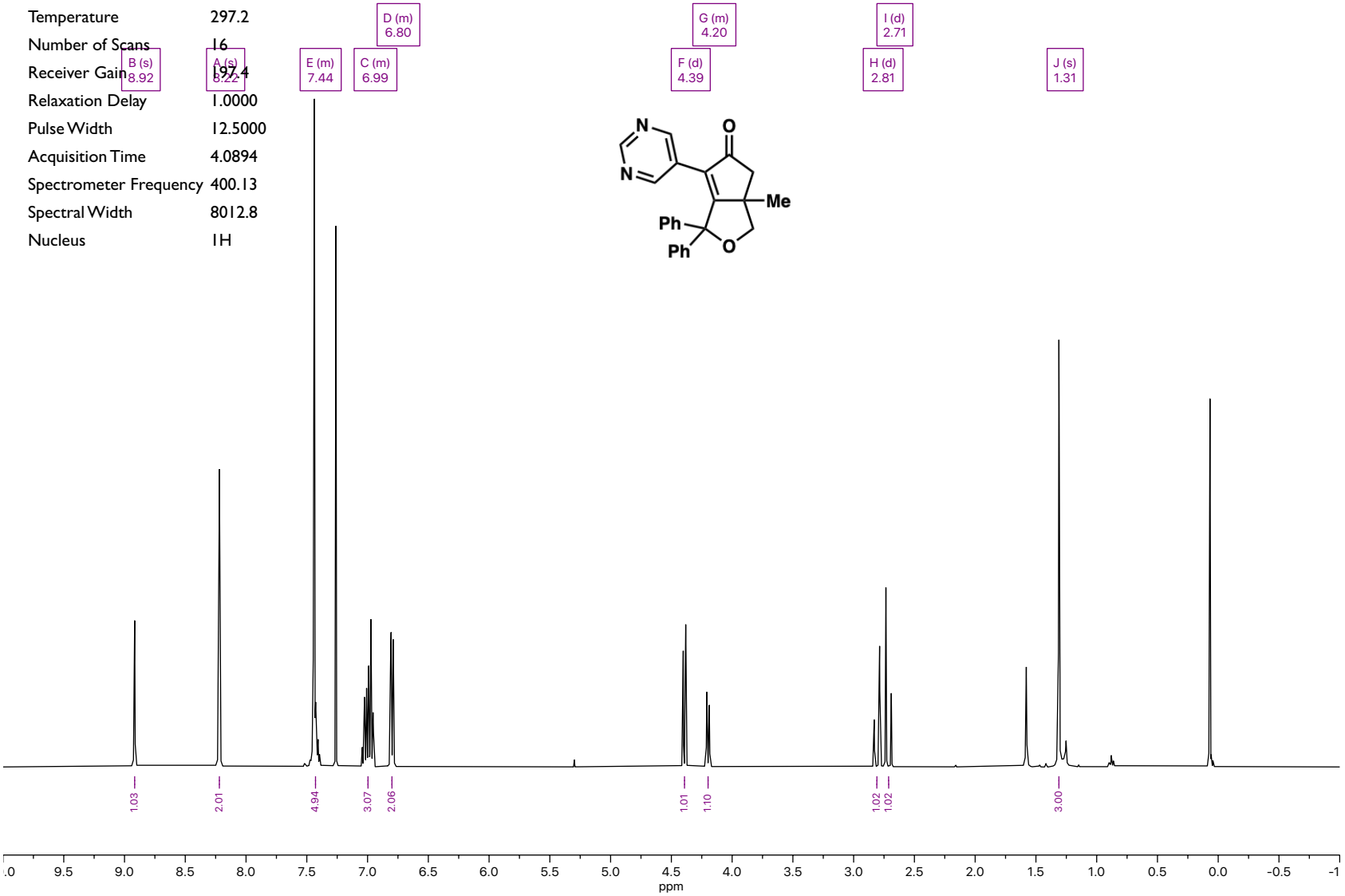
Number of Scans	256
Receiver Gain	72.0
Relaxation Delay	1.0000
Pulse Width	10.0000
Acquisition Time	1.3631
Spectrometer Frequency	100.62
Spectral Width	24038.5
Nucleus	13C



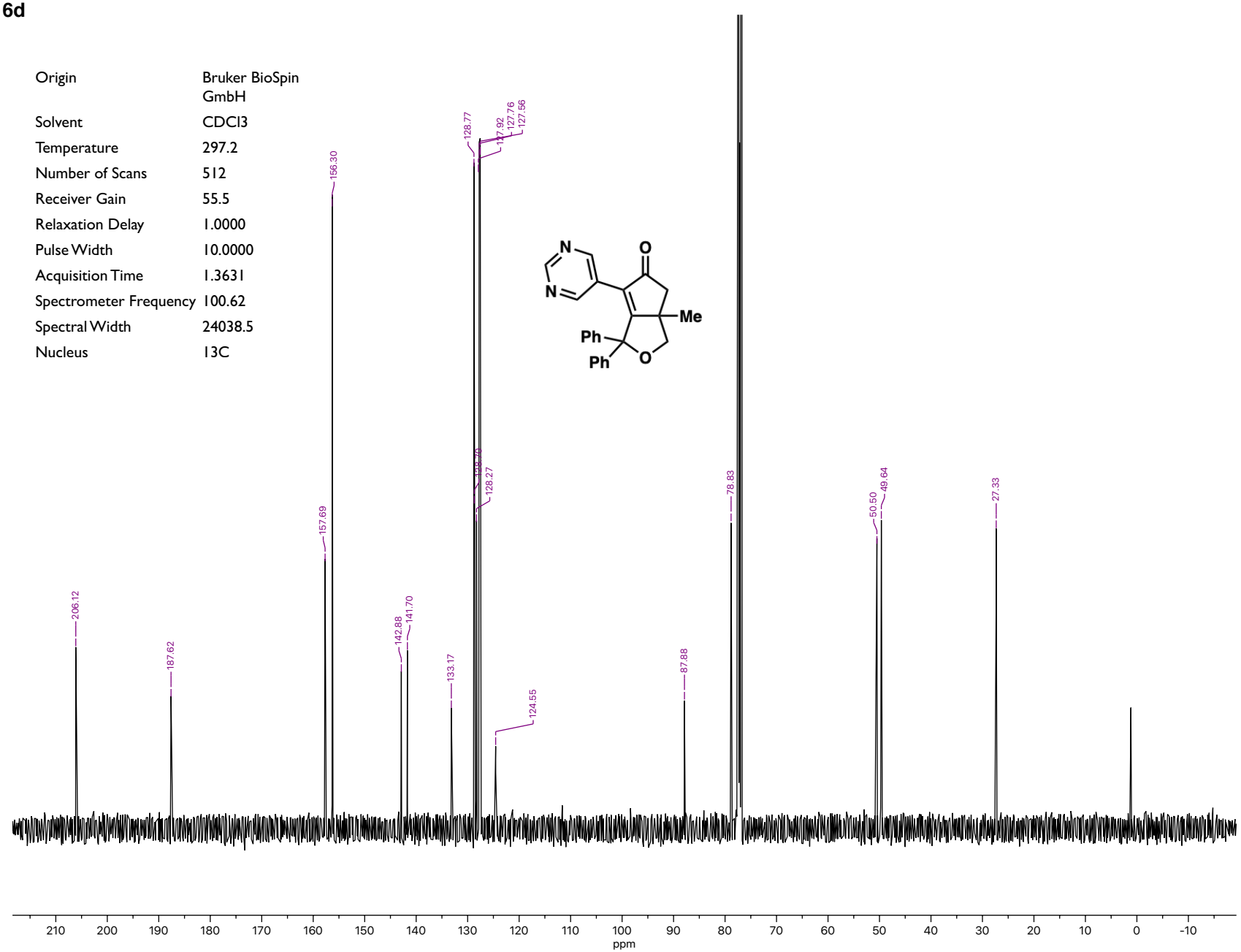
6d

Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	297.2
Number of Scans	16
Receiver Gain	197.4
Relaxation Delay	1.0000
Pulse Width	12.5000
Acquisition Time	4.0894
Spectrometer Frequency	400.13
Spectral Width	8012.8
Nucleus	1H



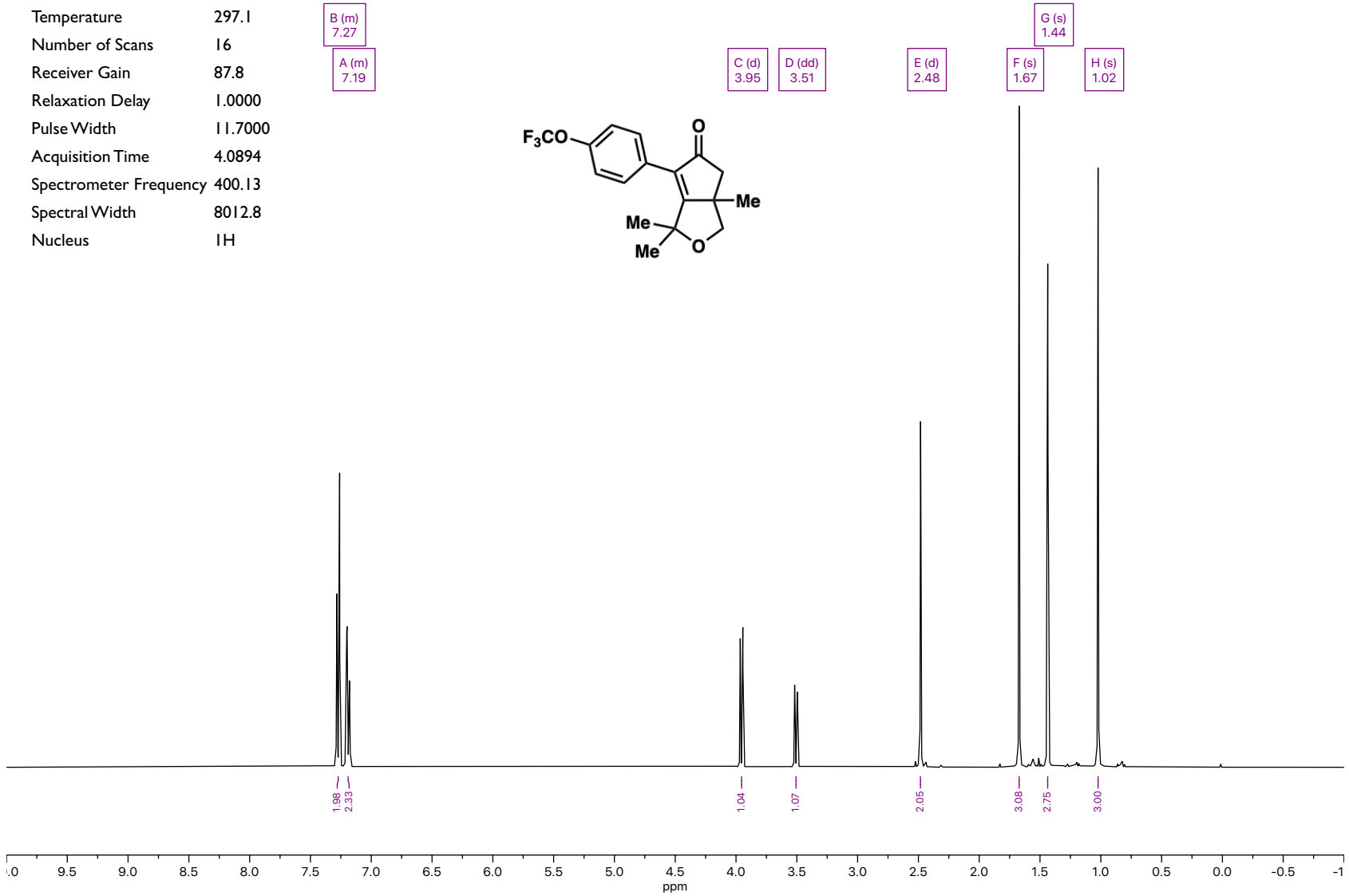
6d

Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	297.2
Number of Scans	512
Receiver Gain	55.5
Relaxation Delay	1.0000
Pulse Width	10.0000
Acquisition Time	1.3631
Spectrometer Frequency	100.62
Spectral Width	24038.5
Nucleus	13C



6e

Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	297.1
Number of Scans	16
Receiver Gain	87.8
Relaxation Delay	1.0000
Pulse Width	11.7000
Acquisition Time	4.0894
Spectrometer Frequency	400.13
Spectral Width	8012.8
Nucleus	1H



6e

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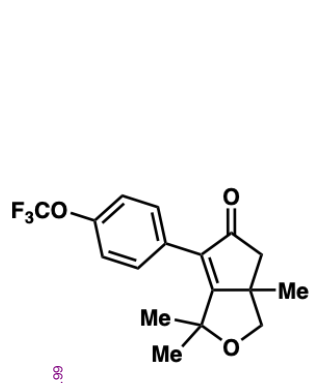
Solvent	CDCl3
Temperature	297.1
Number of Scans	128
Receiver Gain	72.0
Relaxation Delay	1.0000
Pulse Width	10.0000
Acquisition Time	1.3631
Spectrometer Frequency	100.62
Spectral Width	24038.5
Nucleus	13C



6g

Origin	Bruker BioSpin GmbH
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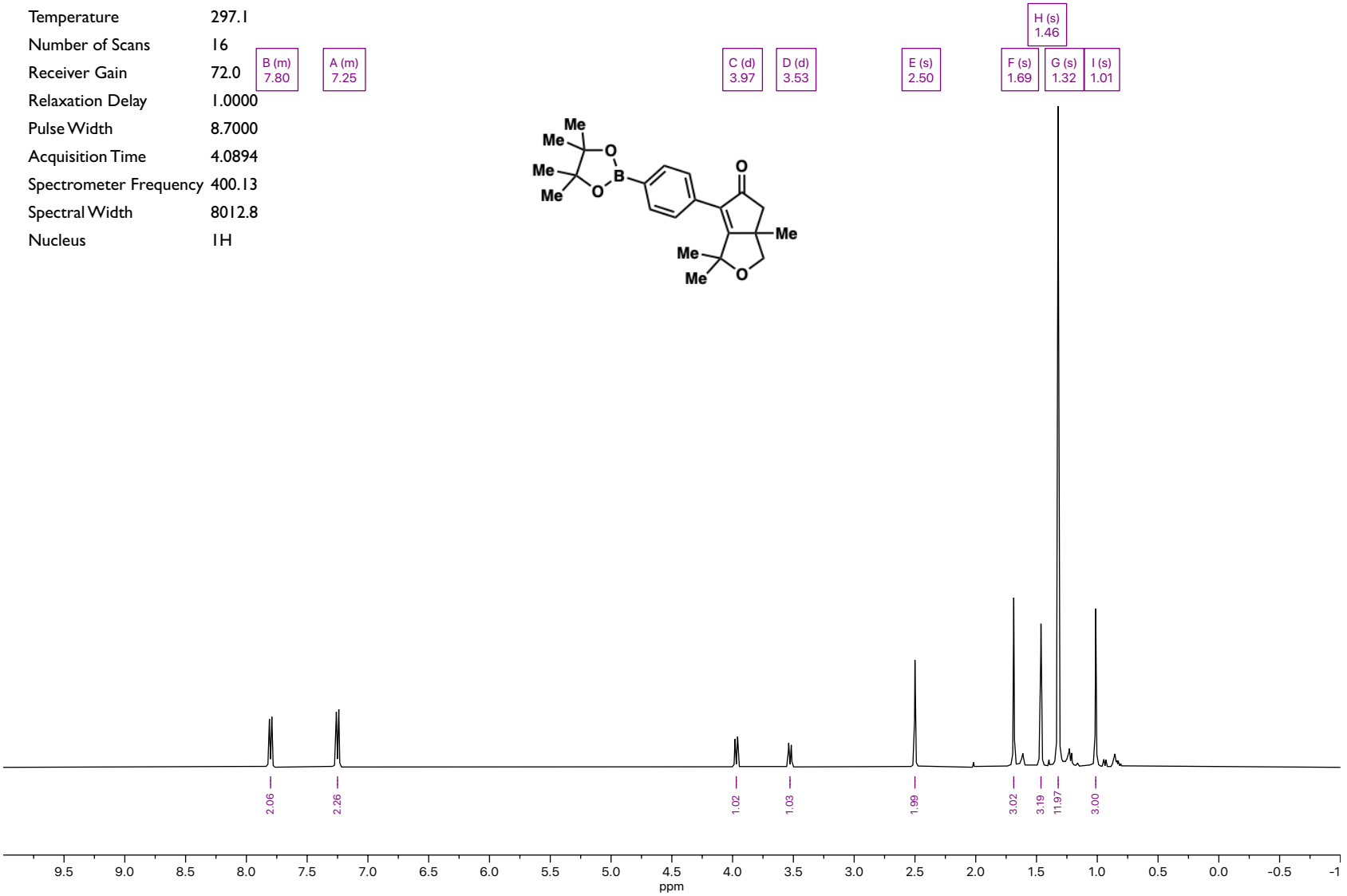
Number of Scans	16
Receiver Gain	72.0
Relaxation Delay	1.0000
Pulse Width	8.7000
Acquisition Time	4.0894
Spectrometer Frequency	400.13
Spectral Width	8012.8
Nucleus	1H



6g

Origin	Bruker BioSpin GmbH
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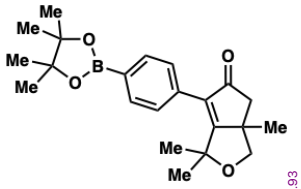
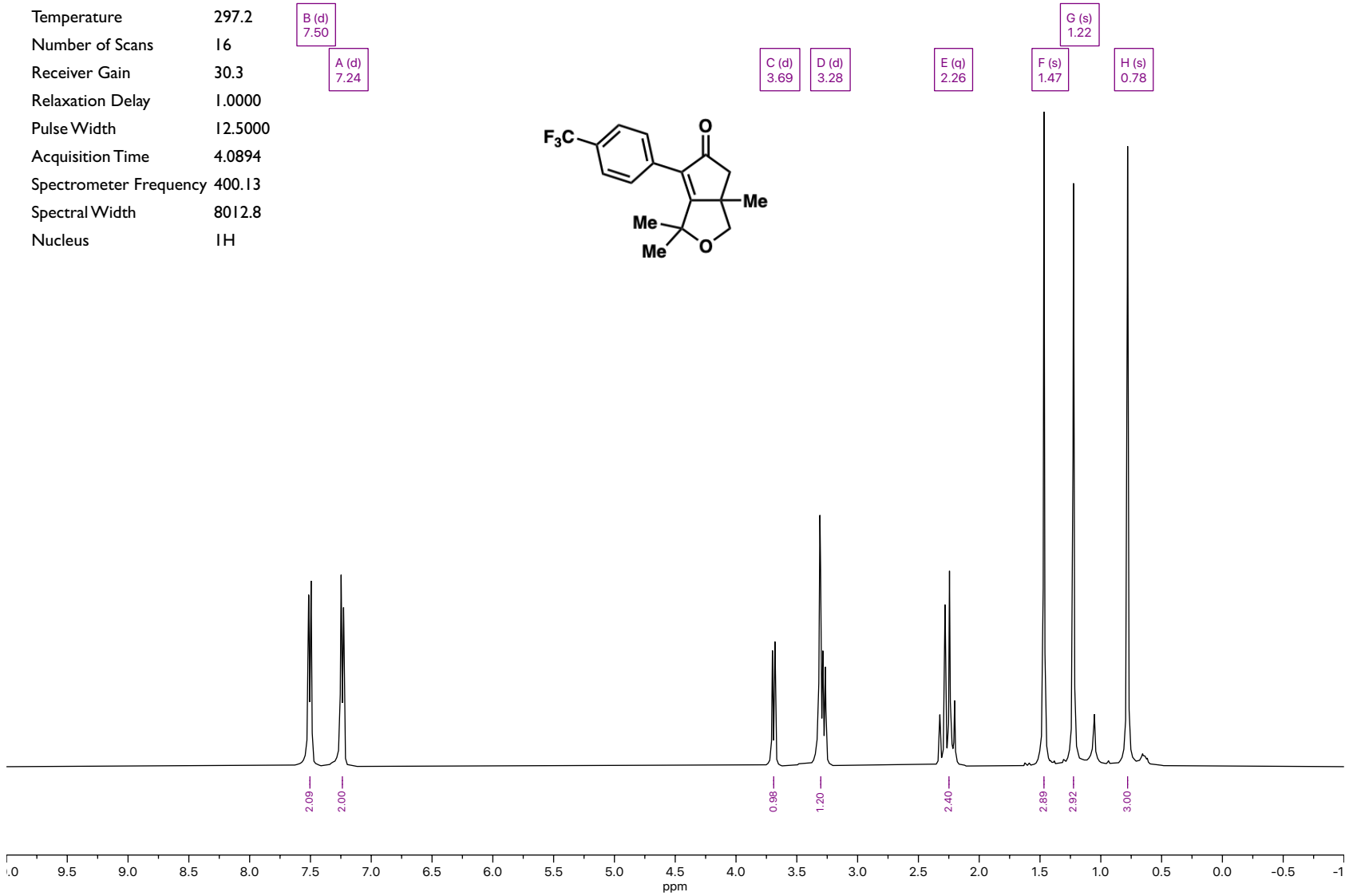
Temperature	297.1
Number of Scans	1024
Receiver Gain	55.5
Relaxation Delay	1.0000
Pulse Width	10.0000
Acquisition Time	1.3631
Spectrometer Frequency	100.62
Spectral Width	24038.5
Nucleus	13C



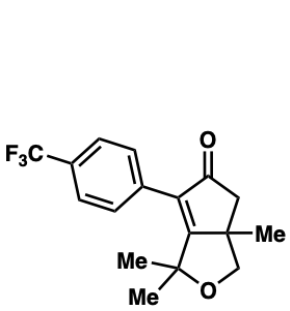
6h

Origin	Bruker BioSpin GmbH
Solvent	Dioxane
Temperature	297.2
Number of Scans	16
Receiver Gain	30.3
Relaxation Delay	1.0000
Pulse Width	12.5000
Acquisition Time	4.0894
Spectrometer Frequency	400.13
Spectral Width	8012.8
Nucleus	1H



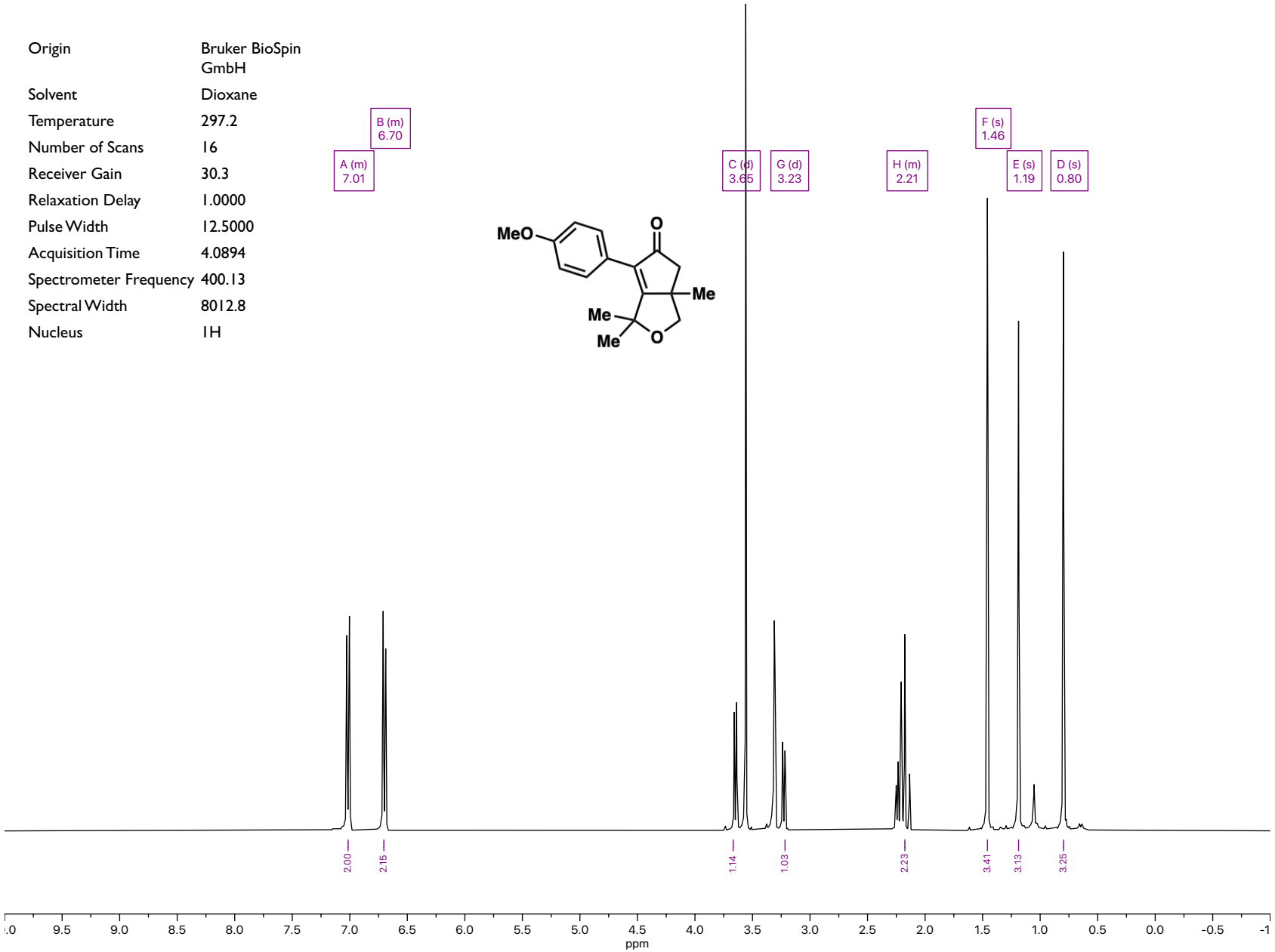
6h

Origin	Bruker BioSpin GmbH
Solvent	Dioxane
Temperature	297.2
Number of Scans	512
Receiver Gain	43.7
Relaxation Delay	1.0000
Pulse Width	10.0000
Acquisition Time	1.3631
Spectrometer Frequency	100.62
Spectral Width	24038.5
Nucleus	13C



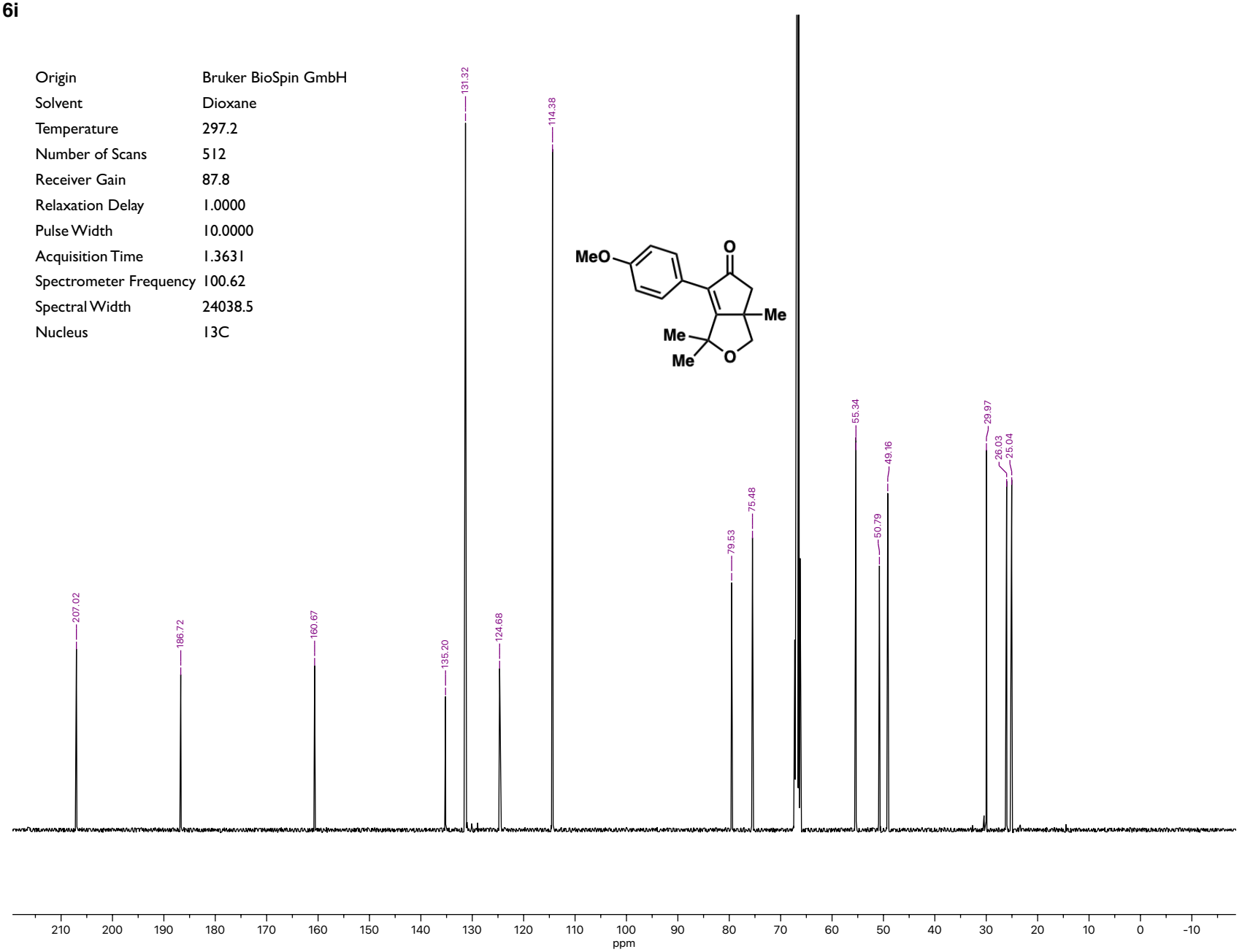
6i

Origin	Bruker BioSpin GmbH
Solvent	Dioxane
Temperature	297.2
Number of Scans	16
Receiver Gain	30.3
Relaxation Delay	1.0000
Pulse Width	12.5000
Acquisition Time	4.0894
Spectrometer Frequency	400.13
Spectral Width	8012.8
Nucleus	1H



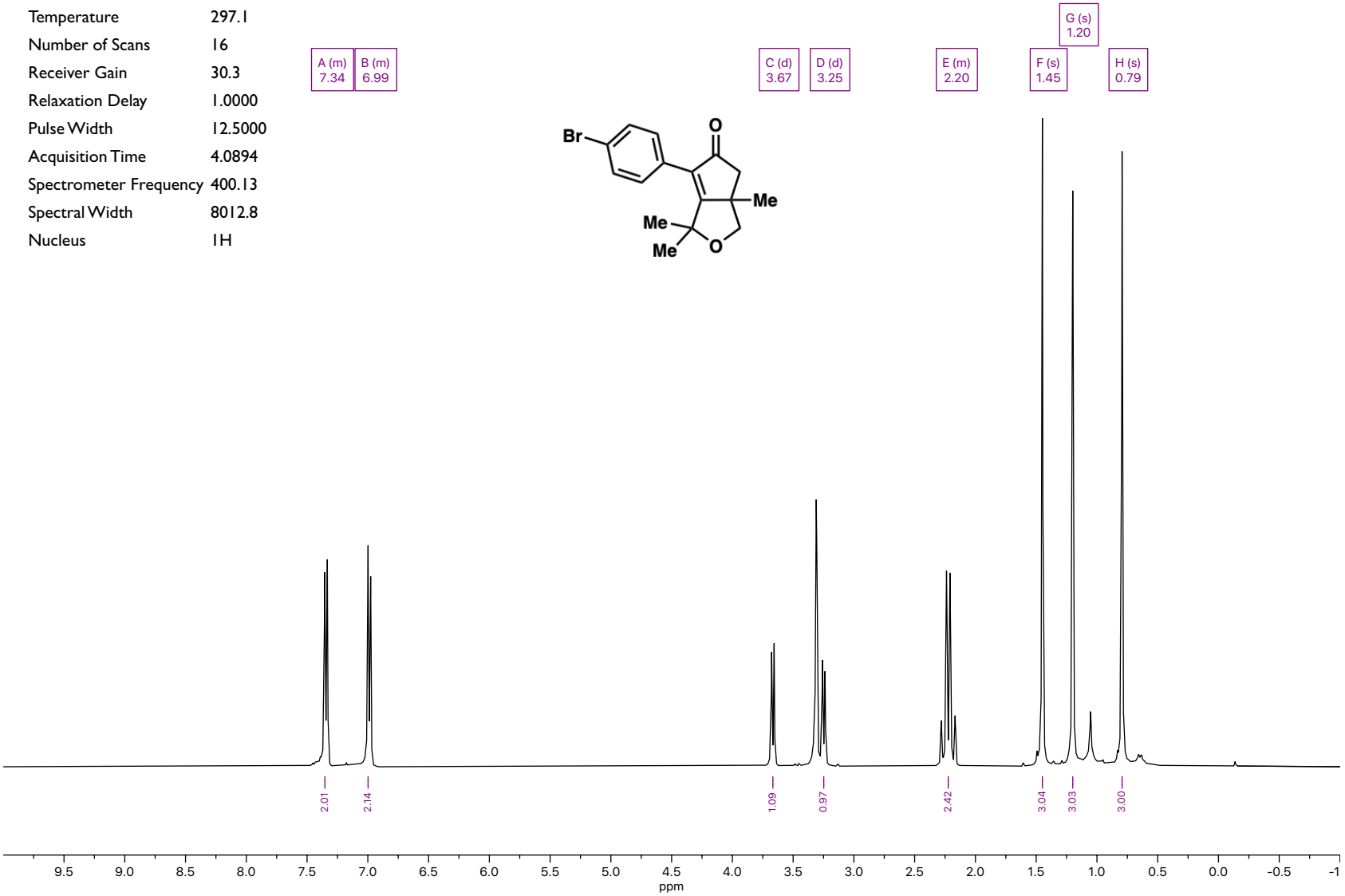
6i

Origin	Bruker BioSpin GmbH
Solvent	Dioxane
Temperature	297.2
Number of Scans	512
Receiver Gain	87.8
Relaxation Delay	1.0000
Pulse Width	10.0000
Acquisition Time	1.3631
Spectrometer Frequency	100.62
Spectral Width	24038.5
Nucleus	13C



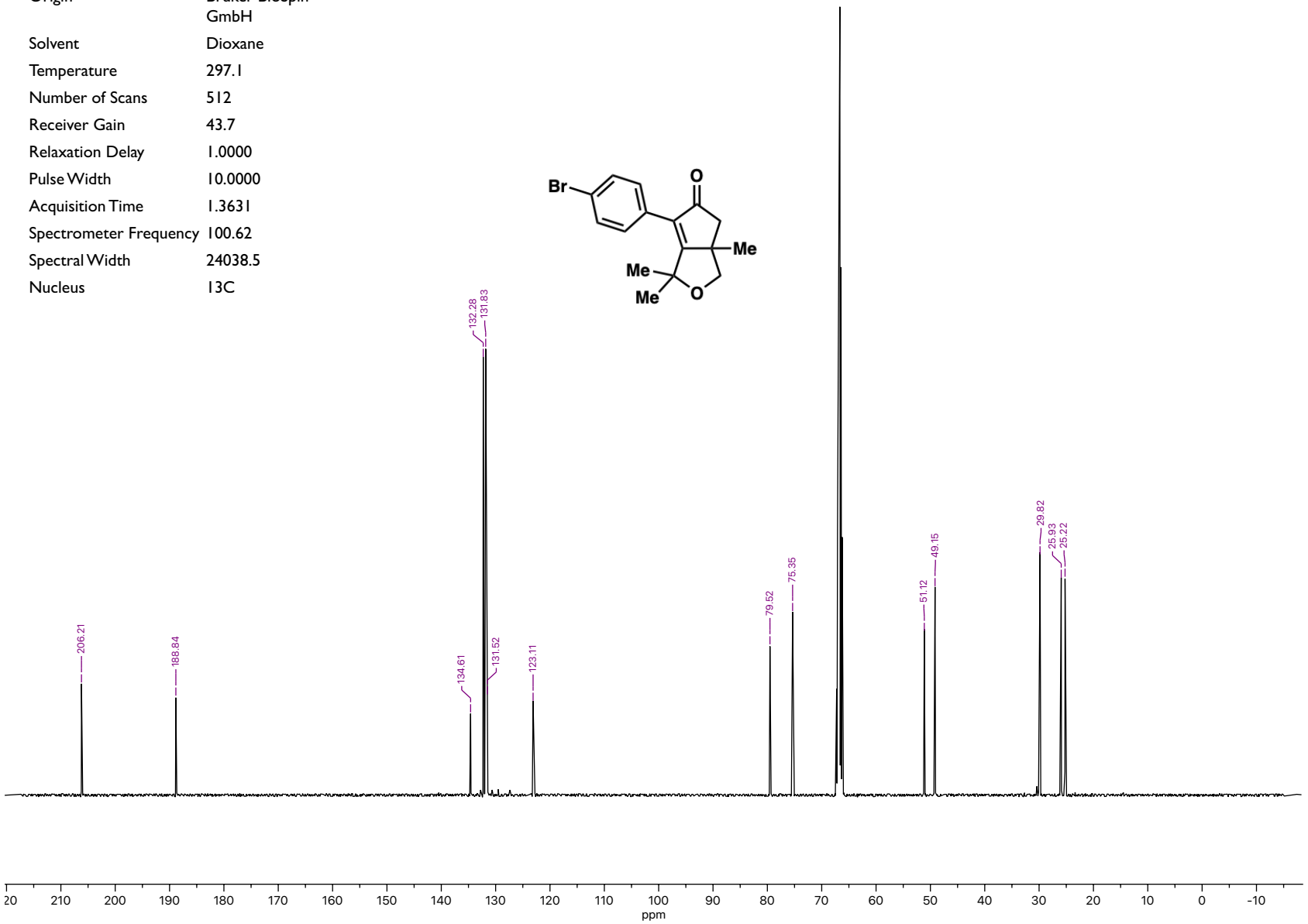
6j

Origin	Bruker BioSpin GmbH
Solvent	Dioxane
Temperature	297.1
Number of Scans	16
Receiver Gain	30.3
Relaxation Delay	1.0000
Pulse Width	12.5000
Acquisition Time	4.0894
Spectrometer Frequency	400.13
Spectral Width	8012.8
Nucleus	1H



6j

Origin	Bruker BioSpin GmbH
Solvent	Dioxane
Temperature	297.1
Number of Scans	512
Receiver Gain	43.7
Relaxation Delay	1.0000
Pulse Width	10.0000
Acquisition Time	1.3631
Spectrometer Frequency	100.62
Spectral Width	24038.5
Nucleus	13C



6k

Origin	Bruker BioSpin GmbH
Solvent	CDCl3
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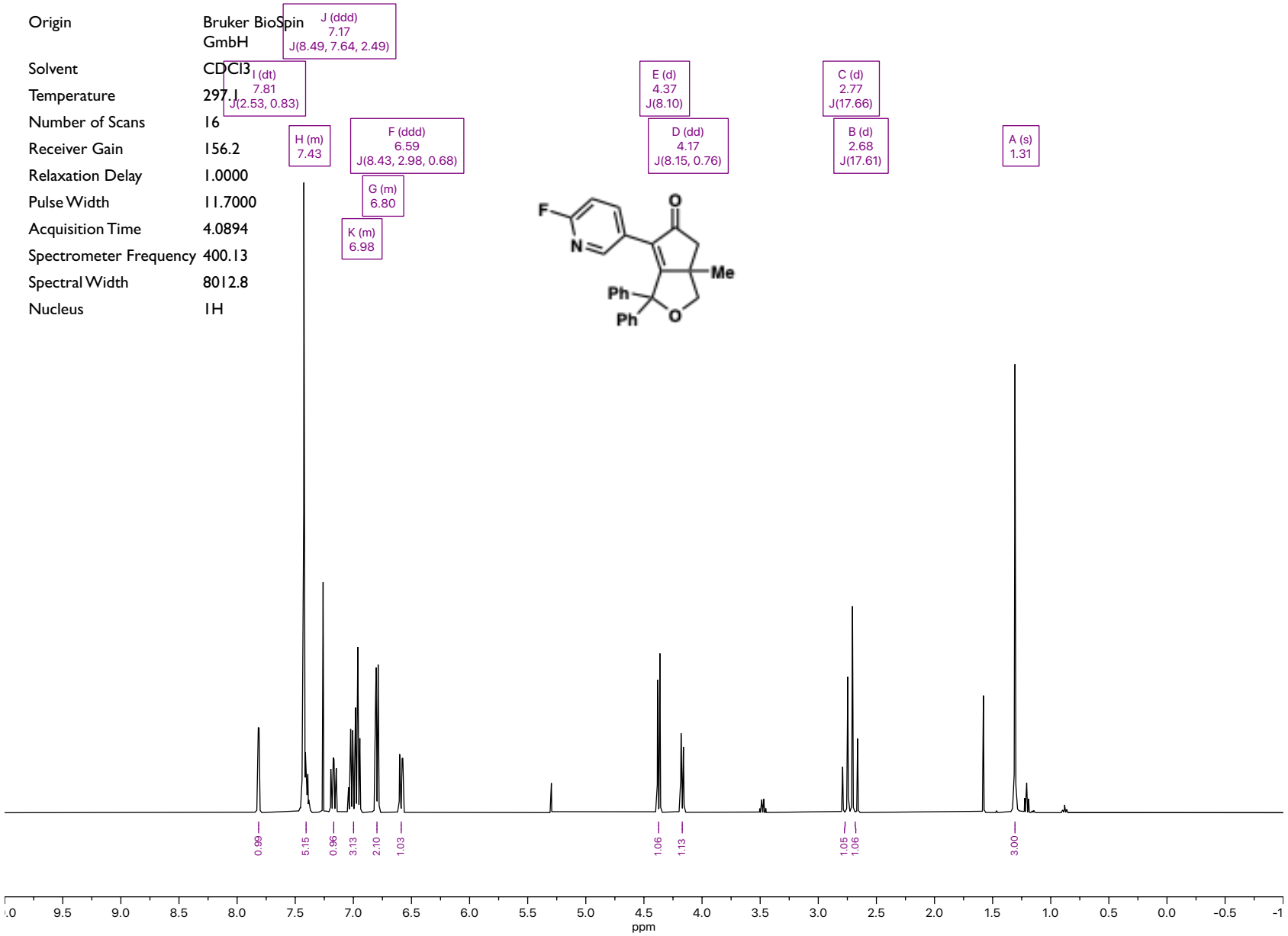
Number of Scans	16
Receiver Gain	156.2
Relaxation Delay	1.0000
Pulse Width	11.7000
Acquisition Time	4.0894
Spectrometer Frequency	400.13
Spectral Width	8012.8
Nucleus	1H



6k

Origin	Bruker BioSpin GmbH
Solvent	CDCl3
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Number of Scans	128
Receiver Gain	78.7
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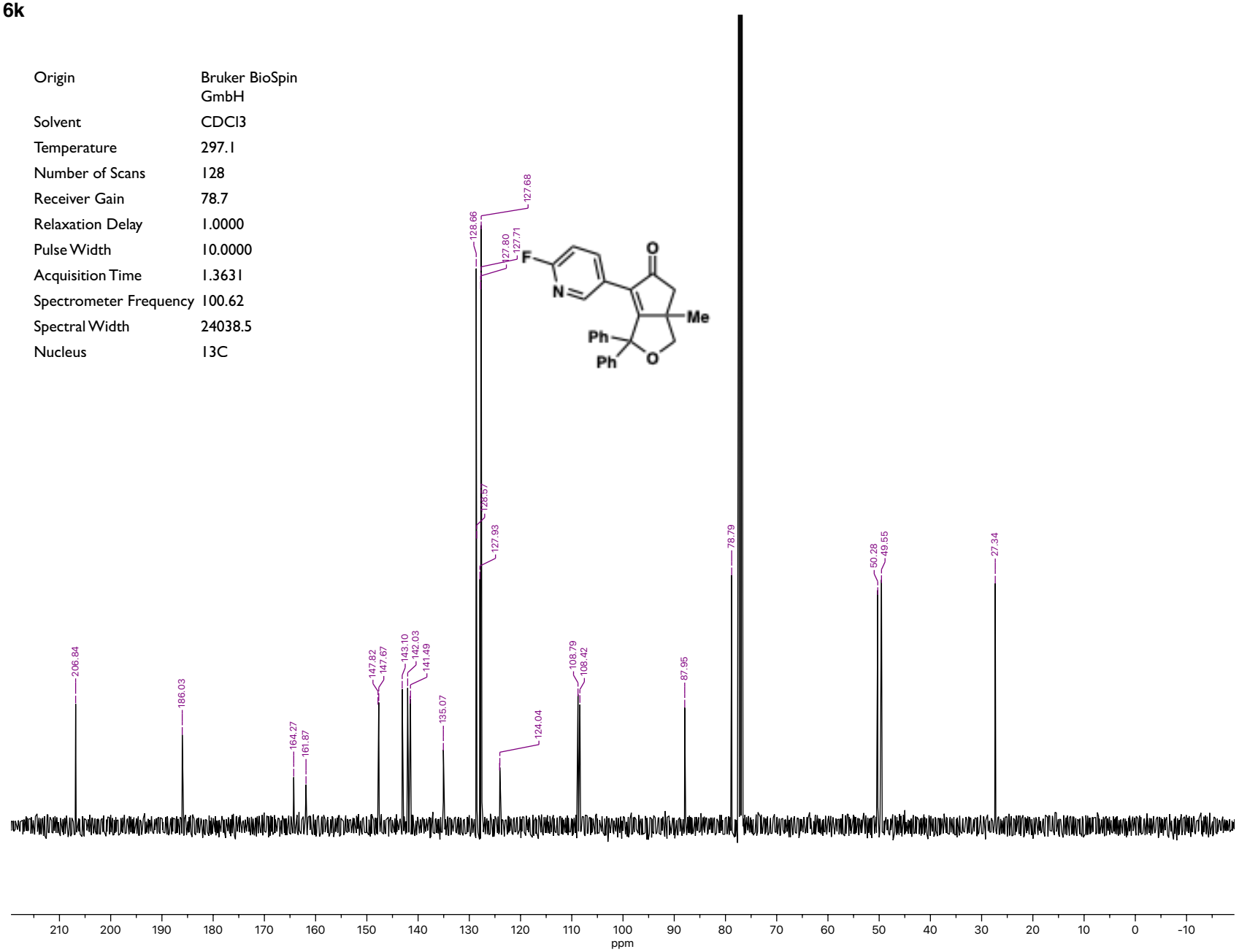
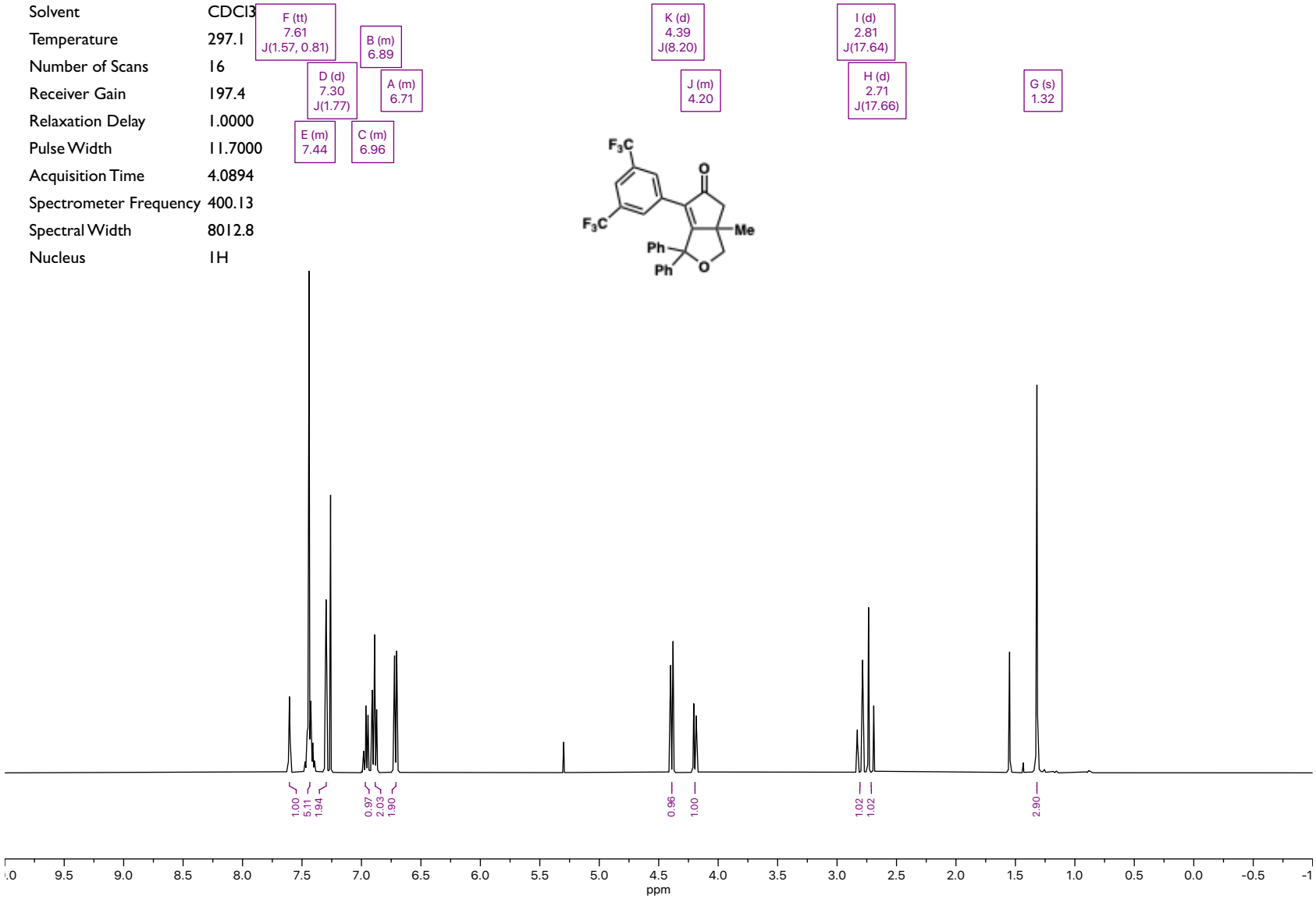
Acquisition Time	1.3631
Spectrometer Frequency	100.62
Spectral Width	24038.5
Nucleus	13C



6l

Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	297.1
Number of Scans	16
Receiver Gain	197.4
Relaxation Delay	1.0000
Pulse Width	11.7000
Acquisition Time	4.0894
Spectrometer Frequency	400.13
Spectral Width	8012.8
Nucleus	1H



6l

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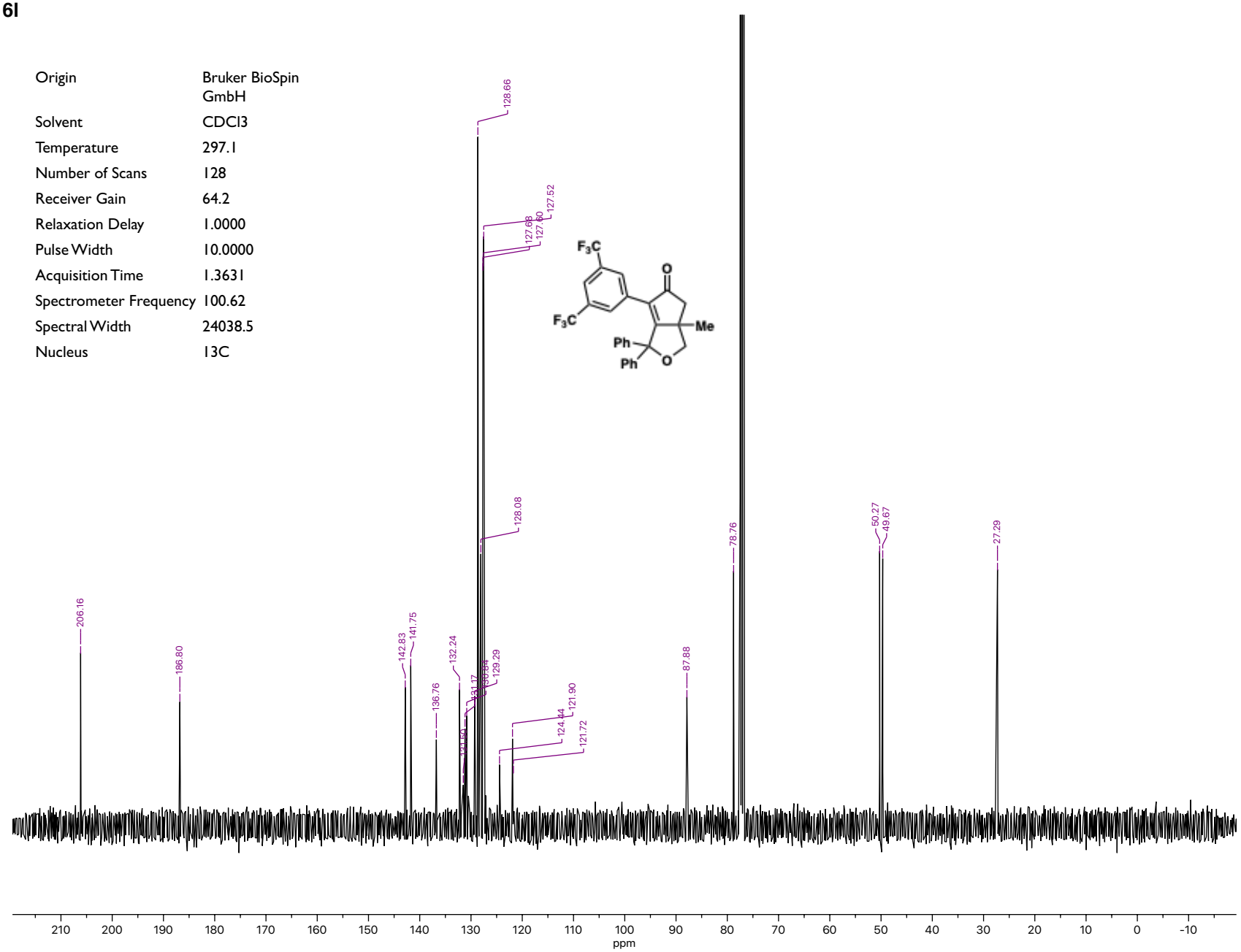
Pulse Width	10.0000
Acquisition Time	1.3631
Spectrometer Frequency	100.62
Spectral Width	24038.5
Nucleus	13C



7a

Origin	Bruker BioSpin GmbH
Solvent	MeOD
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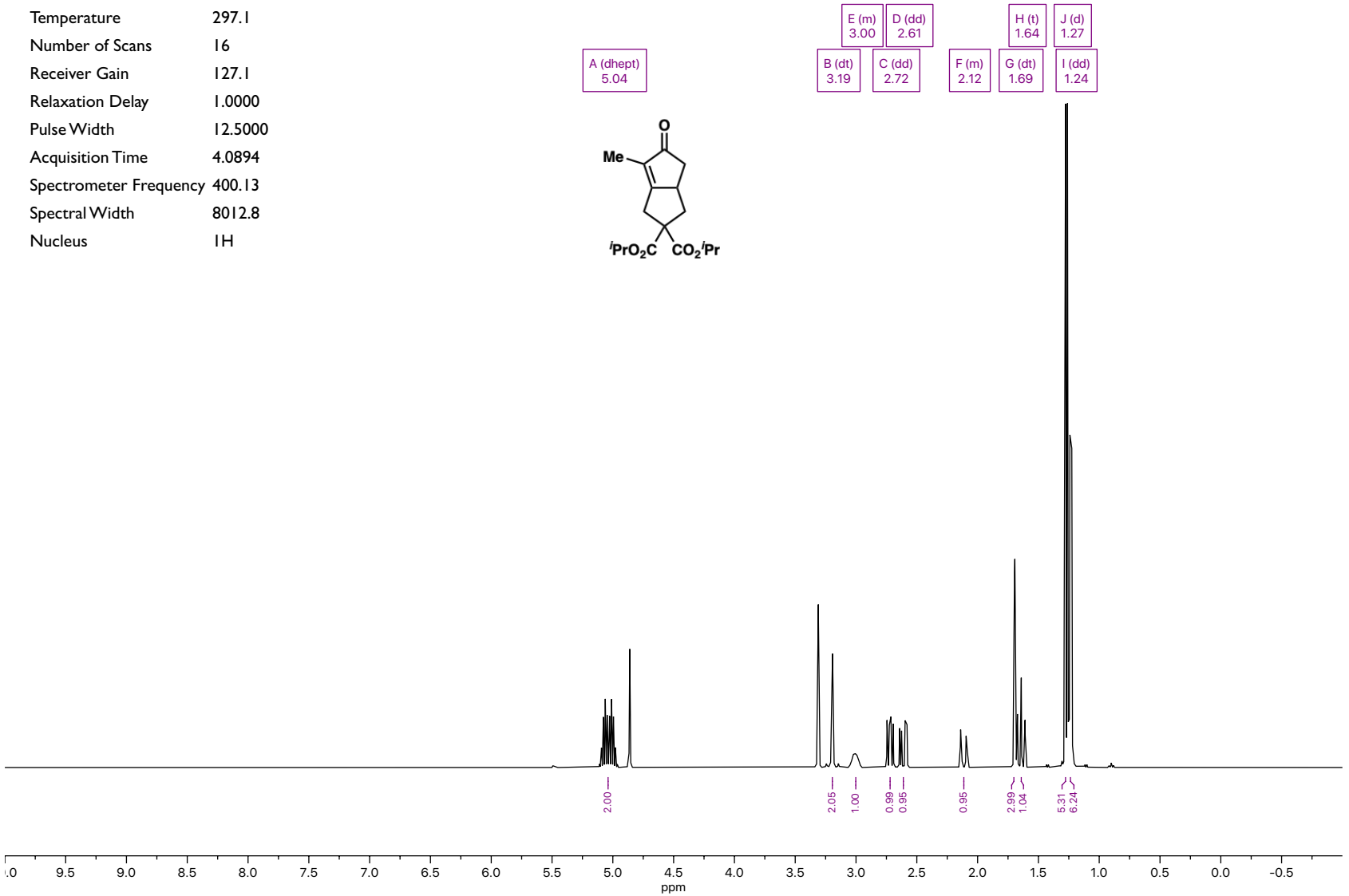
Number of Scans	16
Receiver Gain	127.1
Relaxation Delay	1.0000
Pulse Width	12.5000
Acquisition Time	4.0894
Spectrometer Frequency	400.13
Spectral Width	8012.8
Nucleus	1H



7a

Origin	Bruker BioSpin GmbH
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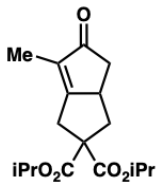
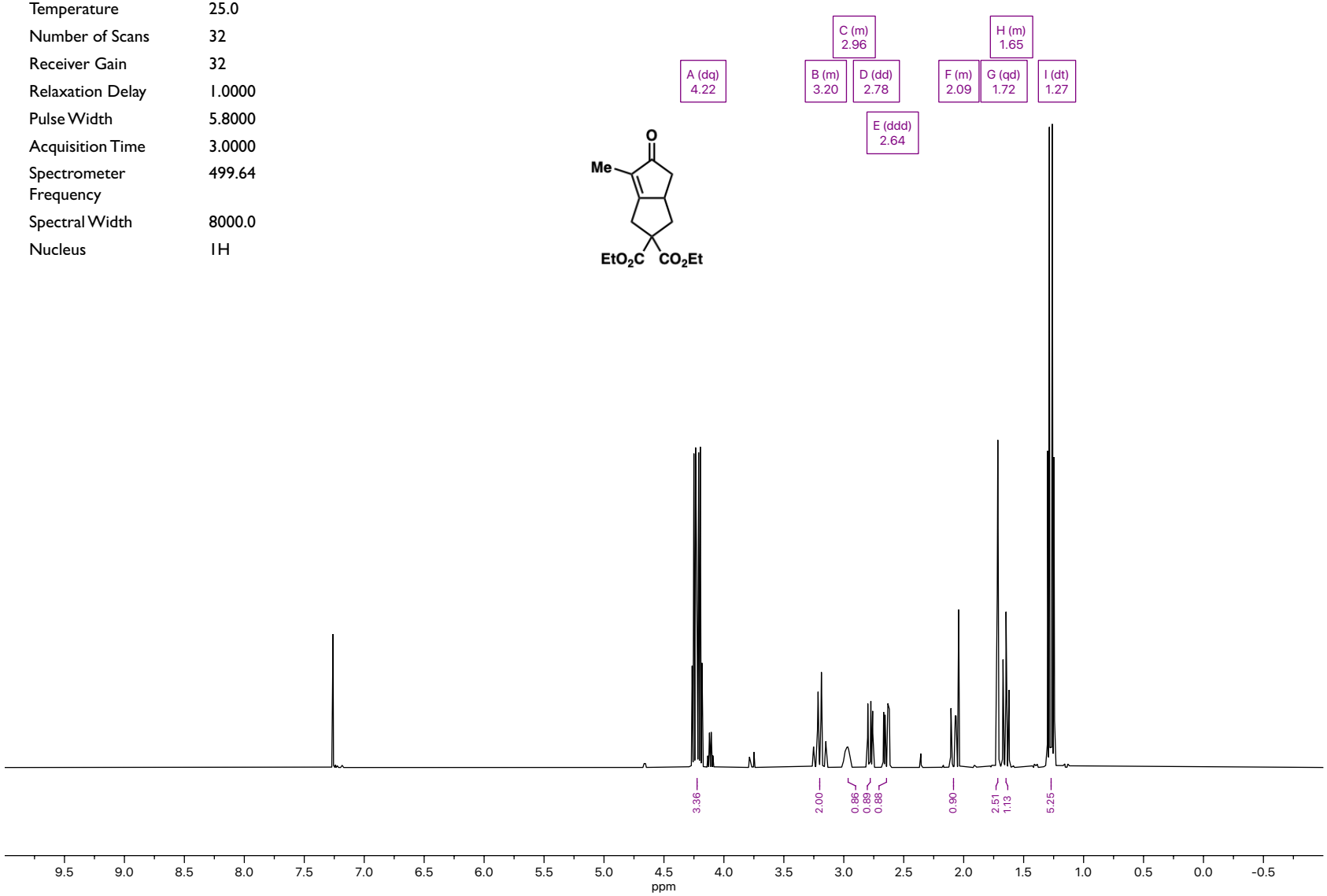
Pulse Width	10.0000
Acquisition Time	1.3631
Spectrometer Frequency	100.62
Spectral Width	24038.5
Nucleus	13C



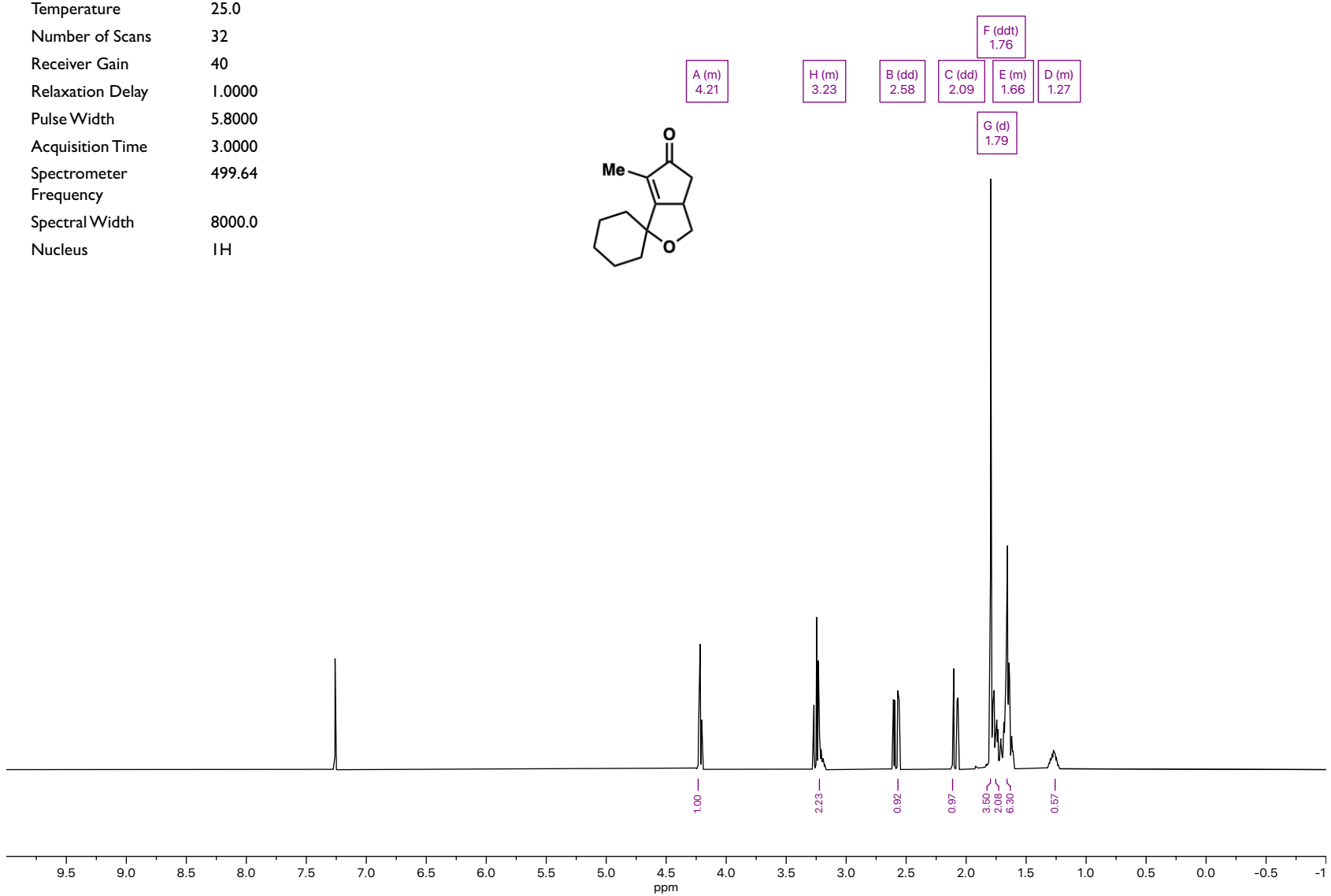
7b

Origin	Varian
Solvent	cdcl3
Temperature	25.0
Number of Scans	32
Receiver Gain	32
Relaxation Delay	1.0000
Pulse Width	5.8000
Acquisition Time	3.0000
Spectrometer Frequency	499.64
Spectral Width	8000.0
Nucleus	1H



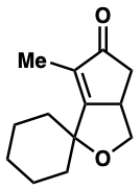
7c

Origin	Varian
Solvent	cdcl3
Temperature	25.0
Number of Scans	32
Receiver Gain	40
Relaxation Delay	1.0000
Pulse Width	5.8000
Acquisition Time	3.0000
Spectrometer Frequency	499.64
Spectral Width	8000.0
Nucleus	1H



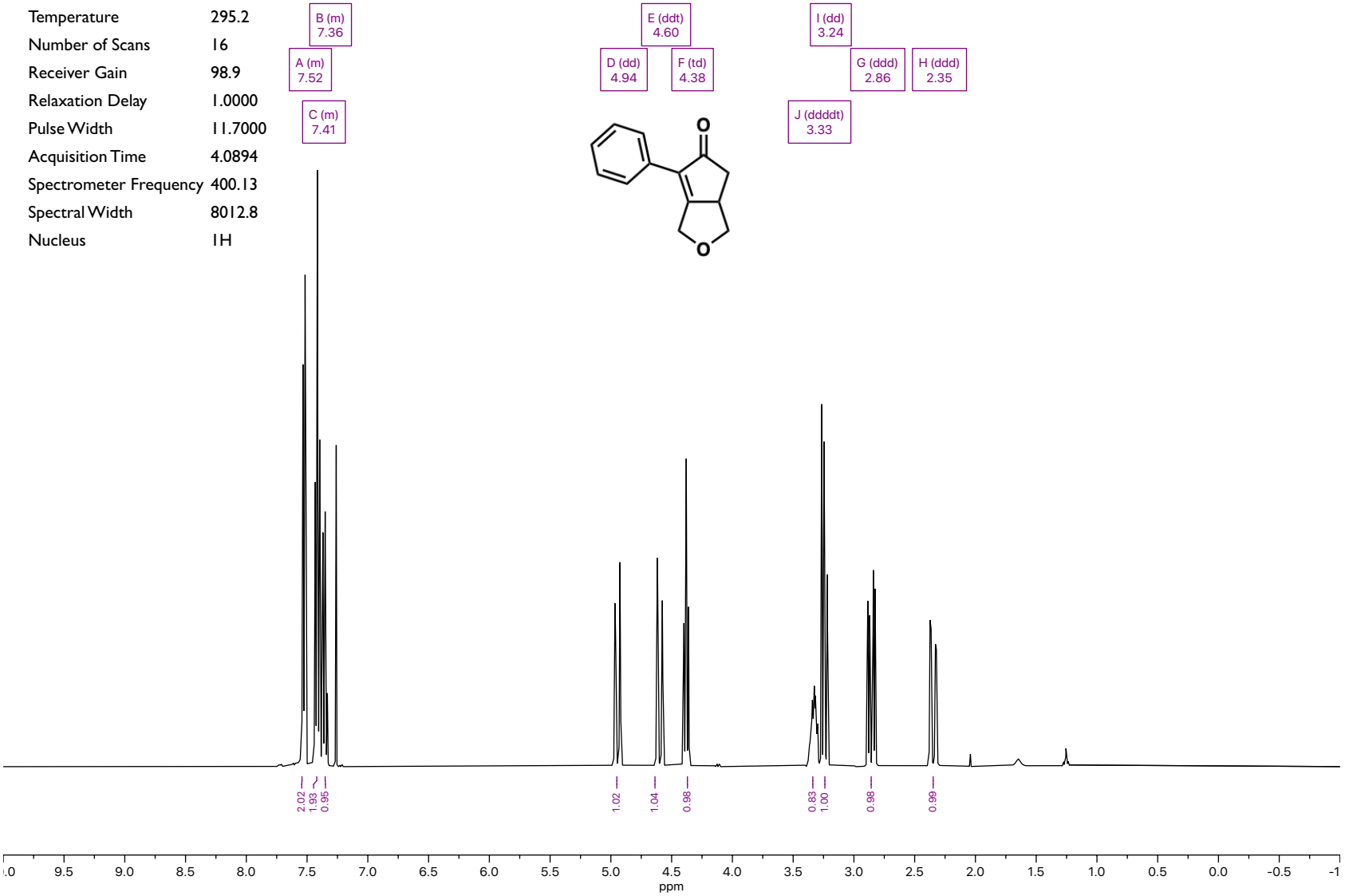
7c

Origin	Varian
Solvent	cdcl3
Temperature	25.0
Number of Scans	64
Receiver Gain	30
Relaxation Delay	1.0000
Pulse Width	4.6125
Acquisition Time	1.0420
Spectrometer Frequency	125.65
Spectral Width	31446.5
Nucleus	13C



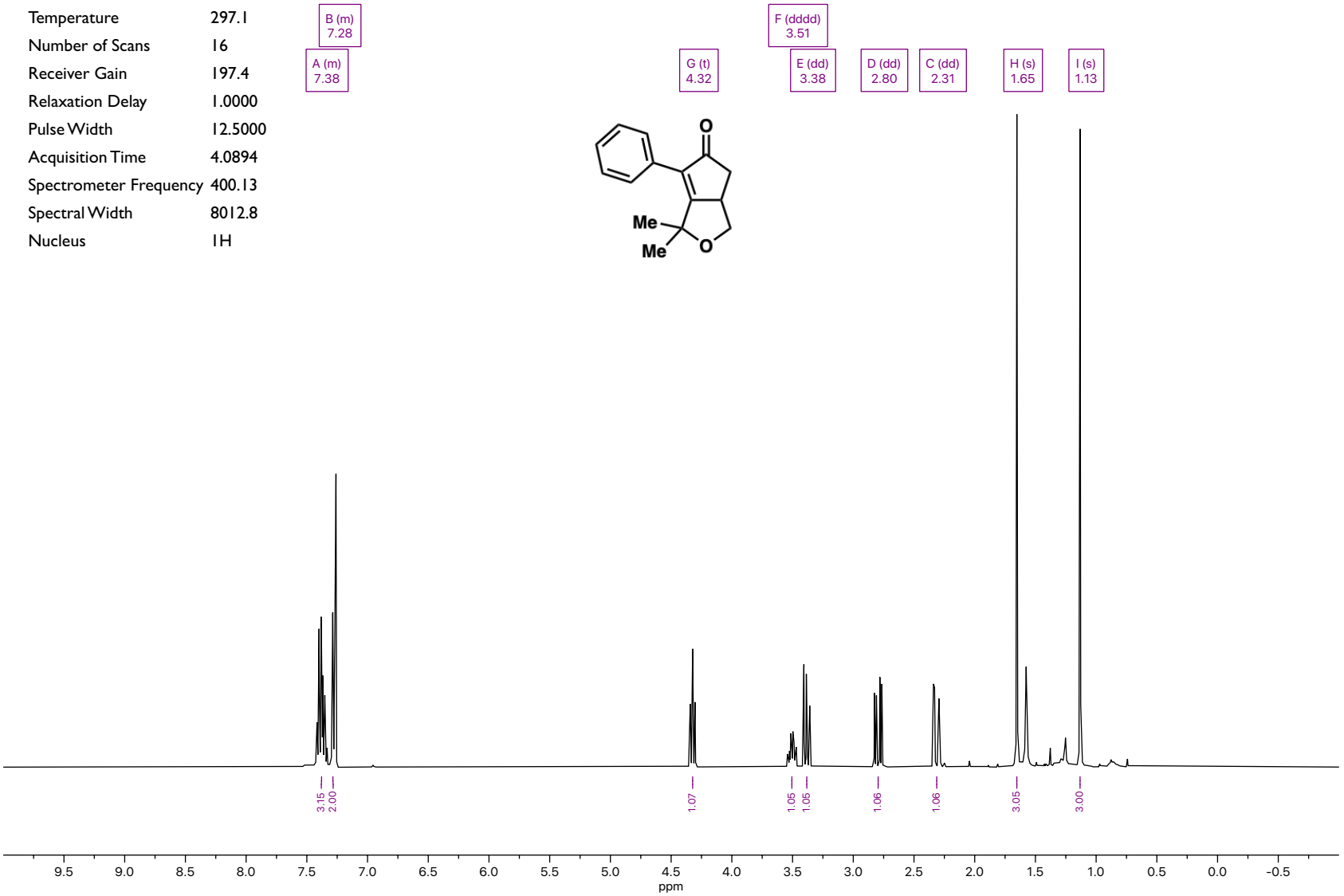
7d

Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	295.2
Number of Scans	16
Receiver Gain	98.9
Relaxation Delay	1.0000
Pulse Width	11.7000
Acquisition Time	4.0894
Spectrometer Frequency	400.13
Spectral Width	8012.8
Nucleus	1H



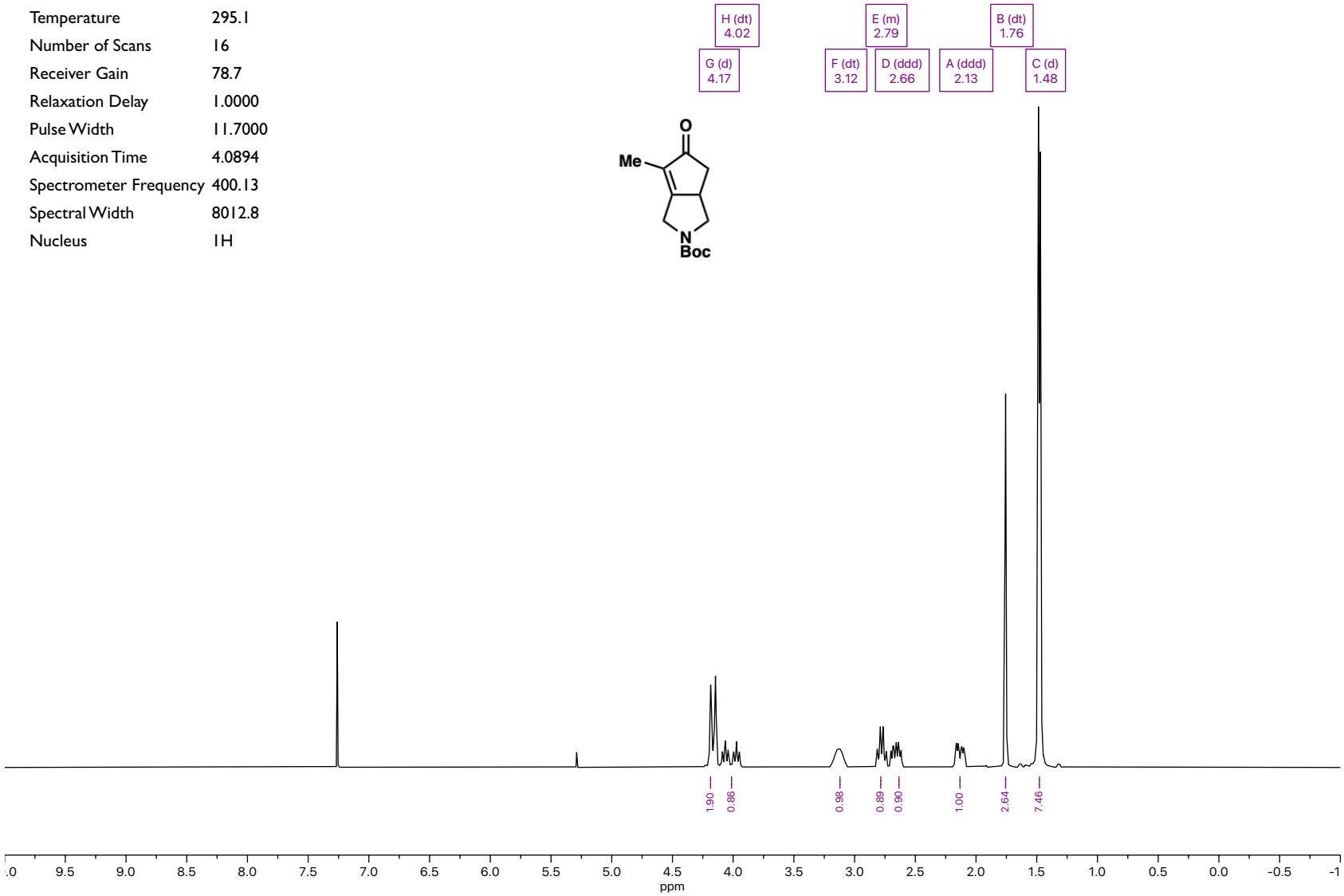
7e

Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	297.1
Number of Scans	16
Receiver Gain	197.4
Relaxation Delay	1.0000
Pulse Width	12.5000
Acquisition Time	4.0894
Spectrometer Frequency	400.13
Spectral Width	8012.8
Nucleus	1H



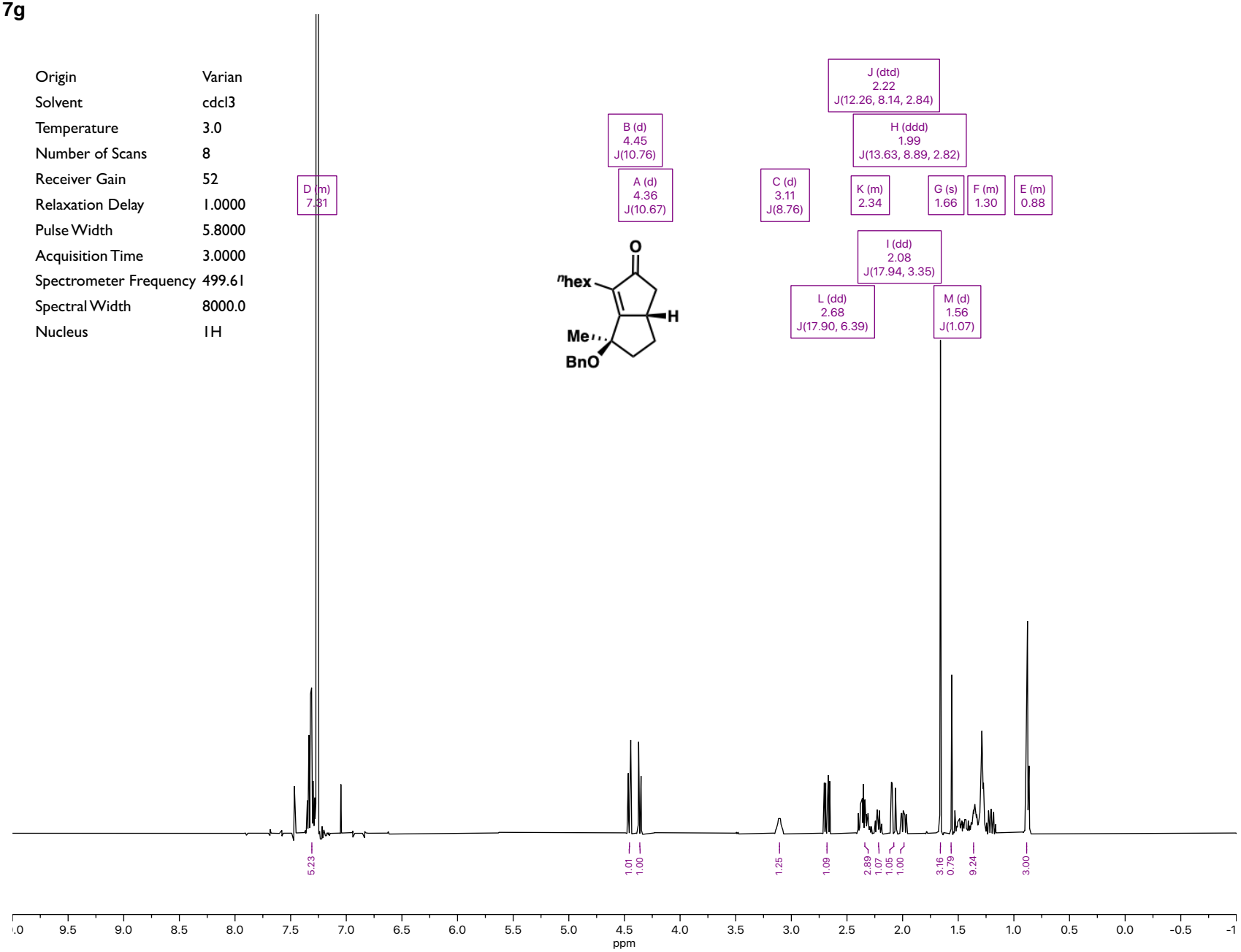
7f

Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	295.1
Number of Scans	16
Receiver Gain	78.7
Relaxation Delay	1.0000
Pulse Width	11.7000
Acquisition Time	4.0894
Spectrometer Frequency	400.13
Spectral Width	8012.8
Nucleus	1H



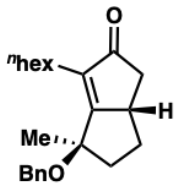
7g

Origin	Varian
Solvent	cdcl3
Temperature	3.0
Number of Scans	8
Receiver Gain	52
Relaxation Delay	1.0000
Pulse Width	5.8000
Acquisition Time	3.0000
Spectrometer Frequency	499.61
Spectral Width	8000.0
Nucleus	1H



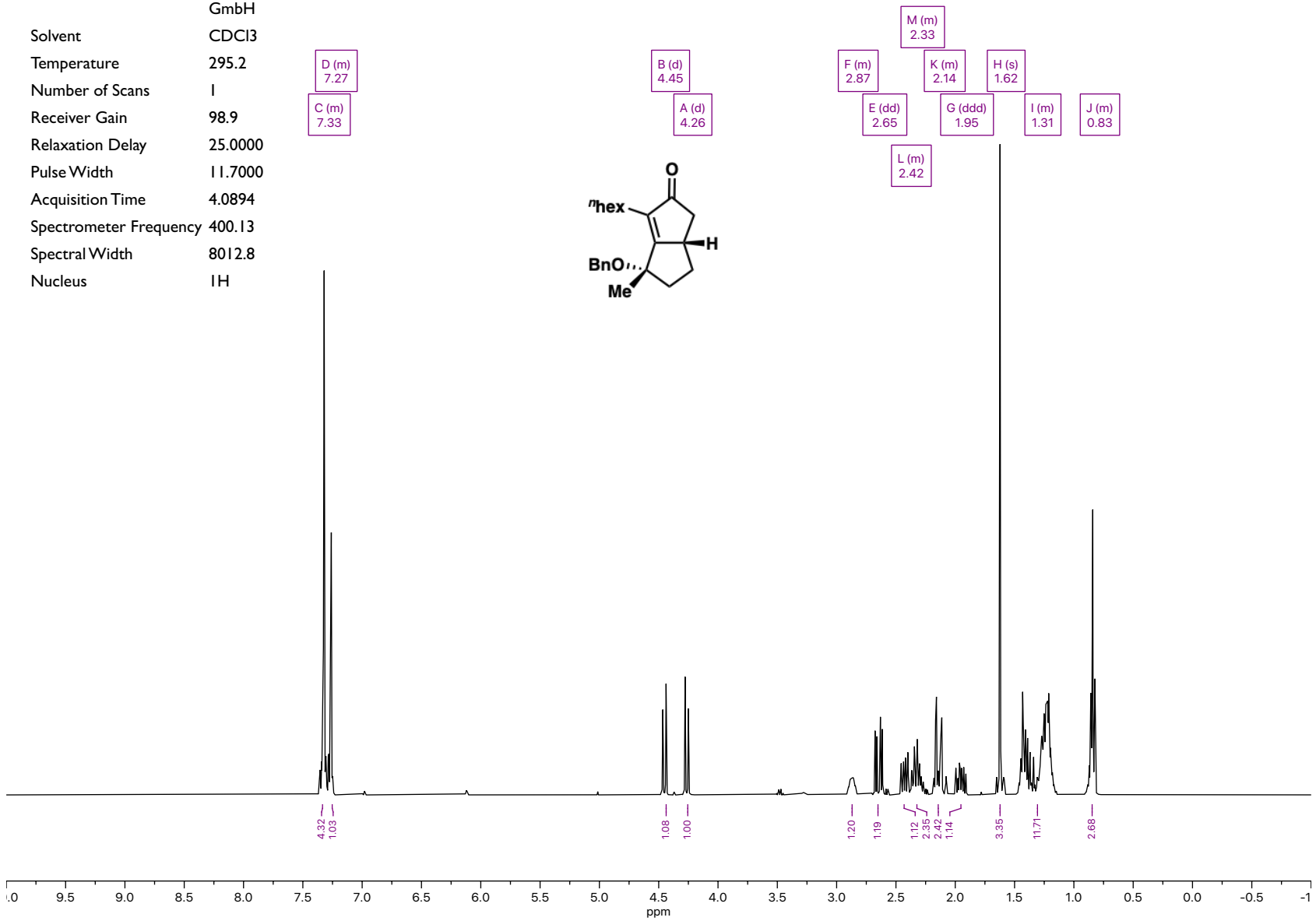
7g

Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	295.2
Number of Scans	128
Receiver Gain	87.8
Relaxation Delay	1.0000
Pulse Width	10.0000
Acquisition Time	1.3631
Spectrometer Frequency	100.62
Spectral Width	24038.5
Nucleus	13C



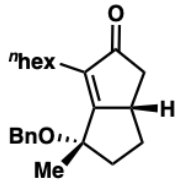
7h

Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	295.2
Number of Scans	1
Receiver Gain	98.9
Relaxation Delay	25.0000
Pulse Width	11.7000
Acquisition Time	4.0894
Spectrometer Frequency	400.13
Spectral Width	8012.8
Nucleus	1H

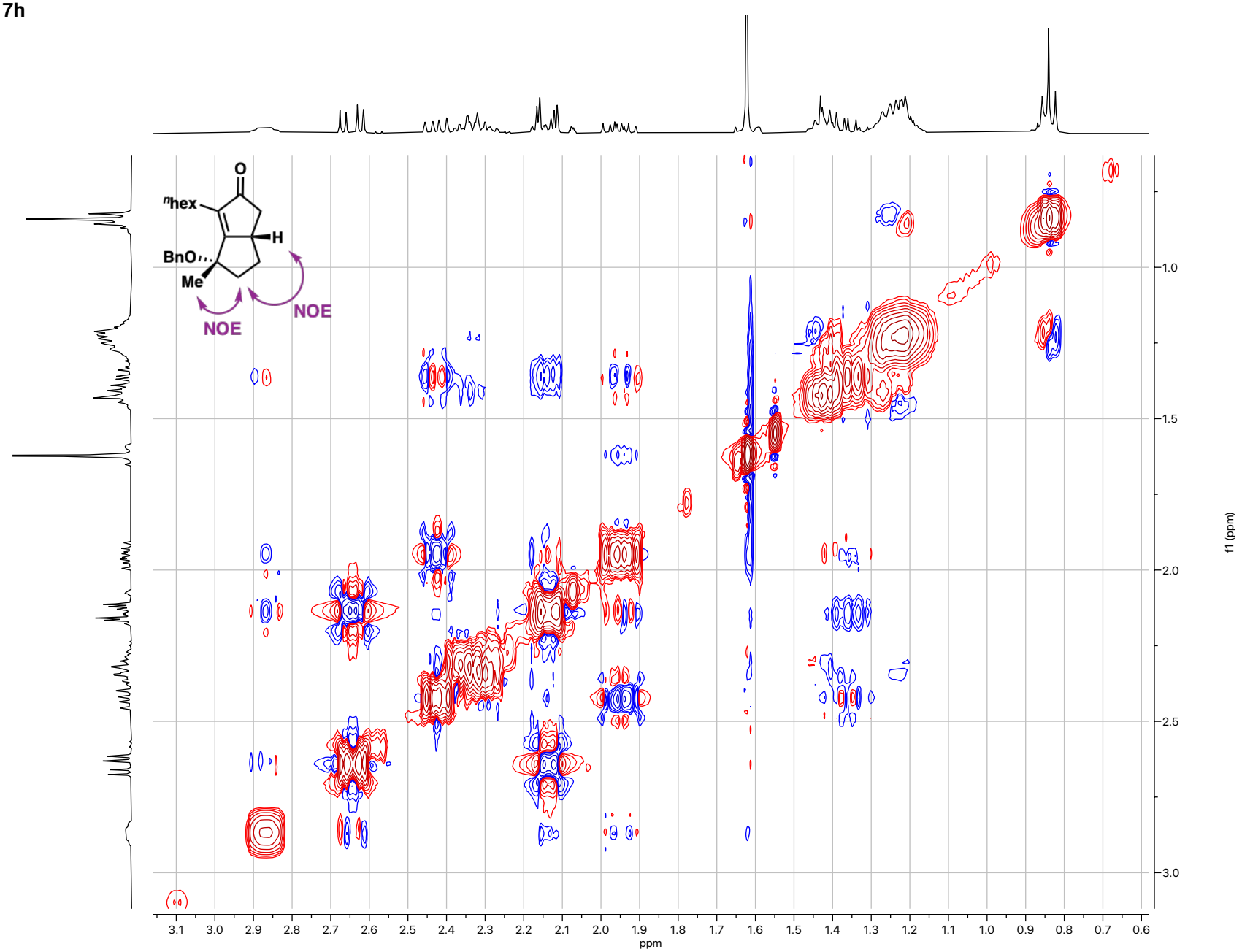


7h

Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	295.1
Number of Scans	128
Receiver Gain	78.7
Relaxation Delay	1.0000
Pulse Width	10.0000
Acquisition Time	1.3631
Spectrometer Frequency	100.62
Spectral Width	24038.5
Nucleus	13C

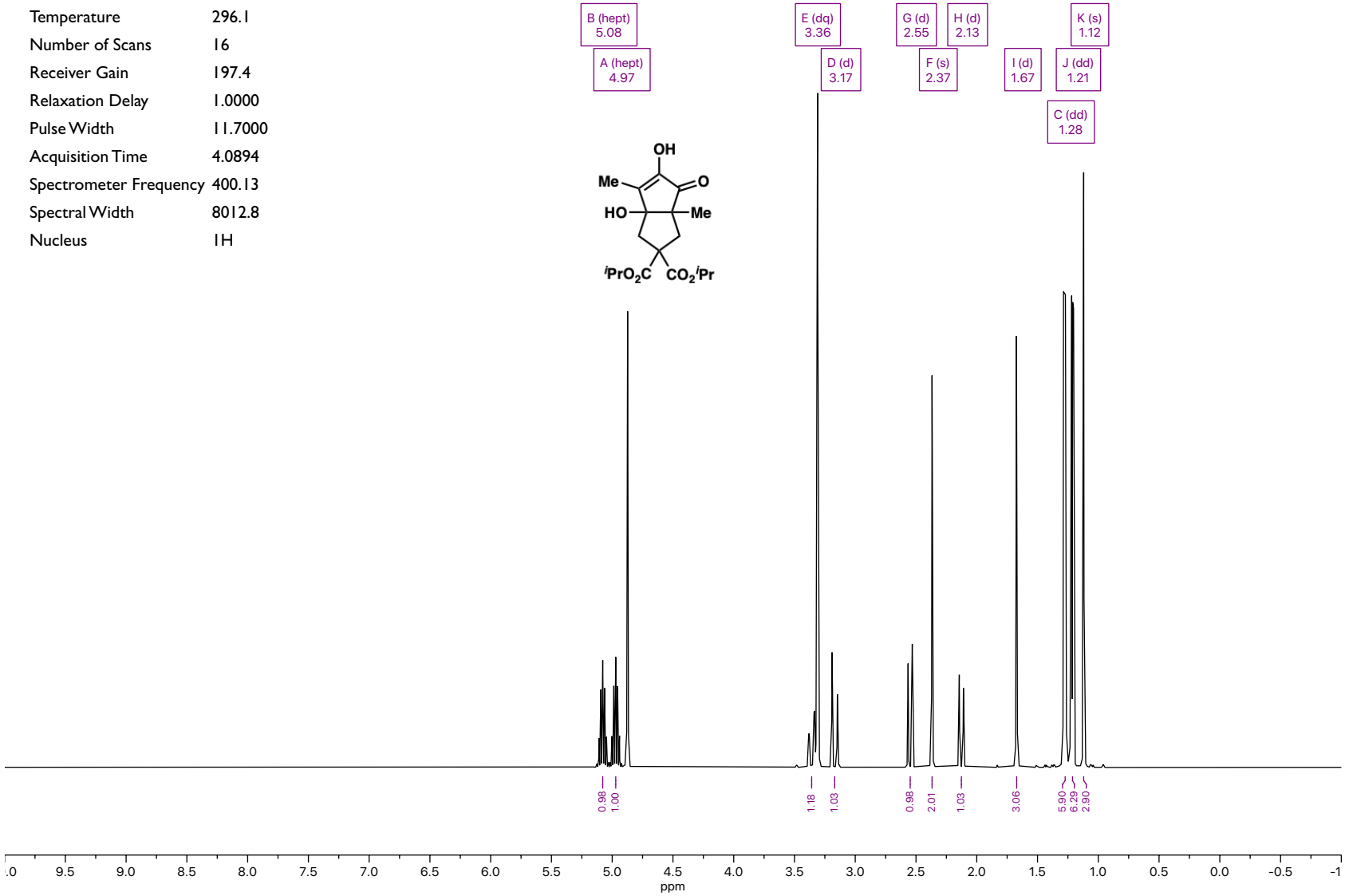


7h


O
nhex
H
BnO
Me
NOE
NOE
3.1 3.0 2.9 2.8 2.7 2.6 2.5 2.4 2.3 2.2 2.1 2.0 1.9 1.8 1.7 1.6 1.5 1.4 1.3 1.2 1.1 1.0 0.9 0.8 0.7 0.6
ppm
1.0
1.5
2.0
2.5
3.0
f1 (ppm)

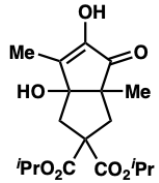
8a

Origin	Bruker BioSpin GmbH
Solvent	MeOD
Temperature	296.1
Number of Scans	16
Receiver Gain	197.4
Relaxation Delay	1.0000
Pulse Width	11.7000
Acquisition Time	4.0894
Spectrometer Frequency	400.13
Spectral Width	8012.8
Nucleus	1H

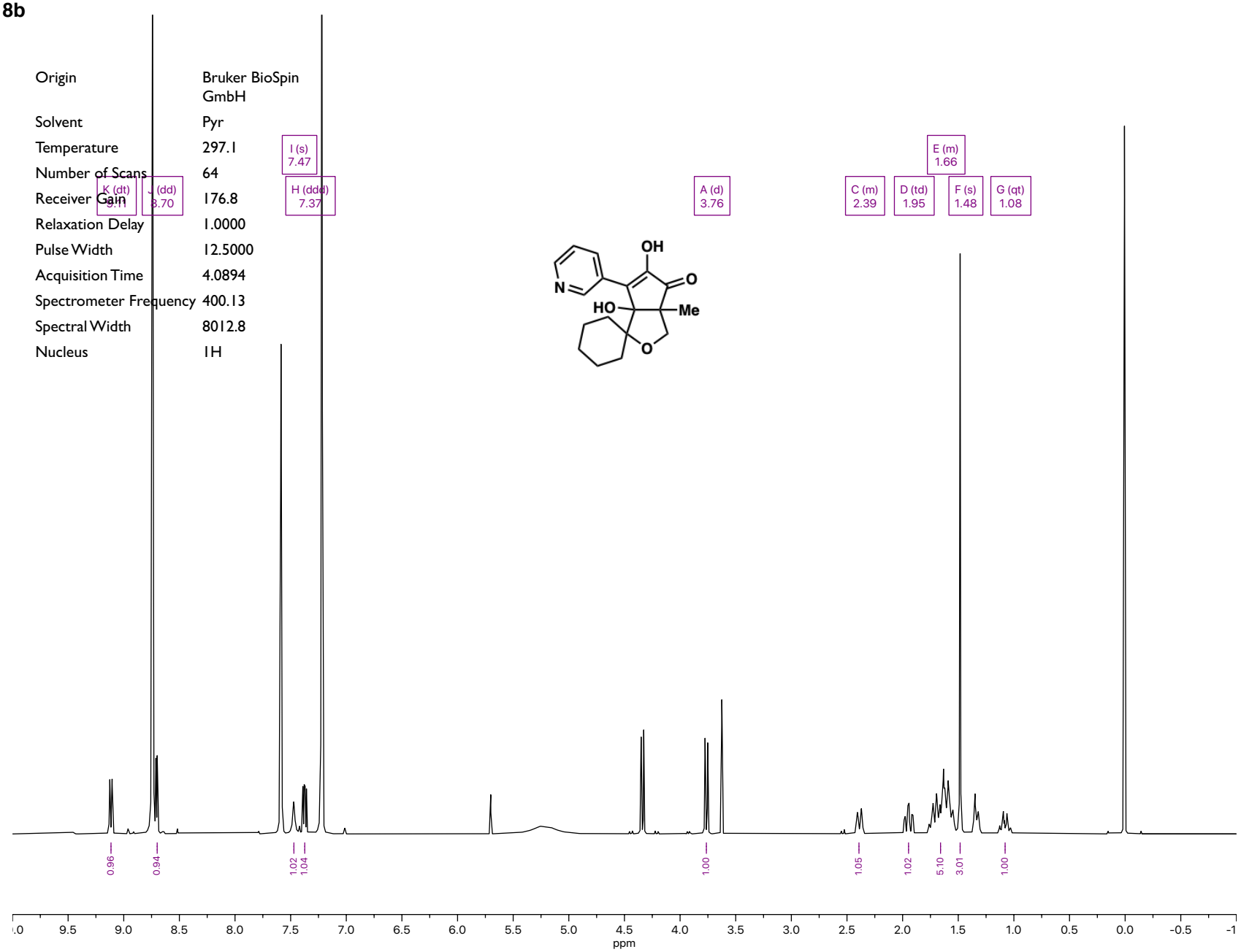


8a

Origin	Varian
Solvent	cdcl3
Temperature	25.0
Number of Scans	256
Receiver Gain	30
Relaxation Delay	1.0000
Pulse Width	4.6125
Acquisition Time	1.0420
Spectrometer Frequency	125.65
Spectral Width	31446.5
Nucleus	13C

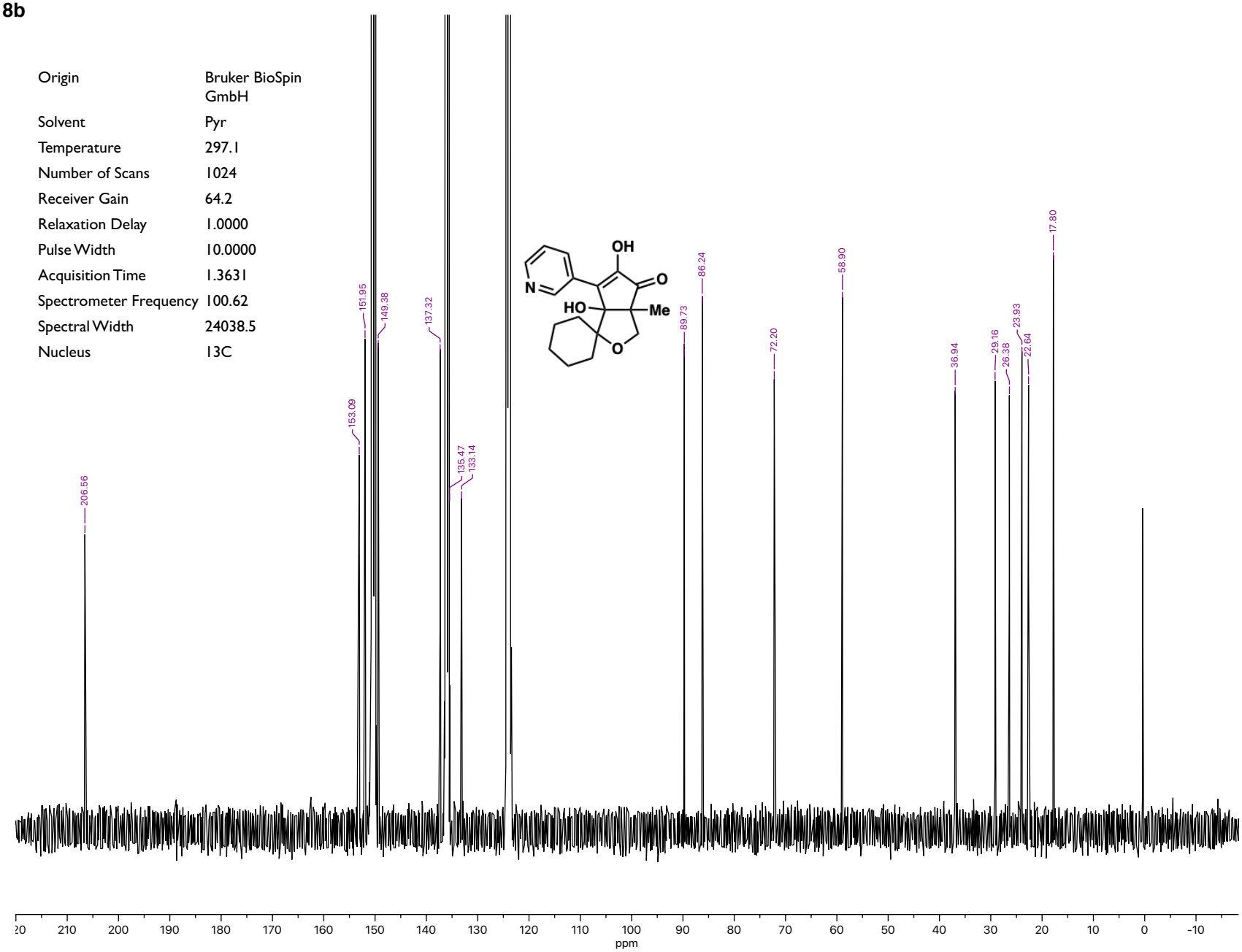


8b


Origin Bruker BioSpin GmbH
Solvent Pyr
Temperature 297.1
Number of Scans 64
Receiver Gain 176.8
Relaxation Delay 1.0000
Pulse Width 12.5000
Acquisition Time 4.0894
Spectrometer Frequency 400.13
Spectral Width 8012.8
Nucleus 1H
K (dt) 9.11
J (dd) 8.70
I (s) 7.47
H (ddd) 7.37
A (d) 3.76
C (m) 2.39
D (td) 1.95
E (m) 1.66
F (s) 1.48
G (qt) 1.08
OH
N
O
HO
Me
O
0.96
0.94
1.02
1.04
1.00
1.05
1.02
5.10
3.01
1.00
ppm

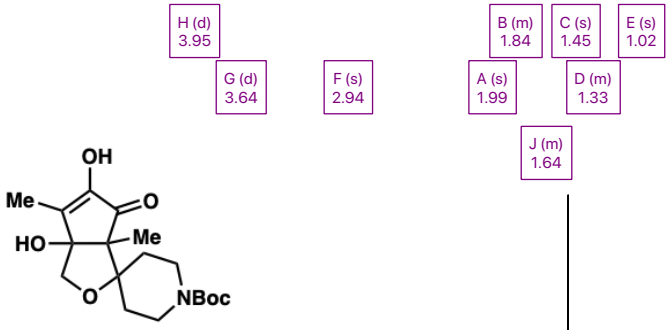
8b

Origin	Bruker BioSpin GmbH
Solvent	Pyr
Temperature	297.1
Number of Scans	1024
Receiver Gain	64.2
Relaxation Delay	1.0000
Pulse Width	10.0000
Acquisition Time	1.3631
Spectrometer Frequency	100.62
Spectral Width	24038.5
Nucleus	13C



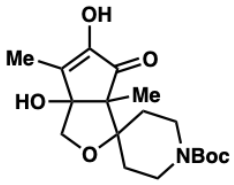
8c

Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	297.2
Number of Scans	64
Receiver Gain	156.2
Relaxation Delay	1.0000
Pulse Width	12.5000
Acquisition Time	4.0894
Spectrometer Frequency	400.13
Spectral Width	8012.8
Nucleus	1H

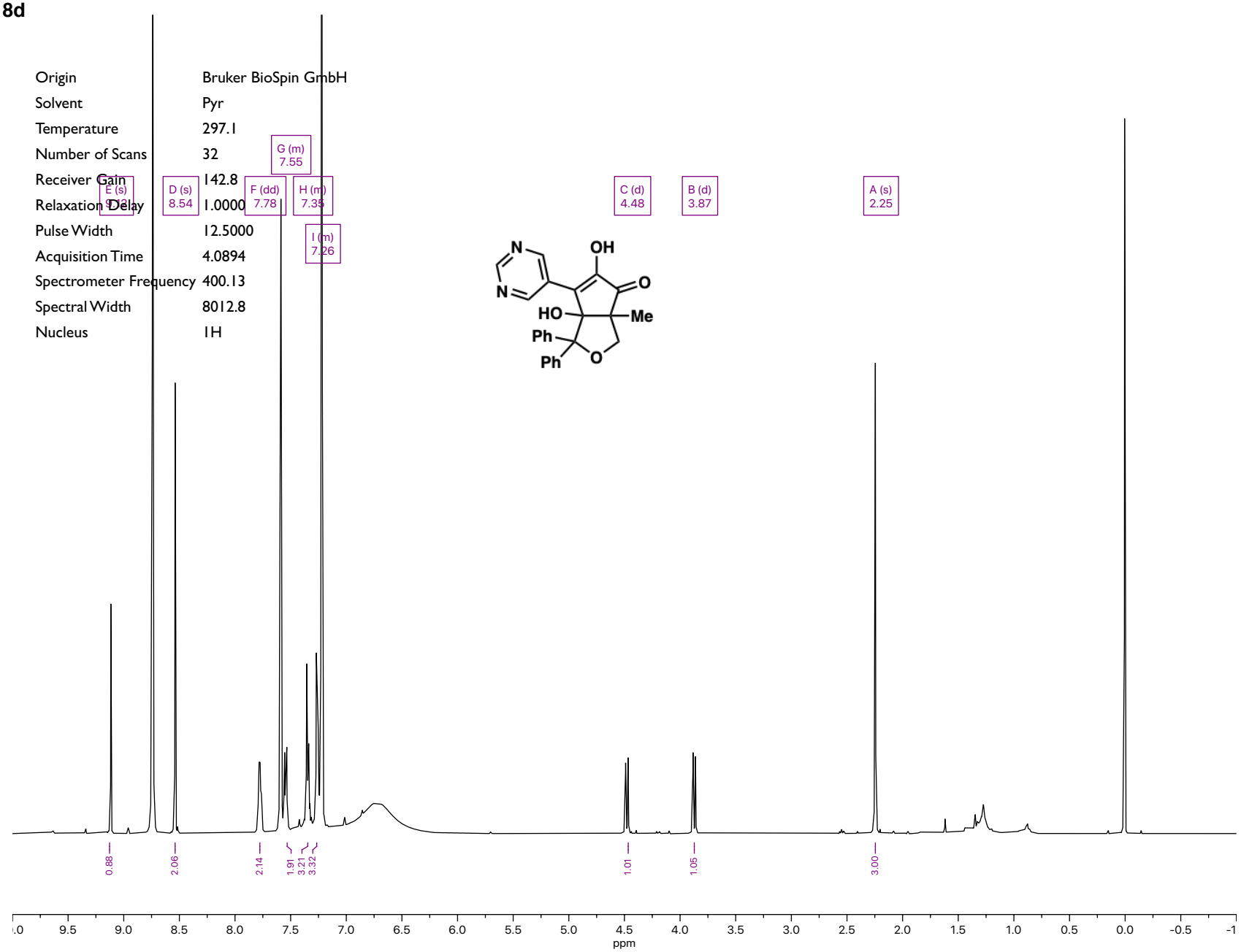


8c

Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	297.2
Number of Scans	1536
Receiver Gain	55.5
Relaxation Delay	1.0000
Pulse Width	10.0000
Acquisition Time	1.3631
Spectrometer Frequency	100.62
Spectral Width	24038.5
Nucleus	13C

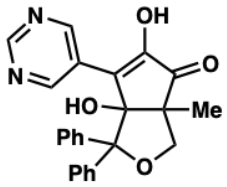


8d


Origin Bruker BioSpin GmbH
Solvent Pyr
Temperature 297.1
Number of Scans 32
Receiver Gain 142.8
Relaxation Delay 1.0000
Pulse Width 12.5000
Acquisition Time 4.0894
Spectrometer Frequency 400.13
Spectral Width 8012.8
Nucleus 1H
E (s) 8.88
D (s) 8.54
F (dd) 7.78
G (m) 7.55
H (m) 7.38
I (m) 7.26
C (d) 4.48
B (d) 3.87
A (s) 2.25
OH
N
N
O
HO
Me
Ph
Ph
O
0.88
2.06
2.14
1.91
3.21
3.32
1.01
1.05
3.00
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
-0.5
-1
ppm

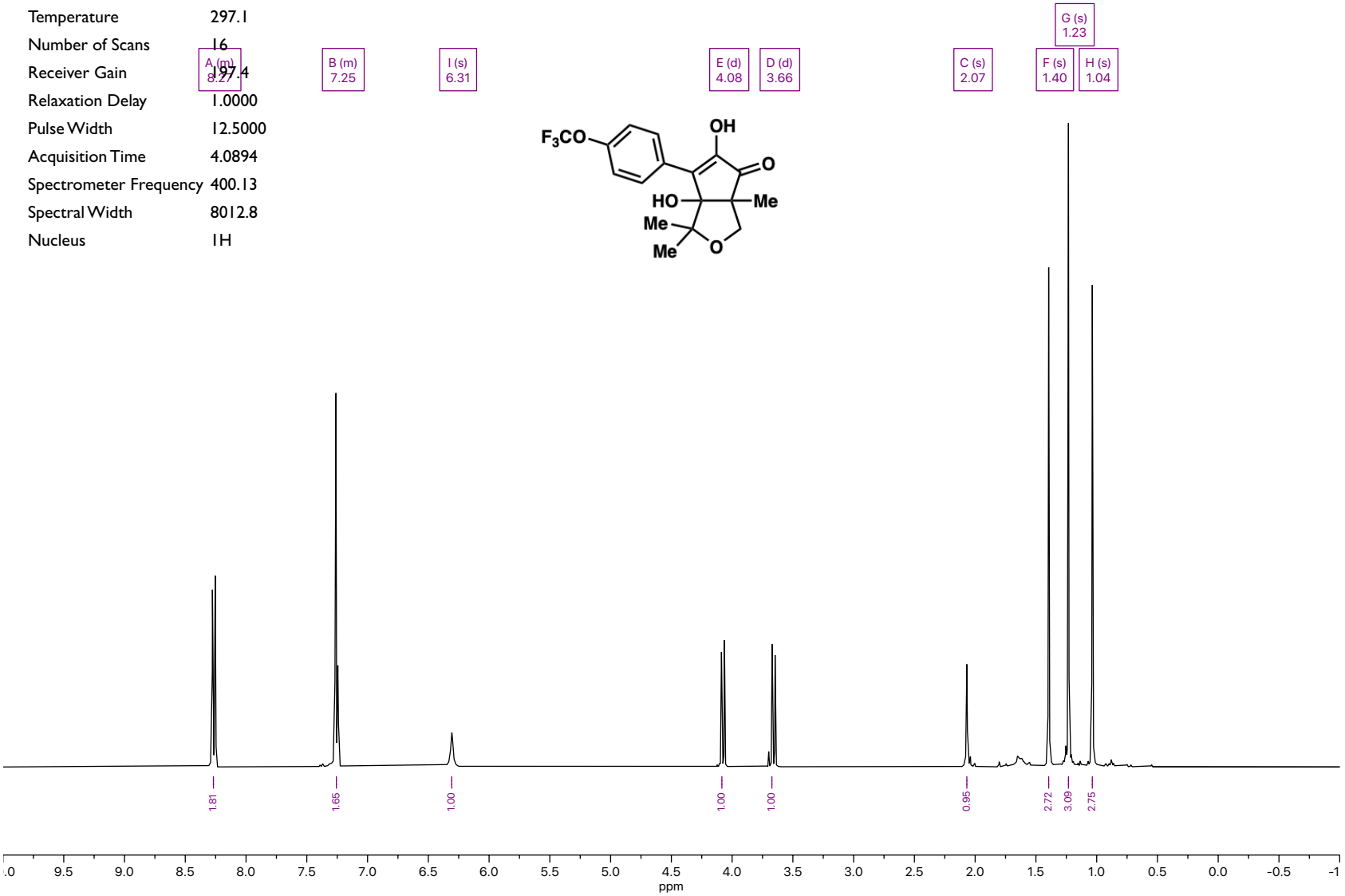
8d

Origin	Bruker BioSpin GmbH
Solvent	Pyr
Temperature	297.1
Number of Scans	1024
Receiver Gain	64.2
Relaxation Delay	1.0000
Pulse Width	10.0000
Acquisition Time	1.3631
Spectrometer Frequency	100.62
Spectral Width	24038.5
Nucleus	13C



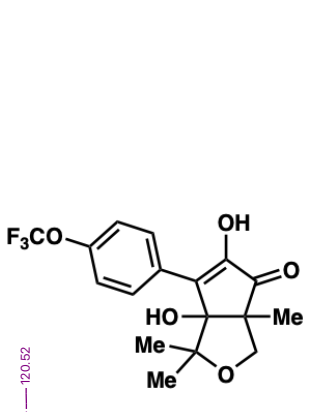
8e

Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	297.1
Number of Scans	16
Receiver Gain	197.4
Relaxation Delay	1.0000
Pulse Width	12.5000
Acquisition Time	4.0894
Spectrometer Frequency	400.13
Spectral Width	8012.8
Nucleus	1H

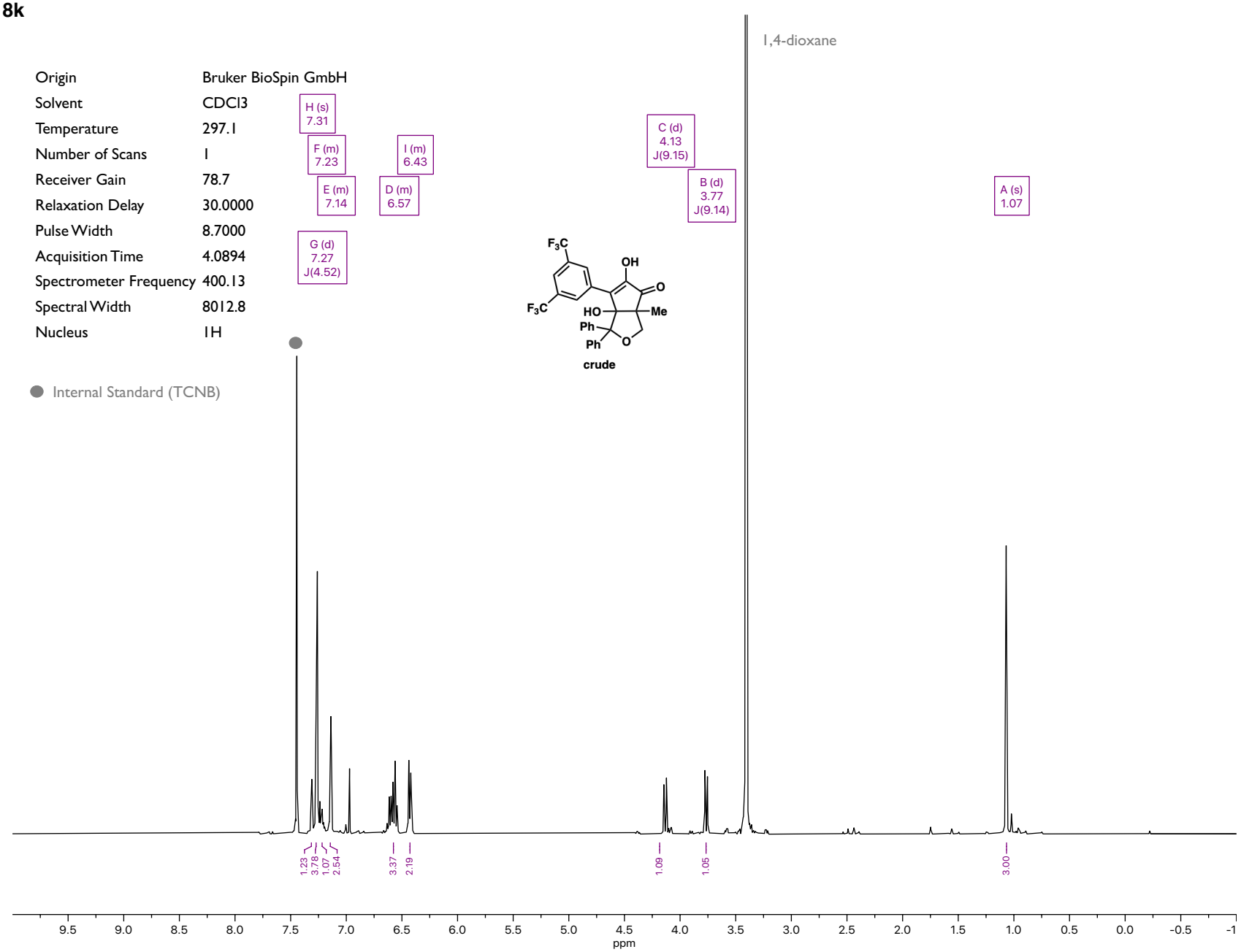


8e

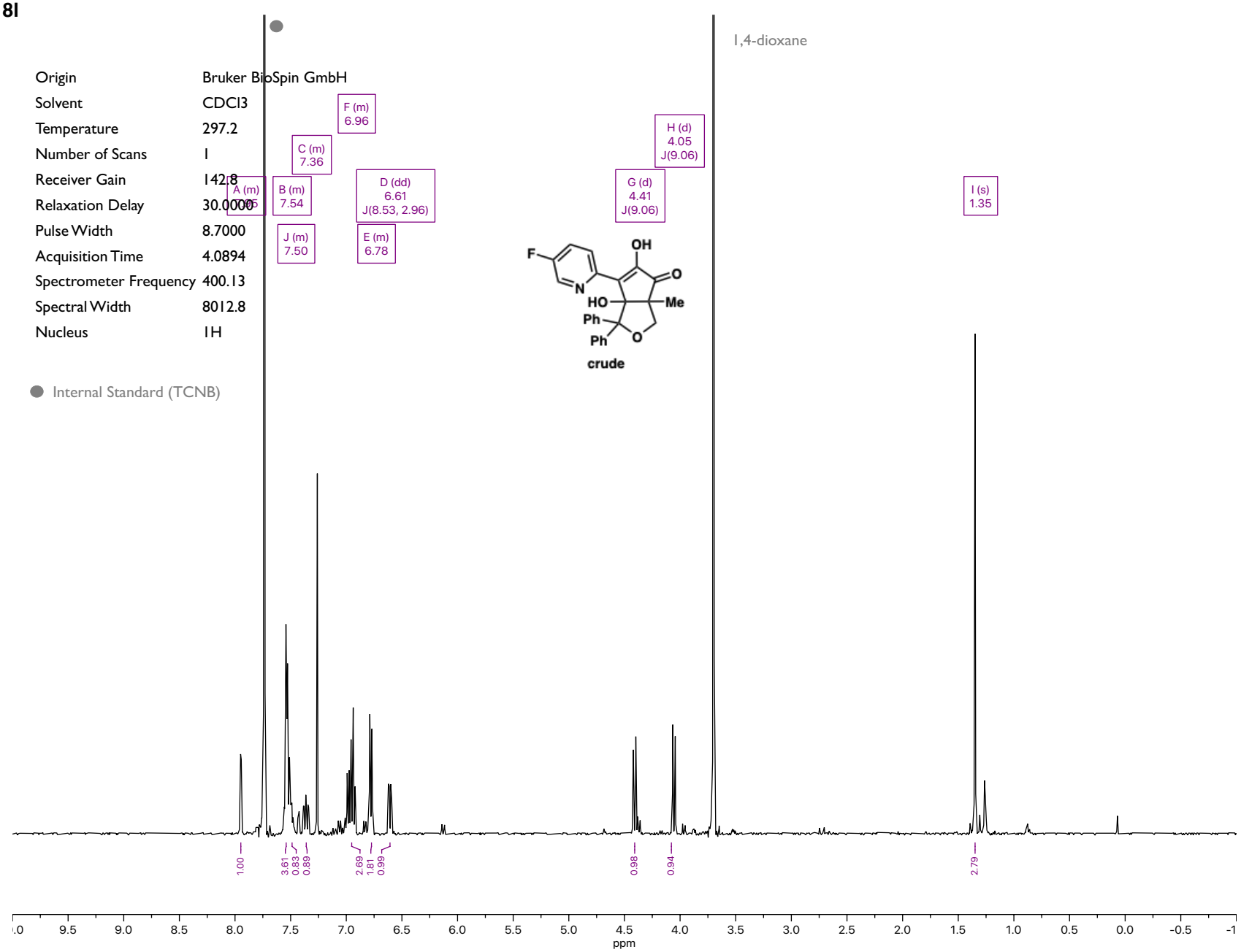
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	297.2
Number of Scans	512
Receiver Gain	55.5
Relaxation Delay	1.0000
Pulse Width	10.0000
Acquisition Time	1.3631
Spectrometer Frequency	100.62
Spectral Width	24038.5
Nucleus	13C



8k

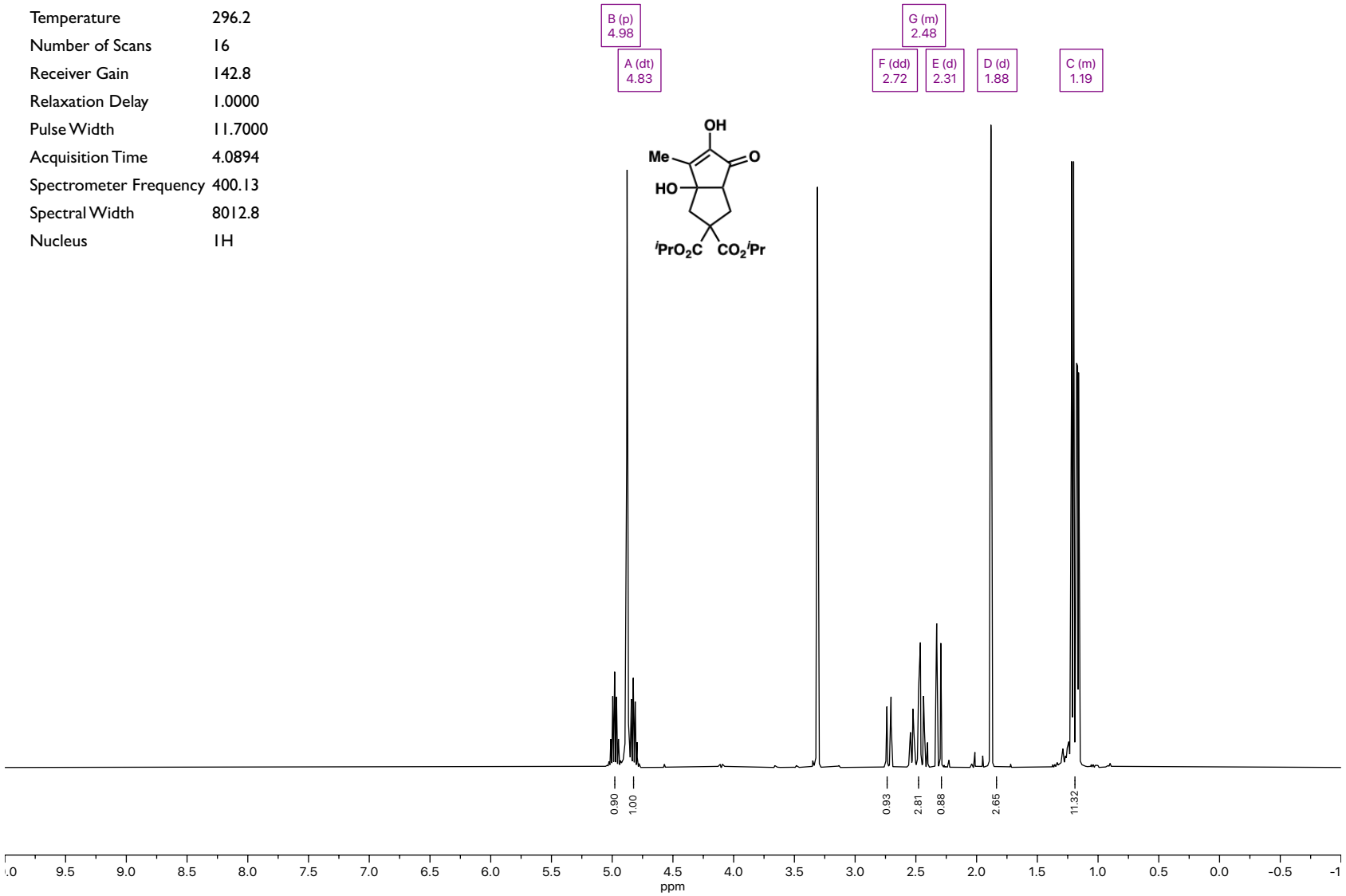

1,4-dioxane
Origin Bruker BioSpin GmbH
Solvent CDCl3
Temperature 297.1
Number of Scans 1
Receiver Gain 78.7
Relaxation Delay 30.0000
Pulse Width 8.7000
Acquisition Time 4.0894
Spectrometer Frequency 400.13
Spectral Width 8012.8
Nucleus 1H
H (s) 7.31
F (m) 7.23
I (m) 6.43
E (m) 7.14
D (m) 6.57
G (d) 7.27 J(4.52)
C (d) 4.13 J(9.15)
B (d) 3.77 J(9.14)
A (s) 1.07
Internal Standard (TCNB)
crude
1.23
3.78
1.07
2.54
3.37
2.19
1.09
1.05
3.00
ppm

8l


Origin Bruker BioSpin GmbH
Solvent CDCl3
Temperature 297.2
Number of Scans 1
Receiver Gain 142.8
Relaxation Delay 30.0000
Pulse Width 8.7000
Acquisition Time 4.0894
Spectrometer Frequency 400.13
Spectral Width 8012.8
Nucleus 1H
Internal Standard (TCNB)
1,4-dioxane
A (m)
B (m) 7.54
C (m) 7.36
D (dd) 6.61 J(8.53, 2.96)
E (m) 6.78
F (m) 6.96
G (d) 4.41 J(9.06)
H (d) 4.05 J(9.06)
I (s) 1.35
J (m) 7.50
F
N
OH
O
HO
Me
Ph
Ph
O
crude
1.00
3.61
0.83
0.89
2.69
1.81
0.99
0.98
0.94
2.79
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 -0.5 -1
ppm

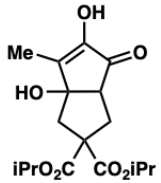
9a

Origin	Bruker BioSpin GmbH
Solvent	MeOD
Temperature	296.2
Number of Scans	16
Receiver Gain	142.8
Relaxation Delay	1.0000
Pulse Width	11.7000
Acquisition Time	4.0894
Spectrometer Frequency	400.13
Spectral Width	8012.8
Nucleus	1H



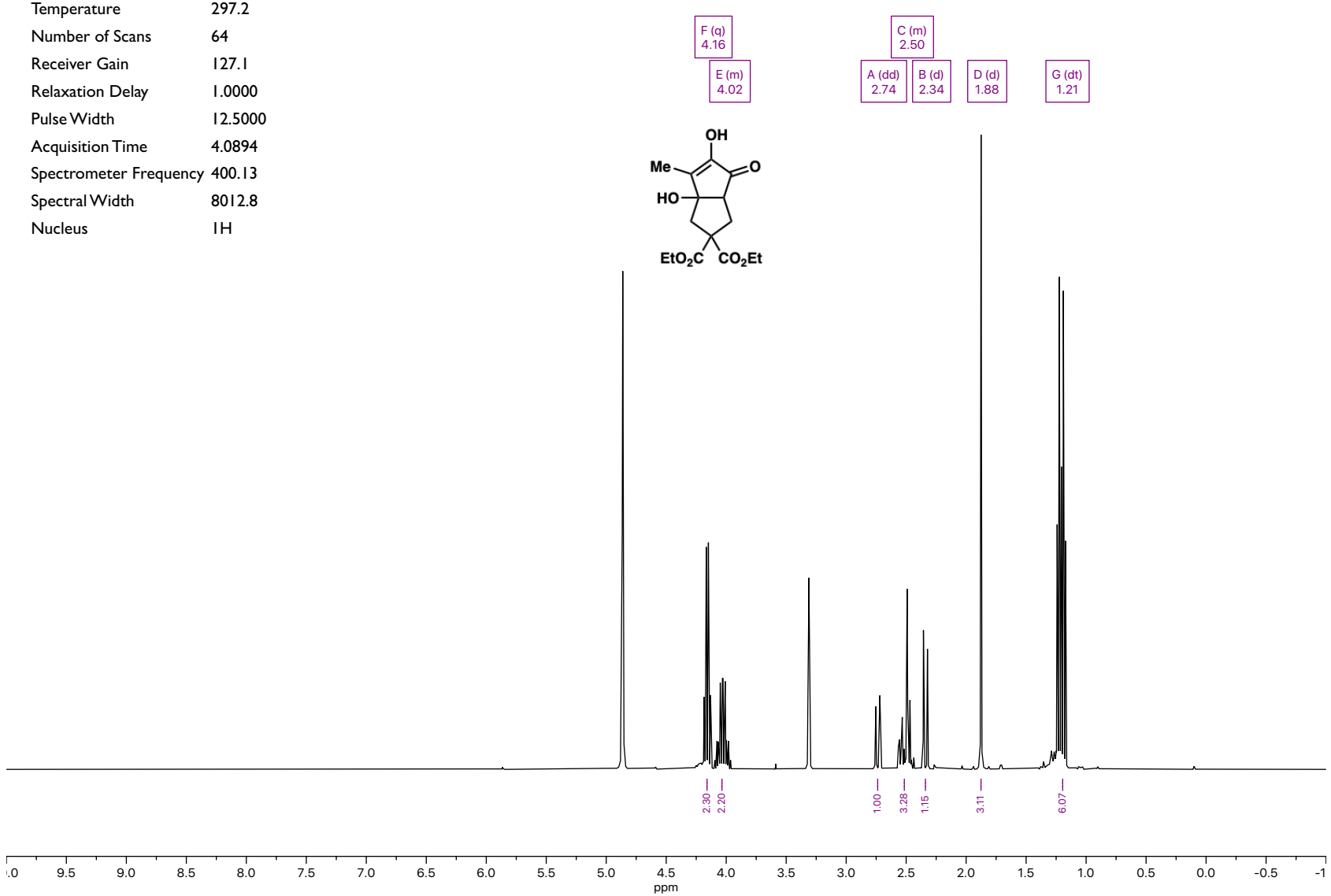
9a

Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	296.2
Number of Scans	1024
Receiver Gain	38.0
Relaxation Delay	1.0000
Pulse Width	10.0000
Acquisition Time	1.3631
Spectrometer Frequency	100.62
Spectral Width	24038.5
Nucleus	13C



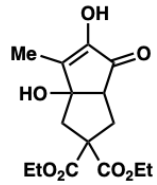
9b

Origin	Bruker BioSpin GmbH
Solvent	MeOD
Temperature	297.2
Number of Scans	64
Receiver Gain	127.1
Relaxation Delay	1.0000
Pulse Width	12.5000
Acquisition Time	4.0894
Spectrometer Frequency	400.13
Spectral Width	8012.8
Nucleus	1H



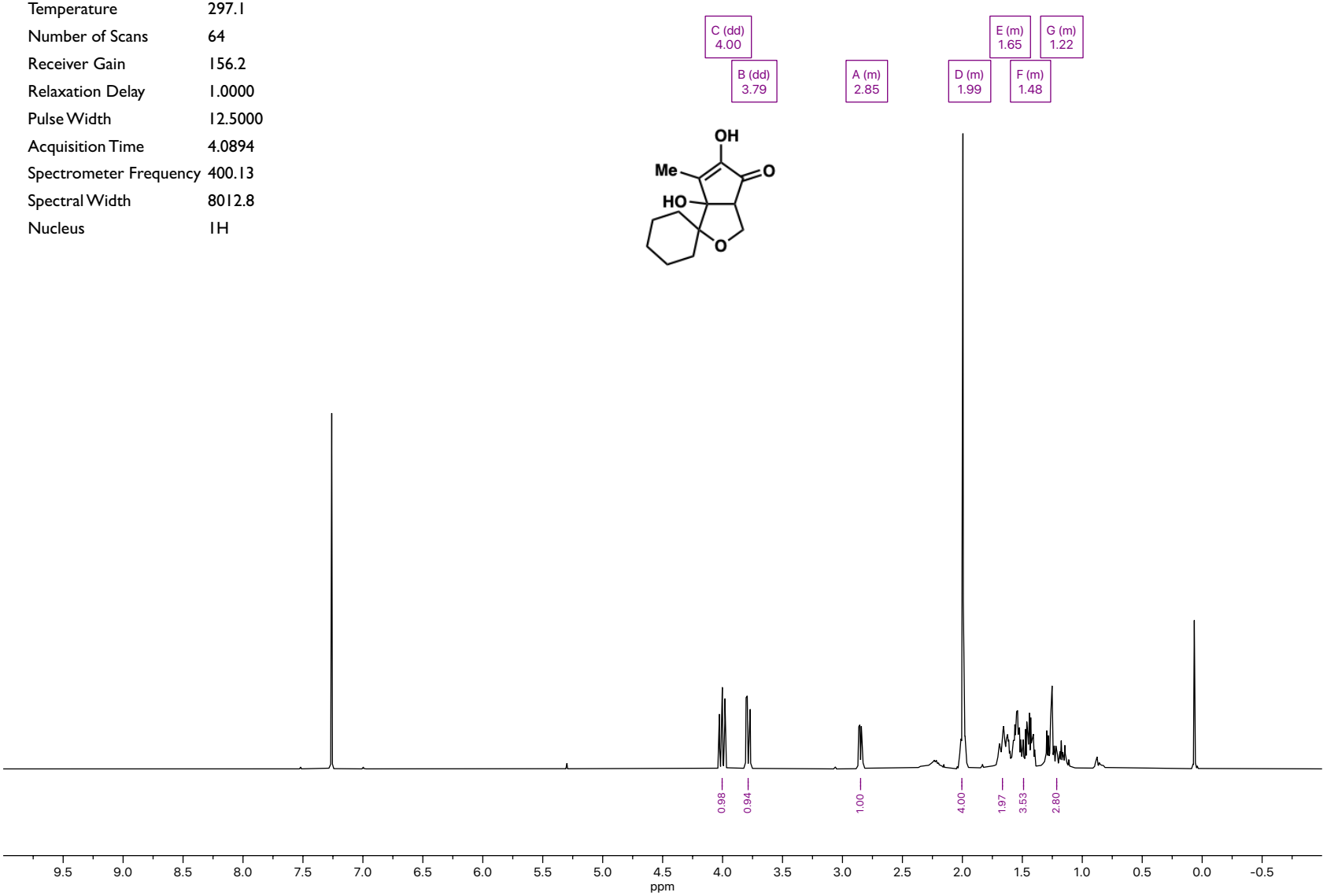
9b

Origin	Bruker BioSpin GmbH
Solvent	MeOD
Temperature	297.1
Number of Scans	1024
Receiver Gain	50.3
Relaxation Delay	1.0000
Pulse Width	10.0000
Acquisition Time	1.3631
Spectrometer Frequency	100.62
Spectral Width	24038.5
Nucleus	13C



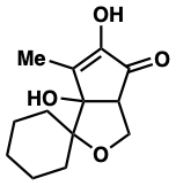
9c

Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	297.1
Number of Scans	64
Receiver Gain	156.2
Relaxation Delay	1.0000
Pulse Width	12.5000
Acquisition Time	4.0894
Spectrometer Frequency	400.13
Spectral Width	8012.8
Nucleus	1H



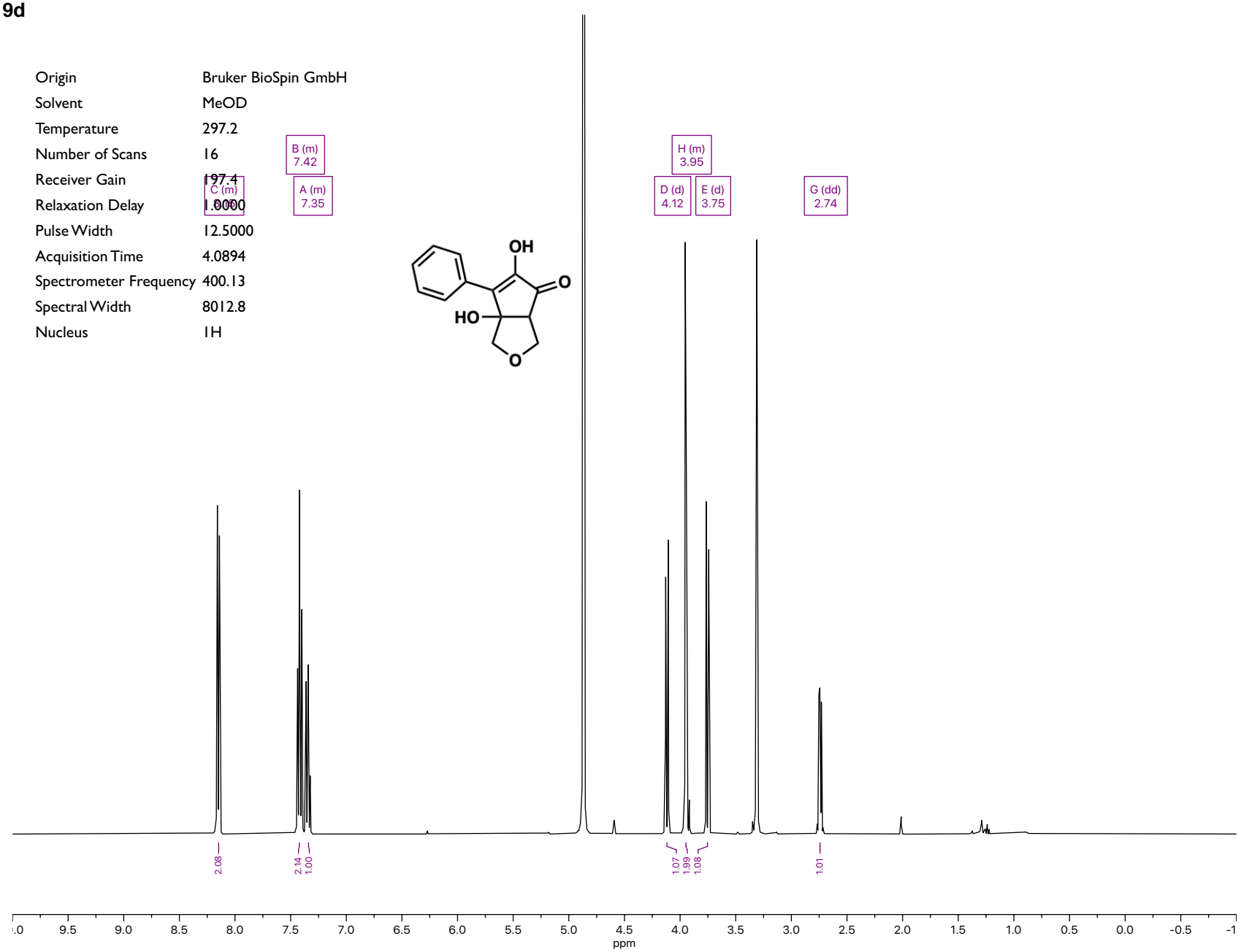
9c

Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	297.2
Number of Scans	1536
Receiver Gain	78.7
Relaxation Delay	1.0000
Pulse Width	10.0000
Acquisition Time	1.3631
Spectrometer Frequency	100.62
Spectral Width	24038.5
Nucleus	13C



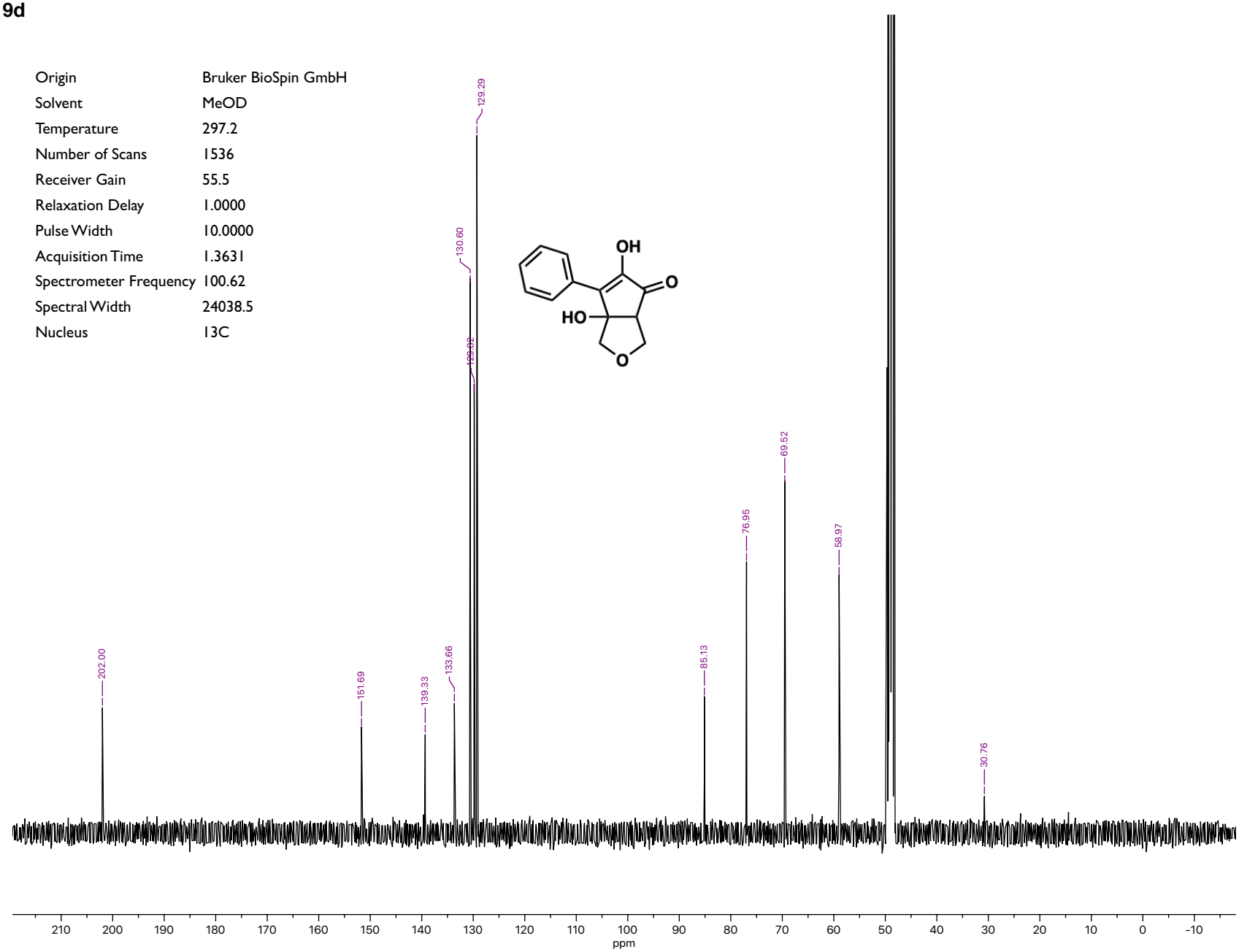
9d

Origin	Bruker BioSpin GmbH
Solvent	MeOD
Temperature	297.2
Number of Scans	16
Receiver Gain	197.4
Relaxation Delay	1.0000
Pulse Width	12.5000
Acquisition Time	4.0894
Spectrometer Frequency	400.13
Spectral Width	8012.8
Nucleus	1H



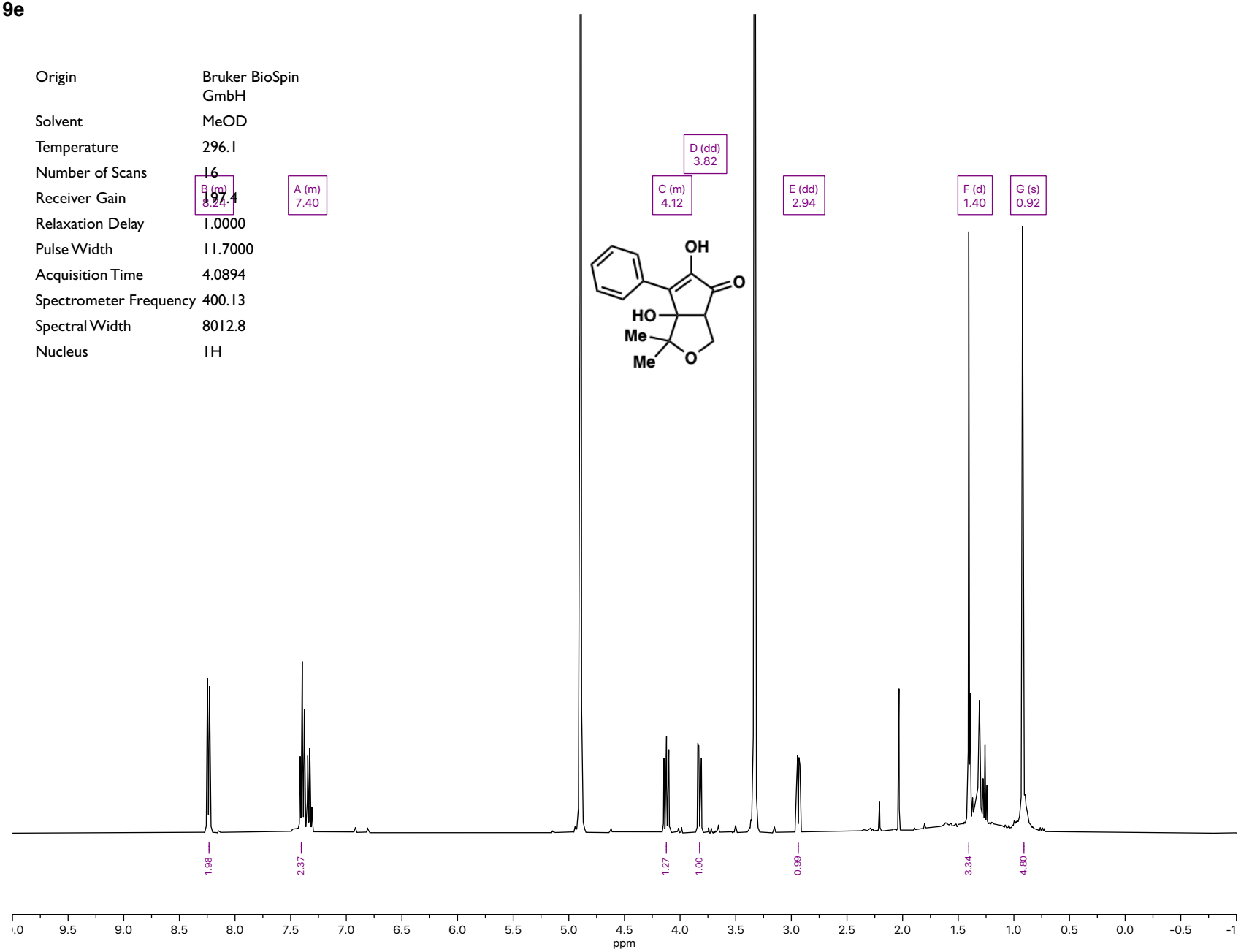
9d

Origin	Bruker BioSpin GmbH
Solvent	MeOD
Temperature	297.2
Number of Scans	1536
Receiver Gain	55.5
Relaxation Delay	1.0000
Pulse Width	10.0000
Acquisition Time	1.3631
Spectrometer Frequency	100.62
Spectral Width	24038.5
Nucleus	13C



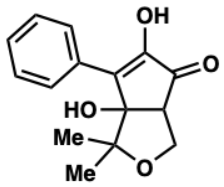
9e

Origin	Bruker BioSpin GmbH
Solvent	MeOD
Temperature	296.1
Number of Scans	16
Receiver Gain	197.4
Relaxation Delay	1.0000
Pulse Width	11.7000
Acquisition Time	4.0894
Spectrometer Frequency	400.13
Spectral Width	8012.8
Nucleus	1H



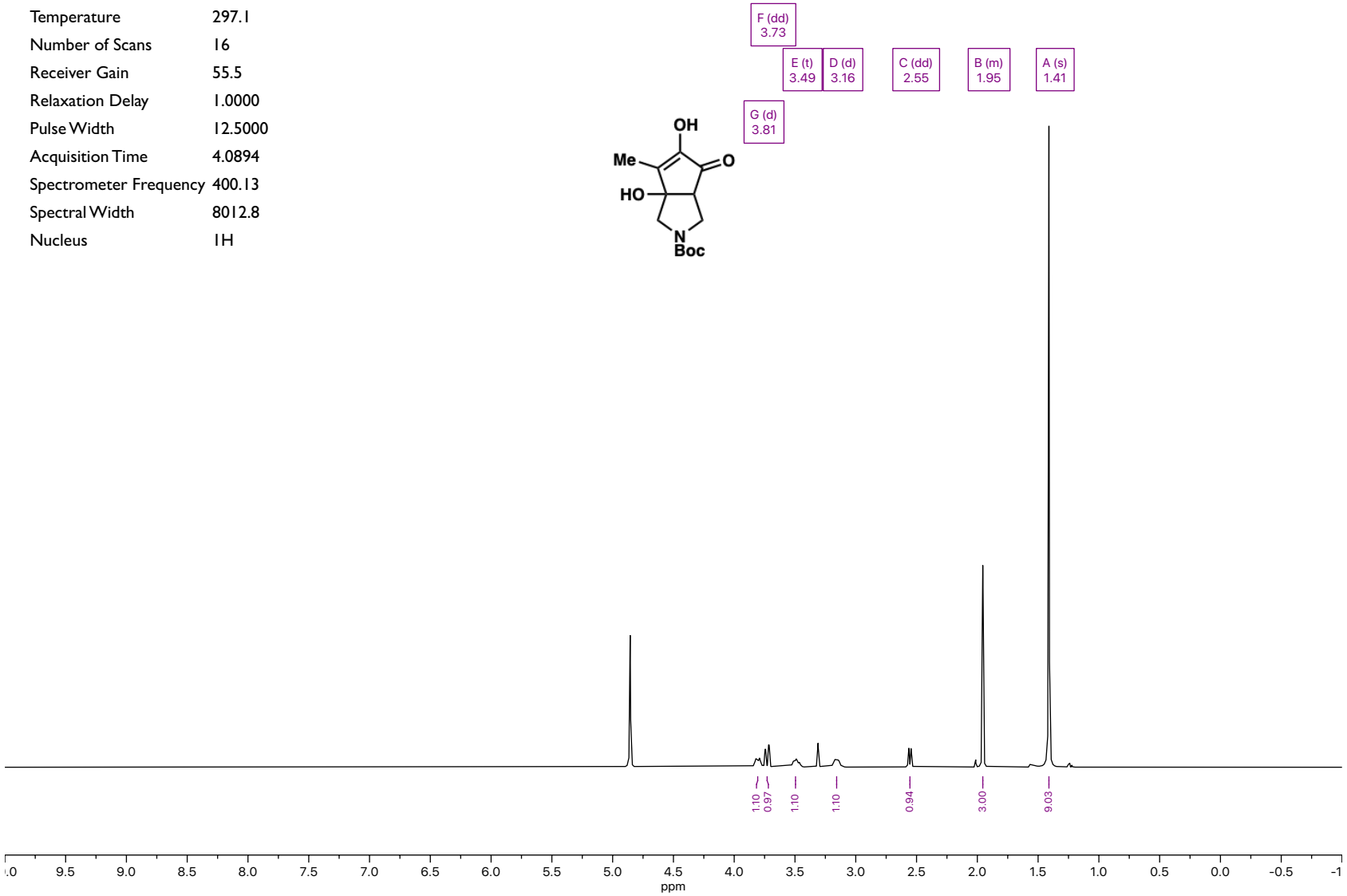
9e

Origin	Bruker BioSpin GmbH
Solvent	MeOD
Temperature	296.2
Number of Scans	2048
Receiver Gain	72.0
Relaxation Delay	1.0000
Pulse Width	10.0000
Acquisition Time	1.3631
Spectrometer Frequency	100.62
Spectral Width	24038.5
Nucleus	13C



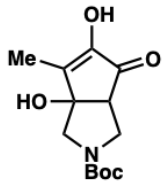
9f

Origin	Bruker BioSpin GmbH
Solvent	MeOD
Temperature	297.1
Number of Scans	16
Receiver Gain	55.5
Relaxation Delay	1.0000
Pulse Width	12.5000
Acquisition Time	4.0894
Spectrometer Frequency	400.13
Spectral Width	8012.8
Nucleus	1H



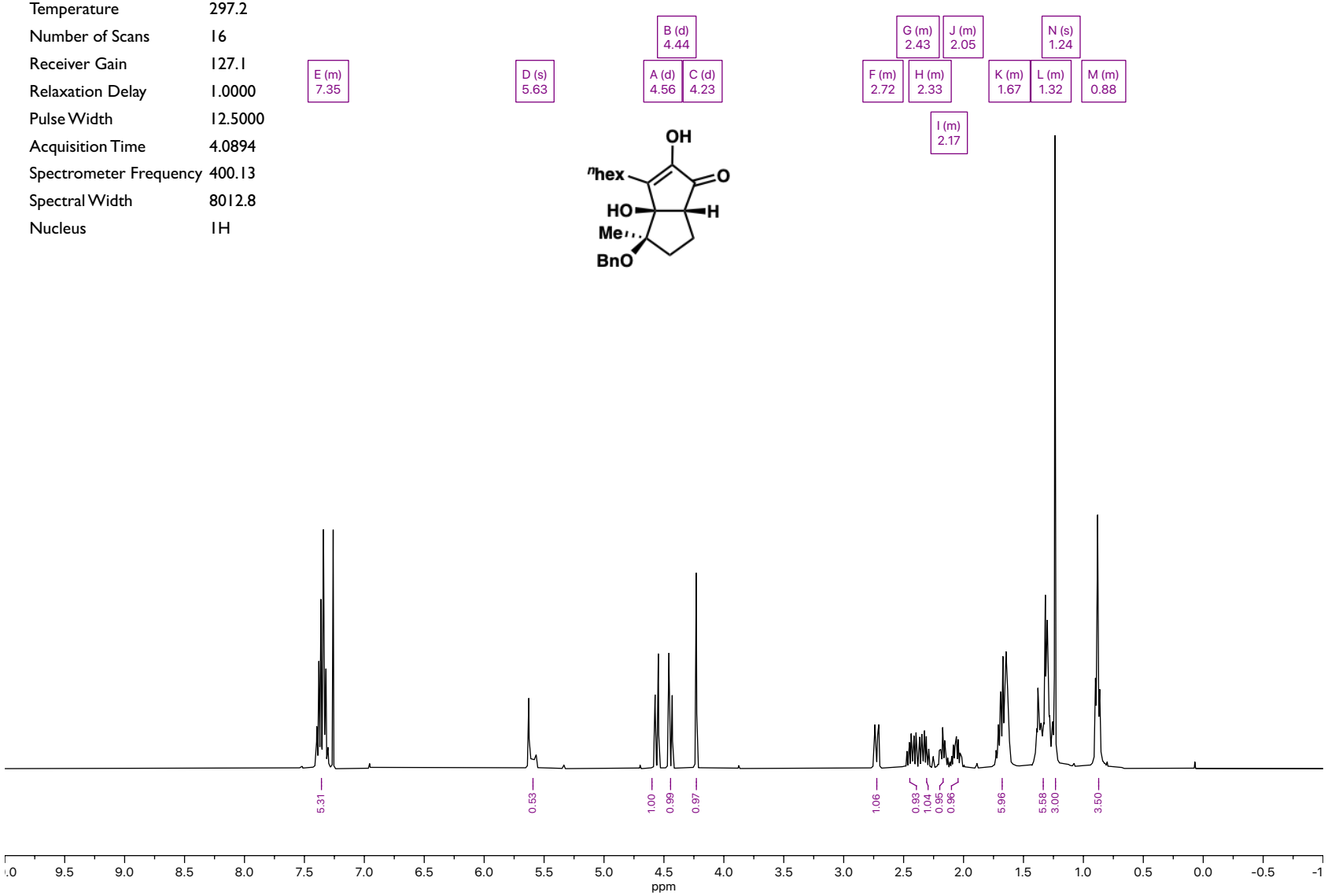
9f

Origin	Bruker BioSpin GmbH
Solvent	MeOD
Temperature	297.1
Number of Scans	2048
Receiver Gain	55.5
Relaxation Delay	1.0000
Pulse Width	10.0000
Acquisition Time	1.3631
Spectrometer Frequency	100.62
Spectral Width	24038.5
Nucleus	13C



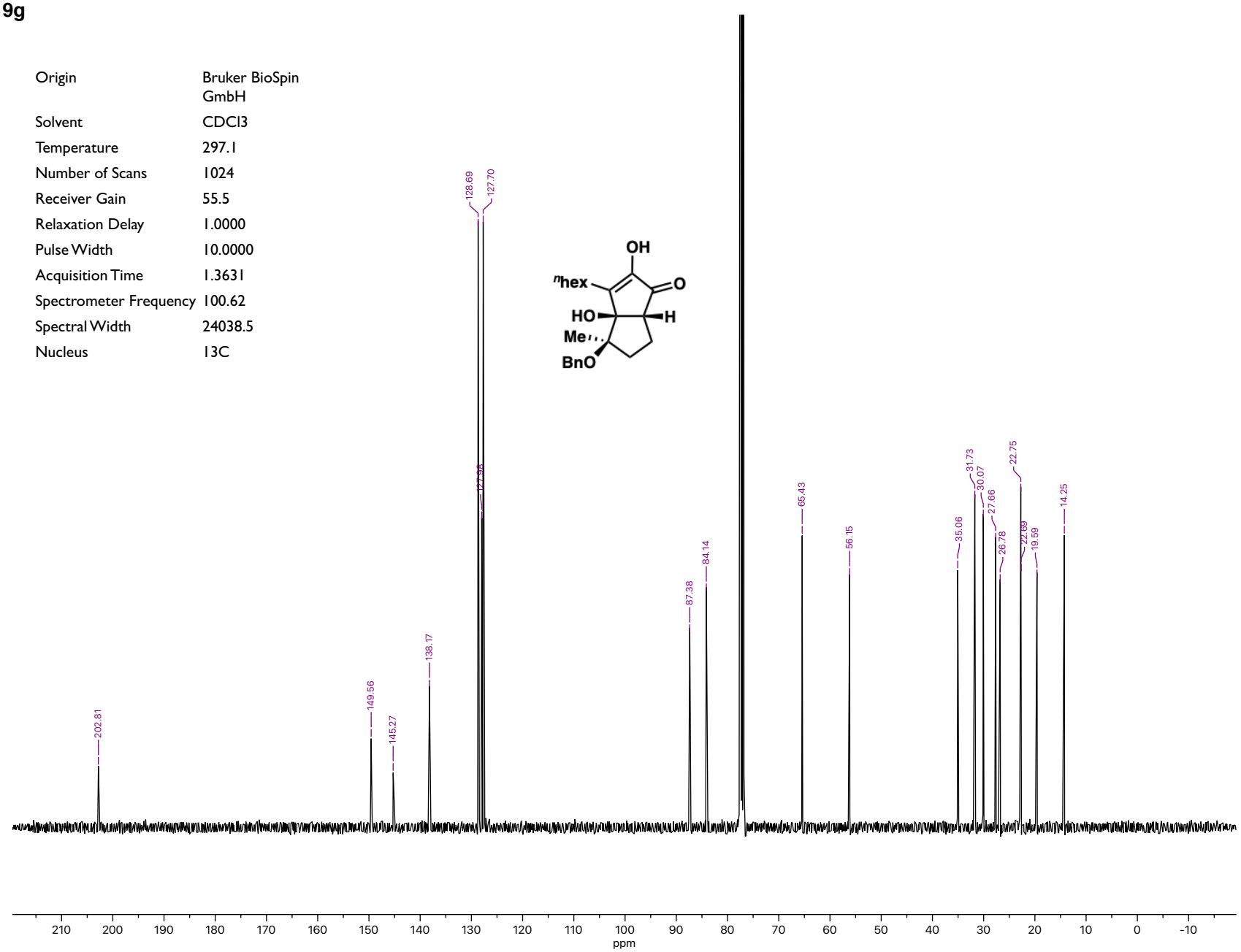
9g

Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	297.2
Number of Scans	16
Receiver Gain	127.1
Relaxation Delay	1.0000
Pulse Width	12.5000
Acquisition Time	4.0894
Spectrometer Frequency	400.13
Spectral Width	8012.8
Nucleus	1H



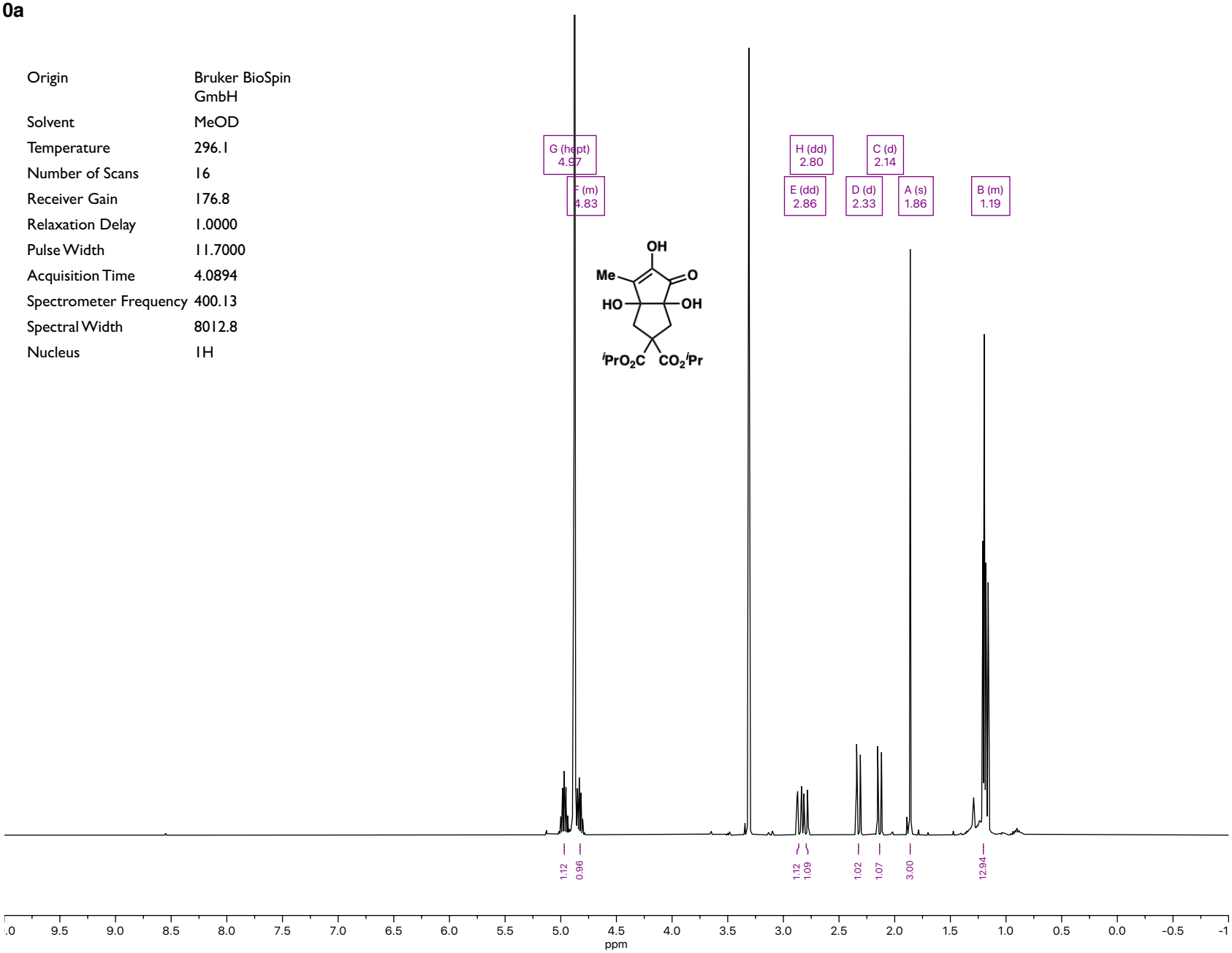
9g

Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	297.1
Number of Scans	1024
Receiver Gain	55.5
Relaxation Delay	1.0000
Pulse Width	10.0000
Acquisition Time	1.3631
Spectrometer Frequency	100.62
Spectral Width	24038.5
Nucleus	13C



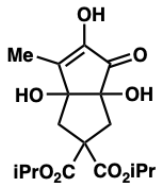
10a

Origin	Bruker BioSpin GmbH
Solvent	MeOD
Temperature	296.1
Number of Scans	16
Receiver Gain	176.8
Relaxation Delay	1.0000
Pulse Width	11.7000
Acquisition Time	4.0894
Spectrometer Frequency	400.13
Spectral Width	8012.8
Nucleus	1H



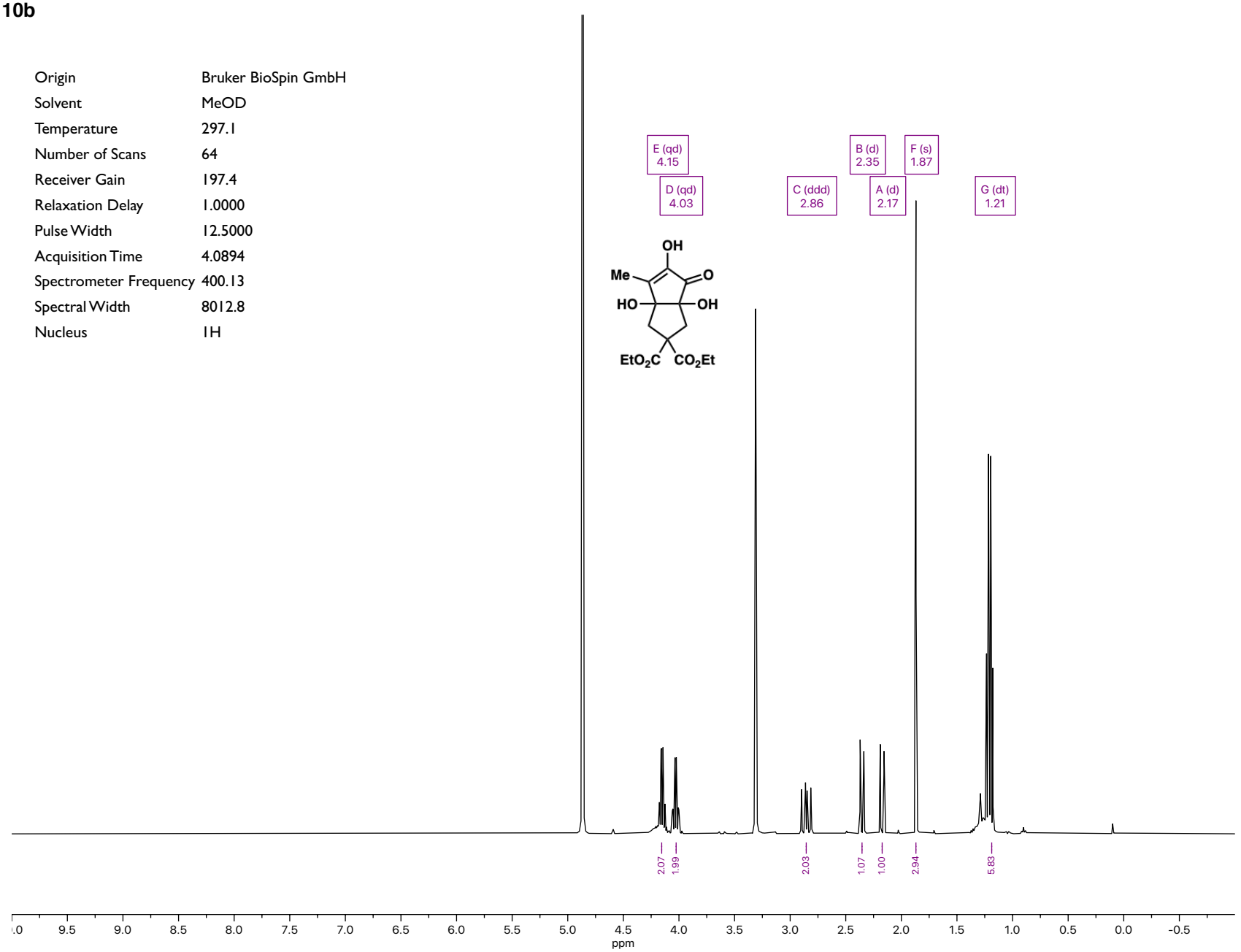
10a

Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	296.2
Number of Scans	512
Receiver Gain	78.7
Relaxation Delay	1.0000
Pulse Width	10.0000
Acquisition Time	1.3631
Spectrometer Frequency	100.62
Spectral Width	24038.5
Nucleus	13C



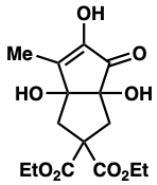
10b

Origin	Bruker BioSpin GmbH
Solvent	MeOD
Temperature	297.1
Number of Scans	64
Receiver Gain	197.4
Relaxation Delay	1.0000
Pulse Width	12.5000
Acquisition Time	4.0894
Spectrometer Frequency	400.13
Spectral Width	8012.8
Nucleus	1H



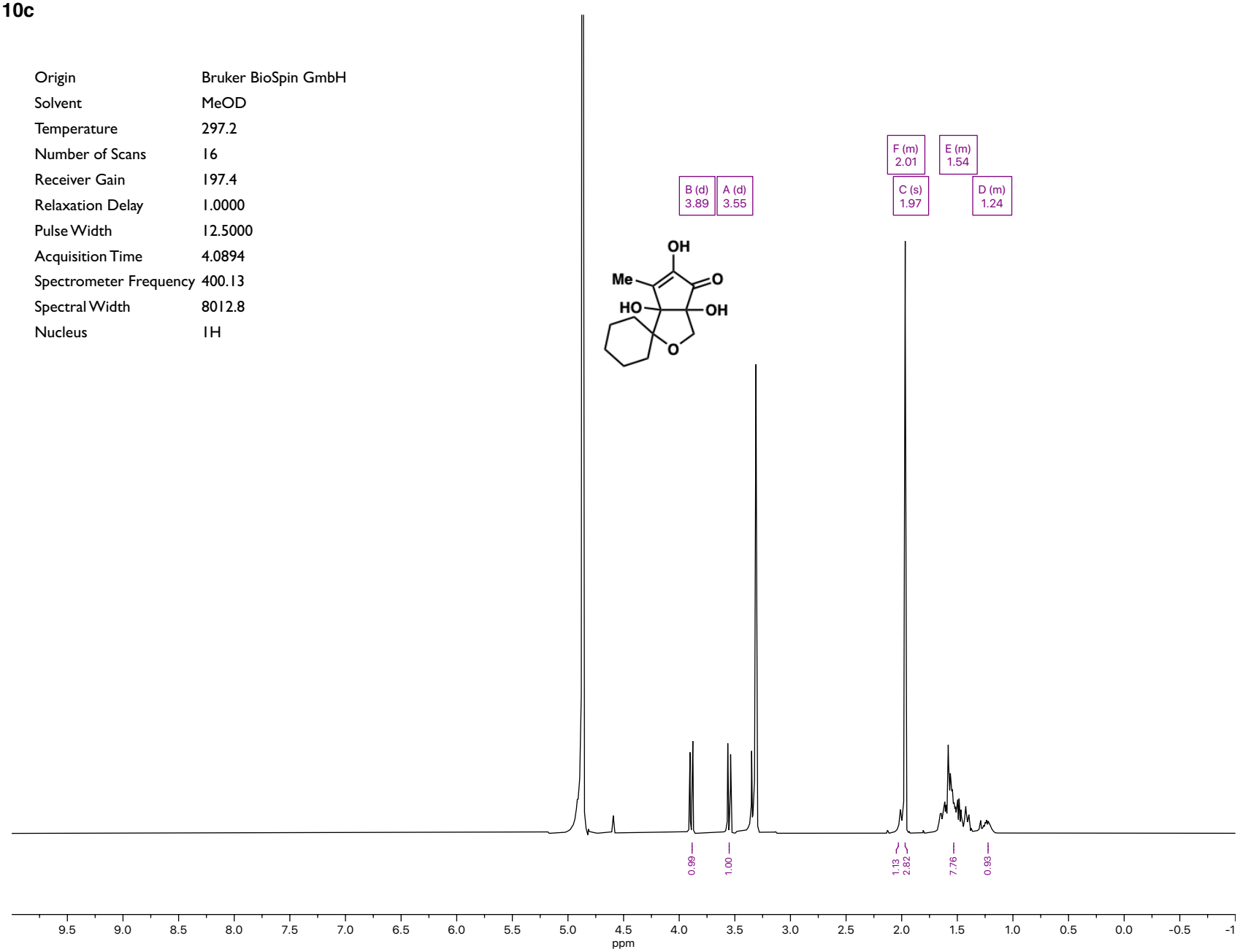
10b

Origin	Bruker BioSpin GmbH
Solvent	MeOD
Temperature	297.2
Number of Scans	1024
Receiver Gain	55.5
Relaxation Delay	1.0000
Pulse Width	10.0000
Acquisition Time	1.3631
Spectrometer Frequency	100.62
Spectral Width	24038.5
Nucleus	13C



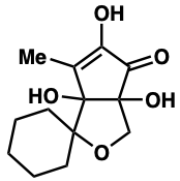
10c

Origin	Bruker BioSpin GmbH
Solvent	MeOD
Temperature	297.2
Number of Scans	16
Receiver Gain	197.4
Relaxation Delay	1.0000
Pulse Width	12.5000
Acquisition Time	4.0894
Spectrometer Frequency	400.13
Spectral Width	8012.8
Nucleus	1H



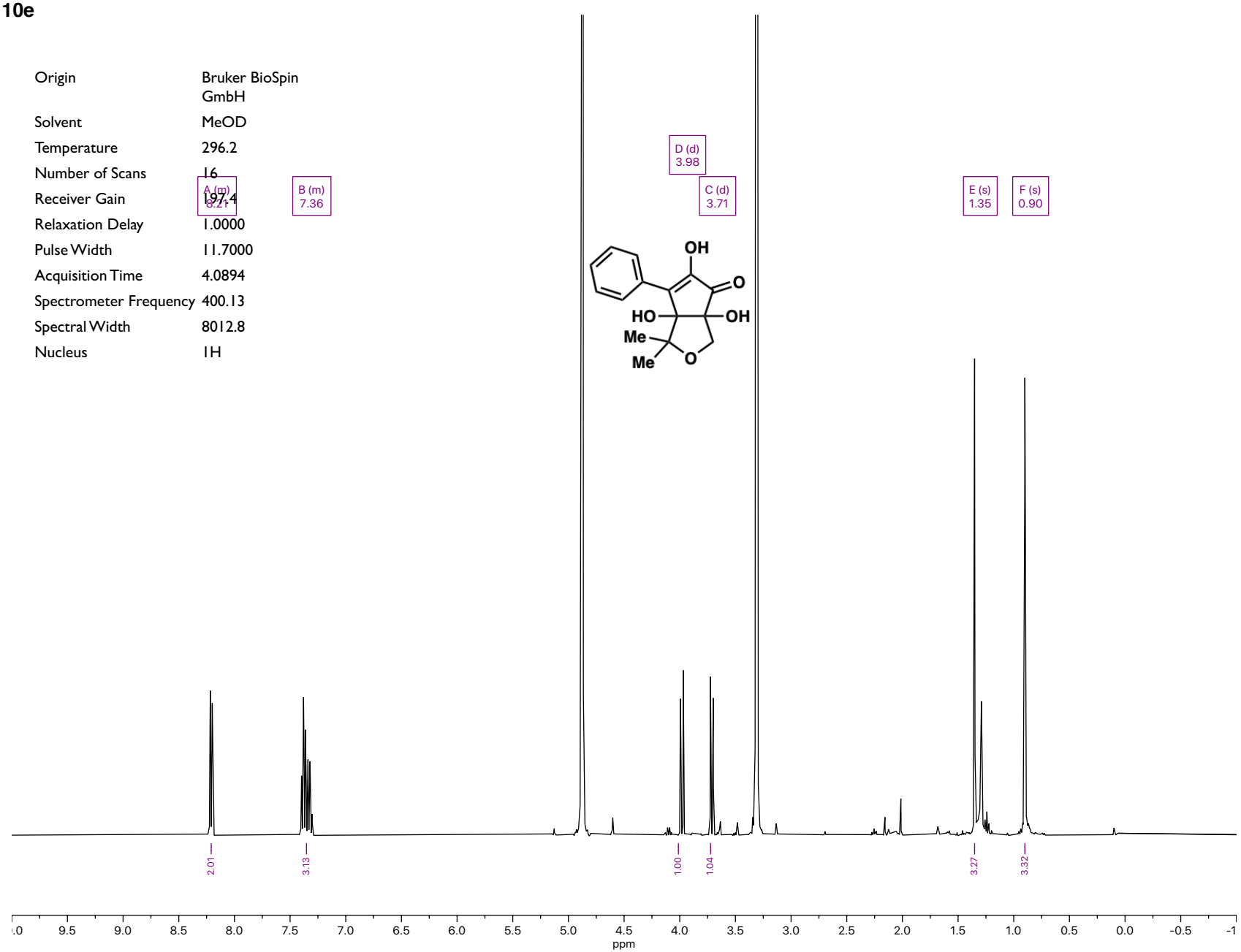
10c

Origin	Bruker BioSpin GmbH
Solvent	MeOD
Temperature	297.1
Number of Scans	1024
Receiver Gain	50.3
Relaxation Delay	1.0000
Pulse Width	10.0000
Acquisition Time	1.3631
Spectrometer Frequency	100.62
Spectral Width	24038.5
Nucleus	13C



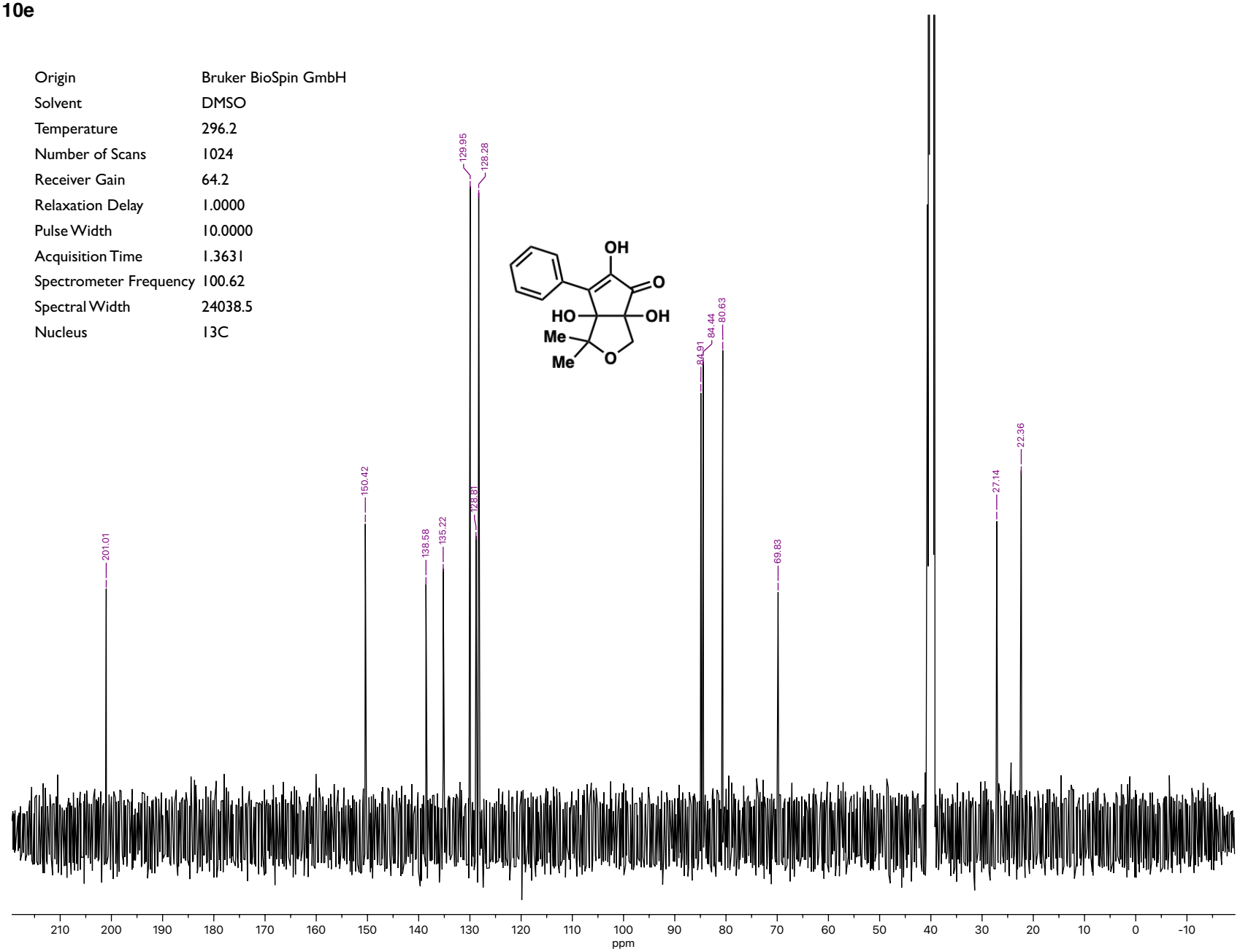
10e

Origin	Bruker BioSpin GmbH
Solvent	MeOD
Temperature	296.2
Number of Scans	16
Receiver Gain	197.4
Relaxation Delay	1.0000
Pulse Width	11.7000
Acquisition Time	4.0894
Spectrometer Frequency	400.13
Spectral Width	8012.8
Nucleus	1H



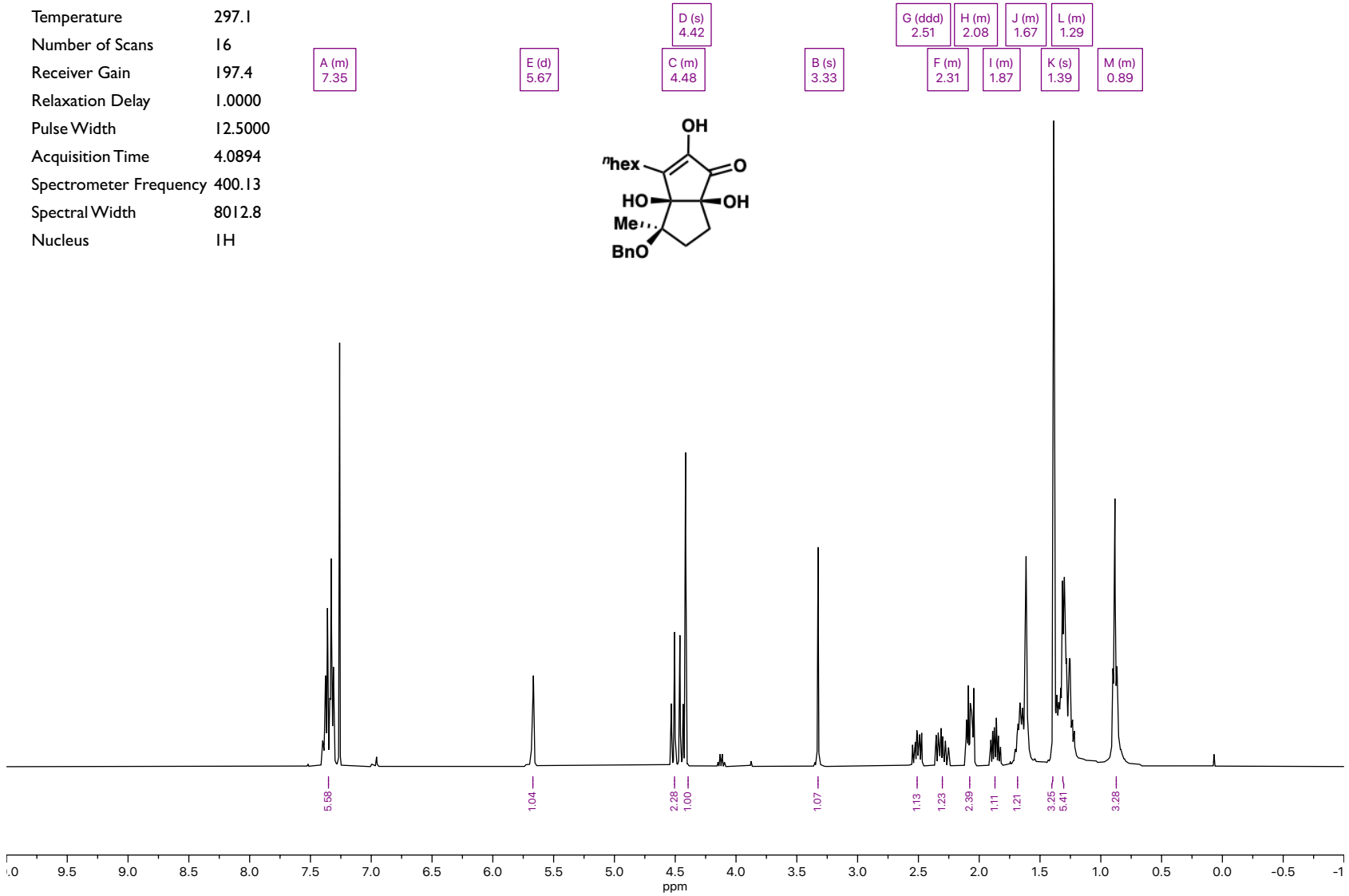
10e

Origin	Bruker BioSpin GmbH
Solvent	DMSO
Temperature	296.2
Number of Scans	1024
Receiver Gain	64.2
Relaxation Delay	1.0000
Pulse Width	10.0000
Acquisition Time	1.3631
Spectrometer Frequency	100.62
Spectral Width	24038.5
Nucleus	13C



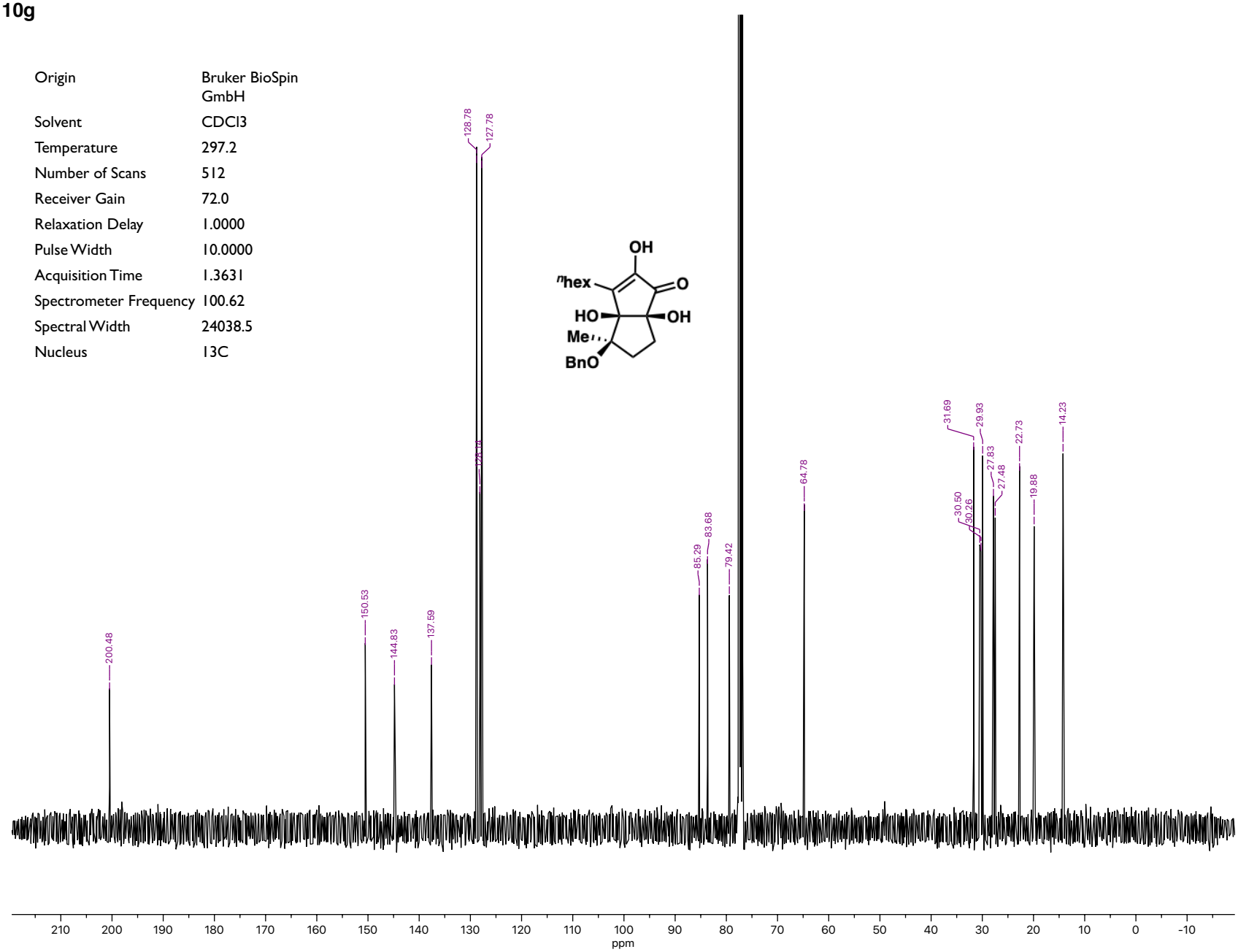
10g

Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	297.1
Number of Scans	16
Receiver Gain	197.4
Relaxation Delay	1.0000
Pulse Width	12.5000
Acquisition Time	4.0894
Spectrometer Frequency	400.13
Spectral Width	8012.8
Nucleus	1H



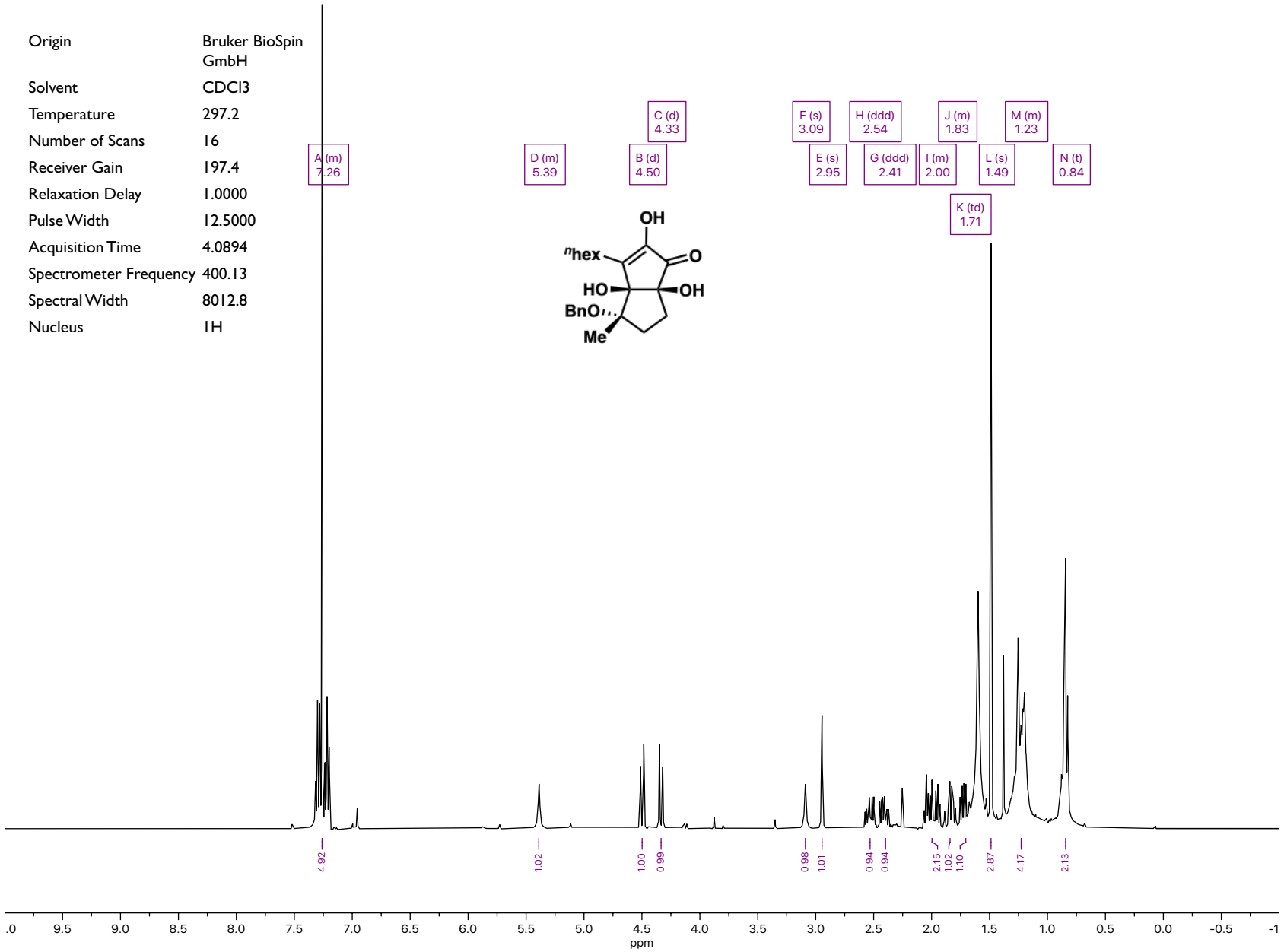
10g

Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	297.2
Number of Scans	512
Receiver Gain	72.0
Relaxation Delay	1.0000
Pulse Width	10.0000
Acquisition Time	1.3631
Spectrometer Frequency	100.62
Spectral Width	24038.5
Nucleus	13C



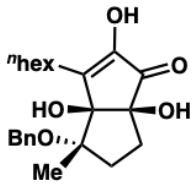
10h

Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	297.2
Number of Scans	16
Receiver Gain	197.4
Relaxation Delay	1.0000
Pulse Width	12.5000
Acquisition Time	4.0894
Spectrometer Frequency	400.13
Spectral Width	8012.8
Nucleus	1H



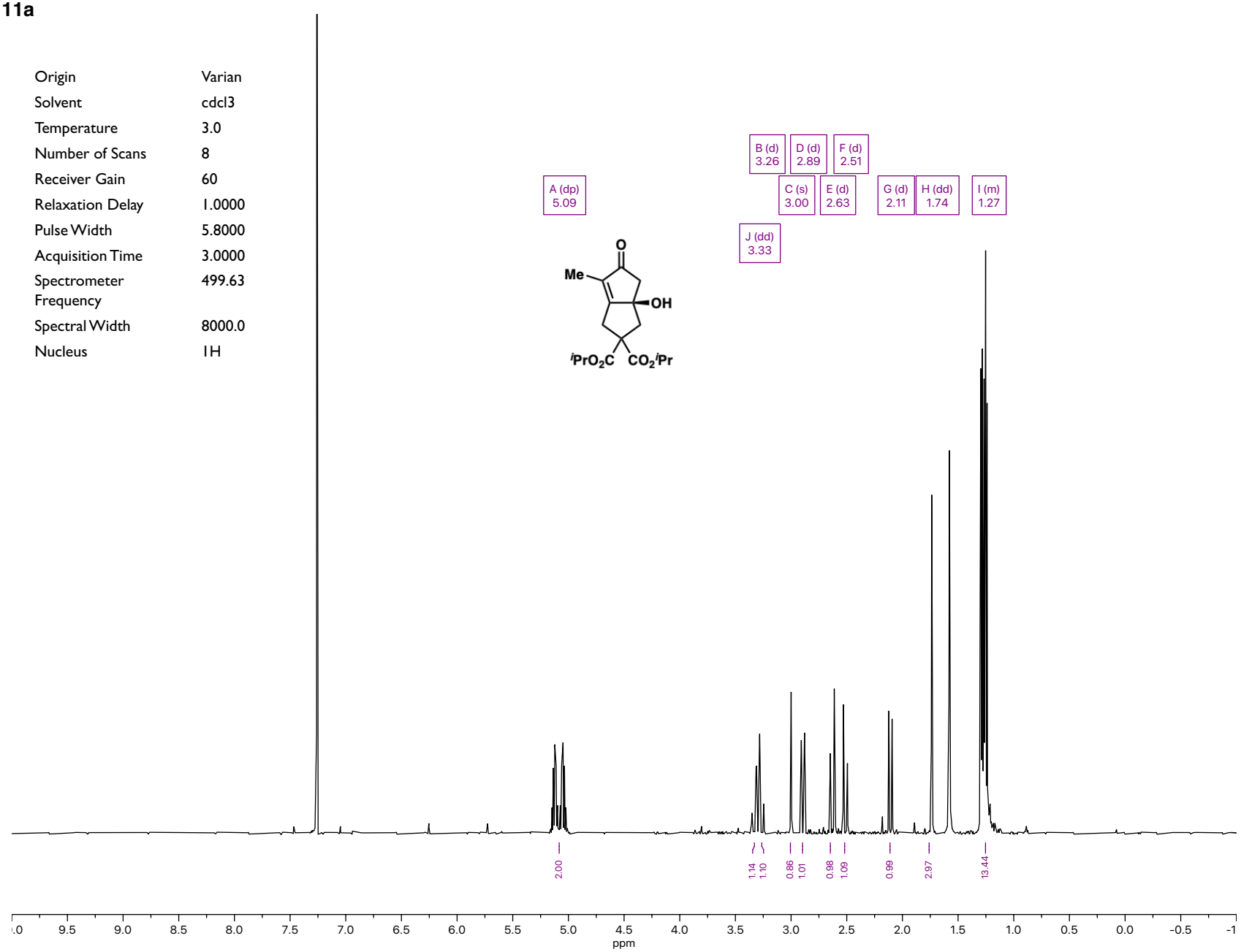
10h

Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	297.1
Number of Scans	512
Receiver Gain	50.3
Relaxation Delay	1.0000
Pulse Width	10.0000
Acquisition Time	1.3631
Spectrometer Frequency	100.62
Spectral Width	24038.5
Nucleus	13C



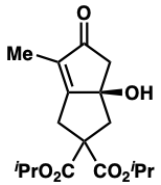
11a

Origin	Varian
Solvent	cdcl3
Temperature	3.0
Number of Scans	8
Receiver Gain	60
Relaxation Delay	1.0000
Pulse Width	5.8000
Acquisition Time	3.0000
Spectrometer Frequency	499.63
Spectral Width	8000.0
Nucleus	1H



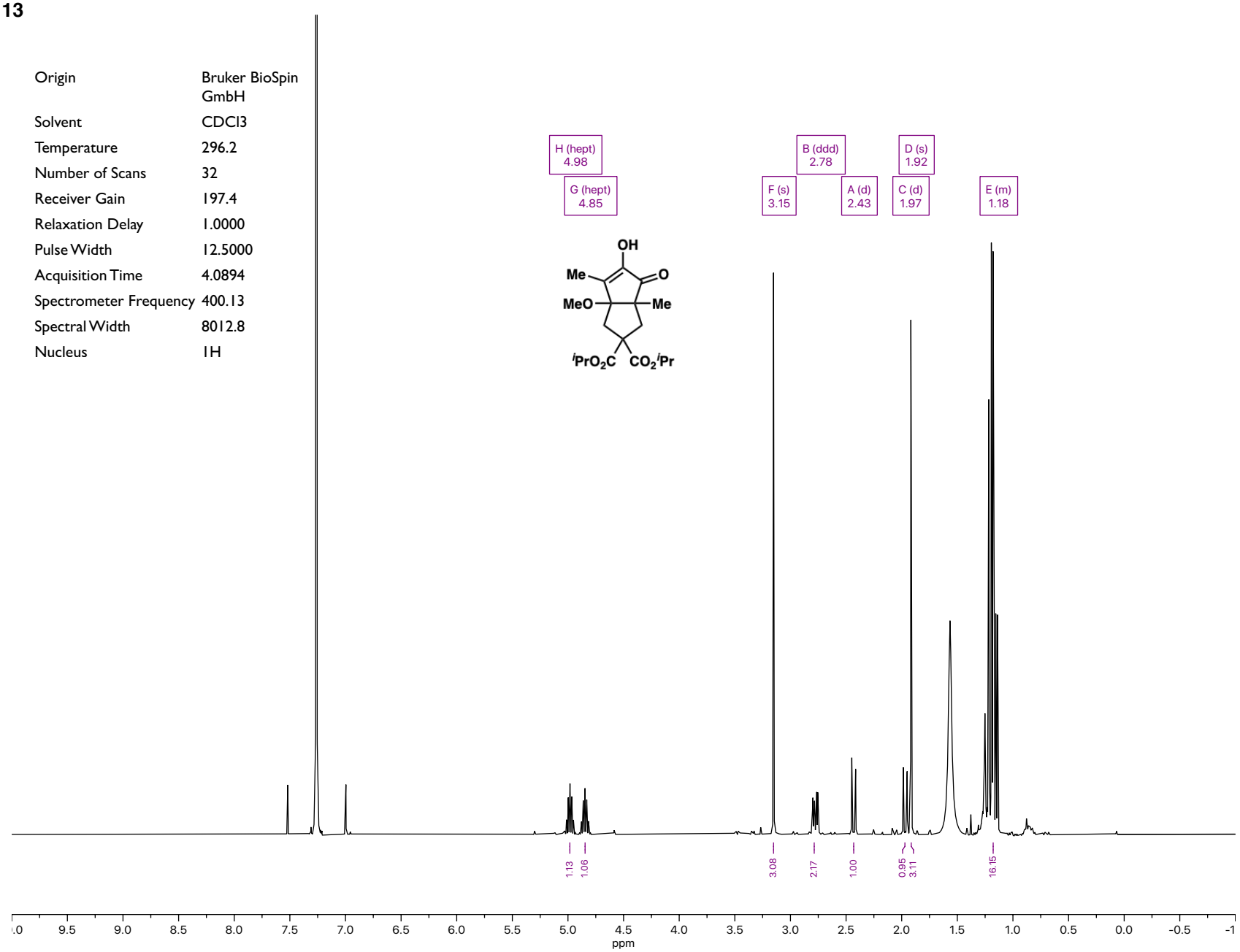
11a

Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	298.2
Number of Scans	512
Receiver Gain	64.2
Relaxation Delay	1.0000
Pulse Width	10.0000
Acquisition Time	1.3631
Spectrometer Frequency	100.62
Spectral Width	24038.5
Nucleus	13C



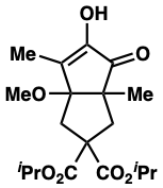
13

Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	296.2
Number of Scans	32
Receiver Gain	197.4
Relaxation Delay	1.0000
Pulse Width	12.5000
Acquisition Time	4.0894
Spectrometer Frequency	400.13
Spectral Width	8012.8
Nucleus	1H



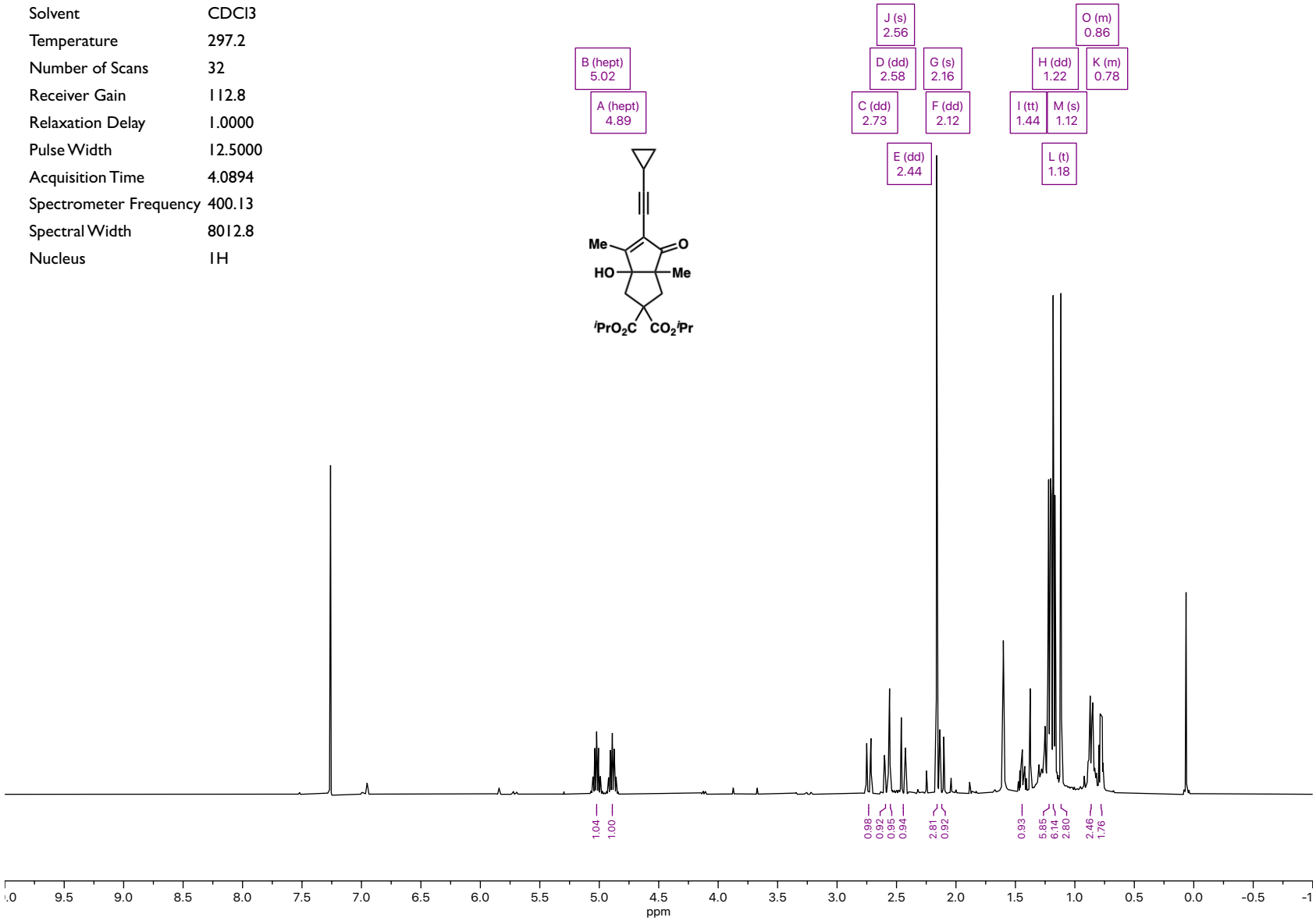
13

Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	296.2
Number of Scans	4096
Receiver Gain	78.7
Relaxation Delay	1.0000
Pulse Width	10.0000
Acquisition Time	1.3631
Spectrometer Frequency	100.62
Spectral Width	24038.5
Nucleus	13C



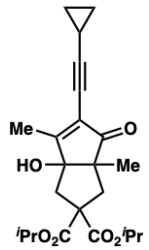
14a

Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	297.2
Number of Scans	32
Receiver Gain	112.8
Relaxation Delay	1.0000
Pulse Width	12.5000
Acquisition Time	4.0894
Spectrometer Frequency	400.13
Spectral Width	8012.8
Nucleus	1H



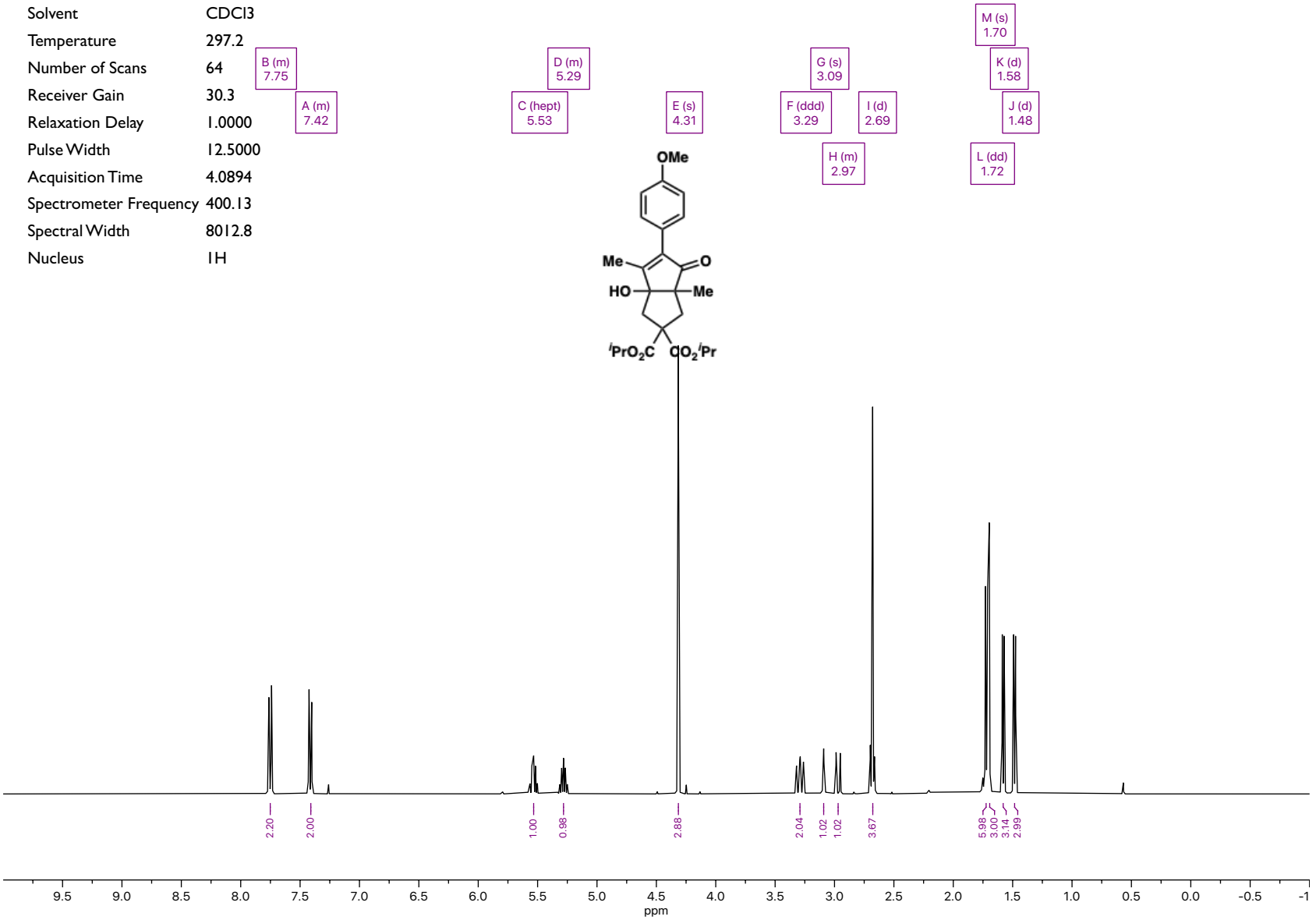
14a

Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	297.2
Number of Scans	1024
Receiver Gain	87.8
Relaxation Delay	1.0000
Pulse Width	10.0000
Acquisition Time	1.3631
Spectrometer Frequency	100.62
Spectral Width	24038.5
Nucleus	13C



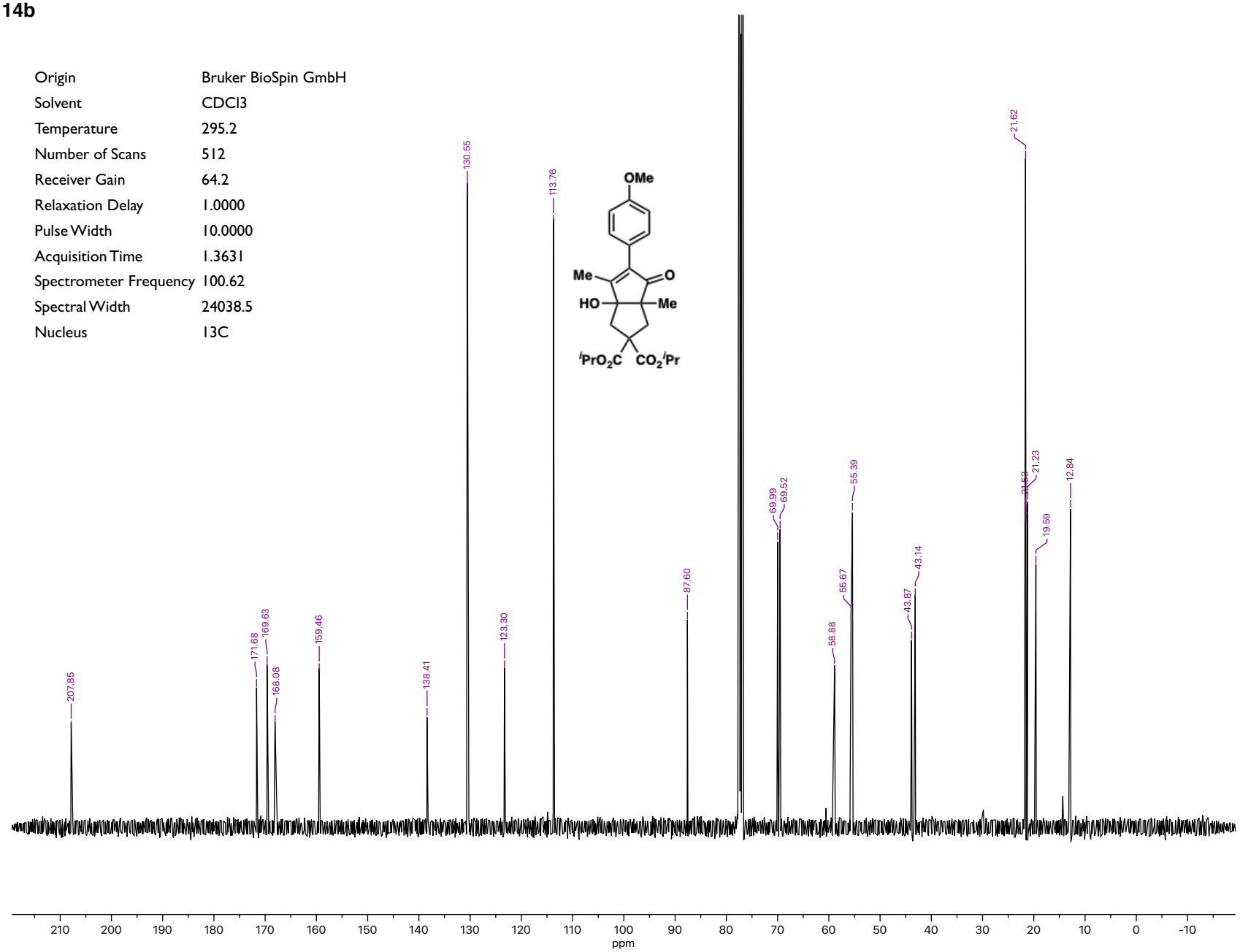
14b

Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	297.2
Number of Scans	64
Receiver Gain	30.3
Relaxation Delay	1.0000
Pulse Width	12.5000
Acquisition Time	4.0894
Spectrometer Frequency	400.13
Spectral Width	8012.8
Nucleus	1H



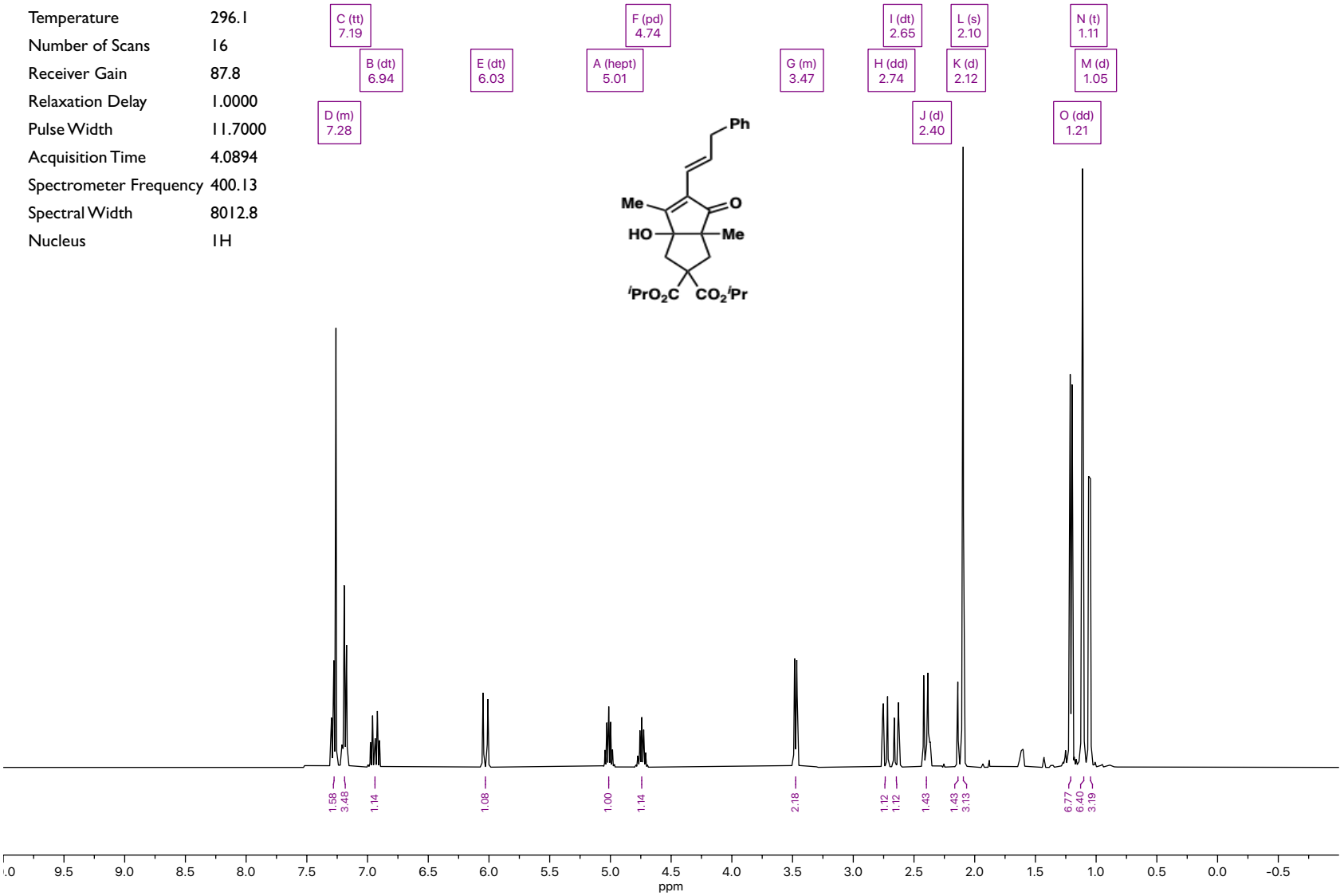
14b

Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	295.2
Number of Scans	512
Receiver Gain	64.2
Relaxation Delay	1.0000
Pulse Width	10.0000
Acquisition Time	1.3631
Spectrometer Frequency	100.62
Spectral Width	24038.5
Nucleus	13C



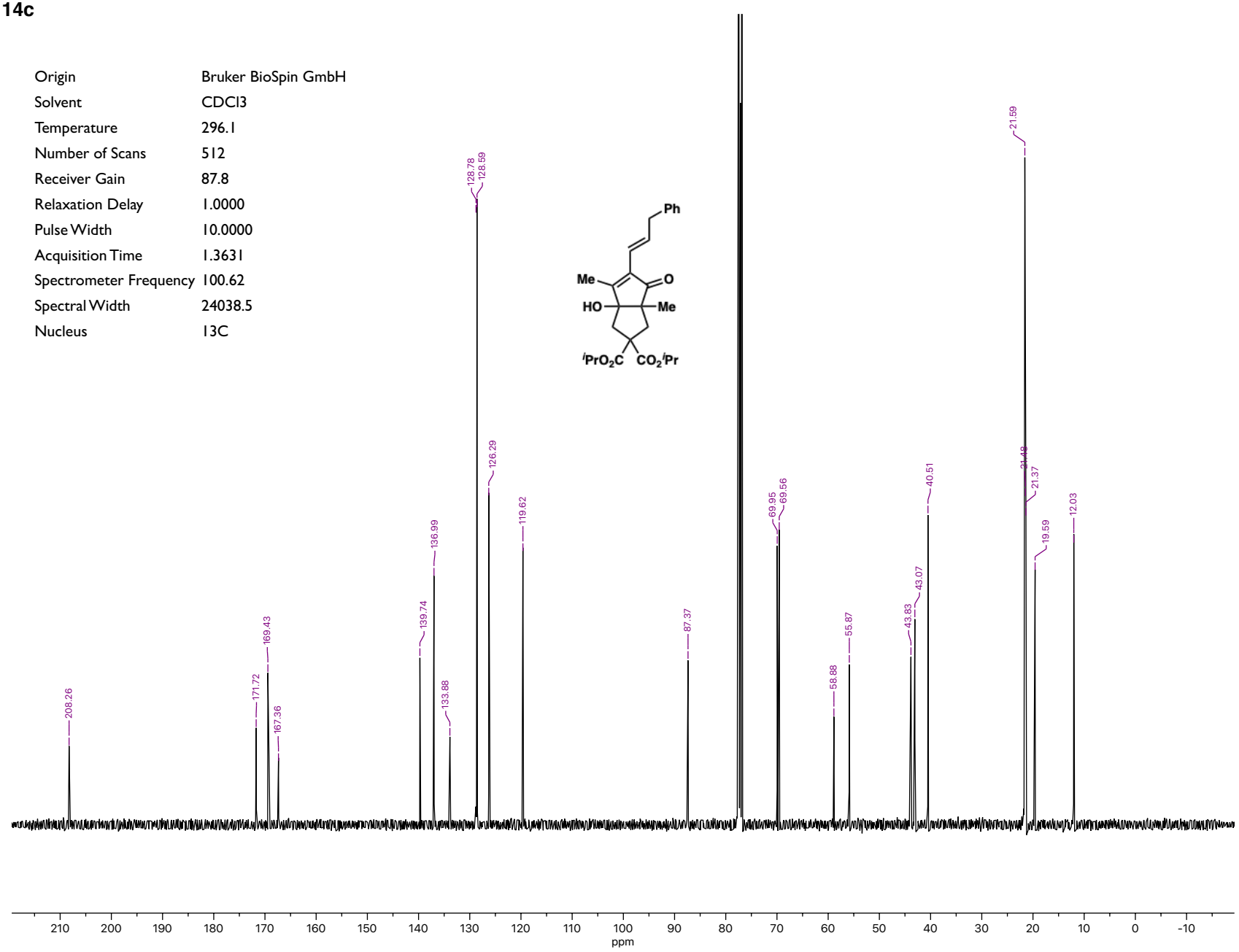
14c

Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	296.1
Number of Scans	16
Receiver Gain	87.8
Relaxation Delay	1.0000
Pulse Width	11.7000
Acquisition Time	4.0894
Spectrometer Frequency	400.13
Spectral Width	8012.8
Nucleus	1H



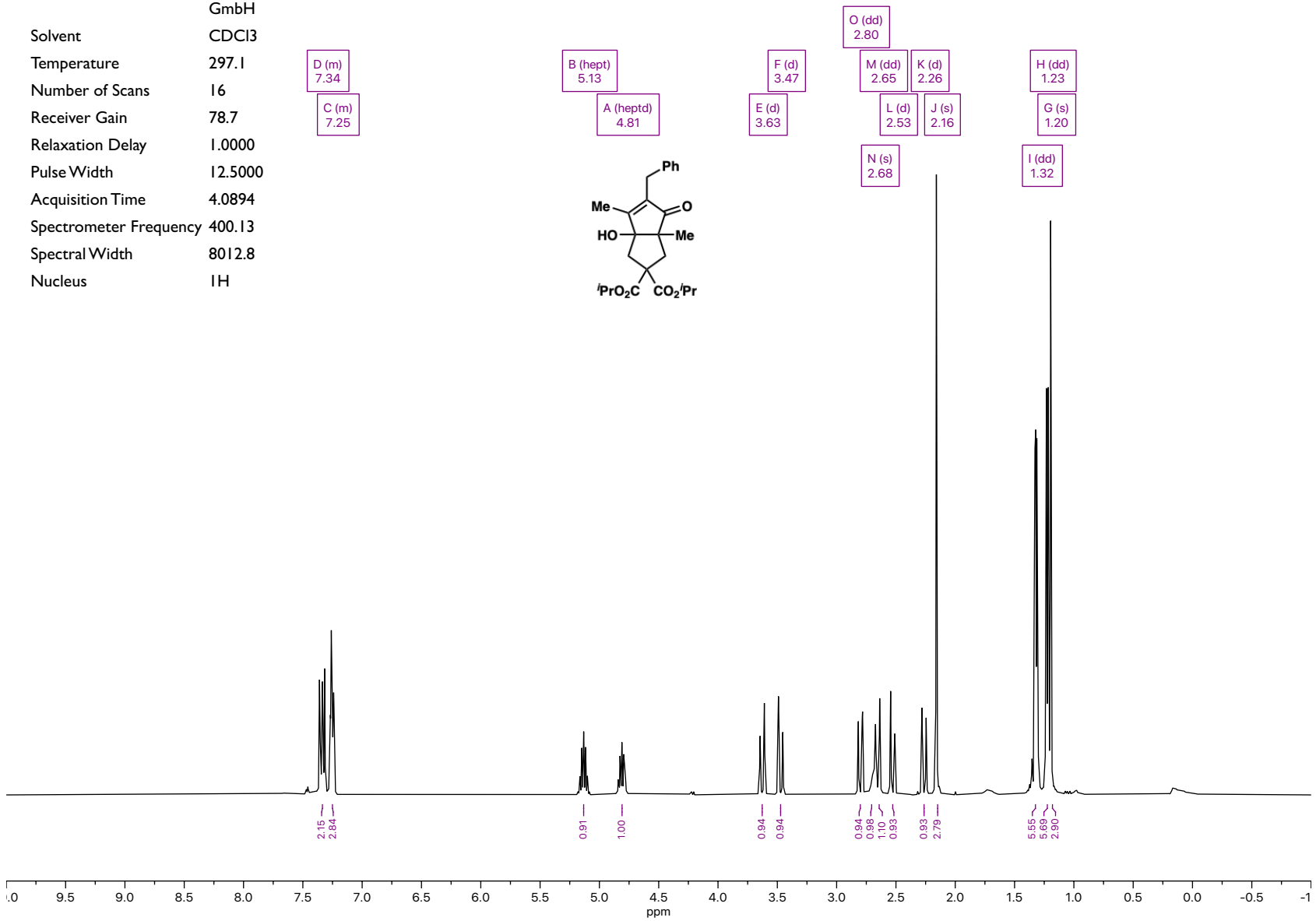
14c

Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	296.1
Number of Scans	512
Receiver Gain	87.8
Relaxation Delay	1.0000
Pulse Width	10.0000
Acquisition Time	1.3631
Spectrometer Frequency	100.62
Spectral Width	24038.5
Nucleus	13C



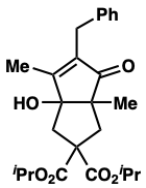
14d

Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	297.1
Number of Scans	16
Receiver Gain	78.7
Relaxation Delay	1.0000
Pulse Width	12.5000
Acquisition Time	4.0894
Spectrometer Frequency	400.13
Spectral Width	8012.8
Nucleus	1H



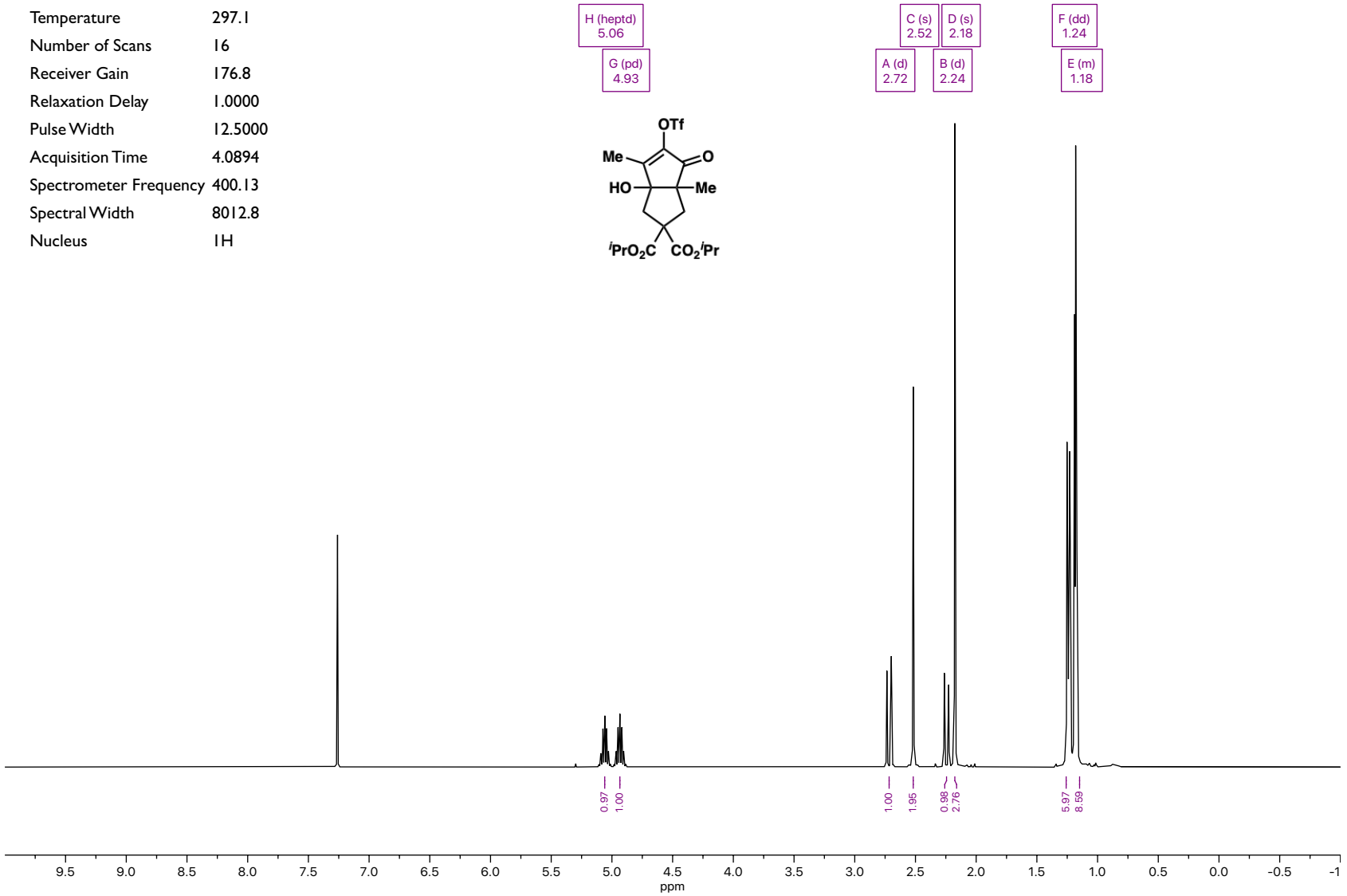
14d

Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	297.1
Number of Scans	512
Receiver Gain	55.5
Relaxation Delay	1.0000
Pulse Width	10.0000
Acquisition Time	1.3631
Spectrometer Frequency	100.62
Spectral Width	24038.5
Nucleus	13C



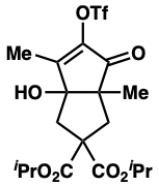
15a

Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	297.1
Number of Scans	16
Receiver Gain	176.8
Relaxation Delay	1.0000
Pulse Width	12.5000
Acquisition Time	4.0894
Spectrometer Frequency	400.13
Spectral Width	8012.8
Nucleus	1H



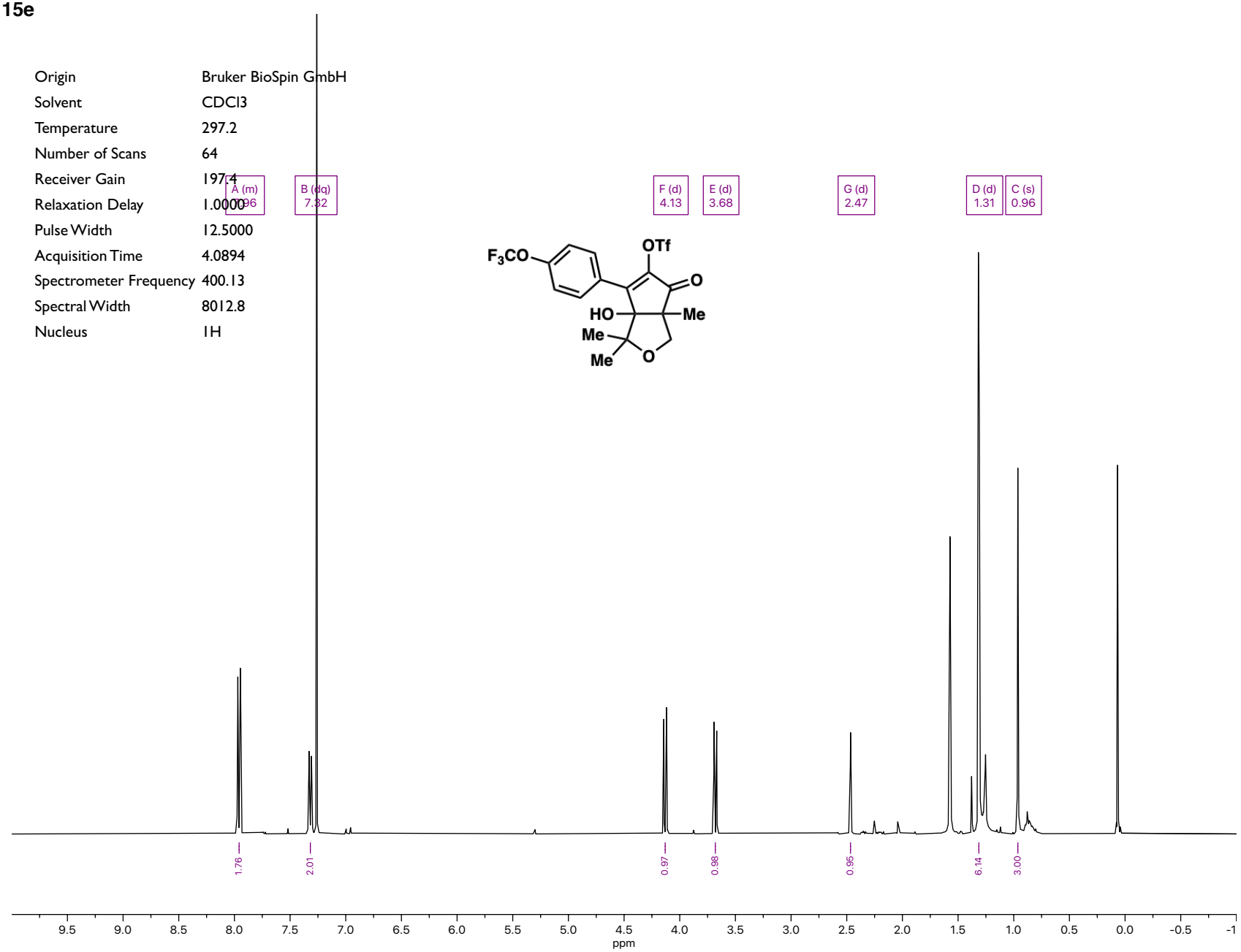
15a

Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	297.2
Number of Scans	512
Receiver Gain	43.7
Relaxation Delay	1.0000
Pulse Width	10.0000
Acquisition Time	1.3631
Spectrometer Frequency	100.62
Spectral Width	24038.5
Nucleus	13C



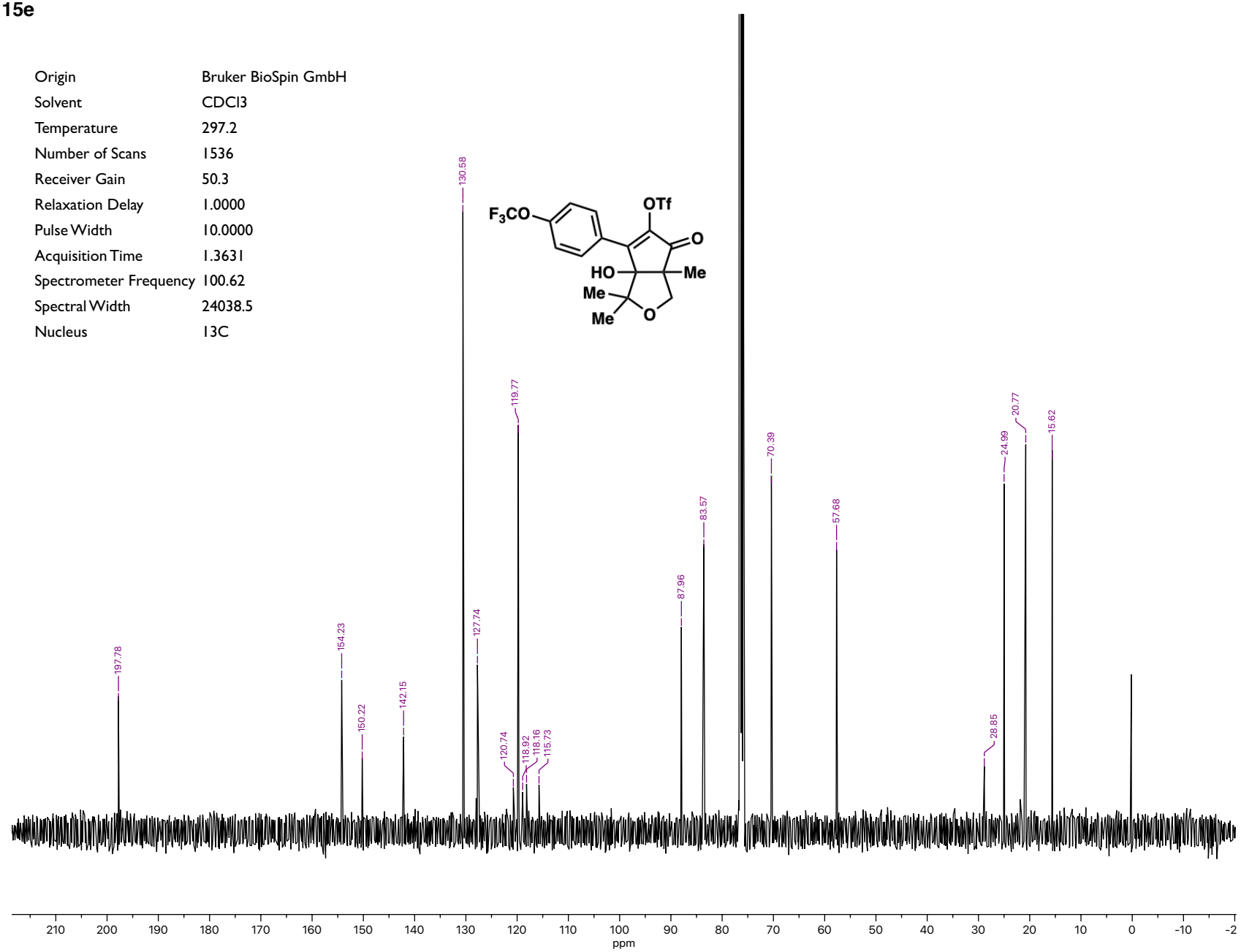
15e

Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	297.2
Number of Scans	64
Receiver Gain	197.4
Relaxation Delay	1.0000
Pulse Width	12.5000
Acquisition Time	4.0894
Spectrometer Frequency	400.13
Spectral Width	8012.8
Nucleus	1H



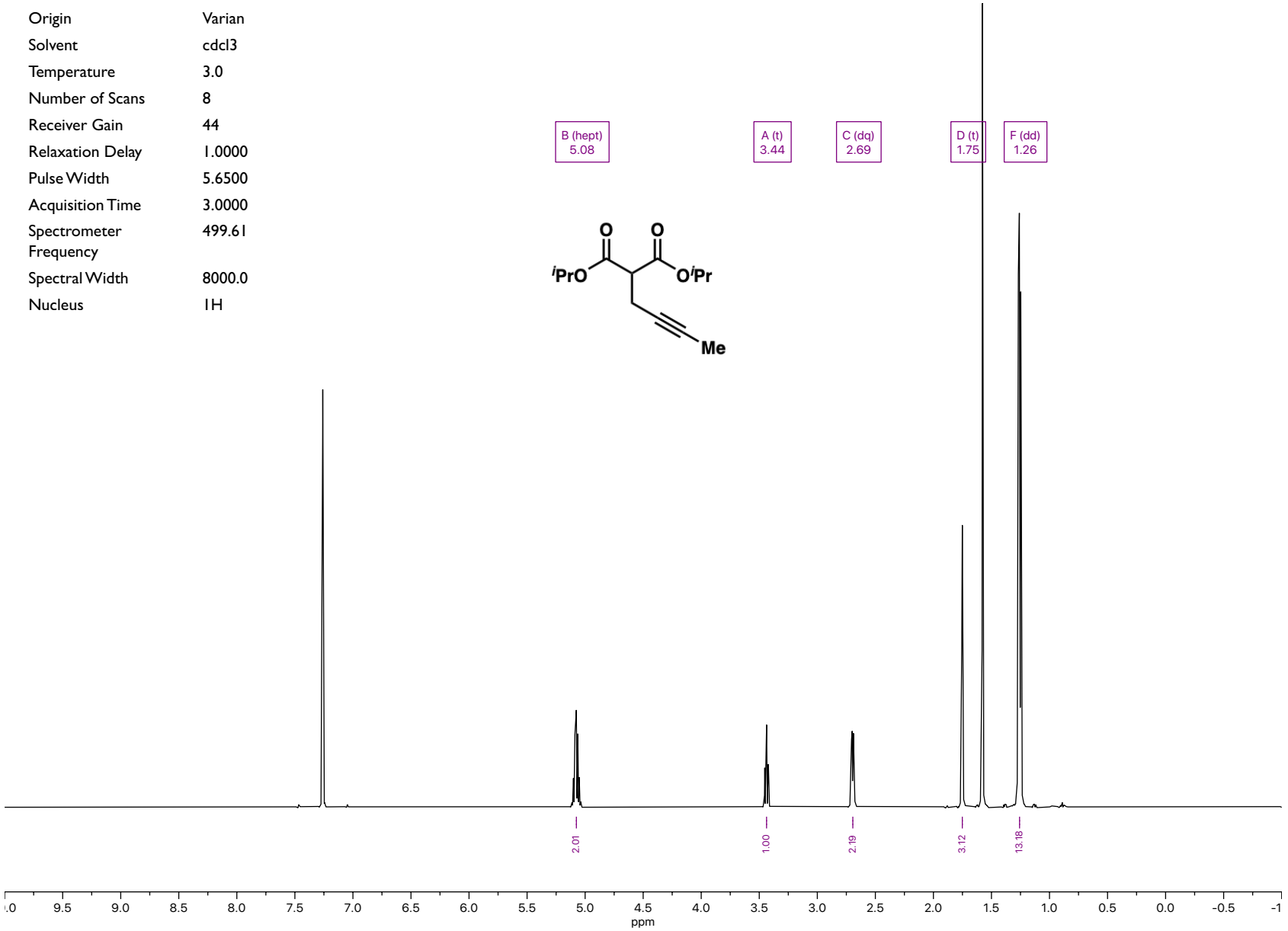
15e

Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	297.2
Number of Scans	1536
Receiver Gain	50.3
Relaxation Delay	1.0000
Pulse Width	10.0000
Acquisition Time	1.3631
Spectrometer Frequency	100.62
Spectral Width	24038.5
Nucleus	13C



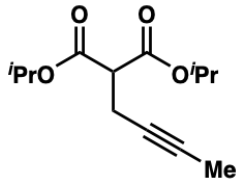
16

Origin	Varian
Solvent	cdcl3
Temperature	3.0
Number of Scans	8
Receiver Gain	44
Relaxation Delay	1.0000
Pulse Width	5.6500
Acquisition Time	3.0000
Spectrometer Frequency	499.61
Spectral Width	8000.0
Nucleus	1H



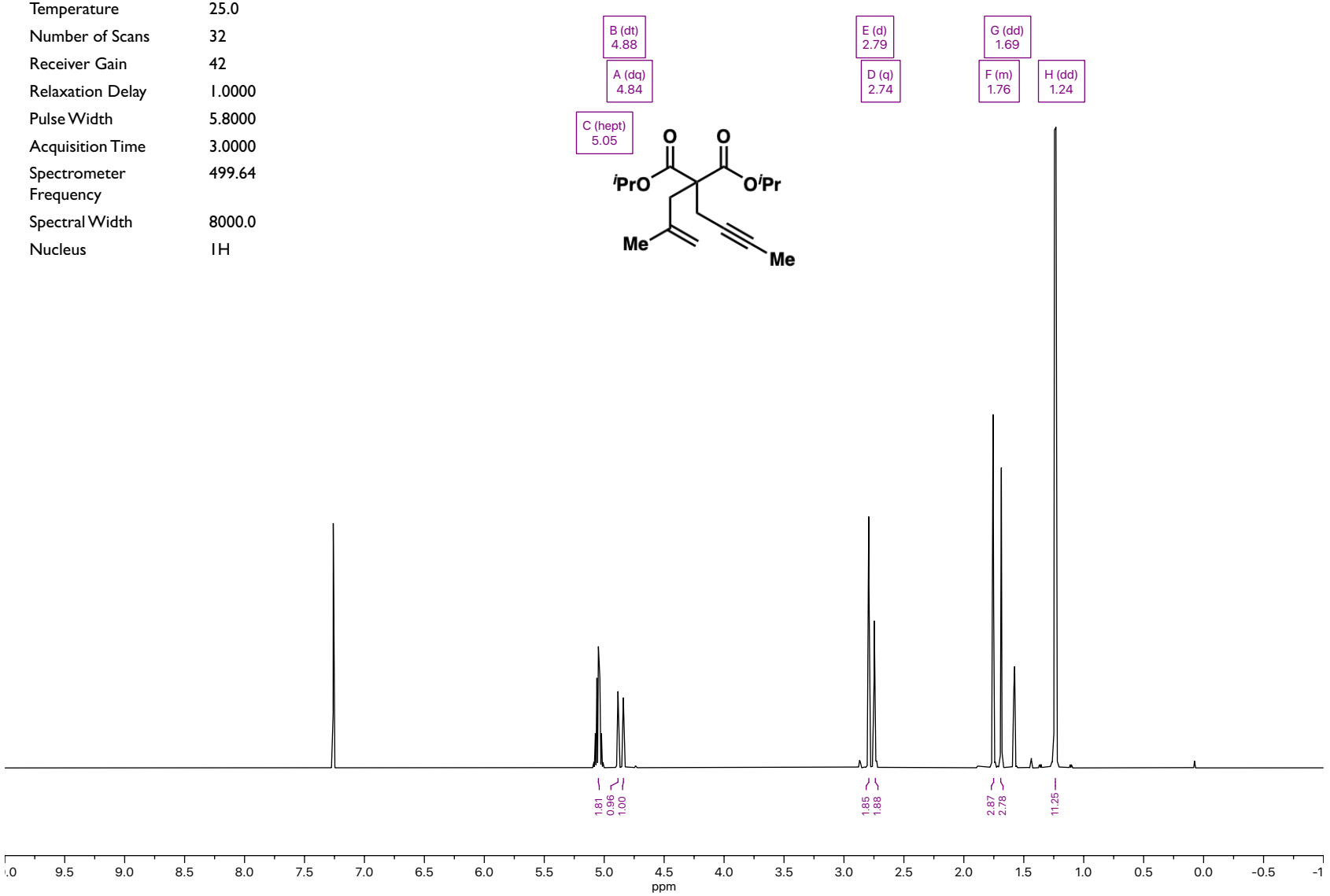
16

Origin	Varian
Solvent	cdcl3
Temperature	25.0
Number of Scans	64
Receiver Gain	30
Relaxation Delay	1.0000
Pulse Width	4.6125
Acquisition Time	1.0420
Spectrometer Frequency	125.65
Spectral Width	31446.5
Nucleus	13C



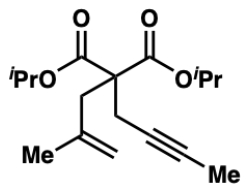
17

Origin	Varian
Solvent	cdcl3
Temperature	25.0
Number of Scans	32
Receiver Gain	42
Relaxation Delay	1.0000
Pulse Width	5.8000
Acquisition Time	3.0000
Spectrometer Frequency	499.64
Spectral Width	8000.0
Nucleus	1H

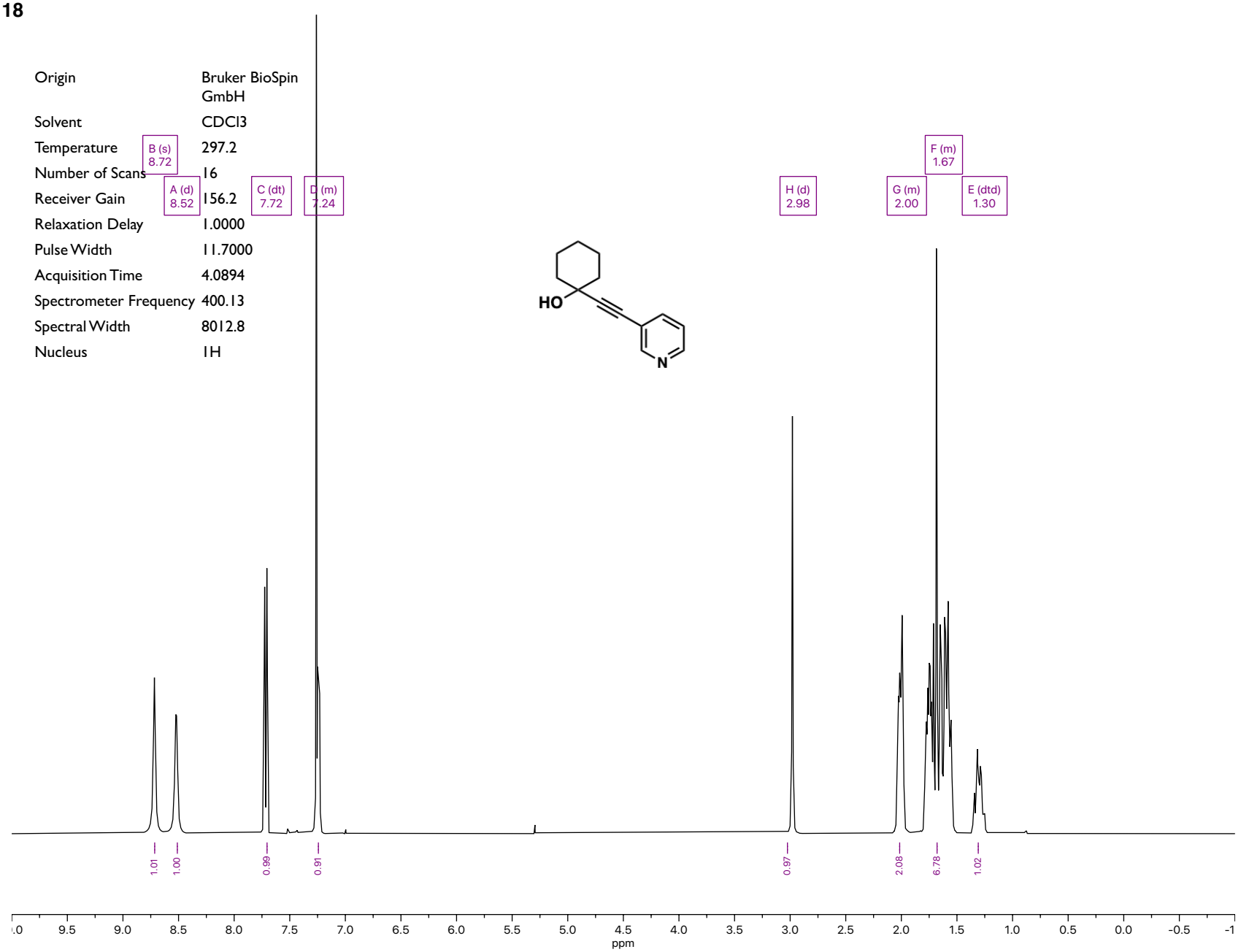


17

Origin	Varian
Solvent	cdcl3
Temperature	25.0
Number of Scans	256
Receiver Gain	30
Relaxation Delay	1.0000
Pulse Width	4.6125
Acquisition Time	1.0420
Spectrometer Frequency	125.65
Spectral Width	31446.5
Nucleus	13C

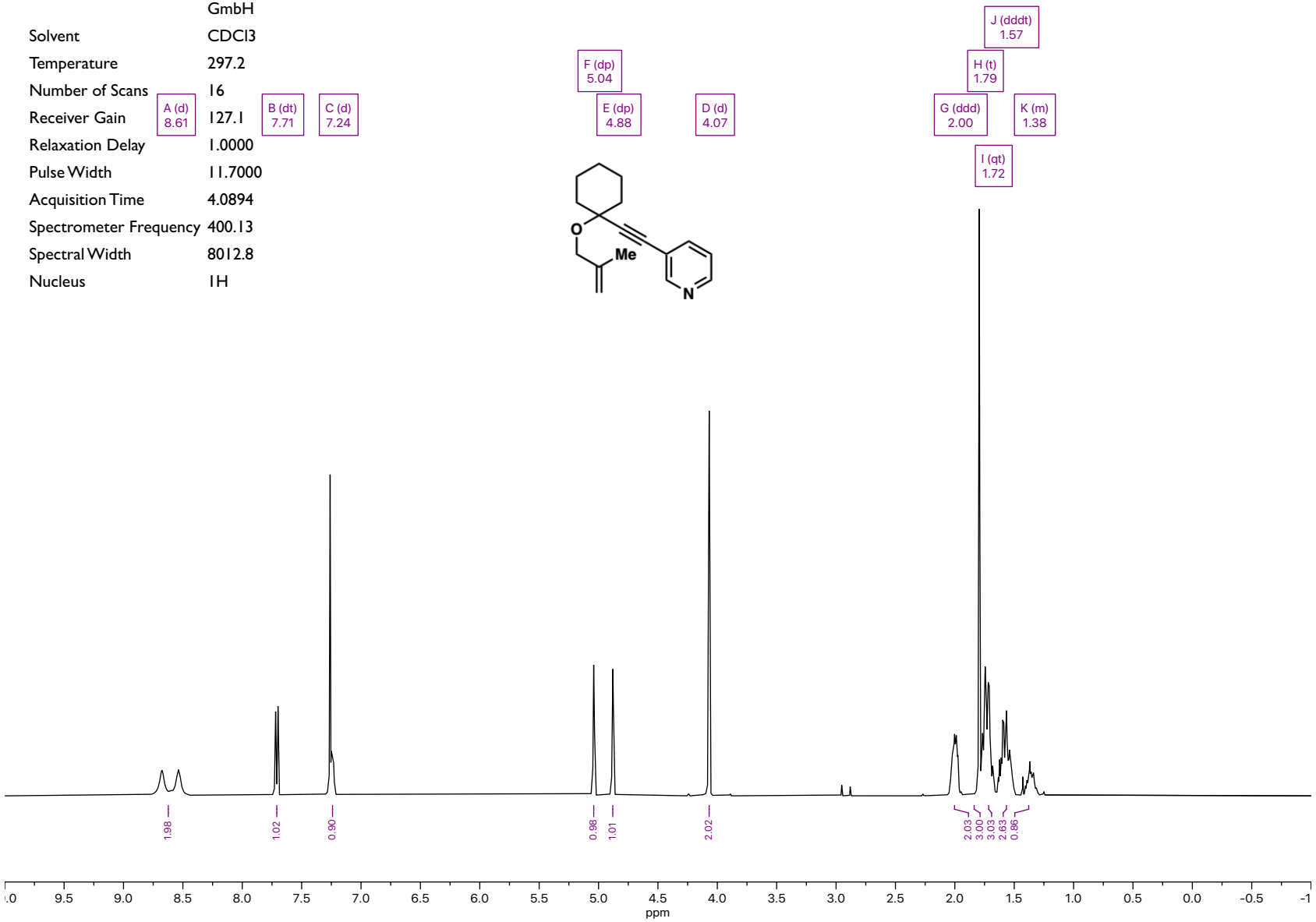


18


Origin Bruker BioSpin GmbH
Solvent CDCl3
Temperature 297.2
Number of Scans 16
Receiver Gain 156.2
Relaxation Delay 1.0000
Pulse Width 11.7000
Acquisition Time 4.0894
Spectrometer Frequency 400.13
Spectral Width 8012.8
Nucleus 1H
B (s) 8.72
A (d) 8.52
C (dt) 7.72
D (m) 7.24
H (d) 2.98
F (m) 1.67
G (m) 2.00
E (dtd) 1.30
HO
N
1.01
1.00
0.99
0.91
0.97
2.08
6.78
1.02
ppm

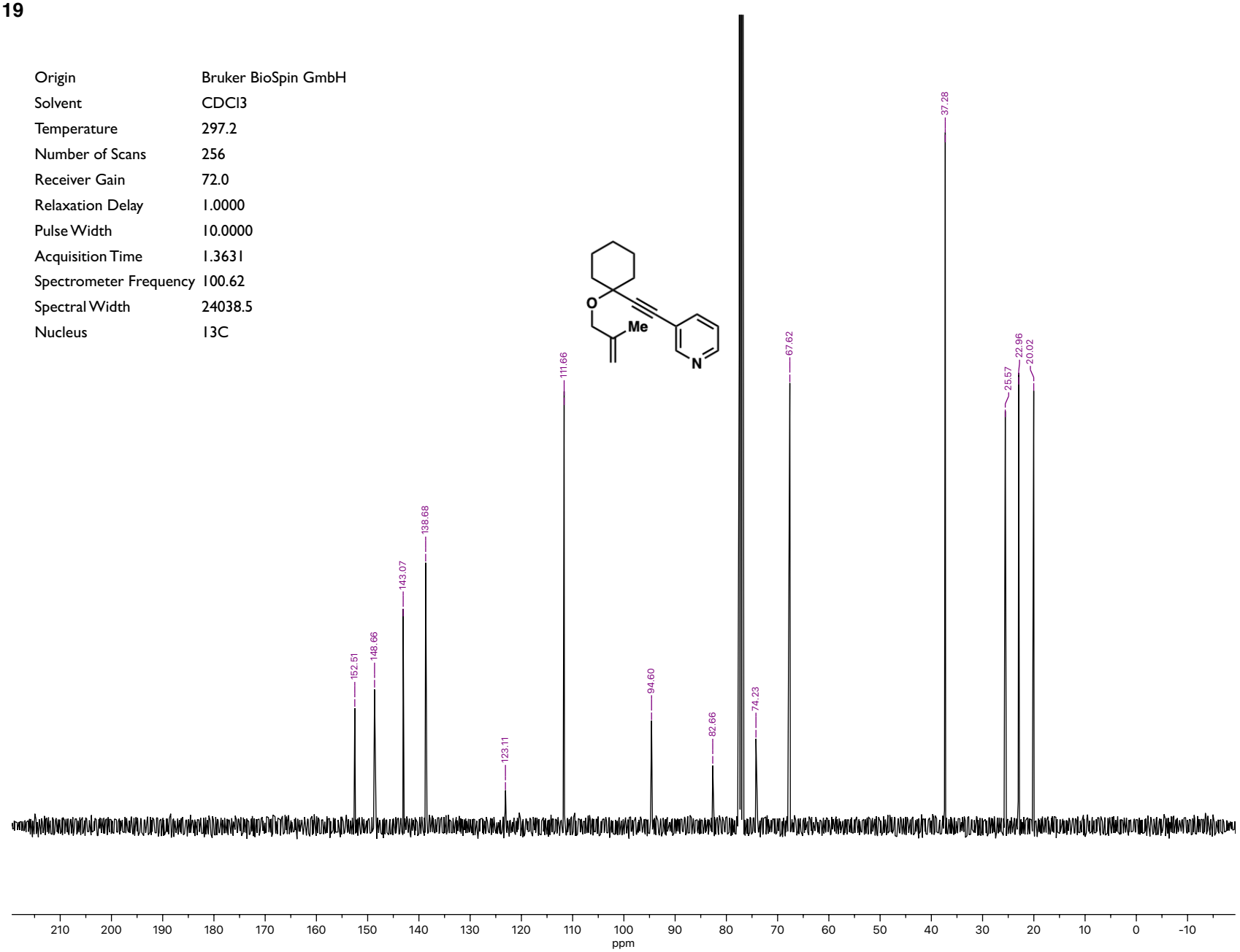
19

Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	297.2
Number of Scans	16
Receiver Gain	127.1
Relaxation Delay	1.0000
Pulse Width	11.7000
Acquisition Time	4.0894
Spectrometer Frequency	400.13
Spectral Width	8012.8
Nucleus	1H



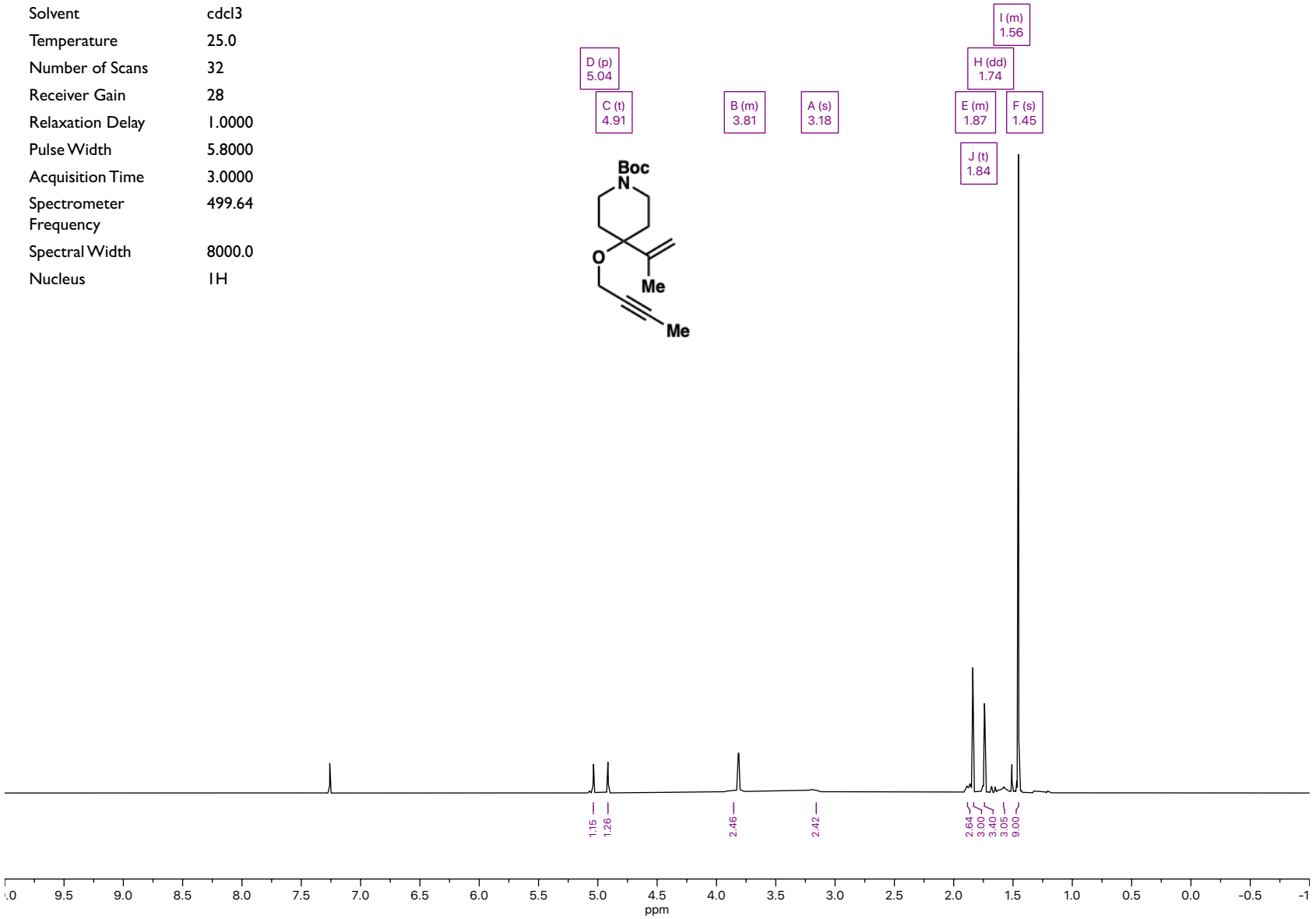
19

Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	297.2
Number of Scans	256
Receiver Gain	72.0
Relaxation Delay	1.0000
Pulse Width	10.0000
Acquisition Time	1.3631
Spectrometer Frequency	100.62
Spectral Width	24038.5
Nucleus	13C



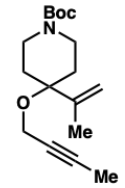
20

Origin	Varian
Solvent	cdcl3
Temperature	25.0
Number of Scans	32
Receiver Gain	28
Relaxation Delay	1.0000
Pulse Width	5.8000
Acquisition Time	3.0000
Spectrometer Frequency	499.64
Spectral Width	8000.0
Nucleus	1H



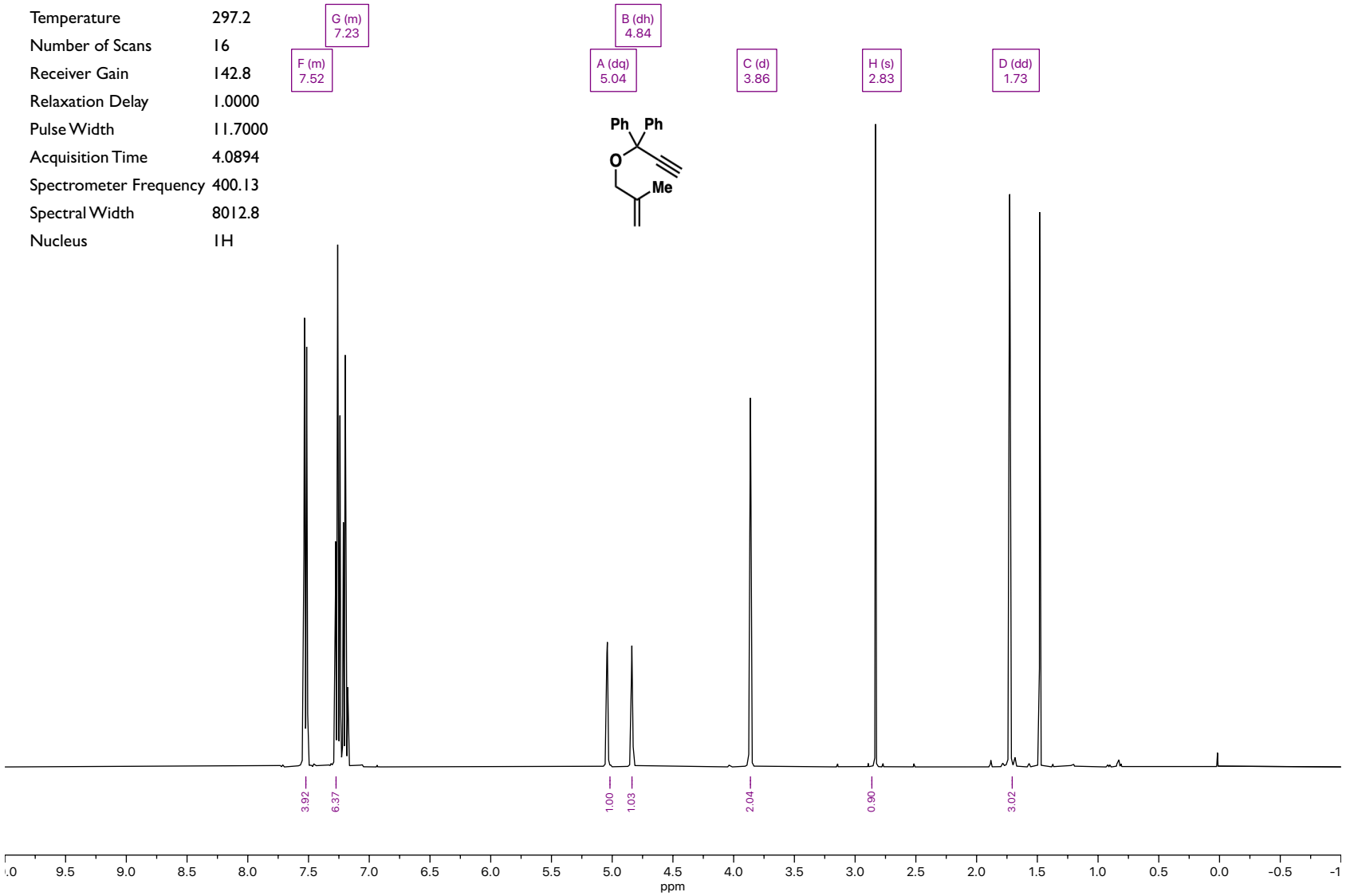
20

Origin	Varian
Solvent	cdcl3
Temperature	25.0
Number of Scans	128
Receiver Gain	30
Relaxation Delay	1.0000
Pulse Width	4.6125
Acquisition Time	1.0420
Spectrometer Frequency	125.65
Spectral Width	31446.5
Nucleus	13C



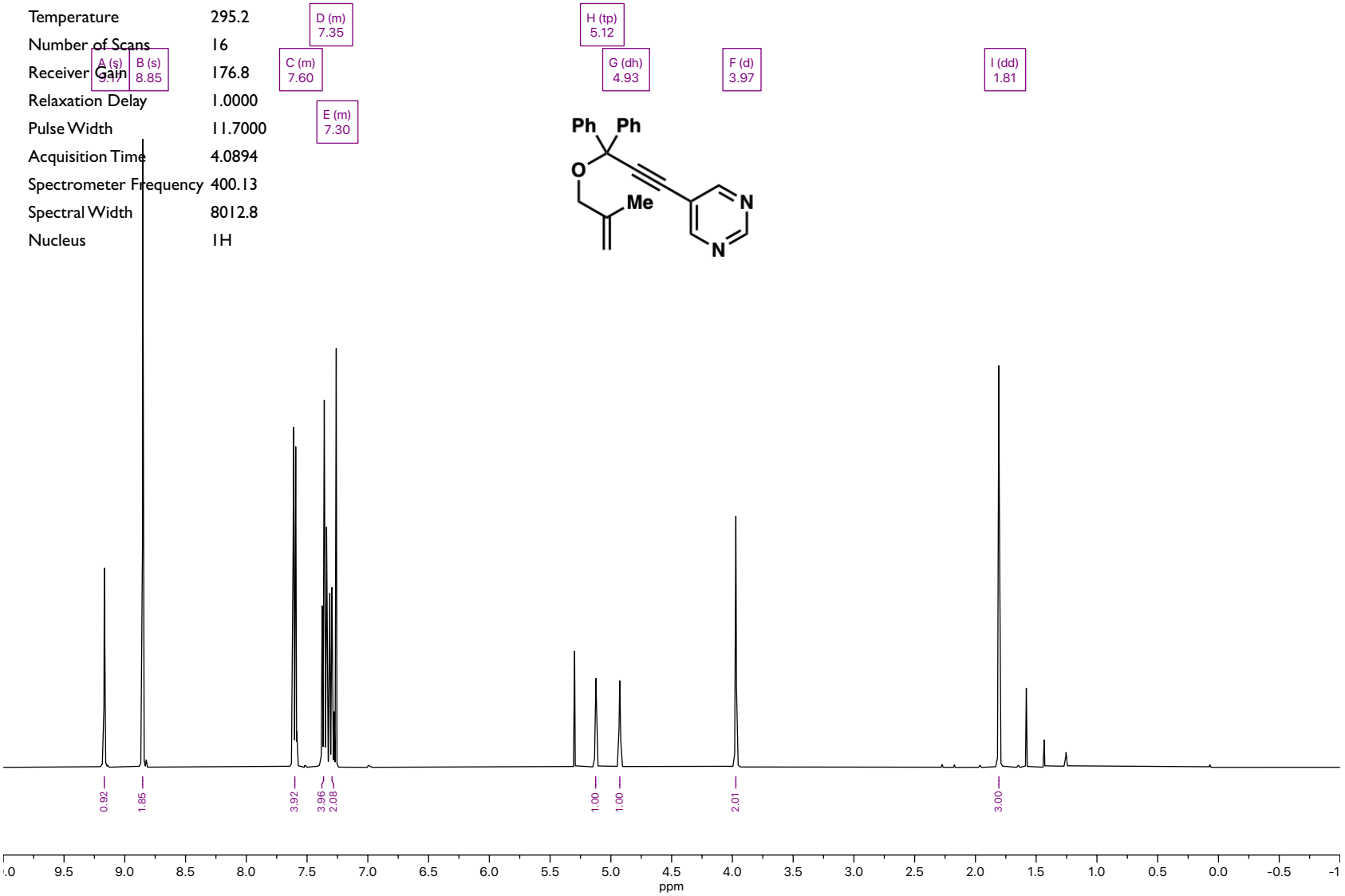
21

Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	297.2
Number of Scans	16
Receiver Gain	142.8
Relaxation Delay	1.0000
Pulse Width	11.7000
Acquisition Time	4.0894
Spectrometer Frequency	400.13
Spectral Width	8012.8
Nucleus	1H



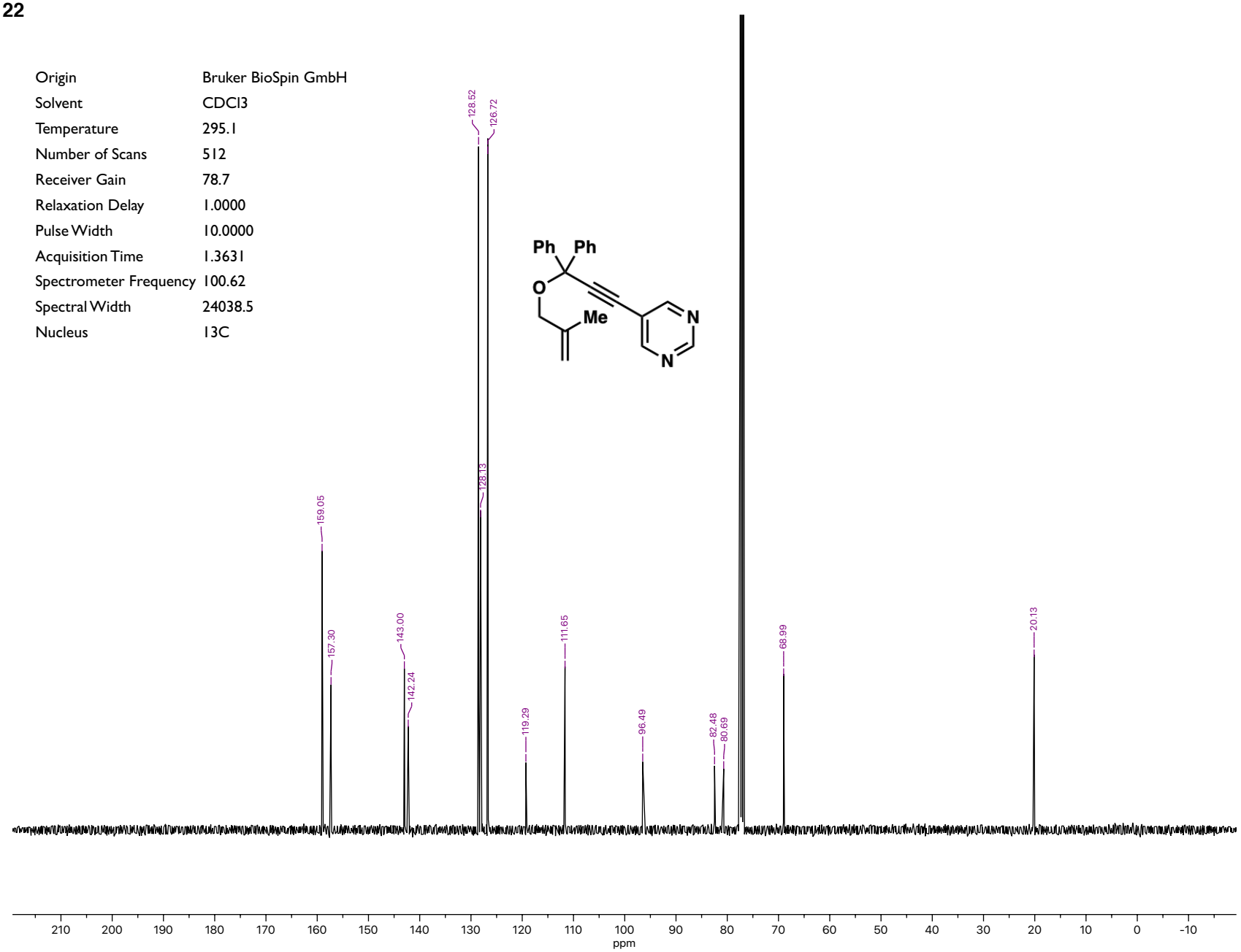
22

Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	295.2
Number of Scans	16
Receiver Gain	176.8
Relaxation Delay	1.0000
Pulse Width	11.7000
Acquisition Time	4.0894
Spectrometer Frequency	400.13
Spectral Width	8012.8
Nucleus	1H



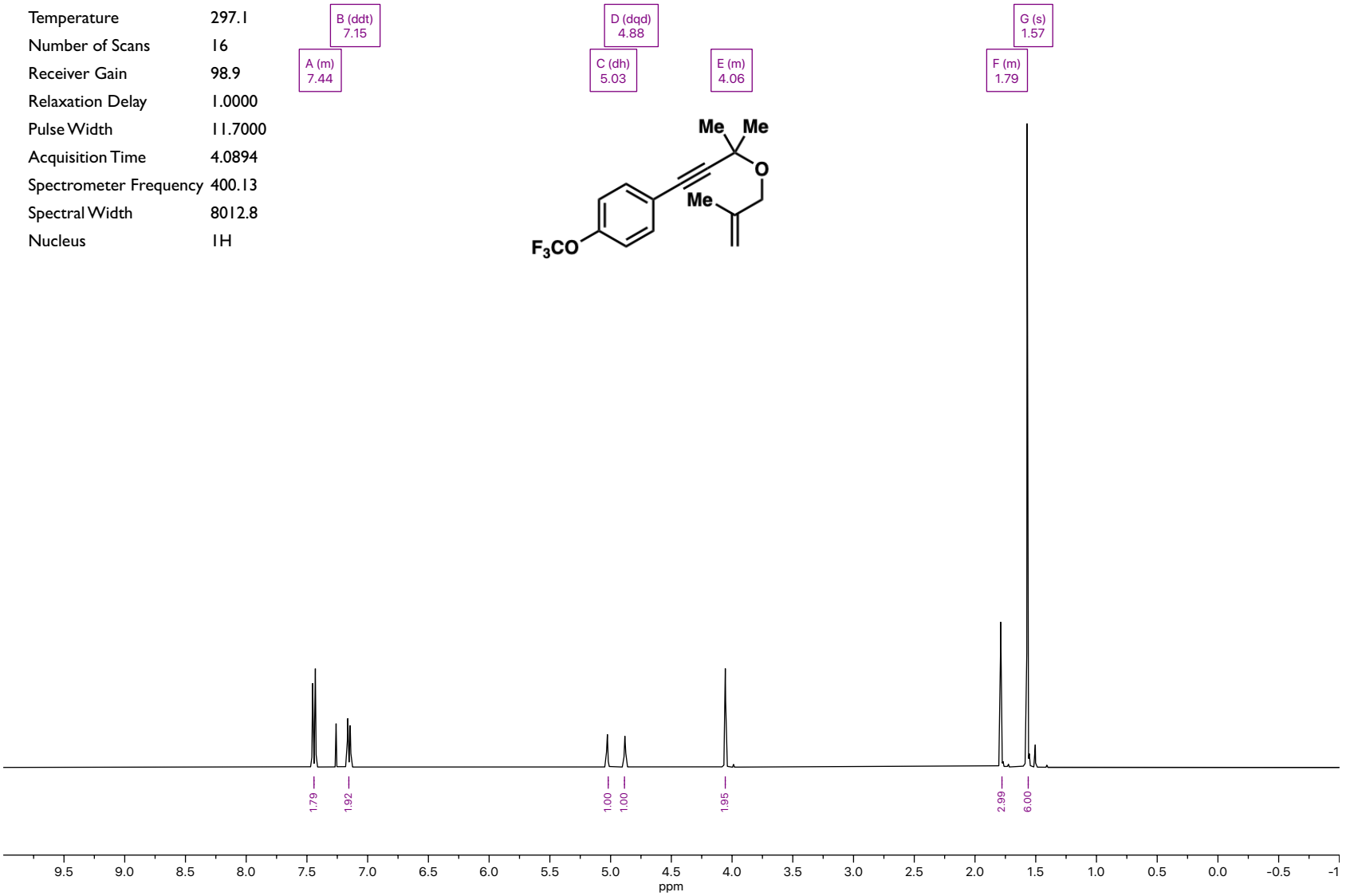
22

Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	295.1
Number of Scans	512
Receiver Gain	78.7
Relaxation Delay	1.0000
Pulse Width	10.0000
Acquisition Time	1.3631
Spectrometer Frequency	100.62
Spectral Width	24038.5
Nucleus	13C



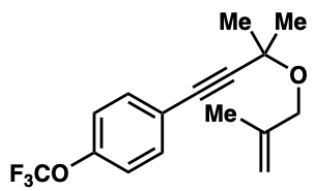
23

Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	297.1
Number of Scans	16
Receiver Gain	98.9
Relaxation Delay	1.0000
Pulse Width	11.7000
Acquisition Time	4.0894
Spectrometer Frequency	400.13
Spectral Width	8012.8
Nucleus	1H



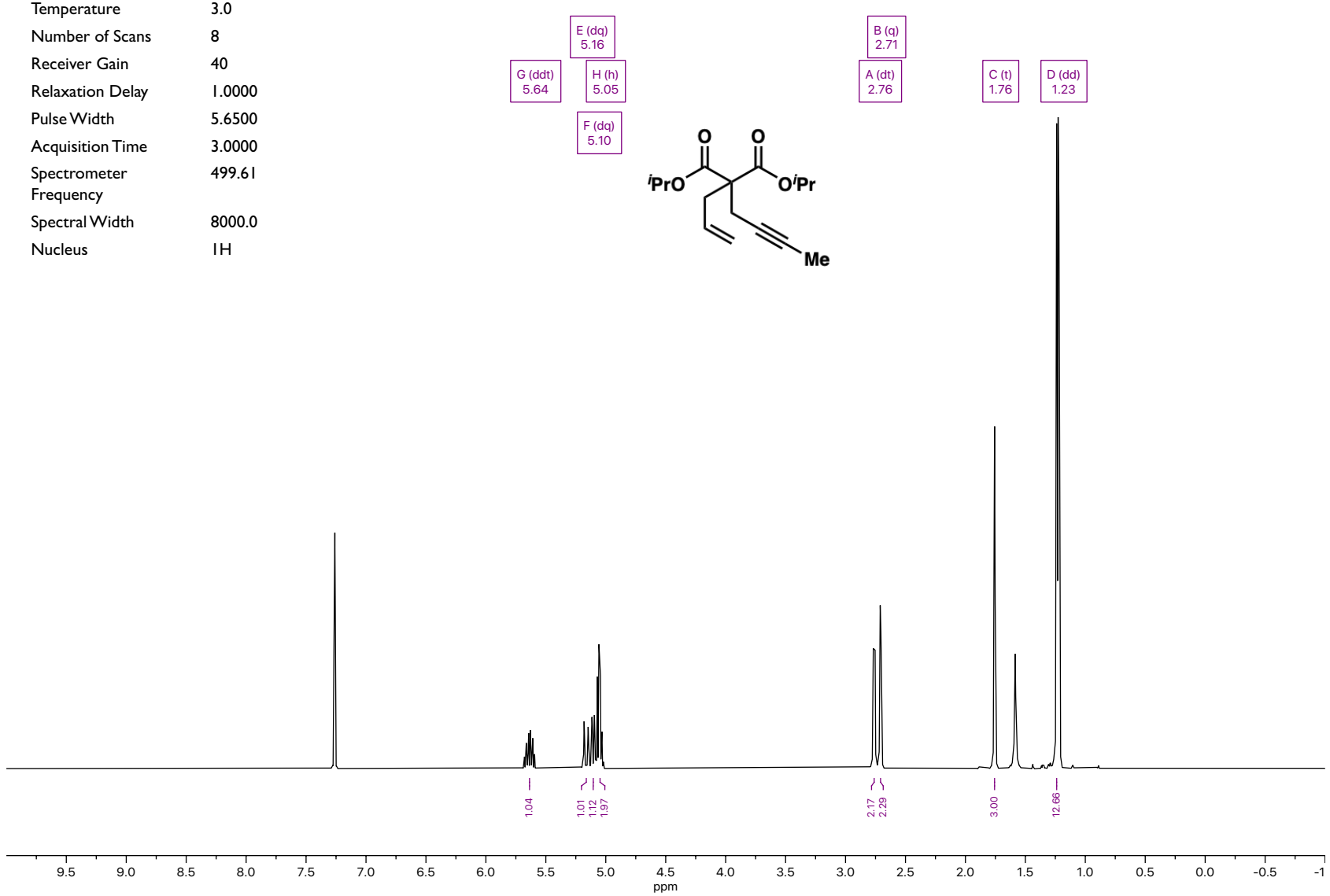
23

Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	297.1
Number of Scans	128
Receiver Gain	78.7
Relaxation Delay	1.0000
Pulse Width	10.0000
Acquisition Time	1.3631
Spectrometer Frequency	100.62
Spectral Width	24038.5
Nucleus	13C



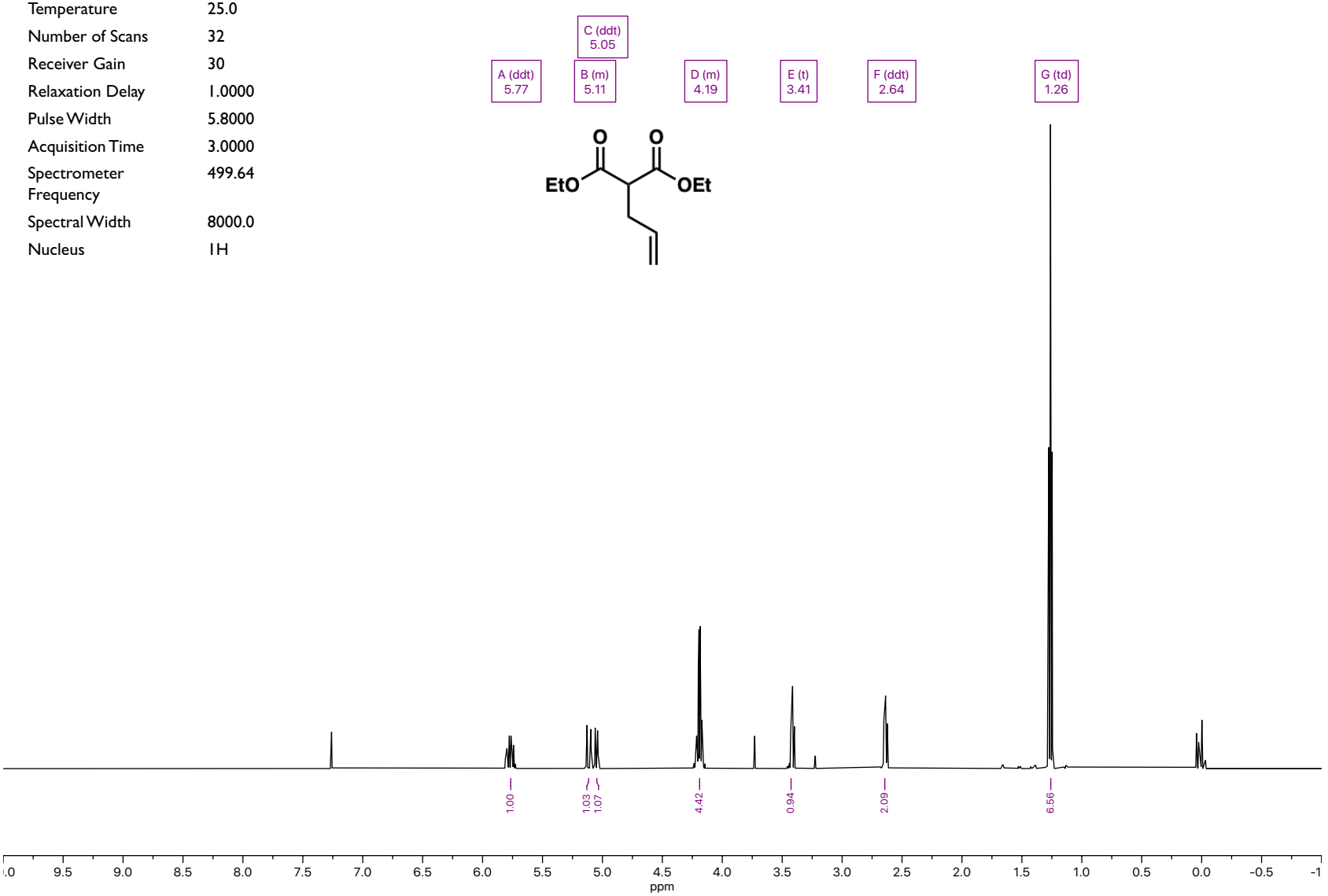
24

Origin	Varian
Solvent	cdcl3
Temperature	3.0
Number of Scans	8
Receiver Gain	40
Relaxation Delay	1.0000
Pulse Width	5.6500
Acquisition Time	3.0000
Spectrometer Frequency	499.61
Spectral Width	8000.0
Nucleus	1H



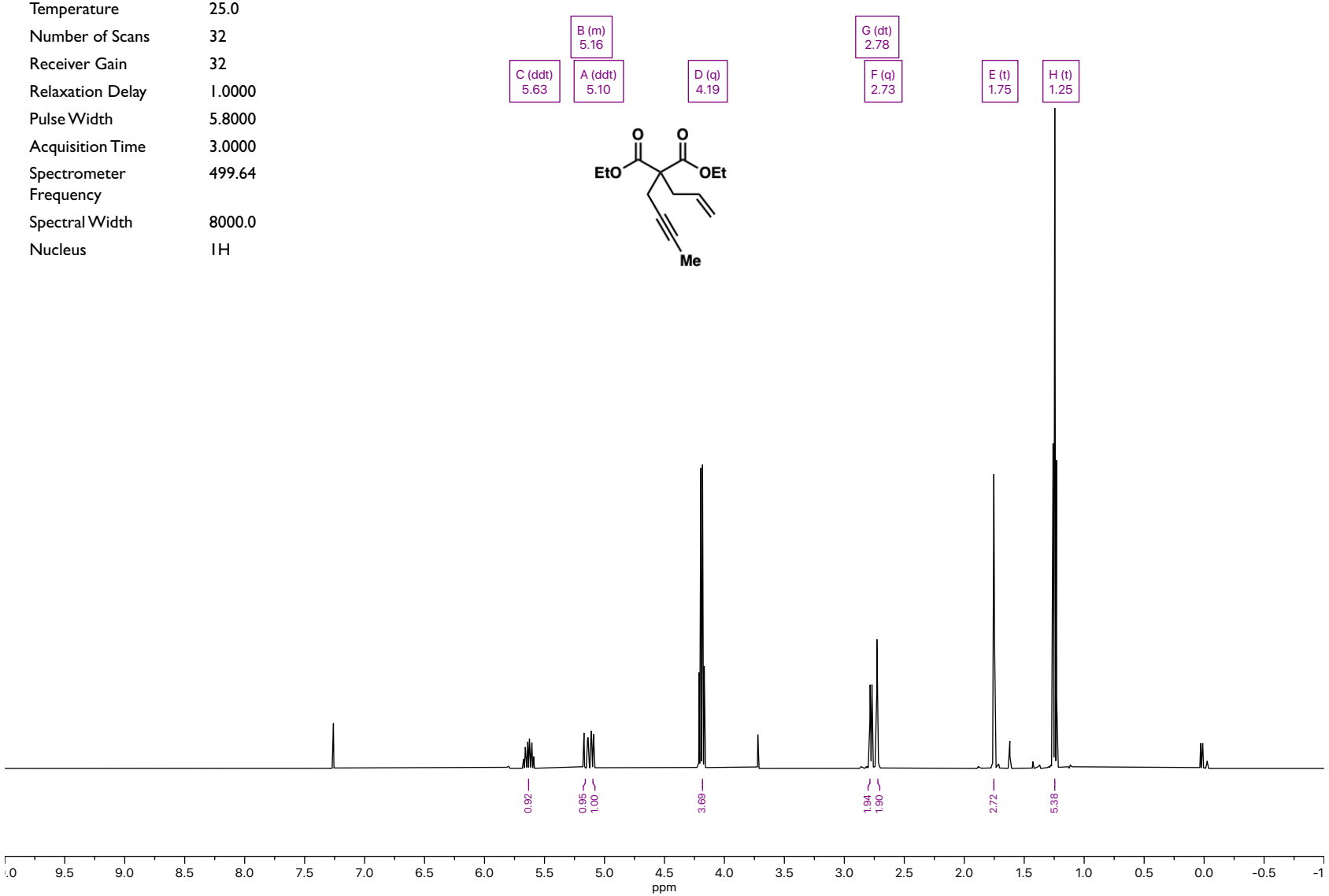
25

Origin	Varian
Solvent	cdcl3
Temperature	25.0
Number of Scans	32
Receiver Gain	30
Relaxation Delay	1.0000
Pulse Width	5.8000
Acquisition Time	3.0000
Spectrometer Frequency	499.64
Spectral Width	8000.0
Nucleus	1H



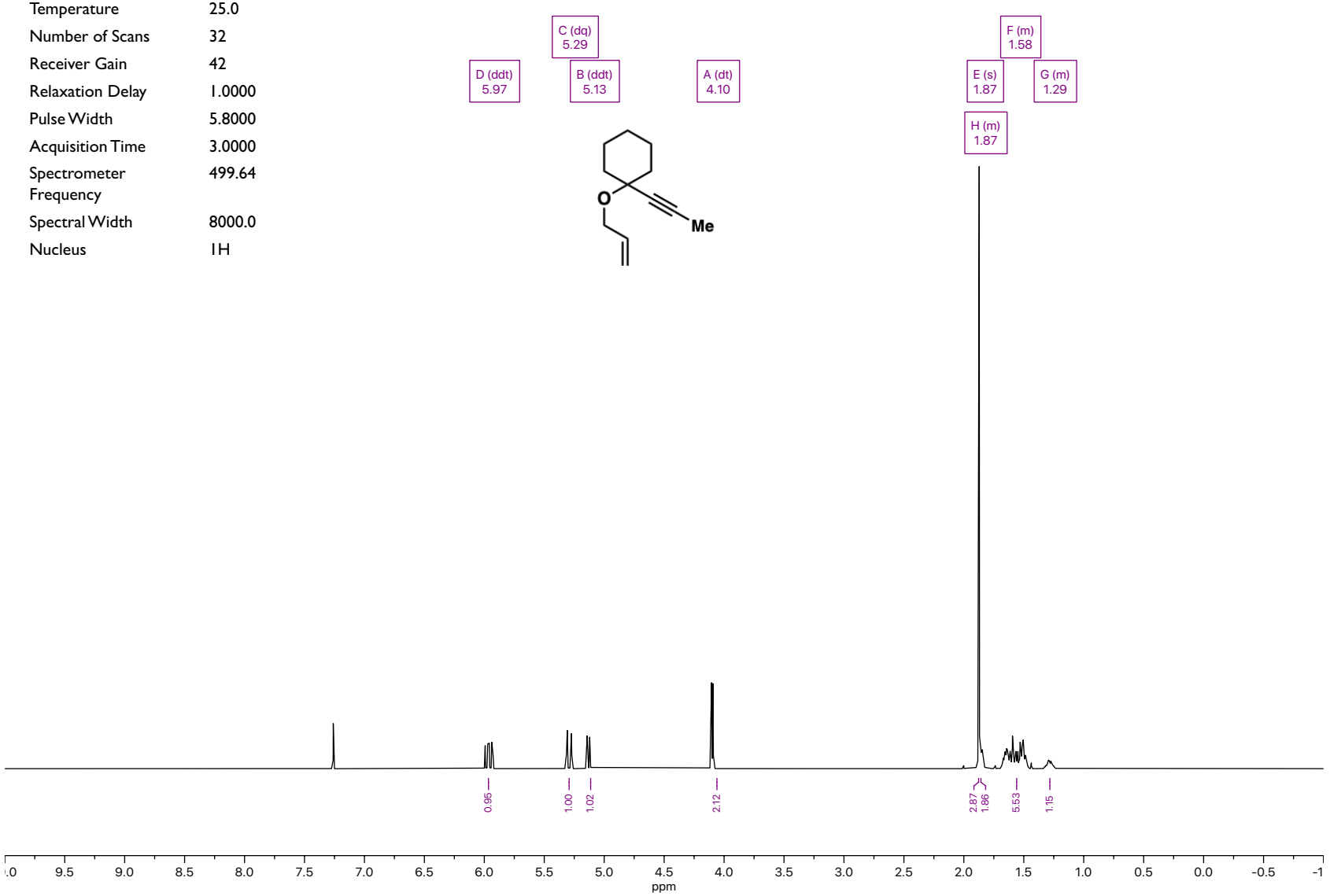
26

Origin	Varian
Solvent	cdcl3
Temperature	25.0
Number of Scans	32
Receiver Gain	32
Relaxation Delay	1.0000
Pulse Width	5.8000
Acquisition Time	3.0000
Spectrometer Frequency	499.64
Spectral Width	8000.0
Nucleus	1H



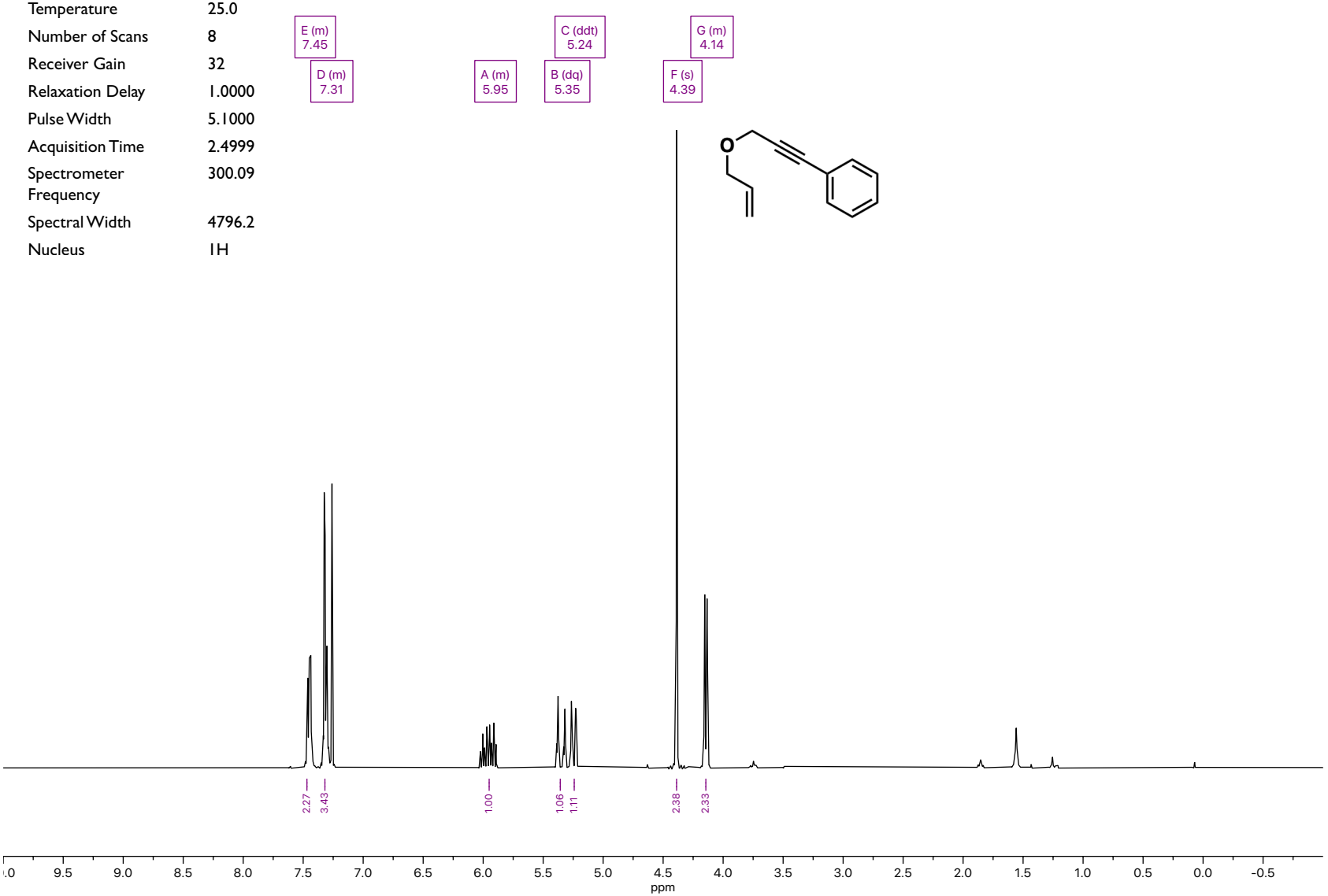
27

Origin	Varian
Solvent	cdcl3
Temperature	25.0
Number of Scans	32
Receiver Gain	42
Relaxation Delay	1.0000
Pulse Width	5.8000
Acquisition Time	3.0000
Spectrometer Frequency	499.64
Spectral Width	8000.0
Nucleus	1H



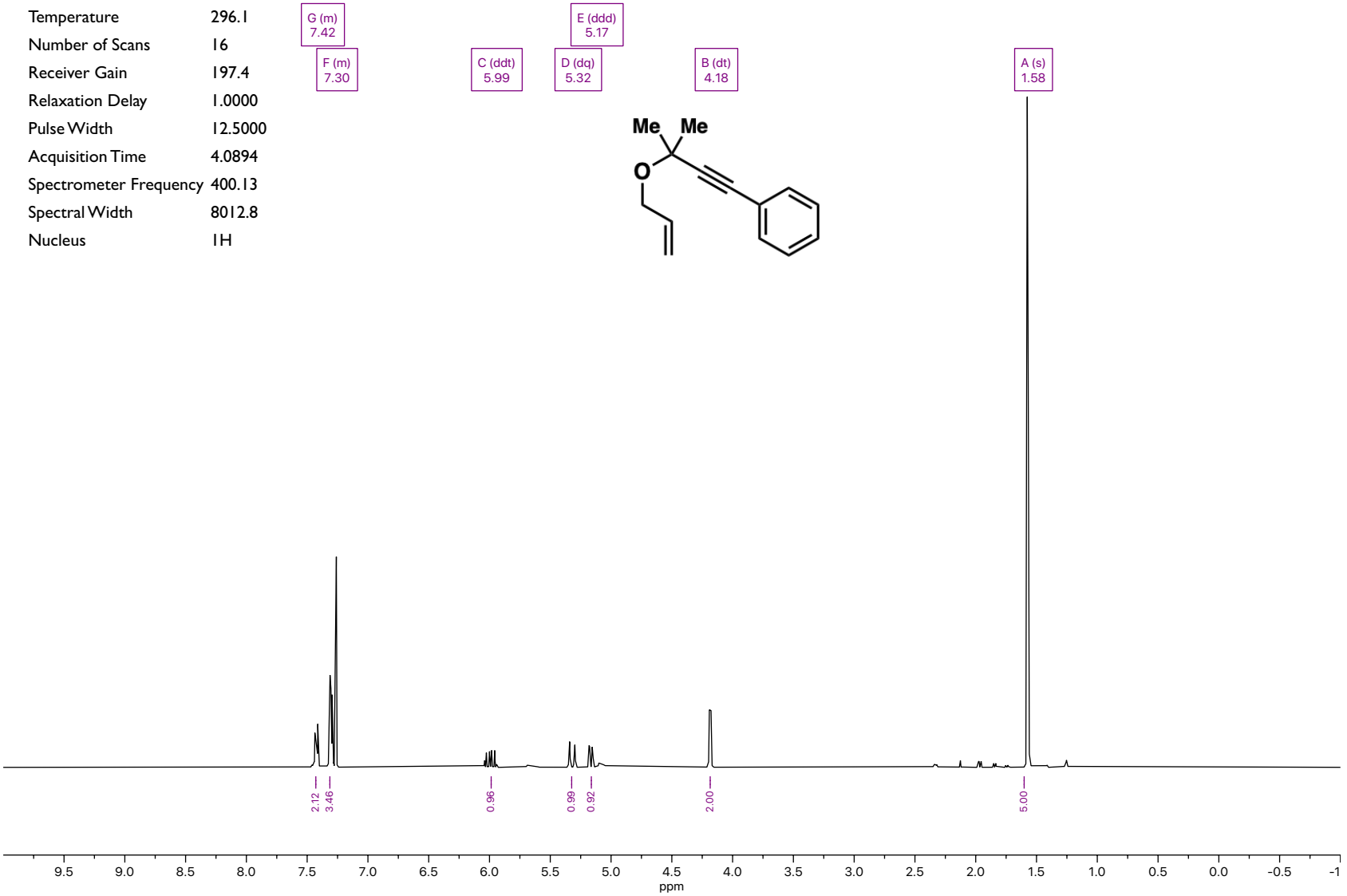
28

Origin	Varian
Solvent	cdcl3
Temperature	25.0
Number of Scans	8
Receiver Gain	32
Relaxation Delay	1.0000
Pulse Width	5.1000
Acquisition Time	2.4999
Spectrometer Frequency	300.09
Spectral Width	4796.2
Nucleus	1H



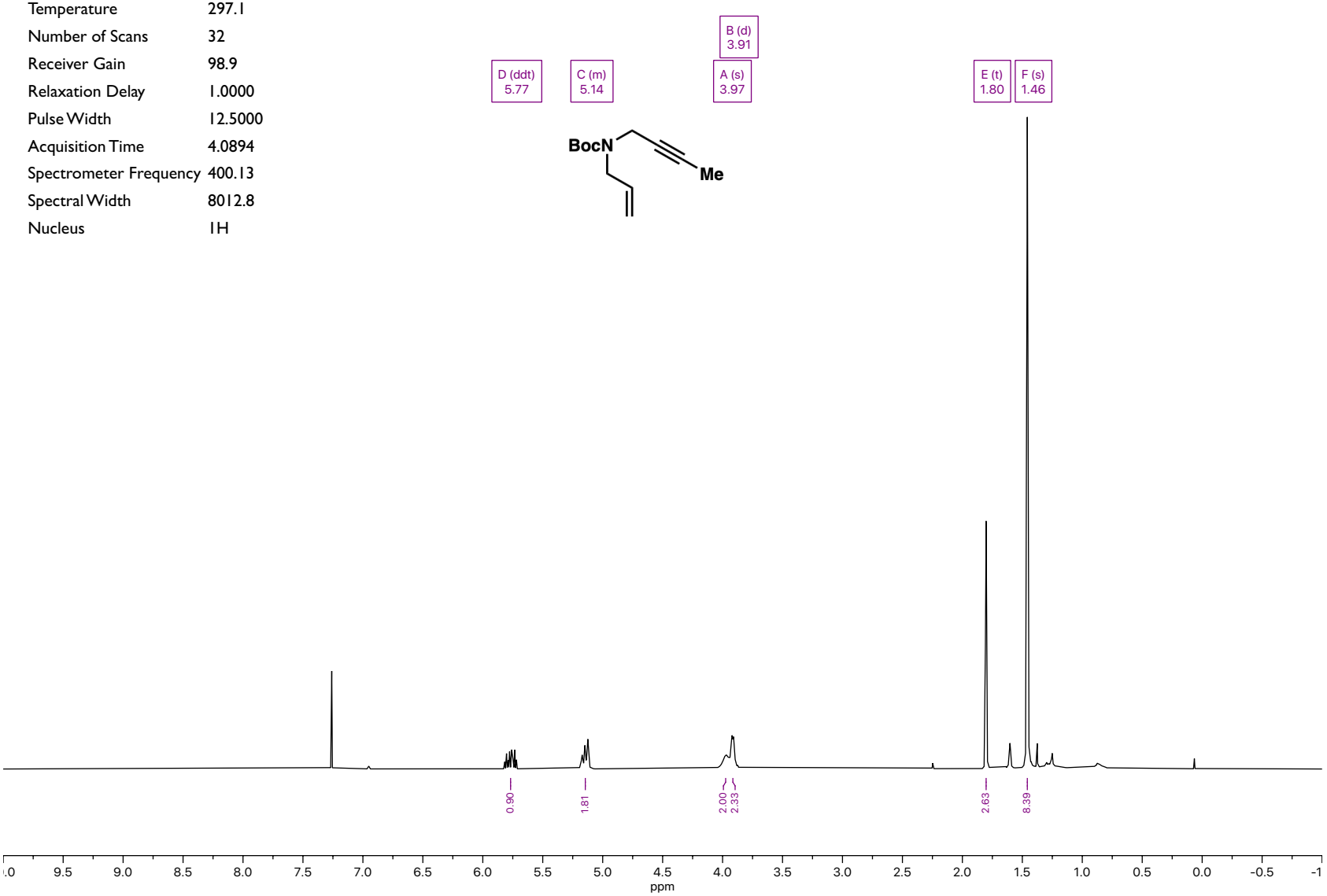
29

Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	296.1
Number of Scans	16
Receiver Gain	197.4
Relaxation Delay	1.0000
Pulse Width	12.5000
Acquisition Time	4.0894
Spectrometer Frequency	400.13
Spectral Width	8012.8
Nucleus	1H



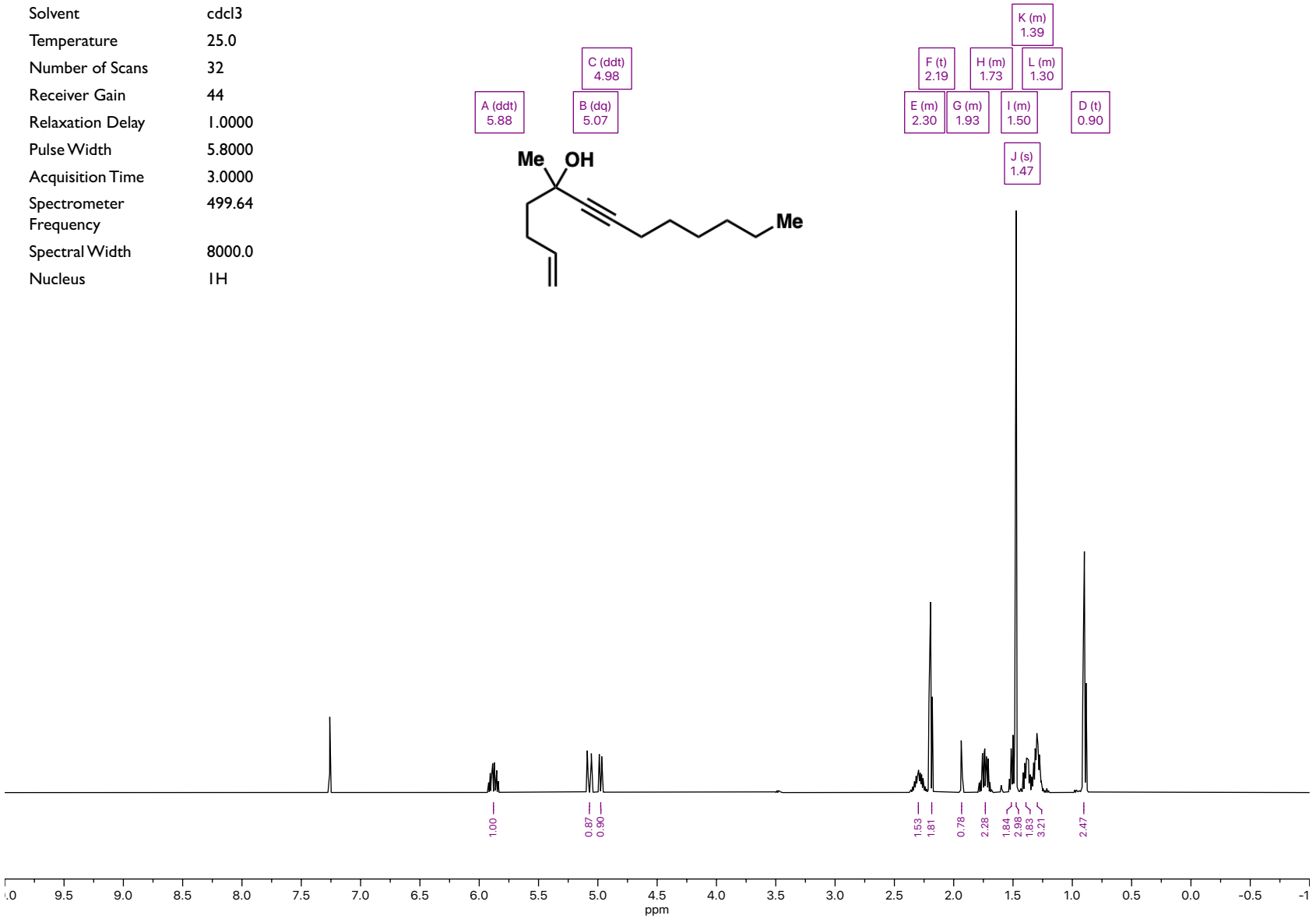
30

Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	297.1
Number of Scans	32
Receiver Gain	98.9
Relaxation Delay	1.0000
Pulse Width	12.5000
Acquisition Time	4.0894
Spectrometer Frequency	400.13
Spectral Width	8012.8
Nucleus	1H



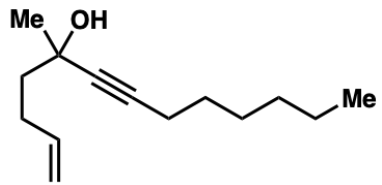
31

Origin	Varian
Solvent	cdcl3
Temperature	25.0
Number of Scans	32
Receiver Gain	44
Relaxation Delay	1.0000
Pulse Width	5.8000
Acquisition Time	3.0000
Spectrometer Frequency	499.64
Spectral Width	8000.0
Nucleus	1H



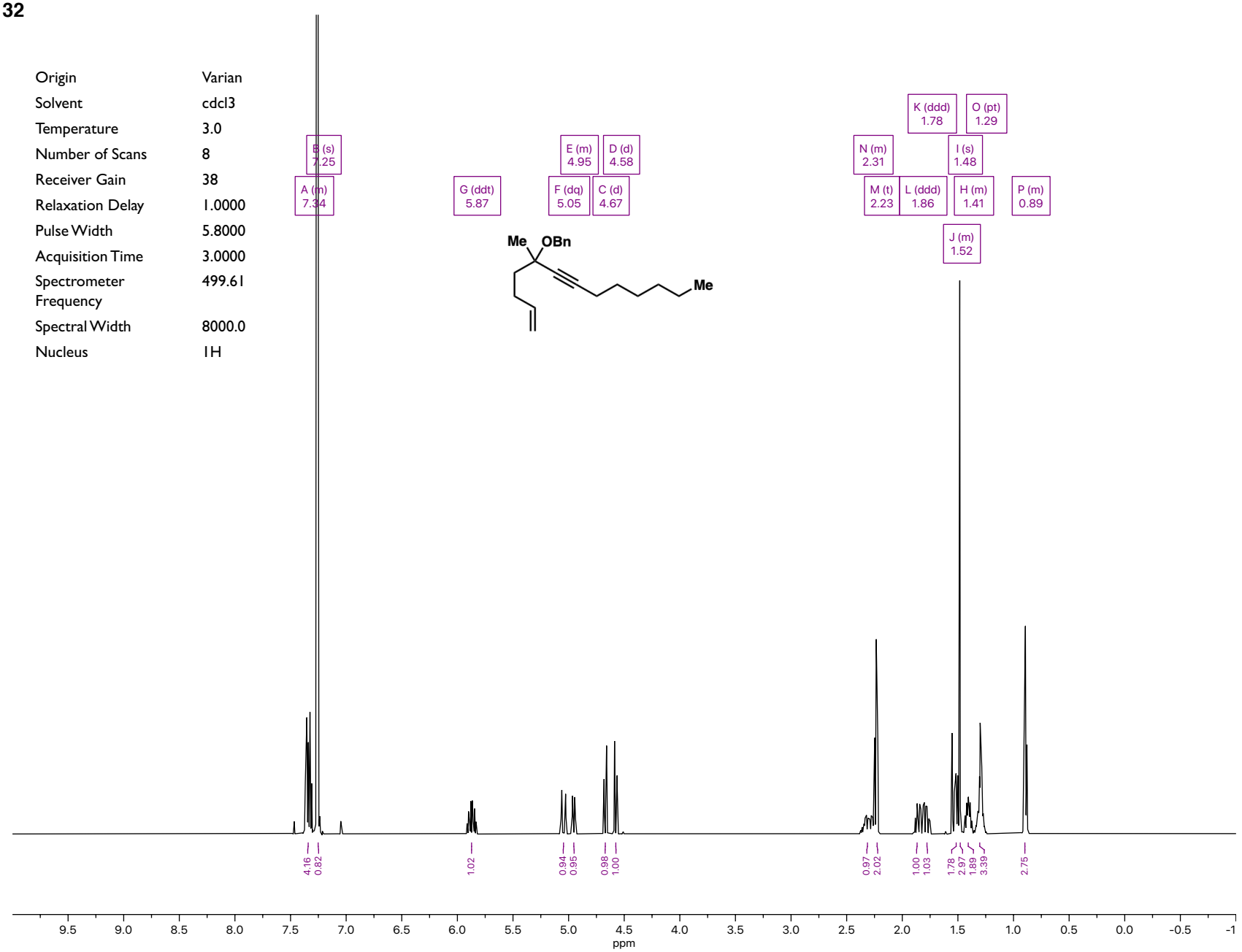
31

Origin	Varian
Solvent	cdcl3
Temperature	25.0
Number of Scans	256
Receiver Gain	30
Relaxation Delay	1.0000
Pulse Width	4.6125
Acquisition Time	1.0420
Spectrometer Frequency	125.65
Spectral Width	31446.5
Nucleus	13C



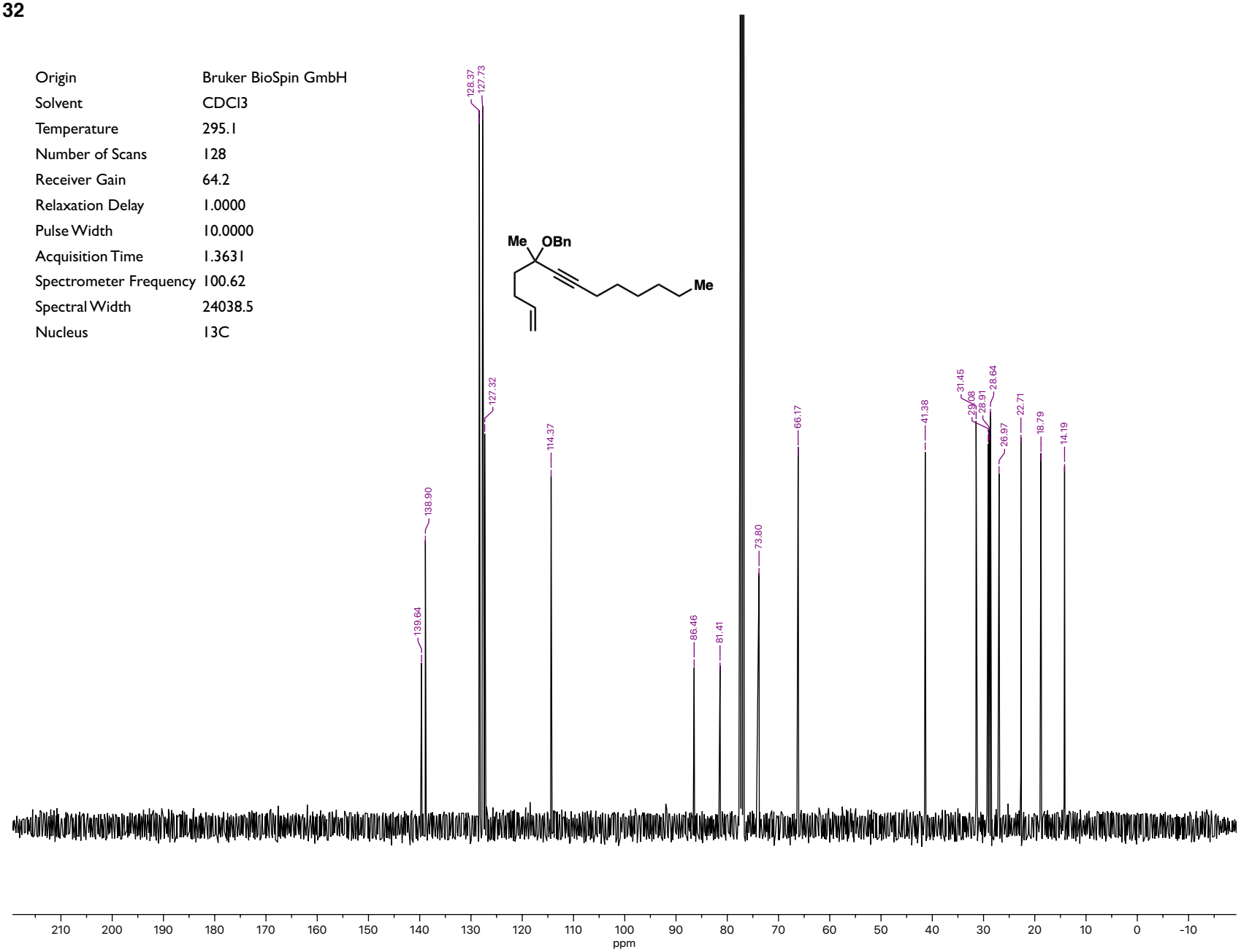
32

Origin	Varian
Solvent	cdcl3
Temperature	3.0
Number of Scans	8
Receiver Gain	38
Relaxation Delay	1.0000
Pulse Width	5.8000
Acquisition Time	3.0000
Spectrometer Frequency	499.61
Spectral Width	8000.0
Nucleus	1H



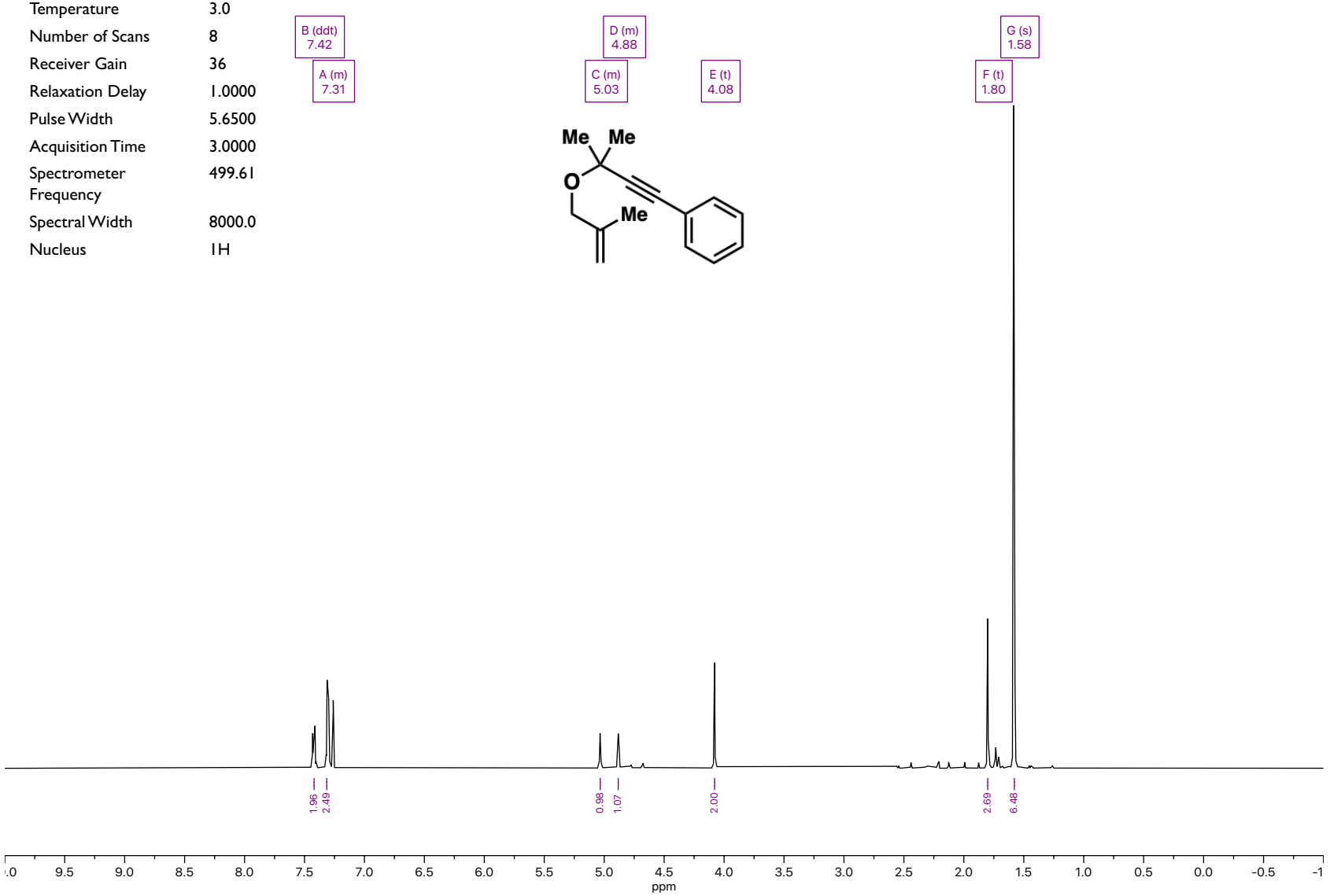
32

Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	295.1
Number of Scans	128
Receiver Gain	64.2
Relaxation Delay	1.0000
Pulse Width	10.0000
Acquisition Time	1.3631
Spectrometer Frequency	100.62
Spectral Width	24038.5
Nucleus	13C



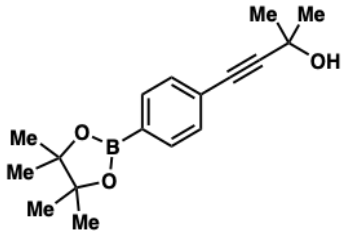
33

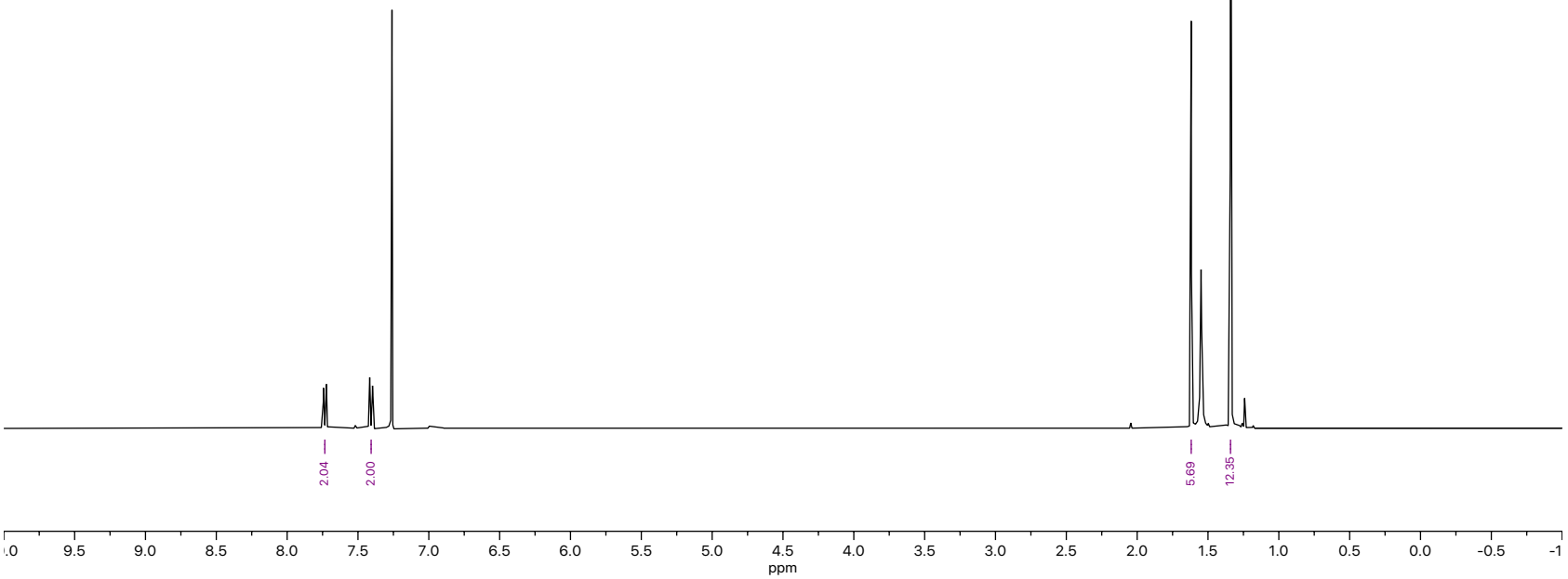
Origin	Varian
Solvent	cdcl3
Temperature	3.0
Number of Scans	8
Receiver Gain	36
Relaxation Delay	1.0000
Pulse Width	5.6500
Acquisition Time	3.0000
Spectrometer Frequency	499.61
Spectral Width	8000.0
Nucleus	1H



34

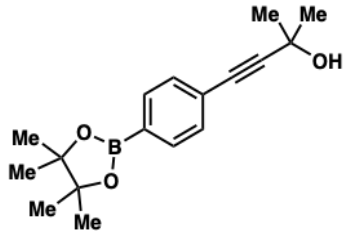
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	297.2
Number of Scans	16
Receiver Gain	197.4
Relaxation Delay	1.0000
Pulse Width	8.7000
Acquisition Time	4.0894
Spectrometer Frequency	400.13
Spectral Width	8012.8
Nucleus	1H





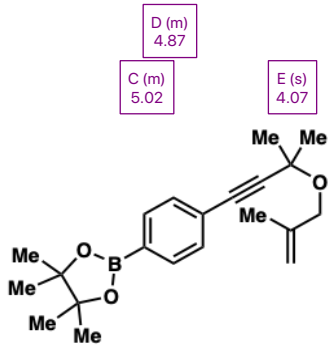
34

Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	297.2
Number of Scans	3000
Receiver Gain	43.7
Relaxation Delay	1.0000
Pulse Width	10.0000
Acquisition Time	1.3631
Spectrometer Frequency	100.62
Spectral Width	24038.5
Nucleus	13C



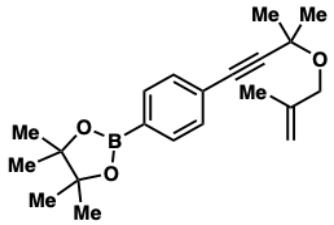
35

Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	297.1
Number of Scans	16
Receiver Gain	197.4
Relaxation Delay	1.0000
Pulse Width	8.7000
Acquisition Time	4.0894
Spectrometer Frequency	400.13
Spectral Width	8012.8
Nucleus	1H



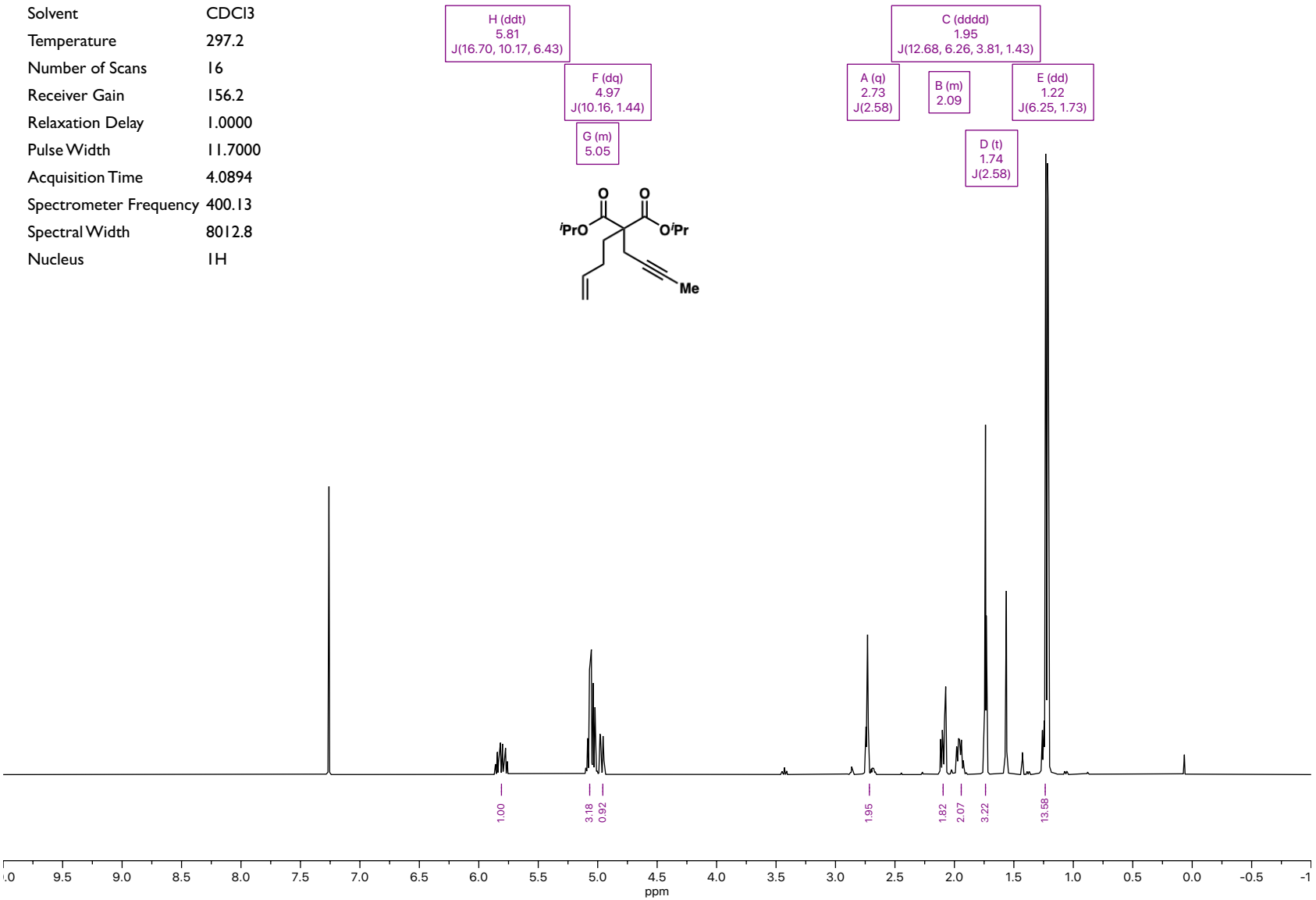
35

Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	297.1
Number of Scans	2048
Receiver Gain	197.4
Relaxation Delay	1.0000
Pulse Width	10.0000
Acquisition Time	1.3631
Spectrometer Frequency	100.62
Spectral Width	24038.5
Nucleus	13C



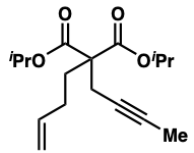
36

Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	297.2
Number of Scans	16
Receiver Gain	156.2
Relaxation Delay	1.0000
Pulse Width	11.7000
Acquisition Time	4.0894
Spectrometer Frequency	400.13
Spectral Width	8012.8
Nucleus	1H



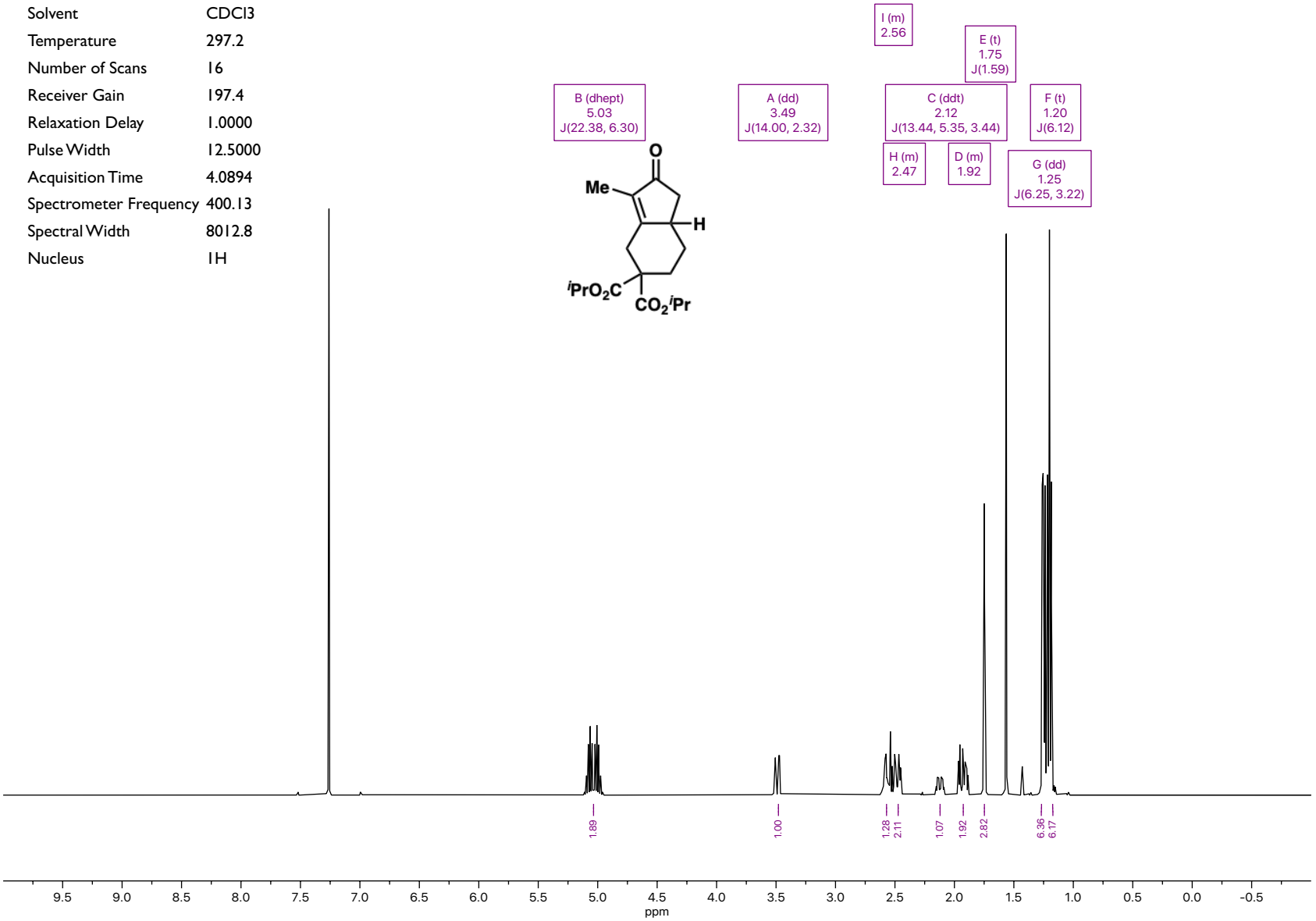
36

Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	297.2
Number of Scans	256
Receiver Gain	72.0
Relaxation Delay	1.0000
Pulse Width	10.0000
Acquisition Time	1.3631
Spectrometer Frequency	100.62
Spectral Width	24038.5
Nucleus	13C



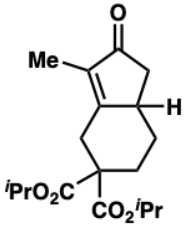
37

Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	297.2
Number of Scans	16
Receiver Gain	197.4
Relaxation Delay	1.0000
Pulse Width	12.5000
Acquisition Time	4.0894
Spectrometer Frequency	400.13
Spectral Width	8012.8
Nucleus	1H



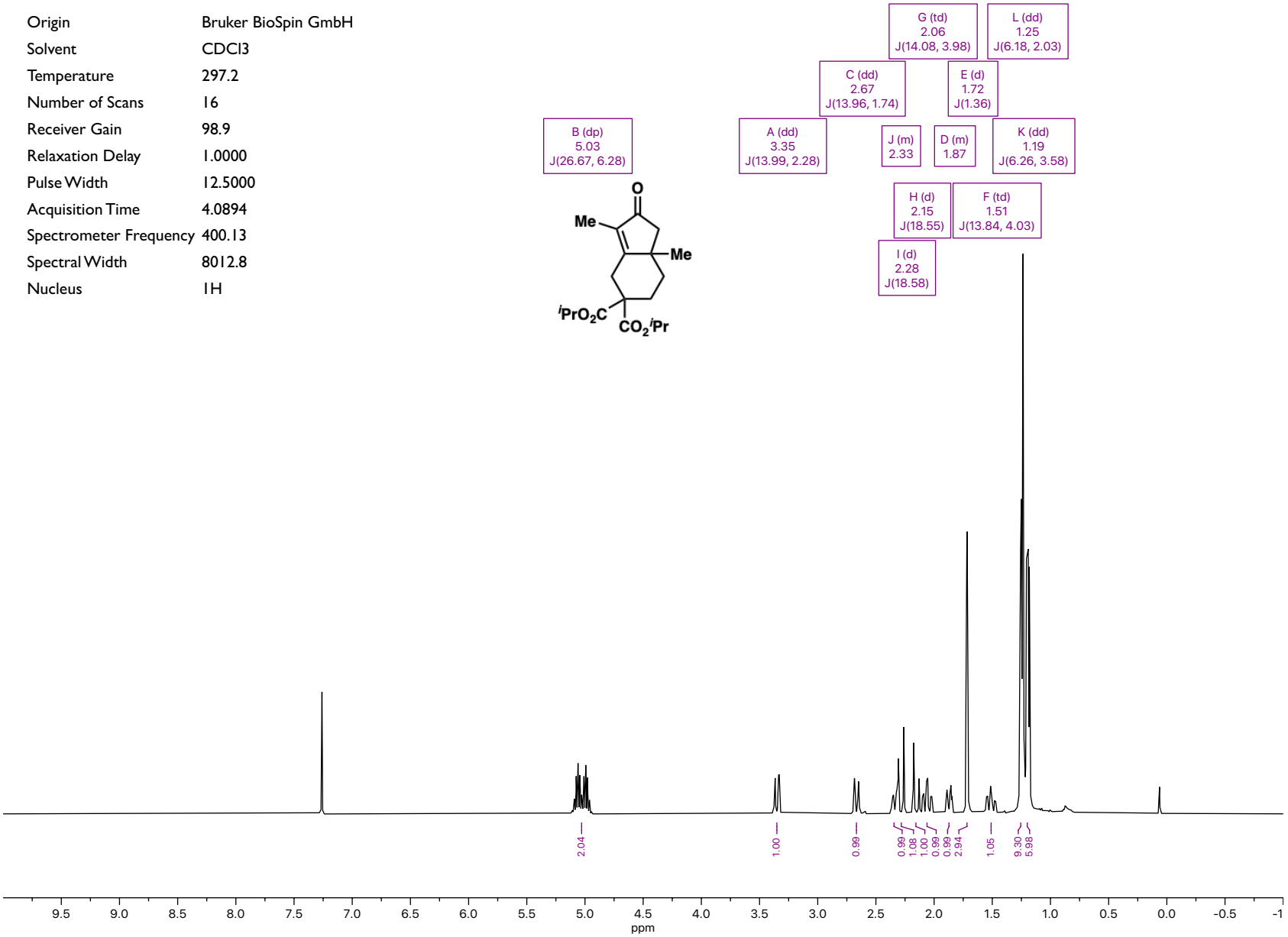
37

Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	297.1
Number of Scans	512
Receiver Gain	78.7
Relaxation Delay	1.0000
Pulse Width	10.0000
Acquisition Time	1.3631
Spectrometer Frequency	100.62
Spectral Width	24038.5
Nucleus	13C



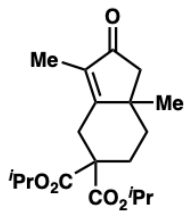
38

Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	297.2
Number of Scans	16
Receiver Gain	98.9
Relaxation Delay	1.0000
Pulse Width	12.5000
Acquisition Time	4.0894
Spectrometer Frequency	400.13
Spectral Width	8012.8
Nucleus	1H



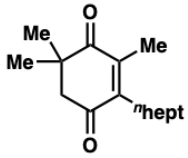
38

Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	297.1
Number of Scans	512
Receiver Gain	72.0
Relaxation Delay	1.0000
Pulse Width	10.0000
Acquisition Time	1.3631
Spectrometer Frequency	100.62
Spectral Width	24038.5
Nucleus	13C



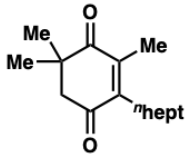
39

Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	297.1
Number of Scans	16
Receiver Gain	98.9
Relaxation Delay	1.0000
Pulse Width	12.5000
Acquisition Time	4.0894
Spectrometer Frequency	400.13
Spectral Width	8012.8
Nucleus	1H



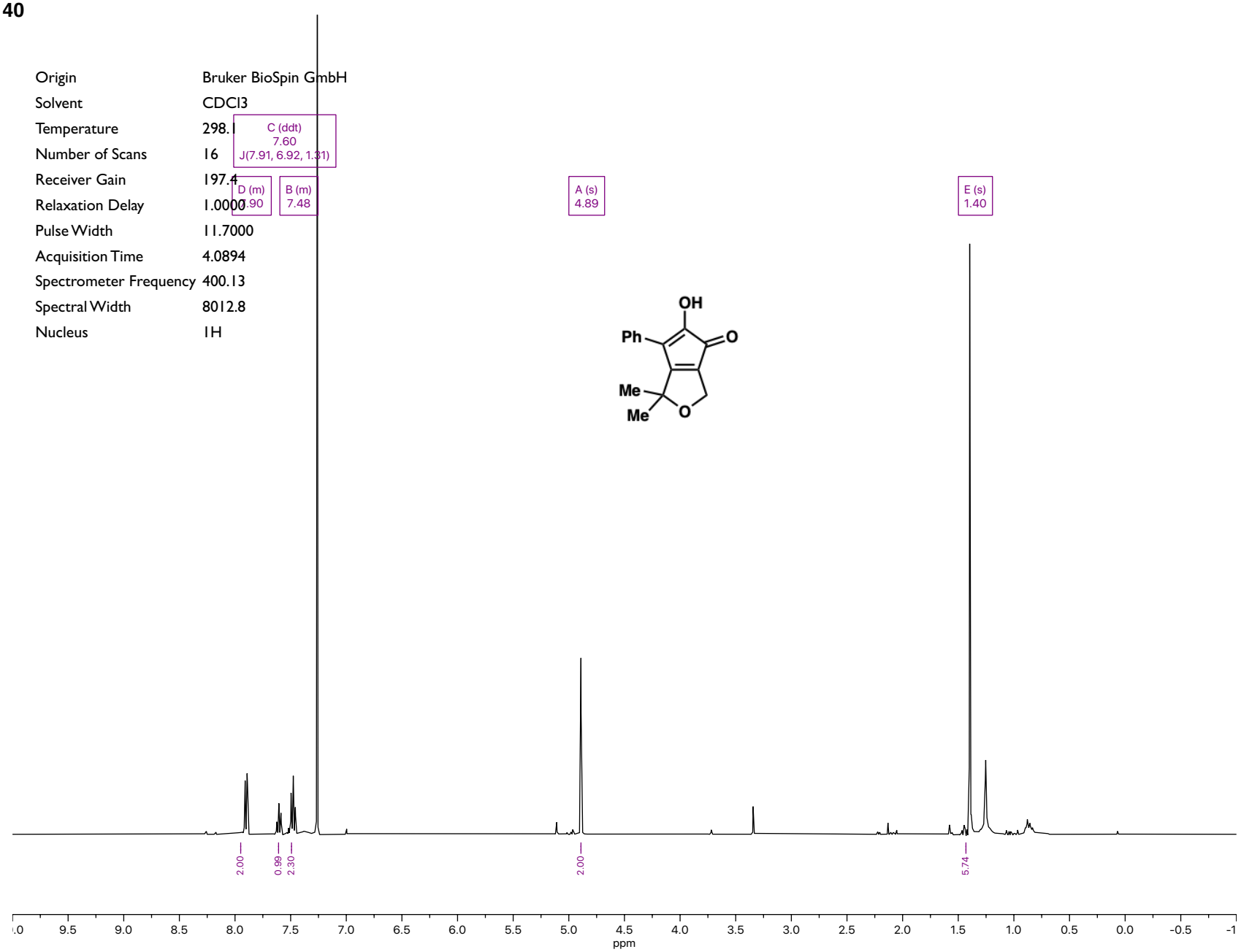
39

Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	297.1
Number of Scans	512
Receiver Gain	72.0
Relaxation Delay	1.0000
Pulse Width	10.0000
Acquisition Time	1.3631
Spectrometer Frequency	100.62
Spectral Width	24038.5
Nucleus	13C



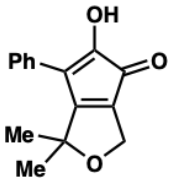
40

Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	298.1
Number of Scans	16
Receiver Gain	197.4
Relaxation Delay	1.0000
Pulse Width	11.7000
Acquisition Time	4.0894
Spectrometer Frequency	400.13
Spectral Width	8012.8
Nucleus	1H

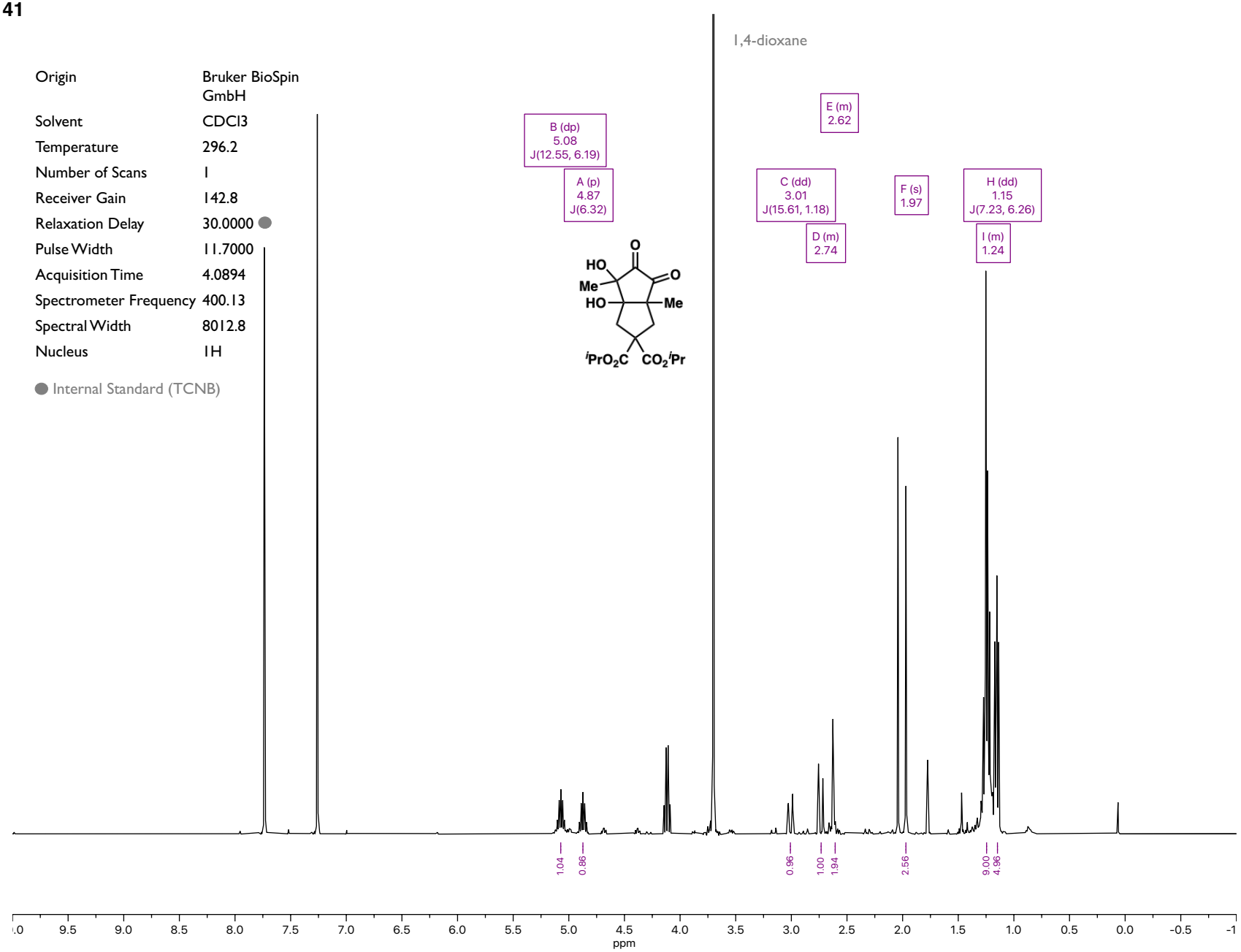


40

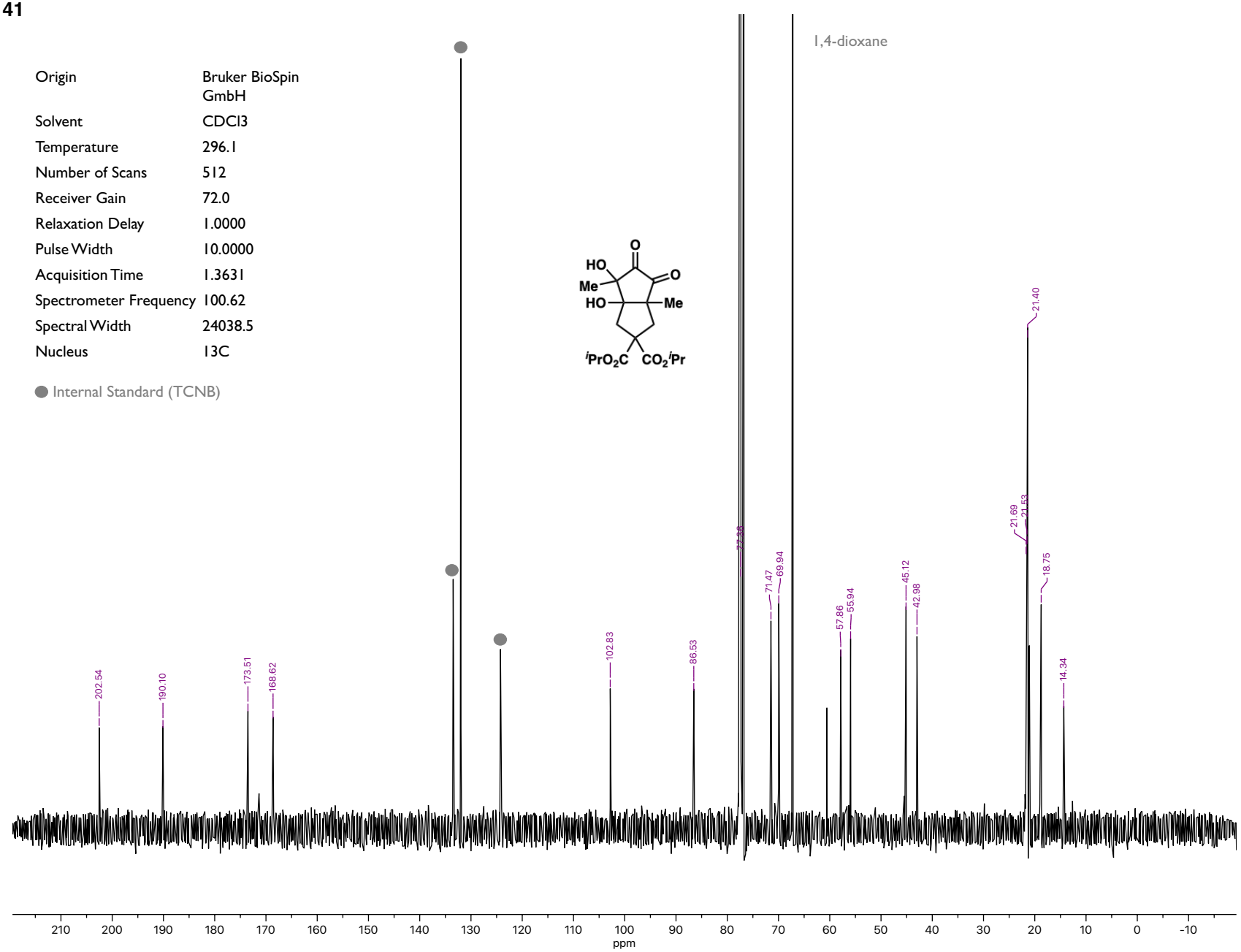
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	298.1
Number of Scans	1024
Receiver Gain	72.0
Relaxation Delay	1.0000
Pulse Width	10.0000
Acquisition Time	1.3631
Spectrometer Frequency	100.62
Spectral Width	24038.5
Nucleus	13C



41

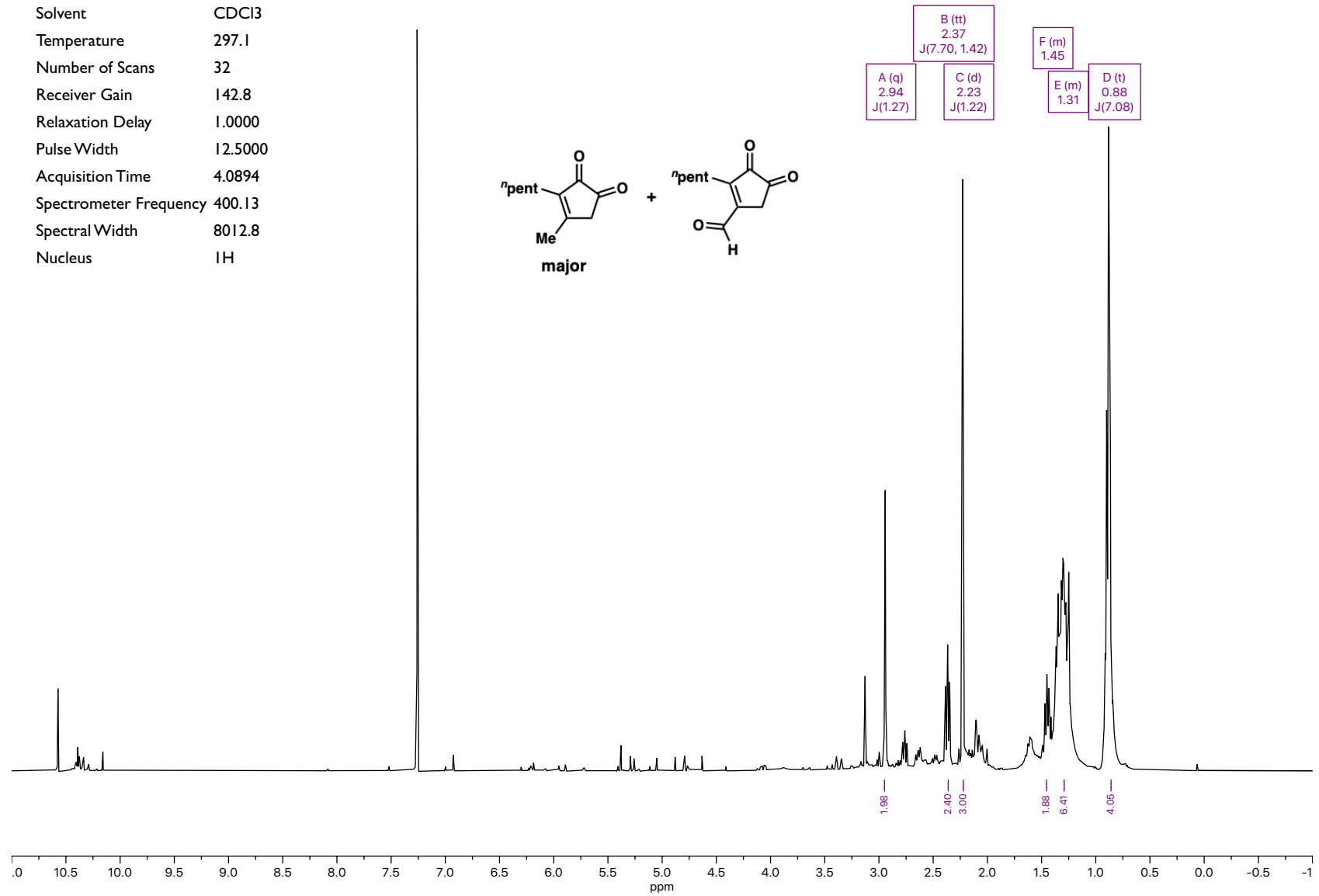

Origin Bruker BioSpin GmbH
Solvent CDCl3
Temperature 296.2
Number of Scans 1
Receiver Gain 142.8
Relaxation Delay 30.0000
Pulse Width 11.7000
Acquisition Time 4.0894
Spectrometer Frequency 400.13
Spectral Width 8012.8
Nucleus 1H
Internal Standard (TCNB)
1,4-dioxane
B (dp) 5.08 J(12.55, 6.19)
A (p) 4.87 J(6.32)
E (m) 2.62
C (dd) 3.01 J(15.61, 1.18)
D (m) 2.74
F (s) 1.97
H (dd) 1.15 J(7.23, 6.26)
I (m) 1.24
HO
Me
HO
O
O
Me
iPrO2C
CO2iPr
1.04
0.86
0.96
1.00
1.94
2.56
9.00
4.96
ppm

41


Origin Bruker BioSpin GmbH
Solvent CDCl3
Temperature 296.1
Number of Scans 512
Receiver Gain 72.0
Relaxation Delay 1.0000
Pulse Width 10.0000
Acquisition Time 1.3631
Spectrometer Frequency 100.62
Spectral Width 24038.5
Nucleus 13C
Internal Standard (TCNB)
1,4-dioxane
HO
Me
HO
Me
O
O
$^{i}PrO_2C$ $CO_2{}^{i}Pr$
202.54
190.10
173.51
168.62
102.83
86.53
77.36
71.47
69.94
57.86
55.94
45.12
42.98
21.69
21.53
21.40
18.75
14.34
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
ppm

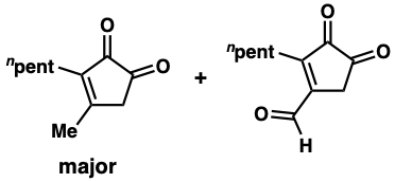
42

Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	297.1
Number of Scans	32
Receiver Gain	142.8
Relaxation Delay	1.0000
Pulse Width	12.5000
Acquisition Time	4.0894
Spectrometer Frequency	400.13
Spectral Width	8012.8
Nucleus	1H



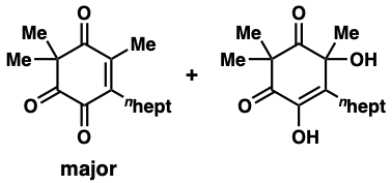
42

Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	297.1
Number of Scans	512
Receiver Gain	64.2
Relaxation Delay	1.0000
Pulse Width	10.0000
Acquisition Time	1.3631
Spectrometer Frequency	100.62
Spectral Width	24038.5
Nucleus	13C



43

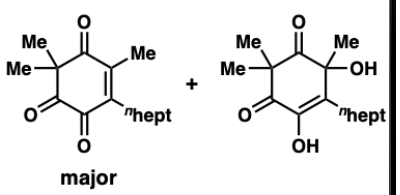
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	297.1
Number of Scans	32
Receiver Gain	72.0
Relaxation Delay	1.0000
Pulse Width	12.5000
Acquisition Time	4.0894
Spectrometer Frequency	400.13
Spectral Width	8012.8
Nucleus	1H



major

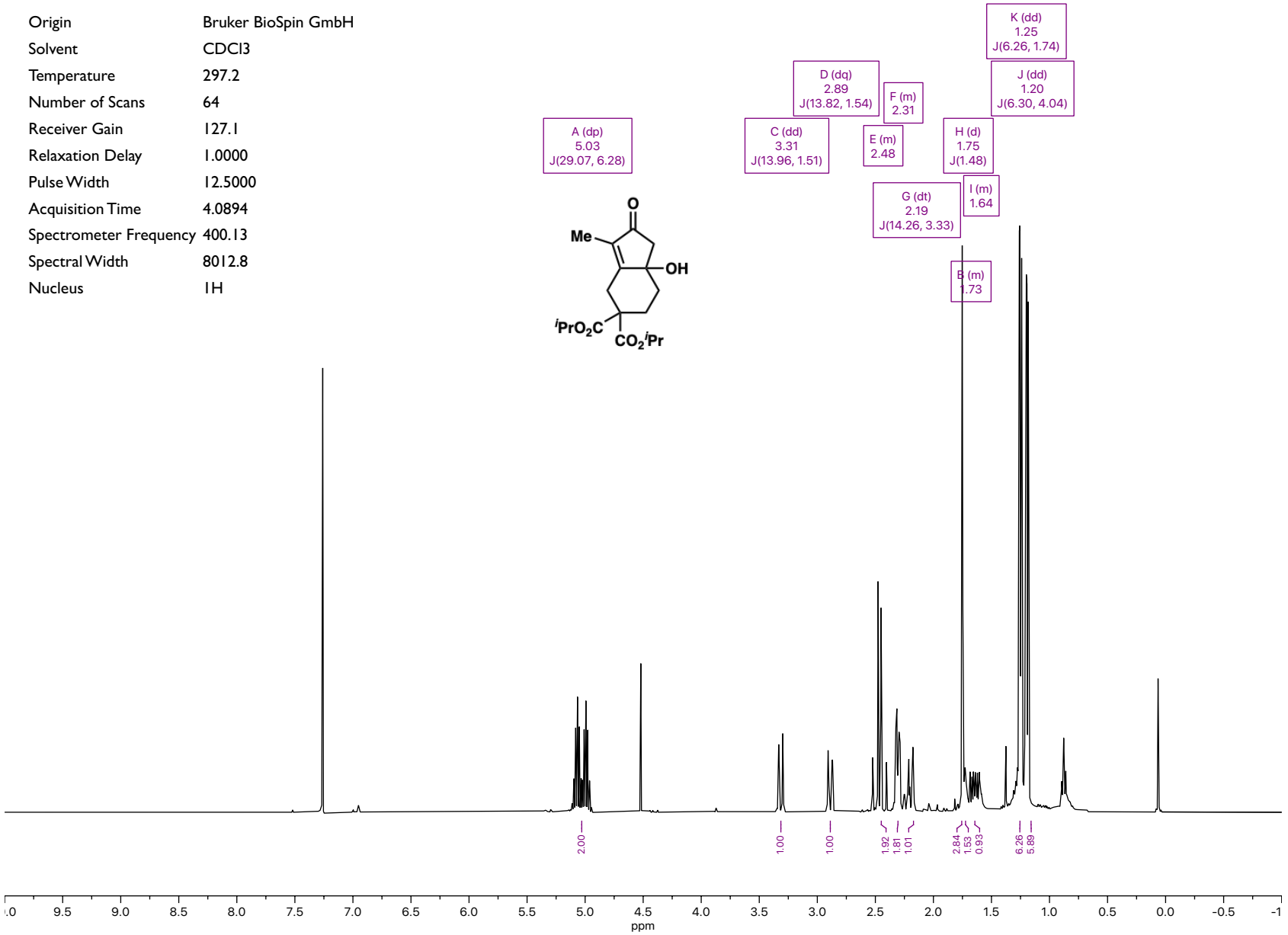
43

Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	297.2
Number of Scans	512
Receiver Gain	72.0
Relaxation Delay	1.0000
Pulse Width	10.0000
Acquisition Time	1.3631
Spectrometer Frequency	100.62
Spectral Width	24038.5
Nucleus	13C



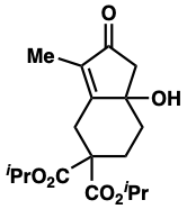
44

Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	297.2
Number of Scans	64
Receiver Gain	127.1
Relaxation Delay	1.0000
Pulse Width	12.5000
Acquisition Time	4.0894
Spectrometer Frequency	400.13
Spectral Width	8012.8
Nucleus	1H



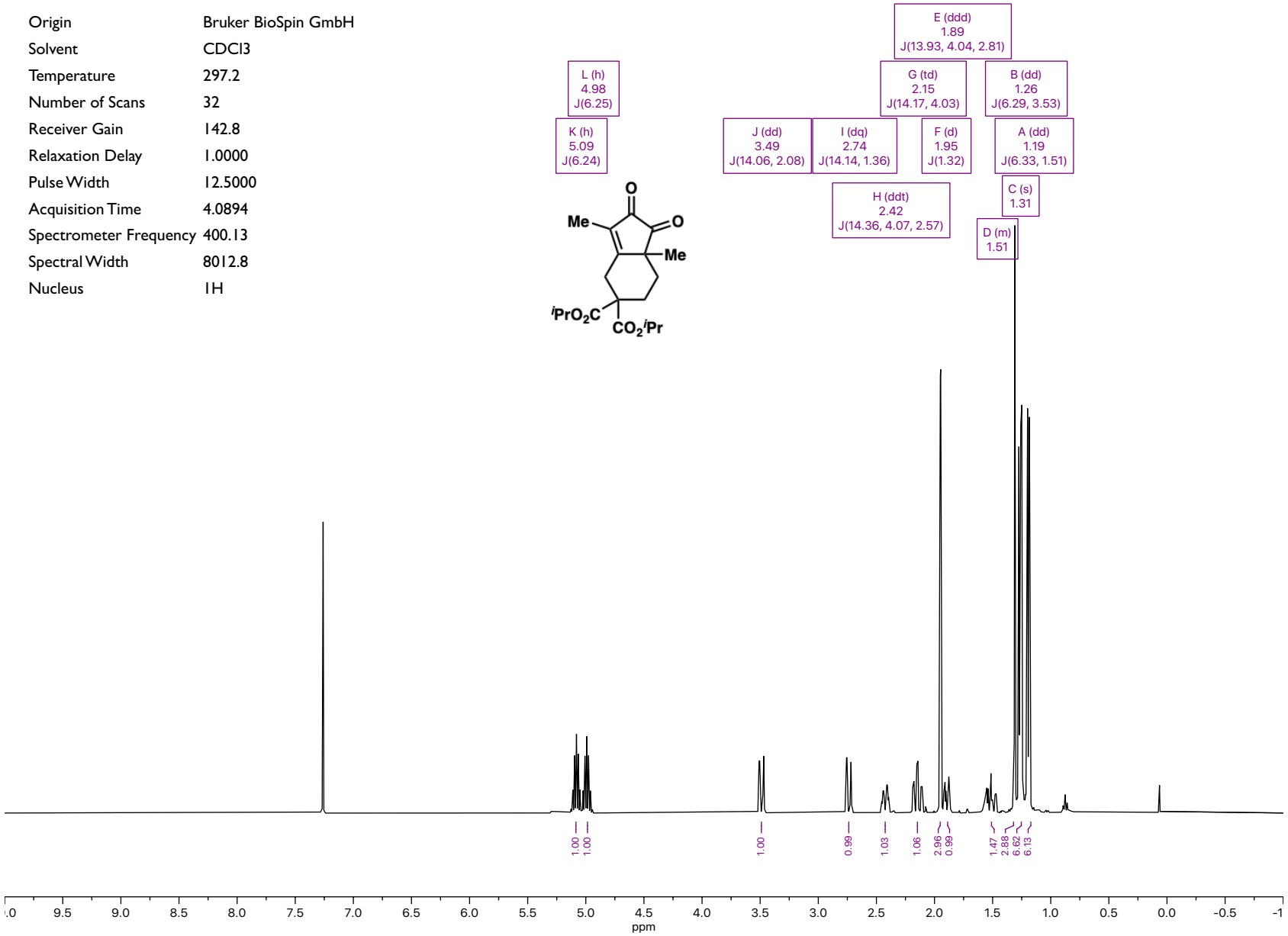
44

Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	297.1
Number of Scans	512
Receiver Gain	72.0
Relaxation Delay	1.0000
Pulse Width	10.0000
Acquisition Time	1.3631
Spectrometer Frequency	100.62
Spectral Width	24038.5
Nucleus	13C



45

Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	297.2
Number of Scans	32
Receiver Gain	142.8
Relaxation Delay	1.0000
Pulse Width	12.5000
Acquisition Time	4.0894
Spectrometer Frequency	400.13
Spectral Width	8012.8
Nucleus	1H



45

Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	297.2
Number of Scans	512
Receiver Gain	50.3
Relaxation Delay	1.0000
Pulse Width	10.0000
Acquisition Time	1.3631
Spectrometer Frequency	100.62
Spectral Width	24038.5
Nucleus	13C