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Supporting Information

Site-Selective *trans*-Hydrostannation of 1,3- and 1,*n*-Diynes: Application to the Total Synthesis of Typhonosides E and F, and a Fluorinated Cerebroside Analogue

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Author Contributions

X.M. Data curation: Equal; Investigation: Lead; Writing – review & editing: Supporting
A.L. Data curation: Equal; Investigation: Equal; Writing – review & editing: Supporting
D.R. Data curation: Equal; Investigation: Equal; Writing – review & editing: Supporting
K.H. Data curation: Equal; Investigation: Equal; Writing – review & editing: Supporting.

SUPPLEMENTARY CRYSTALLOGRAPHIC INFORMATION

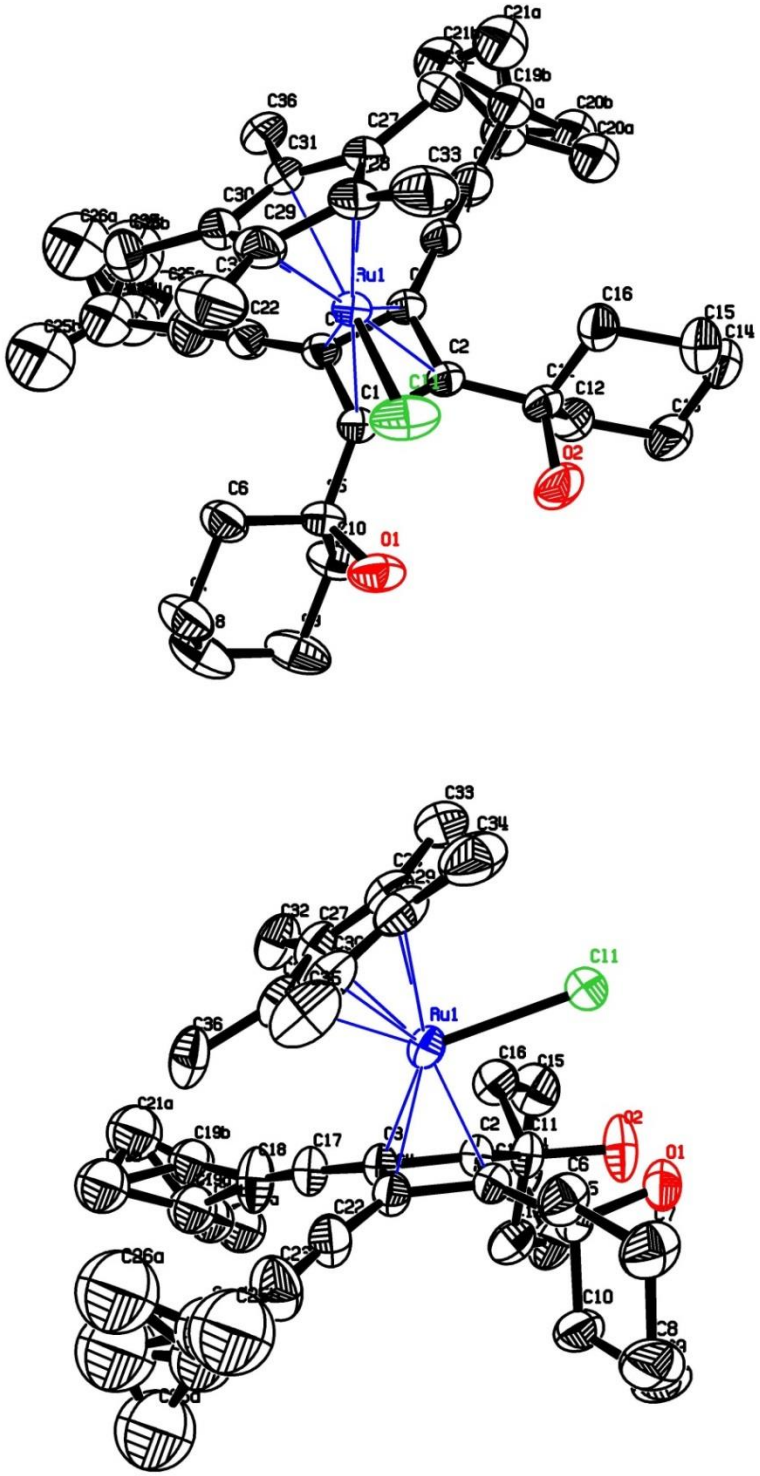


Figure S1. Structure of complex **5** in the solid state in two different projections; hydrogen atoms are omitted for clarity

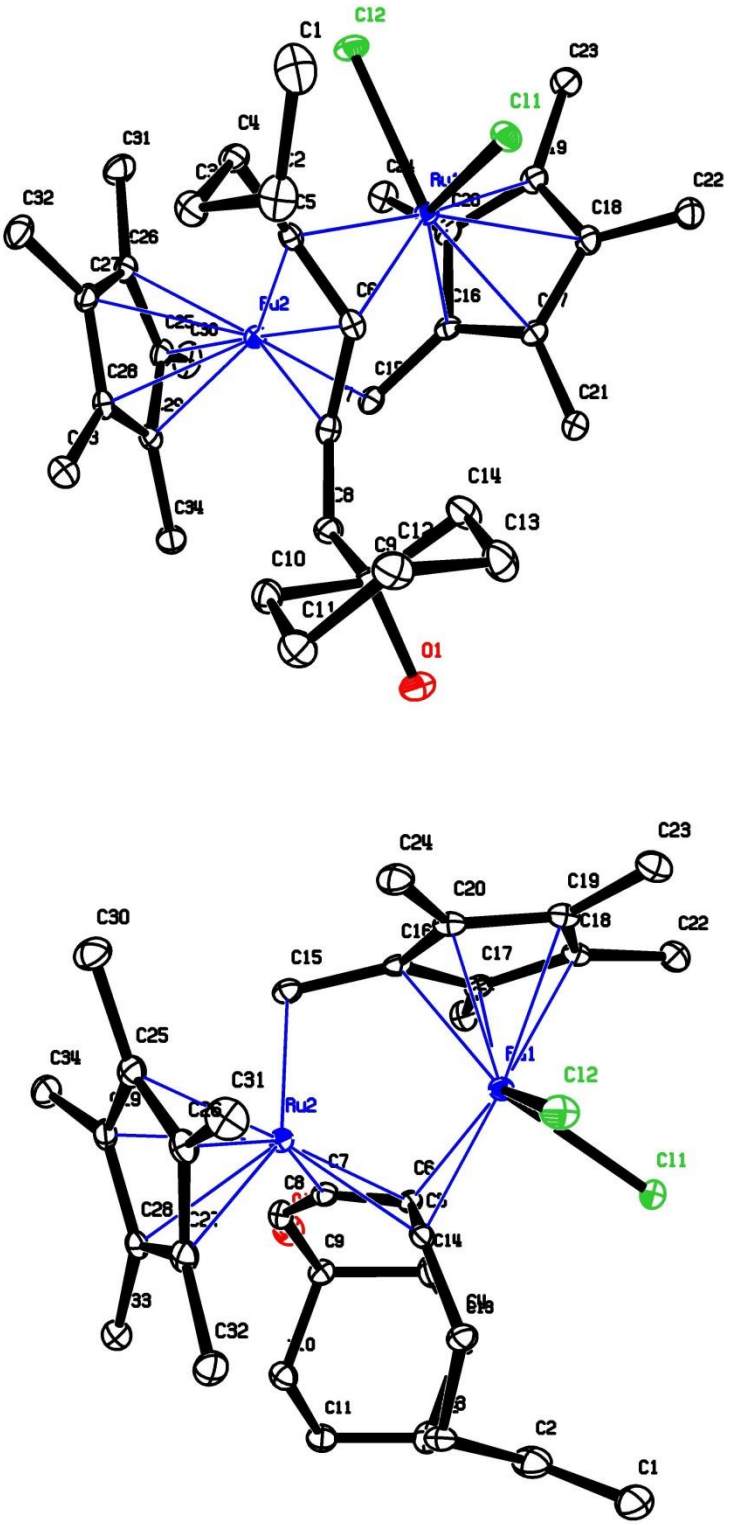
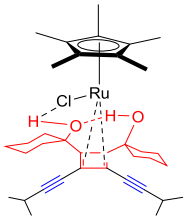


Figure S2. Structure of complex **11** in the solid state in two different projections; hydrogen atoms are omitted for clarity

Preparation and X-ray Crystal Structure Analysis of Complex 5. 1-(5-Methylhexa-1,3-diyn-1-yl)cyclohexan-1-ol (28.6 mg, 0.150 mmol) was added to a solution of $[Cp^*RuCl]_4$ (40.8 mg, 0.037 mmol) in CH_2Cl_2 (5 mL) at -20°C. The mixture was stirred and quickly warmed to 25°C on a water bath, until a colour change from brown to cherry-red was observed. Cooling to -20°C, followed by evaporation of the volatile components at this temperature afforded a purple paste, which was dissolved in pentane (10 mL). The pentane solution was filtered while maintaining the mixture cold, and the supernatant was allowed to stand at -25°C. Brown crystals suitable for X-ray diffraction were collected after 3 days.

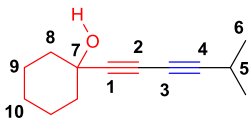


C_{36} H_{51} Cl O_2 Ru, M_r = 652.28 g · mol^{-1}, orange plate, crystal size 0.148 x 0.121 x 0.040 mm^3, orthorhombic, space group *P*bca, *a* = 19.930(2) Å, *b* = 14.4513(16) Å, *c* = 23.442(3) Å, *V* = 6751.5(13) $Å^3$, *T* = 200 K, *Z* = 8, D_{calc} = 1.283 g · cm^3, λ = 0.71073 Å, μ(*Mo-K*$_\alpha$) = 0.572 mm^{-1}, Empirical absorption correction (Tmin = 0.91, Tmax = 0.98), Bruker-AXS Kappa Mach3 APEX-II-diffractometer, 3.466 < θ < 36.481°, 259787 measured reflections, 16470 independent reflections, 8595 reflections with $I > 2\sigma(I)$, R_{int} = 0.129. The structure was solved by direct methods and refined by full-matrix least-squares against F^2 to R_1 = 0.053 [$I > 2\sigma(I)$], wR_2 = 0.150, 367 parameters. H atoms riding, *S* = 1.010, Extinction coefficient = 0.00057(15), residual electron density 0.7 / -1.2 e · $Å^{-3}$. **CCDC-1823583**.

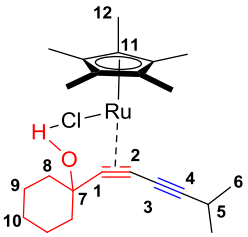
X-ray Crystal Structure Analysis of Complex 11: C_{34} H_{50} Cl_2 O Ru_2, M_r = 747.78 g · mol^{-1}, orange plate, crystal size 0.177 x 0.078 x 0.041 mm^3, triclinic, space group $P\bar{1}$, *a* = 9.7199(12) Å, *b* = 11.4333(14) Å, *c* = 14.5446(18) Å, α = 87.256(2)°, β = 75.124(2)°, γ = 77.318(2)°, *V* = 1524.0(3) $Å^3$, *T* = 100 K, *Z* = 2, D_{calc} = 1.630 g · cm^3, λ = 0.71073 Å, μ(*Mo-K*$_\alpha$) = 1.193 mm^{-1}, Empirical absorption correction (Tmin = 0.95, Tmax = 0.99), Bruker-AXS Kappa Mach3 APEX-II-diffractometer, 2.654 < θ < 31.262°, 45434 measured reflections, 9843 independent reflections, 7663 reflections with $I > 2\sigma(I)$, R_{int} = 0.129. The structure was solved by direct methods and refined by full-matrix least-squares against F^2 to R_1 = 0.030 [$I > 2\sigma(I)$], wR_2 = 0.063, 366 parameters. H atoms riding, *S* = 1.017, residual electron density 0.7 / -0.7 e · $Å^{-3}$. **CCDC-1823582**.

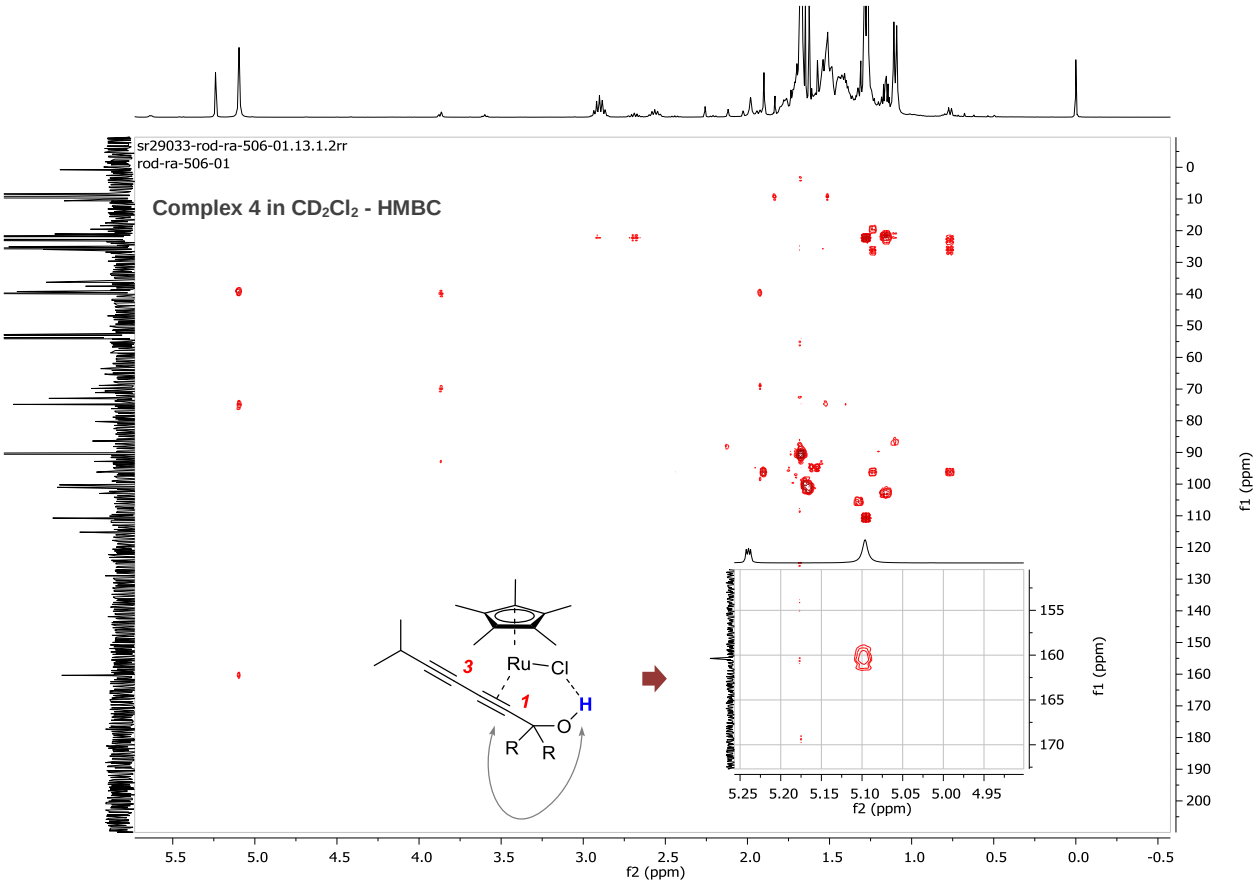
Complex 4 and Reference Data

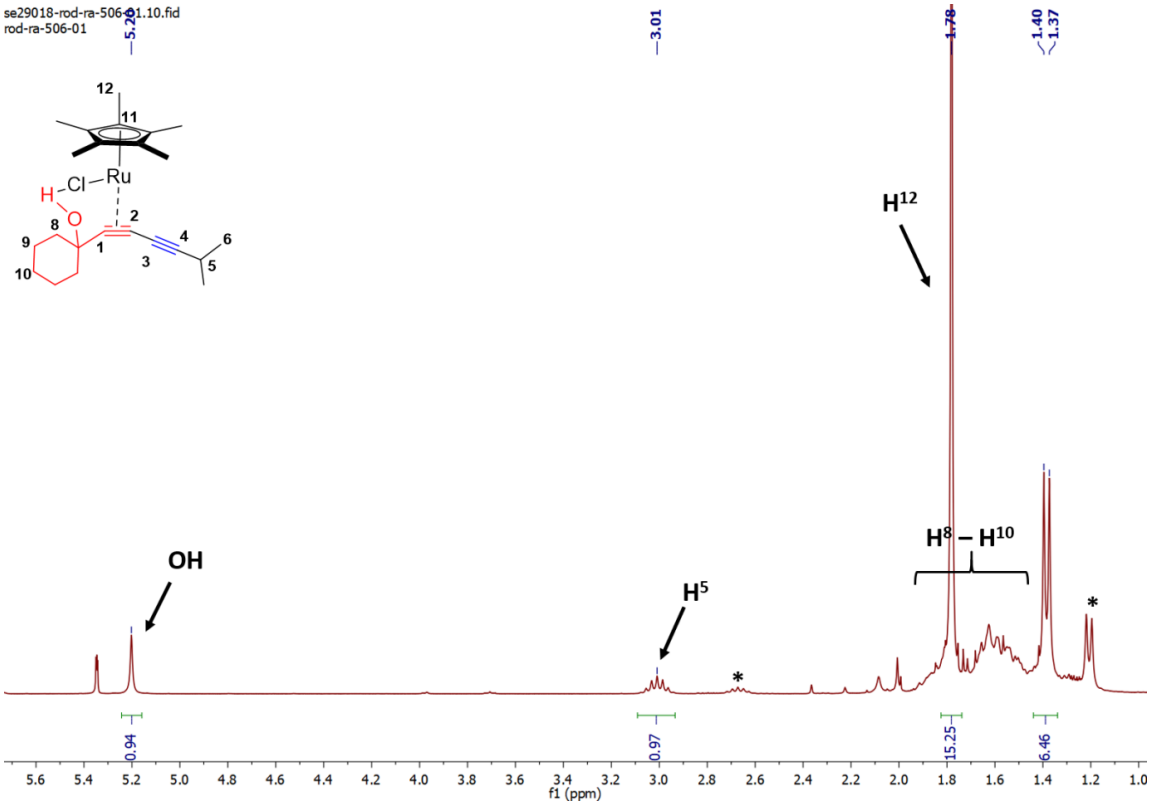
1-(5-Methylhexa-1,3-diyn-1-yl)cyclohexan-1-ol. ^{1}H NMR (400 MHz, CD_2Cl_2, RT) δ 2.65 (hept, *J* = 6.9 Hz, H^5, 1H), 1.99 (s, 1H, OH), 1.91 – 1.22 (m, 10H, H^8-H^{10}), 1.18 (d, *J* = 6.9 Hz, 6H, H^6) ^{13}C{^{1}H} NMR (101 MHz, CD_2Cl_2) δ 86.5 (C^1) , 80.2 (C^4), 68.9 (C^7), 68.7 (C^2), 63.5 (C^3), 39.7 (C^8), 25.0 (C^{10}), 23.1 (C^9), 22.2 (C^6), 21.0 (C^5).



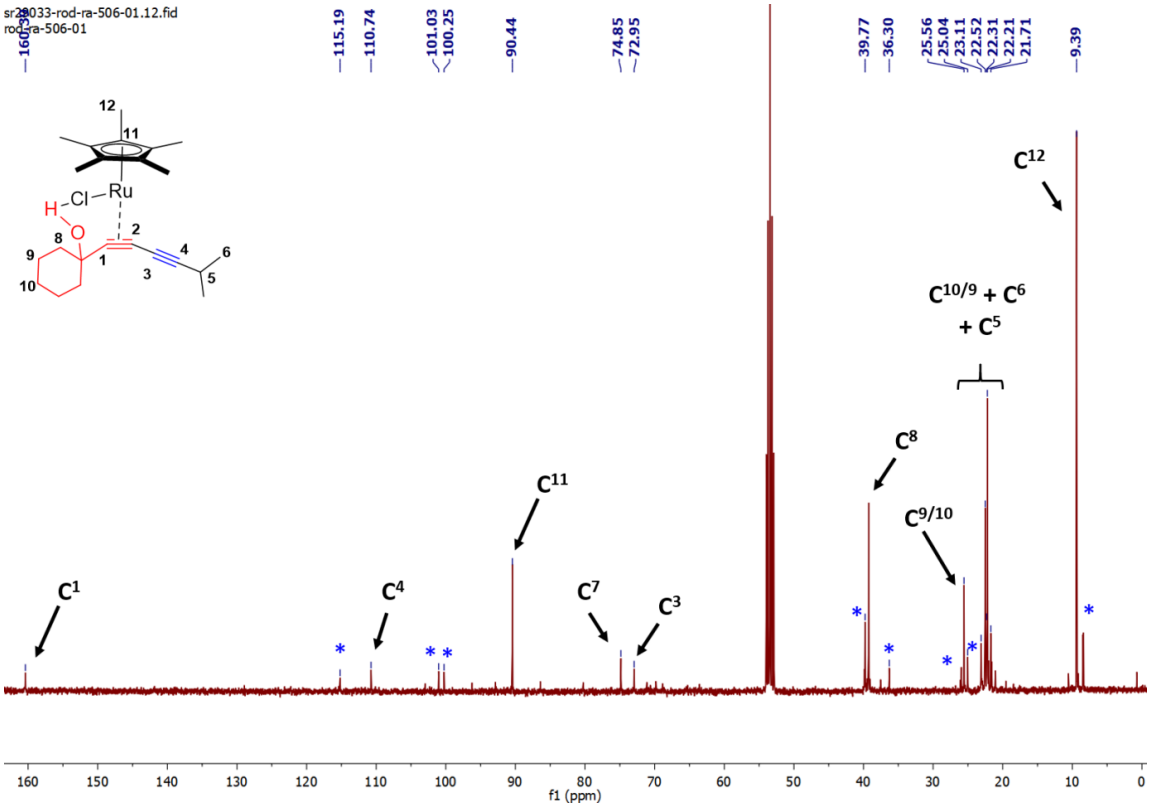
Complex 4. 1-(5-Methylhexa-1,3-diyn-1-yl)cyclohexan-1-ol (8.4 mg, 0.044 mmol) was added to a solution of $[Cp^*RuCl]_4$ (12 mg, 0.011 mmol) in CD_2Cl_2 (0.5 mL) at -20°C in an NMR tube. The mixture was shaken and quickly warmed to 25°C on a water bath. A colour change from brown to cherry-red was observed. NMR spectroscopy indicates full conversion to the title complex. ^{1}H NMR (400 MHz, CD_2Cl_2, RT) δ 5.20 (s, 1H, OH), 3.10 (pseudopent, *J*=7 Hz 1H, H^5), 1.92 – 1.45 (m, 10H, H^8-H^{10}), 1.78 (s, 15H, H^{12}), 1.38 (d, *J* = 6.9 Hz, 6H, H^6). $^{13}C\{^1H\}$ (101 MHz, CD_2Cl_2) 160.4 (C^1), C2 not observed, 110.7 (C^3), 90.4 (C^{11}), 74.9 (C^7), 73.0 (C^3), 39.8 (C^8), 25.6 (C^9 or C^{10}), 23.1 (C^{10} or C^9), 22.6 (C^6), 22.2 (C^5), 9.4 (C^{12}).







* denotes residual resonances of un-coordinated alkyne

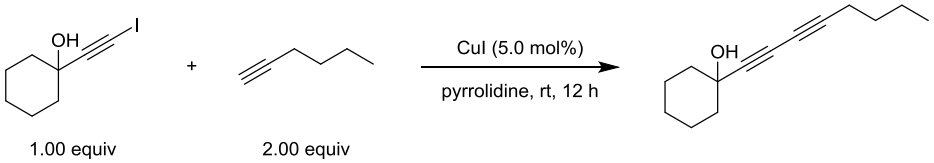


* denotes decomposition during acquisition of the ^{13}C spectrum at RT

General Information

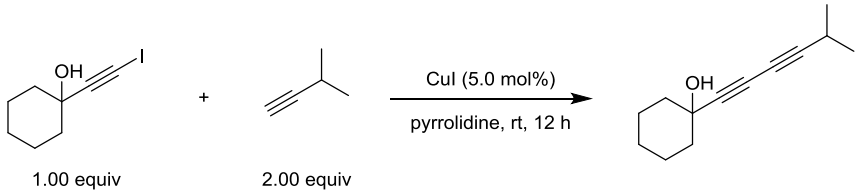
All reactions were carried out under Ar in glassware dried with a heat gun under vacuum (Schlenk line). The solvents were purified by distillation over the indicated drying agents and were transferred under Ar: THF, Et_2O (Mg/anthracene), acetone (B_2O_3), CH_2Cl_2, toluene (Na/K), MeOH (Mg, stored over 3Å MS), DMPU (CaH_2); DMF, CH_3CN, NEt_3 and pyridine were dried by an adsorption solvent purification system based on molecular sieves. Thin layer chromatography (TLC): Macherey-Nagel precoated plates (POLYGRAM®SIL/UV254); Flash chromatography: Merck silica gel 60 (40-63 µm or 15-40 µm (fine)) with pre-distilled or HPLC grade solvents. NMR: Spectra were recorded on a Bruker AV 400, AV 500 or AV 600 spectrometer in the solvents indicated; chemical shifts (δ) are given in ppm relative to TMS, coupling constants (*J*) in Hz. The solvent signals were used as references and the chemical shifts converted to the TMS scale ($CDCl_3$ at 7.26 and 77.16 ppm for ^1H and ^{13}C NMR spectroscopy, respectively; C_6D_6 at 7.16 ppm and 128.06 ppm for ^1H and ^{13}C NMR spectroscopy, respectively; [D_5]-pyridine at 8.70, 7.55 and 7.15 ppm for ^1H NMR and 149.64, 135.26 and 123.25 ppm for ^{13}C NMR spectroscopy, respectively). ^1H NMR data are reported as δ (ppm) (s = singlet, d = doublet, t = triplet, q = quartet, qui = quintet, m = multiplet or unresolved, br = broad signal, app = appearing as; coupling constants (*J*) in Hz; integration). ^{13}C NMR spectra were recorded with broadband ^1H decoupling. ^{119}Sn NMR spectra were recorded using Me_4Sn as external standard. IR: Spectrum One (Perkin-Elmer) spectrometer, wavenumbers ($\tilde{\nu}$) in cm^{-1}. MS (EI): Finnigan MAT 8200 (70 eV), ESIMS: ESQ 3000 (Bruker), accurate mass determinations: Bruker APEX III FT-MS (7 T magnet) or MAT 95 (Finnigan). Unless stated otherwise, all commercially available compounds (ABCR, Acros, Aldrich, Strem, Apollo Scientific, TCI) were used as received. $[Cp^*RuCl_2]_n$ was prepared according to literature procedures and was stored under Argon.[1] $Ph_2PO_2NBu_4$ was prepared according to the literature procedures.[2] Commercial Bu_3SnH is stabilized with 0.05% of 3,5-di-*tert*-butyl-4-hydroxytoluene, which was not removed in the reactions described herein.

Substrates

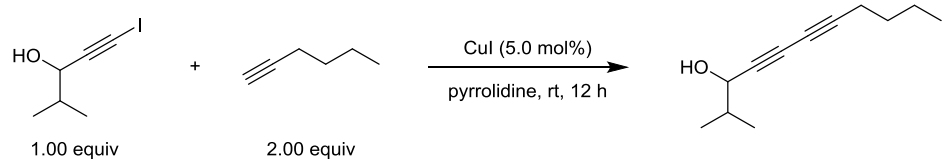


General Procedure for Cadiot-Chodkiewicz Coupling: Preparation of 1-(Octa-1,3-diyn-1-yl)cyclohexan-1-ol (9). CuI (57.0 mg, 0.30 mmol, 5.0 mol%) was added in one portion. at 0°C to a solution of 1-hexyne (1.4 mL, 12.0 mmol) and 1-(iodoethynyl)cyclohexan-1-ol (1.50 g, 6.00 mmol) in pyrrolidine (12 mL). The mixture was allowed to warm to room temperature and was stirred for 12 h. A sat. aqueous solution of NH_4Cl (30 mL) was added and the aqueous phase was extracted with Et_2O (3 × 30 mL). The combined organic phases were dried over $MgSO_4$, filtered and concentrated *in vacuo*. The residue was purified by flash chromatography (hexane/EtOAc: 98/2 to 96/4) to afford the title compound as a colorless

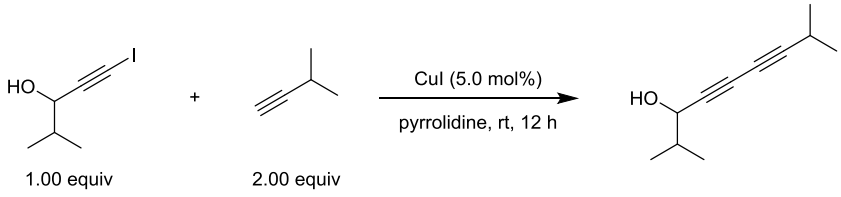
oil (1.20 g, 97%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.29 (t, *J* = 6.9 Hz, 2H), 1.99-1.80 (m, 3H), 1.68 (dt, *J* = 11.6, 4.3 Hz, 2H), 1.62-1.48 (m, 7H), 1.47-1.36 (m, 2H), 1.32-1.17 (m, 1H), 0.91 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 81.8, 79.2, 69.4, 69.3, 64.6, 39.9, 30.4, 25.2, 23.3, 22.1, 19.1, 13.7; IR (neat, cm^{-1}): 3341, 2933, 2859, 2249, 1448, 1342, 1290, 1259, 1065, 964; HRMS (ESI): *m/z* calcd for $C_{14}H_{20}ONa$ $[M+Na]^+$ 227.1406; found: 227.1407.



1-(5-Methylhexa-1,3-diyn-1-yl)cyclohexan-1-ol (1): Prepared analogously as a pale yellow oil (0.74 g, 48%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.63 (hept, *J* = 6.9 Hz, 1H), 2.04 (s, 1H), 1.94-1.84 (m, 2H), 1.73-1.63 (m, 2H), 1.59-1.47 (m, 5H), 1.29-1.21 (m, 1H), 1.19 (s, 3H), 1.17 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 86.6, 80.0, 69.3, 69.2, 63.9, 39.9, 25.2, 23.3, 22.5, 22.5, 21.2; IR (neat, cm^{-1}): 3355, 2971, 2933, 2859, 2249, 1447, 1384, 1343, 1319, 1288, 1259, 1162, 1064, 963, 903, 848; HRMS (ESI): *m/z* calcd for $C_{13}H_{18}ONa$ $[M+Na]^+$ 213.1250; found: 213.1248.

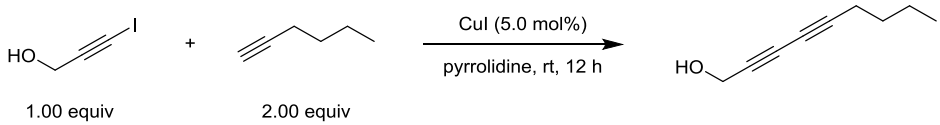


2-Methylundeca-4,6-diyn-3-ol (S1): Prepared analogously as a pale yellow oil (0.76 g, 55%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.21 (t, *J* = 5.8 Hz, 1H), 2.29 (td, *J* = 7.0, 1.0 Hz, 2H), 1.95-1.83 (m, 1H), 1.79-1.70 (m, 1H), 1.59-1.47 (m, 2H), 1.47- 1.34 (m, 2H), 1.01 (d, *J* = 7.6 Hz, 3H), 0.99 (d, *J* = 7.7 Hz, 3H), 0.91 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 81.6, 75.5, 70.8, 68.5, 64.5, 34.8, 30.3, 22.1, 19.1, 18.2, 17.6, 13.7; IR (neat, cm^{-1}): 3337, 2961, 2933, 2873, 2253, 1466, 1382, 1322, 1028; HRMS (ESI): *m/z* calcd for $C_{12}H_{18}ONa$ $[M+Na]^+$ 201.1250; found: 201.1250.

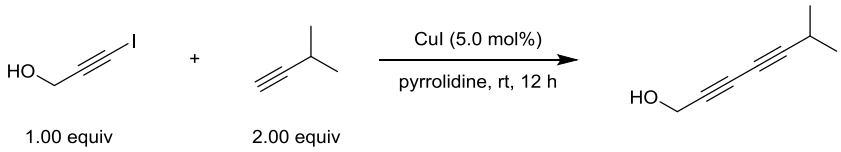


2,8-Dimethylnona-4,6-diyn-3-ol (6): Prepared analogously as a pale yellow oil (0.81 g, 55%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.21 (td, *J* = 5.8, 0.9 Hz, 1H), 2.64 (heptd, *J* = 6.9, 0.9 Hz, 1H), 1.89 (heptd, *J* = 6.8, 5.7 Hz, 1H), 1.74 (d, *J* = 5.8 Hz, 1H), 1.19 (d, *J* = 7.0 Hz, 6H), 1.01 (d, *J* = 6.7 Hz, 3H), 0.99 (d, *J* = 6.7 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 86.5, 76.3, 70.6, 68.5, 63.9, 34.8, 22.5, 21.2, 18.2, 17.6; IR (neat,

cm^{-1}): 3356, 2970, 2932, 2873, 2251, 1467, 1384, 1367, 1318, 1153, 1087, 1025, 951; HRMS (ESI): *m/z* calcd for $C_{11}H_{16}ONa$ $[M+Na]^+$ 187.1093; found: 187.1090.

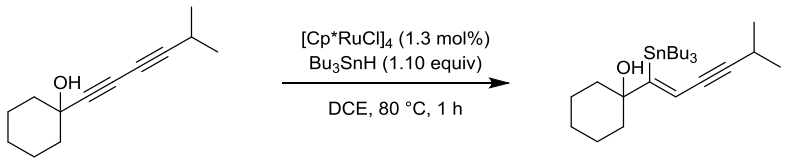


Nona-2,4-diyn-1-ol (S2): Prepared analogously as a pale yellow oil (0.29 g, 59%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.32 (dt, *J* = 6.3, 1.1 Hz, 2H), 2.29 (tt, *J* = 7.1, 1.1 Hz, 2H), 1.57 (s, 1H), 1.56-1.48 (m, 2H), 1.47-1.36 (m, 2H), 0.91 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 82.0, 73.6, 71.1, 64.5, 51.7, 30.3, 22.0, 19.1, 13.7; IR (neat, cm^{-1}): 3332, 2959, 2933, 2872, 2255, 1465, 1426, 1354, 1231, 1022, 633; HRMS (ESI): *m/z* calcd. for $C_9H_{12}ONa$ $[M+Na]^+$ 159.0780; found: 159.0778.



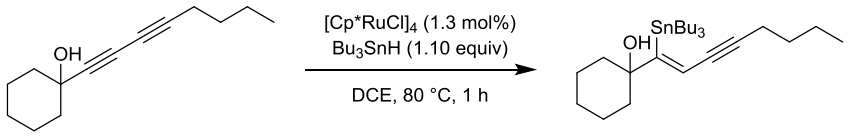
6-Methylhepta-2,4-diyn-1-ol (S3): Prepared analogously as a pale yellow oil (0.78 g, 82%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.32 (d, *J* = 1.0 Hz, 2H), 2.64 (heptt, *J* = 7.0, 1.0 Hz, 1H), 1.62 (s, 1H), 1.20 (s, 3H), 1.18 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 86.9, 74.4, 70.9, 63.8, 51.7, 22.5, 21.2; IR (neat, cm^{-1}): 3324, 2973, 2933, 271, 2255, 1467, 1448, 1364, 1320, 1235, 1152, 1087, 1017, 923, 825; HRMS (ESI): *m/z* calcd for $C_8H_{10}ONa$ $[M+Na]^+$ 145.0624; found: 145.0624.

Ruthenium Catalyzed *trans*-Hydrostannation Reactions

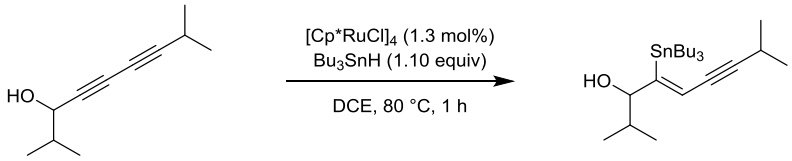


General Procedure for Hydrostannation at 80°C. Preparation of (*Z*)-1-(5-Methyl-1-(tributylstannyl)hex-1-en-3-yn-1-yl)cyclohexan-1-ol (2): A solution of tributyltin hydride (42 µL, 0.16 mmol) in 1,2-dichloroethane (1 mL) was added dropwise (over 60 min) under Argon to a stirred solution of diyne **1** (27.0 mg, 0.14 mmol) and $[Cp^*RuCl]_4$ (1.8 mg, 1.7 µmol, 1.25 mol%) in 1,2-dichloroethane (0.8 mL, 0.2 M) at 80°C, which had been mixed at room temperature and stirred for 1-2 min. Once the addition was complete, stirring was continued for 5 min at the same temperature before the mixture was allowed to reach ambient temperature. The solvent was evaporated and the residue was purified by flash chromatography (hexane/CH_2Cl_2: 80/20 to 70/30) to give the title compound as a light yellow oil (45.0 mg, 66%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.31 (d, *J* = 2.2 Hz, J_{Sn-H} = 119.6 Hz, 1H), 2.69 (hept, *J* = 6.8, 2.1 Hz, 1H), 1.69-1.61 (m, 1H), 1.58 (m, 4H), 1.54-1.47 (m, 10H), 1.39-1.26 (m, 6H), 1.23 (s, 1H), 1.19 (d, *J* = 6.9 Hz, 6H), 1.14-1.09 (m, 1H), 1.08-1.02 (m, 6H), 0.90 (t, *J* = 7.3 Hz, 9H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 169.0, 116.2, 97.9, 80.1, 76.0, 37.4, 29.4, 27.6, 25.6, 23.0, 22.1, 21.5, 13.9, 12.0; ^{119}Sn NMR (149 MHz,

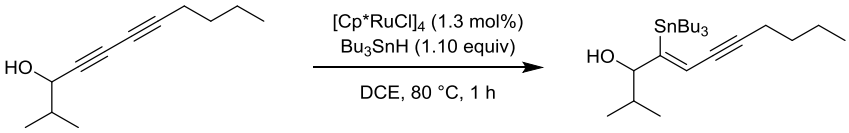
$CDCl_3$): δ -47.9; IR (neat, cm^{-1}): 3412, 2955, 2928, 2854, 2189, 1463, 1376, 1317, 1255, 1161, 1071, 959, 862, 670; HRMS (ESI): *m/z* calcd for $C_{25}H_{46}OSnNa$ $[M+Na]^+$ 505.2462; found: 505.2464.



(*Z*)-1-(1-(Tributylstannyl)oct-1-en-3-yn-1-yl)cyclohexan-1-ol (S4): Prepared analogously as a pale yellow oil (42%, NMR). ^{1}H NMR (600 MHz, $CDCl_3$): δ 6.29 (t, *J* = 2.3 Hz, J_{Sn-H} = 118.9 Hz, 1H), 2.31 (td, *J* = 7.2, 2.2 Hz, 2H), 1.70-1.63 (m, 1H), 1.63-1.56 (m, 4H), 1.55-1.44 (m, 12H), 1.44-1.37 (m, 2H), 1.33 (h, *J* = 7.3 Hz, 6H), 1.24 (s, 1H), 1.20-1.11 (m, 1H), 1.06-1.00 (m, 6H), 0.91 (t, *J* = 7.3 Hz, 3H), 0.89 (t, *J* = 7.3 Hz, 9H); ^{13}C NMR (151 MHz, $CDCl_3$): δ 169.2, 116.2, 92.7, 80.8, 76.0, 37.5, 30.9, 29.4, 27.6, 25.6, 22.3, 22.3, 22.1, 19.6, 13.9, 13.8, 12.0; ^{119}Sn NMR (149 MHz, $CDCl_3$): δ -48.5; IR (neat, cm^{-1}): 3412, 2955, 2928, 2854, 2183, 1571, 1462, 1376, 1257, 1163, 1071, 958, 863, 668, 595; HRMS (ESI): *m/z* calcd for $C_{26}H_{48}OSnNa$ $[M+Na]^+$ 519.2619; found: 519.2616.

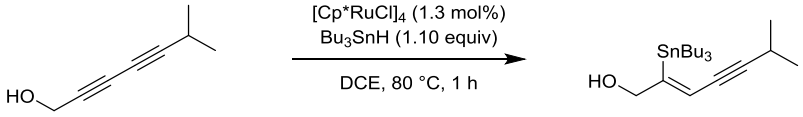


(*Z*)-2,8-Dimethyl-4-(tributylstannyl)non-4-en-6-yn-3-ol (7): Prepared analogously as a pale yellow oil (67.0 mg, 89%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.19 (dd, *J* = 2.1, 1.2 Hz, J_{Sn-H} = 111.5 Hz, 1H), 3.81 (ddd, *J* = 7.3, 3.3, 1.2 Hz, J_{Sn-H} = 51.1 Hz, 1H), 2.69 (heptd, *J* = 6.9, 2.0 Hz, 1H), 1.66-1.57 (m, 1H), 1.56-1.47 (m, 6H), 1.41 (d, *J* = 3.3 Hz, 1H), 1.39-1.27 (m, 6H), 1.19 (d, *J* = 6.9 Hz, 6H), 1.09-1.00 (m, 6H), 0.94 (d, *J* = 6.9 Hz, 3H), 0.90 (t, *J* = 7.3 Hz, 9H), 0.83 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) : δ 163.1, 120.1, 97.1, 85.1, 79.9, 33.3, 29.4, 27.6, 23.0, 23.0, 21.4, 20.0, 17.7, 13.9, 10.9; ^{119}Sn NMR (149 MHz, $CDCl_3$): δ -50.1; IR (neat, cm^{-1}): 3479, 2956, 2922, 2871, 220, 1574, 1464, 1376, 1317, 1262, 1135, 1070, 1014, 595, 870, 667, 596; HRMS (ESI): *m/z* calcd for $C_{23}H_{44}OSnNa$ $[M+Na]^+$ 479.2306; found: 479.2303.

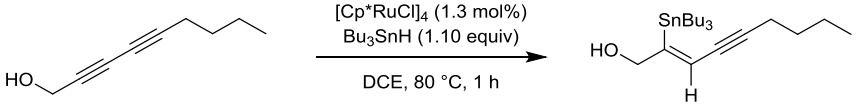


(*Z*)-2-Methyl-4-(tributylstannyl)undec-4-en-6-yn-3-ol (S5): Prepared analogously as a pale yellow oil (45.0 mg, 64%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.18 (q, *J* = 2.2 Hz, J_{Sn-H} = 112.0 Hz, 1H), 3.81 (ddd, *J* = 7.3, 3.4, 1.2 Hz, J_{Sn-H} = 51.1 Hz, 1H), 2.31 (td, *J* = 7.1, 2.2 Hz, 2H), 1.65-1.57 (m, 1H), 1.55-1.47 (m, 8H), 1.44-1.41 (m, 3H), 1.37-1.26 (m, 6H), 1.06-1.00 (m, 6H), 0.94 (d, *J* = 6.6 Hz, 3H), 0.92-0.87 (m, 12H), 0.83 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 163.3, 120.1, 92.0, 85.1, 80.7, 33.3, 30.9, 29.4, 27.6, 22.3, 20.0, 19.5, 17.7, 13.9, 13.8, 10.9; ^{119}Sn NMR (149 MHz, $CDCl_3$): δ -50.5; IR (neat, cm^{-1}): 3492,

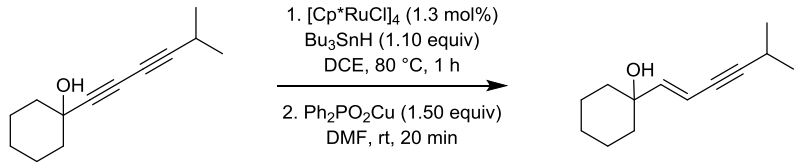
2956, 2928, 2871, 2204, 1573, 1463, 1377, 1262, 1073, 1017, 872, 665; HRMS (ESI): *m/z* calcd for $C_{24}H_{46}OSnNa$ $[M+Na]^+$: 493.2462; found: 493.2462.



(*Z*)-6-Methyl-2-(tributylstannyl)hept-2-en-4-yn-1-ol (S6): Prepared analogously as a pale yellow oil (64.0 mg, 76%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.30 (q, *J* = 1.9 Hz, J_{Sn-H} = 109.8 Hz, 1H), 4.27 (dd, *J* = 6.1, 1.8 Hz, J_{Sn-H} = 30.5 Hz, 2H), 2.68 (heptd, *J* = 6.9, 2.0 Hz, 1H), 1.60-1.46 (m, 6H), 1.38-1.26 (m, 7H), 1.19 (d, *J* = 6.9 Hz, 6H), 1.07-1.01 (m, 6H), 0.90 (t, *J* = 7.3 Hz, 9H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 158.8, 119.3, 96.9, 80.1, 69.6, 29.4, 27.6, 23.0, 21.4, 13.9, 10.1; ^{119}Sn NMR (149 MHz, $CDCl_3$): δ -49.2; IR (neat, cm^{-1}): 3282, 2956, 2921, 2871, 2852, 2221, 1583, 1463, 1376, 1318, 1071, 1003, 961, 861, 665, 596; HRMS (ESI): *m/z* calcd for $C_{20}H_{38}OSnNa$ $[M+Na]^+$ 437.1836; found: 437.1837.

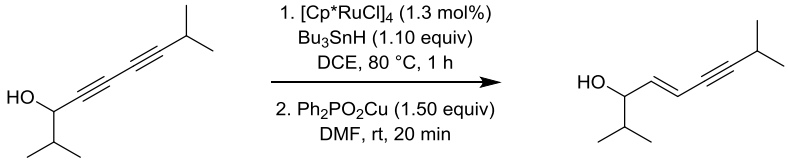


(*Z*)-2-(Tributylstannyl)non-2-en-4-yn-1-ol (S7): Prepared analogously as a pale yellow oil (50.0 mg, 64%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.29 (p, *J* = 2.0 Hz, J_{Sn-H} = 109.1 Hz, 1H), 4.27 (dd, *J* = 6.1, 1.8 Hz, J_{Sn-H} = 29.3 Hz, 2H), 2.31 (td, *J* = 7.1, 2.2 Hz, 2H), 1.57-1.47 (m, 8H), 1.47-1.37 (m, 2H), 1.37-1.25 (m, 7H), 1.13-0.94 (m, 6H), 0.91 (dt, *J* = 8.7, 7.3 Hz, 12H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 159.0, 119.3, 91.7, 80.8, 69.6, 30.9, 29.4, 27.6, 22.3, 19.5, 13.9, 13.8, 10.1; ^{119}Sn NMR (149 MHz, $CDCl_3$): δ -49.6 ; IR (neat, cm^{-1}): 3309, 2955, 2925, 2871, 2854, 2215, 1577, 1463, 1376, 1291, 1075, 1009, 961, 861, 691, 666, 596; HRMS (ESI): *m/z* calcd for $C_{21}H_{40}OSnNa$ $[M+Na]^+$ 451.1993; found: 451.1991.

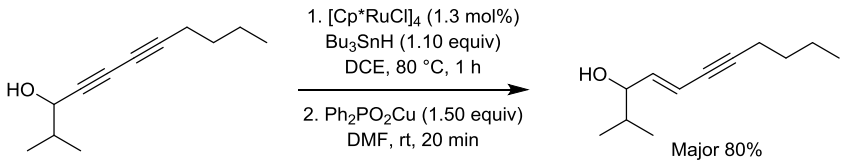


Representative Procedure for One-pot Hydrostannylation/Proto-destannylation: Preparation of (*E*)-1-(5-Methylhex-1-en-3-yn-1-yl)cyclohexan-1-ol (S8): A solution of tributyltin hydride (61 µL, 0.22 mmol) in 1,2-dichloroethane (1 mL) was added dropwise (over 30 min) under Argon to a stirred solution of diyne **1** (25.0 mg, 0.2 mmol) and $[Cp^*RuCl]_4$ (2.7 mg, 2.5 µmol, 1.25 mol%) in 1,2-dichloroethane (1 mL, 0.2 M) at 80°C, which had been mixed at room temperature and stirred for 1-2 min. Once the addition was complete, stirring was continued for 5 min at the same temperature before the reaction mixture was allowed to cool to ambient temperature. A solution of Ph_2PO_2Cu (86.0 mg, 0.3 mmol) in DMF (1 mL) was added and the resulting mixture stirred for 20 min. Et_2O (5 mL) was added before the reaction was quenched with water (5 mL). The aqueous layer was extracted with Et_2O (3 × 10 mL) and the combined extracts were dried over $MgSO_4$, filtered through a pad of SiO_2, and concentrated *in vacuo*. The crude

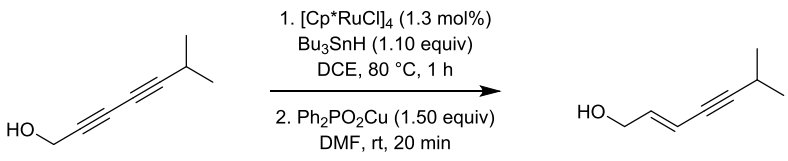
product was purified by flash chromatography (hexane/EtOAc: 90/10) to give the enyne as a colorless oil (21.0 mg, 86%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.16 (d, *J* = 16.0 Hz, 1H), 5.74 (dd, *J* = 16.0, 2.0 Hz, 1H), 2.72 (heptd, *J* = 6.7, 1.8 Hz, 1H), 1.72-1.60 (m, 2H), 1.59-1.46 (m, 7H), 1.38 (br. s, 1H), 1.31-1.21 (m, 1H), 1.19 (s, 3H), 1.17 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 149.1, 107.9, 96.6, 78.0, 71.9, 37.8, 25.5, 23.1, 22.0, 21.3; IR (neat, cm^{-1}): 3377, 2968, 2931, 2860, 2215, 1630, 1448, 1382, 1319, 1265, 1177, 1133, 1056, 988, 958; HRMS (ESI): *m/z* calcd for $C_{13}H_{20}ONa$ $[M+Na]^+$ 215.1406; found: 215.1405.



(*E*)-2,8-Dimethylnon-4-en-6-yn-3-ol (S9): Prepared analogously as a colorless oil (23.0 mg, 76%). ^{1}H NMR (400 MHz, $CDCl_3$) : δ 6.04 (dd, *J* = 15.9, 6.7 Hz, 1H), 5.68 (ddd, *J* = 15.9, 2.0, 1.3 Hz, 1H), 3.87 (ddd, *J* = 6.9, 5.9, 1.3 Hz, 1H), 2.67 (heptd, *J* = 6.8, 2.0 Hz, 1H), 1.74 (heptd, *J* = 6.9, 5.8 Hz, 1H), 1.47 (s, 1H), 1.18 (d, *J* = 6.9 Hz, 6H), 0.93 (d, *J* = 6.8 Hz, 3H), 0.90 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 142.6, 111.6, 96.6, 77.8, 77.7, 33.9, 23.1, 21.3, 18.3, 18.0; IR (neat, cm^{-1}): 3375, 2965, 2933, 2872, 2216, 1632, 1466, 1383, 1365, 1319, 1139, 1074, 1013, 956; HRMS (ESI): *m/z* calcd for $C_{11}H_{18}ONa$ $[M+Na]^+$ 189.1250; found: 189.1249.

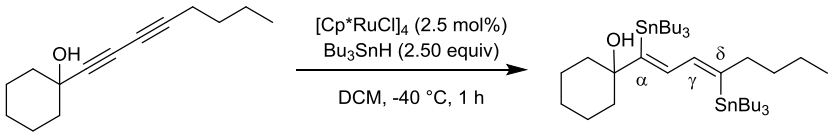


(*E*)-2-Methylundec-4-en-6-yn-3-ol (S10): Prepared analogously as a colorless oil (29.0 mg, 82%, contains some inseparable impurities). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.04 (dd, *J* = 15.9, 6.8 Hz, 1H), 5.68 (dtd, *J* = 15.9, 2.2, 1.3 Hz, 1H), 3.88 (t, *J* = 6.2 Hz, 1H), 2.30 (td, *J* = 6.8, 2.2 Hz, 2H), 1.79-1.69 (m, 1H), 1.54-1.47 (m, 2H), 1.45-1.38 (m, 2H), 0.95-0.88 (m, 9H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 142.6, 111.7, 91.3, 78.6, 77.7, 33.9, 30.9, 22.1, 19.2, 18.3, 18.0, 13.8; IR (neat, cm^{-1}): 3373, 2958, 2931, 2872, 2216, 1632, 1466, 1380, 1367, 1325, 1016, 989, 957; HRMS (ESI): *m/z* calcd for $C_{12}H_{20}ONa$ $[M+Na]^+$ 203.1406; found: 203.1408.

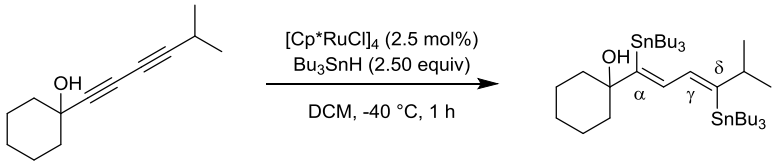


(*E*)-6-Methylhept-2-en-4-yn-1-ol (S11): Prepared analogously as a colorless oil (21.0 mg, 85%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.15 (dt, *J* = 15.8, 5.5 Hz, 1H), 5.72 (dq, *J* = 15.8, 1.9 Hz, 1H), 4.17 (dd, *J* = 5.6, 1.5 Hz, 2H), 2.66 (heptd, *J* = 6.8, 1.9 Hz, 1H), 1.53 (br. s, 1H), 1.18 (d, *J* = 6.9 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 140.2, 111.5, 96.9, 77.6, 63.3, 23.1, 21.2; IR (neat, cm^{-1}): 3342, 2970, 2932, 2871, 2217, 1465,

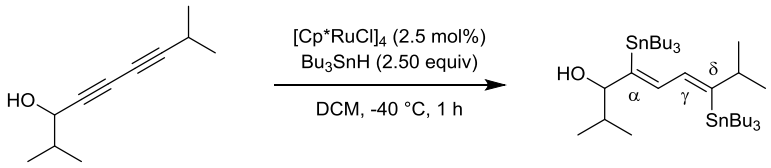
1383, 1364, 1320, 1193, 1093, 1010, 957; HRMS (ESI): *m/z* calcd for $C_8H_{12}ONa$ $[M+Na]^+$ 147.0780; found: 147.0781.



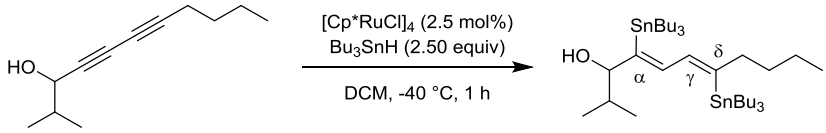
Representative Procedure for the *trans*-Hydrostannation at Low Temperature. Preparation of 1-((1*Z*,3*Z*)-1,4-Bis(tributylstannyl)octa-1,3-dien-1-yl)cyclohexan-1-ol (S12). A solution of tributyltin hydride (0.1 mL, 0.37 mmol) in CH_2Cl_2 (1 mL) was added under Argon via syringe pump over a period of 60 min to a stirred solution of diyne **9** (30.0 mg, 0.15 mmol) and $[Cp^*RuCl]_4$ (4.0 mg, 3.7 µmol, 2.5 mol%) in CH_2Cl_2 (0.75 mL, 0.2 M), which had previously been mixed at room temperature and stirred for 1-2 min. Once the addition was complete, stirring was continued for 5 min before the mixture was warmed to ambient temperature. The solvent was evaporated and the residue was purified by flash chromatography (hexane/CH_2Cl_2: 90/10) to give the distannane (63 mg, 53%) as a pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.66 (m, J_{Sn-H} = 127.5 Hz, J_{Sn-H} = 121.6 Hz, 2H), 2.27 (t, J = 6.6 Hz, J_{Sn-H} = 51.3 Hz, 2H), 1.71-1.55 (m, 7H), 1.53-1.41 (m, 14H), 1.37-1.24 (m, 17H), 1.22-1.10 (m, 1H), 1.00-0.82 (m, 33H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 159.1, 152.5, 141.0, 137.2, 76.2, 41.0, 38.1, 32.8, 29.4, 27.6, 25.8, 22.5, 22.4, 14.2, 13.9, 12.8, 10.7; ^{119}Sn NMR (149 MHz, $CDCl_3$): δ -51.3, -54.3; IR (neat, cm^{-1}): 3490, 2954, 2922, 2853, 1590, 1462, 1376, 1340, 1072, 959, 873, 665, 594; HRMS (ESI): *m/z* calcd for $C_{38}H_{76}OSn_2Na$ $[M+Na]^+$ 811.3831; found: 811.3834.



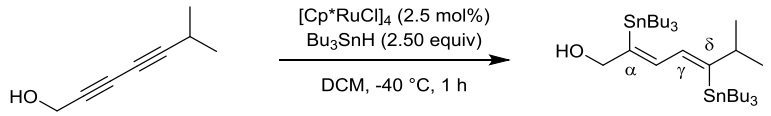
1-((1*Z*,3*Z*)-5-Methyl-1,4-bis(tributylstannyl)hexa-1,3-dien-1-yl)cyclohexan-1-ol (3): Prepared analogously as a pale yellow oil (54 mg, 44%, isomer ratio ≈ 94:6)). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.71 (m, J_{Sn-H} = 129.9 Hz, J_{Sn-H} = 127.8 Hz, 2H), 2.52 (heptd, J = 6.8, 0.8 Hz, 1H), 1.71-1.55 (m, 7H), 1.53-1.40 (m, 14H), 1.37-1.27 (m, 13H), 1.21-1.11 (m, 1H), 1.03 (d, J = 6.7 Hz, 6H), 1.01-0.91 (m, 12H), 0.88 (t, J = 7.2 Hz, 9H), 0.88 (t, J = 7.3 Hz, 9H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 159.3, 159.2, 137.3, 137.1, 76.2, 38.1, 37.8, 29.4, 27.6, 25.8, 23.2, 22.4, 13.9, 13.9, 12.8, 11.2; ^{119}Sn NMR (149 MHz, $CDCl_3$): δ -50.8, -53.6; IR (neat, cm^{-1}): 3400, 2954, 2923, 2870, 2853, 1548, 1462, 1376, 1340, 1292, 1146, 1071, 958, 873, 666, 594; HRMS (ESI): *m/z* calcd for $C_{37}H_{73}OSn_2$ $[M]^-$ 773.3709; found: 773.3729.



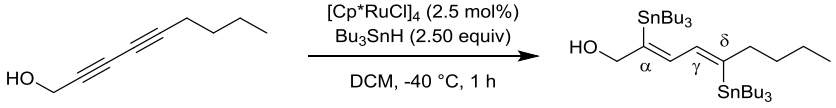
(4*Z*,6*Z*)-2,8-Dimethyl-4,7-bis(tributylstannyl)nona-4,6-dien-3-ol (8): Prepared analogously as a pale yellow oil (59 mg, 52%, isomer ratio ≈ 80:20). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.68 (m, J_{Sn-H} = 129.3 Hz, J_{Sn-H} = 120.4 Hz, 2H), 3.79 (dd, *J* = 7.8, 3.0 Hz, J_{Sn-H} = 57.9 Hz, 1H), 2.60-2.44 (m, 1H), 1.65-1.57 (m, 1H), 1.56-1.37 (m, 12H), 1.37 (d, *J* = 3.0 Hz, 1H), 1.38-1.24 (m, 12H), 1.03 (d, *J* = 6.8 Hz, 6H), 1.03-0.90 (m, 15H), 0.88 (t, *J* = 7.3 Hz, 9H), 0.88 (t, *J* = 7.3 Hz, 9H), 0.82 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 160.2, 152.1, 141.7, 136.6, 86.4, 37.6, 33.9, 29.4, 29.4, 27.6, 27.6, 23.1, 23.1, 20.1, 18.2, 13.8, 11.5, 11.2; ^{119}Sn NMR (149 MHz, $CDCl_3$): δ -50.1; -52.5; IR (neat, cm^{-1}): 3501, 2955, 2923, 2871, 2854, 1551, 1463, 1376, 1290, 1177, 1070, 1008, 881, 666; HRMS (ESI): *m/z* calcd for $C_{35}H_{72}OSn_2Na$ $[M+Na]^+$ 771.3518; found: 771.3525.



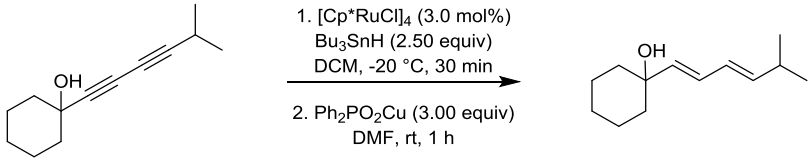
(4*Z*,6*Z*)-2-Methyl-4,7-bis(tributylstannyl)undeca-4,6-dien-3-ol (S13): Prepared analogously as a pale yellow oil (80 mg, 62%, isomer ratio ≈ 60:40). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.63 (m, J_{Sn-H} = 128.1 Hz, J_{Sn-H} = 118.6 Hz, 2H), 3.78 (dd, *J* = 7.8, 3.0 Hz, J_{Sn-H} = 58.2 Hz, 1H), 2.27 (t, *J* = 6.9 Hz, J_{Sn-H} = 49.4 Hz, 2H), 1.67-1.57 (m, 1H), 1.54-1.39 (m, 12H), 1.38 (d, *J* = 3.0 Hz, 1H), 1.36-1.25 (m, 16H), 1.02-0.85 (m, 36H), 0.81 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 153.5, 152.0, 141.5, 140.5, 86.3, 41.0, 33.9, 32.6, 29.4, 29.4, 27.6, 27.6, 22.5, 20.1, 18.2, 14.2, 13.9, 13.8, 11.5, 10.7; ^{119}Sn NMR (149 MHz, $CDCl_3$): δ -50.8, -53.1; IR (neat, cm^{-1}): 3493, 2955, 2923, 2871, 2854, 1463, 1376, 1071, 1009, 960, 874, 664; HRMS (ESI): *m/z* calcd for $C_{36}H_{74}OSn_2Na$ $[M+Na]^+$ 785.3674; found: 785.3674.



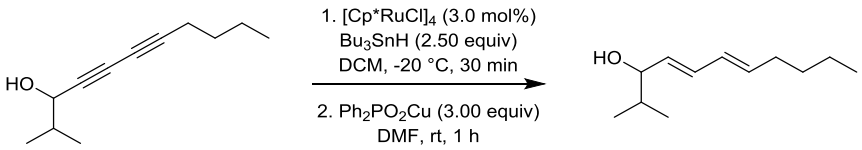
(2*Z*,4*Z*)-6-Methyl-2,5-bis(tributylstannyl)hepta-2,4-dien-1-ol (S14): Prepared analogously as a pale yellow oil (90 mg, 67%, isomer ratio ≈ 86:14). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.79 (m, J_{Sn-H} = 116.9 Hz, 1H), 6.65 (m, J_{Sn-H} = 128.9 Hz, 1H), 4.27 (dd, *J* = 6.1, 1.5 Hz, J_{Sn-H} = 38.7, 2H), 2.53 (heptd, *J* = 6.8, 1.2 Hz, 1H), 1.54-1.43 (m, 12H), 1.39-1.24 (m, 12H), 1.11 (t, *J* = 6.1 Hz, 1H), 1.03 (d, *J* = 6.0 Hz, 6H), 1.01-0.92 (m, 12H), 0.88 (t, *J* = 7.3 Hz, 9H), 0.88 (t, *J* = 7.3 Hz, 9H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 160.9, 147.9, 141.9, 136.8, 70.8, 37.6, 29.4, 29.3, 27.5, 27.5, 23.1, 13.9, 13.8, 11.2, 10.6; ^{119}Sn NMR (149 MHz, $CDCl_3$): δ -50.4; IR (neat, cm^{-1}): 3451, 2955, 2923, 2870, 2852, 1554, 1462, 1418, 1376, 1290, 1180, 1152, 1068, 1001, 960, 873, 689, 665, 594; HRMS (ESI): *m/z* calcd for $C_{32}H_{66}OSn_2Na$ $[M+Na]^+$ 729.3048; found: 729.3052.



(2*Z*,4*Z*)-2,5-Bis(tributylstannyl)nona-2,4-dien-1-ol (S15): Prepared analogously as a pale yellow oil (40 mg, 31%, isomer ratio ≈ 73:27). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.74 (dt, *J* = 10.6, 1.5 Hz, J_{Sn-H} = 114.3 Hz, 1H), 6.64-6.53 (m, J_{Sn-H} = 122.8 Hz, 1H), 4.27 (dd, *J* = 6.5, 1.5 Hz, J_{Sn-H} = 38.8 Hz, 2H), 2.27 (t, *J* = 6.4 Hz, J_{Sn-H} = 48.9 Hz, 2H), 1.54-1.42 (m, 12H), 1.37-1.25 (m, 16H), 1.12 (t, *J* = 6.1 Hz, 1H), 1.03-0.91 (m, 12H), 0.91-0.85 (m, 21H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 154.1, 147.8, 141.7, 140.7, 70.8, 41.0, 32.6, 29.4, 29.4, 27.5, 27.5, 22.4, 14.2, 13.9, 13.8, 10.7, 10.6; ^{119}Sn NMR (149 MHz, $CDCl_3$): δ -50.8, -50.8; IR (neat, cm^{-1}): 3468, 2955, 2922, 2871, 2852, 1556, 1463, 1376, 1291, 1072, 1002, 960, 874, 689, 666, 595; HRMS (ESI): *m/z* calcd for $C_{33}H_{68}OSn_2Na$ $[M+Na]^+$ 743.3205; found: 743.3199.

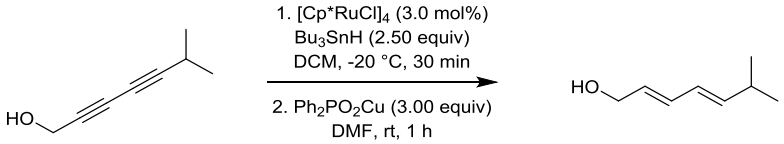


Representative Procedure for One-pot Di-hydrostannation/Proto-destannation. Preparation of 1-((1*E*,3*E*)-5-Methylhexa-1,3-dien-1-yl)cyclohexan-1-ol (S16): A solution of tributyltin hydride (0.14 mL, 0.50 mmol) in CH_2Cl_2 (1 mL) was added dropwise (over 30 min) under Argon at -20°C to a stirred solution of diyne **1** (40.0 mg, 0.2 mmol) and $[Cp^*RuCl]_4$ (6.7 mg, 6.1 μmol, 3.0 mol%) in CH_2Cl_2 (1 mL, 0.2 M), which had previously been mixed at room temperature and stirred for 1-2 min. Once the addition was complete, stirring was continued for 5 min before the mixture was warmed to ambient temperature. A solution of Ph_2PO_2Cu (0.17 g, 0.60 mmol) in DMF (2 mL) was added and stirring continued for 1 h. Et_2O (5 mL) was added and the reaction was quenched with water (5 mL). The aqueous layer was extracted with Et_2O (3 × 10 mL) and the combined extracts were dried over $MgSO_4$, filtered through a pad of SiO_2, and concentrated *in vacuo*. The crude material was purified by flash chromatography (hexane/EtOAc: 90/10) to give the title compound as a colorless oil (32.0 mg, 78%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.23 (ddd, *J* = 15.5, 10.3, 0.7 Hz, 1H), 6.00 (m, 1H), 5.71 (d, *J* = 15.8 Hz, 1H), 5.70 (dd, *J* = 15.2, 6.7 Hz, 1H), 2.33 (appt. octet of doublet, *J* = 6.7, 1.3 Hz, 1H), 1.70-1.44 (m, 10H), 1.38-1.23 (m, 1H), 1.01 (d, *J* = 6.7 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 142.0, 139.0, 128.0, 127.0, 71.6, 38.2, 31.3, 25.7, 22.4, 22.3; IR (neat, cm^{-1}): 3362, 3023, 2958, 2930, 2862, 1448, 1382, 1263, 1171, 989, 955; HRMS (EI): *m/z* calcd for $C_{13}H_{22}O$ $[M]^+$ 194.1665; found: 194.1668.



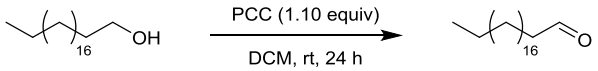
(4*E*,6*E*)-2-Methylundeca-4,6-dien-3-ol (S17): Prepared analogously as a colorless oil (21.0 mg, 85%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.18 (dd, *J* = 15.0, 10.5 Hz, 1H), 6.03 (ddt, *J* = 15.1, 10.7, 1.1 Hz, 1H), 5.69 (dt,

J = 14.7, 7.0 Hz, 1H), 5.57 (dd, *J* = 15.2, 7.2 Hz, 1H), 3.85 (ddd, *J* = 7.1, 5.9, 1.0 Hz, 1H), 2.08 (q, *J* = 7.6, 7.0 Hz, 2H), 1.81-1.65 (octet, *J* = 6.9 Hz, 1H), 1.48 (br. s, 1H), 1.42-1.25 (m, 4H), 0.93 (d, *J* = 6.8 Hz, 3H), 0.92-0.86 (m, 6H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 135.5, 132.1, 131.9, 129.6, 78.1, 34.1, 32.5, 31.5, 22.4, 18.4, 18.2, 14.1; IR (neat, cm^{-1}): 3373, 3017, 2957, 2926, 2872, 1466, 1379, 1257, 1132, 986; HRMS (EI): *m/z* calcd for $C_{12}H_{22}O$ $[M]^+$ 182.1665; found: 182.1666.

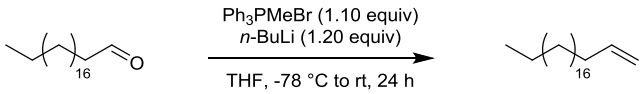


(2*E*,4*E*)-6-Methylhepta-2,4-dien-1-ol (S18): Prepared analogously as a colorless oil (14.0 mg, 56%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.21 (ddt, *J* = 15.1, 10.3, 1.3 Hz, 1H), 6.01 (ddt, *J* = 15.7, 10.4, 0.9 Hz, 1H), 5.80-5.64 (m, 2H), 4.16 (dd, *J* = 6.7, 1.3 Hz, 2H), 2.34 (appt. octet of doublet, *J* = 6.7, 1.2 Hz, 1H), 1.31 (s, 1H), 1.01 (d, *J* = 6.7 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 142.9, 132.4, 129.7, 126.5, 63.7, 31.2, 22.4; IR (neat, cm^{-1}): 3321, 3021, 2959, 2927, 2868, 1464, 1382, 1363, 1087, 987; HRMS (EI): *m/z* calcd for $C_8H_{14}O$ $[M]^+$ 126.1039; found: 126.1041.

Typhonosides E and F

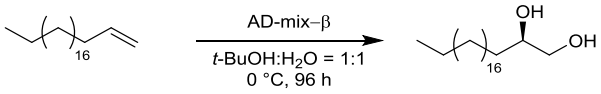


Eicosanal (S19): A flame-dried 100 mL round bottom flask was charged with 1-eicosanol (4.00 g, 13.4 mmol) and CH_2Cl_2 (200 mL). PCC (3.18 g, 14.8 mmol) was added and the mixture stirred at room temperature for 24 h. Celite (5.00 g) was introduced into the brown suspension. The resulting mixture was stirred for 30 min before it was filtered through a pad of Celite. The solid was carefully washed with CH_2Cl_2 (50 mL) and the combined filtrates were concentrated. The title compound was obtained as a white solid by flash chromatography (hexane:EtOAc = 10:1) (3.60 g, 91%) ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.76 (t, *J* = 1.9 Hz, 1H), 2.41 (td, *J* = 7.4, 1.9 Hz, 2H), 1.74-1.50 (m, 2H), 1.25 (m, 32H), 0.91-0.79 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 203.0, 43.9, 31.9, 29.70 (signals unresolved), 29.67, 29.65, 29.6, 29.44, 29.37, 29.2, 22.7, 22.1, 14.1; IR (neat, cm^{-1}): 2961, 2953, 2848, 2747, 1711, 1471, 1410, 1391, 1374, 895, 717; HRMS (EI): *m/z* calcd for $C_{20}H_{40}O$ [M]: 296.3079; found: 296.3078.



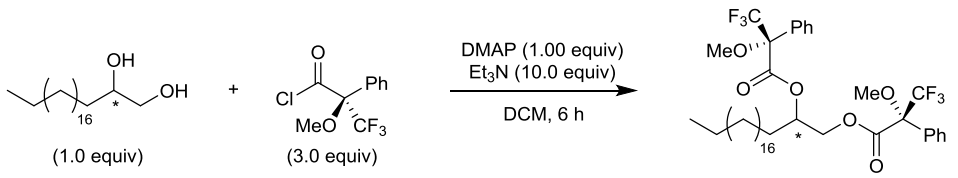
Heneicos-1-ene (S20): A 50 mL Schlenk tube was charged with a solution of methyl(triphenyl)phosphonium bromide (1.96 g, 5.51 mmol) in THF (20 mL). The solution was cooled to −78°C and stirred for 15 min before *n*-BuLi (5.51 mmol, 3.80 mL, 1.45 M in hexane) was added dropwise at

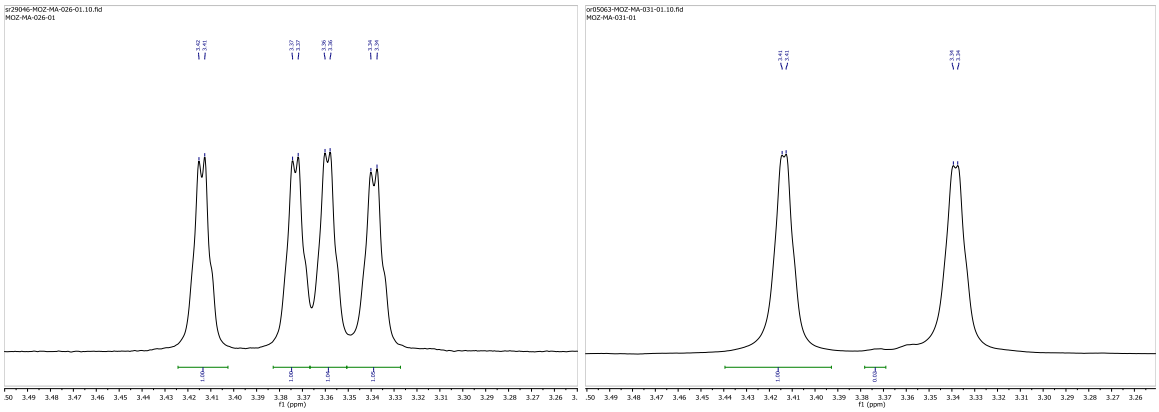
this temperature. The resulting yellow suspension was stirred at -78°C for 15 min before it was warmed to room temperature. After stirring for 15 min, the mixture was cooled again to -78°C. A solution of eicosanal (1.48 g, 5.00 mmol) was added dropwise at -78°C, the mixture was warmed to room temperature and stirring was continued for 24 h. For work up, the mixture was filtered, the filtrated was concentrated and the residue subjected to flash chromatography (hexane) to give the title compound as a waxy solid (1.26 g, 85%).[3] ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.82 (ddt, *J* = 16.9, 10.2, 6.7 Hz, 1H), 4.99 (app dq, 1H), 4.93 (ddt, *J* = 10.2, 2.3, 1.2 Hz, 1H), 2.08-2.00 (m, 2H), 1.42-1.34 (m, 2H), 1.26 (m, 32H), 0.91-0.83 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 139.3, 114.1, 33.8, 32.0, 29.72 (signals unresolved), 29.69, 29.65, 29.5, 29.4, 29.2, 29.0, 22.7, 14.1; IR (neat, cm^{-1}): 2955, 2852, 1641, 1466, 1378, 1057, 922, 907, 735; HRMS (EI): *m/z* calcd for $C_{21}H_{42}$ [M]: 294.3287; found: 294.3281.

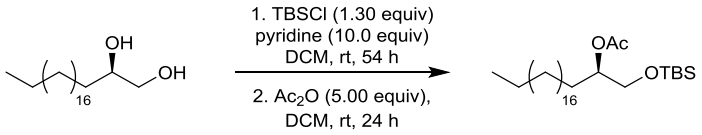


(*R*)-Heneicosane-1,2-diol (S21): A suspension of AD-mix-β (2.25 g) in *t*-BuOH/H_2O (36 mL, v:v = 1:1) was stirred vigorously for 30 min at room temperature. The resulting mixture was then cooled to 0°C before heneicos-1-ene (0.57 g, 1.93 mmol) was added The mixture was vigorously stirred at 0°C for 96 h. Sodium sulfite (2.40 g, 19.0 mmol) was then added to the suspension and stirring was continued for 60 min before the mixture was warmed to room temperature. The suspension was extracted with EtOAc (3 × 50 mL). The combined organic layers were washed with brine (20 mL), dried over $MgSO_4$, filtered and concentrated. The diol product was isolated by flash chromatography (hexane:EtOAc = 1:2 to CH_2Cl_2:MeOH = 20:1) as a white solid (249.9 mg, 39%, 86% *ee*). Recrystallization from EtOAc (40 mL EtOAc per gram of the diol) resulted in enantiomeric enrichment (150.0 mg, >95% *ee*).[4] $[\alpha]_D^{20}$ = +1.9 (c = 2.01, $CHCl_3$:MeOH = 1:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.74-3.61 (m, 2H), 3.44 (ddd, *J* = 12.1, 7.5, 4.7 Hz, 1H), 1.96 (d, *J* = 3.9 Hz, 1H), 1.82 (dd, *J* = 4.7 Hz, 1H), 1.50-1.40 (m, 3H), 1.25 (m, 33H), 0.93-0.80 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 72.3, 66.9, 33.2, 31.9, 29.71 (signals unresolved), 29.68, 29.67, 29.60, 29.56, 29.4, 25.5, 22.7, 14.1; IR (neat, cm^{-1}): 3477, 3309, 3225, 2954, 2915, 2847, 1470, 1073, 873, 719; HRMS (ESI): *m/z* calcd for $C_{21}H_{44}O_2Na$ $[M+Na]^+$: 351.3233; found: 351.3235.

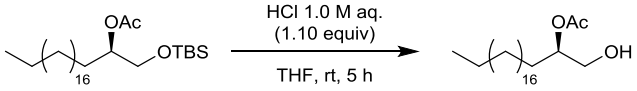
The absolute configuration was assigned as (*R*) in analogy to a similar compound described by Bittman and co-workers.[4] The enantiomeric excess was determined by Mosher ester derivatization. To this end, a flamed-dried 5 mL round bottom flask was charged with the diol (1.6 mg, 0.005 mmol) and DMAP (0.6 mg, 0.005 mmol) in CH_2Cl_2 (0.1 mL). Triethylamine (5.1 mg, 0.152 mmol) was then added, followed by the addition of (*S*)-(+)-MTPA-Cl (3.8 mg, 0.015 mmol). The mixture was allowed to stir at room temperature for 6 h. The solvent was evaporated and the residue subjected to ^{1}H NMR analysis. The enantiomeric excess of the diol was determined to be >95% based on the -OMe signals; for comparison, the racemic diol was derivatized analogously, see the following Figure:



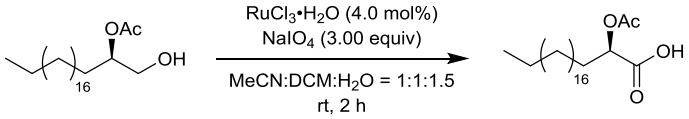




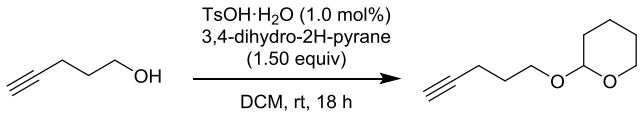
(*R*)-1-((*tert*-Butyldimethylsilyl)oxy)heneicosan-2-yl acetate (S22): To a suspension of the (*R*)-heneicosane-1,2-diol (149.8 mg, 0.46 mmol) in CH_2Cl_2 (7 mL) was added pyridine (361.9 mg, 4.57 mmol) followed by TBSCl (89.3 mg, 0.59 mmol) at 0°C. The mixture was allowed to stir at room temperature for 54 h. The suspension turned into a clear solution at this point. The mixture was cooled to 0°C before acetic anhydride (248.4 mg, 2.43 mmol) was introduced and stirring was continued for 24 h. MeOH (0.1 mL) was added, the solution was diluted with water (5 mL) and CH_2Cl_2 (5 mL). The aqueous layer was extracted with CH_2Cl_2 (3 × 10 mL), the combined organic layers were washed with brine (10 mL), dried over $MgSO_4$, filtered and concentrated. The product was isolated by flash chromatography (EtOAc:hexane = 100:1 to 40:1) as a colorless liquid (130.0 mg, 59%).[5] $[\alpha]_D^{20}$ = -66.7 (c = 0.50, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.88 (dddd, *J* = 7.7, 5.2, 5.2, 5.2 Hz, 1H), 3.62 (d, *J* = 5.1 Hz, 2H), 2.05 (s, 3H), 1.25 (m, 36H), 0.88 (s, 9H), 0.88 (m, 3H), 0.04 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.8, 74.7, 64.3, 31.9, 30.5, 29.71 (signals unresolved), 29.68, 29.67, 29.6, 29.54, 29.50, 29.4, 25.8, 25.2, 22.7, 21.3, 18.3, 14.1, -5.4; IR (neat, cm^{-1}): 2924, 2854, 1744, 1464, 1370, 1238, 1122, 837, 777; HRMS (ESI): *m/z* calcd for $C_{29}H_{60}O_3SiNa$ $[M+Na]^+$: 507.4204; found: 507.4207.



(*R*)-1-Hydroxyheneicosan-2-yl acetate (S23): aq. HCl (1 M, 0.47 mL, 0.47 mmol) was added to a solution of (*R*)-1-((*tert*-butyldimethylsilyl)oxy) heneicosan-2-yl acetate (206.0 mg, 0.42 mmol) in THF (4 mL). The solution was stirred at room temperature for 5 h before $NaHCO_3$ (42 mg, 0.50 mmol) was carefully added. The mixture was diluted with EtOAc (5 mL) and H_2O (5 mL) and the aqueous layer was extracted with EtOAc (3 × 10 mL). The combined organic phases were washed with brine (10 mL), dried over $MgSO_4$, filtered and concentrated. The residue was subjected to flash chromatography (hexane:EtOAc = 1:4) to give the title compound as a viscous liquid (126.0 mg, 80%). $[\boldsymbol{\alpha}]_{\boldsymbol{D}}^{\boldsymbol{20}}$ = -1.1 (c = 0.55, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.91 (ddt, *J* = 9.5, 6.3, 3.2 Hz, 1H), 3.72 (dd, *J* = 12.0, 3.1 Hz, 1H), 3.63 (dd, *J* = 12.0, 6.3 Hz, 1H), 2.09 (s, 3H), 1.84 (s, 1H), 1.62-1.49 (m, 2H), 1.25 (s, 34H), 0.94-0.72 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 171.5, 75.7, 64.9, 31.9, 30.5, 29.71 (signals unresolved), 29.67, 29.64, 29.56, 29.5, 29.4, 25.3, 22.7, 21.2, 14.1; IR (neat, cm^{-1}): 3416, 2916, 2849, 1737, 1467, 1374, 1238, 1051, 1028, 721, 610; HRMS (ESI): *m/z* calcd for $C_{23}H_{46}O_3Na$ $[M+Na]^+$: 393.3339; found: 393.3340.

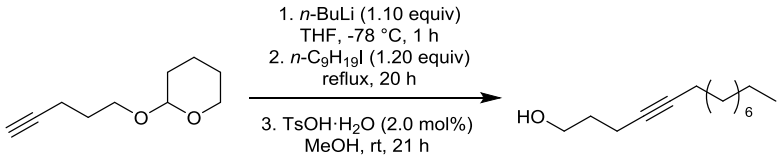


(*R*)-2-Acetoxyheneicosanoic acid (S24): $RuCl_3$ hydrate (2.3 mg, 0.011 mmol) was added to a vigorously stirred mixture of (*R*)-1-hydroxyhenicosan-2-yl acetate (101.2 mg, 0.27 mmol) and $NaIO_4$ (175.2 mg, 0.82 mmol) in CH_2Cl_2/MeCN/H_2O (1:1:1.5, *v/v*). Stirring was continued at room temperature for 2 h before the mixture was diluted with water (5 mL) and EtOAc (15 mL). The aqueous layer was extracted with EtOAc (3 × 15 mL), the combined organic phases were washed with brine and dried over $MgSO_4$, filtered and concentrated. The residue was subjected to flash chromatography (hexane:EtOAc = 2:1 to hexane:EtOAc:CH_3CO_2H = 100:50:1) to provide the title compound as a white solid (85.0 mg, 81%).[6] $[\boldsymbol{\alpha}]_{\boldsymbol{D}}^{\boldsymbol{20}}$ = +11.5 (c = 0.50, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.02 (dd, *J* = 6.3, 6.3 Hz, 1H), 2.15 (s, 3H), 1.91-1.81 (m, 2H), 1.47-1.37 (m, 2H), 1.26 (m, 32H), 0.88 (t, *J* = 6.9 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 176.2, 170.7, 72.0, 31.9, 31.0, 29.71 (signals unresolved), 29.67, 29.63, 29.55, 29.37, 29.36, 29.1, 25.1, 22.7, 20.6, 14.1; IR (neat, cm^{-1}): 2916, 2849, 1734, 1725, 1468, 1374, 1229, 1086, 1049, 907, 649; HRMS (ESI): *m/z* calcd for $C_{23}H_{44}O_4Na$ $[M+Na]^+$: 407.3132; found: 407.3133.



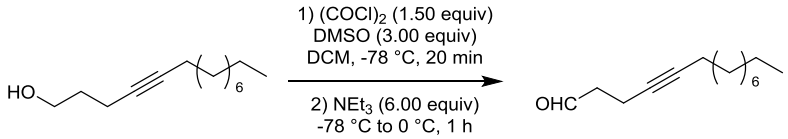
2-(Pent-4-yn-1-yloxy)tetrahydro-2*H*-pyran (S25): 3,4-Dihydro-2*H*-pyrane (75.0 mmol, 6.84 mL) and $TsOH{\cdot}H_2O$ (95.1 mg, 0.50 mmol) were added to a solution of 4-pentyn-1-ol (50.0 mmol, 6.84 mL) in CH_2Cl_2 (100 mL) at 0°C under Ar. After stirring for 18 h at room temperature, the resulting dark brown

mixture was diluted with sat. aq. $NaHCO_3$. The water layer was extracted with EtOAc, the combined organic phases were dried over Na_2SO_4, filtrated, and concentrated. The crude product was purified by flash chromatography (hexane:EtOAc = 98:2) to afford the title compound as a colorless liquid (7.83 g, 93%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.60 (t, *J* = 2.7 Hz, 1H), 3.90-3.80 (m, 2H), 3.55-3.44 (m, 2H), 2.32 (tdd, *J* = 7.0, 2.7, 0.9 Hz, 2H), 1.94 (t, *J* = 5.2 Hz, 1H), 1.88-1.78 (m, 3H), 1.76-1.67 (m, 1H), 1.62-1.48 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 98.8, 84.0, 68.4, 65.8, 62.2, 30.7, 28.7, 25.5, 19.5, 15.3; IR (neat, cm^{-1}): 3295, 2941, 2871, 1441, 1354, 1323, 1261, 1200, 1158, 1136, 1120, 1061, 1033, 1020, 992, 868, 627; HRMS (ESI): *m/z* calcd for $C_{10}H_{16}O_2Na$ $[M+Na]^+$: 191.1048; found: 191.1042.

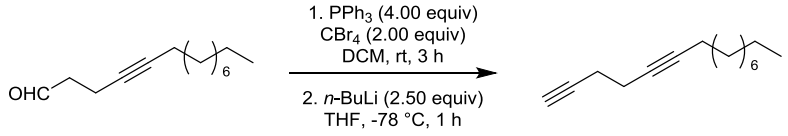


Tetradec-4-yn-1-ol (15): *n*-BuLi (1.6 M in hexane, 30.9 mL, 49.5 mmol) was added dropwise to the solution of 2-(tetradec-4-yn-1-yloxy)tetrahydro-2*H*-pyran (7.57 g, 45.0 mmol) in THF (130 mL) at -78°C under Ar and the resulting pale yellow solution was stirred at -78°C for 1 h. After warming to room temperature, 1-iodononane (10.7 mL, 54.0 mmol) was introduced, and the resulting mixture was stirred at reflux temperature for 20 h. The reaction was quenched with sat. aq. NH_4Cl at 0°C. The water layer was extracted with EtOAc, and the combined organic phases were dried over Na_2SO_4, filtrated, and evaporated under reduced pressure.

$TsOH{\cdot}H_2O$ (171.0 mg, 0.90 mmol) was added to a solution of the pale yellow residue in MeOH (100 mL) under Ar. The mixture was stirred for 21 h at room temperature before NEt_3 (0.5 mL) and water were added. The aqueous layer was extracted with EtOAc and the combined organic phases were dried over Na_2SO_4 and concentrated. The crude material was purified by flash chromatography (hexane:EtOAc = 9:1) to afford the title compound as a colorless liquid (8.80 g, 93%).[7] ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.76 (t, *J* = 6.1 Hz, 2H), 2.28 (tt, *J* = 6.8, 2.4 Hz, 2H), 2.13 (tt, *J* = 7.0, 2.4 Hz, 2H), 1.74 (app qui, *J* = 6.2 Hz, 2H), 1.47 (app qui, *J* = 7.5 Hz, 2H), 1.40-1.22 (m, 12H), 0.88 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 81.2, 79.2, 62.1, 31.9, 31.6, 29.5, 29.3, 29.2, 29.1, 28.9, 22.7, 18.7, 15.5, 14.1; IR (neat, cm^{-1}): 3332, 2924, 2854, 1466, 1434, 1378, 1331, 1056, 908, 733, 648; HRMS (ESI): *m/z* calcd for $C_{14}H_{26}ONa$ $[M+Na]^+$: 233.1881; found: 233.1876.



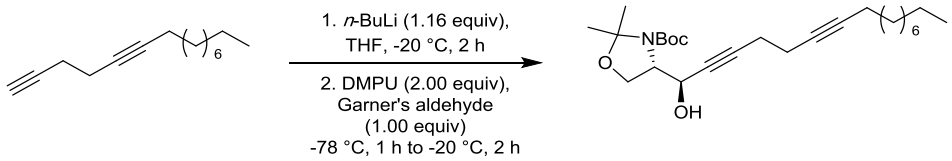
Tetradec-4-ynal (S26): A solution of DMSO (5.3 mL, 75.0 mmol) in CH_2Cl_2 (20 mL) was added dropwise over 20 min to the solution of oxalyl chloride (3.2 mL, 37.5 mmol) in CH_2Cl_2 (40 mL) at -78°C under Ar. The resulting mixture was stirred for 15 min before a solution of tetradec-4-yn-1-ol (5.26 g, 25.0 mmol) in CH_2Cl_2 (20 mL) was added dropwise over 20 min at -78°C. After vigorous stirring for 20 min, NEt_3 (20.9 mL, 150.0 mmol) was introduced and the resulting mixture was vigorously stirred for 30 min at -78°C and for another 30 min at 0°C. The white suspension was diluted with sat. NH_4Cl aq. After separation of the organic phase, the water layer was extracted with CH_2Cl_2, and the combined organic phases were washed twice with brine, dried over Na_2SO_4, and evaporated. The residue was purified by flash chromatography (hexane:EtOAc = 100:0 to 97:3) to give the product as a colorless liquid (3.59 g, 69%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.80 (t, *J* = 1.4 Hz, 1H), 2.61 (tt, *J* = 7.0, 1.3 Hz, 2H), 2.48 (tt, *J* = 7.0, 2.4 Hz, 2H), 2.12 (tt, *J* = 7.2, 2.4 Hz, 2H), 1.46 (app qui, *J* = 7.7 Hz, 2H), 1.38-1.22 (m, 12H), 0.88 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 201.1, 81.7, 77.7, 43.0, 31.9, 29.5, 29.3, 29.2, 28.93, 28.86, 22.7, 18.7, 14.1, 12.2; IR (neat, cm^{-1}): 2923, 2854, 2726, 1728, 1466, 1436, 1411, 1378, 1357, 1333, 1113, 1054, 722; HRMS (ESI): *m/z* calcd for $C_{14}H_{24}ONa$ $[M+Na]^+$: 231.1725; found: 231.1719.



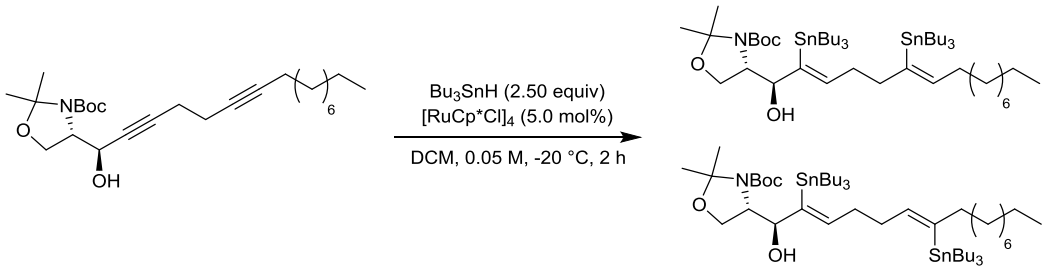
Pentadeca-1,5-diyne (16): PPh_3 (15.7 g, 60.0 mmol) was added to a solution of CBr_4 (9.95 g, 30.0 mmol) in CH_2Cl_2 (75 mL) under Ar at 0°C. A solution of tetradec-4-ynal (3.13 g, 15.0 mmol) in CH_2Cl_2 (25 mL) was added dropwise to the resulting orange mixture at 0°C and stirring was continued for 3 h at room temperature. The dark brown mixture was filtered through the pad of silica, eluting with EtOAc. The combined filtrates were evaporated. The residue was repeatedly triturated with hexane, and the combined hexane extracts were evaporated under reduced pressure.

n-BuLi (1.6 M in hexane, 23.4 mL, 37.5 mmol) was added under Ar atmosphere to the solution of the residue in THF (80 mL) at -78°C. After stirring for 1 h at -78°C, the reaction was quenched at this temperature with sat. aq. NH_4Cl. The water layer was extracted with ether, the combined organic phases were dried over Na_2SO_4, filtrated, and evaporated. The residue was purified by flash chromatography (hexane) to afford pentadeca-1,5-diyne as a pale yellow liquid (2.60 g, 85%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.42-2.38 (m, 4H), 2.15 (tt, *J* = 7.0, 2.0 Hz, 2H), 2.00 (t, *J* = 2.5 Hz, 1H), 1.48 (app qui, *J* = 7.2 Hz, 2H), 1.41-1.24 (m, 12H), 0.88 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 83.1, 81.6, 78.1, 69.0, 31.9,

29.5, 29.3, 29.2, 29.0, 28.8, 22.7, 19.2, 18.9, 18.7, 14.1; IR (neat, cm^{-1}): 3314, 2923, 2854, 1466, 1338, 1257, 722, 632; HRMS (ESI): *m/z* calcd for $C_{15}H_{24}Na$ $[M+Na]^+$: 227.1776; found: 227.1770.



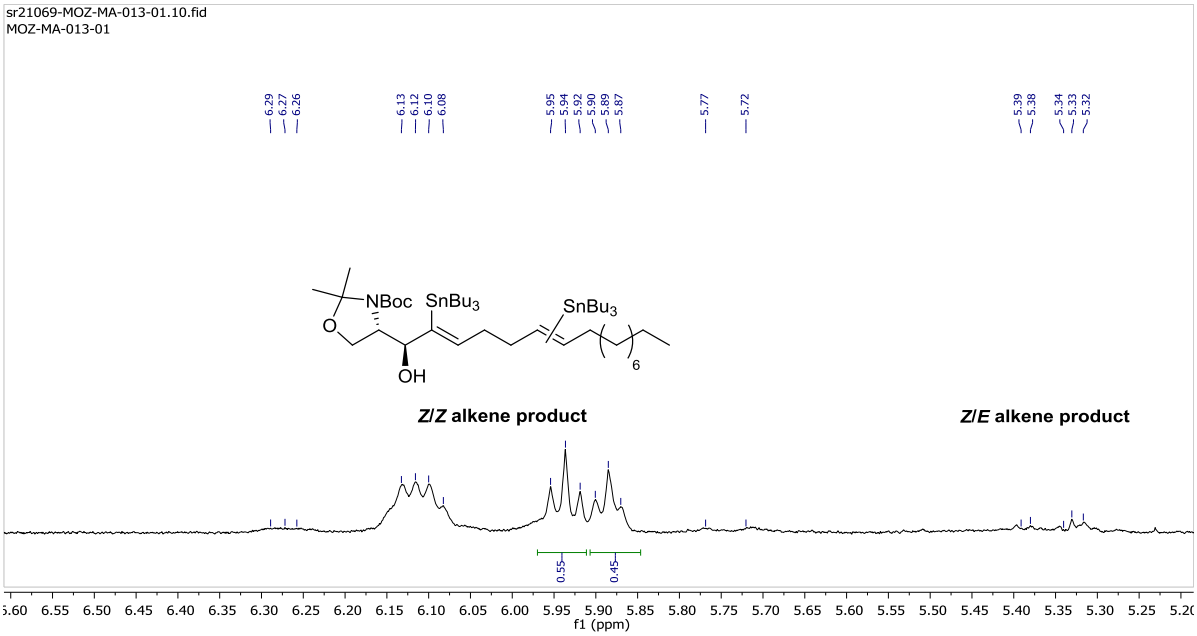
***tert*-Butyl (*S*)-4-((*R*)-1-hydroxyhexadeca-2,6-diyn-1-yl)-2,2-dimethyloxazolidine-3-carboxylate (17)**: *n*-BuLi (1.6 M in hexane, 2.6 mL, 3.78 mmol) was added to a solution of pentadeca-1,5-diyne (866.0 mg, 4.24 mmol) in THF (40 mL) under Ar at -20°C and stirring continued at this temperature for 2 h. Freshly distilled DMPU (835.6 mg, 6.52 mmol)[8] was added, followed by a solution of the Garner's aldehyde (747.4 mg, 3.26 mmol) in THF (15 mL) over a period of 15 min at -78°C. The mixture was allowed to stir at this temperature for 1 h and for another 2 h at -20°C before the reaction was quenched with water and sat. NH_4Cl solution (25 mL). After reaching ambient temperature, the mixture was extracted with EtOAc (3 × 25 mL). The combined organic layers were dried over $MgSO_4$, filtered and concentrated. The crude product was purified by flash chromatography (EtOAc:hexane = 10:1 to 8:1) to afford the title compound as a colorless liquid (1.09 g, 77% yield of the *anti*-isomer).[9] The diastereoselectivity (*anti:syn* > 20:1) was determined by recording the spectrum of the crude material in $[D_6]$-DMSO and comparison of the data with those reported by Herold and co-workers.[9] $[\alpha]_D^{20}$ = -42.5 (c = 0.42, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.75-4.66 (m, 2H), 4.36-3.85 (m, 3H), 2.43-2.32 (m, 4H), 2.16-2.10 (tt, *J* = 7.0, 2.1 Hz, 2H), 1.59 (s, 3H), 1.52-1.43 (m, 14H), 1.38-1.23 (m, 12H), 0.88 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 154.2, 95.0, 85.1, 81.5, 81.3, 78.8, 78.2, 65.1, 64.1, 62.8, 31.9, 29.5, 29.3, 29.2, 29.0, 28.9, 28.4, 25.8, 25.5, 22.7, 19.5, 19.0, 18.7, 14.1; IR (neat, cm^{-1}): 3444, 2925, 2855, 1692, 1457, 1389, 1257, 1207, 1170, 1082, 1065, 847, 769; HRMS (ESI): *m/z* calcd for $C_{26}H_{43}O_4Na$ $[M+Na]^+$: 456.3090; found: 456.3084.



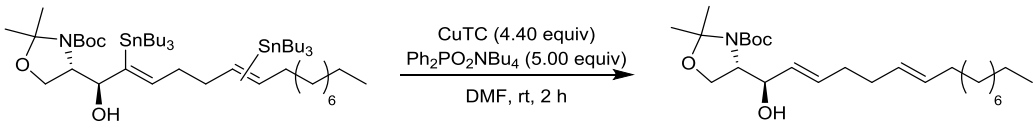
***tert*-Butyl-(S)-4-((S,2Z,6Z)-1-hydroxy-2,6-bis(tributylstannyl)hexadeca-2,6-dien-1-yl)-2,2-dimethyl-oxazolidine-3-carboxylate (18)**: $[Cp^*RuCl]_4$ (2.7 mg, 0.0025 mmol) was added to a solution of the diyne (21.7 mg, 0.05 mmol) in CH_2Cl_2 (1.0 mL) under Ar, causing an immediate color change from brown to slight purple. The mixture was stirred at -20°C for 5 min before a solution of *n*-Bu_3SnH (36.4 mg, 0.13 mmol) in 1,2-dichloroethane (0.5 mL) was added via syringe pump over a period of 2 h. Once the addition

was complete, stirring was continued for an extra 5 min. After removal of the solvent, the resulting crude material was subjected to flash chromatography (hexane:EtOAc = 98:2) to give the distannane product as a pale yellow oil (42.8 mg, 84%). A comparable result (301.9 mg, 80%) was obtained on a 0.30 mmol scale.[10]

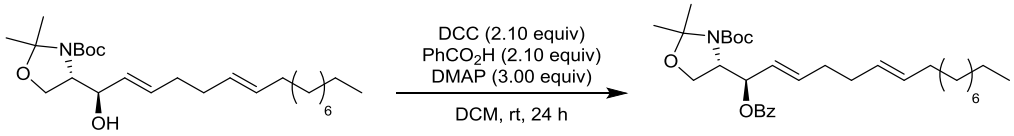
According to ^{1}H NMR analysis of the crude reaction mixture in $CDCl_3$, the *E*/*Z* diastereoselectivity of the diene was determined to be *Z*/*Z*:*Z*/*E* > 20:1. The regioisomeric ratio of the major *Z*/*Z* alkene product was determined to be 55:45; these regioiosmers were not separated.



Compound characterization was performed using C_6D_6 due to gradual decomposition of the distannane in chlorinated solvents. $[\alpha]_D^{20}$ = -2.7 (c = 0.41, $CHCl_3$). ^{1}H NMR (400 MHz, C_6D_6): δ 6.34 (t, *J* = 6.5 Hz, $J_{Sn\text{-}H}$ = 132.8 Hz, 2H), 4.31 (br s, 1H), 4.14 (m, 2H), 3.80-3.57 (m, 1H), 2.57-2.13 (m, 6H), 1.77 (m, 6H), 1.71-1.63 (m, 9H), 1.56-1.26 (m, 44H), 1.16-1.10 (m, 6H), 1.06-0.96 (m, 18H), 0.93-0.89 (m, 3H); ^{13}C NMR (100 MHz, C_6D_6): δ 152.3, 147.0, 146.6, 144.37, 142.4, 141.3, 140.0, 139.8, 93.4, 80.4, 79.2, 64.6, 61.0, 41.4, 41.1, 36.0, 35.6, 35.4, 35.1, 32.0, 31.0, 30.6, 29.84, 29.75, 29.68, 29.65, 29.6, 29.48, 29.46, 28.2, 28.1, 28.0, 27.9, 27.79, 27.75, 27.6, 27.3, 24.4, 22.8, 14.0, 13.74, 13.70, 13.64, 13.63, 12.0, 11.9, 10.5, 10.4; ^{119}Sn NMR (186 MHz, C_6D_6): δ -53.6,. -53.9, -58.7 (br s); IR (neat, cm^{-1}): 2955, 2922, 2853, 1693, 1457, 1386, 1375, 1365, 1248, 1202, 1174, 1099, 1072, 1051, 871, 846, 735; HRMS (ESI): *m/z* calcd for $C_{50}H_{99}NO_4Sn_2Na$ $[M+Na]^+$: 1040.5516; found: 1040.5509.

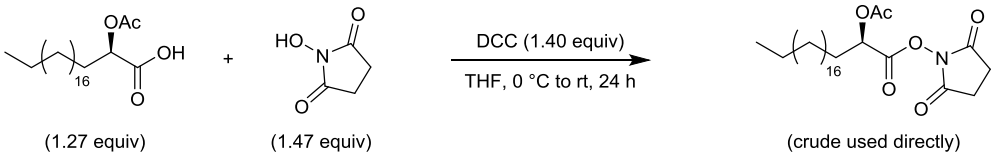


***tert*-Butyl (*S*)-4-((*R*,2*E*,6*E*)-1-hydroxyhexadeca-2,6-dien-1-yl)-2,2-dimethyloxazolidine-3-carboxylate (S27)**: CuTC (170.3 mg, 0.89 mmol) was added to a solution of distannane **18** (184.2 mg, 0.18 mmol) and $Ph_2PO_2NBu_4$ (370.4 mg, 0.81 mmol) in DMF (2.2 mL) and the resulting mixture was stirred at room temperature for 2 h. *tert*-Butyl methyl ether (10 mL) was added before the reaction was quenched with water (10 mL). The resulting yellow mixture was stirred at room temperature for an extra 30 min. The aqueous layer was extracted with *tert*-butyl methyl ether (3 × 30 mL). The combined organic phases were dried over $MgSO_4$ and filtered through a pad of SiO_2. After evaporation of the solvent, the residue was purified by chromatography on silica/KF (20:1, *v:v*; EtOAc:hexane 20:1 to 10:1) as a colorless liquid (67.6 mg, 85%).[2] $[\alpha]_D^{20}$ = -22.4 (c = 0.78, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.74 (dt, *J* = 15.4, 6.2 Hz, 1H), 5.53-5.33 (m, 3H), 4.40-3.78 (br m, 5H), 2.15-2.03 (m, 4H), 1.96 (app q, *J* = 5.4 Hz, 2H), 1.60-1.45 (m, 15H), 1.38-1.22 (m, 14H), 0.88 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 154.2, 132.7, 131.0, 129.3, 128.5, 94.4, 81.0, 74.0, 64.9, 62.3, 32.59, 32.55, 32.2, 31.9, 29.6, 29.5, 29.3, 29.2, 28.4, 26.3, 24.6, 22.7, 14.1; IR (neat, cm^{-1}): 3437, 2957, 2923, 2853, 1698, 1455, 1385, 1376, 1255, 1173, 1097, 1069, 965, 848, 766; HRMS (ESI): *m/z* calcd for $C_{26}H_{47}NO_4Na$ $[M+Na]^+$: 460.3403; found: 460.3397.



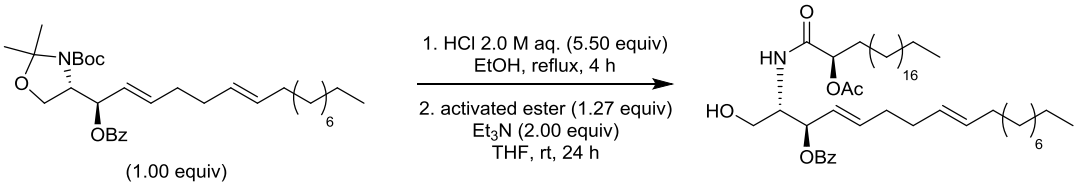
***tert*-Butyl-(*S*)-4-((*R*,2*E*,6*E*)-1-(benzoyloxy)hexadeca-2,6-dien-1-yl)-2,2-dimethyloxazolidine-3-carboxylate (19)**: DCC (18.1 mg, 0.088 mmol) was added to a solution of the allylic alcohol (19.4 mg, 0.044 mmol), benzoic acid (10.7 mg, 0.088 mmol) and DMAP (16.2 mg, 0.13 mmol) in CH_2Cl_2 (2 mL), causing the formation of a white precipitate. The mixture was stirred at room temperature for 24 h before the reaction was quenched with MeOH (0.1 mL). After stirring for an extra 15 min, the mixture was diluted with hexane and insoluble material was filtered off. The solid was washed with hexane/EtOAc (25:1, 10 mL), the combined filtrates were concentrated and the residue was subjected to flash chromatography (EtOAc:hexane = 10:1) to provide the title compound as a colorless liquid (20.6 mg, 86%).[5] ^{1}H NMR (400 MHz, C_6D_6, rotamers at room temperature): δ 8.30 (m, 2H), 7.11-7.03 (m, 3H), 6.38 (br s, 0.4H), 6.32 (br s, 0.6H), 5.88 (dt, *J* = 14.4 Hz, 6.4 Hz, 1H), 5.58-5.29 (m, 3H), 4.27 (br s, 0.4H), 4.17 (d, *J* = 8.9 Hz, 0.6H), 4.11 (d, *J* = 8.9 Hz, 0.4H), 3.89 (br s, 0.6H), 3.80-3.62 (m, 1H), 1.99 (m, 6H), 1.70 (s, 2H), 1.55 (m, 8H), 1.38 (m, 6H), 1.28 (m, 13H), 0.94-0.87 (m, 3H); ^{13}C NMR (100 MHz, C_6D_6, rotamers at room temperature): δ 165.2, 165.0, 152.2, 151.5, 134.6, 134.5, 132.6, 132.4, 131.3, 131.0, 130.7, 129.9, 129.2, 129.0, 128.2, 126.1, 94.7, 93.7, 79.5, 74.1, 73.8, 63.5, 63.4, 60.2, 60.0, 32.7, 32.4, 32.1, 32.0, 29.71, 29.68, 29.6, 29.4, 29.3, 28.1, 28.0, 27.2, 26.3, 24.3, 22.9, 22.8, 14.0. IR (neat, cm^{-1}): 2974, 2925, 2854, 1725, 1703, 1425,

1376, 1269, 1176, 1098, 711; HRMS (ESI): *m/z* calcd for $C_{33}H_{51}NO_5Na$ $[M+Na]^+$: 564.3659; found: 564.3665; $[\alpha]_D^{20}$ = -33.2 (c = 0.51, $CHCl_3$).



(1.27 equiv) (1.47 equiv) (crude used directly)

2,5-Dioxopyrrolidin-1-yl (*R*)-2-acetoxyheneicosanoate. DCC (5.3 mg, 0.026 mmol) was added to a solution of (*R*)-2-acetoxyhenicosanoic acid (9.1 mg, 0.024 mmol) and N-hydroxysuccinimide (3.2 mg, 0.027 mmol) in THF (0.15 mL) at 0°C. The mixture was stirred at 0°C for 1 h and at room temperature overnight. Water (1.5 mg, 0.08 mmol) was added and stirring continued for 1 h. Hexane (1 mL) was introducded, the precipitated dicyclohexylurea was filtered off and rinsed with hexane/EtOAc (10:1, 10 mL). The combined filtrates were dried over $MgSO_4$ and concentrated. The resulting crude 2,5-dioxopyrrolidin-1-yl (*R*)-2-acetoxyheneicosanoate (**23**) was used directly in the next step without further purification.

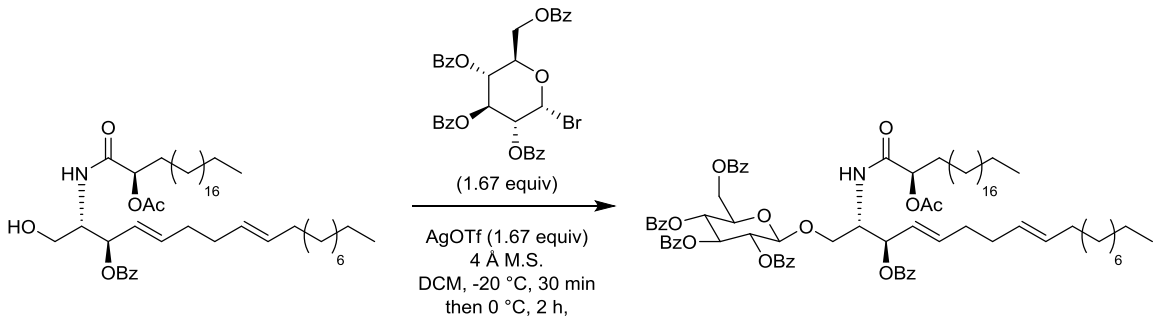


(1.00 equiv)

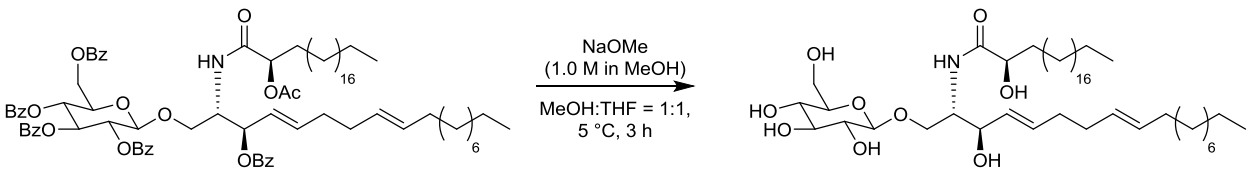
(2*S*,3*R*,4*E*,8*E*)-2-((*R*)-2-Acetoxyhenicosanamido)-1-hydroxyoctadeca-4,8-dien-3-yl benzoate (20). aq HCl (2 M, 0.05 mL) was added to a stirred solution of *tert*-butyl-(*S*)-4-((*R*,2*E*,6*E*)-1-(benzoyloxy)hexadeca-2,6-dien-1-yl)-2,2-dimethyl oxazolidine-3-carboxylate (10.0 mg, 0. 019 mmol) in EtOH (0.2 mL) and the resulting mixture was stirred for 4 h at 70°C. $CHCl_3$/MeOH (7:1, 10 mL) and H_2O (5 mL) were added, the layers were separated and the aqueous phase was extracted with $CHCl_3$/MeOH (7:1, 2 × 10 mL). The combined organic extracts were dried over $MgSO_4$ and concentrated to give the crude amine as a colorless solid.

Crude 2,5-dioxopyrrolidin-1-yl (*R*)-2-acetoxyheneicosanoate was added to a solution of the crude amine in THF (0.50 mL). Et_3N (3.9 mg, 0.039 mmol) was introduced and the mixture was allowed to stir at room temperature for 20 h. EtOAc and H_2O were added, the aqueous phase was extracted with EtOAc (3 × 10 mL), the combined organic layers were dried and concentrated to give yellow oil, which was purified by flash chromatography (hexane:EtOAc = 3:1 to 1:1), furnishing the title compound as a colorless viscous oil (9.3 mg, 66%).[5] $[\boldsymbol{\alpha}]_{\boldsymbol{D}}^{\boldsymbol{20}}$ = +33.1 (c = 0.93, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.03 (m, 2H), 7.60 (m, 1H), 7.46 (m, 2H), 6.77 (d, *J* = 8.5 Hz, 1H), 5.89 (dt, *J* = 14.9, 6.2 Hz, 1H), 5.68-5.53 (m, 2H), 5.45-5.28 (m, 2H), 5.17 (dd, *J* = 7.4, 4.6 Hz, 1H), 4.23 (ddt, *J* = 10.1, 6.8, 3.3 Hz, 1H), 3.77-3.63 (m, 2H), 2.73 (dd, *J* = 8.2, 4.5 Hz, 1H), 2.15 (s, 3H), 2.12-2.03 (m, 4H), 1.98-1.90 (m, 2H), 1.85-1.72 (m, 2H), 1.25 (m, 48H), 0.88 (t, *J* = 6.8 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.2, 169.7, 166.6, 136.8, 133.6, 131.4, 129.8,

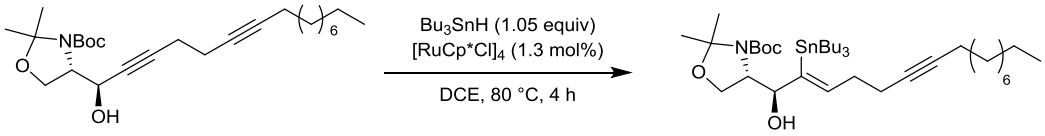
129.5, 128.7, 128.6, 124.9, 74.4, 74.2, 61.6, 53.5, 32.6, 32.3, 31.94, 31.92, 31.8, 29.73 (signals unresolved), 29.67, 29.63, 29.57, 29.5, 29.44, 29.38, 29.36, 29.3, 29.2, 24.8, 22.7, 20.9, 14.1; IR (neat, cm^{-1}): 3310, 2919, 2850, 1743, 1718, 1656, 1544, 1468, 1265, 1233, 1116, 1070, 966, 710; HRMS (ESI): *m/z* calcd for $C_{48}H_{81}NO_6Na$ $[M+Na]^+$: 790.5956; found: 790.5966.



Compound 21. A solution of the amide (9.0 mg, 0.012 mmol), 2,3,4,5-tetraO-benzoyl-α-D-glucopyranosyl bromide (12.9 mg, 0.020 mmol) and 4 Å MS (16.0 mg) in CH_2Cl_2 (0.5 mL) was stirred under Ar at room temperature for 30 min before it was cooled to -20°C. AgOTf (5.0 mg, 0.020 mmol) in toluene (0.1 mL) was added at -20°C and stirring continued at this temperature for 30 min and at 0°C for another 2 h. The mixture was diluted with EtOAc (10 mL) and filtered. The filtrate was extracted with EtOAc (15 mL), and the combined extracts were washed with aqueous $NaHCO_3$ (5 mL), water (5 mL) and brine (5 mL). The combined aqueous phases were extracted with EtOAc (2 × 10 mL), the extracts were dried over $MgSO_4$, filtered and concentrated. The residue was purified by preparative TLC (hexane:EtOAc = 3:1) to give the title compound as a colorless viscous liquid (13.0 mg, 82%).[5] $[\alpha]_D^{20}$ = +16.0 (c = 1.30, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.99 (m, 2H), 7.95 (m, 2H), 7.92 (m, 2H), 7.87 (m, 2H), 7.80 (m, 2H), 7.54-7.27 (m, 15H), 6.47 (d, *J* = 9.1 Hz, 1H), 5.90-5.80 (m, 2H), 5.67-5.59 (m, 2H), 5.54-5.46 (m, 2H), 5.42-5.25 (m, 2H), 5.01 (dd, *J* = 6.8, 5.2 Hz, 1H), 4.85 (d, *J* = 7.8 Hz, 1H), 4.51-4.43 (m, 2H), 4.31 (dd, *J* = 12.2, 4.9 Hz, 1H), 4.16 (dd, *J* = 10.1, 3.2 Hz, 1H), 4.13-4.01 (m, 1H), 3.73 (dd, *J* = 10.1, 4.2 Hz, 1H), 2.01 (m, 4H), 1.92 (m, 5H), 1.70 (m, 2H), 1.25 (m, 48H), 0.88 (t, *J* = 6.3 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.58, 169.55, 166.0, 165.7, 165.2, 165.1, 165.0, 136.9, 133.42, 133.40, 133.3, 133.1, 133.0, 131.2, 130.1, 129.8, 129.7, 129.6, 129.5, 129.0, 128.9, 128.7, 128.5, 128.38, 128.37, 128.33, 128.29, 124.8, 100.81, 74.0, 73.9, 72.9, 72.36, 72.1, 69.5, 67.5, 62.9, 50.7, 32.6, 32.4, 31.94, 31.93, 31.87, 31.8, 29.73 (signals unresolved), 29.68, 29.63, 29.59, 29.54, 29.46, 29.4, 29.3, 24.7, 22.7, 20.7, 14.1; IR (neat, cm^{-1}): 2923, 2853, 1730, 1689, 1602, 1515, 1452, 1266, 1095, 1027, 709; HRMS (ESI): *m/z* calcd for $C_{82}H_{107}NO_{15}Na$ $[M+Na]^+$: 1368.7533; found: 1368.7545.

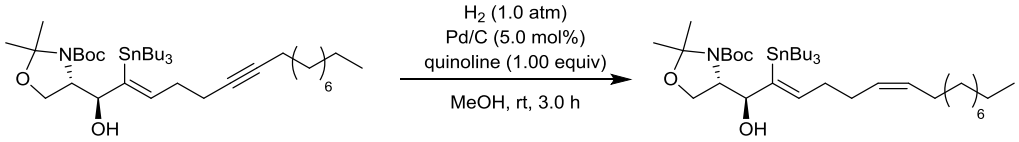


Typhonoside F (13): NaOMe (1.0 M in methanol, 13 µL) was added to a solution of compound **21** (12.5 mg) in MeOH (0.2 mL) and THF (0.2 mL). After 2 h, additional NaOMe (1.0 M in methanol, 3 µL) was added every 30 min until TLC showed complete conversion of the substrate. Stirring was continued at 5°C for 3 h before the reaction was neutralized with acetic acid. All volatile materials were evaporated and the residue was purified by flash chromatography (CH_2Cl_2:MeOH = 9:1 to 7:1) to give the title compound as a white amorphous solid (6.1 mg, 83%).[5] $[\boldsymbol{\alpha}]_{\boldsymbol{D}}^{\boldsymbol{20}}$ = +3.4 (c = 0.61, $CHCl_3$:MeOH = 1:1). ^{1}H NMR (400 MHz, [D_5]-pyridine): δ 8.35 (d, *J* = 8.7 Hz, 1H), 7.65 (d, *J* = 5.1 Hz, 1H), 6.87 (d, *J* = 4.9 Hz, 1H), 6.38 (t, *J* = 6.2 Hz, 1H), 5.99 (dd, *J* = 15.4, 5.8 Hz, 1H), 5.92 (dt, *J* = 15.5, 5.6 Hz, 1H), 5.49 (m, 2H), 4.91 (d, *J* = 7.6 Hz, 1H), 4.82 (m, 1 H), 4.76 (t, *J* = 5.6 Hz, 1H), 4.71 (dd, *J* = 10.5, 5.9 Hz, 1H), 4.58 (m, 1H), 4.51 (m, 1H), 4.36 (dt, *J* = 11.6, 5.7 Hz, 1H), 4.24 (dd, *J* = 10.5, 3.7 Hz, 1H), 4.21 (m, 2H), 4.03 (m, 1H), 3.90 (m, 1H), 2.15 (m, 4H), 2.04-1.98 (m, 2H), 1.76 (m, 2H), 1.35-1.26 (m, 48H), 0.86 (t, *J* = 6.4 Hz, 3H), 0.86 (t, *J* = 6.4 Hz, 3H); ^{13}C NMR (100 MHz, [D_5]-pyridine): δ 175.4, 131.84, 131.79, 130.9, 129.7, 105.5, 78.4, 78.2, 74.9, 72.3, 72.1, 71.3, 70.0, 62.4, 54.4, 35.5, 32.73, 32.66, 32.5, 31.9, 29.81 (signals unresolved), 29.76, 29.75, 29.70, 29.69, 29.65, 29.6, 29.4, 29.3, 25.7, 22.7, 14.1; IR (neat, cm^{-1}): 3341, 2919, 2850, 1646, 1541, 1468, 1080, 721; HRMS (ESI): *m/z* calcd for $C_{45}H_{84}NO_9$ $[M\text{-}H]^-$: 782.6152; found: 782.6158.

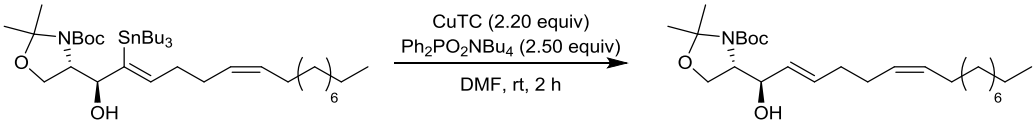


***tert*-Butyl-(*S*)-4-((*S*,*Z*)-1-hydroxy-2-(tributylstannyl)hexadec-2-en-6-yn-1-yl)-2,2-dimethyloxazolidine-3-carboxylate (25)**: [Cp*RuCl]$_4$ (2.7 mg, 0.0025 mmol) was added to a solution of the diyne (86.7 mg, 0.20 mmol) in 1,2-dichloroethane (1.0 mL) under Ar, causing a color change from brown to purple. The mixture was stirred at 80°C for 5 min before a solution of *n*-Bu_3SnH (61.1 mg, 0.21 mmol) in 1,2-dichloroethane (0.5 mL) was added via syringe pump over the course of 8 h. Once the addition was complete, stirring was continued for an extra 5 min. After removal of the solvent, the crude product was subjected to flash chromatography (hexane:EtOAc = 97:3) to give the monostannylated product as a pale yellow oil (72.6 mg, 50%, 71% brsm) and a second fraction of recovered starting material (17.6 mg).[10] The large $J_{Sn\text{-}H}$ value (126.4 Hz) indicated that *trans*-hydrostannation had occurred. $[\boldsymbol{\alpha}]_{\boldsymbol{D}}^{\boldsymbol{20}}$ = +1.2 (c = 1.47, $CHCl_3$). ^{1}H NMR (400 MHz, C_6D_6): δ 6.29 (t, *J* = 6.6 Hz, $J_{Sn\text{-}H}$ = 126.4 Hz, 1H), 4.31 (br s, 1H), 4.18-4.06 (m, 2H), 3.72 (dd, *J* = 8.8, 5.8 Hz, 1H), 2.40 (m, 2H), 2.30 (m, 2H), 2.15 (tt, *J* = 7.0, 2.1 Hz, 2H), 1.79-1.68 (m, 6H), 1.67 (s, 3H), 1.54-1.46 (m, 9H), 1.38 (m, 14H), 1.27 (m, 15H), 1.01 (t, *J* = 7.3 Hz, 9H), 0.91 (t, *J* = 6.9 Hz, 3H); ^{13}C NMR (100 MHz, C_6D_6): δ 152.3, 147.6, 139.0, 93.5, 80.8, 80.1, 79.4, 79.1, 64.5, 60.9, 34.1, 31.9, 29.6, 29.5 (signal unresolved), 29.4, 29.28, 29.26, 29.0, 28.1 (signals unresolved), 27.7, 24.4,

22.7, 19.8, 18.9, 14.0, 13.7, 11.9; ^{119}Sn NMR (186 MHz, C_6D_6): δ -58.3; IR (neat, cm^{-1}): 3495, 2955, 2923, 2871, 2855, 1693, 1457, 1386, 1375, 1365, 1247, 1170, 1099, 1070, 1050, 871, 844; HRMS (ESI): *m/z* calcd for $C_{38}H_{71}NO_4SnNa$ $[M+Na]^+$: 748.4303; found: 748.4297.

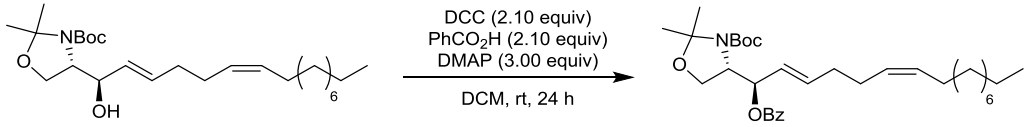


***tert*-Butyl-(*S*)-4-((*S*,2*Z*,6*Z*)-1-hydroxy-2-(tributylstannyl)hexadeca-2,6-dien-1-yl)-2,2-dimethyl-oxazolidine-3-carboxylate (26)**: A flame-dried round bottom flask was charged with Lindlar catalyst (13.0 mg, 5% palladium to the substrate) under argon. The flask was evacuated and back filled with hydrogen gas from a balloon. Methanol (2.5 mL) and quinoline (15.8 mg, 0.12 mmol) were added and the resulting suspension was stirred for 10 min. A solution of the alkyne substrate (87.0 mg, 0.12 mmol) in MeOH (2.5 mL) was introduced and the reaction was monitored by TLC. After 3 h, the flask was vented and the mixture was filtered through a pad of silica, eluting with EtOAc. The combined filtrates were evaporated and the crude product was purified by flash chromatography (hexane:EtOAc = 40:1) to give the title compound as a colorless oil (81.4 mg, 93%). $[\boldsymbol{\alpha}]_{\boldsymbol{D}}^{\boldsymbol{20}}$ = +2.1 (c = 0.54, $CHCl_3$). ^{1}H NMR (400 MHz, C_6D_6): δ 6.26 (br s, J_{Sn-H} = 127.2 Hz, 1H), 5.60-5.36 (m, 2H), 4.35 (br s, 1H), 4.19-4.06 (m, 2H), 3.72 (dd, *J* = 8.9, 5.9 Hz, 1H), 2.26 (m, 4H), 2.19-2.13 (m, 2H), 1.79-1.65 (m, 9H), 1.50 (qt, *J* = 14.9, 7.4 Hz, 6H), 1.40 (m, 14H), 1.30 (m, 18H), 1.01 (t, *J* = 7.3 Hz, 9H), 0.9- 0.88 (m, 3H); ^{13}C NMR (100 MHz, C_6D_6): δ 152.3, 146.6, 140.1, 130.5, 128.9, 93.5, 80.1, 79.1, 64.4, 61.0, 34.5, 32.0, 29.9, 29.7 (signals unresolved), 29.6, 29.48, 29.45, 28.1 (signals unresolved), 27.9, 27.7, 27.5, 22.8, 14.0, 13.7, 11.9; ^{119}Sn NMR (186 MHz, C_6D_6): δ -58.2; IR (neat, cm^{-1}): 3501, 2954, 2922, 2853, 1693, 1615, 1455, 1386, 1249, 1171, 1099, 871; HRMS (ESI): *m/z* calcd for $C_{38}H_{74}NO_4Sn$ $[M+H]^+$: 728.4634; found: 728.4636.

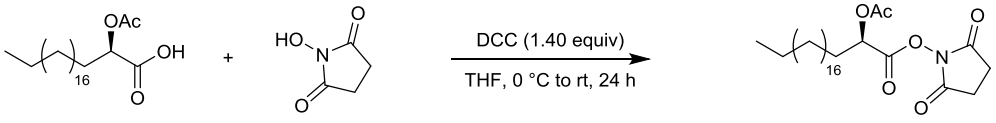


***tert*-Butyl (*S*)-4-((*R*,2*E*,6*E*)-1-hydroxyhexadeca-2,6-dien-1-yl)-2,2-dimethyloxazolidine-3-carboxylate (S28)**: CuTC (53.4 mg, 0.28 mmol) was added to a solution of the stannane (81.4 mg, 0.11 mmol) and $Ph_2PO_2NBu_4$ (113.1 mg, 0.25 mmol) in DMF (1.5 mL). The mixture was allowed to stir at room temperature for 2 h before *tert*-butyl methyl ether (10 mL) was added and the reaction was quenched with water (10 mL). The resulting yellow mixture was stirred at room temperature for an extra 30 min. The aqueous layer was extracted with *tert*-butyl methyl ether (3 × 30 mL), the combined organic layers were dried over $MgSO_4$ and filtered through a pad of SiO_2. Evaporation of the solvent and purification of the pure material by flash chromatography on silica/KF (20:1 *v:v*; EtOAc:hexane 20:1 to 10:1) furnished the title compound as a colorless liquid (44.5 mg, 91%).[2] $[\boldsymbol{\alpha}]_{\boldsymbol{D}}^{\boldsymbol{20}}$ = -24.3 (c = 0.73, $CHCl_3$). ^{1}H NMR (400 MHz,

$CDCl_3$): δ 5.68 (dt, *J* = 15.2 Hz, 5.6 Hz, 1H), 5.41 (dd, *J* = 15.2, 5.3 Hz, 1H), 5.35-5.23 (m, 2H), 4.16-3.64 (br m, 5H), 2.07-2.00 (m, 4H), 1.93 (m, 2H), 1.42 (m, 14H), 1.19 (m, 15H), 0.81 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 154.2, 132.7, 130.5, 128.8, 128.6, 94.5, 81.1, 74.1, 64.9, 62.3, 32.6, 31.9, 29.7, 29.62, 29.58, 29.4, 28.4, 27.3, 26.9, 26.3, 24.6, 22.7, 14.1; IR (neat, cm^{-1}): 3453, 3006, 2956, 2925, 2854, 1699, 1675, 1457, 1386, 1256, 1174, 1099, 1070, 965, 848, 766; HRMS (ESI): *m/z* calcd for $C_{26}H_{48}NO_4$ $[M+H]^+$: 438.3578; found: 438.3578.

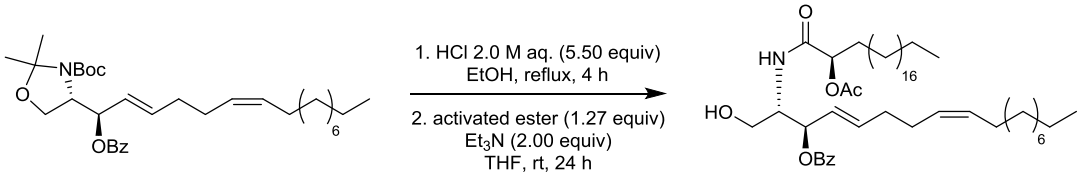


***tert*-Butyl-(*S*)-4-((*R*,2*E*,6*Z*)-1-(benzoyloxy)hexadeca-2,6-dien-1-yl)-2,2-dimethyloxazolidine-3-carboxylate (27)**: DCC (44.1 mg, 0.21 mmol) was added to a solution of the allylic alcohol (44.5 mg, 0.10 mmol), benzoic acid (26.1 mg, 0.21 mmol) and DMAP (41.5 mg, 0.34 mmol) in CH_2Cl_2 (5 mL), causing the formation of a white precipitate. The mixture was stirred at room temperature for 24 h before the reaction was quenched with MeOH (0.1 mL). After stirring for an extra 15 min, the mixture was diluted with hexane and filtered, and the remaining solid was washed with hexane/EtOAc (25:1, 10 mL). The combined filtrates were concentrated and the residue was subjected to flash chromatography (EtOAc:hexane = 10:1) to provide the title compound as a colorless liquid (51.5 mg, 93%).[5] $[\boldsymbol{\alpha}]_{\boldsymbol{D}}^{\mathbf{20}}$ = -35.8 (c = 0.84, $CHCl_3$). ^{1}H NMR (400 MHz, C_6D_6, rotamers): δ 8.30 (m, 2H), 7.12-7.01 (m, 3H), 6.40 (br s, 0.4H), 6.33 (br s, 0.6H), 5.89 (dt, *J* = 16.1, 6.4 Hz, 1H), 5.61-5.31 (m, 3H), 4.27 (br s, 0.4H), 4.17 (d, *J* = 8.8 Hz, 0.6H), 4.11 (d, *J* = 8.8 Hz, 0.4H), 3.87 (br s, 0.6H), 3.79-3.66 (m, 1H), 2.09-1.87 (m, 6H), 1.70 (s, 2H), 1.55 (m, 8H), 1.39 (s, 6H), 1.28 (m, 13H), 0.91 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, C_6D_6, rotamers): δ 165.2, 165.1, 152.2, 151.5, 134.5, 134.3, 132.6, 132.4, 130.6, 130.4, 129.9, 128.6, 128.4, 128.2, 126.2, 126.1, 94.7, 93.7, 79.5, 74.0, 73.7, 63.5, 63.4, 60.3, 60.0, 32.5, 32.0, 29.8, 29.71, 29.67, 29.44, 29.38, 28.13, 27.97, 27.35, 27.22, 26.72, 26.65, 26.31, 24.25, 22.83, 22.75, 14.01; IR (neat, cm^{-1}): 3005, 2974, 2925, 2854, 1725, 1702, 1602, 1452, 1376, 1268, 1176, 1097, 711; HRMS (ESI): *m/z* calcd for $C_{33}H_{51}NO_5Na$ $[M+Na]^+$: 564.3659; found: 564.3662.



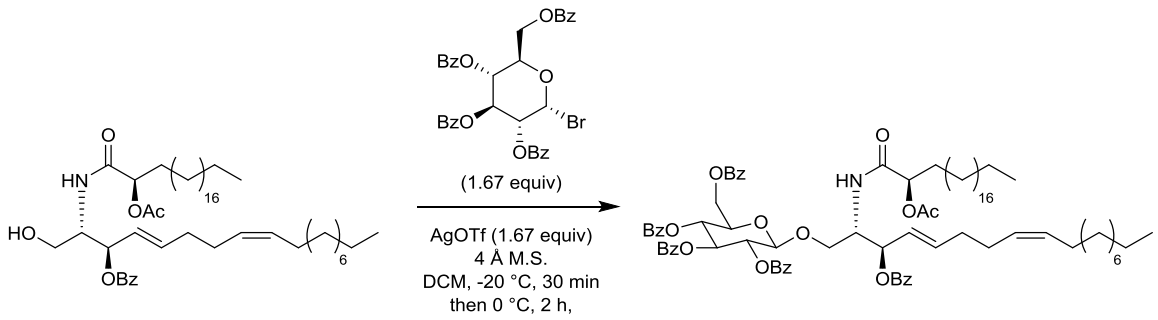
2,5-Dioxopyrrolidin-1-yl (*R*)-2-acetoxyheneicosanoate. DCC (5.3 mg, 0.026 mmol) was added to a solution of (*R*)-2-acetoxyheneicosanoic acid (9.1 mg, 0.024 mmol) and N-hydroxysuccinimide (3.2 mg, 0.027 mmol) in THF (0.15 mL) at 0°C. The mixture was stirred at 0°C for 1 h and then at ambient temperature overnight. Water (1.5 mg, 0.08 mmol) was added and stirring continued for 1 h before the mixture was diluted with hexane (1 mL). The precipitated dicyclohexylurea was filtered and washed with hexane/EtOAc (10:1, 10 mL). The combined filtrates were dried over $MgSO_4$, filtered and concentrated.

The resulting crude 2,5-dioxopyrrolidin-1-yl (*R*)-2-acetoxyhenicosanoate (**23**) was used directly in the next step without further purification.

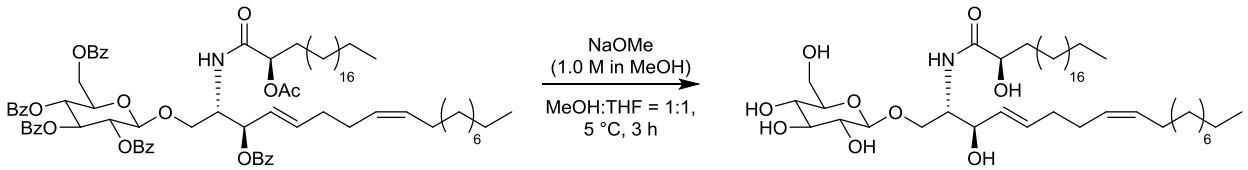


(2*S*,3*R*,4*E*,8*Z*)-2-((*R*)-2-Acetoxyhenicosanamido)-1-hydroxyoctadeca-4,8-dien-3-yl benzoate (28). aq HCl (2 M, 0.05 mL) was added to a stirred solution of *tert*-butyl-(*S*)-4-((*R*,2*E*,6*E*)-1-(benzoyloxy)hexadeca-2,6-dien-1-yl)-2,2-dimethyl oxazolidine-3-carboxylate (10.0 mg, 0.019 mmol) in EtOH (0.2 mL) and the mixture was stirred for 4 h at 70°C. $CHCl_3$/MeOH (7:1, 10 mL) and H_2O (5 mL) was introduced, the layers were separated and the aqueous phase was extracted with $CHCl_3$/MeOH (7:1, 2 × 10 mL). The combined organic extracts were dried over $MgSO_4$ and concentrated to give the crude amine as a colorless solid.

Crude **23** and the crude amine were dissolved in THF (0.50 mL), Et_3N (3.9 mg, 0.039 mmol) was introduced and the resulting mixture was stirred at room temperature for 20 h. The mixture was diluted with EtOAc and H_2O, and the aqueous layer was extracted with EtOAc (3 × 10 mL). The combined organic phases were dried and concentrated to give a yellow oil which was purified by flash chromatography (hexane:EtOAc = 3:1 to 1:1) to furnish the title compound as a colorless viscous oil (10.0 mg, 70%).[5] $[\boldsymbol{\alpha}]_{\boldsymbol{D}}^{\mathbf{20}}$ = +26.7 (c = 0.27, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.04 (m, 2H), 7.60 (m, 1H), 7.46 (m, 2H), 6.78 (d, *J* = 8.4 Hz, 1H), 5.90 (dt, *J* = 14.5, 5.9 Hz, 1H), 5.70-5.51 (m, 2H), 5.43-5.25 (m, 2H), 5.17 (dd, *J* = 7.5, 4.6 Hz, 1H), 4.23 (ddt, *J* = 10.1, 6.8, 3.4 Hz, 1H), 3.78-3.63 (m, 2H), 2.74 (br s, 1H), 2.15 (s, 3H), 2.14-2.07 (m, 4H), 2.02-1.94 (m, 2H), 1.88-1.69 (m, 2H), 1.25 (m, 48H), 0.88 (t, *J* = 6.5 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.2, 169.7, 166.6, 136.7, 133.6, 130.9, 129.8, 129.5, 128.6, 128.2, 125.0, 74.4, 74.2, 61.6, 53.6, 32.4, 31.94, 31.92, 30.6, 29.72 (signals unresolved), 29.70, 29.67, 29.66, 29.62, 29.59, 29.5, 29.38, 29.35, 29.3, 27.3, 26.5, 24.9, 22.7, 20.9, 14.1; IR (neat, cm^{-1}): 3296, 2952, 2921, 2851, 1744, 1720, 1654, 1546, 1452, 1467, 1266, 1233, 1115, 1071, 711; HRMS (ESI): *m/z* calcd for $C_{48}H_{81}NO_6Na$ $[M+Na]^+$: 790.5956; found: 790.5959.

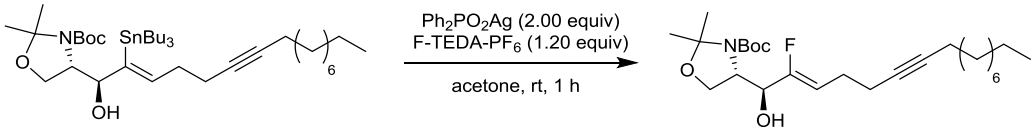


Compound 29. A solution of amide **28** (9.0 mg, 0.012 mmol), 2,3,4,5-tetraO-benzoyl-α-D-glucopyranosyl bromide (12.9 mg, 0.020 mmol) and 4 Å MS (16.0 mg) in CH_2Cl_2 (0.5 mL) was prepared and stirred under Ar at room temperature for 30 min before it was cooled to -20°C. AgOTf (5.0 mg, 0.020 mmol) in toluene (0.1 mL) was introduced at -20°C. The mixture was stirred at -20°C for 30 min and for 2 h at 0°C before it was diluted with EtOAc (10 mL). Insoluble material was filtered off and rinsed with EtOAc (15 mL). The combined organic layers were washed with aqueous $NaHCO_3$ solution (5 mL), water (5 mL) and brine (5 mL). The combined aqueous phases were extracted with EtOAc (2 × 10 mL) and the combined extracts were dried over $MgSO_4$, filtered and concentrated. Purification of the residue by preparative TLC (hexane:EtOAc = 3:1) gave the title compound as a colorless viscous liquid (13.0 mg, 82%).[5] $[\boldsymbol{\alpha}]_{\boldsymbol{D}}^{\boldsymbol{20}}$ = +9.8 (c = 0.21, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.99 (m, 2H), 7.95 (m, 2H), 7.92 (m, 2H), 7.87 (m, 2H), 7.80 (m, 2H), 7.54-7.27 (m, 15H), 6.47 (d, *J* = 9.1 Hz, 1H), 5.92-5.81 (m, 2H), 5.69-5.59 (m, 2H), 5.56-5.46 (m, 2H), 5.39-5.24 (m, 2H), 4.99 (dd, *J* = 7.1, 4.9 Hz, 1H), 4.85 (d, *J* = 7.8 Hz, 1H), 4.53-4.43 (m, 2H), 4.33 (dd, *J* = 11.6, 4.8 Hz, 1H), 4.16 (dd, *J* = 10.2, 3.5 Hz, 1H), 4.11 (ddd, *J* = 9.6, 4.9, 3.3 Hz, 1H), 3.73 (dd, *J* = 10.0, 4.4 Hz, 1H), 2.04 (m, 4H), 1.93 (m, 5H), 1.77-1.65 (m, 2H), 1.25 (m, 48H), 0.88 (t, *J* = 6.8 Hz, 3H), 0.87 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.59, 169.55, 166.0, 165.7, 165.2, 165.1, 165.0, 136.7, 133.42, 133.39, 133.3, 133.1, 133.0, 130.7, 130.1, 129.8, 129.7, 129.6, 129.5, 129.0, 128.7, 128.5, 128.4, 128.33, 128.29, 124.9, 100.8, 74.0, 73.8, 72.9, 72.4, 72.1, 69.5, 67.5, 62.9, 50.8, 32.4, 31.9, 31.8, 29.73 (signals unresolved), 29.7, 29.6, 29.5, 29.37, 29.36, 27.3, 26.5, 24.7, 22.7, 20.7, 14.1; IR (neat, cm^{-1}): 2924, 2853, 1733, 1687, 1602, 1521, 1451, 1368, 1266, 1177, 1094, 1070, 709; HRMS (ESI): *m/z* calcd for $C_{82}H_{107}NO_{15}Na$ $[M+Na]^+$: 1368.7533; found: 1368.7530.



Typhonoside E (12): NaOMe (1.0 M in methanol, 13 µL) was added to a solution of compound **29** (12.5 mg) in MeOH (0.2 mL) and THF (0.2 mL). After 2 h, additional NaOMe (1.0 M in methanol, 3 µL) was added every 30 min until TLC indicated complete conversion. The resulting mixture was then allowed to stir at 5°C for 3 h before the reaction was quenched with acetic acid (2.5 mg). All volatile materials were

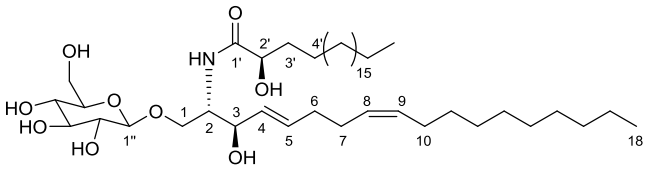
removed in vacuo and the residue was purified by flash chromatography. (CH_2Cl_2:MeOH = 9:1 to 7:1) to give the title compound as a white amorphous solid (5.9 mg, 81%).[5] $[\alpha]_D^{20}$ = +2.0 (c = 0.56, $CHCl_3$:MeOH = 1:1). ^{1}H NMR (400 MHz, [D_5]-pyridine): δ 8.35 (d, *J* = 8.6 Hz, 1H), 7.64 (d, *J* = 5.0 Hz, 1H), 6.88 (d, *J* = 4.8 Hz, 1H), 6.37 (t, *J* = 5.9 Hz, 1H), 5.99 (dd, *J* = 15.4, 6.0 Hz, 1H), 5.91 (dt, *J* = 15.4, 5.6 Hz, 1H), 5.47 (m, 2H), 4.91 (d, *J* = 7.9 Hz, 1H), 4.80 (m, 1H), 4.76 (m, 1H), 4.70 (dd, *J* = 10.5, 5.8 Hz, 1H), 4.57 (m, 1H), 4.50 (m, 1H), 4.35 (dt, *J* = 11.4, 5.6 Hz, 1H), 4.23 (dd, *J* = 10.6, 3.7 Hz, 1H), 4.20 (m, 2H), 4.02 (m, 1H), 3.89 (m, 1H), 2.17 (m, 4H), 2.05-2.01 (m, 2H), 1.76 (m, 2H), 1.35-1.27 (m, 48H), 0.85 (t, *J* = 6.4 Hz, 3H), 0.85 (t, *J* = 6.4 Hz, 3H); ^{13}C NMR (100 MHz, [D_5]-pyridine): δ 175.6, 132.2, 132.0, 130.6, 129.4, 105.7, 78.6, 78.46, 75.1, 72.5, 72.3, 71.5, 70.2, 62.6, 54.6, 35.7, 32.9, 32.1, 30.02, 29.98, 29.97, 29.91, 29.88, 29.6, 27.6, 27.3, 25.9, 22.9, 14.3; IR (neat, cm^{-1}): 3336, 2959, 2920, 2851, 1641, 1534, 1466, 1377, 1260, 1076, 799; HRMS (ESI): *m/z* calcd for $C_{45}H_{84}NO_9$ [M-H]$^-$: 782.6152; found: 782.6156.



***tert*-Butyl-(*S*)-4-((*S*,*Z*)-2-fluoro-1-hydroxyhexadec-2-en-6-yn-1-yl)-2,2-dimethyloxazolidine-3-carboxylate (31)**: A flame-dried Schlenk tube was charged with a stir bar, solid silver diphenylphosphinate (13.0 mg, 0.04 mmol) and F-TEDA-PF_6 (11.3 mg, 0.024 mmol). The mixture was stirred under Argon for 10 min to form a homogenous grey powder which was then suspended in anhydrous acetone (0.3 mL). A solution of the stannane (14.5 mg, 0.02 mmol) in anhydrous acetone (0.4 mL) was added dropwise over 1 h. The reaction mixture was quenched with sat. NH_4Cl (5 mL) and *tert*-butyl methyl ether (5 mL), the aqueous phase was extracted with *tert*-butyl methyl ether (3 times, 10 mL each). The combined organic layers were washed with brine (10 mL), dried over $MgSO_4$, filtered and concentrated. The residue was purified by flash chromatography (*tert*-butyl methyl ether:hexane = 1:10) followed by preparative HPLC (MeOH:water = 90:10) to give the fluoroalkene as a pale yellow oil (4.5 mg, 50%). $[\alpha]_D^{20}$ = -16.0 (c = 0.44, $CHCl_3$). ^{1}H NMR (500 MHz, [D_6]-Benzene, 343 K): δ 5.06 (dt, *J* = 37.7, 7.4 Hz, 1H), 4.39 (t, *J* = 10.3, 7.0 Hz, 1H), 4.15-4.01 (m, 1H), 3.95 (s, 1H), 3.64 (dd, *J* = 9.3, 6.7 Hz, 1H), 2.40-2.25 (m, 2H), 2.19-2.14 (m, 2H), 2.14-2.08 (m, 2H), 1.63 (s, 3H), 1.48 (p, *J* = 7.1 Hz, 2H), 1.44 (s, 3H), 1.40 (s, 9H), 1.38-1.22 (m, 12H), 0.90 (t, *J* = 6.7 Hz, 3H); ^{13}C NMR (126 MHz, [D_6]-Benzene, 343 K): δ 158.6 (d, *J* = 258.4 Hz), 105.8 (d, *J* = 11.9 Hz), 94.3, 80.8, 79.9, 79.1, 71.0 (d, *J* = 32.0 Hz), 63.9 (signals unresolved), 31.8, 29.5, 29.21, 29.15, 29.1, 28.8, 28.0 (signals unresolved), 26.2, 23.5 (d, *J* = 4.6 Hz), 22.6, 18.9 (d, *J* = 2.0 Hz), 18.8, 13.7; ^{19}F NMR (470 MHz, [D_6]-Benzene, 280 K): δ -119.4 (dd, *J* = 37.3, 9.9 Hz, major rotamer), -122.4 (dd, *J* = 37.6, 9.1 Hz, minor rotamer). IR (neat, cm^{-1}): 3460, 2927, 2856, 1703, 1456, 1387, 1366, 1257, 1173, 1092, 848; HRMS (ESI): *m/z* calcd for $C_{26}H_{44}NO_4FNa$ [M+Na]$^+$: 476.3147; found: 476.3149.

Tabular Survey

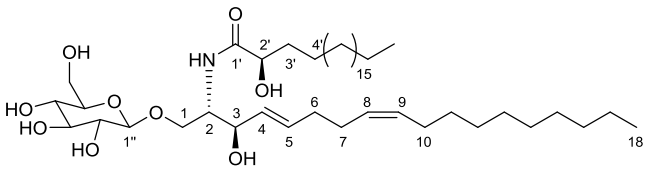
Comparison of ^{1}H NMR Data ([D_5]-pyridine) of Typhonoside E[11]



position	δ_H (J in Hz)		
	natural[a]	synthetic[b]	Δδ (ppm)
1	4.71 (dd, 10.8, 6.0)	4.70 (dd, 10.5, 5.8)	0.01
	4.24 (dd, 10.8, 4.4)	4.23 (dd, 10.6, 3.7)	0.01
2	4.80 (m)	4.80 (m)	-
3	4.76 (t, 6.0)	4.76 (m)	-
4	5.99 (dd, 15.3, 6.6)	5.99 (dd, 15.4, 6.0)	-
5	5.92 (dt, 15.3, 6.6)	5.91 (dt, 15.4, 5.6)	0.01
6	2.16 (m)	2.17 (m)	0.01
7	2.03 (m)	2.01-2.05	-
8	5.47 (m)	5.47 (m)	-
9	5.46 (m)	5.47 (m)	0.01
10	2.18 (m)	2.17 (m)	0.01
11-15	1.24-1.36 (m)	1.27-1.35 (m)	-
16	1.27 (m)	1.27-1.35 (m)	-
17	1.27 (m)	1.27-1.35 (m)	-
18	0.85 (t, 6.6)	0.85 (t, 6.4)	-
1’			
2’	4.56 (m)	4.57 (m)	0.01
3’	2.01 (m)	2.01-2.05	-
4’	1.78 (m)	1.76 (m)	0.02
5’-18’	1.24-1.36 (m)	1.27-1.35 (m)	-
19’	1.27 (m)	1.27-1.35 (m)	-
20’	1.27 (m)	1.27-1.35 (m)	-
21’	0.85 (t, 6.6)	0.85 (t, 6.4)	-
1”	4.91 (d, 7.8)	4.91 (d, 7.9)	-
2”	4.02 (m)	4.02 (m)	-
3”	4.22 (m)	4.20 (m)	0.02
4”	4.21 (m)	4.20 (m)	0.01
5”	3.89 (m)	3.89 (m)	-
6”	4.50 (m)	4.50 (m)	-
	4.34 (dd, 11.7, 5.4)	4.35 (dt, 11.4, 5.6)	0.01
N-H	8.35 (d, 9.0)	8.35 (d, 8.6)	-
	-	7.64 (d, 5.0)	-
unassigned signals[c]	-	6.68 (d, 4.8)	-
(-OH)	-	6.37 (d, 5.9)	-

[a]Data were recorded at 600 MHz. [b]Data were recorded at 400 MHz. [c]These signals were found on the original spectrum but not assigned by the authors.

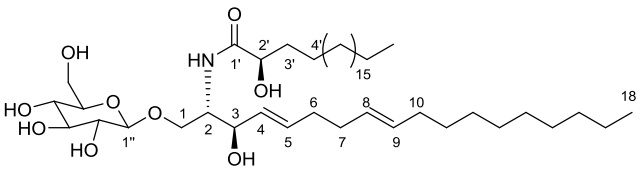
Comparison of ^{13}C NMR Data ([D_5]-pyridine) of Typhonoside E[11]



position	δ_C		
	natural[a]	synthetic[b]	Δδ (ppm)
1	70.1	70.2	0.1
2	54.6	54.6	-
3	72.3	72.3	-
4	132.2	132.2	-
5	132.1	132.0	0.1
6	32.9	32.9	-
7	27.6	27.6	-
8	130.6	130.6	-
9	129.4	129.4	-
10	27.3	27.3	-
11-15	29.6-30.0	29.6-30.0	-
16	32.1	32.1	-
17	22.9	22.9	-
18	14.3	14.3	-
1’	175.6	175.6	-
2’	72.5	72.5	-
3’	35.6	35.7	0.1
4’	25.9	25.9	-
5’-18’	29.6-30.0	29.6-30.0	-
19’	32.1	32.1	-
20’	22.9	22.9	-
21’	14.2	14.3	0.1
1”	105.7	105.7	-
2”	75.1	75.1	-
3”	78.4	78.5	0.1
4”	71.5	71.5	-
5”	78.6	78.6	-
6”	62.6	62.6	-

[a]Data were recorded at 600 MHz. [b]Data were recorded at 400 MHz.

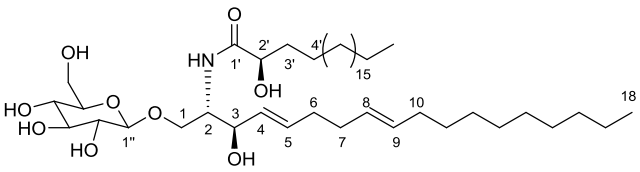
Comparison of ^{1}H NMR Data ([D_5]-pyridine) of Typhonoside F[11]



position	δ_H (*J* in Hz)		
	natural[a]	synthetic[b]	Δδ (ppm)
1	4.71 (dd, 10.2, 6.0)	4.71 (dd, 10.5, 5.9)	-
	4.25 (dd, 10.8, 4.2)	4.24 (dd, 10.5, 3.7)	0.01
2	4.82 (m)	4.82 (m)	-
3	4.76 (t, 6.0)	4.76 (t, 5.6)	-
4	5.99 (15.6, 6.0)	5.99 (dd, 15.4, 5.8)	-
5	5.92 (dt, 15.6, 6.0)	5.92 (dt, 15.5, 5.6)	-
6	2.17 (m)	2.15 (m)	0.02
7	2.06 (m)	1.98-2.04 (m)	0.02
8	5.50 (m)	5.49 (m)	-
9	5.50 (m)	5.49 (m)	-
10	2.14 (m)	21.5 (m)	0.01
11-15	1.24-1.36 (m)	1.26-1.35 (m)	-
16	1.27 (m)	1.26-1.35 (m)	-
17	1.27 (m)	1.26-1.35 (m)	-
18	0.86 (t, 6.6)	0.86 (t, 6.4)	-
1’			
2’	4.58 (m)	4.58 (m)	-
3’	2.02 (m)	1.98-2.04 (m)	-
4’	1.78 (m)	1.76 (m)	-
5’-18’	1.24-1.36 (m)	1.26-1.35 (m)	-
19’	1.27 (m)	1.26-1.35 (m)	-
20’	1.27 (m)	1.26-1.35 (m)	-
21’	0.86 (t, 6.6)	0.86 (t, 6.4)	-
1”	4.92 (7.8)	4.91 (d, 7.6)	0.01
2”	4.02 (m)	4.03 (m)	-
3”	4.21 (m)	4.21 (m)	-
4”	4.21 (m)	4.21 (m)	-
5”	3.90 (m)	3.90 (m)	
6”	4.51 (m)	4.51 (m)	-
	4.36 (dd, 11.4, 5.4)	4.36 (dt, 11.6, 5.7)	-
N-H	8.36 (d, 9.0)	8.35 (d, 8.7)	0.01
	-	7.65 (d, 5.1)	-
Unassigned signals[c]	-	6.87 (d, 4.9)	-
(-OH)	-	6.38 (d, 6.2)	-

[a]Data were recorded at 600 MHz. [b]Data were recorded at 400 MHz. [c]These signals were found on the original spectrum but not assigned by the authors.

Comparison of ^{13}C NMR Data ([D_5]-pyridine) of Typhonoside F[11]



position	δ_C		
	natural[a]	synthetic[b]	Δδ (ppm)
1	69.9	70.0	0.1
2	54.3	54.4	0.1
3	72.1	72.1	-
4	131.9	131.84	0.04
5	131.8	131.8	-
6	32.7	32.7	-
7	32.7	32.7	-
8	129.7	129.7	-
9	130.9	130.9	-
10	32.5	32.5	-
11-15	29.3-29.9	29.3-29.8	-
16	31.9	31.9	-
17	22.7	22.7	-
18	14.1	14.1	-
1’	175.4	175.4	-
2’	72.3	72.3	-
3’	35.4	35.5	0.1
4’	25.7	25.7	-
5’-18’	29.3-29.9	29.3-29.8	0.1
19’	31.9	31.9	-
20’	22.7	22.7	-
21’	14.1	14.1	-
1”	105.4	105.5	-
2”	74.9	74.9	-
3”	78.2	78.2	-
4”	71.3	71.3	-
5”	78.4	78.4	-
6”	62.4	62.4	-

[a]Data were recorded at 600 MHz. [b]Data were recorded at 400 MHz.

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10. (a) Rummelt, S. M.; Fürstner. A.; *Angew. Chem. Int. Ed.* **2014**, *53*, 3626-3630. (b) Rummelt, S. M.; Radkowski, K.; Roşca, D. -A.; Fürstner. A. *J. Am. Chem. Soc.* **2015**, *137*, 5506-5519. (c) Roşca, D. -A.; Radkowski, K.; Wolf, L. M.; Wagh, M.; Goddard, R.; Thiel, W.; Fürstner. A. *J. Am. Chem. Soc.* **2017***, 139*, 2443-2455.

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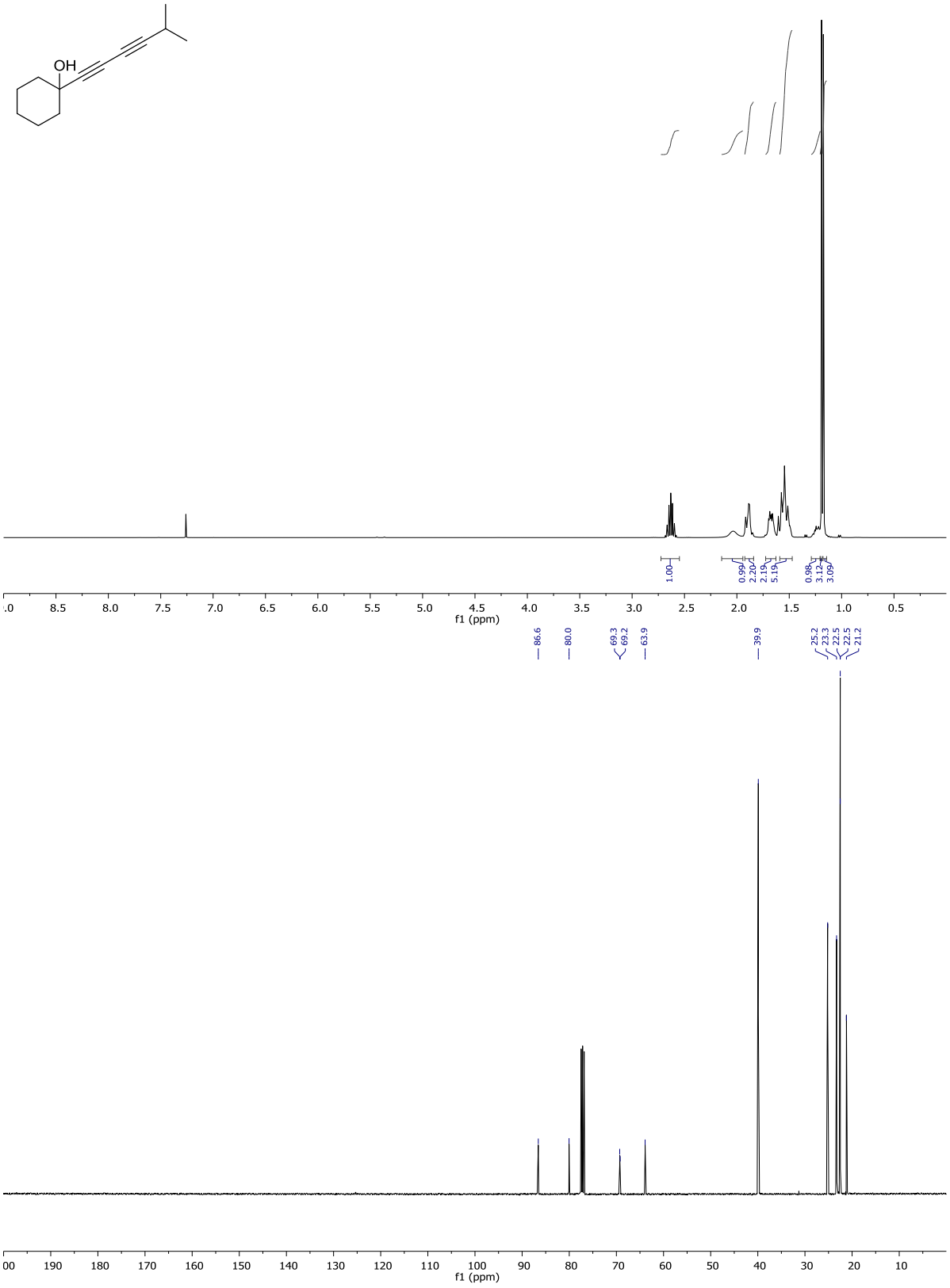
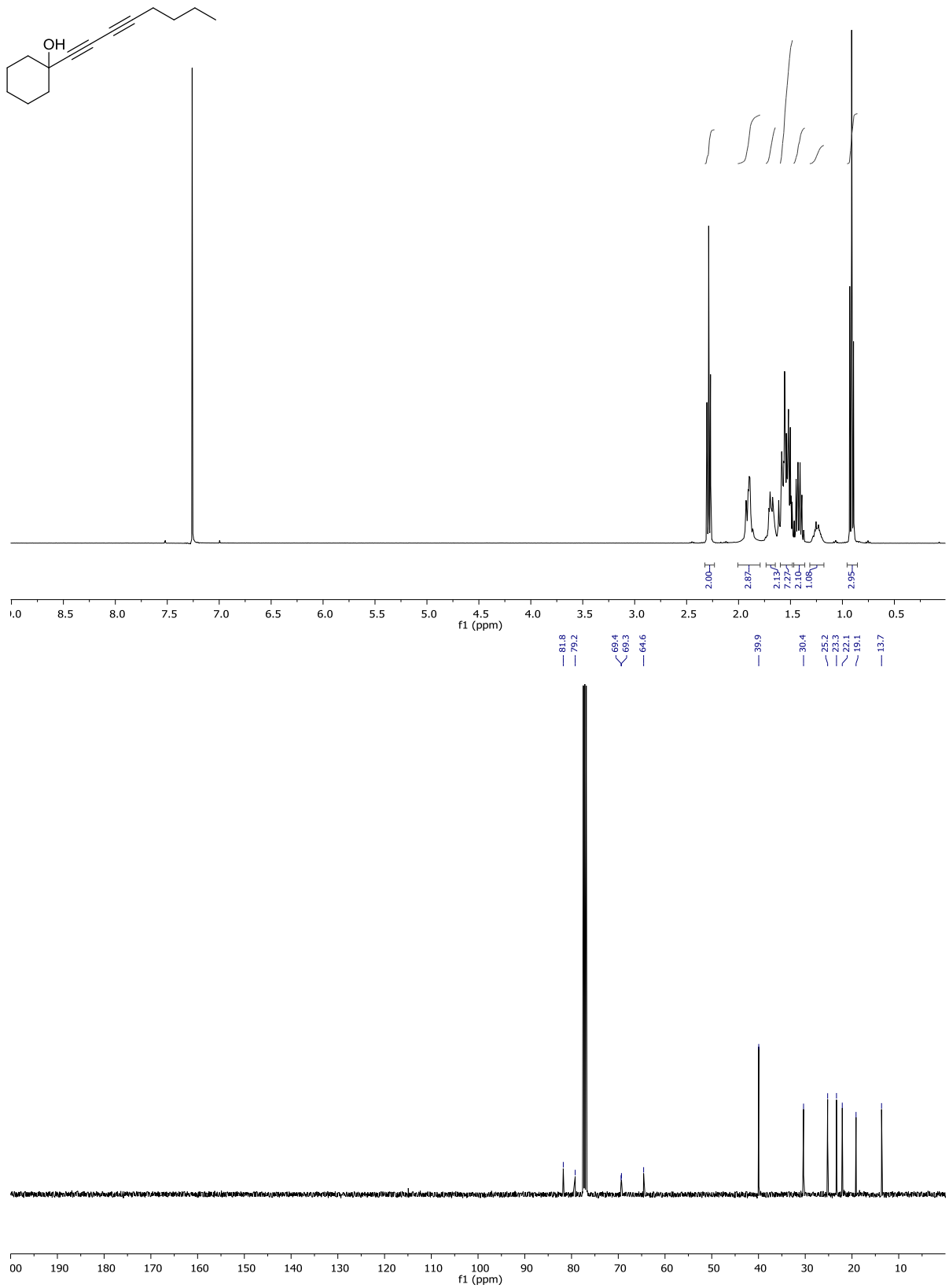
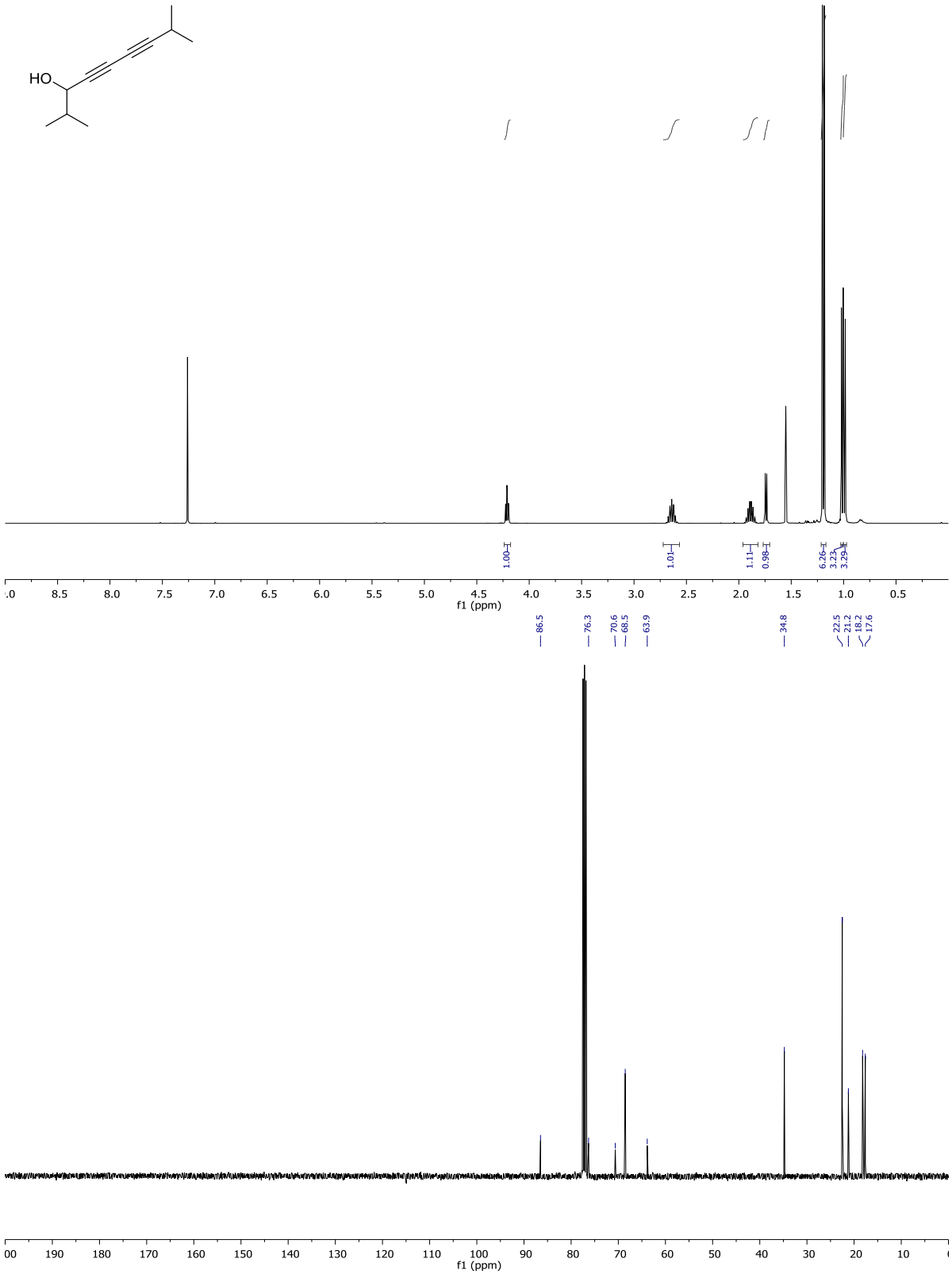
NMR spectra of 1. Top: ^{1}H NMR ($CDCl_3$, 400 MHz). Bottom: ^{13}C NMR ($CDCl_3$, 100 MHz)



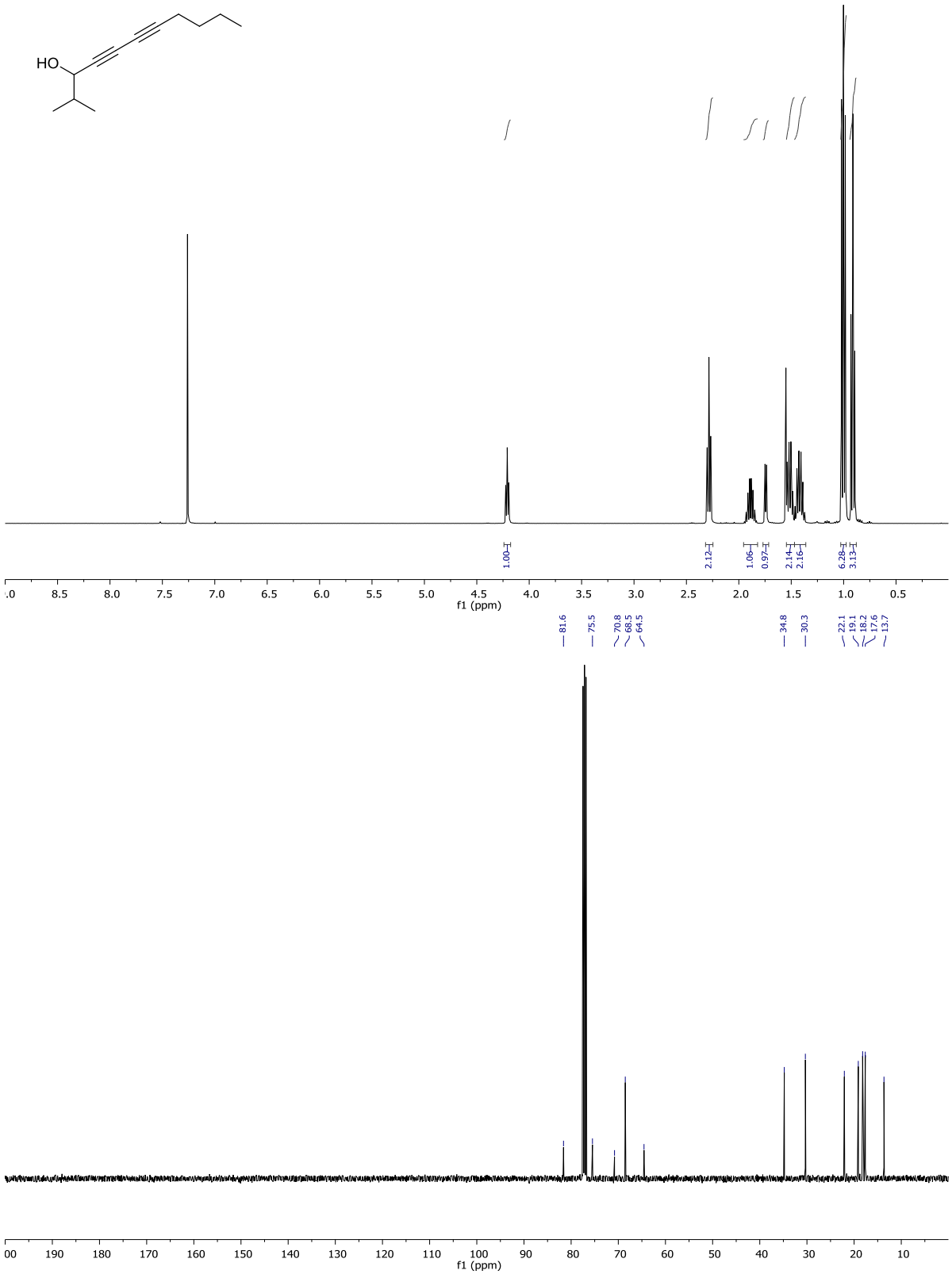
NMR spectra of 9. Top: ^{1}H NMR ($CDCl_3$, 400 MHz). Bottom: ^{13}C NMR ($CDCl_3$, 100 MHz)



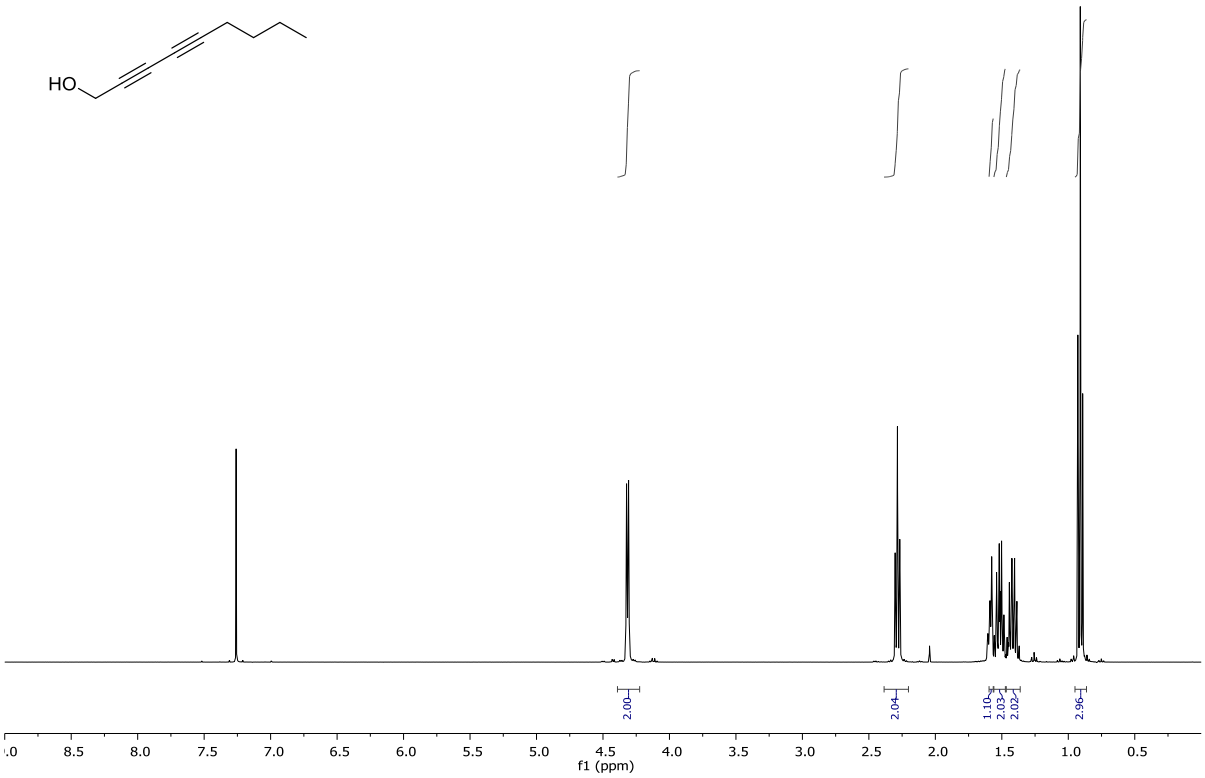
NMR spectra of 6. Top: ^{1}H NMR ($CDCl_3$, 400 MHz). Bottom: ^{13}C NMR ($CDCl_3$, 100 MHz)

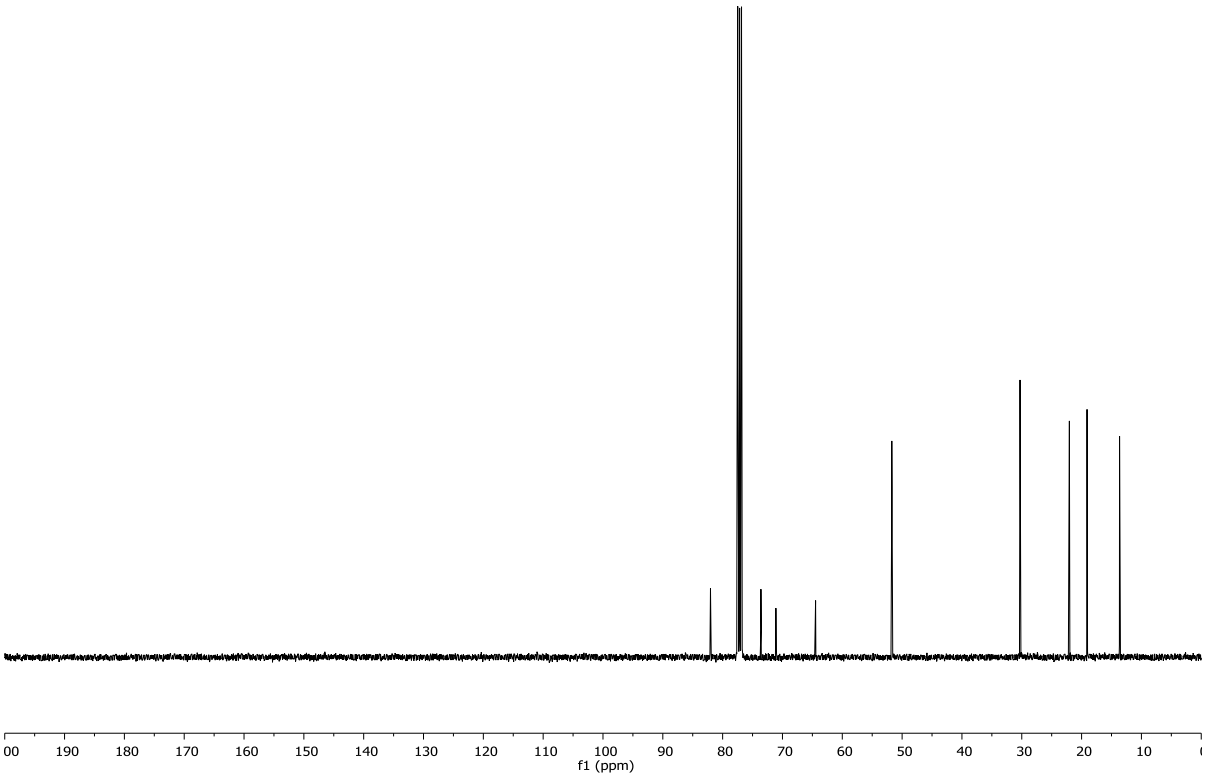


NMR spectra of S1. Top: ^{1}H NMR ($CDCl_3$, 400 MHz). Bottom: ^{13}C NMR ($CDCl_3$, 100 MHz)

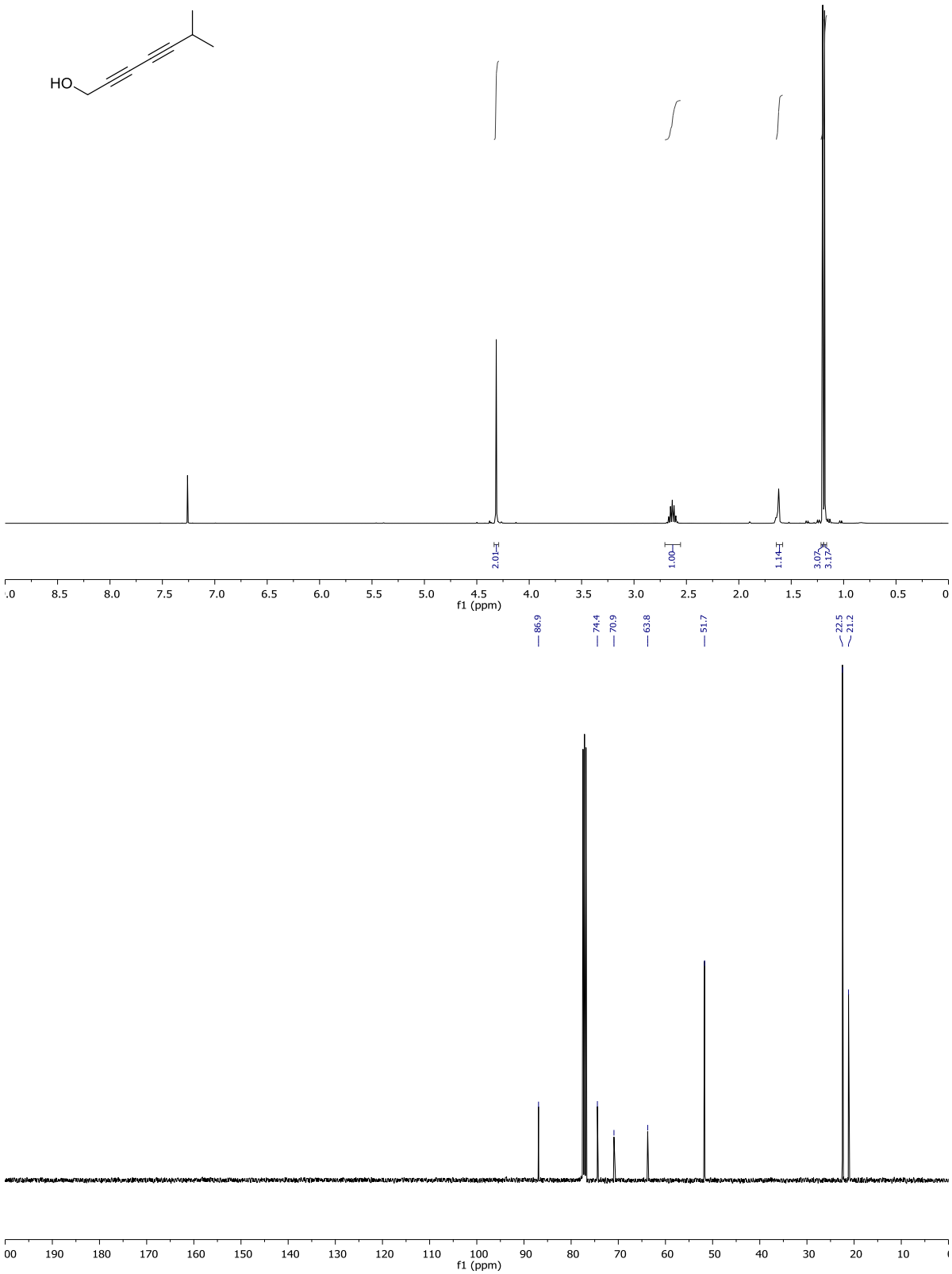


NMR spectra of S2. Top: ^{1}H NMR ($CDCl_3$, 400 MHz). Bottom: ^{13}C NMR ($CDCl_3$, 100 MHz)

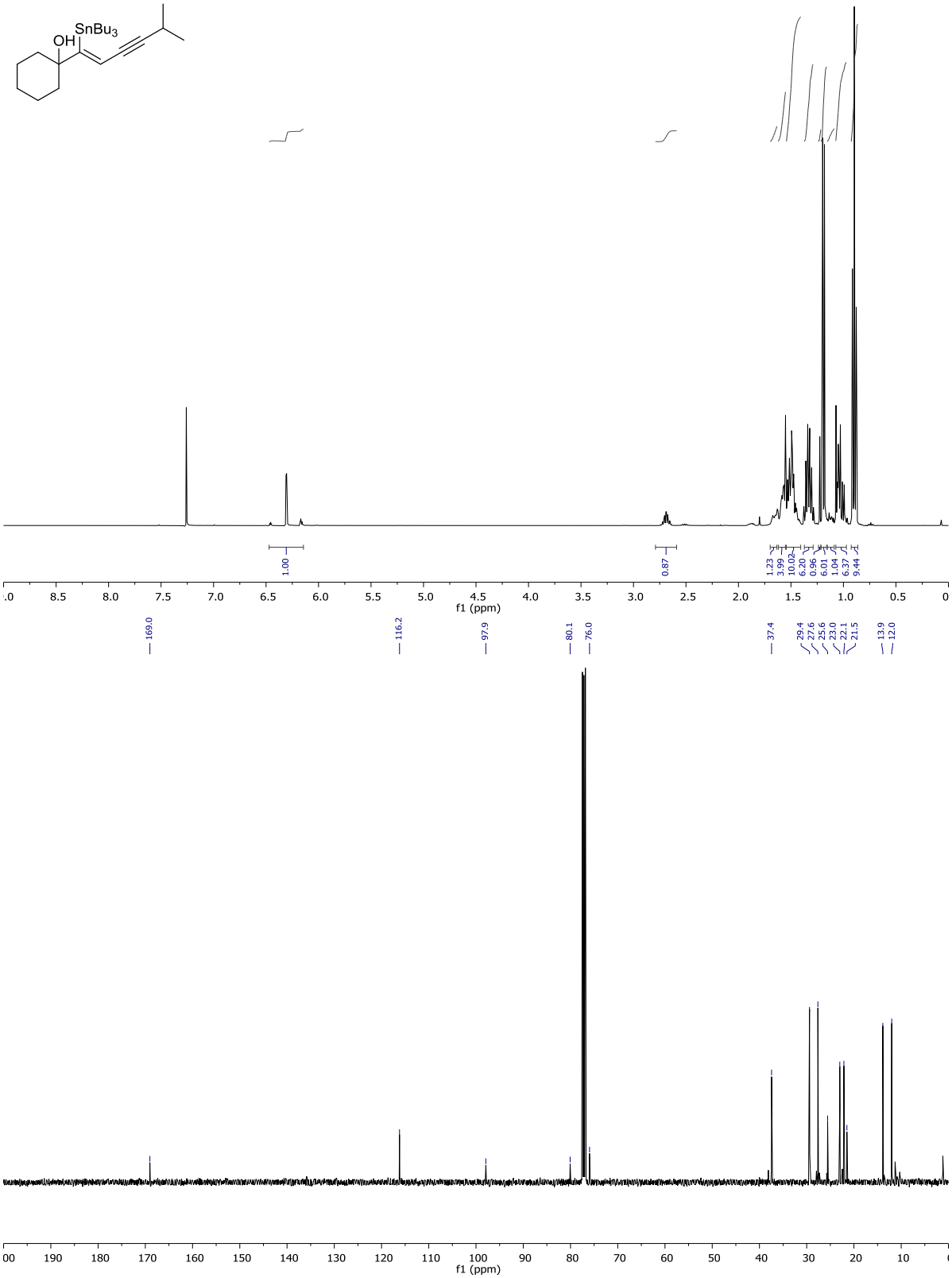




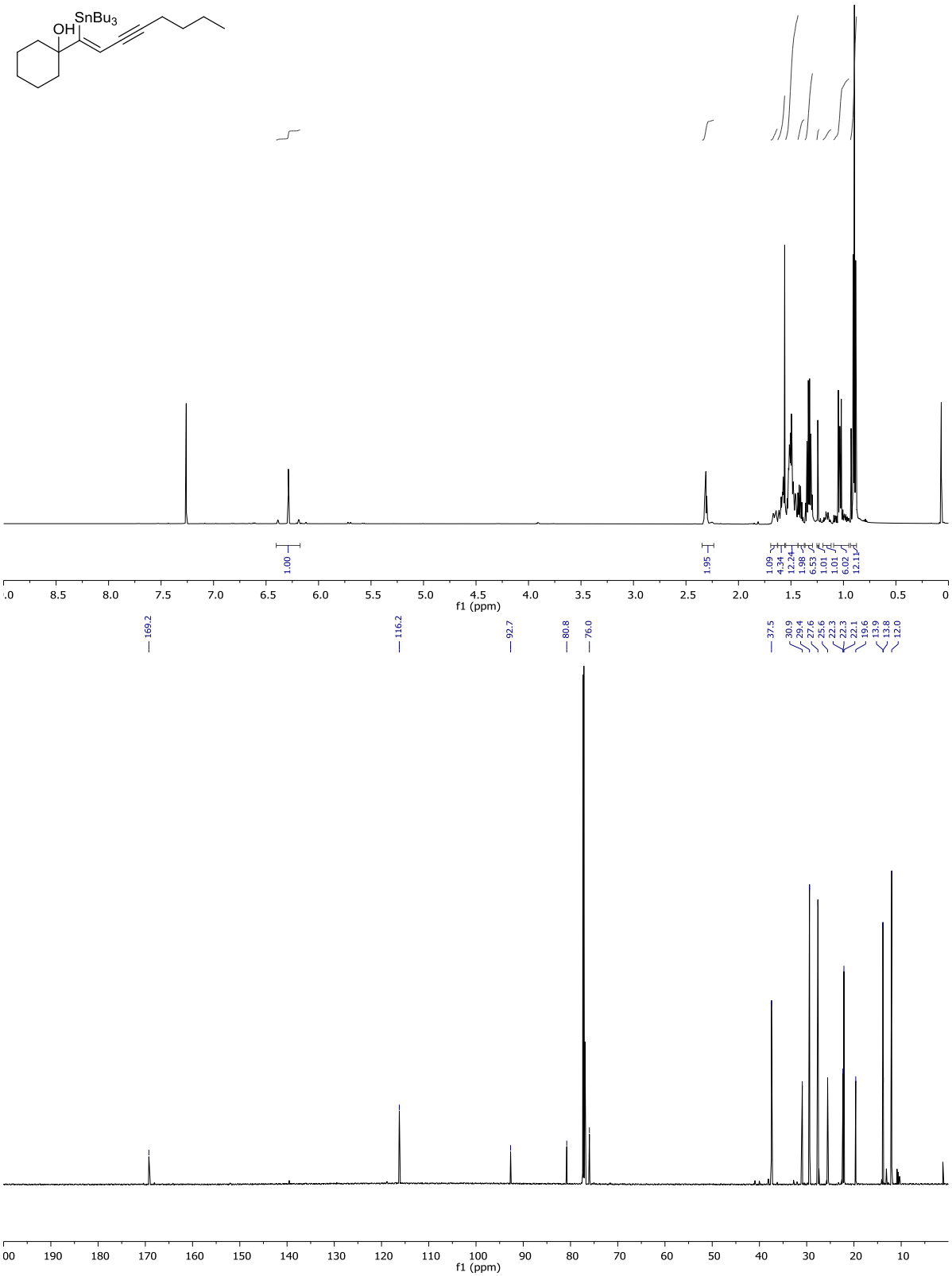
NMR spectra of S3. Top: ^{1}H NMR ($CDCl_3$, 400 MHz). Bottom: ^{13}C NMR ($CDCl_3$, 100 MHz)



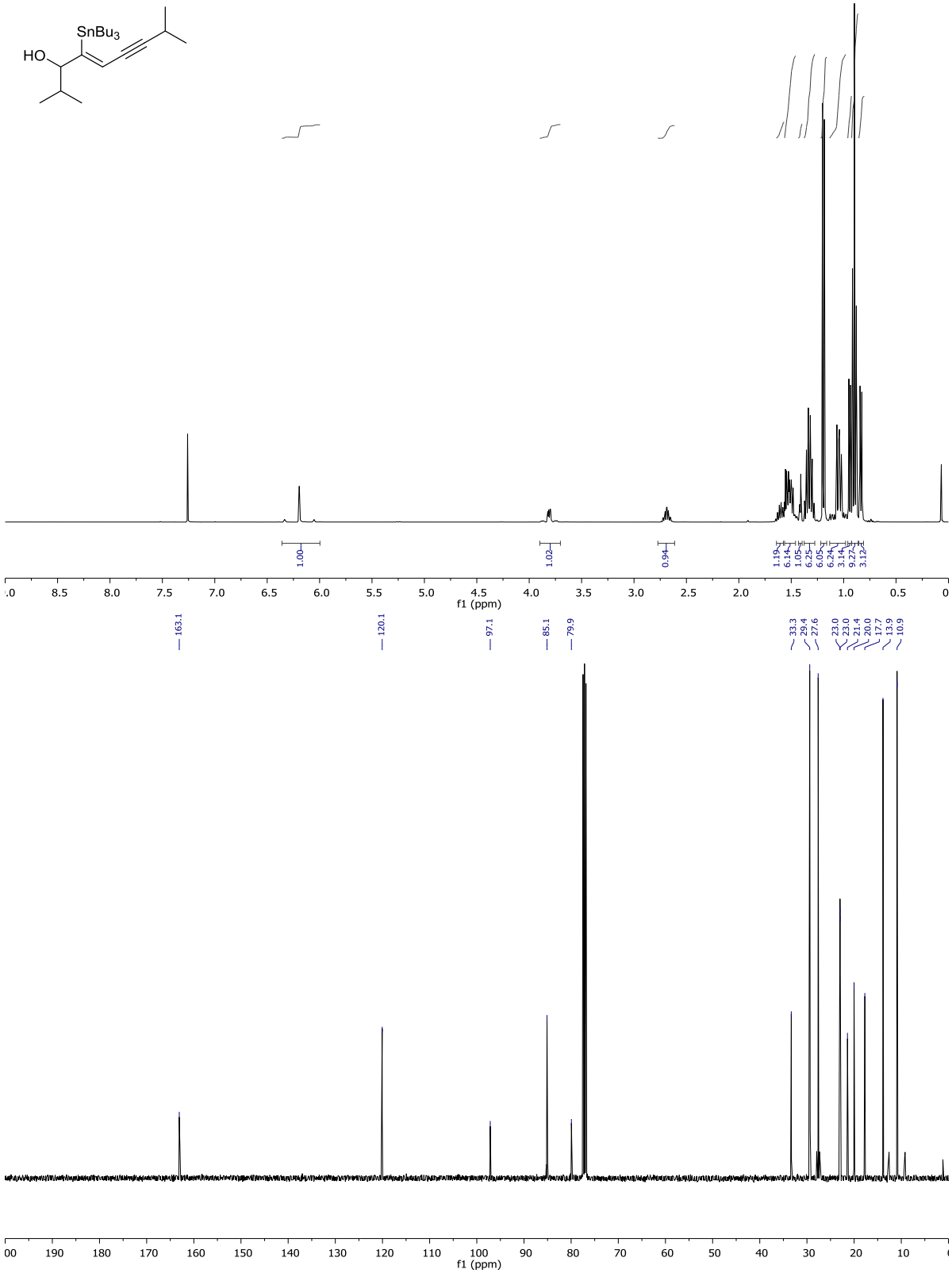
NMR spectra of 2. Top: ^{1}H NMR ($CDCl_3$, 400 MHz). Bottom: ^{13}C NMR ($CDCl_3$, 100 MHz)



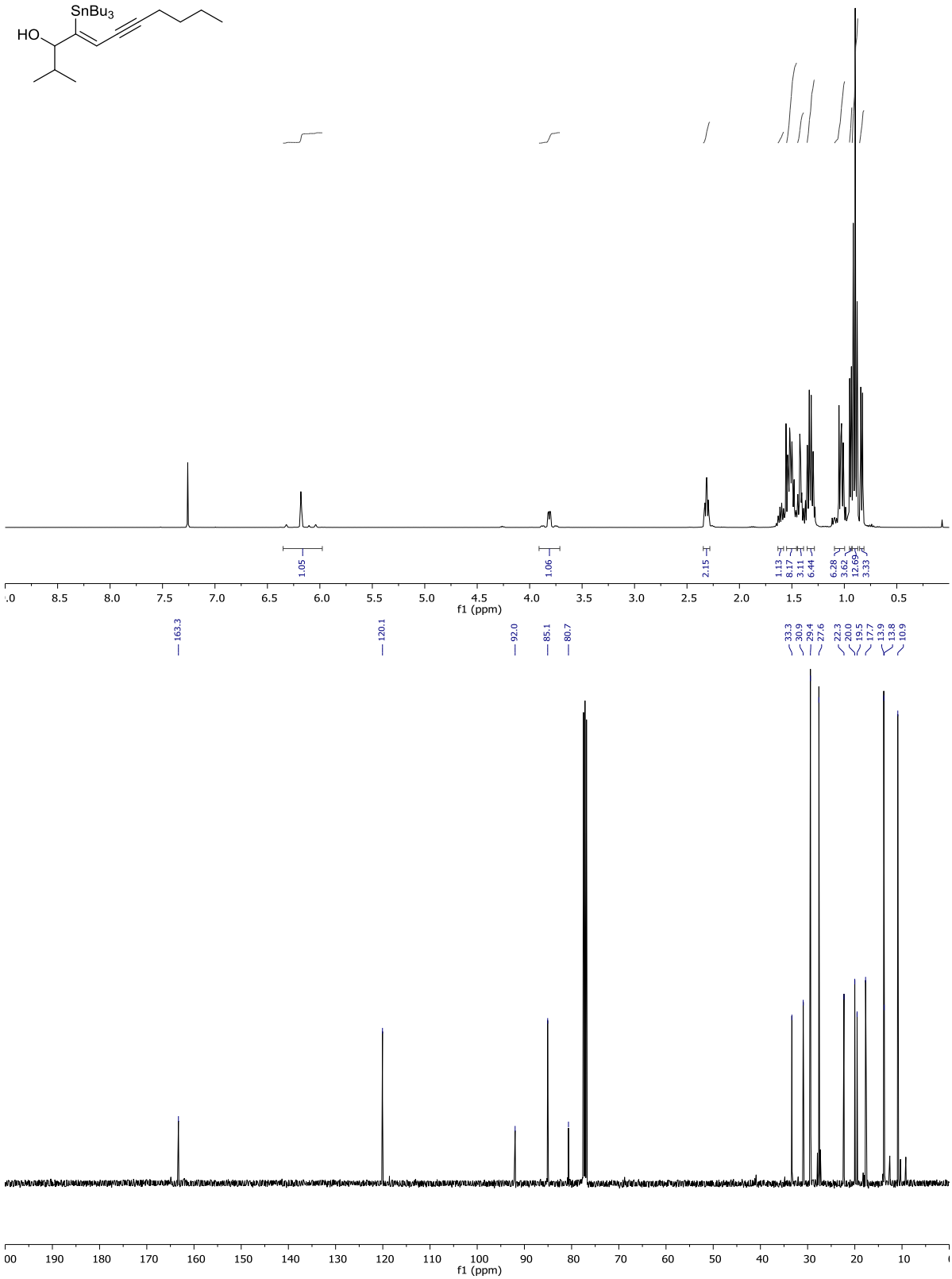
NMR spectra of S4. Top: ^{1}H NMR ($CDCl_3$, 600 MHz). Bottom: ^{13}C NMR ($CDCl_3$, 150 MHz)



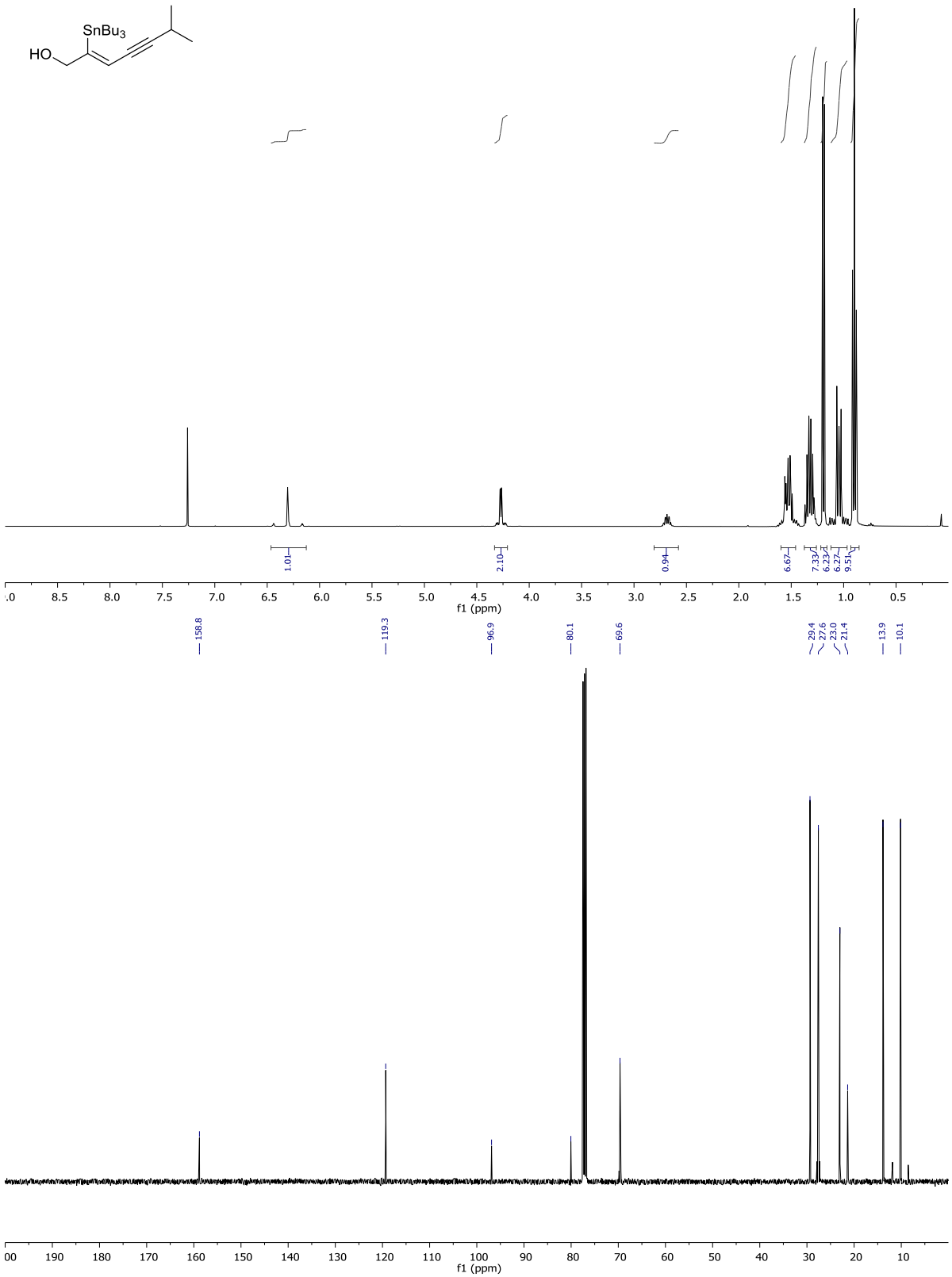
NMR spectra of 7. Top: ^{1}H NMR ($CDCl_3$, 400 MHz). Bottom: ^{13}C NMR ($CDCl_3$, 100 MHz)



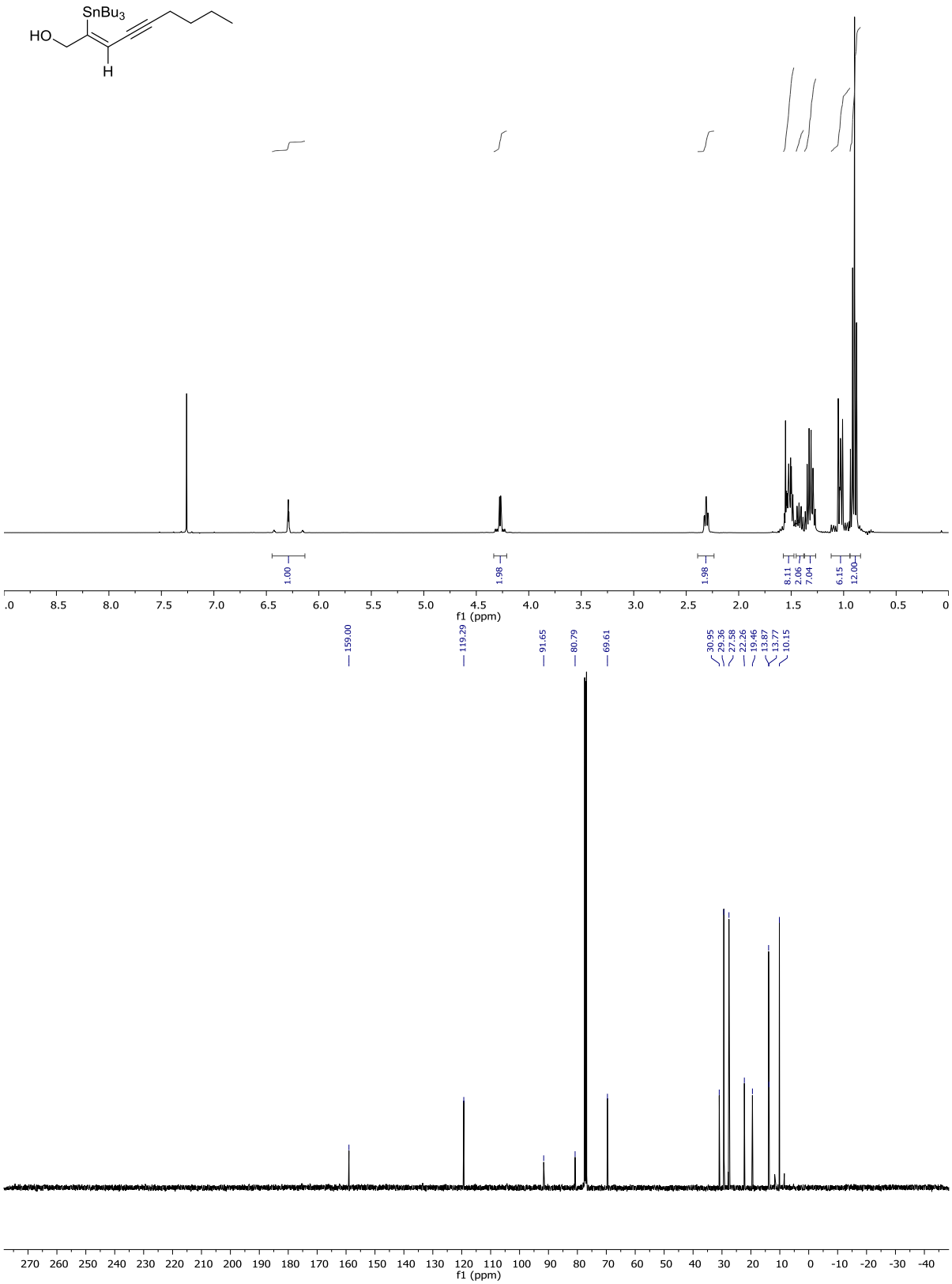
NMR spectra of S5. Top: ^{1}H NMR ($CDCl_3$, 400 MHz). Bottom: ^{13}C NMR ($CDCl_3$, 100 MHz)



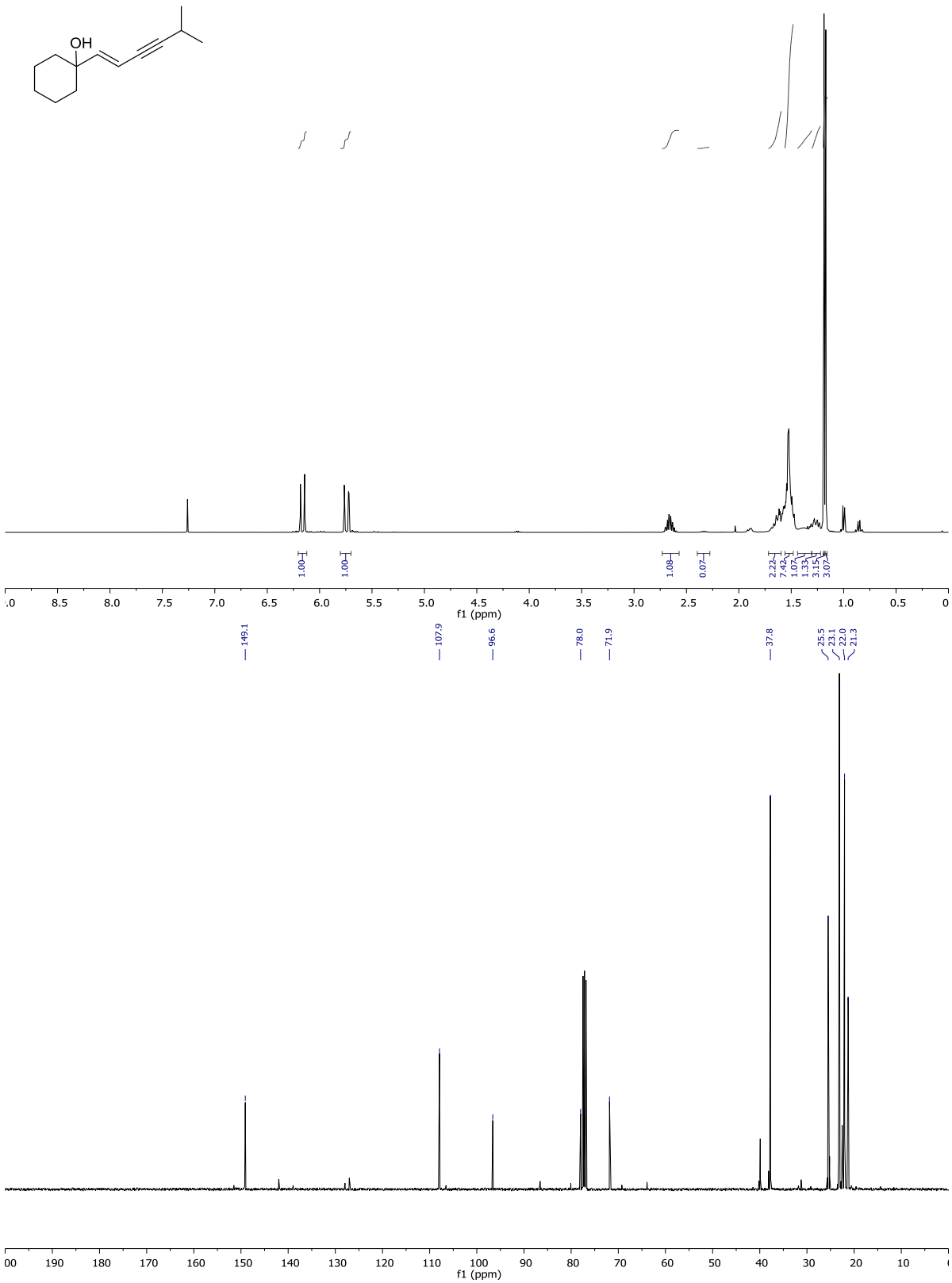
NMR spectra of S6. Top: ^{1}H NMR ($CDCl_3$, 400 MHz). Bottom: ^{13}C NMR ($CDCl_3$, 100 MHz)



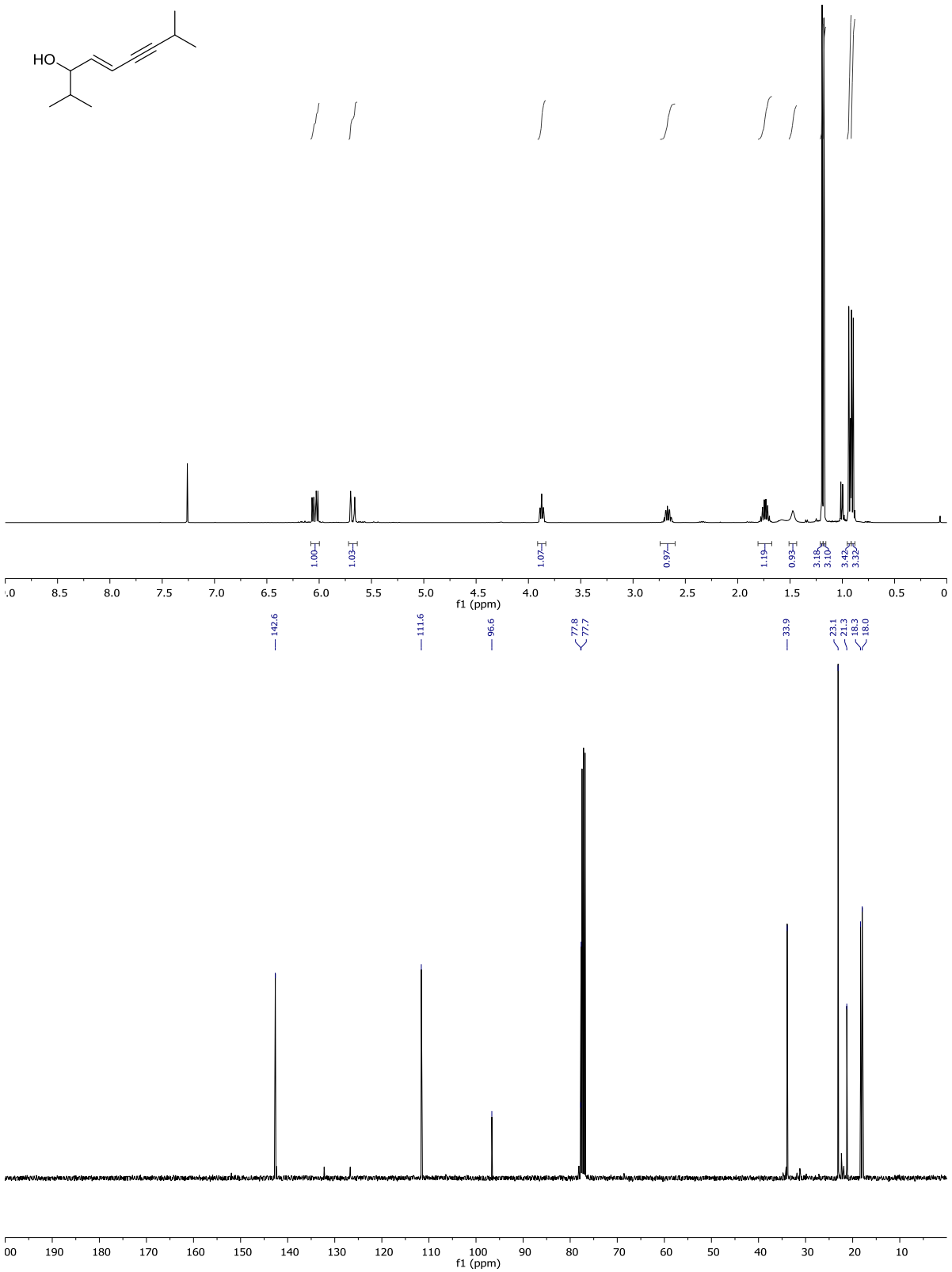
NMR spectra of S7. Top: ^{1}H NMR ($CDCl_3$, 400 MHz). Bottom: ^{13}C NMR ($CDCl_3$, 100 MHz)



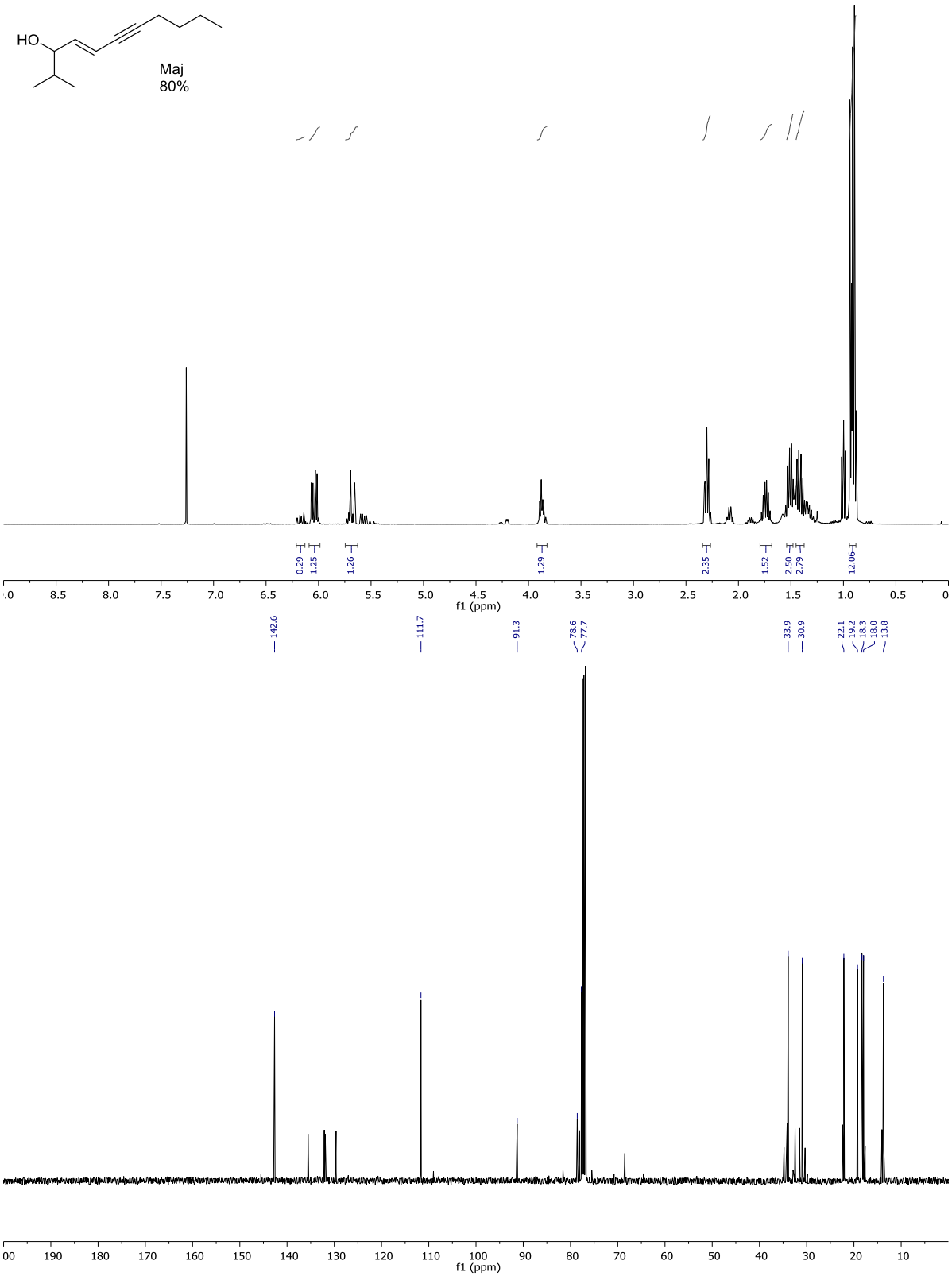
NMR spectra of S8. Top: ^{1}H NMR ($CDCl_3$, 400 MHz). Bottom: ^{13}C NMR ($CDCl_3$, 100 MHz)



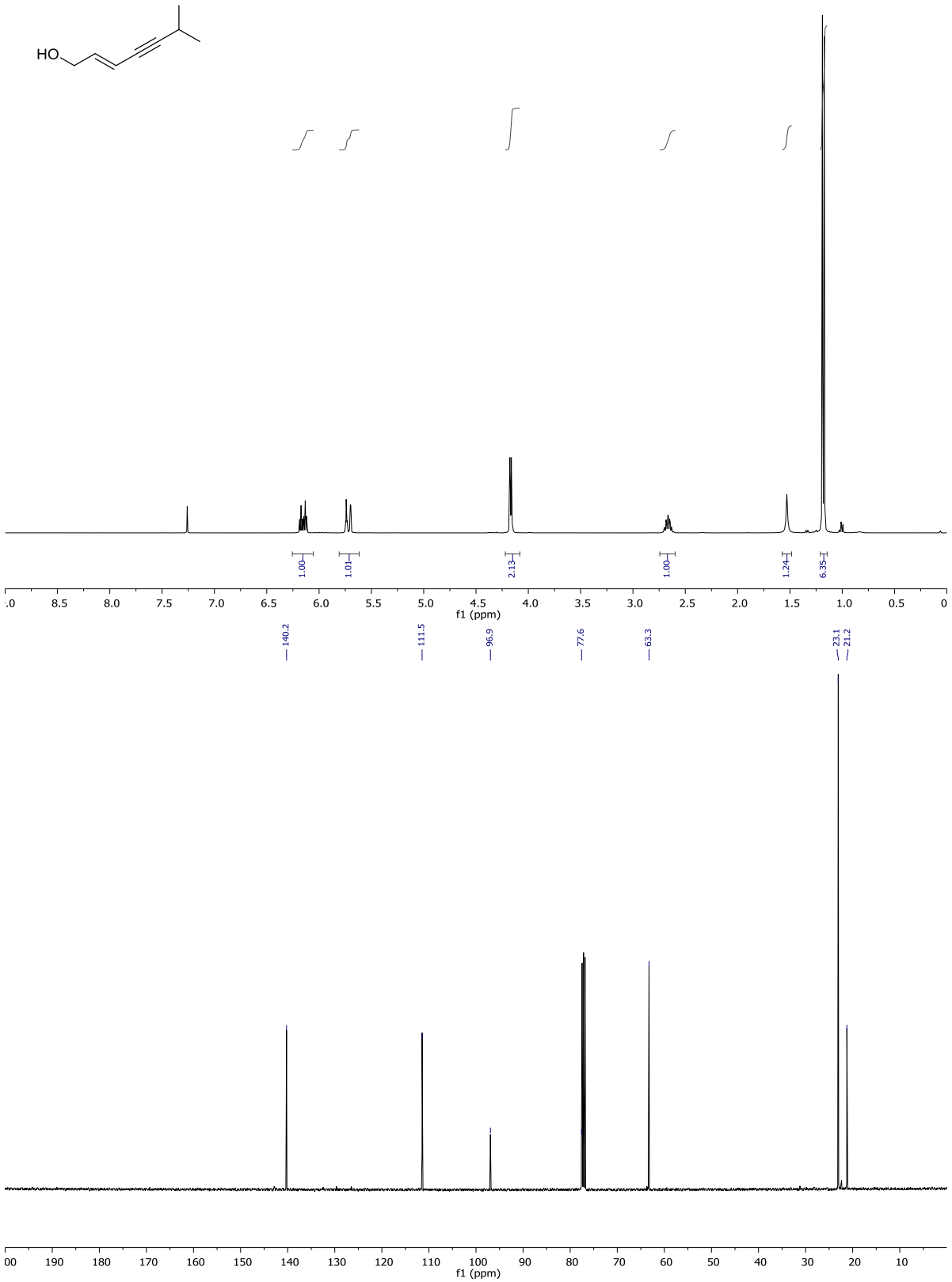
NMR spectra of S9. Top: ^{1}H NMR ($CDCl_3$, 400 MHz). Bottom: ^{13}C NMR ($CDCl_3$, 100 MHz)



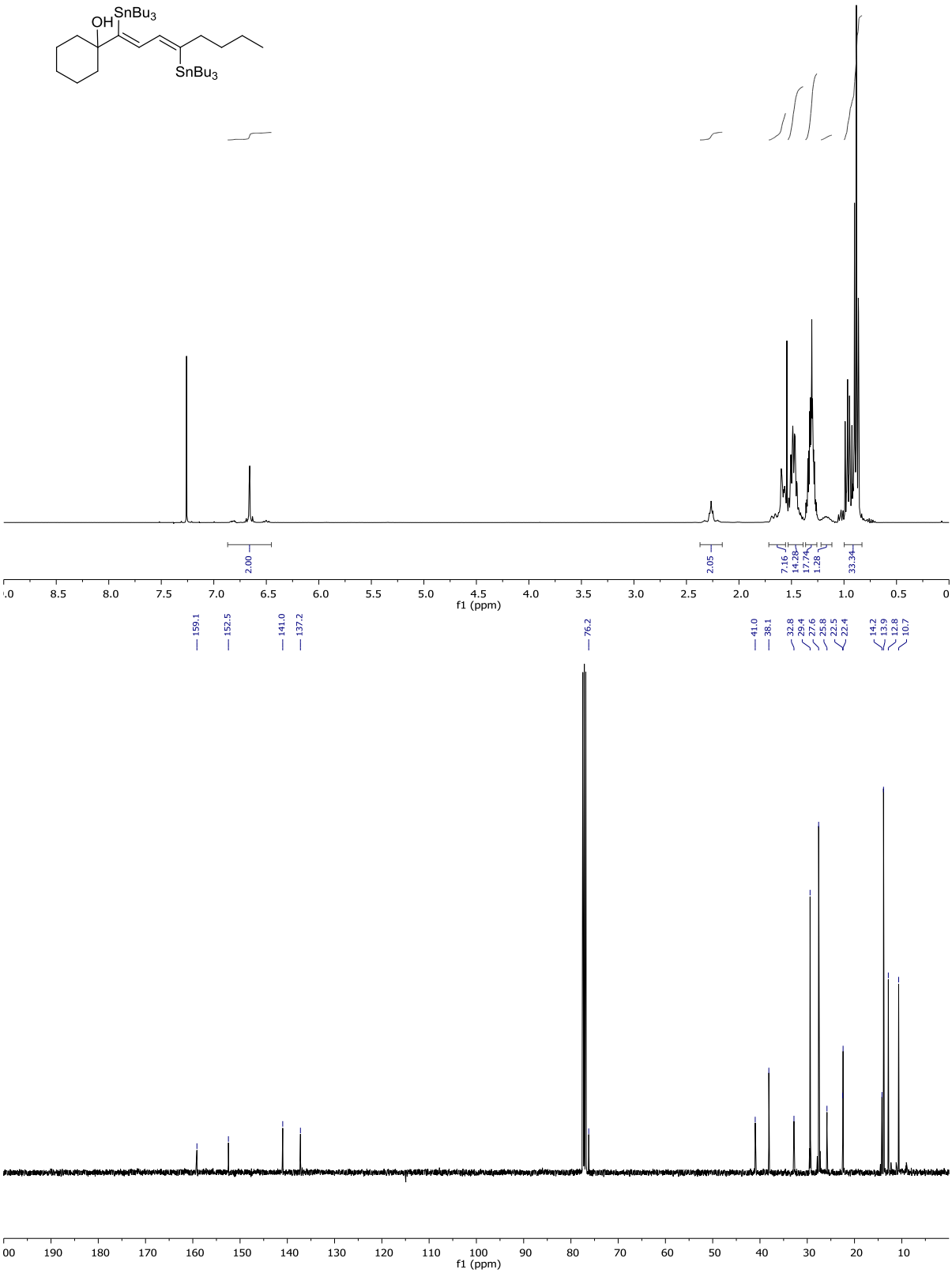
NMR spectra of S10. Top: ^{1}H NMR ($CDCl_3$, 400 MHz). Bottom: ^{13}C NMR ($CDCl_3$, 100 MHz)



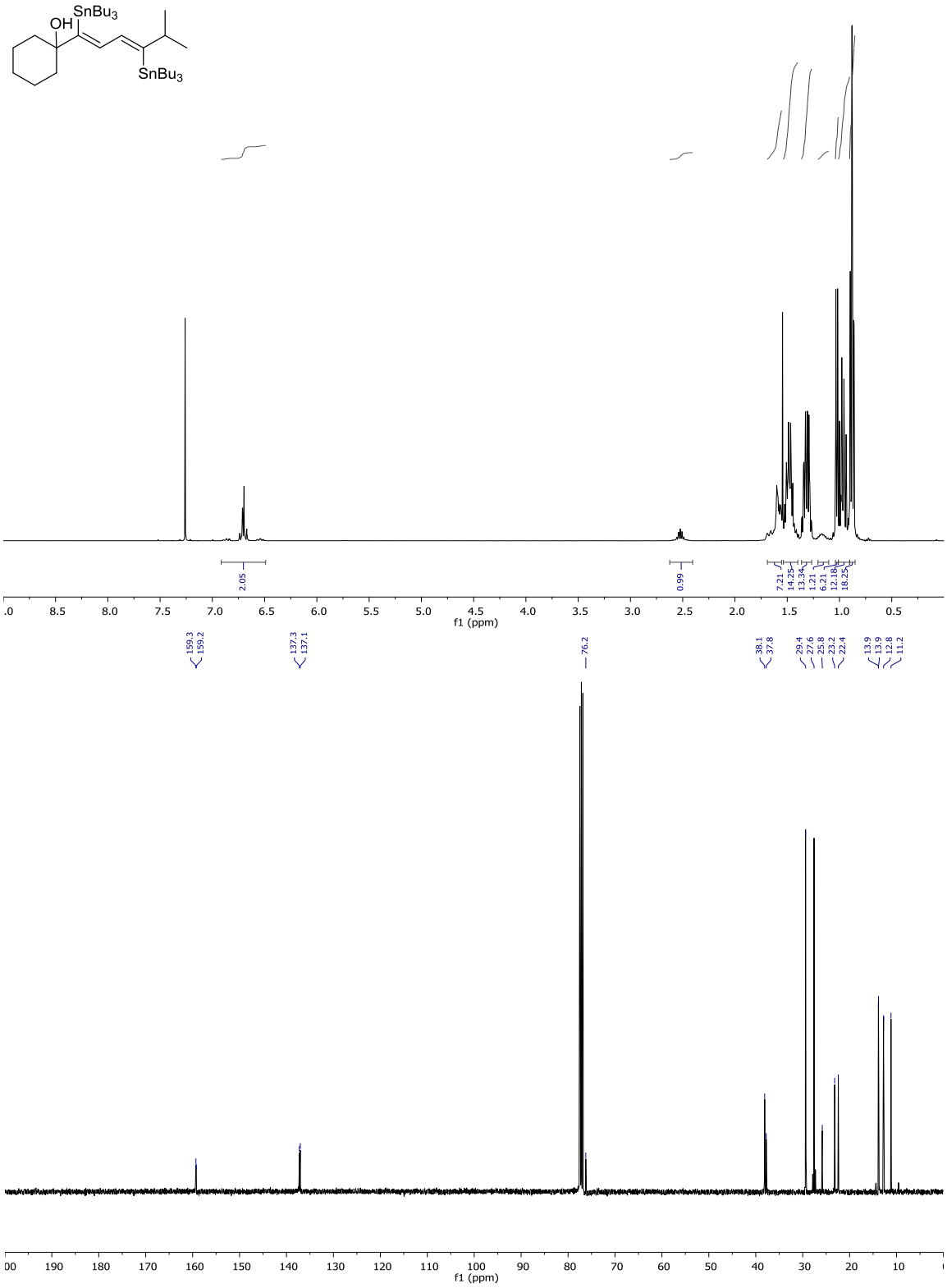
NMR spectra of S11. Top: ^{1}H NMR ($CDCl_3$, 400 MHz). Bottom: ^{13}C NMR ($CDCl_3$, 100 MHz)



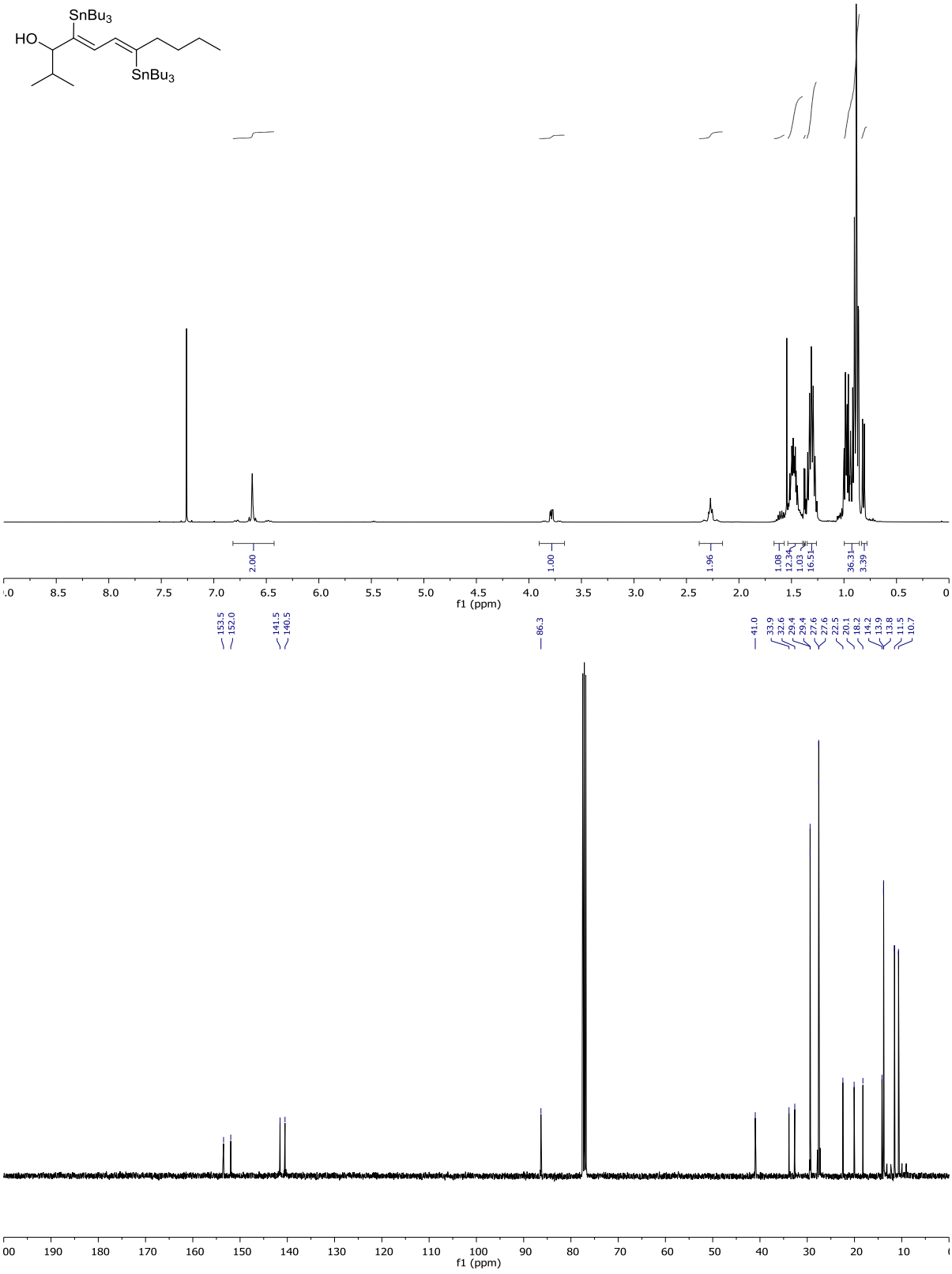
NMR spectra of S12. Top: ^{1}H NMR ($CDCl_3$, 400 MHz). Bottom: ^{13}C NMR ($CDCl_3$, 100 MHz)

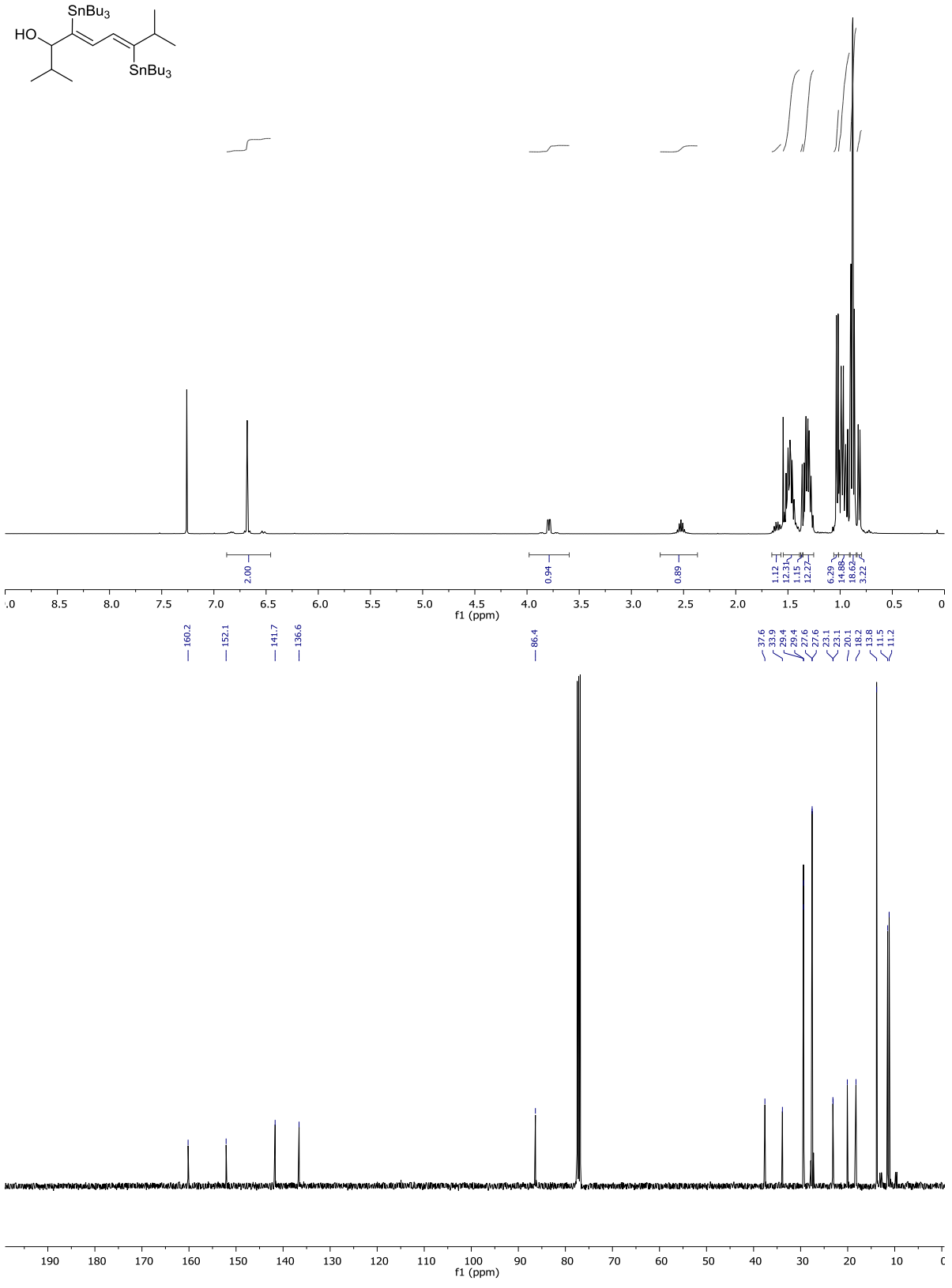


NMR spectra of 3. Top: ^{1}H NMR ($CDCl_3$, 400 MHz). Bottom: ^{13}C NMR ($CDCl_3$, 100 MHz)



NMR spectra of S13. Top: ^{1}H NMR ($CDCl_3$, 400 MHz). Bottom: ^{13}C NMR ($CDCl_3$, 100 MHz)

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HO
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0.89
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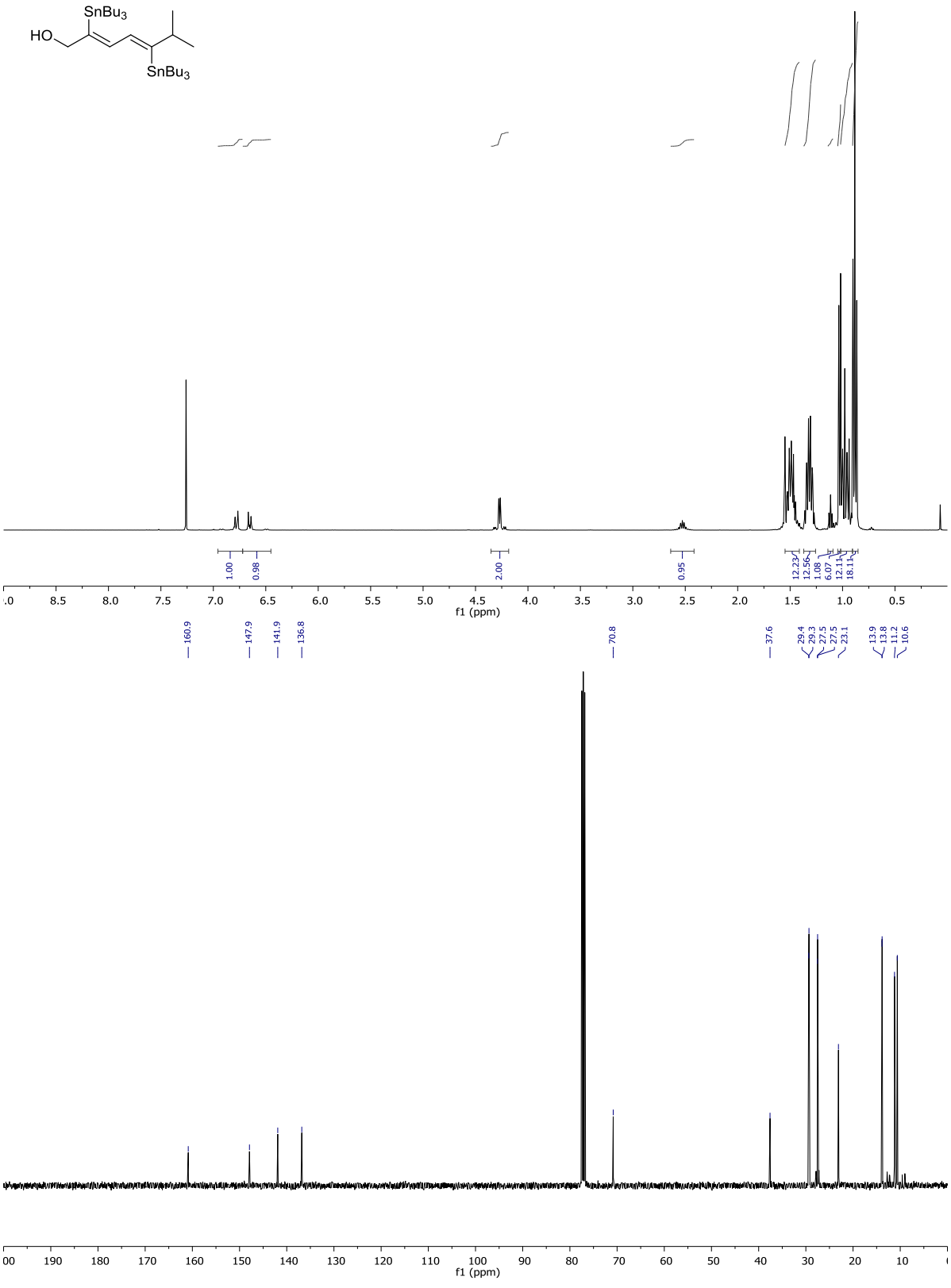
12.31
1.15
12.22
6.29
14.88
18.62
3.22
f1 (ppm)
160.2
152.1
141.7
136.6
86.4
37.6
33.9
29.4
29.4
27.6
27.6
23.1
23.1
20.1
18.2
13.8
11.5
11.2
f1 (ppm)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1.08
6.07
12.11
18.11
f1 (ppm)
160.9
147.9
141.9
136.8
70.8
37.6
29.4
29.3
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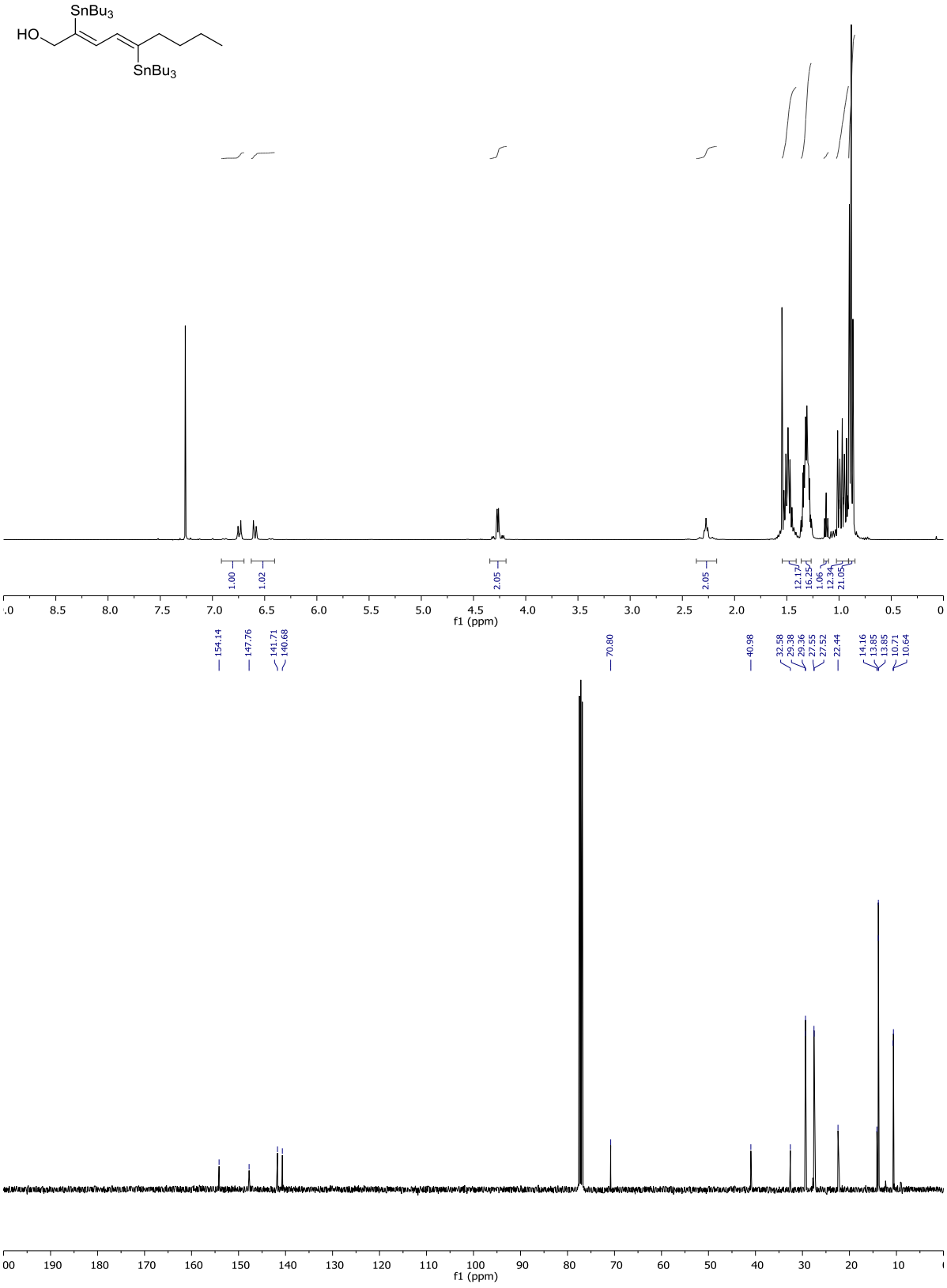
27.5
23.1
13.9
13.8
11.2
10.6
f1 (ppm)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70.80
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13.85
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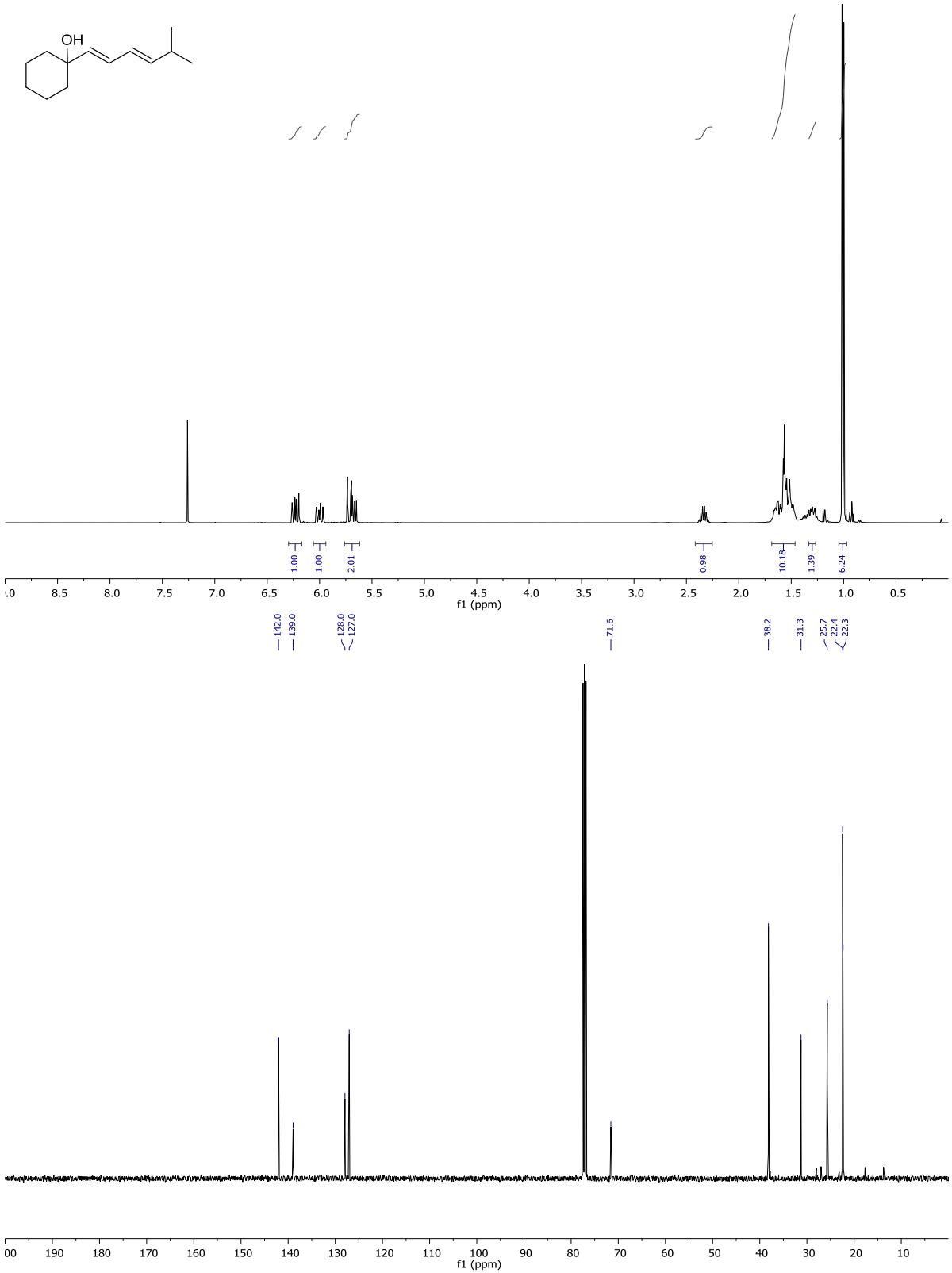
10.64
f1 (ppm)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6.24
f1 (ppm)
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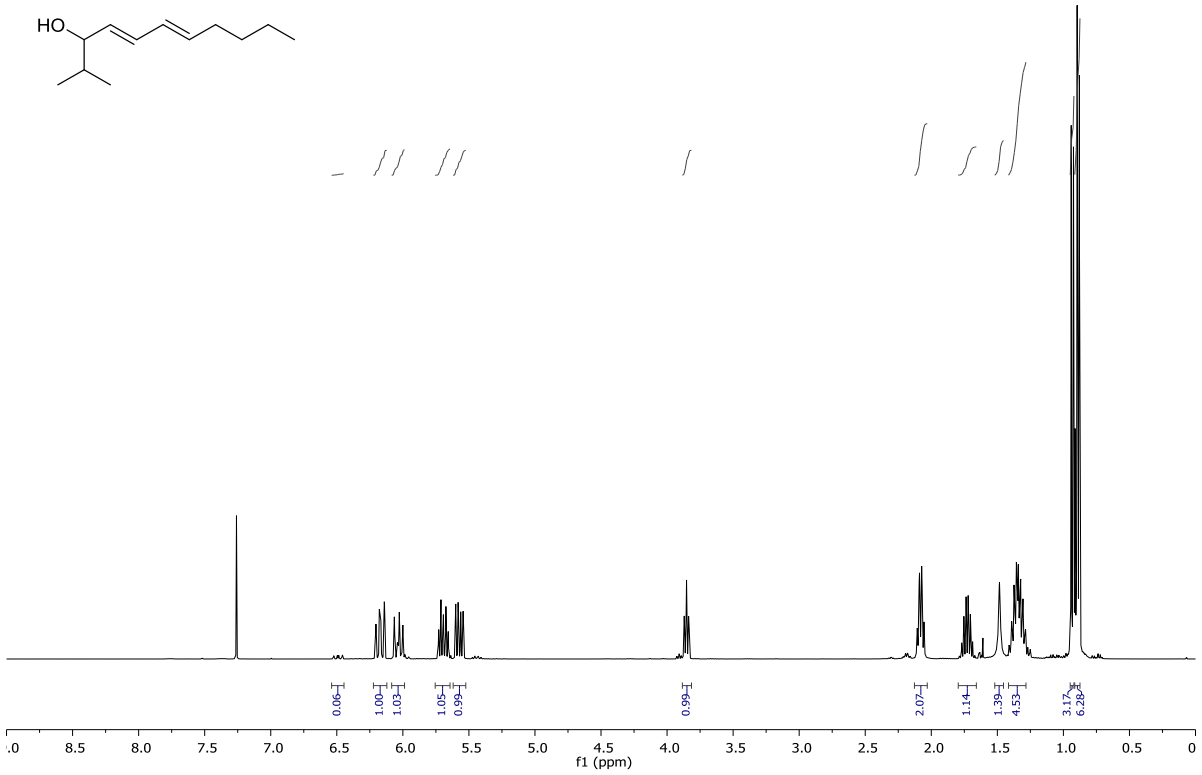
31.3
25.7
22.4
22.3
f1 (ppm)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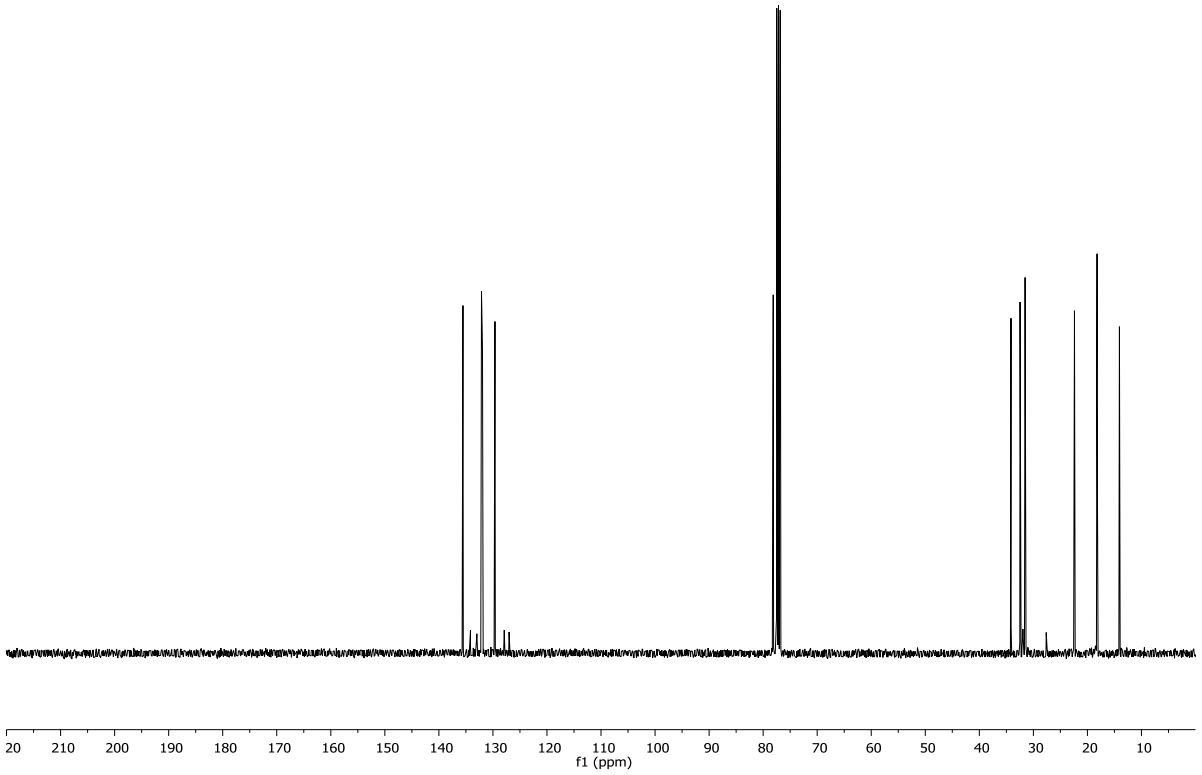
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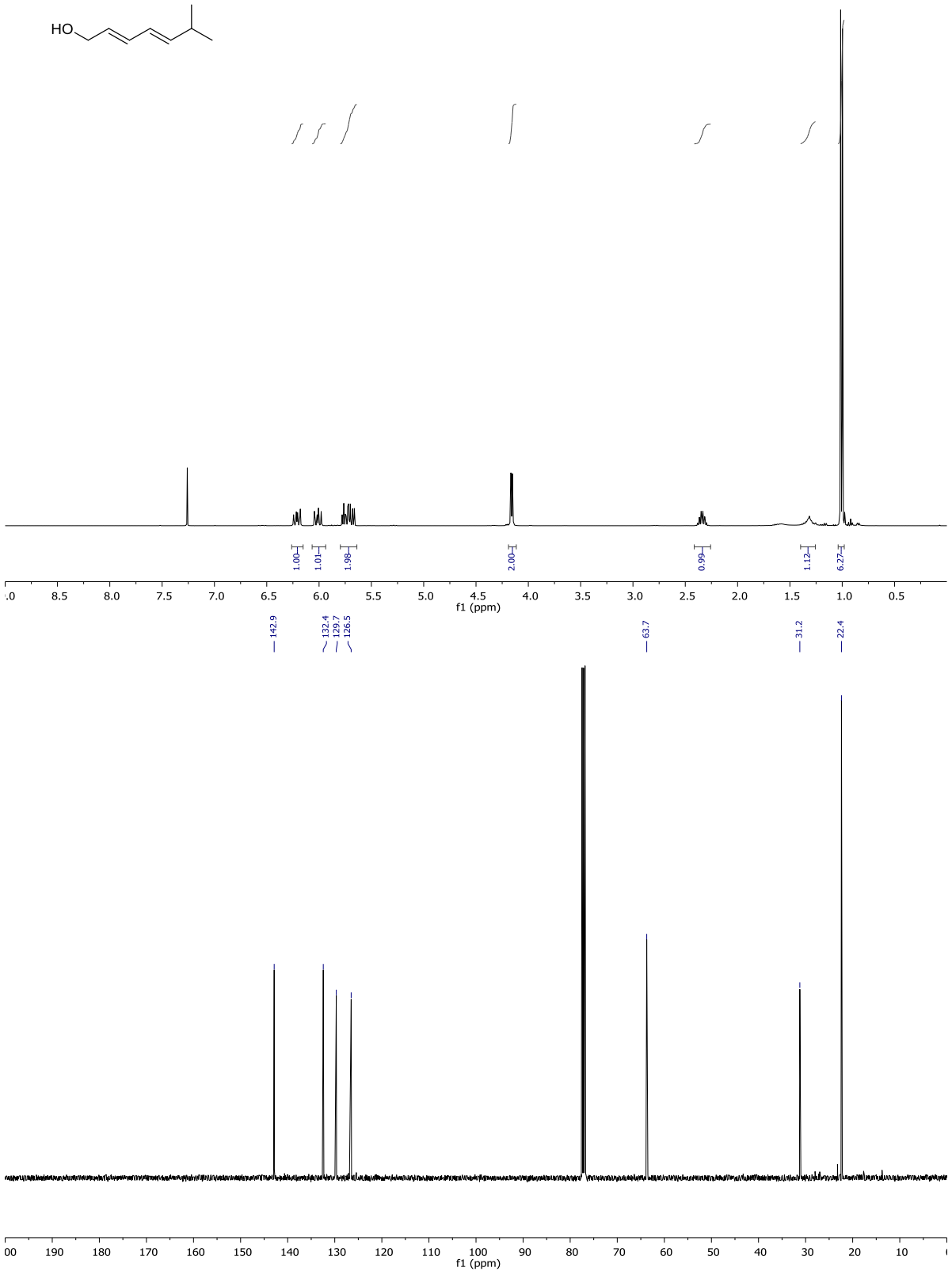
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f1 (ppm)
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22.4
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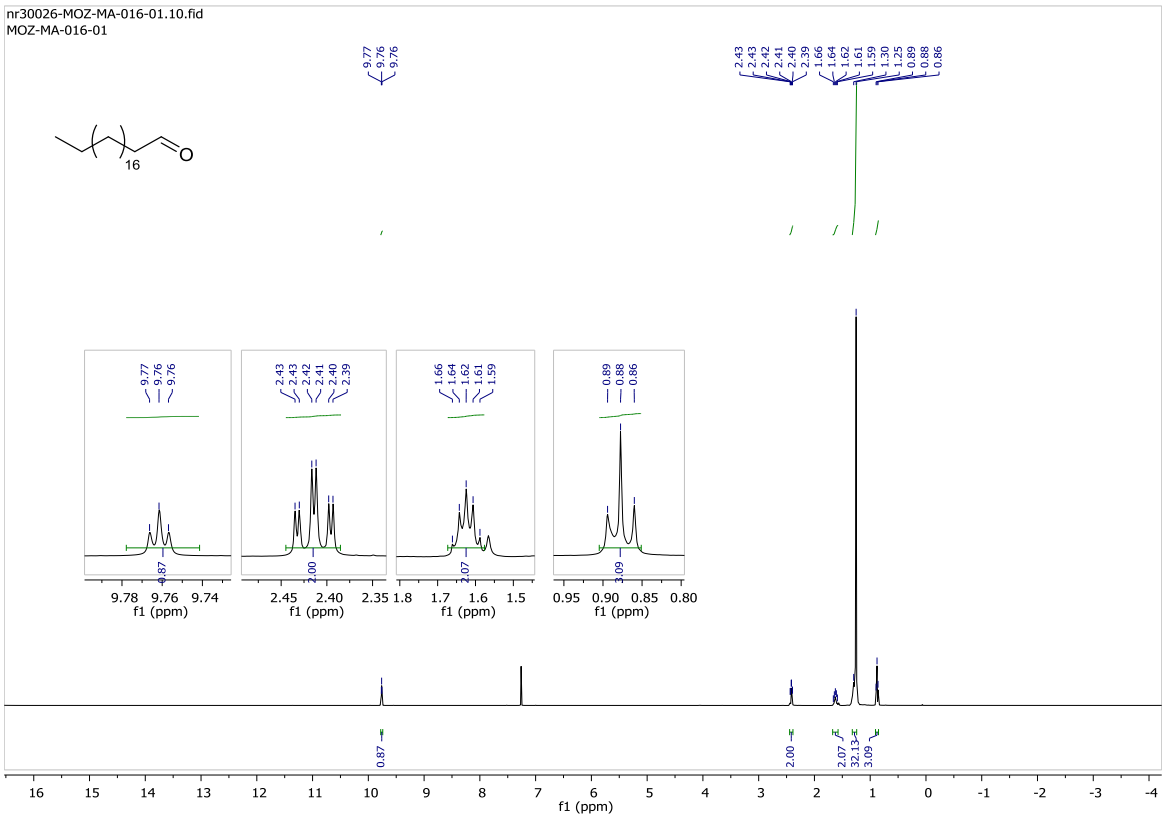
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1.64
1.62
1.61
1.59
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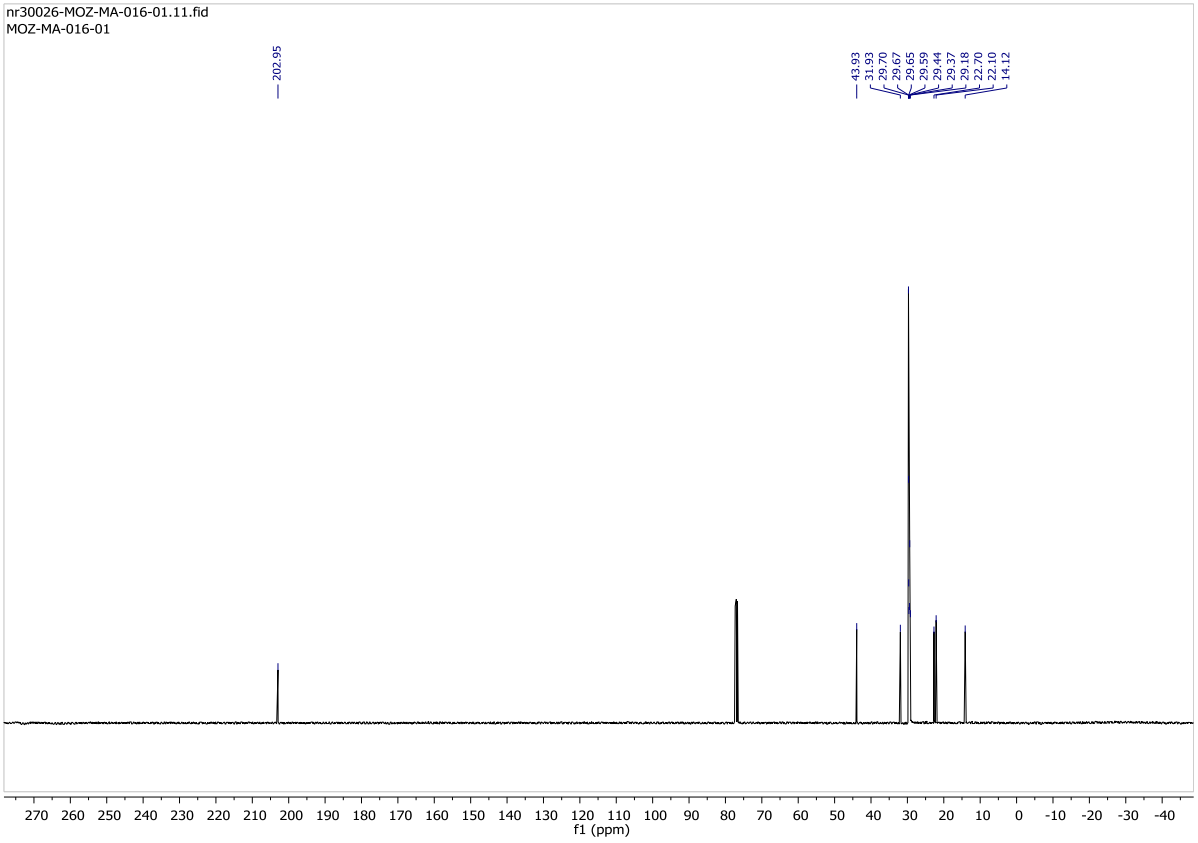
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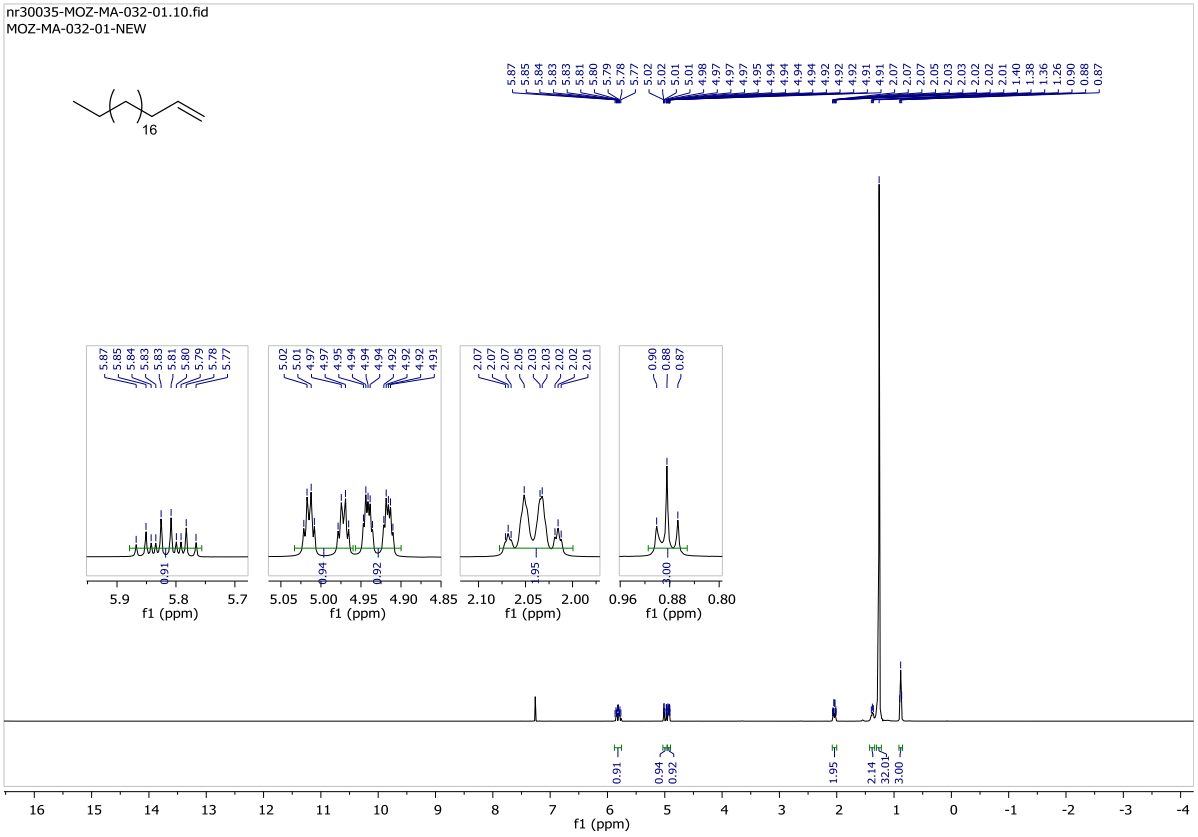
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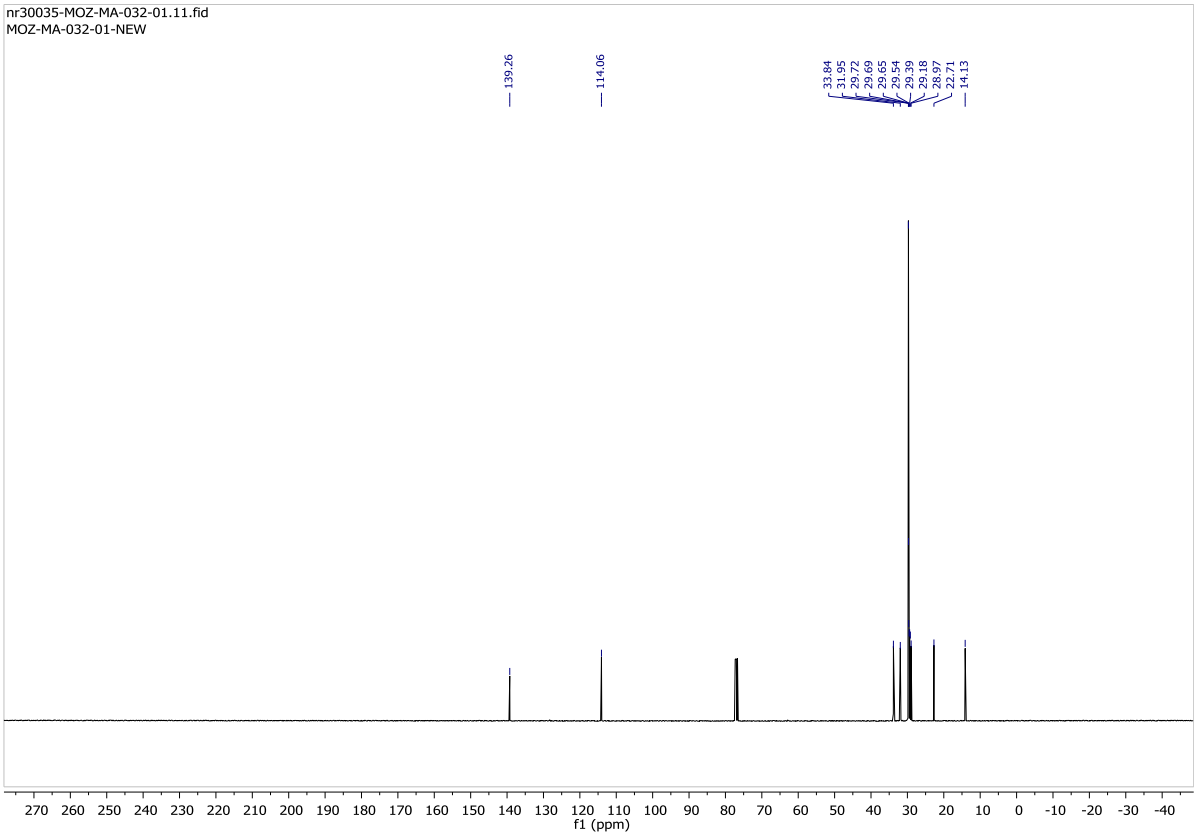
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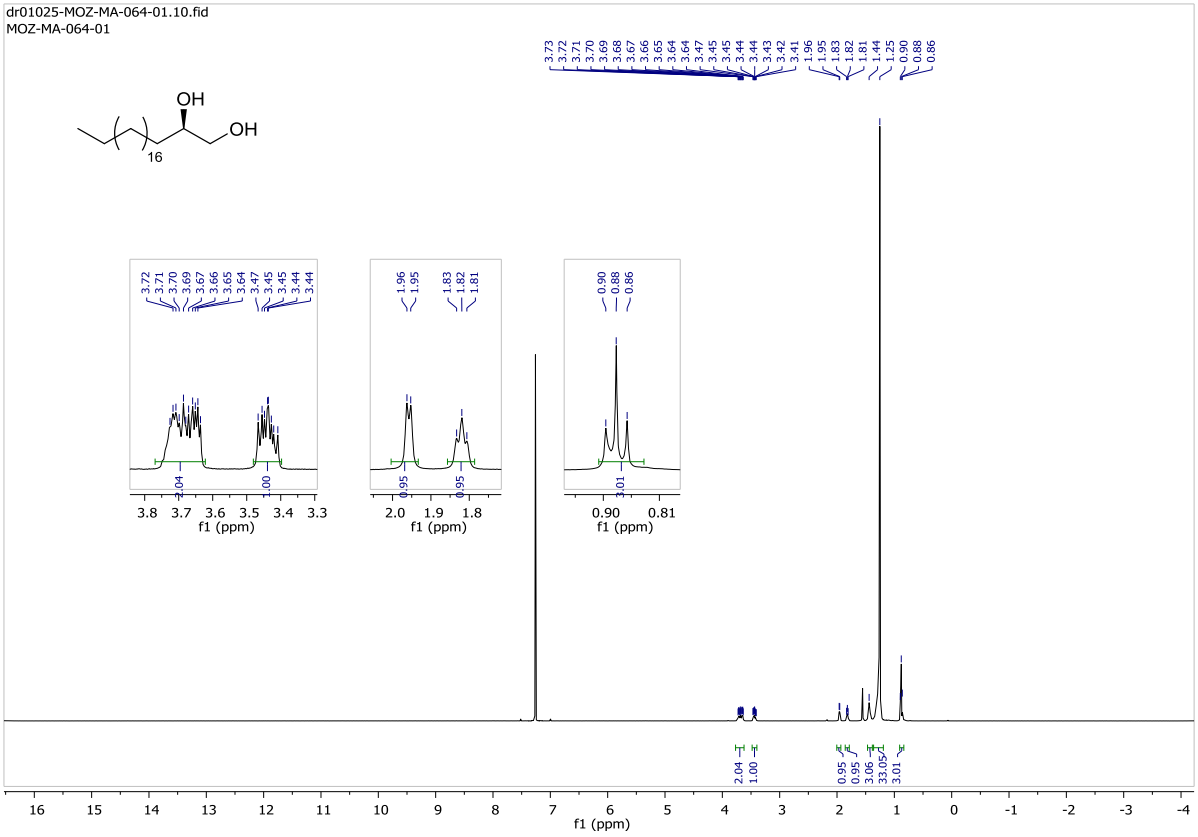
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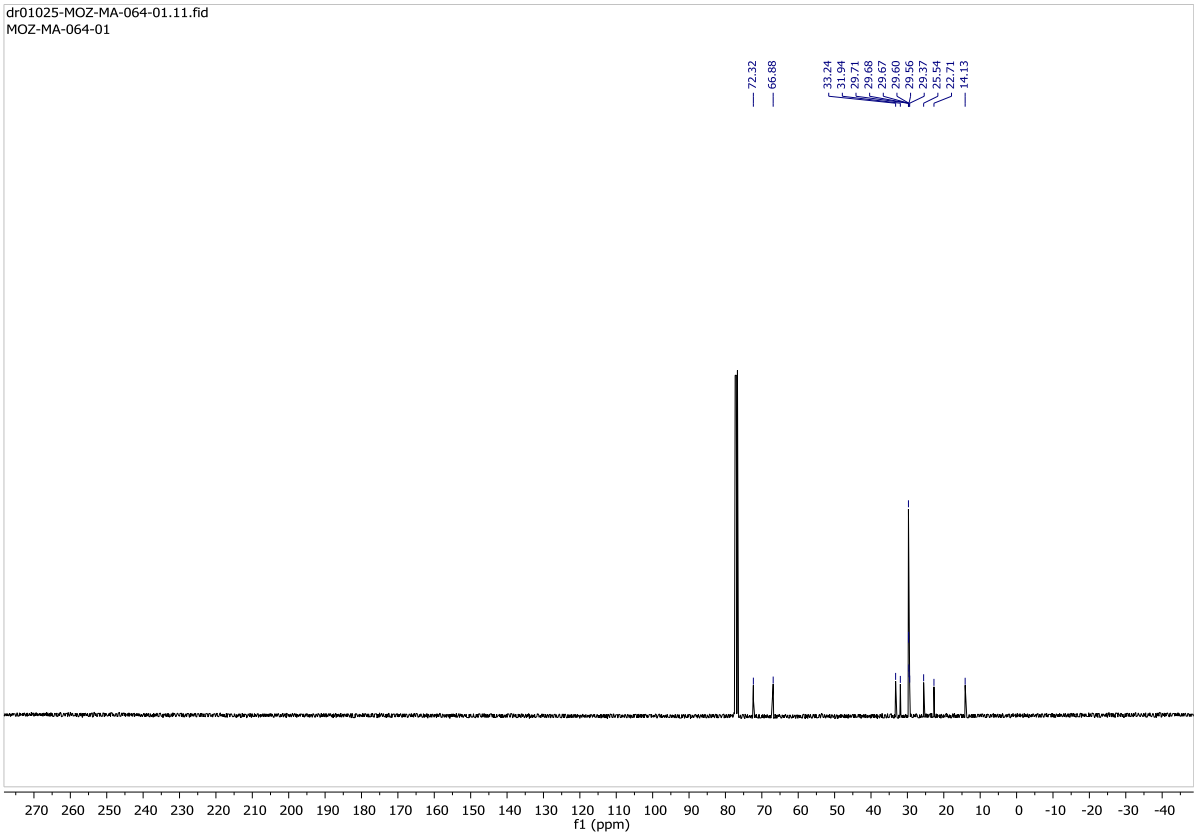
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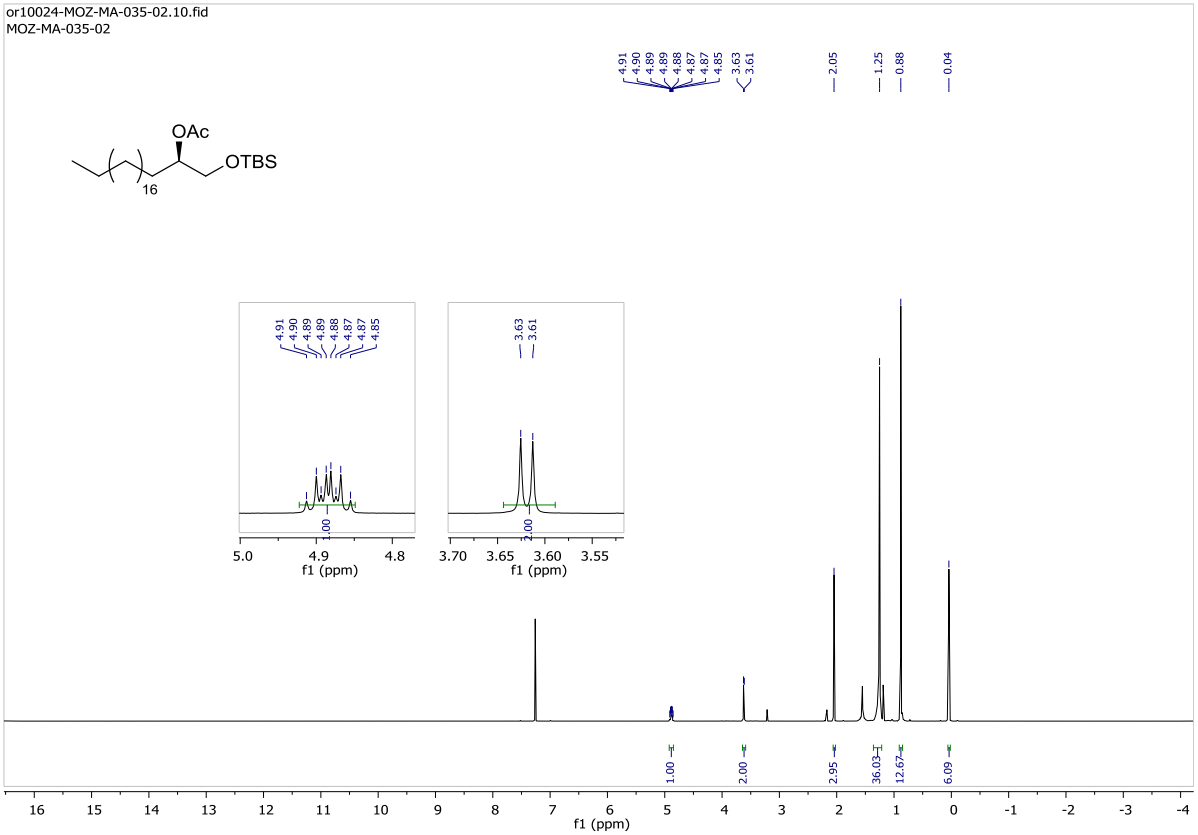
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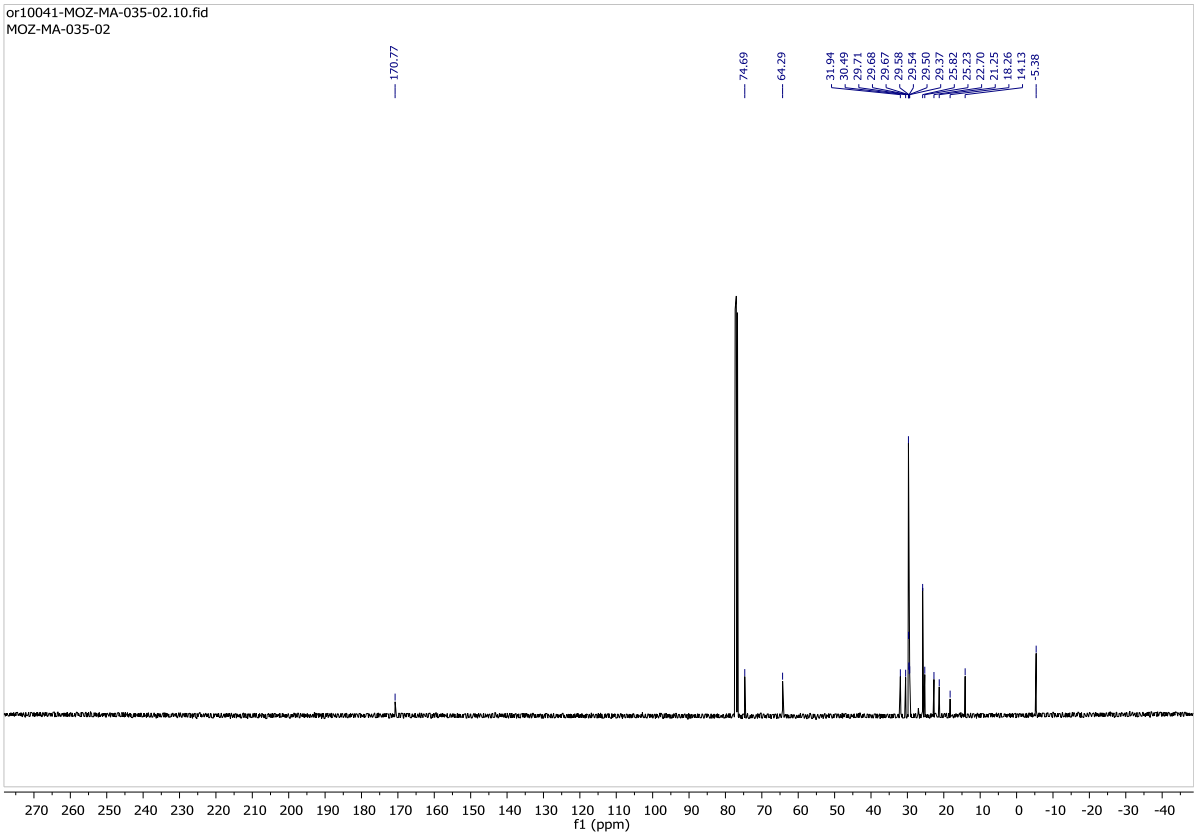
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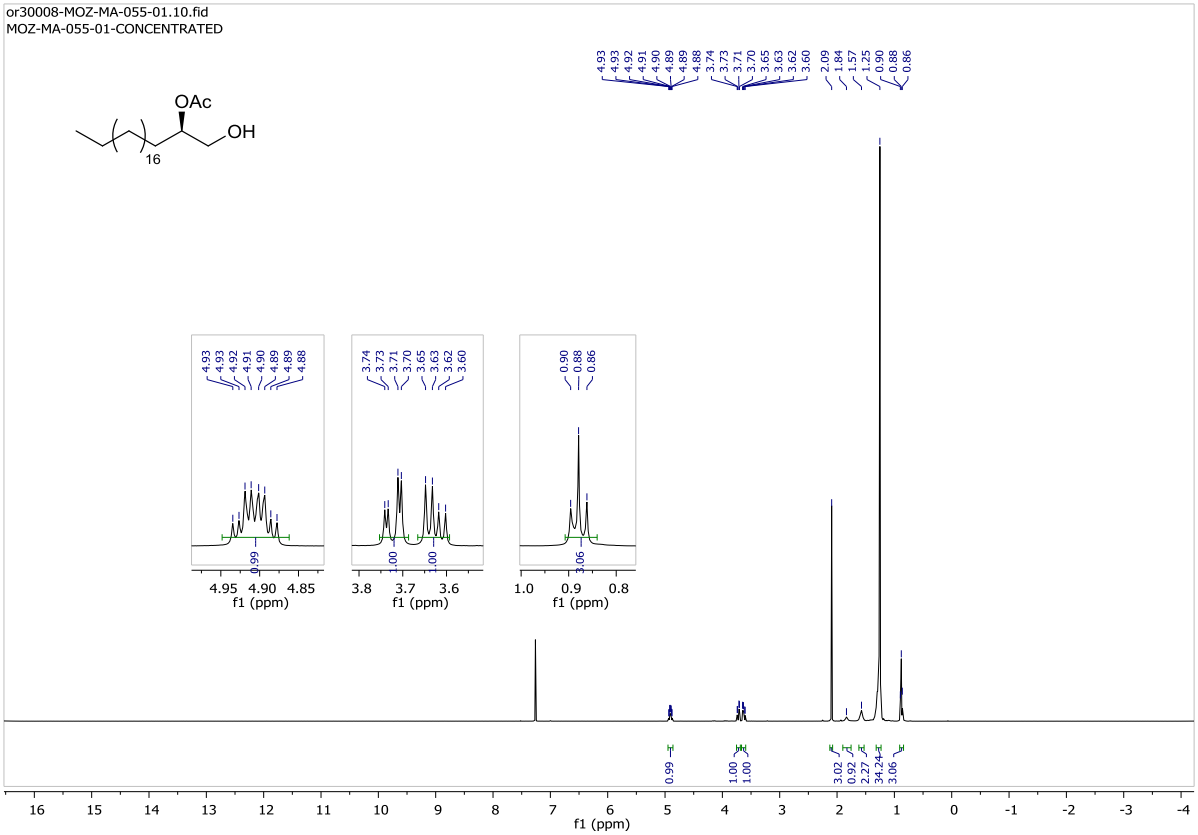
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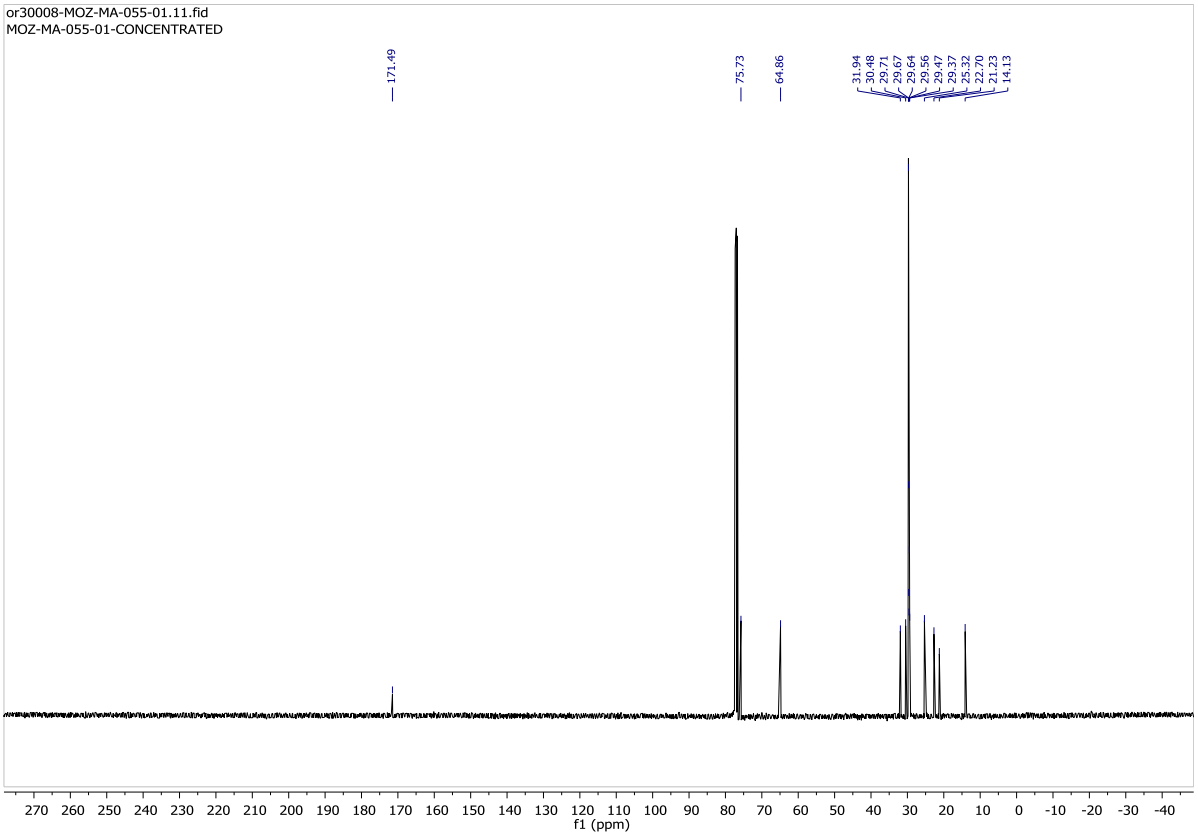
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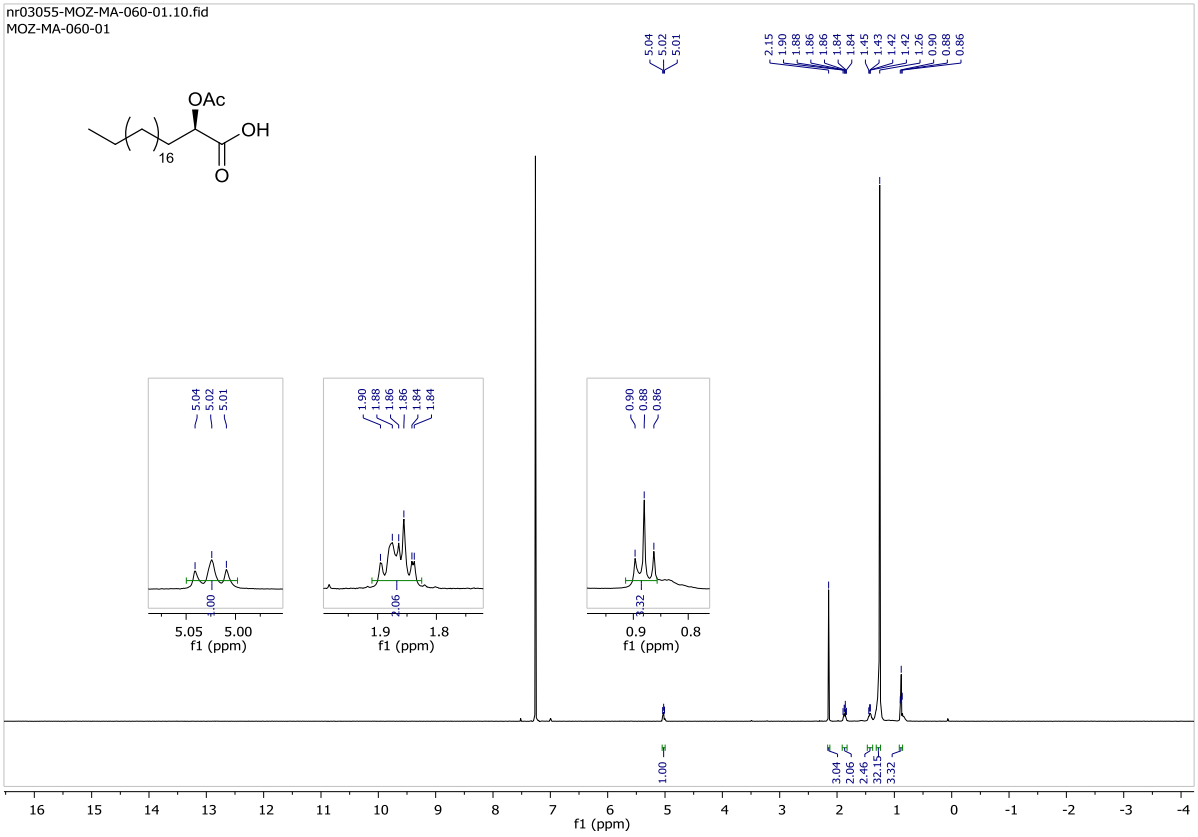
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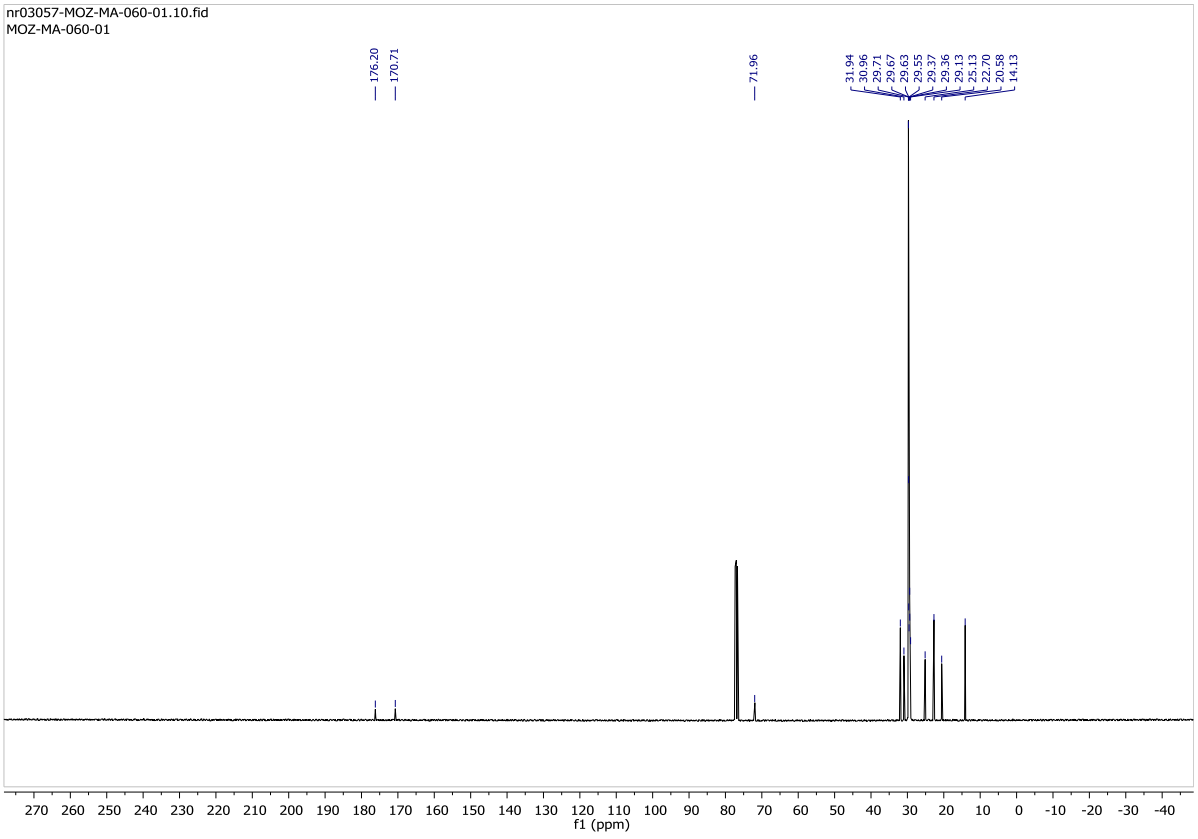
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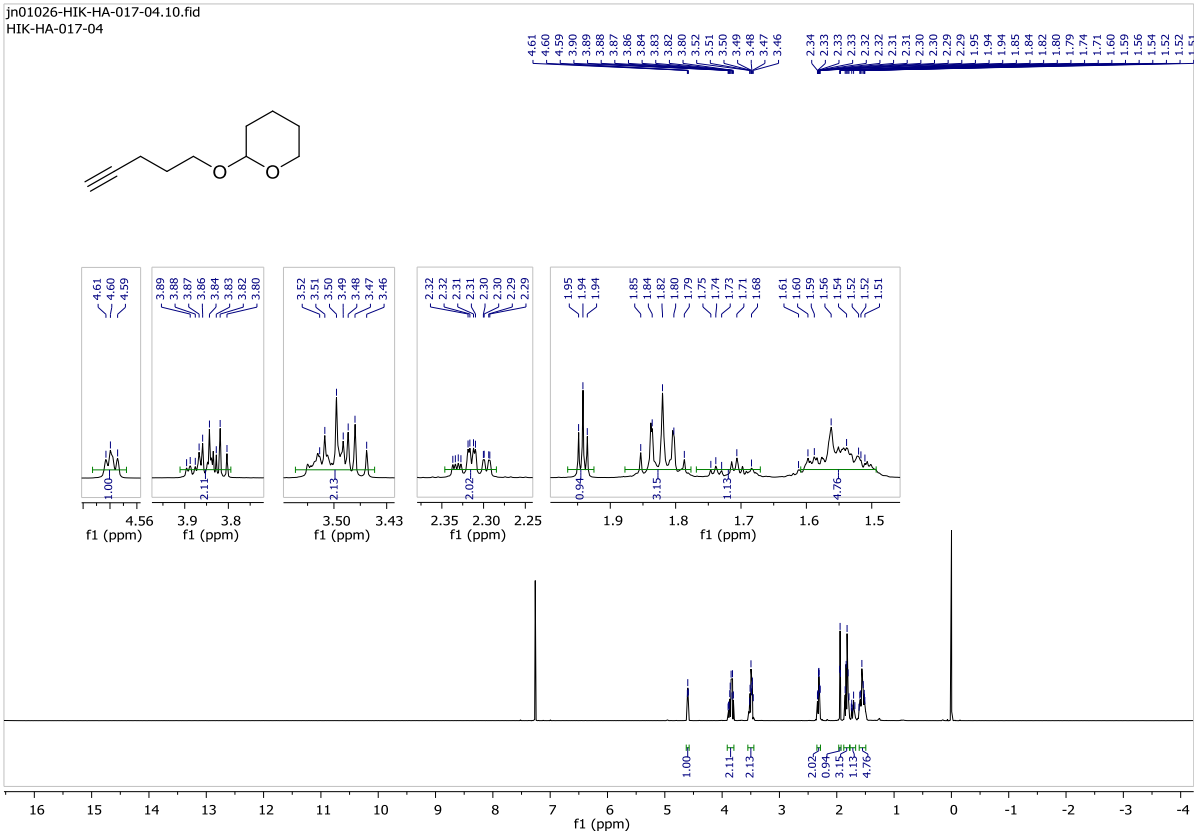
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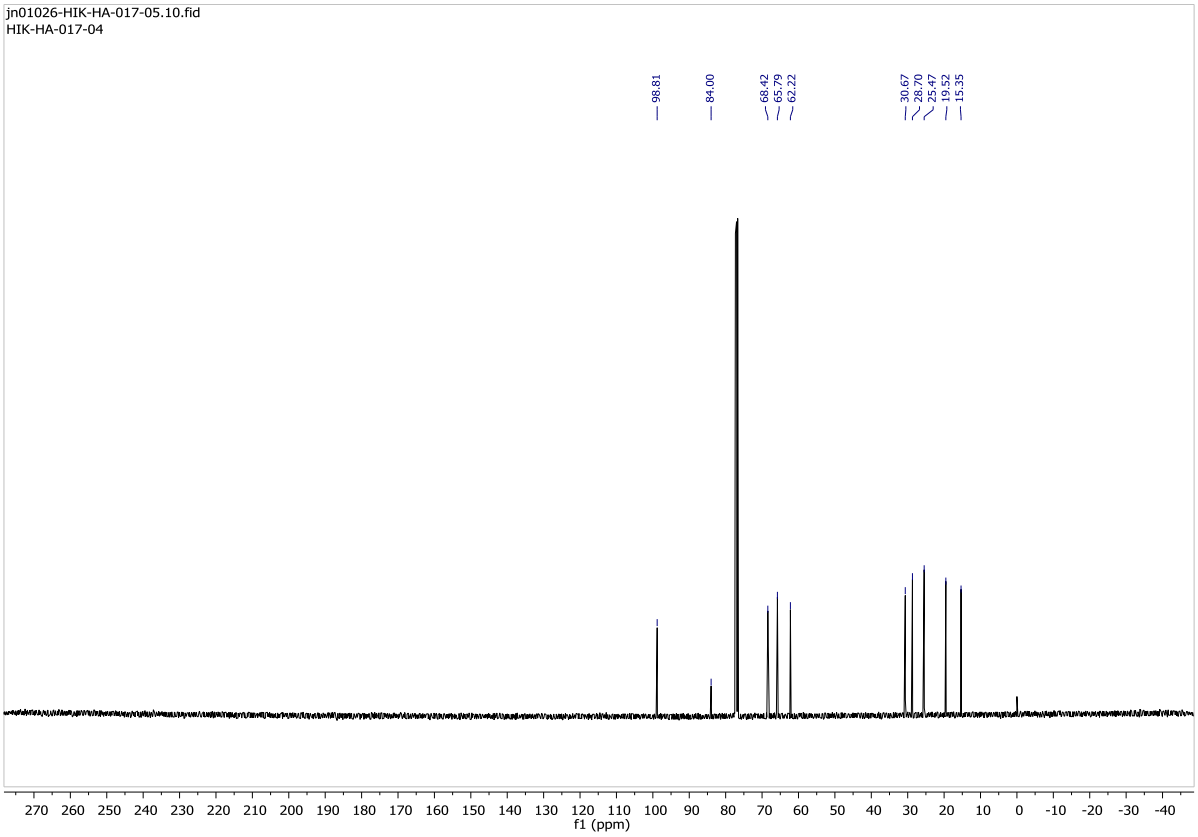
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HIK-HA-017-04
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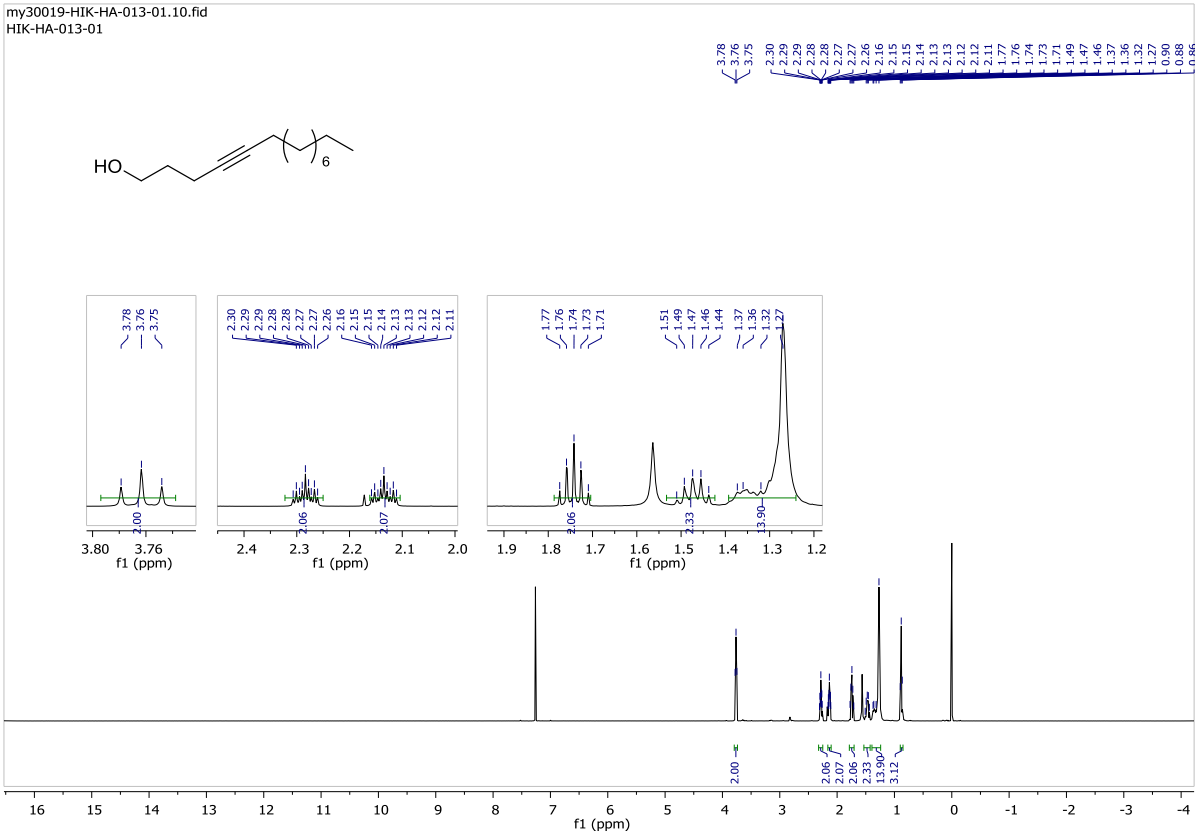
84.00
68.42
65.79
62.22
30.67
28.70
25.47
19.52
15.35
f1 (ppm)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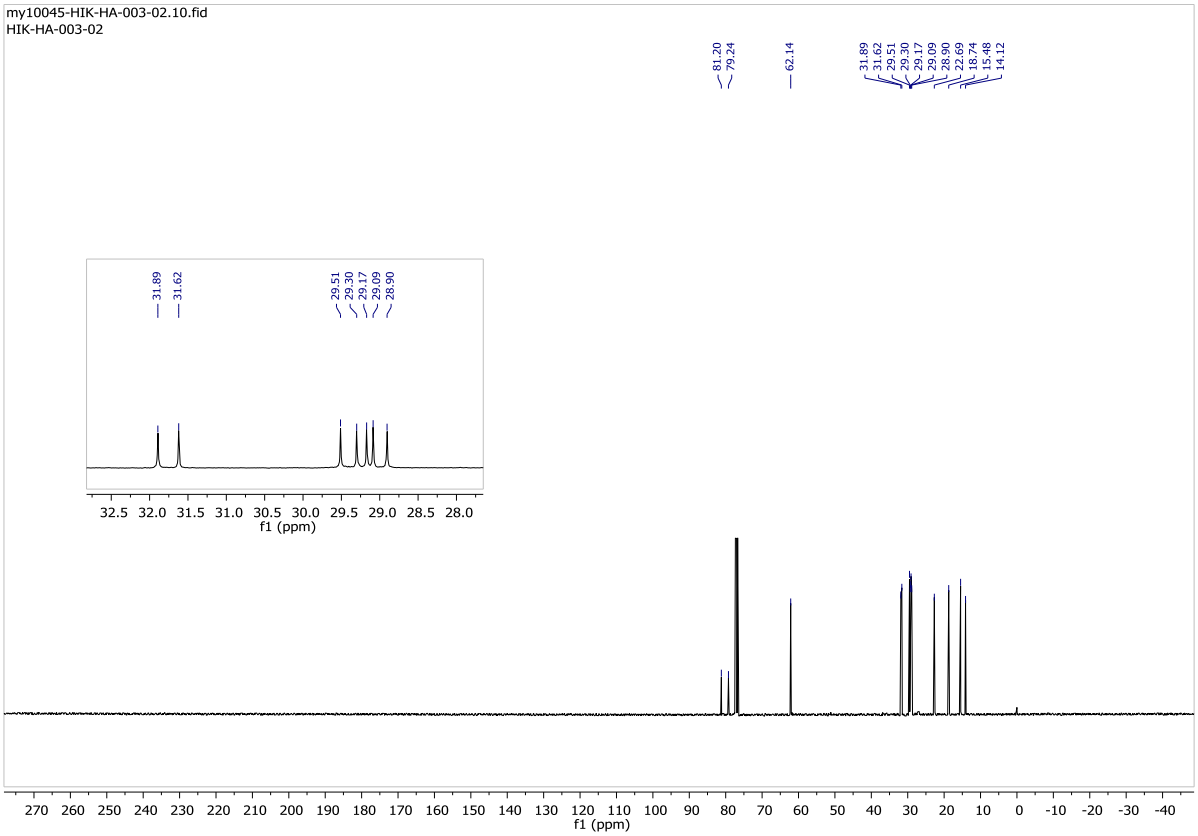
HO
6
f1 (ppm)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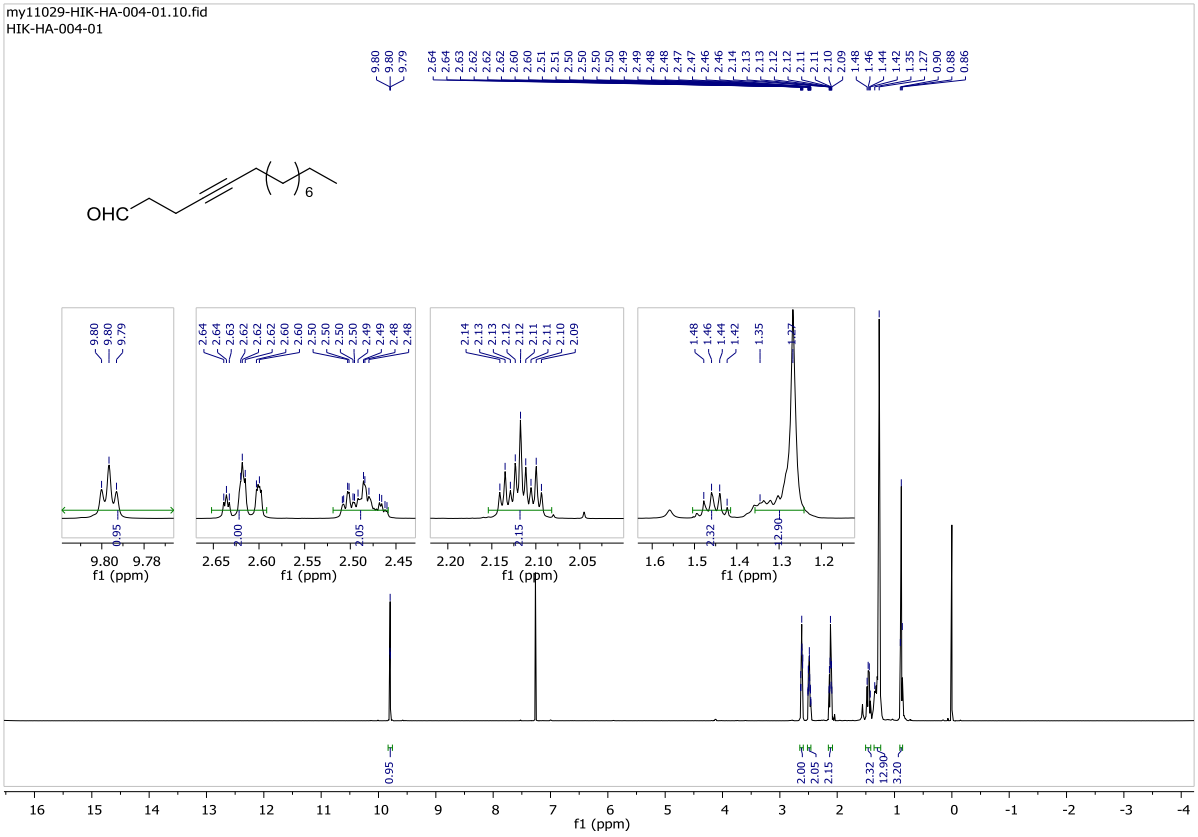
f1 (ppm)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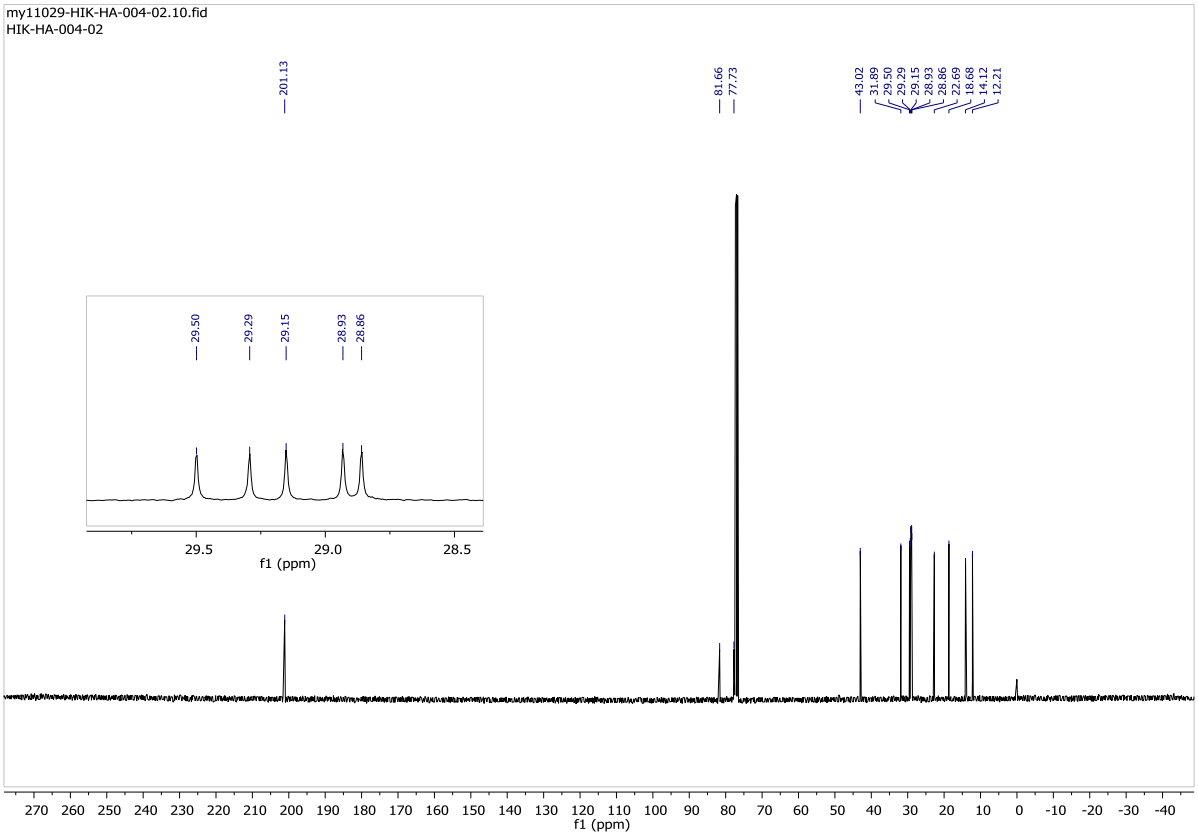
f1 (ppm)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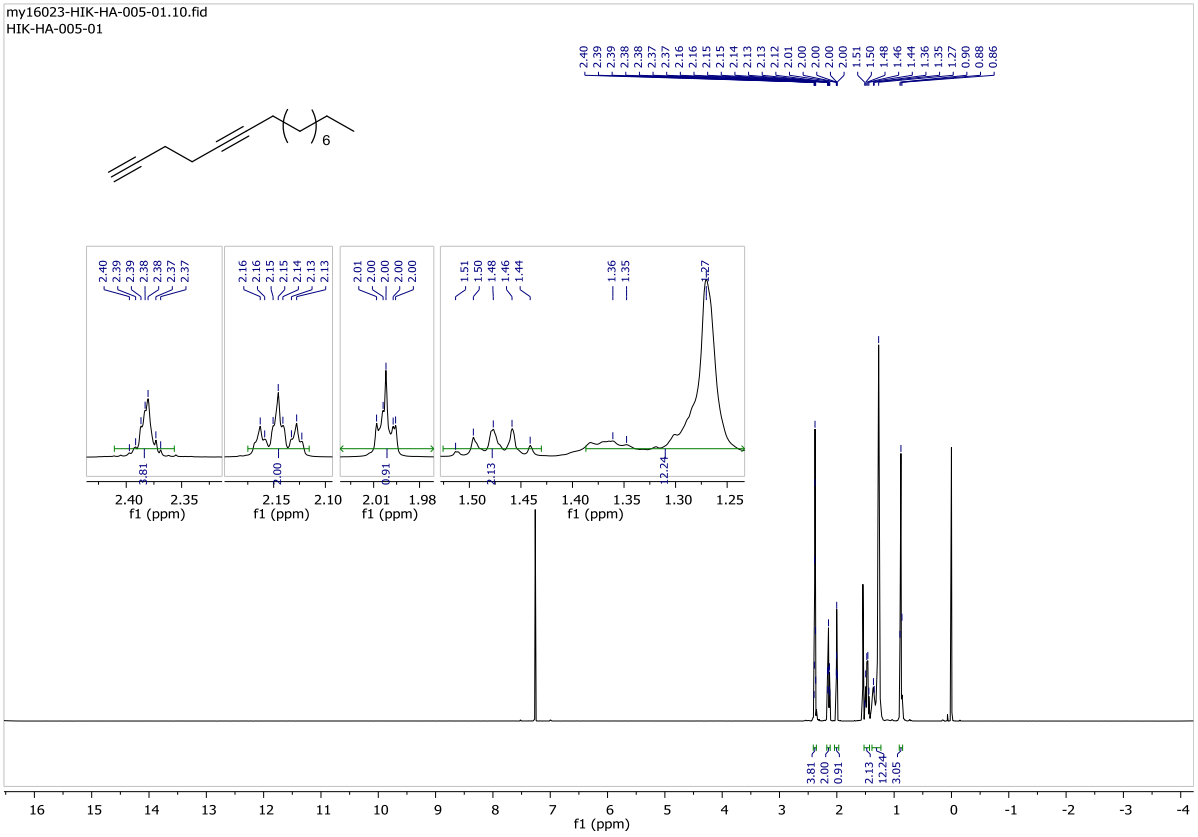
HIK-HA-004-02
f1 (ppm)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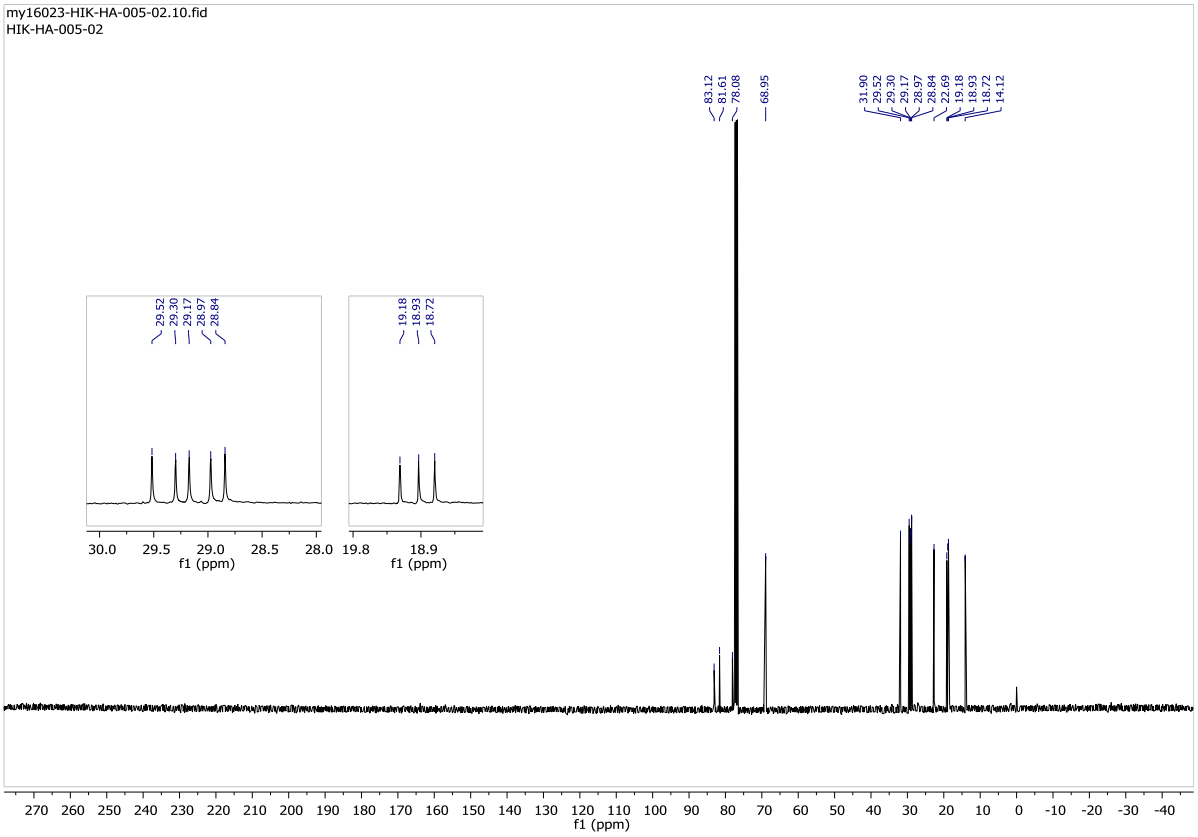
6
f1 (ppm)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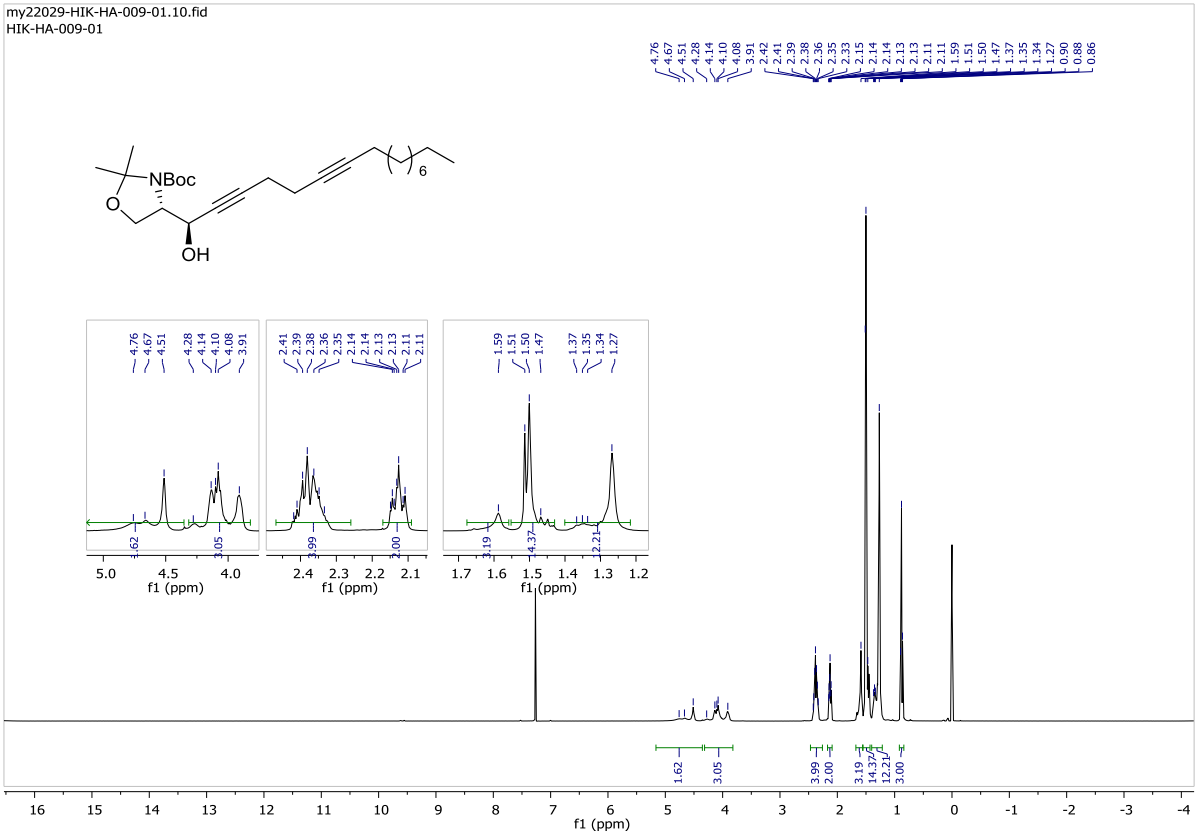
HIK-HA-005-02
f1 (ppm)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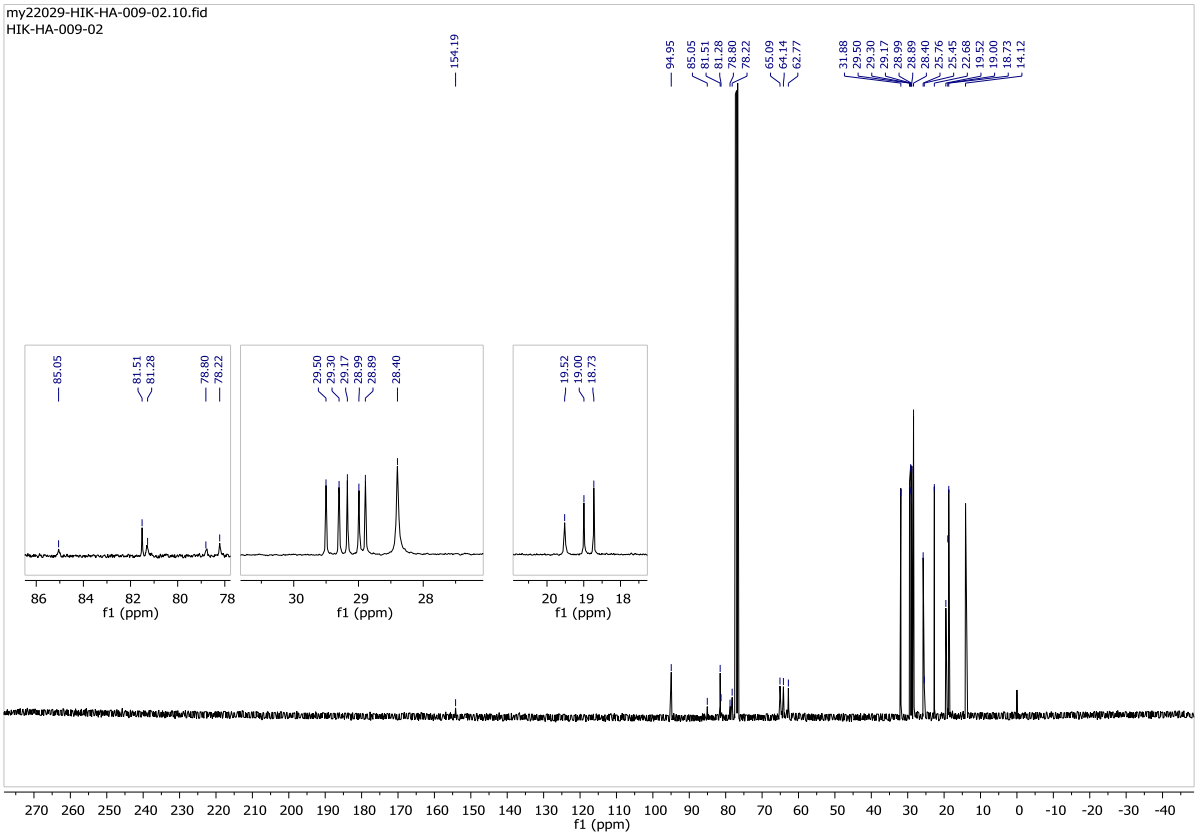
HIK-HA-009-01
NBoc
O
OH
6
f1 (ppm)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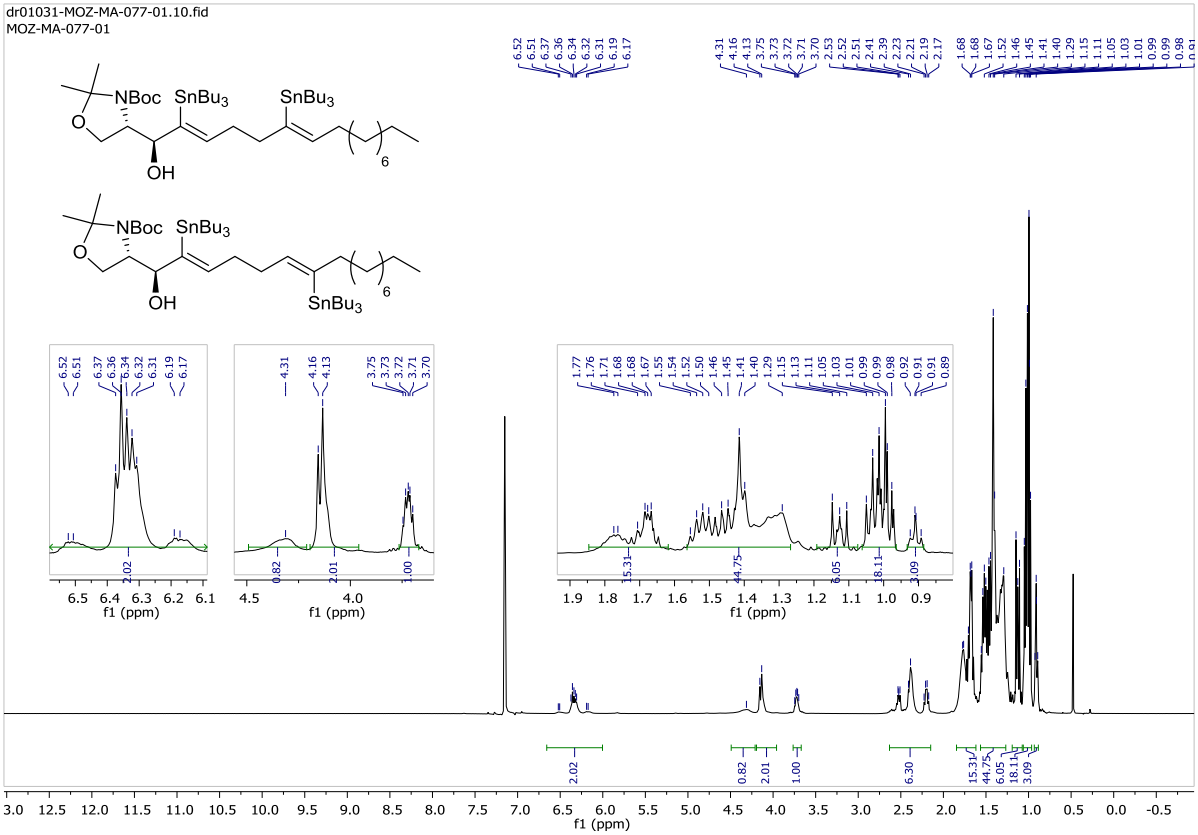
f1 (ppm)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NBoc SnBu3 SnBu3
OH
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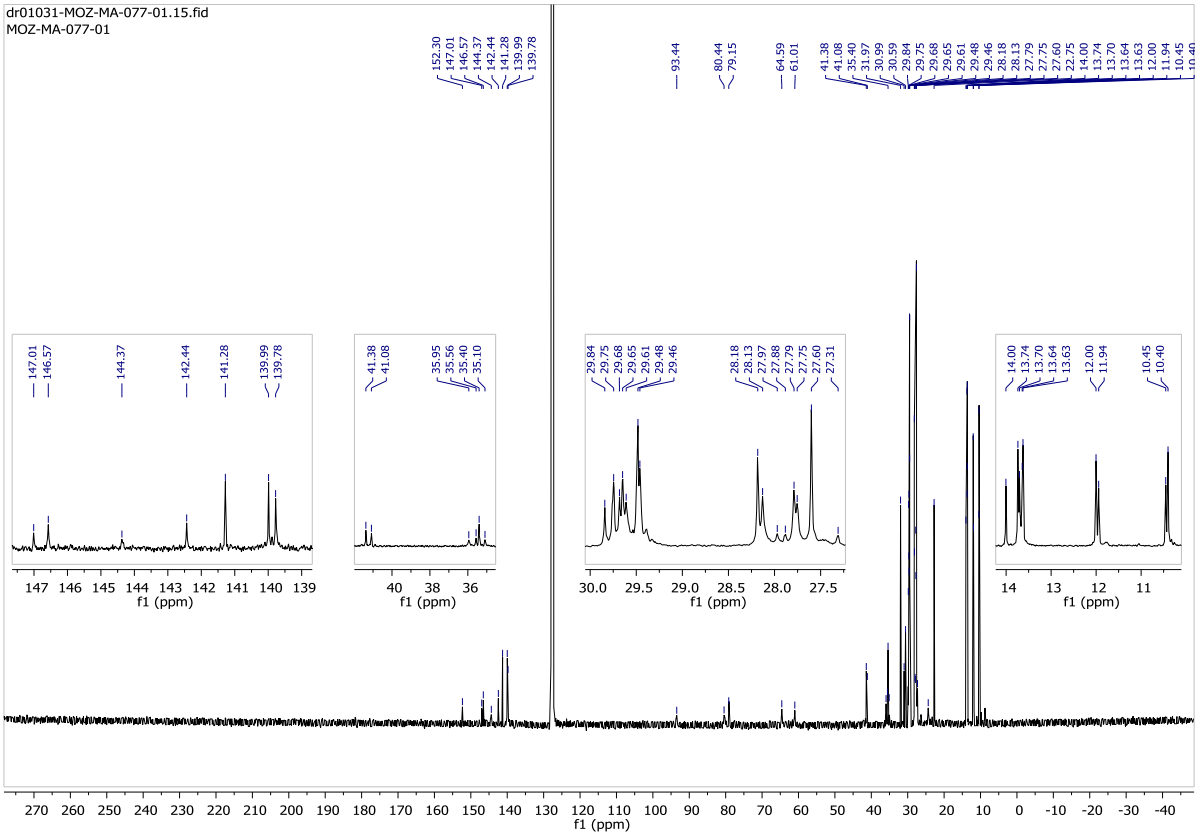
NBoc SnBu3
OH
SnBu3
6
f1 (ppm)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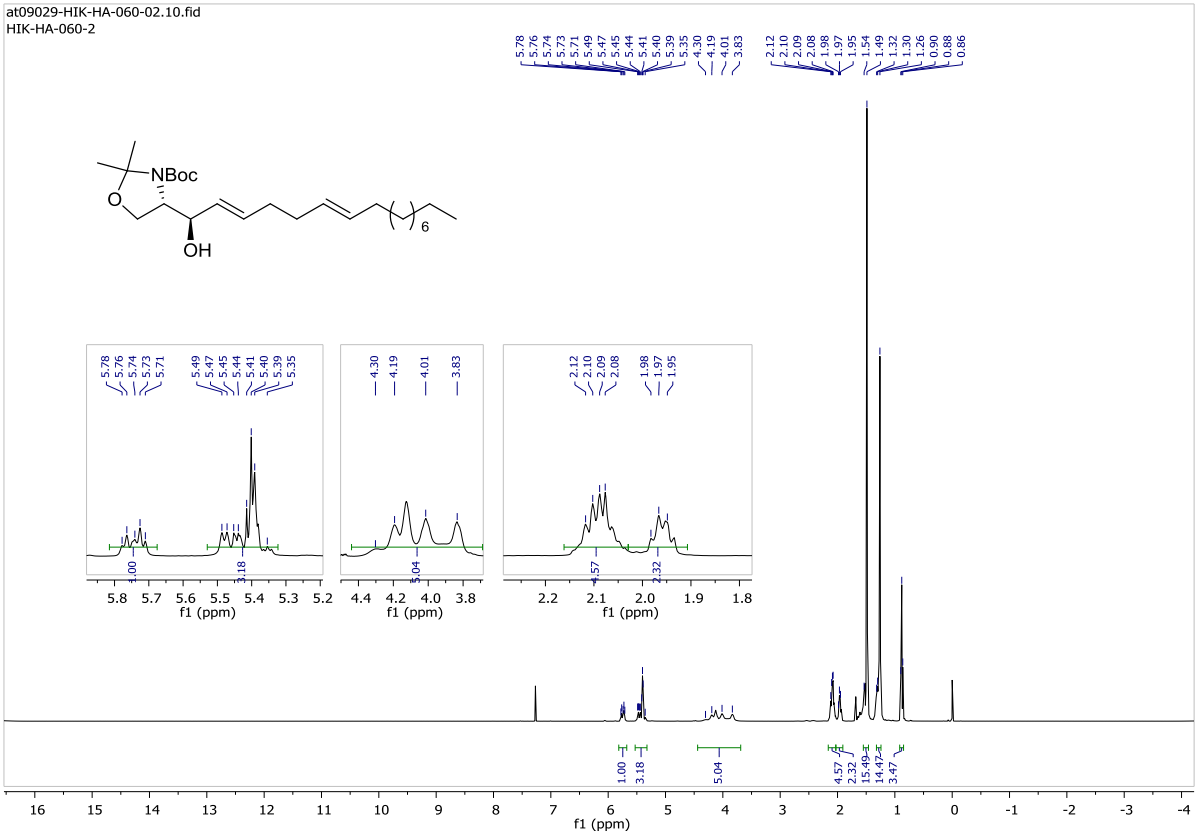
f1 (ppm)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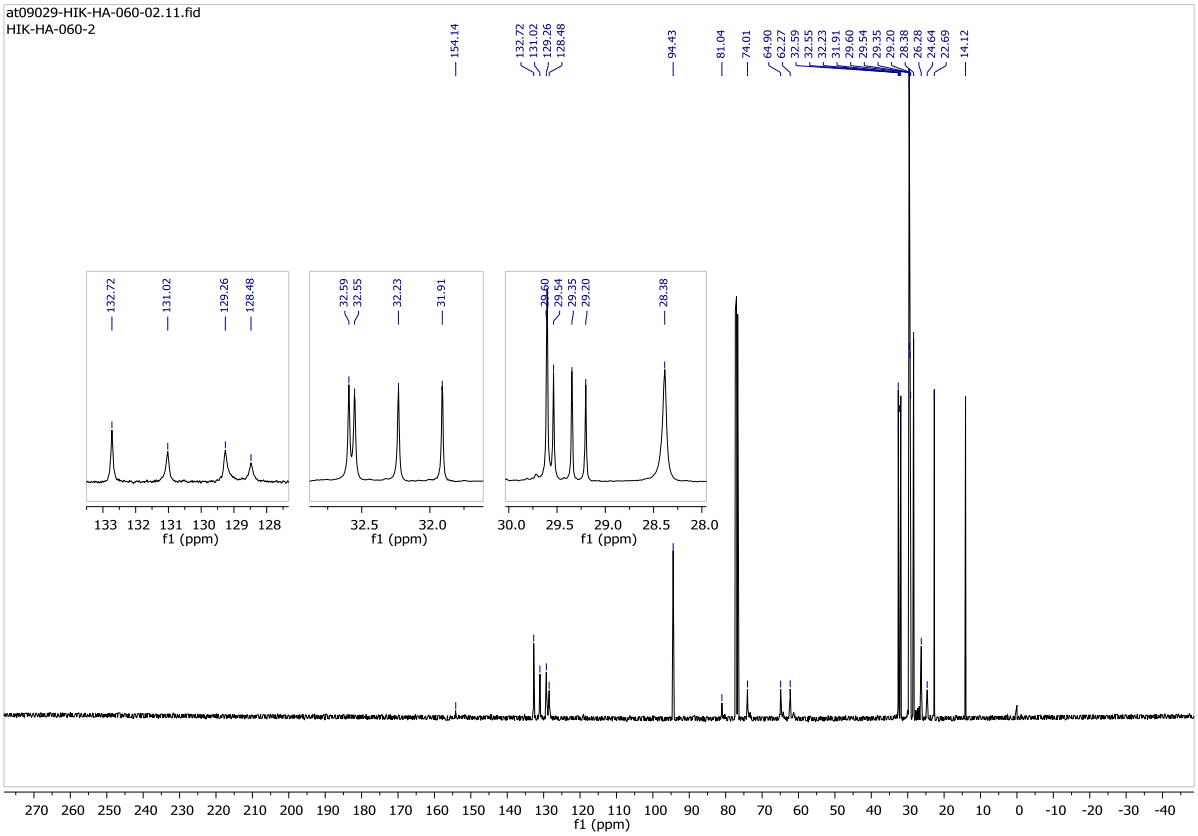
HIK-HA-060-2
NBoc
O
OH
6
f1 (ppm)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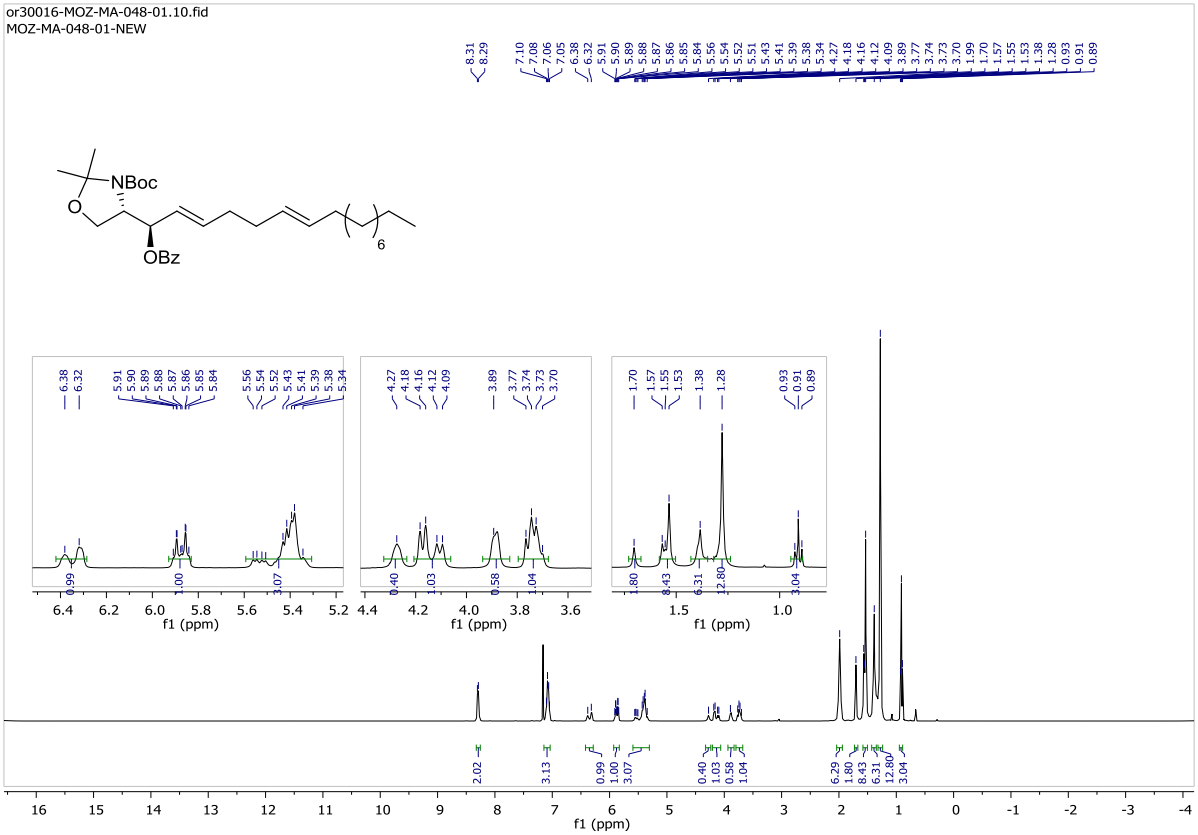
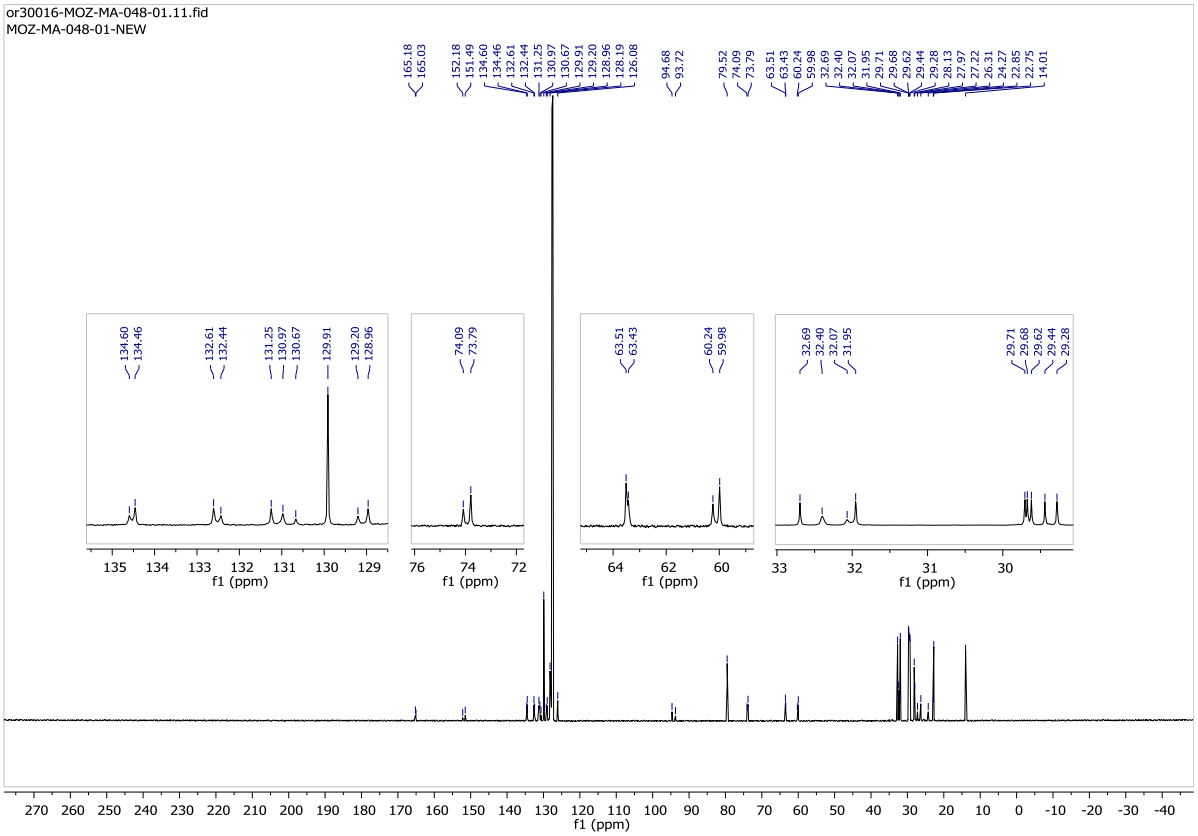
HIK-HA-060-2
f1 (ppm)


or30016-MOZ-MA-048-01.10.fid
MOZ-MA-048-01-NEW
NBoc
O
OBz
6
f1 (ppm)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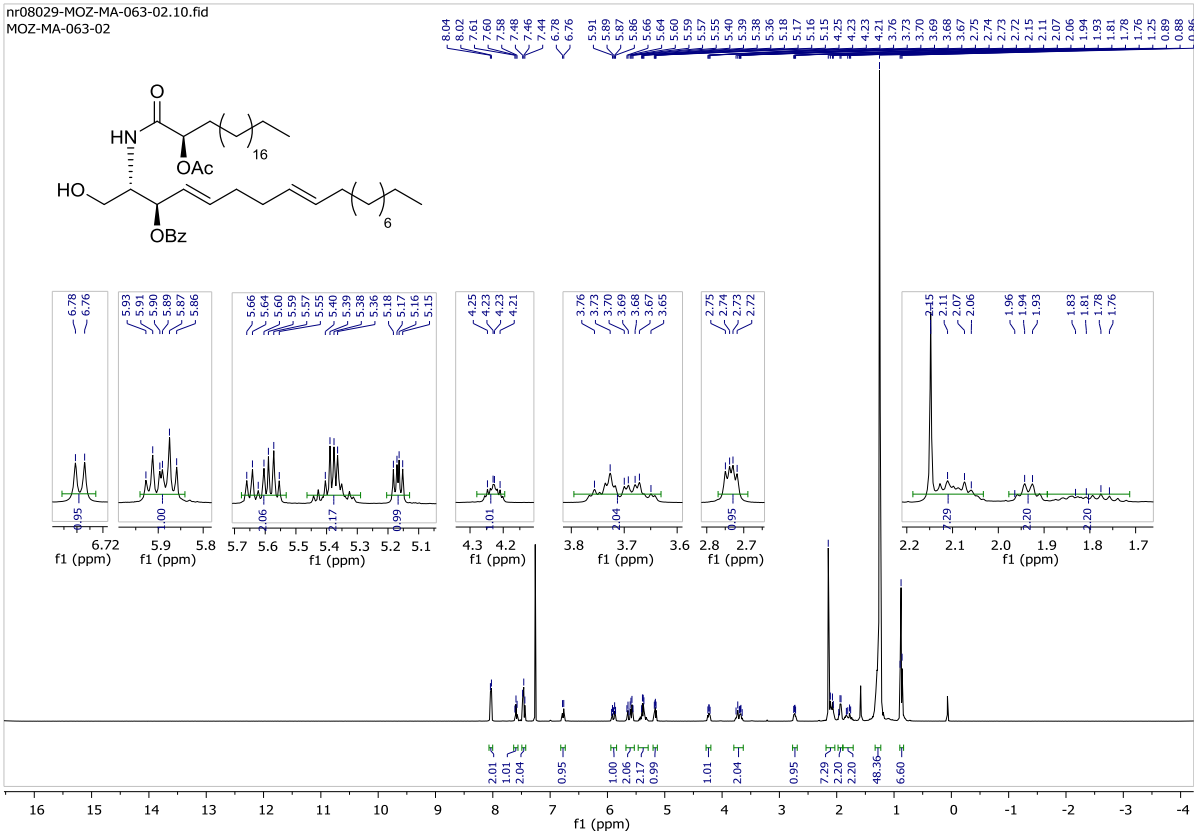
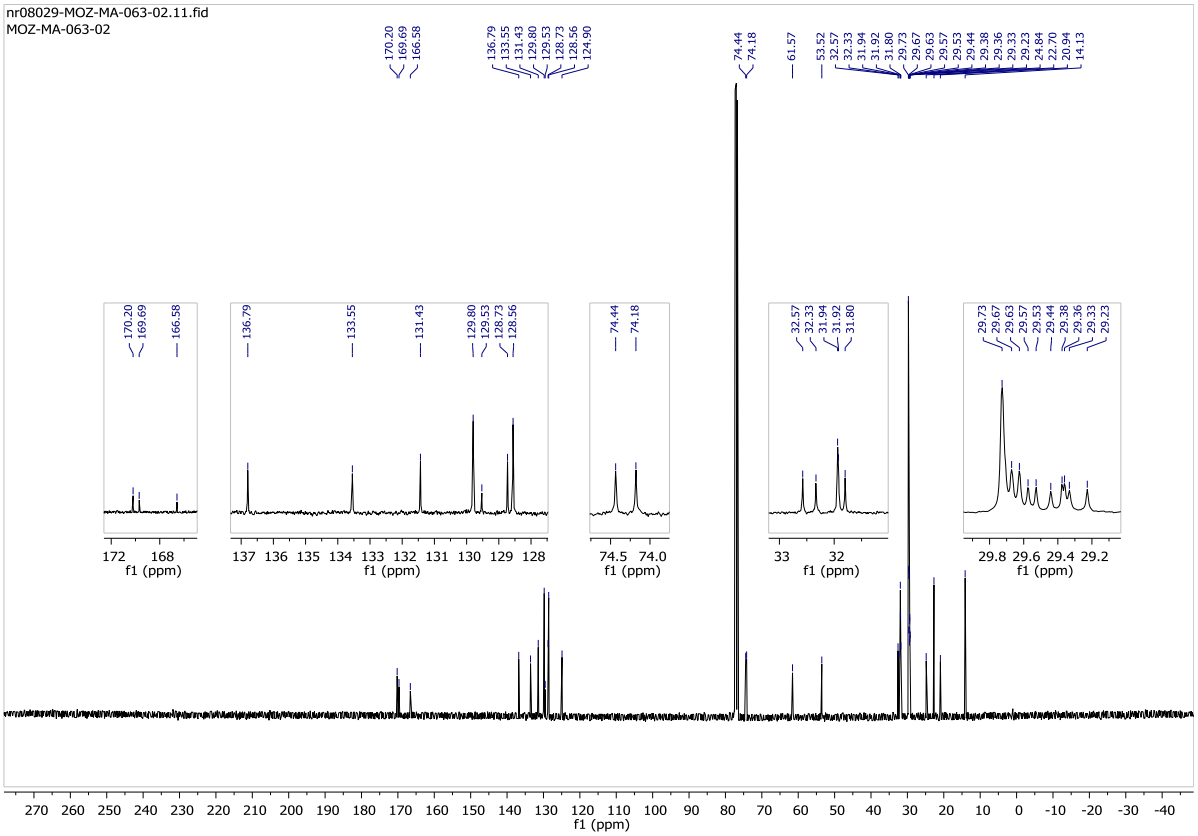
MOZ-MA-048-01-NEW
f1 (ppm)


nr08029-MOZ-MA-063-02.10.fid
MOZ-MA-063-02
HN
O
OAc
16
HO
OBz
6
f1 (ppm)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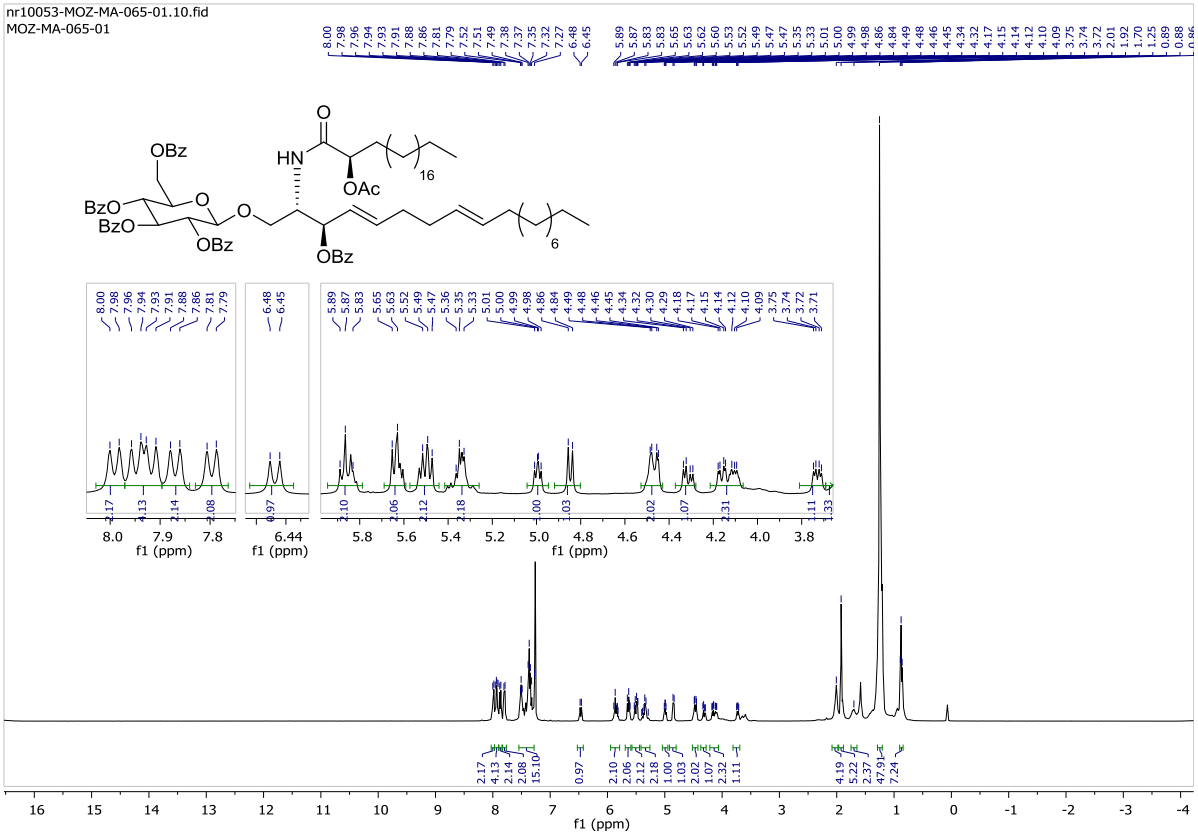
MOZ-MA-063-02
f1 (ppm)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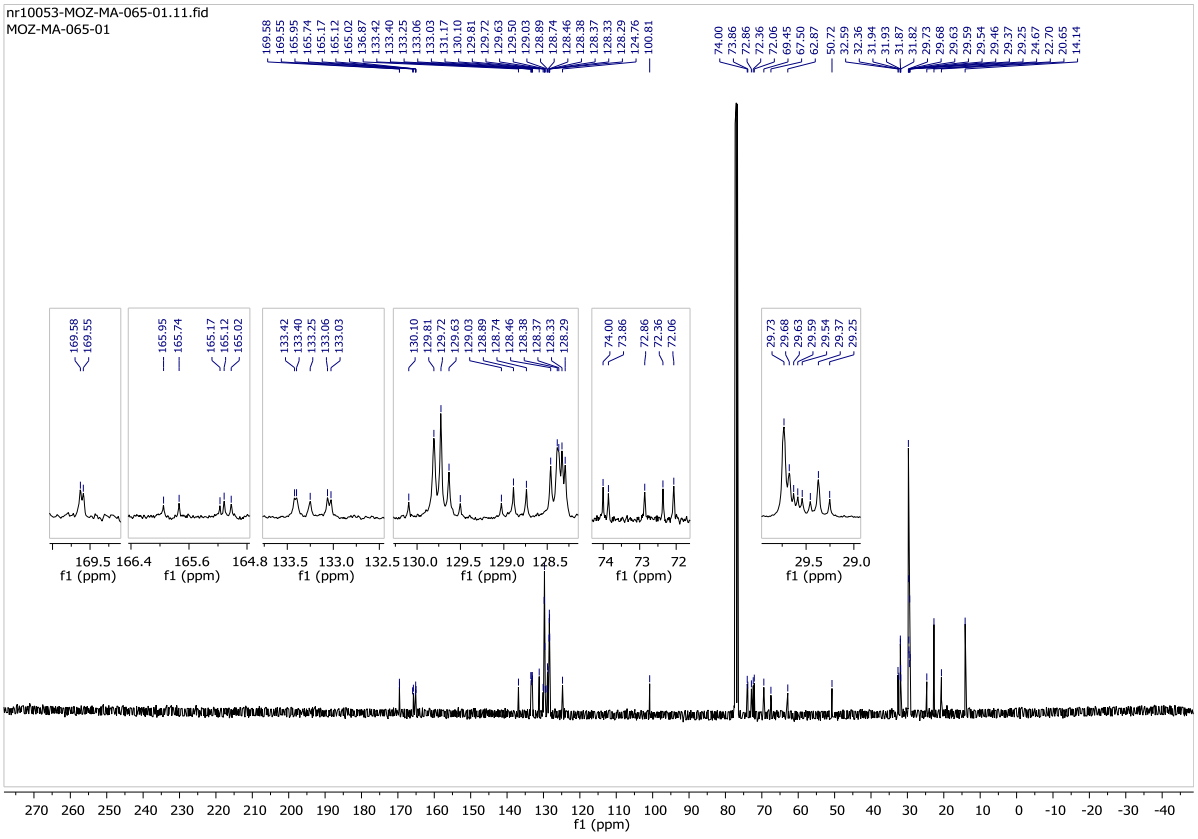
MOZ-MA-065-01
OBz
BzO
BzO
OBz
O
O
HN
OAc
16
OBz
6
f1 (ppm)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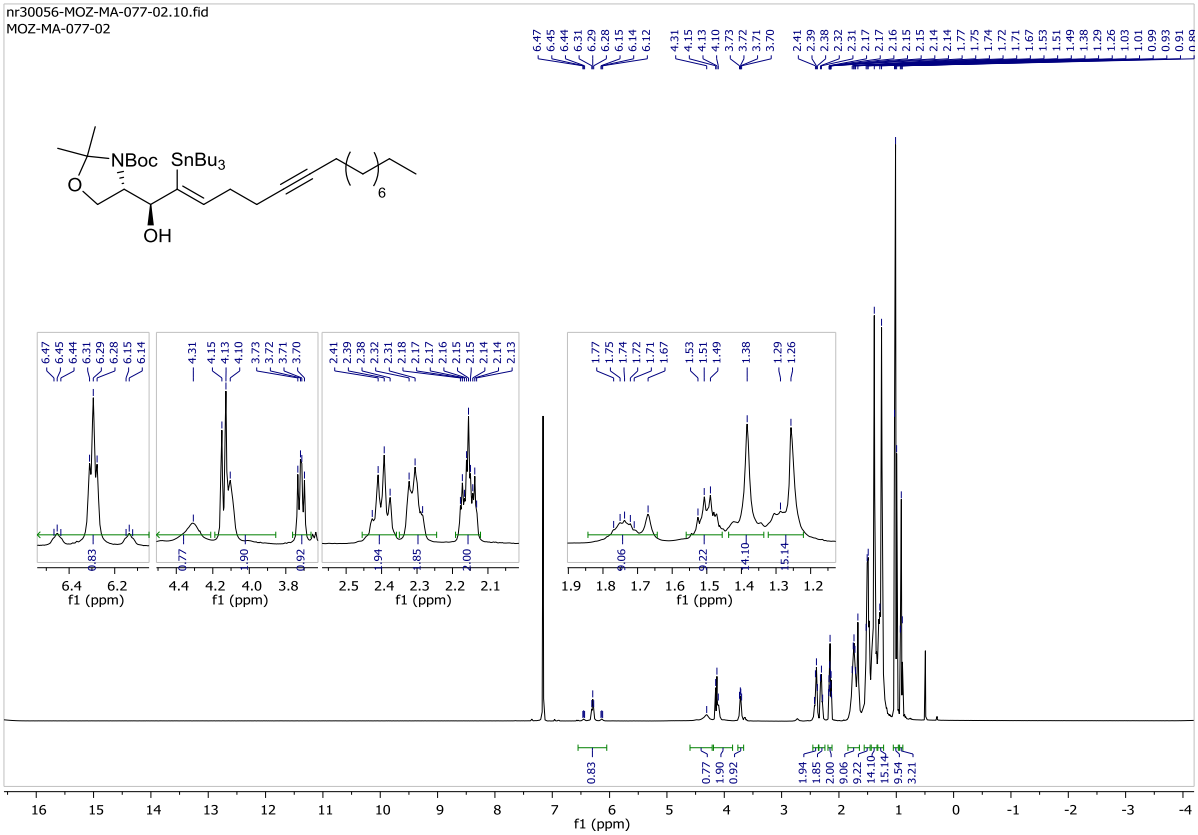
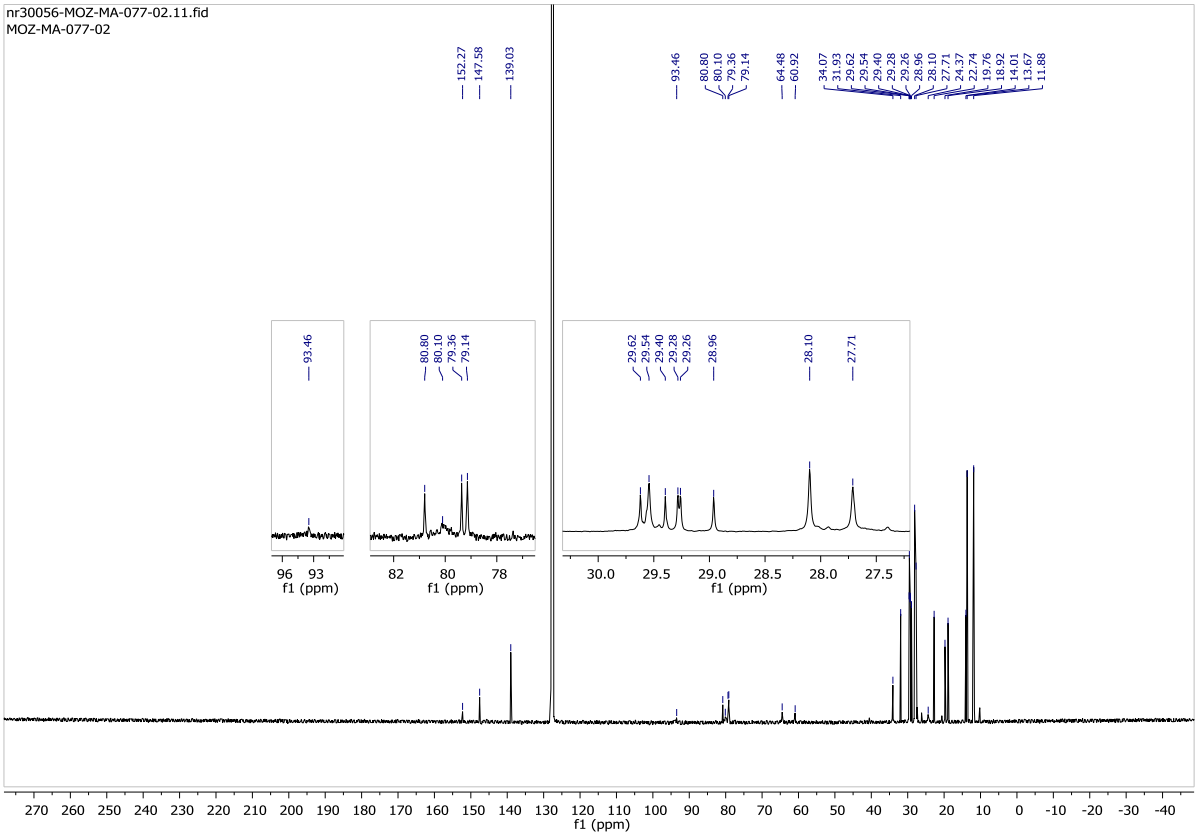
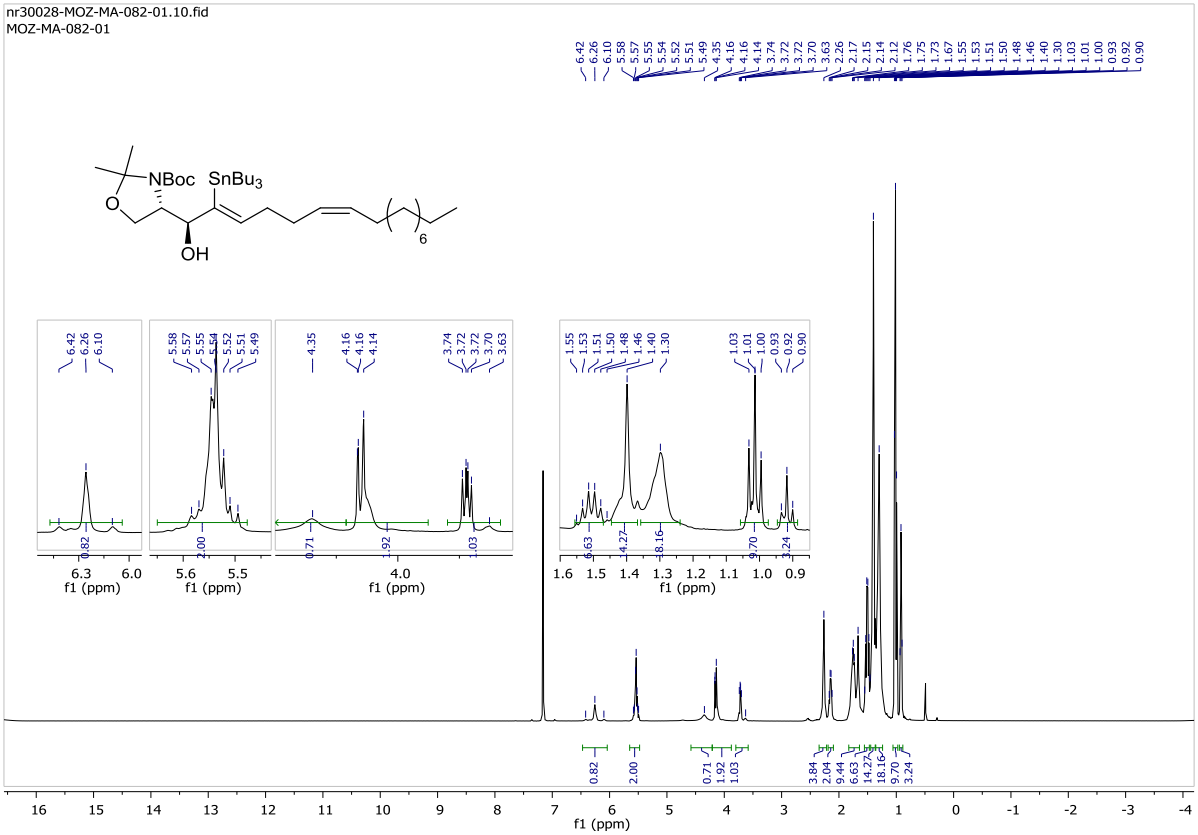
MOZ-MA-065-01
f1 (ppm)


nr30056-MOZ-MA-077-02.10.fid
MOZ-MA-077-02
NBoc
SnBu3
O
OH
6
f1 (ppm)


nr30056-MOZ-MA-077-02.11.fid
MOZ-MA-077-02
f1 (ppm)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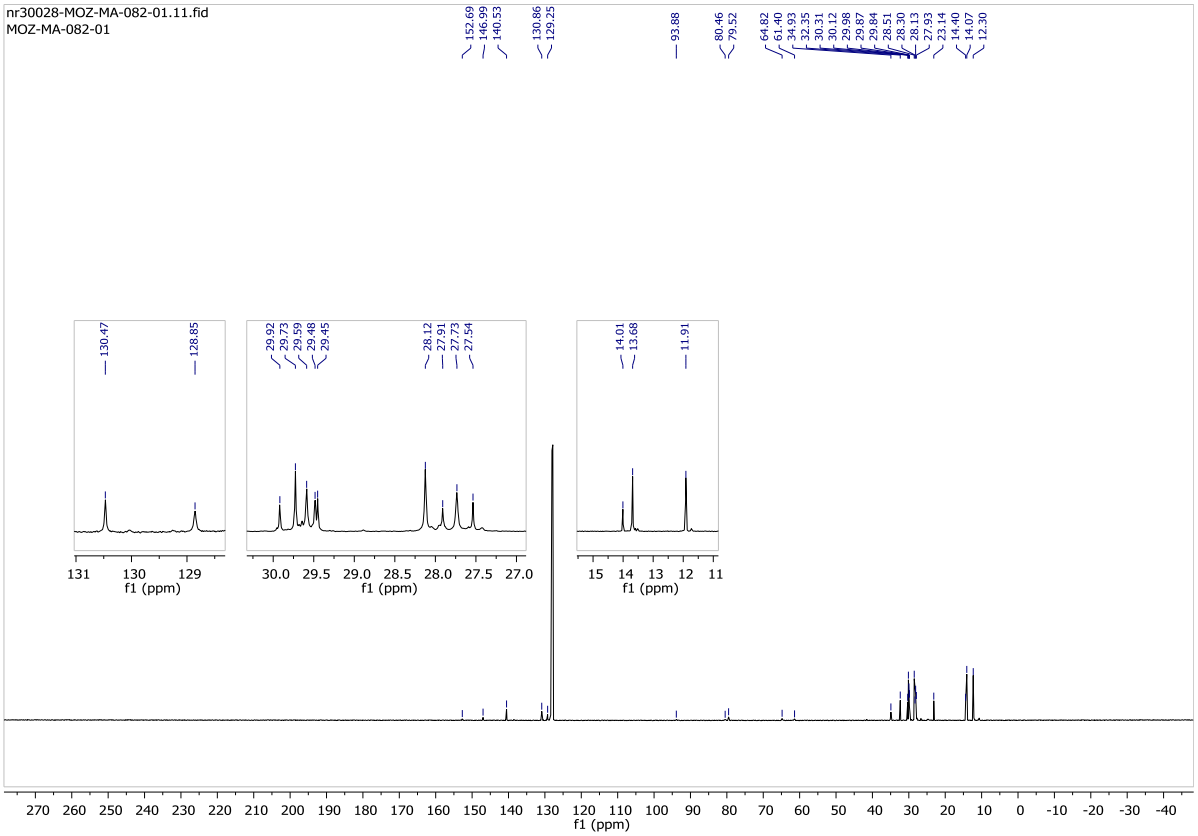
MOZ-MA-082-01
NBoc
SnBu3
O
OH
6
f1 (ppm)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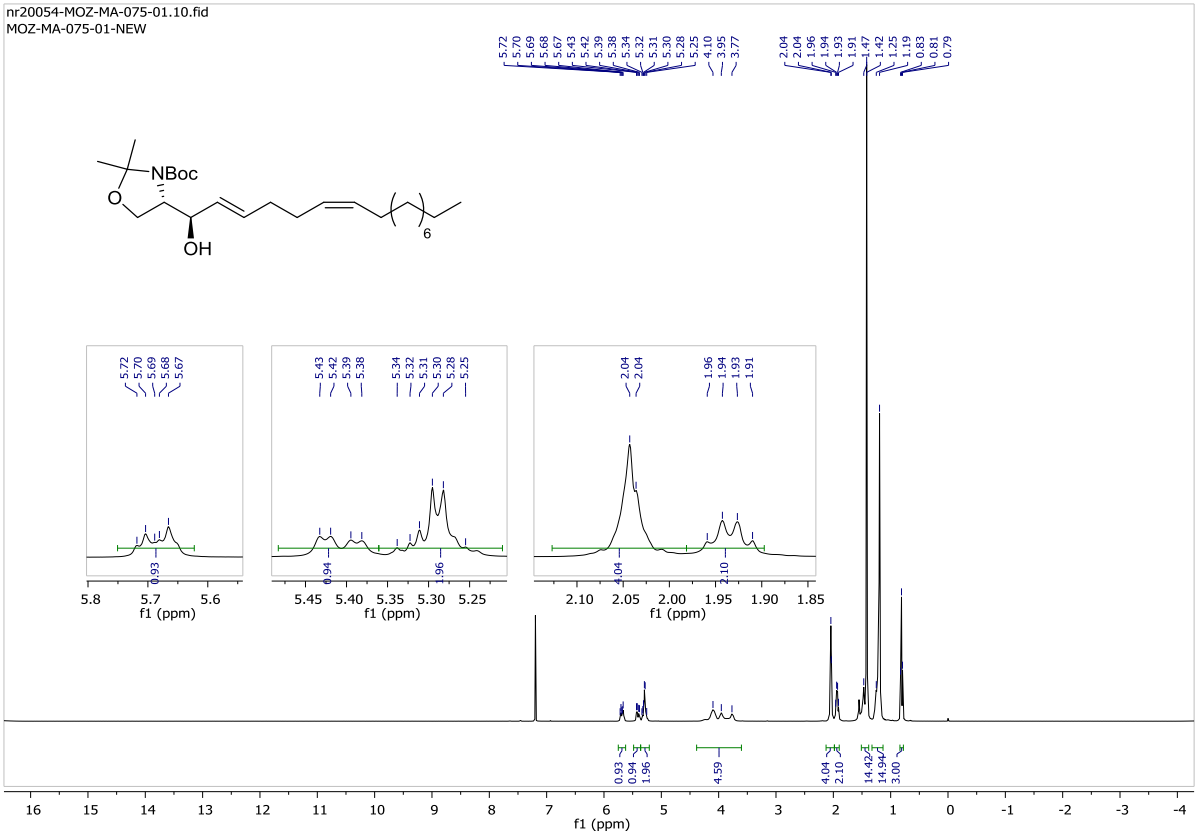
MOZ-MA-082-01
f1 (ppm)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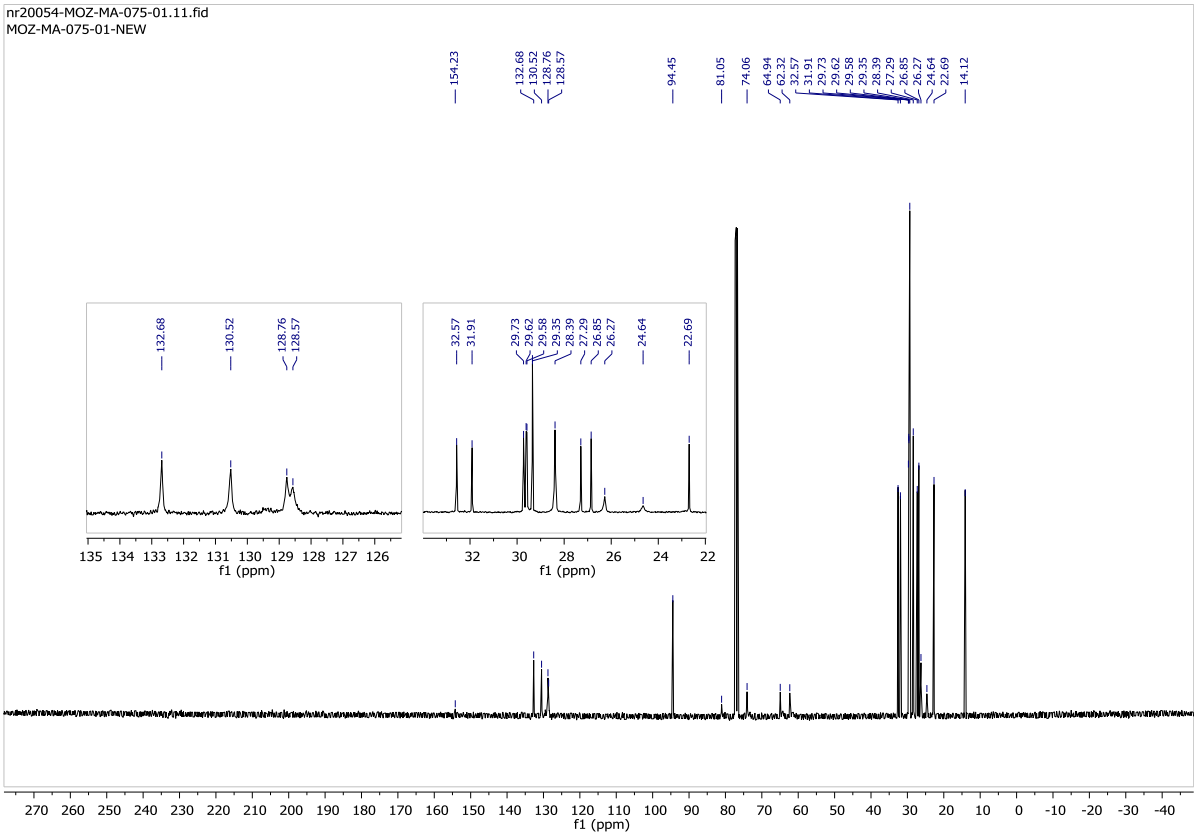
MOZ-MA-075-01-NEW
NBoc
O
OH
6
f1 (ppm)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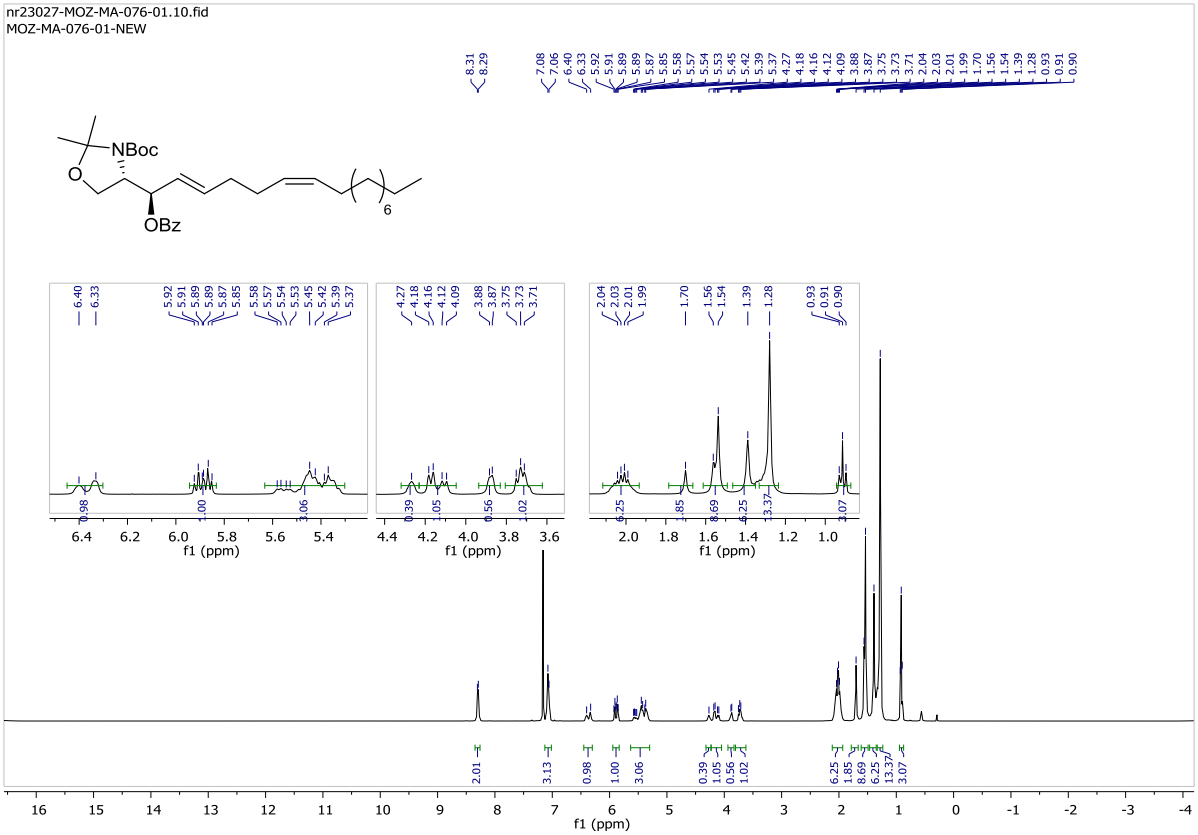
MOZ-MA-075-01-NEW
f1 (ppm)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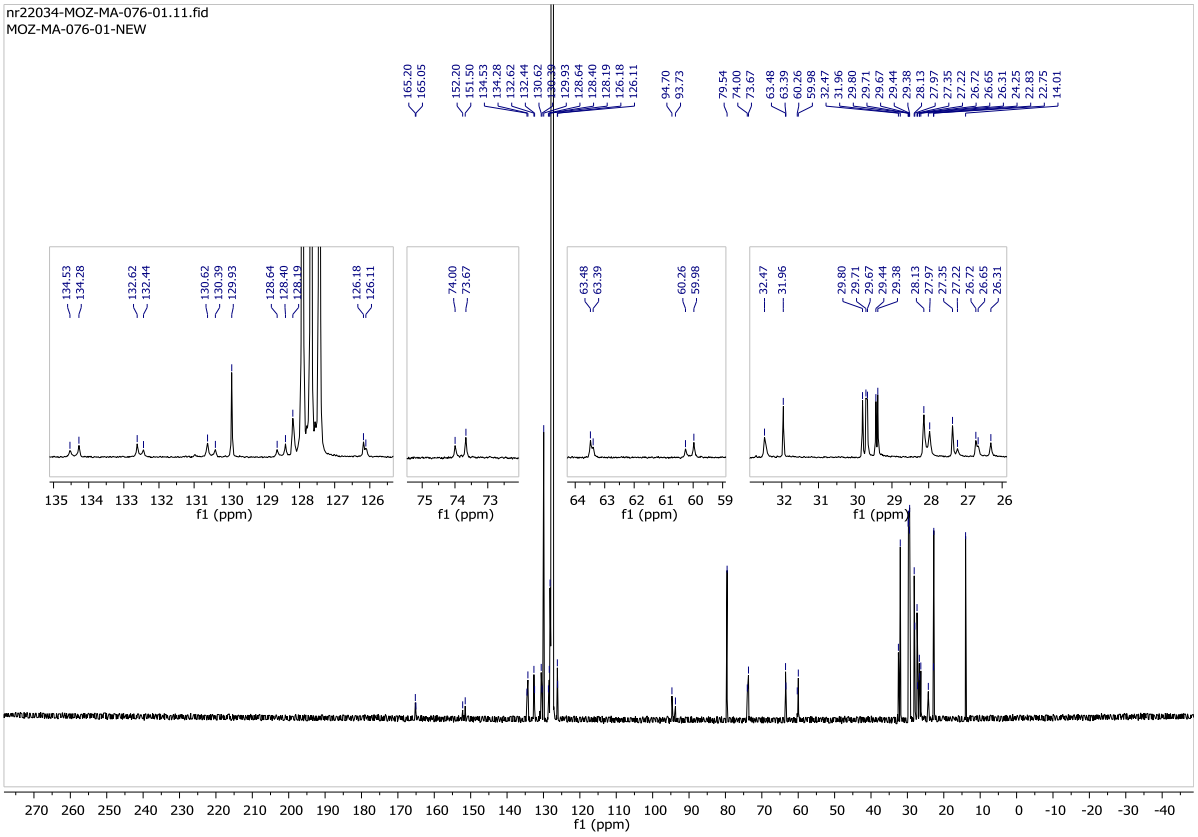
MOZ-MA-076-01-NEW
NBoc
O
OBz
6
f1 (ppm)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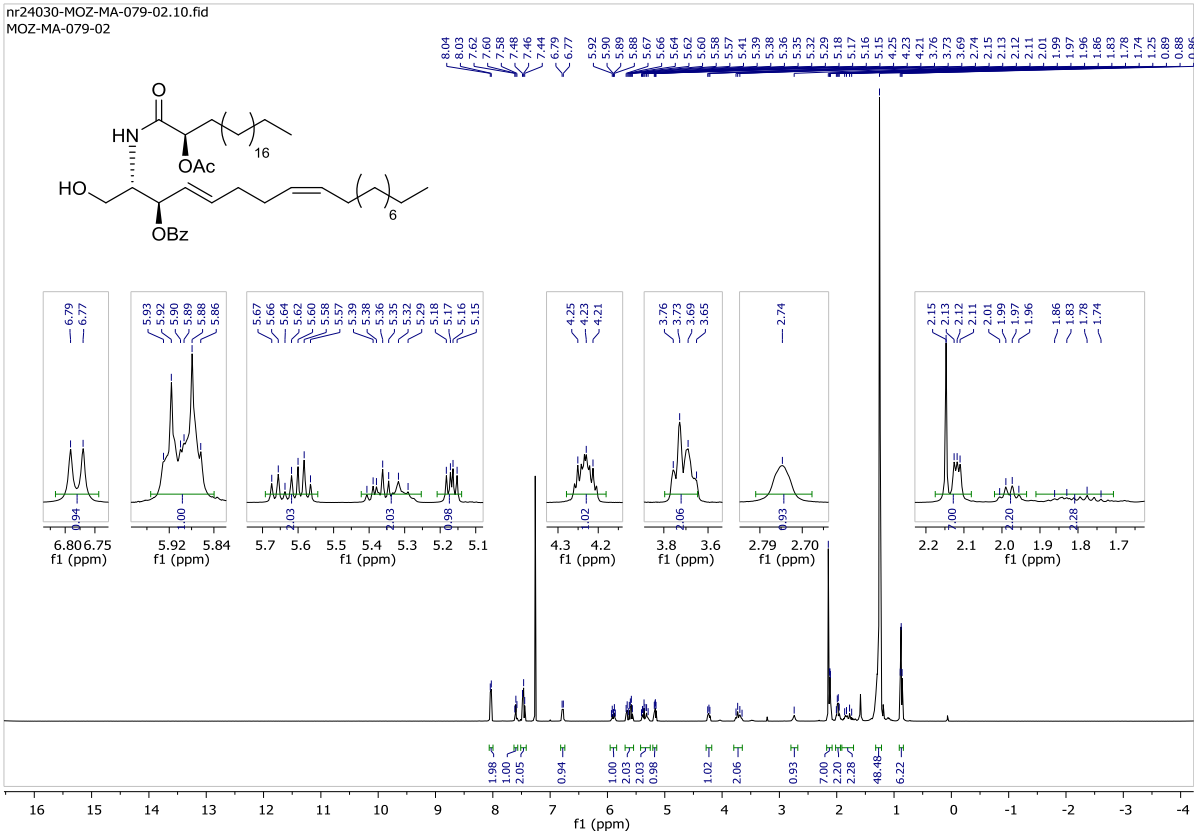
MOZ-MA-076-01-NEW
f1 (ppm)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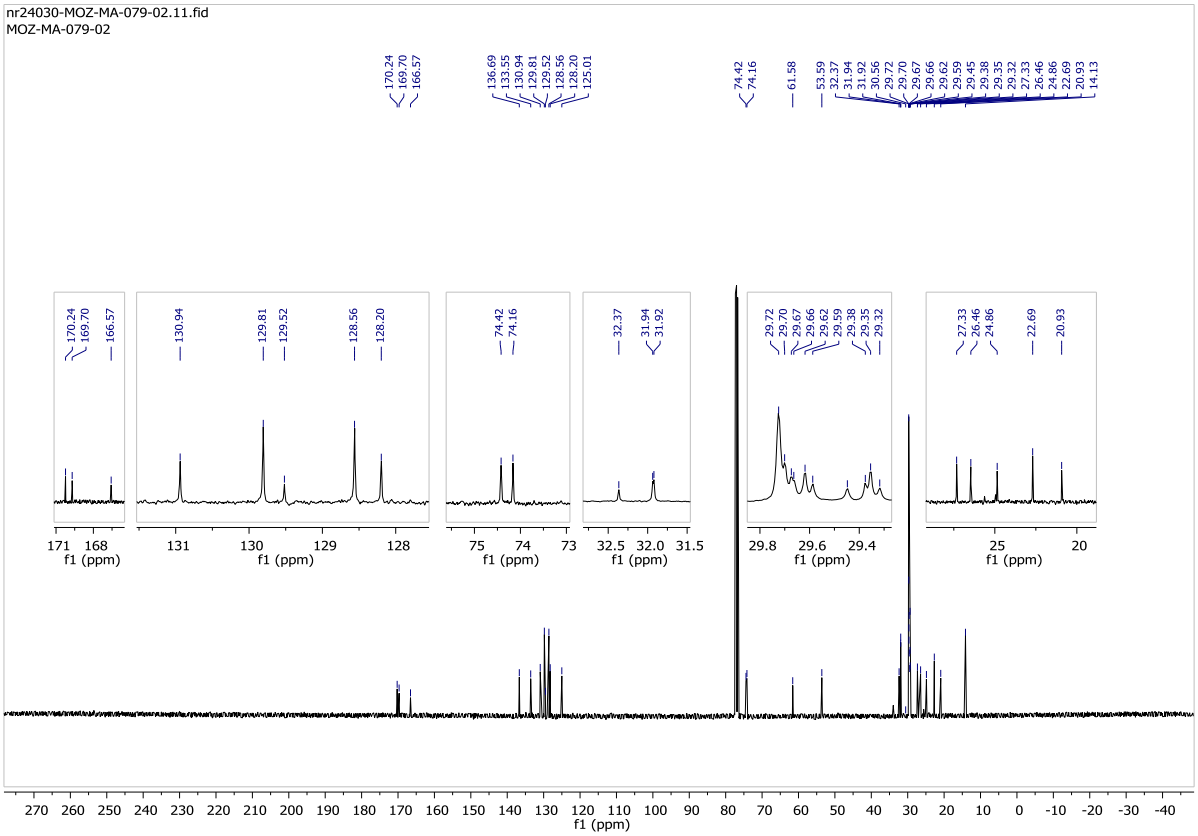
MOZ-MA-079-02
HN
OAc
16
HO
OBz
6
f1 (ppm)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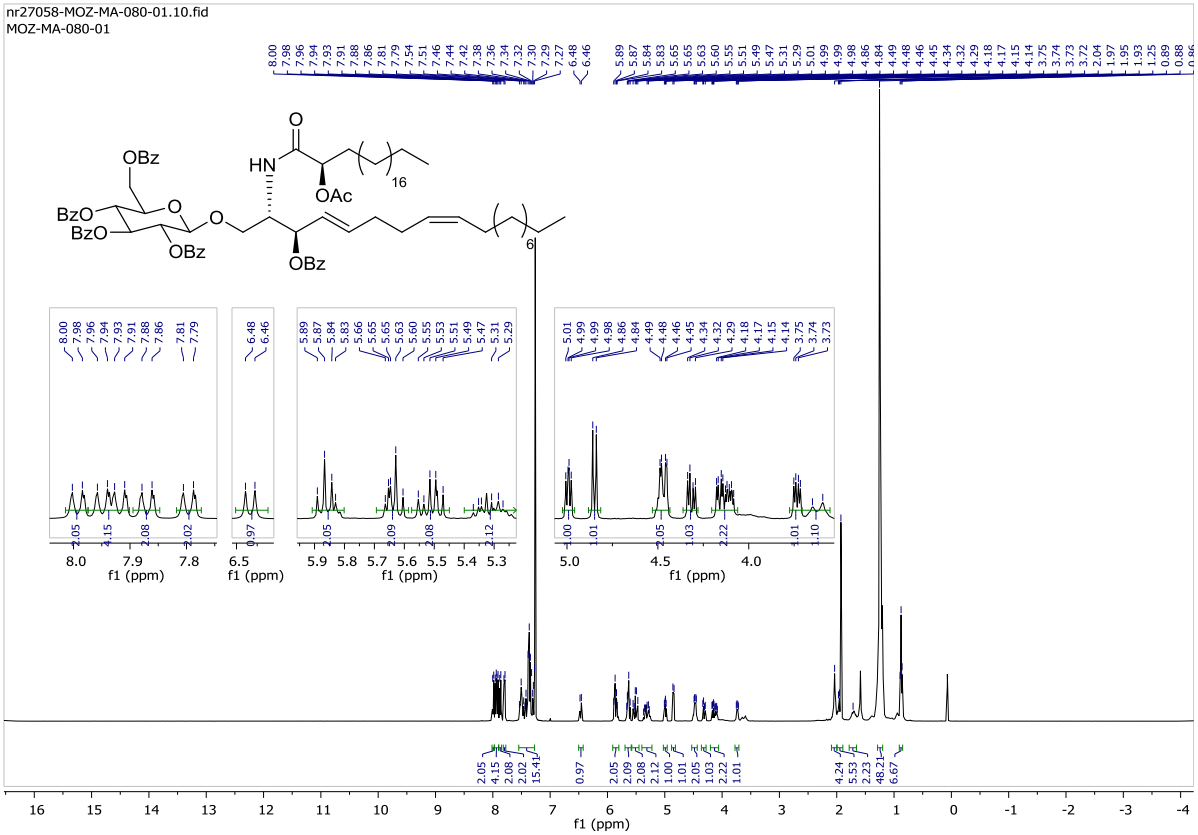
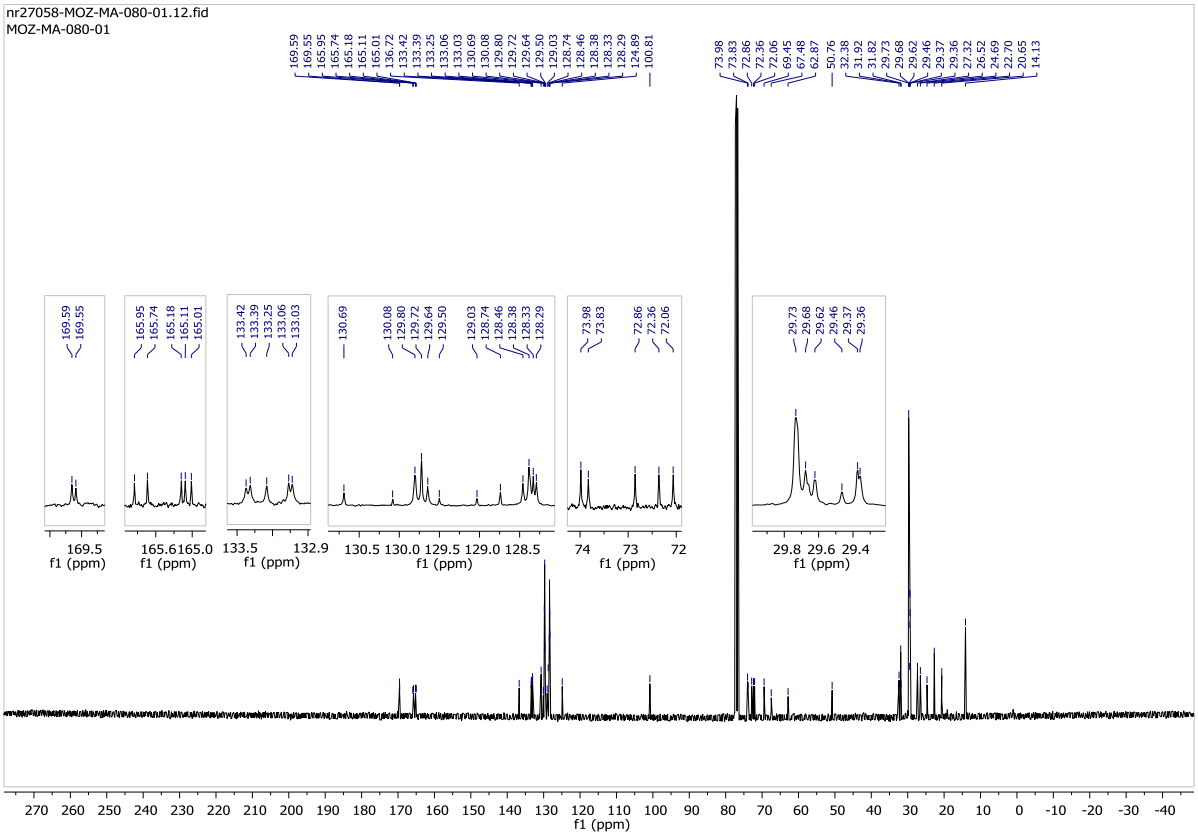
MOZ-MA-079-02
f1 (ppm)


nr27058-MOZ-MA-080-01.10.fid
MOZ-MA-080-01
OBz
BzO
BzO
OBz
O
HN
OAc
16
OBz
6
f1 (ppm)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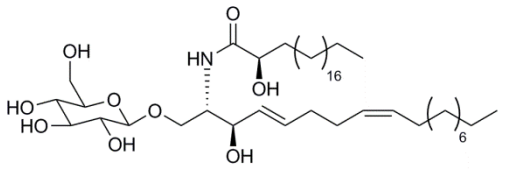
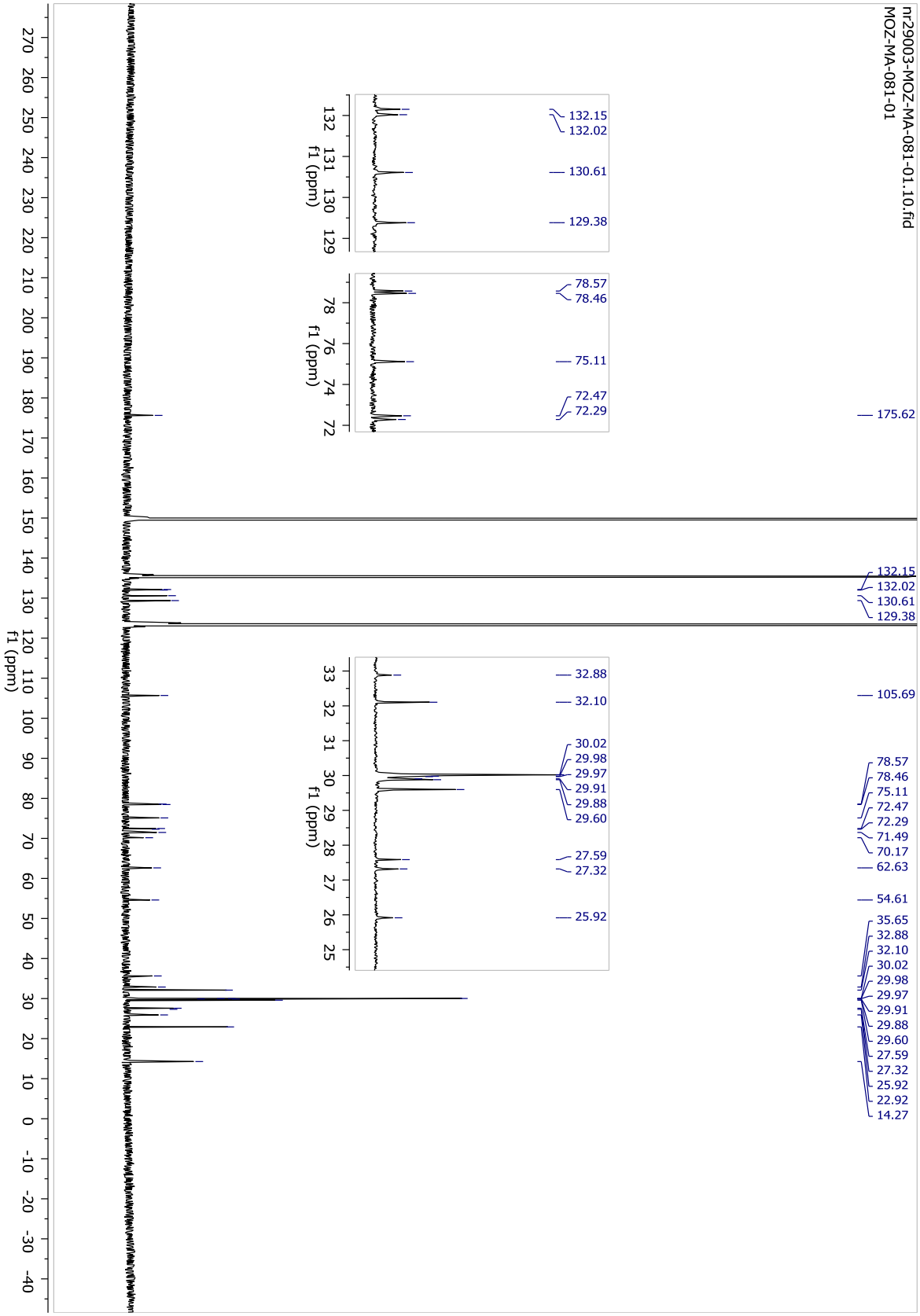
MOZ-MA-080-01
f1 (ppm)

nr29003-MOZ-MA-081-01.11.fid
MOZ-MA-081-01

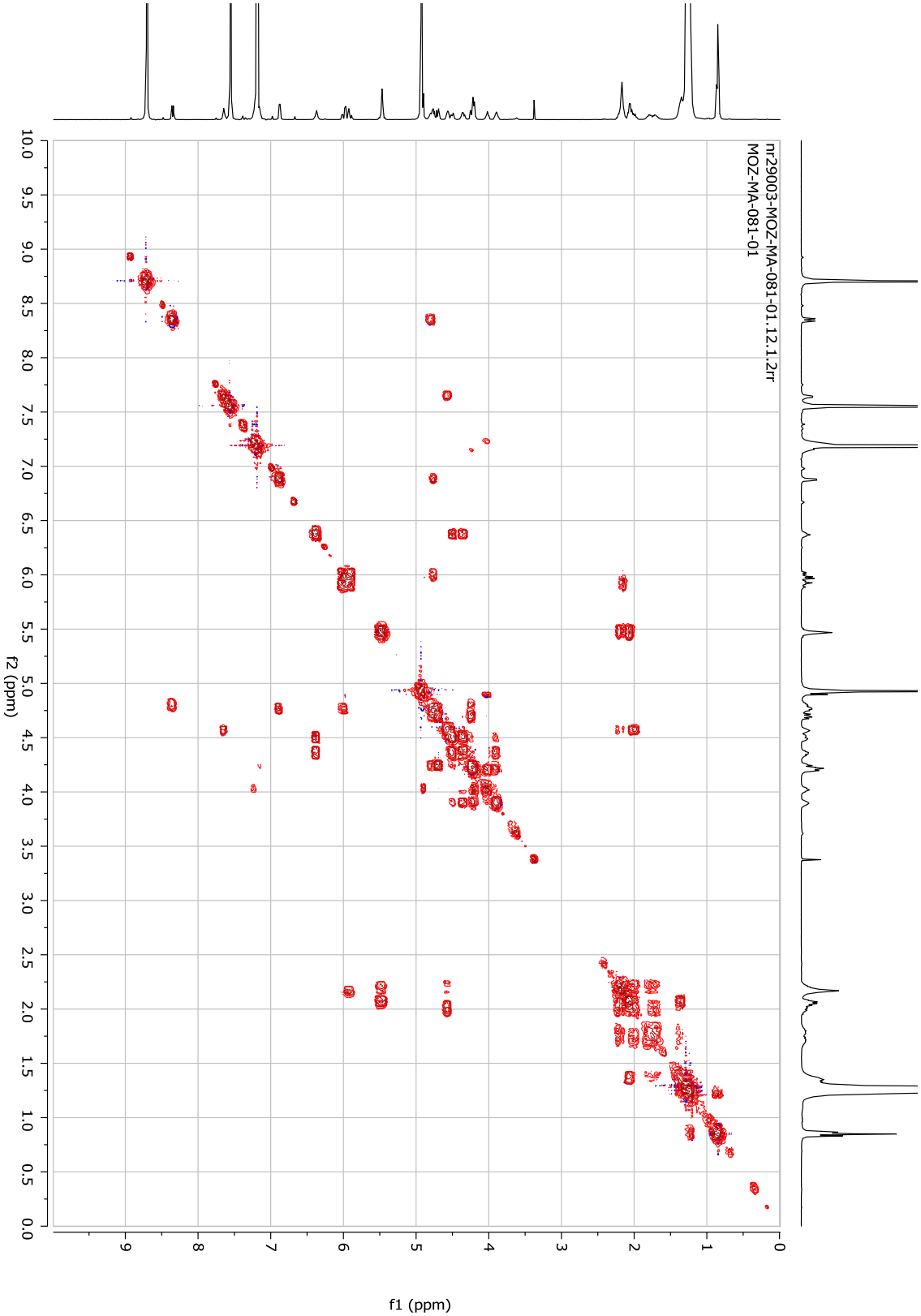


Typhonoside E

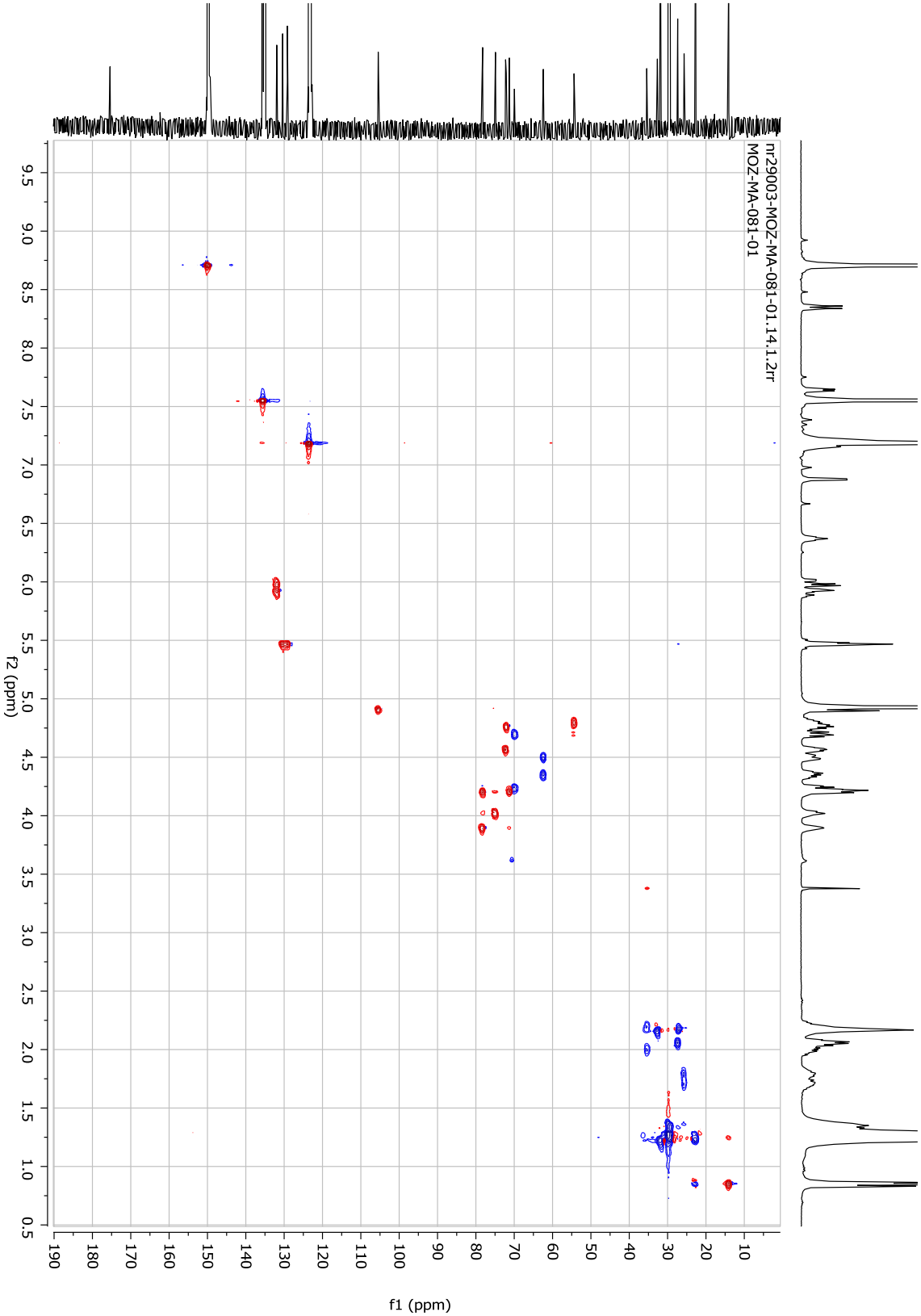
f1 (ppm)


nr29003-MOZ-MA-081-01.10.fid
MOZ-MA-081-01
f1 (ppm)
175.62
132.15
132.02
130.61
129.38
105.69
78.57
78.46
75.11
72.47
72.29
71.49
70.17
62.63
54.61
35.65
32.88
32.10
30.02
29.98
29.97
29.91
29.88
29.60
27.59
27.32
25.92
22.92
14.27

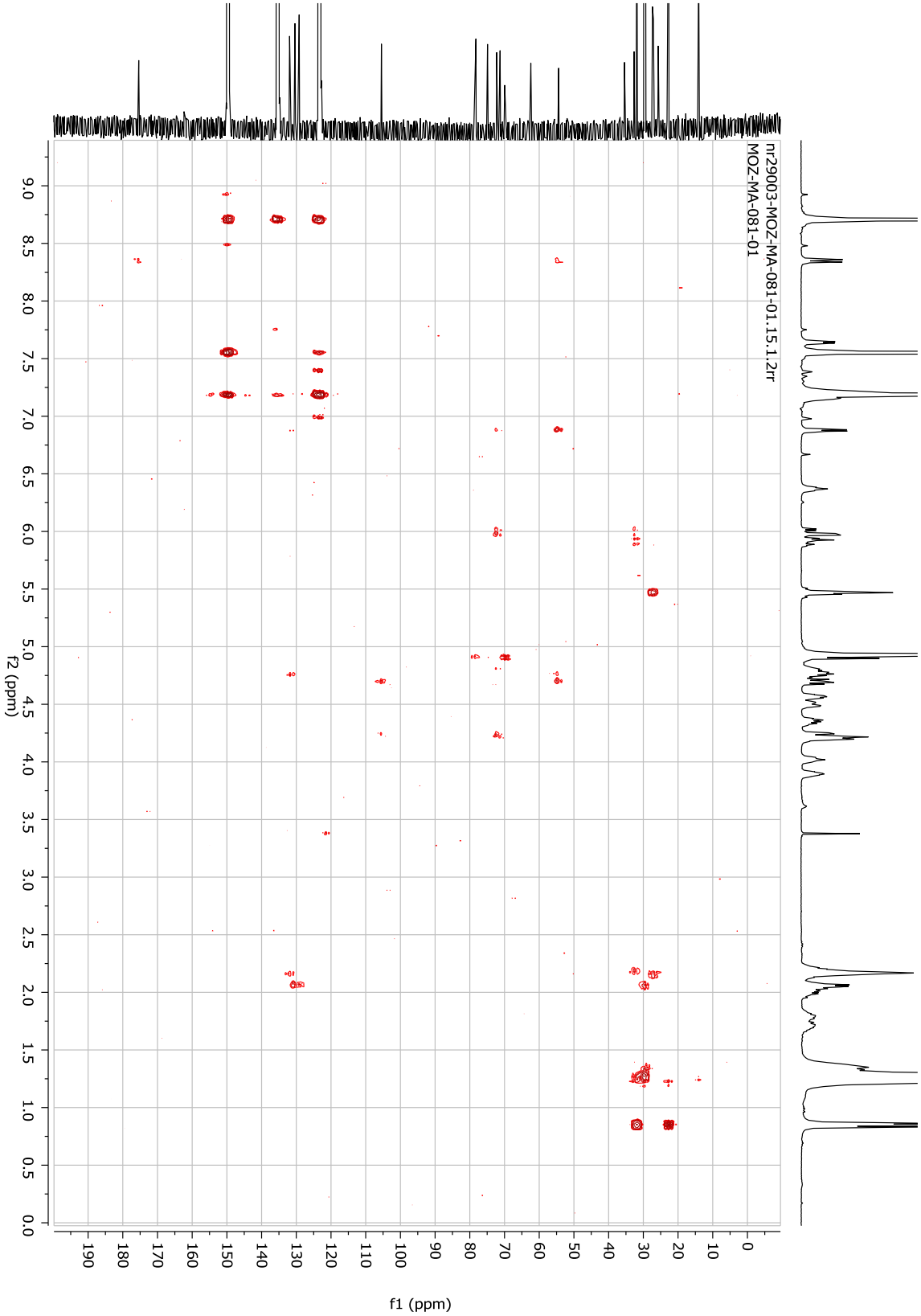
NMR of Typhonoside E. COSY (pyridine-*d5*, 400 MHz).



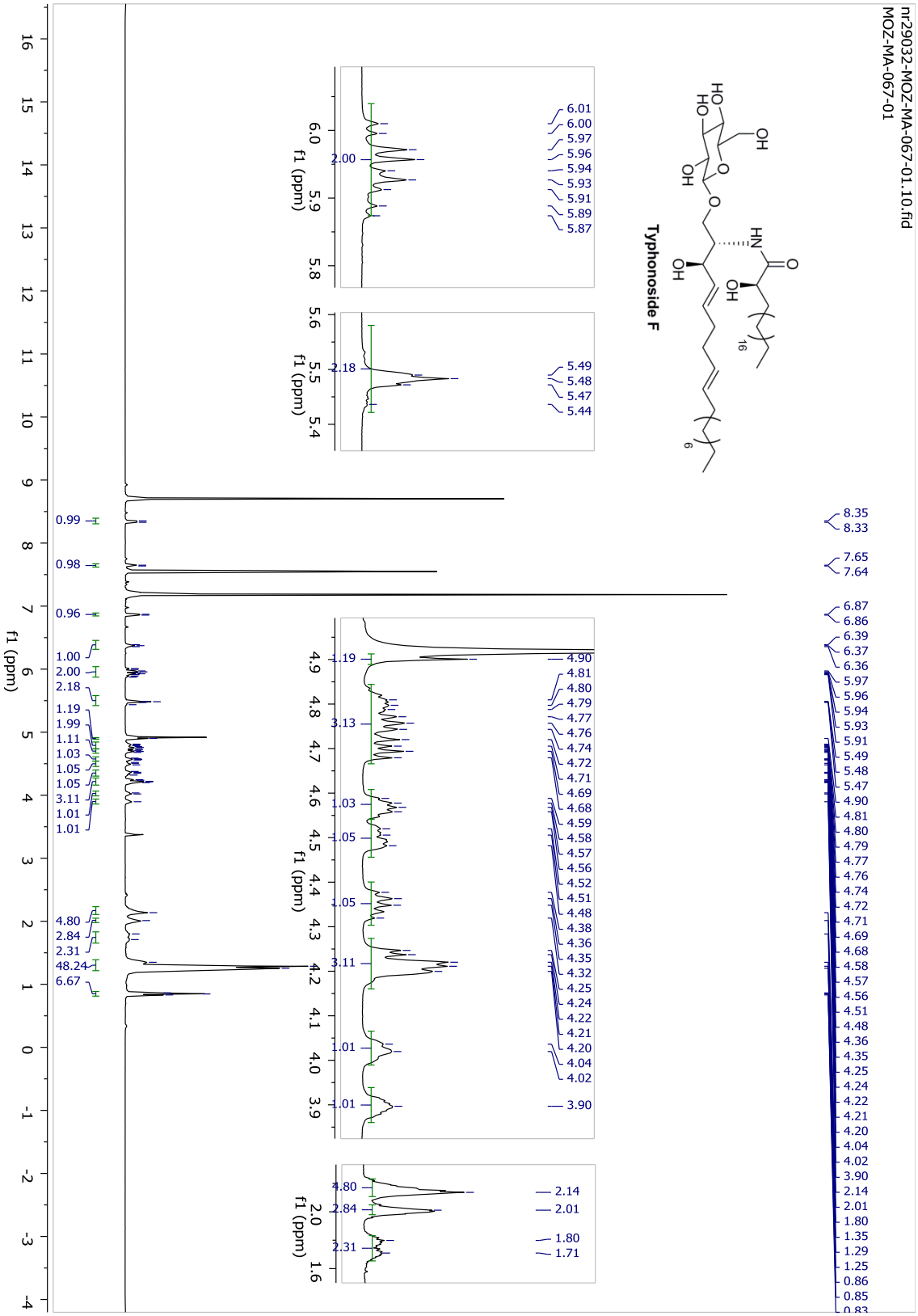
NMR of Typhonoside E. HSQC (pyridine-*d5*, 100 MHz).



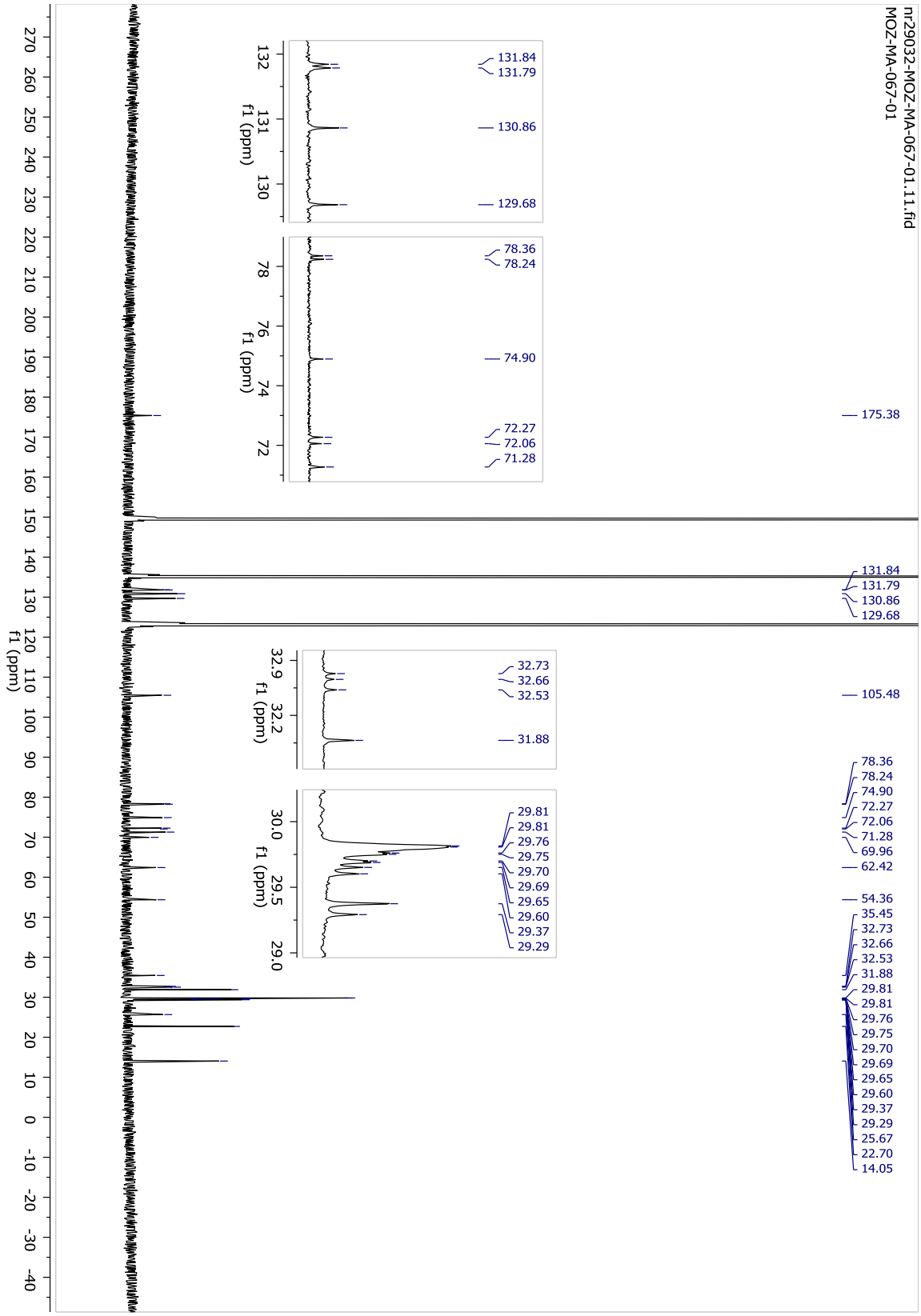
NMR of Typhonoside E. HMBC (pyridine-*d5*, 400 MHz).



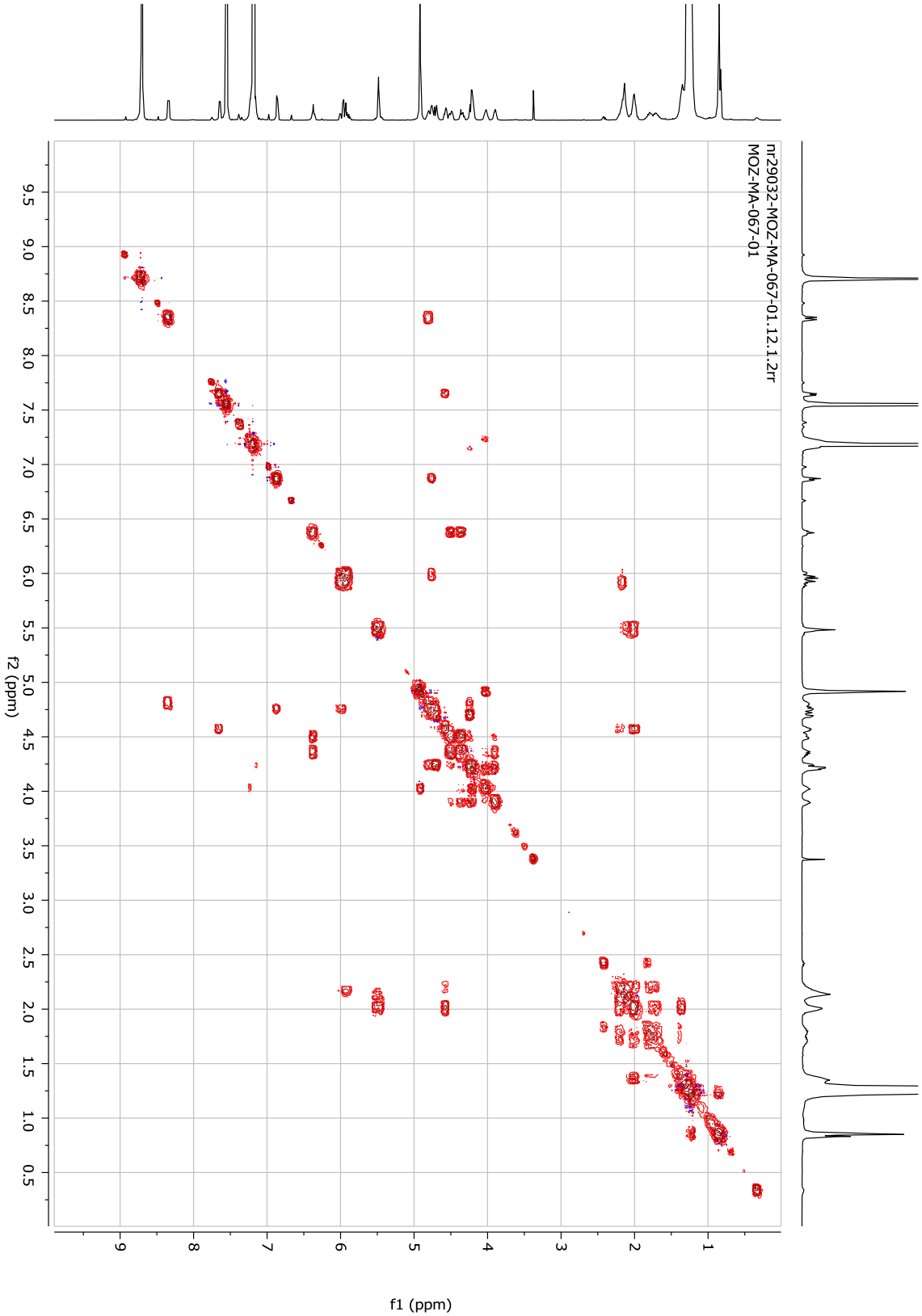
NMR of Typhonoside F. ^{1}H NMR (pyridine-*d5*, 400 MHz).



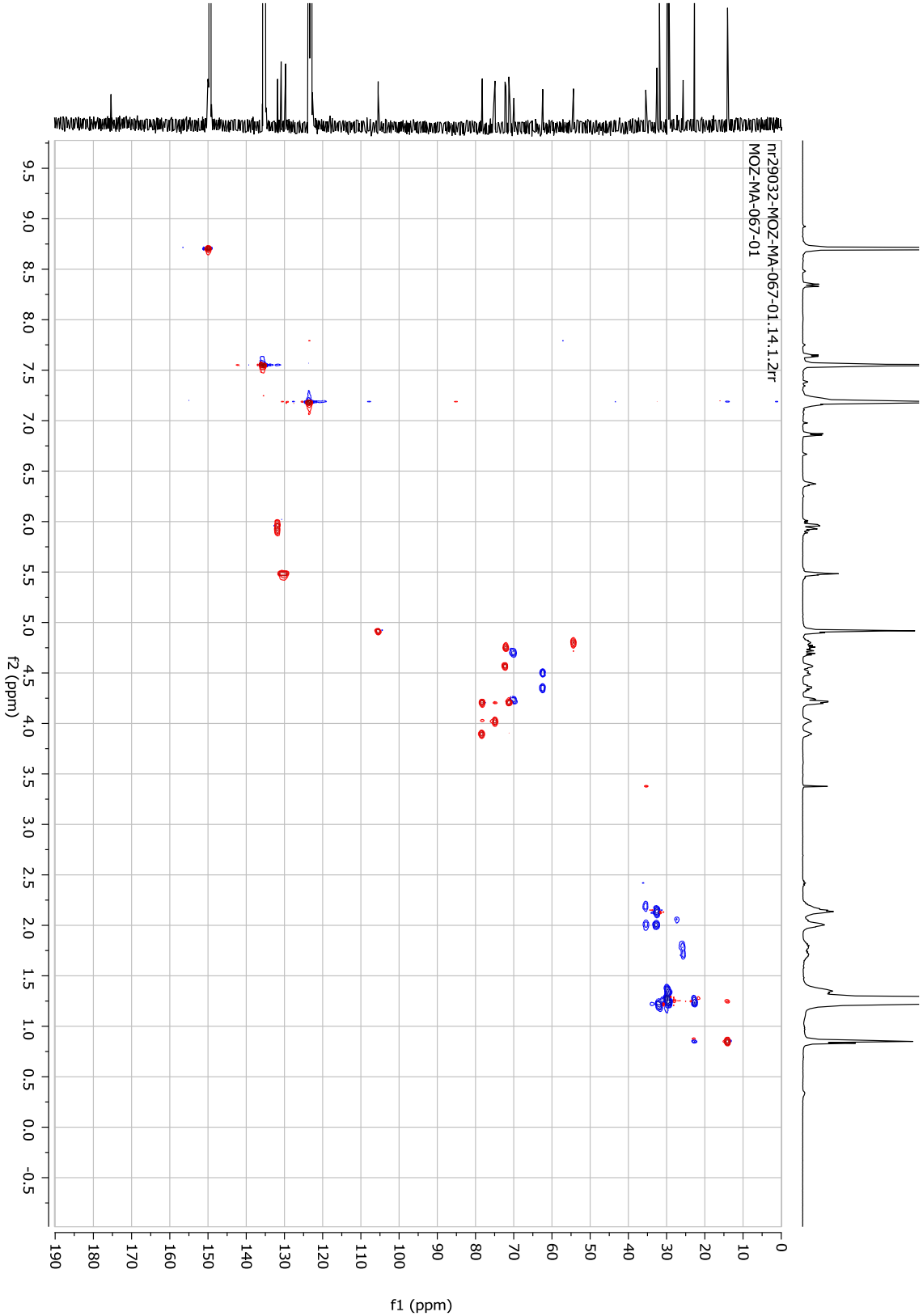
NMR of Typhonoside F. ^{13}C NMR (pyridine-*d5*, 100 MHz).



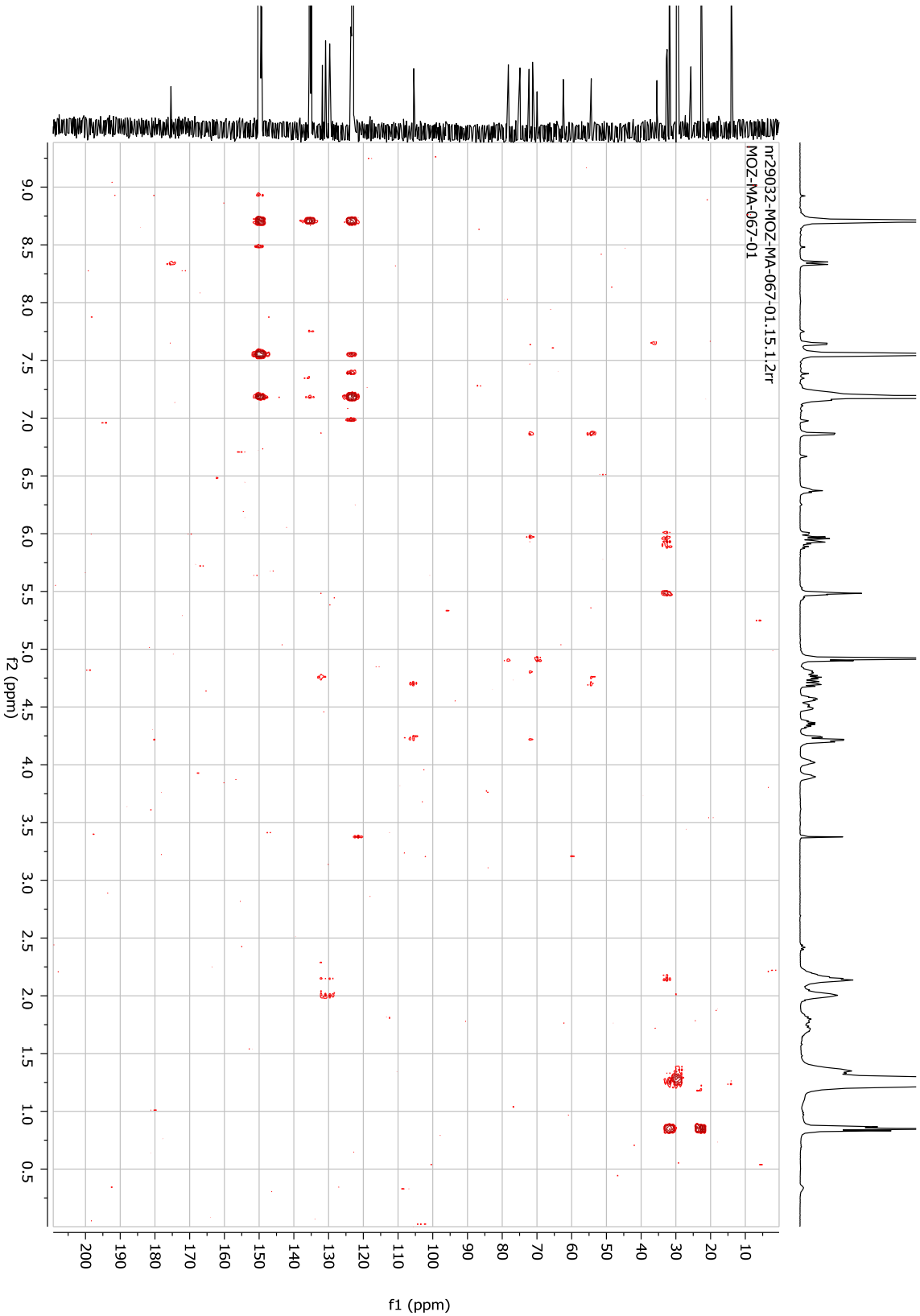
NMR of Typhonoside F. COSY (pyridine-*d5*, 400 MHz).



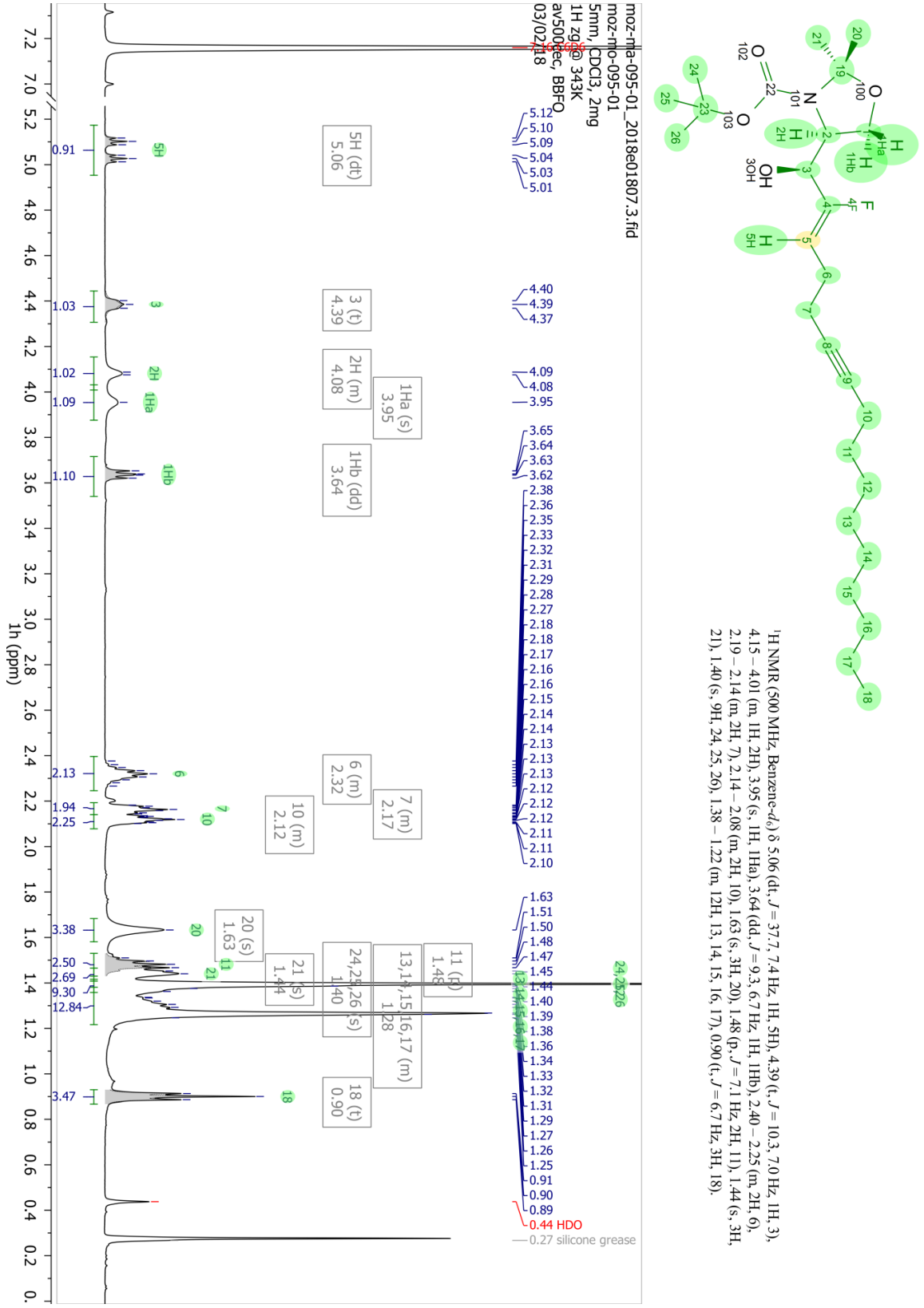
NMR of Typhonoside F. HSQC (pyridine-*d5*, 100 MHz).



NMR of Typhonoside F. HMBC (pyridine-*d5*, 400 MHz).

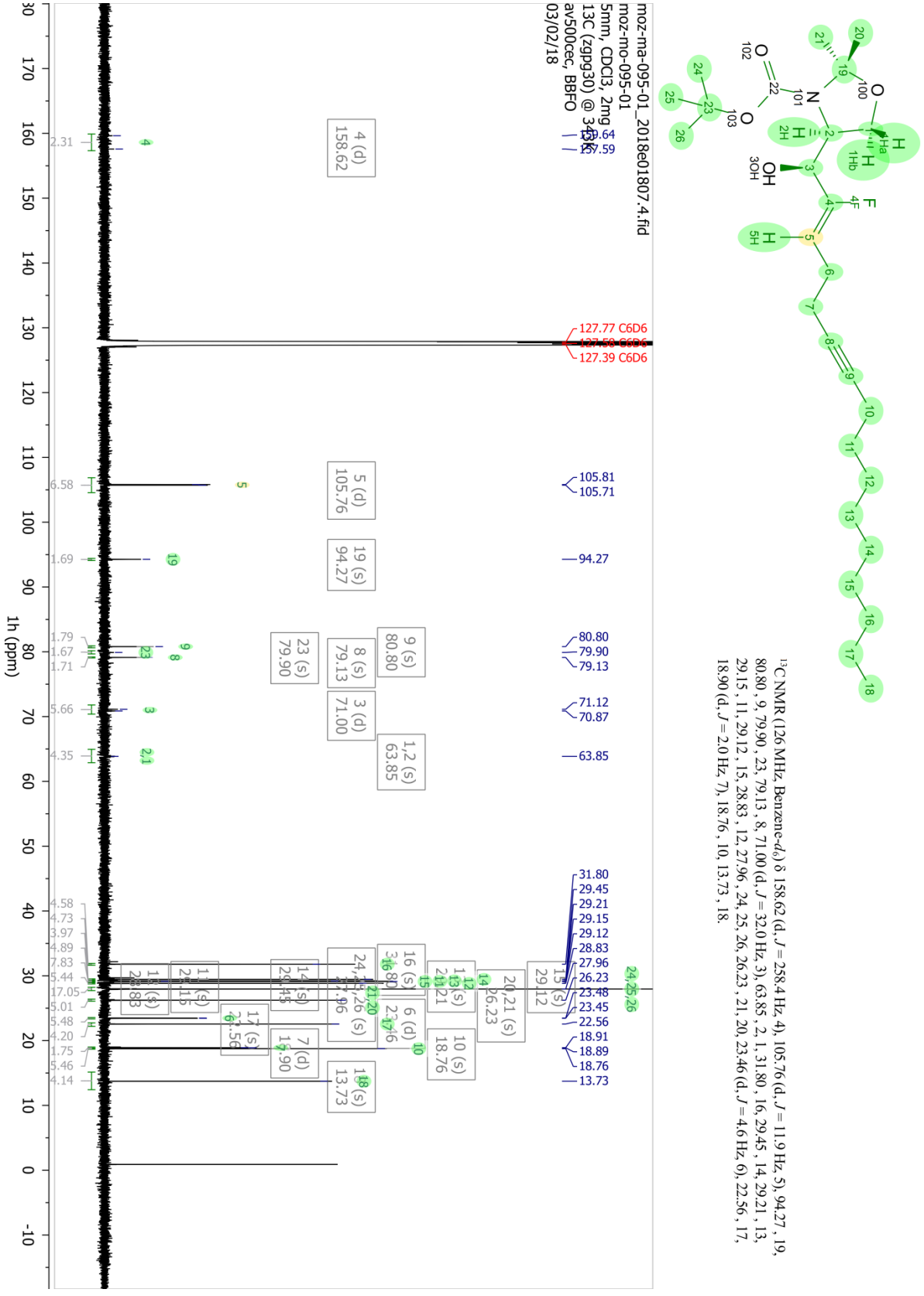


NMR spectra of 31. ^{1}H NMR (C_6D_6, 500 MHz, 343 K).



^{1}H NMR (500 MHz, Benzene-d_6) δ 5.06 (dt, J = 37.7, 7.4 Hz, 1H, 5H), 4.39 (t, J = 10.3, 7.0 Hz, 1H, 3), 4.15 – 4.01 (m, 1H, 2H), 3.95 (s, 1H, 1Ha), 3.64 (dd, J = 9.3, 6.7 Hz, 1H, 1Hb), 2.40 – 2.25 (m, 2H, 6), 2.19 – 2.14 (m, 2H, 7), 2.14 – 2.08 (m, 2H, 10), 1.63 (s, 3H, 20), 1.48 (p, J = 7.1 Hz, 2H, 11), 1.44 (s, 3H, 21), 1.40 (s, 9H, 24, 25, 26), 1.38 – 1.22 (m, 12H, 13, 14, 15, 16, 17), 0.90 (t, J = 6.7 Hz, 3H, 18).

NMR spectra of 31. ^{13}C NMR (C_6D_6, 126 MHz, 343 K).



^{13}C NMR (126 MHz, Benzene-d_6) δ 158.62 (d, J = 258.4 Hz, 4), 105.76 (d, J = 11.9 Hz, 5), 94.27 , 19, 80.80 , 9, 79.90 , 23, 79.13 , 8, 71.00 (d, J = 32.0 Hz, 3), 63.85 , 2, 1, 31.80 , 16, 29.45 , 14, 29.21 , 13, 29.15 , 11, 29.12 , 15, 28.83 , 12, 27.96 , 24, 25, 26, 26.23 , 21, 20, 23.46 (d, J = 4.6 Hz, 6), 22.56 , 17, 18.90 (d, J = 2.0 Hz, 7), 18.76 , 10, 13.73 , 18.