SUPPORTING INFORMATION

Hydroxyl-Assisted Carbonylation of Alkenyltin Derivatives: Development and Application to a Formal Synthesis of Tubelactomicin A

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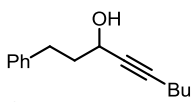
General. All reactions were carried out under Ar in flame-dried glassware. The solvents were purified by distillation over the drying agents indicated and were transferred under Ar: THF, Et_2O (Mg/anthracene), CH_2Cl_2, MeCN, pyridine (CaH_2), toluene, benzene (Na/K), MeOH (Mg). DMF and Et_3N were dried by an absorption solvent purification system based on molecular sieves. Flash chromatography: Merck silica gel 60 (40–63 µm). NMR: Spectra were recorded on a Bruker AV 400 spectrometer or a Bruker AV VIII 300 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 ($CDCl_3$: $\delta_C \equiv 77.16$ ppm; residual $CHCl_3$ in $CDCl_3$: $\delta_H \equiv 7.26$ ppm). ^{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] 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

Representative Procedure for the Preparation of Propargyl Alcohols from Aldehydes or Ketones. A flame-dried 250 mL two-necked flask equipped with a dropping funnel was charged with THF (100 mL) and 1-hexyne (6.61 mL, 57.5 mmol). The flask was immersed in a dry-ice/acetone bath. *n*BuLi (1.6 M in hexanes, 34.4 mL, 55 mmol) was slowly added via the dropping funnel and the resulting mixture was stirred for 1 h before neat hydrocinnamaldehyde (6.58 mL, 50 mmol) was added in one portion. After being stirred for 30 minutes at dry-ice temperature, the cooling bath was removed and the mixture allowed to warm to room temperature. The reaction was quenched with saturated ammonium chloride solution, the mixture extracted two times with *tert*-butyl methyl ether, and the combined organic layers were washed with brine, dried over magnesium sulfate and concentrated under reduced pressure. Pure products were obtained by flash chromatography (hexanes/ethyl acetate).

1-Phenylnon-4-yn-3-ol (S1). 99% yield (10.7 g). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 – 7.27 (m, 2H), 7.25 – 7.17 (m, 3H), 4.37 (tt, *J* = 6.4, 2.0 Hz, 1H), 2.80 (t, *J* = 7.9 Hz, 2H), 2.24 (td, *J* = 7.0, 2.0 Hz, 2H), 2.01 (tt, *J* = 7.8, 6.2 Hz, 2H), 1.62 – 1.48 (m, 2H), 1.48 – 1.35 (m, 2H), 0.93 (t, *J* = 7.2 Hz, 3H) ppm.



^{13}C NMR (101 MHz, $CDCl_3$) δ 141.6, 128.6, 128.5, 126.0, 86.1, 81.1, 62.2, 39.8, 31.6, 30.8, 22.1, 18.5, 13.7 ppm. IR (film, $CHCl_3$) 3338, 3027, 2955, 2931, 2861, 1603, 1496, 1454, 1379, 1328, 1134, 1030 1054, 914, 746, 699 cm^{-1}. The data are in accordance with those reported in the literature.[2]

The following compounds were prepared analogously:

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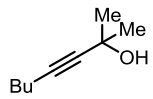
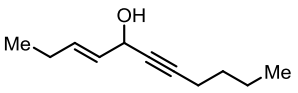
1 a) N. Oshima, H. Suzuki, Y. Moro-oka, *Chem. Lett*. **1984**, *13*, 1161-1164; b) T. D. Tilley, R. H. Grubbs, J. E. Bercaw, *Organometallics* **1984**, *3*, 274-278.

2 M. Egi, Y. Yamaguchi, N. Fujiwara, S. Akai, *Org. Lett.*, **2008**, 1867-1870.

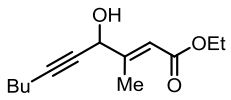
2-Methyloct-3-yn-2-ol (S2). 99% yield (2.80 g). ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.18 (t, *J* = 7.0 Hz, 2H), 1.88 – 1.81 (m, 1H), 1.49 (s, 7H), 1.48 – 1.35 (m, 3H), 0.90 (t, *J* = 7.2 Hz, 3H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 85.2, 82.7, 65.5, 31.9, 30.9, 22.1, 18.4, 13.8 ppm. The data are in accordance with those reported in the literature.[3]



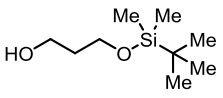
(*E*)-Undec-3-en-6-yn-5-ol (S3). 67% yield (2.23 g). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.90 (dtd, *J* = 15.3, 6.3, 1.2 Hz, 1H), 5.58 (ddt, *J* = 15.3, 6.2, 1.6 Hz, 1H), 4.88 – 4.69 (m, 1H), 2.24 (td, *J* = 7.1, 2.0 Hz, 2H), 2.13 – 2.04 (m, 2H), 1.80 – 1.75 (m, 1H), 1.54 – 1.46 (m, 2H), 1.46 – 1.36 (m, 2H), 1.01 (t, *J* = 7.5 Hz, 3H), 0.91 (t, *J* = 7.2 Hz, 3H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 135.3, 128.7, 87.0, 79.8, 63.4, 30.8, 25.1, 22.1, 18.6, 13.7, 13.3 ppm. IR (film, $CHCl_3$) 3337, 2961, 2933, 2873, 1460, 1432, 1379, 1328, 1147, 1083, 998, 966 cm^{-1}. HRMS (ESI): *m/z* calculated for $C_{11}H_{18}ONa$ [M+Na$^+$]: 189.12498; found 189.12509.



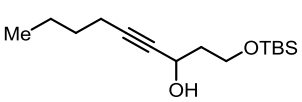
Ethyl (*E*)-4-hydroxy-3-methyldec-2-en-5-ynoate (S4). 86% yield (3.87). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.06 (pent., *J* = 1.3 Hz, 1H), 4.77 (q, *J* = 1.8 Hz, 1H), 4.16 (q, *J* = 7.1 Hz, 2H), 2.26 – 2.15 (m, 6H), 1.56 – 1.42 (m, 2H), 1.42 – 1.30 (m, 2H), 1.27 (t, *J* = 7.1 Hz, 3H), 0.90 (t, *J* = 7.2 Hz, 3H ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.9, 155.9, 116.0, 87.8, 78.1, 67.2, 60.1, 30.6, 22.1, 18.5, 15.2, 14.4, 13.7 ppm. IR (film, $CHCl_3$) 3434, 2959, 2934, 2873, 1717, 1699, 1657, 1432, 1368, 1344, 1295, 1210, 1146, 1096, 1040, 876 cm^{-1}.



3-((*tert*-Butyldimethylsilyl)oxy)propan-1-ol (S5). A solution of 1,3-propanediol (7.23 mL, 100 mmol), triethylamine (6.97 mL, 50 mmol) and *tert*-butyldimethylchlorosilane (7.54 g, 50 mmol) in reagent grade dichloromethane (150 mL) was stirred at room temperature for 12 h. The reaction was quenched with saturated ammonium chloride solution and the mixture extracted two times with dichloromethane. The combined extracts were washed with water, dried over magnesium sulfate and concentrated under reduced pressure to give a crude yellow oil. Flash chromatography (hexanes/ethyl acetate, 6:1 to 4:1) yielded the product as a colorless liquid (7.74 g, 81% yield). ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.83 (m, 4H), 2.24 (s, 1H), 1.88 – 1.69 (m, 2H), 0.90 (s, 9H), 0.08 (s, 6H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 63.0, 62.6, 34.4, 26.0, 18.3, -5.3 ppm. The data are in accordance with those reported in the literature.[4]



1-((*tert*-Butyldimethylsilyl)oxy)non-4-yn-3-ol (S6). A solution of oxalyl chloride (1.99 mL, 23.2 mmol) in dichloromethane (50 mL) was stirred at −60°C in a flame-dried Schlenk flask. A solution of DMSO (3.41 mL, 48 mmol) in dichloromethane (10 mL) was added. After stirring for 5 minutes, 3-(*tert*-butyl-dimethyl-silanyloxy)-propan-1-ol (3.81 g, 20 mmol) was added dropwise at −60°C, followed by the dropwise addition of triethylamine (14.1 mL, 101 mmol). The mixture was allowed to warm to room temperature and the reaction was quenched with water (100 mL). The aqueous phase was extracted with dichloromethane, the combined organic layers were washed



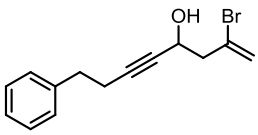
[3] X. C. Gonzalez-Avion, A. Mourino, N. Rochel, D. Moras, *J. Med. Chem.*, **2006**, 1509-1516.

[4] C. D. Donner, *Org. Lett.*, **2013**, 1258-1261.

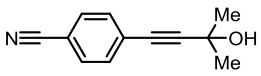
with brine, water and a second time with brine before being dried over magnesium sulfate. The solvents were removed under reduced pressure, the residue was dissolved in diethyl ether, the solution filtrated through a pad of Celite®, and the filtrate evaporated. The resulting crude aldehyde was used without further purification for the next step.

1-Hexyne (1.38 mL, 12 mmol) was dissolved in THF (25 mL) and the solution cooled in an acetone/dry ice bath. *n*BuLi (1.6 M in hexanes, 7.5 mL, 12 mmol) was added and stirring continued for 1 h at the same temperature before freshly prepared 3-((*tert*-butyldimethylsilyl)oxy)propanal (1.88 g, 10 mmol) was introduced. After another 1 h the mixture was allowed to warm to room temperature and the reaction was quenched with saturated ammonium chloride solution. The mixture was extracted two times with ethyl acetate, the combined organic layers were washed with brine, dried over magnesium sulfate and concentrated under reduced pressure. Flash chromatography (hexanes/ethyl acetate, 10:1) yielded the product as a pale yellow oil (2.29 g, 85% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.54 (tt, *J* = 4.3, 2.2 Hz, 1H), 3.97 (ddd, *J* = 10.2, 7.6, 4.2 Hz, 1H), 3.77 (ddd, *J* = 10.4, 6.2, 4.5 Hz, 1H), 3.37 (s, 1H), 2.17 (td, *J* = 7.0, 2.0 Hz, 2H), 1.91 (ddt, *J* = 14.1, 7.6, 4.5 Hz, 1H), 1.80 (dtd, *J* = 14.1, 6.3, 4.2 Hz, 1H), 1.53 – 1.29 (m, 4H), 0.89 – 0.83 (m, 12H), 0.04 (s, 3H), 0.04 (s, 3H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 85.4, 80.7, 61.9, 61.2, 39.2, 30.8, 25.9, 22.0, 18.5, 18.2, 13.7, -5.5 ppm. IR (film, $CHCl_3$) 2955, 2929, 2858, 1470, 1253, 1099, 1006, 939, 832, 775 cm^{-1}. HRMS (ESI): *m/z* calculated for $C_{15}H_{30}O_2SiNa$ [M+Na^+]: 293.19073; found 293.19070.

2-Bromo-8-phenyloct-1-en-5-yn-4-ol (S7). Sn powder (2.04 g, 17.2 mmol) was suspended in H_2O/Et_2O (25 mL/25 mL). 2,3-Dibromopropene (3.95 mL, 34 mmol, 85% purity) was added to the vigorously stirred suspension, followed by a few drops of concentrated aqueous HBr and 5-phenylpent-2-ynal (1.81 g, 11.4 mmol).[5] Stirring was continued at room temperature until TLC showed complete conversion. The mixture was diluted with water and extracted two times with *tert*-butyl methyl ether. The combined organic layers were dried over magnesium sulfate and the volatile materials were removed under reduced pressure to give an orange oil. The crude material was purified by flash chromatography (hexanes/ethyl acetate, 9:1 to 4:1) to give the product as a yellow oil (2.4 g, 75% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.31 (m, 2H), 7.26 (td, *J* = 6.5, 1.6 Hz, 3H), 5.72 (dt, *J* = 1.9, 1.1 Hz, 1H), 5.56 (d, *J* = 1.7 Hz, 1H), 4.69 (ddt, *J* = 7.6, 5.7, 1.9 Hz, 1H), 2.86 (t, *J* = 7.5 Hz, 2H), 2.84 – 2.71 (m, 2H), 2.55 (td, *J* = 7.5, 2.0 Hz, 2H), 2.41 (s, 1H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.5, 128.6, 128.5, 128.4, 126.4, 120.2, 85.7, 80.5, 60.5, 49.7, 34.9, 20.9 ppm. IR (film, $CHCl_3$) 3349, 3027, 2924, 1632, 1603, 1496, 1427, 1453, 1340, 1200, 1113, 1141, 1032, 891, 746, 697 cm^{-1}. HRMS (ESI): *m/z* calculated for $C_{14}H_{15}OBrNa$ [M+Na^+]: 301.01986; found 301.01972.



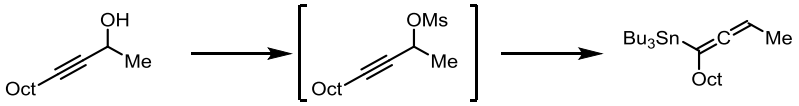
4-(3-Hydroxy-3-methylbut-1-yn-1-yl)benzonitrile (S8). Triethylamine (25 mL), bis(triphenylphosphine)-palladium(II) dichloride (105 mg, 0.15 mmol, 1 mol%) and copper iodide (86 mg, 0.45 mmol, 3 mol%) were successively added to a solution of *p*-bromobenzonitrile (2.73 g, 15 mmol) and 2-methyl-3-butyn-2-ol (1.74 mL, 18 mmol) in THF (5 mL). The Schlenk flask was sealed and the mixture heated to 60°C for 18 h before being left to cool to room temperature. The reaction was



[5] C. K.-W. Kwong, M. Y. Fu, H. C.-H. Law, P. H. Toy, *Synlett* **2010**, 2617-2620.

quenched with ammonium chloride solution, the mixture was extracted two times with *tert*-butyl methyl ether, the combined extracts were washed with HCl (2 M) and brine, dried over magnesium sulfate and concentrated under reduced pressure. Flash chromatography (hexanes/ethyl acetate, 4:1) yielded the product as an orange solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 – 7.56 (m, 2H), 7.53 – 7.45 (m, 2H), 2.01 (s, 1H), 1.63 (s, 6H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 131.4, 131.2, 127.0, 117.7, 110.9, 97.4, 79.9, 64.9, 30.5 ppm. IR (film, $CHCl_3$) 3404, 2979, 2240, 2225, 1600, 1497, 1456, 1401, 1361, 1272, 1161, 962, 905, 836, 560 cm^{-1}. HRMS (ESI): *m/z* calculated for $C_{12}H_{11}NONa$ [M+Na^{+}]: 208.07328; found 208.07350.

Tributyl(dodeca-2,3-dien-4-yl)stannane (S9).



Et_3N (3.14 mL, 22.5 mmol) and MsCl (1.51 mL, 19.5 mmol) were slowly added to a solutioin of dodec-3-yn-2-ol (2.73 g, 15 mmol)[6] in CH_2Cl_2 (20 mL) at −78°C and the mixture was stirred for 15 minutes at this temperature before it was placed into an ice bath. After another 30 minutes the mixture was poured onto HCl (1 M), the aqueous phase was extracted two times with CH_2Cl_2, and the combined extracts were washed with water, dried over magnesium sulfate and concentrated under reduced pressure to give the crude mesylate which was used in the next step without further purification.

*n*BuLi (1.6 M in hexanes, 9.4 mL, 15 mmol) was slowly added at 0°C to a solution of diisopropylamine (2.31 mL, 16.5 mmol) in THF (100 mL). After stirring for 30 minutes, Bu_3SnH (4.04 mL, 15 mmol) was introduced and stirring continued for another 20 minutes. The mixture was cooled to −78°C before CuBr·Me_2S (3.08 g, 15 mmol) was added. Another 30 minutes later, a solution of the crude mesylate in THF (10 mL) was added and stirring continued for 30 minutes before the mixture was poured onto vigorously stirred aqueous NH_4Cl/NH_4OH (9:1). After 10 minutes the mixture was allowed to settle for 12 h. The layers were separated, the aqueous phase was extracted with *tert*-butyl methyl ether, the combined organic layers were washed with brine, dried over magnesium sulfate and concentrated under reduced pressure. Flash chromatography (hexanes/Et_3N, 100:1) yielded the product as a colorless liquid contaminated with small amounts of $(Bu_3Sn)_2$ (6.02 g, 88% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.67 – 4.43 (m, 1H), 2.05 (td, *J* = 7.8, 7.4, 2.8 Hz, 2H), 1.59 (d, *J* = 6.8 Hz, 3H), 1.54 – 1.45 (m, 7H), 1.44 – 1.15 (m, 24H), 1.02 – 0.80 (m, 29H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 203.2, 93.0, 76.2, 33.3, 32.1, 30.8, 30.1, 29.6, 29.5, 29.4, 29.2, 27.5, 22.9, 14.3, 13.9, 10.3 ppm. ^{119}Sn NMR (149 MHz, $CDCl_3$) δ -31.9 ppm.

[6] X. Li, H. Jiang, E. W. Uffman, L. Guo, Y. Zhang, X. Yang, V. B. Birman, *J. Org. Chem.*, **2012**, 1722–1737.

trans-Hydrostannation

Representative Procedure for the *trans*-Hydrostannation of Propargyl Alcohols. (*Z*)-1-Phenyl-4-(tributylstannyl)non-4-en-3-ol (1). $Cp^*RuCl_2]_n$ (77 mg, 0.25 mmol, 1 mol%) was added to a solution of 1-phenylnon-4-yn-3-ol (5.4 g, 25 mmol) in CH_2Cl_2 (100 mL), followed by slow addition of tributyltin hydride (7.1 mL, 26.3 mmol) over 1 h via syringe pump. Stirring was continued for another 5 minutes before all volatile materials were removed under reduced pressure. The crude material was purified by flash chromatography (hexanes/ethyl acetate) to give the product as a pale brown syrup (11.8 g, 93%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 – 7.24 (m, 2H), 7.23 – 7.12 (m, 3H), 6.38 – 5.96 (m, 1H), 4.35 – 4.01 (m, 1H), 2.64 (qdd, *J* = 13.8, 9.8, 6.1 Hz, 2H), 2.13 – 1.95 (m, 2H), 1.83 (dddd, *J* = 13.3, 9.7, 7.2, 6.0 Hz, 1H), 1.71 (ddt, *J* = 13.5, 10.0, 6.3 Hz, 1H), 1.60 – 1.40 (m, 8H), 1.40 – 1.21 (m, 9H), 1.04 – 0.79 (m, 18H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.6, 142.3, 141.4, 128.6, 128.5, 125.9, 79.6, 39.4, 34.2, 32.5, 29.4, 27.6, 22.7, 14.2, 13.8, 11.2 ppm. ^{119}Sn NMR (149 MHz, $CDCl_3$) δ -55.09 ppm. IR (film, $CHCl_3$) 2955, 2923, 2871, 2854, 1616, 1496, 1456, 1419, 1376, 1340, 1290, 1201, 1072, 1048, 1002, 961, 926, 863, 746, 697, 664 cm^{-1}. HRMS (ESI): *m/z* calculated for $C_{27}H_{48}OSnNa$ [M+Na$^+$]: 531.26186; found 531.26185.

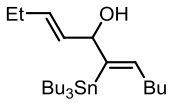
The following compounds were prepared analogously:

(*Z*)-2-(Tributylstannyl)dec-2-en-1-ol (S10). 97% yield (3.1 g). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.25 (tt, *J* = 7.2, 1.4 Hz, 1H), 4.28 – 4.12 (m, 2H), 2.04 (q, *J* = 7.4 Hz, 2H), 1.61 – 1.44 (m, 6H), 1.43 – 1.25 (m, 16H), 1.22 (t, *J* = 6.0 Hz, 1H), 1.02 – 0.94 (m, 6H), 0.94 – 0.87 (m, 12H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.0, 142.2, 70.7, 34.8, 32.0, 30.2, 29.6, 29.4, 29.4, 27.6, 22.8, 14.3, 13.9, 10.3 ppm. ^{119}Sn NMR (149 MHz, $CDCl_3$) δ -52.7 ppm. IR (film, $CHCl_3$) 3305, 2955, 2922, 2871, 2852, 1462, 1418, 1376, 1340, 1290, 1181, 1148, 1072, 1000, 960, 862, 806, 769 cm^{-1}. HRMS (ESI): *m/z* calculated for $C_{22}H_{45}OSn$ [M-H$^+$]: 445.24972; found 445.25028.

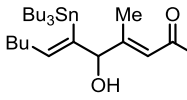
(*Z*)-2-methyl-3-(tributylstannyl)oct-3-en-2-ol (S11). 90% yield (3.11 g). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.36 – 5.86 (m, 1H), 2.11 – 1.94 (m, 2H), 1.57 – 1.40 (m, 6H), 1.38 – 1.30 (m, 12H), 1.29 (s, 6H), 0.97 – 0.83 (m, 17H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.0, 136.6, 75.4, 33.8, 32.6, 30.9, 29.4, 27.6, 22.8, 14.3, 13.9, 12.3 ppm. ^{119}Sn NMR (149 MHz, $CDCl_3$) δ -55.51 ppm. IR (film, $CHCl_3$) 3456, 2955, 2921, 2871, 2854, 1616, 1462, 1376, 1360, 1133, 1071, 1002, 960, 911, 860, 761, 665 cm^{-1}. HRMS (ESI): *m/z* calculated for $C_{21}H_{44}OSnNa$ [M+Na$^+$]: 455.23056; found 455.23087.

(*Z*)-1-((*tert*-Butyldimethylsilyl)oxy)-4-(tributylstannyl)non-4-en-3-ol (S12). 81% yield (1.86 g). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.20 (td, *J* = 7.2, 1.2 Hz, 1H), 4.48 – 4.18 (m, 1H), 3.94 – 3.72 (m, 3H), 3.16 (d, *J* = 2.2 Hz, 1H), 2.02 (td, *J* = 8.9, 8.1, 5.9 Hz, 2H), 1.79 – 1.64 (m, 2H), 1.58 – 1.40 (m, 7H), 1.40 – 1.20 (m, 11H), 1.01 – 0.76 (m, 21H), 0.07 (s, 9H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.2, 140.1, 79.3, 62.5, 39.7, 34.1, 32.5, 29.4, 27.6, 26.0, 22.7, 18.3, 14.2, 13.8, 11.2, -5.4 ppm. ^{119}Sn NMR (149 MHz, $CDCl_3$) δ -55.1 ppm. IR (film, $CHCl_3$) 2954, 2926, 2856, 1463, 1377, 1254, 1093, 1004, 961, 939, 834, 775, 729, 664 cm^{-1}. HRMS (ESI): *m/z* calculated for $C_{27}H_{58}O_2SiSnNa$ [M+Na$^+$]: 585.31196; found 585.31235.

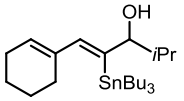
(3*E*,6*Z*)-6-(tributylstannyl)undeca-3,6-dien-5-ol (S13). 41% yield (1.3 g). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.20 (td, *J* = 7.2, 1.1 Hz, 1H), 5.64 (dtd, *J* = 15.5, 6.2, 1.3 Hz, 1H), 5.43 (ddt, *J* = 15.4, 5.9, 1.6 Hz, 1H), 4.63 (ddt, *J* = 5.9, 3.5, 1.1 Hz, 1H), 2.12 – 1.93 (m, 3H), 1.54 – 1.40 (m, 6H), 1.39 – 1.22 (m, 10H), 0.99 (t, *J* = 7.4 Hz, 3H), 0.97 – 0.84 (m, 20H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.3, 141.1, 133.3, 131.9, 80.2, 34.2, 32.4, 29.4, 27.6, 25.4, 22.8, 14.2, 13.9, 13.5, 11.2 ppm. ^{119}Sn NMR (149 MHz, $CDCl_3$) δ -53.6 ppm. IR (film, $CHCl_3$) 2956, 2922, 2853, 2871, 1458, 1376, 1071, 1001, 966, 863, 666, 594 cm^{-1}. HRMS (ESI): *m/z* calculated for $C_{23}H_{46}OSnNa$ [M+Na$^+$]: 481.24621; found 481.24621.



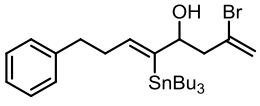
Ethyl (2*E*,5*Z*)-4-hydroxy-3-methyl-5-(tributylstannyl)deca-2,5-dienoate (S14). 72% yield (2.96 g). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.24 (td, *J* = 7.2, 1.0 Hz, 1H), 6.04 (p, *J* = 1.4 Hz, 1H), 4.71 – 4.45 (m, 1H), 4.16 (q, *J* = 7.1 Hz, 2H), 2.11 – 2.03 (m, 2H), 2.02 (d, *J* = 1.2 Hz, 3H), 1.66 (d, *J* = 3.4 Hz, 1H), 1.44 (dddd, *J* = 14.1, 8.4, 7.1, 4.0 Hz, 5H), 1.40 – 1.19 (m, 13H), 0.97 – 0.83 (m, 19H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.1, 158.9, 145.1, 144.0, 114.9, 83.7, 59.7, 34.1, 32.3, 29.3, 27.5, 22.7, 16.3, 14.5, 14.2, 13.8, 11.3 ppm. ^{119}Sn NMR (149 MHz, $CDCl_3$) δ -49.65 ppm. IR (film, $CHCl_3$) 3482, 2955, 2923, 2871, 2854, 1718, 1698, 1650, 1463, 1377, 1340, 1288, 1210, 1142, 1093, 1043 cm^{-1}. HRMS (ESI): *m/z* calculated for $C_{25}H_{48}O_3SnNa$ [M+Na$^+$]: 539.25169; found 539.25226.



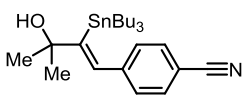
(*Z*)-1-(Cyclohex-1-en-1-yl)-4-methyl-2-(tributylstannyl)pent-1-en-3-ol (S15). 72% yield (3.36 g). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.53 (h, *J* = 1.1 Hz, 1H), 5.58 (dh, *J* = 3.5, 1.5 Hz, 1H), 4.03 – 3.64 (m, 1H), 2.18 – 1.86 (m, 4H), 1.68 – 1.53 (m, 6H), 1.53 – 1.36 (m, 7H), 1.36 – 1.25 (m, 6H), 0.99 – 0.78 (m, 20H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.4, 143.3, 139.3, 123.8, 85.3, 33.6, 29.4, 28.9, 27.7, 25.6, 22.7, 22.2, 20.2, 17.7, 13.9, 12.0 ppm. ^{119}Sn NMR (149 MHz, $CDCl_3$) δ -51.6 ppm. IR (film, $CHCl_3$) 3449, 2955, 2924, 2871, 1597, 1459, 1364, 1266, 1236, 1201, 1137, 1076, 1021, 960, 924, 848, 802, 724, 665, cm^{-1}. HRMS (ESI): *m/z* calculated for $C_{24}H_{45}OSn$ [M-H$^+$]: 469.24972; found 469.24941.



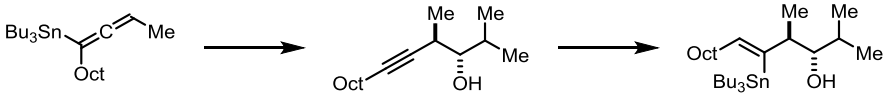
(*Z*)-2-Bromo-8-phenyl-5-(tributylstannyl)octa-1,5-dien-4-ol (S16). 45% yield (1.55 g). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 – 7.25 (m, 2H), 7.24 – 7.13 (m, 3H), 6.33 (td, *J* = 7.2, 1.1 Hz, 1H), 5.66 (q, *J* = 1.0 Hz, 1H), 5.53 (d, *J* = 1.6 Hz, 1H), 4.61 – 4.38 (m, 1H), 2.75 – 2.62 (m, 2H), 2.60 – 2.47 (m, 2H), 2.43 – 2.29 (m, 2H), 1.69 (d, *J* = 2.7 Hz, 1H), 1.60 – 1.38 (m, 6H), 1.38 – 1.23 (m, 6H), 1.10 – 0.93 (m, 6H), 0.89 (t, *J* = 7.3 Hz, 9H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.8, 141.8, 140.5, 130.8, 128.5, 128.5, 126.1, 119.6, 76.4, 50.0, 36.5, 36.3, 29.4, 27.6, 13.9, 11.3 ppm. ^{119}Sn NMR (149 MHz, $CDCl_3$) δ -53.85 ppm. IR (film, $CHCl_3$) 2954, 2922, 2870, 2853, 1629, 1496, 1454, 1376, 1290, 1199, 1123, 1072, 1029, 961, 884, 746, 697 cm^{-1}. HRMS (ESI): *m/z* calculated for $C_{26}H_{43}BrOSnNa$ [M+Na$^+$]: 593.14109; found 593.14118.



(*Z*)-4-(3-Hydroxy-3-methyl-2-(tributylstannyl)but-1-en-1-yl)benzonitrile (S17). 78% yield (2.63 g). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 – 7.53 (m, 2H), 7.29 (s, 1H), 7.27 – 7.23 (m, 2H), 1.61 (s, 1H), 1.41 (s, 6H), 1.39 – 1.26 (m, 6H), 1.26 – 1.15 (m, 6H), 0.83 (t, *J* = 7.2 Hz, 9H), 0.79 – 0.55 (m, 6H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.5, 146.0, 135.4, 131.9, 129.0, 119.1, 110.4, 76.2, 31.1, 29.2, 27.5, 13.8, 12.9 ppm. ^{119}Sn NMR (149 MHz, $CDCl_3$) δ -53.0 ppm. IR (film, $CHCl_3$) 3507, 2955, 2921, 2871, 2228, 1602, 1500, 1462, 1362, 1201, 1142, 1073, 1020, 959, 931, 876, 849, 823, 797, 724, 667, 594 cm^{-1}. HRMS (ESI): *m/z* calculated for $C_{24}H_{39}NOSnNa$ [M+Na$^+$]: 500.19451; found 500.19430.



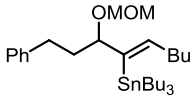
***anti-(Z)*-2,4-Dimethyl-5-(tributylstannyl)tetradec-5-en-3-ol (S18)**



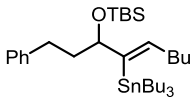
$SnCl_4$ (1 M in CH_2Cl_2, 6.0 mL, 6 mmol) was slowly added at −78°C to a solution of tributyl(dodeca-2,3-dien-4-yl)stannane (2.73 g, 6.0 mmol) in CH_2Cl_2 (5 mL) and the resulting mixture was stirred for 40 minutes before a solution of isobutyraldehyde (1.64 mL, 18 mmol) in CH_2Cl_2 (5 mL) was slowly introduced. After being stirred at the same temperature for 1 h, the reaction was quenched with saturated ammonium chloride solution. The mixture was extracted two times with CH_2Cl_2, the combined extracts were washed with water, dried over magnesium sulfate and concentrated under reduced pressure. Flash chromatography (hexanes/ethyl acetate, 30:1) yielded the product as a pale yellow oil (1.44 g, quant.).

Bu_3SnH (1.78 mL, 6.6 mmol) was added over 1 h by means of a syringe pump to a solution of *anti*-2,4-dimethyltetradec-5-yn-3-ol (1.44 g, 6.0 mmol) and $[Cp^*RuCl]_4$ (82 mg, 0.3 mmol, 5 mol%) in CH_2Cl_2 (25 mL). Upon complete addition, all volatile materials were removed and the residue loaded onto a column. Flash chromatography (hexanes/ethyl acetate, 30:1) yielded the product as a slightly impure pale brown oil (1.56 g, 49% yield over 2 steps, α/β = 10:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.37 – 5.94 (m, 1H), 3.16 (dt, *J* = 9.5, 2.1 Hz, 1H), 2.38 – 2.26 (m, 1H), 2.02 (p, *J* = 6.4, 5.7 Hz, 2H), 1.87 – 1.75 (m, 1H), 1.52 – 1.41 (m, 6H), 1.40 – 1.19 (m, 20H), 1.03 (d, *J* = 6.9 Hz, 3H), 0.99 – 0.79 (m, 23H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.7, 143.8, 77.9, 49.6, 34.9, 32.0, 30.5, 29.7, 29.7, 29.4, 29.4, 28.0, 27.6, 27.0, 22.8, 21.1, 18.0(2C), 17.7, 14.3(2C), 13.8, 11.6 ppm. ^{119}Sn NMR (149 MHz, $CDCl_3$) δ -54.9 ppm. IR (film, $CHCl_3$) 2956, 2923, 2872, 2853, 1462, 1377, 1174, 1073, 991, 875, 758, 666, 594, 504 cm^{-1}. HRMS (ESI): *m/z* calculated for $C_{28}H_{57}OSn$ [M^-]: 529.34362; found 529.34430.

(*Z*)-Tributyl(3-(methoxymethoxy)-1-phenylnon-4-en-4-yl)stannane (S19). TBAI (185 mg, 0.5 mmol, 10 mol%) and Hünig's base (1.74 mL, 10 mmol) were added to a solution of (*Z*)-1-phenyl-4-(tributylstannyl)non-4-en-3-ol (2.53 g, 5.0 mmol) in CH_2Cl_2 (20 mL) followed by dropwise addition of MOMCl (570 µL, 7.5 mmol). The mixture was stirred for 18 h at ambient temperature. The reaction was quenched with saturated ammonium chloride solution. The mixture was extracted two times with *tert*-butyl methyl ether, the combined organic phases were washed with brine, dried over magnesium sulfate and concentrated under reduced pressure. Flash chromatography (hexanes/ethyl acetate, 30:1) yielded the product as a colorless oil (2.62 g, 95% yield). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.32 – 7.24 (m, 2H), 7.22 – 7.13 (m, 3H), 6.46 – 5.87 (m, 1H), 4.66 (d, *J* = 6.5 Hz, 1H), 4.47 (d, *J* = 6.5 Hz, 1H), 4.25 – 3.92 (m, 1H), 3.37 (s, 3H), 2.80 – 2.51 (m, 2H), 2.07 (dddd, *J* = 8.8, 7.0, 4.9, 1.8 Hz, 2H), 1.91 (dddd, *J* = 13.2, 10.5, 7.2, 5.9 Hz, 1H), 1.68 (ddt, *J* = 13.5, 10.6, 6.1 Hz, 1H), 1.60 – 1.41 (m, 6H), 1.41 – 1.14 (m, 10H), 1.01 – 0.79 (m, 18H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 144.9, 144.1, 142.5, 128.5, 128.5, 93.4, 84.0, 55.6, 38.4, 34.3, 32.6, 29.4, 27.6, 22.8, 14.2, 13.8, 11.3 ppm. IR (film, $CHCl_3$) 2954, 2923, 2871, 2855, 1614, 1496, 1455, 1376, 1177, 1147, 1094, 1030, 960, 920, 863, 746, 697 cm^{-1}. HRMS (ESI): *m/z* calculated for $C_{29}H_{52}O_2SnNa$ [$M+Na^+$]: 575.28808; found 575.28862.

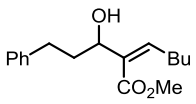


(*Z*)-*tert*-Butyldimethyl((1-phenyl-4-(tributylstannyl)non-4-en-3-yl)oxy)silane (S20). DMAP (61 mg, 0.5 mmol, 10 mol%), imidazole (681 mg, 10 mmol) and *tert*-butyldimethylsilyl chloride (1.13 g, 7.5 mmol) were successively added to a solution of (*Z*)-1-phenyl-4-(tributylstannyl)non-4-en-3-ol (2.53 g, 5.0 mmol) in CH_2Cl_2 (20 mL). The mixture was stirred for 18 h at ambient temperature before the reaction was quenched with saturated ammonium chloride solution. The mixture was extracted two times with *tert*-butyl methyl ether, the combined extracts were washed with brine, dried over magnesium sulfate and concentrated under reduced pressure. Flash chromatography (hexanes/ethyl acetate, 30:1) yielded the product as a colorless oil (2.89 g, 93% yield). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.32 – 7.22 (m, 2H), 7.22 – 7.11 (m, 3H), 6.08 (td, *J* = 7.2, 1.0 Hz, 1H), 4.11 (td, *J* = 6.6, 0.9 Hz, 1H), 2.63 – 2.43 (m, 2H), 2.13 – 1.90 (m, 2H), 1.76 (ddt, *J* = 13.5, 10.8, 6.2 Hz, 1H), 1.65 (dddd, *J* = 13.4, 10.8, 6.7, 5.6 Hz, 1H), 1.60 – 1.40 (m, 6H), 1.40 – 1.23 (m, 10H), 1.03 – 0.71 (m, 27H), 0.00 (d, *J* = 17.2 Hz, 6H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 148.1, 142.8, 140.41, 128.5, 128.4, 125.7, 81.1, 41.0, 34.2, 32.6, 32.5, 29.5, 27.7, 26.2, 22.8, 18.4, 14.3, 13.8, 11.3, -3.9, -4.6 ppm. ^{119}Sn NMR (149 MHz, $CDCl_3$) δ -57.69 ppm. IR (film, $CHCl_3$) 3027, 2926, 2855, 1616, 1496, 1462, 1417, 1377, 1360, 1291, 1251, 1175, 1152, 1066, 1004, 963, 938, 875, 834, 773, 746, 697, 666 cm^{-1}. HRMS (ESI): *m/z* calculated for $C_{33}H_{62}OSiSnNa$ [M+Na$^+$]: 645.34834; found 645.34898.



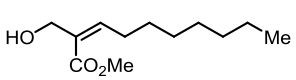
Methoxycarbonylation

Representative Procedure for the Oxidative Methoxycarbonylation of Alkenyl Stannanes. Methyl (*Z*)-2-(1-hydroxy-3-phenylpropyl)hept-2-enoate (2). *p*-Benzoquinone (405 mg, 3.75 mmol), Ph_3As (77 mg, 0.25 mmol, 10 mol%) and $Pd(OAc)_2$ (28 mg, 0.125 mmol, 5 mol%) were added to a solution of (*Z*)-1-phenyl-4-(tributylstannyl)non-4-en-3-ol (**1**) (1.27 g, 2.5 mmol) in TFA in MeOH (0.1 M, 10 mL). The Schlenk flask was flushed for 2 minutes with CO before the mixture was stirred under CO atmosphere (balloon) at room temperature for 12 h. The flask was vented, the mixture was diluted with *tert*-butyl methyl ether and filtered through a plug of Celite®. The filtrate was evaporated and the crude material purified by flash chromatography (hexanes/ethyl acetate, 19:1) to give the product as a colorless oil (660 mg, 86% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 – 7.25 (m, 2H), 7.22 – 7.15 (m, 3H), 6.13 (td, *J* = 7.5, 0.9 Hz, 1H), 4.23 (d, *J* = 8.7 Hz, 1H), 3.77 (s, 3H), 2.83 – 2.60 (m, 3H), 2.42 (q, *J* = 7.3 Hz, 2H), 2.04 – 1.86 (m, 2H), 1.47 – 1.24 (m, 4H), 0.91 (t, *J* = 7.2 Hz, 3H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.2, 143.5, 141.9, 133.7, 128.6, 128.5, 126.0, 74.0, 51.5, 38.2, 32.4, 31.5, 29.3, 22.5, 14.0 ppm. IR (film, $CHCl_3$) 3435, 3027, 2954, 2927, 2859, 1706, 1496, 1454, 1435, 1378, 1205, 1143, 1032, 748, 700 cm^{-1}. HRMS (ESI): *m/z* calculated for $C_{17}H_{24}O_3Na$ [M+Na$^+$]: 299.16176; found 299.16188.



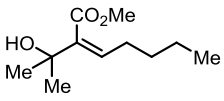
The following compounds were prepared analogously:

Methyl (*Z*)-2-(hydroxymethyl)dec-2-enoate (4). 68% yield (145 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.23 (tt, *J* = 7.3, 1.0 Hz, 1H), 4.21 (q, *J* = 1.0 Hz, 2H), 3.76 (s, 3H), 2.58 – 2.46 (m, 2H), 2.43 (s, 1H), 1.49 – 1.35 (m, 2H), 1.35 – 1.16 (m, 8H), 1.00 – 0.70 (m, 3H) ppm. ^{13}C NMR

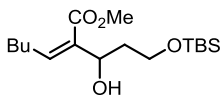


(101 MHz, $CDCl_3$) δ 167.7, 147.0, 130.5, 65.3, 51.5, 31.9, 29.6, 29.2, 22.7, 14.2 ppm. IR (film, $CHCl_3$) 3432, 2954, 2924, 2855, 1706, 1650, 1435, 1380, 1339, 1204, 1145, 1103, 1046, 1011 cm^{-1}. HRMS (ESI): *m/z* calculated for $C_{12}H_{22}O_3Na$ [M+Na^+]: 237.14611; found 237.14618.

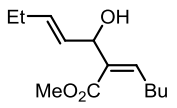
Methyl (*Z*)-2-(2-hydroxypropan-2-yl)hept-2-enoate (5). 63% yield (63 mg). ^1H NMR (400 MHz, $CDCl_3$) δ 5.99 (t, *J* = 7.5 Hz, 1H), 3.80 (s, 3H), 3.01 (s, 1H), 2.20 (q, *J* = 7.4 Hz, 2H), 1.41 (s, 6H), 1.40 – 1.22 (m, 4H), 0.90 (t, *J* = 7.1 Hz, 3H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.0, 139.4, 135.3, 71.8, 51.7, 31.5, 29.6, 29.4, 22.5, 14.0 ppm. IR (film, $CHCl_3$) 3436, 2956, 2931, 2860, 1719, 1458, 1434, 1356, 1255, 1204, 1127, 1038, 966 cm^{-1}. HRMS (ESI): *m/z* calculated for $C_{11}H_{20}O_3Na$ [M+Na^+]: 223.13046; found 223.13068.



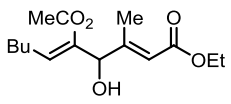
Methyl (*Z*)-2-(3-((*tert*-butyldimethylsilyl)oxy)-1-hydroxypropyl)hept-2-enoate (6). 77% yield (128 mg). ^1H NMR (400 MHz, $CDCl_3$) δ 6.28 (td, *J* = 7.5, 1.3 Hz, 1H), 4.63 – 4.53 (m, 1H), 3.88 – 3.75 (m, 3H), 3.74 (s, 3H), 2.45 (qdd, *J* = 7.4, 2.1, 1.0 Hz, 2H), 1.93 – 1.83 (m, 1H), 1.81 – 1.69 (m, 1H), 1.49 – 1.27 (m, 4H), 0.94 – 0.84 (m, 13H), 0.10 – 0.01 (m, 6H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.0, 142.4, 133.5, 72.3, 62.1, 51.4, 38.2, 31.6, 29.3, 26.0, 22.6, 18.3, 14.1, -5.4 ppm. IR (film, $CHCl_3$) 3487, 2929, 2954, 2858, 1708, 1435, 1464, 1379, 1254, 1202, 1151, 1096, 1006, 914, 833, 776, 732 cm^{-1}. HRMS (ESI): *m/z* calculated for $C_{17}H_{35}O_4Si$ [M+H^+]: 331.22991; found 331.22998.



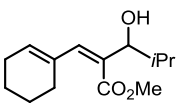
Methyl (*Z*)-2-((*E*)-1-hydroxypent-2-en-1-yl)hept-2-enoate (7). 72% yield (81 mg). ^1H NMR (400 MHz, $CDCl_3$) δ 6.17 (td, *J* = 7.5, 1.0 Hz, 1H), 5.73 (dtd, *J* = 15.5, 6.3, 1.2 Hz, 1H), 5.54 (ddt, *J* = 15.4, 6.3, 1.5 Hz, 1H), 4.76 (t, *J* = 6.5 Hz, 1H), 3.77 (s, 3H), 2.72 (d, *J* = 6.8 Hz, 1H), 2.43 (q, *J* = 7.3 Hz, 2H), 2.10 – 1.99 (m, 2H), 1.50 – 1.25 (m, 4H), 0.98 (t, *J* = 7.5 Hz, 3H), 0.90 (t, *J* = 7.2 Hz, 3H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.1, 143.6, 134.7, 133.3, 129.5, 74.6, 51.5, 31.4, 29.3, 25.4, 22.5, 14.0, 13.5 ppm. IR (film, $CHCl_3$) 3434, 2959, 2929, 2873, 1707, 1435, 1377, 1204, 1150, 1081, 1021, 966, 911, 799, 731 cm^{-1}. HRMS (ESI): *m/z* calculated for $C_{13}H_{22}O_3Na$ [M+Na^+]: 249.14611; found 249.14620.



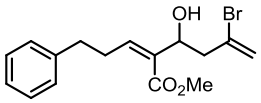
Ethyl (2*E*,5*Z*)-5-acetoxy-4-hydroxy-3-methyldeca-2,5-dienoate (8). 80% yield (113 mg). ^1H NMR (400 MHz, $CDCl_3$) δ 6.20 (td, *J* = 7.6, 0.7 Hz, 1H), 6.07 (p, *J* = 1.4 Hz, 1H), 4.81 – 4.73 (m, 1H), 4.16 (qd, *J* = 7.1, 1.2 Hz, 2H), 3.76 (s, 3H), 3.00 (d, *J* = 7.2 Hz, 1H), 2.47 (q, *J* = 7.4 Hz, 2H), 2.05 (dd, *J* = 1.4, 0.6 Hz, 3H), 1.49 – 1.30 (m, 4H), 1.28 (t, *J* = 7.1 Hz, 3H), 0.91 (t, *J* = 7.2 Hz, 3H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.7, 166.9, 157.3, 146.7, 130.9, 116.1, 77.8, 60.0, 51.8, 31.3, 29.5, 22.6, 16.0, 14.4, 14.0 ppm. IR (film, $CHCl_3$) 3488, 2957, 2930, 2873, 1775, 1713, 1654, 1435, 1368, 1344, 1206, 1144, 1095, 1039 cm^{-1}. HRMS (ESI): *m/z* calculated for $C_{15}H_{24}O_5Na$ [M+Na^+]: 307.15159; found 307.15176.



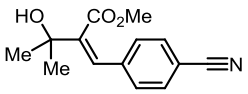
Methyl (*Z*)-2-(cyclohex-1-en-1-ylmethylene)-3-hydroxy-4-methylpentanoate (9). 55% yield (65 mg). ^1H NMR (400 MHz, $CDCl_3$) δ 6.17 (p, *J* = 1.0 Hz, 1H), 5.86 (ddt, *J* = 4.0, 2.7, 1.2 Hz, 1H), 3.80 (ddd, *J* = 8.0, 6.2, 0.9 Hz, 1H), 3.76 (s, 3H), 2.22 (d, *J* = 6.2 Hz, 1H), 2.18 – 2.09 (m, 2H), 2.09 – 2.01 (m, 2H), 1.83 – 1.70 (m, 1H), 1.66 – 1.57 (m, 4H), 1.00 (d, *J* = 6.6 Hz, 3H), 0.88 (d, *J* = 6.7 Hz, 3H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.3, 137.4, 134.5, 133.7, 130.9, 81.7, 51.8, 33.1, 26.4, 26.2, 22.8, 22.0, 19.6, 18.6 ppm. IR (film, $CHCl_3$) 3482, 2931, 2868, 1774, 1716, 1635, 1435, 1366, 1214, 1180, 1135, 1102, 1017, 981, 927, 872 cm^{-1}. HRMS (ESI): *m/z* calculated for $C_{14}H_{22}O_3Na$ [M+Na^+]: 261.14611; found 261.14632.



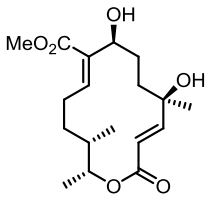
Methyl (*Z*)-5-bromo-3-hydroxy-2-(3-phenylpropylidene)hex-5-enoate (10). 87% yield (147 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (ddd, *J* = 9.1, 6.4, 0.9 Hz, 2H), 7.20 (td, *J* = 6.5, 1.7 Hz, 3H), 6.35 – 6.27 (m, 1H), 5.63 (dt, *J* = 1.9, 1.0 Hz, 1H), 5.49 (d, *J* = 1.6 Hz, 1H), 4.59 (tdd, *J* = 7.1, 6.0, 0.9 Hz, 1H), 3.78 (s, 3H), 2.83 – 2.68 (m, 7H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.5, 143.5, 141.2, 132.5, 130.25, 128.5, 126.2, 119.8, 72.2, 51.7, 48.7, 35.4, 31.3 ppm. IR (film, $CHCl_3$) 3463,3026, 2949, 1703, 1631, 1603, 1496, 1435, 1453, 1381, 1332, 1200, 1111, 1050, 1005, 890, 793, 748, 698 cm^{-1}. HRMS (ESI): *m/z* calculated for $C_{16}H_{19}BrO_3Na$ [M+Na^+]: 361.04099; found 361.04241.



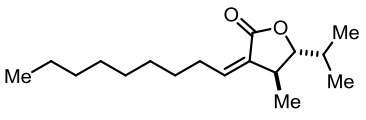
Methyl (*Z*)-2-(4-cyanobenzylidene)-3-hydroxy-3-methylbutanoate (11). 73% yield (89 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 – 7.54 (m, 2H), 7.36 – 7.29 (m, 2H), 6.86 (s, 1H), 3.64 (s, 3H), 2.49 (s, 1H), 1.52 (s, 6H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.7, 145.0, 140.6, 132.2, 128.6, 127.1, 118.7, 111.5, 72.3, 52.3, 29.4 ppm. IR (film, $CHCl_3$) 3430, 2977, 2228, 1721, 1638, 1605, 1512, 1435, 1353, 1313, 1286, 1206, 1175, 1041, 966, 944, 893, 824, 759, 677 cm^{-1}. HRMS (ESI): *m/z* calculated for $C_{14}H_{15}NO_3Na$ [M+Na^+]: 268.09441; found 268.09435.



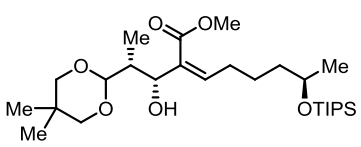
Methyl (2*R*,3*S*,6*Z*,8*S*,11*R*,12*E*)-8,11-dihydroxy-2,3,11-trimethyl-14-oxooxacyclotetra-deca-6,12-diene-7-carboxylate (12). 69% yield (10.3 mg). $[\alpha]_D^{20}$: -58.3° (c 0.83 in $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.77 (d, *J* = 15.7 Hz, 1H), 6.25 (dd, *J* = 9.2, 5.0 Hz, 1H), 5.98 (d, *J* = 15.7 Hz, 1H), 4.63 (dq, *J* = 9.9, 6.2 Hz, 1H), 4.21 (s, 1H), 3.77 (s, 3H), 2.76 (dddd, *J* = 16.2, 9.3, 6.8, 4.5 Hz, 1H), 2.60 (s, 1H), 2.31 – 2.10 (m, 1H), 1.96 – 1.81 (m, 2H), 1.81 – 1.65 (m, 2H), 1.65 – 1.40 (m, 2H), 1.35 (s, 4H), 1.31 (d, *J* = 6.3 Hz, 4H), 0.96 (d, *J* = 6.9 Hz, 3H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 168.1, 165.8, 153.4, 145.6, 132.3, 120.2, 76.3, 75.6, 73.6, 51.7, 39.3, 38.9, 33.3, 31.6, 28.8, 27.4, 19.2, 18.0 ppm. IR (film, $CHCl_3$) 3434, 2954, 2933, 2874, 1703, 1642, 1439, 1377, 1267, 1226, 1153, 1107, 1041, 987 cm^{-1}. HRMS (ESI): *m/z* calculated for $C_{18}H_{28}O_6Na$ [M+Na^+]: 363.17781; found 363.17801.



***anti-(Z)*-5-Isopropyl-4-methyl-3-nonylidenedihydrofuran-2(3*H*)-one (13)**. 60% yield (79 mg). ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.08 (td, *J* = 7.6, 2.2 Hz, 1H), 3.75 (t, *J* = 5.7 Hz, 1H), 2.72 (tdd, *J* = 7.6, 5.2, 1.6 Hz, 3H), 1.84 (pd, *J* = 6.8, 5.7 Hz, 1H), 1.54 – 1.37 (m, 2H), 1.37 – 1.23 (m, 10H), 1.19 (d, *J* = 6.7 Hz, 3H), 0.98 (d, *J* = 6.8 Hz, 6H), 0.94 – 0.82 (m, 3H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.1, 143.7, 131.0, 89.1, 37.9, 32.5, 32.0, 29.6, 29.4, 27.6, 22.8, 20.1, 18.3, 17.4, 14.2 ppm. IR (film, $CHCl_3$) 2960, 2924, 2855, 1751, 1667, 1466, 1370, 1170, 1126, 1094, 1005 953 cm^{-1}. HRMS (ESI): *m/z* calculated for $C_{17}H_{30}O_2$ [M^+]: 266.22403; found 266.22367.



Methyl (*R*,*Z*)-2-((1*R*,2*R*)-2-(5,5-dimethyl-1,3-dioxan-2-yl)-1-hydroxypropyl)-7-((triisopropylsilyl)oxy)oct-2-enoate (15). 87% yield (345 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.28 (td, *J* = 7.5, 1.5 Hz, 1H), 4.84 (dq, *J* = 2.9, 1.5 Hz, 1H), 4.53 (d, *J* = 2.8 Hz, 1H), 3.93 (q, *J* = 5.6 Hz, 1H), 3.73 (s, 3H), 3.68 – 3.59 (m, 2H), 3.47 – 3.38 (m, 3H), 2.57 – 2.33 (m, 2H), 2.04 – 1.91 (m, 1H), 1.58 – 1.30 (m, 4H), 1.19 (s, 3H), 1.14 (dd, *J* = 8.4, 6.1 Hz, 3H), 1.05 (s, 18H), 0.99 (dt, *J* = 9.7, 7.0 Hz, 3H), 0.89 (d, *J* = 7.2 Hz, 3H), 0.72 (s, 3H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.8, 142.6, 131.5, 104.5, 77.4, 70.9, 68.5, 51.4, 40.6, 39.8, 30.5, 29.8, 25.4, 23.7, 23.0, 21.9, 18.3, 18.3, 12.6, 6.9 ppm. IR (film, $CHCl_3$) 3514, 2943, 2866, 1719, 1462, 1365, 1202, 1136, 1097, 1061,



1038, 1017, 993, 923, 882, 851, 724, 676, 654 cm^{-1}. HRMS (ESI): *m/z* calculated for $C_{27}H_{52}O_6SiNa$ [M+Na^+]: 523.34254; found 523.34334.

Formal Total Synthesis of Tubelactomicin A

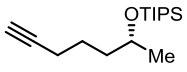
***(R)*-Hept-4-yn-2-ol (S21)**. 1-Butyne was condensed into a 500 mL two-necked flask equipped with a dropping funnel and a gas bubbler under dry-ice cooling until about 10 g of liquid 1-butyne were obtained. THF (50 mL) was added followed by slow addition of *n*BuLi (1.6 M in hexanes, 66 mL, 105 mmol). After being stirred at −78°C for 10 minutes, the flask was placed on an ice bath for 1 h. DMPU (50 mL) was introduced and the resulting mixture was cooled to -30°C. A solution of *(R)*-propylene oxide (4.90 mL, 70 mmol) in DMPU (50 mL) was added and the mixture allowed to reach room temperature over the course of 18 h. The reaction was quenched by slow addition of saturated ammonium chloride solution. The mixture was extracted two times with diethyl ether, and the combined organic phases were washed with brine, dried over magnesium sulfate and concentrated under reduced pressure. Flash chromatography of the residue (pentane/diethyl ether, 4:1) yielded the product after careful evaporation of the volatiles as a pale yellow liquid (6.7 g, 85% yield). $[\alpha]_D^{20}$: +22.2° (c 1.02 in MeOH); -18.7° (c 1.13 in $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.98 – 3.81 (m, 1H), 2.36 (ddt, *J* = 16.3, 4.8, 2.4 Hz, 1H), 2.25 (ddt, *J* = 16.3, 6.8, 2.4 Hz, 1H), 2.18 (qt, *J* = 7.5, 2.4 Hz, 2H), 2.03 (s, 1H), 1.23 (d, *J* = 6.2 Hz, 3H), 1.12 (t, *J* = 7.5 Hz, 3H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 84.8, 77.5, 66.6, 29.5, 22.3, 14.4, 12.5 ppm. HRMS (ESI): *m/z* calculated for $C_7H_{12}ONa$ [M+Na^+]: 135.07803; found 135.07811.

***(R)*-Hept-6-yn-2-ol (S22)**.[7] Lithium granula (1.25 g, 180 mmol) were added in one portion to distilled 1,3-diaminopropane (100 mL) and the mixture was stirred until a dark blue solution was obtained. This mixture was then stirred at 70°C until the color faded and a pale blueish/grey mixture was formed which was allowed to reach room temperature. KOtBu (13.1 g, 117 mmol) [dried for 2 h under high vacuum at 120°C] was added in one portion and stirring was continued for 30 minutes while the mixture turned into yellowish green. *(R)*-Hept-4-yn-2-ol (3.36 g, 30 mmol) was added dropwise, causing a color change to red. Once the addition was complete, stirring was continued for 30 minutes before the reaction was slowly poured onto ice/water (250 mL). The aqueous phase was extracted three times with diethyl ether, the combined organic layer were successively washed with HCl (2 M), saturated sodium bicarbonate solution and brine, dried over magnesium sulfate and concentrated under reduced pressure to give a pale yellow oil. Flash chromatography of this material (pentane/diethyl ether, 3:1 to 2:1) yielded the product after careful concentration as a colorless liquid which was directly used in the next step. $[\alpha]_D^{20}$: -14.5° (c 0.99 in $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.77 (qd, *J* = 5.9, 1.4 Hz, 1H), 2.17 (tdd, *J* = 6.7, 2.7, 1.3 Hz, 2H), 2.08 (s, 1H), 1.92 (td, *J* = 2.7, 1.2 Hz, 1H), 1.69 – 1.54 (m, 1H), 1.54 – 1.44 (m, 3H), 1.15 (dd, *J* = 6.2, 1.4 Hz, 3H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 84.5, 68.6, 67.5, 38.2, 24.7, 23.6, 18.4 ppm. IR (film, $CHCl_3$) 3297, 2930, 1457, 1433, 1374, 1327,

[7] Y. Wu, J. Gao, *Org. Lett*. **2008**, *10*, 1533-1536.

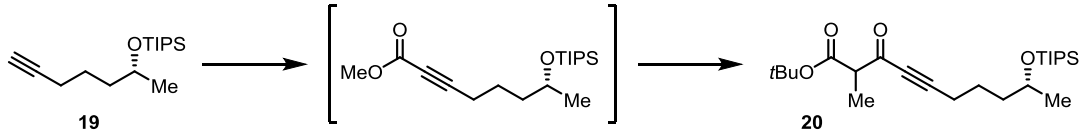
1183, 1128, 1085, 977, 944, 923, 862, 819, 624 cm^{-1}. HRMS (ESI): *m/z* calculated for $C_7H_{12}ONa$ [M+Na^+]: 135.07803; found 135.07809.

***(R)*-(Hept-6-yn-2-yloxy)triisopropylsilane (19)**. Triisopropylsilyl chloride (9.63 mL, 45 mmol) was slowly added



to a solution of *(R)*-hept-6-yn-2-ol (3.36, 30 mmol) and imidazole (4.08 g, 60 mmol) in DMF (60 mL) and the resulting mixture was stirred for 18 h until TLC showed complete consumption of the starting material. The reaction was quenched with saturated ammonium chloride solution, the aqueous phase was extracted three times with *tert*-butyl methyl ether, and the combined organic layers were washed with brine, dried over magnesium sulfate and concentrated under reduced pressure. Flash chromatography of the residue (pentane) yielded the product as a colorless oil (6.4 g, 79% yield over 2 steps). $[a]_D^{20}$: -3.4° (c 1.08 in $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.04 – 3.91 (m, 1H), 2.26 – 2.11 (m, 2H), 1.94 (t, *J* = 2.6 Hz, 1H), 1.66 – 1.49 (m, 4H), 1.17 (d, *J* = 6.1 Hz, 3H), 1.06 (s, 21H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 84.7, 68.4, 68.2, 39.0, 24.4, 23.6, 18.8, 18.3, 12.6 ppm. IR (film, $CHCl_3$) 3314, 2942, 2866, 1462, 1375, 1245, 1136, 1097, 1028, 996, 918, 881, 750, 675, 627 cm^{-1}. HRMS (ESI): *m/z* calculated $C_{16}H_{32}OSiNa$ [M+Na^+]: 291.21146; found 291.21157.

***tert*-Butyl (9*R*)-2-methyl-3-oxo-9-((triisopropylsilyl)oxy)dec-4-ynoate (20)**

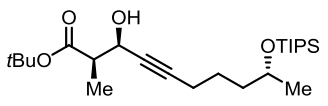


*n*BuLi (1.6 M in hexanes, 7.93 mL, 12.7 mmol) was slowly added at −78°C to a solution of *(R)*-(hept-6-yn-2-yloxy)triisopropylsilane **19** (2.27 g, 8.45 mmol) in THF (40 mL). The mixture was stirred for 30 minutes before neat methyl chloroformate (1.31 mL, 16.9 mmol) was introduced. The mixture was allowed to reach room temperature. After stirring for another 30 minutes, the reaction was quenched with saturated ammonium chloride solution. The mixture was extracted two times with *tert*-butyl methyl ether, the combined organic layers were washed with brine, dried over magnesium sulfate and concentrated under reduced pressure. The crude material was used in the next step without purification.

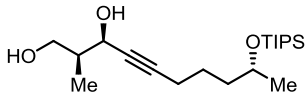
*n*BuLi (1.6 M in hexanes, 15.9 mL, 25.4 mmol) was added dropwise at 0°C to a solution of diisopropyl amine (3.55 mL, 25.4 mmol) in THF (40 mL) and the resulting mixture was stirred for 10 minutes before it was cooled to −78°C. *tert*-Butyl propionate (3.82 mL, 25.4 mmol) was added and stirring continued for 30 minutes at this temperature before a solution of the above alkynoate in a minimum amount of THF was added dropwise. After stirring at −78°C for 2 h the reaction was quenched with saturated ammonium chloride solution while cold, and the resulting mixture was warmed to room temperature. The mixture was extracted two times with *tert*-butyl methyl ether, and the combined organic layers were washed with brine, dried over magnesium sulfate and concentrated under reduced pressure. Flash chromatography of the residue (hexanes/ethyl acetate, 40:1) yielded the product as a mixture of tautomers (3.40 g, 95% yield). $[a]_D^{20}$: -1.6° (c 1.10 in $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 12.28 (s, 0.65H), 4.03 – 3.90 (m, 1H), 3.48 – 3.38 (m, 0.35H), 2.41 (dt, *J* = 16.5, 6.8 Hz, 2H), 1.82 (s, 2H), 1.71 – 1.52 (m, 3H), 1.50 (s, 6H), 1.46 (s, 4H), 1.36 (d, *J* = 7.2 Hz, 1H), 1.16 (d, *J* = 6.1 Hz, 3H), 1.05 (s, 21H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 183.7, 173.1, 169.0, 152.0, 104.5, 99.8, 96.4, 82.0, 81.8, 75.4, 68.2,

68.0, 56.0, 39.2, 28.4, 28.0, 24.1, 23.7, 19.9, 19.5, 18.3, 18.3, 13.6, 12.9, 12.6 ppm. IR (film, $CHCl_3$) 2942, 2866, 2215, 1737, 1680, 1645, 1601, 1459, 1369, 1353, 1252, 1151, 1120, 1026, 995, 882, 846, 817, 757, 675 cm^{-1}. HRMS (ESI): *m/z* calculated $C_{24}H_{44}O_4SiNa$ [M+Na^+]: 447.29011; found 447.29049.

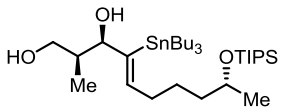
***tert*-Butyl (*2R,3R,9R*)-3-hydroxy-2-methyl-9-((triisopropylsilyl)oxy)dec-4-ynoate (22)**. [(*R,R*)-Teth-TsDpen RuCl] (**21**)[8] (24.8 mg, 0.04 mmol, 0.5 mol%) and formic acid/triethylamine complex (5:2, 7.1 g) were placed in an oven-dried Schlenk flask under an argon atmosphere. A solution of *tert*-butyl (9*R*)-2-methyl-3-oxo-9-((triisopropylsilyl)oxy)dec-4-ynoate **20** (3.4 g, 8.0 mmol) in CH_2Cl_2 (40 mL) was added and the mixture was stirred at room temperature for 48 h. For work up, all volatile materials were removed under reduced pressure and the residue purified by flash chromatography (hexanes/ethyl acetate, 19:1) to give the title compound as a colorless oil (2.81 g, 82% yield). $[\alpha]_D^{20}$: +2.5° (c 1.22 in $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.52 (ddt, *J* = 7.2, 4.0, 2.0 Hz, 1H), 4.06 – 3.81 (m, 1H), 3.10 (dd, *J* = 7.4, 2.3 Hz, 1H), 2.62 (qd, *J* = 7.2, 4.0 Hz, 1H), 2.21 (tt, *J* = 4.9, 2.0 Hz, 2H), 1.54 (dddt, *J* = 8.3, 6.9, 4.4, 2.3 Hz, 4H), 1.47 (d, *J* = 1.8 Hz, 9H), 1.23 (dd, *J* = 7.2, 1.8 Hz, 3H), 1.15 (dd, *J* = 6.1, 1.8 Hz, 3H), 1.05 (d, *J* = 1.9 Hz, 21H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.8, 86.2, 81.6, 78.8, 68.2, 64.3, 46.3, 39.2, 28.2, 24.5, 23.6, 19.1, 18.3, 18.3, 12.6, 12.2 ppm. IR (film, $CHCl_3$) 3475, 2942, 2866, 1729, 1460, 1368, 1350, 1254, 1216, 1152, 1095, 1026, 918, 882, 849, 755, 709, 675 cm^{-1}. HRMS (ESI): *m/z* calculated $C_{24}H_{46}O_4SiNa$ [M+Na^+]: 449.30576; found 449.30589.



(2*S*,3*R*,9*R*)-2-Methyl-9-((triisopropylsilyl)oxy)dec-4-yne-1,3-diol (23). $LiBH_4$ (4 M in THF, 4.5 mL, 18 mmol) was slowly added at 0°C to a solution of *tert*-butyl (*2R,3R,9R*)-3-hydroxy-2-methyl-9-((triisopropylsilyl)oxy)dec-4-ynoate **22** (2.56 g, 6.0 mmol) THF (25 mL) and MeOH (2.5 mL). The resulting mixture was then stirred at 70°C (CAUTION: vigorous foaming when the reaction starts!). After 15 minutes, TLC indicated complete consumption of starting material. For work up, the mixture was allowed to reach room temperature before it was poured onto ice water which was carefully acidified with HCl (2 M). The aqueous layer was extracted three times with ethyl acetate, and the combined extracts were washed with brine, dried over magnesium sulfate and concentrated under reduced pressure. Flash chromatography of the residue (hexanes/ethyl acetate, 2:1) yielded the product as a colorless oil (1.97 g, 92% yield). $[\alpha]_D^{20}$: +7.8° (c 1.06 in $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.50 (ddt, *J* = 5.9, 4.0, 2.0 Hz, 1H), 4.01 – 3.91 (m, 1H), 3.87 (ddd, *J* = 10.4, 8.3, 3.6 Hz, 1H), 3.68 (dt, *J* = 10.7, 4.2 Hz, 1H), 2.79 (d, *J* = 5.9 Hz, 1H), 2.25 (tt, *J* = 6.6, 1.9 Hz, 3H), 2.08 (dqt, *J* = 8.3, 7.0, 3.9 Hz, 1H), 1.65 – 1.45 (m, 4H), 1.16 (d, *J* = 6.1 Hz, 3H), 1.05 (s, 21H), 0.93 (d, *J* = 7.0 Hz, 3H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 87.2, 79.2, 68.3, 67.2, 66.2, 40.5, 39.2, 24.7, 23.7, 19.1, 18.3, 18.3, 12.6 ppm. IR (film, $CHCl_3$) 3348, 2942, 2866, 1462, 1376, 1256, 1135, 1094, 1013, 917, 882, 756, 674 cm^{-1}. HRMS (ESI): *m/z* calculated $C_{20}H_{40}O_3SiNa$ [M+Na^+]: 379.26389; found 379.26384.



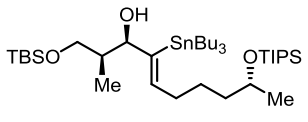
(2*S*,3*R*,9*R*,*Z*)-2-Methyl-4-(tributylstannyl)-9-((triisopropylsilyl)oxy)dec-4-ene-1,3-diol (24). $[Cp^*RuCl_2]_n$ (84 mg, 0.27 mmol, 5 mol%) was added to a solution of (2*S*,3*R*,9*R*)-2-methyl-9-((triisopropylsilyl)oxy)dec-4-yne-1,3-diol **23** (1.95 g, 5.47 mmol) in CH_2Cl_2 (25 mL),



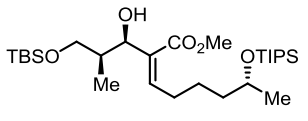
[8] Z. Fang, M. Wills, *J. Org. Chem*. **2013**, *78*, 8594-8605.

followed by the dropwise addition of tributyltin hydride (1.62 mL, 6.01 mmol) over 1 h by means of a syringe pump. Once the addition was complete, all volatile materials were removed under reduced pressure and the residue was purified by flash chromatography (hexanes/ethyl acetate, 9:1) to give the product as a colorless oil (3.11 g, 88% yield). $[\alpha]_D^{20}$: +12.0° (c 1.16 in $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.43 – 6.00 (m, 1H), 4.37 – 4.18 (m, 1H), 3.99 – 3.86 (m, 1H), 3.63 (dd, *J* = 5.7, 4.8 Hz, 2H), 2.17 (s, 3H), 2.05 (qt, *J* = 10.3, 5.1 Hz, 2H), 1.96 (t, *J* = 5.7 Hz, 1H), 1.80 (d, *J* = 3.1 Hz, 1H), 1.73 – 1.63 (m, 1H), 1.58 – 1.37 (m, 8H), 1.36 – 1.26 (m, 6H), 1.15 (d, *J* = 6.1 Hz, 3H), 1.05 (s, 21H), 0.97 – 0.91 (m, 8H), 0.88 (t, *J* = 7.3 Hz, 9H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 207.2, 146.7, 140.1, 80.7, 68.6, 67.1, 39.9, 34.9, 29.4, 27.6, 26.1, 23.6, 18.3, 18.3, 13.8, 12.6, 11.0, 10.7 ppm. ^{119}Sn NMR (149 MHz, $CDCl_3$) δ -55.5 ppm. IR (film, $CHCl_3$) 3385, 2925, 2866, 1462, 1376, 1247, 1187, 1133, 1098, 1029, 1013, 970, 918, 881, 758, 674 cm^{-1}. HRMS (ESI): *m/z* calculated $C_{32}H_{68}O_3SiSnNa$ [M+Na$^+$]: 671.38512; found 671.38501.

(6*S*,7*R*,13*R*,*Z*)-15,15-Diisopropyl-2,2,3,3,6,13,16-heptamethyl-8-(tributylstannyl)-4,14-dioxa-3,15-disilahepta-dec-8-en-7-ol (S23). *tert*-Butyldimethylsilyl chloride (796 mg, 5.28 mmol) was added at 0°C to a solution of (2*S*,3*R*,9*R*,Z)-2-methyl-4-(tributylstannyl)-9-((triisopropylsilyl)-oxy)dec-4-ene-1,3-diol (3.11 g, 4.8 mmol) in CH_2Cl_2 (25 mL). Et_3N (736 µL, 5.28 mmol) was then introduced over 20 minutes via syringe and stirring continued until TLC showed complete conversion. The reaction was quenched with saturated ammonium chloride solution, the mixture was extracted two times with CH_2Cl_2, and the combined extracts were dried over magnesium sulfate and concentrated under reduced pressure. Flash chromatography of the residue (hexanes/ethyl acetate, 40:1) yielded the product as a colorless oil (3.34 g, 91% yield). $[\alpha]_D^{20}$: +5.7° (c 1.10 in $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.24 (td, *J* = 7.2, 1.5 Hz, 1H), 4.36 (ddd, *J* = 4.0, 2.5, 1.4 Hz, 1H), 4.00 – 3.86 (m, 1H), 3.70 – 3.58 (m, 3H), 2.52 (d, *J* = 2.4 Hz, 1H), 2.15 – 1.94 (m, 2H), 1.68 – 1.57 (m, 1H), 1.56 – 1.37 (m, 9H), 1.37 – 1.24 (m, 6H), 1.15 (d, *J* = 6.1 Hz, 3H), 1.05 (s, 21H), 1.00 – 0.79 (m, 26H), 0.06 (s, 7H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.4, 139.5, 79.1, 68.6, 67.6, 40.0, 39.6, 35.0, 29.4, 27.6, 26.2, 26.0, 23.6, 18.3, 13.9, 12.6, 11.0, 10.1, -5.4, -5.4 ppm. ^{119}Sn NMR (149 MHz, $CDCl_3$) δ -55.9 ppm. IR (film, $CHCl_3$) 2955, 2927, 2865, 1463, 1376, 1252, 1202, 1133, 1095, 1005, 918, 882, 835, 775, 724, 673 cm^{-1}. HRMS (ESI): *m/z* calculated $C_{38}H_{82}O_3Si_2SnNa$ [M+Na$^+$]: 785.47160; found 785.47165.

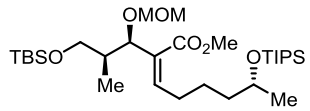


Methyl (*R*,*Z*)-2-((1*R*,2*S*)-3-((*tert*-butyldimethylsilyl)oxy)-1-hydroxy-2-methylpropyl)-7-((triisopropylsilyl)oxy)-oct-2-enoate (25). 1,4-Benzoquinone (162 mg, 1.5 mmol), $AsPh_3$ (31 mg, 0.1 mmol, 10 mol%) and $Pd(OAc)_2$ (12 mg, 0.05 mmol, 5 mol%) were added to a solution of (6*S*,7*R*,13*R*,Z)-15,15-diisopropyl-2,2,3,3,6,13,16-heptamethyl-8-(tributylstannyl)-4,14-dioxa-3,15-disilaheptadec-8-en-7-ol (761 mg, 1.0 mmol) in a solution of TFA in MeOH (0.1 M, 10 mL). The solution was flushed with CO for 2 minutes before stirring was continued under a CO atmosphere (balloon) at 50°C. For work up, the flask was vented and the mixture filtered through a pad of Celite® which was carefully rinsed with *tert*-butyl methyl ether. The combined filtrates were evaporated and the residue purified by flash chromatography (hexanes/ethyl acetate, 25:1) to give the product as a pale yellow oil (373 mg, 70% yield). $[\alpha]_D^{20}$: +6.0° (c 1.15 in $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.24 (td, *J* = 7.5, 1.4 Hz, 1H), 4.65 (tt, *J* = 3.6, 1.4 Hz, 1H), 3.93 (hept, *J* = 5.2, 4.7 Hz, 1H), 3.79 (dd, *J* = 9.8, 3.6 Hz, 1H), 3.72 (s, 3H), 3.65 (dd, *J* = 9.8, 4.2

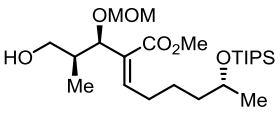


Hz, 1H), 3.54 (d, *J* = 3.7 Hz, 1H), 2.45 (qq, *J* = 14.1, 6.6 Hz, 2H), 1.85 (tp, *J* = 7.1, 3.2 Hz, 1H), 1.59 – 1.43 (m, 4H), 1.15 (d, *J* = 6.0 Hz, 3H), 1.05 (s, 21H), 0.90 (s, 9H), 0.86 (d, *J* = 7.1 Hz, 3H), 0.06 (d, *J* = 1.0 Hz, 6H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.0, 142.5, 132.2, 74.7, 68.5, 68.1, 51.3, 39.8, 38.3, 29.8, 26.0, 25.3, 23.6, 18.3, 18.3, 12.6, 10.1, -5.45, -5.51 ppm. IR (film, $CHCl_3$) 3497, 2930, 2865, 1721, 1463, 1435, 1374, 1252, 1195, 1134, 1096, 1063, 1005, 918, 882, 835, 775, 723 cm^{-1}. HRMS (ESI): *m/z* calculated $C_{28}H_{59}O_5Si_2$ [M+H$^+$]: 531.38956; found 531.38965.

Methyl (*R*,*Z*)-2-((1*R*,2*S*)-3-((*tert*-butyldimethylsilyl)oxy)-1-hydroxy-2-methylpropyl)-7-((triisopropylsilyl)oxy)-oct-2-enoate (S24). Hünig's base (860 µL, 4.93 mmol) and MOMCl (281 µL, 3.70 mmol,) were added at 0°C in that order to a solution of methyl (*R*,Z)-2-((1*R*,2*S*)-3-((*tert*-butyldimethylsilyl)oxy)-1-hydroxy-2-methylpropyl)-7-((triisopropylsilyl)oxy)oct-2-enoate (655 mg, 1.23 mmol) in CH_2Cl_2 (7 mL). The resulting mixture was stirred at room temperature for 24 h before it was diluted with CH_2Cl_2 and the reaction was quenched with saturated ammonium chloride solution. The aqueous layer was extracted two times with CH_2Cl_2, and the combined organic phases were washed with brine, dried over magnesium sulfate and concentrated under reduced pressure. Flash chromatographic purification of the residue (hexanes/ethyl acetate, 19:1) yielded the product as a colorless oil (605 mg, 85% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.05 (td, *J* = 7.5, 1.0 Hz, 1H), 4.61 (d, *J* = 6.6 Hz, 1H), 4.52 (d, *J* = 6.6 Hz, 1H), 4.48 – 4.38 (m, 1H), 4.02 – 3.86 (m, 1H), 3.71 (s, 3H), 3.58 (dd, *J* = 9.9, 6.1 Hz, 1H), 3.48 (dd, *J* = 9.9, 6.0 Hz, 1H), 3.37 (s, 3H), 2.42 (dq, *J* = 14.7, 7.6 Hz, 2H), 1.98 – 1.82 (m, 1H), 1.58 – 1.39 (m, 4H), 1.14 (d, *J* = 6.1 Hz, 3H), 1.05 (s, 22H), 0.89 (s, 13H), 0.03 (d, *J* = 2.6 Hz, 6H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.7, 142.7, 131.1, 94.8, 77.0, 68.4, 65.4, 56.1, 51.4, 39.7, 39.6, 29.7, 26.0, 25.3, 23.7, 18.4, 18.3, 12.6, 11.5, -5.2 ppm.



Methyl (*R*,*Z*)-2-((1*R*,2*S*)-3-((*tert*-butyldimethylsilyl)oxy)-1-hydroxy-2-methylpropyl)-7-((triisopropylsilyl)oxy)-oct-2-enoate (26). HCl (2 M) was added to a solution of methyl (*R*,*Z*)-2-((1*R*,2*S*)-3-((*tert*-butyldimethylsilyl)oxy)-1-hydroxy-2-methylpropyl)-7-((triisopropylsilyl)oxy)oct-2-enoate (450 mg, 0.78 mmol) in THF (10 mL) at 0°C. The ice bath was removed and stirring continued until TLC indicated complete conversion The mixture was diluted with water and extracted two times with CH_2Cl_2. The combined organic layers were dried over magnesium sulfate and concentrated under reduced pressure. Flash chromatographic purification of the residue (hexanes/ethyl acetate, 4:1) yielded the product as a colorless oil (359 mg, 85%). $[\alpha]_D^{20}$: +77.8° (c 1.18 in $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.12 (td, *J* = 7.5, 1.1 Hz, 1H), 4.57 (d, *J* = 6.6 Hz, 1H), 4.55 – 4.48 (m, 2H), 3.97 – 3.87 (m, 1H), 3.73 (s, 3H), 3.64 – 3.51 (m, 2H), 3.39 (s, 3H), 2.54 – 2.37 (m, 2H), 2.35 (t, *J* = 6.0 Hz, 1H), 1.99 – 1.87 (m, 1H), 1.58 – 1.37 (m, 4H), 1.14 (d, *J* = 6.1 Hz, 3H), 1.04 (s, 21H), 0.87 (d, *J* = 7.0 Hz, 3H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.0, 143.2, 130.6, 95.1, 77.1, 68.4, 65.5, 56.2, 51.6, 39.7, 29.7, 25.3, 23.6, 18.3, 12.6, 11.4 ppm. IR (film, $CHCl_3$) 3468, 2942, 2891, 2866, 1720, 1462, 1436, 1377, 1210, 1136, 1096, 1029, 919, 882, 850, 675 cm^{-1}. HRMS (ESI): *m/z* calculated $C_{24}H_{48}O_6SiNa$ [M+Na$^+$]: 483.31124; found 483.31142.



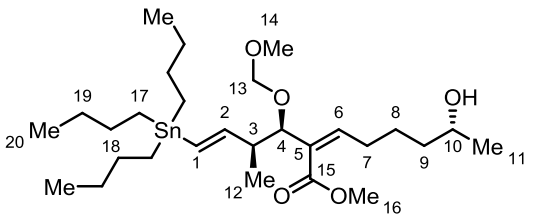
Methyl (*R*,*Z*)-2-((1*R*,2*S*,E)-1-(methoxymethoxy)-2-methyl-4-(tributylstannyl)but-3-en-1-yl)-7-((triisopropylsilyl)oxy)oct-2-enoate (16). $NaHCO_3$ (341 mg, 4.06 mmol) and Dess-Martin periodinane (345 mg, 0.81 mmol) were weighed at 0°C into an oven-dried Schlenk flask under argon and were suspended in CH_2Cl_2 (4 mL). A solution of methyl (*R*,Z)-2-((1*R*,2*S*)-3-((*tert*-butyldimethylsilyl)oxy)-1-hydroxy-2-methylpropyl)-7-((triisopropylsilyl)oxy)oct-2-enoate (234 mg, 0.51 mmol) in CH_2Cl_2 (2 mL) was added and the resulting mixture stirred for 6 h. The reaction was quenched with saturated sodium bicarbonate solution and the resulting mixture was diluted with saturated sodium thiosulfate solution. The aqueous phase was extracted two times with CH_2Cl_2, and the combined organic layers were washed with saturated sodium bicarbonate solution, dried over magnesium sulfate and concentrated under reduced pressure. The crude aldehyde was used in the next step without further purification.

$CrCl_2$·THF (990 mg, 5.08 mmol) was weighed under argon into an oven-dried Schlenk flask. THF (10 mL) was added and the mixture stirred at room temperature. DMF (393 µL, 5.08 mmol) was dropwise added and stirring continued for 15 minutes. A second oven-dried Schlenk flask was charged with the crude aldehyde and tributyl(dibromomethyl)stannane (517 mg, 1.12 mmol). The mixture was dissolved in 2 mL THF and added under argon to the chromium suspension via canula. The reaction flask was covered with aluminum foil. A third Schlenk flask was charged with LiI (272 g, 2.03 mmol) which was melted at ≈10 mbar with a Bunsenburner. Upon cooling to room temperature, a stirring bar was added and the salt was solubilized in THF (2 mL) before the resulting solution was added to the reaction mixture. The resulting mixture was vigorously stirred for 18 h before the reaction was quenched with water. The aqueous phase was extracted two times with *tert*-butyl methyl ether, and the combined organic layers were washed with brine, dried over magnesium sulfate and concentrated under reduced pressure. Flash chromatographic purification of the residue (hexanes/ethyl acetate, 40:1) yielded the product as a colorless oil (225 mg, *E:Z* = 85:15, 60% yield). $[\alpha]_D^{20}$: +21.5° (c 0.87 in $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.05 (td, *J* = 7.5, 0.9 Hz, 1H), 5.93 (d, *J* = 19.0 Hz, 1H), 5.90 – 5.83 (m, 1H), 4.60 (d, *J* = 6.7 Hz, 1H), 4.49 (d, *J* = 6.7 Hz, 1H), 4.24 (d, *J* = 6.6 Hz, 1H), 3.92 (tt, *J* = 7.2, 3.6 Hz, 1H), 3.71 (s, 3H), 3.36 (s, 3H), 2.56 – 2.47 (m, 1H), 2.47 – 2.28 (m, 2H), 1.57 – 1.36 (m, 10H), 1.36 – 1.22 (m, 6H), 1.14 (d, *J* = 6.0 Hz, 3H), 1.04 (s, 24H), 0.88 (t, *J* = 7.3 Hz, 9H), 0.86 – 0.81 (m, 6H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.6, 151.0, 143.7, 131.2, 127.9, 94.5, 79.9, 68.4, 56.0, 51.4, 45.7, 39.8, 29.8, 29.2, 27.4, 25.3, 23.6, 18.3, 18.3, 15.1, 13.9, 12.6, 9.5 ppm. ^{119}Sn NMR (149 MHz, $CDCl_3$) δ -49.1 ppm. IR (film, $CHCl_3$) 2926, 2867, 1723, 1462, 1376, 1291, 1246, 1194, 1152, 1097, 1030, 991, 920, 882, 675 cm^{-1}. HRMS (ESI): *m/z* calculated $C_{37}H_{74}O_5SiSnNa$ [M+Na$^+$]: 769.42190; found 769.42204.

Methyl (*R*,*Z*)-7-hydroxy-2-((1*R*,2*S*,*E*)-1-(methoxymethoxy)-2-methyl-4-(tributylstannyl)but-3-en-1-yl)oct-2-enoate (S25). TBAF (1 M in THF, 343 µL, 0.343 mmol) was added at 0°C to a solution of methyl (*R*,Z)-2-((1*R*,2*S*,E)-1-(methoxymethoxy)-2-methyl-4-(tributylstannyl)but-3-en-1-yl)-7-((triisopropylsilyl)oxy)oct-2-enoate (160 mg, 0.21 mmol) in THF (2 mL) and the resulting mixture was stirred for 18 h at ambient temperature. The mixture was diluted with *tert*-butyl methyl ether and the reaction quenched with saturated ammonium chloride solution. The mixture was extracted two times with *tert*-butyl methyl ether, the combined organic layers were

washed with brine, dried over magnesium sulfate and concentrated under reduced pressure. Flash chromatographic purification of the residue (hexanes/ethyl acetate, 4:1) yielded the product as a colorless oil (76 mg, 60% yield). $[\alpha]_D^{20}$: +27.6° (c 1.20 in $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.07 (td, *J* = 7.7, 0.9 Hz, 1H), 5.92 (d, *J* = 19.0 Hz, 1H), 5.85 (dd, *J* = 19.0, 5.9 Hz, 1H), 4.60 (d, *J* = 6.7 Hz, 1H), 4.49 (d, *J* = 6.7 Hz, 1H), 4.24 (d, *J* = 6.6 Hz, 1H), 3.87 – 3.74 (m, 1H), 3.72 (s, 3H), 3.35 (s, 3H), 2.51 (dddd, *J* = 13.4, 8.3, 5.8, 3.9 Hz, 2H), 2.41 – 2.30 (m, 1H), 1.57 (d, *J* = 2.7 Hz, 1H), 1.54 – 1.40 (m, 10H), 1.33 – 1.22 (m, 6H), 1.18 (d, *J* = 6.2 Hz, 3H), 1.03 (d, *J* = 6.8 Hz, 3H), 0.87 (t, *J* = 7.3 Hz, 9H), 0.85 – 0.80 (m, 6H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.6, 150.9, 143.5, 131.4, 128.0, 94.5, 79.9, 67.7, 56.0, 51.5, 45.7, 38.9, 29.3, 29.2, 27.4, 25.6, 23.6, 15.1, 13.8, 9.5 ppm. ^{119}Sn NMR (149 MHz, $CDCl_3$) δ −49.1 ppm. IR (film, $CHCl_3$) 2955, 2925, 2871, 1720, 1458, 1436, 1375, 1291, 1211, 1153, 1096, 1029, 991, 961, 921, 863 cm^{-1}. HRMS (ESI): *m/z* calculated $C_{28}H_{54}O_5SnNa$ [M+Na$^+$]: 613.28847; found 613.28840.

Table S-1. Comparison of the recorded spectra ($CDCl_3$) of compound 16 with the published ^{13}C NMR data; numbering scheme as shown in the Insert



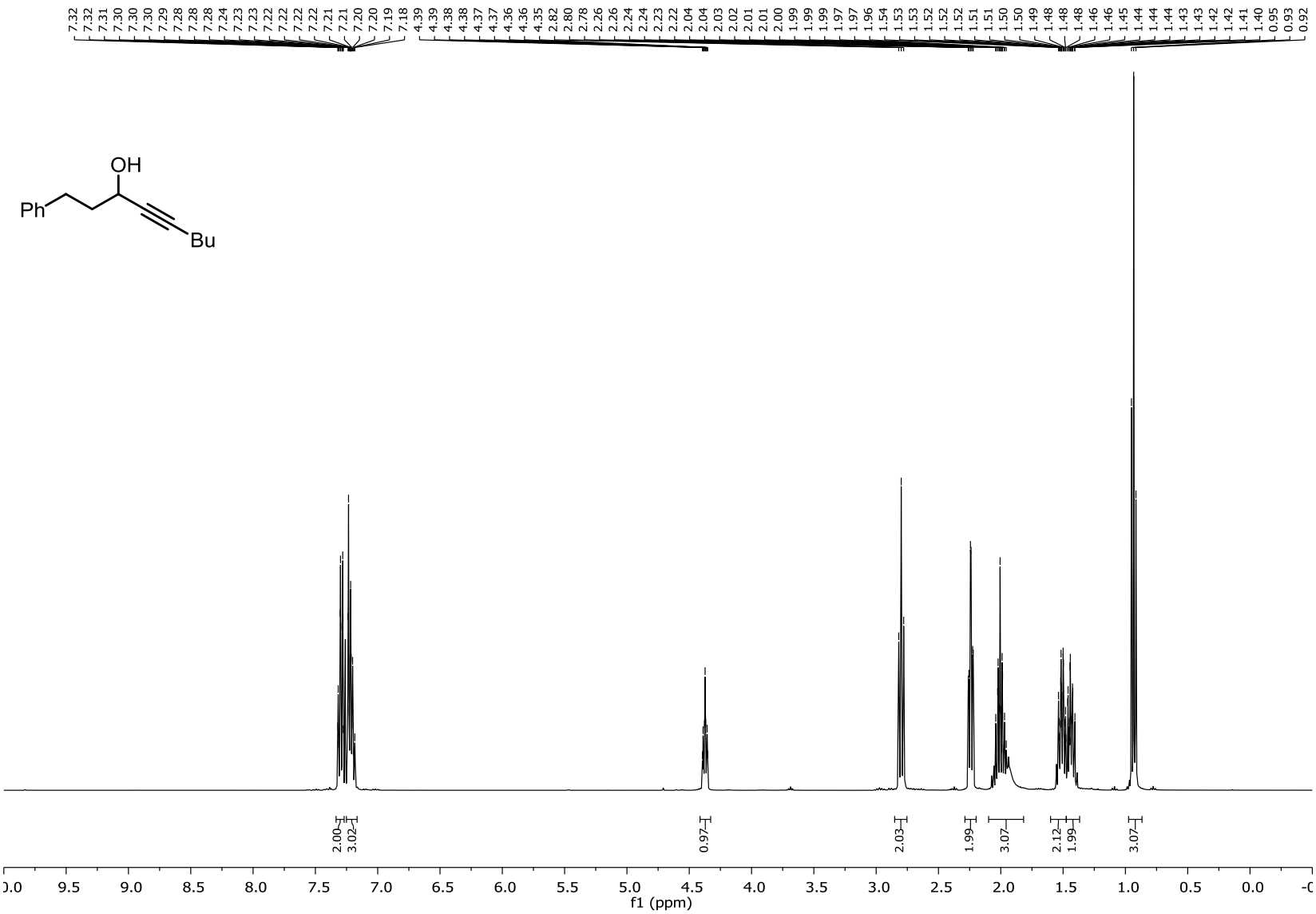
Position	Tadano et al.[9]	this work	Δ
1	150.8	150.9	-0.1
2	127.9	128.0	-0.1
3	29.2	29.3	-0.1
4	79.8	79.9	-0.1
5	131.3	131.4	-0.1
6	143.4	143.5	-0.1
7	45.6	45.7	-0.1
8	38.8	38.9	-0.1
9	29.1	29.2	-0.1
10	67.6	67.7	-0.1
11	25.5	25.6	-0.1
12	15.0	15.1	-0.1
13a	94.4	94.5	-0.1
13b	94.4	94.5	-0.1
14	55.8	56.0	-0.2
15	167.4	167.6	-0.2
16	51.3	51.5	-0.2
17	23.5	23.6	-0.1
18	27.2	27.4	-0.2
19	9.3	9.5	-0.2
20	13.7	13.8	-0.1

[9] a) T. Motozaki, K. Sawamura, A. Suzuki, K. Yoshida, T. Ueki, A. Ohara, R. Munakata, K. Takao, K. Tadano, *Org. Lett*. **2005**, *7*, 2265-2257; b) K. Sawamura, K. Yoshida, A. Suzuki, T. Motozaki, I. Kozawa, T. Hayamizu, R. Munakata, K. Takao, K. Tadano, *J. Org. Chem*. **2007**, *72*, 6143-6148.

Table S-2. Comparison of the recorded spectra ($CDCl_3$) of compound 16 with the published ^{1}H NMR data; numbering scheme as shown in the Insert of Table S-2

Position	Tadano *et al.* [ppm][9]	multiplicity	this work [ppm]	multiplicity	Δ [ppm]
1	5.94	(d, *J* = 19.1 Hz, 1H)	5.92	(d, *J* = 19.0 Hz, 1H)	0.04
2	5.86	(dd, *J* = 19.1, 5.5 Hz, 1H)	5.85	(dd, *J* = 19.0, 5.9 Hz, 1H)	0.01
3	2.37	(m, 1H)	2.41 – 2.30	(m, 1H)	0.01
4	4.25	(d, *J* = 6.6 Hz, 1H)	4.24	(d, *J* = 6.6 Hz, 1H)	0.01
5	-	-	-	-	-
6	6.08	(t, *J* = 7.6 Hz, 1H)	6.07	(td, *J* = 7.7, 0.9 Hz, 1H)	0.01
7	2.42-2.61	(m, 2H)	2.51	(dddd, *J* = 13.4, 8.3, 5.8, 3.9 Hz, 2H)	0.01
8	1.40-1.59	(m, 2H)	1.40-1.54	(m, 2H)	0.02
9	1.40-1.59	(m, 2H)	1.40-1.54	(m, 2H)	0.02
10	3.82	(m, 1H)	3.74-3.87	(m, 1H)	0.01
11	1.19	(d, *J* = 6.2 Hz, 3H)	1.18	(d, *J* = 6.2 Hz, 3H)	0.01
12	1.04	(d, *J* = 6.8 Hz, 3H)	1.03	(d, *J* = 6.8 Hz, 3H)	0.01
13a	4.62	(d, *J* = 6.8 Hz, 1H)	4.60	(d, *J* = 6.7 Hz, 1H)	0.02
13b	4.51	(d, *J* = 6.8 Hz, 1H)	4.49	(d, *J* = 6.7 Hz, 1H)	0.02
14	3.37	(s, 3H)	3.35	(s, 3H)	0.02
15	-	-	-	-	-
16	3.73	(s, 3H)	3.72	(s, 3H)	0.01
17	1.40-1.59	(m, 6H)	1.40-1.54	(m, 6H)	0.02
18	1.22-1.37	(m, 6H)	1.22-1.33	(m, 6H)	0.02
19	0.79-0.94	(m, 6H)	0.80-0.85	(m, 6H)	0.03
20	0.89	(t, *J* = 7.2 Hz, 9H)	0.87	(t, *J* = 7.3 Hz, 9H)	0.02

1-phenylnon-4-yn-3-ol (S1)



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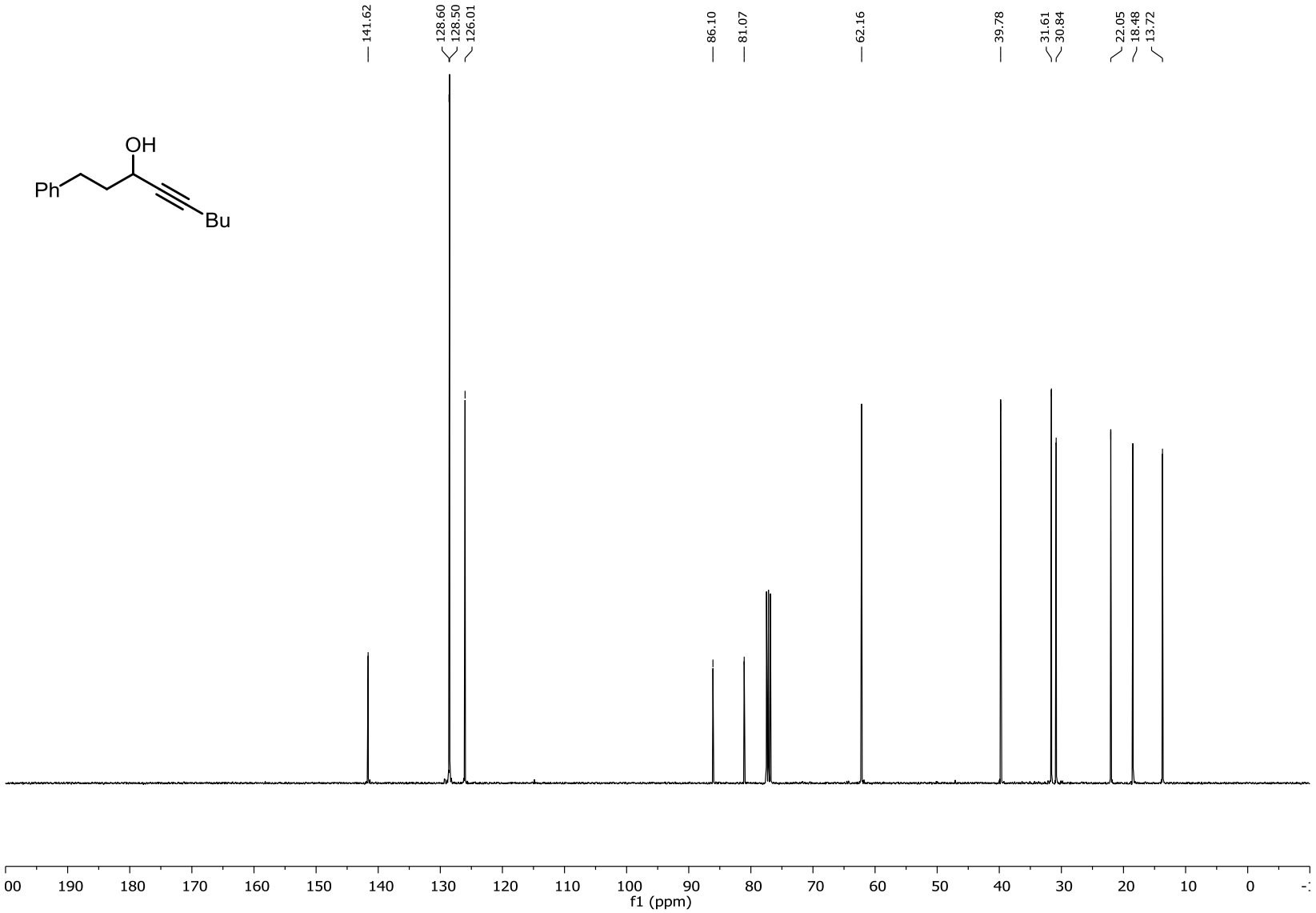
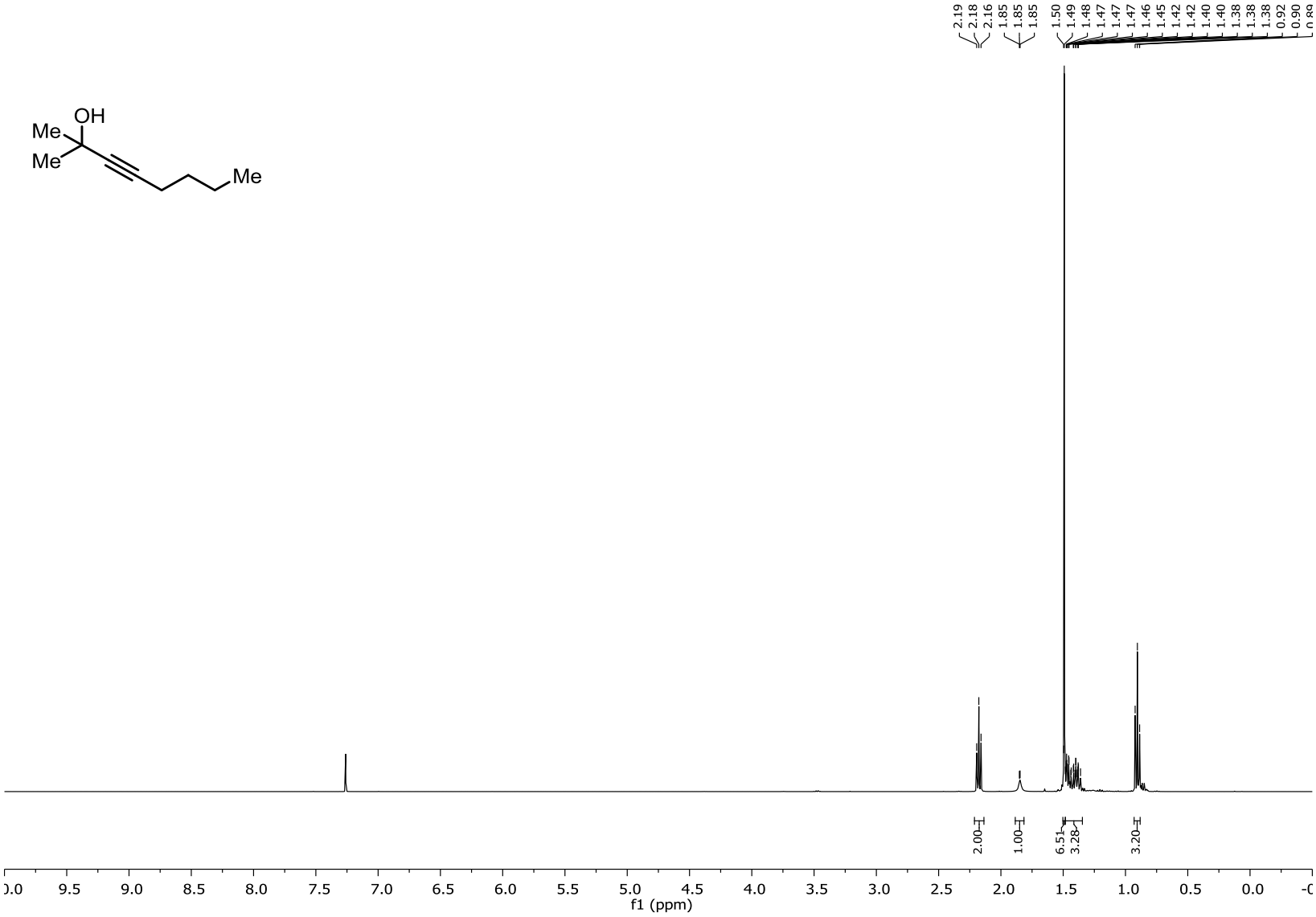
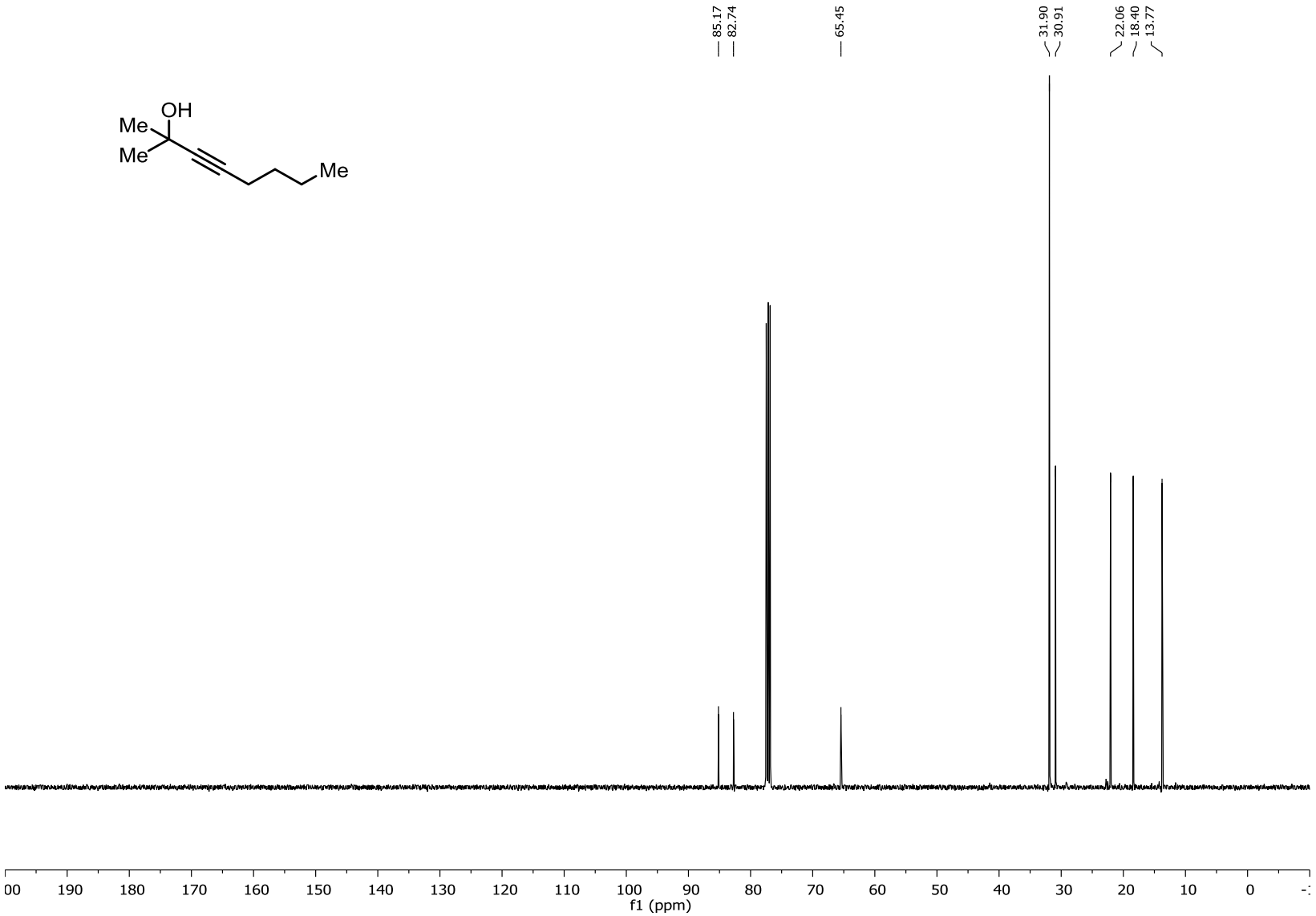


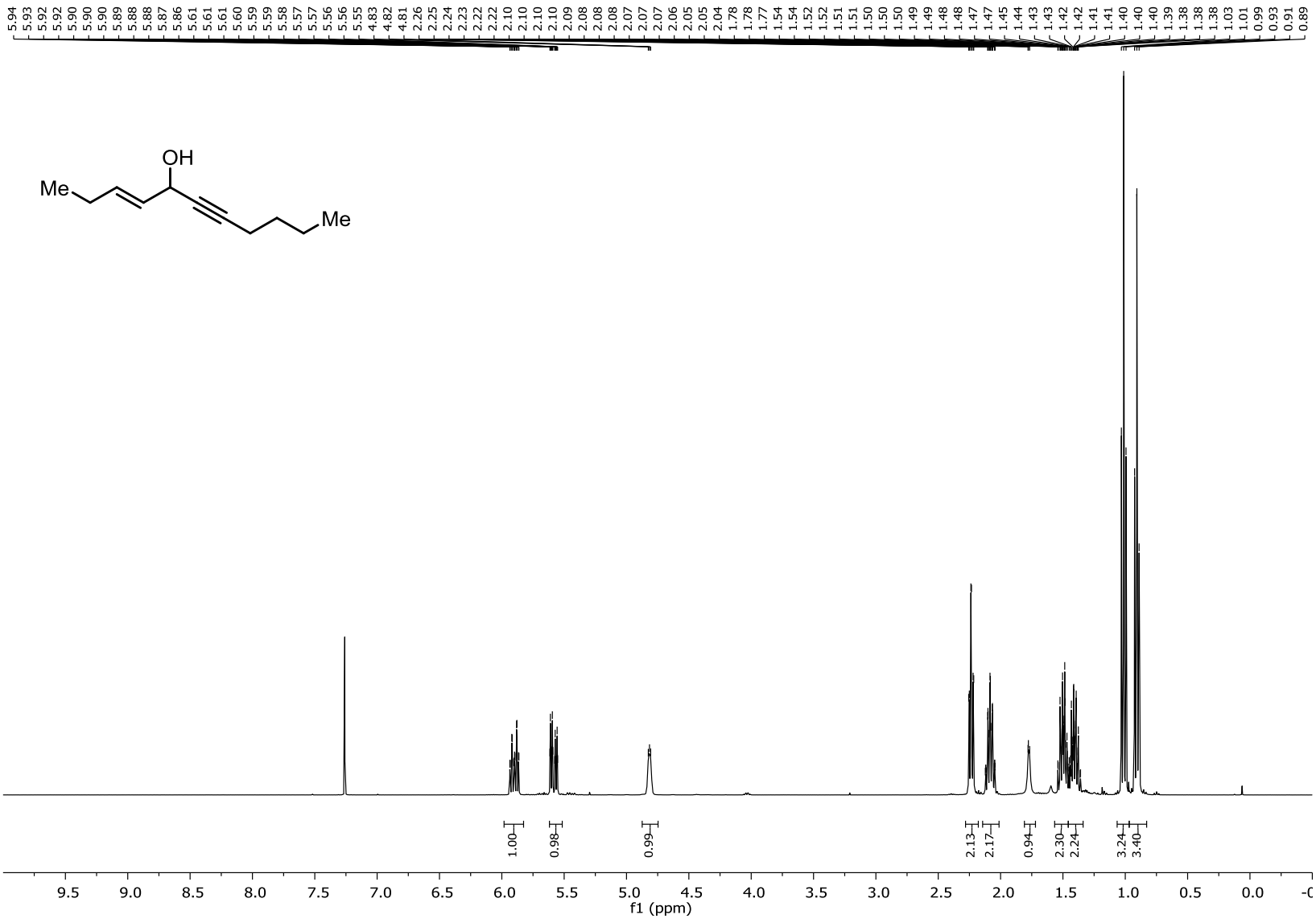
2-Methyloct-3-yn-2-ol (S2)



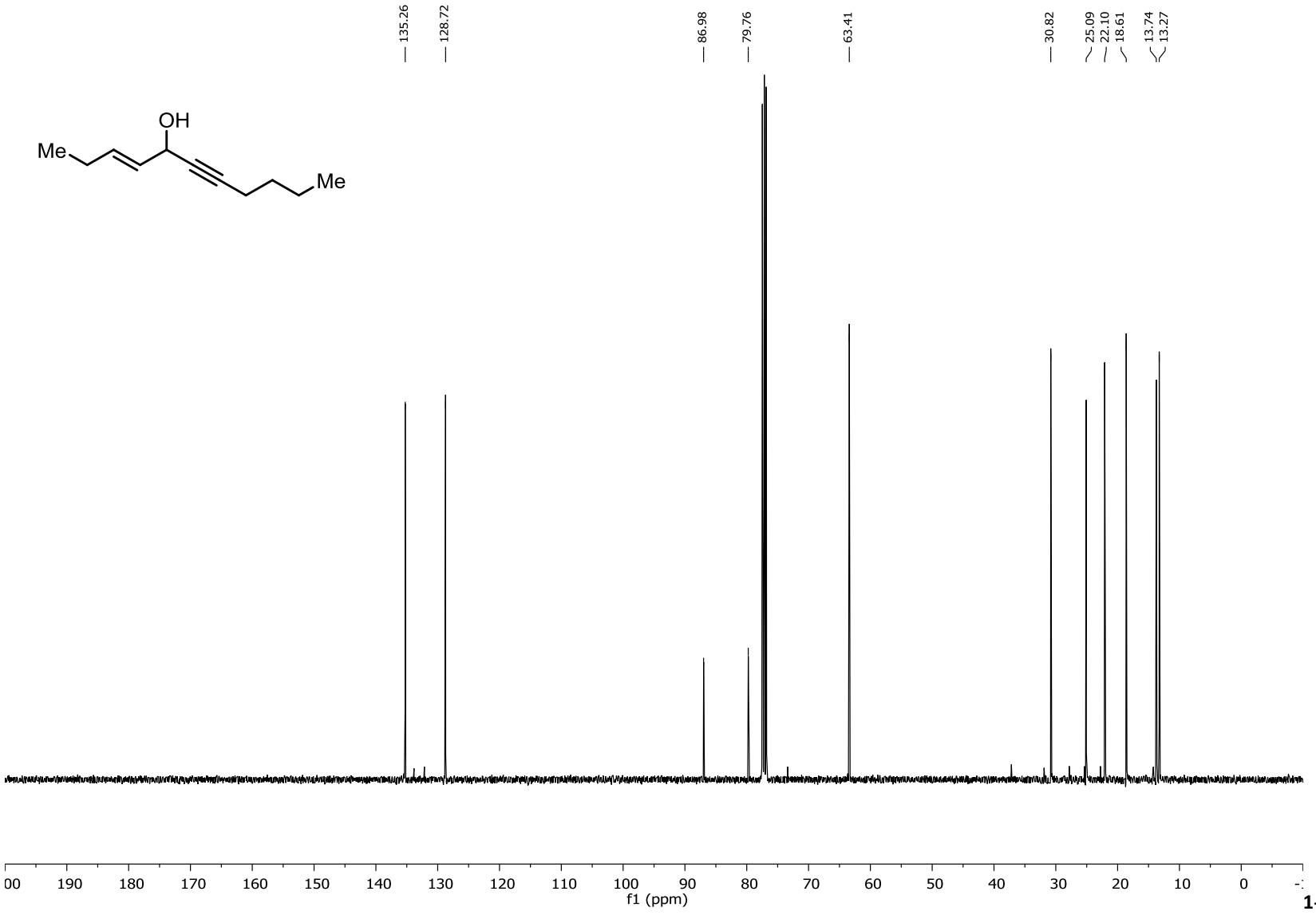
2-Methyloct-3-yn-2-ol (S2)



(E)-undec-3-en-6-yn-5-ol (S3)

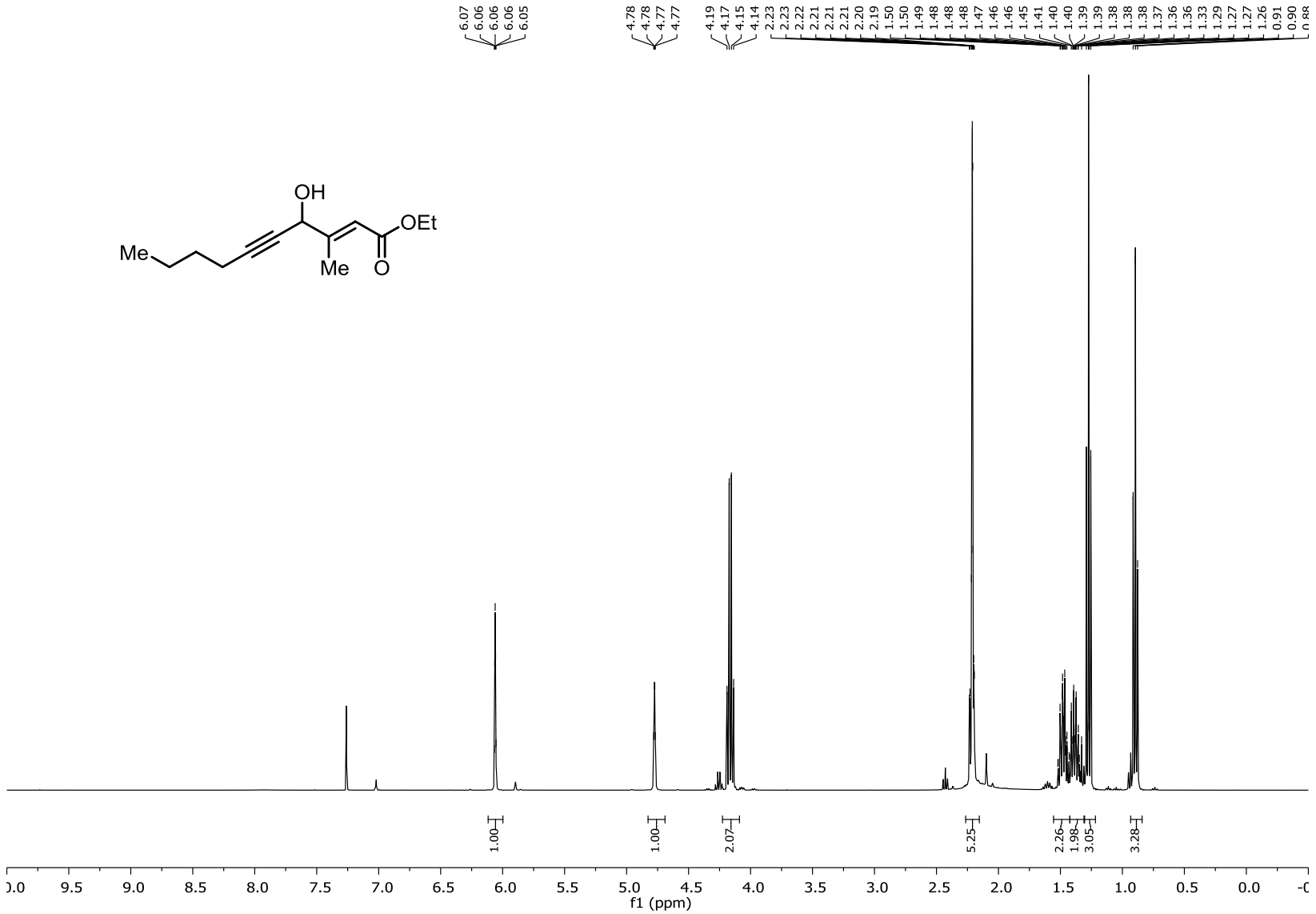


(E)-undec-3-en-6-yn-5-ol (S3)



1-((tert-

Ethyl (*E*)-4-hydroxy-3-methy ldec-2-en-5-ynoate (S4)



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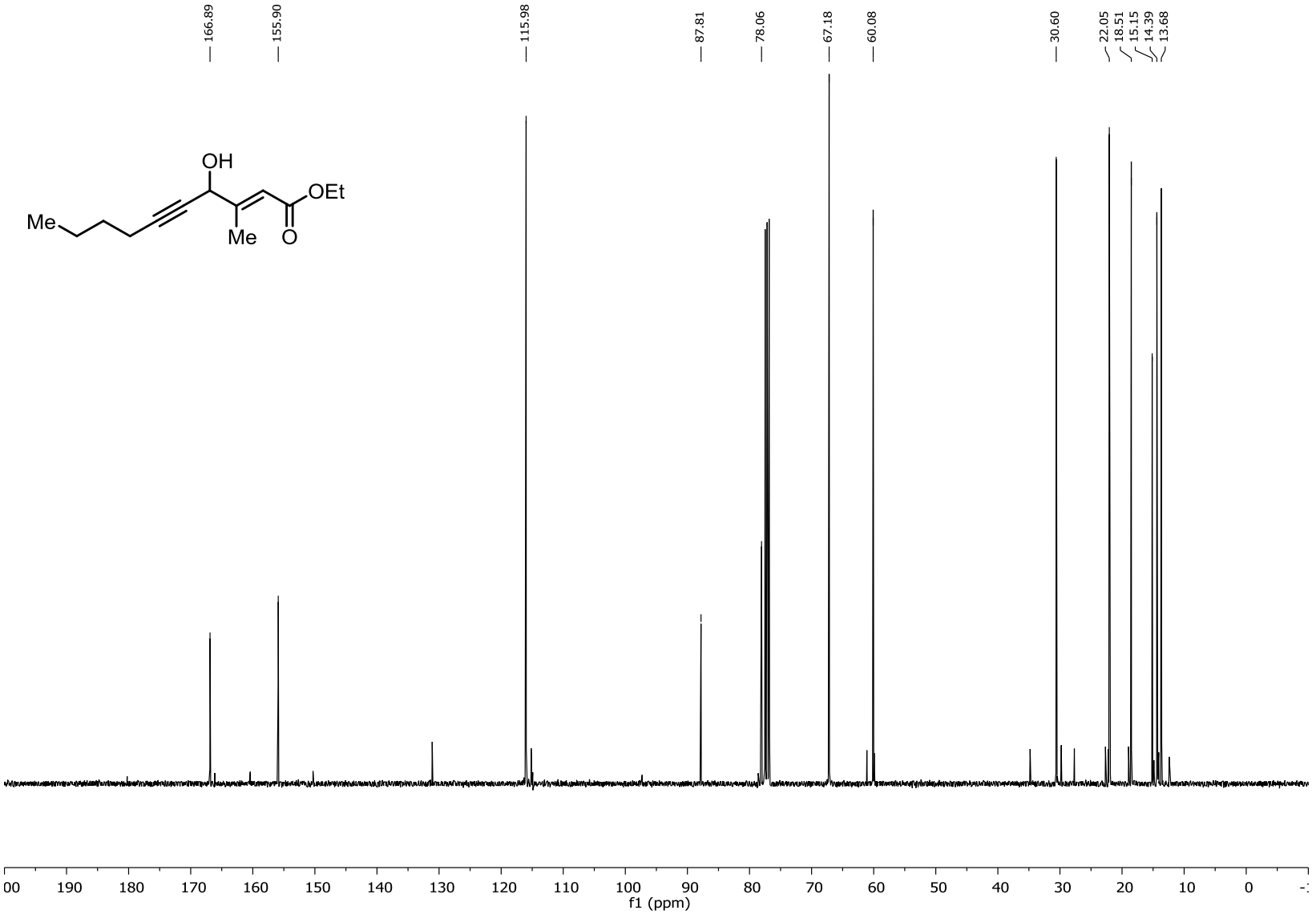
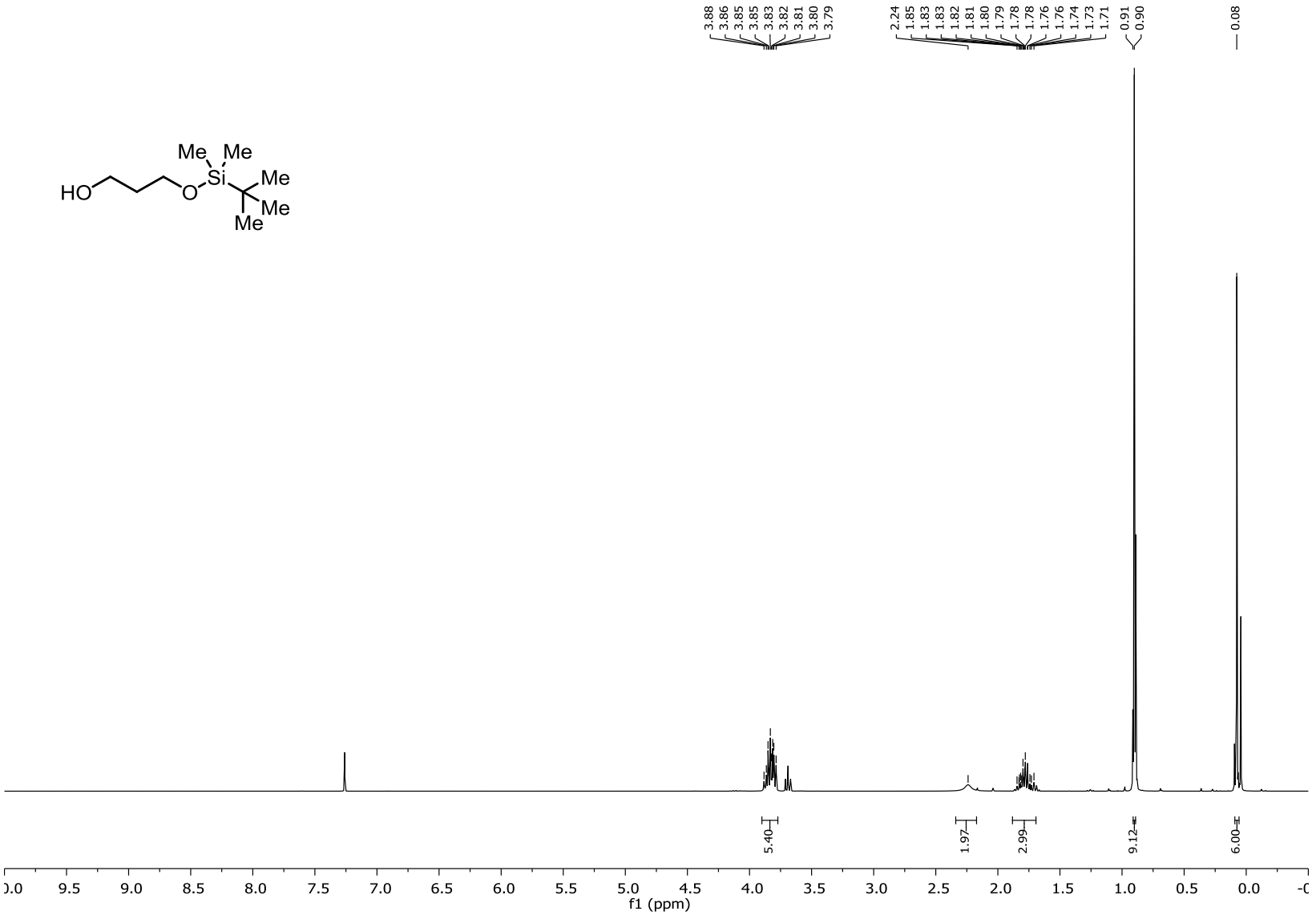


3-((*tert*-Butyldimethylsilyl)oxy)propan-1-ol (S5)



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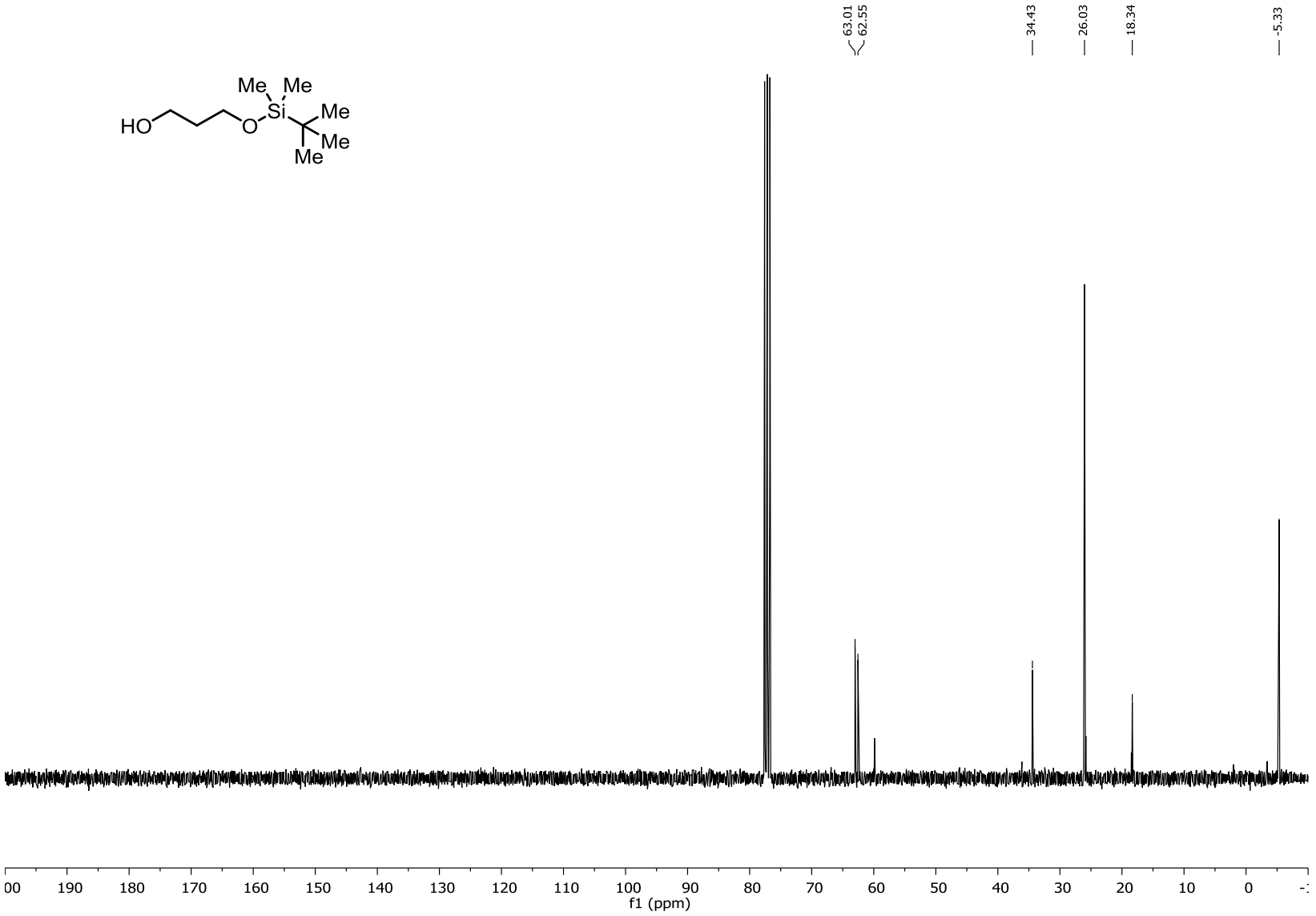
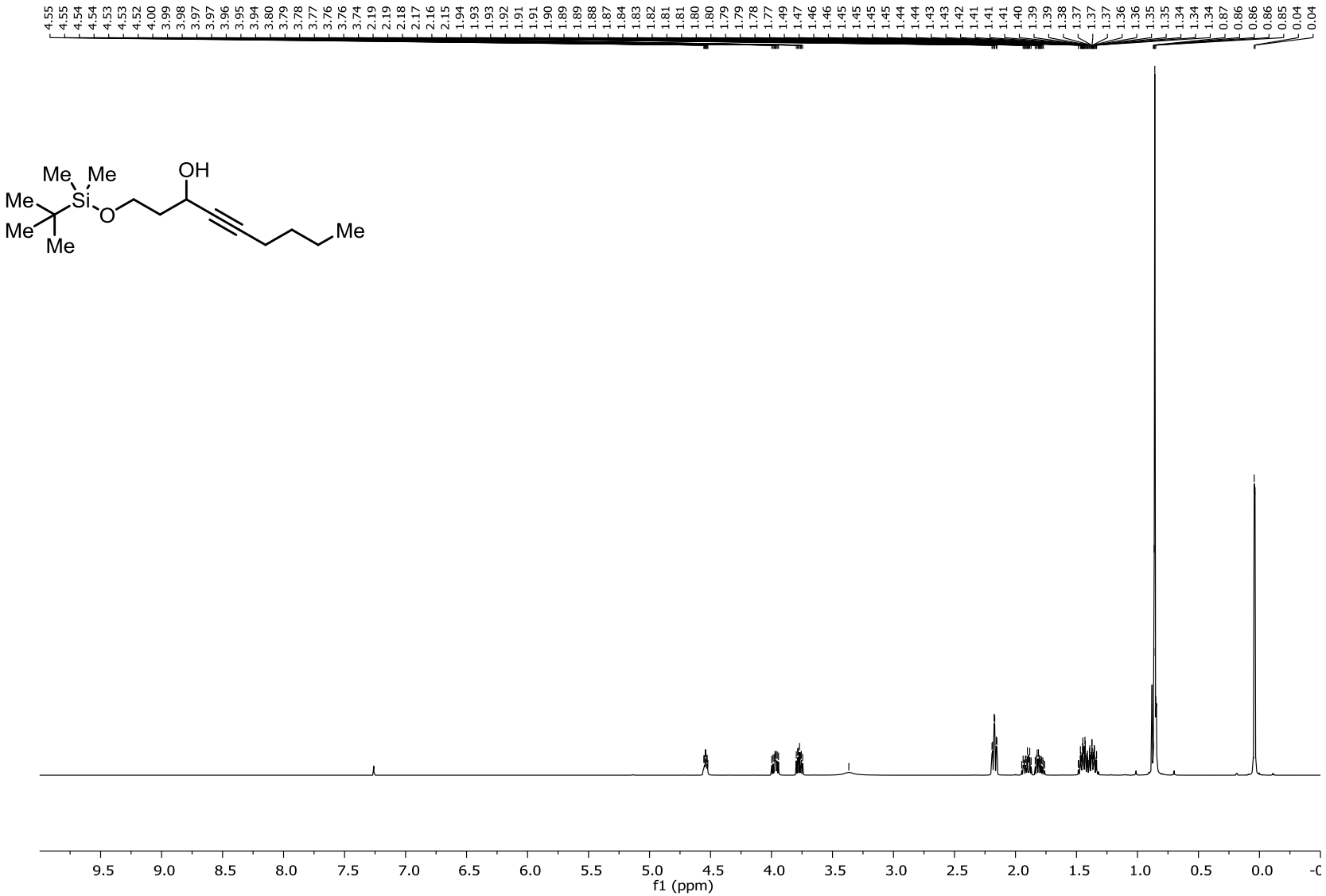
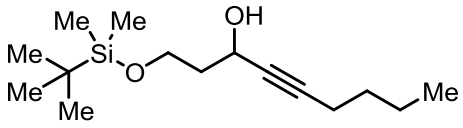


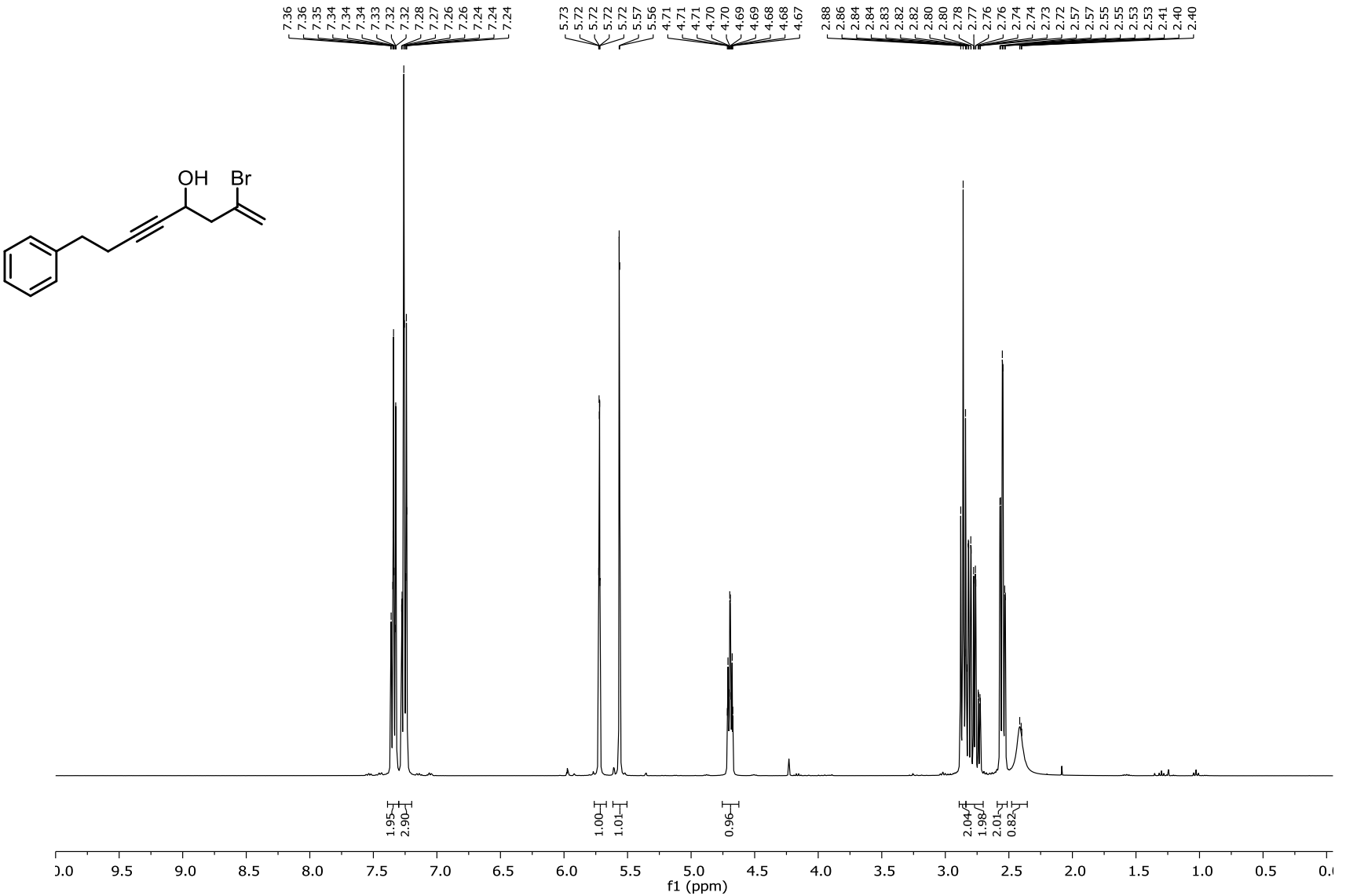
butyldimethylsilyl)oxy)non-4-yn-3-ol (S6)



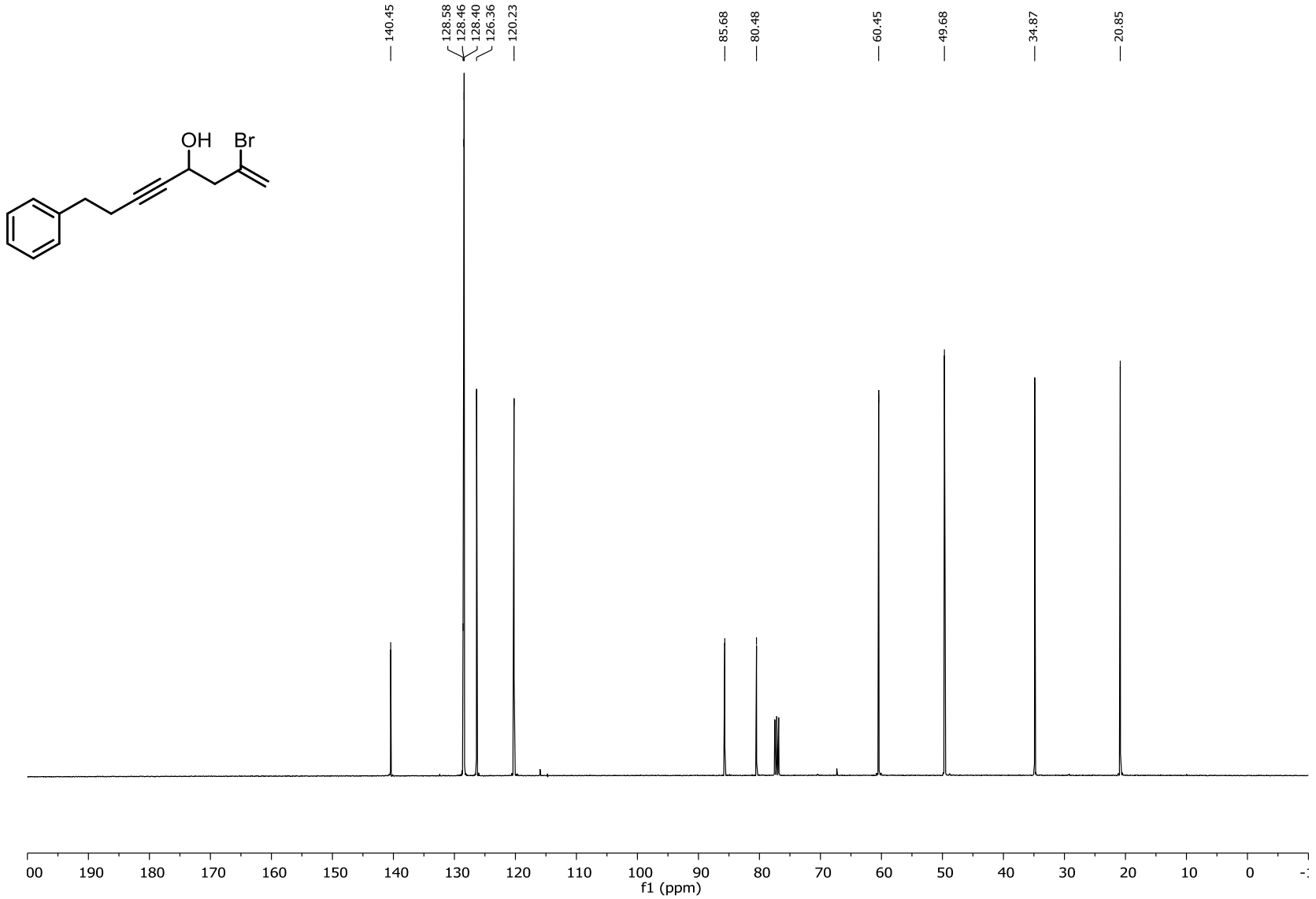
1-((tert-butyldimethylsilyl)oxy)non-4-yn-3-ol (S6)



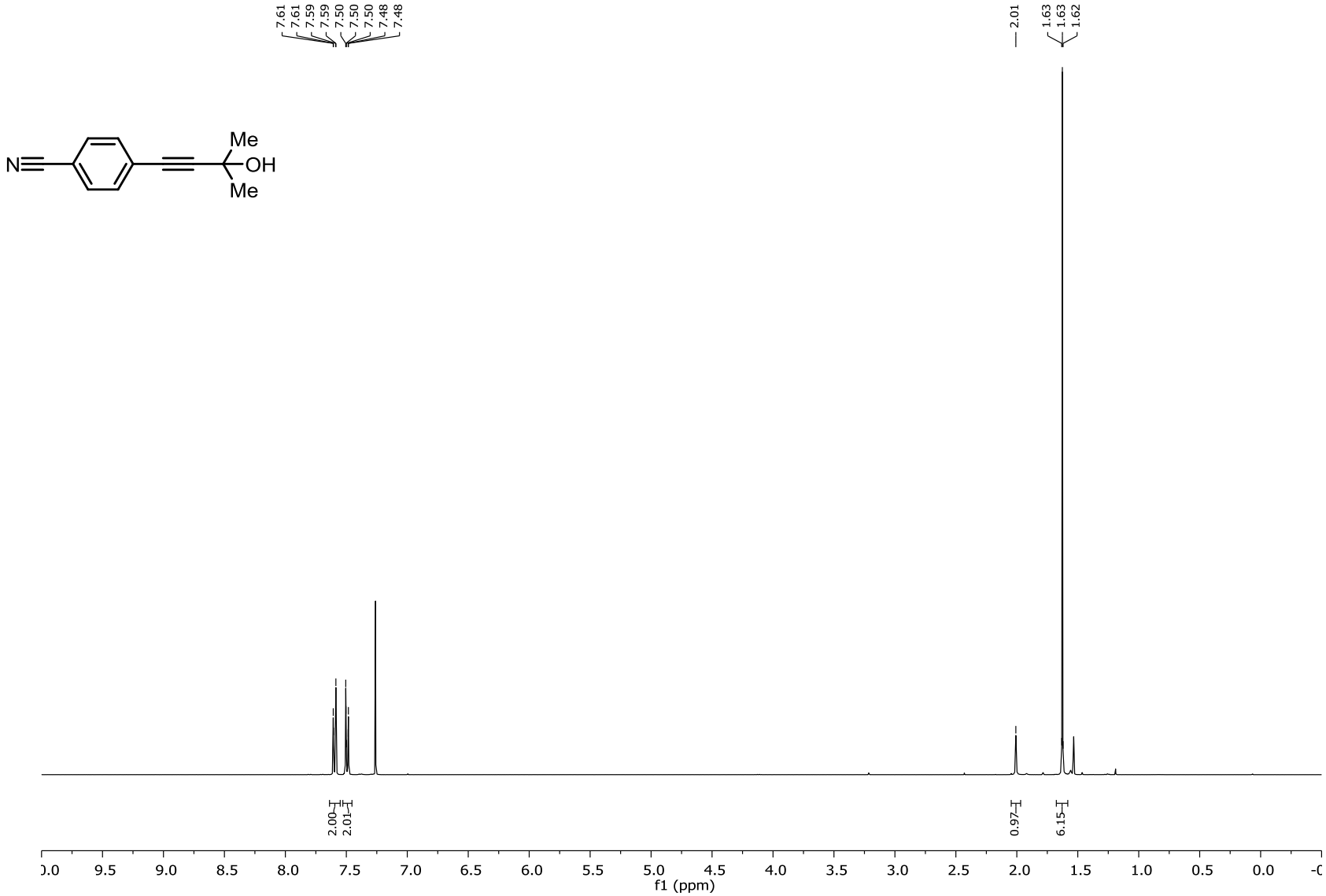
2-bromo-8-phenyloct-1-en-5-yn-4-ol (S7)



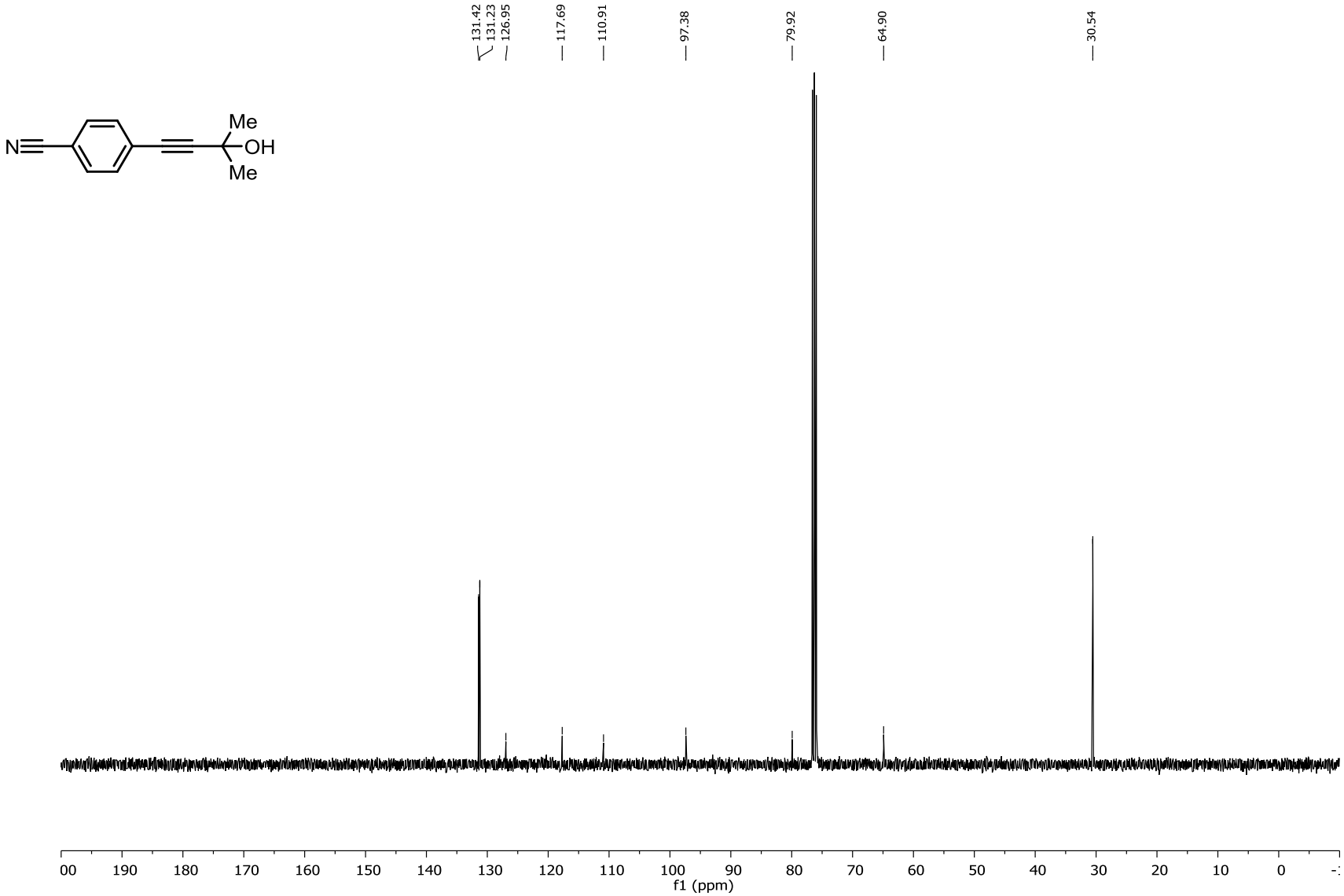
2-bromo-8-phenyloct-1-en-5-yn-4-ol (S7)



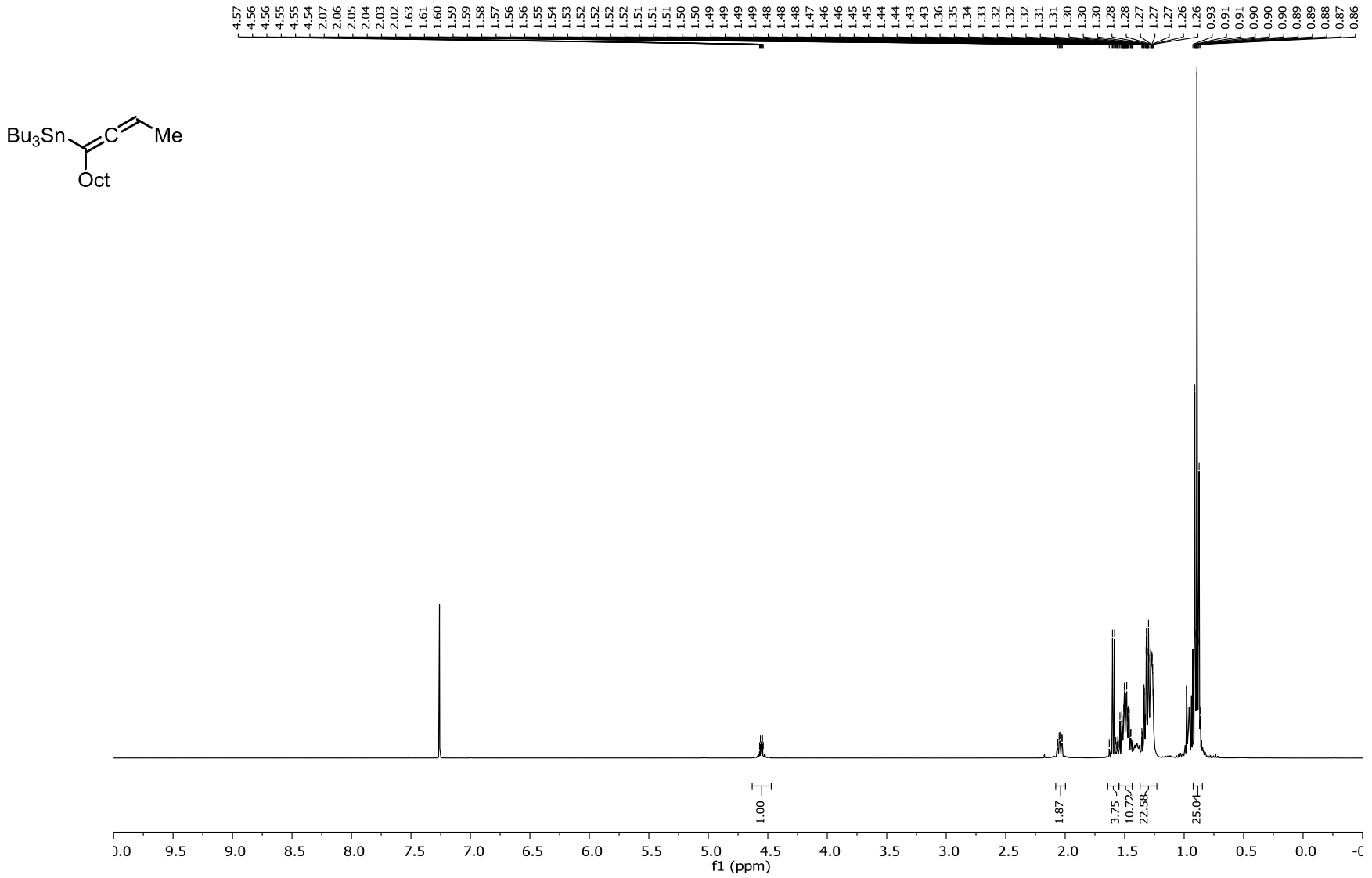
4-(3-hydroxy-3-methylbut-1-yn-1-yl)benzonitrile (S8)



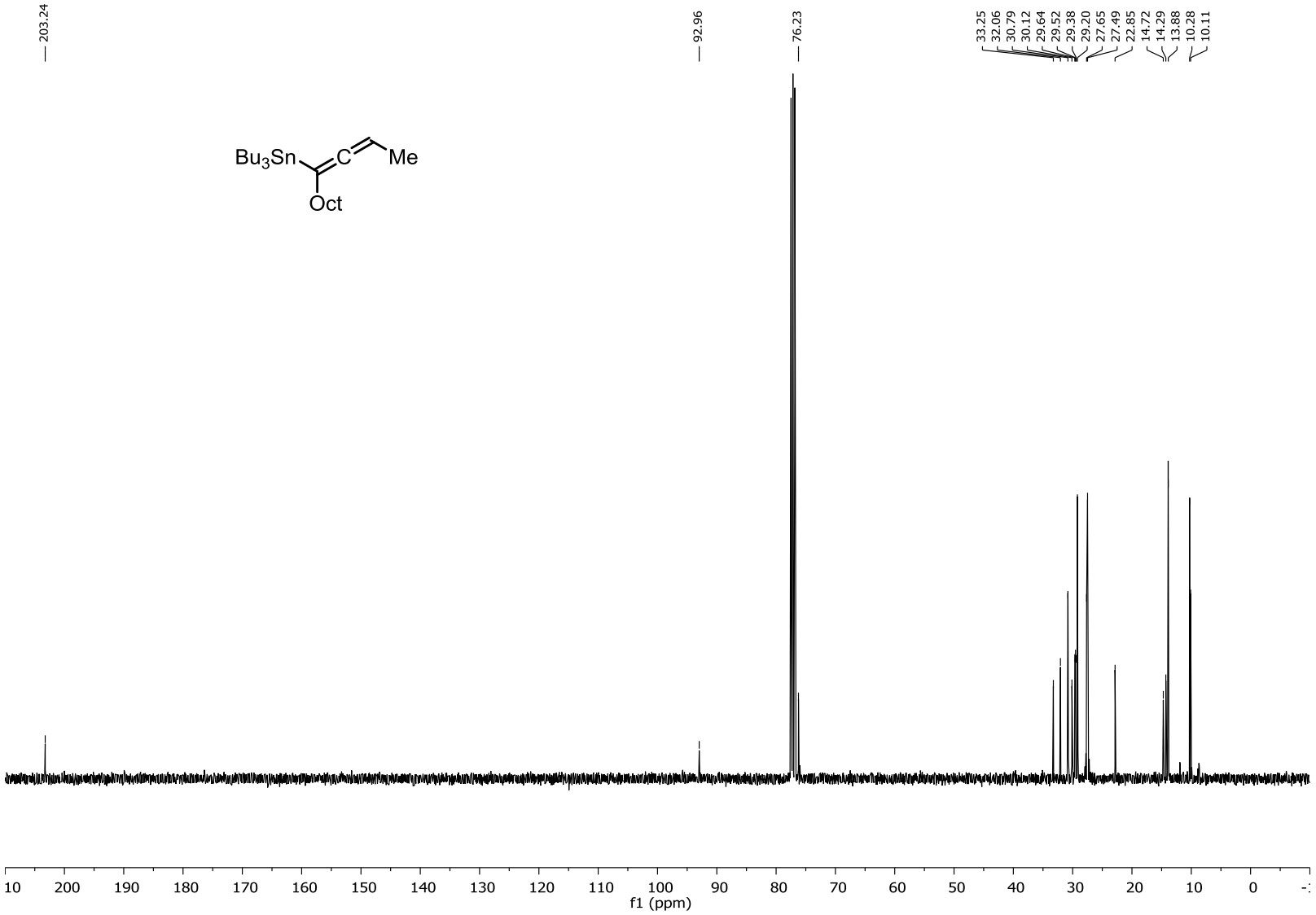
4-(3-hydroxy-3-methylbut-1-yn-1-yl)benzonitrile (S8)



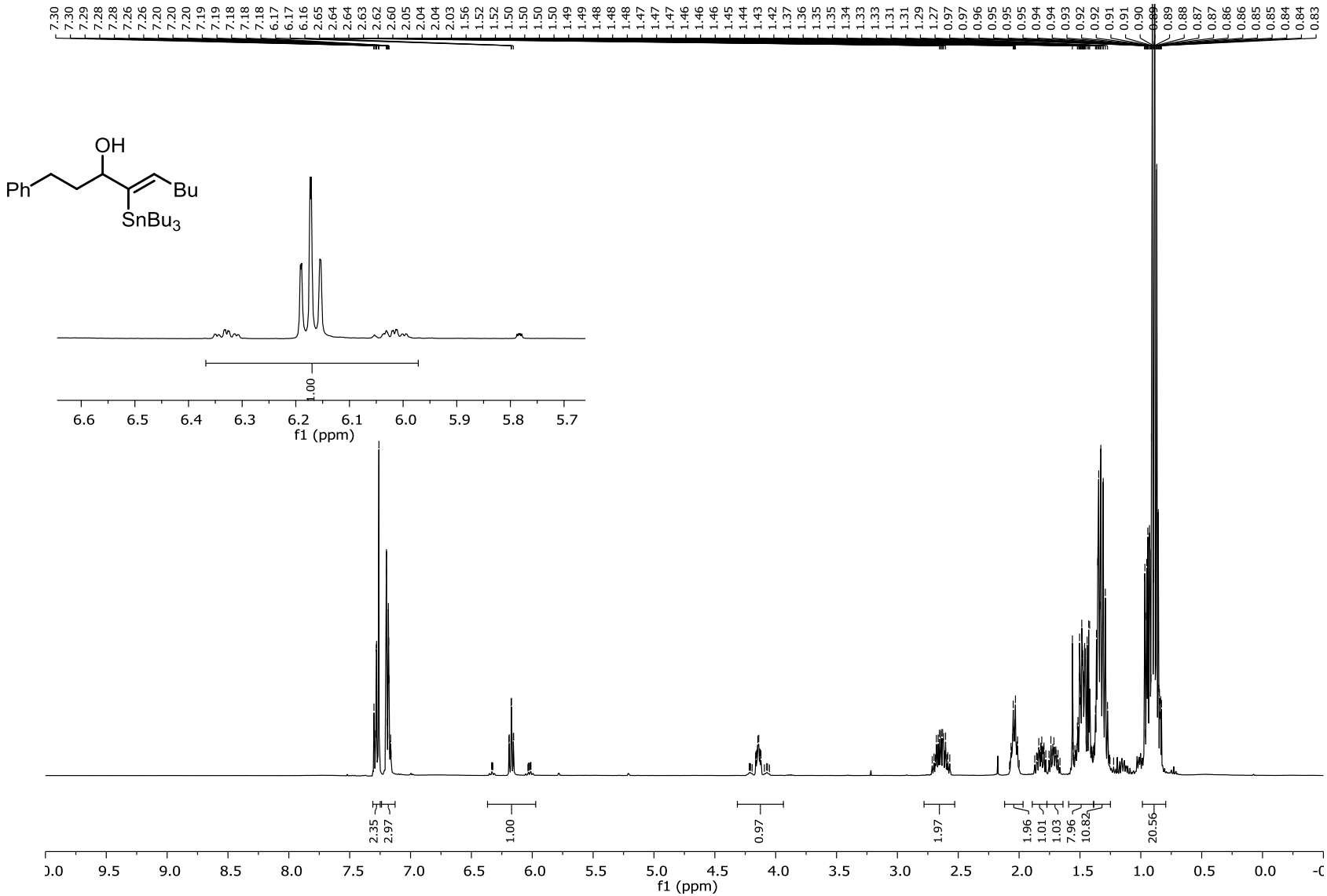
tributyl(dodeca-2,3-dien-4-yl)stannane (S9)



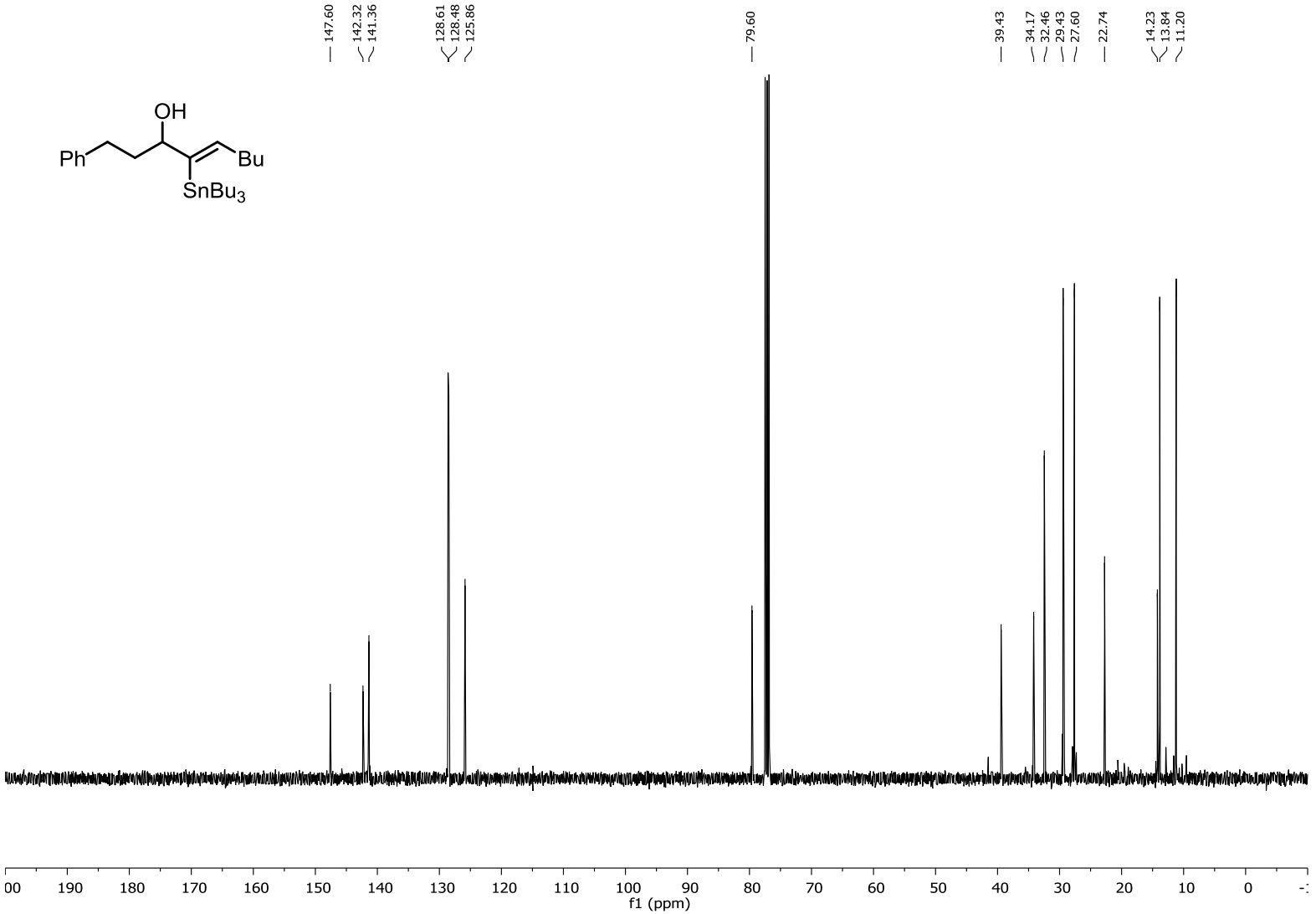
tributyl(dodeca-2,3-dien-4-yl)stannane (S9)



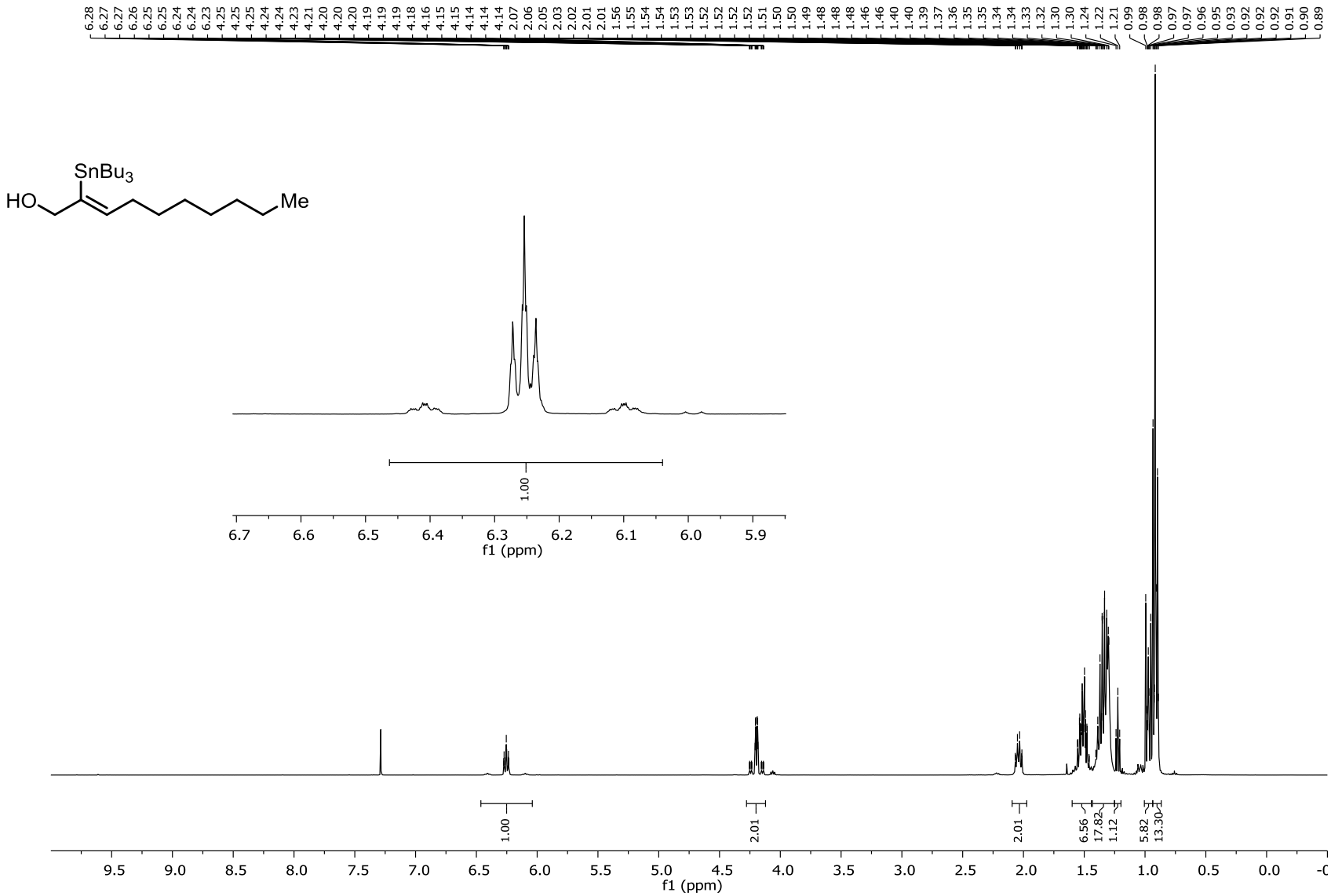
(Z)-1-Phenyl-4-(tributylstannyl)non-4-en-3-ol (1)



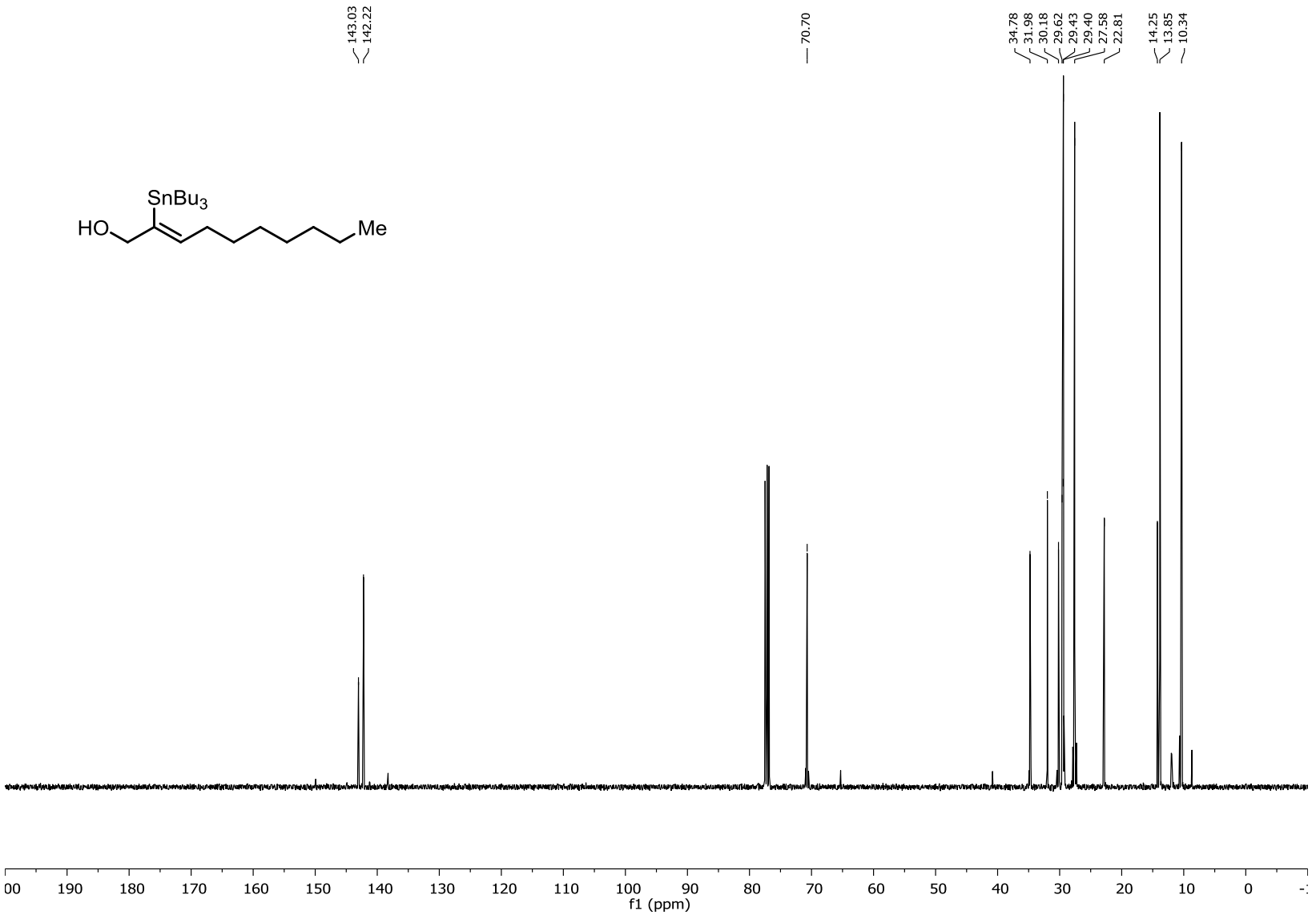
(Z)-1-Phenyl-4-(tributylstannyl)non-4-en-3-ol (1)



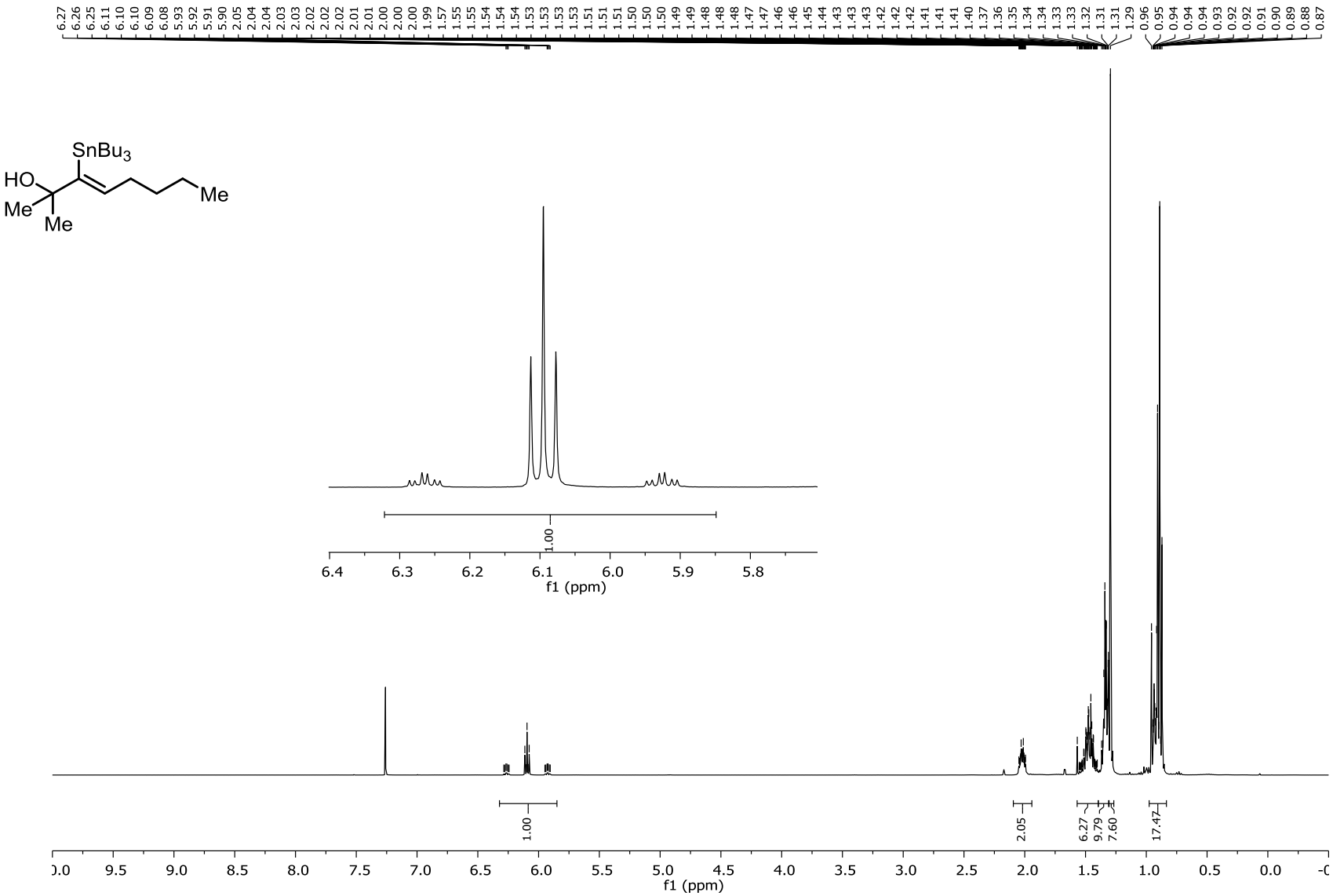
(Z)-2-(tributylstannyl)dec-2-en-1-ol (S10)



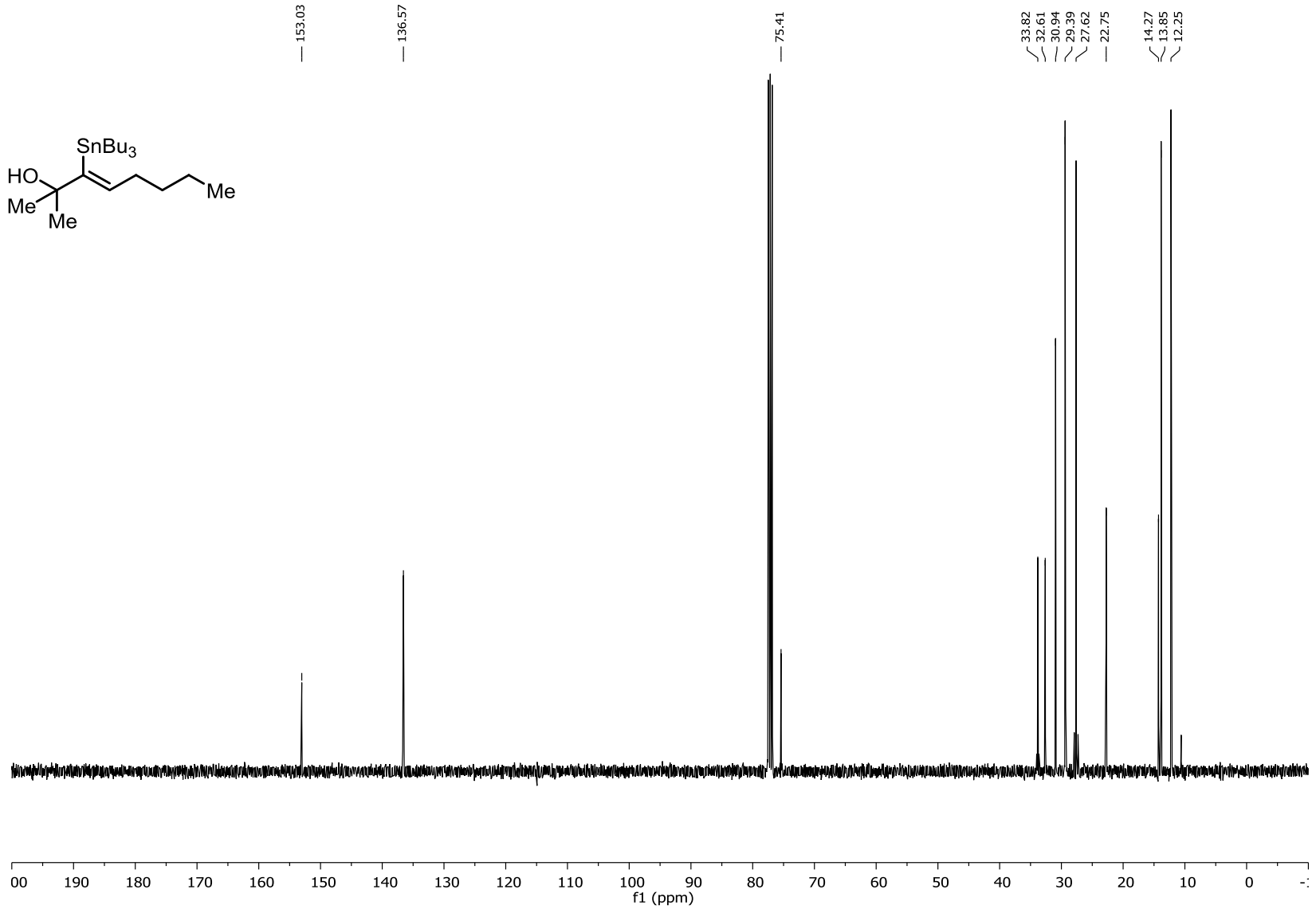
(Z)-2-(tributylstannyl)dec-2-en-1-ol (S10)



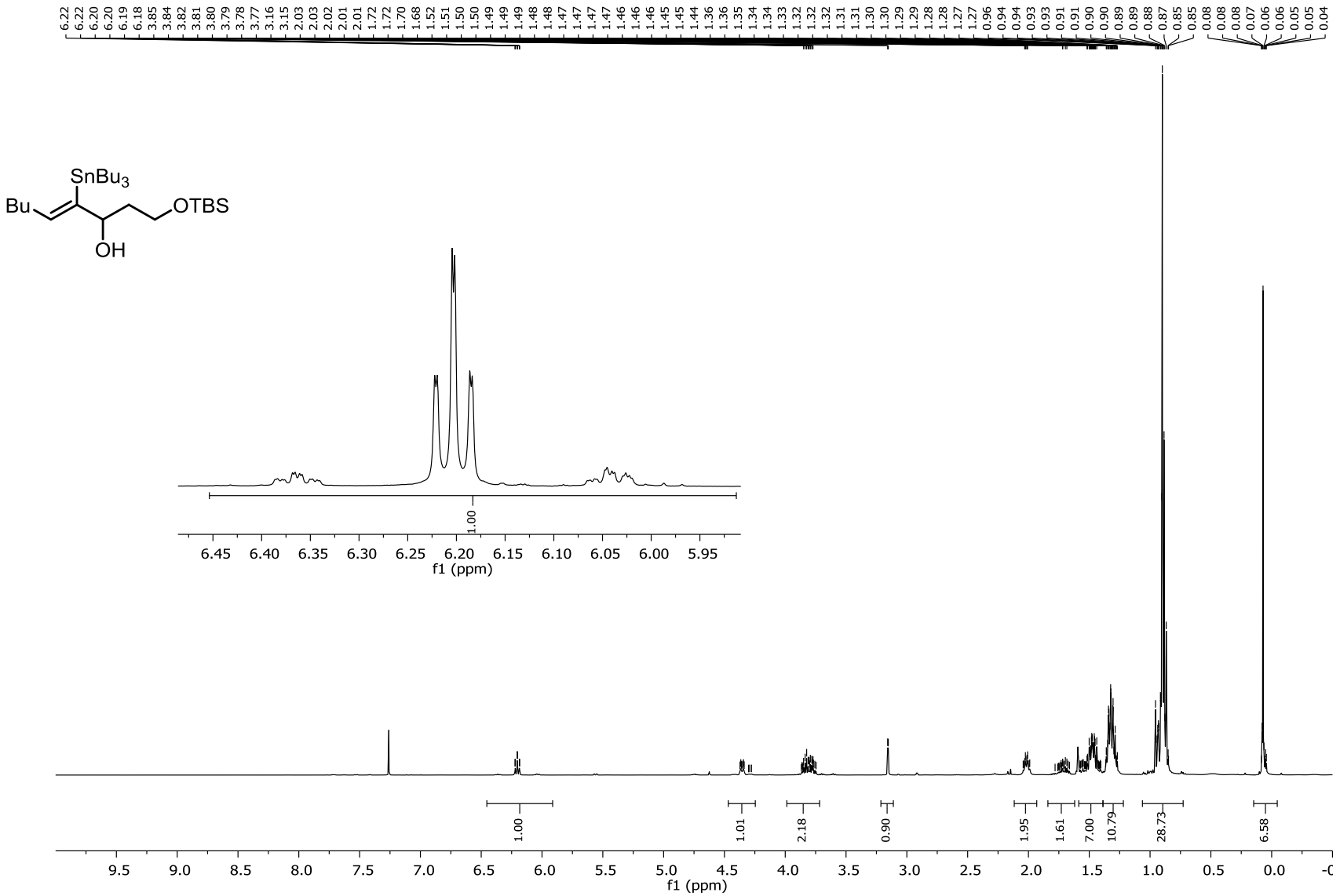
(Z)-2-methyl-3-(tributylstannyl)oct-3-en-2-ol (S11)



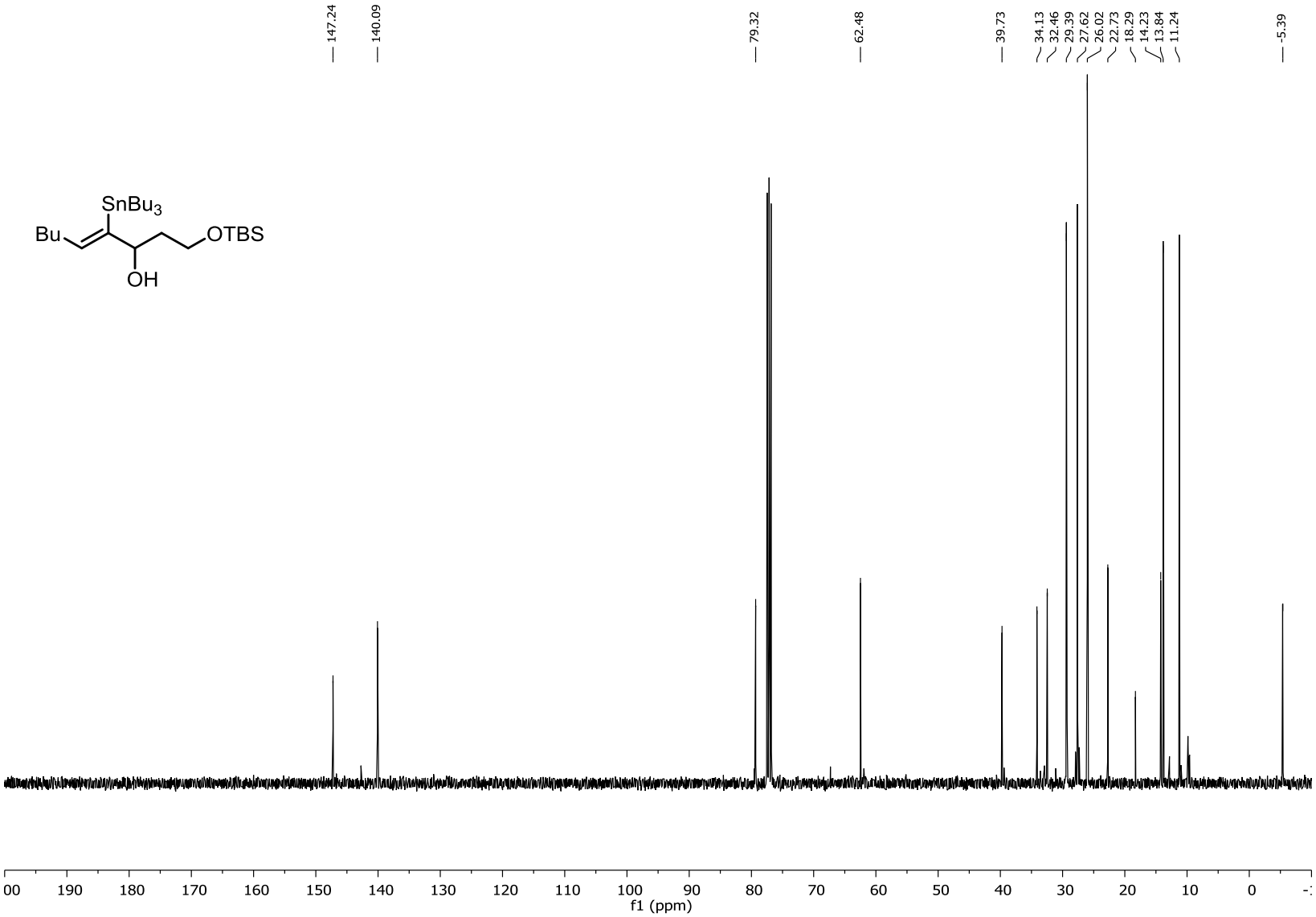
(Z)-2-methyl-3-(tributylstannyl)oct-3-en-2-ol (S11)



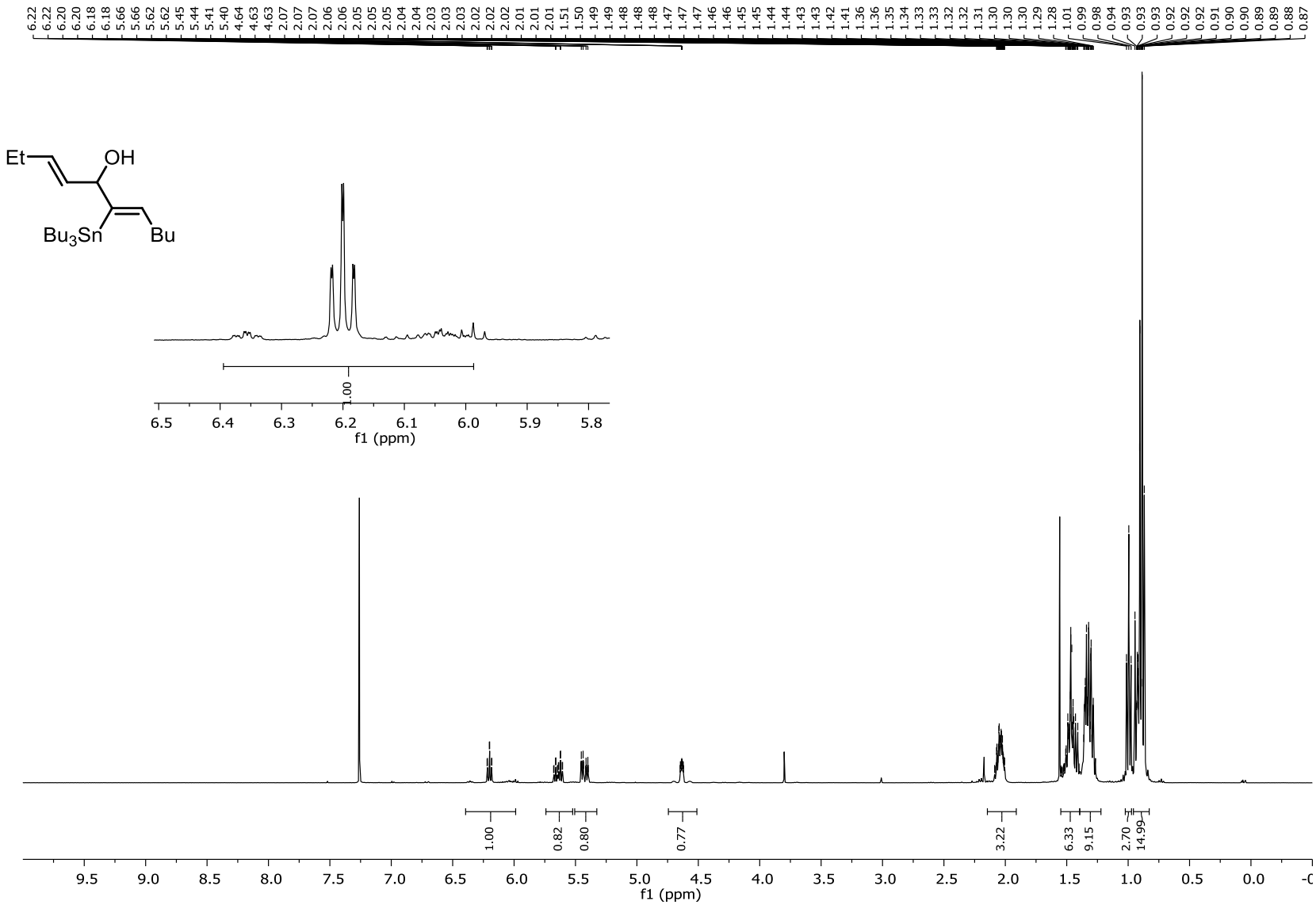
(Z)-1-((tert-butyldimethylsilyl)oxy)-4-(tributylstannyl)non-4-en-3-ol (S12)



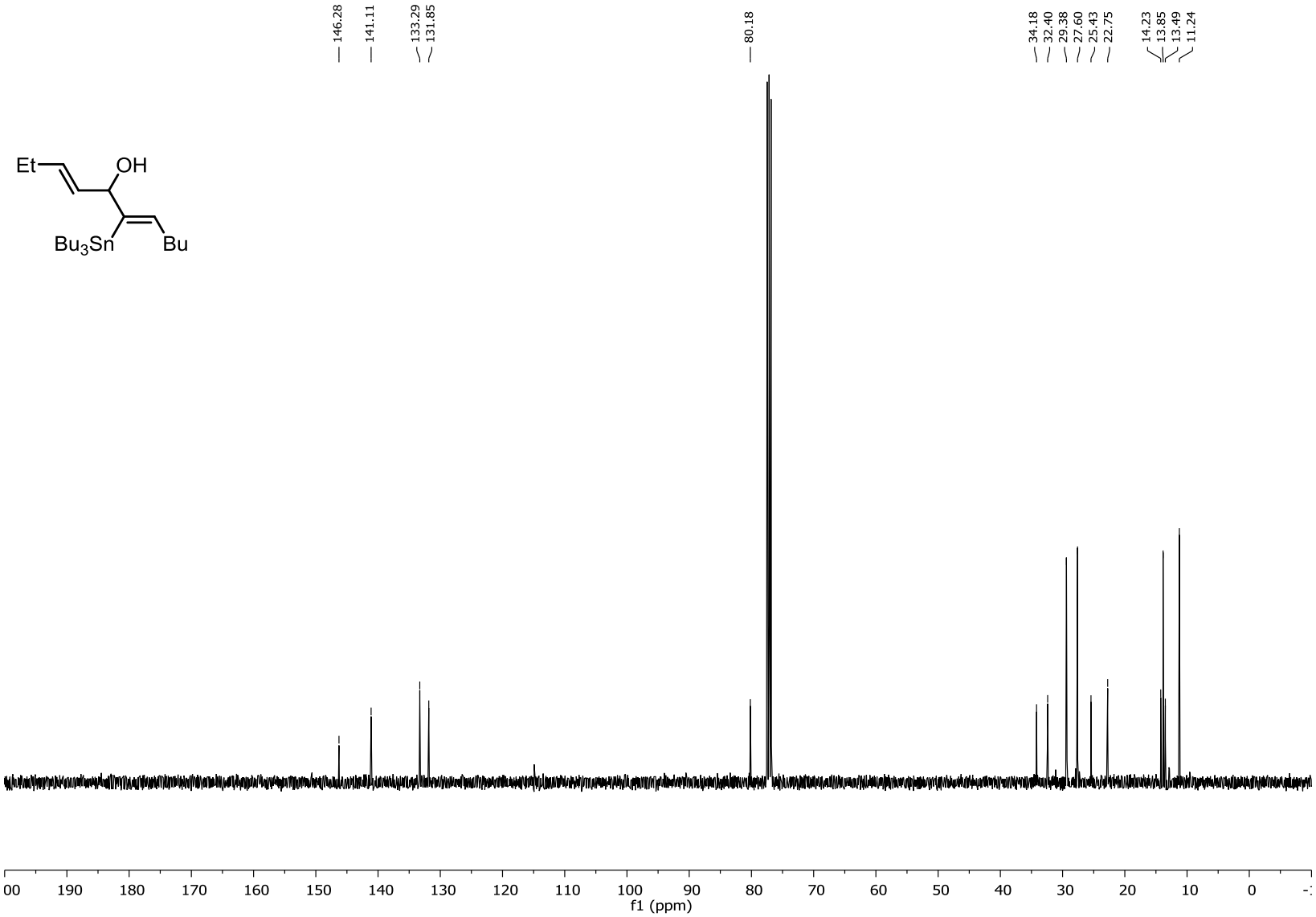
(Z)-1-((tert-butyldimethylsilyl)oxy)-4-(tributylstannyl)non-4-en-3-ol (S12)



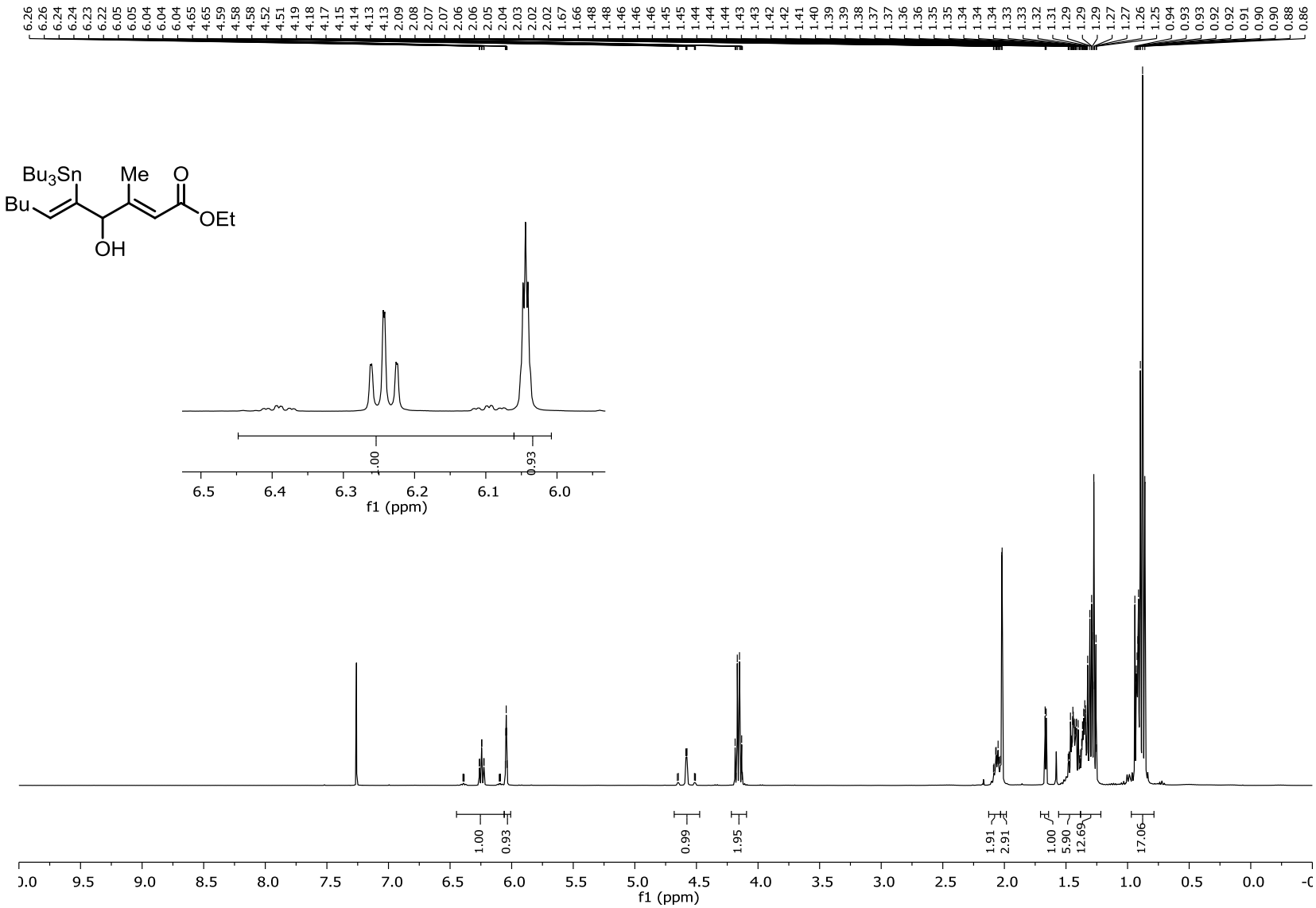
(3E,6Z)-6-(tributylstannyl)undeca-3,6-dien-5-ol (S13)



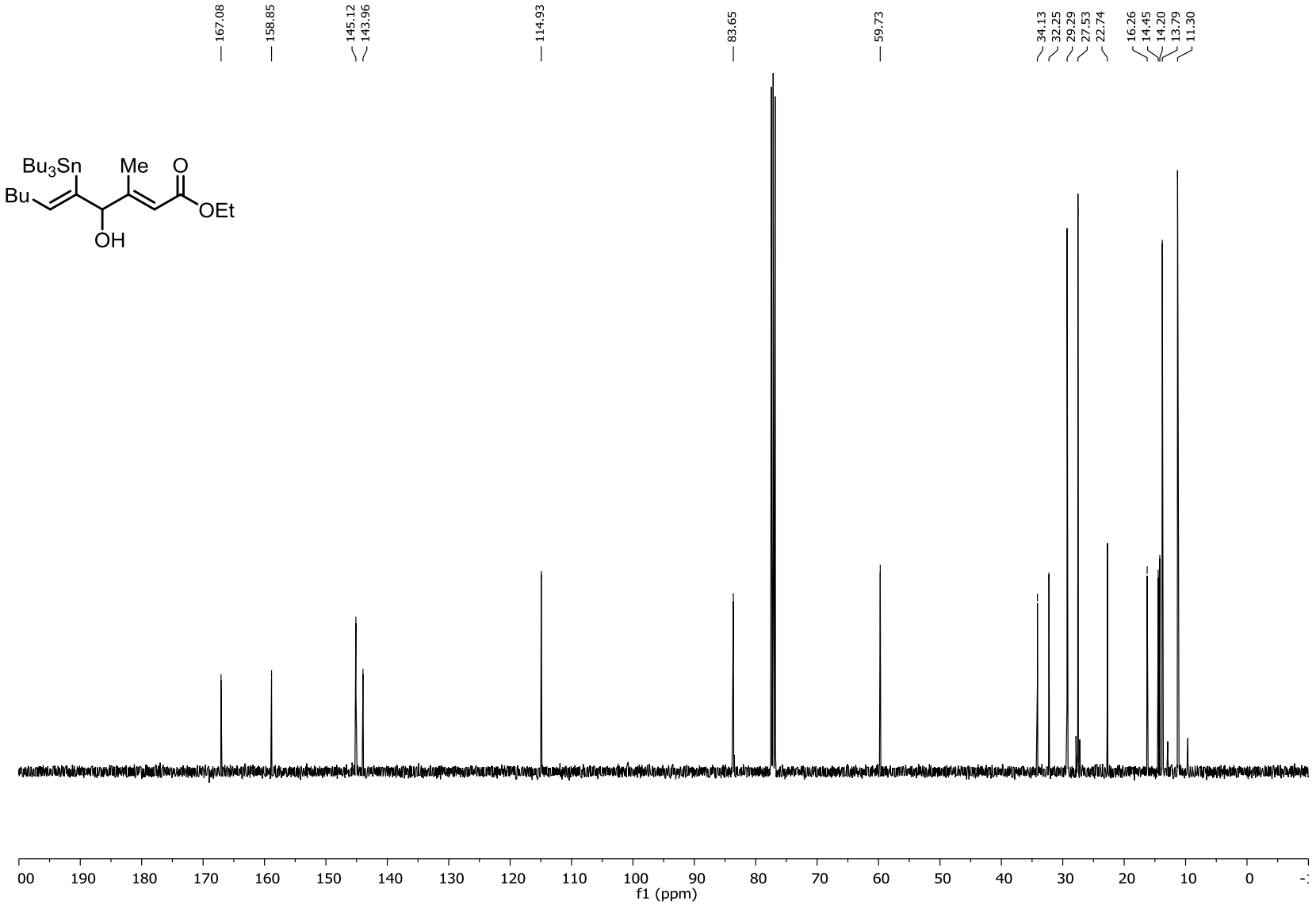
(3E,6Z)-6-(tributylstannyl)undeca-3,6-dien-5-ol (S13)



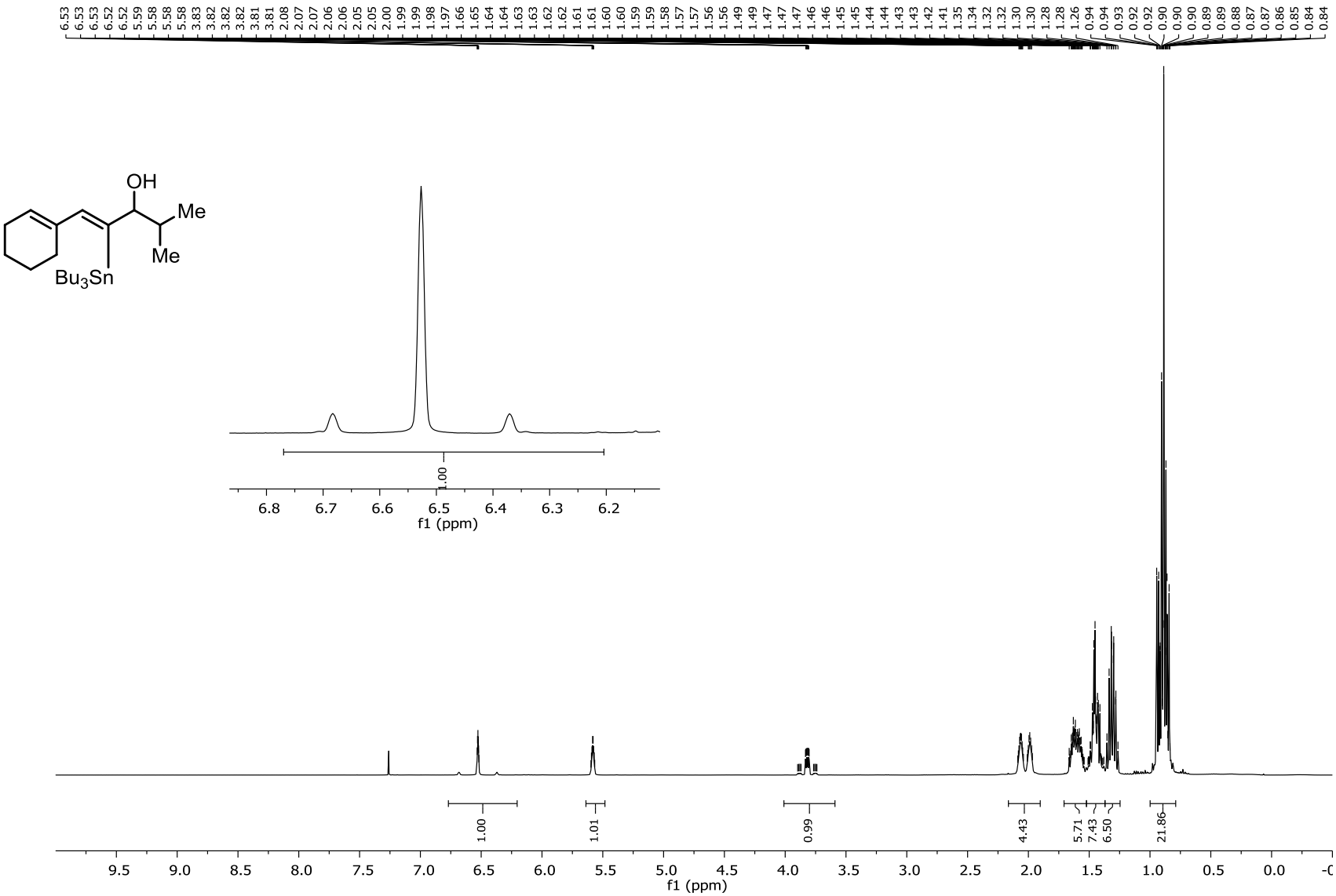
ethyl (2E,5Z)-4-hydroxy-3-methyl-5-(tributylstannyl)deca-2,5-dienoate (S14)



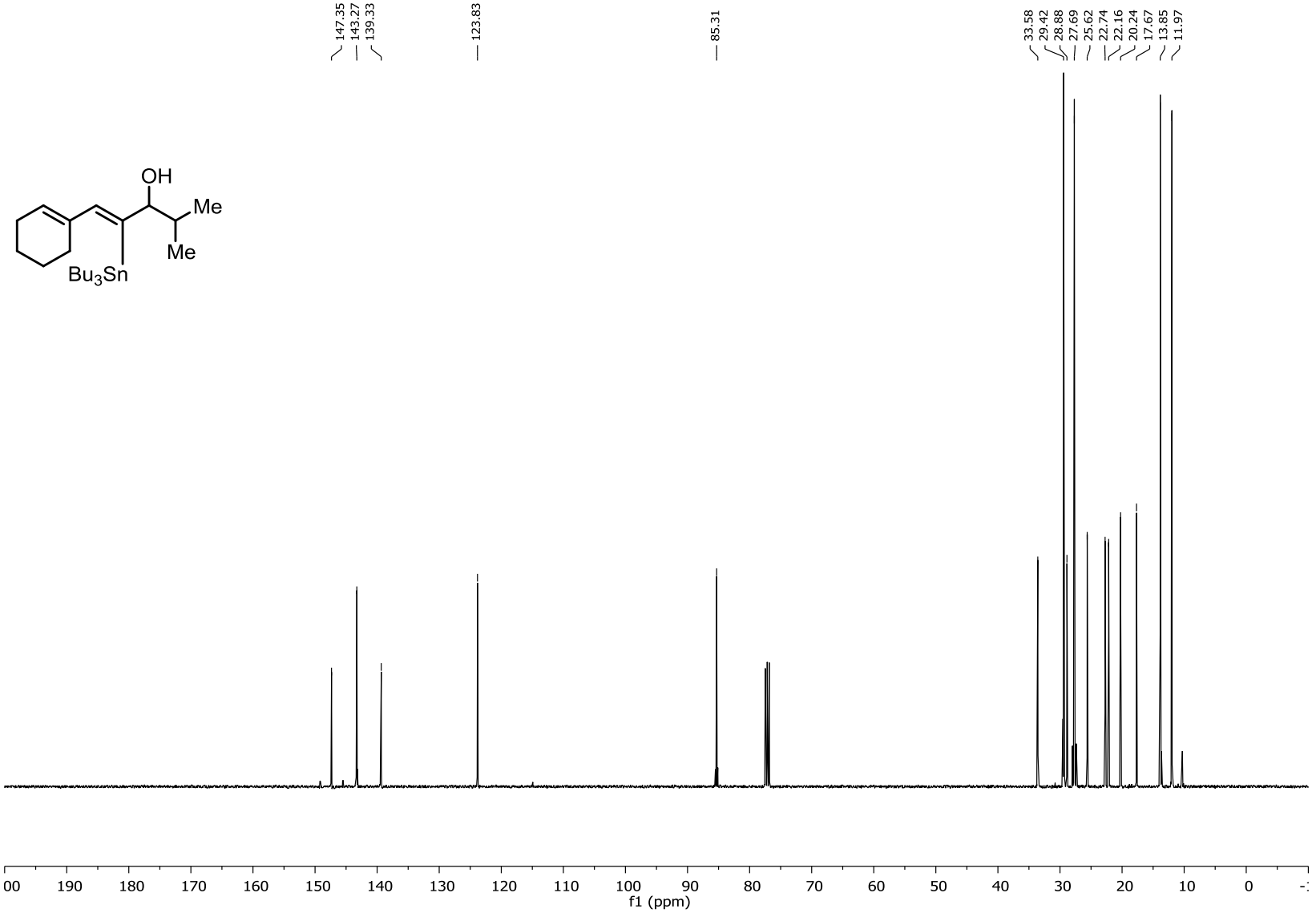
ethyl (2E,5Z)-4-hydroxy-3-methyl-5-(tributylstannyl)deca-2,5-dienoate (S14)



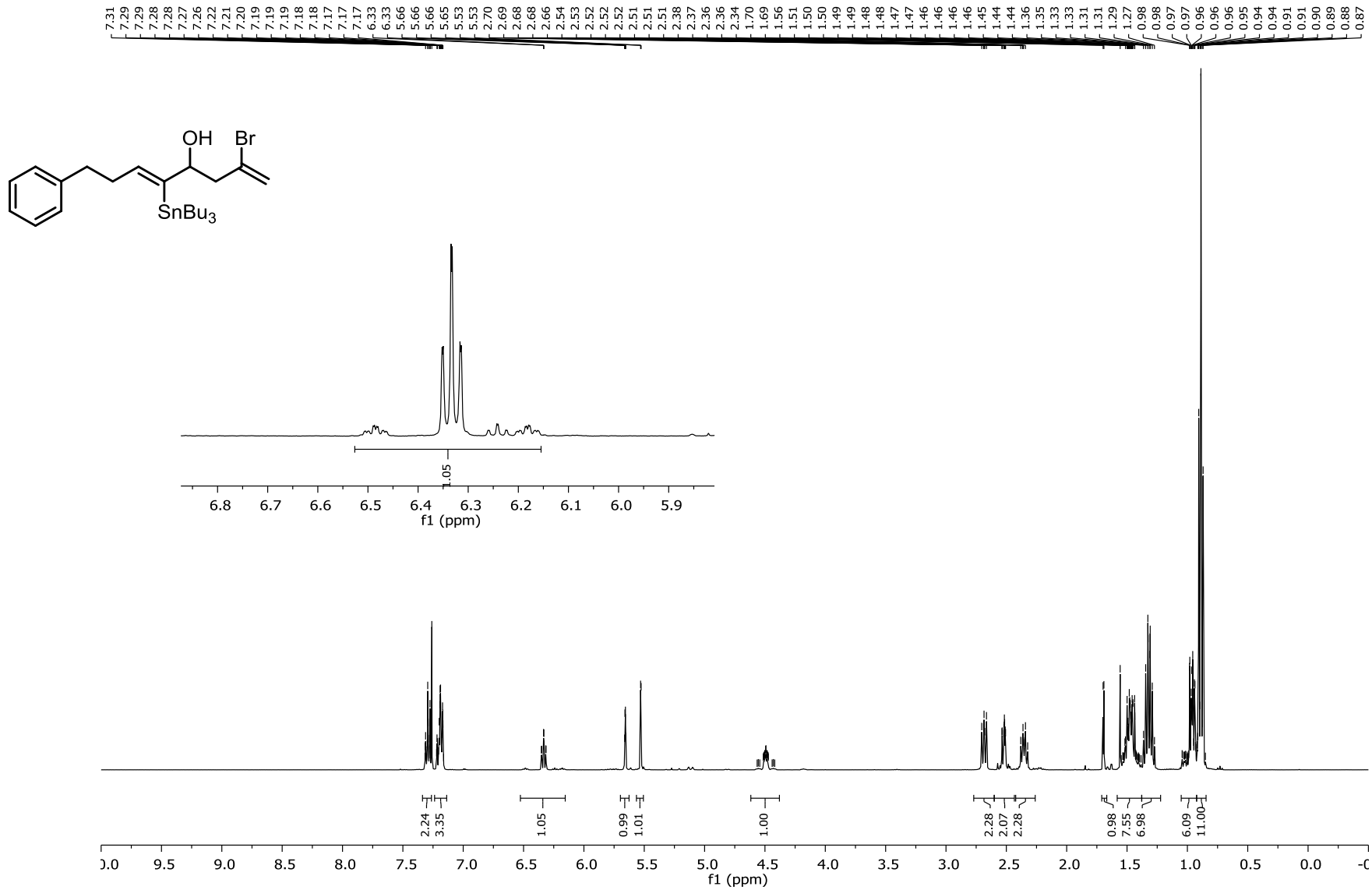
(Z)-1-(cyclohex-1-en-1-yl)-4-methyl-2-(tributylstannyl)pent-1-en-3-ol (S15)



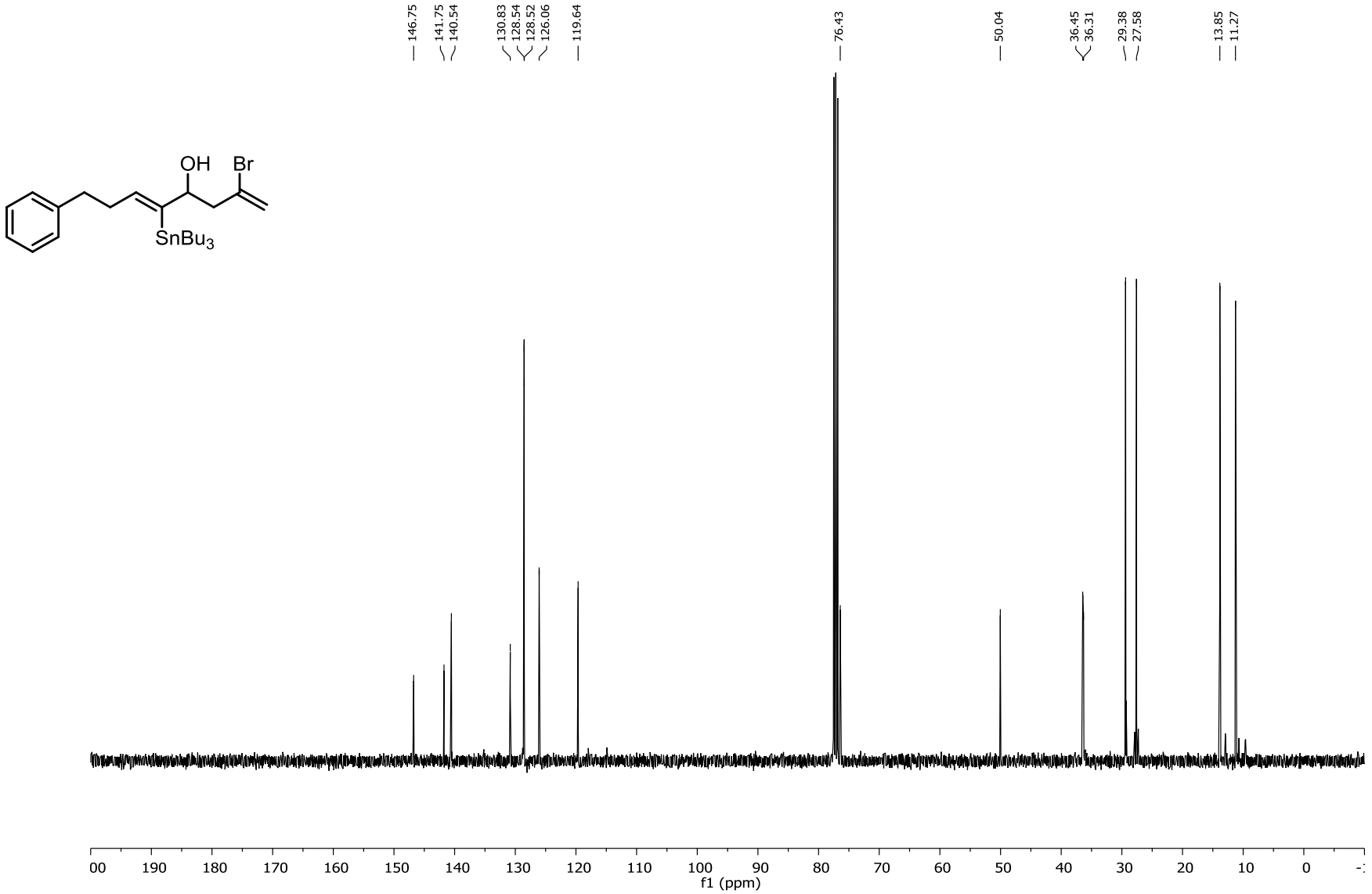
(Z)-1-(cyclohex-1-en-1-yl)-4-methyl-2-(tributylstannyl)pent-1-en-3-ol (S15)



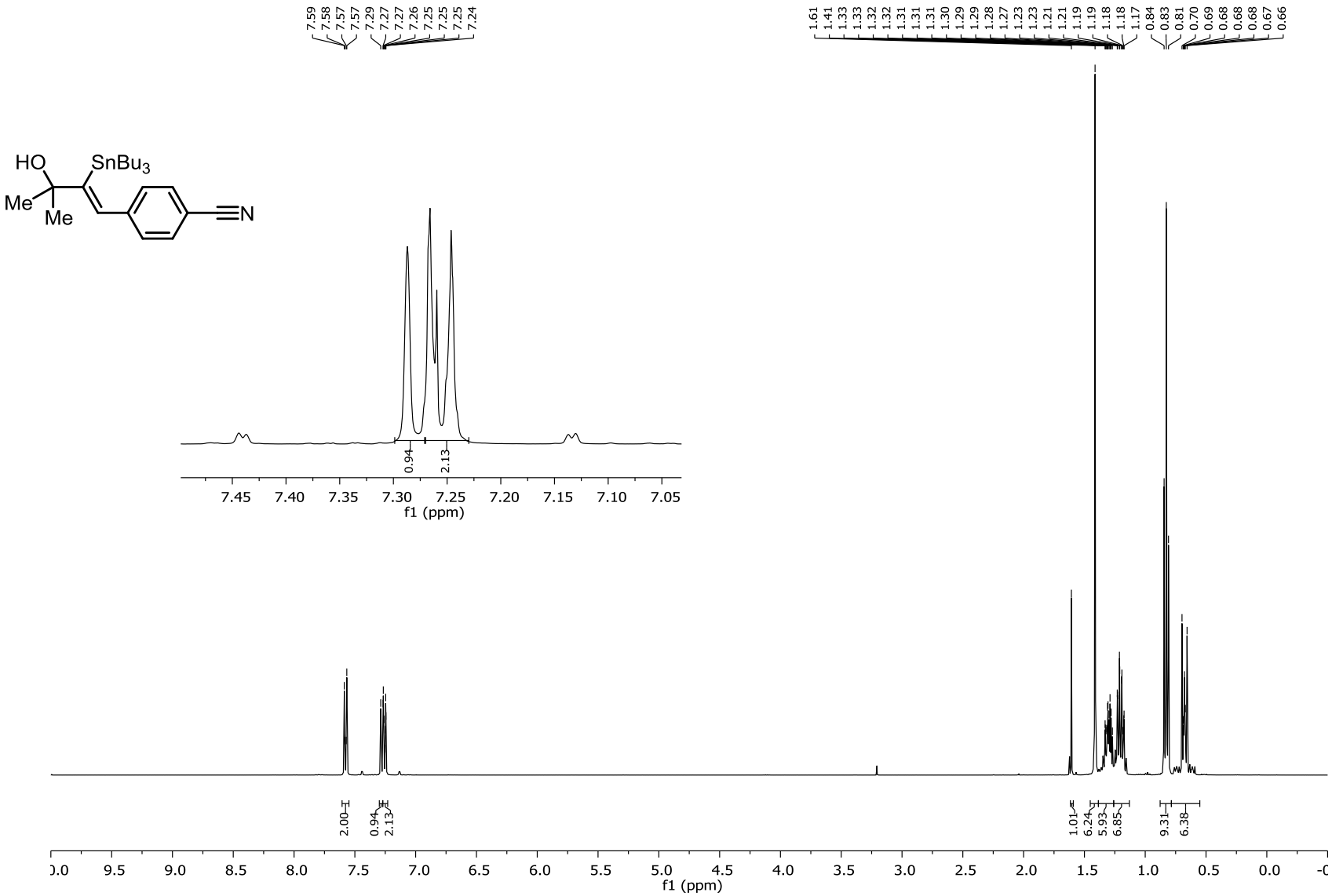
(Z)-2-bromo-8-phenyl-5-(tributylstannyl)octa-1,5-dien-4-ol (S16)



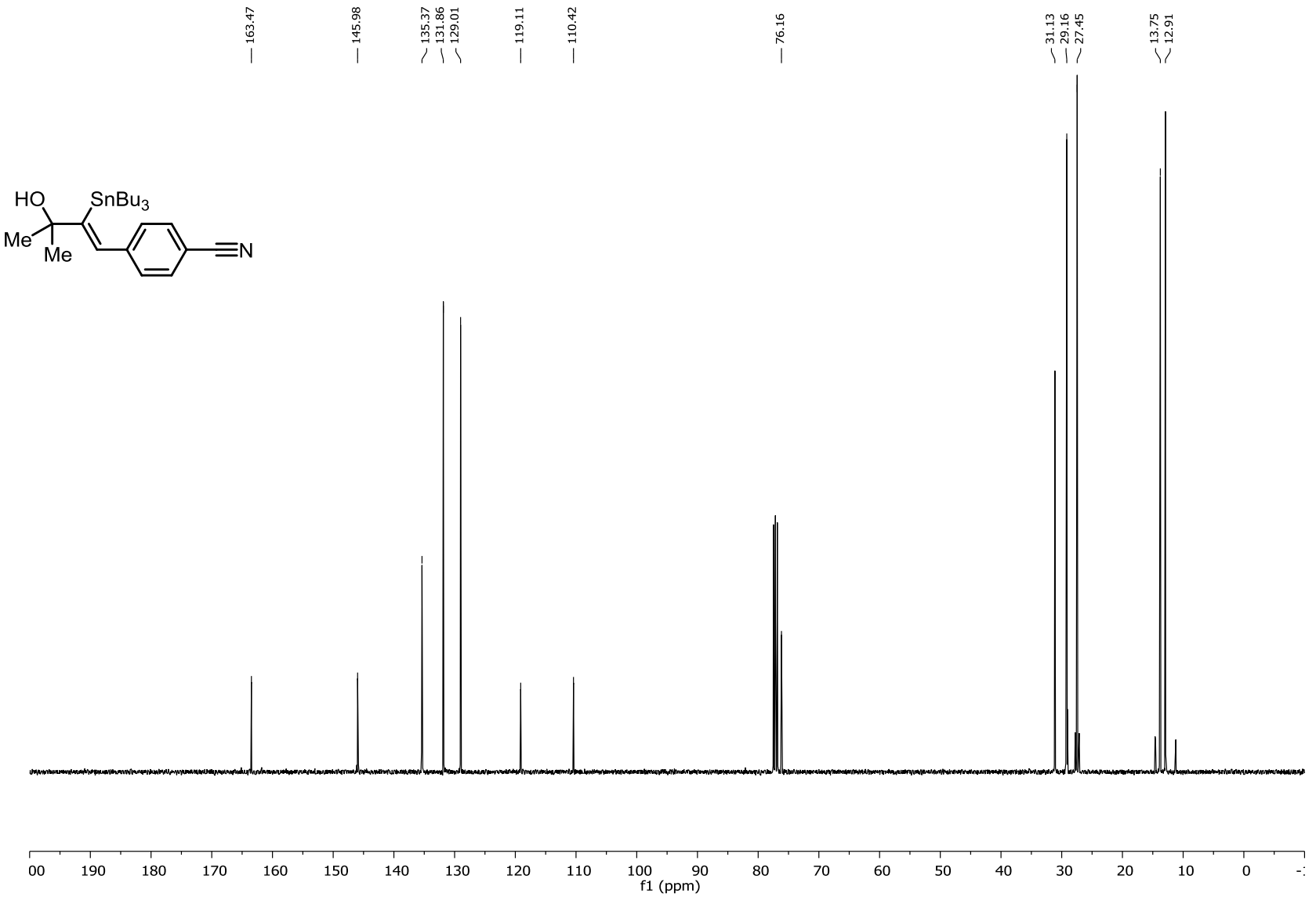
(Z)-2-bromo-8-phenyl-5-(tributylstannyl)octa-1,5-dien-4-ol (S16)



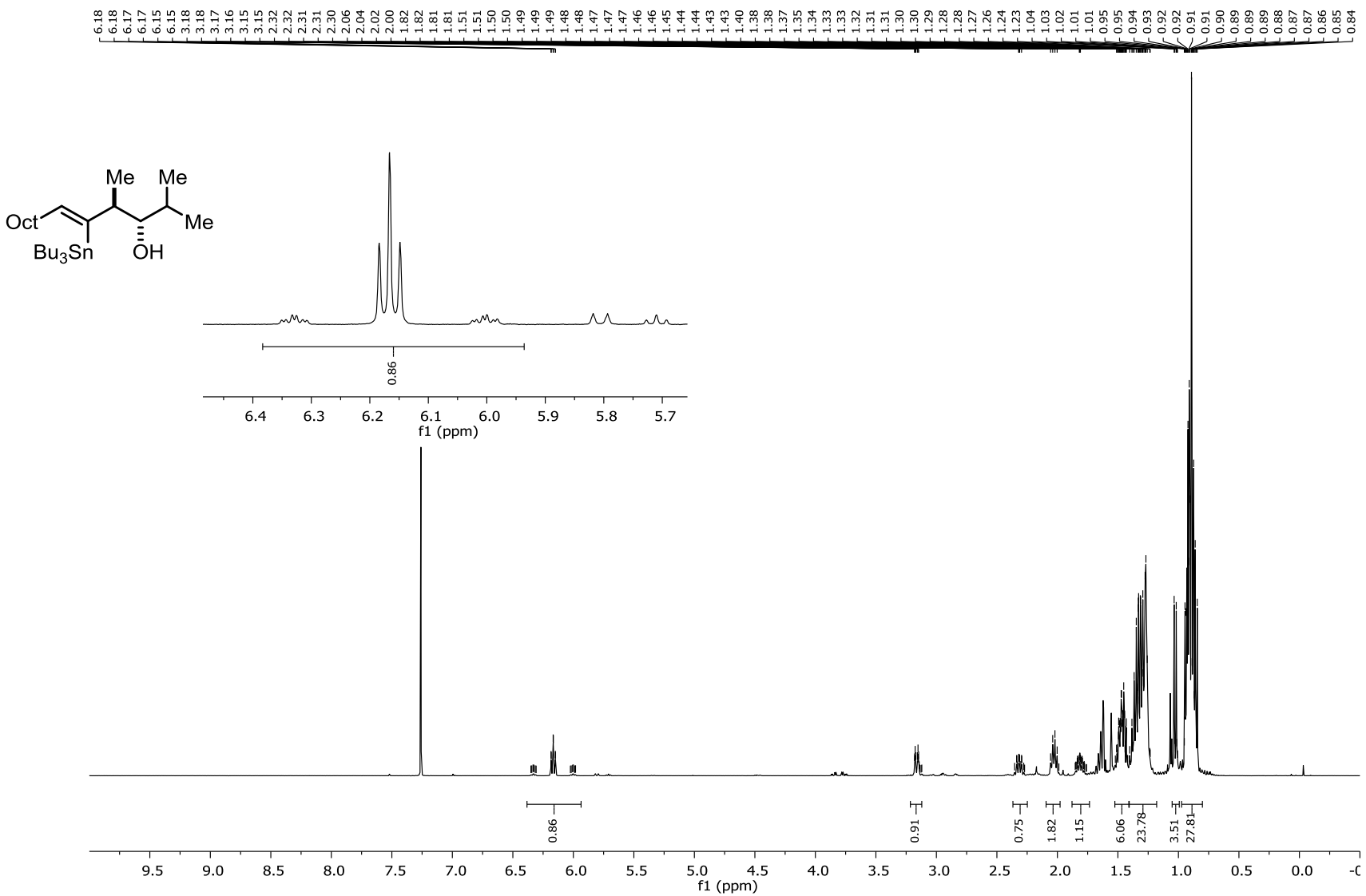
(Z)-4-(3-hydroxy-3-methyl-2-(tributylstannyl)but-1-en-1-yl)benzonitrile (S17)



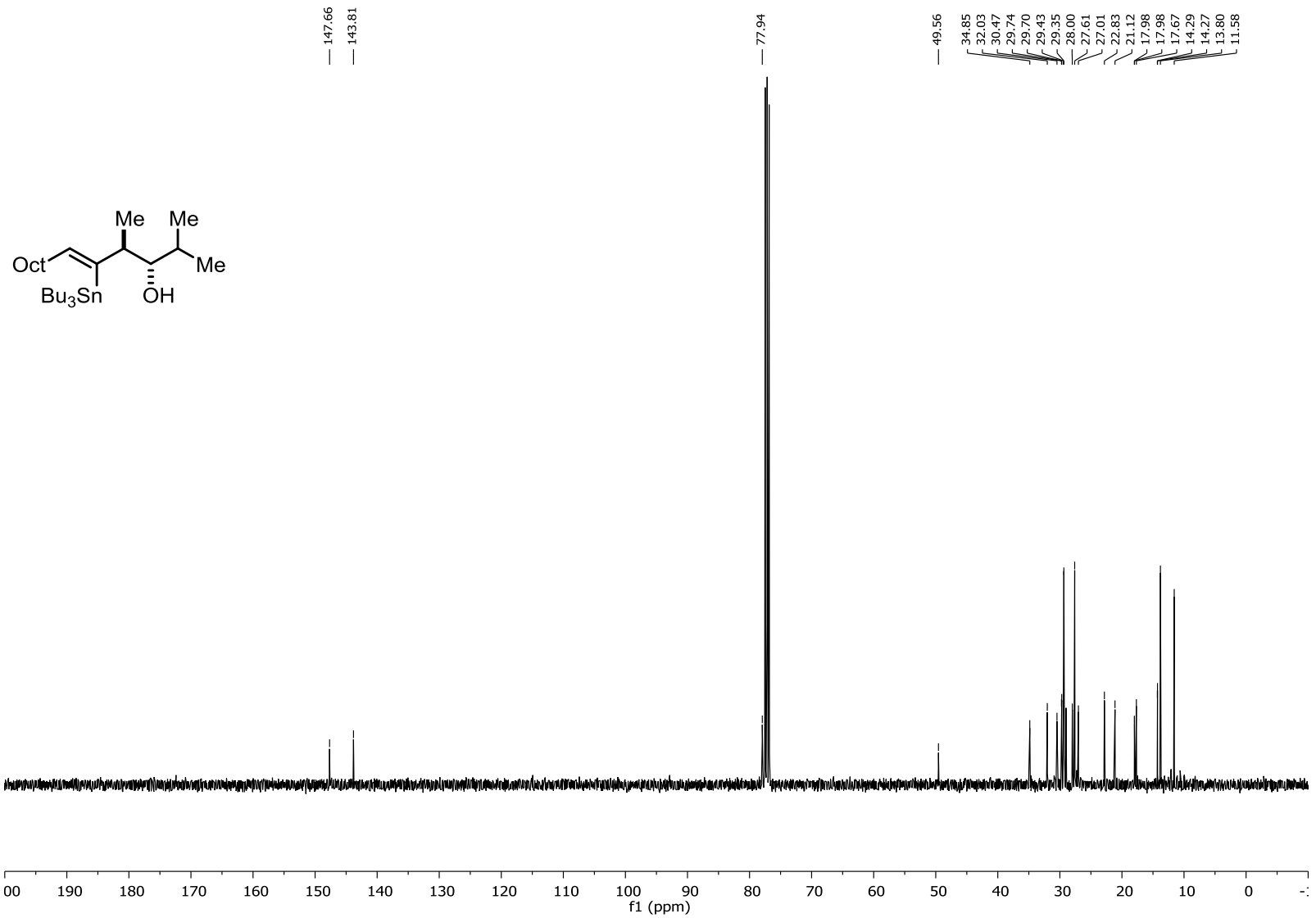
(Z)-4-(3-hydroxy-3-methyl-2-(tributylstannyl)but-1-en-1-yl)benzonitrile (S17)



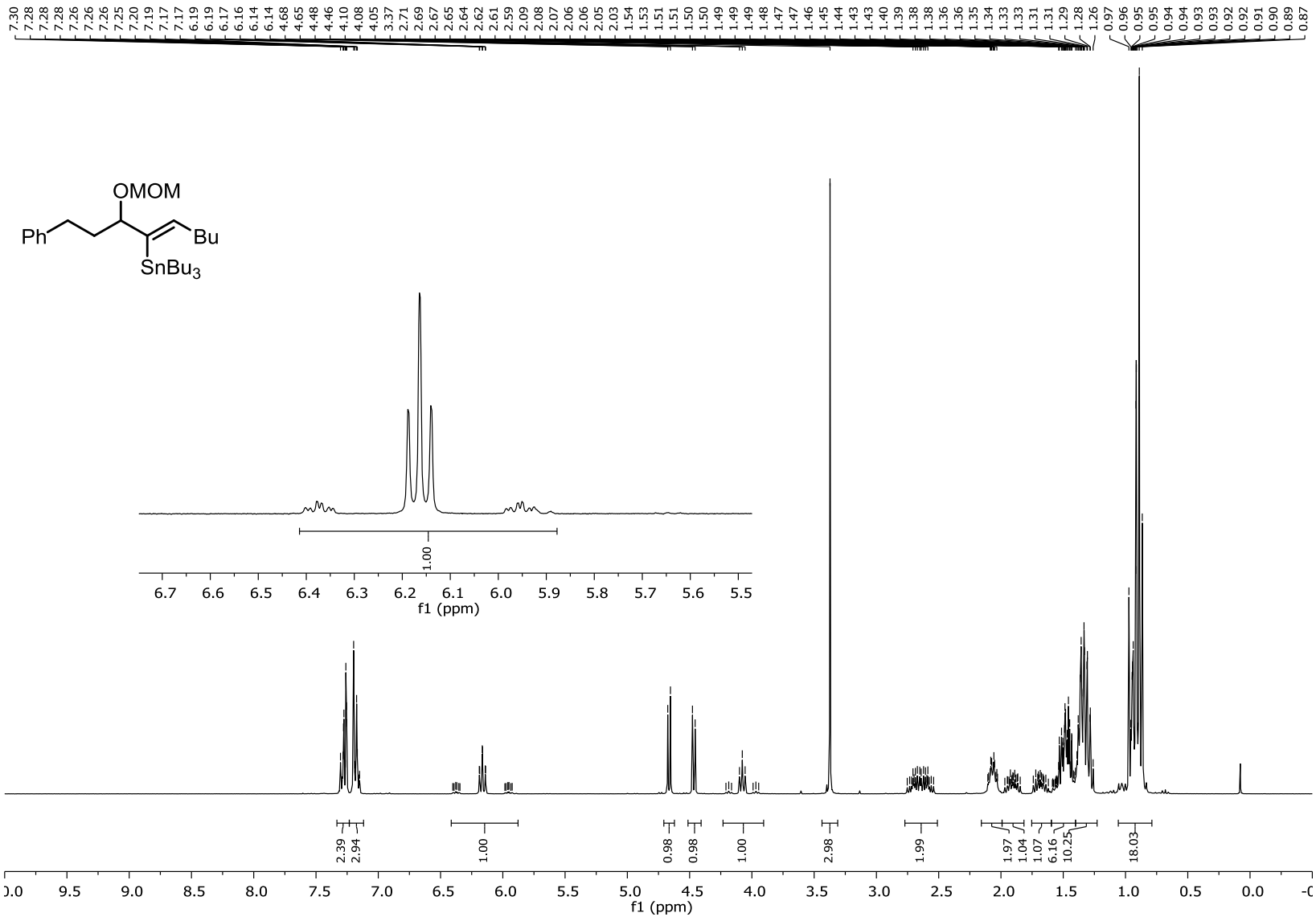
(anti,Z)-2,4-dimethyl-5-(tributylstannyl)tetradec-5-en-3-ol (S18)



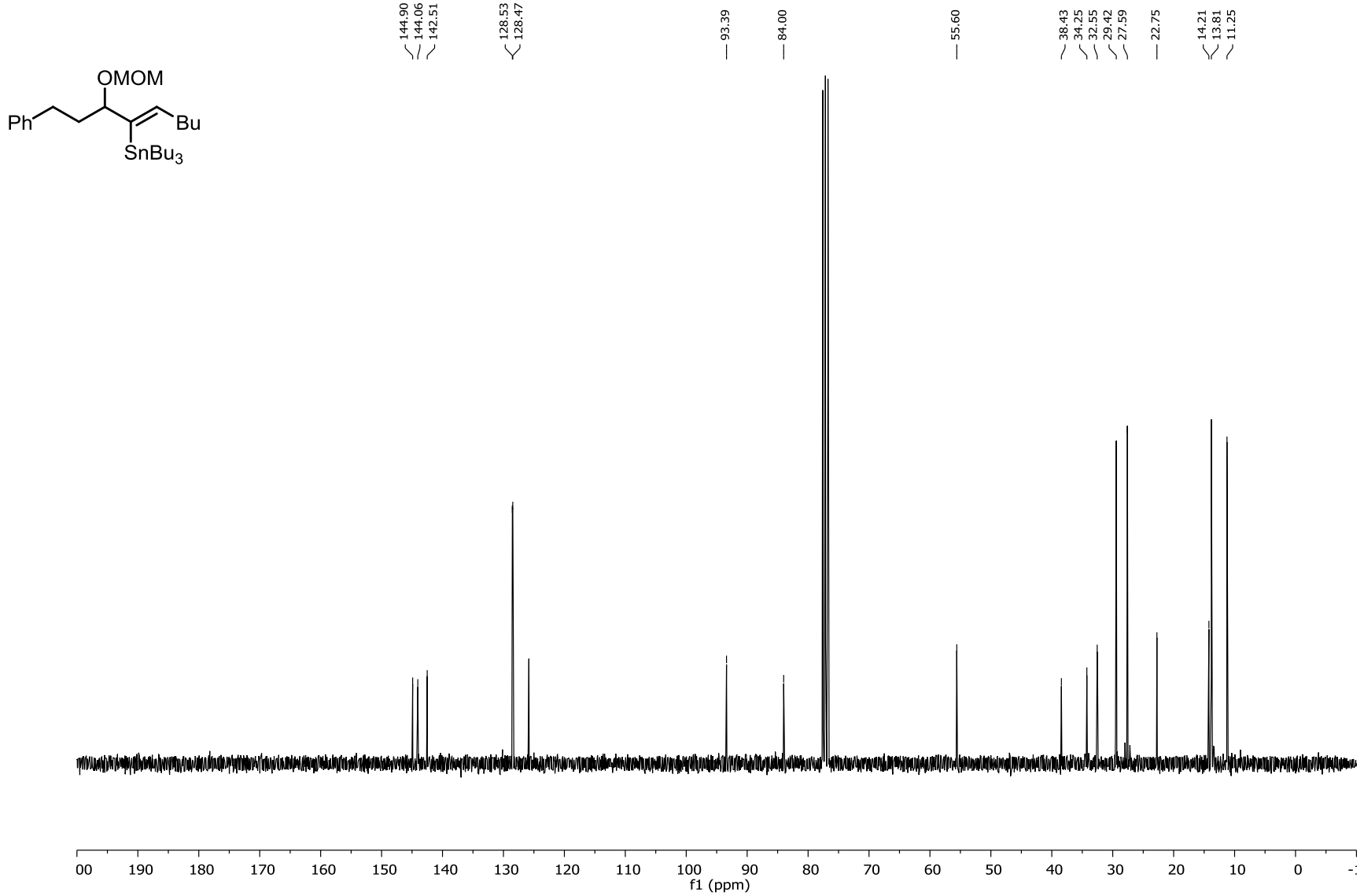
(anti,Z)-2,4-dimethyl-5-(tributylstannyl)tetradec-5-en-3-ol (S18)



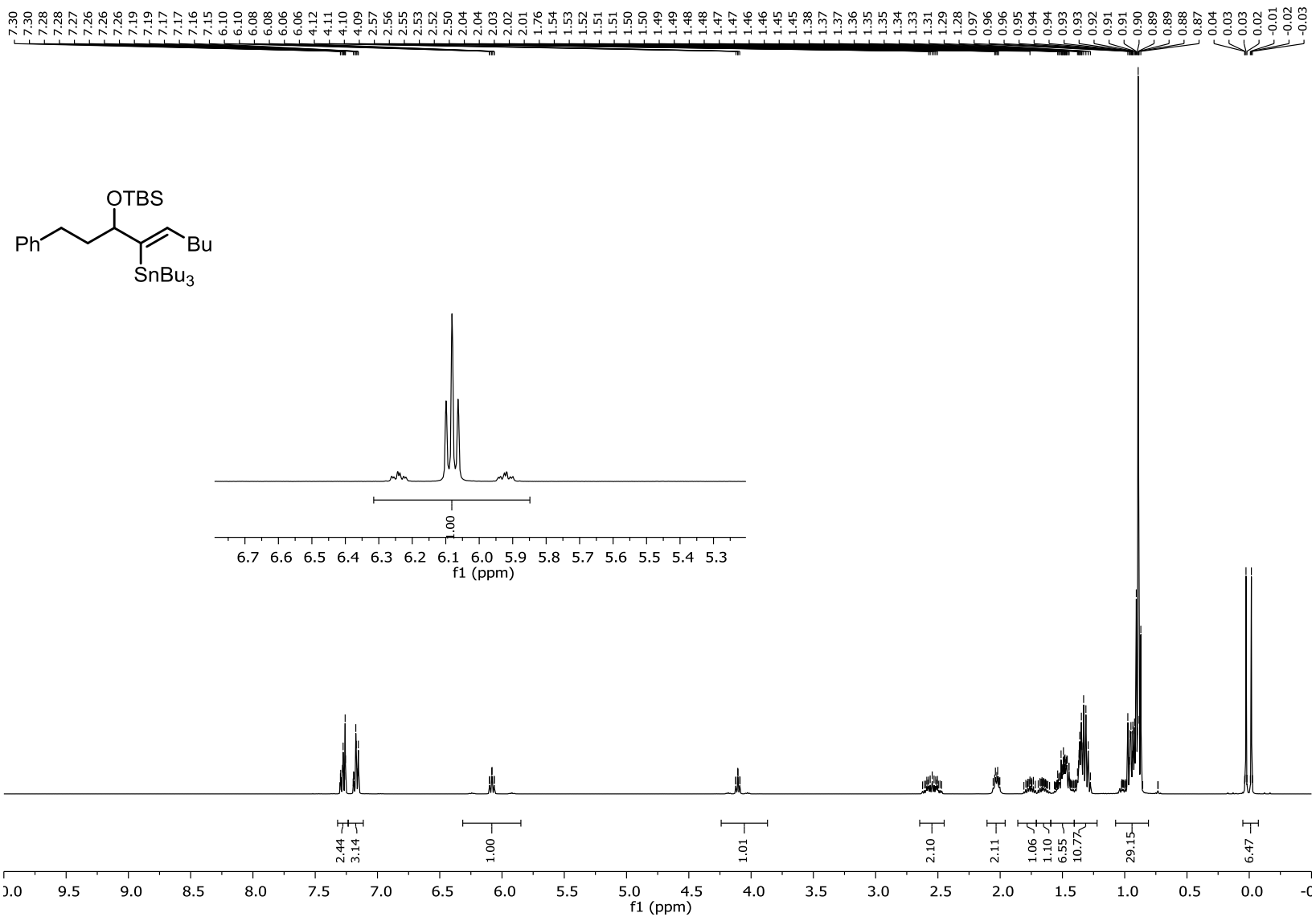
(Z)-tributyl(3-(methoxymethoxy)-1-phenylnon-4-en-4-yl)stannane (S19)



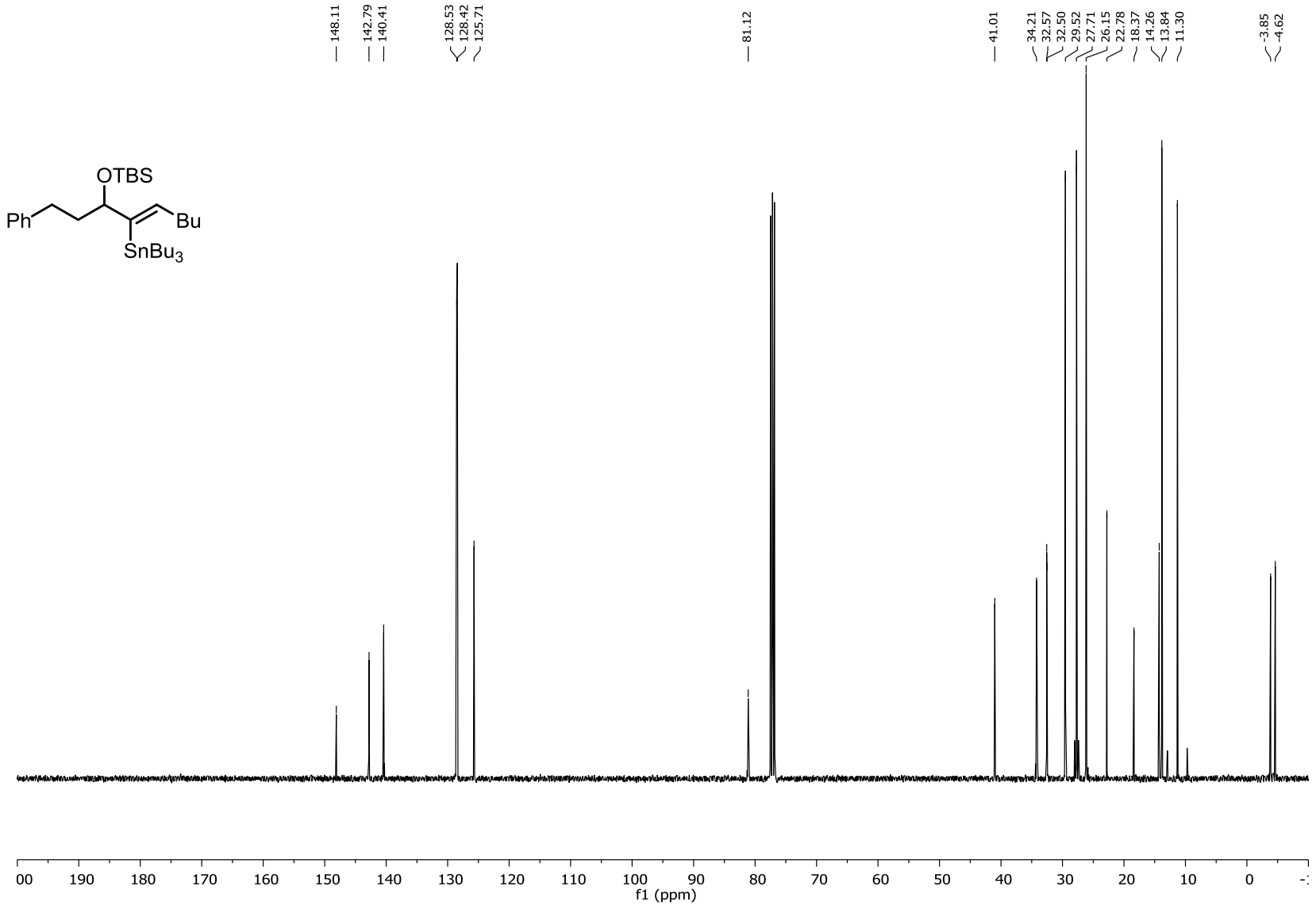
(Z)-tributyl(3-(methoxymethoxy)-1-phenylnon-4-en-4-yl)stannane (S19)



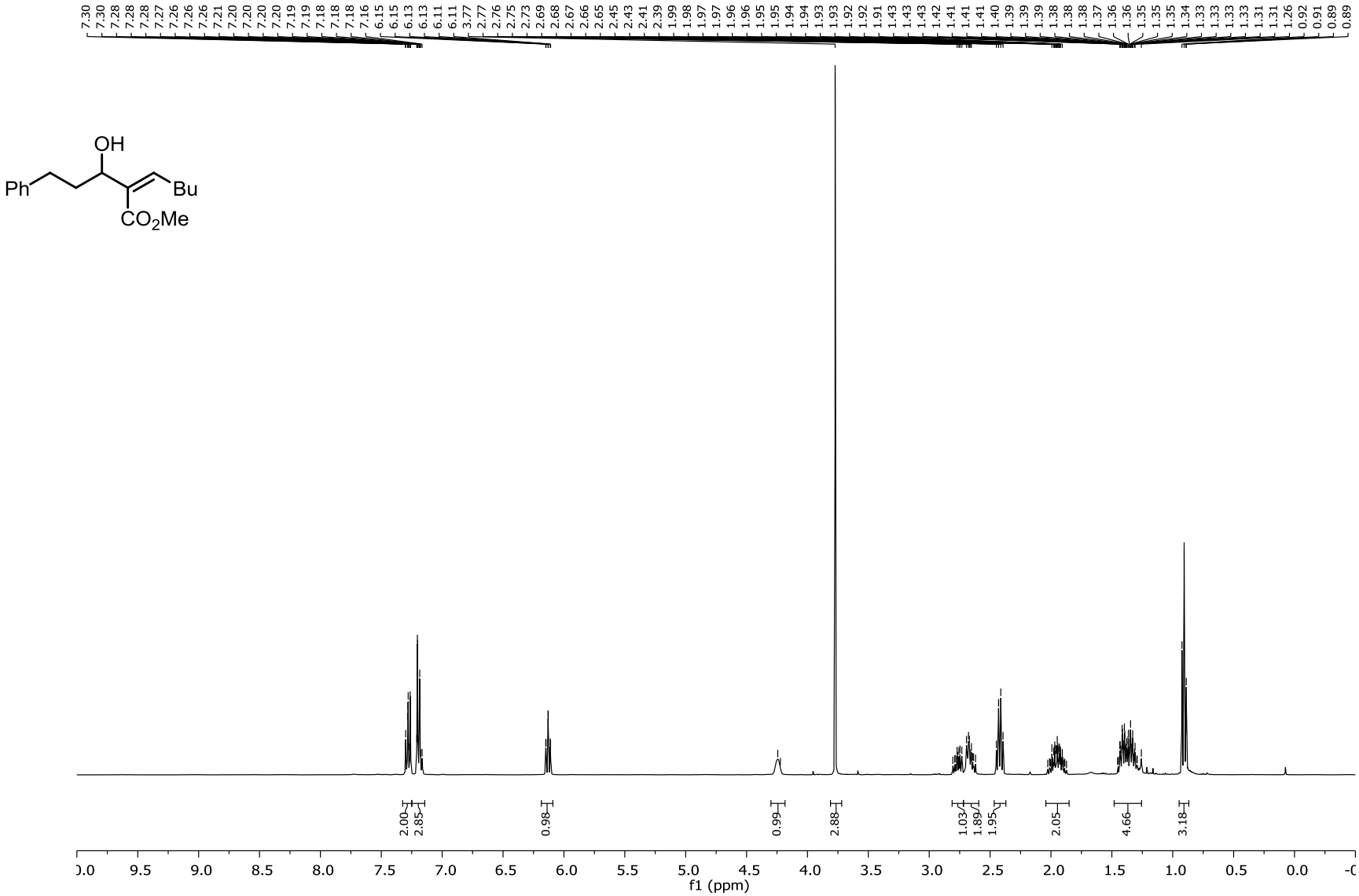
(Z)-tert-butyldimethyl((1-phenyl-4-(tributylstannyl)non-4-en-3-yl)oxy)silane (S20)



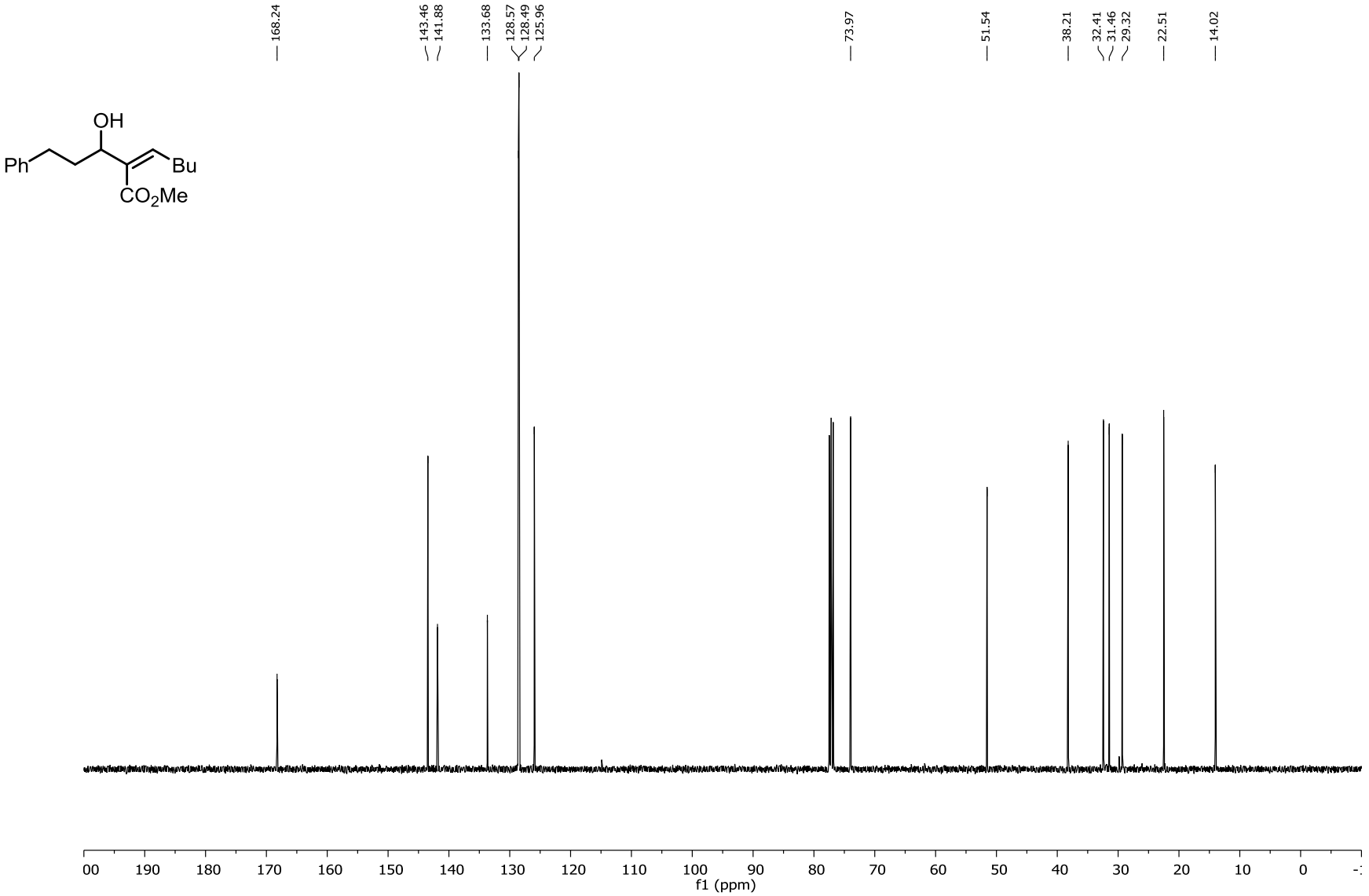
(Z)-tert-butyldimethyl((1-phenyl-4-(tributylstannyl)non-4-en-3-yl)oxy)silane (S20)



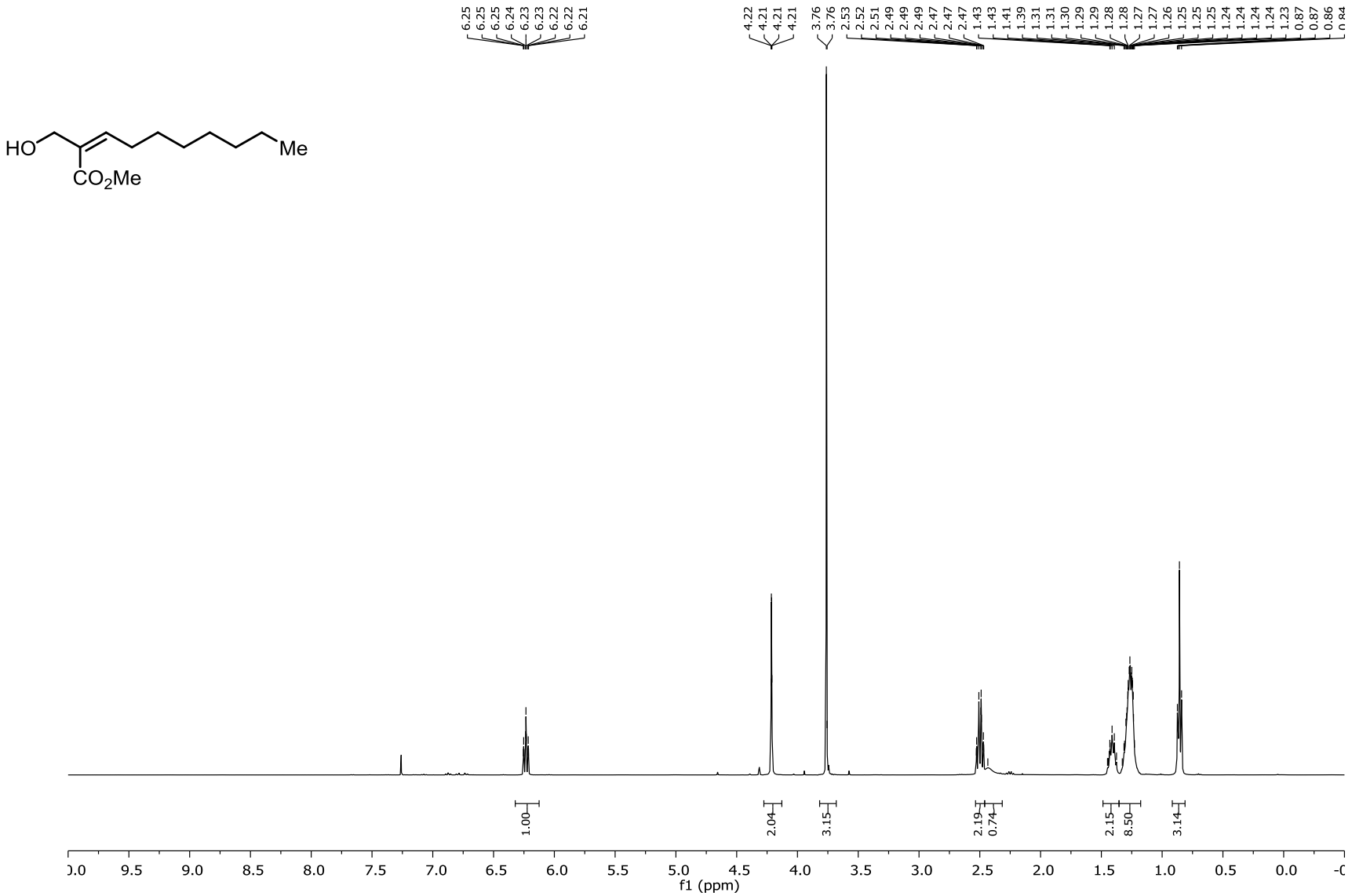
methyl (Z)-2-(1-hydroxy-3-phenylpropyl)hept-2-enoate (2)



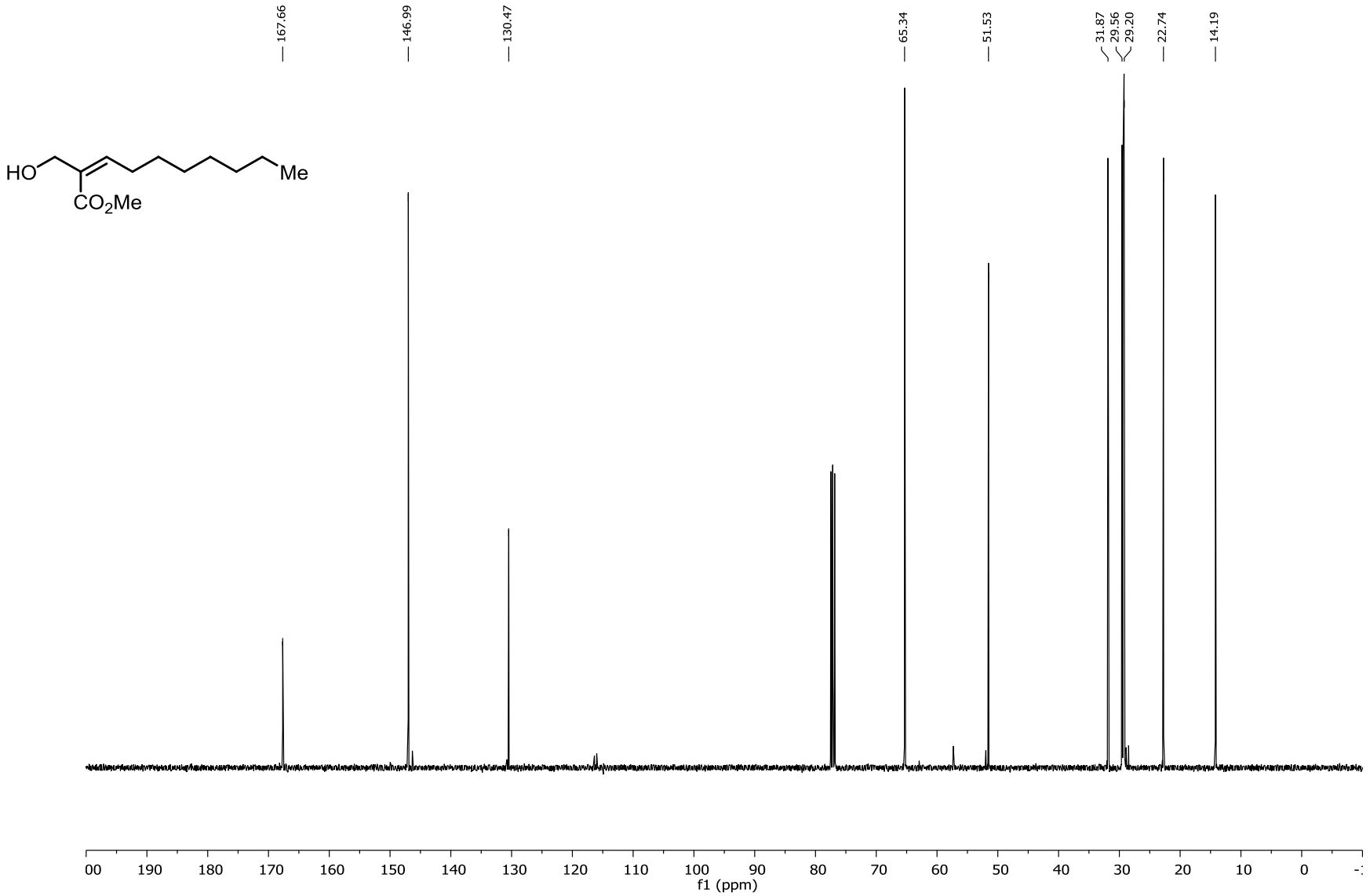
methyl (Z)-2-(1-hydroxy-3-phenylpropyl)hept-2-enoate (2)



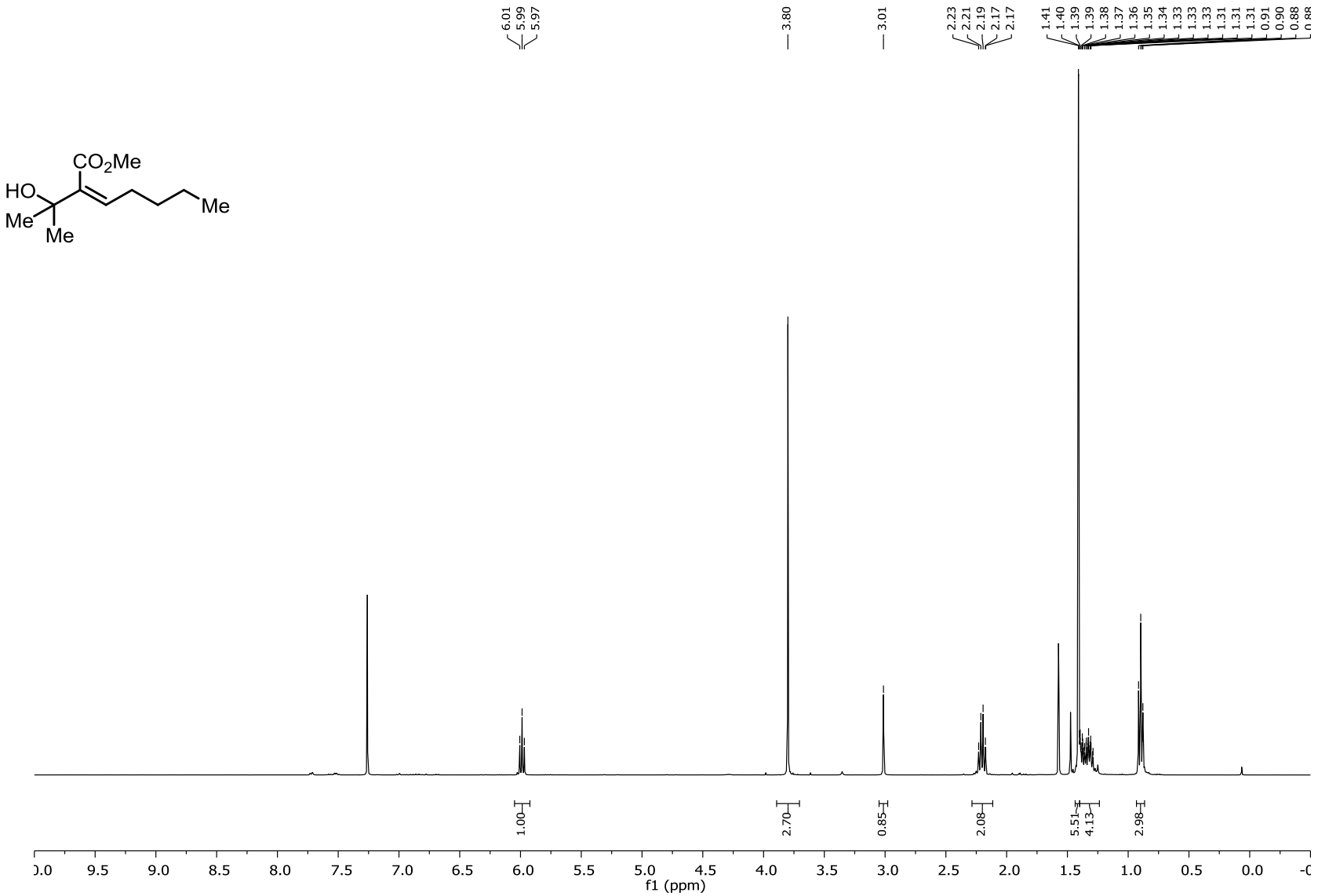
methyl (Z)-2-(hydroxymethyl)dec-2-enoate (4)



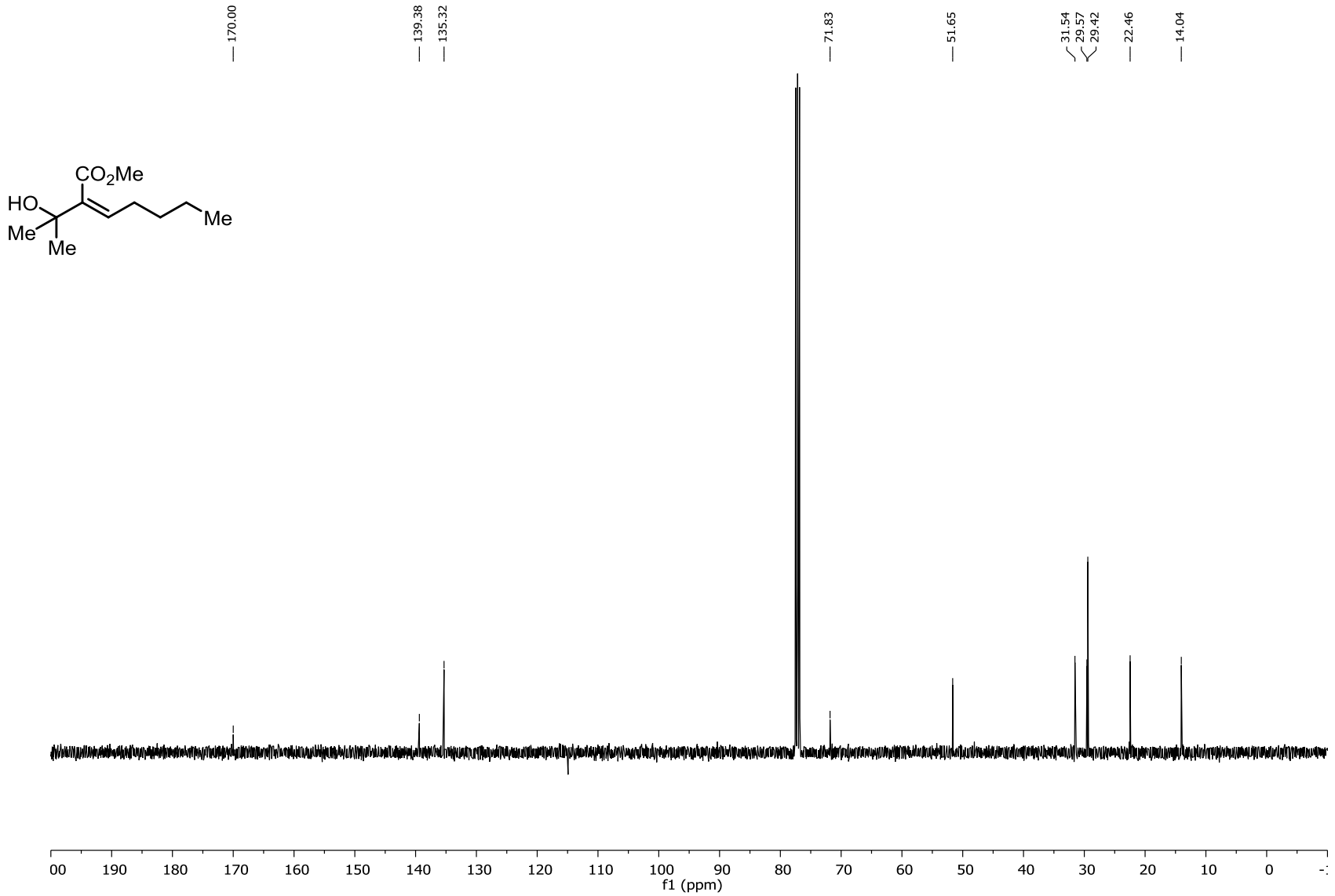
methyl (Z)-2-(hydroxymethyl)dec-2-enoate (4)



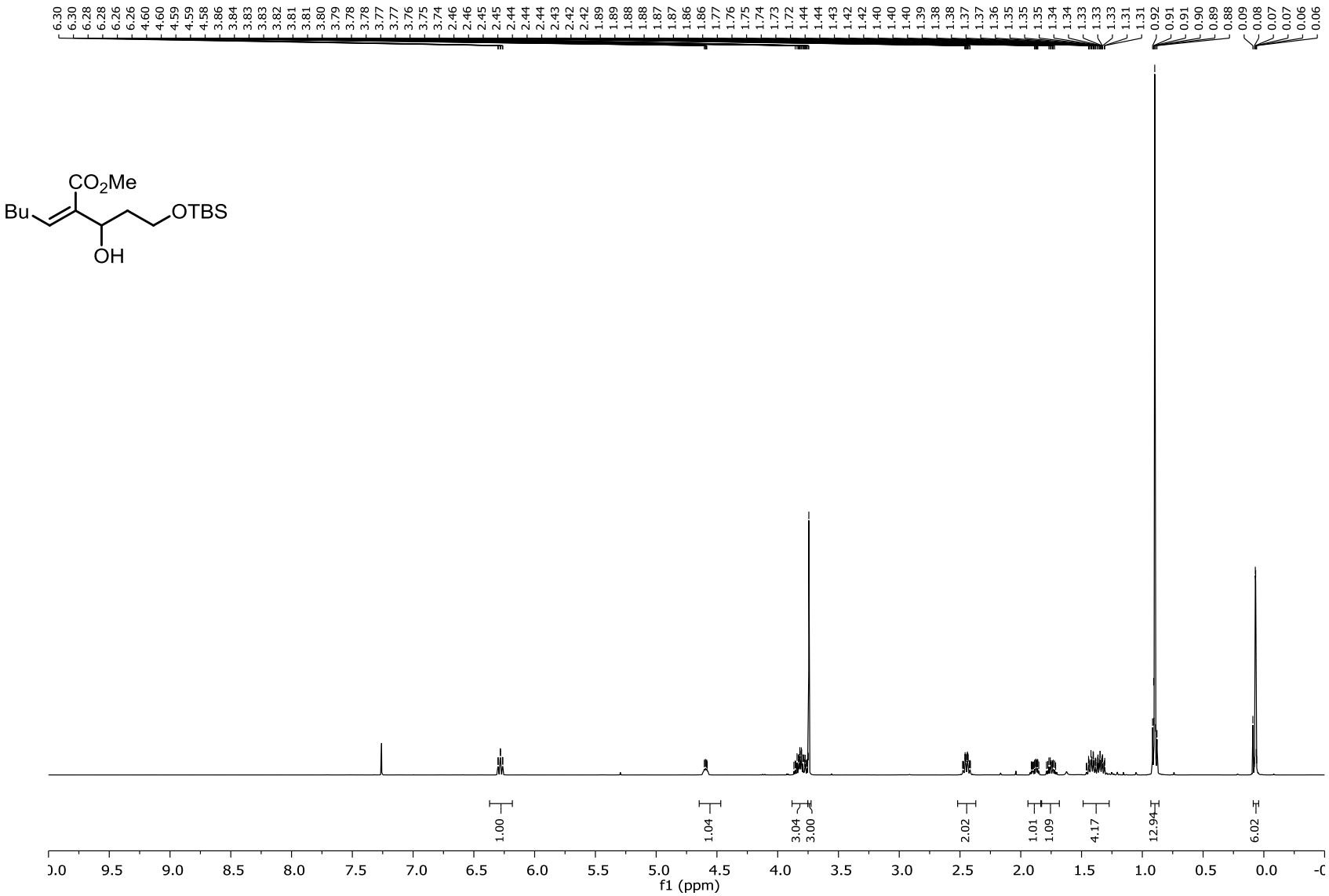
methyl (Z)-2-(2-hydroxypropan-2-yl)hept-2-enoate (5)



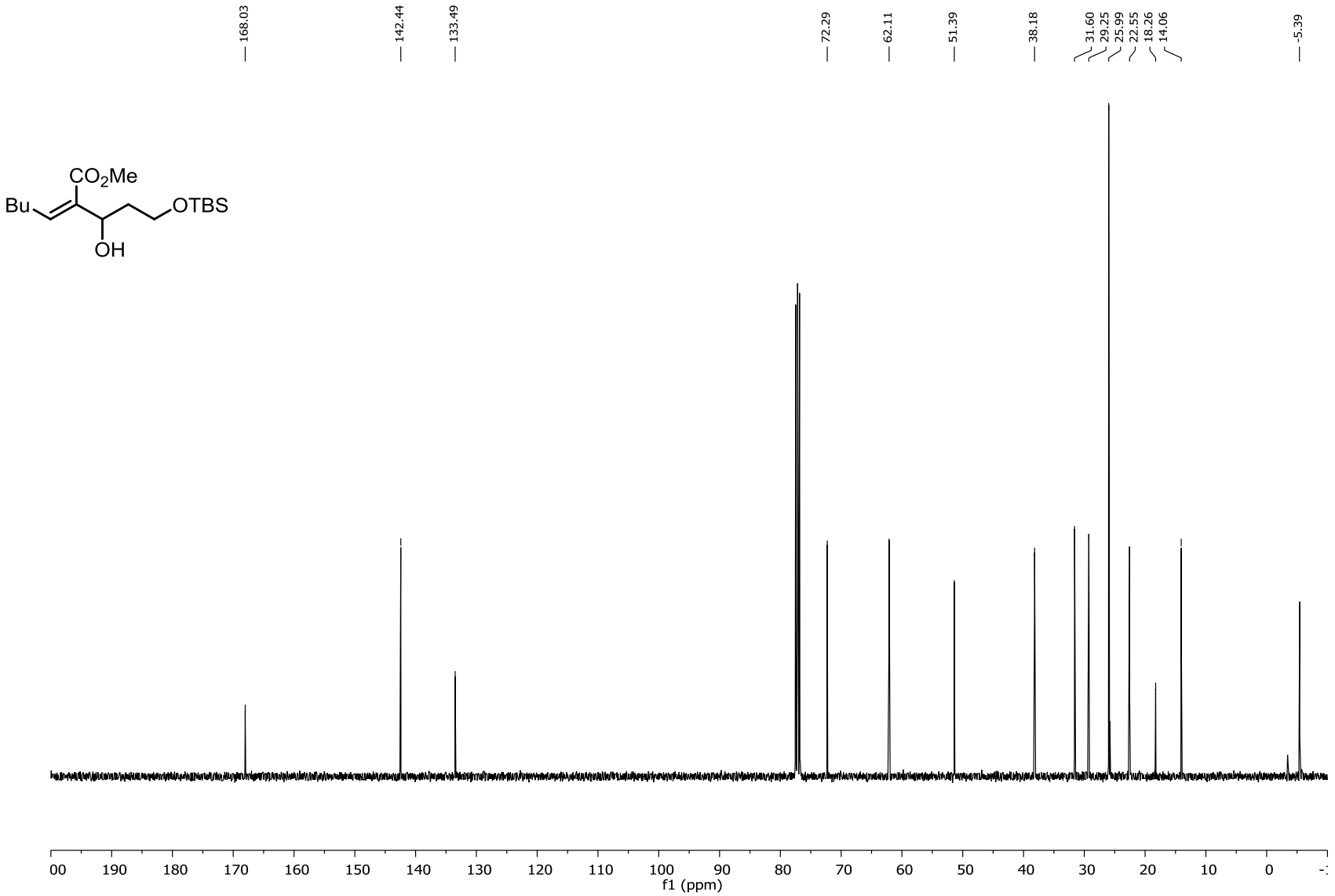
methyl (Z)-2-(2-hydroxypropan-2-yl)hept-2-enoate (5)



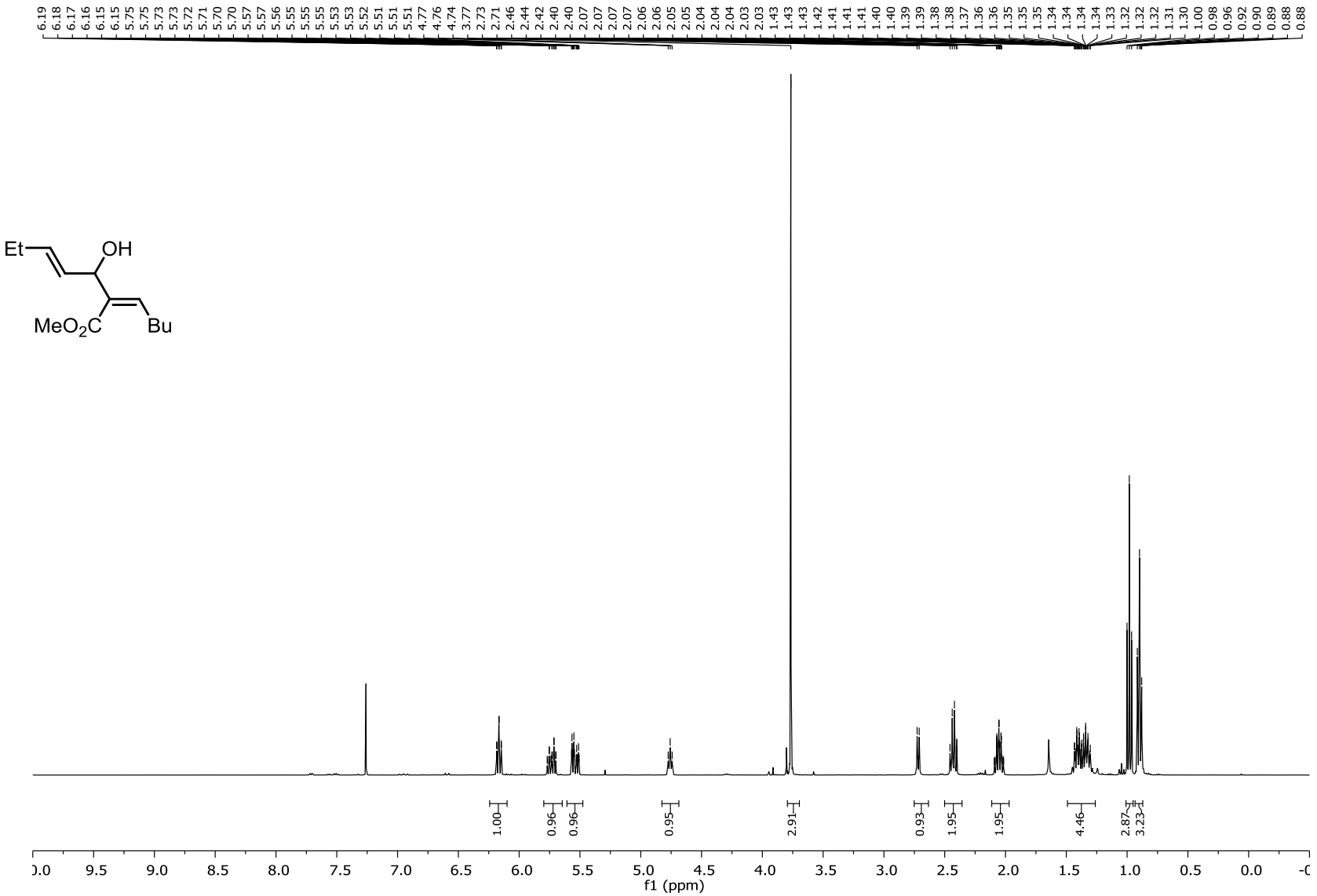
methyl (Z)-2-(3-((tert-butyldimethylsilyl)oxy)-1-hydroxypropyl)hept-2-enoate (6)



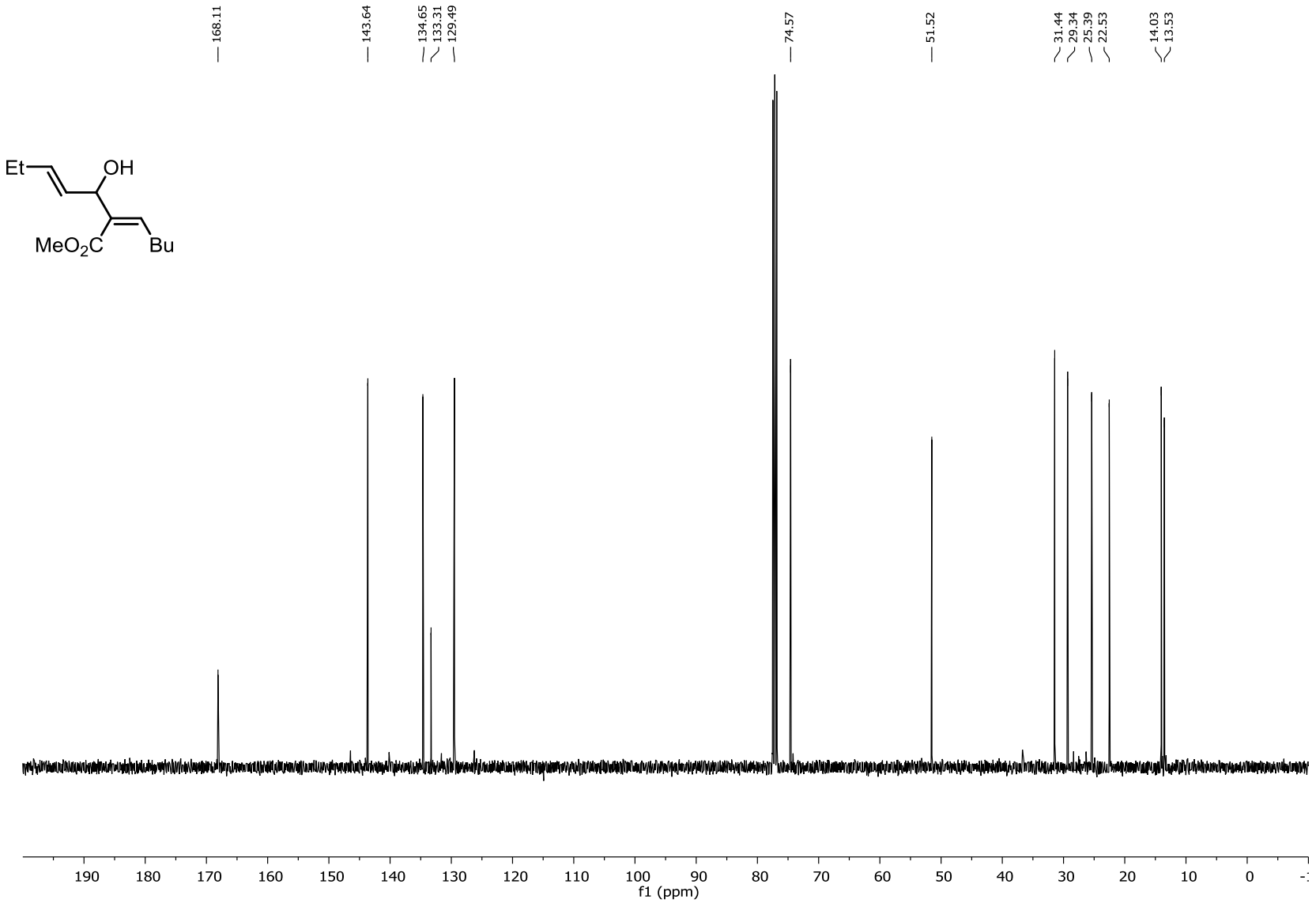
methyl (Z)-2-(3-((tert-butyldimethylsilyl)oxy)-1-hydroxypropyl)hept-2-enoate (6)



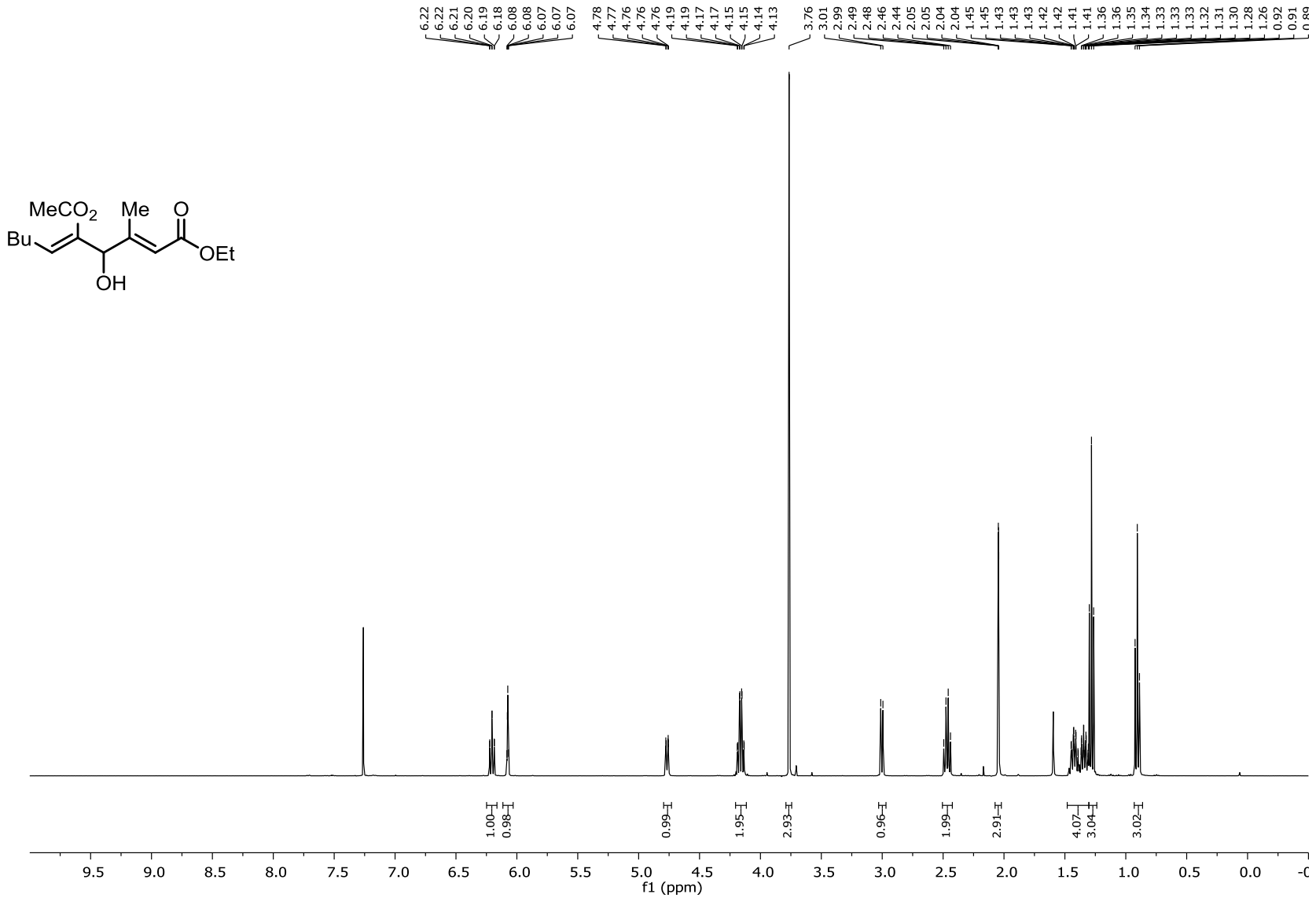
methyl (Z)-2-((E)-1-hydroxypent-2-en-1-yl)hept-2-enoate (7)



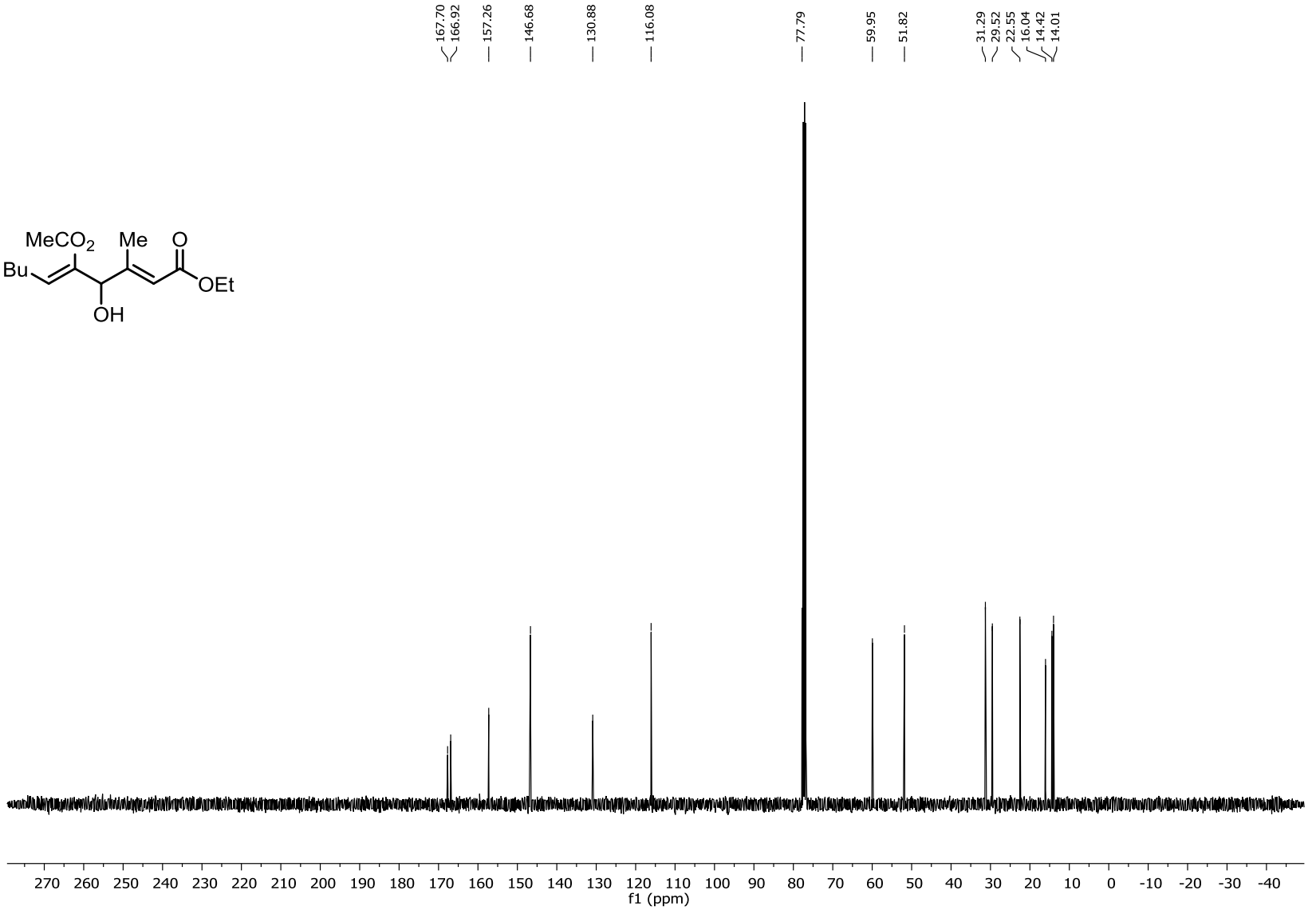
methyl (Z)-2-((E)-1-hydroxypent-2-en-1-yl)hept-2-enoate (7)



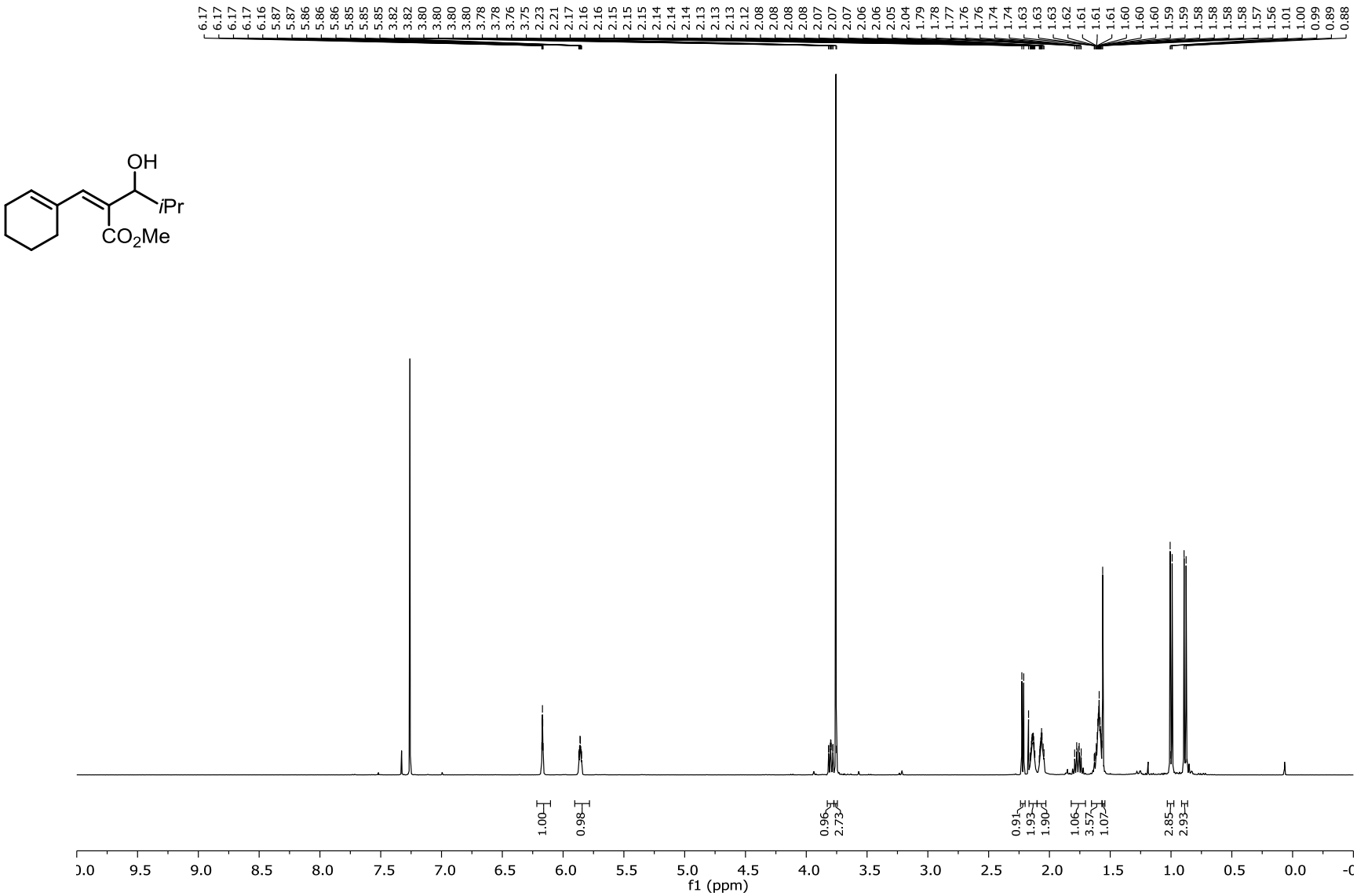
ethyl (2E,5Z)-5-acetoxy-4-hydroxy-3-methyldeca-2,5-dienoate (8)



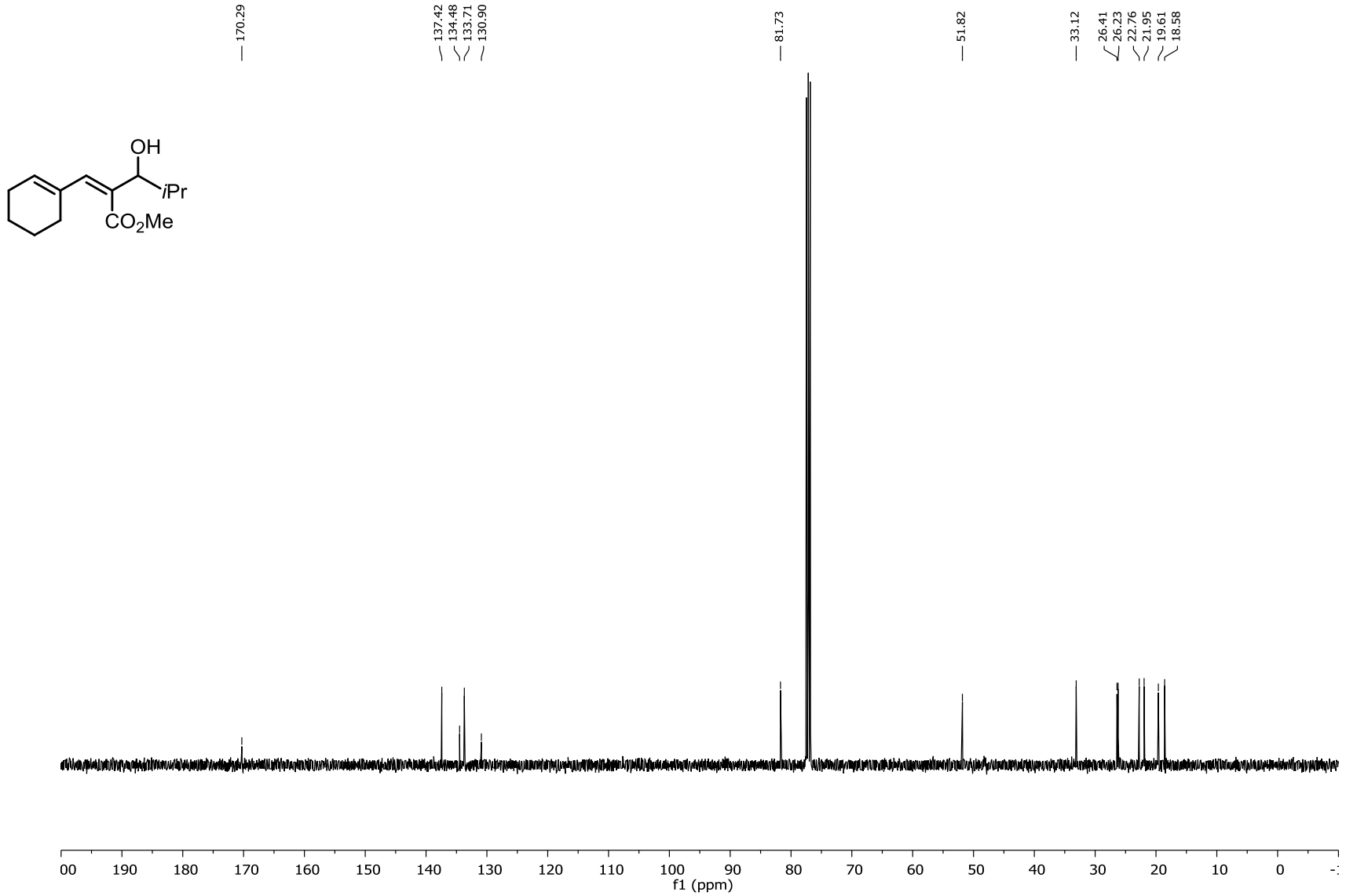
ethyl (2E,5Z)-5-acetoxy-4-hydroxy-3-methyldeca-2,5-dienoate (8)



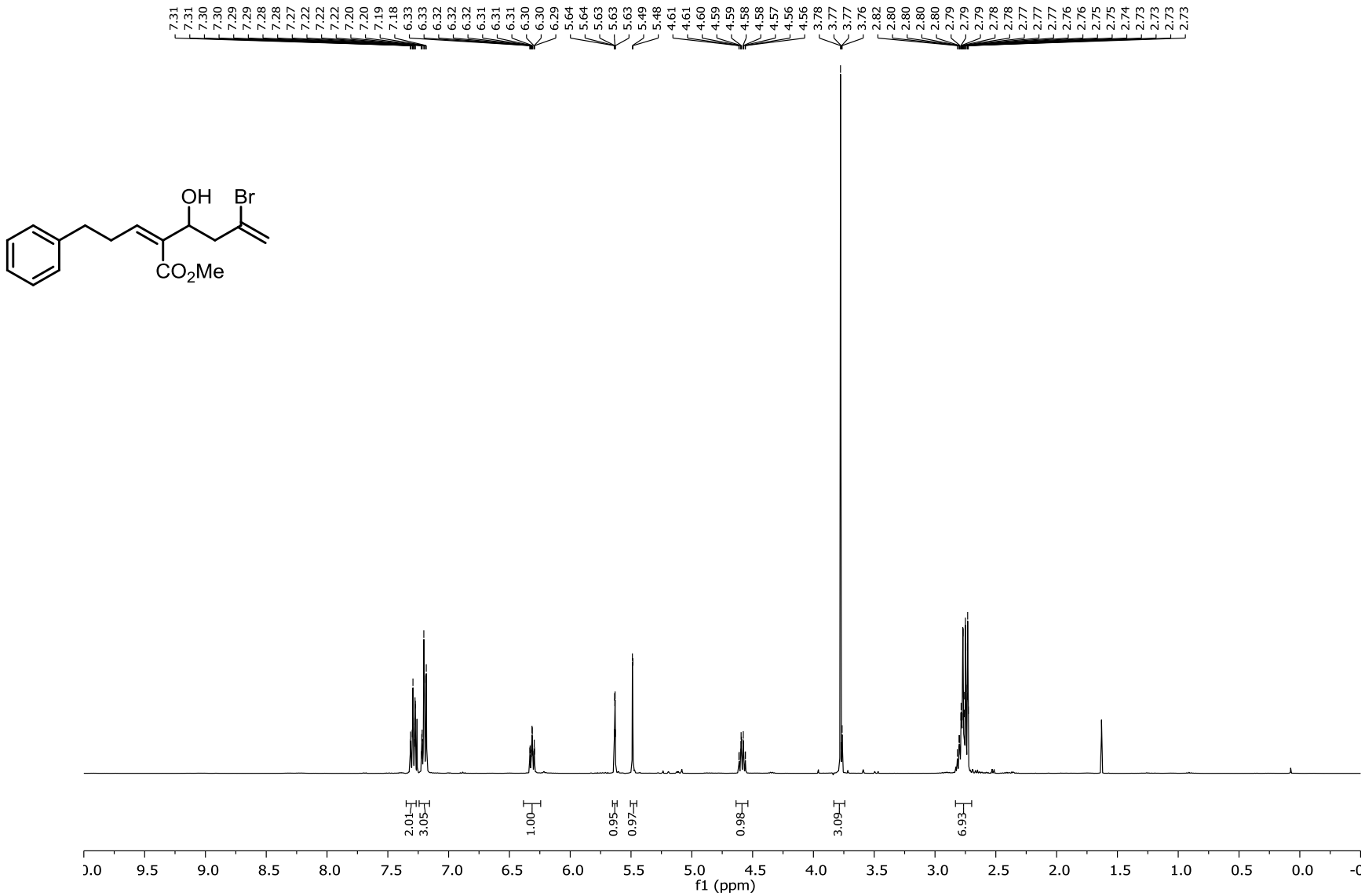
methyl (Z)-2-(cyclohex-1-en-1-ylmethylene)-3-hydroxy-4-methylpentanoate (9)



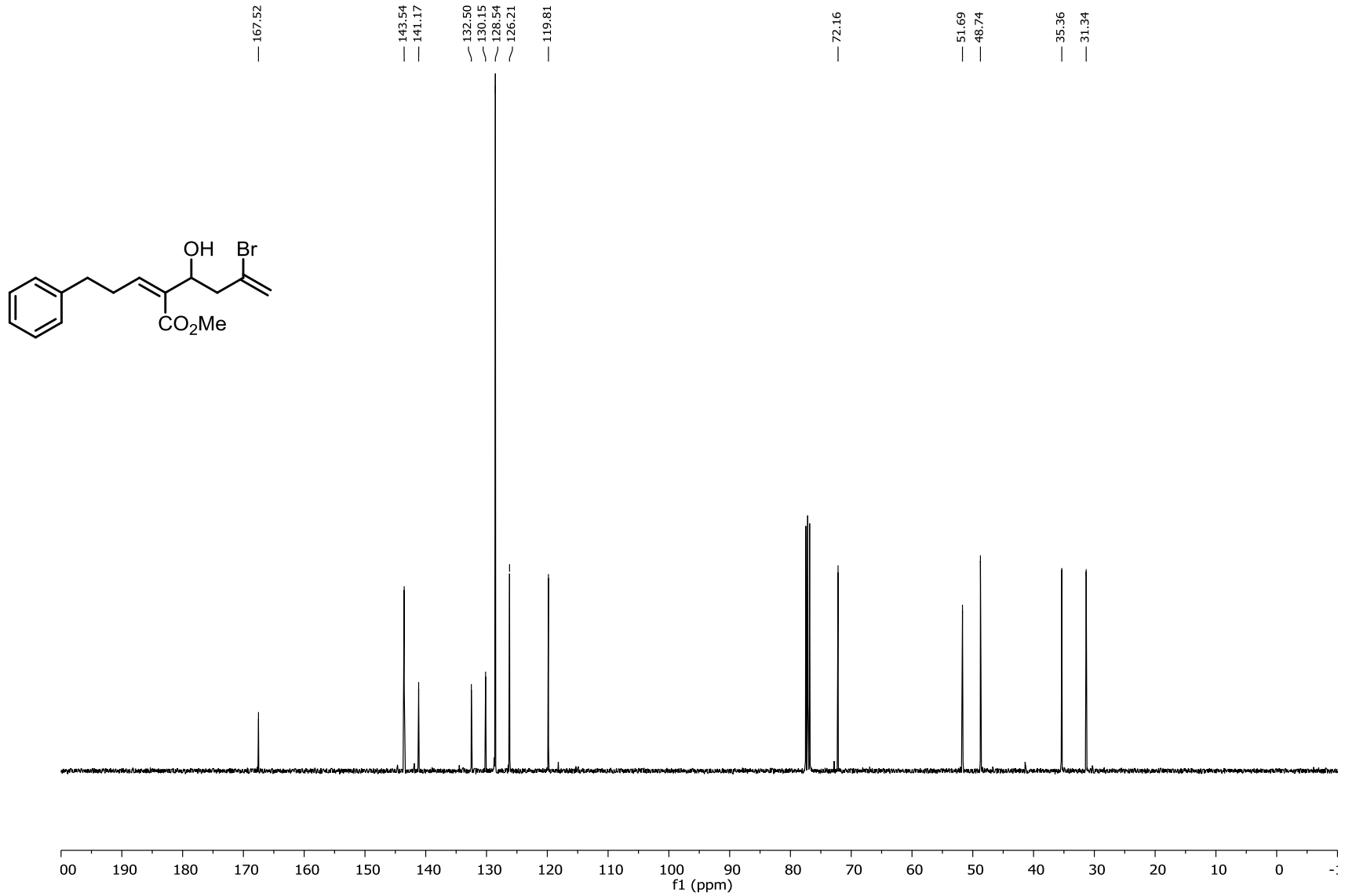
methyl (Z)-2-(cyclohex-1-en-1-ylmethylene)-3-hydroxy-4-methylpentanoate (9)



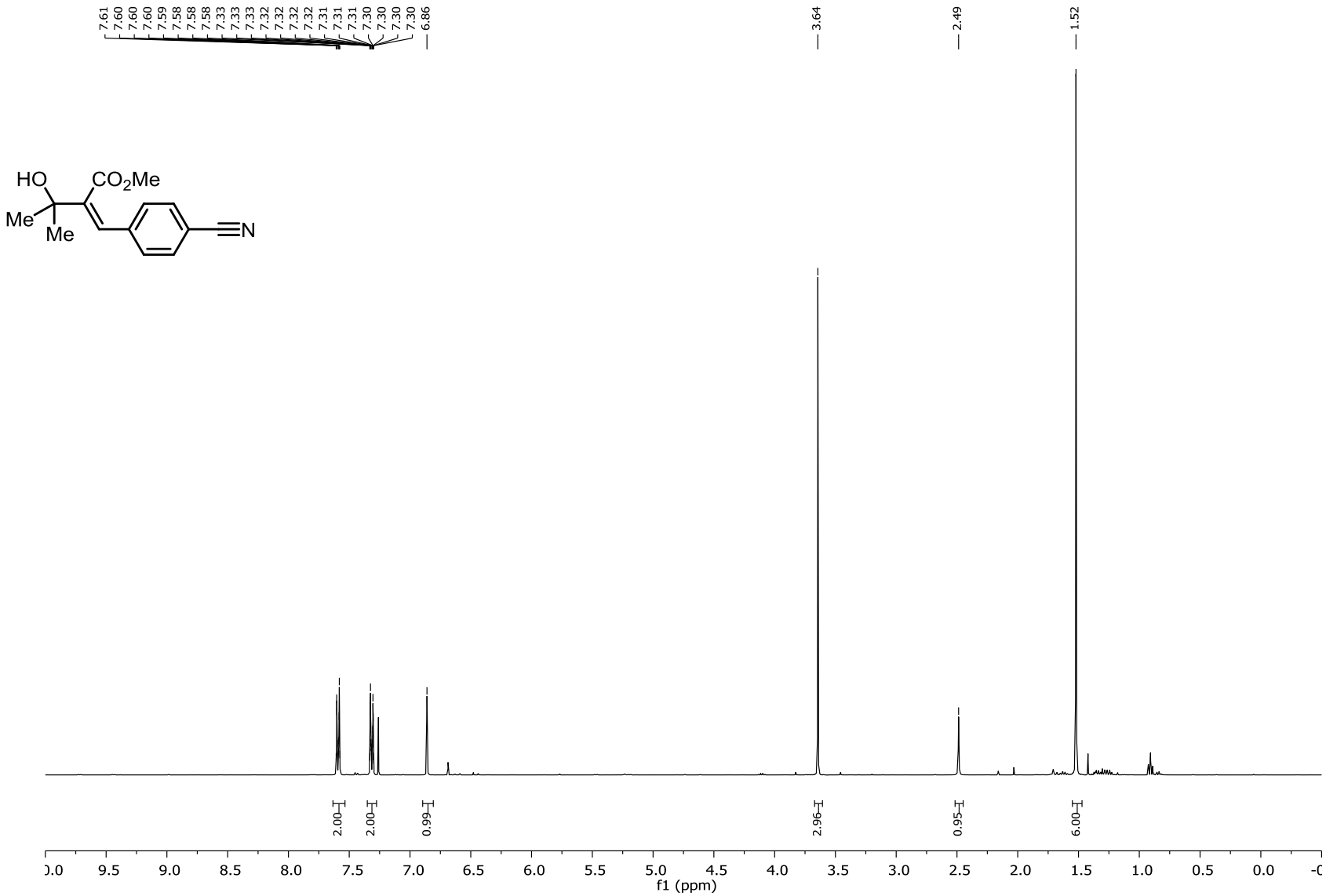
methyl (Z)-5-bromo-3-hydroxy-2-(3-phenylpropylidene)hex-5-enoate (10)



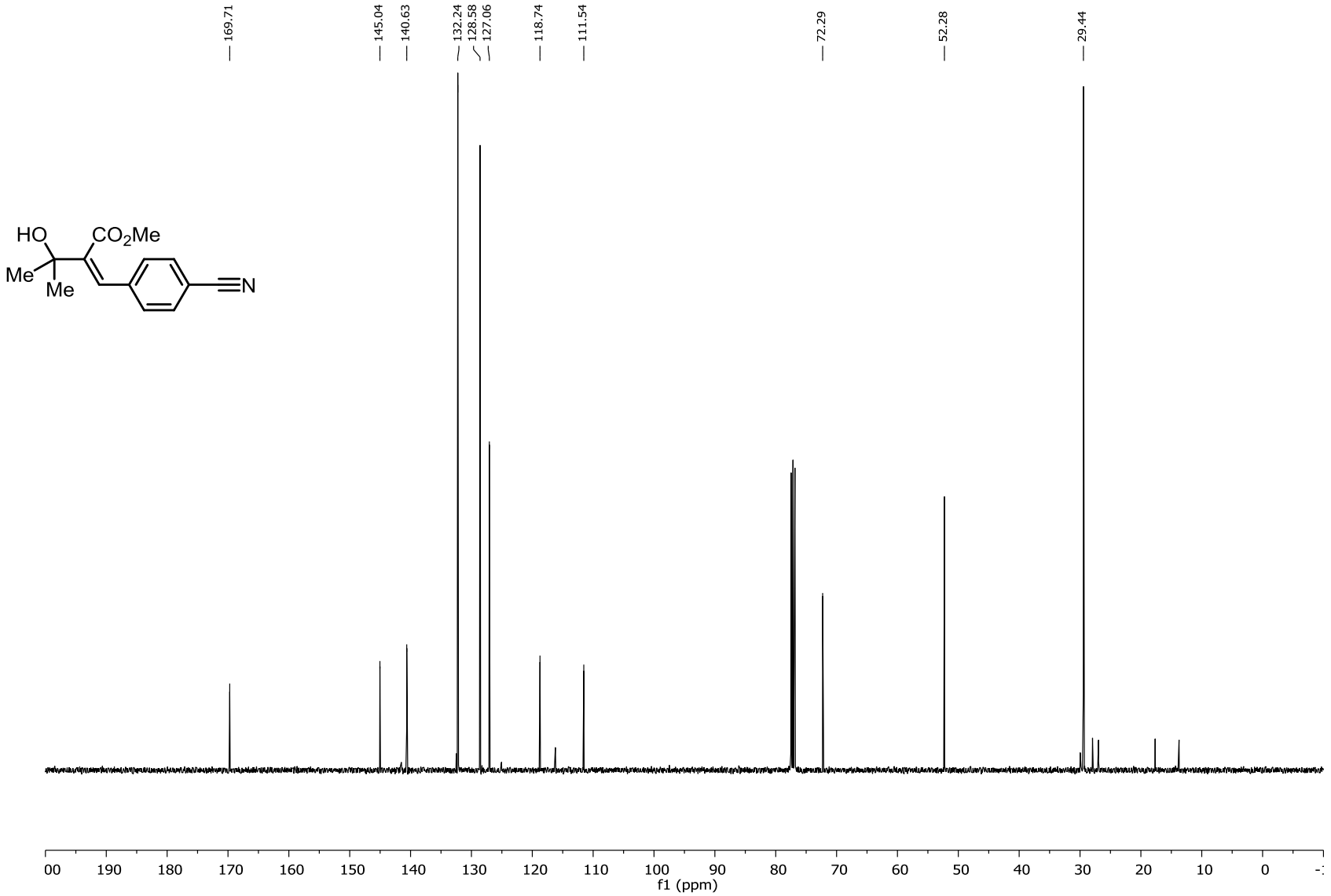
methyl (Z)-5-bromo-3-hydroxy-2-(3-phenylpropylidene)hex-5-enoate (10)



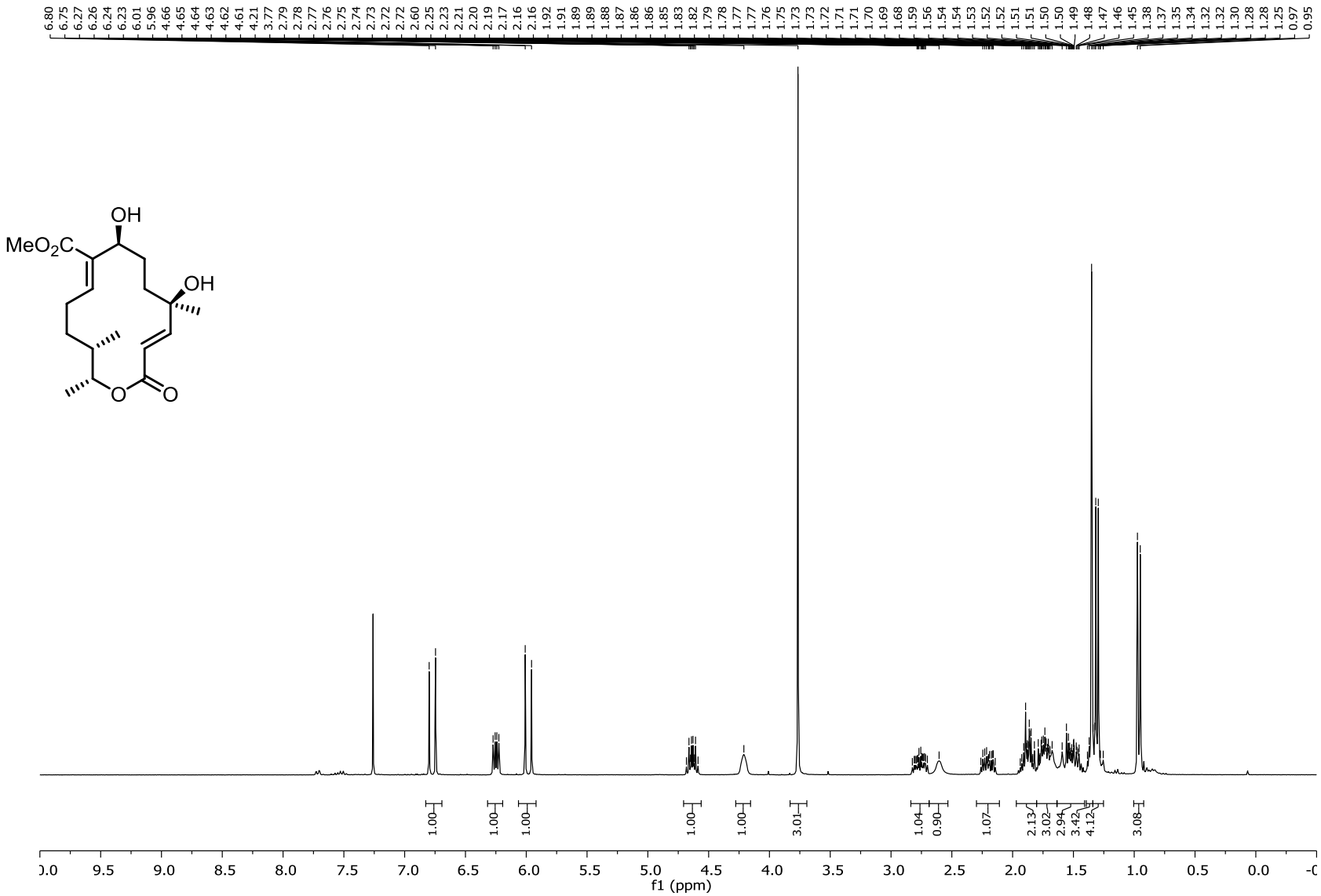
methyl (Z)-2-(4-cyanobenzylidene)-3-hydroxy-3-methylbutanoate (11)



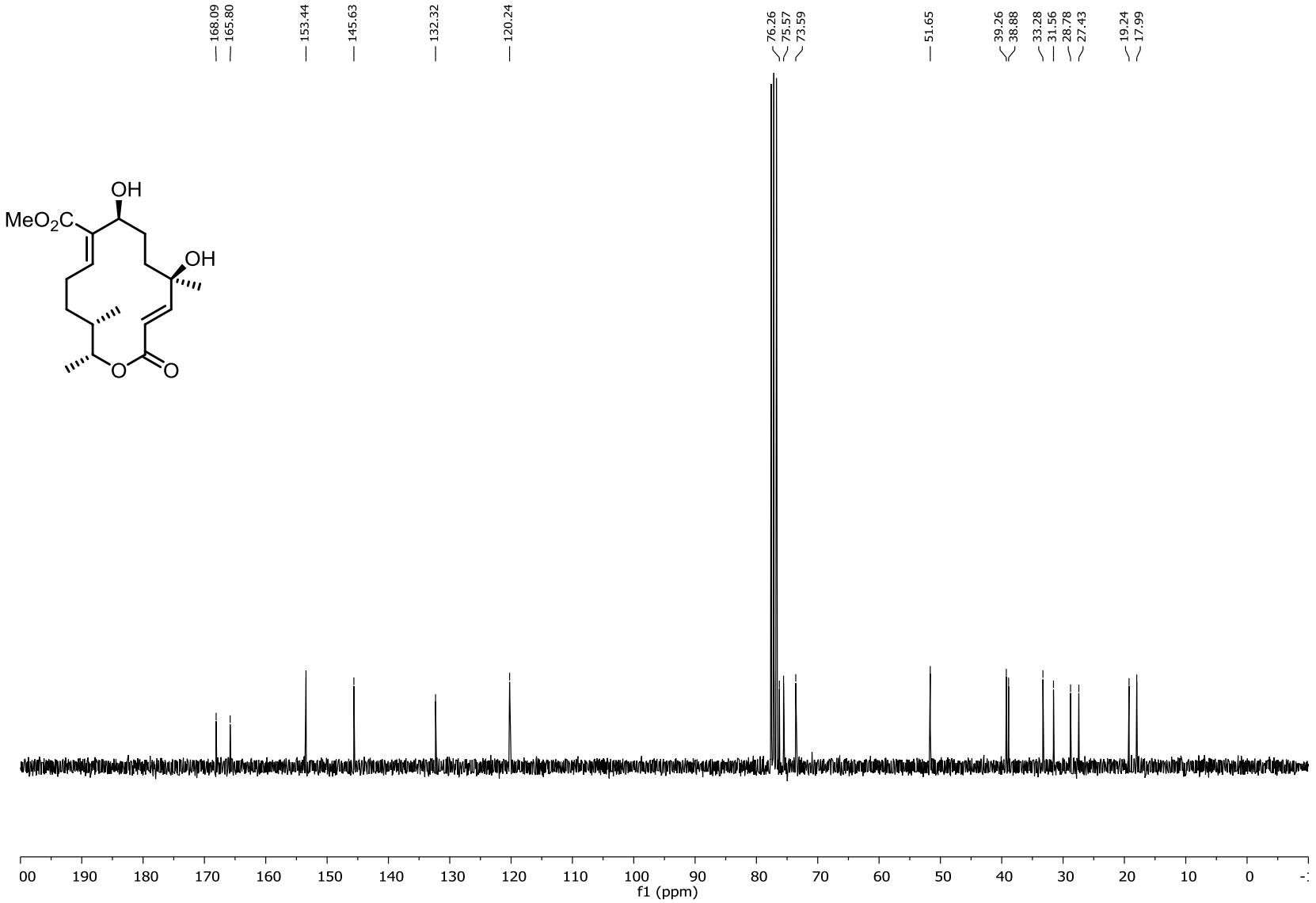
methyl (Z)-2-(4-cyanobenzylidene)-3-hydroxy-3-methylbutanoate (11)



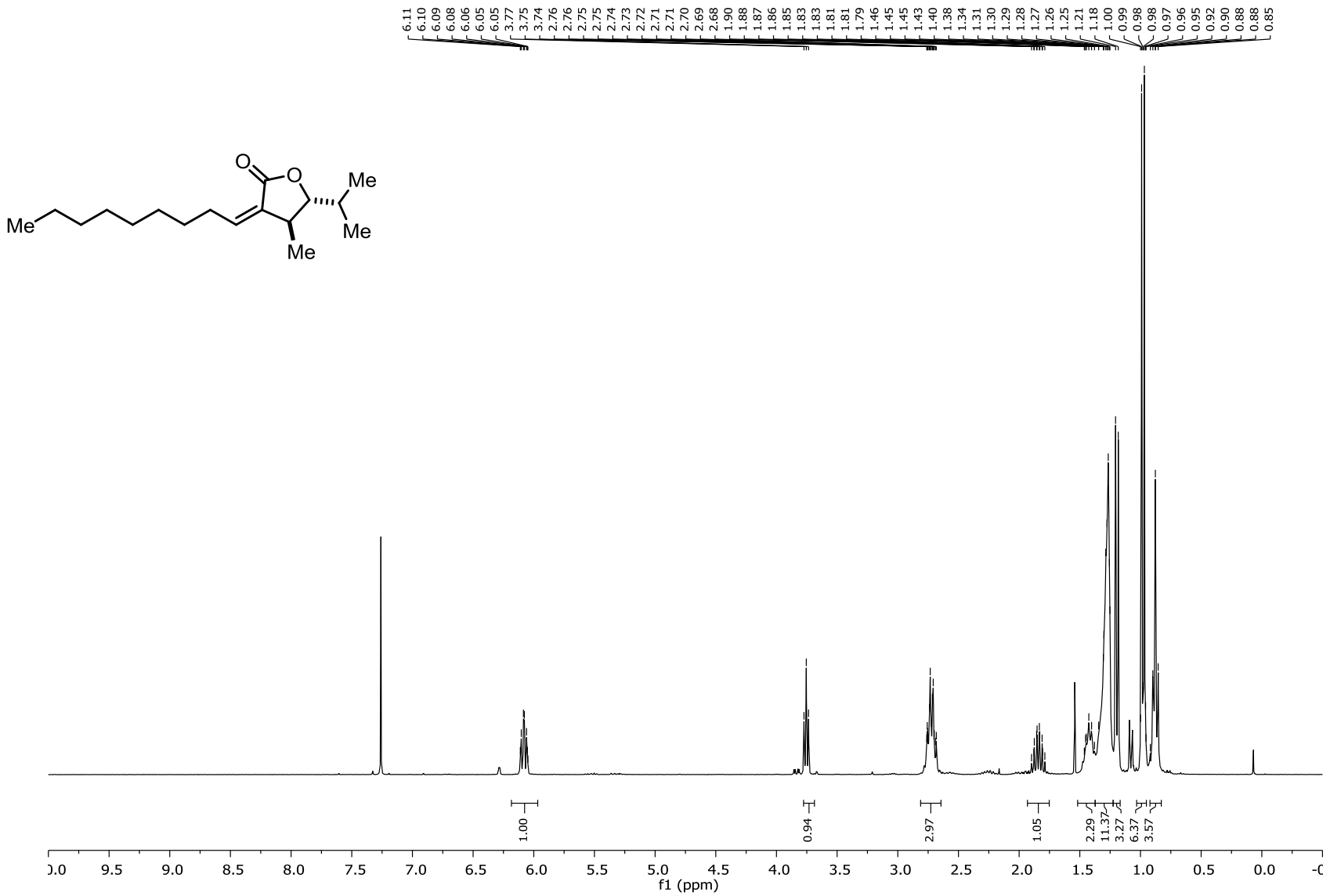
methyl (2R,3S,6Z,8S,11R,12E)-8,11-dihydroxy-2,3,11-trimethyl-14-oxooxacyclotetradeca-6,12-diene-7-carboxylate (12)



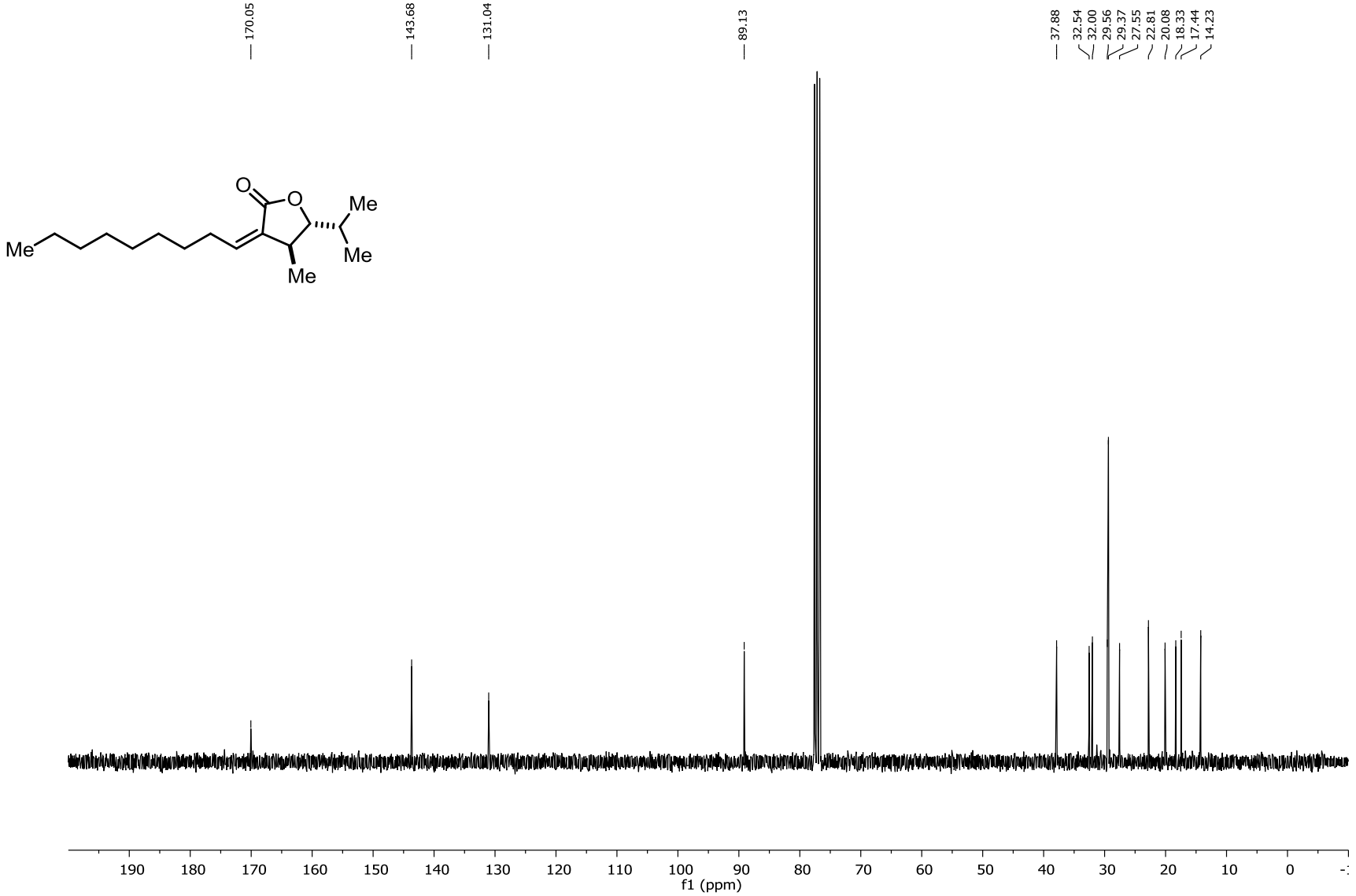
methyl (2R,3S,6Z,8S,11R,12E)-8,11-dihydroxy-2,3,11-trimethyl-14-oxooxacyclotetradeca-6,12-diene-7-carboxylate (12)



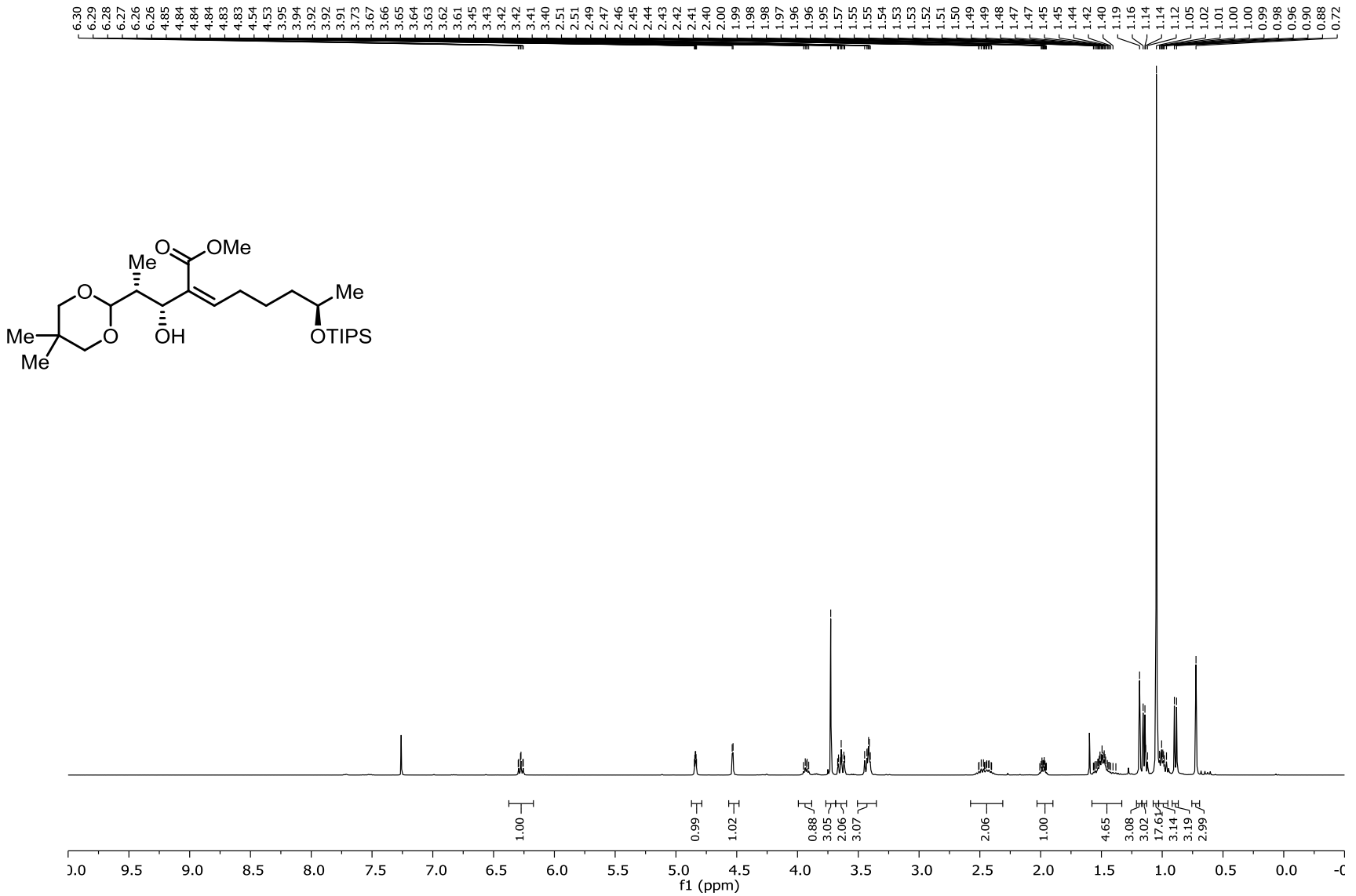
(*anti,Z*)-5-isopropyl-4-methyl-3-nonylidenedihydrofuran-2(3H)-one (13)



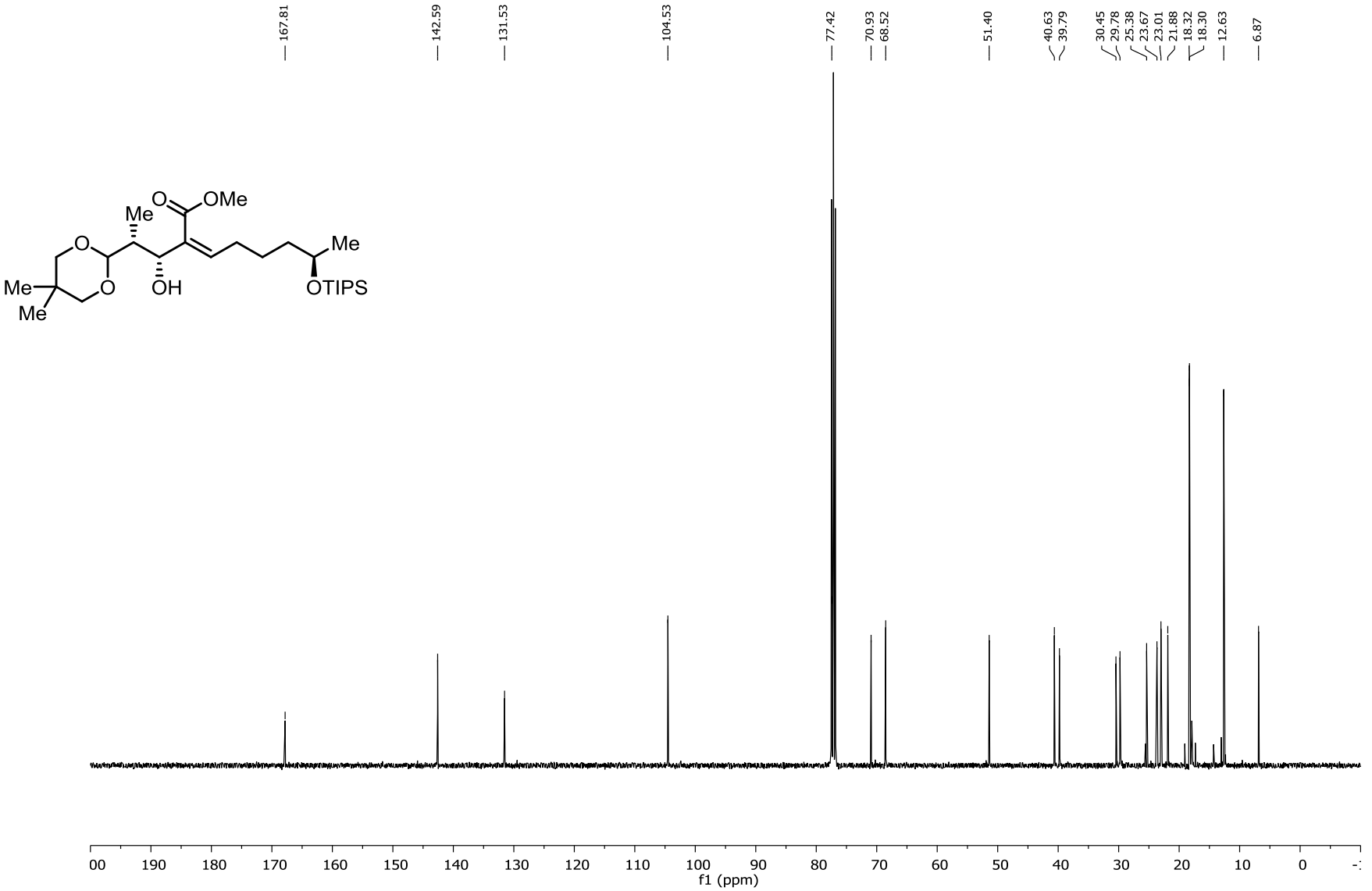
(*anti,Z*)-5-isopropyl-4-methyl-3-nonylidenedihydrofuran-2(3H)-one (13)



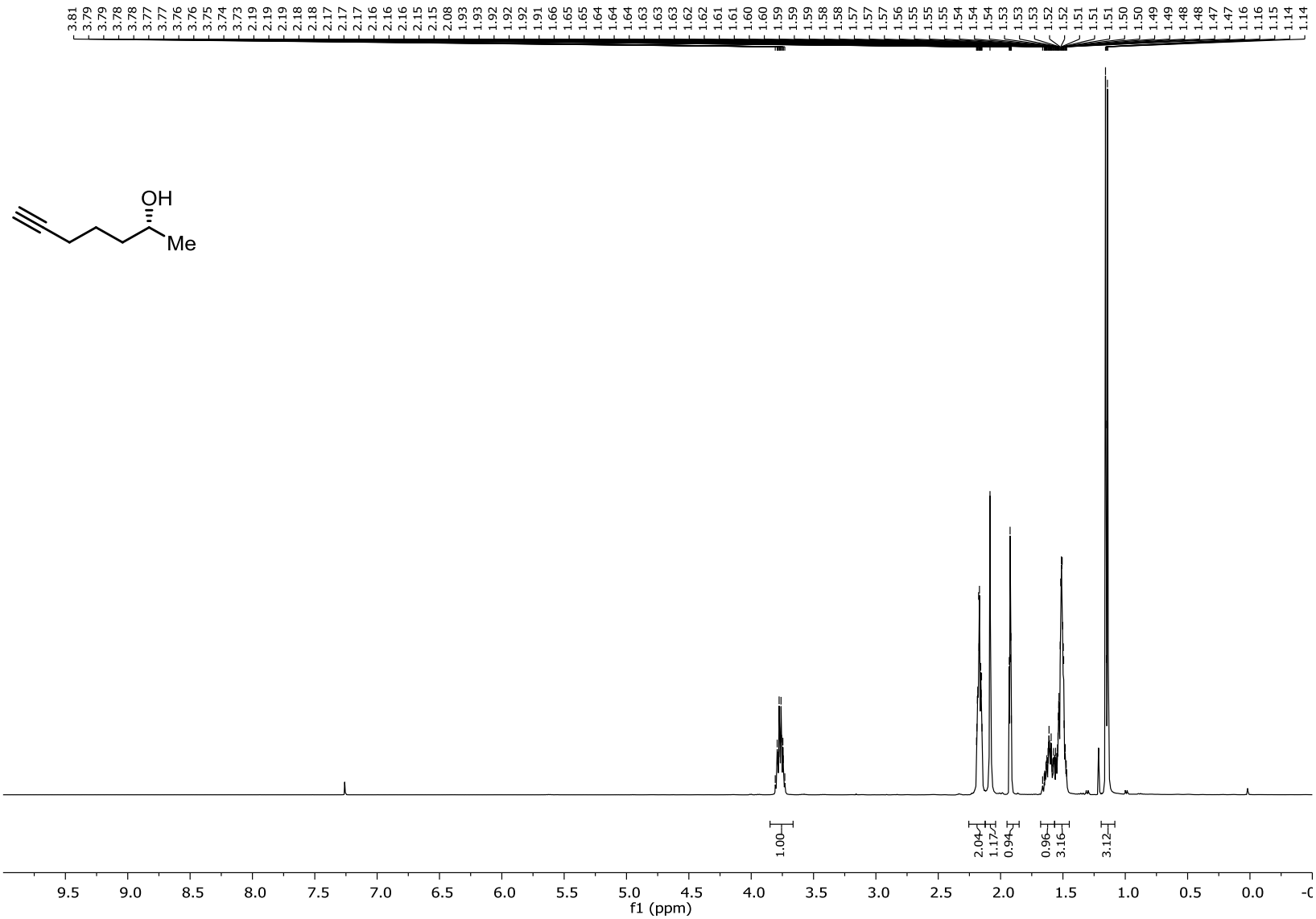
methyl (R,Z)-2-((1R,2R)-2-(5,5-dimethyl-1,3-dioxan-2-yl)-1-hydroxypropyl)-7-((triisopropylsilyl)oxy)oct-2-enoate (15)



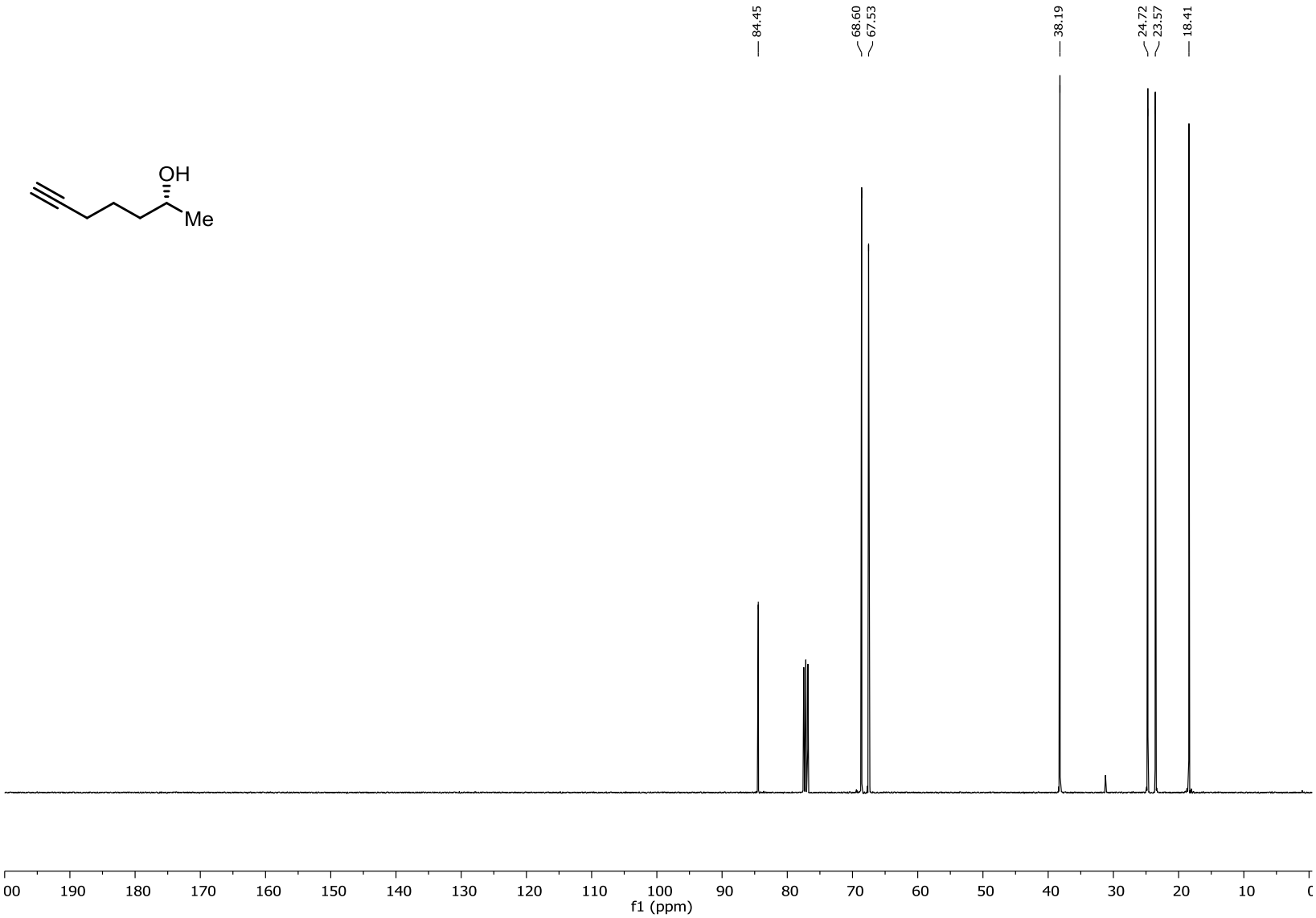
methyl (R,Z)-2-((1R,2R)-2-(5,5-dimethyl-1,3-dioxan-2-yl)-1-hydroxypropyl)-7-((triisopropylsilyl)oxy)oct-2-enoate (15)



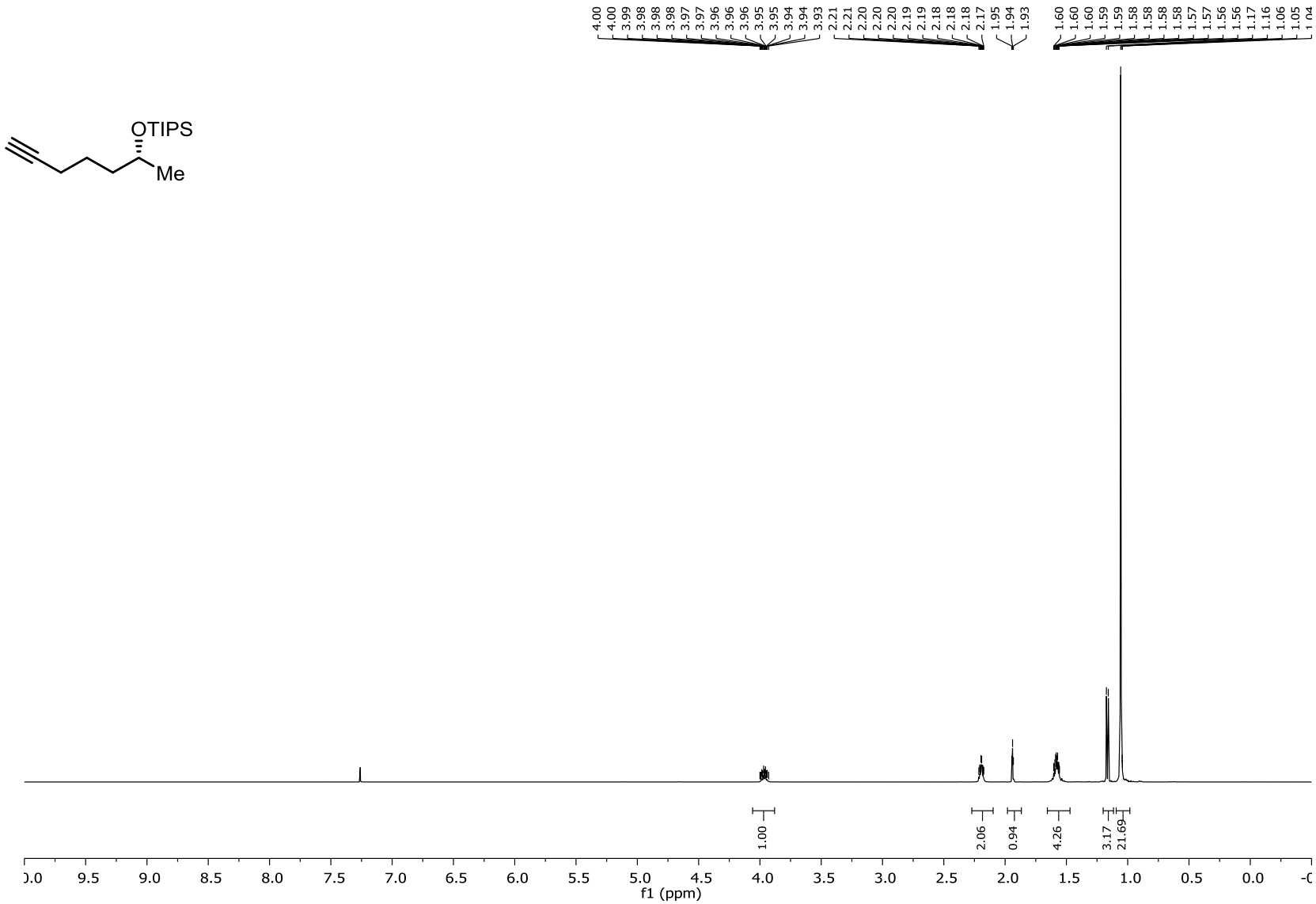
(SOI-SA-1018) - (R)-hept-6-yn-2-ol (S22)



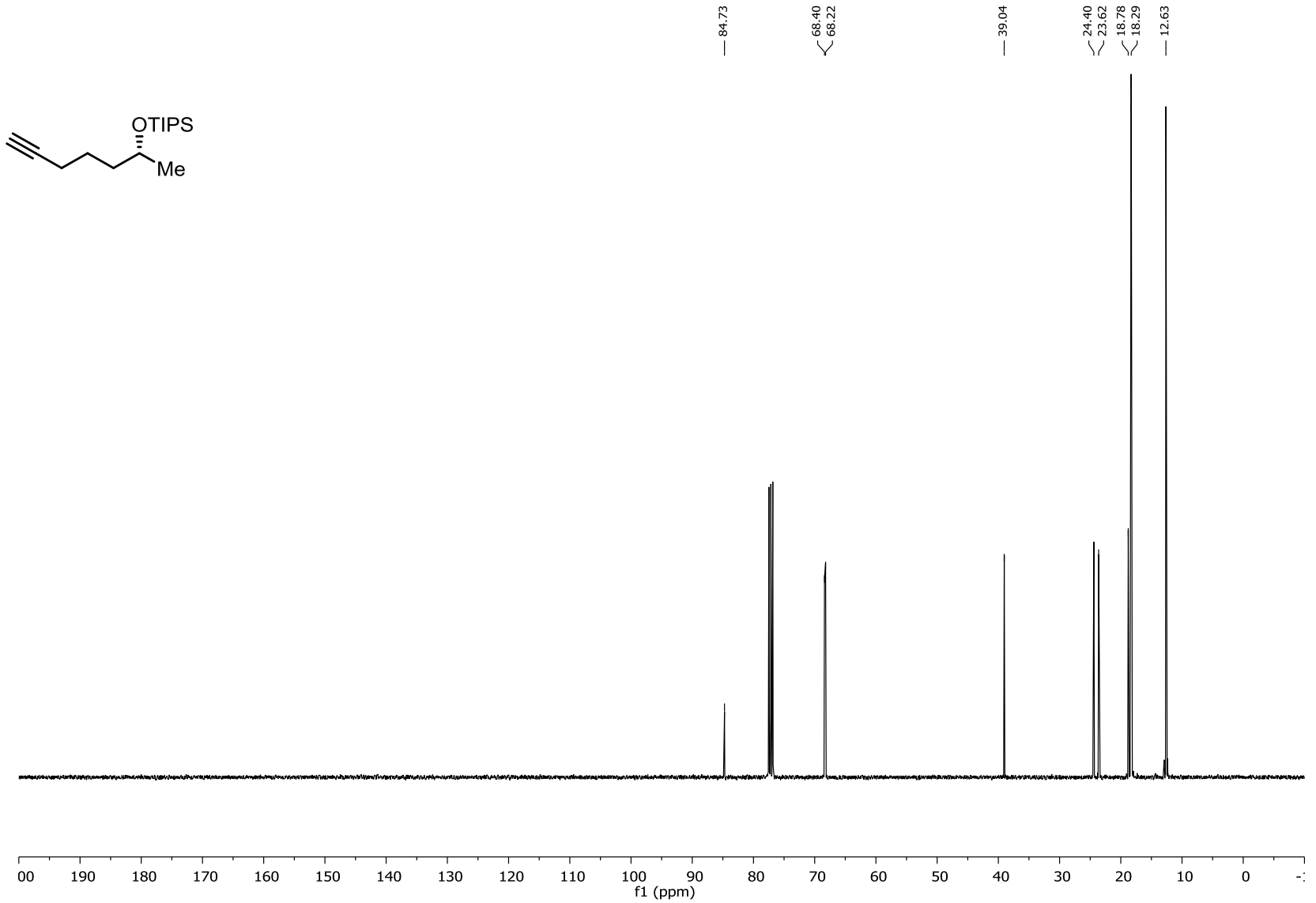
(R)-hept-6-yn-2-ol (S22)



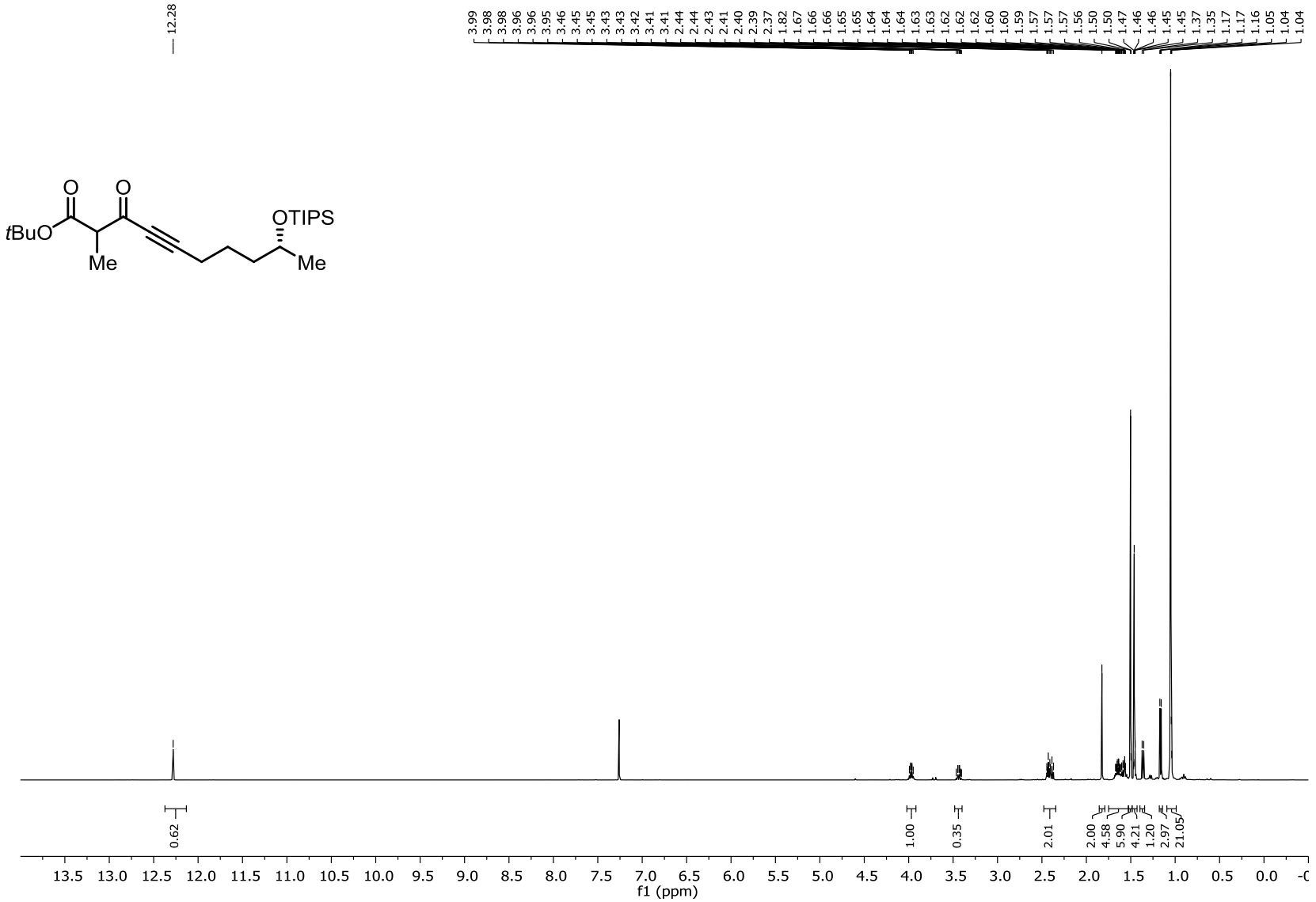
***(R)*-(hept-6-yn-2-yloxy)triisopropylsilane (19)**



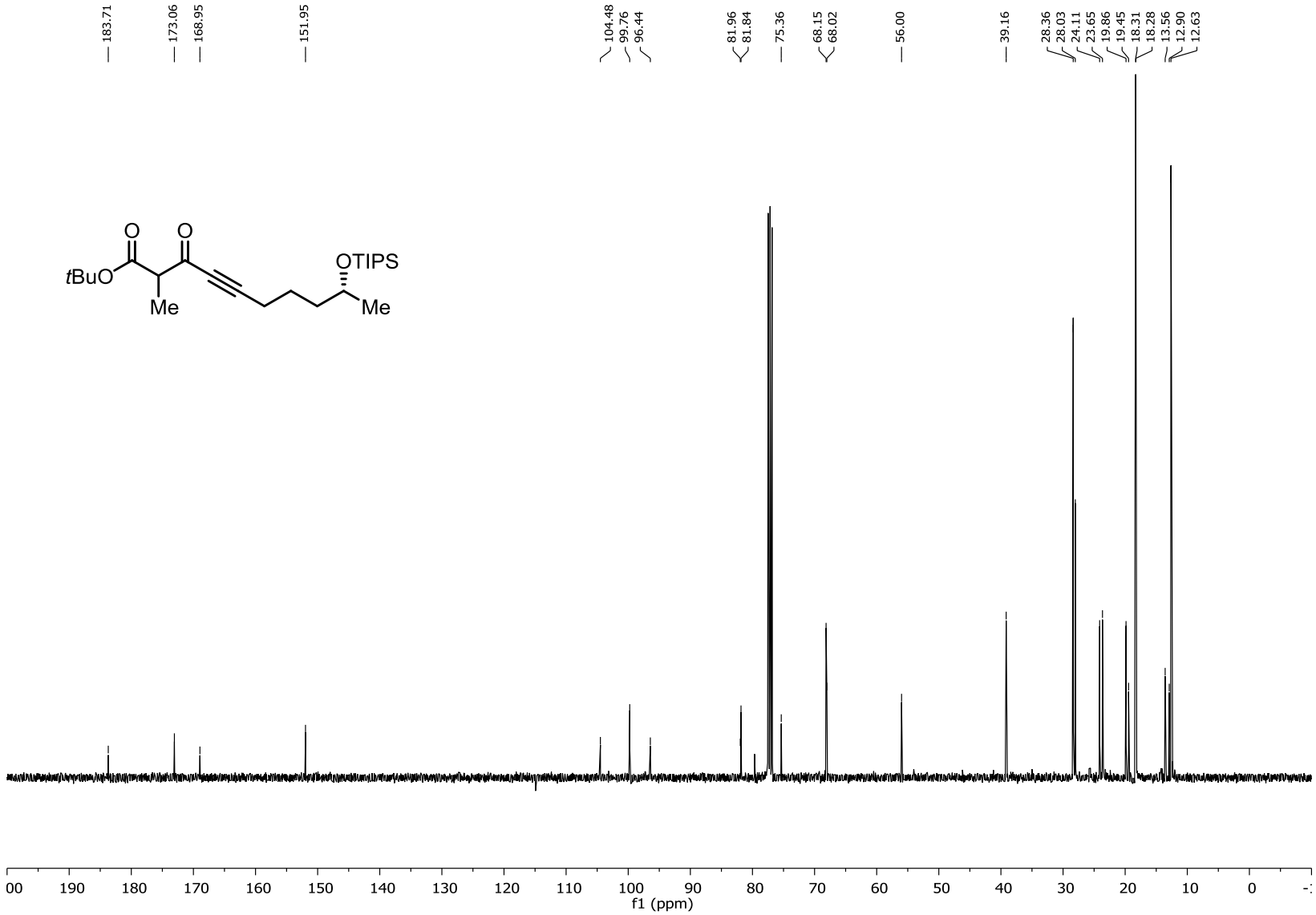
***(R)*-(hept-6-yn-2-yloxy)triisopropylsilane (19)**



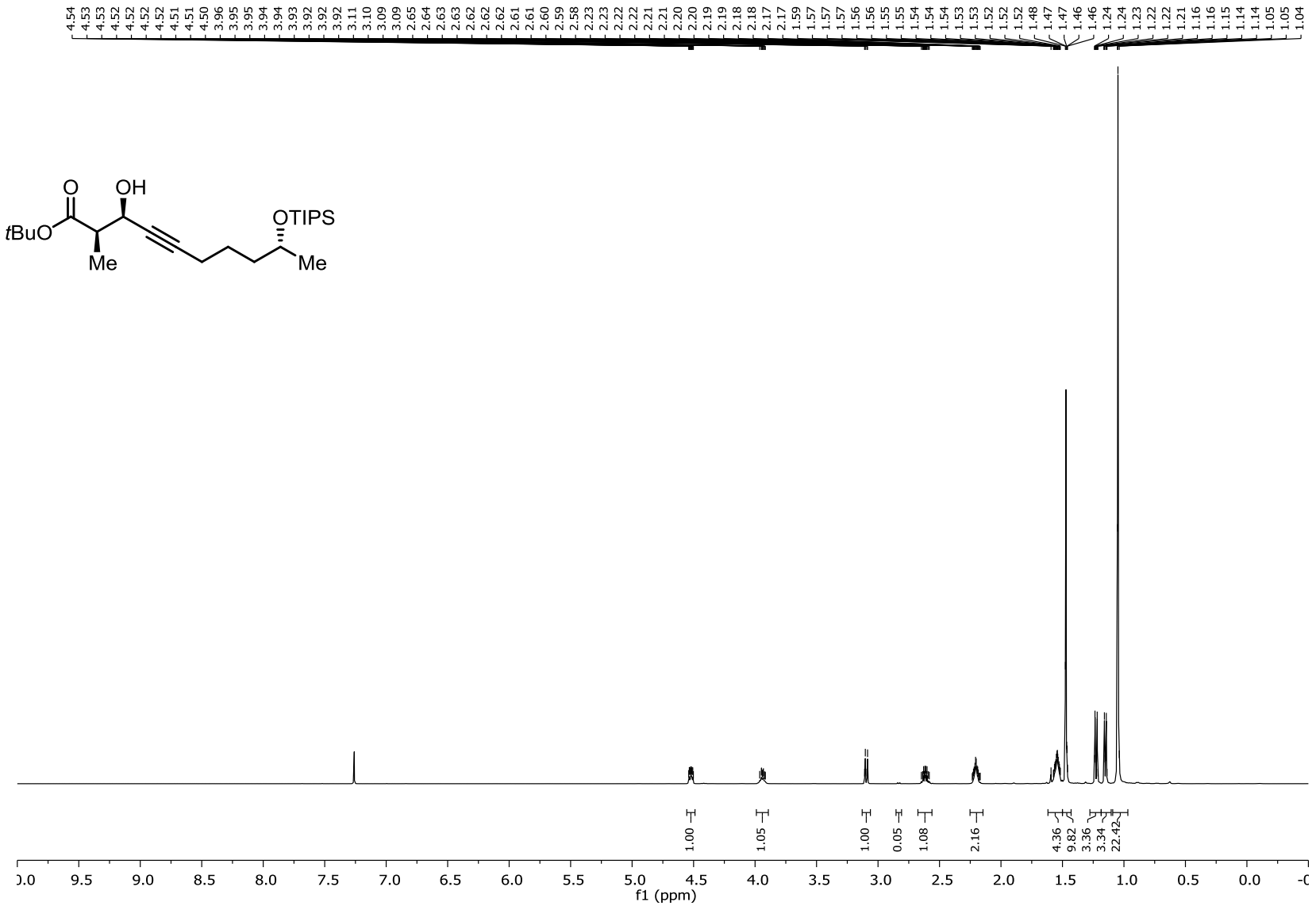
tert-butyl (9R)-2-methyl-3-oxo-9-((triisopropylsilyl)oxy)dec-4-ynoate (20)



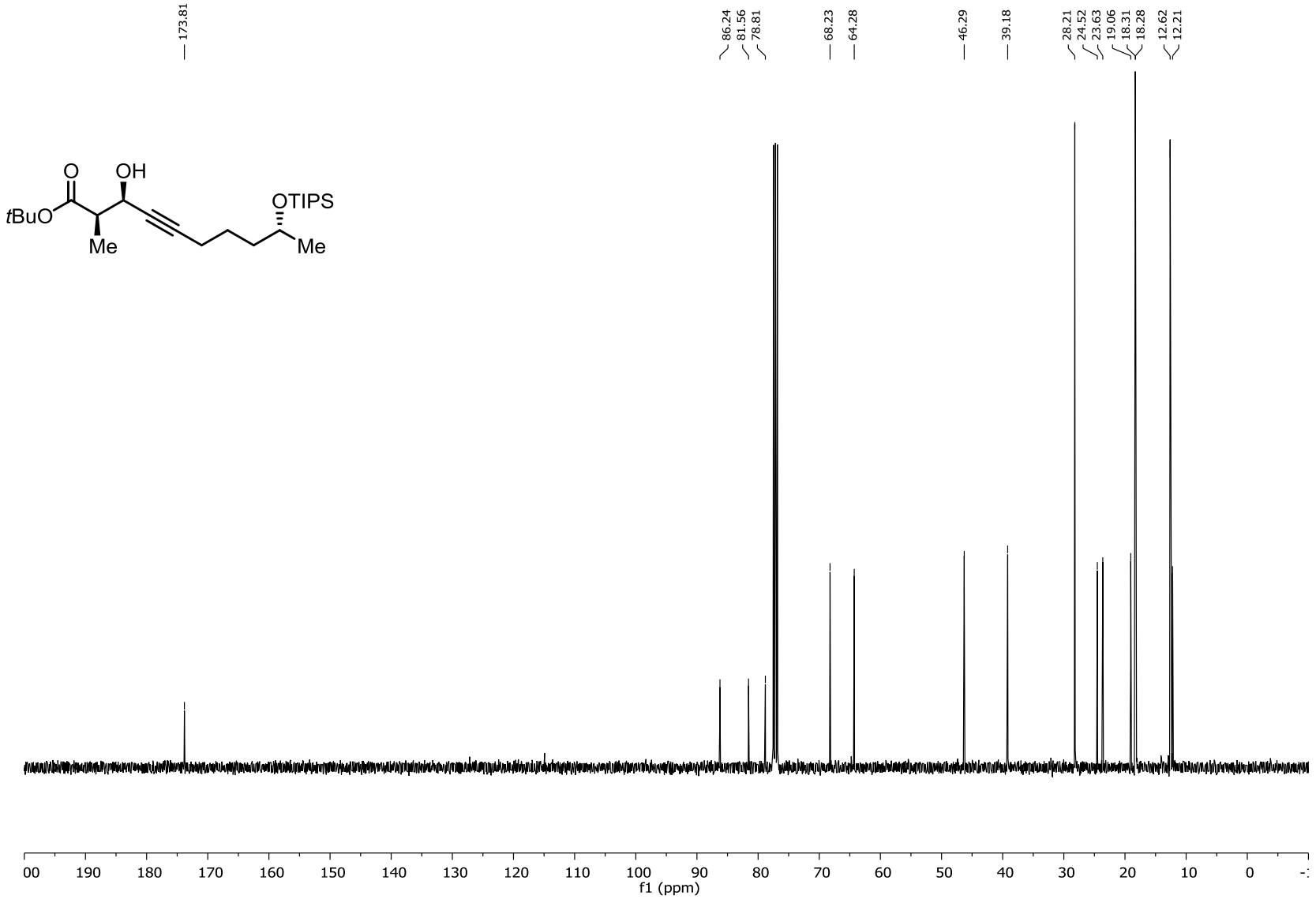
tert-butyl (9R)-2-methyl-3-oxo-9-((triisopropylsilyl)oxy)dec-4-ynoate (20)



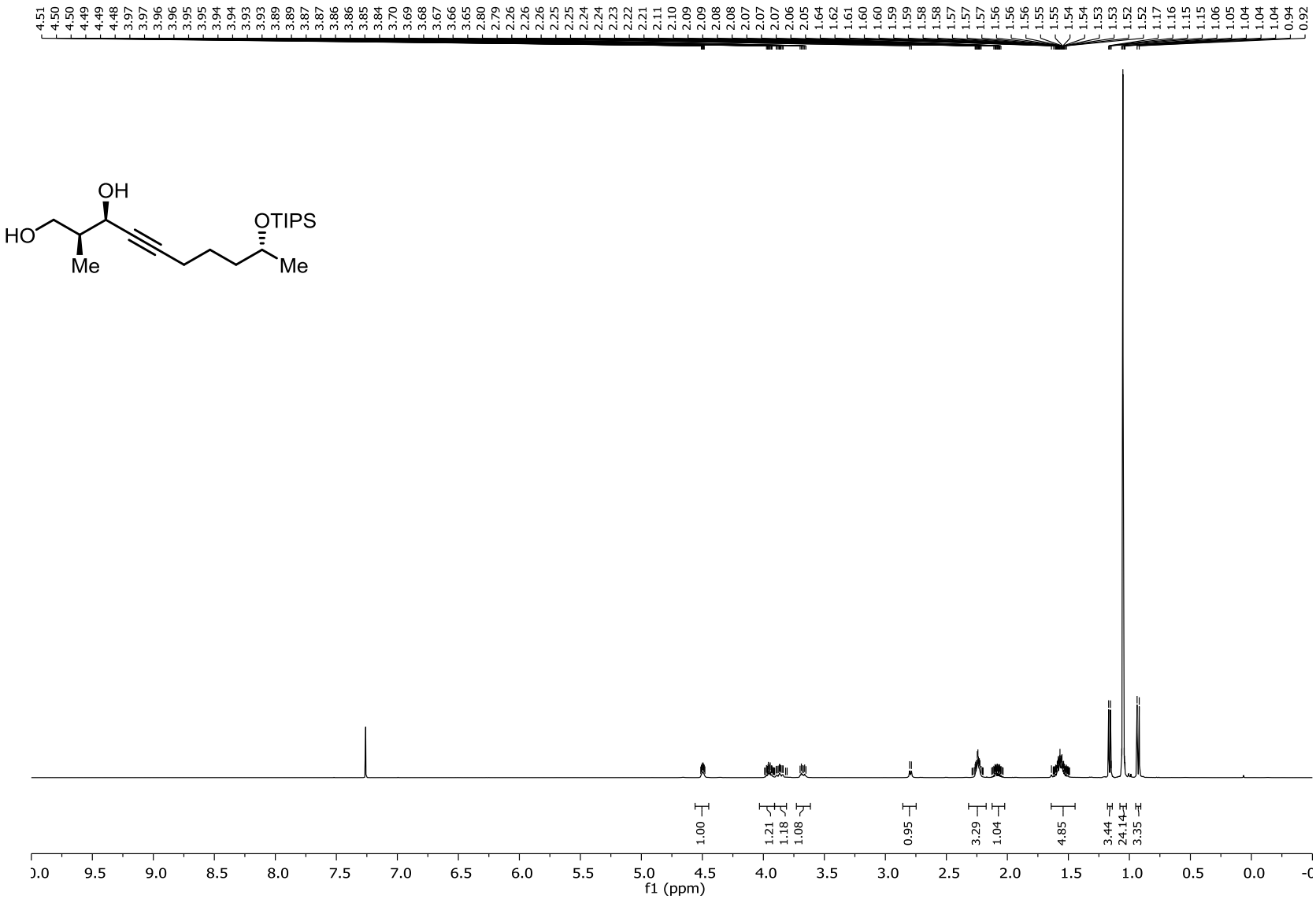
***tert*-butyl (*2R,3R,9R*)-3-hydroxy-2-methyl-9-((triisopropylsilyl)oxy)dec-4-ynoate (22)**



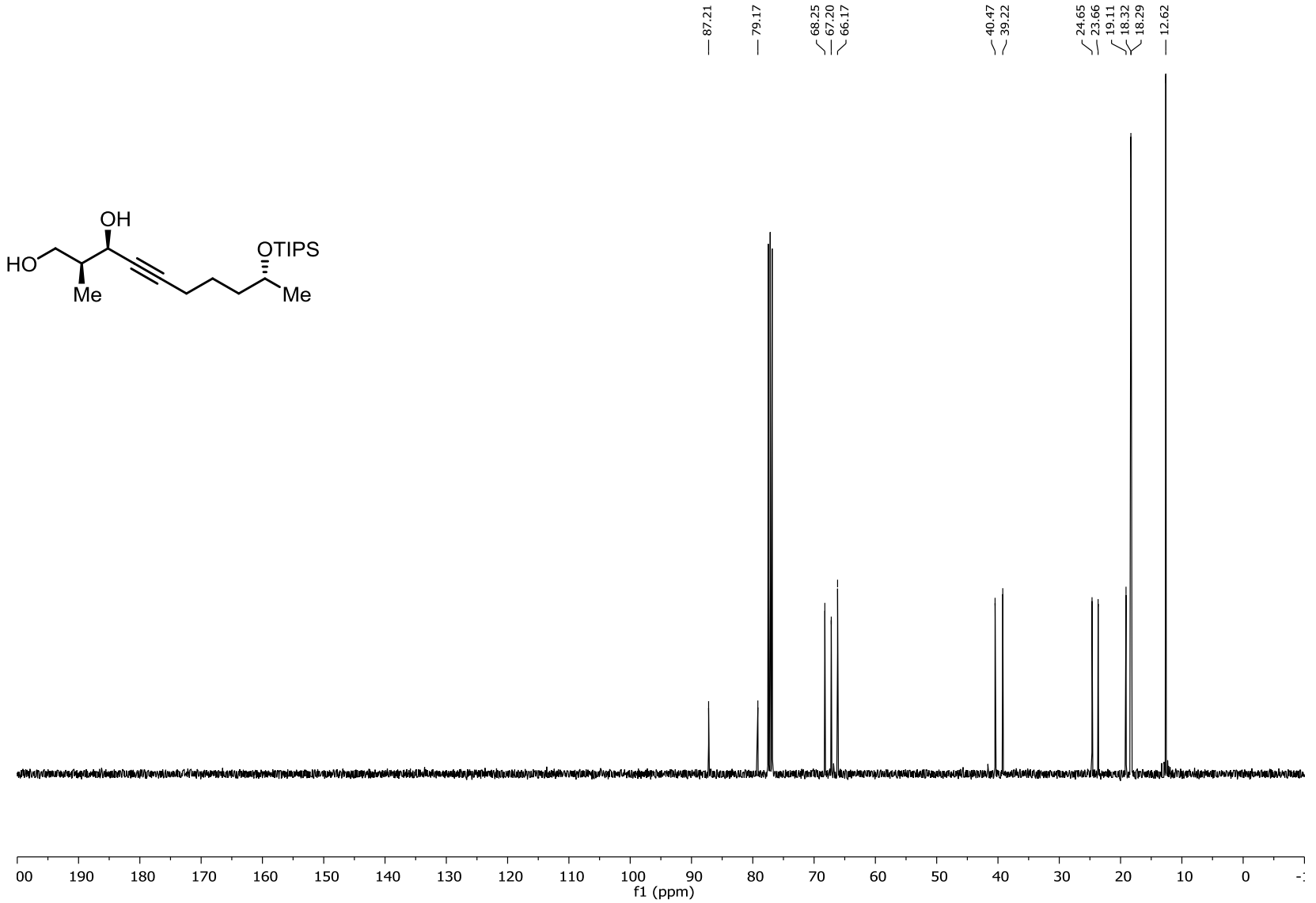
***tert*-butyl (*2R,3R,9R*)-3-hydroxy-2-methyl-9-((triisopropylsilyl)oxy)dec-4-ynoate (22)**



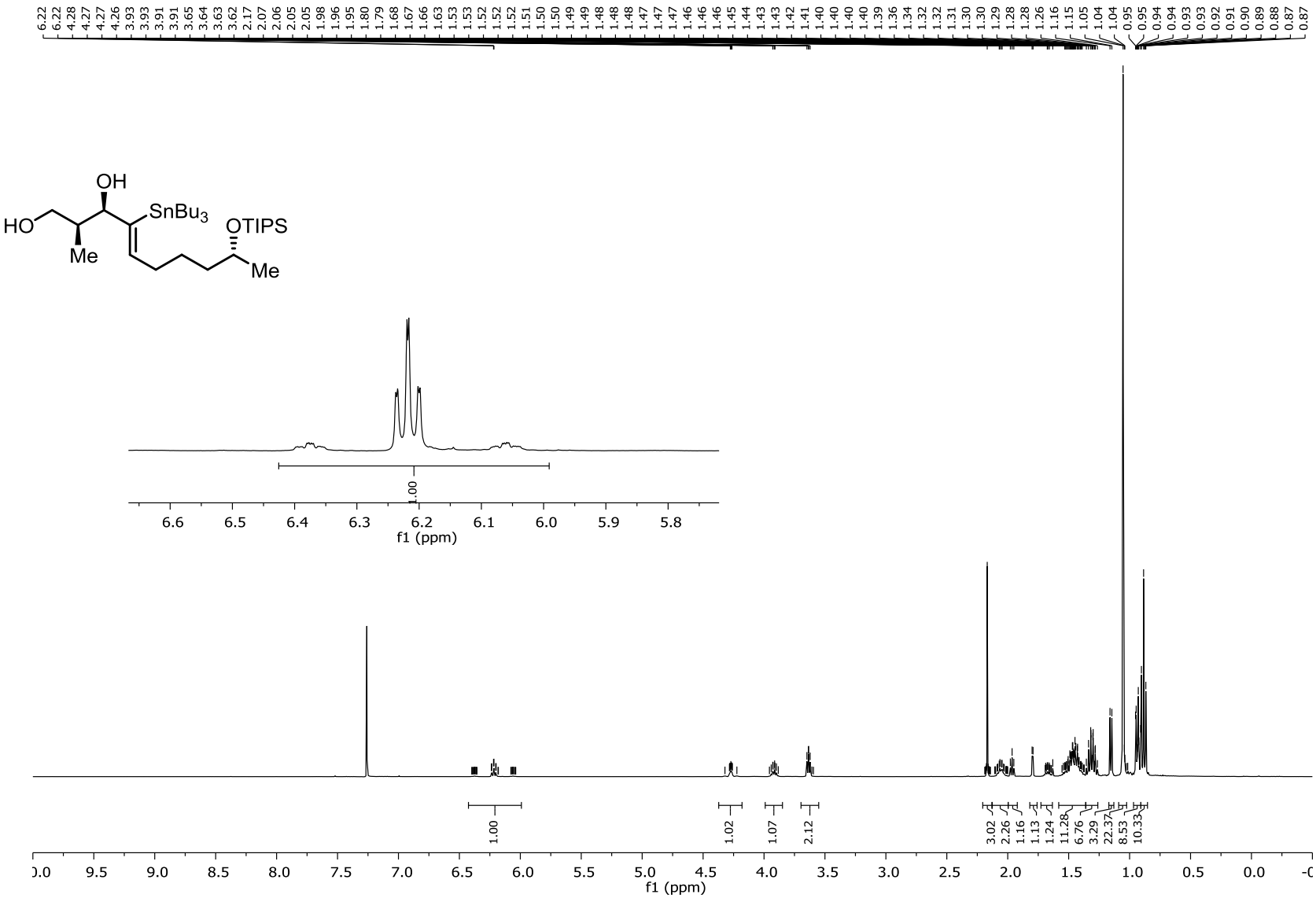
(2*S*,3*R*,9*R*)-2-methyl-9-((triisopropylsilyl)oxy)dec-4-yne-1,3-diol (23)



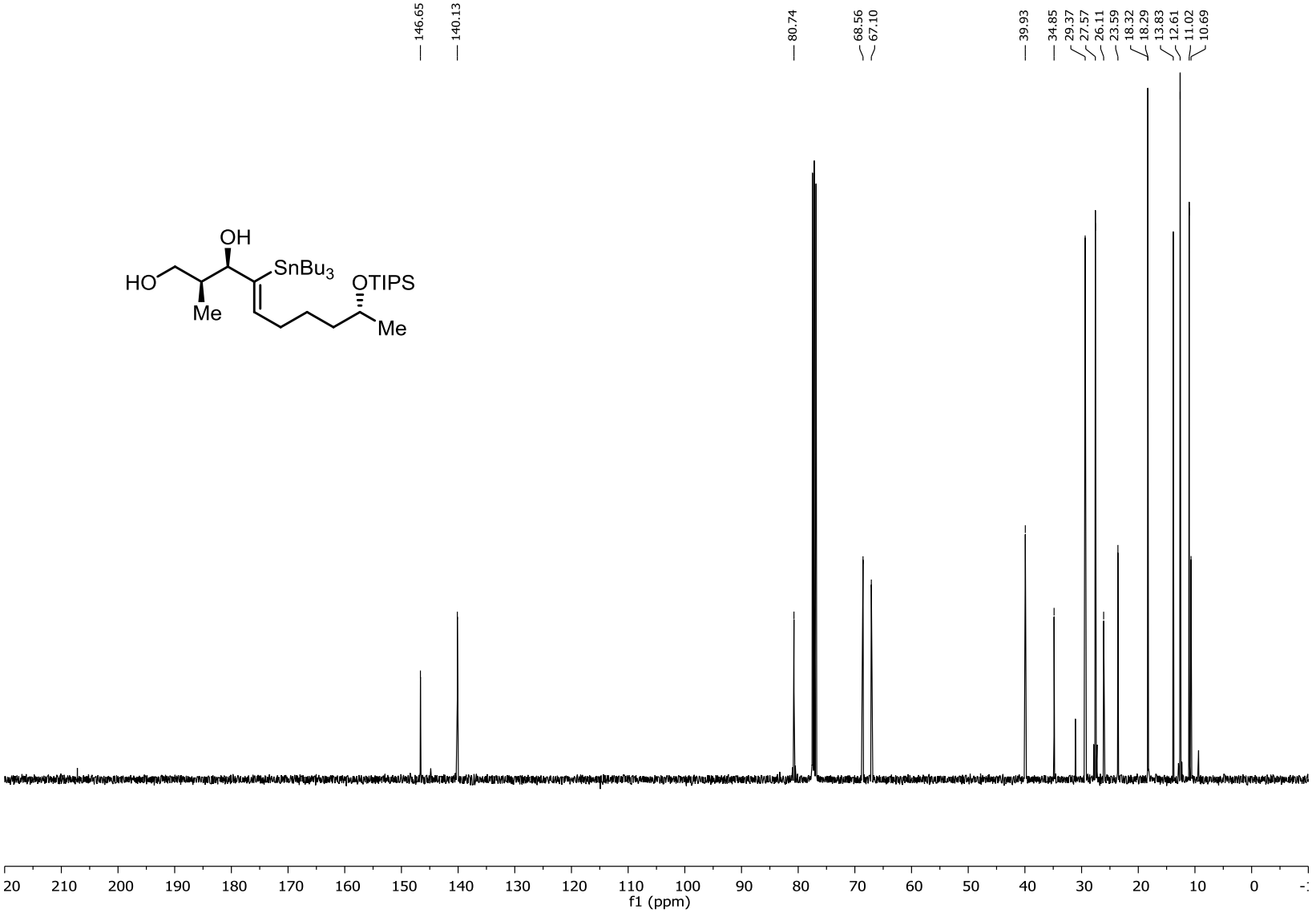
(2*S*,3*R*,9*R*)-2-methyl-9-((triisopropylsilyl)oxy)dec-4-yne-1,3-diol (23)



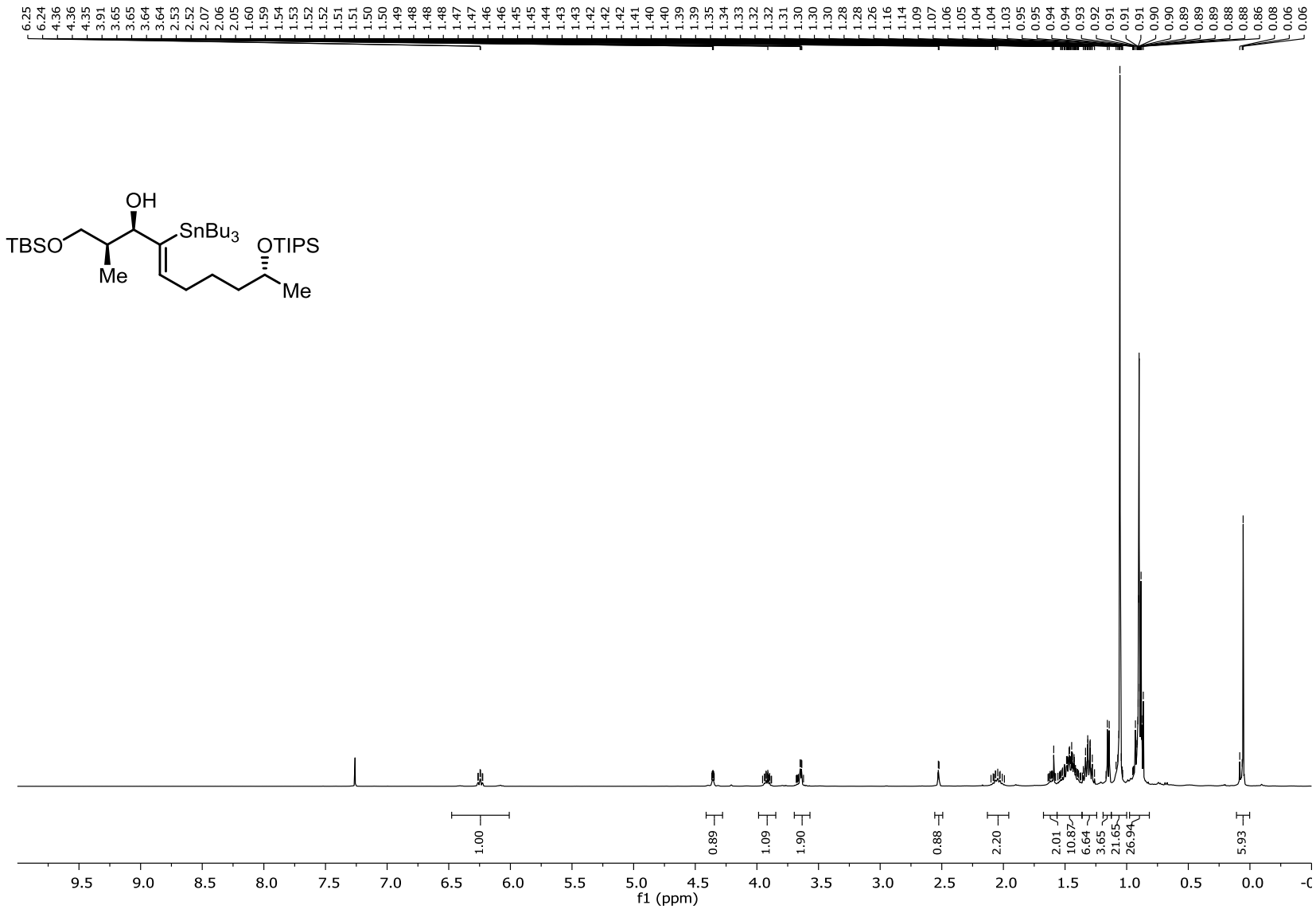
(2*S*,3*R*,9*R*,*Z*)-2-methyl-4-(tributylstannyl)-9-((triisopropylsilyl)oxy)dec-4-ene-1,3-diol (24)



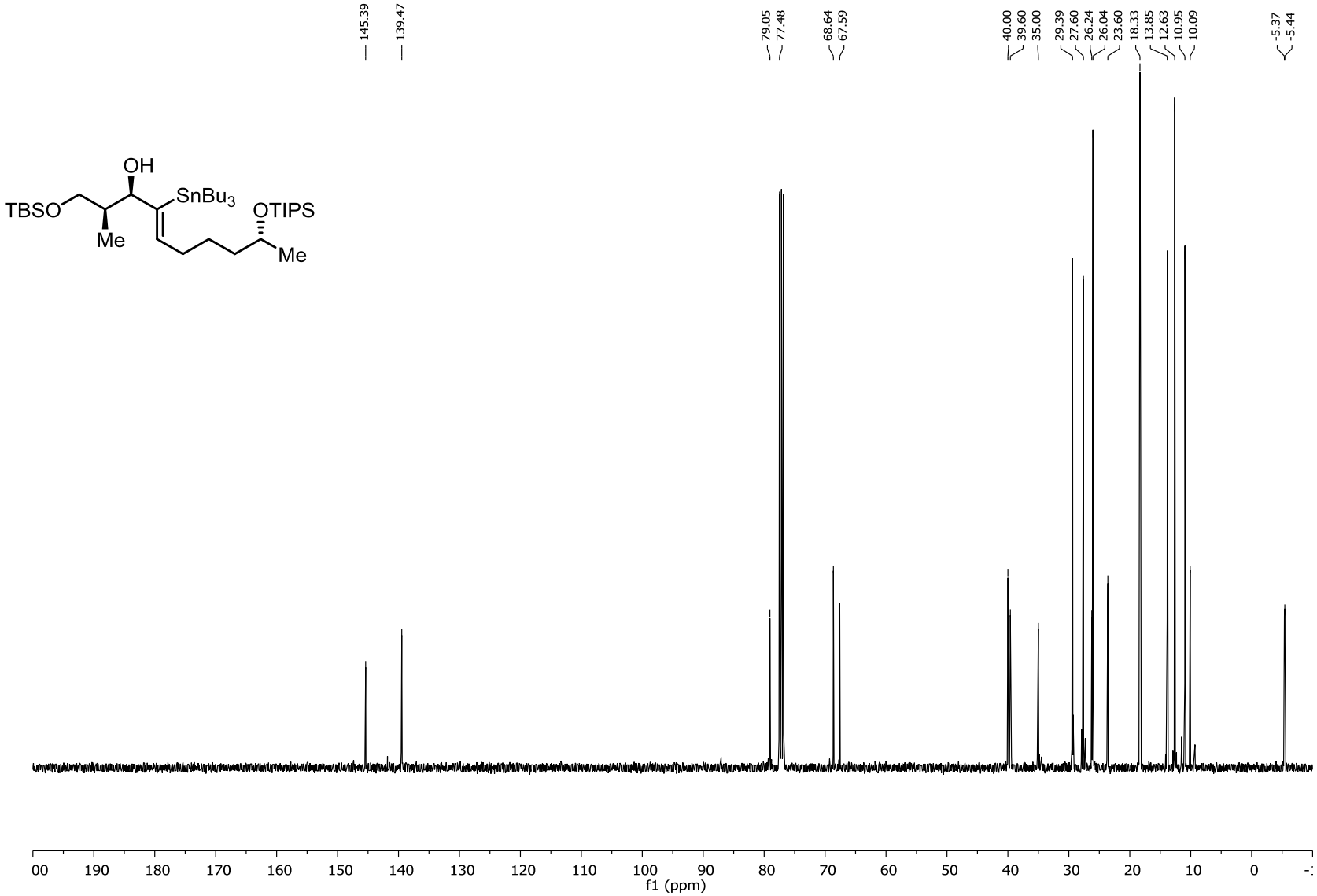
(2*S*,3*R*,9*R*,*Z*)-2-methyl-4-(tributylstannyl)-9-((triisopropylsilyl)oxy)dec-4-ene-1,3-diol (24)



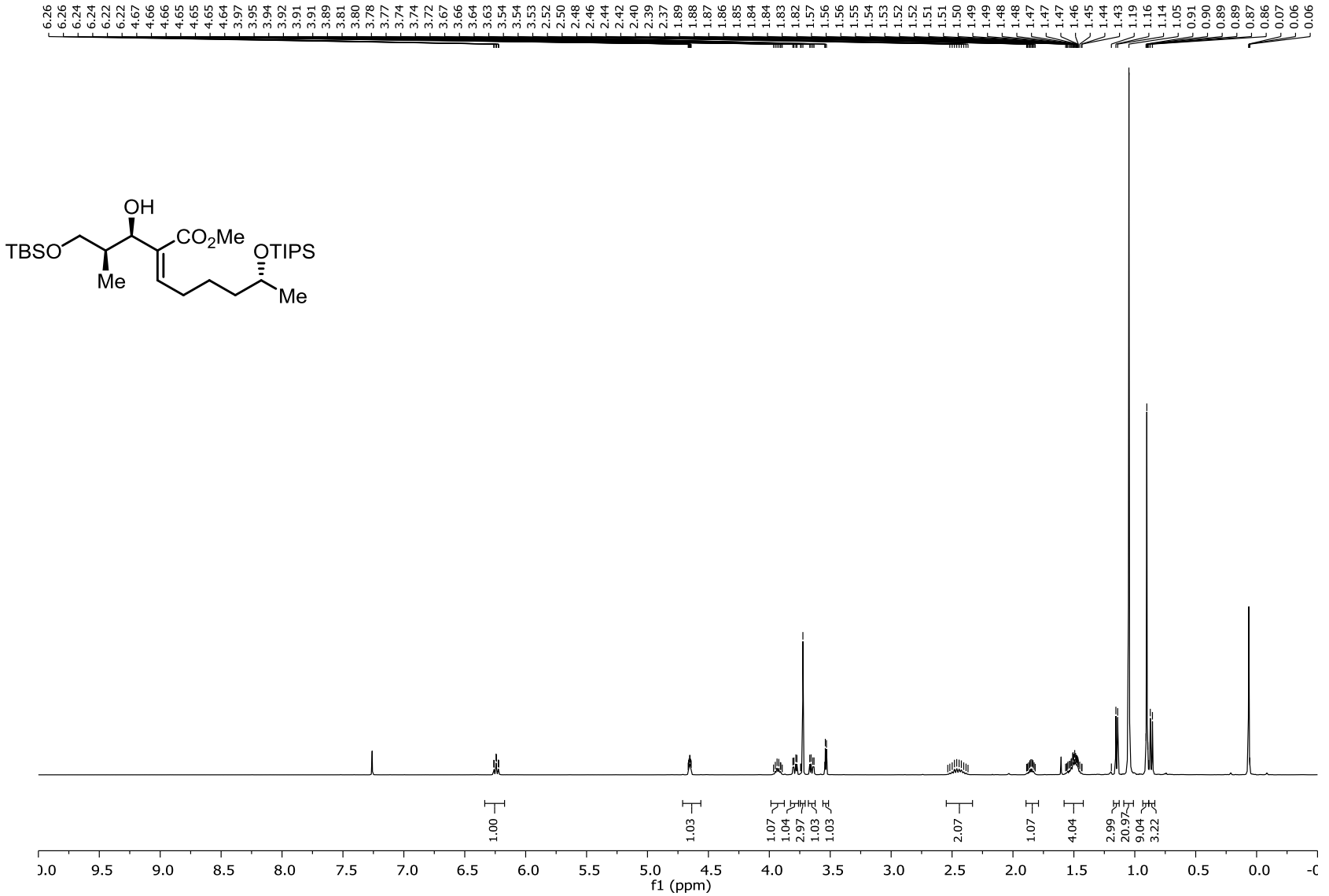
(6*S*,7*R*,13*R*,*Z*)-15,15-diisopropyl-2,2,3,3,6,13,16-heptamethyl-8-(tributylstannyl)-4,14-dioxa-3,15-disilaheptadec-8-en-7-ol (S23)



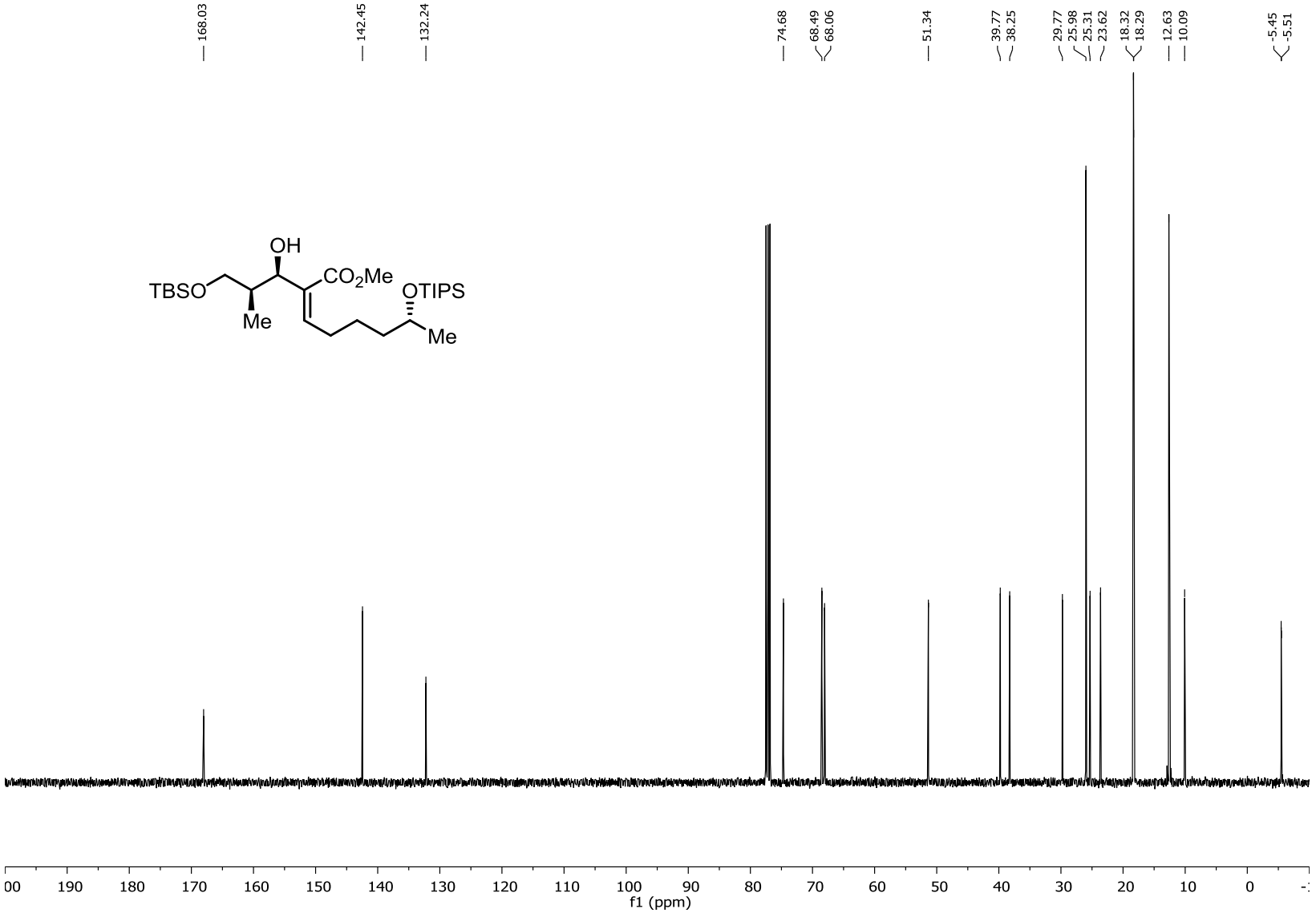
(6*S*,7*R*,13*R*,*Z*)-15,15-diisopropyl-2,2,3,3,6,13,16-heptamethyl-8-(tributylstannyl)-4,14-dioxa-3,15-disilaheptadec-8-en-7-ol (S23)



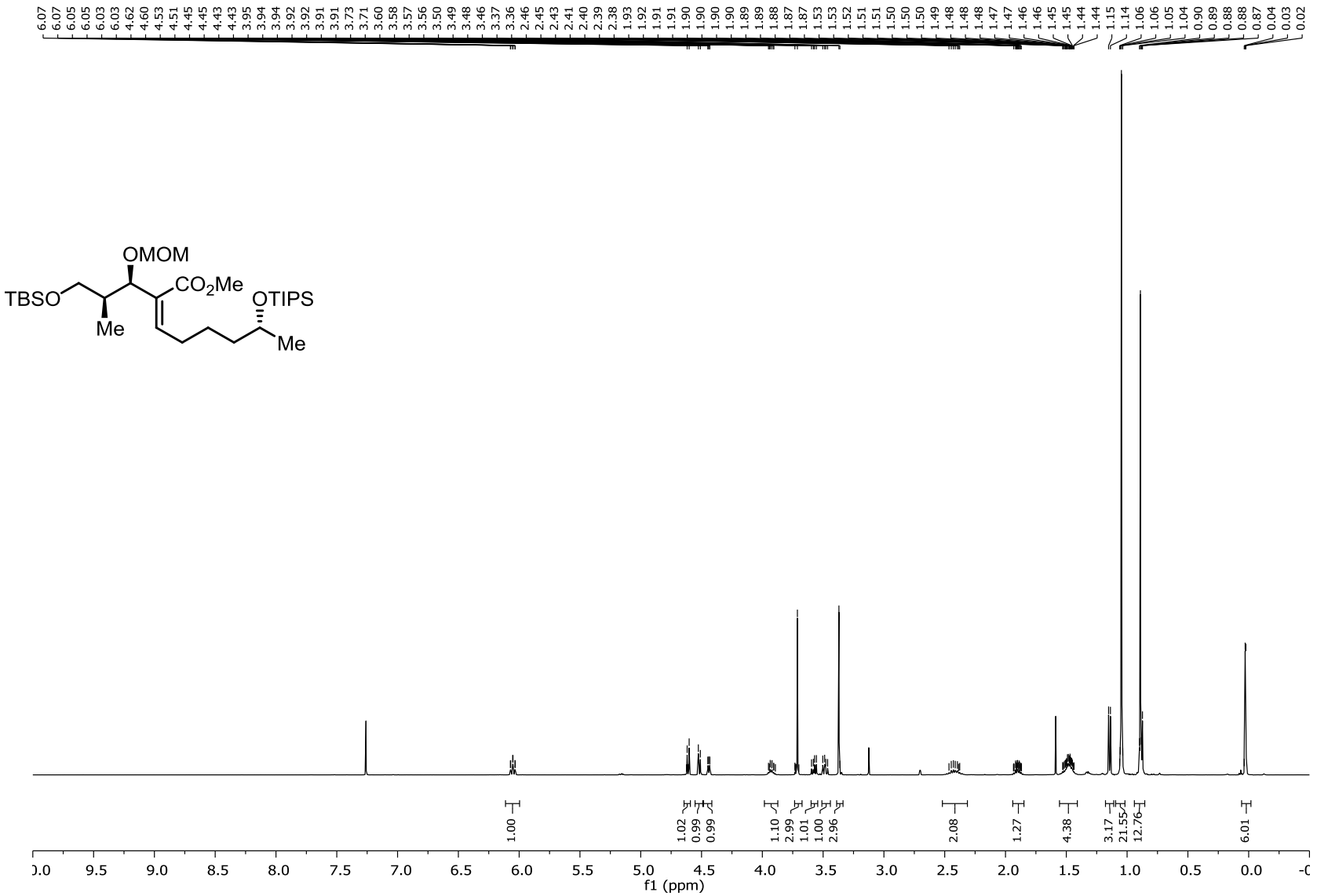
methyl (*R*,*Z*)-2-((1*R*,2*S*)-3-((tert-butyldimethylsilyl)oxy)-1-hydroxy-2-methylpropyl)-7-((triisopropylsilyl)oxy)oct-2-enoate (25)



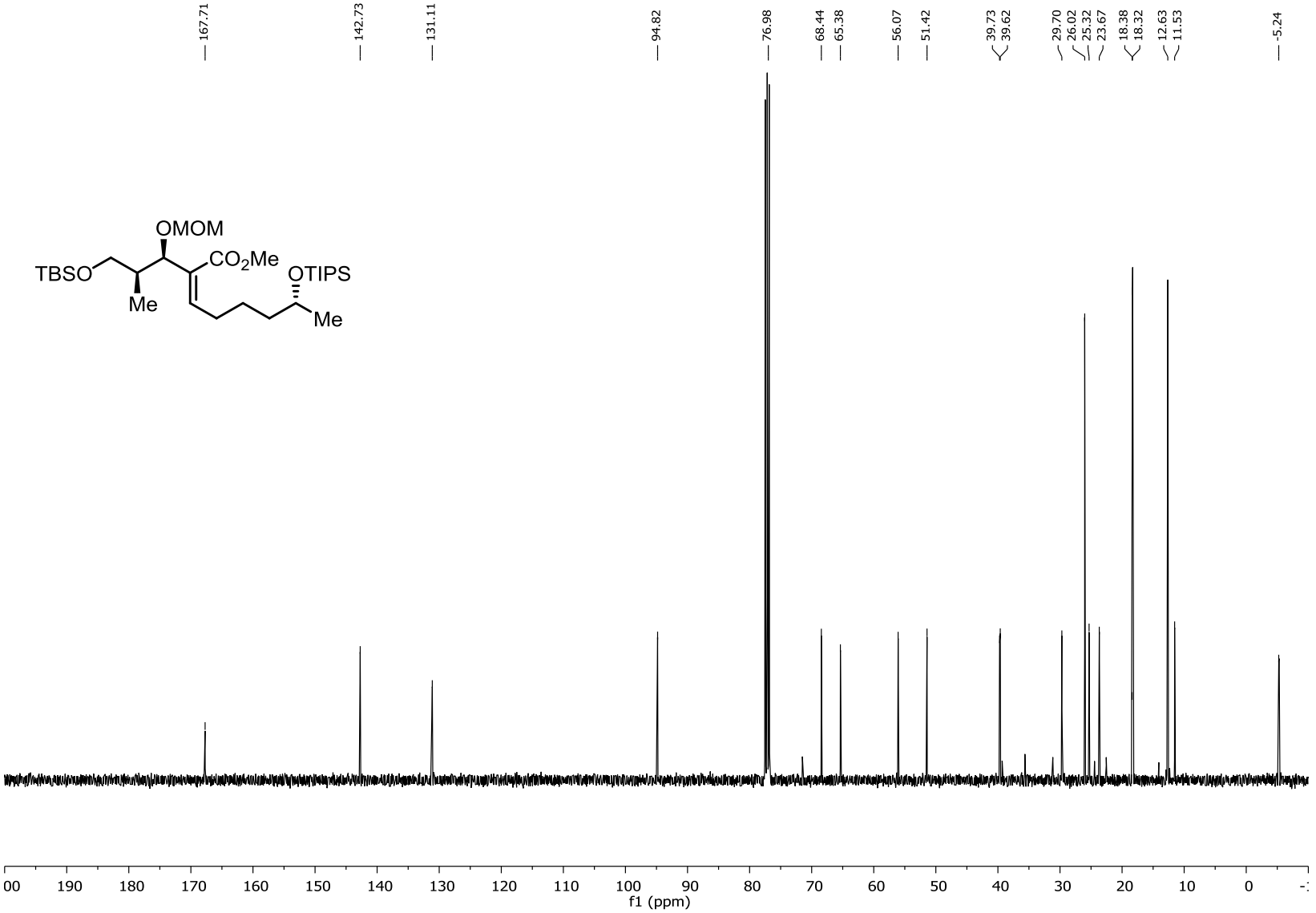
methyl (*R*,*Z*)-2-((1*R*,2*S*)-3-((tert-butyldimethylsilyl)oxy)-1-hydroxy-2-methylpropyl)-7-((triisopropylsilyl)oxy)oct-2-enoate (25)



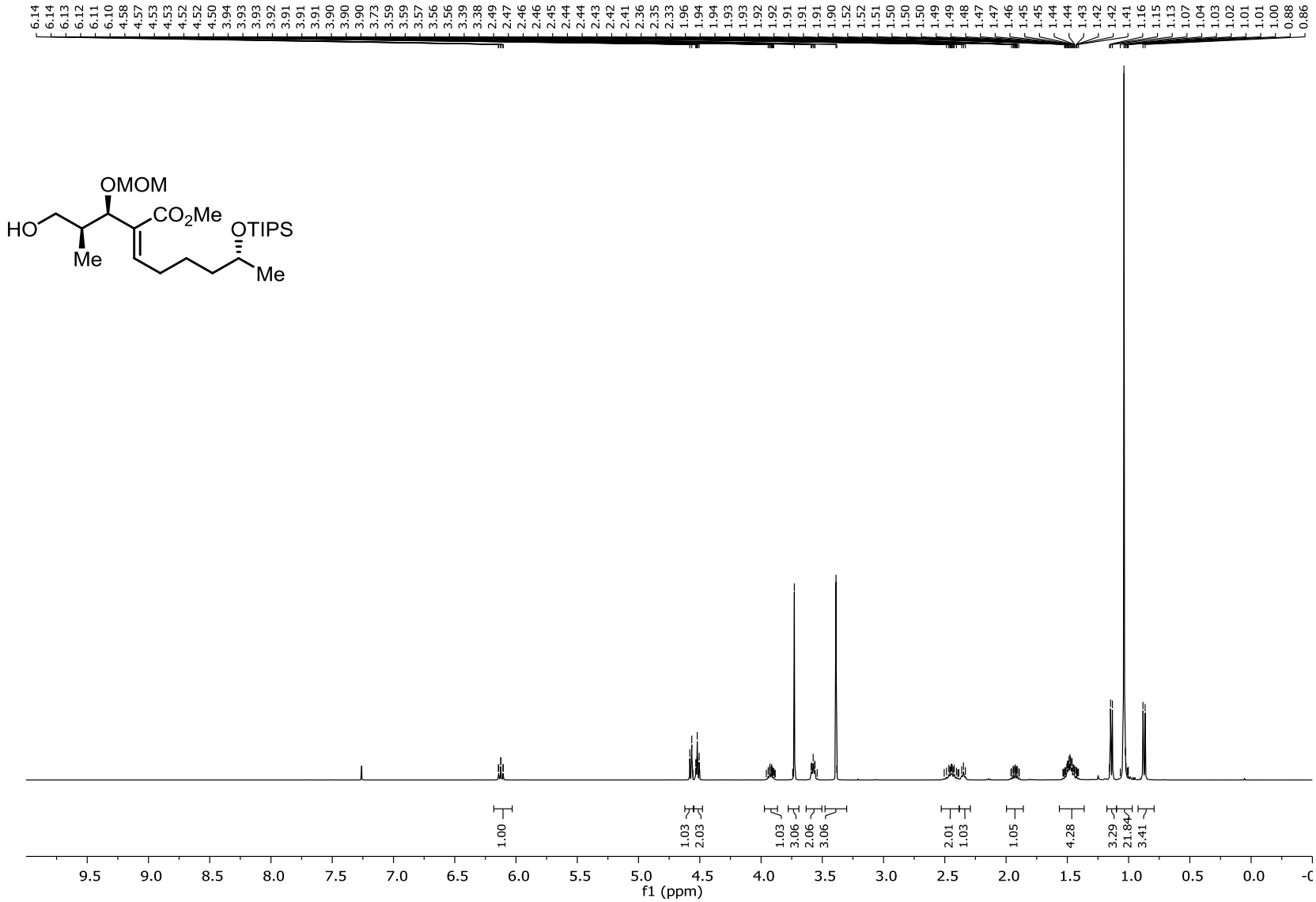
methyl (*R*,*Z*)-2-((1*R*,2*S*)-3-((tert-butyldimethylsilyl)oxy)-1-hydroxy-2-methylpropyl)-7-((triisopropylsilyl)oxy)oct-2-enoate (S24)



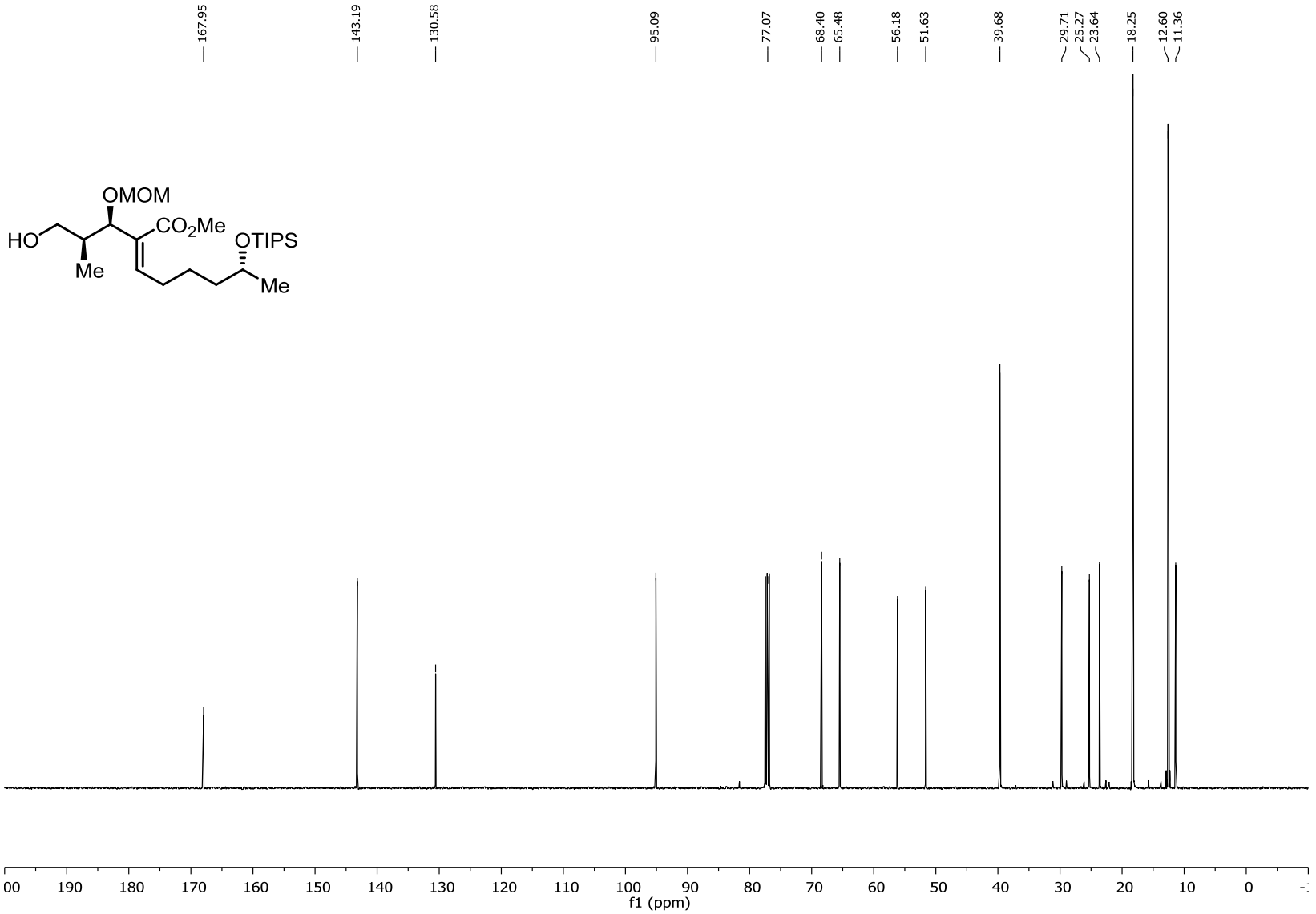
methyl (*R*,Z)-2-((1*R*,2*S*)-3-((tert-butyldimethylsilyl)oxy)-1-hydroxy-2-methylpropyl)-7-((triisopropylsilyl)oxy)oct-2-enoate (S24)



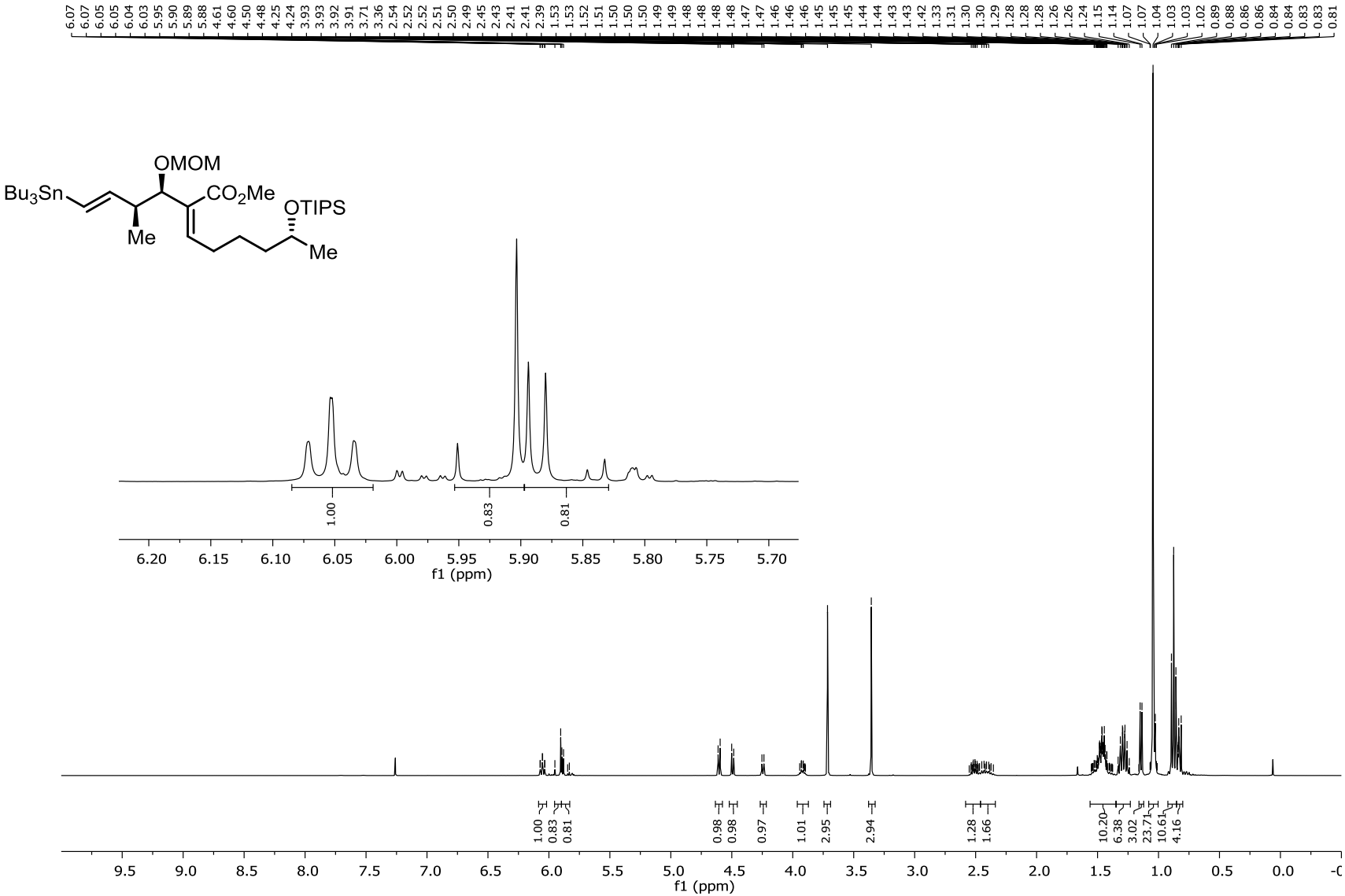
methyl (*R*,*Z*)-2-((1*R*,2*S*)-3-((tert-butyldimethylsilyl)oxy)-1-hydroxy-2-methylpropyl)-7-((triisopropylsilyl)oxy)oct-2-enoate (26)



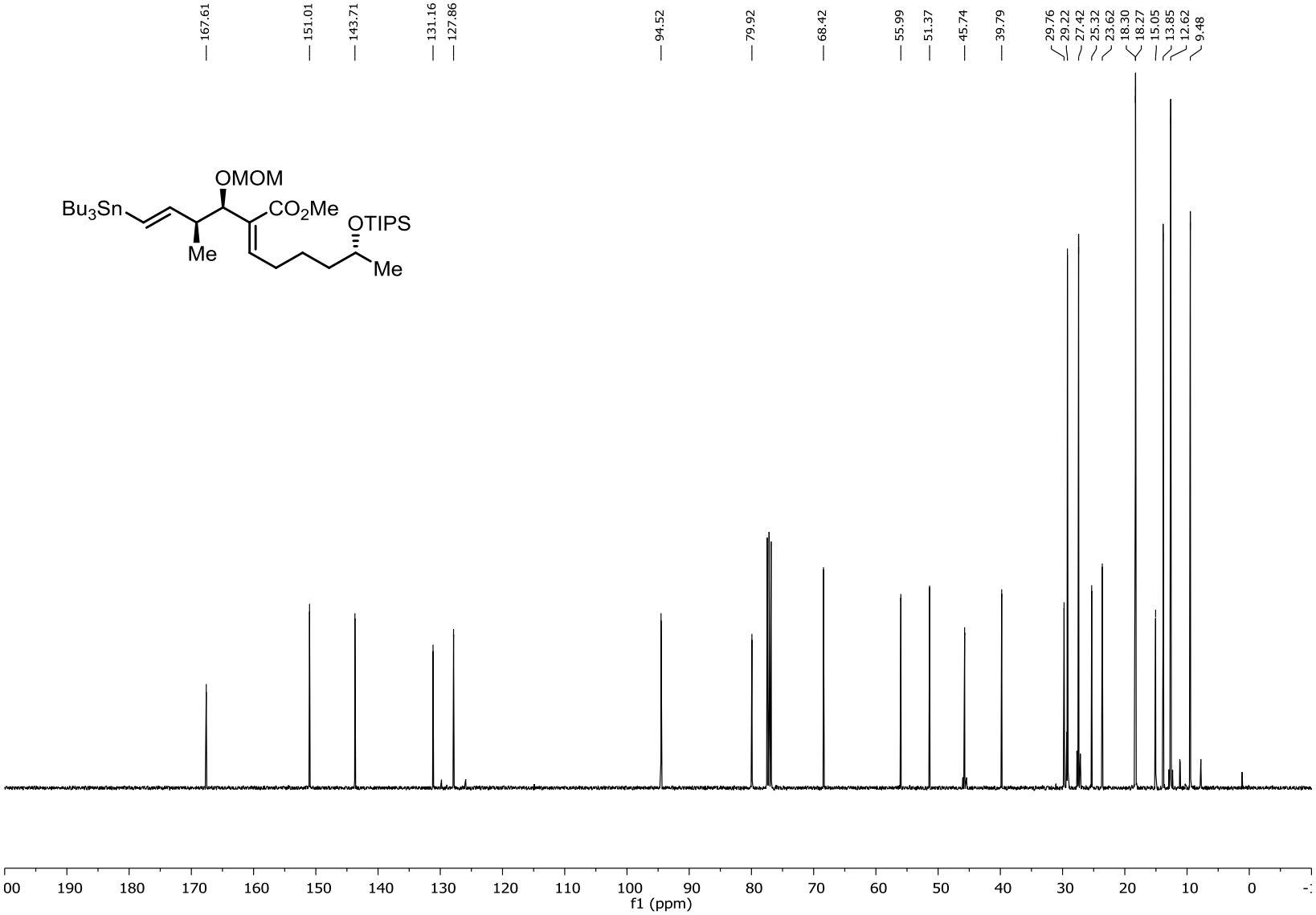
methyl (*R*,Z)-2-((1*R*,2*S*)-3-((tert-butyldimethylsilyl)oxy)-1-hydroxy-2-methylpropyl)-7-((triisopropylsilyl)oxy)oct-2-enoate (26)



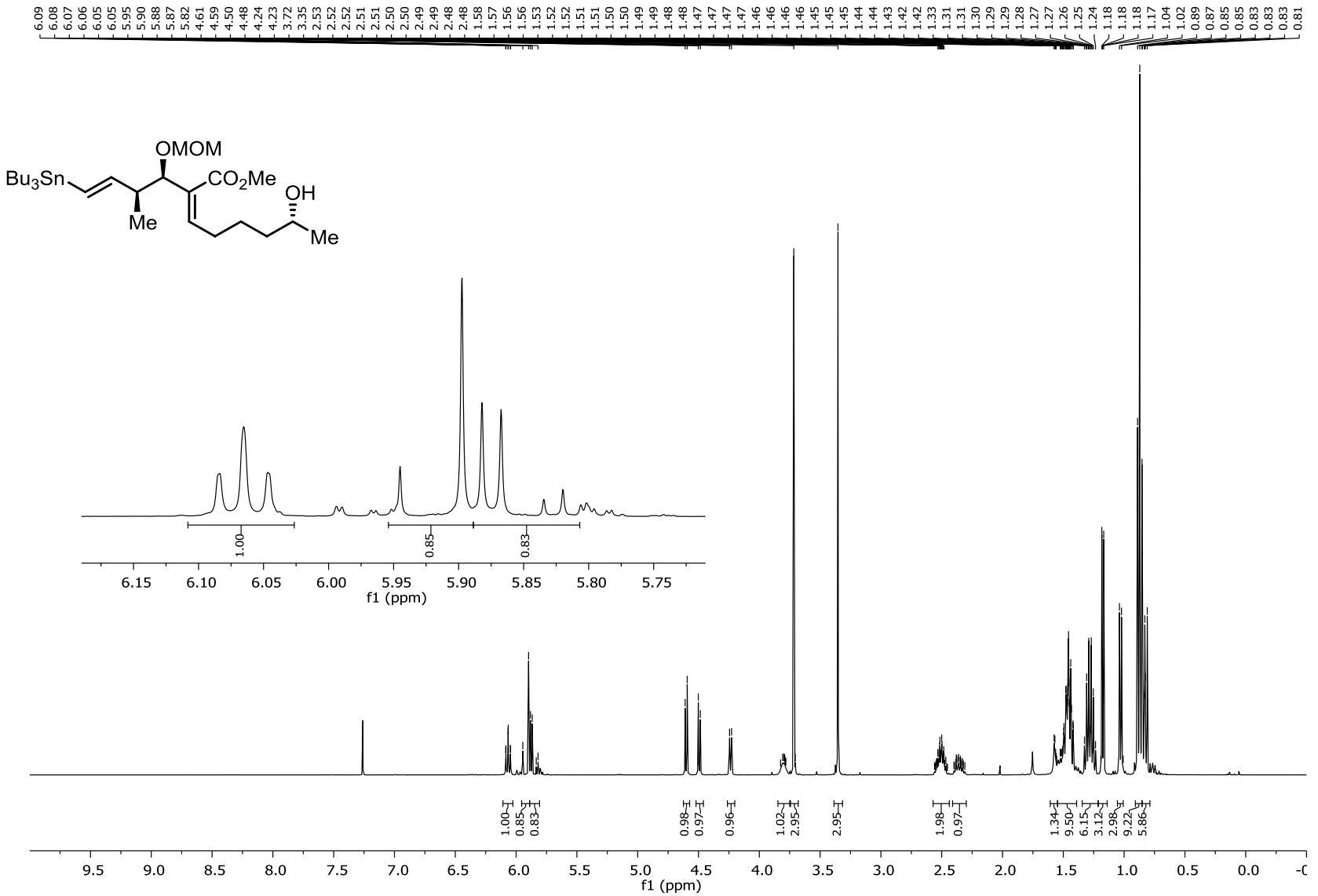
methyl (*R*,Z)-2-((1*R*,2*S*,E)-1-(methoxymethoxy)-2-methyl-4-(tributylstannyl)but-3-en-1-yl)-7-((triisopropylsilyl)oxy)oct-2-enoate (16)



methyl (*R*,Z)-2-((1*R*,2*S*,E)-1-(methoxymethoxy)-2-methyl-4-(tributylstannyl)but-3-en-1-yl)-7-((triisopropylsilyl)oxy)oct-2-enoate (16)



methyl (*R*,Z)-7-hydroxy-2-((1*R*,2*S*,E)-1-(methoxymethoxy)-2-methyl-4-(tributylstannyl)but-3-en-1-yl)oct-2-enoate (S25)



methyl (*R*,Z)-7-hydroxy-2-((1*R*,2*S*,E)-1-(methoxymethoxy)-2-methyl-4-(tributylstannyl)but-3-en-1-yl)oct-2-enoate (S25)