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Supporting Information

Stereospecific Synthesis of Fluoroalkenes by Silver-Mediated Fluorination of Functionalized Alkenylstannanes

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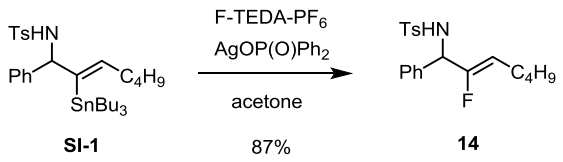
Crystallographic Information



SI-1 **14**

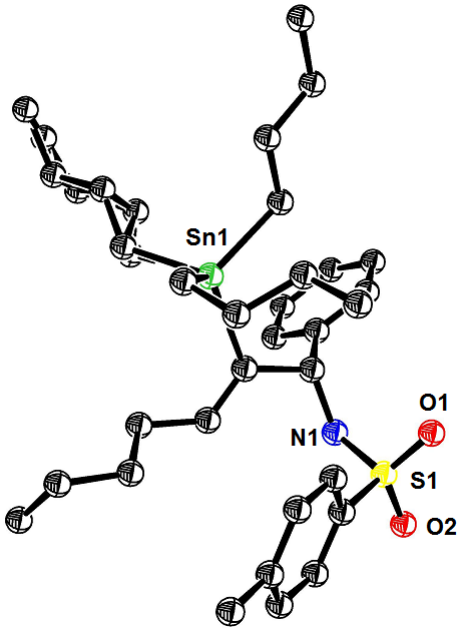


Figure S-1. Structure of Stannane **SI-1** in the Solid State

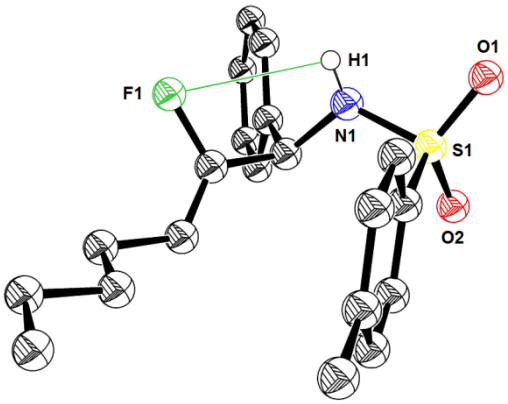


Figure S-2. Structure of Fluoroalkene **14** in the Solid State

X-ray Crystal Structure Analysis of 9954: $C_{32}H_{51}NO_2SSn$, M_r = 632.48 g · mol^{-1}, colorless plate, crystal size 0.26 x 0.14 x 0.06 mm, monoclinic, space group *P2$_1$/c*, *a* = 15.041(3) Å, *b* = 22.972(3) Å, *c* = 9.4505(2) Å, β = 97.301(7)°, *V* = 3239.0(7) Å^3, *T* = 100 K, *Z* = 4, D_{calc} = 1.297 g · cm^3, λ = 0.71073 Å, μ(*MoK*$_\alpha$) = 0.880 mm^{-1}, Empirical absorption correction (T_{min} = 0.83, T_{max} = 0.95), Bruker AXS Enraf-Nonius KappaCCD diffractometer, 2.805 < θ < 36.045°, 86733 measured reflections, 15364 independent reflections, 12313 reflections with $I > 2\sigma(I)$, structure solved by direct methods and refined by full-matrix least-squares against F^2 to R_1 = 0.039 [$I > 2\sigma(I)$], wR_2 = 0.095, 335 parameters, H atoms riding, *S* = 1.051, residual electron density 1.5 / -2.5 e Å^{-3}. **CCDC-1511736**.

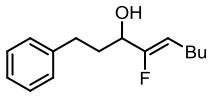
X-ray Crystal Structure Analysis of Fluoroalkene 14: $C_{20}H_{24}FNO_2S$, M_r = 361.46 g · mol^{-1}, colorless plate, crystal size 0.25 x 0.07 x 0.05 mm, monoclinic, space group *C2*, *a* = 25.7470(12) Å, *b* = 5.272(2) Å, *c* = 15.2010(19) Å, β = 114.977(13)°, *V* = 1870.4(8) Å^3, *T* = 100 K, *Z* = 4, D_{calc} = 1.284 g · cm^3, λ = 0.71073 Å, μ(*MoK*$_\alpha$) = 0.195 mm^{-1}, Empirical absorption correction (T_{min} = 0.97, T_{max} = 0.99), Bruker AXS Enraf-Nonius KappaCCD diffractometer, 2.726 < θ < 33.162°, 27424 measured reflections, 7129 independent reflections, 6241 reflections with $I > 2\sigma(I)$, structure solved by direct methods and refined by full-matrix least-squares against F^2 to R_1 = 0.046 [$I > 2\sigma(I)$], wR_2 = 0.105, 232 parameters, H atoms riding, absolute structure parameter = 0.08(5), *S* = 1.035, residual electron density 0.4 / -0.4 e Å^{-3}. **CCDC-1511735**.

Procedures

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, Fluorochem) were used as received. $[Cp^*RuCl_2]_n$ was prepared according to literature procedures and was stored under Argon.[10] 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.

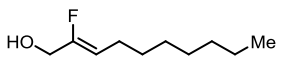
Synthesis of Silver(I) Diphenylphosphinate ($AgOP(O)Ph_2$).[1] Diphenylphosphinic acid (5.73 g, 26.3 mmol, 1.05 equiv.) was added to a stirred solution of NaOH (1.1 g, 27.5 mmol, 1.1 equiv.) in water (10 mL) and stirring continued until complete dissolution was achieved (occasionally, a few extra drops of aqueous NaOH were necessary). Next, a solution of $AgNO_3$ (4.25 g, 25 mmol, 1.0 equiv.) in a minimum amount water was rapidly added to the vigorously stirred mixture, causing the immediate formation of a grey precipitate. The solid material was filtered off with suction; it was successively washed twice with water, acetone and *tert*-butyl methyl ether before it was dried under high vacuum to give the title compound as a grey powder (83%, 6.72 g). The material obtained was used without further purification.

Representative procedure for the Silver Mediated Fluorination of Alkenylstannanes. (*Z*)-1-Phenyl-4-(tributylstannyl)non-4-en-3-ol (2). $AgOP(O)Ph_2$ (390 mg, 1.2 mmol, 1.2 equiv.) and F-TEDA-PF_6 (941 mg, 2.0 mmol, 2.0 equiv.) were stirred under argon in an oven-dried Schlenk at room temperature for 10 minutes until a homogenous greyish powder had formed. This material was suspended in dry acetone (15 mL). A solution of (Z)-1-phenyl-4-(tributylstannyl)non-4-en-3-ol (507 mg, 1.0 mmol, 1.0 equiv.) in dry acetone (5 mL) was added over 60 min via syringe pump to this suspension. Once the addition was complete, the mixture was diluted with *tert*-butyl methyl ether and the reaction quenched with saturated ammonium chloride solution. The mixture was extracted twice with *tert*-butyl methyl ether, the combined extracts were washed with brine, dried over magnesium sulfate and concentrated under reduced pressure. Flash chromatography of the residue (SiO_2, hexanes/ethyl acetate) provided the title compound as a colorless oil (78%, 184 mg). ^{1}H NMR (300 MHz, Chloroform-d) δ 7.34 – 7.26 (m, 2H), 7.21 (m, 3H), 4.82 (dt, *J* = 37.8, 7.5 Hz, 1H), 4.08 (dt, *J* = 16.6, 6.7 Hz, 1H), 2.86 – 2.63 (m, 2H), 2.24 – 2.06 (m, 2H), 2.06 – 1.91 (m, 2H), 1.80 (s, 1H), 1.44 – 1.26 (m, 4H), 1.01 – 0.79 (m, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.3 (d, *J* = 255.9 Hz), 141.6, 128.6, 128.5, 126.1, 107.1 (d, *J* = 14.1 Hz), 70.4 (d, *J* = 30.5 Hz), 35.6, 31.8, 31.6 (d, *J* = 1.8 Hz), 23.1 (d, *J* = 4.5 Hz), 22.4, 14.0 ppm; ^{19}F NMR (282 MHz, $CDCl_3$) δ −126.7 ppm; IR (film, $CHCl_3$) 3342, 3027, 2955, 2927, 2859, 1706, 1604, 1496, 1455, 1298, 1179, 1031, 936, 830, 746, 698 cm^{-1}; HRMS (ESI): *m/z* calcd. for $C_{15}H_{21}OFNa$ [M+Na$^+$]: 259.14686, found 259.14691.



The following compounds were prepared analogously:

(Z)-2-Fluorodec-2-en-1-ol (4). Colorless oil (74%, 64 mg). ^{1}H NMR (300 MHz, Chloroform-d) δ 4.82 (dt, *J* = 37.0, 7.6 Hz, 1H), 4.09 (dd, *J* = 16.0, 6.2 Hz, 2H), 2.09 (qd, *J* = 7.4, 1.8 Hz, 2H), 1.98 (t, *J* = 6.3 Hz, 1H), 1.53 – 1.18 (m, 10H), 0.94 – 0.79 (m, 3H) ppm; ^{13}C NMR (75 MHz, Chloroform-d) δ 157.5 (d, *J* = 253.2 Hz), 131.3 (d, *J* = 377.8 Hz), 108.4 (d, *J* = 14.1 Hz), 61.5 (d, *J* = 32.6 Hz), 31.9, 29.3 (d, *J* = 1.7 Hz), 29.2 (d, *J* = 4.9 Hz), 23.5 (d, *J* = 4.2 Hz), 22.8, 14.2 ppm; ^{19}F NMR (282 MHz, $CDCl_3$) δ −121.4 ppm; IR (film, $CHCl_3$) 3328, 2924, 2856, 1709, 1458, 1378, 1214,1114, 1067, 1012, 919, 856, 723, 683 cm^{-1}; HRMS (EI): *m/z* calcd. for $C_{10}H_{19}OF$ [M]: 174.14199, found 174.14206.



(Z)-3-Fluoro-2-methyl-6-phenylhex-3-en-2-ol (5). Colorless oil (68%, 71 mg). ^{1}H NMR (300 MHz, Chloroform-d) δ 7.35 – 7.26 (m, 2H), 7.25 – 7.15 (m, 3H), 4.91 (dt, *J* = 37.9, 7.5 Hz, 1H), 2.70 (dd, *J* = 8.7, 6.7 Hz, 2H), 2.47 – 2.35 (m, 2H), 1.86 (s, 1H), 1.38 (d, *J* = 1.2 Hz, 6H). ^{13}C NMR (75 MHz, Chloroform-d) δ 163.4 (d, *J* = 257.7 Hz), 141.7, 128.6, 128.4, 126.0, 102.1 (d, *J* = 14.9 Hz), 70.4 (d, *J* = 29.3 Hz), 35.7 (d, *J* = 1.7 Hz), 27.4, 25.2 (d, *J* = 5.2 Hz) ppm; ^{19}F NMR (282 MHz, $CDCl_3$) δ −122.6 ppm; IR (film, $CHCl_3$) 3380, 2930, 2858, 1702, 1496, 1454, 1364, 1280, 1171, 1094, 1053, 1030, 1002, 955, 877, 841, 782, 747 cm^{-1}; HRMS (ESI): *m/z* calcd. for $C_{13}H_{17}OFNa$ [M+Na$^+$]: 231.11556, found 231.11565.

(Z)-1-((*tert*-Butyldimethylsilyl)oxy)-4-fluorononon-4-en-3-ol (6). Colorless oil (57% , 82 mg). ^{1}H NMR (300 MHz, Chloroform-d) δ 4.89 (dtd, *J* = 38.4, 7.6, 0.8 Hz, 1H), 4.44 – 4.23 (m, 1H), 3.91 (ddd, *J* = 10.5, 6.5, 4.2 Hz, 1H), 3.79 (ddd, *J* = 10.2, 7.1, 4.1 Hz, 1H), 3.59 (d, *J* = 4.4 Hz, 1H), 2.17 – 2.03 (m, 2H), 2.01 – 1.73 (m, 2H), 1.47 – 1.22 (m, 4H), 0.97 – 0.83 (m, 12H), 0.08 (s, 6H) ppm; ^{13}C NMR (75 MHz, Chloroform-d) δ 159.3 (d, *J* = 254.3 Hz), 105.9 (d, *J* = 13.3 Hz), 70.4 (d, *J* = 33.7 Hz), 61.8, 35.5, 31.6, 26.0, 23.0 (d, *J* = 4.7 Hz), 22.4, 18.2, 14.0, -5.5 ppm; ^{19}F NMR (282 MHz, $CDCl_3$) δ −125.1 ppm; IR (film, $CHCl_3$) 3408, 2955, 2929, 2858, 1709, 1470, 1389, 1362, 1254, 1099, 1006, 939, 832, 775, 732, 664 cm^{-1}; HRMS (ESI): *m/z* calcd. for $C_{15}H_{31}O_2FSiNa$ [M+Na$^+$]: 313.19696, found 313.19696.

(Z)-6-Fluoro-9-phenylnon-5-ene-1,7-diol (7). Colorless oil (62%, 78 mg). ^{1}H NMR (300 MHz, Chloroform-d) δ 7.33 – 7.25 (m, 2H), 7.20 (m, 3H), 4.81 (dt, *J* = 37.6, 7.6 Hz, 1H), 4.06 (dt, *J* = 16.4, 6.7 Hz, 1H), 3.64 (t, *J* = 6.4 Hz, 2H), 2.71 (dh, *J* = 13.9, 7.1 Hz, 2H), 2.14 (qd, *J* = 7.4, 1.7 Hz, 2H), 2.07 – 1.85 (m, 2H), 1.68 – 1.52 (m, 2H), 1.52 – 1.32 (m, 2H) ppm; ^{13}C NMR (75 MHz, Chloroform-d) δ 159.6 (d, *J* = 256.6 Hz), 141.5, 128.6, 128.5, 126.1, 106.5 (d, *J* = 14.1 Hz), 70.2 (d, *J* = 30.4 Hz), 62.7, 35.6, 32.2, 31.7, 25.5 (d, *J* = 1.8 Hz), 23.1 (d, *J* = 4.6 Hz) ppm; ^{19}F NMR (282 MHz, $CDCl_3$) δ −125.9 ppm; IR (film, $CHCl_3$) 3338, 2932, 2861, 1707, 1496, 1454, 1262, 1032, 933, 836, 748, 698, 494 cm^{-1}; HRMS (ESI): *m/z* calcd. for $C_{15}H_{21}O_2FNa$ [M+Na$^+$]: 275.14178, found 275.14184.

(Z)-6-Fluoro-7-hydroxy-9-phenylnon-5-enenitrile (8). Colorless oil (60%, 74 mg). ^{1}H NMR (400 MHz, Chloroform-d) δ 7.36 – 7.27 (m, 2H), 7.21 (m, 3H), 4.82 (dt, *J* = 36.9, 7.6 Hz, 1H), 4.09 (dt, *J* = 14.3, 6.6 Hz, 1H), 2.83 – 2.63 (m, 2H), 2.34 (t, *J* = 7.2 Hz, 2H), 2.30 – 2.22 (m, 2H), 2.21 – 2.15 (m, 1H), 2.08 – 1.90 (m, 2H), 1.75 (p, *J* = 7.2 Hz, 2H) ppm; ^{13}C NMR (101 MHz, Chloroform-d) δ 161.1 (d, *J* = 259.1 Hz), 141.3, 128.6, 128.5, 126.1, 119.7, 103.9 (d, *J* = 13.6 Hz), 69.80 (d, *J* = 30.4 Hz), 35.5, 31.6, 25.0 (d, *J* = 2.1 Hz), 22.5 (d, *J* = 5.0 Hz), 16.7 ppm; ^{19}F NMR (282 MHz, $CDCl_3$) δ −122.9 ppm; IR (film, $CHCl_3$) 3429, 3027, 2936, 2865, 2249, 1707, 1603, 1496, 1454, 1424, 1295, 1140, 1063, 1030, 1013, 925, 851, 749, 699 cm^{-1}; HRMS (ESI): *m/z* calcd. for $C_{15}H_{18}NOFNa$ [M+Na$^+$]: 270.12646, found 270.12649.

(Z)-2-(6-Fluoro-7-hydroxy-9-phenylnon-5-en-1-yl)isoindoline-1,3-dione (9). Colorless solid (50%, 96 mg). ^{1}H NMR (300 MHz, Chloroform-d) δ 7.86 – 7.77 (m, 2H), 7.73 – 7.65 (m, 2H), 7.32 – 7.22 (m, 2H), 7.22 – 7.12 (m, 3H), 4.79 (dt, *J* = 37.4, 7.6 Hz, 1H), 4.18 – 3.96 (m, 1H), 3.67 (t, *J* = 7.3 Hz, 2H), 2.70 (hept, *J* = 7.1 Hz, 2H), 2.29 (d, *J* = 5.2 Hz, 1H), 2.15 (qd, *J* = 7.4, 1.7 Hz, 2H), 2.05 – 1.83 (m, 2H), 1.82 – 1.63 (m, 2H), 1.54 – 1.33 (m, 2H) ppm; ^{13}C NMR (75 MHz, Chloroform-d) δ 168.5, 159.9 (d, *J* = 257.2 Hz), 141.5, 134.0, 132.2, 128.5, 128.5, 126.0, 123.3, 106.0 (d, *J* = 14.0 Hz), 70.1 (d, *J* = 30.5 Hz), 37.8, 35.5, 31.7, 28.0, 26.4, 22.8 (d, *J* = 4.7 Hz) ppm; ^{19}F NMR (282 MHz, $CDCl_3$) δ −125.5 pm. IR (film, $CHCl_3$) 3463, 2940, 2861, 1770, 1702, 1604, 1496, 1437, 1396, 1371, 1239, 1187, 1116, 1037, 925, 862, 793, 751, 718, 699 cm^{-1}; HRMS (EI): *m/z* calcd. for $C_{23}H_{24}NO_3FNa$ [M+Na$^+$]: 404.16324, found 404.16349.

Ethyl (2E,5Z)-5-fluoro-4-hydroxy-3-methyldeca-2,5-dienoate (10). Colorless oil (71%, 87 mg). ^{1}H NMR (300 MHz, Chloroform-d) δ 6.07 (p, *J* = 1.4 Hz, 1H), 4.91 (dt, *J* = 37.0, 7.6 Hz, 1H), 4.55 (d, *J* = 16.0 Hz, 1H), 4.16 (q, *J* = 7.1 Hz, 2H), 2.37 (s, 1H), 2.18 – 2.00 (m, 5H), 1.34 (m, 4H), 1.28 (t, *J* = 7.1 Hz, 3H), 0.94 – 0.82 (m, 3H) ppm; ^{13}C NMR (75 MHz, Chloroform-d) δ 166.7, 158.1, 154.7, 117.3, 109.5 (d, *J* = 13.7 Hz), 75.2 (d, *J* = 31.6 Hz), 60.1, 31.3 (d, *J* = 1.8 Hz), 23.2 (d, *J* = 4.0 Hz), 22.3, 15.4, 14.4, 13.9 ppm; ^{19}F NMR (282 MHz, $CDCl_3$) δ −124.3 ppm; IR (film, $CHCl_3$) 3436, 2958, 2931, 2861, 1698, 1657, 1445, 1369, 1345, 1279, 1212, 1146, 1113, 1096, 1040, 938, 880, 826 cm^{-1}; HRMS (ESI): *m/z* calcd. for $C_{13}H_{21}O_3FNa$ [M+Na$^+$]: 267.13669, found 267.13679.

(*anti*,Z)-4-Fluoro-3-methylnon-4-en-2-ol (11). Colorless oil (54%, 47 mg, 6:1 mixture of α:β). Analytical of data of the pure promixal (α) isomer: ^{1}H NMR (400 MHz, Chloroform-d) δ 4.61 (dt, *J* = 38.7, 7.5 Hz, 1H), 3.86 – 3.69 (m, 1H), 2.22 (dp, *J* = 24.7, 7.2 Hz, 1H), 2.13 – 2.00 (m, 2H), 1.76 – 1.64 (m, 1H), 1.40 – 1.25 (m, 4H), 1.19 (dd, *J* = 6.2, 0.7 Hz, 3H), 1.08 (d, *J* = 7.1 Hz, 3H), 0.93 – 0.84 (m, 3H) ppm; ^{13}C NMR (101 MHz, Chloroform-d) δ 160.1 (d, *J* = 255.6 Hz), 107.5 (d, *J* = 15.6 Hz), 68.9, 45.1 (d, *J* = 24.4 Hz), 31.8 (d, *J* = 1.8 Hz), 23.3 (d, *J* = 5.1 Hz), 22.4, 20.3, 14.0, 13.9 (d, *J* = 2.9 Hz) ppm; ^{19}F NMR (282 MHz, $CDCl_3$) δ −116.9 ppm; IR (film, $CHCl_3$) 3371, 2959, 2927, 2860, 1702, 1458, 1379, 1277, 1171, 1096, 999, 959, 934, 909, 869, 841, 730 cm^{-1}; HRMS (EI): *m/z* calcd. for $C_{10}H_{19}OF$ [M$^+$]: 174.14199, found 174.14209.

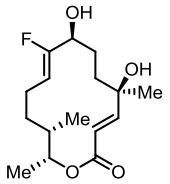
(Z)-4-(2-Fluoro-3-hydroxy-3-methylbut-1-en-1-yl)benzonitrile (12). Colorless oil (70%, 72 mg). ^{1}H NMR (300 MHz, Chloroform-d) δ 7.66 – 7.48 (m, 4H), 5.97 (d, *J* = 38.8 Hz, 1H), 1.96 (s, 1H), 1.52 (d, *J* = 1.3 Hz, 6H) ppm; ^{13}C NMR (75 MHz, Chloroform-d) δ 166.9 (d, *J* = 276.1 Hz), 138.1, 132.3, 129.2 (d, *J* = 8.0 Hz), 119.1, 110.5 (d, *J* = 3.0 Hz), 102.2 (d, *J* = 6.5 Hz), 71.0 (d, *J* = 29.0 Hz), 27.7 ppm; ^{19}F NMR (282 MHz, $CDCl_3$) δ -110.1 ppm; IR (film, $CHCl_3$) 3432, 2981, 2933, 2872, 2226, 1685, 1605, 1504, 1413, 1072, 1019, 1003, 958, 895, 578 cm^{-1}; HRMS (ESI): *m/z* calcd. for $C_{12}H_{12}NOFNa$ [M+Na$^+$]: 228.07951, found 228.07953.

(Z)-4-(2-Fluoro-3-hydroxy-3-methylbut-1-en-1-yl)benzaldehyde (13). Colorless oil (68%, 71 mg). ^{1}H NMR (500 MHz, Chloroform-d) δ 9.97 (s, 1H), 7.88 – 7.80 (m, 2H), 7.67 – 7.59 (m, 2H), 6.01 (d, *J* = 39.2 Hz, 1H), 1.52 (d, *J* = 1.2 Hz, 6H) ppm; ^{13}C NMR (126 MHz, Chloroform-d) δ 191.9, 166.7 (d, *J* = 275.9 Hz), 139.7 (d, *J* = 2.5 Hz), 134.9 (d, *J* = 2.0 Hz), 130.1, 129.2 (d, *J* = 7.8 Hz), 102.6 (d, *J* = 6.5 Hz), 71.0 (d, *J* = 29.2 Hz), 27.71 ppm; ^{19}F NMR (282 MHz, $CDCl_3$) δ −110.2 ppm; IR (film, $CHCl_3$) 3430, 2979, 1677, 1600, 1566, 1463, 1421, 1363, 1311, 1299, 1254, 1213, 1190, 1169 1071, 1004, 959, 895, 866, 809, 779, 720 cm^{-1}; HRMS (EI): *m/z* calcd. for $C_{12}H_{13}O_2F$ [M$^+$]: 208.08996, found 208.08988.

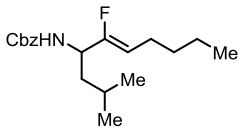
(Z)-N-(2-Fluoro-1-phenylhept-2-en-1-yl)-4-methylbenzenesulfonamide (14). Colorless solid (87%, 158 mg). ^{1}H NMR (500 MHz, Chloroform-d) δ 7.86 – 7.60 (m, 2H), 7.45 – 7.11 (m, 7H), 5.09 (d, *J* = 25.0 Hz, 1H), 5.02 (d, *J* = 18.0 Hz, 1H), 4.69 (dt, *J* = 36.9, 7.5 Hz, 1H), 2.88 (d, *J* = 7.5 Hz, 1H), 2.41 (s, 3H), 1.97 – 1.81 (m, 2H), 1.33 – 1.09 (m, 6H), 0.85 (t, *J* = 7.1 Hz, 3H) ppm; ^{13}C NMR (126 MHz, Chloroform-d) δ 154.8 (d, *J* = 255.3 Hz), 143.6, 137.4 (d, *J* = 56.9 Hz), 129.6, 128.8, 128.3, 127.3, 127.1, 109.9 (d, *J* = 14.0 Hz), 58.4 (d, *J* = 29.8 Hz), 46.1, 31.2, 23.2 (d, *J* = 4.1 Hz), 22.3, 21.7, 13.9 ppm; ^{19}F NMR (282 MHz, $CDCl_3$) δ −123.2 ppm; IR (film, $CHCl_3$) 3293, 2951, 2858, 1598, 1496, 1440, 1382, 1330, 1249, 1155, 1117, 1089, 1054, 1030, 928, 875, 850, 813, 754, 699, 685 cm^{-1}; HRMS (ESI): *m/z* calcd. for $C_{20}H_{23}NO_2FS$ [M-H$^+$]: 360.14391, found 360.14397.

N-(3-Fluoro-1-phenylbut-3-en-1-yl)-4-methylbenzenesulfonamide (15). Colorless solid (65%, 103 mg). ^{1}H NMR (500 MHz, Chloroform-d) δ 7.59 – 7.52 (m, 2H), 7.22 – 7.11 (m, 5H), 7.08 (m, 2H), 5.33 (s, 1H), 4.54 (t, *J* = 7.2 Hz, 1H), 4.49 (dd, *J* = 17.2, 3.1 Hz, 1H), 4.17 (dd, *J* = 49.6, 3.0 Hz, 1H), 2.71 – 2.50 (m, 2H), 2.36 (s, 3H) ppm; ^{13}C NMR (126 MHz, Chloroform-d) δ 161.9 (d, *J* = 257.1 Hz), 143.3, 139.7, 137.3, 129.5, 128.6, 127.8, 127.3, 126.6, 93.7, 55.3, 40.5 (d, *J* = 26.9 Hz), 21.6 ppm; ^{19}F NMR (282 MHz, $CDCl_3$) δ −95.7 ppm; IR (film, $CHCl_3$) 3245, 1675, 1600, 1497, 1458, 1319, 1290, 1242, 1157, 1095, 1060, 940, 874, 843, 811, 758, 700, 671, 597 cm^{-1}; HRMS (EI): *m/z* calcd. for $C_{17}H_{17}NO_2FS$ [M-H$^+$]: 318.09696, found 318.09694.

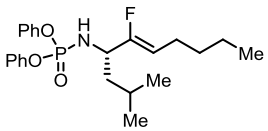
(Z)-7-Fluorotetradec-7-ene-1,14-diyl dihexanoate (16). Colorless oil (60%, 133 mg). ^{1}H NMR (400 MHz, Chloroform-d) δ 4.44 (dt, *J* = 38.2, 7.4 Hz, 1H), 4.05 (td, *J* = 6.7, 1.2 Hz, 4H), 2.28 (t, *J* = 7.6 Hz, 4H), 2.12 (dt, *J* = 17.4, 7.4 Hz, 2H), 2.03 (p, *J* = 6.1 Hz, 2H), 1.68 – 1.53 (m, 8H), 1.53 – 1.41 (m, 2H), 1.31 (ddtd, *J* = 12.1, 9.9, 6.8, 3.1 Hz, 18H), 0.96 – 0.81 (m, 6H) ppm; ^{13}C NMR (101 MHz, Chloroform-d) δ 174.2, 174.2, 159.6 (d, *J* = 252.5 Hz), 105.0 (d, *J* = 16.1 Hz), 64.4 (d, *J* = 8.9 Hz), 34.5, 32.2, 31.9, 31.5, 29.6, 28.9, 28.7, 28.7, 28.7, 26.3, 25.9, 25.8, 24.8, 23.5, 23.5, 22.5, 14.1 ppm; ^{19}F NMR (282 MHz, $CDCl_3$) δ −110.0 ppm; IR (film, $CHCl_3$) 2930, 2859, 1734, 1707, 1463, 1354, 1244, 1168, 1098, 1050, 992, 891, 729 cm^{-1}; HRMS (EI): *m/z* calcd. for $C_{26}H_{47}O_4FNa$ [M+Na$^+$]: 465.33506, found 465.33544.

(3E,*5R,8S,9Z,13S,14R*)-9-Fluoro-5,8-dihydroxy-5,13,14-trimethyloxacyclo-tetra-deca-3,9-dien-2-one (20). 

Colorless solid (84%, 11 mg). $[\alpha]_D^{20}$: −53.0° (c=1.10 in $CHCl_3$). ^{1}H NMR (500 MHz, Chloroform-d) δ 6.76 (d, *J* = 15.7 Hz, 1H), 5.99 (d, *J* = 15.6 Hz, 1H), 4.86 (ddd, *J* = 36.2, 10.1, 4.9 Hz, 1H), 4.59 (dq, *J* = 10.1, 6.1 Hz, 1H), 3.93 (ddd, *J* = 20.7, 10.0, 3.1 Hz, 1H), 2.19 (dddd, *J* = 14.6, 10.0, 7.8, 4.2 Hz, 1H), 2.03 – 1.92 (m, 2H), 1.87 (ddd, *J* = 14.9, 9.9, 5.0 Hz, 1H), 1.83 – 1.75 (m, 1H), 1.71 (dddd, *J* = 14.4, 9.9, 5.5, 3.2 Hz, 2H), 1.54 (tdd, *J* = 12.2, 6.1, 3.0 Hz, 1H), 1.50 – 1.38 (m, 2H), 1.36 (s, 3H), 1.31 (d, *J* = 6.1 Hz, 3H), 0.94 (d, *J* = 6.9 Hz, 3H), 0.93 – 0.86 (m, 1H) ppm; ^{13}C NMR (126 MHz, Chloroform-d) δ 165.9, 157.0 (d, *J* = 257.1 Hz), 152.4, 120.0, 109.1 (d, *J* = 14.2 Hz), 74.7, 73.0, 72.1 (d, *J* = 27.7 Hz), 38.8, 37.1, 32.5, 28.9, 27.9, 19.3, 18.6 (d, *J* = 5.1 Hz), 16.7 ppm; ^{19}F NMR (282 MHz, $CDCl_3$) δ −124.9 ppm; IR (film, $CHCl_3$) 3408, 2958, 2927, 2873, 1697, 1643, 1456, 1377, 1261, 1152, 1103, 1043, 976, 871, 727, 678, 559, 438 cm^{-1}; HRMS (EI): *m/z* calcd. for $C_{16}H_{25}O_4FNa$ [M+Na$^+$]: 323.16291, found 323.16327.

Benzyl (Z)-(5-fluoro-2-methyldec-5-en-4-yl)carbamate (32a). 

Colorless solid (77%, 124 mg). ^{1}H NMR (400 MHz, Chloroform-d) δ 7.43 – 7.27 (m, 5H), 5.10 (s, 2H), 4.93 – 4.84 (m, 1H), 4.77 (dt, *J* = 37.9, 7.7 Hz, 1H), 4.26 (dq, *J* = 22.2, 8.2 Hz, 1H), 2.14 – 1.96 (m, 2H), 1.70 – 1.57 (m, 1H), 1.52 (dt, *J* = 13.9, 7.1 Hz, 1H), 1.47 – 1.37 (m, 1H), 1.37 – 1.20 (m, 4H), 0.95 – 0.91 (m, 6H), 0.89 (t, *J* = 7.2 Hz, 3H) ppm; ^{13}C NMR (101 MHz, Chloroform-d) δ 157.3 (d, *J* = 255.4 Hz), 155.6, 136.5, 128.7, 128.3, 128.2, 107.2 (d, *J* = 14.6 Hz), 67.0, 51.2 (d, *J* = 28.1 Hz), 41.5, 31.5, 24.9, 23.2 (d, *J* = 4.4 Hz), 22.6 (d, *J* = 6.5 Hz), 22.3, 14.0 ppm; ^{19}F NMR (282 MHz, $CDCl_3$) δ −127.4. ppm; IR (film, $CHCl_3$) 3322, 2956, 2930, 2871, 1696, 1527, 1250, 1112, 1027, 1039, 735, 696 cm^{-1}; HRMS (EI): *m/z* calcd. for $C_{19}H_{28}NO_2FNa$ [M+Na$^+$]: 344.19963, found 344.19941.

Diphenyl (*S*,Z)-(5-fluoro-2-methyldec-5-en-4-yl)phosphoramidate (32b). 

Colorless solid (84%, 176 mg). $[\alpha]_D^{20}$: −6.5° (c=1.11 in $CHCl_3$). ^{1}H NMR (400 MHz, Chloroform-d) δ 7.39 – 7.28 (m, 4H), 7.28 – 7.19 (m, 4H), 7.19 – 7.11 (m, 2H), 4.71 (dt, *J* = 37.7, 7.5 Hz, 1H), 3.89 (ddq, *J* = 23.4, 10.2, 7.7 Hz, 1H), 3.16 (dd, *J* = 12.3, 10.2 Hz, 1H), 1.99 (dddt, *J* = 7.5, 5.9, 3.5, 2.1 Hz, 2H), 1.65 – 1.45 (m, 2H), 1.38 (dt, *J* = 13.5, 7.4 Hz, 1H), 1.33 – 1.18 (m, 4H), 0.87 (d, *J* = 1.5 Hz, 3H), 0.87 – 0.83 (m, 6H) ppm; ^{13}C NMR (101 MHz, Chloroform-d) δ 157.6 (dd, *J* = 255.5, 3.3 Hz), 151.0 (d, *J* = 1.6 Hz), 150.9 (d, *J* = 2.1 Hz), 129.8, 129.7, 125.08 – 125.03 (m), 125.04 – 124.99 (m), 120.4 (d, *J* = 3.1 Hz), 120.3 (d, *J* = 3.1 Hz), 107.2 (d, *J* = 14.7 Hz), 52.4 (d, *J* = 28.6 Hz), 43.4 (d, *J* = 7.1 Hz), 31.4 (d, *J* = 1.7 Hz), 24.7, 23.1 (d, *J* = 4.3 Hz), 22.4 (d, *J* = 25.5 Hz), 22.4, 14.0 ppm; ^{19}F NMR (282 MHz, $CDCl_3$) δ −128.8 ppm; IR (film, $CHCl_3$) 3212, 2952, 2927, 2869, 1592, 1486, 1456, 1249, 1197, 1158, 1084, 1017, 925, 906, 779, 690 cm^{-1}; HRMS (EI): *m/z* calcd. for $C_{23}H_{30}NO_3FP$ [M-H$^+$]: 418.19529, found 418.19579.

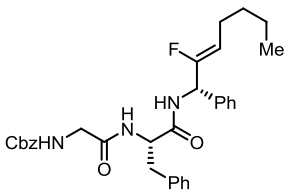
(*S*,Z)-N-(5-Fluoro-2-methyldec-5-en-4-yl)-2-methylpropane-2-sulfonamide (32c). Colorless solid (81%, 125 mg). $[a]_D^{20}$: −10.2° (c = 1.21 in $CHCl_3$). ^1H NMR (400 MHz, Chloroform-d) δ 4.76 (dt, *J* = 37.7, 7.6 Hz, 1H), 4.06 – 3.89 (m, 2H), 2.13 – 2.00 (m, 2H), 1.73 – 1.44 (m, 3H), 1.37 (s, 9H), 1.35 – 1.23 (m, 4H), 0.95 (d, *J* = 6.5 Hz, 3H), 0.93 – 0.86 (m, 6H) ppm; ^{13}C NMR (101 MHz, Chloroform-d) δ 157.1 (d, *J* = 255.0 Hz), 108.0, 59.8, 54.7 (d, *J* = 27.5 Hz), 43.6, 31.4 (d, *J* = 1.6 Hz), 24.9, 24.3, 23.2 (d, *J* = 4.4 Hz), 22.7, 22.3 (d, *J* = 12.6 Hz), 13.9 ppm; ^{19}F NMR (282 MHz, $CDCl_3$) δ −128.2 ppm; IR (film, $CHCl_3$) 3274, 2957, 2872, 2931, 1706, 1458, 1367, 1301, 1172, 1127, 1061, 1006, 964, 921, 817, 680 cm^{-1}; HRMS (EI): *m/z* calcd. for $C_{15}H_{29}NO_2FS$ [M-H$^+$]: 306.19086, found 306.19105.

(*S*,Z)-N-(5-Fluoro-2-methyldec-5-en-4-yl)-4-nitrobenzenesulfonamide (32d). Colorless solid (54%, 100 mg). $[a]_D^{20}$: +40.7° (c=1.11 in $CHCl_3$). ^1H NMR (400 MHz, Chloroform-d) δ 8.36 – 8.27 (m, 2H), 8.06 – 7.94 (m, 2H), 4.77 (d, *J* = 8.8 Hz, 1H), 4.52 (dt, *J* = 37.5, 7.5 Hz, 1H), 3.97 (ddt, *J* = 24.2, 8.9, 7.8 Hz, 1H), 1.79 (dtdd, *J* = 14.3, 8.0, 6.6, 1.6 Hz, 1H), 1.73 – 1.60 (m, 2H), 1.49 (td, *J* = 7.7, 7.2, 1.1 Hz, 2H), 1.22 – 1.00 (m, 4H), 0.92 (d, *J* = 4.9 Hz, 3H), 0.91 (d, *J* = 4.9 Hz, 3H), 0.81 (t, *J* = 7.1 Hz, 3H) ppm; ^{13}C NMR (101 MHz, Chloroform-d) δ 154.8 (d, *J* = 255.7 Hz), 150.1, 146.9, 128.5, 124.2, 109.0 (d, *J* = 14.5 Hz), 54.2 (d, *J* = 27.6 Hz), 42.0, 31.2, 24.6, 22.9 (d, *J* = 4.2 Hz), 22.4, 22.3 (d, *J* = 2.6 Hz), 13.8 ppm; ^{19}F NMR (282 MHz, $CDCl_3$) δ −128.6 ppm; IR (film, $CHCl_3$) 3301, 2932, 2959, 2871, 1609, 1527, 1352, 1332, 1308, 1158, 856, 813, 738, 682 cm^{-1}; HRMS (EI): *m/z* calcd. for $C_{17}H_{24}N_2O_4FS$ [M-H$^+$]: 371.14463, found 371.14485.

Benzyl (Z)-(4-fluoro-2-methylnon-4-en-3-yl)carbamate (33). Colorless solid (76%, 116 mg). ^1H NMR (400 MHz, Chloroform-d) δ 7.43 – 7.28 (m, 5H), 5.11 (s, 2H), 4.96 (d, *J* = 9.6 Hz, 1H), 4.73 (dt, *J* = 38.1, 7.5 Hz, 1H), 3.95 (ddd, *J* = 22.9, 9.6, 7.9 Hz, 1H), 2.15 – 1.96 (m, 2H), 1.88 (dq, *J* = 13.9, 6.9 Hz, 1H), 1.43 – 1.23 (m, 4H), 0.95 (d, *J* = 2.7 Hz, 3H), 0.94 (d, *J* = 2.9 Hz, 3H), 0.92 – 0.85 (m, 3H) ppm; ^{13}C NMR (101 MHz, Chloroform-d) δ 156.5 (d, *J* = 255.5 Hz), 155.9, 136.5, 128.7, 128.3, 128.2, 108.0 (d, *J* = 14.4 Hz), 67.0, 58.6 (d, *J* = 27.4 Hz), 31.5 (d, *J* = 1.7 Hz), 30.4, 23.1 (d, *J* = 4.6 Hz), 22.3, 19.5, 18.8, 14.0 ppm; ^{19}F NMR (282 MHz, $CDCl_3$) δ −125.5 ppm; IR (film, $CHCl_3$) 3326, 2959, 2930, 2873, 1697, 1510, 1455, 1264, 1228, 1096, 1022, 936, 836, 736, 696 cm^{-1}; HRMS (EI): *m/z* calcd. for $C_{18}H_{26}NO_2FNa$ [M+Na$^+$]: 330.18398, found 330.18378.

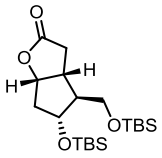
(*S*,Z)-N-(2-Fluoro-1-phenylhept-2-en-1-yl)-2-methylpropane-2-sulfonamide (34). Colorless solid (76%, 125 mg). $[a]_D^{20}$: +3.7° (c = 1.01 in MeOH). ^1H NMR (400 MHz, Chloroform-d) δ 7.45 – 7.28 (m, 5H), 5.17 (dd, *J* = 18.2, 9.3 Hz, 1H), 4.92 (dt, *J* = 36.9, 7.6 Hz, 1H), 4.50 (d, *J* = 9.2 Hz, 1H), 2.14 (tdq, *J* = 8.5, 7.0, 2.3, 1.9 Hz, 2H), 1.39 (s, 9H), 1.38 – 1.21 (m, 4H), 0.95 – 0.86 (m, 3H) ppm; ^{13}C NMR (101 MHz, Chloroform-d) δ 156.6 (d, *J* = 255.8 Hz), 138.5, 129.0, 128.3, 127.0, 109.5 (d, *J* = 14.2 Hz), 60.3, 59.2 (d, *J* = 29.1 Hz), 31.3, 24.3, 23.4 (d, *J* = 4.1 Hz), 22.4, 13.9 ppm; ^{19}F NMR (282 MHz, $CDCl_3$) δ −122.1 ppm; IR (film, $CHCl_3$) 3287, 2957, 2931, 2858, 1705, 1495, 1451, 1438, 1369,

1302, 1249, 1182, 1129, 1061, 1026, 923, 852, 738, 694, 605, 512 cm^{-1}; HRMS (EI): *m/z* calcd. for $C_{17}H_{26}NO_2FSNa$ [M+Na^+]: 350.15605, found 350.15569.

Benzyl (2-(((*S*)-1-(((*S*,*Z*)-2-fluoro-1-phenylhept-2-en-1-yl)amino)-1-oxo-3-phenylpropan-2-yl)amino)-2-oxoethyl)carbamate (35). 

Colorless solid (83%, 91 mg; only ~80% pure); an analytically pure sample was obtained by preparative HPLC. $[\alpha]_D^{25}$: −19.0° (c = 1.40 in $CHCl_3$). ^{1}H NMR (400 MHz, Chloroform-d) δ 7.31 (dq, *J* = 7.3, 4.1, 3.3 Hz, 5H), 7.27 – 7.18 (m, 7H), 7.15 (dd, *J* = 7.6, 1.9 Hz, 2H), 6.93 (t, *J* = 8.5 Hz, 2H), 5.63 (dd, *J* = 17.9, 8.6 Hz, 1H), 5.47 (q, *J* = 5.7, 4.2 Hz, 1H), 5.07 – 4.96 (m, 3H), 4.86 – 4.76 (m, 1H), 4.72 (dt, *J* = 36.9, 7.6 Hz, 1H), 3.74 (d, *J* = 5.7 Hz, 2H), 3.04 (dt, *J* = 13.5, 7.2 Hz, 2H), 2.07 (qt, *J* = 7.2, 1.8 Hz, 2H), 1.32 (dq, *J* = 7.5, 3.9 Hz, 4H), 0.97 – 0.82 (m, 3H) ppm; ^{13}C NMR (101 MHz, Chloroform-d) δ 169.9, 169.1, 156.7, 155.8 (d, *J* = 255.7 Hz), 137.7, 136.2, 136.2, 129.5, 128.78, 128.76, 128.7, 128.4, 128.2, 128.0, 127.2, 127.0, 109.0 (d, *J* = 14.0 Hz), 67.3, 54.6, 54.2 (d, *J* = 29.6 Hz), 44.6, 38.6, 31.4 (d, *J* = 1.0 Hz), 23.4 (d, *J* = 4.1 Hz), 22.4, 14.0 ppm; ^{19}F NMR (282 MHz, $CDCl_3$) δ −120.9 ppm; IR (film, $CHCl_3$) 3282, 3064, 3032, 2955, 2928, 2859, 1705, 1644, 1521, 1497, 1454, 1395, 1233, 1164, 1104, 1081, 1048, 1030, 987, 938, 742, 696 cm^{-1}; HRMS (ESI): *m/z* calcd. for $C_{32}H_{36}N_3O_4FNa$ [M+Na^+]: 568.25820, found 568.25823.

Formal Synthesis of (+)-14-Fluoroprostaglandin $F_{2\alpha}$[2]

(3a*R*,4*S*,5*R*,6a*S*)-5-((*tert*-Butyldimethylsilyl)oxy)-4-(((*tert*-butyldimethylsilyl)oxy)-methyl)hexahydro-2H-cyclopenta[b]furan-2-one (22).[3] 

Corey lactone (**21**) (5.83 g, 33.9 mmol, 1.0 equiv.) was suspended in dry DMF (50 mL) and the solution stirred in a single-necked flask under an argon atmosphere. Imidazole (6.92 g, 102 mmol, 3.0 equiv.) and *tert*-butyldimethylsilyl chloride (12.8 g, 85 mmol, 2.5 equiv.) were successfully added and stirring was continued for 3 h when TLC showed complete consumption of starting material. The reaction was quenched with saturated ammonium chloride solution and the mixture extracted two times with *tert*-butyl methyl ether. The combined extracts were washed with water and brine, dried over magnesium sulfate and concentrated under reduced pressure. Flash chromatography (SiO_2, hexanes/ethyl acetate, 4:1) yielded the product as a colorless solid (13.6 g, 34 mmol, quant.). $[\alpha]_D^{25}$: −39.3° (c 1.15 in $CHCl_3$). ^{1}H NMR (400 MHz, Chloroform-d) δ 4.92 (td, *J* = 7.1, 2.3 Hz, 1H), 4.12 (dt, *J* = 5.7, 4.7 Hz, 1H), 3.55 (dd, *J* = 10.3, 5.2 Hz, 1H), 3.48 (dd, *J* = 10.3, 5.6 Hz, 1H), 2.78 (dd, *J* = 17.8, 10.5 Hz, 1H), 2.66 (dddd, *J* = 10.4, 7.6, 5.5, 2.8 Hz, 1H), 2.54 (dd, *J* = 17.8, 2.9 Hz, 1H), 2.23 (ddd, *J* = 14.8, 6.9, 5.7 Hz, 1H), 2.03 – 1.91 (m, 2H), 0.89 (s, 9H), 0.87 (s, 9H), 0.05 (d, *J* = 0.7 Hz, 6H), 0.04 (d, *J* = 1.0 Hz, 6H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 177.4, 84.3, 74.7, 62.7, 57.1, 41.2, 39.3, 35.8, 26.0, 25.9, 18.4, 18.1, -4.6, -4.9, -5.3, -5.4 ppm; IR (film, $CHCl_3$) 2929, 2885, 2856, 1752, 1462, 1388, 1360, 1251, 1192, 1167, 1096, 1032, 1006, 960, 868, 832, 773 cm^{-1}; HRMS (ESI): *m/z* calcd. for $C_{20}H_{40}O_4Si_2Na$ [M+Na^+]: 423.23574, found 423.23544.

(3a*R*,4*S*,5*R*,6a*S*)-5-((*tert*-Butyldimethylsilyl)oxy)-4-(hydroxymethyl)hexahydro-2H-cyclopenta[b]furan-2-one (SI-2). Water (42 ml) and AcOH (78 mL) were added to a solution of compound **22** (13.6 g, 33.9 mmol, 1.0 equiv.) in THF (20 mL) and the resulting mixture was stirred at ambient temperature for 15 h. The reaction was quenched with saturated sodium bicarbonate solution. The mixture was extracted two times with ethyl acetate, the combined extracts were washed with brine, dried over magnesium sulfate and concentrated under reduced pressure. Flash chromatography (SiO_2, hexanes/ethyl acetate, 1:1) yielded the product as a colorless solid (5.64 g, 19.7 mmol, 58%). $[\alpha]_D^{25}$: –85.9° (c 1.61 in $CHCl_3$). ^{1}H NMR (400 MHz, Chloroform-d) δ 4.93 (td, *J* = 7.1, 2.5 Hz, 1H), 4.12 (q, *J* = 5.4 Hz, 1H), 3.58 (d, *J* = 6.0 Hz, 2H), 2.79 (dd, *J* = 17.8, 10.4 Hz, 1H), 2.73 – 2.63 (m, 1H), 2.53 (dd, *J* = 17.9, 2.6 Hz, 1H), 2.26 (ddd, *J* = 14.7, 6.9, 5.8 Hz, 1H), 2.05 – 1.94 (m, 2H), 1.81 (s, 1H), 0.87 (s, 9H), 0.06 (s, 6H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 177.4, 83.8, 75.1, 62.9, 56.5, 41.1, 39.1, 35.6, 25.8, 18.0, -4.5, -4.9 ppm; The analytical data are in accordance with those reported in the literature.[3]

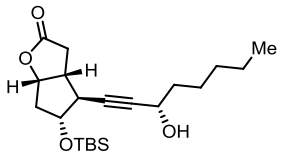
The aqueous extracts were dried under reduced pressure and extracted with ethanol. The concentrated ethanol extracts provided colorless solids which were taken over with acetone, filtered again and concentrated under reduced pressure to give a thick oil. This syrup was again dissolved in a minimum amount of acetone and *tert*-butyl methyl ether was slowly added until some precipitate formed. About 100 mL of *tert*-butyl methyl ether were then added, the supernatant solution was decanted, the solids were washed again with *tert*-butyl methyl ether and hexanes and dried under reduced pressure to give pure Corey lactone (**21**) (1.52 g, 8.83 mmol, 26%).

(3a*R*,4*S*,5*R*,6a*S*)-5-((*tert*-Butyldimethylsilyl)oxy)-4-ethynylhexahydro-2H-cyclopenta[b]-furan-2-one (SI-3). Oxalyl chloride (791 µL, 9.2 mmol, 1.3 equiv.) was dissolved in dry CH_2Cl_2 (25 mL) and the solution stirred in an oven-dried Schlenk flask under an argon atmosphere at –60°C. A solution of DMSO (1.26 mL, 17.7 mmol, 2.5 equiv.) in CH_2Cl_2 (10 mL) was added and stirring continued for 15 minutes before a solution of compound **SI-2** (2.03 g, 7.1 mmol, 1.0 equiv.) in dry CH_2Cl_2 (10 mL) was added dropwise. After stirring at this temperature for another 15 minutes, neat Et_3N (5.3 mL, 38.3 mmol, 5.4 equiv.) was introduced and 2 minutes later the mixture was allowed to warm to room temperature. The reaction was then quenched with water, 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. Characteristic data of the resulting crude aldehyde which was used in the next step without further purification: ^{1}H NMR (400 MHz, Chloroform-d) δ 9.72 (d, *J* = 0.8 Hz, 1H), 5.03 (ddd, *J* = 7.5, 6.6, 1.3 Hz, 1H), 4.58 (dt, *J* = 5.1, 2.6 Hz, 1H), 3.41 – 3.28 (m, 1H), 3.01 – 2.94 (m, 1H), 2.89 (dd, *J* = 18.3, 11.3 Hz, 1H), 2.51 (dd, *J* = 18.4, 3.5 Hz, 1H), 2.20 – 2.08 (m, 1H), 1.86 (ddd, *J* = 15.1, 6.5, 4.8 Hz, 1H), 0.88 (s, 10H), 0.10 (d, *J* = 0.6 Hz, 6H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 199.4, 176.5, 84.3, 73.9, 68.2, 46.3, 41.2, 36.6, 35.9, 25.7, 18.0, -4.6, -5.0 ppm;

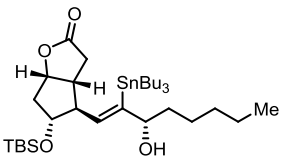
KO*t*Bu (1.08 g, 9.6 mmol, 1.35 equiv.) was placed in an oven-dried Schlenk flask and dried for 1 h under high vacuum at 100 °C. After cooling to room temperature, THF (20 mL) was added and the mixture was placed on a dry-ice bath. A solution of the Gilbert-Seyferth reagent[4] (1.13 g, 9.9 mmol, 1.4 equiv.) in THF (20 mL) was added dropwise and stirring was continued for 15 minutes at the same temperature to give a red solution. Next, a solution of the crude aldehyde in THF (20 mL) was added over 30 minutes by means of a syringe pump. Stirring was continued for another 30 minutes before the mixture was allowed to reach room temperature. 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 (SiO_2, hexanes/ethyl acetate, 4:1) yielded the product as a colorless solid (1.31 g, 4.7 mmol, 66%). $[a]_D^{25}$: −55.5° (c 1.31 in $CHCl_3$). ^{1}H NMR (400 MHz, Chloroform-d) δ 5.17 – 5.01 (m, 1H), 4.37 – 4.24 (m, 1H), 3.14 – 3.01 (m, 1H), 2.83 (dd, *J* = 18.4, 11.3 Hz, 1H), 2.76 – 2.69 (m, 1H), 2.56 (dd, *J* = 18.5, 3.7 Hz, 1H), 2.31 (ddd, *J* = 14.9, 6.7, 4.6 Hz, 1H), 2.19 (d, *J* = 2.6 Hz, 1H), 2.14 – 2.01 (m, 1H), 0.87 (s, 9H), 0.09 (s, 3H), 0.08 (s, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 176.7, 84.2, 83.9, 78.9, 72.0, 46.4, 44.7, 40.8, 35.9, 25.8, 18.1, -4.8, -4.9 ppm; IR (film, $CHCl_3$) 3242, 2956, 2928, 2856, 1760, 1471, 1414, 1362, 1254, 1186, 1083, 1053, 1006, 900, 832, 774, 712 cm^{-1}; HRMS (ESI): *m/z* calcd. for $C_{15}H_{24}O_3SiNa$ [M+Na$^+$]: 303.13869, found 303.13855.

(3a*R*,4*S*,5*R*,6a*S*)-5-((*tert*-Butyldimethylsilyl)oxy)-4-(3-oxooct-1-yn-1-yl)hexahydro-2H-cyclopenta[b]furan-2-one (23).[5] An oven-dried Schlenk flask was charged with tri-(2-furyl)-phosphine (271 mg, 1.17 mmol, 25 mol%) and copper(I) iodide (1.51 g, 7.94 mmol, 1.7 equiv.) under argon atmosphere. [1,1'-Bis-(diphenylphosphino)-ferrocene]-palladium(II)-chloride-methylenchloride-complex (1:1) (381 mg, 0.47 mmol, 10 mol%) was added, followed by DMF (35 mL), S-phenyl hexanethioate[6] (1.94 g, 9.34 mmol, 2.0 equiv.), Et_3N (7 mL) and compound **SI-2** (1.31 g, 4.67 mmol, 1.0 equiv.) in that order. The resulting mixture was stirred for 18 h until TLC showed complete consumption of the starting material. Celite(R) was added to the orange suspension which was filtered through a plug of Celite(R), eluting with *tert*-butyl methyl ether. The reaction was quenched with water, the organic layer was separated, the aqueous layer extracted with *tert*-butyl methyl ether, the combined organic phases were washed with brine, dried over magnesium sulfate and concentrated under reduced pressure. Flash chromatography (SiO_2, hexanes/ethyl acetate, 6:1) yielded the product as a yellow oil (1.20 g, 3.2 mmol, 68%). $[a]_D^{20}$: −74.6° (c 1.80 in $CHCl_3$). ^{1}H NMR (400 MHz, Chloroform-d) δ 5.19 – 4.94 (m, 1H), 4.36 (dt, *J* = 4.6, 3.0 Hz, 1H), 3.11 (ddt, *J* = 11.1, 7.3, 3.6 Hz, 1H), 2.94 – 2.75 (m, 2H), 2.56 (dd, *J* = 18.5, 3.6 Hz, 1H), 2.51 (t, *J* = 7.4 Hz, 2H), 2.28 (ddd, *J* = 15.0, 6.6, 4.7 Hz, 1H), 2.17 – 2.09 (m, 1H), 1.63 (p, *J* = 7.4 Hz, 2H), 1.37 – 1.21 (m, 4H), 0.91 – 0.87 (m, 3H), 0.87 (s, 9H), 0.09 (s, 3H), 0.08 (s, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 187.9, 176.1, 91.1, 83.8, 83.3, 78.4, 46.5, 45.6, 44.2, 41.1, 35.8, 31.2, 25.7, 23.8, 22.5, 18.1, 14.0, -4.8, -5.0 ppm; IR (film, $CHCl_3$) 2955, 2930, 2857, 2211, 1773, 1673, 1464, 1412, 1363, 1312, 1253, 1168, 1096, 1056, 1033, 1006, 976, 955,

897, 833, 776 cm^{-1}; HRMS (ESI): *m/z* calcd. for $C_{21}H_{34}O_4SiNa$ [M+Na^+]: 401.21186, found 401.21180.

(3a*R*,4*S*,5*R*,6a*S*)-5-((*tert*-Butyldimethylsilyl)oxy)-4-((*S*)-3-hydroxyoct-1-yn-1-yl)hexahydro-2H-cyclopenta[b]furan-2-one (25).[7] 

Compound **23** (681 mg, 1.8 mmol, 1.0 equiv.) was placed in an oven-dried cooling Schlenk under an argon atmosphere. Dry THF (17 mL) was added followed by (*S*)-(−)-2-methyl-CBS-oxazaborolidine (**24**) (1.0 g, 3.6 mmol, 2.0 equiv.) and the solution was stirred vigorously while being cooled to −30 °C. Borane dimethylsulfide (243 µL, 2.7 mmol, 1.5 equiv.) was added and stirring continued until complete conversion was reached as judged by TLC (hexanes/ethyl acetate, 2:1). After 1 h, MeOH was added, the mixture warmed to room temperature and saturated ammonium chloride solution was introduced. The mixture was extracted two times with ethyl acetate, the combined extracts were washed with brine, dried over magnesium sulfate and concentrated under reduced pressure. Flash chromatography (SiO_2, hexanes/ethyl acetate, 3:1) yielded the product as a pale yellow oil (560 mg, 1.47 mmol, 82%). $[a]_D^{20}$ –6.4°(c 0.25 in $CHCl_3$). ^{1}H NMR (400 MHz, Chloroform-d) δ 5.06 (td, *J* = 7.1, 1.3 Hz, 1H), 4.32 (qd, *J* = 6.6, 1.9 Hz, 1H), 4.26 (dt, *J* = 4.8, 2.9 Hz, 1H), 3.02 (ddt, *J* = 11.1, 7.3, 3.6 Hz, 1H), 2.80 (dd, *J* = 18.4, 11.3 Hz, 1H), 2.74 (dp, *J* = 3.4, 1.7 Hz, 1H), 2.54 (dd, *J* = 18.4, 3.7 Hz, 1H), 2.26 (ddd, *J* = 14.9, 6.7, 4.6 Hz, 1H), 2.07 (ddt, *J* = 14.8, 3.1, 1.6 Hz, 1H), 1.71 – 1.56 (m, 3H), 1.48 – 1.33 (m, 2H), 1.33 – 1.23 (m, 4H), 0.88 (t, *J* = 7.2 Hz, 3H), 0.86 (s, 9H), 0.07 (s, 3H), 0.06 (s, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 176.8, 84.9, 84.6, 84.2, 78.9, 62.7, 46.6, 44.8, 40.9, 38.1, 35.9, 31.5, 25.8, 25.0, 22.7, 18.1, 14.1, -4.8, -4.9 ppm; IR (film, $CHCl_3$) 2954, 2857, 1768, 1464, 1412, 1363, 1310, 1254, 1183, 1093, 1030, 1006, 983, 900, 833, 776, 731 cm^{-1}; HRMS (ESI): *m/z* calcd. for $C_{21}H_{36}O_4SiNa$ [M+Na^+]: 403.22751, found 403.22757.

(3a*R*,4*S*,5*R*,6a*S*)-5-((*tert*-Butyldimethylsilyl)oxy)-4-((*S*,Z)-3-hydroxy-2-(tributylstannyl)-oct-1-en-1-yl)hexahydro-2H-cyclopenta[b]furan-2-one (SI-4). 

Compound **25** (520 mg, 1.37 mmol, 1.0 equiv.) and (1,2,3,4,5-pentamethylcyclopenta-2,4-dien-1-yl)ruthenium(II) chloride (19 mg, 0.07 mmol, 5.0 mol%) were dissolved in CH_2Cl_2 (6 mL) and the solution was stirred in an oven-dried Schlenk flask under an argon atmosphere at room temperature. Bu_3SnH (404 µL, 1.5 mmol, 1.1 equiv.) was dropwise added over 60 minutes by means of a syringe pump before the volatile materials were removed under reduced pressure. The residue was purified by flash chromatography (SiO_2, hexanes/ethyl acetate, 6:1) to give the product as a pale yellow oil. $[a]_D^{20}$ + 23.1° (c 2.40 in $CHCl_3$). ^{1}H NMR (400 MHz, Chloroform-d) δ 5.98 – 5.51 (m, 1H), 5.04 (td, *J* = 7.0, 1.6 Hz, 1H), 4.12 – 3.93 (m, 2H), 2.83 – 2.71 (m, 1H), 2.62 (dt, *J* = 10.3, 3.3 Hz, 1H), 2.60 – 2.56 (m, 1H), 2.56 – 2.53 (m, 1H), 2.51 (tt, *J* = 4.2, 2.2 Hz, 1H), 2.21 (ddd, *J* = 15.1, 6.8, 4.7 Hz, 1H), 2.09 (ddt, *J* = 15.1, 3.2, 1.4 Hz, 1H), 1.56 – 1.40 (m, 9H), 1.40 – 1.18 (m, 14H), 1.03 – 0.94 (m, 6H), 0.90 (t, *J* = 7.3 Hz, 9H), 0.87 (s, 9H), 0.07 (s, 3H), 0.05 (s, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 177.1, 151.6, 139.0, 84.3, 79.9, 78.9, 59.5, 44.6, 40.9, 37.9, 35.6, 31.9,

29.4, 27.6, 25.9, 25.8, 22.8, 18.1, 14.2, 13.9, 11.6, –4.2, –4.8 ppm; ^{119}Sn NMR (149 MHz, $CDCl_3$) δ –56.7 ppm; IR (film, $CHCl_3$) 2954, 2855, 1768, 1463, 1362, 1253, 1183, 1125, 1088, 1004, 1029, 973, 893, 832, 775 cm^{-1}; HRMS (ESI): *m/z* calcd. for $C_{33}H_{64}O_4SiSnNa$ [M+Na$^+$]: 695.34874, found 695.34881.

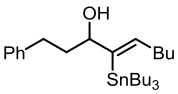
(3a*R*,4*S*,5*R*,6a*S*)-5-Hydroxy-4-((*S*,Z)-3-hydroxy-2-(tributylstannyl)oct-1-en-1-yl)hexahydro-2H-cyclopenta[b]furan-2-one (26). Tetrabutylammonium fluoride trihydrate (282 mg, 0.90 mmol, 2.0 equiv.) was added to a solution of compound **SI-4** (300 mg, 0.45 mmol, 1.0 equiv.) in THF (4 mL) at 0°C. The cooling bath was removed and the mixture stirred for 18 h. The reaction was quenched with saturated ammonium chloride solution, the mixture was extracted two times with ethyl acetate, the combined extracts were washed with brine, dried over magnesium sulfate and concentrated under reduced pressure. Flash chromatography (SiO_2, hexanes/ethyl acetate, 3:2 to 2:1) yielded the product as a pale yellow oil (192 mg, 0.34 mmol, 77%). $[\alpha]_D^{20}$ + 2.4° (c 1.02 in $CHCl_3$). ^{1}H NMR (400 MHz, Chloroform-d) δ 5.99 – 5.57 (m, 1H), 5.00 (td, *J* = 7.0, 2.2 Hz, 1H), 4.08 (ddd, *J* = 7.1, 5.8, 1.1 Hz, 1H), 3.99 (q, *J* = 5.1 Hz, 1H), 2.75 (dd, *J* = 18.0, 10.4 Hz, 1H), 2.61 (dddd, *J* = 10.2, 7.3, 5.5, 2.5 Hz, 1H), 2.49 (dd, *J* = 18.0, 2.6 Hz, 1H), 2.45 – 2.31 (m, 2H), 2.11 (s, 1H), 2.06 (ddd, *J* = 15.1, 5.2, 2.1 Hz, 1H), 1.72 (s, 1H), 1.57 – 1.39 (m, 8H), 1.38 – 1.20 (m, 12H), 1.08 – 0.92 (m, 6H), 0.92 – 0.86 (m, 12H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 177.0, 152.8, 138.7, 83.7, 80.1, 77.9, 58.6, 43.9, 40.3, 37.9, 34.9, 31.8, 29.4, 27.6, 25.8, 22.8, 14.2, 13.8, 11.7 ppm; ^{119}Sn NMR (149 MHz, $CDCl_3$) δ –55.6 ppm; IR (film, $CHCl_3$) 3428, 2954, 2924, 2854, 1757, 1459, 1417, 1375, 1290, 1176, 1073, 1028, 968, 910 881, 733, 666, 594, 543, 501 cm^{-1}; HRMS (ESI): *m/z* calcd. for $C_{27}H_{50}O_4SnNa$ [M+Na$^+$]: 581.26226, found 581.26237.

(3a*R*,4*S*,5*R*,6a*S*)-4-((*S*,Z)-2-Fluoro-3-hydroxyoct-1-en-1-yl)-5-hydroxyhexahydro-2H-cyclopenta[b]furan-2-one (27). $AgOP(O)Ph_2$ (115 mg, 0.36 mmol, 1.2 equiv.) and F-TEDA-PF_6 (279 mg, 0.59 mmol, 2.0 equiv.) were stirred vigorously at room temperature under an argon atmosphere in an oven-dried Schlenk flask until a homogenous grey powder was obtained. Dry acetone (4.5 mL) was added, followed by slow addition of a solution of stannane **26** (165 mg, 0.30 mmol, 1.0 equiv.) in dry acetone (1.5 mL) over 60 minutes by means of a syringe pump. The mixture was diluted with ethyl acetate and the reaction quenched with saturated ammonium chloride solution. The organic layer was separated, the aqueous layer extracted two times with ethyl acetate, the combined extracts were washed with brine, dried over magnesium sulfate and concentrated under reduced pressure. Flash chromatography (SiO_2, hexanes/ethyl acetate, 1:1 [to remove tin residues], then pure ethyl acetate) gave the product as a colorless oil (57 mg, 0.20 mmol, 67%). $[\alpha]_D^{20}$ − 9.1° (c 0.76 in MeOH). ^{1}H NMR (400 MHz, Acetone-d_6) δ 4.94 (td, *J* = 7.0, 2.7 Hz, 1H), 4.81 (dd, *J* = 37.7, 9.4 Hz, 1H), 4.22 (d, *J* = 5.3 Hz, 1H), 4.10 (d, *J* = 4.6 Hz, 1H), 4.09 – 4.03 (m, 1H), 3.99 (qd, *J* = 6.5, 4.8 Hz, 1H), 2.76 (dd, *J* = 17.6, 9.9 Hz, 1H), 2.74 (dd, *J* = 9.2, 6.8 Hz, 1H), 2.66 (dtd, *J* = 9.7, 7.1, 2.1 Hz, 1H), 2.45 – 2.33 (m, 2H), 1.86 (ddd, *J* = 14.5, 6.4, 2.7 Hz, 1H),

1.71 – 1.50 (m, 2H), 1.50 – 1.23 (m, 6H), 0.93 – 0.84 (m, 3H) ppm; ^{13}C NMR (101 MHz, Acetone-d_6) δ 177.0, 163.4 (d, *J* = 259.5 Hz), 106.3 (d, *J* = 12.4 Hz), 83.5, 77.8 (d, *J* = 1.5 Hz), 70.4 (d, *J* = 30.5 Hz), 49.5 (d, *J* = 2.9 Hz), 44.3 (d, *J* = 1.9 Hz), 41.1, 35.2, 34.9, 32.4, 25.8, 23.2, 14.3 ppm; ^{19}F NMR (282 MHz, Acetone-d_6) δ −123.16 (dd, *J* = 37.6, 14.8 Hz) ppm; IR (film, $CHCl_3$) 3406, 2955, 2931, 2860, 1756, 1459, 1417, 1353, 1306, 1241, 1215, 1178, 1077, 1033, 973,913 846, 749, 667 cm^{-1}; HRMS (ESI): *m/z* calcd. for $C_{15}H_{23}FO_4Na$ [M+Na$^+$]: 309.14726, found 309.14754.

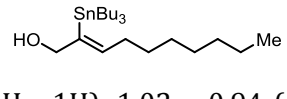
Ruthenium-catalyzed *trans*-Hydrostannation

Representative Procedure for the Ruthenium Catalyzed *trans*-Hydrostannation of Propargyl Alcohols.[8] **(Z)-1-Phenyl-4-(tributylstannyl)non-4-en-3-ol.** Bu_3SnH (7.1 ml, 26.3 mmol, 1.05 equiv.) was added over 1 h via syringe pump to a solution of 1-phenylnon-4-yn-3-ol (5.4 g, 25 mmol, 1.0 equiv.) and $[Cp^*RuCl_2]_n$ (77 mg, 0.25 mmol, 1.0 mol%) in dry CH_2Cl_2 (100 mL). Once the addition was complete, stirring was continued for 5 min before the volatile materials were removed under reduced pressure. The crude material was purified by flash chromatography (SiO_2, hexanes/ethyl acetate) to give the product as a pale-brown syrup (11.8 g, 93%). ^{1}H NMR (400 MHz, Chloroform-d) 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, 10H), 1.04 – 0.79 (m, 20H) 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* calcd. for $C_{27}H_{48}OSnNa$ [M+Na$^+$]: 531.26186, found 531.26185.

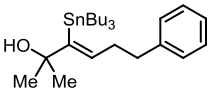


The following compounds were prepared analogously:

(Z)-2-(Tributylstannyl)dec-2-en-1-ol. Colorless oil (97%, 3.1 g). ^{1}H NMR (400 MHz, Chloroform-d) 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* calcd. for $C_{22}H_{45}OSn$ [M-H$^+$]: 445.24972, found 445.25028.

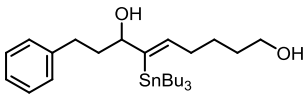


(Z)-2-Methyl-6-phenyl-3-(tributylstannyl)hex-3-en-2-ol. Colorless oil (quant., 5.16 g). ^{1}H NMR (400 MHz, Chloroform-d) δ 7.36 – 7.27 (m, 2H), 7.24 – 7.12 (m, 3H), 6.16 (t, *J* = 7.2 Hz, 1H), 2.78 – 2.60 (m, 2H), 2.41 – 2.28 (m, 2H), 1.57 – 1.41 (m, 6H), 1.39 – 1.31 (m, 6H), 1.31 (s, 7H), 0.99 – 0.92 (m, 6H), 0.89 (t, *J* = 7.3 Hz, 9H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.2, 142.0, 135.6, 128.6, 128.5, 126.0, 75.5, 36.7, 35.9, 30.9,

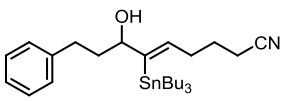


29.4, 27.6, 13.9, 12.3 ppm; ^{119}Sn NMR (149 MHz, $CDCl_3$) δ –55.6 ppm; IR (film, $CHCl_3$) 2955, 2853, 2871, 2815, 1624, 1463, 1419 , 1366, 1376, 1349, 1267, 1291, 1192, 1148, 1110, 1094, 1072, 1002, 1019, 960, 915, 860 cm^{-1}; HRMS (ESI): *m/z* calcd. for $C_{25}H_{44}OSnNa$ [M+Na$^+$]: 503.23056, found 503.23061.

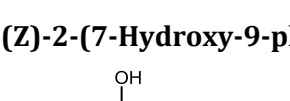
(Z)-9-Phenyl-6-(tributylstannyl)non-5-ene-1,7-diol. Colorless oil (68%, 2.68 g). ^{1}H NMR (300 MHz, Chloroform-d) δ 7.39 – 7.29 (m, 2H), 7.29 – 7.19 (m, 3H), 6.24 (td, *J* = 7.1, 1.1 Hz, 1H), 4.37 – 4.04 (m, 1H), 3.70 (td, *J* = 6.4, 5.0 Hz, 2H), 2.86 – 2.53 (m, 2H), 2.15 (q, *J* = 7.3 Hz, 2H), 1.99 – 1.74 (m, 2H), 1.72 – 1.60 (m, 4H), 1.60 – 1.48 (m, 4H), 1.48 – 1.28 (m, 6H), 1.13 – 0.85 (m, 18H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 148.4, 142.2, 140.5, 128.5, 128.4, 125.8, 79.3, 62.8, 39.4, 34.0, 32.6, 32.4, 29.4, 27.5, 26.4, 13.8, 11.2 ppm; ^{119}Sn NMR (112 MHz, $CDCl_3$) δ –55.3 ppm; IR (film, $CHCl_3$) 3391, 2954, 2924, 2854, 1742, 1727, 1496, 1455, 1374, 1241, 1046, 864, 747, 698 cm^{-1}; HRMS (ESI): *m/z* calcd. for $C_{27}H_{48}O_2SnNa$ [M+Na$^+$]: 547.25678, found 547.25751.



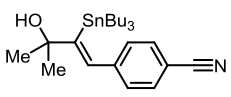
(Z)-7-Hydroxy-9-phenyl-6-(tributylstannyl)non-5-enenitrile. Colorless oil (89%, 2.3 g). ^{1}H NMR (400 MHz, Chloroform-d) δ 7.34 – 7.26 (m, 2H), 7.20 (m, 3H), 6.13 (td, *J* = 7.1, 1.1 Hz, 1H), 4.27 – 4.03 (m, 1H), 2.76 – 2.56 (m, 2H), 2.35 (t, *J* = 7.2 Hz, 2H), 2.20 (q, *J* = 7.2 Hz, 2H), 1.89 – 1.64 (m, 4H), 1.55 (d, *J* = 3.3 Hz, 1H), 1.53 – 1.38 (m, 6H), 1.38 – 1.26 (m, 6H), 1.04 – 0.92 (m, 6H), 0.90 (t, *J* = 7.3 Hz, 9H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.9, 142.0, 137.5, 128.5, 128.5, 125.9, 119.6, 79.0, 39.4, 33.1, 32.4, 29.4, 27.5, 25.9, 16.9, 13.8, 11.2 ppm; ^{119}Sn NMR (149 MHz, $CDCl_3$) δ –54.7 ppm; IR (film, $CHCl_3$) 3500, 3027, 2954, 2924, 2870, 2853, 1738, 1604, 1495, 1455, 1422, 1375, 1339, 1243, 1180, 1151, 1046, 961, 915, 877, 748 cm^{-1}; HRMS (ESI): *m/z* calcd. for $C_{27}H_{45}NOSnNa$ [M+Na$^+$]: 542.24146, found 542.24170.



(Z)-2-(7-Hydroxy-9-phenyl-6-(tributylstannyl)non-5-en-1-yl)isoindoline-1,3-dione. Colorless solid (76%, 1.02 g). ^{1}H NMR (400 MHz, Chloroform-d) δ 7.87 – 7.77 (m, 2H), 7.74 – 7.64 (m, 2H), 7.26 (ddd, *J* = 7.8, 7.1, 0.9 Hz, 2H), 7.22 – 7.13 (m, 3H), 6.15 (td, *J* = 7.2, 1.1 Hz, 1H), 4.28 – 4.00 (m, 1H), 3.69 (t, *J* = 7.2 Hz, 2H), 2.64 (qdd, *J* = 13.8, 9.8, 6.1 Hz, 2H), 2.10 (q, *J* = 7.3 Hz, 2H), 1.87 – 1.77 (m, 1H), 1.71 (dq, *J* = 9.8, 6.9 Hz, 4H), 1.58 – 1.37 (m, 8H), 1.37 – 1.18 (m, 6H), 1.08 – 0.90 (m, 6H), 0.86 (t, *J* = 7.3 Hz, 9H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.4, 148.6, 142.2, 140.0, 133.9, 132.1, 128.5, 128.3, 125.7, 123.2, 79.2, 39.3, 37.9, 33.8, 32.3, 29.3, 28.4, 27.4, 27.3, 13.7, 11.1 ppm; ^{119}Sn NMR (149 MHz, $CDCl_3$) δ –55.2 ppm; IR (film, $CHCl_3$) 2925, 2854, 1773, 1739, 1712, 1455, 1438, 1395, 1371, 1238, 1044, 961, 918, 873, 849, 792, 747 cm^{-1}; HRMS (ESI): *m/z* calcd. for $C_{35}H_{51}NO_3SnNa$ [M+Na$^+$]: 676.27824, found 676.27876.



(Z)-4-(3-Hydroxy-3-methyl-2-(tributylstannyl)but-1-en-1-yl)benzonitrile. Colorless oil (78%, 2.63 g). ^{1}H NMR (400 MHz, Chloroform-d) 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* calcd. for $C_{24}H_{39}NOSnNa$ [M+Na$^+$]: 500.19451, found 500.19430.

(Z)-4-(3-Hydroxy-3-methyl-2-(tributylstannyl)but-1-en-1-yl)benzaldehyde. Colorless oil (79%, 3.04 g). ^{1}H NMR (400 MHz, Chloroform-d) δ 10.00 (s, 1H), 7.84 – 7.75 (m, 2H), 7.40 – 7.29 (m, 3H), 1.57 (d, *J* = 0.8 Hz, 1H), 1.43 (s, 6H), 1.40 – 1.25 (m, 6H), 1.25 – 1.12 (m, 6H), 0.82 (t, *J* = 7.2 Hz, 9H), 0.78 – 0.57 (m, 6H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 192.0, 162.9, 147.7, 136.0, 135.0, 129.7, 129.0, 76.2, 31.2, 29.2, 27.5, 13.8, 12.9 ppm; ^{119}Sn NMR (149 MHz, $CDCl_3$) δ –52.8 ppm; IR (film, $CHCl_3$) 2955, 2921, 2871, 2853, 1700, 1600, 1565, 1462, 1418, 1139, 1074, 1048, 1018, 959, 932, 877, 723, 652, 628 cm^{-1}; HRMS (ESI): *m/z* calcd. for $C_{24}H_{39}O_2Sn$ [M-H$^+$]: 479.19769, found 479.19782.

(*anti*,Z)-3-Methyl-4-(tributylstannyl)non-4-en-2-ol. Colorless oil (91%, 9.43 g; α/β = 12:1). ^{1}H NMR (300 MHz, Chloroform-d) δ 6.17 (td, *J* = 7.1, 0.8 Hz, 1H), 3.48 (dqt, *J* = 8.0, 4.6, 1.9 Hz, 1H), 2.26 – 2.12 (m, 1H), 2.12 – 1.97 (m, 2H), 1.86 (dd, *J* = 1.7, 0.8 Hz, 1H), 1.55 – 1.42 (m, 6H), 1.42 – 1.21 (m, 8H), 1.16 (d, *J* = 6.0 Hz, 3H), 1.09 – 0.51 (m, 23H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 147.0, 143.7, 70.6, 53.9, 34.6, 32.6, 29.4, 27.6, 22.7, 20.1, 18.0, 14.2, 13.8, 11.5 ppm; ^{119}Sn NMR (112 MHz, $CDCl_3$) δ –54.4 ppm; IR (film, $CHCl_3$) 2923, 2871, 2854, 1457, 1419, 1376, 1340, 1264, 1120, 1071, 1046, 1002, 961, 926, 666 cm^{-1}; HRMS (ESI): *m/z* calcd. for $C_{22}H_{46}OSnNa$ [M+Na$^+$]: 469.24621, found 469.24663.

(Z)-4-Methyl-N-(1-phenyl-2-(tributylstannyl)hept-2-en-1-yl)benzene-sulfonamide (SI-1). Colorless solid (56%, 1.41 mg). ^{1}H NMR (400 MHz, Chloroform-d) δ 7.70 – 7.60 (m, 2H), 7.21 (tdd, *J* = 7.1, 5.6, 3.3 Hz, 5H), 7.15 – 7.07 (m, 2H), 6.22 – 5.77 (m, 1H), 5.15 – 4.98 (m, 1H), 4.53 (d, *J* = 7.9 Hz, 1H), 2.40 (s, 3H), 1.92 (qd, *J* = 7.0, 1.9 Hz, 2H), 1.44 – 1.08 (m, 10H), 0.90 (t, *J* = 7.1 Hz, 3H), 0.83 (t, *J* = 7.0 Hz, 15H), 0.66 (ddd, *J* = 9.1, 5.8, 1.3 Hz, 6H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.1, 142.5, 141.8, 140.8, 138.3, 129.5, 128.5, 127.6, 127.6, 127.5, 65.0, 34.4, 32.3, 29.1, 27.5, 22.8, 21.6, 14.2, 13.7, 10.8 ppm; ^{119}Sn NMR (149 MHz, $CDCl_3$) δ –51.9 ppm; IR (film, $CHCl_3$) 3250, 2952, 2922, 2869, 2853, 1453, 1437, 1324, 1303, 1160, 1095, 1067, 1051, 995, 937, 912, 870, 813, 765, 750, 700, 658, 633, 595, 569 cm^{-1}; HRMS (ESI): *m/z* calcd. for $C_{32}H_{50}NO_2SSn$ [M-H$^+$]: 632.25891, found 632.25941.

N-(3-Fluoro-1-phenylbut-3-en-1-yl)-4-methylbenzenesulfonamide. Colorless solid (47%, 1.12 g). ^{1}H NMR (400 MHz, Chloroform-d) δ 7.48 – 7.39 (m, 2H), 7.20 – 7.11 (m, 3H), 7.11 – 7.02 (m, 4H), 5.70 (dt, *J* = 2.5, 1.3 Hz, 1H), 5.29 (d, *J* = 2.3 Hz, 1H), 4.74 (d, *J* = 3.8 Hz, 1H), 4.29 (ddd, *J* = 9.1, 5.4, 3.8 Hz, 1H), 2.68 – 2.48 (m, 2H), 2.35 (s, 3H), 1.54 – 1.39 (m, 6H), 1.39 – 1.25 (m, 6H), 0.98 – 0.81 (m, 15H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.2, 143.0, 140.7, 137.7, 130.1, 129.3, 128.4, 127.5, 127.4, 127.2, 57.2, 49.7, 29.2, 27.5, 21.6, 13.8, 9.8 ppm; ^{119}Sn NMR (149 MHz, $CDCl_3$) δ –43.6 ppm; IR (film, $CHCl_3$) 3273, 2955, 2924,

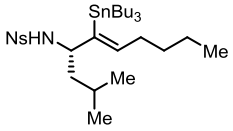
2871, 2852, 1599, 1495, 1455, 1376, 1325, 1243, 1157, 1094, 1052, 959, 921, 863, 812, 757, 698, 665 cm^{-1}; HRMS (ESI): *m/z* calcd. for $C_{29}H_{44}NO_2SSn$ [M-H^+]: 590.21086, found 590.21190.

(Z)-7-(Tributylstannyl)tetradec-7-ene-1,14-diyl dihexanoate. Tetradec-7-yne-1,14-diyl dihexanoate (1.69 g, 4.0 mmol, 1.0 equiv.) and $[Cp^*Ru(MeCN)_3]PF_6$ (100 mg, 0.2 mmol, 5.0 mol%) were dissolved in dry CH_2Cl_2 (10 mL) and the solution was stirred at room temperature under an argon atmosphere (high concentration necessary for good conversion). Bu_3SnH was added over 2 h via syringe pump. Upon complete addition, the volatile materials were removed and the residue purified by flash chromatography (SiO_2, hexanes/ethyl acetate, 19:1) to yield the product as a pale brown oil (2.3 g, 81%). ^{1}H NMR (400 MHz, Chloroform-d) δ 4.02 (td, *J* = 6.7, 1.3 Hz, 4H), 2.25 (t, *J* = 7.5 Hz, 4H), 2.15 – 2.04 (m, 2H), 1.93 (q, *J* = 6.6 Hz, 2H), 1.70 – 1.49 (m, 6H), 1.51 – 1.36 (m, 6H), 1.28 (dddd, *J* = 14.4, 11.9, 8.5, 5.4 Hz, 22H), 1.04 – 0.65 (m, 28H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.9, 143.4, 140.6, 64.4, 40.7, 35.0, 34.4, 31.4, 30.6, 30.3, 29.4, 29.2, 28.9, 28.8, 28.7, 27.5, 26.0, 25.9, 24.8, 22.4, 14.0, 13.8, 10.3 ppm; ^{119}Sn NMR (149 MHz, $CDCl_3$) δ –53.2 ppm; IR (film, $CHCl_3$) 2955, 2925, 2855, 1737, 1462, 1377, 1360, 1244, 1205, 1169, 1098, 1000, 862 cm^{-1}; HRMS (ESI): *m/z* calcd. for $C_{38}H_{74}O_4SnNa$ [M+Na^+]: 737.45006, found 737.45014.

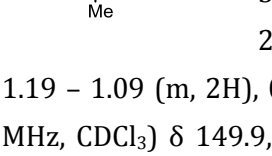
Ethyl (2E,5Z)-4-hydroxy-3-methyl-5-(tributylstannyl)deca-2,5-dienoate. Colorless oil (72%, 2.96 g). ^{1}H NMR (400 MHz, Chloroform-d) δ 6.24 (td, *J* = 7.2, 1.0 Hz, 1H), 6.04 (p, *J* = 1.4 Hz, 1H), 4.71 – 4.45 (m, 1H), 4.16 (q, *J* = 7.1 Hz, 2H), 2.11 – 2.03 (m, 2H), 2.02 (d, *J* = 1.2 Hz, 3H), 1.66 (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 –49.7 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* calcd. for $C_{25}H_{48}O_3SnNa$ [M+Na^+]: 539.25169, found 539.25226.

(Z)-1-((*tert*-Butyldimethylsilyl)oxy)-4-(tributylstannyl)non-4-en-3-ol. Colorless oil (81%, 1.86 g). ^{1}H NMR (400 MHz, Chloroform-d) 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* calcd. for $C_{27}H_{58}O_2SiSnNa$ [M+Na^+]: 585.31196, found 585.31235.

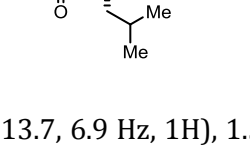
(*S*,Z)-N-(2-Methyl-5-(tributylstannyl)dec-5-en-4-yl)-4-nitrobenzene-sulfonamide. Colorless solid (67%, 1.39 g). $[a]_D^{20}$: +9.6° (c=1.35 in $CHCl_3$). ^1H NMR (400 MHz, Chloroform-d) δ 8.30 (dq, *J* = 9.0, 2.1 Hz, 2H), 8.05 – 7.88 (m, 2H), 6.15 – 5.64 (m, 1H), 4.45 (d, *J* = 7.6 Hz, 1H), 4.18 – 3.82 (m, 1H), 1.90 – 1.71 (m, 2H), 1.62 (dq, *J* = 13.4, 6.7 Hz, 1H), 1.49 – 1.33 (m, 7H), 1.33 – 1.19 (m, 12H), 1.19 – 1.09 (m, 2H), 0.91 – 0.87 (m, 9H), 0.86 (s, 6H), 0.83 – 0.77 (m, 6H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.9, 147.4, 143.7, 142.3, 128.7, 124.2, 62.1, 46.7, 34.3, 32.3, 29.3, 27.5, 24.7, 22.7, 22.6, 22.3, 14.1, 13.7, 11.1 ppm; ^{119}Sn NMR (149 MHz, $CDCl_3$) δ –55.3 ppm; IR (film, $CHCl_3$) 3285, 2956, 2925, 2871, 1608, 1531, 1464, 1417, 1347, 1310, 1164, 854, 811, 735, 747, 758, 685, 667, 612, 580, 535, 462 cm^{-1}; HRMS (ESI): *m/z* calcd. for $C_{29}H_{52}N_2O_4SSnNa$ [M+Na$^+$]: 667.25613, found 667.25650.



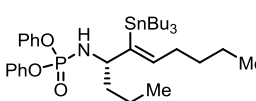
Diphenyl (*S*,Z)-(2-methyl-5-(tributylstannyl)dec-5-en-4-yl)phosphor-amidate. Colorless solid (65%, 1.62 g). $[a]_D^{20}$: –14.2° (c=1.34 in $CHCl_3$). ^1H NMR (400 MHz, Chloroform-d) δ 7.37 – 7.25 (m, 5H), 7.22 (tt, *J* = 8.7, 1.1 Hz, 3H), 7.18 – 7.08 (m, 2H), 6.13 (td, *J* = 7.2, 0.9 Hz, 1H), 4.07 – 3.81 (m, 1H), 2.92 (dd, *J* = 12.5, 9.2 Hz, 1H), 1.98 (dtd, *J* = 12.9, 7.1, 5.8, 3.8 Hz, 2H), 1.60 (dq, *J* = 13.7, 6.9 Hz, 1H), 1.53 – 1.39 (m, 6H), 1.38 – 1.21 (m, 12H), 0.95 – 0.84 (m, 24H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.2, 151.2, 151.2, 151.1, 145.9, 145.8, 141.3, 129.7, 129.6, 124.7, 120.5, 120.4, 120.3, 120.2, 60.2, 47.9, 47.8, 34.3, 32.3, 29.3, 27.6, 24.7, 22.7, 22.7, 22.4, 14.2, 13.7, 11.2 ppm; ^{119}Sn NMR (149 MHz, $CDCl_3$) δ –56.3 ppm; IR (film, $CHCl_3$) 3200, 2924, 2955, 2870, 1593, 1491, 1457, 1422, 1376, 1255, 1195, 1220, 1162, 1071, 1025, 929, 899, 753, 687 cm^{-1}; HRMS (ESI): *m/z* calcd. for $C_{35}H_{58}NO_3PSnNa$ [M+Na$^+$]: 714.30678, found 714.30658.



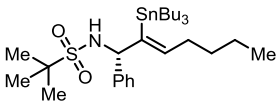
Benzyl (Z)-(2-methyl-5-(tributylstannyl)dec-5-en-4-yl)carbamate. Colorless oil (68%, 1.86 g). ^1H NMR (400 MHz, Chloroform-d) δ 7.43 – 7.27 (m, 5H), 6.15 (t, *J* = 7.2 Hz, 1H), 5.15 – 4.99 (m, 2H), 4.56 (d, *J* = 8.5 Hz, 1H), 4.21 (q, *J* = 7.8 Hz, 1H), 1.99 (tt, *J* = 13.6, 7.1 Hz, 2H), 1.68 – 1.54 (m, 1H), 1.54 – 1.38 (m, 6H), 1.38 – 1.19 (m, 10H), 1.01 – 0.77 (m, 26H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.4, 144.4, 141.4, 136.9, 128.6, 128.3, 128.2, 66.5, 58.2, 45.6, 34.4, 32.4, 29.3, 27.6, 24.9, 22.7, 14.2, 13.8, 11.0 ppm; ^{119}Sn NMR (149 MHz, $CDCl_3$) δ –53.4 ppm; IR (film, $CHCl_3$) 2954, 2924, 2870, 1707, 1497, 1455, 1403, 1337, 1213, 1027, 864, 734, 695 cm^{-1}; HRMS (ESI): *m/z* calcd. for $C_{31}H_{55}NO_2SnNa$ [M+Na$^+$]: 616.31463, found 616.31451.

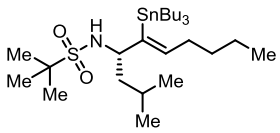


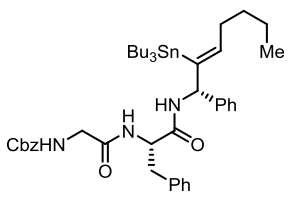
Benzyl (Z)-(2-methyl-4-(tributylstannyl)non-4-en-3-yl)carbamate. Colorless oil (81%, 2.85 g). ^1H NMR (400 MHz, Chloroform-d) δ 7.42 – 7.27 (m, 5H), 6.26 – 5.87 (m, 1H), 5.18 – 4.98 (m, 2H), 4.66 (dd, *J* = 19.2, 8.8 Hz, 1H), 4.05 – 3.74 (m, 1H), 2.12 – 1.92 (m, 1H), 1.62 – 1.38 (m, 6H), 1.31 (h, *J* = 7.2 Hz, 10H), 0.99 – 0.79 (m, 26H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.8, 143.7, 141.3, 136.9, 128.6, 128.2, 128.1, 66.6, 65.6, 34.5, 32.5, 29.3, 27.6, 22.7, 20.7, 17.9, 14.2, 13.8, 10.9 ppm; ^{119}Sn NMR (149 MHz, $CDCl_3$) δ –54.1 ppm; IR (film, $CHCl_3$) 2955, 2924, 2871, 1705, 1497, 1456, 1402, 1338, 1213,



1072, 1024, 873, 752, 695 cm^{-1}; HRMS (ESI): *m/z* calcd. for $C_{30}H_{53}NO_2SnNa$ [M+Na^+]: 602.29898, found 602.29917.

Representative Procedure for the Oxidation of Sulfinimides to the Corresponding Sulfonamides. (*S*,Z)-2-Methyl-N-(1-phenyl-2-(tributylstannyl)hept-2-en-1-yl)propane-2-sulfonamide.  *m*CPBA (1.62 g, 80% purity, 7.5 mmol, 1.5 equiv.) was added in one portion to a solution of (*S*)-2-methyl-N-((S)-1-phenylhept-2-yn-1-yl)propane-2-sulfinamide (1.46 g, 5.0 mmol, 1.0 equiv.) in 25 mL of CH_2Cl_2 at 0°C. The ice bath was removed after 5 min and stirring was continued with the conversion monitored by TLC (hexanes/ethyl acetate, 2:1). After 1 h, saturated sodium bicarbonate solution was added and stirring continued for 30 min before the mixture was extracted twice with CH_2Cl_2. The combined organics were washed with saturated sodium bicarbonate solution and water, dried over magnesium sulfate and concentrated under reduced pressure. The crude material was used as such for the ensuing hydrostannation (56% over 2 steps, 1.67 g, 2.79 mmol). $[a]_D^{20}$: +20.6° (c=1.38 in $CHCl_3$). ^{1}H NMR (400 MHz, Chloroform-d) δ 7.40 – 7.28 (m, 4H), 7.28 – 7.17 (m, 2H), 6.43 (td, *J* = 7.2, 1.4 Hz, 1H), 5.32 – 5.12 (m, 1H), 4.02 (d, *J* = 9.5 Hz, 1H), 2.17 (q, *J* = 7.1 Hz, 2H), 1.52 – 1.41 (m, 2H), 1.39 (s, 8H), 1.37 – 1.11 (m, 13H), 1.00 – 0.90 (m, 4H), 0.82 (t, *J* = 7.1 Hz, 9H), 0.73 – 0.62 (m, 6H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.0, 142.1, 141.3, 128.8, 127.8, 127.7, 65.6, 60.1, 34.5, 32.5, 29.1, 27.5, 24.4, 22.8, 14.3, 13.8, 10.8 ppm; ^{119}Sn NMR (149 MHz, $CDCl_3$) δ –52.5 ppm; IR (film, $CHCl_3$) 3279, 2924, 2955, 2854, 2871, 1454, 1377, 1302, 1182, 1127, 1067, 1003, 939, 874, 757, 698, 654, 560 594, 513 cm^{-1}; HRMS (ESI): *m/z* calcd. for $C_{29}H_{53}NO_2SSnNa$ [M+Na^+]: 622.27105, found 622.27143.

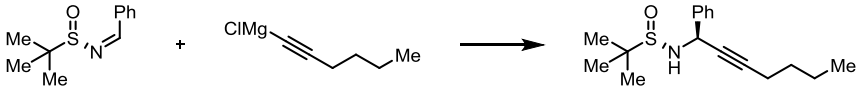
(*S*,Z)-2-Methyl-N-(2-methyl-5-(tributylstannyl)dec-5-en-4-yl)propane-2-sulfonamide.  Prepared analogously (62% over 2 steps, 1.78 g). $[a]_D^{20}$: –8.6° (c=1.23 in $CHCl_3$). ^{1}H NMR (400 MHz, Chloroform-d) δ 6.34 – 5.86 (m, 1H), 4.17 – 3.89 (m, 1H), 3.63 (d, *J* = 8.9 Hz, 1H), 2.12 – 1.87 (m, 2H), 1.81 – 1.59 (m, 2H), 1.55 – 1.39 (m, 6H), 1.35 (s, 9H), 1.35 – 1.27 (m, 14H), 0.98 – 0.92 (m, 9H), 0.89 (t, *J* = 7.2 Hz, 12H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.3, 141.7, 62.1, 59.5, 48.5, 34.5, 32.3, 29.4, 27.6, 24.8, 24.5, 22.7, 22.6, 14.2, 13.8, 11.1 ppm; ^{119}Sn NMR (149 MHz, $CDCl_3$) δ –55.1 ppm; IR (film, $CHCl_3$) 3273, 2925, 2955, 2871, 1457, 1420, 1377, 1301, 1125, 1061, 692, 663, 594, 539, 512 cm^{-1}; HRMS (ESI): *m/z* calcd. for $C_{27}H_{57}NO_2SSnNa$ [M+Na^+]: 602.30235, found 602.30270.

Benzyl (2-oxo-2-(((*S*)-1-oxo-3-phenyl-1-(((S,Z)-1-phenyl-2-(tri-butylstannyl)hept-2-en-1-yl)amino)propan-2-yl)amino)ethyl)-carbamate. Colorless oil (796 mg, 47%, 72% brsm).  $[a]_D^{20}$: +4.3° (c 1.42 in $CHCl_3$). ^{1}H NMR (400 MHz, Chloroform-d) δ 7.33 (q, *J* = 4.8, 4.3 Hz, 5H), 7.27 – 7.05 (m, 10H), 6.83 (d, *J* = 8.1 Hz, 1H), 6.37 (d, *J* = 8.5 Hz, 1H), 5.96 (t, *J* = 7.0 Hz, 1H), 5.64 (d, *J* = 8.5 Hz, 1H), 5.42 (t, *J* = 5.6 Hz, 1H), 5.13 – 4.95 (m, 2H), 4.67 (q, *J* = 7.2 Hz, 1H), 3.66 (qd, *J* = 16.8, 5.6 Hz, 2H), 3.13 – 2.95 (m, 2H), 2.12 – 1.96 (m, 2H), 1.75 – 1.56

(m, 2H), 1.43 – 1.29 (m, 6H), 1.29 – 1.15 (m, 5H), 0.93 (td, *J* = 7.2, 3.4 Hz, 6H), 0.84 (t, *J* = 7.1 Hz, 9H), 0.72 (d, *J* = 7.3 Hz, 3H), 0.70 (d, *J* = 8.1 Hz, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.2, 169.0, 156.6, 141.8, 141.2, 140.9, 136.5, 136.2, 129.4, 128.7, 128.6, 128.5, 128.3, 128.2, 127.9, 127.5, 127.0, 67.3, 60.0, 54.5, 44.4, 38.2, 34.6, 32.5, 29.1, 28.0, 27.5, 27.0, 22.8, 17.6, 14.2, 13.7, 10.7 ppm; ^{119}Sn NMR (149 MHz, $CDCl_3$) δ –51.1 ppm; IR (film, $CHCl_3$) 3282, 2955, 2923, 2871, 2853, 1707, 1643, 1521, 1455, 1376, 1238, 1155, 1105, 1029, 961, 914, 875, 745, 697, 666 cm^{-1}; HRMS (ESI): *m/z* calcd. for $C_{44}H_{63}N_3O_4SnNa$ [M+Na$^+$]: 840.37321, found 840.37341.

Alkyne Substrates

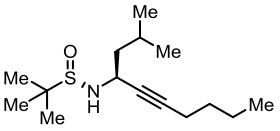
Representative Procedure for the Diastereoselective Addition of Magnesium Acetylides to Sulfinimides.[9] (*S*)-2-Methyl-N-((*S*)-1-phenylhept-2-yn-1-yl)propane-2-sulfinamide

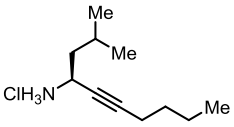


iso-Propylmagnesium chloride (17.3 mL, 2 M solution in THF, 34.5 mmol, 2.0 equiv.) was added to a solution of 1-hexyne (4.36 mmol, 38 mmol, 2.2 equiv.) in THF (5 mL) at 0°C. The cooling bath was removed and stirring continued for 60 min. The resulting solution vas added via canula over 15 min to a solution of (*S*,*E*)-N-benzylidene-2-methylpropane-2-sulfinamide (3.6 g, 17.2 mmol, 1.0 equiv.) in dry CH_2Cl_2 (80 mL) at –78°C. The resulting mixture was stirred at that temperature for 2 h and for another 12 h at room temperature. The reaction was then 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 (SiO_2, hexanes/ethyl acetate, 4:1) yielded the product as a yellow thick oil (3.4 g, 11.7 mmol, > 20:1 d.r., 68%). $[a]_D^{20}$: +32.3° (c=1.24 in $CHCl_3$). ^{1}H NMR (400 MHz, Chloroform-d) δ 7.53 – 7.45 (m, 2H), 7.39 – 7.27 (m, 3H), 5.20 (dt, *J* = 5.7, 2.2 Hz, 1H), 3.59 (d, *J* = 5.8 Hz, 1H), 2.25 (td, *J* = 7.1, 2.1 Hz, 2H), 1.60 – 1.46 (m, 2H), 1.46 – 1.32 (m, 2H), 1.20 (s, 9H), 0.90 (t, *J* = 7.3 Hz, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 139.9, 128.7, 128.2, 127.8, 87.6, 78.9, 56.3, 51.2, 30.7, 22.7, 22.1, 18.7, 13.8 ppm; IR (film, $CHCl_3$) 3186, 2931 2956, 2870, 1493, 1455, 1381, 1327, 1251, 1188, 1139, 1061, 1005, 923, 792, 751, 697 cm^{-1}; HRMS (ESI): *m/z* calcd. for $C_{17}H_{25}NOSNa$ [M+Na$^+$]: 314.15491, found 314.15462.

The following compound was prepared analogously:

(*S*)-2-Methyl-N-((*S*)-2-methyldec-5-yn-4-yl)propane-2-sulfinamide. Colorless solid (74%, 3.85 g, >20:1 d.r.). $[a]_D^{20}$: +49.5° (c=1.35 in $CHCl_3$). ^{1}H NMR (400 MHz, Chloroform-d) δ 4.02 (dddd, *J* = 8.4, 7.2, 4.2, 2.1 Hz, 1H), 3.18 (d, *J* = 6.5 Hz, 1H), 2.18 (td, *J* = 7.1, 2.1 Hz, 2H), 1.83 (dp, *J* = 13.5, 6.7 Hz, 1H), 1.57 – 1.51 (m, 2H), 1.51 – 1.42 (m, 2H), 1.42 – 1.31 (m, 2H), 1.20 (s, 9H), 0.93 – 0.86 (m, 9H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 85.4, 80.1, 56.1, 46.6, 30.9, 25.1, 22.8, 22.7, 22.2, 22.1, 18.6, 13.7 ppm; IR (film, $CHCl_3$) 3198, 2956, 2931, 2869, 1467, 1364 1385, 1159, 1057, 877, 795, 752, 663, 605, 478 cm^{-1}; HRMS (ESI): *m/z* calcd. for $C_{15}H_{29}NOSNa$ [M+Na$^+$]: 294.18621, found 294.18593.



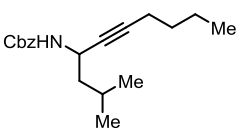
Representative Procedure for the Acid Mediated Deprotection of Sulfonamides.[9] **(*S*)-2-Methyldec-5-yn-4-aminium chloride.**  HCl (4.5 mL, 4 M in 1,4-dioxane, 18 mmol, 2.0 equiv.) was added in one portion to a solution of (*S*)-2-methyl-N-((S)-2-methyldec-5-yn-4-yl)propane-2-sulfinamide (1.61 g, 5.5 mmol, 1.0 equiv.) in MeOH (20 mL) at 0°C and stirring was continued until TLC indicated complete conversion (hexanes/ethyl acetate, 2:1). All volatile materials were removed under reduced pressure and the crude ammonium salt used in the next step without further purification.

(*S*)-N-(2-Methyldec-5-yn-4-yl)-4-nitrobenzenesulfonamide. (*S*)-2-Methyldec-5-yn-4-amin hydrochloride (917 mg, 4.5 mmol, 1.0 equiv.) was dissolved in dry DMF (20 mL) and stirred at room temperature in an oven-dried Schlenk flask under an argon atmosphere. Et_3N (1.88 mL, 13.5 mmol, 3.0 equiv.) and 4-nitrobenzenesulfonyl chloride (1.2 g, 5.4 mmol, 1.2 equiv.) were added and stirring was continued for 12 h. The mixture was then poured onto saturated ammonium chloride solution, which 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 (SiO_2, hexanes/ethyl acetate) yielded the product as an orange solid (1.13 g, 3.2 mmol, 71%). $[a]_D^{20}$: –94.2° (c=1.74 in $CHCl_3$). ^{1}H NMR (400 MHz, Chloroform-d) δ 8.35 (dq, *J* = 9.0, 2.1 Hz, 2H), 8.22 – 7.96 (m, 2H), 4.65 (d, *J* = 9.4 Hz, 1H), 4.35 – 3.97 (m, 1H), 1.89 – 1.74 (m, 3H), 1.62 – 1.44 (m, 2H), 1.23 – 1.08 (m, 4H), 0.92 (dd, *J* = 9.0, 6.6 Hz, 6H), 0.85 – 0.75 (m, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.2, 146.7, 128.9, 124.1, 85.8, 77.9, 46.3, 45.1, 30.6, 24.8, 22.3, 22.2, 22.0, 18.1, 13.6 ppm; IR (film, $CHCl_3$) 3271, 2933 2958, 2871, 1524, 1346, 1311, 1155, 1090, 1053, 855, 739, 619, 550 cm^{-1}; HRMS (ESI): *m/z* calcd. for $C_{17}H_{24}N_2O_4SNa$ [M+Na$^+$]: 375.13490, found 375.13471.

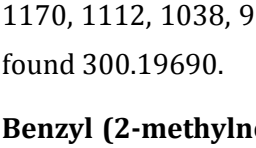
(*S*)-N-(2-Methyldec-5-yn-4-yl)-4-nitrobenzenesulfonamide. (*S*)-2-Methyldec-5-yn-4-amin hydrochloride (917 mg, 4.5 mmol, 1.0 equiv.) was dissolved in dry DMF (20 mL) and the solution stirred at room temperature in an oven-dried Schlenk flask under an argon atmosphere. Et_3N (1.88 mL, 13.5 mmol, 3.0 equiv.) and diphenylchlorophosphate (1.2 mL, 5.4 mmol, 1.2 equiv.) were added and stirring was continued for 12 h. The mixture was then poured onto saturated ammonium chloride solution, which 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 (SiO_2, hexanes/ethyl acetate, 9:1) yielded the product as an orange solid (1.45 g, 3.6 mmol, 81%). $[a]_D^{20}$: –33.1° (c=1.21 in $CHCl_3$).^{1}H NMR (400 MHz, Chloroform-d) δ 7.38 – 7.23 (m, 8H), 7.16 (dddd, *J* = 8.0, 5.9, 4.2, 1.1 Hz, 2H), 4.14 (dtdt, *J* = 10.5, 8.7, 6.9, 2.1 Hz, 1H), 3.16 (dd, *J* = 12.6, 10.1 Hz, 1H), 2.10 (td, *J* = 6.9, 2.1 Hz, 2H), 1.77 (ddt, *J* = 13.1, 8.0, 6.6 Hz, 1H), 1.56 – 1.28 (m, 6H), 0.89 (d, *J* = 1.7 Hz, 4H), 0.88 – 0.84 (m, 5H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.0, 151.0, 150.9, 129.7, 129.7, 125.0, 120.6, 120.6, 120.4, 120.4, 84.1, 80.4, 80.4, 47.7, 47.7, 43.2, 30.8, 25.0, 22.8, 22.0, 18.4, 13.7 ppm; IR (film, $CHCl_3$) 3204,

2932 2956, 2870, 1591, 1489, 1255, 1219, 1191, 1162 , 928, 752, 688 cm^{-1}; HRMS (ESI): *m/z* calcd. for $C_{23}H_{30}NO_3PNa$ [M+Na^+]: 422.18555, found 422.18526.

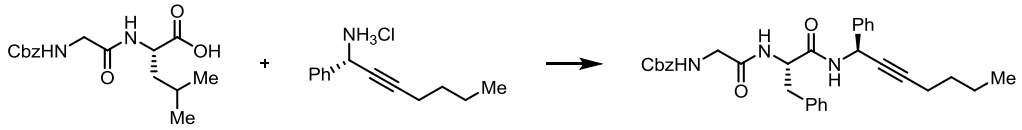
Benzyl (2-methyldec-5-yn-4-yl)carbamate. Colorless solid (97%, 1.46 g). ^{1}H NMR (400 MHz, Chloroform-d) δ 7.40 – 7.27 (m, 5H), 5.24 – 5.00 (m, 2H), 4.82 (d, *J* = 8.8 Hz, 1H), 4.48 (q, *J* = 8.2 Hz, 1H), 2.22 – 2.09 (m, 2H), 1.77 (dq, *J* = 13.4, 6.7 Hz, 1H), 1.57 – 1.31 (m, 6H), 1.00 – 0.78 (m, 9H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.5, 136.5, 128.6, 128.3 (2C), 83.7, 79.5, 66.9, 45.9, 42.3, 30.9, 25.2, 22.9, 22.0, 18.4, 13.7 ppm; IR (film, $CHCl_3$) 3327, 2956, 2932, 2871, 1697, 1500, 1455, 1368, 1325, 1278, 1241, 1170, 1112, 1038, 912, 751, 696 cm^{-1}; HRMS (ESI): *m/z* calcd. for $C_{19}H_{26}NO_2$ [M-H^+]: 300.19718, found 300.19690.



Benzyl (2-methylnon-4-yn-3-yl)carbamate. Colorless solid (91%, 1.76 g). ^{1}H NMR (400 MHz, Chloroform-d) δ 7.44 – 7.28 (m, 5H), 5.17 – 5.04 (m, 2H), 4.94 (d, *J* = 9.0 Hz, 1H), 4.35 (dq, *J* = 7.5, 2.7 Hz, 1H), 2.17 (td, *J* = 6.9, 2.2 Hz, 2H), 1.96 – 1.81 (m, 1H), 1.53 – 1.30 (m, 4H), 0.96 (dd, *J* = 6.8, 4.4 Hz, 6H), 0.90 (t, *J* = 7.2 Hz, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.6, 136.5, 128.6, 128.3, 128.3, 84.6, 77.6, 66.9, 49.6, 33.3, 30.9, 22.0, 19.0, 18.4, 17.6, 13.7 ppm; IR (film, $CHCl_3$) 3325, 2959, 2931, 2872, 1696, 1499, 1455, 1386, 1332, 1302, 1229, 1126, 1026, 736, 696 cm^{-1}; HRMS (ESI): *m/z* calcd. for $C_{18}H_{25}NO_2Na$ [M+Na^+]: 310.17775, found 310.17765.



Benzyl (2-oxo-2-(((*S*)-1-oxo-3-phenyl-1-(((*S*)-1-phenylhept-2-yn-1-yl)amino)propan-2-yl)amino)ethyl)carbamate.



Z-Gly-Phe (891 mg, 2.5 mmol, 1.0 equiv.), EDCI (575 mg, 3.0 mmol, 1.2 equiv.), HOBT (405 mg, 3.0 mmol, 1.2 equiv.) and Et_3N (1.05 mL, 7.5 mmol, 3.0 equiv.) were added in that order to a solution of (*S*)-1-phenylhept-2-yn-1-amin hydrochloride (559 mg, 2.5 mmol, 1.0 equiv.) in 20 mL of dry DMF at 0°C. Stirring was continued while the mixture was allowed to reach room temperature. The mixture was then poured onto saturated ammonium chloride solution, the resulting mixture was extracted two times with CH_2Cl_2, the combined organic layers were washed with water, dried over magnesium sulfate and concentrated under reduced pressure. Flash chromatography (hexanes/ethyl acetate) yielded the product as a syrup (1.10 g, 84%). $[a]_D^{20}$: –5.5° (c 1.39 in $CHCl_3$). ^{1}H NMR (400 MHz, Chloroform-d) δ 7.44 – 7.31 (m, 6H), 7.31 – 7.15 (m, 9H), 6.71 (d, *J* = 7.9 Hz, 1H), 6.40 (d, *J* = 8.4 Hz, 1H), 5.86 (dt, *J* = 8.4, 2.2 Hz, 1H), 5.35 (s, 1H), 5.05 (s, 2H), 4.65 (q, *J* = 7.2 Hz, 1H), 3.77 (d, *J* = 5.7 Hz, 2H), 3.11 (dd, *J* = 13.7, 5.7 Hz, 1H), 3.03 (dd, *J* = 13.5, 7.5 Hz, 1H), 2.22 (td, *J* = 7.1, 2.2 Hz, 2H), 1.56 – 1.46 (m, 2H), 1.46 – 1.33 (m, 2H), 0.91 (t, *J* = 7.2 Hz, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.2, 168.8, 156.6, 139.2, 136.3, 136.2, 129.6, 128.8, 128.7, 128.4, 128.3, 128.1, 127.2, 127.1, 85.9, 67.4, 54.4, 45.2, 44.6, 38.6, 30.8, 22.2,

18.6, 13.8 ppm; IR (film, $CHCl_3$) 3402, 3275, 2930 2955, 1724, 1681, 1644, 1524, 1249, 1223, 745, 698 cm^{-1}; HRMS (ESI): *m/z* calcd. for $C_{32}H_{35}N_3O_4Na$ [M+Na^+]: 548.25198, found 548.25181.

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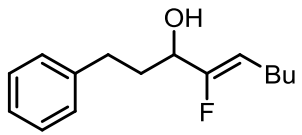
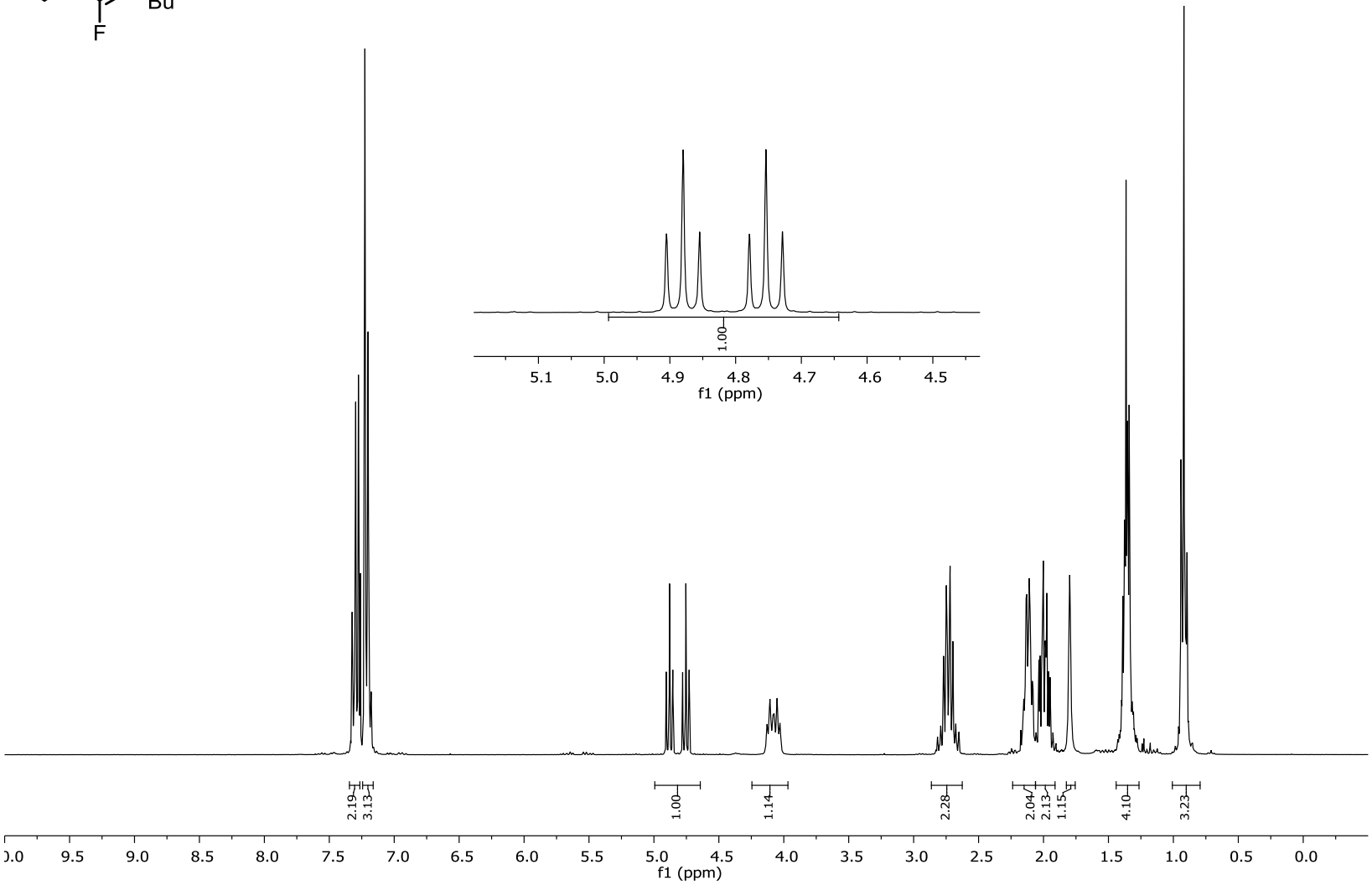
(Z)-1-Phenyl-4-(tributylstannyl)non-4-en-3-ol





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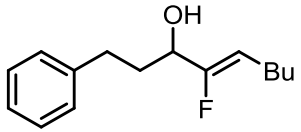
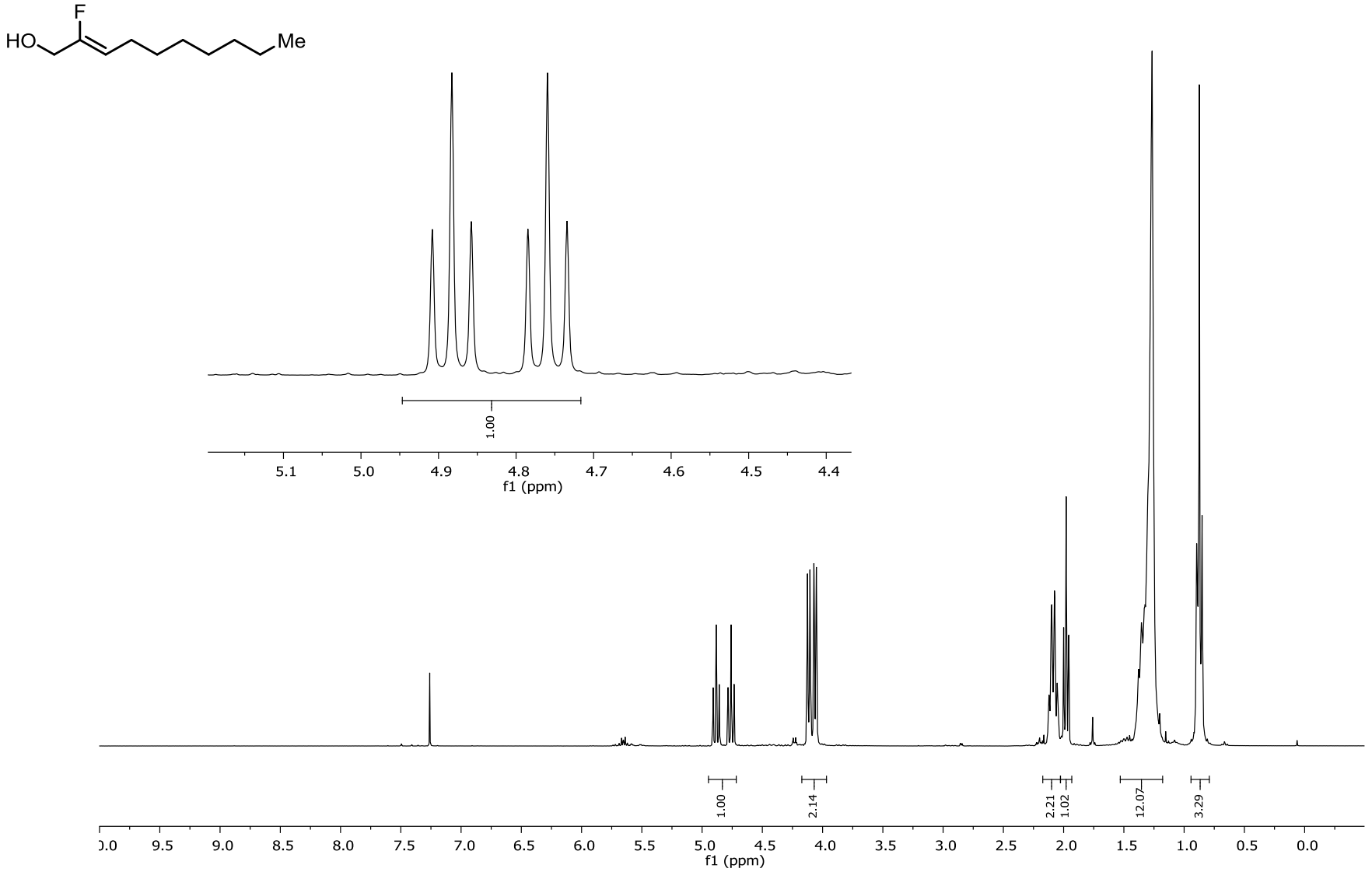


(Z)-2-Fluorodec-2-en-1-ol



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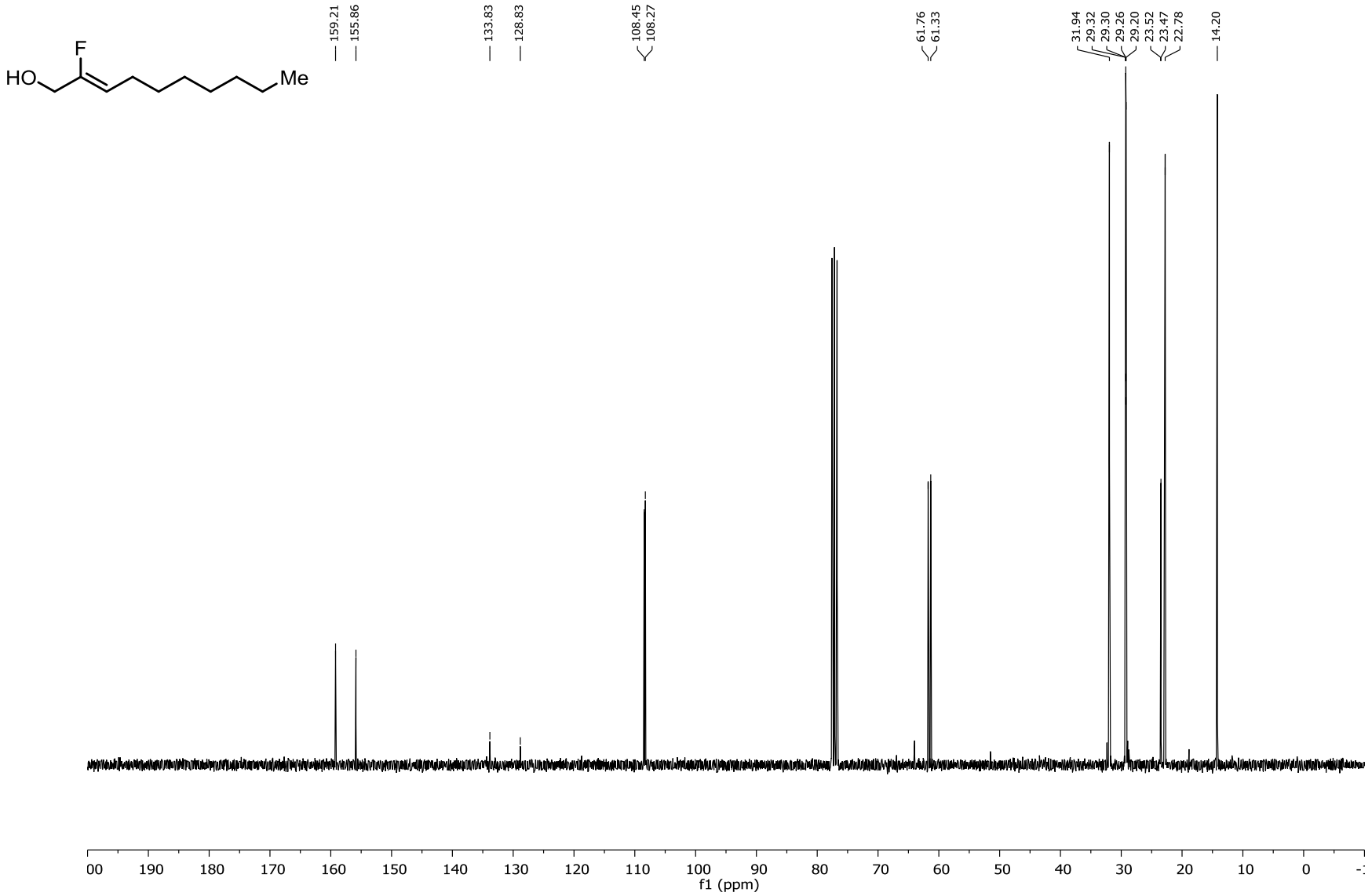

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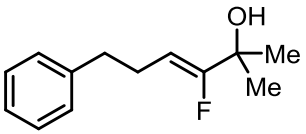

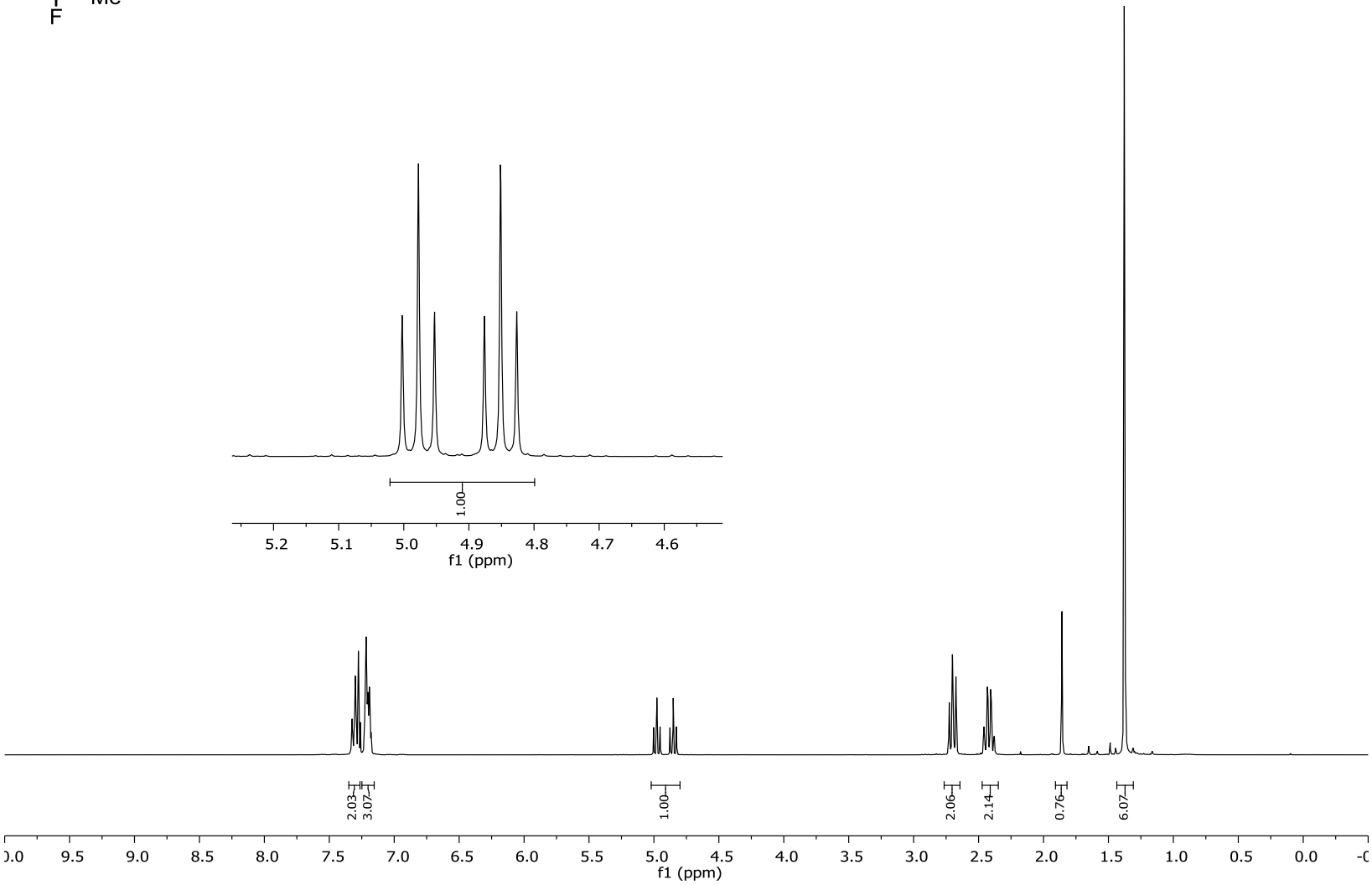

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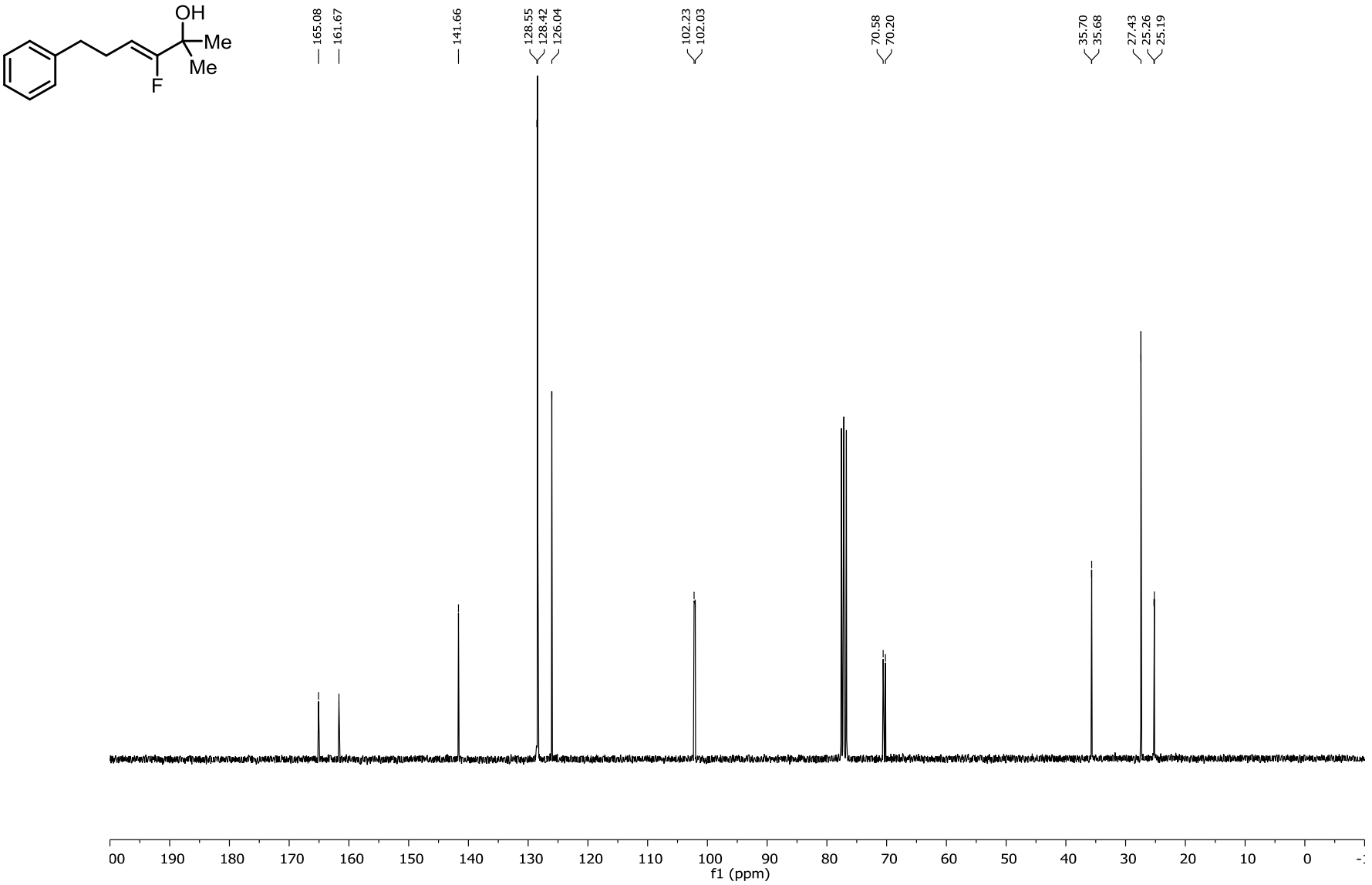

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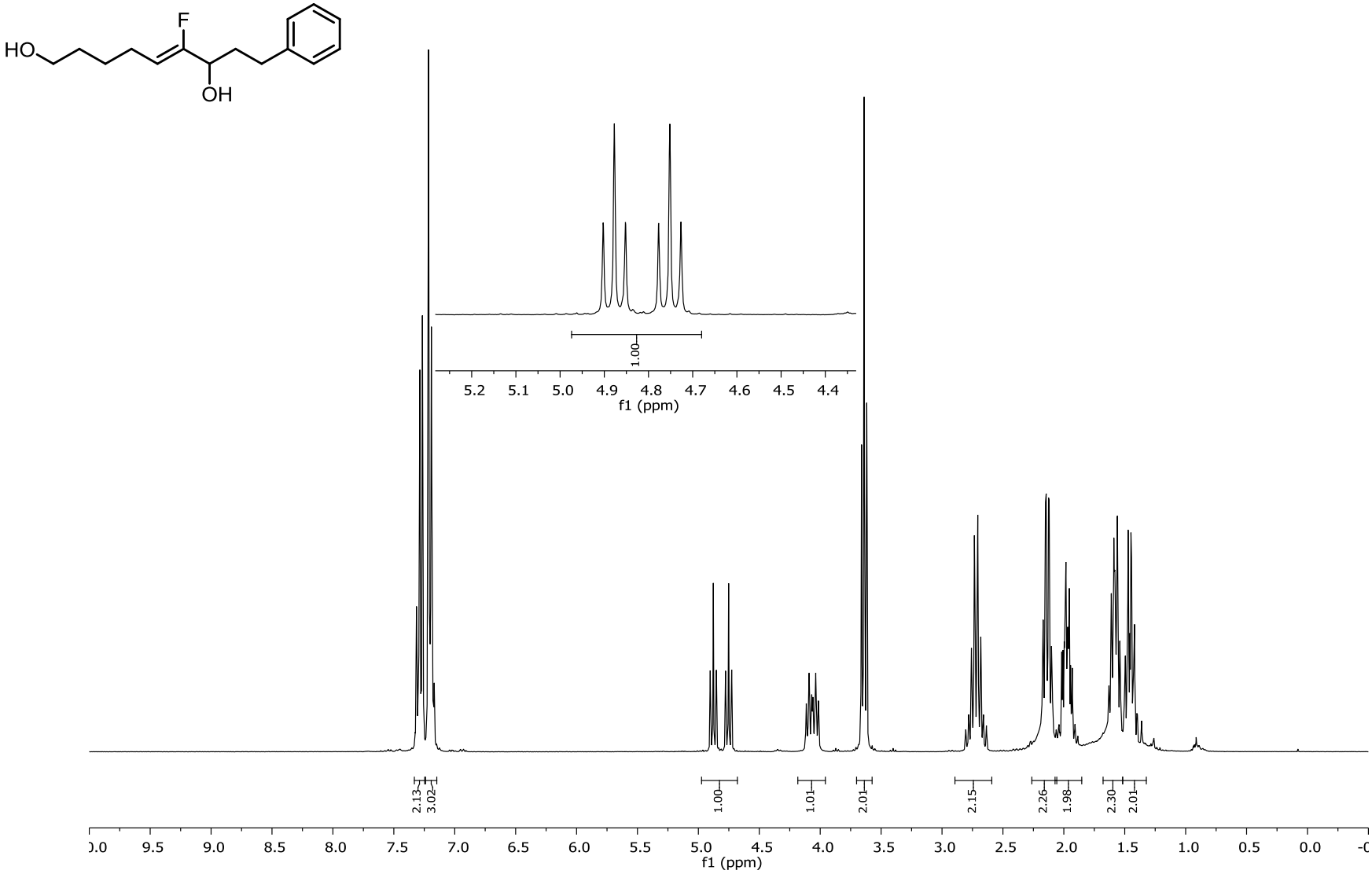

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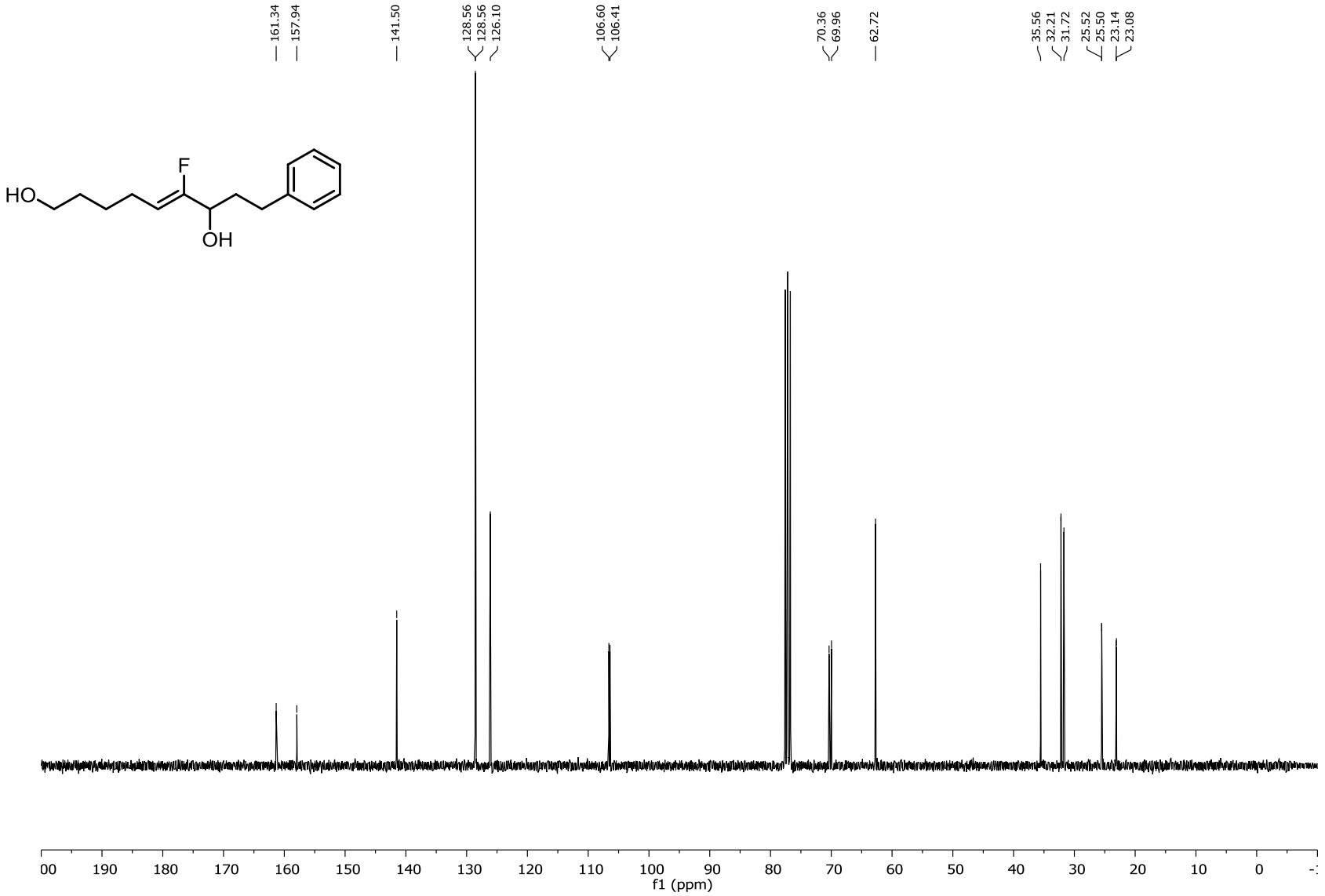

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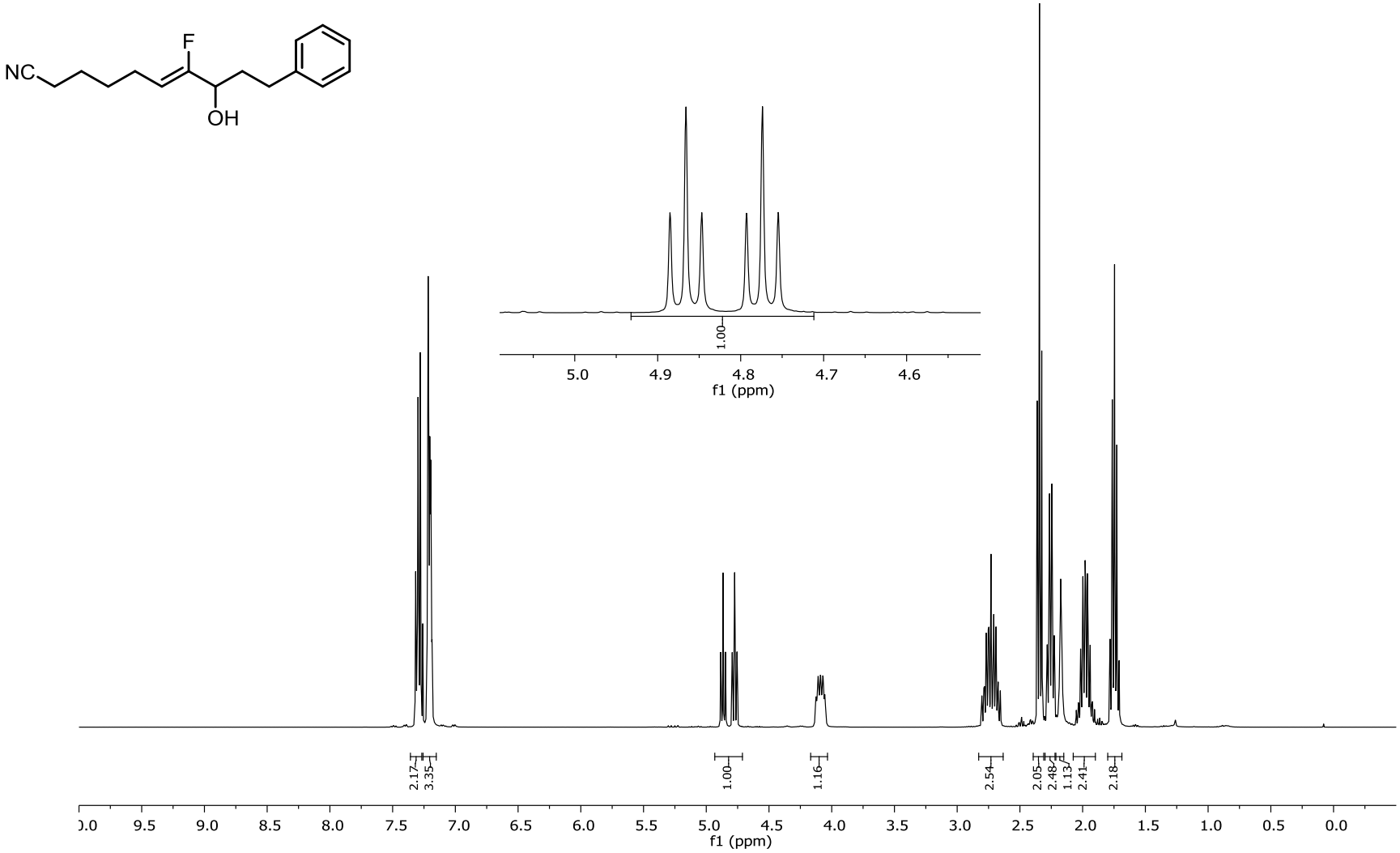

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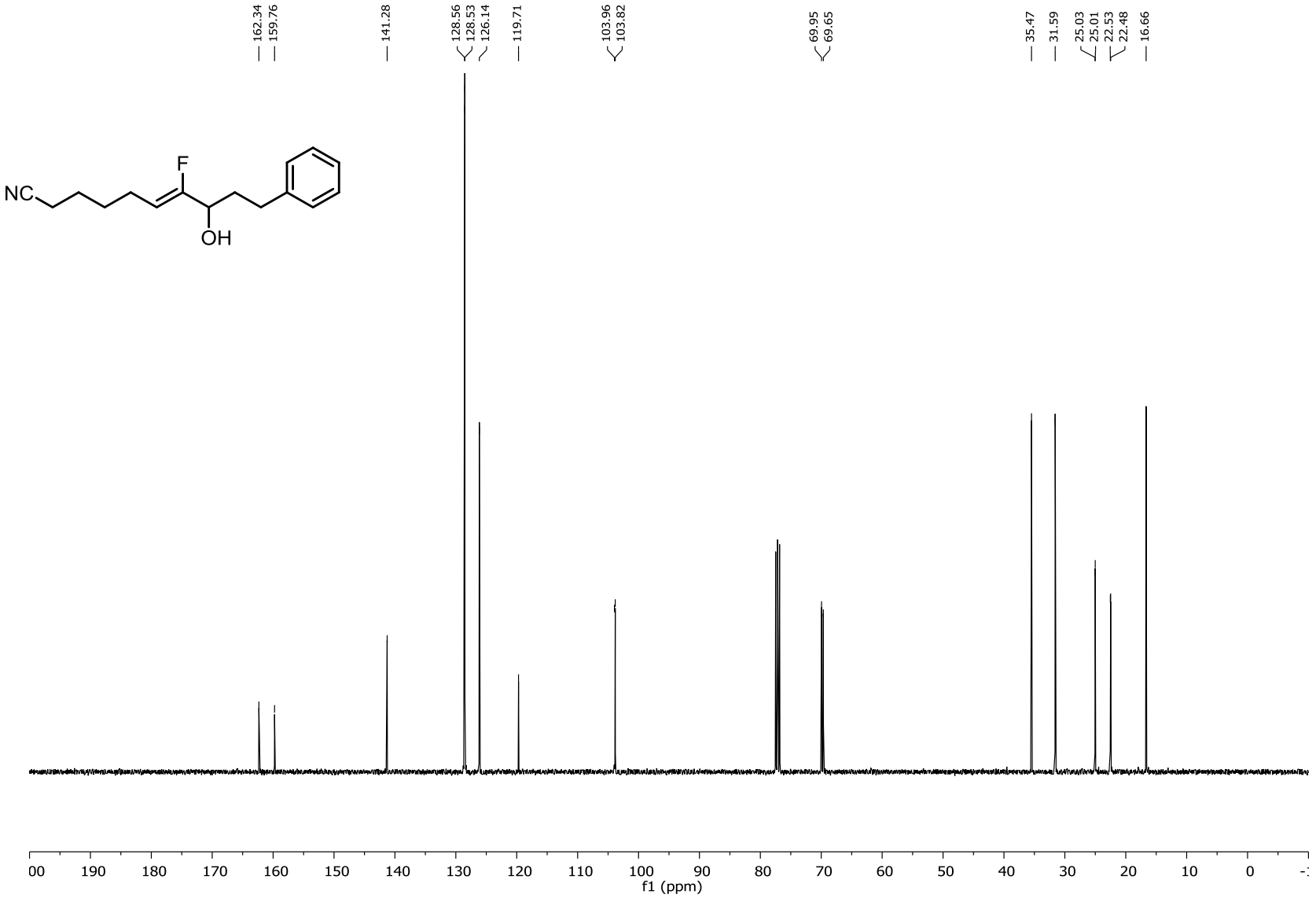

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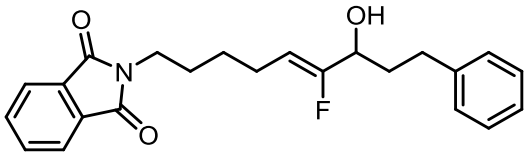

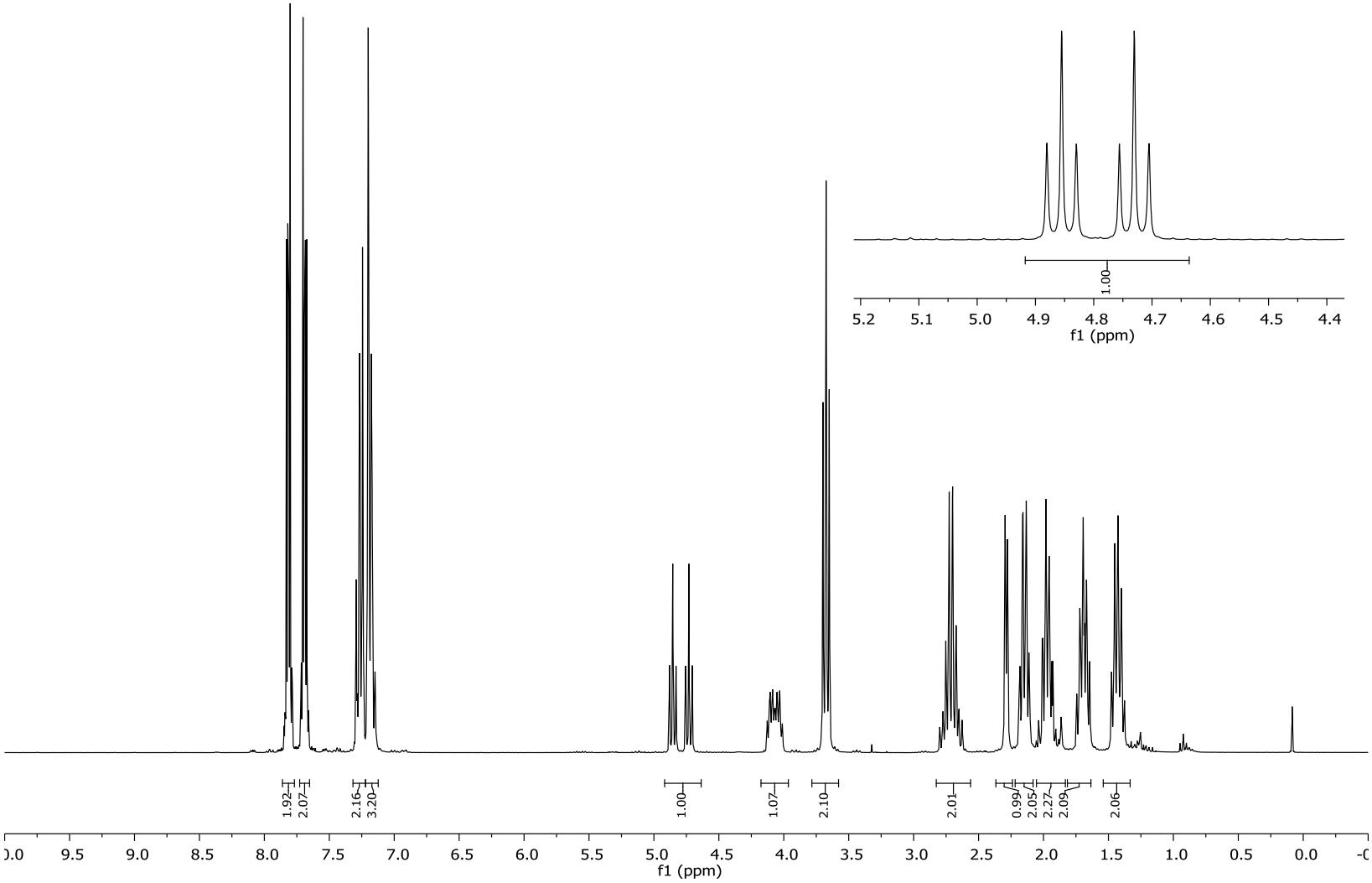

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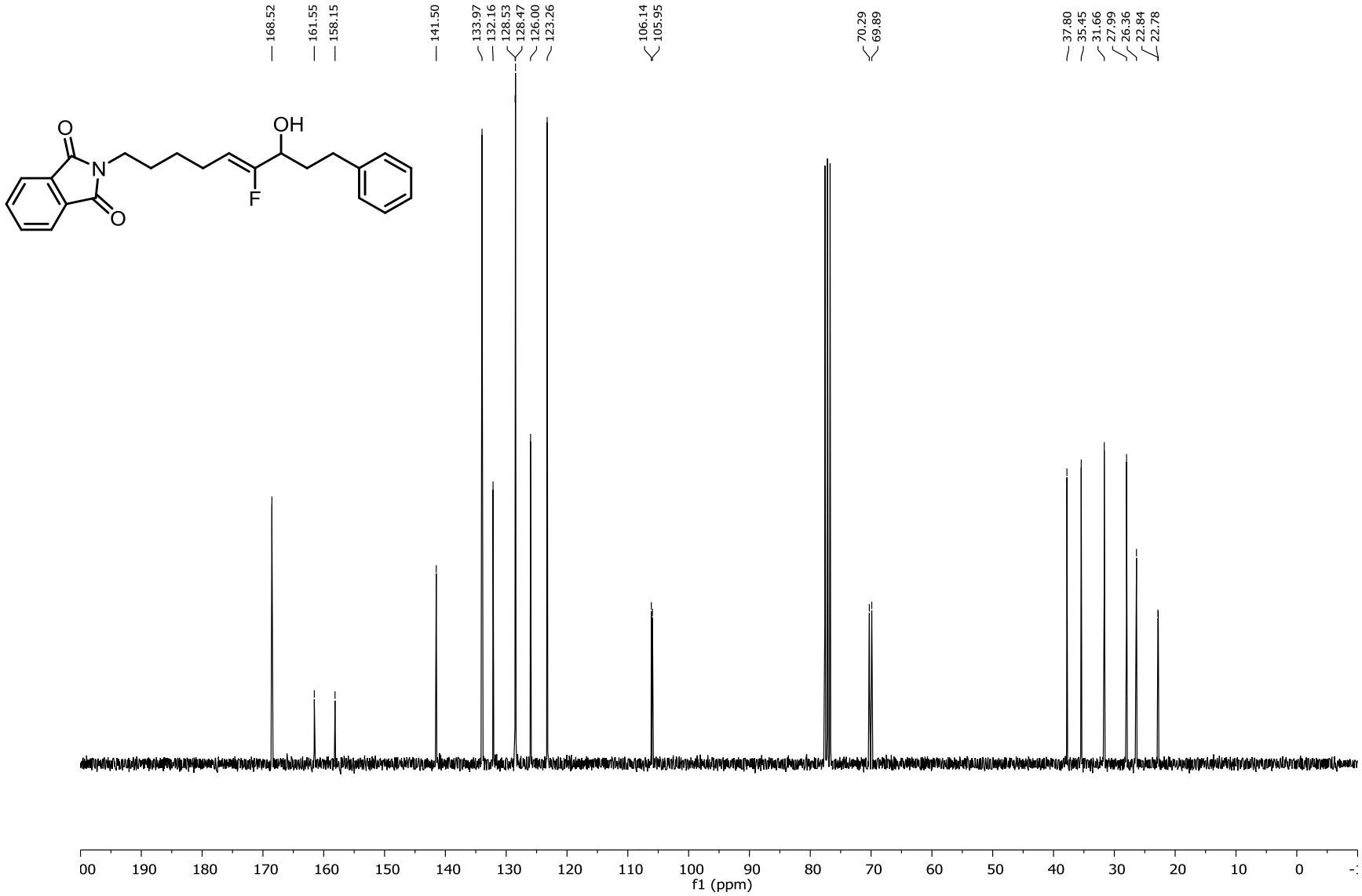
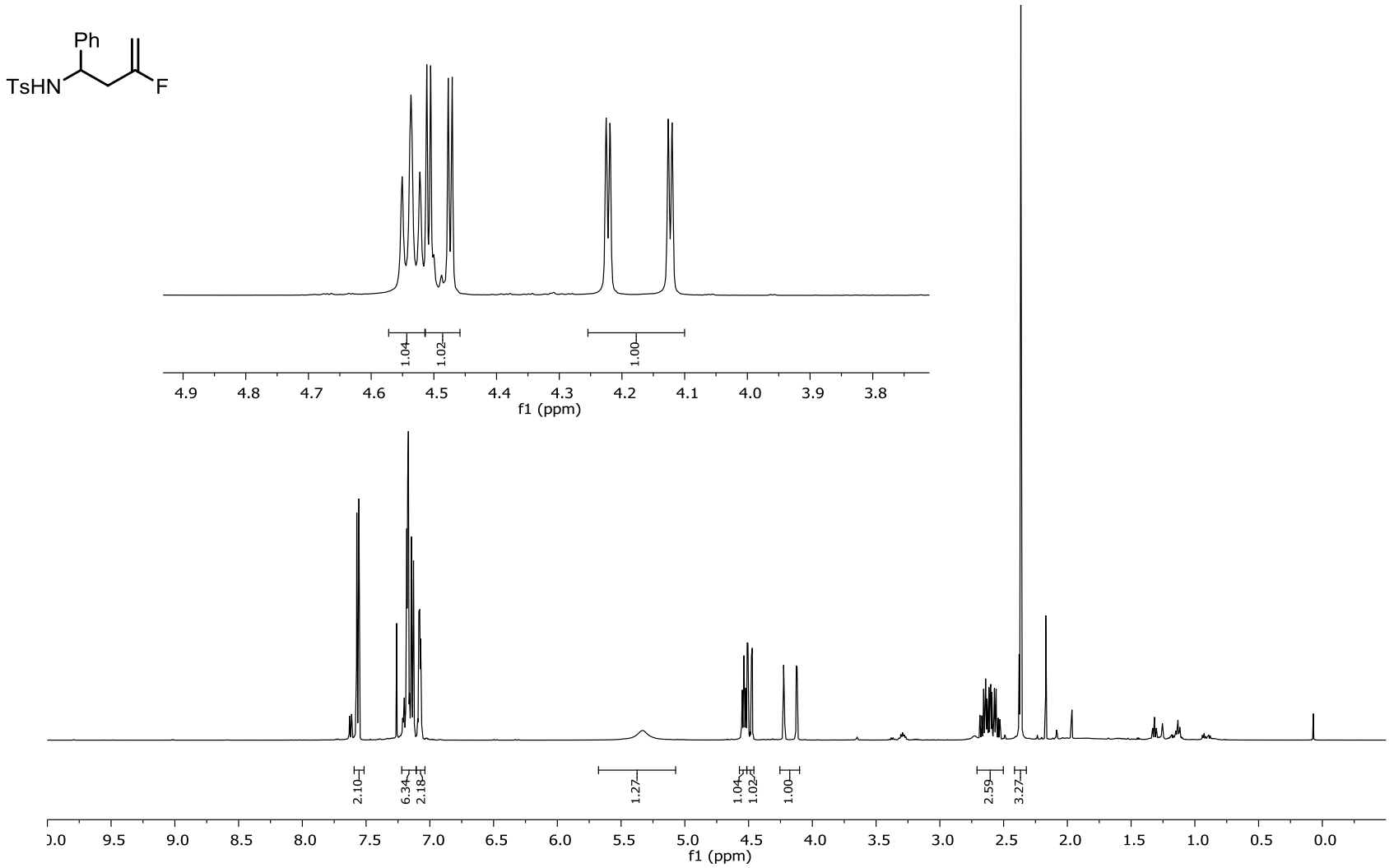


N-(3-Fluoro-1-phenylbut-3-en-1-yl)-4-methylbenzenesulfonamide



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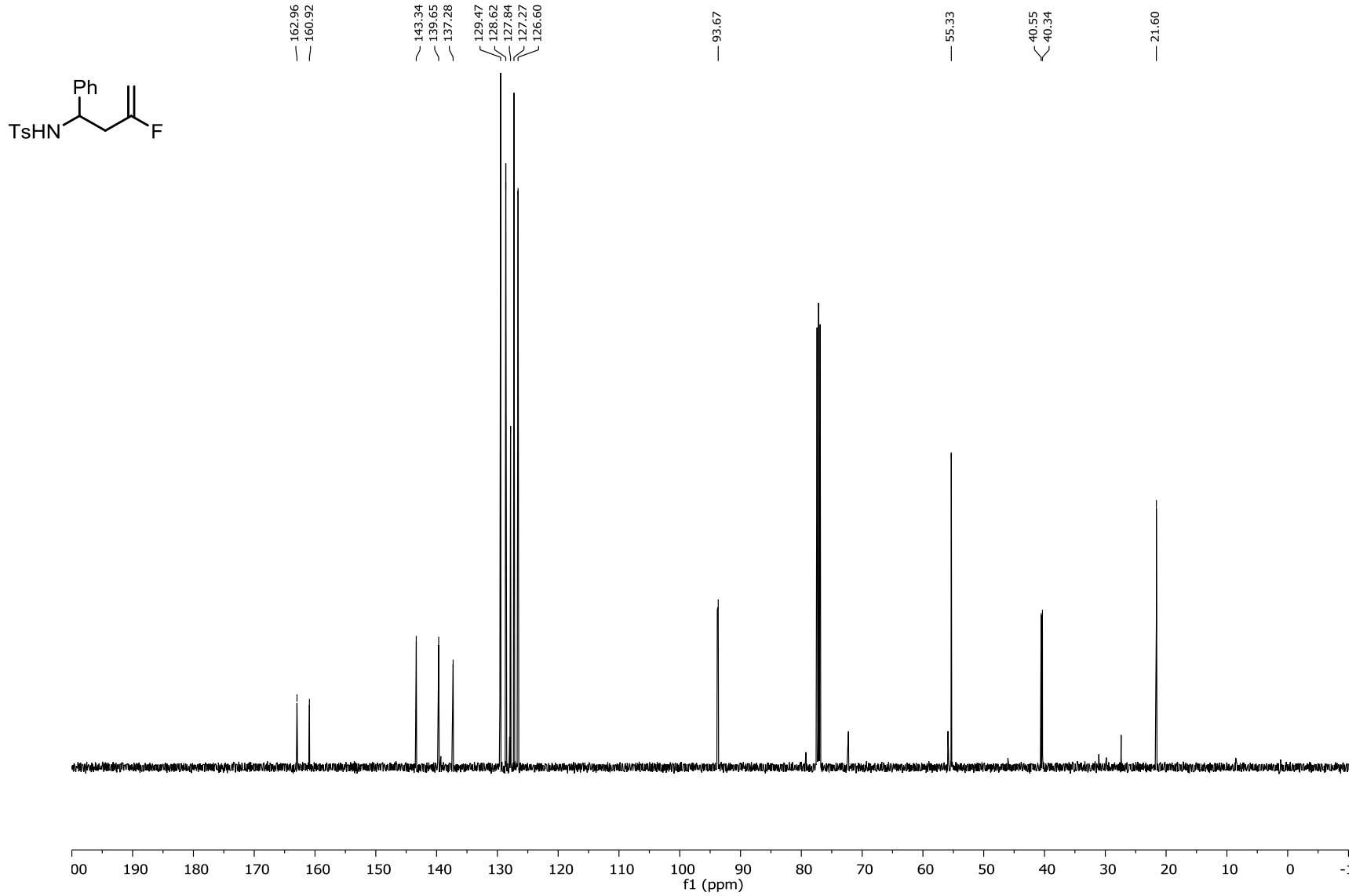

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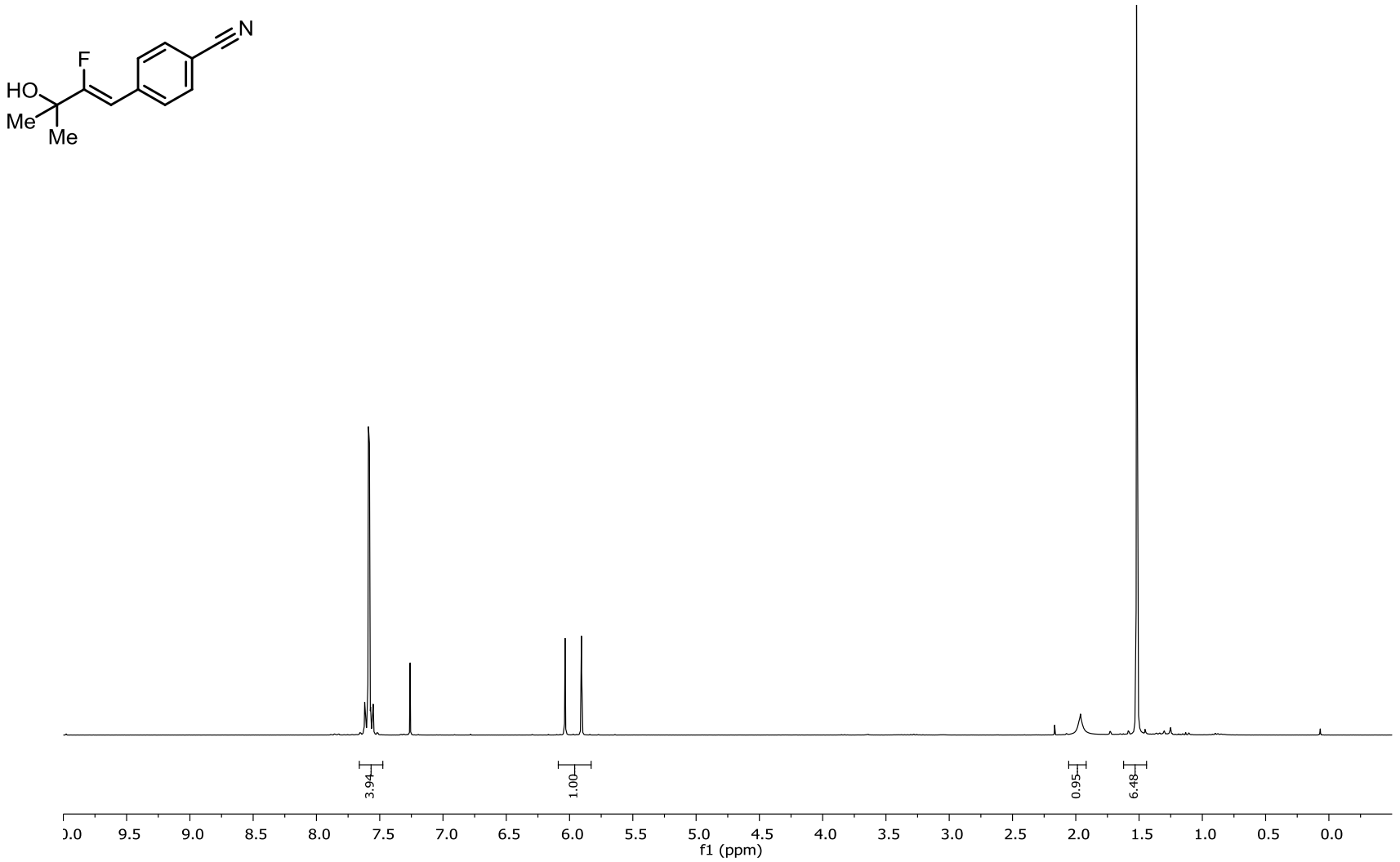

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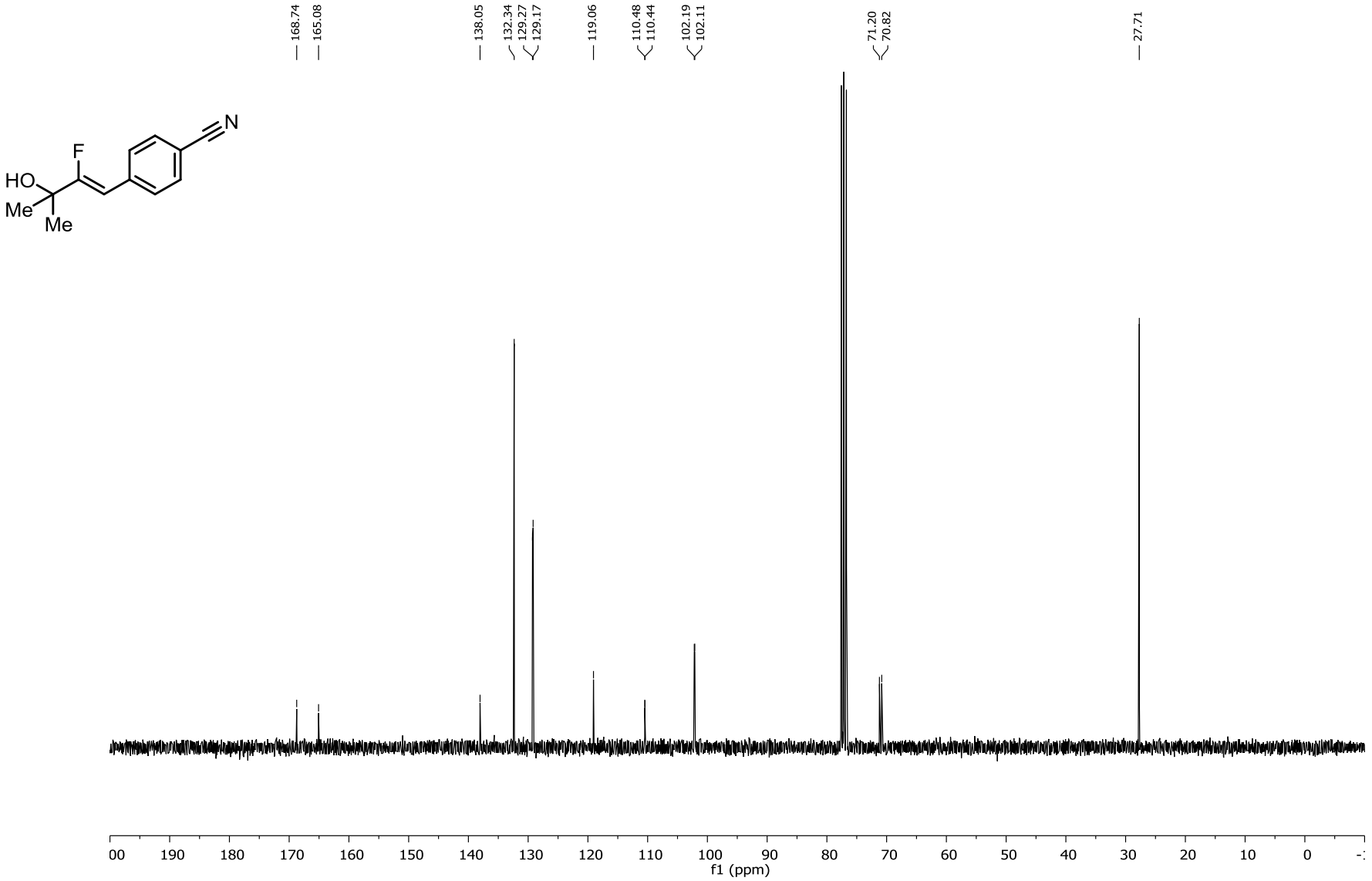
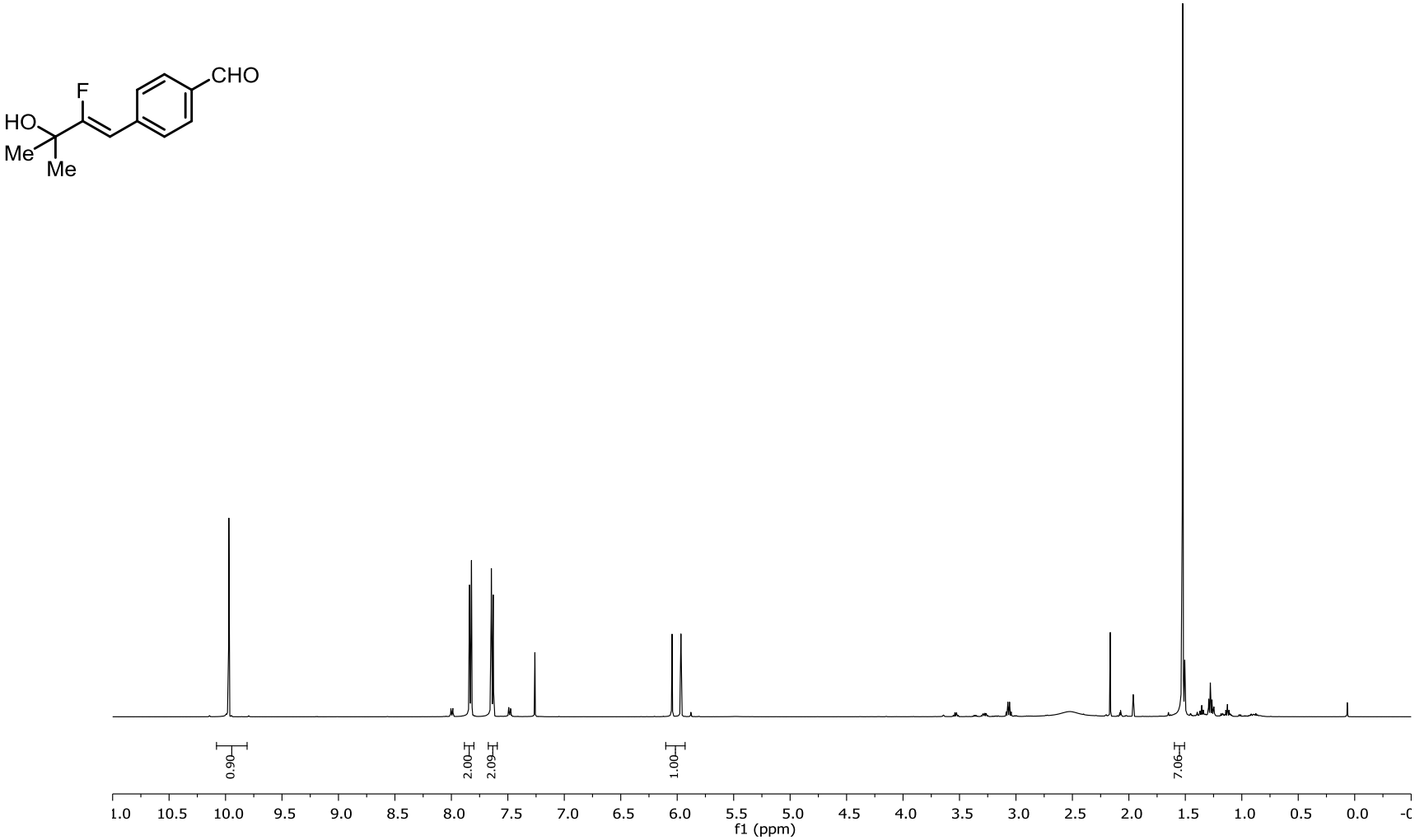


(Z)-4-(2-Fluoro-3-hydroxy-3-methylbut-1-en-1-yl)benzaldehyde



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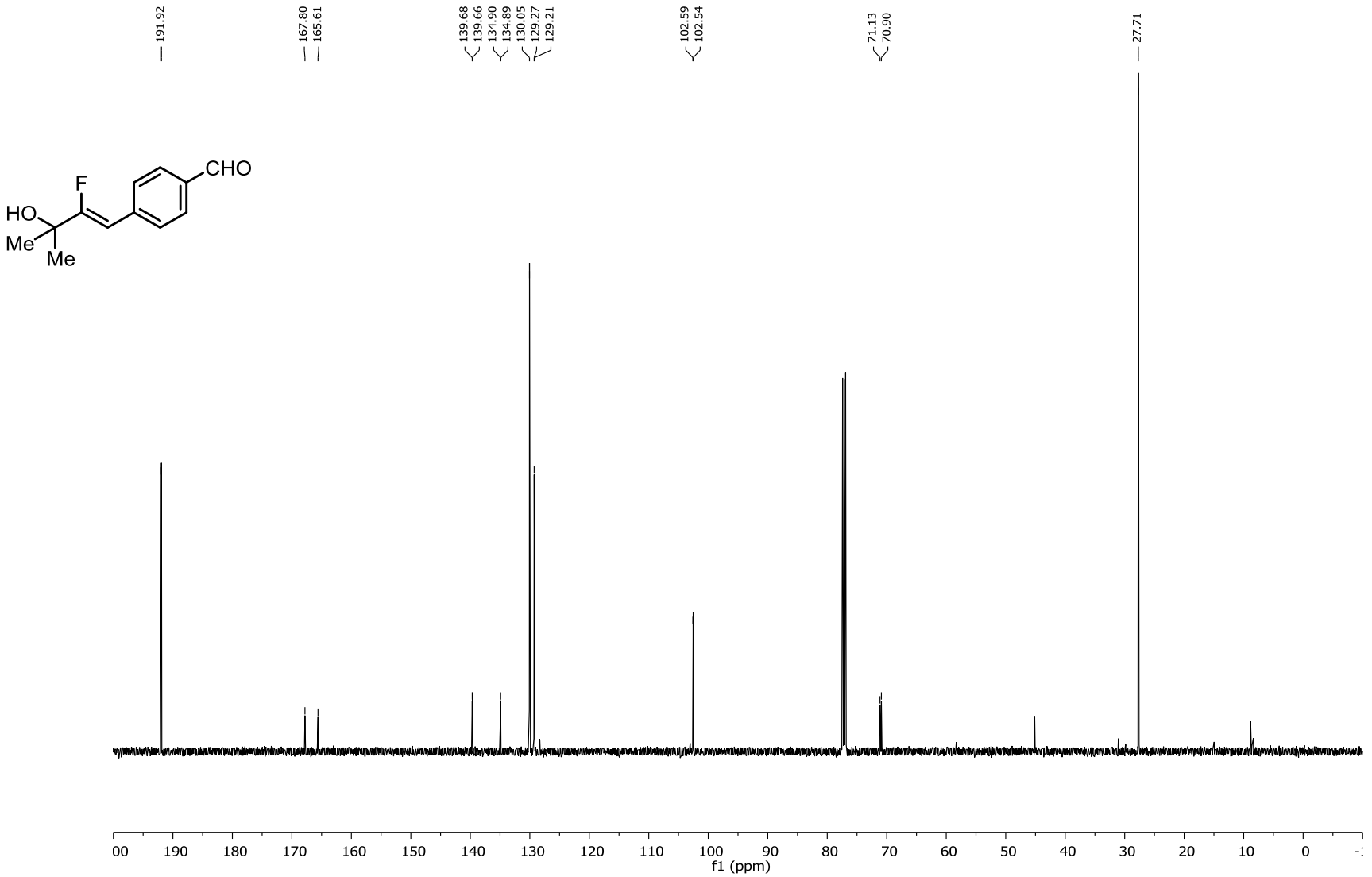
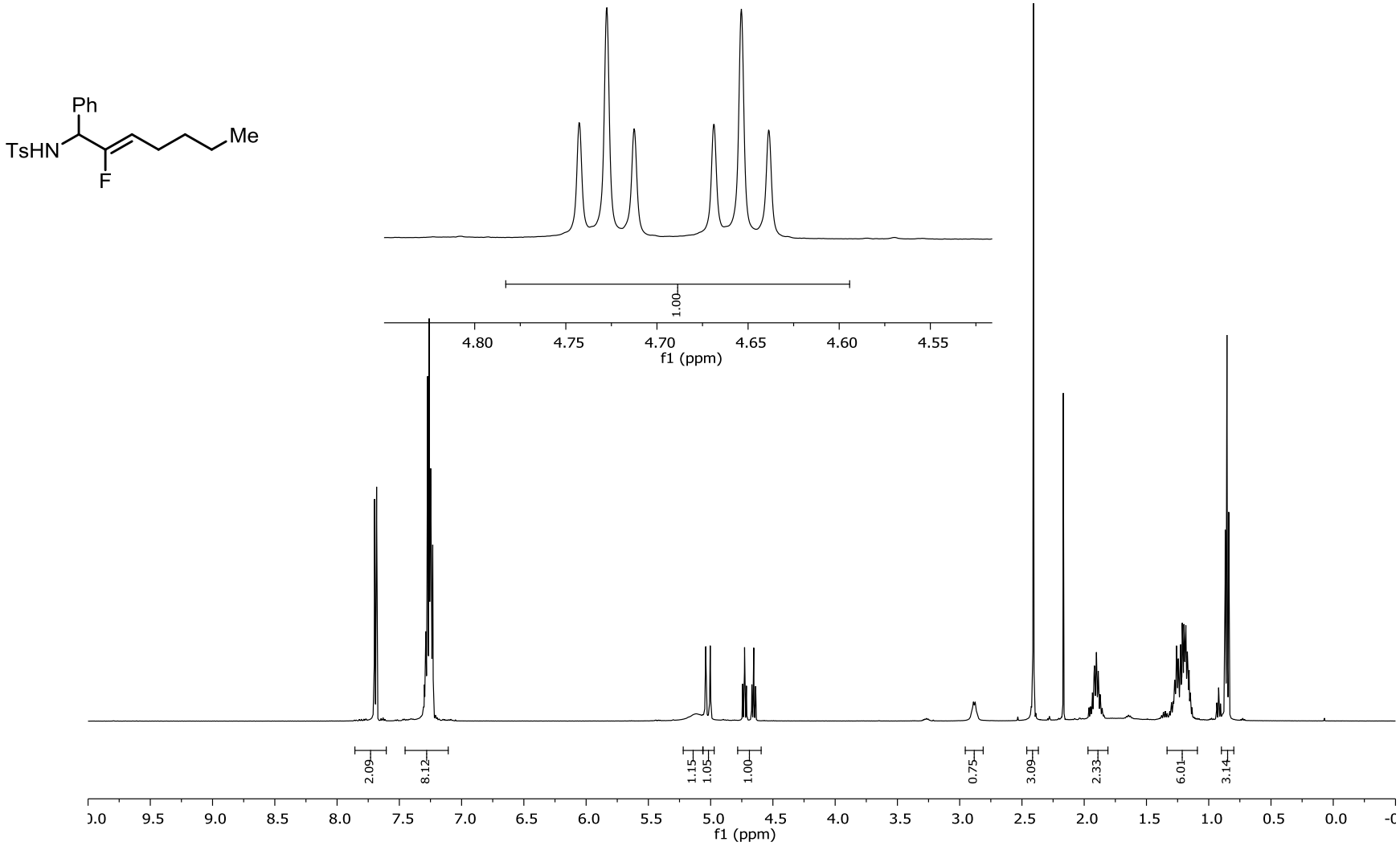


(SOI-SA-1600) – (Z)-N-(2-Fluoro-1-phenylhept-2-en-1-yl)-4-methylbenzenesulfonamide



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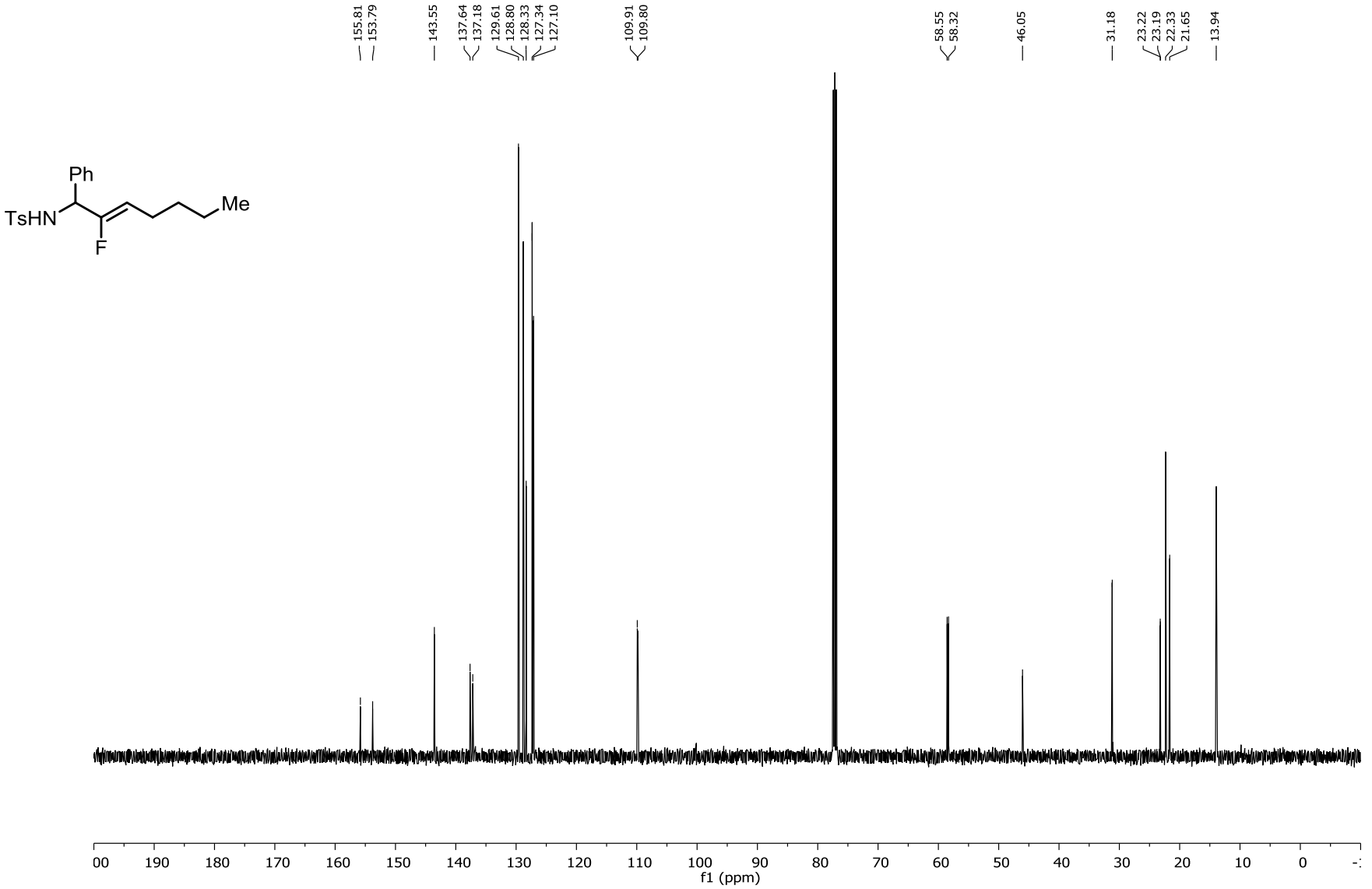

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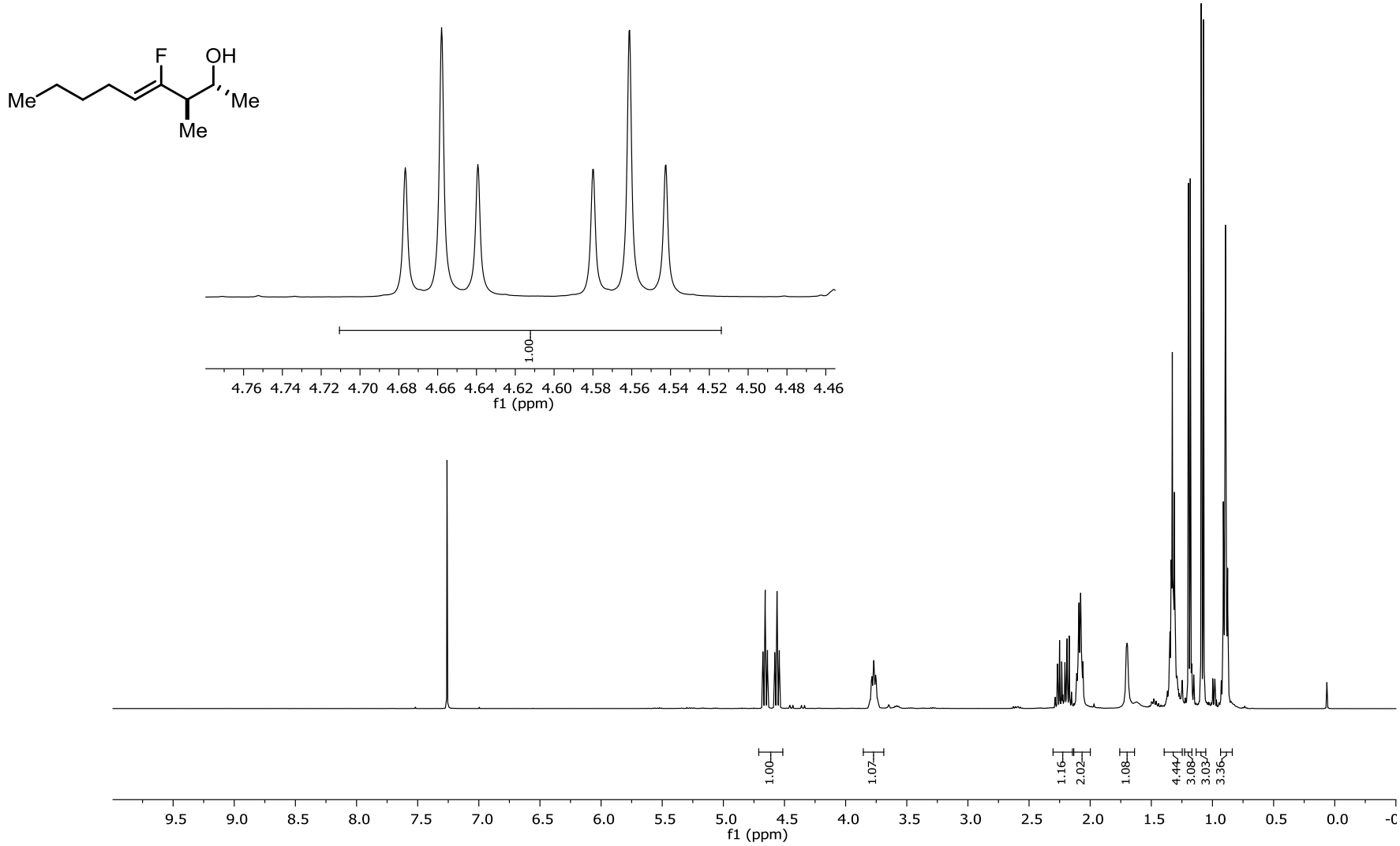

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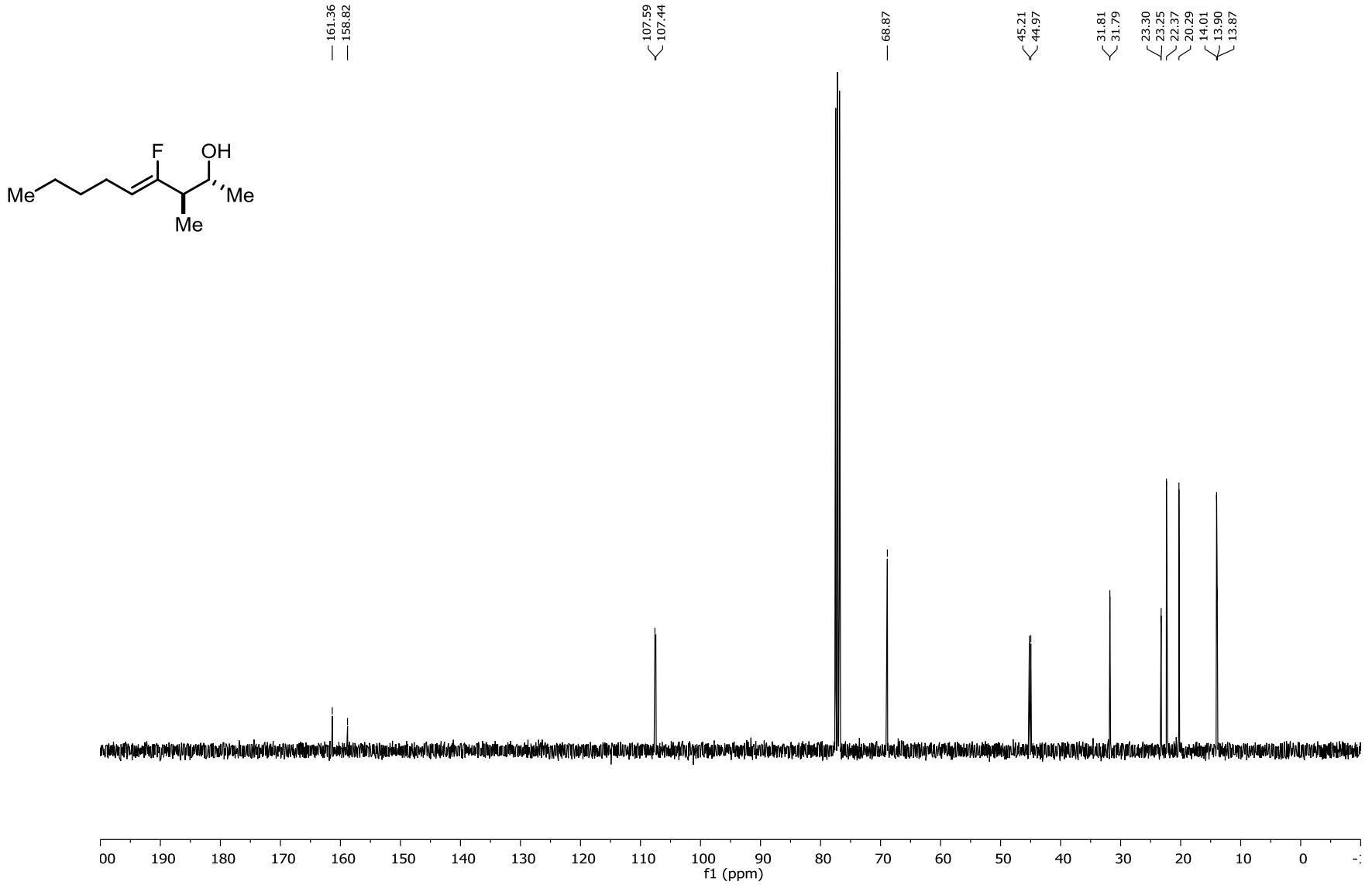
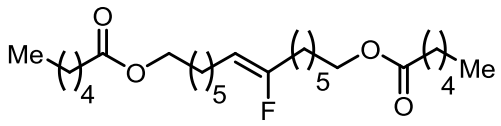
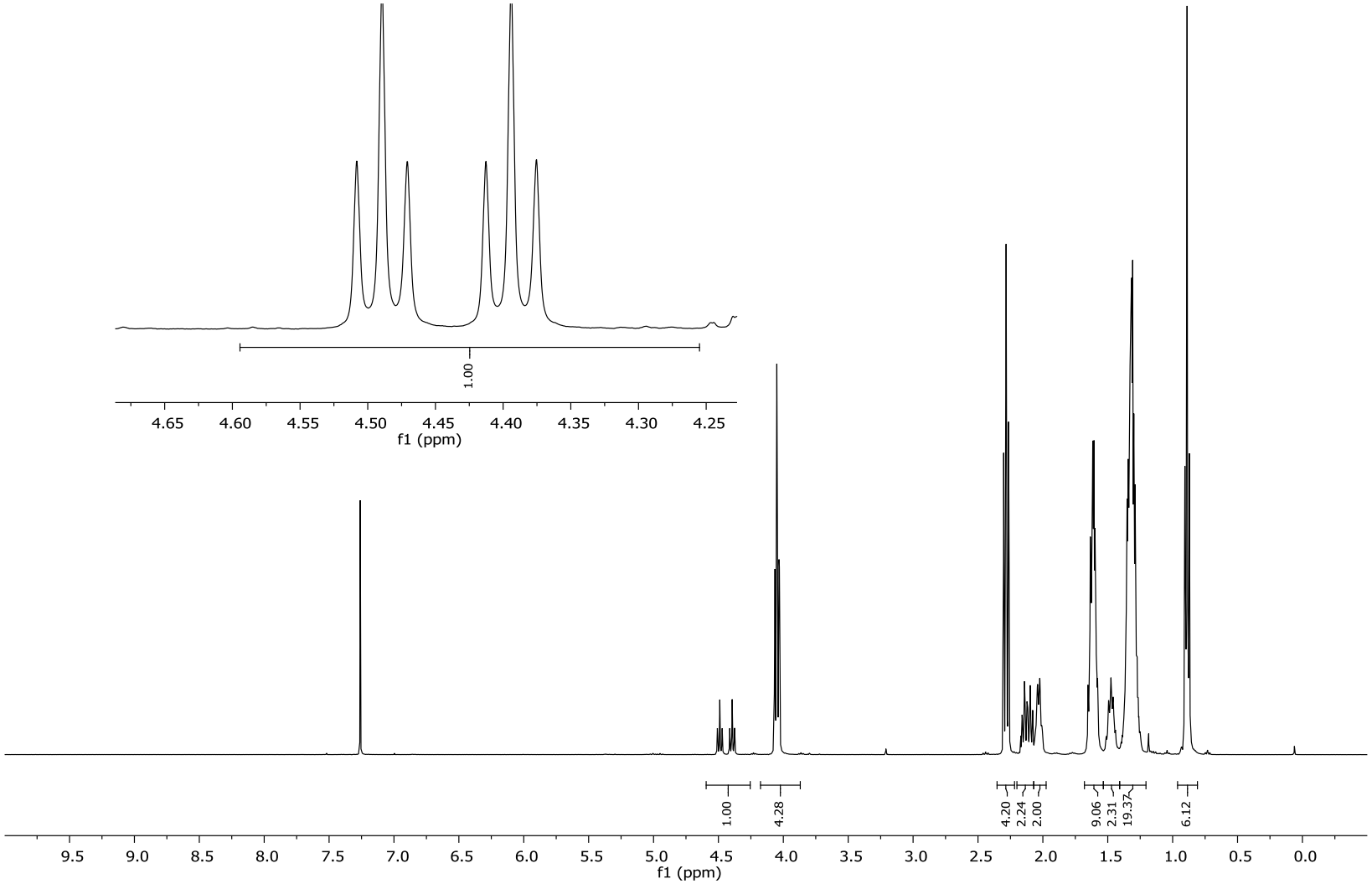


(Z)-7-Fluorotetradec-7-ene-1,14-diyl dihexanoate





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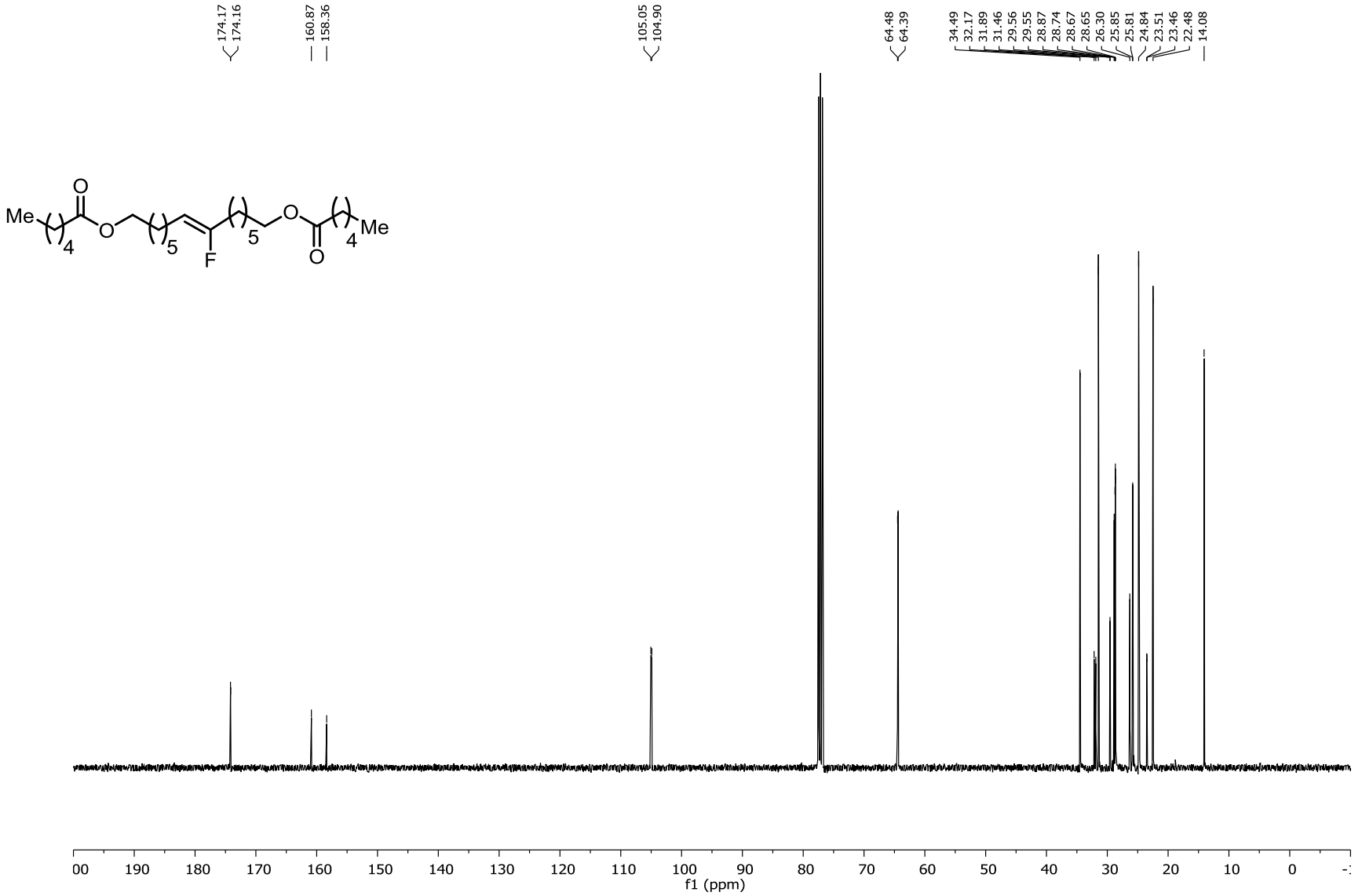
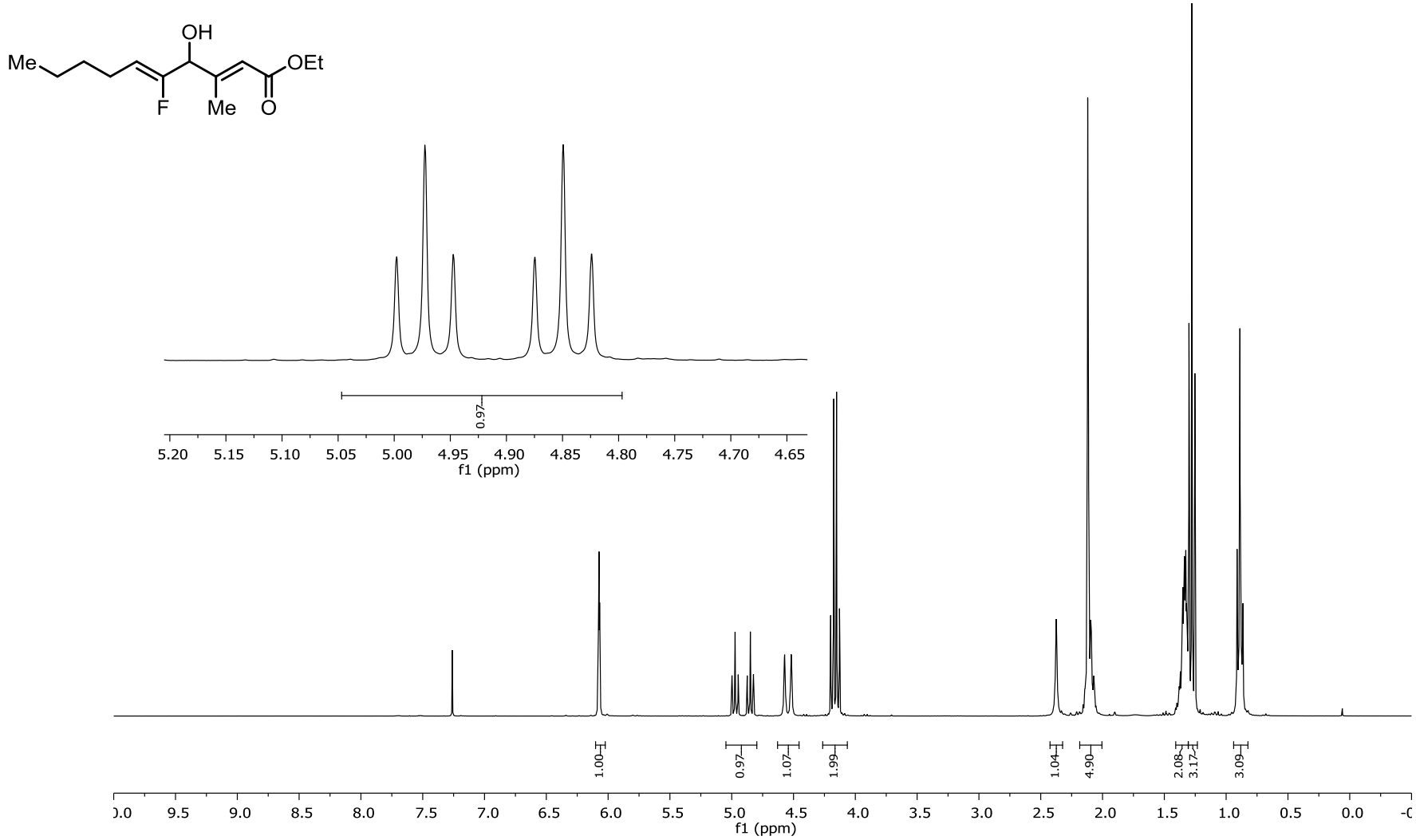


Ethyl (2E,5Z)-5-fluoro-4-hydroxy-3-methyldeca-2,5-dienoate



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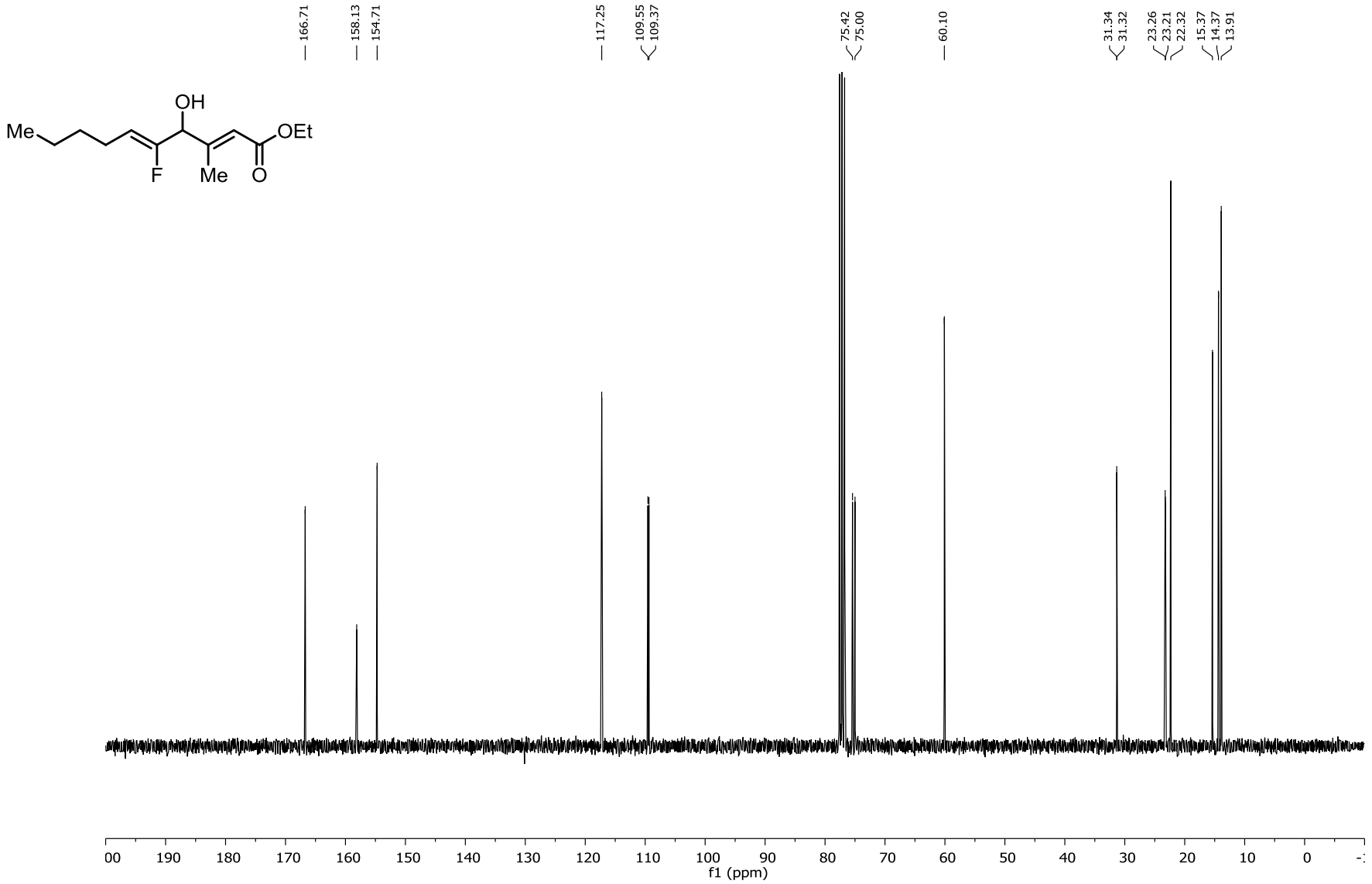
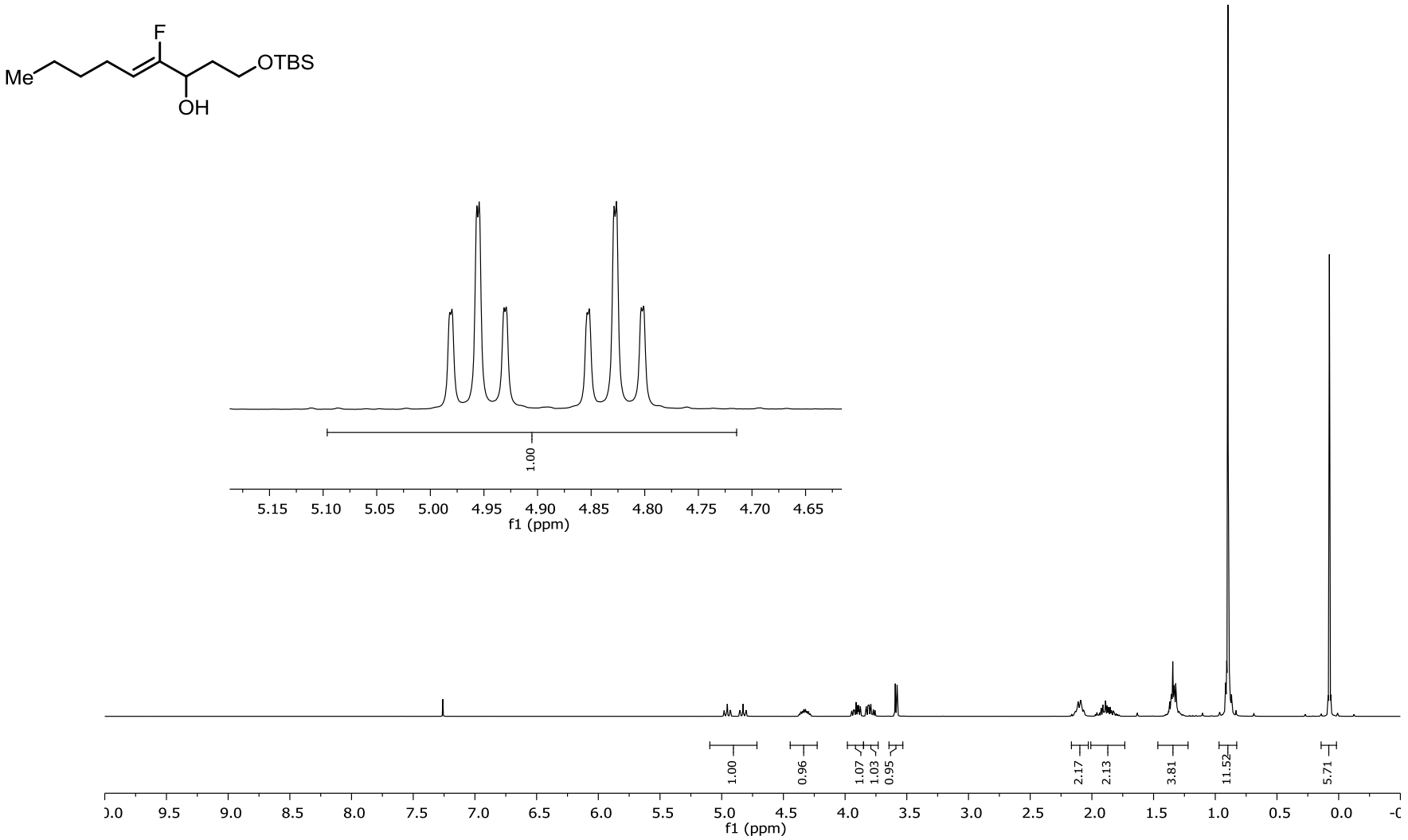


(Z)-1-((*tert*-Butyldimethylsilyl)oxy)-4-fluoronon-4-en-3-ol



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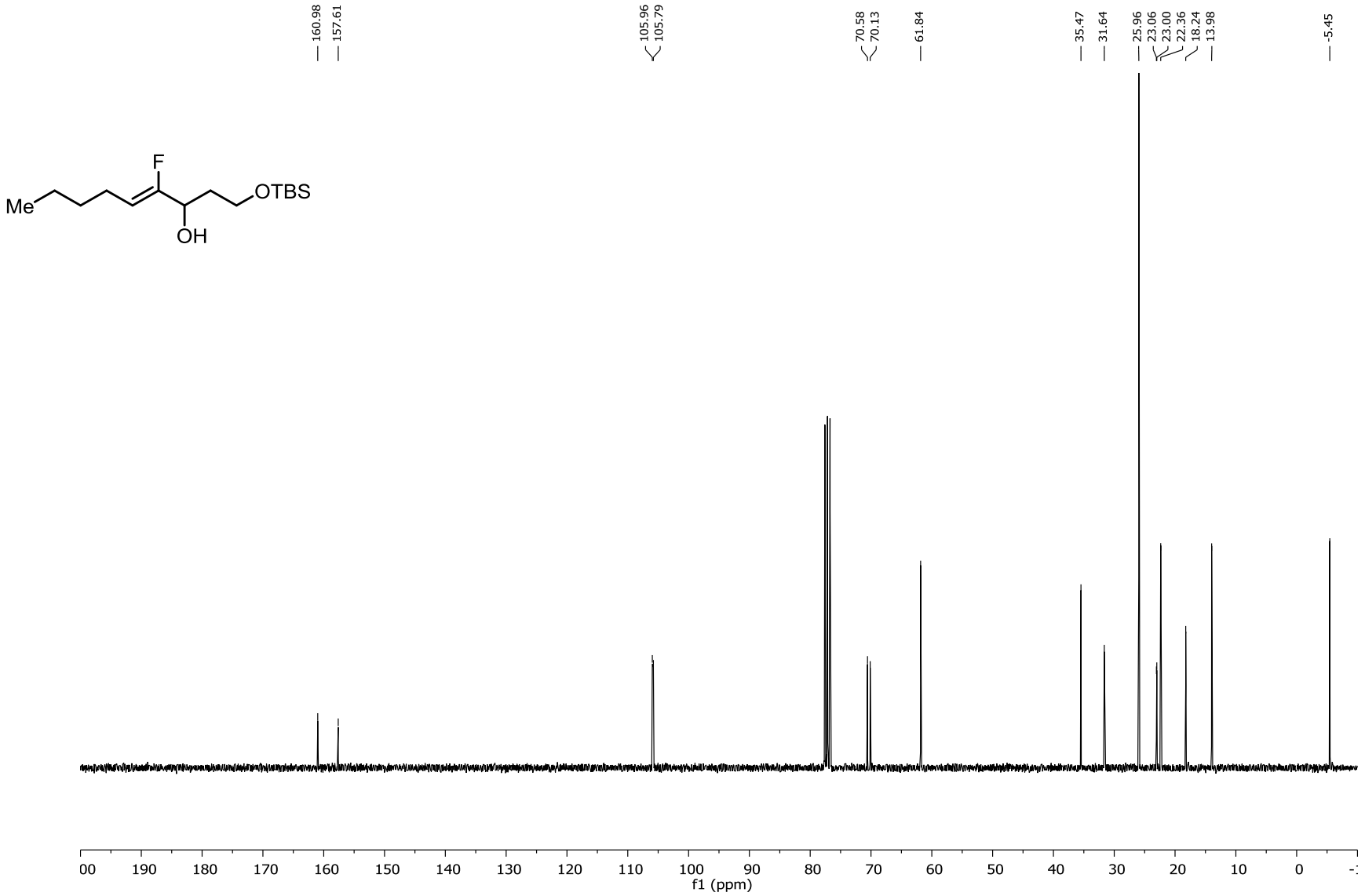
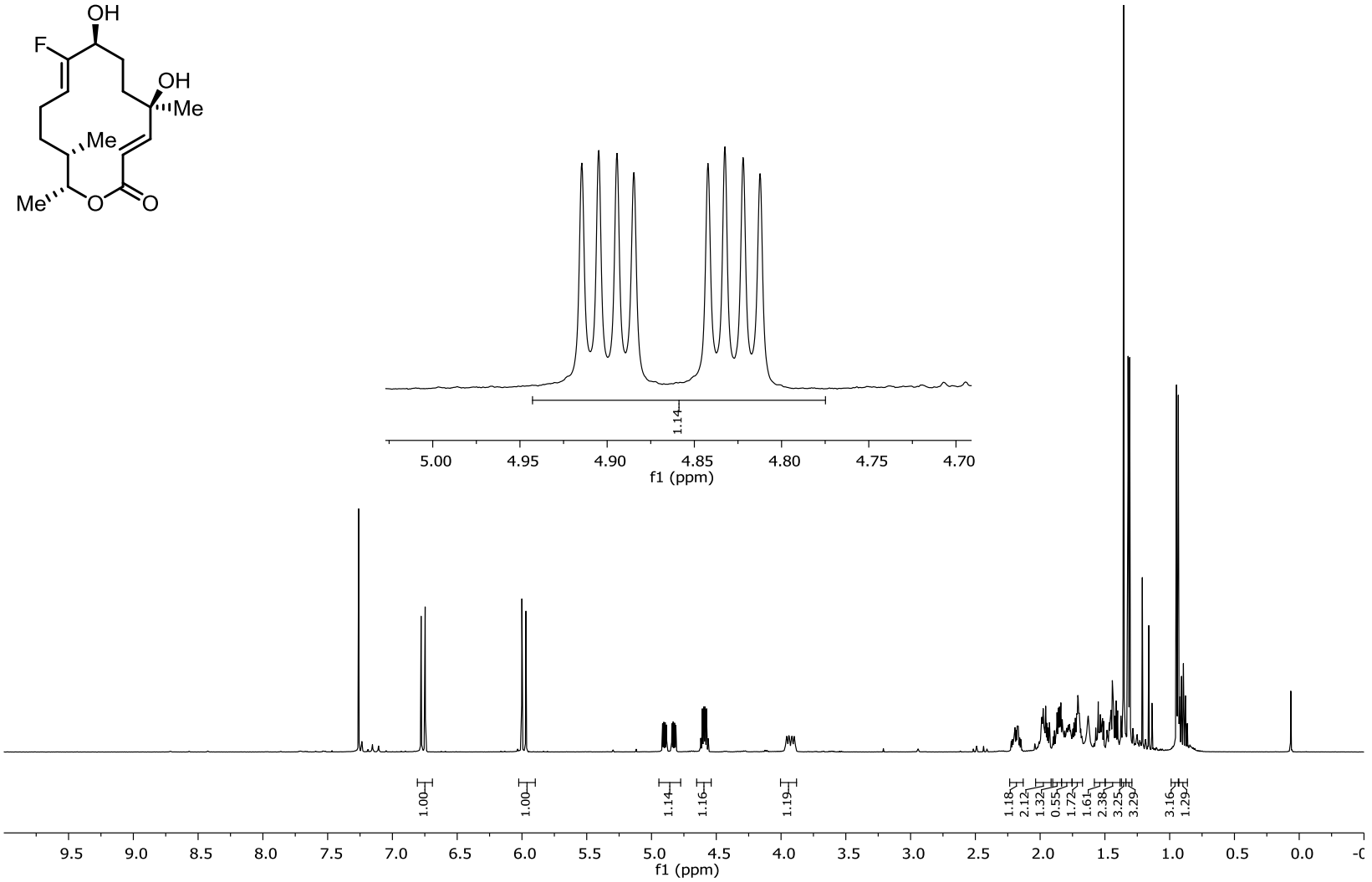
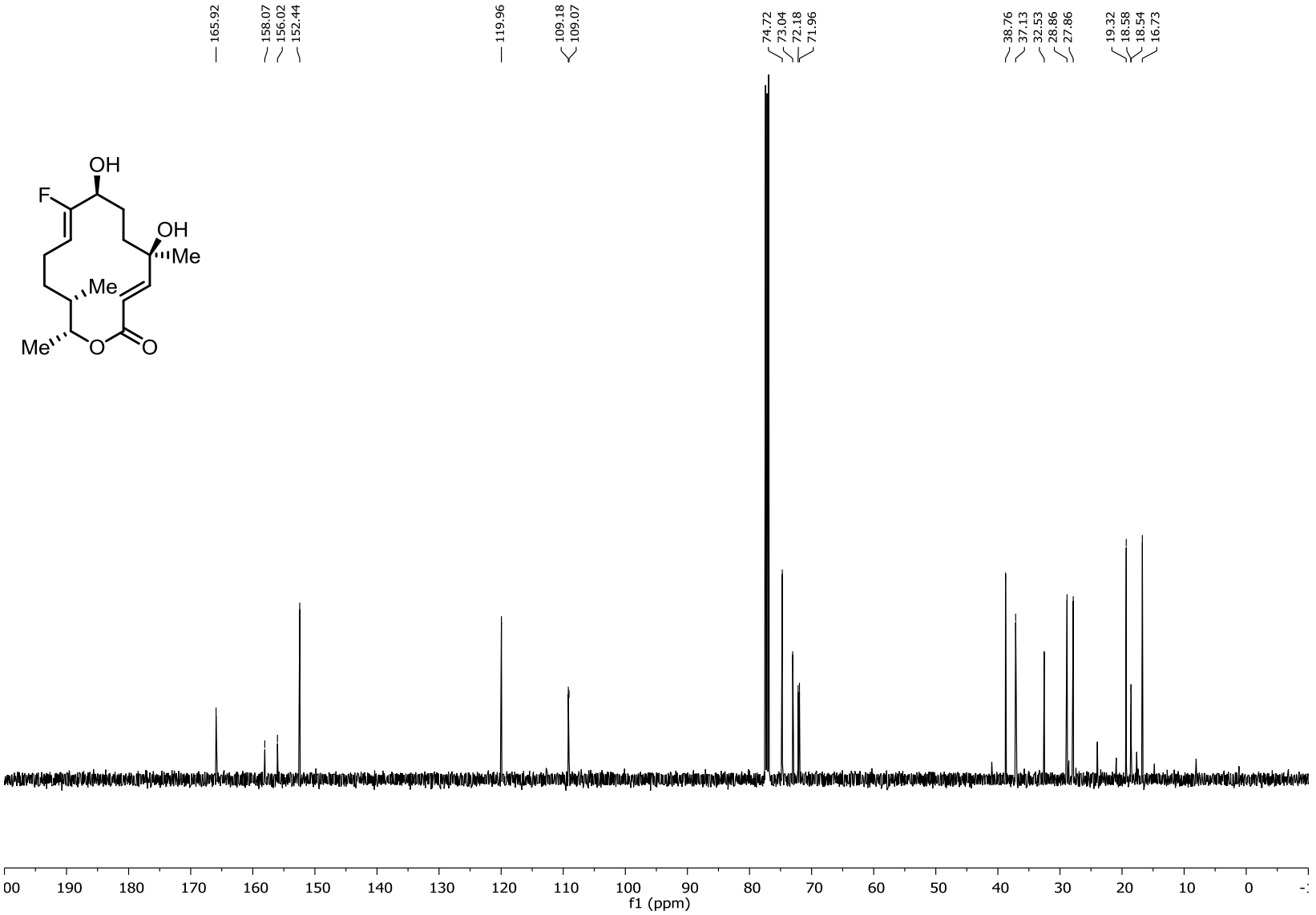


(3E,5R,8S,9Z,13S,14R)-9-Fluoro-5,8-dihydroxy-5,13,14-trimethyloxacyclotetradeca-3,9-dien-2-one



(3E,5R,8S,9Z,13S,14R)-9-Fluoro-5,8-dihydroxy-5,13,14-trimethyloxacyclotetradeca-3,9-dien-2-one



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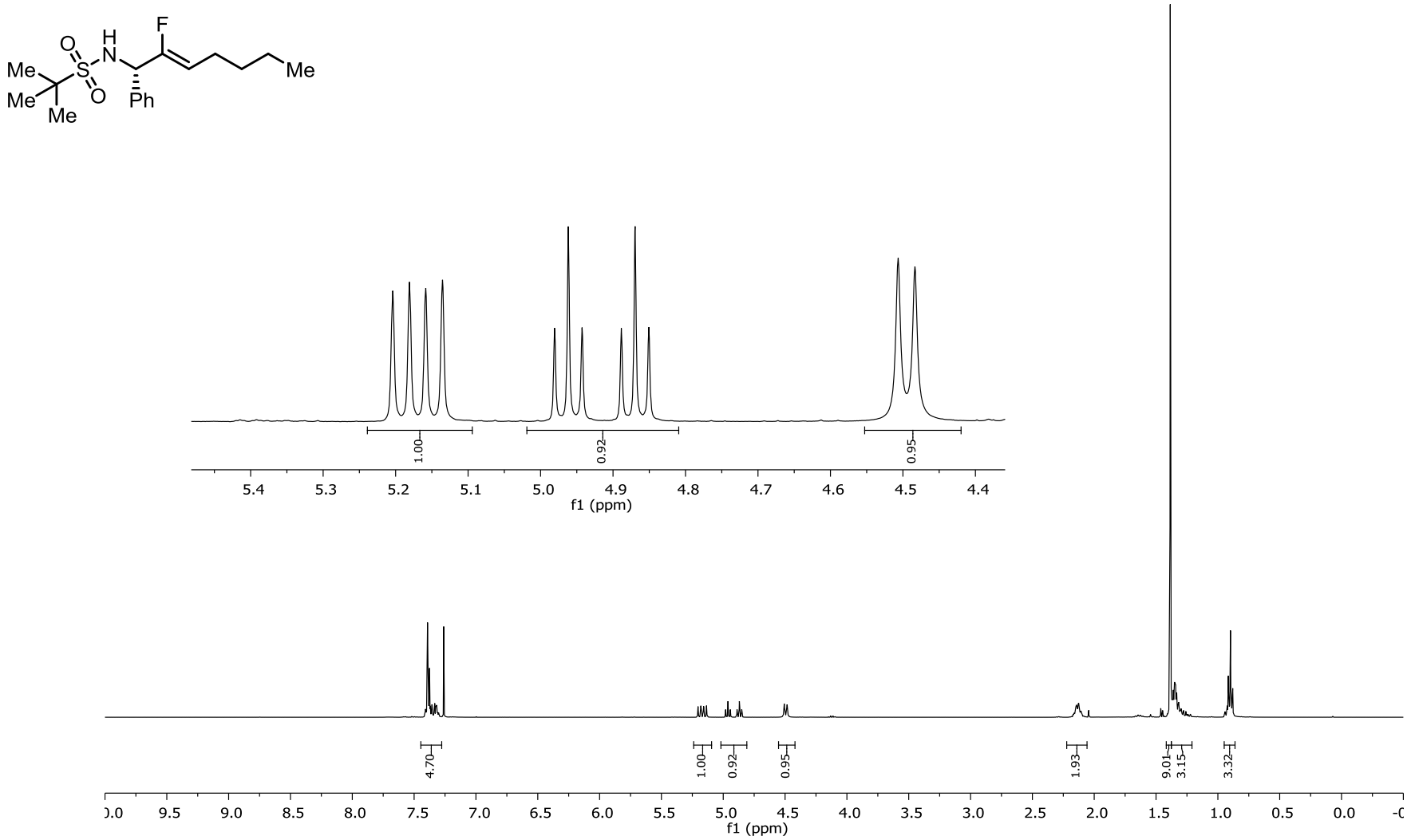

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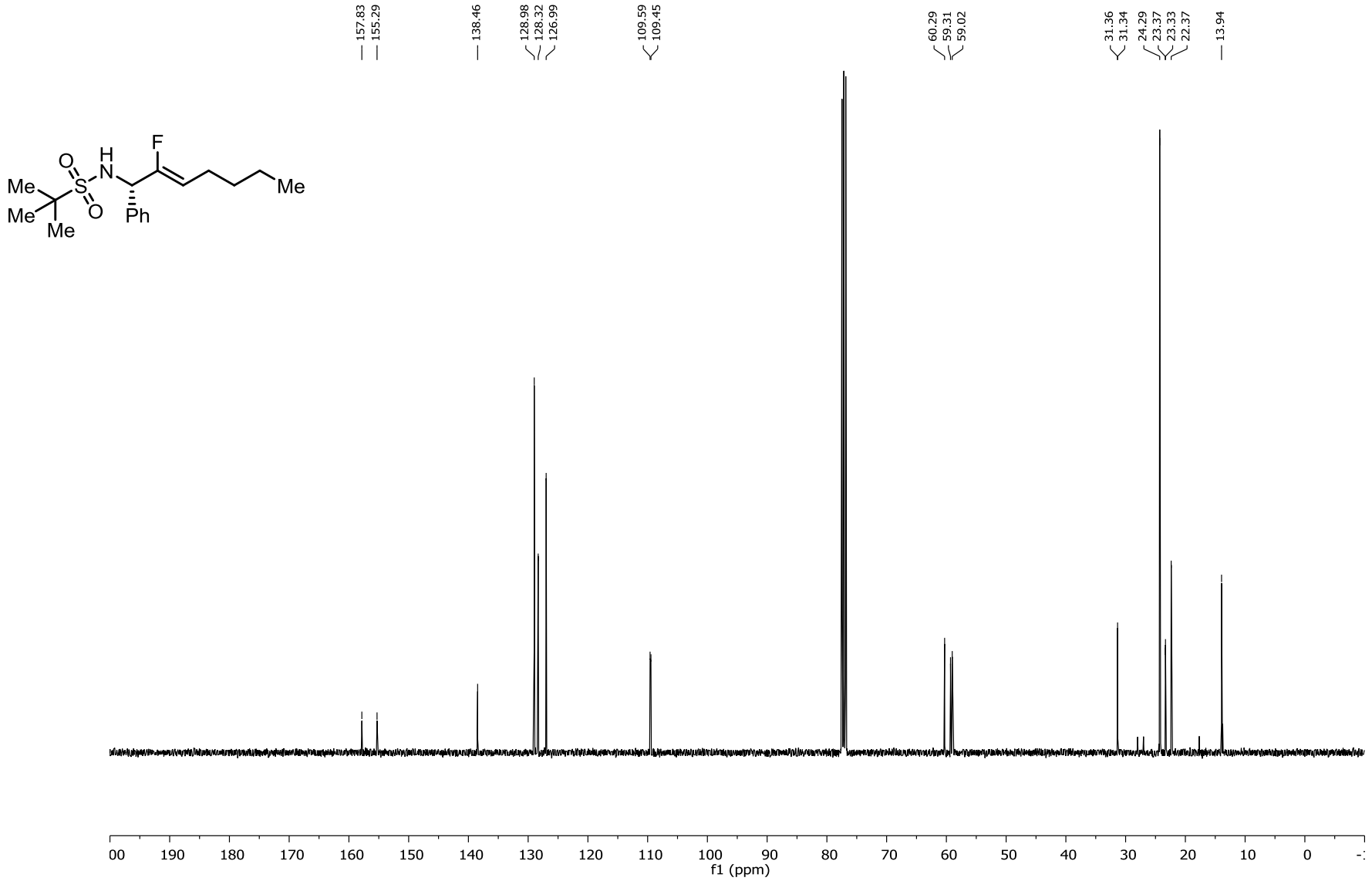

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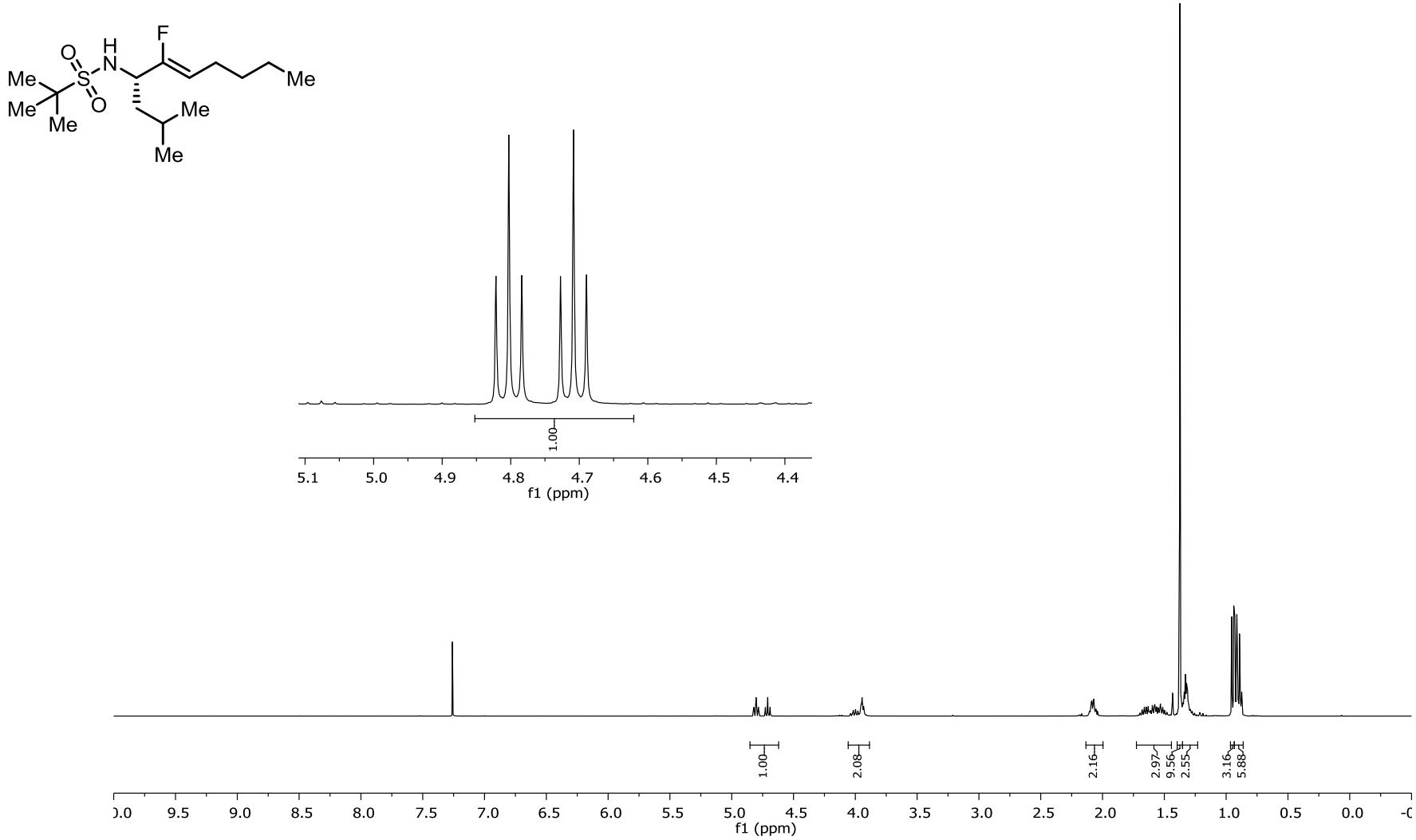

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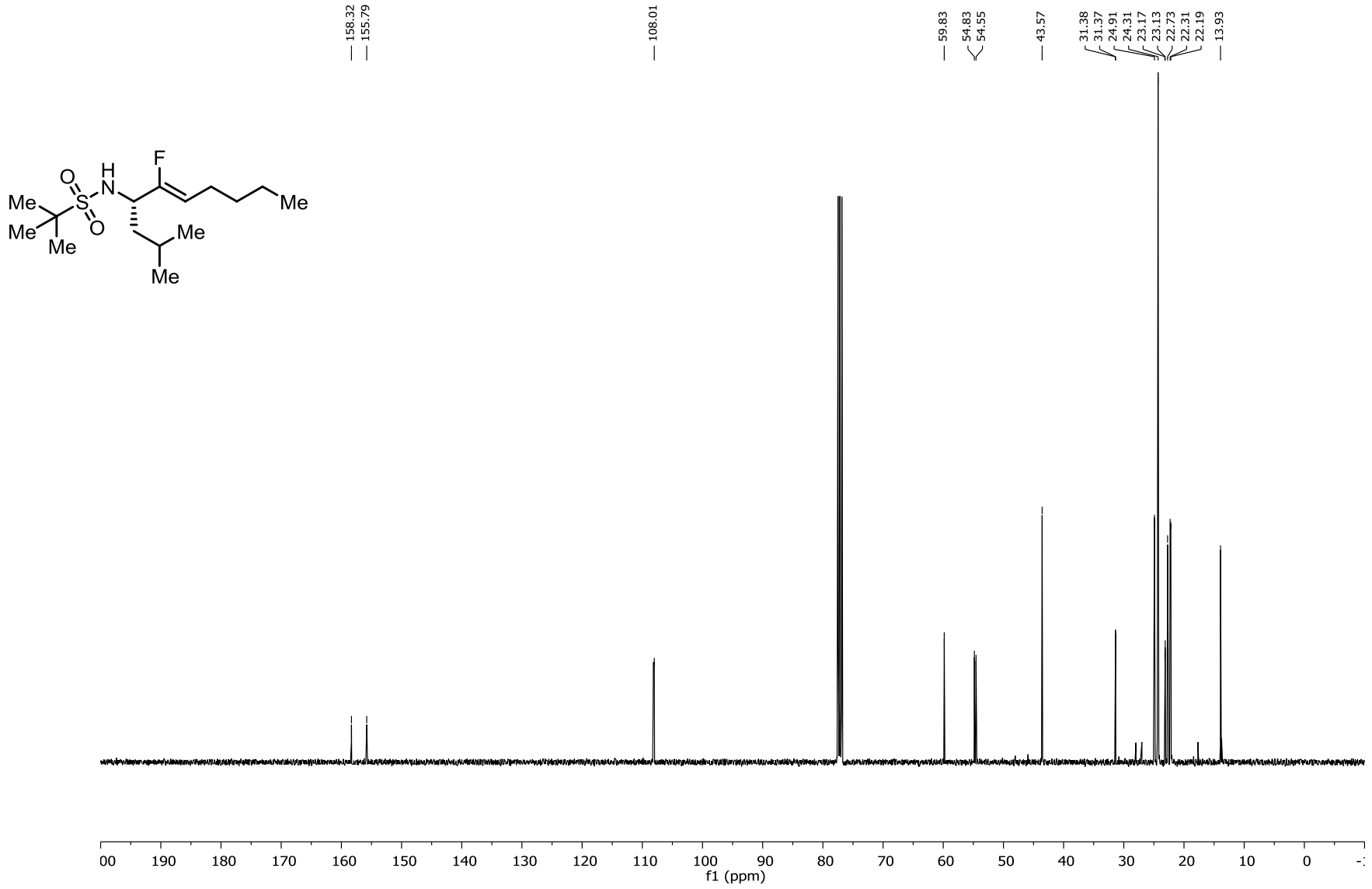
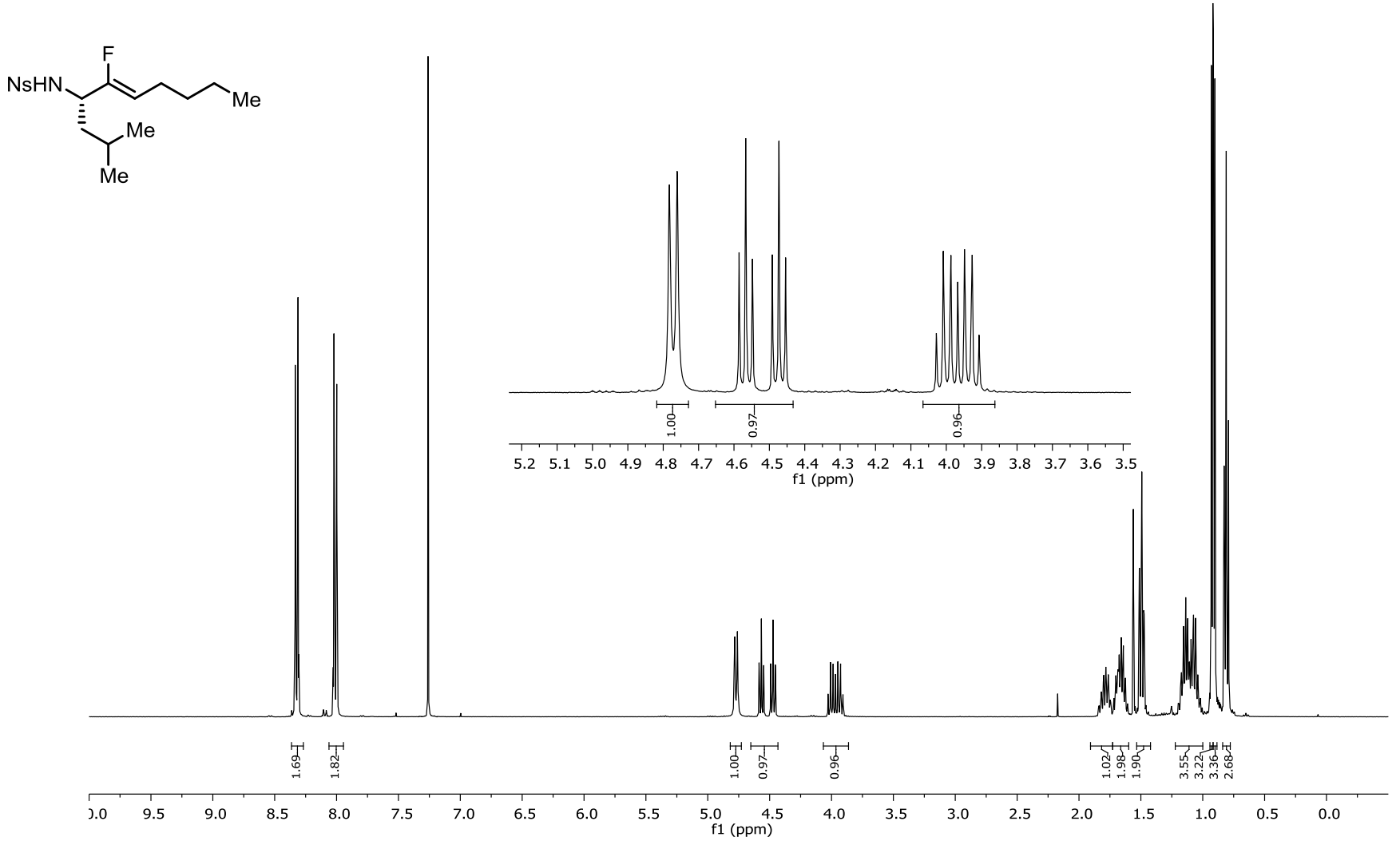
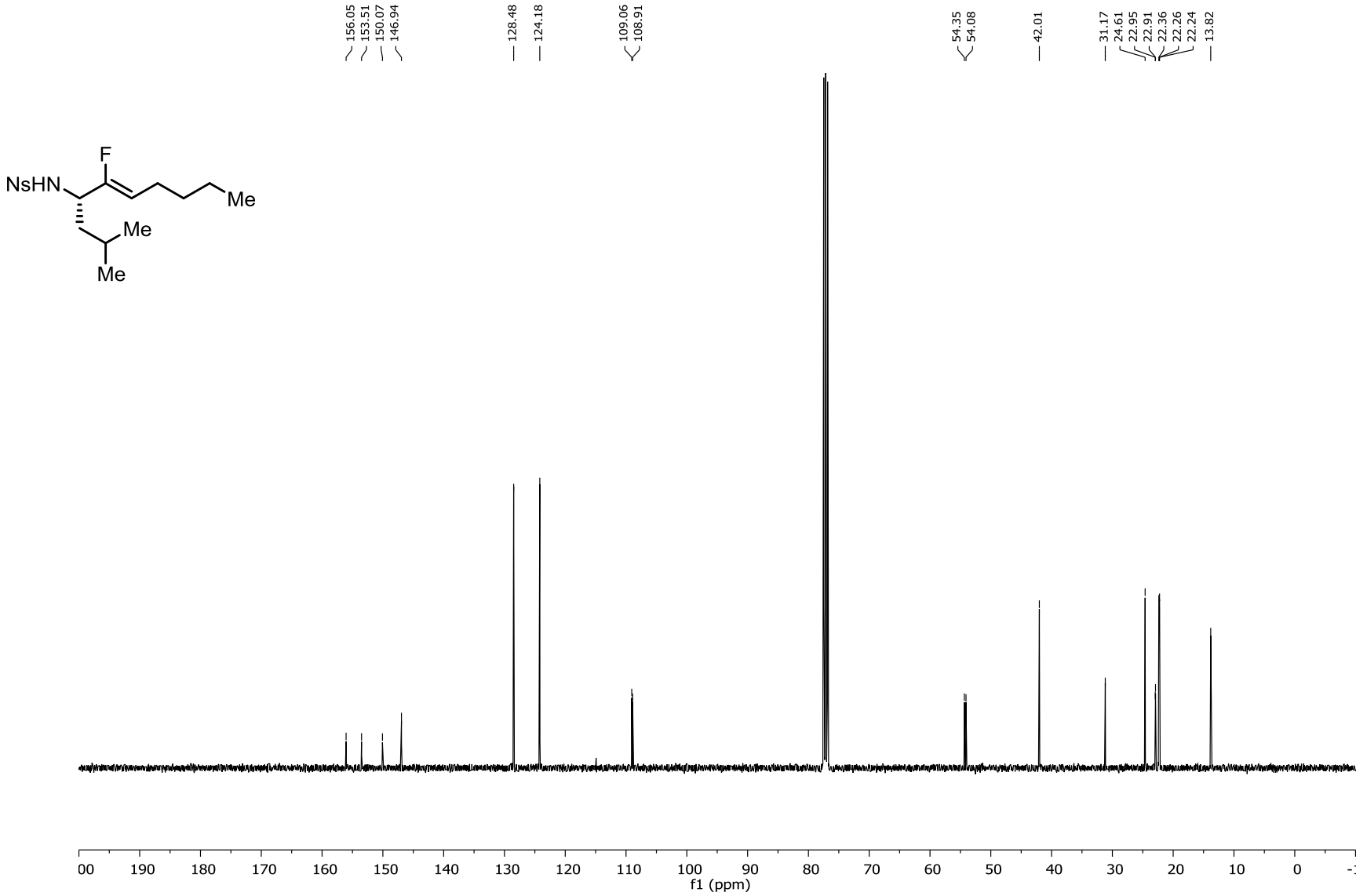


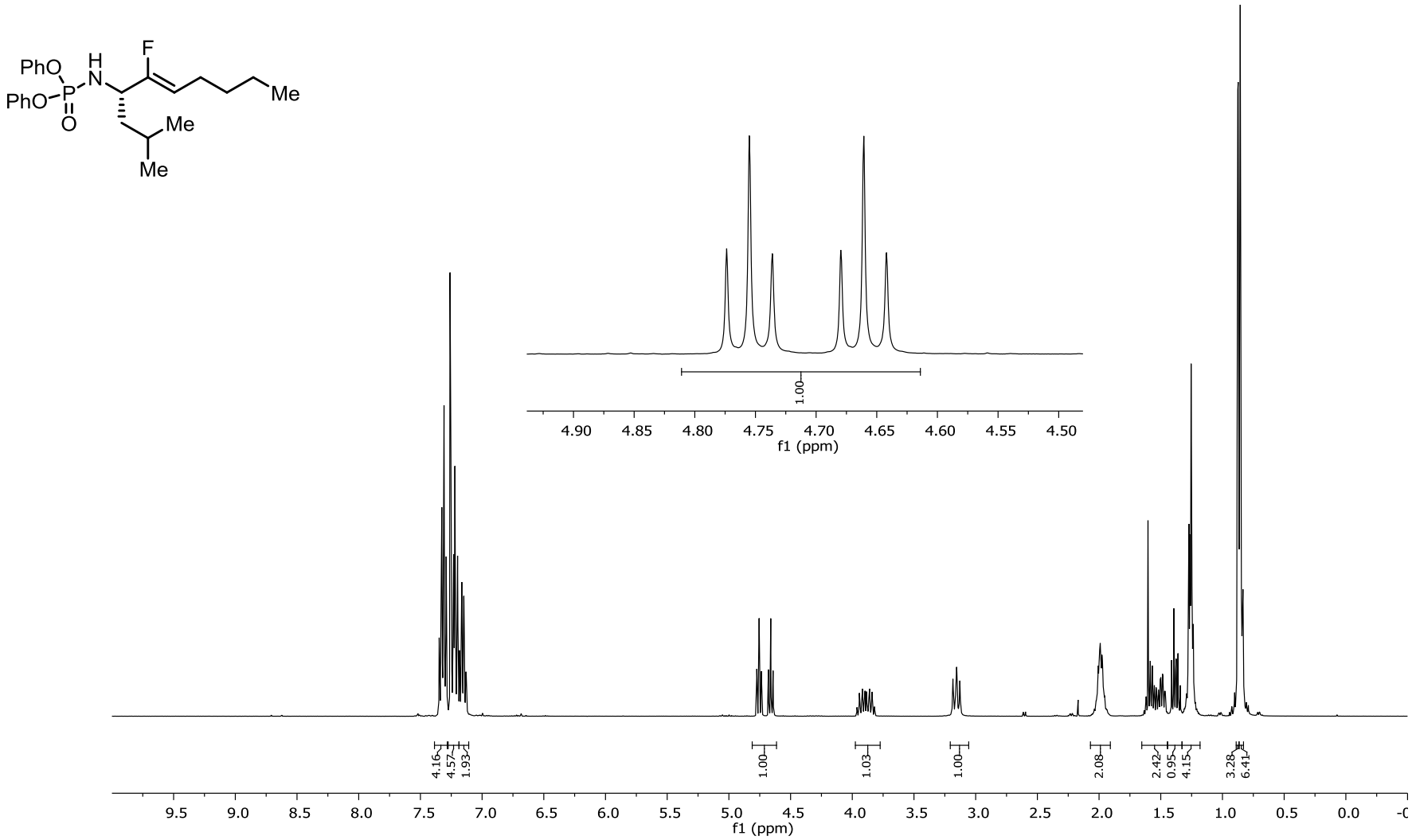
(S,Z)-N-(5-fluoro-2-methyldec-5-en-4-yl)-4-nitrobenzenesulfonamide



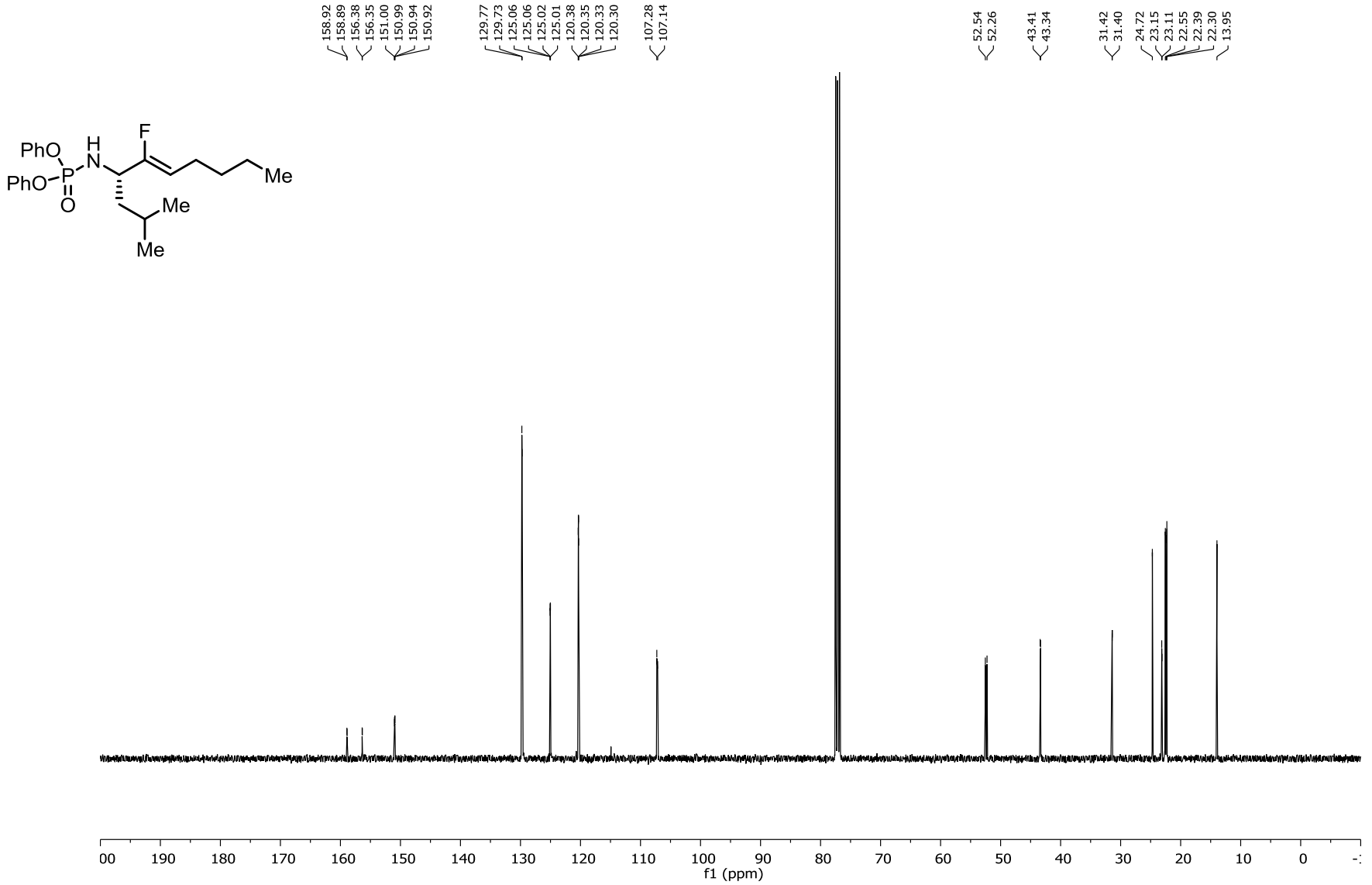
(S,Z)-N-(5-fluoro-2-methyldec-5-en-4-yl)-4-nitrobenzenesulfonamide



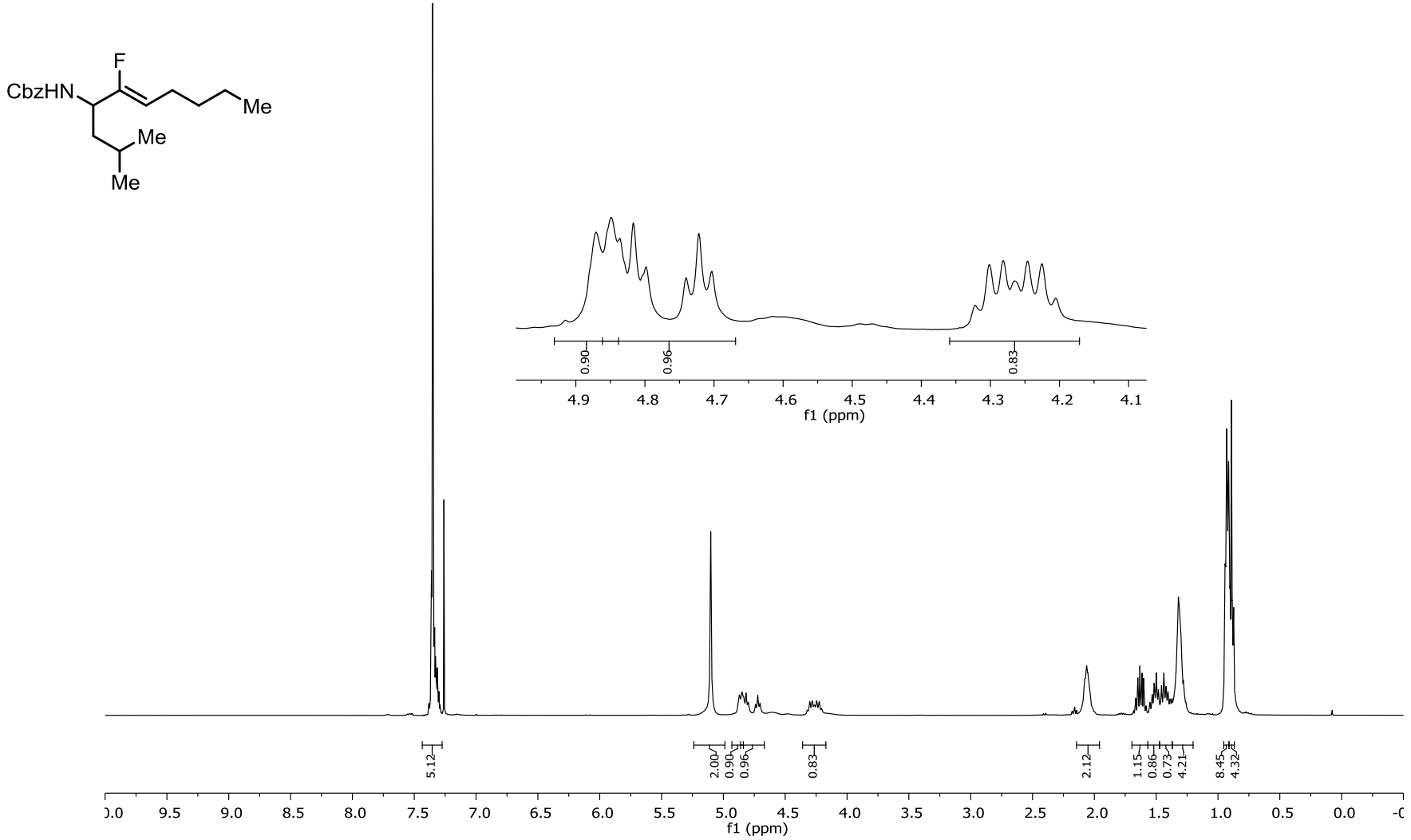
Diphenyl (*S*,*Z*)-(5-fluoro-2-methyldec-5-en-4-yl)phosphoramidate



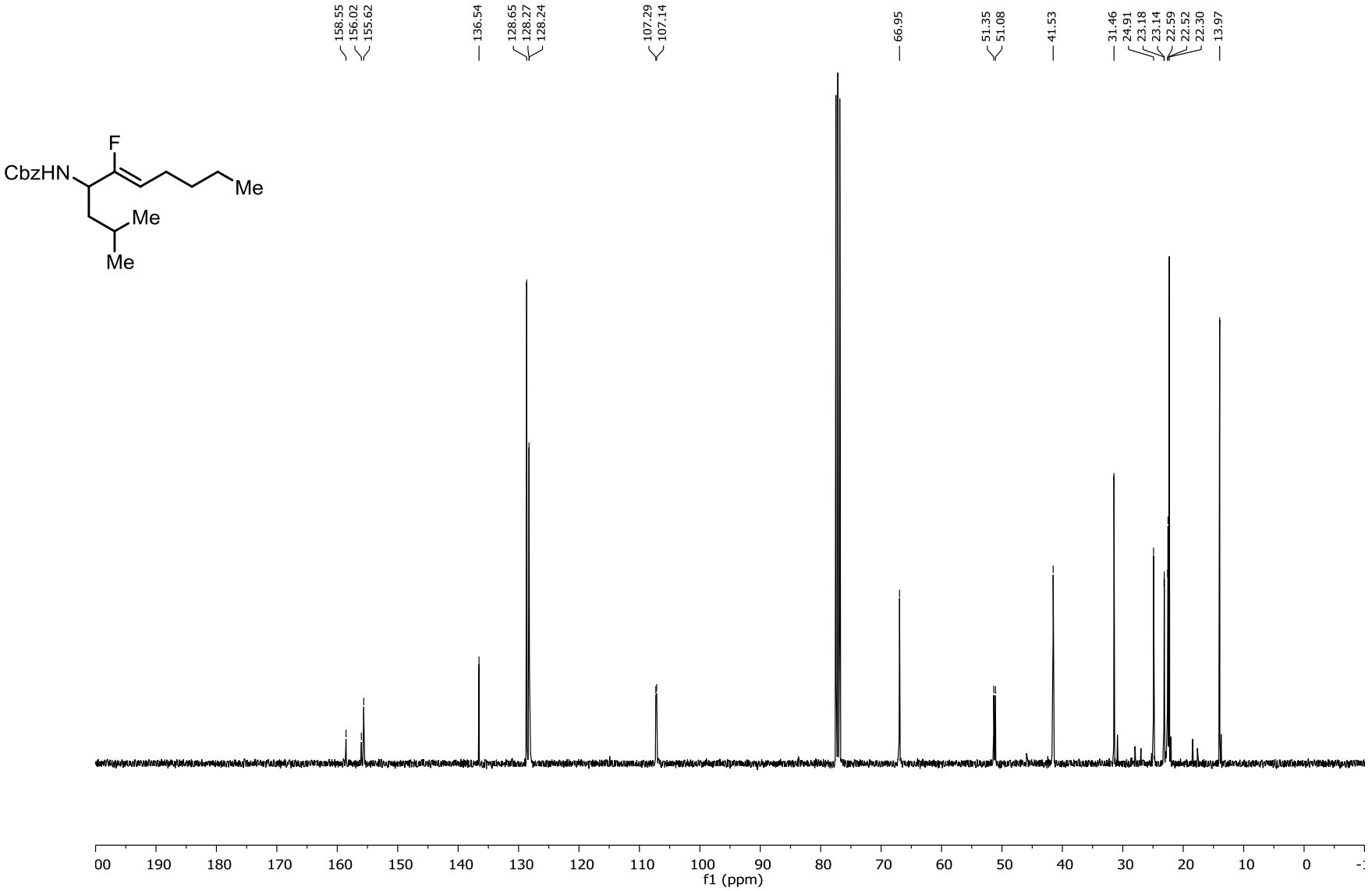
Diphenyl (*S*,*Z*)-(5-fluoro-2-methyldec-5-en-4-yl)phosphoramidate



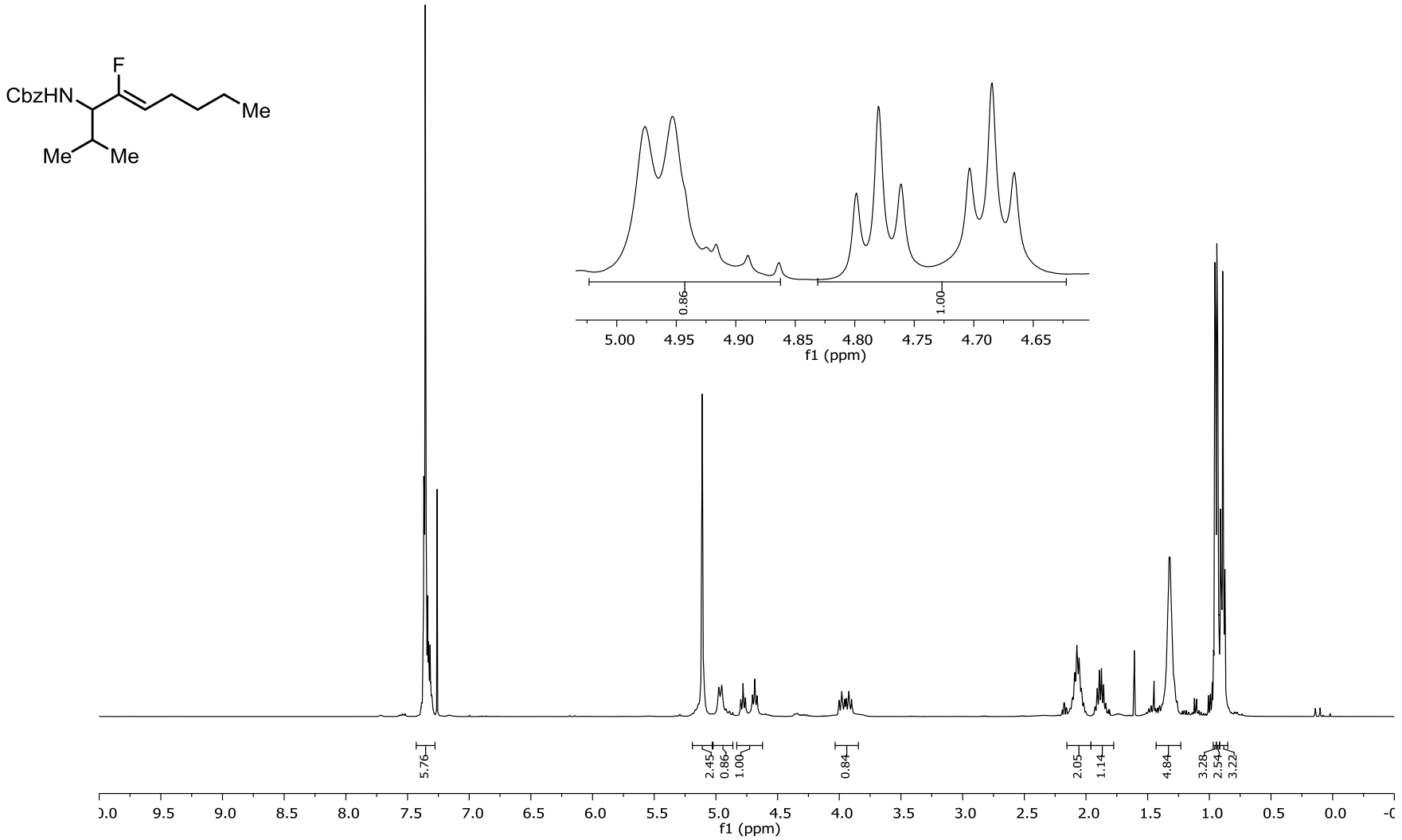
Benzyl (Z)-(5-fluoro-2-methyldec-5-en-4-yl)carbamate



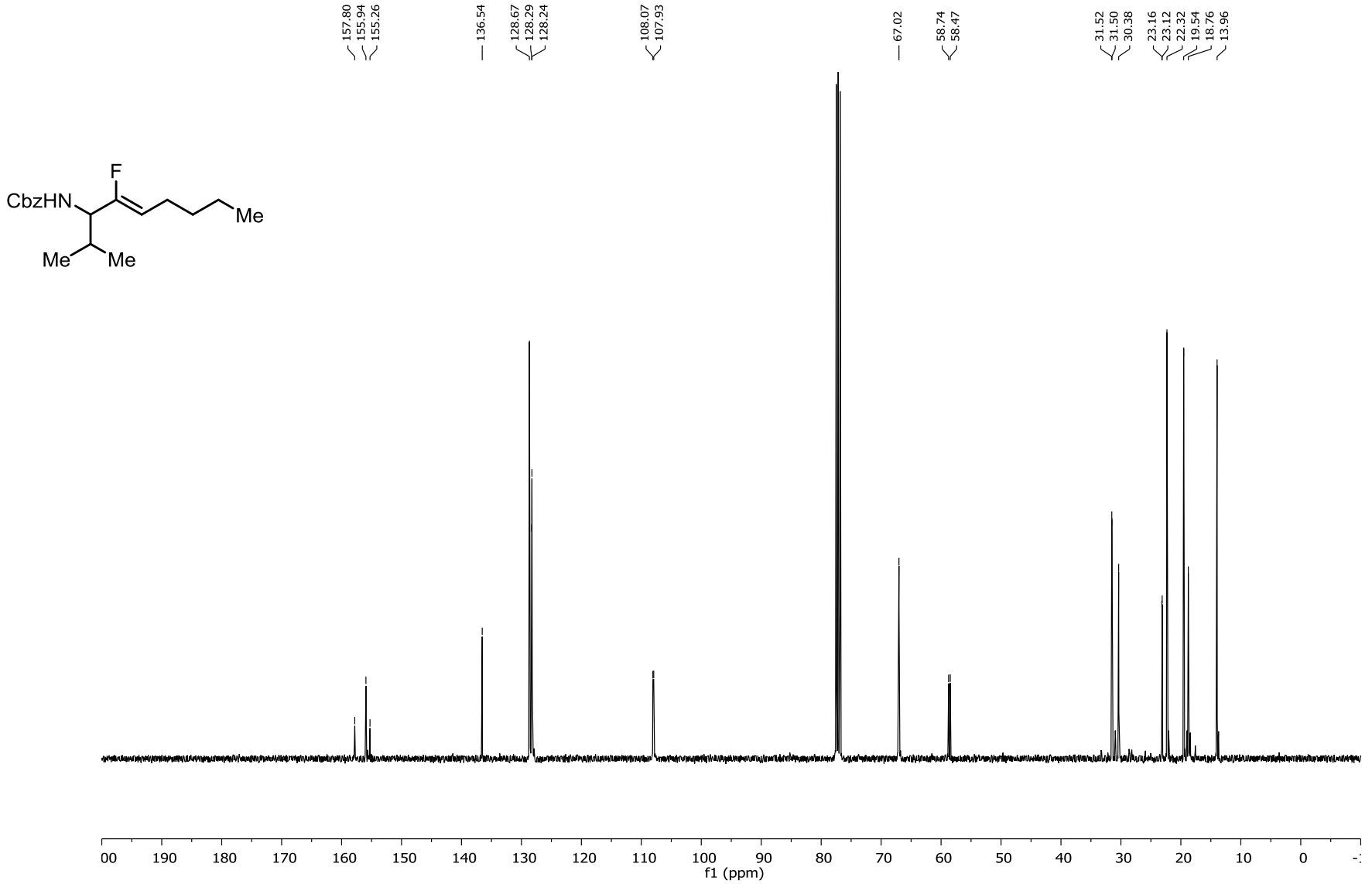
Benzyl (Z)-(5-fluoro-2-methyldec-5-en-4-yl)carbamate



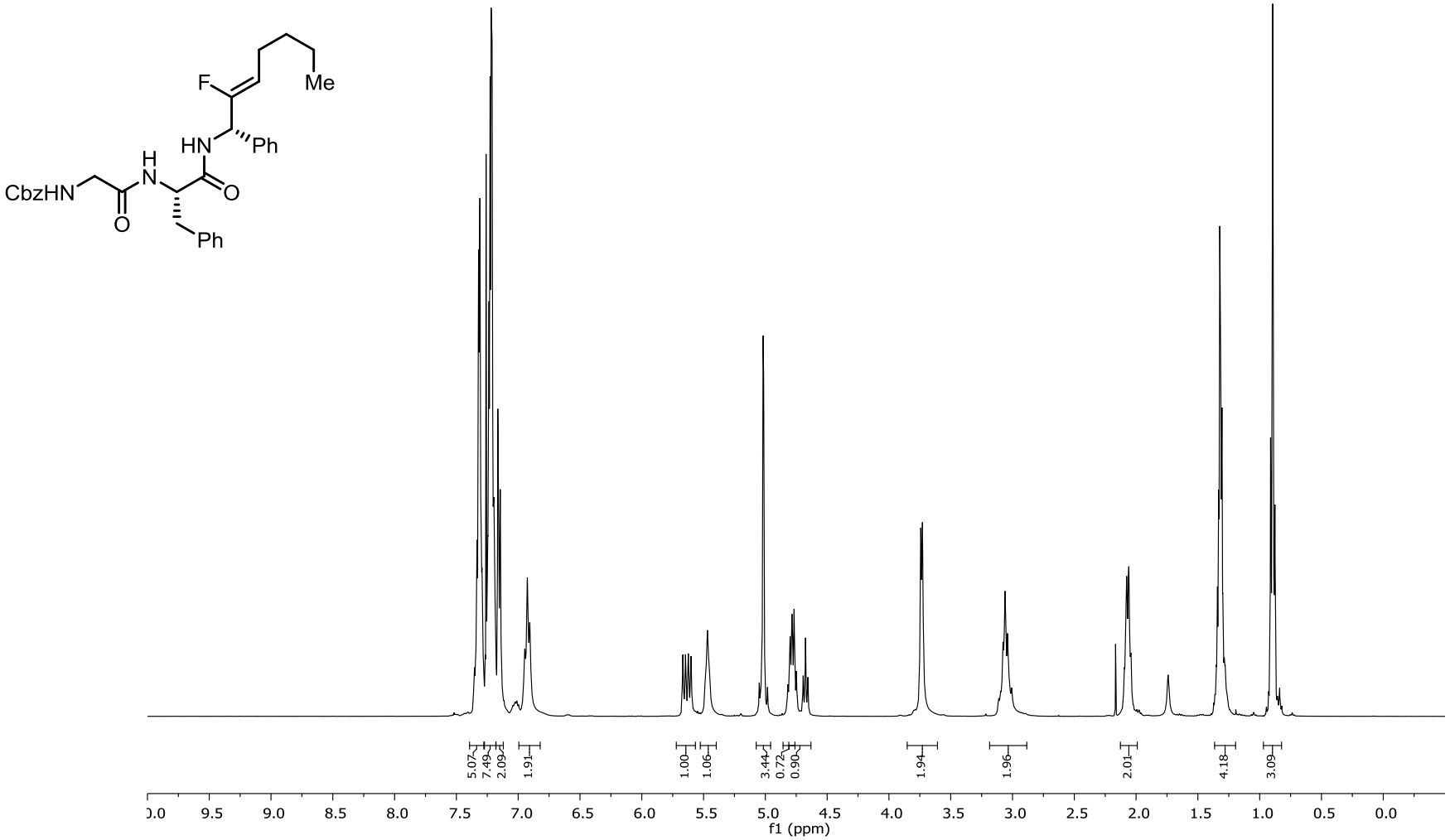
Benzyl (Z)-(4-fluoro-2-methylnon-4-en-3-yl)carbamate



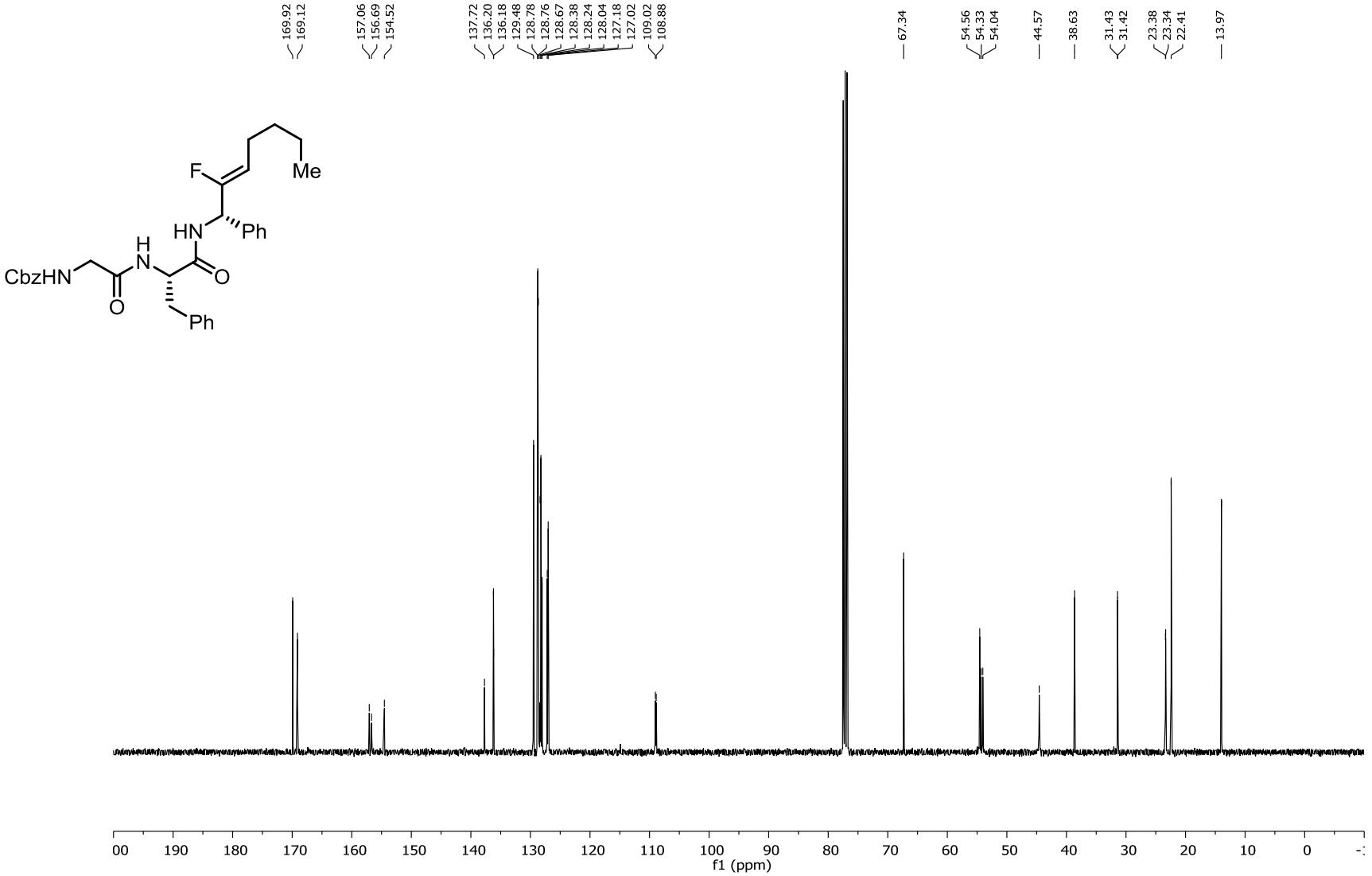
Benzyl (Z)-(4-fluoro-2-methylnon-4-en-3-yl)carbamate



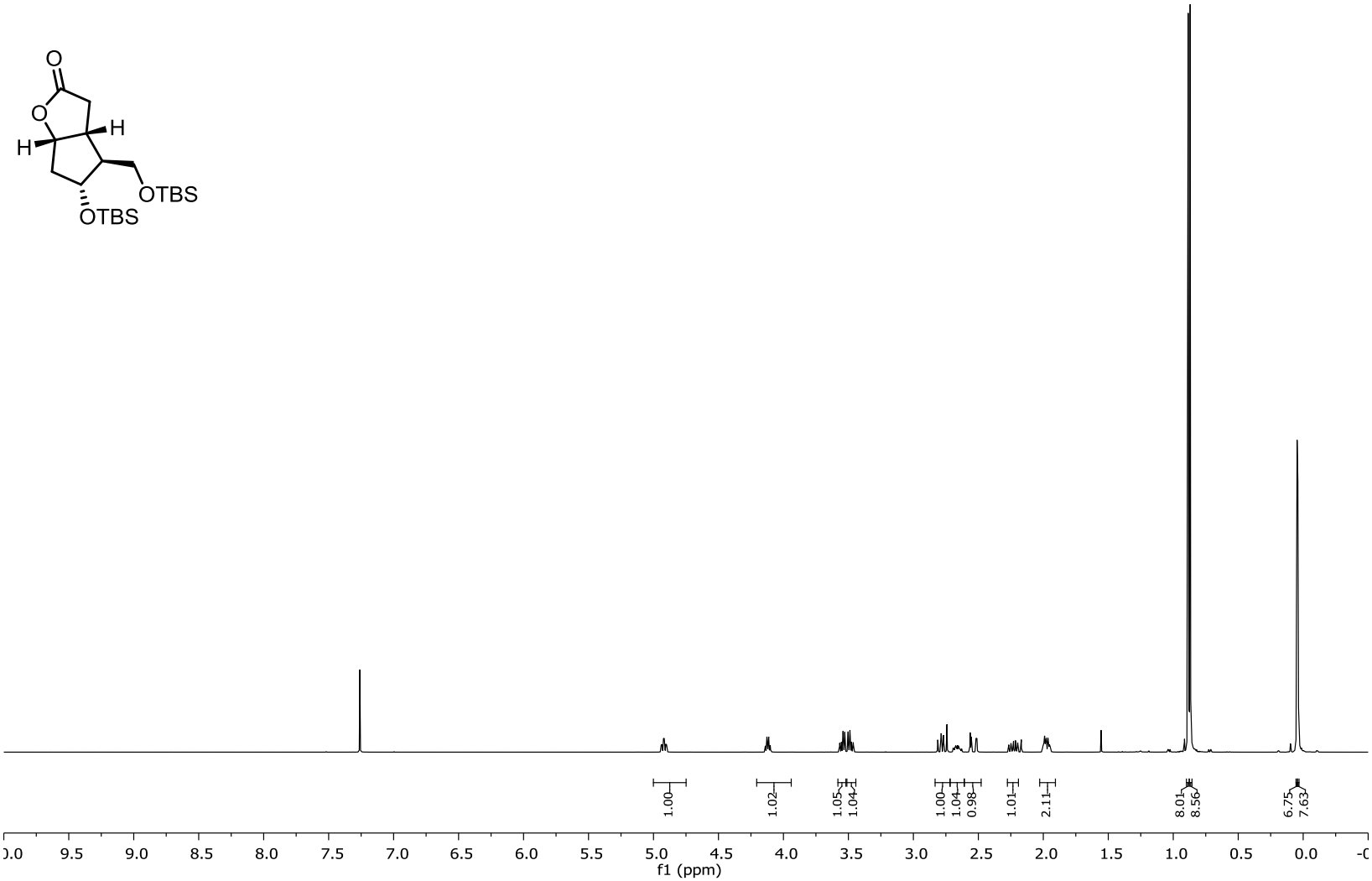
Benzyl (2-(((S)-1-(((S,Z)-2-fluoro-1-phenylhept-2-en-1-yl)amino)-1-oxo-3-phenylpropan-2-yl)amino)-2-oxoethyl)carbamate



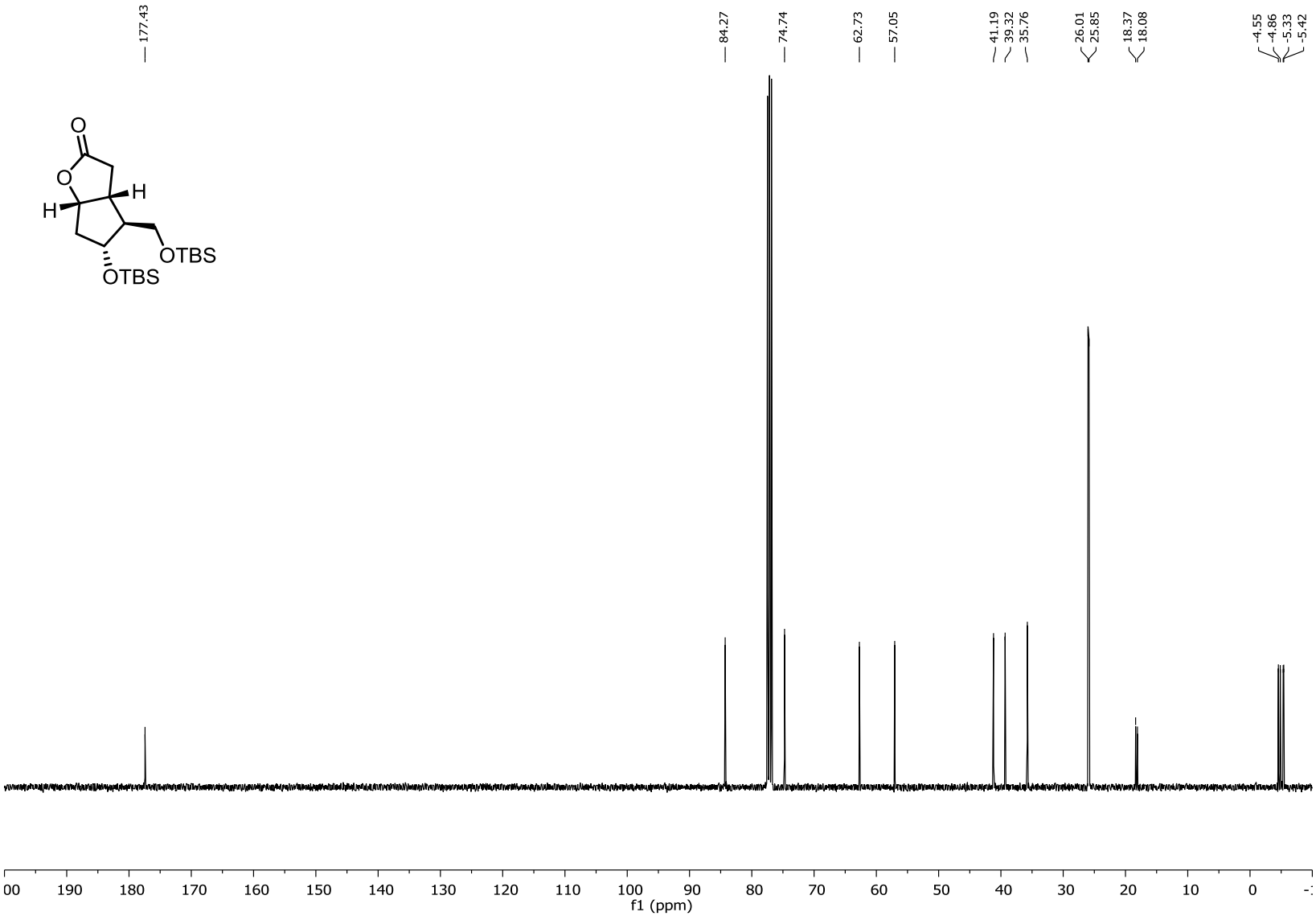
(SOI-SA-1738) - Benzyl (2-(((S)-1-(((S,Z)-2-fluoro-1-phenylhept-2-en-1-yl)amino)-1-oxo-3-phenylpropan-2-yl)amino)-2-oxoethyl)carbamate



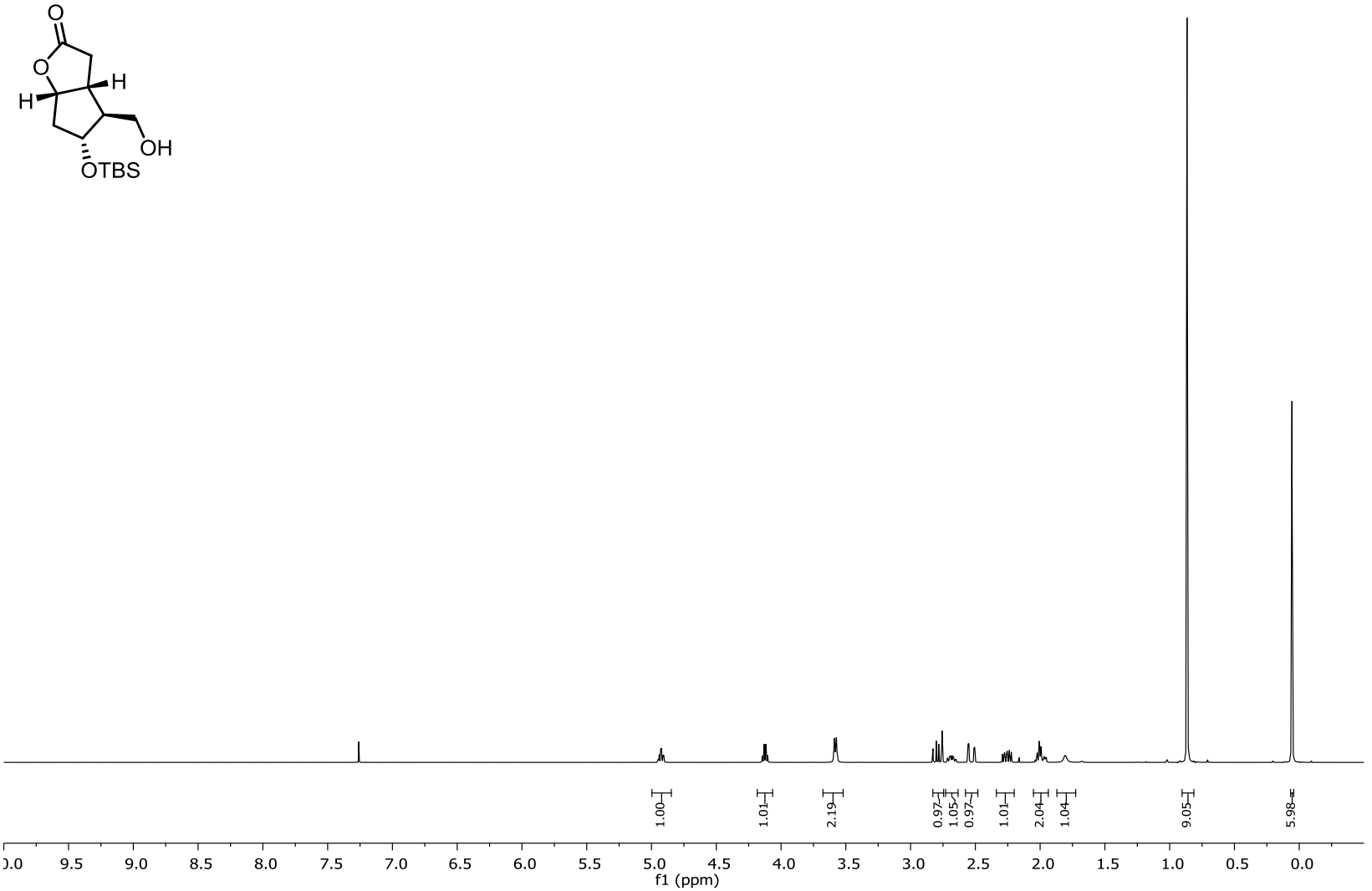
(3aR,4S,5R,6aS)-5-((*tert*-Butyldimethylsilyl)oxy)-4-(((*tert*-butyldimethylsilyl)oxy)methyl)hexahydro-2H-cyclopenta[b]furan-2-one



(3aR,4S,5R,6aS)-5-((*tert*-Butyldimethylsilyl)oxy)-4-(((*tert*-butyldimethylsilyl)oxy)methyl)hexahydro-2H-cyclopenta[b]furan-2-one



(3aR,4S,5R,6aS)-5-((*tert*-Butyldimethylsilyl)oxy)-4-(hydroxymethyl)hexahydro-2H-cyclopenta[b]furan-2-one



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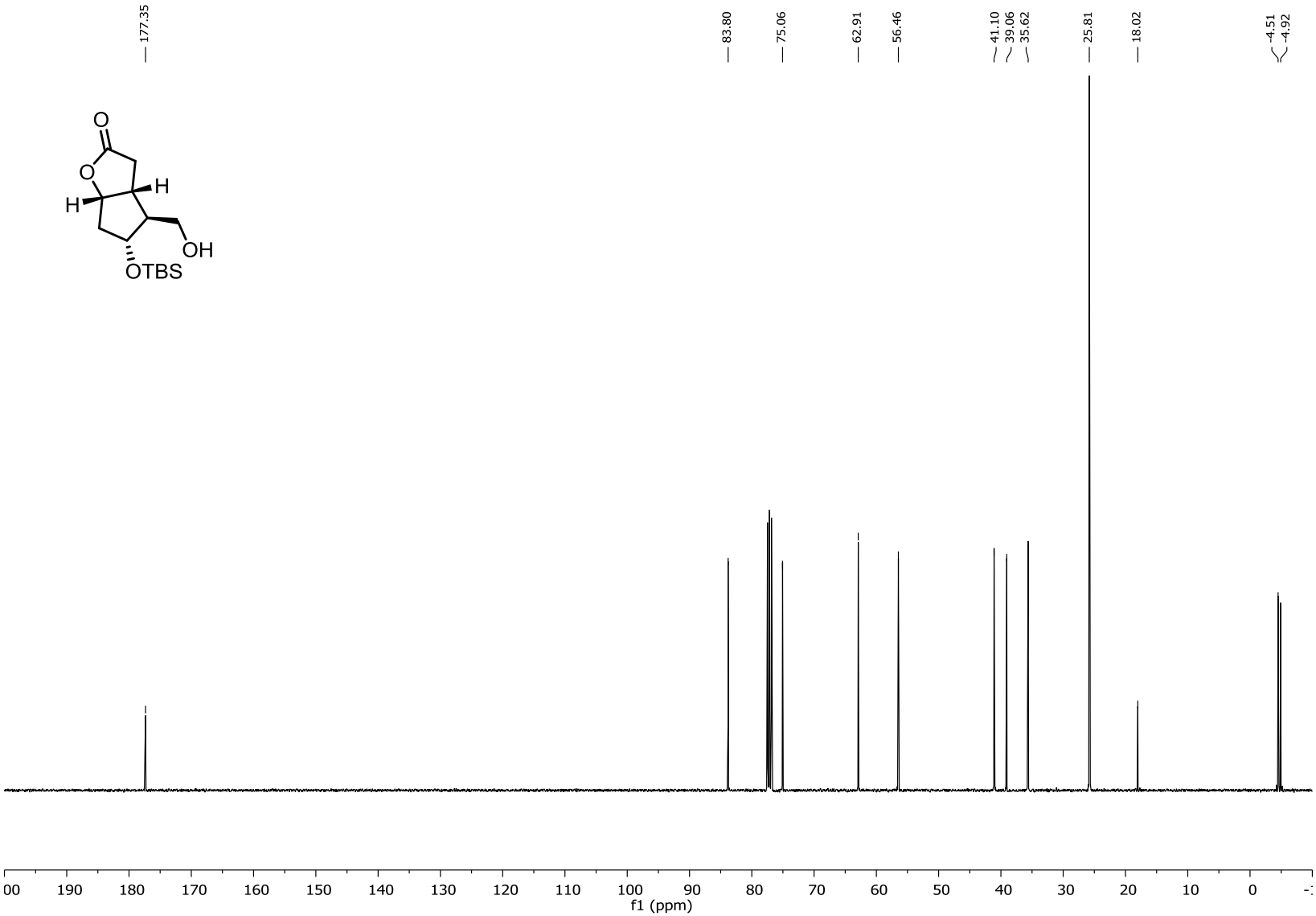
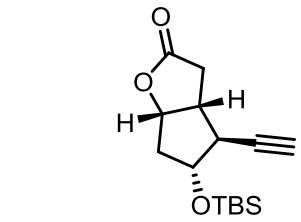


(3aR,4S,5R,6aS)-5-((*tert*-Butyldimethylsilyl)oxy)-4-ethynylhexahydro-2H-cyclopenta[b]furan-2-one



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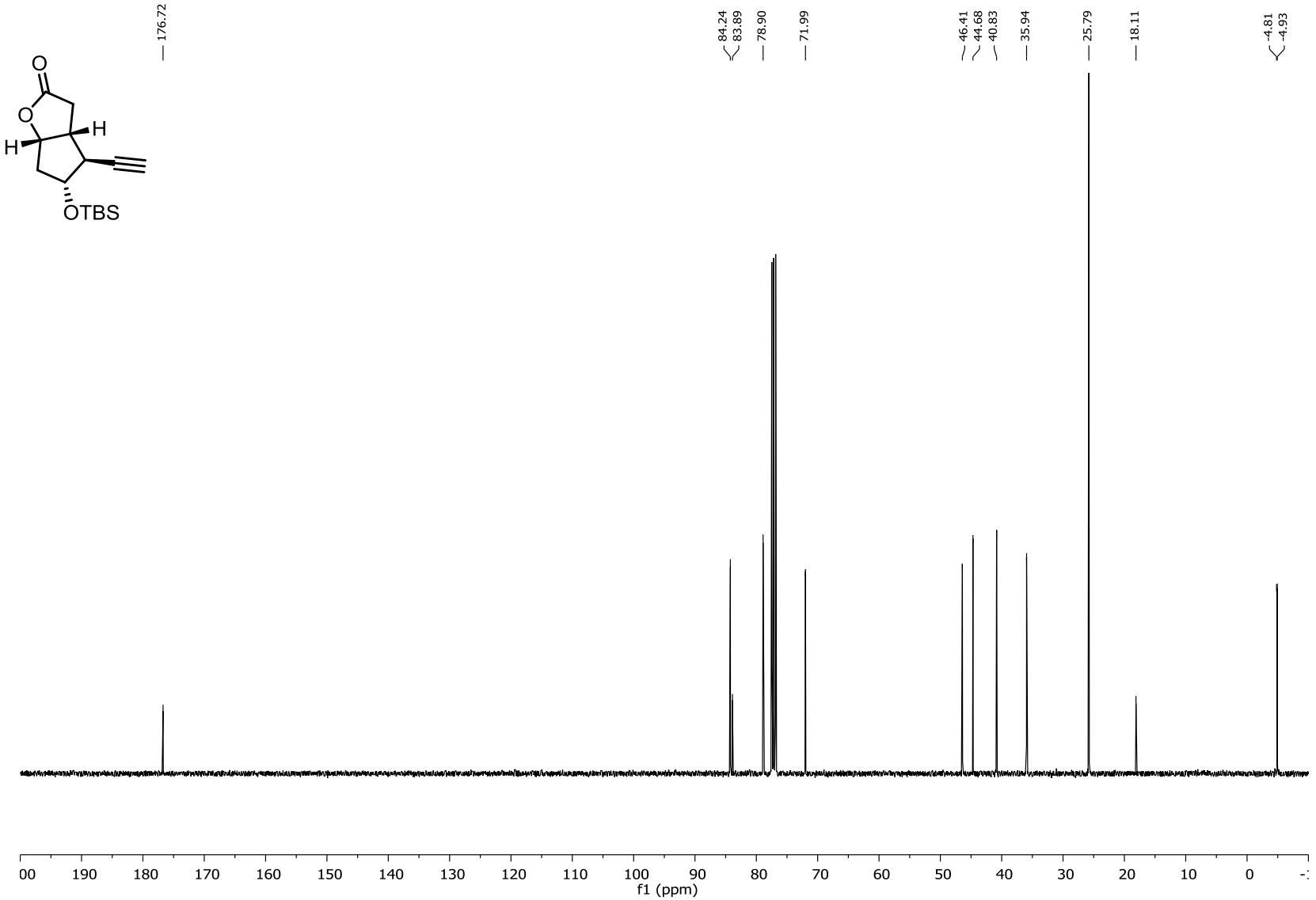
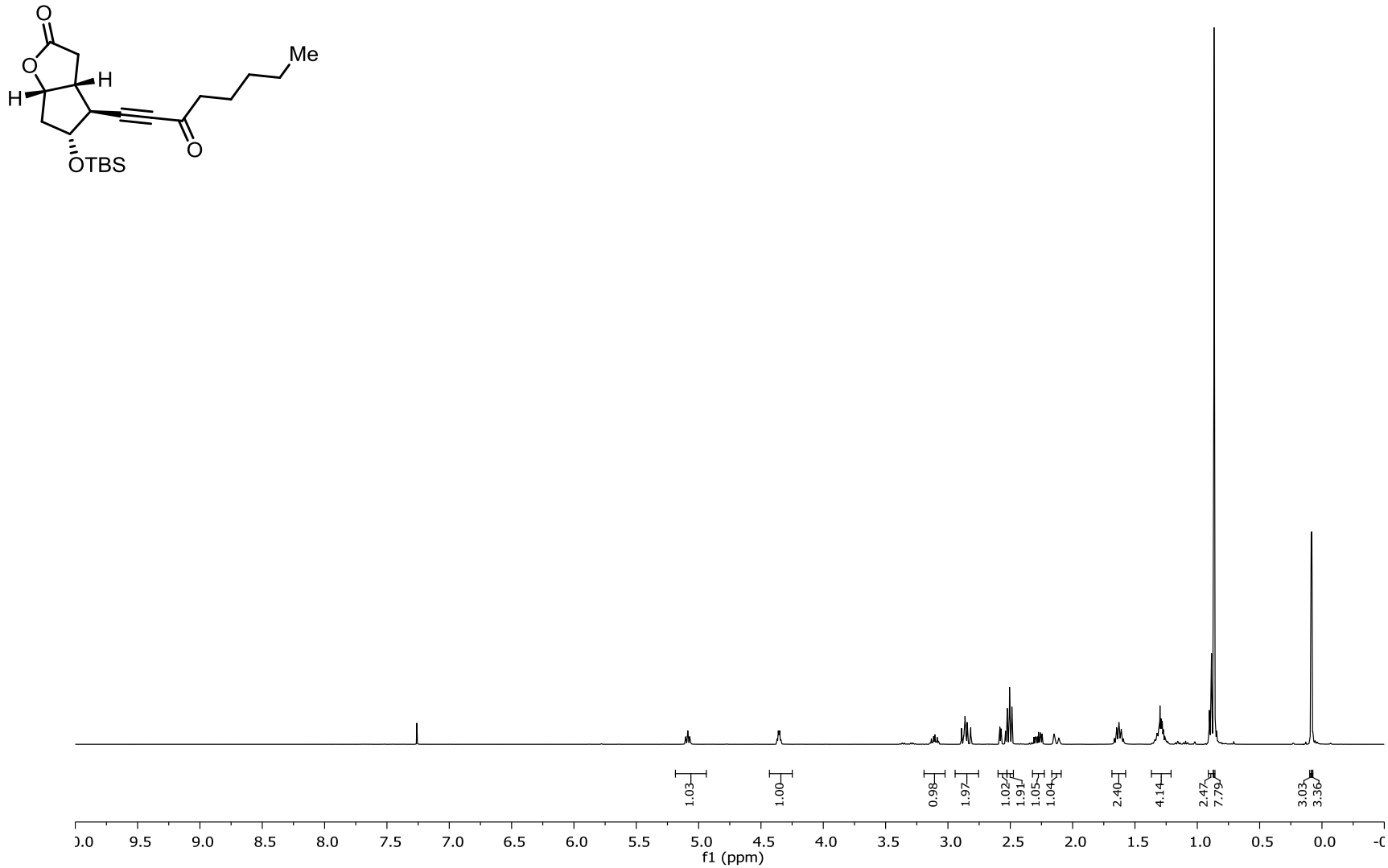


(3aR,4S,5R,6aS)-5-((*tert*-Butyldimethylsilyl)oxy)-4-(3-oxooct-1-yn-1-yl)hexahydro-2H-cyclopenta[b]furan-2-one



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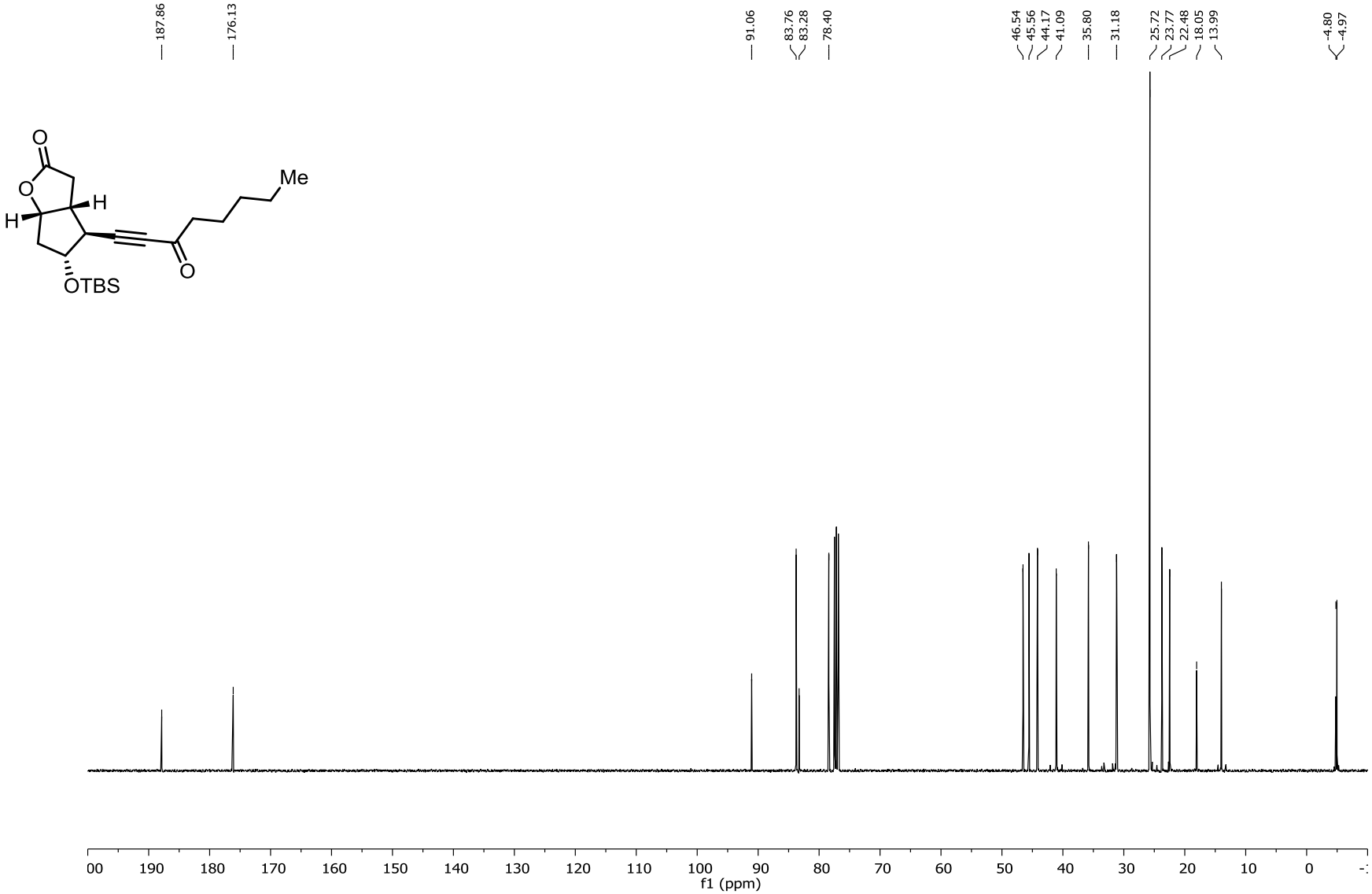
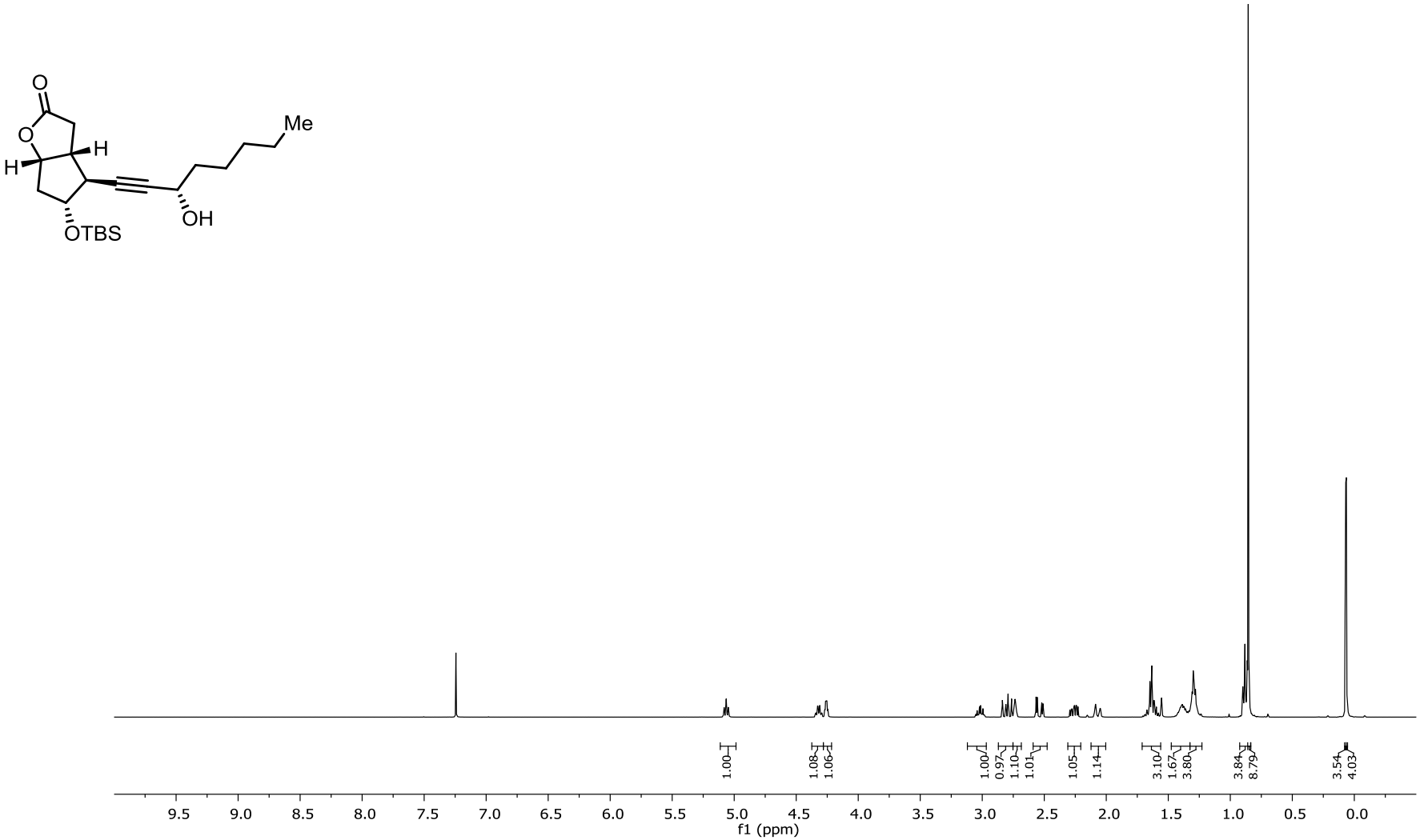


(3aR,4S,5R,6aS)-5-((*tert*-Butyldimethylsilyl)oxy)-4-((S)-3-hydroxyoct-1-yn-1-yl)hexahydro-2H-cyclopenta[b]furan-2-one



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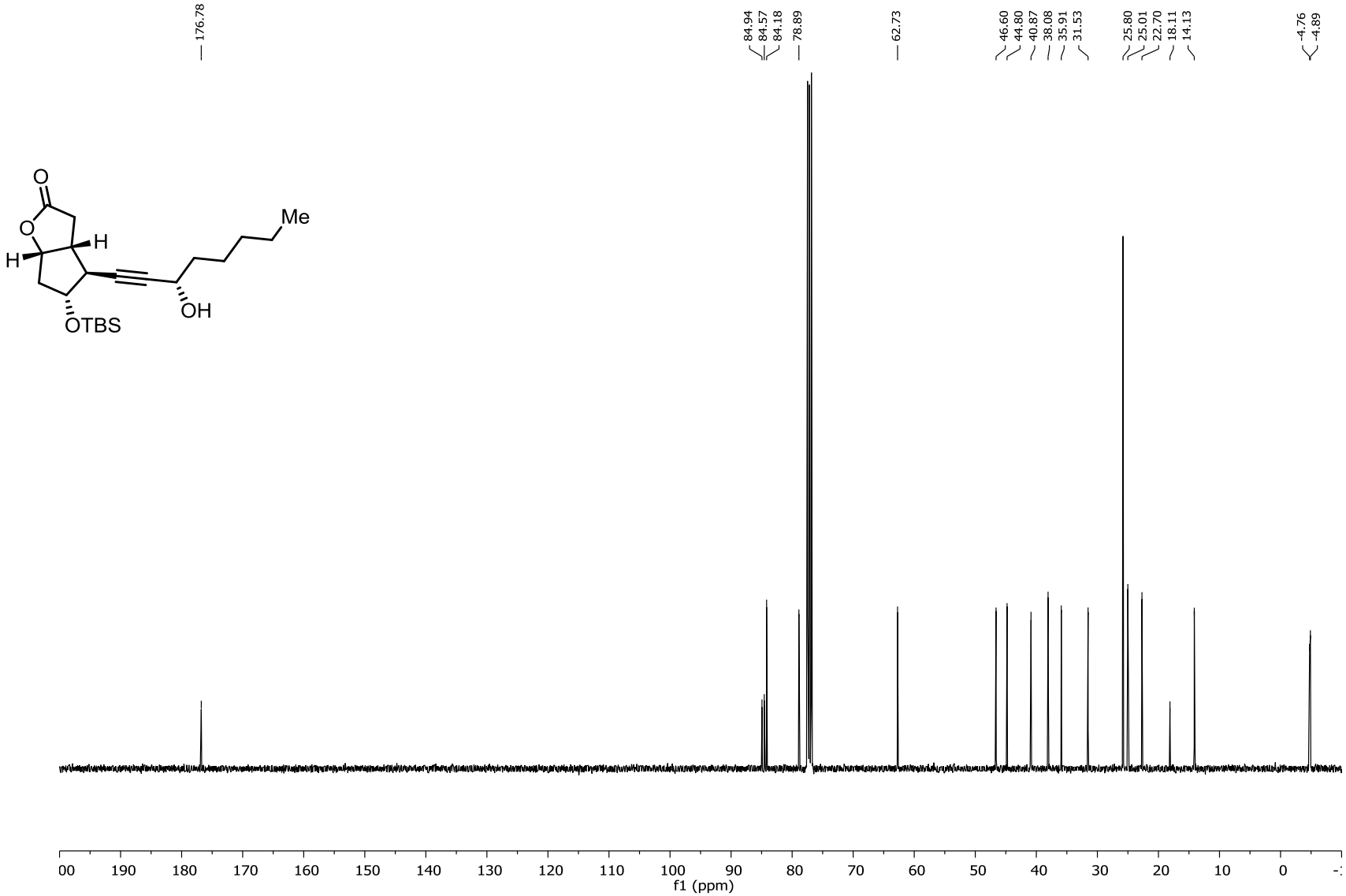
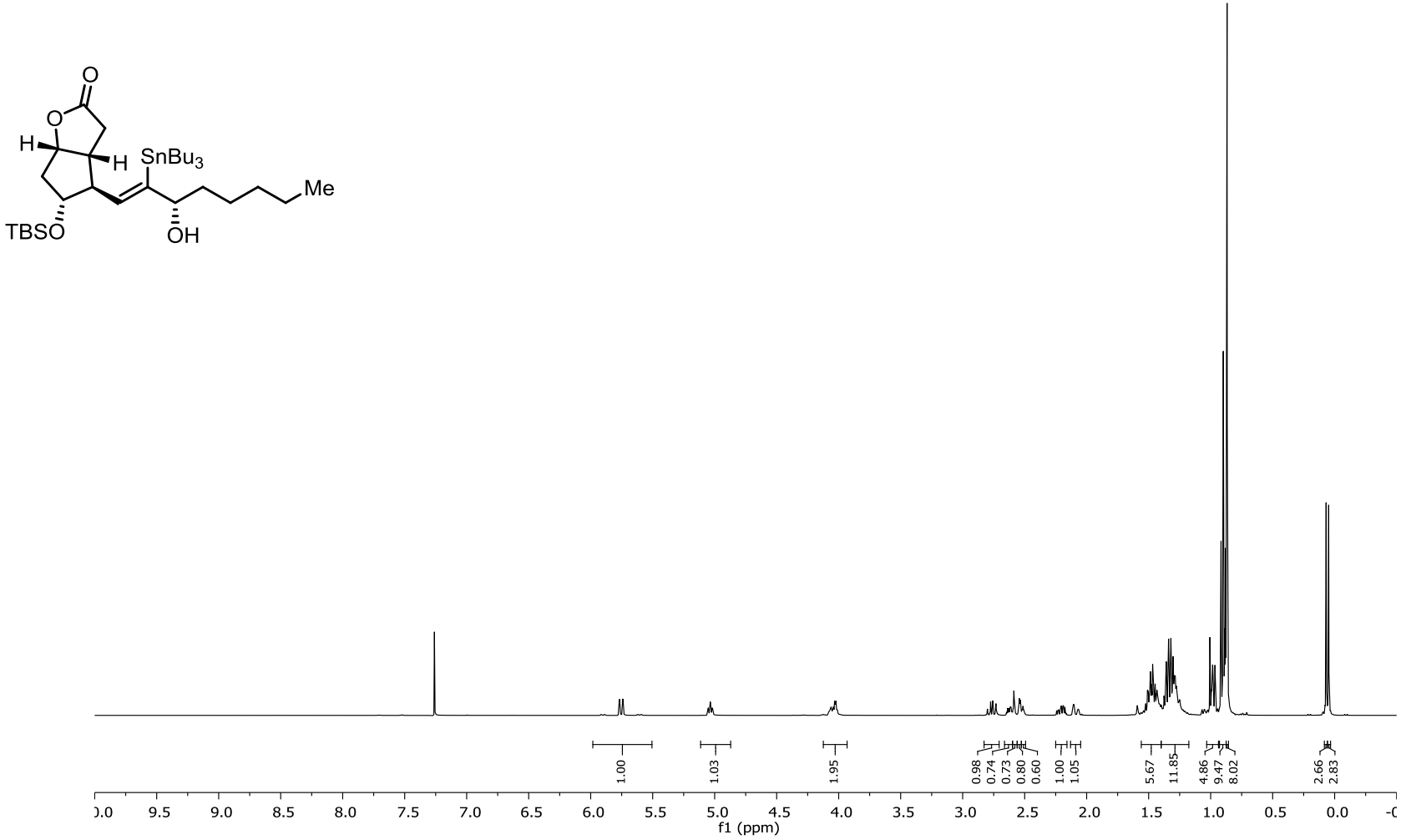
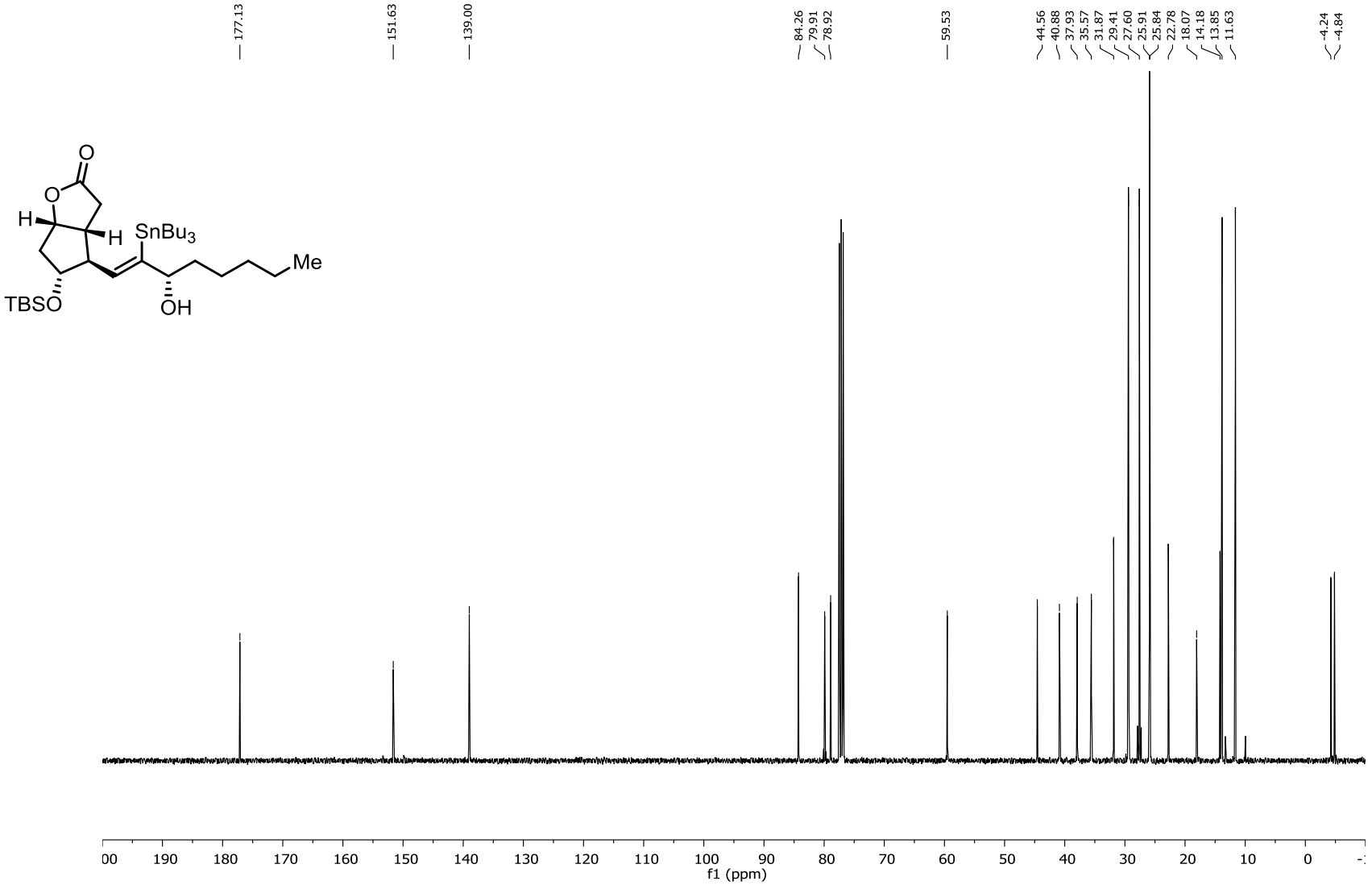


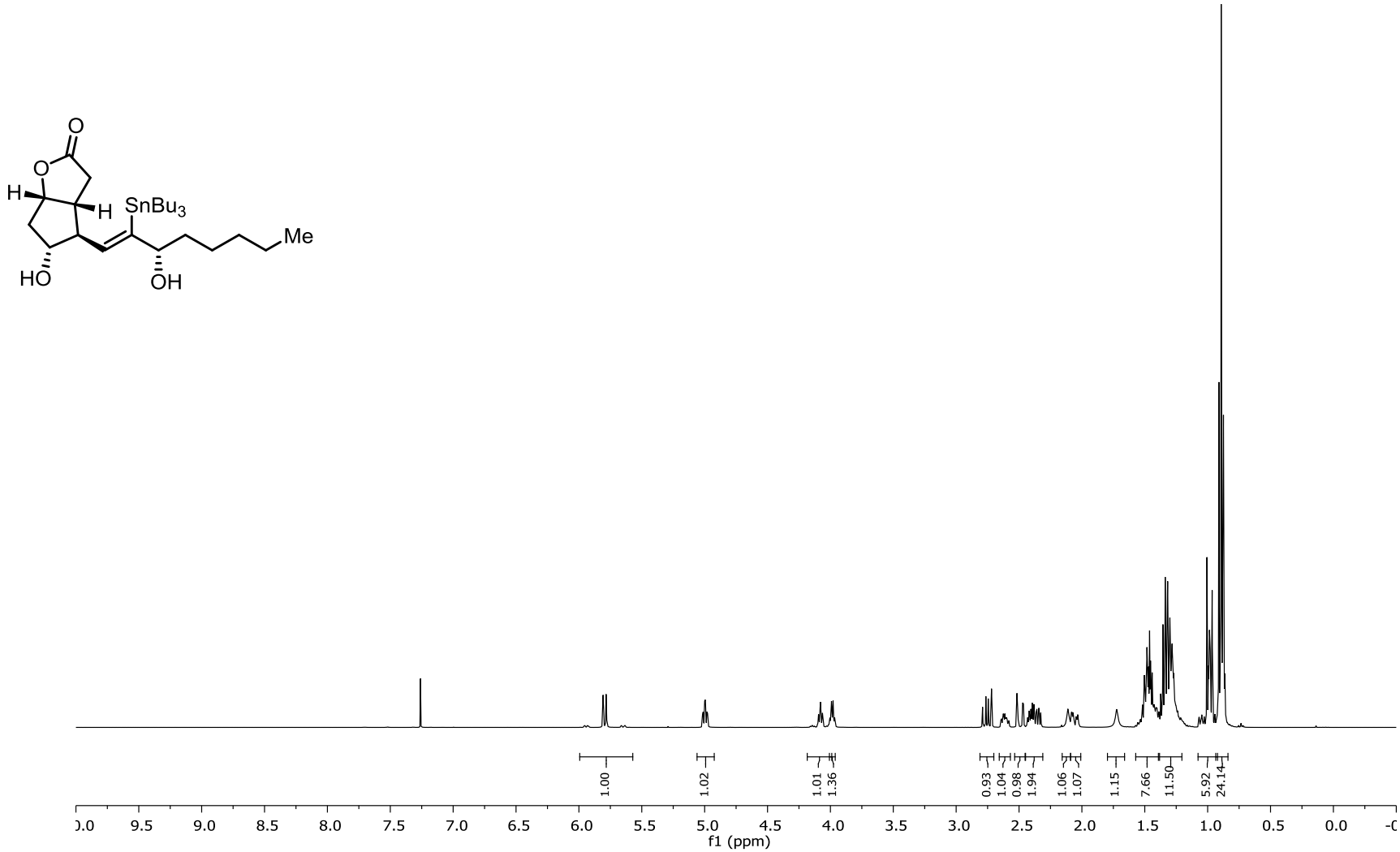
(3aR,4S,5R,6aS)-5-((*tert*-Butyldimethylsilyl)oxy)-4-((S,Z)-3-hydroxy-2-(tributylstannyl)oct-1-en-1-yl)hexahydro-2H-cyclopenta[b]furan-2-one



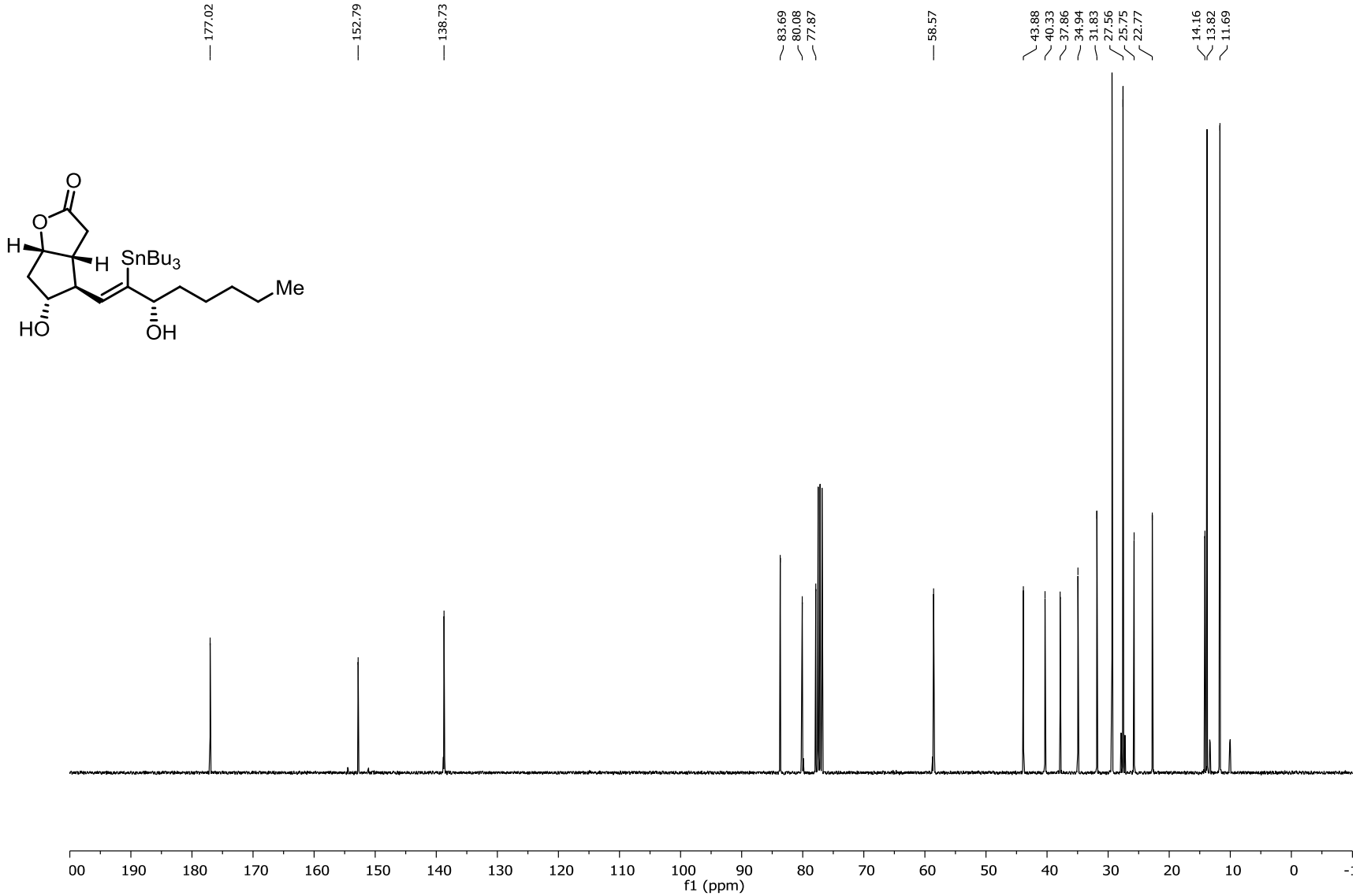
(3aR,4S,5R,6aS)-5-((*tert*-Butyldimethylsilyl)oxy)-4-((S,Z)-3-hydroxy-2-(tributylstannyl)oct-1-en-1-yl)hexahydro-2H-cyclopenta[b]furan-2-one



(3aR,4S,5R,6aS)-5-Hydroxy-4-((S,Z)-3-hydroxy-2-(tributylstannyl)oct-1-en-1-yl)hexahydro-2H-cyclopenta[b]furan-2-one



(3aR,4S,5R,6aS)-5-Hydroxy-4-((S,Z)-3-hydroxy-2-(tributylstannyl)oct-1-en-1-yl)hexahydro-2H-cyclopenta[b]furan-2-one



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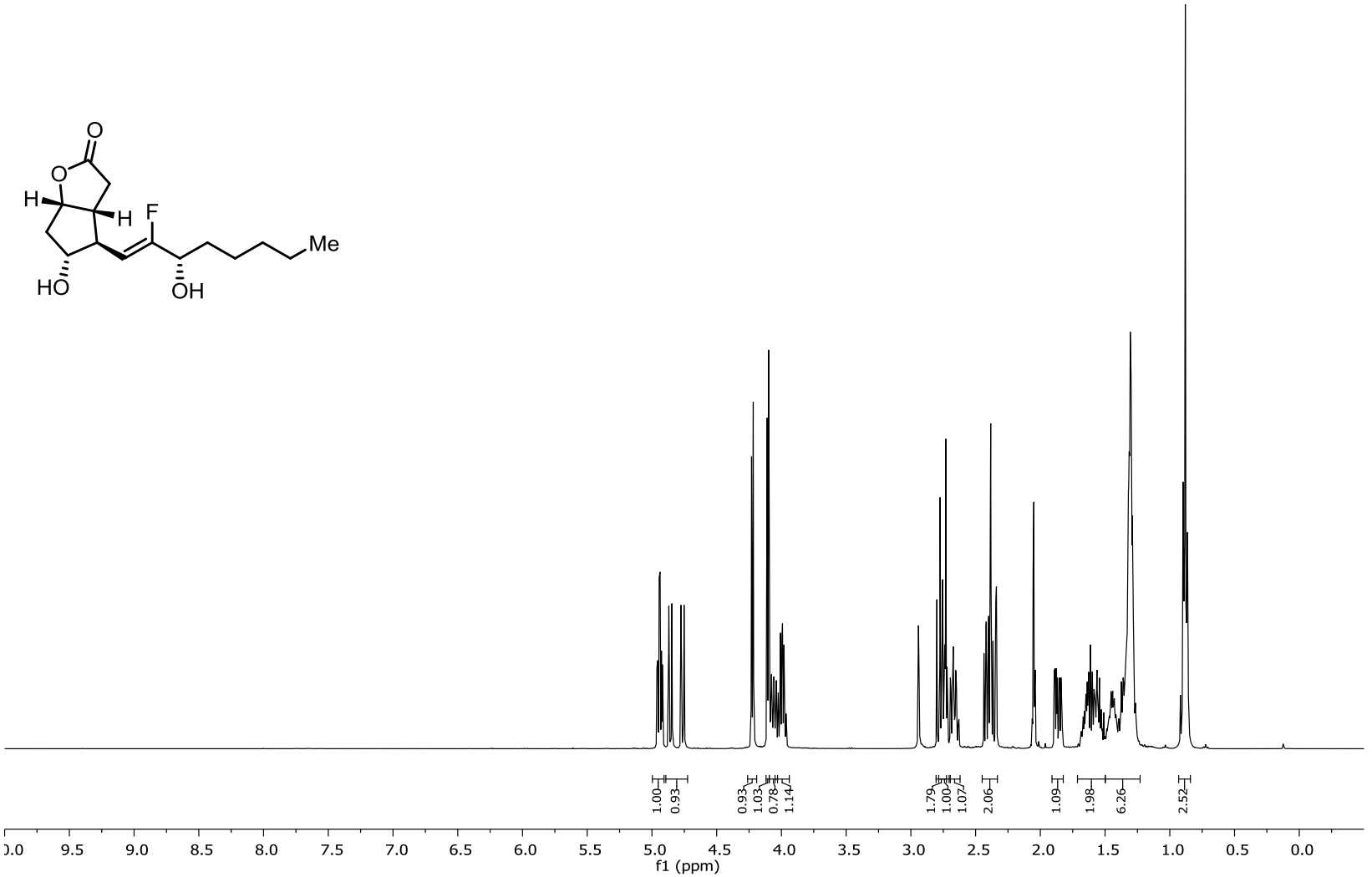
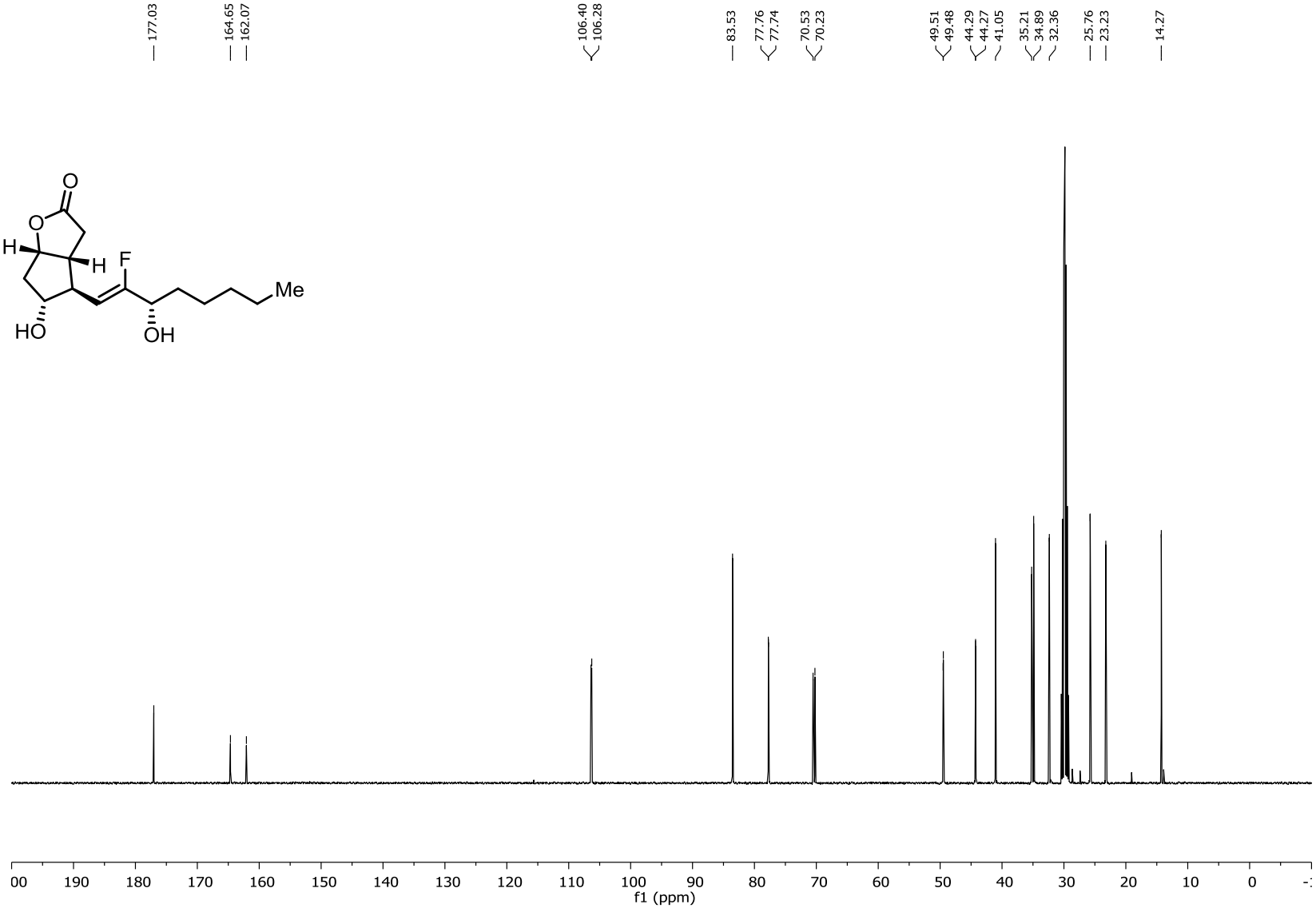
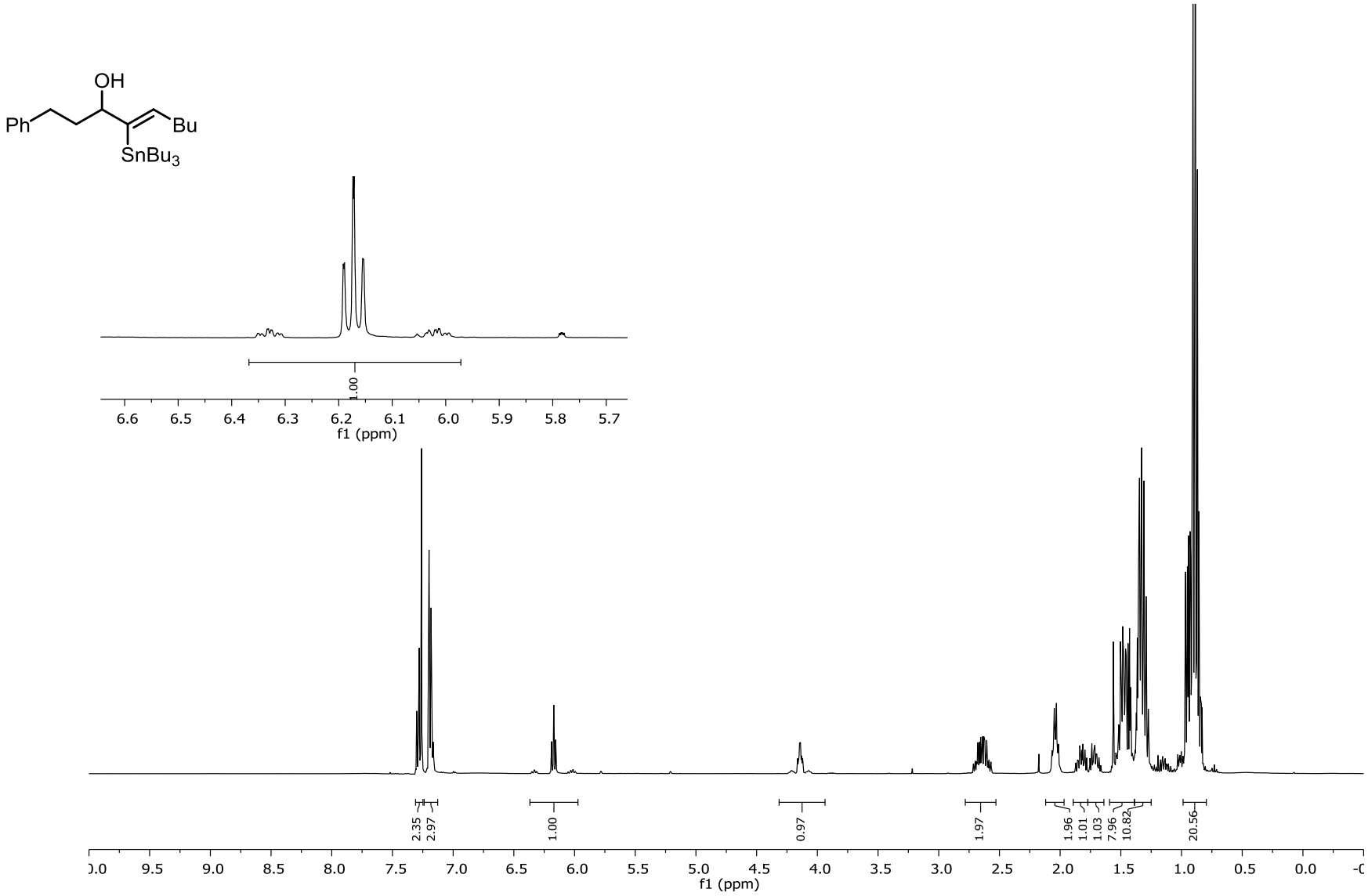


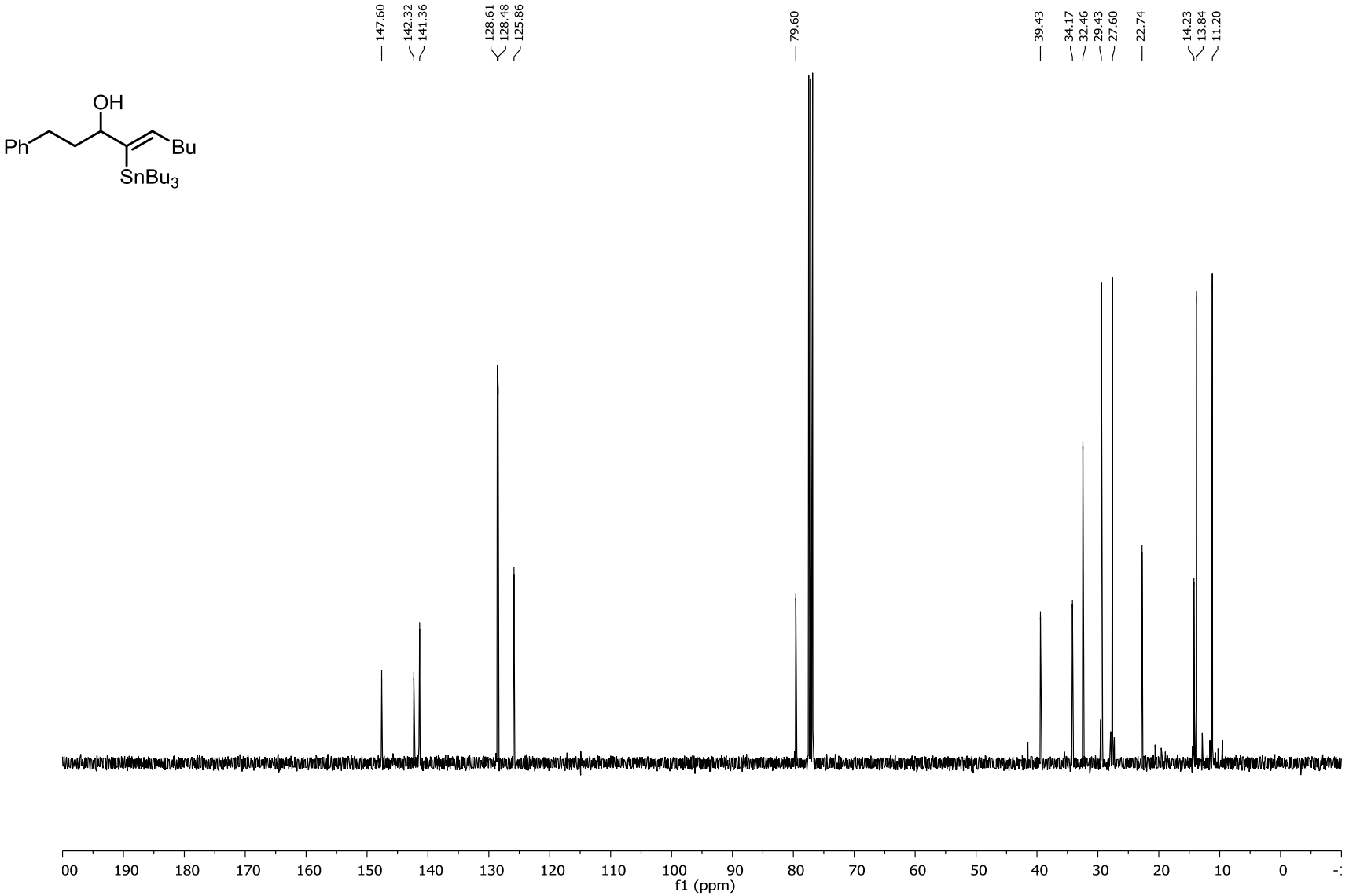
(3aR,4S,5R,6aS)-4-((S,Z)-2-Fluoro-3-hydroxyoct-1-en-1-yl)-5-hydroxyhexahydro-2H-cyclopenta[b]furan-2-one



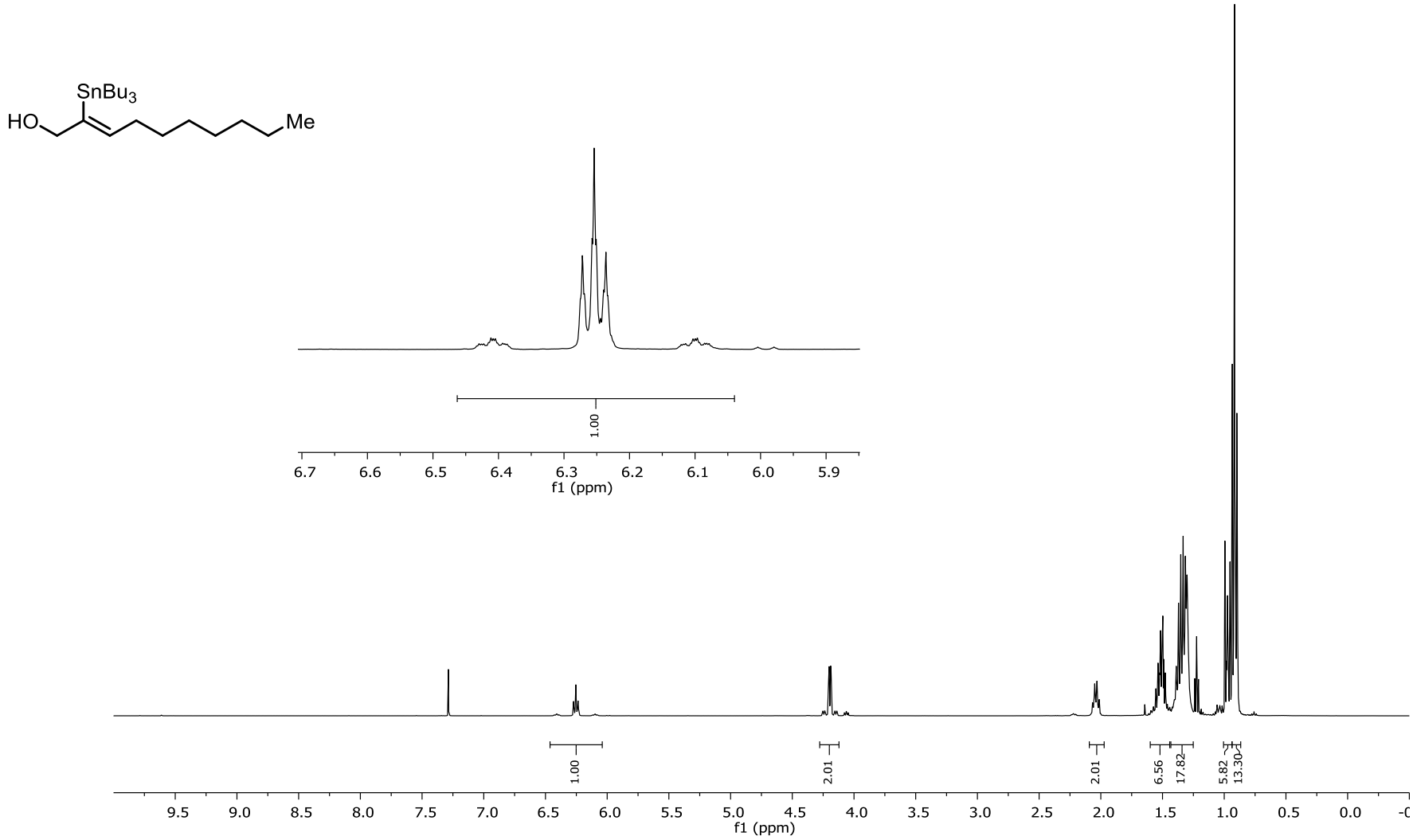
(Z)-1-Phenyl-4-(tributylstannyl)non-4-en-3-ol



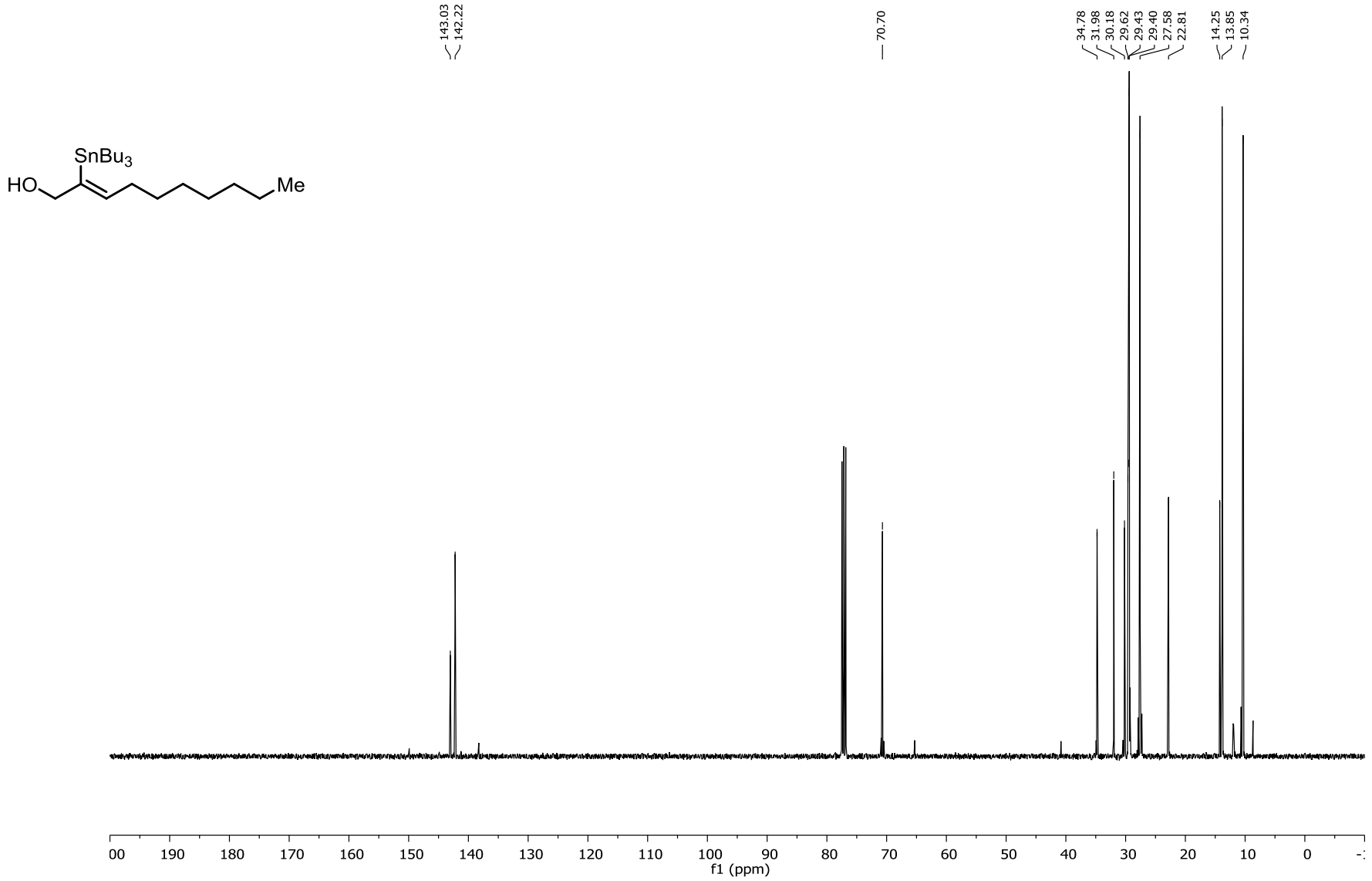
(Z)-1-Phenyl-4-(tributylstannyl)non-4-en-3-ol



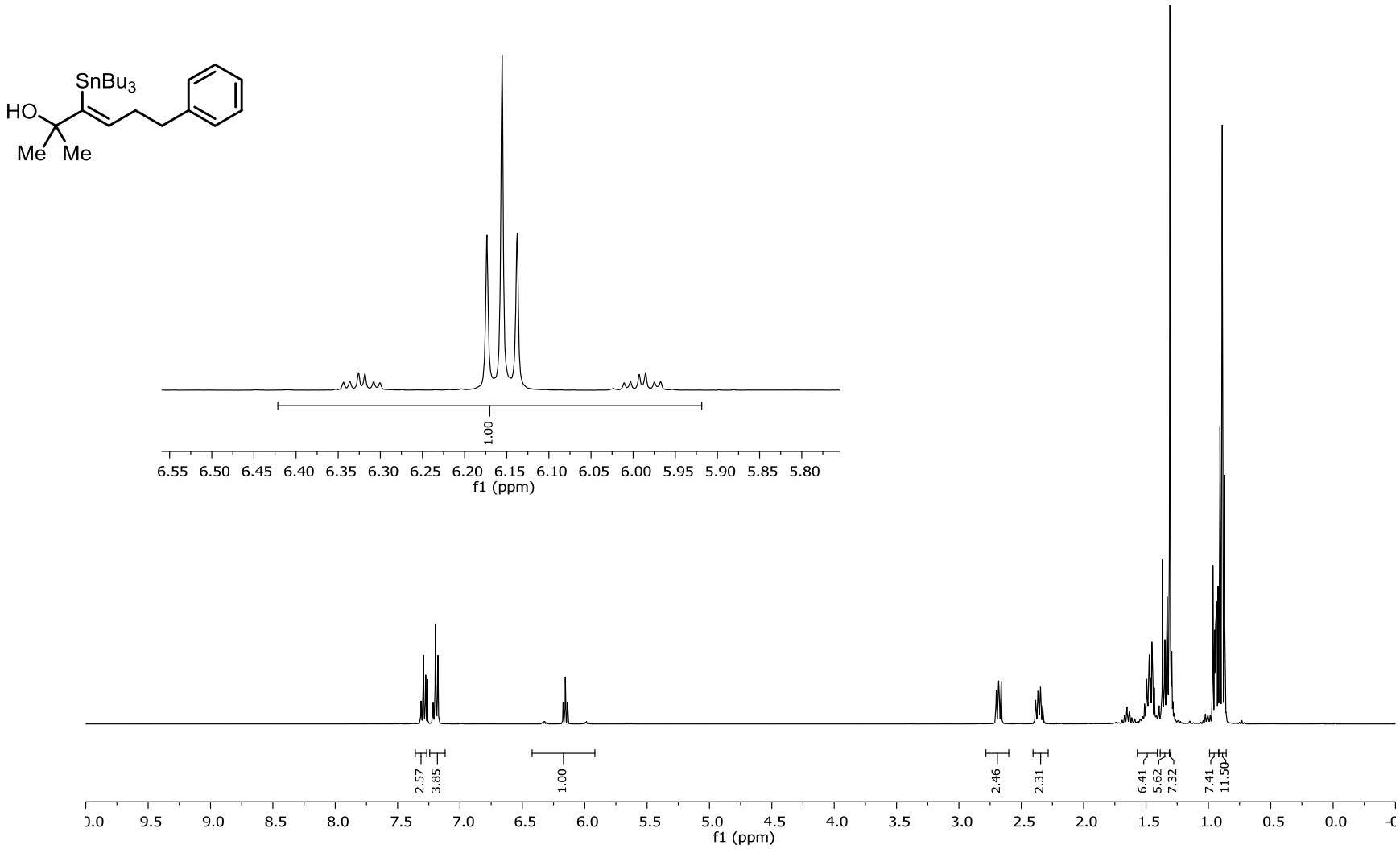
(Z)-2-(Tributylstannyl)dec-2-en-1-ol



(Z)-2-(Tributylstannyl)dec-2-en-1-ol



(Z)-2-Methyl-6-phenyl-3-(tributylstannyl)hex-3-en-2-ol



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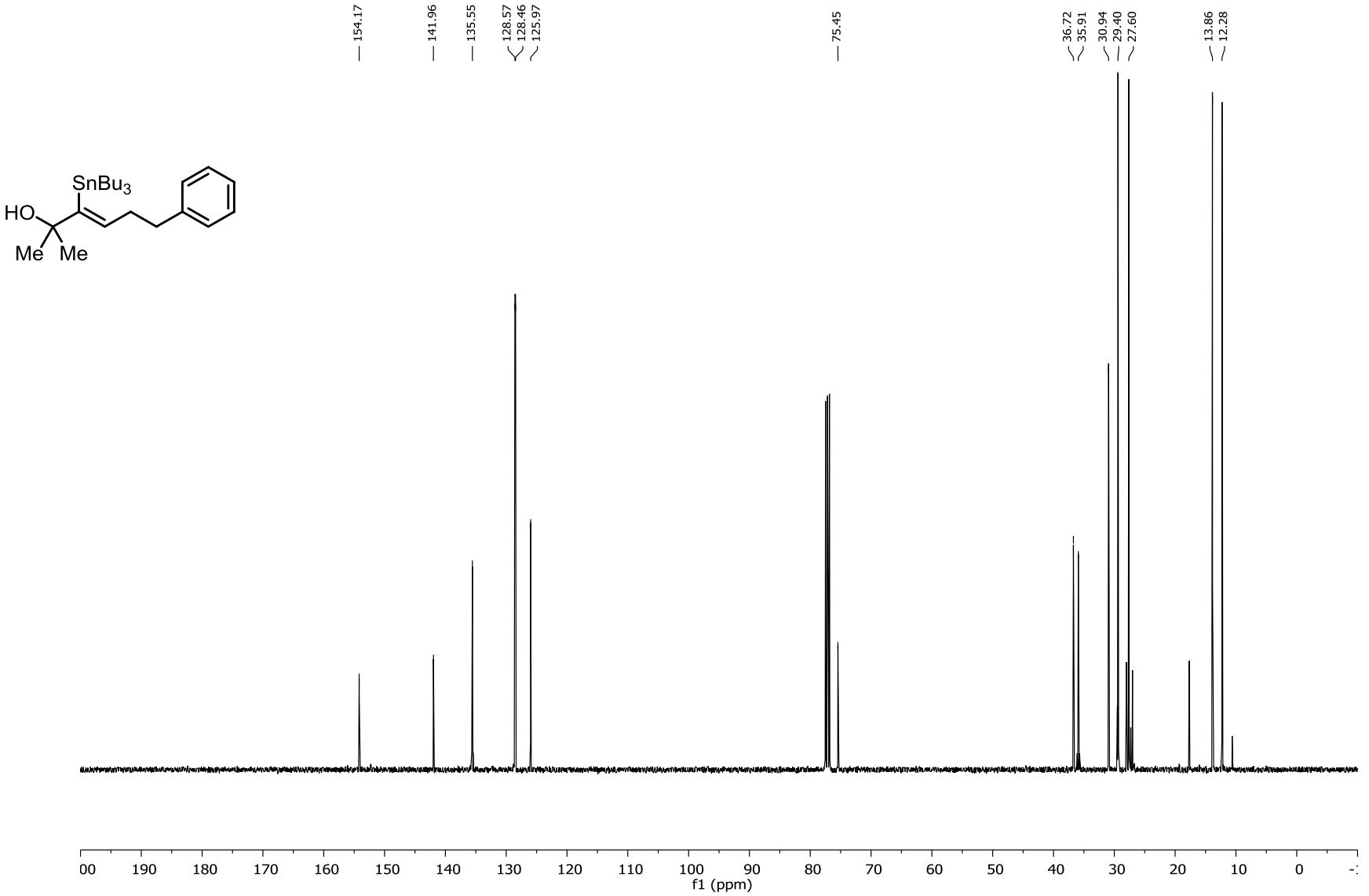
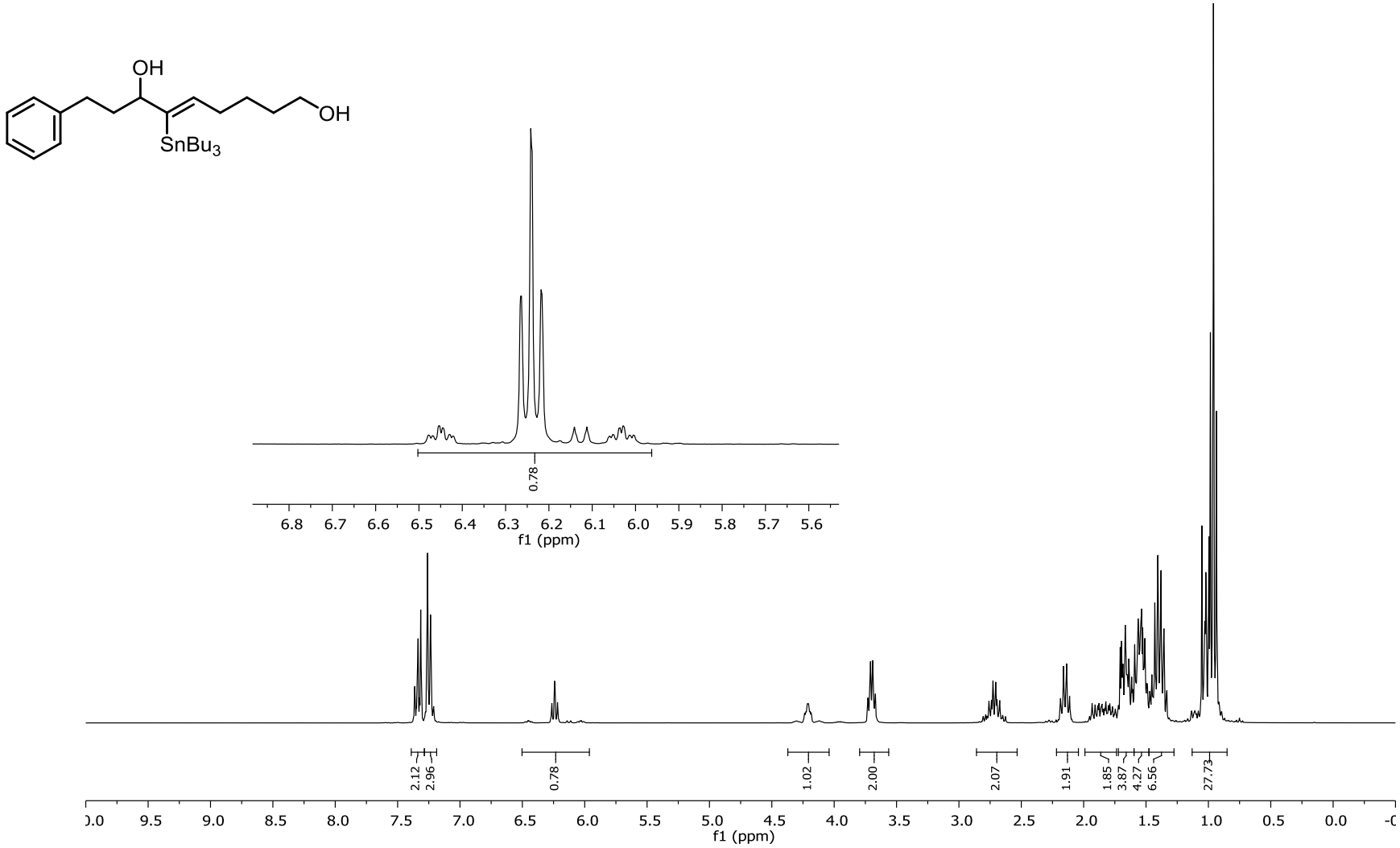
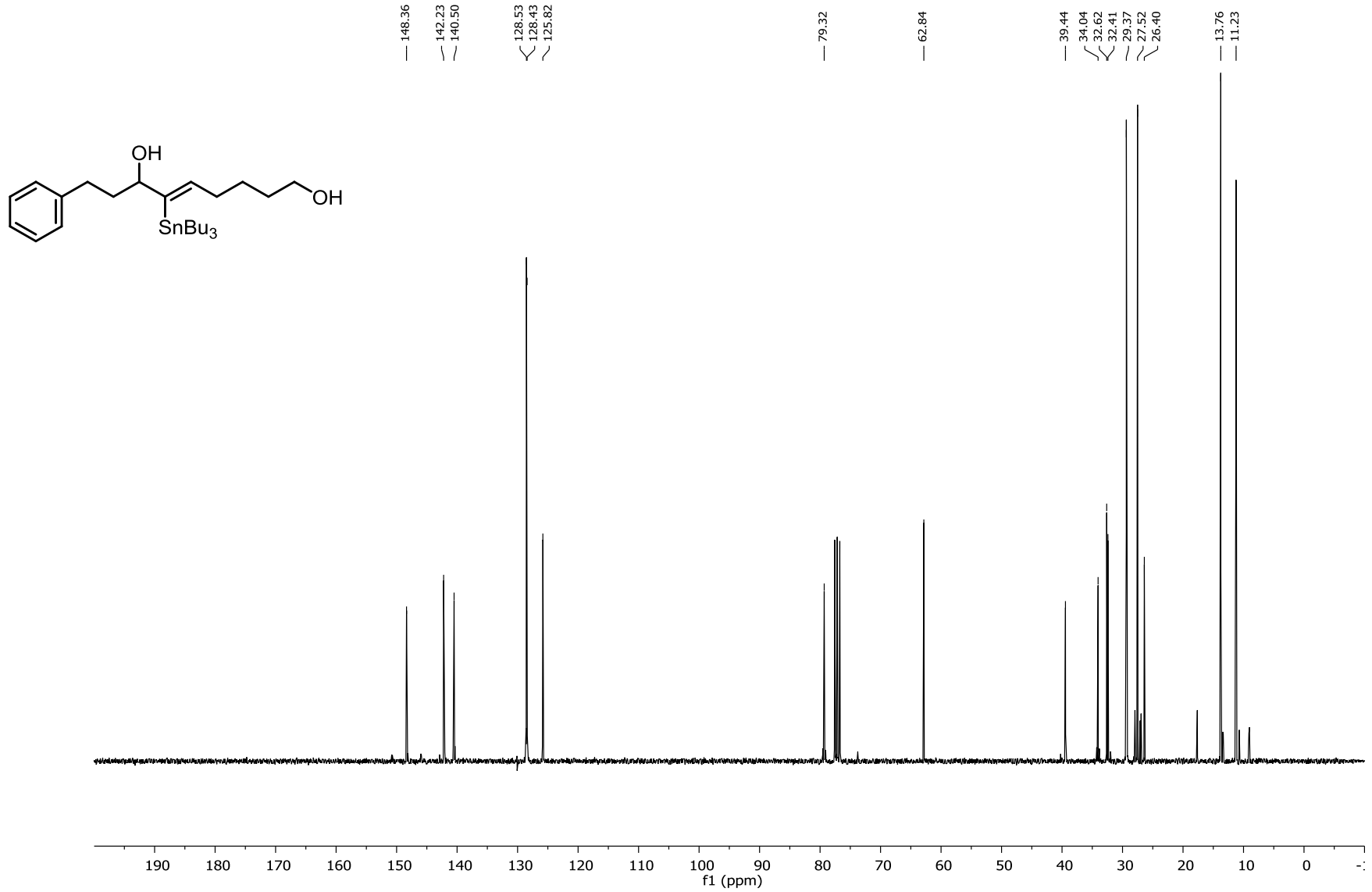


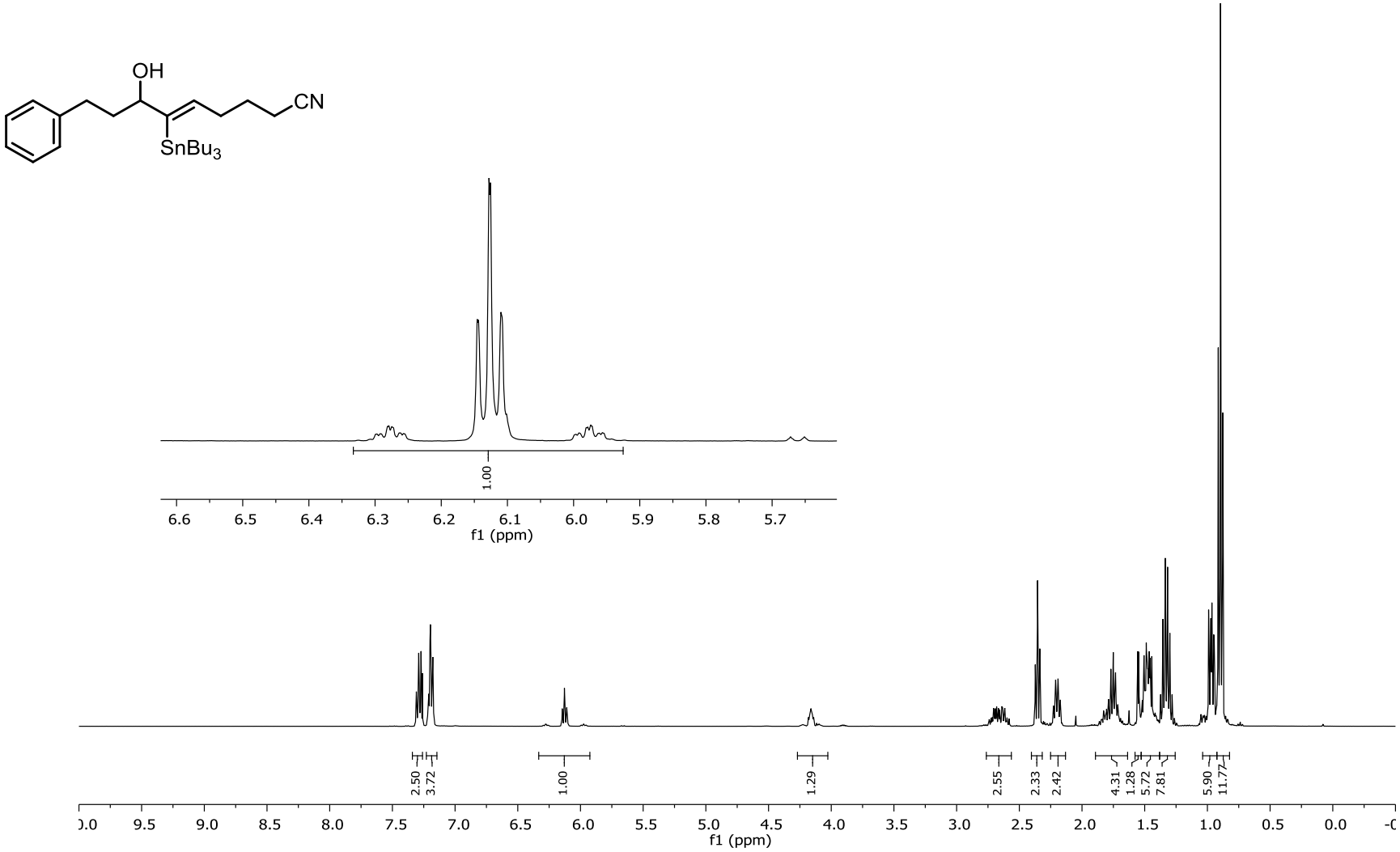
(Z)-9-Phenyl-6-(tributylstannyl)non-5-ene-1,7-diol



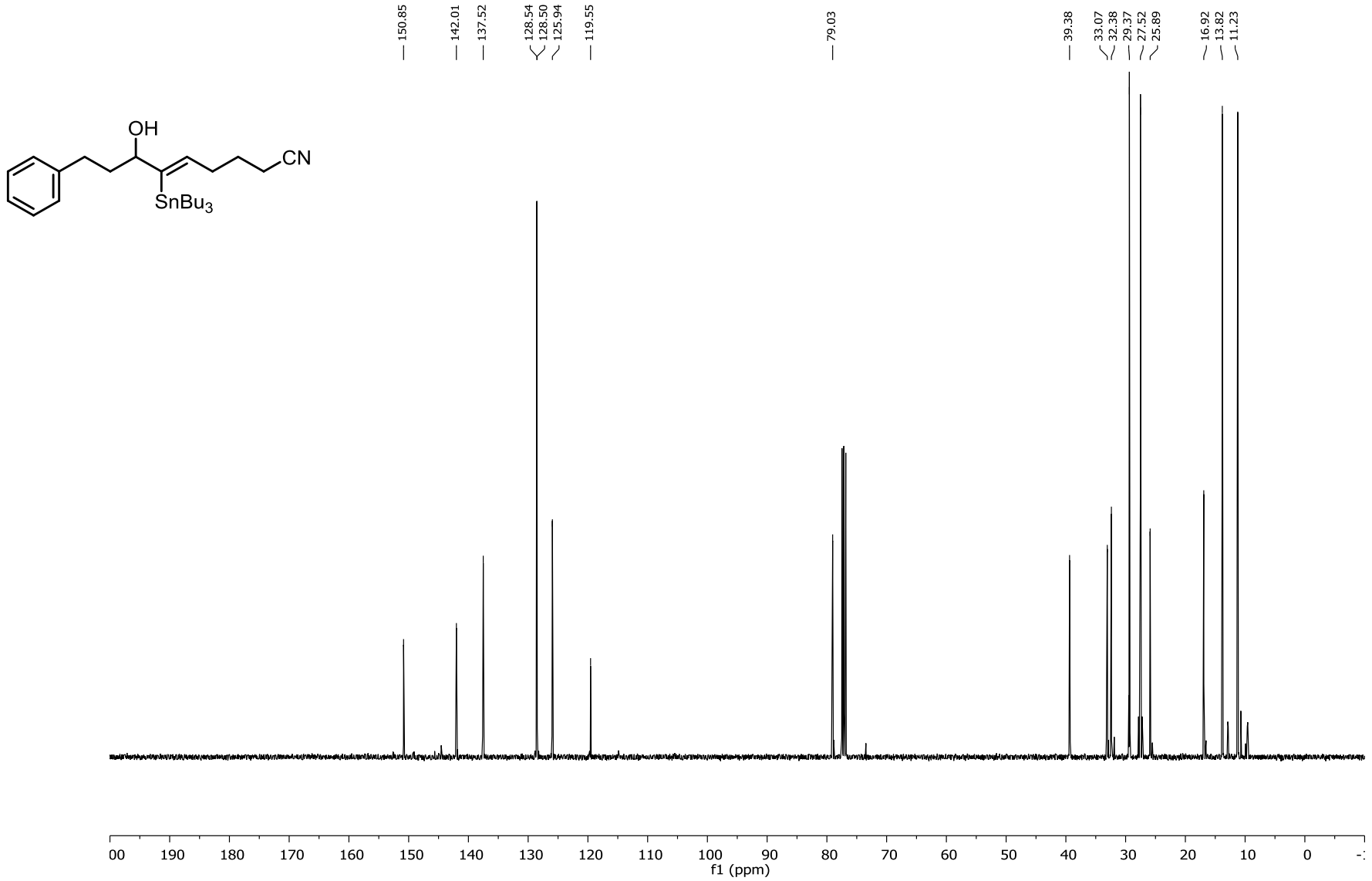
(Z)-9-Phenyl-6-(tributylstannyl)non-5-ene-1,7-diol



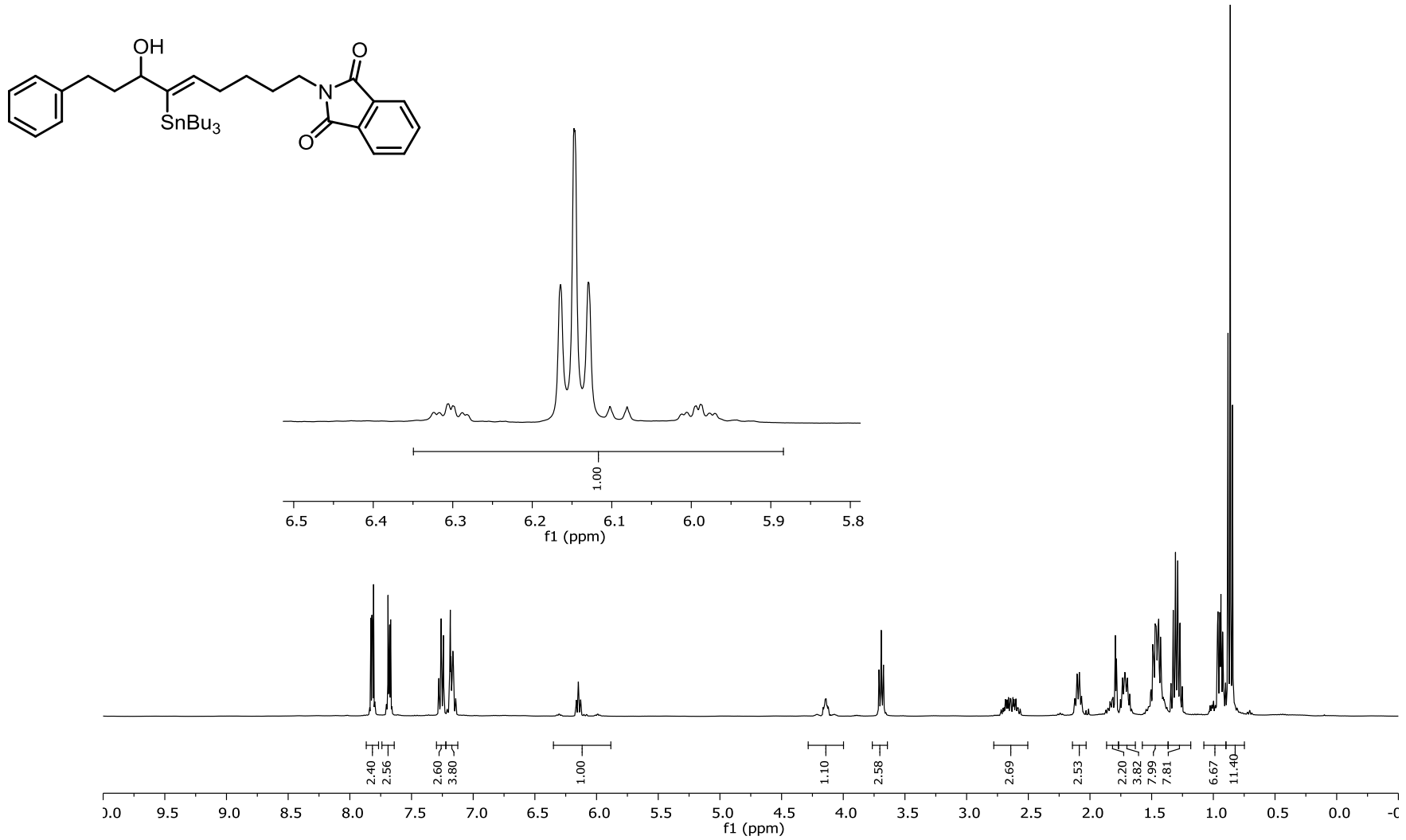
(Z)-7-Hydroxy-9-phenyl-6-(tributylstannyl)non-5-enenitrile



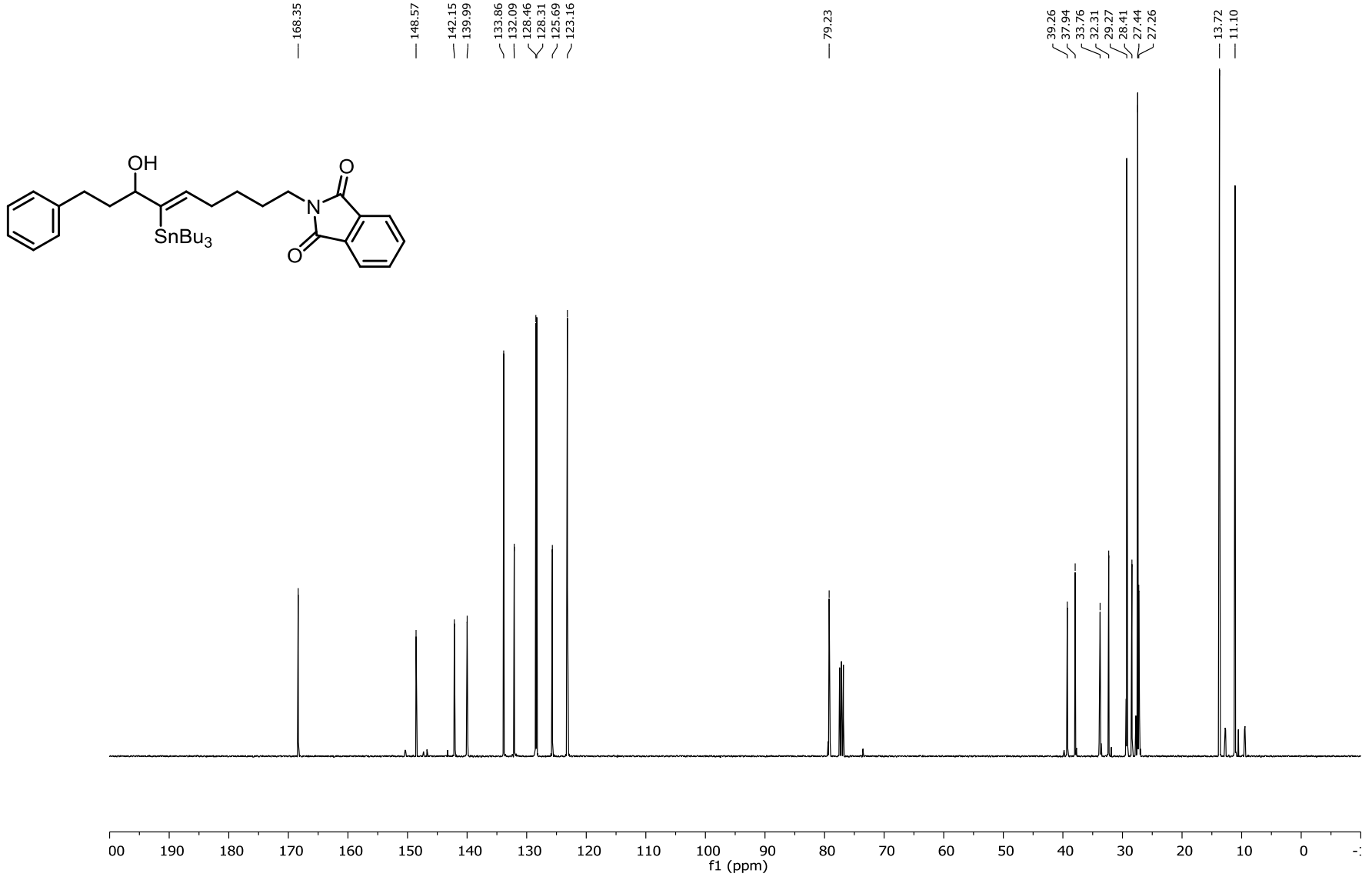
(Z)-7-Hydroxy-9-phenyl-6-(tributylstannyl)non-5-enenitrile



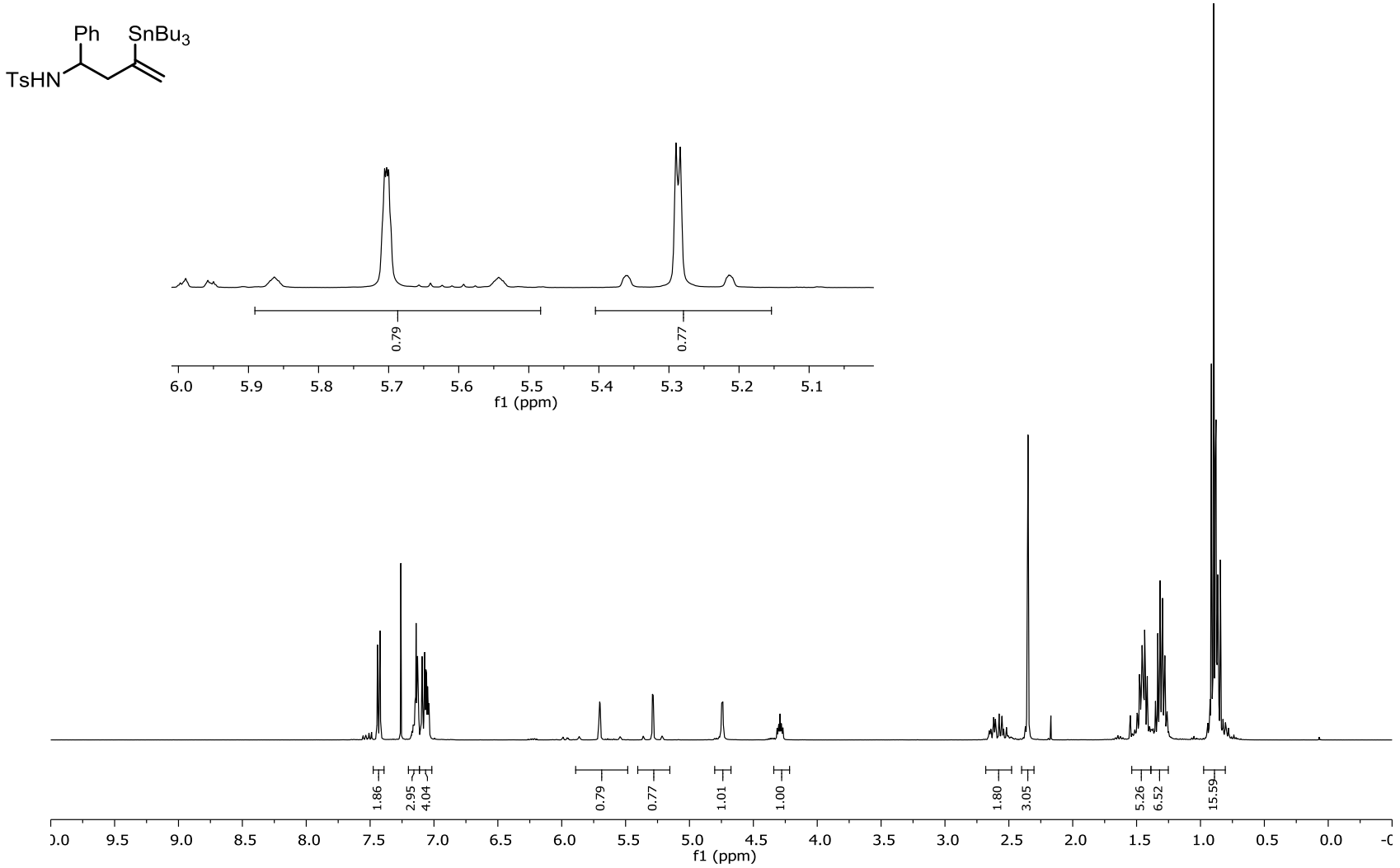
(Z)-2-(7-Hydroxy-9-phenyl-6-(tributylstannyl)non-5-en-1-yl)isoindoline-1,3-dione



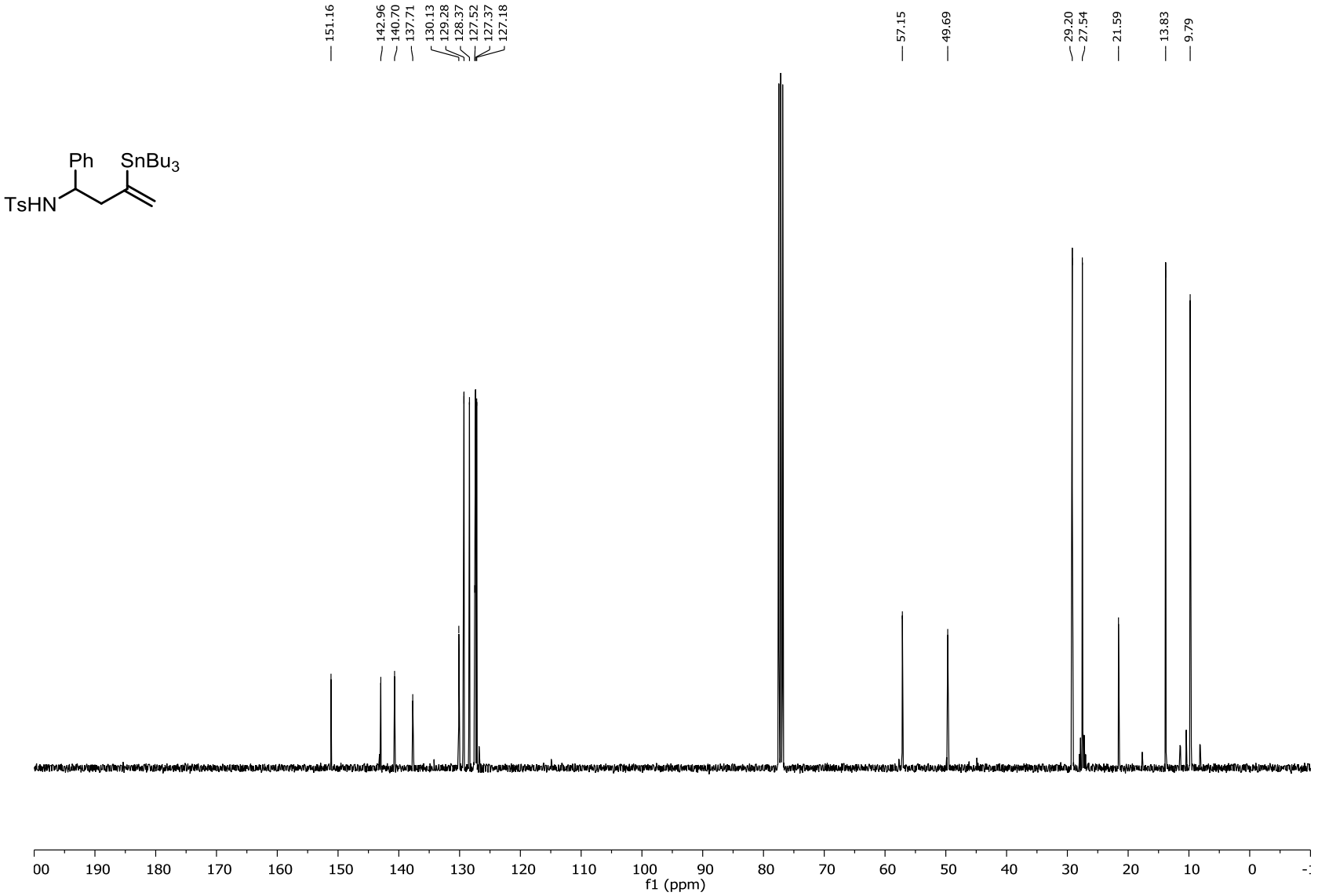
(Z)-2-(7-Hydroxy-9-phenyl-6-(tributylstannyl)non-5-en-1-yl)isoindoline-1,3-dione



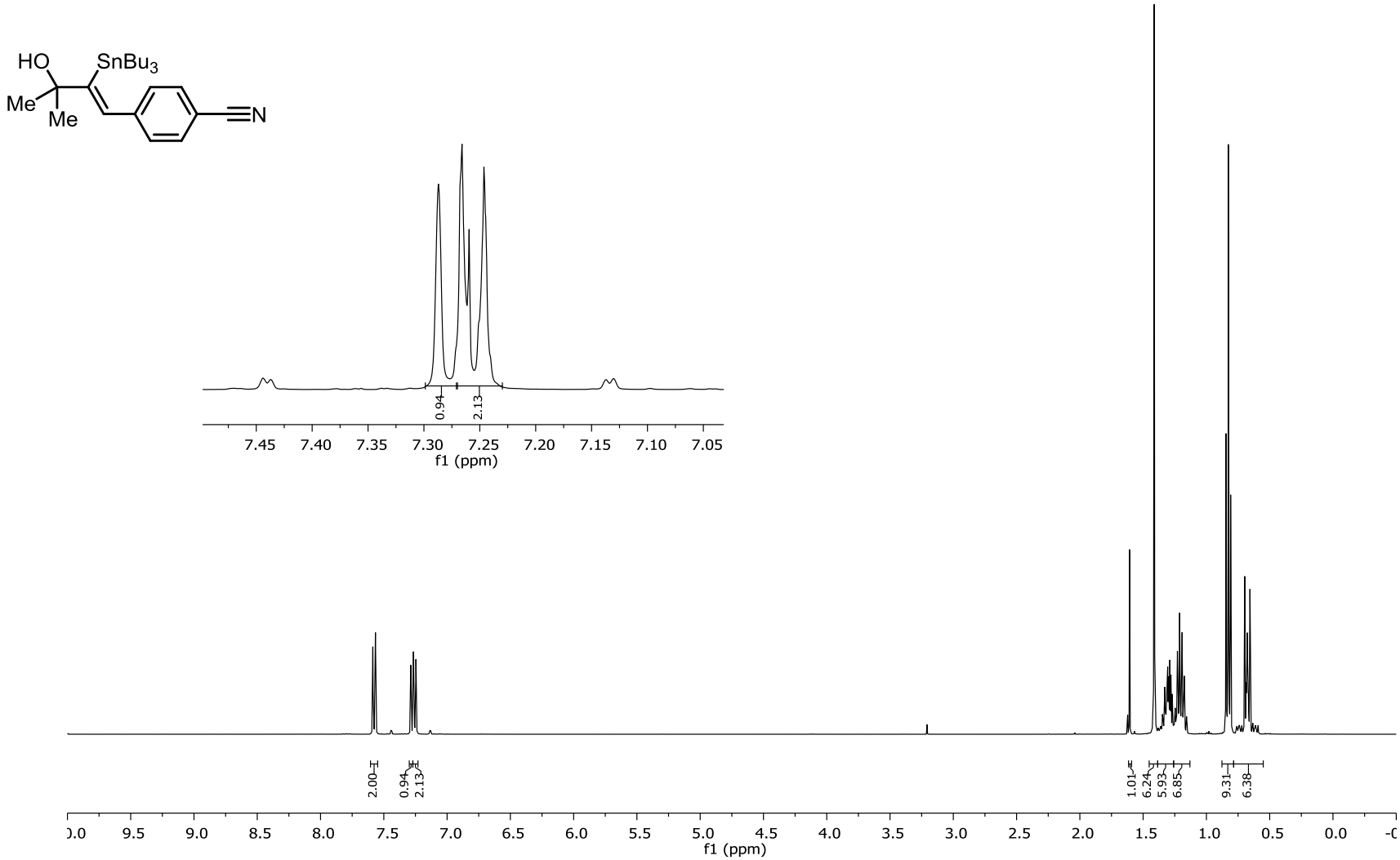
N-(3-Fluoro-1-phenylbut-3-en-1-yl)-4-methylbenzenesulfonamide



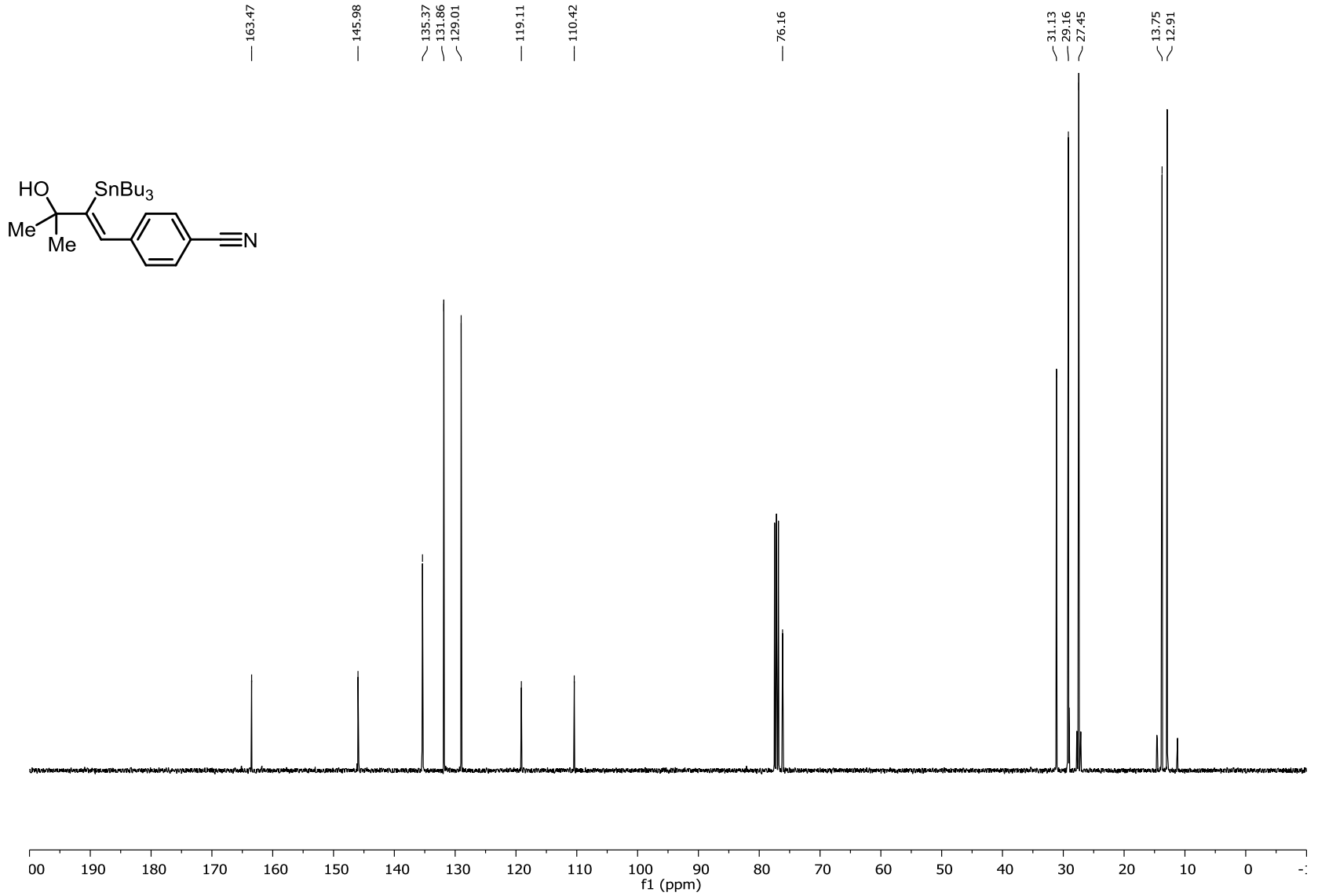
N-(3-Fluoro-1-phenylbut-3-en-1-yl)-4-methylbenzenesulfonamide



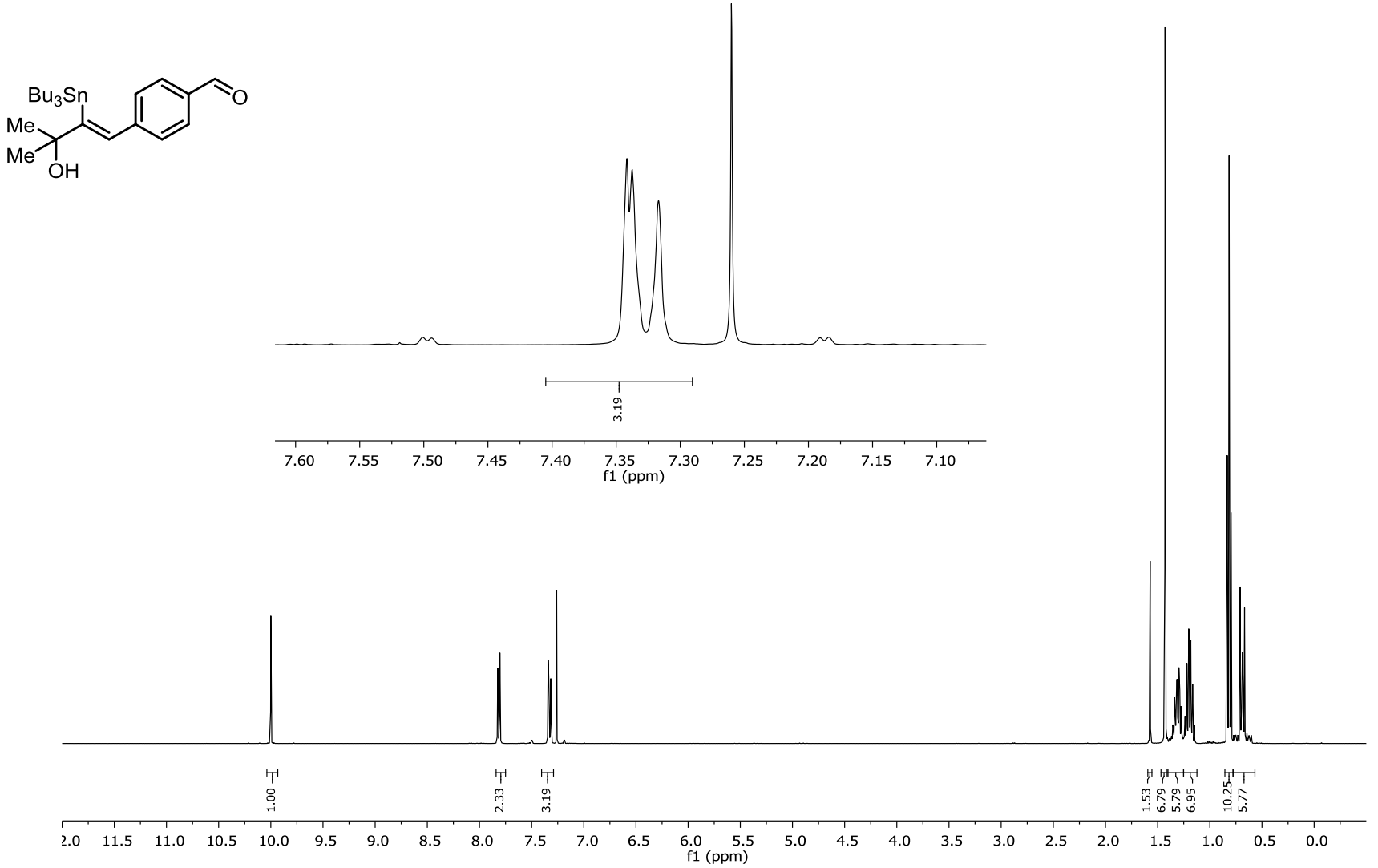
(Z)-4-(3-Hydroxy-3-methyl-2-(tributylstannyl)but-1-en-1-yl)benzonitrile



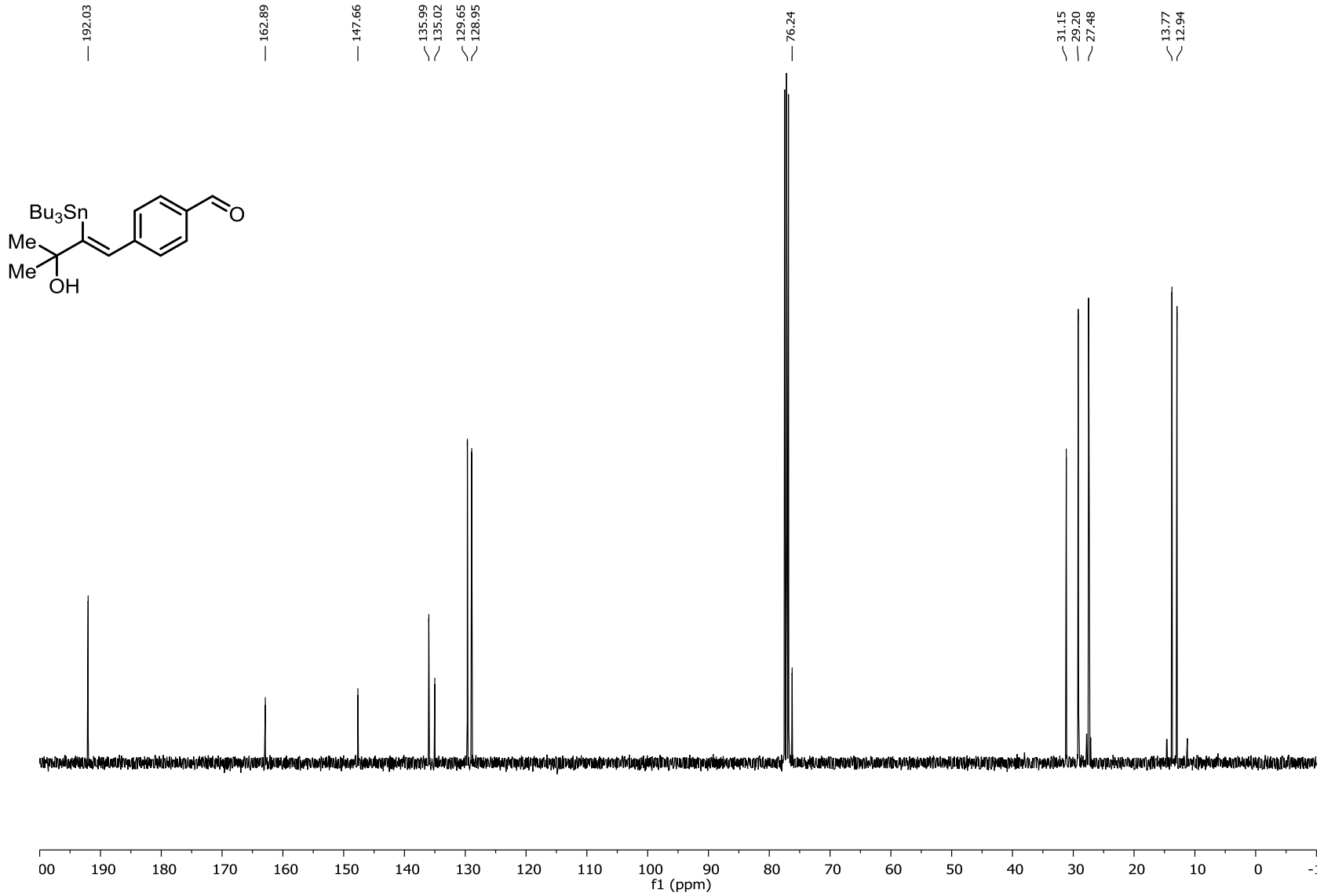
(Z)-4-(3-Hydroxy-3-methyl-2-(tributylstannyl)but-1-en-1-yl)benzonitrile



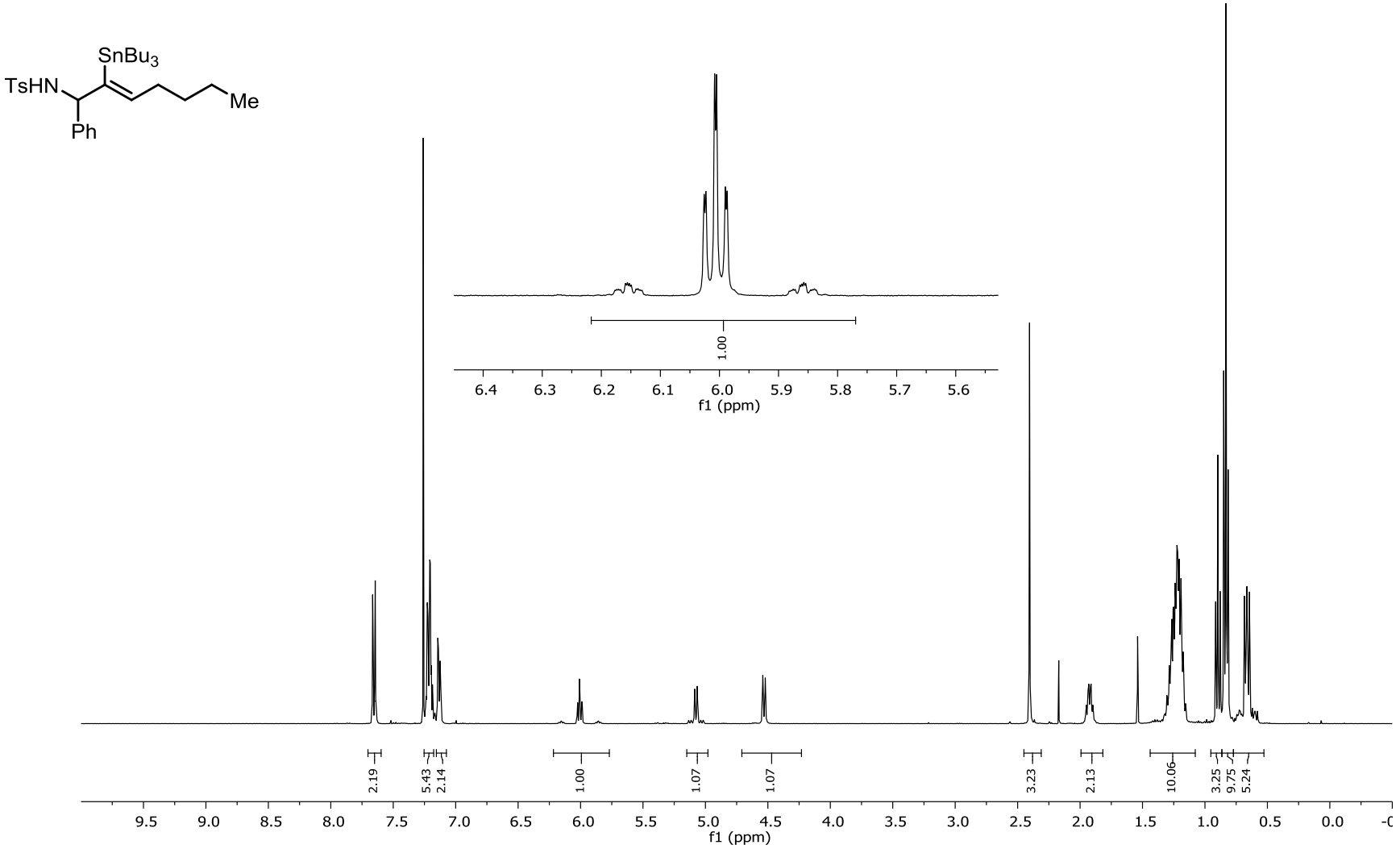
(Z)-4-(3-Hydroxy-3-methyl-2-(tributylstannyl)but-1-en-1-yl)benzaldehyde



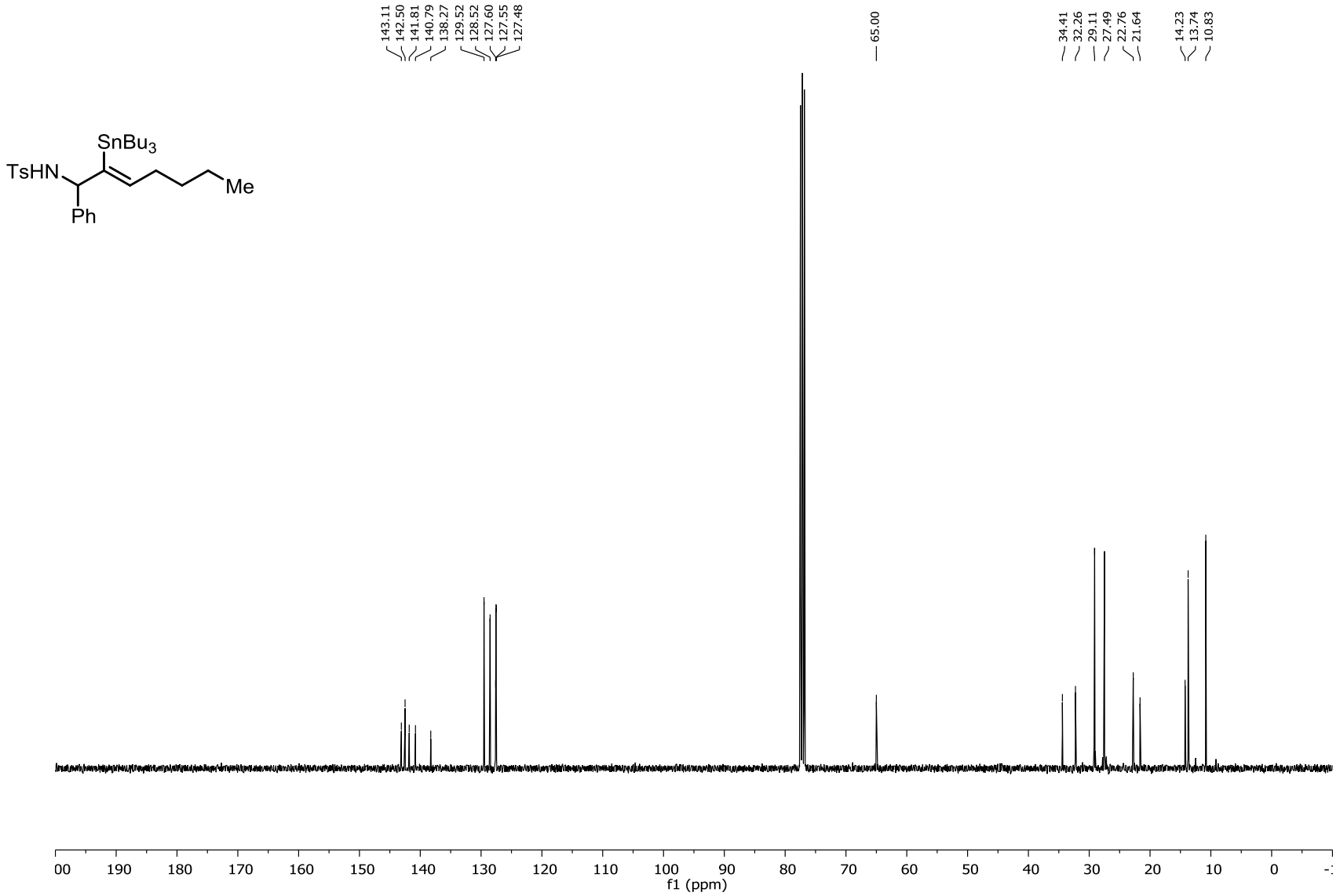
(Z)-4-(3-Hydroxy-3-methyl-2-(tributylstannyl)but-1-en-1-yl)benzaldehyde



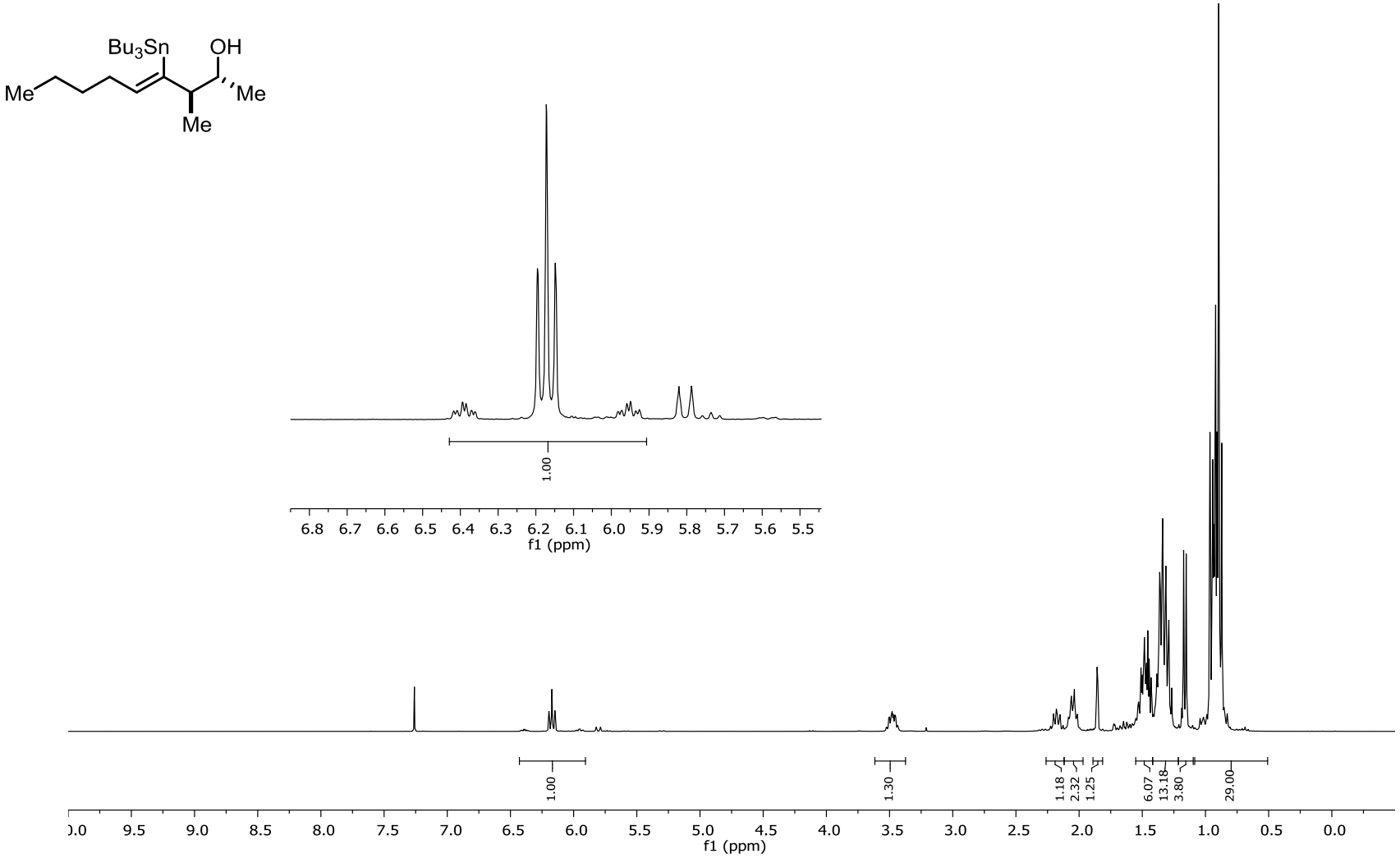
(Z)-4-Methyl-N-(1-phenyl-2-(tributylstannyl)hept-2-en-1-yl)benzenesulfonamide



(Z)-4-Methyl-N-(1-phenyl-2-(tributylstannyl)hept-2-en-1-yl)benzenesulfonamide



(*anti*,Z)-3-Methyl-4-(tributylstannyl)non-4-en-2-ol



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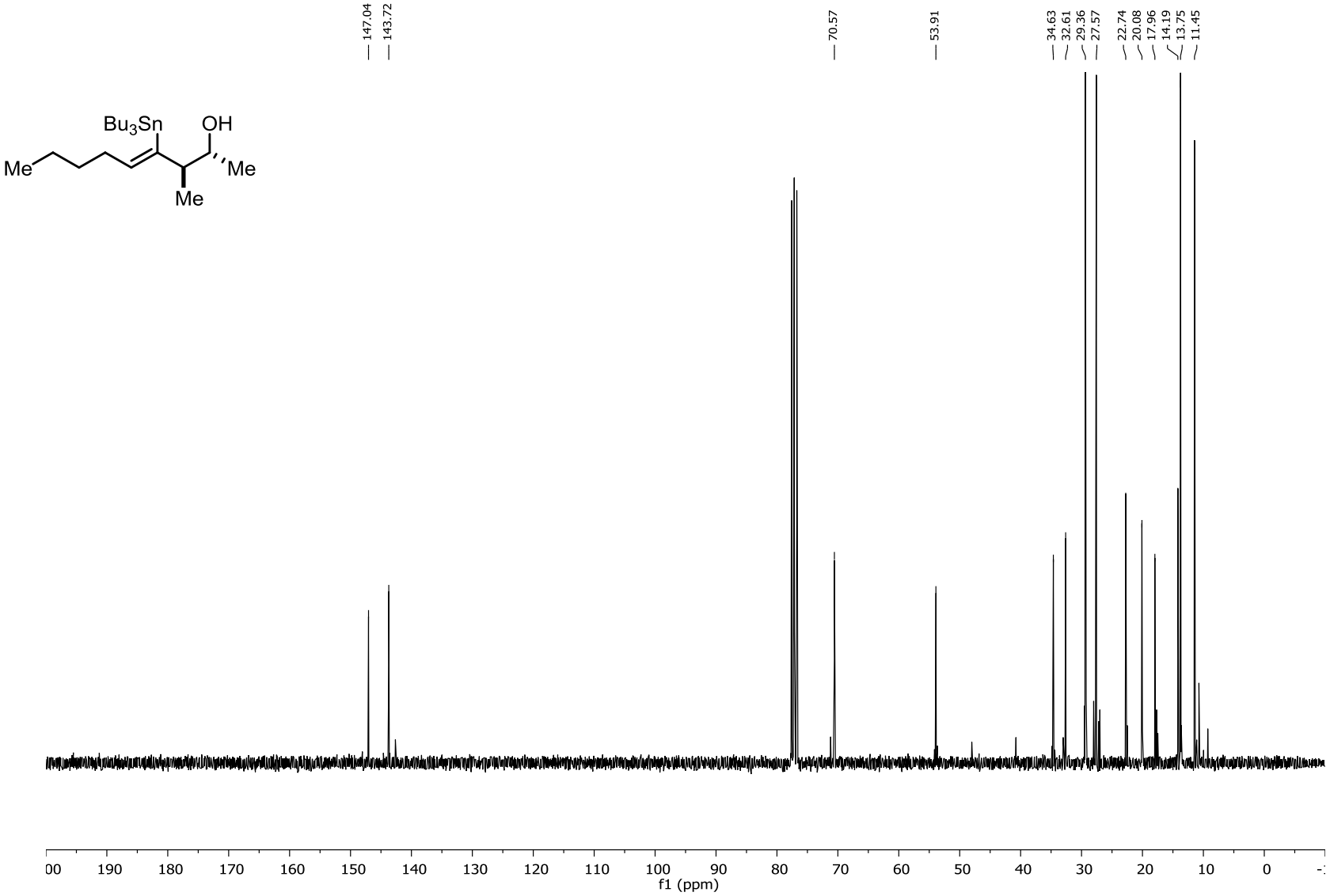
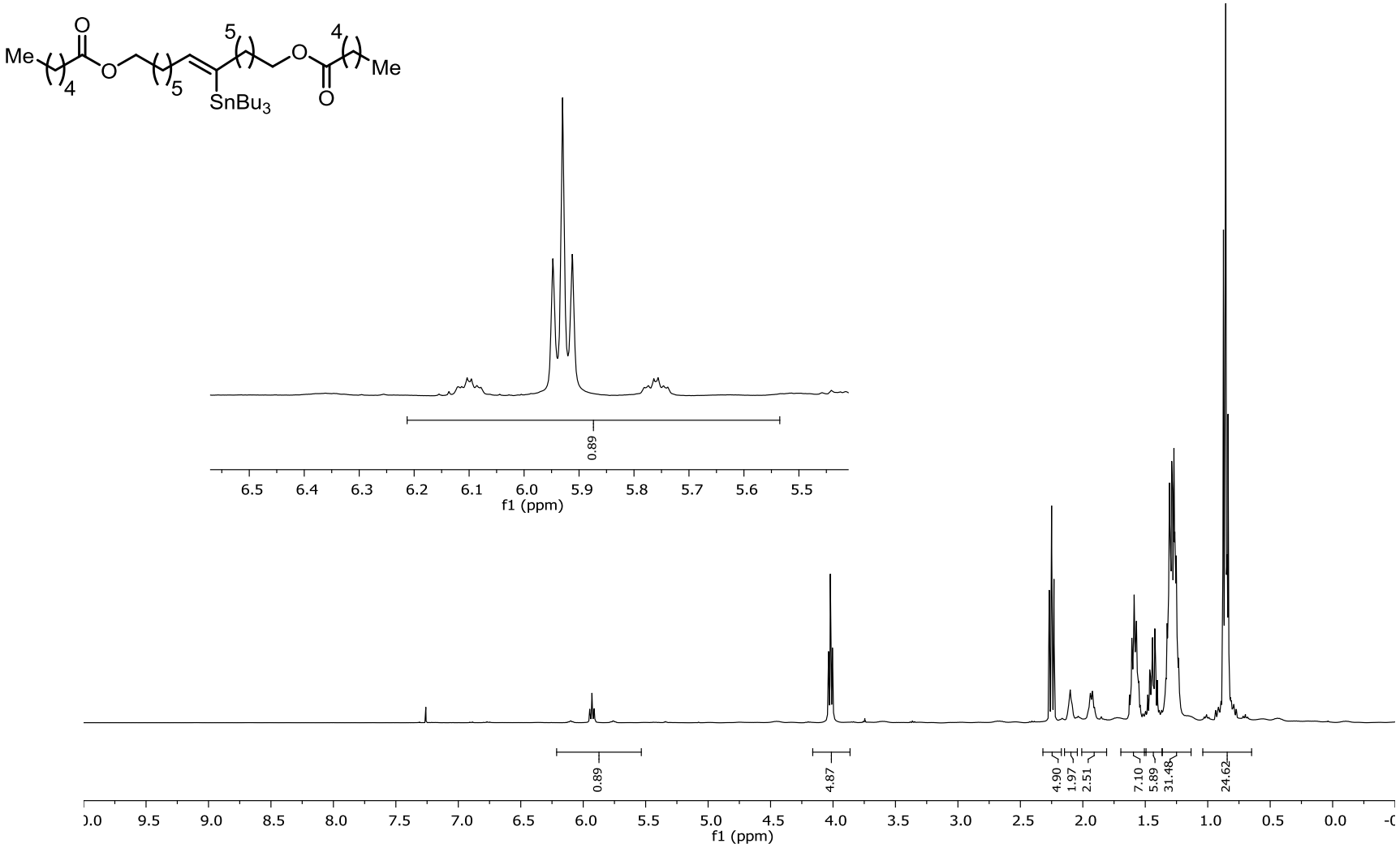
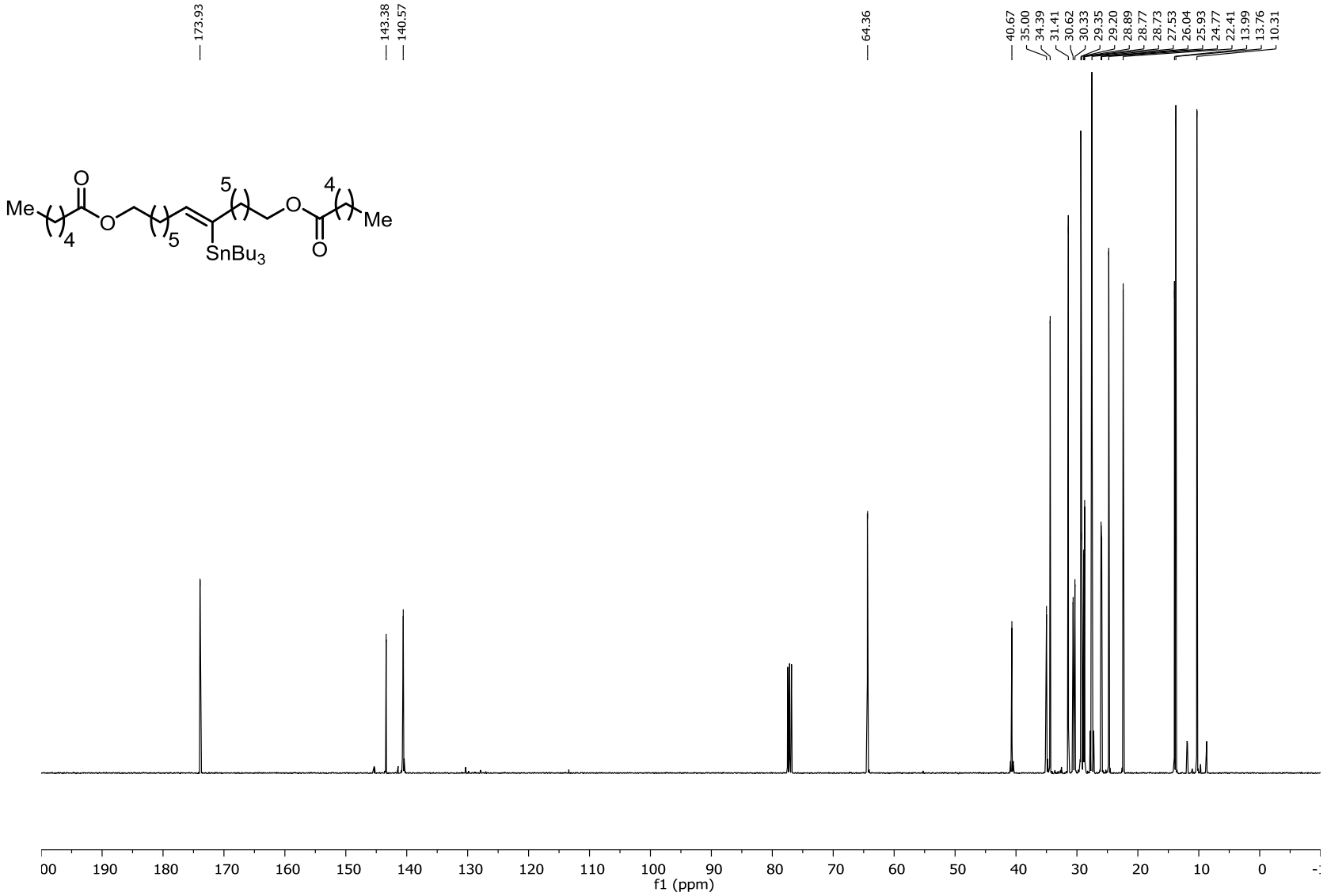


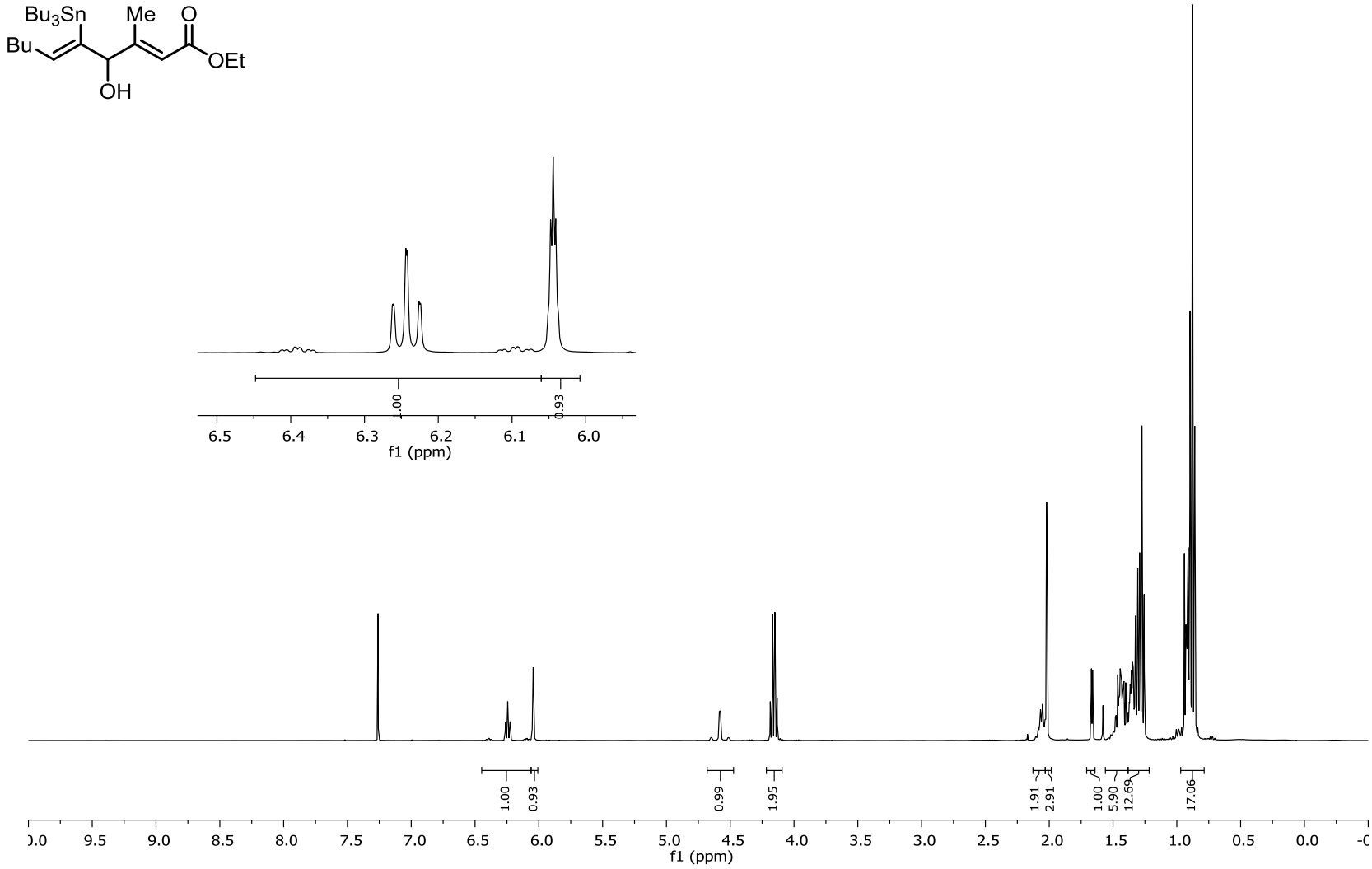
(Z)-7-(Tributylstannyl)tetradec-7-ene-1,14-diyl dihexanoate



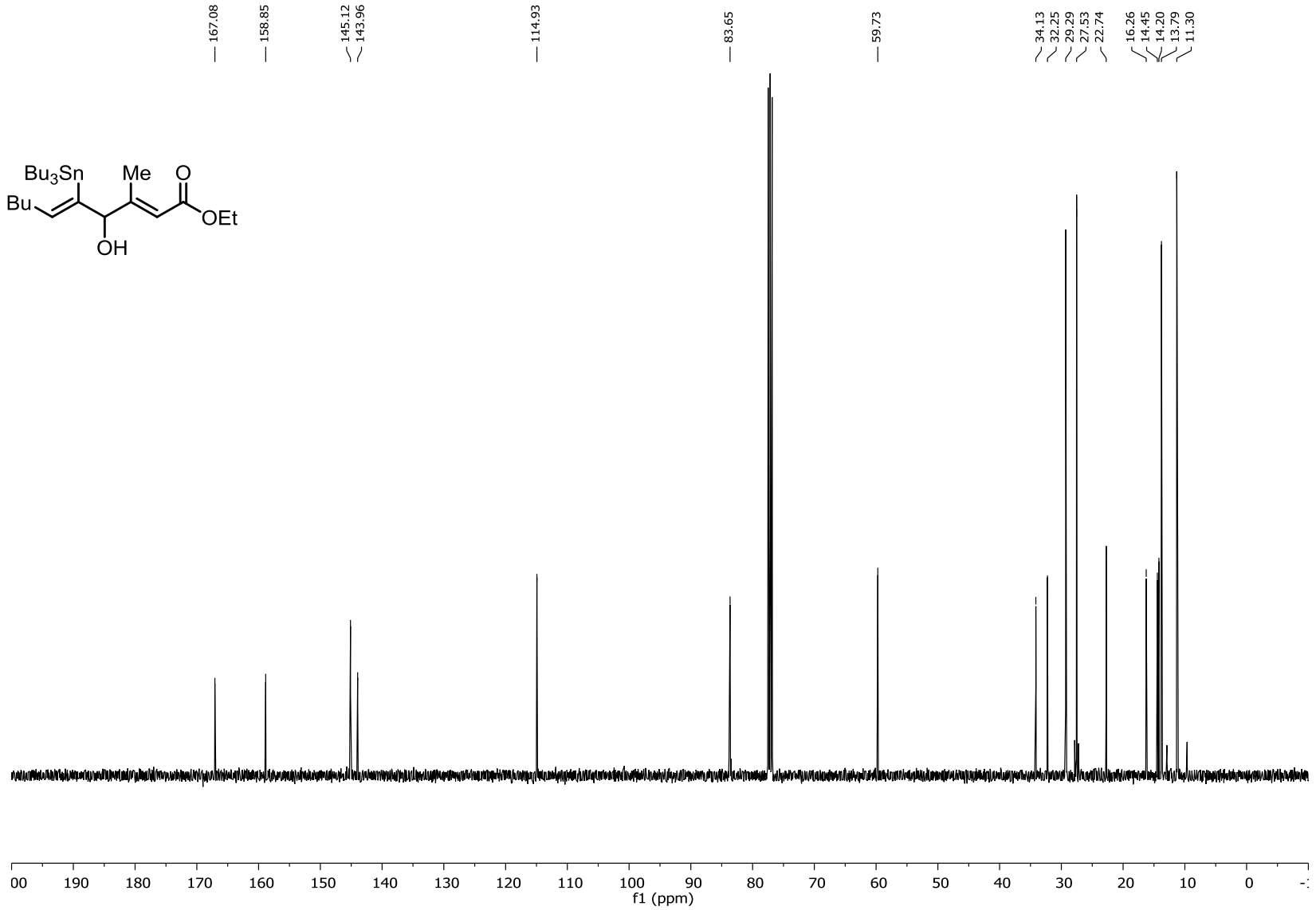
(Z)-7-(Tributylstannyl)tetradec-7-ene-1,14-diyl dihexanoate



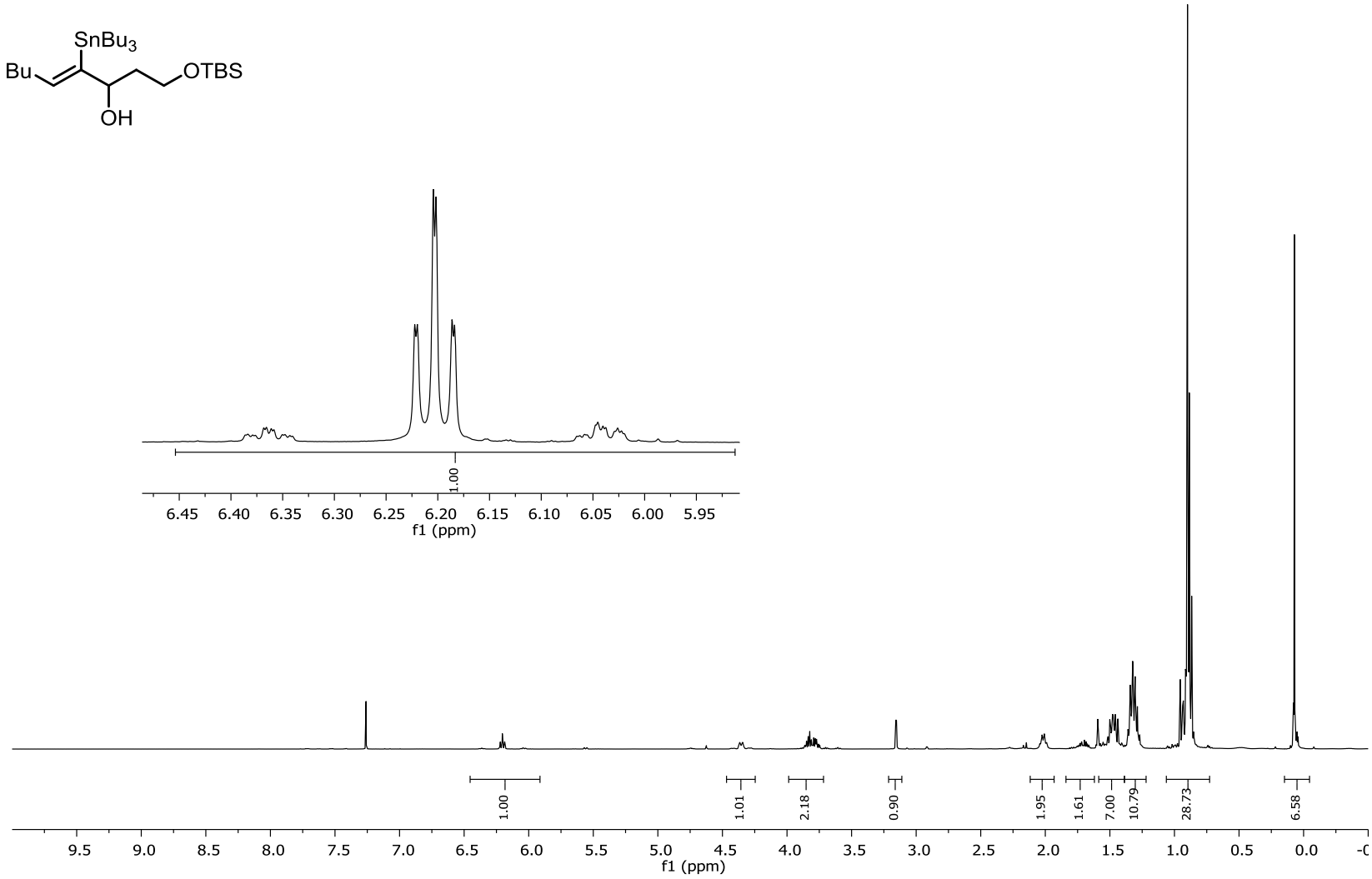
Ethyl (2E,5Z)-4-hydroxy-3-methyl-5-(tributylstannyl)deca-2,5-dienoate



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



(Z)-1-((*tert*-Butyldimethylsilyl)oxy)-4-(tributylstannyl)non-4-en-3-ol



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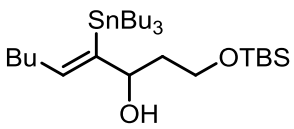
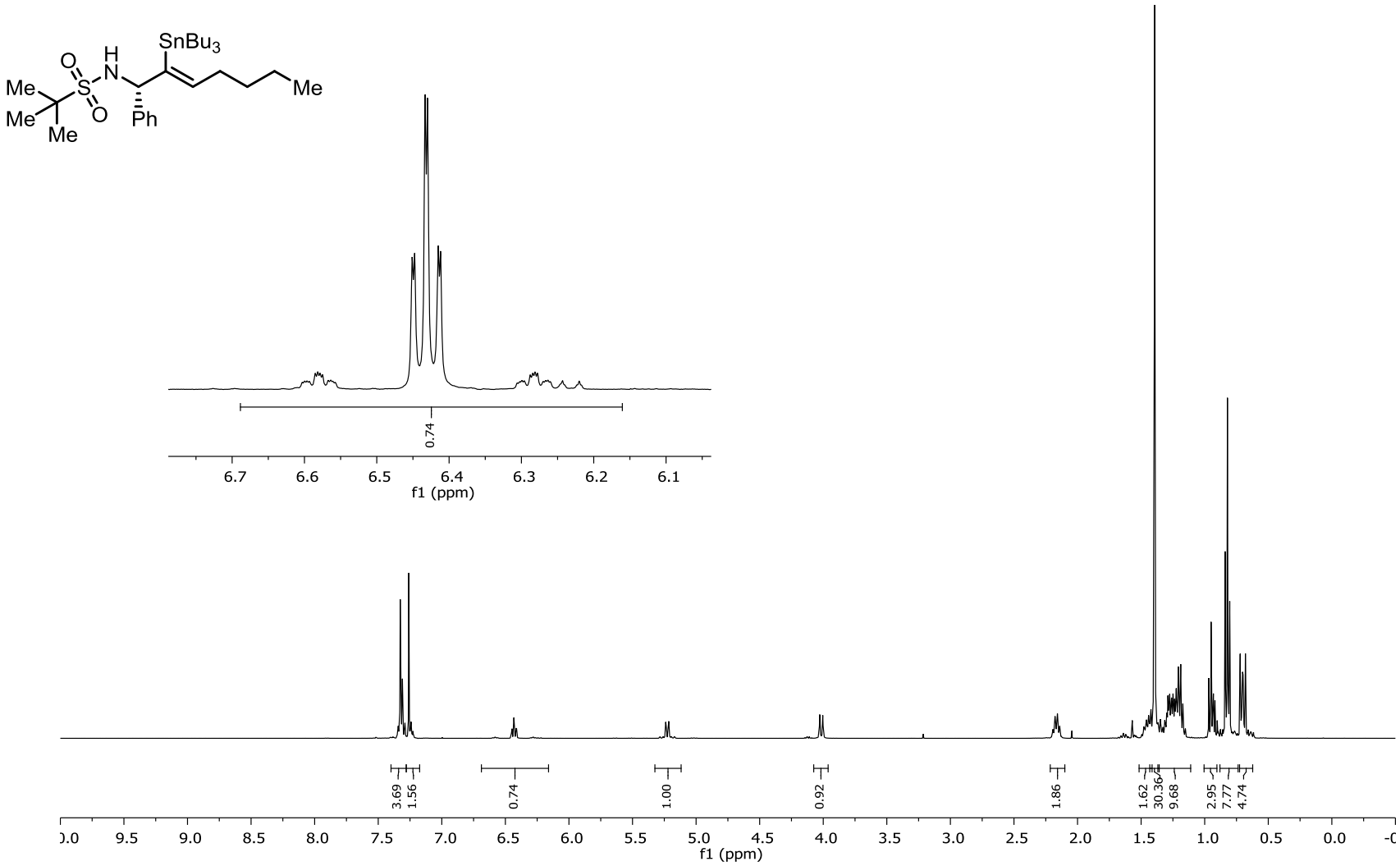


(S,Z)-2-Methyl-N-(1-phenyl-2-(tributylstannyl)hept-2-en-1-yl)propane-2-sulfonamide



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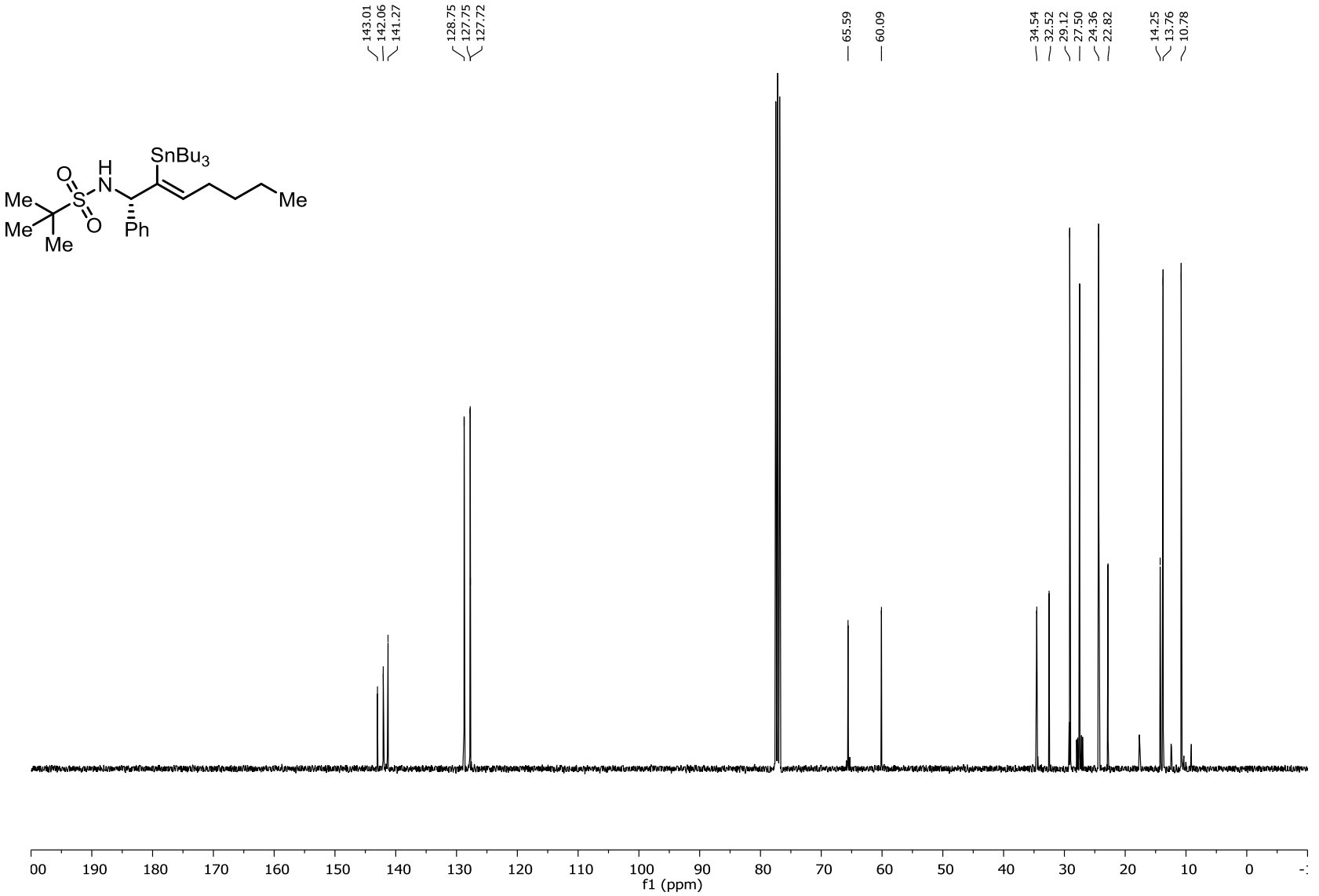
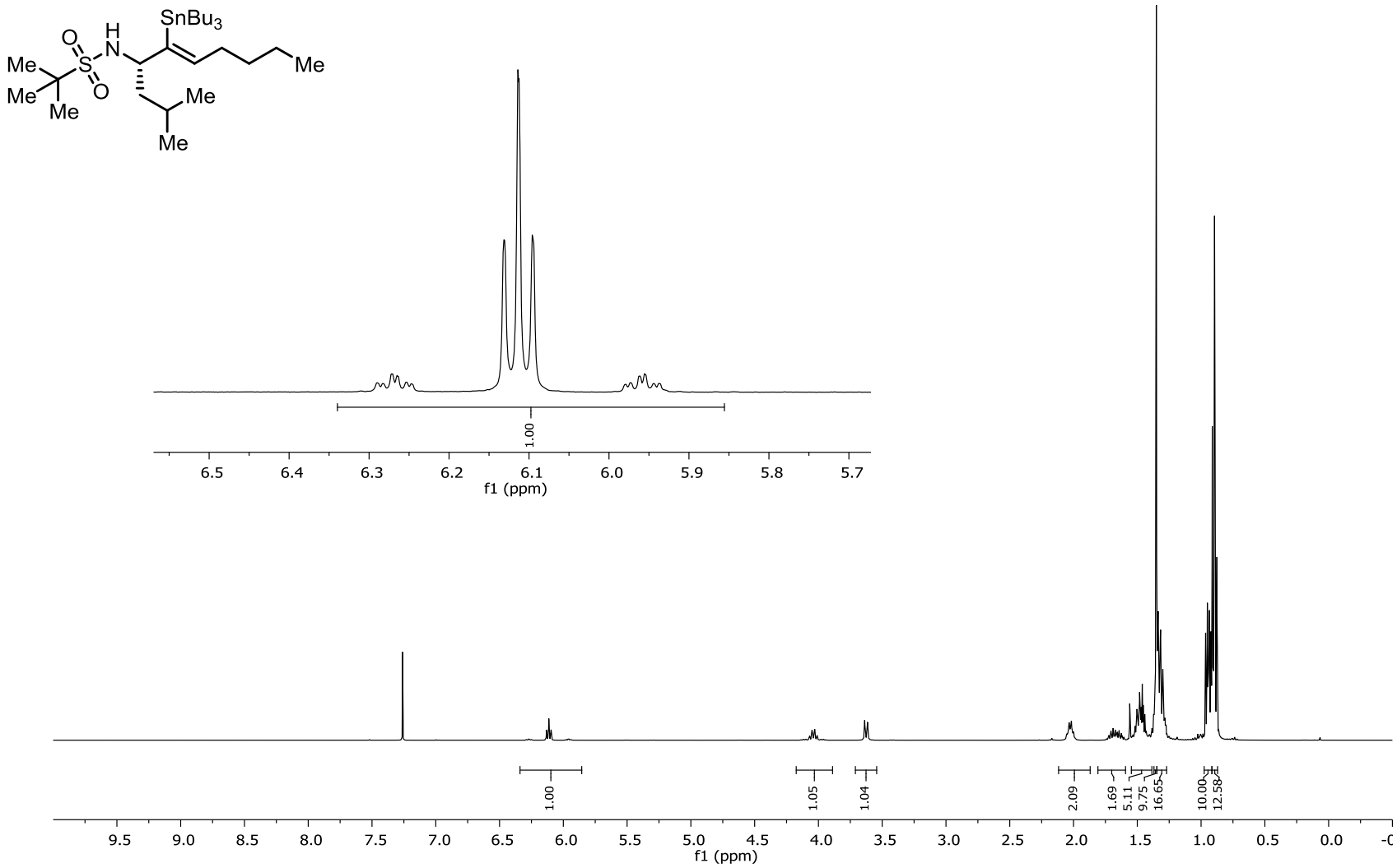
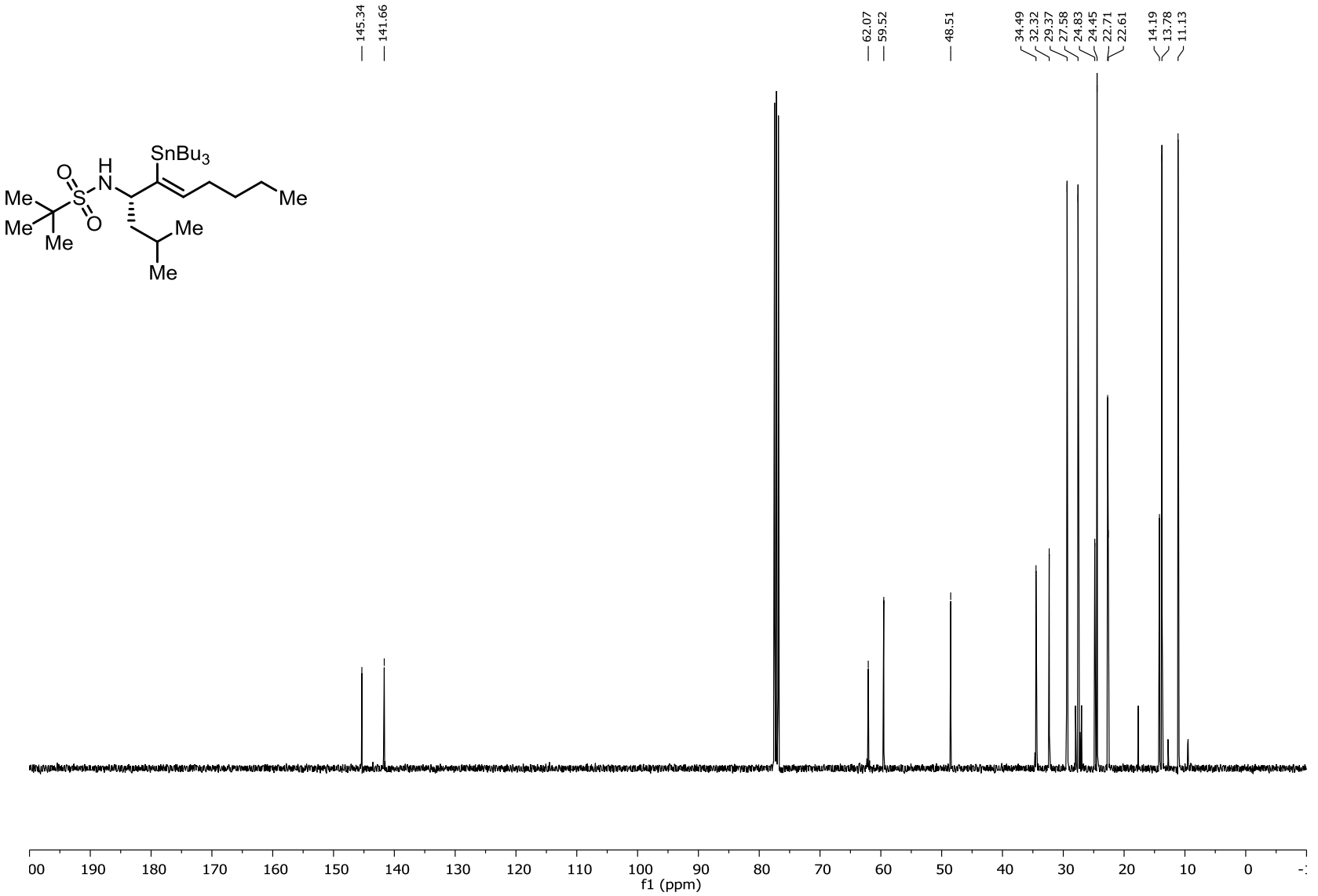


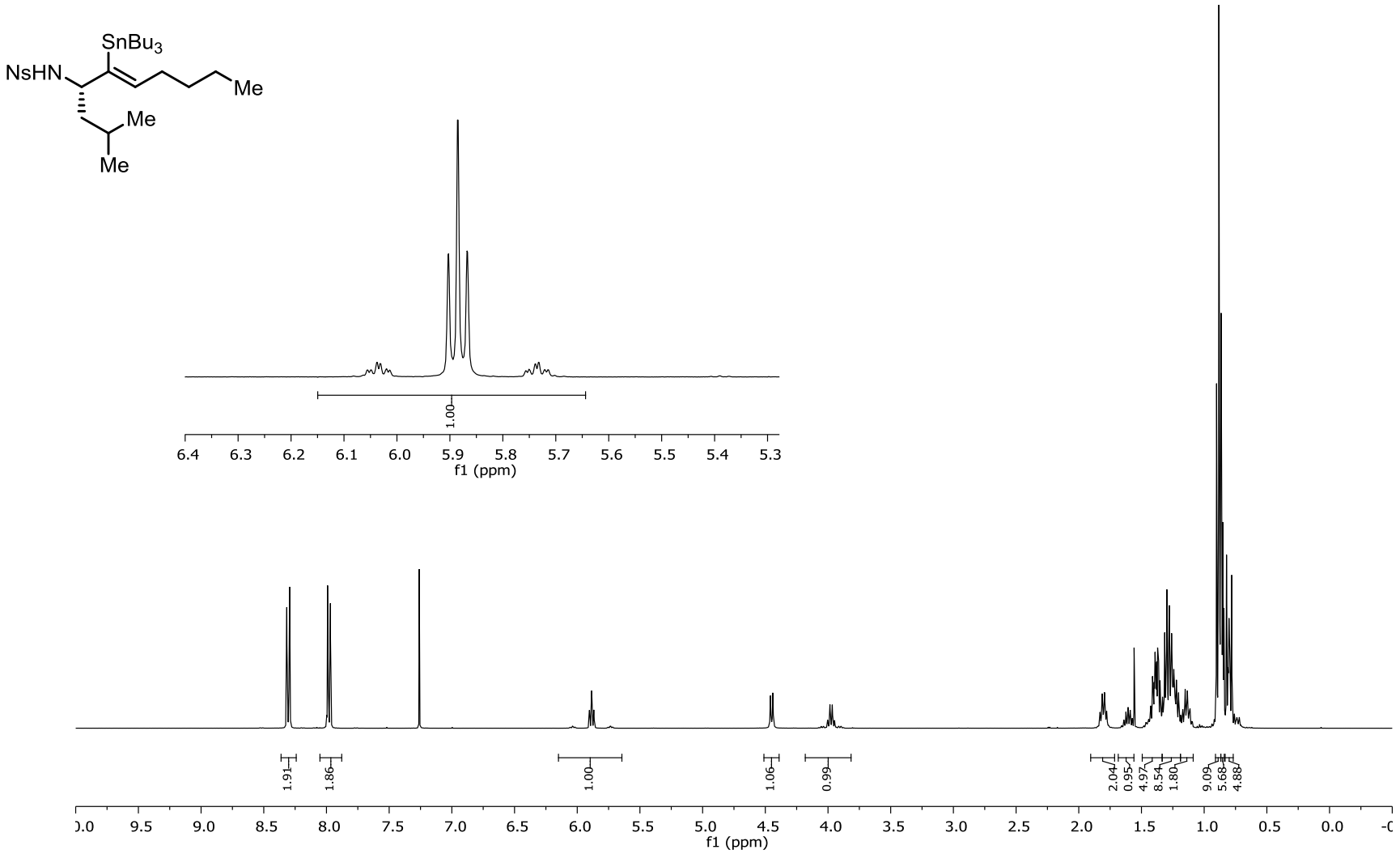
(S,Z)-2-Methyl-N-(2-methyl-5-(tributylstannyl)dec-5-en-4-yl)propane-2-sulfonamide



(S,Z)-2-Methyl-N-(2-methyl-5-(tributylstannyl)dec-5-en-4-yl)propane-2-sulfonamide



(S,Z)-N-(2-Methyl-5-(tributylstannyl)dec-5-en-4-yl)-4-nitrobenzenesulfonamide



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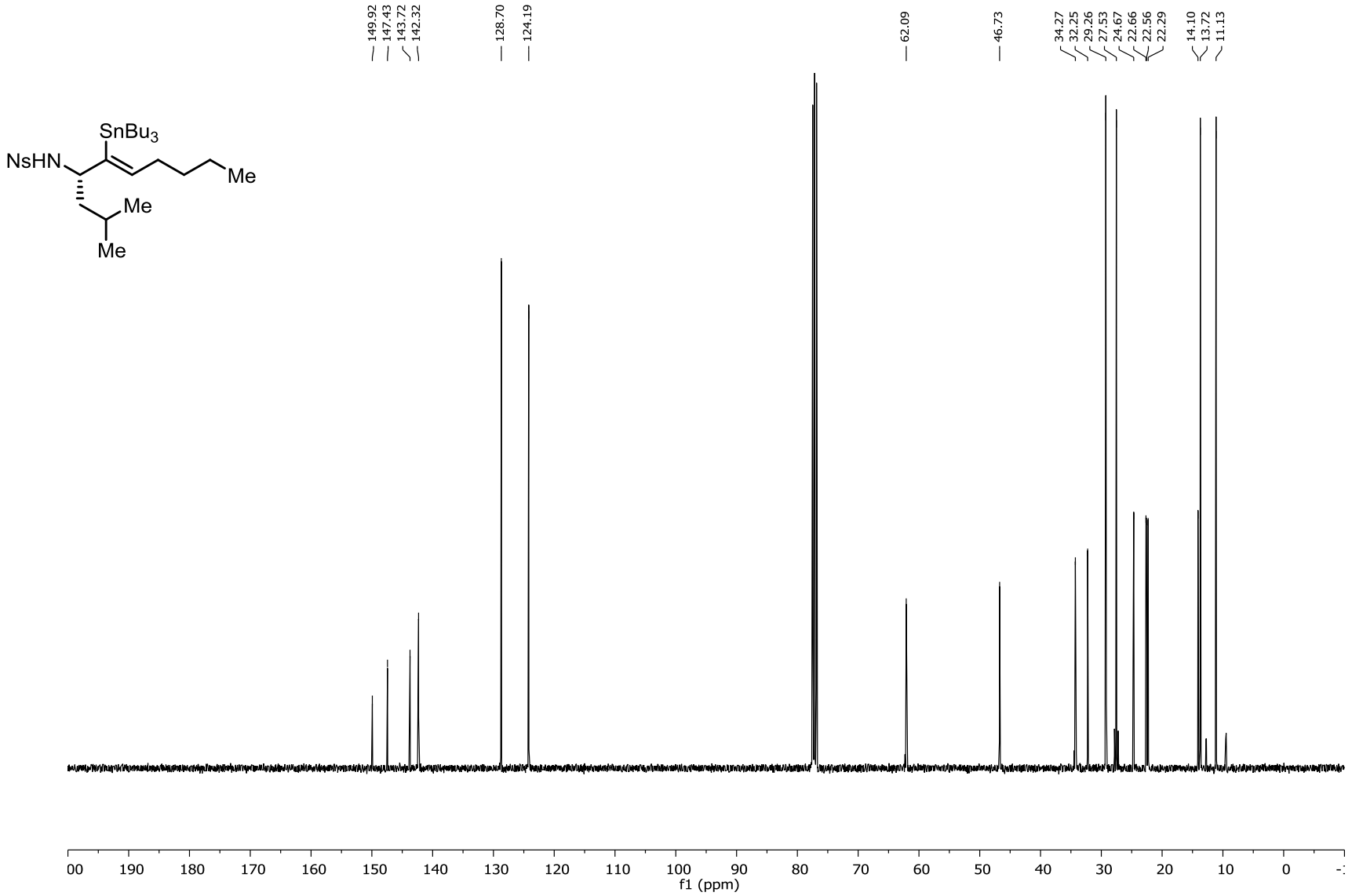
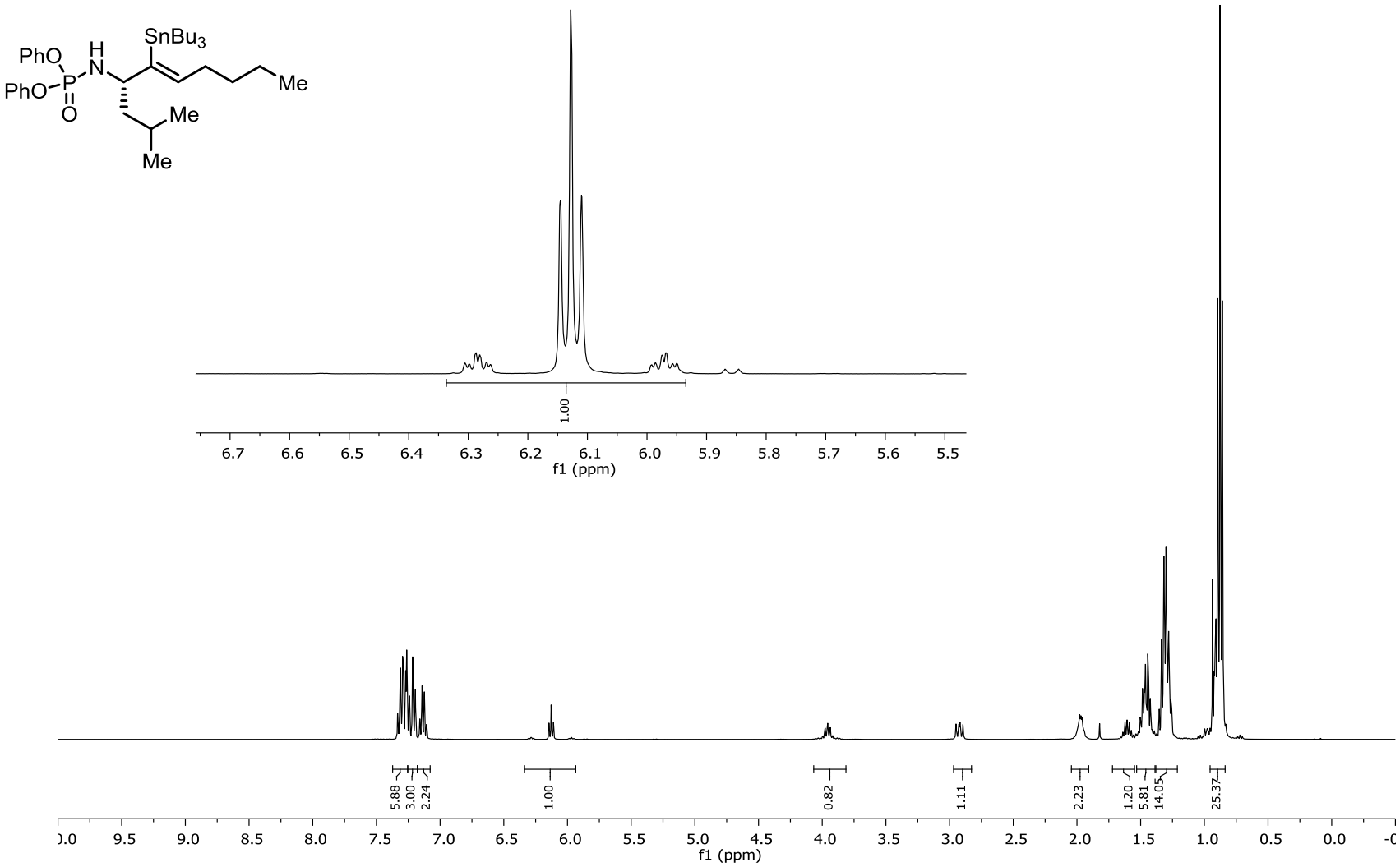
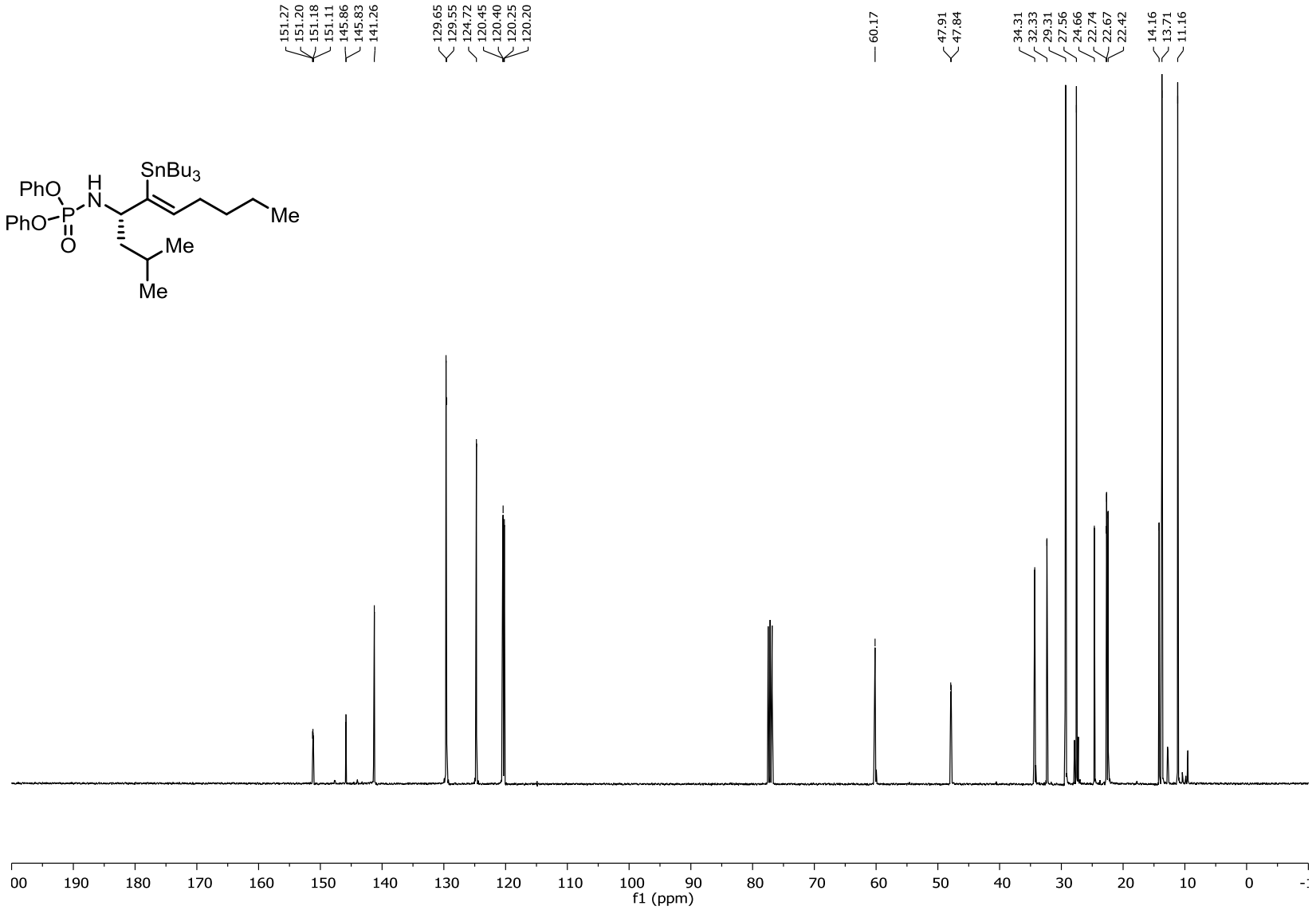


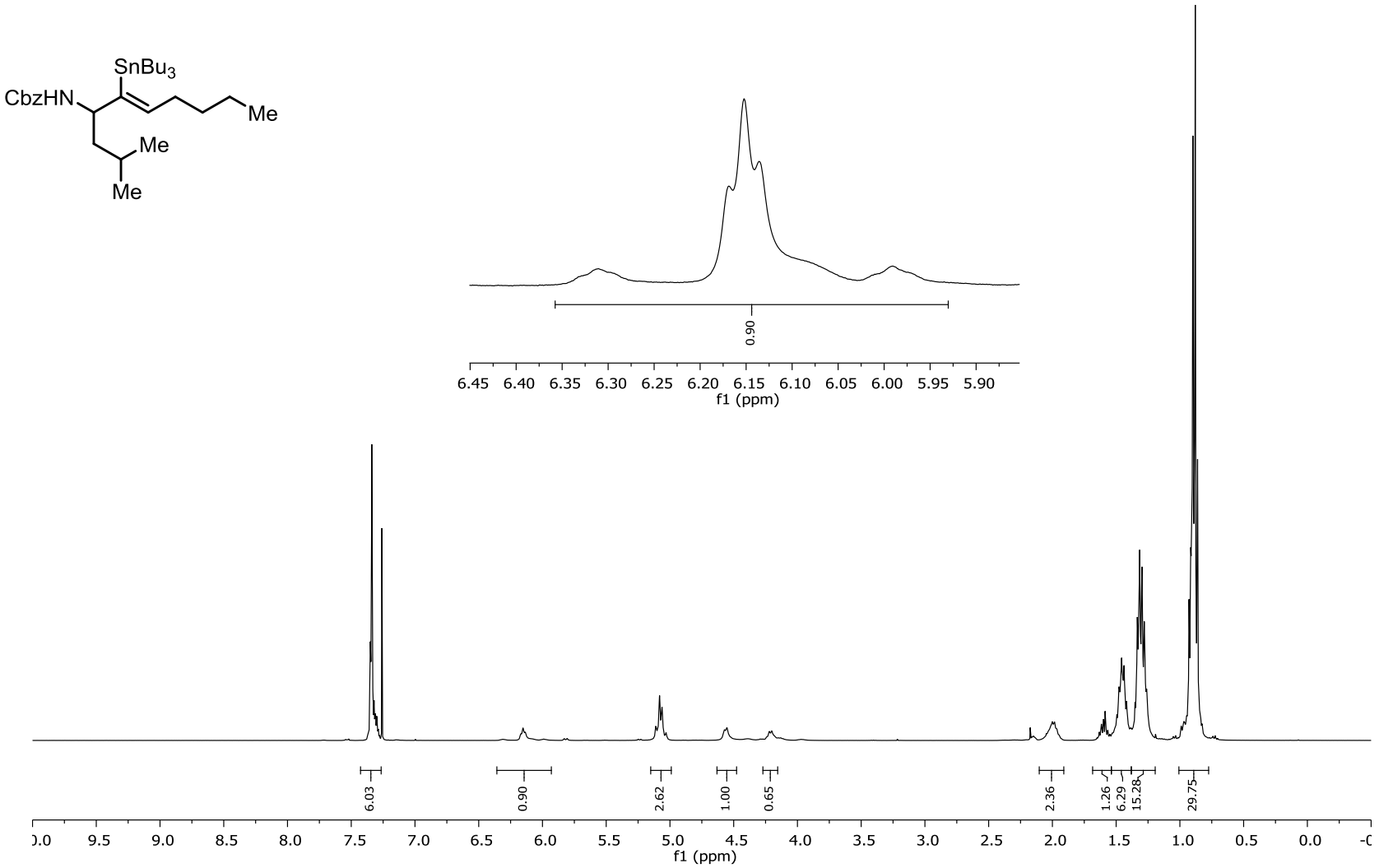
Diphenyl (*S*,*Z*)-(2-methyl-5-(tributylstannyl)dec-5-en-4-yl)phosphoramidate



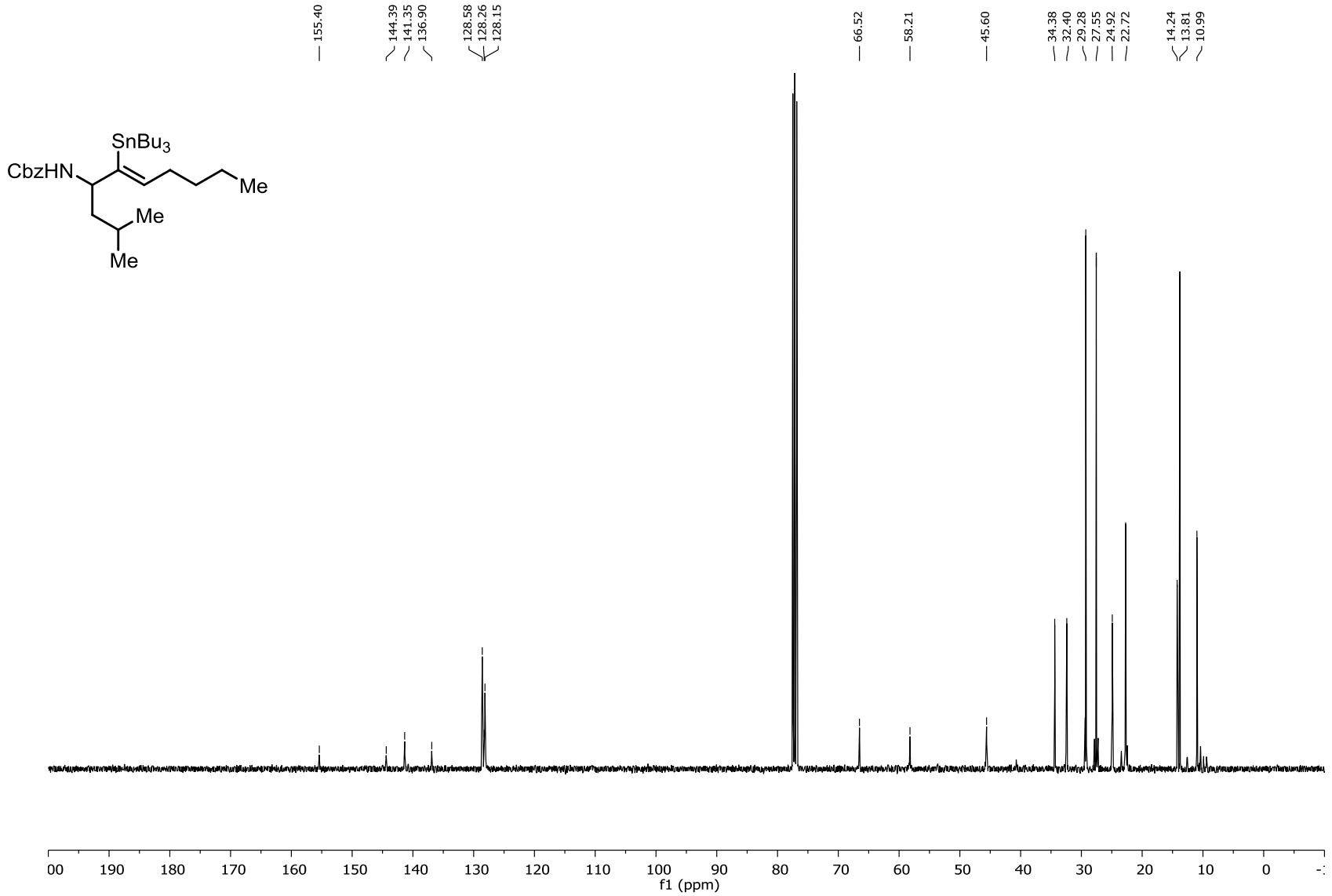
Diphenyl (*S*,*Z*)-(2-methyl-5-(tributylstannyl)dec-5-en-4-yl)phosphoramidate



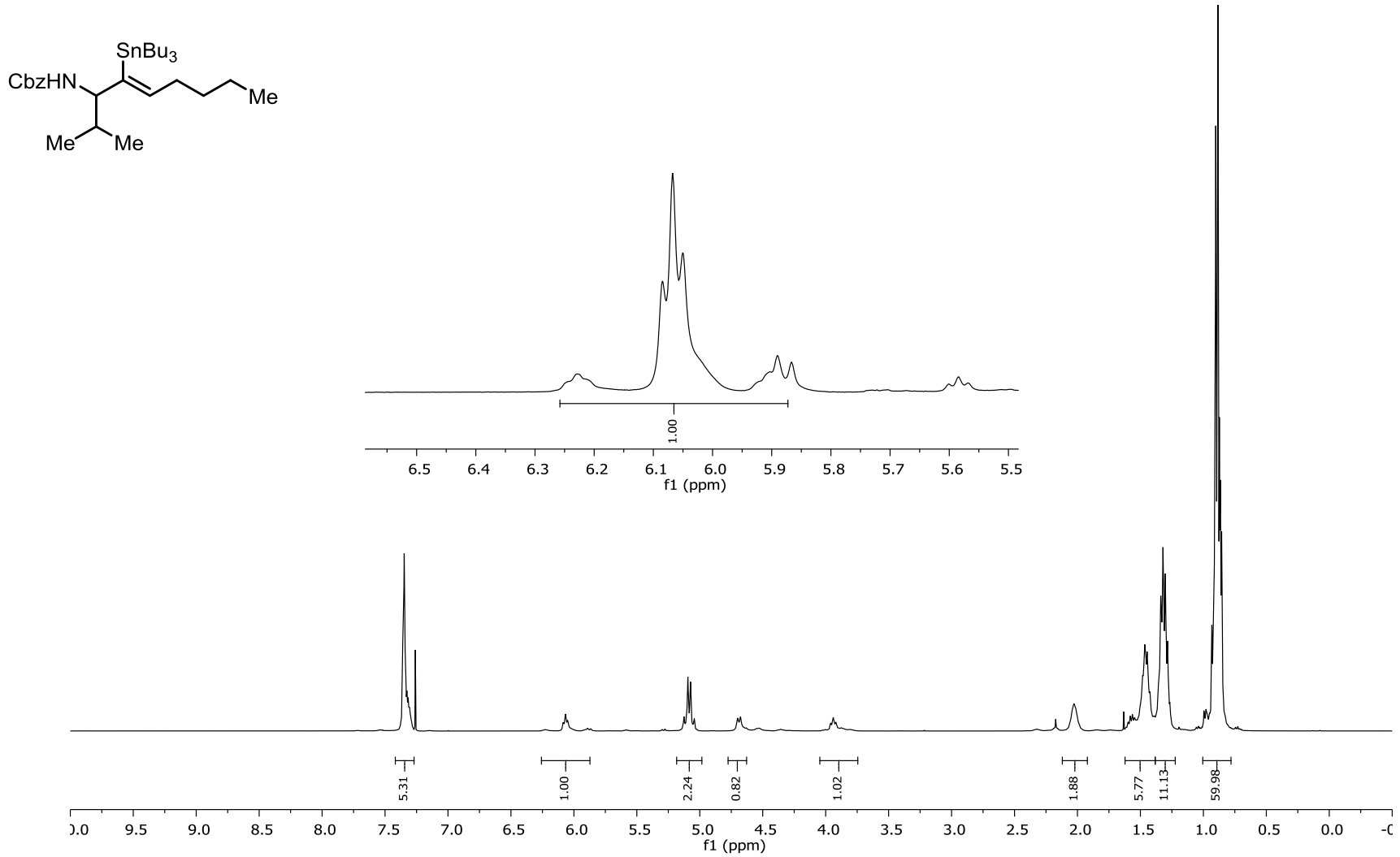
Benzyl (Z)-(2-methyl-5-(tributylstannyl)dec-5-en-4-yl)carbamate



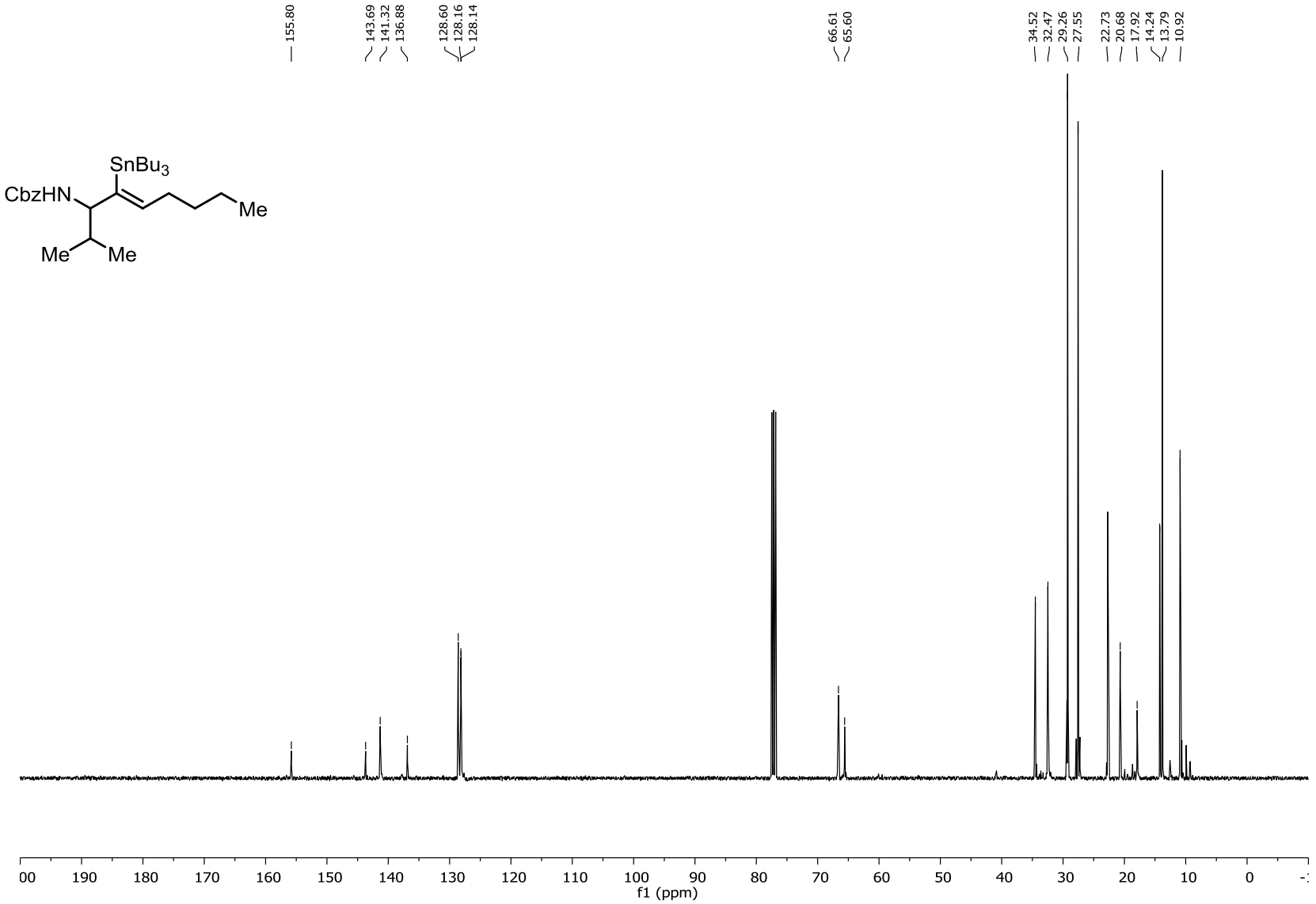
Benzyl (Z)-(2-methyl-5-(tributylstannyl)dec-5-en-4-yl)carbamate



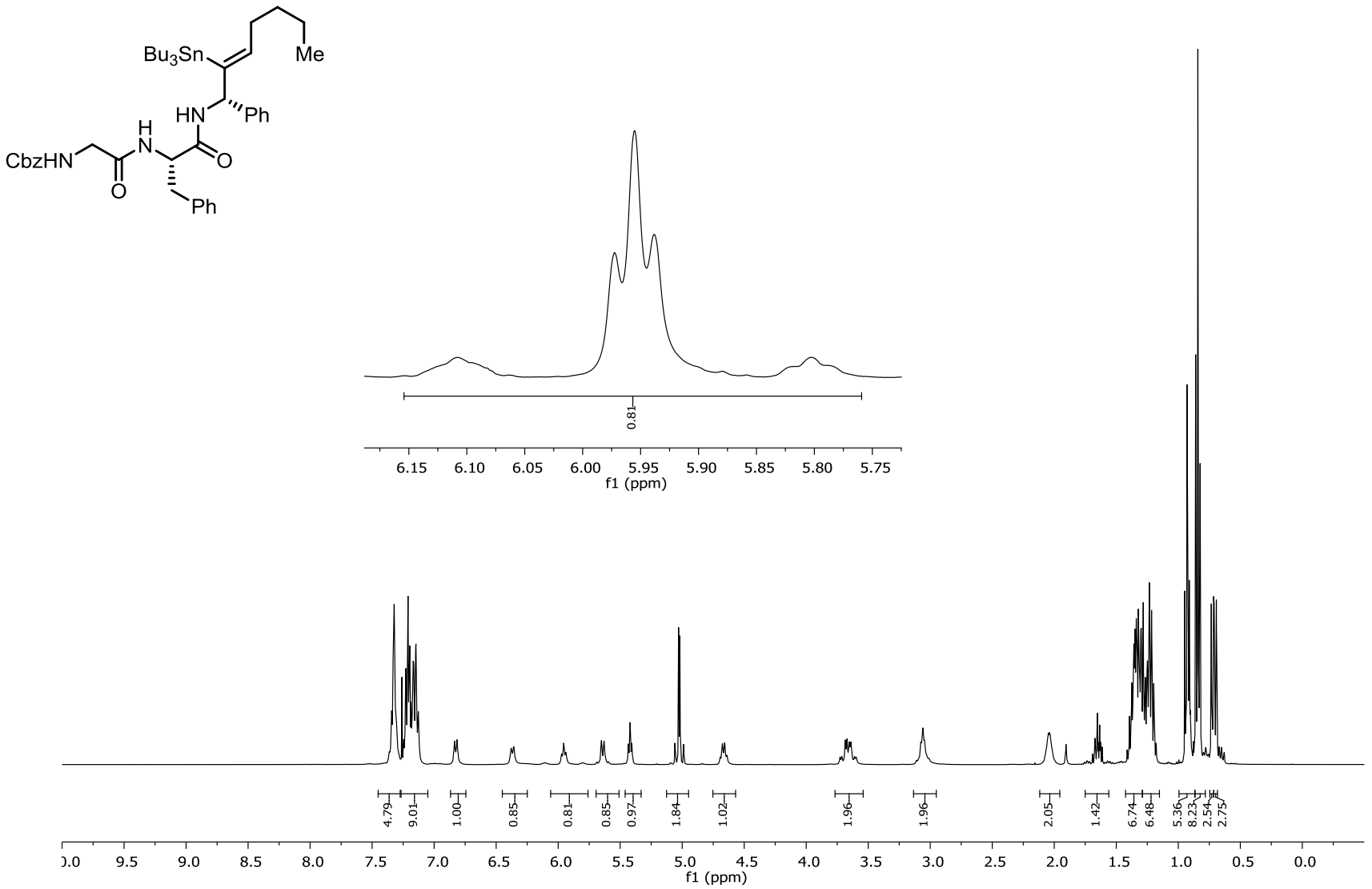
Benzyl (Z)-(2-methyl-4-(tributylstannyl)non-4-en-3-yl)carbamate



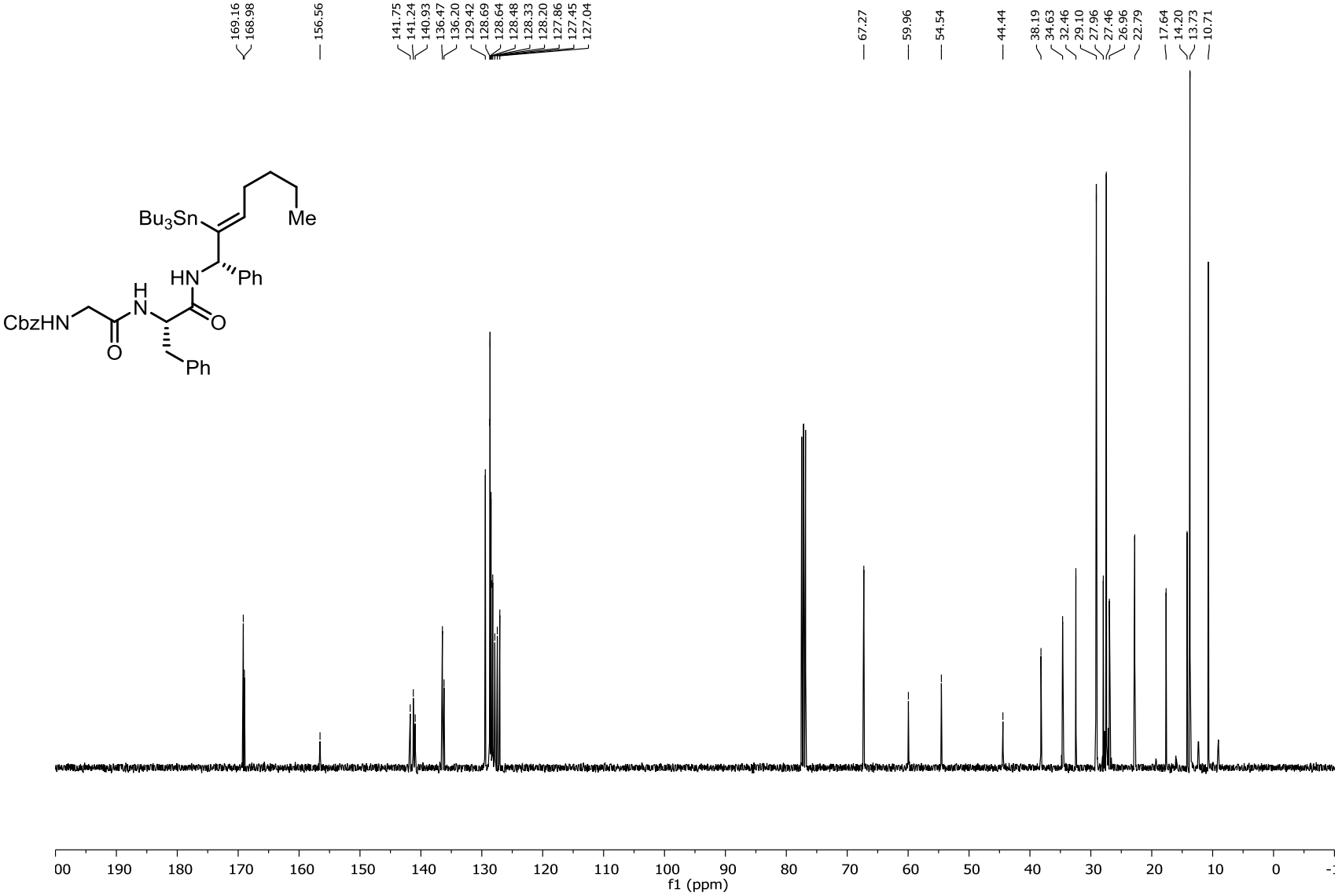
Benzyl (Z)-(2-methyl-4-(tributylstannyl)non-4-en-3-yl)carbamate



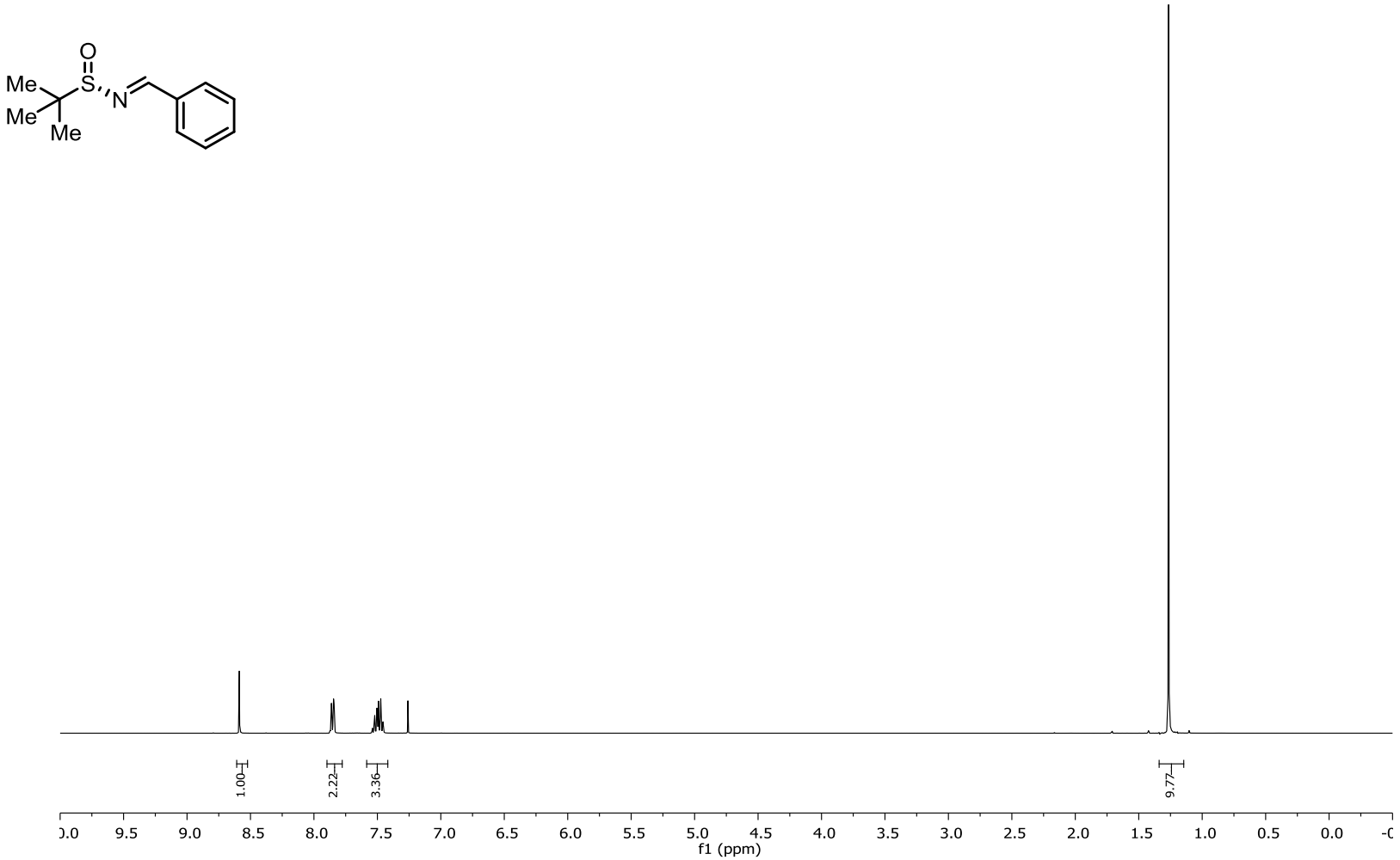
Benzyl (2-oxo-2-(((S)-1-oxo-3-phenyl-1-(((S,Z)-1-phenyl-2-(tributylstannyl)hept-2-en-1-yl)amino)propan-2-yl)amino)ethyl)carbamate



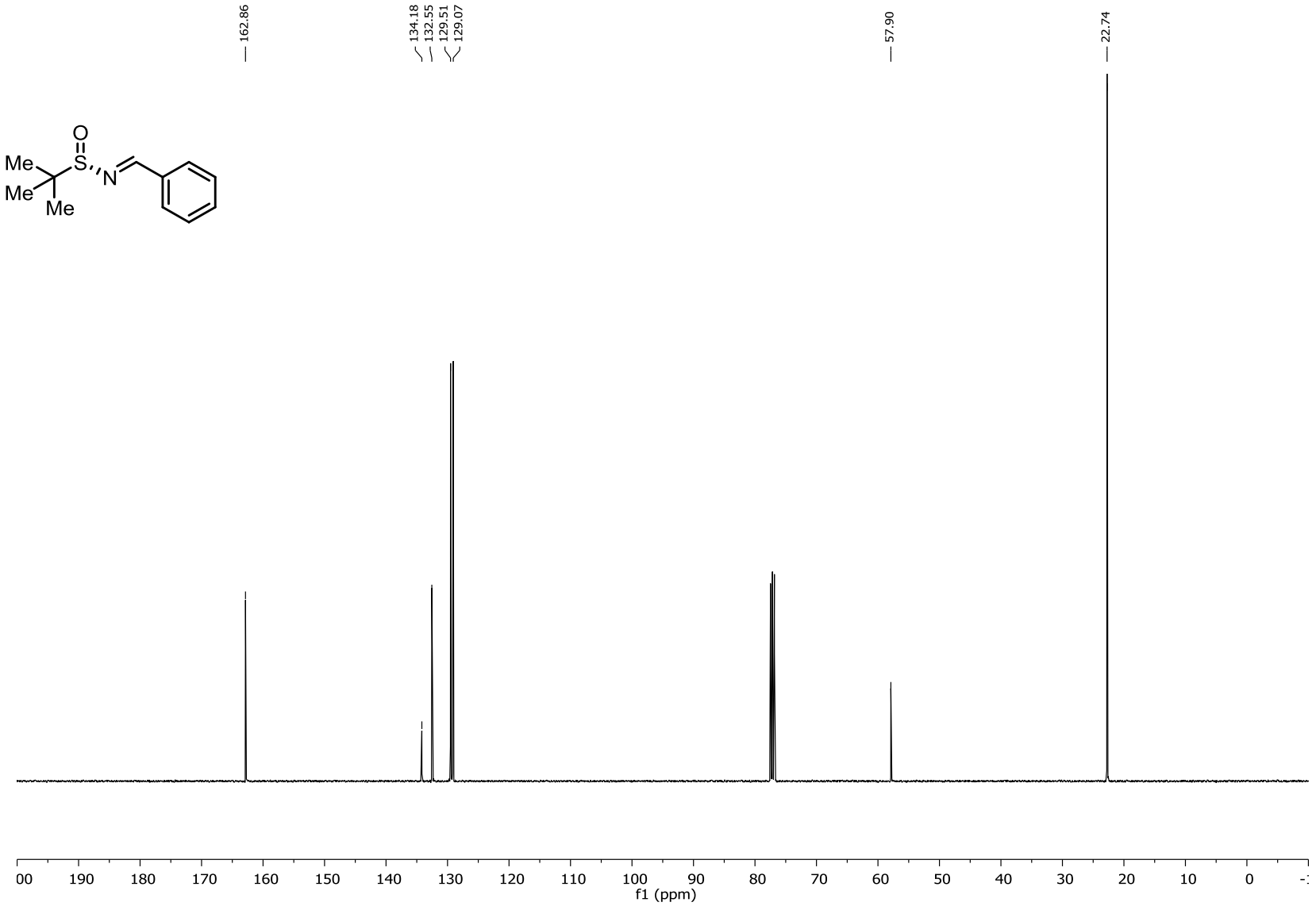
Benzyl (2-oxo-2-(((S)-1-oxo-3-phenyl-1-(((S,Z)-1-phenyl-2-(tributylstannyl)hept-2-en-1-yl)amino)propan-2-yl)amino)ethyl)carbamate



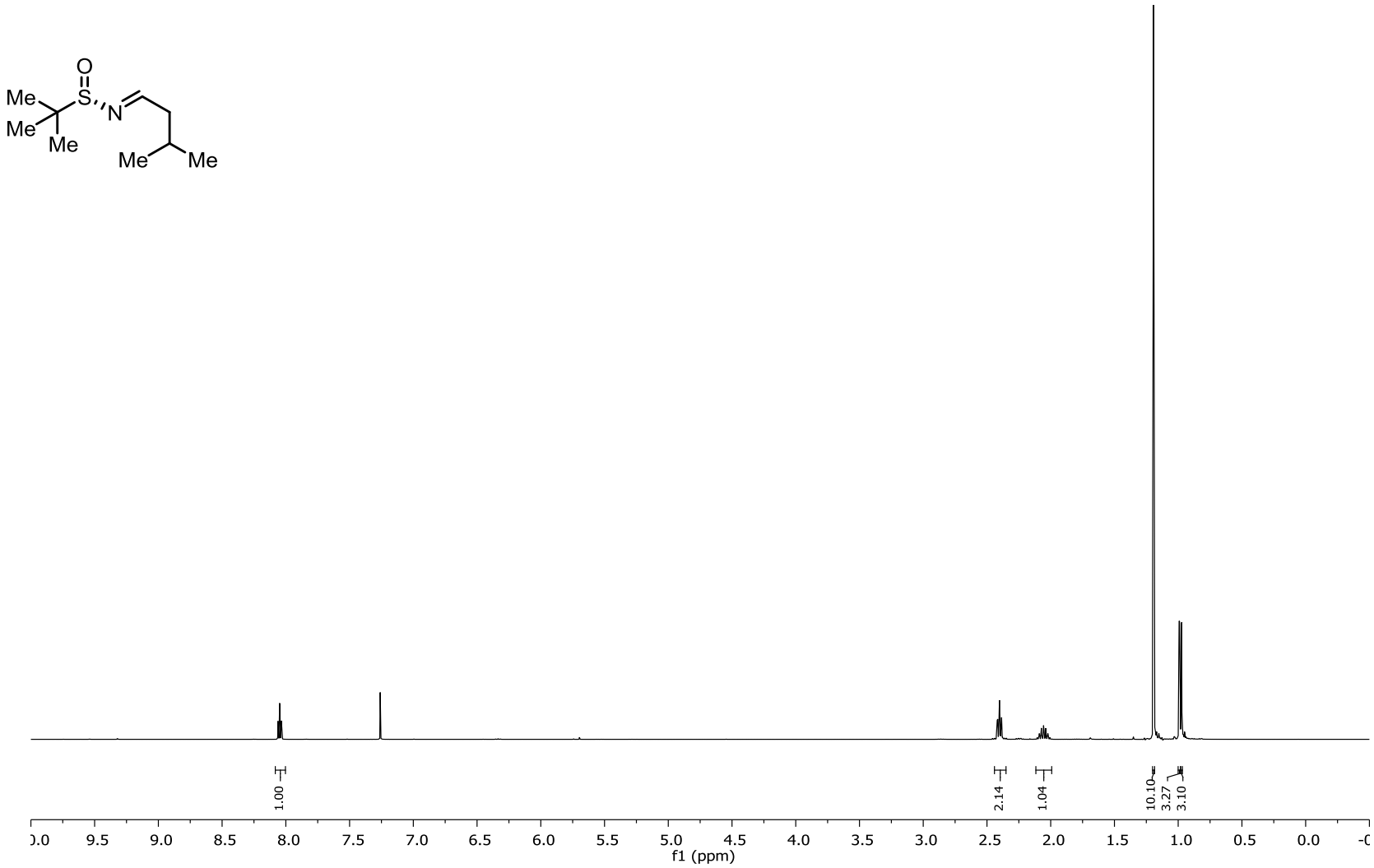
(S,E)-N-Benzylidene-2-methylpropane-2-sulfinamide



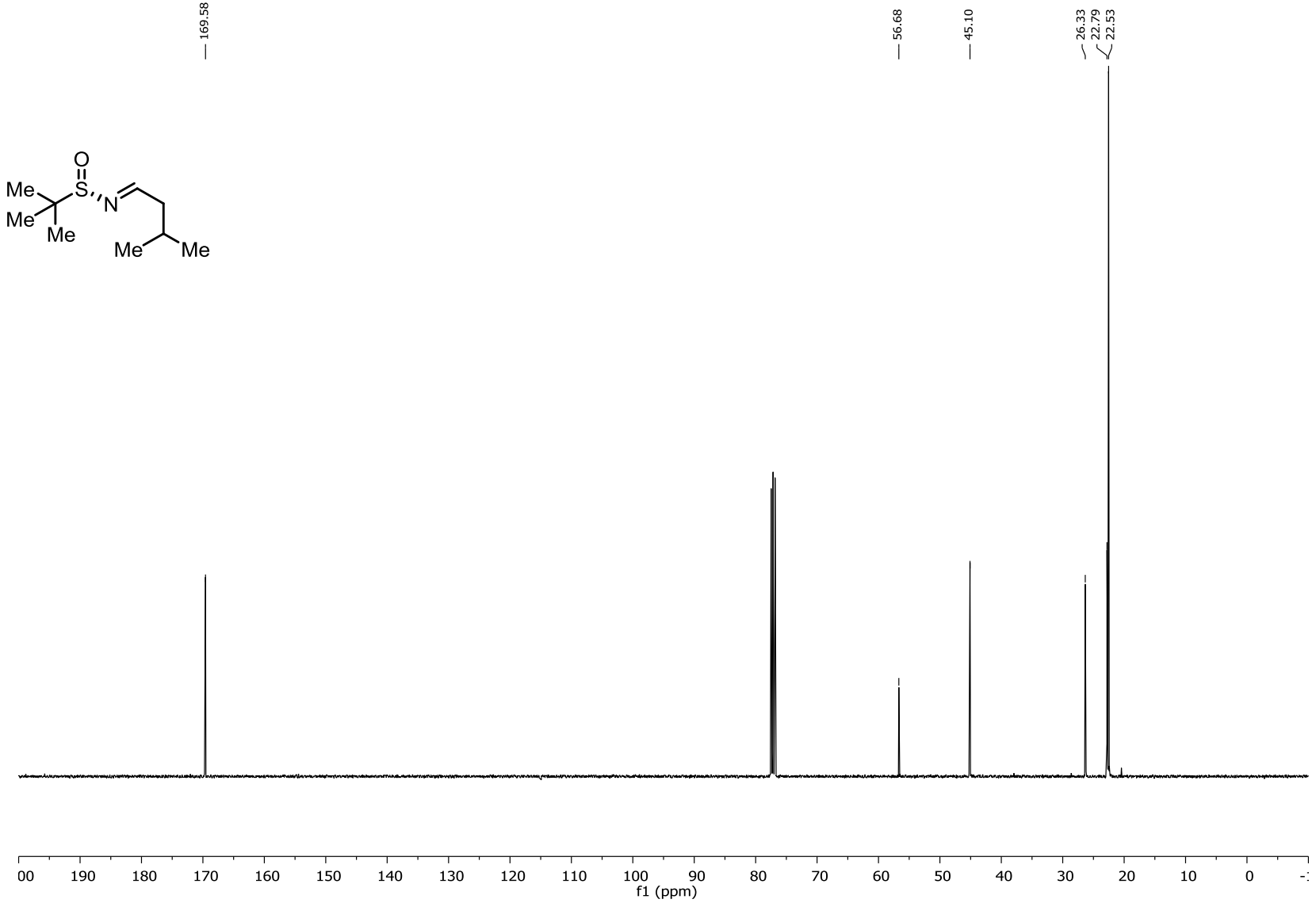
(S,E)-N-Benzylidene-2-methylpropane-2-sulfinamide



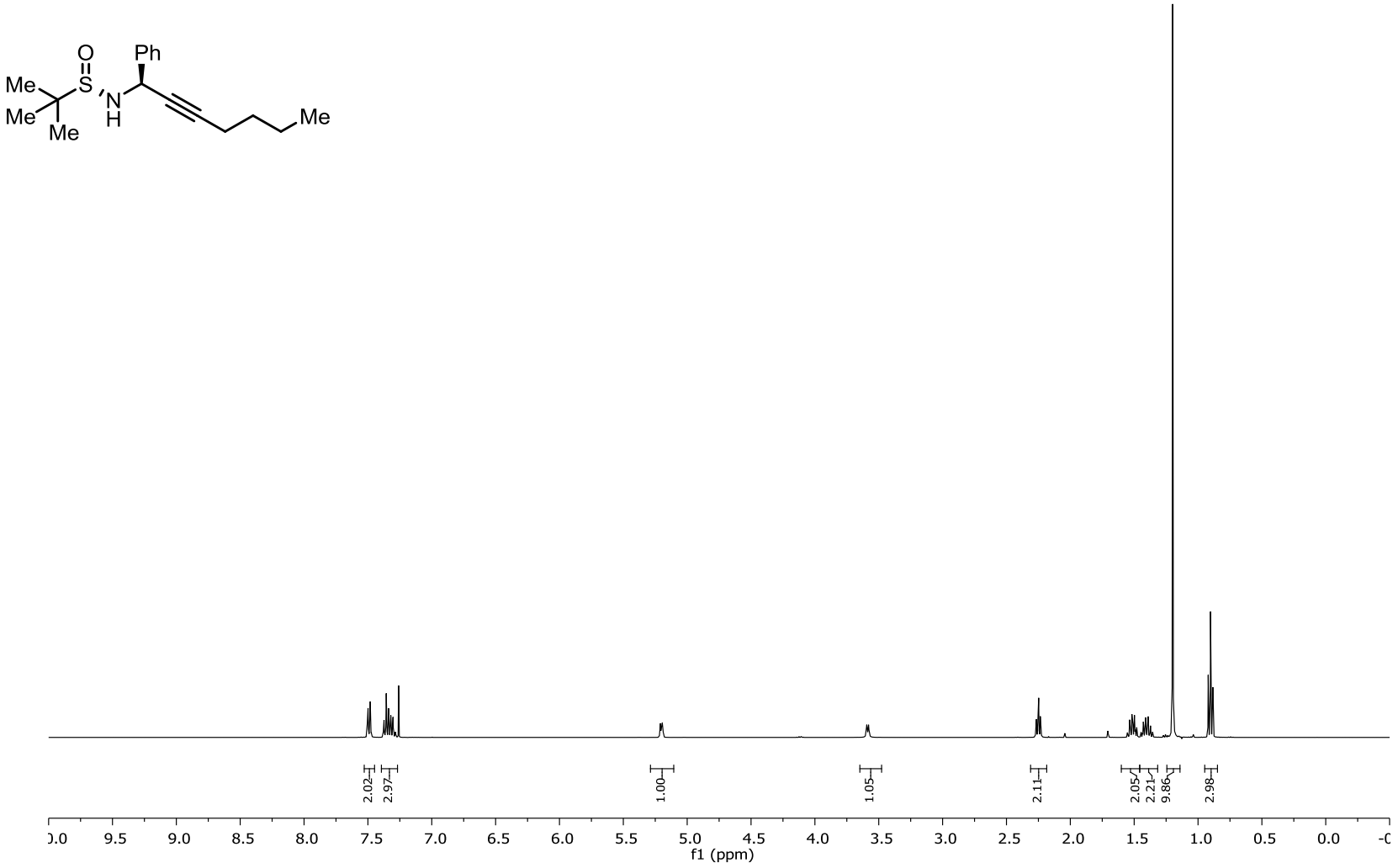
(S,E)-2-Methyl-N-(3-methylbutylidene)propane-2-sulfinamide



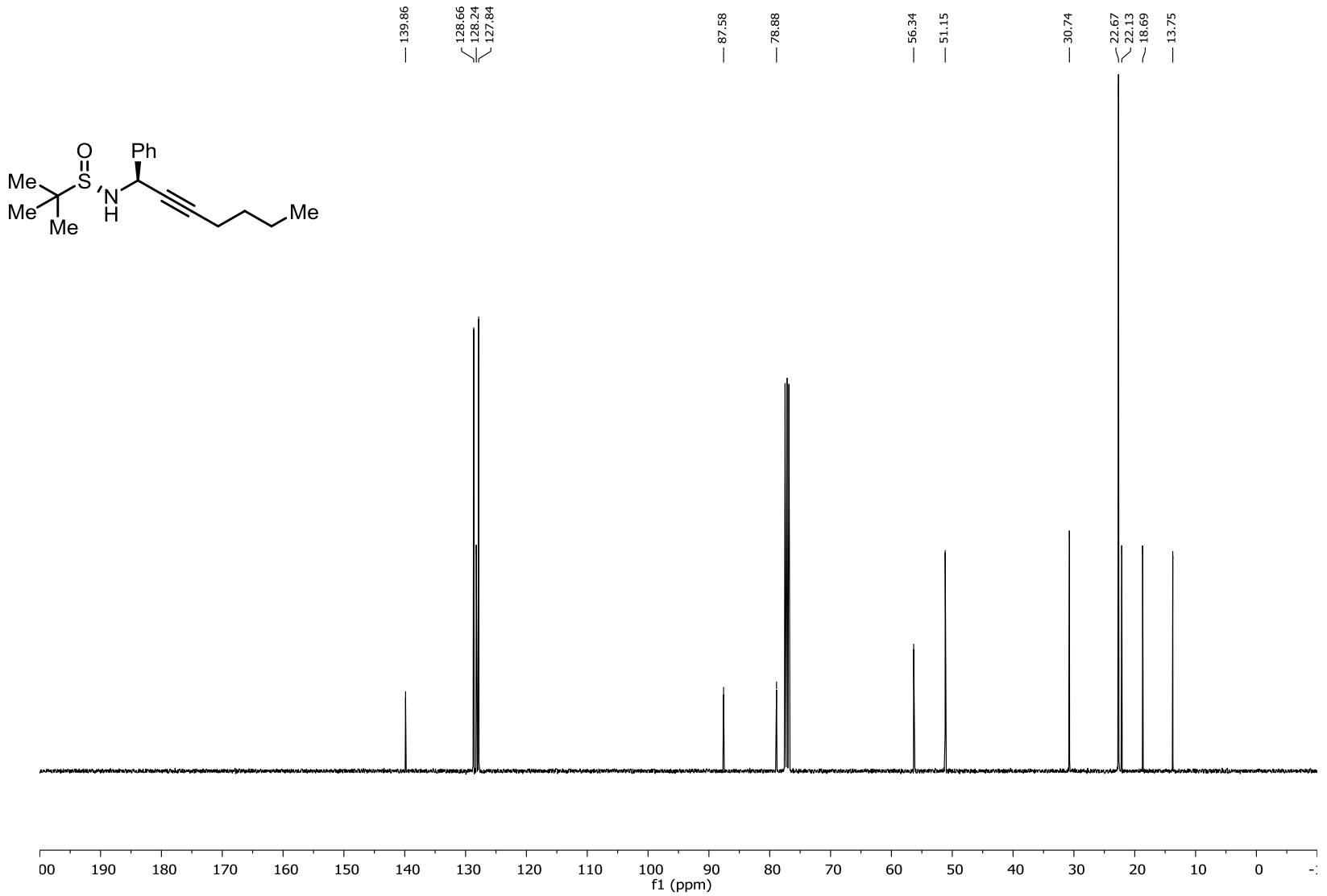
(S,E)-2-Methyl-N-(3-methylbutylidene)propane-2-sulfinamide



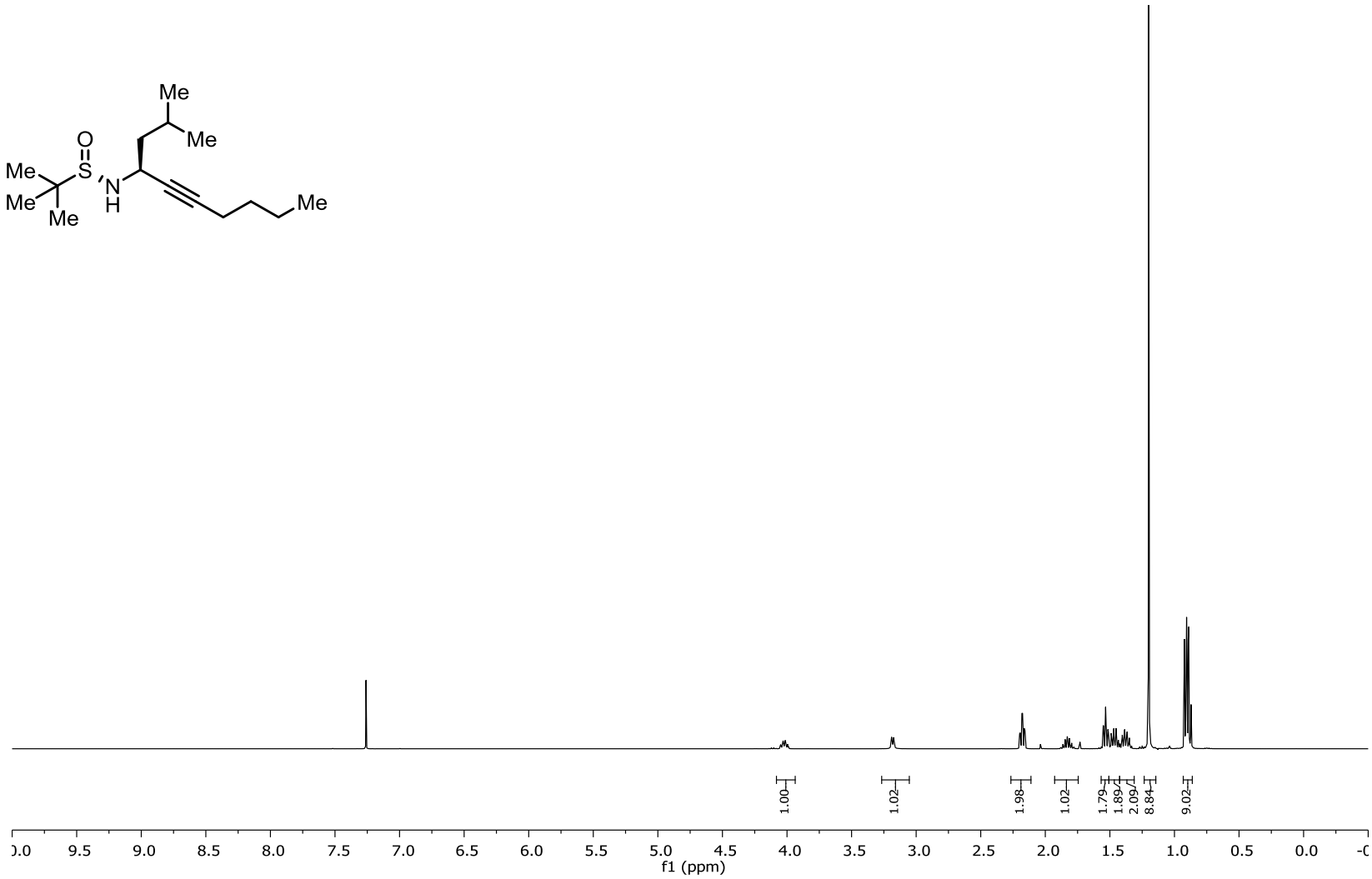
(S)-2-Methyl-N-((S)-1-phenylhept-2-yn-1-yl)propane-2-sulfinamide



(S)-2-Methyl-N-((S)-1-phenylhept-2-yn-1-yl)propane-2-sulfinamide



(S)-2-Methyl-N-((S)-2-methyldec-5-yn-4-yl)propane-2-sulfinamide



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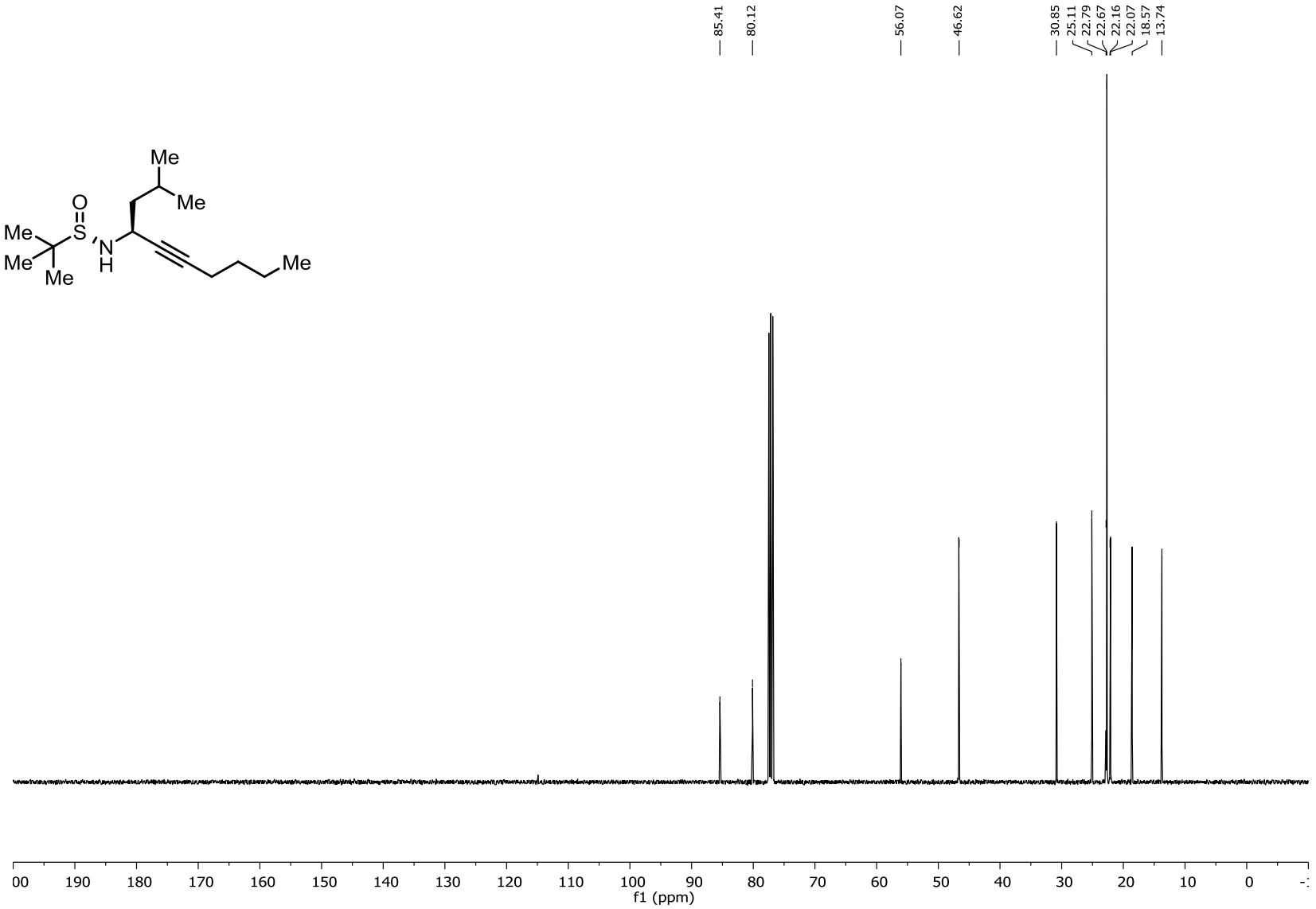
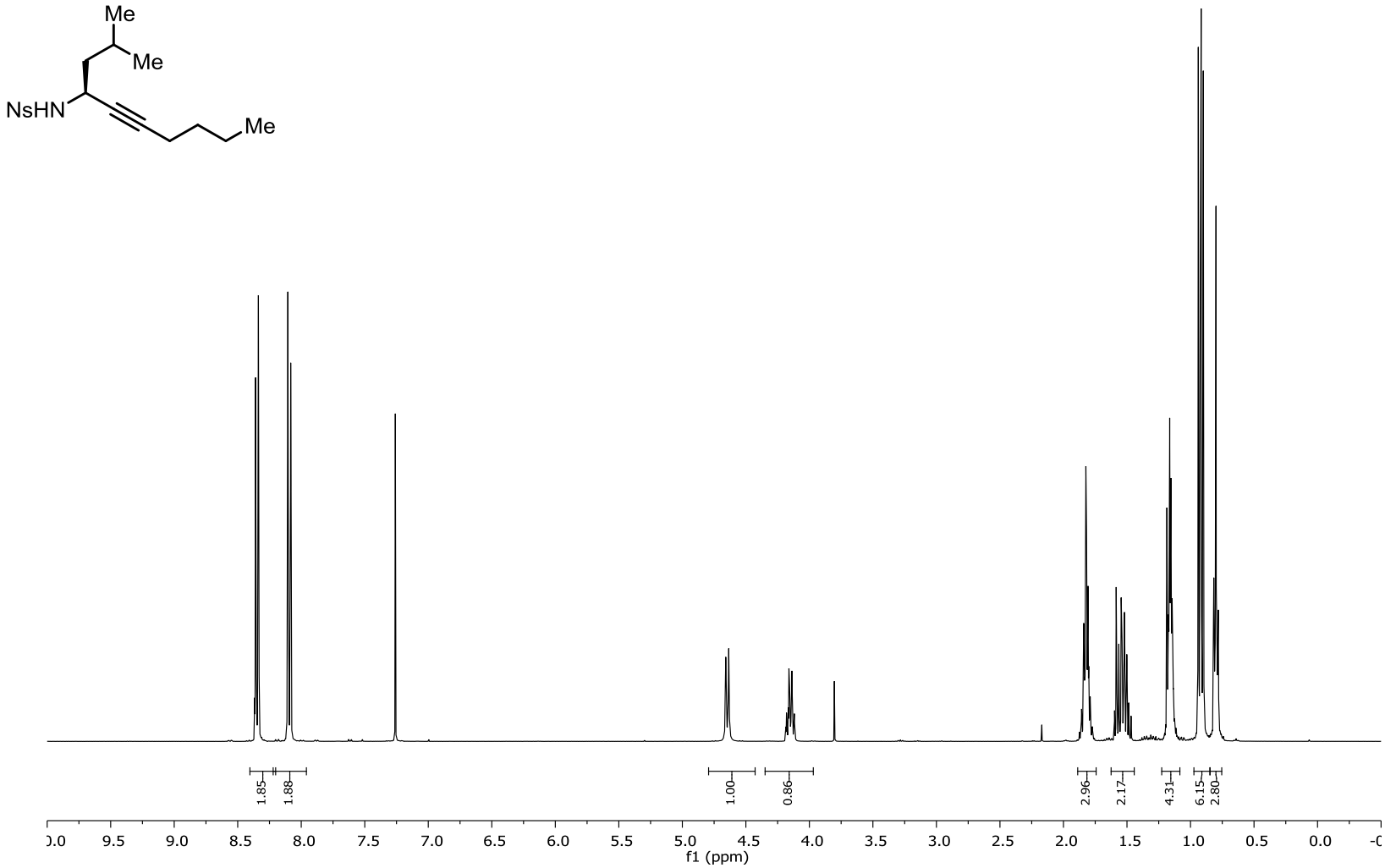
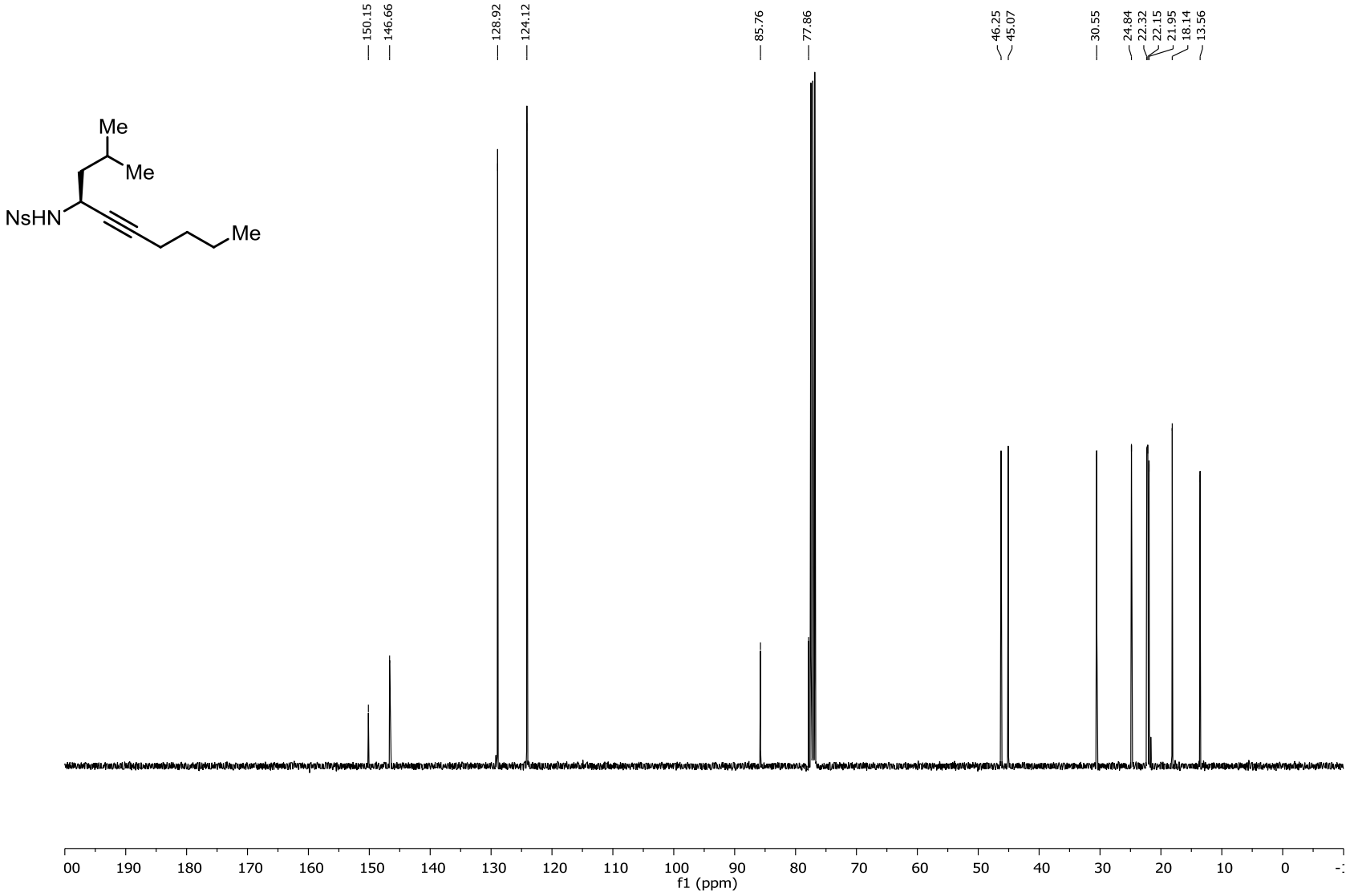


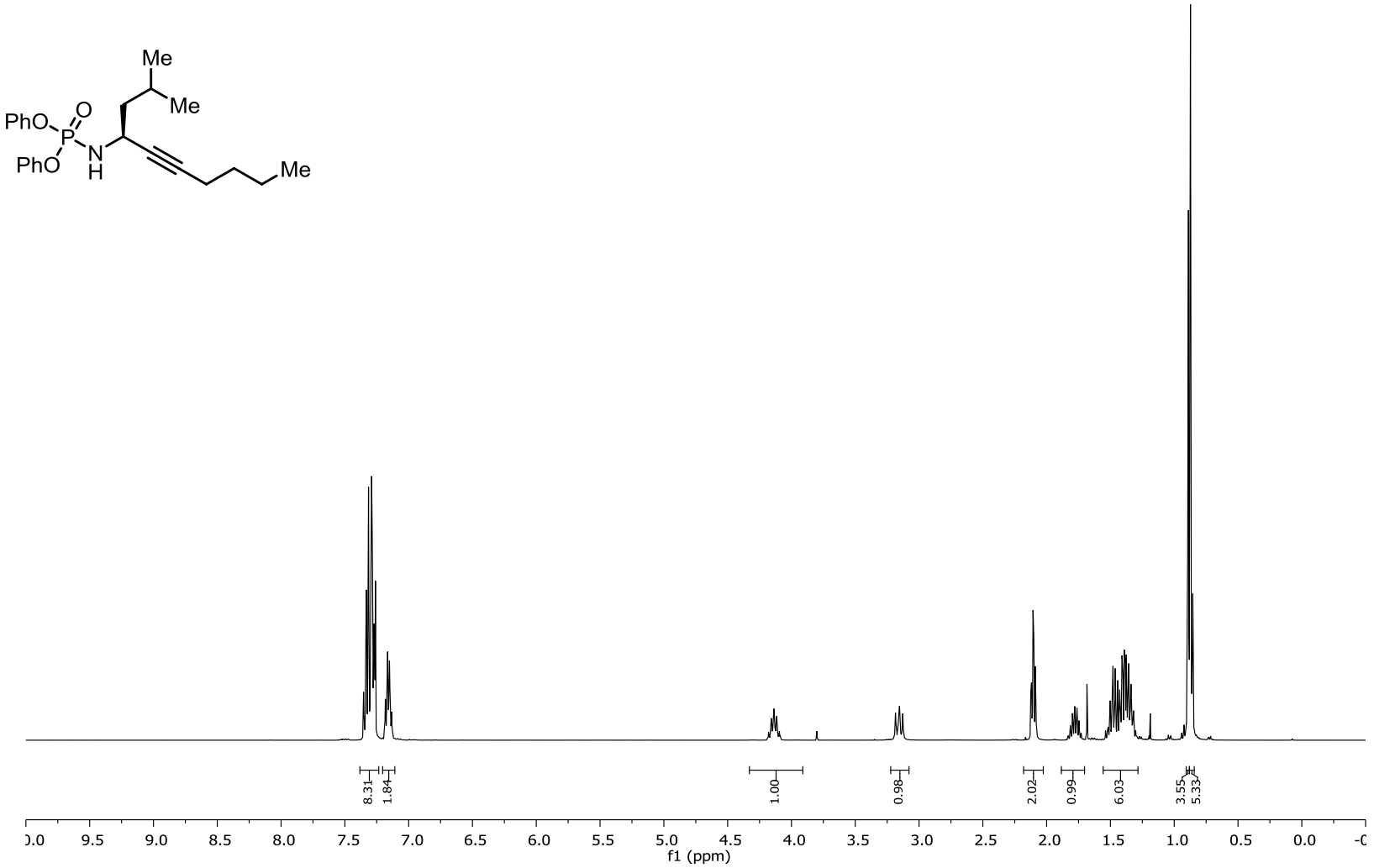
(S)-N-(2-Methyldec-5-yn-4-yl)-4-nitrobenzenesulfonamide



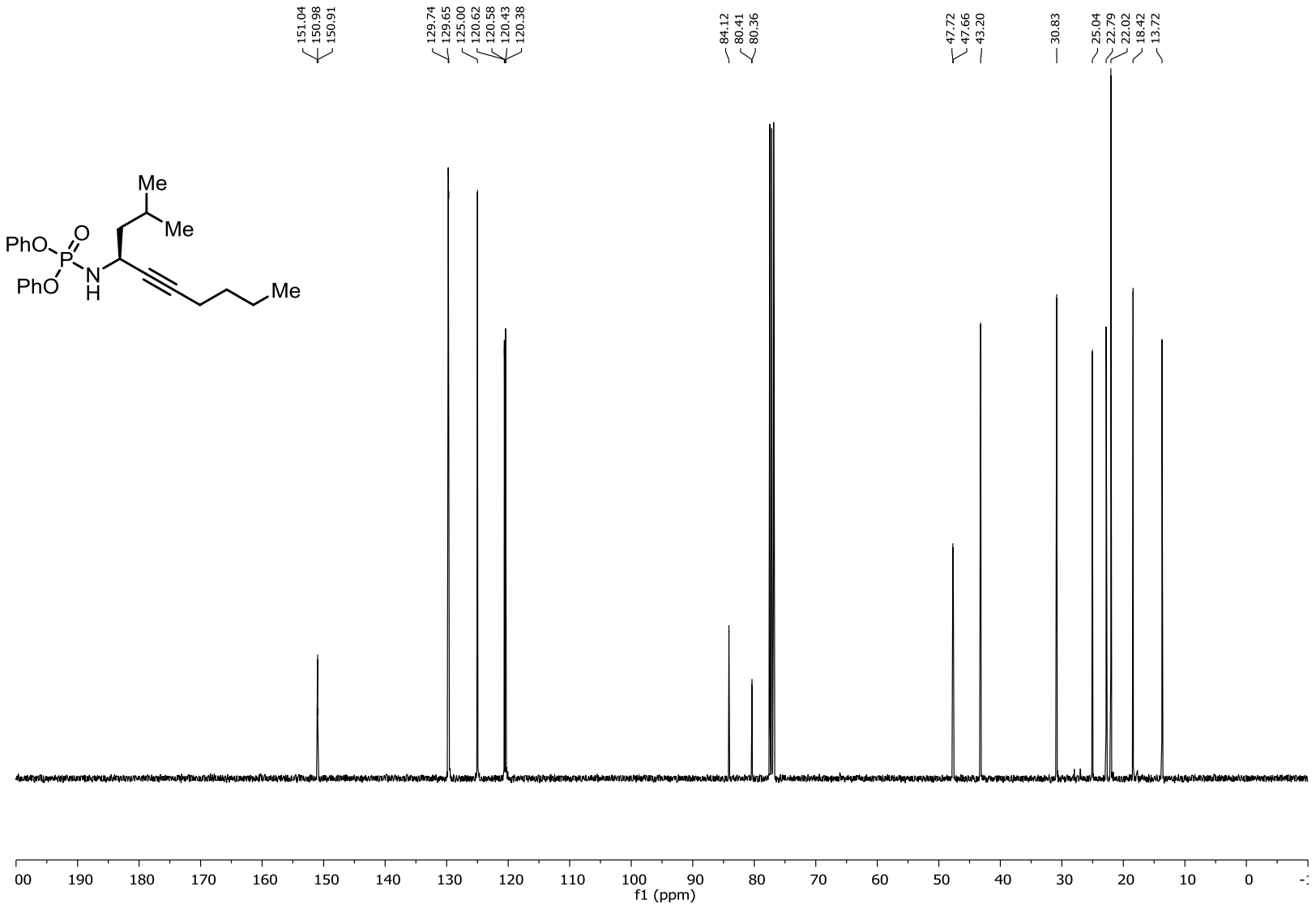
(S)-N-(2-Methyldec-5-yn-4-yl)-4-nitrobenzenesulfonamide



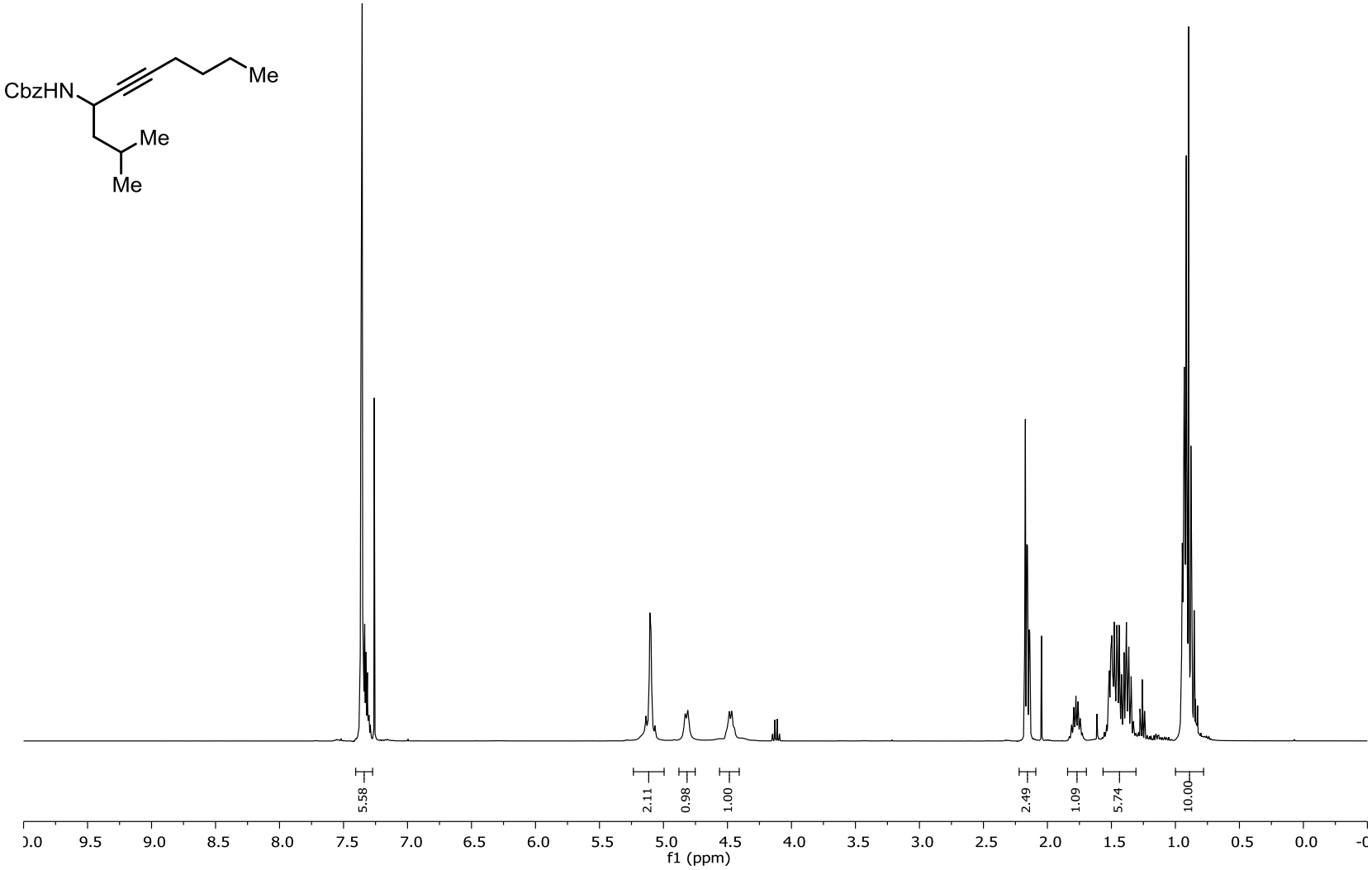
(S)-N-(2-Methyldec-5-yn-4-yl)-4-nitrobenzenesulfonamide



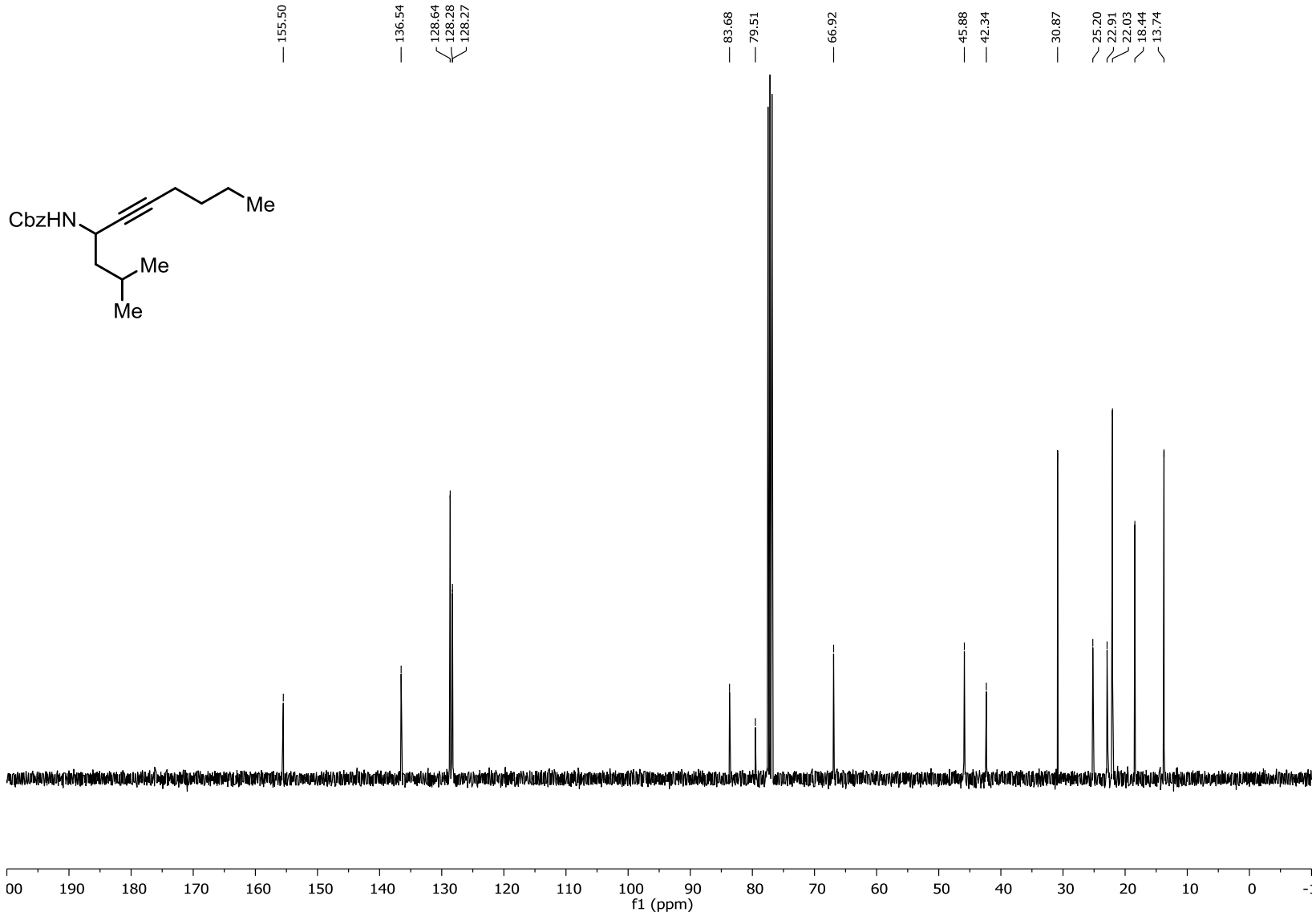
(S)-N-(2-Methyldec-5-yn-4-yl)-4-nitrobenzenesulfonamide



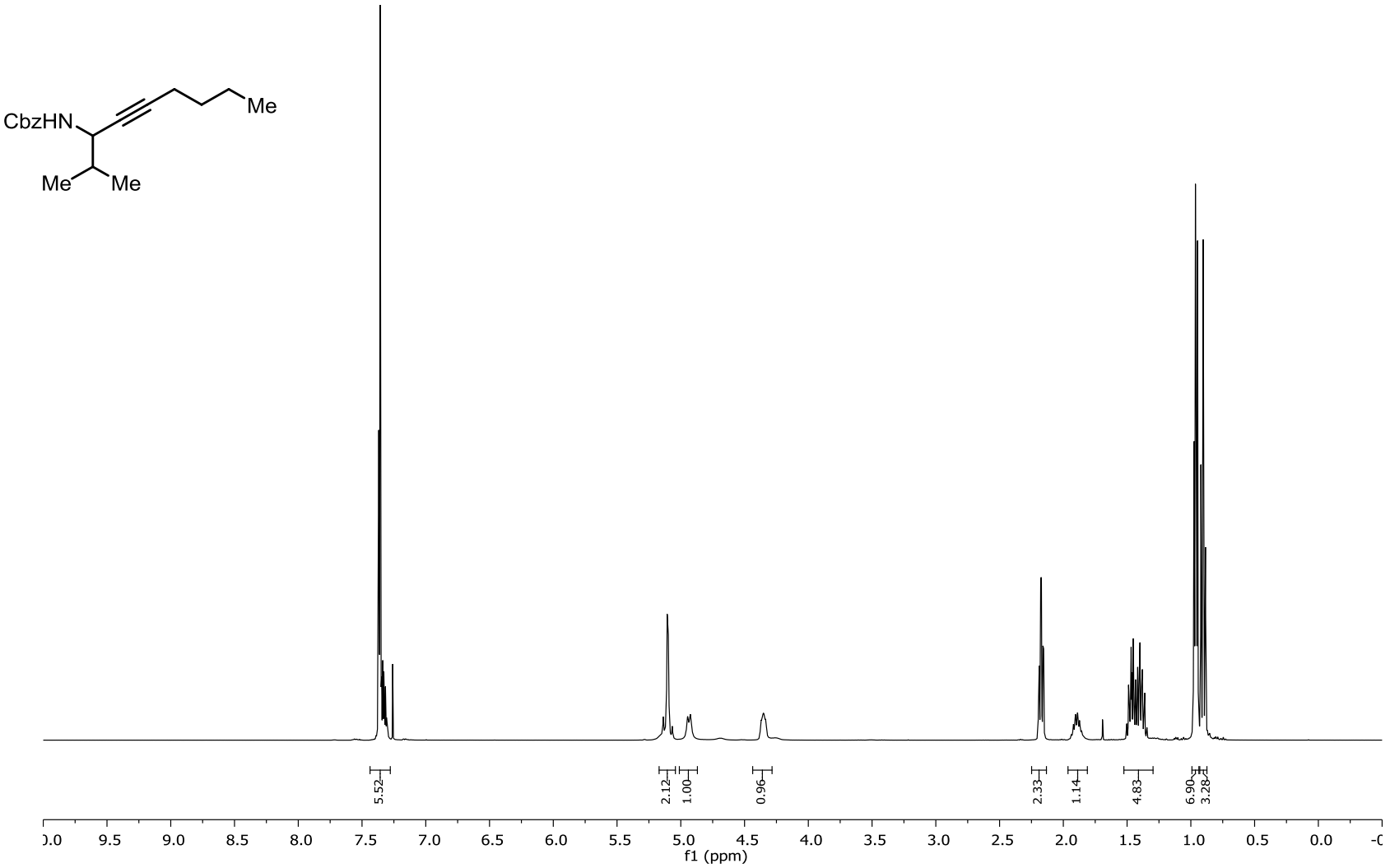
Benzyl (2-methyldec-5-yn-4-yl)carbamate



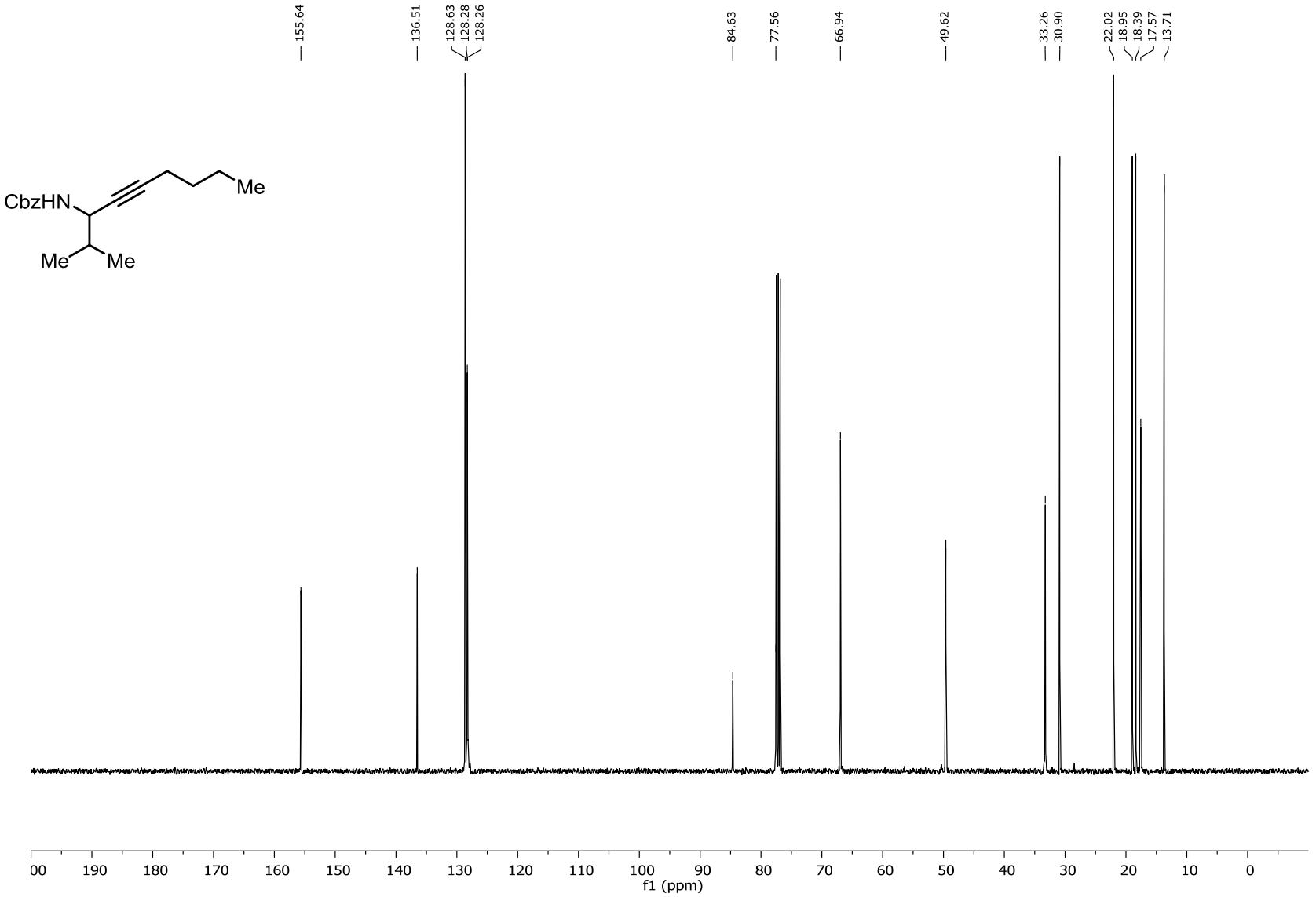
Benzyl (2-methyldec-5-yn-4-yl)carbamate



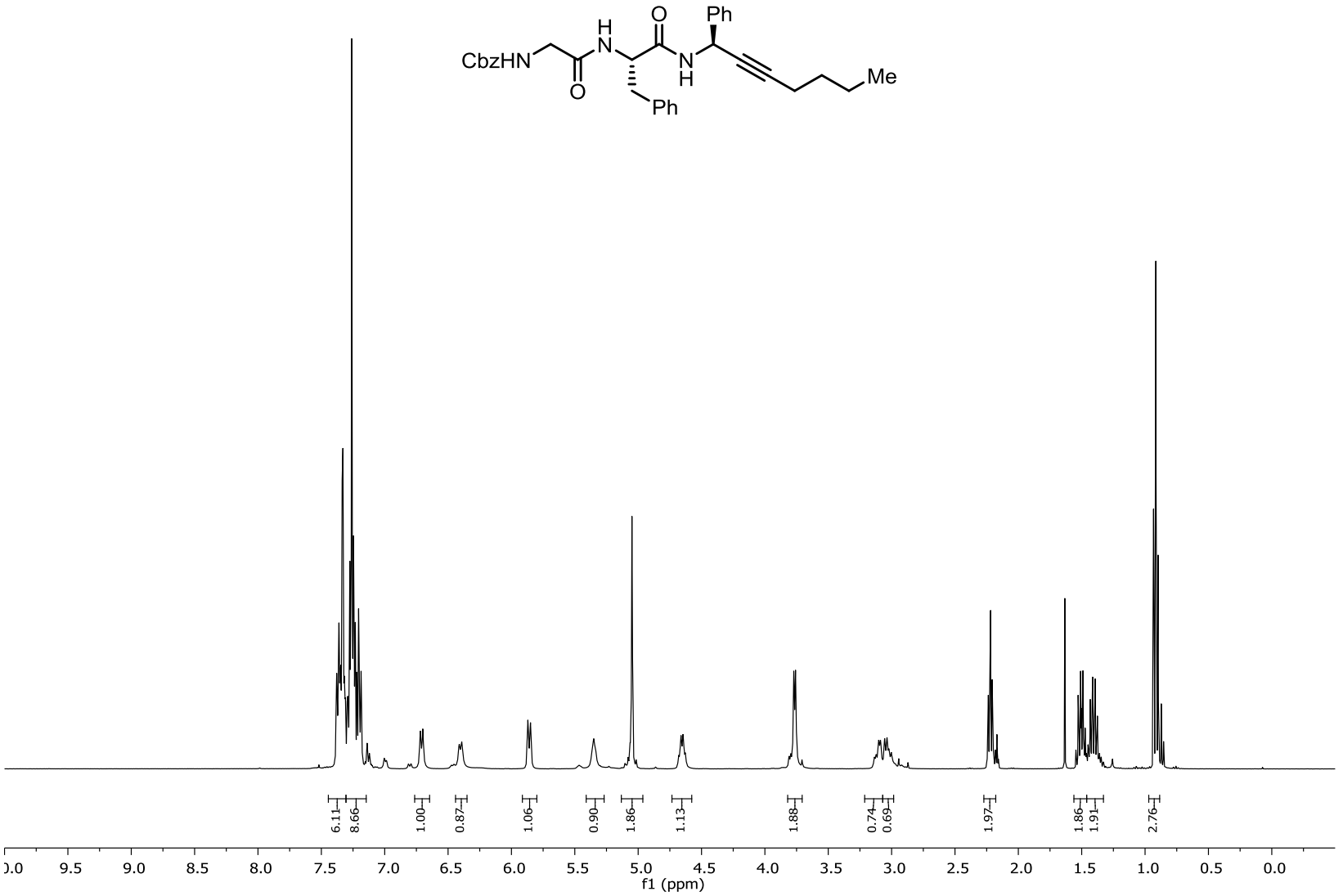
Benzyl (2-methylnon-4-yn-3-yl)carbamate



Benzyl (2-methylnon-4-yn-3-yl)carbamate



Benzyl (2-oxo-2-(((S)-1-oxo-3-phenyl-1-(((S)-1-phenylhept-2-yn-1-yl)amino)propan-2-yl)amino)ethyl)carbamate



Benzyl (2-oxo-2-(((S)-1-oxo-3-phenyl-1-(((S)-1-phenylhept-2-yn-1-yl)amino)propan-2-yl)amino)ethyl)carbamate