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Supporting Information

A Method for the Late-Stage Formation of Ketones, Acyloins, and Aldols from Alkenylstannanes: Application to the Total Synthesis of Paecilonic Acid A

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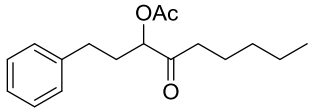
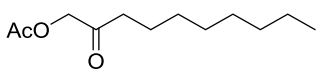
General: Unless otherwise noted, all reactions were carried out under Ar in flamed-dried glassware using anhydrous solvents. Anhydrous solvents were prepared by distillation over the indicated drying agents prior to use and were transferred under Ar: THF/Et_2O (Mg/anthracene), CH_2Cl_2, MeOH (Mg); DMF and Et_3N were dried by an adsorption solvent purification system based on molecular sieves. Thin layer chromatography (TLC): Macherey-Nagel precoated plates (POLYGRAM®SIL/UV254). Flash chromatography: Merck silica gel 60 (40−63 μm) with reagent grade solvents. NMR: Spectra were recorded on Bruker AV VIII 300, 400, or 600 spectrometers in solvents indicated. The solvent signals were used as references, and the chemical shifts were converted to the TMS scale ($CDCl_3$: δ_C = 77.16 ppm; residual $CHCl_3$ in $CDCl_3$: δ_H = 7.26 ppm; CD_3OD: δ_C = 49.0 ppm; residual CHD_2OD in CD_3OD: δ_H = 3.31 ppm). ^{119}Sn NMR spectra were recorded using Me_4Sn as an external standard. IR: Bruker ALPHA Platinum-ATR, wavenumbers ($\tilde{\nu}$) in cm^{-1}. MS: Finnigan MAT 8200 (EI, 70 eV), Bruker ESQ 3000 (ESI); accurate mass determinations: Bruker APEX III FT-MS (7 T magnet) or Finnigan Mat 95. Optical rotation ($[\alpha]_D$): Krüss P8000-T, 10 cm/1 mL cell. Chiral GC: Agilent 7890B GC. Unless otherwise noted, all commercially available compounds (ABCR, Acros, Aldrich, Alfa Aesar, TCI) were used as received. $[Cp^*RuCl_2]_n$ was prepared following a literature precedence and was stored under Ar.[1]

Representative procedure: Copper Acetate Mediated Oxidation of Alkenylstannanes. 4-Oxo-1-phenylnonan-3-yl acetate (2). 

Copper(II) acetate monohydrate (998 mg, 5.0 mmol) and reagent grade Et_3N (1.74 mL, 12.5 mmol) were added to a stirred solution of (*Z*)-1-phenyl-4-(tributylstannyl)non-4-en-3-ol (1.27 g, 2.5 mmol) in reagent grade DMSO (20 mL). The mixture was stirred at 45 °C to 50 °C until TLC analysis (hexane/EtOAc = 15/1) showed complete consumption of the starting material. The mixture was diluted with *tert*-butyl methyl ether and washed with saturated aqueous NH_4Cl solution. The organic layer was separated and the aqueous layer was extracted with *tert*-butyl methyl ether. The combined extracts were washed with brine, dried over magnesium sulfate, and concentrated under reduced pressure. Flash chromatographic purification of the residue (hexane/EtOAc = 15/1) yielded the product as a colorless oil (527 mg, 76%). ^1H NMR (400 MHz, $CDCl_3$) δ 7.33 – 7.27 (m, 2H), 7.24 – 7.14 (m, 3H), 4.99 (dd, *J* = 8.7, 4.1 Hz, 1H), 2.84 – 2.61 (m, 2H), 2.47 (ddd, *J* = 17.4, 7.8, 7.0 Hz, 1H), 2.36 (dt, *J* = 17.4, 7.4 Hz, 1H), 2.16 (s, 3H), 2.14 – 1.93 (m, 2H), 1.56 (dddd, *J* = 13.6, 9.0, 6.8, 1.2 Hz, 2H), 1.37 – 1.17 (m, 4H), 0.88 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 207.5, 170.7, 140.6, 128.7, 128.5, 126.4, 77.9, 38.7, 32.2, 31.7, 31.4, 22.9, 22.6, 20.8, 14.0. IR (film, $CHCl_3$) 3028, 2931 2956, 2861, 1727, 1742, 1604, 1497, 1455, 1373, 1230, 1041, 749, 700 cm^{-1}. HRMS (ESI): *m/z* calculated for $C_{17}H_{24}O_3Na$ $[M+Na^+]$: 299.1618, found 299.1619.

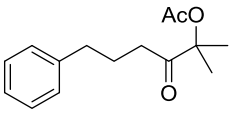
The following compounds were prepared analogously:

2-Oxodecyl acetate (5). 

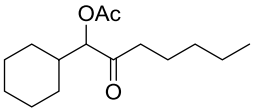
74% yield (79 mg). ^1H NMR (400 MHz, $CDCl_3$) δ 4.65 (s, 2H), 2.40 (t, *J* = 7.4 Hz, 2H), 2.17 (s, 3H), 1.59 (dt, *J* = 5.2, 4.6 Hz, 2H), 1.38 – 1.17 (m, 10H), 0.95 – 0.75 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 203.3, 169.5, 67.2, 38.1, 31.1, 28.6, 28.4, 28.4, 22.6, 21.9, 19.8, 13.4. IR (film, $CHCl_3$) 2913, 2848, 2873, 1723, 1750, 1459, 1475, 1407, 1430, 1375, 1335, 1279, 1293, 1259, 1211, 1130, 1105, 1075, 1050, 1009, 982, 960, 897, 857 cm^{-1}. HRMS (ESI): *m/z* calculated for $C_{12}H_{22}O_3Na$ $[M+Na^+]$: 237.1461, found 237.1461.

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

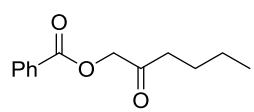
2-Methyl-3-oxo-6-phenylhexan-2-yl acetate (6). 76% yield (83 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 – 7.23 (m, 2H), 7.18 (ddt, *J* = 7.1, 3.1, 1.3 Hz, 3H), 2.62 (dd, *J* = 8.3, 6.9 Hz, 2H), 2.45 (t, *J* = 7.3 Hz, 2H), 2.03 (s, 3H), 1.99 – 1.83 (m, 2H), 1.45 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 208.8, 170.4, 141.8, 128.6, 128.4, 126.0, 83.7, 35.1, 34.9, 25.1, 23.8, 21.3. IR (film, $CHCl_3$) 2937, 1733, 1719, 1603, 1497, 1454, 1367, 1253, 1146, 1085, 1018, 963, 911, 849, 745, 699 cm^{-1}. HRMS (ESI): *m/z* calculated for $C_{15}H_{20}O_3Na$ [M+Na$^+$]: 271.1305, found 271.1303.



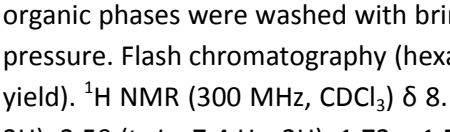
1-Cyclohexyl-2-oxoheptyl acetate (7). 65% yield (82 mg). ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.86 (dd, *J* = 5.0, 1.7 Hz, 1H), 2.55 – 2.26 (m, 2H), 2.14 (d, *J* = 1.0 Hz, 3H), 1.87 (tq, *J* = 6.9, 4.3, 3.6 Hz, 1H), 1.80 – 1.70 (m, 2H), 1.70 – 1.47 (m, 4H), 1.41 – 1.06 (m, 10H), 1.00 – 0.82 (m, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 207.7, 170.9, 82.6, 39.8, 39.4, 31.5, 29.6, 27.5, 26.3, 26.1, 26.1, 22.9, 22.6, 20.8, 14.0. IR (film, $CHCl_3$) 2928, 2855, 1742, 1726, 1451, 1371, 1232, 1082, 1023, 990, 958, 920 cm^{-1}. HRMS (ESI): *m/z* calculated for $C_{15}H_{26}O_3Na$ [M+Na$^+$]: 277.1774, found 277.1775.



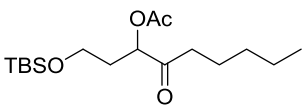
2-Oxohexyl benzoate (8). To a stirred solution of (*Z*)-2-(tributylstannyl)hex-2-en-1-ol (389 mg, 1.0 mmol) in reagent grade DMSO (8 mL) was added copper(II) trifluoroacetate hydrate (475 mg, 2.0 mmol), sodium benzoate (576 mg, 4.0 mmol), and reagent grade Et_3N (697 µL, 5.0 mmol). The resulting mixture was stirred at 45 °C to 50 °C until TLC analysis (hexane/EtOAc = 15/1) indicated complete consumption of the starting material. The mixture was diluted with *tert*-butyl methyl ether and washed with saturated aqueous NH_4Cl solution. The organic layer was separated, and the aqueous layer was 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 (hexane/EtOAc = 25/1) yielded the product as a colorless oil (136 mg, 62% yield). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.17 – 8.00 (m, 2H), 7.65 – 7.54 (m, 1H), 7.52 – 7.38 (m, 2H), 4.88 (s, 2H), 2.50 (t, *J* = 7.4 Hz, 2H), 1.72 – 1.56 (m, 2H), 1.43 – 1.28 (m, 2H), 0.92 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 204.3, 166.0, 133.5, 130.0, 129.4, 128.6, 68.5, 38.8, 25.5, 22.4, 13.9. IR (film, $CHCl_3$) 2959, 2933, 2873, 1718, 1601, 1452, 1414, 1377, 1315, 1272, 1177, 1115, 1060, 1027, 804, 709 cm^{-1}. HRMS (ESI): *m/z* calculated for $C_{13}H_{16}O_3Na$ [M+Na$^+$]: 243.0992, found 243.0993.



9-(1,3-Dioxoisoindolin-2-yl)-4-oxo-1-phenylnonan-3-yl acetate (9). 63% yield (132 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 – 7.79 (m, 2H), 7.70 (m, 2H), 7.31 – 7.24 (m, 2H), 7.23 – 7.13 (m, 3H), 4.96 (dd, *J* = 8.7, 4.2 Hz, 1H), 3.66 (t, *J* = 7.2 Hz, 2H), 2.81 – 2.58 (m, 2H), 2.47 (dt, *J* = 17.6, 7.3 Hz, 1H), 2.36 (dt, *J* = 17.7, 7.3 Hz, 1H), 2.14 (s, 3H), 2.12 – 1.94 (m, 2H), 1.71 – 1.51 (m, 4H), 1.38 – 1.24 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 207.1, 170.7, 168.5, 140.5, 134.0, 132.2, 128.7, 128.5, 126.4, 123.3, 77.9, 38.4, 37.9, 32.1, 31.6, 28.5, 26.4, 22.7, 20.8. IR (film, $CHCl_3$) 2937, 2864, 1771, 1740, 1706, 1604, 1497, 1466, 1455, 1436, 1395, 1369, 1229, 1188, 1081, 1041, 947, 874, 851, 794, 750 cm^{-1}. HRMS (ESI): *m/z* calculated for $C_{25}H_{27}NO_5Na$ [M+Na$^+$]: 444.1781, found 444.1785.



1-((*tert*-Butyldimethylsilyl)oxy)-4-oxononan-3-yl acetate (10). 64% yield (106 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.15 (dd, *J* = 9.1, 3.7 Hz, 1H), 3.88 – 3.51 (m, 2H), 2.62 – 2.35 (m, 2H), 2.13 (s, 3H), 1.99 (dddd, *J* = 14.2, 8.1, 6.0, 3.7 Hz, 1H), 1.86 (ddt, *J* = 14.0, 9.3, 4.8 Hz, 1H), 1.66 – 1.52 (m, 2H), 1.38 – 1.20 (m, 4H), 0.88 (s, 12H), 0.04 (d, *J* = 1.2 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 207.5, 170.6, 75.4, 58.6, 38.8, 33.4, 31.5, 26.0, 23.1, 22.6, 20.8,



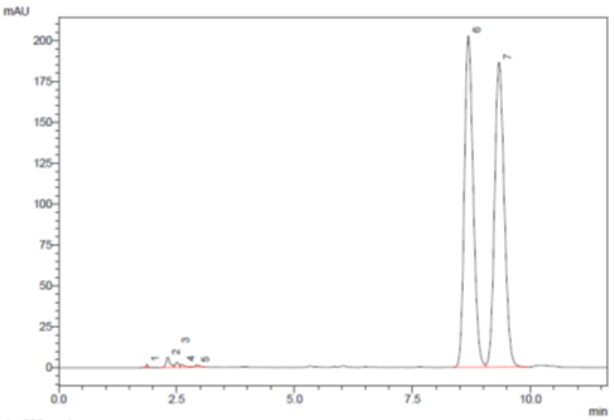
18.4, 14.1, −5.3, −5.4. IR (film, $CHCl_3$) 2955, 2929, 2858, 1730, 1745, 1471, 1373, 1234, 1094, 1022, 939, 834, 775, 730 cm^{-1}. HRMS (ESI): *m/z* calculated for $C_{17}H_{35}O_4Si$ [M+H^+]: 331.2299, found 331.2301.

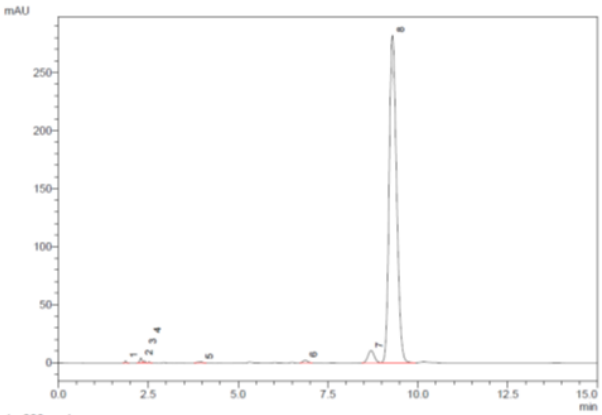
6-Chloro-2-oxohexyl acetate (11). 68% yield (65 mg). ^1H NMR (400 MHz, $CDCl_3$) δ 4.64 (s, 2H), 3.64 – 3.47 (m, 2H), 2.46 (td, *J* = 6.1, 5.3, 1.3 Hz, 2H), 2.16 (s, 3H), 1.91 – 1.67 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 203.4, 170.4, 68.0, 44.6, 37.9, 31.8, 20.6 (two signals unresolved). IR (film, $CHCl_3$) 2938, 1729, 1416, 1373, 1273, 1228, 1073, 1048, 1026, 982, 844, 725, 647 cm^{-1}. HRMS (ESI): *m/z* calculated for $C_8H_{13}O_3ClNa$ [M+Na^+]: 215.0445, found 215.0447.

8-Cyano-4-oxo-1-phenyloctan-3-yl acetate (12). 54% yield (78 mg). ^1H NMR (400 MHz, $CDCl_3$) δ 7.34 – 7.27 (m, 2H), 7.25 – 7.19 (m, 1H), 7.19 – 7.12 (m, 2H), 4.99 – 4.91 (m, 1H), 2.82 – 2.65 (m, 2H), 2.54 (dt, *J* = 18.0, 6.8 Hz, 1H), 2.42 (dt, *J* = 17.9, 6.6 Hz, 1H), 2.33 (t, *J* = 6.9 Hz, 2H), 2.16 (s, 3H), 2.11 – 1.99 (m, 2H), 1.84 – 1.56 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 206.4, 170.8, 140.4, 128.7, 128.5, 126.5, 119.5, 77.8, 37.5, 32.1, 31.6, 24.8, 22.2, 20.8, 17.2. IR (film, $CHCl_3$) 3028, 2932, 1724, 1603, 1497, 1454, 1373, 1229, 1080, 1028, 950, 911, 750, 700 cm^{-1}. HRMS (ESI): *m/z* calculated for $C_{17}H_{21}NO_3Na$ [M+Na^+]: 310.1414, found 310.1412.

(*R*)-2-Methyl-4-oxo-7-phenylheptan-3-yl acetate (13). 61% yield (80 mg). $[\alpha]_D^{20}$ = +4.7 (c = 2.25, $CHCl_3$). ^1H NMR (300 MHz, $CDCl_3$) δ 7.33 – 7.24 (m, 2H), 7.23 – 7.13 (m, 3H), 4.86 (d, *J* = 4.3 Hz, 1H), 2.63 (t, *J* = 7.6 Hz, 2H), 2.58 – 2.31 (m, 2H), 2.26 – 2.14 (m, 1H), 2.13 (s, 3H), 2.02 – 1.85 (m, 2H), 0.98 (d, *J* = 6.9 Hz, 3H), 0.90 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 207.2, 170.9, 141.7, 128.6, 128.5, 126.1, 82.8, 38.7, 35.1, 29.6, 24.8, 20.7, 19.4, 17.0. IR (film, $CHCl_3$) 2966, 1742, 1724, 1603, 1496, 1454, 1371, 1231, 1028, 949, 908, 746, 699 cm^{-1}. HRMS (ESI): *m/z* calculated for $C_{16}H_{22}O_3Na$ [M+Na^+]: 285.1461, found 285.1463.

The enantiomeric excess was determined to be 94% by HPLC analysis (150 mm Chiralpak IC-3, 4.6 mm i.D., *n*-heptane/2-propanol = 98:2, 1.0 mL/min, 4.9 MPa, 298 K, UV 220 nm).





6-Hydroxy-8,8,12-trimethyl-1-phenyltridec-11-en-5-one (14). 77% yield (564 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 – 7.24 (m, 2H), 7.21 – 7.14 (m, 3H), 5.11 – 5.02 (m, 2H), 2.62 (t, *J* = 7.0 Hz, 2H), 2.55 – 2.36 (m, 2H), 2.11 (s, 3H), 2.01 – 1.89 (m, 2H), 1.73 – 1.49 (m, 12H), 1.33 – 1.18 (m, 2H), 0.941 (s, 3H), 0.936 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 207.5, 170.7, 142.3, 131.4, 128.5, 128.4, 125.9, 124.7, 76.5, 42.4, 40.9, 38.2, 35.9, 33.1, 31.0, 27.4, 27.3, 25.8, 23.0, 22.8, 20.9, 17.8. IR (neat) 2931, 2859, 1742, 1729, 1453, 1372, 1231, 1084, 1050, 1025, 935, 829, 746, 699 cm^{-1}. HRMS (ESI): *m/z* calculated for $C_{24}H_{36}O_3Na$ [M+Na$^+$]: 395.2559, found 395.2557.

(2*R*,3*S*,8*S*,11*R*,*E*)-11-Hydroxy-2,3,11-trimethyl-7,14-dioxooxacyclotetradec-12-en-8-yl acetate (15). 81% yield (12 mg). The reaction was performed with $Cu(OAc)_2$ (4 equiv.) and Et_3N (10 equiv.). $[\alpha]_D^{20} = -59.5$ (c = 1.20, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.68 (d, *J* = 15.8 Hz, 1H), 5.98 (d, *J* = 15.7 Hz, 1H), 4.73 – 4.59 (m, 2H), 2.51 (dt, *J* = 17.2, 7.3 Hz, 1H), 2.16 (dt, *J* = 17.3, 6.6 Hz, 1H), 2.11 (s, 3H), 1.87 – 1.75 (m, 2H), 1.74 – 1.47 (m, 5H), 1.38 (s, 3H), 1.28 (d, *J* = 6.3 Hz, 3H), 1.22 – 1.07 (m, 1H), 1.02 (ddt, *J* = 13.4, 9.0, 7.3 Hz, 1H), 0.90 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 208.1, 170.7, 165.7, 153.0, 120.7, 78.9, 76.9, 73.4, 40.4, 36.8, 36.0, 34.2, 28.9, 24.5, 22.3, 20.9, 19.4, 17.1. IR (film, $CHCl_3$) 3488, 2969, 2934, 2876, 1739, 1711, 1644, 1455, 1374, 1234, 1156, 1107, 1036, 992, 918, 876, 812, 777, 731, 686 cm^{-1}. HRMS (ESI): *m/z* calculated for $C_{18}H_{28}O_6Na$ [M+Na$^+$]: 363.1778, found 363.1776.

***anti*-3-Methyl-4-oxononan-2-yl acetate (21).** 57% yield based on pure α-alkenylstannane (111 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.07 (dq, *J* = 7.9, 6.3 Hz, 1H), 2.77 (dq, *J* = 7.9, 7.1 Hz, 1H), 2.49 – 2.35 (m, 2H), 1.97 (s, 3H), 1.62 – 1.48 (m, 2H), 1.34 – 1.21 (m, 4H), 1.18 (d, *J* = 6.3 Hz, 3H), 1.04 (d, *J* = 7.1 Hz, 3H), 0.87 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 212.1, 170.2, 71.8, 50.9, 42.1, 31.5, 23.3, 22.6, 21.3, 17.1, 14.0, 12.3. IR (film, $CHCl_3$) 2957, 2933, 2873, 1736, 1714, 1457, 1408, 1372, 1235, 1090, 1036, 1017, 965, 946, 850 cm^{-1}. HRMS (ESI): *m/z* calculated for $C_{12}H_{22}O_3Na$ [M+Na$^+$]: 237.1461, found 237.1463.

***syn*-3-Methyl-4-oxononan-2-yl acetate (23).** 59% yield based on pure α-alkenylstannane (114 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.13 (p, *J* = 6.3 Hz, 1H), 2.70 (qd, *J* = 7.0, 6.1 Hz, 1H), 2.43 (td, *J* = 7.3, 4.5 Hz, 2H), 2.01 (s, 3H), 1.58 – 1.48 (m, 2H), 1.37 – 1.19 (m, 4H), 1.17 (d, *J* = 6.4 Hz, 3H), 1.07 (d, *J* = 7.0 Hz, 3H), 0.86 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 211.9, 170.4, 71.2, 50.7, 42.6, 31.5, 23.3, 22.6, 21.3, 17.9, 14.0, 12.3. IR (film, $CHCl_3$) 2957, 2933, 2873, 1736, 1714, 1457, 1408, 1372, 1235, 1090, 1036, 1017, 965, 946, 850 cm^{-1}. HRMS (ESI): *m/z* calculated for $C_{12}H_{22}O_3Na$ [M+Na$^+$]: 237.1461, found 237.1463.

1-((2*S*,3*S*,*Z*)-3-Hydroxy-4-(3-phenylpropylidene)oxetan-2-yl)octan-1-one (26). 58% yield (87 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 – 7.25 (m, 2H), 7.20 (dt, *J* = 8.2, 2.0 Hz, 3H), 4.99 (ddq, *J* = 8.7, 5.9, 1.3 Hz, 1H), 4.70 (td, *J* = 7.0, 5.9 Hz, 1H), 4.43 (td, *J* = 7.5, 1.5 Hz, 1H), 2.78 – 2.58 (m, 2H), 2.32 (qd, *J* = 7.5, 1.1 Hz, 2H), 2.01 (d, *J* = 9.2 Hz, 1H), 1.68 (q, *J* = 6.9 Hz, 2H), 1.49 – 1.18 (m, 12H), 0.95 – 0.83 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.1, 142.0, 128.7, 128.3, 125.9, 96.9, 86.5, 69.6, 36.0, 32.0, 29.7, 29.6, 29.4, 29.2, 24.7, 24.6, 22.8, 14.3. IR (film, $CHCl_3$) 3407, 3027, 2924, 2855, 1716, 1604, 1496, 1454, 1365, 1304, 1234, 1201, 1144, 1069, 984, 940, 893, 848, 746, 724 cm^{-1}. HRMS (ESI): *m/z* calculated for $C_{20}H_{30}O_2Na$ [M+Na$^+$]: 325.2138, found 325.2140.

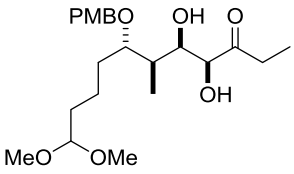
(*Z*)-1-Methoxydec-2-en-2-yl acetate (33). 82% yield (94 mg). ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.31 (tt, *J* = 7.3, 0.7 Hz, 1H), 3.93 (q, *J* = 0.9 Hz, 2H), 3.32 (s, 3H), 2.18 (s, 3H), 1.97 (q, *J* = 7.2 Hz, 2H), 1.48 – 1.10 (m, 10H), 0.91 – 0.78 (m, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 169.0, 144.2, 121.3, 72.2, 58.0, 31.9, 29.3, 29.2, 28.9, 25.5, 22.8, 20.8, 14.2. IR (film, $CHCl_3$) 2925, 2855, 1756, 1457, 1369, 1203, 1090, 1017, 942, 914, 587 cm^{-1}. HRMS (ESI): *m/z* calculated for $C_{13}H_{24}O_3Na$ [M+Na$^+$]: 251.1618, found 251.1619.

Representative procedure: Copper Trifluoroacetate Mediated Oxidation of Alkenylstannanes. 3-(Methoxymethoxy)-1-phenylnonan-4-one (17). **C**opper(II) trifluoroacetate hydrate (290 mg, 1.0 mmol) and reagent grade Et_3N (349 µL, 2.5 mmol) were added to a stirred solution of tributyl(4-((tetrahydro-2*H*-pyran-2-yl)oxy)but-1-en-2-yl)stannane (223 mg, 0.5 mmol) in reagent grade DMSO (4 mL). The mixture was stirred at 45 °C to 50 °C until TLC analysis (hexane/EtOAc = 15/1) showed complete consumption of the starting material. The mixture was diluted with *tert*-butyl methyl ether and washed with saturated aqueous NH_4Cl solution. The organic layer was separated, and the aqueous layer was extracted with *tert*-butyl methyl ether. The combined extracts were washed with brine, dried over magnesium sulfate, and concentrated under reduced pressure. Purification of the residue by flash chromatography (hexane/EtOAc = 9/1) yielded the product as a colorless oil (95 mg, 68%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.34 – 7.24 (m, 2H), 7.24 – 7.14 (m, 3H), 4.66 (d, *J* = 0.7 Hz, 2H), 4.06 – 3.93 (m, 1H), 3.40 (s, 3H), 2.87 – 2.61 (m, 2H), 2.49 (dd, *J* = 7.8, 7.0 Hz, 2H), 2.04 – 1.91 (m, 2H), 1.69 – 1.49 (m, 2H), 1.43 – 1.18 (m, 4H), 0.93 – 0.83 (m, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 211.6, 141.3, 128.6, 128.6, 126.3, 96.8, 82.2, 56.3, 38.6, 34.0, 31.7, 31.6, 23.1, 22.6, 14.0. IR (film, $CHCl_3$) 2929, 1715, 1497, 1455, 1148, 1104, 1027, 920, 747, 699, 494 cm^{-1}. HRMS (ESI): *m/z* calculated for $C_{17}H_{26}O_3Na$ [M+Na$^+$]: 301.1774, found 301.1775.

4-((Tetrahydro-2*H*-pyran-2-yl)oxy)butan-2-one (19). Prepared analogously (70% yield, 60 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.55 (dd, *J* = 4.5, 2.9 Hz, 1H), 4.01 – 3.91 (m, 1H), 3.87 – 3.75 (m, 1H), 3.70 – 3.60 (m, 1H), 3.53 – 3.41 (m, 1H), 2.67 (td, *J* = 6.2, 1.5 Hz, 2H), 2.15 (s, 3H), 1.81 – 1.69 (m, 1H), 1.69 – 1.57 (m, 1H), 1.57 – 1.41 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 207.3, 99.2, 62.7, 62.4, 43.8, 30.7, 30.6, 25.5, 19.6. IR (film, $CHCl_3$) 2942, 1714, 1355, 1324, 1260, 1201, 1161, 1135, 1120, 1065, 1032, 1019, 979, 904, 869, 813, 755 cm^{-1}. HRMS (ESI): *m/z* calculated for $C_9H_{16}O_3Na$ [M+Na$^+$]: 195.0992, found 195.0992.

(5*S*,6*R*)-5,6-Dihydroxy-1-phenyltetradecan-4-one (27). Pyridinium *p*-toluenesulfonate (10.3 mg, 40.9 µL) was added to a stirred solution of compound **26** (13.7 mg, 45.3 µL) in wet benzene (3 mL) under air. The mixture was stirred for 12 h before it was diluted with *tert*-butyl methyl ether (5 mL). The organic phase was washed with saturated aqueous $NaHCO_3$ solution (2 x 2 mL) and H_2O (2 mL), and concentrated in vacuo. Purification of the residue by flash chromatography (5/1 = hexane/EtOAc) gave the product as a white amorphous solid (9.7 mg, 67%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 – 7.26 (m, 2H), 7.23 – 7.15 (m, 3H), 4.02 (s, 1H), 3.91 (s, 1H), 3.71 (d, *J* = 3.2 Hz, 1H), 2.70 – 2.58 (m, 3H), 2.53 – 2.43 (m, 1H), 2.09 – 1.91 (m, 2H), 1.72 – 1.55 (m, 3H), 1.50 – 1.21 (m, 12H), 0.90 (t, *J* = 6.7 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 210.4, 141.4, 128.6 (two signals unresolved), 126.2, 79.0, 72.1, 37.1, 35.1, 34.6, 32.0, 29.7, 29.6, 29.4, 26.0, 25.0 22.8, 14.3. IR (neat) 3420, 2924, 2853, 1711, 1455, 1393, 1362, 1265, 1104, 1070, 1017, 737, 698, 492 cm^{-1}. HRMS (ESI): *m/z* calculated for $C_{20}H_{32}O_3Na$ [M+Na$^+$]: 343.2243, found 343.2244.

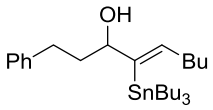
(4*S*,5*R*,6*R*,7*S*)-4,5-Dihydroxy-11,11-dimethoxy-7-((4-methoxybenzyl)oxy)-6-methylundecan-3-one (31).



Prepared analogously (68% yield, 9.0 mg). $[\alpha]_D^{25}$ = +31.4 (c = 0.9, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 – 7.22 (m, 2H), 6.89 – 6.84 (m, 2H), 4.51 (d, *J* = 10.7 Hz, 1H), 4.41 (d, *J* = 10.7 Hz, 1H), 4.35 (t, *J* = 5.6 Hz, 1H), 4.12 (dd, *J* = 4.6, 2.3 Hz, 1H), 4.06 (ddd, *J* = 7.7, 4.3, 2.3 Hz, 1H), 3.80 (s, 3H), 3.73 (d, *J* = 4.6 Hz, 1H), 3.62 (q, *J* = 5.6 Hz, 1H), 3.32 (s, 6H), 3.10 (d, *J* = 7.7 Hz, 1H), 2.65 (dq, *J* = 18.0, 7.3 Hz, 1H), 2.45 (dq, *J* = 18.0, 7.3 Hz, 1H), 2.13 – 2.02 (m, 1H), 1.66 – 1.55 (m, 4H), 1.50 – 1.36 (m, 2H), 1.09 (t, *J* = 7.3 Hz, 3H), 1.02 (d, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 211.9, 159.4, 130.5, 129.7, 114.0, 104.6, 82.2, 78.2, 72.8, 71.7, 55.4, 53.0, 52.9, 39.0, 32.8, 31.5, 30.6, 19.8, 12.5, 7.6. IR (neat): 3439, 2939, 1713, 1612, 1513, 1459, 1381, 1302, 1246, 1174, 1033, 821, 756, 578, 516 cm^{-1}. HRMS (ESI): *m/z* calcd for $C_{22}H_{36}O_7Na$ [M+Na^+]: 435.2353, found: 435.2353.

Substrates

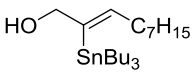
Representative Procedure for the Ruthenium Catalyzed *trans*-Hydrostannation.[2] (*Z*)-1-Phenyl-4-(tributylstannyl)non-4-en-3-ol (1).



1-Phenylnon-4-yn-3-ol (5.4 g, 25 mmol) was dissolved in CH_2Cl_2 (100 mL) and the solution was stirred in an oven-dried Schlenk flask. $[Cp^*RuCl_2]_n$ (77 mg, 0.25 mmol) was added, followed by addition of Bu_3SnH (7.1 ml, 26.3 mmol) over 1 h via a syringe pump. Stirring was continued for additional 5 min before the volatile materials were removed under reduced pressure. The crude product was purified by flash chromatography (hexane/EtOAc) to give the product as a viscous oil (11.8 g, 93%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 – 7.24 (m, 2H), 7.23 – 7.12 (m, 3H), 6.38 – 5.96 (m, 1H), 4.35 – 4.01 (m, 1H), 2.64 (qdd, *J* = 13.8, 9.8, 6.1 Hz, 2H), 2.13 – 1.95 (m, 2H), 1.83 (dddd, *J* = 13.3, 9.7, 7.2, 6.0 Hz, 1H), 1.71 (ddt, *J* = 13.5, 10.0, 6.3 Hz, 1H), 1.60 – 1.40 (m, 8H), 1.40 – 1.21 (m, 9H), 1.04 – 0.79 (m, 18H). ^{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. ^{119}Sn NMR (149 MHz, $CDCl_3$) δ −55.09. IR (film, $CHCl_3$) 2955, 2923, 2871, 2854, 1616, 1496, 1456, 1419, 1376, 1340, 1290, 1201, 1072, 1048, 1002, 961, 926, 863, 746, 697, 664 cm^{-1}. HRMS (ESI): *m/z* calculated for $C_{27}H_{48}OSnNa$ [M+Na^+]: 531.2619, found 531.2618.

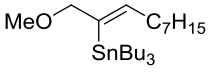
Unless stated otherwise, the following compounds were prepared analogously:

(*Z*)-2-(Tributylstannyl)dec-2-en-1-ol (32a).



97% yield (3.1 g). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.25 (tt, *J* = 7.2, 1.4 Hz, 1H), 4.28 – 4.12 (m, 2H), 2.04 (q, *J* = 7.4 Hz, 2H), 1.61 – 1.44 (m, 6H), 1.43 – 1.25 (m, 16H), 1.22 (t, *J* = 6.0 Hz, 1H), 1.02 – 0.94 (m, 6H), 0.94 – 0.87 (m, 12H). ^{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. ^{119}Sn NMR (149 MHz, $CDCl_3$) δ −52.7. IR (film, $CHCl_3$) 3305, 2955, 2922, 2871, 2852, 1462, 1418, 1376, 1340, 1290, 1181, 1148, 1072, 1000, 960, 862, 806, 769 cm^{-1}. HRMS (ESI): *m/z* calculated for $C_{22}H_{45}OSn$ [M−H^+]: 445.2497, found 445.2503.

(*Z*)-Tributyl(1-methoxydec-2-en-2-yl)stannane (32b).

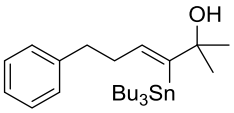


An oven-dried Schlenk flask was charged with NaH (180 mg, 7.5 mmol) and THF (20 mL), and the suspension was cooled with an ice bath. (*Z*)-2-(Tributylstannyl)dec-2-en-1-ol (**32a**) (2.23 g, 5.0 mmol) in a minimal amount of THF was added dropwise. Stirring was continued for 30 min at 0 °C before MeI (622 µL, 10.0 mmol) was slowly added, and the reaction mixture was allowed to warm to room temperature.

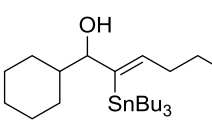
[2] S. M. Rummelt, A. Fürstner, *Angew. Chem. Int. Ed.* **2014**, *53*, 3626-3630; *Angew. Chem*. **2014**, *126*, 3700-3704.

After stirring for 12 h, the reaction was quenched with water at 0 °C and the solution acidified with saturated aqueous NH_4Cl solution. The mixture was extracted twice with *tert*-butyl methyl ether, and the combined organic layers were dried over magnesium sulfate and concentrated under reduced pressure. Flash chromatography (hexane/EtOAc = 30/1) yielded the product as a colorless oil (2.14 g, 93% yield). 1H NMR (400 MHz, $CDCl_3$) δ 6.23 (tt, *J* = 7.1, 1.2 Hz, 1H), 4.00 – 3.88 (m, 2H), 3.25 (d, *J* = 0.9 Hz, 3H), 2.02 (q, *J* = 7.1 Hz, 2H), 1.55 – 1.41 (m, 6H), 1.41 – 1.19 (m, 16H), 1.01 – 0.73 (m, 18H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.5, 140.6, 80.6, 57.4, 34.8, 32.0, 30.2, 29.6, 29.4, 29.4, 27.6, 22.8, 14.3, 13.9, 10.4. ^{119}Sn NMR (149 MHz, $CDCl_3$) δ −52.5. 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* calculated for $C_{23}H_{48}OSnNa$ [M+Na^+]: 483.2619, found 483.2624.

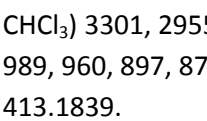
(*Z*)-2-Methyl-6-phenyl-3-(tributylstannyl)hex-3-en-2-ol. quant. (5.16 g). ^1H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.27 (m, 2H), 7.24 – 7.12 (m, 3H), 6.16 (t, *J* = 7.2 Hz, 1H), 2.78 – 2.60 (m, 2H), 2.41 – 2.28 (m, 2H), 1.57 – 1.41 (m, 6H), 1.39 – 1.31 (m, 6H), 1.31 (s, 7H), 0.99 – 0.92 (m, 6H), 0.89 (t, *J* = 7.3 Hz, 9H). ^{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. ^{119}Sn NMR (149 MHz, $CDCl_3$) δ −55.6. 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* calculated for $C_{25}H_{44}OSnNa$ [M+Na^+]: 503.2306, found 503.2306.



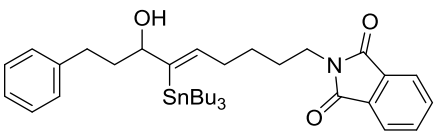
(*Z*)-1-Cyclohexyl-2-(tributylstannyl)hept-2-en-1-ol. 66% yield (3.2 g). ^1H NMR (400 MHz, $CDCl_3$) 6.29 – 5.84 (m, 1H), 3.87 – 3.61 (m, 1H), 2.10 – 1.89 (m, 2H), 1.83 – 1.58 (m, 3H), 1.58 – 1.39 (m, 6H), 1.38 – 1.25 (m, 12H), 1.18 (dtt, *J* = 20.5, 9.1, 3.3 Hz, 2H), 1.02 – 0.68 (m, 22H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.0, 142.1, 85.4, 43.1, 34.2, 32.5, 30.3, 29.4, 28.8, 27.6, 26.7, 26.3, 26.3, 22.8, 14.2, 13.9, 11.3. ^{119}Sn NMR (149 MHz, $CDCl_3$) δ −55.5. IR (film, $CHCl_3$) 3482, 2955, 2921, 2851, 1615, 1451, 1376, 1257, 1202, 1148, 1069, 1001, 961, 890, 862 cm^{-1}. HRMS (ESI): *m/z* calculated for $C_{25}H_{49}OSn$ [M−H^+]: 485.2810, found 485.2810.



(*Z*)-2-(Tributylstannyl)hex-2-en-1-ol. 92% yield (7.19 g). ^1H NMR (300 MHz, $CDCl_3$) δ 6.52 – 5.93 (m, 1H), 4.28 – 4.09 (m, 2H), 2.10 – 1.87 (m, 2H), 1.63 – 1.41 (m, 6H), 1.41 – 1.23 (m, 7H), 1.16 (t, *J* = 6.0 Hz, 1H), 0.99 – 0.92 (m, 7H), 0.89 (t, *J* = 7.3 Hz, 12H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 143.4, 142.0, 70.7, 36.8, 29.4, 27.6, 23.3, 14.0, 13.8, 10.4. ^{119}Sn NMR (112 MHz, $CDCl_3$) δ −52.8. IR (film, $CHCl_3$) 3301, 2955, 2924, 2871, 2853, 1622, 1462, 1418, 1376, 1340, 1291, 1182, 1148, 1073, 1045, 1021, 989, 960, 897, 875, 741, 664 cm^{-1}. HRMS (ESI): *m/z* calculated for $C_{18}H_{38}OSnNa$ [M+Na^+]: 413.1836, found 413.1839.

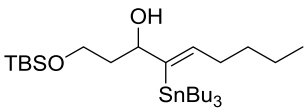


(*Z*)-2-(7-Hydroxy-9-phenyl-6-(tributylstannyl)non-5-en-1-yl)isoindoline-1,3-dione. 76% yield (1.02 g). ^1H NMR (400 MHz, $CDCl_3$) δ 7.87 – 7.77 (m, 2H), 7.74 – 7.64 (m, 2H), 7.26 (ddd, *J* = 7.8, 7.1, 0.9 Hz, 2H), 7.22 – 7.13 (m, 3H), 6.15 (td, *J* = 7.2, 1.1 Hz, 1H), 4.28 – 4.00 (m, 1H), 3.69 (t, *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). ^{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. ^{119}Sn NMR (149 MHz, $CDCl_3$) δ −55.2.

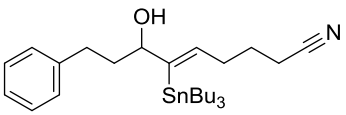


IR (film, $CHCl_3$) 2925, 2854, 1773, 1739, 1712, 1455, 1438, 1395, 1371, 1238, 1044, 961, 918, 873, 849, 792, 747 cm^{-1}. HRMS (ESI): *m/z* calculated for $C_{35}H_{51}NO_3SnNa$ [M+Na^+]: 676.2782, found 676.2788.

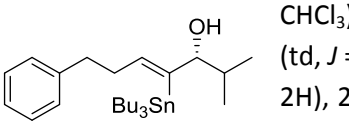
(*Z*)-1-((*tert*-Butyldimethylsilyl)oxy)-4-(tributylstannyl)non-4-en-3-ol. 81% yield (1.86 g). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.20 (td, *J* = 7.2, 1.2 Hz, 1H), 4.48 – 4.18 (m, 1H), 3.94 – 3.72 (m, 3H), 3.16 (d, *J* = 2.2 Hz, 1H), 2.02 (td, *J* = 8.9, 8.1, 5.9 Hz, 2H), 1.79 – 1.64 (m, 2H), 1.58 – 1.40 (m, 7H), 1.40 – 1.20 (m, 11H), 1.01 – 0.76 (m, 21H), 0.07 (s, 9H). ^{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. ^{119}Sn NMR (149 MHz, $CDCl_3$) δ −55.1. IR (film, $CHCl_3$) 2954, 2926, 2856, 1463, 1377, 1254, 1093, 1004, 961, 939, 834, 775, 729, 664 cm^{-1}. HRMS (ESI): *m/z* calculated for $C_{27}H_{58}O_2SiSnNa$ [M+Na^+]: 585.3120, found 585.3123.



(*Z*)-6-Chloro-2-(tributylstannyl)hex-2-en-1-ol. 75% yield (1.58 g). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.21 (tt, *J* = 7.1, 1.5 Hz, 1H), 4.28 – 4.12 (m, 2H), 3.54 (q, *J* = 6.7 Hz, 2H), 2.19 (dddd, *J* = 7.8, 6.9, 6.0, 1.2 Hz, 2H), 2.00 – 1.74 (m, 2H), 1.70 – 1.38 (m, 6H), 1.38 – 1.27 (m, 6H), 1.24 (d, *J* = 5.9 Hz, 1H), 1.07 – 0.93 (m, 6H), 0.89 (t, *J* = 7.3 Hz, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.1, 139.4, 70.5, 44.7, 32.9, 31.8, 29.4, 27.6, 13.9, 10.4. ^{119}Sn NMR (149 MHz, $CDCl_3$) δ −52.3. IR (film, $CHCl_3$) 3312, 2955, 2923, 2871, 2851, 1622, 1458, 1376 1340, 1290, 1182, 1072, 999, 961, 866, 767, 727, 657 cm^{-1}. HRMS (ESI): *m/z* calculated for $C_{18}H_{36}OClSn$ [M−H^+]: 423.1481, found 423.1481.



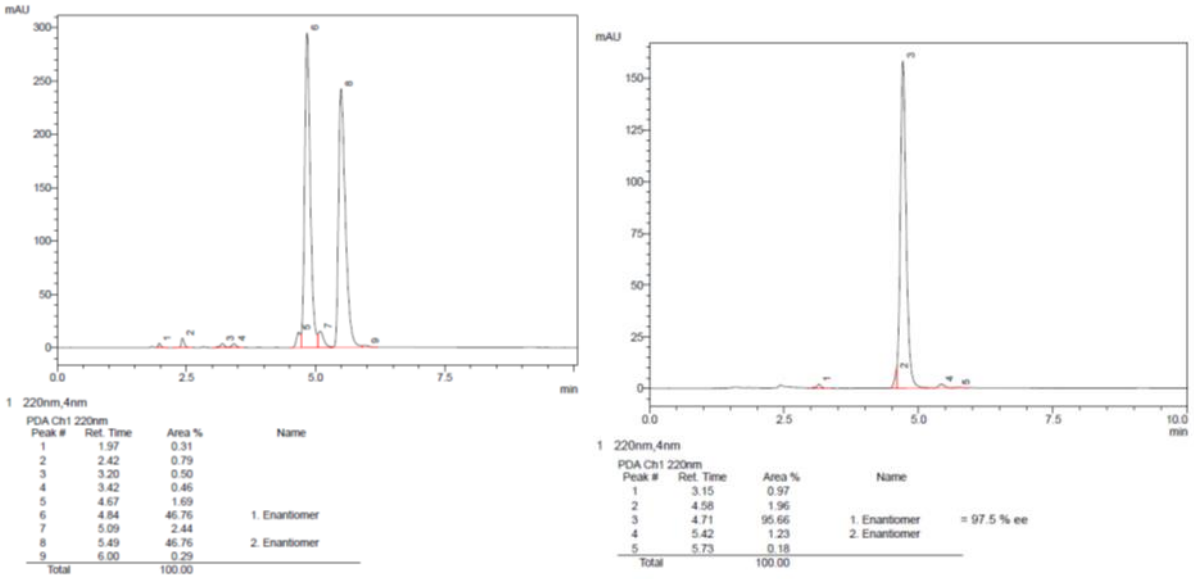
(*Z*)-7-Hydroxy-9-phenyl-6-(tributylstannyl)non-5-enenitrile. 89% yield (2.3 g). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 – 7.26 (m, 2H), 7.20 (m, 3H), 6.13 (td, *J* = 7.1, 1.1 Hz, 1H), 4.27 – 4.03 (m, 1H), 2.76 – 2.56 (m, 2H), 2.35 (t, *J* = 7.2 Hz, 2H), 2.20 (q, *J* = 7.2 Hz, 2H), 1.89 – 1.64 (m, 4H), 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). ^{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. ^{119}Sn NMR (149 MHz, $CDCl_3$) δ −54.7. 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* calculated for $C_{27}H_{45}NOSnNa$ [M+Na^+]: 542.2415, found 542.2417.



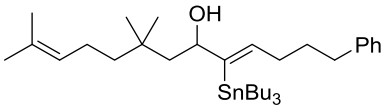
(*R*,*Z*)-2-Methyl-7-phenyl-4-(tributylstannyl)hept-4-en-3-ol. 91% yield (2.05 g). $[\alpha]_D^{20}$ = −9.7 (c = 2.23, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 – 7.24 (m, 2H), 7.24 – 7.11 (m, 3H), 6.16 (td, *J* = 7.2, 1.1 Hz, 1H), 3.71 (ddd, *J* = 8.1, 3.2, 1.1 Hz, 1H), 2.69 (dd, *J* = 9.1, 6.6 Hz, 2H), 2.45 – 2.30 (m, 2H), 1.60 – 1.41 (m, 7H), 1.40 (d, *J* = 3.2 Hz, 1H), 1.37 – 1.25 (m, 6H), 0.99 – 0.91 (m, 9H), 0.89 (t, *J* = 7.2 Hz, 9H), 0.79 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.4, 141.9, 140.6, 128.6, 128.5, 126.0, 86.3, 36.6, 36.3, 33.5, 29.4, 27.6, 20.1, 18.3, 13.8, 11.3. ^{119}Sn NMR (149 MHz, $CDCl_3$) δ −55.2. IR (film, $CHCl_3$) 3480, 3027, 2954, 2922, 2870, 2853, 1614, 1496, 1455, 1376, 1273, 1178, 1071, 1004, 959, 874, 745, 697 cm^{-1}. HRMS (ESI): *m/z* calculated for $C_{26}H_{46}OSnNa$ [M+Na^+]: 517.2462, found 517.2465.

The racemic sample was prepared analogously.

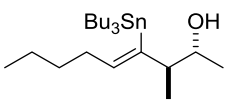
The enantiomeric excess was determined to be 98%by HPLC analysis (150 mm Chiralpak IA-3, 4.6 mm i.D., Säule 3, *n*-Heptane/2-Propanol = 99.9:0.1 (v/v), 1.0 ml/min, 6.3 MPa, 298 K, UV 220 nm).



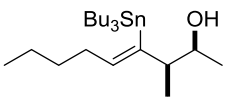
(*Z*)-8,8,12-Trimethyl-1-phenyl-5-(tributylstannyl)trideca-4,11-dien-6-ol. 90% yield (1.22 g). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 – 7.24 (m, 2H), 7.21 – 7.13 (m, 3H), 6.13 (t, *J* = 7.1 Hz, 1H), 5.13 – 5.06 (m, 1H), 4.30 (dt, *J* = 6.9, 2.9 Hz, 1H), 2.63 (t, *J* = 7.6 Hz, 2H), 2.08 – 1.99 (m, 2H), 1.92 (p, *J* = 8.8 Hz, 2H), 1.73 – 1.63 (m, 5H), 1.59 (s, 3H), 1.51 – 1.41 (m, 7H), 1.37 – 1.23 (m, 9H), 1.21 (d, *J* = 2.9 Hz, 1H), 0.98 – 0.83 (m, 21H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.6, 142.4, 139.5, 131.0, 128.6, 128.5, 125.9, 125.4, 78.0, 49.6, 43.3, 36.0, 33.9, 33.2, 32.0, 29.4, 28.0, 27.8, 27.6, 25.9, 23.0, 17.7, 13.9, 11.3. ^{119}Sn NMR (149 MHz, $CDCl_3$) δ −54.33. IR (neat) 3496, 2954, 2922, 2854, 1613, 1454, 1376, 1070, 1050, 875, 743, 697, 666, 594, 531, 495 cm^{-1}. HRMS (ESI): *m/z* calculated for $C_{34}H_{60}OSnNa$ [M+Na$^+$]: 627.3559, found 627.3558.

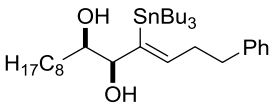


(*anti*,*Z*)-3-Methyl-4-(tributylstannyl)non-4-en-2-ol (20). 91% yield (9.43 g; α/β = 12:1). ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.17 (td, *J* = 7.1, 0.8 Hz, 1H), 3.48 (dqt, *J* = 8.0, 4.6, 1.9 Hz, 1H), 2.26 – 2.12 (m, 1H), 2.12 – 1.97 (m, 2H), 1.86 (dd, *J* = 1.7, 0.8 Hz, 1H), 1.55 – 1.42 (m, 6H), 1.42 – 1.21 (m, 8H), 1.16 (d, *J* = 6.0 Hz, 3H), 1.09 – 0.51 (m, 23H). ^{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. ^{119}Sn NMR (112 MHz, $CDCl_3$) δ −54.4. 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* calculated for $C_{22}H_{46}OSnNa$ [M+Na$^+$]: 469.2462, found 469.2466.



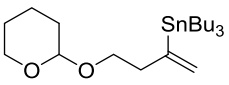
(*syn*,*Z*)-3-Methyl-4-(tributylstannyl)non-4-en-2-ol (22). 62% yield (5.76 g; α/β = 10:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.30 – 5.86 (m, 1H), 3.60 (dddd, *J* = 9.6, 8.6, 6.3, 3.2 Hz, 1H), 2.40 – 2.19 (m, 1H), 2.01 (pd, *J* = 6.8, 2.0 Hz, 2H), 1.58 – 1.41 (m, 6H), 1.41 – 1.24 (m, 11H), 1.15 (d, *J* = 6.3 Hz, 3H), 1.05 – 0.99 (m, 3H), 0.95 – 0.78 (m, 18H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.0, 141.1, 69.7, 49.7, 35.1, 32.7, 29.4, 27.6, 22.8, 21.2, 14.4, 14.3, 13.8, 11.0. ^{119}Sn NMR (149 MHz, $CDCl_3$) δ −52.00. IR (film, $CHCl_3$) 3341, 2956, 2923, 2871, 2854, 1458, 1418, 1376, 1340, 1291, 1249, 1151, 1076, 1047, 1019, 960, 923, 899, 862, 768 cm^{-1}. HRMS (ESI): *m/z* calculated for $C_{22}H_{45}OSn$ [M−H$^+$]: 445.2497, found 445.2500.



(5*S*,6*R*,*Z*)-1-Phenyl-4-(tributylstannyl)tetradec-3-ene-5,6-diol (25). 54% yield (1.26 g). ^{1}H NMR (400 MHz, 

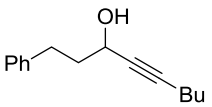
$CDCl_3$) δ 7.33 – 7.26 (m, 2H), 7.24 – 7.14 (m, 3H), 6.47 – 6.05 (m, 1H), 4.04 – 3.80 (m, 1H), 3.44 – 3.27 (m, 1H), 2.71 (dd, *J* = 8.8, 6.6 Hz, 2H), 2.45 – 2.34 (m, 2H), 2.29 (dd, *J* = 16.8, 3.4 Hz, 2H), 1.57 – 1.40 (m, 6H), 1.40 – 1.16 (m, 20H), 0.99 – 0.92 (m, 6H), 0.92 – 0.85 (m, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.5, 142.9, 141.6, 128.5, 128.5, 126.1, 83.5, 74.2, 36.4, 36.3, 33.0, 32.0, 29.9, 29.7, 29.5, 29.4, 27.6, 26.0, 22.8, 14.3, 13.8, 11.3. ^{119}Sn NMR (149 MHz, $CDCl_3$) δ −53.8. IR (film, $CHCl_3$) 3397, 2922, 2954, 2853, 2870, 1615, 1496, 1455, 1376, 1339, 1288, 1199, 1072, 1029, 961, 904, 866, 746, 723, 697 cm^{-1}. HRMS (ESI): *m/z* calculated for $C_{32}H_{58}O_2SnNa$ [M+Na^+]: 617.3350, found 617.3355.

(*Z*)-Tributyl(3-(methoxymethoxy)-1-phenylnon-4-en-4-yl)stannane (16). Tetrabutylammonium iodide (185 mg, 0.5 mmol) and Hünig base (1.74 mL, 10 mmol) were added to a solution of (*Z*)-1-phenyl-4-(tributylstannyl)-non-4-en-3-ol (**1**) (2.53 g, 5.0 mmol) in CH_2Cl_2 (20 mL) at 0°C, followed by dropwise addition of chloromethyl methyl ether (570 µL, 7.5 mmol). The mixture was stirred for 18 h while being gradually warmed to room temperature. The reaction was then quenched with saturated aqueous NH_4Cl solution. The mixture was extracted twice with *tert*-butyl methyl ether, and the combined extracts were washed with brine, dried over magnesium sulfate, and concentrated under reduced pressure. Flash chromatography (hexane/EtOAc = 30/1) yielded the product as a colorless oil (2.62 g, 95% yield). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.32 – 7.24 (m, 2H), 7.22 – 7.13 (m, 3H), 6.46 – 5.87 (m, 1H), 4.66 (d, *J* = 6.5 Hz, 1H), 4.47 (d, *J* = 6.5 Hz, 1H), 4.25 – 3.92 (m, 1H), 3.37 (s, 3H), 2.80 – 2.51 (m, 2H), 2.07 (dddd, *J* = 8.8, 7.0, 4.9, 1.8 Hz, 2H), 1.91 (dddd, *J* = 13.2, 10.5, 7.2, 5.9 Hz, 1H), 1.68 (ddt, *J* = 13.5, 10.6, 6.1 Hz, 1H), 1.60 – 1.41 (m, 6H), 1.41 – 1.14 (m, 10H), 1.01 – 0.79 (m, 18H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 144.9, 144.1, 142.5, 128.5, 128.5, 93.4, 84.0, 55.6, 38.4, 34.3, 32.6, 29.4, 27.6, 22.8, 14.2, 13.8, 11.3. IR (film, $CHCl_3$) 2954, 2923, 2871, 2855, 1614, 1496, 1455, 1376, 1177, 1147, 1094, 1030, 960, 920, 863, 746, 697 cm^{-1}. HRMS (ESI): *m/z* calculated for $C_{29}H_{52}O_2SnNa$ [M+Na^+]: 575.2881, found 575.2886.

Tributyl(4-((tetrahydro-2H-pyran-2-yl)oxy)but-1-en-2-yl)stannane (18). A solution of 2-(3-butynyloxy)-tetrahydro-2*H*-pyran (784 µL, 5.0 mmol) and Bu_3SnH (1.41 mL, 5.25 mmol) in CH_2Cl_2 

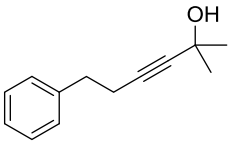
(5 mL) was added over 1 h via syringe pump to a stirred solution of [Cp*Ru(MeCN)$_3$]PF_6 (63 mg, 0.125 mmol) in CH_2Cl_2 (20 mL) at room temperature. Upon complete addition, the volatile materials were removed under vacuum, and the residue was purified by flash chromatography (hexane/EtOAc = 50/1) to give the product as a pale yellow oil (1.88 g, 84% yield). TLC (hexane/EtOAc = 20:1), Rf = 0.45. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.94 – 5.49 (m, 1H), 5.31 – 5.09 (m, 1H), 4.58 (dd, *J* = 4.3, 2.7 Hz, 1H), 3.92 – 3.81 (m, 1H), 3.78 (ddd, *J* = 9.7, 7.8, 6.7 Hz, 1H), 3.55 – 3.47 (m, 1H), 3.41 (ddd, *J* = 9.7, 7.9, 7.0 Hz, 1H), 2.54 (ddq, *J* = 8.0, 6.7, 1.3 Hz, 2H), 1.90 – 1.79 (m, 1H), 1.77 – 1.68 (m, 1H), 1.67 – 1.39 (m, 10H), 1.39 – 1.24 (m, 6H), 1.04 – 0.79 (m, 15H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.5, 127.1, 99.0, 67.5, 62.5, 41.2, 30.9, 29.3, 27.6, 25.7, 19.8, 13.8, 9.7. ^{119}Sn NMR (149 MHz, $CDCl_3$) δ −43.8. IR (film, $CHCl_3$) 2923, 2871, 2852, 1463, 1377, 1351, 1323, 1260, 1201, 1183, 1135, 1120, 1071, 1031, 981, 960, 915 cm^{-1}. HRMS (ESI): *m/z* calculated for $C_{21}H_{42}O_2SnNa$ [M+Na^+]: 469.2098, found 469.2102.

Representative procedure: Synthesis of Propargyl Alcohols. 1-Phenylnon-4-yn-3-ol. A flame-dried 250 mL two-necked flask was equipped with a dropping funnel and charged with THF (100 mL) and 1-hexyne (6.61 mL, 57.5 mmol). The solution was cooled with a dry ice/acetone bath before *n*-butyllithium (34.4 mL, 1.6 M in hexane, 55 mmol) was slowly added via the dropping funnel. Once the addition was complete, stirring was continued for 1 h before neat hydrocinnamaldehyde (6.58 mL, 50 mmol) was added in one portion. After being stirred for 30 min, the mixture was warmed to room temperature, the reaction was quenched with saturated aqueous NH_4Cl solution, and the aqueous phase was extracted twice with *tert*-butyl methyl ether. The combined organic layers were washed with brine, dried over magnesium sulfate, and concentrated under reduced pressure. The product was obtained after flash chromatographic purification of the residue (hexane/EtOAc) (10.7 g, 99%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 – 7.27 (m, 2H), 7.25 – 7.17 (m, 3H), 4.37 (tt, *J* = 6.4, 2.0 Hz, 1H), 2.80 (t, *J* = 7.9 Hz, 2H), 2.24 (td, *J* = 7.0, 2.0 Hz, 2H), 2.01 (tt, *J* = 7.8, 6.2 Hz, 2H), 1.62 – 1.48 (m, 2H), 1.48 – 1.35 (m, 2H), 0.93 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.6, 128.6, 128.5, 126.0, 86.1, 81.1, 62.2, 39.8, 31.6, 30.8, 22.1, 18.5, 13.7. IR (film, $CHCl_3$): 3338, 3027, 2955, 2931, 2861, 1603, 1496, 1454, 1379, 1328, 1134, 1030 1054, 914, 746, 699 cm^{-1}. The recorded data were in accordance with literature.[3]

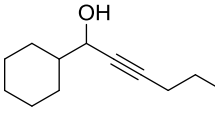


Unless stated otherwise, the following compounds were prepared analogously:

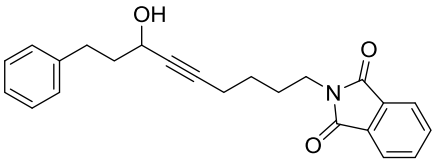
2-Methyl-6-phenylhex-3-yn-2-ol. 97% yield (2.75 g). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 – 7.27 (m, 2H), 7.26 – 7.16 (m, 3H), 2.82 (t, *J* = 7.5 Hz, 2H), 2.48 (t, *J* = 7.6 Hz, 2H), 2.07 (s, 1H), 1.49 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.7, 128.6, 128.4, 126.4, 86.1, 81.8, 65.3, 35.2, 31.7, 21.0. IR (film, $CHCl_3$): 3379, 3028, 2979, 2930, 2863, 1739, 1604, 1496, 1454, 1362, 1341, 1239, 1163, 1047, 1078, 1030, 949, 833, 861, 748, 698 cm^{-1}. HRMS (ESI): *m/z* calculated for $C_{13}H_{16}ONa$ [M+Na$^+$]: 211.1093, found 211.1093.



1-Cyclohexylhept-2-yn-1-ol. 98% yield (5.28 g). ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.13 (dt, *J* = 6.0, 2.1 Hz, 1H), 2.21 (td, *J* = 7.0, 2.0 Hz, 2H), 1.79 (ddtd, *J* = 29.2, 12.6, 3.2, 1.7 Hz, 3H), 1.67 (dddd, *J* = 12.8, 5.1, 3.1, 1.7 Hz, 1H), 1.58 – 1.44 (m, 3H), 1.44 – 1.33 (m, 2H), 1.32 – 0.94 (m, 7H), 0.91 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 86.4, 80.2, 67.6, 44.5, 30.9, 28.7, 28.2, 26.6, 26.1, 26.0, 22.1, 18.5, 13.7. The recorded data were in accordance with the literature.[4]



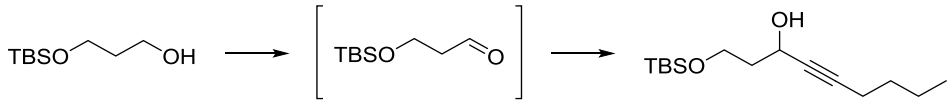
2-(7-Hydroxy-9-phenylnon-5-yn-1-yl)isoindoline-1,3-dione. *n*-Butyllithium (8.13 mL, 1.6 M in hexane, 13 mmol) was added dropwise to a solution of HMDS (3.13 mL, 15 mmol) in THF (20 mL) at 0°C. The resulting mixture was stirred for 30 min before it was cooled to −78 °C. *n*-(5-Hexynyl)-phthalimide (2.5 g, 11 mmol) was added, and stirring was continued for 1 h before neat phenylpropionaldehyde (1.31 mL, 10 mmol) was added in one portion. The mixture was allowed to warm to room temperature. After being stirred for another 30 min, saturated aqueous NH_4Cl solution was added, followed by aqueous HCl (2 M) to give a clear solution. The mixture was extracted twice with EtOAc, and the combined extracts were washed



[3] M. Egi, Y. Yamaguchi, N. Fujiwara, S. Akai, *Org. Lett.* **2008**, *10*, 1867-1870.
[4] R. B. Lettan, K. A. Scheidt, *Org. Lett.* **2005**, *7*, 3227-3230.

with brine, dried over magnesium sulfate, and concentrated under reduced pressure. Purification of the residue by flash chromatography (hexane/EtOAc = 2/1) delivered the title compound (746 mg, 21% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (m, 2H), 7.64 – 7.55 (m, 2H), 7.23 – 7.14 (m, 2H), 7.14 – 7.04 (m, 3H), 4.26 (dt, *J* = 4.6, 2.1 Hz, 1H), 3.62 (t, *J* = 7.2 Hz, 2H), 2.68 (t, *J* = 7.9 Hz, 2H), 2.40 (d, *J* = 4.8 Hz, 1H), 2.19 (td, *J* = 7.0, 2.0 Hz, 2H), 1.99 – 1.80 (m, 2H), 1.73 (tt, *J* = 7.9, 6.4 Hz, 2H), 1.47 (dq, *J* = 9.7, 7.0 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.5, 141.6, 134.0, 132.1, 128.5, 128.4, 125.9, 123.3, 84.8, 82.0, 61.9, 39.6, 37.5, 31.5, 27.5, 25.6, 18.2. IR (film, $CHCl_3$) 3463, 2940, 2864, 1771, 1736, 1704, 1604, 1496, 1467, 1437, 1396, 1372, 1335, 1239, 1188, 1115, 1039, 915, 847, 792 cm^{-1}. HRMS (ESI): *m/z* calculated for $C_{23}H_{23}NO_3Na$ [M+Na$^+$]: 384.1570, found 384.1573.

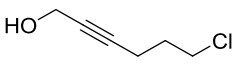
1-((*tert*-Butyldimethylsilyl)oxy)non-4-yn-3-ol



A solution of oxalyl chloride (1.99 mL, 23.2 mmol) in CH_2Cl_2 (50 mL) and stirred at −60 °C in a flame-dried Schlenk flask. A solution of DMSO (3.41 mL, 48 mmol) in CH_2Cl_2 (10 mL) was added. After 5 min, 3-(*tert*-butyl-dimethyl-silanyloxy)-propan-1-ol (3.81 g, 20 mmol) was added dropwise at −60 °C, followed by dropwise addition of Et_3N (14.1 mL, 101 mmol). The mixture was allowed to reach room temperature, and the reaction was quenched with water (100 mL). The phases were separated and the aqueous layer was extracted with CH_2Cl_2. The combined organic layers were washed with brine, water, and again with brine before being dried over magnesium sulfate. The solvents were removed under reduced pressure, and the residue was dissolved in diethyl ether and filtered over Celite. The crude aldehyde, which was obtained after concentration under reduced pressure, was used in the next step without further purification.

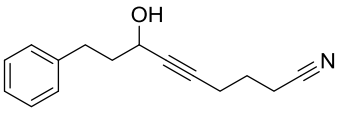
n-Butyllithium (7.5 mL, 1.6 M in hexane, 12 mmol) was added to a solution of 1-hexyne (1.38 mL, 12 mmol) in THF (25 mL) at −78°C and stirring was continued for 1 h at the same temperature before freshly prepared 3-((*tert*-butyldimethyl-silyl)oxy)propanal (1.88 g, 10 mmol) was introduced. After an additional 1 h, the mixture was warmed to room temperature and the reaction was quenched with saturated aqueous NH_4Cl. The mixture was extracted twice with EtOAc, and the combined organic layers were washed with brine, dried over magnesium sulfate, and concentrated under reduced pressure. Purification of the residue by flash chromatography (hexane/EtOAc = 10:1) yielded the product as a pale yellow oil (2.29 g, 85% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.54 (tt, *J* = 4.3, 2.2 Hz, 1H), 3.97 (ddd, *J* = 10.2, 7.6, 4.2 Hz, 1H), 3.77 (ddd, *J* = 10.4, 6.2, 4.5 Hz, 1H), 3.37 (s, 1H), 2.17 (td, *J* = 7.0, 2.0 Hz, 2H), 1.91 (ddt, *J* = 14.1, 7.6, 4.5 Hz, 1H), 1.80 (dtd, *J* = 14.1, 6.3, 4.2 Hz, 1H), 1.53 – 1.29 (m, 4H), 0.89 – 0.83 (m, 12H), 0.04 (s, 3H), 0.04 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 85.4, 80.7, 61.9, 61.2, 39.2, 30.8, 25.9, 22.0, 18.5, 18.2, 13.7, −5.5. IR (film, $CHCl_3$): 2955, 2929, 2858, 1470, 1253, 1099, 1006, 939, 832, 775 cm^{-1}. HRMS (ESI): *m/z* calculated for $C_{15}H_{30}O_2SiNa$ [M+Na$^+$]: 293.1907, found 293.1907.

6-Chlorohex-2-yn-1-ol. *n*-Butyllithium (12.5 mL, 1.6 M in hexane, 20 mmol) was added dropwise to a solution of 5-chloro-1-pentyne (2.14 mL, 20 mmol) in THF (20 mL) at −78°C and the resulting mixture was stirred for 15 min. Paraformaldehyde (1.62 g, 54 mmol) was added in one portion and the mixture was stirred at 45 °C for 2 h. After being cooled to room temperature, saturated aqueous NH_4Cl solution was added. The mixture was extracted

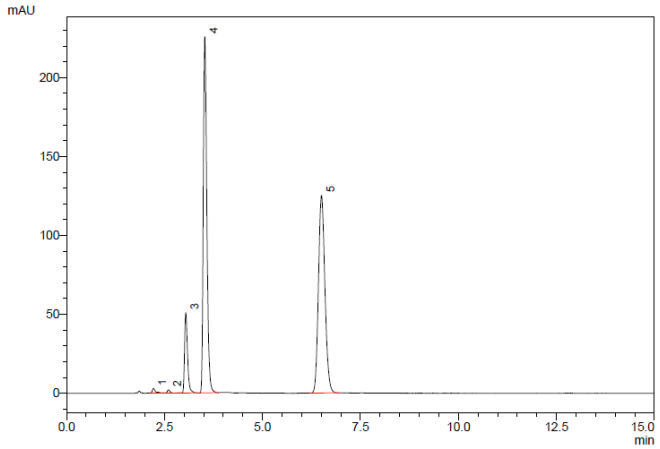


twice with *tert*-butyl methyl ether, and the combined organic layers were washed with brine, dried over magnesium sulfate, and concentrated under reduced pressure. Flash chromatography (hexane/*tert*-butyl methyl ether = 3:1) yielded the product as a colorless oil (2.15 g, 95% purity, 77% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.25 (t, *J* = 2.2 Hz, 2H), 3.65 (t, *J* = 6.3 Hz, 2H), 2.42 (tt, *J* = 6.8, 2.2 Hz, 2H), 1.96 (p, *J* = 6.6 Hz, 2H), 1.83 – 1.74 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 84.5, 79.5, 51.4, 43.8, 31.3, 16.3. IR (film, $CHCl_3$) 3340, 2918, 1433, 1354, 1290, 1230, 1131, 1010, 859, 726, 652 cm^{-1}. HRMS (ESI): *m/z* calculated for C_6H_9OClNa [M+Na$^+$]: 155.0234, found 155.0235.

7-Hydroxy-9-phenylnon-5-ynenitrile. 96% yield (2.19 g). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 – 7.26 (m, 2H), 7.25 – 7.15 (m, 3H), 4.36 (tdd, *J* = 6.5, 4.7, 3.3 Hz, 1H), 2.78 (t, *J* = 7.8 Hz, 2H), 2.49 (t, *J* = 7.1 Hz, 2H), 2.43 (td, *J* = 6.8, 2.0 Hz, 2H), 2.12 – 1.93 (m, 2H), 1.93 – 1.78 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.3, 128.6, 126.2, 119.3, 83.2, 82.9, 77.4, 62.0, 39.6, 31.6, 24.5, 18.0, 16.4. IR (film, $CHCl_3$) 3415, 3025, 2944, 2863, 2249, 1603, 1496, 1454, 1432, 1334, 1218, 1155, 1132, 1056, 1030, 915, 749 cm^{-1}. HRMS (ESI): *m/z* calculated for $C_{15}H_{17}NONa$ [M+Na$^+$]: 250.1202, found 250.1203.



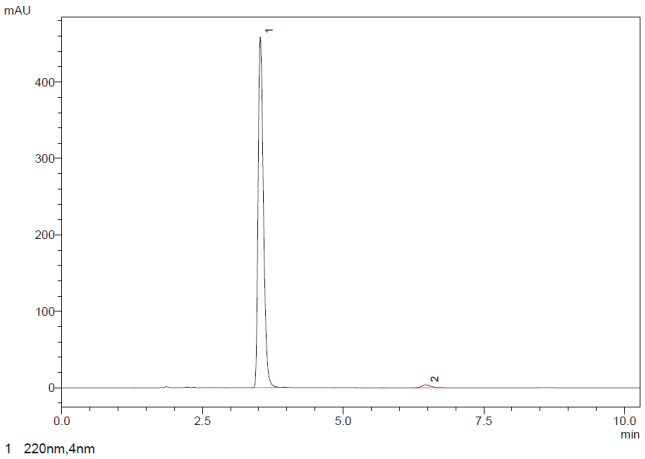
(*R*)-2-Methyl-7-phenylhept-4-yn-3-ol.[5] An oven-dried Schlenk flask was charged with $Zn(OTf)_2$ (2.0 g, 5.5 mmol), (+)-*N*-methylephedrine (1.08 g, 6.0 mmol) and toluene (15 mL), and the mixture was stirred for 15 min before Et_3N (836 µL, 6.0 mmol) was added. After being stirred for 2 h, the reaction mixture was treated with 4-phenyl-1-butyne (844 µL, 6.0 mmol) and stirring was continued for 15 min, followed by addition of iso-butyraldehyde (456 µL, 5.0 mmol). The mixture was vigorously stirred for 18 h before the reaction was quenched with saturated aqueous NH_4Cl solution. The mixture was extracted twice with *tert*-butyl methyl ether, and the combined extracts were washed with brine, dried over magnesium sulfate, and concentrated under reduced pressure. Flash chromatography (hexane/EtOAc = 9:1) yielded the product as a pale yellow oil (925 mg, 92% yield).



1 220nm,4nm

PDA Ch1 220nm

Peak #	Ret. Time	Area %	Name
1	2.22	0.52	
2	2.60	0.32	
3	3.04	8.48	
4	3.53	44.95	1. Enantiomer
5	6.51	45.73	2. Enantiomer
Total		100.00	



1 220nm,4nm

PDA Ch1 220nm

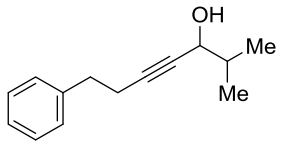
Peak #	Ret. Time	Area %	Name
1	3.53	98.58	1. Enantiomer
2	6.47	1.42	2. Enantiomer
Total		100.00	

ee = 97.2 %

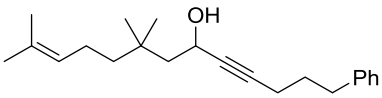
[5] D. E. Frantz, R. Fässler, E. M. Carreira, *J. Am. Chem. Soc.* **2000**, *122*, 1806-1807.

The enantiomeric excess was determined to be 97%by HPLC analysis (150 mm Chiralcel OD-3, 4.6 mm i.D., *n*-Heptane/2-Propanol = 90:10, 1.0 ml/min, 7.0 MPa, 298 K, UV 220 nm).

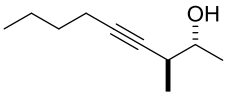
2-Methyl-7-phenylhept-4-yn-3-ol. 89% yield (1.08 g). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.34 – 7.25 (m, 2H), 7.25 – 7.17 (m, 3H), 4.13 (ddt, *J* = 5.6, 3.7, 2.2 Hz, 1H), 2.83 (t, *J* = 7.5 Hz, 2H), 2.59 – 2.48 (m, 2H), 1.81 (pd, *J* = 6.7, 5.6 Hz, 1H), 1.63 (d, *J* = 5.4 Hz, 1H), 0.95 (dd, *J* = 6.7, 3.6 Hz, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 140.7, 128.6, 128.5, 126.4, 85.5, 80.9, 68.3, 35.3, 34.8, 21.0, 18.2, 17.6. IR (film, $CHCl_3$) 3382, 3028, 2959, 2929, 2871, 1726, 1604, 1496, 1468, 1454, 1430, 1367, 1256, 1146, 1108, 1077, 1021, 959, 816, 745, 697 cm^{-1}. HRMS (ESI): *m/z* calculated for $C_{14}H_{18}O$ [M]: 202.1352, found 202.1350.



8,8,12-Trimethyl-1-phenyltridec-11-en-4-yn-6-ol. *n*BuLi (1.76 mL, 1.6 M in hexane, 2.82 mmol) was added dropwise at −78 °C to a stirred solution of pent-4-yn-1-ylbenzene (0.408 mL, 2.68 mmol) in THF (9.8 mL). After stirring for 1 h, a solution of 3,3,7-trimethyloct-6-enal[6] in THF (0.9 mL) was added and stirring was continued at −78 °C for 1 h. The mixture was warmed to ambient temperature before being quenched with saturated aqueous NH_4Cl solution (5 mL). The mixture was diluted with H_2O (10 mL) and the aqueous phase was extracted with *tert*-butyl methyl ether (3 x 10 mL). The combined organic layers were washed with H_2O (10 mL), dried over $MgSO_4$, and concentrated in vacuo. Purification by gradient flash chromatography (hexane/EtOAc = 14/1 to 9/1) gave the product as a colorless oil (0.777 g, 93%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 – 7.24 (m, 2H), 7.21 – 7.14 (m, 3H), 5.08 (t, *J* = 7.1 Hz, 1H), 4.45 (t, *J* = 6.3 Hz, 1H), 2.69 (t, *J* = 7.6 Hz, 2H), 2.21 (td, *J* = 7.1, 2.0 Hz, 2H), 1.99 – 1.90 (m, 2H), 1.81 (p, *J* = 7.1 Hz, 2H), 1.71 – 1.64 (m, 6H), 1.59 (s, 3H), 1.33 – 1.25 (m, 2H), 0.97 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 141. 7, 131.1, 128.6, 128.5, 126.0, 125.2, 84.9, 83.4, 60.2, 49.9, 42.8, 35.0, 32.7, 30.3, 27.7, 27.6, 25.8, 22.9, 18.3, 17.7. IR (neat) 3387, 2927, 2861, 1496, 1453, 1376, 1345, 1054, 1028, 992, 834, 744, 698, 491 cm^{-1}. HRMS (ESI): *m/z* calculated for $C_{22}H_{32}ONa$ [M+Na^{+}]: 335.2346, found 335.2345.



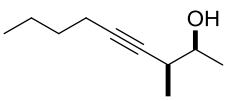
***anti*-3-Methylnon-4-yn-2-ol.** *n*-Butyllithium (23.4 mL, 1.6 M in hexane, 37.5 mmol) was added dropwise to a solution of 1-hexyne (4.3 mL, 37.5 mmol) in THF (50 mL) at −78°C and stirring was continued for 10 min. $BF_3{\cdot}Et_2O$ (4.6 mL, 37.5 mmol) was then introduced; 15 min later, *syn*-2,3-dimethyloxirane (2.18 mL, 25 mmol) was added and the mixture was stirred at −78°C for 2 h before the reaction was quenched with saturated aqueous NH_4Cl solution. The mixture was allowed to warm to room temperature and extracted twice with EtOAc. The combined extracts were washed with brine, dried over magnesium sulfate, and concentrated under reduced pressure. Flash chromatography (hexane/EtOAc = 9/1) yielded the product as a pale yellow liquid (3.6 g, 93% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.57 (h, *J* = 6.0 Hz, 1H), 2.41 (tddd, *J* = 7.0, 5.6, 4.6, 2.2 Hz, 1H), 2.19 (td, *J* = 6.9, 2.2 Hz, 2H), 1.96 (d, *J* = 5.7 Hz, 1H), 1.53 – 1.44 (m, 2H), 1.44 – 1.34 (m, 2H), 1.22 (d, *J* = 6.2 Hz, 3H), 1.16 (d, *J* = 7.0 Hz, 3H), 0.91 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 83.7, 80.7, 71.1, 35.2, 31.3, 22.1, 20.9, 18.5, 17.9, 13.8. IR (film, $CHCl_3$) 3386, 2932 2960, 2874, 1454, 1376, 1300, 1265,



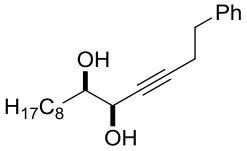
[6] D. L. J. Clive, V. Farina, P. L. Beaulieu, *J. Org. Chem.* **1982**, *47*, 2572-2582.

1173, 1098, 997, 1011, 955, 913 cm^{-1}. HRMS (ESI): *m/z* calculated for $C_{10}H_{18}ONa$ [M+Na^+]: 177.1250, found 177.1250.

***syn*-3-Methylnon-4-yn-2-ol.** Prepared analogously from *anti*-2,3-dimethyloxirane (2.18 mL, 25 mmol) as a pale yellow liquid (3.2 g, 83% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.76 – 3.60 (m, 1H), 2.56 (ttd, *J* = 7.0, 4.9, 2.2 Hz, 1H), 2.16 (td, *J* = 7.0, 2.3 Hz, 2H), 1.80 (d, *J* = 6.0 Hz, 1H), 1.53 – 1.31 (m, 4H), 1.21 (d, *J* = 6.2 Hz, 3H), 1.11 (d, *J* = 7.1 Hz, 3H), 0.90 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 83.1, 81.2, 70.6, 34.3, 31.3, 22.1, 19.5, 18.5, 16.7, 13.8. IR (film, $CHCl_3$) 3384, 2962, 2932, 2874, 1742, 1727, 1454, 1374, 1328, 1298, 1246, 1202, 1168, 1083, 1008, 972, 911 cm^{-1}. HRMS (ESI): *m/z* calculated for $C_{10}H_{18}ONa$ [M+Na^+]: 177.1250, found 177.1250.

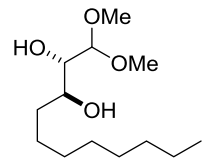


(5*R*,6*R*)-1-Phenyltetradec-3-yne-5,6-diol (24).[7] AD-mix-β (7.5 g) was dissolved in *t*-BuOH (25 mL) and the solution was stirred at 4°C in air. A solution of $MeSO_2NH_2$ (514 mg, 5.4 mmol) in water (25 mL) was added, followed by (*E*)-tetradec-5-en-3-yn-1-ylbenzene (1.45 g, 5.4 mmol). After being stirred at the same temperature for 12 h, the reaction was quenched with saturated aqueous Na_2SO_3 solution at 4 °C. The mixture was then extracted three times with EtOAc. The combined extracts were washed with brine, dried over magnesium sulfate, and concentrated under reduced pressure. Purification of the residue by flash chromatography (hexane/EtOAc = 4/1 to 2/1) yielded the product as a colorless oil, which solidified upon standing (1.18 g, 72% yield). $[\alpha]_D^{20}$ = +13.3 (c = 1.60, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 – 7.27 (m, 2H), 7.25 – 7.17 (m, 3H), 4.10 (dt, *J* = 6.3, 2.0 Hz, 1H), 3.51 (ddd, *J* = 8.0, 6.3, 3.4 Hz, 1H), 2.83 (t, *J* = 7.4 Hz, 2H), 2.53 (td, *J* = 7.4, 1.9 Hz, 4H), 1.65 – 1.16 (m, 14H), 0.97 – 0.84 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.5, 128.5, 128.5, 126.5, 86.4, 79.6, 75.2, 66.4, 34.9, 32.4, 32.0, 29.7, 29.7, 29.4, 25.7, 22.8, 20.9, 14.3. IR (film, $CHCl_3$) 3361, 2922, 2854, 1496, 1454, 1260, 1129, 1031, 745, 697, 579, 507 cm^{-1}. HRMS (ESI): *m/z* calculated for $C_{20}H_{30}O_2Na$ [M+Na^+]: 325.2138, found 325.2137.



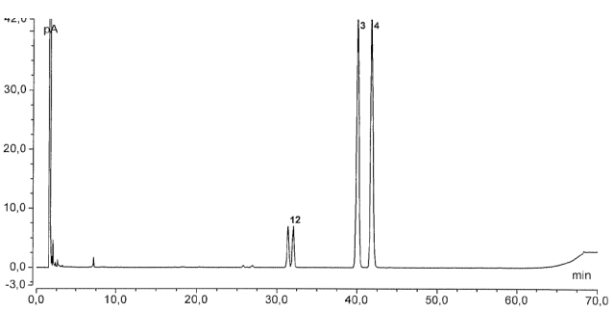
Total Synthesis of Paecilonic Acid A

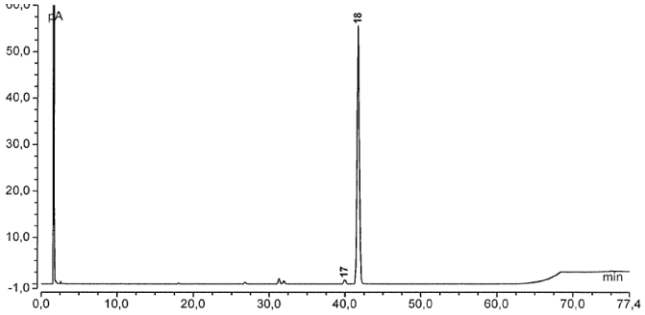
(2*S*,3*S*)-1,1-Dimethoxyundecane-2,3-diol (40). A 1 L round-bottom flask was charged with (*R*)-α,α-bis[3,5-bis(trifluoromethyl)phenyl]-2-pyrrolidinemethanol trimethylsilyl ether (0.485 g, 0.811 mmol), CH_2Cl_2 (65 mL), and *trans*-2-undecenal (6.43 mL, 32.4 mmol) under an ambient atmosphere. After being stirred for 5 min, the mixture was treated with H_2O_2 (35% (*w*/*w*) in H_2O, 4.1 mL, 42.2 mmol) and stirring was continued for 24 h. MeOH (650 mL) and sodium methoxide (17.5 g, 324 mmol) were added, and the resulting mixture was vigorously stirred for 24 h. The mixture was concentrated in vacuo, the residue was redissolved in H_2O (250 mL), and the aqueous phase was extracted with CH_2Cl_2 (3 x 100 mL). The combined organic layers were dried over Na_2SO_4 and concentrated in vacuo. Purification of the crude product by gradient flash chromatography (hexane/EtOAc = 2/1 to 1/1) gave the title compound as a colorless oil (4.78 g, 59%). $[\alpha]_D^{25}$ = −22.8 (c = 2.0, $CHCl_3$). ^{1}H NMR (400 MHz, CD_3OD) δ 4.37 (d, *J* = 4.9 Hz, 1H), 3.59 (ddd, *J* = 9.1, 6.0, 2.5 Hz, 1H), 3.50 – 3.44 (m, 4H), 3.41 (s, 3H), 1.66 – 1.22 (m, 14H), 0.90 (t, *J* = 6.6 Hz, 3H). ^{13}C NMR (101 MHz, CD_3OD) δ 106.3, 75.2, 72.6, 55.54, 55.48, 33.2, 33.1, 30.8, 30.7, 30.5, 26.7, 23.7, 14.5. IR (neat): 3415, 2922, 2854, 1464, 1378, 1312, 1192, 1124, 1060, 972, 913, 722, 571 cm^{-1}. HRMS (ESI): *m/z* calcd for $C_{13}H_{28}O_4Na$ [M+Na^+]: 271.1880, found: 271.1878.



[7] T. Honda, S. Horiuchi, H. Mizutani, K. Kanai, *J. Org. Chem.* **1996**, *61*, 4944-4948.

GC chromatogram on chiral column [Macherey-Nagel Hydrodex-beta-TBDAc-CD G681 (25.0 m, i.D. 0.25 mm); FID; Temperature: 230 °C (injector), 350 °C (detector), 155 °C (60 min iso) to 220 °C (8 °C/min, 3 min iso); Gas: H_2 (0.5 bar); 97% ee (t_R(major) = 41.8 min, t_R(minor) = 40.1 min)].

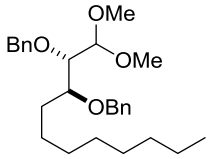




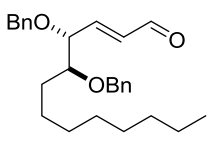
No.	Ret.Time min	area-% %
1	31,39	5,00
2	32,05	5,14
3	40,09	44,79
4	41,80	45,08

No.	Ret.Time min	Rel.Area %	Peak Name
17	39,95	1,54	
18	41,70	98,46	

((((2*S*,3*S*)-1,1-Dimethoxyundecane-2,3-diyl)bis(oxy))bis(methylene))dibenzene (S1). A solution of compound **40** (3.50 g, 14.1 mmol) in DMF (20.5 mL) was added dropwise to a stirred solution of sodium hydride (1.02 g, 42.3 mmol) in DMF (50 mL) at 0 °C. The resulting mixture was stirred at 0 °C for 15 min before addition of benzyl bromide (4.20 mL, 35.3 mmol). After being stirred at ambient temperature for 3 h, the reaction was quenched by addition of H_2O (10 mL) and the mixture was diluted with *tert*-butyl methyl ether (300 mL). The resulting solution was washed with H_2O (2 x 100 mL) and brine (100 mL), dried over $MgSO_4$, and concentrated in vacuo. Purification of the crude product by gradient flash chromatography (hexane/EtOAc = 19/1 to 9/1) gave the title compound as a colorless oil (5.42 g, 90%). $[\alpha]_D^{25}$ = −35.8 (c = 2.0, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 – 7.19 (m, 10H), 4.80 – 4.71 (m, 2H), 4.58 (d, *J* = 11.6 Hz, 1H), 4.47 (d, *J* = 11.6 Hz, 1H), 4.35 (d, *J* = 5.7 Hz, 1H), 3.70 – 3.64 (m, 1H), 3.62 – 3.56 (m, 1H), 3.44 (s, 3H), 3.39 (s, 3H), 1.78 – 1.64 (m, 1H), 1.60 – 1.40 (m, 2H), 1.34 – 1.17 (m, 11H), 0.88 (t, *J* = 6.8 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 139.0, 138.9, 128.4, 128.3, 128.1, 128.0, 127.6, 127.5, 105.7, 79.8, 79.7, 74.2, 72.0, 55.8, 55.4, 32.0, 30.2, 29.9, 29.7, 29.4, 25.9, 22.8, 14.3. IR (neat): 2924, 2854, 1497, 1454, 1376, 1327, 1204, 1065, 1028, 962, 912, 733, 696, 607, 461 cm^{-1}. HRMS (ESI): *m/z* calcd for $C_{27}H_{44}NO_4$ [M+NH_4^+]: 446.3265, found: 446.3259.

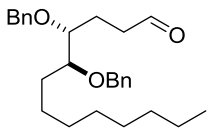


(4*R*,5*S*,*E*)-4,5-Bis(benzyloxy)tridec-2-enal (43). *Step 1*: A mixture of H_2O and trifluoroacetic acid (1:1 (*v*/*v*), 38 mL) was added to a stirred solution of compound **S1** (5.42 g, 12.6 mmol) in CH_2Cl_2 (38 mL). After being vigorously stirred for 24 h, the reaction was carefully quenched with saturated aqueous $NaHCO_3$ solution (30 mL) and the mixture was diluted with *tert*-butyl methyl ether (200 mL). The mixture was then washed with saturated aqueous $NaHCO_3$ solution (3 x 70 mL) and brine (70 mL), dried over $MgSO_4$, and concentrated in vacuo to afford aldehyde **41** as a pale yellow oil, which was used directly in the subsequent step.



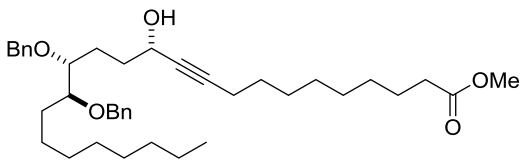
Step 2: Diethylzinc (15% (*w*/*w*) in toluene, 19.9 mL, 22.1 mmol) was added to tris(ethoxyvinyl)borane[8] (0.28 M in toluene, 22.1 mL, 6.19 mmol) at −78 °C. After being stirred for 20 min at −78 °C, a solution of aldehyde **41** in toluene (6.3 mL) was added dropwise. The mixture was gradually warmed to RT over 3 h and then further kept at ambient temperature for 30 min before being cooled to 0 °C. The solution was diluted with Et_2O (22 mL) and the reaction carefully quenched with brine (22 mL). Aqueous HCl (2 M) was added dropwise to the heterogeneous mixture until complete dissolution of all precipitates was reached (at approximately pH 2). This biphasic mixture was stirred for 19 h and then quenched by addition of saturated aqueous $NaHCO_3$ solution (15 mL). The resulting mixture was diluted with *tert*-butyl methyl ether (100 mL), washed with saturated aqueous $NaHCO_3$ solution (30 mL) and H_2O (30 mL), the organic phase was dried over $MgSO_4$, and concentrated in vacuo. Purification of the crude product by flash chromatography (hexane/EtOAc = 9/1) gave the title compound as a colorless oil (3.81 g, 74%). $[\alpha]_D^{25}$ = −25.2 (c = 2.0, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.59 (d, *J* = 7.9 Hz, 1H), 7.39 – 7.26 (m, 10H), 6.87 (dd, *J* = 15.9, 6.0 Hz, 1H), 6.34 (ddd, *J* = 15.9, 7.9, 1.1 Hz, 1H), 4.69 – 4.55 (m, 3H), 4.47 (d, *J* = 12.0 Hz, 1H), 4.13 (ddd, *J* = 6.0, 4.2, 1.1 Hz, 1H), 3.62 (dt, *J* = 8.1, 4.2 Hz, 1H), 1.67 – 1.18 (m, 14H), 0.89 (t, *J* = 6.8 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 193.5, 154.6, 138.4, 137.8, 134.0, 128.6, 128.5, 128.2, 128.0, 127.9 (two signals unresolved), 81.1, 80.7, 73.1, 71.9, 32.0, 31.4, 29.8, 29.7, 29.4, 25.5, 22.8, 14.3. IR (neat): 2924, 2854, 1691, 1496, 1454, 1352, 1207, 1095, 1027, 978, 734, 696, 607, 462 cm^{-1}. HRMS (ESI): *m/z* calcd for $C_{27}H_{40}NO_3$ [M+NH_4^+]: 426.3003, found: 426.2999.

(4*R*,5*S*)-4,5-Bis(benzyloxy)tridecanal (S2). H_2SO_4 (1 M in H_2O, 465 µL, 0.465 mmol) and triethylsilane



(2.23 mL, 14.0 mmol) were sequentially added to a stirred solution of compound **43** (3.80 g, 9.30 mmol) and Pd/C (10% (*w*/*w*), 99.0 mg, 93.0 µmol) in THF (31 mL). After being stirred for 45 min, the mixture was neutralized by addition of Et_3N (64.8 µL, 0.465 mmol), the suspension was filtered through Celite, and the filtrate was concentrated in vacuo. Purification of the crude product by flash chromatography (hexane/EtOAc = 9/1) gave the title compound as a colorless oil (2.46 g, 64%). $[\alpha]_D^{25}$ = +11.9 (c = 2.0, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.71 (t, *J* = 1.6 Hz, 1H), 7.37 – 7.26 (m, 10H), 4.69 (d, *J* = 11.6 Hz, 1H), 4.65 (d, *J* = 11.5 Hz, 1H), 4.56 (d, *J* = 11.6 Hz, 1H), 4.45 (d, *J* = 11.5 Hz, 1H), 3.55 (dt, *J* = 7.5, 3.4 Hz, 1H), 3.49 (dt, *J* = 8.4, 3.4 Hz, 1H), 2.58 – 2.43 (m, 2H), 2.02 – 1.84 (m, 2H), 1.68 – 1.58 (m, 1H), 1.53 – 1.40 (m, 2H), 1.36 – 1.20 (m, 11H), 0.90 (t, *J* = 6.7 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 202.7, 138.9, 138.5, 128.53, 128.47, 128.2, 128.0, 127.8, 127.7, 80.1, 80.0, 72.6, 72.2, 40.5, 32.0, 31.1, 29.9, 29.7, 29.4, 26.0, 23.0, 22.8, 14.3. IR (neat): 2924, 2854, 1723, 1496, 1454, 1351, 1206, 1094, 1061, 1027, 733, 696, 607, 460 cm^{-1}. HRMS (ESI): *m/z* calcd for $C_{27}H_{38}O_3Na$ [M+Na^+]: 433.2713, found: 433.2710.

Methyl (12*S*,15*R*,16*S*)-15,16-bis(benzyloxy)-12-hydroxytetracos-10-ynoate (35). (−)-*N*-Methylephedrine

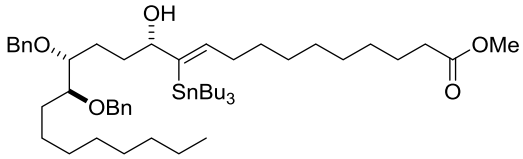


(0.458 g, 2.56 mmol) and Et_3N (0.356 mL, 2.56 mmol) were added to a stirred suspension of $Zn(OTf)_2$ (0.885 g, 2.44 mmol) in toluene (8.4 mL). The heterogeneous mixture was stirred for 2 h, treated with methyl 10-undecynoate (0.526 mL, 2.44 mmol), and further stirred for 1 h. A solution of compound **S2** (0.500 g, 1.22 mmol) in toluene (1.2 mL) was added dropwise. The resulting mixture was stirred for additional 24 h before the reaction was quenched by addition of saturated aqueous NH_4Cl

[8] P. Valenta, N. A. Drucker, J. W. Bode, P. J. Walsh, *Org. Lett.* **2009**, *11*, 2117-2119.

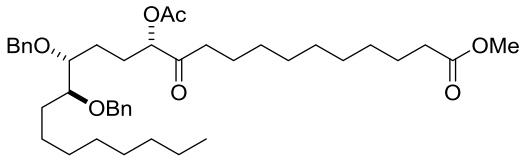
solution (10 mL). The aqueous phase was extracted with *tert*-butyl methyl ether (3 x 15 mL) and the combined organic layers were dried over $MgSO_4$ and concentrated in vacuo. Purification of the crude product by gradient flash chromatography (hexane/EtOAc = 6/1 to 5/1) gave the title compound as a colorless oil (0.553 g, 75%). $[\alpha]_D^{25}$ = −0.9 (c = 2.0, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.21 (m, 10H), 4.69 (dd, *J* = 11.6, 1.8 Hz, 2H), 4.54 (dd, *J* = 11.6, 1.4 Hz, 2H), 4.34 (t, *J* = 5.8 Hz, 1H), 3.66 (s, 3H), 3.56 – 3.50 (m, 2H), 2.29 (t, *J* = 7.5 Hz, 2H), 2.18 (td, *J* = 7.1, 2.0 Hz, 2H), 1.91 – 1.69 (m, 4H), 1.68 – 1.56 (m, 3H), 1.56 – 1.41 (m, 4H), 1.41 – 1.19 (m, 19H), 0.88 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.4, 139.0, 138.7, 128.5, 128.4, 128.1, 128.0, 127.7, 127.6, 85.6, 81.3, 80.6, 80.5, 72.4, 72.2, 62.8, 51.6, 34.6, 34.2, 32.0, 30.9, 29.9, 29.7, 29.4, 29.21, 29.18, 29.0, 28.9, 28.8, 26.2, 26.1, 25.0, 22.8, 18.8, 14.3. IR (neat): 3439, 2924, 2854, 1738, 1454, 1354, 1204, 1172, 1095, 1061, 1027, 734, 697, 609, 460 cm^{-1}. HRMS (ESI): *m/z* calcd for $C_{39}H_{58}O_5Na$ [M+Na^+]: 629.4176, found: 629.4173.

Methyl (12*S*,15*R*,16*S*,*Z*)-15,16-bis(benzyloxy)-12-hydroxy-11-(tributylstannyl)tetracos-10-enoate (44).



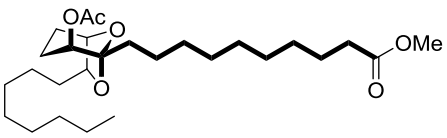
Tributyltin hydride (0.83 mL, 3.09 mmol) was added over 1 h to a stirred solution of compound **35** (1.71 g, 2.81 mmol) and $[Cp^*RuCl_2]_n$ (21.6 mg, 70.3 µmol) in CH_2Cl_2 (12 mL). Upon complete addition, the reaction mixture was further stirred for 5 min and concentrated in vacuo. The residue was subjected to flash chromatography (hexane/EtOAc = 9/1) to afford the title compound as a pale yellow oil (2.08 g, 83%). $[\alpha]_D^{25}$ = −0.8 (c = 2.0, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.24 (m, 10H), 6.12 (t, *J* = 7.1, J_{Sn-H} = 122.9 Hz, 1H), 4.70 (d, *J* = 11.6 Hz, 2H), 4.54 (d, *J* = 11.6 Hz, 1H), 4.53 (d, *J* = 11.6 Hz, 1H), 4.08 (s, 1H), 3.67 (s, 3H), 3.55 – 3.48 (m, 2H), 2.30 (t, *J* = 7.5 Hz, 2H), 2.01 (q, *J* = 7.1 Hz, 2H), 1.71 – 1.57 (m, 7H), 1.57 – 1.40 (m, 9H), 1.38 – 1.21 (m, 27H), 1.05 – 0.80 (m, 18H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.4, 147.9, 140.9, 139.1, 138.9, 128.4 (two signals unresolved), 128.0, 127.9, 127.6, 127.5, 80.9, 80.8, 80.3, 72.4, 72.3, 51.6, 34.41, 34.38, 34.2, 32.0, 30.9, 30.3, 29.9, 29.7, 29.61, 29.57, 29.44, 29.39, 29.37, 29.3, 27.6, 27.2, 26.3, 25.1, 22.8, 14.3, 13.8, 11.2. ^{119}Sn NMR (149 MHz, $CDCl_3$) δ −55.39. IR (neat): 3497, 2923, 2853, 1740, 1455, 1357, 1204, 1173, 1066, 1027, 874, 754, 696, 666, 595, 499, 454 cm^{-1}. HRMS (ESI): *m/z* calcd for $C_{51}H_{85}O_5Sn$ [M−H^+]: 897.5424, found: 897.5436.

Methyl (12*S*,15*R*,16*S*)-12-acetoxy-15,16-bis(benzyloxy)-11-oxotetracosanoate (45). Et_3N (1.59 mL, 11.4 mmol) was added to a stirred solution of compound **44** (2.05 g, 2.28 mmol) and $Cu(OAc)_2{\cdot}H_2O$ (0.912 g, 4.57 mmol) in reagent grade DMSO (18 mL) under an ambient atmosphere. After being vigorously stirred at 70 °C for 22 h, the heterogeneous mixture was diluted with *tert*-butyl methyl ether (100 mL) and the suspension was filtered through Celite. The filtrate was washed with saturated aqueous NH_4Cl solution (2 x 40 mL) and H_2O (40 mL), the organic phase was dried over $MgSO_4$ and concentrated in vacuo. Purification of the crude product by flash chromatography (hexane/EtOAc = 7/1) gave the title compound as a yellow oil (1.18 g, 77%). $[\alpha]_D^{25}$ = +5.2 (c = 2.0, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.24 (m, 10H), 4.98 – 4.91 (m, 1H), 4.67 (d, *J* = 11.5 Hz, 2H), 4.55 (d, *J* = 11.5 Hz, 1H), 4.48 (d, *J* = 11.5 Hz, 1H), 3.66 (s, 3H), 3.52 (dt, *J* = 7.4, 2.9 Hz, 1H), 3.45 (dt, *J* = 7.3, 2.9 Hz, 1H), 2.49 – 2.25 (m, 4H), 2.11 (s, 3H), 2.05 – 1.94 (m, 1H), 1.77 – 1.39 (m, 10H), 1.39 – 1.19 (m, 21H), 0.89 (t, *J* = 6.7 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 207.4, 174.4, 170.7, 138.9, 138.6, 128.53, 128.48, 128.1, 128.0, 127.8, 127.7,



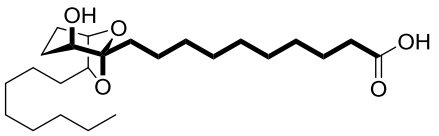
80.7, 80.3, 78.9, 72.6, 72.3, 51.6, 38.8, 34.3, 32.0, 31.1, 29.9, 29.7, 29.5, 29.43, 29.39, 29.35, 29.27 (two signals unresolved), 27.0, 26.5, 26.1, 25.1, 23.3, 22.8, 20.8, 14.3. IR (neat): 2925, 2854, 1737, 1454, 1372, 1233, 1171, 1094, 1061, 1027, 735, 697, 606, 463 cm^{-1}. HRMS (ESI): *m/z* calcd for $C_{41}H_{62}O_7Na$ [M+Na^+]: 689.4388, found: 689.4389.

Methyl 10-((1*R*,4*S*,5*S*,7*S*)-4-acetoxy-7-octyl-6,8-dioxabicyclo[3.2.1]octan-5-yl)decanoate (46). A



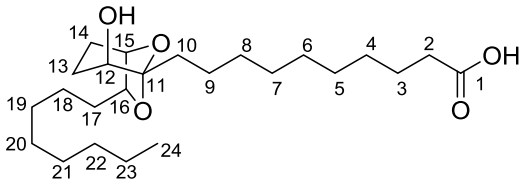
suspension containing Pd/C (10% (*w*/*w*), 96.0 mg, 90.2 µmol) and compound **45** (0.602 g, 0.902 mmol) in THF (9 mL) was stirred under an atmosphere of H_2 (balloon) for 40 h. The catalyst was removed by filtration through Celite, rinsing with additional THF (9 mL) to aid the complete transfer. The obtained colorless filtrate was treated with HCl (4 M in 1,4-dioxane, 1.13 mL, 4.51 mmol) and stirred for 3 h before the reaction was quenched with saturated aqueous $NaHCO_3$ solution (5 mL). The mixture was diluted with H_2O (30 mL) and extracted with CH_2Cl_2 (3 x 20 mL). The combined organic layers were dried over $MgSO_4$ and concentrated in vacuo. Purification of the crude product by flash chromatography (hexane/EtOAc = 9/1) gave the title compound as a coloress oil (0.352 g, 83%). $[\alpha]_D^{25}$ = +45.8 (c = 2.0, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.68 (d, *J* = 4.4 Hz, 1H), 4.25 (t, *J* = 4.0 Hz, 1H), 4.00 – 3.93 (m, 1H), 3.64 (s, 3H), 2.28 (t, *J* = 7.5 Hz, 2H), 2.24 – 2.12 (m, 1H), 2.09 (s, 3H), 2.03 – 1.90 (m, 1H), 1.82 – 1.17 (m, 32H), 0.87 (d, *J* = 6.7 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.4, 170.7, 106.8, 80.3, 76.2, 70.0, 51.5, 34.2, 34.0, 32.0, 29.8 (two signals unresolved), 29.61, 29.56, 29.5, 29.34, 29.32, 29.26, 29.2, 26.8, 25.1, 23.5, 22.8, 22.0, 21.5, 20.9, 14.2. IR (neat): 2925, 2854, 1736, 1436, 1371, 1240, 1168, 1102, 1021, 917, 756, 608, 515 cm^{-1}. HRMS (ESI): *m/z* calcd for $C_{27}H_{48}O_6Na$ [M+Na^+]: 491.3343, found: 491.3340.

Paecilonic acid A (34). NaOH (4 M in H_2O, 1.21 mL, 4.84 mmol) was added to a stirred solution of



compound **46** (247 mg, 0.527 mmol) in MeOH/THF (1:1.5 (*v*/*v*), 5.4 mL) in air. The mixture was stirred for 14 h and concentrated in vacuo. The residue was redissolved in H_2O (20 mL), acidified with aqueous HCl (2 M) to approximately pH 2, and extracted with CH_2Cl_2 (3 x 10 mL). The combined organic layers were dried over $MgSO_4$ and concentrated in vacuo. Purification of the crude product by flash chromatography (CH_2Cl_2/MeOH = 49/1 with 0.5% AcOH) gave paecilonic acid A (**34**) as a white amorphous solid (0.207 g, 95%). $[\alpha]_D^{25}$ = +35.5 (c = 2.0, $CHCl_3$). ^{1}H NMR (600 MHz, CD_3OD) δ 4.19 (t, *J* = 4.0 Hz, 1H), 3.93 (dddd, *J* = 7.5, 6.3, 4.1, 1.0 Hz, 1H), 3.42 (dt, *J* = 4.6, 1.1 Hz, 1H), 2.27 (t, *J* = 7.5 Hz, 2H), 2.13 (tdd, *J* = 13.9, 6.7, 4.6 Hz, 1H), 2.03 (tddd, *J* = 13.9, 6.1, 3.8, 0.8 Hz, 1H), 1.79 (dt, *J* = 14.3, 8.0 Hz, 1H), 1.77 – 1.69 (m, 1H), 1.66 – 1.45 (m, 7H), 1.45 – 1.38 (m, 2H), 1.38 – 1.25 (m, 21H), 0.90 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (151 MHz, CD_3OD) δ 177.8, 109.6, 81.6, 77.9, 69.4, 35.1, 35.0, 33.1, 31.1, 30.9, 30.8, 30.7, 30.6, 30.51, 30.48, 30.3 (two signals unresolved), 28.0, 27.2, 26.2, 23.8, 23.3, 21.5, 14.5. IR (neat): 3277, 2920, 2851, 2650, 1695, 1467, 1388, 1282, 1251, 1177, 1095, 1017, 960, 926, 907, 723, 638, 483 cm^{-1}. HRMS (ESI): *m/z* calcd for $C_{24}H_{45}O_5$ [M+H^+]: 413.3262, found: 413.3259.

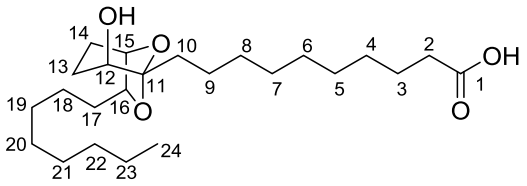
Comparison of ^{1}H NMR Data (CD_3OD) of Paecilonic Acid A (34)[9]



position	δ_H (*J* in Hz)		
	natural	synthetic	Δδ (ppm)
1	-	-	-
2	2.29, t (7.2)	2.27, t (7.5)	0.02
3	1.62, quint	1.45 – 1.66, m	-
4 – 8	1.30 – 1.36, m	1.25 – 1.38, m	-
9	1.45, quint	1.38 – 1.45, m	-
10	1.66, dt (15.2, 7.2); 1.82, dt (15.2, 7.2)	1.45 – 1.66, m; 1.79, dt (14.3, 8.0)	- 0.03
11	-	-	-
12	3.44, br d (4.8)	3.42, dt (4.6, 1.1)	0.02
13	1.54, m; 2.16, tdd (14.4, 7.2, 4.8)	1.45 – 1.66, m; 2.13, tdd (13.9, 6.7, 4.6)	- 0.03
14	1.53, m; 2.05, tdd (14.4, 6.4, 4.8)	1.45 – 1.66, m; 2.03, tdd (13.9, 6.1, 3.8, 0.8)	- 0.02
15	4.22, br t (4.0)	4.19, t (4.0)	0.03
16	3.96, dt (4.0, 7.2)	3.93, dddd (7.5, 6.3, 4.1, 1.0)	0.03
17	1.58, m; 1.75, m	1.45 – 1.66, m; 1.69 – 1.77, m	-
18	1.36, m; 1.51, m	1.25 – 1.38, m; 1.45 – 1.66, m	-
19 – 21	1.30 – 1.36, m	1.25 – 1.38, m	-
22	1.28, m	1.25 – 1.38, m	-
23	1.31, m	1.25 – 1.38, m	-
24	0.92, t (7.2)	0.90, t (7.1)	0.02

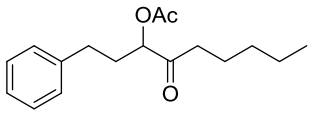
[9] H. Wang, J. Hong, J. Yin, J. Liu, Y. Liu, J. S. Choi, J. H. Jung, *Bioorg. Med. Chem. Lett.* **2016**, *26*, 2220-2223.

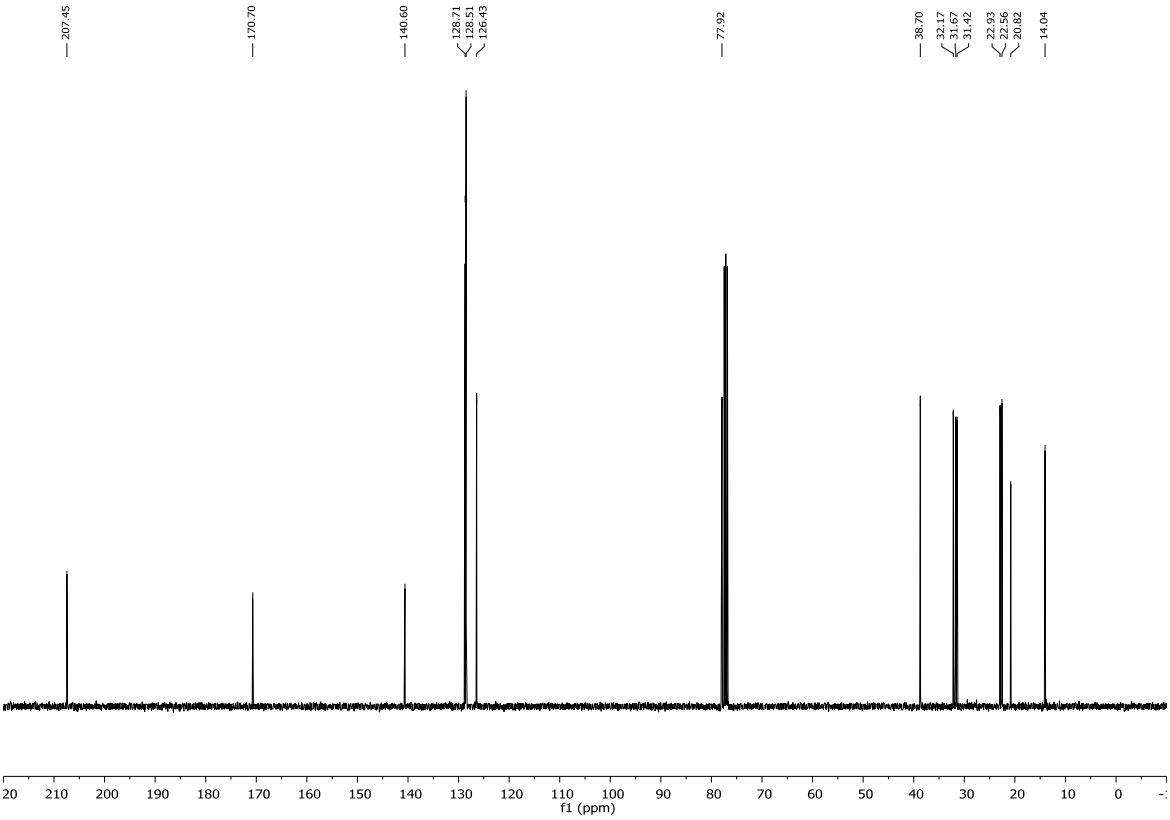
Comparison of ^{13}C NMR Data (CD_3OD) of Paecilonic Acid A (34)[9]



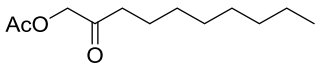
position	δ_C type		
	natural	synthetic	Δδ (ppm)
1	176.5, C	177.8, C	1.3
2	34.2, CH_2	35.1, CH_2	0.9
3	25.1, CH_2	26.2, CH_2	1.1
4 – 8	29.0 – 29.8, CH_2	30.3 – 31.1, CH_2	-
9	22.0, CH_2	23.3, CH_2	1.3
10	33.7, CH_2	35.0, CH_2	1.3
11	108.3, C	109.6, C	1.3
12	68.1, CH	69.4, CH	1.3
13	25.9, CH_2	27.2, CH_2	1.3
14	20.2, CH_2	21.5, CH_2	1.3
15	76.6, CH	77.9, CH	1.3
16	80.3, CH	81.6, CH	1.3
17	29.1, CH_2	30.3, CH_2	1.2
18	26.7, CH_2	28.0, CH_2	1.3
19 – 21	29.0 – 29.8, CH_2	30.3 – 31.1, CH_2	-
22	31.8, CH_2	33.1, CH_2	1.3
23	22.5, CH_2	23.8, CH_2	1.3
24	13.2, CH_3	14.5, CH_3	1.3

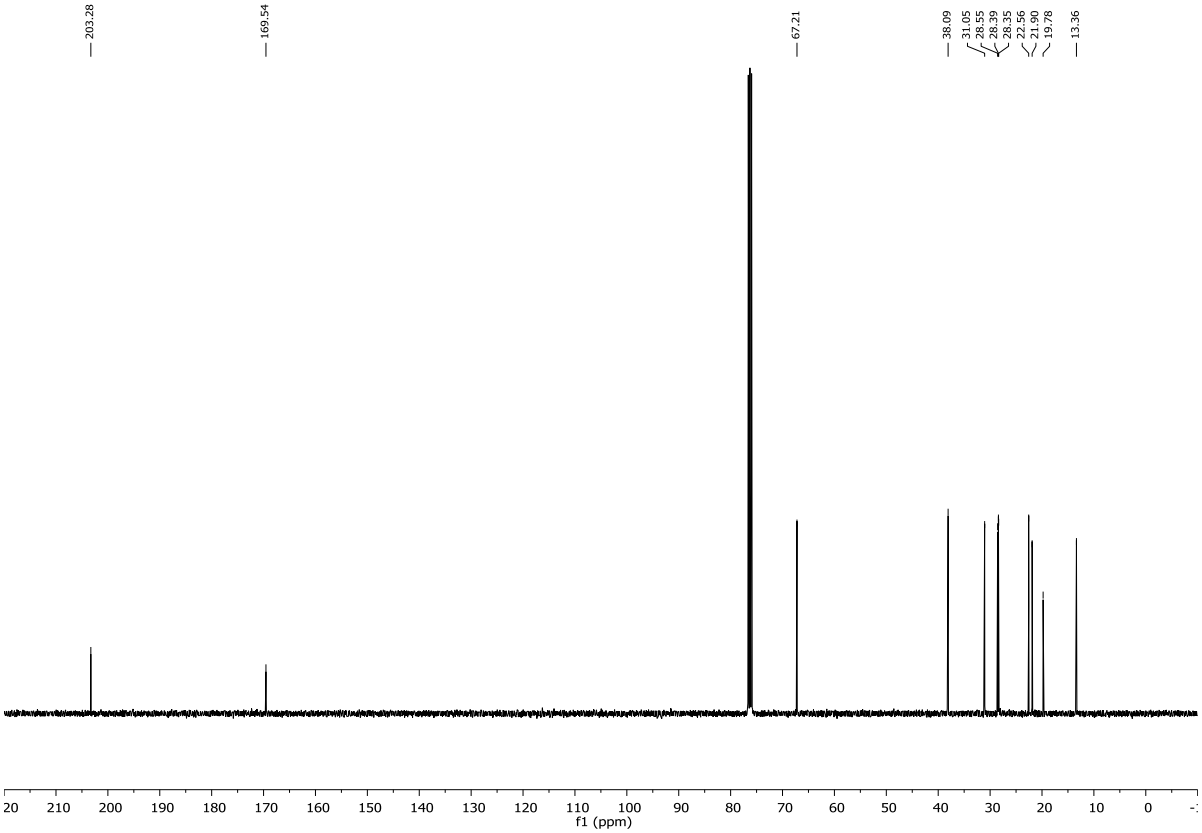
4-Oxo-1-phenylnonan-3-yl acetate (2)



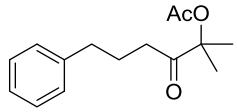


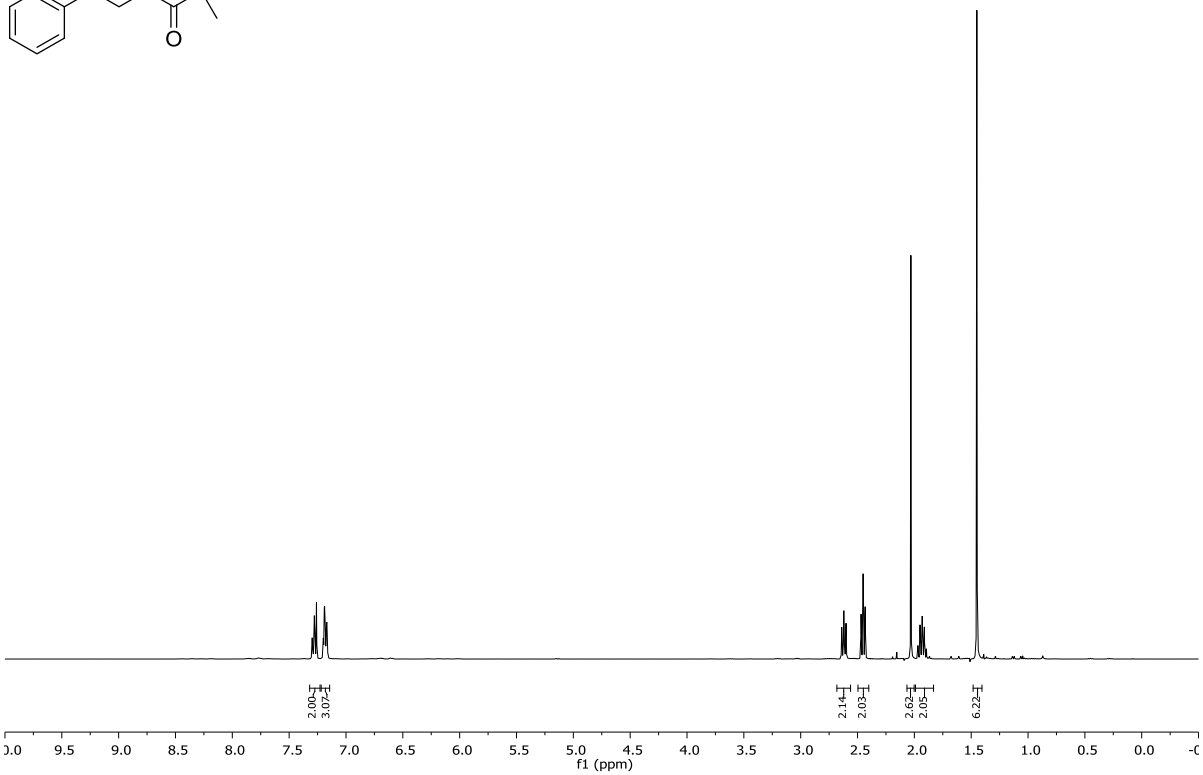
2-Oxodecyl acetate (5)

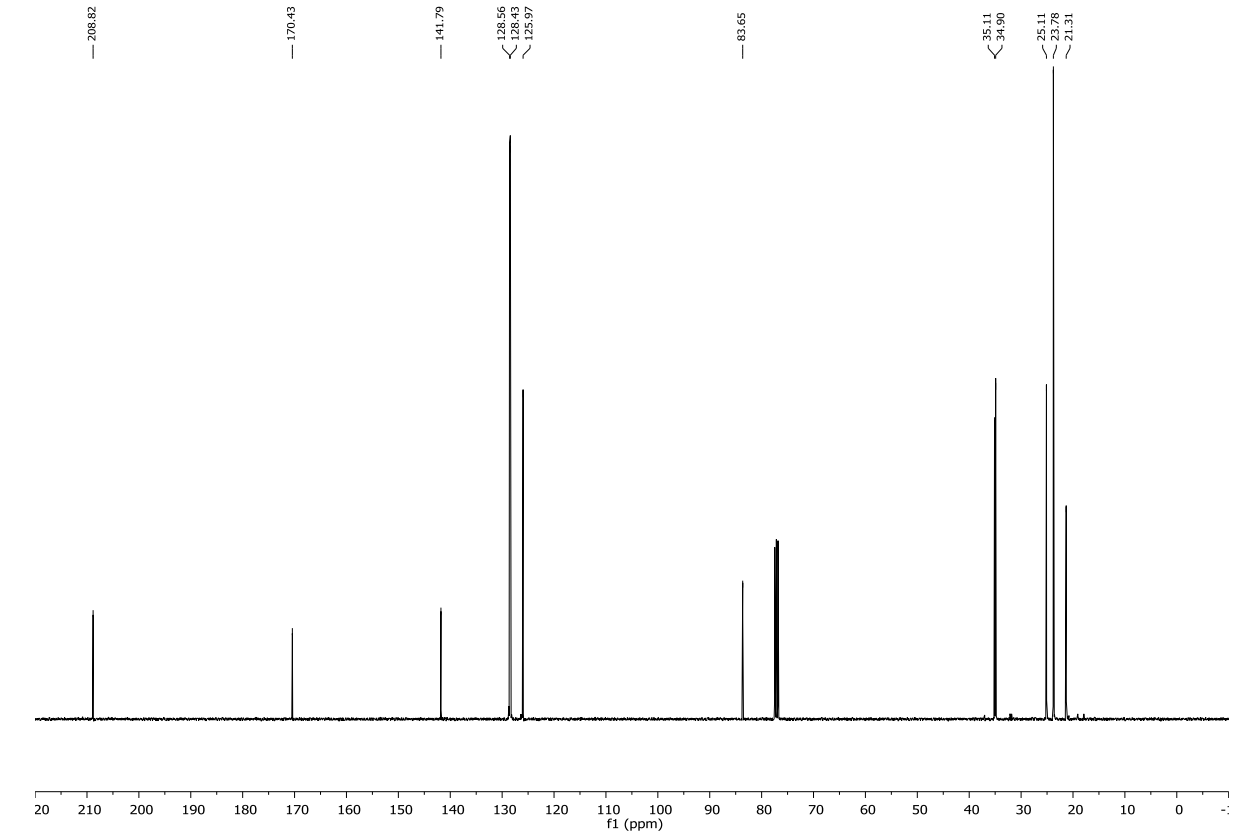




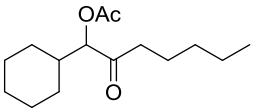
2-Methyl-3-oxo-6-phenylhexan-2-yl acetate (6)

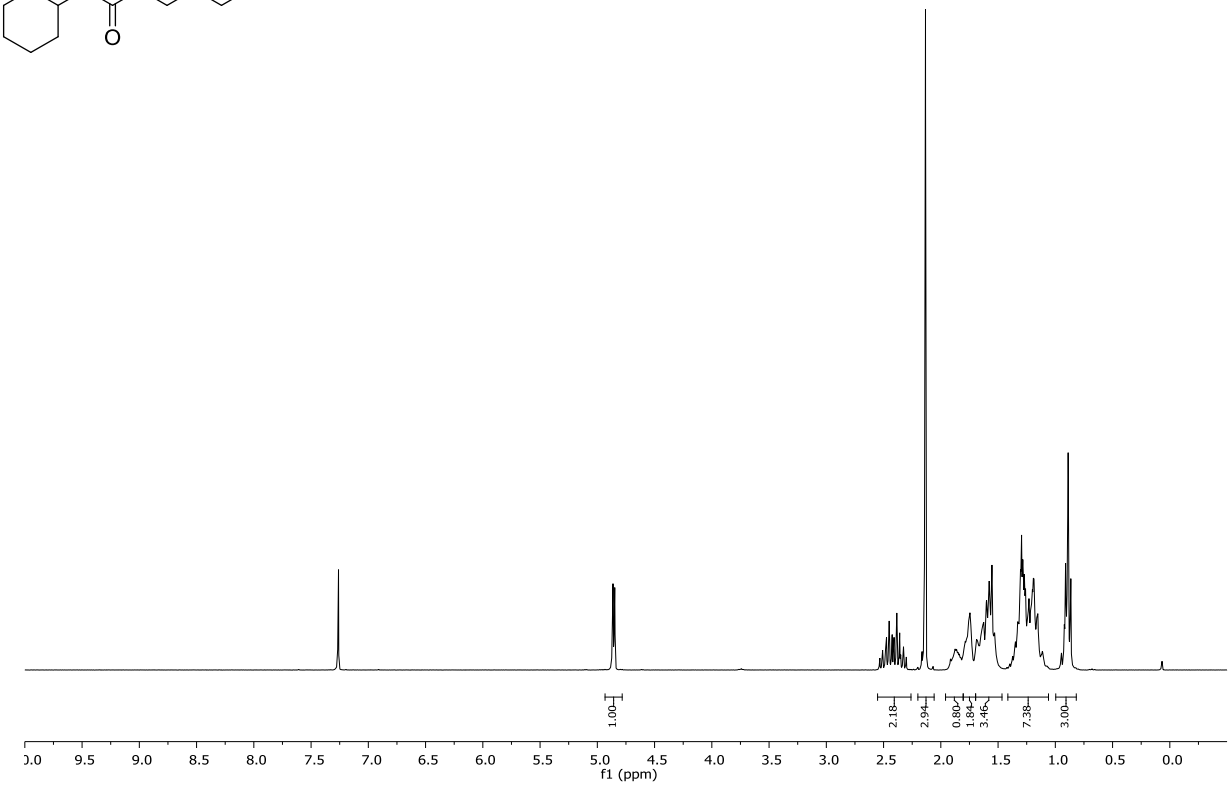


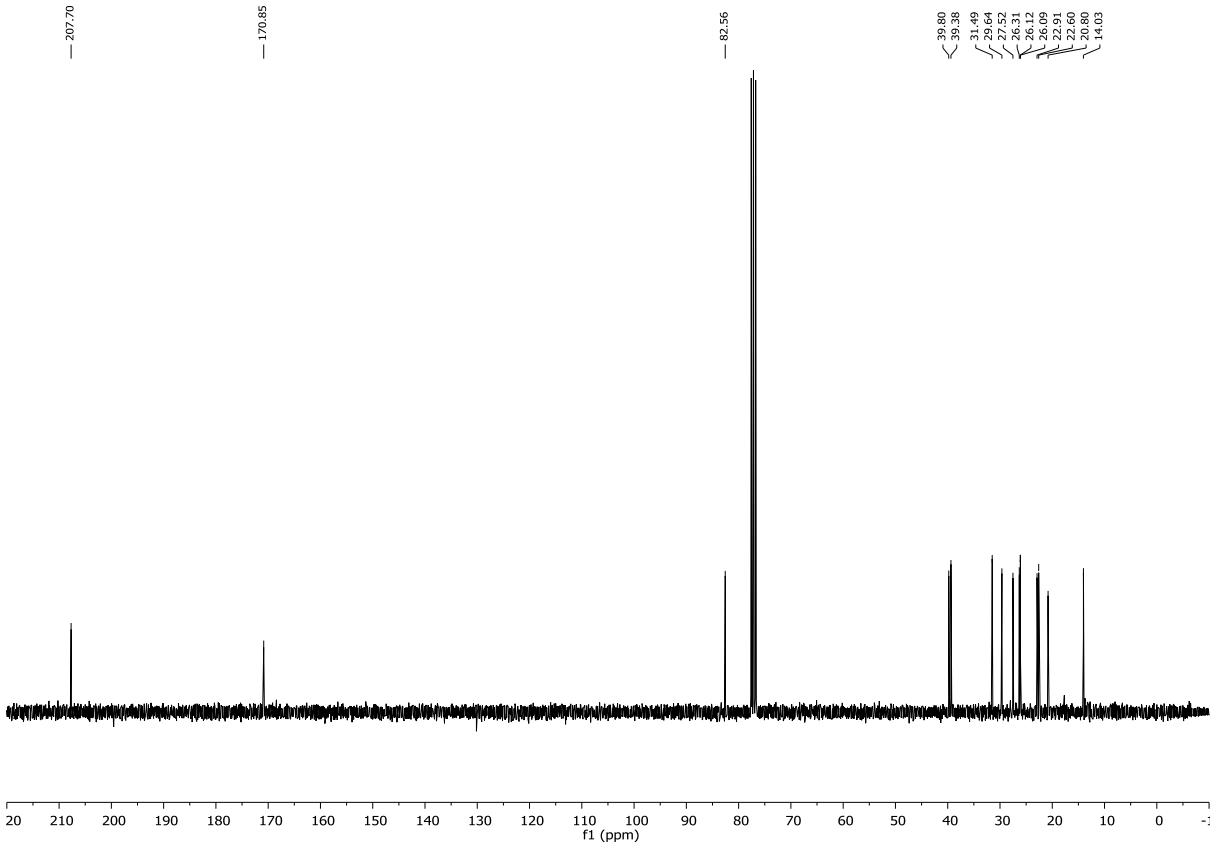




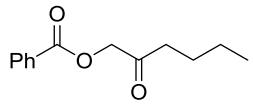
1-Cyclohexyl-2-oxoheptyl acetate (7)

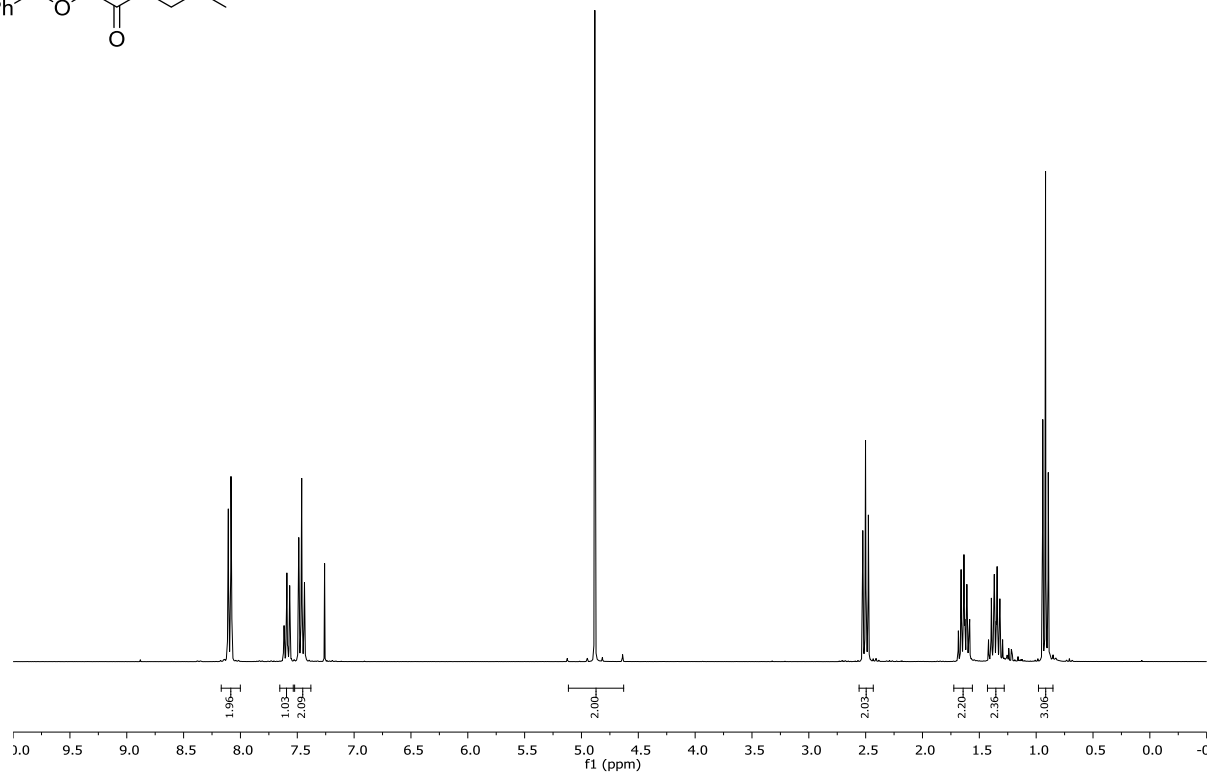


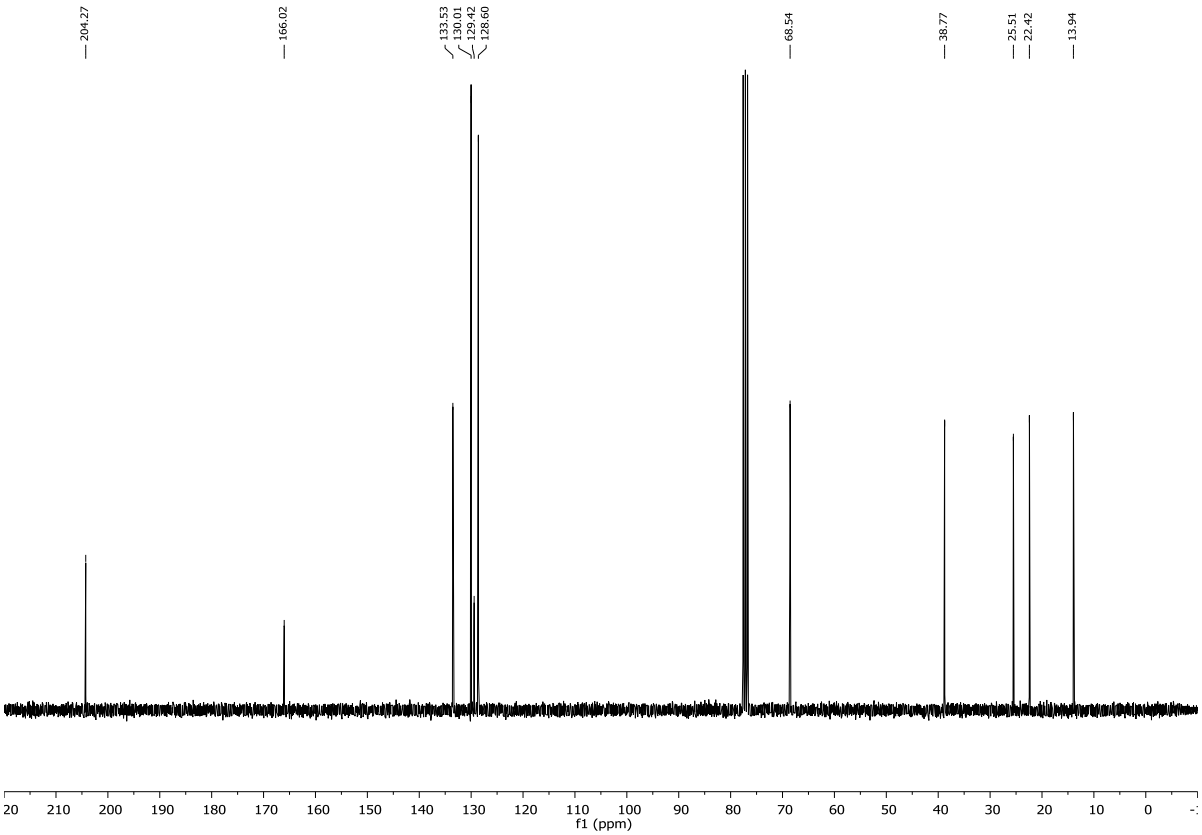




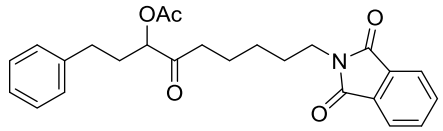
2-Oxohexyl benzoate (8)

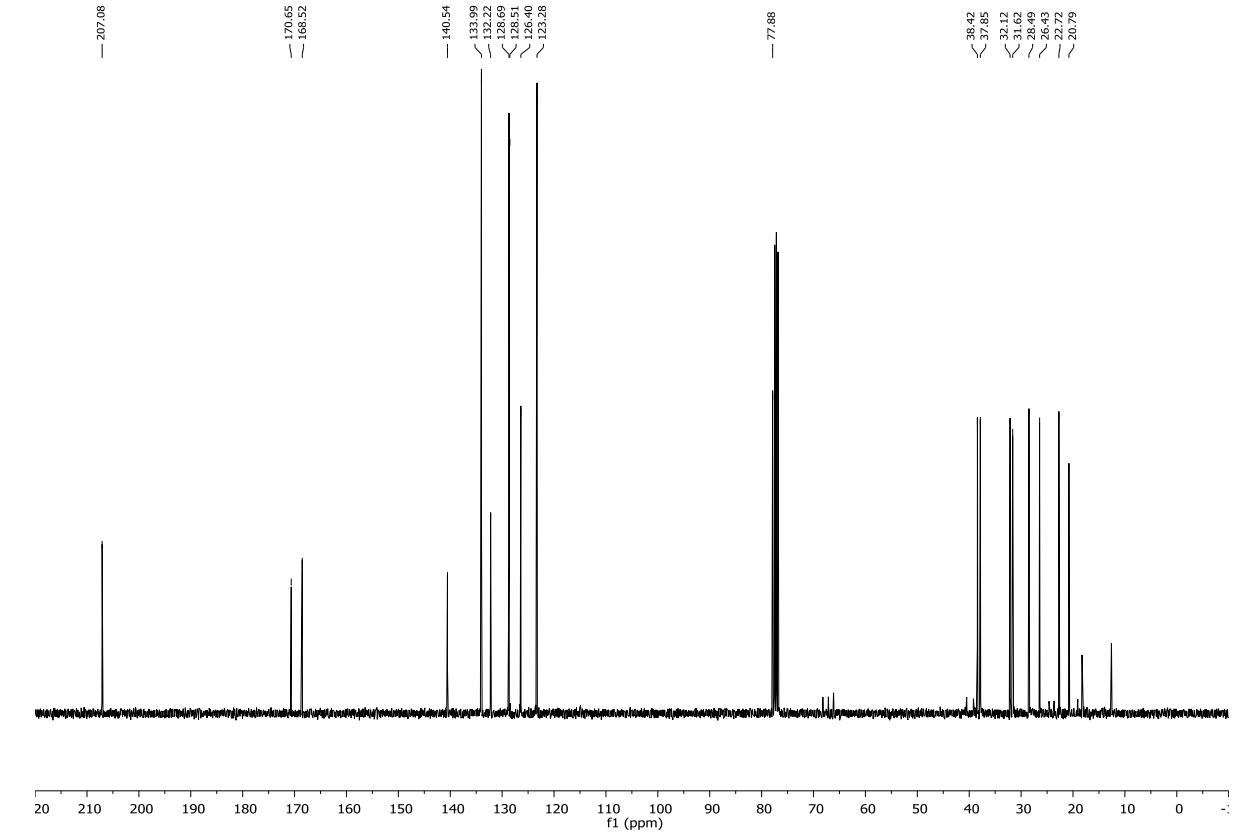




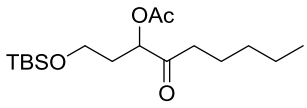


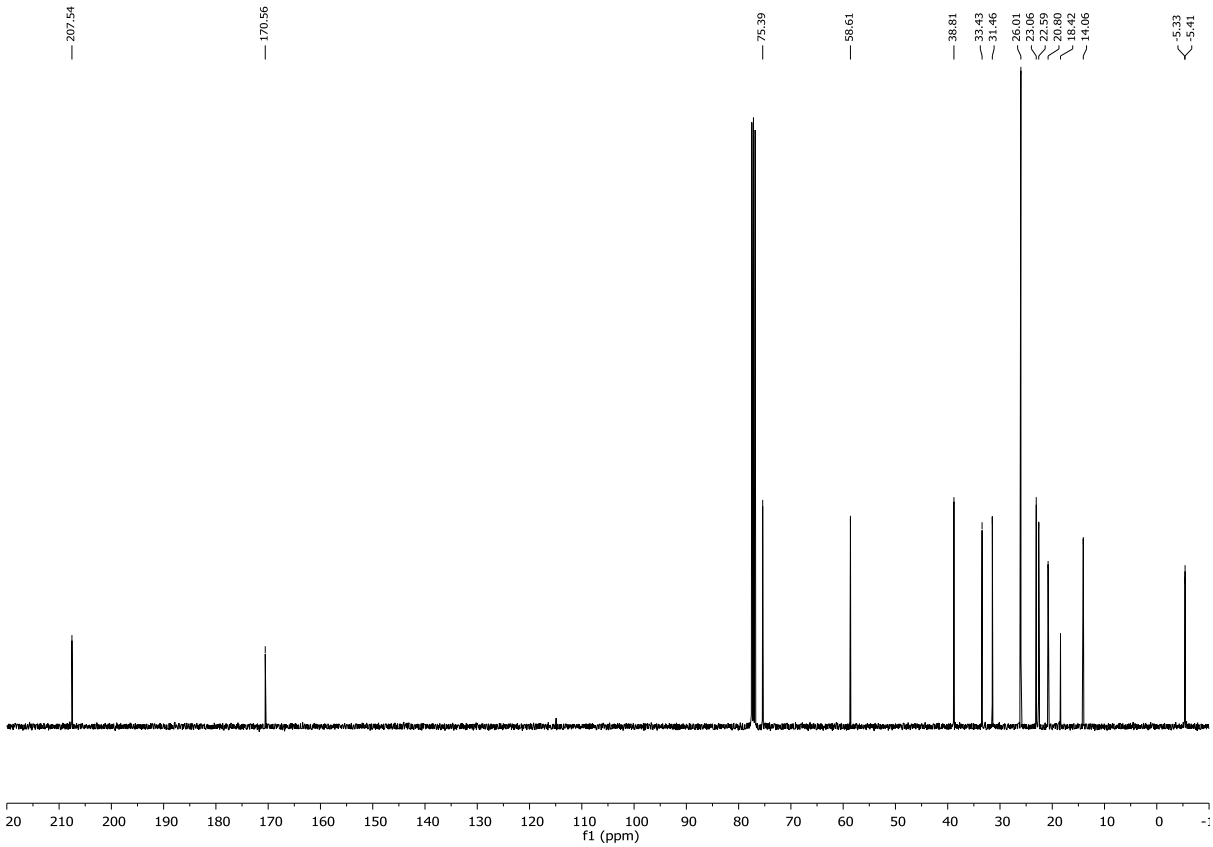
9-(1,3-Dioxoisoindolin-2-yl)-4-oxo-1-phenylnonan-3-yl acetate (9)



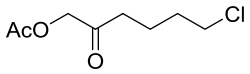


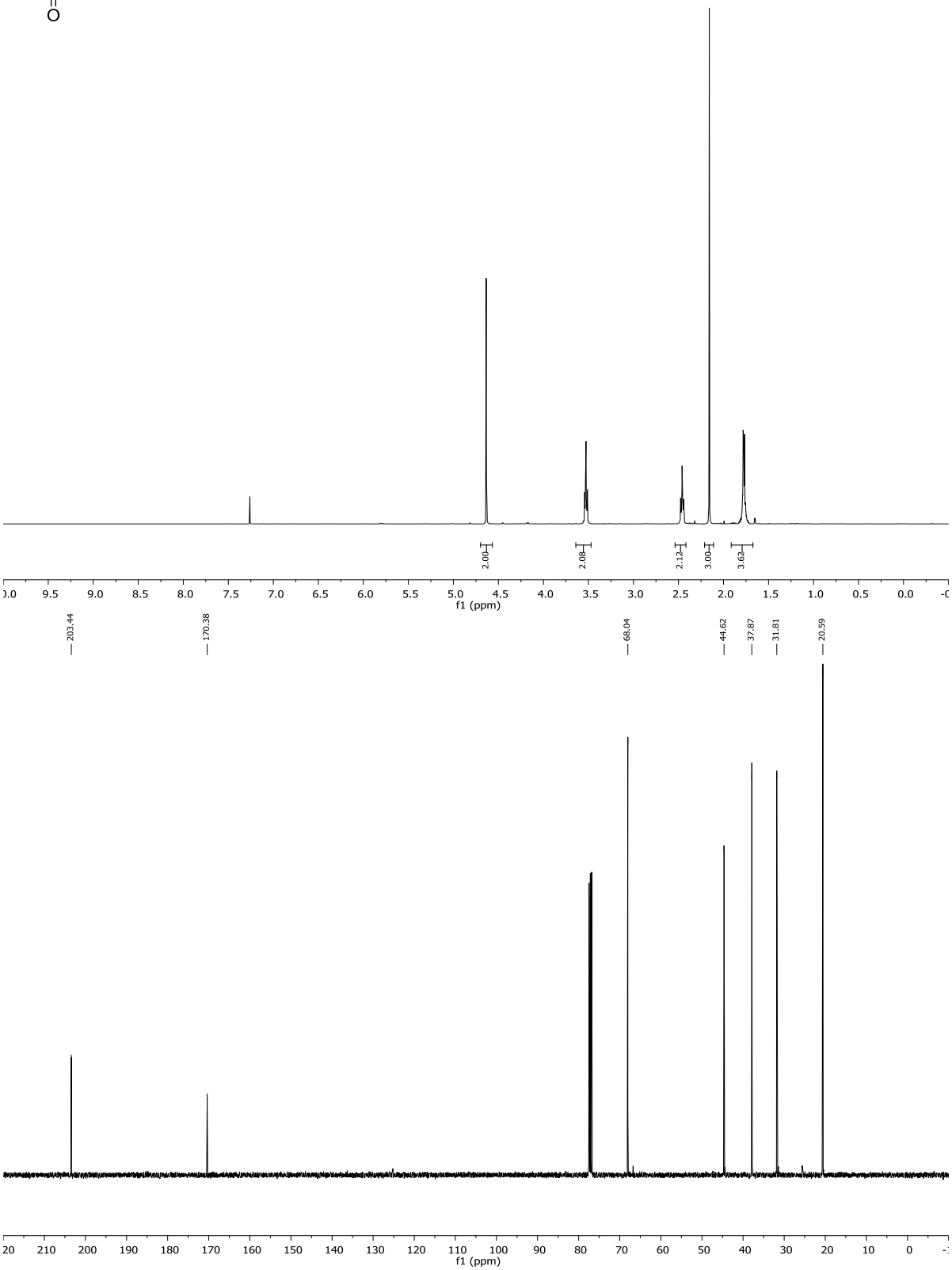
1-((*tert*-Butyldimethylsilyl)oxy)-4-oxononan-3-yl acetate (10)



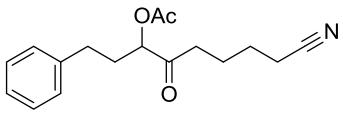


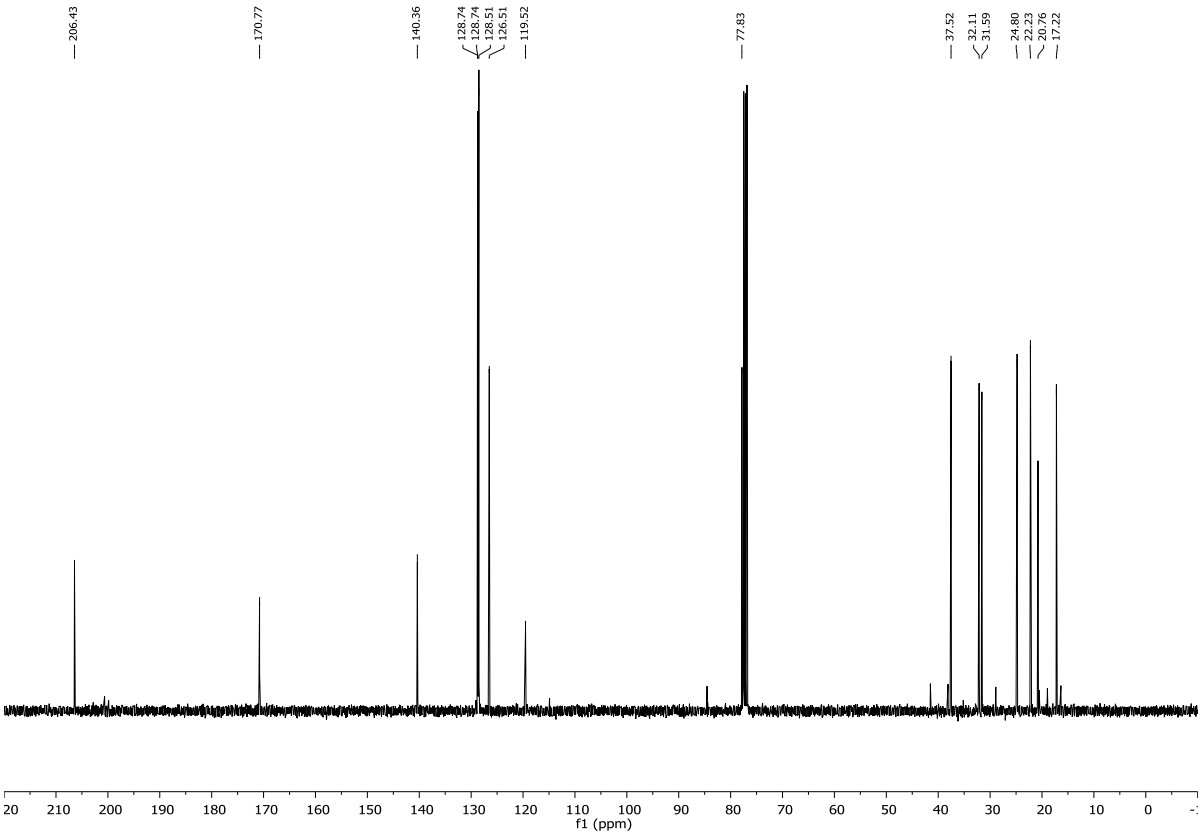
6-Chloro-2-oxohexyl acetate (11)



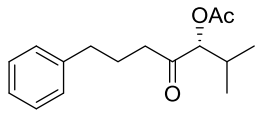


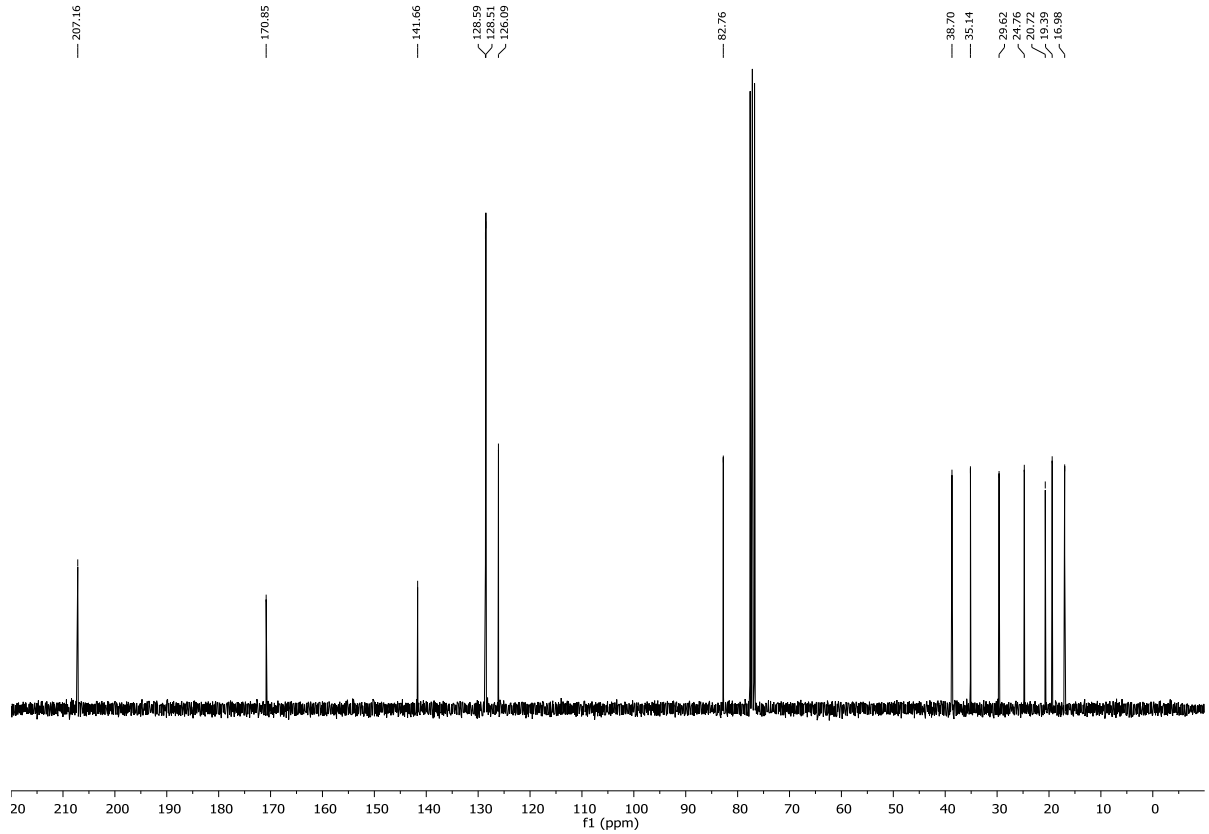
8-Cyano-4-oxo-1-phenyloctan-3-yl acetate (12)



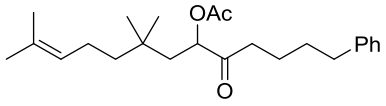


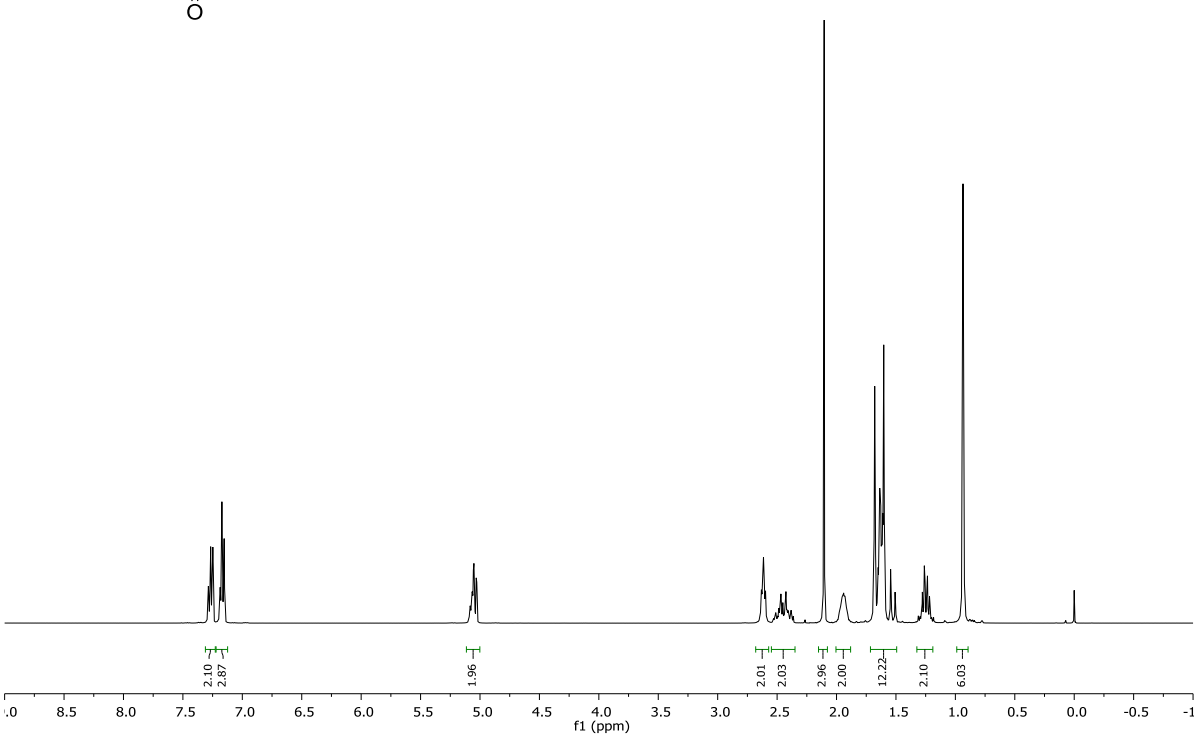
(*R*)-2-Methyl-4-oxo-7-phenylheptan-3-yl acetate (13)

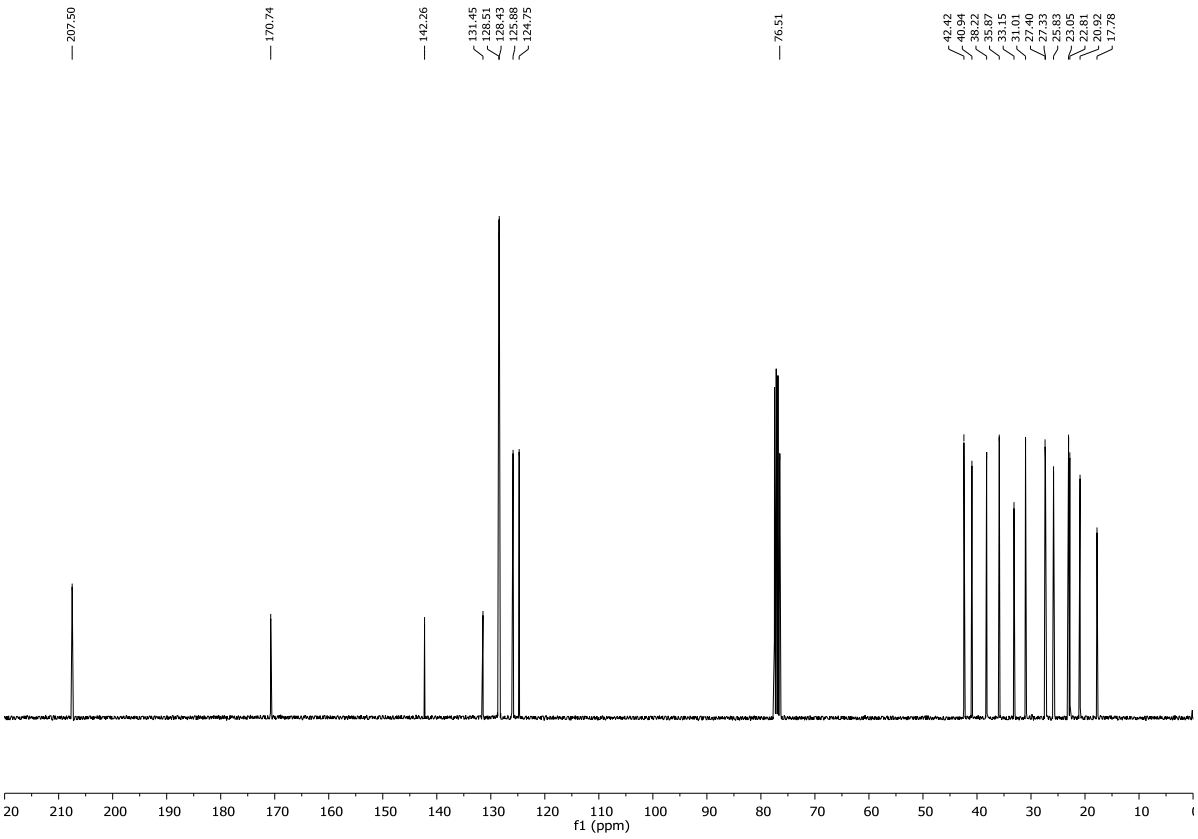




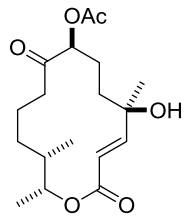
6-Hydroxy-8,8,12-trimethyl-1-phenyltridec-11-en-5-one (14)

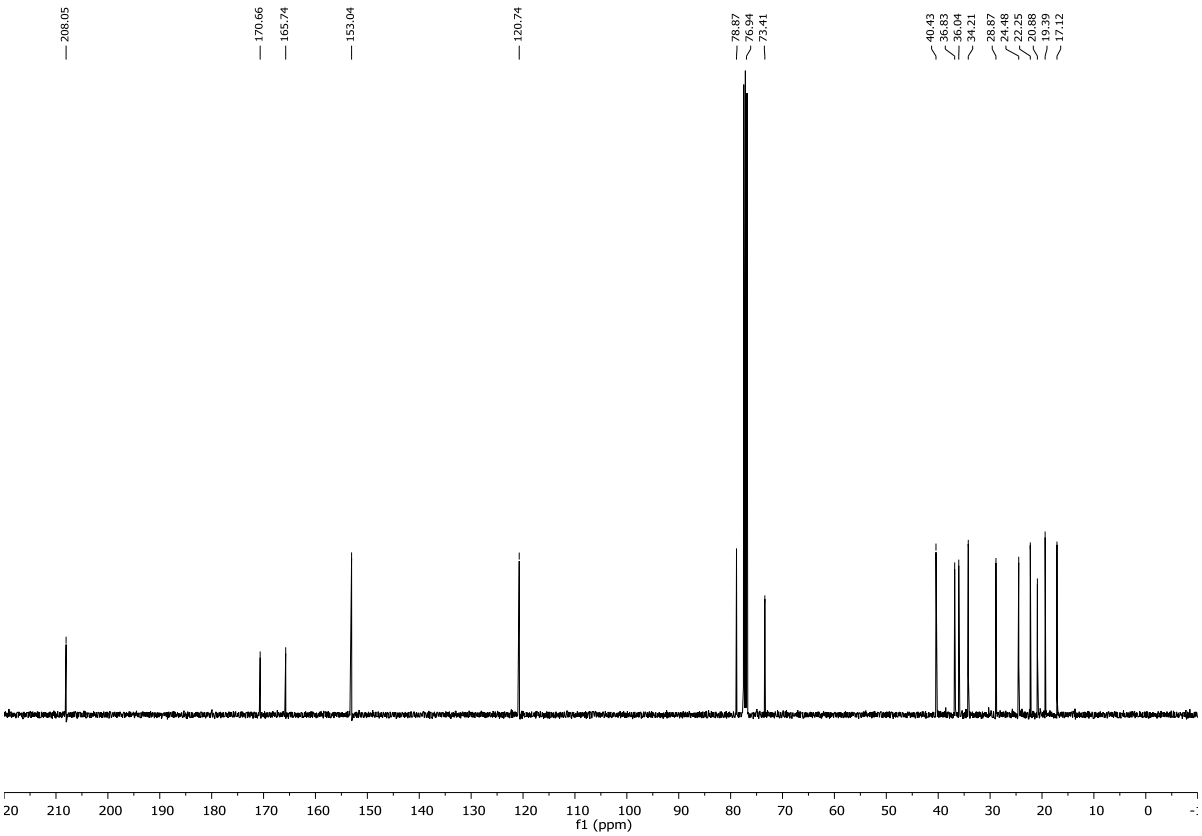




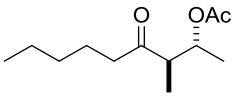


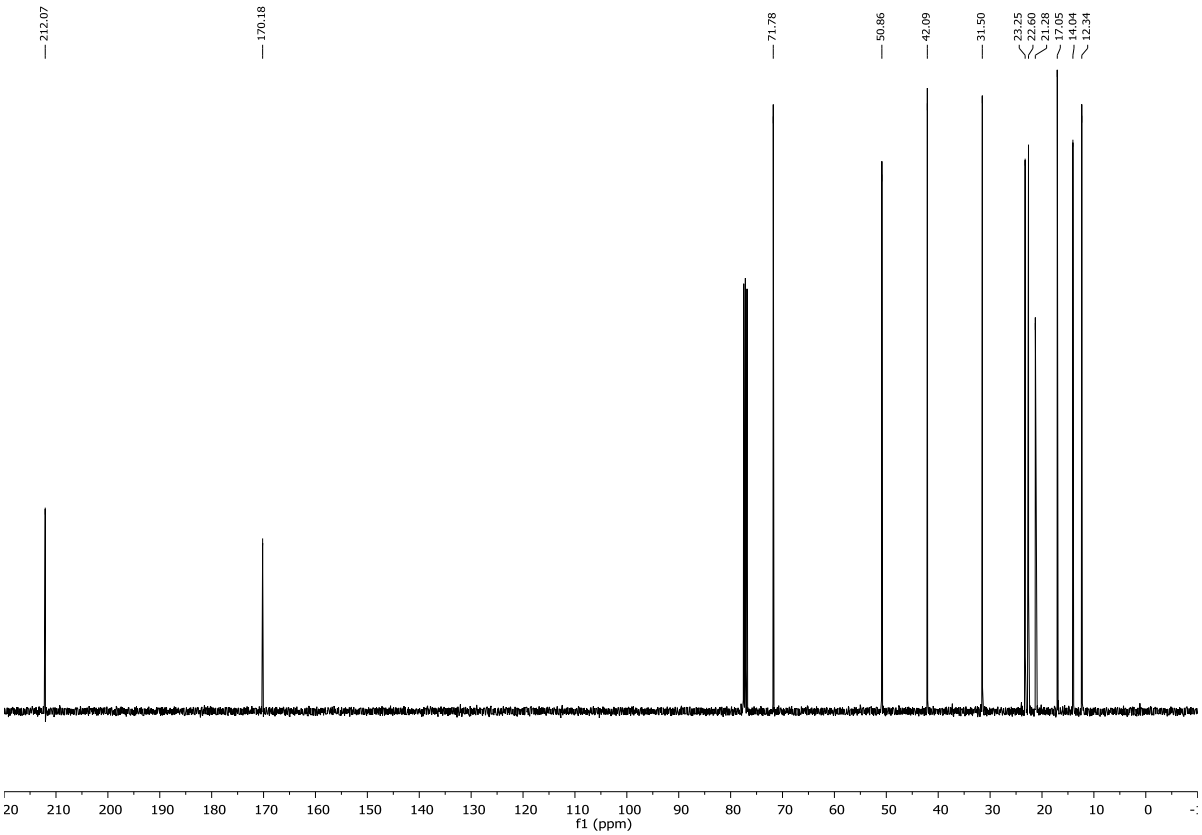
(2*R*,3*S*,8*S*,11*R*,*E*)-11-Hydroxy-2,3,11-trimethyl-7,14-dioxooxacyclotetradec-12-en-8-yl acetate (15)



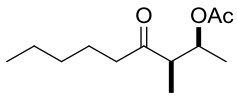


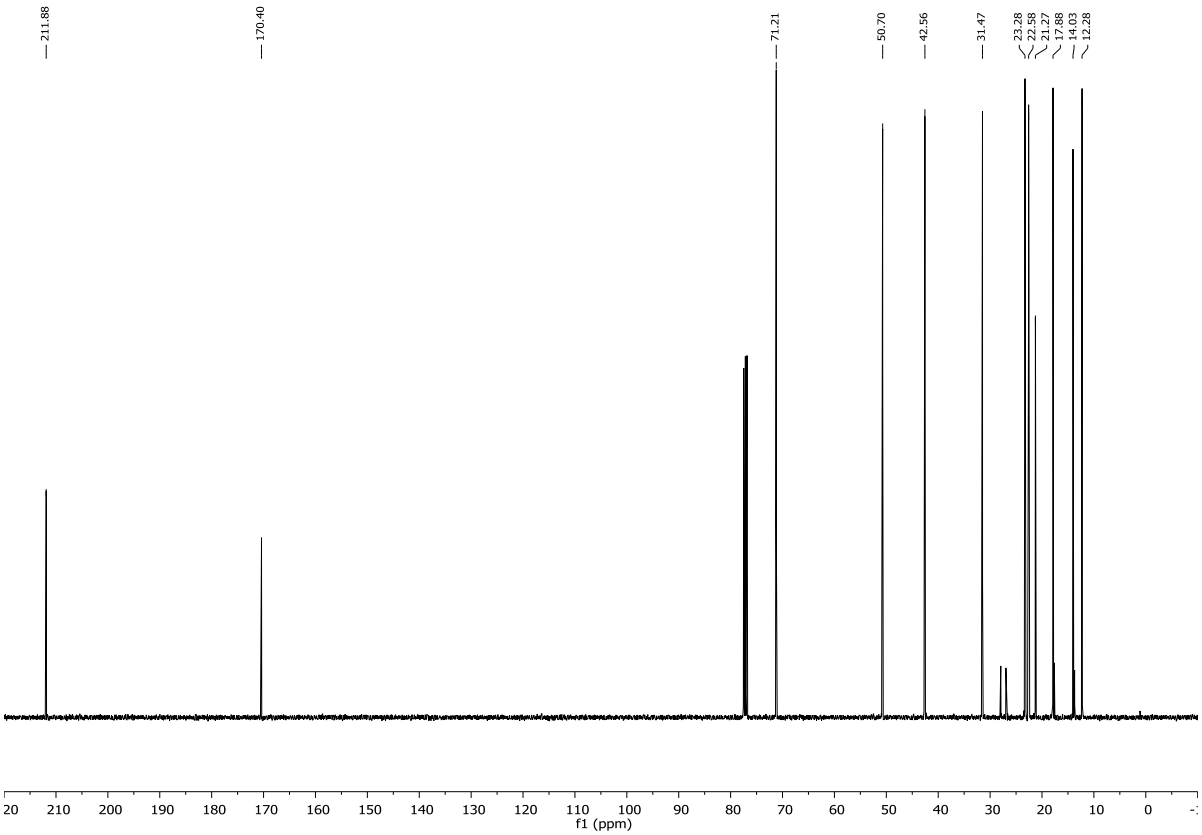
anti-3-Methyl-4-oxononan-2-yl acetate (21)



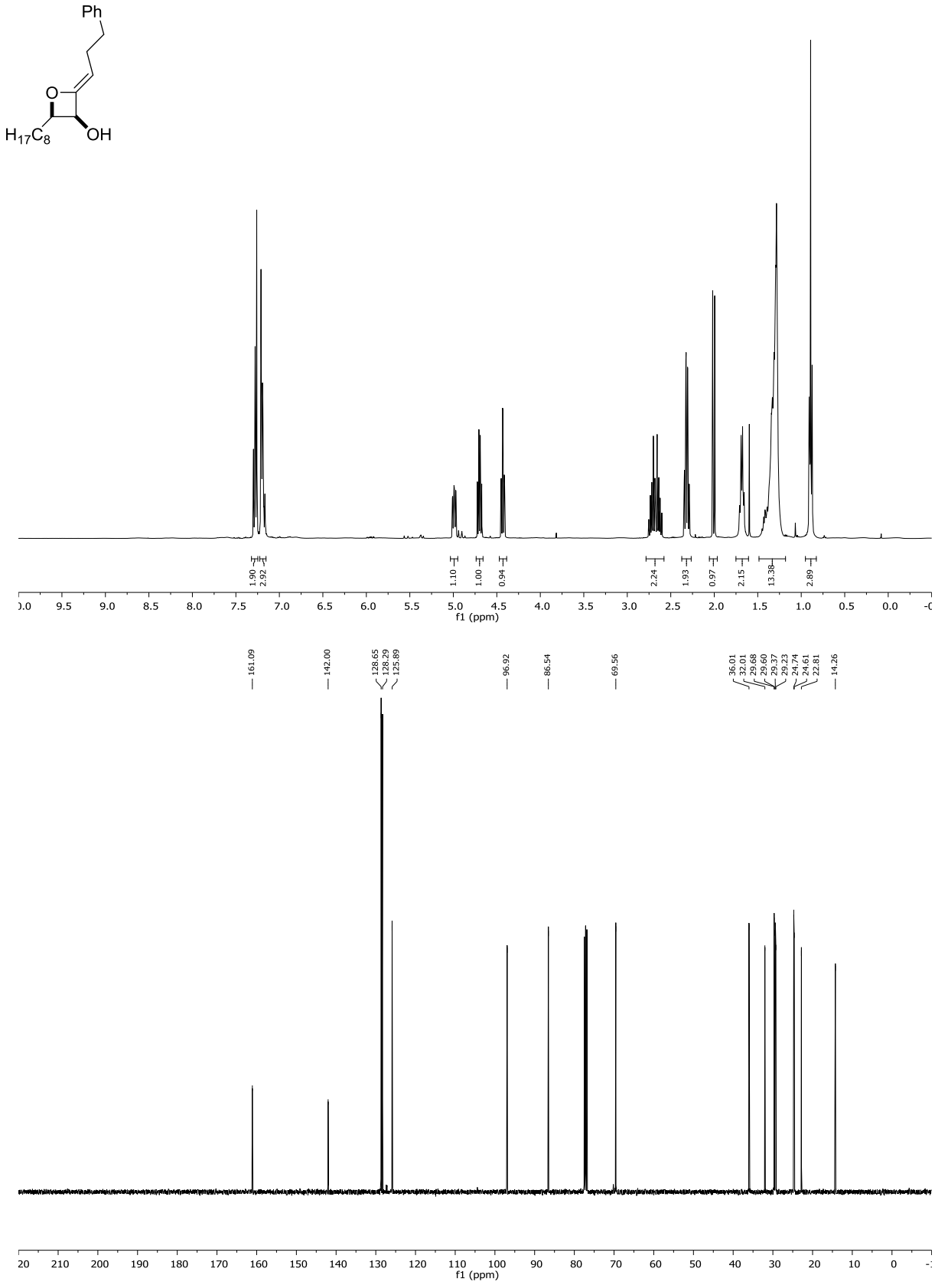


syn-3-Methyl-4-oxononan-2-yl acetate (23)



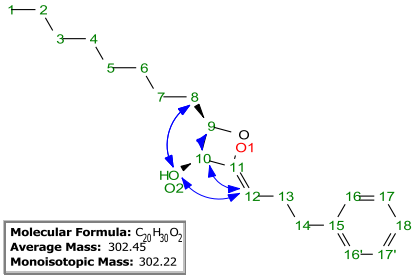


1-((2*S*,3*S*,*Z*)-3-Hydroxy-4-(3-phenylpropylidene)oxetan-2-yl)octan-1-one (26)



SOI-SA-1318

15 mg $CDCl_3$ 298 K



Molecular Formula: $C_{20}H_{30}O_2$
Average Mass: 302.45
Monoisotopic Mass: 302.22

P-ID:	CW00231
Measured on:	14.12.2015
CHIFFRE:	SOI-SA-1318
Client:	Sommer
Group:	Fürstner
Analyst:	Wirtz
Assignment Date:	15.12.2015
Amount:	15 mg
Solvent:	$CDCl_3$
Reference:	solvent
Temperature:	298K
Spectrometer:	AV-400 + BBFO
Experiments:	1H, 13C{1H}, COSYPH
	HSQCed, HMBC,NOESY

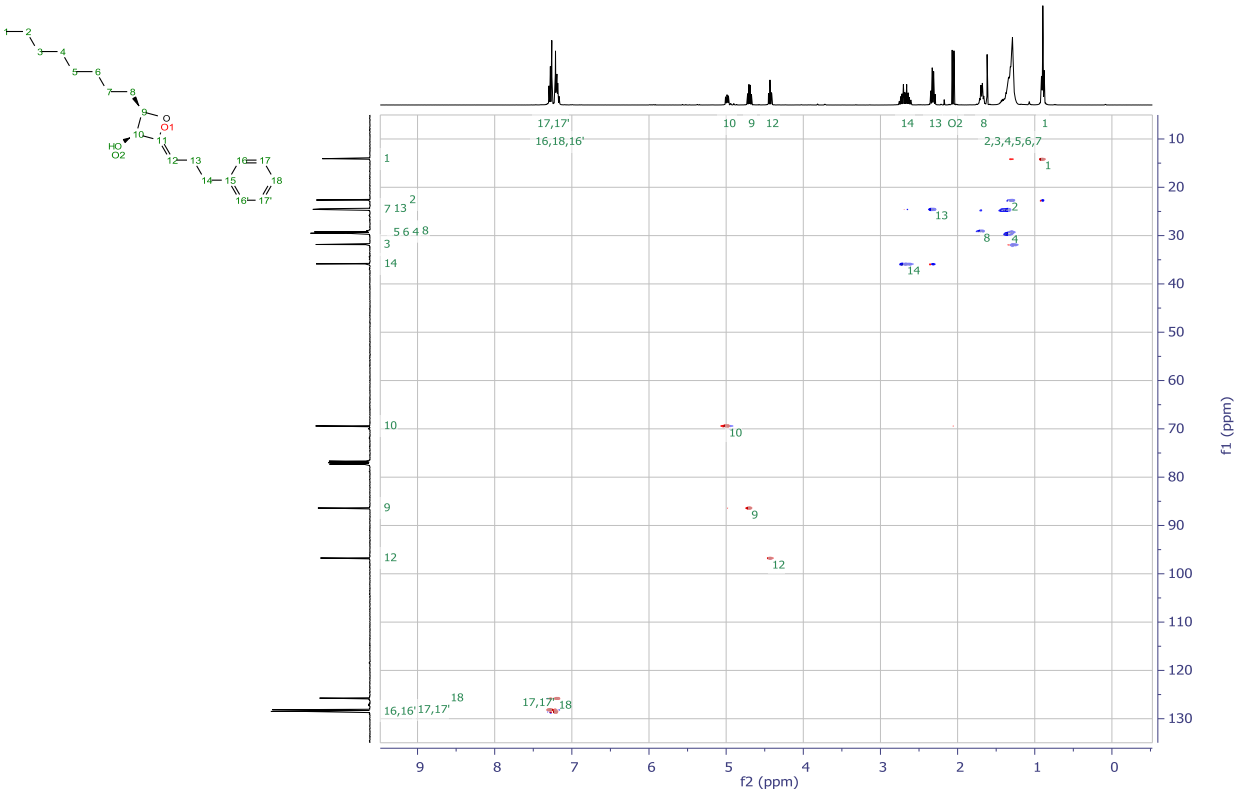
^{13}C NMR (101 MHz, $CDCl_3$) δ 160.98 (11), 141.87 (15), 128.50 (16, 16'), 128.14 (17, 17'), 125.74 (18), 96.74 (12), 86.39 (9), 77.32, 77.00, 76.68, 69.40 (10), 35.85 (14), 31.84 (3), 29.51, 29.43, 29.20, 29.07 (8), 24.58 (7), 24.43 (13), 22.64 (2), 14.08 (1).

^{1}H NMR (400 MHz, Chloroform-d) δ = 7.33 – 7.23 (m, 2H), 7.23 – 7.15 (m, 3H), 4.99 (dd, J=8.6, 5.9, 1.3, 1H), 4.70 (td, J=6.9, 6.0, 1H), 4.43 (td, J=7.5, 1.5, 1H), 2.76 – 2.60 (m, 2H), 2.39 – 2.25 (m, 2H), 2.06 (d, J=9.1, 1H), 1.73 – 1.64 (m, 2H), 1.50 – 1.06 (m, 12H), 0.90 (t, 3H).

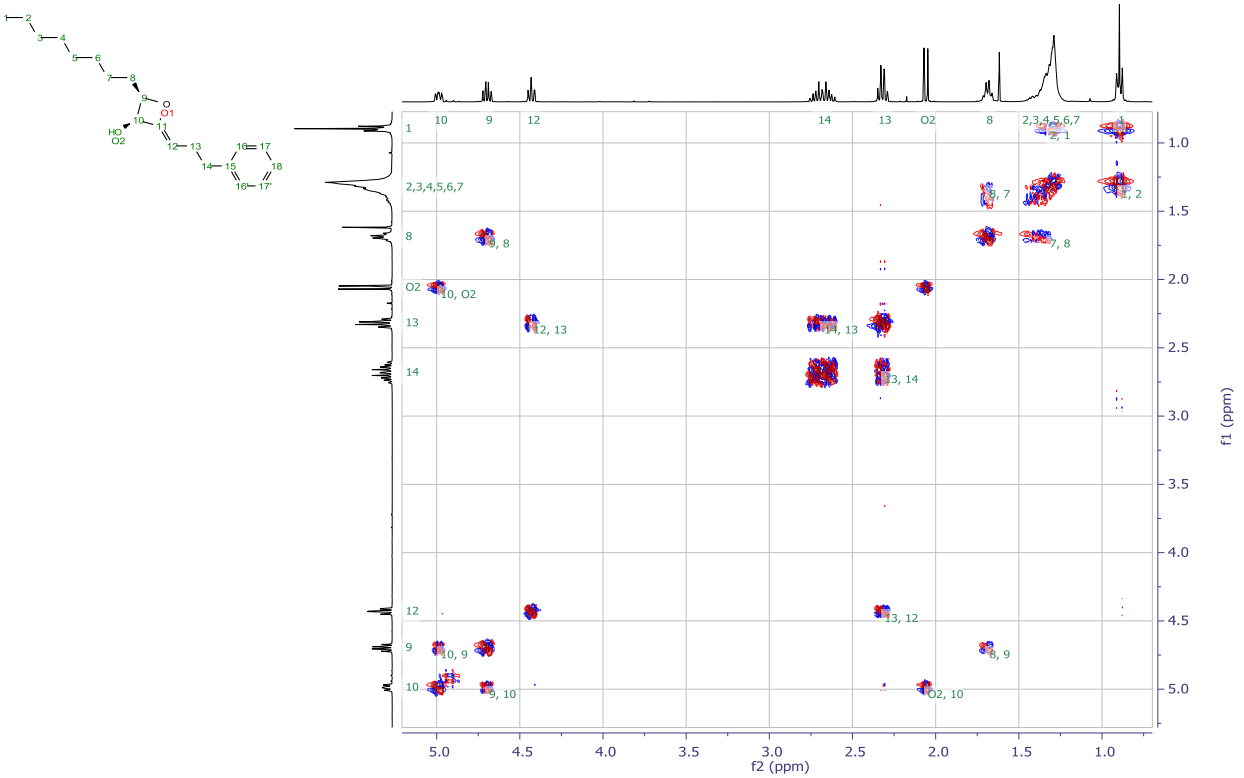
Atom	Chemical Shift	J	COSY	HSQC	HMBC	NOESY
O2 O					9	
H	2.06	9.00(10)	10		11, 9, 10	12, 8
1 C	14.08			1		
H3	0.90		2	1	3, 2	
2 C	22.64			2	1	
H2	1.21..1.49		1	2		
3 C	31.84			3	1	
H2	1.19..1.47			3		
4 C	29.17..29.54			4		
H2	1.21..1.45			4		
5 C	29.18..29.54			5		
H2	1.19..1.49			5		
6 C	29.18..29.54			6		
H2	1.22..1.46			6		
7 C	24.58			7	8, 9	
H2	1.21..1.48		8	7		
8 C	29.07			8		
H2	1.69	6.90(9)	7, 9	8	9, 10, 7	O2
9 C	86.39			9	8, O2	
H	4.70	6.90(8), 6.00(10)	8, 10	9	11, 12, O2, 7	10
10 C	69.40			10	8, 12, O2	
H	4.99	6.00(9), 9.00(O2), 1.30(?)	O2, 9	10	11, 12	9, 12
11 C	160.98				10, 12, 13, 9, O2	
12 C	96.74			12	10, 13, 14, 9	
H	4.43	7.50(13), 1.50(?)	13	12	11, 10, 14	10, O2
13 C	24.43			13	14	
H2	2.32	7.50(12)	12, 14	13	11, 15, 12, 14	
14 C	35.85			14	12, 13, 16, 16'	
H2	2.68		13	14	15, 16', 16, 12, 13	
15 C	141.87				13, 14, 17, 17'	
16 C	128.50			16	16', 18, 14	
H	7.20		17	16	16', 18, 14	
16' C	128.50			16'	16, 18, 14	
H	7.20		17'	16'	16, 18, 14	
17 C	128.14			17	17'	
H	7.28		18, 16	17	15, 17'	
17' C	128.14			17'	17	
H	7.28		18, 16'	17'	15, 17	
18 C	125.74			18	16, 16'	
H	7.20		17, 17'	18	16', 16	

SOI-SA-1318

15 mg $CDCl_3$ 298 K

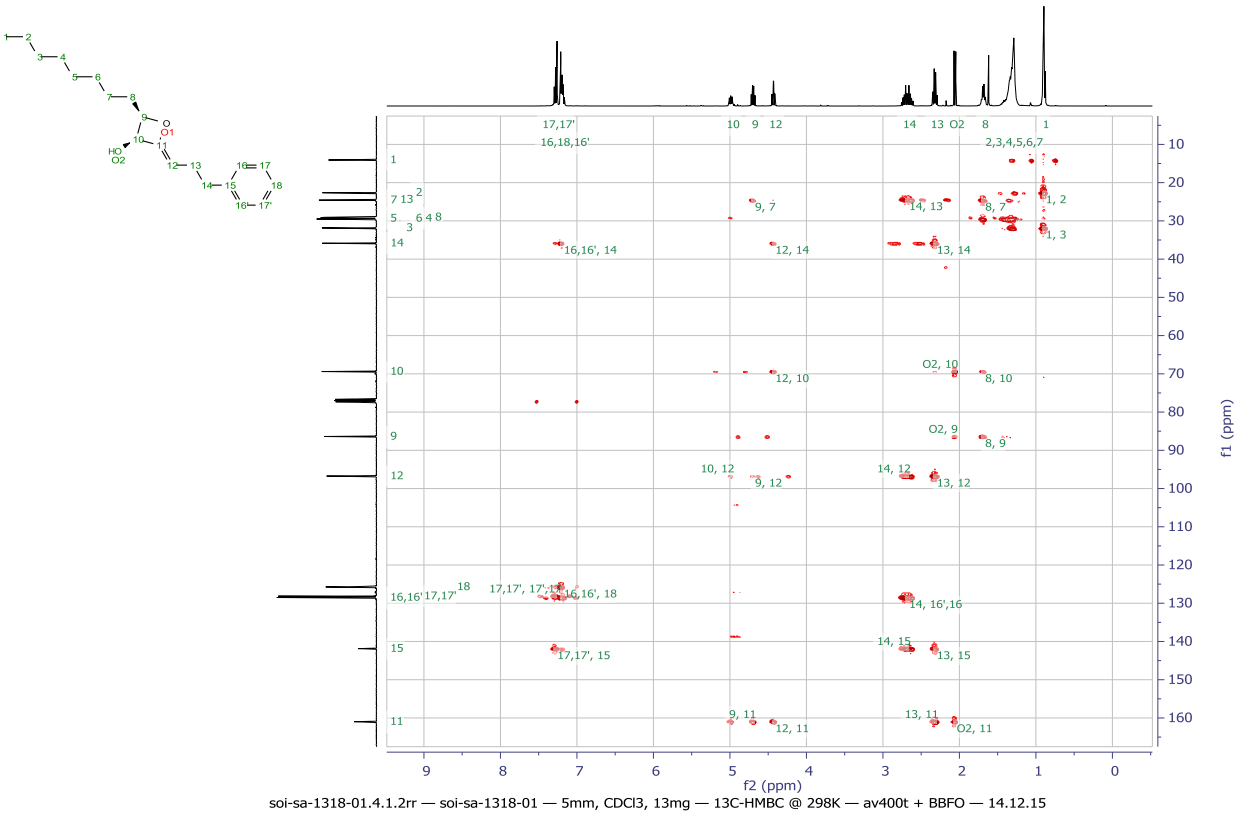


SOI-SA-1318 15 mg $CDCl_3$ 298 K

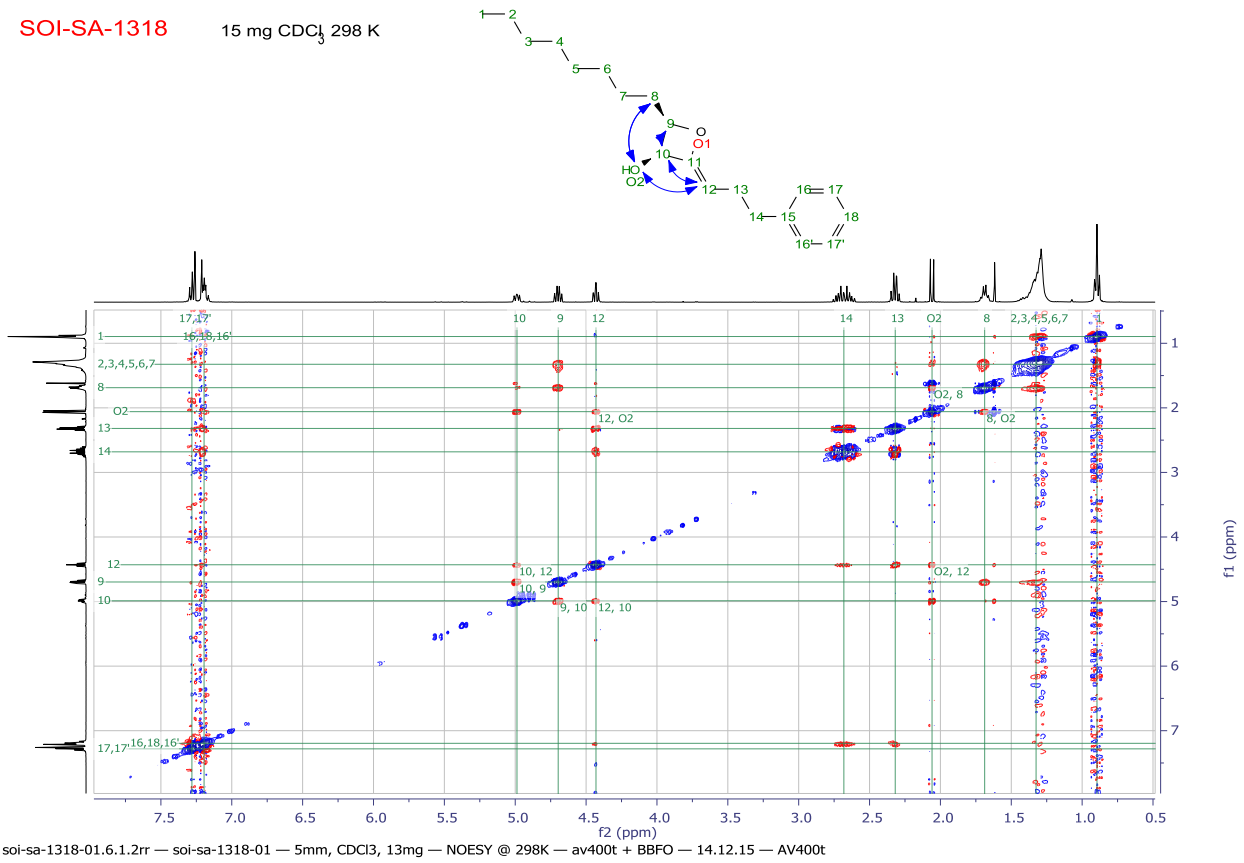


soi-sa-1318-01.5.1.2rr — soi-sa-1318-01 — 5mm, CDCl3, 13mg — COSY @ 298K — av400t + BBFO — 14.12.15

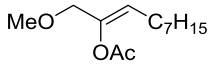
SOI-SA-1318 15 mg $CDCl_3$ 298 K

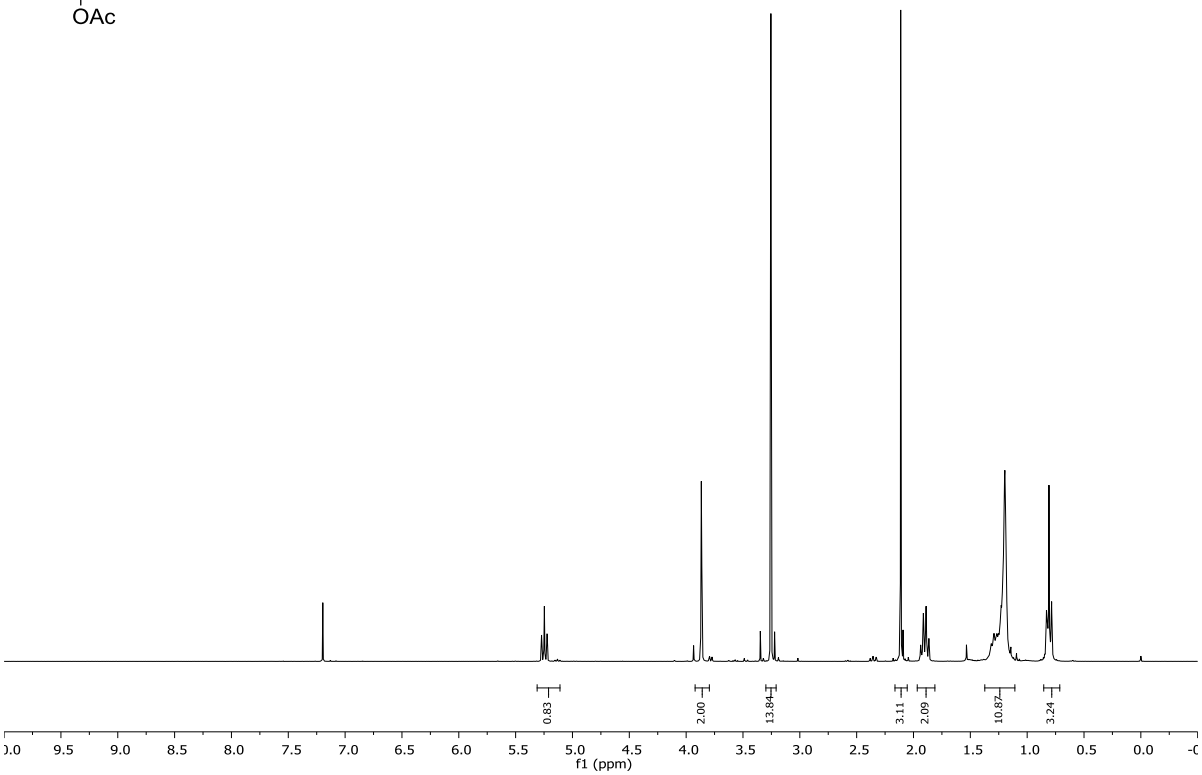


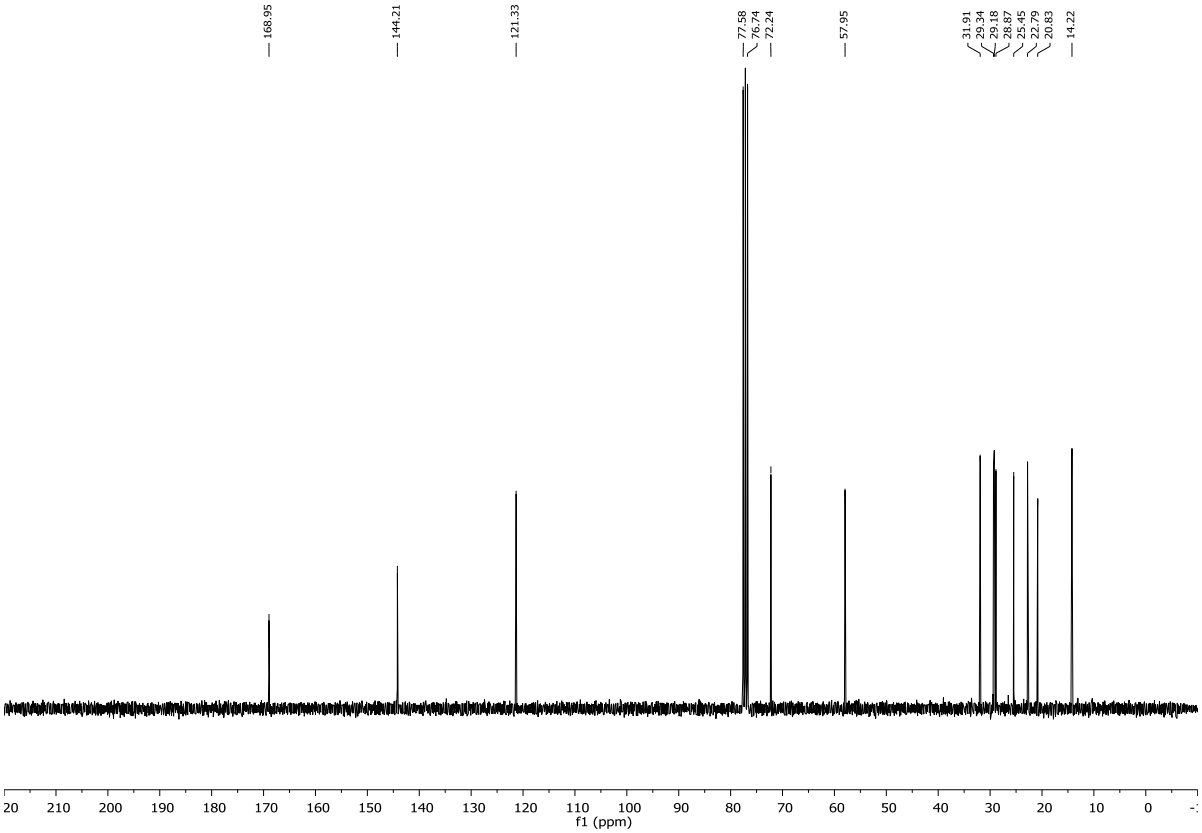
soi-sa-1318-01.4.1.2rr — soi-sa-1318-01 — 5mm, CDCl3, 13mg — 13C-HMBC @ 298K — av400t + BBFO — 14.12.15


SOI-SA-1318
15 mg CDCl3 298 K
f2 (ppm)
f1 (ppm)
soi-sa-1318-01.6.1.2rr — soi-sa-1318-01 — 5mm, CDCl3, 13mg — NOESY @ 298K — av400t + BBFO — 14.12.15 — AV400t

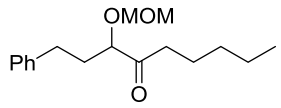
(*Z*)-1-Methoxydec-2-en-2-yl acetate (33)

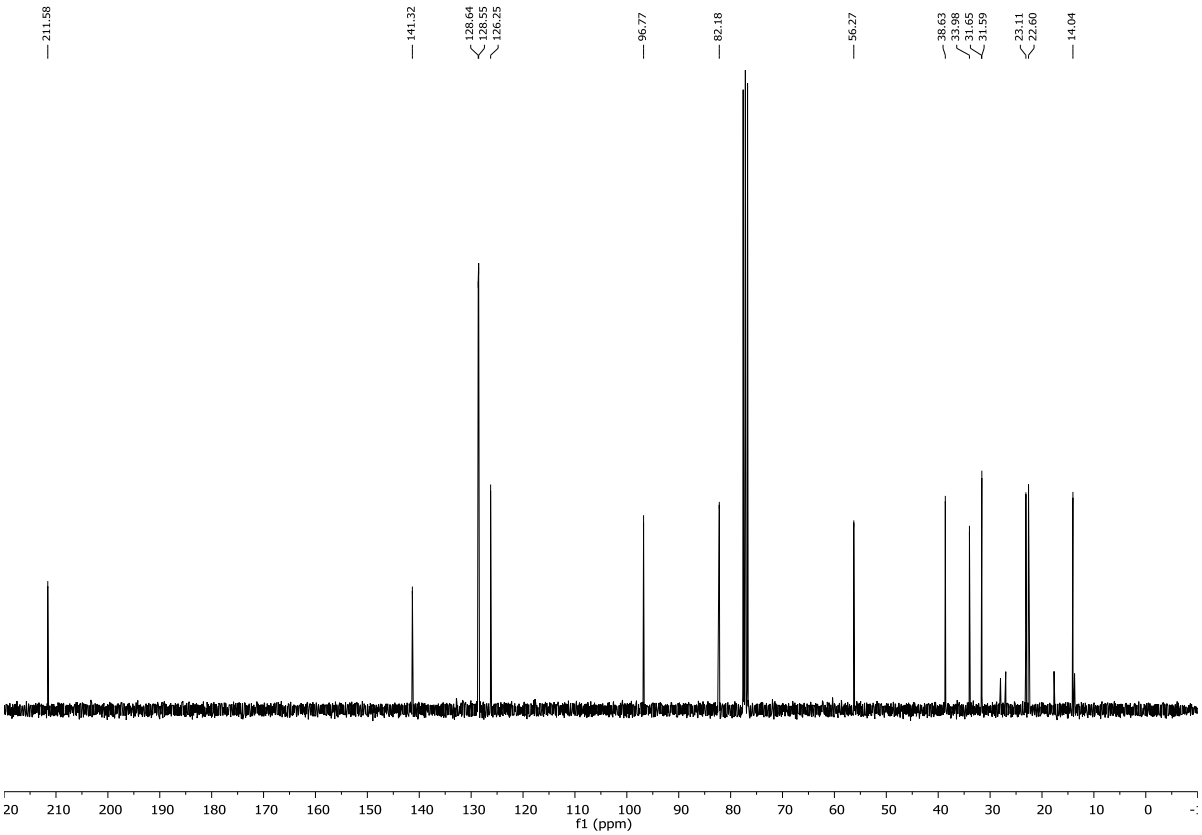




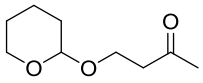


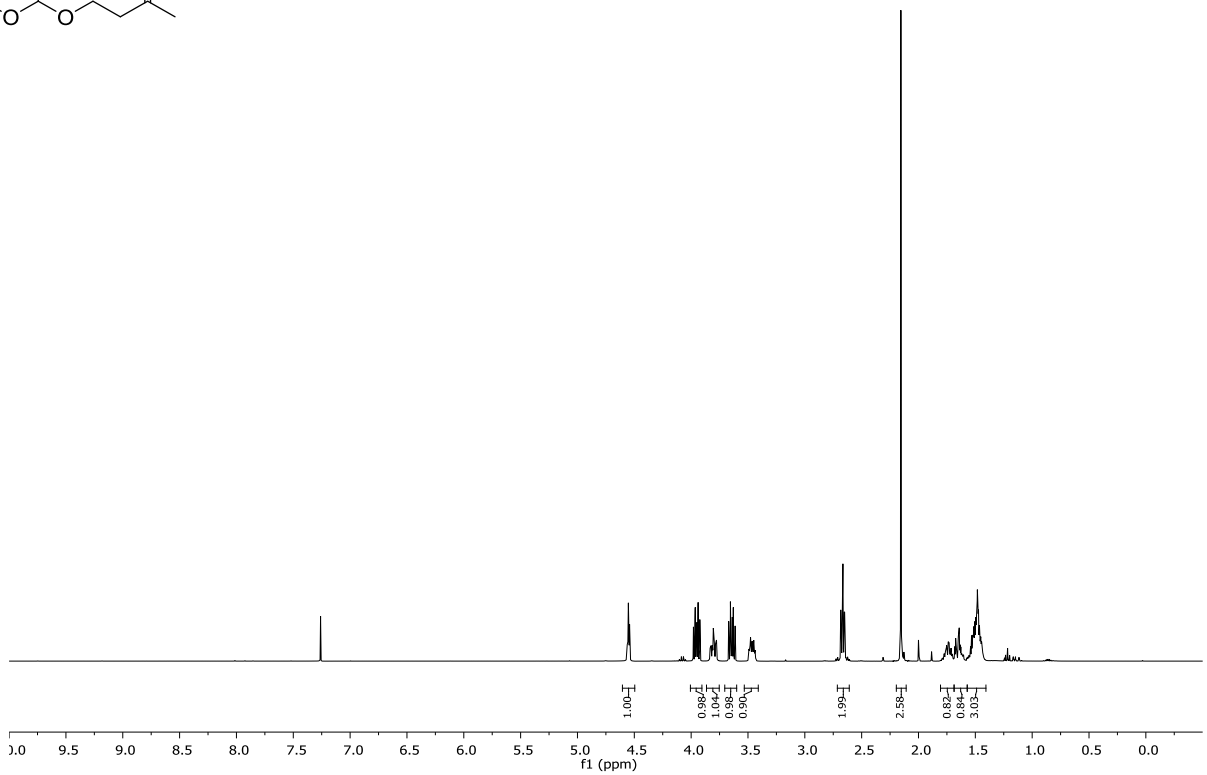
3-(Methoxymethoxy)-1-phenylnonan-4-one (17)

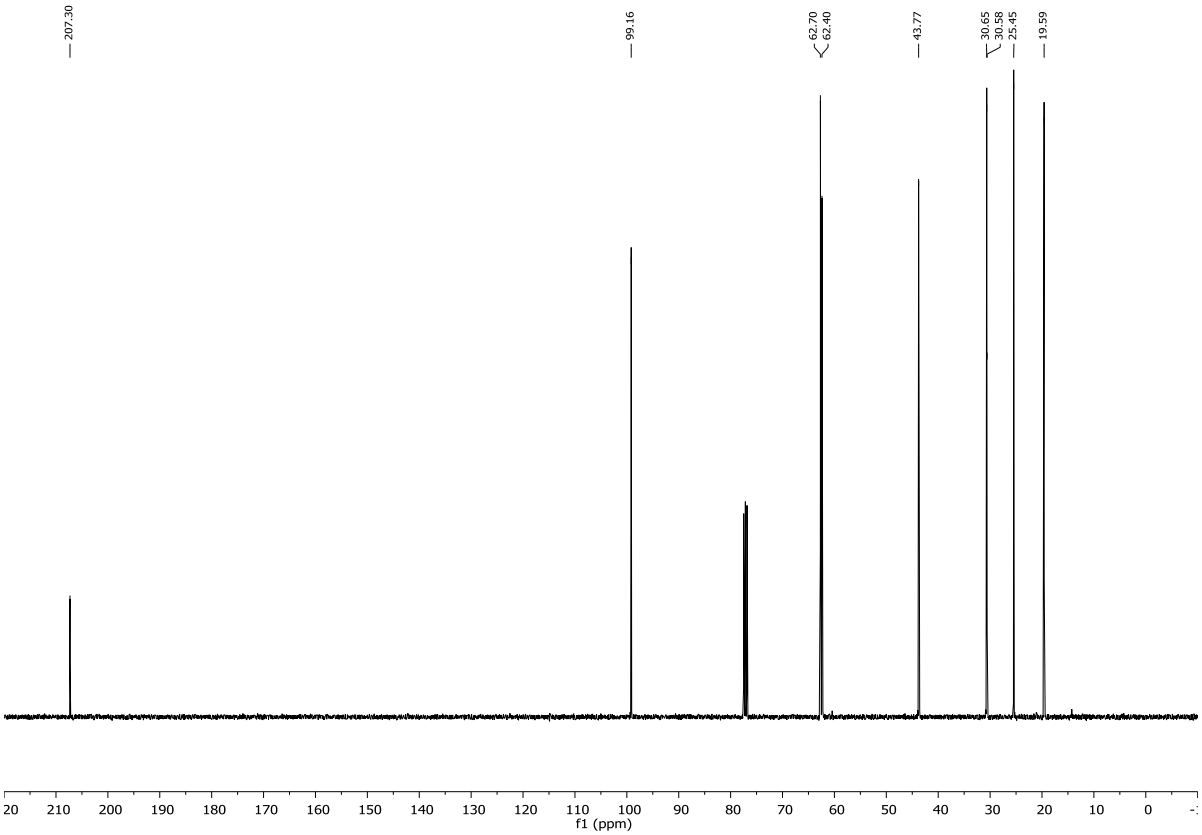




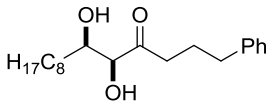
4-((Tetrahydro-2*H*-pyran-2-yl)oxy)butan-2-one (19)

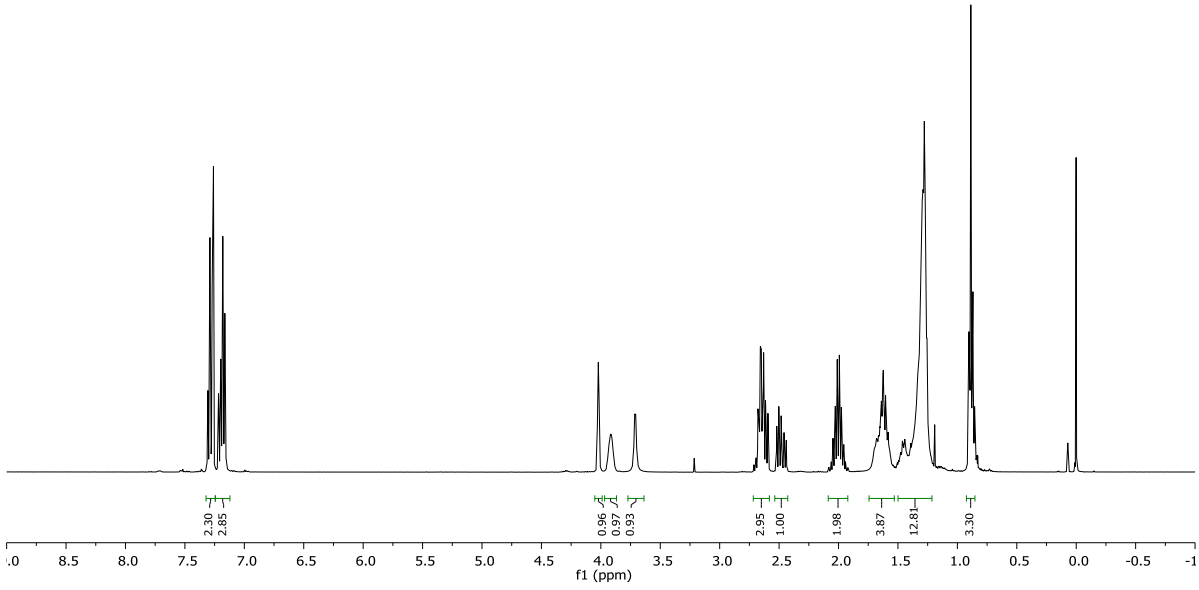


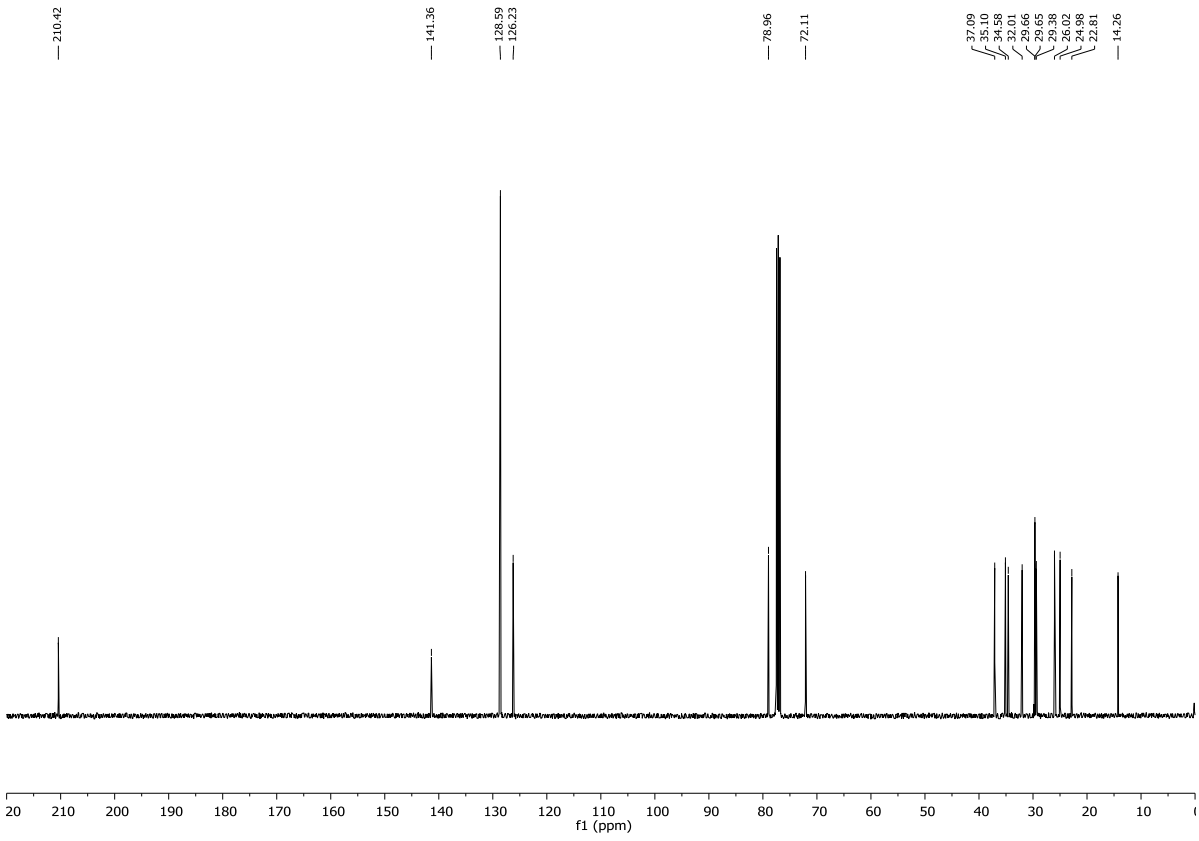




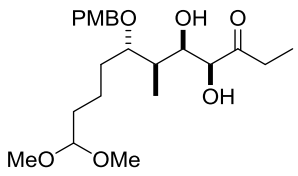
(5*S*,6*R*)-5,6-Dihydroxy-1-phenyltetradecan-4-one (27)



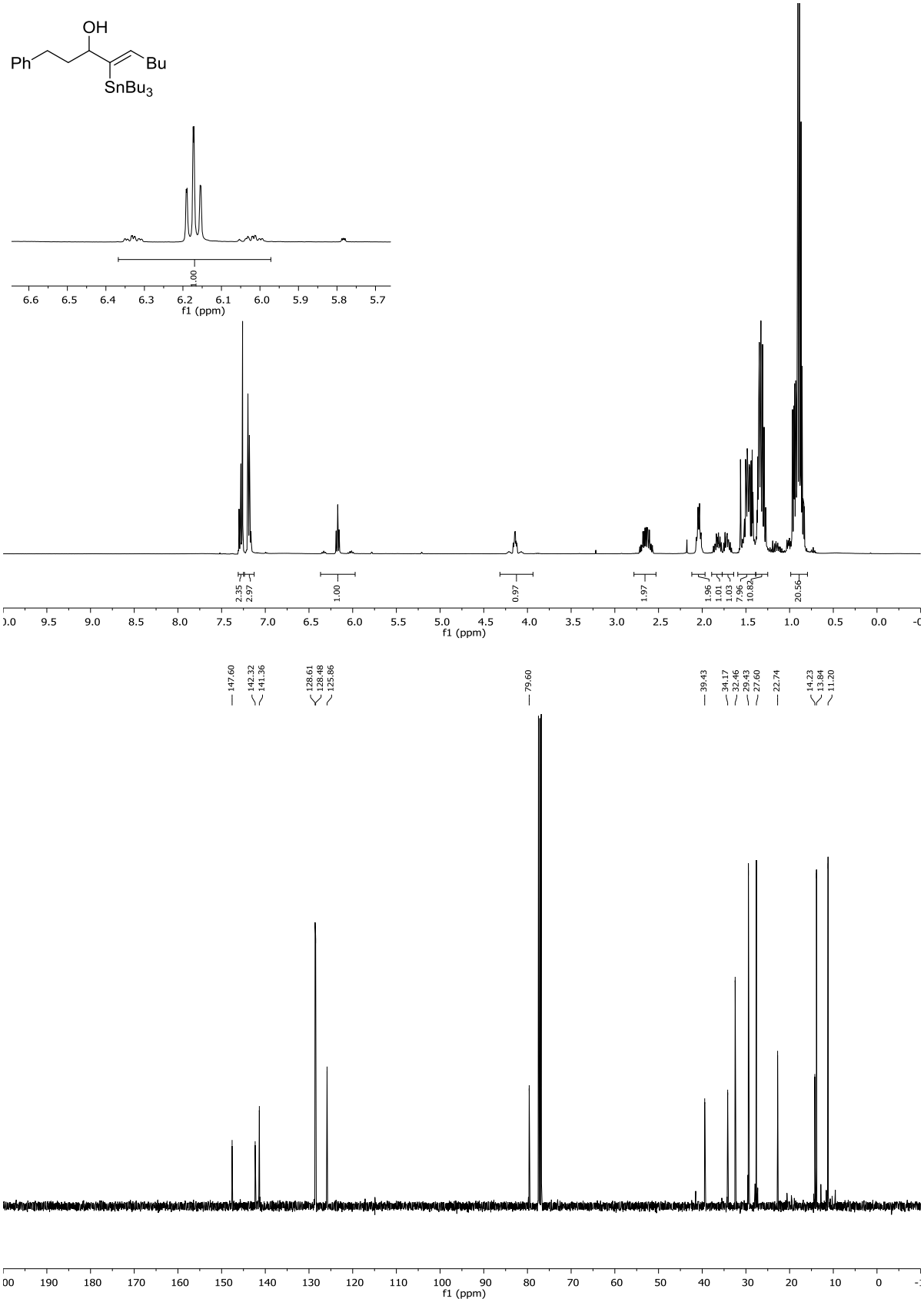




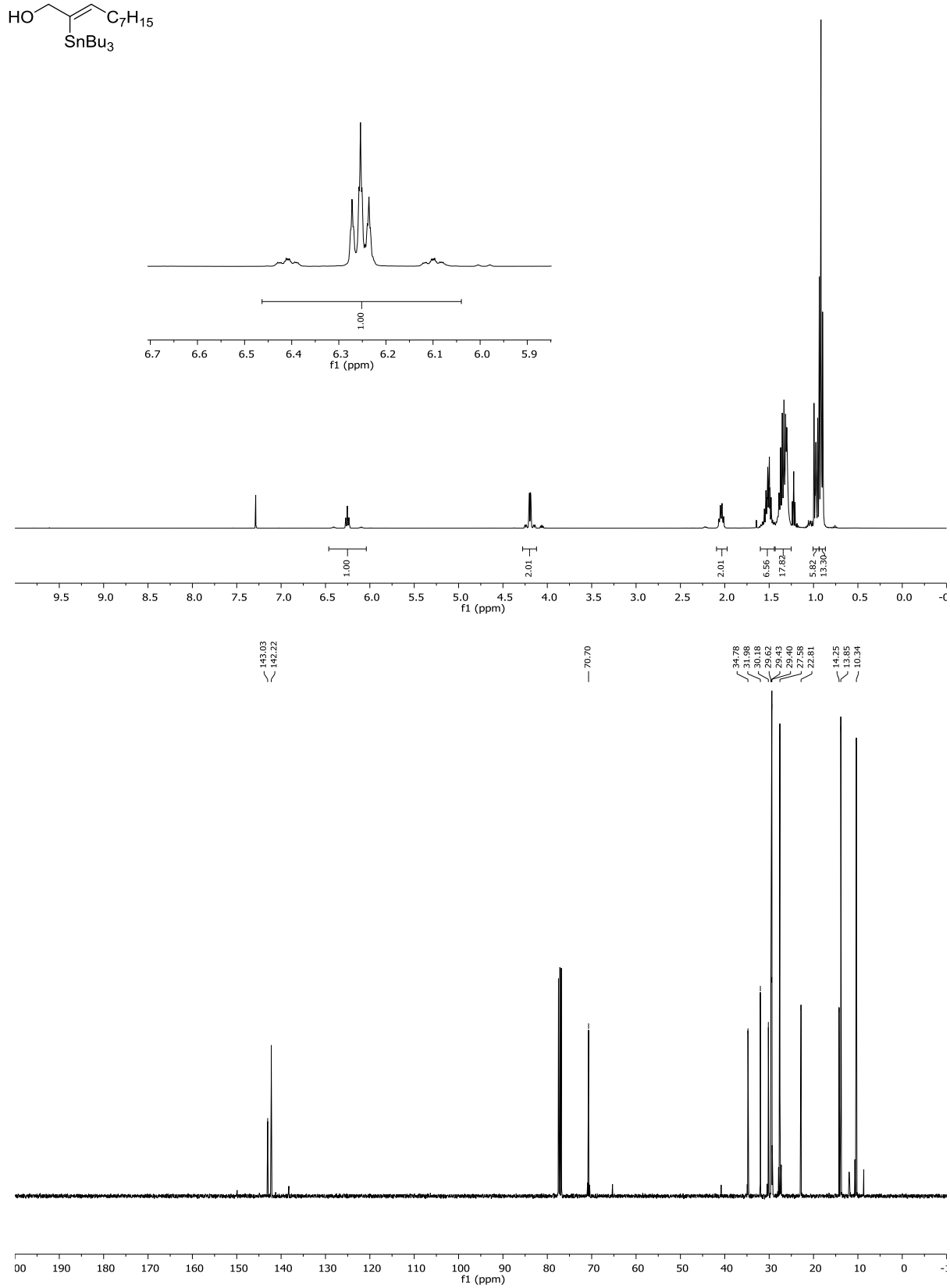
(4*S*,5*R*,6*R*,7*S*)-4,5-Dihydroxy-11,11-dimethoxy-7-((4-methoxybenzyl)oxy)-6-methylundecan-3-one (31)



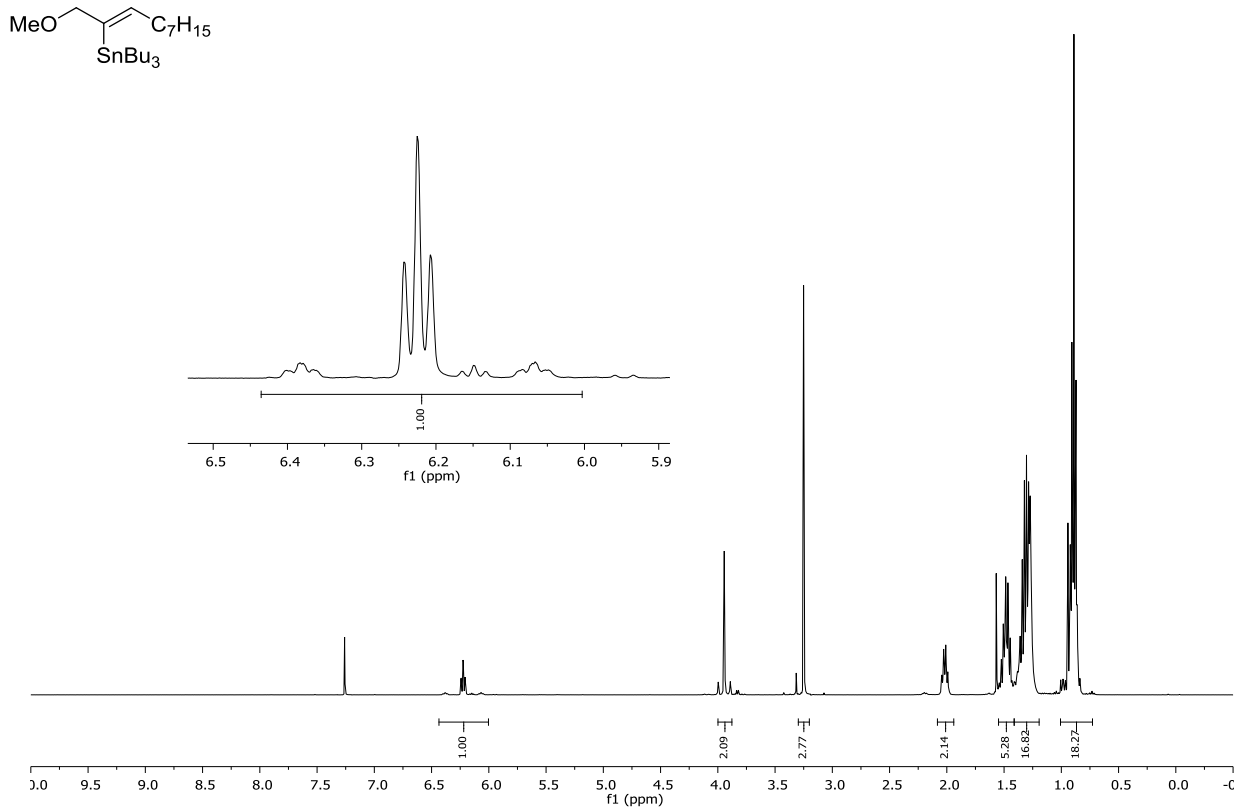
(*Z*)-1-Phenyl-4-(tributylstannyl)non-4-en-3-ol (1)

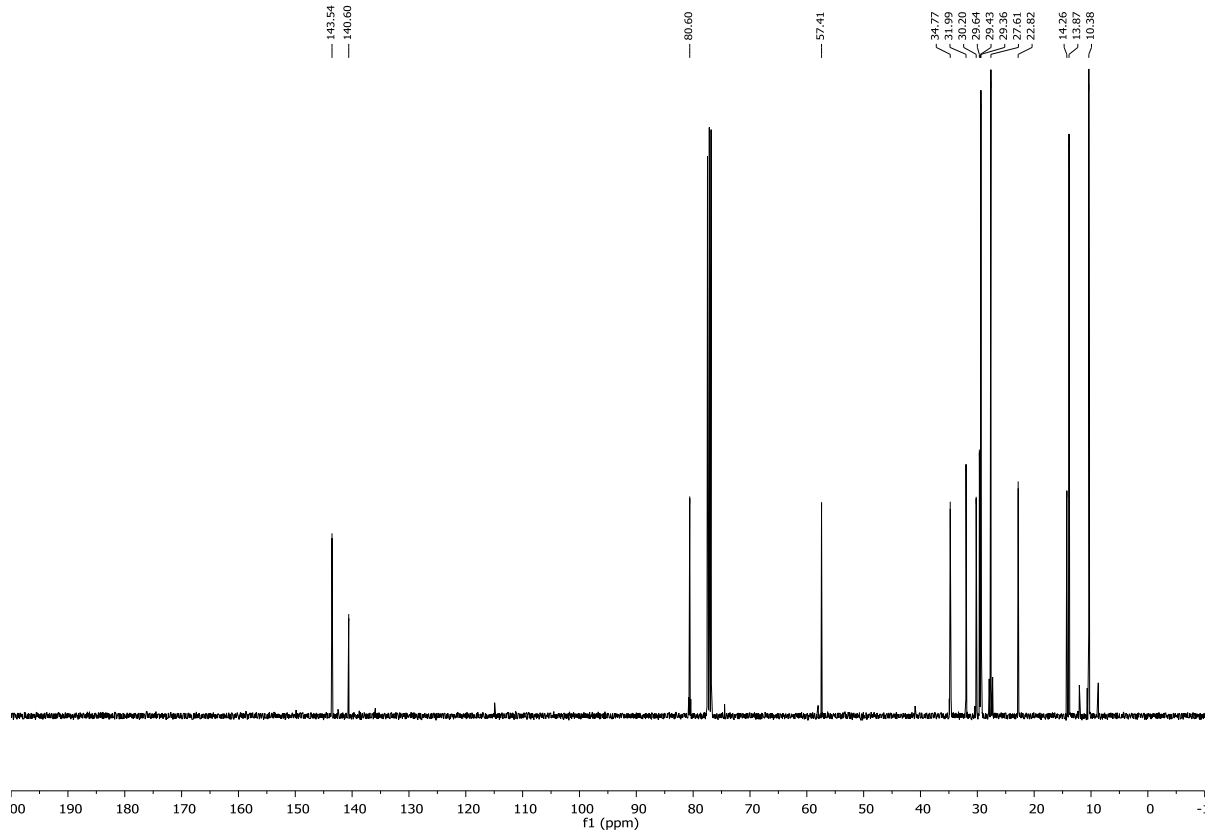


(*Z*)-2-(Tributylstannyl)dec-2-en-1-ol (32a)

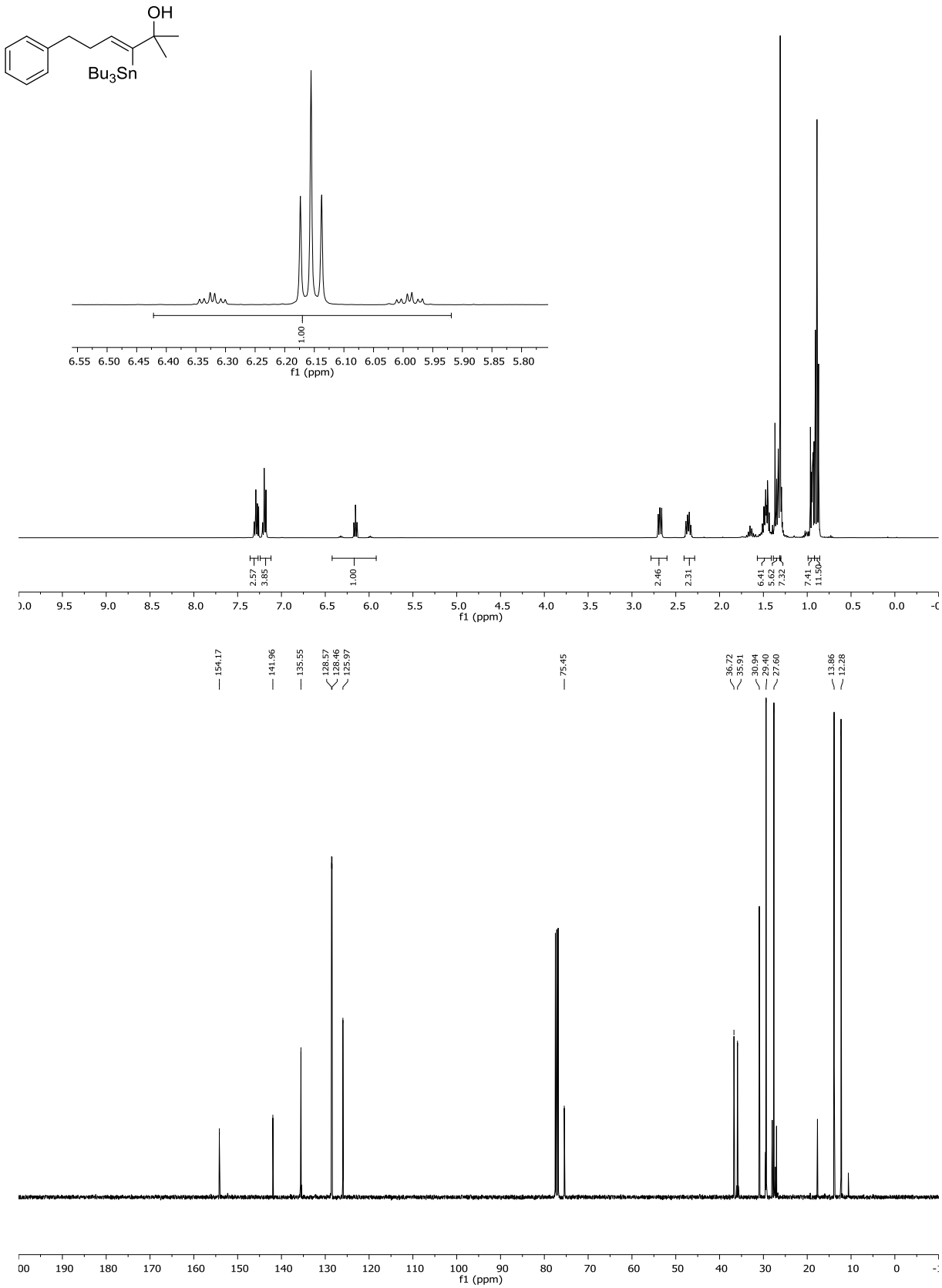


(*Z*)-Tributyl(1-methoxydec-2-en-2-yl)stannane (32b)

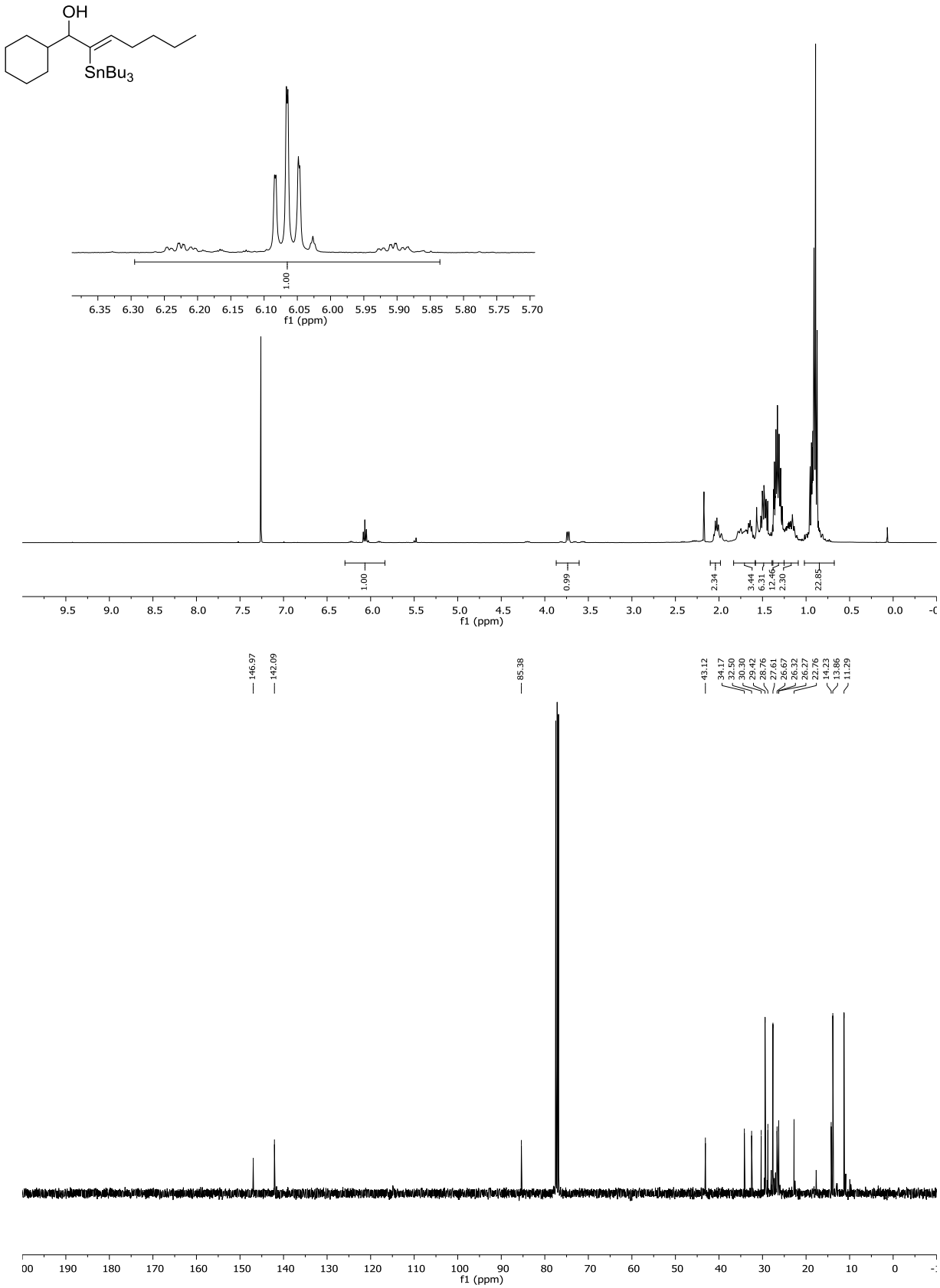




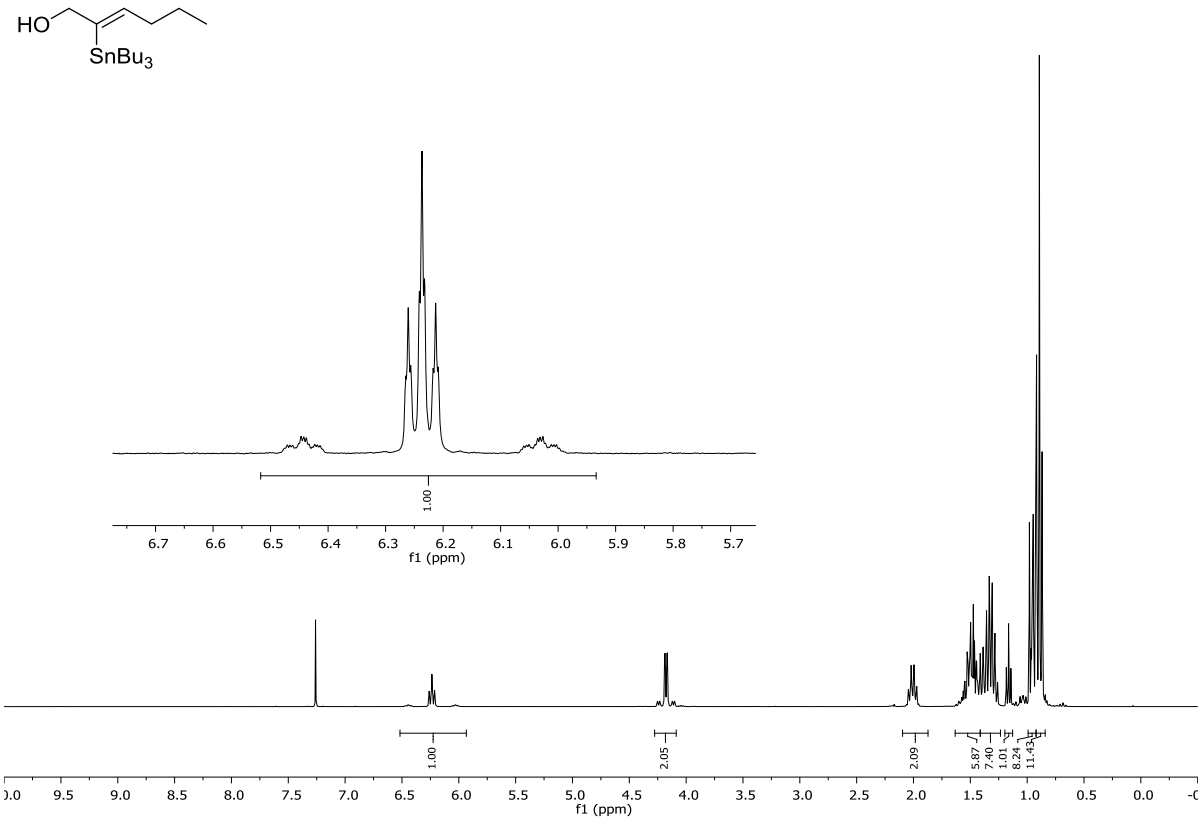
(*Z*)-2-Methyl-6-phenyl-3-(tributylstannyl)hex-3-en-2-ol

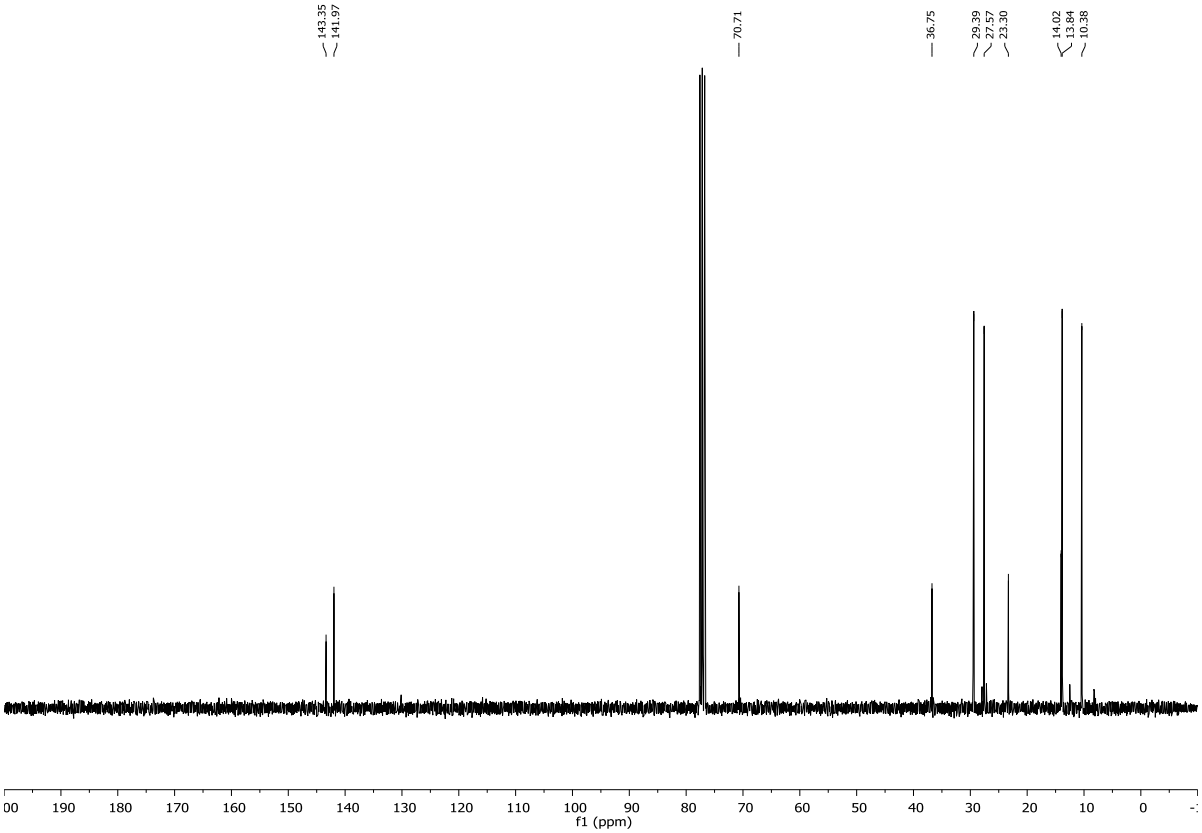


(*Z*)-1-Cyclohexyl-2-(tributylstannyl)hept-2-en-1-ol

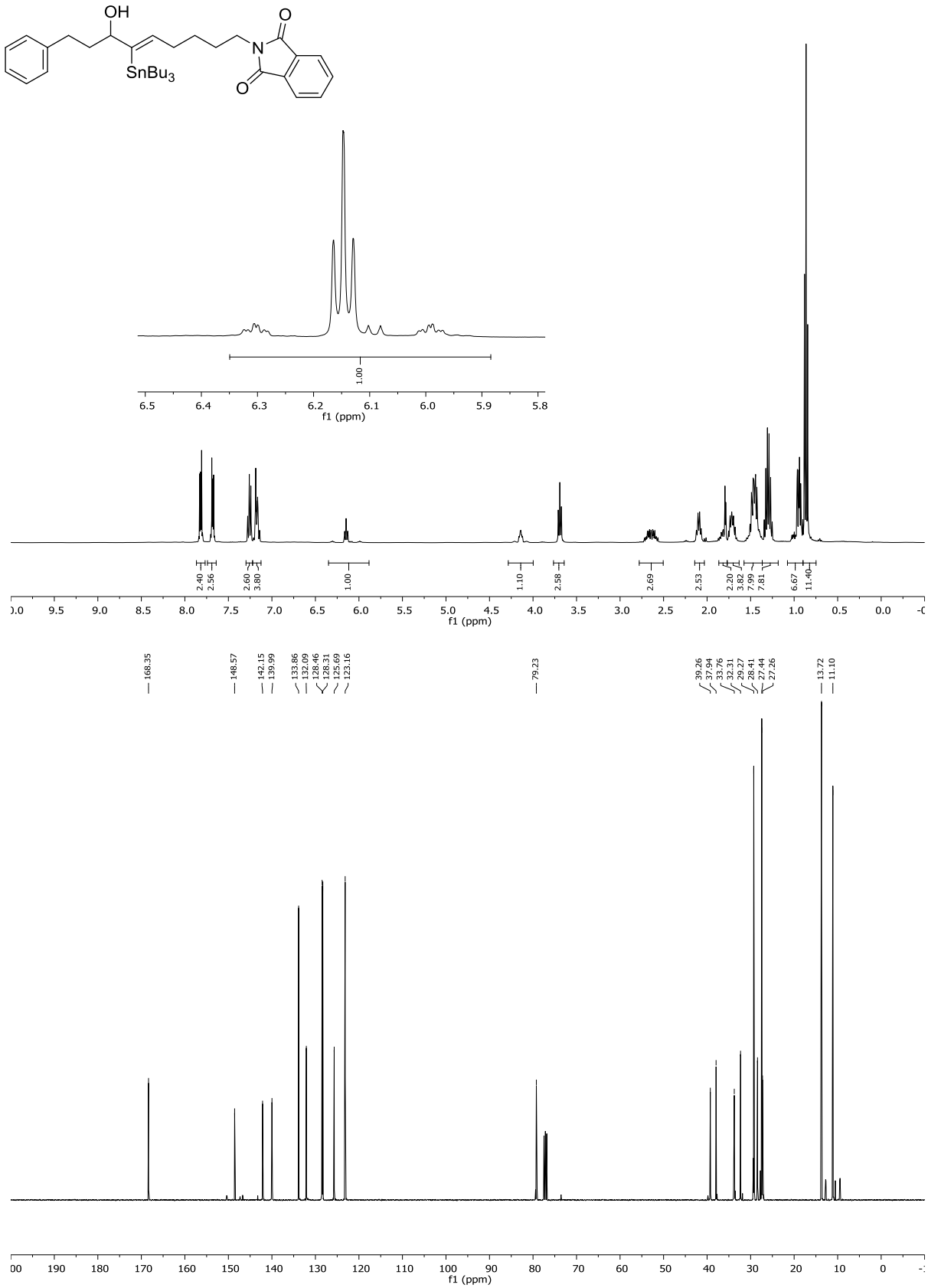


(*Z*)-2-(Tributylstannyl)hex-2-en-1-ol

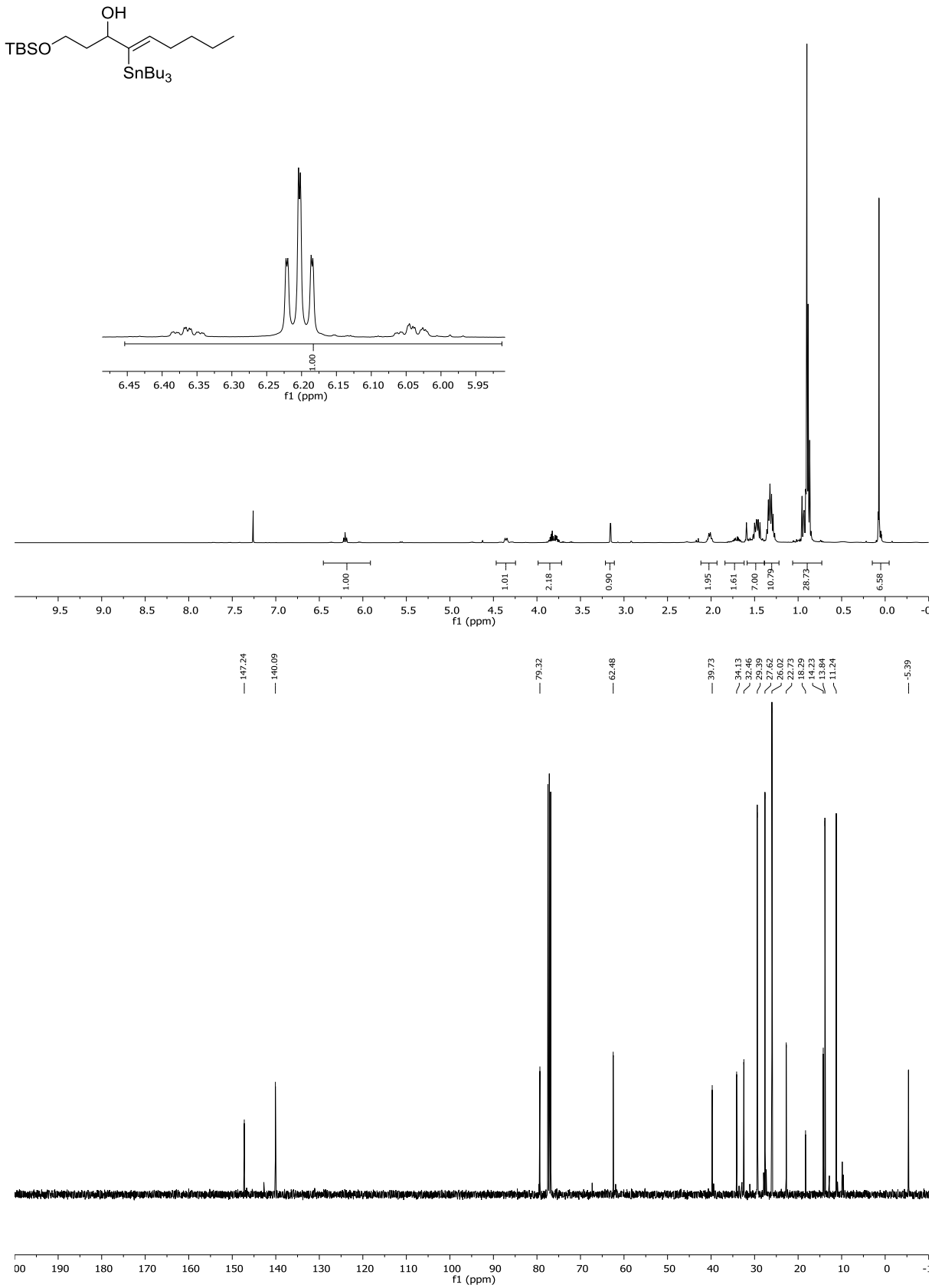




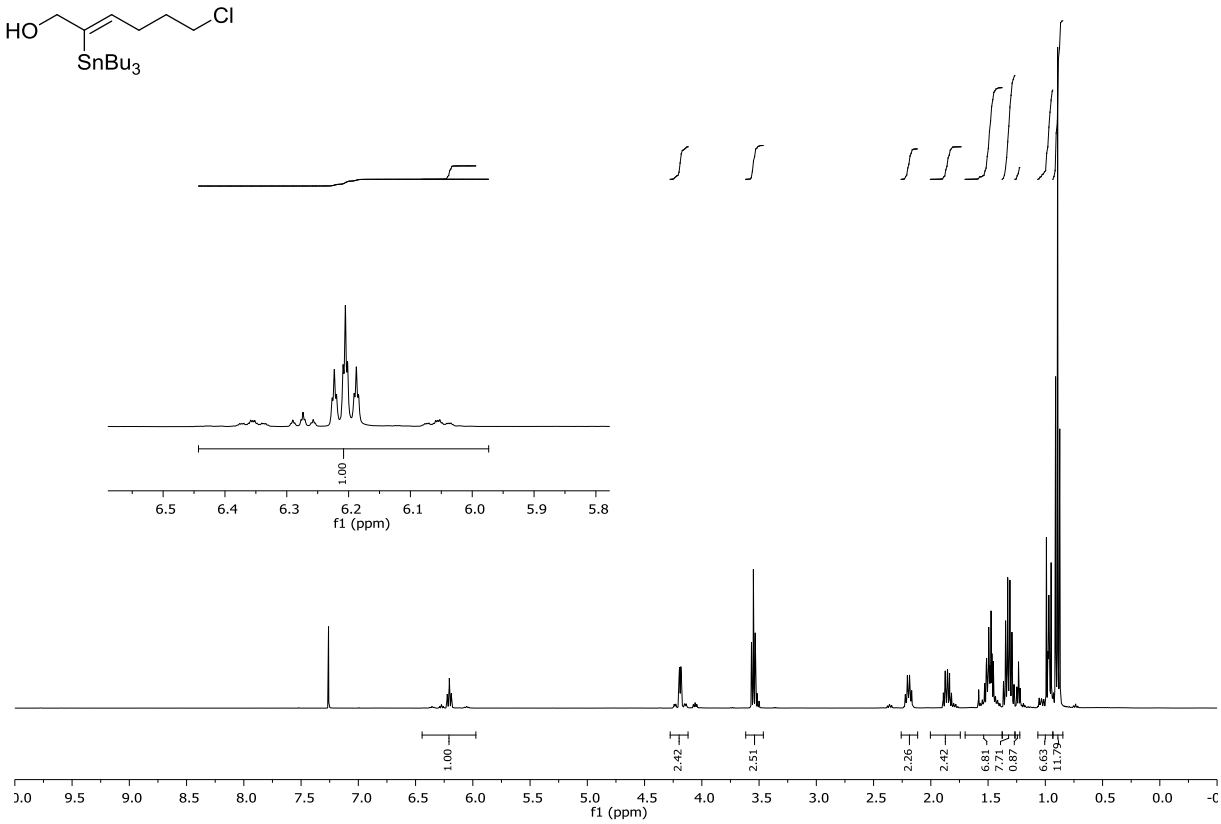
(*Z*)-2-(7-Hydroxy-9-phenyl-6-(tributylstannyl)non-5-en-1-yl)isoindoline-1,3-dione

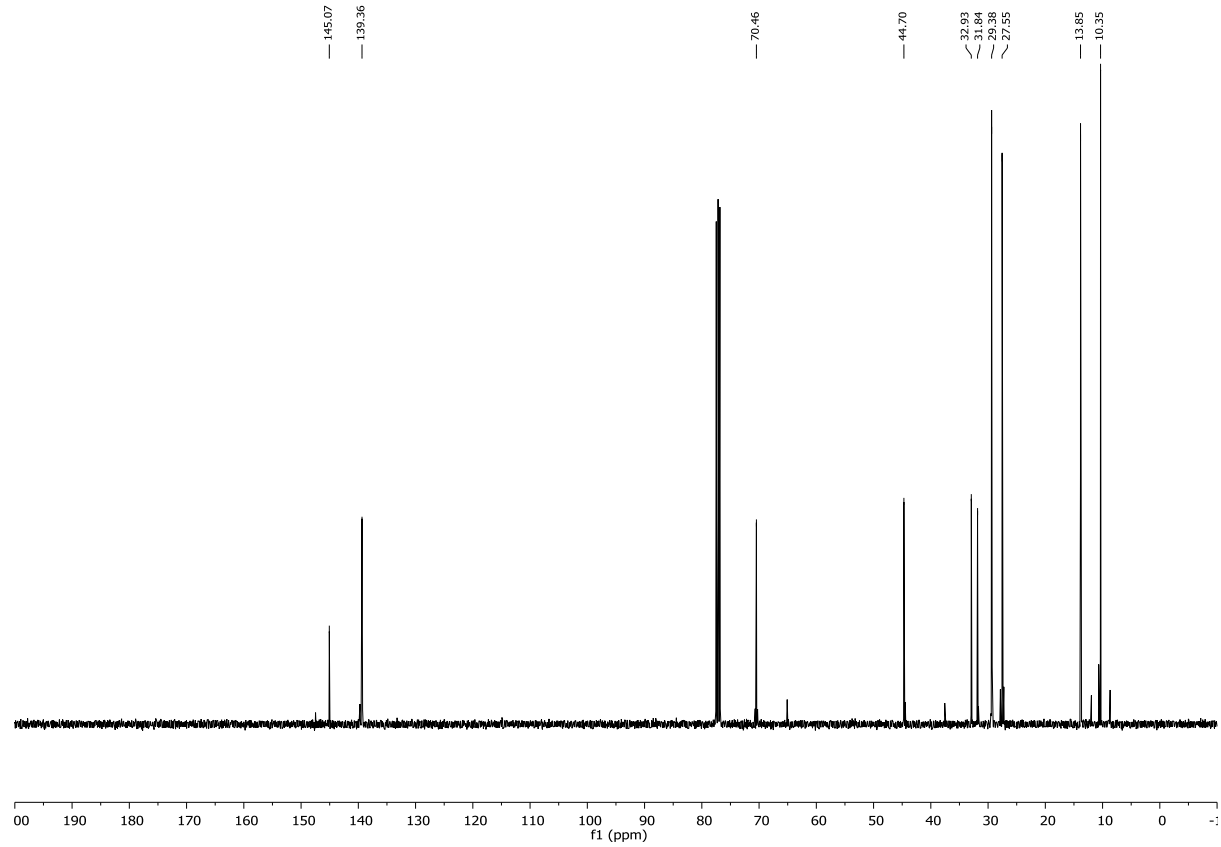


(*Z*)-1-((*tert*-Butyldimethylsilyl)oxy)-4-(tributylstannyl)non-4-en-3-ol

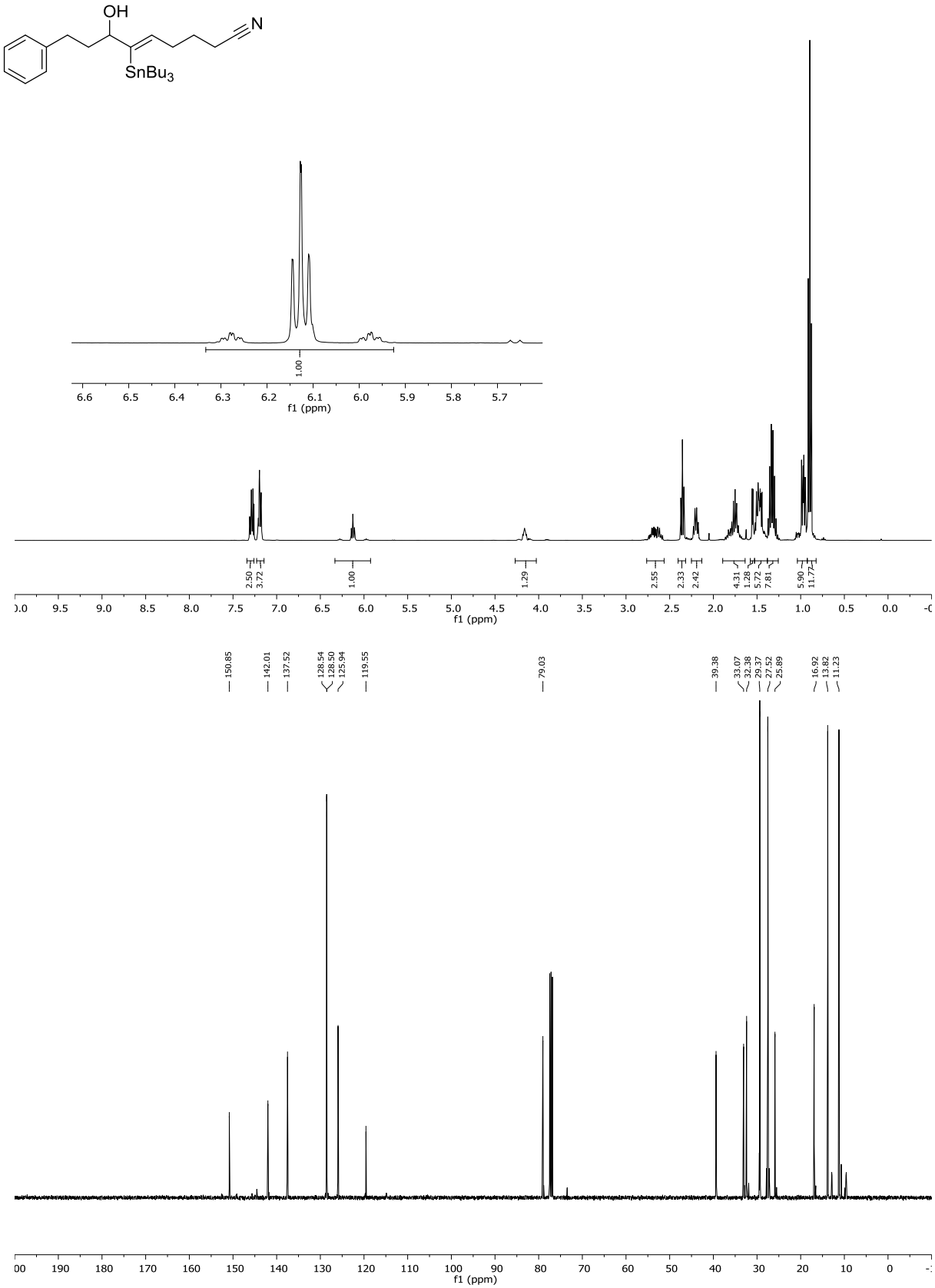


(*Z*)-6-Chloro-2-(tributylstannyl)hex-2-en-1-ol

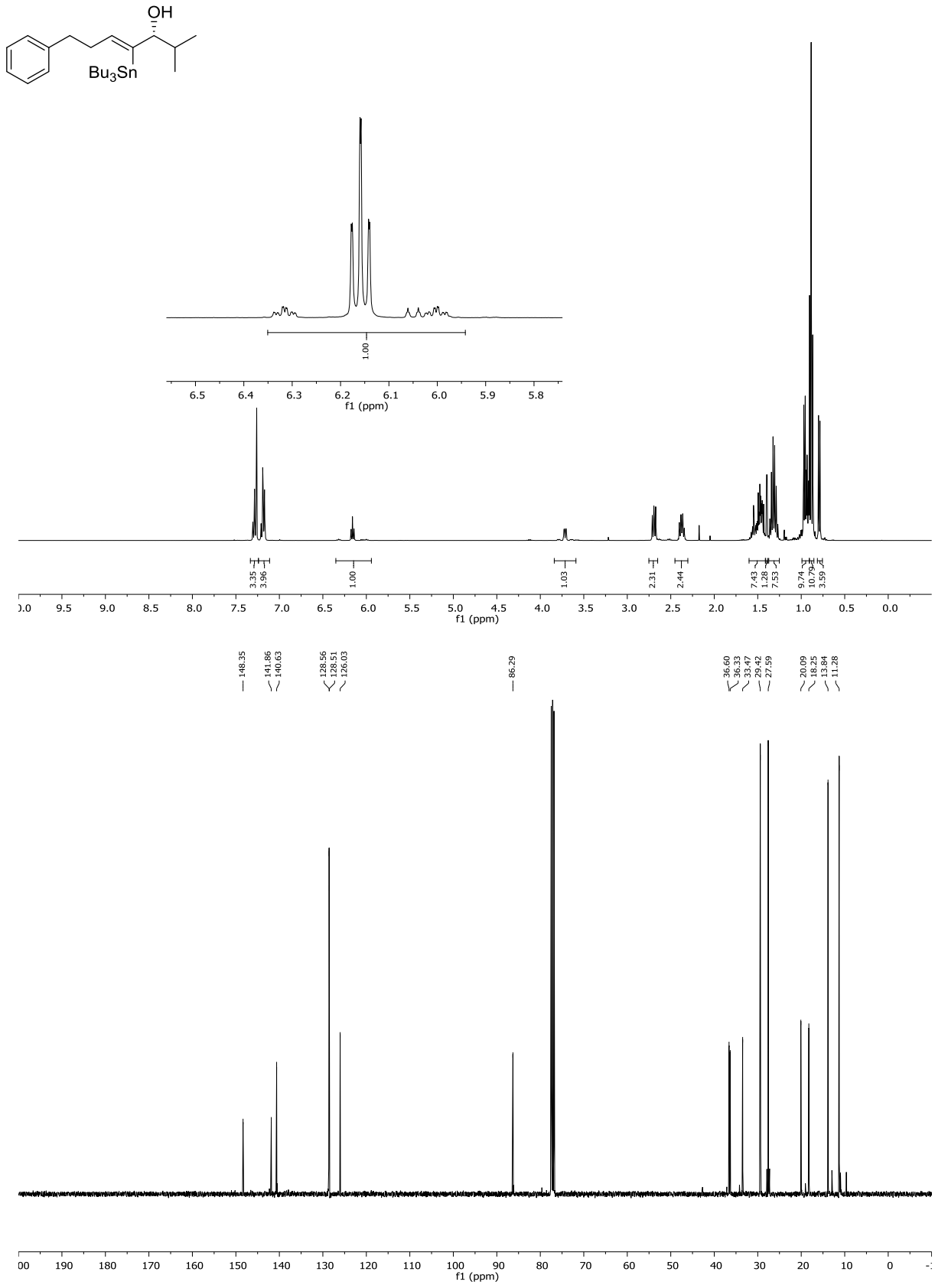




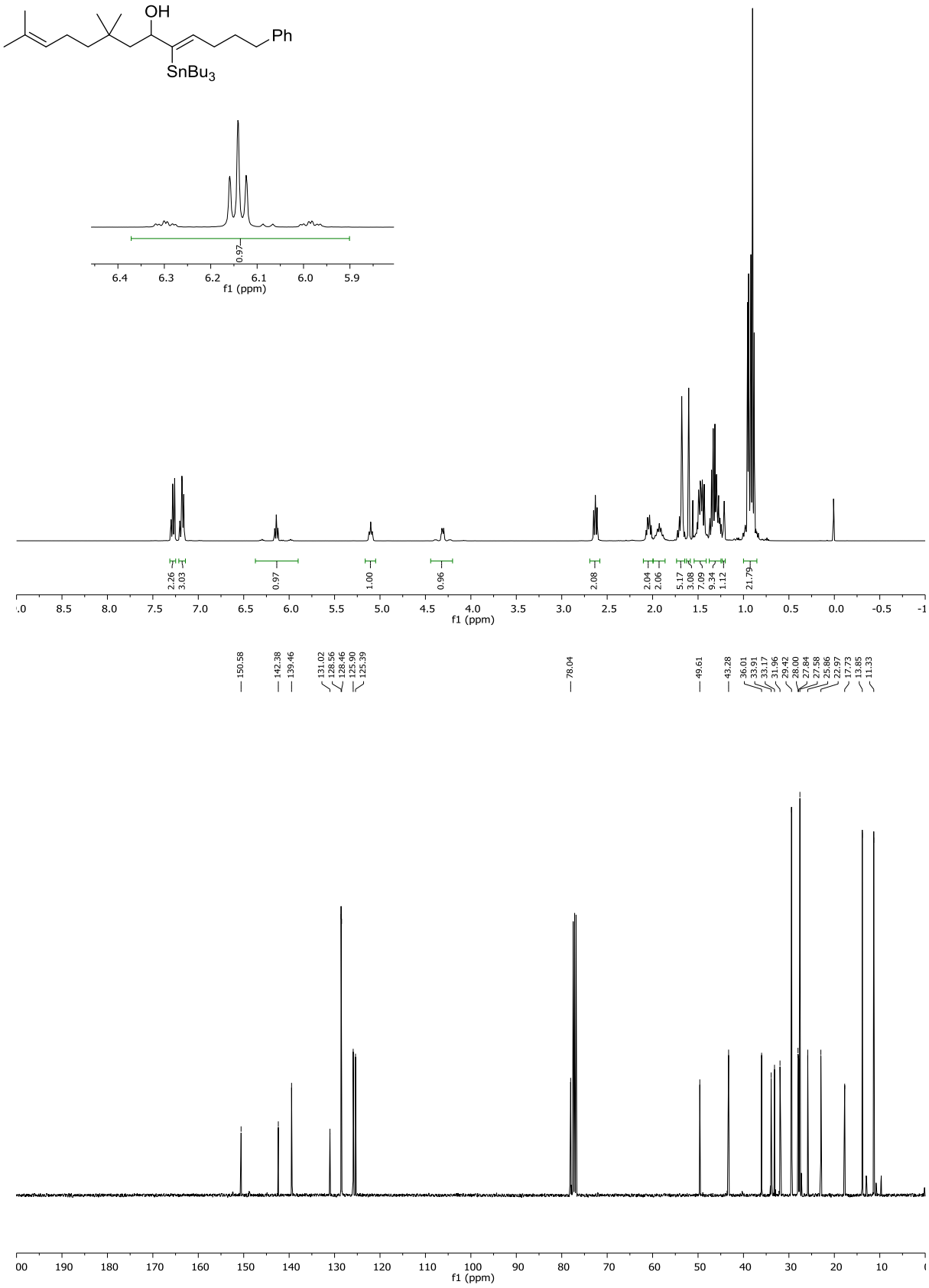
(*Z*)-7-Hydroxy-9-phenyl-6-(tributylstannyl)non-5-enenitrile



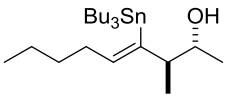
(*R*,*Z*)-2-Methyl-7-phenyl-4-(tributylstannyl)hept-4-en-3-ol

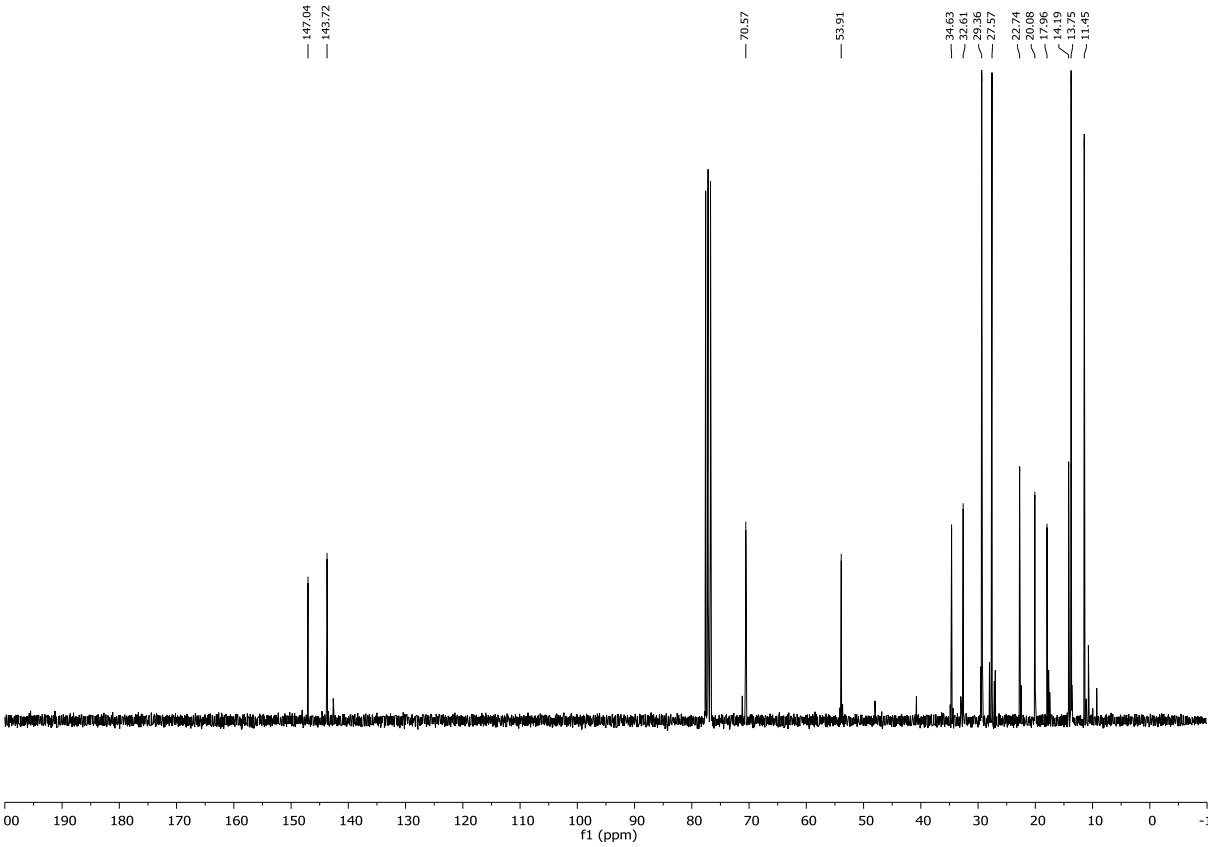


(*Z*)-8,8,12-Trimethyl-1-phenyl-5-(tributylstannyl)trideca-4,11-dien-6-ol

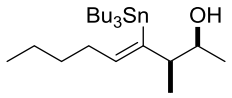


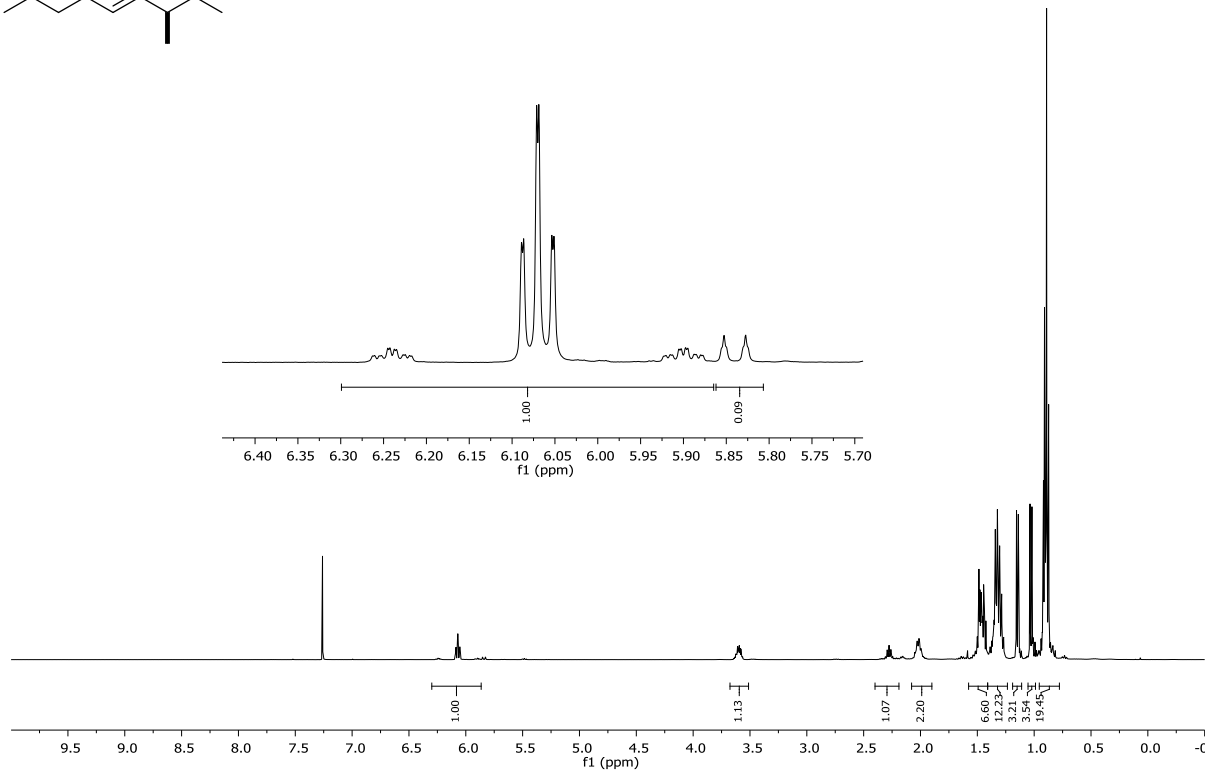
(*anti*,*Z*)-3-Methyl-4-(tributylstannyl)non-4-en-2-ol (20)

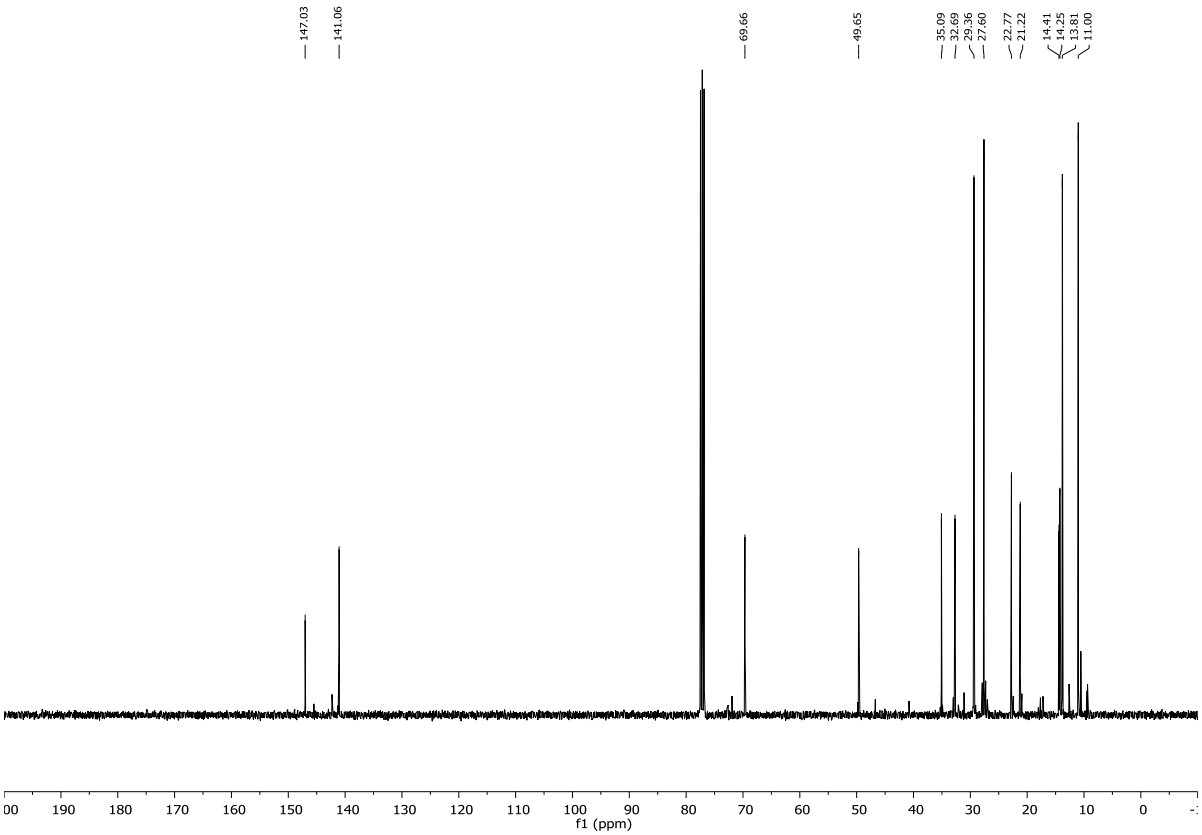




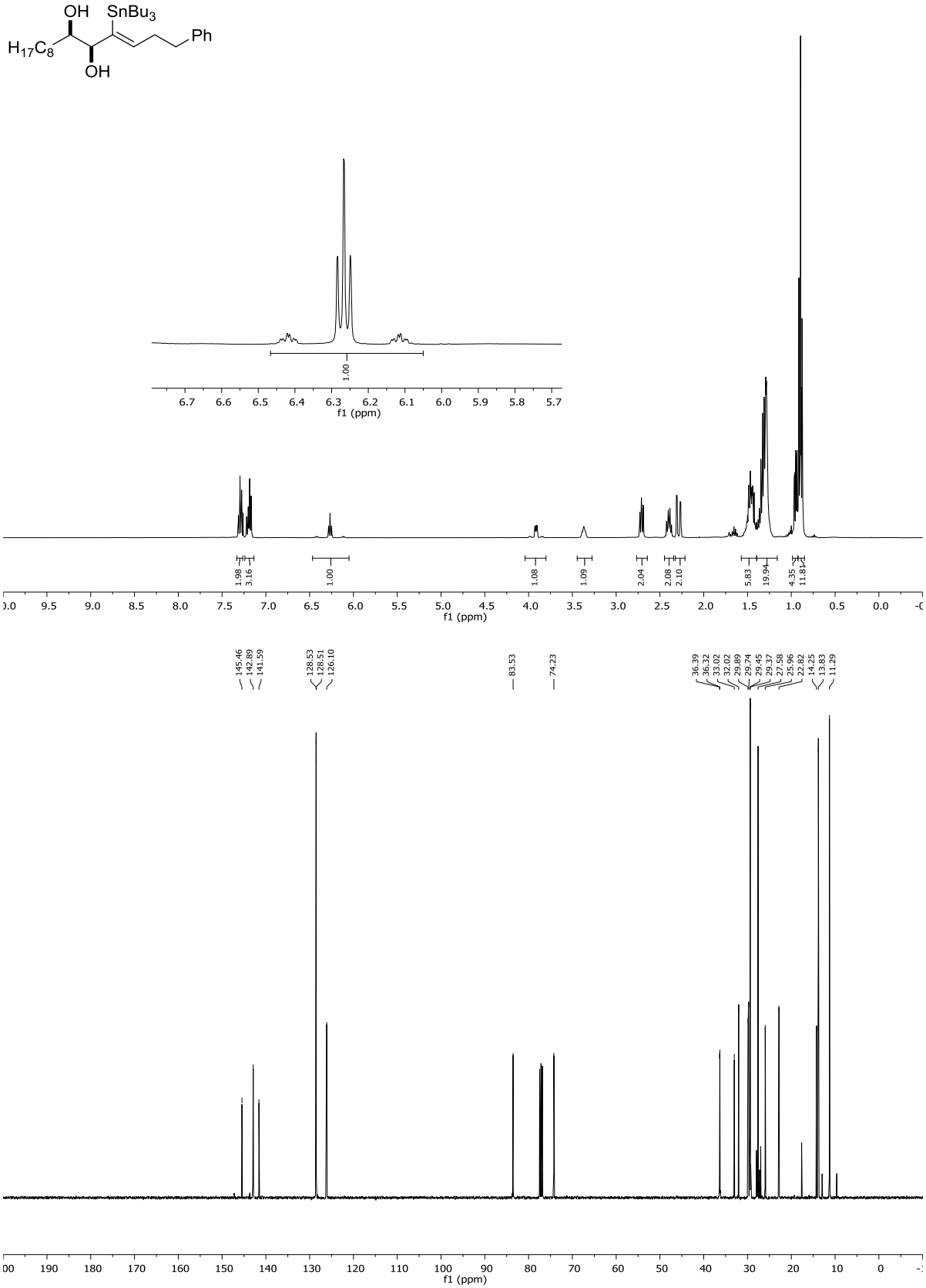
(*syn*,*Z*)-3-Methyl-4-(tributylstannyl)non-4-en-2-ol (22)



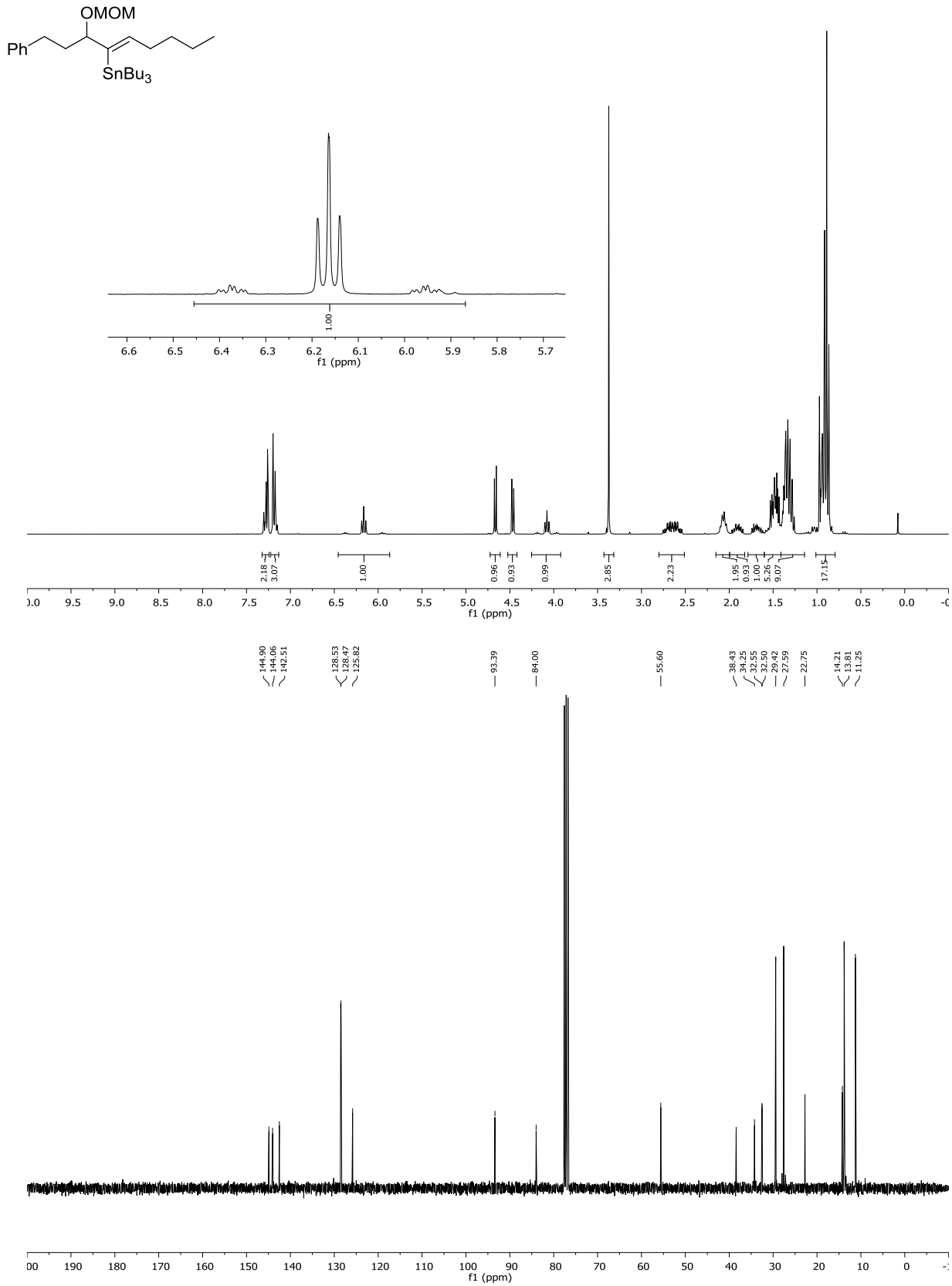




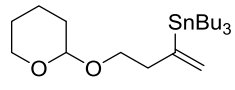
(5*S*,6*R*,*Z*)-1-Phenyl-4-(tributylstannyl)tetradec-3-ene-5,6-diol (25)

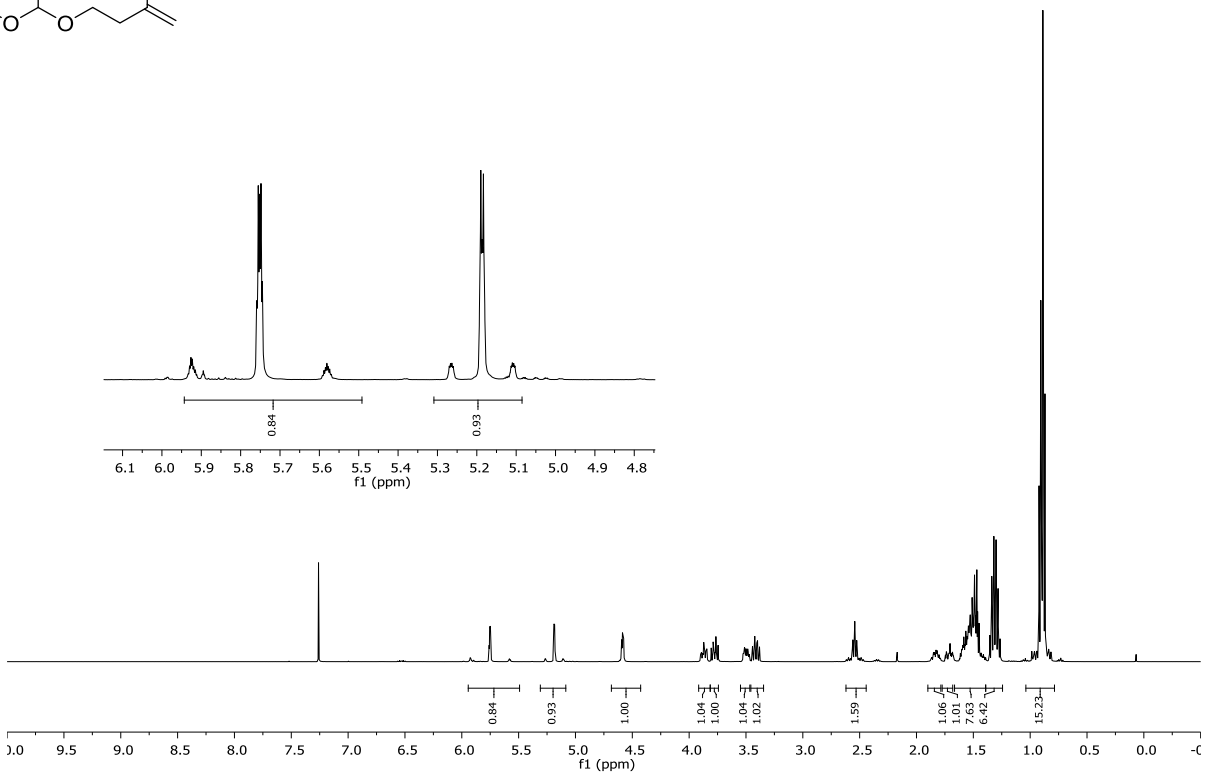


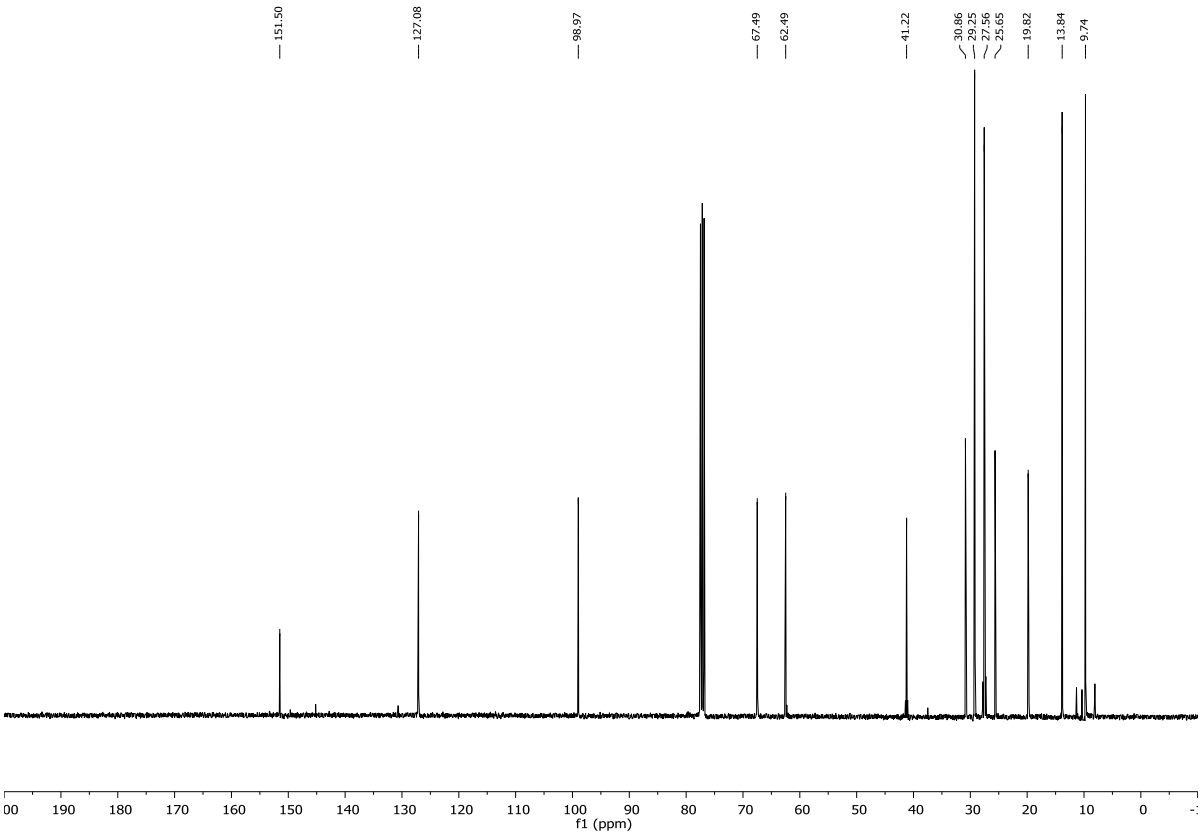
(*Z*)-Tributyl(3-(methoxymethoxy)-1-phenylnon-4-en-4-yl)stannane (16)



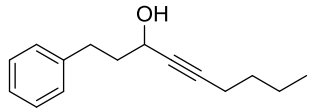
Tributyl(4-((tetrahydro-2H-pyran-2-yl)oxy)but-1-en-2-yl)stannane (18)

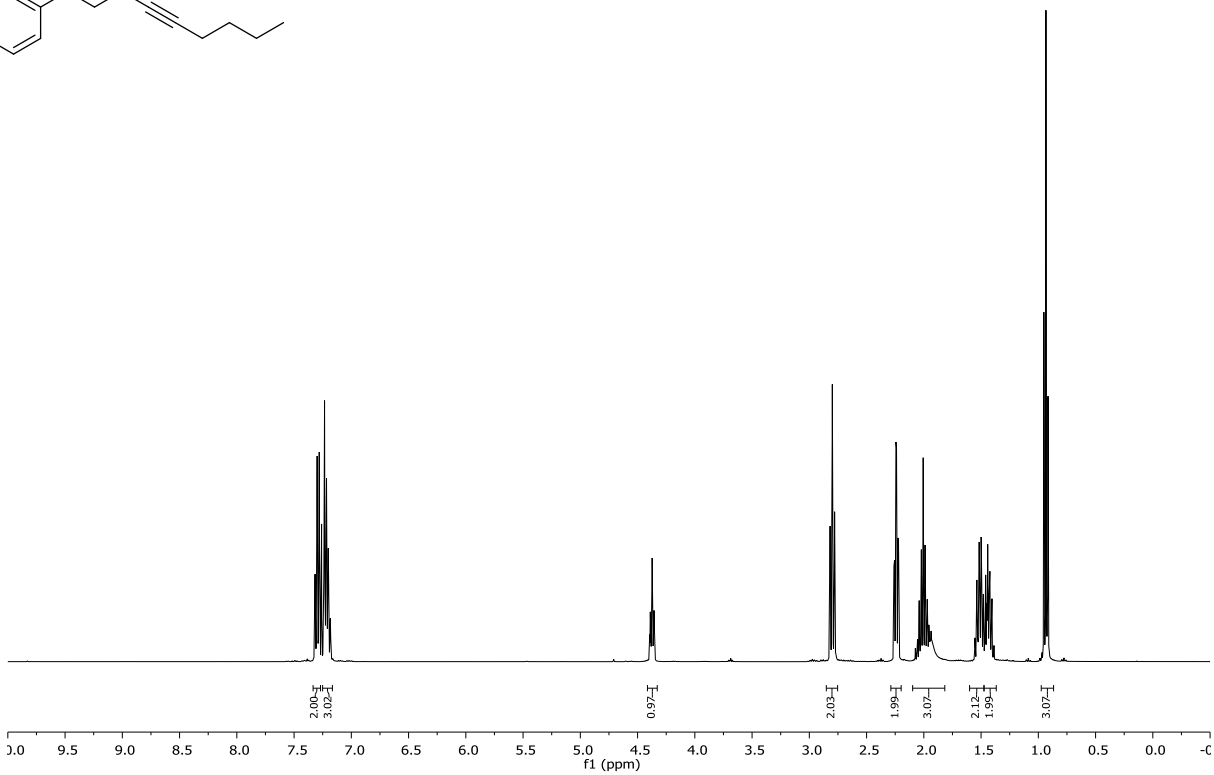


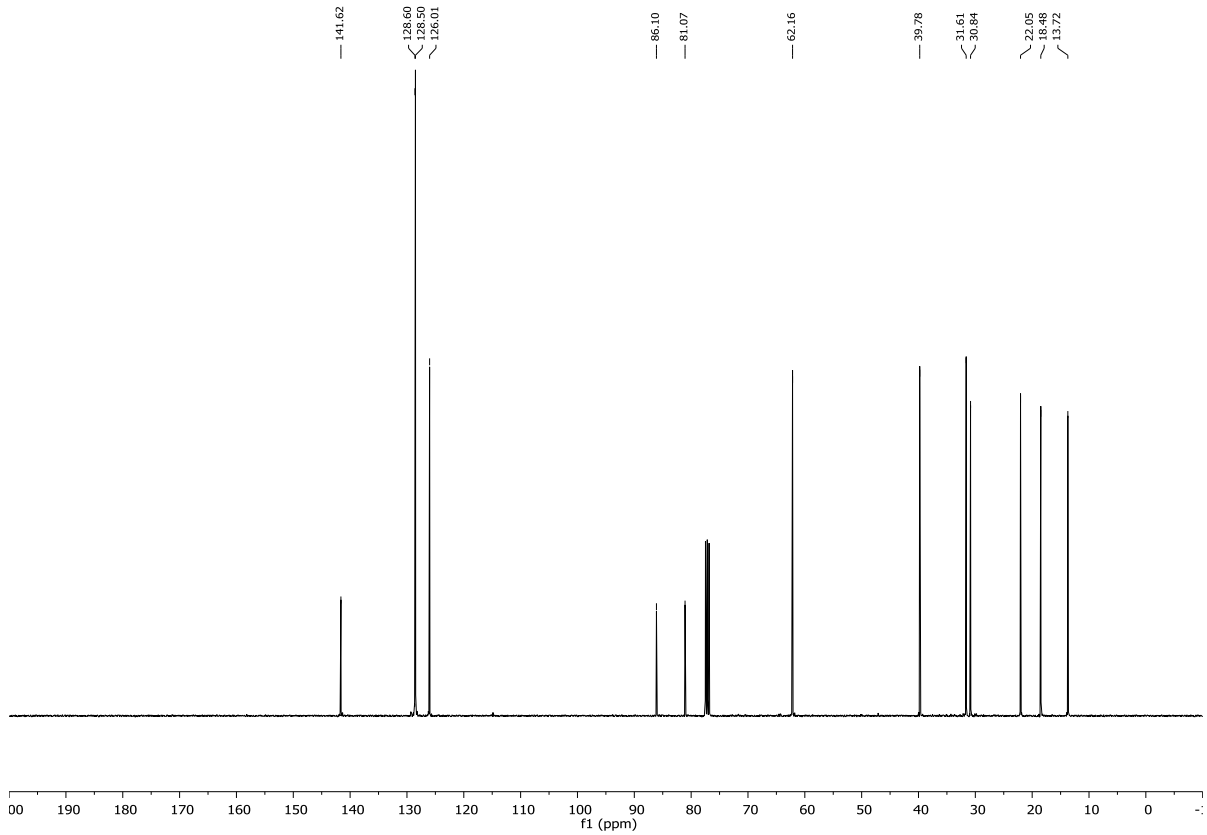




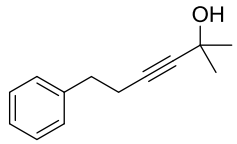
1-Phenylnon-4-yn-3-ol

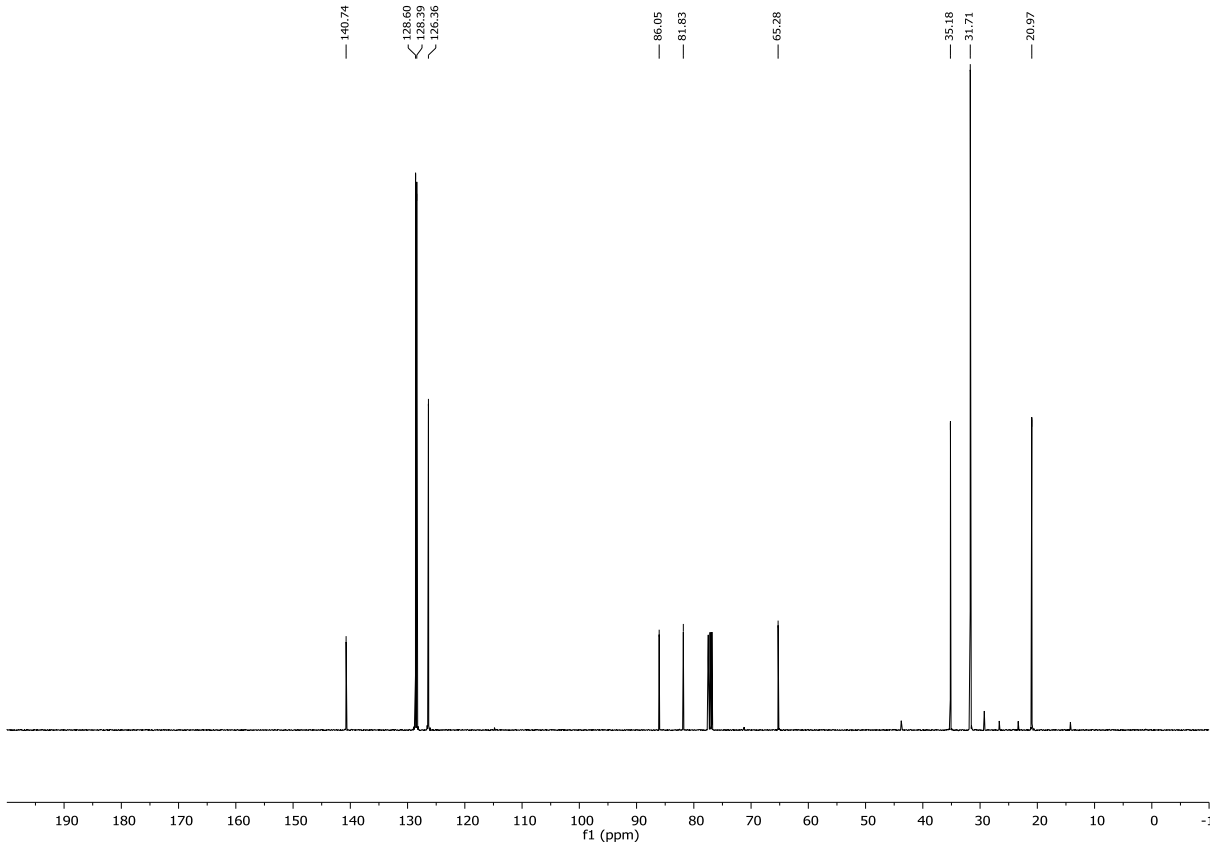




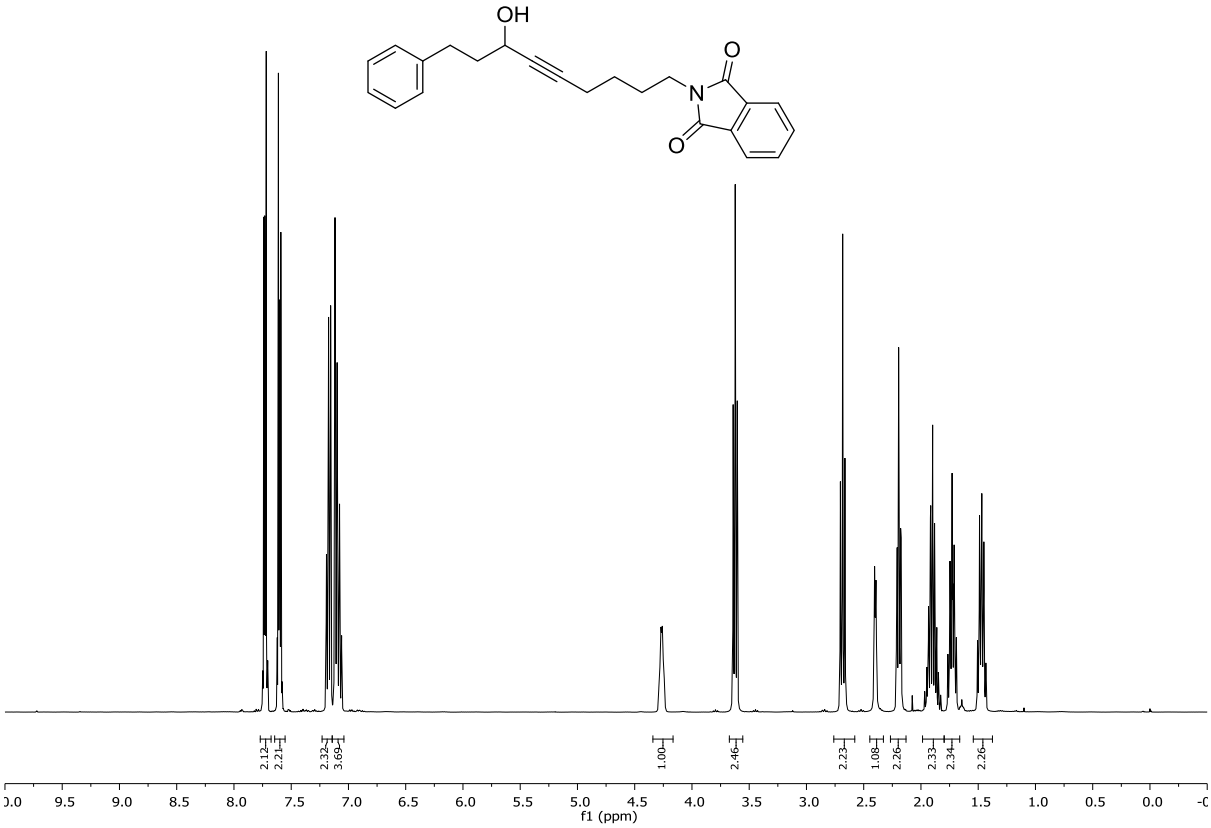


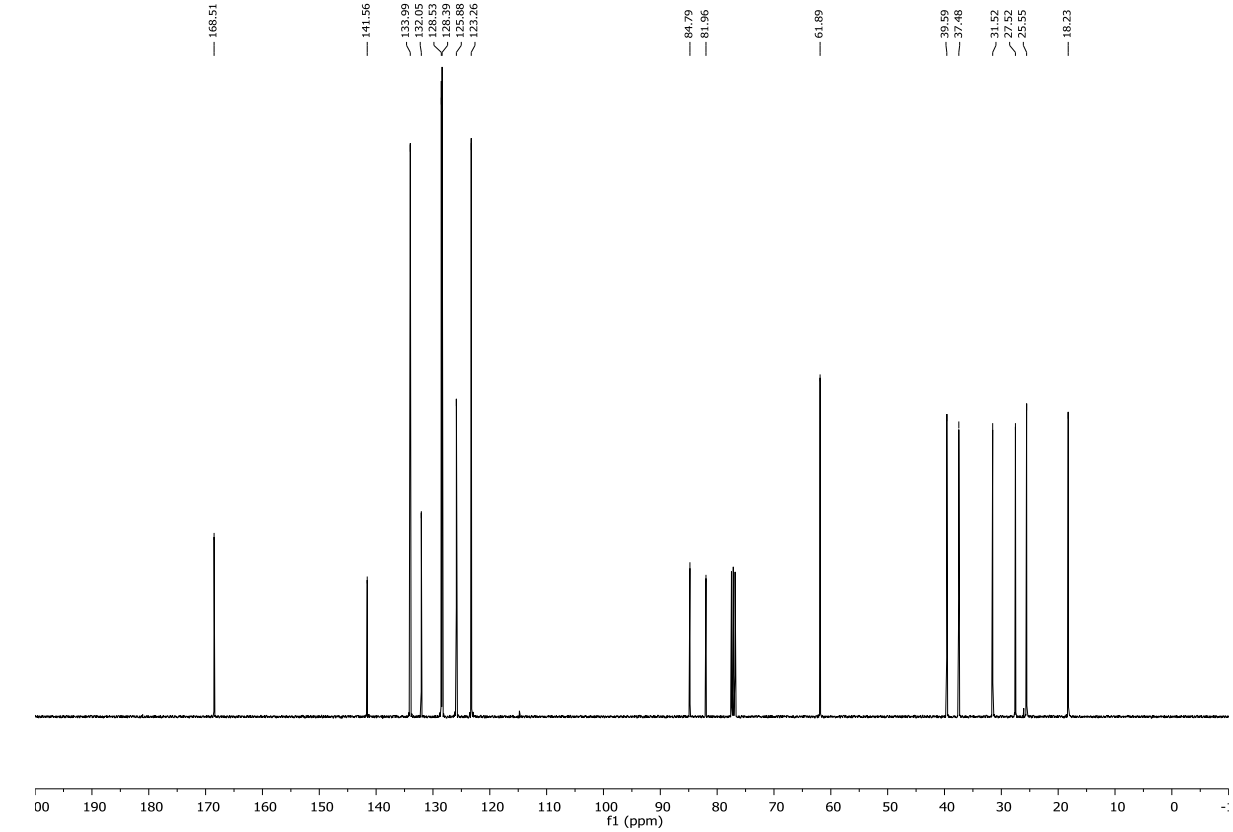
2-Methyl-6-phenylhex-3-yn-2-ol



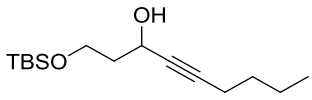


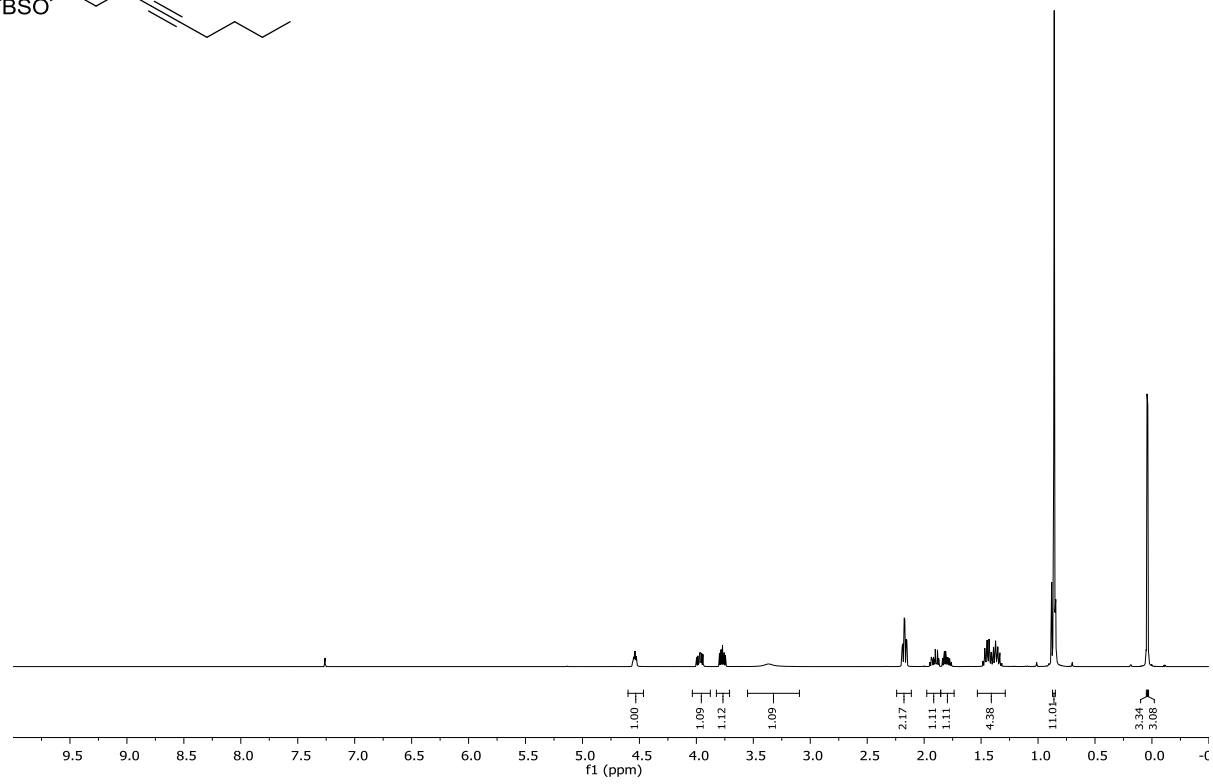
2-(7-Hydroxy-9-phenylnon-5-yn-1-yl)isoindoline-1,3-dione

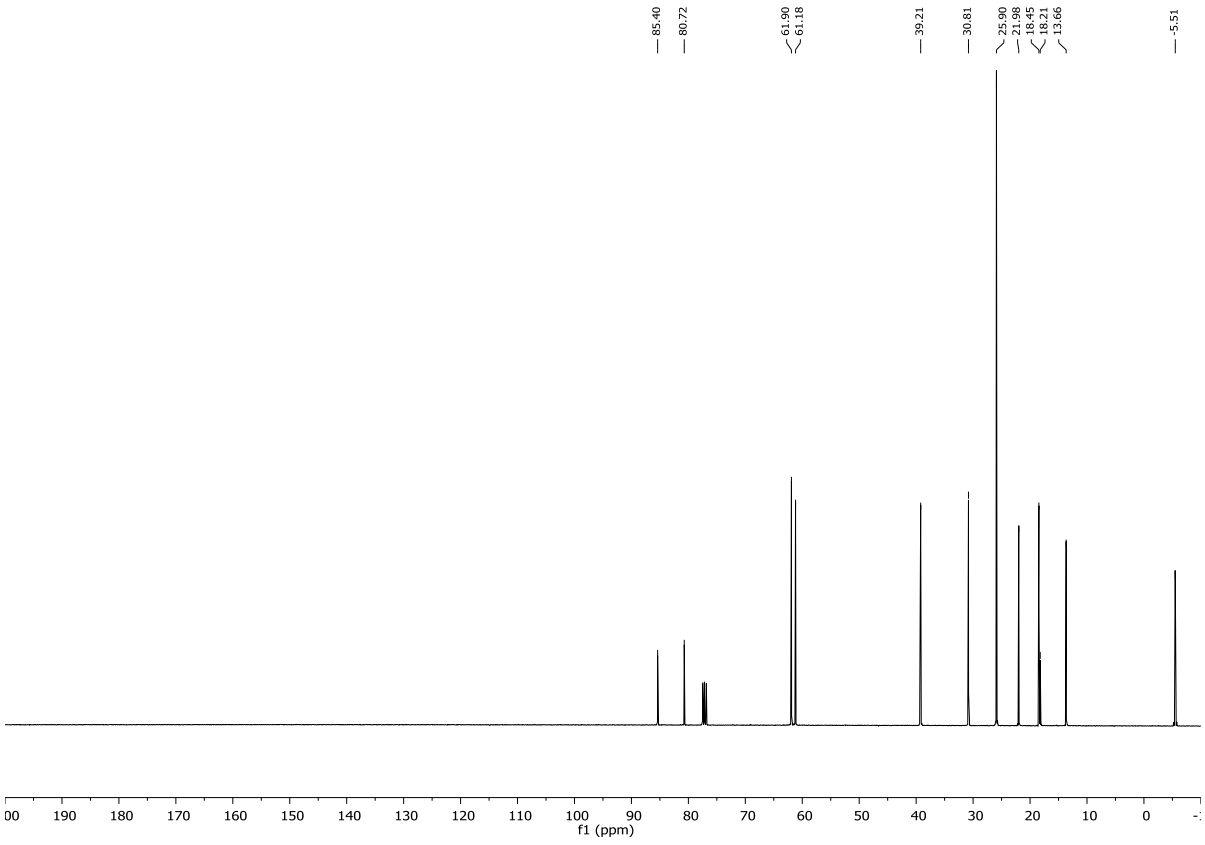




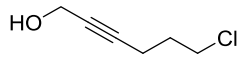
1-((*tert*-Butyldimethylsilyl)oxy)non-4-yn-3-ol

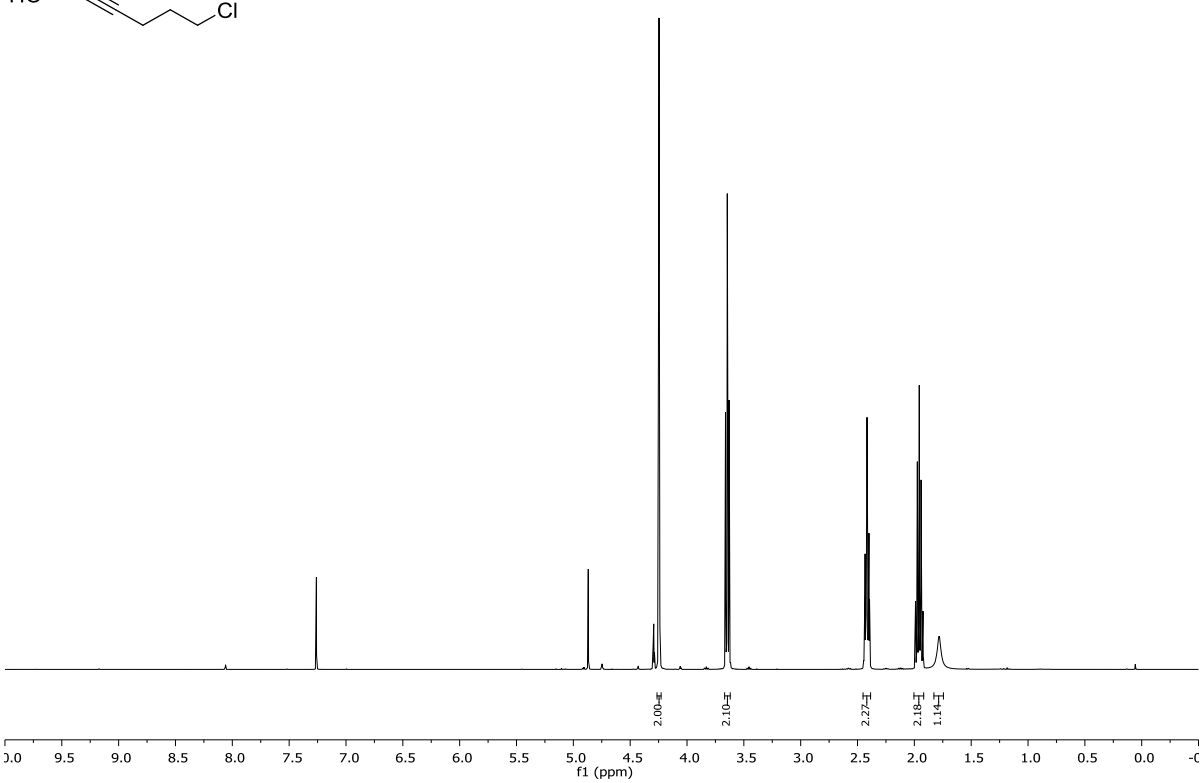


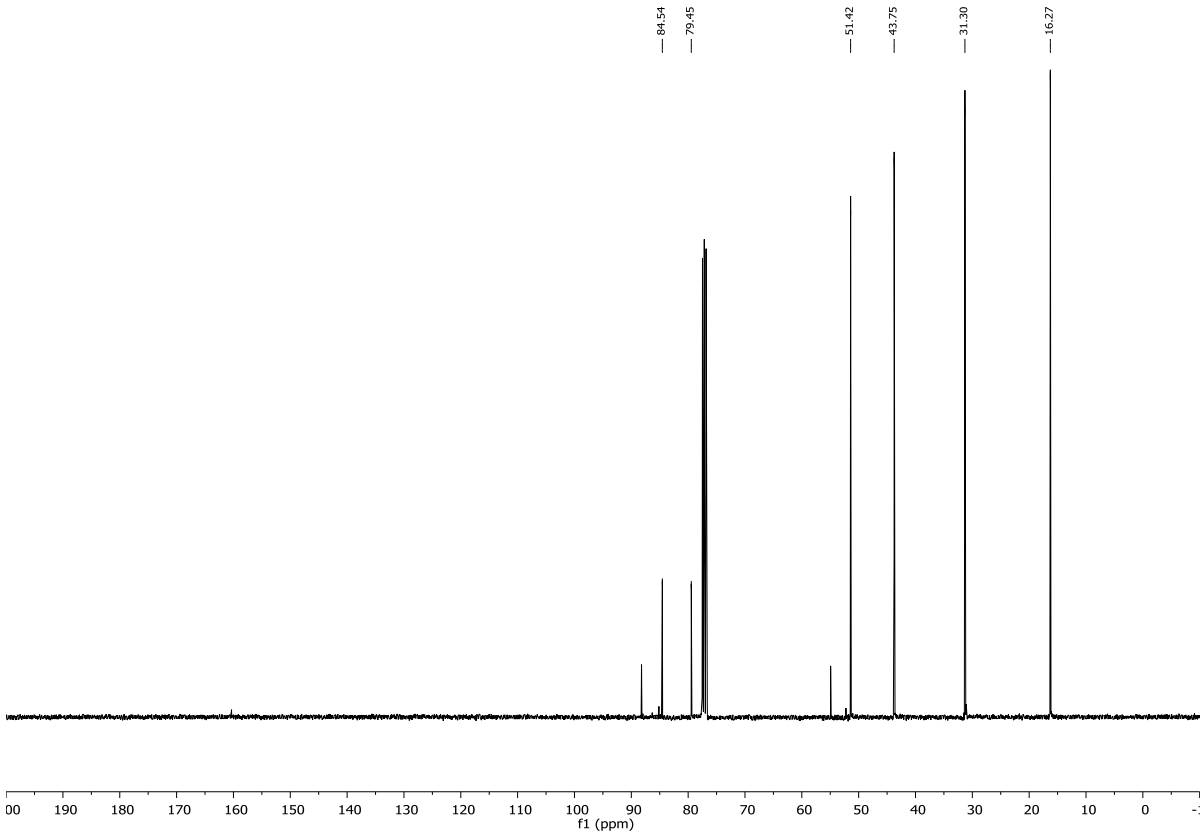




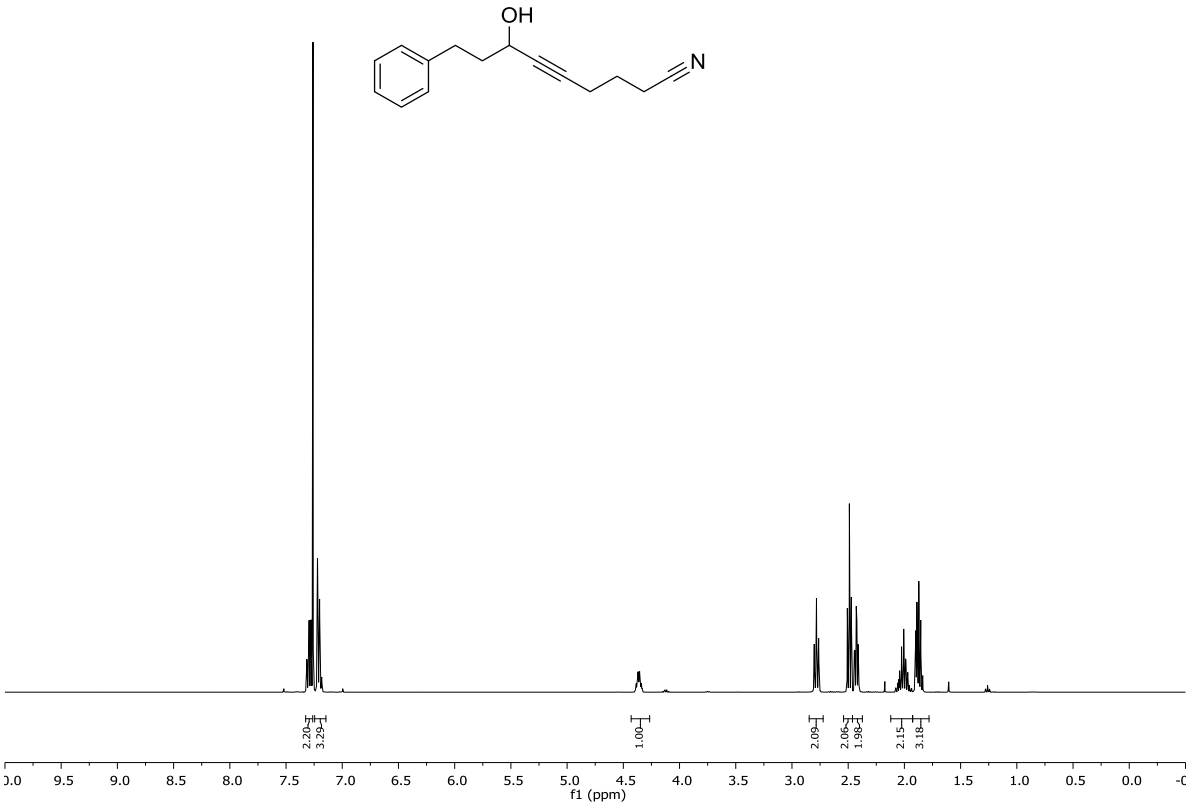
6-Chlorohex-2-yn-1-ol

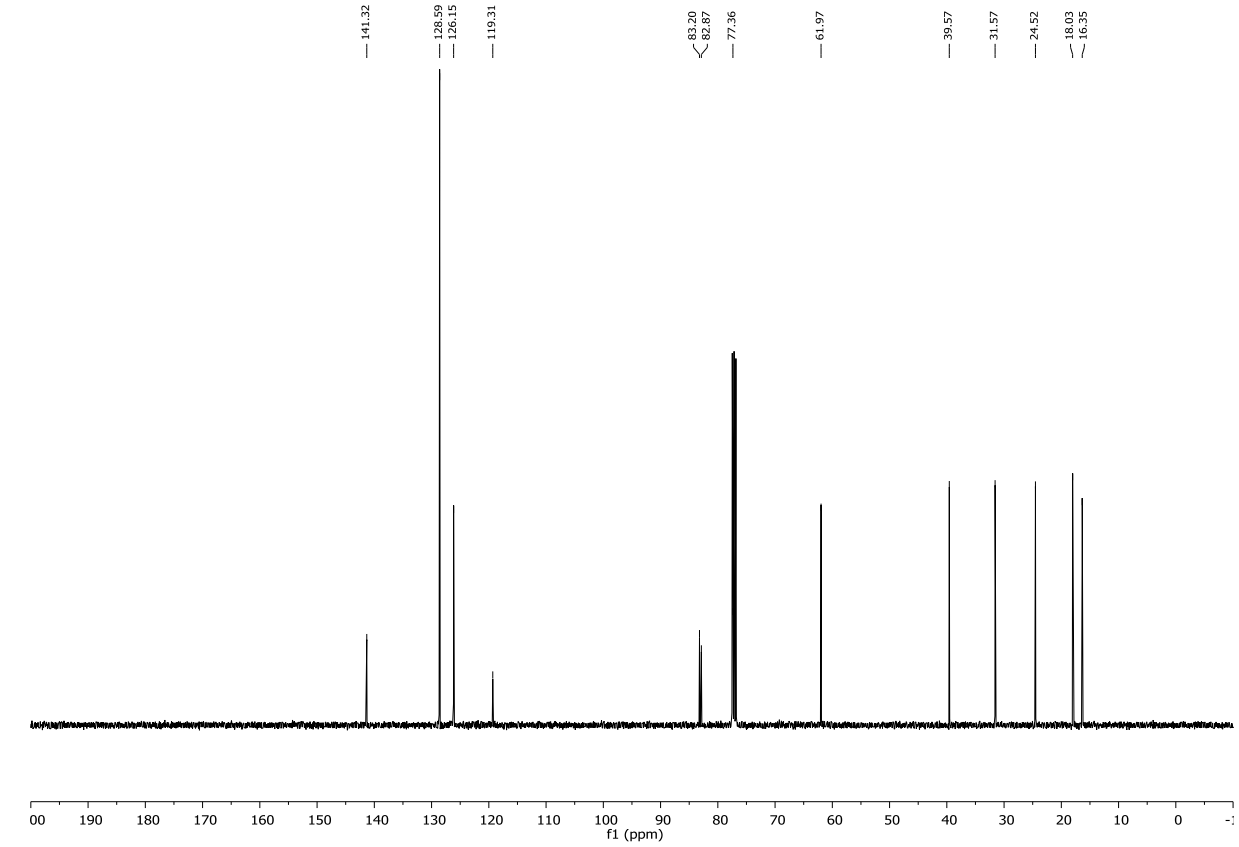




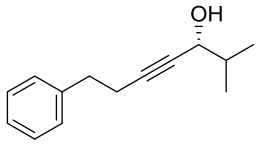


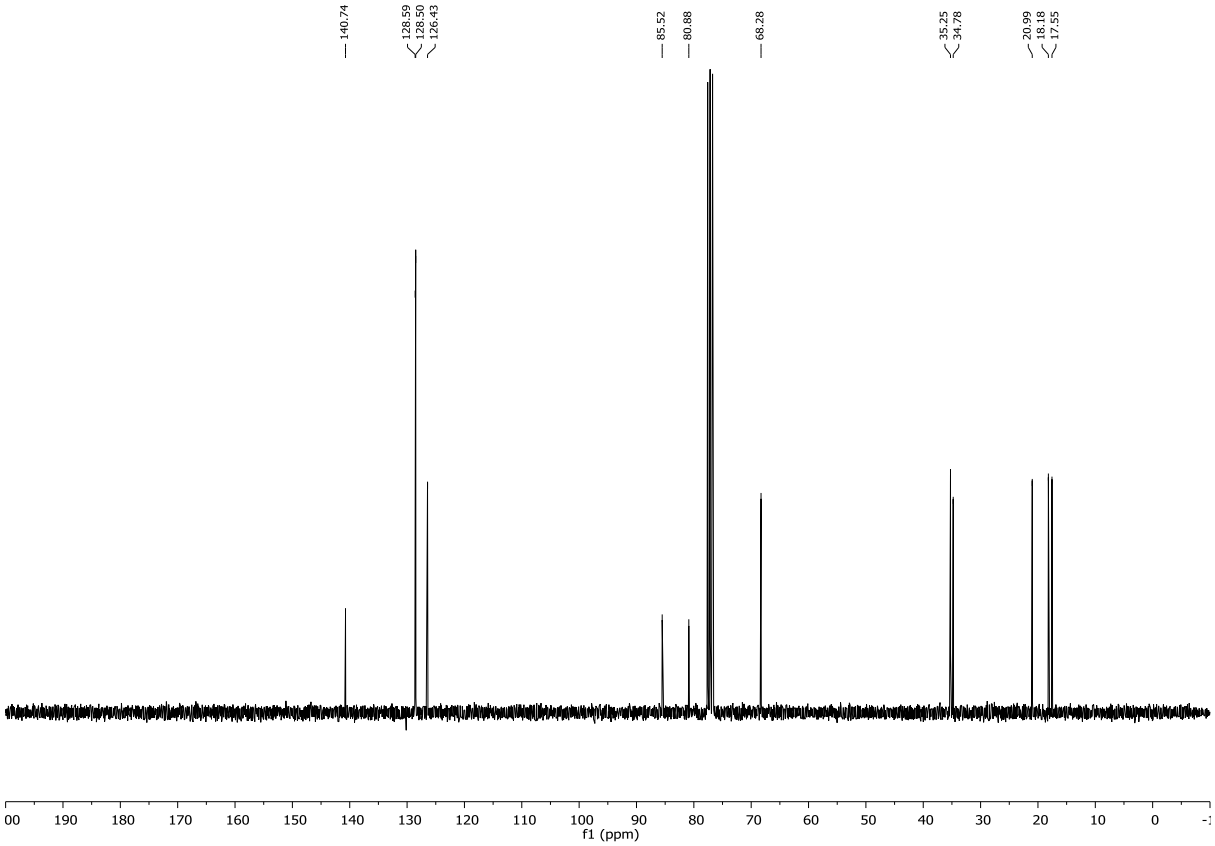
7-Hydroxy-9-phenylnon-5-ynenitrile



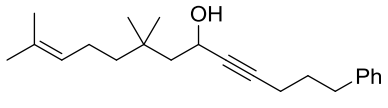


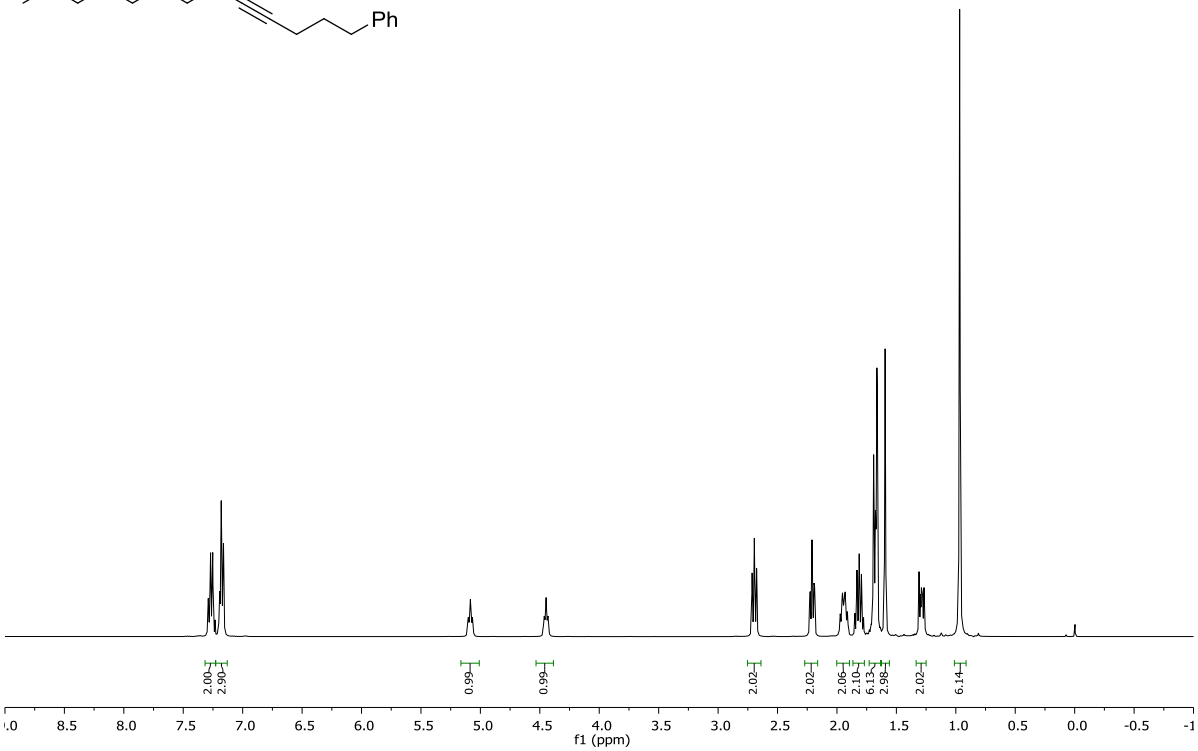
(*R*)-2-Methyl-7-phenylhept-4-yn-3-ol

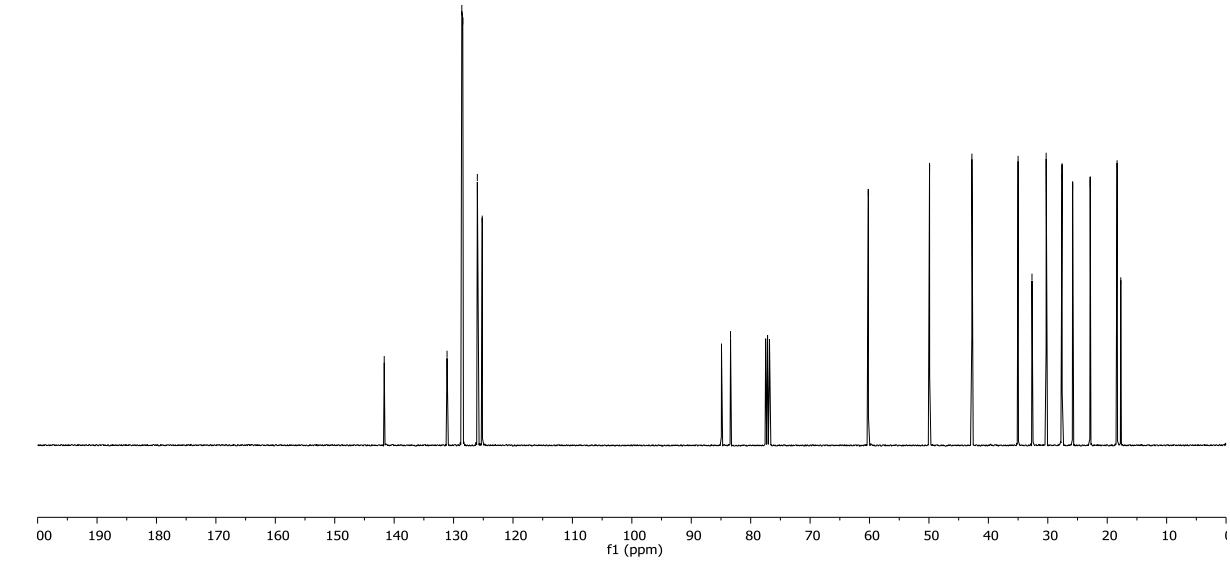




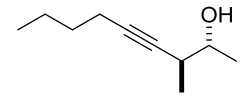
8,8,12-Trimethyl-1-phenyltridec-11-en-4-yn-6-ol

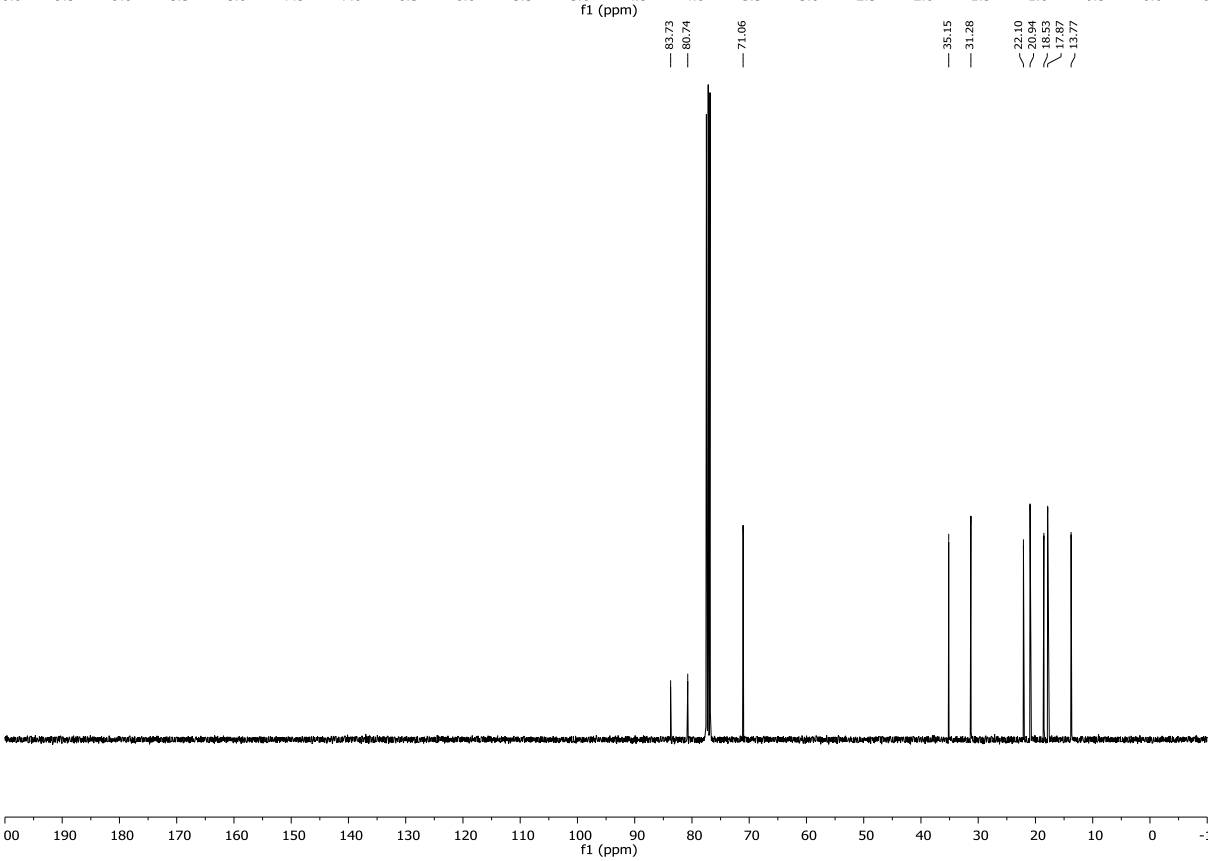




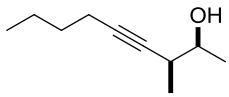


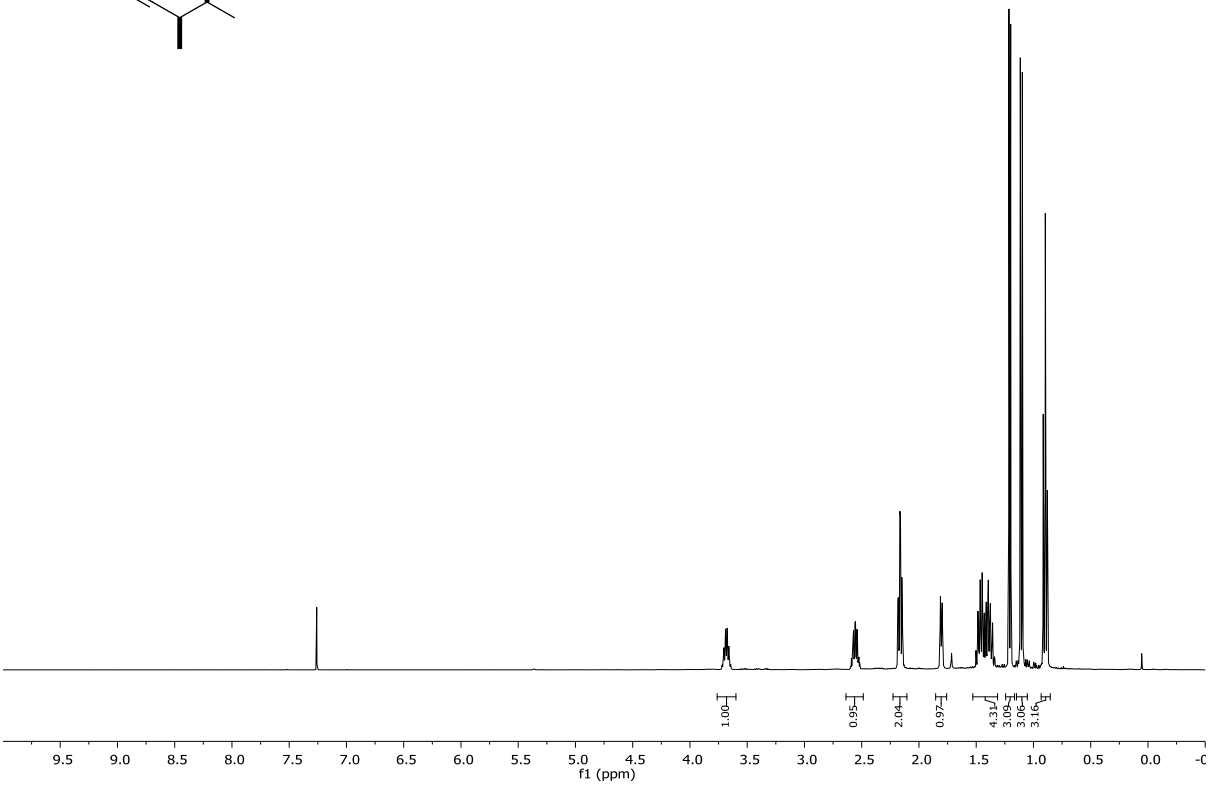
***anti*-3-Methylnon-4-yn-2-ol**

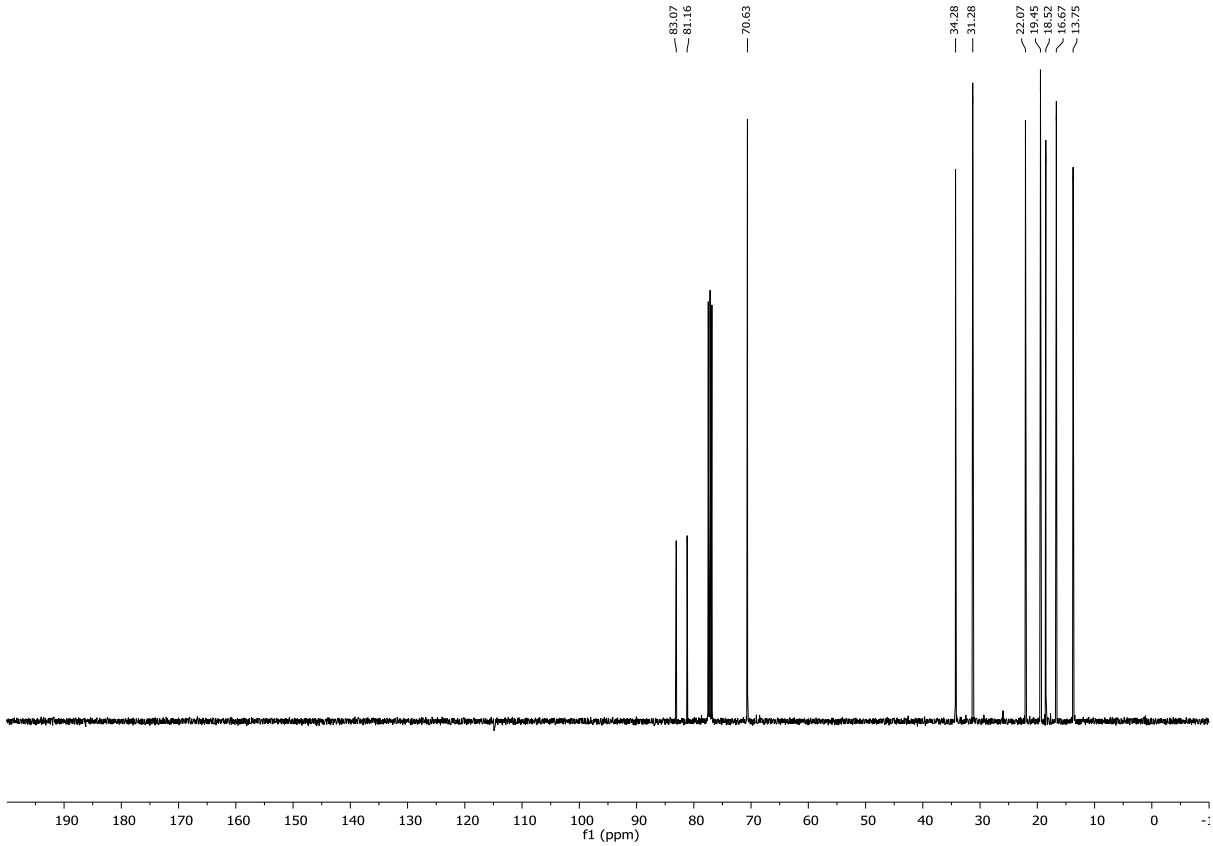




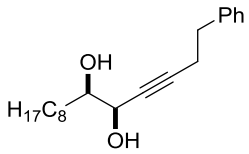
***syn*-3-Methylnon-4-yn-2-ol**

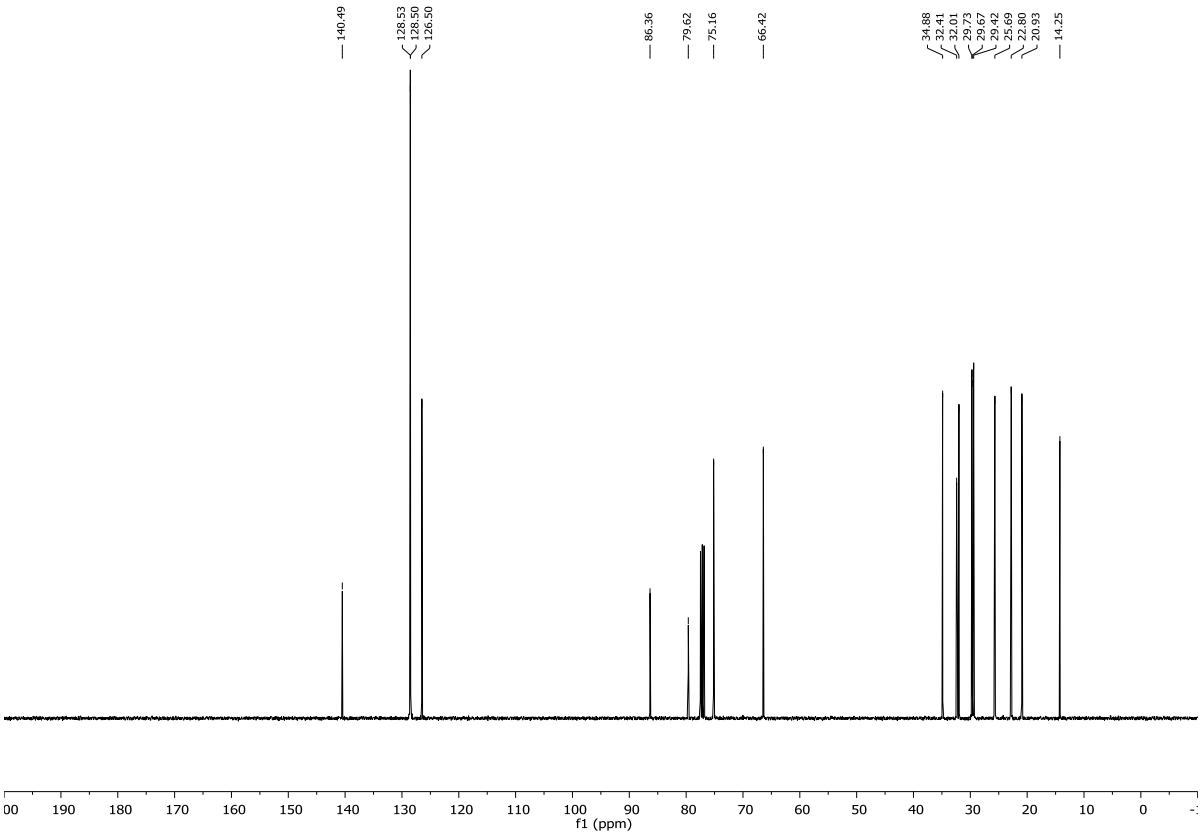




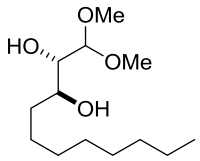


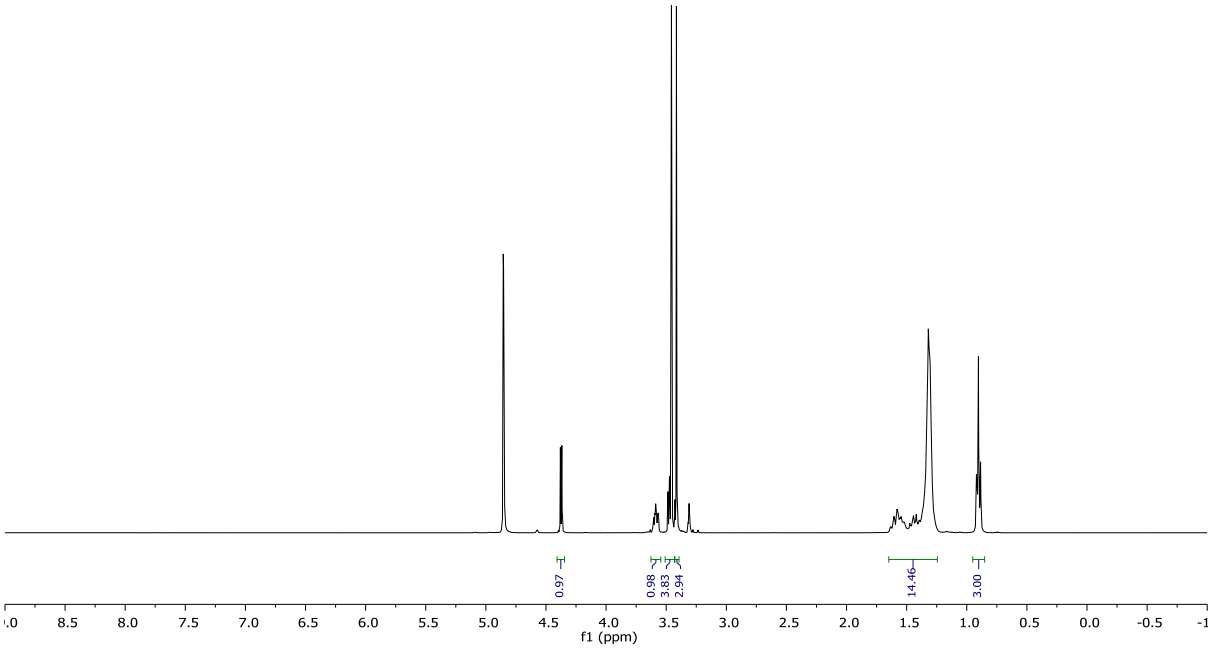
(5*R*,6*R*)-1-Phenyltetradec-3-yne-5,6-diol (24)

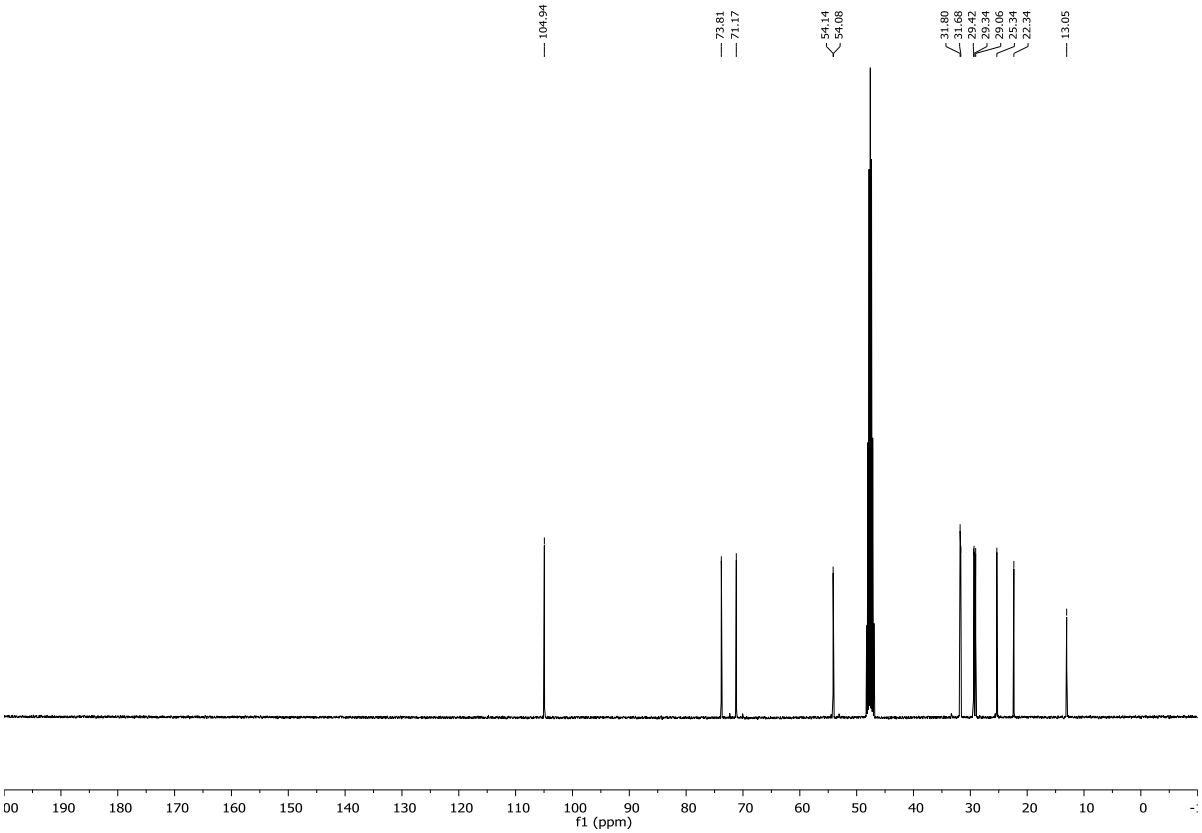




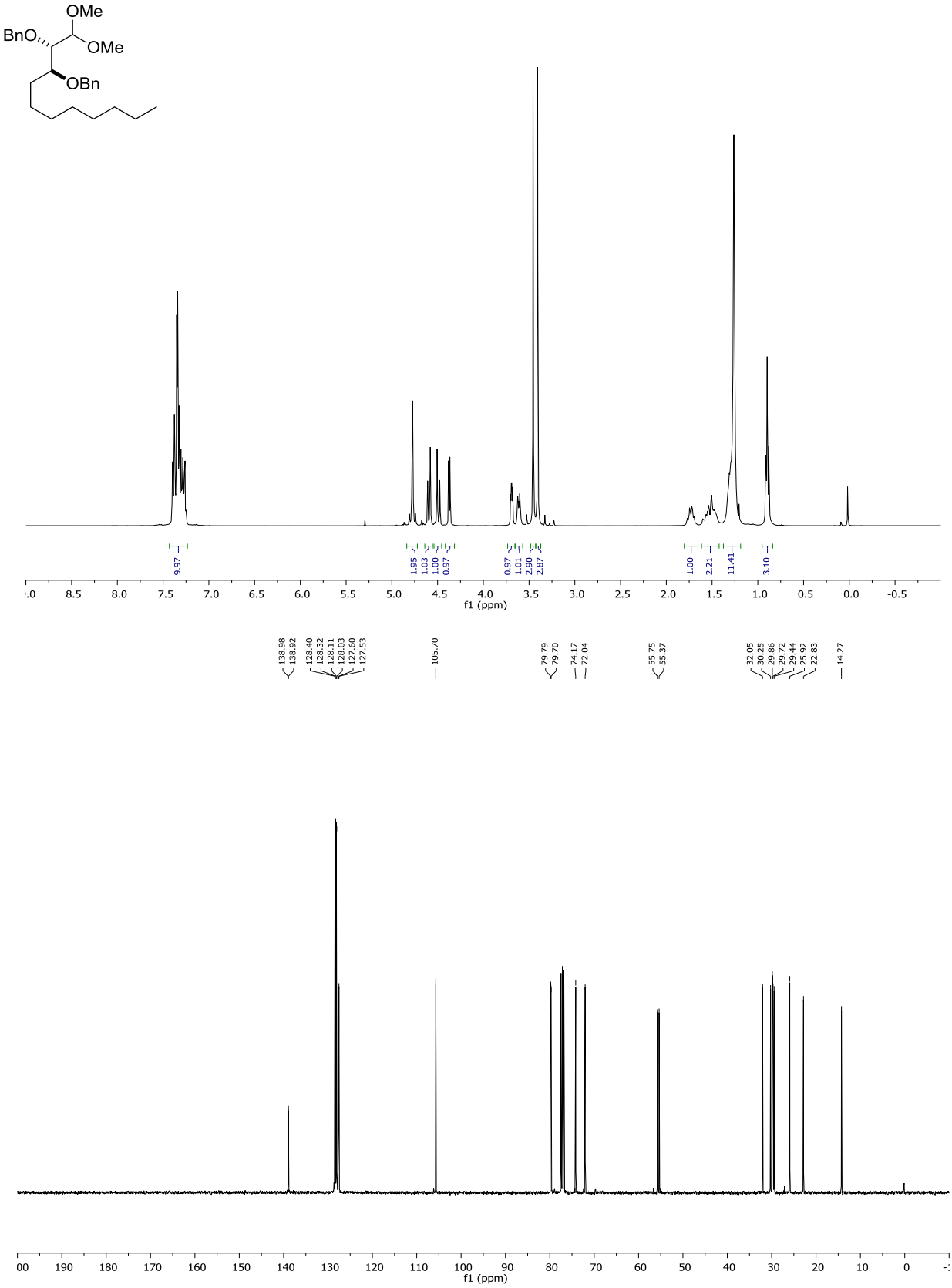
(2*S*,3*S*)-1,1-Dimethoxyundecane-2,3-diol (40)



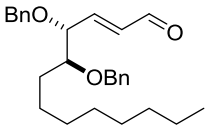


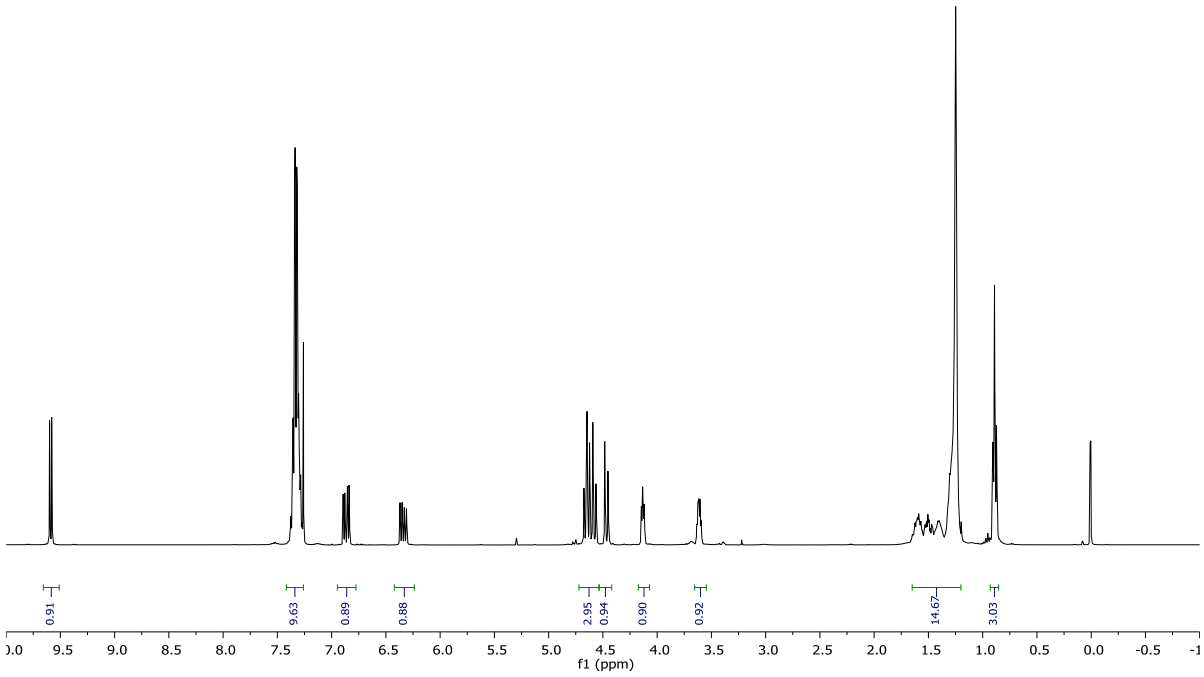


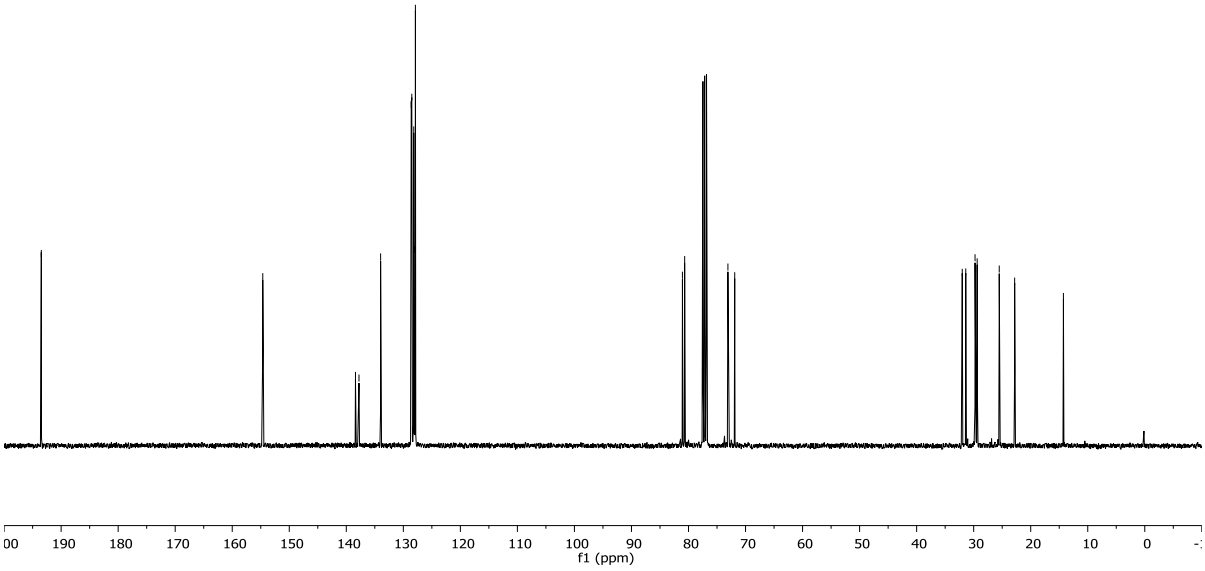
((((2*S*,3*S*)-1,1-Dimethoxyundecane-2,3-diyl)bis(oxy))bis(methylene))dibenzene (S1)



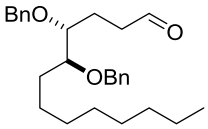
(4*R*,5*S*,*E*)-4,5-Bis(benzyloxy)tridec-2-enal (43)

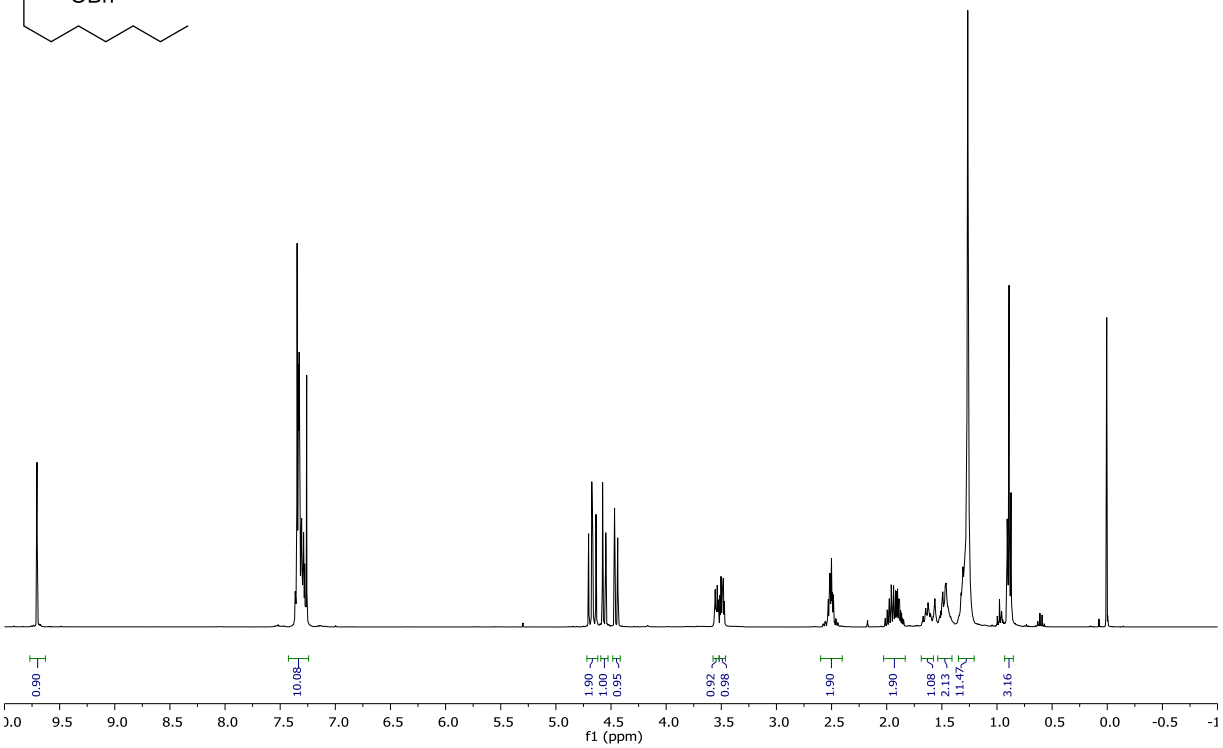


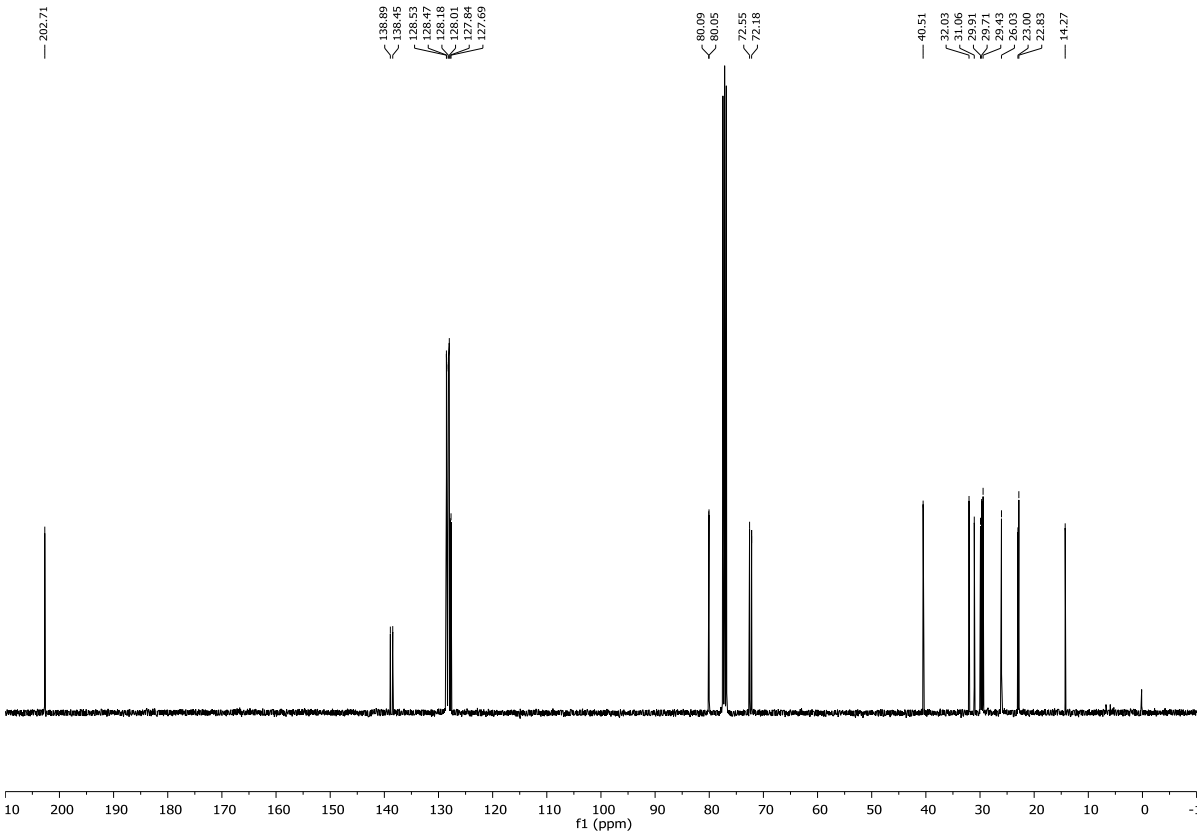




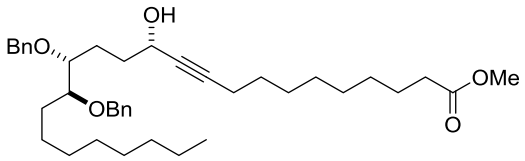
(4*R*,5*S*)-4,5-Bis(benzyloxy)tridecanal (S2)

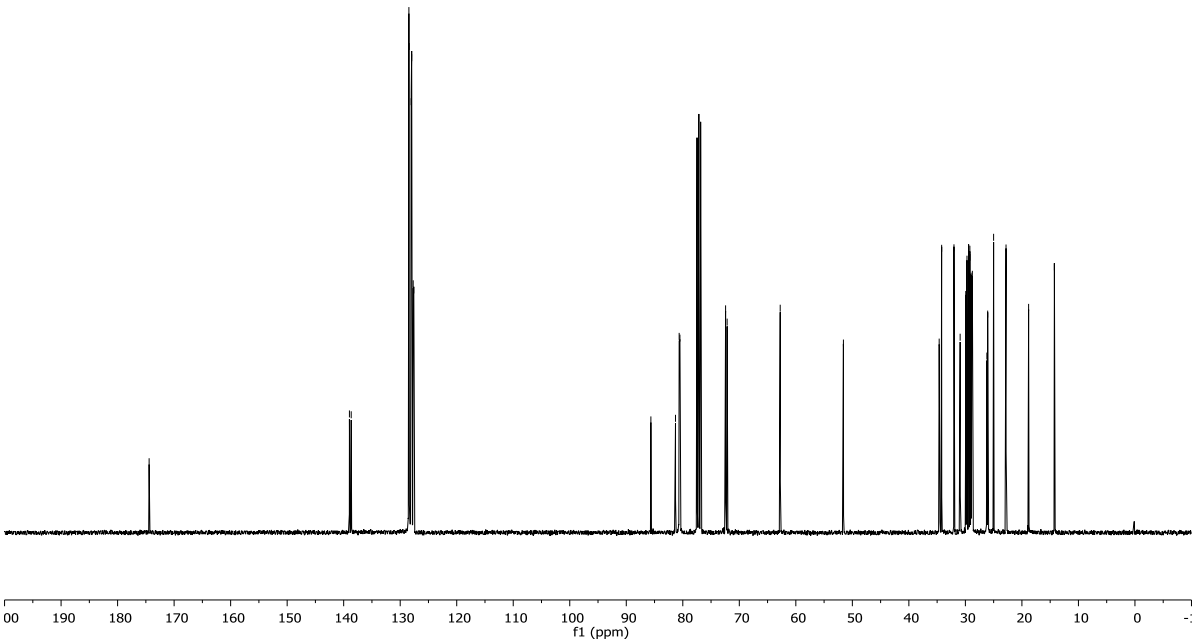




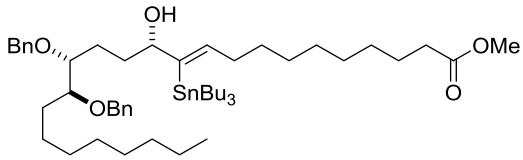


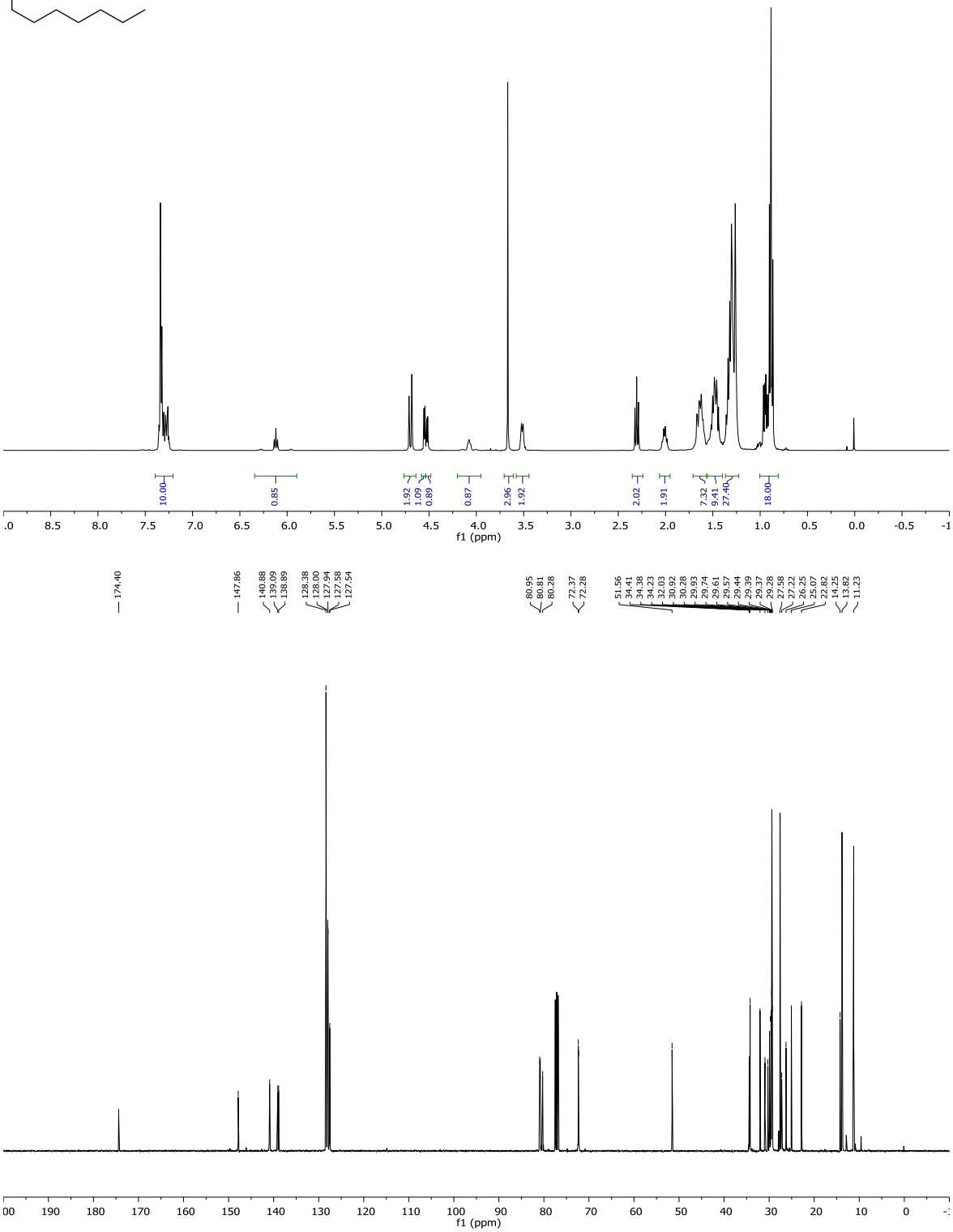
Methyl (12*S*,15*R*,16*S*)-15,16-bis(benzyloxy)-12-hydroxytetracos-10-ynoate (35)



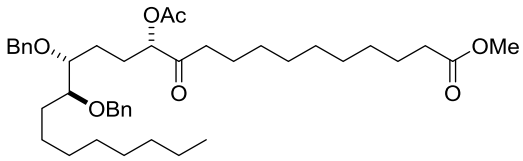


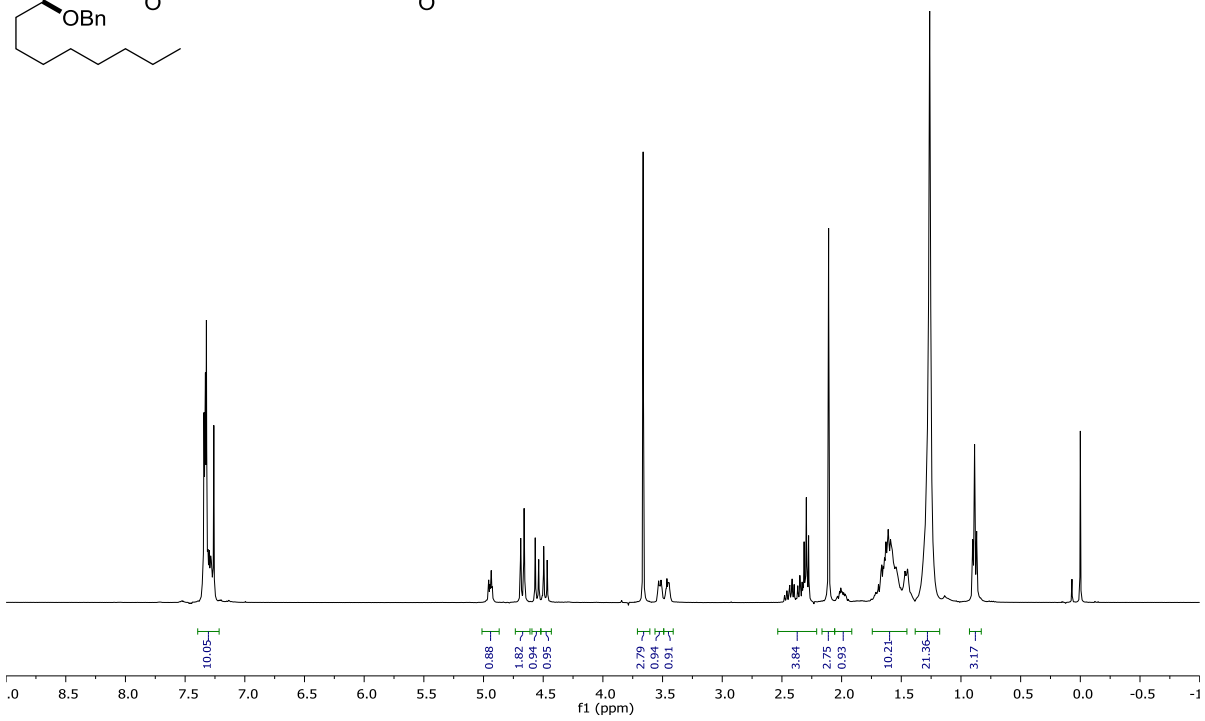
Methyl (12*S*,15*R*,16*S*,*Z*)-15,16-bis(benzyloxy)-12-hydroxy-11-(tributylstannyl)tetracos-10-enoate (44)

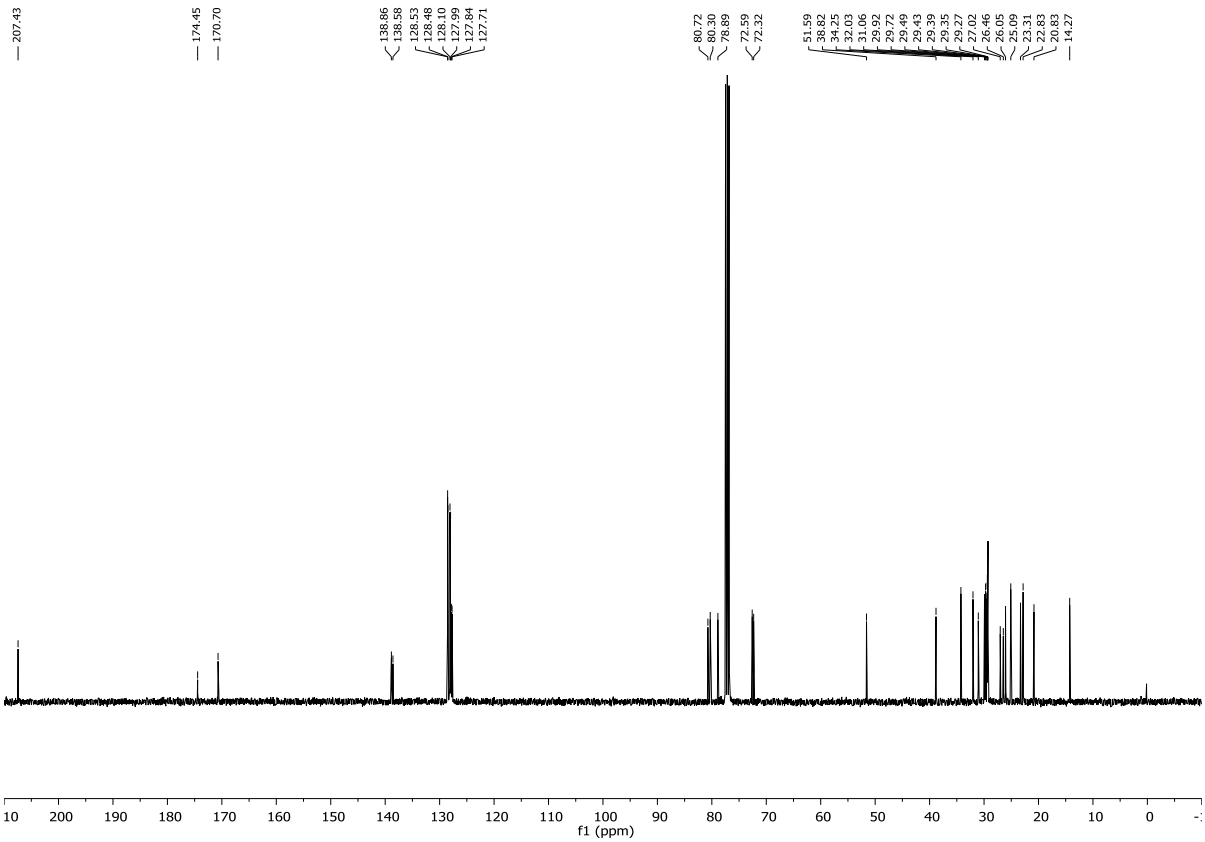




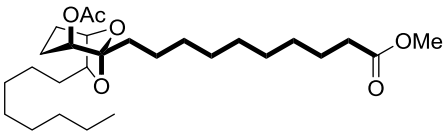
Methyl (12*S*,15*R*,16*S*)-12-acetoxy-15,16-bis(benzyloxy)-11-oxotetracosanoate (45)

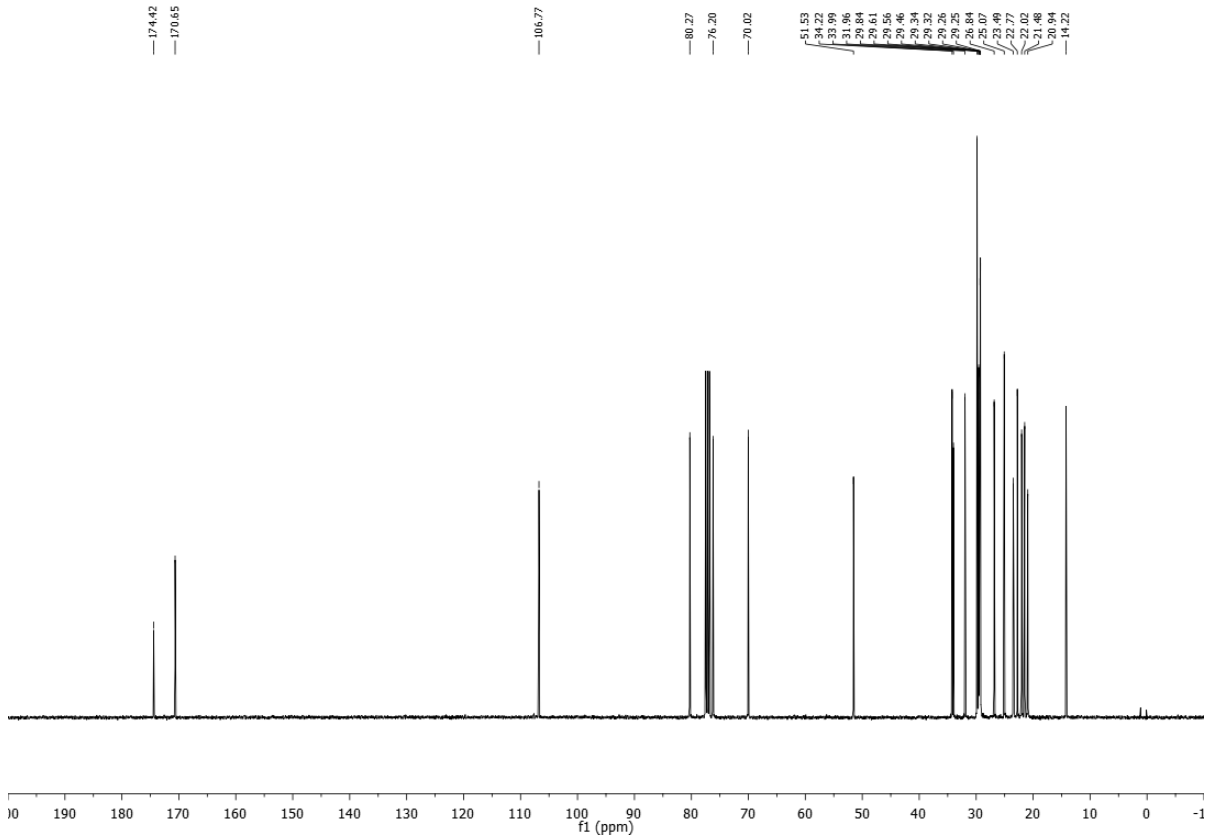




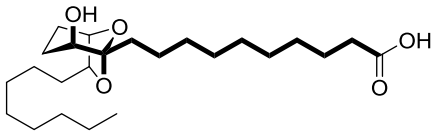


Methyl 10-((1*R*,4*S*,5*S*,7*S*)-4-acetoxy-7-octyl-6,8-dioxabicyclo[3.2.1]octan-5-yl)decanoate (46)



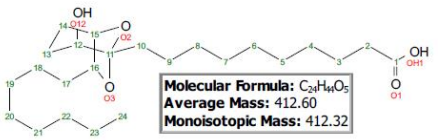


Paecilonic acid A (34)



HAP-HB-205-01 17 mg d_4-MeOD 298 K

see notes on next page



Molecular Formula: $C_{24}H_{44}O_5$
Average Mass: 412.60
Monoisotopic Mass: 412.32

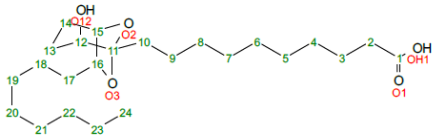
P-ID:	CW00289	
Measured on:	10.11.2016	
CHIFFRE:	HAP-HB-205-01	
Client:	James Hamilton	
Group:	Fürstner	
Analyst:	Wirtz	
Assignment Date:	21.11.2016	
Amount:	17 mg	
Solvent:	MeOD	
Reference:	solvent	
Temperature:	298K	
Spectrometer:	AV-600I	
Experiments:	1H, 13C{1H}, Dept135, COSY, HSQC	
	HMBC, 1D-NOESY, 1D-COSY, HSQC-TOCSY	

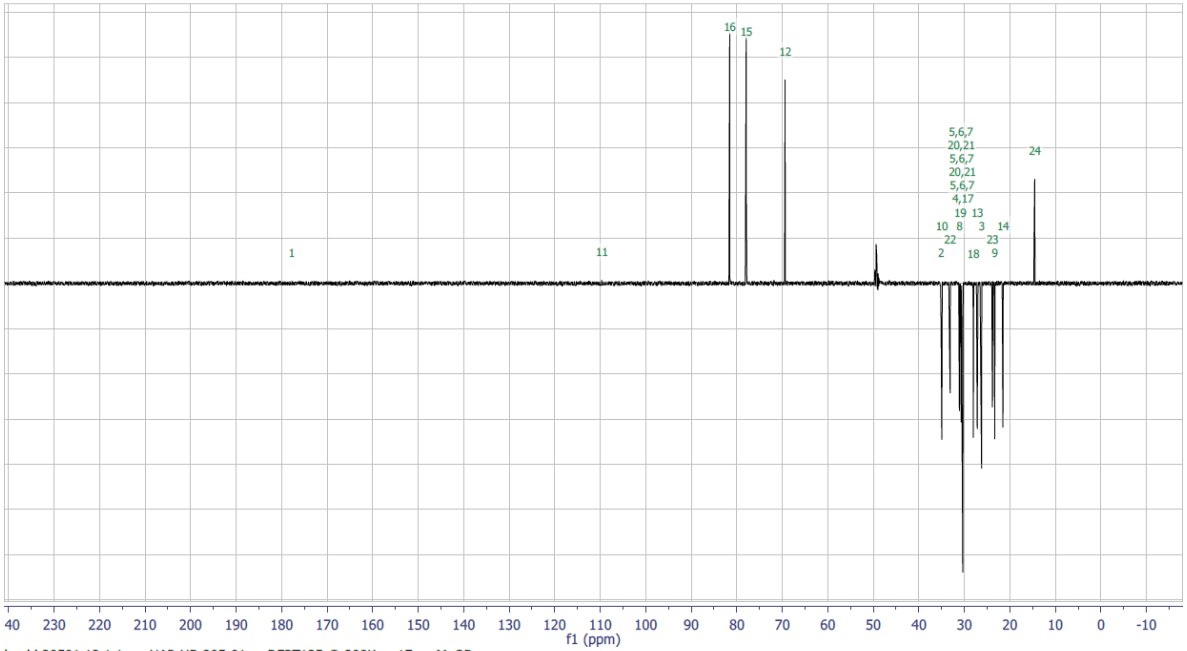
^{1}H NMR (600 MHz, Methanol-d_4) δ 4.19 (t, J = 4.0 Hz, 1H), 3.93 (dddd, J = 7.5, 6.3, 4.1, 1.0 Hz, 1H), 3.42 (dt, J = 4.6, 1.1 Hz, 1H), 2.27 (t, J = 7.5 Hz, 2H), 2.13 (tdd, J = 13.9, 6.7, 4.6 Hz, 1H), 2.03 (tddd, J = 13.9, 6.1, 3.8, 0.8 Hz, 1H), 1.79 (dt, J = 14.3, 8.0 Hz, 1H), 1.72 (dtd, J = 12.5, 9.1, 7.8, 4.9 Hz, 1H), 1.66 – 1.45 (m, 2H), 1.45 – 1.37 (m, 1H), 1.31 (q, J = 6.4 Hz, 21H), 0.90 (t, J = 7.1 Hz, 2H).

^{13}C NMR (151 MHz, MeOD) δ 177.81 (1), 109.65 (11), 81.56 (16), 77.94 (15), 69.39 (12), 35.11 (2), 34.96 (10), 33.13 (22), 31.09 (8), 30.90 (19), 30.77 (5, 6 or 7), 30.72 (20 or 21), 30.63 (5, 6 or 7), 30.51 (5, 6 or 7), 30.48 (20 or 21), 30.35 (4, 17), 28.04 (18), 27.17 (13), 26.22 (3), 23.83 (23), 23.31 (9), 21.53 (14), 14.55 (24).

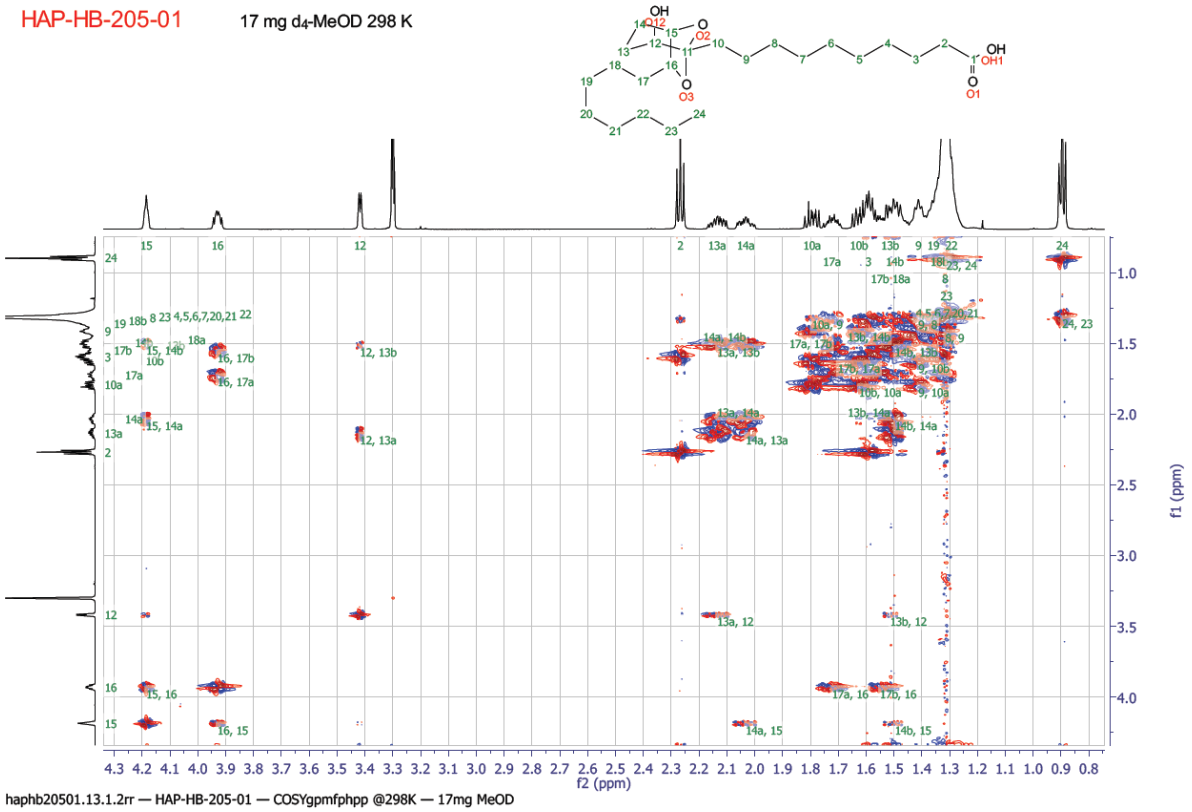
Atom	Chemical Shift	J	COSY	HSQC	HMBC	NOESY	HSQC-TOCSY
1 C	177.81				2, 3		
2 C	35.11			2			
H2	2.27			2	1, 3, 4		2, 3, 4, 5, 6, 7, 8, 9, 10
3 C	26.22			3	2, 4, 5		
H2	1.59			3	1, 4		
4 C	30.35				2, 3		
H2	1.31				3		
5 C	30.51, 30.63, 30.77						
H2	1.31				3		
6 C	30.51, 30.63, 30.77						
H2	1.31						
7 C	30.51, 30.63, 30.77						
H2	1.31						
8 C	31.09			8	9, 10a, 10b		
H2	1.32		9	8	9		
9 C	23.31			9	10a, 10b, 8		
H2	1.41		10a, 10b, 8	9	10, 8, 11	10a, 16, 12	
10 C	34.96			10b, 10a	9, 12		
Ha	1.79		10b, 9	10	8, 12, 9, 11	9, 12	
Hb	1.63		10a, 9	10	8, 12, 9, 11	12	
11 C	109.65				13, 10a, 10b, 13b, 9, 12		
12 C	69.39			12	16, 13a, 10a, 10b, 14b		
H	3.42		13a, 13b	12	10, 14, 13, 11	13a, 14a, 10a, 10b, 13b, 9	
13 C	27.17			13a, 13b	15, 12, 14a, 14b		
Ha	2.14		12, 14b, 13b, 14a	13	12, 14	17b, 13b, 17a, 15, 12	
Hb	1.51		12, 13a, 14b, 14a	13	15, 11	13a, 12	
14 C	21.53			14a, 14b	14a, 14b, 16, 12, 13a		
Ha	2.04	4.00(15)	15, 13a, 13b, 14b	14	16, 15, 14, 13	14b, 15, 12	
Hb	1.50		15, 13a, 13b, 14a	14	16, 15, 12, 14, 13	14a, 17a, 15	
15 C	77.94			15	16, 14a, 17a, 13b, 14b		
H	4.19	4.00(14a), 4.00(16)	14b, 14a, 16	15	16, 13, 11	14a, 13a, 17b, 14b, 19, 16	
16 C	81.56			16	15, 14a, 14b, 17a, 13a, 13b		
H	3.93	4.00(15), 7.50(17a), 6.30(17b)	15, 17b, 17a	16	15, 12, 14, 18	15, 17a, 17b, 18a, 19, 9	
17 C	30.35			17b, 17a			
Ha	1.72	7.50(16)	16, 17b	17	16, 15, 18, 19	18a, 17b, 14b, 13a, 19, 16	
Hb	1.55	6.30(16)	16, 17a	17	18, 19	13a, 17a, 15, 16	
18 C	28.04			18a, 18b	16, 17a, 17b		
Ha	1.47			18	16, 19	17a, 16	
Hb	1.34			18	16		
19 C	30.90			19	17a, 17b, 18a		
H2	1.36			19		17a, 13, 16	
20 C	30.48, 30.72			20			
H2	1.31			20			
21 C	30.48, 30.72			21			
H2	1.31			21			
22 C	33.13			22	23, 24		
H2	1.29			22	23		
23 C	23.83			23	22, 24		
H2	1.31		24	23	22, 24		
24 C	14.55			24	23		15, 16
H3	0.89		23	24	22, 23		23, 22, 21, 20, 19, 18, 17

HAP-HB-205-01 17 mg d_4-MeOD 298 K

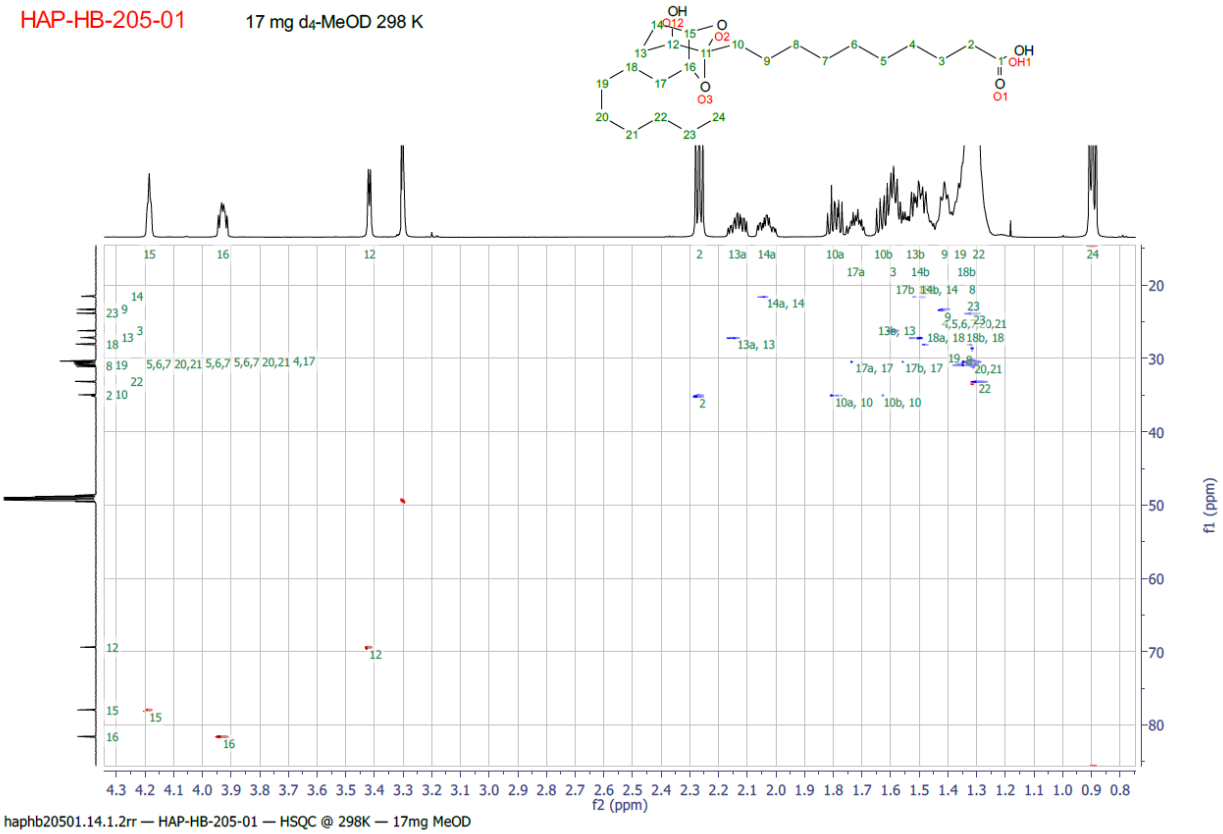




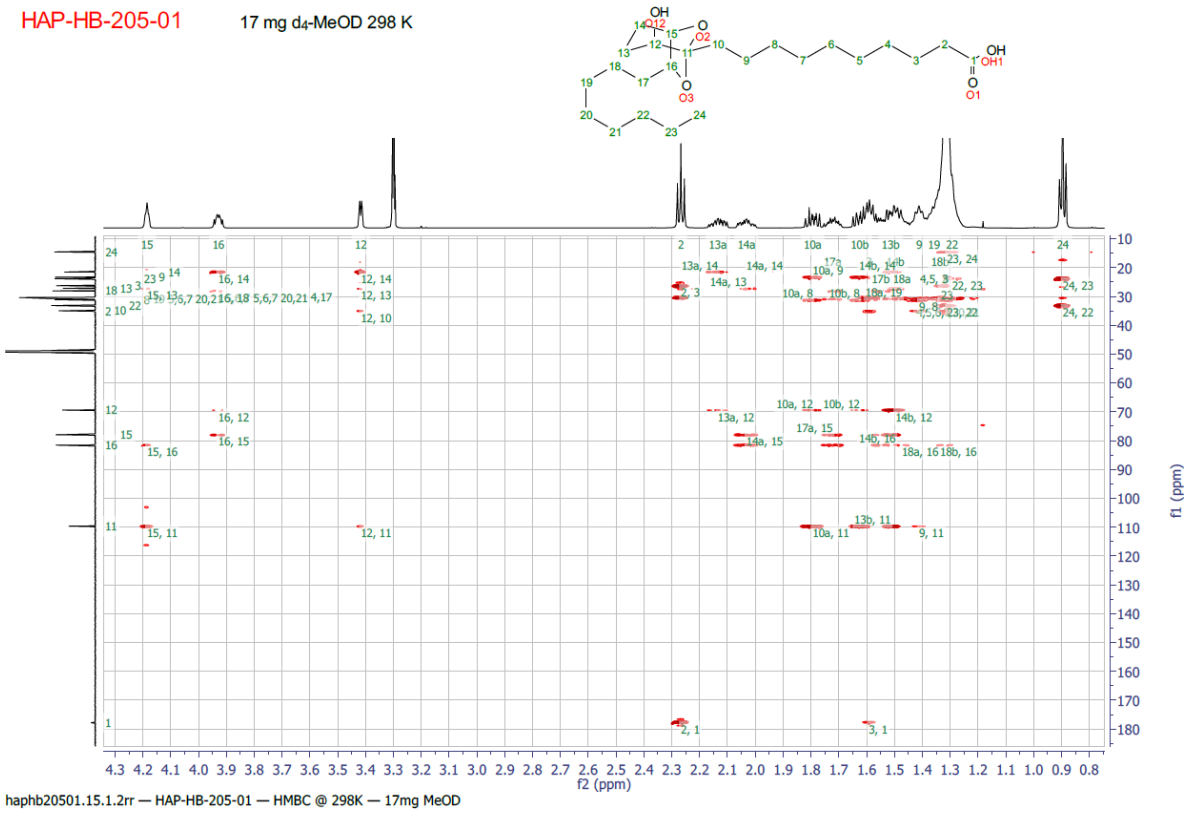
haphb20501.12.1.1r — HAP-HB-205-01 — DEPT135 @ 298K — 17mg MeOD



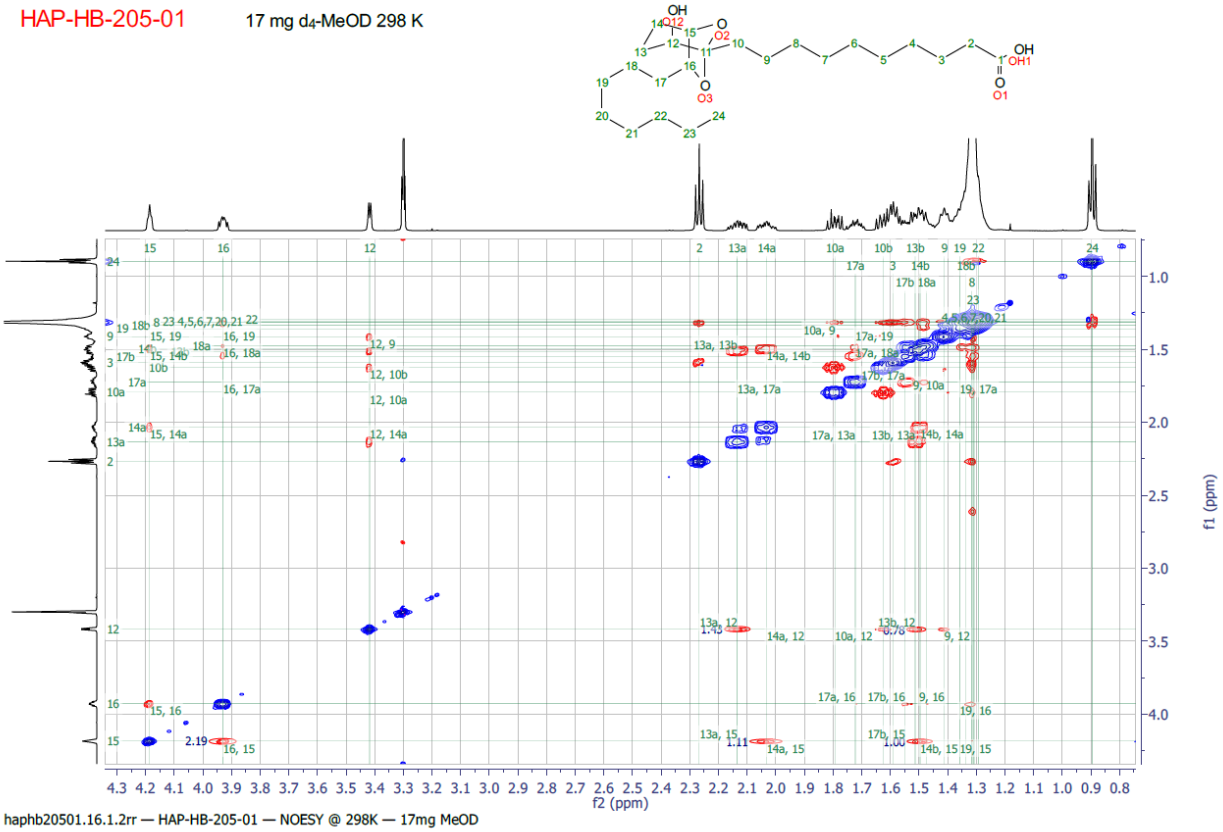
haphb20501.13.1.2rr — HAP-HB-205-01 — COSYgpmfphpp @298K — 17mg MeOD



haphb20501.14.1.2rr — HAP-HB-205-01 — HSQC @ 298K — 17mg MeOD

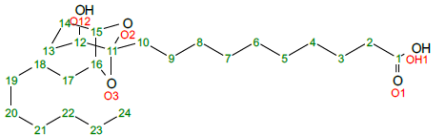


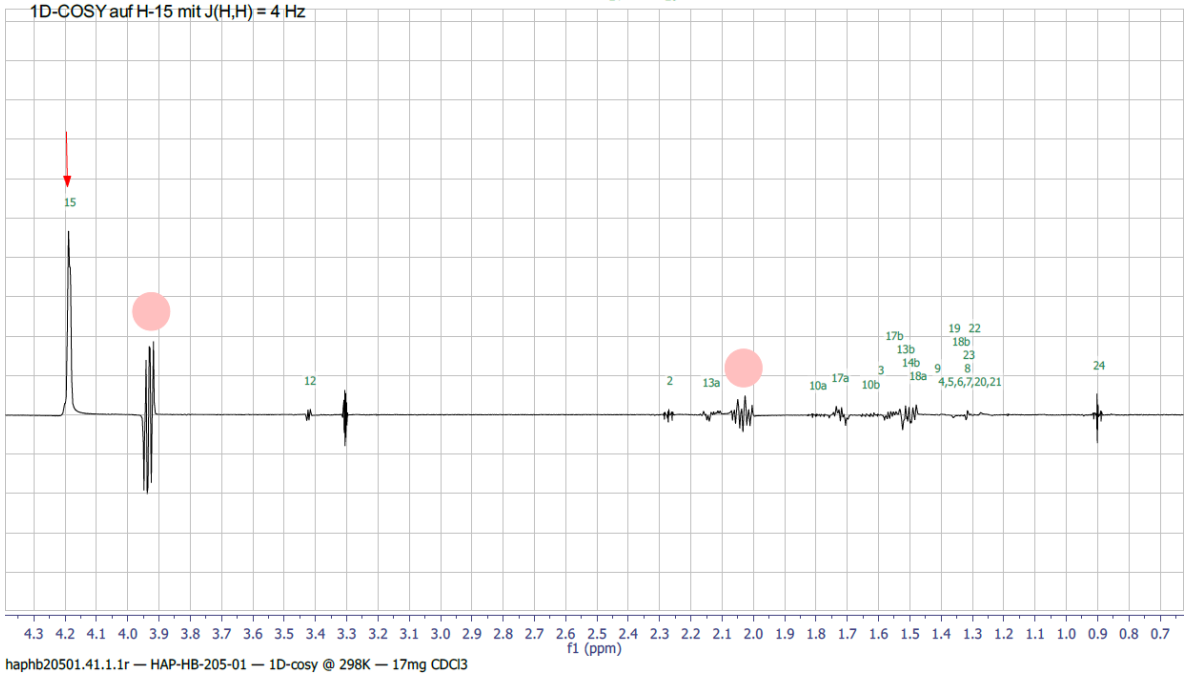
haphb20501.15.1.2rr — HAP-HB-205-01 — HMBC @ 298K — 17mg MeOD



haphb20501.16.1.2rr — HAP-HB-205-01 — NOESY @ 298K — 17mg MeOD

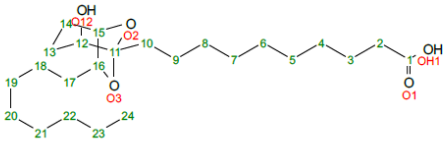
HAP-HB-205-01 17 mg d_4-MeOD 298 K

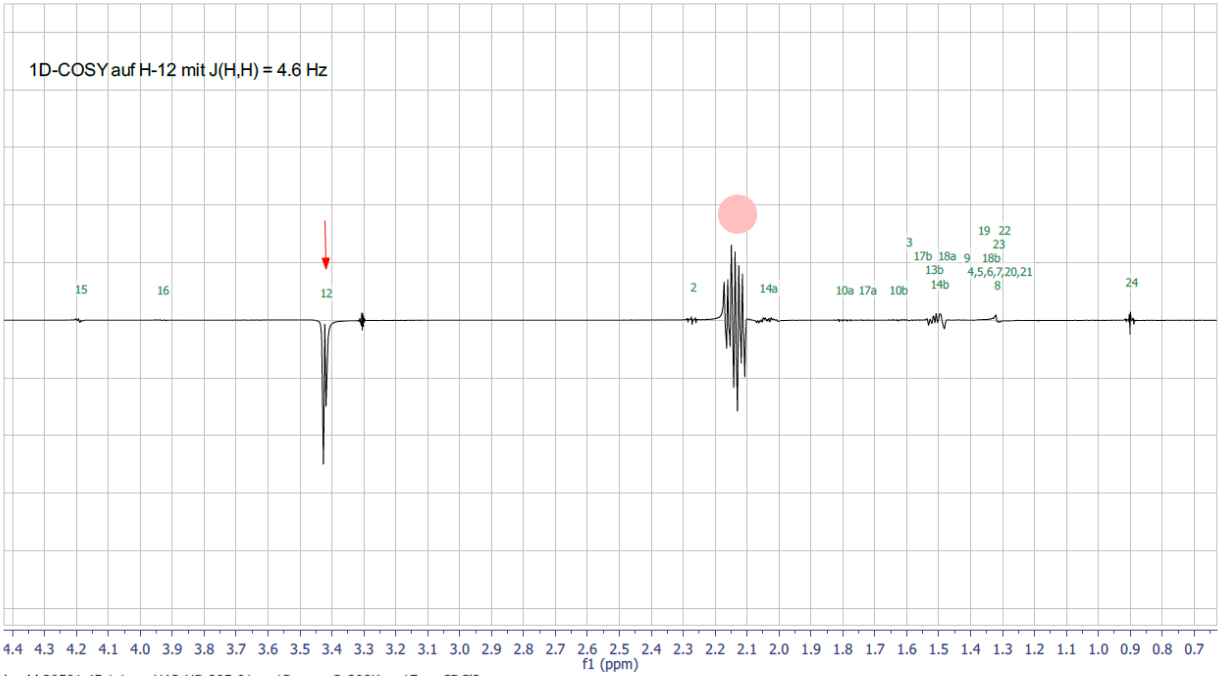




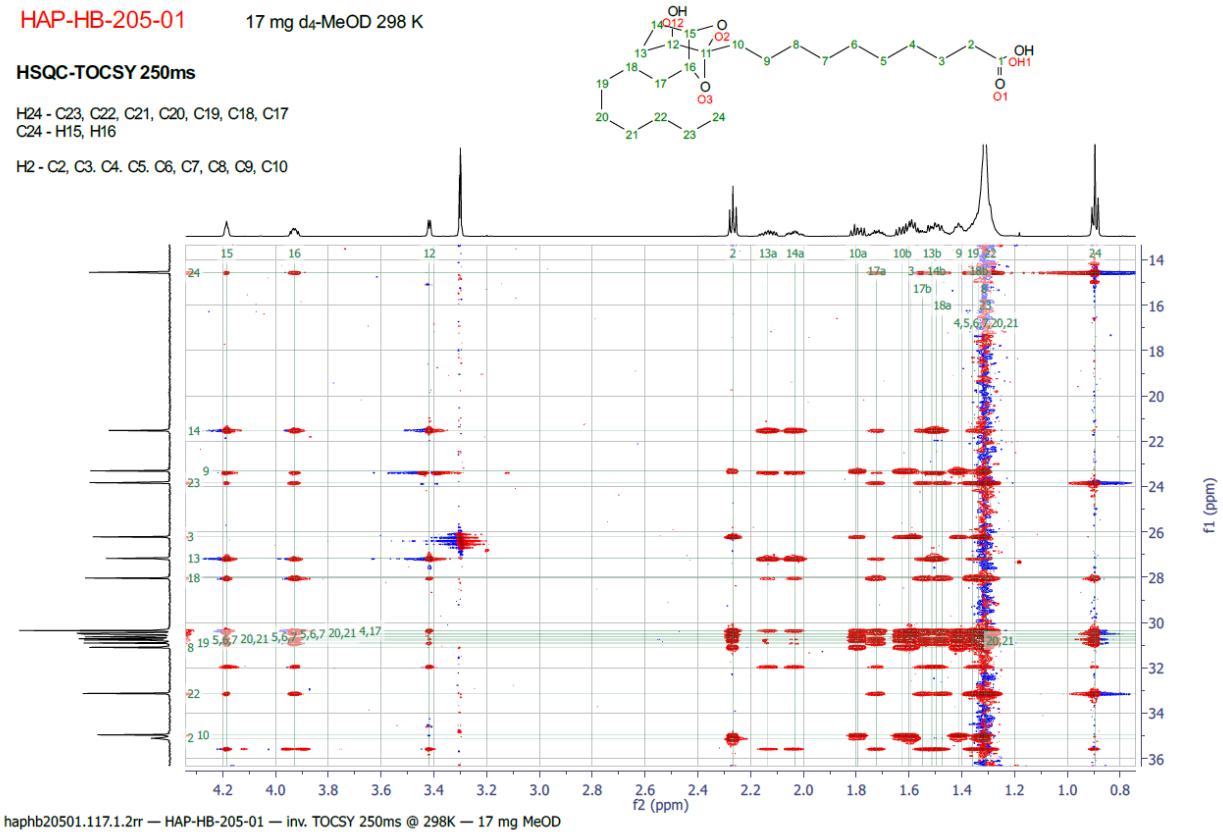
haphb20501.41.1.1r — HAP-HB-205-01 — 1D-cosy @ 298K — 17mg CDCl3

HAP-HB-205-01 17 mg d_4-MeOD 298 K





haphb20501.45.1.1r — HAP-HB-205-01 — 1D-cosy @ 298K — 17mg CDCl3


HAP-HB-205-01
17 mg d4-MeOD 298 K
HSQC-TOCSY 250ms
H24 - C23, C22, C21, C20, C19, C18, C17
C24 - H15, H16
H2 - C2, C3. C4. C5. C6, C7, C8, C9, C10
f2 (ppm)
f1 (ppm)
haphb20501.117.1.2rr — HAP-HB-205-01 — inv. TOCSY 250ms @ 298K — 17 mg MeOD