20 years

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Addition of Chiral and Achiral Allyltrichlorostannanes to Chiral α-Alkoxy Aldehydes

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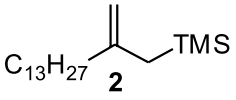
General Informations: All reactions were carried out under an atmosphere of argon or nitrogen in flame-dried glassware with magnetic stirring. Dichloromethane, triethylamine, 2,6-lutidine, diisopropylamine, dimethylformamide and *N*-methylpyrrolidone were distilled from CaH_2. Dimethyl sulfoxide was distilled under reduced pressure from calcium hydride and stored over molecular sieves. THF and toluene were distilled from sodium/benzophenone ketyl. Petrol refers to the fraction boiling between 40-60 ºC. Purification of reaction products was carried out by flash chromatography using silica-gel (230-400 mesh). Analytical thin layer chromatography was performed on silica gel 60 and GF (5-40 μm thickness) plates. Visualization was accomplished with UV light and anisaldehyde, ceric ammonium nitrate stain or phosphomolybdic acid followed by heating or I_2 staining. ^{1}H-NMR spectra were taken in $CDCl_3$ at 300 MHz or at 500 MHz spectrometer and are reported in ppm using solvent as an internal standard ($CDCl_3$ at 7.26 ppm) unless otherwise indicated. Data are reported as (ap = apparent, s = singlet, d = doublet, t = triplet, q = quartet, quint = quintet, sext = sextet, ap t = apparent triplet, m = multiplet, br = broad, td = triplet of doublets, quint d = quintet of doublets, coupling constant(s) in Hz; integration. Proton-decoupled ^{13}C-NMR spectra were taken in $CDCl_3$ at 75 MHz spectrometer and are recorded in ppm using solvent as an internal standard ($CDCl_3$ at 77.0 ppm) unless otherwise indicated.

Allylsilanes 2-4 (General Procedure): In a 3-necked 500 mL round bottomed flask powdered $CeCl_3.7H_2O$ (15.44 g, 41.4 mmol) was heated under vacuum (1 Torr) at 160 °C for 12 h with vigorous stirring, resulting in the formation of a mobile white solid. The reaction flask was flushed with argon and allowed to cool to rt when anhydrous THF (65 mL) was added to the vigorously stirred anhydrous cerium(III) chloride forming a uniform white suspension, which was kept under stirring for 2 h. During this time, a separate three-necked 100 mL flask, fitted with a condenser and a pressure-equalizing dropping funnel, was charged with Mg turnings (1 g, 41.4 mmol), and the whole apparatus was flame dried under a flow of argon. To this flask was added dropwise a solution of $ClCH_2SiMe_3$ (5.8 mL, 41.4 mmol) in anhydrous THF (27 mL). This mixture was stirred for 3 h until almost all of the Mg had dissolved. The anhyd $CeCl_3$ suspension was now cooled to –78 °C. To this suspension was added dropwise the previously prepared Grignard reagent, forming an off-white suspension, which was stirred at –78 °C for 2 h. At this time, a solution of the corresponding ester (13.8 mmol) in anhydrous THF (8 mL) was added to the Grignard-cerium chloride complex dropwise over 5 min, and the resulting mixture was warmed gradually to r.t. When consumption of the starting ester was complete, as determined by TLC (3 h), the resulting grey solution was cooled to 0 °C and quenched by the addition of a sat. aq solution of NH_4Cl (30 mL). The organic layer was separated, and the aqueous layer was extracted with Et_2O (2 x 50 mL). The combined organic layers were washed with brine (2 x 50 mL) and dried ($MgSO_4$). The solvent was removed under reduced pressure to give a slightly yellow liquid that was dissolved in CH_2Cl_2 (100 mL). To this flask was added Amberlyst 15 (1.0 g) and this mixture was stirred at rt until complete consumption of starting material. The resin was then removed by filtration and washed with CH_2Cl_2 (100 mL). The solvent was removed under reduced pressure to give allylsilanes **2-4**.



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Trimethyl(2-methylenepentadecyl)silane (2): yellow oil; Yield: 68%; TLC: R_f 0.75 (EtOAc/hexane 20%); IR (Film): ν 3072, 2953, 2926, 2854, 1633, 1466, 1248, 1157 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.04 (s, 9H), 0.91 (t, J = 7.0 Hz, 3H), 1.29 (brs, 20H), 1.39-1.49 (m, 2H), 1.57 (s, 2H), 1.97 (t, J = 7.0 Hz, 2H), 4.52 (brs, 1H), 4.60 (d, J = 1.0 Hz, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 2.1 (CH_3), 14.2 (CH_2), 22.5 (CH_3), 22.8 (CH_2), 27.8 (CH_2), 29.4 (CH_2), 29.6 (CH_2), 29.8 (CH_2), 32.0 (CH_2), 37.9 (CH_2), 109.4 (CH_2), 146.2 (C_0).

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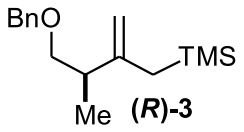
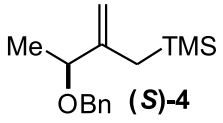
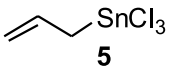


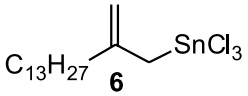
(*R*)-(4-(benzyloxy)-3-methyl-2-methylenebutyl) trimethylsilane (3): Yield: 88%; R*f* = 0.38 (EtOAc/hexanes 5%); $[\alpha]_D^{22}$: +12.6 (*c* 1.3, $CHCl_3$); IR (film) ν (cm^{-1}): 3069, 3030, 2957, 2851, 1632, 1497, 1453, 1414, 1364, 1247, 1158, 1097, 1031, 952, 852, 735, 696, 634 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ (ppm): 0.03 (s, 9H), 1.04 (d, *J* = 6.8 Hz, 3H), 1.46 (d, *J* = 13.6 Hz, lH), 1.52 (d, *J* = 13.6 Hz, lH), 2.28 (m, lH), 3.26 (dd, *J* = 9.3, 8.3 Hz, 1H), 3.53 (dd, *J* = 9.3, 5.4 Hz, lH), 4.52 (d, *J* = 12.1 Hz, lH), 4.53 (d, *J* = 12.1 Hz, lH), 4.62 (s, lH), 4.64 (s, lH), 7.25-7.40 (m, 5H); ^{13}C NMR ($CDCl_3$, 75 MHz), δ (ppm): −1.3, 17.1, 26.6, 41.0, 72.9, 75.0, 106.5, 127.4, 127.5, 128.3, 138.7, 149.7; Elemental analysis: calcd. for $C_{16}H_{26}OSi$: C, 73.22%; H, 9.98%; found: C, 73.15%; H, 10.02%.



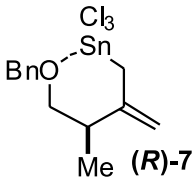
(*S*)-(3-(benzyloxy)-2-methylenebutyl)trimethylsilane (4): R*f* = 0.34 (EtOAc/hexanes 5%); $[\alpha]_D^{22}$: +12.6 (*c* 1.3, $CHCl_3$); IR (film) ν (cm^{-1}): 3068, 3023, 2951, 1720, 1603, 1495, 1454, 1248, 1093; ^1H NMR ($CDCl_3$, 300 MHz), δ (ppm): 0.08 (s, 9H), 1.30 (d, *J* = 6.6 Hz, 3H), 1.48 (d, *J* = 14.5 Hz, 1H), 1.62 (d, *J* = 14.5 Hz, 1H), 3.84 (q, *J* = 6.6 Hz, 1H), 4.35 (d, *J* = 11.7 Hz, 1H), 4.57 (d, *J* = 11.7 Hz, 1H), 4.80 (s, 1H), 5.00 (s, 1H), 7.25-7.40 (m, 5H); ^{13}C NMR ($CDCl_3$, 75 MHz), δ (ppm): −0.8, 20.6, 21.1, 70.0, 78.8, 108.7, 127.2, 127.5, 128.2, 138.8, 147.6.



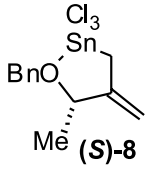
Allyltrichlorostannane (5): ^1H NMR ($CDCl_3$, 300 MHz) δ (ppm): 3.06 (d, *J* = 5,2 Hz, lH), 5.33 (d, *J* = 5.6 Hz, lH), 5.40 (d, *J* = 6.6 Hz, 1H), 5.97 (m, lH); ^{13}C NMR ($CDCl_3$, 75 MHz) δ (ppm): 35.0, 121.0, 127.0. Obs. The signal at 0.45 ppm corresponds to TMSCl.



Trichloro(2-methylenepentadecyl)stannane (6): ^1H NMR ($CDCl_3$, 300 MHz): δ 0.89 (t, *J* = 6.0 Hz, 3H), 1.30 (brs, 20H), 1.51 (m, 2H), 2.14 (t, *J* = 8.0 Hz, 2H), 3.15 (s, 2H), 5.07 (brs, 1H), 5.10 (brs, 1H). Obs. The signal at 0.45 ppm corresponds to TMSCl.

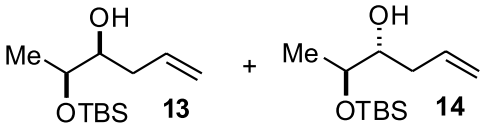


(*R*)-(4-(benzyloxy)-3-methyl-2-methylenebutyl) trichlorostannane (7): ^1H NMR ($CDCl_3$, 300 MHz) δ (ppm): 0.95 (d, *J* = 7.0 Hz, 3H), 2.48 (m, lH), 3.19 (d, *J* = 11.2 Hz, lH), 3.36 (d, *J* = 11.2 Hz, lH), 3.53 (dd, *J* = 9.9, 8.4 Hz, 1H), 3.70 (dd, *J* = 9.9, 4.4 Hz, lH), 4.71 (d, *J* = 13.2 Hz, lH), 4.77 (d, *J* = 13.2 Hz, lH), 5.04 (s, lH), 5.18 (s, lH), 7.30-7.50 (m, 5H). Obs. The signal at 0.45 ppm corresponds to TMSCl; ^{13}C NMR ($CDCl_3$, 75 MHz) δ (ppm): 15.7, 39.9, 42.7, 73.0, 74.5, 114.6, 127.5, 128.3, 128.7, 138.7, 144.0. Obs. The signal at 3.6 ppm corresponds to TMSCl.



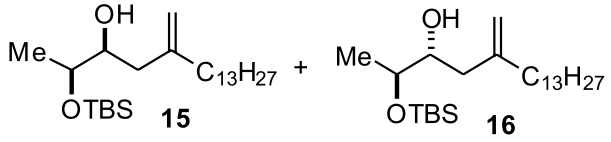
(*S*)-(3-(benzyloxy)-2-methylenebutyl) trichlorostannane (8): ^1H NMR ($CDCl_3$, 300 MHz, −60 ºC) δ (ppm): 1.28 (d, *J* = 6.6 Hz, 3H), 2.91 (d, *J* = 14.5 Hz, 1H), 3.05 (d, *J* = 14.5 Hz, 1H), 4.17 (q, *J* = 6.6 Hz, 1H), 4.68 (d, *J* = 11.7 Hz, 1H), 5.01 (s, 1H), 5.05 (s, 1H), 5.10 (d, *J* = 11.7 Hz, 1H), 7.20-7.40 (m, 5H). Obs. The signal at 0.45 ppm corresponds to TMSCl.

Homoallylic Alcohols (General Procedure): To a solution of the corresponding allylsilane (1.5 mmol) in CH_2Cl_2 (5 mL) at rt was added $SnCl_4$ (1.1 mmol). The resulting solution was stirred at rt for 2 h and then cooled to –78 °C when a solution of aldehyde (1.2 mmol) in CH_2Cl_2 (2 mL) was added. This mixture was stirred for 2 h at –78 °C and quenched by the slow addition of a sat. aq solution of $NaHCO_3$ (5 mL) followed by CH_2Cl_2 (5 mL). The layers were separated and the aqueous layer was extracted with CH_2Cl_2 (2 x 5 mL). The combined organic layers were dried ($MgSO_4$), filtered, and concentrated in vacuo. Purification by flash chromatography on silica gel (30% EtOAc–hexane) gave the corresponding homoallylic alcohols.

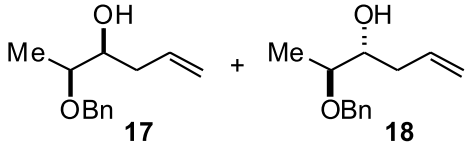


(2*S*,3*S*)-2-(*tert*-butyldimethylsilyloxy)hex-5-en-3-ol (13) and (2*S*,3*R*)-2-(*tert*-butyldimethylsilyloxy)hex-5-en-3-ol (14): Yield: 45%; R*f* = 0.26 (EtOAc/hexanes 5%); IR (film) ν (cm^{-1}): 3568, 3468, 2956, 2957, 2932, 2858, 1641,

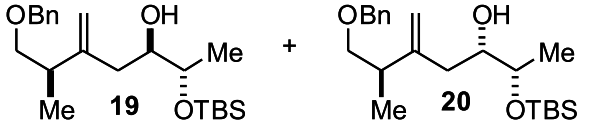
1473, 1389, 1074, 1005, 968, 912, 777; ^{1}H NMR ($CDCl_3$, 300 MHz) δ (ppm): 0.08 (s, 3H), 0.09 (s, 3H), 0.91 (s, 9H), 1.17 (d, J = 6.2 Hz, 3H), 2.18-2.32 (m, 2H), 3.33-3.43 (m, 1H), 3.70-3.82 (m, 1H), 5.01-5.16 (m, 2H), 5.81-5.59 (m, 1H). Minor isomer: 0.07 (s, 3H), 1.12 (d, J = 6.2 Hz, 3H), 3.53-3.60 (m, 1H), 3.76-3.82 (m, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ (ppm): –4.7, –4.0, 18.2, 20.2, 25.9, 38.1, 70.9, 75.2, 116.8, 135.1; Minor isomer (**14**): 17.5, 36.8, 74.5, 117.2.



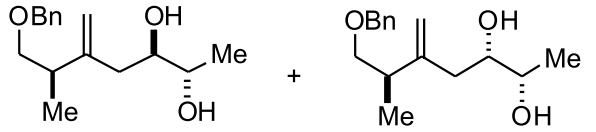
(2*S*,3*S*)-2-(*tert*-butyldimethylsilyloxy)-5-methyleneoctadecan-3-ol (15) and (2*S*,3*R*)-2-(*tert*-butyldimethylsilyloxy)-5-methyleneoctadecan-3-ol (16): Yield: 40%; R*f* = 0.36 (EtOAc/hexane 5%); IR (film) ν (cm^{-1}): 3465, 3067, 2957, 2930, 2857, 1645, 1371, 1255, 1092, 835, 775; ^{1}H NMR ($CDCl_3$, 300 MHz) δ (ppm): 0.08 (s, 6H), 0.88 (m, 3H), 0.89 (s, 9H), 1.16 (d, J = 6.0 Hz, 3H), 1.25 (brs, 22H), 1.36-1.49 (m, 2H), 2.01-2.18 (m, 2H), 3.49 (dq, J = 4.4 Hz, 6.6 Hz, 1H), 3.66-3.75 (m,1H), 4.81 (d, J = 4.7 Hz, 2H); Minor isomer: 0.06 (s, 6H), 1.12 (d, J = 6.0 Hz, 3H), 3.56-3.66 (m,1H); ^{13}C NMR ($CDCl_3$, 63 MHz) δ (ppm): –4.8, –4.1, 14.1, 18.0, 22.7, 25.8, 27.7, 29.4, 29.7, 31.9, 71.0, 73.4, 111.3. Minor isomer: 20.0, 29.7, 73.0.



(2*S*,3*S*)-2-(benzyloxy)hex-5-en-3-ol (17) and (2*S*,3*R*)-2-(benzyloxy)hex-5-en-3-ol (18): Yield: 40%; R*f* = 0.44 (EtOAc/hexane 10%); IR (film) ν (cm^{-1}): 3566, 3453, 3062, 3030, 2969, 2871, 1603, 1645, 1454, 1072, 1028, 993, 914, 737, 698; ^{1}H NMR ($CDCl_3$, 500 MHz) δ (ppm): 1.21 (d, J = 6.0 Hz, 3H), 2.15-2.26 (m, 1H), 2.31-2.40 (m, 1H), 3.44 (apqt, J = 6.2 Hz, 1H), 3.52 (ddd, J = 4.4 Hz, 6.2 Hz, 7.7 Hz, 1H), 4.38 (d, J = 11.7 Hz, 1H), 4.66 (d, J = 11.7 Hz, 1H), 5.09 (d, J = 9.5 Hz, 1H), 5.12(d, J = 20.3 Hz, 1H), 5.87 (ddt, J = 7.3 Hz, 9.5 Hz, 20.5 Hz), 7.26-7.38 (m, 5H). Minor isomer: 1.15 (d, J = 6.2 Hz, 3H); ^{13}C NMR ($CDCl_3$, 63 MHz) δ (ppm): 15.4, 37.5, 71.0, 74.2, 117.2, 127.8, 128.4, 134.7, 138.3. Minor isomer: 13.8, 36.9, 70.7.

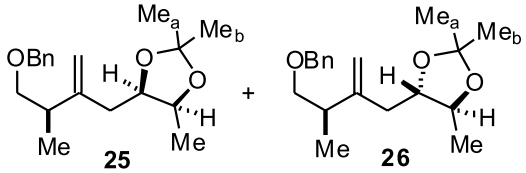


(2*S*,3*R*,6*R*)-7-(benzyloxy)-2-(*tert*-butyldimethylsilyloxy)-6-methyl-5-methyleneheptan-3-ol (19) and (2*S*,3*S*,6*R*)-7-(benzyloxy)-2-(*tert*-butyldimethylsilyloxy)-6-methyl-5-methyleneheptan-3-ol (20): Yield: 55%; R*f* = 0.28 (EtOAc/hexanes 10%); IR (film) ν (cm^{-1}): 3465, 3067, 2957, 2930, 2857, 1645, 1371, 1092, 835, 775; ^{1}H NMR ($CDCl_3$, 300 MHz) δ (ppm): 0.08 (s, 6H), 0.9 (s, 9H), 1.07 (d, J = 7.0 Hz, 3H), 1.15 (d, J = 6.2 Hz, 3H), 2.07 (dd, J = 9.2, 14.3 Hz, 1H), 2.31 (dd, J = 4.0, 14.3 Hz, 1H), 2.50 (m, 1H), 3.39 (dd, J = 6.6, 9.2 Hz, 2H), 3.42 (dd, J = 7.0, 9.2 Hz, 2H), 3.63 (m, 1H), 3.72 (m, 1H), 4.93 (s, 1H), 4.95 (s, 1H), 7.26-7.32 (m, 5H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ (ppm): –4.6, –4.2, 17.5, 18.1, 18.7, 25.9, 38.7, 39.3, 71.4, 73.0, 73.5, 74.5, 111.6, 127.4, 128.2, 138.2, 149.0.

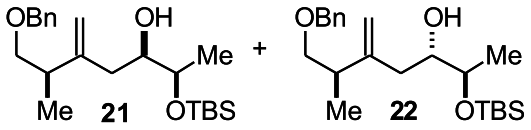


23 (1,2-*anti*) **24** (1,2-s*yn*)

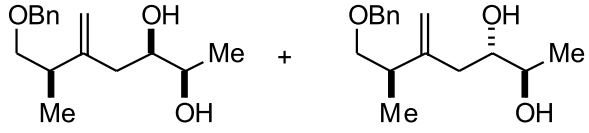
(2*S*,6*R*)-7-(benzyloxy)-6-methyl-5-methyleneheptane-2,3-diols (23) and (24): Yield: 67%; *Rf* = 0.26 (EtOAc/hexanes 50%); ^{1}H NMR ($CDCl_3$, 300 MHz) δ (ppm): 1.02 (d, J = 7.0 Hz, 3H), 1.17 (d, J = 6.2 Hz, 3H), 2.13-2.29 (m, 2H), 2.51-2.55 (m, 1H), 3.39-3.51 (m, 2H), 3.70-3.77 (m, 1H), 3.84-3.92 (m, 1H) 4.51 (s, 2H), 5.00 (s, 2H); 5.30 (s, 2H), 7.28-7.38 (m, 5H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ (ppm): 17.5, 36.8, 39.0, 69.9, 72.0, 73.1, 74.3, 112.8, 127.8, 128.2, 137.8, 148,8.



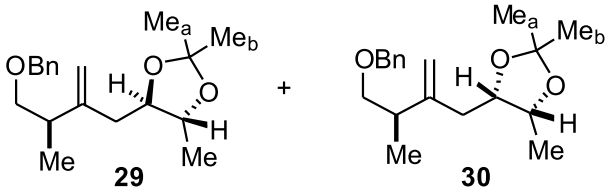
(4*R*,5*S*)-4-((*R*)-4-(benzyloxy)-3-methyl-2-methylenebutyl)-2,2,5-trimethyl-1,3-dioxolane (25) and (4*S*,5*S*)-4-((*R*)-4-(benzyloxy)-3-methyl-2-methylenebutyl)-2,2,5-trimethyl-1,3-dioxolane (26): *Rf* = 0.72 (EtOAc/hexanes 20%); IR (film) ν (cm^{-1}): 3047, 2986, 2934, 2872, 1645, 1454, 1377, 1223, 1080; ^{1}H NMR($CDCl_3$, 300 MHz) δ (ppm): 1.02 (d, J = 6.4 Hz, 3H), 1.12 (d, J = 6.7 Hz, 3H), 1.31 (s, 3H), 1.49 (s, 3H), 2.07 (dd, J = 4.9, 15.6 Hz, 1H), 2.34 (dd, J = 8.4, 15.6 Hz, 1H), 2.07 (st, J = 6.7 Hz, 1H), 3.25 (dd, J = 7.2, 8.9 Hz, 1H), 3.43 (dd, J = 5.8, 8.9 Hz, 1H), 4.09 (qt, J = 6.4 Hz, 1H), 4.21 (dt, J = 5.3, 8.5 Hz, 1H), 4.33 (s, 2H), 4,93 (d, J = 13.7 Hz, 2H), 7.28-7.38 (m, 5H); ^{13}C NMR (benzene-d6, 75 MHz) δ (ppm): 16.1, 17.4, 26.0, 28.9, 35.9, 40.4, 73.1, 74.0, 75.1, 76.9, 107.4, 110.7, 126.5, 127.6, 128.5, 139.3, 149.3.



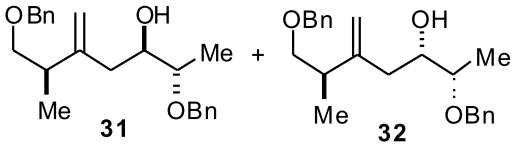
(2*R*,3*R*,6*R*)-7-(benzyloxy)-2-(*tert*-butyldimethylsilyloxy)-6-methyl-5-methyleneheptan-3-ol (21) and (2*R*,3*S*,6*R*)-7-(benzyloxy)-2-(*tert*-butyldimethylsilyloxy)-6-methyl-5-methyleneheptan-3-ol (22): *Rf* = 0.53 (hexanes: EtOAc, 95:05); IR (film) ν (cm^{-1}): 3463, 3031, 2950, 2857, 1645, 1559, 1497, 1455, 1255, 1092, 895; ^{1}H NMR ($CDCl_3$, 300 MHz) δ (ppm): 0.09 (s, 3H), 0.09 (s, 3H), 0.91 (s, 9H), 1.09 (d, *J* = 7.0 Hz, 3H), 1.16 (d, *J* = 6.2 Hz, 3H) 2.03-2.35 (m, 2H); 2.50 (qt, *J* = 7.0 Hz,1H), 3.32-3.39 (m, 1H), 3.45-3.64 (m, 2H), 3.72-3.80 (m, 1H), 4.52 (s, 2H), 4.91 (s, 1H), 4.94 (s, 1H), 7.33-7.34 (m, 5H).Minor isomer: 0.07 (s, 3H), 0.08 (s, 3H), 0.90 (s, 9H), 1.11 (d, *J* = 2.2 Hz, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ (ppm): –4.8, –4.2, 17.4, 18.0, 18.3, 19.7, 25.8, 38.9, 39.4, 71.0, 73.0, 79.7, 74.6, 111.4, 127.5, 128.3, 138.4, 149.2. Minor isomer: 17.2, 38.5, 39.6, 71.4, 74.8, 79.7, 74.6, 111.8.



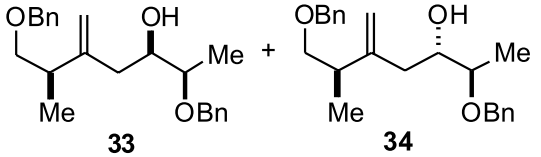
(2*R*,6*R*)-7-(benzyloxy)-6-methyl-5-methyleneheptane-2,3-diol (27) and (28): *Rf* = 0.65 (EtOAc/hexanes 50%); ^{1}H NMR ($CDCl_3$, 500 MHz) δ (ppm): 1.01 (d, *J* = 7.0 Hz, 3H), 1.18 (d, *J* = 6.0 Hz, 3H); 2.02-2.57 (m, 3H); 3.87-3.34 (m, 4H) 4.49 (d, *J* = 2.3 Hz, 1H), 4.97 (d, *J* = 2.3 Hz, 1H), 7.28-736 (m, 5H). Minor isomer: 1.08 (d, *J* = 7.0 Hz, 3H), 1.15 (d, *J* = 6.0 Hz, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ (ppm): 17.8, 19.0, 38.5, 40.1, 70.7, 73.2, 74.8, 113.0, 127.8, 128.4, 138.0, 148.8. Minor isomer: 17.3, 37.3, 39.7, 69.9, 75.0, 112.7, 127.7, 128.4.



(4*R*,5*R*)-4-((*R*)-4-(benzyloxy)-3-methyl-2-methylenebutyl)-2,2,5-trimethyl-1,3-dioxolane (29) and (4*S*,5*R*)-4-((*R*)-4-(benzyloxy)-3-methyl-2-methylenebutyl)-2,2,5-trimethyl-1,3-dioxolane (30): Yield: 50%; *Rf* = 0.38 (EtOAc/hexanes 5%); IR (film) ν (cm^{-1}): 3055, 2986, 2936, 2874, 1645, 1454, 1379, 1090, 898, 842; ^{1}H NMR (C_6D_6, 500 MHz) δ (ppm): 1.10 (d, *J* = 6.1 Hz, 3H), 1.13 (d, *J* = 7.0 Hz, 3H), 1,40 (s, 6H), 2.13 (dd, *J* = 4.0, 15.0 Hz, 1H), 2.32 (dd, *J* = 7.6, 15.0 Hz, 1H), 2.55 (apsex, *J* = 6.4 Hz, 1H), 3.23 (dd, *J* = 7.3, 8.8 Hz, 1H), 3.42 (dd, *J* = 5.8, 8.8 Hz, 1H), 3.62 (dq, *J* = 5.8, 8.2 Hz, 1H), 3.68-3.72 (m,1H), 4.33 (s, 2H), 4.91 (s, 2H), 4.91 (s, 1H), 5.02 (s, 1H), 7.15-7.31 (m, 5H). Minor isomer: 1.11 (d, *J* = 6.0 Hz, 3H), 1.31 (s, 3H), 1.49 (s, 3H), 2.06 (dd, J = 4.6, 15.4 Hz, 1H), 4.20 (m,1H), 4.25 (m,1H), 7.08-7.11 (m, 5H); ^{13}C NMR (C_6D_6, 125 MHz) δ (ppm): 17.2, 17.8, 27.5, 27.6, 39.0, 40.0, 73.1, 75.1, 77.3, 81.6, 111.5, 128.0, 128.5, 139.3, 149.0. Minor isomer: 16.0, 17.4, 26.0, 28.9, 35.7, 40.2, 74.0, 75.0, 76.4, 108.0, 110.8.

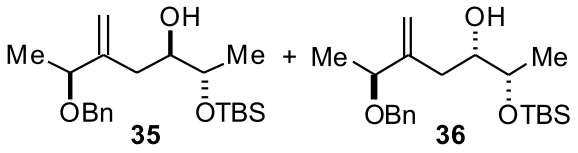


(2*S*,3*R*,6*R*)-2,7-bis(benzyloxy)-6-methyl-5-methyleneheptan-3-ol (31) and (2*S*,3*S*,6*R*)-2,7-bis(benzyloxy)-6-methyl-5-methyleneheptan-3-ol (32): Yield: 70%; *Rf* = 0.36 (EtOAc/hexanes 20%); IR (film) ν (cm^{-1}): 3454, 3061, 3026, 2970, 2872, 1643, 1498, 1454, 1367, 1264, 1090; ^{1}H NMR ($CDCl_3$, 250 MHz) δ (ppm): 1.04 (d, *J* = 7.0 Hz, 3H), 1.22 (d, *J* = 6.3 Hz, 3H), 2.09-2.53 (m, 3H), 3.33- 3.54 (m, 3H), 3.80-3.88 (m, 1H), 4.50 (s, 2H), 4.52 (d, *J* = 12.0 Hz, 1H), 4.63 (d, *J* = 12.0 Hz, 1H), 4.93 (s, 1H), 4.97 (s, 1H), 7.29-7.35 (m, 10H). Minor isomer: 1.09 (d, *J* = 7.0 Hz, 3H), 1.17 (d, *J* = 6.0 Hz, 3H), 3.62-3.72 (m, 1H), 4.00-4.10 (m, 1H); ^{13}C NMR ($CDCl_3$, 63 MHz) δ (ppm): 14.8, 17.5, 39.0, 70.9, 73.0, 74.5, 112.0, 127.5, 127.7, 128.3, 138.1, 149.0. Minor isomer: 15.5, 17.2, 71.0, 71.7, 74.9, 138.7.

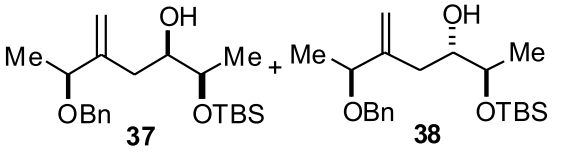


(2*R*,3*R*,6*R*)-2,7-bis(benzyloxy)-6-methyl-5-methyleneheptan-3-ol (33) and (2*R*,3*S*,6*R*)-2,7-bis(benzyloxy)-6-methyl-5-methyleneheptan-3-ol (34): Yield: 60%; *Rf* = 0.18 (EtOAc/hexanes 10%); IR (film) ν (cm^{-1}): 3695, 3055, 2976, 2930, 1715, 1452, 1072, 897; ^{1}H NMR ($CDCl_3$, 250 MHz) δ (ppm): 1.06 (d, *J* = 7.0 Hz, 3H), 1.21 (d, *J* = 6.0 Hz, 3H), 2.08-2.71 (m, 3H), 3.31-3.55 (m, 3H), 3.65-3.76 (m, 1H), 4.48 (d, *J* = 9.2 Hz, 1H), 4.51 (s, 2H), 4.66 (d, *J* = 11.3 Hz, 1H), 4.92 (s, 1H), 4.94 (s, 1H), 7.10-7.37 (m, 10H). Minor isomer: 1.20 (d, *J* = 6.3 Hz, 3H), 3.79-3.87 (m, 1H), 4.00-4.10 (m, 1H); ^{13}C NMR ($CDCl_3$, 63 MHz) δ (ppm): 15.5, 17.4, 38.8, 39.1, 39.5, 71.1, 72.6,

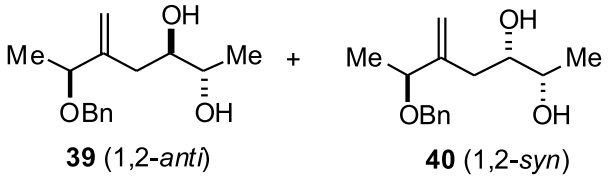
74.5, 111.8, 127.7, 128.3, 138.3, 148.9. Minor isomer: 14.5, 17.2, 38.7, 70.8, 72.0, 74.8, 112.0, 126.0.



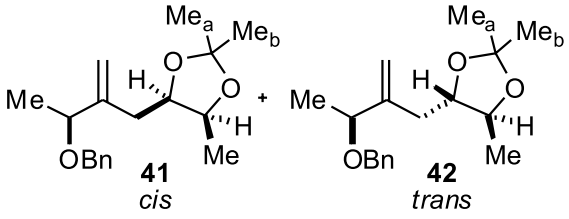
(2*S*,3*R*,6*S*)-6-(benzyloxy)-2-(*tert*-butyldimethylsilyloxy)-5-methyleneheptan-3-ol (35) and (2*S*,3*S*,6*S*)-6-(benzyloxy)-2-(*tert*-butyldimethylsilyloxy)-5-methyleneheptan-3-ol (36): Yield: 35%; *Rf* = 0.17 (EtOAc/hexanes 5%); IR (film) ν (cm^{-1}): 3564, 3445, 3052, 2955, 2931, 2858, 1651, 1454, 1372, 1092; ^{1}H NMR ($CDCl_3$, 500 MHz) δ (ppm): 0.08 (s, 3H); 0.09 (s, 3H); 0.90 (s, 9 H); 1.16 (d, *J* = 6.2 Hz, 3H); 1.31 (d, *J* = 6.6 Hz, 3H); 2.03-2.34 (m, 2H); 3.55 (dq, *J* = 3.3, 1.5 Hz, 1H); 3.71-3.81 (m, 1H); 3.95-4.03 (m, 1H); 4.36 (d, *J* = 11.7 Hz, 1H); 4.56 (d, *J* = 11.7 Hz, 1H); 5.07 (s, 1H); 5.12 (s, 1H); 7.27-7.33 (m, 5H). Minor isomer: 0.07 (s, 3H); 0.08 (s, 3H); 0.89 (s, 9 H); 1.13 (d, *J* = 5.9 Hz, 3H); 1.32 (d, *J* = 6.2 Hz, 3H);); 4.36 (d, *J* = 11.7 Hz, 1H); 4.53 (d, *J* = 11.7 Hz, 1H); 5.10 (s, 1H); 5.14 (s, 1H). ^{13}C NMR (C_6D_6, 75 MHz) δ (ppm): -4.7, -4.2, 18.2, 19.2, 20.5, 26.0, 34.7, 70.2, 71.6, 74.9, 78.9, 113.7, 114.1, 127.8, 128.5, 139.2, 148.0. Minor isomer: –4.6, –4.3, 18.5, 21.2, 72.1, 74.6, 79.1.



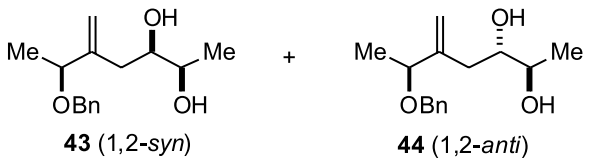
(2*R*,3*R*,6*S*)-6-(benzyloxy)-2-(*tert*-butyldimethylsilyloxy)-5-methyleneheptan-3-ol (37) and (2*R*,3*S*,6*S*)-6-(benzyloxy)-2-(*tert*-butyldimethylsilyloxy)-5-methyleneheptan-3-ol (38): Yield: 47%; *Rf* = 0.25 (EtOAc/hexanes 10%); IR (film) ν (cm^{-1}): 3564, 3435, 3052, 2960, 2931, 2862, 1647, 1454, 1371, 1090; ^{1}H NMR ($CDCl_3$, 250 MHz) δ (ppm): 0.09 (s, 6H), 0.90 (s, 9 H), 1.16 (d, *J* = 6.3 Hz, 3H), 1.31 (d, *J* = 6.6 Hz, 3H), 2.03-2.49 (m, 2H), 3.57 (dq, *J* = 4.1, 1.3 Hz, 1H), 3.65-3.76 (m, 1H), 3.92-4.05 (m, 1H), 4.36 (d, *J* = 11.7 Hz, 1H), 4.52 (d, *J* = 11.7 Hz, 1H), 5.10 (d, *J* = 1.6 Hz, 1H), 5.14 (s, 1H), 7.26-7.35 (m, 5H). Minor isomer: 0.08 (s, 3H), 0.89 (s, 9H), 1.15 (d, *J* = 6.3 Hz, 3H), 1.32 (d, *J* = 6.6 Hz, 3H), 4.36 (d, *J* = 11.7 Hz, 1H), 4.53 (d, *J* = 11.7 Hz, 1H), 5.07 (d, *J* = 1.6 Hz, 1H); ^{13}C ($CDCl_3$, 63 MHz) δ (ppm): –4.8, –4.2, 18.0, 20.0, 20.1, 25.8, 35.3, 70.0, 71.5, 74.3, 78.4, 113.2, 127.7, 128.4, 138.7, 147.2; Minor isomer: 18.6, 20.3, 34.3, 74.6, 114.1.



(2*S*,6*S*)-6-(benzyloxy)-5-methyleneheptane-2,3-diol (39) and (40): Yield: 67%; *Rf* = 0.36 (EtOAc/hexanes 50%); ^{1}H NMR ($CDCl_3$, 300 MHz) δ (ppm): 1.18 (d, *J* = 6.6 Hz, 3H), 1.32 (d, *J* = 6.6 Hz, 3H), 2.14-2.45 (m, 2H), 3.61 (dt, *J* = 3.7, 8.8 Hz, 1H), 3.70 (br, 2H), 3.79-3.87 (m, 1H), 4.00 (q, *J* = 6.6 Hz, 1H), 4.41 (d, *J* = 11.7, 1H), 4.56 (d, *J* = 11.7, 1H), 5.07 (s, 1H), 5.10 (s, 1H), 7.27-7.37 (m, 5H). Minor isomer: 1.19 (d, *J* = 6.0 Hz, 3H), 1.33 (d, *J* = 6.6 Hz, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ (ppm): 17.4, 19.9, 33.6, 70.1, 74.6, 78.7, 115.9, 127.7, 128.5, 137.8, 146.8. Minor isomer: 19.2, 19.4, 35.6, 70.3, 78.5.

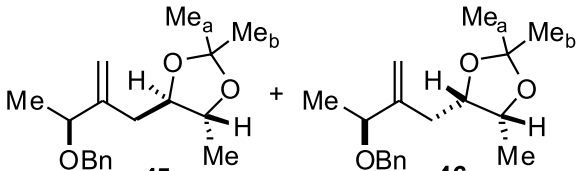


(4*R*,5*S*)-4-((*S*)-3-(benzyloxy)-2-methylenebutyl)-2,2,5-trimethyl-1,3-dioxolane (41) and (4*S*,5*S*)-4-((*S*)-3-(benzyloxy)-2-methylenebutyl)-2,2,5-trimethyl-1,3-dioxolane (42): Yield: 50%; *Rf* = 0.55 (EtOAc/hexanes 20%); IR (film) ν (cm^{-1}): 3055, 2986, 2934, 2872, 1647, 1454, 1371, 1086; ^{1}H NMR (C_6D_6, 300 MHz) δ (ppm): 1.01 (d, *J* = 6.2 Hz, 3H), 1.28 (d, *J* = 6.6 Hz, 3H), 1.31 (s, 3H), 1.48 (s, 3H), 2.10-2.33 (m, 2H), 3.55-3.93 (m, 1H), 3.91 (q, *J* = 6.6 Hz, 1H), 4.06 (apquint, *J* = 6.2 Hz, 1H), 4.30 (d, *J* = 12.0 Hz, 1H), 4.53 (d, *J* = 12.0 Hz, 1H), 5.10 (s, 1H), 5.14 (s, 1H), 7.07-7.37 (m, 5H). Minor isomer: 1.08 (d, *J* = 5.9 Hz, 3H), 1.39 (s, 3H), 1.41 (s, 3H), 3.75 (ddd, *J* = 3.3, 8.4 Hz, 1H), 4.21-4.40 (m, 2H); ^{13}C NMR (C_6D_6, 75 MHz) δ (ppm): 15.9, 20.6, 27.5, 27.6, 31.4, 70.1, 74.0, 76.9, 77.2, 81.1, 107.4, 112.9, 139.6, 147.1. Minor isomer: 17.6, 26.0, 28.9, 33.4, 78.9, 78.6, 108.0, 113.2.



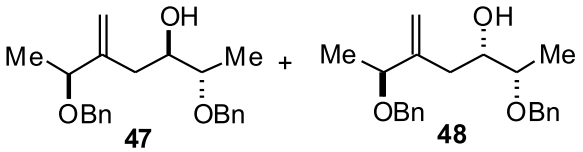
(2*R*,6*S*)-6-(benzyloxy)-5-methyleneheptane-2,3-diol (43) and (44): Yield: 90%; *Rf* = 0.40 (EtOAc/hexanes 50%); IR (film) ν (cm^{-1}): 3416, 3069, 2976, 2930, 2867, 1722, 1647, 1454, 1371, 1275, 1070; ^{1}H NMR ($CDCl_3$,

300 MHz) δ (ppm): 1.19 (d, J = 6.6 Hz, 3H), 1.34 (d, J = 6.6 Hz, 3H), 2.14-2.27 (m, 2H), 2.40 (d, J = 3.3 Hz, OH), 3.49-3.55 (m, 1H), 3.61 (apqt, J = 6.2 Hz, 1H), 4.01 (q, J = 6.6 Hz, 1H), 4.44 (d, J = 12.0 Hz, 1H), 4.52 (d, J = 12.0 Hz, 1H), 5.05 (s, 1H), 5.14 (s, 1H), 7.26-7.37 (m, 5H). Minor isomer: 1.18 (d, J = 6.6 Hz, 3H), 1.32 (d, J = 6.6 Hz, 3H), 2.44 (d, J = 3.3 Hz, OH), 3.80-3.88 (m, 1H), 5.11 (s, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ (ppm): 19.3, 19.5, 35.7, 70.3, 74.3, 78.5, 115.4, 127.7, 128.4, 137.8, 145.9. Minor isomer: 17.5, 20.0, 74.6, 78.7.



45 *trans* **46** *cis*

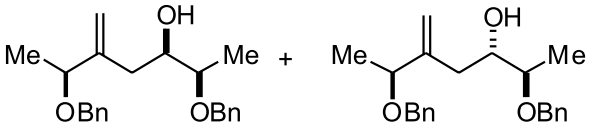
(4*R*,5*R*)-4-((*S*)-3-(benzyloxy)-2-methylenebutyl)-2,2,5-trimethyl-1,3-dioxolane (45) and (4*S*,5*R*)-4-((*S*)-3-(benzyloxy)-2-methylenebutyl)-2,2,5-trimethyl-1,3-dioxolane (46): Yield: 90%; *Rf* = 0.27 (EtOAc/hexanes 5%); IR (film) ν (cm^{-1}): 3053, 2963,2936, 2874, 1724, 1649, 1454, 1379, 1265, 1089, 912, 842; ^{1}H NMR ($CDCl_3$, 300 MHz) δ (ppm): 1.26 (d, J = 6.0 Hz, 3H), 1.31 (d, J = 6.6 Hz, 3H), 1.39 (s, 6H), 2.13-2.38 (m, 2H), 3.68-3.79 (m, 1H), 3.95-4.09 (m, 1H), 4.31-4.41 (m, 1H), 4.33 (d, J = 12.0 Hz, 1H), 4.50 (d, J = 12.0 Hz, 1H), 5.15 (s, 2H), 7.23-7.36 (m, 5H); Minor isomer: 0.99 (d, J = 6.6 Hz, 3H), 1.17 (d, J = 6.2 Hz, 3H), 1.35 (s, 3H), 1.46 (s, 3H), 5.06 (s, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ (ppm): 17.9, 20.5, 27.6, 33.5, 70.2, 78.7, 81.2, 108.1, 113.7, 127.8, 128.5, 138.8, 146.6. Minor isomer: 16.1, 19.5, 26.1, 28.9, 30.8, 72.0, 74.0, 76.2, 112.9, 115.1.



47 **48**

1,4-*syn*-1,2-*anti* 1,4-*anti*-**1,2-*syn***

(2*S*,3*R*,6*S*)-2,6-bis(benzyloxy)-5-methyleneheptan-3-ol (47) and (2*S*,3*S*,6*S*)-2,6-bis(benzyloxy)-5-methyleneheptan-3-ol (48): Yield: 70%; *Rf* = 0.55 (EtOAc/hexanes 20%); IR (film) ν (cm^{-1}): 3695, 3055, 2986, 2930, 2685, 1715, 1603, 1452, 1265, 1072, 744; ^{1}H NMR ($CDCl_3$, 250 MHz) δ (ppm): 1.20 (d, J = 6.3 Hz, 3H), 1.32 (d, J = 6.6 Hz, 3H), 2.12-2.46 (m, 2H), 3.51 (ddd, J = 4.3, 6.3, 12.6 Hz, 1H), 3.87-4.13 (m, 2H), 4.37 (d, J = 12.0, 1H), 4.49 (d, J = 11.7 Hz, 1H), 4.51 (d, J = 11.7 Hz, 1H), 4.61 (d, J = 11.7 Hz, 1H), 5.08 (s, 1H), 5.14 (s, 1H), 7.26-7.37 (m, 10H). Minor isomer: 1.22 (d, J = 6.3 Hz, 1H); ^{13}C NMR ($CDCl_3$, 63 MHz) δ (ppm): 14.1, 19.9, 34.1, 70.7, 72.0, 77.5, 78.5, 114.0, 127.6, 128.4, 138.6, 146.7.Minor isomer: 15.2, 20.3, 34.5, 70.0, 71.0, 73.3, 78.4, 79.4, 114.2, 127.5, 126.9, 138.5, 146.9.



49 **50**

1,4-*syn*-1,2-*syn* 1,4-*anti*-1,2-*anti*

(2*R*,3*R*,6*S*)-2,6-bis(benzyloxy)-5-methyleneheptan-3-ol (49) and (2*R*,3*S*,6*S*)-2,6-bis(benzyloxy)-5-methyleneheptan-3-ol (50): Yield: 88%; *Rf* = 0.55 (EtOAc/hexanes 10%); ^{1}H NMR ($CDCl_3$, 250 MHz) δ (ppm): 1.22 (d, J = 6.3 Hz, 3H), 1.32 (d, J = 6.3 Hz, 3H), 2.11-2.42 (m, 1H), 3.42-3.54 (m,1H), 3.68-3.83 (m,1H), 3.93- 4.08 (m, 1 H), 4.34- 4.69 (m, 4H), 5.09 (d, J = 15 Hz, 1H), 5.14 (d, J = 5.4 Hz, 1H), 7.23-7.35 (m, 10H). Minor isomer: 1.23 (d, J = 6.3 Hz, 1H); ^{13}C NMR ($CDCl_3$, 63 MHz) δ (ppm): 15.6, 20.2, 34.9, 70.0, 71.1, 73.4, 77.8, 78.4, 113.5, 127.7, 127.8, 128.3, 128.4, 138.6, 146.9. Minor isomer: 14.7, 34.7, 70.9, 73.0, 114.6, 127.4, 127.5, 138.3.

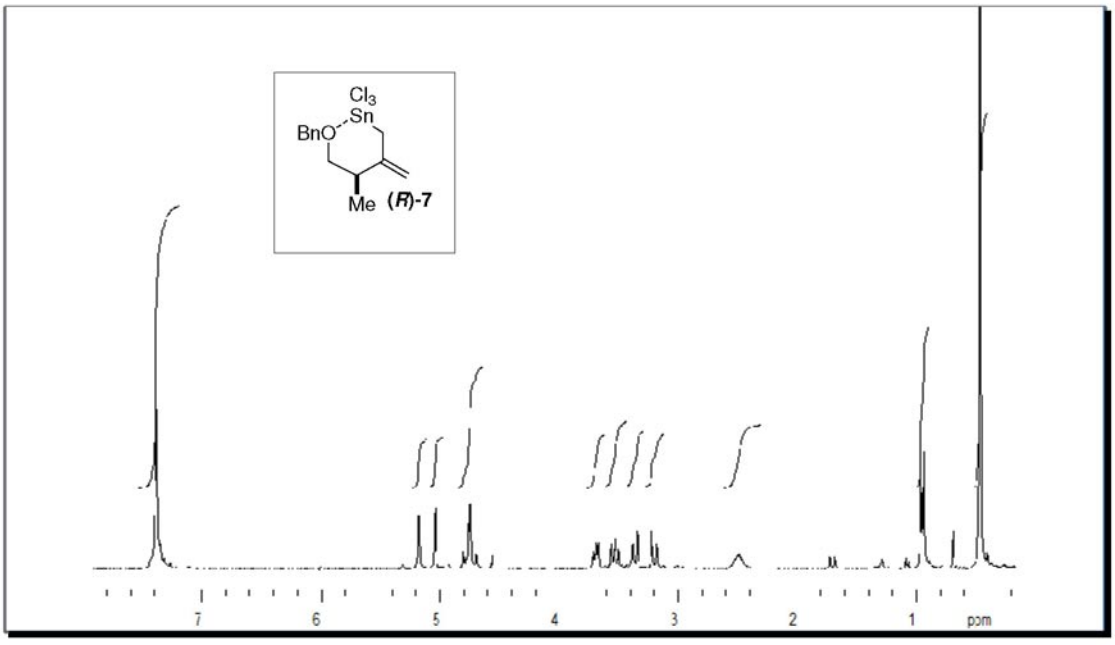


Figure 1S. ^{1}H NMR ($CDCl_3$, 300 MHz) - (*R*)-(4-(benzyloxy)-3-methyl-2-methylenebutyl)trichlorostannane (**7**).

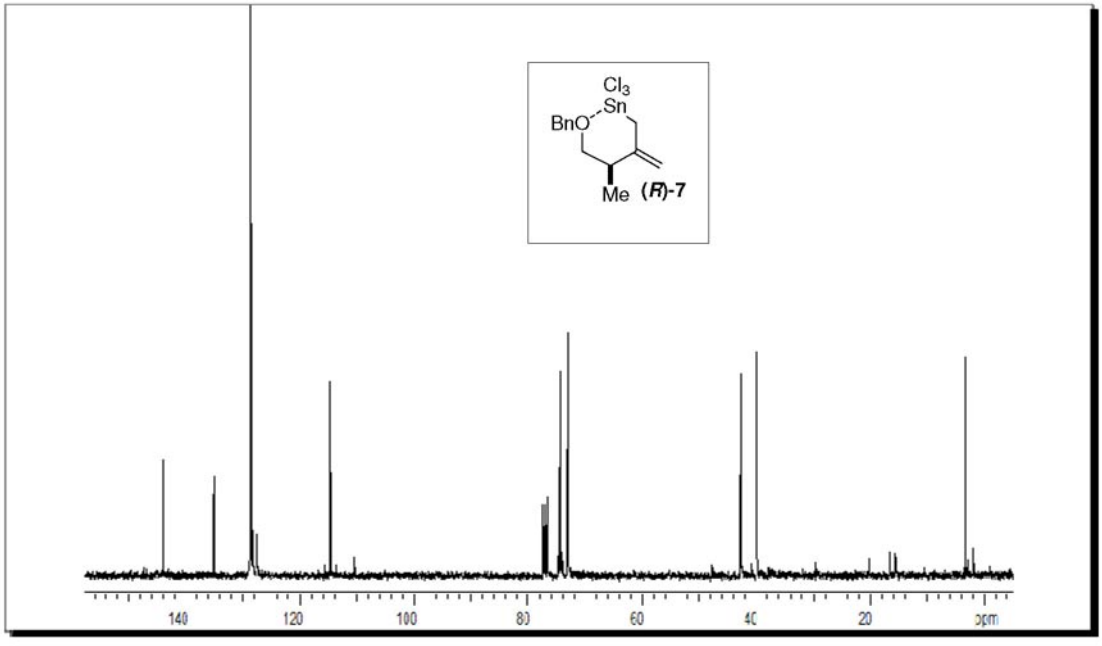


Figure 2S. ^{13}C NMR ($CDCl_3$, 75 MHz) - (*R*)-(4-(benzyloxy)-3-methyl-2-methylenebutyl)trichlorostannane (**7**).

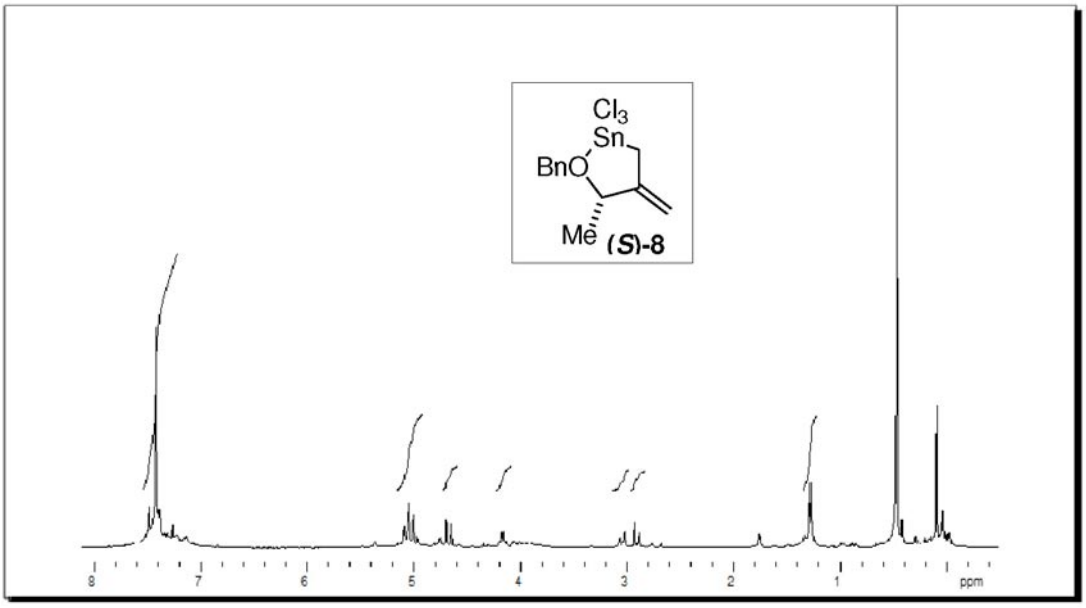


Figure 3S. ^{1}H NMR ($CDCl_3$, 300 MHz) - (*S*)-(3-(benzyloxy)-2-methylenebutyl)trichlorostannane (**8**).

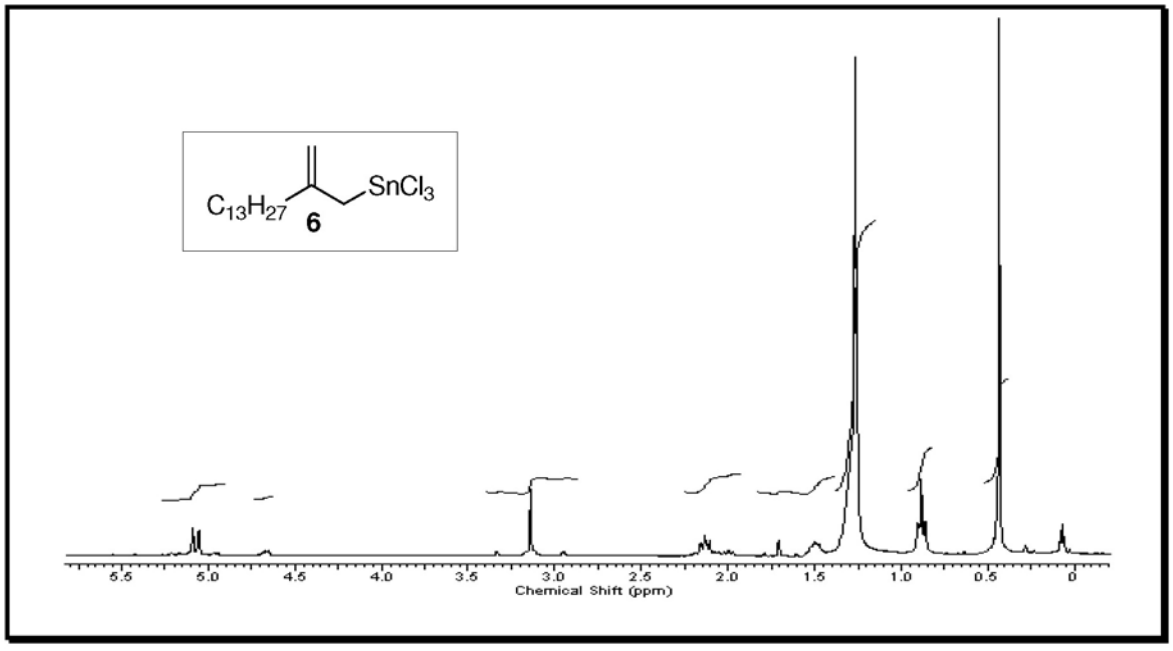


Figure 4S. ^{1}H NMR ($CDCl_3$, 300 MHz) - Trichloro(2-methylenepentadecyl)stannane (**6**).

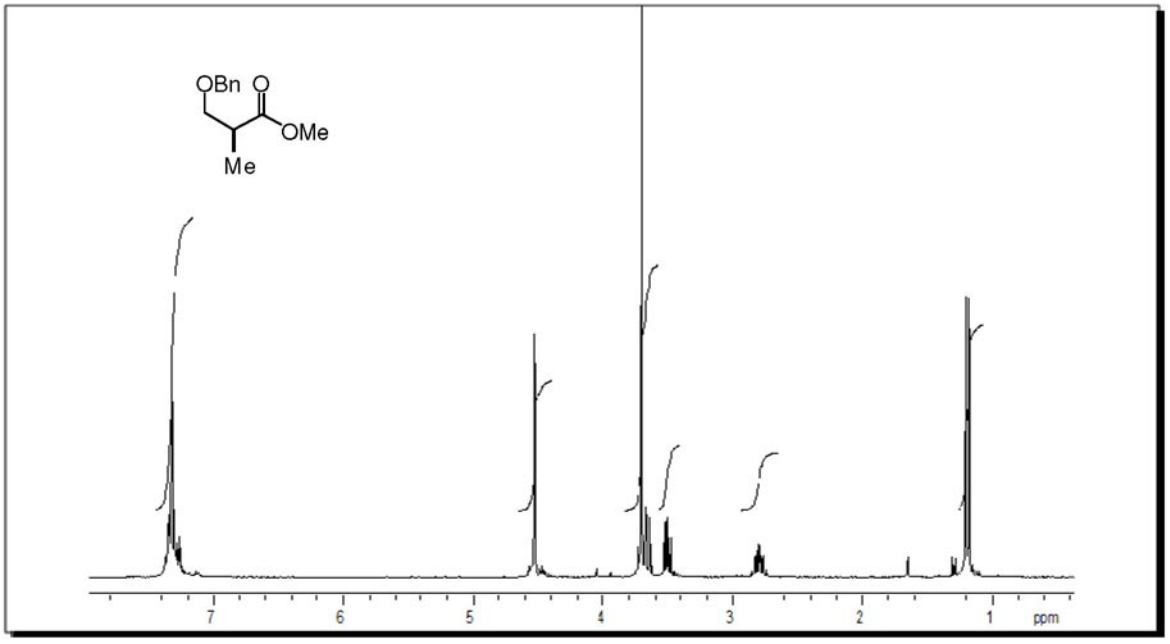


Figure 5S. ^{1}H NMR ($CDCl_3$, 300 MHz).

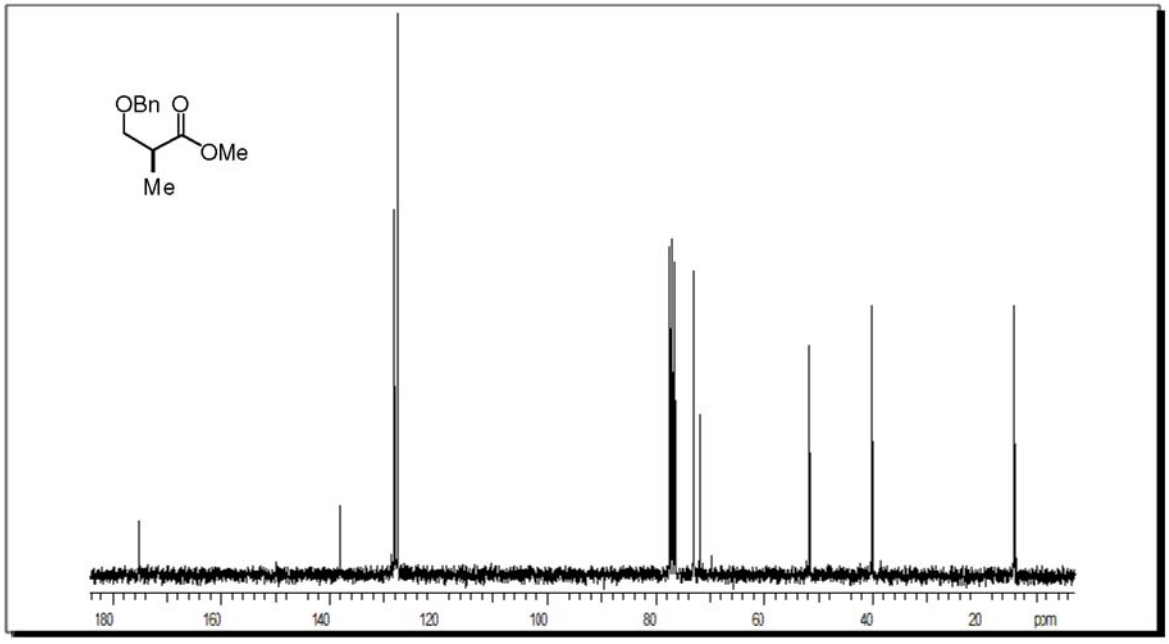


Figure 6S. ^{13}C NMR ($CDCl_3$, 75 MHz).

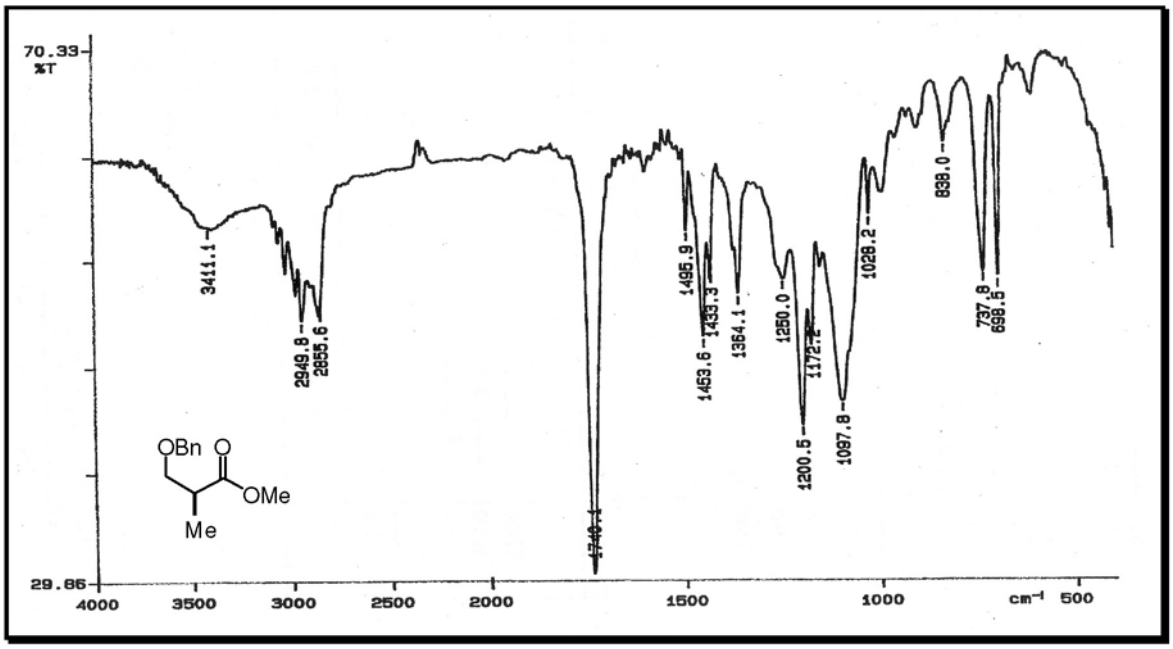


Figure 7S. IR (film).

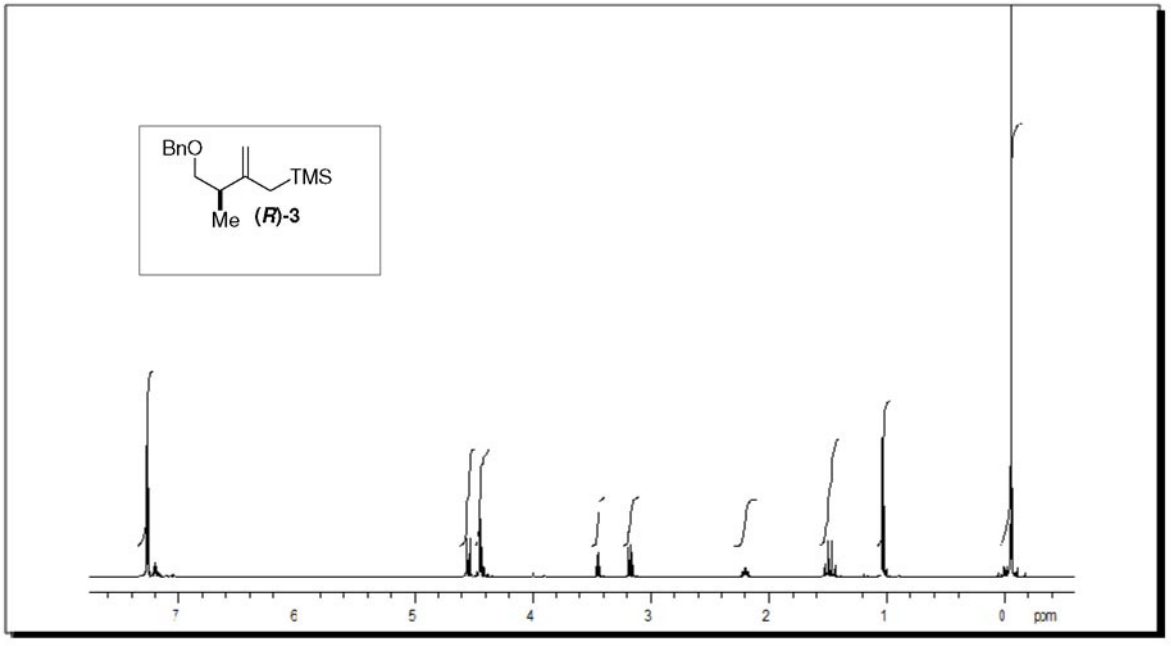


Figure 8S. ^{1}H NMR ($CDCl_3$, 300 MHz) - (*R*)-(4-(benzyloxy)-3-methyl-2-methylenebutyl)trimethylsilane (**3**).

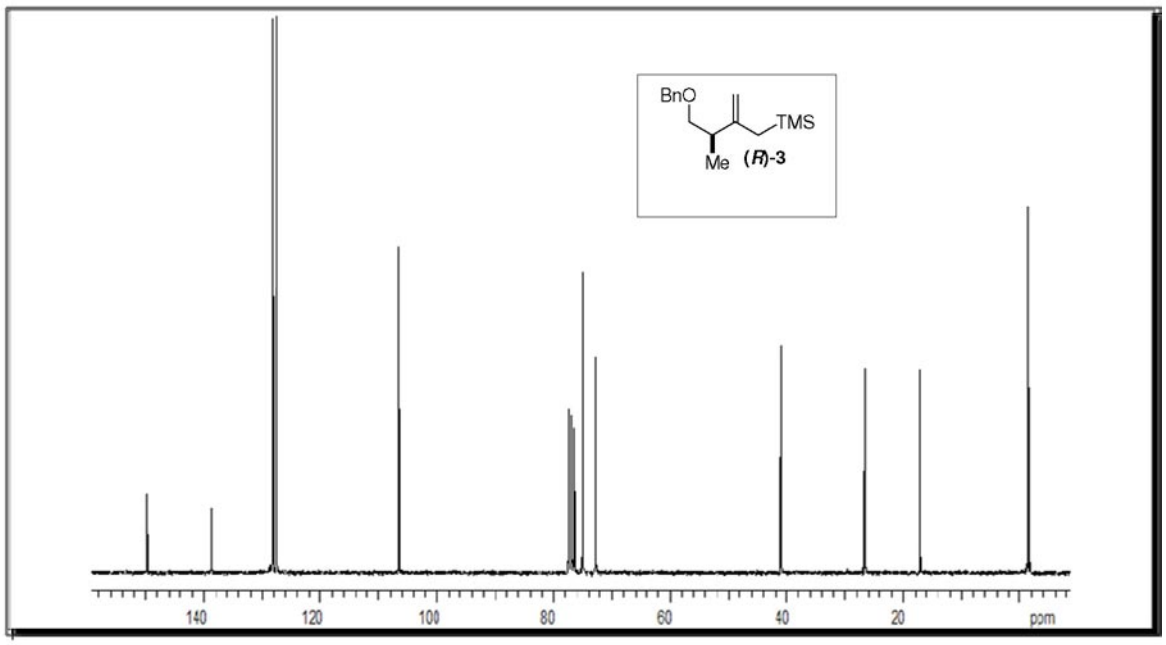


Figure 9S. ^{13}C NMR ($CDCl_3$, 75 MHz) - (*S*)-(3-(benzyloxy)-2-methylenebutyl)trimethylsilane (**4**).

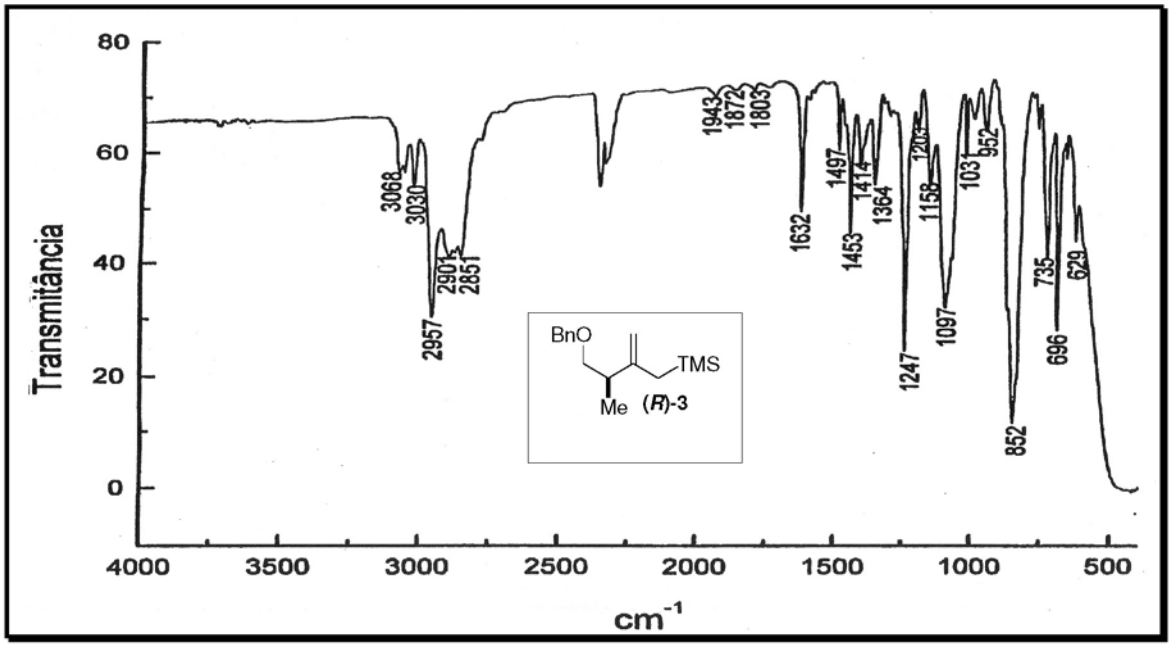


Figure 10S. IR (film) - (*S*)-(3-(benzyloxy)-2-methylenebutyl)trimethylsilane (**4**).

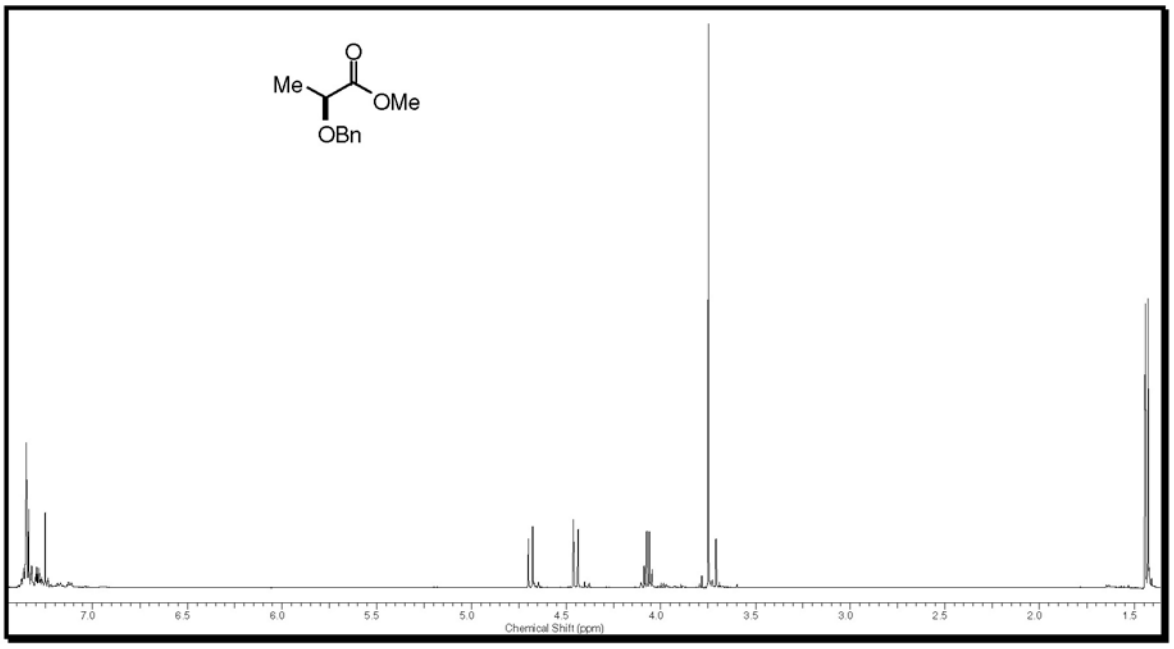


Figure 11S. ^{1}H NMR ($CDCl_3$, 300 MHz).

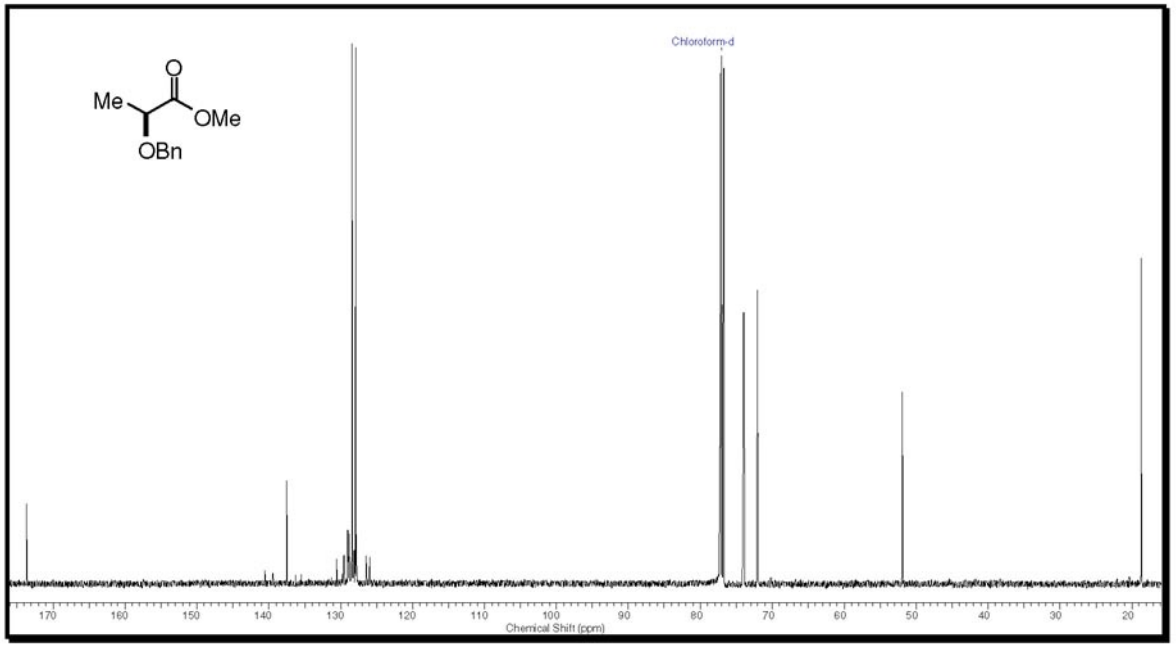


Figure 12S. ^{13}C NMR ($CDCl_3$, 75 MHz).

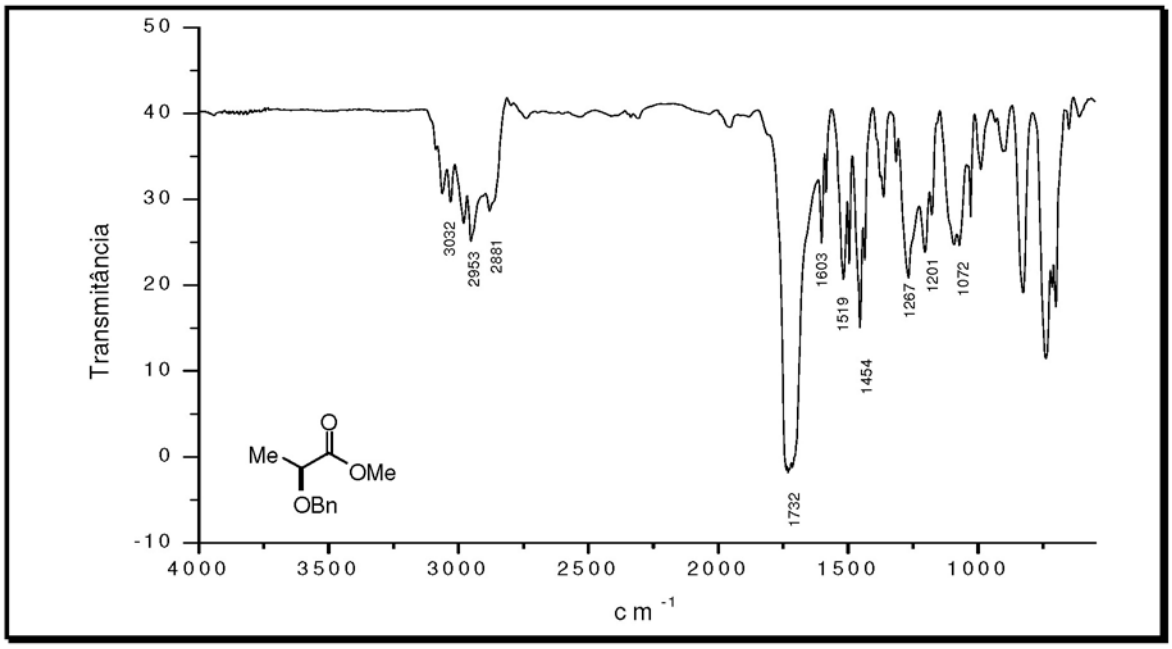


Figure 13S. IR (film).

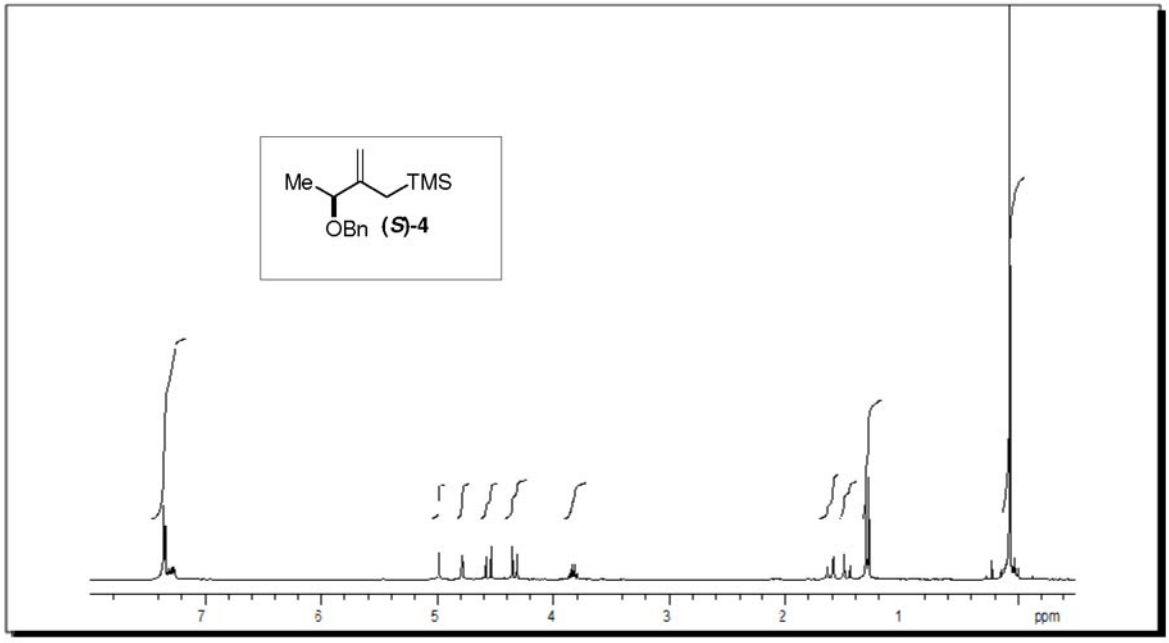


Figure 14S. ^{1}H NMR ($CDCl_3$, 300 MHz) - (*S*)-(3-(benzyloxy)-2-methylenebutyl)trimethylsilane (**4**).

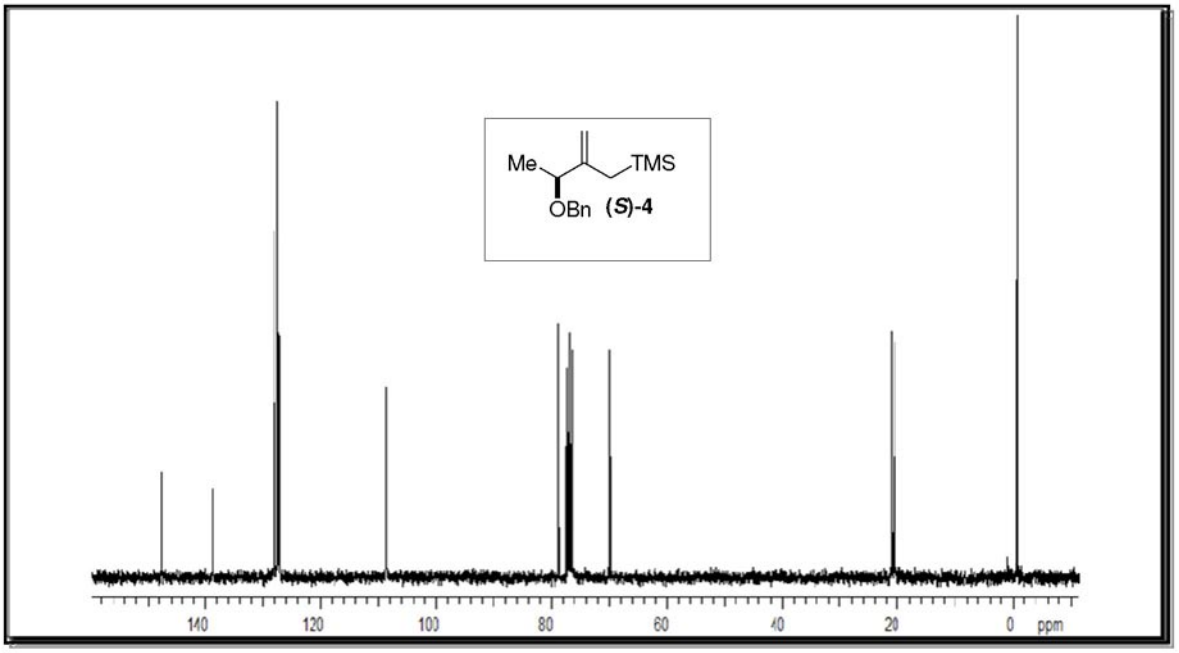


Figure 15S. ^{13}C NMR ($CDCl_3$, 75 MHz) - (*S*)-(3-(benzyloxy)-2-methylenebutyl)trimethylsilane (**4**).

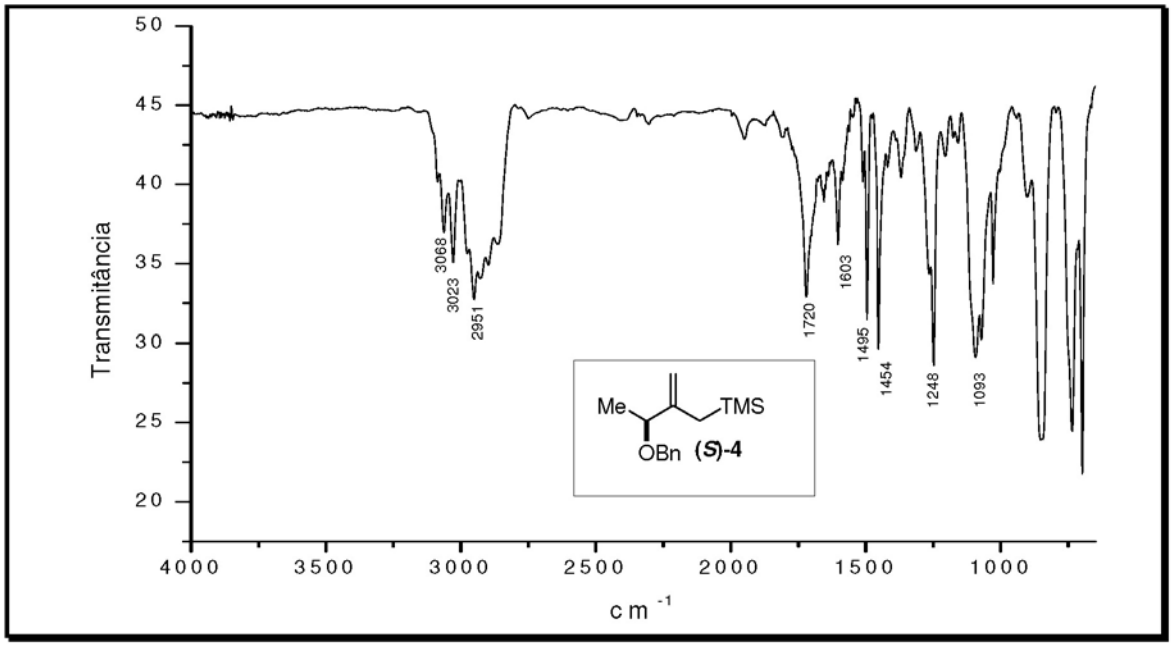


Figure 16S. IR (film) - (*S*)-(3-(benzyloxy)-2-methylenebutyl)trimethylsilane (**4**).

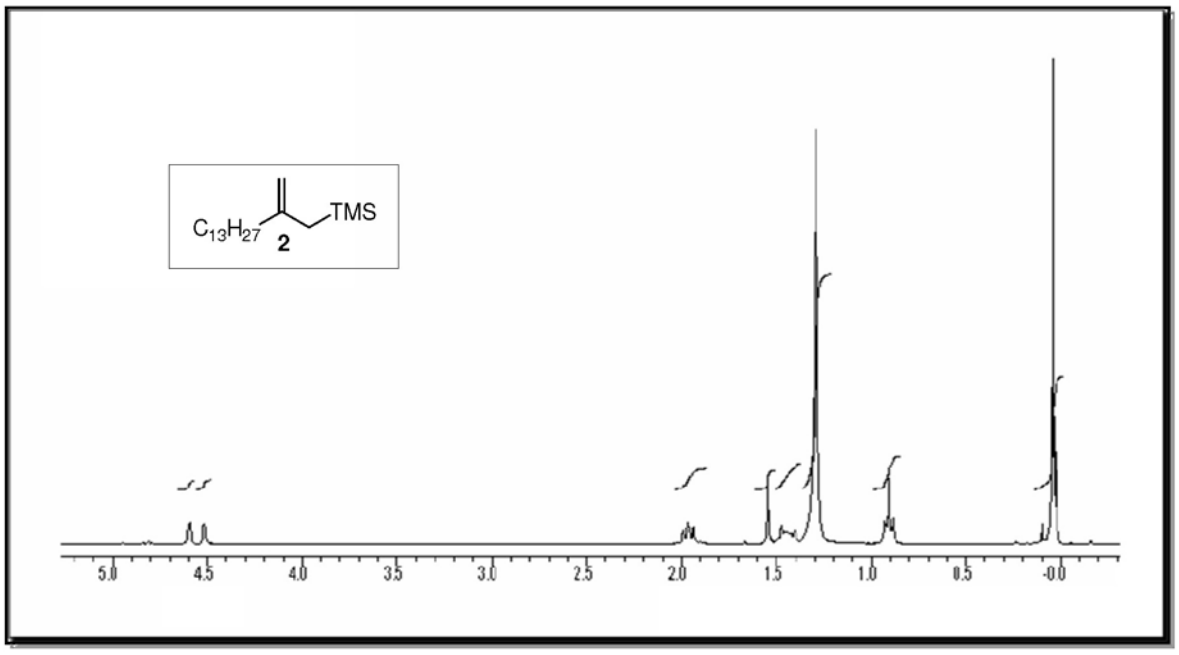


Figure 17S. ^{1}H NMR ($CDCl_3$, 300 MHz) - Trimethyl(2-methylenepentadecyl)silane (**2**).

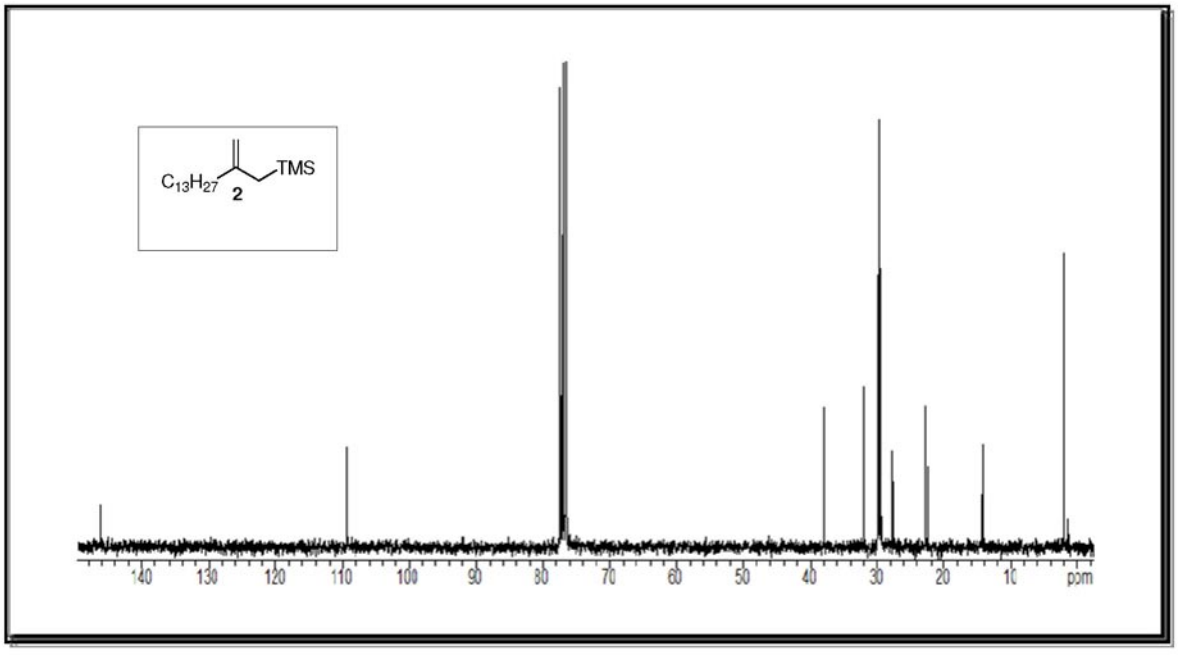


Figure 18S. ^{13}C NMR ($CDCl_3$, 75 MHz) - Trimethyl(2-methylenepentadecyl)silane (**2**).

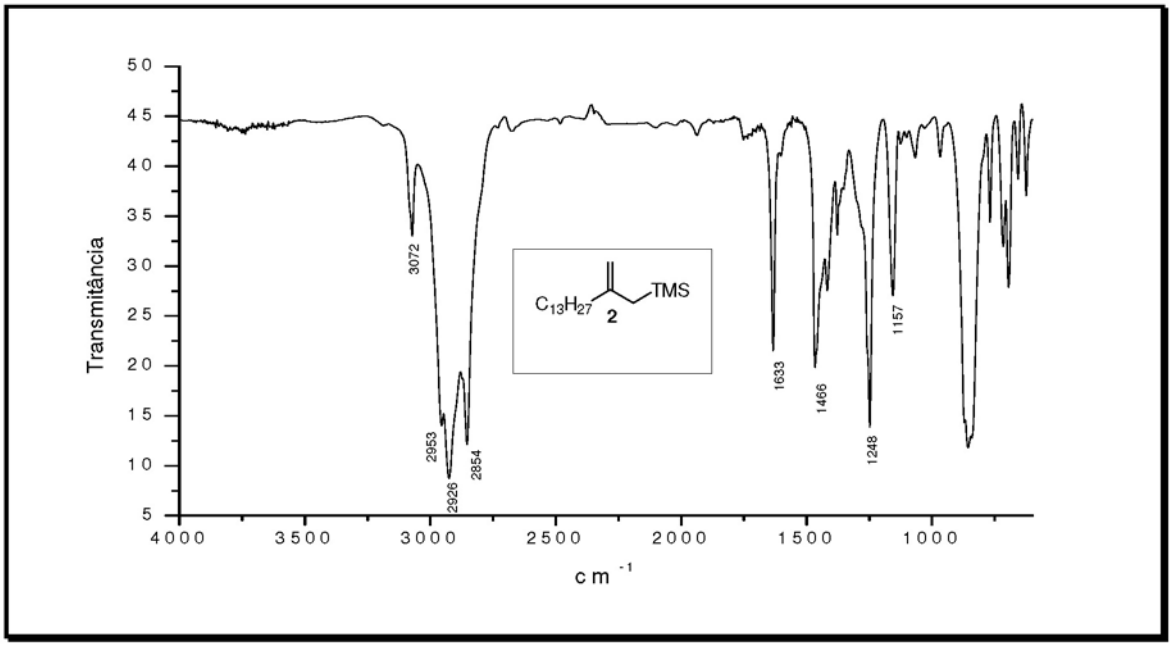


Figure 19S. IR (film) - Trimethyl(2-methylenepentadecyl)silane (**2**).

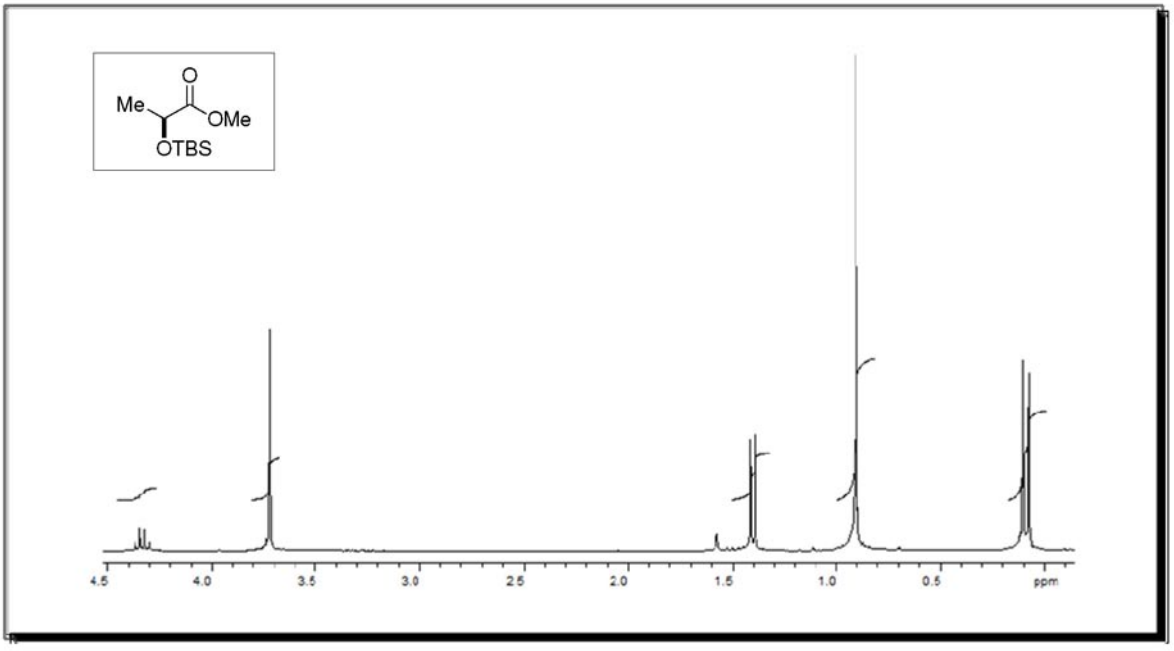


Figure 20S. ^{1}H NMR ($CDCl_3$, 300 MHz).

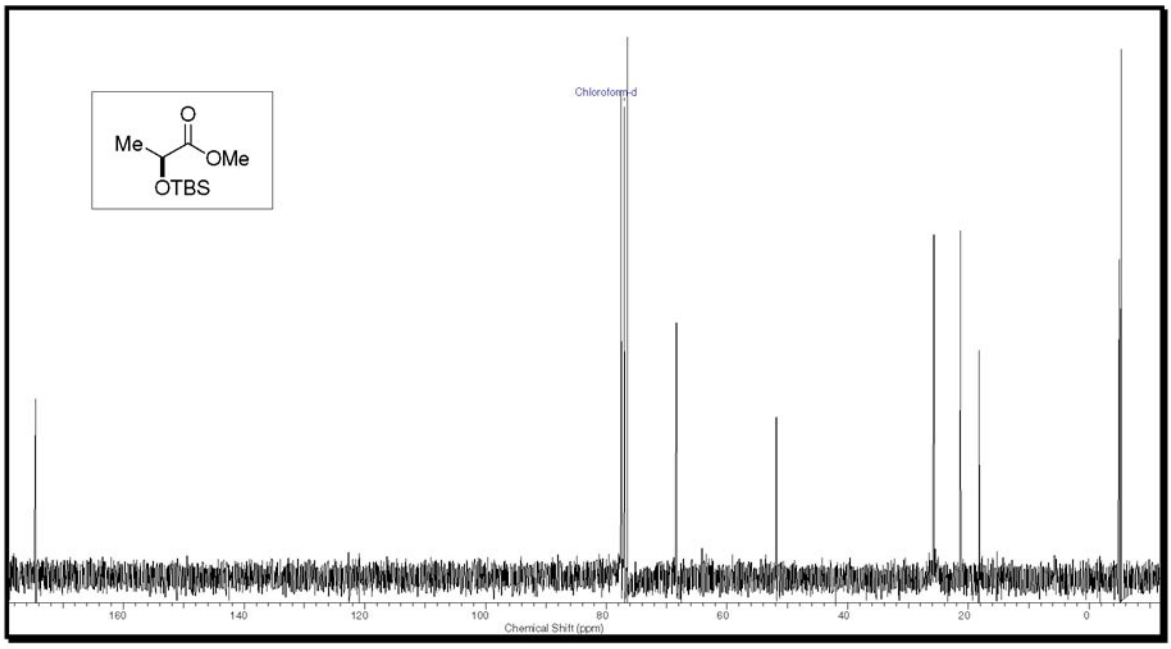


Figure 21S. ^{13}C NMR ($CDCl_3$, 63 MHz).

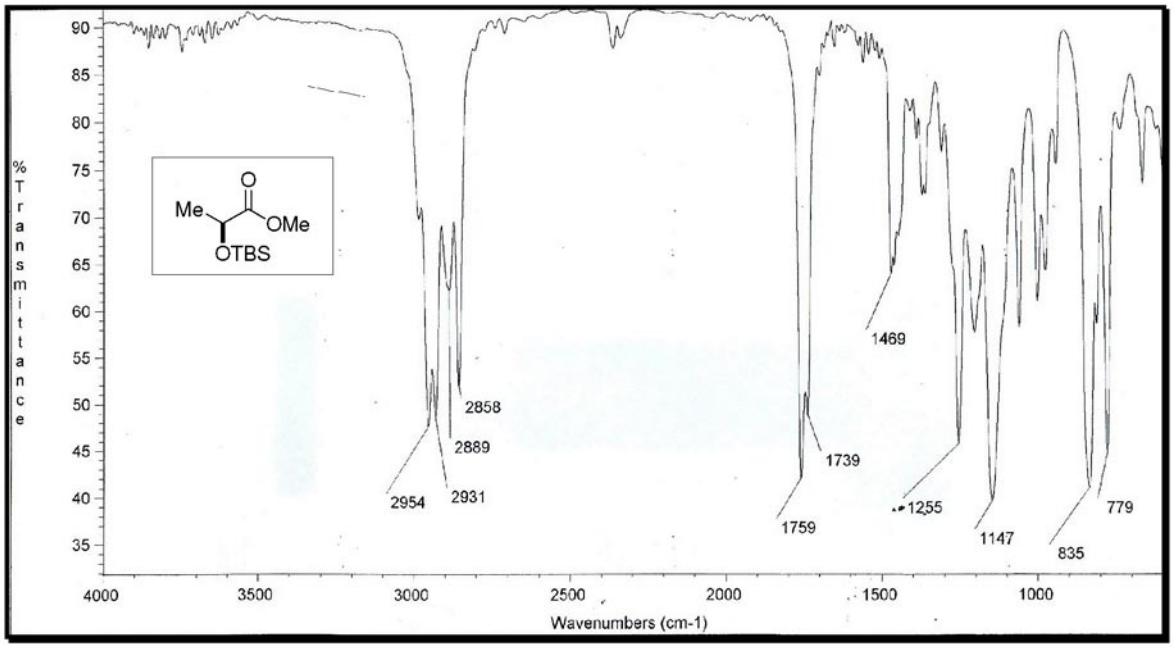


Figure 22S. IR (film).

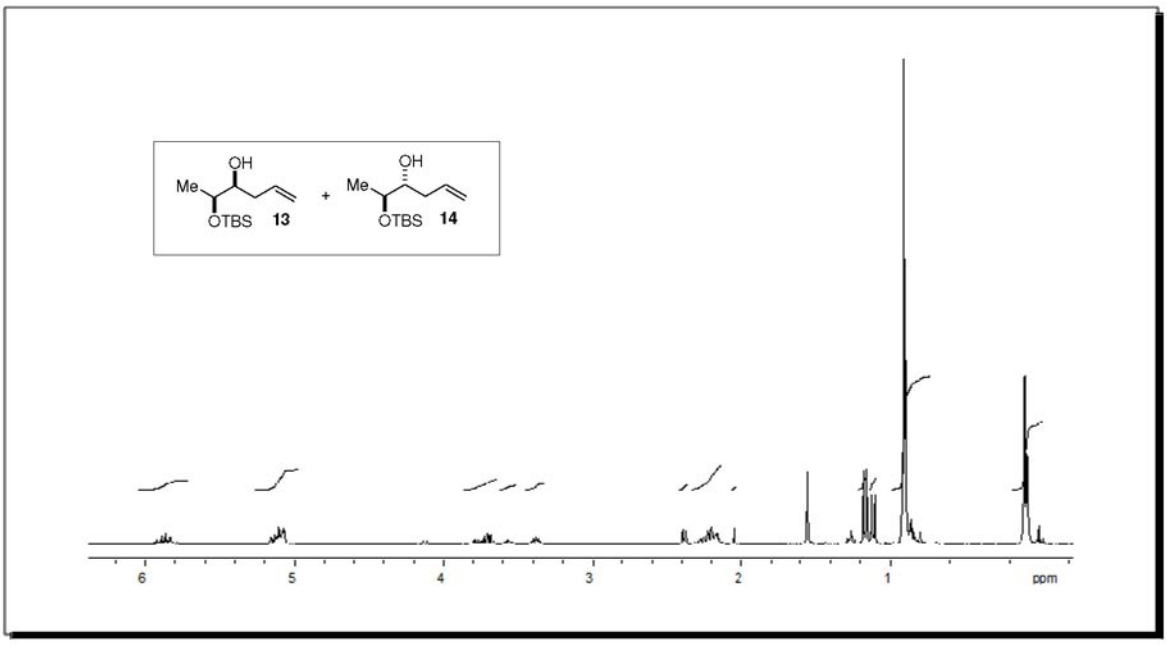


Figure 23S. ^{1}H NMR ($CDCl_3$, 300 MHz) - (2*S*,3*S*)-2-(*tert*-butyldimethylsilyloxy)hex-5-en-3-ol (**13**) and (2*S*,3*R*)-2-(*tert*-butyldimethylsilyloxy)hex-5-en-3-ol (**14**).

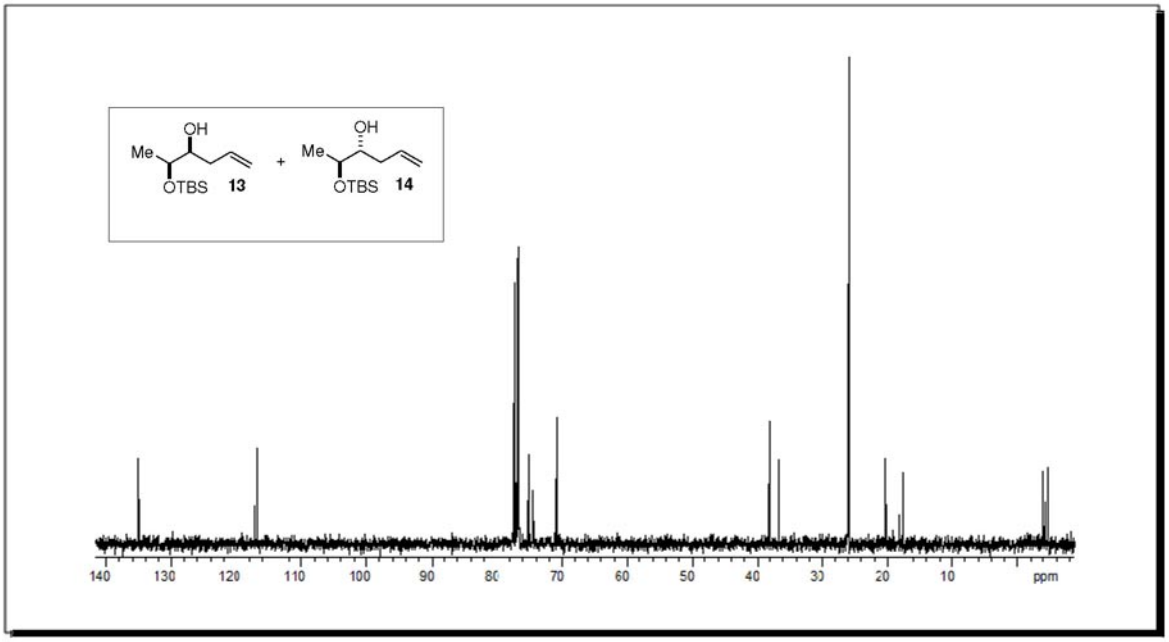


Figure 24S. ^{13}C NMR ($CDCl_3$, 75 MHz) - (2*S*,3*S*)-2-(*tert*-butyldimethylsilyloxy)hex-5-en-3-ol (**13**) and (2*S*,3*R*)-2-(*tert*-butyldimethylsilyloxy)hex-5-en-3-ol (**14**).

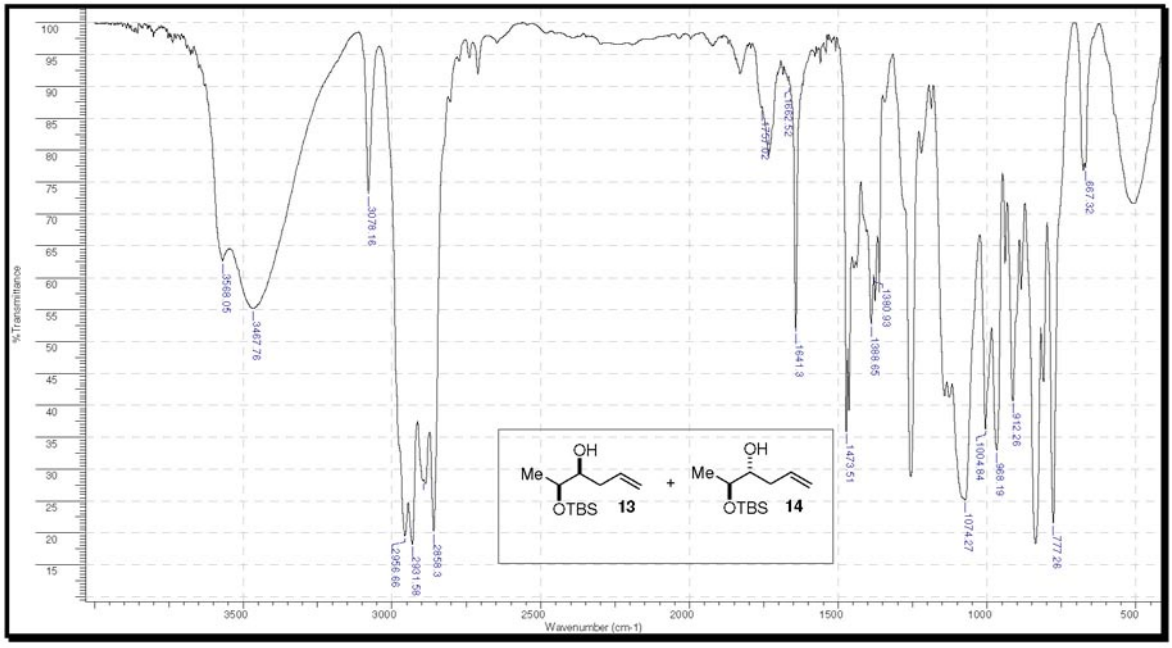


Figure 25S. IR (film) - (2*S*,3*S*)-2-(*tert*-butyldimethylsilyloxy)hex-5-en-3-ol (**13**) and (2*S*,3*R*)-2-(*tert*-butyldimethylsilyloxy)hex-5-en-3-ol (**14**).

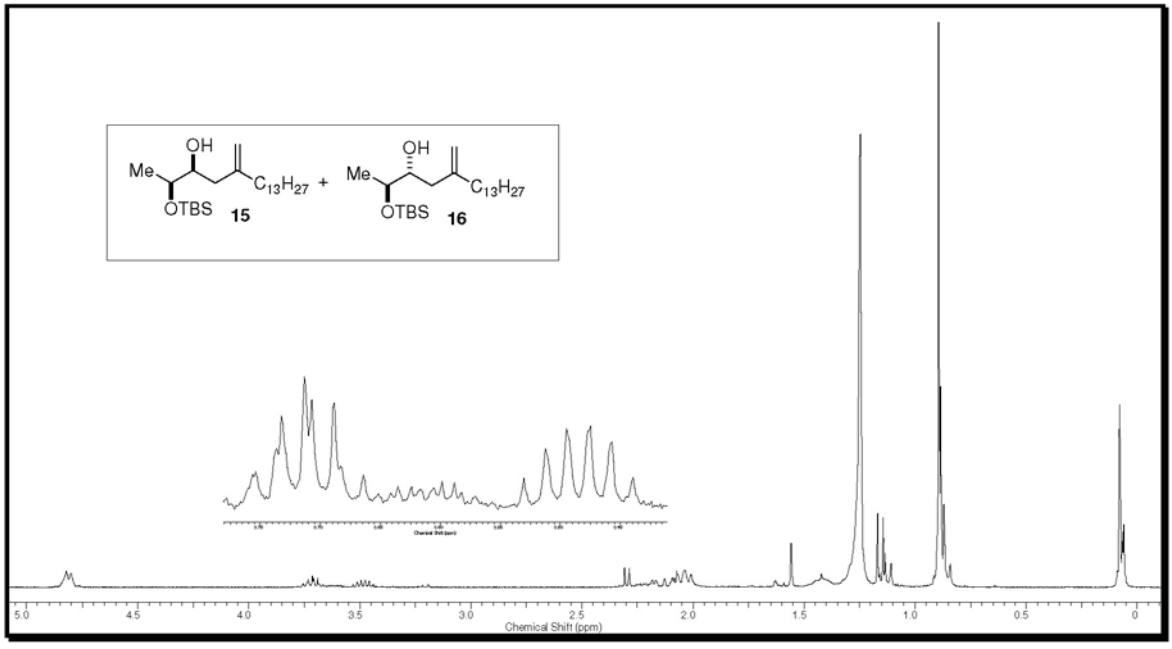


Figure 26S. ^{1}H NMR ($CDCl_3$, 300 MHz) - (2*S*,3*S*)-2-(*tert*-butyldimethylsilyloxy)-5-methyleneoctadecan-3-ol (**15**) and (2*S*,3*R*)-2-(*tert*-butyldimethylsilyloxy)-5-methyleneoctadecan-3-ol (**16**).

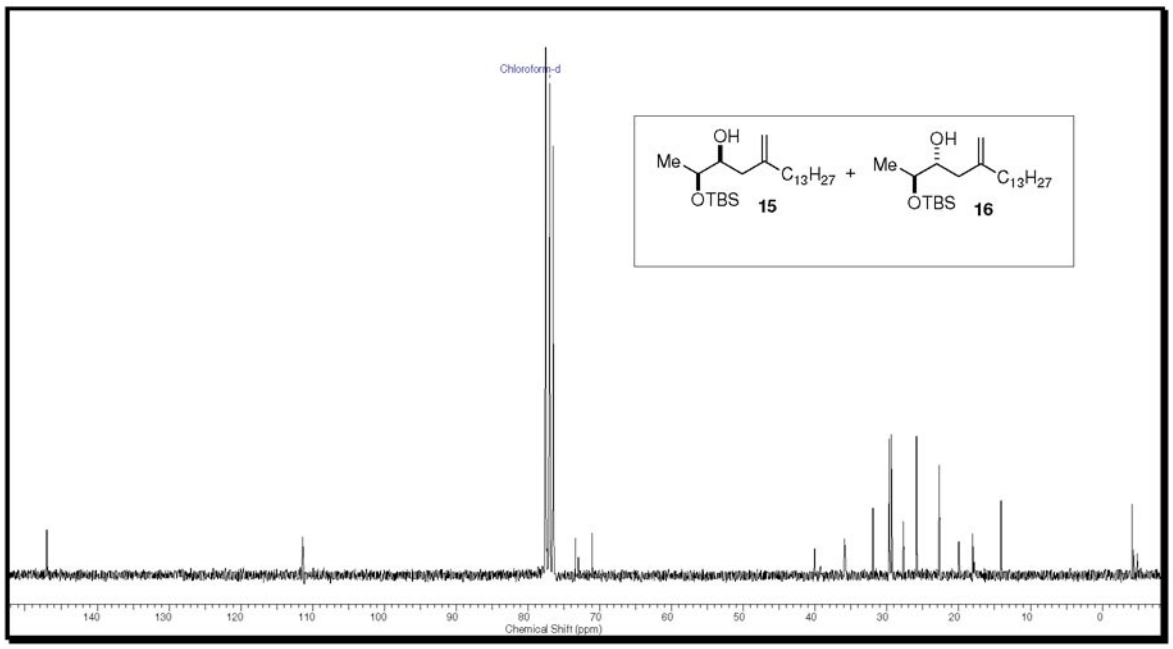


Figure 27S. ^{13}C NMR ($CDCl_3$, 63 MHz) - (2*S*,3*S*)-2-(*tert*-butyldimethylsilyloxy)-5-methyleneoctadecan-3-ol (**15**) and (2*S*,3*R*)-2-(*tert*-butyldimethylsilyloxy)-5-methyleneoctadecan-3-ol (**16**).

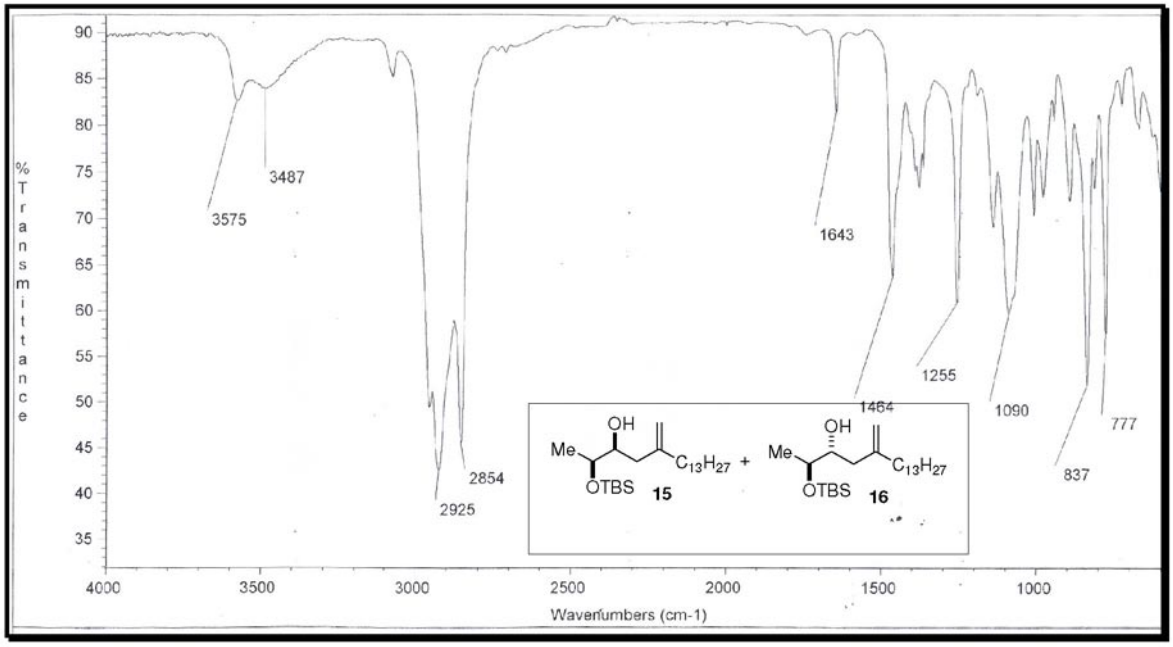


Figure 28S. IR (film) - (2*S*,3*S*)-2-(*tert*-butyldimethylsilyloxy)-5-methyleneoctadecan-3-ol (**15**) and (2*S*,3*R*)-2-(*tert*-butyldimethylsilyloxy)-5-methyleneoctadecan-3-ol (**16**).

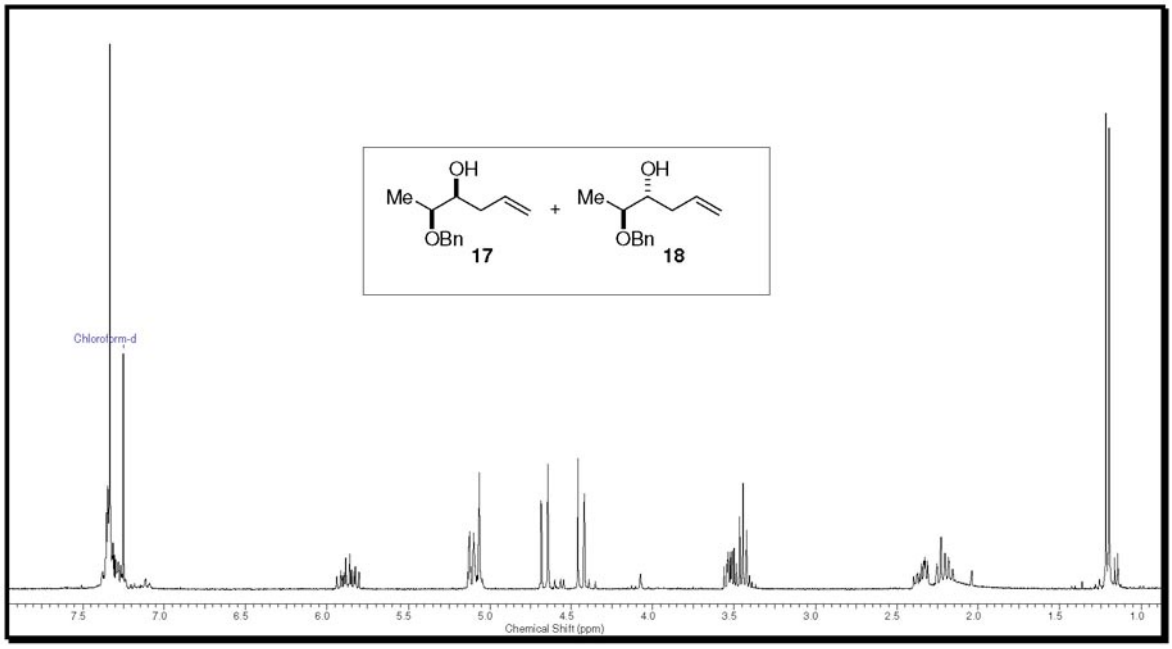


Figure 29S. ^{1}H NMR ($CDCl_3$, 500 MHz) (2*S*,3*S*)-2-(benzyloxy)hex-5-en-3-ol (**17**) and (2*S*,3*R*)-2-(benzyloxy)hex-5-en-3-ol (**18**).

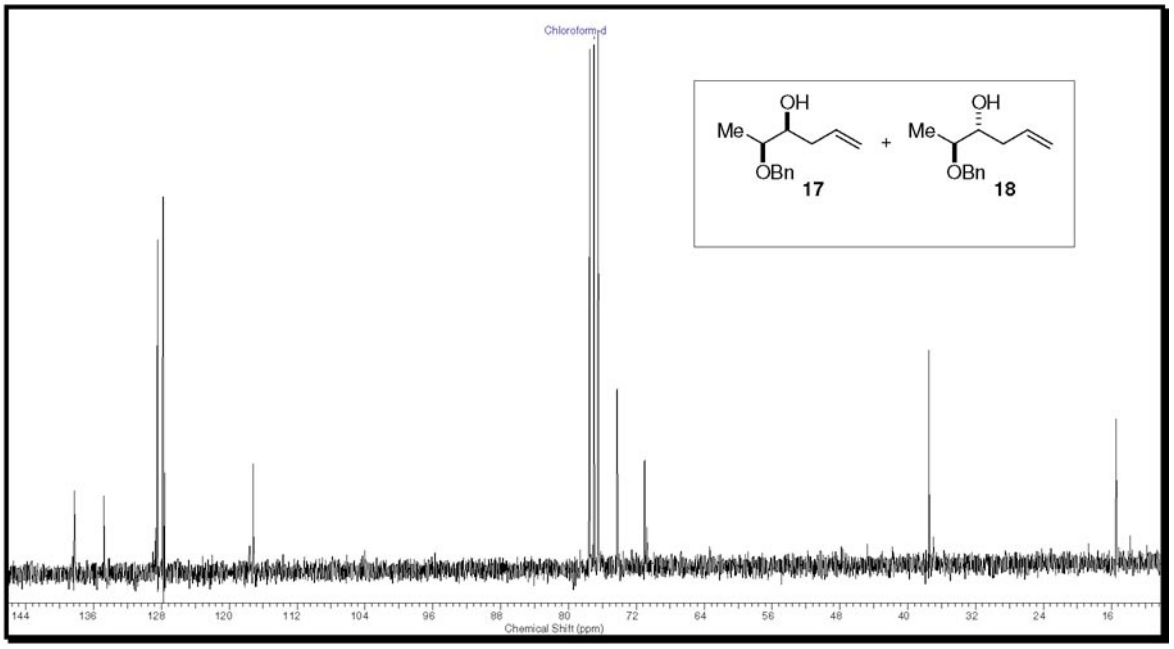


Figure 30S. ^{13}C NMR ($CDCl_3$, 63 MHz) - (2*S*,3*S*)-2-(benzyloxy)hex-5-en-3-ol (**17**) and (2*S*,3*R*)-2-(benzyloxy)hex-5-en-3-ol (**18**).

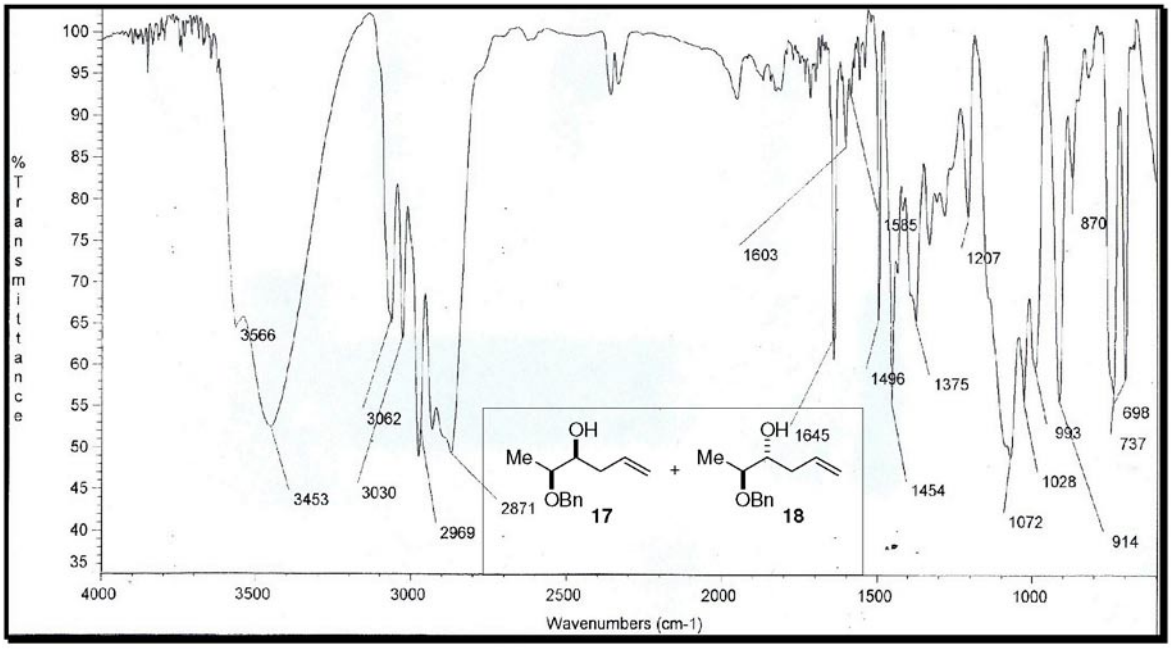


Figure 31S. IR (film) - (2*S*,3*S*)-2-(benzyloxy)hex-5-en-3-ol (**17**) and (2*S*,3*R*)-2-(benzyloxy)hex-5-en-3-ol (**18**).

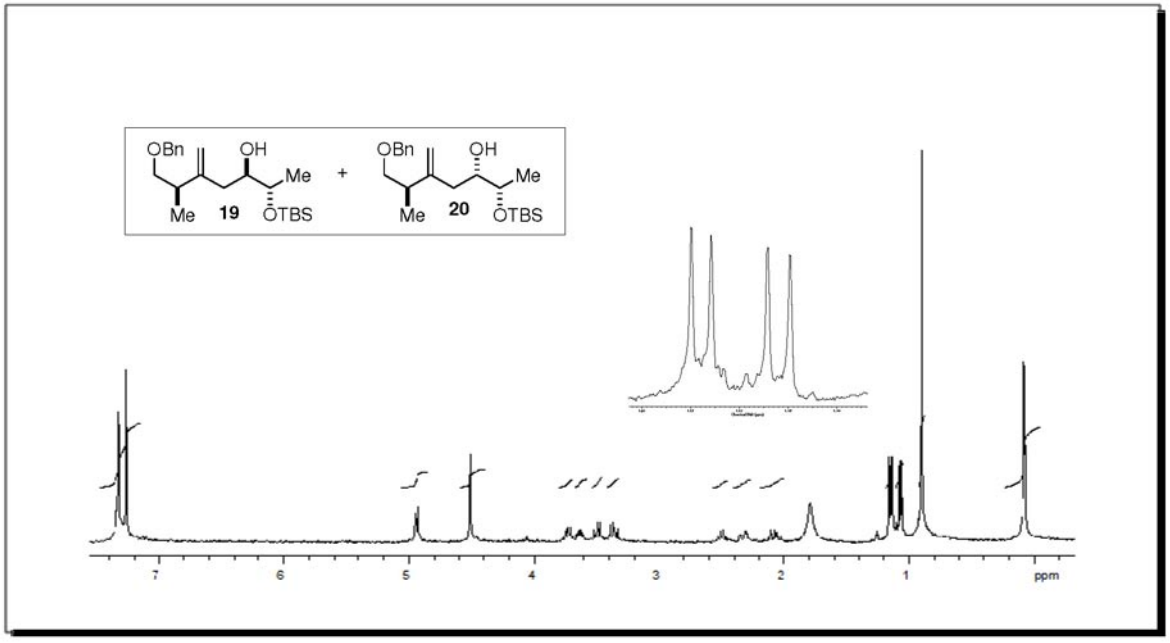


Figure 32S. ^{1}H NMR ($CDCl_3$, 300 MHz) - (2*S*,3*R*,6*R*)-7-(benzyloxy)-2-(*tert*-butyldimethylsilyloxy)-6-methyl-5-methyleneheptan-3-ol (**19**) and (2*S*,3*S*,6*R*)-7-(benzyloxy)-2-(*tert*-butyldimethylsilyloxy)-6-methyl-5-methyleneheptan-3-ol (**20**).

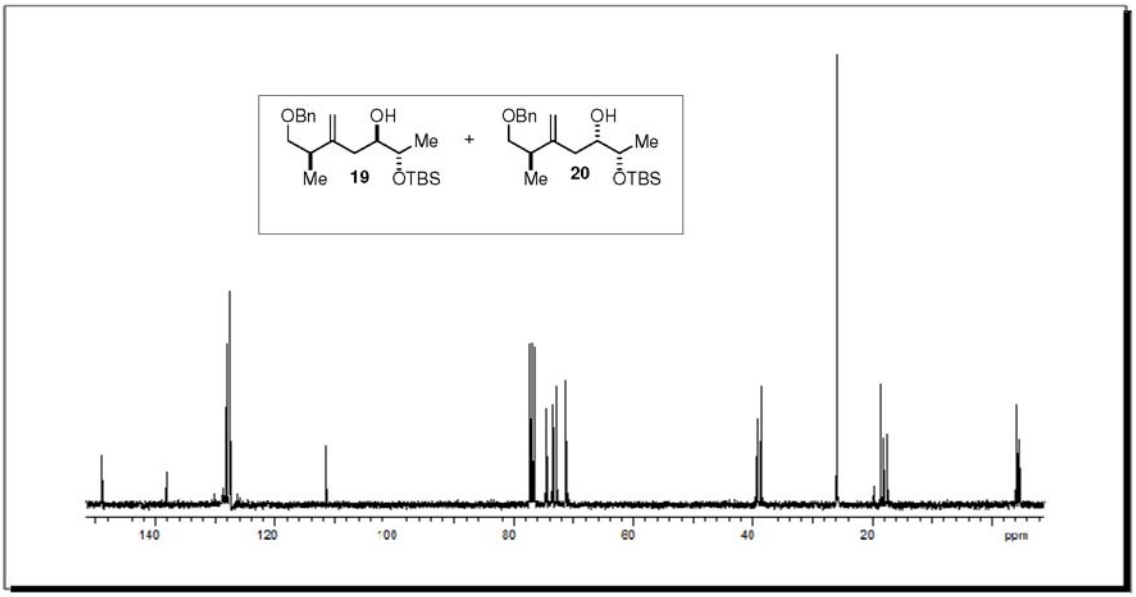


Figure 33S. ^{13}C NMR ($CDCl_3$, 75 MHz) - (2*S*,3*R*,6*R*)-7-(benzyloxy)-2-(*tert*-butyldimethylsilyloxy)-6-methyl-5-methyleneheptan-3-ol (**19**) and (2*S*,3*S*,6*R*)-7-(benzyloxy)-2-(*tert*-butyldimethylsilyloxy)-6-methyl-5-methyleneheptan-3-ol (**20**).

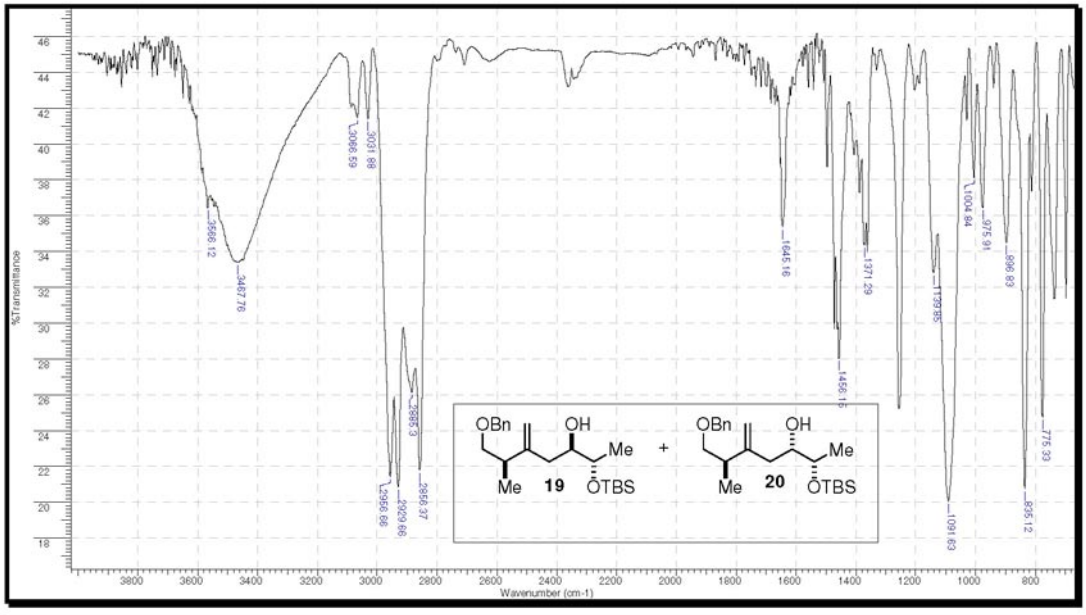


Figure 34S. IR (film) - (2*S*,3*R*,6*R*)-7-(benzyloxy)-2-(*tert*-butyldimethylsilyloxy)-6-methyl-5-methyleneheptan-3-ol (**19**) and (2*S*,3*S*,6*R*)-7-(benzyloxy)-2-(*tert*-butyldimethylsilyloxy)-6-methyl-5-methyleneheptan-3-ol (**20**).

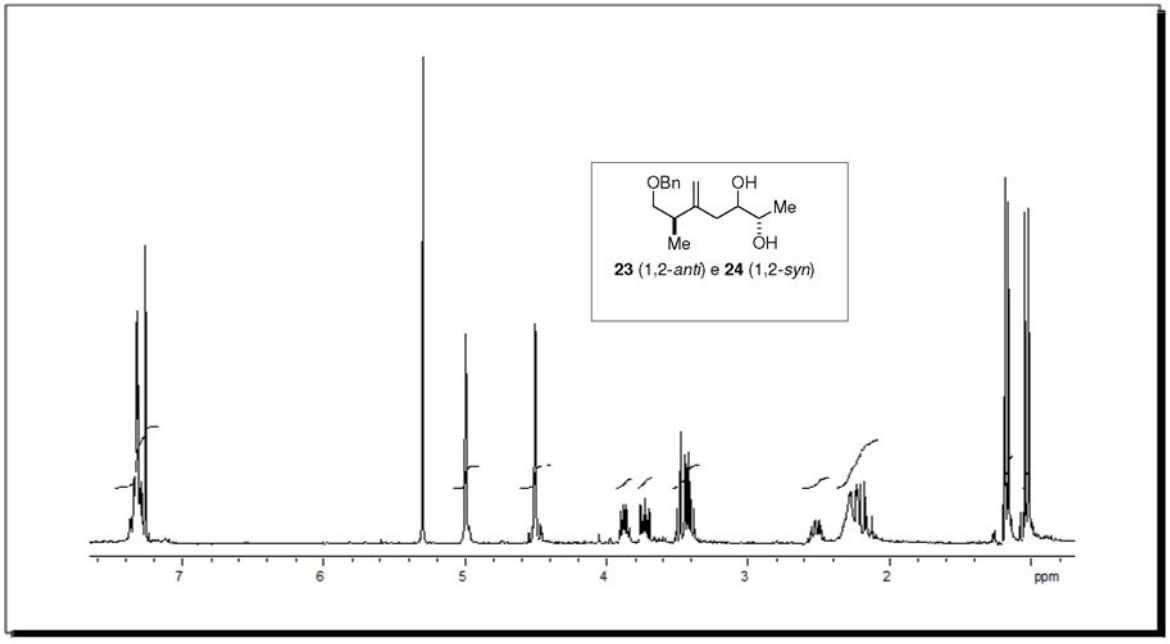


Figure 35S. ^{1}H NMR ($CDCl_3$, 300 MHz) - (2*S*,6*R*)-7-(benzyloxy)-6-methyl-5-methyleneheptane-2,3-diols (**23**) and (**24**).

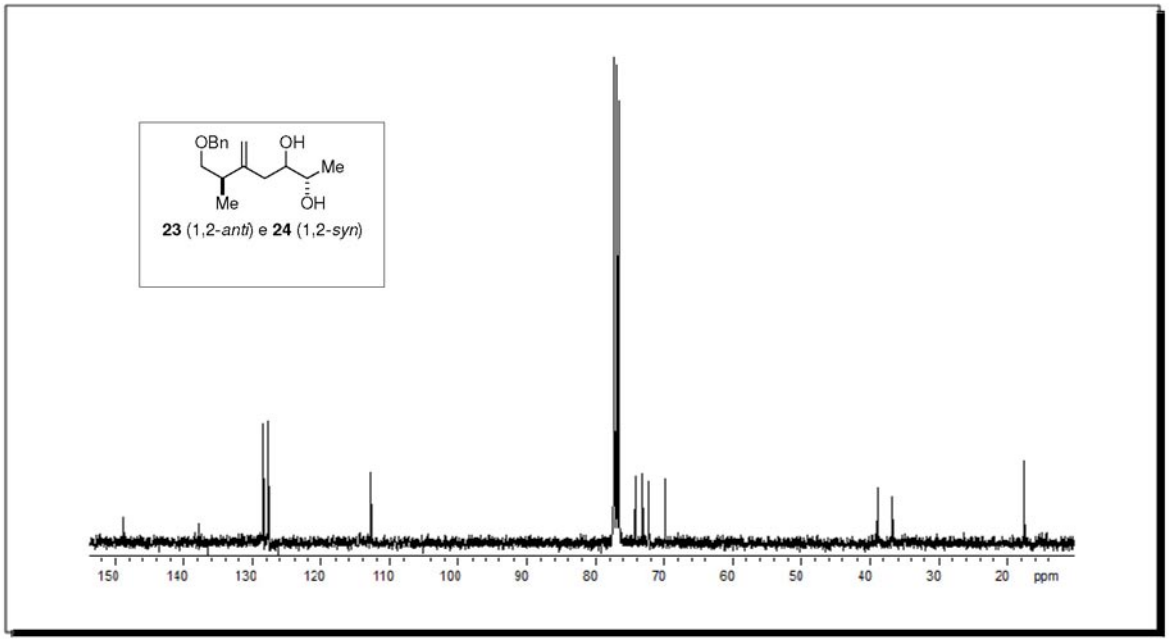


Figure 36S. ^{13}C NMR ($CDCl_3$, 75 MHz) - (2*S*,6*R*)-7-(benzyloxy)-6-methyl-5-methyleneheptane-2,3-diols (**23**) and (**24**).

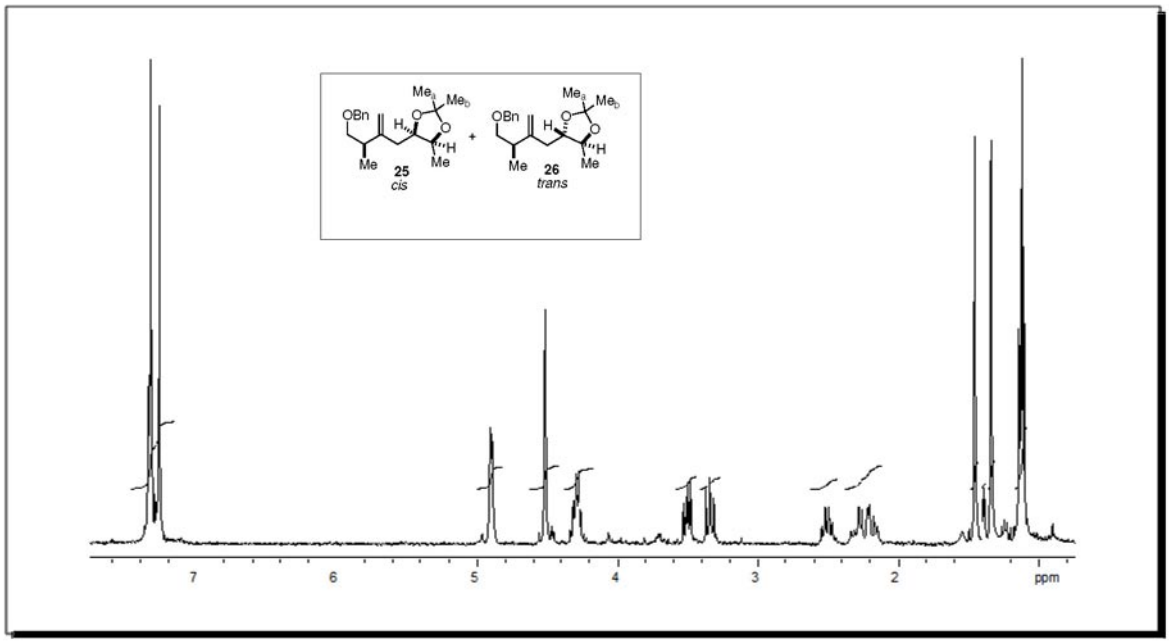


Figure 37S. ^{1}H NMR ($CDCl_3$, 300 MHz) - (4*R*,5*S*)-4-((*R*)-4-(benzyloxy)-3-methyl-2-methylenebutyl)-2,2,5-trimethyl-1,3-dioxolane (**25**) and (4*S*,5*S*)-4-((*R*)-4-(benzyloxy)-3-methyl-2-methylenebutyl)-2,2,5-trimethyl-1,3-dioxolane (**26**).

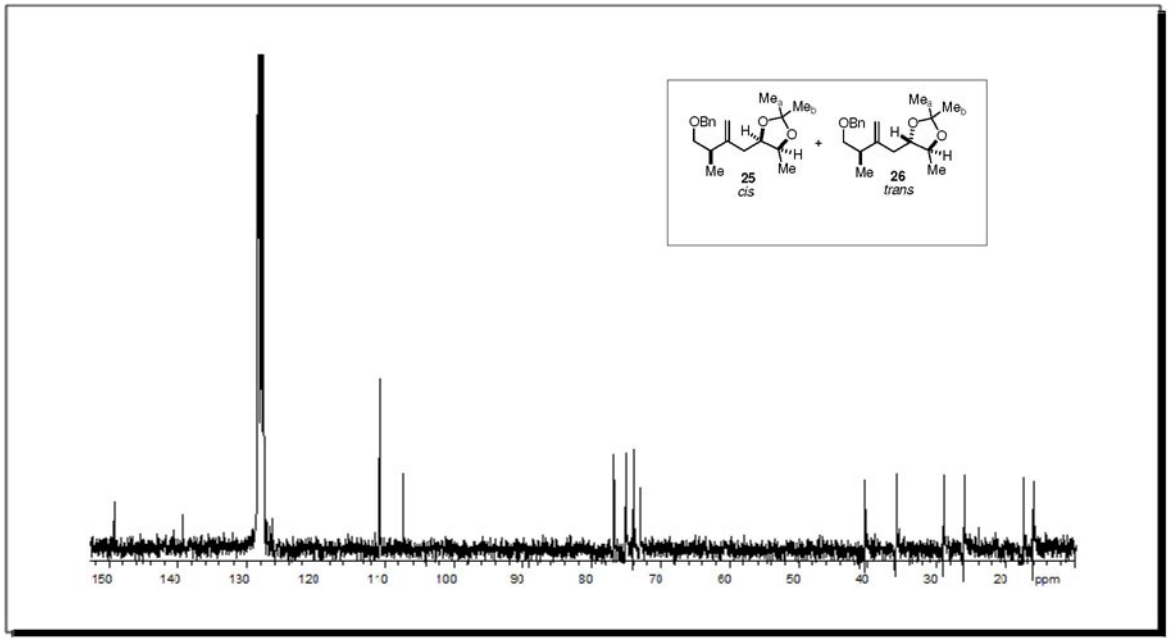


Figure 38S. ^{13}C NMR ($CDCl_3$, 75 MHz) - (4*R*,5*S*)-4-((*R*)-4-(benzyloxy)-3-methyl-2-methylenebutyl)-2,2,5-trimethyl-1,3-dioxolane (**25**) and (4*S*,5*S*)-4-((*R*)-4-(benzyloxy)-3-methyl-2-methylenebutyl)-2,2,5-trimethyl-1,3-dioxolane (**26**).

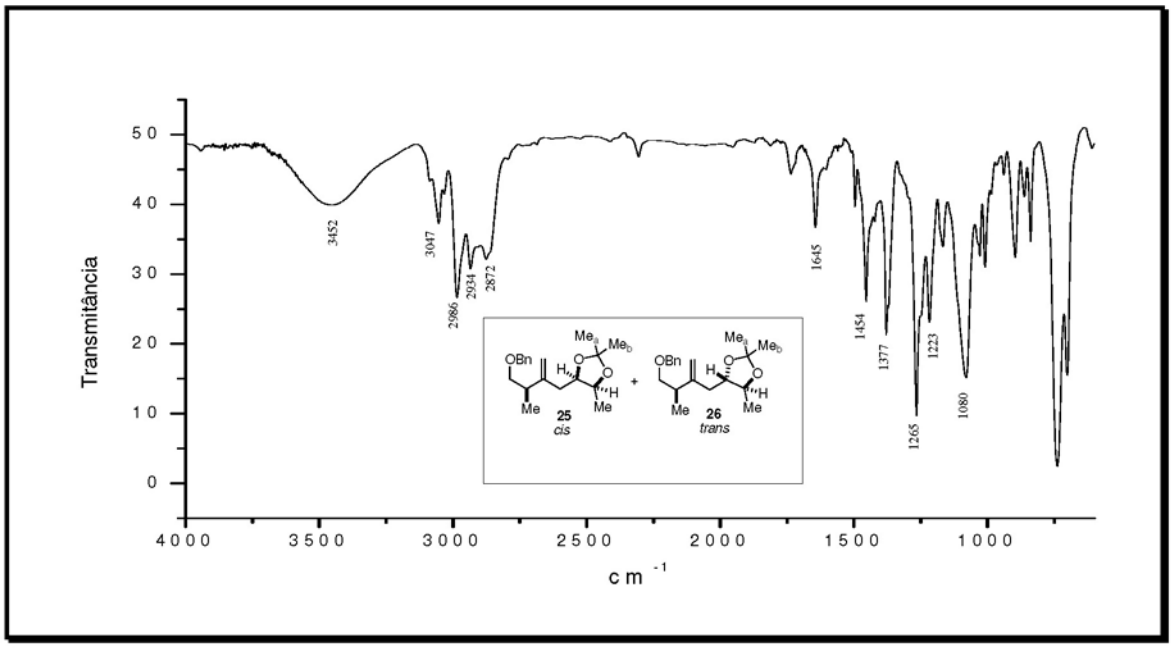


Figure 39S. IR (film) - (4*R*,5*S*)-4-((*R*)-4-(benzyloxy)-3-methyl-2-methylenebutyl)-2,2,5-trimethyl-1,3-dioxolane (**25**) and (4*S*,5*S*)-4-((*R*)-4-(benzyloxy)-3-methyl-2-methylenebutyl)-2,2,5-trimethyl-1,3-dioxolane (**26**).

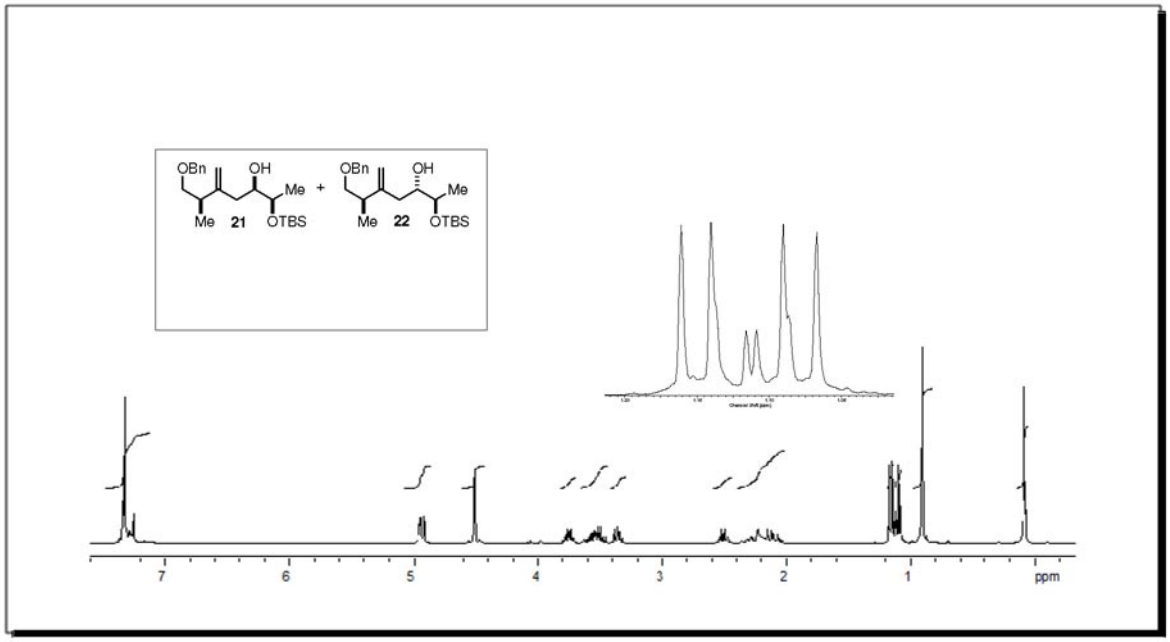


Figure 40S. ^{1}H NMR ($CDCl_3$, 300 MHz) (2*R*,3*R*,6*R*)-7-(benzyloxy)-2-(*tert*-butyldimethylsilyloxy)-6-methyl-5-methyleneheptan-3-ol (**21**) and (2*R*,3*S*,6*R*)-7-(benzyloxy)-2-(*tert*-butyldimethylsilyloxy)-6-methyl-5-methyleneheptan-3-ol (**22**).

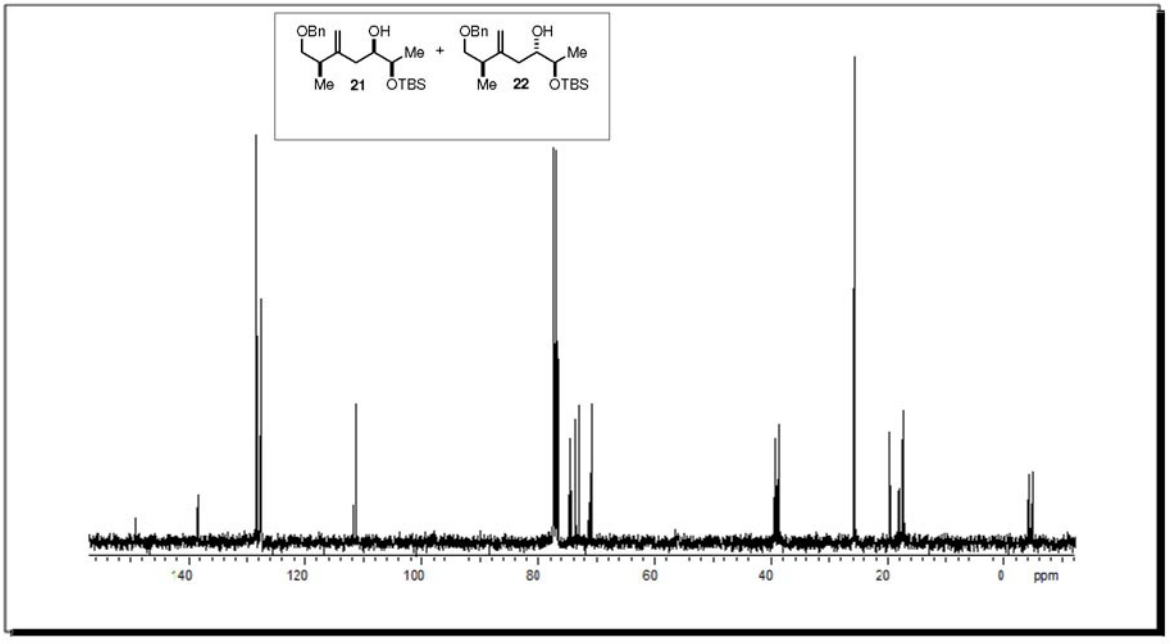


Figure 41S. ^{13}C NMR ($CDCl_3$, 75 MHz) - (2*R*,3*R*,6*R*)-7-(benzyloxy)-2-(*tert*-butyldimethylsilyloxy)-6-methyl-5-methyleneheptan-3-ol (**21**) and (2*R*,3*S*,6*R*)-7-(benzyloxy)-2-(*tert*-butyldimethylsilyloxy)-6-methyl-5-methyleneheptan-3-ol (**22**).

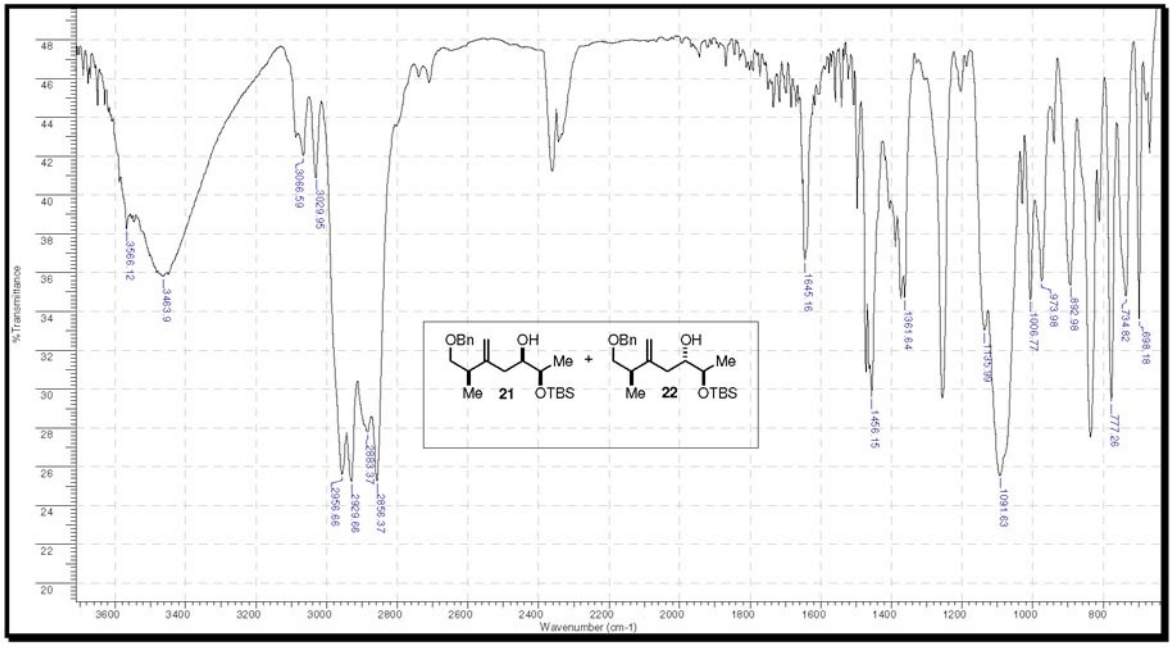


Figure 42S. IR (film) - (2*R*,3*R*,6*R*)-7-(benzyloxy)-2-(*tert*-butyldimethylsilyloxy)-6-methyl-5-methyleneheptan-3-ol (**21**) and (2*R*,3*S*,6*R*)-7-(benzyloxy)-2-(*tert*-butyldimethylsilyloxy)-6-methyl-5-methyleneheptan-3-ol (**22**).

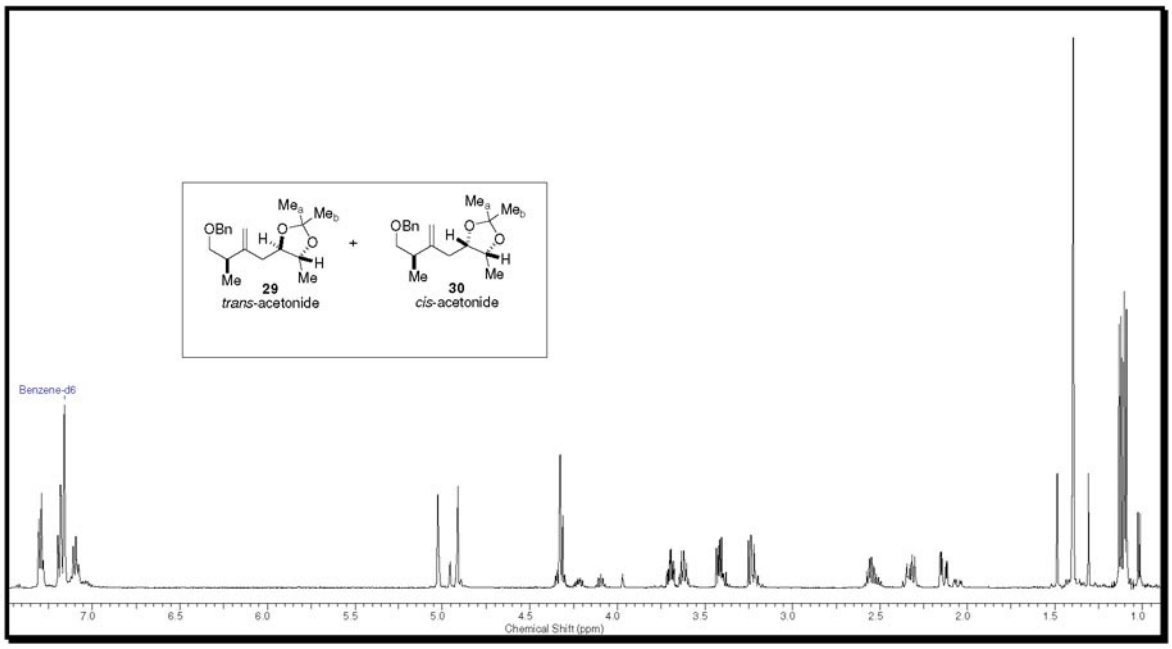


Figure 43S. ^{1}H NMR (C_6D_6, 500 MHz) - (4*R*,5*R*)-4-((*R*)-4-(benzyloxy)-3-methyl-2-methylenebutyl)-2,2,5-trimethyl-1,3-dioxolane (**29**) and (4*S*,5*R*)-4-((*R*)-4-(benzyloxy)-3-methyl-2-methylenebutyl)-2,2,5-trimethyl-1,3-dioxolane (**30**).

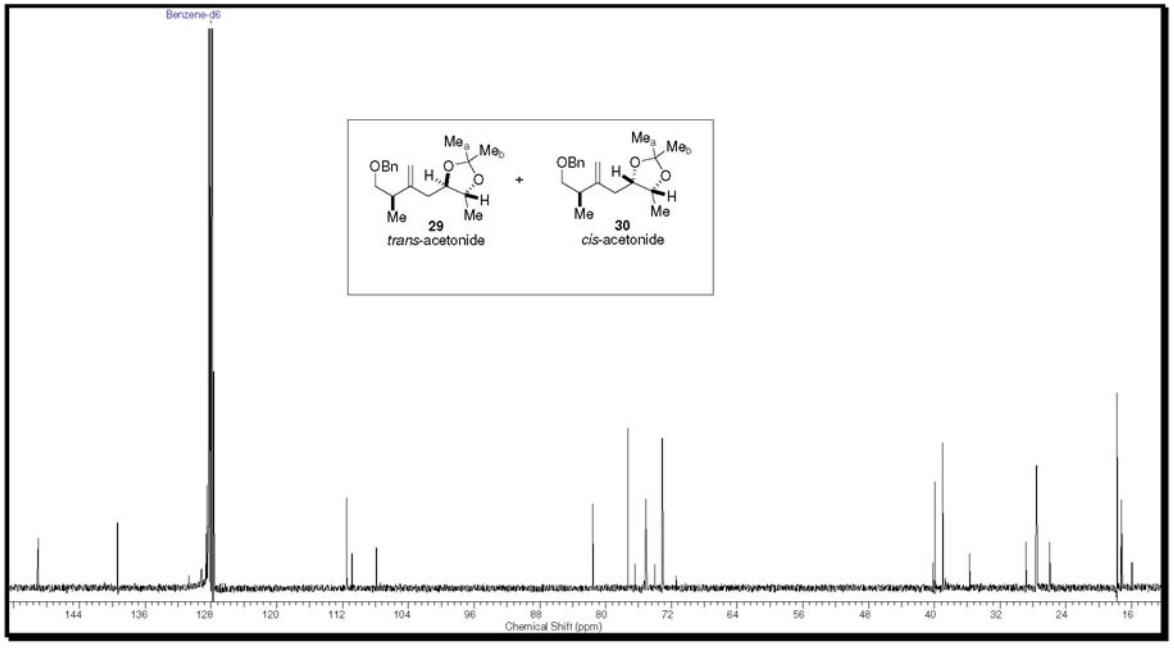


Figure 44S. ^{13}C NMR (C_6D_6, 125 MHz) - (4*R*,5*R*)-4-((*R*)-4-(benzyloxy)-3-methyl-2-methylenebutyl)-2,2,5-trimethyl-1,3-dioxolane (**29**) and (4*S*,5*R*)-4-((*R*)-4-(benzyloxy)-3-methyl-2-methylenebutyl)-2,2,5-trimethyl-1,3-dioxolane (**30**).

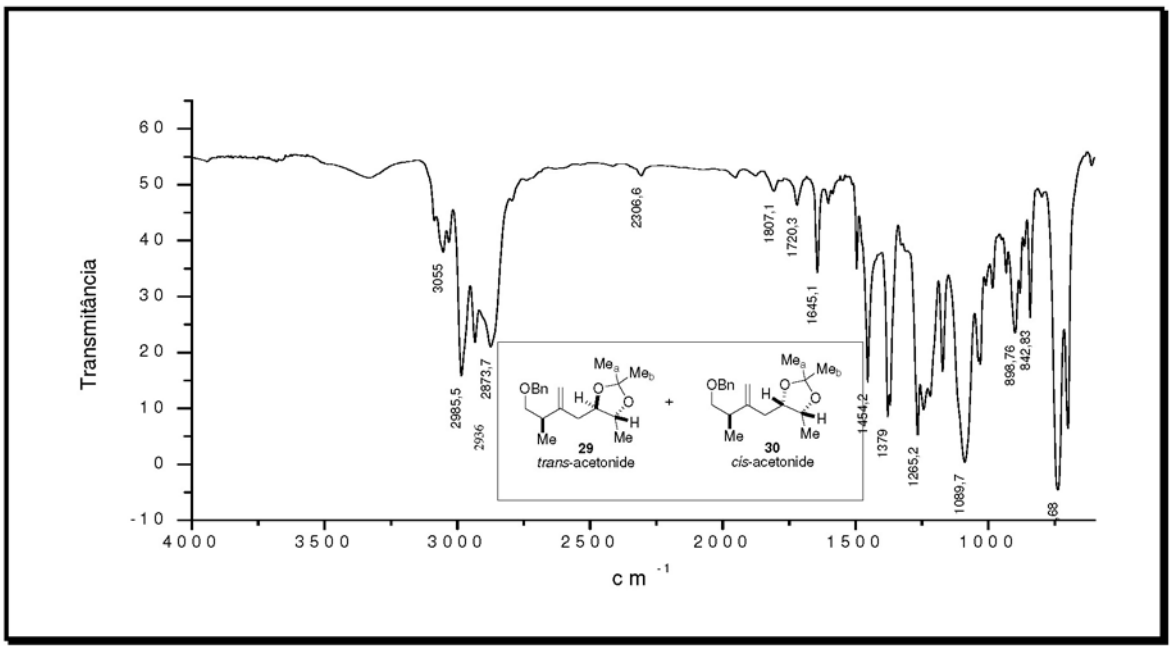


Figure 45S. IR (film) - (4*R*,5*R*)-4-((*R*)-4-(benzyloxy)-3-methyl-2-methylenebutyl)-2,2,5-trimethyl-1,3-dioxolane (**29**) and (4*S*,5*R*)-4-((*R*)-4-(benzyloxy)-3-methyl-2-methylenebutyl)-2,2,5-trimethyl-1,3-dioxolane (**30**).

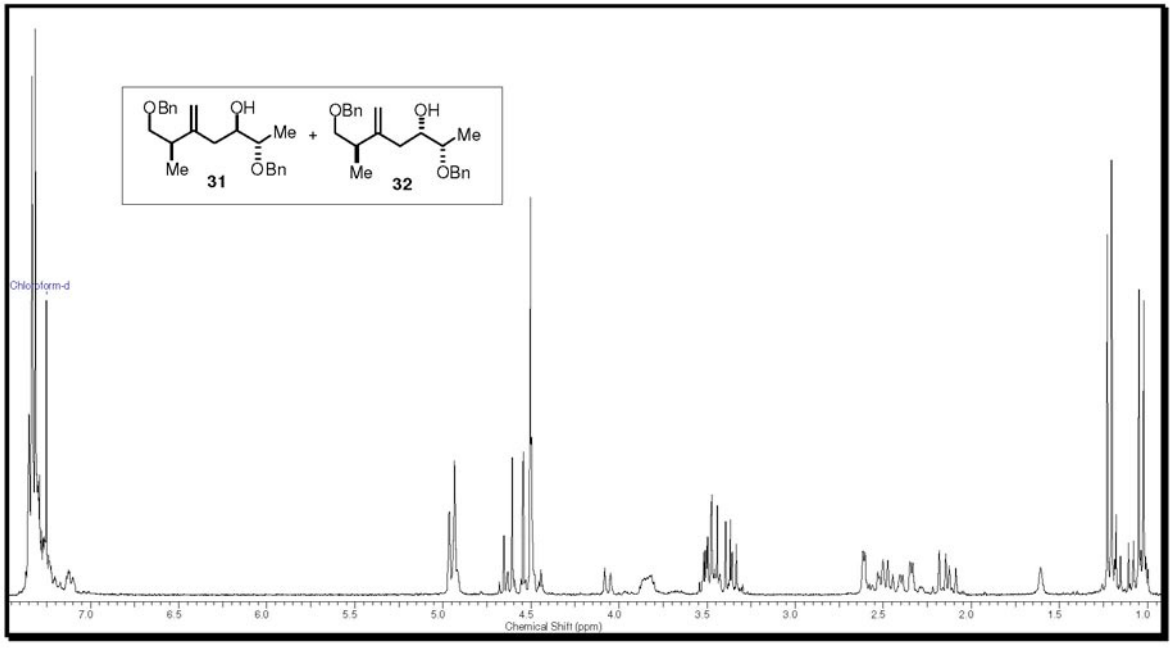


Figure 46S. ^{1}H NMR ($CDCl_3$, 250 MHz) - (2*S*,3*R*,6*R*)-2,7-bis(benzyloxy)-6-methyl-5-methyleneheptan-3-ol (**31**) and (2*S*,3*S*,6*R*)-2,7-bis(benzyloxy)-6-methyl-5-methyleneheptan-3-ol (**32**).

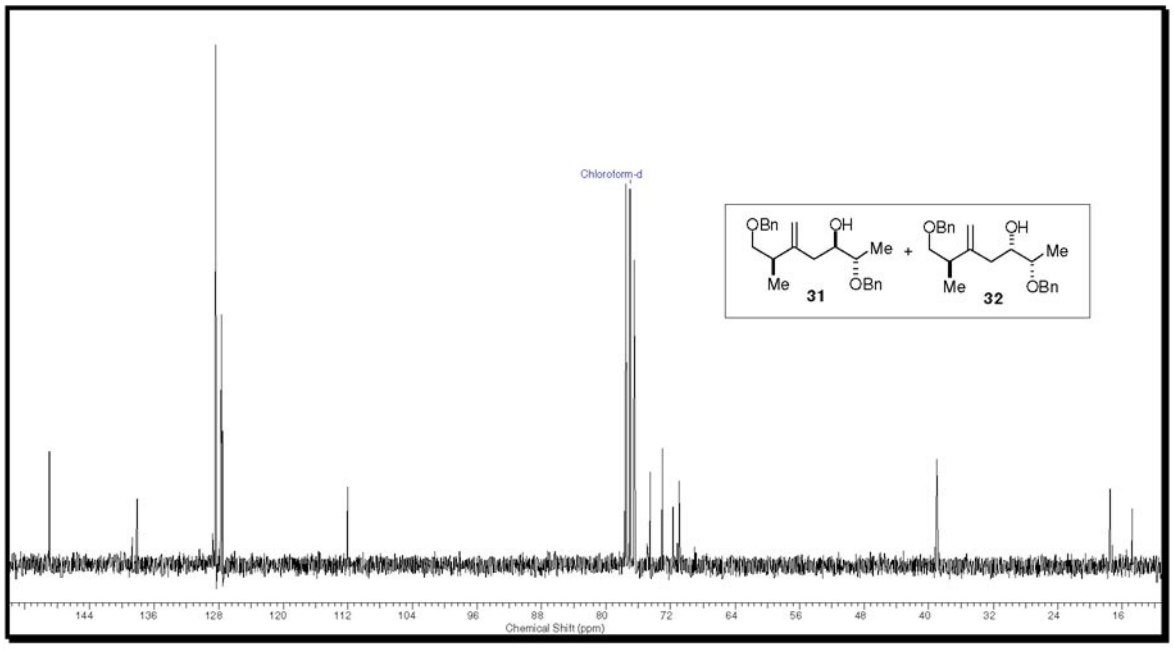


Figure 47S. ^{13}C NMR ($CDCl_3$, 63 MHz) - (2*S*,3*R*,6*R*)-2,7-bis(benzyloxy)-6-methyl-5-methyleneheptan-3-ol (**31**) and (2*S*,3*S*,6*R*)-2,7-bis(benzyloxy)-6-methyl-5-methyleneheptan-3-ol (**32**).

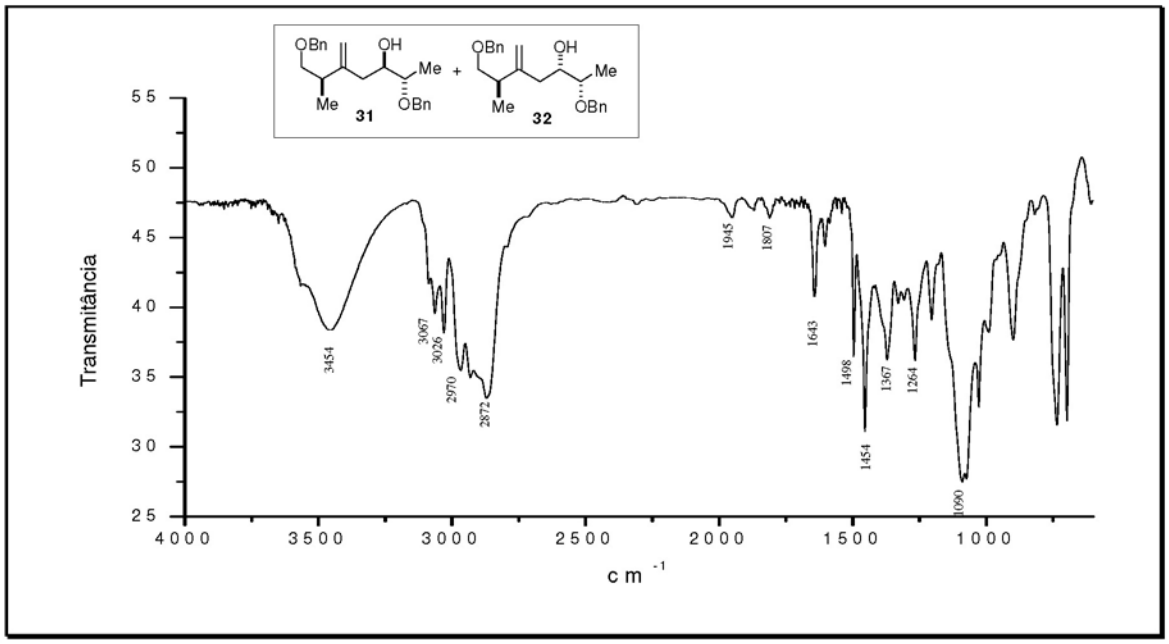


Figure 48S. IR (film) - (2*S*,3*R*,6*R*)-2,7-bis(benzyloxy)-6-methyl-5-methyleneheptan-3-ol (**31**) and (2*S*,3*S*,6*R*)-2,7-bis(benzyloxy)-6-methyl-5-methyleneheptan-3-ol (**32**).

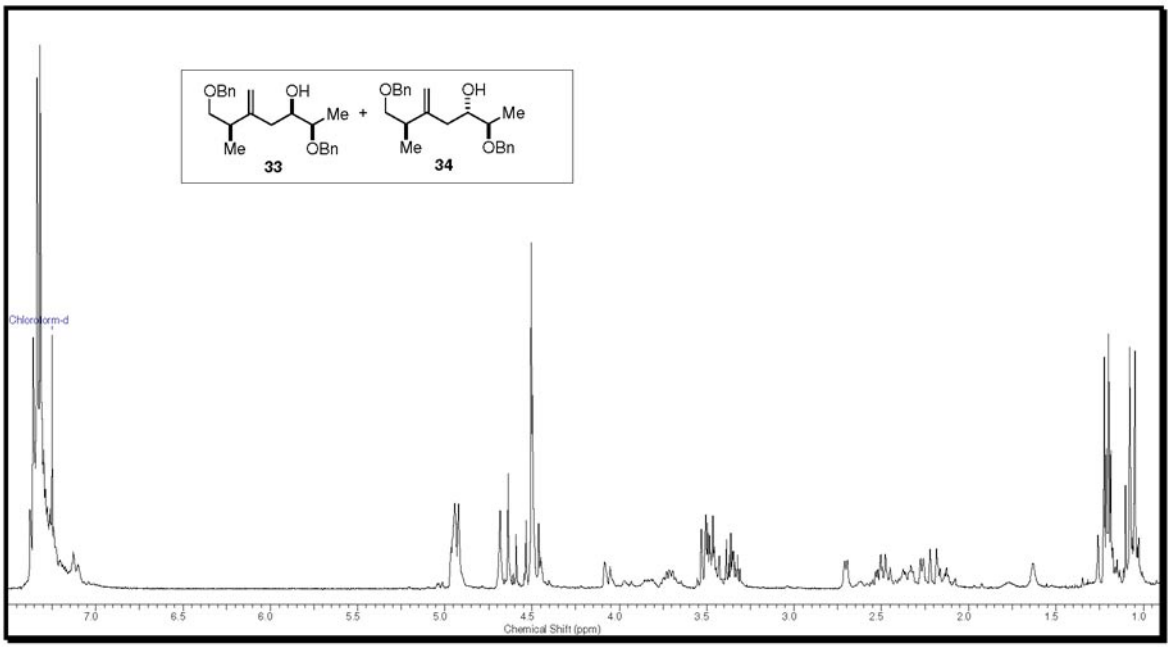


Figure 49S. ^{1}H NMR ($CDCl_3$, 250 MHz) - (2*R*,3*R*,6*R*)-2,7-bis(benzyloxy)-6-methyl-5-methyleneheptan-3-ol (**33**) and (2*R*,3*S*,6*R*)-2,7-bis(benzyloxy)-6-methyl-5-methyleneheptan-3-ol (**34**).

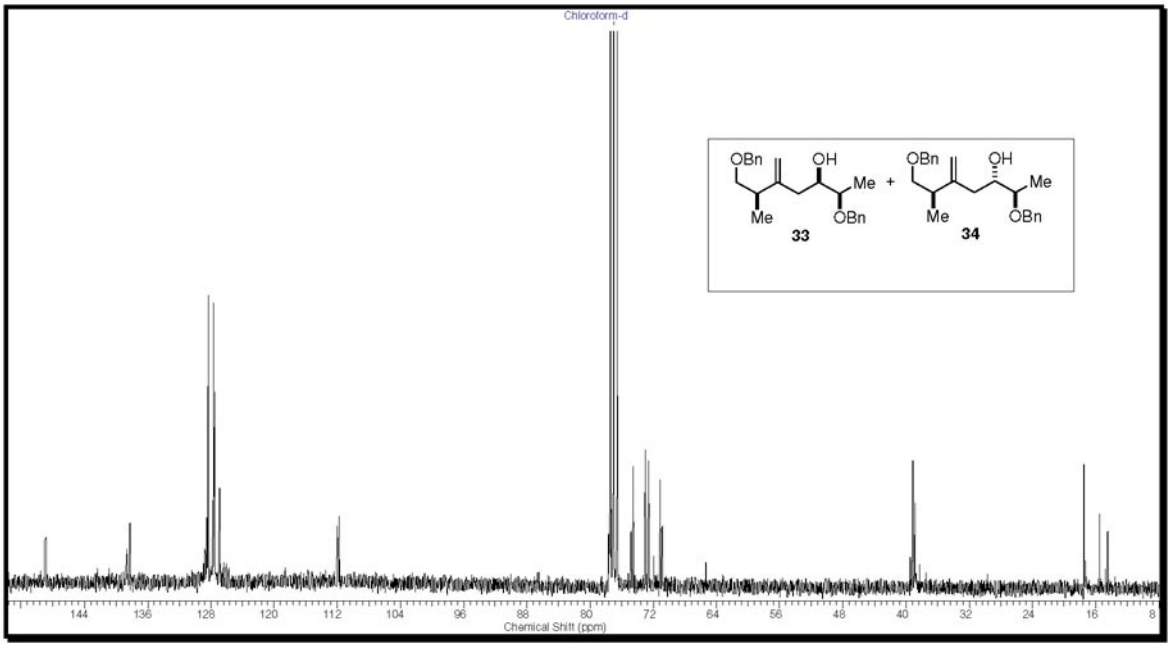


Figure 50S. ^{13}C NMR $CDCl_3$, 75 MHz) - (2*R*,3*R*,6*R*)-2,7-bis(benzyloxy)-6-methyl-5-methyleneheptan-3-ol (**33**) and (2*R*,3*S*,6*R*)-2,7-bis(benzyloxy)-6-methyl-5-methyleneheptan-3-ol (**34**).

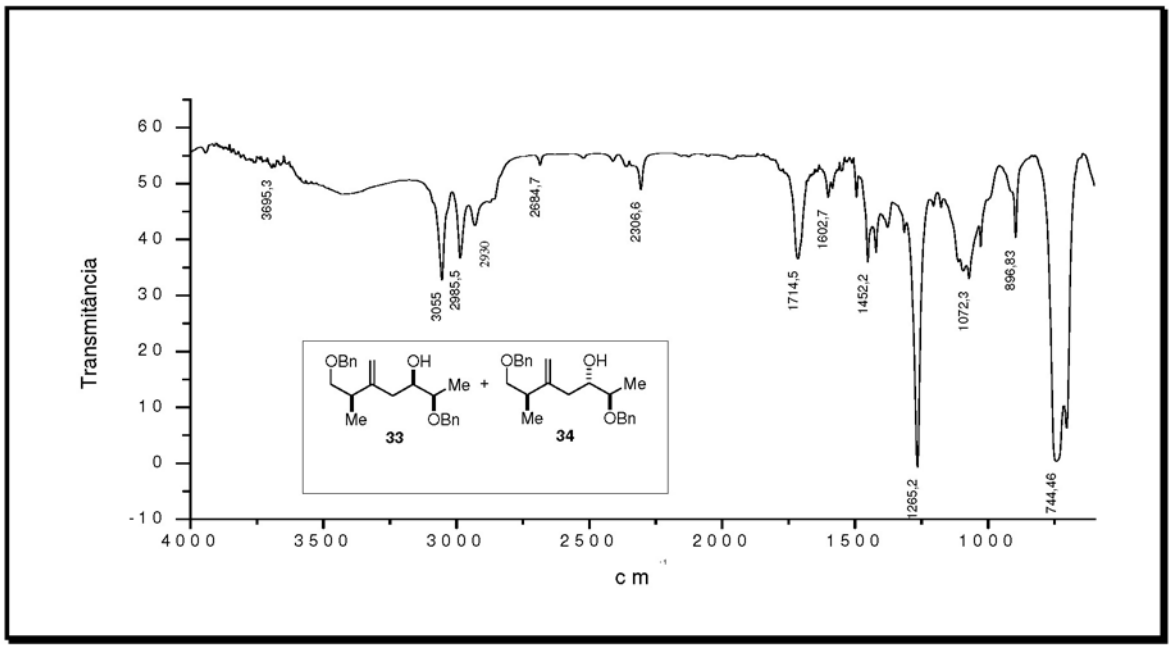


Figure 51S. IR (film) - (2*R*,3*R*,6*R*)-2,7-bis(benzyloxy)-6-methyl-5-methyleneheptan-3-ol (**33**) and (2*R*,3*S*,6*R*)-2,7-bis(benzyloxy)-6-methyl-5-methyleneheptan-3-ol (**34**).

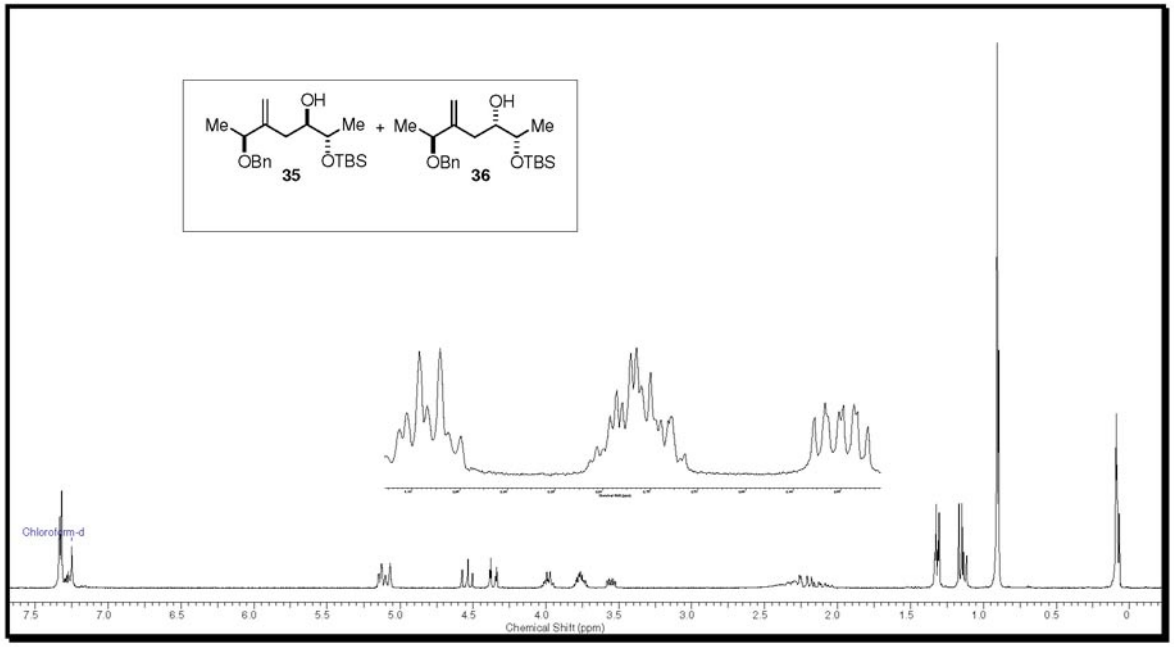


Figure 52S. ^{1}H NMR ($CDCl_3$, 300 MHz) - (2*S*,3*R*,6*S*)-6-(benzyloxy)-2-(*tert*-butyldimethylsilyloxy)-5-methyleneheptan-3-ol (**35**) and (2*S*,3*S*,6*S*)-6-(benzyloxy)-2-(*tert*-butyldimethylsilyloxy)-5-methyleneheptan-3-ol (**36**).

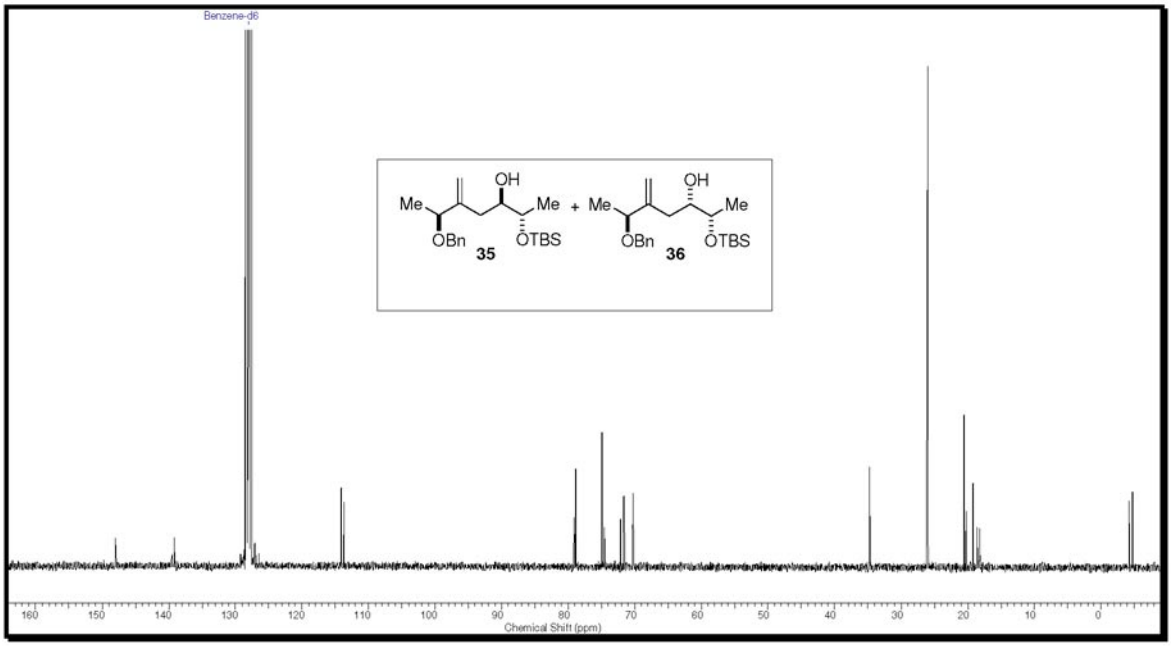


Figure 53S. ^{13}C NMR (C_6D_6, 75 MHz) - (2*S*,3*R*,6*S*)-6-(benzyloxy)-2-(*tert*-butyldimethylsilyloxy)-5-methyleneheptan-3-ol (**35**) and (2*S*,3*S*,6*S*)-6-(benzyloxy)-2-(*tert*-butyldimethylsilyloxy)-5-methyleneheptan-3-ol (**36**).

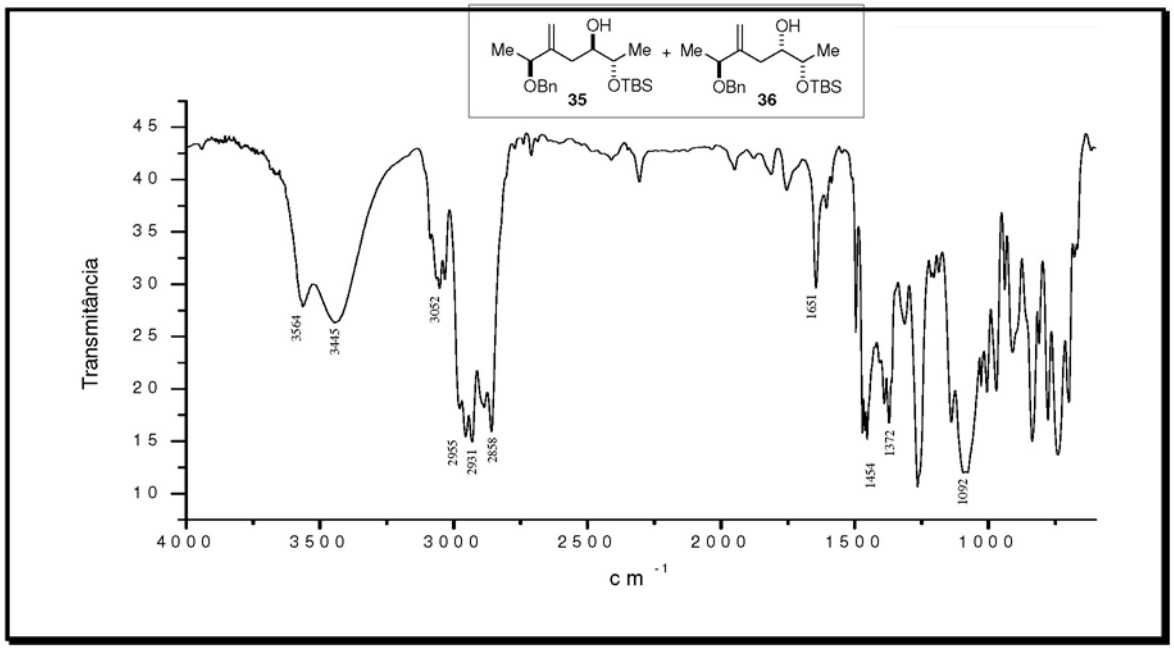


Figure 54S. IR (film) - (2*S*,3*R*,6*S*)-6-(benzyloxy)-2-(*tert*-butyldimethylsilyloxy)-5-methyleneheptan-3-ol (**35**) and (2*S*,3*S*,6*S*)-6-(benzyloxy)-2-(*tert*-butyldimethylsilyloxy)-5-methyleneheptan-3-ol (**36**).

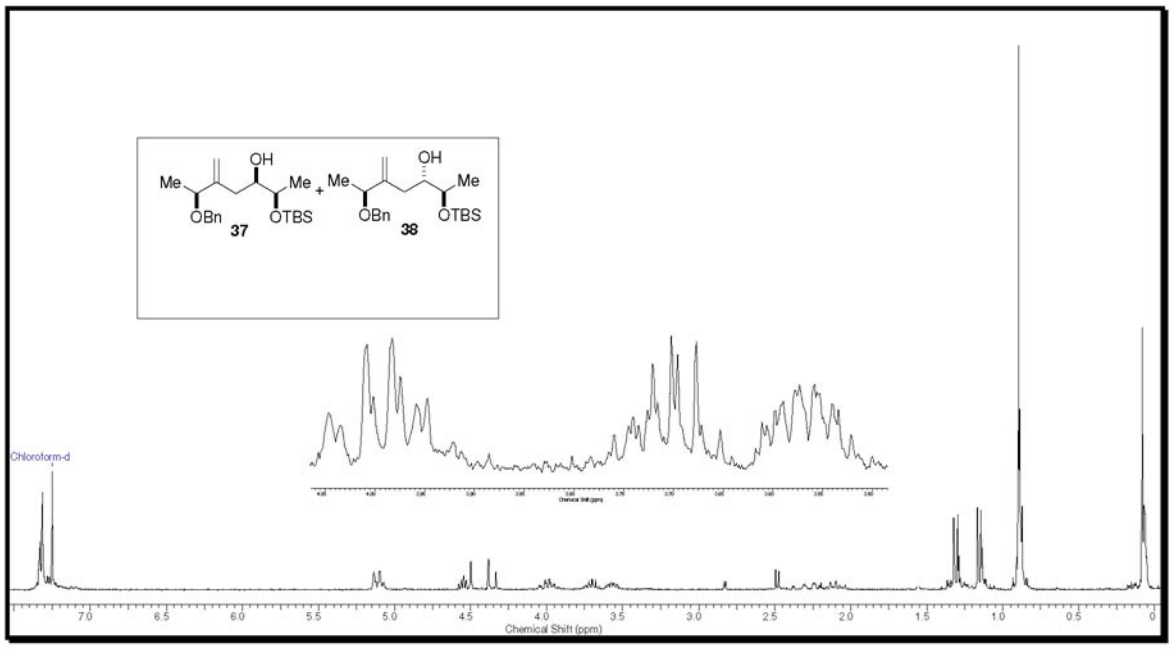


Figure 55S. ^{1}H NMR ($CDCl_3$, 250 MHz) - (2*R*,3*R*,6*S*)-6-(benzyloxy)-2-(*tert*-butyldimethylsilyloxy)-5-methyleneheptan-3-ol (**37**) and (2*R*,3*S*,6*S*)-6-(benzyloxy)-2-(*tert*-butyldimethylsilyloxy)-5-methyleneheptan-3-ol (**38**).

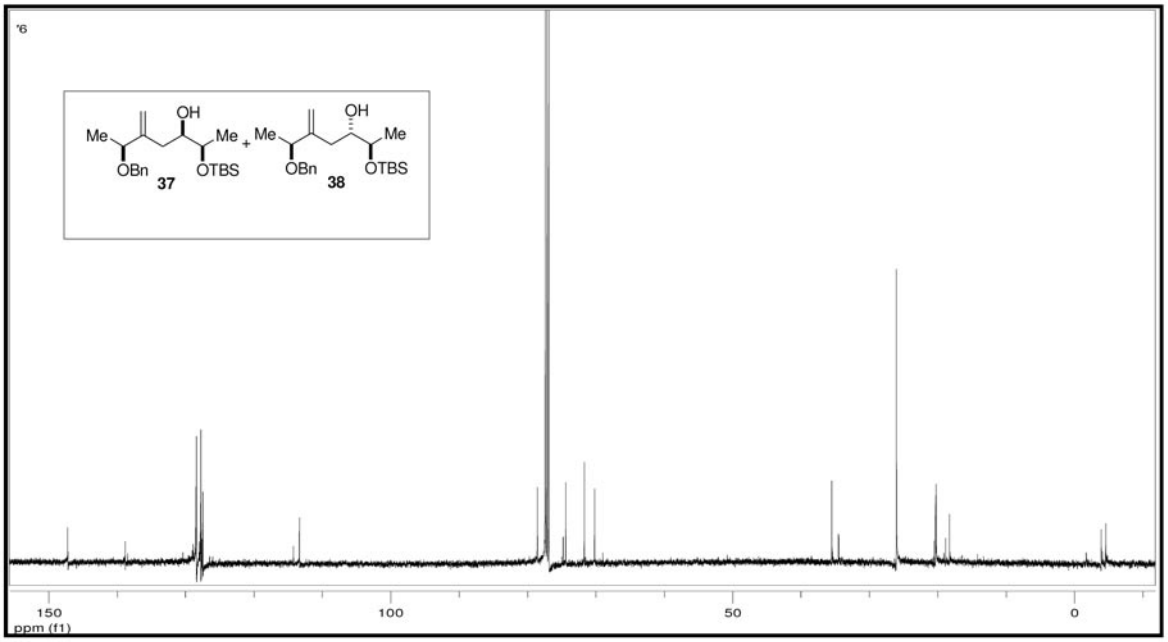


Figure 56S. ^{13}C NMR ($CDCl_3$, 63 MHz) - (2*R*,3*R*,6*S*)-6-(benzyloxy)-2-(*tert*-butyldimethylsilyloxy)-5-methyleneheptan-3-ol (**37**) and (2*R*,3*S*,6*S*)-6-(benzyloxy)-2-(*tert*-butyldimethylsilyloxy)-5-methyleneheptan-3-ol (**38**).

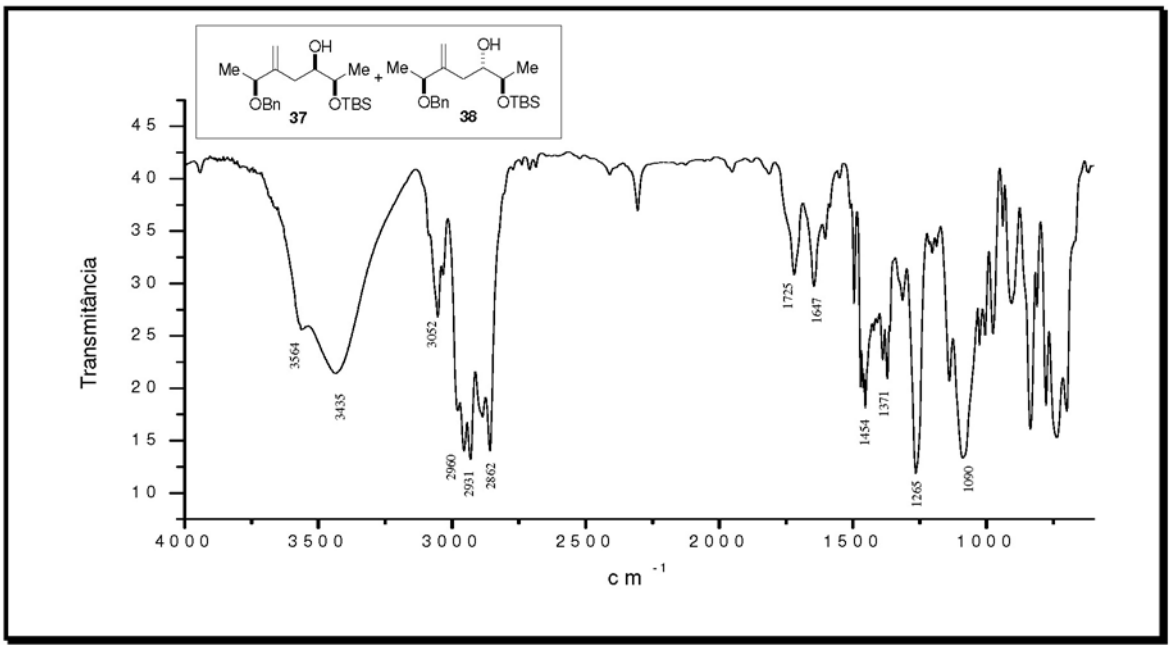


Figure 57S. IR (film) - (2*R*,3*R*,6*S*)-6-(benzyloxy)-2-(*tert*-butyldimethylsilyloxy)-5-methyleneheptan-3-ol (**37**) and (2*R*,3*S*,6*S*)-6-(benzyloxy)-2-(*tert*-butyldimethylsilyloxy)-5-methyleneheptan-3-ol (**38**).

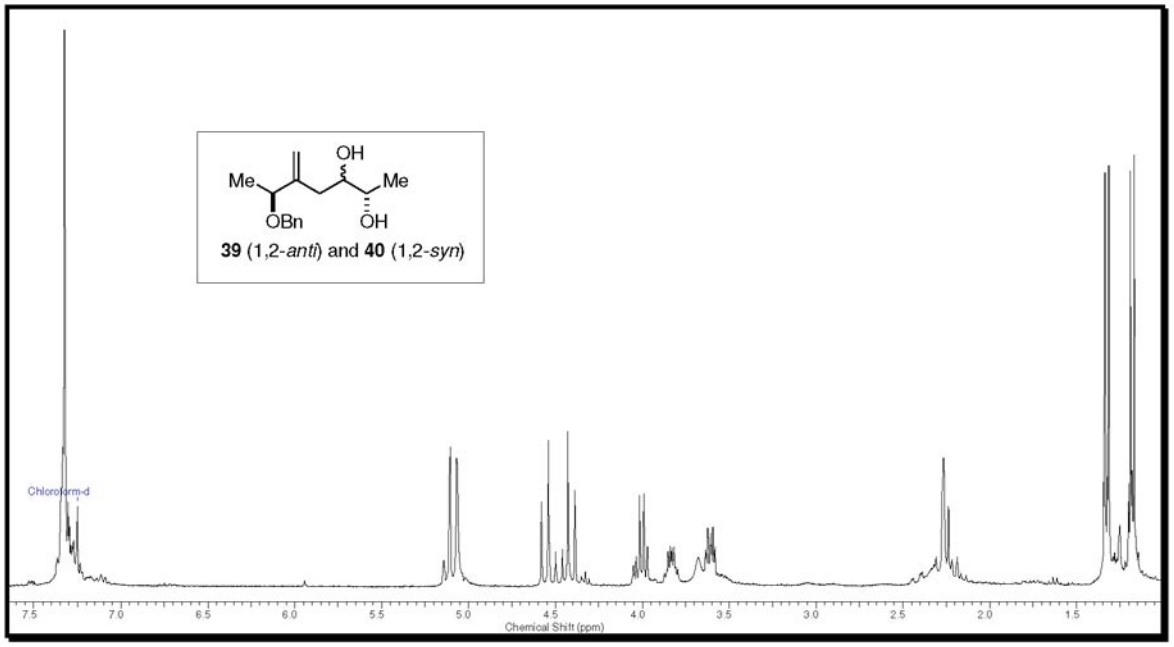


Figure 58S. ^{1}H NMR ($CDCl_3$, 300 MHz) - (2*S*,6*S*)-6-(benzyloxy)-5-methyleneheptane-2,3-diol (**39**) and (**40**).

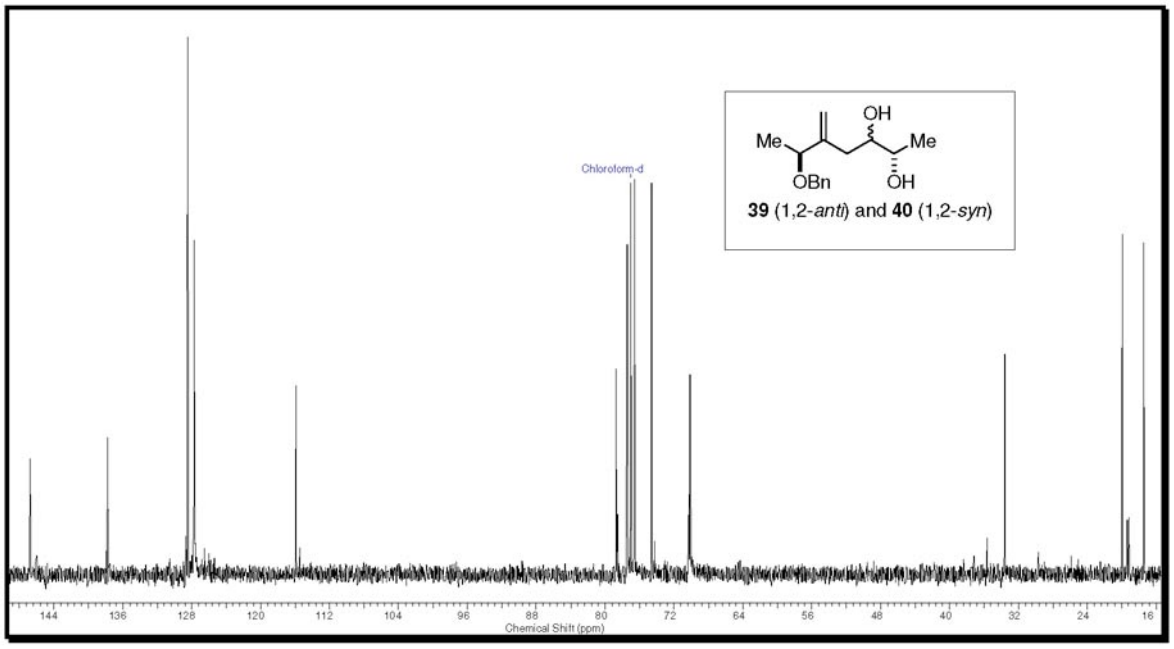


Figure 59S. ^{13}C NMR ($CDCl_3$, 75 MHz) - (2*S*,6*S*)-6-(benzyloxy)-5-methyleneheptane-2,3-diol (**39**) and (**40**).

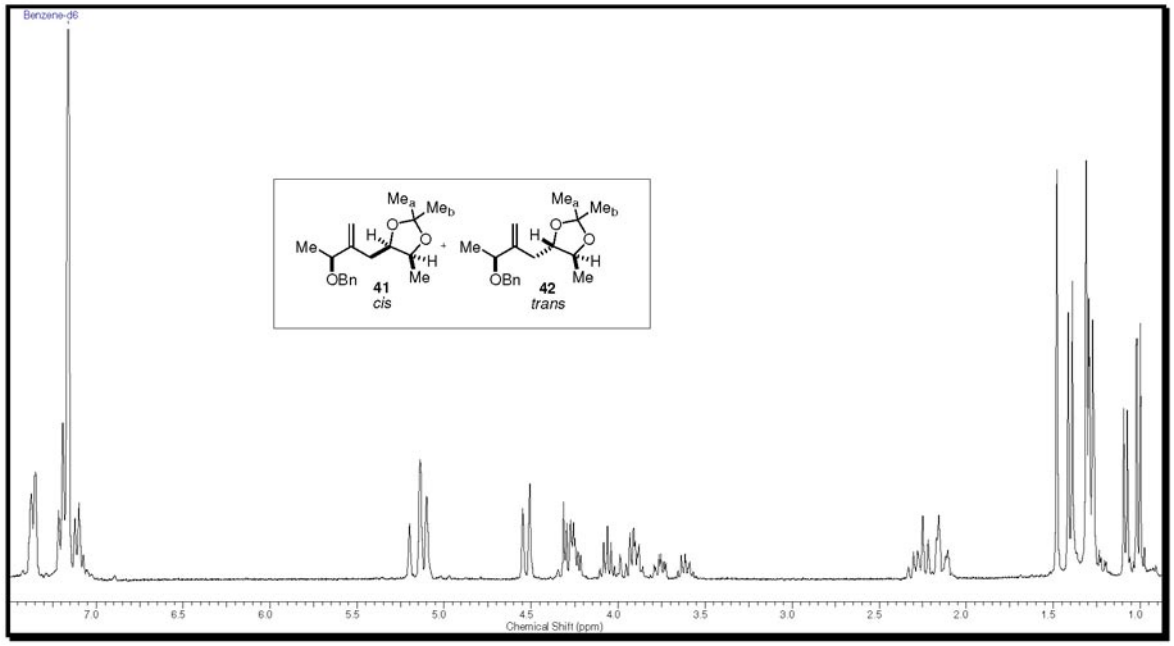


Figure 60S. ^{1}H NMR (C_6D_6, 300 MHz) - (4*R*,5*S*)-4-((*S*)-3-(benzyloxy)-2-methylenebutyl)-2,2,5-trimethyl-1,3-dioxolane (**41**) and (4*S*,5*S*)-4-((*S*)-3-(benzyloxy)-2-methylenebutyl)-2,2,5-trimethyl-1,3-dioxolane (**42**).

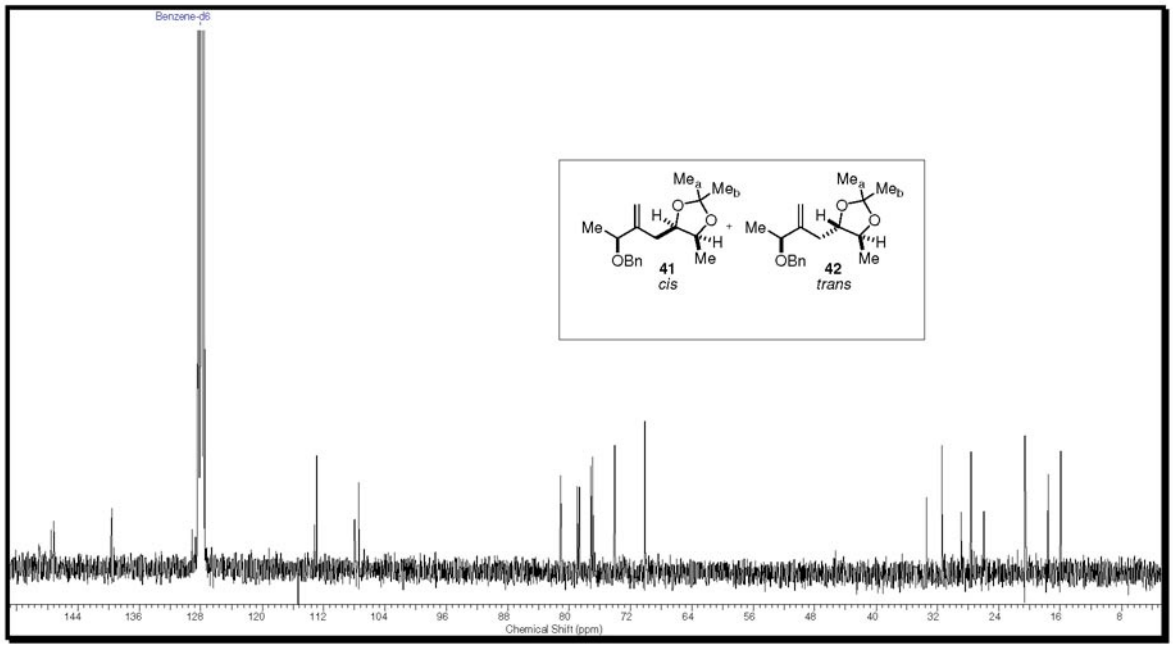


Figure 61S. ^{13}C NMR (C_6D_6, 300 MHz) - (4*R*,5*S*)-4-((*S*)-3-(benzyloxy)-2-methylenebutyl)-2,2,5-trimethyl-1,3-dioxolane (**41**) and (4*S*,5*S*)-4-((*S*)-3-(benzyloxy)-2-methylenebutyl)-2,2,5-trimethyl-1,3-dioxolane (**42**).

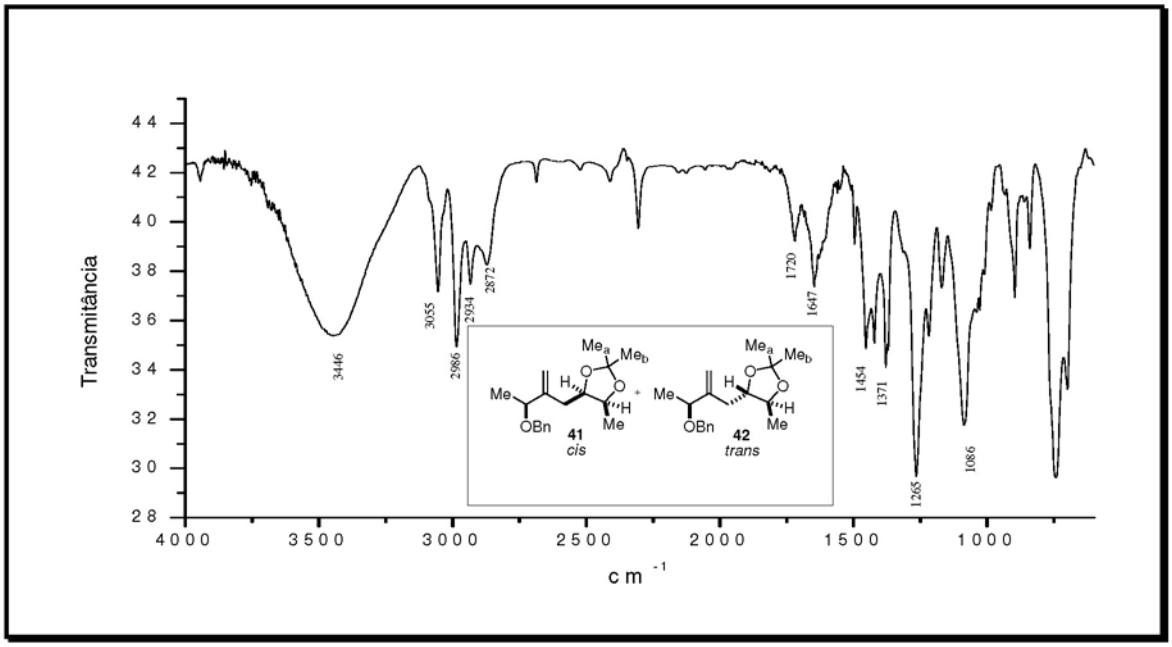


Figure 62S. IR (film) - (4*R*,5*S*)-4-((*S*)-3-(benzyloxy)-2-methylenebutyl)-2,2,5-trimethyl-1,3-dioxolane (**41**) and (4*S*,5*S*)-4-((*S*)-3-(benzyloxy)-2-methylenebutyl)-2,2,5-trimethyl-1,3-dioxolane (**42**).

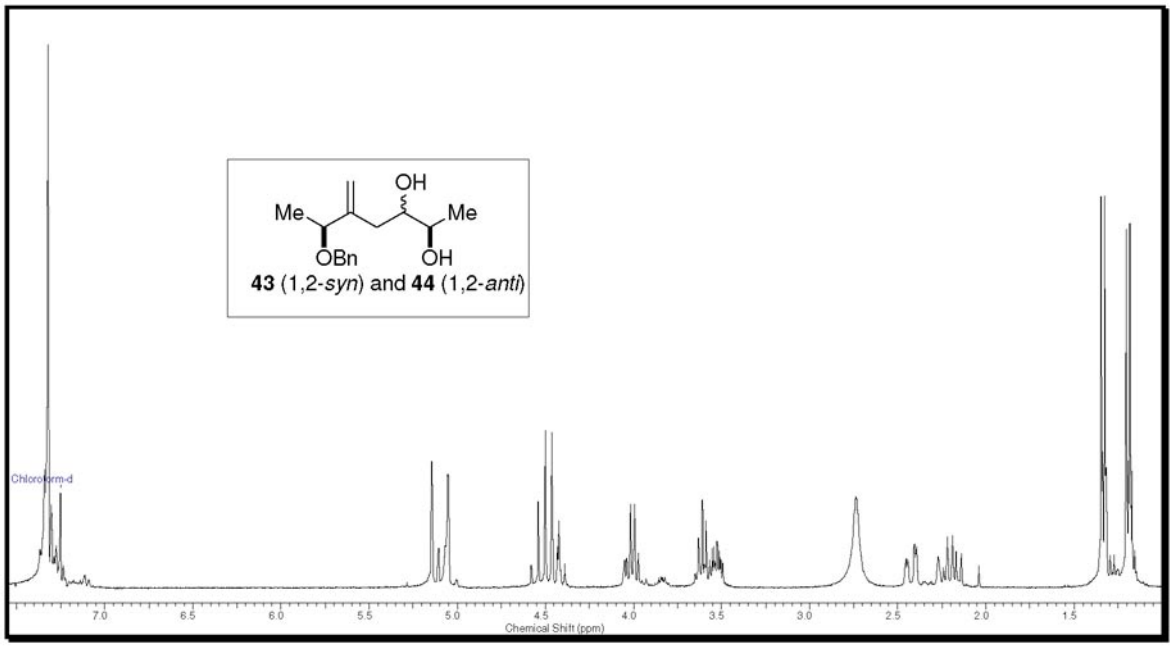


Figure 63S. ^{1}H NMR ($CDCl_3$, 300 MHz) - (2*R*,6*S*)-6-(benzyloxy)-5-methyleneheptane-2,3-diol (**43**) and (**44**).

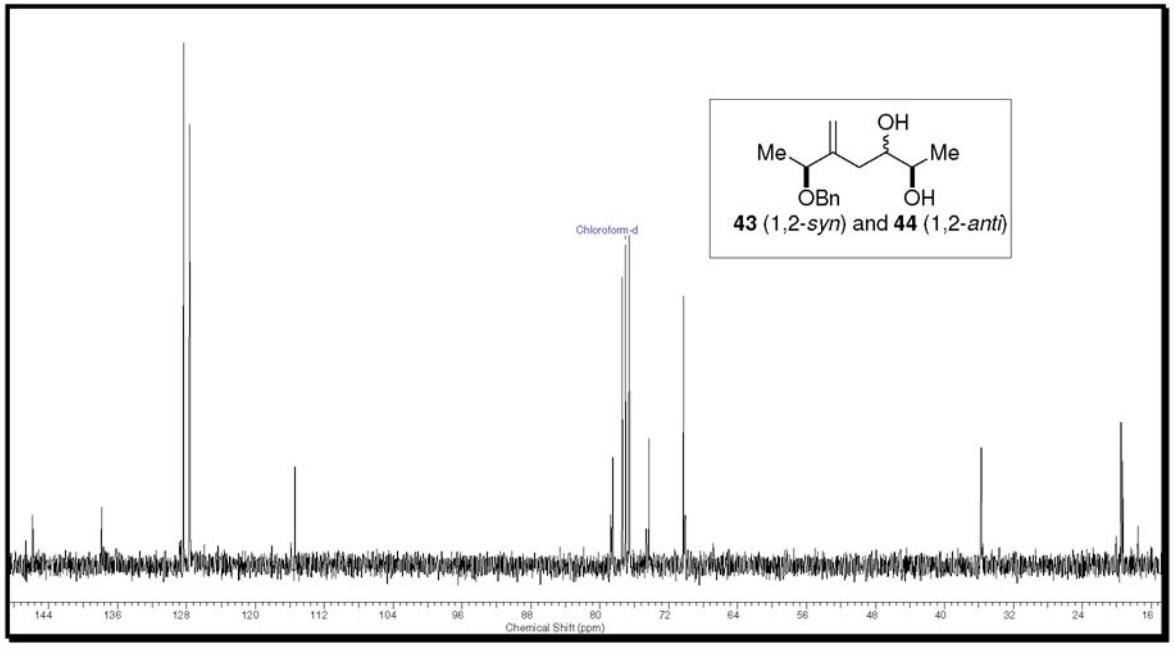


Figure 64S. ^{13}C NMR ($CDCl_3$, 75 MHz) - (2*R*,6*S*)-6-(benzyloxy)-5-methyleneheptane-2,3-diol (**43**) and (**44**).

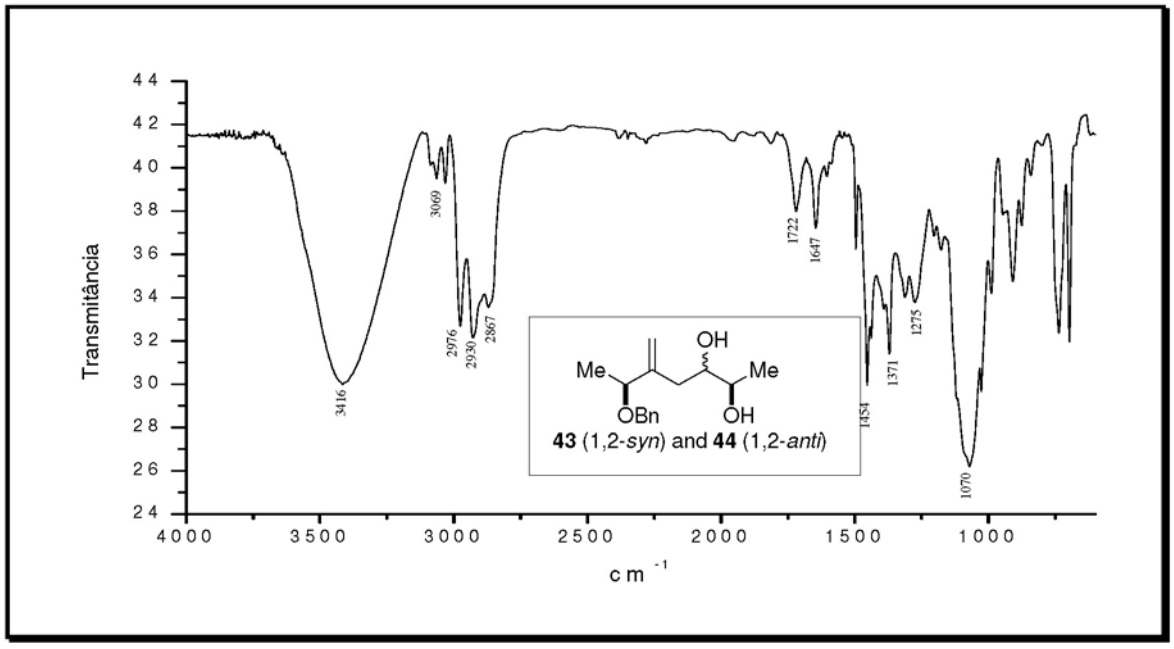


Figure 65S. IR (film) - (2*R*,6*S*)-6-(benzyloxy)-5-methyleneheptane-2,3-diol (**43**) and (**44**).

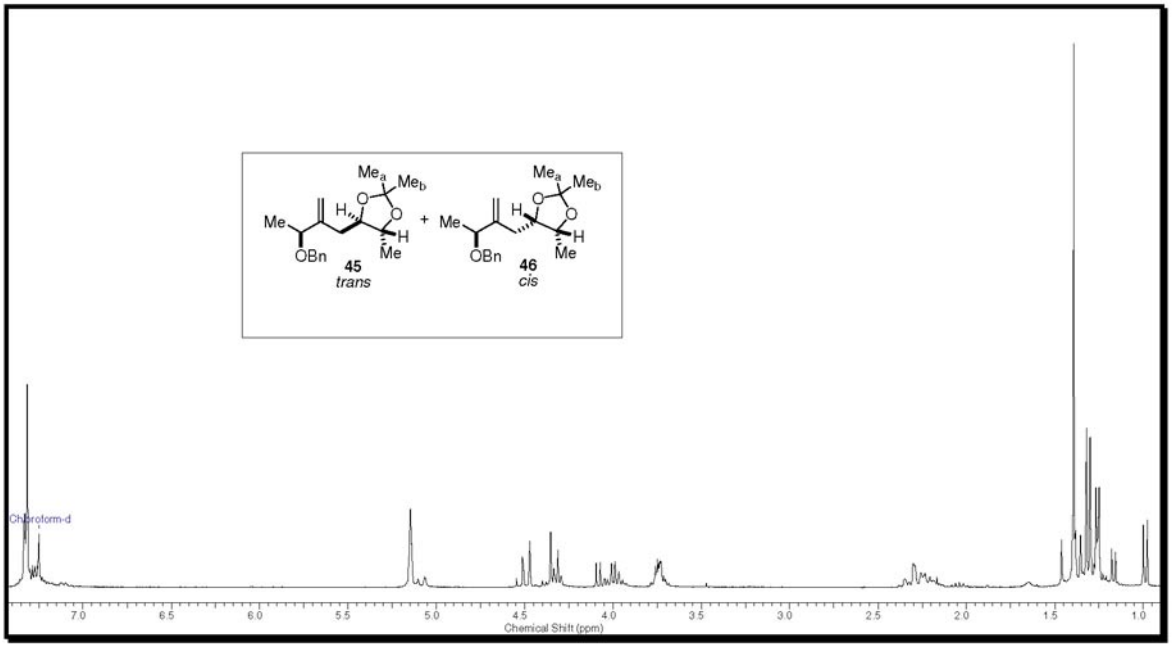


Figure 66S. ^{1}H NMR ($CDCl_3$, 250 MHz) - (4*R*,5*R*)-4-((*S*)-3-(benzyloxy)-2-methylenebutyl)-2,2,5-trimethyl-1,3-dioxolane (**45**) and (4*S*,5*R*)-4-((*S*)-3-(benzyloxy)-2-methylenebutyl)-2,2,5-trimethyl-1,3-dioxolane (**46**).

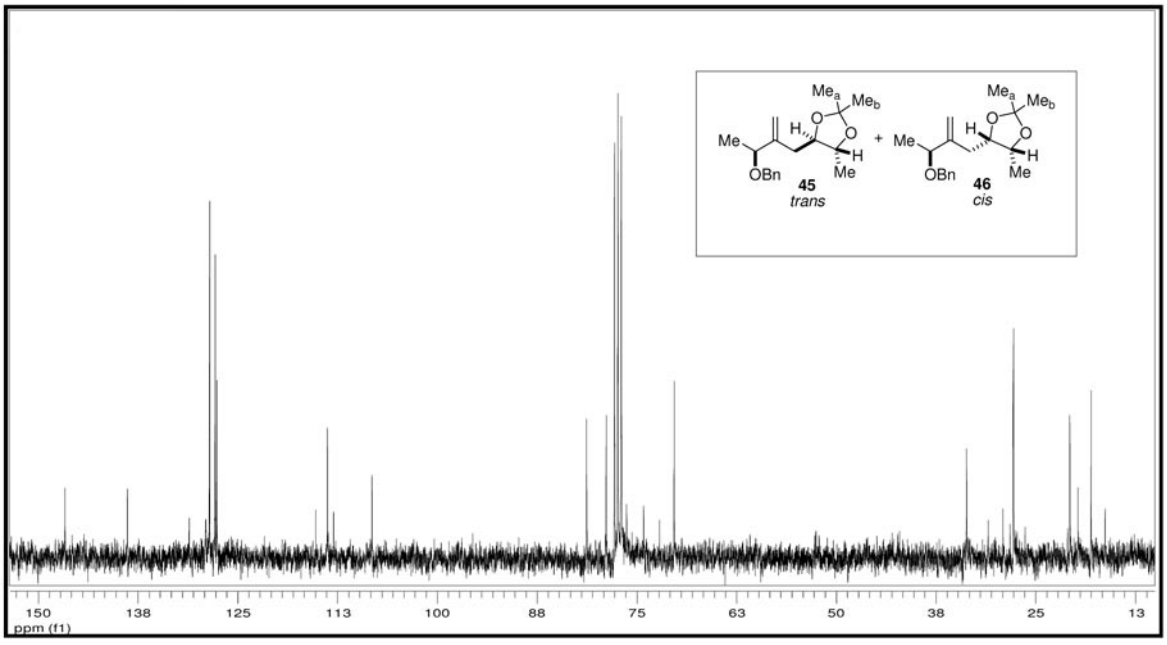


Figure 67S. ^{13}C NMR ($CDCl_3$, 63 MHz) - (4*R*,5*R*)-4-((*S*)-3-(benzyloxy)-2-methylenebutyl)-2,2,5-trimethyl-1,3-dioxolane (**45**) and (4*S*,5*R*)-4-((*S*)-3-(benzyloxy)-2-methylenebutyl)-2,2,5-trimethyl-1,3-dioxolane (**46**).

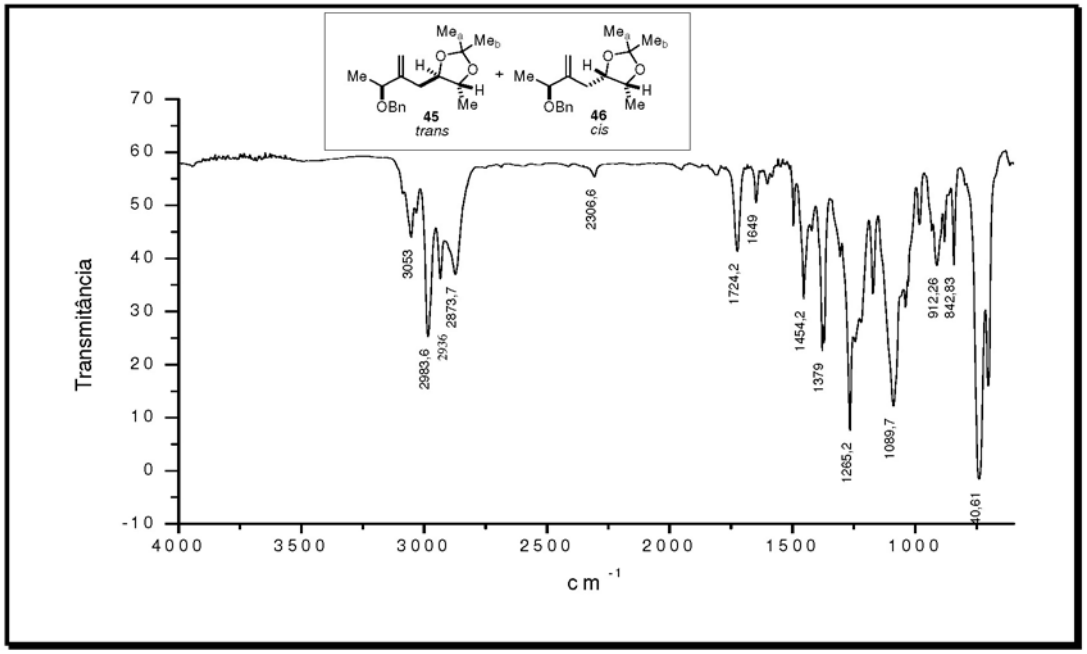


Figure 68S. IR (film) - (4*R*,5*R*)-4-((*S*)-3-(benzyloxy)-2-methylenebutyl)-2,2,5-trimethyl-1,3-dioxolane (45) and (4*S*,5*R*)-4-((*S*)-3-(benzyloxy)-2-methylenebutyl)-2,2,5-trimethyl-1,3-dioxolane (46).

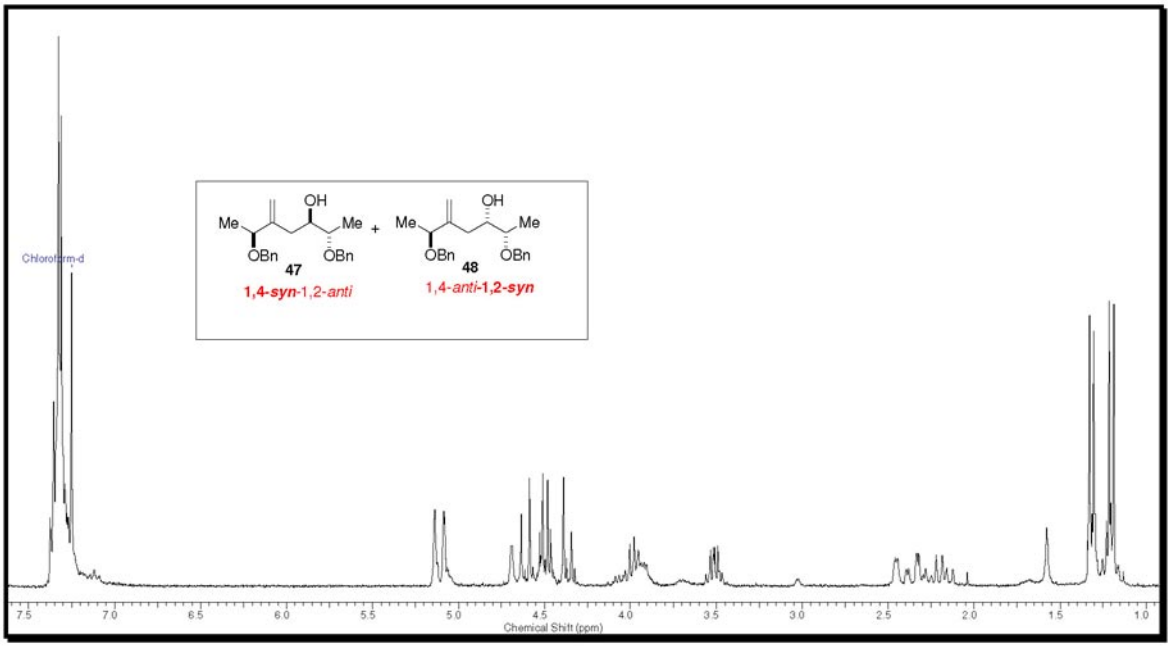


Figure 69S. ^{1}H NMR ($CDCl_3$, 250 MHz) - (2*S*,3*R*,6*S*)-2,6-bis(benzyloxy)-5-methyleneheptan-3-ol (**47**) and (2*S*,3*S*,6*S*)-2,6-bis(benzyloxy)-5-methyleneheptan-3-ol (**48**).

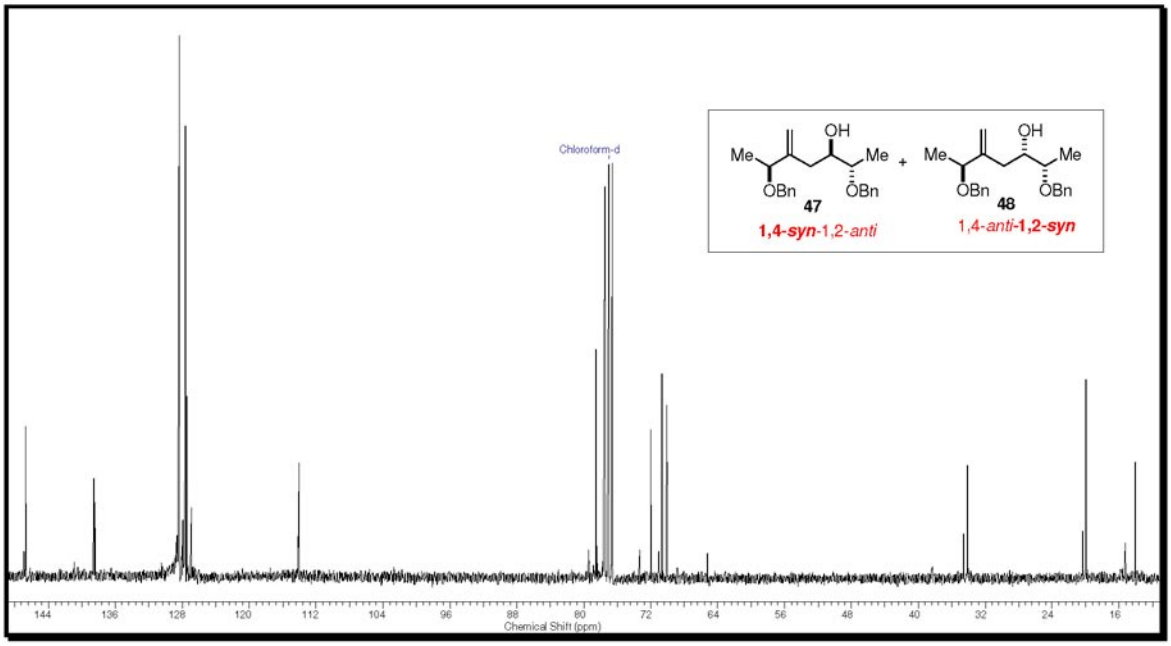


Figure 70S. ^{13}C NMR ($CDCl_3$, 63 MHz) - (2*S*,3*R*,6*S*)-2,6-bis(benzyloxy)-5-methyleneheptan-3-ol (**47**) and (2*S*,3*S*,6*S*)-2,6-bis(benzyloxy)-5-methyleneheptan-3-ol (**48**).

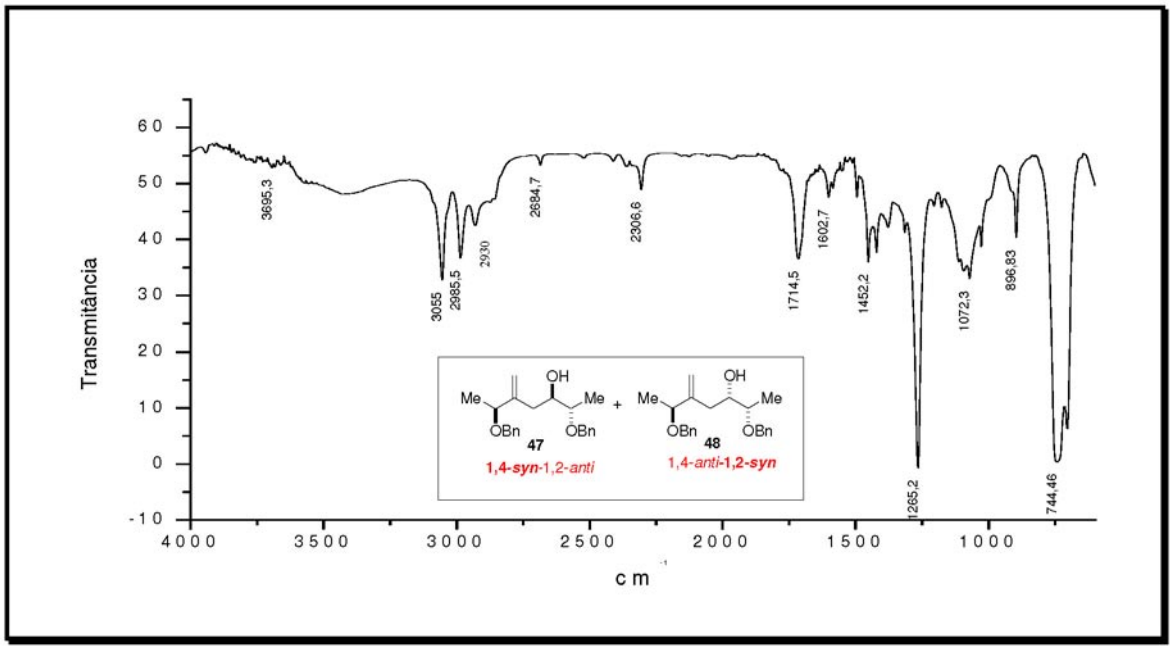


Figure 71S. IR (film) - (2*S*,3*R*,6*S*)-2,6-bis(benzyloxy)-5-methyleneheptan-3-ol (**47**) and (2*S*,3*S*,6*S*)-2,6-bis(benzyloxy)-5-methyleneheptan-3-ol (**48**).

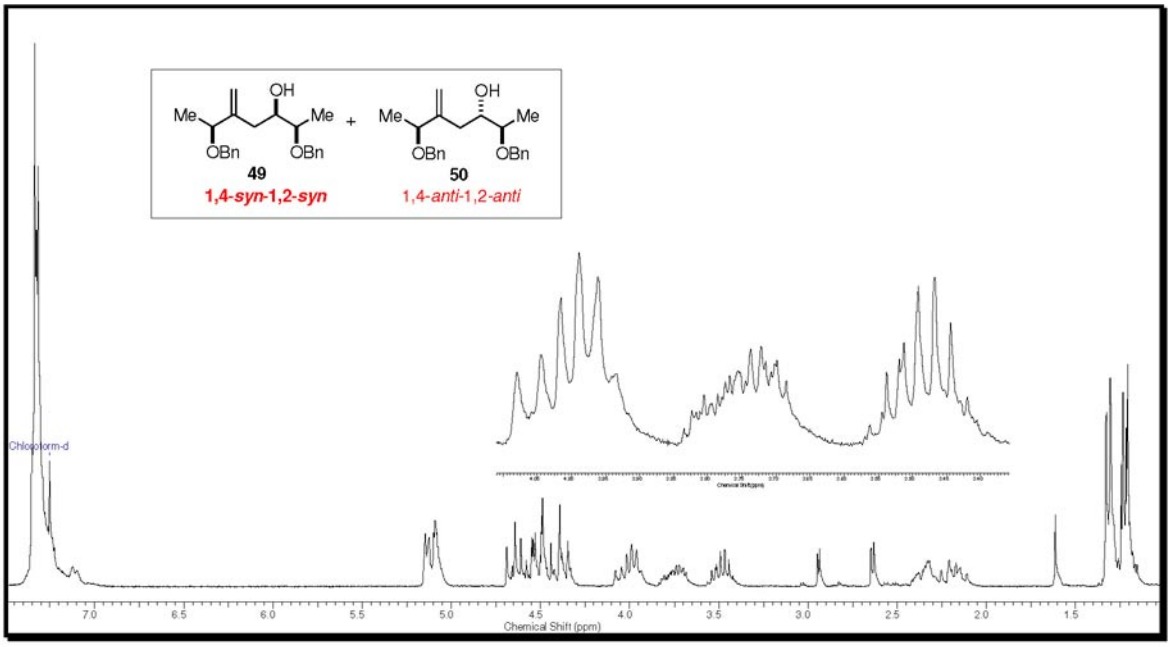


Figure 72S. ^{1}H NMR ($CDCl_3$, 250 MHz) - (2*R*,3*R*,6*S*)-2,6-bis(benzyloxy)-5-methyleneheptan-3-ol (**49**) and (2*R*,3*S*,6*S*)-2,6-bis(benzyloxy)-5-methyleneheptan-3-ol (**50**).

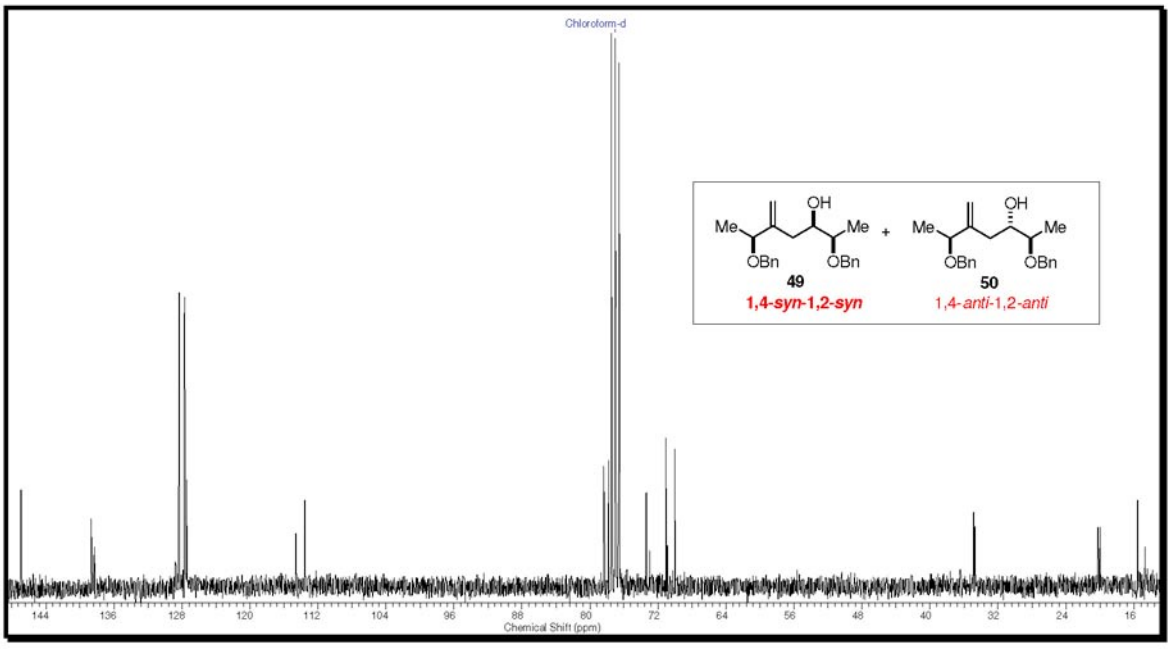


Figure 73S. ^{13}C NMR ($CDCl_3$, 63 MHz) (2*R*,3*R*,6*S*)-2,6-bis(benzyloxy)-5-methyleneheptan-3-ol (**49**) and (2*R*,3*S*,6*S*)-2,6-bis(benzyloxy)-5-methyleneheptan-3-ol (**50**).

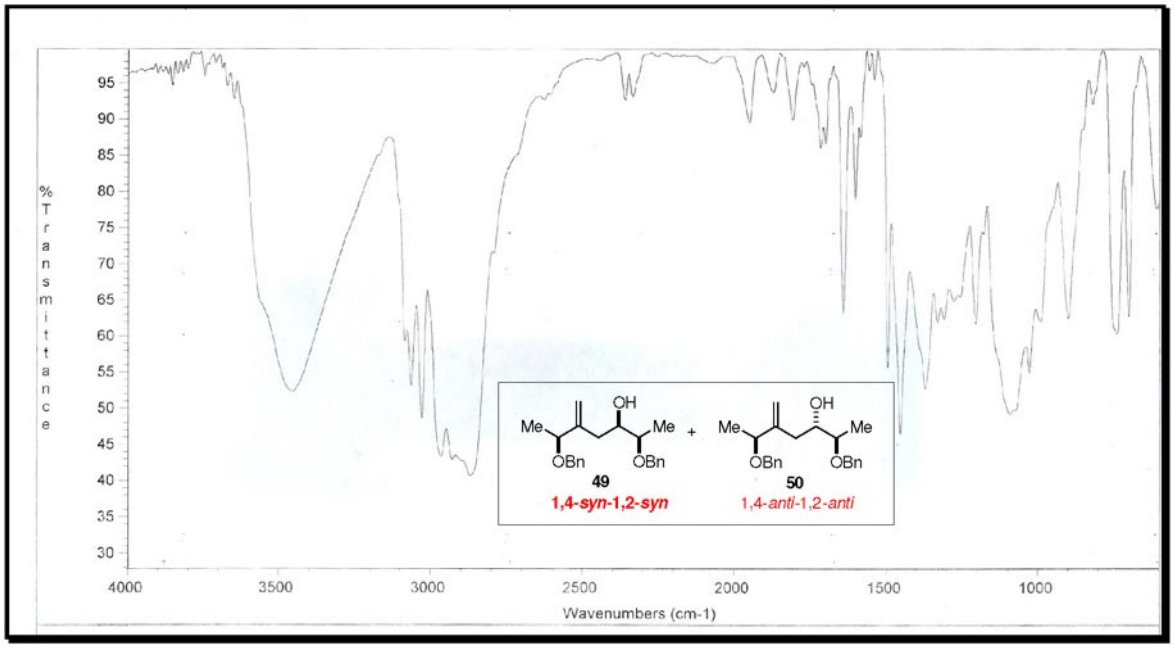


Figure 74S. IR (film) - (2*R*,3*R*,6*S*)-2,6-bis(benzyloxy)-5-methyleneheptan-3-ol (**49**) and (2*R*,3*S*,6*S*)-2,6-bis(benzyloxy)-5-methyleneheptan-3-ol (**50**).