SUPPORTING INFORMATION

Total Synthesis of Limaol

Stephan N. Hess, Xiaobin Mo, Conny Wirtz, Alois Fürstner*

Max-Planck-Institut für Kohlenforschung, 45470 Mülheim/Ruhr, Germany

Email: fuerstner@kofo.mpg.de

Table of Contents

Additional Screening Data and Pathfinding Experiments

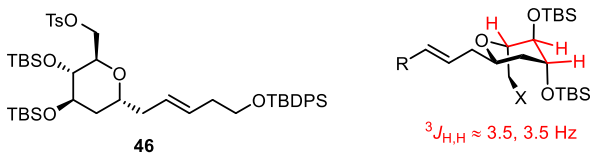


Figure S1. ^{1}H NMR data show that compound **46** adopts a conformation in which the bulky –OTBS groups and the –CH_2OTs substituent are axially disposed; this conformation is likely accountable for the reluctance of **46** to undergo nucleophilic substitution reactions with external nucleophiles

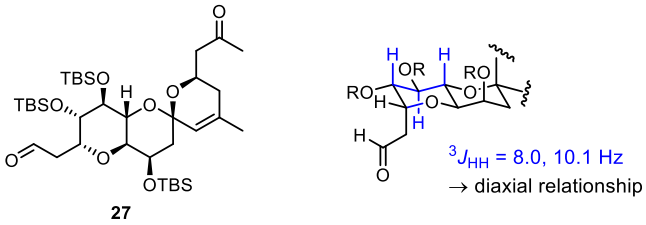
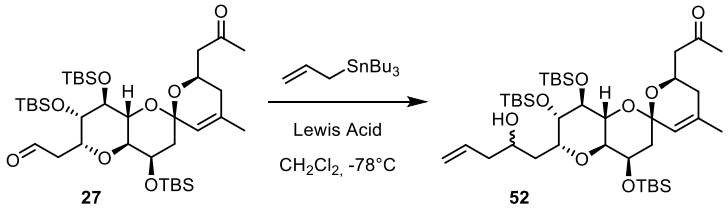


Figure S2. ^{1}H NMR data show the regular *trans*-decaline-type conformation adopted by the central fragment **27**, in which the aldehyde to be allylated is axially disposed and the large –OTBS groups remain equatorially oriented

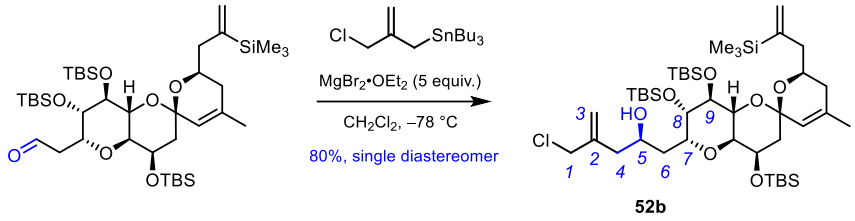
Table S1. Screening of Additional Lewis Acid Promotors in the Allylation of the Central Fragment[a]



Entry	Lewis Acid	d. r.	Yield
1	$MgBr_2$ (5 equiv.)	1:14	76%
2	$SnCl_4$ (1 equiv.)	4:3	28% (NMR)
3	$SnCl_4$ (2 equiv.)	---	decomposition
4	$BF_3{\cdot}OEt_2$ (1 equiv.)	1:1	56% (NMR)

[a] For the stereochemical assignment of the major isomer of product **52**, see the Mosher Ester Analysis compiled in Table S4

Table S2. Additional Control Experiment Concerning the Stereochemical Course of the Allylation Reaction: Reaction of a Modified Central Fragment with a Functionalized Allyl Stannane Donor: Analysis of the Mosher Esters of the Resulting Product **52b**;[1] arbitrary numbering as shown

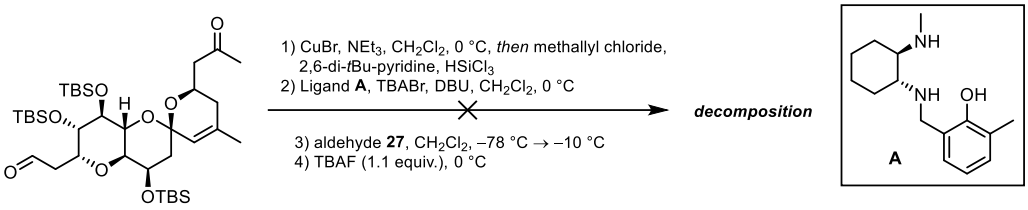


52b

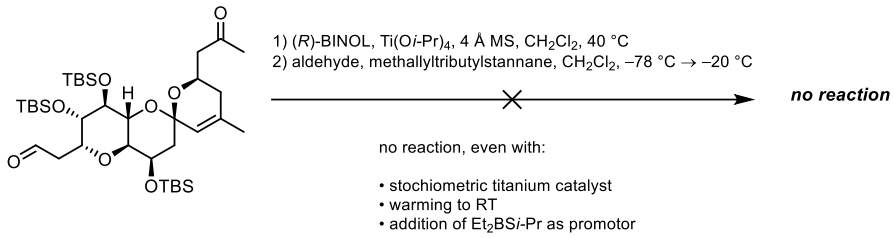
Atom number	(*S*)-MTPA-Ester δ [ppm]	(*R*)-MTPA-Ester δ [ppm]	Δδ [ppm]
1	4.02	3.87	+0.15
1'	3.96	3.83	+0.13
3	5.21	5.06	+0.15
3'	5.02	4.90	+0.12
4	2.69	2.65	+0.04
4'	2.39	2.35	+0.04
5	5.38	5.34	+0.04
6	2.10	2.21	−0.11
6'	1.74	1.88	−0.14
7	3.93	3.98	−0.05
8	3.61	3.63	−0.02
9	3.62	3.65	−0.03

Attempted Reagent- or Catalyst-Controlled Allylation Reactions of the Central Fragment[2]

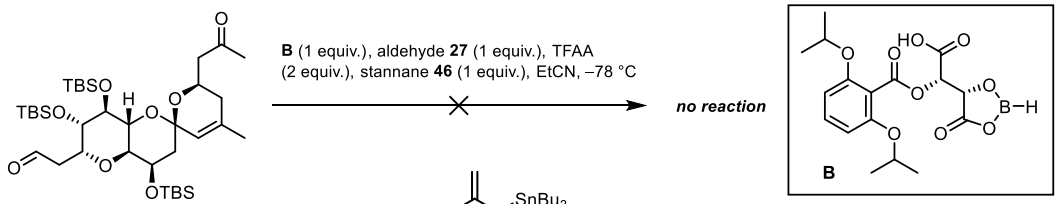
Leighton allylation (model reaction):



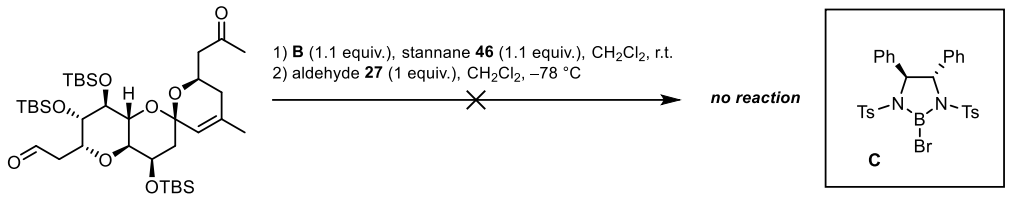
Keck allylation (model reaction):

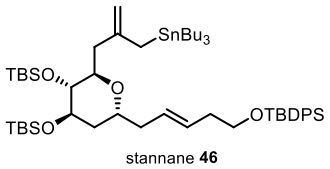


Yamamoto's Chiral (Acyloxy)borane as Promotor



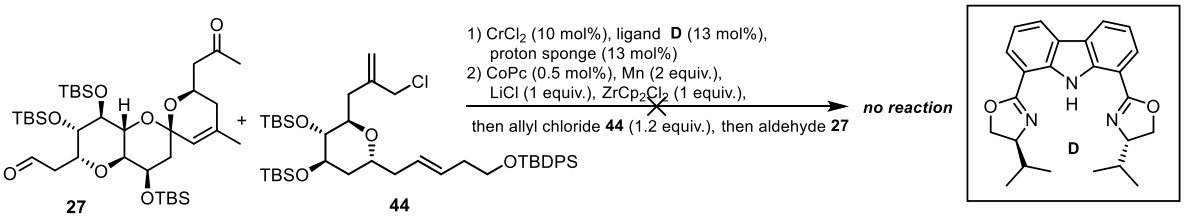
Corey's Chiral Bromoborane as Promotor





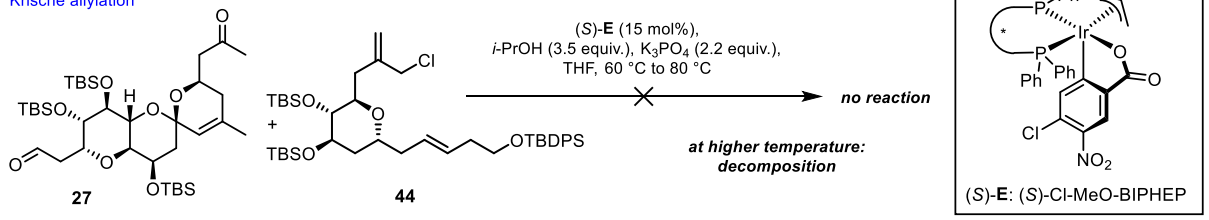
stannane **46**

Asymmetric NHK



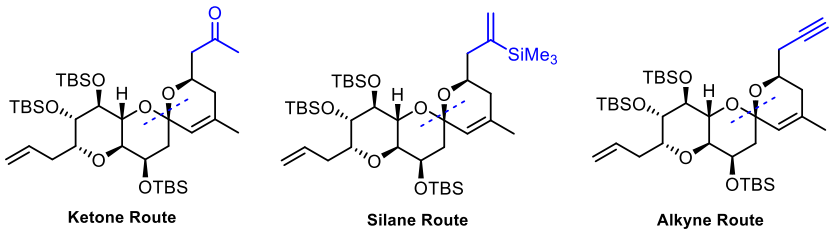
27 **44**

Krische allylation

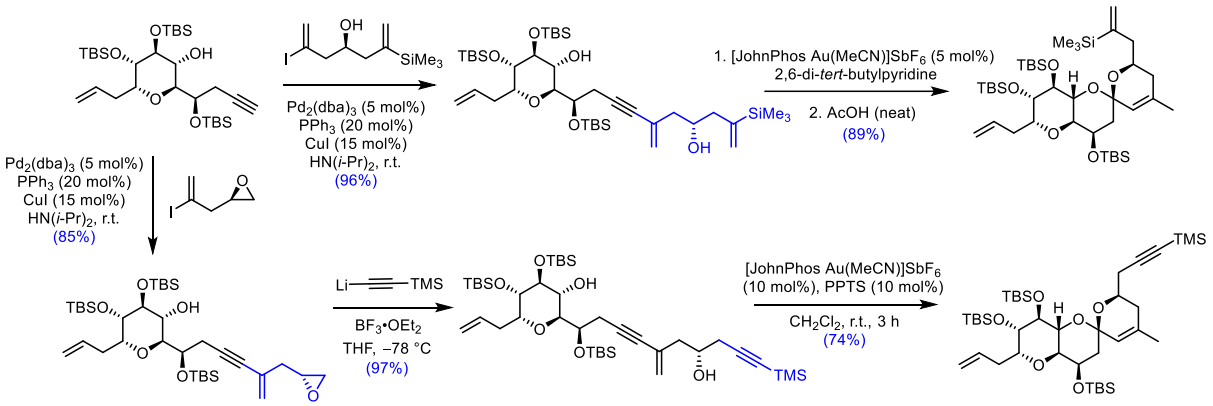


27 **44**

All Central Fragments Considered & Key Steps of the Syntheses of the Alternative Modules



Ketone Route **Silane Route** **Alkyne Route**



General Information

All reactions were carried out under argon in glassware that was flame-dried under vacuum. The solvents were purified by distillation over the indicated drying agents and were transferred under Ar: THF, Et_2O (Mg/anthracene); hexanes, toluene (Na/K); NEt_3, diisopropylamine, diisopropylethylamine, 2,6-lutidine, pyridine, *tert*-butyl methyl ether, CH_2Cl_2, NMP, DMPU (CaH_2); MeOH (Mg, stored over 3Å MS); DMF, 1,4-dioxane, and CH_3CN were dried by an adsorption solvent purification system based on molecular sieves.

Thin layer chromatography (TLC): Macherey-Nagel precoated plates (POLYGRAM®SIL/UV254); Flash chromatography: Merck silica gel 60 (40-63 µm or 15-40 µm (referred to as "fine silica")) with pre-distilled or HPLC grade solvents.

NMR: Spectra were recorded on a Bruker AV 400 or Bruker AVIII 600 or AV600neo spectrometer in the solvents indicated; chemical shifts (δ) are given in ppm relative to TMS, coupling constants (*J*) in Hz. The solvent signals were used as references and the chemical shifts converted to the TMS scale ($CDCl_3$ at 7.26 and 77.16 ppm for ^1H and ^{13}C NMR spectroscopy, respectively; CD_2Cl_2 at 5.32 ppm and 53.84 ppm for ^1H and ^{13}C NMR spectroscopy, respectively; C_6D_6 at 7.16 ppm and 128.06 ppm for ^1H and ^{13}C NMR spectroscopy, respectively; CD_3OD at 4.87 and 3.31 ppm for ^1H NMR and 49.00 ppm for ^{13}C NMR spectroscopy, respectively). ^1H NMR data are reported as δ (ppm) (s = singlet, d = doublet, t = triplet, q = quartet, qui = quintet, m = multiplet or unresolved, br = broad signal, app = appearing as; coupling constant (*J*) in Hz; integration). ^{13}C NMR spectra were recorded with broadband ^1H decoupling. ^{119}Sn NMR spectra were recorded using Me_4Sn as external standard.

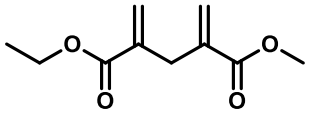
IR: Spectrum One (Perkin-Elmer) spectrometer, wavenumbers ($\tilde{\nu}$) in cm^{-1}.

MS (EI): Finnigan MAT 8200 (70 eV), ESIMS: ESQ 3000 (Bruker), accurate mass determinations: Bruker APEX III FT-MS (7 T magnet) or MAT 95 (Finnigan).

Unless stated otherwise, all commercially available compounds (ABCR, Acros, Aldrich, Apollo Scientific, Strem, TCI) were used as received. $CuBr{\cdot}SMe_2$ was recrystallized from dimethylsulfide and stored under Argon. *t*-BuOK was sublimed and stored under Argon.

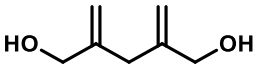
The following reagents and compounds were prepared according to the cited literature procedures: 2-Allenyl-1,3,2-dioxaborinane,[3] tetrabutylammonium diphenylphosphinate,[4] trityl potassium.[5]

Synthesis of the Northern Fragment



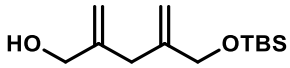
1-Ethyl 5-methyl 2,4-dimethylenepentanedioate (5).[6] A solution of DABCO (897 mg, 8.00 mmol) in methyl acrylate (4 mL) was slowly added to methyl 2-(bromomethyl)prop-2-enoate (**4**) (772 mg, 4.00 mmol), leading to the formation of a white precipitate. The resulting suspension was stirred at room temperature for 7 d. The reaction mixture was diluted with *tert*-butyl methyl ether (30 mL) and washed successively with HCl (2 M) and water. The organic layer was dried over anhydrous Na_2SO_4 and concentrated. The crude product was purified by flash chromatography (hexanes/EtOAc 15:1) to provide the desired product (557 mg, 70%). **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 6.25 (m, 2H), 5.60 (app q, J = 1.3 Hz, 1H), 5.58 (app q, J = 1.4 Hz, 1H), 4.20 (q, J = 7.1 Hz, 2H), 3.75 (s, 3H), 3.35 – 3.29 (m, 2H), 1.29 (t, J = 7.1 Hz, 3H); **^{13}C NMR** ($CDCl_3$, 100 MHz): δ 166.9, 166.4, 137.8, 137.6, 126.7, 126.5, 60.6, 51.8, 33.6, 14.0; **IR** (Microscope, cm^{-1}): 2984, 2954, 1700, 1632, 1438, 1211, 1137, 951; **HRMS** (EI) for $C_{10}H_{14}O_4$ [M+H]: calcd. 198.0887; found 198.0884.

Note: Compound **5** is rather unstable upon contact with silica; therefore the yield after flash chromoatography is variable. It is therefore recommended to skip the purification and reduce the crude material with DIBAL-H as described below.

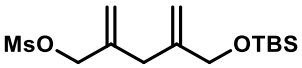


2,4-Dimethylenepentane-1,5-diol (S1). A solution of DABCO (1.80 g, 16.0 mmol) in methyl acrylate (8 mL) was slowly added to methyl 2-(bromomethyl)prop-2-enoate (**4**) (1.54 g, 8.00 mmol) slowly, leading to the formation of a white precipitate. The resulting suspension was stirred at room temperature for 7 d before the mixture was diluted with *tert*-butyl methyl ether (50 mL) and washed successively with HCl (2 M) and water. The organic layer was dried over anhydrous Na_2SO_4. *tert*-Butyl methyl ether was carefully removed under vacuum (300 mbar) at 25 °C. Next, the pressure was gradually reduced and excess methyl acrylate was distilled off at 80 mbar at 25 °C (an aliquot of the crude material was examined by ^{1}H NMR to ensure that most of the methyl acrylate had been removed).

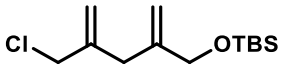
A solution of DIBAL-H (40 mmol, 1.0 M in THF, 40 mL) was slowly added to a solution of the residue in THF (60 mL) at 0 °C. The cooling bath was removed and the mixture was stirred for 5 h. The reaction was quenched at 0 °C with Rochelle's salt solution (20 mL) and the resulting mixture was vigorously stirred overnight before the aqueous layer was exacted with EtOAc (6 × 30 mL). It was essential to use EtOAc and the extraction must be performed repeatedly to recover the diol from the aqueous phase. The combined organic layers were dried over Na_2SO_4, filtered and concentrated. The residue was purified by flash chromatography (hexanes/EtOAc 1:2) to give the title compound as a colorless oil (581 mg, 57%). **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 5.13 (d, J = 1.5 Hz, 2H), 4.98 – 4.97 (m, 2H), 4.09 (d, J = 4.2 Hz, 4H), 2.90 (s, 2H), 1.64 (t, J = 5.0 Hz, 2H); **^{13}C NMR** ($CDCl_3$, 100 MHz): δ 146.3, 112.5, 65.7, 37.4; **IR** (Microscope, cm^{-1}): 3300, 3088, 2917, 2858, 1646, 1433, 1261, 1055, 1021, 899; **HRMS** (ESI) for $C_7H_{12}O_2Na$ $[M+Na]^+$: calcd. 151.0729; found 151.0730.



4-(((*tert*-Butyldimethylsilyl)oxy)methyl)-2-methylenepent-4-en-1-ol (6). A solution of diol **S1** (760 mg, 5.93 mmol) in THF (5 mL) was added dropwise at 0 °C to a suspension of NaH (157 mg, 6.52 mmol) in THF (15 mL). The resulting mixture was stirred for 45 min at ambient temperature before. *tert*-butylchlorodimethylsilane (983 mg, 6.52 mmol) was added in one batch and stirring was continued for an additional 2 h. The reaction was carefully quenched with H_2O and the resulting mixture extracted with ethyl acetate (3 × 15 mL). The combined organic layers were washed with brine, dried over Na_2SO_4, filtered and concentrated. The residue was purified by flash chromatography (hexanes/EtOAc 9:1 to 4:1) to provide the title compound as a colorless oil (1.25 g, 87 % yield). **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 5.14 (d, *J* = 1.8 Hz, 1H), 5.11 (d, *J* = 1.5 Hz, 1H), 4.94 (d, *J* = 1.3 Hz, 1H), 4.92 (d, *J* = 1.9 Hz, 1H), 4.07 (d, *J* = 6.2 Hz, 2H), 4.06 (s, 2 H), 2.83 (s, 2H), 1.64 (t, *J* = 6.2 Hz, 1H), 0.91 (s, 9H), 0.07 (s, 6H); **^{13}C NMR** ($CDCl_3$, 100 MHz): δ 146.4, 145.9, 111.9, 111.5, 65.7, 37.2, 26.1, 18.5, −5.2; **IR** (Microscope, cm^{-1}): 3329, 3079, 2929, 2857, 1648, 1472, 1255, 1109, 836; **HRMS** (ESI) for $C_{13}H_{26}O_2SiNa$ $[M+Na]^+$: calcd. 265.1594; found 265.1594.

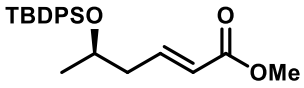


4-(((*tert*-Butyldimethylsilyl)oxy)methyl)-2-methylenepent-4-en-1-yl methanesulfonate (S2). MsCl (344 mg, 3.00 mmol) was added dropwise to a solution of the allylic alcohol **6** (364 mg, 1.50 mmol) and triethylamine (455 mg, 4.50 mmol) in CH_2Cl_2 (6 mL) at 0 °C. The cooling bath was removed after 15 min and stirring continued for 2 h. Water (10 mL) was added to quench the reaction. The resulting mixture was extracted with CH_2Cl_2 (3 × 10 mL), the combined organic layers were washed with brine (20 mL), dried over Na_2SO_4, and concentrated. The residue was subjected to flash chromatography (hexanes/EtOAc 10:1) to give the title compound as pale yellow oil (421 mg, 88%). **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 5.29 – 5.26 (m, 1H), 5.19 (d, *J* = 1.7 Hz, 1H), 5.16 – 5.14 (m, 1H), 4.92 (d, *J* = 1.5 Hz, 1H), 4.64 (s, 2H), 4.04 (s, 2H), 3.01 (s, 3H), 2.87 (s, 2H), 0.91 (s, 9H), 0.06 (s, 6H); **^{13}C NMR** ($CDCl_3$, 100 MHz): δ 144.8, 139.6, 117.6, 112.1, 71.5, 65.3, 38.0, 36.8, 26.0, 18.5, −5.3; **IR** (Microscope, cm^{-1}): 2955, 2857, 1649, 1463, 1359, 1176, 1109, 836; **HRMS** (ESI) for $C_{14}H_{28}O_4SSiNa[M+Na]^+$: calcd. 343.1370; found 343.1370.

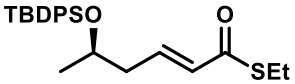


***tert*-Butyl((4-(chloromethyl)-2-methylenepent-4-en-1-yl)oxy)dimethylsilane (7).** Anhydrous LiCl (30 mg, 0.70 mmol) was added to a solution of mesylate **S2** (75 mg, 0.23 mmol) in THF (0.8 mL). The mixture was stirred at 40 °C for 24 h, causing the formation of a white suspension. After reaching ambient temperature, the reaction was quenched with brine (2 mL) and the resulting mixture was extracted with *tert*-butyl methyl ether (3 × 5 mL). The combined organic layers were dried over Na_2SO_4, filtered, and concentrated to afford the desired allyl chloride (59 mg, 98%) as a colorless oil, which was used without further purification. **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 5.21 (s, 1H), 5.18 (d, *J* = 1.8 Hz, 1H), 5.03 (d, *J* = 1.3 Hz, 1H), 4.93 (d, *J* = 1.8 Hz, 1H), 4.04 (s, 2H), 4.03 (d, *J* = 0.9 Hz, 2H), 2.92 (s, 2H), 0.91 (s, 9H), 0.06 (s, 6H); **^{13}C NMR** ($CDCl_3$, 100 MHz): δ 145.1, 142.8, 116.7, 111.8, 65.3, 47.5, 37.1,

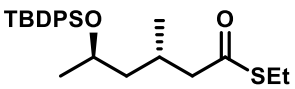
26.1, 18.5, −5.2; **IR** (Microscope, cm^{-1}): 2955, 2929, 2857, 1645, 1463, 1256, 1109, 836; **HRMS** (ESI) for $C_{13}H_{25}OClSiNa$ $[M+Na]^+$: calcd. 283.1255; found 283.1258.



Methyl (*R*,*E*)-5-((*tert*-butyldiphenylsilyl)oxy)hex-2-enoate (10). Compound **9** (325 mg, 1.00 mmol)[7] was dissolved in CH_2Cl_2 (7.0 ml) and the resulting solution was degassed for fifteen minutes by bubbling Ar through it, at which point there was only a total volume of ≈3.5 mL left. Freshly distilled methyl acrylate (215 mg, 2.50 mmol, freshly distilled) was added, followed by Grubbs II catalyst (8.5 mg, 10 µmol). The resulting mixture was stirred at reflux temperature for 20 h. After full consumption of the starting material, stirring was continued under air for 1 h to destroy the catalyst. The dark brown solution was concentrated and the residue was purified by flash chromatography (hexanes/EtOAc 20:1 to 10:1) to give the title compound as a colorless syrup (383 mg, 86%). $[\boldsymbol{\alpha}]_{\boldsymbol{D}}^{\boldsymbol{20}}$ = 35.1 (c = 0.27, $CHCl_3$). **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.71 – 7.61 (m, 4H), 7.49 – 7.30 (m, 6H), 6.92 (dt, *J* = 15.3, 7.5 Hz, 1H), 5.76 (dt, *J* = 15.7, 1.4 Hz, 1H), 3.96 (app h, *J* = 6.1 Hz, 1H), 3.72 (s, 3H), 2.41 – 2.20 (m, 2H), 1.09 (d, *J* = 6.1 Hz, 3H), 1.05 (s, 9H); **^{13}C NMR** ($CDCl_3$, 100 MHz): δ 167.0, 146.0, 136.0, 136.0, 134.5, 134.1, 129.8, 129.7, 127.7, 127.7, 123.2, 68.6, 51.5, 42.3, 27.1, 23.3, 19.4; **IR** (Microscope, cm^{-1}): 2932, 2858, 1725, 1659, 1428, 1270, 1110, 702; **HRMS** (ESI) for $C_{23}H_{30}O_3SiNa$ $[M+Na]^+$: calcd. 405.1856; found 405.1856.

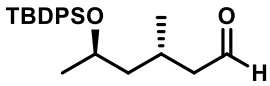


S-Ethyl (*R*,*E*)-5-((*tert*-butyldiphenylsilyl)oxy)hex-2-enethioate (11). Me_3SiSEt (263 mg, 1.76 mmol) and $AlCl_3$ (141 mg, 1.06 mmol) were added to a solution of enoate **10** (337 mg, 0.880 mmol) in THF (4.0 mL). The resulting mixture was stirred at reflux temperature for 3 h before the reaction was carefully quenched at room temperature with aqueous phosphate buffer solution (pH 7). The mixture was extracted with *tert*-butyl methyl ether (3 × 10 mL) and the combined organic layers were washed with water (10 mL), dried over Na_2SO_4, filtered and concentrated. The residue was purified by flash chromatography (hexanes/EtOAc 20:1) to afford the title compound as a colorless liquid (313 mg, 86%). $[\boldsymbol{\alpha}]_{\boldsymbol{D}}^{\boldsymbol{20}}$ = 52.5 (c = 0.56, $CHCl_3$). **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.69 – 7.64 (m, 4H), 7.46 – 7.34 (m, 6H), 6.85 (dt, *J* = 15.2, 7.5 Hz, 1H), 6.03 (dt, *J* = 15.5, 1.4 Hz, 1H), 3.97 (h, *J* = 6.0 Hz, 1H), 2.94 (q, *J* = 7.4 Hz, 2H), 2.37 – 2.10 (m, 2H), 1.28 (t, *J* = 7.4 Hz, 3H), 1.09 (d, *J* = 6.1 Hz, 3H), 1.05 (s, 9H); **^{13}C NMR** ($CDCl_3$, 100 MHz): δ 190.0, 141.6, 135.9, 135.8, 134.3, 133.9, 130.8, 129.7, 129.6, 127.6, 127.5, 68.5, 42.1, 27.0, 23.3, 23.1, 19.2, 14.8; **IR** (Microscope, cm^{-1}): 3070, 2964, 2857, 1670, 1634, 1427, 1377, 1262, 1109, 991; **HRMS** (ESI) for $C_{24}H_{32}O_2SSiNa$ $[M+Na]^+$: calcd. 435.1785; found 435.1783.



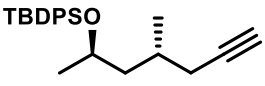
S-Ethyl (3*S*,5*R*)-5-((*tert*-butyldiphenylsilyl)oxy)-3-methylhexanethioate (12). $CuBr{\cdot}SMe_2$ (36 mg, 0.17 mmol) and (*S*)-(*R*)-Josiphos **19** (0.12 g, 0.21 mmol) were added to *tert*-butyl methyl ether (69 mL)

and the mixture was stirred at room temperature for 30 min to form a clear solution. The mixture was cooled to −75 °C before methyl magnesium bromide (3.0 M in Et_2O, 5.20 mL, 15.6 mmol) was added dropwise. After stirring for another 10 min, a solution of thioester **11** (3.56 g, 8.62 mmol) in *tert*-butyl methyl ether (17.2 mL) was added via syringe pump over the course of 2 h. Once the addition was complete, stirring was continued at −75 °C for 18 h. The reaction mixture was quenched with MeOH at −75 °C and the mixture was warmed to room temperature. Saturated aq. NH_4Cl solution (50 mL) was then added, the phases were separated and the aqueous layer extracted with *tert*-butyl methyl ether (3 × 50 mL). The combined organic layers were dried over Na_2SO_4, filtered and concentrated. The residue was purified by flash chromatography (hexanes/EtOAc 100:1) to afford the title compound as a colorless liquid (3.34 g, 90%, dr > 20:1 (^{1}H NMR)). $[\alpha]_D^{20}$ = 13.2 (c = 0.53, $CHCl_3$). **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.72 – 7.65 (m, 4H), 7.46 – 7.33 (m, 6H), 3.85 (app dq, *J* = 12.2, 6.1 Hz, 1H), 2.85 (q, *J* = 7.4 Hz, 2H), 2.40 – 2.26 (m, 1H), 2.25 – 2.10 (m, 2H), 1.61 – 1.47 (m, 1H), 1.23 (t, *J* = 7.4 Hz, 3H), 1.21 – 1.12 (m, 1H), 1.06 (m, 12H), 0.78 (d, *J* = 6.3 Hz, 3H); **^{13}C NMR** ($CDCl_3$, 100 MHz): δ 199.0, 136.0, 134.9, 134.2, 129.6, 129.4, 127.6, 127.4, 67.4, 51.6, 46.7, 27.8, 27.1, 24.0, 23.2, 19.6, 19.3, 14.8; **IR** (Microscope, cm^{-1}): 3070, 2963, 2931, 2857, 1689, 1428, 1110, 702; **HRMS** (ESI) for $C_{25}H_{36}O_2SSiNa$ $[M+Na]^+$: calcd. 451.2098; found 451.2098.



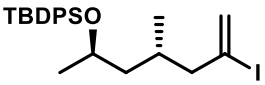
(3*S*,5*R*)-5-((*tert*-Butyldiphenylsilyl)oxy)-3-methylhexanal (13).[8] A solution of compound **12** (3.34 g, 7.80 mmol) in CH_2Cl_2 (8 mL) was sequentially added to a stirred suspension of Pd/C (10% *w/w*, 0.41 g, 0.39 mmol) in CH_2Cl_2 (8 mL) at room temperature, followed by Et_3SiH (2.72 g, 23.4 mmol). After stirring for 30 min, the mixture was filtered through a pad of Celite which was carefully rinsed with CH_2Cl_2 (100 mL). The combined filtrates were concentrated under reduced pressure and the residue was purified by flash chromatography (hexanes/EtOAc 100:1 to 20:1) to afford the title compound as a colorless liquid (2.45 g, 85%). $[\alpha]_D^{20}$ = 5.4 (c = 0.24, $CHCl_3$). **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 9.64 – 9.61 (m, 1H), 7.73 – 7.63 (m, 4H), 7.45 – 7.32 (m, 6H), 3.86 (app dq, *J* = 12.2, 6.1 Hz, 1H), 2.28 – 2.13 (m, 2H), 2.14 – 2.00 (m, 1H), 1.60 – 1.45 (m, 1H), 1.23 (ddd, *J* = 13.5, 8.2, 4.7 Hz, 1H), 1.08 (d, *J* = 6.1 Hz, 3H), 1.05 (s, 9H), 0.78 (d, *J* = 6.6 Hz, 3H); **^{13}C NMR** ($CDCl_3$, 100 MHz): δ 203.0, 136.1, 136.1, 134.8, 134.3, 129.8, 129.6, 127.7, 127.6, 67.6, 51.4, 47.2, 27.2, 25.0, 24.2, 20.1, 19.4; **IR** (Microscope, cm^{-1}): 3071, 2930, 2857, 2712, 1725, 1462, 1427, 1109, 822; **HRMS** (ESI) for $C_{23}H_{32}O_2SiNa$ $[M+Na]^+$: calcd. 391.2064; found 391.2061.

Note: *Comparison of the recorded data of **12** with the data of this aldehyde as reported by Nelson and co-workers confirmed the relative and absolute stereochemistry*.[7]

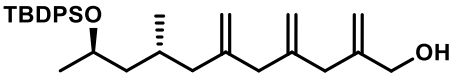


***tert*-Butyl(((2*R*,4*R*)-4-methylhept-6-yn-2-yl)oxy)diphenylsilane (14).** K_2CO_3 (9.19 g, 66.5 mmol) was added to a solution of aldehyde **13** (2.45 mg, 6.65 mmol) in MeOH (66 mL), followed by addition of the

Bestmann-Ohira reagent **18** (1.53 g, 7.98 mmol) in one portion. The mixture was stirred at room temperature for 16 h before the reaction was quenched with water (30 mL). The aqueous phase was extracted with *tert*-butyl methyl ether (3 × 50 mL), and the combined organic layers were washed with brine (30 mL), dried over Na_2SO_4, filtered and concentrated. Purification of the residue by flash chromatography (hexanes/*tert*-butyl methyl ether 100:1) afforded the product as a colorless liquid (2.27 g, 94%). $[\alpha]_D^{20}$ = 13.0 (c = 0.68, $CHCl_3$). **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.73 – 7.65 (m, 4H), 7.47 – 7.32 (m, 6H), 3.89 (app h, *J* = 5.9 Hz, 1H), 2.10 – 2.01 (m, 1H), 1.99 – 1.90 (m, 2H), 1.85 (app dq, *J* = 14.4, 6.5 Hz, 1H), 1.69 (app dt, *J* = 13.4, 6.5 Hz, 1H), 1.30 – 1.17 (m, 1H), 1.06 (m, 12H), 0.84 (d, *J* = 6.6 Hz, 3H); **^{13}C NMR** ($CDCl_3$, 100 MHz): δ 136.1, 135.1, 134.4, 129.7, 129.5, 127.7, 127.5, 83.3, 69.3, 67.8, 46.3, 29.0, 27.2, 26.3, 24.2, 19.5; **IR** (Microscope, cm^{-1}): 3309, 3071, 2930, 2858, 1461, 1427, 1375, 1109, 1061, 702; **HRMS** (ESI) for $C_{24}H_{32}OSiNa$ $[M+Na]^+$: calcd. 387.2115; found 387.2111.



***tert*-Butyl(((2*R*,4*S*)-6-iodo-4-methylhept-6-en-2-yl)oxy)diphenylsilane (15).** 9-I-9-BBN (0.32 mL, 1.0 M in hexane, 0.32 mmol) was added over the course of 1 h to a stirred solution of alkyne **14** (91 mg, 0.25 mmol) in anhydrous hexane (2.5 mL) at 0 °C. Once the addition was complete, stirring was continued at room temperature for 16 h. At this point, HOAc (56 mg, 0.93 mmol) was added and the mixture stirred for another 1 h. The reaction was then quenched with aq. NaS_2O_3 (1 M) and $NaHCO_3$ until the mixture was colorless and showed a pH = 7. The aqueous layer was separated and extracted with *tert*-butyl methyl ether (3 × 10 mL), and the combined organic layers were washed with brine, dried over Na_2SO_4, filtered and concentrated. The residue was purified by flash chromatography (hexanes/Et_3N, 100:1) to give the title compound as a colorless liquid (121 mg, 99%). **Note**: It was critical to ensure that the silica was neutralized. $[\alpha]_D^{20}$ = 19.8 (c = 0.30, $CHCl_3$). **^{1}H NMR** (C_6D_6, 400 MHz): δ 7.88 – 7.76 (m, 4H), 7.27 – 7.20 (m, 6H), 5.64 (d, *J* = 1.2 Hz, 1H), 5.58 – 5.52 (s, 1H), 3.99 – 3.89 (m, 1H), 2.19 – 2.00 (m, 2H), 1.78 (dd, *J* = 14.3, 7.7 Hz, 1H), 1.57 (ddd, *J* = 13.1, 8.1, 4.7 Hz, 1H), 1.23 (s, 9H), 1.08 (d, *J* = 6.1 Hz, 3H), 0.97 (ddd, *J* = 13.4, 8.8, 4.5 Hz, 1H), 0.66 (d, *J* = 6.5 Hz, 3H); **^{13}C NMR** (C_6D_6, 100 MHz): δ 136.4, 135.3, 134.6, 130.0, 129.9, 126.5, 112.3, 67.8, 53.1, 46.5, 29.1, 27.5, 24.5, 19.6, 18.7; **IR** (Microscope, cm^{-1}): 3070, 2962, 2929, 2857, 1616, 1427, 1110, 509; **HRMS** (ESI) for $C_{24}H_{33}OISiNa$ $[M+Na]^+$: calcd. 515.1238; found 515.1245.



Compound 16.

Pre-Activation of the Zinc Dust: Commercial Zn dust was pre-activated by sequential washing with HCl (1.0 M), water, *i*-PrOH, MeOH and Et_2O and was then dried under high vacuum.

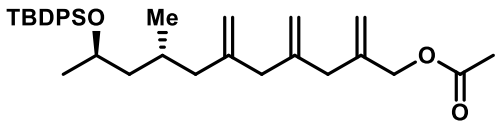
***Preparation of the Organozinc Compound Derived from Iodide* 15**: A Schlenk tube charged with LiCl (67.8 mg, 1.60 mmol) and pre-activated Zn dust (105 mg, 1.60 mmol) was evacuated and dried with

a heat gun. After reaching room temperature, the flask was flushed with Argon. THF was introduced (2 mL) and the resulting suspension was vigorously stirred. TMSCl (4.5 mg, 40 µmol) was added and stirring was continued at reflux temperature for 2 min. 1,2-Dibromoethane (7.5 mg, 40 µmol) was introduced at room temperature before the resulting suspension was stirred again at reflux temperature for another 2 min. Once again, the mixture was cooled to ambient temperature before alkenyl iodide **15** (0.39 g, 0.80 mmol) was added. The reaction mixture was then stirred at 65 °C bath temperature for 18 h before it was cooled to room temperature and filtered under Argon.

The solution of the organozinc reagent (3.0 mL) was titrated with I_2, which suggested a concentration of ≈0.135 M, corresponding to a yield of 51% yield.

Negishi Cross-coupling Reaction/Deprotection: A flame-dried Schlenk tube was charged with allyl chloride 7 (26 mg, 0.10 mmol) and THF (0.5 mL). This solution was degassed by purging with Argon for 15 min, leading to a reduced total volume (ca. 0.25 mL). $Pd(PPh_3)_4$ (5.8 mg, 5.0 µmol) was added followed by the solution of the organozinc reagent (0.74 mL, 0.10 mmol). The mixture was stirred at ambient temperature and the reaction monitored by TLC. Once full conversion was reached (ca. 8 h), saturated NH_4Cl solution was added and the resulting mixture was extracted with *tert*-butyl methyl ether (3 × 10 mL). The combined organic layers were washed with brine, dried over Na_2SO_4, filtered and concentrated.

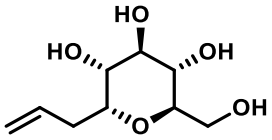
TBAF solution (1 M in THF, 0.11 mL, 0.11 mmol) was added to a solution of the crude materail (59 mg) in THF (1.0 mL) at 0 °C and the resulting mixture was stirred for 1.5 h. The reaction was quenched with saturated aq. NH_4Cl solution (2.0 mL) and the aqueous phase extracted with *tert*-butyl methyl ether (3 × 5 mL). The combined organic layers were washed with brine (10 mL), dried over Na_2SO_4, filtered and concentrated. The residue was subjected to flash chromatography (hexanes/*tert*-butyl methyl ether 6:1) to give the title compound as a colorless liquid (36 mg, 76% over two steps). $[\alpha]_D^{20}$ = −4.8 (c = 0.45, $CHCl_3$). **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.72 – 7.65 (m, 4H), 7.44 – 7.32 (m, 6H), 5.12 (s, 1H), 4.91 (s, 1H), 4.87 (s, 1H), 4.84 (s, 1H), 4.77 (s, 1H), 4.76 (s, 1H), 4.03 (s, 2H), 3.90 (app dq, *J* = 12.1, 6.0 Hz, 1H), 2.75 (s, 2H), 2.66 (s, 2H), 1.89 – 1.76 (m, 2H), 1.65 (m, 1H), 1.57 (ddd, *J* = 12.6, 8.0, 4.5 Hz, 1H), 1.04 (d, *J* = 2.2 Hz, 13H), 0.69 (d, *J* = 6.4 Hz, 3H); **^{13}C NMR** ($CDCl_3$, 100 MHz): δ 146.3, 145.6, 144.6, 136.0, 135.9, 135.0, 134.3, 129.5, 129.4, 127.5, 127.3, 113.8, 113.1, 111.8, 67.7, 65.4, 47.3, 43.6, 42.5, 39.5, 27.1, 27.0, 24.3, 19.5, 19.3; **IR** (Microscope, cm^{-1}): 3330, 3071, 2962, 2928, 2857, 1638, 1428, 1375, 1110, 1060, 897; **HRMS** (ESI) for $C_{31}H_{44}O_2SiNa$ $[M+Na]^+$: calcd. 499.3003; found 499.3008.



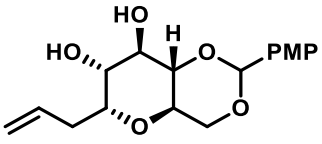
(8*R*,10*R*)-10-((*tert*-Butyldiphenylsilyl)oxy)-8-methyl-2,4,6-trimethyleneundecyl acetate (17). Pyridine (30 µL, 0.37 mmol), acetic anhydride (44 µL, 0.47 mmol), and DMAP (3.8 mg, 31 µmol) were sequentially added to a stirred solution of alcohol **16** (0.15 g, 0.31 mmol) in CH_2Cl_2 (4 mL) at 0 °C. The

cooling bath was removed and the mixture stirred for 2 h at room temperature. The reaction was quenched with saturated aqueous NH_4Cl solution (4 mL) and the mixture diluted with *tert*-butyl methyl ether (8 mL). The aqueous phase was extracted with *tert*-butyl methyl ether (3 × 4 mL). The combined organic fractions were washed with brine (4 mL), dried over anhydrous Na_2SO_4, filtered and concentrated. The residue was purified by flash chromatography (hexanes/EtOAc 20:1) to give the allylic acetate **17** as a colorless oil (0.15 g, 96%). $[\alpha]_D^{20}$ = −5.2 (c = 1.00, $CHCl_3$). **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.69 (ddd, *J* = 8.2, 6.8, 1.6 Hz, 4H), 7.47 – 7.32 (m, 6H), 5.12 (s, 1H), 5.02 – 4.95 (m, 1H), 4.86 (s, 2H), 4.79 – 4.73 (m, 2H), 4.49 (s, 2H), 3.90 (dqd, *J* = 8.1, 6.1, 4.6 Hz, 1H), 2.75 (s, 2H), 2.66 (s, 2H), 2.08 (s, 3H), 1.91 – 1.76 (m, 2H), 1.72 – 1.50 (m, 2H), 1.10 – 1.07 (m, 1H), 1.05 (s, 9H), 1.04 (d, *J* = 6.1 Hz, 3H), 0.69 (d, *J* = 6.2 Hz, 3H); **^{13}C NMR** ($CDCl_3$, 100 MHz): δ 170.8, 145.6, 143.9, 141.5, 136.1, 136.1, 135.1, 134.5, 129.6, 129.5, 127.6, 127.5, 114.6, 114.3, 113.2, 67.8, 66.3, 47.4, 43.8, 42.6, 39.7, 27.2, 27.1, 24.4, 21.1, 19.6, 19.5; **IR** (Microscope, cm^{-1}): 3072, 2962, 2929, 2858, 1744, 1638, 1472, 1459, 1428, 1374, 1227, 1155, 1129, 1110, 1058, 1027, 996, 951, 899, 822, 741, 728, 703, 685, 612, 500; **HRMS** (ESI) for $C_{33}H_{46}O_3SiNa$ $[M+Na]^+$: calcd. 541.3108; found 541.3112.

Synthesis of the Central Fragment

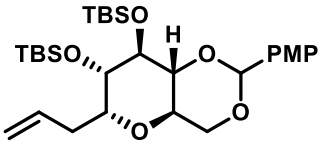


(2*R*,3*R*,4*R*,5*S*,6*R*)-2-Allyl-6-(hydroxymethyl)tetrahydro-2*H*-pyran-3,4,5-triol (S3). The compound was prepared according to a procedure previously described by our group.[9] **^{1}H NMR** (CD_3OD, 400 MHz): δ 5.88 (ddt, *J* = 17.1, 10.2, 6.9 Hz, 1H), 5.12 (dq, *J* = 17.1, 1.5 Hz, 1H), 5.04 (ddt, *J* = 10.2, 2.2, 1.1 Hz, 1H), 3.95 (ddd, *J* = 10.5, 5.6, 4.3 Hz, 1H), 3.74 (dd, *J* = 11.8, 2.5 Hz, 1H), 3.64 (dd, *J* = 11.7, 5.2 Hz, 1H), 3.60 (dd, *J* = 9.4, 5.7 Hz, 1H), 3.53 (dd, *J* = 9.5, 8.4 Hz, 1H), 3.45 (ddd, *J* = 9.6, 5.3, 2.6 Hz, 1H), 3.28 (dd, *J* = 9.6, 8.4 Hz, 1H), 2-53 – 2.36 (m, 2H); **^{13}C NMR** (CD_3OD, 101 MHz): δ 136.6, 116.9, 77.1, 75.1, 74.4, 72.9, 72.2, 62.9, 30.5.

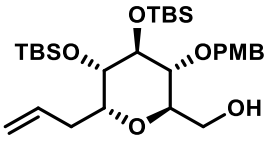


Compound 21. Anisaldehyde dimethyl acetal (1.3 mL, 7.6 mmol) and camphorsulfonic acid (0.15 g, 0.64 mmol) were added to a stirred solution of **S3** (1.3 g, 6.4 mmol) in anhydrous DMF (10 mL). The mixture was stirred at 85 °C under reduced pressure (250 mbar) for 3 h. Additional anisaldehyde dimethyl acetal (0.65 mL, 3.8 mmol) was added and stirring continued at 85 °C under reduced pressure (250 mbar) for another 1 h. The reaction was quenched with triethylamine (0.5 mL) and the solvent was removed in vacuo. The residue was purified by flash chromatography (hexanes/EtOAc 2:3 to 0:1) to give the title compound (1.6 g, 79%) as a pale yellow solid. $[\alpha]_D^{20}$ = +56.6 (c = 1.22, $CHCl_3$); **m.p.** 193.0-193.5 °C. **^{1}H NMR** (CD_3OD, 400 MHz): δ 7.42 (d, *J* = 8.7 Hz, 2H), 6.89 (d, *J* = 8.9 Hz, 2H), 5.84 (dddd,

J = 16.8, 10.2, 7.5, 6.4 Hz, 1H), 5.51 (s, 1H), 5.15 (dq, *J* = 17.2, 1.6 Hz, 1H), 5.07 (ddt, *J* = 10.1, 2.2, 1.2 Hz, 1H), 4.11 (dd, *J* = 9.6, 4.3 Hz, 1H), 4.02 (ddd, *J* = 10.4, 6.3, 3.8 Hz, 1H), 3.79 (s, 3H), 3.77 – 3.70 (m, 2H), 3.65 (t, *J* = 9.8 Hz, 1H), 3.59 (td, *J* = 9.8, 9.4, 4.3 Hz, 1H), 3.46 – 3.36 (m, 1H), 2.61 – 2.43 (m, 2H); **^{13}C NMR** (CD_3OD, 101 MHz): δ 161.6, 136.3, 131.5, 128.8, 117.0, 114.3, 103.0, 83.6, 78.2, 73.7, 72.2, 70.3, 64.8, 55.7, 30.8; **IR** (Microscope, cm^{-1}): 3504, 3314, 2915, 1614, 1519, 1385, 1250, 1129, 1108, 1072, 1034, 1020, 973, 926, 829, 616, 599; **HRMS** (ESI) for $C_{17}H_{22}O_6Na$ [M+Na]: calcd. 345.1309; found 345.1310.

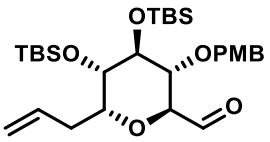


Compound S4. 2,6-Lutidine (1.2 mL, 10 mmol) and TBSOTf (1.5 mL, 6.4 mmol) were added to a solution of compound **21** (0.82 g, 2.5 mmol) in CH_2Cl_2 (14 mL) at −40 °C. After stirring at this temperature for 2 h, the reaction was quenched at −40 °C with saturated aqueous sodium bicarbonate (10 mL) and the mixture was allowed to reach room temperature over 30 min. The aqueous phase was extracted with EtOAc (3 × 15 mL), the combined organic fractions were dried over anhydrous Na_2SO_4, filtered and concentrated in vacuum. The residue was purified by flash chromatography (hexanes/EtOAc 20:1) to give the title compound (1.2 g, 86%) as a colorless oil. $[\alpha]_D^{20}$ = +21.7 (c = 0.93, $CHCl_3$). **^{1}H NMR** ($CDCl_3$, 400 MHz,): δ 7.39 (d, *J* = 8.7 Hz, 2H), 6.87 (d, *J* = 8.8 Hz, 2H), 5.80 (ddt, *J* = 17.1, 10.2, 6.9 Hz, 1H), 5.39 (s, 1H), 5.15 (dq, *J* = 17.2, 1.3 Hz, 1H), 5.12 – 5.08 (m, 1H), 4.20 (dd, *J* = 9.6, 4.3 Hz, 1H), 3.97 (td, *J* = 7.5, 5.0 Hz, 1H), 3.85 – 3.57 (m, 7H), 3.39 (dd, *J* = 9.4, 8.3 Hz, 1H), 2.50 (t, *J* = 7.4 Hz, 2H), 0.92 (s, 9H), 0.82 (s, 9H), 0.12 (s, 3H), 0.09 (s, 3H), 0.04 (s, 3H), 0.00 (s, 3H); **^{13}C NMR** ($CDCl_3$, 101 MHz): δ 160.1, 134.9, 130.1, 127.8, 117.1, 113.6, 102.2, 83.5, 72.9, 69.8, 63.7, 55.4, 30.4, 26.3, 26.2, 26.0, 25.9, 18.4, 18.2, −3.4, −3.9, −4.0, −4.3; **IR** (Microscope, cm^{-1}): 2954, 2930, 2895, 2857, 1519, 1251, 1171, 1080, 1035, 1003, 858, 837, 777; **HRMS** (ESI) for $C_{29}H_{50}O_6Si_2Na$ [M+Na]: calcd. 573.3038; found 573.3042.

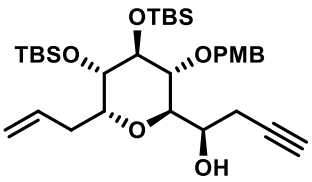


Compound S5. Diisobutylaluminum hydride in CH_2Cl_2 (1.0 M, 6.6 mL, 6.6 mmol) was added dropwise to a solution of acetal **S4** (1.2 g, 2.2 mmol) in CH_2Cl_2 (10 mL) at −78 °C. After stirring at −78 °C for 2 h, the mixture was allowed to warm to 0 °C and maintained at this temperature for 14 h. The reaction was carefully quenched with water (1 mL), and the mixture diluted with EtOAc (30 mL) and warmed to room temperature. Saturated aqueous sodium potassium tartrate (20 mL) was added and the biphasic mixture was vigorously stirred for 8 h. The layers were separated and the aqueous phase was extracted with EtOAc (3 × 10 mL). The combined organic fractions were dried over anhydrous Na_2SO_4, filtered and the solvent was evaporated. The residue was purified by flash chromatography (hexanes/EtOAc 4:1) to give the title compound (1.2 g, quant.) as a colorless oil. $[\alpha]_D^{20}$ = +41.8 (c = 1.09, $CHCl_3$). **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.24 (d, *J* = 8.7 Hz, 2H), 6.86 (d, *J* = 8.6 Hz, 2H), 5.81 (ddt, *J* = 17.2, 10.2, 6.8 Hz, 1H),

5.16 – 5.06 (m, 2H), 4.67 (d, *J* = 11.4 Hz, 1H), 4.49 (d, *J* = 11.4 Hz, 1H), 3.90 (dt, *J* = 10.5, 3.8 Hz, 1H), 3.84 – 3.69 (m, 6H), 3.64 – 3.55 (m, 2H), 3.24 (t, *J* = 6.9, 6.1 Hz, 1H), 2.51 – 2.41 (m, 1H), 2.36 – 2.28 (m, 1H), 1.89 (t, *J* = 5.9 Hz, 1H), 0.92 (s, 9H), 0.91 (s, 9H), 0.12 (s, 3H), 0.10 (s, 3H), 0.08 (s, 3H), 0.05 (s, 3H); **^{13}C NMR** ($CDCl_3$, 101 MHz): δ 159.2, 135.1, 130.3, 129.2, 117.1, 113.8, 78.1, 73.2, 73.2, 73.1, 73.0, 73.0, 61.9, 55.3, 31.8, 26.2, 26.1, 18.3, 18.0, −3.6, −3.7, −4.2, −4.5; **IR** (Microscope, cm^{-1}): 3498, 2954, 2930, 2893, 2857, 1613, 1514, 1472, 1250, 1088, 837, 776, 686; **HRMS** (ESI) for $C_{29}H_{52}O_6Si_2Na$ [M+Na]: calcd. 575.3195; found 575.3195.



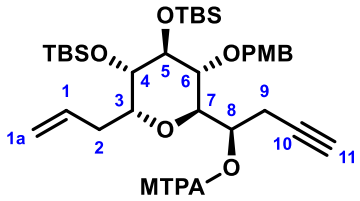
Aldehyde 22. DMSO (0.31 mL, 4.3 mmol) was added dropwise to a stirred solution of oxalyl chloride (0.18 mL, 2.1 mmol) in CH_2Cl_2 (8 mL) at −78 °C. The reaction mixture was stirred at −78 °C for 10 min before a solution of alcohol **S5** (0.59 g, 1.1 mmol) in CH_2Cl_2 (2 mL, rinse 2 × 1 mL) was added dropwise. After stirring for another 20 min at −78 °C, triethylamine (1.5 mL, 11 mmol) was slowly added at this temperature over the course of 5 min. After an additional 5 min at −78 °C, the mixture was allowed to warm to room temperature and stirring was continued for 30 min. The reaction was quenched with water and the aqueous phase was extracted with EtOAc (3 × 10 mL). The combined organic fractions were washed with brine (10 mL), dried over anhydrous Na_2SO_4, filtered and concentrated. The residue was purified by flash chromatography (hexanes/EtOAc 12:1) to afford the title compound (0.51 g, 87%) as a pale yellow oil. This experiment was repeated on a 2.2 mmol-scale to give the desired product in 84% yield. $[\boldsymbol{\alpha}]_{\boldsymbol{D}}^{\boldsymbol{20}}$ = +40.1 (c = 1.12, $CHCl_3$). **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 9.74 (s, 1H), 7.28 (d, *J* = 8.6 Hz, 2H), 6.87 (d, *J* = 8.7 Hz, 2H), 5.94 (ddt, *J* = 17.2, 10.2, 6.8 Hz, 1H), 5.17 (dq, *J* = 17.2, 1.7 Hz, 1H), 5.10 (ddt, *J* = 10.3, 2.1, 1.2 Hz, 1H), 4.59 (d, *J* = 12.2 Hz, 1H), 4.43 (d, *J* = 12.2 Hz, 1H), 4.32 (d, *J* = 0.8 Hz, 1H), 4.09 (ddd, *J* = 8.5, 5.0, 1.6 Hz, 1H), 3.84 (t, *J* = 3.2 Hz, 1H), 3.81 (s, 3H), 3.59 (ddd, *J* = 2.8, 1.5, 1.0 Hz, 1H), 3.36 – 3.34 (m, 1H), 2.57 (dddt, *J* = 14.9, 8.2, 6.4, 1.5 Hz, 1H), 2.21 (dddt, *J* = 14.8, 6.6, 5.0, 1.4 Hz, 1H), 0.93 (s, 9H), 0.78 (s, 9H), 0.10 (s, 3H), 0.09 (s, 3H), −0.04 (s, 3H), −0.13 (s, 3H); **^{13}C NMR** ($CDCl_3$, 101 MHz): δ 200.8, 159.5, 135.2, 130.0, 129.9, 117.0, 114.0, 80.0, 74.4, 71.3, 71.2, 70.1, 69.0, 55.5, 35.8, 26.1, 25.7, 18.5, 18.0, −3.9, −4.5, −5.0, −5.1; **IR** (Microscope, cm^{-1}): 2952, 2929, 2857, 1733, 1513, 1250, 1139, 1087, 1038, 835, 775; **HRMS** (ESI) for $C_{29}H_{50}O_6Si_2Na$ [M+Na]: calcd. 573.3038; found 573.3042.



Compound 23. 2-Allenyl-1,3,2-dioxaborinane (**33**) (0.13 mL, 1.4 mmol) and (*R*)-(+)-3,3'-dibromo-1,1'-bi-2-naphthol (**32**) (42 mg, 0.093 mmol) were added to a solution of aldehyde **22** (0.51 g, 0.93 mmol) in toluene (2 mL). The mixture was stirred at room temperature for 15 h. The reaction mixture was adsorped on silica and the product purified by flash chromatography (fine silica, hexanes/EtOAc 10:1) to give the title compound as a colorless oil (0.53 g, 96%, single diastereomer by ^{1}H NMR). $[\boldsymbol{\alpha}]_{\boldsymbol{D}}^{\boldsymbol{20}}$ =

+22.6 (c = 0.94, $CHCl_3$).**^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.26 (d, *J* = 8.6 Hz, 2H), 6.85 (d, *J* = 8.6 Hz, 2H), 5.86 (ddt, *J* = 17.2, 10.2, 7.0 Hz, 1H), 5.17 – 5.04 (m, 2H), 4.57 – 4.49 (m, 2H), 4.10 – 4.02 (m, 1H), 3.88 (dd, *J* = 4.2, 3.0 Hz, 1H), 3.86 – 3.73 (m, 5H), 3.56 – 3.51 (m, 2H), 2.57 – 2.35 (m, 4H), 2.13 (dddd, *J* = 14.4, 7.1, 3.3, 2.0 Hz, 1H), 2.00 (t, *J* = 2.6 Hz, 1H), 0.91 (s, 9H), 0.87 (s, 9H), 0.11 (s, 3H), 0.08 (s, 3H), 0.05 (s, 3H), 0.02 (s, 3H); **^{13}C NMR** ($CDCl_3$, 101 MHz): δ 159.4, 135.6, 130.2, 129.8, 117.1, 113.9, 81.2, 74.6, 72.0, 72.0, 71.7, 71.6, 70.7, 69.5, 55.4, 34.8, 26.1, 26.0, 24.0, 18.4, 18.0, −3.8, −4.2, −4.6, −4.6; **IR** (Microscope, cm^{-1}): 3505, 2953, 2930, 2857, 1514, 1472, 1250, 1089, 1038, 915, 835, 775, 635; **HRMS** (ESI) for $C_{32}H_{54}O_6Si_2Na$ [M+Na]: calcd. 613.3351; found 613.3354.

The absolute configuration was determined by Mosher ester analysis:[1]

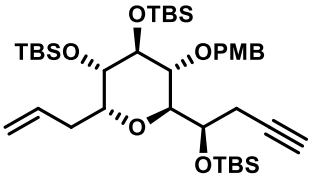


Preparation of the (*S*)-and (*R*)-MTPA Esters (S6) of Alcohol 23. *R*-(−)-MTPA-Cl (7.3 mg, 29 µmol) was added to a stirred solution of **23** (8.5 mg, 14 µmol) and pyridine (3.6 µL, 45 µmol) in CH_2Cl_2 (0.3 mL) After stirring for 16 h at room temperature, the reaction was quenched with H_2O (1 mL) and the mixture was diluted with *tert*-butyl methyl ether (3 mL). The aqueous phase was extracted with *tert*-butyl methyl ether (2 × 3 mL). The combined organic fractions were dried over anhydrous Na_2SO_4, filtered and evaporated. The residue was purified via flash chromatography (hexanes/EtOAc 15:1) to give the the desired *S*-MTPA ester **(*S*-S6**) (8.1 mg, 70%) as a pale yellow oil. **^{1}H NMR** ($CDCl_3$, 600 MHz): δ 7.64 (dd, *J* = 6.7, 3.0 Hz, 2H), 7.48 – 7.34 (m, 3H), 7.29 (d, *J* = 8.6 Hz, 2H), 6.87 (d, *J* = 8.6 Hz, 2H), 5.75 (ddt, *J* = 17.2, 10.8, 6.9 Hz, 1H), 5.70 (q, *J* = 6.0 Hz, 1H), 5.10 – 5.05 (m, 1H), 5.01 – 4.97 (m, 1H), 4.53 (d, *J* = 11.4 Hz, 1H), 4.40 (d, *J* = 11.3 Hz, 1H), 4.16 (t, *J* = 5.6 Hz, 1H), 4.00 (ddd, *J* = 8.3, 5.9, 2.8 Hz, 1H), 3.85 (t, *J* = 4.1 Hz, 1H), 3.80 (s, 3H), 3.53 (dd, *J* = 4.6, 2.8 Hz, 1H), 3.42 (d, *J* = 1.3 Hz, 3H), 3.23 – 3.20 (m, 1H), 2.50 (ddd, *J* = 16.9, 5.9, 2.7 Hz, 1H), 2.43 (ddd, *J* = 16.9, 6.5, 2.7 Hz, 1H), 2.35 (dt, *J* = 14.7, 7.3 Hz, 1H), 2.29 (dd, *J* = 14.0, 7.1 Hz, 1H), 1.87 (t, *J* = 2.6 Hz, 1H), 0.92 (s, 9H), 0.88 (s, 9H), 0.12 (s, 3H), 0.10 (s, 3H), 0.06 (s, 3H), −0.01 (s, 3H).

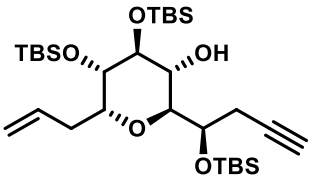
The *R*-MTPA ester **(*R*)-S6** was prepared analogously using *S*-(+)-MTPA-Cl as the reagent. **^{1}H NMR** ($CDCl_3$, 600 MHz): δ 7.67 – 7.63 (m, 2H), 7.40 – 7.38 (m, 3H), 7.31 – 7.27 (m, 2H), 6.91 – 6.86 (m, 2H), 5.76 (ddt, *J* = 17.0, 10.2, 6.8 Hz, 1H), 5.56 (td, *J* = 6.5, 3.8 Hz, 1H), 5.08 (dq, *J* = 17.2, 1.7 Hz, 1H), 5.00 (dq, *J* = 10.2, 2.2, 1.1 Hz, 1H), 4.53 (d, *J* = 10.9 Hz, 1H), 4.27 (d, *J* = 11.0 Hz, 1H), 4.09 (dd, *J* = 7.6, 3.8 Hz, 1H), 3.89 (ddd, *J* = 8.8, 5.1, 3.3 Hz, 1H), 3.81 (s, 3H), 3.80 – 3.78 (m, 1H), 3.60 – 3.57 (m, 3H), 3.46 (dd, *J* = 5.4, 3.4 Hz, 1H), 3.10 (dd, *J* = 7.6, 4.4 Hz, 1H), 2.67 – 2.61 (m, 2H), 2.35 (dt, *J* = 15.6, 7.7 Hz, 1H), 2.30 – 2.21 (m, 1H), 2.00 (t, *J* = 2.7 Hz, 1H), 0.90 (s, 9H), 0.88 (s, 9H), 0.10 (s, 3H), 0.07 (s, 3H), 0.05 (s, 3H), 0.00 (s, 3H).

Table S3. Analysis of the Mosher esters **S6** according to Hoye and co-workers;[1] arbitrary numbering scheme as shown in the insert.

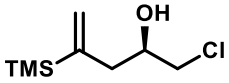
Atom number	**23** δ [ppm]	(***S***)-**S6** δ [ppm]	(***R***)-**S6** δ [ppm]	**Δδ** [ppm]
11	2.00	1.87	2.00	−0.13
9'	2.40	2.43	2.64	−0.21
9''	2.52	2.50	2.64	−0.14
8	3.88	5.70	5.56	+0.14
7a	3.83	4.16	4.09	+0.07
6	2.53	3.21	3.10	+0.11
5	3.77	3.85	3.79	+0.06
4	3.53	3.53	3.46	+0.07
3	4.06	4.00	3.89	+0.11
2'	2.47	2.35	2.35	±0.00
2''	2.13	2.26	2.26	±0.00



Compound S7. *tert*-Butyldimethylsilyl trifluoromethanesulfonate (0.46 mL, 2.0 mmol) was added dropwise to a solution of alcohol **23** (0.98 g, 1.7 mmol) and 2,6-lutidine (0.39 mL, 3.3 mmol) in CH_2Cl_2 (10 mL) at 0 °C and the mixture was stirred at 0 °C for 30 min. The reaction was quenched at 0 °C with saturated aqueous NH_4Cl (15 mL) and the mixture was diluted with *tert*-butyl methyl ether (20 mL). The aqueous phase was extracted with *tert*-butyl methyl ether (3 × 10 mL). The organic layers were combined, dried over anhydrous Na_2SO_4, and filtered. The solvent was evaporated and the residue purified by flash chromatography (hexanes/EtOAc 30:1) to give the title compound (1.2 g, 99%) as a colorless oil. $[\boldsymbol{\alpha}]_{\boldsymbol{D}}^{\boldsymbol{20}}$ = +39.2 (c = 1.03, $CHCl_3$). **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.24 (d, *J* = 8.6 Hz, 2H), 6.86 (d, *J* = 8.6 Hz, 2H), 5.86 (dddd, *J* = 16.6, 10.2, 7.5, 6.3 Hz, 1H), 5.17 – 5.02 (m, 2H), 4.67 (d, *J* = 11.4 Hz, 1H), 4.53 (d, *J* = 11.4 Hz, 1H), 4.05 (ddd, *J* = 6.9, 6.0, 2.7 Hz, 1H), 3.90 – 3.79 (m, 6H), 3.60 (dd, *J* = 5.7, 3.7 Hz, 1H), 3.51 (dd, *J* = 8.2, 4.4 Hz, 1H), 2.50 – 2.40 (m, 2H), 2.35 (ddd, *J* = 16.9, 6.9, 2.7 Hz, 1H), 2.23 (dddd, *J* = 14.7, 7.5, 3.3, 2.1 Hz, 1H), 1.92 (t, *J* = 2.6 Hz, 1H), 0.90 (s, 9H), 0.90 (s, 9H), 0.89 (s, 9H), 0.09 (s, 9H), 0.08 (s, 3H), 0.08 (s, 3H), 0.06 (s, 3H); **^{13}C NMR** ($CDCl_3$, 101 MHz): δ 159.0, 135.6, 130.9, 128.7, 116.7, 113.7, 82.9, 79.3, 74.4, 74.0, 73.5, 72.9, 72.3, 72.2, 69.8, 55.4, 33.0, 26.2, 26.2, 26.1, 24.1, 18.4, 18.3, 18.1, −3.5, −3.6, −4.0, −4.1, −4.5, −4.5; **IR** (Microscope, cm^{-1}): 2953, 2929, 2895, 2857, 1515, 1472, 1250, 1094, 1040, 1004, 836, 776, 672, 637; **HRMS** (ESI) for $C_{38}H_{68}O_6Si_3Na$ [M+Na]: calcd. 727.4216; found 727.4213.

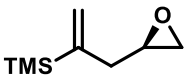


Compound 24. Water (3.0 mL) and 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (0.52 g, 2.3 mmol) were added to a solution of **S7** (1.2 g, 1.6 mmol) in CH_2Cl_2 (30 mL) at 0 °C. The mixture was stirred for 1 h at room temperature before it was diluted with water (20 mL) and extracted with *tert*-butyl methyl ether (3 × 15 mL). The combined organic fractions were washed with water (20 mL) and brine (20 mL), dried over anhydrous Na_2SO_4, and filtered. The solvent was evaporated and the crude product purified by flash chromatography (hexanes/*tert*-butyl methyl ether 50:1) to yield the title compound (0.95 g, 99%) as a colorless oil. $[\boldsymbol{\alpha}]_D^{\mathbf{20}}$ = +20.8 (c = 1.00, $CHCl_3$). **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 5.84 (ddt, *J* = 17.1, 10.2, 7.0 Hz, 1H), 5.19 – 5.04 (m, 2H), 4.14 (dt, *J* = 8.5, 4.4 Hz, 1H), 3.89 – 3.76 (m, 2H), 3.69 (dd, *J* = 8.1, 5.5 Hz, 1H), 3.61 (q, *J* = 5.7 Hz, 1H), 3.58 – 3.52 (m, 1H), 3.40 (d, *J* = 6.5 Hz, 1H), 2.59 – 2.38 (m, 3H), 2.29 – 2.19 (m, 1H), 1.97 (t, *J* = 2.6 Hz, 1H), 0.92 (s, 9H), 0.90 (s, 9H), 0.90 (s, 9H), 0.15 (s, 3H), 0.13 (s, 3H), 0.13 (s, 3H), 0.12 (s, 3H), 0.10 (s, 3H), 0.09 (s, 3H); **^{13}C NMR** ($CDCl_3$, 101 MHz): δ 135.1, 117.3, 81.2, 73.2, 72.9, 72.6, 72.1, 71.7, 70.6, 27.1, 26.2, 26.1, 25.9, 24.6, 18.3, 18.3, 18.2, −3.7, −3.9, −3.9, −4.0, −4.2, −4.5; **IR** (Microscope, cm^{-1}): 3505, 2954, 2930, 2896, 2858, 1472, 1254, 1096, 1033, 1005, 914, 836, 776, 680, 638; **HRMS** (ESI) for $C_{30}H_{60}O_5Si_3Na$ [M+Na]: calcd. 607.3641; found 607.3644.

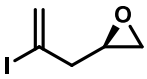


(*R*)-1-Chloro-4-(trimethylsilyl)pent-4-en-2-ol (28). A two-necked flask equipped with a reflux condenser was charged with Mg turnings (0.46 g, 19 mmol) and THF (4 mL). The suspension was stirred at reflux temperature for 1 min before 1,2-dibromoethane (16 µL, 0.19 mmol) was added and stirring was continued for 5 min. (1-Bromovinyl)trimethylsilane (0.70 mL, 4.5 mmol) was then added dropwise over 15 min at such a rate as to maintain gentle reflux but avoid strong foaming. Once the addition was complete, the mixture was stirred for 1 h at room temperature. The resulting solution of the Grignard reagent was transferred into a separate two-necked jacketed Schlenk vessel via cannula. Complete transfer was ensured by washing the flask with THF (2 × 2 mL). The solution was cooled to −50 °C and copper(I) cyanide (34 mg, 0.38 mmol) and (*R*)-(−)-epichlorohydrin (0.30 mL, 3.8 mmol) were successively added at this temperature. The resulting mixture was warmed to −20 °C and stirred was continued at this temperature for 2 h. The solution gradually turned red and then brown during this time. Saturated aqueous NH_4Cl (15 mL) and *tert*-butyl methyl ether (15 mL) were added and the mixture was warmed to room temperature over 10 min, giving a biphasic mixture. The aqueous phase was extracted with *tert*-butyl methyl ether (3 × 10 mL). The combined organic fractions were washed with brine, dried over anhydrous Na_2SO_4, filtered and concentrated. The residue was purified by bulb-to-bulk distillation under vacuum to give the desired chlorohydrin (0.73 g, 99%) as a colorless oil. $[\boldsymbol{\alpha}]_D^{\mathbf{20}}$ = −0.9 (c = 1.16, $CHCl_3$). **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 5.71 (dt, *J* = 2.7, 1.4 Hz, 1H), 5.52 (dt, *J* = 2.8, 0.8 Hz, 1H), 3.92 (dddt, *J* = 7.9, 6.3, 5.5, 4.0 Hz, 1H), 3.62 (dd, *J* = 11.1, 3.9 Hz, 1H), 3.52 (dd, *J* = 11.0, 6.3 Hz, 1H), 2.49

(dddd, *J* = 14.0, 5.6, 1.4, 0.7 Hz, 1H), 2.36 (dddd, *J* = 13.9, 7.9, 1.3, 0.8 Hz, 1H), 2.15 (d, *J* = 4.0 Hz, 1H), 0.12 (s, 9H).; **^{13}C NMR** ($CDCl_3$, 101 MHz): δ 148.2, 128.4, 70.1, 49.7, 41.5, −1.3; **IR** (Microscope, cm^{-1}): 3411, 2956, 1429, 1249, 1049, 934, 837, 758, 692, 658; **HRMS** (ESI) for $C_8H_{17}ClOSiNa$ [M+Na]: calcd. 215.0629; found 215.0629.



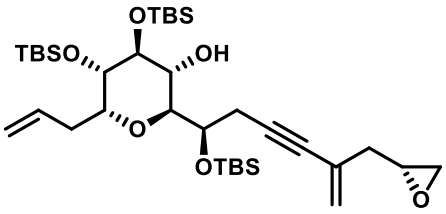
(*R*)-Trimethyl(3-(oxiran-2-yl)prop-1-en-2-yl)silane (29). Freshly powdered sodium hydroxide (0.23 g, 5.7 mmol) was added to a solution of chlorohydrin **28** (0.73 g, 3.8 mmol) in Et_2O (8 mL). The suspension was stirred for 27 h at room temperature before the mixture was filtered and the residue was washed with Et_2O (3 × 2 mL). The combined filtrates were dried over anhydrous Na_2SO_4 and concentrated by distilling the solvent off at atmospheric pressure (bath temperature ≤ 40 °C). The residue was purified by bulb-to-bulk distillation under vacuum to afford the desired epoxide (0.59 g, 99%) as a colorless liquid. The spectral data and specific rotation were in good agreement with those reported in the literature.[10] $[\alpha]_D^{20}$ = −4.1 (c = 0.96, $CHCl_3$), literature: $[\alpha]_D^{18}$ = −6.0 (c = 1.00, $CHCl_3$). **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 5.73 (dt, *J* = 2.9, 1.5 Hz, 1H), 5.45 (dt, *J* = 2.8, 1.0 Hz, 1H), 3.00 (tdd, *J* = 5.7, 3.9, 2.7 Hz, 1H), 2.79 (ddd, *J* = 5.1, 3.9, 0.7 Hz, 1H), 2.50 (dd, *J* = 5.1, 2.7 Hz, 1H), 2.46 – 2.38 (m, 1H), 2.29 (ddt, *J* = 15.1, 5.5, 1.3 Hz, 1H), 0.11 (s, 9H); **^{13}C NMR** ($CDCl_3$, 101 MHz): δ 148.1, 126.6, 51.9, 47.4, 39.0, −1.6; **IR** (Microscope, cm^{-1}): 2956, 1402, 1248, 1042, 930, 905, 833, 756, 691, 654; **HRMS** (CI) for $C_8H_{17}OSi$ [M+H]: calcd. 157.1049; found 157.1047.



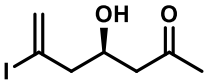
(*R*)-2-(2-Iodoallyl)oxirane (30). A solution of iodine monochloride (1.3 mL, 25 mmol) in degassed CH_2Cl_2 (20 mL) was added dropwise to a solution of alkenylsilane **29** (3.6 g, 23 mmol) in degassed CH_2Cl_2 (100 mL) at −78 °C. After stirring at −78 °C for 30 min, saturated aqueous $Na_2S_2O_3$ (100 mL) was added and the mixture was vigorously stirred until the yellow color had disappeared. The aqueous phase was extracted with CH_2Cl_2 (3 × 100 mL) and the combined organic layers were dried over anhydrous Na_2SO_4, filtered and concentrated in vacuum (bath temperature ≤ 30 °C).

The residue was taken up in Et_2O/THF (4:1, 100 mL) and solid tetrabutylammonium fluoride trihydrate (8.7 g, 28 mmol) was added at 0 °C. The mixture was stirred at 0 °C for 1 h before the reaction was quenched with saturated aqueous $NaHCO_3$ (100 mL). The mixture was diluted with pentane (150 mL) and the aqueous phase was extracted with pentane (3 × 100 mL). The combined organic fractions were washed with saturated aqueous NH_4Cl (100 mL) and brine (100 mL), dried over anhydrous Na_2SO_4, filtered and concentrated by distilling the solvent off at atmospheric pressure (bath temperature 45 °C). The residue was purified by flash chromatography (pentane/Et_2O 10:1) and the combined fractions were carefully concentrated at atmospheric pressure (bath temperature 45 °C). The residue was purified by bulb-to-bulk distillation under vacuum (1.0×10^{-3} mbar, receiving flask cooled to −78 °C) to give the desired alkenyl iodide (3.8 g, 79%) as a pale yellow oil. $[\alpha]_D^{20}$ = −11.9 (c = 1.00, $CHCl_3$). **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 6.20 (q, *J* = 1.5 Hz, 1H), 5.88 – 5.82 (m, 1H), 3.14 (dddd, *J* = 5.9, 5.2, 3.9, 2.6 Hz, 1H),

2.85 (ddd, *J* = 4.7, 3.9, 0.6 Hz, 1H), 2.81 – 2.70 (m, 1H), 2.70 – 2.60 (m, 1H), 2.62 (dd, *J* = 4.9, 2.7 Hz, 1H); **^{13}C NMR** ($CDCl_3$, 101 MHz): δ 128.1, 103.8, 51.3, 48.2, 46.9; **IR** (Microscope, cm^{-1}): 3050, 2992, 2922, 1618, 1404, 1257, 1135, 1116, 969, 896, 835, 799, 760, 616, 545, 492; **HRMS** (GC-EI) for C_5H_7OI [$M^{\bullet+}$]: calcd. 209.9536; found 209.9534.

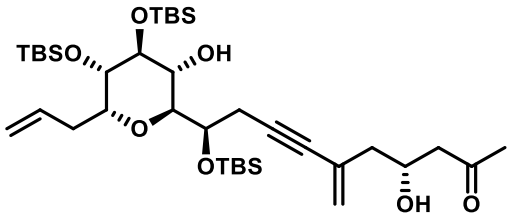


Compound S8. Copper(I) iodide (62 mg, 0.33 mmol) was added to a solution of alkyne **24** (0.95 g, 1.6 mmol) in degassed diisopropylamine (10 mL). The mixture was stirred at room temperature for 10 min. A solution of alkenyl iodide **30** (0.41 g, 2.0 mmol) in diisopropylamine (2 mL, 2 × 2 mL wash) was added, followed by triphenylphosphine (86 mg, 0.33 mmol) and tris(dibenzylideneacetone)-dipalladium(0) (75 mg, 82 µmol). The resulting mixture was stirred for 1 h at room temperature before the reaction was quenched at 0°C by addition of saturated aqueous NH_4Cl (30 mL). The mixture was diluted with *tert*-butyl methyl ether (30 mL) and the aqueous phase was extracted with *tert*-butyl methyl ether (3 × 20 mL) once room temperature had been reached. The combined organic extracts were washed with brine (30 mL), dried over anhydrous Na_2SO_4, and concentrated. The residue was purified by flash chromatography (hexanes/*tert*-butyl methyl ether 50:1 to 20:1) to afford the desired enyne (1.1 g, 97%) as a colorless oil. $[\boldsymbol{\alpha}]_{\boldsymbol{D}}^{\boldsymbol{20}}$ = +44.1 (c = 1.10, $CHCl_3$). **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 5.85 (ddt, *J* = 17.1, 10.2, 7.0 Hz, 1H), 5.37 – 5.33 (m, 1H), 5.27 (d, *J* = 1.5 Hz, 1H), 5.16 – 5.06 (m, 2H), 4.16 (dt, *J* = 8.4, 4.5 Hz, 1H), 3.83 – 3.76 (m, 2H), 3.68 – 3.58 (m, 2H), 3.56 (dd, *J* = 6.2, 3.4 Hz, 1H), 3.41 (d, *J* = 6.1 Hz, 1H), 3.13 (tdd, *J* = 5.7, 3.9, 2.6 Hz, 1H), 2.80 (ddd, *J* = 4.7, 3.9, 0.6 Hz, 1H), 2.67 (dd, *J* = 17.2, 4.3 Hz, 1H), 2.61 – 2.53 (m, 2H), 2.50 – 2.37 (m, 2H), 2.25 (ddd, *J* = 14.6, 5.8, 1.2 Hz, 2H), 0.92 (s, 9H), 0.90 (s, 9H), 0.90 (s, 9H), 0.15 (s, 3H), 0.13 (s, 3H), 0.13 (s, 3H), 0.13 (s, 3H), 0.10 (s, 3H), 0.09 (s, 3H); **^{13}C NMR** ($CDCl_3$, 101 MHz): δ 135.1, 127.4, 122.3, 117.2, 87.7, 82.7, 76.6, 73.3, 72.9, 72.6, 72.5, 71.7, 50.9, 47.2, 40.6, 26.2, 26.2, 25.9, 25.4, 18.3, 18.3, 18.2, −3.7, −3.9, −3.9, −4.0, −4.2, −4.5; **IR** (Microscope, cm^{-1}): 3517, 2953, 2929, 2896, 2857, 1472, 1254, 1125, 1096, 1037, 1005, 903, 836, 812, 777, 681; **HRMS** (ESI) for $C_{35}H_{66}O_6Si_3Na$ [M+Na]: calcd. 689.4059; found 689.4062.

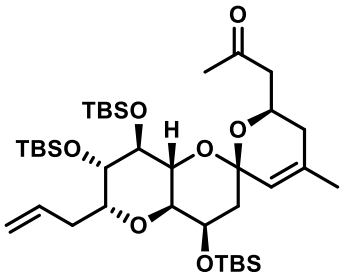


(*S*)-4-Hydroxy-6-iodohept-6-en-2-one (31). *tert*-Butyllithium (1.9 M solution in pentane, 5.5 mL, 10 mmol) was added dropwise to a solution of ethyl vinyl ether (1.5 mL, 16 mmol) in THF (12 mL) at −78 °C. The resulting mixture was allowed to slowly warm to 5 °C over 40 min (programmed cryostat) and then recooled to −78 °C. This solution of the lithium species (−78 °C) was added dropwise *via* cannula to a stirred solution of boron trifluoride etherate (1.3 mL, 10 mmol) in THF (20 mL) at −78 °C. A solution of epoxide **S8** (0.73 g, 3.5 mmol) in THF (4 mL, 2 x 2 mL washes) was added quickly via cannula at −78 °C. After 30 min of stirring at this temperature, the reaction was quenched at −78 °C by addition of saturated aqueous $NaHCO_3$ (30 mL) and the resulting mixture was warmed to room temperature. The

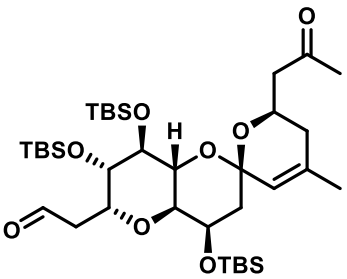
aqueous phase was extracted with *tert*-butyl methyl ether (3 × 20 mL). The combined organic fractions were washed with brine (30 mL), dried over Na_2SO_4, filtered and evaporated. The residue was taken up in THF (8 mL) and aqueous HCl (0.1 M, 2 mL) and the mixture was stirred at room temperature for 2 h. The reaction was quenched with saturated aqueous $NaHCO_3$ (10 mL) and the aqueous phase was extracted with *tert*-butyl methyl ether (3 × 10 mL). The combined organic fractions were washed with brine (10 mL), dried over Na_2SO_4, filtered and evaporated. The residue was purified by flash chromatography (hexanes/EtOAc 3:2) to give the title compound as pale yellow oil (0.56 g, 63% over two steps). $[\alpha]_D^{20}$ = −18.4 (c = 0.92, $CHCl_3$).**^{1}H NMR** ($CDCl_3$, 400 MHz): δ 6.17 (q, *J* = 1.3 Hz, 1H), 5.84 (d, *J* = 1.5 Hz, 1H), 4.39 – 4.28 (m, 1H), 3.01 (d, *J* = 3.8 Hz, 1H), 2.72 – 2.54 (m, 3H), 2.47 (ddd, *J* = 14.4, 5.5, 1.3 Hz, 1H), 2.20 (s, 3H); **^{13}C NMR** ($CDCl_3$, 101 MHz): δ 209.2, 128.8, 106.3, 66.5, 51.5, 48.5, 30.9; **IR** (Microscope, cm^{-1}): 3416, 2929, 1708, 1617, 1419, 1359, 1295, 1261, 1190, 1164, 1119, 1078, 901, 870, 551, 515, 421; **HRMS** (GC-CI) for $C_7H_{12}O_2I$ $[M+H]^+$: calcd. 254.9877; found 254.9874.



Compound 25. Copper(I) iodide (57 mg, 0.30 mmol) was added to a solution of alkyne **24** (1.2 g, 2.0 mmol) in degassed diisopropylamine (10 mL). The mixture was stirred at room temperature for 10 min. A solution of alkenyl iodide **31** (0.55 g, 2.2 mmol) in diisopropylamine (2 mL, 2 × 2 mL wash) was added, followed by triphenylphosphine (0.11 g, 0.40 mmol) and tris(dibenzylideneacetone)-dipalladium(0) (91 mg, 0.10 mmol). The resulting mixture was stirred for 4 h at room temperature before the reaction was quenched at 0°C with saturated aqueous NH_4Cl (30 mL). The mixture was diluted with *tert*-butyl methyl ether (30 mL), allowed to warm to room temperature, and the aqueous phase was extracted with *tert*-butyl methyl ether (3 × 20 mL). The combined organic extracts were washed with brine (30 mL), dried over anhydrous Na_2SO_4, and concentrated *in vacuo*. The residue was purified by flash chromatography (hexanes/EtOAc 5:1) to afford the desired enyne (1.3 g, 93%) as a colorless oil. $[\alpha]_D^{20}$ = +21.9 (c = 1.00, $CHCl_3$). **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 5.85 (ddt, *J* = 17.1, 10.2, 6.9 Hz, 1H), 5.35 (d, *J* = 2.0 Hz, 1H), 5.26 – 5.23 (m, 1H), 5.18 – 5.07 (m, 2H), 4.32 (tdt, *J* = 7.1, 6.1, 3.5 Hz, 1H), 4.14 (dt, *J* = 8.2, 4.3 Hz, 1H), 3.87 – 3.74 (m, 2H), 3.68 – 3.57 (m, 2H), 3.56 (dd, *J* = 6.3, 3.5 Hz, 1H), 3.42 (d, *J* = 6.1 Hz, 1H), 3.03 (d, *J* = 3.8 Hz, 1H), 2.72 – 2.51 (m, 4H), 2.49 – 2.33 (m, 2H), 2.30 – 2.20 (m, 2H), 2.18 (s, 3H), 0.92 (s, 9H), 0.90 (s, 9H), 0.90 (s, 9H), 0.15 (s, 3H), 0.13 (s, 3H), 0.13 (s, 3H), 0.12 (s, 3H), 0.10 (s, 3H), 0.09 (s, 3H); **^{13}C NMR** ($CDCl_3$, 101 MHz): δ 209.4, 135.1, 128.1, 123.2, 117.3, 88.0, 82.5, 73.3, 73.1, 72.6, 72.4, 71.8, 66.4, 49.2, 44.5, 32.6, 30.9, 26.3, 26.2, 25.9, 25.4, 18.4, 18.3, 18.2, −3.7, −3.9, −3.9, −4.0, −4.2, −4.4; **IR** (Microscope, cm^{-1}): 3523, 2953, 2930, 2896, 2857, 1712, 1472, 1410, 1389, 1361, 1254, 1125, 1096, 1035, 1005, 937, 902, 860, 837, 777, 680; **HRMS** (ESI) for $C_{37}H_{70}O_7Si_3Na$ $[M+Na]^+$: calcd. 733.4322; found 733.4320.



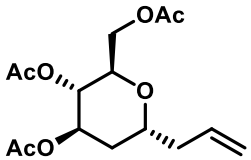
Compound 26. (Acetonitrile)[(2-biphenyl)di-*tert*-butylphosphine]gold(I) hexafluoroantimonate (3.8 mg, 4.9 µmol) and pyridinium *p*-toluenesulfonate (1.2 mg, 4.9 µmol) were added to a solution of enyne **25** (35 mg, 49 µmol) in CH_2Cl_2 (0.5 mL). The mixture was stirred at room temperature for 2 h before the reaction was quenched with trimethylamine (0.1 mL). Saturated aqueous NH_4Cl (2 mL) and *tert*-butyl methyl ether (2 mL) were added and the aqueous phase was extracted with *tert*-butyl methyl ether (3 × 2 mL). The combined organic fractions were washed with brine (3 mL), dried over anhydrous Na_2SO_4, filtered and concentrated. The residue was purified by flash chromatography (hexanes/EtOAc 30:1) to give the title compound (27 mg, 78%) as a pale yellow oil. The reaction was repeated on a 1.7 mmol-scale to afford the desired product in 65% yield (730 mg). $[\alpha]_D^{20}$ = +51.1 (c = 1.00, $CHCl_3$). **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 5.80 (ddt, *J* = 17.0, 10.2, 6.7 Hz, 1H), 5.17 (p, *J* = 1.2 Hz, 1H), 5.14 – 4.99 (m, 2H), 4.34 (dtd, *J* = 10.5, 6.4, 4.0 Hz, 1H), 4.01 (q, *J* = 3.0 Hz, 1H), 3.95 – 3.79 (m, 2H), 3.69 – 3.56 (m, 2H), 3.30 (dd, *J* = 10.1, 2.8 Hz, 1H), 2.74 (dd, *J* = 16.0, 6.1 Hz, 1H), 2.52 (dd, *J* = 16.1, 6.8 Hz, 1H), 2.42 (ddt, *J* = 8.3, 6.8, 1.5 Hz, 2H), 2.23 (s, 3H), 1.96 – 1.76 (m, 3H), 1.74 – 1.65 (m, 4H), 0.91 (s, 9H), 0.89 (s, 9H), 0.88 (s, 9H), 0.11 (s, 3H), 0.08 (s, 3H), 0.05 (s, 6H), 0.02 (s, 3H), 0.01 (s, 3H); **^{13}C NMR** ($CDCl_3$, 101 MHz): δ 207.2, 135.7, 135.5, 124.4, 116.3, 95.2, 76.3, 74.3, 73.2, 70.3, 68.8, 66.8, 64.0, 50.2, 42.5, 34.8, 30.9, 29.7, 26.4, 26.1, 22.8, 18.6, 18.4, 18.3, −3.5, −3.5, −3.6, −4.2, −4.2, −5.1; **IR** (Microscope, cm^{-1}): 2953, 2928, 2887, 2856, 1720, 1472, 1463, 1387, 1361, 1252, 1204, 1156, 1130, 1089, 1060, 1039, 1005, 971, 913, 858, 835, 807, 776, 672; **HRMS** (ESI) for $C_{37}H_{70}O_7Si_3Na$ $[M+Na]^+$: calcd. 733.4322; found 733.4320.



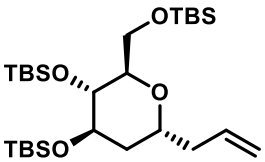
Compound 27. 2,6-Lutidine (0.16 mL, 1.4 mmol), osmium tetroxide (51 µL, 4% in water, 70 µmol) and sodium periodate (0.60 g, 2.8 mmol) were sequentially added to a stirred solution of spiroketal **26** (0.50 g, 0.70 mmol) in 1,4-dioxane/H_2O (3:1, 12 mL) at room temperature. The resulting mixture was stirred for 20 h before the reaction was quenched with saturated aqueous $Na_2S_2O_3$ (10 mL). The aqueous layer was extracted with *tert*-butyl methyl ether (3 × 10 mL), and the combined organic layers were washed with saturated aqueous NH_4Cl (10 mL) and brine (10 mL), dried over Na_2SO_4 and concentrated. The residue was purified by flash chromatography (pentane/*tert*-butyl methyl ether 20:1 to 15:1) to afford the title compound (0.43 g, 87%) as a pale yellow oil. When performed on a 0.04 mmol-

scale, the desired product was obtained in 93% yield. $[\alpha]_D^{20}$ = +35.9 (c = 1.00, $CHCl_3$). **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 9.75 (dd, *J* = 3.8, 1.4 Hz, 1H), 5.15 (s, 1H), 4.53 (dt, *J* = 9.9, 4.3 Hz, 1H), 4.32 (dp, *J* = 10.5, 3.9, 3.3 Hz, 1H), 3.97 (d, *J* = 3.0 Hz, 1H), 3.87 (dd, *J* = 10.1, 8.1 Hz, 1H), 3.71 – 3.51 (m, 2H), 3.32 (dd, *J* = 10.1, 2.8 Hz, 1H), 2.86 – 2.66 (m, 3H), 2.51 (dd, *J* = 16.2, 6.9 Hz, 1H), 2.21 (s, 3H), 1.97 – 1.76 (m, 3H), 1.74 – 1.63 (m, 4H), 0.91 (s, 9H), 0.88 (s, 9H), 0.88 (s, 9H), 0.13 (s, 3H), 0.11 (s, 3H), 0.05 (s, 6H), 0.00 (s, 3H), −0.01 (s, 3H); **^{13}C NMR** ($CDCl_3$, 101 MHz): δ 206.9, 201.4, 135.6, 124.2, 95.2, 73.6, 73.2, 71.9, 71.0, 68.4, 66.5, 64.1, 50.1, 42.4, 41.3, 34.8, 30.9, 26.4, 26.0, 22.7, 18.6, 18.3, 18.3, −3.5, −3.6, −3.6, −4.2, −4.3, −5.0; **IR** (Microscope, cm^{-1}): 2954, 2929, 2888, 2856, 1729, 1472, 1463, 1387, 1361, 1252, 1204, 1157, 1130, 1093, 1042, 1006, 979, 959, 836, 807, 776, 671; **HRMS** (ESI) for $C_{36}H_{68}O_8Si_3Na$ $[M+Na]^+$: calcd. 735.4114; found 735.4112.

Synthesis of the Southern Fragment



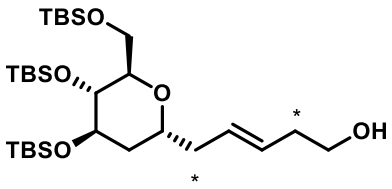
(2*R*,3*S*,4*R*,6*R*)-2-(Acetoxymethyl)-6-allyltetrahydro-2H-pyran-3,4-diyl diacetate (38). Prepared according to the cited literature procedure.[11] **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 5.77 (ddt, *J* = 17.1, 10.2, 6.9 Hz, 1H), 5.17 – 5.07 (m, 3H), 4.87 (t, *J* = 7.3 Hz, 1H), 4.37 (dd, *J* = 12.0, 6.3 Hz, 1H), 4.14 – 4.01 (m, 2H), 3.90 (td, *J* = 6.7, 3.3 Hz, 1H), 2.57 – 2.45 (m, 1H), 2.34 – 2.24 (m, 1H), 2.08 (s, 3H), 2.06 (s, 3H), 2.05 (s, 3H), 1.99 (dt, *J* = 13.6, 4.8 Hz, 1H), 1.85 (ddd, *J* = 13.7, 8.9, 4.9 Hz, 1H); **^{13}C NMR** ($CDCl_3$, 100 MHz): δ 170.9, 170.2, 169.9, 133.9, 117.8, 70.8, 70.0, 68.8, 62.3, 36.8, 32.2, 21.2, 21.0, 21.0.



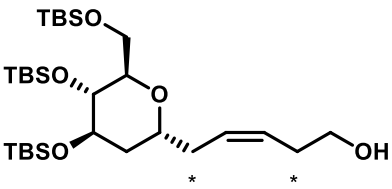
(((2*R*,3*R*,4*R*,6*R*)-6-Allyl-2-(((*tert*-butyldimethylsilyl)oxy)methyl)tetrahydro-2*H*-pyran-3,4-diyl)bis-(oxy))bis(*tert*-butyldimethylsilane) (39). K_2CO_3 (165 mg, 1.19 mmol) was added to a solution of triacetate **37** (3.75 g, 11.9 mmol) in methanol (12 mL) at room temperature. After 1 h, the yellow mixture was filtered through a silica plug, rinsing with 10% MeOH/EtOAc. The combined filtrates were concentrated and the crude material dried in high vacuum overnight to remove any residual methanol.

TBSOTf (12.4 mL, 53.6 mmol) was slowly added to a solution of the crude triol and 2,6-lutidine (8.35 mL, 71.7 mmol) in CH_2Cl_2 (50 mL) at 0 °C. The mixture was stirred at room temperature for 24 h before the reaction was quenched with saturated aq. NH_4Cl solution (100 mL) and the aqueous phase extracted with *tert*-butyl methyl ether (3 × 100 mL). The combined organic layers were washed with brine (100 mL), dried over Na_2SO_4, filtered and concentrated. The residue was subjected to flash chromatography (hexanes/*tert*-butyl methyl ether 200:1 to 100:1) to furnish the title compound as a pale yellow liquid (6.01 g, 95% over two steps). $[\alpha]_D^{20}$ = +8.8 (c = 0.58, $CHCl_3$). **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 5.82 (ddt, *J*

= 17.2, 10.2, 6.9 Hz, 1H), 5.08 (dq, *J* = 17.2, 1.5 Hz, 1H), 5.05 – 5.00 (m, 1H), 3.89 (d, *J* = 7.0 Hz, 2H), 3.87 – 3.82 (m, 1H), 3.80 (d, *J* = 3.4 Hz, 1H), 3.74 (t, *J* = 7.0 Hz, 1H), 3.58 (d, *J* = 3.5 Hz, 1H), 2.36 – 2.27 (m, 1H), 2.15 (app dt, *J* = 14.1, 6.5 Hz, 1H), 1.82 (ddd, *J* = 13.5, 11.0, 2.6 Hz, 1H), 1.38 (d, *J* = 13.4 Hz, 1H), 0.89 (s, 27H), 0.05 (m, 18H); **^{13}C NMR** ($CDCl_3$, 100 MHz): δ 135.2, 116.7, 80.3, 69.9, 68.3, 65.2, 61.8, 40.4, 33.8, 26.1, 26.0, 26.0, 18.4, 18.2, 18.1, −4.5, −4.6, −4.8, −5.1, −5.1; **IR** (Microscope, cm^{-1}): 2953, 2929, 2885, 2857, 1643, 1472, 1361, 1253, 1087, 669; **HRMS** (ESI) for $C_{27}H_{58}O_4Si_3Na$ $[M+Na]^+$: calcd. 553.3535; found 553.3539.



(*E*)-5-((2*R*,4*R*,5*R*,6*R*)-4,5-Bis((*tert*-butyldimethylsilyl)oxy)-6-(((*tert*-butyldimethylsilyl)oxy)methyl) tetrahydro-2*H*-pyran-2-yl)pent-3-en-1-ol (40). A solution of compound **39** (0.65 g, 1.2 mmol) and 3-buten-1-ol (0.44 g, 6.1 mmol) in CH_2Cl_2 (11 mL) was purged with argon for 15 min. A solution of complex **47** (35 mg, 61 µmol) in CH_2Cl_2 (1.0 mL) was added and the resulting mixture was stirred at reflux temperature for 5 h. Stirring was continued in air for 30 min at room temperature to destroy most of the catalyst. Volatile materials were evaporated and the crude product was subjected to flash chromatography (hexanes/*tert*-butyl methyl ether 20:1 to 10:1) to give *E*-**40** as a colorless liquid (0.53 g, 75%). A second fraction contained the undesired *Z*-isomer (50 mg, 7%). Analytical and spectral data of the major isomer *E*-**40**: $[\alpha]_D^{20}$ = +3.2 (c = 0.72, $CHCl_3$).**^{1}H NMR** ($CDCl_3$, 400 MHz): δ 5.62 – 5.53 (m, 1H), 5.50 – 5.41 (m, 1H), 3.90 – 3.87 (m, 2H), 3.84 – 3.77 (m, 2H), 3.73 (t, *J* = 6.9 Hz, 1H), 3.62 (t, *J* = 6.3 Hz, 2H), 3.57 (d, *J* = 3.5 Hz, 1H), 2.27 (p, *J* = 5.8, 5.3 Hz, 3H), 2.14 (dt, *J* = 13.4, 6.2 Hz, 1H), 1.82 (ddd, *J* = 13.5, 11.0, 2.6 Hz, 1H), 1.35 (d, *J* = 13.4 Hz, 1H), 0.89 (s, 27H), 0.07 – 0.01 (m, 18H); **^{13}C NMR** ($CDCl_3$, 100 MHz): δ 130.2, 128.3, 80.3, 69.8, 68.3, 65.3, 62.1, 61.8, 39.2, 36.2, 33.8, 26.1, 26.0, 26.0, 18.5, 18.2, 18.1, −4.5, −4.6, −4.8, −5.1, −5.1; **IR** (Microscope, cm^{-1}): 3421, 2954, 2929, 2857, 1463, 1361, 1255, 1090, 835; **HRMS** (ESI) for $C_{29}H_{62}O_5Si_3Na$ $[M+Na]^+$: calcd. 597.3797; found 597.3801.



Analytical and spectral data of the minor isomer *Z*-**40**: $[\alpha]_D^{20}$ = +1.7 (c = 0.71, $CHCl_3$).**^{1}H NMR** ($CDCl_3$, 400 MHz): δ 5.60 (dt, *J* = 10.9, 7.2 Hz, 1H), 5.48 (dt, *J* = 10.9, 7.5 Hz, 1H), 3.89 – 3.78 (m, 4H), 3.73 (t, *J* = 7.0 Hz, 1H), 3.68 – 3.61 (m, 2H), 3.57 (d, *J* = 3.4 Hz, 1H), 2.42 – 2.28 (m, 3H), 2.22 – 2.09 (m, 1H), 1.86 (ddd, *J* = 13.6, 11.3, 2.6 Hz, 1H), 1.35 (d, *J* = 13.3 Hz, 1H), 0.89 (m, 27H), 0.05 (m, 18H); **^{13}C NMR** ($CDCl_3$, 100 MHz): δ 129.1, 127.6, 80.3, 69.8, 68.1, 65.1, 62.2, 61.6, 34.0, 31.1, 26.1, 26.0, 26.0, 18.4, 18.2, 18.1, −4.6, −4.6, −4.6, −4.8, −5.1, −5.1; **IR** (Microscope, cm^{-1}): 3418, 2953, 2929, 2886, 2857,

1472, 1389, 1361, 1089, 775; **HRMS** (ESI) for $C_{29}H_{62}O_5Si_3Na$ $[M+Na]^+$: calcd. 597.3797; found 597.3740.

Note: The configuration of the double bond was assigned based on the ^{13}C NMR shifts of the carbon signals vicinal to the alkenes: the CH_2 groups (as labeled with stars) adjacent to *E*-alkenes are more deshielded (Figure S3).

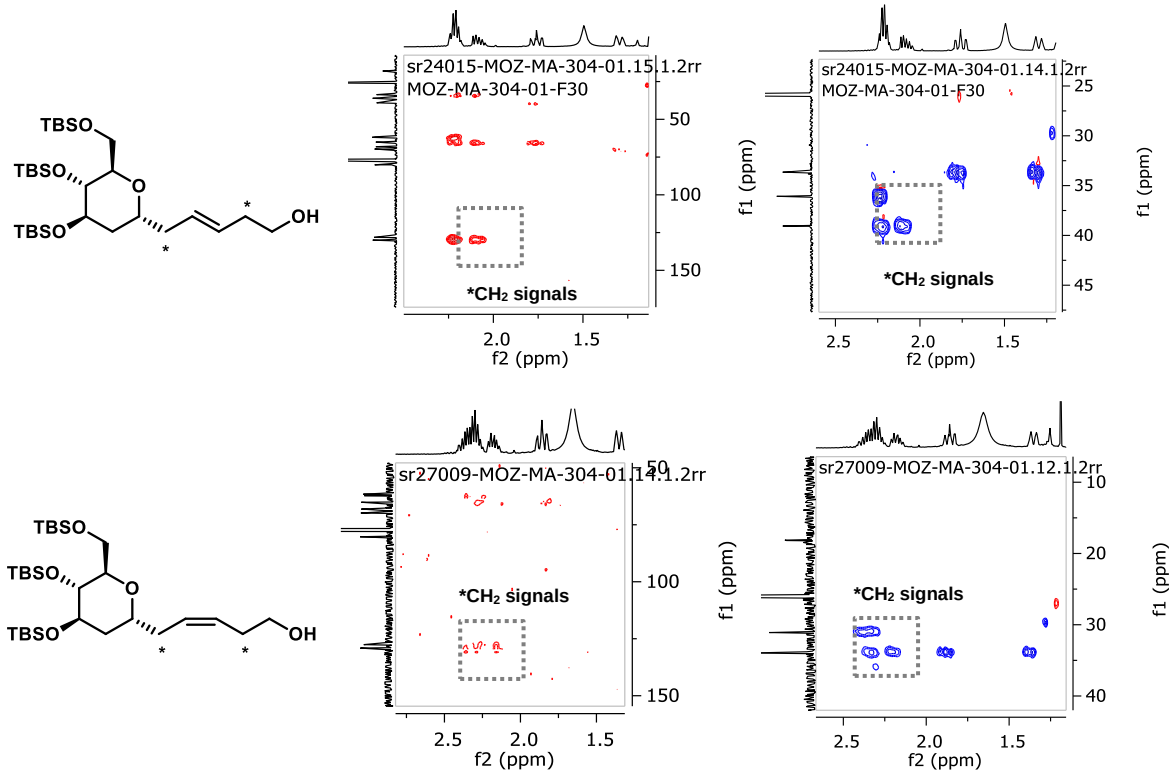
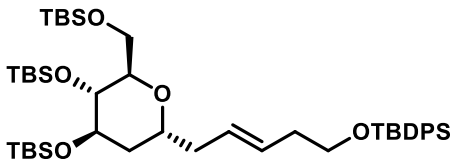
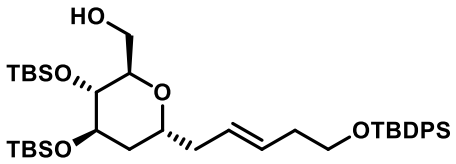


Figure S3. Determination of the *E*/*Z* isomers of **40** based on ^{13}C NMR data.

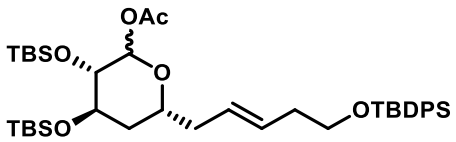


Compound S9. Imidazole (85 mg, 1.3 mmol) was added to a solution of alcohol **40** (0.36 g, 0.63 mmol) in CH_2Cl_2 (5 mL) at 0 °C. After 5 min, TBDPSCl (0.19 g, 0.69 mmol) was added in one portion. The cooling bath was removed and the mixture stirred at room temperature for 2 h. The reaction was quenched with saturated aq. NH_4Cl solution (10 mL), the aqueous phase was extracted with CH_2Cl_2 (3 × 15 mL), and the combined organic layers were washed with water (20 mL), dried over Na_2SO_4, filtered and concentrated. The residue was purified by flash chromatography (hexanes/*tert*-butyl methyl ether 100:1) to afford the title compound as a colorless liquid (507 mg, 99%). $[\alpha]_D^{20}$ = +5.0 (c = 1.10, $CHCl_3$). **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.69 – 7.63 (m, 4H), 7.43 – 7.32 (m, 6H), 5.46 (t, *J* = 3.7 Hz, 2H), 3.88 (d, *J* = 6.9 Hz, 2H), 3.81 – 3.70 (m, 3H), 3.66 (t, *J* = 6.9 Hz, 2H), 3.56 (d, *J* = 3.3 Hz, 1H), 2.31 – 2.19 (m, 3H), 2.07 (app dt, *J* = 14.0, 6.2 Hz, 1H), 1.78 (ddd, *J* = 13.4, 11.0, 2.5 Hz, 1H), 1.35 (d, *J* = 13.6 Hz, 1H),

1.04 (s, 9H), 0.89 (s, 18H), 0.87 (s, 9H), 0.05 (s, 3H), 0.05 (s, 3H), 0.04 (s, 3H), 0.04 (s, 3H), 0.03 (s, 3H), 0.01 (s, 3H); **^{13}C NMR** ($CDCl_3$, 100 MHz): δ 135.7, 134.2, 129.7, 128.9, 128.5, 127.7, 80.2, 69.9, 68.4, 65.5, 64.2, 61.8, 39.3, 36.3, 33.7, 27.0, 26.1, 26.0, 26.0, 19.4, 18.4, 18.2, 18.1, −4.5, −4.6, −4.6, −4.8, −5.1, −5.1; **IR** (Microscope, cm^{-1}): 3072, 2954, 2929, 2857, 1472, 1361, 1254, 1087, 938; **HRMS** (ESI) for $C_{45}H_{80}O_5Si_4Na$ $[M+Na]^+$: calcd. 835.4975; found 835.4979.

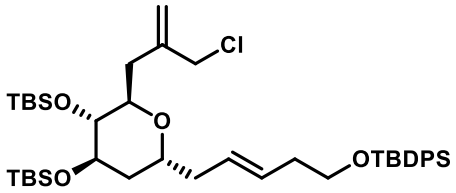


((2*R*,3*R*,4*R*,6*R*)-3,4-Bis((*tert*-butyldimethylsilyl)oxy)-6-((*E*)-5-((*tert*-butyldiphenylsilyl)oxy)pent-2-en-1-yl)tetrahydro-2*H*-pyran-2-yl)methanol (41). (*R*)-Camphor-10-sulfonic acid (18 mg, 0.077 mmol) was added to a solution of **S9** (0.63 g, 0.77 mmol) in a solvent mixture of MeOH/CH_2Cl_2 (1:1 *v/v*, 7.6 mL) at −20 °C. The mixture was stirred at this temperature for 18 h, the reaction was quenched with saturated $NaHCO_3$ solution (10 mL), and the aqueous phase was extracted with CH_2Cl_2 (3 × 15 mL). The combined organic layers were washed with water (20 mL), dried over Na_2SO_4, filtered and concentrated. The crude material was subjected to flash chromatography (hexanes/*tert*-butyl methyl ether 20:1 to 10:1) to afford the title compound as a colorless liquid (0.42 g, 77%). $[\alpha]_D^{20}$ = +1.3 (c = 0.56, $CHCl_3$). **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.68 – 7.64 (m, 4H), 7.44 – 7.34 (m, 6H), 5.55 – 5.39 (m, 2H), 4.09 (dd, *J* = 11.5, 9.1 Hz, 1H), 3.87 (app q, *J* = 9.2 Hz, 1H), 3.81 – 3.71 (m, 2H), 3.66 (t, *J* = 6.8 Hz, 2H), 3.46 (dd, *J* = 11.6, 3.3 Hz, 1H), 3.38 – 3.30 (m, 1H), 2.27 (app q, *J* = 6.6 Hz, 3H), 2.11 (dt, *J* = 13.3, 6.4 Hz, 1H), 1.83 (ddd, *J* = 12.8, 9.8, 2.8 Hz, 1H), 1.47 – 1.36 (m, 1H), 1.04 (s, 9H), 0.89 (s, 9H), 0.87 (s, 9H), 0.06 (s, 3H), 0.06 (s, 3H), 0.05 (s, 3H), 0.03 (s, 3H); **^{13}C NMR** ($CDCl_3$, 100 MHz): δ 135.7, 134.2, 129.7, 129.6, 128.1, 127.7, 79.2, 70.0, 69.7, 65.9, 64.1, 61.0, 38.5, 36.3, 34.2, 27.0, 26.0, 26.0, 19.4, 18.2, 18.2, −4.4, −4.4, −4.6; **IR** (Microscope, cm^{-1}): 3469, 3071, 2954, 2929, 2893, 2857, 1472, 1428, 1255, 1038, 835; **HRMS** (ESI) for $C_{39}H_{66}O_5Si_3Na$ $[M+Na]^+$: calcd. 721.4110; found 721.4116.



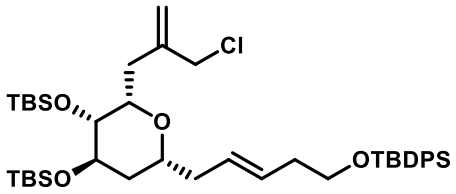
(3*S*,4*R*,6*R*)-3,4-Bis((*tert*-butyldimethylsilyl)oxy)-6-((*E*)-5-((*tert*-butyldiphenylsilyl)oxy)pent-2-en-1-yl)tetrahydro-2H-pyran-2-yl acetate (42). Lead(IV) acetate (1.6 g, 3.6 mmol) was added in one portion to a solution of alcohol **41** (0.71 g, 1.0 mmol) in THF (10 mL) at room temperature. After stirring for 4.5 h, the reaction was quenched with saturated aqueous $Na_2S_2O_3$ (10 mL) and the mixture was diluted with *tert*-butyl methyl ether (20 mL). The aqueous phase was extracted with *tert*-butyl methyl ether (3 × 5 mL). The combined organic fractions were washed with saturated aqueous $NaHCO_3$ (10 mL) and brine (10 mL), dried over anhydrous Na_2SO_4, filtered, and concentrated. The residue was purified by flash chromatography (hexanes/*tert*-butyl methyl ether 20:1) to give the title compound as an inconsequential mixture of diastereoisomers (0.45 g, 61%). $[\alpha]_D^{20}$ = +12.9 (c = 1.33, $CHCl_3$). Spectral data of the major diastereoisomer: **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.69 – 7.64 (m, 4H), 7.46 – 7.33 (m, 6H), 5.79 (d, *J* = 1.4 Hz, 1H), 5.55 – 5.37 (m, 2H), 4.23 – 4.08 (m, 1H), 3.79 (q, *J* = 3.3 Hz, 1H), 3.66 (t, *J* = 6.9 Hz, 2H),

3.53 – 3.41 (m, 1H), 2.37 – 2.21 (m, 3H), 2.18 – 2.07 (m, 1H), 2.04 (s, 3H), 1.81 (ddd, *J* = 13.9, 11.5, 2.6 Hz, 1H), 1.46 – 1.39 (m, 1H), 1.04 (s, 9H), 0.89 (s, 9H), 0.88 (s, 9H), 0.11 (s, 3H), 0.06 (s, 3H), 0.03 (s, 3H), 0.01 (s, 3H); **^{13}C NMR** ($CDCl_3$, 101 MHz): δ 170.1, 135.7, 134.2, 129.7, 129.5, 127.7, 127.7, 96.0, 68.6, 68.4, 65.8, 64.1, 38.7, 36.3, 33.0, 27.0, 25.9, 25.8, 21.5, 19.4, 18.1, −4.7, −4.7, −4.8, −4.9; **IR** (Microscope, cm^{-1}): 2954, 2929, 2857, 1734, 1472, 1428, 1362, 1254, 1166, 1107, 1008, 939, 836, 777, 739, 702, 614, 505; **HRMS** (ESI) for $C_{40}H_{66}O_6Si_3Na$ $[M+Na]^+$: calcd. 749.4059; found 749.4047.

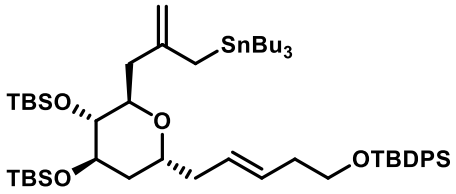


Compound 44. Tin(IV) chloride (1.0 M in CH_2Cl_2 , 0.92 mL, 0.92 mmol) was added dropwise with a graduated glass pipette to a solution of compound **42** (0.45 g, 0.61 mmol) and 2-(chloromethyl)allyl-trimethylsilane (**43**) (0.22 mL, 1.2 mmol) in CH_2Cl_2 (6 mL) at −78 °C. Once the addition was complete, stirring was continued at this temperature for 1.5 h. The reaction was quenched by addition of trimethylamine (0.5 mL) at −78 °C before the mixture was allowed to reach room temperature. Saturated aqueous NH_4Cl (10 mL) and *tert*-butyl methyl ether (10 mL) were added, followed by addition of water until all solid materials had been dissolved. The aqueous phase was extracted with *tert*-butyl methyl ether (3 x 10 mL). The combined organic extracts were washed with brine (10 mL), dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by flash chromatography (hexanes/EtOAc 50:1) to give the title compound as a colorless oil (0.39 g, 83%, d.r. ≈ 5:1 (^{1}H NMR)).

Analytically pure samples of both diastereomers were obtained by preparative HPLC (column: 250 mm MultoKrom Si 3 µm, 4.6 mm i.D.; gradient: 1.0 mL/min, *n*-heptane/isopropanol = 99.9:0.1; R_t (minor) = 6.89 min; R_t (major) = 7.57 min). Analytical and spectral data of the major diastereoisomer: $[\boldsymbol{\alpha}]_{\boldsymbol{D}}^{\boldsymbol{20}}$ = +6.1 (c = 1.00, $CHCl_3$). **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.67 (dd, *J* = 7.9, 1.7 Hz, 4H), 7.44 – 7.35 (m, 6H), 5.52 – 5.34 (m, 2H), 5.09 (d, *J* = 1.5 Hz, 1H), 4.96 (d, *J* = 1.3 Hz, 1H), 4.12 – 4.02 (m, 2H), 3.88 – 3.78 (m, 3H), 3.65 (t, *J* = 7.1 Hz, 2H), 3.35 (ddd, *J* = 3.9, 2.0, 0.8 Hz, 1H), 3.02 (ddd, *J* = 15.0, 11.0, 1.0 Hz, 1H), 2.38 – 2.14 (m, 4H), 2.11 – 1.95 (m, 1H), 1.78 (ddd, *J* = 13.4, 10.4, 2.8 Hz, 1H), 1.44 – 1.35 (m, 1H), 1.05 (s, 9H), 0.90 (s, 9H), 0.90 (s, 9H), 0.06 (s, 6H), 0.06 (s, 3H), 0.04 (s, 3H); **^{13}C NMR** ($CDCl_3$, 101 MHz): δ 143.7, 135.7, 134.2, 129.7, 128.8, 128.6, 127.7, 116.4, 71.7, 70.2, 64.9, 64.1, 48.3, 38.9, 36.2, 34.2, 33.7, 27.0, 26.0, 26.0, 19.4, 18.2, 18.1, 14.8, −4.5, −4.5, −4.7; **IR** (Microscope, cm^{-1}): 2954, 2929, 2894, 2857, 1472, 1428, 1361, 1256, 1091, 1006, 970, 835, 776, 740, 702, 613, 505; **HRMS** (ESI) for $C_{42}H_{69}O_4Si_3ClNa$ $[M+Na]^+$: calcd. 779.4084; found 779.4085.



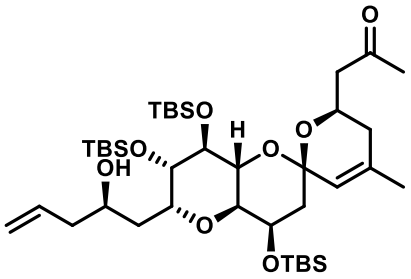
Spectral data of the minor diastereoisomer: **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.69 – 7.64 (m, 4H), 7.45 – 7.34 (m, 6H), 5.51 – 5.37 (m, 2H), 5.23 – 5.13 (m, 1H), 4.99 (d, *J* = 1.3 Hz, 1H), 4.18 – 4.03 (m, 2H), 3.92 – 3.78 (m, 3H), 3.65 (td, *J* = 6.9, 0.9 Hz, 2H), 3.37 (ddd, *J* = 3.6, 1.8, 0.8 Hz, 1H), 3.07 (ddd, *J* = 15.0, 10.9, 0.9 Hz, 1H), 2.39 – 2.25 (m, 3H), 2.23 – 2.06 (m, 2H), 1.79 (ddd, *J* = 13.4, 10.6, 2.7 Hz, 1H), 1.39 (dt, *J* = 13.5, 3.0 Hz, 1H), 1.04 (s, 9H), 0.90 (s, 18H), 0.07 (s, 6H), 0.06 (s, 3H), 0.05 (s, 3H); **^{13}C NMR** ($CDCl_3$, 101 MHz): δ 143.7, 135.7, 134.1, 129.7, 127.7, 127.6, 127.4, 116.4, 77.3, 71.5, 70.2, 64.6, 63.7, 48.4, 34.2, 33.7, 33.6, 31.2, 29.9, 27.0, 26.1, 26.0, 19.3, 18.3, 18.1, −4.5, −4.7.



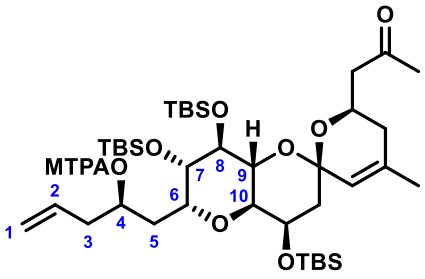
Compound 45. *n*-Butyllithium (1.6 M in hexanes, 0.96 mL, 1.5 mmol) was added to a solution of bis(tributyltin) (0.83 mL, 1.6 mmol) in THF (1.5 mL) at −20 °C. The mixture was stirred at this temperature for 15 min to give a clear solution of tributylstannyllithium.[12]

This solution was added dropwise to a solution of allyl chloride **44** (0.39 g, 0.51 mmol, d.r. = 5:1) in THF (3.5 mL) at −78 °C. The mixture was stirred at this temperature for 20 min. The reaction was quenched at −78°C with water (5 mL), before the mixture was warmed to room temperature. The aqueous phase was extracted with *tert*-butyl methyl ether (3 × 5 mL) and the combined organic fractions were washed with brine (5 mL), dried over anhydrous Na_2SO_4, filtered, and concentrated. The residue was purified by flash chromatography (hexanes/*tert*-butyl methyl ether/triethylamine 200:1:2) to give the title compound as a colorless oil (0.47 g, 91%, d.r. = 5:1 (^{1}H NMR)). An analytically pure sample was obtained by reacting isomerically pure **44** under the same conditions; it analyzed as follows: $[\alpha]_D^{20}$ = +7.5 (c = 1.00, $CHCl_3$). **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.67 (dd, *J* = 7.8, 1.7 Hz, 4H), 7.45 – 7.32 (m, 6H), 5.50 – 5.42 (m, 2H), 4.56 (d, *J* = 2.2 Hz, 1H), 4.48 (d, *J* = 2.2 Hz, 1H), 3.88 – 3.78 (m, 3H), 3.66 (t, *J* = 6.9 Hz, 2H), 3.41 (dd, *J* = 3.7, 1.6 Hz, 1H), 2.57 (dd, *J* = 14.0, 8.7 Hz, 1H), 2.34 – 2.16 (m, 4H), 2.11 – 2.02 (m, 1H), 1.88 – 1.73 (m, 3H), 1.59 – 1.38 (m, 6H), 1.41 – 1.36 (m, 1H), 1.30 (dq, *J* = 14.3, 7.2 Hz, 6H), 1.05 (s, 9H), 0.95 – 0.72 (m, 33H), 0.06 (s, 3H), 0.05 (s, 3H), 0.04 (s, 3H), 0.03 (s, 3H); **^{13}C NMR** ($CDCl_3$, 101 MHz): δ 147.5, 135.7, 134.2, 129.6, 128.8, 128.6, 127.7, 107.4, 77.5, 71.2, 70.4, 64.5, 64.2, 39.2, 39.1, 36.3, 34.0, 29.3, 27.5, 27.0, 26.1, 26.0, 19.4, 18.8, 18.2, 18.2, 13.9, 9.6, −4.4, −4.5, −4.6, −4.7; **^{119}Sn NMR** ($CDCl_3$, 149 MHz): δ −16.3; **IR** (Microscope, cm^{-1}): 2955, 2928, 2857, 1471, 1463, 1428, 1378, 1361, 1255, 1091, 1006, 973, 939, 835, 775, 738, 702, 688, 672, 666, 614, 505; **HRMS** (ESI) for $C_{54}H_{97}O_4Si_3Sn$ $[M+H]^+$: calcd. 1013.5711; found 1013.5729.

Fragment Coupling and Completion of the Total Synthesis



Model Compound 52a. Solid magnesium bromide diethyl etherate (14 mg, 53 µmol) was added in one portion to a solution of aldehyde **27** (7.6 mg, 11 µmol) and allyltributylstannane (3.5 µL, 11 µmol) in CH_2Cl_2 (0.3 mL) at −78 °C and the resulting mixture was stirred at this temperature for 3 h. The reaction was quenched by addition of triethylamine (0.1 mL) at –78°C before the mixture was warmed to room temperature and diluted with *tert*-butyl methyl ether (1 mL) and saturated aqueous NH_4Cl (1 mL). The aqueous layer was extracted with *tert*-butyl methyl ether (3 x 1 mL). The combined organic phases were dried over anhydrous Na_2SO_4 and concentrated, and the residue was purified by flash chromatography (hexanes/EtOAc 15:1) to give the title compound as a colorless oil (6.1 mg, 76%, d.r. = 14:1 (^{1}H NMR)). **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 5.84 (ddt, *J* = 17.2, 10.1, 7.1 Hz, 1H), 5.15 (dd, *J* = 2.6, 1.6 Hz, 2H), 5.14 – 5.05 (m, 1H), 4.34 (dddd, *J* = 10.9, 7.0, 5.9, 3.8 Hz, 1H), 4.16 – 4.06 (m, 1H), 4.01 (q, *J* = 3.0 Hz, 1H), 3.87 (dd, *J* = 10.1, 8.0 Hz, 1H), 3.88 – 3.80 (m, 1H), 3.66 – 3.52 (m, 2H), 3.49 (dd, *J* = 10.1, 2.8 Hz, 1H), 3.39 (d, *J* = 1.1 Hz, 1H), 2.75 (dd, *J* = 16.2, 6.0 Hz, 1H), 2.52 (dd, *J* = 16.2, 7.0 Hz, 1H), 2.36 – 2.20 (m, 2H), 2.21 (s, 3H), 1.98 – 1.75 (m, 5H), 1.75 – 1.67 (m, 1H), 1.68 (s, 3H), 0.89 (s, 18H), 0.88 (s, 9H), 0.10 (s, 3H), 0.07 (s, 3H), 0.05 (s, 3H), 0.05 (s, 3H), 0.02 (s, 3H), 0.01 (s, 3H); **^{13}C NMR** ($CDCl_3$, 101 MHz): δ 206.9, 135.7, 134.9, 124.2, 117.6, 95.2, 78.4, 73.9, 72.9, 72.8, 71.1, 68.4, 66.6, 64.1, 50.1, 42.5, 42.0, 34.8, 30.8, 30.4, 26.4, 26.4, 26.0, 22.7, 18.5, 18.3, 18.3, −3.5, −3.6, −3.7, −4.3, −4.3, −4.8.



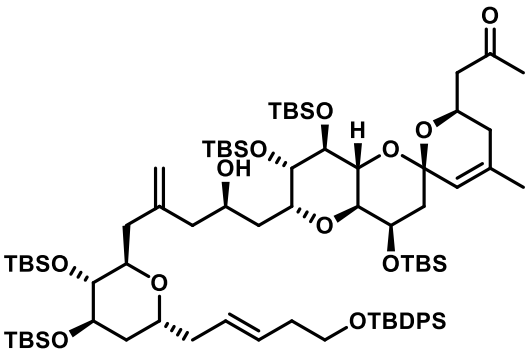
Preparation of the (*S*)-and (*R*)-MTPA Esters (S10) of Alcohol 52a. *R*-(−)-MTPA-Cl (2.0 mg, 7.9 µmol) and DMAP (0.1 mg, 0.8 µmol) were added to a stirred solution of **52a** (3.0 mg, 4.0 µmol) and pyridine (1.0 µL, 12 µmol) in CH_2Cl_2 (0.2 mL) at room temperature. After stirring for 16 h at room temperature, the reaction was quenched with H_2O (1 mL) and the mixture was diluted with *tert*-butyl methyl ether (2 mL). The aqueous phase was extracted with *tert*-butyl methyl ether (2 × 2 mL). The combined organic fractions were dried over anhydrous Na_2SO_4, filtered and concentrated via vacuum evaporation. The residue was purified via flash chromatography (hexanes/EtOAc 15:1) to give **(*S*)-S10** (3.8 mg, 3.9 µmol, 98%) as a pale yellow oil. **^{1}H NMR** ($CDCl_3$, 600 MHz): δ 7.58 – 7.51 (m, 2H), 7.45 – 7.34 (m, 3H), 5.76

(dddd, *J* = 16.5, 10.2, 7.8, 6.0 Hz, 1H), 5.29 – 5.23 (m, 1H), 5.22 (dt, *J* = 2.3, 1.1 Hz, 1H), 5.12 (dd, *J* = 17.1, 1.5 Hz, 1H), 5.10 (d, *J* = 10.2 Hz, 1H), 4.34 (ddd, *J* = 10.5, 6.4, 4.1 Hz, 1H), 4.10 (q, *J* = 3.0 Hz, 1H), 3.93 (dt, *J* = 12.2, 4.0 Hz, 1H), 3.82 (dd, *J* = 9.9, 7.5 Hz, 1H), 3.64 – 3.57 (m, 2H), 3.55 (d, *J* = 1.2 Hz, 3H), 3.40 (dd, *J* = 10.1, 2.9 Hz, 1H), 2.74 (dd, *J* = 16.1, 6.1 Hz, 1H), 2.60 – 2.55 (m, 1H), 2.51 (dd, *J* = 16.1, 6.7 Hz, 1H), 2.42 – 2.29 (m, 1H), 2.23 (s, 3H), 2.15 – 2.04 (m, 1H), 1.96 – 1.79 (m, 3H), 1.79 – 1.71 (m, 2H), 1.69 (s, 3H), 0.90 (s, 9H), 0.88 (s, 9H), 0.86 (s, 9H), 0.09 (s, 3H), 0.06 (s, 3H), 0.03 (s, 9H), 0.02 (s, 3H).

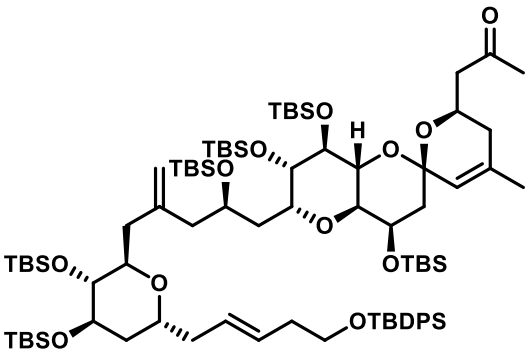
(*R*)-S10 was prepared analogously using *S*-(+)-MTPA-Cl. **^{1}H NMR** ($CDCl_3$, 600 MHz): δ 7.61 – 7.50 (m, 2H), 7.47 – 7.31 (m, 3H), 5.62 (ddt, *J* = 16.6, 10.2, 7.2, 7.0 Hz, 1H), 5.27 – 5.18 (m, 1H), 5.22 – 5.16 (m, 1H), 5.02 (dd, *J* = 17.2, 1.7 Hz, 1H), 4.99 (dt, *J* = 10.0, 1.4 Hz, 1H), 4.33 (dtd, *J* = 10.5, 6.5, 3.9 Hz, 1H), 4.08 (q, *J* = 3.0 Hz, 1H), 3.97 (dt, *J* = 12.1, 4.0 Hz, 1H), 3.84 (dd, *J* = 10.1, 7.4 Hz, 1H), 3.67 – 3.56 (m, 2H), 3.56 (d, *J* = 1.2 Hz, 3H), 3.40 (dd, *J* = 10.4, 3.5 Hz, 1H), 2.74 (dd, *J* = 16.1, 6.1 Hz, 1H), 2.51 (dd, *J* = 16.1, 6.8 Hz, 1H), 2.48 (s, 1H), 2.38 – 2.25 (m, 1H), 2.22 (s, 3H), 2.23 – 2.11 (m, 1H), 1.96 – 1.76 (m, 4H), 1.72 (dd, *J* = 14.4, 3.4 Hz, 1H), 1.68 (s, 3H), 0.90 (s, 9H), 0.90 (s, 9H), 0.87 (s, 9H), 0.11 (s, 3H), 0.06 (s, 3H), 0.05 (s, 3H), 0.04 (s, 3H), 0.03 (s, 3H), 0.02 (s, 3H).

Table S4. Analysis of the Mosher esters **S10** according to Hoye and co-workers;[1] arbitrary numbering scheme as shown in the insert.

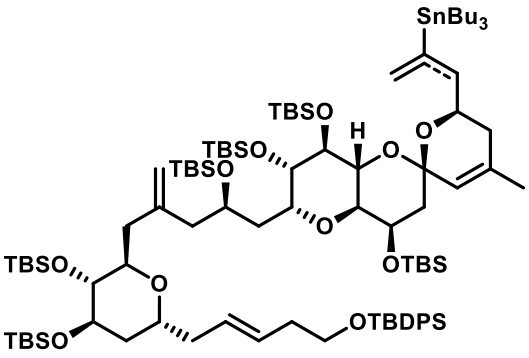
Atom number	**52a** δ [ppm]	**(*S*)-S10** δ [ppm]	**(*R*)-S10** δ [ppm]	**Δδ** [ppm]
1-*cis*	5.10	5.10	5.02	+0.08
1-*trans*	5.13	5.12	4.99	+0.13
2	5.84	5.76	5.62	+0.14
3'	2.27	2.57	2.48	+0.09
3''	2.27	2.34	2.31	+0.03
4	3.84	5.25	5.23	+0.02
5'	1.85	2.09	2.17	−0.08
5''	1.85	1.74	1.86	−0.12
6	4.11	3.93	3.97	−0.04
7	3.59	3.59	3.62	−0.03
8	3.87	3.82	3.84	−0.02
9	3.59	3.59	3.62	−0.03
10	3.49	3.40	3.40	±0.00



Compound 48. Solid magnesium bromide diethyl etherate (574 mg, 2.22 mmol) was added in one portion to a solution of aldehyde **27** (317 mg, 0.445 mmol) and allyl stannane **45** (540 mg, 0.533 mmol, *dr* 5:1) in CH_2Cl_2 (12 mL) at −78 °C. The resulting mixture was stirred at this temperature for 3 h before the reaction was quenched at −78°C with triethylamine (0.5 mL). The mixture was warmed to room temperature and diluted with *tert*-butyl methyl ether (20 mL) and saturated aqueous NH_4Cl (20 mL). The aqueous phase was extracted with *tert*-butyl methyl ether (3 x 20 mL). The combined organic phases were dried over anhydrous Na_2SO_4 and concentrated, and the residue was purified by flash chromatography (hexanes/EtOAc 15:1) to give the title compound as a colorless oil (561 mg, 88%). $[\alpha]_D^{20}$ = +22.1 (c = 1.00, $CHCl_3$). **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.70 – 7.63 (m, 4H), 7.48 – 7.32 (m, 6H), 5.53 – 5.33 (m, 2H), 5.15 (s, 1H), 4.90 (s, 2H), 4.35 (dtd, *J* = 10.5, 6.5, 3.9 Hz, 1H), 4.14 – 4.02 (m, 1H), 4.00 (q, *J* = 3.0 Hz, 1H), 3.94 (dt, *J* = 9.7, 5.0 Hz, 1H), 3.90 – 3.74 (m, 4H), 3.65 (td, *J* = 8.5, 7.7, 5.5 Hz, 3H), 3.56 (dd, *J* = 8.7, 5.2 Hz, 1H), 3.49 (dd, *J* = 10.1, 2.7 Hz, 1H), 3.42 (s, 1H), 3.36 (dd, *J* = 3.9, 2.7 Hz, 1H), 2.81 – 2.60 (m, 2H), 2.52 (dd, *J* = 16.2, 6.9 Hz, 1H), 2.37 (dd, *J* = 14.3, 4.9 Hz, 1H), 2.33 – 2.15 (m, 7H), 2.14 – 2.03 (m, 1H), 1.98 – 1.69 (m, 7H), 1.70 – 1.65 (m, 3H), 1.46 – 1.36 (m, 1H), 1.04 (s, 9H), 0.89 (s, 9H), 0.89 (s, 27H), 0.88 (s, 9H), 0.10 (s, 3H), 0.07 (s, 3H), 0.05 (s, 15H), 0.03 (s, 3H), 0.02 (s, 3H), 0.01 (s, 3H); **^{13}C NMR** ($CDCl_3$, 101 MHz): δ 207.0, 144.0, 135.7, 135.5, 134.2, 129.7, 128.9, 128.5, 127.7, 124.2, 114.9, 95.1, 77.7, 76.3, 73.9, 72.8, 71.9, 71.0, 70.6, 70.5, 68.4, 66.6, 65.5, 64.1, 64.0, 50.2, 43.4, 42.5, 38.5, 37.2, 36.3, 34.8, 34.2, 30.8, 27.0, 26.6, 26.5, 26.4, 26.4, 26.1, 26.0, 22.7, 19.4, 18.5, 18.4, 18.3, 18.2, 18.2, −3.5, −3.6, −3.6, −4.0, −4.2, −4.3, −4.3, −4.3, −4.4, −4.7, −4.7, −4.8; **IR** (Microscope, cm^{-1}): 2953, 2929, 2893, 2857, 1719, 1472, 1463, 1428, 1388, 1361, 1253, 1205, 1091, 1040, 1007, 961, 836, 776, 738, 703, 688, 672, 667, 613, 506; **HRMS** (ESI) for $C_{78}H_{138}O_{12}Si_6Na$ $[M+Na]^+$: calcd. 1457.8696; found 1457.8698.



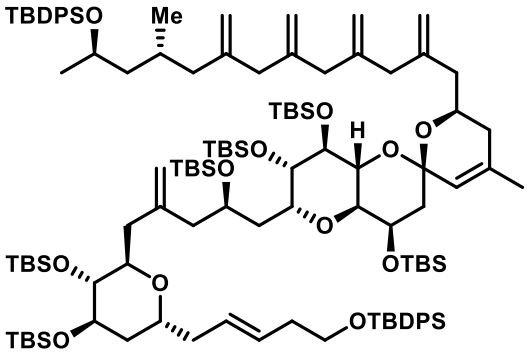
Compound S11. A solution of TBSOTf (1.0 M in CH_2Cl_2, 0.29 mL, 0.29 mmol) was added dropwise to a solution of alcohol **48** (0.38 g, 0.27 mmol) and 2,6-lutidine (93 µL, 0.80 mmol) in CH_2Cl_2 (2.5 mL) at −78 °C using a glas pipette. Stirring was continued at −78 °C for 6 h before the reaction was quenched with saturated aqueous NH_4Cl (3 mL). The mixture was warmed to room temperature and stirred until all solids had dissolved. The aqueous phase was extracted with *tert*-butyl methyl ether (3 × 3 mL). The combined organic fractions were washed with brine (3 mL), dried over Na_2SO_4, filtered and concentrated. The residue was purified by flash chromatography (hexanes/EtOAc 25:1) to give the title compound as a colorless syrup (0.35 g, 84%). $[\alpha]_D^{20}$ = +27.1 (c = 1.00, $CHCl_3$). **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.70 – 7.63 (m, 4H), 7.45 – 7.32 (m, 6H), 5.48 – 5.41 (m, 2H), 5.16 (s, 1H), 4.87 (s, 1H), 4.85 (s, 1H), 4.35 (dtd, *J* = 10.5, 6.4, 4.0 Hz, 1H), 4.02 (q, *J* = 3.0 Hz, 1H), 3.95 – 3.71 (m, 6H), 3.65 (dd, *J* = 7.5, 6.3 Hz, 3H), 3.54 (dd, *J* = 7.9, 4.9 Hz, 1H), 3.42 (dd, *J* = 3.6, 1.6 Hz, 1H), 3.36 (d, *J* = 10.0 Hz, 1H), 2.74 (dd, *J* = 15.9, 6.0 Hz, 1H), 2.72 – 2.63 (m, 1H), 2.51 (dd, *J* = 16.0, 6.8 Hz, 1H), 2.41 (dd, *J* = 14.3, 6.0 Hz, 1H), 2.23 (s, 7H), 2.08 (dd, *J* = 13.5, 7.8 Hz, 2H), 1.96 – 1.69 (m, 6H), 1.68 (s, 3H), 1.65 (dd, *J* = 14.5, 3.6 Hz, 1H), 1.37 (dt, *J* = 13.7, 2.8 Hz, 1H), 1.04 (s, 9H), 0.90 (s, 9H), 0.90 (s, 9H), 0.89 – 0.88 (m, 36H), 0.10 (s, 3H), 0.06 – 0.02 (m, 27H), 0.02 (s, 3H), 0.01 (s, 3H); **^{13}C NMR** ($CDCl_3$, 101 MHz): δ 207.2, 144.2, 144.1, 135.7, 135.4, 134.2, 134.2, 129.7, 128.8, 128.6, 127.7, 124.5, 115.1, 95.2, 74.2, 73.3, 70.9, 70.8, 70.3, 69.6, 68.9, 66.9, 64.4, 64.2, 64.1, 50.2, 42.8, 42.6, 39.1, 37.6, 36.3, 34.9, 33.9, 30.8, 27.0, 26.5, 26.5, 26.2, 26.0, 26.0, 22.7, 19.4, 19.3, 18.6, 18.4, 18.2, 18.2, 18.1, −3.5, −3.6, −3.7, −3.9, −4.1, −4.3, −4.3, −4.4, −4.5, −4.8, −4.9; **IR** (Microscope, cm^{-1}): 2954, 2929, 2894, 2857, 1721, 1472, 1463, 1428, 1388, 1361, 1253, 1205, 1093, 1041, 1006, 963, 835, 809, 775, 738, 702, 671, 666, 505; **HRMS** (ESI) for $C_{84}H_{152}O_{12}Si_7Na$ $[M+Na]^+$: calcd. 1571.9561; found 1571.9561.



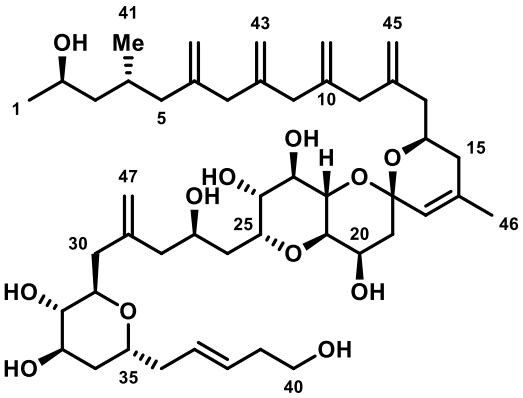
Alkenyl Stannane 49. *n*-Butyllithium (1.6 M in hexanes, 0.15 mL, 0.24 mmol) was added to a solution of hexabutylditin (0.13 mL, 0.25 mmol) in THF (1.8 mL) at −20 °C. The mixture was stirred at this temperature for 15 min to give a pale yellow solution of tributylstannyllithium. This solution was cooled to −78 °C and solid copper(I) cyanide (11 mg, 0.12 mmol) was added in one portion. The mixture was allowed to warm to −55 °C and stirred at this temperature for 15 min to give a green-yellow solution of the bis(tributylstannyl) cuprate reagent.[11,13]

In a separate flask, trityl potassium (0.20 M in 1,2-dimethoxyethane, 0.90 mL, 0.18 mmol) was added dropwise to a stirred solution of ketone **48** (62 mg, 0.040 mmol) and bis(trifluoromethanesulfonyl)aniline (29 mg, 0.080 mmol) in THF (3.0 mL) at −78 °C until the red color of the trityl anion persisted. Stirring was continued at −78 °C for 15 min and the resulting solution of the alkenyl triflate was transferred via canula into the cooled (−55 °C) stannylcuprate solution. The mixture was kept at −55 °C for 15 min before the reaction was quenched with saturated aqueous NH_4Cl (6 mL). The mixture was diluted with *tert*-butyl methyl ether (6 mL) and then warmed to room temperature. Stirring was continued until all solid materials had dissolved. The aqueous phase was extracted with *tert*-butyl methyl ether (3 × 6 mL) and the combined organic fractions were washed with brine (10 mL), dried over Na_2SO_4, filtered and concentrated. The residue was purified by flash chromatography (hexanes/toluene 2:1 + 1% NEt_3) to give the title compound and its internal double bond isomer as an inseperable mixture (4:1, 57 mg, 77%). Analytical and spectral data of the mixture of double bond isomers: $[\alpha]_D^{20}$ = +27.9 (c = 1.02, $CHCl_3$). **^{1}H NMR** (CD_2Cl_2, 400 MHz): δ 7.72 – 7.60 (m, 4H), 7.51 – 7.34 (m, 6H), 5.85 (d, *J* = 2.0 Hz, 1H), 5.64 (dd, *J* = 6.7, 1.9 Hz; *resolved signal of minor isomer*), 5.55 – 5.40 (m, 2H), 5.26 (s, 1H), 5.19 (q, *J* = 1.2 Hz, 1H), 4.87 (d, *J* = 4.8 Hz, 2H), 4.16 (ddt, *J* = 12.7, 8.7, 4.4 Hz, 1H), 4.05 (q, *J* = 3.0 Hz, 1H), 4.02 – 3.78 (m, 5H), 3.78 – 3.64 (m, 4H), 3.60 (dd, *J* = 8.0, 4.8 Hz, 1H), 3.45 (dd, *J* = 3.6, 1.5 Hz, 1H), 3.42 – 3.33 (m, 1H), 2.79 – 2.64 (m, 1H), 2.46 (dd, *J* = 14.3, 6.2 Hz, 1H), 2.38 – 2.24 (m, 4H), 2.19 (ddt, *J* = 11.1, 5.3, 2.5 Hz, 1H), 2.08 (dt, *J* = 14.6, 7.5 Hz, 2H), 2.01 – 1.70 (m, 7H), 1.72 – 1.61 (m, 3H), 1.60 – 1.40 (m, 7H), 1.34 (dq, *J* = 14.4, 7.2 Hz, 6H), 1.28 (s, 3H), 1.05 (s, 9H), 0.95 – 0.87 (m, 69H), 0.14 – 0.11 (m, 3H), 0.11 – 0.09 (m, 3H), 0.09 (s, 3H), 0.08 (s, 3H), 0.07 – 0.05 (m, 16H), 0.04 (s, 3H), 0.03 (s, 3H); **^{13}C NMR** ($CDCl_3$, 101 MHz): δ 150.9, 144.9, 144.7, 142.5, 136.0, 135.8, 134.5, 134.5, 130.0, 129.2, 128.9, 128.0, 127.1, 124.9, 114.9, 95.4, 77.0, 74.6, 74.0, 71.5, 71.2, 70.6, 70.0, 69.2, 67.2, 66.7, 64.6, 46.4, 43.1, 39.5, 38.1, 36.6, 35.2, 34.2, 32.4, 31.5, 30.2, 29.8, 29.7, 29.6, 29.5, 27.9, 27.1, 26.8, 26.7, 26.6, 26.3, 26.2, 26.1, 26.1, 23.2, 22.9, 20.7, 19.5, 18.9, 18.8, 18.7, 18.5, 18.4, 18.3, 14.0, 9.9, 9.4, −3.3,

−3.5, −3.6, −3.7, −4.0, −4.1, −4.2, −4.3, −4.4, −4.5, −4.7, −4.8; **^{119}Sn NMR** (CD_2Cl_2, 149 MHz): δ −40.6 (minor), −44.2 (major); **IR** (Microscope, cm^{-1}): 2956, 2928, 2857, 1489, 1466, 1446, 1361, 1288, 1247, 1215, 1184, 1157, 1086, 1037, 1007, 974, 962, 941, 922, 897, 856, 834, 814, 788, 753, 702, 664, 507; **HRMS** (ESI) for $C_{96}H_{178}O_{11}Si_7SnNa$ $[M+Na]^+$: calcd. 1846.0668; found 1846.0677.



Compound 50. A degassed solution of stannane **49** (10 mg, 5.5 µmol, 4:1 mixture of isomers) and allylic acetate **17** (3.4 mg, 6.6 µmol) in NMP (0.3 mL) was added to a Schlenk tube containing flame-dried tetrabutylammonium diphenylphosphinate (10 mg, 22 µmol). Copper-thiophene carboxylate complex (CuTC, 3.1 mg, 16 µmol) was then introduced followed by $Pd(PPh_3)_4$ (1.3 mg, 1.1 µmol). The resulting mixture was stirred for 2 h at ambient temperature before the reaction was quenched with aqueous saturated NH_4Cl (1 mL). The aqueous phase was extracted with *tert*-butyl methyl ether (3 x 1 mL), the combined organic layers were washed with brine (1 mL), dried over anhydrous Na_2SO_4, and evaporated. The residue was purified twice by flash chromatography (fine silica, hexanes/toluene, 3:2) to afford the fully protected polyol **50** as a colorless oil (single isomer, 8.4 mg, 77%). $[\alpha]_D^{20}$ = +9.8 (c = 0.98, CH_2Cl_2). **^{1}H NMR** (CD_2Cl_2, 400 MHz): δ 7.75 – 7.61 (m, 8H), 7.48 – 7.32 (m, 12H), 5.46 (t, *J* = 3.9 Hz, 2H), 5.19 (q, *J* = 1.6 Hz, 1H), 4.97 (dd, *J* = 3.7, 2.1 Hz, 2H), 4.90 – 4.82 (m, 6H), 4.77 (s, 1H), 4.75 (s, 1H), 4.16 (tt, *J* = 8.1, 5.9 Hz, 1H), 4.04 (q, *J* = 3.0 Hz, 1H), 3.98 – 3.79 (m, 6H), 3.76 – 3.69 (m, 2H), 3.67 (t, *J* = 6.9 Hz, 2H), 3.58 (dd, *J* = 8.5, 5.1 Hz, 1H), 2.74 (s, 2H), 2.66 (s, 5H), 2.41 (ddd, *J* = 16.5, 14.3, 5.8 Hz, 2H), 2.33 – 2.23 (m, 3H), 2.22 – 2.13 (m, 1H), 2.05 (dt, *J* = 14.5, 8.3 Hz, 3H), 2.00 – 1.48 (m, 17H), 1.38 (dt, *J* = 13.6, 2.7 Hz, 1H), 1.04 (s, 9H), 1.04 (s, 9H), 0.92 (s, 9H), 0.90 (s, 9H), 0.89 (s, 36H), 0.70 (d, *J* = 6.3 Hz, 3H), 0.11 (s, 3H), 0.09 – 0.03 (m, 33H), 0.02 (s, 3H); **^{13}C NMR** (CD_2Cl_2, 101 MHz): δ 146.3, 145.4, 145.1, 144.7, 143.9, 136.4, 136.3, 136.0, 135.9, 135.5, 134.8, 134.5, 129.9, 129.9, 129.8, 129.1, 128.9, 128.0, 127.9, 127.7, 124.8, 114.9, 114.6, 114.0, 113.9, 113.2, 95.4, 77.0, 74.4, 73.6, 71.6, 71.1, 70.6, 70.0, 68.8, 68.2, 67.2, 65.7, 64.5, 64.5, 47.7, 44.1, 43.9, 43.2, 42.8, 41.9, 41.6, 39.5, 38.0, 36.6, 35.2, 34.2, 27.4, 27.3, 27.1, 26.7, 26.6, 26.2, 26.1, 26.1, 26.1, 24.4, 22.8, 19.8, 19.6, 19.5, 18.9, 18.7, 18.5, 18.4, 18.3, 18.3, 1.2, −3.3, −3.6, −3.6, −3.8, −4.0, −4.1, −4.2, −4.3, −4.5, −4.5, −4.8, −4.8; **IR** (Microscope, cm^{-1}): 3072, 2954, 2928, 2894, 2857, 1640, 1472, 1462, 1428, 1379, 1361, 1253, 1206, 1095, 1038, 1007, 965, 896, 835, 775, 739, 702, 686, 613, 505; **HRMS** (ESI) for $C_{115}H_{194}O_{12}Si_8Na$ $[M+Na]^+$: calcd. 2014.2617; found 2014.2636.

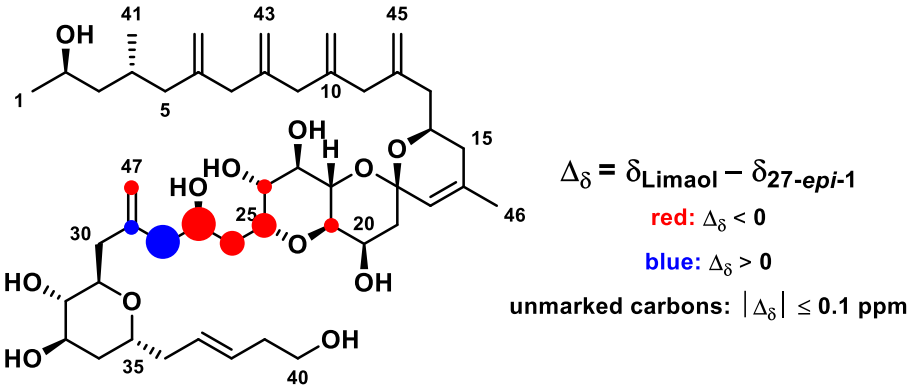


27-*epi*-1. Water (9.4 µL, 0.52 mmol) and TASF (48 mg, 0.17 mmol) were added to a solution of silyl ether **50** (14 mg, 7.2 µmol) in DMF/THF (1:1, 0.4 mL) at room temperature. After 24 h, additional TASF (48 mg, 0.17 mmol) was introduced and stirring continued for another 24 h. The reaction was quenched with pH 7.4 phosphate buffer (1 mL) and the aqueous phase was extracted with EtOAc (5 × 1 mL). The combined organic fractions were washed with brine (1 mL), dried over anhydrous Na_2SO_4, filtered and concentrated. The residue was taken up in pyridine/THF (3:1, 0.4 mL) and HF-pyridine complex (0.1 mL) was added at 0 °C. The cooling bath was removed and the mixture was stirred at this temperature for 11 d. The reaction was quenched by dropwise addition of pH 7.4 phosphate buffer (1 mL) and the aqueous phase was extracted with EtOAc (5 × 1 mL). The combined organic fractions were washed with brine (1 mL), dried over anhydrous Na_2SO_4, filtered and concentrated. The residue was purified by preparative HPLC (column: YMC-Actus ODS-A, S-5 µm, 150 mm length, 20.0 mm ID; gradient: 20.0 mL/min, MeCN/H_2O 50:50 for 10 min, then 100:0 for 50 min; R_t = 6.65 min) to afford 27-*epi*-**1** as a colorless oil (2.2 mg, 37%). **^{1}H NMR** (CD_3OD, 600 MHz): δ 5.56 – 5.49 (m, 1H), 5.49 – 5.43 (m, 1H), 5.30 (p, *J* = 1.3 Hz, 1H), 5.01 (t, *J* = 1.5 Hz, 1H), 4.96 (d, *J* = 2.2 Hz, 1H), 4.93 – 4.86 (m, 7H), 4.82 – 4.80 (m, 1H), 4.80 (q, *J* = 1.2 Hz, 1H), 4.25 (ddt, *J* = 10.7, 9.5, 3.8 Hz, 1H), 4.13 (ddd, *J* = 10.1, 5.6, 4.7 Hz, 1H), 3.99 (q, *J* = 3.1 Hz, 1H), 3.97 – 3.88 (m, 2H), 3.82 (dqd, *J* = 12.4, 6.1, 3.9 Hz, 1H), 3.74 (ddd, *J* = 10.7, 8.1, 4.7 Hz, 1H), 3.69 – 3.58 (m, 4H), 3.54 (t, *J* = 6.8 Hz, 2H), 3.41 (m, 1H), 3.04 – 2.98 (m, 2H), 2.88 (d, *J* = 14.7 Hz, 1H), 2.77 – 2.66 (m, 6H), 2.45 (ddd, *J* = 14.5, 8.3, 6.4 Hz, 1H), 2.39 (dd, *J* = 14.2, 3.9 Hz, 1H), 2.29 (dd, *J* = 13.8, 4.1 Hz, 1H), 2.27 – 2.19 (m, 4H), 2.14 (dd, *J* = 14.5, 9.4 Hz, 2H), 2.00 – 1.79 (m, 8H), 1.71 (d, *J* = 1.3 Hz, 3H), 1.63 (ddd, *J* = 13.1, 10.8, 5.6 Hz, 1H), 1.46 (ddd, *J* = 13.7, 9.1, 4.3 Hz, 1H), 1.14 (d, *J* = 6.2 Hz, 3H), 1.07 (ddd, *J* = 13.4, 9.1, 3.9 Hz, 1H), 0.87 (d, *J* = 6.3 Hz, 3H); **^{13}C NMR** (CD_3OD, 151 MHz): δ 147.1, 146.1, 146.0, 145.3, 145.1, 138.3, 130.2, 130.0, 123.8, 115.7, 115.1, 114.9, 114.7, 113.9, 97.8, 77.1, 76.1, 73.7, 73.4, 73.3, 72.6, 70.8, 70.0, 69.9, 68.3, 68.0, 66.8, 66.1, 62.8, 47.6, 45.0, 44.8, 43.3, 43.2, 42.5, 42.3, 41.2, 38.9, 37.1, 36.5, 36.2, 35.8, 33.7, 28.2, 24.4, 22.8, 19.8; **HRMS** (ESI) for $C_{47}H_{74}O_{12}Na$ $[M+Na]^+$: calcd. 853.5072; found 853.5073.

Table S5. NMR data of 27-*epi*-**1**; numbering scheme as shown in the insert.

atom number	**^{1}H NMR** (CD_3OD, 600 MHz)				**^{13}C NMR** (CD_3OD, 151 MHz)	
	δ [ppm]	**m**	***J*** [Hz]	**COSY**	δ [ppm]	**HMBC**
1	1.14	d	6.2	2	24.4	3ab
2	3.82	dqd	12.4, 6.1, 3.9	1, 3a, 3b	66.1	1, 3ab
3a	1.46	ddd	13.7, 9.1, 4.3	2, 3b, 4	47.6	1, 5ab, 41
3b	1.07	ddd	13.4, 9.1, 3.9	2, 3a, 4		
4	1.87	m	-	3a, 3b, 41	28.2	3ab, 5ab, 41
5a	1.98	m	-	42'	45.0	3ab, 7, 41, 42', 42"
5b	1.82	m	-	42'		
6	-	-	-	-	147.1	5ab, 7, 42', 42"
7	2.73	m	-	42', 42", 43', 43"	43.4	9, 5ab, 42', 42", 43', 43"
8	-	-	-	-	146.1	7, 9, 43', 43"
9	2.70	m	-	43', 43", 44', 44"	42.3	7, 11ab, 43', 43", 44', 44"
10	-	-	-	-	146.0	9, 11ab, 44', 44"
11a	3.01	m	14.7	11b, 44', 45', 45"	43.2	9, 13ab, 44', 44", 45', 45"
11b	2.88	d	14.7	11a, 44', 44", 45"		
12	-	-	-	-	145.3	11ab, 13ab, 45'
13a	2.29	dd	13.8, 4.1	13b, 14, 45'	42.5	11ab, 45', 45"
13b	2.22	m	-	13a, 14, 45'		
14	4.25	ddt	10.7, 9.5, 3.8, 3.8	13ab, 15ab	66.8	13ab
15a	1.93	m	-	14, 15b, 17, 46	36.2	13ab, 17, 46
15b	1.84	m	-	14, 15a, 17, 46		
16	-	-	-	-	138.3	15ab, 46
17	5.30	p	1.3	15ab, 19a, 46	123.8	15ab, 19b, 46
18	-	-	-	-	97.8	17, 19ab, 20
19a	1.94	m	-	17, 19b, 20	41.2	20
19b	1.89	m	-	19a, 20		
20	3.99	q	3.1	19ab, 21	68.0	19a, 22
21	3.41	m	-	20, 22	70.8	19a, 20, 22, 25
22	3.66	m	-	21, 23	69.9	20, 21, 23
23	3.66	m	-	22, 24	72.6	21, 22, 24, 25
24	3.62	m	-	23, 25	73.4	23, 25
25	4.13	ddd	10.1, 5.6, 4.7	24, 26ab	76.1	26ab
26a	1.89	m	-	25, 26b, 27	33.7	24, 25, 28b
26b	1.84	m	-	25, 26a, 27		
27	3.94	m	-	26ab, 28ab	68.3	25, 26ab, 28a

28a	2.39	dd	14.2, 3.9	27, 28b, 47', 47"	44.8	30b, 47', 47"
28b	2.14	m	-	27, 28a, 47', 47"		
29	-	-	-	-	145.1	28ab, 30ab, 47'
30a	2.69	m	-	30b, 31, 47', 47"	38.9	28b, 32, 47', 47"
30b	2.14	dd	14.5, 9.4	30a, 31, 47', 47"		
31	3.60	m	-	30ab, 32	73.8	30ab, 32, 35
32	3.00	m	8.3, 8.3	31, 33	77.1	30b, 33, 34ab
33	3.74	ddd	10.7, 8.1, 4.7	32, 34ab	70.0	32, 34ab, 35
34a	1.90	m	-	33, 34b, 35	36.5	36a
34b	1.63	ddd	13.1, 10.8, 5.6	33, 34a, 35		
35	3.91	m	-	34ab, 36ab	73.3	34b, 36ab
36a	2.45	ddd	14.5, 8.3, 6.4	35, 36b, 37	35.8	34b, 37, 38
36b	2.24	m	-	35, 36a, 37		
37	5.47	m	-	36ab, 38	130.0	36ab, 39
38	5.52	m	-	37, 39	130.2	36ab, 39, 40
39	2.22	m	-	38, 40	37.1	37, 38, 40
40	3.54	t	6.8	39	62.8	38, 39
41	0.87	d	6.3	4	19.8	3ab, 5ab
42'	4.81	m	-	5ab, 7, 42"	113.9	5ab, 7
42"	4.80	q	1.2	7, 42'		
43'	4.90	m	-	7, 9, 43"	114.7	7, 9
43"	4.88	m	-	7, 9, 43'		
44'	5.01	t	1.5	9, 11ab, 44"	115.1	9, 11ab
44"	4.88	m	-	9, 11b, 44'		
45'	4.96	d	2.2	11a, 13ab, 45"	115.8	11ab, 13ab
45"	4.91	m	-	11ab, 45'		
46	1.71	d	1.3	15ab, 17	22.8	15b, 17
47'	4.91	m	-	28ab, 30ab, 47"	114.9	28ab, 30a
47"	4.88	m	-	28ab, 30ab, 47'		

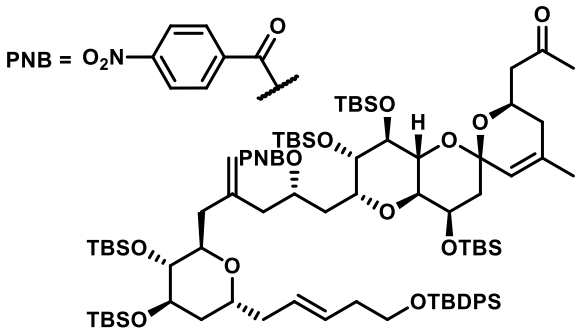


Graphical Comparison of the ^{13}C NMR data of Synthetic 27-*epi*-1 with those of Authentic Limaol (1)[14] (for the Exact Numbers and a Tabular Survey, see Table S6)

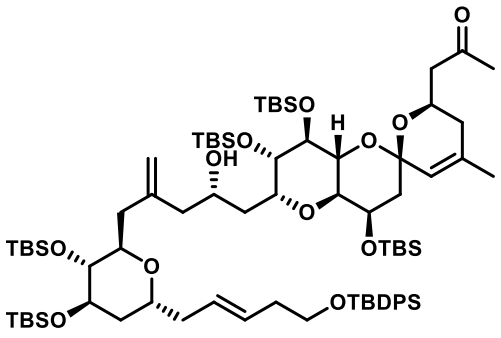
Table S6. Comparison of ^{13}C NMR shifts of synthetic polyol 27-*epi*-**1** with authentic Limaol;[13] color code: $\Delta\delta \leq 0.1$ ppm; $\Delta\delta > 0.1$ ppm.

atom number	Limaol (1)	27-*epi*-1	Δδ
1	24.4	24.4	0.0
2	66.1	66.1	0.0
3	47.6	47.6	0.0
4	28.1	28.2	-0.1
5	45.0	45.0	0.0
6	147.1	147.1	0.0
7	43.3	43.4	-0.1
8	146.1	146.1	0.0
9	42.3	42.3	0.0
10	146.0	146.0	0.0
11	43.2	43.2	0.0
12	145.3	145.3	0.0
13	42.5	42.5	0.0
14	66.8	66.8	0.0
15	36.2	36.2	0.0
16	138.4	138.3	0.1
17	123.7	123.8	-0.1
18	97.8	97.8	0.0
19	41.2	41.2	0.0
20	68.1	68.0	0.1
21	70.5	70.8	-0.3
22	69.9	69.9	0.0
23	72.6	72.6	0.0
24	73.1	73.4	-0.3

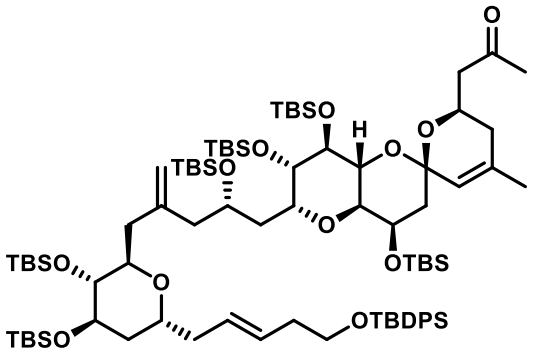
25	74.8	76.1	-1.3
26	32.5	33.7	-1.2
27	66.4	68.3	-1.9
28	46.5	44.8	1.7
29	145.4	145.1	0.3
30	39.0	38.9	0.1
31	73.7	73.8	-0.1
32	77.1	77.1	0.0
33	70.0	70.0	0.0
34	36.5	36.5	0.0
35	73.3	73.3	0.0
36	35.9	35.8	0.1
37	129.9	130.0	-0.1
38	130.3	130.2	0.1
39	37.1	37.1	0.0
40	62.8	62.8	0.0
41	19.8	19.8	0.0
42	113.9	113.9	0.0
43	114.7	114.7	0.0
44	115.1	115.1	0.0
45	115.9	115.8	0.1
46	22.8	22.8	0.0
47	114.5	114.9	-0.4



Compound S12. Diethyl azodicarboxylate (888 µL, 40% in toluene, 1.95 mmol) was added dropwise to a solution of alcohol **48** (560 mg, 0.390 mmol), triphenylphosphine (516 mg, 1.95 mmol), and 4-nitrobenzoic acid (293 mg, 1.75 mmol) in toluene (4.0 mL) at 0 °C. The cooling bath was removed and the mixture was stirred at this temperature for 4 h. The reaction was quenched with saturated aqueous NH_4Cl (5 mL). The mixture was diluted with *tert*-butyl methyl ether (10 mL), the aqueous phase was extracted with *tert*-butyl methyl ether (3 × 10 mL), and the combined organic fractions were washed with brine (10 mL), dried over anhydrous Na_2SO_4, filtered, and concentrated. The residue was purified by flash chromatography (hexanes/EtOAc 25:1) to give the title compound as a colorless oil (417 mg, 67%). $[\alpha]_D^{20}$ = +24.6 (c = 0.98, $CHCl_3$). **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 8.32 – 8.20 (m, 2H), 8.18 – 8.09 (m, 2H), 7.70 – 7.64 (m, 4H), 7.45 – 7.32 (m, 6H), 5.51 – 5.33 (m, 2H), 5.22 – 5.12 (m, 1H), 4.85 (dd, *J* = 9.0, 1.8 Hz, 2H), 4.34 (dtd, *J* = 10.4, 6.3, 3.8 Hz, 1H), 4.00 (dq, *J* = 7.4, 4.4, 3.6 Hz, 2H), 3.92 – 3.76 (m, 5H), 3.65 (t, *J* = 7.0 Hz, 2H), 3.60 (dd, *J* = 5.5, 1.9 Hz, 2H), 3.38 (dd, *J* = 3.7, 1.8 Hz, 1H), 3.21 (dd, *J* = 10.2, 2.7 Hz, 1H), 2.83 (dd, *J* = 14.5, 9.7 Hz, 1H), 2.73 (dd, *J* = 16.1, 6.1 Hz, 1H), 2.59 – 2.45 (m, 2H), 2.42 – 2.34 (m, 2H), 2.30 – 2.14 (m, 6H), 2.10 – 1.99 (m, 3H), 1.97 – 1.71 (m, 4H), 1.69 – 1.61 (m, 5H), 1.37 (dt, *J* = 13.6, 3.0 Hz, 1H), 1.04 (s, 9H), 0.92 (s, 9H), 0.90 (s, 9H), 0.88 (s, 18H), 0.84 (s, 9H), 0.11 (s, 3H), 0.08 (s, 3H), 0.07 (s, 9H), 0.04 (s, 3H), 0.03 (s, 6H), −0.01 (s, 3H), −0.08 (s, 3H); **^{13}C NMR** ($CDCl_3$, 101 MHz): δ 207.0, 163.8, 150.5, 143.1, 136.2, 135.7, 135.6, 134.2, 134.2, 130.7, 129.7, 128.7, 128.5, 127.7, 124.2, 123.5, 115.6, 95.1, 76.7, 73.9, 73.0, 71.1, 70.9, 70.8, 70.3, 68.6, 66.7, 64.7, 64.1, 64.0, 62.1, 50.1, 42.5, 41.4, 38.9, 36.5, 36.3, 34.8, 34.0, 30.8, 27.0, 26.5, 26.4, 26.0, 26.0, 26.0, 22.7, 19.3, 18.5, 18.3, 18.3, 18.2, 18.1, 14.4, −3.5, −3.6, −3.6, −4.2, −4.4, −4.4, −4.6, −4.8, −5.2; **IR** (Microscope, cm^{-1}): 2953, 2929, 2889, 2857, 1726, 1531, 1472, 1463, 1428, 1388, 1360, 1349, 1273, 1254, 1205, 1156, 1095, 1044, 1006, 978, 836, 776, 720, 703, 506; **HRMS** (ESI) for $C_{85}H_{141}NO_{15}Si_6Na$ $[M+Na]^+$: calcd. 1606.8809; found 1606.8799.

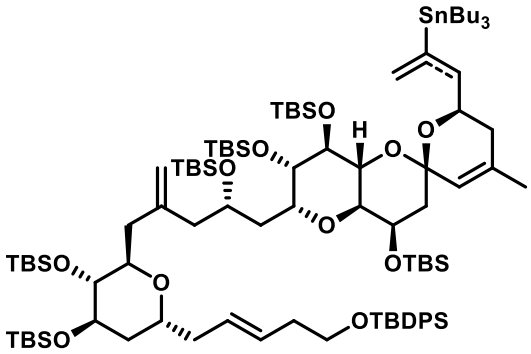


Compound 53. Powdered NaOH (13 mg, 0.33 mmol) was added in one portion to a solution of p-nitrobenzoate ester **S12** (75 mg, 0.047 mmol) in MeOH/THF (3:1, 2 mL) at room temperature. After stirring for 14 h at this temperature, the reaction was quenched with saturated aqueous NH_4Cl (3 mL) and the mixture was diluted with *tert*-butyl methyl ether (4 mL). The aqueous phase was extracted with *tert*-butyl methyl ether (3 × 4 mL). The combined organic fractions were washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated. The residue was purified by flash chromatography (hexanes/EtOAc 20:1) to give the title compound as a colorless oil (62 mg, 0.043 mmol, 91%). $[\alpha]_D^{20}$ = +15.5 (c = 1.03, $CHCl_3$). **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.71 – 7.63 (m, 4H), 7.46 – 7.33 (m, 6H), 5.53 – 5.35 (m, 2H), 5.17 (s, 1H), 4.93 (s, 1H), 4.90 (s, 1H), 4.35 (dtd, *J* = 10.5, 6.5, 4.0 Hz, 1H), 4.23 – 4.14 (m, 1H), 4.01 (q, *J* = 3.0 Hz, 1H), 3.84 (ddd, *J* = 21.0, 9.2, 5.7 Hz, 5H), 3.70 – 3.56 (m, 4H), 3.38 (dd, *J* = 3.8, 2.2 Hz, 1H), 3.32 (dd, *J* = 10.0, 2.8 Hz, 1H), 2.74 (dd, *J* = 16.1, 6.1 Hz, 1H), 2.72 – 2.64 (m, 1H), 2.52 (dd, *J* = 16.1, 6.7 Hz, 1H), 2.41 (dd, *J* = 14.4, 5.5 Hz, 1H), 2.34 – 2.13 (m, 9H), 2.09 (dt, *J* = 13.2, 6.6 Hz, 1H), 1.98 – 1.62 (m, 10H), 1.40 (ddd, *J* = 13.5, 4.4, 2.5 Hz, 1H), 1.05 (s, 9H), 0.92 (s, 9H), 0.90 (s, 9H), 0.89 (s, 9H), 0.89 (s, 9H), 0.88 (s, 9H), 0.11 (s, 3H), 0.10 (s, 3H), 0.08 (s, 3H), 0.06 (s, 6H), 0.05 (s, 6H), 0.04 (s, 3H), 0.03 (s, 3H), 0.03 (s, 3H); **^{13}C NMR** ($CDCl_3$, 101 MHz): δ 207.1, 144.5, 135.7, 135.5, 134.2, 130.9, 129.7, 129.0, 128.4, 127.7, 124.4, 123.7, 114.7, 95.2, 77.0, 74.2, 73.5, 73.1, 71.3, 70.8, 70.4, 68.9, 66.9, 66.8, 65.1, 64.1, 64.0, 50.2, 44.6, 42.5, 38.8, 37.4, 36.3, 34.9, 34.0, 32.7, 30.8, 27.0, 26.5, 26.4, 26.0, 22.7, 19.3, 18.6, 18.4, 18.3, 18.2, 18.1, 1.2, −3.5, −3.6, −3.7, −4.1, −4.1, −4.3, −4.4, −4.7, −4.9; **IR** (Microscope, cm^{-1}): 2954, 2929, 2887, 2857, 1718, 1472, 1463, 1428, 1388, 1361, 1254, 1204, 1089, 1006, 961, 939, 835, 808, 775, 741, 702, 688, 671, 667, 613, 505, 489, 459, 446, 433, 421; **HRMS** (ESI) for $C_{78}H_{138}O_{12}Si_6Na$ $[M+Na]^+$: calcd. 1457.8696; found 1457.8706.



Compound S13. TBSOTf (11 µL, 0.047 mmol) was added dropwise to a solution of alcohol **53** (62 mg, 0.043 mmol) and 2,6-lutidine (15 µL, 0.13 mmol) in CH_2Cl_2 (0.4 mL) at −78 °C. The mixture was stirred

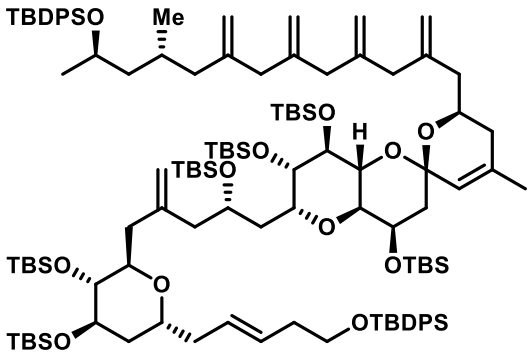
at this temperature for 1 h before the reaction was quenched at −78°C with saturated aqueous NH_4Cl (2 mL). The mixture was warmed to room temperature and stirring was continued until all solids had dissolved. The aqueous phase was extracted with *tert*-butyl methyl ether (3 × 2 mL). The combined organic fractions were washed with brine (2 mL), dried over anhydrous Na_2SO_4, filtered and concentrated. The residue was purified by flash chromatography (hexanes/EtOAc 25:1) to give the title compound as a colorless oil (56 mg, 84%). $[\boldsymbol{\alpha}]_{\boldsymbol{D}}^{\boldsymbol{20}}$ = +18.9 (c = 1.00, $CHCl_3$). **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.69 – 7.65 (m, 4H), 7.46 – 7.34 (m, 6H), 5.52 – 5.37 (m, 2H), 5.15 (s, 1H), 4.83 (s, 1H), 4.80 (s, 1H), 4.36 (dtd, *J* = 10.5, 6.5, 3.8 Hz, 1H), 4.09 (dt, *J* = 10.7, 2.8 Hz, 1H), 3.98 (q, *J* = 3.0 Hz, 1H), 3.92 (p, *J* = 5.1, 4.5 Hz, 1H), 3.80 (td, *J* = 6.8, 5.9, 2.6 Hz, 4H), 3.66 (t, *J* = 7.0 Hz, 2H), 3.63 – 3.55 (m, 2H), 3.38 (dd, *J* = 3.6, 1.8 Hz, 1H), 3.22 – 3.10 (m, 1H), 2.76 (dd, *J* = 16.0, 5.9 Hz, 1H), 2.72 – 2.66 (m, 1H), 2.51 (dd, *J* = 16.1, 6.8 Hz, 1H), 2.39 – 2.19 (m, 8H), 2.19 – 2.02 (m, 2H), 1.95 – 1.72 (m, 5H), 1.67 (s, 3H), 1.65 – 1.54 (m, 2H), 1.39 (dt, *J* = 13.8, 2.9 Hz, 1H), 1.05 (s, 9H), 0.91 (s, 9H), 0.90 (s, 9H), 0.90 (s, 18H), 0.88 (s, 9H), 0.87 (s, 9H), 0.10 (s, 3H), 0.08 (s, 3H), 0.06 (s, 6H), 0.06 (s, 9H), 0.05 (s, 12H), 0.03 (s, 3H); **^{13}C NMR** ($CDCl_3$, 101 MHz): δ 207.2, 144.1, 135.7, 135.3, 134.2, 129.7, 128.8, 128.6, 127.7, 124.5, 114.2, 95.0, 76.6, 73.9, 73.1, 71.2, 70.5, 70.4, 68.8, 67.2, 67.0, 64.6, 64.2, 64.0, 50.3, 44.6, 42.7, 39.0, 37.8, 36.3, 34.9, 33.9, 30.8, 27.0, 26.6, 26.5, 26.2, 26.1, 26.0, 22.7, 19.4, 18.6, 18.4, 18.4, 18.2, 18.1, 1.2, −3.3, −3.4, −3.6, −3.9, −4.1, −4.2, −4.3, −4.4, −4.5, −4.7, −4.9; **IR** (Microscope, cm^{-1}): 2954, 2929, 2887, 2857, 1720, 1472, 1463, 1428, 1388, 1361, 1253, 1204, 1086, 1060, 1006, 973, 939, 835, 808, 775, 739, 702, 686, 613, 505, 488, 467; **HRMS** (ESI) for $C_{84}H_{152}O_{12}Si_7Na$ $[M+Na]^+$: calcd. 1571.9561; found 1571.9569.



Compound 54. *n*-Butyllithium (1.6 M in hexanes, 0.19 mL, 0.31 mmol) was added to a solution of hexabutylditin (0.16 mL, 0.32 mmol) in THF (2.0 mL) at −20 °C. The mixture was stirred at −20 °C for 15 min to give a pale yellow solution of tributylstannyllithium. This solution was cooled to −78 °C and solid copper(I) cyanide (14 mg, 0.15 mmol) was added in one portion. The mixture was allowed to reach −55 °C and stirring was continued at this temperature for 15 min to give a green-yellow solution of the bis(tributylstannyl) cuprate reagent.[11,12]

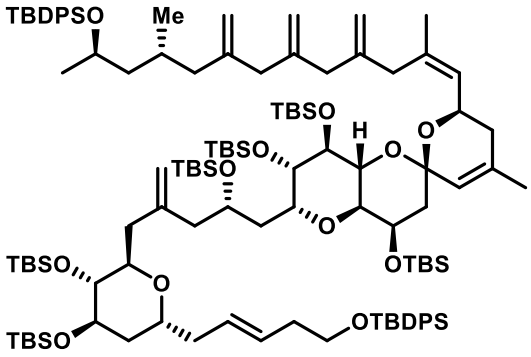
In a separate flask, a solution of trityl potassium (0.20 M in 1,2-dimethoxyethane, 1.2 mL, 0.23 mmol) was added dropwise to a stirred solution of ketone **53** (80 mg, 0.052 mmol) and bis(trifluoromethanesulfonyl)aniline (37 mg, 0.10 mmol) in THF (3.5 mL) at −78 °C until the red color of the trityl anion persisted. The resulting mixture was stirred at this temperature for 15 min to give a solution of the vinyl triflate, which was transferred via canula into the flask containing the cooled (−55 °C)

stannylcuprate solution. Stirring was continued at −55 °C for 15 min before the reaction was quenched with saturated aqueous NH_4Cl (8 mL). The mixture was diluted with *tert*-butyl methyl ether (8 mL) and warmed to room temperature. Stirring was continued until all solid materials had dissolved. The aqueous phase was extracted with *tert*-butyl methyl ether (3 × 8 mL) and the combined organic fractions were washed with brine (15 mL), dried over Na_2SO_4, filtered and concentrated. The residue was purified by flash chromatography (hexanes/ CH_2Cl_2 4:1 + 1% NEt_3) to give the desired alkenyl stannane **54** and its internal double bond isomer as an inseperable mixture (3:1, 58 mg, 62%). Analytical and spectral data of the mixture of double bond isomers: $[\alpha]_D^{20}$ = +23.2 (c = 0.93, $CHCl_3$). **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.70 – 7.64 (m, 4H), 7.47 – 7.32 (m, 6H), 5.84 (s, 1H), 5.63 – 5.55 (m, *resolved signal of the minor isomer*), 5.50 – 5.36 (m, 2H), 5.23 (s, 1H), 5.16 (s, 1H), 4.84 (s, 1H), 4.80 (s, 1H), 4.22 – 4.02 (m, 2H), 4.03 – 3.77 (m, 6H), 3.74 – 3.57 (m, 4H), 3.38 (s, 1H), 3.14 (t, *J* = 9.9 Hz, 1H), 2.72 (dt, *J* = 14.8, 7.2 Hz, 2H), 2.41 – 2.17 (m, 6H), 2.11 (ddd, *J* = 17.6, 13.8, 8.1 Hz, 2H), 2.00 – 1.71 (m, 7H), 1.72 – 1.64 (m, 3H), 1.63 – 1.23 (m, 19H), 1.05 (s, 9H), 0.94 – 0.86 (m, 63H), 0.11 (s, 3H), 0.09 (s, 3H), 0.08 – 0.02 (m, 30H); **^{13}C NMR** ($CDCl_3$, 101 MHz): δ 150.4, 144.2, 142.2, 135.7, 135.3, 134.2, 129.7, 128.7, 128.6, 127.7, 127.2, 124.6, 114.3, 94.9, 76.5, 73.9, 73.4, 73.3, 73.0, 71.2, 71.1, 71.0, 70.9, 70.4, 68.8, 67.3, 67.2, 66.9, 66.4, 64.5, 64.2, 46.1, 44.6, 42.9, 39.1, 37.7, 36.3, 35.0, 34.9, 33.9, 29.3, 27.6, 27.5, 27.0, 26.7, 26.6, 26.2, 26.0, 22.9, 22.8, 20.5, 19.4, 18.7, 18.6, 18.5, 18.5, 18.4, 18.4, 18.2, 18.1, 13.9, 9.7, 9.2, −3.3, −3.4, −3.4, −3.5, −3.5, −3.6, −3.9, −4.2, −4.2, −4.3, −4.3, −4.4, −4.4, −4.5, −4.7, −4.8; **^{119}Sn NMR** ($CDCl_3$, 149 MHz): −40.7 (minor isomer), −44.4 (major isomer); **IR** (Microscope, cm^{-1}): 2955, 2928, 2896, 2857, 1472, 1463, 1428, 1378, 1361, 1253, 1205, 1088, 1060, 1006, 971, 939, 861, 836, 811, 775, 738, 702, 671, 666, 506; **HRMS** (ESI) for $C_{96}H_{178}O_{11}Si_7SnNa$ $[M+Na]^+$: calcd. 1846.0668; found 1846.0692.



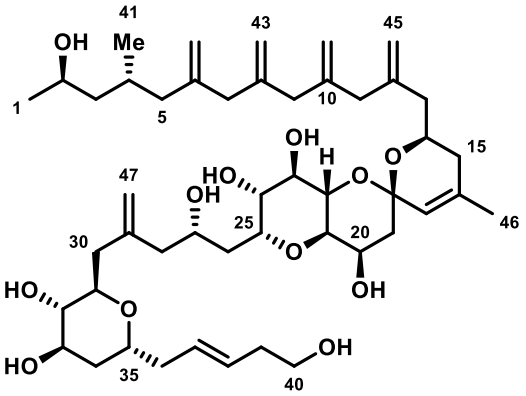
Compound 55. A degassed solution of stannane **54** (0.11 g, 0.060 mmol, 3:1 mixture of isomers) and allylic acetate **17** (31 mg, 0.060 mmol) in DMF/THF (1:1, 0.6 mL) was added to a Schlenk tube containing flame-dried tetrabutylammonium diphenylphosphinate (0.11 g, 0.24 mmol). Copper-thiophene carboxylate complex (CuTC, 35 mg, 0.18 mmol) was then introduced, followed by $Pd(PPh_3)_4$ (7.0 mg, 6.0 µmol). The mixture was stirred for 2 h at ambient temperature before the reaction was quenched with aqueous saturated NH_4Cl (2 mL). The aqueous phase was extracted with *tert*-butyl methyl ether (3 x 2 mL), the combined organic layers were washed with brine (2 mL), dried over anhydrous Na_2SO_4, and evaporated *in vacuo*. The residue was purified twice by flash chromatography (first column: fine silica, hexanes/acetone 90:1; second column: fine silica, hexanes/toluene, 3:2) to

afford **55** (72 mg, 60%) and the internal double bond isomer **S14** (16 mg, 13%) as a colorless oil each. Analytical and spectral data of the desired isomer **55**: $[\alpha]_D^{20}$ = +8.9 (c = 1.00, $CHCl_3$). **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.73 – 7.64 (m, 8H), 7.45 – 7.32 (m, 12H), 5.51 – 5.37 (m, 2H), 5.16 (s, 1H), 4.97 (s, 2H), 4.88 – 4.73 (m, 8H), 4.18 – 4.12 (m, 1H), 4.11 – 4.04 (m, 1H), 3.97 (q, *J* = 3.0 Hz, 1H), 3.90 (ddd, *J* = 7.8, 6.0, 4.7 Hz, 2H), 3.84 – 3.78 (m, 4H), 3.66 (t, *J* = 7.0 Hz, 2H), 3.63 – 3.60 (m, 2H), 3.37 (dd, *J* = 3.5, 1.8 Hz, 1H), 3.11 (d, *J* = 10.0 Hz, 1H), 2.76 – 2.68 (m, 4H), 2.65 (s, 3H), 2.44 – 2.18 (m, 6H), 2.17 – 1.98 (m, 3H), 1.94 – 1.71 (m, 7H), 1.66 (s, 4H), 1.64 – 1.53 (m, 5H), 1.42 – 1.35 (m, 1H), 1.05 (s, 8H), 1.05 (s, 9H), 0.91 (s, 9H), 0.89 (s, 18H), 0.89 (s, 9H), 0.88 (s, 9H), 0.87 (s, 9H), 0.70 (d, *J* = 6.2 Hz, 3H), 0.10 (s, 3H), 0.08 (s, 3H), 0.07 – 0.01 (m, 33H); **^{13}C NMR** ($CDCl_3$, 101 MHz): δ 145.9, 145.0, 144.7, 144.2, 143.5, 136.1, 136.1, 135.7, 135.6, 135.2, 134.5, 134.2, 129.7, 129.6, 129.5, 128.7, 128.6, 127.7, 127.6, 127.5, 124.6, 114.5, 114.3, 113.9, 113.8, 113.1, 94.9, 76.5, 73.9, 73.2, 71.2, 70.9, 70.4, 68.5, 67.8, 67.3, 66.9, 65.3, 64.6, 64.2, 47.5, 44.6, 43.9, 43.7, 42.7, 41.7, 41.4, 39.0, 37.7, 36.3, 34.9, 33.9, 27.2, 27.1, 27.1, 27.0, 26.6, 26.6, 26.2, 26.1, 26.0, 24.4, 22.9, 19.7, 19.5, 19.4, 18.7, 18.5, 18.4, 18.2, 18.1, −3.3, −3.7, −3.9, −4.2, −4.2, −4.3, −4.4, −4.4, −4.5, −4.7, −4.8; **IR** (Microscope, cm^{-1}): 3072, 2954, 2928, 2894, 2857, 1641, 1472, 1463, 1428, 1379, 1361, 1253, 1205, 1090, 1060, 1006, 970, 939, 895, 836, 775, 739, 702, 686, 672, 666, 612, 506; **HRMS** (ESI) for $C_{115}H_{194}O_{12}Si_8Na$ $[M+Na]^+$: calcd. 2014.2617; found 2014.2636.



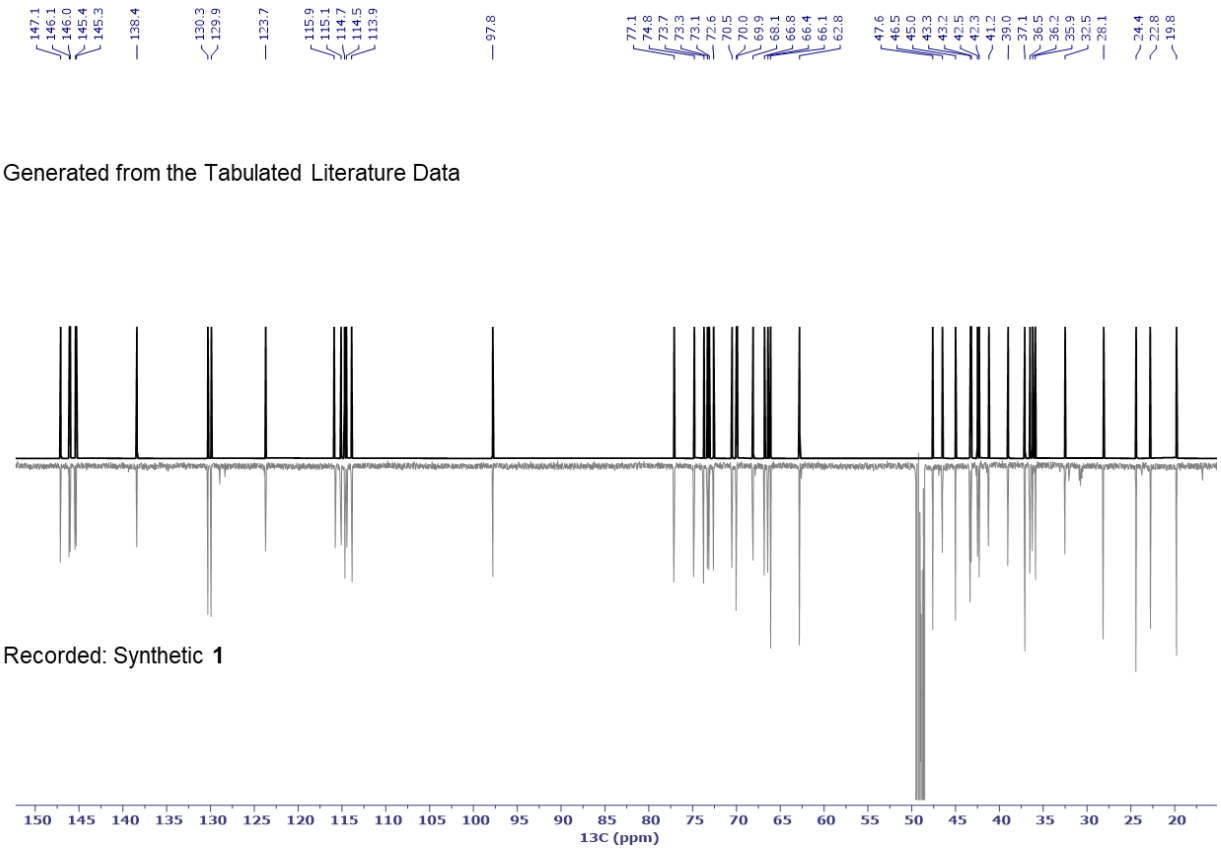
Spectral data of the double bond isomer **S14**: **^{1}H NMR** ($CDCl_3$, 600 MHz): δ 7.70 (ddt, *J* = 9.5, 6.7, 1.5 Hz, 4H), 7.69 – 7.64 (m, 4H), 7.45 – 7.38 (m, 4H), 7.40 – 7.33 (m, 9H), 5.49 – 5.38 (m, 2H), 5.25 (dq, *J* = 7.6, 1.2 Hz, 1H), 5.17 (q, *J* = 2.5, 1.3 Hz, 1H), 4.86 – 4.82 (m, 4H), 4.82 (d, *J* = 2.1 Hz, 1H), 4.80 – 4.78 (m, 1H), 4.78 (d, *J* = 2.2 Hz, 1H), 4.75 (d, *J* = 2.4 Hz, 1H), 4.69 (ddd, *J* = 11.3, 7.7, 3.9 Hz, 1H), 4.07 (ddd, *J* = 12.2, 5.4, 2.1 Hz, 1H), 3.96 (q, *J* = 3.0 Hz, 1H), 3.94 – 3.88 (m, 2H), 3.86 (t, *J* = 9.3 Hz, 1H), 3.84 – 3.78 (m, 4H), 3.66 (t, *J* = 7.0 Hz, 2H), 3.63 (t, *J* = 8.7 Hz, 1H), 3.59 (dd, *J* = 9.1, 5.3 Hz, 1H), 3.37 (dd, *J* = 3.6, 1.8 Hz, 1H), 3.12 (d, *J* = 9.7 Hz, 1H), 2.72 (dd, *J* = 15.4, 10.0 Hz, 1H), 2.68 (d, *J* = 15.0 Hz, 1H), 2.65 (s, 2H), 2.64 (s, 2H), 2.60 (d, *J* = 14.5 Hz, 1H), 2.32 (dd, *J* = 14.1, 4.2 Hz, 1H), 2.30 – 2.19 (m, 4H), 2.13 (dd, *J* = 13.9, 9.1 Hz, 1H), 2.10 – 2.04 (m, 1H), 1.93 (ddm, *J* = 17.1, 10.9 Hz, 1H), 1.90 – 1.80 (m, 5H), 1.79 – 1.71 (m, 3H), 1.71 – 1.64 (m, 7H), 1.62 – 1.55 (m, 6H), 1.38 (dt, *J* = 13.9, 2.9 Hz, 1H), 1.05 (d, *J* = 2.0 Hz, 19H), 1.03 (d, *J* = 6.1 Hz, 4H), 0.70 (d, *J* = 6.1 Hz, 3H), 0.09 – 0.01 (m, 37H); **^{13}C NMR** ($CDCl_3$, 151 MHz): δ 145.7, 144.9, 144.8, 144.0, 136.0, 135.9, 135.7, 135.6, 135.4, 135.0, 134.3, 134.0, 129.5, 129.5, 129.3, 129.1, 128.6, 128.4, 127.6, 127.5, 127.3, 124.4, 114.1, 113.8,

113.3, 112.9, 94.6, 77.2, 77.0, 76.8, 76.4, 76.4, 73.7, 73.0, 73.0, 71.0, 70.8, 70.2, 68.3, 67.7, 67.1, 66.7, 64.4, 64.1, 64.0, 47.2, 45.9, 44.5, 43.7, 42.5, 42.4, 41.7, 38.9, 37.5, 36.1, 35.1, 33.8, 31.9, 29.7, 29.7, 29.7, 29.6, 29.4, 27.1, 27.0, 27.0, 26.9, 26.9, 26.4, 26.0, 25.9, 25.8, 24.3, 22.7, 22.7, 22.7, 19.6, 19.6, 19.3, 19.2, 18.6, 18.3, 18.2, 18.0, 18.0, 16.8, 14.1, −3.6, −3.8, −4.1, −4.3, −4.4, −4.5, −4.5, −4.6, −4.7, −4.9, −5.0.



Limaol (1). Silyl ether **55** (25 mg, 13 µmol) was dissolved in pyridine/THF (3:1, 0.8 mL) and HF–pyridine complex (0.2 mL) was added at 0 °C. The cooling bath was removed and the mixture was stirred at room temperature for 11 d. The reaction was quenched by dropwise addition of pH 7.4 phosphate buffer (2 mL) and the aqueous phase was extracted with EtOAc (5 × 2 mL). The combined organic fractions were washed with brine (5 mL), dried over anhydrous Na_2SO_4, filtered and concentrated. The residue was purified by preparative HPLC (column: YMC-Actus ODS-A, S-5 µm, 150 mm length, 20.0 mm ID; gradient: 20.0 mL/min, MeCN/H_2O 50:50 for 10 min, then 100:0 for 50 min; R_t = 6.59 min) to afford Limaol as a colorless oil (3.3 mg, 32%). $[\alpha]_D^{20}$ = +40 (c = 0.1, MeOH); literature: $[\alpha]_D^{20}$ = +63 (c = 0.1, MeOH).[13] **^{1}H NMR** (CD_3OD, 600 MHz): 5.58 – 5.44 (m, 2H), 5.29 (dq, *J* = 2.6, 1.4 Hz, 1H), 5.02 – 4.99 (m, 1H), 4.96 (d, *J* = 2.2 Hz, 1H), 4.92 – 4.90 (m, 3H), 4.89 – 4.87 (m, 2H), 4.86 (d, *J* = 2.0 Hz, 1H), 4.81 (d, *J* = 2.4 Hz, 1H), 4.80 (q, *J* = 1.2 Hz, 1H), 4.28 – 4.20 (m, 2H), 3.95 (q, *J* = 3.1 Hz, 1H), 3.96 – 3.88 (m, 2H), 3.82 (dqd, *J* = 9.0, 6.2, 3.9 Hz, 1H), 3.73 (ddd, *J* = 10.8, 8.2, 4.7 Hz, 1H), 3.66 (dd, *J* = 10.3, 9.0 Hz, 1H), 3.65 (dd, *J* = 9.3, 6.3 Hz, 1H), 3.60 (d, *J* = 9.1 Hz, 1H), 3.60 – 3.57 (m, 1H), 3.55 (t, *J* = 6.8 Hz, 2H), 3.26 (dd, *J* = 10.2, 2.9 Hz, 1H), 3.01 (d, *J* = 14.7 Hz, 1H), 2.98 (t, *J* = 8.4 Hz, 1H), 2.88 (d, *J* = 14.6 Hz, 1H), 2.73 (d, *J* = 2.3 Hz, 2H), 2.70 (s, 2H), 2.61 (d, *J* = 14.8 Hz, 1H), 2.50 – 2.42 (m, 1H), 2.36 (dd, *J* = 13.7, 6.5 Hz, 1H), 2.32 – 2.18 (m, 6H), 2.12 (dd, *J* = 15.1, 9.7 Hz, 1H), 2.01 – 1.78 (m, 9H), 1.71 (d, *J* = 1.2 Hz, 3H), 1.68 – 1.58 (m, 2H), 1.46 (ddd, *J* = 13.7, 9.1, 4.3 Hz, 1H), 1.14 (d, *J* = 6.1 Hz, 3H), 1.07 (ddd, *J* = 13.9, 9.1, 3.9 Hz, 1H), 0.87 (d, *J* = 6.4 Hz, 3H); **^{13}C NMR** (CD_3OD, 151 MHz): δ 147.1, 146.1, 146.0, 145.5, 145.3, 138.4, 130.3, 129.9, 123.7, 115.8, 115.1, 114.7, 114.4, 113.8, 97.8, 77.1, 74.9, 73.7, 73.3, 73.1, 72.6, 70.5, 70.0, 70.0, 68.1, 66.8, 66.4, 66.1, 62.8, 47.6, 46.5, 45.0, 43.3, 43.2, 42.5, 42.3, 41.3, 39.1, 37.1, 36.5, 36.2, 35.9, 32.5, 28.2, 24.4, 22.8, 19.8; **IR** (Microscope, cm^{-1}): 3383, 2924, 2856, 1638, 1430, 1379, 1176, 1069, 996, 967, 895; **HRMS** (ESI) for $C_{47}H_{74}O_{12}Na$ $[M+Na]^+$: calcd. 853.5072; found 853.5075

Visual Comparison of the ^{13}C NMR Data of Authentic Limaol (**1**) with those of Synthetic **1**[a]



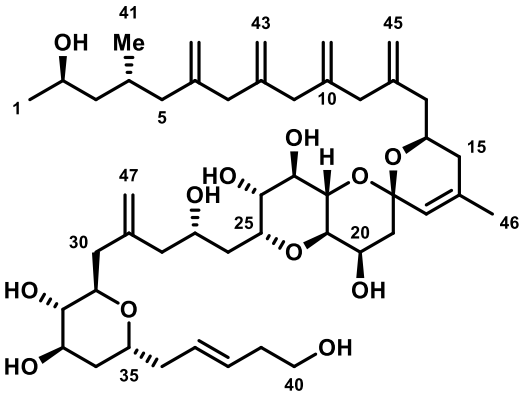
[a] Note that the literature does ***not*** depict the ^{13}C NMR spectrum of limaol (**1**); the shown spectrum (up) was generated (MestReNova) by converting the tabulated ^{13}C NMR data[13] into a formal spectrum; the intensity of the lines is arbitrarily set to be identical for all signals; for a tabular survey of the exact numbers, see Table S8

Table S7. NMR data of synthetic Limaol (**1**); numbering scheme as shown in the insert.

atom number	**^{1}H NMR** (CD_3OD, 600 MHz)				**^{13}C NMR** (CD_3OD, 151 MHz)	
	δ [ppm]	**m**	***J*** [Hz]	**COSY**	δ [ppm]	**HMBC**
1	1.14	d	6.1	2	24.4	3ab
2	3.82	dqd	9.0, 6.2, 3.9	1, 3ab	66.1	1, 3ab
3a	1.46	ddd	13.7, 9.1, 4.3	2, 3b, 4, 41	47.6	1, 5ab, 41
3b	1.07	ddd	13.9, 9.1, 3.9	2, 3a, 4, 41		
4	1.87	m	-	3ab, 5b, 41	28.2	3ab, 5ab, 41
5a	1.98	m	13.3, 5.8	5b, 41, 42'	45.0	3ab, 7, 41, 42', 42"
5b	1.82	m	13.2, 8.2	4, 5a, 41, 42'		
6	-	-	-	-	147.1	5ab, 7, 42', 42"
7	2.73	m	-	42', 42", 43'	43.4	5ab, 9, 42', 42", 43', 43"
8	-	-	-	-	146.1	7, 9, 43', 43"
9	2.70	m	-	43', 43", 44', 44"	42.3	7, 11ab, 43', 43", 44', 44"
10	-	-	-	-	146.0	9, 11ab, 44', 44"
11a	3.01	d	14.7	11b, 44', 45', 45"	43.2	9, 13ab, 44', 44", 45', 45"
11b	2.88	d	14.6	11a, 44', 44", 45"		
12	-	-	-	-	145.3	11ab, 13ab, 14, 45', 45"
13a	2.29	dd	14.0, 3.8	13b, 14, 45'	42.5	11ab, 45', 45"
13b	2.21	m	-	13a, 14, 45'		
14	4.24	m	-	13ab, 15ab	66.8	13ab, 15a
15a	1.93	m	-	14, 15b, 17, 46	36.2	13ab, 17, 46
15b	1.84	m	-	14, 15a, 46		
16	-	-	-	-	138.4	15ab, 46
17	5.29	m	-	15ab, 19a, 46	123.7	15ab, 46
18	-	-	-	-	97.8	17, 19ab, 20, 22
19a	1.94	m	-	17, 20	41.3	20
19b	1.86	m	-	20		
20	3.95	m	3.1	19ab, 21	68.1	19a, 22
21	3.26	dd	10.2, 2.9	20, 22	70.5	19a, 20, 22, 25
22	3.66	dd	10.3, 9.0	21	70.0	20, 21, 23
23	3.59	d	9.1	24	72.6	21, 22, 25
24	3.64	dd	9.3, 6.3	23, 25	73.1	23, 25
25	4.25	m	-	24, 26ab	74.9	24, 26a
26a	1.88	m	-	25, 26b, 27	32.5	22, 28ab

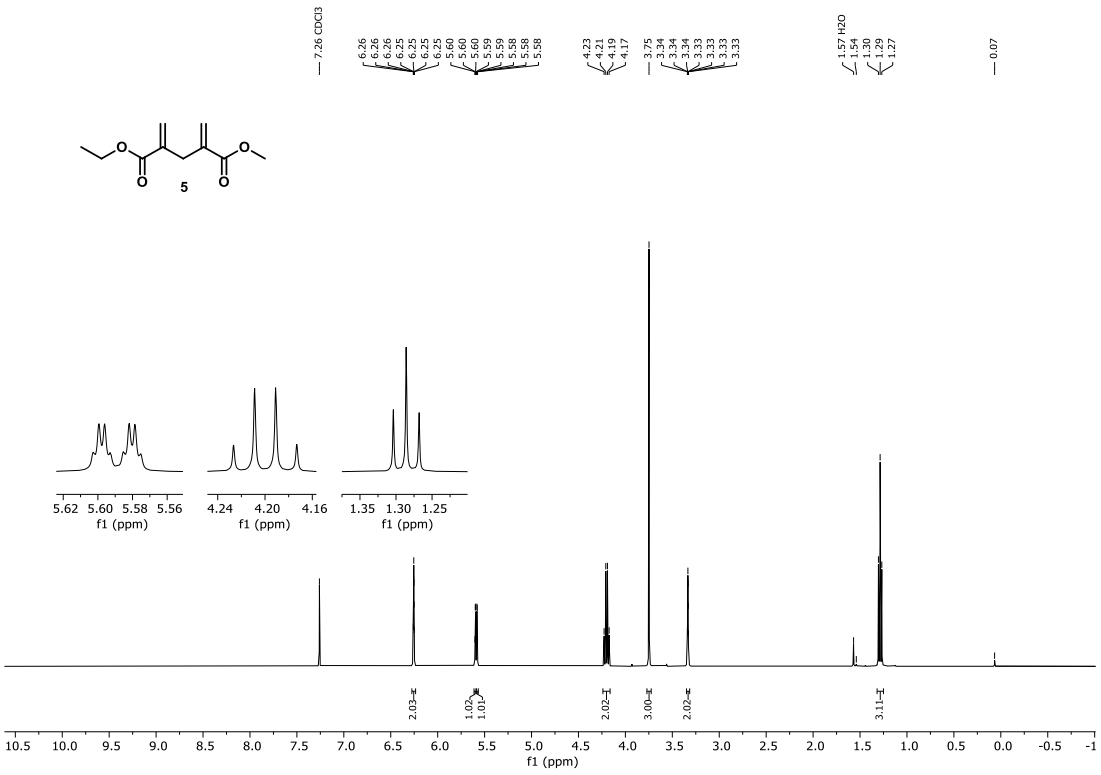
26b	1.62	m	-	25, 26a, 27		
27	3.92	m	-	26ab, 28ab	66.4	26b, 28ab
28a	2.36	dd	13.7, 6.5	27, 28b, 47''	46.5	30ab, 47', 47''
28b	2.23	m	-	27, 28a, 47''		
29	-	-	-	-	145.5	28ab, 30ab, 31, 47', 47''
30a	2.61	d	14.8	30b, 31, 47', 47''	39.1	28ab, 32, 47', 47''
30b	2.12	dd	15.1, 9.7	30a, 31, 47'		
31	3.59	m	-	30ab, 32	73.8	30ab, 32, 35
32	2.98	t	8.4	31, 33	77.1	30b, 31, 33, 34ab
33	3.73	ddd	10.8, 8.2, 4.7	32, 34ab	70.0	32, 34ab
34a	1.92	m	-	33, 34b, 35	36.5	32, 35, 36ab
34b	1.63	m	-	33, 34a, 35		
35	3.92	m	-	34ab, 36ab	73.3	34b, 36ab, 37
36a	2.46	m	-	35, 36b, 37	35.9	34b, 35, 37, 38
36b	2.25	m	-	35, 36a, 37		
37	5.48	m	-	36ab, 38	139.9	35, 36ab, 38
38	5.54	m	-	37, 39	130.3	36ab, 37, 40
39	2.23	m	-	38, 40	37.1	37, 38, 40
40	3.55	t	6.8	39	62.8	38, 39
41	0.87	d	6.4	3ab, 4, 5ab	19.8	3ab, 5ab
42'	4.81	d	2.4	5ab, 7	113.8	5ab, 7
42''	4.80	q	1.2	7		
43'	4.90	m	-	7, 9	114.7	7, 9
43''	4.88	m	-	9		
44'	5.01	m	-	9, 11ab, 44''	115.1	9, 11ab
44''	4.88	m	-	9, 11b, 44'		
45'	4.96	d	2.2	11a, 13ab, 45''	115.8	11ab, 13ab
45''	4.91	m	-	11ab, 45'		
46	1.71	d	1.2	15ab, 17	22.8	15b, 17
47'	4.91	m	-	30ab, 47''	114.4	28ab, 30ab
47''	4.86	d	2.0	28ab, 30a, 47'		

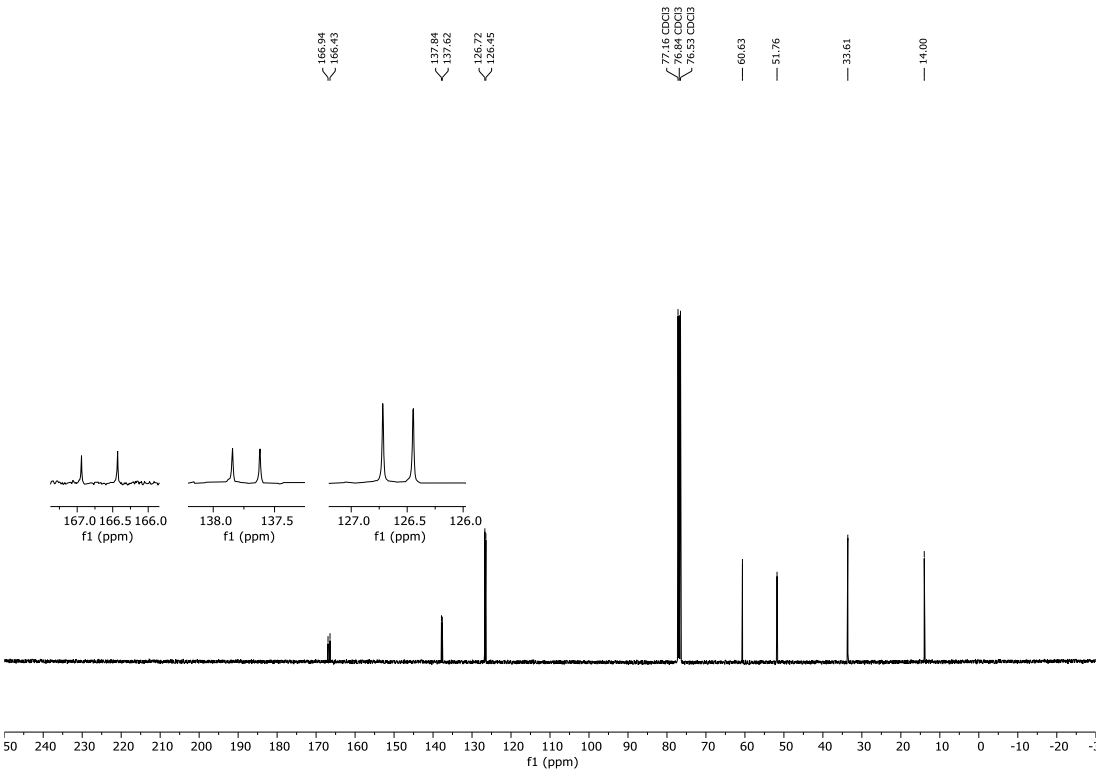
Table S8. Comparison of ^{13}C NMR Data of Synthetic **1** with Authentic Limaol.[13]

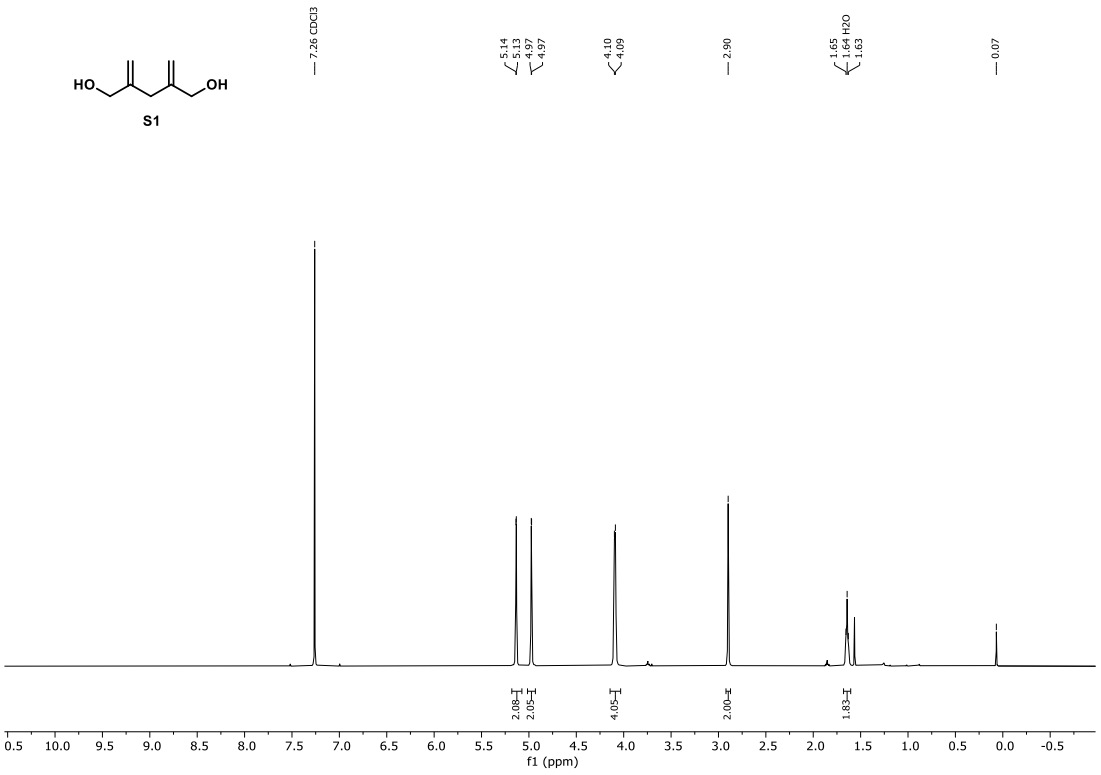


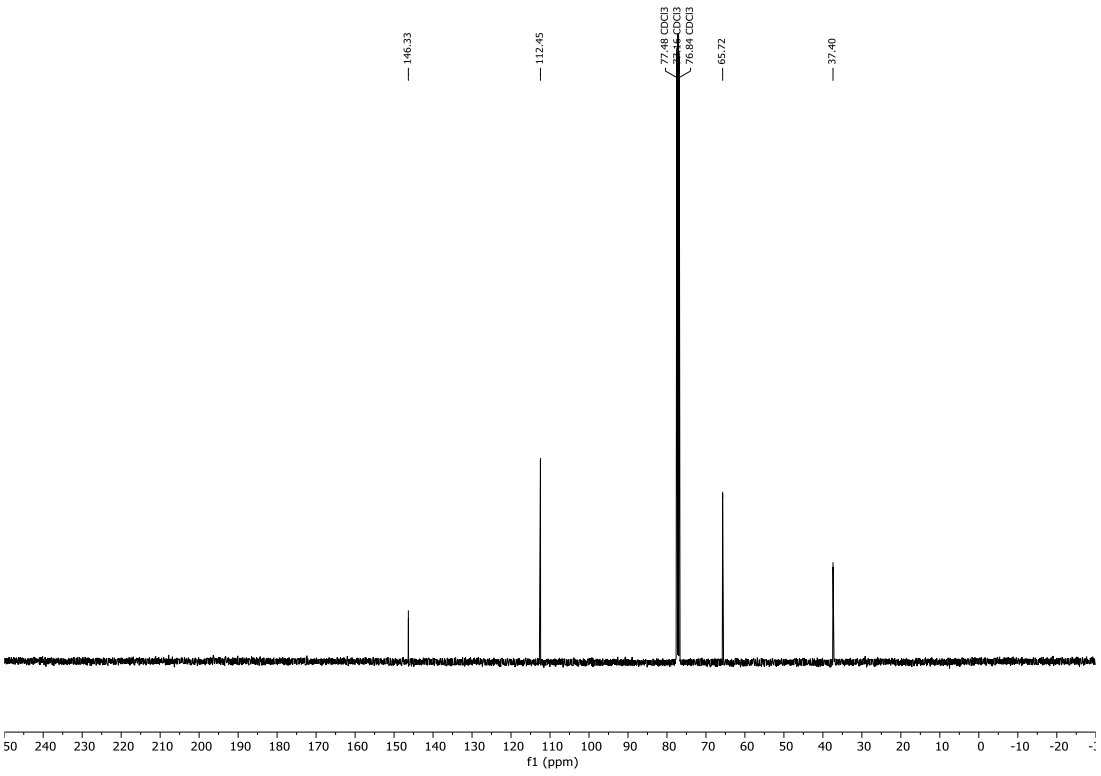
atom number	Limaol	1	Δδ
1	24.4	24.4	±0.0
2	66.1	66.1	±0.0
3	47.6	47.6	±0.0
4	28.1	28.2	−0.1
5	45.0	45.0	±0.0
6	147.1	147.1	±0.0
7	43.3	43.3	±0.0
8	146.1	146.1	±0.0
9	42.3	42.3	±0.0
10	146.0	146.0	±0.0
11	43.2	43.2	±0.0
12	145.3	145.3	±0.0
13	42.5	42.5	±0.0
14	66.8	66.8	±0.0
15	36.2	36.2	±0.0
16	138.4	138.4	±0.0
17	123.7	123.7	±0.0
18	97.8	97.8	±0.0
19	41.2	41.2	±0.0
20	68.1	68.1	±0.0
21	70.5	70.5	±0.0
22	69.9	70.0	−0.1
23	72.6	72.6	±0.0
24	73.1	73.1	±0.0
25	74.8	74.9	−0.1
26	32.5	32.5	±0.0
27	66.4	66.4	±0.0
28	46.5	46.5	±0.0

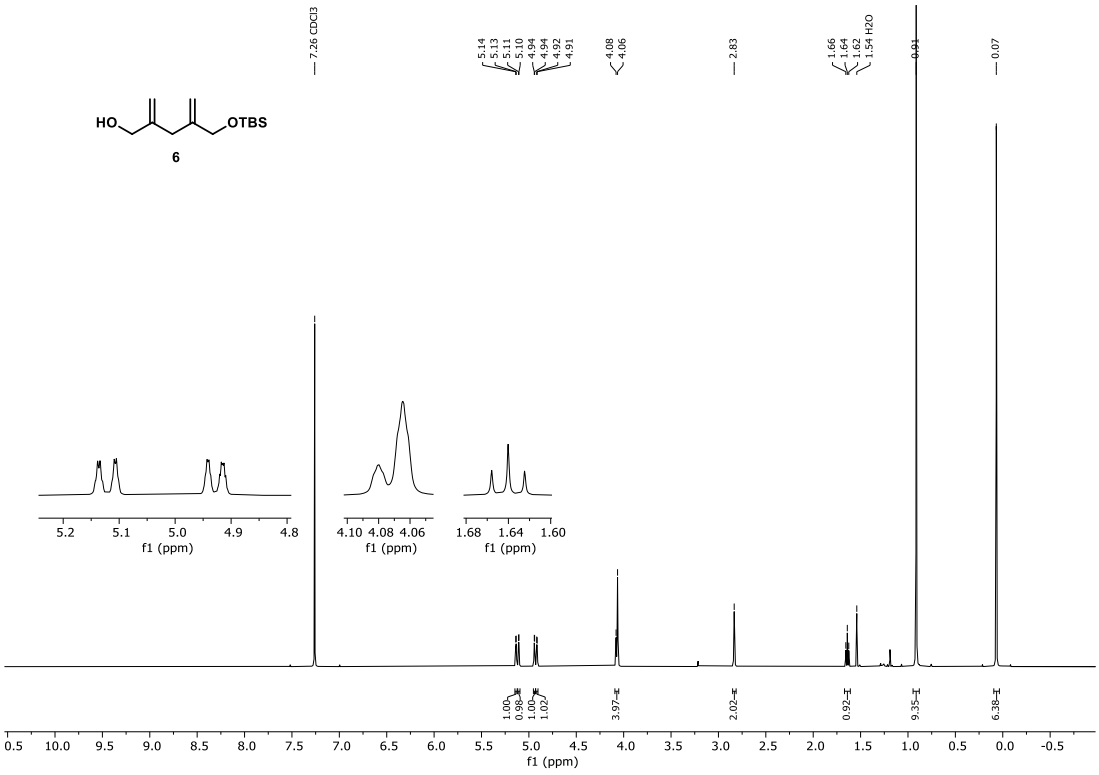
29	145.4	145.5	−0.1
30	39.0	39.1	−0.1
31	73.7	73.7	±0.0
32	77.1	77.1	±0.0
33	70.0	70.0	±0.0
34	36.5	36.5	±0.0
35	73.3	73.3	±0.0
36	35.9	35.9	±0.0
37	129.9	129.9	±0.0
38	130.3	130.3	±0.0
39	37.1	37.1	±0.0
40	62.8	62.8	±0.0
41	19.8	19.8	±0.0
42	113.9	113.8	+0.1
43	114.7	114.7	±0.0
44	115.1	115.1	±0.0
45	115.9	115.8	+0.1
46	22.8	22.8	±0.0
47	114.5	114.4	+0.1

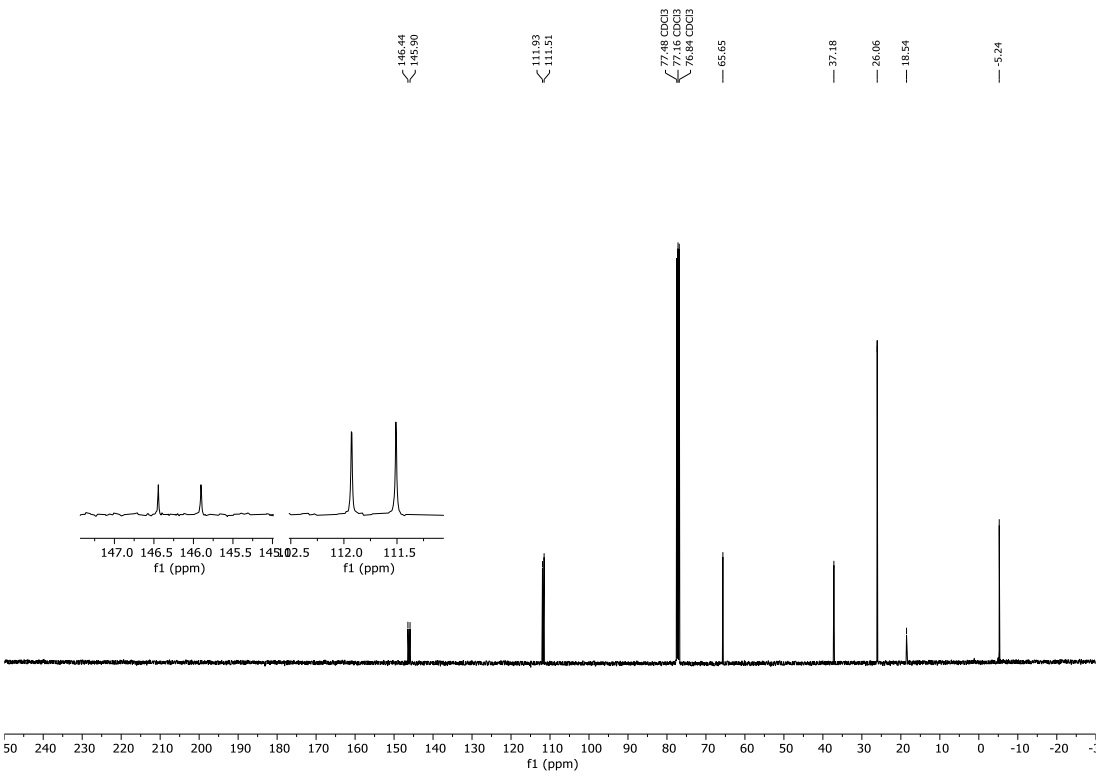

7.26 CDCl3
6.26
6.26
6.26
6.25
6.25
6.25
5.60
5.60
5.59
5.59
5.58
5.58
5.58
4.23
4.21
4.19
4.17
3.75
3.34
3.34
3.34
3.33
3.33
3.33
3.33
1.57 H2O
1.54
1.30
1.29
1.27
0.07
O
O
O
O
5
5.62 5.60 5.58 5.56
f1 (ppm)
4.24 4.20 4.16
f1 (ppm)
1.35 1.30 1.25
f1 (ppm)
2.03
1.02
1.01
2.02
3.00
2.02
3.11
f1 (ppm)

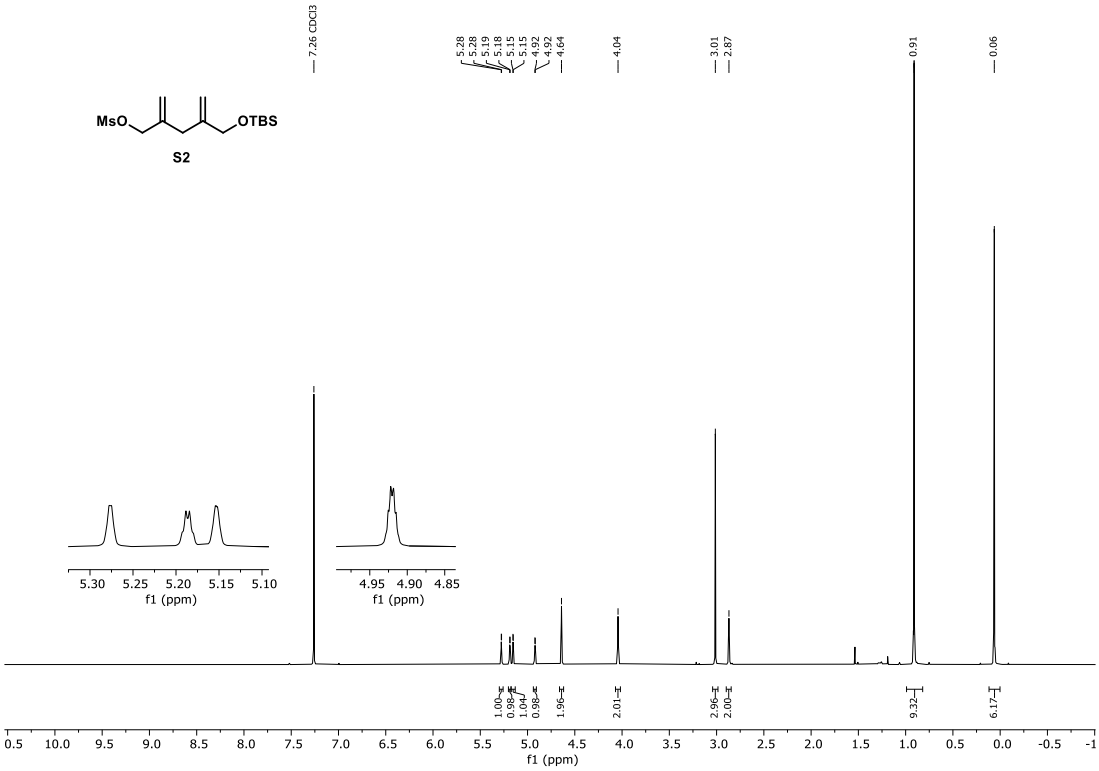

166.94
166.43
137.84
137.62
126.72
126.45
77.16 CDCl3
76.84 CDCl3
76.53 CDCl3
60.63
51.76
33.61
14.00
167.0 166.5 166.0
f1 (ppm)
138.0 137.5
f1 (ppm)
127.0 126.5 126.0
f1 (ppm)
f1 (ppm)

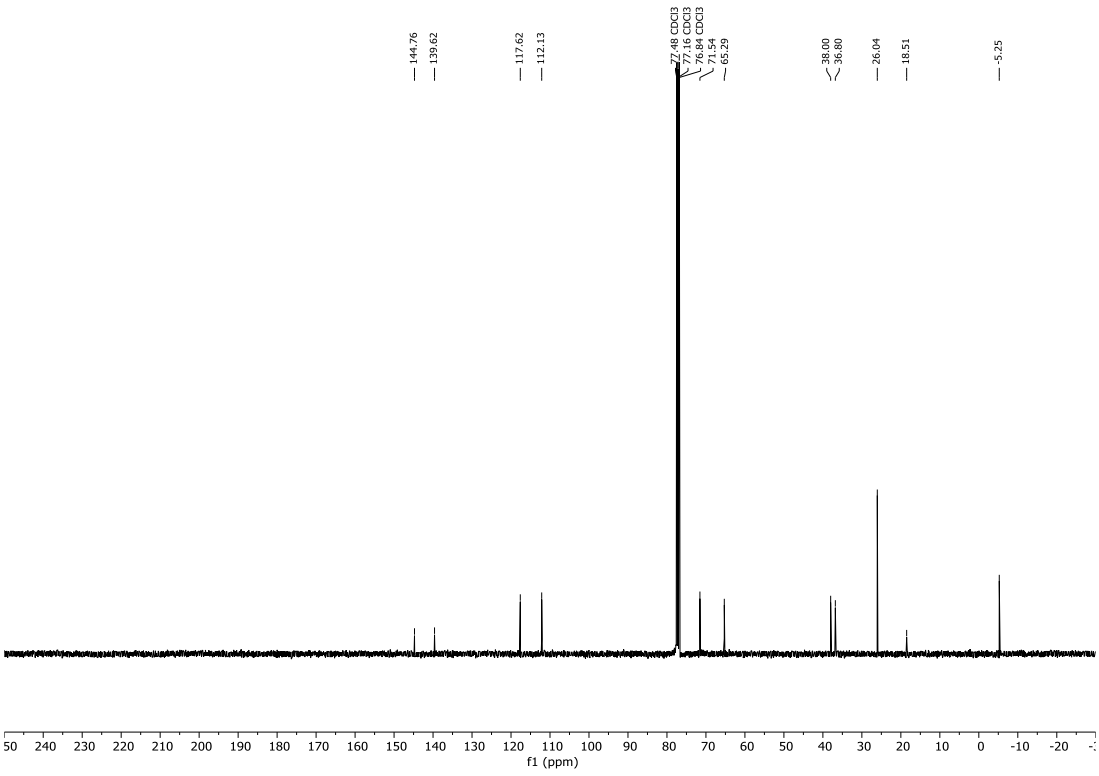

HO
OH
S1
7.26 CDCl3
5.14
5.13
4.97
4.97
4.10
4.09
2.90
1.65
1.64 H2O
1.63
0.07
2.08
2.05
4.05
2.00
1.83
f1 (ppm)

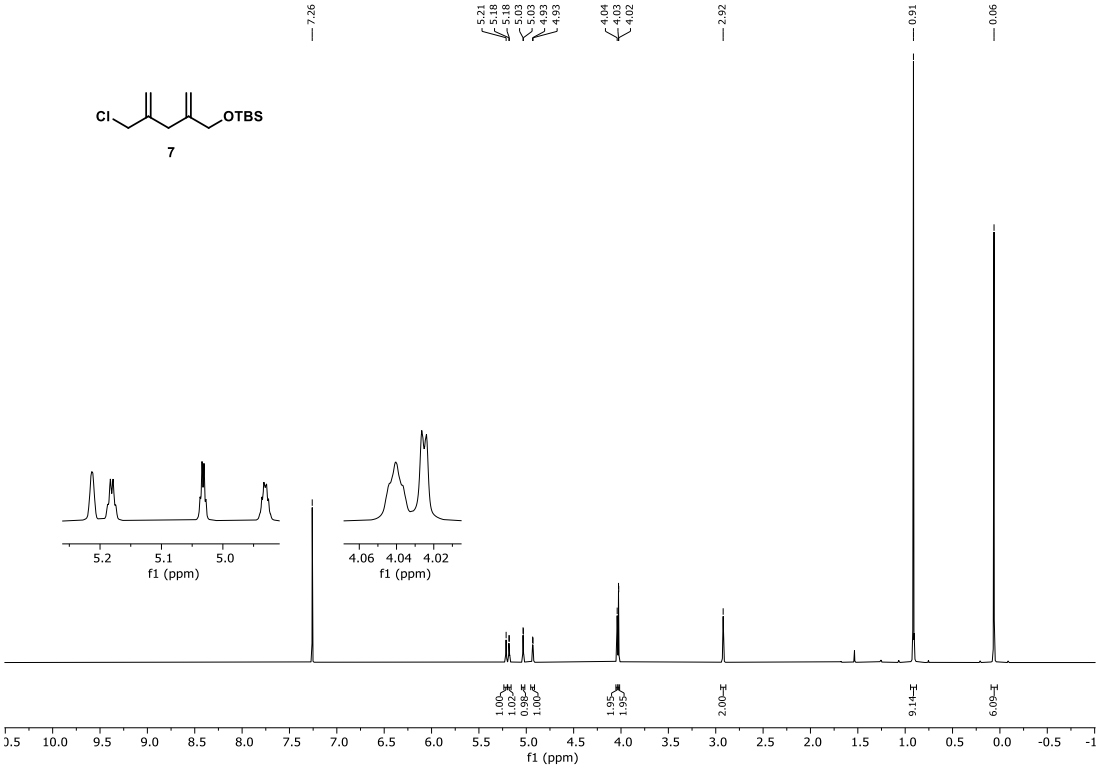

146.33
112.45
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
65.72
37.40
f1 (ppm)

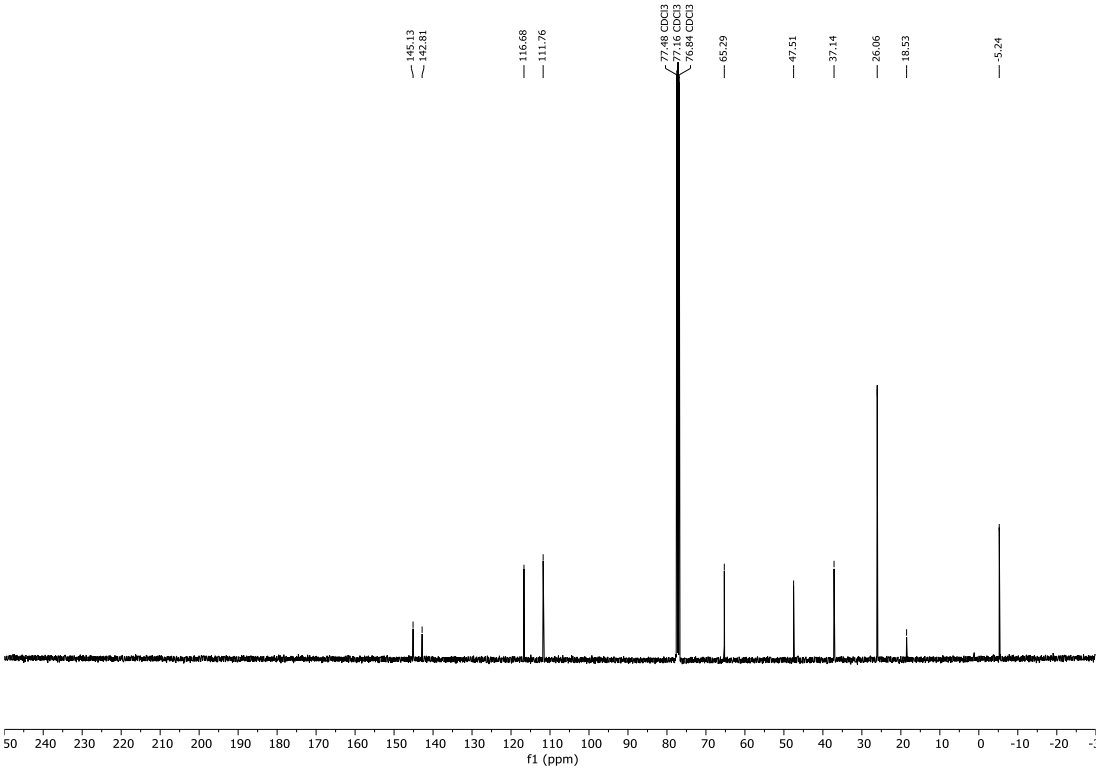

HO
OTBS
6
7.26 CDCl3
5.14
5.13
5.11
5.10
4.94
4.94
4.92
4.91
4.08
4.06
2.83
1.66
1.64
1.62
1.54 H2O
0.91
0.07
f1 (ppm)

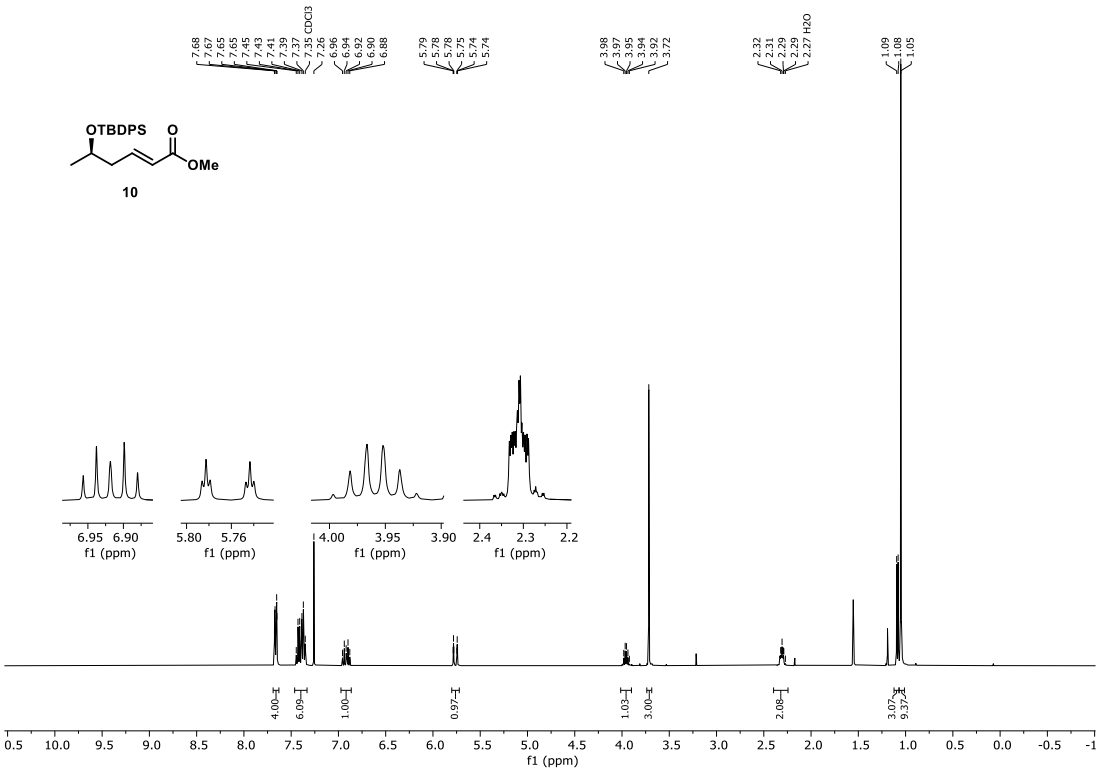

146.44
145.90
111.93
111.51
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
65.65
37.18
26.06
18.54
-5.24
f1 (ppm)

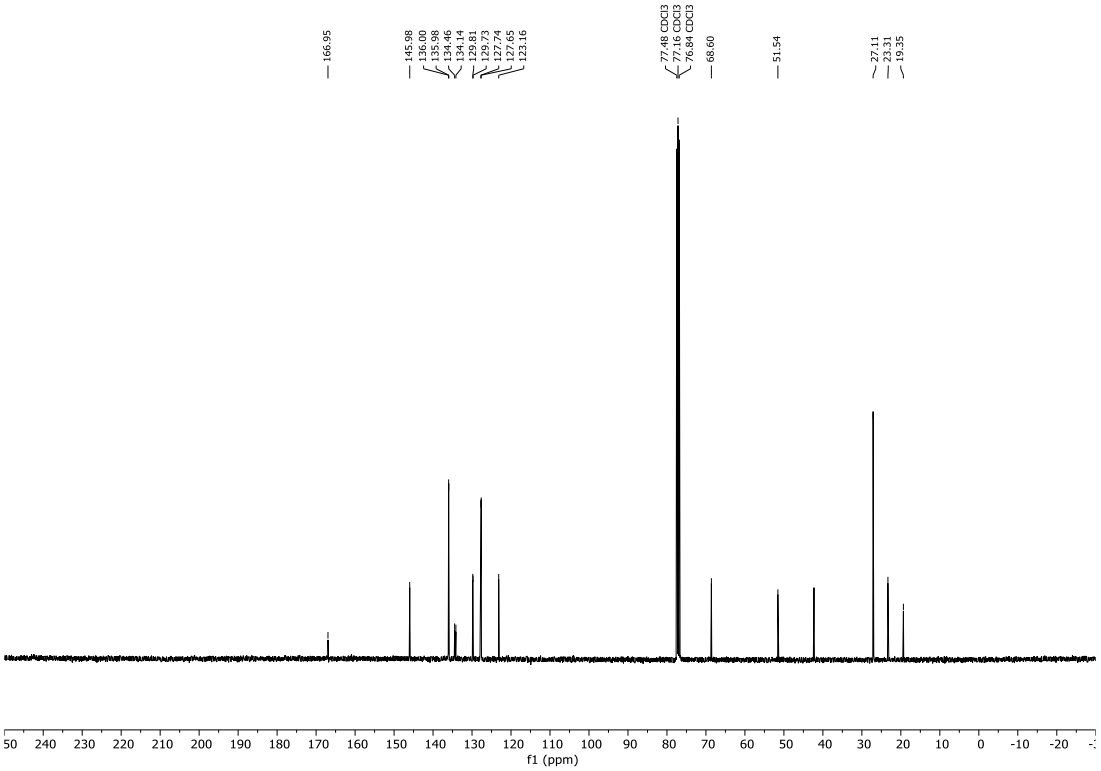

MsO
OTBS
S2
7.26 CDCl3
5.28
5.28
5.19
5.18
5.15
4.92
4.92
4.64
4.04
3.01
2.87
0.91
0.06
5.30 5.25 5.20 5.15 5.10
f1 (ppm)
4.95 4.90 4.85
f1 (ppm)
1.00
0.98
1.04
0.98
1.96
2.01
2.96
2.00
9.32
6.17
f1 (ppm)

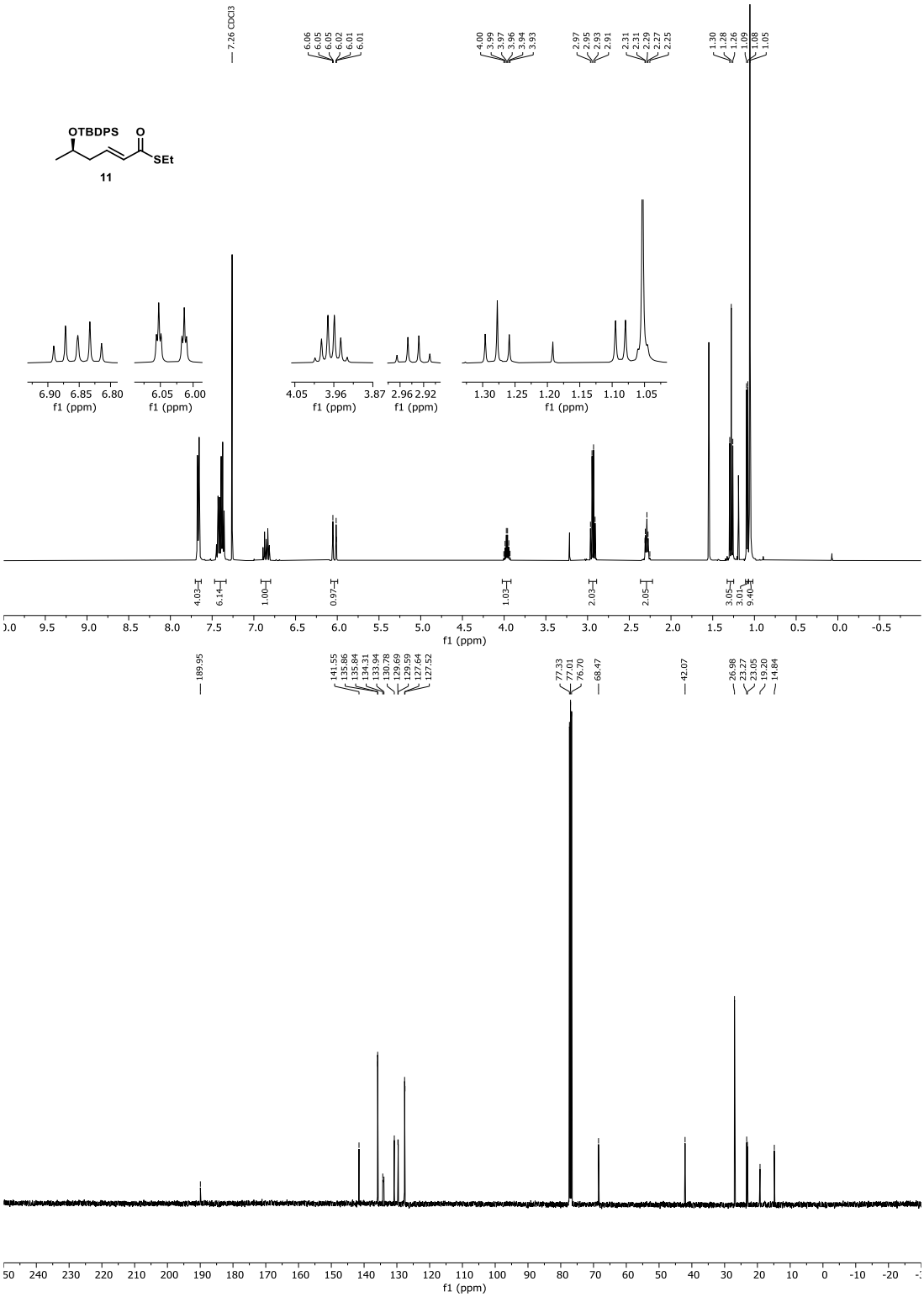

144.76
139.62
117.62
112.13
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
71.54
65.29
38.00
36.80
26.04
18.51
-5.25
f1 (ppm)

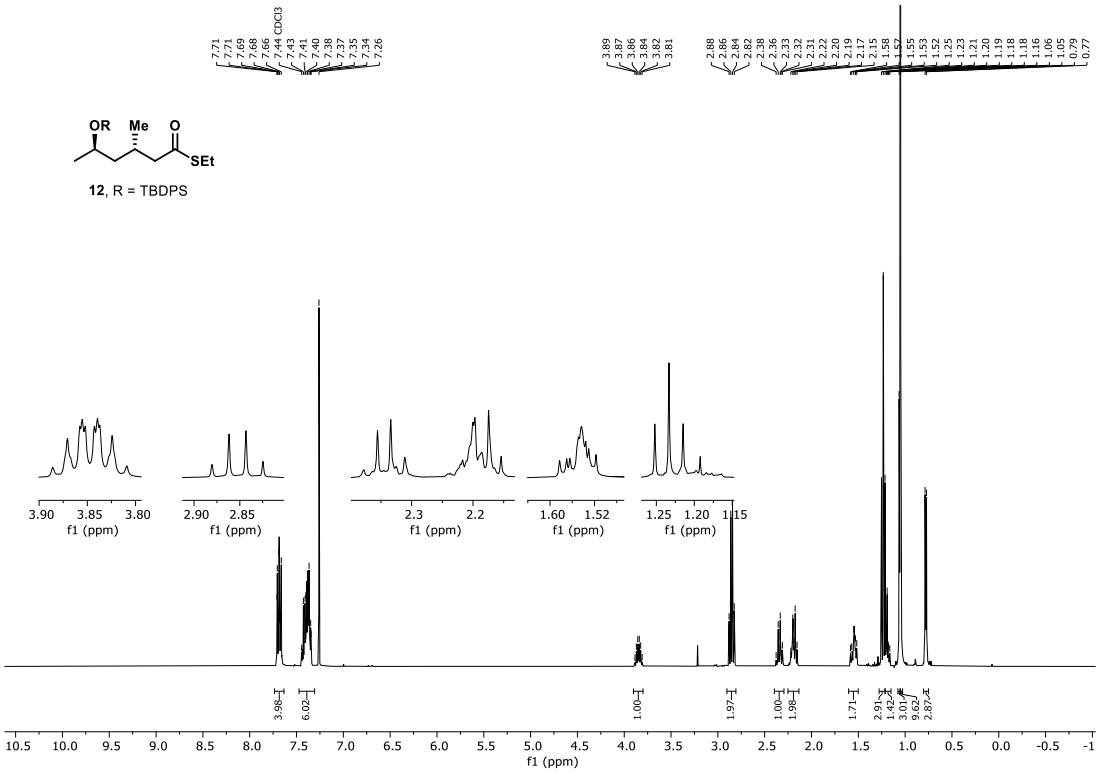

7.26
5.21
5.18
5.18
5.03
5.03
4.93
4.93
4.04
4.03
4.02
2.92
0.91
0.06
Cl
OTBS
7
5.2
5.1
5.0
f1 (ppm)
4.06
4.04
4.02
f1 (ppm)
1.00
1.02
0.98
1.00
1.95
1.95
2.00
9.14
6.09
f1 (ppm)

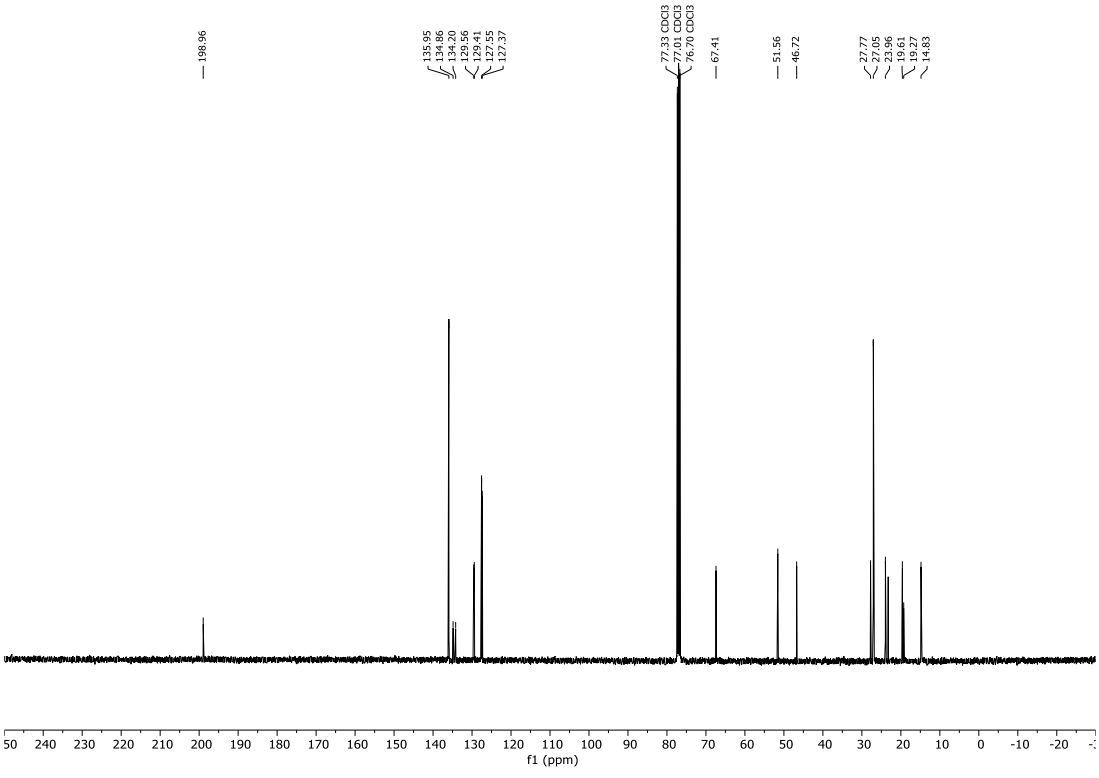

145.13
142.81
116.68
111.76
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
65.29
47.51
37.14
26.06
18.53
-5.24
f1 (ppm)

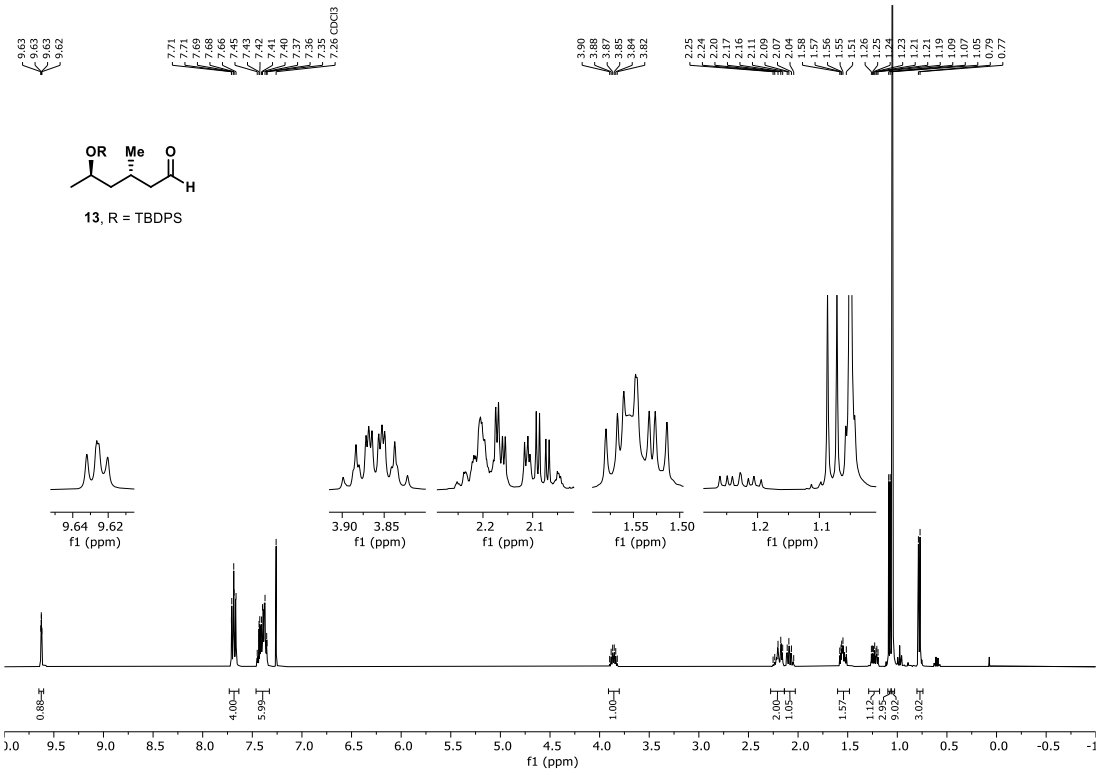

7.68
7.67
7.65
7.65
7.45
7.43
7.41
7.39
7.37
7.35 CDCl3
7.26
6.96
6.94
6.92
6.90
6.88
5.79
5.78
5.78
5.75
5.74
5.74
3.98
3.97
3.95
3.94
3.92
3.72
2.32
2.31
2.29
2.29
2.27 H2O
1.09
1.08
1.05
OTBDPS
O
OMe
10
6.95 6.90
f1 (ppm)
5.80 5.76
f1 (ppm)
4.00 3.95 3.90
f1 (ppm)
2.4 2.3 2.2
f1 (ppm)
4.00
6.09
1.00
0.97
1.03
3.00
2.08
3.07
9.37
f1 (ppm)

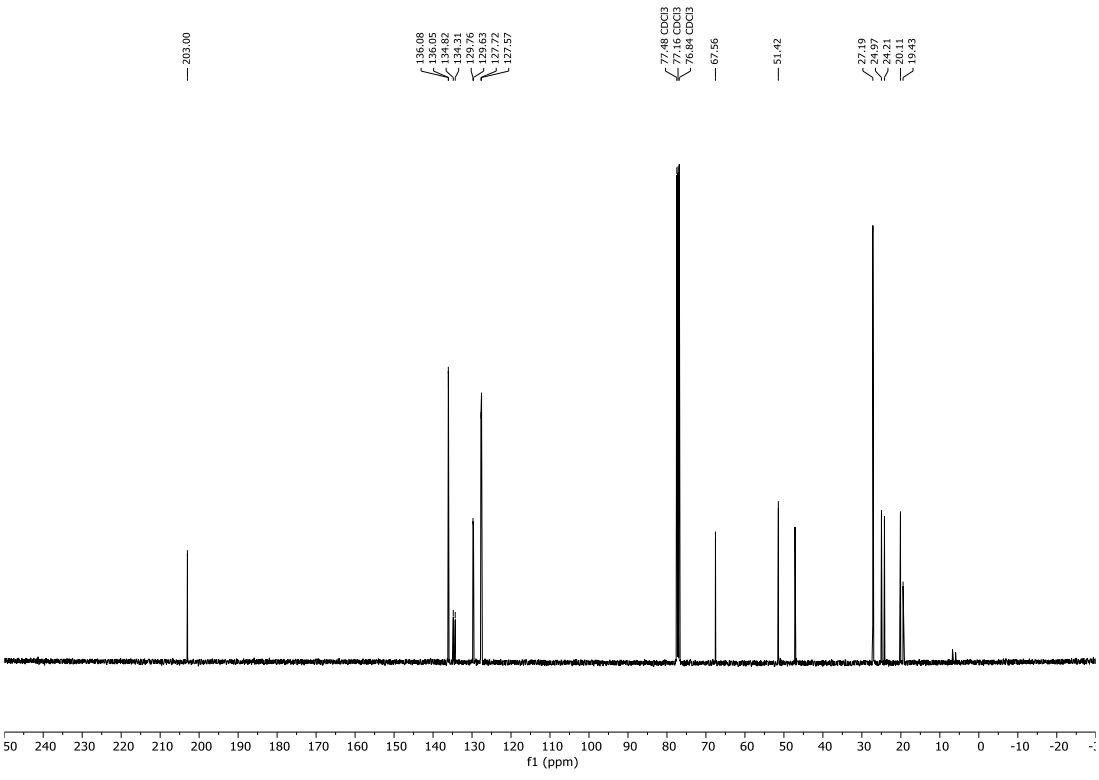

166.95
145.98
136.00
135.98
134.46
134.14
129.81
129.73
127.74
127.65
123.16
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
68.60
51.54
27.11
23.31
19.35
f1 (ppm)

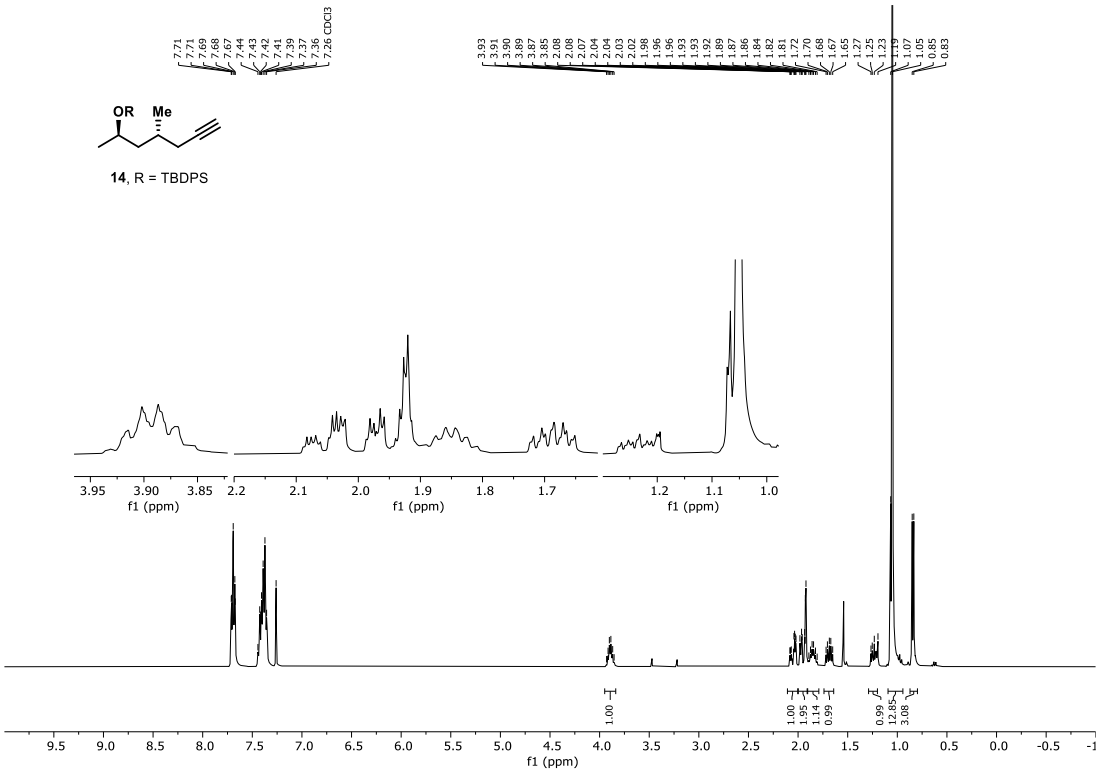

OTBDPS
O
SEt
11
7.26 CDCl3
6.06
6.05
6.02
6.01
6.01
4.00
3.99
3.97
3.96
3.94
3.93
2.97
2.95
2.93
2.91
2.31
2.31
2.29
2.27
2.25
1.30
1.28
1.26
1.09
1.08
1.05
f1 (ppm)
4.03
6.14
1.00
0.97
1.03
2.03
2.05
3.05
3.01
9.40
189.95
141.55
135.86
135.84
134.31
133.94
130.78
129.69
129.59
127.64
127.52
77.33
77.01
76.70
68.47
42.07
26.98
23.27
23.05
19.20
14.84

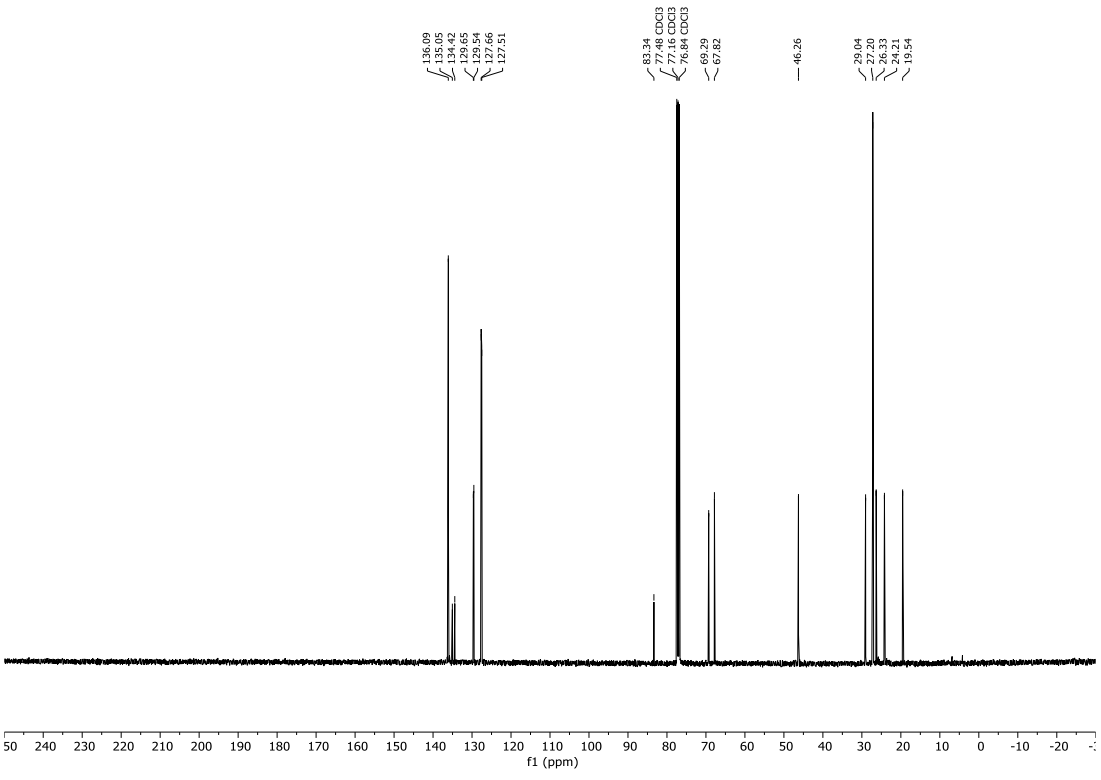

OR
Me
O
SEt
12, R = TBDPS
f1 (ppm)

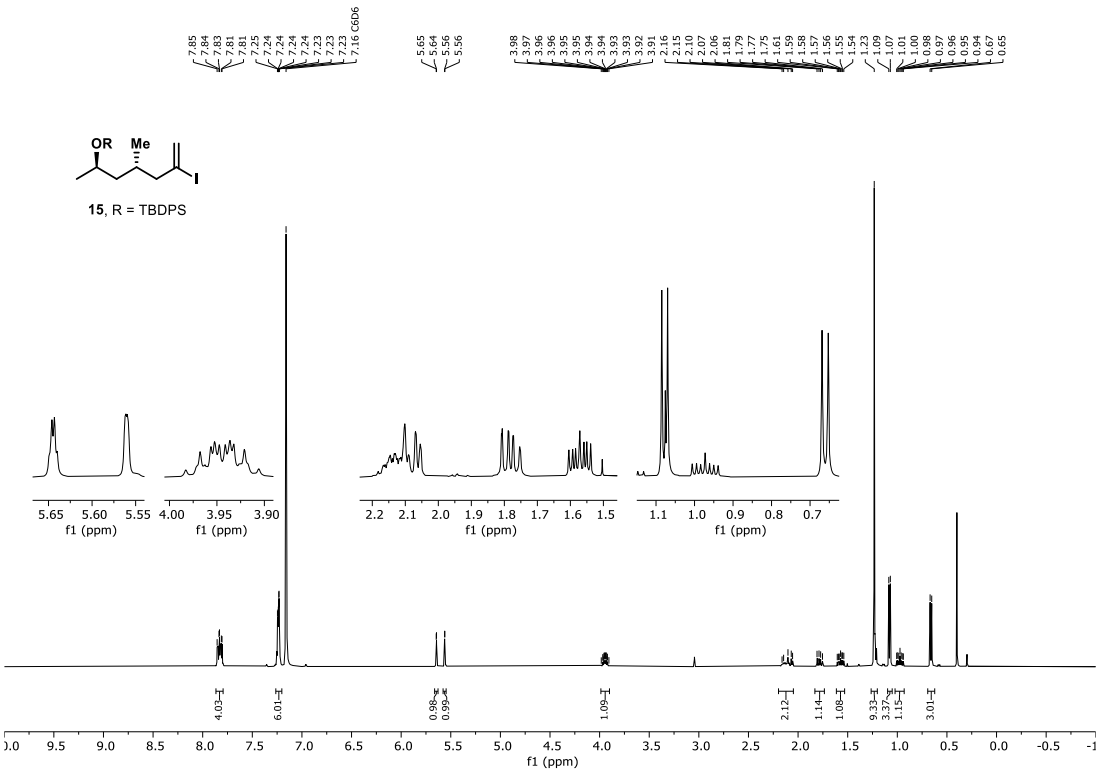

f1 (ppm)

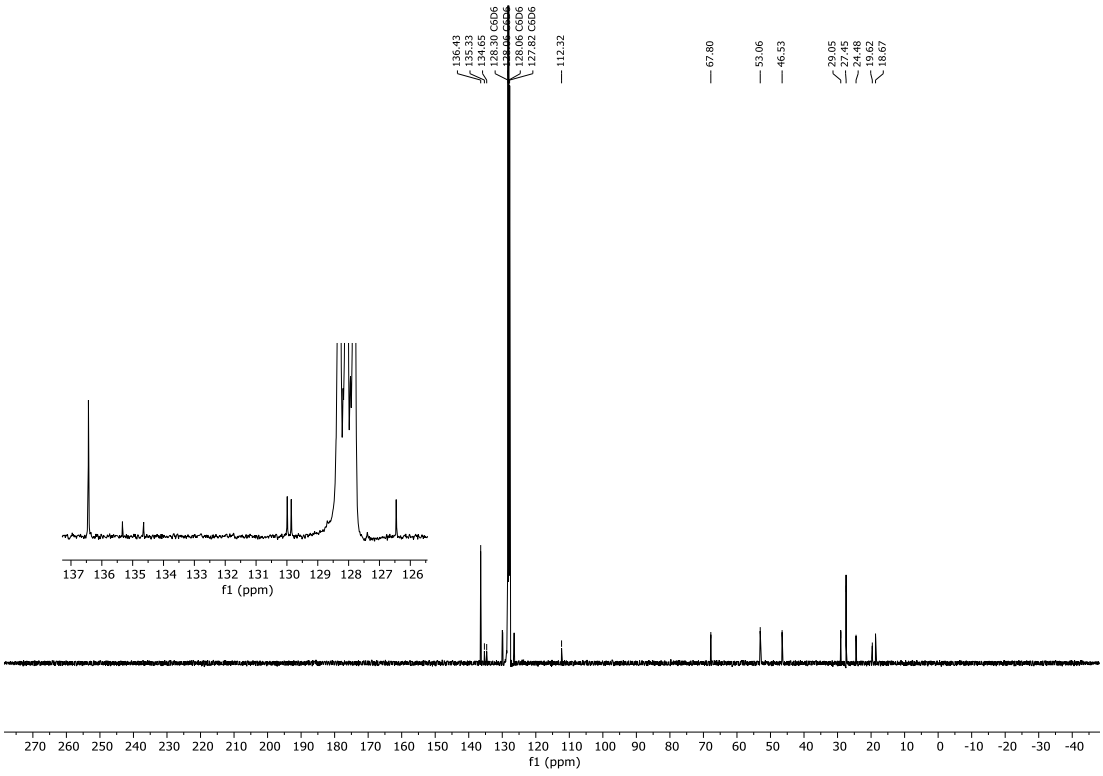

OR
Me
O
H
13, R = TBDPS
f1 (ppm)

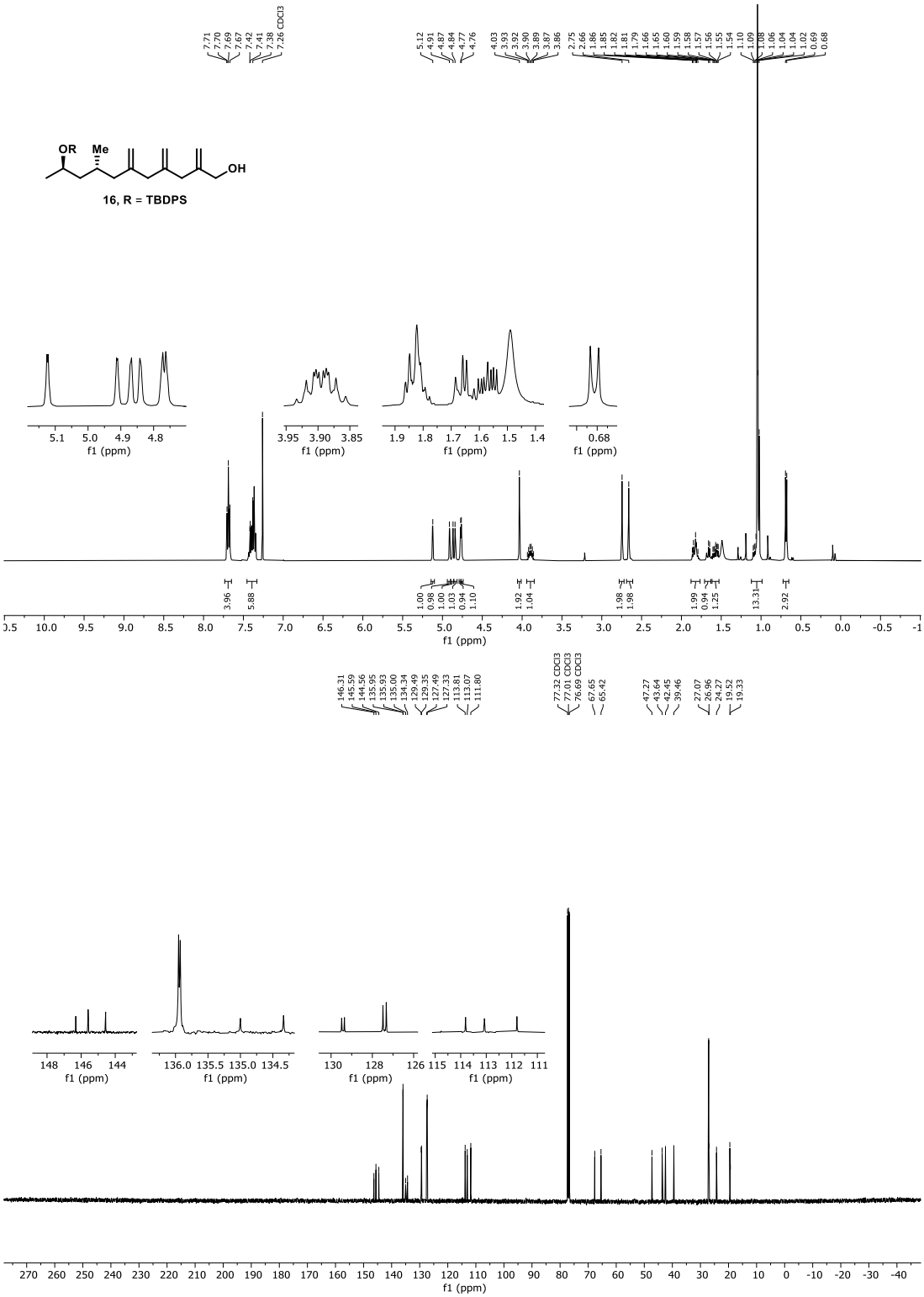

f1 (ppm)

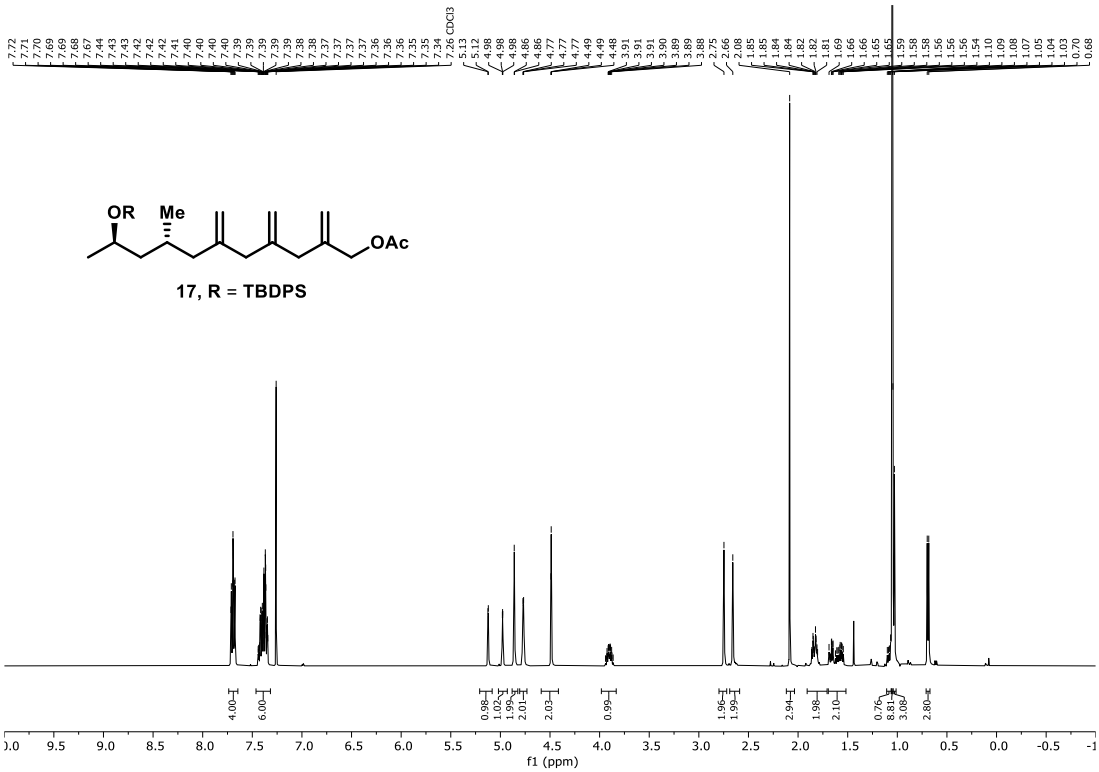

7.71
7.71
7.69
7.68
7.67
7.44
7.43
7.42
7.41
7.39
7.37
7.36
7.26 CDCl3
3.93
3.91
3.90
3.89
3.87
3.85
2.08
2.08
2.07
2.04
2.04
2.03
2.02
1.98
1.96
1.96
1.93
1.93
1.92
1.89
1.87
1.86
1.84
1.82
1.81
1.72
1.70
1.68
1.67
1.65
1.27
1.25
1.23
1.19
1.07
1.05
0.85
0.83
OR
Me
14, R = TBDPS
f1 (ppm)
1.00
1.00
1.95
1.14
0.99
0.99
12.85
3.08


136.09
135.05
134.42
129.65
129.54
127.66
127.51
83.34
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
69.29
67.82
46.26
29.04
27.20
26.33
24.21
19.54
f1 (ppm)

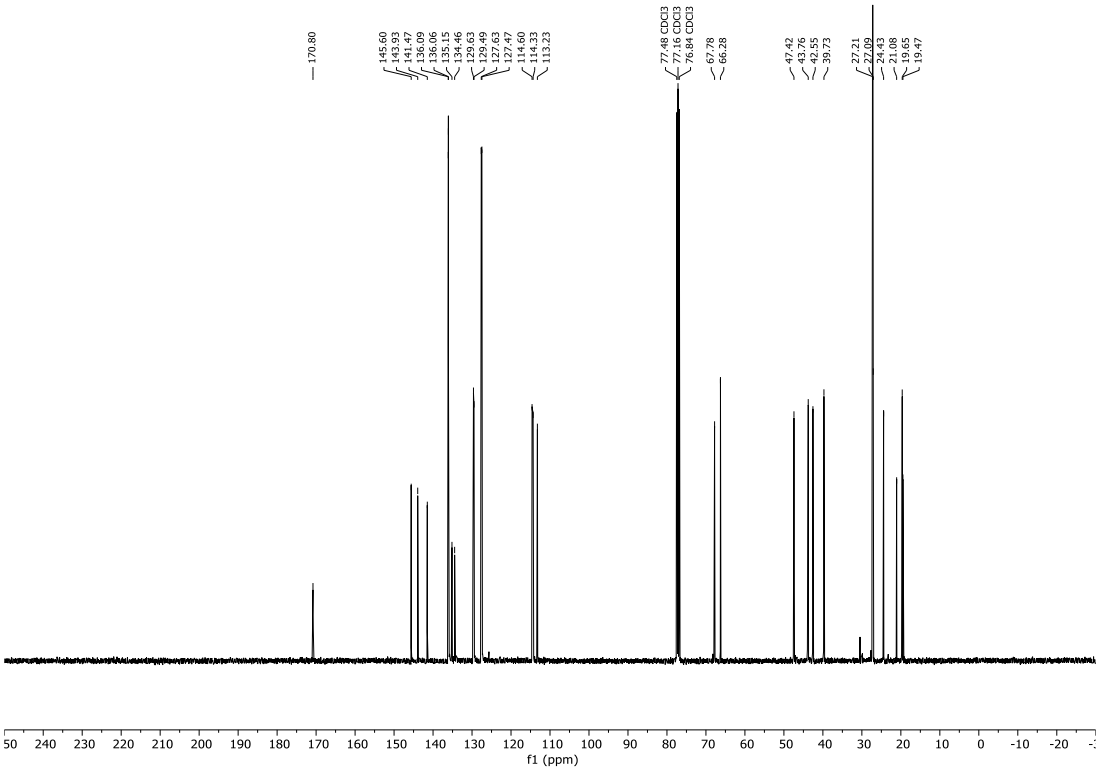

OR
Me
I
15, R = TBDPS
f1 (ppm)

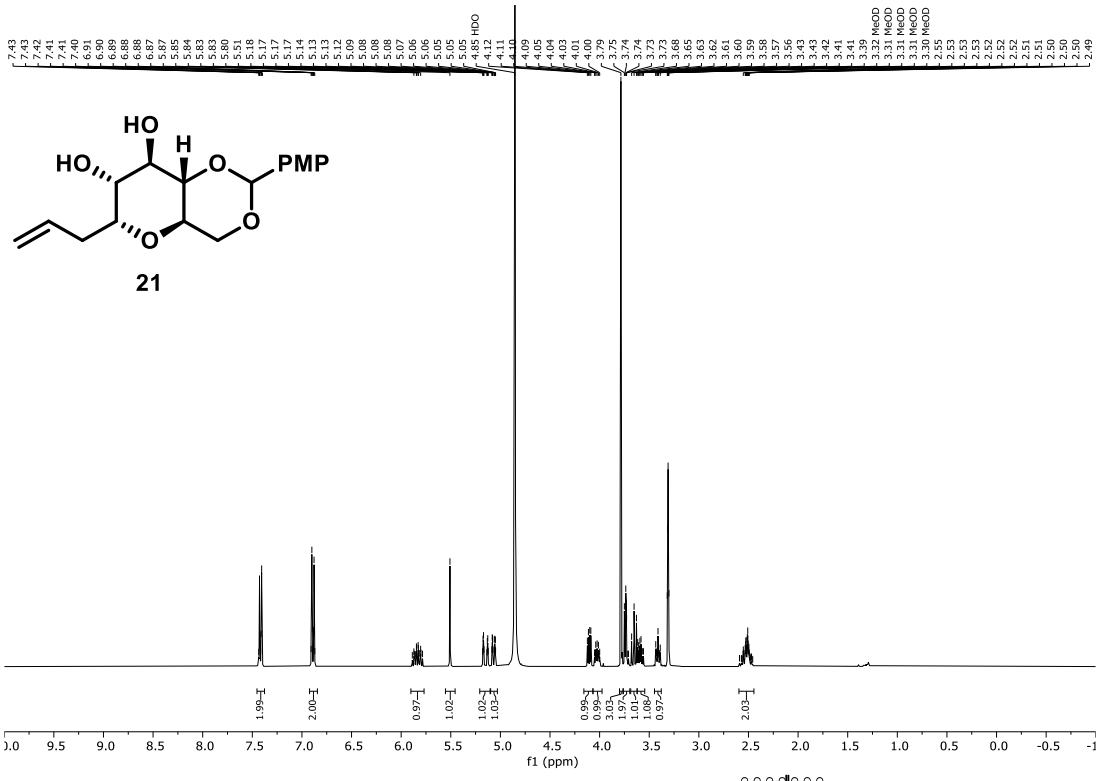

f1 (ppm)

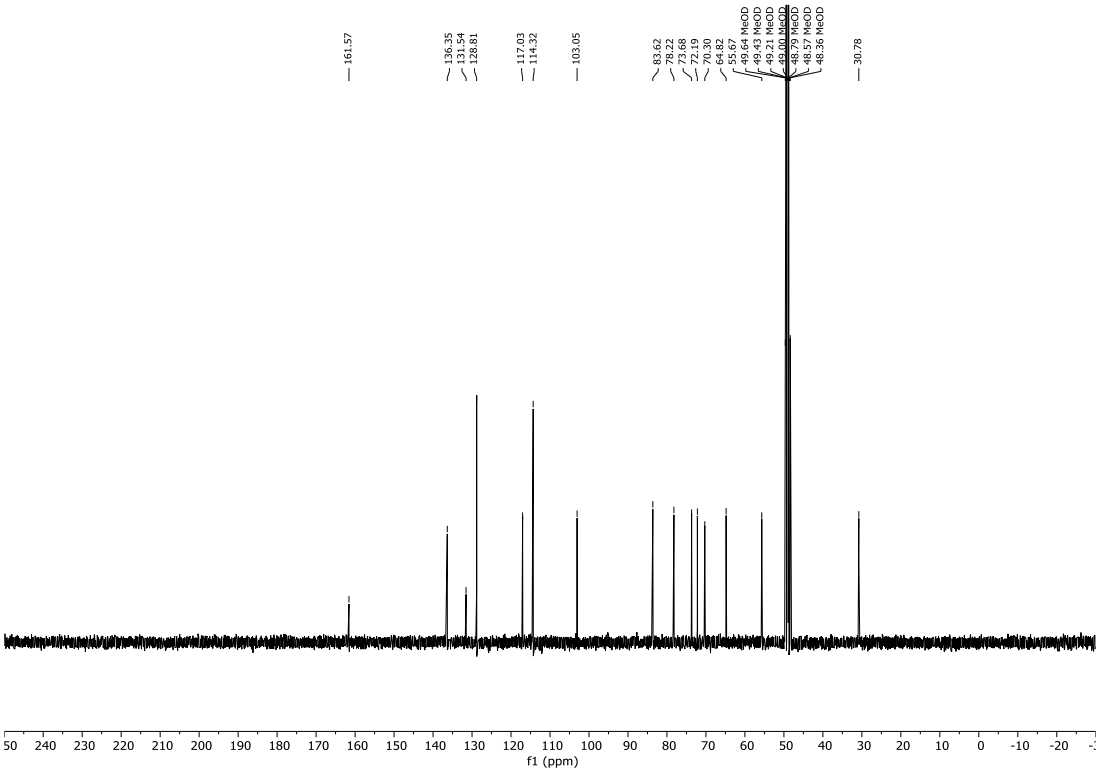

OR
Me
OH
16, R = TBDPS
f1 (ppm)

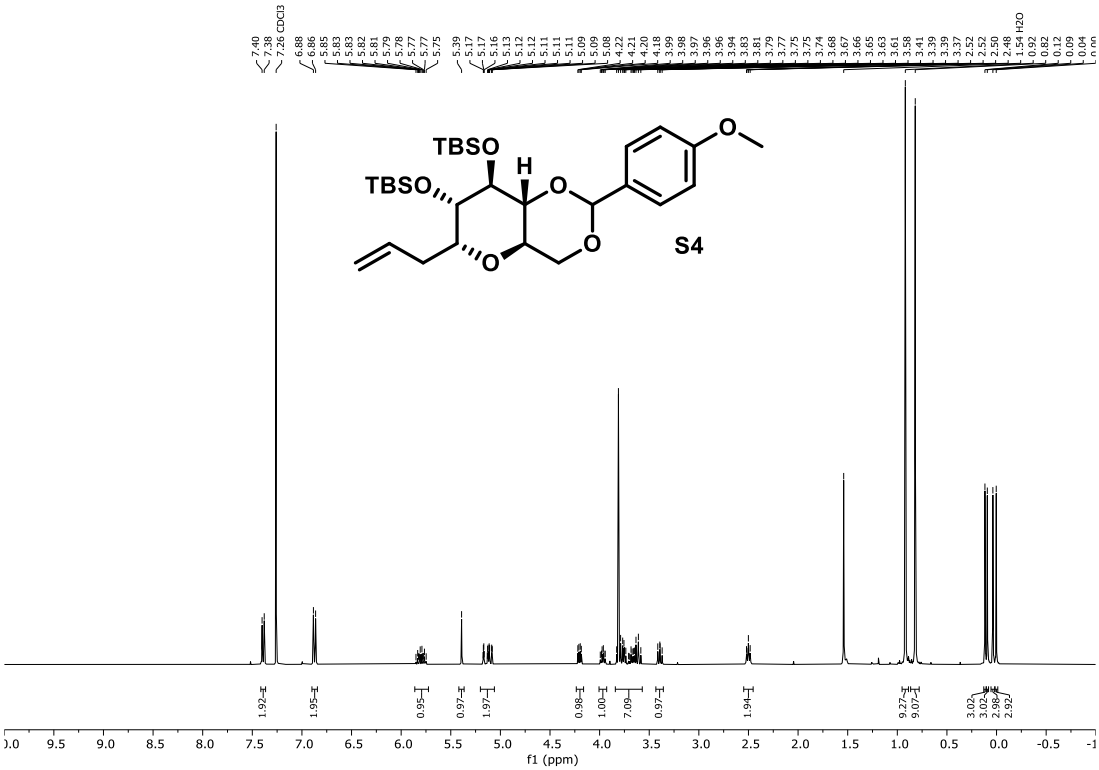


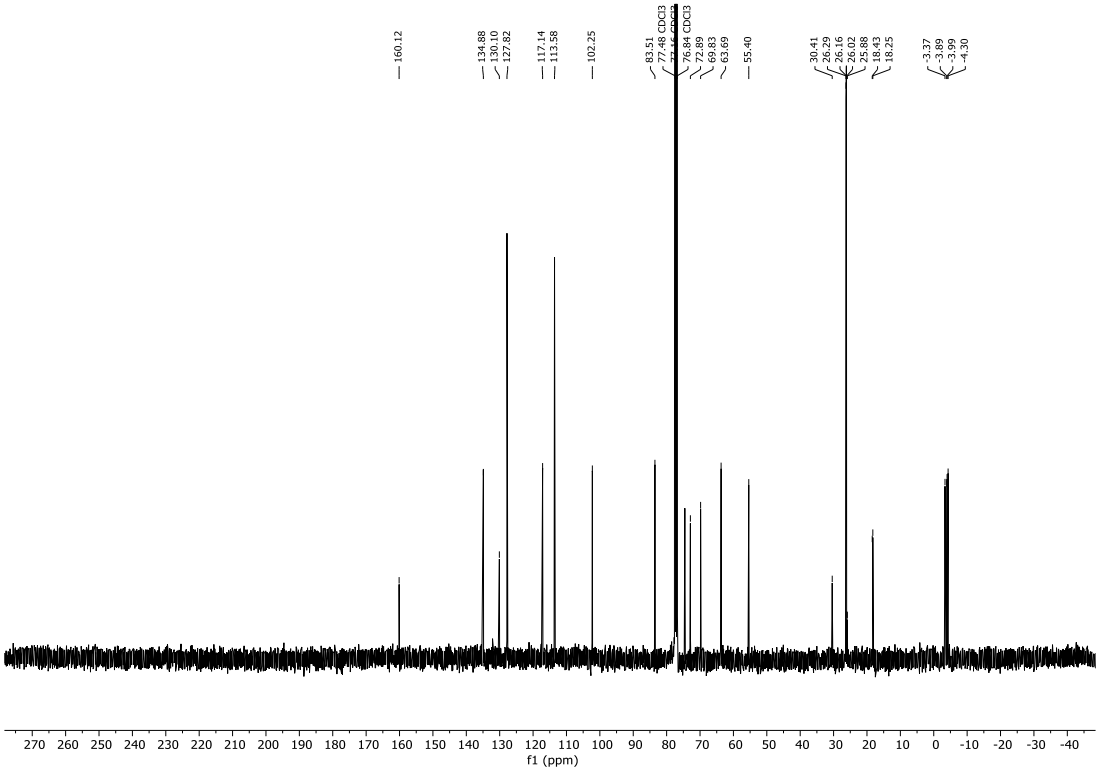
17, R = TBDPS

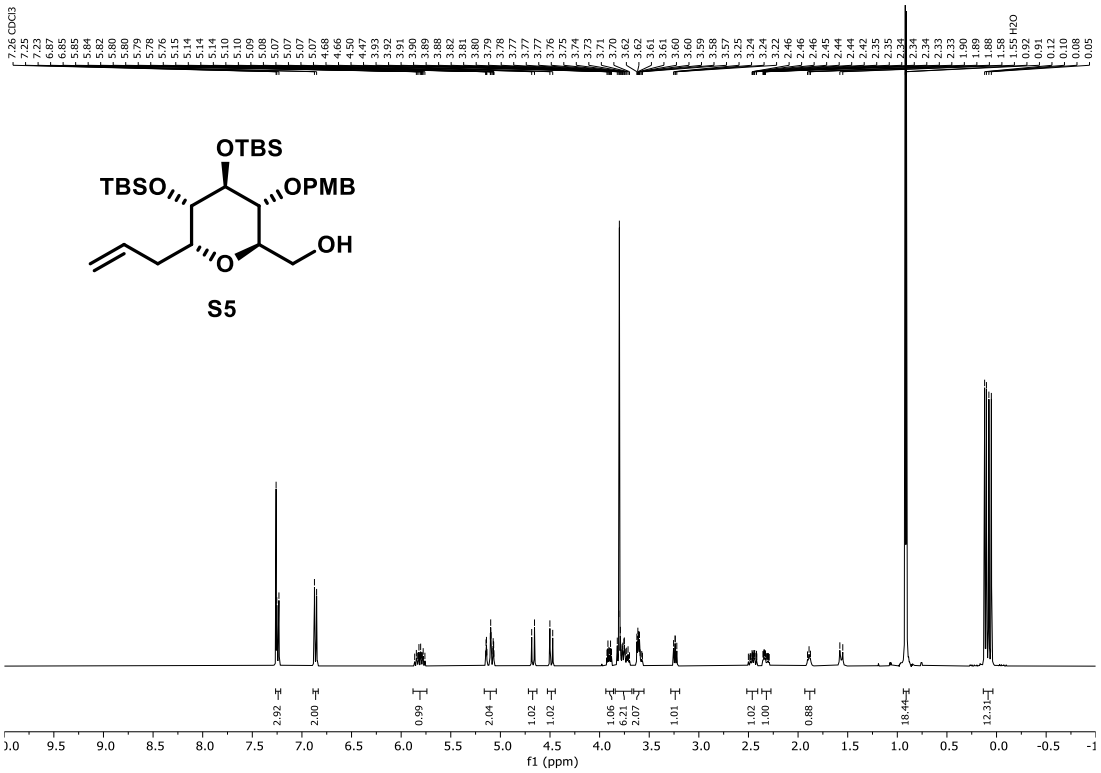


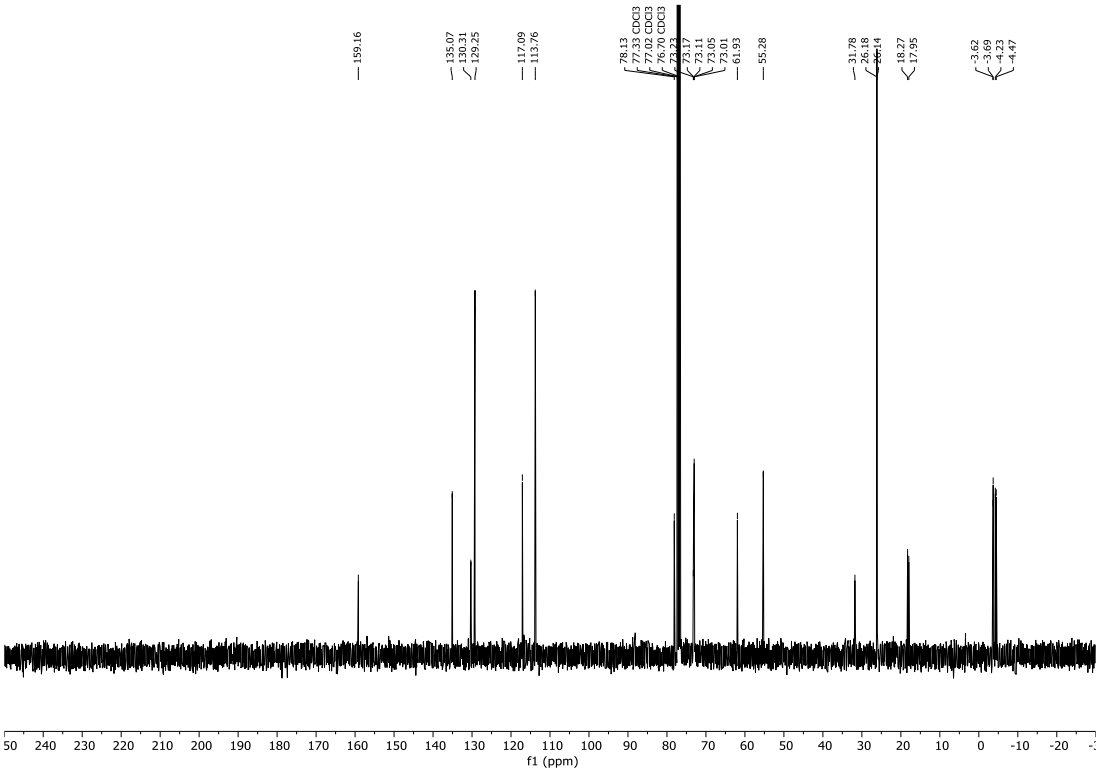

HO
H
HO
O
PMP
O
O
21
f1 (ppm)

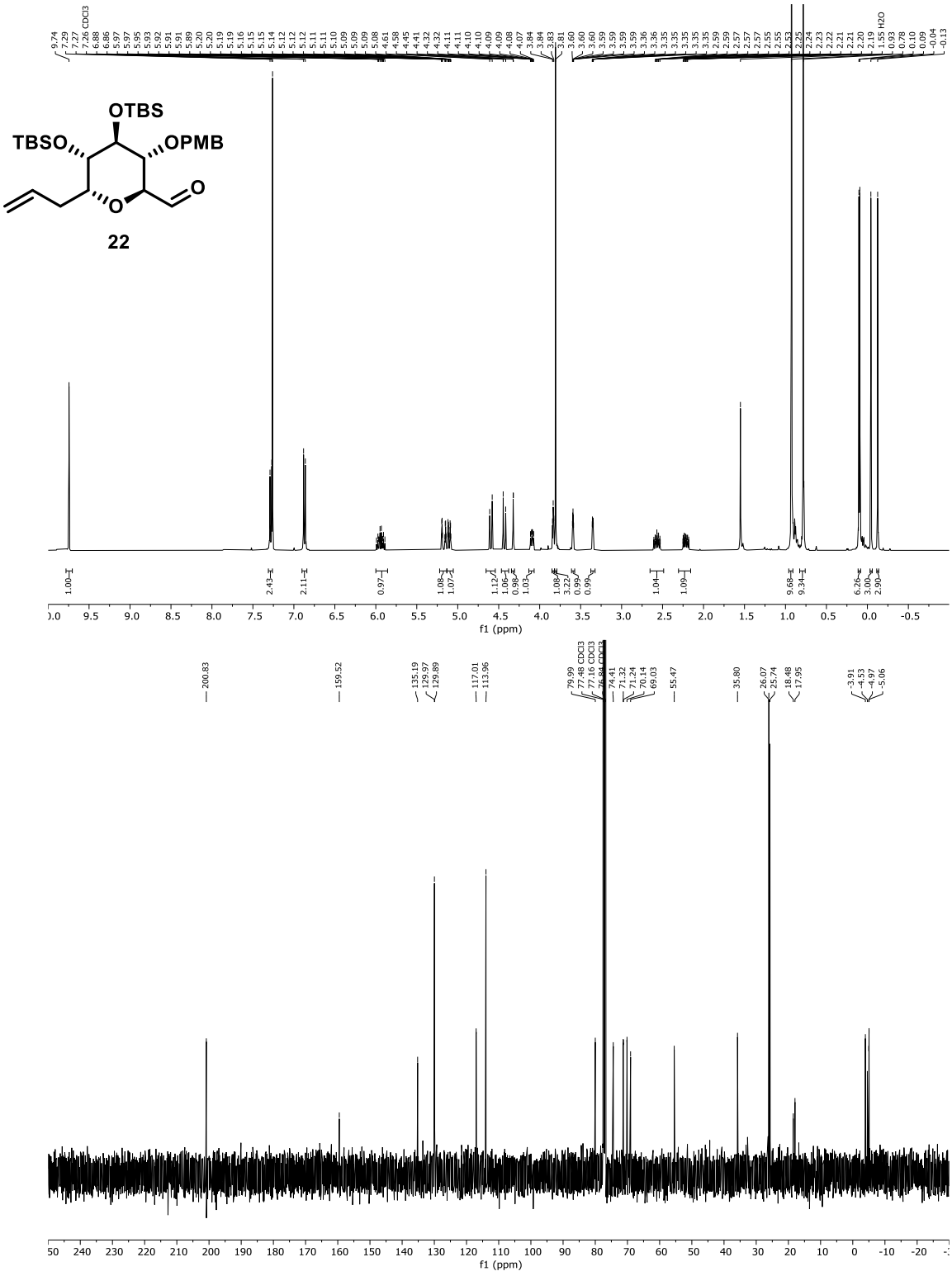

161.57
136.35
131.54
128.81
117.03
114.32
103.05
83.62
78.22
73.68
72.19
70.30
64.82
55.67
49.64 MeOD
49.43 MeOD
49.21 MeOD
49.00 MeOD
48.79 MeOD
48.57 MeOD
48.36 MeOD
30.78
f1 (ppm)

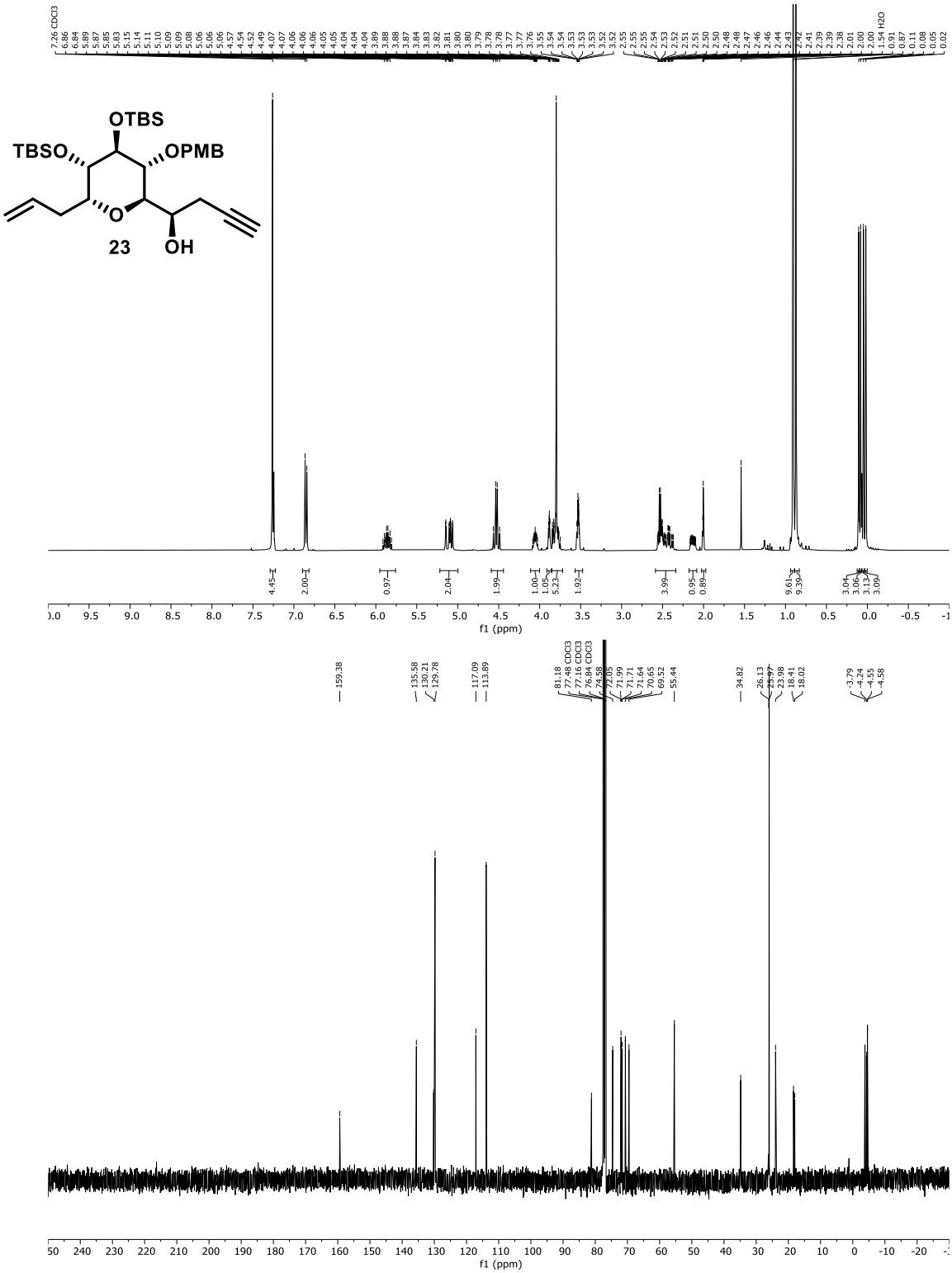

TBSO
TBSO
H
O
O
O
O
S4
f1 (ppm)

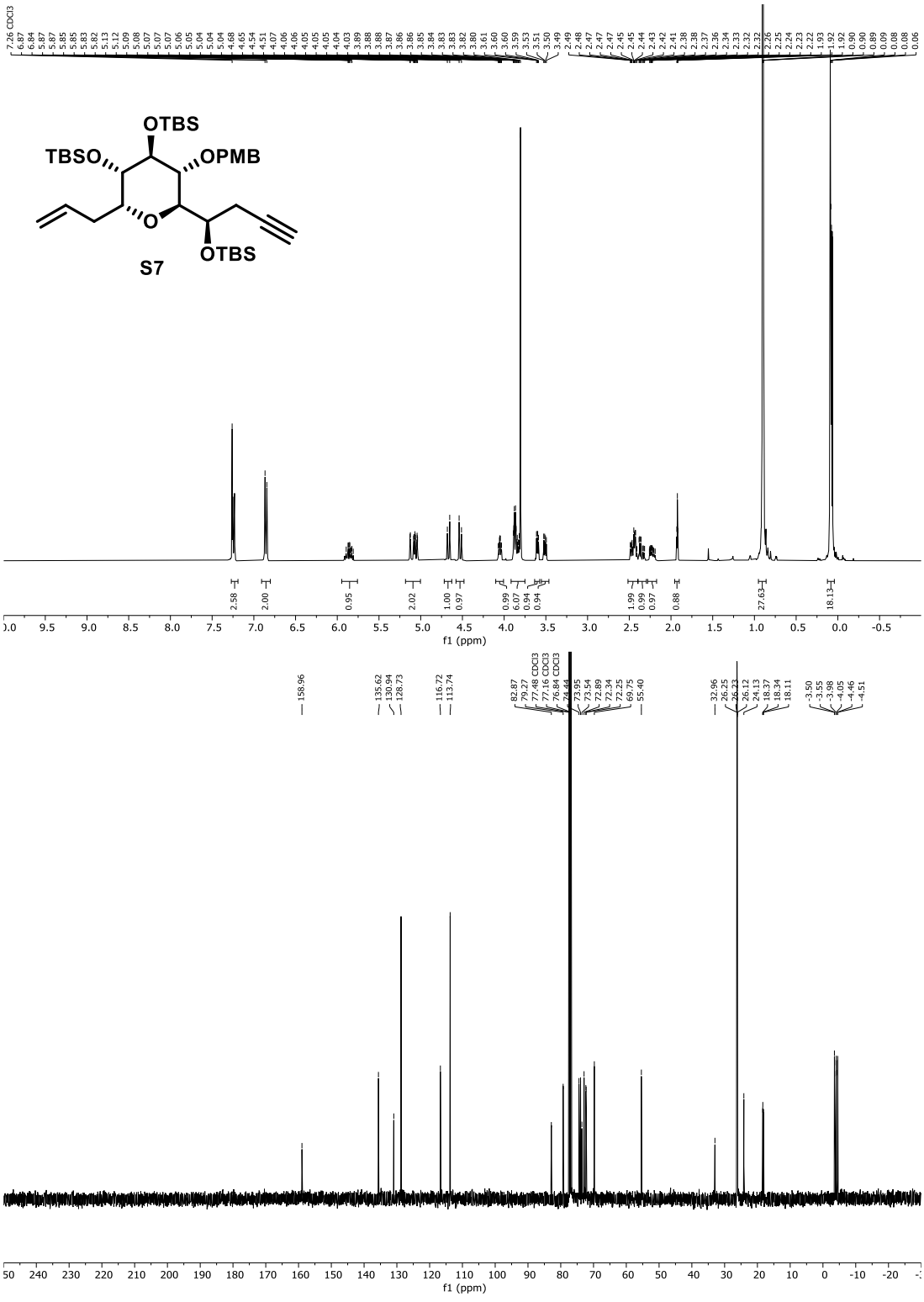

160.12
134.88
130.10
127.82
117.14
113.58
102.25
83.51
77.48 CDCl3
76.84 CDCl3
72.89
69.83
63.69
55.40
30.41
26.29
26.16
26.02
25.88
18.43
18.25
-3.37
-3.89
-3.99
-4.30
f1 (ppm)

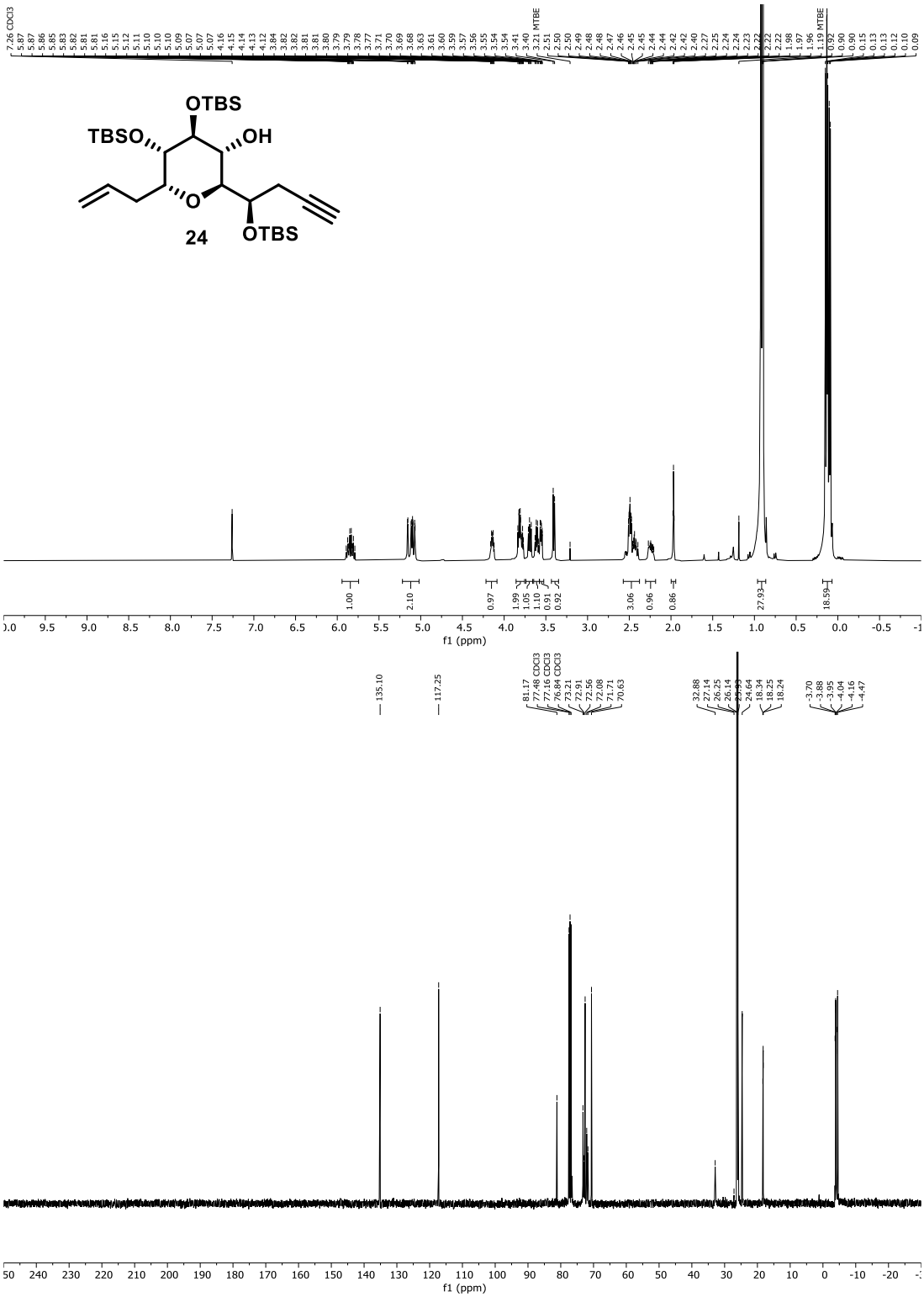

OTBS
TBSO
OPMB
OH
O
S5
f1 (ppm)

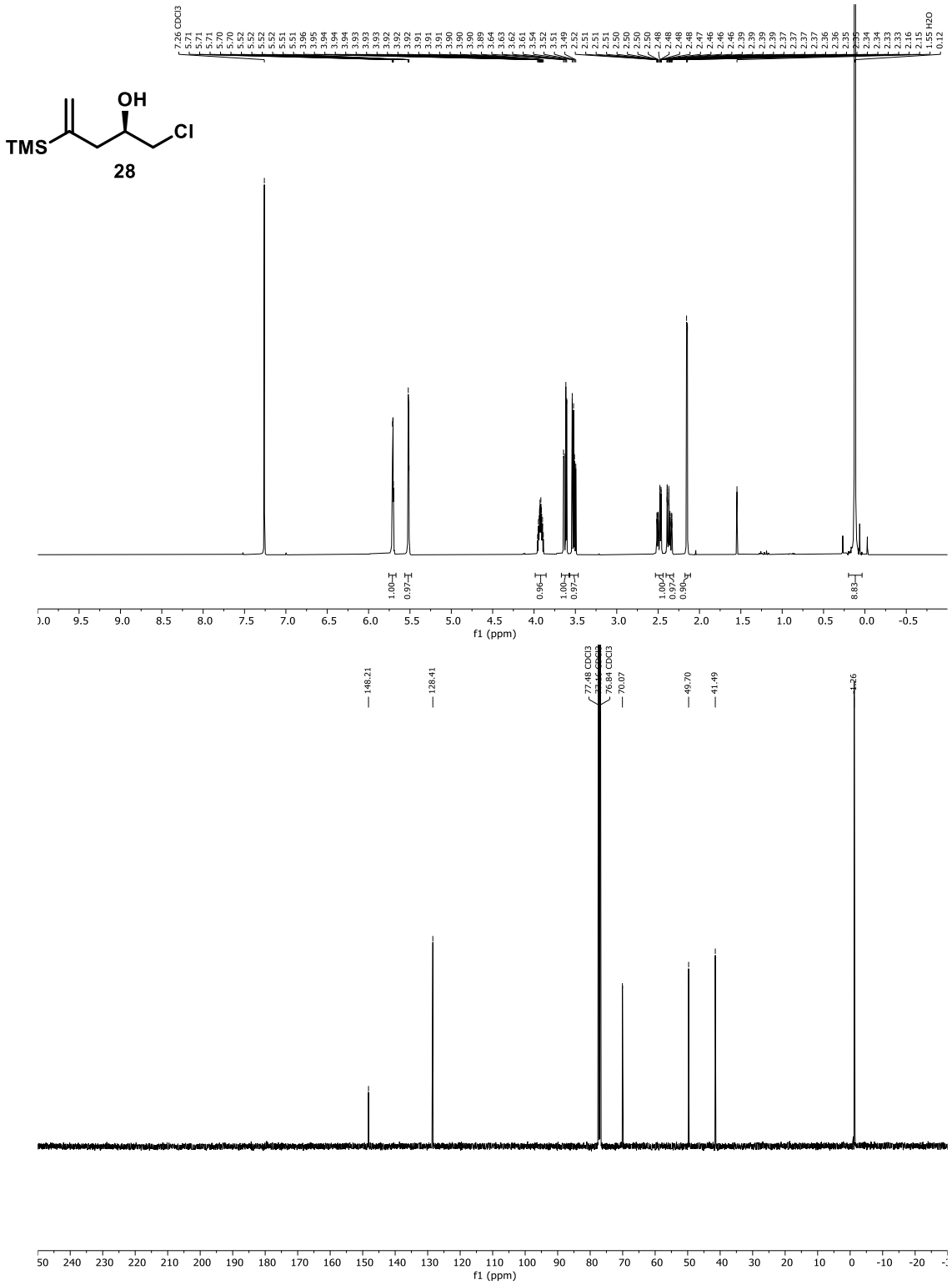

f1 (ppm)

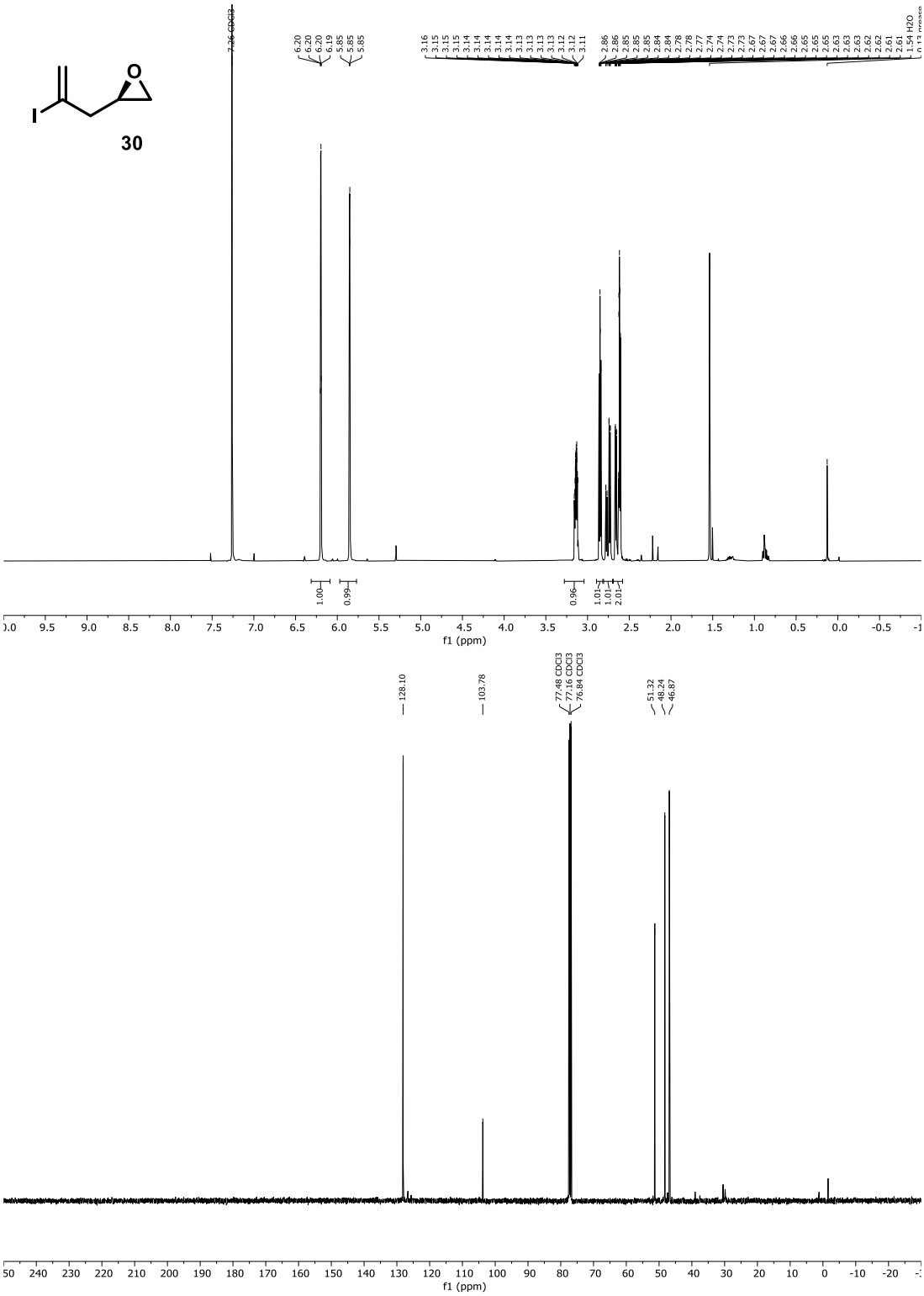

OTBS
TBSO
OPMB
O
O
22
f1 (ppm)
f1 (ppm)

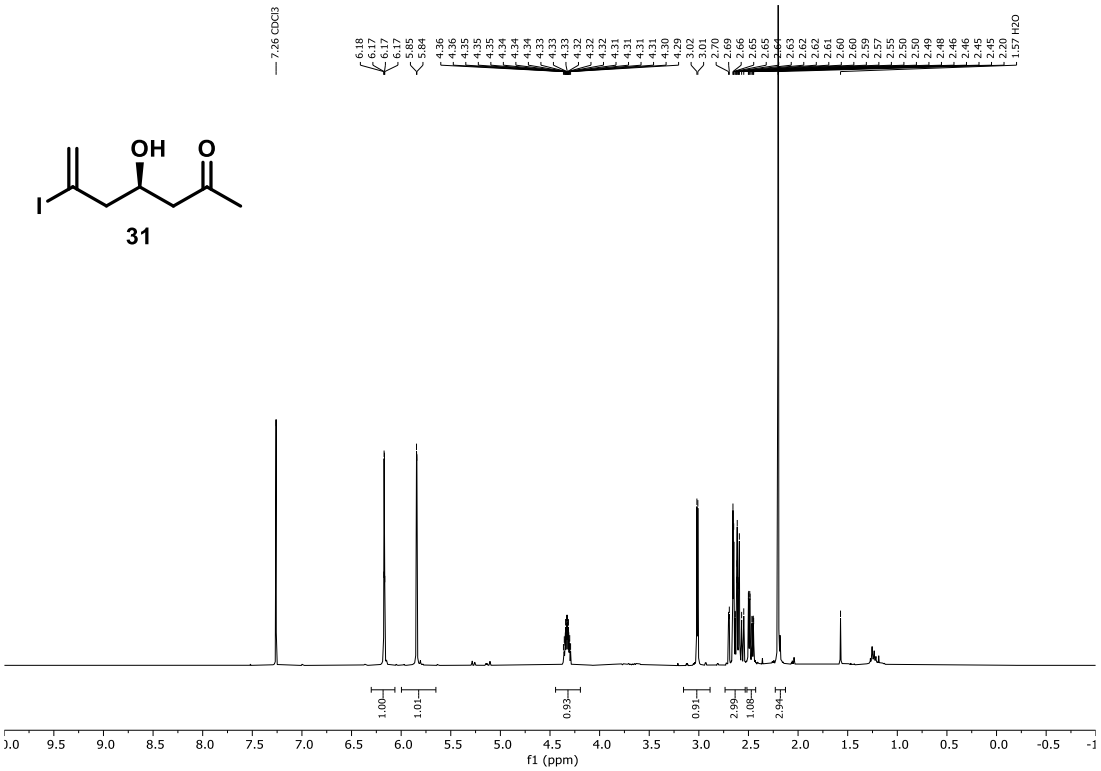

OTBS
TBSO
OPMB
O
23
OH
f1 (ppm)
f1 (ppm)

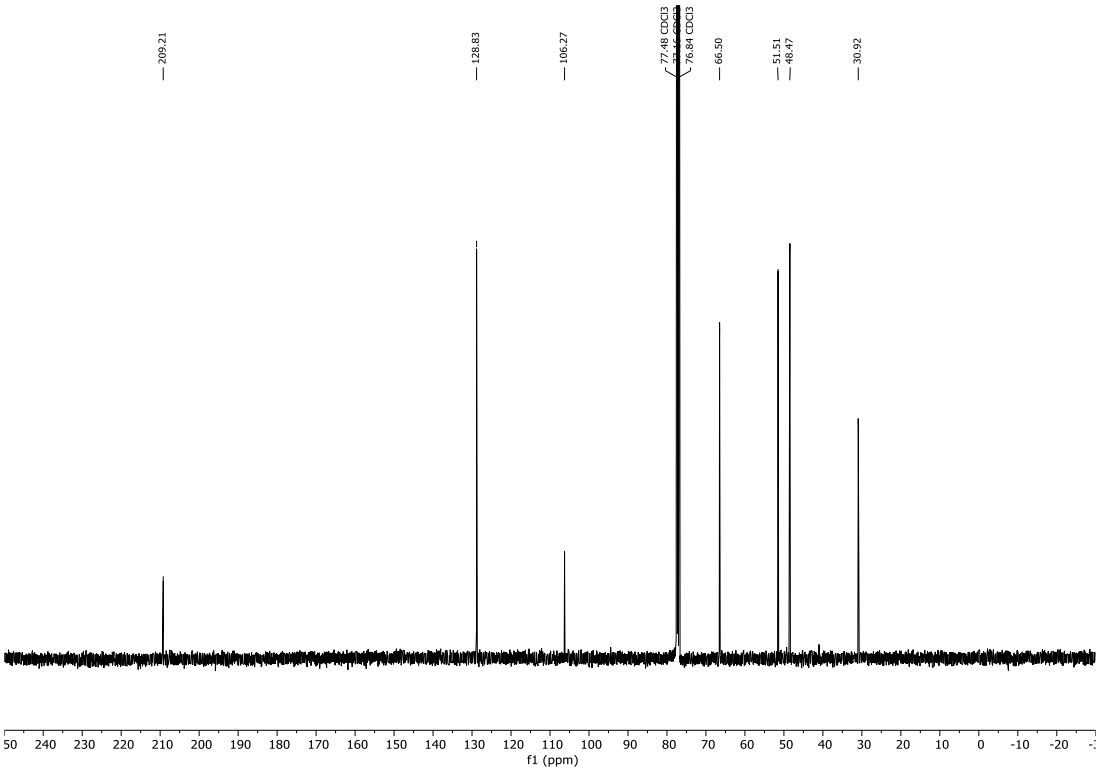

OTBS
TBSO
OPMB
O
OTBS
S7
f1 (ppm)
f1 (ppm)

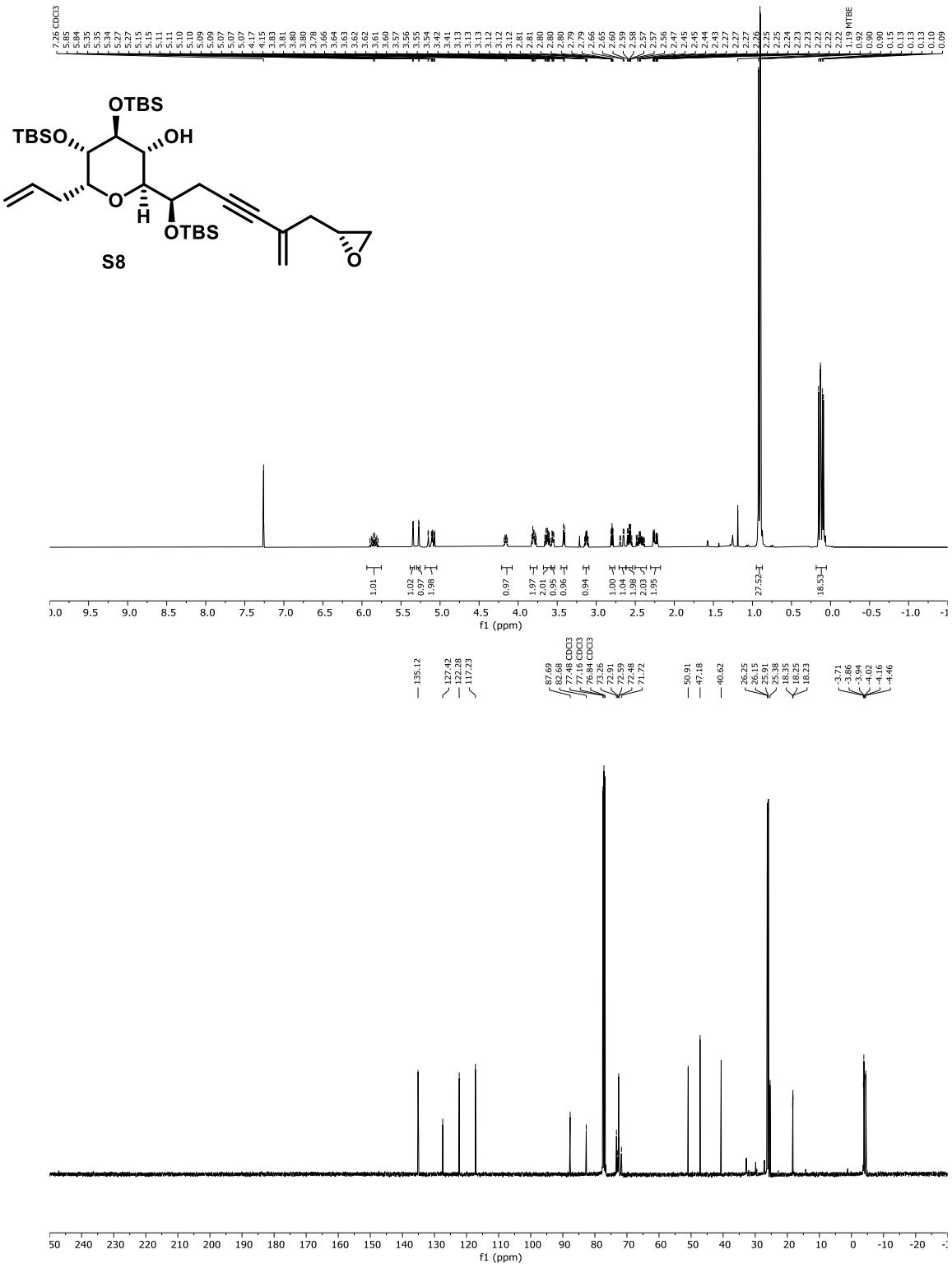

OTBS
TBSO
OH
O
OTBS
24
f1 (ppm)
f1 (ppm)

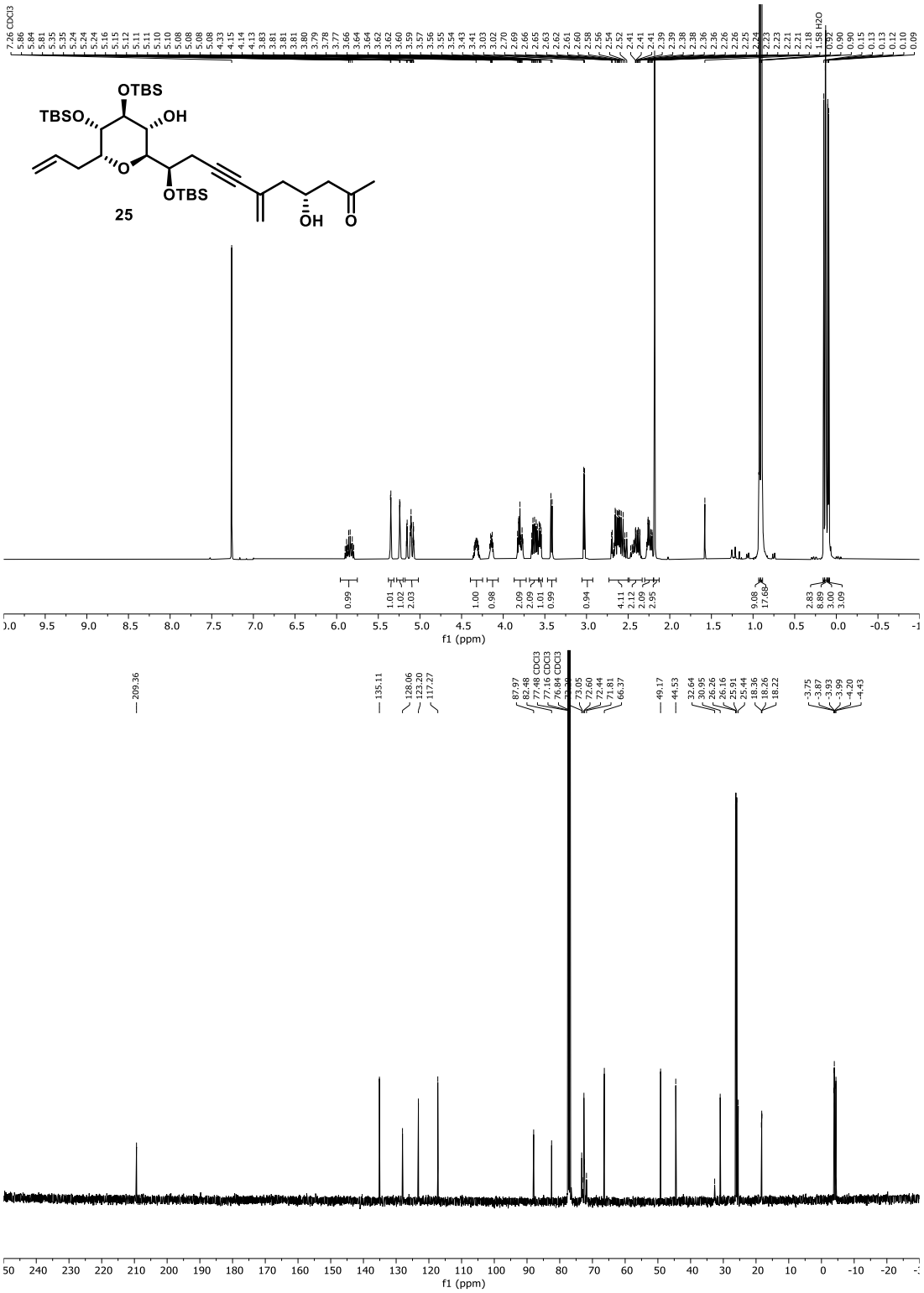

OH
TMS
Cl
28
f1 (ppm)
f1 (ppm)

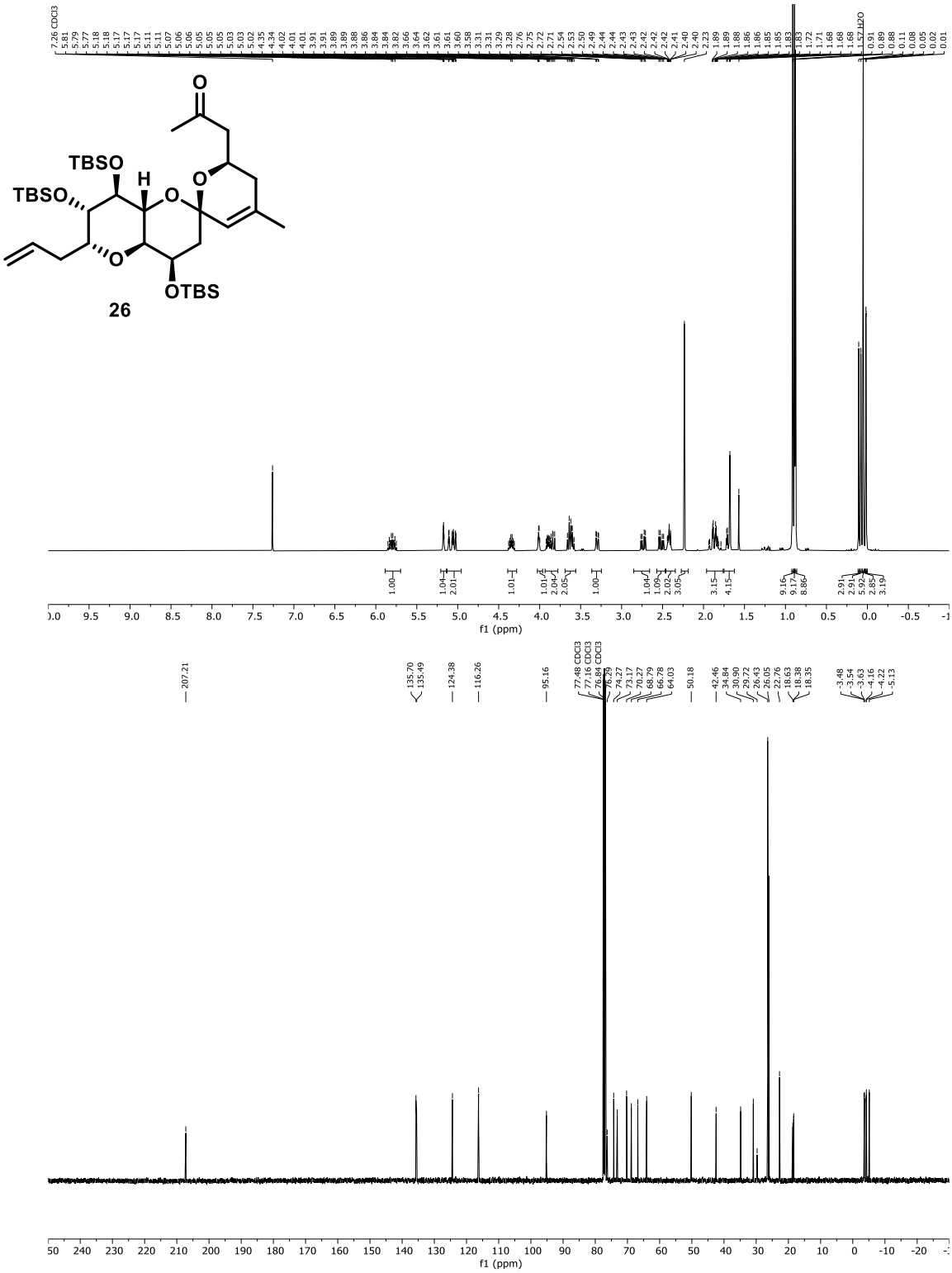

30
7.26 CDCl3
6.20
6.20
6.20
6.19
5.85
5.85
5.85
3.16
3.15
3.15
3.15
3.14
3.14
3.14
3.14
3.14
3.13
3.13
3.13
3.13
3.12
3.12
3.11
2.86
2.86
2.85
2.85
2.85
2.84
2.84
2.78
2.78
2.77
2.74
2.74
2.73
2.73
2.67
2.67
2.67
2.66
2.66
2.65
2.65
2.65
2.63
2.63
2.63
2.62
2.62
2.61
1.54 H2O
1.00
0.99
0.96
1.01
1.01
2.01
f1 (ppm)
128.10
103.78
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
51.32
48.24
46.87
f1 (ppm)

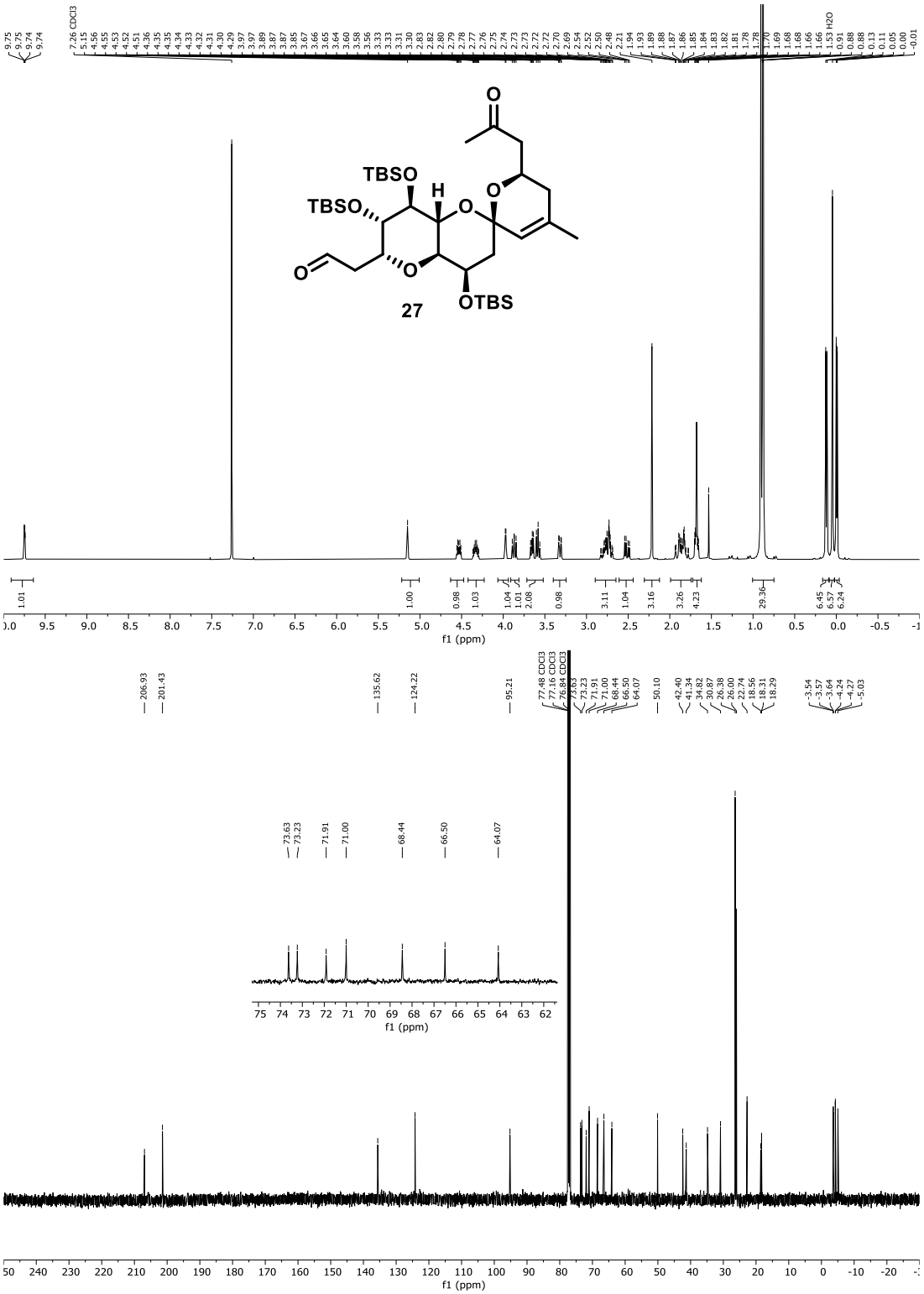

OH
O
I
31
7.26 CDCl3
1.57 H2O
1.00
1.01
0.93
0.91
2.99
1.08
2.94
f1 (ppm)

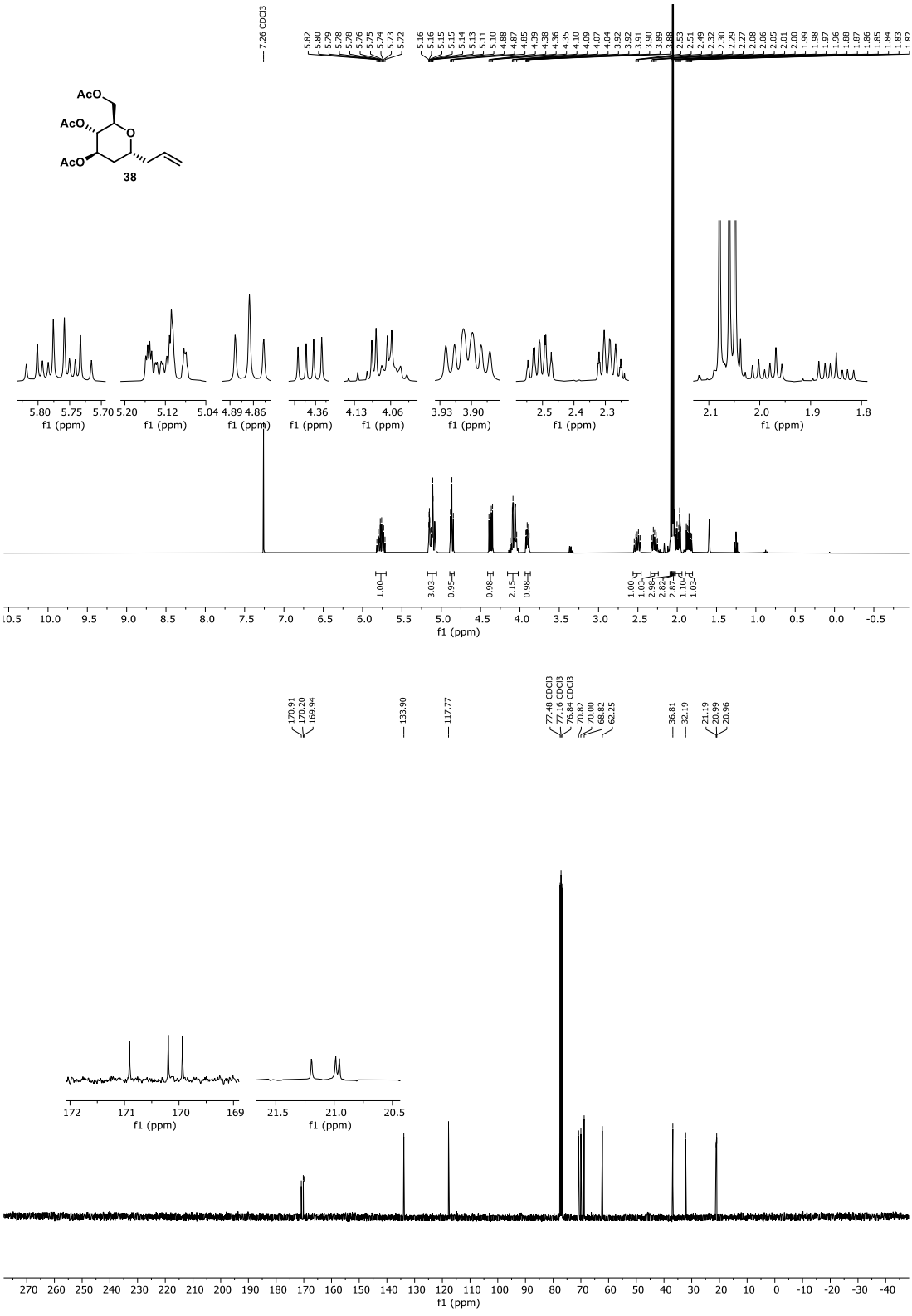

209.21
128.83
106.27
77.48 CDCl3
76.84 CDCl3
66.50
51.51
48.47
30.92
f1 (ppm)

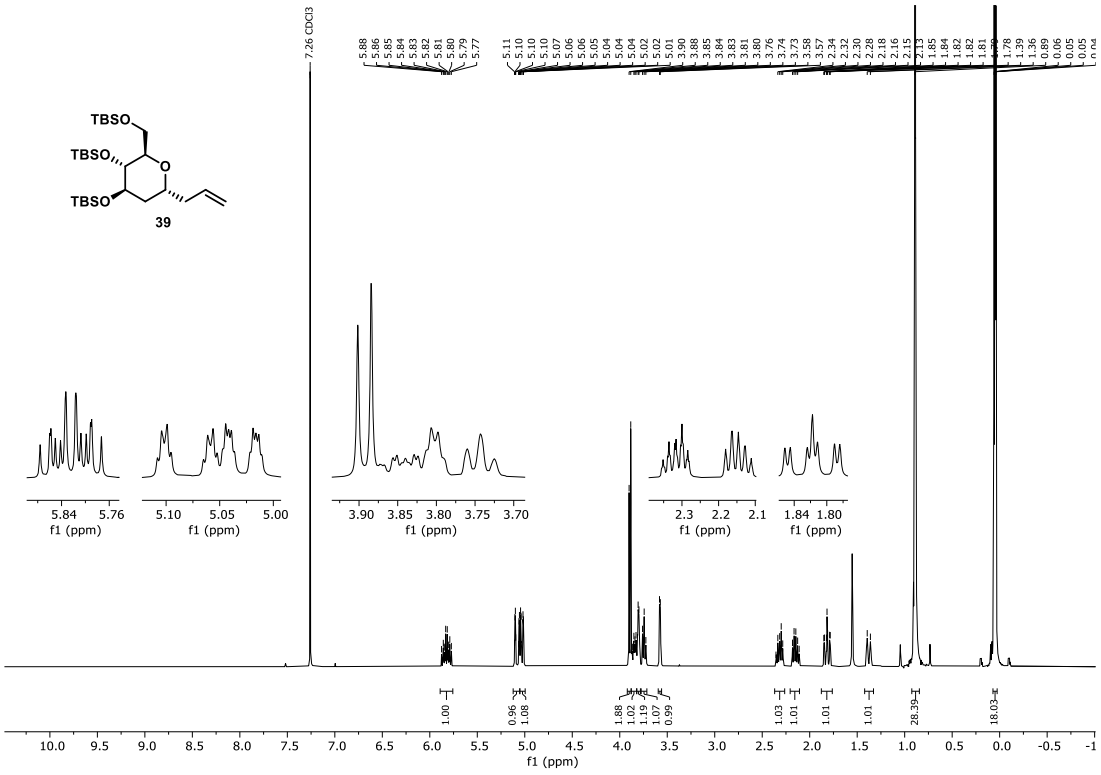

OTBS
TBSO
OH
O
H
OTBS
O
S8
f1 (ppm)
f1 (ppm)

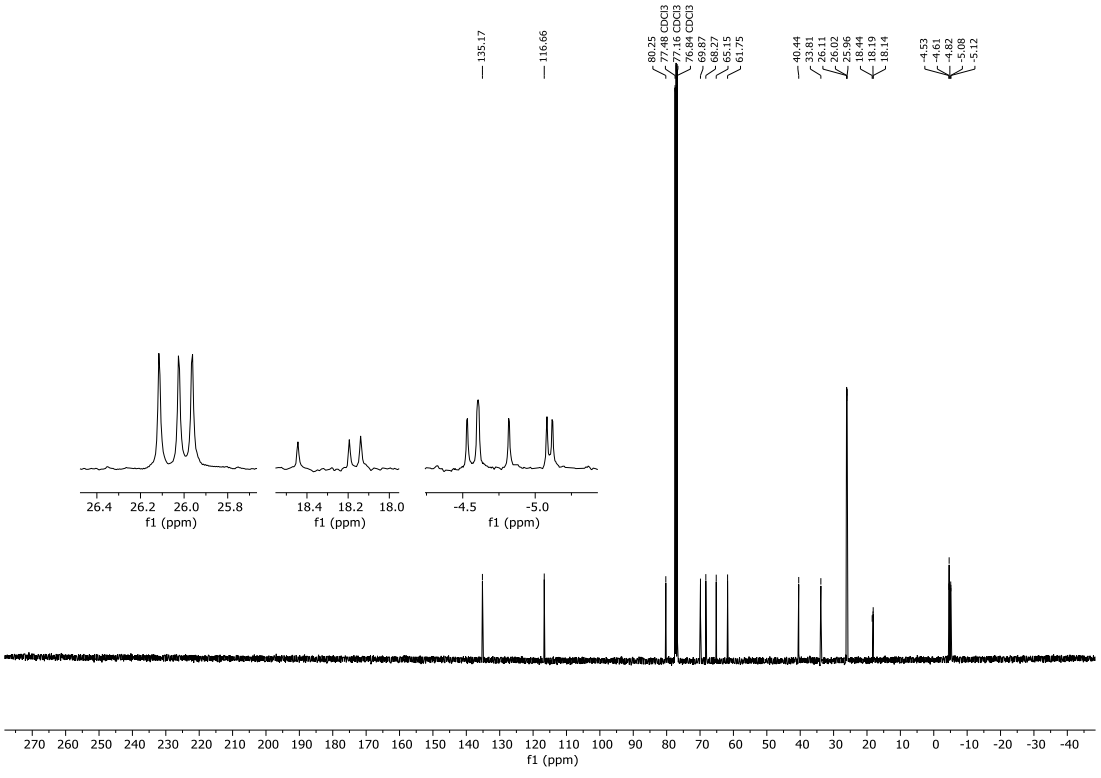

OTBS
TBSO
OH
O
OTBS
25
OH
O
f1 (ppm)
f1 (ppm)

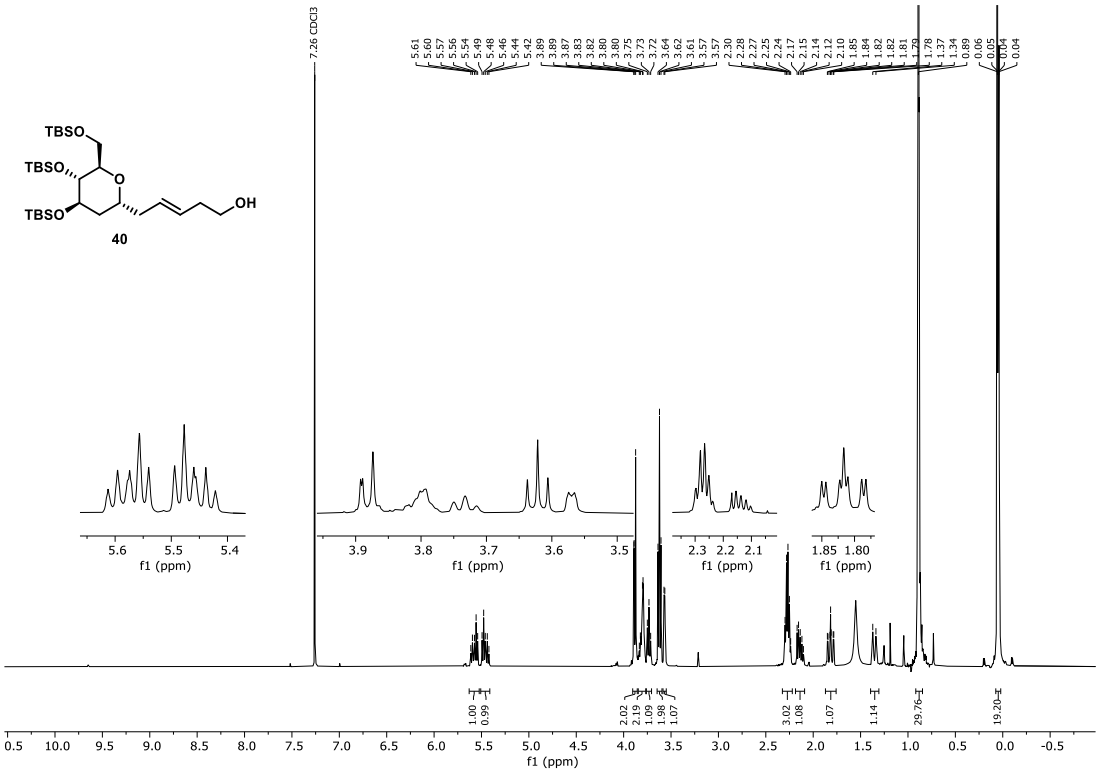

TBSO
TBSO
H
O
O
O
O
OTBS
26
f1 (ppm)
f1 (ppm)

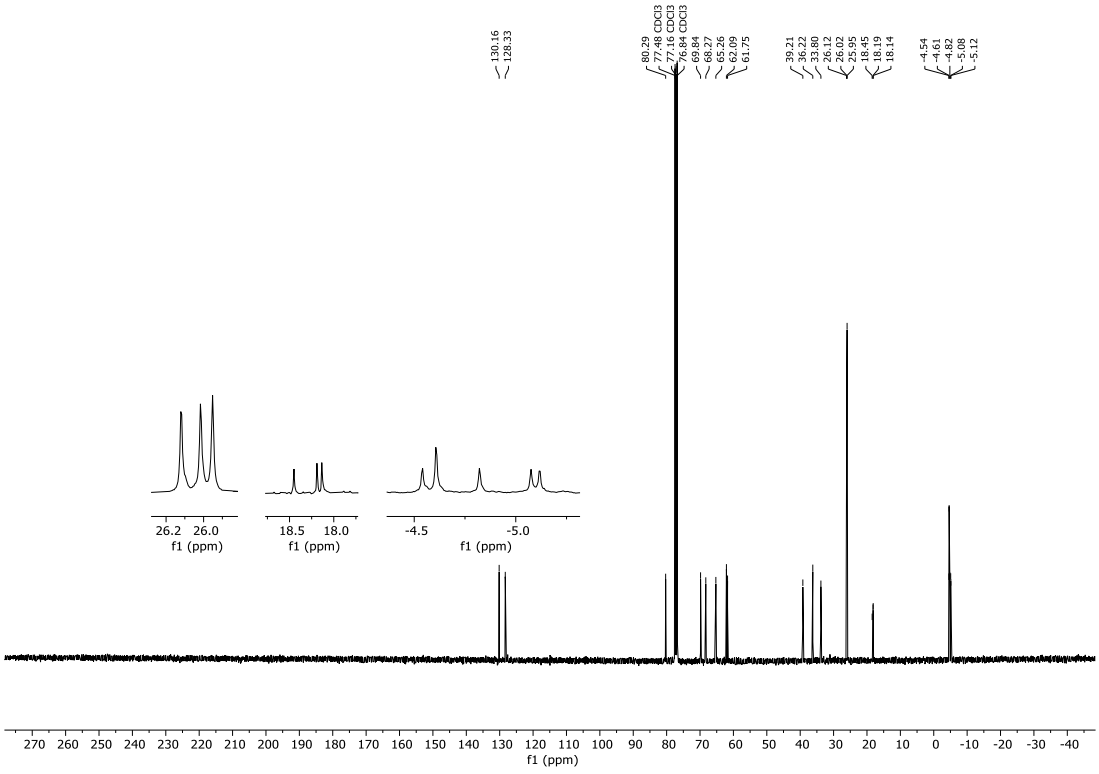

TBSO
TBSO
H
O
O
O
O
O
OTBS
27
f1 (ppm)
f1 (ppm)
f1 (ppm)

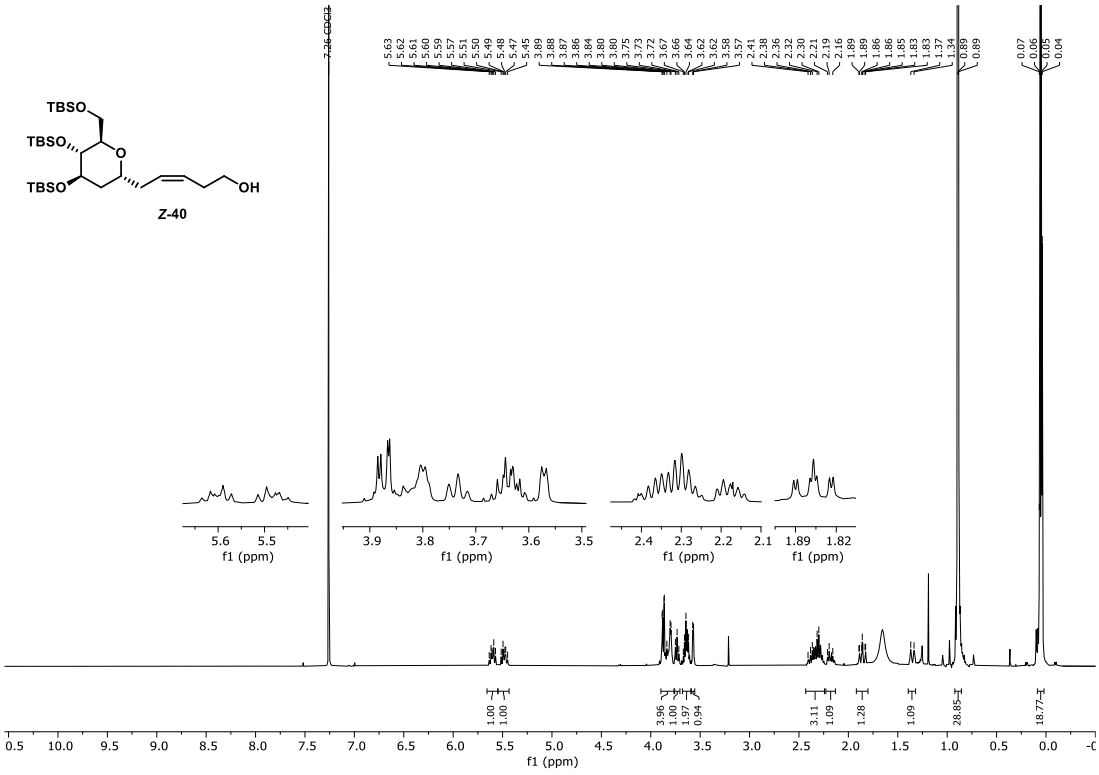

AcO
AcO
AcO
O
38
7.26 CDCl3
f1 (ppm)
170.91
170.20
169.94
133.90
117.77
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
70.82
70.00
68.82
62.25
36.81
32.19
21.19
20.99
20.96

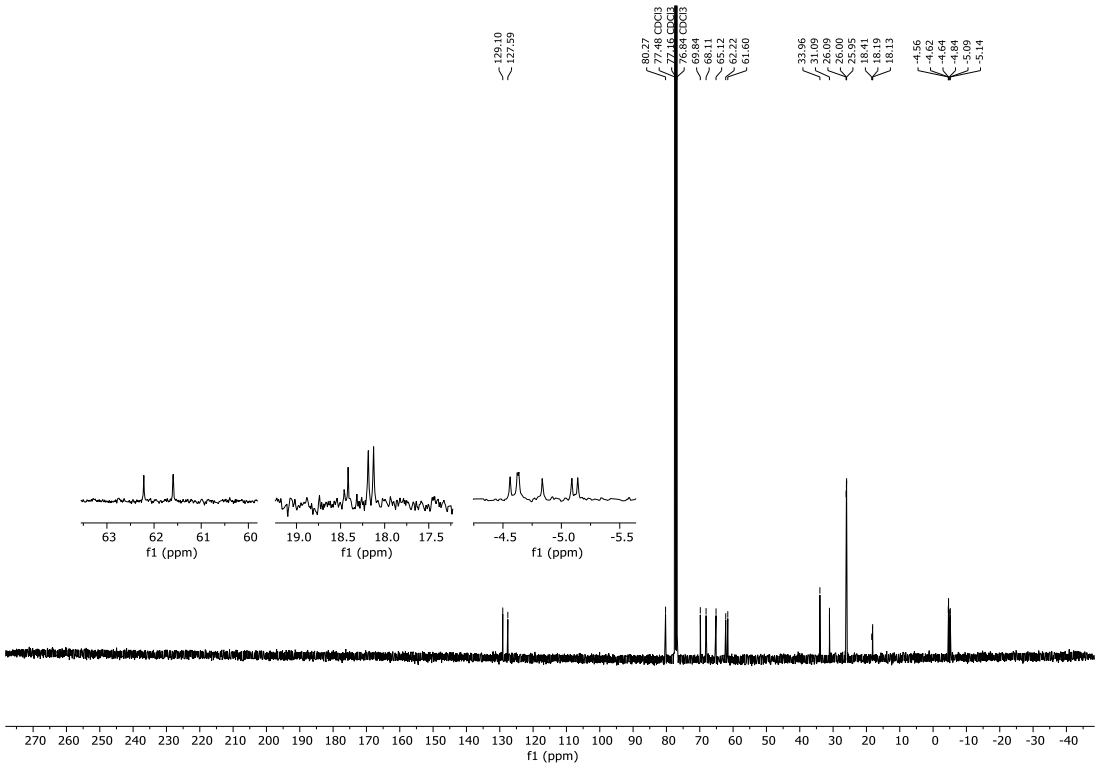

TBSO
TBSO
TBSO
O
39
7.26 CDCl3
f1 (ppm)

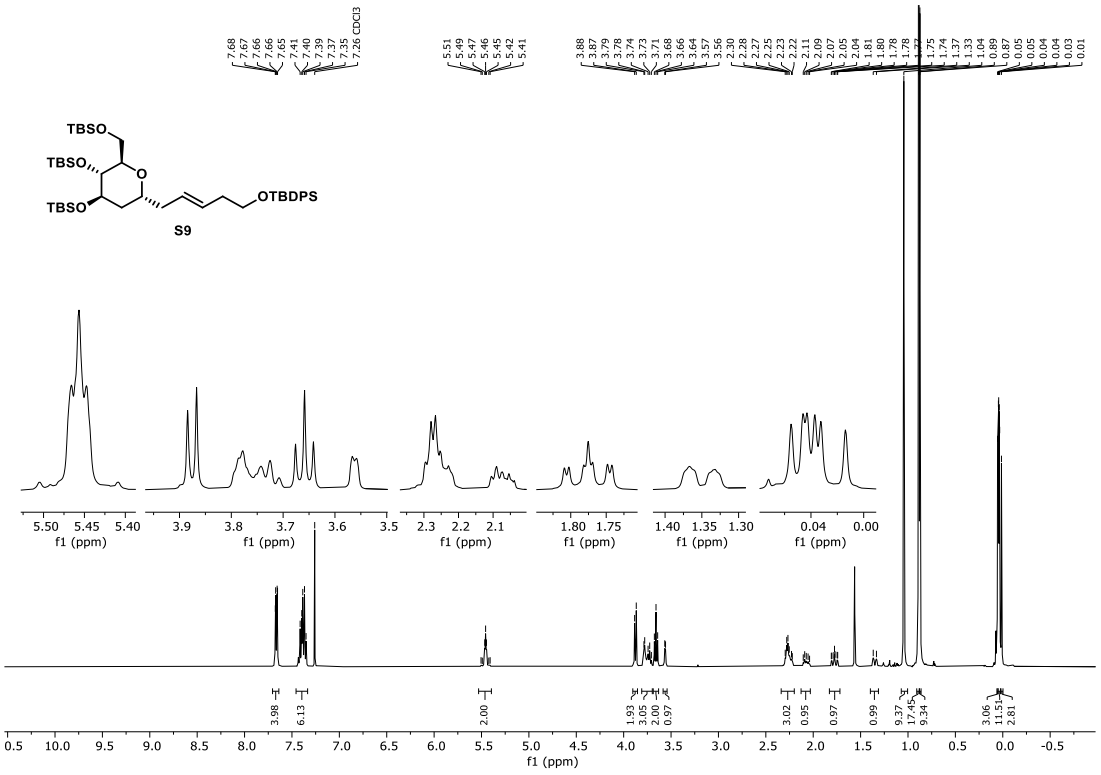

135.17
116.66
80.25
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
69.87
68.27
65.15
61.75
40.44
33.81
26.11
26.02
25.96
18.44
18.19
18.14
-4.53
-4.61
-4.82
-5.08
-5.12
f1 (ppm)

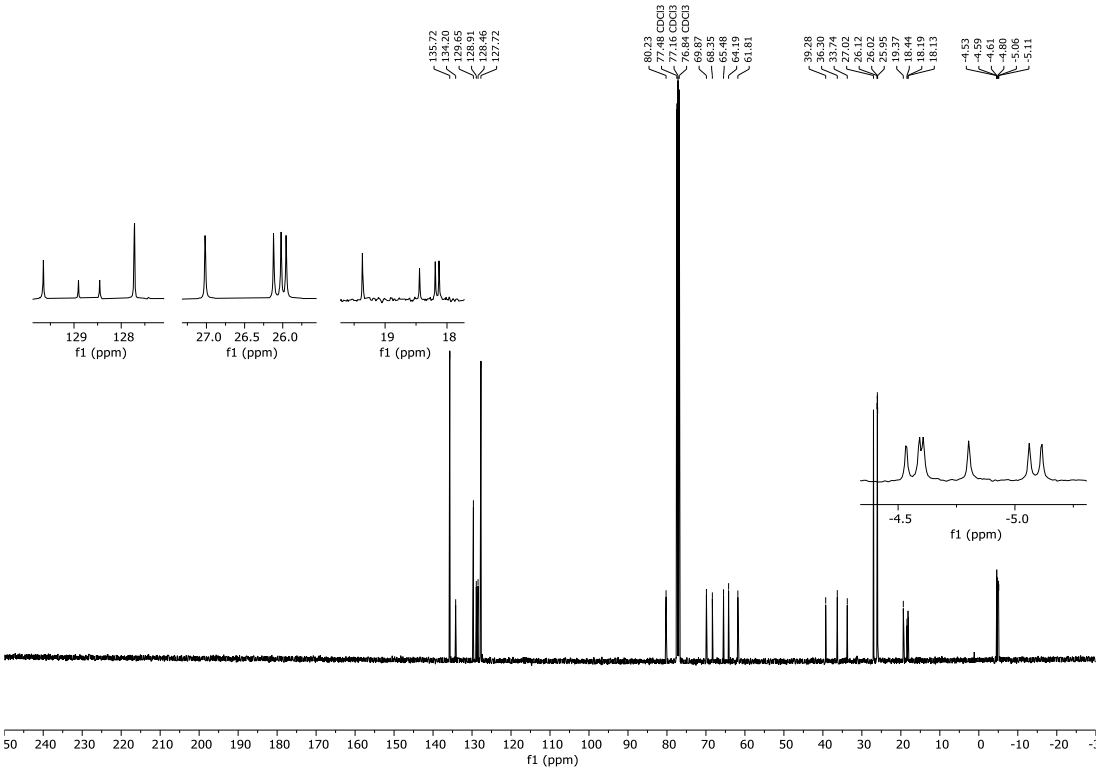

TBSO
TBSO
TBSO
O
OH
40
7.26 CDCl3
f1 (ppm)

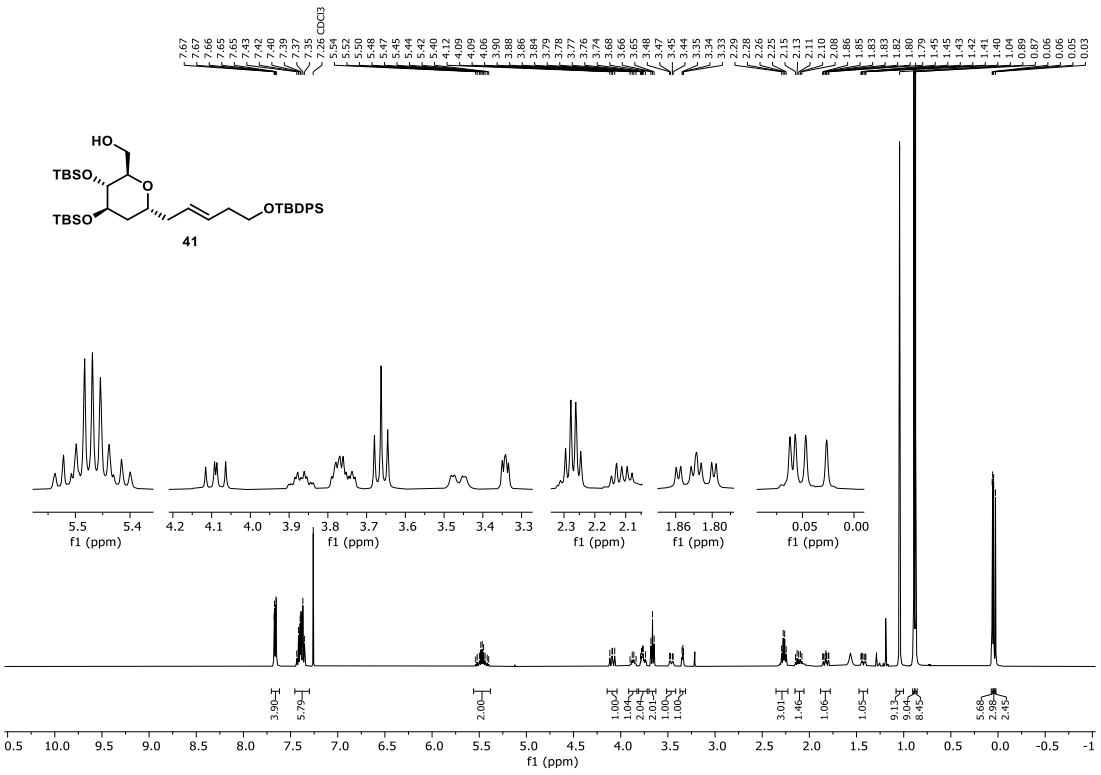

130.16
128.33
80.29
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
69.84
65.27
65.26
62.09
61.75
39.21
36.22
33.80
26.12
26.02
25.95
18.45
18.19
16.14
-4.54
-4.61
-4.82
-5.08
-5.12
f1 (ppm)

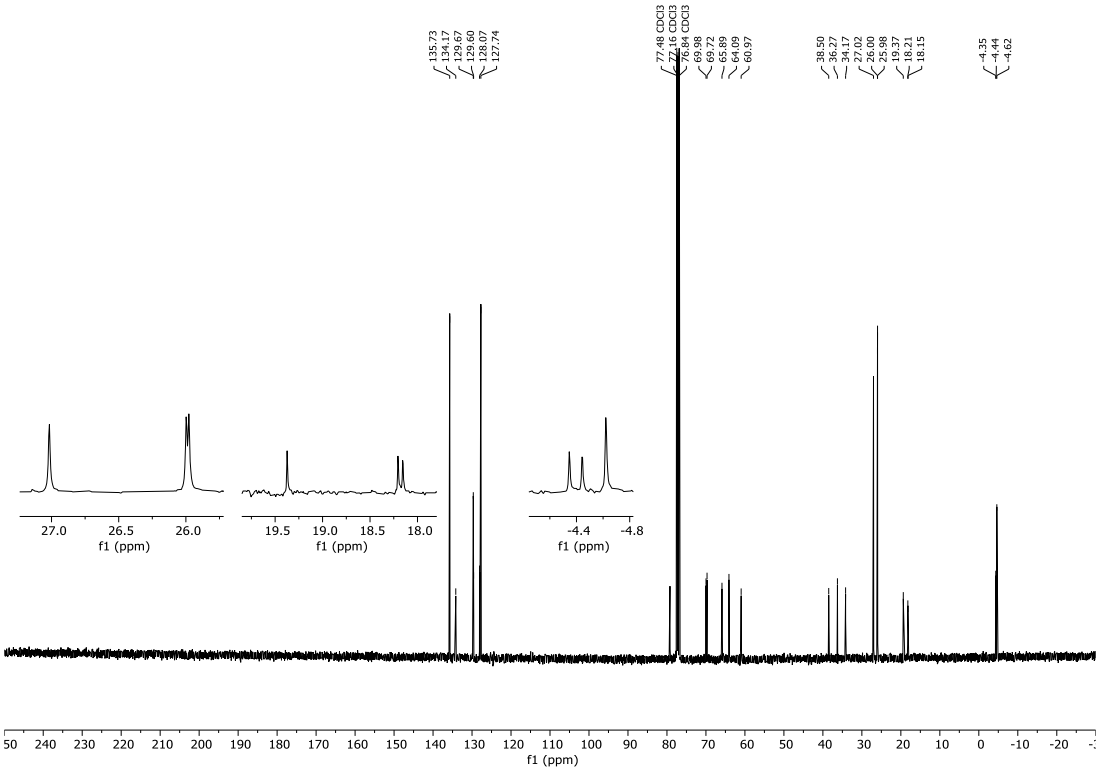

TBSO
TBSO
TBSO
O
OH
Z-40
f1 (ppm)

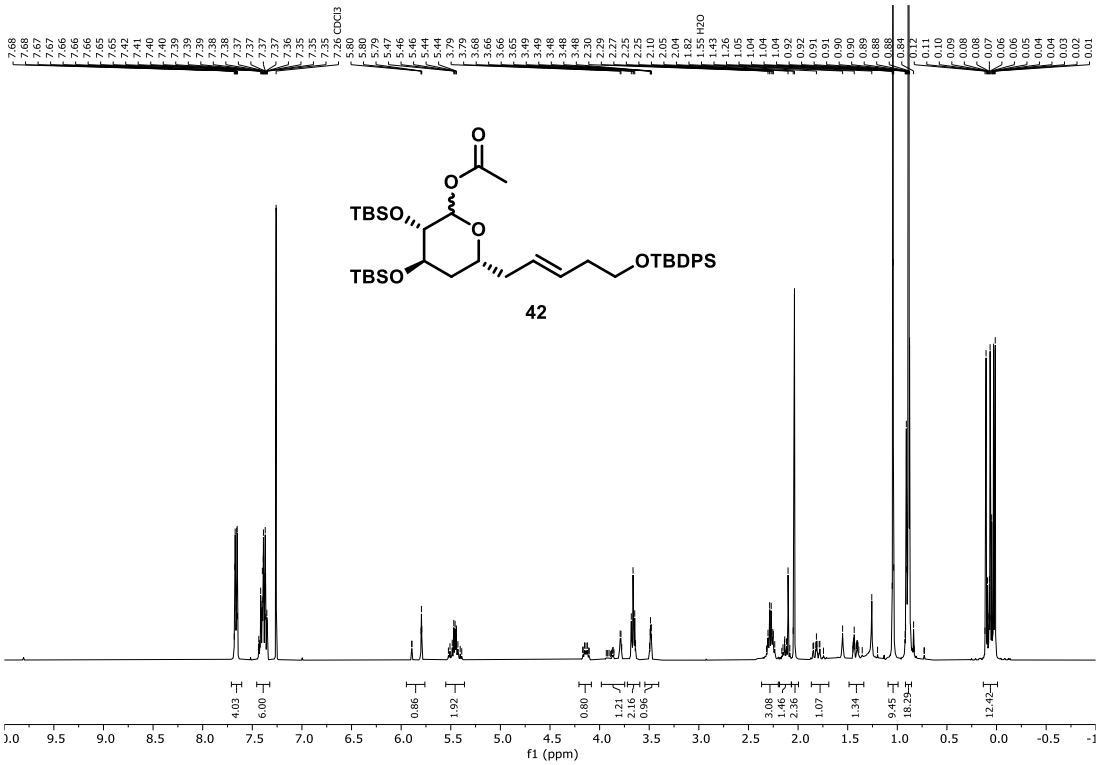

f1 (ppm)

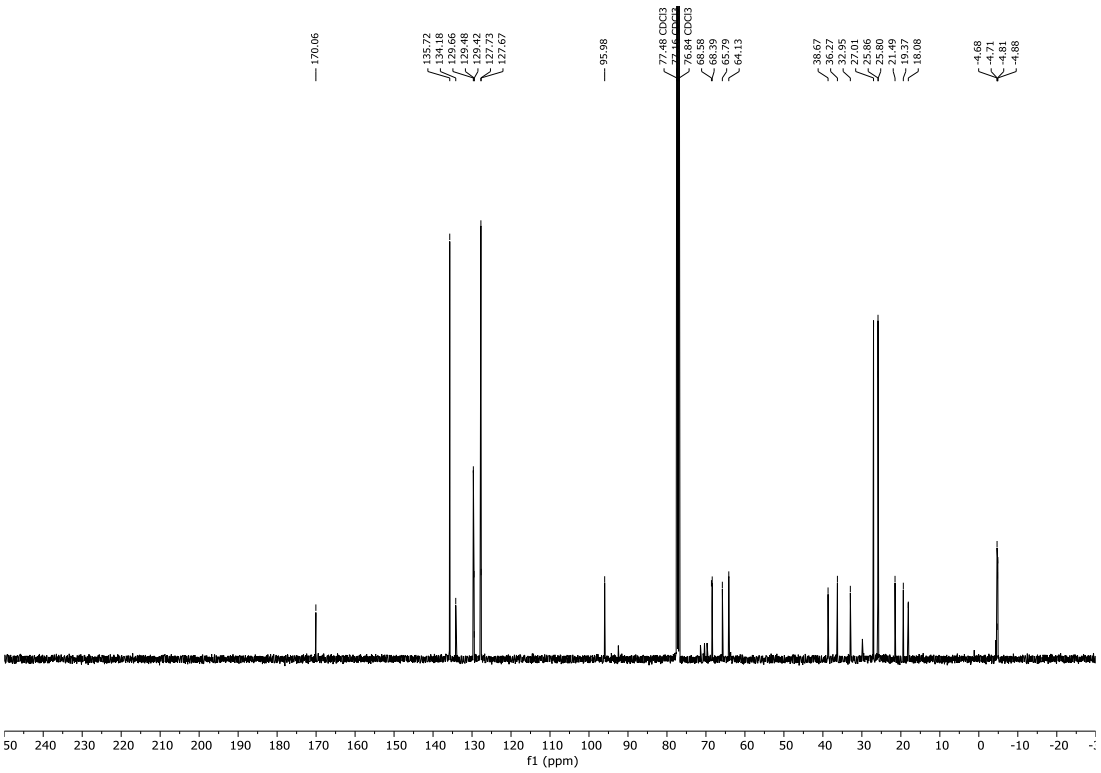

TBSO
TBSO
TBSO
O
OTBDPS
S9
f1 (ppm)

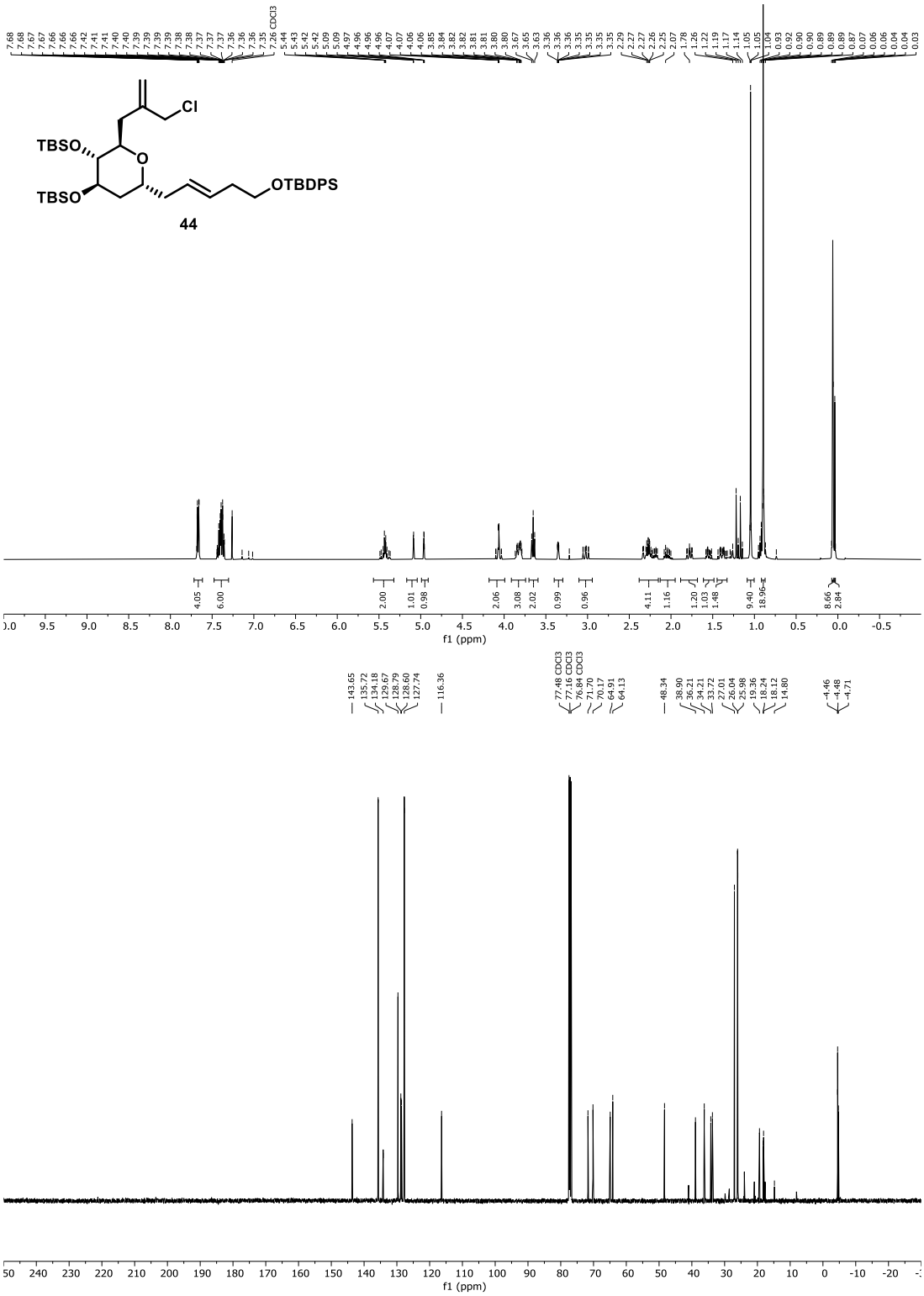

f1 (ppm)

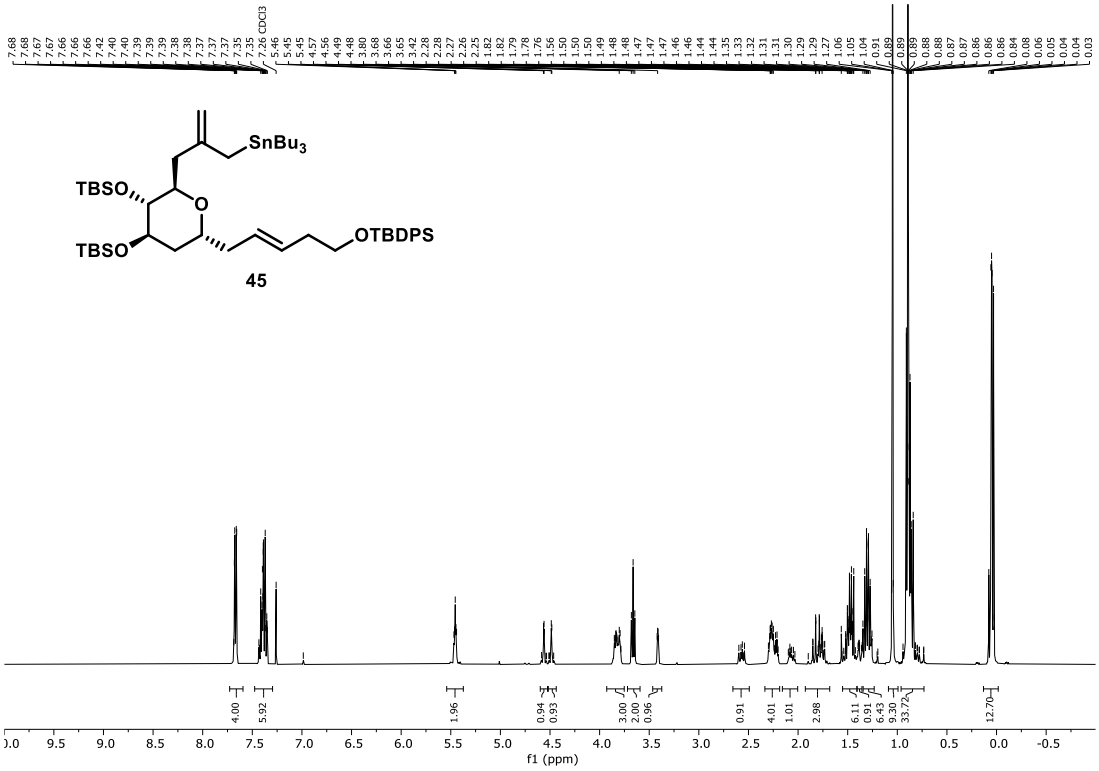

HO
TBSO
TBSO
O
OTBDPS
41
f1 (ppm)

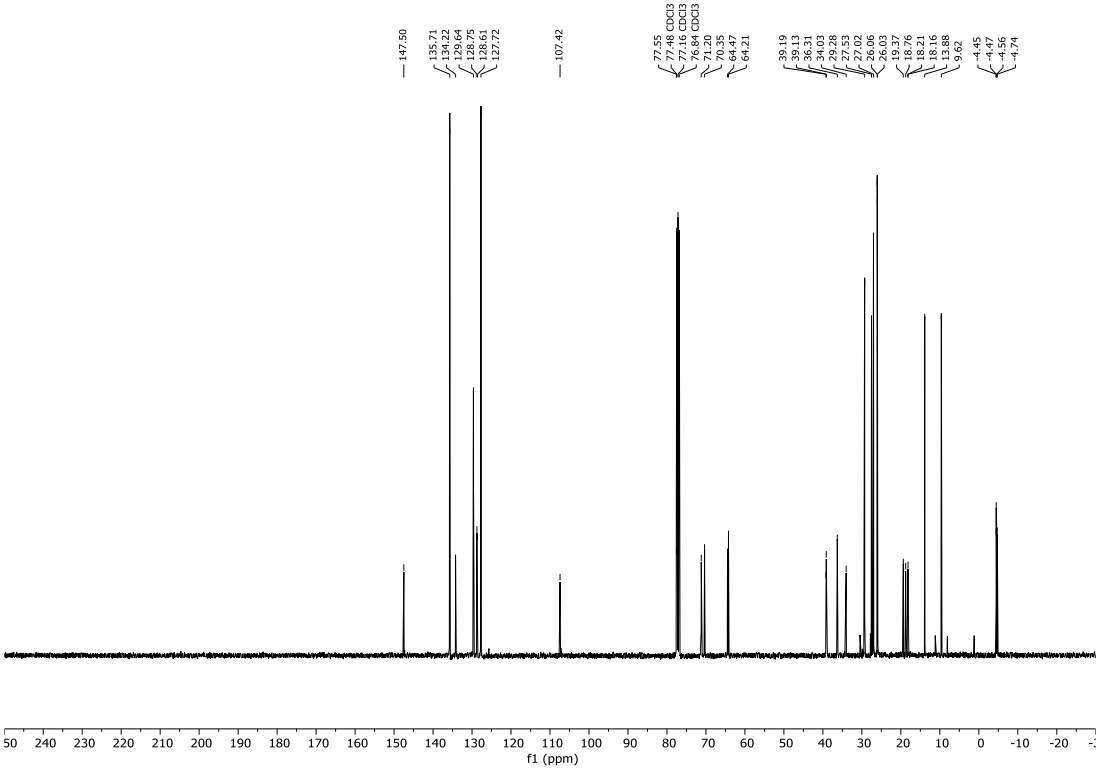

f1 (ppm)


TBSO
TBSO
OTBDPS
42
f1 (ppm)

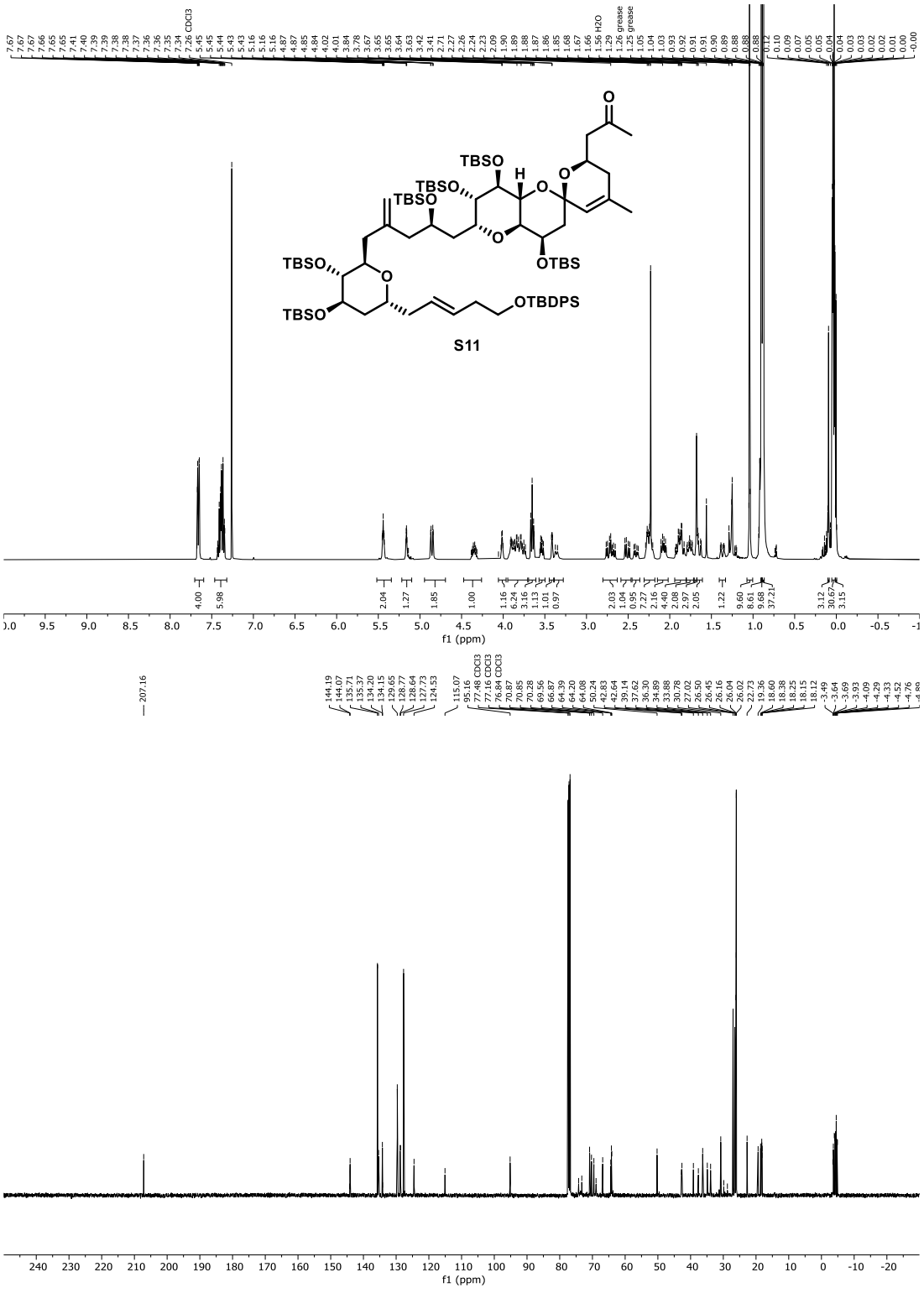

f1 (ppm)

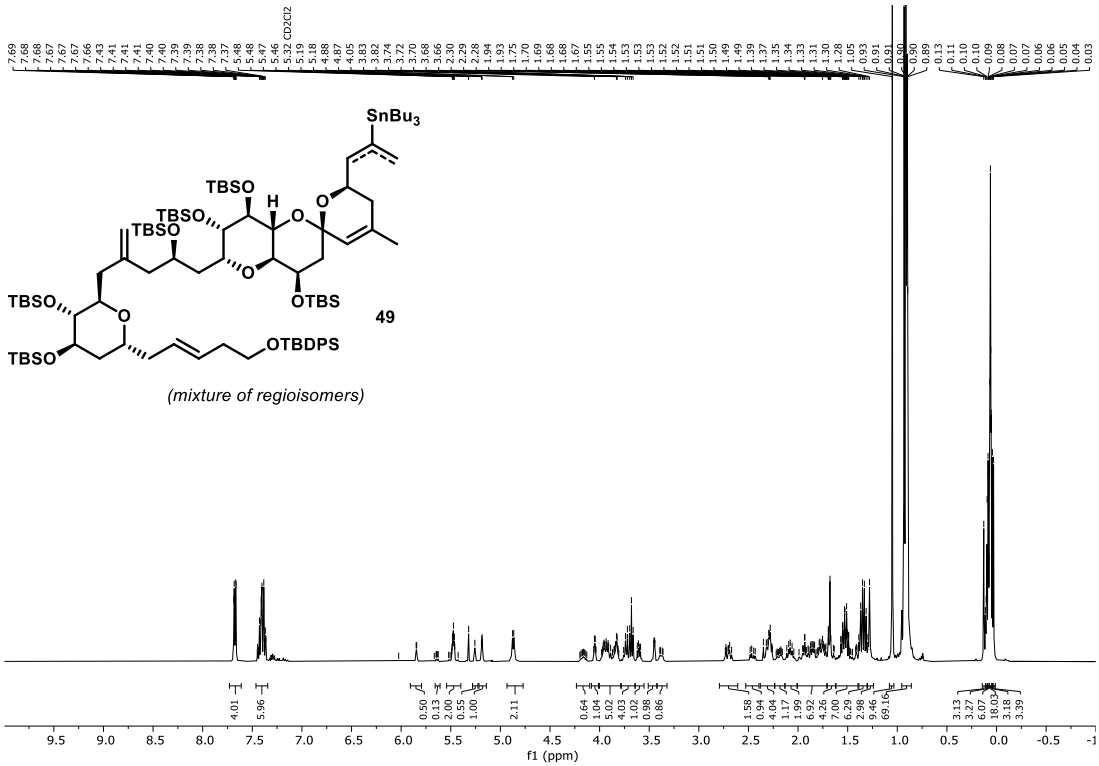

Cl
TBSO
O
TBSO
OTBDPS
44
f1 (ppm)
f1 (ppm)


SnBu3
TBSO
TBSO
O
OTBDPS
45
f1 (ppm)

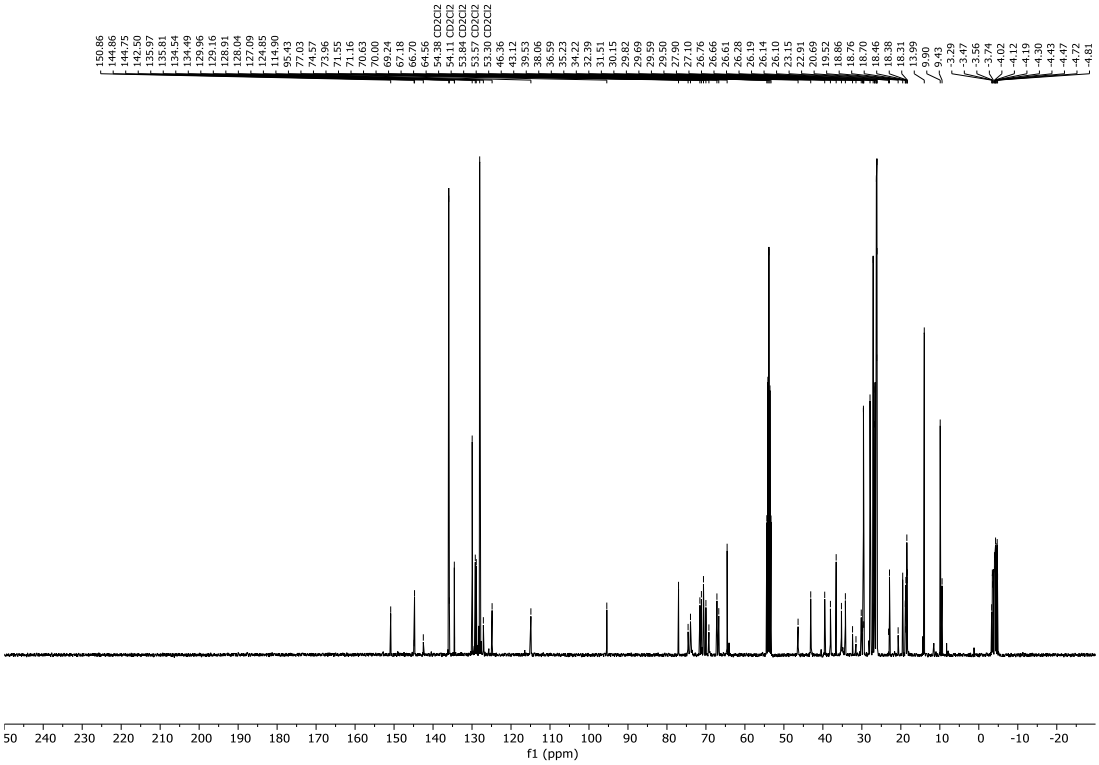

f1 (ppm)

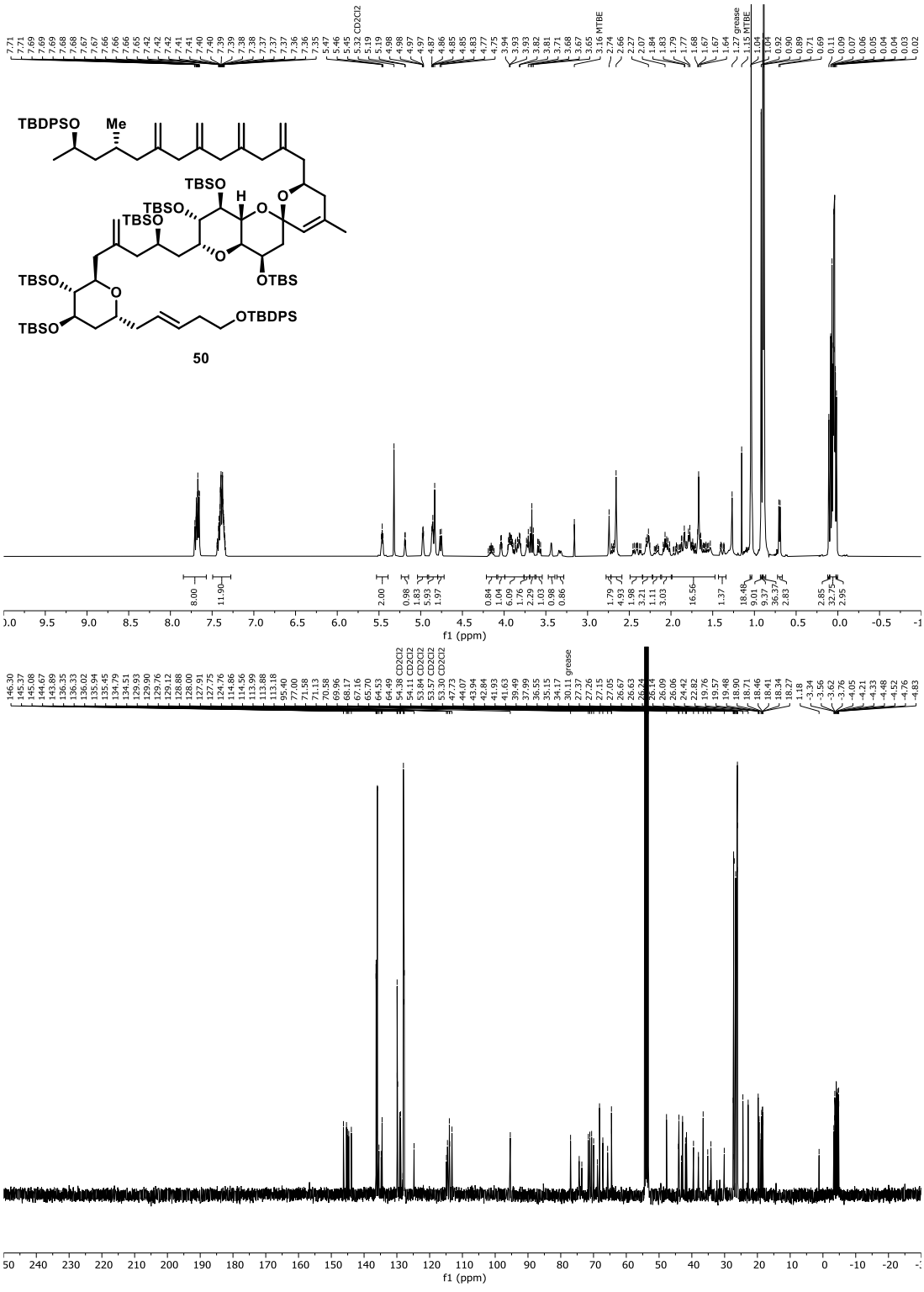

TBSO
H
O
TBSO
OH
O
O
OTBS
TBSO
O
TBSO
OTBDPS
48
f1 (ppm)
f1 (ppm)

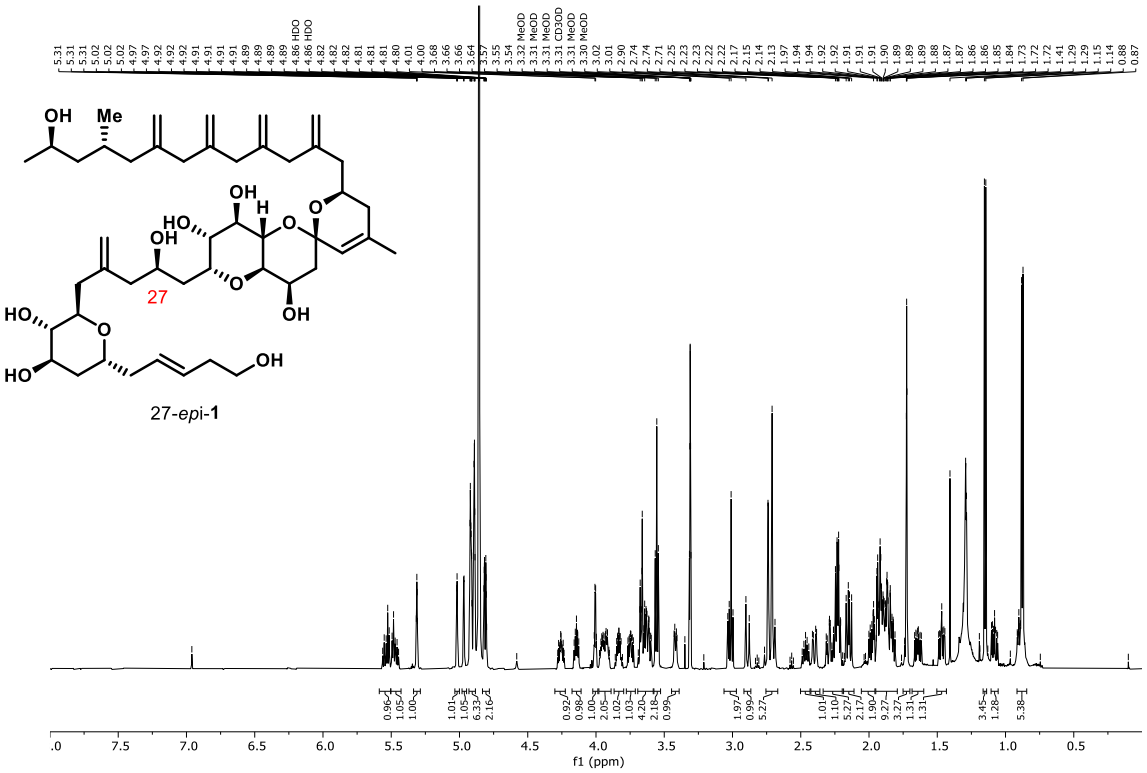

TBSO
H
O
TBSO
TBSO
O
O
OTBS
TBSO
O
TBSO
OTBDPS
S11
f1 (ppm)
f1 (ppm)



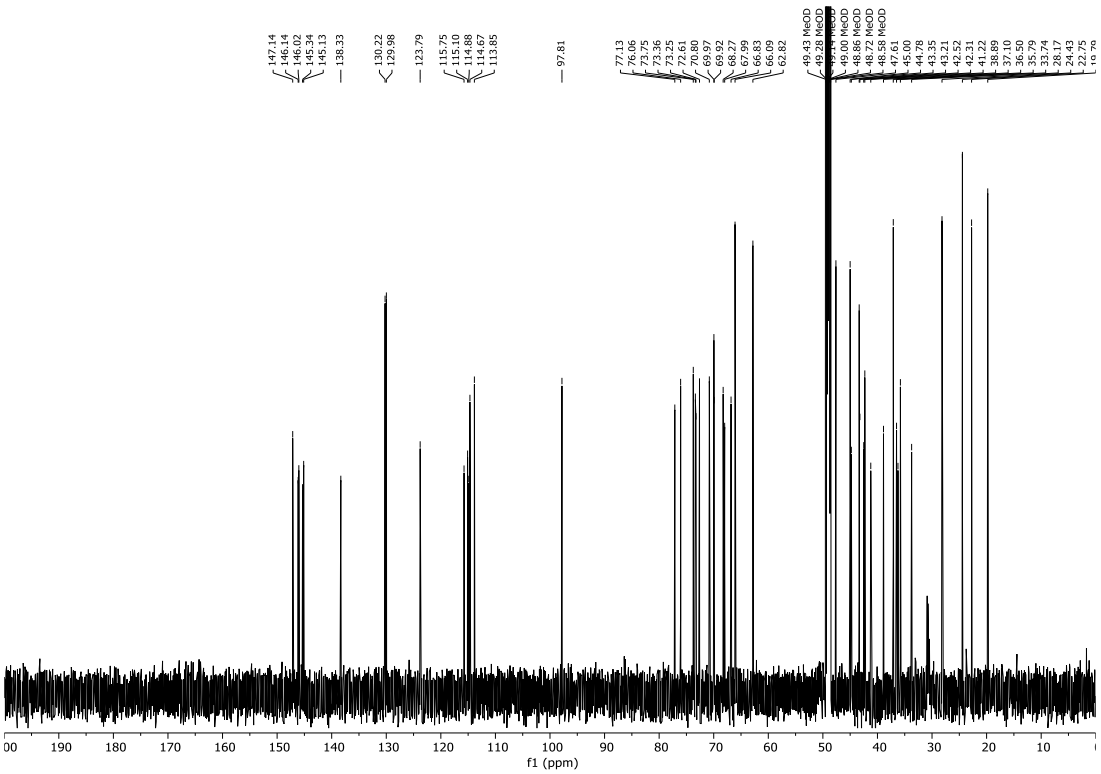
(mixture of regioisomers)

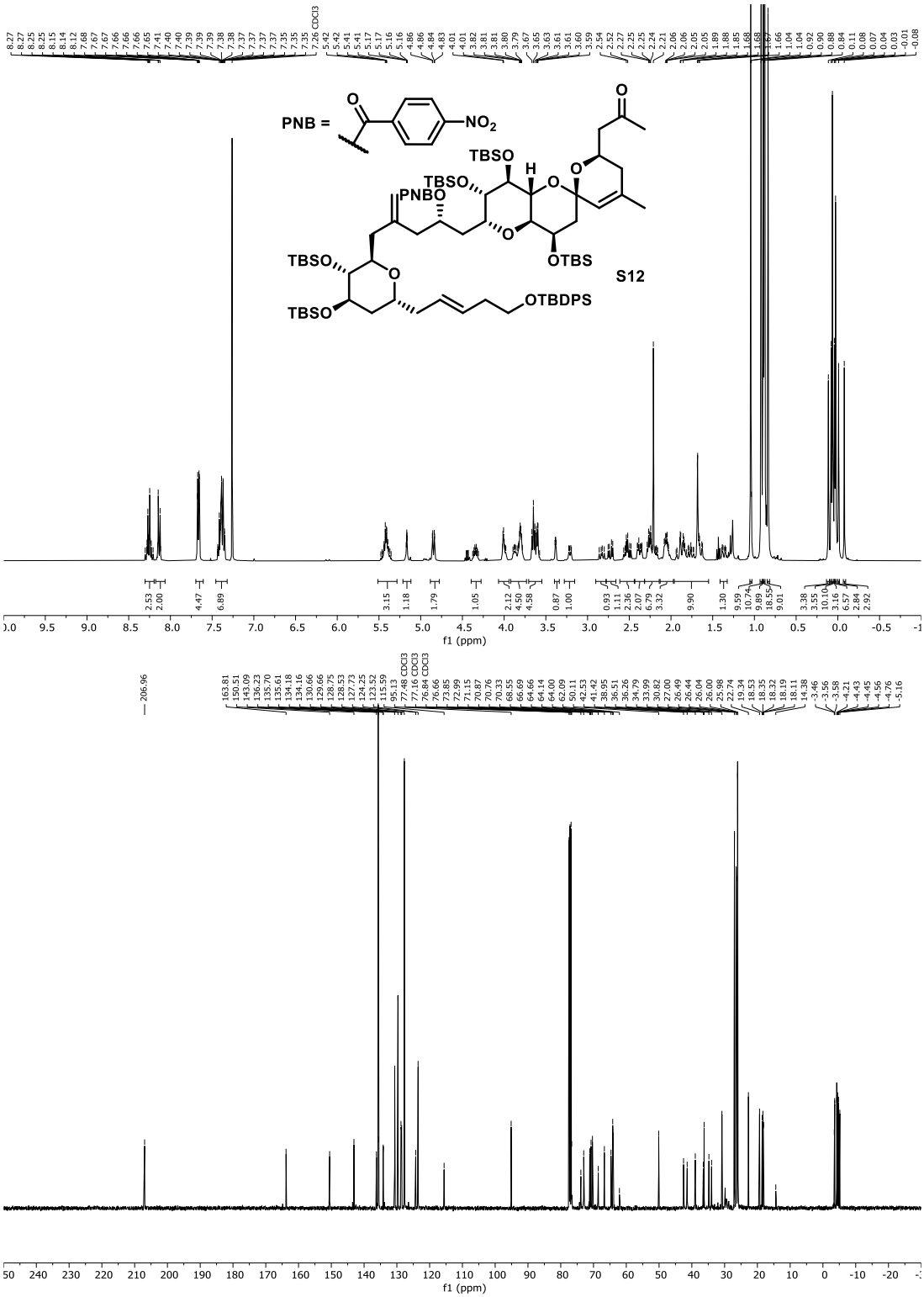


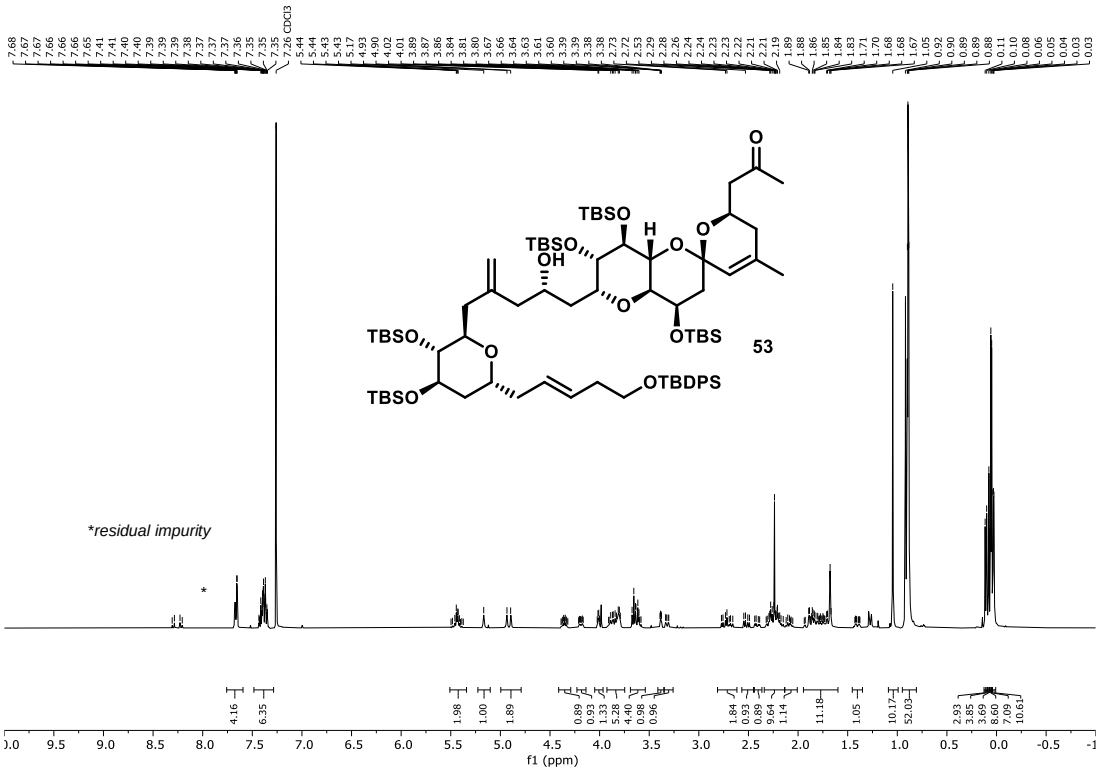

TBDPSO
Me
TBSO
H
O
TBSO
TBSO
O
O
TBSO
OTBS
O
TBSO
OTBDPS
50
f1 (ppm)
f1 (ppm)

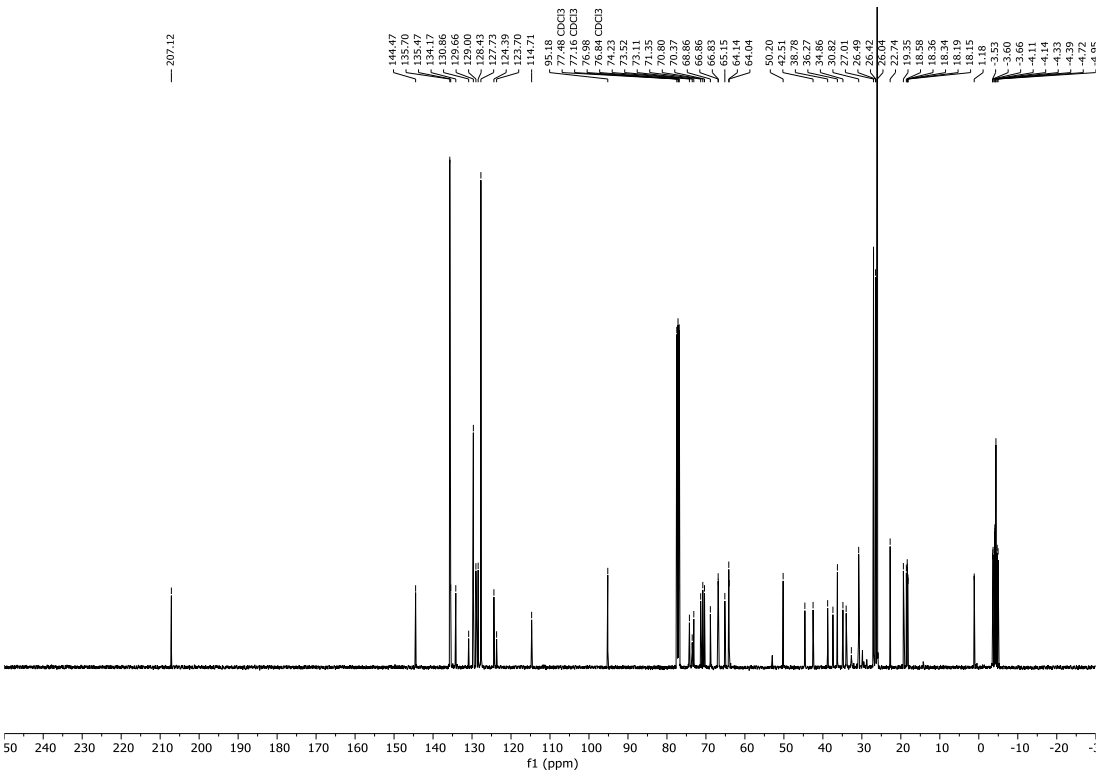


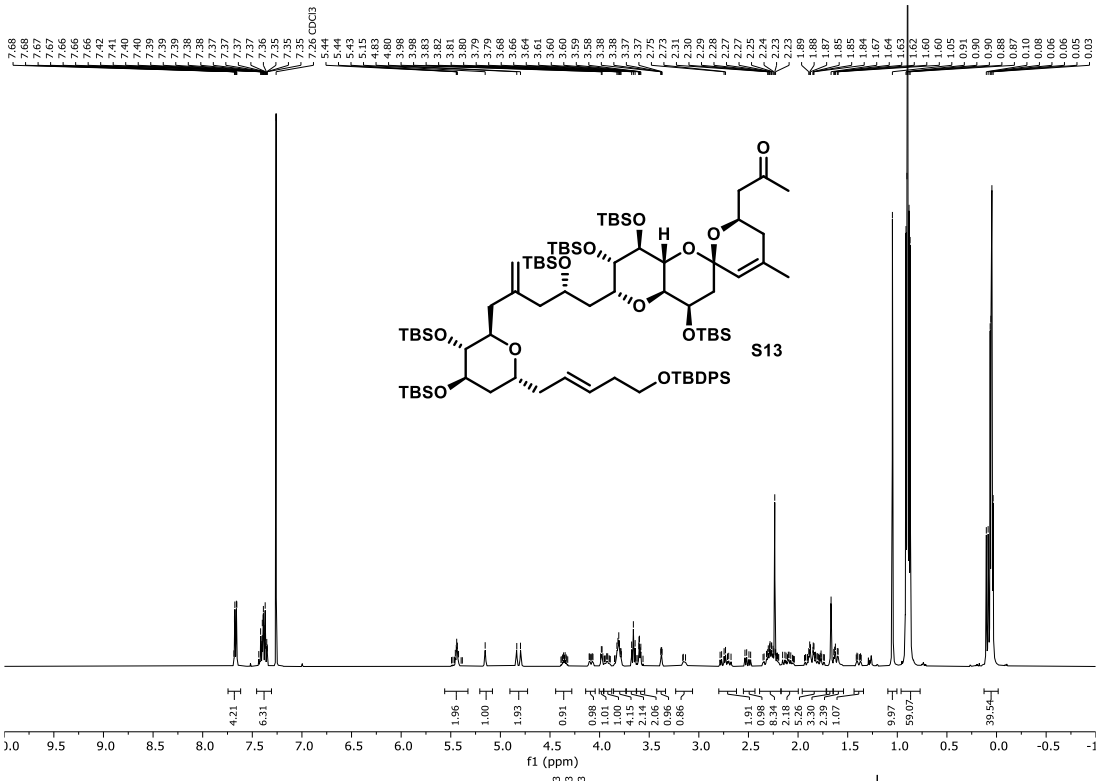
27-*epi*-**1**

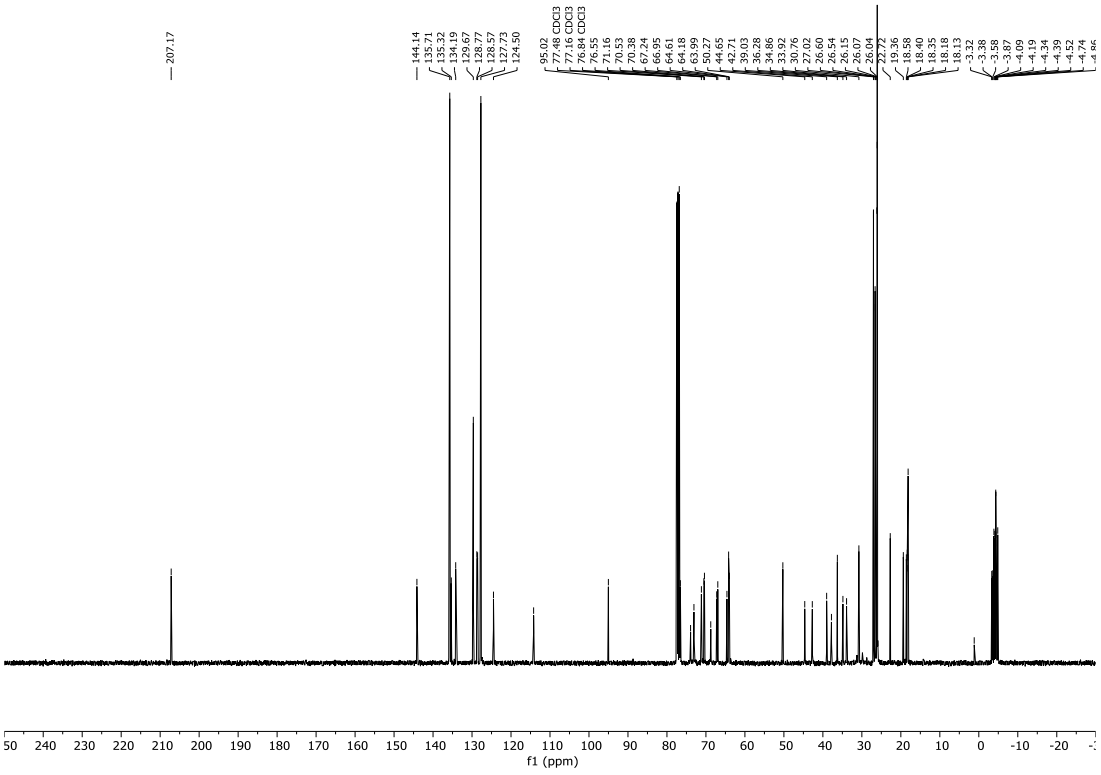


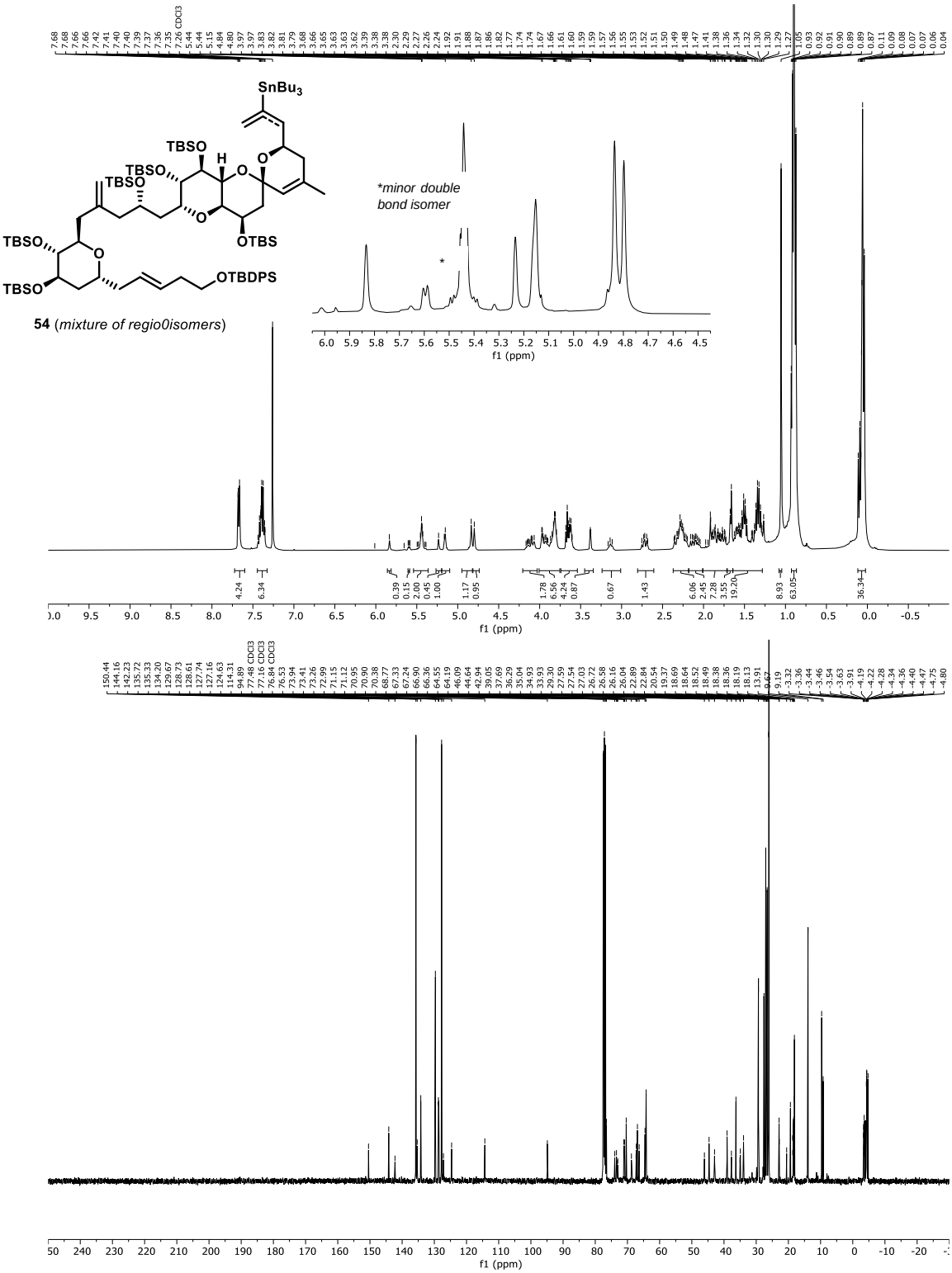

PNB =
O
NO2
TBSO
H
O
TBSO
PNBO
O
O
OTBS
S12
TBSO
O
TBSO
OTBDPS
f1 (ppm)
f1 (ppm)


TBSO
H
O
TBSO
OH
O
O
OTBS
TBSO
O
TBSO
OTBDPS
53
*residual impurity
*
f1 (ppm)

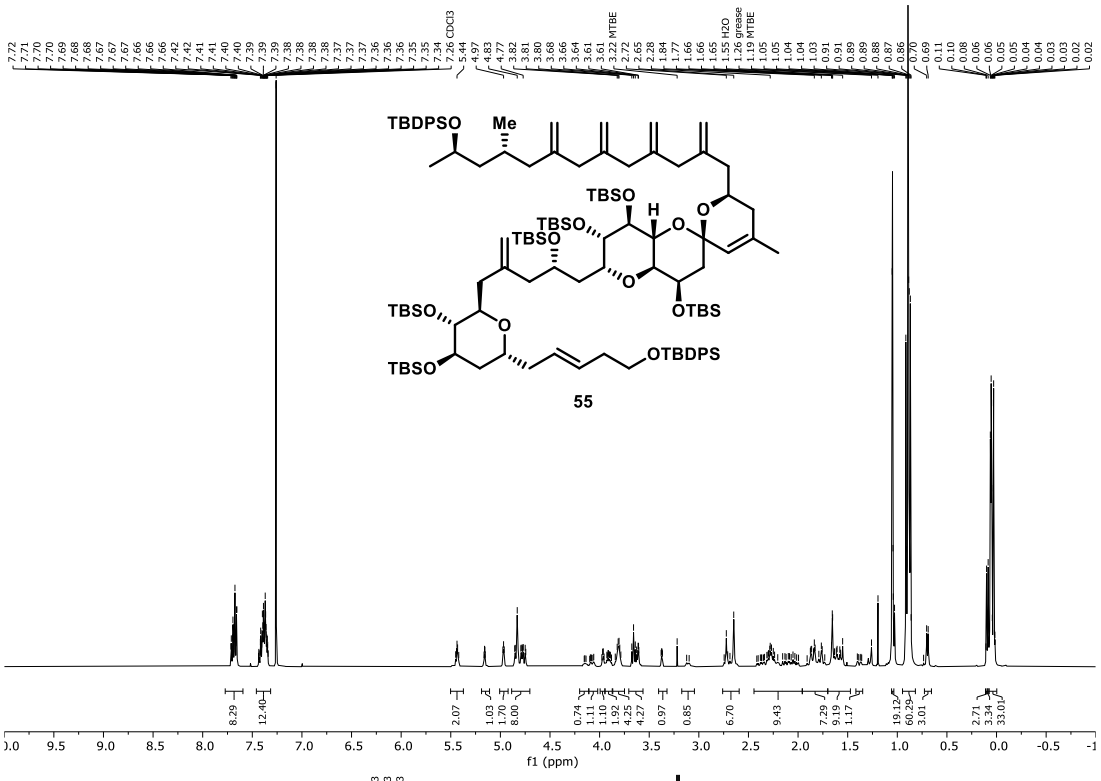

f1 (ppm)


TBSO
H
O
TBSO
TBSO
O
O
OTBS
S13
TBSO
O
TBSO
OTBDPS
f1 (ppm)

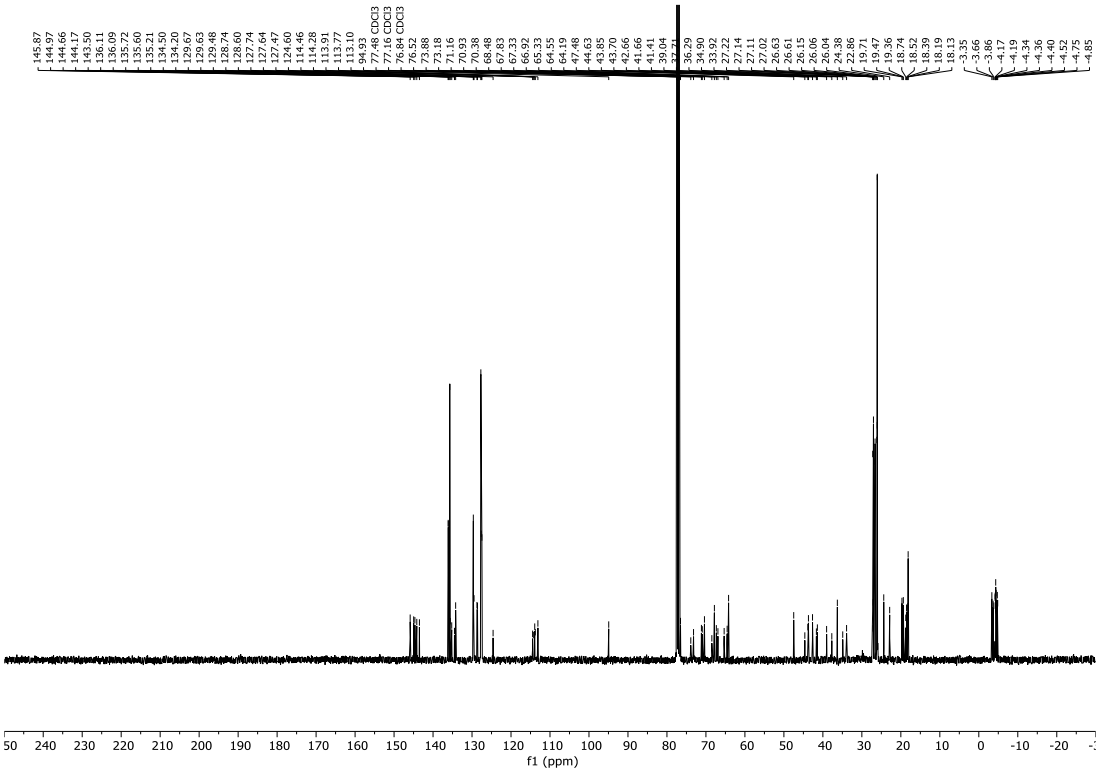

207.17
f1 (ppm)

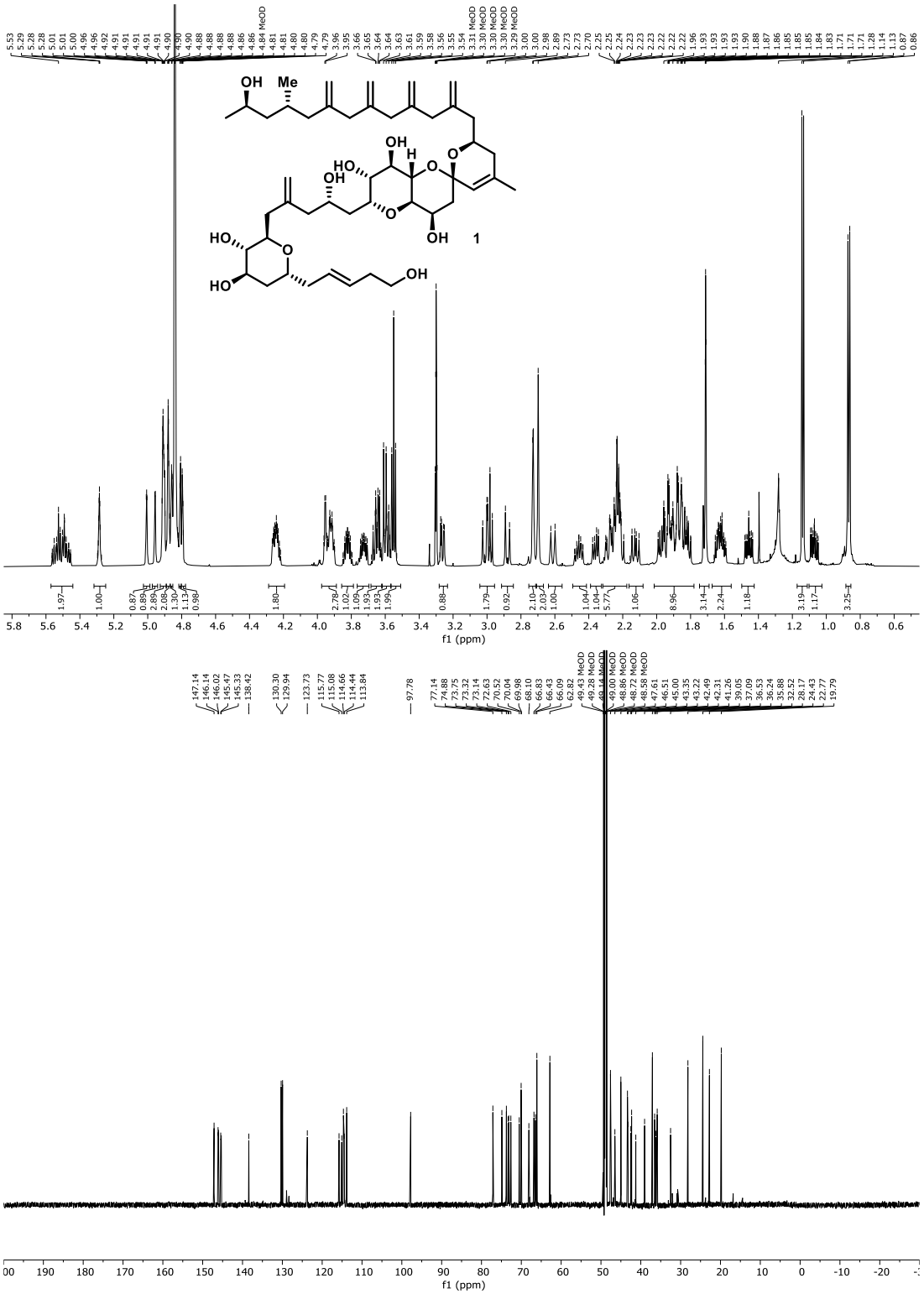


54 (*mixture of regio0isomers*)



55




OH
Me
OH
H
HO
OH
O
O
OH
1
HO
O
HO
OH
f1 (ppm)
f1 (ppm)

References

[1] Hoye, T. R.; Jeffrey, C. S.; Shao, F. Mosher Ester Analysis for the Determination of Absolute Configuration of Stereogenic (Chiral) Carbinol Carbons. *Nat. Protocols* **2007**, *2*, 2451-2458.

[2] (a) Tekle-Smith, M. A.; Williamson, K. S.; Hughes, I. F.; Leighton, J. Direct, Mild, and General *n*-Bu_4NBr-Catalyzed Aldehyde Alllylsilation with Allyl Chlorides. *Org. Lett*. **2017**, *19*, 6024-6027. (b) Keck, G. E.; Geraci, L. S. Catalytic Asymmetric Allylation (CAA) Reactions. II. A New Enantioselective Allylation Procedure. *Tetrahedron Lett*. **1993**, *34*, 7827-7828. (c) Ishihara, K.; Mouri, M.; Gao, G.; Maruyama, T.; Furuta, K.; Yamamoto, H. Catalytic Asymmetric Allylation Using a Chiral (Acyloxy)borane Complex as a Versatile Lewis Acid Catalyst. *J. Am. Chem. Soc*. **1993**, *115*, 11490-11495. (d) Williams, D. R.; Meyer, K. G. Total Synthesis of (+)-Amphidinolide K. *J. Am. Chem. Soc*. **2001**, *123*, 765-766. (e) Inoue, M.; Suzuki, T.; Nakada, M. Asymmetric Catalysis of Nozaki−Hiyama Allylation and Methallylation with A New Tridentate Bis(oxazolinyl)carbazole Ligand. *J. Am. Chem. Soc*. **2003**, *125*, 1140-1141.

[3] Barnett, D. S.; Schaus, S. E. Asymmetric Propargylation of Ketones Using Allenylboronates Catalyzed by Chiral Biphenols. *Org. Lett*. **2011**, *13*, 4020-4023.

[4] Huwyler, N.; Radkowski, K.; Rummelt, S. M.; Fürstner, A. Two Enabling Strategies fort he Stereoselective Conversion of Internal Alkynes into Trisubstituted Alkenes. *Chem. Eur. J.* **2017**, *23*, 12412-12419.

[5] (a) Huffmann, J. W.; Harris, P. G. Potassium Triphenylmethide. A Strong Base for Organic Synthesis. *Synth. Commun*. **1977**, *7*, 137-141. (b) Matthews, F. J. Methylation of Isobutyrophenone Using Potassium Triphenylmethide: An Advanced Organic Chemistry Laboratory Experiment. *J. Chem. Educ.* **1997**, *74*, 996.

[6] Basavaiah, D.; Sharada, D. S.; Kumaragurubaran, N.; Reddy, R. M. The Baylis−Hillman Reaction: One-Pot Facile Synthesis of 2,4-Functionalized 1,4-Pentadienes. *J. Org. Chem*. **2002**, *67*, 7135-7137.

[7] Thirupathi, B.; Gundapaneni, R. R.; Mohapatra, D. K., First Total Syntheses of (3*R*,5*R*)-Sonnerlactone and (3*R*,5*S*)-Sonnerlactone. *Synlett* **2011**, 2667-2670.

[8] Nelson, S. G.; Cheung, W. S.; Kassick, A. J.; Hilfiker, M. A. A de Novo Enantioselective Total Synthesis of (−)-Laulimalide. *J. Am. Chem. Soc.* **2002**, *124*, 13654-13655.

[9] Anderl, F.; Größl, S.; Wirtz, C.; Fürstner, A. Total Synthesis of Belizentrin Methyl Ester: Report on a Likely Conquest. *Angew. Chem. Int. Ed*. **2018**, *57*, 10712-10717.

[10] Smith, A. B.; Kim, W.-S.; Tong, R. Uniting Anion Relay Chemistry with Pd-Mediated Cross Coupling: Design, Synthesis and Evaluation of Bifunctional Aryl and Vinyl Silane Linchpins. *Org. Lett.* **2010**, *12*, 588-591.

[11] Ghosh, A. K.; Veitschegger, A. M.; Nie, S.; Pelitti, N.; MacRae, A. J.; Jurica, M. S. Enantioselective Synthesis of Thailanstatin A Methyl Ester and Evaluation of *in Vitro* Splicing Inhibition. *J. Org. Chem*. **2018**, *83*, 5187-5198.

[12] Still, W. C. Stannylation/destannylation. New Syntheses of Carbonyl Compounds via Organotin Intermediates. *J. Am. Chem. Soc.* **1977**, *99*, 4836-4838.

[13] Gilbertson, S. R.; Challener, C. A.; Bos, M. E.; Wulff, W. D. An Examination of the Coupling of Vinyl and Aryl triflates with Stannyl Cuprates for the Purpose of Providing Regioselective Access to Vinyl Lithiums. *Tetrahedron Lett.* **1988**, *29*, 4795-4798.

[14] Yang, A. R.; Lee, S.; Yoo, Y. D.; Kim, H. S.; Jeong, E. J.; Rho, J.-R. Limaol: A Polyketide from the Benthic Marine Dinoflagellate *Prorocentrum lima*. *J. Nat. Prod*. **2017**, *80*, 1688-1692.