

Supporting Information

Double Diastereoselection in Aldol Reactions Mediated by Dicyclohexylchloroborane between Chiral Aldehydes and A Chiral Ethyl Ketone Derived from L-Erythrulose. Synthesis of A C₁-C₉ Fragment of the Structure of the Antifungal Metabolite Soraphen A_{1α}

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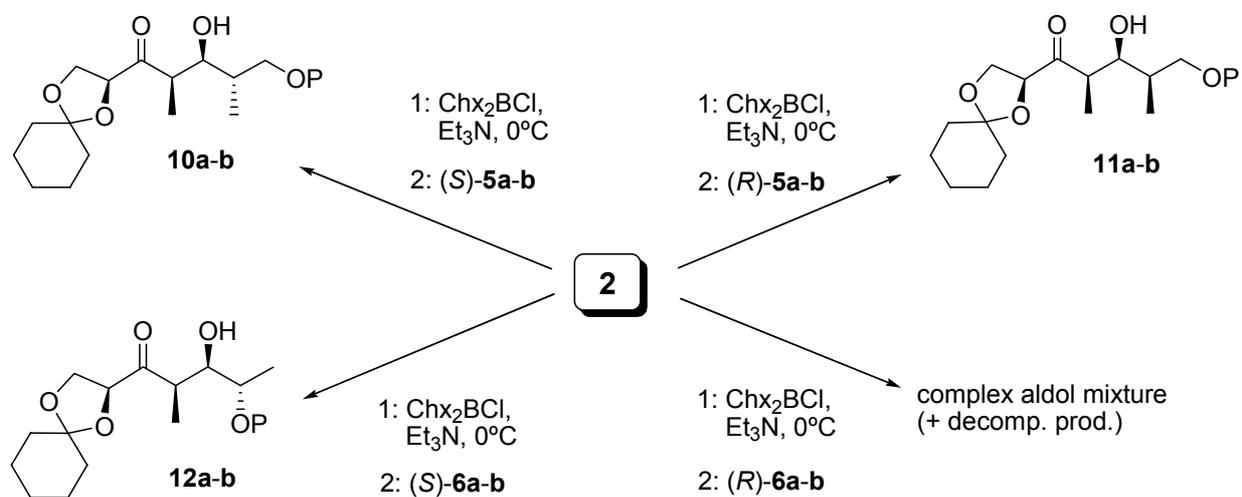
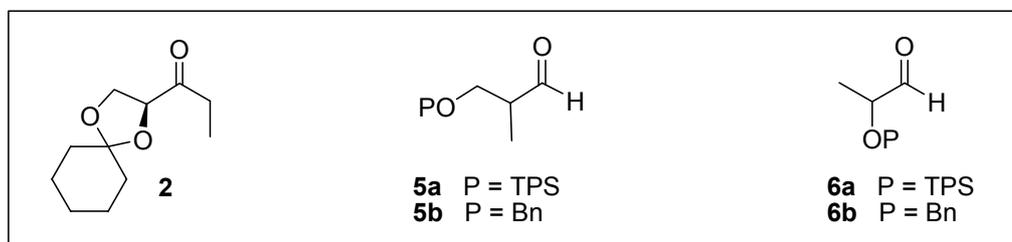
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General features

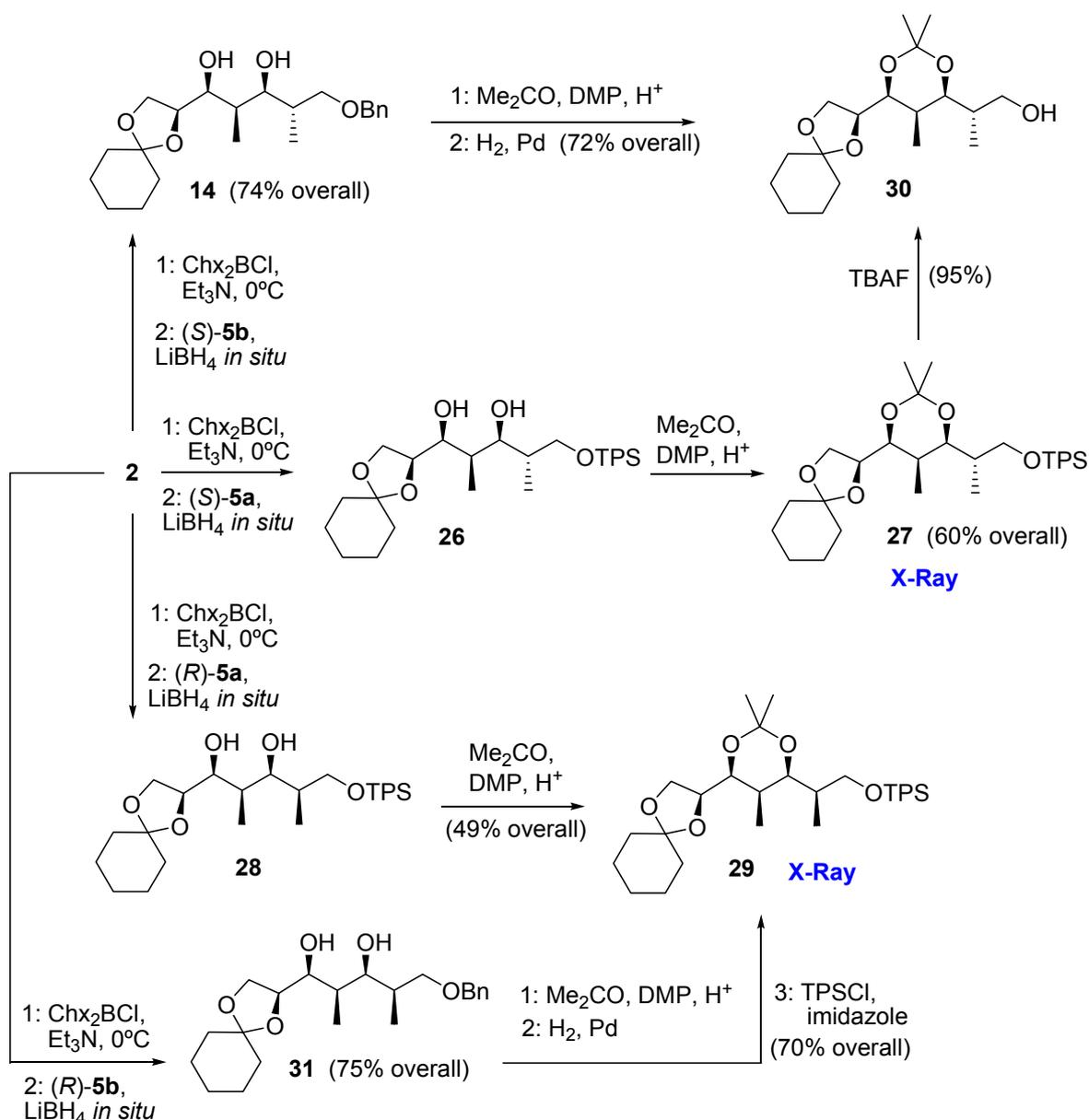
NMR spectra were recorded at 500 MHz (^1H NMR) and 125 MHz (^{13}C NMR) in CDCl_3 solution at 30°C (unless otherwise indicated). ^{13}C NMR signal multiplicities were determined with the DEPT pulse sequence. Mass spectra were run in the electron impact (EIMS, 70 eV) or the by fast atom bombardment mode (FAB MS, *m*-nitrobenzyl alcohol matrix). IR data, which were measured as films on NaCl plates (oils) or as KBr pellets (solids), are given only when relevant functions (C=O, OH) are present. Optical rotations were measured at 25°C . Reactions which required an inert atmosphere were carried out under dry N_2 with flame-dried glassware. Commercial reagents were used as received. THF and Et_2O were freshly distilled from sodium-benzophenone ketyl. Dichloromethane was freshly distilled from CaH_2 . Tertiary amines were freshly distilled from KOH. Unless detailed otherwise, "work-up" means pouring the reaction mixture into brine, followed by extraction with the solvent indicated in parenthesis. If the reaction medium was acidic (basic), an additional washing with 5% aq NaHCO_3 (aq NH_4Cl) was performed. New washing with brine, drying over anhydrous Na_2SO_4 and elimination of the solvent under reduced pressure were followed by chromatography on a silica gel column (60-200 μm) with the indicated eluent. Where solutions were filtered through a Celite pad, the pad was additionally washed with the same solvent used, and the washings incorporated to the main organic layer. Column chromatography was performed on silica gel (60-200 μ).

Aldol reactions studied in this paper



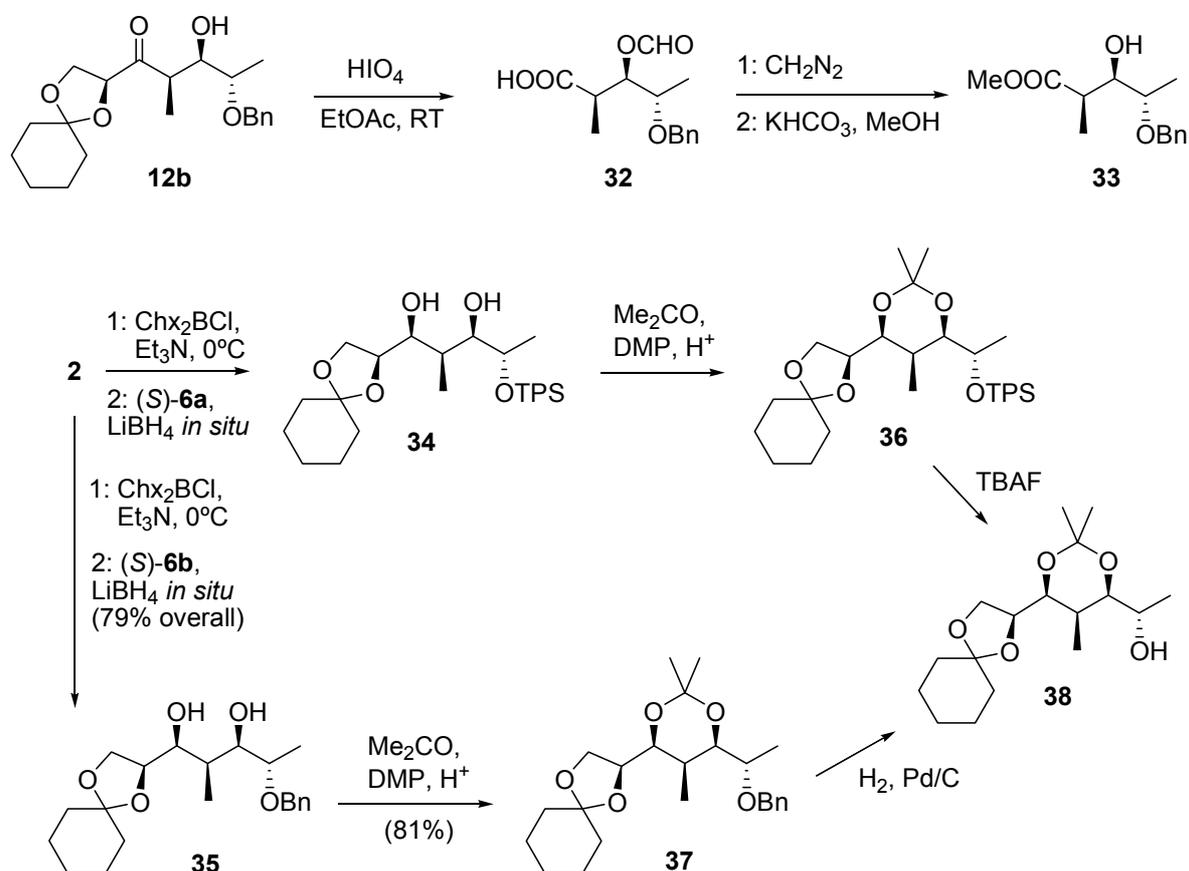
Chemical correlations

The stereostructures of the aldols were established with the aid of the chemical correlations depicted in the following schemes. The aldol reaction mixture of **2** with aldehydes (*S*)-**5a** and (*R*)-**5a** (which gives rise to aldols **10a** and **11a**, respectively) was reduced *in situ* with LiBH₄ according to the reported procedure (Paterson, I.; Channon, J. A. *Tetrahedron Lett.* **1992**, *33*, 797-800). This yielded *syn*-1,3-diols **26** and **28**, respectively, which were then converted into the corresponding acetonides **27** and **29**. **These were solid compounds and gave crystals suitable for X-ray diffraction analysis.** This unequivocally established the absolute configuration of the five consecutive stereocenters in both compounds.



The stereostructures of aldols **10b** and **11b** were established through chemical correlation with compounds **27** and **29**. Thus, the reaction mixtures generating these aldols were reduced *in situ* as above with LiBH_4 to yield *syn*-1,3-diols **14** and **31**, respectively. Acetonide formation in the former followed by hydrogenolytic cleavage of the benzyl group furnished alcohol **30**, also obtained from **27** by means of desilylation. Likewise, acetonide formation in **31** followed by hydrogenolytic cleavage of the benzyl group furnished an alcohol, silylation of which afforded **29**.

The stereostructures of aldols **12a** and **12b** were established through chemical correlations. Aldol **12b** was oxidized with periodic acid to the β -formyloxy acid **32**.¹ Methylation of the carboxyl function and saponification of the formyl group afforded the known ester **33**.² Furthermore, the reaction mixtures generating aldols **12a** and **12b** were reduced *in situ* with LiBH_4 to yield *syn*-1,3-diols **34** and **35**, respectively, which were subsequently transformed into their respective acetonides **36** and **37**. These were then converted into the same alcohol **38** after cleavage of the appropriate protecting groups.



¹ Carda, M.; Murga, J.; Falomir, E.; González, F.; Marco, J. A. *Tetrahedron* **2000**, *56*, 677-683.

² Zhao, C.-X.; Duffey, M. O.; Taylor, S. J.; Morken, J. P. *Org. Lett.* **2001**, *3*, 1829-1831. The product described here is the enantiomer of **33**.

Experimental procedures

Experimental procedure for aldol additions of ketone 2 mediated by dicyclohexyl boron chloride. Ch_2BCl (neat, 395 μL , ca. 1.8 mmol) was added under N_2 via syringe to an ice-cooled solution of Et_3N (280 μL , 2 mmol) in anhydrous Et_2O (5 mL). Ketone **2** (1 mmol) was dissolved in anhydrous ether (5 mL) and added dropwise via syringe to the reagent solution. The reaction mixture was then stirred for 30 min. After addition of a solution of the appropriate aldehyde (1.5 mmol) in ether (6 mL), the reaction mixture was stirred at 0°C for 5 h. Then phosphate buffer solution (pH 7, 6 mL) and MeOH (6 mL) were added, followed by 30% aq H_2O_2 solution (3 mL). After stirring for 1 h at room temperature, the mixture was worked up (extraction with Et_2O). Solvent removal *in vacuo* and column chromatography of the residue on silica gel (hexanes-EtOAc mixtures) afforded the corresponding aldol addition product. Chemical yields and d.r.'s (the latter determined by means of ^1H and ^{13}C NMR) are given in the main text.

Experimental procedure for the one-pot aldolization/reduction. Procedure as above until aldehyde addition. After stirring at 0°C for 5 h, the solution was cooled to -78°C and treated dropwise with a 2M solution of LiBH_4 in THF (1.5 mL, 3 mmol). The stirring was then continued at -78°C for 2 h. The reaction was quenched with pH 7 phosphate buffer (6 mL) and MeOH (6 mL), followed by a 30% aq H_2O_2 solution (3 mL). After stirring for 1 h at room temperature, the mixture was poured into satd. aq NaHCO_3 and extracted with Et_2O . The organic layer was washed with brine and dried on anhydrous Na_2SO_4 . Solvent removal *in vacuo* afforded an oily residue which was chromatographed on silica gel (hexanes-EtOAc mixtures) to yield the expected *syn*-1,3-diols.

Formation of acetonides. The 1,3-diol (1 mmol) and *p*-toluenesulfonic acid (19 mg, 0.1 mmol) were dissolved in a 4:1 acetone/2,2-dimethoxypropane (DMP) mixture (5 mL). The mixture was then stirred at room temp. until consumption of the starting material (TLC monitoring). After adding Et_3N (0.1 mL), all volatiles were removed *in vacuo*, and the residue was chromatographed on silica gel (hexanes-EtOAc mixtures).

Formation of TPS derivatives. A solution of the alcohol (1 mmol) and imidazole (170 mg, 2.5 mmol) in dry CH_2Cl_2 (4 mL) was treated dropwise under N_2 with a solution of TPS chloride (1.5 mmol) in dry CH_2Cl_2 (2 mL). The reaction mixture was stirred overnight at room temp., then diluted with CH_2Cl_2 and worked up. Column chromatography on silica gel (hexanes-EtOAc mixtures) afforded the desired silyl derivative.

Desilylation of silyl derivatives. The silyl derivative (1 mmol) was dissolved under N_2 in dry THF (3 mL). Tetra-*n*-butylammonium fluoride trihydrate (TBAF, 315 mg, 1.2 mmol) dissolved in dry THF (1 mL) was then added. The reaction mixture was stirred at room temp. until consumption of the starting material (TLC monitoring). After addition of an aqueous satd. NH_4Cl solution (2 mL), the mixture was stirred for 5 min., worked up and chromatographed on silica gel (hexanes-EtOAc mixtures).

Hydrogenolysis of benzyl ethers. A solution of the appropriate benzyl ether (1 mmol) was dissolved in EtOAc (5 mL) and stirred for 48 h under H_2 (1 atm) in the presence of 20% palladium hydroxide on

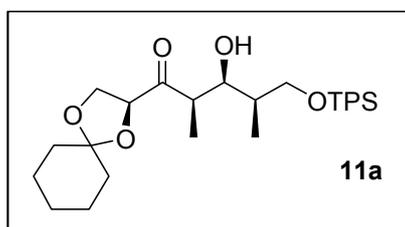
carbon (Pearlman's catalyst) (50 mg). After filtration through Celite and removal of all volatiles under reduced pressure, the residue was chromatographed on silica gel (hexanes-EtOAc, 7:3) to yield the debenzylated product.

Oxidative cleavage of aldol 12b with periodic acid hydrate and subsequent conversion into methyl ester 33. Aldol **12b** (363 mg, 1 mmol) was dissolved in dry EtOAc (10 mL) and treated with H_5IO_6 (800 mg, 3.5 mmol). The mixture was then stirred at room temperature until consumption of the starting material (ca. 2-3 h, TLC monitoring!). After this, solid sodium thiosulfate pentahydrate (500 mg, ca. 2 mmol) was added to the reaction mixture, which was then stirred for 15 min., filtered through Celite and evaporated under reduced pressure. The oily residue was then subjected to column chromatography on silica gel (CH_2Cl_2 -MeOH, 19:1) to yield acid **32** (171 mg, 64%).

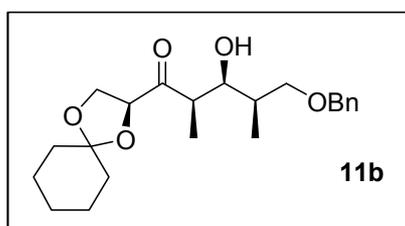
The acid from above was dissolved in ether (5 mL) and treated with excess ethereal diazomethane. After stirring for 15 minutes at room temperature, the volatiles were eliminated in vacuo. The oily residue was then dissolved in MeOH (3 mL) and treated with KHCO_3 (75 mg, 0.75 mmol). After stirring at room temperature for about 1 h (TLC monitoring), the mixture was worked up (extraction with CH_2Cl_2) and evaporated in vacuo. Column chromatography on silica gel (hexanes-EtOAc, 7:3) provided methyl ester **33** (102 mg, 63%).

Physical data of selected correlation products

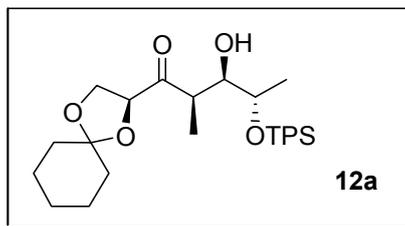
Aldols



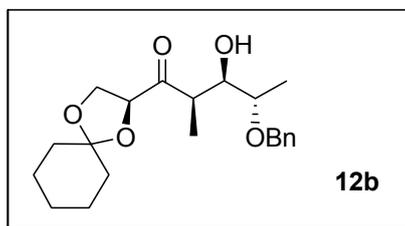
(2R,3S,4R)-5-(tert-Butyldiphenylsilyloxy)-1-[(2S)-(1,4-dioxaspiro[4.5]dec-2-yl)]-3-hydroxy-2,4-dimethylpentan-1-one (11a). Oil, $[\alpha]_D -29.8$ (c 1.8; CHCl_3). IR 3500 (br), 1711 cm^{-1} . ^1H NMR (500 MHz) δ 7.70-7.65 (4H, br m), 7.45-7.35 (6H, br m), 4.46 (1H, dd, $J = 7.7, 5.7$ Hz), 4.18 (1H, t, $J = 8.5, 7.7$ Hz), 4.05 (1H, m), 3.98 (1H, dd, $J = 8.5, 5.7$ Hz), 3.69 (1H, dd, $J = 10.2, 4.3$ Hz), 3.62 (1H, dd, $J = 10.2, 5$ Hz), 3.37 (1H, quint, $J = 7$ Hz), 2.90 (1H, br d, $J = 3$ Hz, OH), 1.75-1.55 (9H, br m), 1.40 (2H, m), 1.18 (3H, d, $J = 7$ Hz), 1.07 (9H, s), 1.02 (3H, d, $J = 7$ Hz); ^{13}C NMR (125 MHz) δ 214.2, 133.2, 133.1, 111.7, 19.1 (C), 135.6, 135.5, 129.8, 129.7, 127.7, 127.6, 79.6, 74.3, 44.8, 37.8 (CH), 68.2, 66.3, 35.6, 34.4, 25.1, 24.0, 23.8 (CH_2), 26.9 (x 3), 12.1, 11.5 (CH_3). HR EIMS m/z 467.2170 ($\text{M}^+ - t\text{Bu}$, 1), 269 (100), 239 (96), 183 (62). Calcd. for $\text{C}_{31}\text{H}_{44}\text{O}_5\text{Si} - t\text{Bu}$, 467.2253. Anal. Calcd. for $\text{C}_{31}\text{H}_{44}\text{O}_5\text{Si}$: C, 70.95; H, 8.45. Found, C, 71.02; H, 8.38.



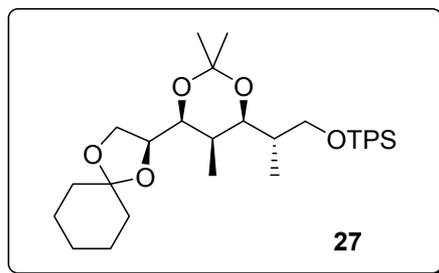
(2R,3S,4R)-5-Benzyloxy-1-[(2S)-(1,4-dioxaspiro[4.5]dec-2-yl)]-3-hydroxy-2,4-dimethylpentan-1-one (11b). Oil; $[\alpha]_D -43.8$ (c 0.9; CHCl_3). IR 3490 (br), 1711 cm^{-1} . ^1H NMR (500 MHz) δ 7.35-7.25 (5H, br m), 4.45-4.40 (3H, m), 4.10 (1H, t, $J = 8$ Hz), 3.90 (2H, m), 3.40 (2H, m), 3.28 (1H, quint, $J = 7$ Hz), 2.80 (1H, br s, OH), 1.75 (1H, m), 1.65-1.50 (8H, br m), 1.35 (2H, m), 1.11 (3H, d, $J = 7$ Hz), 0.97 (3H, d, $J = 7$ Hz); ^{13}C NMR (125 MHz) δ 214.2, 138.1, 111.6 (C), 128.4, 127.7, 127.5, 79.6, 74.2, 44.7, 36.3 (CH), 74.6, 73.3, 66.4, 35.6, 34.4, 25.1, 24.0, 23.8 (CH_2), 12.0, 11.9 (CH_3). HR FABMS m/z (rel. int.) 377.2322 ($\text{M} + \text{H}^+$). Calcd. for $\text{C}_{22}\text{H}_{33}\text{O}_5$, 377.2328. Anal. Calcd. for $\text{C}_{22}\text{H}_{32}\text{O}_5$: C, 70.18; H, 8.57. Found, C, 70.32; H, 8.48.



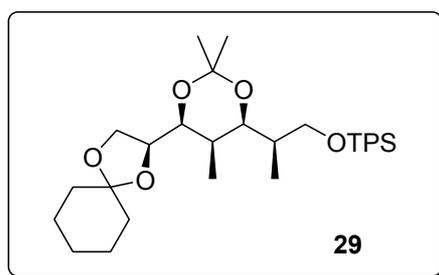
(2R,3R,4S)-4-(tert-Butyldiphenylsilyloxy)-1-[(2S)-(1,4-dioxaspiro[4.5]dec-2-yl)]-3-hydroxy-2-methylpentan-1-one (12a). Oil; $[\alpha]_D -25.6$ (c 1.5; CHCl_3). IR 3500 (br), 1712 cm^{-1} . ^1H NMR (500 MHz) δ 7.70-7.65 (4H, br m), 7.45-7.35 (6H, br m), 4.49 (1H, dd, $J = 8.5, 6$ Hz), 4.19 (1H, t, $J = 8.5$ Hz), 3.97 (1H, dd, $J = 8.5, 6$ Hz), 3.94 (1H, m), 3.80 (1H, quint, $J = 6$ Hz), 3.55 (dq, $J = 4, 7$ Hz), 2.70 (1H, br s, OH), 1.70-1.55 (8H, br m), 1.40 (2H, m), 1.11 (3H, d, $J = 6$ Hz), 1.09 (9H, s), 1.07 (3H, d, $J = 7$ Hz); ^{13}C NMR (125 MHz) δ 214.4, 134.3, 133.2, 111.5, 19.2 (C), 135.8, 135.7, 129.8, 129.6, 127.7, 127.5, 79.2, 75.1, 70.1, 42.8 (CH), 66.3, 35.6, 34.2, 25.0, 23.9, 23.7 (CH_2), 27.0 (x 3), 19.3, 10.1 (CH_3). HR EIMS m/z 453.2089 ($\text{M}^+ - t\text{Bu}$, 2), 255 (69), 199 (100). Calcd. for $\text{C}_{30}\text{H}_{42}\text{O}_5\text{Si} - t\text{Bu}$, 453.2097. Anal. Calcd. for $\text{C}_{30}\text{H}_{42}\text{O}_5\text{Si}$: C, 70.55; H, 8.29. Found, C, 70.42; H, 8.30.



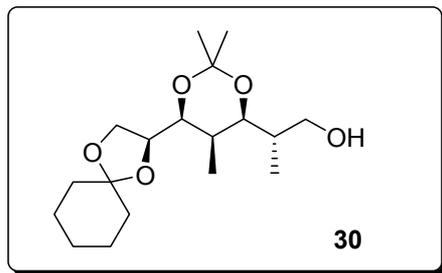
(2R,3R,4S)-4-Benzyloxy-1-[(2S)-(1,4-dioxaspiro[4.5]dec-2-yl)]-3-hydroxy-2-methylpentan-1-one (12b). Oil; $[\alpha]_D -3.1$ (c 1.75; CHCl_3). IR 3460 (br), 1710 cm^{-1} . ^1H NMR (500 MHz) δ 7.35-7.25 (5H, br m), 4.60 (1H, d, $J = 11.5$ Hz), 4.44 (1H, dd, $J = 8, 6$ Hz), 4.40 (1H, d, $J = 11.5$ Hz), 4.13 (1H, t, $J = 8$ Hz), 3.95-3.90 (2H, m), 3.45-3.40 (2H, m), 2.60 (1H, br s, OH), 1.70-1.50 (8H, br m), 1.40 (2H, m), 1.27 (3H, d, $J = 6$ Hz), 1.07 (3H, d, $J = 7$ Hz); ^{13}C NMR (125 MHz) δ 214.5, 138.3, 111.7 (C), 128.4, 127.7, 127.6, 79.4, 75.4, 74.0, 43.0 (CH), 70.7, 66.5, 35.7, 34.3, 25.1, 24.0, 23.8 (CH_2), 15.6, 10.7 (CH_3). HR EIMS m/z 362.2079 (M^+ , 1), 141 (58), 91 (100). Calcd. for $\text{C}_{21}\text{H}_{30}\text{O}_5$, 362.2093. Anal. Calcd. for $\text{C}_{21}\text{H}_{30}\text{O}_5$: C, 69.59; H, 8.34. Found, C, 69.36; H, 8.50.



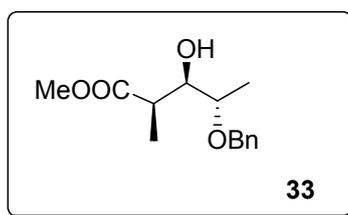
Solid, mp 118-119 °C (from CH₂Cl₂-Et₂O); [α]_D +6.5 (*c* 2.5; CHCl₃). ¹H NMR (500 MHz) δ 7.75-7.70 (4H, br m), 7.45-7.35 (6H, br m), 4.23 (1H, td, *J* = 7.2, 6.5 Hz), 4.07 (1H, dd, *J* = 8.2, 6.5 Hz), 3.95-3.90 (3H, m), 3.74 (1H, dd, *J* = 8.2, 7.2 Hz), 3.62 (1H, dd, *J* = 9.5, 2.4 Hz), 1.80-1.30 (12H, br m), 1.48 (6H, s), 1.11 (9H, s), 0.99 (3H, d, *J* = 7 Hz), 0.91 (3H, d, *J* = 7 Hz); ¹³C NMR (125 MHz) δ 133.8, 133.7, 110.2, 99.1, 19.3 (C), 135.6, 135.5, 129.5, 129.4, 127.5, 127.4, 76.7, 76.0, 72.5, 36.4, 30.6 (CH), 64.7, 64.5, 36.7, 35.3, 25.1, 24.0, 23.8 (CH₂), 29.8, 26.9 (\times 3), 19.5, 12.4, 5.6 (CH₃). HR EIMS *m/z* 566.3402 (M⁺, 20), 551 (15), 353 (45), 269 (77), 199 (100), 135 (22). Calcd. for C₃₄H₅₀O₅Si, 566.3427.



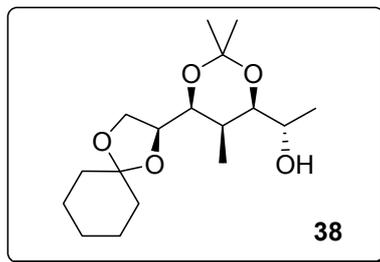
Solid, mp 123-124 °C (from pentane-Et₂O); [α]_D -19.9 (*c* 1.6; CHCl₃). ¹H NMR (500 MHz) δ 7.70-7.65 (4H, br m), 7.45-7.35 (6H, br m), 4.13 (1H, td, *J* = 8, 6 Hz), 3.96 (1H, dd, *J* = 8, 6 Hz), 3.78 (1H, dd, *J* = 8, 2 Hz), 3.73 (1H, dd, *J* = 9.7, 1.5 Hz), 3.55 (2H, m), 3.49 (1H, t, *J* = 8 Hz), 1.80-1.30 (12H, br m), 1.48 (3H, s), 1.47 (3H, s), 1.07 (9H, s), 1.05 (3H, d, *J* = 6.5 Hz), 0.82 (3H, d, *J* = 6.5 Hz); ¹³C NMR (125 MHz) δ 133.6, 133.5, 110.2, 99.4, 19.3 (C), 135.6, 135.5, 129.7, 129.6, 127.7, 127.6, 76.7, 76.1, 75.7, 36.4, 31.6 (CH), 65.3, 64.8, 36.3, 35.4, 25.1, 24.0, 23.8 (CH₂), 29.9, 26.9 (\times 3), 19.4, 14.3, 6.3 (CH₃). HR EIMS *m/z* 566.3452 (M⁺, 2), 551 (1), 353 (8), 269 (33), 199 (92), 135 (100). Calcd. for C₃₄H₅₀O₅Si, 566.3427.



Oil; $[\alpha]_D +4.8$ (c 2.7; CHCl_3). IR 3500 (br) cm^{-1} . ^1H NMR (500 MHz) δ 4.09 (1H, td, $J = 7.2, 6.5$ Hz), 3.95 (1H, dd, $J = 8.2, 6.5$ Hz), 3.78 (1H, dd, $J = 8, 2$ Hz), 3.66 (1H, dd, $J = 10, 2$ Hz), 3.58 (1H, dd, $J = 8.2, 7.2$ Hz), 3.54 (1H, dd, $J = 10.8, 7.3$ Hz), 3.46 (1H, dd, $J = 10.8, 3.5$ Hz), 3.00 (1H, br s, OH), 1.80 (1H, m), 1.60-1.20 (11H, br m), 1.41 (3H, s), 1.38 (3H, s), 0.84 (3H, d, $J = 7$ Hz), 0.71 (3H, d, $J = 7$ Hz); ^{13}C NMR (125 MHz) δ 110.2, 99.2 (C), 78.4, 76.4, 75.7, 35.9, 30.9 (CH), 67.8, 64.6, 36.2, 35.1, 25.0, 23.8, 23.6 (CH_2), 29.7, 19.4, 11.8, 5.6 (CH_3). HR EIMS m/z 328.2282 (M^+ , 30), 313 (15), 285 (45), 269 (17), 155 (62), 55 (100). Calcd. for $\text{C}_{18}\text{H}_{32}\text{O}_5$, 328.2249.

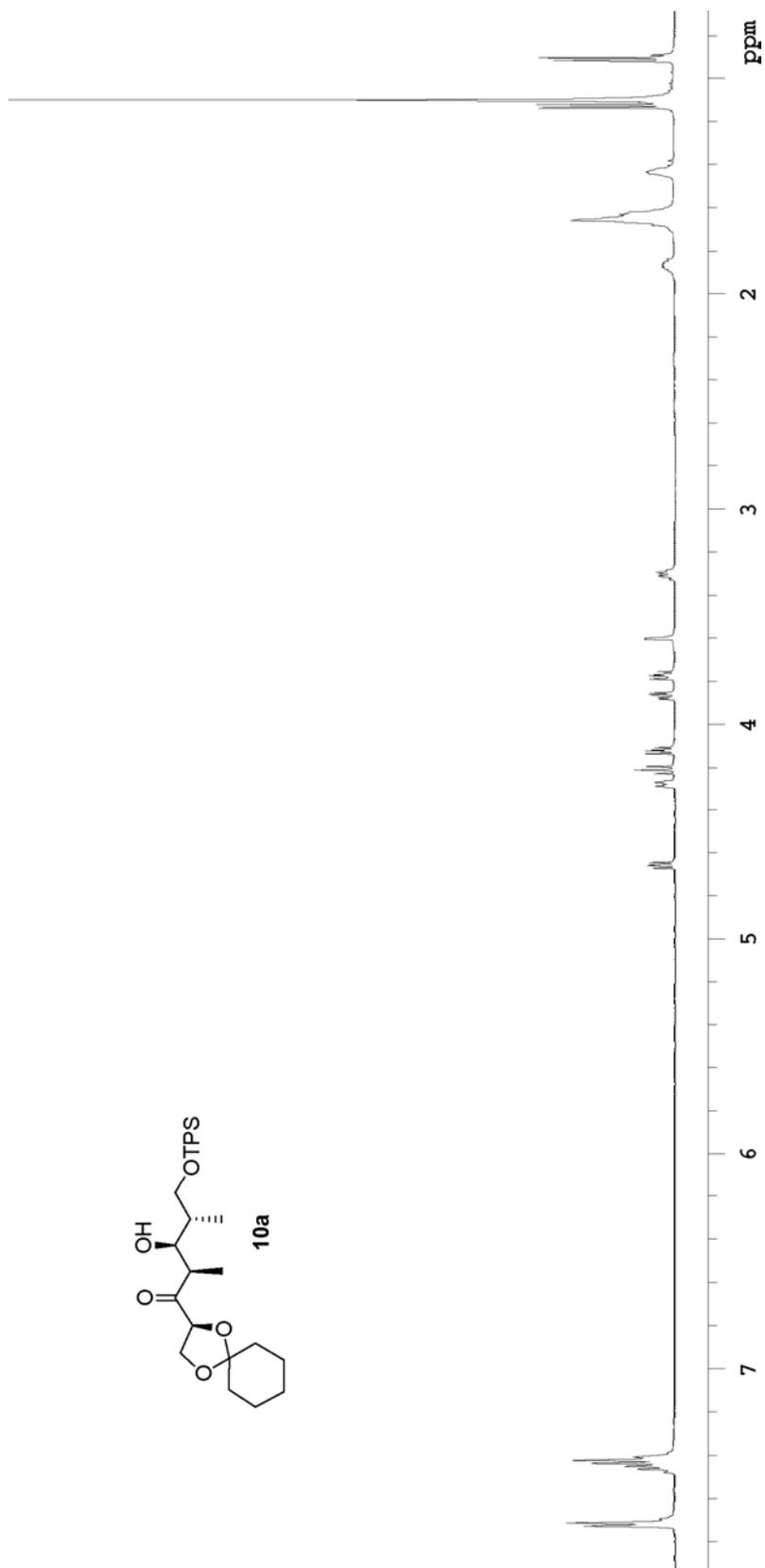
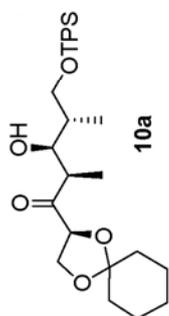


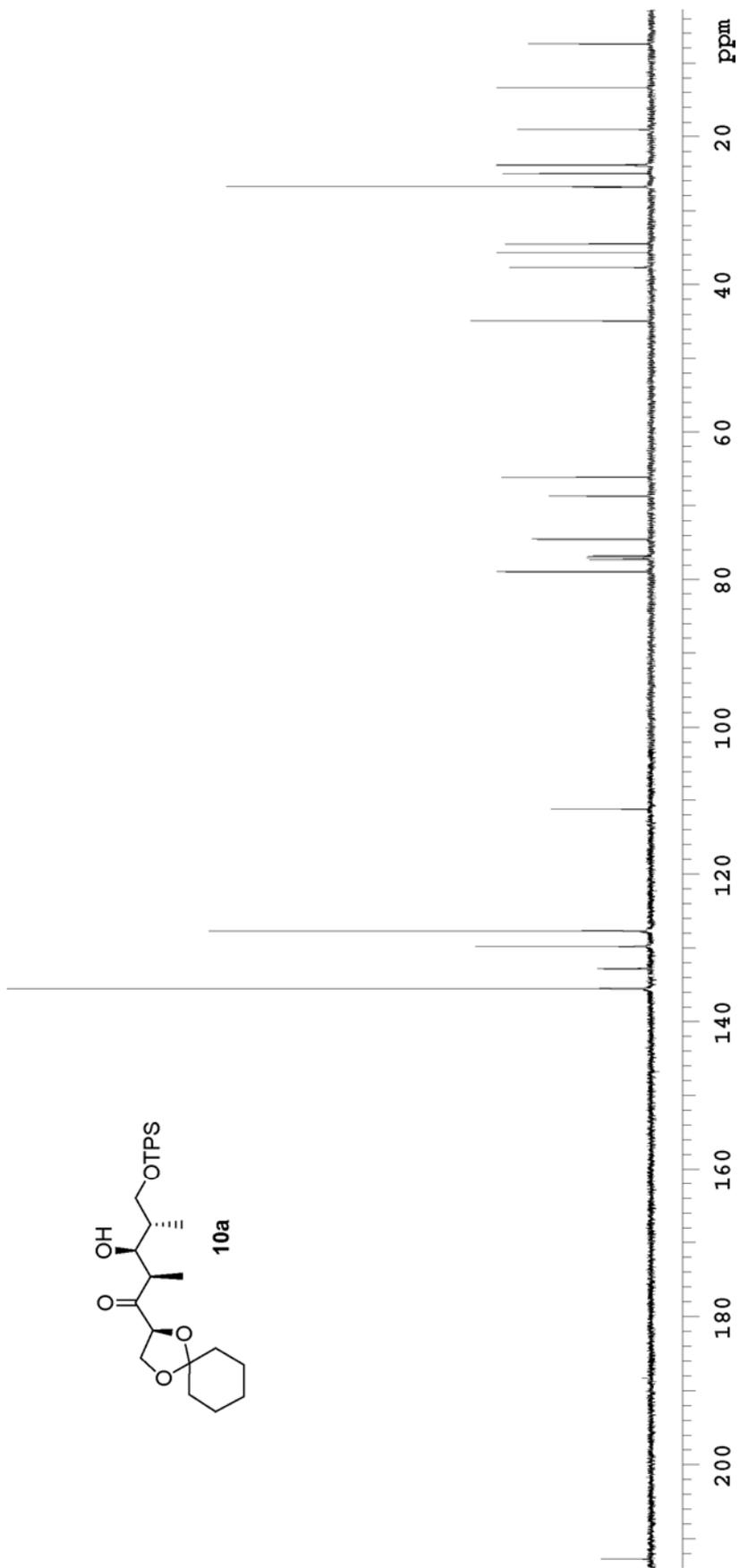
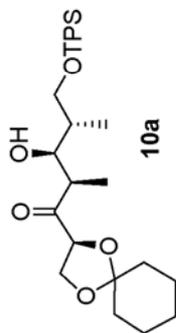
Oil; $[\alpha]_D +30.7$ (c 0.4; CHCl_3). IR 3500 (br), 1733 cm^{-1} . ^1H NMR (500 MHz) δ 7.35-7.25 (5H, br m), 4.61 (1H, d, $J = 11.6$ Hz), 4.41 (1H, d, $J = 11.6$ Hz), 3.90 (1H, dd, $J = 5, 6$ Hz), 3.65 (3H, s), 3.46 (1H, quint, $J = 6$ Hz), 2.80 (1H, dq, $J = 5, 7$ Hz), 2.60 (1H, br s), 1.25 (3H, d, $J = 6$ Hz), 1.16 (3H, d, $J = 7$ Hz); ^{13}C NMR (125 MHz) δ 176.5, 138.3 (C), 128.5, 127.8, 127.7, 74.9, 74.0, 41.0 (CH), 70.7 (CH_2), 51.8, 15.1, 11.7 (CH_3). HR FABMS m/z (rel. int.) 253.1422 ($\text{M}+\text{H}^+$). Calcd. for $\text{C}_{14}\text{H}_{21}\text{O}_4$, 253.1439. NMR data essentially identical to those reported in ref. 2 of page S-5 except that the signal at δ 4.61 is reported there at δ 4.71. This is likely a typographic mistake.

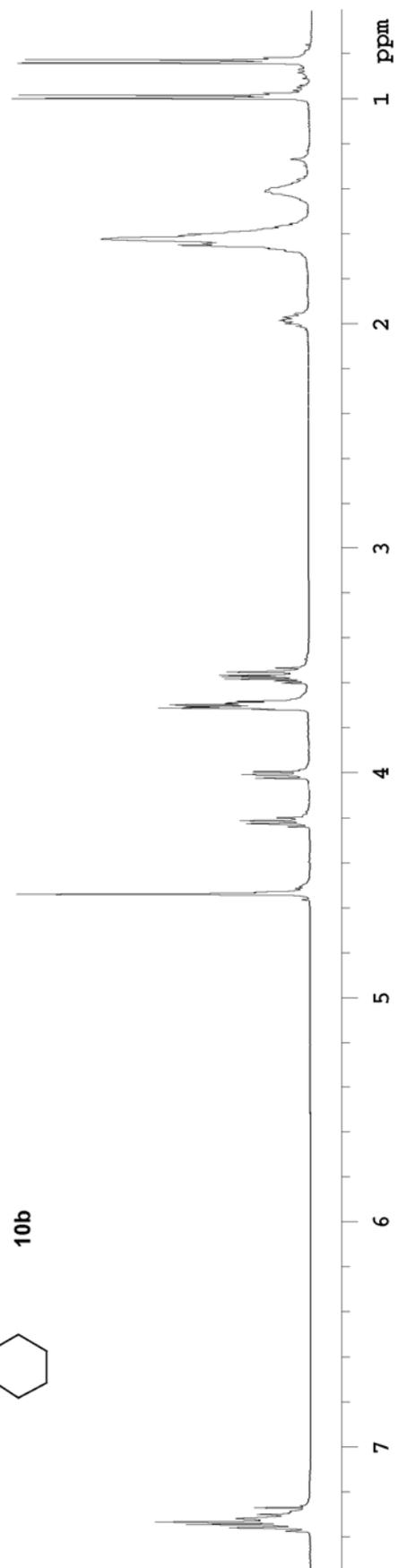
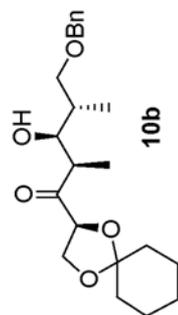


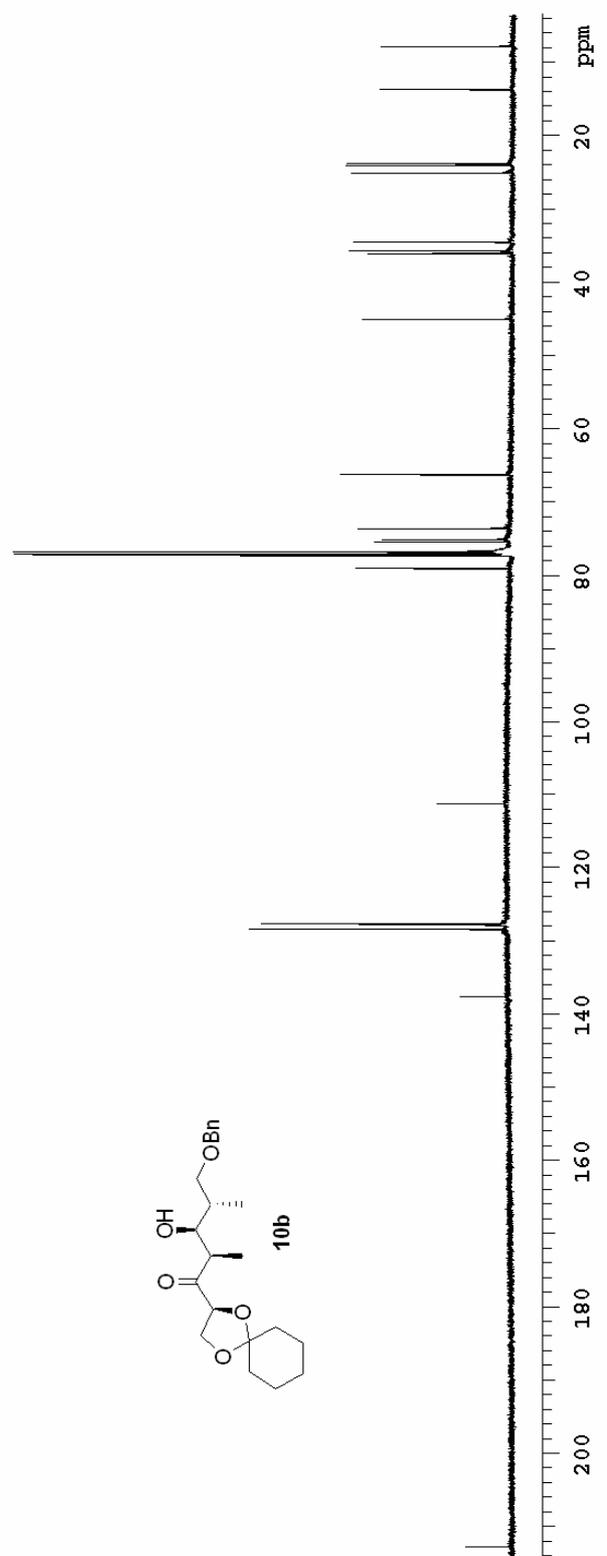
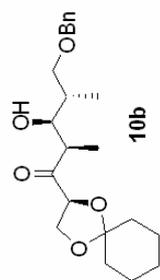
Oil; $[\alpha]_D +2$ (c 1.3; CHCl_3). IR 3480 (br) cm^{-1} . ^1H NMR (500 MHz) δ 4.10 (1H, td, $J = 8, 6.3$ Hz), 3.99 (1H, dd, $J = 8, 6.3$ Hz), 3.76 (1H, dd, $J = 8, 2$ Hz), 3.66 (1H, dq, $J = 8.2, 6$ Hz), 3.59 (1H, t, $J = 8$ Hz), 3.48 (1H, dd, $J = 8.2, 2$ Hz), 2.10 (1H, br s, OH), 1.65-1.40 (11H, br m), 1.39 (6H, s), 1.16 (3H, d, $J = 6$ Hz), 0.88 (3H, d, $J = 7$ Hz); ^{13}C NMR (125 MHz) δ 110.2, 99.2 (C), 77.0, 76.5, 75.7, 66.3, 29.9 (CH), 64.6, 36.2, 35.2, 25.0, 23.8, 23.7 (CH_2), 29.6, 20.4, 19.4, 6.2 (CH_3). HR FABMS m/z (rel. int.) 315.2139 ($\text{M}+\text{H}^+$). Calcd. for $\text{C}_{17}\text{H}_{31}\text{O}_5$, 315.2171.

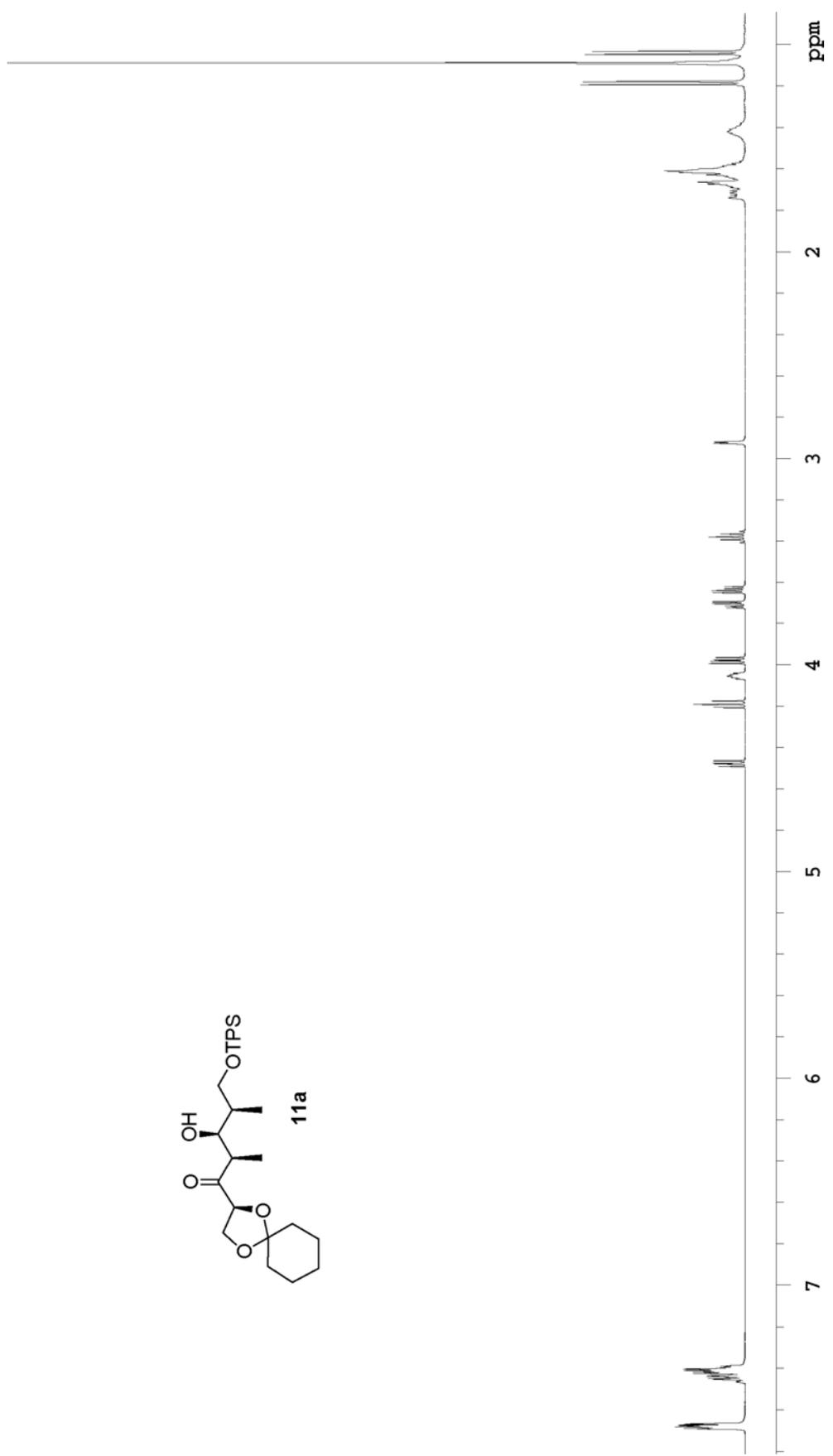
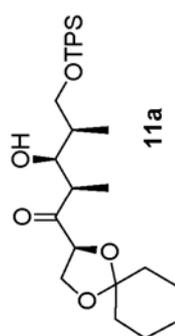
NMR spectra of selected compounds

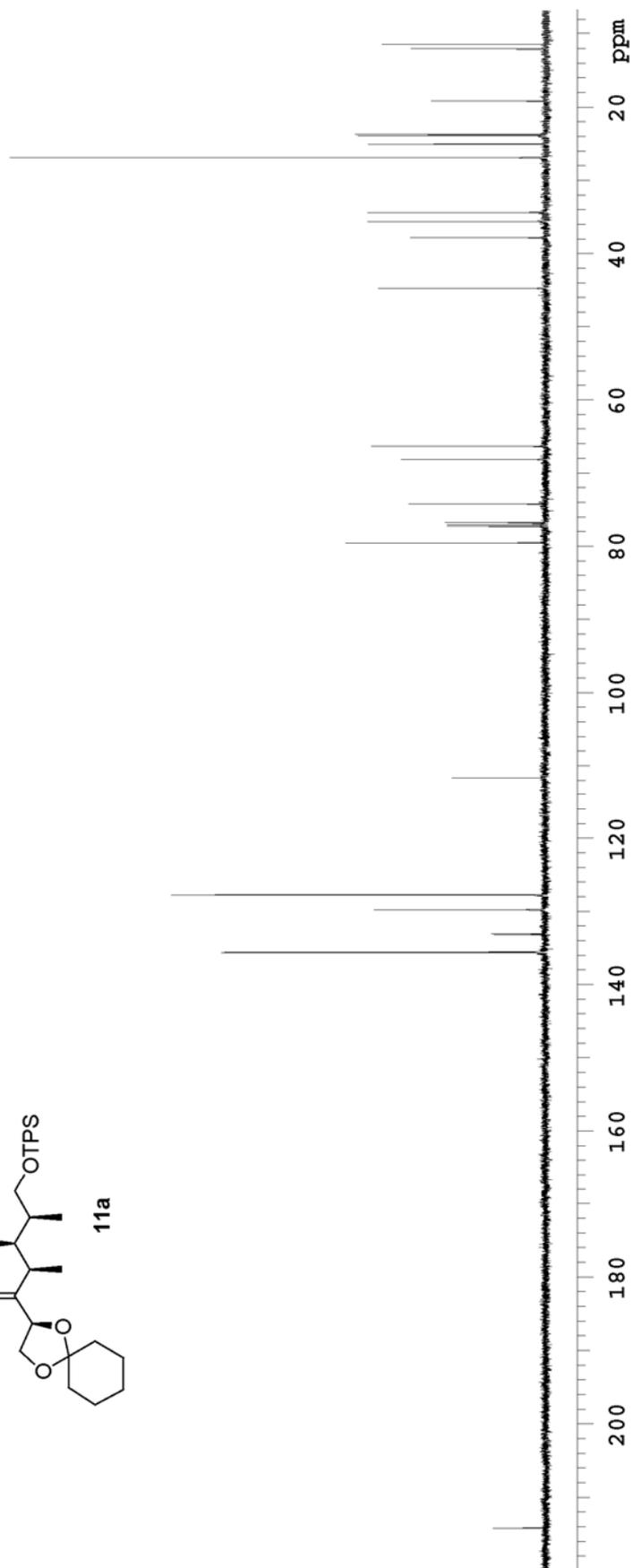
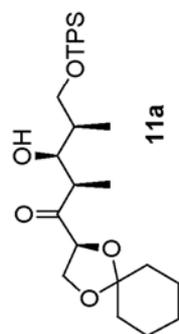


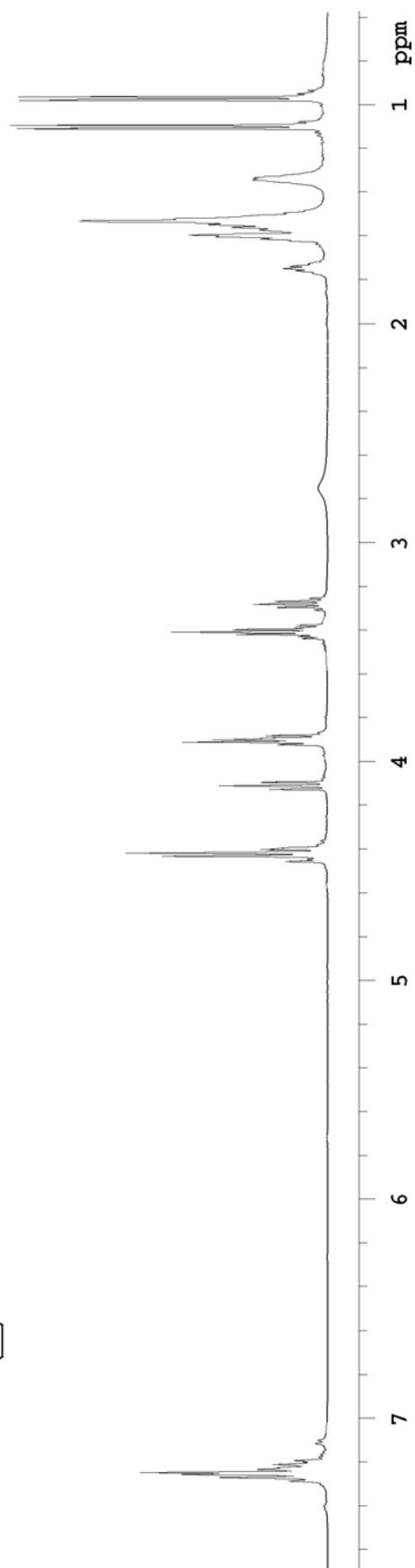
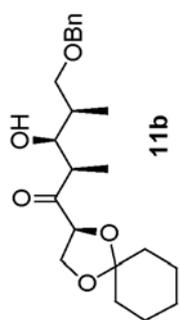


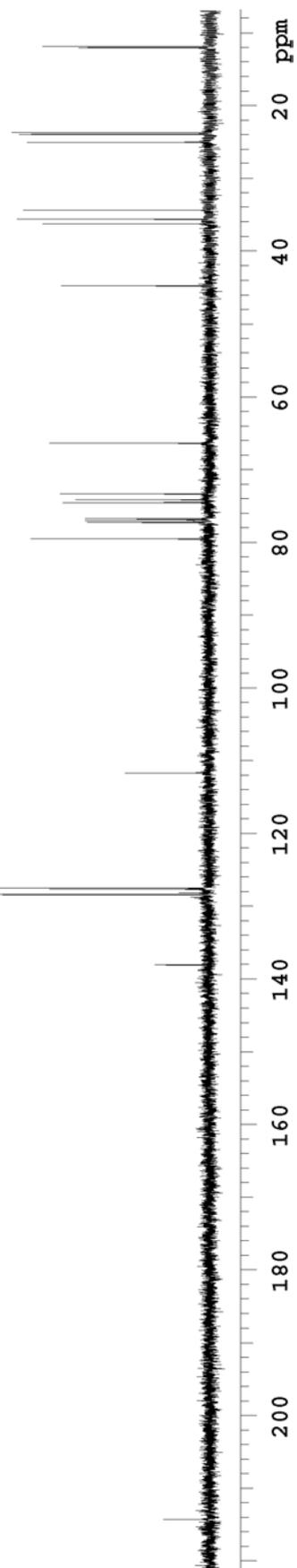
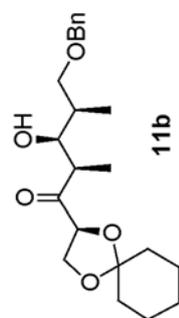


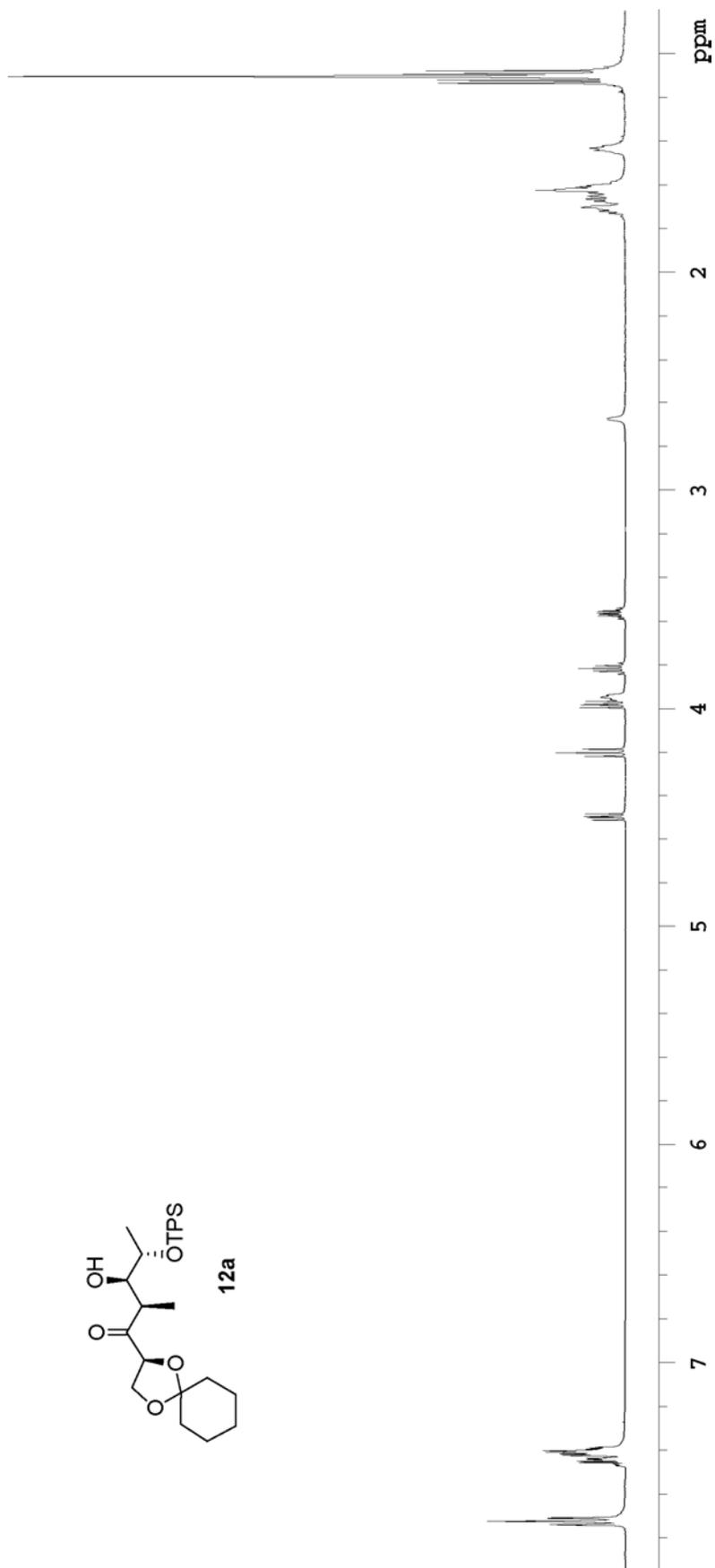
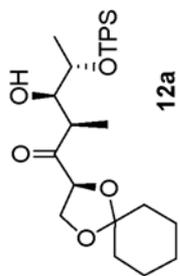


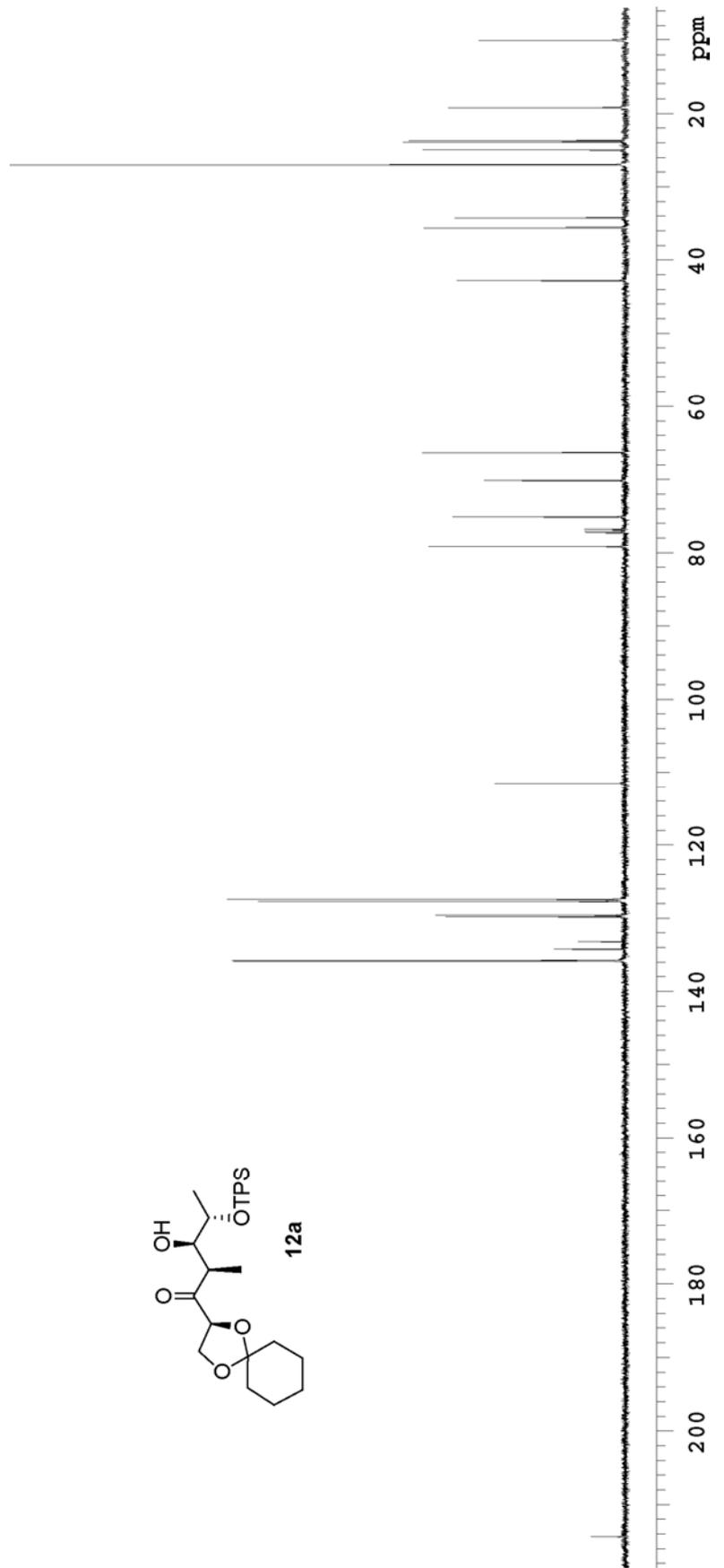
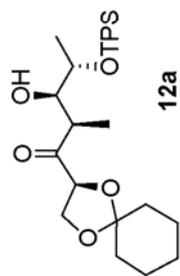


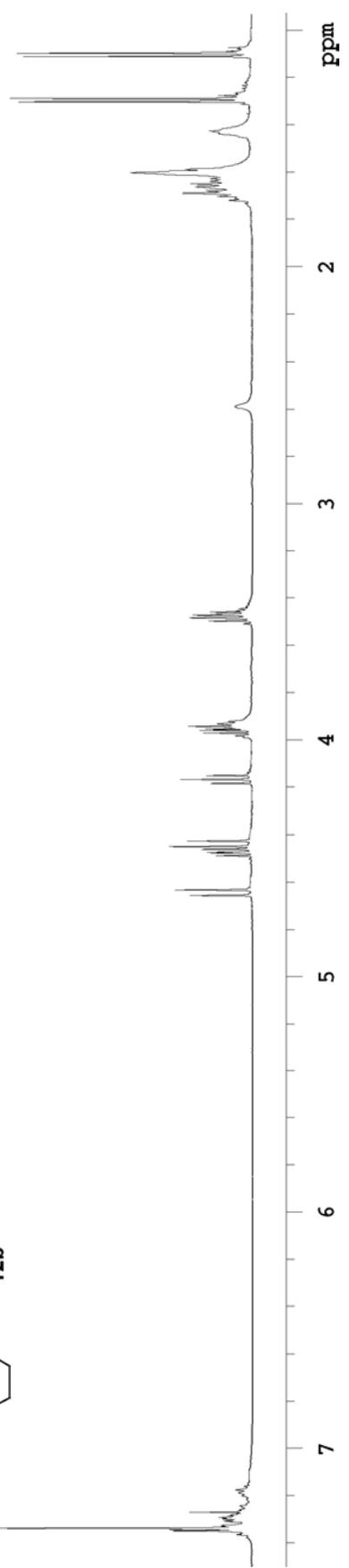
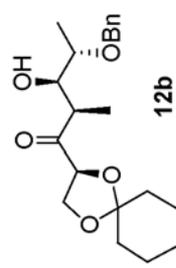


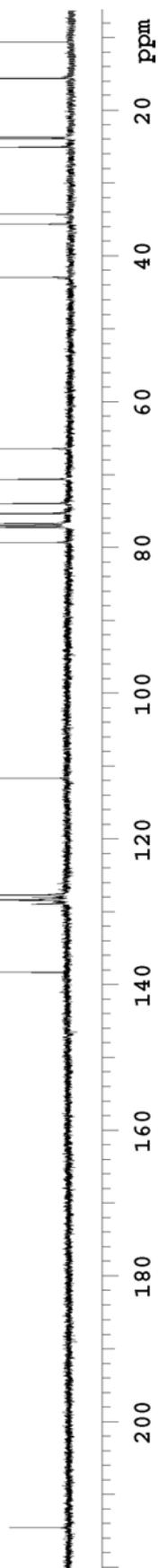
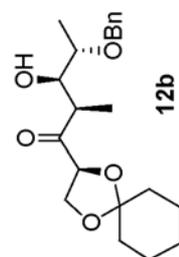


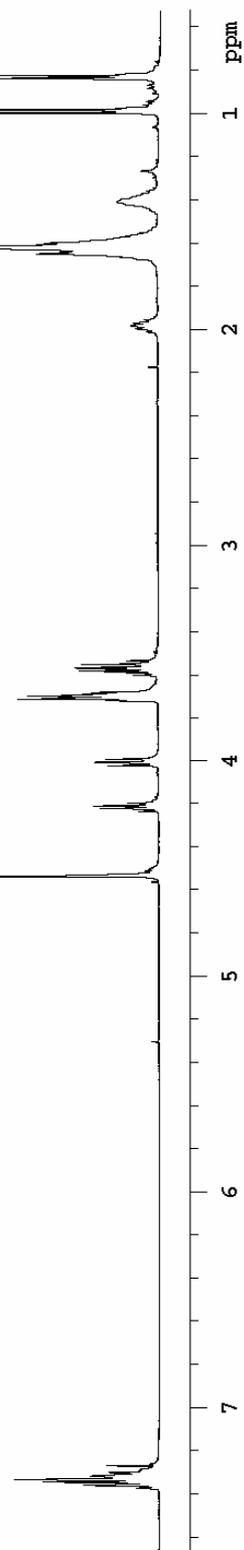
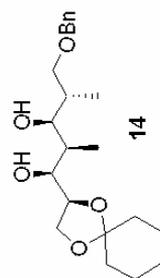


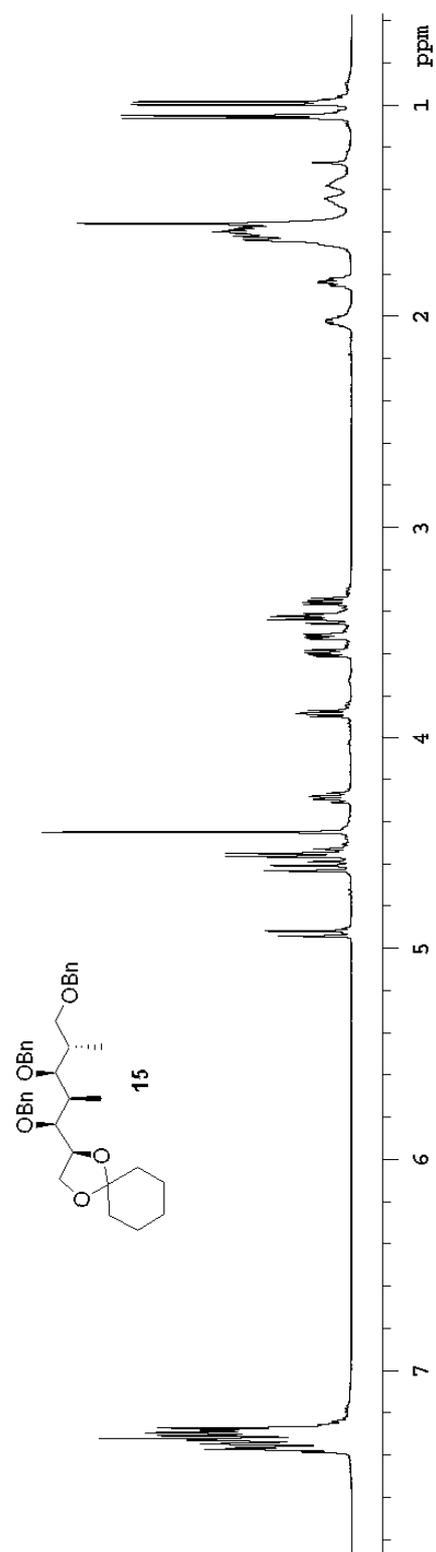


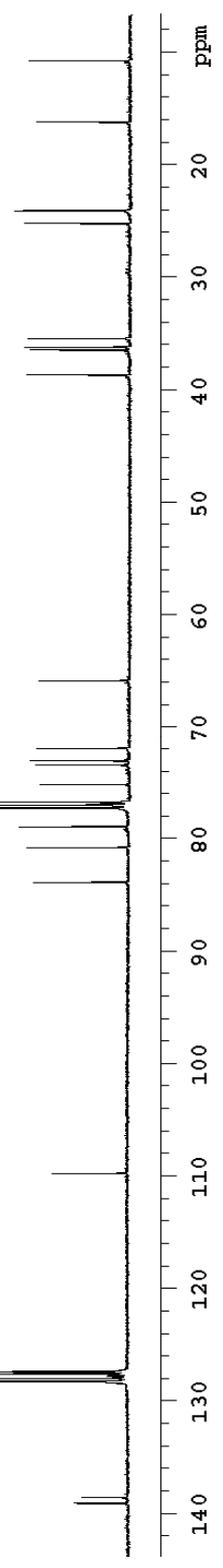
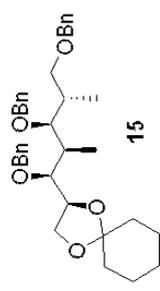


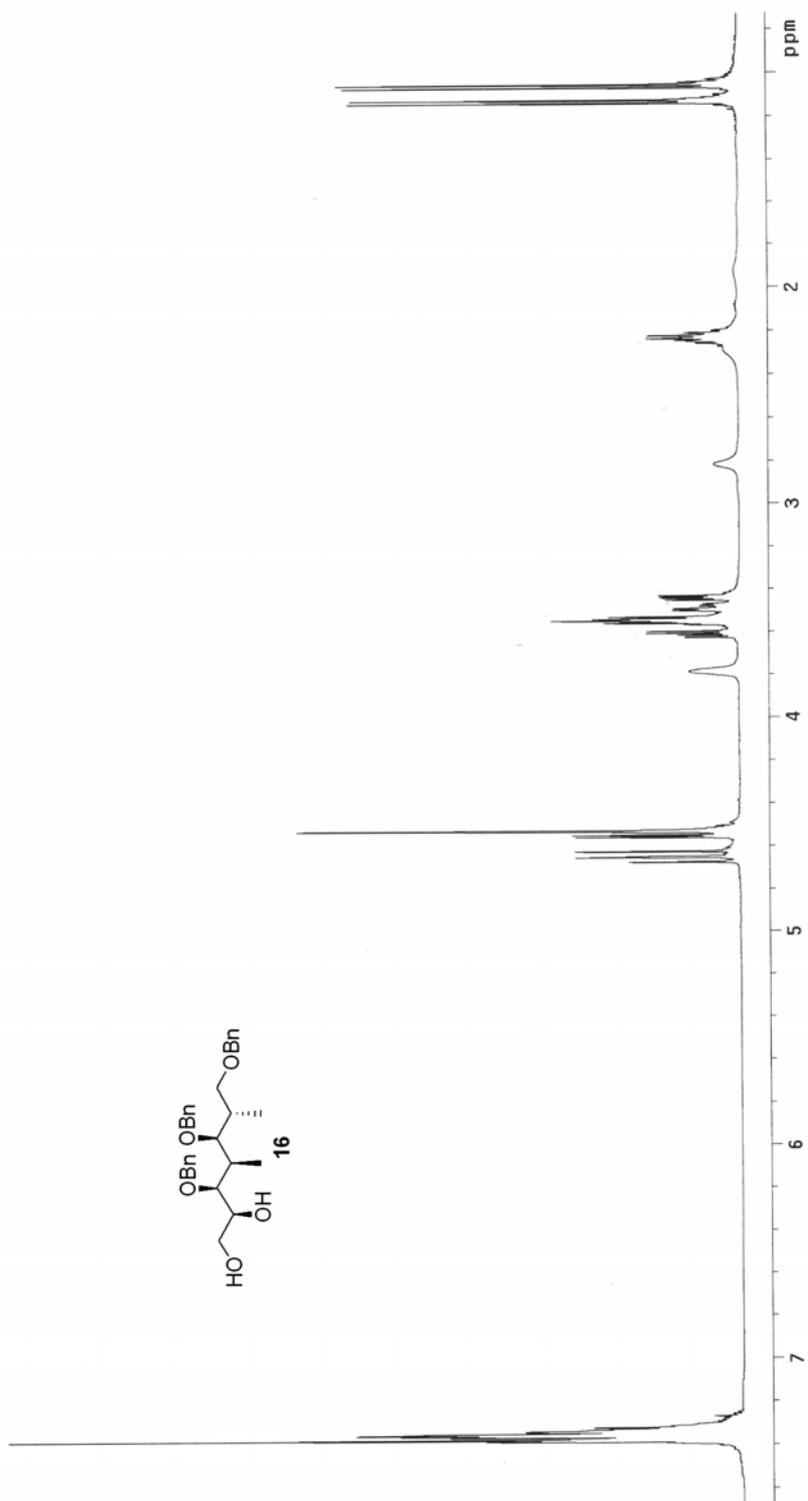


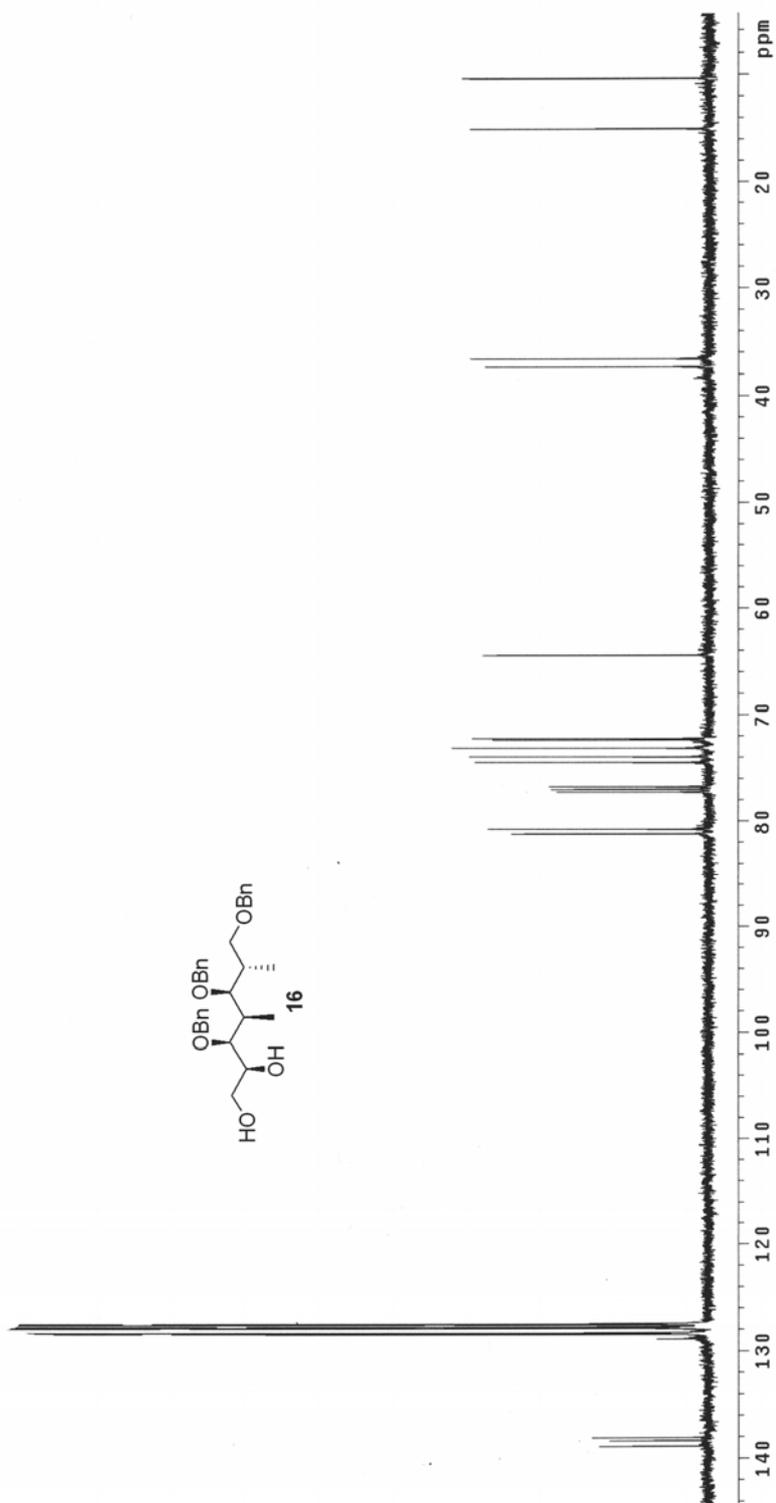


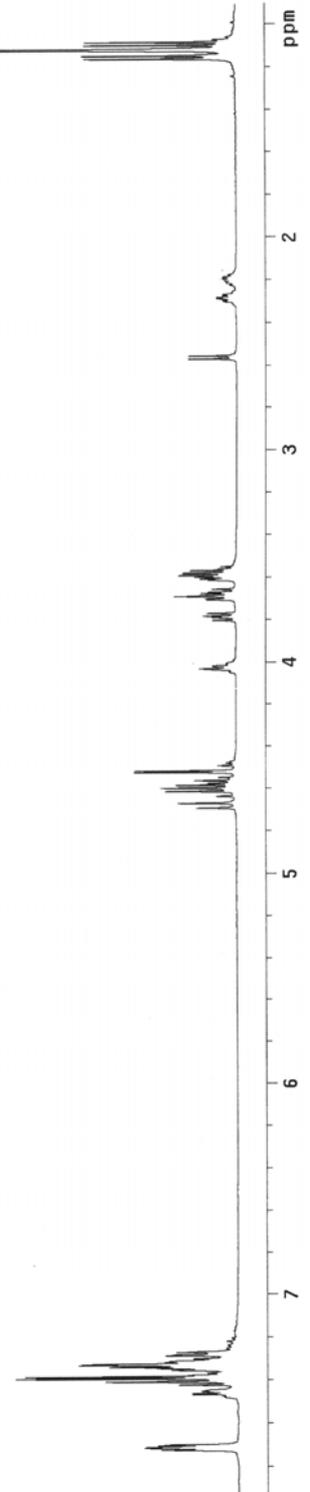
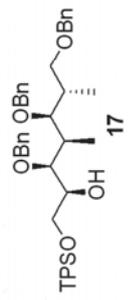


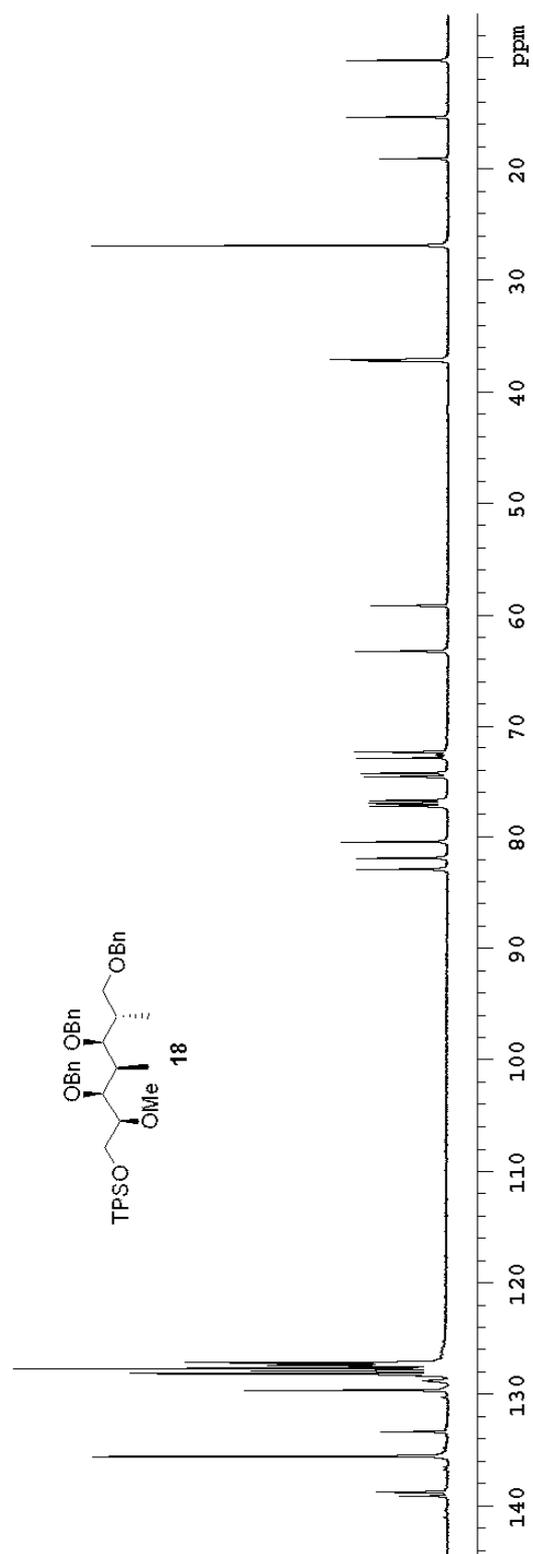


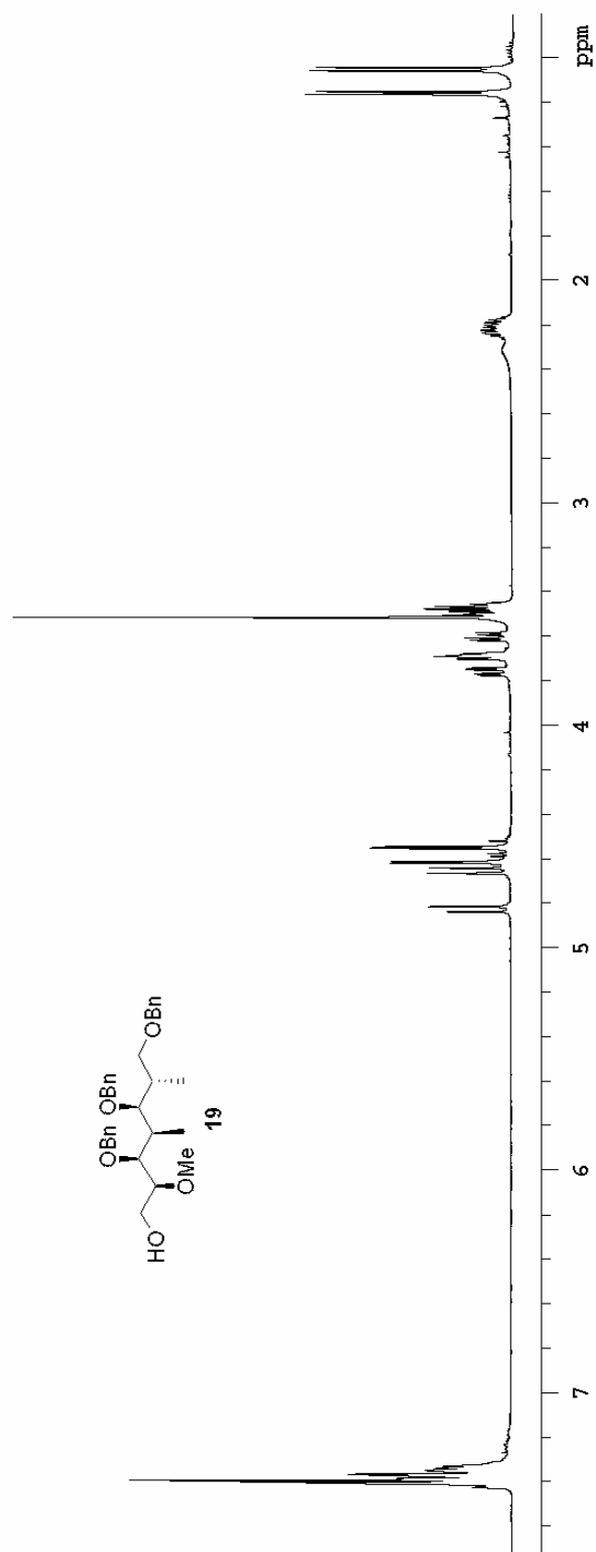


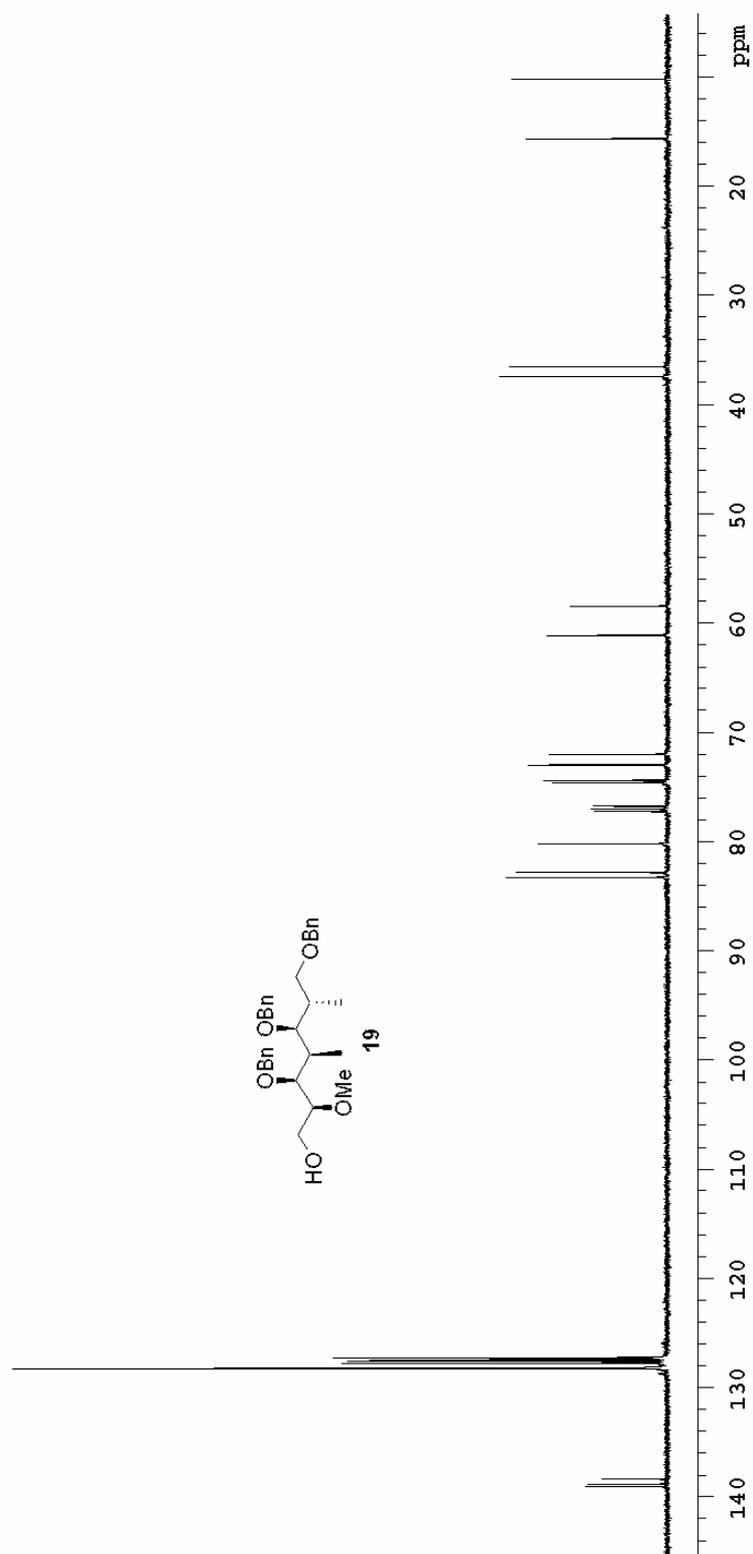


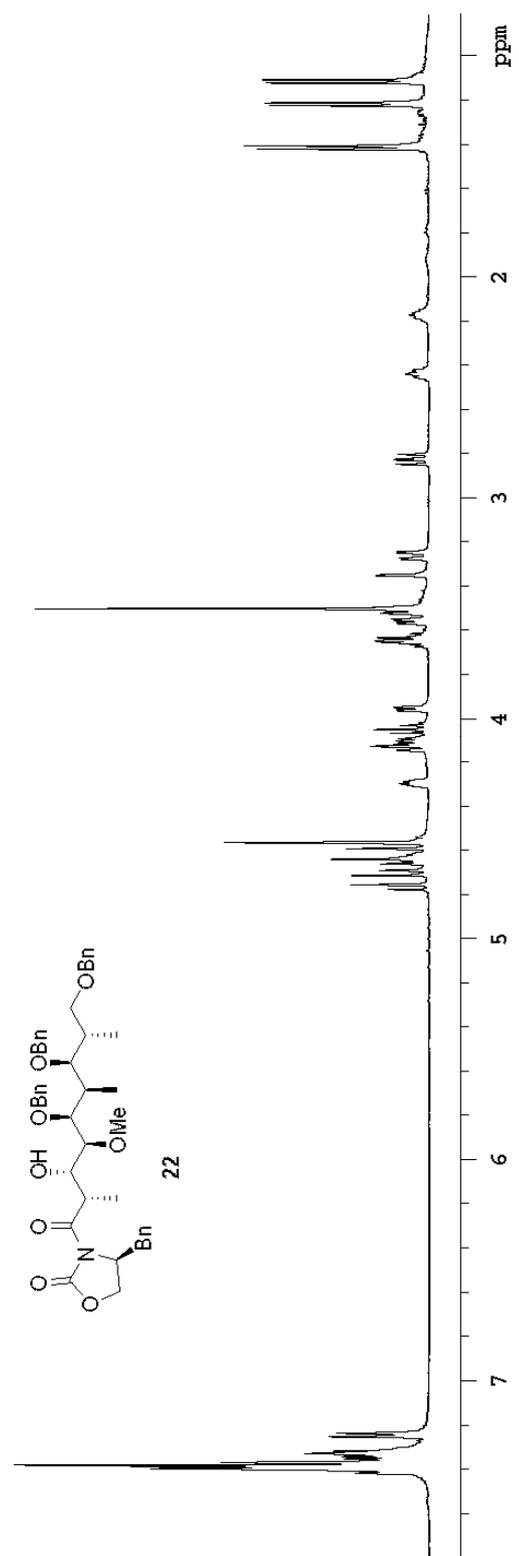


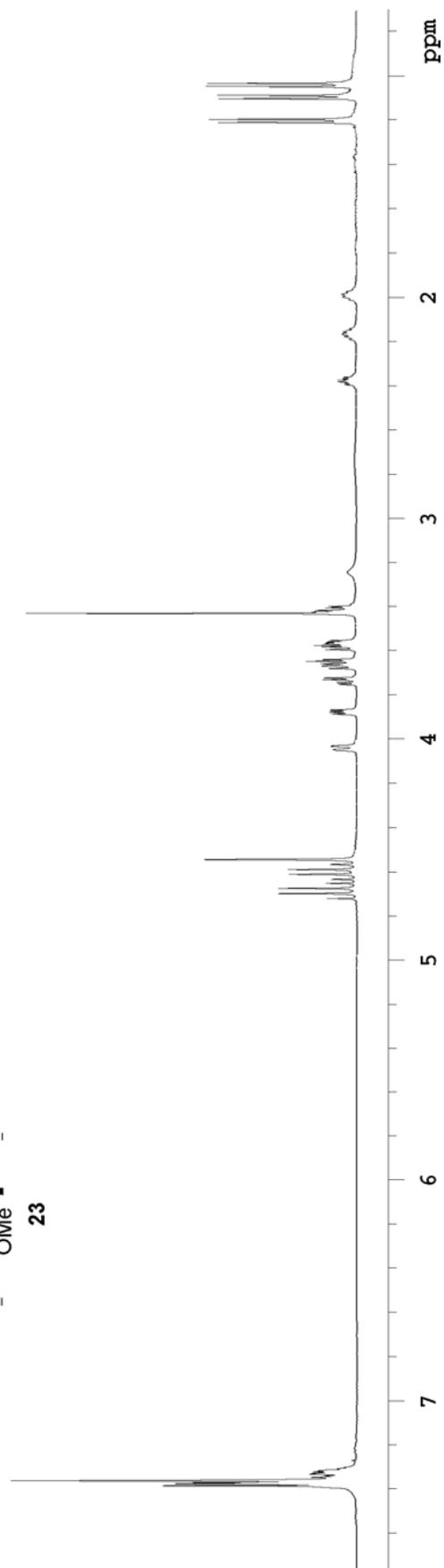
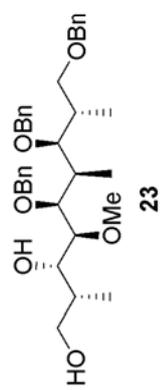


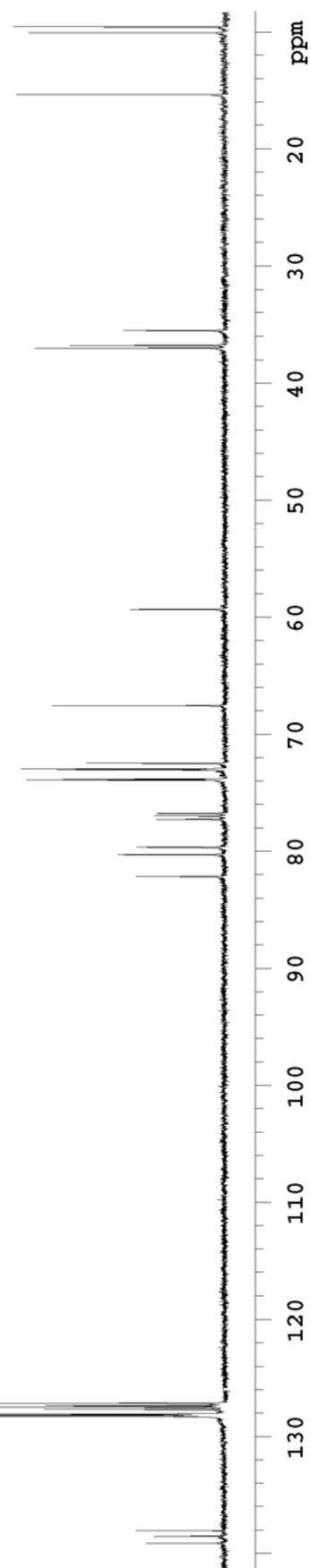
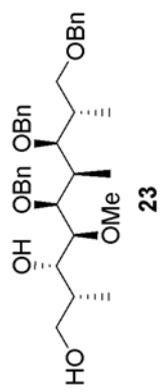


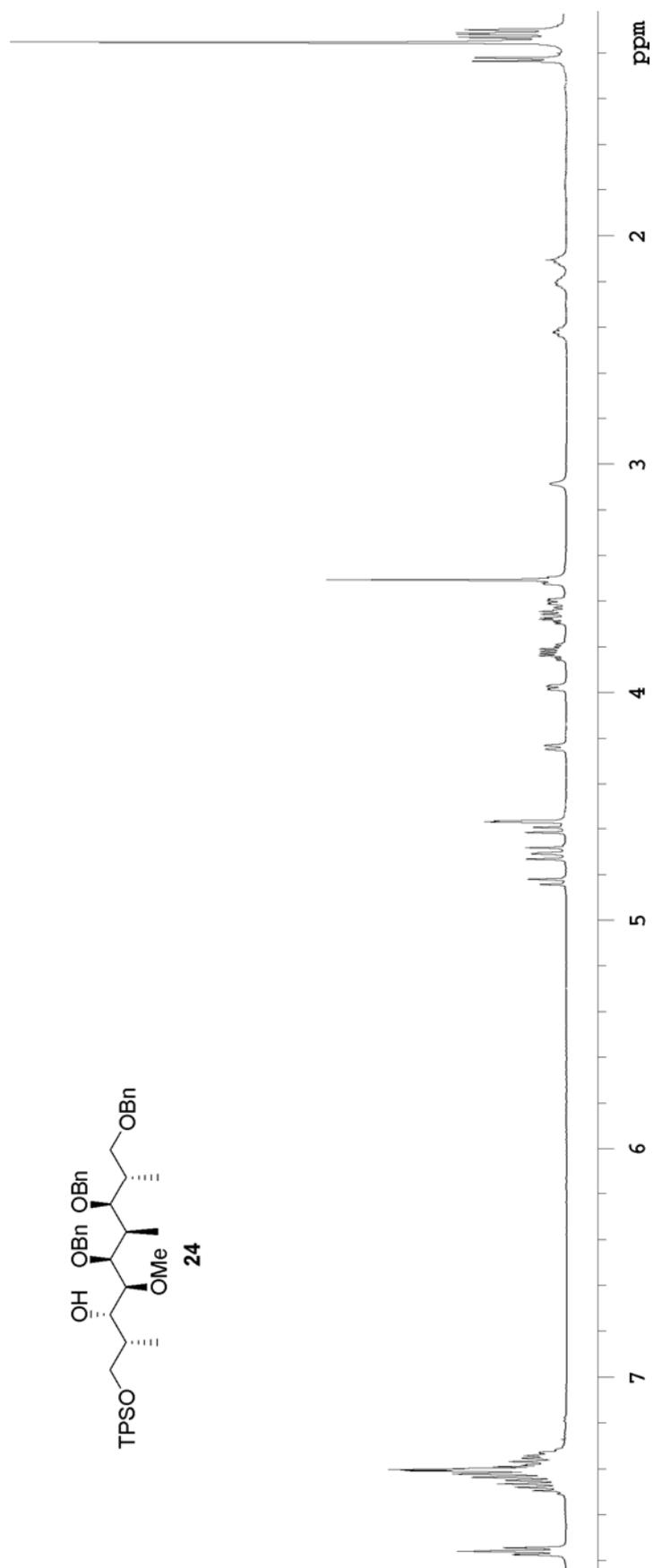


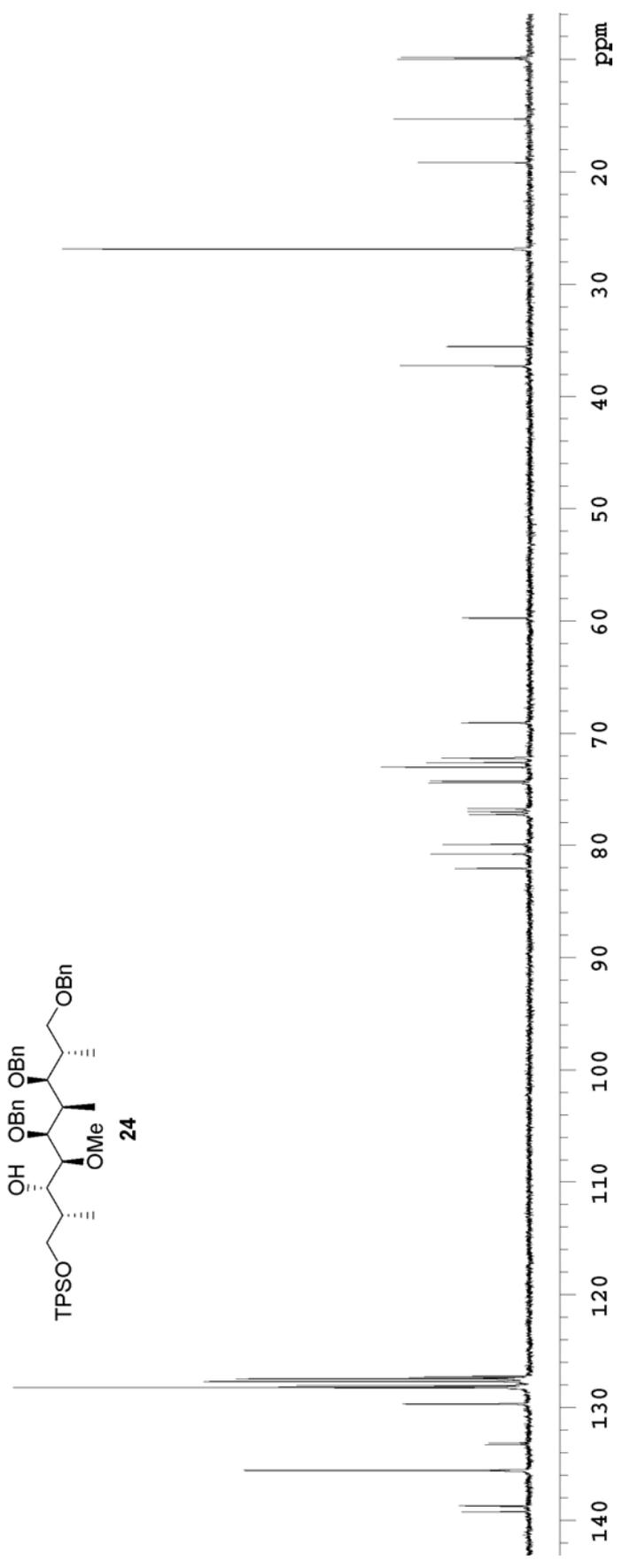
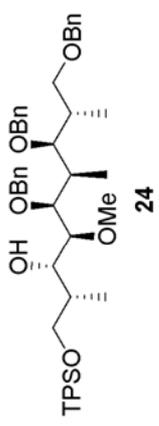


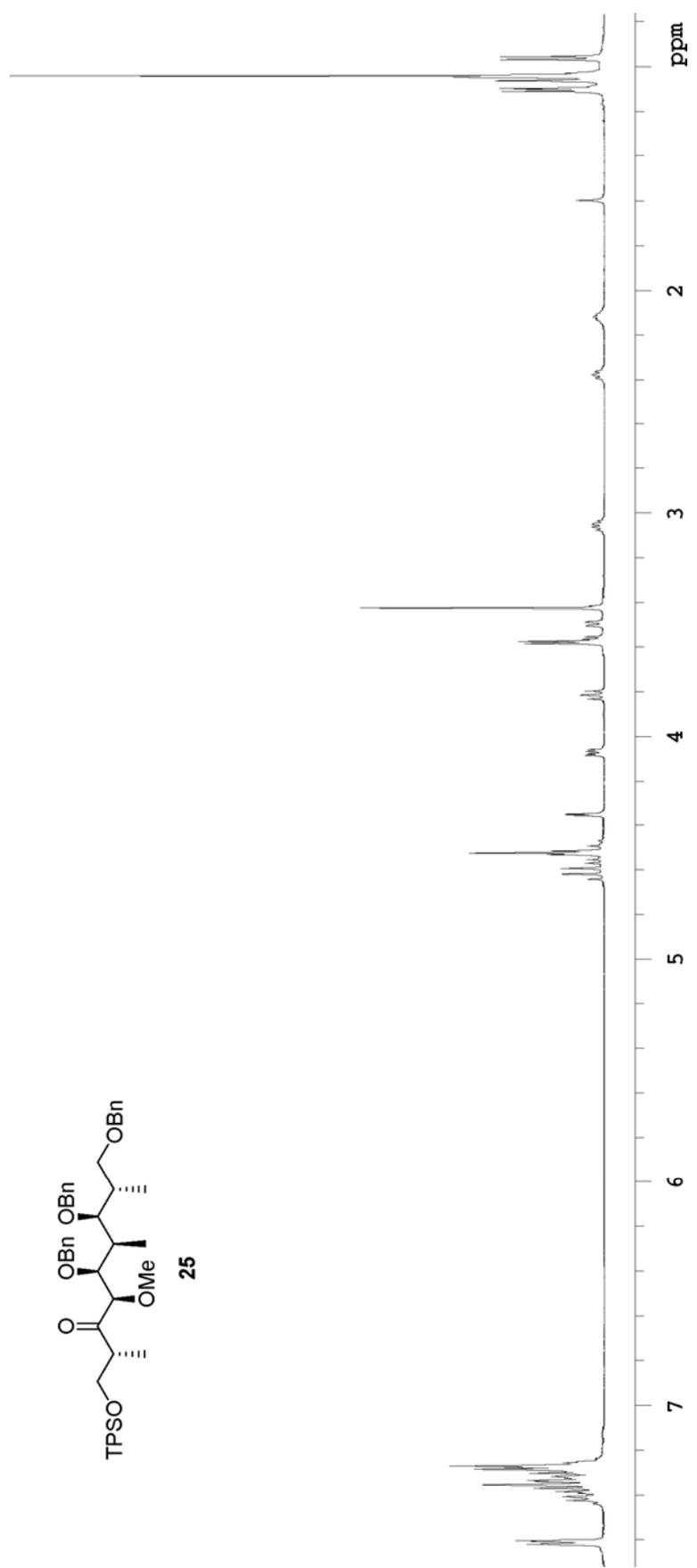
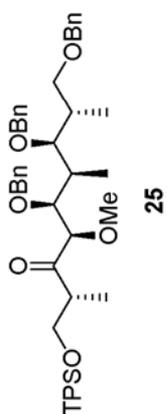


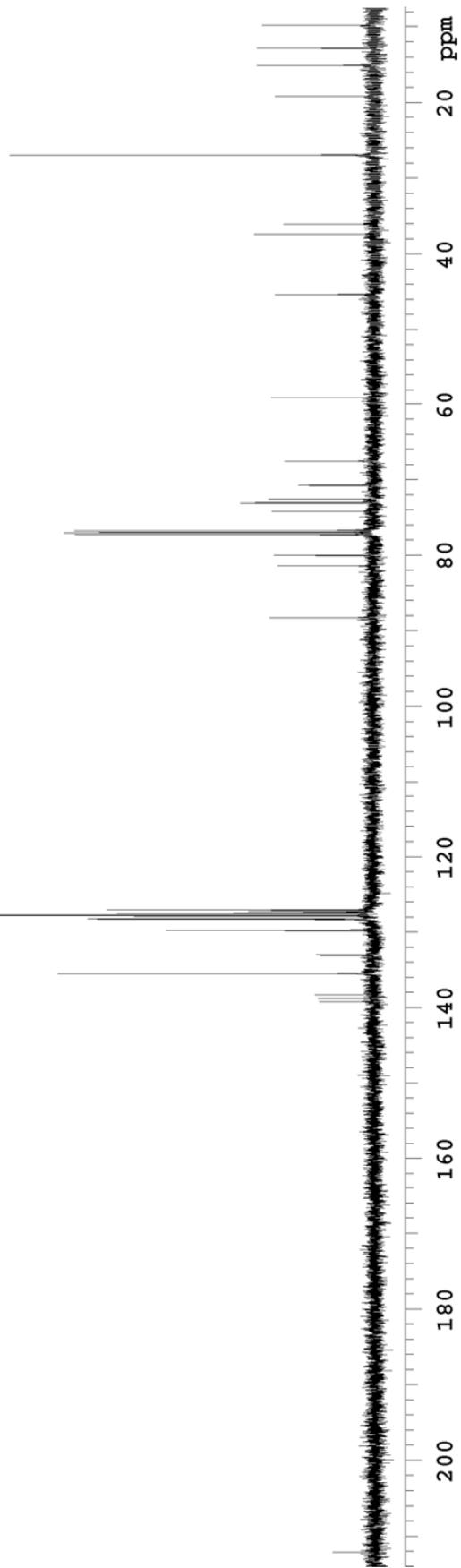
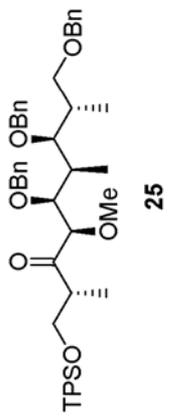


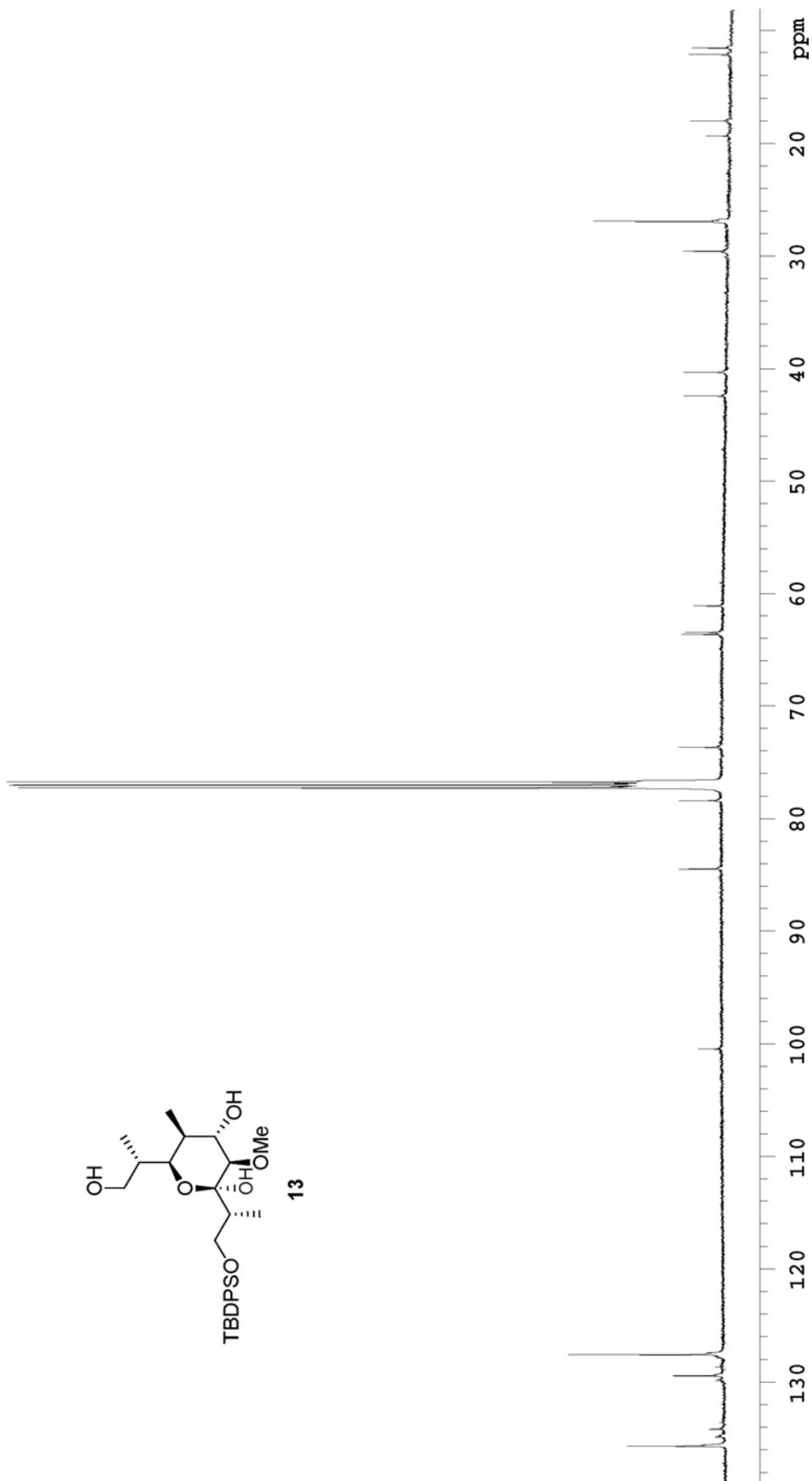
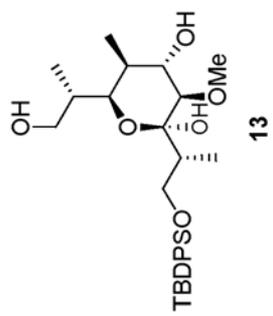


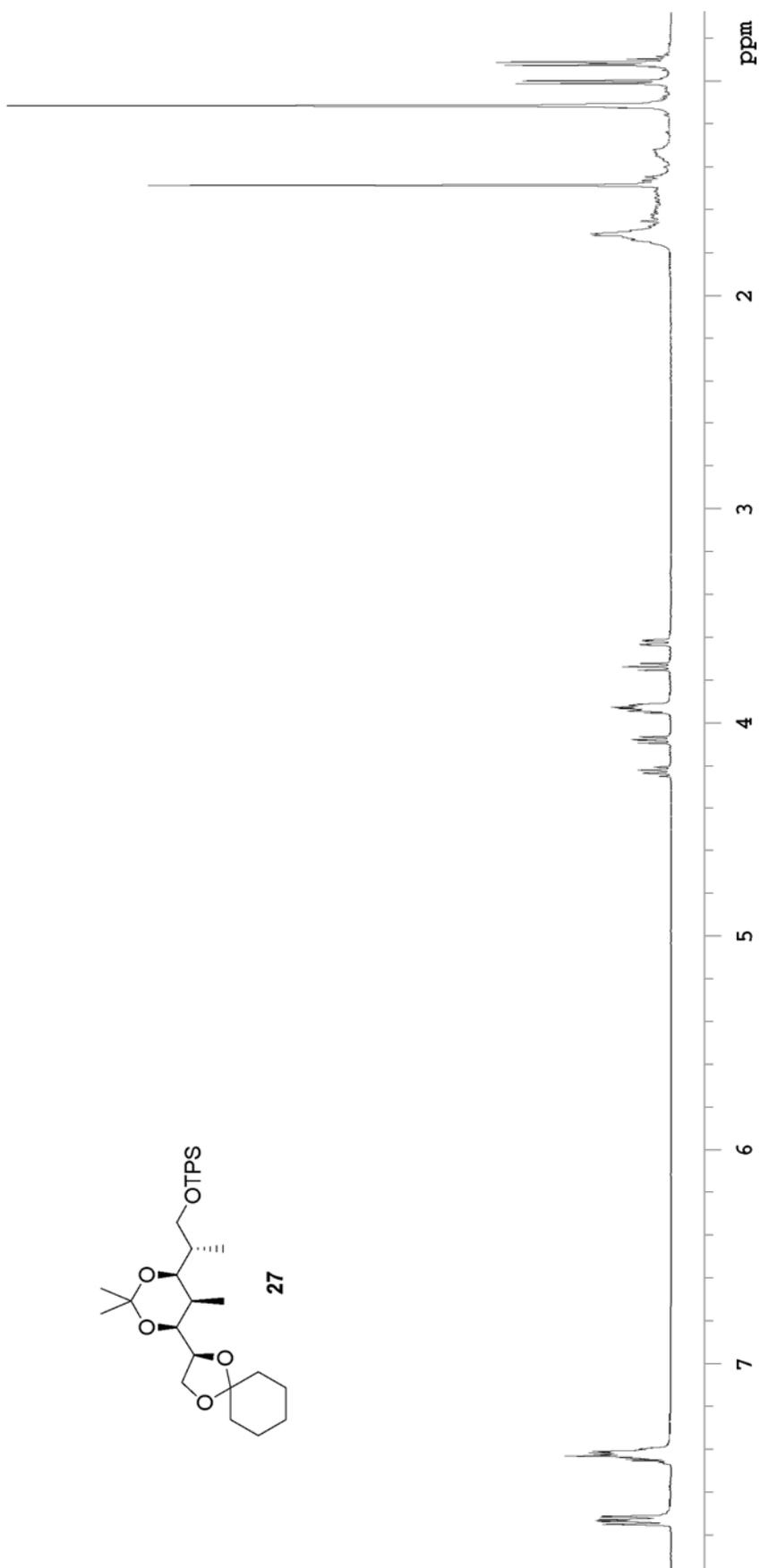
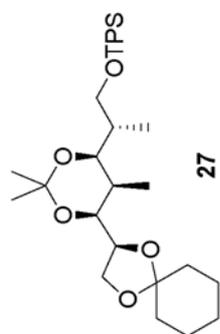


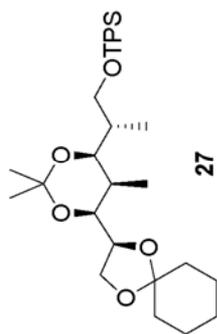












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