Supporting Information

Boron-Catalyzed Site-Selective Reduction of Carbohydrate Derivatives with Catecholborane

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General Experimental

General Methods: All catalytic reactions were performed in oven (130 °C) and/or flame-dried glassware in a nitrogen-filled glovebox. All reactions were performed at ambient temperature (25 ºC, RT) unless otherwise specified. All workup procedures were performed under air with reagent grade reagents unless otherwise specified. Alumina refers to Brockmann activity I neutral alumina gel (Aldrich) that was treated with 10% deionzed water as previously disclosed.[1] Protection of polyol substrates with chlorosilanes has been previously described[2,3] and products were purified via column chromatography using alumina. Column chromatography of isolated products was performed using SilaFlash P60 40-63 μm (230-400 mesh). Thin layer chromatography (TLC) was performed on SiliCycle Silica Gel 60 F254 plates and was visualized with UV light and cerium ammonium molybdate (CAM) stain.

All NMR spectra were recorded on a Bruker Avance 600 MHz, 500 MHz, or 400 MHz spectrometer at standard temperature and pressure, unless otherwise specified. All deuterated solvents were used as received from Cambridge Isotope Laboratories, Inc. The residual solvent protons (^{1}H) or the solvent carbons (^{13}C) were used as internal referencing standards.[4] The following abbreviations are used in reporting NMR data: s, singlet; d, doublet; t, triplet; q, quartet; quint, quintet; dd, doublet of doublets; dt, doublet of triplets; dq, doublet of quartets; td, triplet of doublets; tt, triplet of triplets; quint d, quintet of doublets; ddd, doublet of doublet of doublets; m, multiplet. Where necessary, HSQC, HMBC, COSY, DEPT and APT data were used for peak assignment.

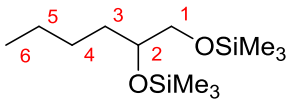
High resolution mass spectra were obtained on a Thermo Scientific Q Exactive HF-X Hybrid Quadrupole-Orbitrap MS System operating in positive ion mode with an electrospray ionization source (ESI).

Chemicals:
Tris(pentafluorophenyl)borane ($B(C_6F_5)_3$) and trityl tetra(pentafluorophenyl)borate ($[C(C_6H_5)_3][B(C_6F_5)_4]$) were purchased from Strem Chemicals and used as received. Catecholborane was purchased from Sigma-Aldrich, distilled prior to use, taken into a nitrogen-filled glovebox and stored at -48 ^{o}C, though it should be noted that it begins to decompose slowly over the course of weeks. Pinacolborane was purchased from Oakwood Chemicals and distilled prior to use, then taken into a nitrogen-filled glovebox and stored under sieves at room temperature. Ethers were purchased from Sigma-Aldrich, Alfa-Aesar, and TCI, dried with CaH_2, and distilled prior to use. Hexanediol was purchased from Sigma-Aldrich and used as received. D-galactitol was purchased from ChemImpex and used as received. D-sorbitol, D-mannitol, isosorbide, and isomannide were purchased from Sigma-Aldrich and used as received. Pyridine (anhydrous, 99%), 4-(dimethylamino)pyridine (DMAP), and copper sulfate (anhydrous) were purchased from Sigma-Aldrich and used as received. Methanol was purchased from Fisher and used as received. CH_2Cl_2 for the catalytic reactions was passed through an alumina column in a solvent purification system prior to use and stored in a nitrogen-filled glovebox under sieves.

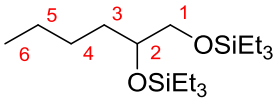
Characterization Data for Reduced Products:
Numbering (in red) in the figures are based on standard sugar labeling from the parent substrate and is provided to track carbons from the starting material. Names provided are IUPAC-based and do not necessarily correlate to the numbering shown in red.

Special Note:
NMR spectra of all sugar derived substrates synthesized in this publication and others from the Gagné lab are available on our website at, http://gagnegroup.web.unc.edu/sugars/. Here you can search for structures by oxygen count and download spectra that are readable in MNova and other data processing programs in order to facilitate future research in this area.

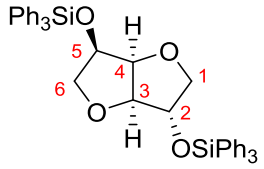
Characterization of Substrates



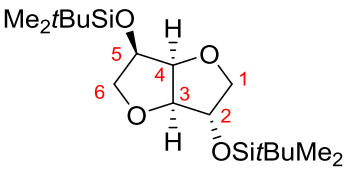
Me_3Si-1,2-hexanediol: $^{13}C\{^1H\}$ NMR(151 MHz, CD_2Cl_2) δ 73.7 (s, C_2), 67.4 (s, C_1), 34.1 (s, C_3), 28.2 (s, C_4), 23.3 (s, C_5), 14.3 (s, C_6), 0.5 (s, -Si(CH_3)$_3$), -0.4 (s, -Si(CH_3)$_3$). ^1H NMR (600 MHz, CD_2Cl_2) δ 3.63 (dtd, *J* = 7.6, 5.5, 4.2 Hz, 1H, H_2), 3.46 – 3.38 (m, 2H, H_1), 1.52 – 1.45 (m, 1H, H_3), 1.43 – 1.18 (m, 5H, $H_{3',4,5}$), 0.90 (t, *J* = 7.2 Hz, 3H, H_6), 0.10 (s, 9H, -Si(CH_3)$_3$), 0.10 (s, 9H, -Si(CH_3)$_3$).



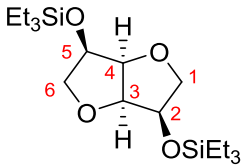
Et_3Si-1,2-hexanediol: $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$) δ 73.4 (s, C_2), 67.4 (s, C_1), 34.3 (s, C_3), 27.6 (s, C_4), 23.1 (s, C_5), 14.2 (s, C_1), 7.1, 6.9, 5.2, 4.5 (each an s, -SiCH_2CH_3 or -SiCH_2CH_3) . ^1H NMR (600 MHz,$CDCl_3$) δ 3.69 – 3.64 (m, 1H, H_2), 3.51 (dd, *J* = 9.9, 5.7 Hz, 1H, H_1), 3.41 (dd, *J* = 9.9, 6.2 Hz, 1H, $H_{1'}$), 1.61 – 1.52 (m, 1H, H_3), 1.43 – 1.24 (m, 5H, $H_{3',4,5}$), 0.96 (app m, 18H, -SiCH_2CH_3), 0.90 (t, *J* = 7.1 Hz, 1H, H_6), 0.64 – 0.57 (m, 12H, -SiCH_2C_3).



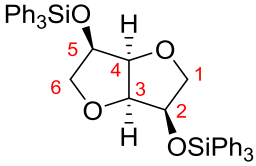
Ph_3Si-isosorbide: $^{13}C\{^1H\}$ NMR (151 MHz, CD_2Cl_2) δ 135.8, 135.7, 130.7, 130.7, 128.4, 128.4 (each an s, -SiPh_3), 88.4 (s, C_3), 82.1 (s, C_4), 79.0 (s, C_2), 76.3 (s, C_1), 75.0 (s, C_5), 71.4 (s, C_6). ^1H NMR (600 MHz, CD_2Cl_2) δ 7.70 – 7.65 (m, 6H, -SiPh_3), 7.64 – 7.60 (m, 6H, -SiPh_3), 7.50 – 7.46 (m, 6H, -SiPh_3), 7.42 (m, 12H, -SiPh_3), 4.50 (app t, *J* = 4.3 Hz, 1H, H_4), 4.44 (dd, *J* = 3.3, 1.6 Hz, 1H, H_2), 4.41 (ddd, *J* = 8.0, 6.5, 4.5 Hz, 1H, H_5), 4.34 (app d, *J* = 4.1 Hz, 1H, H_3), 3.93 (app d, 10 Hz, 1H, H_1), 3.87 (dd, *J* = 9.9, 3.4 Hz, 1H, $H_{1'}$), 3.61 (dd, *J* = 8.5, 6.6 Hz, 1H, H_6), 3.49 (app t, *J* = 8.2 Hz, 1H, $H_{6'}$).



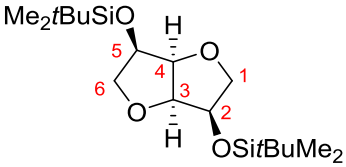
***t*BuMe$_2$Si-isosorbide:** $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$) δ 88.8 (s, C_3), 81.9 (s, C_4), 77.7 (s, C_2), 76.5 (s, C_1), 74.2 (s, C_5), 71.6 (s, C_6), 26.1 (s, -SiC(*C*H$_3$)$_3$), 25.9 (s, -SiC(*C*H$_3$)$_3$), 18.6 (s, -Si*C*(CH$_3$)$_3$), 18.3 (s, -Si*C*(CH$_3$)$_3$), -4.9, -4.7, -4.7, -4.6 (each an s, -Si*C*H$_3$) . ^{1}H NMR (600 MHz, $CDCl_3$) δ 4.46 (app t, *J* = 4.4 Hz, 1H, H_4), 4.29 (app d, *J* = 4.2 Hz, 1H, H_3), 4.27 (ddd, *J* = 7.7, 6.4, 4.5 Hz, 1H, H_5), 4.25 – 4.22 (m, 1H, H_2), 3.93 (dd, *J* = 9.5, 3.8 Hz, 1H, H_1), 3.79 (app d, *J* = 9.7 Hz, 1H, $H_{1'}$), 3.76 (dd, *J* = 8.4, 6.3 Hz, 1H, H_6), 3.50 (app t, *J* = 8.2 Hz, 1H, $H_{6'}$) , 0.90 (s, 9H, -SiC(C*H*$_3$)$_3$), 0.88 (s, 9H, -SiC(C*H*$_3$)$_3$), 0.11 (s, 3H, -SiC*H*$_3$), 0.10 (s, 3H, -SiC*H*$_3$), 0.07 (s, 3H, -SiC*H*$_3$), 0.07 (s, 3H, -SiC*H*$_3$).



Et$_3$Si-isomannide: $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$) δ 81.9 (s, C_3 & C_4), 74.1 (s, C_2 & C_5), 72.6 (s, C_1 & C_6), 6.8 (s, -SiCH$_2$*C*H$_3$), 4.7 (s, -Si*C*H$_2$CH$_3$). ^{1}H NMR (600 MHz, $CDCl_3$) δ 4.31 (app dt, *J* = 4.1, 2.0 Hz, 2H, H_3 & H_4), 4.27 (m, 2H, H_2 & H_5), 3.89 (dd, *J* = 8.3, 6.8 Hz, 2H, H_1 & H_6), 3.60 (app t, *J* = 8.4 Hz, 2H, $H_{1'}$ & H_6'), 0.95 (t, *J* = 8.0 Hz, 18H, -SiCH$_2$C*H*$_3$), 0.62 (q, *J* = 8.1 Hz, 12H, -SiC*H*$_2$CH$_3$).



Ph$_3$Si-isomannide: $^{13}C\{^1H\}$ NMR (151 MHz, CD_2Cl_2) δ 135.7, 130.6, 128.3 (each an s, -Si*Ph*$_3$), 81.6 (s, C_3 & C_4), 75.0 (s, C_2 & C_5), 72.8 (s, C_1 & C_6). ^{1}H NMR (600 MHz, CD_2Cl_2) δ 7.67 – 7.63 (m, 12H, -Si*Ph*$_3$), 7.48 – 7.44 (m, 6H, -Si*Ph*$_3$), 7.42 – 7.37 (m, 12H, -Si*Ph*$_3$), 4.41 – 4.36 (m, 2H, H_2 & H_5), 4.08 – 4.06 (m, 2H, H_3 & H_4), 3.81 (dd, *J* = 8.5, 6.8 Hz, 2H, H_1 & H_6), 3.75 (app t, *J* = 8.5 Hz, 2H, $H_{1'}$ & $H_{6'}$).



***t*BuMe$_2$Si-isomannide:** $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$) δ 81.7 (s, C_3 & C_4), 74.3 (s, C_2 & C_5), 72.8 (s, C_1 & C_6), 26.1 (s, -SiC(*C*H$_3$)$_3$), 18.6 (s, -Si*C*(CH$_3$)$_3$), -4.8 (s, -Si*C*H$_3$), -4.6 (s, -Si*C*H$_3$). ^{1}H NMR (600 MHz, $CDCl_3$) δ 4.30 (m, 2H, H_3 & H_4), 4.26 (m, 2H, H_2 & H_5), 3.85 (dd, *J* = 8.5, 6.6 Hz, 2H, H_1 & H_6), 3.59 (app t, *J* = 8.3 Hz, 2H, $H_{1'}$ & $H_{6'}$), 0.90 (s, 18H, -SiC(C*H*$_3$)$_3$), 0.10 (s, 6H, -SiC*H*$_3$), 0.09 (s, 6H, -SiC*H*$_3$).

Substrates not characterized here have been previously reported.[5]

Reduction of Simple Ethers

General Procedure: In a nitrogen-filled glovebox, a 1-dram vial was charged with $B(C_6F_5)_3$ (5.1 mg, 0.01 mmol, 0.05 equiv.) and hexamethylbenzene (3.7 mg, 0.22 mmol, 1.1 equiv.) and dichloromethane was added by syringe. To the $B(C_6F_5)_3$ solution was added ether (0.2 mmol, 1.0 equiv.) and hydroborane (0.3 mmol, 1.5 equiv.) both by microliter syringe or microliter pipet with the hydroborane in excess to ensure full reduction. The vial was capped and shaken manually for 30 seconds. The solution was subsequently transferred by syringe to an NMR tube, which was capped with a septum and removed from the box. The NMR tube was allowed to stand for the appropriate time until the reaction was complete. Peaks identified as the borate ester were integrated relative to the methyl peak of hexamethylbenzene to determine yield.

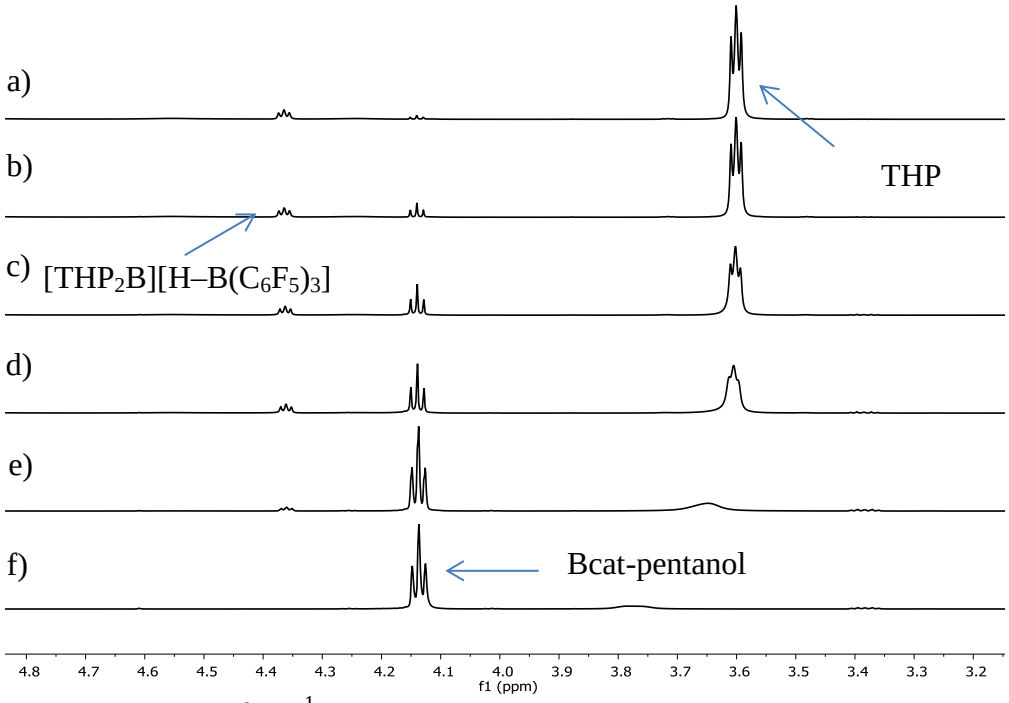


Figure S1: Stacked region of the ^1H NMR spectrum monitoring tetrahydropyran (THP) reduction using HBcat ($B(C_6F_5)_3$-catalyzed), after: a) 1 hr, b) 1 day, c) 2 days, d) 3 days, e) 4 days, f) 5 days. The most downfield resonance integrates for, and is assigned to, the bis-THP adduct of $Bcat^+$.

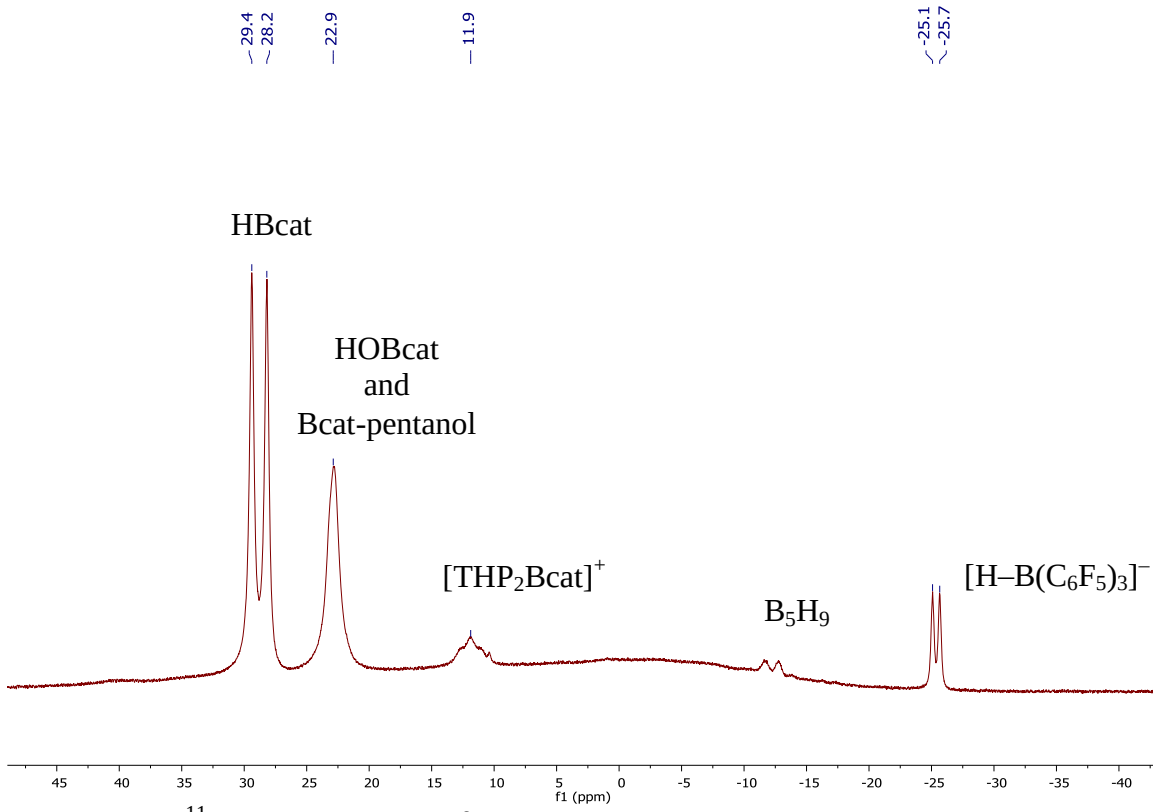


Figure S2: *in situ* ^{11}B NMR spectrum of a $B(C_6F_5)_3$ catalyzed THP reaction (Table 1, Entry 5). The peak at ~12 ppm is consistent with a 4-coordinate boron species.

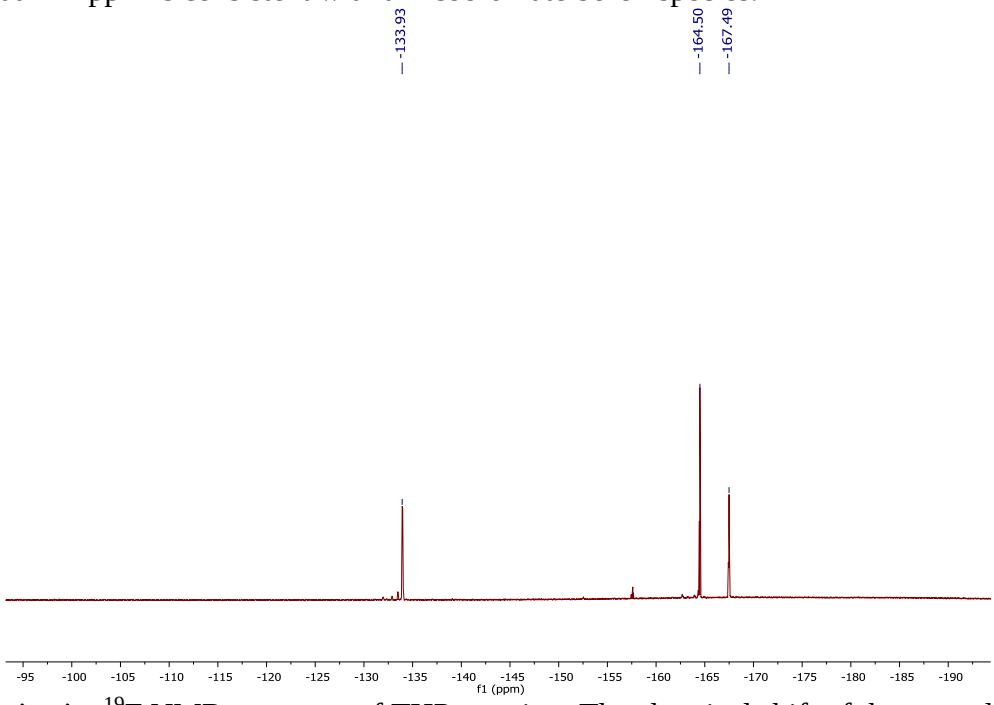


Figure S3: *in situ* ^{19}F NMR spectrum of THP reaction. The chemical shift of the central peak is highly diagnostic, and the species is identical to $[H–B(C_6F_5)_3]^-$.

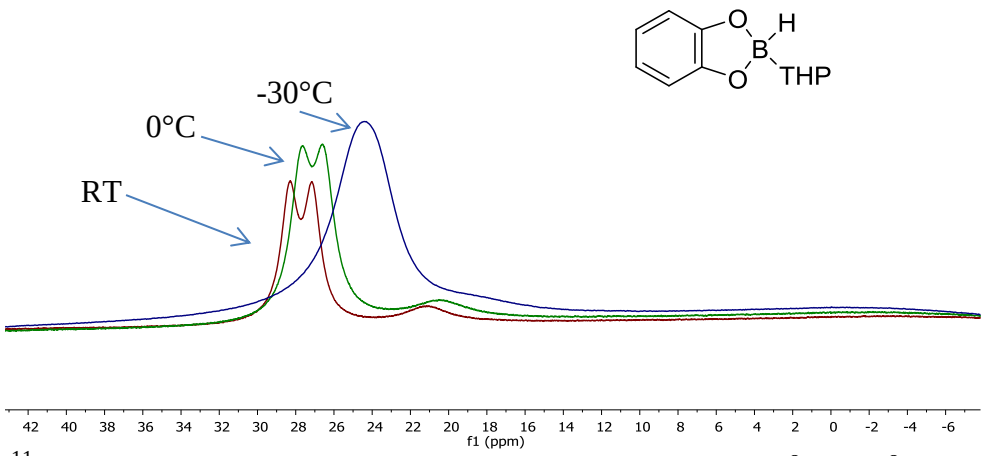


Figure S4: ^{11}B NMR spectrum of HBcat (1 eq.) and THP (1 eq.) (RT, 0 ^{o}C, -30 ^{o}C). A shift in the HBcat peak suggests adduct formation to THP. This effect has been shown elsewhere.[6,7] In the absence of THP, no shifting occurs on cooling.

Reduction of Silyl Ethers

General Procedure: In a nitrogen-filled glovebox, a 1-dram vial was charged with $B(C_6F_5)_3$ (5.1 mg, 0.01 mmol, 0.10 equiv.) and hexamethylbenzene (1.1 mg, 0.067 mmol) and dichloromethane was added by syringe. To the $B(C_6F_5)_3$ solution was added silyl ether (0.1 mmol, 1.0 equiv) and hydroborane (0.4 mmol, ~2 equiv. per -OSi) both by microliter syringe or microliter pipet. The vial was capped and shaken manually for 30 seconds. The solution was subsequently transferred by syringe to an NMR tube, which was capped with a septum and removed from the box. The NMR tube was allowed to stand for at least 16 hours and monitored by NMR intermittently. Peaks identified as the fully reduced alkane were integrated relative to the methyl peak of hexamethylbenzene to determine yield.

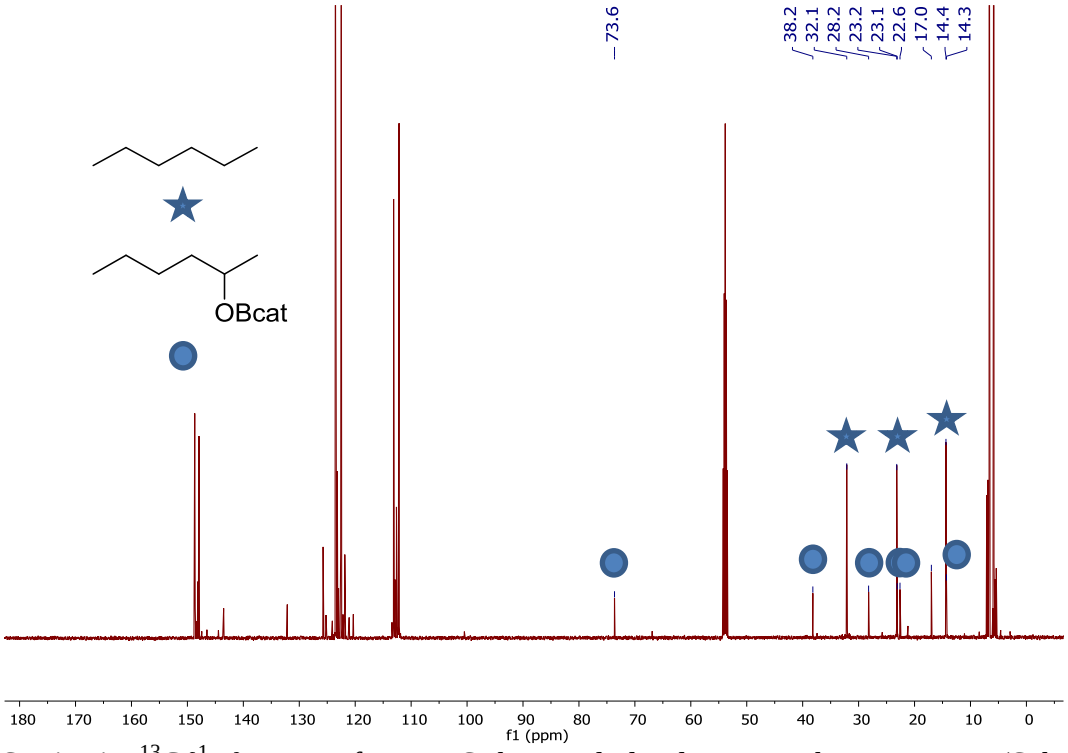


Figure S5: *in situ* $^{13}C\{^{1}H\}$ NMR of 1,2-Et_3Si-hexanediol reduction with 4 eq. HBcat (Scheme 2b). The peak at 17.0 ppm is from hexamethylbenzene.

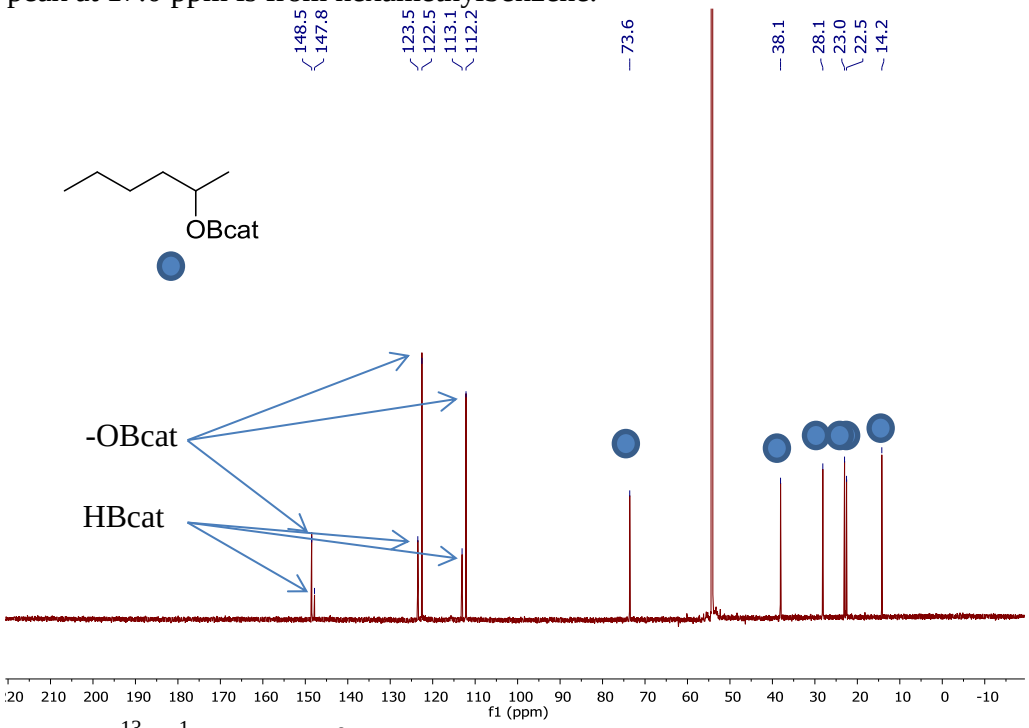


Figure S6: *in situ* $^{13}C\{^{1}H\}$ NMR of 2-Bcat-hexanol. The C–O peak at 73.6 ppm matches that in Figure S5.

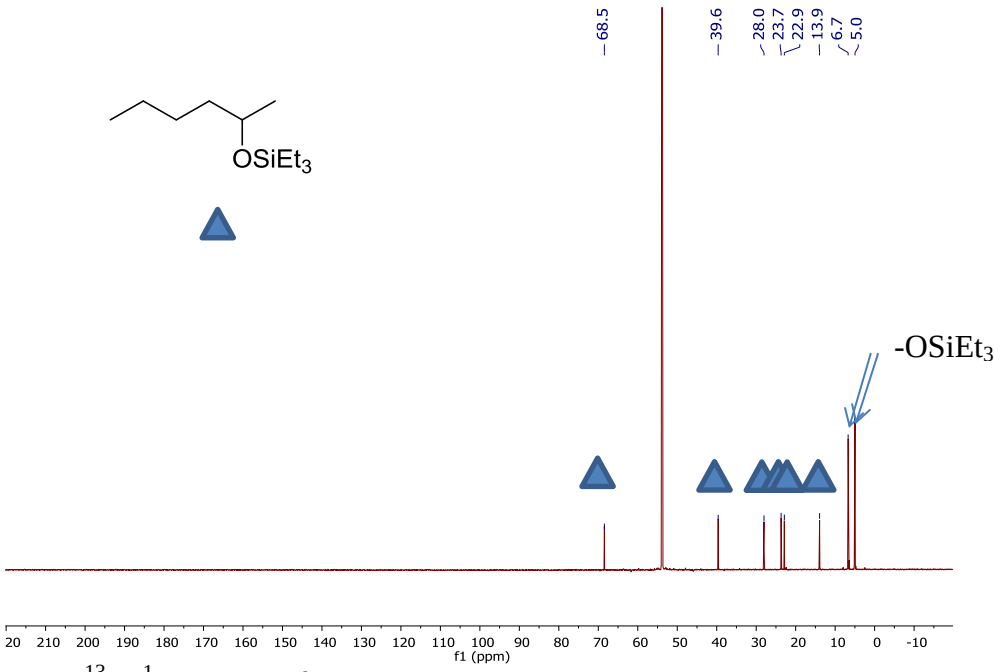
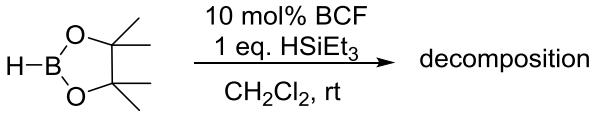


Figure S7: *in situ* $^{13}C\{^{1}H\}$ NMR of 2-Et_3Si-hexanol. The C–O peak at 68.5 ppm does not match that in Figure S5.

Stability of Hydroboranes with Triethylsilane



In a nitrogen-filled glovebox, a 1-dram vial was charged with $B(C_6F_5)_3$ (5.1 mg, 0.01 mmol, 0.10 equiv.) and dichloromethane (0.5 mL), followed by triethylsilane (0.1 mmol, 1.0 equiv.). To the $B(C_6F_5)_3$ solution pinacolborane (1.0 equiv) was added and the vial was capped and shaken manually for 30 seconds. The solution was transferred by syringe to an NMR tube, which was capped with a septum and removed from the box. The solution was monitored by NMR after 24 hours, revealing decomposition of the borane by silane.

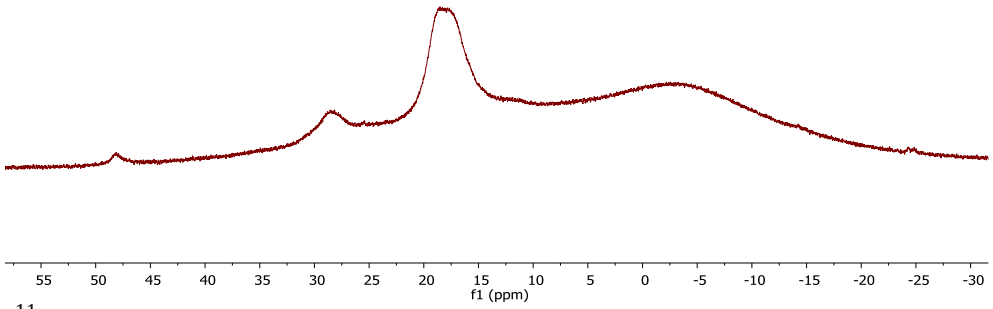


Figure S8: ^{11}B NMR of HBpin and Et_3SiH with $B(C_6F_5)_3$ after 24 hours. Note the trace amount of $[H–B(C_6F_5)_3]^-$ at -25 ppm and disappearance of the HBpin doublet at 28 ppm (Figure S10) the other peaks have not been fully characterized.

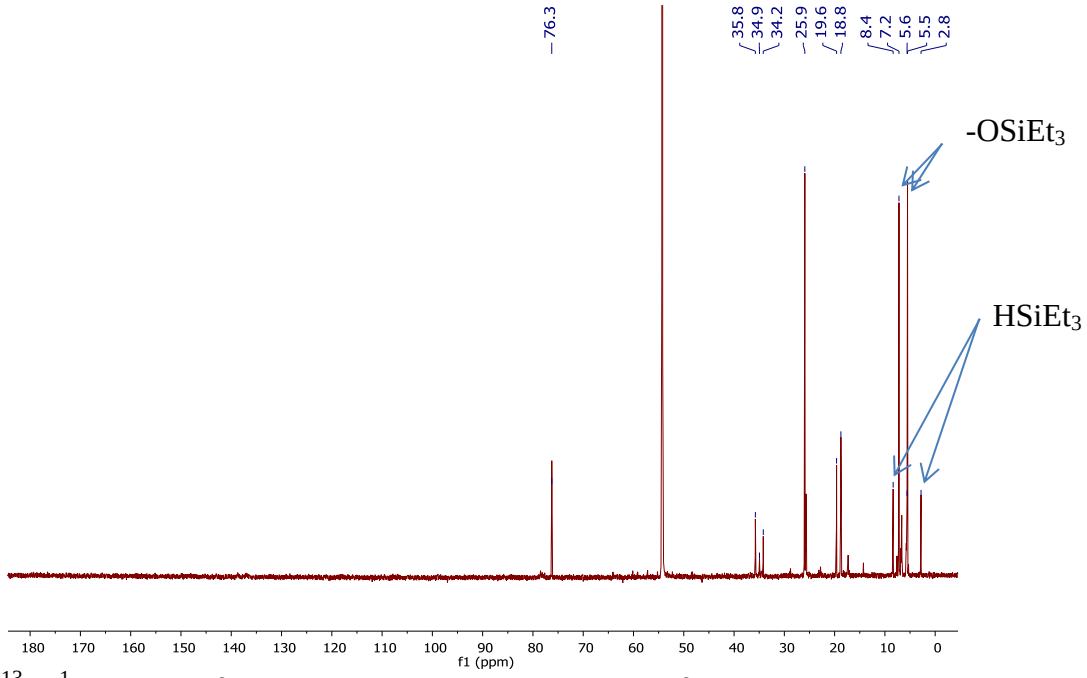


Figure S9: $^{13}C\{^1H\}$ NMR of HBpin and Et_3SiH with $B(C_6F_5)_3$ after 24 hours. The appearance of -$OSiEt_3$ peaks suggests a reductive pinacol rearrangement because HBpin is the only source of oxygen in this reaction. The appearance of additional peaks compared to HBpin also suggests rearrangement, though they have not been fully characterized (Figure S11).

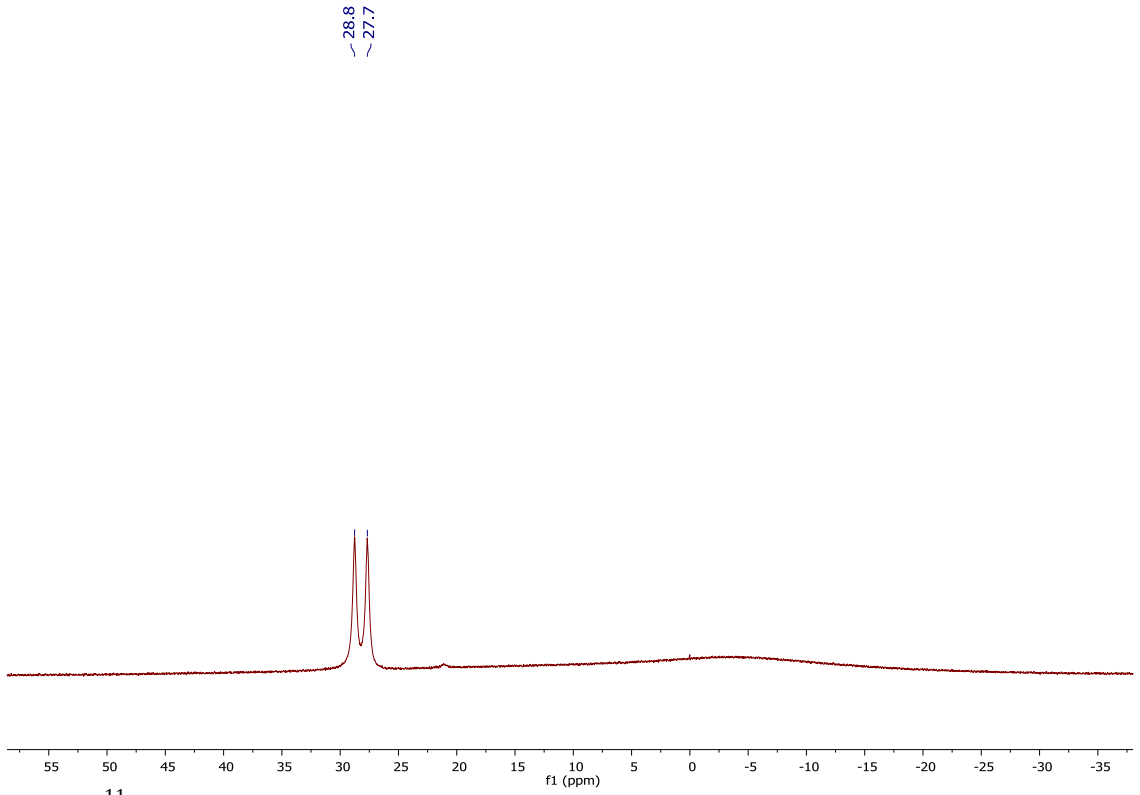


Figure S10: ^{11}B NMR of HBpin in $CDCl_3$.

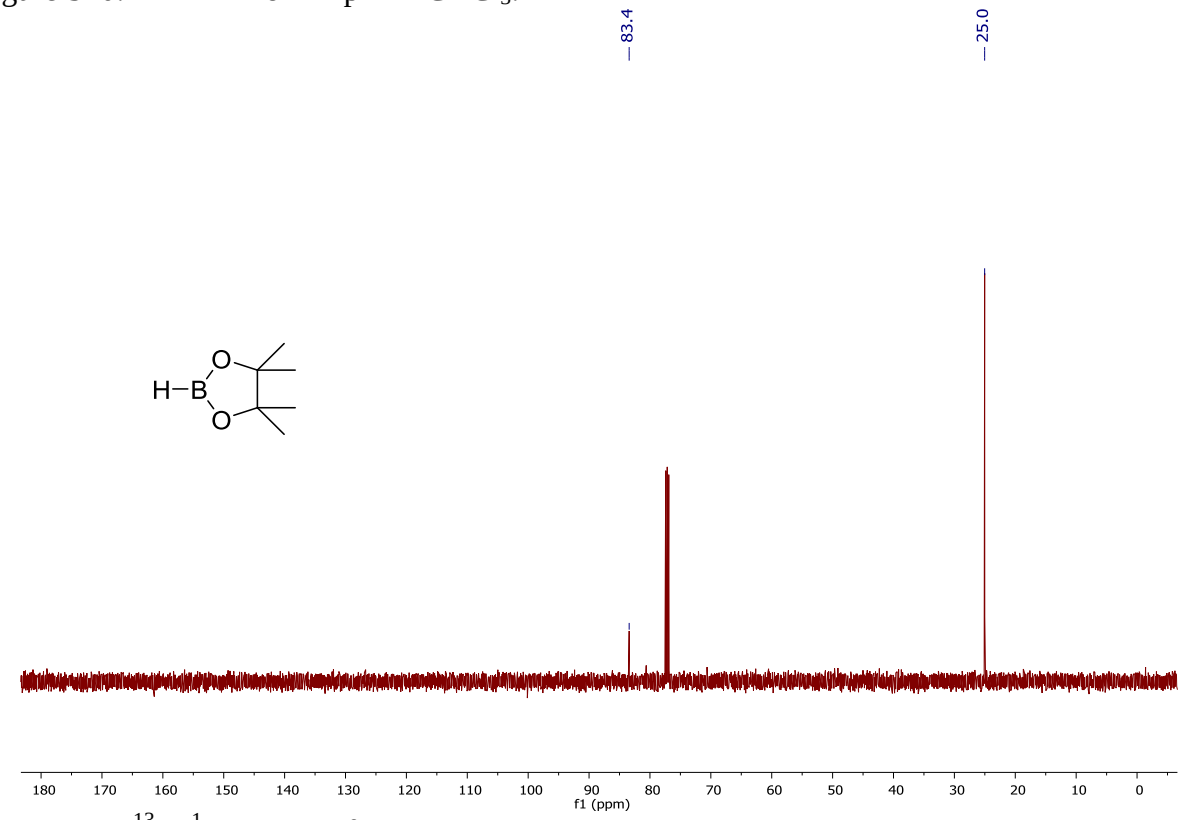
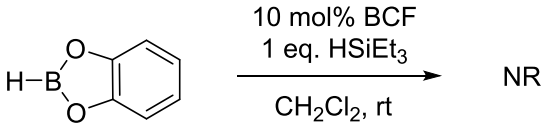


Figure S11: $^{13}C\{^1H\}$ NMR of HBpin in $CDCl_3$, which shows only two peaks: the quaternary carbon peak at 83.4 ppm and the methyl peak at 25.0 ppm.



In a nitrogen-filled glovebox, a 1-dram vial was charged with $B(C_6F_5)_3$ (5.1 mg, 0.01 mmol, 0.10 equiv.) and dichloromethane (0.5 mL), followed by triethylsilane (0.1 mmol, 1.0 equiv.). To the solution of $B(C_6F_5)_3$ catecholborane (1.0 equiv) was added and the vial was capped and shaken manually for 30 seconds. The solution was transferred by syringe to an NMR tube, which was capped with a septum and removed from the box. The solution was monitored by NMR after 24 hours, revealing no appreciable decomposition.

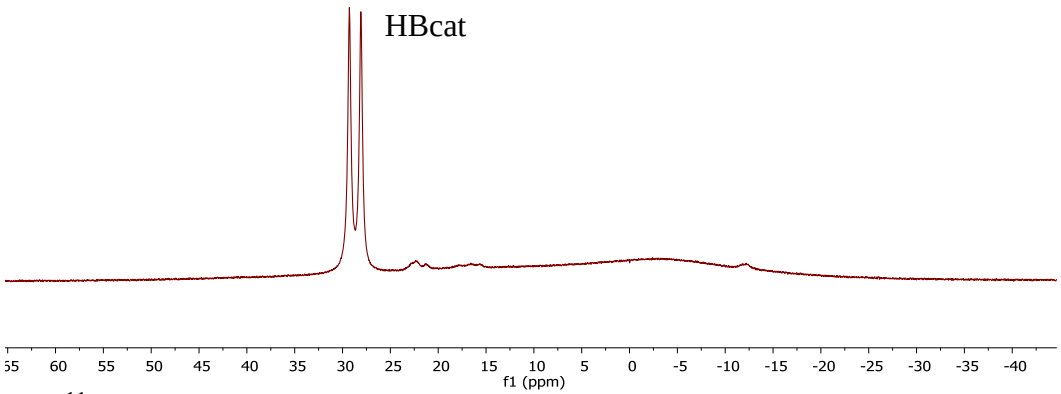


Figure S12: ^{11}B NMR of HBcat and Et_3SiH with $B(C_6F_5)_3$ after 24 hours. The HBcat is unchanged under these conditions.

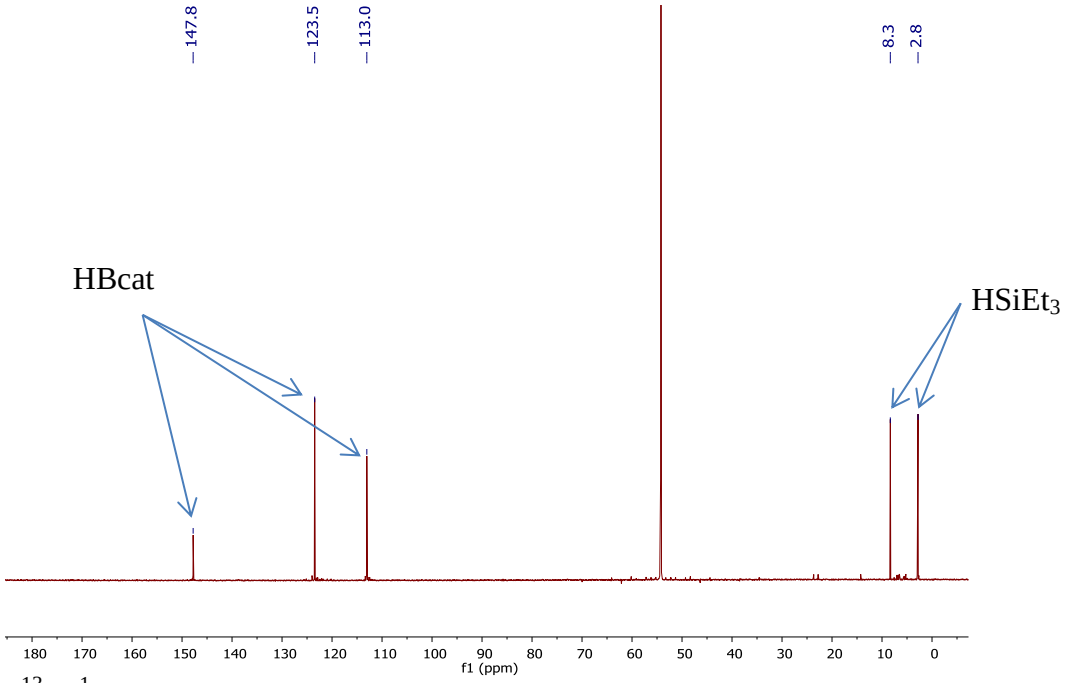
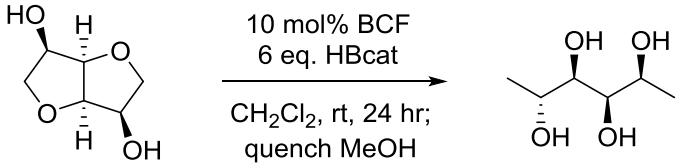


Figure S13: $^{13}C\{^{1}H\}$ NMR of HBcat and Et_3SiH with $B(C_6F_5)_3$ after 24 hours. Both reagents are unchanged under these conditions.

Isosorbide Reductions

Reduction of Unprotected Isosorbide with HBcat to form 2

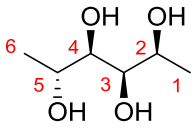


2

71%

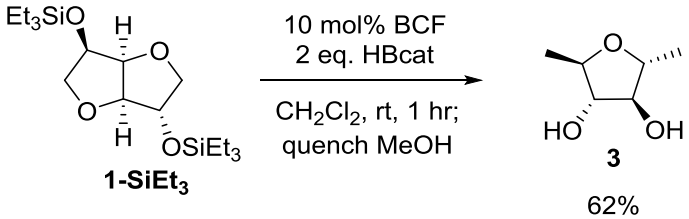
In a nitrogen-filled glovebox, a 1-dram vial was charged with isosorbide (14.6 mg, 0.10 mmol, 1.0 equiv.). A separate 1-dram vial was charged with $B(C_6F_5)_3$ (5.1 mg, 0.01 mmol, 0.10 equiv.) and dichloromethane (0.5 mL) was added by syringe. The $B(C_6F_5)_3$ solution was then transferred to the starting material vial. Catecholborane (64 µL, 0.60 mmol, 6.0 equiv.) was added by microliter syringe and the vial was capped and shaken manually until rapid bubbling ceased. Subsequently the solution was transferred by syringe to an NMR tube, which was capped with a septum and removed from the box. The NMR tube was allowed to stand for 24 hr. The reaction mixture was transferred to a scintillation vial and dichloromethane was used to collect the remaining residue (3 x 1 mL). The reaction was quenched and silyl-groups deprotected when methanol (0.5 mL) was added. Subsequently the solvent was removed by vacuum, to afford a cloudy oil. The residue was purified by silica gel chromatography (5 x 1 cm

column) with gradient elution (50:1, 25:1, 10:1, 5:1 DCM: methanol) to afford tetraol **2** (10.6 mg, 71%).

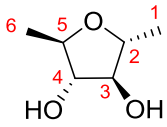


(2*R*,3*R*,4*R*,5*S*)-hexane-2,3,4,5-tetraol: $^{13}C\{^{1}H\}$ NMR (151 MHz, CD_3OD) δ 77.0 (s, C_4), 74.9 (s, C_3), 70.4 (s, C_2), 68.7 (s, C_5), 20.2 (s, C_6), 19.5 (s, C_1). 1H NMR (600 MHz, CD_3OD) δ 3.85 (app t, *J* = 6.2 Hz, 1H, H_2), 3.80 (dq, *J* = 6.3, 7.8 Hz, 1H, H_5), 3.57 (dd, *J* = 6.0, 1.9 Hz, 1H, H_3), 3.31 (dd, *J* = 7.8, 1.5 Hz, 1H, H_4), 1.24 (d, *J* = 6.3 Hz, 3H, H_6), 1.19 (d, *J* = 6.3 Hz, 3H, H_1). NMR spectra match those previously reported in the literature.[5]

Reduction of 1-$SiEt_3$ to form 3



In a nitrogen-filled glovebox, a 1-dram vial was charged with triethylsilane-isosorbide (37.5 mg, 0.10 mmol, 1.0 equiv.) by Pasteur pipet. A separate 1-dram vial was charged with $B(C_6F_5)_3$ (5.1 mg, 0.01 mmol, 0.10 equiv.) and dichloromethane (0.5 mL) was added by syringe. The $B(C_6F_5)_3$ solution was then transferred to the starting material vial. Catecholborane (21.3 µL, 0.20 mmol, 2.0 equiv.) was added by microliter syringe and the vial was capped and shaken manually for 30 seconds. Subsequently the solution was transferred by syringe to an NMR tube, which was capped with a septum and removed from the box. The NMR tube was allowed to stand for 1 hr. The reaction mixture was transferred to a scintillation vial and dichloromethane was used to collect the remaining residue (3 x 1 mL). The reaction was quenched and silyl-groups deprotected when methanol (0.5 mL) was added. Subsequently the solvent was removed by vacuum, to afford a cloudy oil. The residue was purified by silica gel chromatography (5 x 1 cm column) with gradient elution (50:1, 25:1, 10:1, 5:1 DCM: methanol) to afford **3** (8.2 mg, 62% yield).



(2*R*,3*S*,4*S*,5*R*)-2,5-dimethyltetrahydrofuran-3,4-diol: $^{13}C\{^{1}H\}$ NMR (151 MHz, CD_3OD) δ 84.3 (s, C_3 & C_4), 79.4 (s, C_2 & C_5), 19.3 (s, C_1 & C_6). ^{1}H NMR (600 MHz, CD_3OD) δ 3.86-3.81 (m 2H, H_2 & H_5), 3.65 – 3.61 (m, 2H, H_3 & H_4), 1.26 (d, *J* = 6.3 Hz, 6H, H_1 & H_6). NMR spectra match those previously reported in the literature.[5]

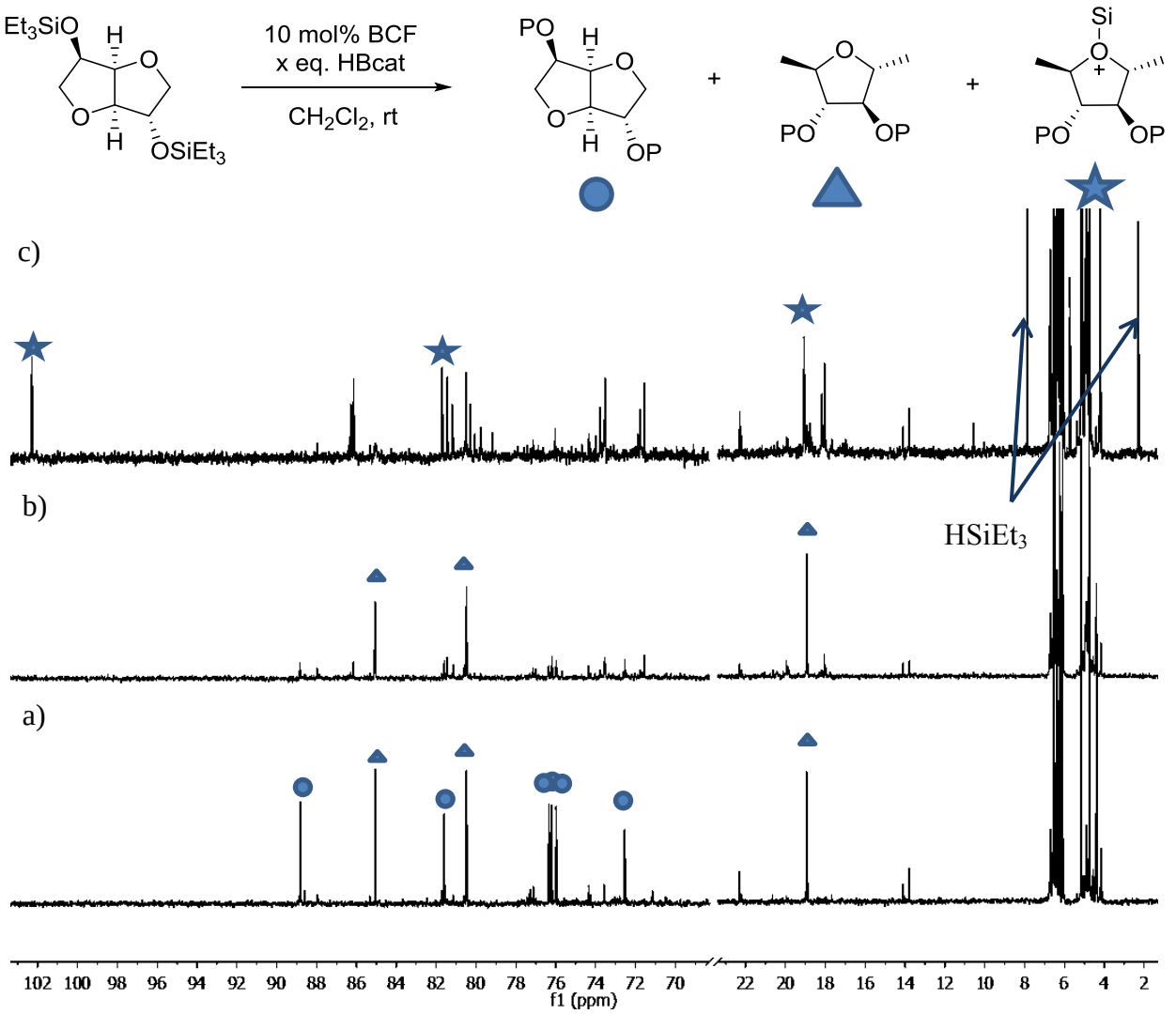
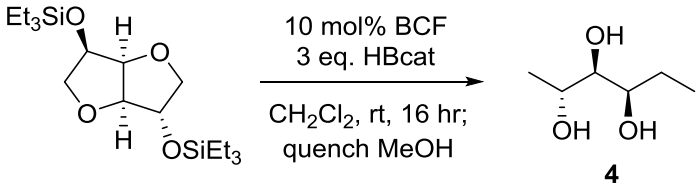


Figure S14: *in situ* ^{13}C NMR data for reduction of **1-SiEt$_3$** using a) 0.5 eq. HBcat b) 1.5 eq. HBcat c) 2 eq. HBcat.

Reduction of 1-SiEt$_3$ to form 4

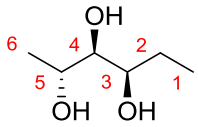


1-SiEt$_3$ **4**

48%

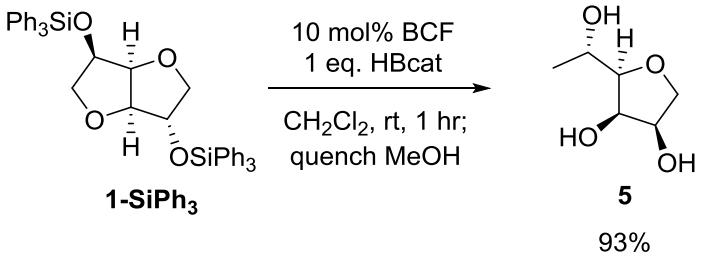
In a nitrogen-filled glovebox, a 1-dram vial was charged with triethylsilane-isosorbide (37.5 mg, 0.10 mmol, 1.0 equiv.) by Pasteur pipet. A separate 1-dram vial was charged with $B(C_6F_5)_3$ (5.1 mg, 0.01 mmol, 0.10 equiv.) and dichloromethane (0.5 mL) was added by syringe. The $B(C_6F_5)_3$ solution was then transferred to the starting material vial. Catecholborane (32.0 µL, 0.30 mmol, 3.0 equiv.) was added by microliter syringe and the vial was capped and shaken manually for 30 seconds. Subsequently the solution was transferred by syringe to an NMR tube,

which was capped with a septum and removed from the box. The NMR tube was allowed to stand for 16 hr. The reaction mixture was transferred to a scintillation vial and dichloromethane was used to collect the remaining residue (3 x 1 mL). The reaction was quenched and silyl-groups deprotected when methanol (0.5 mL) was added. Subsequently the solvent was removed by vacuum, to afford a cloudy oil. The residue was purified by silica gel chromatography (5 x 1 cm column) with gradient elution (50:1, 25:1, 10:1, 5:1 DCM: methanol) to afford triol **4** (6.4 mg, 48% yield), with amounts of **2** and **5** (4 mg, 26%).

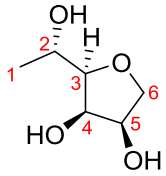


(2*R*,3*R*,4*R*)-hexane-2,3,4-triol: $^{13}C\{^{1}H\}$ NMR (151 MHz, CD_3OD) δ 77.9 (s, C_4), 73.1 (s, C_3), 68.8 (s, C_5), 27.5 (s, C_2), 20.2 (s, C_2), 10.8 (s, C_1). 1H NMR (600 MHz, CD_3OD) δ 3.81 – 3.75 (m, 1H, H_5), 3.68 (ddd, J = 8.0, 5.7, 2.4 Hz, 1H, H_3), 3.14 (dd, J = 7.4, 2.4 Hz, 1H, H_4), 1.61 – 1.50 (m, 2H, H_2), 1.23 (d, J = 6.3 Hz, 3H, H_6), 0.97 (t, J = 7.4 Hz, 3H, H_1). NMR spectra match those previously reported in the literature.[5]

Reduction of 1-SiPh$_3$ to form 5

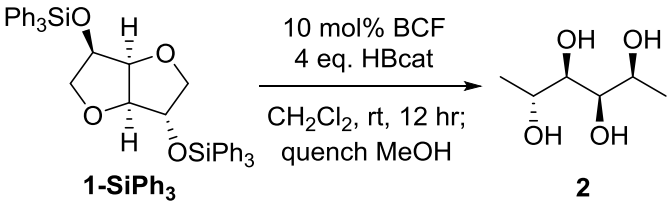


In a nitrogen-filled glovebox, a 1-dram vial was charged with triphenylsilane-isosorbide (66.3 mg, 0.10 mmol, 1.0 equiv.). A separate 1-dram vial was charged with $B(C_6F_5)_3$ (5.1 mg, 0.01 mmol, 0.10 equiv.) and dichloromethane (0.5 mL) was added by syringe. The $B(C_6F_5)_3$ solution was then transferred to the starting material vial. Catecholborane (10.7 µL, 0.10 mmol, 1.0 equiv.) was added by microliter syringe and the vial was capped and shaken manually for 30 seconds. Subsequently the solution was transferred by syringe to an NMR tube, which was capped with a septum and removed from the box. The NMR tube was allowed to stand for 1 hr. The reaction mixture was transferred to a scintillation vial and dichloromethane was used to collect the remaining residue (3 x 1 mL). The reaction was quenched and silyl-groups deprotected when methanol (0.5 mL) was added. Subsequently the solvent was removed by vacuum, to afford a cloudy oil. The residue was purified by silica gel chromatography (5 x 1 cm column) with gradient elution (50:1, 25:1, 10:1, 5:1 DCM: methanol) to afford **5** (13 mg, 93% yield).



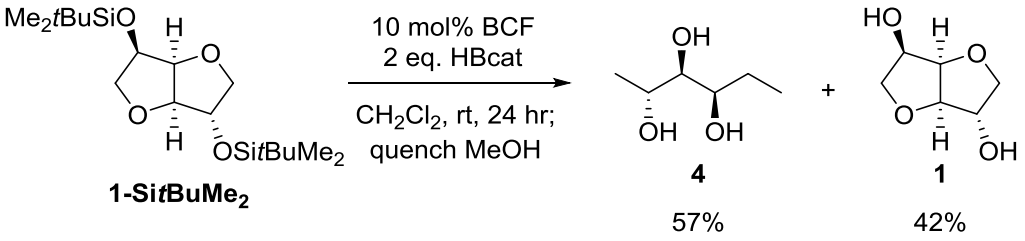
(3*R*,4*R*,5*R*)-5-((*S*)-1-hydroxyethyl)tetrahydrofuran-3,4-diol: $^{13}C\{^{1}H\}$ NMR (151 MHz, CD_3OD) δ 86.1 (s, C_3), 73.2 (s, C_4 or C_5), 73.0 (s, C_4 or C_5), 72.3 (s, C_6), 67.7 (s, C_2), 19.6 (s, C_1). ^{1}H NMR (600 MHz, CD_3OD) δ 4.26 (td, *J* = 6.4, 4.8 Hz, 1H, H_5), 4.11 (app t, *J* = 4.7 Hz, 1H, H_4), 4.00 (dq, *J* = 6.5, 6.1 Hz, 1H, H_2), 3.88 (dd, *J* = 8.7, 6.5 Hz, 1H, H_6), 3.70 (dd, *J* = 8.6, 6.3 Hz, 1H, $H_{6'}$), 3.60 (dd, *J* = 6.1, 4.5 Hz, 1H, H_3), 1.21 (d, *J* = 6.5 Hz, 3H, C_1). HRMS (ESI^+): Calculated for $C_6H_{12}O_4Na$ $[M+Na]^+$: 171.0628; Found: 171.0627. Stereochemistry was supported by full deprotection of previously reported compounds.[5]

Reduction of 1-SiPh$_3$ to form 2



In a nitrogen-filled glovebox, a 1-dram vial was charged with triphenylsilane-isosorbide (66.3 mg, 0.10 mmol, 1.0 equiv.). A separate 1-dram vial was charged with $B(C_6F_5)_3$ (5.1 mg, 0.01 mmol, 0.10 equiv.) and dichloromethane (0.5 mL) was added by syringe. The $B(C_6F_5)_3$ solution was then transferred to the starting material vial. Catecholborane (42.6 µL, 0.40 mmol, 4.0 equiv.) was added by microliter syringe and the vial was capped and shaken manually for 30 seconds. Subsequently the solution was transferred by syringe to an NMR tube, which was capped with a septum and removed from the box. The NMR tube was allowed to stand for 12 hr. The reaction mixture was transferred to a scintillation vial and dichloromethane was used to collect the remaining residue (3 x 1 mL). The reaction was quenched and silyl-groups deprotected when methanol (0.5 mL) was added. Subsequently the solvent was removed by vacuum, to afford a cloudy oil. The residue was purified by silica gel chromatography (5 x 1 cm column) with gradient elution (50:1, 25:1, 10:1, 5:1 DCM: methanol) to afford tetraol **2** (10.4 mg, 69% yield).

Reduction of 1-Si*t*BuMe$_2$ to form 4

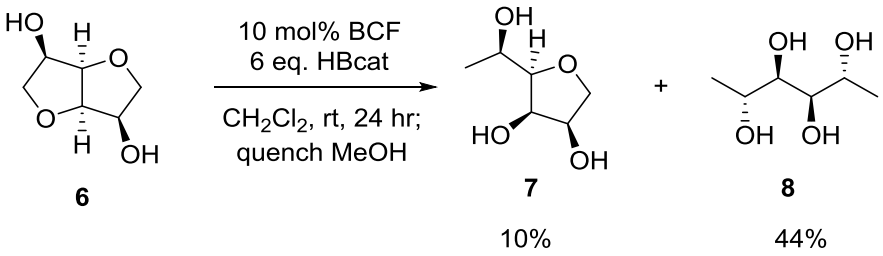


In a nitrogen-filled glovebox, a 1-dram vial was charged with tertbutyldimethylsilane-isosorbide (37.5 mg, 0.10 mmol, 1.0 equiv.). A separate 1-dram vial was charged with $B(C_6F_5)_3$

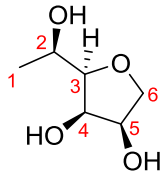
(5.1 mg, 0.01 mmol, 0.10 equiv.) and dichloromethane (0.5 mL) was added by syringe. The $B(C_6F_5)_3$ solution was then transferred to the starting material vial. Catecholborane (21.3 μL, 0.20 mmol, 2.0 equiv.) was added by microliter syringe and the vial was capped and shaken manually for 30 seconds. Subsequently the solution was transferred by syringe to an NMR tube, which was capped with a septum and removed from the box. The NMR tube was allowed to stand for 24 hr. The reaction mixture was transferred to a scintillation vial and dichloromethane was used to collect the remaining residue (3 x 1 mL). The reaction was quenched and silyl-groups deprotected when methanol (0.5 mL) was added. Subsequently the solvent was removed by vacuum, to afford a cloudy oil. The residue was purified by silica gel chromatography (5 x 1 cm column) with gradient elution (50:1, 25:1, 10:1, 5:1 DCM: methanol) to afford triol **4** (7.6 mg, 57% yield) and deprotected isosorbide **1** (6.2 mg, 42% recovered).

Isomannide Reductions

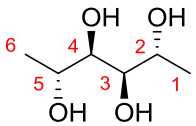
Reduction of unprotected isomannide with HBcat to form 7 and 8



In a nitrogen-filled glovebox, a 1-dram vial was charged with isomannide (14.6 mg, 0.10 mmol, 1.0 equiv.). A separate 1-dram vial was charged with $B(C_6F_5)_3$ (5.1 mg, 0.01 mmol, 0.1 equiv.) and dichloromethane (0.5 mL) was added by syringe. The $B(C_6F_5)_3$ solution was then transferred to the starting material vial. Catecholborane (64 µL, 0.60 mmol, 6.0 equiv.) was added by microliter syringe and the vial was capped and shaken manually for 30 seconds. Subsequently the solution was transferred by syringe to an NMR tube, which was capped with a septum and removed from the box. The NMR tube was allowed to stand for 24 hr. The reaction mixture was transferred to a scintillation vial and dichloromethane was used to collect the remaining residue (3 x 1 mL). The reaction was quenched and silyl-groups deprotected when methanol (0.5 mL) was added. Subsequently the solvent was removed by vacuum, to afford a cloudy oil. The residue was purified by silica gel chromatography (5 x 1 cm column) with gradient elution (25:1, 15:1, 10:1, 5:1 DCM: methanol) to afford 1-deoxysorbitan **7** (1.5 mg, 10%) and tetraol **8** (6.6 mg, 44%).

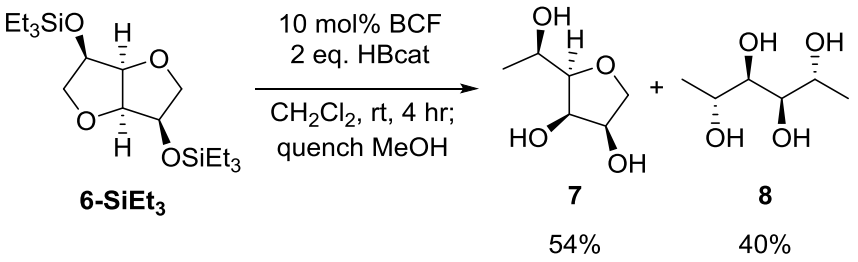


(3*R*,4*R*,5*R*)-5-((*R*)-1-hydroxyethyl)tetrahydrofuran-3,4-diol: $^{13}C\{^1H\}$ NMR (151 MHz, CD_3OD) δ 86.0 (s, C_3), 73.2 (s, C_5), 72.7 (s, C_4), 72.2 (s, C_6), 67.2 (s, C_2), 20.4 (s, C_1). ^1H NMR (600 MHz, CD_3OD) δ 4.29 (ddd, *J* = 6.9, 6.9, 4.7 Hz, 1H, H_5), 4.20 (dd, *J* = 4.3, 4.3 Hz, 1H, H_4), 4.01 (dq, *J* = 7.8, 6.4 Hz, 1H, H_2), 3.86 (dd, *J* = 8.5, 6.8 Hz, 1H, H_6), 3.65 (dd, *J* = 8.5, 6.9 Hz, 1H, $H_{6'}$), 3.52 (dd, *J* = 7.7, 3.9 Hz, 1H, H_3), 1.23 (d, *J* = 6.4 Hz, 3H, H_1). HRMS (ESI^+): Calculated for $C_6H_{12}O_4Na$ $[M+Na]^+$: 171.0628; Found: 171.0627. Stereochemistry was not established by NMR but assumed on the basis of the established stereochemistry of the starting material.



(2*R*,3*R*,4*R*,5*R*)-hexane-2,3,4,5-tetraol: $^{13}C\{^1H\}$ NMR (151 MHz, CD_3OD) δ 74.9 (s, C_3 & C_4), 69.1 (s, C_2 & C_5), 20.3 (s, C_1 &C_6). ^1H NMR (600 MHz, CD_3OD) δ 3.78 (app q, *J* = 6.5 Hz, 2H, H_2 & H_5), 3.52 (d, *J* = 7.1 Hz, 2H, H_3 & H_4), 1.24 (d, *J* = 6.3 Hz, 6H, H_1 & H_6). NMR spectra match those previously found in the literature.[5]

Reduction of 6-SiEt$_3$ to form 7 and 8

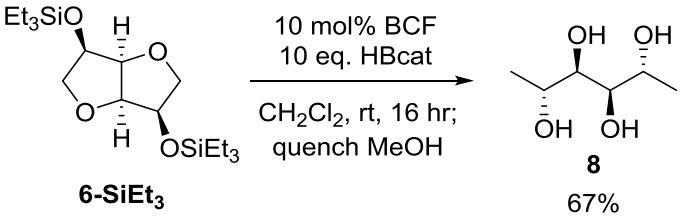


6-SiEt$_3$ **7** **8**

54% 40%

In a nitrogen-filled glovebox, a 1-dram vial was charged with triethylsilane-isomannide (37.4 mg, 0.10 mmol, 1.0 equiv.) by Pasteur pipet. A separate 1-dram vial was charged with B(C_6F_5)$_3$ (5.1 mg, 0.01 mmol, 0.10 equiv.) and dichloromethane (0.5 mL) was added by syringe. The B(C_6F_5)$_3$ solution was then transferred to the starting material vial. Catecholborane (21.3 µL, 0.20 mmol, 2.0 equiv.) was added by microliter syringe and the vial was capped and shaken manually for 30 seconds. Subsequently the solution was transferred by syringe to an NMR tube, which was capped with a septum and removed from the box. The NMR tube was allowed to stand for 4 hr. The reaction mixture was transferred to a scintillation vial and dichloromethane was used to collect the remaining residue (3 x 1 mL). The reaction was quenched and silyl-groups deprotected when methanol (0.5 mL) was added. Subsequently the solvent was removed by vacuum, to afford a cloudy oil. The residue was purified by silica gel chromatography (5 x 1 cm column) with gradient elution (50:1, 25:1, 10:1, 5:1 DCM: methanol) to afford 1-deoxysorbitan **7** (8 mg, 54%) tetraol **8** (6 mg, 40%).

Reduction of 6-SiEt$_3$ with excess HBcat to form 8

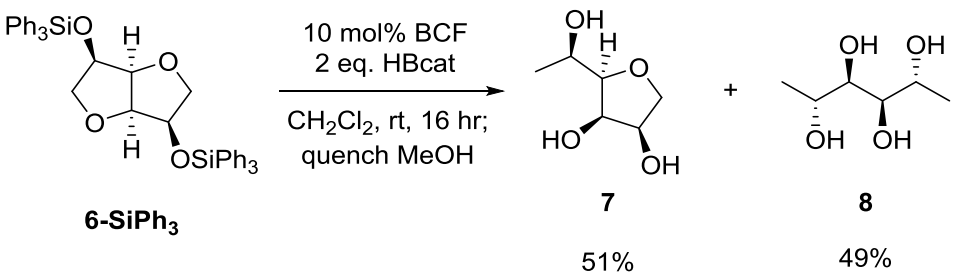


6-SiEt$_3$ **8**

67%

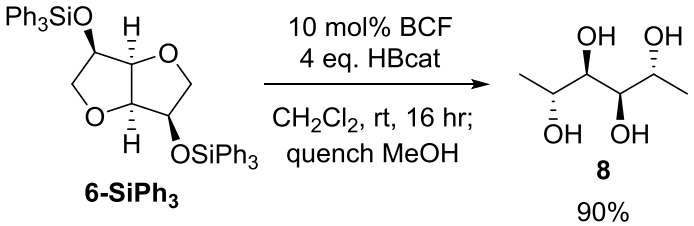
In a nitrogen-filled glovebox, a 1-dram vial was charged with triethylsilane-isomannide (37.4 mg, 0.10 mmol, 1.0 equiv.). A separate 1-dram vial was charged with B(C_6F_5)$_3$ (5.1 mg, 0.01 mmol, 0.10 equiv.) and dichloromethane (0.5 mL) was added by syringe. The B(C_6F_5)$_3$ solution was then transferred to the starting material vial. Catecholborane (106.6 µL, 1.0 mmol, 10.0 equiv.) was added by microliter syringe and the vial was capped and shaken manually for 30 seconds. Subsequently the solution was transferred by syringe to an NMR tube, which was capped with a septum and removed from the box. The NMR tube was allowed to stand for 16 hr. The reaction mixture was transferred to a scintillation vial and dichloromethane was used to collect the remaining residue (3 x 1 mL). The reaction was quenched and silyl-groups deprotected when methanol (0.5 mL) was added. Subsequently the solvent was removed by vacuum, to afford a cloudy oil (the large excess of HOBcat crystallized). The residue was purified by silica gel chromatography (5 x 1 cm column) with gradient elution (50:1, 25:1, 10:1, 5:1 DCM: methanol) to afford tetraol **8** (10 mg, 67%).

Reduction of 6-$SiPh_3$ to form 7 and 8



In a nitrogen-filled glovebox, a 1-dram vial was charged with triphenylsilane-isomannide (66.3 mg, 0.10 mmol, 1.0 equiv.). A separate 1-dram vial was charged with $B(C_6F_5)_3$ (5.1 mg, 0.01 mmol, 0.10 equiv.) and dichloromethane (0.5 mL) was added by syringe. The $B(C_6F_5)_3$ solution was then transferred to the starting material vial. Catecholborane (21.3 µL, 0.20 mmol, 2.0 equiv.) was added by microliter syringe and the vial was capped and shaken manually for 30 seconds. Subsequently the solution was transferred by syringe to an NMR tube, which was capped with a septum and removed from the box. The NMR tube was allowed to stand for 16 hr. The reaction mixture was transferred to a scintillation vial and dichloromethane was used to collect the remaining residue (3 x 1 mL). The reaction was quenched and silyl-groups deprotected when methanol (0.5 mL) was added. Subsequently the solvent was removed by vacuum, to afford a cloudy oil. The residue was purified by silica gel chromatography (5 x 1 cm column) with gradient elution (50:1, 25:1, 10:1, 5:1 DCM: methanol) to afford a 1-deoxysorbitan **7** (8 mg, 54%) and tetraol **8** (6 mg, 40%).

Reduction of 6-$SiPh_3$ with 4 eq. of HBcat to form 8



In a nitrogen-filled glovebox, a 1-dram vial was charged with triphenylsilane-isomannide (66.3 mg, 0.10 mmol, 1.0 equiv.). A separate 1-dram vial was charged with $B(C_6F_5)_3$ (5.1 mg, 0.01 mmol, 0.10 equiv.) and dichloromethane (0.5 mL) was added by syringe. The $B(C_6F_5)_3$ solution was then transferred to the starting material vial. Catecholborane (42.6 µL, 0.40 mmol, 4.0 equiv.) was added by microliter syringe and the vial was capped and shaken manually for 30 seconds. Subsequently the solution was transferred by syringe to an NMR tube, which was capped with a septum and removed from the box. The NMR tube was allowed to stand for 16 hr. The reaction mixture was transferred to a scintillation vial and dichloromethane was used to collect the remaining residue (3 x 1 mL). The reaction was quenched and silyl-groups deprotected when methanol (0.5 mL) was added. Subsequently the solvent was removed by vacuum, to afford a cloudy oil. The residue was purified by silica gel chromatography (5 x 1 cm

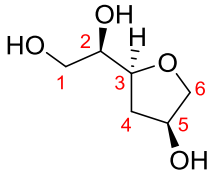
column) with gradient elution (50:1, 25:1, 10:1, 5:1 DCM: methanol) to afford tetraol **8** (13.5 mg, 90%).

Reduction of 6-Si*t*BuMe$_2$ to form 9

6-Si*t*BuMe$_2$ **9**

47%

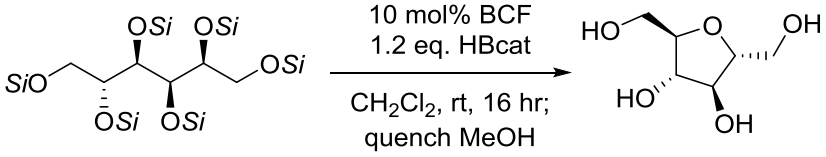
In a nitrogen-filled glovebox, a 1-dram vial was charged with tert-butyldimethylsilane-isomannide (37.4 mg, 0.10 mmol, 1.0 equiv.). A separate 1-dram vial was charged with $B(C_6F_5)_3$ (5.1 mg, 0.01 mmol, 0.10 equiv.) and dichloromethane (0.5 mL) was added by syringe. The $B(C_6F_5)_3$ solution was then transferred to the starting material vial. Catecholborane (21.3 µL, 0.20 mmol, 2.0 equiv.) was added by microliter syringe and the vial was capped and shaken manually for 30 seconds. Subsequently the solution was transferred by syringe to an NMR tube, which was capped with a septum and removed from the box. The NMR tube was allowed to stand for 2 hr. The reaction mixture was transferred to a scintillation vial and dichloromethane was used to collect the remaining residue (3 x 1 mL). The reaction was quenched and silyl-groups deprotected when methanol (0.5 mL) was added. Subsequently the solvent was removed by vacuum, to afford a cloudy oil. The residue was purified by silica gel chromatography (5 x 1 cm column) with gradient elution (50:1, 25:1, 10:1, 5:1 DCM: methanol) to afford a 4-deoxysorbitan **9** (7 mg, 47%).



4-deoxysorbitan: $^{13}C\{^1H\}$ NMR (151 MHz, CD_3OD) δ 80.4 (s, C_3), 76.4 (s, C_6), 74.8 (s, C_2), 72.5 (s, C_5), 64.9 (s, C_1), 36.7 (s, C_4). ^1H NMR (600 MHz, CD_3OD) δ 4.38 (ddt, *J* = 6.4, 4.4, 2.3 Hz, 1H, H_5), 3.97 (dt, *J* = 8.6, 5.4 Hz, 1H, H_3), 3.79 (dt, *J* = 9.4, 1.7 Hz, 1H, H_6), 3.75 (dt, *J* = 6.4, 4.9 Hz, 1H, H_2), 3.70 (dd, *J* = 9.4, 4.1 Hz, 1H, $H_{6'}$), 3.63 (dd, *J* = 11.4, 4.6 Hz, 1H, H_1), 3.53 (m, 1H, $H_{6'}$), 2.24 (ddd, *J* = 13.7, 8.5, 6.2 Hz, 1H, H_4), 1.93 (ddd, *J* = 13.6, 5.7, 2.7, 1.4 Hz, 1H, $H_{4'}$). NMR spectra match those previously reported in the literature.[5]

Hexitol Reductions

Reduction of 10-SiMe$_2$Et (sorbitol) to form 11



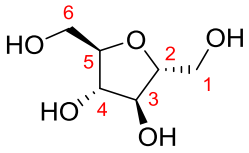
10

Si = SiMe$_2$Et

11

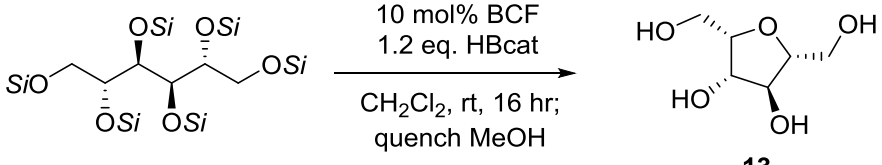
60%

In a nitrogen-filled glovebox, a 1-dram vial was charged with dimethylethylsilane-sorbitol (70.0 mg, 0.10 mmol, 1.0 equiv.) by Pasteur pipet. A separate 1-dram vial was charged with B(C_6F_5)$_3$ (5.1 mg, 0.01 mmol, 0.10 equiv.) and dichloromethane (0.5 mL) was added by syringe. The B(C_6F_5)$_3$ solution was then transferred to the starting material vial. Catecholborane (12.8 µL, 0.12 mmol, 1.2 equiv.) was added by microliter syringe and the vial was capped and shaken manually for 30 seconds. Subsequently the solution was transferred by syringe to an NMR tube, which was capped with a septum and removed from the box. The NMR tube was allowed to stand for 16 hr. The reaction mixture was transferred to a scintillation vial and dichloromethane was used to collect the remaining residue (3 x 1 mL). The reaction was quenched and silyl-groups deprotected when methanol (0.5 mL) was added. Subsequently the solvent was removed by vacuum, to afford a cloudy oil. The residue was purified by silica gel chromatography (5 x 1 cm column) with gradient elution (50:1, 25:1, 10:1, 5:1 DCM: methanol) to afford a 2,5-sorbitan **11** (9.8 mg, 47%)



(2*R*,3*S*,4*S*,5*R*)-2,5-bis(hydroxymethyl)tetrahydrofuran-3,4-diol (2,5-anhydro-D-mannitol): $^{13}C\{^1H\}$ NMR (151 MHz, CD_3OD) δ 85.2 (s), 78.8 (s), 63.3 (s). ^1H NMR (600 MHz, CD_3OD) δ 3.96 (dt, *J* = 5.4, 2.7 Hz, 1H), 3.84 – 3.80 (m, 1H), 3.71 (dd, *J* = 11.8, 3.4 Hz, 1H), 3.62 (dd, *J* = 11.8, 5.5 Hz, 1H). NMR spectra in D_2O match those previously reported in the literature.[8]

Reduction of 12-SiMe$_2$Et (mannitol) to form 13



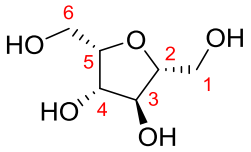
12-SiMe$_2$Et

Si=SiMe$_2$Et

13

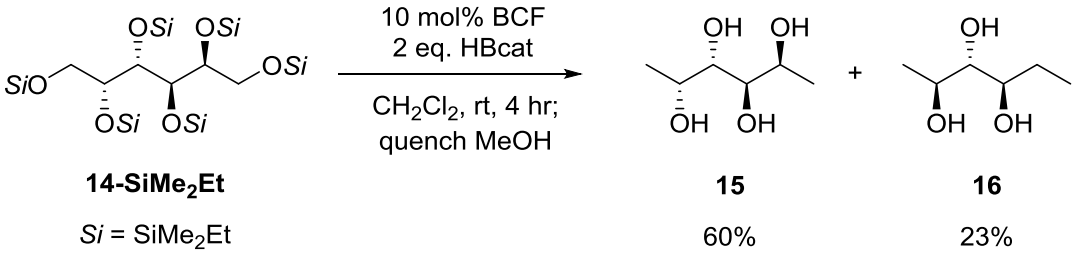
60%

In a nitrogen-filled glovebox, a 1-dram vial was charged with dimethylethylsilane-mannitol (70.0 mg, 0.10 mmol, 1.0 equiv.). A separate 1-dram vial was charged with $B(C_6F_5)_3$ (5.1 mg, 0.010 mmol, 0.10 equiv.) and dichloromethane (0.5 mL) was added by syringe. The $B(C_6F_5)_3$ solution was then transferred to the starting material vial. Catecholborane (12.8 µL, 0.12 mmol, 1.2 equiv.) was added by microliter syringe and the vial was capped and shaken manually for 30 seconds. Subsequently the solution was transferred by syringe to an NMR tube, which was capped with a septum and removed from the box. The NMR tube was allowed to stand for 16 hr. The reaction mixture was transferred to a scintillation vial and dichloromethane was used to collect the remaining residue (3 x 1 mL). The reaction was quenched and silyl-groups deprotected when methanol (0.5 mL) was added. Subsequently the solvent was removed by vacuum, to afford a cloudy oil. The residue was purified by silica gel chromatography (5 x 1 cm column) with gradient elution (50:1, 25:1, 10:1, 5:1 DCM: methanol) to afford a 2,5-sorbitan **13** (9.8 mg, 47%)

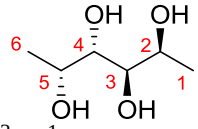


(2*R*,3*S*,4*S*,5*S*)-2,5-bis(hydroxymethyl)tetrahydrofuran-3,4-diol (2,5-anhydro-D-glucitol): $^{13}C\{^1H\}$ NMR (151 MHz, CD_3OD) δ 87.1 (s), 82.8 (s), 79.9 (s), 78.8 (s), 63.5 (s), 61.8 (s). ^1H NMR (600 MHz, CD_3OD) δ 4.06 (dt, *J* = 6.3, 4.4 Hz, 1H), 4.03 (dd, *J* = 4.1, 2.1 Hz, 1H), 3.99 (dd, *J* = 3.4, 2.1 Hz, 1H), 3.82 – 3.79 (m, 2H), 3.77 – 3.66 (m, 3H). NMR spectra in D_2O match those previously reported in the literature.[9]

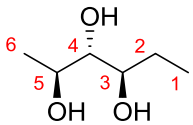
Reduction of 14-$SiMe_2Et$ (galactitol) to form 15 and 16



In a nitrogen-filled glovebox, a 1-dram vial was charged with dimethylethylsilane-galactitol (70.0 mg, 0.10 mmol, 1.0 equiv.). A separate 1-dram vial was charged with $B(C_6F_5)_3$ (5.1 mg, 0.01 mmol, 0.10 equiv.) and dichloromethane (0.5 mL) was added by syringe. The $B(C_6F_5)_3$ solution was then transferred to the starting material vial. Catecholborane (21.3 µL, 0.20 mmol, 2.0 equiv.) was added by microliter syringe and the vial was capped and shaken manually for 30 seconds. Subsequently the solution was transferred by syringe to an NMR tube, which was capped with a septum and removed from the box. The NMR tube was allowed to stand for 4 hr. The reaction mixture was transferred to a scintillation vial and dichloromethane was used to collect the remaining residue (3 x 1 mL). The reaction was quenched and silyl-groups deprotected when methanol (0.5 mL) was added. Subsequently the solvent was removed by vacuum, to afford a cloudy oil. The residue was purified by silica gel chromatography (5 x 1 cm column) with gradient elution (50:1, 25:1, 10:1, 5:1 DCM: methanol) to afford a tetraol **15** (9 mg, 60%) and triol **16** (3 mg, 23%).



(2*R*,3*S*,4*R*,5*S*)-hexane-2,3,4,5-tetraol: $^{13}C\{^{1}H\}$ NMR (151 MHz, CD_3OD) δ 75.0 (s, C_3 & C_4), 67.8 (s, C_2 & C_5), 19.9 (s, C_1 & C_6). ^{1}H NMR (600 MHz, CD_3OD) δ 4.03 (app q, J = 6.5 Hz, 2H, H_2 & H_5), 3.40 (app s, 2H, H_2 & H_4), 1.23 (d, J = 6.6 Hz, 6H, H_1 & H_6). NMR spectra match those previously reported in the literature.[5]



(2*R*,3*S*,4*R*)-hexane-2,3,4-triol: $^{13}C\{^{1}H\}$ NMR (151 MHz, CD_3OD) δ 78.5 (s, C_4), 75.5 (s, C_3), 70.0 (s, C_5), 26.8 (s, C_2), 18.4 (s, C_6), 10.2 (s, C_1). ^{1}H NMR (600 MHz, CD_3OD) δ 3.85 (app quint, J = 6.2 Hz, 1H, H_5), 3.43 (ddd, J = 9.0, 7.4, 2.8 Hz, 1H, H_3), 3.28 (dd, J = 7.4, 5.8 Hz, 1H, H_4), 1.77 (ddq, J = 14.0, 7.6, 2.8 Hz, 1H, H_2), 1.41 (ddq, J = 14.4, 8.9, 7.3 Hz, 1H, $H_{2'}$), 1.19 (d, J = 6.3 Hz, 3H, H_6), 0.99 (t, J = 7.5 Hz, 3H, H_1). NMR spectra match those previously reported in the literature.[5]

Full Gaussian Reference

Gaussian 09, Revision E.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M Caricato, A. Marenich, J. Bloino, B. G. Janeska, R. Gomperts, B. Mennucci, H. P. Hratchian, J. B. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, R. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, B. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreve, K. Throssel, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farka, J. B. Foresman, and D. J. Fox, Gaussian, Inc., Wallingford CT, **2016**.

Computational Method

Calculations were carried out with the Gaussian 09 program package, revision E.01. Geometry optimizations and frequency analysis were performed with the M06-2X functional with the 6-311+G(d,p) basis set (M06-2X/6-31+G(d,p). The conductor-like polarizable continuum (CPCM) solvation model was used with solvent parameters for dichloromethane.[10,11]

Table of Summarized Energies

Compound	Absolute E (a. u.)	# imaginary freq	Zero Point E (a. u.)	G (a. u.)
HBcat	-406.895593	0	-406.792111	-406.822291
Me_3SiH	-409.75735	0	-409.638458	-409.669094
$(Me_3Si)_2$-2-propanol$^+$	-1011.91886	0	-1011.591494	-1011.636815
$Me_3SiBcat$-2-propanol$^+$	-1009.045706	0	-1008.73668	-1008.784521
$Bcat_2$-2-propanol$^+$	-1006.16223	0	-1005.871412	-1005.920136
Me_3Si-propane-1,2-diol (Me_3Si^+ on C2)	-1495.735267	0	-1495.300402	-1495.356844
Me_3Si-propane-1,2-diol ($Bcat^+$ chelate)	-1492.894576	0	-1492.478059	-1492.535527

References

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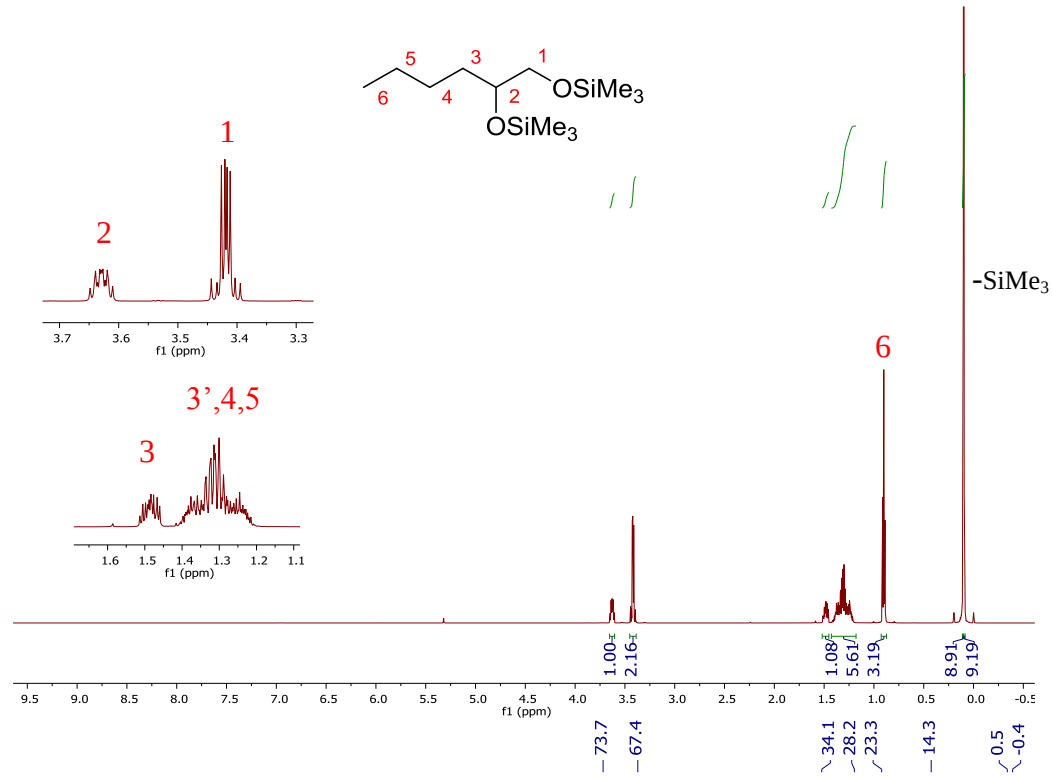
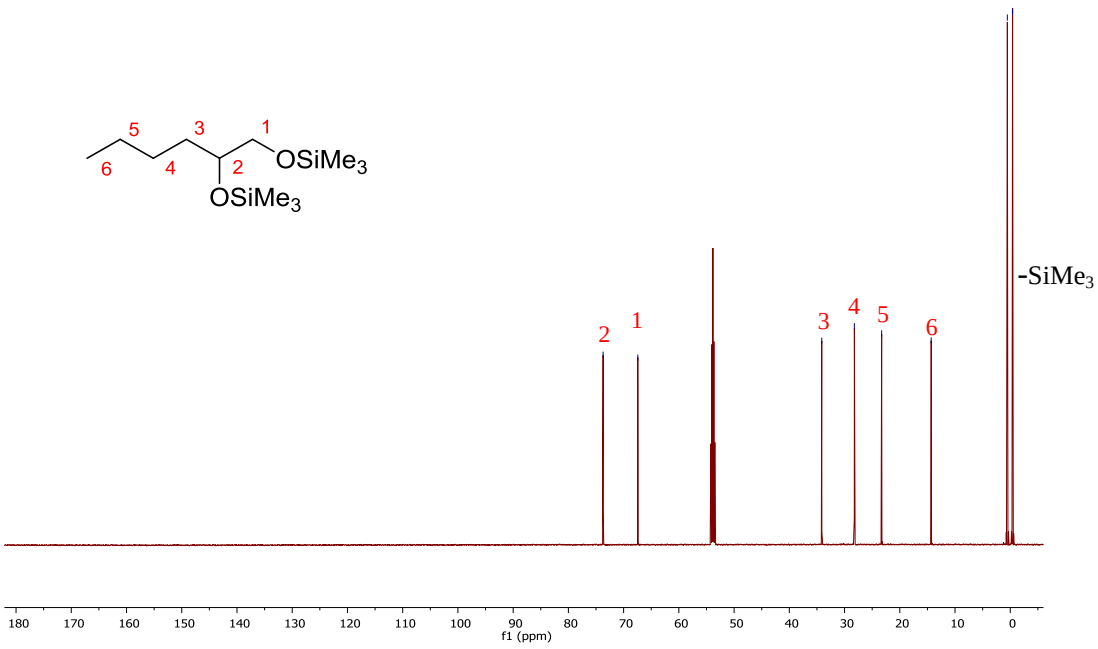
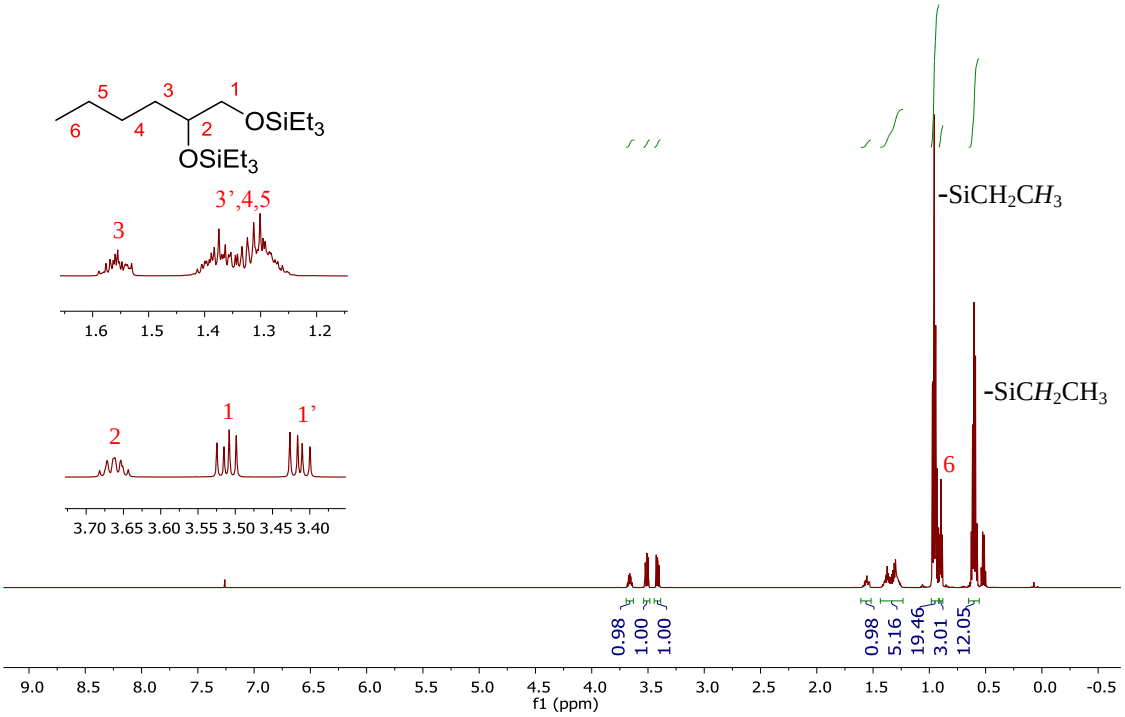
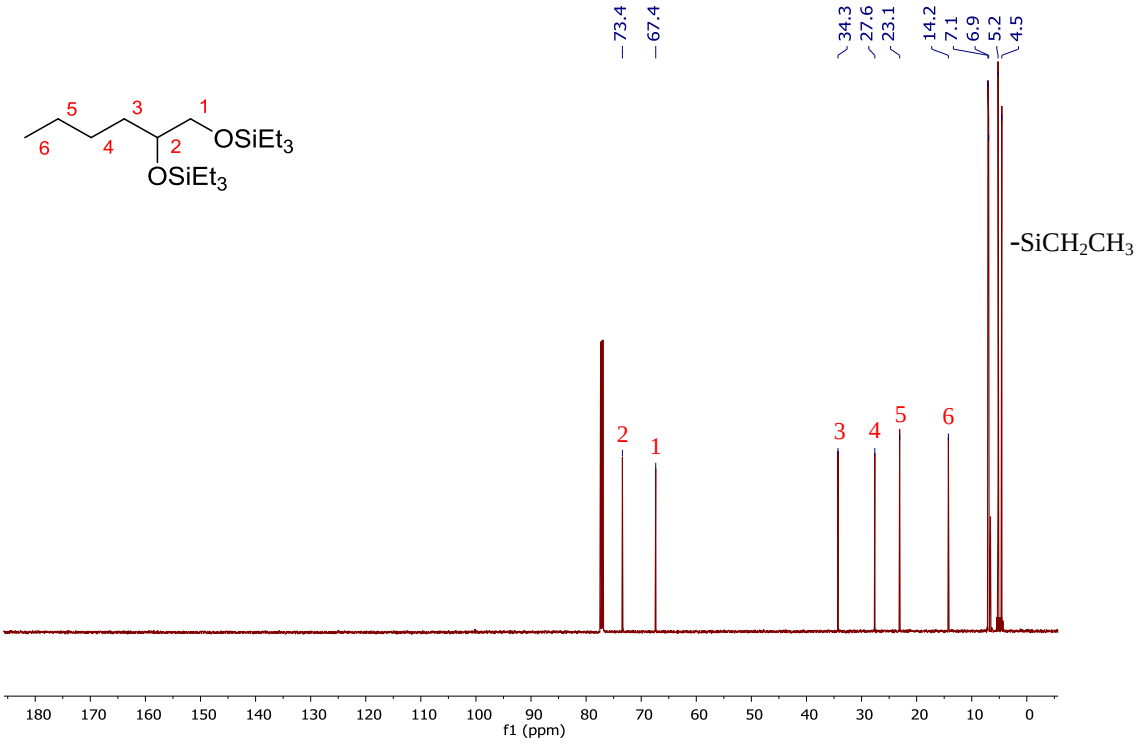
NMR Data


5
3
1
6
4
2
OSiMe3
OSiMe3
1
2
3’,4,5
3
-SiMe3
6
1.00
2.16
1.08
5.61
3.19
8.91
9.19
f1 (ppm)
73.7
67.4
34.1
28.2
23.3
14.3
0.5
-0.4


5
3
1
6
4
2
OSiMe3
OSiMe3
-SiMe3
2
1
3
4
5
6
f1 (ppm)


OSiEt3
OSiEt3
3',4,5
3
1.6 1.5 1.4 1.3 1.2
1
1'
2
3.70 3.65 3.60 3.55 3.50 3.45 3.40
-SiCH2CH3
-SiCH2CH3
6
0.98 1.00 1.00 0.98 5.16 19.46 3.01 12.05
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


73.4
67.4
34.3
27.6
23.1
14.2
7.1
6.9
5.2
4.5
OSiEt3
OSiEt3
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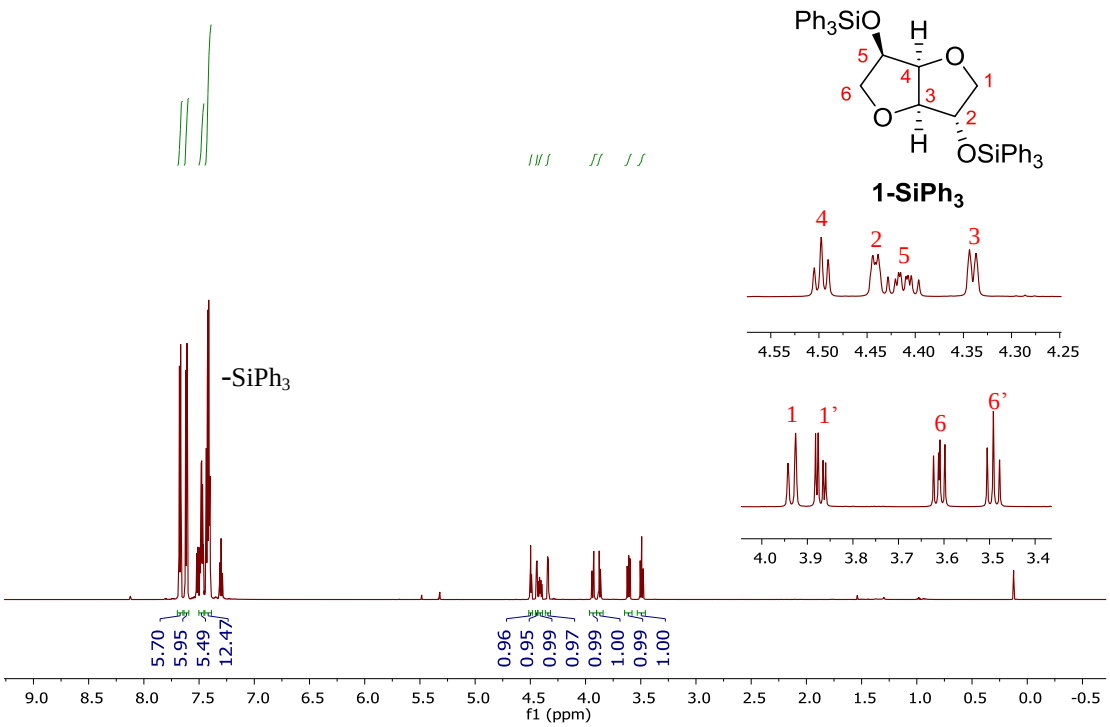
2
1
3
4
5
6
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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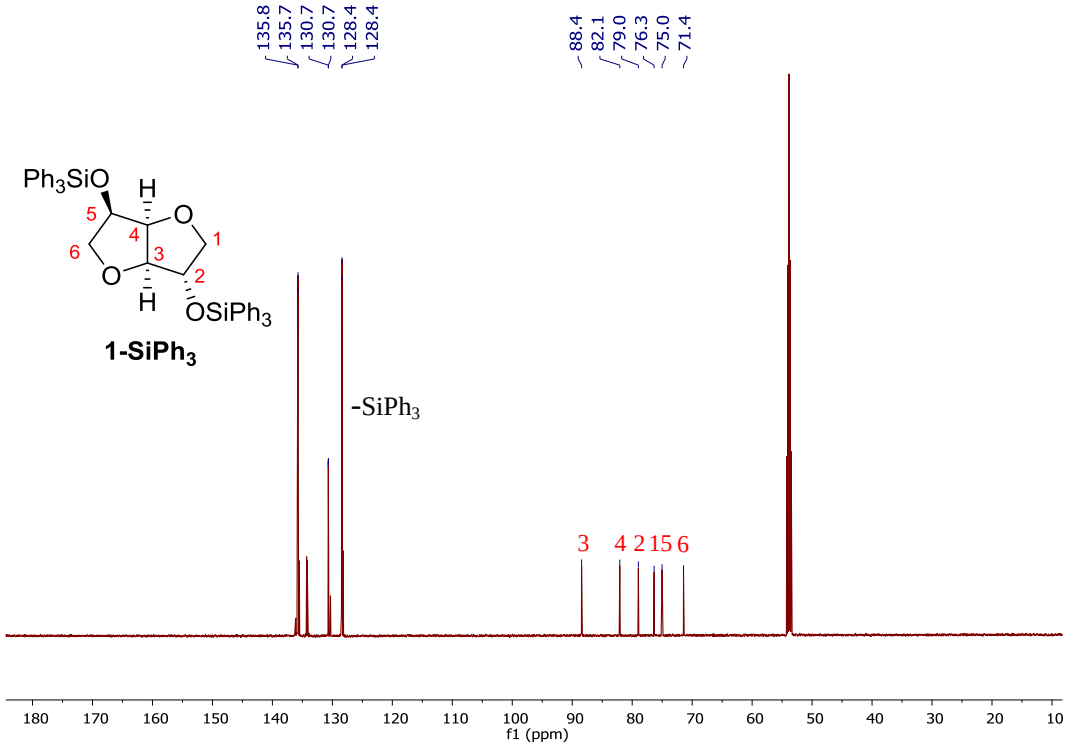
H
5
4
O
1
6
3
2
O
H
OSiPh3
1-SiPh3
4
2
5
3
4.55 4.50 4.45 4.40 4.35 4.30 4.25
1
1'
6
6'
4.0 3.9 3.8 3.7 3.6 3.5 3.4
-SiPh3
5.70
5.95
5.49
12.47
0.96
0.95
0.99
0.97
0.99
1.00
0.99
1.00
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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135.7
130.7
130.7
128.4
128.4
88.4
82.1
79.0
76.3
75.0
71.4
Ph3SiO
H
5
4
O
1
6
3
2
O
H
OSiPh3
1-SiPh3
-SiPh3
3
4
2
1
5
6
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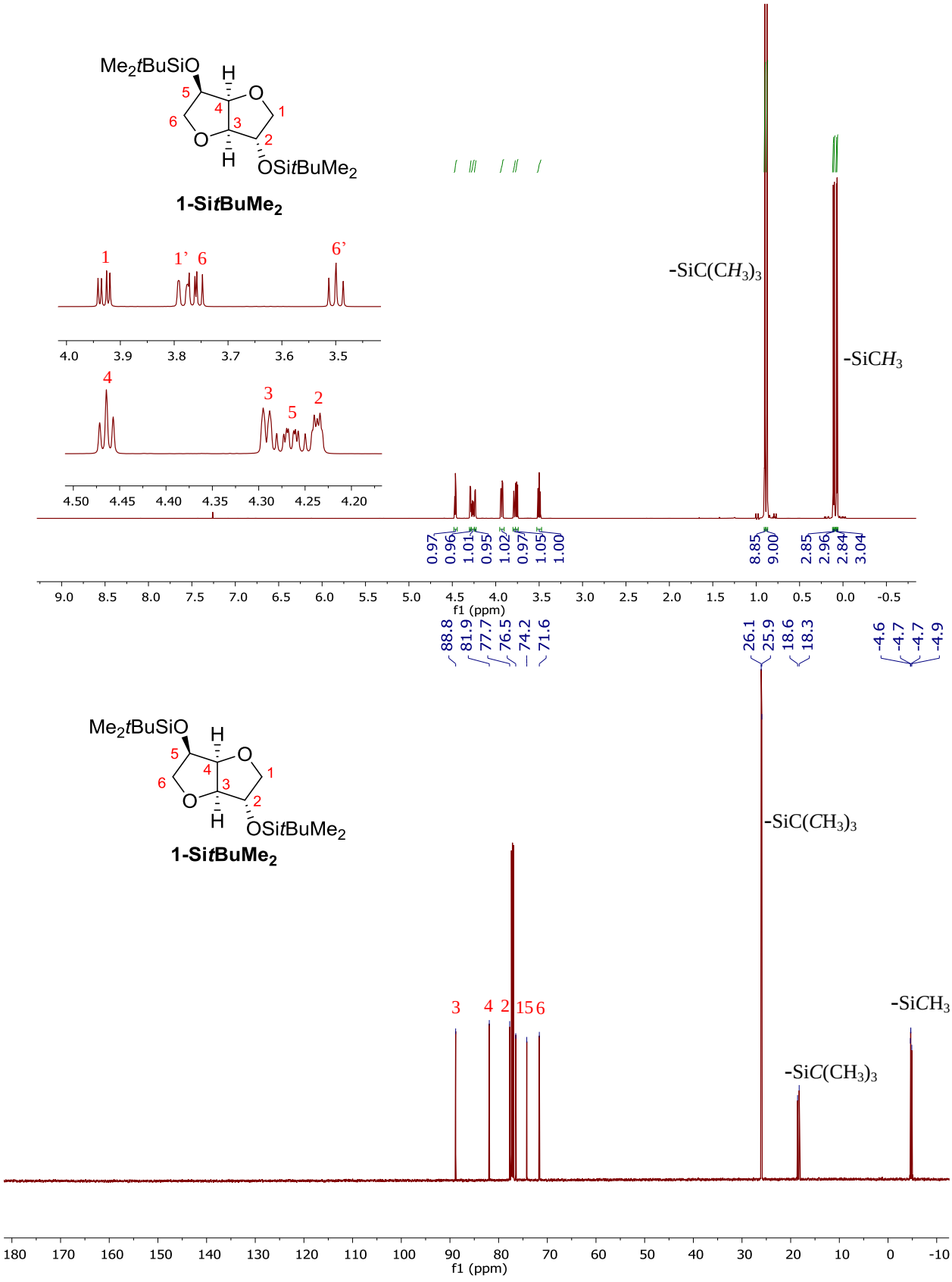
f1 (ppm)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1-SitBuMe2
-SiC(CH3)3
-SiCH3
f1 (ppm)
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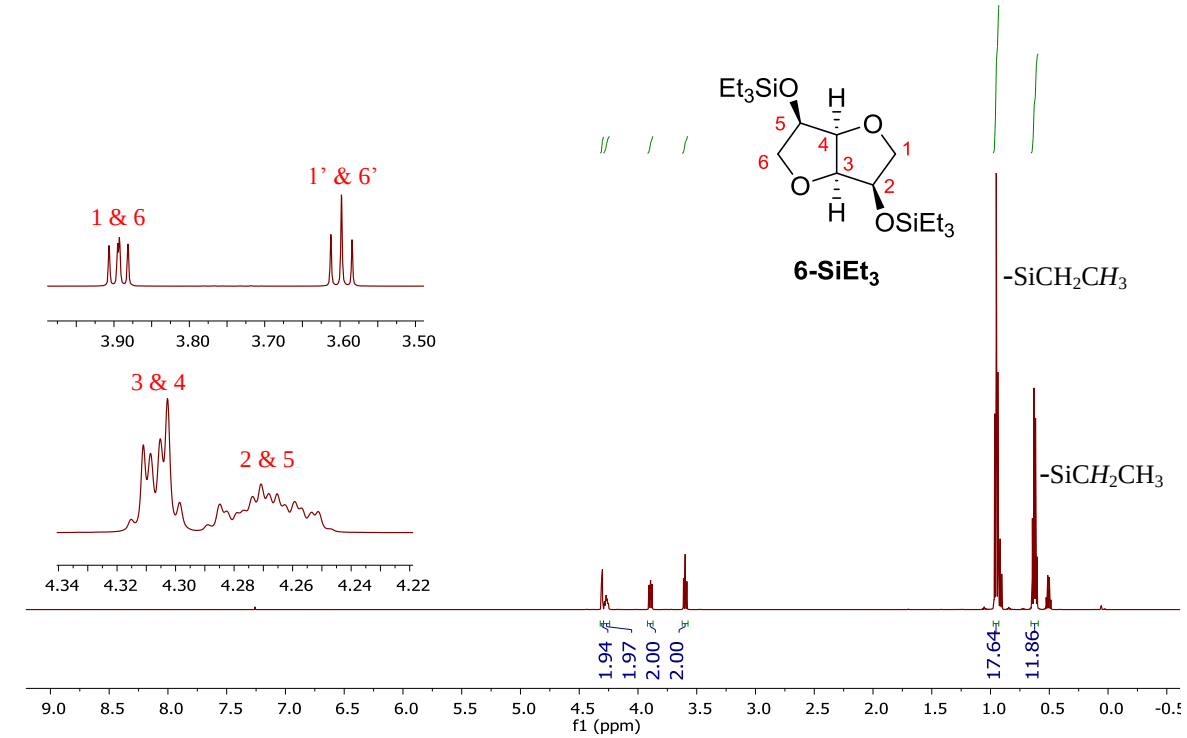
-SiC(CH3)3
-SiCH3
f1 (ppm)


1 & 6
1' & 6'
3 & 4
2 & 5
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OSiEt3
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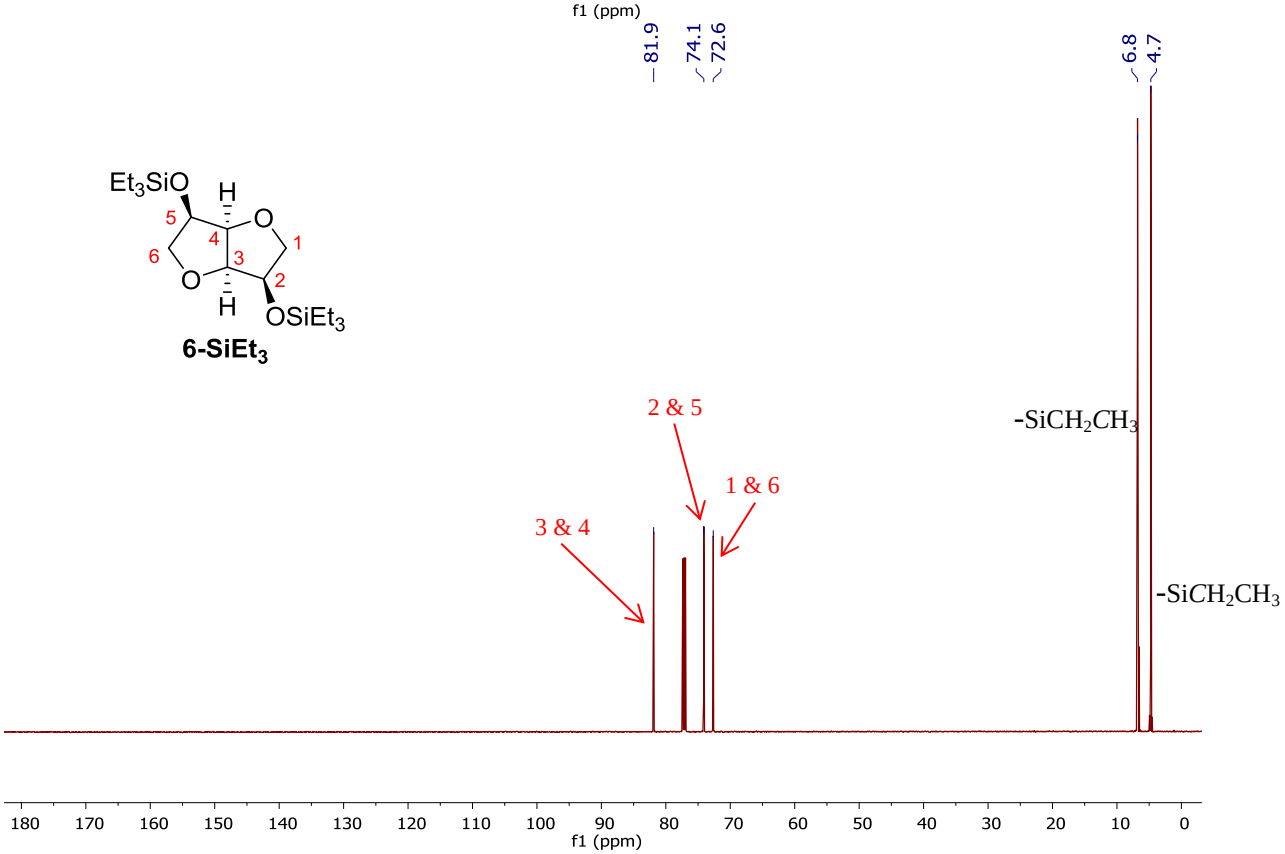
2.00
2.00
17.64
11.86
f1 (ppm)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72.6
6.8
4.7
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2 & 5
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3 & 4
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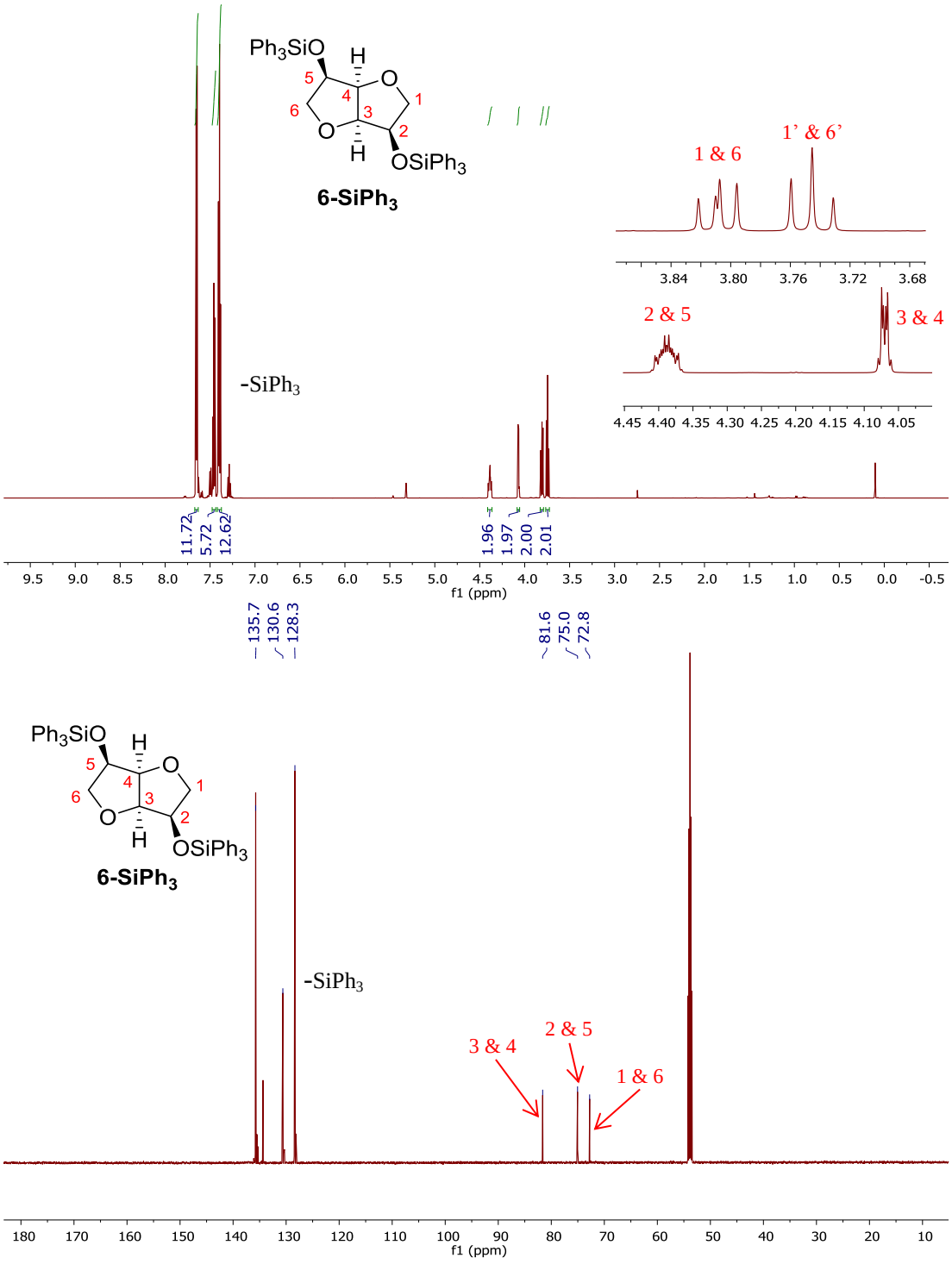
f1 (ppm)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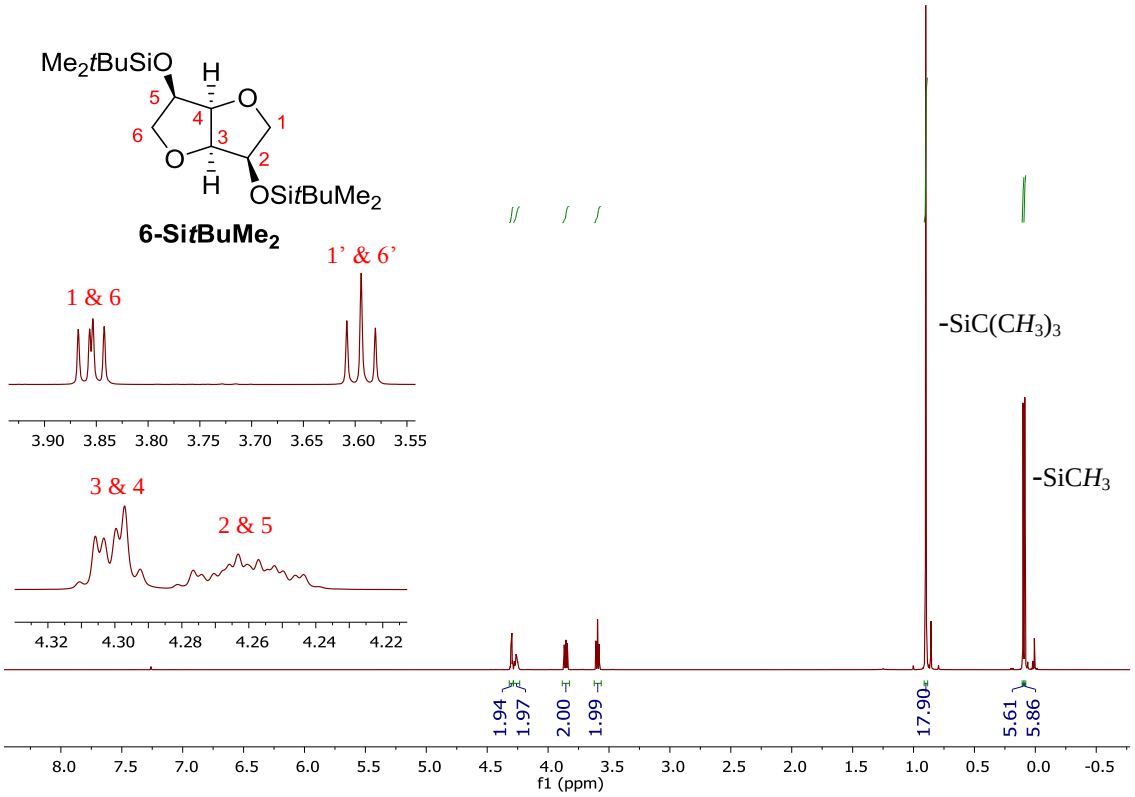
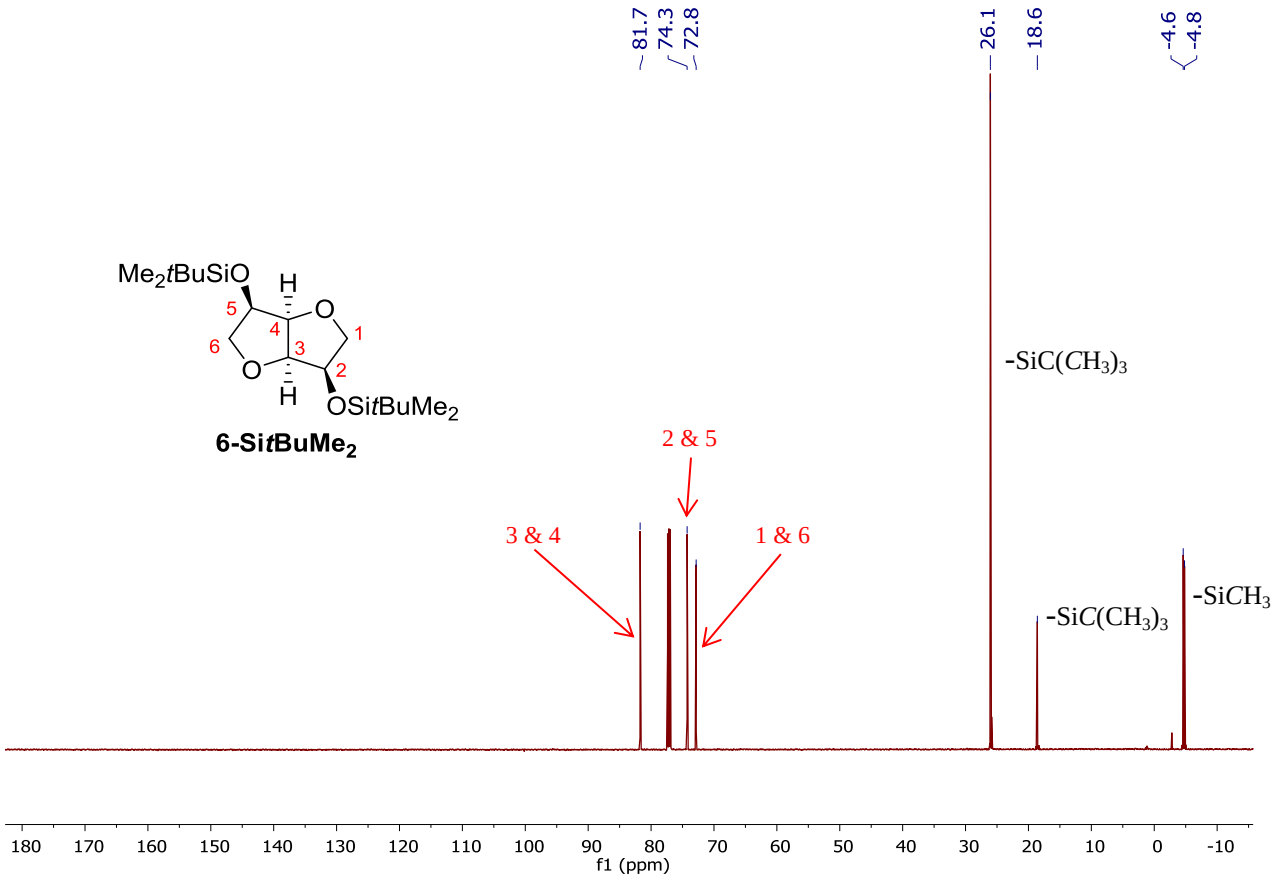
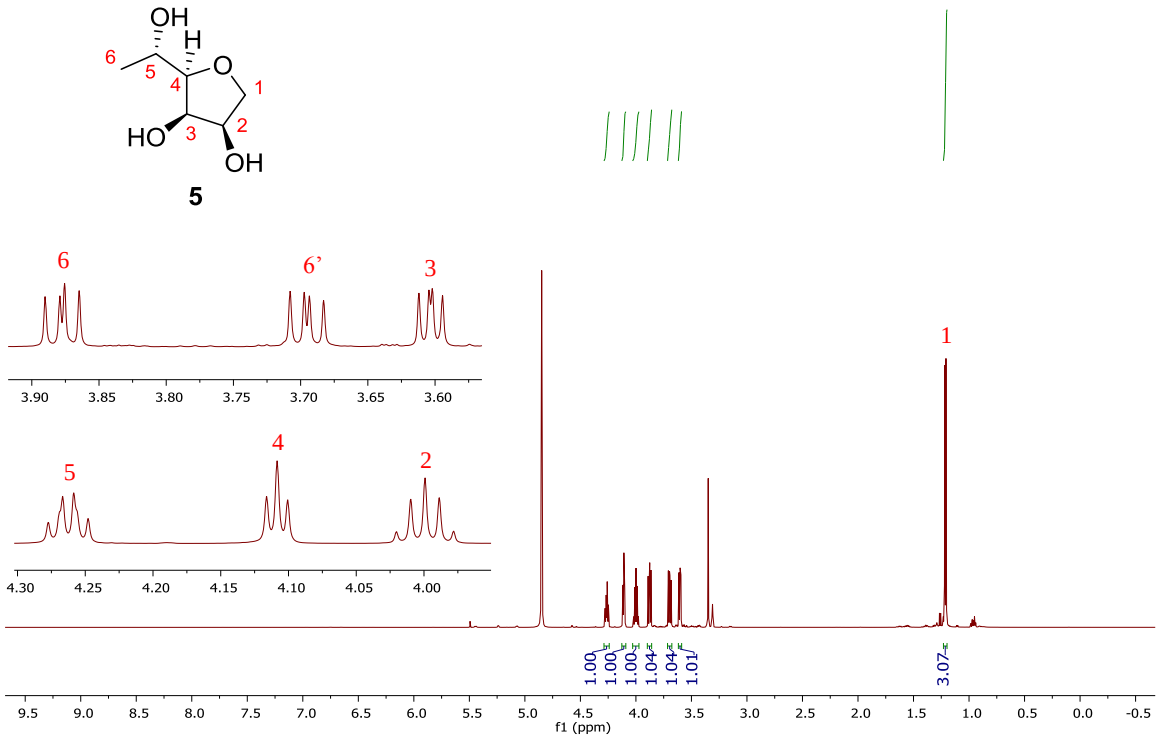
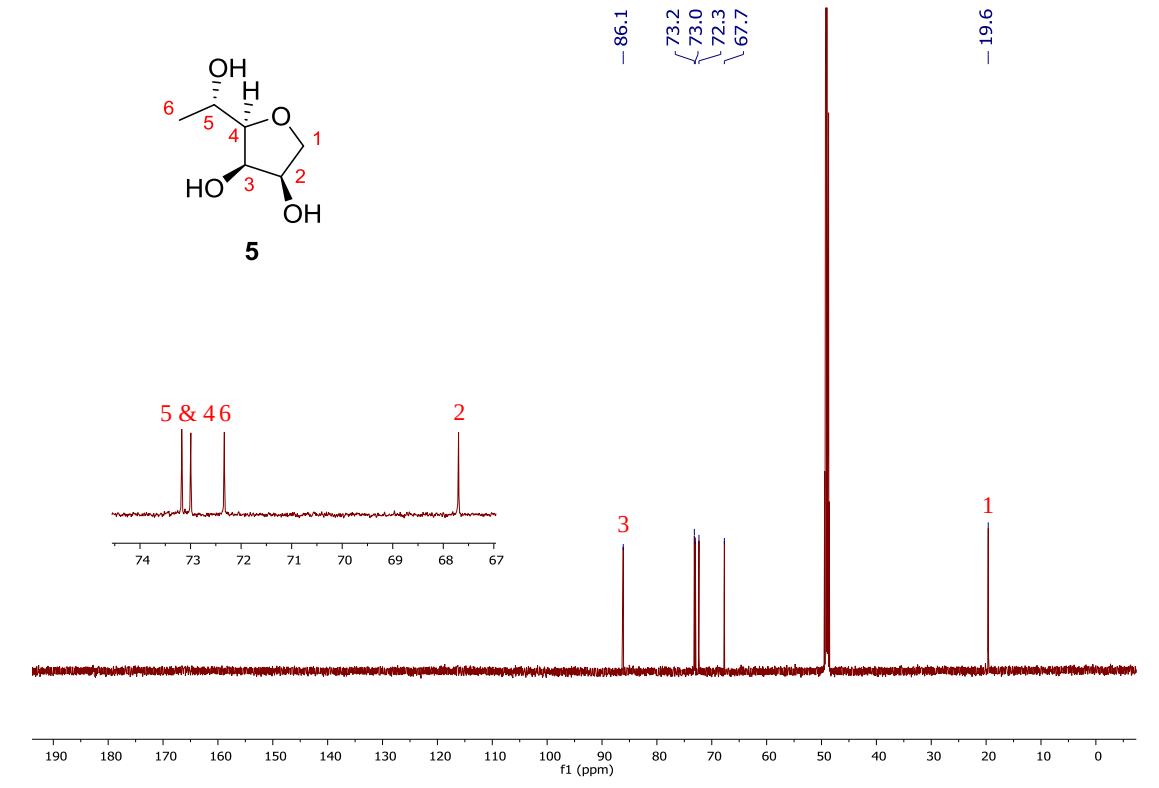
H
5
4
O
1
6
3
2
O
H
OSiPh3
6-SiPh3
1 & 6
1' & 6'
3.84
3.80
3.76
3.72
3.68
2 & 5
3 & 4
4.45 4.40 4.35 4.30 4.25 4.20 4.15 4.10 4.05
-SiPh3
11.72
5.72
12.62
1.96
1.97
2.00
2.01
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)
135.7
130.6
128.3
81.6
75.0
72.8
Ph3SiO
H
5
4
O
1
6
3
2
O
H
OSiPh3
6-SiPh3
-SiPh3
3 & 4
2 & 5
1 & 6
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)


Me2tBuSiO
OSitBuMe2
6-SitBuMe2
1 & 6
1' & 6'
3 & 4
2 & 5
-SiC(CH3)3
-SiCH3
1.94
1.97
2.00
1.99
17.90
5.61
5.86
f1 (ppm)

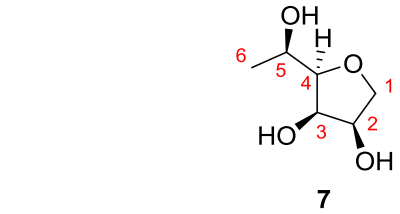

81.7
74.3
72.8
26.1
18.6
-4.6
-4.8
Me2tBuSiO
OSitBuMe2
6-SitBuMe2
-SiC(CH3)3
2 & 5
3 & 4
1 & 6
-SiC(CH3)3
-SiCH3
f1 (ppm)


OH
H
O
HO
OH
1
2
3
4
5
6
5
6
6'
3
4
2
1
3.90
3.85
3.80
3.75
3.70
3.65
3.60
4.30
4.25
4.20
4.15
4.10
4.05
4.00
1.00
1.00
1.00
1.04
1.04
1.01
3.07
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

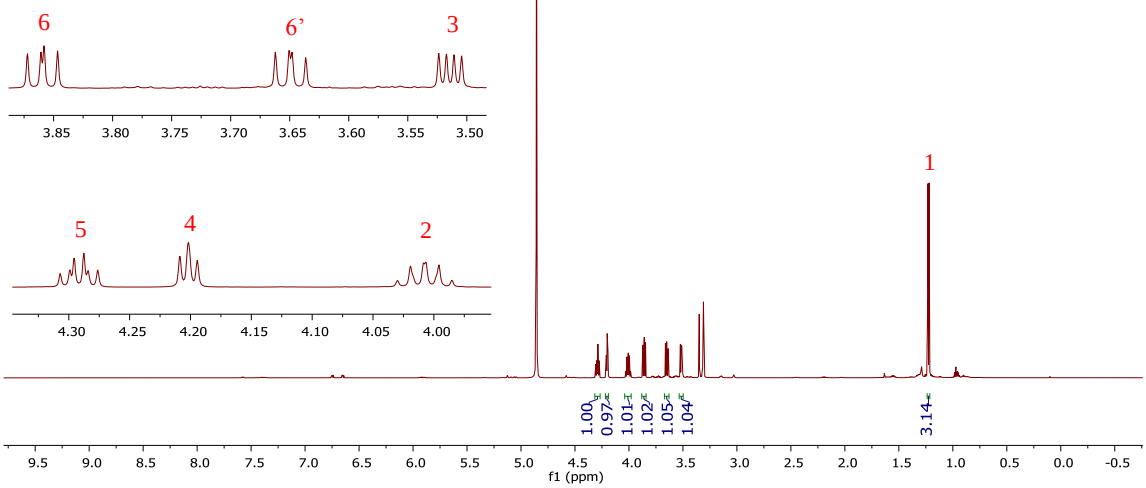
5

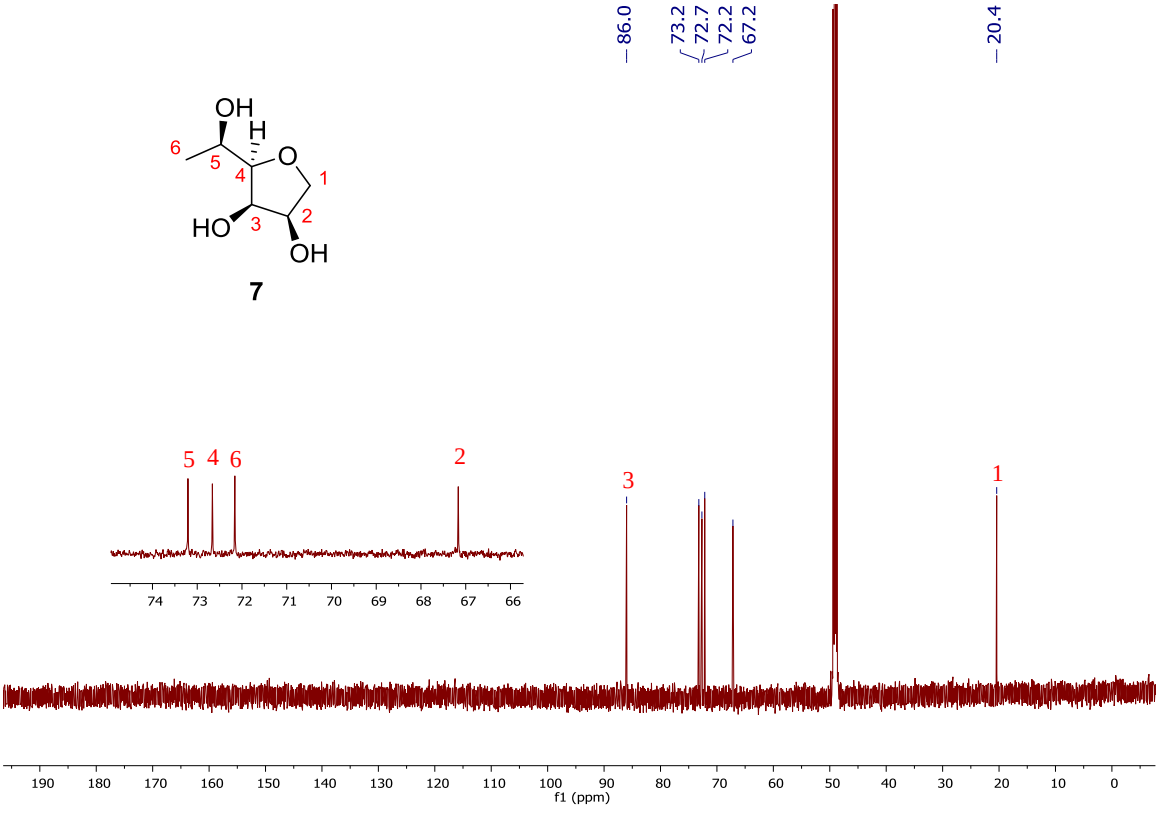

OH
H
O
HO
OH
1
2
3
4
5
6
86.1
73.2
73.0
72.3
67.7
19.6
5 & 4 6
2
3
1
74
73
72
71
70
69
68
67
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

5


OH
H
6
5
4
O
1
HO
3
2
OH

7


6
6'
3
5
4
2
1
1.00
0.97
1.01
1.02
1.05
1.04
3.14
f1 (ppm)


86.0
73.2
72.7
72.2
67.2
20.4
OH
H
6
5
4
O
1
HO
3
2
OH
5 4 6
2
3
1
f1 (ppm)

7

Optimized Coordinates for each structure

HBcat

C	-0.52181800	0.81002400	0.20865400
C	0.80476500	0.67181500	0.60412300
C	1.71610400	1.70468000	0.49816700
C	1.23127200	2.90688000	-0.03229200
C	-0.10208200	3.04577300	-0.43011500
C	-1.01441700	1.98926900	-0.31643000
H	2.74726800	1.58564900	0.81065200
H	1.90819500	3.74830700	-0.13493300
H	-0.44069500	3.99333200	-0.83543500
H	-2.05020900	2.08583200	-0.62121000
O	-1.18149000	-0.37825900	0.43529600
O	0.99727400	-0.60476900	1.08472200
B	-0.23196800	-1.22773100	0.97230800
H	-0.44479800	-2.34164400	1.29462200

Me_3SiH

Si	-0.46651400	0.24076800	-0.00003400
H	-1.95788700	0.24126600	-0.00012500
C	0.14262600	1.12986800	1.54273900
H	-0.21156000	2.16491600	1.56916100
H	-0.20472000	0.62755400	2.45083100
H	1.23751500	1.14586800	1.56244400
C	0.14059400	-1.54128500	0.00007800
H	-0.21085100	-2.07853600	0.88637800
H	-0.21076700	-2.07862300	-0.88620100
H	1.23539700	-1.56742500	0.00013100
C	0.14282200	1.12974700	-1.54279800
H	-0.20436700	0.62733200	-2.45089400
H	-0.21140400	2.16477700	-1.56937100
H	1.23771300	1.14579100	-1.56233900

$(Me_3Si)_2$-2-propanol$^+$

C	-0.73765500	2.19866300	-1.28493100
H	-0.68006000	3.28657100	-1.37532000
H	-1.79134900	1.91740800	-1.33250700
H	-0.20892000	1.75612200	-2.13268800
C	-0.09210100	1.80021700	0.02535500
H	0.95108600	2.12101100	0.00809400
C	-0.73319100	2.35609800	1.27947500
H	-1.81410400	2.22044500	1.29347400
H	-0.29580000	1.89822300	2.17021500
H	-0.52881200	3.42958500	1.31197900
O	0.00368100	0.29974200	0.11441300

Si	1.72711700	-0.25634600	0.02167300
C	1.79312000	-2.11362300	0.01936900
H	1.16425000	-2.59236600	-0.73453500
H	2.83401100	-2.35200100	-0.23154200
H	1.58279400	-2.54560300	0.99899700
C	2.35898700	0.42404700	-1.59237000
H	3.38607500	0.06772500	-1.72594000
H	1.76705000	0.04770600	-2.43273700
H	2.38005900	1.51565100	-1.63730100
C	2.50624800	0.45303400	1.55302300
H	1.96468600	0.11887200	2.44339000
H	3.53243700	0.07748800	1.62346900
H	2.55046500	1.54500900	1.55638000
Si	-1.43765800	-0.78791100	-0.01328100
C	-1.45866100	-1.30659900	-1.80005700
H	-2.21941200	-2.08286000	-1.93313000
H	-1.71554200	-0.46616700	-2.45120900
H	-0.50069100	-1.71768700	-2.13010300
C	-1.15023800	-2.15568700	1.22042600
H	-2.13221400	-2.45849400	1.59867100
H	-0.66993200	-3.03534100	0.79031900
H	-0.56231900	-1.80977800	2.07636300
C	-2.99319400	0.10570200	0.48592500
H	-3.00294900	0.33551300	1.55429400
H	-3.24300500	1.00105100	-0.08377100
H	-3.78958100	-0.62754500	0.30506000

$Me_3SiBcat\text{-}2\text{-}propanol^+$

C	-2.40339400	-1.89392800	1.46674300
H	-2.70160800	-2.93017200	1.64651700
H	-3.31008500	-1.28592900	1.45674300
H	-1.75813900	-1.57739300	2.28885400
C	-1.66984900	-1.85441200	0.14787400
H	-0.75518400	-2.44225400	0.20770800
C	-2.46020700	-2.25816700	-1.07300600
H	-3.44178200	-1.78684100	-1.11111600
H	-1.90631400	-2.03801000	-1.98807800
H	-2.60889700	-3.33992700	-1.01859700
O	-1.12977700	-0.42881800	-0.05336500
Si	-2.16689000	1.13704900	-0.07388900
C	-1.36332400	2.14400000	-1.40915600
H	-1.13190300	1.52439300	-2.28134000
H	-2.08607500	2.90296700	-1.72715300
H	-0.45457500	2.64397700	-1.07313800
C	-3.90276800	0.69340000	-0.55543000
H	-4.44850700	1.64351500	-0.49170300

H	-3.96390100	0.35298300	-1.59159800
H	-4.41213900	-0.01463100	0.09901600
C	-1.97625300	1.75366300	1.66277300
H	-0.92269700	1.88345500	1.92341600
H	-2.46907600	2.72821800	1.74194700
H	-2.44383100	1.07810700	2.38394400
B	0.26713700	-0.30239100	-0.04165100
O	0.88725100	0.90234100	0.14432100
O	1.12724800	-1.35337200	-0.19783200
C	2.24058800	0.59551500	0.09113300
C	2.38595000	-0.77249300	-0.11364900
C	3.32051100	1.44379500	0.21417200
C	3.62088200	-1.37847200	-0.20740600
C	4.58324400	0.84407400	0.12114000
H	3.19414600	2.50805200	0.37392100
C	4.72951600	-0.53076700	-0.08433800
H	3.72138400	-2.44543000	-0.36739700
H	5.46767000	1.46492600	0.21133700
H	5.72513100	-0.95520500	-0.15068500

$Bcat_2$-2-propanol$^+$

C	-0.66698400	3.12879700	-1.29578200
H	-0.50066800	4.20705400	-1.38288500
H	-1.74149300	2.95048900	-1.25298300
H	-0.23259600	2.65248300	-2.17629500
C	0.03176600	2.70446700	-0.03591500
H	1.10445900	2.87654700	-0.08465700
C	-0.55870900	3.14785000	1.27163400
H	-1.63022700	2.95380000	1.32563800
H	-0.04375600	2.69322500	2.11943500
H	-0.40056200	4.22955200	1.32404700
O	0.03563300	1.08192100	-0.02065700
B	1.30355400	0.43142900	-0.01203400
O	2.46051200	1.14569500	-0.01881300
O	1.45474900	-0.91641200	0.00699900
C	3.44716900	0.16299400	-0.00334300
C	2.83627100	-1.08576000	0.01243200
C	4.81675900	0.31909200	-0.00304500
C	3.55665500	-2.26108100	0.02945900
C	5.56393300	-0.86539600	0.01429100
H	5.27994900	1.29845100	-0.01556100
C	4.95021600	-2.12166400	0.03010400
H	3.06929200	-3.22866900	0.04141700
H	6.64644900	-0.80321800	0.01528800
H	5.56687800	-3.01344700	0.04307900
B	-1.19872100	0.36994200	-0.00999500

O	-2.39503800	1.01179100	0.05762800
O	-1.27206100	-0.98410100	-0.06785700
C	-3.32215000	-0.02678300	0.04010400
C	-2.64022400	-1.23574900	-0.03544600
C	-4.69785000	0.04799200	0.08709400
C	-3.29118800	-2.45064800	-0.06935400
C	-5.37489800	-1.17754100	0.05346200
H	-5.21659800	0.99734100	0.14652400
C	-4.68981000	-2.39410200	-0.02289000
H	-2.74913800	-3.38687300	-0.12875300
H	-6.45866500	-1.17955200	0.08762300
H	-5.25358600	-3.32000900	-0.04700600

Me_3Si-propane-1,2-diol (Me_3Si^+ on C2)

C	-1.09239000	-1.14210100	2.73807100
H	-0.55769100	-1.00306400	3.68110700
H	-1.10290100	-2.20743000	2.51265600
H	-2.11661200	-0.78856000	2.87647100
C	-0.38640600	-0.31301200	1.68506600
H	-0.15664000	0.66226800	2.10730900
C	0.89820800	-0.90756400	1.14597900
H	0.70704600	-1.88276300	0.67001000
H	1.56272500	-1.08611900	2.00361200
O	-1.27345500	0.00062900	0.52215100
O	1.44625300	0.00090400	0.22153000
Si	-1.35360800	1.74800300	0.00168000
Si	3.08046600	-0.05052600	-0.23033700
C	-0.17420300	2.74729300	1.03784900
H	-0.19436500	3.75663400	0.60899500
H	-0.47880300	2.83301800	2.08444800
H	0.85007800	2.37146100	0.97749600
C	-3.11168100	2.26393500	0.33845400
H	-3.12622100	3.35135500	0.46725700
H	-3.80492800	2.00925200	-0.46455500
H	-3.46986100	1.81238100	1.26904100
C	-0.81694700	1.78617700	-1.77897400
H	-1.44161100	1.21468800	-2.46782400
H	-0.84829400	2.83447600	-2.09726000
H	0.21708200	1.43823800	-1.85960800
C	3.18339000	1.13860100	-1.66470300
H	4.22125000	1.26144900	-1.98973400
H	2.60329100	0.77354100	-2.51859400
H	2.79860900	2.12338700	-1.37963100
C	3.50152500	-1.80678100	-0.72559500
H	4.53347600	-1.86002600	-1.08763500

H	3.41132500	-2.49530700	0.12121900
H	2.84382900	-2.15904800	-1.52713500
C	4.12094400	0.50426700	1.22298200
H	5.18081600	0.51264500	0.94815000
H	3.84270500	1.51554900	1.53597000
H	4.00640100	-0.16559800	2.08127400
Si	-1.84866700	-1.29060200	-0.61828800
C	-0.51453700	-1.51186400	-1.90577100
H	-0.25646400	-2.57279200	-1.98321200
H	-0.85642300	-1.16931500	-2.88644500
H	0.38781800	-0.95475900	-1.63930100
C	-3.46549300	-0.64341800	-1.27561600
H	-3.38465400	0.23457300	-1.91868000
H	-3.88811500	-1.45325800	-1.88173700
H	-4.16874300	-0.43344500	-0.46484200
C	-2.17491400	-2.87030700	0.30981800
H	-2.88856700	-2.75056500	1.12764900
H	-2.63223500	-3.53120700	-0.43737700
H	-1.27536700	-3.37154100	0.67332400

Me_3Si-propane-1,2-diol ($Bcat^+$ chelate)

C	-1.47921100	-2.45343900	-1.91914800
H	-1.48471600	-3.53294400	-2.08758200
H	-0.60059400	-2.02152400	-2.40653300
H	-2.37862000	-2.02582400	-2.36541800
C	-1.44644200	-2.17991300	-0.43146000
H	-2.30302600	-2.60922100	0.09132300
C	-0.14821600	-2.57736400	0.24814200
H	0.26445800	-3.50634500	-0.14508000
H	-0.24584900	-2.61564300	1.33586500
O	-1.45166200	-0.73213800	-0.20136700
O	0.73540000	-1.47842700	-0.10381100
Si	-2.91946800	0.14505800	0.36605300
Si	2.49798300	-1.61640400	0.26324900
C	-4.30454500	-0.62260200	-0.60943000
H	-5.23781600	-0.14294100	-0.29487500
H	-4.18352900	-0.44103000	-1.68106700
H	-4.41748900	-1.69661500	-0.43817200
C	-2.61870500	1.91480100	-0.10308400
H	-3.58174100	2.43593500	-0.09787900
H	-1.95149900	2.42585500	0.59500700
H	-2.20280100	1.99016300	-1.11281000
C	-2.98196100	-0.20280600	2.18855400
H	-2.08337000	0.18505900	2.67637900
H	-3.85598500	0.28584900	2.63039600
H	-3.05877700	-1.27560400	2.39030300

C	3.26407900	-0.10613200	-0.49030900
H	4.35095700	-0.23862500	-0.45719800
H	2.96614400	0.02066800	-1.53450300
H	3.02207300	0.80551000	0.06295500
C	2.97425800	-3.19766400	-0.59030200
H	4.06664800	-3.26071900	-0.62488300
H	2.60945400	-4.08474200	-0.06559400
H	2.60459300	-3.21301400	-1.62016500
C	2.58010800	-1.67716500	2.11762900
H	3.62827100	-1.67230300	2.43323100
H	2.08785300	-0.80009500	2.54814800
H	2.11474900	-2.58123200	2.52057000
B	-0.03750100	-0.15051400	-0.16676700
O	0.29194000	0.60869800	-1.33052800
O	0.17112800	0.66918600	0.98962500
C	0.68257300	1.84209100	-0.87901200
C	0.62027100	1.87766500	0.51672600
C	1.09877800	2.93163100	-1.61522100
C	0.97329100	2.99974900	1.23641900
C	1.45946100	4.08324600	-0.89492100
H	1.14593500	2.89406800	-2.69795100
C	1.39946900	4.11662300	0.49728500
H	0.92120700	3.01355900	2.31953800
H	1.79215300	4.96185600	-1.43725500
H	1.68591900	5.02044500	1.02429500