Supporting Information

Ketone Hydrosilylation with Sugar Silanes Followed by Intramolecular Aglycone Delivery: An Orthogonal Glycosylation Strategy

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All reagents were used as received unless otherwise noted. Solvents were purified under nitrogen using a solvent purification system (Innovative Technology, inc., Model # SPS-400-3 and PS-400-3). $Ni(COD)_2$ (Strem Chemicals, Inc., used as received), CuCl (Sigma-Aldrich, used as received), 1,3-dimesitylimidazolium chloride (IMes·HCl)[1] were stored and weighed in an inert atmosphere glovebox. $Ti(O\text{-}i\text{-}Pr)_4$ and $Me_2Si(H)Cl$ were distilled and stored under inert atmosphere in Schlenk flasks. All nickel reactions were conducted in flame-dried glassware under a nitrogen atmosphere. ^1H and ^{13}C spectra were obtained in $CDCl_3$ at rt, unless otherwise noted, on a Varian Mercury 400 or Varian Unity 500 MHz instrument. Chemical shifts of ^1H NMR spectra were recorded in parts per million (ppm) on the δ scale from an internal standard of residual chloroform (7.27 ppm). Chemical shifts of ^{13}C NMR spectra were recorded in ppm from the central peak of $CDCl_3$ (77.0 ppm) on the δ scale. High resolution mass spectra (HRMS) were obtained on a VG-70-250-s spectrometer manufactured by Micromass Corp. (Manchester UK) at the University of Michigan Mass Spectrometry Laboratory.

General Procedure for the Preparation of Sugar Silanes

The respective 2-OH sugar (1.0 equiv) was dissolved in dry CH_2Cl_2 (0.2M) and cooled to 0 °C in an ice bath. Freshly distilled NEt_3 (2.0 equiv) was added and stirred for 3 minutes, $Me_2Si(H)Cl$ (1.5 equiv) was then added. This was allowed to stir for 4 hours then volatiles were removed by rotary evaporation, the resulting oil was extracted from $NaHCO_3$ (aq.) (diluted over ice) 3 times with CH_2Cl_2. The combined organic extracts were dried quickly over $MgSO_4$, filtered, concentrated, and the resulting oil was either used directly or stored frozen in C_6H_6. Note – the sugar silanes are stable for months when stored frozen in benzene, alternatively the corresponding 2-OH sugars are very stable to be stored for long periods of time on the bench top.

General Procedure for the $Ni(COD)_2$/IMes Promoted Hydrosilylation of Ketones

A solid mixture of $Ni(COD)_2$ (10%), IMes·HCl (10%), and KO-*t*-Bu (10%) was dissolved in dry THF (0.02M) at rt under an inert atmoshphere (N_2), and stirred for 10-15 minutes until the catalyst mixture was a dark blue color. $Ti(Oi\text{-}Pr)_4$ (1.1-2.2 equiv) was

then added to the catalyst mixture followed by the addition of the sugar silane (1.1 equiv), and ketone (1.0 equiv) as a solution in dry THF (0.2M). Upon completion of the reaction, as monitored by TLC, the reaction mixture was filtered through a short plug of silica gel with a mixture of EtOAc/hexanes and concentrated by rotary evaporation. The resulting residue was purified via flash chromatography (SiO_2) to afford the desired product. Note – When doing the site-selective hydrosilylation of a ketone in the presense of a free hydroxyl group, the use of 2.2 equiv of Ti(O-*i*-Pr)$_4$, and a 0.05 M solution in THF results in higher yields of the desired product.

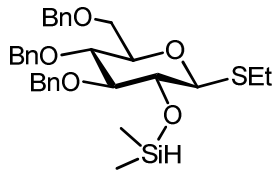
General Procedure for the CuCl/IMes Promoted Hydrosilylation of Ketones

A solid mixture of CuCl (5%), IMes·HCl (5%) and KO-*t*-Bu (10%) was dissolved in dry toluene (0.015M) at rt under an inert atmosphere (N_2), and stirred for 20 minutes. A mixture of ketone (1.0 equiv) and silane (1.1 equiv) was dissolved in dry toluene (0.2M), the catalyst was then added to this mixture as a solution in a minimum of dry toluene. Upon completion of the reaction, as monitored by TLC, the reaction mixture was filtered through a short plug of silical gel with a mixture of EtOAc/Hexanes and concentrated by rotary evaporation. The resulting residue was purified via flash chromatography (SiO_2) to afford the desired product.

General Procedure for the NIS/TMSOTf Mediated Glycosylation of Silyl-linked Compounds

The respective silyl-linked compound (1.0 equiv) was dissolved in dry CH_2Cl_2 (0.02M) and cooled to -40 °C. *N*-iodosuccinimide (NIS) (1.3-1.4 equiv) and 2,6-di-*tert*-butyl-4-methyl pyridine (2,6-DTBMP) (2.0-4.0 equiv) were added and stirred for 3 minutes. To this solution, trimethylsilyl trifluoromethanesulfonate (TMSOTf) (1.2-2.4 equiv) was added, this is stirred for 10-15 minutes and then warmed to 0 °C. Upon disappearance of the silyl-linked compound, as monitored by TLC (generally 30 to 90 min), *n*-Bu_4NF (5-10 equiv, 1M THF) was added, and the reaction was warmed to rt and stirred overnight. The reaction mixture was then quenched with sat. $Na_2S_2O_3$ (aq.) and extracted three times from sat. NH_4Cl (aq.) with EtOAc. The combined organic extracts were dried over $MgSO_4$, filtered, concentrated, and purified by flash chromatography on SiO_2 to afford the desired product.

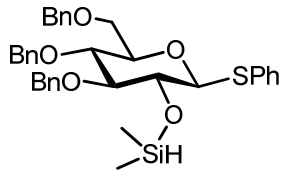
Ethyl 2-*O*-dimethylsilane-3,4,6-tri-*O*-benzyl-1-thio-β-D-glucopyranoside (Scheme 1, compound 1a)



Following the general procedure, ethyl 3,4,6-tri-*O*-benzyl-1-thio-β-D-glucopyranoside (1.237 g, 2.50 mmol),[2] NEt_3 (0.697 mL, 5.00 mmol), and $Me_2Si(H)Cl$ (0.416 mL, 3.75

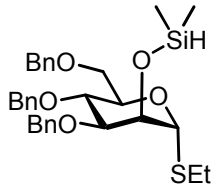
mmol) were stirred for 4 hours at 0 °C. The product (1.38 g, 2.50 mmol, 100%) was obtained as a red oil after aqueous work up. ^{1}H NMR (500MHz, $CDCl_3$) δ 7.25-7.28 (m, 13H), 7.12-7.16 (m, 2H), 4.91 (d, *J* = 11.5 Hz, 1H), 4.85 (d, *J* = 11.0 Hz, 1H), 4.82 (sept, *J* = 3.0 Hz, 1H), 4.78 (d, *J* = 10.5 Hz, 1H), 4.61 (d, *J* = 12.5 Hz, 1H), 4.553 (d, *J* = 12.5 Hz, 1H), 4.546 (d, *J* = 11.0 Hz, 1H), 4.37 (d, *J* = 9.0 Hz, 1H anomeric), 3.75 (dd, *J* = 10.5, 1.5 Hz, 1H), 3.69 (dd, *J* = 11.0, 4.5 Hz, 1H), 3.53-3.62 (m, 3H), 3.49 (ddd, *J* = 9.5, 5.0, 2.0 Hz, 1H), 2.77 (dq, *J* = 12.5, 7.5 Hz, 1H), 2.71 (dq, *J* = 12.0, 8.0 Hz, 1H), 1.32 (t, *J* = 7.5 Hz, 3H), 0.31 (d, *J* = 3.0 Hz, 3H), 0.25 (d, *J* = 2.5 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.5, 138.2, 138.0, 128.34, 128.30, 128.27, 127.9, 127.71, 127.69, 127.52, 127.48, 127.45, 87.2, 86.1, 79.2, 77.9, 75.9, 75.6, 75.0, 73.4, 69.1, 24.7, 15.0, -0.6, -0.8; IR (film, cm^{-1}) 2956, 2926, 2864, 2129, 1651, 1385, 1083; HRMS (ES) *m/z* calcd for $C_{31}H_{40}O_5SSi$ $[M+Na]^+$ 575.2263, found 575.2269.

Phenyl 2-*O*-dimethylsilane-3,4,6-tri-*O*-benzyl-1-thio-β-D-glucopyranoside (Scheme 1, compound 1b)



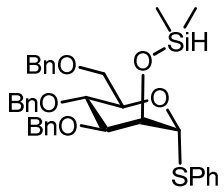
Following the general procedure, phenyl 3,4,6-tri-*O*-benzyl-1-thio-β-D-glucopyranoside (1.00 g, 1.8 mmol),[2] NEt_3 (0.513 μL, 3.7 mmol), and $Me_2Si(H)Cl$ (307 μL, 2.8 mmol) were stirred for 4 hours at 0 °C. The product (1.10 g, 1.8 mmol, 99%) was obtained as a red oil after aqueous work up. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.56-7.59 (m, 2H), 7.24-7.38 (m, 16H), 7.15-7.20 (m, 2H), 4.91 (d, *J* = 11.0 Hz, 1H), 4.87 (d, *J* = 11.5 Hz, 1H), 4.85 (sept, *J* = 3.0 Hz, 1H), 4.79 (d, *J* = 10.5 Hz, 1H), 4.62 (d, *J* = 12.0 Hz, 1H), 4.61 (d, *J* = 9.5 Hz, 1H anomeric) 4.59 (d, *J* = 12.0 Hz, 1H), 4.55 (d, *J* = 12.5 Hz, 1H), 3.80 (dd, *J* = 10.5, 1.5 Hz, 1H), 3.73 (dd, *J* = 11.0, 5.0 Hz, 1H), 3.67 (t, *J* = 9.0 Hz, 1H), 3.65 (t, *J* = 9.0 Hz, 1H), 3.58 (t, *J* = 8.25 Hz, 1H), 3.54 (ddd, *J* = 9.5, 4.5, 1.5 Hz, 1H), 0.29 (d, *J* = 2.5 Hz, 3H), 0.24 (d, *J* = 3.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.4, 138.2, 138.0, 134.1, 131.5, 128.8, 128.4, 128.3, 127.9, 127.8, 127.7, 127.53, 127.49, 127.48, 127.2, 88.8, 87.2, 79.2, 77.8, 75.6, 75.1, 75.0, 73.4, 69.0, -0.6, -0.9; IR (film, cm^{-1}) 3060, 3028, 2864, 2129, 1452, 1362, 1066; HRMS (ES) *m/z* calcd for $C_{35}H_{40}O_5SSi$ $[M+Na]^+$ 623.2263, found 623.2274.

Ethyl 2-*O*-dimethylsilane-3,4,6-tri-*O*-benzyl-1-thio-α-D-mannopyranoside (Scheme 1, compound 2a)



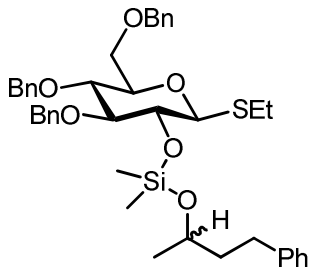
Following the general procedure, ethyl 3,4,6-tri-*O*-benzyl-1-thio-α-D-mannopyranoside (1.74 g, 3.5 mmol),[2] NEt_3 (0.98 mL, 7.0 mmol), and $Me_2Si(H)Cl$ (587 μL, 5.3 mmol) were stirred for 4 hours at 0 °C. The product (1.93 g, 3.5 mmol, 100%) was obtained as a red oil after aqueous work up. ^{1}H NMR (500MHz, $CDCl_3$) δ 7.25-7.39 (m, 13H), 7.15-7.18 (m, 2H), 5.27 (d, *J* = 2.0 Hz, 1H anomeric), 4.84 (d, *J* = 11.0 Hz, 1H), 4.76 (sept, *J* = 2.5 Hz, 1H), 4.73 (d, *J* = 11.5 Hz, 1H), 4.68 (d, *J* = 12.0 Hz, 1H), 4.62 (d, *J* = 11.5 Hz, 1H), 4.50 (d, *J* = 11.5 Hz, 1H), 4.49 (d, *J* = 11.0 Hz, 1H), 4.18 (t, *J* = 2.25 Hz, 1H), 4.13 (ddd, *J* = 10.0, 5.0, 2.0 Hz, 1H), 3.95 (t, *J* = 9.5 Hz, 1H), 3.76-3.83 (m, 2H), 3.70 (dd, *J* = 11.0, 2.0 Hz, 1H), 2.67 (dq, *J* = 13.0, 7.0 Hz, 1H), 2.59 (dq, *J* = 13.0, 7.5 Hz, 1H), 1.29 (t, *J* = 7.5 Hz, 3H), 0.26 (d, *J* = 2.5 Hz, 3H), 0.24 (d, *J* = 2.5 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.43, 138.40, 138.1, 128.28, 128.25, 128.20, 127.89, 127.65, 127.59, 127.50, 127.4, 85.0, 80.7, 74.9, 74.6, 73.2, 72.5, 72.2, 72.1, 69.1, 25.2, 15.0, -0.6, -0.7; IR (film, cm^{-1}) 3030, 2870, 2122, 1453, 1384, 1250, 1097; HRMS (ES) *m/z* calcd for $C_{31}H_{40}O_5SSi$ $[M+Na]^+$ 575.2263, found 575.2273.

Phenyl 2-*O*-dimethylsilane-3,4,6-tri-*O*-benzyl-1-thio-α-D-mannopyranoside (Scheme 1, compound 2b)



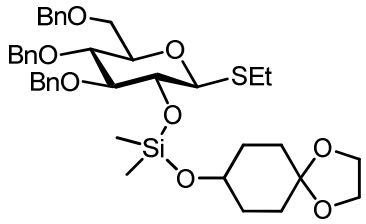
Following the general procedure, phenyl 3,4,6-tri-*O*-benzyl-1-thio-α-D-mannopyranoside (0.765 g, 1.4 mmol),[2] NEt_3 (0.390 mL, 2.8 mmol), and $Me_2Si(H)Cl$ (0.233 mL, 2.1 mmol) were stirred for 4 hours at 0 °C. The product (0.828 g, 1.4 mmol, 98%), was obtained as a red oil after aqueous work up. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.48-7.51 (m, 2H), 7.39-7.42 (m, 2H), 7.23-7.37 (m, 14H), 7.18-7.21 (m, 2H), 5.50 (d, *J* = 1.5 Hz, 1H anomeric), 4.87 (d, *J* = 11.0 Hz, 1H), 4.78 (d, *J* = 11.5 Hz, 1H), 4.76 (sept, *J* = 3.0 Hz, 1H), 4.68 (d, *J* = 11.5 Hz, 1H), 4.67 (d, *J* = 12.0 Hz, 1H), 4.52 (d, *J* = 11.0 Hz, 1H),. 4.48 (d, *J* = 12.0 Hz, 1H), 4.34 (t, *J* = 2.0 Hz, 1H), 4.29 (ddd, *J* = 9.5, 4.5, 1.5 Hz, 1H), 4.00 (t, *J* = 9.5 Hz, 1H), 3.79-3.86 (m, 2H), 3.74 (dd, *J* = 11.0, 2.0 Hz, 1H), 0.26 (d, *J* = 3.0 Hz, 3H), 0.22 (d, *J* = 3.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.36, 138.31, 134.4, 131.3, 128.9, 128.32, 128.28, 128.18, 127.9, 127.65, 127.57, 127.4, 127.2, 88.7, 80.5, 75.0, 74.5, 73.2, 72.8, 72.5, 72.3, 69.1, -0.6, -0.7; IR (film, cm^{-1}) 3061, 3030, 2869, 2123, 1453, 1368, 1251, 1101; HRMS (ES) *m/z* calcd for $C_{35}H_{40}O_5SSi$ $[M+Na]^+$ 623.2263, found 623.2248.

Ethyl 2-*O*-dimethyl[(4-phenylbutan-2-yloxy)silane]-3,4,6-tri-*O*-benzyl-1-thio-β-D-glucopyranoside (Table 1, compound 4a)



Following the general procedure, **1a** (182 mg, 0.33 mmol), freshly distilled (bulb-to-bulb) benzylacetone (45 μL, 0.30 mmol), $Ni(COD)_2$ (8 mg, 0.03 mmol), IMes·HCl (10 mg, 0.03 mmol), and KO-*t*-Bu (3 mg, 0.03 mmol) were stirred at rt for 13 hours. The desired product was obtained as an inseparable mixture of diastereomers (54:46) (204 mg, 0.29 mmol, 97%, 54:46) as a clear oil, upon purification by flash chromatography on SiO_2 (10% EtOAc/Hex). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.24-7.40 (m, 16H), 7.14-7.19 (m, 2H), 7.09-7.13 (m, 2H), 4.98 (d, *J* = 11.5 Hz, 1H), 4.89 (d, *J* = 11.5 Hz, 0.5H), 4.88 (d, *J* = 11.0 Hz, 0.5H), 4.75 (d, *J* = 10.5 Hz, 0.5H), 4.74 (d, *J* = 11.0 Hz, 0.5H), 4.52-4.63 (m, 3H), 4.40 (d, *J* = 9.5 Hz, 0.5H anomeric), 4.39 (d, *J* = 9.5 Hz, 0.5H anomeric), 4.00-4.08 (m, 1H), 3.67-3.78 (m, 3H), 3.54-3.64 (m, 2H), 3.48-3.52 (m, 1H), 2.66-2.80 (m, 3H), 2.55-2.62 (m, 1H), 1.74-1.84 (m, 1H), 1.65-1.73 (m, 1H), 1.31 (t, *J* = 7.5 Hz, 3H), 1.21 (d, *J* = 6.0 Hz, 1.5H), 1.19 (d, *J* = 6.0 Hz, 1.5H), 0.23 (s, 1.5H), 0.22 (s, 1.5H), 0.19 (s, 1.5H), 0.18 (s, 1.5H), Note – diastereomers are reported as a 1:1 ratio of the total amount of protons; ^{13}C NMR (100 MHz, $CDCl_3$) major and minor diastereomer signals reported δ 142.53, 142.50, 138.8, 138.2, 137.9, 128.3,4, 128.32, 128.24, 128.19, 127.9, 127.7, 127.5, 127.26, 127.24, 127.21, 127.1, 125.58, 125.56, 87.1, 86.2, 79.1, 78.2, 75.18, 75.15, 74.9, 74.48, 74.43, 73.4, 69.1, 68.3, 68.1, 41.0, 32.04, 32.02, 24.7, 23.7, 23.6, 15.1, -0.8, -0.9, -1.2, -1.3; IR (film, cm^{-1}) 3029, 2965, 2923, 2865, 1496, 1453, 1366, 1256, 1134, 1086; HRMS (ES) *m/z* calcd for $C_{41}H_{52}0_6SSi$ $[M+Na]^+$ 723.3152, found 723.3162.

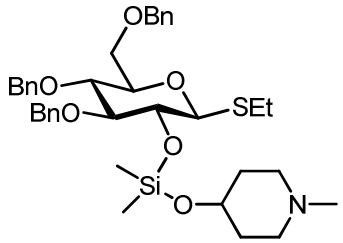
Ethyl 2-*O*-[(1,4-dioxaspiro[4.5]decan-8-yloxy)dimethylsilane]-3,4,6-tri-*O*-benzyl-1-thio-β-D-glucopyranoside (Table 1, compound 4b)



Following the general procedure, **1a** (182 mg, 0.33 mmol), 1,4-cyclohexanedione monoethylene acetal (47 mg, 0.30 mmol), $Ni(COD)_2$ (8 mg, 0.03 mmol), IMes·HCl (10 mg, 0.03 mmol), KO-*t*-Bu (3.4 mg, 0.03 mmol), and $Ti(O\text{-}i\text{-}Pr)_4$ (98 μL, 0.33 mmol) were stirred for 3 hr at rt. The product (197 mg, 0.28 mmol, 93%) was obtained as a viscous yellow oil after purification by flash chromatography on SiO_2 (10 to 20% EtOAc/Hex). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.24-7.38 (m, 13H), 7.08-7.12 (m, 2H), 4.93 (d, *J* = 11.5 Hz, 1H), 4.89 (d, *J* = 11.5 Hz, 1H), 4.73 (d, *J* = 11.0 Hz, 1H), 4.61 (d, *J* = 12.0 Hz, 1H), 4.56 (d, *J* = 12.0 Hz, 1H) 4.53 (d, *J* = 11.0 Hz, 1H) 4.40 (d, *J* = 9.5 Hz, 1H

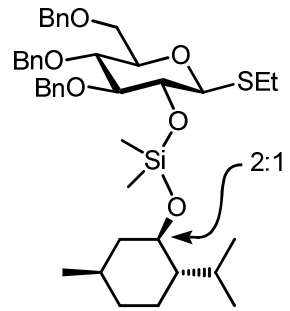
anomeric), 4.01 (tt, J = 7.5, 3.5 Hz, 1H), 3.90-3.96 (m, 4H), 3.75 (dd, J = 11.0, 2.0 Hz, 1H), 3.66-3.73 (m, 2H), 3.60 (t, J = 9.25, 1H), 3.55 (t, J = 8.75 Hz, 1H), 3.49 (ddd, J = 9.5, 5.0, 2.0 Hz, 1H), 2.77 (dq, J = 12.75, 7.5 Hz, 1H), 2.71 (dq, J = 13.5, 7.5 Hz, 1H), 1.64-1.85 (m, 6H), 1.46-1.54 (m, 2H), 1.31 (t, J = 7.5 Hz, 3H), 0.21 (s, 3H), 0.16 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.7, 138.2, 138.0, 128.32, 128.30, 128.2, 127.9, 127.72, 127.69, 127.5, 127.2, 127.0, 108.4, 87.0, 86.2, 79.1, 78.3, 75.1, 74.9, 74.4. 73.4, 69.1, 68.3, 64.17, 64.15, 32.03, 32.00, 31.34, 31.32, 24.6, 15.0, -0.9, -1.3; IR (film, cm^{-1}) 3030, 2929, 1497, 1453, 1363, 1255, 1094; HRMS (ES) *m/z* calcd for $C_{39}H_{52}O_8SSi$ $[M+Na]^+$ 731.3050, found 731.3062.

Ethyl 2-*O*-[4-(dimethylsilyloxy)-1-methylpiperidine]-3,4,6-tri-*O*-benzyl-1-thio-β-D-glucopyranoside (Table 1, compound 3c)



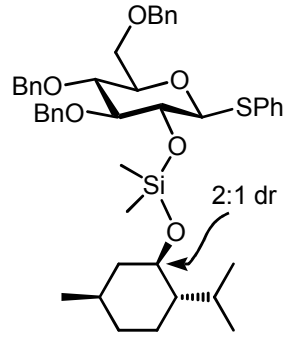
Following the general procedure, **1a** (182 mg, 0.33 mmol), N-methyl-4-piperidone (37 μL, 0.30 mmol), Ti(O-*i*-Pr)$_4$ (98 μL, 0.33 mmol), Ni(COD)$_2$ (8 mg, 0.03 mmol), IMes·HCl (10 mg, 0.03 mmol), and KO-*t*-Bu (3 mg, 0.03 mmol) were stirred for 6 hours at rt. The product (200 mg, 0.30 mmol, 100%) was obtained after flash chromatography on SiO_2 (15% MeOH/EtOAc w/ ~1% NEt_3) as a viscous light orange oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.24-7.38 (m, 13H), 7.08-7.12 (m, 2H), 4.95 (d, J = 11.0 Hz, 1H), 4.89 (d, J = 11.5 Hz, 1H), 4.73 (d, J = 10.5 Hz, 1H), 4.61 (d, J = 12.0 Hz, 1H), 4.56 (d, J = 12.0 Hz, 1H), 4.53 (d, J = 10.5 Hz, 1H), 4.39 (d, J = 9.5 Hz, 1H anomeric), 3.88 (br s, 1H), 3.75 (dd, J = 11.0, 1.5 Hz, 1H), 3.67-3.72 (m, 2H), 3.60 (t, J = 9.25 Hz, 1H), 3.55 (t, J = 8.75 Hz, 1H), 3.49 (ddd, J = 10.0, 5.0, 1.5 Hz, 1H), 2.77 (dq, J = 12.5, 7.5 Hz, 1H), 2.72 (dq, J = 12.5, 7.5 Hz, 1H), 2.65 (br s, 2H), 2.23 (s, 3H), 1.98-2.10 (m, 2H), 1.74-1.86 (m, 2H), 1.58 (m, 2H), 1.32 (t, J = 7.25 Hz, 3H), 0.22 (s, 3H), 0.17 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.7, 138.1, 137.9, 128.33, 128.31, 128.2, 127.9, 127.7, 127.5, 127.3, 127.1, 87.0, 86.1, 79.1, 78.2, 75.1, 74.9, 74.5, 73.4, 69.1, 52.9, 45.9, 34.2, 24.6, 15.1, -0.9, -1.3; IR (film, cm^{-1}) 3030, 2927, 2864, 2780, 1452, 1362, 1255, 1148, 1087; HRMS (ES) *m/z* calcd for $C_{37}H_{51}NO_6SSi$ $[M+H]^+$ 666.3285, found 666.3284.

Ethyl 2-*O*-[((1R,2S,5R)-2-isopropyl-5-methylcyclohexyloxy)dimethylsilane]-3,4,6-tri-*O*-benzyl-1-thio-β-D-glucopyranoside (Table 1, compound 4d)



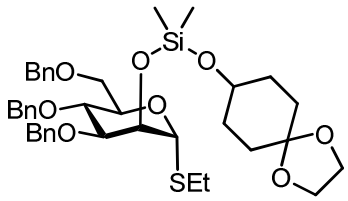
Following the general procedure, **1a** (243 mg, 0.30 mmol), (-)-menthone[3] (62 mg, 0.40 mmol), CuCl (2 mg, 0.015 mmol), IMes·HCl (7 mg, 0.015 mmol) and NaO-*t*-Bu (3 mg, 0.03 mmol) were stirred for 8 hours at rt to give the product as an inseparable 2:1 mixture of diastereomers. The product (192 mg, 0.27 mmol, 68%, 2:1) was obtained as a clear oil upon purification by flash chromatography on SiO_2 (10% EtOAc/Hex). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.23-7.41 (m, 13 H), 7.07-7.14 (m, 2H), 5.01 (d, *J* = 11.0 Hz, 0.67H), 4.97 (d, *J* = 11.5 Hz, 0.33H) 4.88 (d, *J* = 12.0 Hz, 0.33H), 4.86 (d, *J* = 11.0 Hz, 0.67H), 4.75 (d, *J* = 11.0 Hz, 0.67H), 4.72 (d, *J* = 11.0 Hz, 0.33H), 4.50-4.63 (m, 3 H), 4.39 (d, *J* = 9.5 Hz, 0.67H anomeric), 4.38 (d, *J* = 9.5 Hz, 0.33H anomeric), 4.26 (br s, 0.33H), 3.66-3.78 (m, 3H), 3.53-3.62 (m, 2.67H), 3.48-3.53 (m, 1H), 2.68-2.81 (m, 2H), 2.20 (septd, *J* = 7.0, 2.5 Hz, 0.67H), 1.99-2.04 (m, 0.67H), 1.78-1.88 (m, 0.67H), 1.48-1.65 (m, 2.33H), 1.26-1.40 (m, 1H), 1.32 (t, *J* = 7.5 Hz, $3H_{major}$), 1.31 (t, *J* = 7.5 Hz, $3H_{minor}$), 0.74-1.15 (m, 10.67H), 0.73 (d, *J* = 7.0 Hz, $3H_{major}$), 0.23 (s, $3H_{major}$), 0.19 (s, $3H_{minor}$), 0.15 (s, $3H_{major + minor}$), Note – diastereomers are reported as a 2:1 ratio of the total amount of protons, the stereochemistry of the major diastereomer and the dr of the reduction was determined on a crude reaction mixture of the silyl-linked compound after complete desilylation by *n*-Bu_4NF and comparison to known compounds;[4,5] ^{13}C NMR (100 MHz, $CDCl_3$) major and minor diastereomer signals reported δ 138.9, 138.8, 138.24, 138.22, 138.0, 128.34, 128.31, 128.16, 128.13, 127.94, 127.89, 127.7, 127.5, 127.3, 127.2, 127.11, 127.96, 87.2, 87.0, 86.4, 86.3, 79.1, 78.3, 78.2, 75.2, 75.1, 74.9, 74.5, 74.3, 73.4, 72.6, 69.3, 69.2, 68.8, 49.7, 48.8, 45.4, 43.1, 42.6, 35.3, 34.5, 31.6, 28.7, 25.5, 25.2, 24.8, 24.6, 24.0, 22.8, 22.4, 22.2, 21.2, 21.1, 20.9, 15.9, 15.0, -0.4, -1.0, -1.5; IR (film, cm^{-1}) 3029, 2953, 2921, 2866, 1453, 1365, 1254, 1067; HRMS (ES) *m/z* calcd for $C_{41}H_{58}O_6SSi$ $[M+Na]^+$ 729.3621, found 729.3639.

Phenyl 2-*O*-[((1R,2S,5R)-2-isopropyl-5-methylcyclohexyloxy)dimethylsilane]-3,4,6-tri-*O*-benzyl-1-thio-β-D-glucopyranoside (Table 1, compound 4e)



Following the general procedure, **1b** (198 mg, 0.33 mmol), (-)-menthone[3] (46 mg, 0.30 mmol), CuCl (2 mg, 0.015 mmol), IMes·HCl (5 mg, 0.015 mmol), and NaO-*t*-Bu (3 mg, 0.03 mmol) were stirred for 5 hours at rt to give the desired product as an inseparable 2:1 mixture of diastereomers. The product (144 mg, 0.19 mmol, 64%, 2:1) was obtained as a clear viscous oil upon purification by flash chromatography on SiO_2 (5% EtOAc/Hex). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.52-7.57 (m, 2H), 7.21-7.41 (m, 16H), 7.10-7.17 (m, 2H), 5.02 (d, *J* = 11.0 Hz, 0.67H), 4.98 (d, *J* = 11.5 Hz, 0.33H), 4.89 (d, *J* = 11.5 Hz, 0.33H), 4.86 (d, *J* = 10.5 Hz, 0.67H) , 4.78 (d, *J* = 11.0 Hz, 0.67H) 4.73 (d, *J* = 10.5 Hz, 0.33H), 4.52-4.66 (m, 4H), 4.27 (br s, 0.33H), 3.76-3.86 (m, 2H), 3.69-3.74 (m, 1H), 3.51-3.66 (m, 3.67H), 2.21 (septd, *J* = 6.75, 2.25 Hz, 0.67H), 2.01 (d, *J* = 12.0 Hz, 0.67H), 1.80-1.89 (m, 0.67H), 1.48-1.64 (m, 2.33H), 1.26-1.41 (m, 1.33H), 1.09-1.18 (m, 0.67H), 0.75-1.07 (m, 5.67H), 0.87 (d, *J* = 7.0 Hz, $3H_{minor}$), 0.85 (d, *J* = 7.0Hz, $3H_{major}$), 0.84 (d, *J* = 6.5 Hz, $3H_{minor}$), 0.74 (d, *J* = 7.0 Hz, $3H_{major}$), 0.25 (s, $3H_{major}$), 0.20 (s, $3H_{minor}$), 0.16 (s, $3H_{minor}$), 0.13 (s, $3H_{major}$), Note – diastereomers are reported as a 2:1 ratio of the total amount of protons, the stereochemistry of the major diastereomer and the dr of the reduction was determined on a crude reaction mixture of the silyl-linked compound after complete desilylation by *n*-Bu_4NF and comparison to known compounds;[4,5] ^{13}C NMR (100 MHz, $CDCl_3$) δ major and minor diastereomer signals reported 138.8, 138.7, 138.26, 138.24, 138.0, 137.0, 134.5, 131.1, 131.0, 128.8, 128.37, 128.33, 128.30, 128.18, 128.15, 127.90, 127.8, 127.73, 127.69, 127.67, 127.52, 127.51, 127.3, 127.2, 126.97, 126.96, 126.91, 89.1, 88.8, 87.2, 87.0, 79.03, 78.98, 78.16, 78.12, 75.2, 75.1, 74.9, 73.9, 73.8, 73.4, 72.7, 69.14, 69.07, 68.9, 49.7, 48.8, 45.4, 43.2, 35.2, 34.5, 31.6, 28.7, 25.6, 25.2, 24.0, 22.8, 22.3, 22.2, 21.2, 21.1, 20.9, 15.9, -0.4, -1.1, -1.2, -1.4; IR (film, cm^{-1}) 3030, 2953, 2919, 2867, 1454, 1383, 1256, 1067; HRMS (ES) *m/z* calcd for $C_{45}H_{58}O_6SSi$ $[M+Na]^+$ 777.3621, found 777.3635.

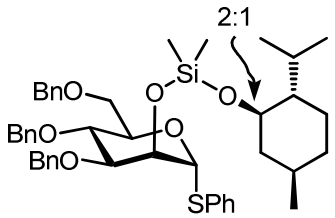
Ethyl 2-*O*-[(1,4-dioxaspiro[4.5]decan-8-yloxy)dimethylsilane]-3,4,6-tri-*O*-benzyl-1-thio-α-D-mannopyranoside (Table 1, compound 5a)



Following the general procedure, **2a** (182 mg, 0.33 mmol), 1,4-cyclohexanedione monoethylene acetal (47 mg, 0.30 mmol), Ti(O-*i*-Pr)$_4$ (98 μL, 0.33 mmol), Ni(COD)$_2$ (8 mg, 0.03 mmol), IMes·HCl (10 mg, 0.03 mmol), and KO-*t*-Bu (3 mg, 0.03 mmol) were stirred at room temperature for 4 hours. The product (183 mg, 0.26 mmol, 86%) was obtained as a colorless oil after purification by flash chromatography on SiO_2 (10 to 20% EtOAc/Hex). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.24-7.37 (m, 13H), 7.15-7.18 (m, 2H), 5.28 (d, *J* = 1.5 Hz, 1H anomeric), 4.83 (d, *J* = 10.5 Hz, 1H), 4.71 (d, *J* = 11.5 Hz, 1H), 4.68 (d, *J* = 12.0 Hz, 1H), 4.64 (d, *J* = 11.5 Hz, 1H), 4.52 (d, *J* = 12.0 Hz, 1H), 4.50 (d, *J* = 10.5 Hz, 1H), 4.28 (t, *J* = 2.25 Hz, 1H), 4.13 (ddd, *J* = 10.0, 5.0, 1.5 Hz, 1H), 3.90-4.00 (m, 5H), 3.82 (dd, *J* = 11.0, 5.0 Hz, 1H), 3.77 (dd, *J* = 9.0, 2.5 Hz, 1H), 3.71 (dd, *J* =

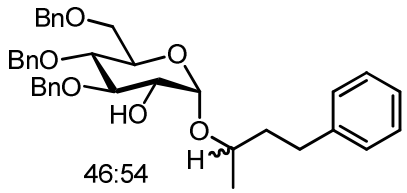
10.5, 1.5 Hz, 1H), 2.66 (dq, *J* = 13.0, 7.5 Hz, 1H), 2.58 (dq, *J* = 13.0, 7.5 Hz, 1H), 1.64-1.86 (m, 6H), 1.46-1.55 (m, 2H), 0.17 (s, 3H), 0.15 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.49, 138.47, 138.3, 128.27, 128.25, 128.21, 127.9, 127.8, 127.6, 127.52, 127.49, 127.36, 108.4, 85.4, 80.3, 74.9, 74.8, 73.2, 72.2, 71.0, 69.2, 68.1, 64.20, 64.17, 32.05, 32.00, 31.2, 25.2, 15.0, -1.5, -1.7; IR (film, cm^{-1}) 3030, 2938, 2874, 1452, 1378, 1256, 1099, 1036; HRMS (ES) *m/z* calcd for $C_{39}H_{52}O_8SSi$ $[M+Na]^+$ 731.3050, found 731.3055.

Phenyl 2-*O*-[((1R,2S,5R)-2-isopropyl-5-methylcyclohexyloxy)dimethylsilane]-3,4,6-tri-*O*-benzyl-1-thio-α-D-mannopyranoside (Table 1, compound 5b)



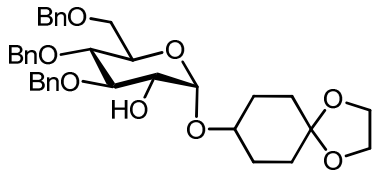
Following the general procedure, **2b** (198 mg, 0.33 mmol), (-)-menthone[3] (46 mg, 0.30 mmol), CuCl (1.5 mg, 0.015 mmol), IMes·HCl (5 mg, 0.015 mmol), and NaO-*t*-Bu (3 mg, 0.03 mmol) were stirred for 4 hours at rt to give the desired product as an inseparable 2:1 mixture of diastereomers. The product (171 mg, 0.23 mmol, 75%, 2:1) was isolated as a colorless oil upon purification by flash chromatography on SiO_2 (5% EtOAc/Hex). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.47-7.51 (m, 2H), 7.38-7.41 (m, 2H), 7.20-7.36 (m, 16H), 5.54 (d, *J* = 2.0 Hz, 0.33H anomeric), 5.53 (d, *J* = 2.0 Hz, 0.67H anomeric), 4.88 (d, *J* = 11.0 Hz, 0.33H), 4.87 (d, *J* = 10.5 Hz, 0.67H), 4.77 (d, *J* = 11.5 Hz, 1H), 4.65-4.70 (m, 2H), 4.46-4.56 (m, 3H), 4.28-4.34 (m, 1H), 4.19 (br s, 0.33H), 3.97-4.02 (m, 1H), 3.74-3.88 (m, 3H), 3.53 (td, *J* = 10.5, 4.5 Hz, 0.67H), 2.14 (septd, *J* = 7.0, 3.0 Hz, 0.67H), 1.92-1.97 (m, 0.67H), 1.66-1.77 (m, 0.67H), 1.43-1.63 (m, 1.67H), 1.20-1.35 (m, 1.67H), 1.11 (ddt, *J* = 12.25, 9.75, 2.75 Hz, 0.67H), 0.72-1.04 (m, 4H), 0.83 (d, *J* = 7.0 Hz, $3H_{major}$), 0.82 (d, *J* = 6.5 Hz, $3H_{major}$), 0.80 (d, *J* = 7.0 Hz, $3H_{minor}$), 0.78 (d, *J* = 6.5 Hz, $3H_{minor}$), 0.71 (d, *J* = 7.0 Hz, $3H_{major}$), 0.17 (s, $3H_{major}$), 0.16 (s, $3H_{minor}$), 0.15 (s, $3H_{major + minor}$), Note – diastereomers are reported as a 2:1 ratio of the total amount of protons, the stereochemistry of the major diastereomer and the dr of the reduction was determined on a crude reaction mixture of the silyl-linked compound after complete desilylation by *n*-Bu_4NF and comparison to known compounds;[4,5] ^{13}C NMR (100 MHz, $CDCl_3$) major and minor diastereomer signals reported δ 138.53, 138.47, 138.43, 138.3, 138.2, 134.74, 134.66, 131.7, 131.4, 131.3, 128.9, 128.8, 128.3, 128.2, 127.92, 127.85, 127.77, 127.66, 127.63, 127.58, 127.35, 127.12, 127.09, 89.3, 89.0, 80.3, 75.03, 74.85, 73.16, 73.13, 72.99, 72.86, 72.6, 72.2, 72.1, 70.7, 70.6, 69.28, 69.24, 68.8, 49.8, 48.6, 45.3, 43.1, 35.1, 34.4, 31.6, 28.8, 25.7, 25.5, 25.3, 24.0, 22.8, 22.4, 22.2, 21.1, 21.0, 20.8, 15.8, -1.20, -1.22, -1.36, -1.40; IR (film, cm^{-1}) 3029, 2952, 2915, 2866, 1453, 1255, 1099; HRMS (ES) *m/z* calcd for $C_{45}H_{58}O_8SSi$ $[M+Na]^+$ 777.3621, found 777.3640.

[4-phenylbutan-2]-3,4,6-tri-*O*-benzyl-α-D-glucopyranoside (Table 1, compound 6a)



Following the general procedure, compound **4a** (112 mg, 0.16 mmol), NIS (47 mg, 0.21 mmol), TMSOTf (35 μL, 0.19 mmol), 2,6-DTBMP (66 mg, 0.32 mmol) were stirred for 10 min at -40 °C, and 30 min at 0 °C, then excess *n*-Bu_4NF (0.96 mmol, 0.96 mL) was added as a 1M solution in THF and stirred overnight to afford the desired products as a 46:54 mixture of diastereomers as clear oils, which were separated and characterized independently (combined 90 mg, 0.15 mmol, 97%, 54:46) upon purification by flash chromatography on SiO_2 (20% EtOAc/Hex). **Major diastereomer** ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39-7.42 (m, 2H), 7.25-7.36 (m, 13H), 7.13-7.21 (m, 5H), 5.02 (d, *J* = 3.0 Hz, 1H anomeric), 4.97 (d, *J* = 11.0 Hz, 1H), 4.85 (d, *J* = 10.0 Hz, 1H), 4.83 (d, *J* = 10.5 Hz, 1H), 4.62 (d, *J* = 12.5 Hz, 1H), 4.49 (d, *J* = 10.5 Hz, 1H), 4.47 (d, *J* = 12.0 Hz, 1H), 3.83-3.92 (m, 2H), 3.58-3.76 (m, 5H), 2.70-2.78 (m, 1H), 2.60-2.68 (m, 1H), 1.92-2.07 (m, 2H), 1.77-1.85 (m, 1H), 1.23 (d, *J* = 6.5 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.8, 138.8, 138.2, 137.9, 128.35, 128.34, 128.32, 128.27, 127.9, 127.8, 127.66, 127.63, 127.56, 125.8, 96.0, 83.6, 77.3, 75.3, 75.0, 73.5, 72.8, 72.7, 70.8, 68.4, 38.6, 32.0, 19.1; IR (film, cm^{-1}) 3461, 3061, 3029, 2924, 1495, 1453, 1381, 1129, 1065, 1034 ; HRMS (ES) *m/z* calcd for $C_{37}H_{42}O_6$ $[M+Na]^+$ 605.2879, found 605.2877. **Minor diastereomer** ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39-7.42 (m, 2H), 7.26-7.36 (m, 13H), 7.18-7.22 (m, 3H), 7.14-7.17 (m, 2H), 4.99 (d, *J* = 3.5 Hz, 1H anomeric), 4.96 (d, *J* = 11.5 Hz, 1H), 4.84 (d, *J* = 10.5 Hz, 1H), 4.83 (d, *J* = 10.5 Hz, 1H), 4.65 (d, *J* = 12.5 Hz, 1H), 4.50 (d, *J* = 12 Hz, 1H), 4.49 (d, *J* = 10.5 Hz, 1H), 3.89 (d, *J* = 9.0 Hz, 1H), 3.62-3.83 (m, 6H), 2.64-2.75 (m, 2H), 1.90-1.98 (m, 2H), 1.74-1.82 (m, 1H), 1.28 (d, *J* = 6.5 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.7, 138.8, 138.1, 137.9, 128.42, 128.35, 128.32, 128.27, 127.93, 127.87, 127.83, 127.70, 127.63, 127.59, 125.9, 98.5, 83.5, 77.4, 75.28, 75.26, 75.0, 73.5, 73.2, 70.6, 68.5, 38.0, 31.5, 21.3; IR (film, cm^{-1}) 3559, 3471, 3029, 2922, 2864, 1454, 1363, 1129, 1066, 1036; HRMS (ES) *m/z* calcd for $C_{37}H_{42}O_6$ $[M+Na]^+$ 605.2879, found 605.2876.

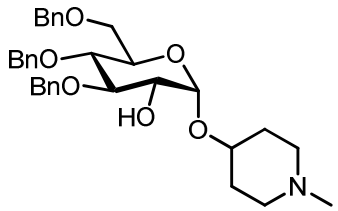
8-(1,4-dioxaspiro[4.5]decane)-3,4,6-tri-*O*-benzyl-α-D-glucopyranoside (Table 1, compound 6b)



Following the general procedure, compound **4b** (425 mg, 0.60 mmol), NIS (175 mg, 0.78 mmol), 2,6-DTBMP (185 mg, 0.90 mmol), TMSOTf (142 μL, 0.78 mmol) were stirred for 10 min at -40 °C, then warmed to 0 °C and allowed to stir for 1 hour. *n*-Bu_4NF (3.0 mL, 3.0 mmol) was added as a 1M solution in THF, warmed to rt and stirred overnight.

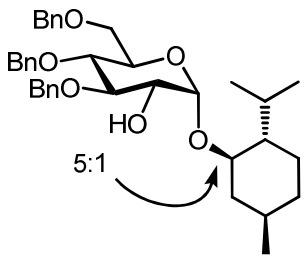
The product (289 mg, 0.49 mmol, 82%) was obtained as a colorless oil after flash chromatography on SiO_2 (33% EtOAc/Hex w/ 5% NEt_3). ^1H NMR (400 MHz, $CDCl_3$) δ 7.22-7.38 (m, 13 H), 7.10-7.14 (m, 2H), 4.98 (d, *J* = 3.2 Hz, 1H anomeric), 4.94 (d, *J* = 11.2 Hz, 1H), 4.80 (d, J = 10.8 Hz, 2H), 4.61 (d, *J* = 12.0 Hz, 1H) 4.47 (d, *J* = 12.0 Hz, 1H) 4.45 (d, *J* = 10.8 Hz, 1H), 3.89-3.93 (m, 4H), 3.84 (ddd, *J* = 10.0, 3.2, 2.0 Hz, 1H), 3.57-3.66 (m, 6H), 1.96 (d, *J* = 10.0 Hz, 1H) 1.66-1.91 (m, 6H), 1.50-1.59 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.7, 138.1, 137.9, 128.33, 128.31, 127.9, 127.84, 127.80, 127.7, 127.63, 127.56, 108.0, 97.0, 83.6, 75.3, 75.0, 73.5, 73.4, 72.9, 70.6, 68.4, 64.3, 64.2, 31.6, 31.3, 29.9, 28.1; IR (film, cm^{-1}) 3476, 3029, 2937, 1496, 1453, 1365, 1134, 1068, 1028; HRMS (ES) *m/z* calcd for $C_{35}H_{42}O_8$ $[M+Na]^+$ 613.2777, found 613.2786.

4-(methylpiperidin-1)-3,4,6-tri-*O*-benzyl-α-D-glucopyranoside (Table 1, compound 6c)



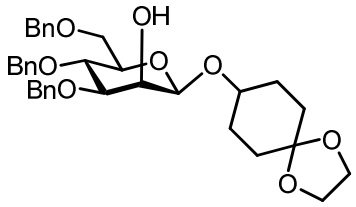
Following the general procedure, compound **4c** (125 mg, 0.19 mmol), NIS (55 mg, 0.24 mmol), 2,6-DTBMP (77 mg, 0.38 mmol), TMSOTf (41 μL, 0.23 mmol) were stirred at -40 °C for 10 min, then warmed to 0 °C and stirred for 1 hour, then excess *n*-Bu_4NF was added (1.14 mL, 1.14 mmol) as a 1M solution in THF, warmed to rt and allowed to stir overnight. The product (73 mg, 0.13 mmol, 70%) was obtained after purification by flash chromatography on SiO_2 (7:1:2 to 3:1:1 EtOAc:MeOH:MeCN w/ ~ 1% NEt_3). ^1H NMR (500 MHz, $CDCl_3$) δ 7.39-7.42 (m, 2H), 7.26-7.37 (m, 11H), 7.13-7.16 (m, 2H), 5.03 (d, *J* = 3.5 Hz, 1H anomeric), 4.99 (d, *J* = 11.0 Hz, 1H), 4.85 (d, *J* = 11.0 Hz, 1H), 4.84 (d, *J* = 10.5 Hz, 1H), 4.64 (d, *J* = 12.0 Hz, 1H), 4.51 (d, *J* = 11.5 Hz, 1H), 4.49 (d, *J* = 10.5 Hz, 1H), 3.87 (ddd, *J* = 10.0, 3.75, 1.75 Hz, 1H), 3.61-3.79 (m, 6H), 2.68 (br s, 2H), 2.28 (s, 3H), 2.20 (br s, OH), 2.16 (br s, 2H), 1.92 (br s, 1H), 1.62-1.77 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.7, 138.0, 137.9, 128.40, 128.37, 128.36, 128.0, 127.9, 127.84, 127.77, 127.69, 127.6, 97.1, 83.6, 77.3, 75.3, 75.1, 73.5, 72.9, 70.7, 68.5, 53.1, 46.1, 32.5, 30.8; IR (film, cm^{-1}) 3453, 3030, 2920, 2850, 2784, 1452, 1384, 1155, 1068, 1043; HRMS (ES) *m/z* calcd for $C_{33}H_{41}NO_6$ $[M+H]^+$ 548.3012, found 548.3019.

(1R,2S,4S)-2-isopropyl-4-methylcyclohexan-3,4,6-tri-*O*-benzyl-α-D-glucopyranoside (Table 1, compound 6d)



Following the general procedure, compound **4e** (87 mg, 0.12 mmol), NIS (34 mg, 0.15 mmol), 2,6-DTBMP (47 mg, 0.24 mmol) and TMSOTf (25 μL, 0.14 mmol) were stirred for 10 min at -40 °C, warmed to 0 °C and stirred for 45 min, then excess *n*-Bu_4NF was added (0.72 mL, 0.72 mmol) as a 1M solution in THF, warmed to rt, and stirred overnight. The product (49 mg, 0.08 mmol, 72%, 5:1) was obtained as an inseparable 5:1 mixture of diastereomers as a colorless oil after purification by flash chromatography on SiO_2 (10 to 20% EtOAc/Hex). ^{1}H NMR (500 MHz, $CDCl_3$) **Major diastereomer** δ 7.26-7.43 (m, 13H), 7.14-7.18 (m, 2H), 4.99 (d, *J* = 4.0 Hz, 1H anomeric), 4.98 (d, *J* = 12.0 Hz, 1H), 4.85 (d, *J* = 11.5 Hz, 1H), 4.84 (d, *J* =10.5 Hz, 1H), 4.66 (d, *J* = 12.0 Hz, 1H), 4.51 (d, *J* = 11.0 Hz, 1H), 4.48 (d, *J* = 10.5 Hz, 1H), 3.95 (d, *J* = 10.0 Hz, 1H), 3.60-3.84 (m, 5H), 3.41 (td, *J* = 10.5, 4.0 Hz, 1H), 2.21 (d, *J* =12.5 Hz, 1H), 2.15 (septd, *J* =7.0, 2.0 Hz, 1H), 1.97 (d, *J* = 9.0 Hz, 1H), 1.56-1.80 (m, 2H), 1.24-1.46 (m, 2H), 0.78-1.05 (m, 3H), 0.93 (d, *J* = 7.0 Hz, 3H), 0.87 (d, *J* = 7.0 Hz, 3H), 0.78 (d, *J* = 7.0 Hz, 3H), diagnostic peaks of the minor diastereomer at 5.03 (d, *J* = 3.5 Hz, 0.2H anomeric), and 4.11 (br s, 0.2H) (aglycone carbinol); ^{13}C NMR (100 MHz, $CDCl_3$) major and minor diastereomer signals reported δ 138.8, 138.2, 138.0, 128.36, 128.33, 128.11, 127.96, 127.92, 127.85, 127.7, 127.64, 127.60, 100.1, 95.4, 83.5, 81.1, 77.5, 75.2, 75.0, 73.6, 73.5, 73.0, 72.6, 70.6, 68.6, 48.7, 48.2, 42.9, 37.3, 34.9, 34.2, 31.6, 28.4, 26.4, 25.5, 22.8, 22.2, 21.2, 21.1, 20.9, 15.7; IR (film, cm^{-1}) 3564, 3030, 2922, 2867, 1453, 1384, 1132, 1067, 1027; HRMS (ES) *m/z* calcd for $C_{37}H_{48}O_6$ $[M+Na]^+$ 611.3349, found 611.3355.

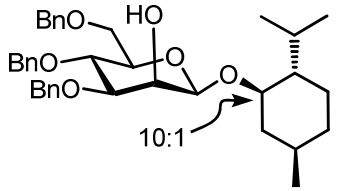
8-(1,4-dioxaspiro[4.5]decane)-3,4,6-tri-*O*-benzyl-β-D-mannopyranoside (Table 1, compound 7a)



Following the general procedure, compound **5a** (144 mg, 0.20 mmol) NIS (59 mg, 0.26 mmol), 2,6-DTBMP (83 mg, 0.41 mmol) and TMSOTf (44 μL, 0.24 mmol) were stirred at -40 °C for 15 minutes, warmed to 0 °C and stirred for 45 min, then *n*-Bu_4NF (1.2 mL, 1.2 mmol) was added as a 1M solution in THF and the reaction was warmed to rt and stirred overnight. The product (67 mg, 0.11 mmol, 57%) was obtained as a colorless oil upon purification by flash chromatography on SiO_2 (40 to 50% EtOAc/Hex). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38-7.41 (m, 2H), 7.26-7.36 (m, 11H), 7.21-7.24 (m, 2H), 4.91 (d, *J* = 11.0 Hz, 1H), 4.79 (d, *J* = 12.0 Hz, 1H), 4.68 (d, *J* = 12.0 Hz, 1H), 4.56 (d, *J* = 12.0 Hz, 1H), 4.55 (d, *J* = 11.0 Hz, 1H), 4.52 (s, 1H anomeric), 4.07 (br s, 1H), 3.89-3.98 (m, 5H), 3.86 (t, *J* = 9.5 Hz, 1H), 3.78 (dd, *J* = 10.5, 1.5 Hz, 1H), 3.69 (dd, *J* = 10.5, 5.5 Hz, 1H), 3.58 (dd, *J* = 9.0, 3.0 Hz, 1H), 3.43 (ddd, *J* = 9.5, 5.5, 1.5 Hz, 1H), 2.45 (d, *J* = 1.5 Hz, 1H), 1.70-1.98 (m, 6H), 1.52-1.61 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.3, 138.2, 137.9, 128.5, 128.35, 128.31, 128.1, 127.9, 127.8, 127.7, 127.5, 108.2, 97.4, 81.6, 75.23, 75.16, 74.3, 73.7, 73.4, 71.3, 69.3, 68.8, 64.3, 31.4, 31.3, 29.9, 27.9; IR (film, cm^-

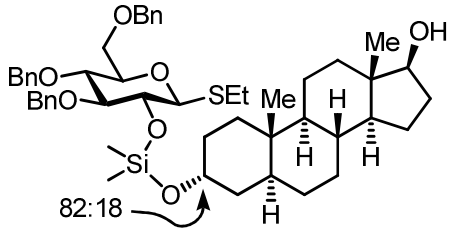
[1]) 3476, 3029, 2940, 2872, 1452, 1372, 1100; HRMS (ES) *m/z* calcd for $C_{35}H_{42}O_8$ $[M+Na]^+$ 613.2777, found 613.2781.

(1R,2S,4S)-2-isopropyl-4-methylcyclohexan-3,4,6-tri-*O*-benzyl-β-D-mannopyranoside (Table 1, compound 7b)



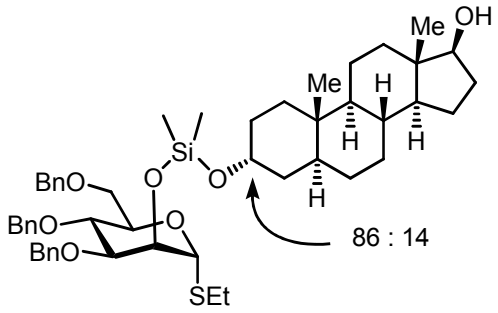
Following the general procedure, compound **5b** (68 mg, 0.09 mmol), NIS (26 mg, 0.12 mmol), 2,6-DTBMP (37 mg, 0.18 mmol), and TMSOTf (20 μL, 0.11 mmol) were stirred at -40 °C for 10 min, then warmed to 0 °C and stirred for 1.5 hours. *n*-Bu_4NF (0.63 mL, 0.63 mmol) was added as a 1M solution in THF and stirred at rt overnight to give the products as a 10:1 mixture of diastereomers. The products (combined 39 mg, 0.07 mmol, 74%, 10:1) were isolated as a white solid and clear oil respectively, and characterized independently after purification by flash chromatography on SiO_2 (10 to 20% EtOAc/Hex). Data for the major diastereomer matches that previously reported.[6] **Major diastereomer** ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38-7.41 (m, 2H), 7.24-7.36 (m, 13H), 4.91 (d, *J* = 11.0 Hz, 1H), 4.80 (d, *J* = 12.0 Hz, 1H), 4.69 (d, *J* = 12.0 Hz, 1H), 4.62 (d, *J* = 12.5 Hz, 1H), 4.60 (d, *J* = 12.0 Hz, 1H), 4.55 (d, *J* = 12.0 Hz, 1H), 4.54 (s, 1H anomeric), 4.04 (br s, 1H), 3.87 (t, *J* = 9.5 Hz, 1H), 3.75 (dd, *J* = 10.5, 1.5 Hz, 1H), 3.71 (dd, *J* = 10.5, 5.0 Hz, 1H), 3.55-3.63 (m, 2H), 3.41 (ddd, *J* = 10.0, 5.0, 2.0 Hz, 1H), 2.38 (s, 1H), 2.29 (septd, *J* = 7.0, 2.0 Hz, 1H), 1.99 (d, *J* = 12.0 Hz, 1H), 1.62-1.70 (m, 2H), 1.24-1.41 (m, 2H), 0.80-1.05 (m, 3H), 0.92 (d, *J* = 6.5 Hz, 3H), 0.91 (d, *J* = 7.0 Hz, 3H), 0.83 (d, *J* = 6.5 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.4, 138.3, 138.0, 128.44, 128.35, 128.29, 128.16, 127.8, 127.75, 127.71, 127.68, 127.5, 96.1, 81.9, 76.5, 75.3, 75.2, 74.4, 73.6, 71.2, 69.7, 69.2, 47.7, 40.4, 34.3, 31.3, 25.3, 23.1, 22.3, 21.0, 15.8; IR (film, cm^{-1}) 3472, 3028, 2950, 2920, 2865, 1452, 1383, 1102; HRMS (ES) *m/z* calcd for $C_{37}H_{48}O_6$ $[M+Na]^+$ 611.3349, found 611.3337. **Minor diastereomer** ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38-7.42 (m, 2H), 7.23-7.36 (m, 13H), 4.91 (d, *J* =11 Hz, 1H), 4.81 (d, *J* = 12 Hz, 1H), 4.69 (d, *J* = 11.5 Hz, 1H), 4.64 (d, *J* = 12 Hz, 1H), 4.58 (d, *J* = 11 Hz, 1H), 4.57 (d, *J* = 12 Hz, 1H), 4.44 (s, 1H anomeric), 4.07 (d, *J* = 2.5 Hz, 1H), 4.02 (br s, 1H), 3.69 (t, *J* = 9.0 Hz, 1H), 3.74 (dd, *J* = 11, 2.0 Hz, 1H), 3.70 (dd, *J* = 11, 5.5 Hz, 1H), 3.56 (dd, *J* = 9.5, 3.0 Hz, 1H), 3.41 (ddd, *J* = 9.5, 5.0, 2.0 Hz, 1H), 2.39 (br s, 1H), 2.16-2.22 (m, 1H), 1.81-1.91 (m, 1H), 1.69-1.86 (m, 1H), 1.60-1.68 (m, 1H), 1.20-1.44 (m, 2H), 0.80-1.00 (m, 3H), 0.90 (d, *J* = 7.0 Hz, 3H), 0.89 (d, *J* = 7.0 Hz, 3H), 0.85 (d, *J* = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.4, 138.3, 138.0, 128.42, 128.35, 128.31, 128.1, 127.9, 127.73, 127.69, 127.65, 127.5, 101.3, 81.8, 78.5, 75.3, 75.2, 74.3, 73.6, 71.3, 69.5, 69.0, 48.3, 41.1, 35.0, 28.9, 26.2, 24.6, 22.4, 21.3, 20.9; IR (film, cm^{-1}) 3444, 3027, 2917, 2848, 1452, 1383, 1103; HRMS (ES) *m/z* calcd for $C_{37}H_{48}O_6$ $[M+Na]^+$ 611.3349, found 611.3359.

Ethyl 2-*O*-[(3R,5S,8R,9S,10S,13S,14S,17S)-3-(dimethylsilyloxy)-10,13-dimethylhexadecahydro-1H-cyclopenta[a]phenanthren-17-ol]-3,4,6-tri-*O*-benzyl-1-thio-β-D-glucopyranoside (Scheme 3, compound 8a)



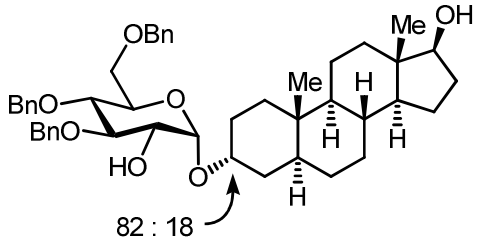
Following the general procedure, **1a** (182 mg, 0.33 mmol), dihydrotestosterone[7] (87 mg, 0.30 mmol), $Ni(COD)_2$ (8 mg, 0.03 mmol), IMes·HCl (10 mg, 0.03 mmol), KO-*t*-Bu (3.4 mg, 0.03 mmol), and $Ti(O\text{-}i\text{-}Pr)_4$ (195 μL, 0.66 mmol) were stirred for 6.5 hr at rt to give the product as an inseparable 5:1 mixture of diastereomers. The product (226 mg, 0.27 mmol, 89%, 5:1) was obtained as a viscous yellow oil after flash chromatography on SiO_2 (20 to 25% EtOAc/Hex). ^{1}H NMR 7.24-7.40 (m, 13H), 7.06 (m, 2H), 5.03 (d, J = 11.5 Hz, 1H), 4.86 (d, J = 11.5 Hz, 1H), 4.71 (d, J = 11.0 Hz, 1H), 4.61 (d, J = 12.5 Hz, 1H), 4.56 (d, J = 12.5 Hz, 1H), 4.51 (d, J = 10.5 Hz, 1H), 4.40 (d, J = 9.5 Hz, 1H anomeric), 4.17 (t, J = 2.5 Hz, 1H) 3.47-3.81 (m, $7H_{major + minor}$), 2.68-2.81 (m, 2H), 2.00-2.10 (m, 1H), 0.56-1.82 (m, $31H_{major + minor}$) {assignable peaks within this multiplet: 1.32 (t, J = 7.5 Hz, $3H_{major}$), 0.73 (s, $3H_{major}$), 0.71 (s, $3H_{major}$)}, 0.21 (s, 3H), 0.19 (s, 3H), diagnostic peaks for minor diastereomer 4.97 (d, J = 11.5 Hz, $1H_{minor}$), 4.90 (d, J = 11 Hz, $1H_{minor}$) benzylic, Note – the stereochemistry of the major diastereomer and the dr of the reduction was determined on a crude reaction mixture of the silyl-linked compound after complete desilylation by *n*-Bu_4NF and comparison to known compounds;[8,9] ^{13}C NMR (100 MHz, $CDCl_3$) major and minor diastereomer signals reported δ 138.9, 138.2, 138.0, 128.34, 128.31, 128.2, 127.95, 127.93, 127.72, 127.69, 127.5, 127.3, 127.0, 87.2, 87.0, 86.2, 82.0, 79.1, 78.3, 78.1, 75.3, 75.1, 74.9, 74.6, 73.4, 71.7, 69.1, 67.2, 54.5, 54.1, 51.01, 50.95, 44.9, 42.9, 38.8, 38.2, 37.1, 36.74, 36.67, 36.4, 35.9, 35.5, 35.4, 32.3, 31.64, 31.57, 31.47, 30.5, 29.7, 29.4, 28.6, 28.4, 24.7, 23.4, 23.3, 20.7, 20.3, 15.1, 12.3, 11.4, 11.1, -0.9, -1.0, -1.1, -1.2; IR (film, cm^{-1}) 3429, 3028, 2925, 2867, 1496, 1452, 1362, 1253, 1133, 1067, 1027; HRMS (ES) *m/z* calcd for $C_{50}H_{70}O_7SSi$ $[M+Na]^+$ 865.4509, found 865.4501.

Ethyl 2-*O*-[(3R,5S,8R,9S,10S,13S,14S,17S)-3-(dimethylsilyloxy)-10,13-dimethylhexadecahydro-1H-cyclopenta[a]phenanthren-17-ol]-3,4,6-tri-*O*-benzyl-1-thio-α-D-mannopyranoside (Scheme 3, compound 8b)



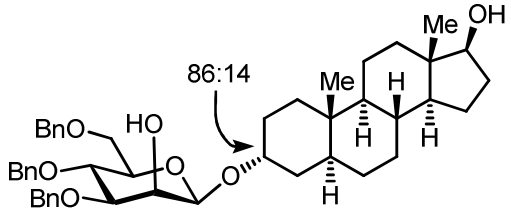
Following the general procedure, **2a** (182 mg, 0.33 mmol) dihydrotestosterone[7] (87 mg, 0.30 mmol), $Ni(COD)_2$ (8 mg, 0.03 mmol), IMes·HCl (10 mg, 0.03 mmol), KO-*t*-Bu (3.4 mg, 0.03 mmol), and $Ti(O\text{-}i\text{-}Pr)_4$ (195 μL, 0.66 mmol) were stirred for 6.5 hr at rt to give the desired product as an inseparable 6:1 mixture of diastereomers. The product (202 mg, 0.24 mmol, 80%, 6:1) was obtained as a viscous off-white oil after flash chromatography on SiO_2 (10 to 20% EtOAc/hexanes). ^{1}H NMR (500 MHz, $CDCl_3$) **Major diastereomer** δ 7.24-7.38 (m, 13H), 7.15-7.18 (m, 2H), 5.32 (d, *J* = 1.5 Hz, 1H anomeric), 4.84 (d, *J* = 11.0 Hz, 1H), 4.73 (d, *J* = 11.5 Hz, 1H), 4.69 (d, *J* = 12.0 Hz, 1H), 4.62 (d, *J* = 12.0 Hz, 1H), 4.52 (d, *J* = 11.0 Hz, 1H), 4.50 (d, *J* = 10.5 Hz, 1H), 4.30 (dd, *J* = 2.5, 2.0 Hz, 1H), 4.12-4.16 (m, 2H), 3.98 (t, 9.5 Hz, 1H), 4.83 (dd, *J* = 11.0, 5.0 Hz, 1H), 3.77 (dd, *J* = 9.0, 2.25 Hz, 1H), 3.72 (dd, *J* = 11.0, 2.0 Hz, 1H), 3.62 (t, *J* = 8.25 Hz, 1H), 2.54-2.70 (m, 2H), 2.01-2.11 (m, 1H), 1.78 (dt, *J* = 12.5, 3.5 Hz, 1H), 1.09-1.66 (m, 17H), 1.29 (t, *J* = 7.5 Hz, 3H), 1.02, (td, *J* = 13.0, 4.0 Hz, 1H), 0.80-0.96 (m, 2H), 0.69-0.78 (m, 1H), 0.76 (s, 3H), 0.73 (s, 3H), 0.16 (s, 3H), 0.15 (s, 3H); diagnostic peak for minor diastereomer at 5.28 (d, *J* = 1.5 Hz, 0.15H anomeric), Note – the stereochemistry of the major diastereomer and the dr of the reduction was determined on a crude reaction mixture of the silyl-linked compound after complete desilylation by *n*-Bu_4NF and comparison to known compounds;[8,9] ^{13}C NMR (100 MHz, $CDCl_3$) major and minor diastereomer signals reported δ 138.5, 138.3, 128.3, 128.2, 127.9, 127.7, 127.6, 127.5, 127.4, 85.5, 82.0, 80.4, 74.9, 74.8, 73.2, 72.1, 72.0, 70.6, 69.2, 67.0, 54.3, 51.1, 44.9, 43.0, 39.0, 36.7, 36.4, 36.0, 35.5, 25.3, 23.3, 20.3, 15.1, 11.4, 11.1, -1.4, -1.5, -1.7; IR (film, cm^{-1}) 3465, 3030, 2925, 1452, 1371, 1255, 1097, 1047; HRMS (ES) *m/z* calcd for $C_{50}H_{70}O_7SSi$ $[M+Na]^+$ 865.4509, found 865.4484.

3-(3R,5S,8R,9S,10S,13S,14S,17S)-10,13-dimethylhexadecahydro-1H-cyclopenta[a]phenanthrene-17-ol 3,4,6-tri-*O*-benzyl-α-D-glucopyranoside (Scheme 3, compound 9a)



Following the general procedure, compound **8a** (145 mg, 0.17 mmol), NIS (54 mg, 0.24 mmol), TMSOTf (75 μL, 0.41 mmol), 2,6-DTBMP (141 mg, 0.69 mmol) were stirred for 5 minutes at -40 °C, and 1 hour at 0 °C then excess *n*-Bu_4NF (1.7 mL, 1.7 mmol) was added as a 1M solution in THF and stirred overnight to afford the desired products as a 5:1 mixture of diastereomers. The products (combined 117 mg, 0.16 mg, 95%, 5:1) were obtained as colorless viscous oils, separated and characterized independently upon purification by flash chromatography on SiO_2 (30 to 40% EtOAc/Hex). **Major diastereomer** ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.41-7.44 (m, 2H), 7.26-7.38 (m, 11H), 7.14-7.17 (m, 2H), 5.02 (d, *J* = 11.0 Hz, 1H), 4.97 (d, *J* = 3.5 Hz, 1H anomeric), 4.87 (d, *J* = 11.0 Hz, 1H), 4.84 (d, *J* = 10.5 Hz, 1H), 4.64 (d, *J* = 12.0 Hz, 1H), 4.51 (d, *J* = 12.0 Hz, 1H), 4.50 (d, *J* = 10.5 Hz, 1H), 3.91 (m, 1H), 3.85 (ddd, *J* = 10.0, 3.5, 1.5 Hz, 1H), 3.78 (dd, *J* = 10.5, 3.5 Hz, 1H), 3.68-3.75 (m, 2H), 3.61-3.68 (m, 3H), 2.02-2.11 (m, 1H), 1.96 (d, *J* = 9.5 Hz, 1H), 1.78-1.81 (m, 2H), 1.52-1.70 (m, 4H), 1.13-1.52 (m, 12 H), 1.07 (td, *J* = 13.0, 4.0 Hz, 1H), 0.85-1.02 (m, 2H), 0.80 (s, 3H), 0.74 (s, 3H), 0.70-0.78 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.9, 138.1, 138.0, 128.44, 128.37, 128.2, 127.90, 127.87, 127.83, 127.7, 127.6, 97.3, 83.8, 82.0, 77.4, 75.2, 73.5, 73.3, 73.1, 70.7, 68.6, 54.3, 51.0, 43.0, 40.2, 36.7, 36.0, 35.5, 33.1, 32.5, 31.4, 30.5, 28.4, 27.4, 23.3, 20.4, 11.4, 11.1; IR (film, cm^{-1}) 3453, 3063, 3030, 2928, 1496, 1453, 1358, 1135, 1067; HRMS (ES) *m/z* calcd for $C_{46}H_6O_7$ $[M+Na]^+$ 747.4237, found 747.4250. **Minor diastereomer** ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37-7.41 (m , 2H), 7.26-7.36 (m, 11H), 7.14-7.17 (m, 2H), 5.03 (d, *J* = 3.5 Hz, 1H anomeric), 4.98 (d, *J* = 11.0 Hz, 1H), 4.84 (d, *J* = 11.0 Hz, 1H), 4.64 (d, *J* = 12.5 Hz), 4.51 (d, *J* = 12.0 Hz, 1H), 4.49 (d, *J* = 10.5 Hz, 1H), 3.90 (ddd, *J* = 10.0, 4.0, 2.0 Hz, 1H), 3.55-3.78 (m, 7H), 2.05 (d, *J* = 9.5 Hz, 1H), 2.02-2.10 (m, 1H), 1.84-1.90 (m, 1H), 1.80 (dt, *J* = 12, 3.5 Hz, 1H), 1.74 (dt, *J* = 13.5, 3.5 Hz, 1H), 1.54-1.68 (m, 3H), 1.20-1.47 (m, 10H), 1.01-1.12 (m, 2H), 0.80-0.98 (m, 3H), 0.82 (s,3H), 0.74 (s, 3H), 0.60-0.98 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.8, 138.2, 138.0, 128.35, 128.33, 127.9, 127.8, 127.7, 127.6, 127.5, 97.0, 83.8, 81.9, 77.4, 75.3, 75.0, 73.5, 73.0, 70.5, 68.7, 54.4, 51.0, 45.0, 43.0, 36.8, 36.7, 36.0, 35.6, 35.5, 31.6, 30.5, 29.7, 28.5, 27.8, 23.4, 20.8, 12.3, 11.1; IR (film, cm^{-1}) 3439, 3029, 2928, 1452, 1356, 1207, 1131, 1067, 1025; HRMS (ES) *m/z* calcd for $C_{46}H_{60}O_7$ $[M+Na]^+$ 747.4237, found 747.4258.

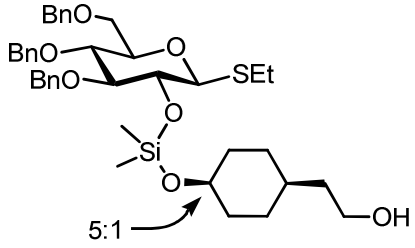
3-(3R,5S,8R,9S,10S,13S,14S,17S)-10,13-dimethylhexadecahydro-1H-cyclopenta[a]phenanthrene-17-ol 3,4,6-tri-*O*-benzyl-β-D-mannopyranoside (Scheme 3, compound 9b)



Following the general procedure, compound **8b** (131 mg, 0.16 mmol), NIS (49 mg, 0.22 mmol), 2,6-DTBMP (128 mg, 0.62 mmol), and TMSOTf (68 μL, 0..37 mmol), were stirred at -40 °C for 10 min, then warmed to 0 °C and stirred for 1.5 hours. *n*-Bu_4NF (1.6 mL, 1.6 mmol) was then added as a 1M solution in THF, and the reaction was taken to rt

and stirred overnight to give the products as a 6:1 mixture of diastereomers. The products (combined 103 mg, 0.14 mmol, 92%, 6:1) were isolated as viscous, colorless oils, which were separated and characterized independently upon purification by flash chromatography on SiO_2 (30% EtOAc/Hex). **Major diastereomer** ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38-7.41 (m, 2H), 7.24-7.36 (m, 13H), 7.20-7.23 (m, 2H), 4.91 (d, *J* = 11.0 Hz, 1H), 4.81 (d, *J* = 12.0 Hz, 1H), 4.68 (d, *J* = 11.5 Hz, 1H), 4.61 (d, *J* = 12.5 Hz, 1H), 4.56 (d, *J* = 12.5 Hz, 1H), 4.55 (d, *J* = 10.5 Hz, 1H), 4.49 (s, 1H anomeric), 4.09 (br s, 1H), 4.04-4.07 (m, 1H), 3.87 (t, *J* = 9.0 Hz, 1H), 3.76 (dd, *J* = 10.5, 2.0 Hz, 1H), 3.68 (dd, *J* = 11.0, 5.5 Hz, 1H), 3.64 (t, *J* = 8.5 Hz, 1H), 3.59 (dd, *J* = 9.0, 2.5 Hz, 1H), 3.41 (ddd, *J* = 9.5, 5.0, 2.0 Hz, 1H), 2.52 (s, 1H), 2.02-2.11 (m, 1H), 1.79 (dt, *J* = 12.0, 3.0 Hz, 1H), 1.72 (d, *J* = 14.5 Hz, 1H), 1.10-1.68 (m, 18H), 1.05 (td, *J* = 13.0, 4.0 Hz, 1H), 0.85-1.00 (m, 1H), 0.72-0.82 (m, 1H), 0.80 (s, 3H), 0.74 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.3, 138.2, 137.9, 128.4, 128.33, 128.28, 128.1, 127.8, 127.74, 127.69, 127.5, 97.2, 81.9, 81.8, 75.2, 75.1, 74.3, 73.5, 72.8, 71.2, 69.3, 68.9, 54.2, 51.0, 42.9, 39.4, 36.7, 35.9, 35.5, 34.2, 32.5, 31.4, 30.5, 28.2, 25.0, 23.3, 20.3, 11.4, 11.1; IR (film, cm^{-1}) 3452, 3028, 2926, 2866, 1452, 1363, 1105, 1056; HRMS (ES) *m/z* calcd for $C_{46}H_{60}O_7$ $[M+Na]^+$ 747.4237, found 747.4250. **Minor diastereomer** ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37-7.40 (m, 2H), 7.27-7.36 (m, 11H), 7.21-7.24 (m, 2H), 4.90 (d, *J* = 11.0 Hz, 1H), 4.78 (d, *J* = 12.0 Hz, 1H), 4.68 (d, *J* = 11.5 Hz, 1H), 4.62 (d, *J* = 12.0 Hz, 1H), 4.57 (d, *J* = 12.0 Hz, 1H), 4.56 (s, 1H anomeric), 4.55 (d, *J* = 11.5 Hz, 1H), 4.06 (s, 1H), 3.83 (t, *J* = 9.75 Hz, 1H), 3.79 (dd, *J* = 10.75, 1.75 Hz, 1H), 3.60-3.75 (m, 2H), 3.68 (dd, *J* = 10.5, 6.0 Hz, 1H), 3.57 (dd, *J* = 9.0, 3.0 Hz, 1H), 3.43 (ddd, *J* = 9.5, 5.75, 1.75 Hz, 1H), 2.46 (d, *J* = 2.0 Hz, 1H), 2.01-2.10 (m, 1H), 1.92-1.98 (m, 1H), 1.80 (dt, *J* = 12.0, 3.25 Hz, 1H), 1.73 (dt, *J* = 13.25, 2.5 Hz, 1H), 1.67 (dq, *J* = 12.75, 3.25 Hz. 1H), 1.20-1.62 (m, 11H), 0.75-1.10 (m, 6H), 0.82 (s, 3H), 0.74 (s, 3H), 0.58-0.65 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.4, 138.2, 137.9, 128.5, 128.4, 128.3, 128.1, 127.9, 127.8, 127.7, 127.5, 97.2, 82.0, 81.7, 77.4, 75.3, 75.2, 74.4, 73.4, 71.3, 69.4, 68.8, 54.5, 51.0, 44.7, 43.0, 37.0, 36.7, 35.7, 35.5, 34.2, 31.6, 30.5, 29.2, 28.7, 23.4, 20.8, 12.3, 11.1; IR (film, cm^{-1}) 3462, 3028, 2926, 2848, 1452, 1383, 1101, 1071, 1026; HRMS (ES) *m/z* calcd for $C_{46}H_{60}O_7$ $[M+Na]^+$ 747.4237, found 747.4247.

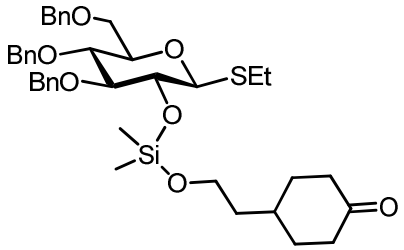
Ethyl 2-*O*- 2-(4-(dimethylsilyloxy)cyclohexyl)ethanol -3,4,6-tri-*O*-benzyl-1-thio-β-D-glucopyranoside (Compound 11, Scheme 4)



Following the general procedure, **1a** (182 mg, 0.33 mmol), hydroxyketone **10**[10] (43 mg, 0.30 mmol), $Ni(COD)_2$ (8 mg, 0.03 mmol), IMes·HCl (10 mg, 0.03 mmol), KO-*t*-Bu (3.4 mg, 0.03 mmol), and $Ti(O\text{-}i\text{-}Pr)_4$ (195 μL, 0.66 mmol) were stirred for 3 hr at rt to give the desired product **11** as an inseparable 5:1 mixture of diastereomers. Compound **11** (187 mg, 0.26 mmol, 86%, 5:1) was obtained as a viscous colorless oil after purification

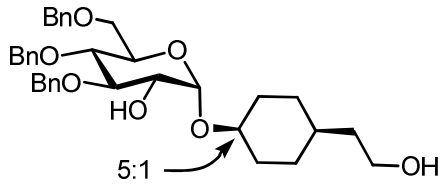
by flash chromatography on SiO_2 (25 to 30% EtOAc/hexanes). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.23-7.39 (m, 13H), 7.07-7.12 (m, 2H), 4.98 (d, *J* = 11.5 Hz, 1H), 4.88 (d, *J* = 11.5 Hz, 1H), 4.73 (d, *J* = 10.5 Hz, 1H), 4.61 (d, *J* = 12.0 Hz, 1H), 4.56 (d, *J* = 12.5 Hz, 1H), 4.52 (d, *J* = 10.5 Hz, 1 H), 4.40 (d, *J* = 9.5 Hz, 1H anomeric), 4.10-4.12 (m, 1H), 3.53-3.78 (m, 7H), 3.49 (ddd, *J* = 9.0, 5.0, 1.75 Hz, 1H), 2.77 (dq, *J* = 12.5, 7.5 Hz, 1H), 2.72 (dq, *J* = 12.5, 7.5 Hz, 1H), 1.59-1.74 (m, 2H), 1.37-1.49 (m, 8H), 1.25-1.39 (m, 1H), 1.32 (t, *J* = 7.5 Hz, 3H), 1.15 (br s, 1H), 0.20 (s, 3H), 0.18 (s, 3H); diagnostic peaks for minor diastereomer: 4.74 (d, *J* = 10.5 Hz, 1H), 1.85-1.97 (m, 1H), 0.22 (s, 3H), 0.17 (s, 3H) Note – the relative stereochemistry of the major and minor diastereomers was confirmed based on the Karplus correlations of the carbinol methine proton of the desilylated diol; ^{13}C NMR (100 MHz, $CDCl_3$) major and minor diastereomer signals reported δ 138.9, 138.2, 138.0, 129.1, 128.34, 128.32, 128.2, 127.9, 127.74, 127.70, 127.6, 127.2, 127.1, 87.1, 87.0, 86.3, 86.1, 79.1, 78.5, 78.2, 75.1, 74.9, 74.5, 73.4, 71.5, 69.2, 67.6, 60.9, 61.1, 39.6, 38.9, 35.5, 33.2, 32.7, 31.4, 27.13, 27.09, 24.7, 15.1, -0.89, -0.90, -1.16, -1.17; IR (film, cm^{-1}) 3437, 3031, 2926, 2858, 1454, 1364, 1255, 1057, 1028; HRMS (ES) *m/z* calcd for $C_{39}H_{54}O_7SSi$ $[M+Na]^+$ 717.3257, found 717.3283.

Ethyl 2-*O*- 4-(2-(dimethylsilyloxy)ethyl)cyclohexanone -3,4,6-tri-*O*-benzyl-1-thio-β-D-glucopyranoside (Compound 12, Scheme 4)



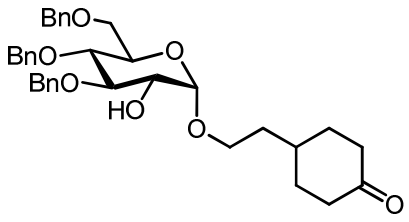
Following the general procedure, **1a** (182 mg, 0.33 mmol), hydroxyketone **10**[10] (43 mg, 0.30 mmol), CuCl (1.5 mg, 0.015 mmol), IMes·HCl (5 mg, 0.015 mmol), and NaO-*t*-Bu) (3 mg, 0.03 mmol) were stirred for 3 hr at rt to give the desired product. Compound **12** (119 mg, 0.17 mmol, 57%) was obtained as a colorless oil after purification by flash chromatography on SiO_2 (20% EtOAc/hexanes). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.23-7.38 (m, 13H), 7.08-7.11 (m, 2H), 4.94 (d, *J* = 11.5 Hz, 1H), 4.89 (d, *J* = 11.5 Hz, 1H), 4.73 (d, *J* = 11.0 Hz, 1H), 4.61 (d, *J* = 12.5 Hz, 1H), 4.56 (d, *J* = 12.0 Hz, 1H), 4.53 (d, *J* = 10.5 Hz, 1H), 4.40 (d, *J* = 9.5 Hz, 1H anomeric), 3.74-3.78 (m, 3H), 3.67-3.72 (m, 2H), 3.62 (t, *J* = 9.25 Hz, 1H), 3.55 (t, *J* = 8.75 Hz, 1H), 3.49 (ddd, *J* = 9.75, 4.75, 1.75 Hz, 1H), 2.77 (dq, *J* = 12.5, 7.5 Hz, 1H), 2.72 (dq, *J* = 12.5, 7.5 Hz, 1H), 2.20-2.38 (m, 4H), 1.93-2.01 (m, 2H), 1.77-1.86 (m, 1H), 1.49 (q, *J* = 7.0 Hz, 2H), 1.28-1.39 (m, 2H), 1.32 (t, *J* = 7.5 Hz, 3H), 0.22 (s, 3H), 0.20 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 212.3, 138.7, 138.2, 137.9, 128.4, 128.34, 128.26, 127.9, 127.78, 127.76, 127.6, 127.3, 127.1, 87.1, 86.2, 79.2, 78.2, 75.2, 75.0, 74.6, 73.5, 69.1, 60.5, 40.8, 38.0, 32.7, 32.6, 32.4, 24.7, 15.1, -1.95, -2.02; IR (film, cm^{-1}) 3031, 2925, 2865, 1715, 1453, 1384, 1256, 1089, 1029; HRMS (ES) *m/z* calcd for $C_{39}H_{52}O_7SSi$ $[M+Na]^+$ 715.3101, found 715.3095.

2-(4-cyclohexyl)ethanol-3,4,6-tri-*O*-benzyl-α-D-glucopyranoside (Compound 13, Scheme 4)



Following the general procedure, silyl-linked compound **11** (81 mg, 0.12 mmol), NIS (37 mg, 0.16 mmol), 2,6-DTBMP (96 mg, 0.47 mmol), and TMSOTf (51 μL, 0.28 mmol) were stirred at -40 °C for 10 min, then warmed to 0 °C and stirred for 1.5 hr. *n*-Bu_4NF (1.2 mL, 1.2 mmol) was added as a 1M solution in THF, warmed to room temperature and stirred over night. The products **13** (combined 67 mg, 0.11 mmol, 97%, 5:1) were isolated as a clear oil and white crystalline solid respectively, and independently characterized after purification by flash chromatography on SiO_2 (50 to 65% EtOAc/hexanes). **Major diastereomer** ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.41-7.44 (m, 2H), 7.26-7.37 (m, 11H), 7.14-7.18 (m, 2H), 5.00 (d, *J* = 11.0 Hz, 1H), 4.99 (d, *J* = 4.0 Hz, 1H anomeric), 4.86 (d, *J* = 11.0 Hz, 1H), 4.85 (d, *J* = 10.5 Hz, 1H), 4.65 (d, *J* = 12.0 Hz, 1H), 4.52 (d, *J* = 12.5 Hz, 1H), 4.51 (d, *J* = 11.0 Hz, 1H), 3.85-3.91 (m, 2H), 3.63-3.80 (m, 7H), 2.00 (d, *J* = 10.0 Hz, 1H), 1.81-1.89 (m, 2H), 1.44 -1.60 (m, 7H), 1.22-1.37 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.8, 138.1, 137.9, 128.39, 128.35, 128.34, 128.0, 127.9, 127.85, 127.76, 127.66, 127.58, 97.0, 83.7, 77.3, 75.25, 75.15, 73.5, 73.03, 72.97, 70.6, 68.5, 60.7, 39.0, 32.7, 30.8, 28.7, 27.6, 27.5; IR (film, cm^{-1}) 3436, 3031, 2926, 2860, 1453, 1363, 1132, 1067, 1028; HRMS (ES) *m/z* calcd for $C_{35}H_{44}O_7$ $[M+Na]^+$ 599.2985, found 599.2974. **Minor diastereomer** ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38-7.41 (m, 2H), 7.25-7.36 (m, 11H), 7.13-7.17 (m, 2H), 5.04 (d, *J* = 4.0 Hz 1H anomeric), 4.98 (d, *J* = 11.0 Hz, 1H), 4.84 (d, *J* = 11.5 Hz, 1H), 4.83 (d, *J* = 11.0 Hz, 1H), 4.64 (d, *J* = 12.0 Hz, 1H), 4.51 (d, *J* = 11.5 Hz, 1H), 4.49 (d, *J* = 10.5 Hz, 1H), 3.88 (ddd, *J* = 10.0, 3.75, 1.75 Hz, 1H), 3.60-3.79 (m, 7H), 3.56 (tt, *J* = 11.0, 4.25 Hz, 1H), 1.99-2.08 (m, 3H), 1.76-1.85 (m, 2H), 1.48 (q, *J* = 6.5 Hz, 2H), 1.14-1.44 (m, 4H), 0.92-1.04 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.8, 138.2, 138.0, 128.38, 128.37, 128.35, 128.0, 127.8, 127.72, 127.66, 127.57, 97.0, 83.7, 77.4, 75.3, 75.1, 73.5, 73.0, 70.5, 68.6, 60.9, 39.4, 33.33, 33.29, 31.7, 31.3, 31.1; IR (film, cm^{-1}) 3401, 3032, 2924, 2853, 1452, 1353, 1130, 1070, 1040; HRMS (ES) *m/z* calcd for $C_{35}H_{44}O_7$ $[M+Na]^+$ 599.2985, found 599.2971.

4-(2-ethyl)cyclohexanone-3,4,6-tri-*O*-benzyl-α-D-glucopyranoside (Compound 14, Scheme 4)



Following the general procedure, silyl-linked compound **12** (80 mg, 0.12 mmol), NIS (36 mg, 0.16 mmol), 2,6-DTBMP (95 mg, 0.46 mmol), and TMSOTf (50 μL, 0.28 mmol)

were stirred at -40 °C for 10 min, then warmed to 0 °C and stirred for 30 min. *n*-Bu_4NF (1.2 mL, 1.2 mmol) was added as a 1M solution in THF, warmed to rt and stirred over night. Compound **14** (41 mg, 0.07 mmol, 62%) was obtained as white crystalline solid after purification by flash chromatography on SiO_2 (50 to 60% EtOAc/hexanes). ^1H NMR (500 MHz, $CDCl_3$) δ 7.38-7.41 (m, 2H), 7.22-7.37 (m, 11H), 7.15-7.19 (m, 2H), 4.95 (d, *J* = 11.0 Hz, 1H), 4.91 (d, *J* = 3.0 Hz, 1H anomeric), 4.88 (d, *J* = 11.0 Hz, 1H), 4.84 (d, *J* = 10.5 Hz, 1H), 4.63 (d, *J* = 12.0 Hz, 1H), 4.54 (d, *J* = 12.0 Hz, 1H), 4.52 (d, *J* = 10.5 Hz, 1H), 3.71-3.85 (m, 5H), 3.68 (dd, *J* = 10.25, 2.25 Hz, 1H), 3.62 (dd, *J* = 9.5, 9.0 Hz 1H), 3.56 (dt, *J* = 10.0, 6.5 Hz, 1H), 2.28 (m, 4H), 2.01-2.10 (m, 3H), 1.81-1.91 (m, 1H), 1.60-1.72 (m, 2H), 1.36-1.48 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 211.7, 138.6, 138.0, 137.9, 128.42, 128.37, 128.0, 127.85, 127.82, 127.74, 127.69, 98.5, 83.4, 77.5, 75.3, 75.1, 73.6, 72.9, 70.8, 68.6, 66.2, 40.62, 40.60, 35.1, 32.9, 32.7, 32.4; IR (film, cm^{-1}) 3450, 3031, 2926, 1713, 1453, 1357, 1135, 1068, 1028; HRMS (ES) *m/z* calcd for $C_{35}H_{44}O_7$ $[M+Na]^+$ 597.2828, found 597.2818.

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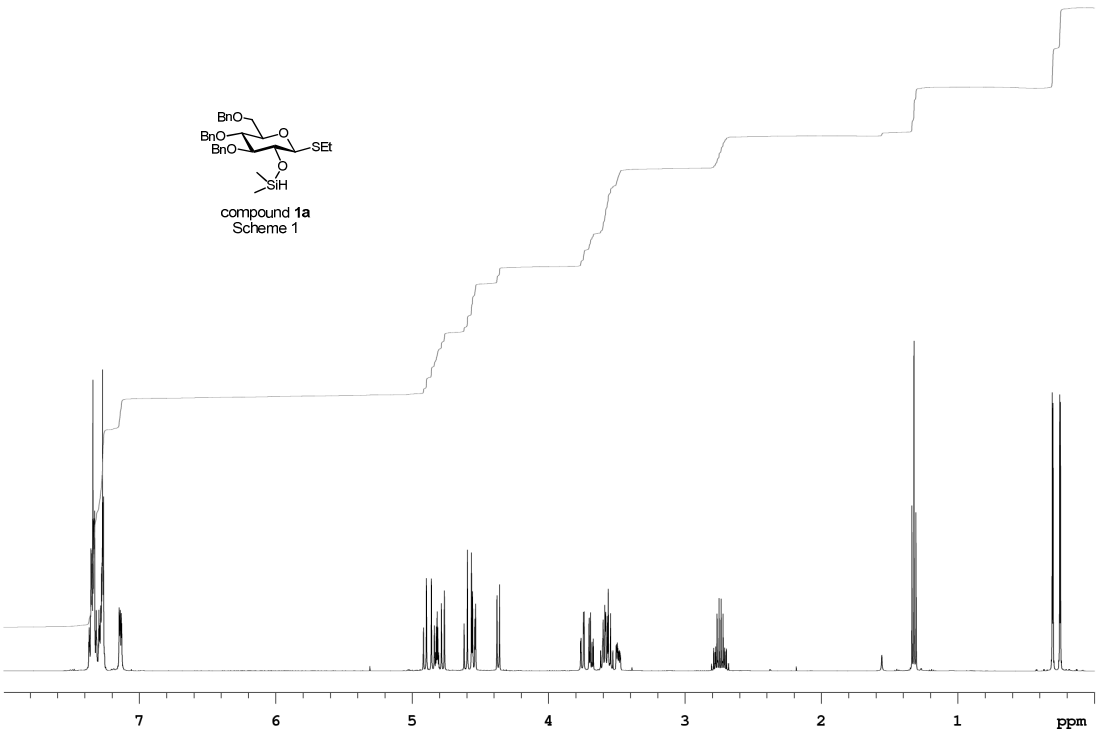
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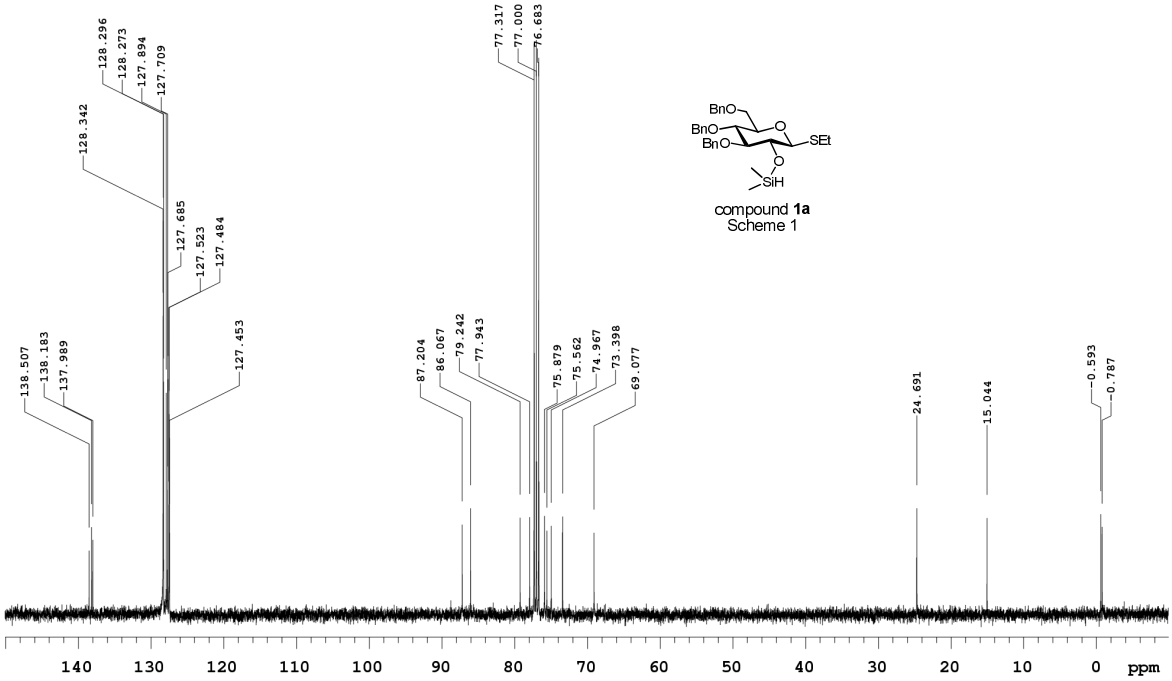
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69.077
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BnO
BnO
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SEt
O
SiH
compound 1a
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60
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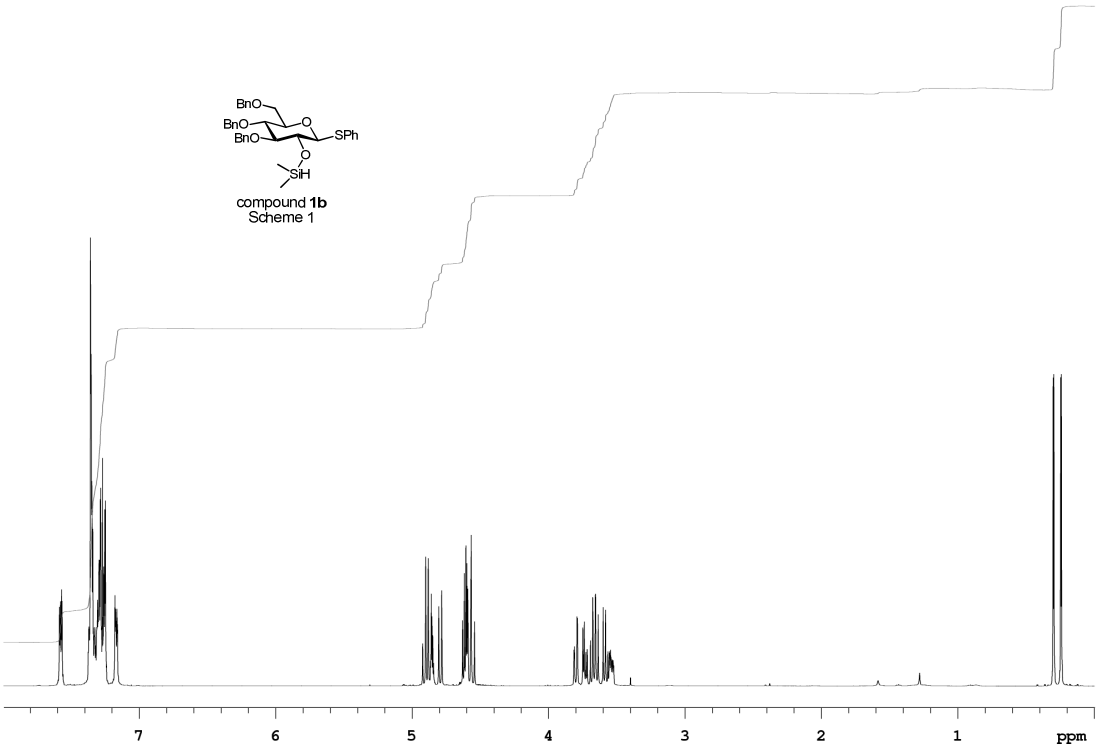
ppm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compound 1b
Scheme 1
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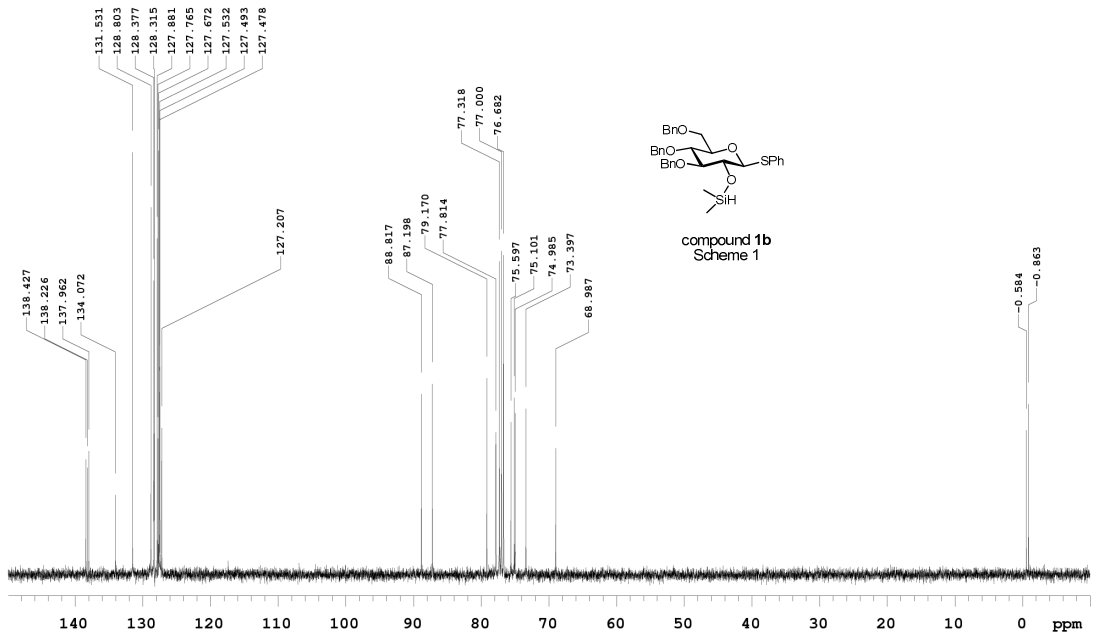
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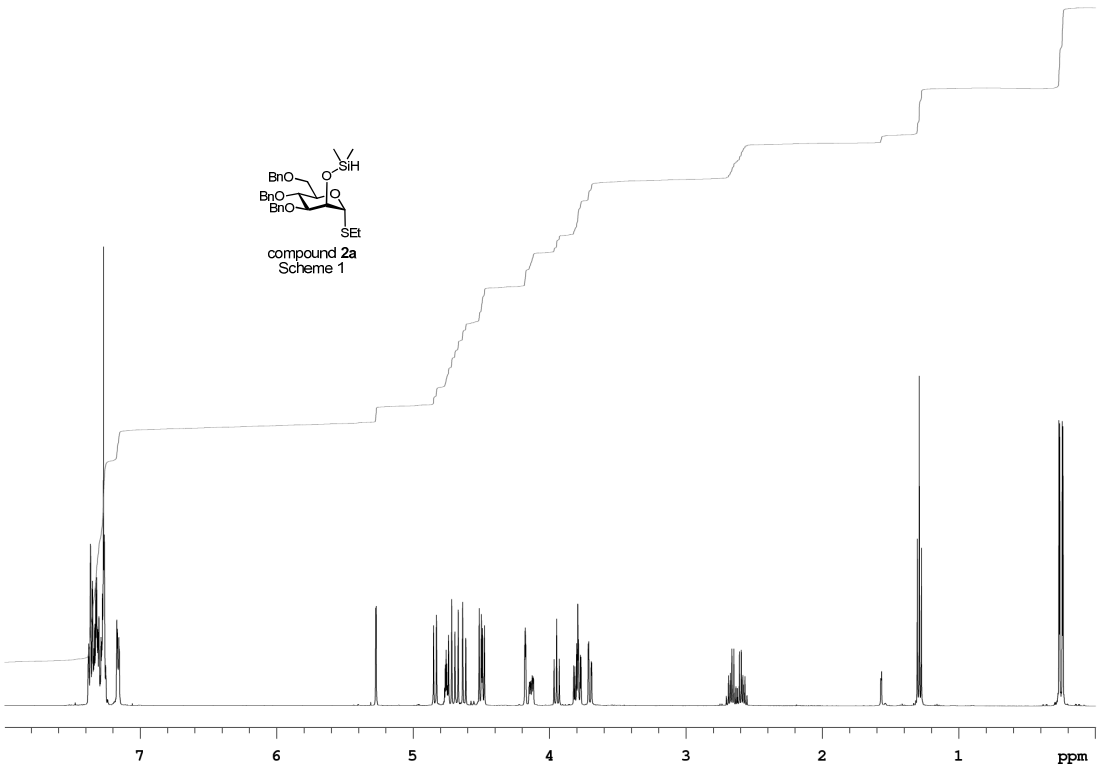
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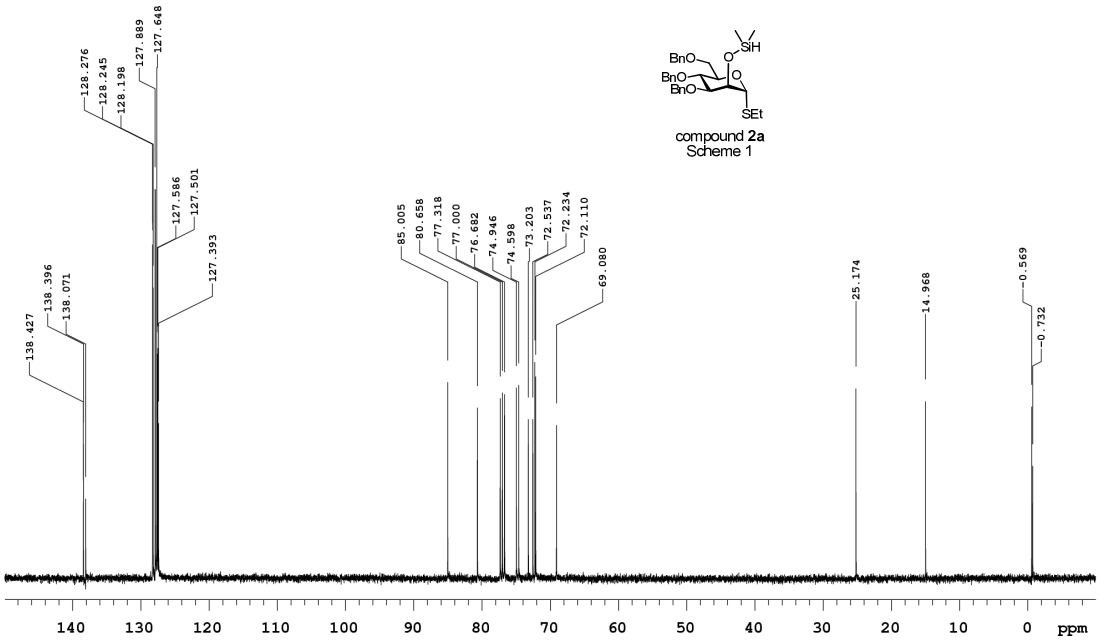
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85.005
80.658
77.318
77.000
76.682
74.946
74.598
73.203
72.537
72.234
72.110
69.080
25.174
14.968
0.569
-0.732
BnO
BnO
BnO
O
SiH
O
SEt
compound 2a
Scheme 1
140
130
120
110
100
90
80
70
60
50
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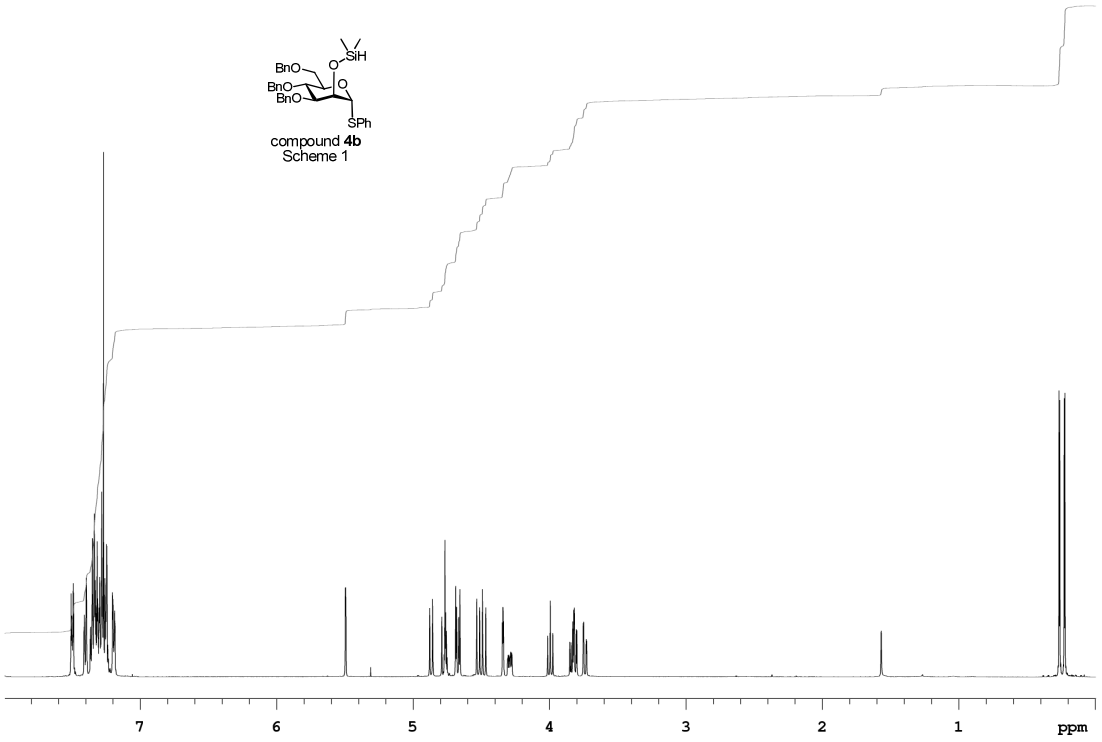
30
20
10
0
ppm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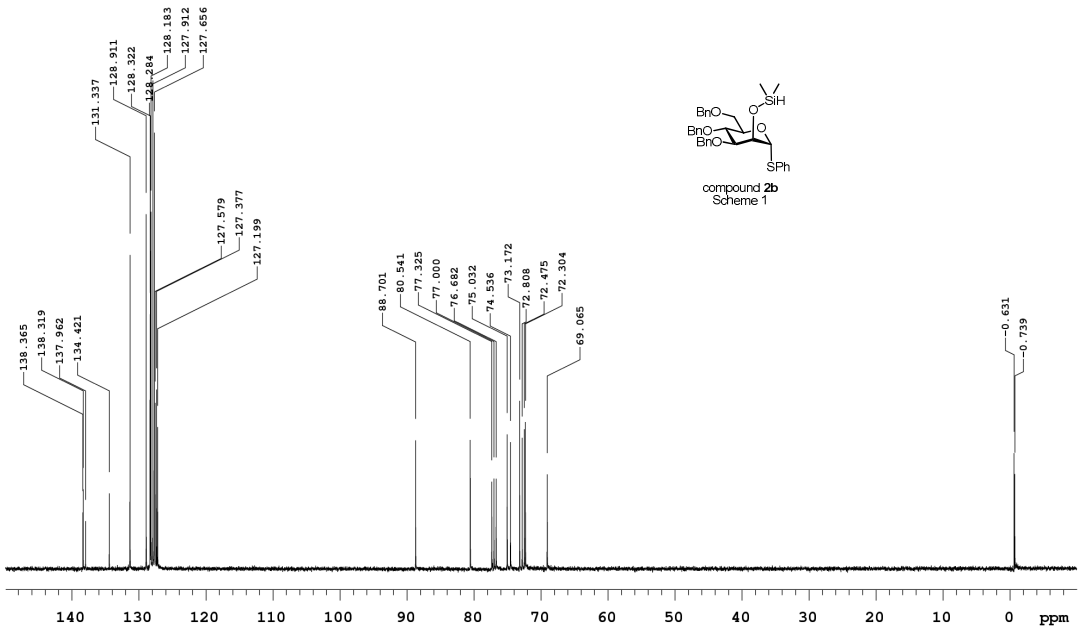
BnO
BnO
O
SiH
O
SPh
compound 4b
Scheme 1
7
6
5
4
3
2
1
ppm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128.284
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127.579
127.377
127.199
88.701
80.541
77.325
77.000
76.682
75.032
74.536
73.172
72.808
72.475
72.304
69.065
0.631
0.739
BnO
BnO
BnO
O
SiH
O
SPh
compound 2b
Scheme 1
140
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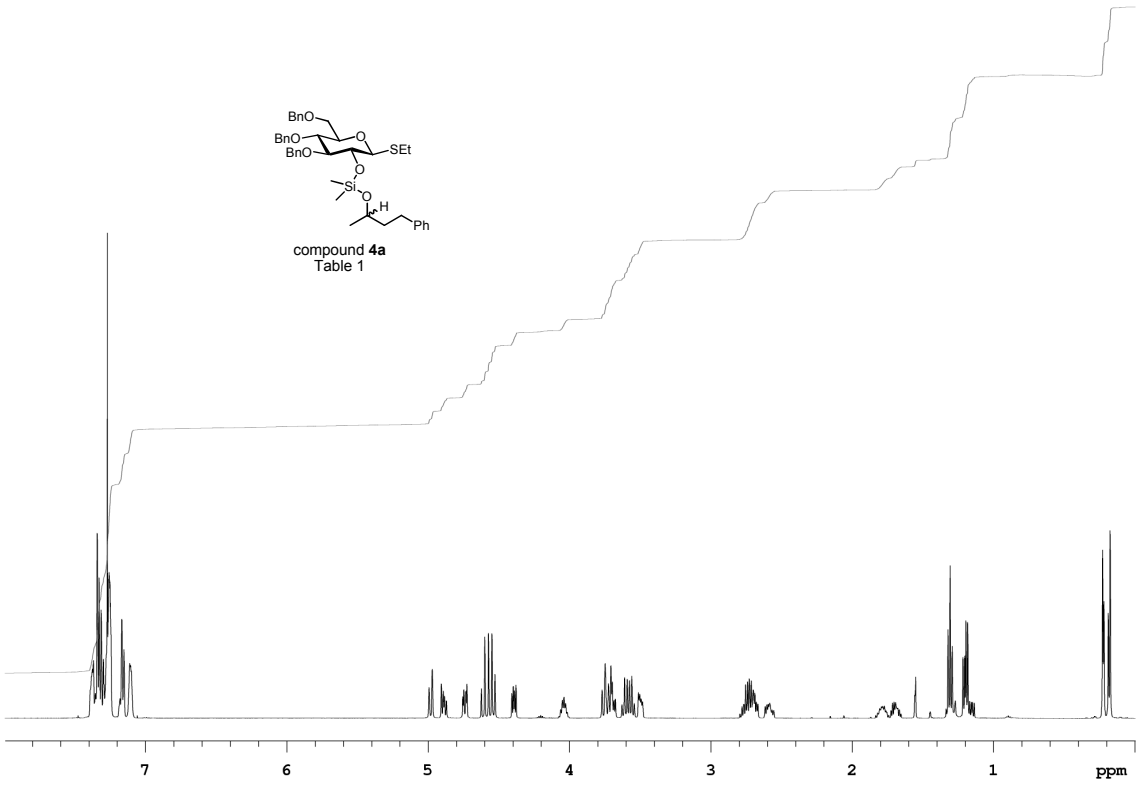
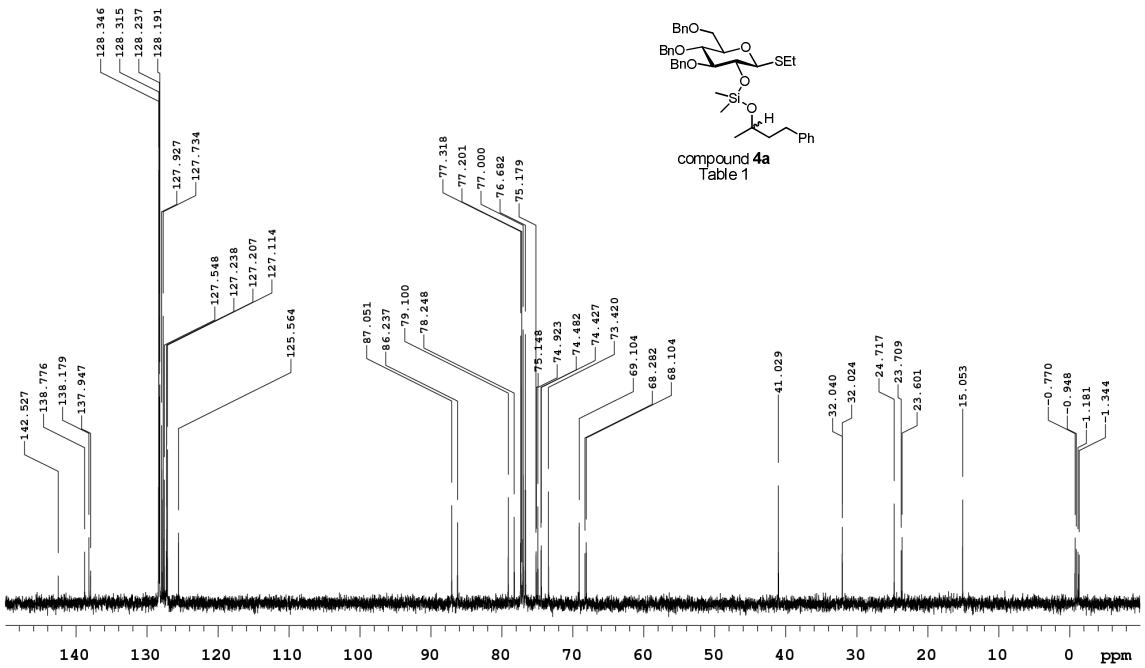
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


BnO
BnO
BnO
O
SEt
O
Si
O
H
Ph
compound 4a
Table 1
7
6
5
4
3
2
1
ppm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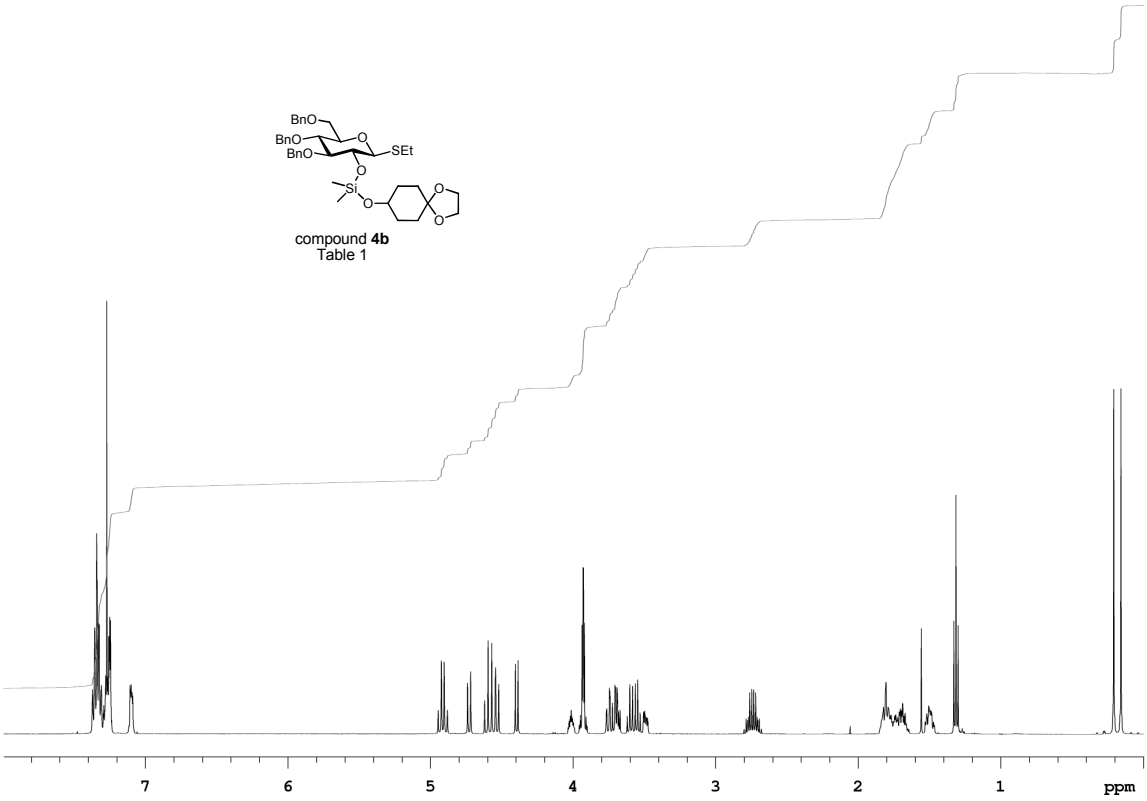
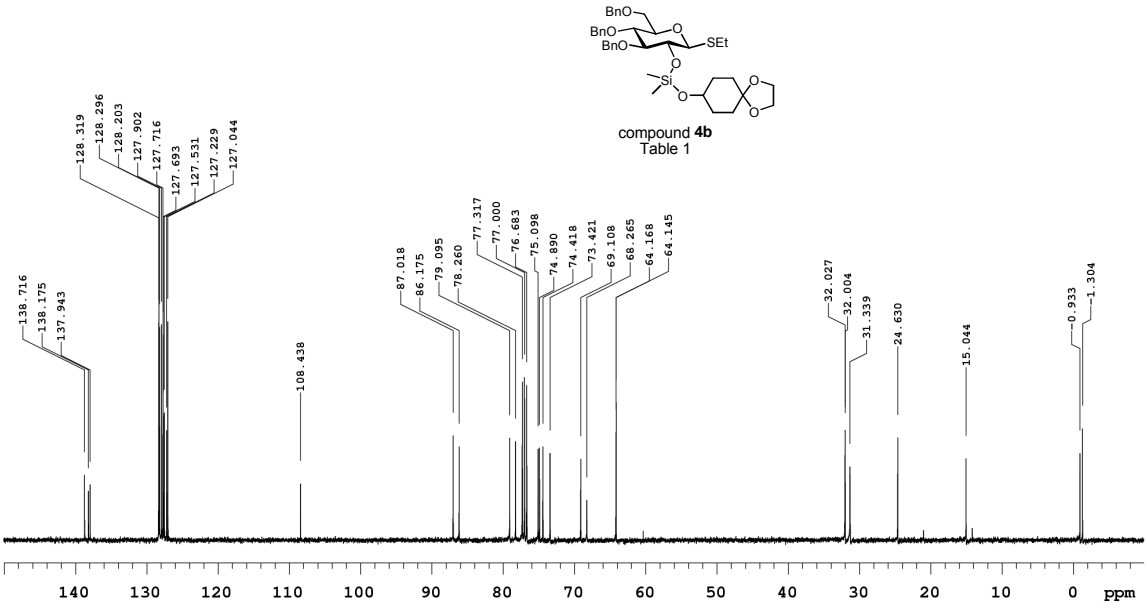
127.548
127.238
127.207
127.114
125.564
142.527
138.776
138.179
137.947
87.051
86.237
79.100
78.248
77.318
77.201
77.000
76.682
75.179
75.148
74.923
74.482
74.427
73.420
69.104
68.282
68.104
41.029
32.040
32.024
24.717
23.709
23.601
15.053
0.770
0.948
1.181
1.344
BnO
BnO
BnO
O
SEt
O
Si
O
H
Ph
compound 4a
Table 1
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


BnO
BnO
BnO
O
SEt
O
Si
O
O
O
compound 4b
Table 1
7
6
5
4
3
2
1
ppm


BnO
BnO
BnO
O
SEt
O
Si
O
O
O
compound 4b
Table 1
128.319
128.296
128.203
127.902
127.716
127.693
127.531
127.229
127.044
138.716
138.175
137.943
108.438
87.018
86.175
79.095
78.260
77.317
77.000
76.683
75.098
74.890
74.418
73.421
69.108
68.265
64.168
64.145
32.027
32.004
31.339
24.630
15.044
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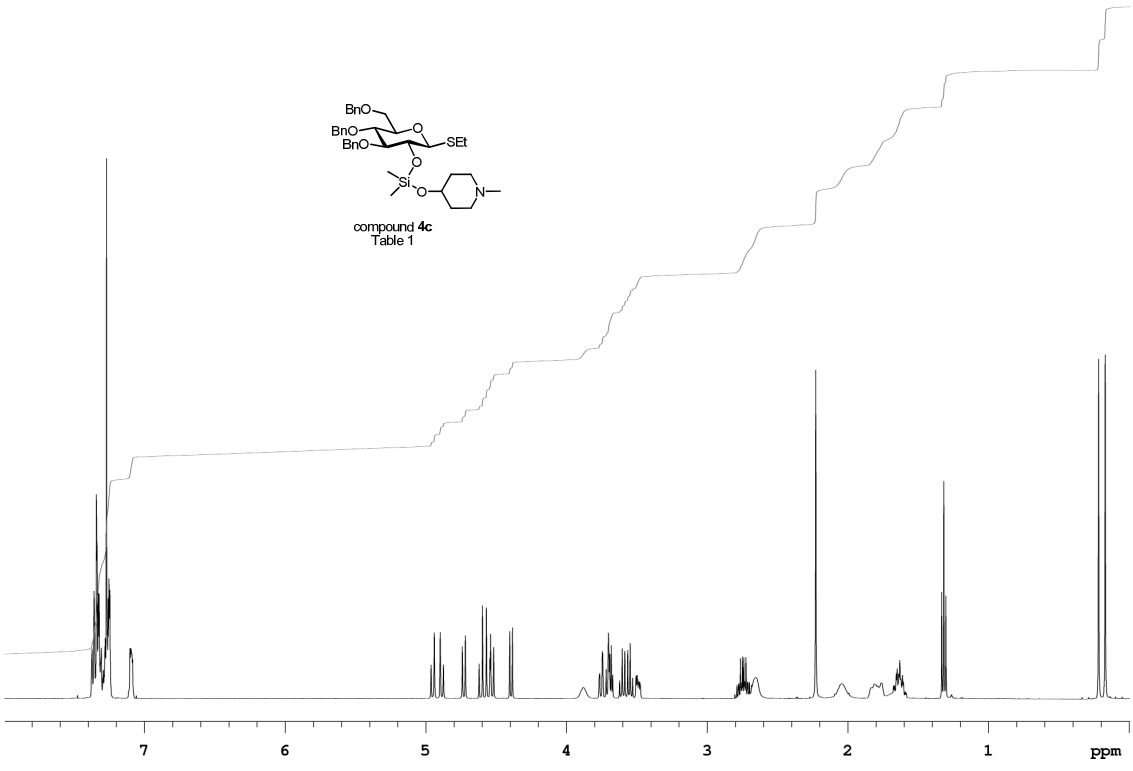
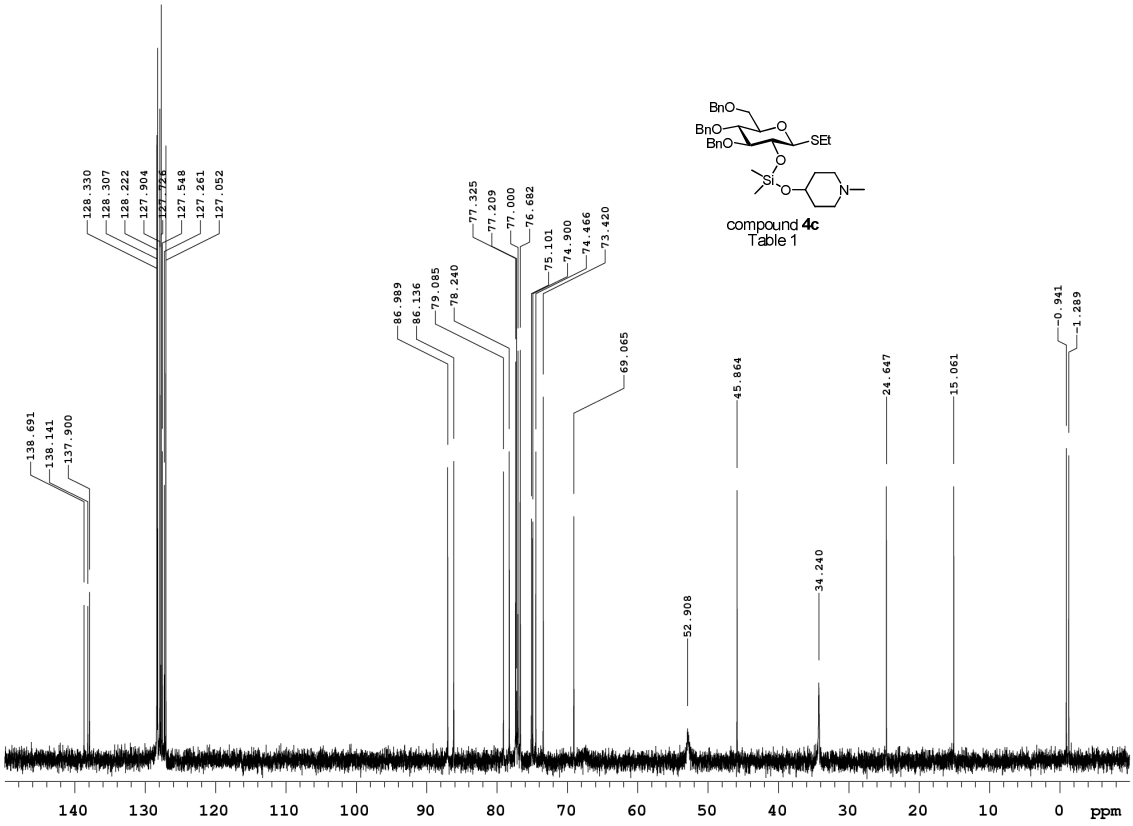
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


BnO
BnO
BnO
SEt
Si
O
N
compound 4c
Table 1
7
6
5
4
3
2
1
ppm


BnO
BnO
BnO
SEt
Si
O
N
compound 4c
Table 1
128.330
128.307
128.222
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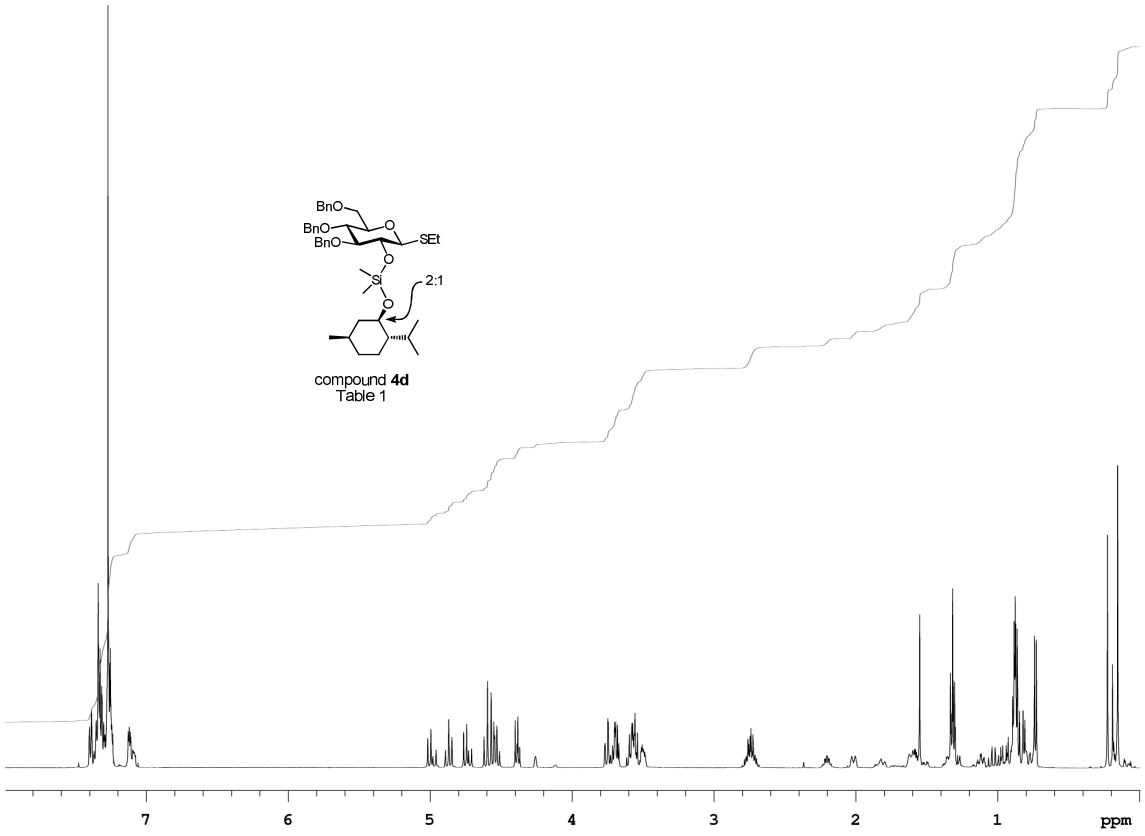
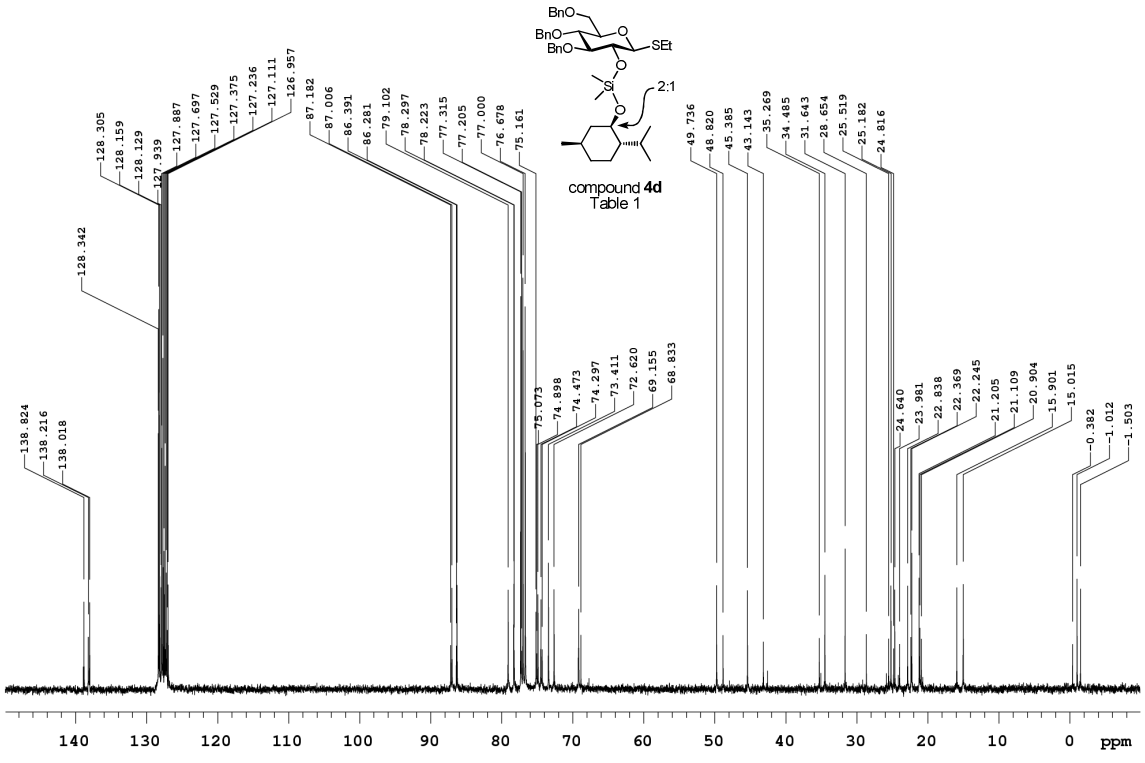
127.726
127.548
127.261
127.052
138.691
138.141
137.900
86.989
86.136
79.085
78.240
77.325
77.209
77.000
76.682
75.101
74.900
74.466
73.420
69.065
52.908
45.864
34.240
24.647
15.061
0.941
-1.289
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


BnO
BnO
BnO
O
SEt
O
Si
O
2:1
compound 4d
Table 1
7
6
5
4
3
2
1
ppm


BnO
BnO
BnO
O
SEt
O
Si
O
2:1
compound 4d
Table 1
128.342
128.305
128.159
128.129
127.939
127.887
127.697
127.529
127.375
127.236
127.111
126.957
87.182
87.006
86.391
86.281
79.102
78.297
78.223
77.315
77.205
77.000
76.678
75.161
75.073
74.898
74.473
74.297
73.411
72.620
69.155
68.833
49.736
48.820
45.385
43.143
35.269
34.485
31.643
28.654
25.519
25.182
24.816
24.640
23.981
22.838
22.369
22.245
21.205
21.109
20.904
15.901
15.015
0.382
1.012
1.503
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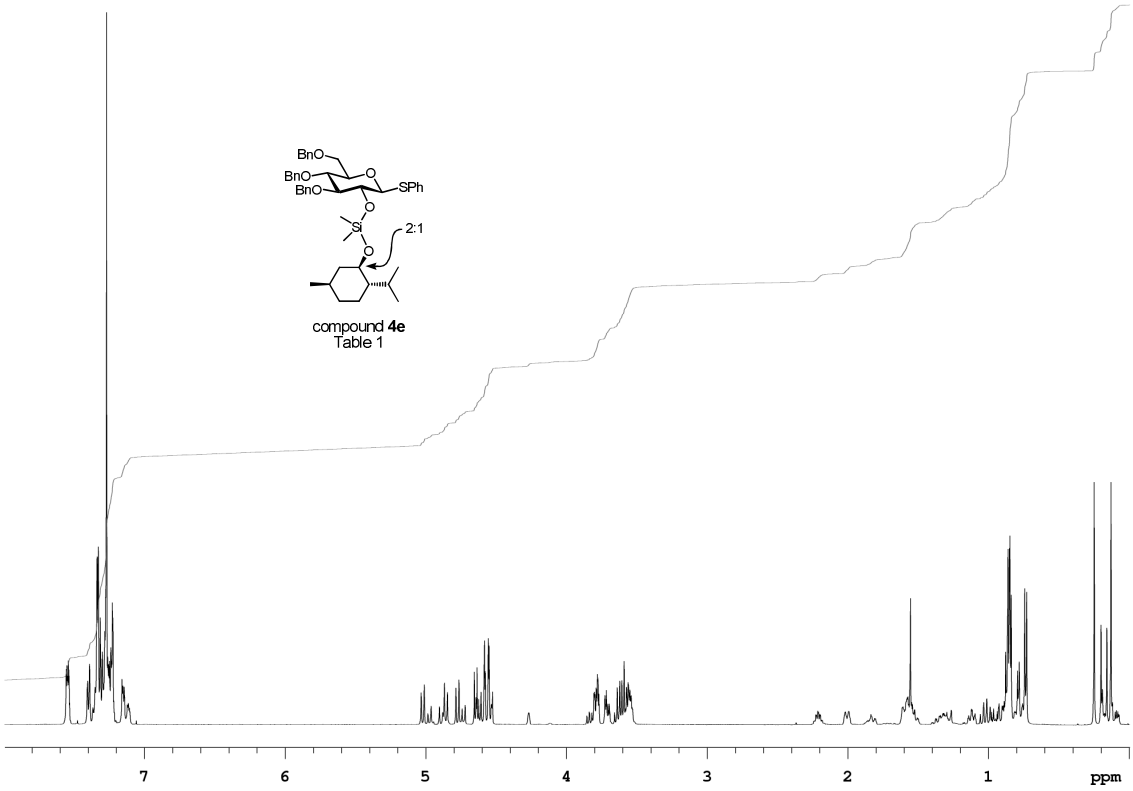
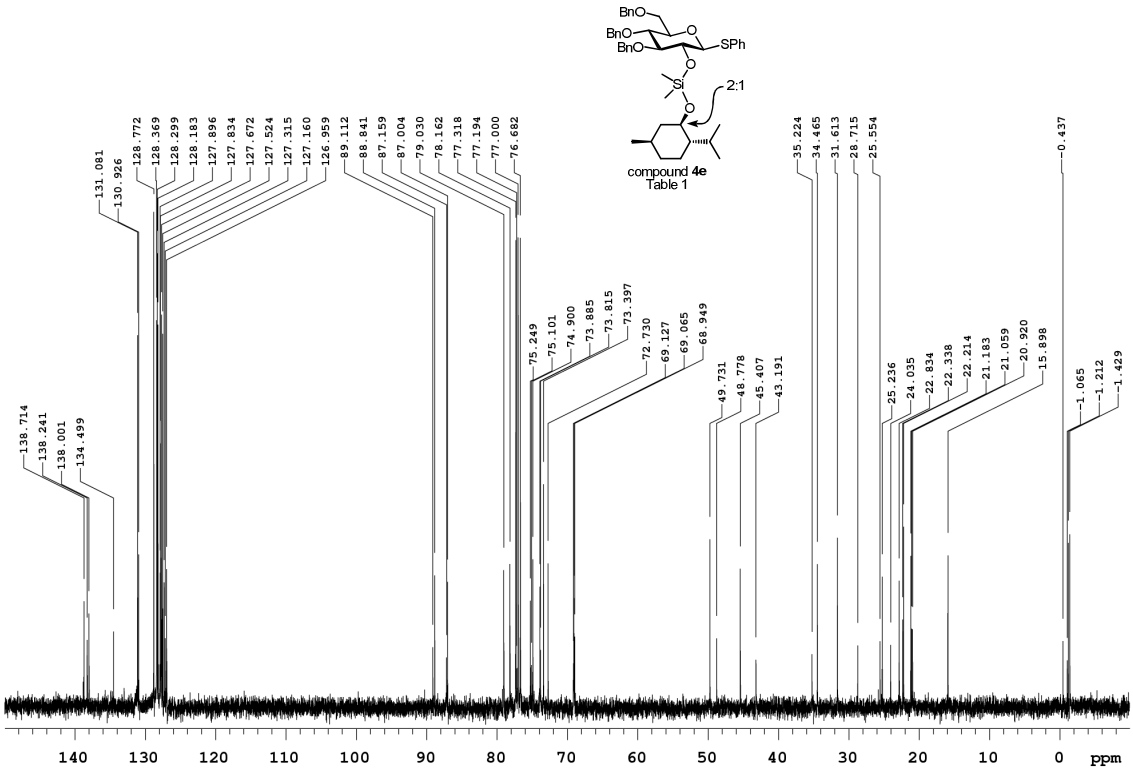
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


BnO
BnO
BnO
O
SPh
O
Si
O
2:1
compound 4e
Table 1
7
6
5
4
3
2
1
ppm


BnO
BnO
BnO
O
SPh
O
Si
O
2:1
compound 4e
Table 1
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138.241
138.001
134.499
131.081
130.926
128.772
128.369
128.299
128.183
127.896
127.834
127.672
127.524
127.315
127.160
126.959
89.112
88.841
87.159
87.004
79.030
78.162
77.318
77.194
77.000
76.682
75.249
75.101
74.900
73.885
73.815
73.397
72.730
69.127
69.065
68.949
49.731
48.778
45.407
43.191
35.224
34.465
31.613
28.715
25.554
25.236
24.035
22.834
22.338
22.214
21.183
21.059
20.920
15.898
0.437
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1.212
1.429
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130
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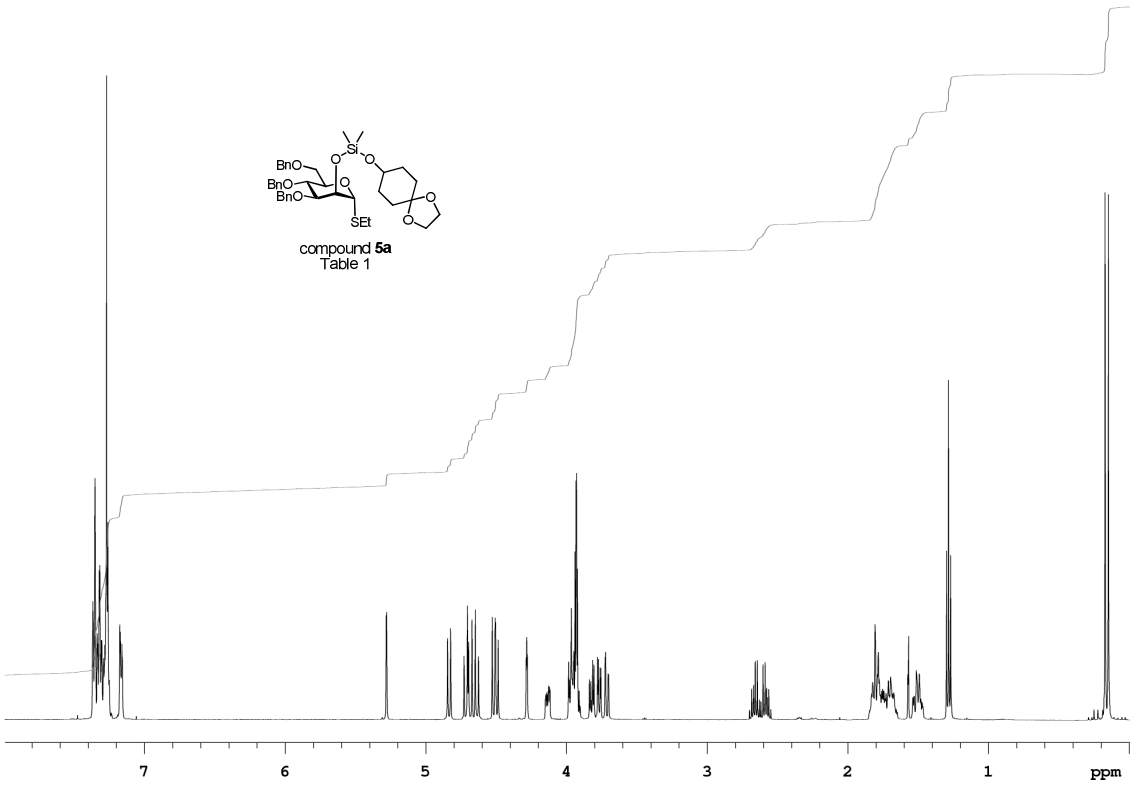
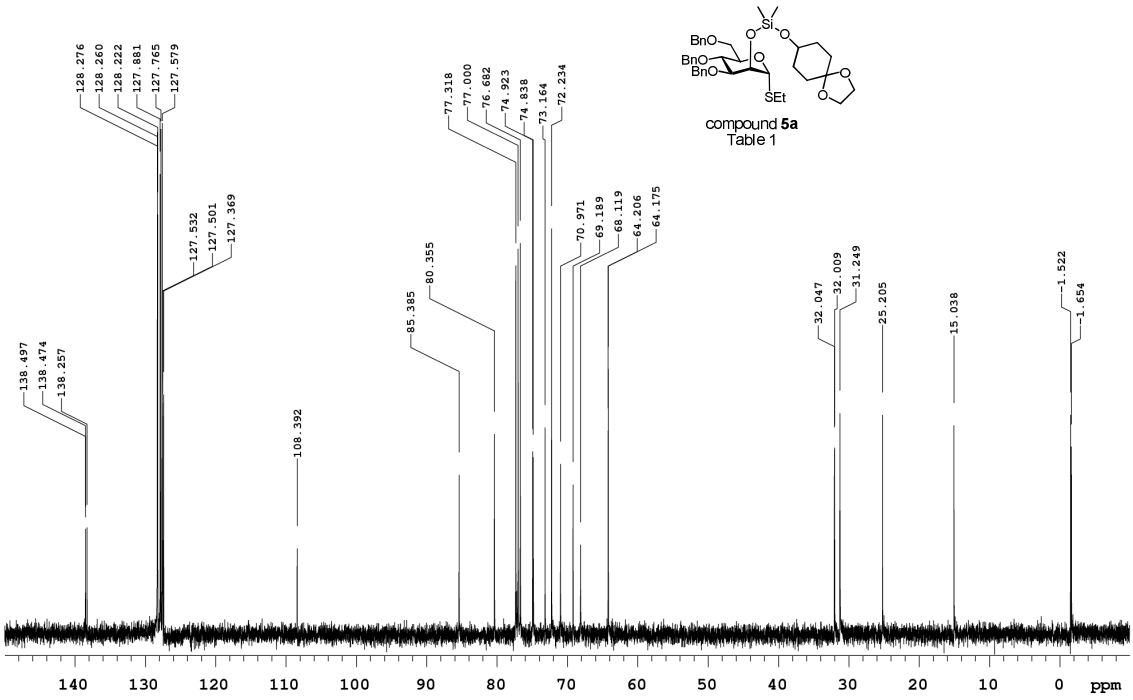
110
100
90
80
70
60
50
40
30
20
10
0
ppm


BnO
BnO
BnO
O
Si
O
O
O
O
SEt
compound 5a
Table 1
7
6
5
4
3
2
1
ppm


BnO
BnO
BnO
O
Si
O
O
O
O
SEt
compound 5a
Table 1
128.276
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127.881
127.765
127.579
127.532
127.501
127.369
138.497
138.474
138.257
108.392
85.385
80.355
77.318
77.000
76.682
74.923
74.838
73.164
72.234
70.971
69.189
68.119
64.206
64.175
32.047
32.009
31.249
25.205
15.038
1.522
1.654
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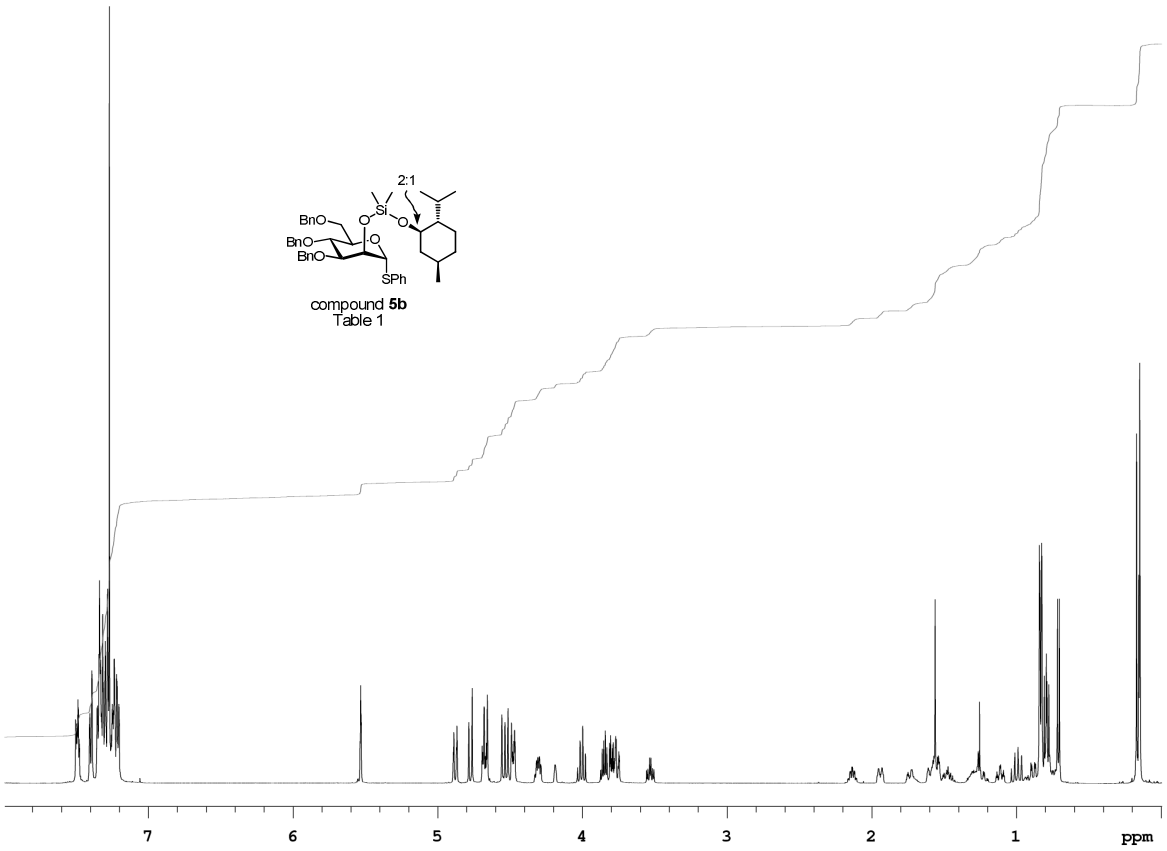
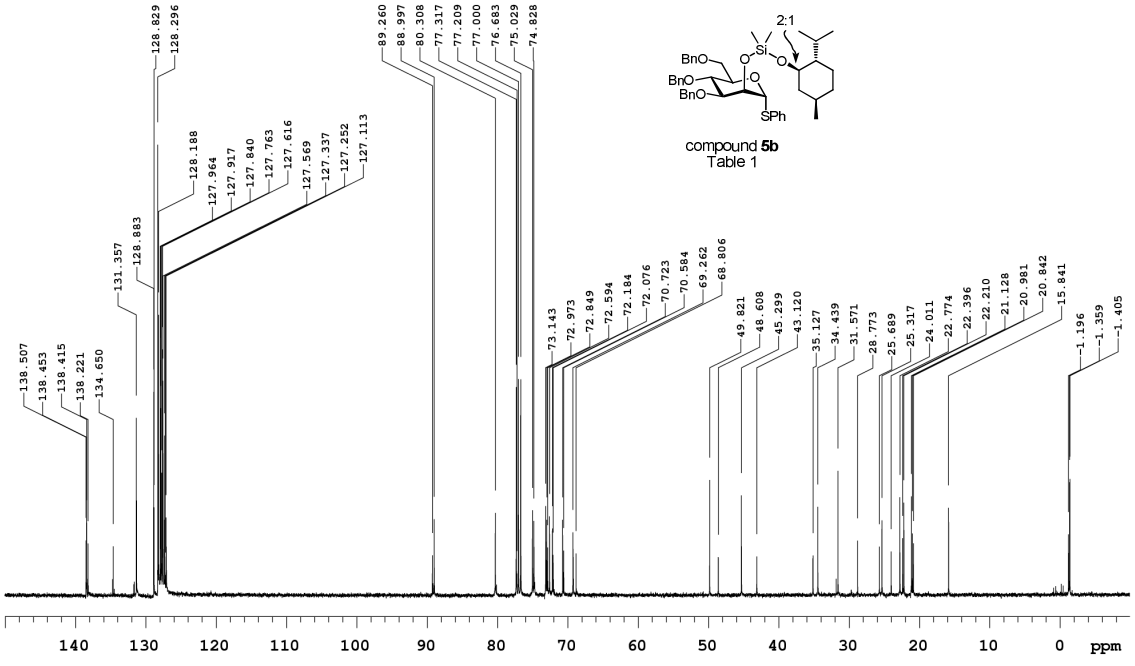
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


2:1
BnO
BnO
BnO
SPh
compound 5b
Table 1
7
6
5
4
3
2
1
ppm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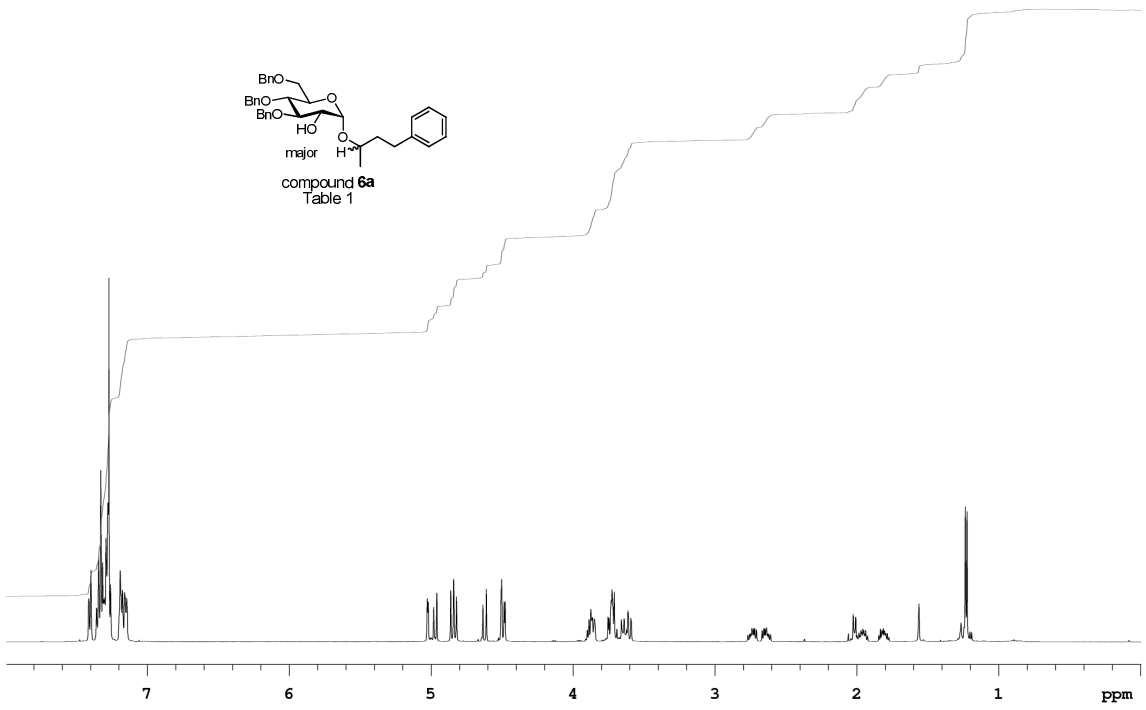
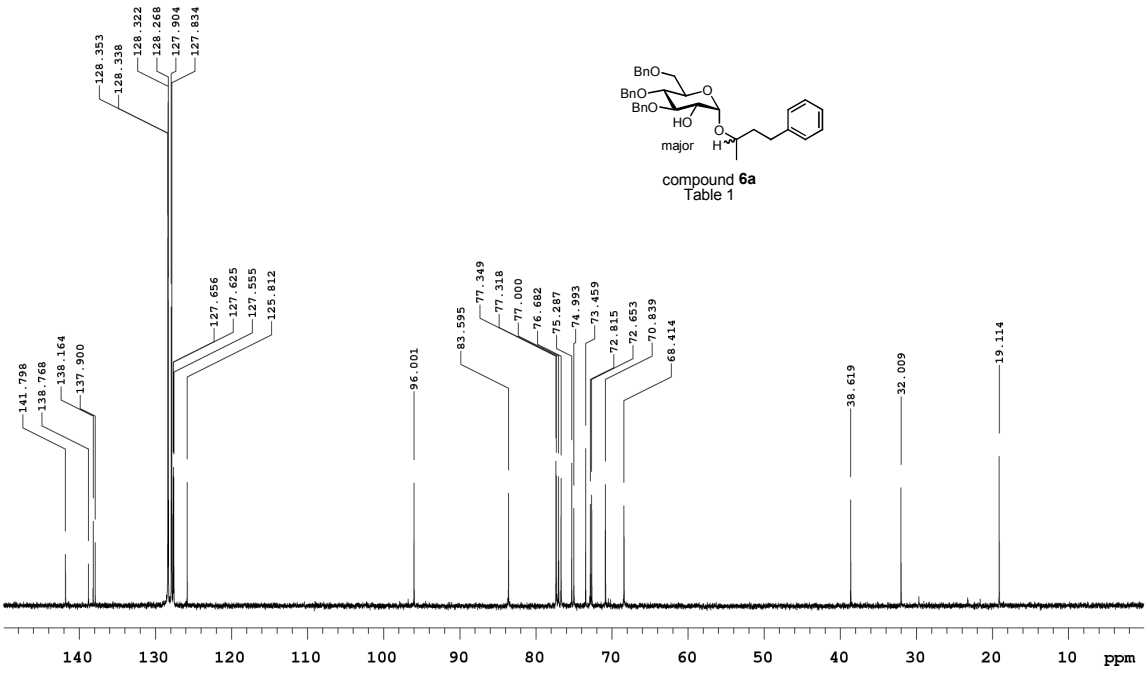
127.616
127.569
127.337
127.252
127.113
131.357
128.883
138.507
138.453
138.415
138.221
134.650
89.260
88.997
80.308
77.317
77.209
77.000
76.683
75.029
74.828
73.143
72.973
72.849
72.594
72.184
72.076
70.723
70.584
69.262
68.806
49.821
48.608
45.299
43.120
35.127
34.439
31.571
28.773
25.689
25.317
24.011
22.774
22.396
22.210
21.128
20.981
20.842
15.841
1.196
1.359
1.405
2:1
BnO
BnO
BnO
SPh
compound 5b
Table 1
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


BnO
BnO
BnO
HO
O
major
H
compound 6a
Table 1
7
6
5
4
3
2
1
ppm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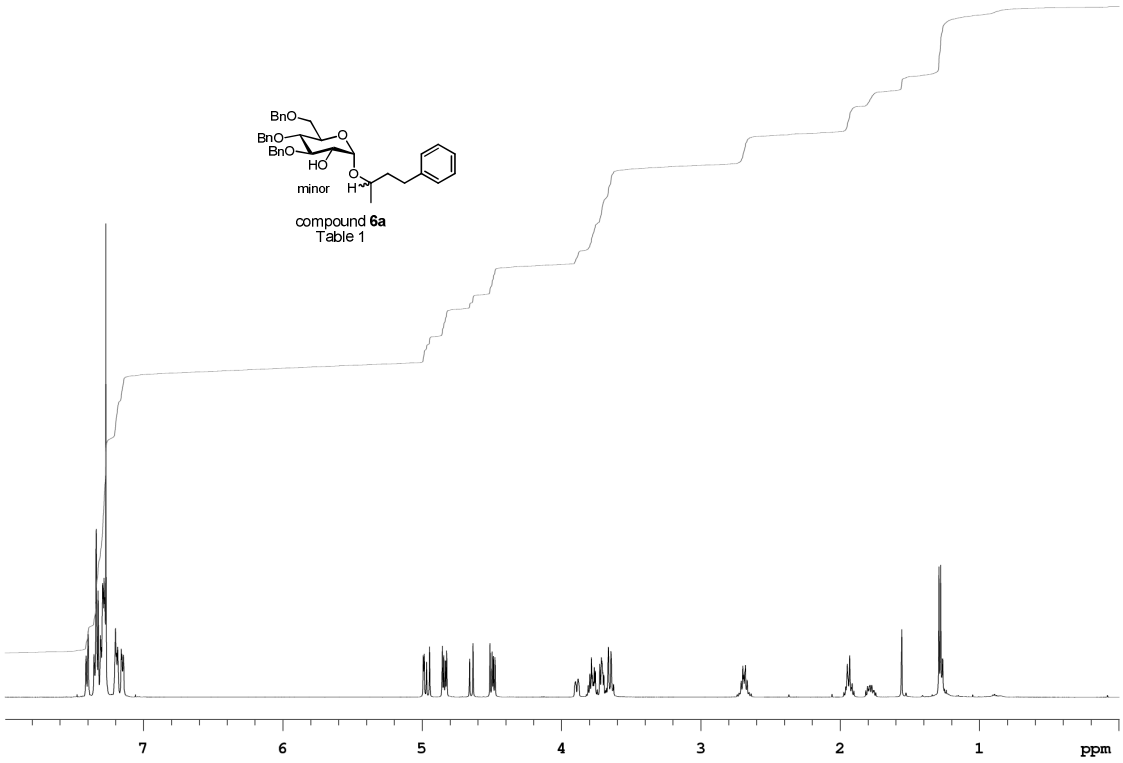
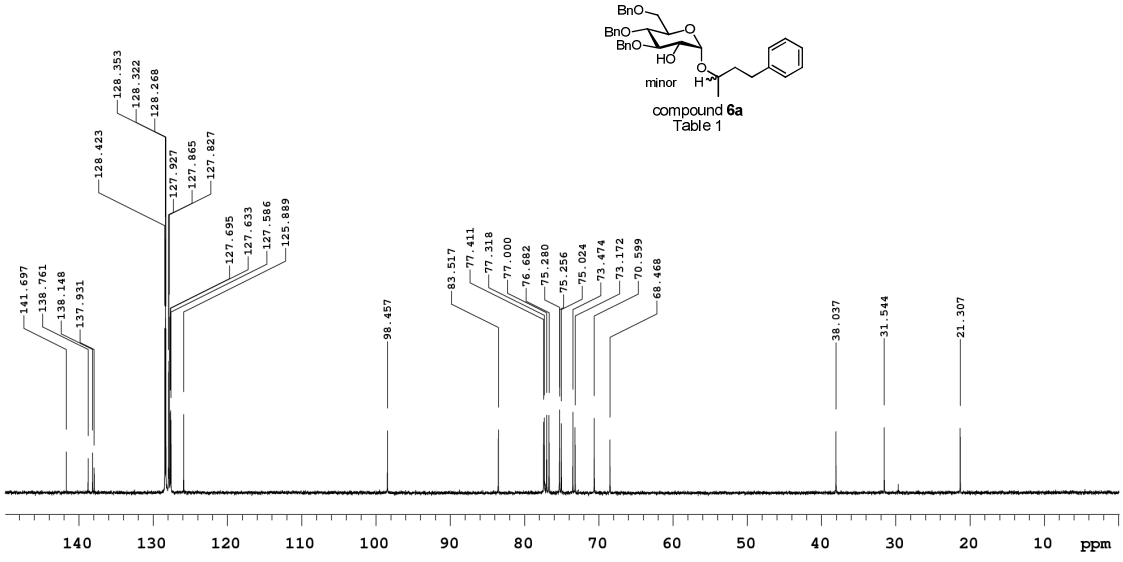
138.164
137.900
96.001
83.595
77.349
77.318
77.000
76.682
75.287
74.993
73.459
72.815
72.653
70.839
68.414
38.619
32.009
19.114
BnO
BnO
BnO
HO
O
major
H
compound 6a
Table 1
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


BnO
BnO
BnO
HO
O
minor
H
compound 6a
Table 1
7
6
5
4
3
2
1
ppm


BnO
BnO
BnO
HO
O
minor
H
compound 6a
Table 1
141.697
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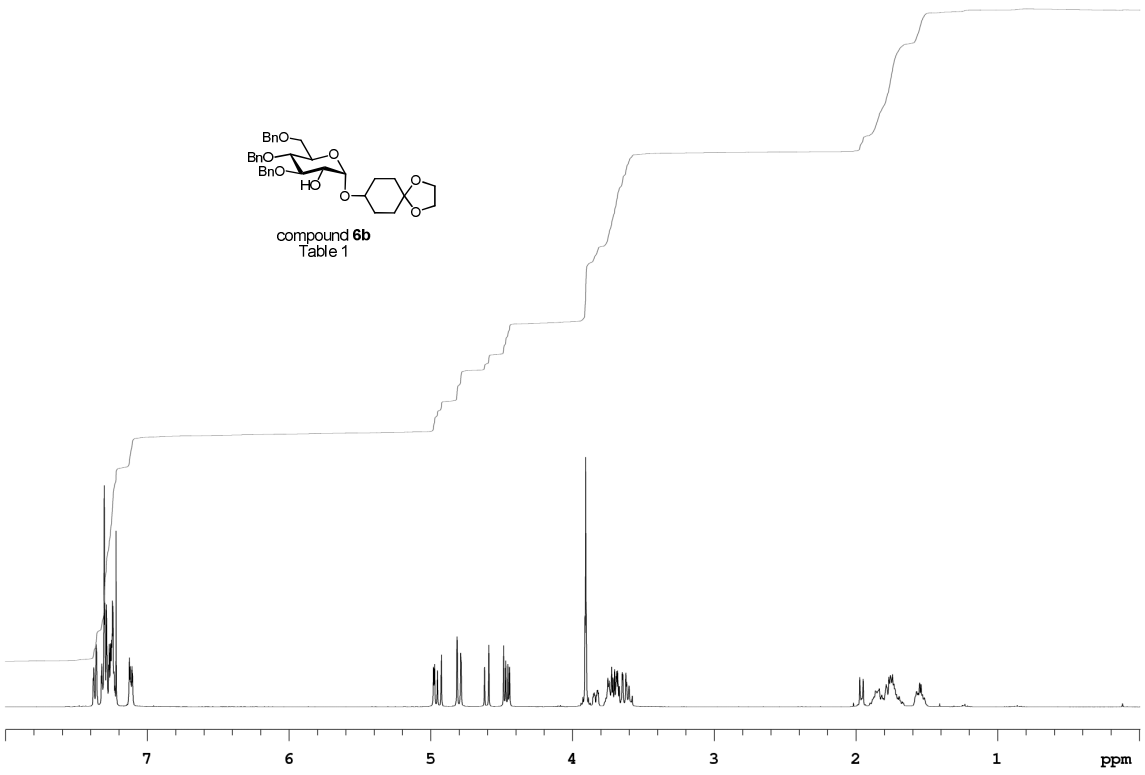
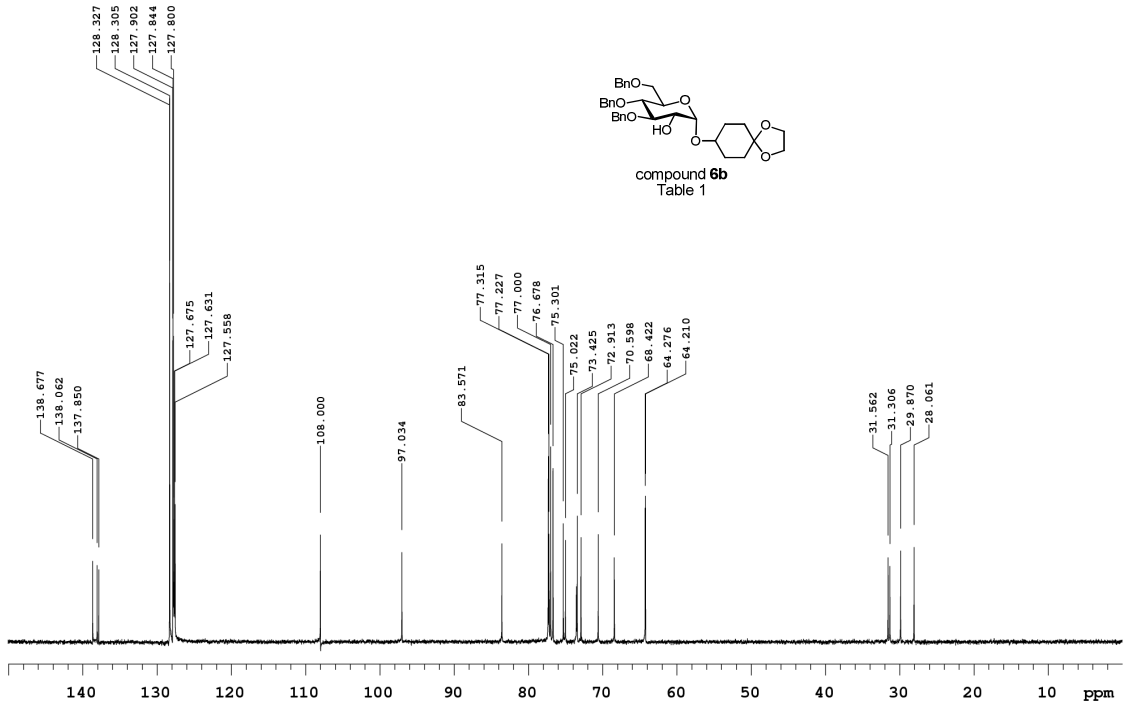
138.148
137.931
128.423
128.353
128.322
128.268
127.927
127.865
127.827
127.695
127.633
127.586
125.889
98.457
83.517
77.411
77.318
77.000
76.682
75.280
75.256
75.024
73.474
73.172
70.599
68.468
38.037
31.544
21.307
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


BnO
BnO
BnO
HO
O
O
O
compound 6b
Table 1
7
6
5
4
3
2
1
ppm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127.675
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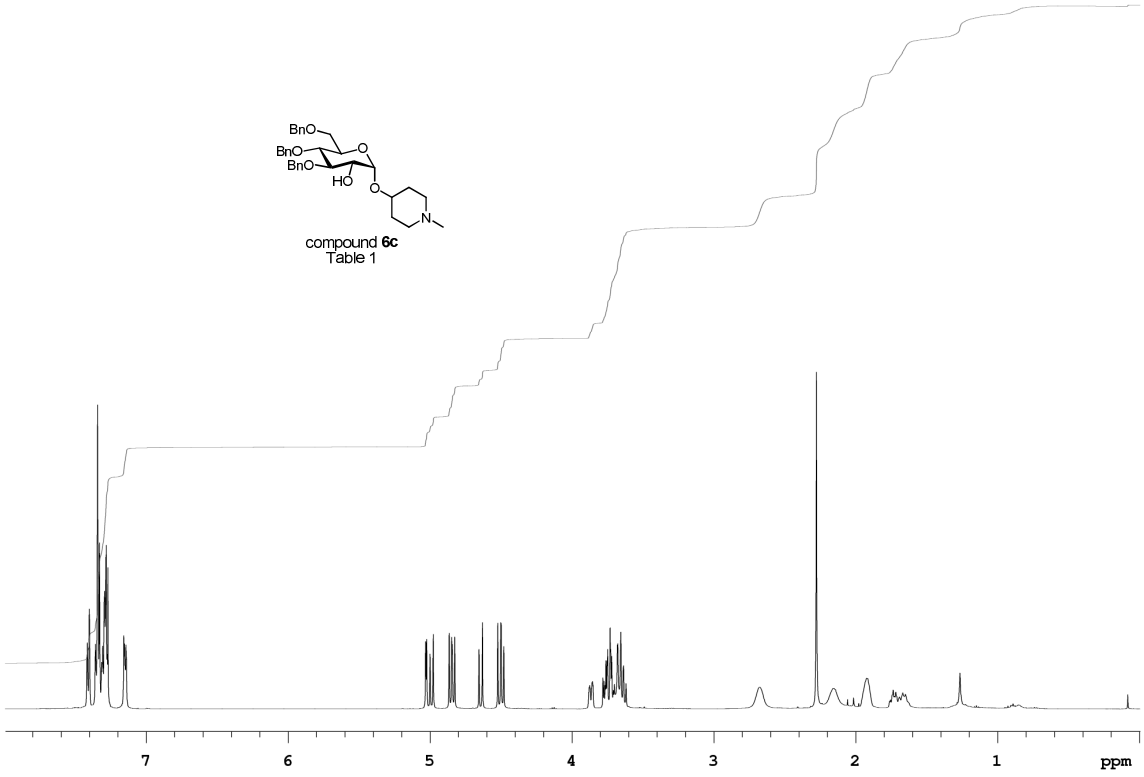
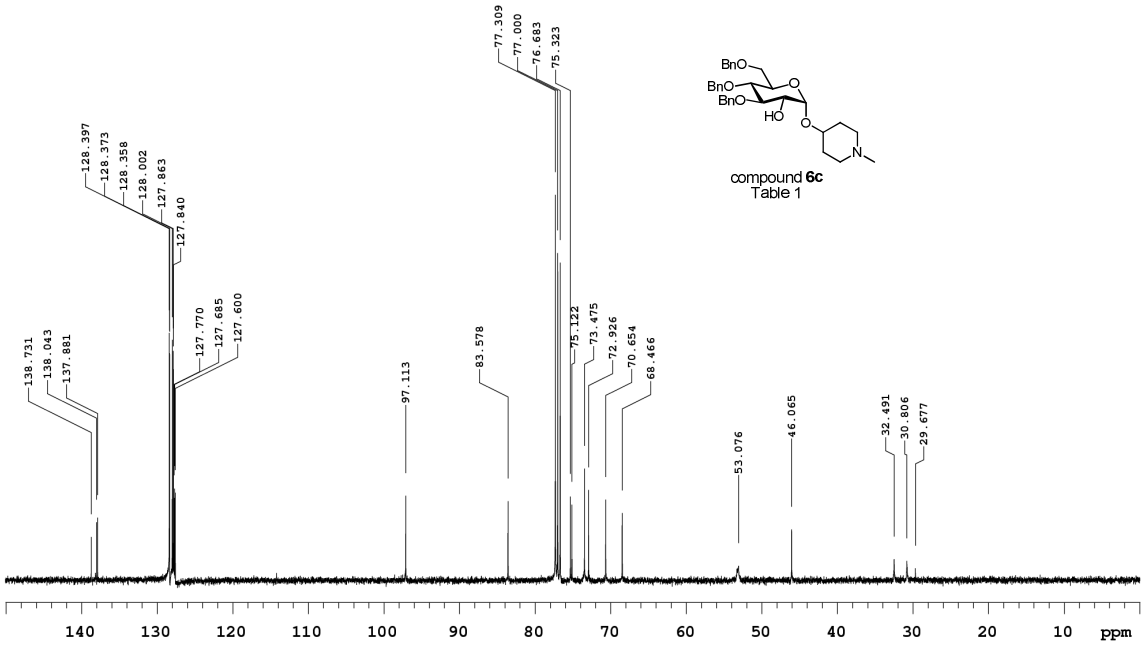
127.558
138.677
138.062
137.850
108.000
97.034
83.571
77.315
77.227
77.000
76.678
75.301
75.022
73.425
72.913
70.598
68.422
64.276
64.210
31.562
31.306
29.870
28.061
BnO
BnO
BnO
HO
O
O
O
compound 6b
Table 1
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


BnO
BnO
BnO
HO
O
N
compound 6c
Table 1
7
6
5
4
3
2
1
ppm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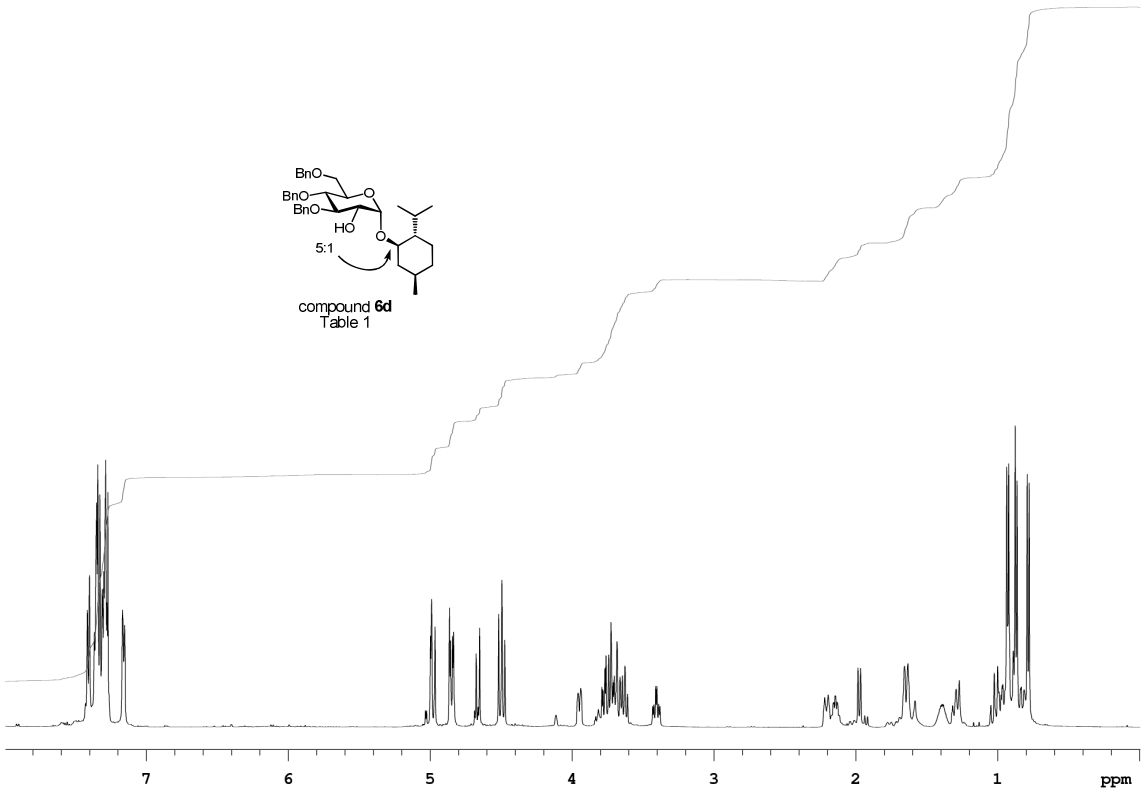
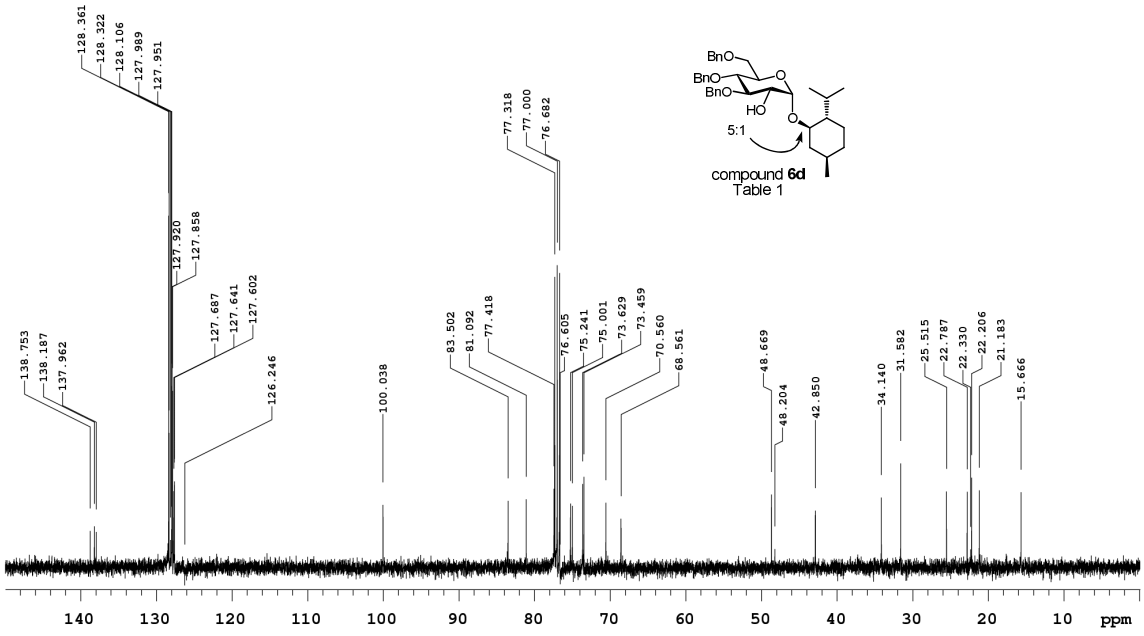
76.683
75.323
128.397
128.373
128.358
128.002
127.863
127.840
127.770
127.685
127.600
138.731
138.043
137.881
97.113
83.578
75.122
73.475
72.926
70.654
68.466
53.076
46.065
32.491
30.806
29.677
BnO
BnO
BnO
HO
O
N
compound 6c
Table 1
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


BnO
BnO
BnO
HO
O
O
5:1
compound 6d
Table 1
7
6
5
4
3
2
1
ppm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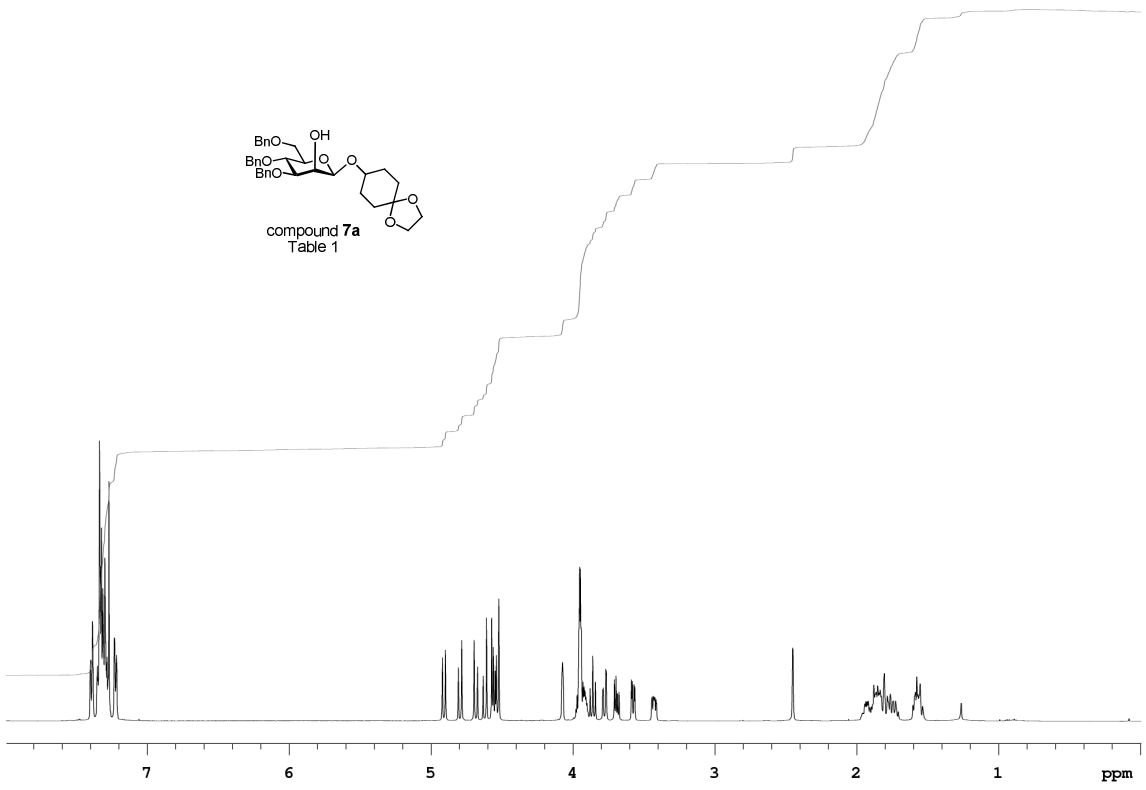
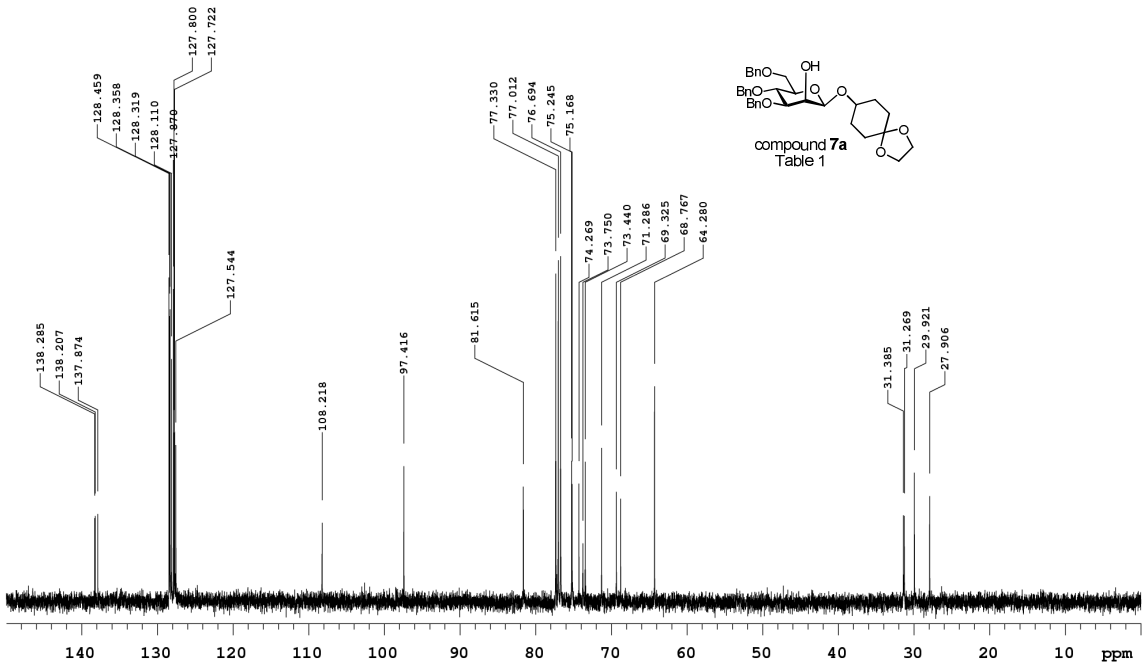
127.951
127.920
127.858
127.687
127.641
127.602
126.246
138.753
138.187
137.962
100.038
83.502
81.092
77.418
77.318
77.000
76.682
76.605
75.241
75.001
73.629
73.459
70.560
68.561
48.669
48.204
42.850
34.140
31.582
25.515
22.787
22.330
22.206
21.183
15.666
BnO
BnO
BnO
HO
O
O
5:1
compound 6d
Table 1
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


BnO
OH
BnO
BnO
compound 7a
Table 1
7
6
5
4
3
2
1
ppm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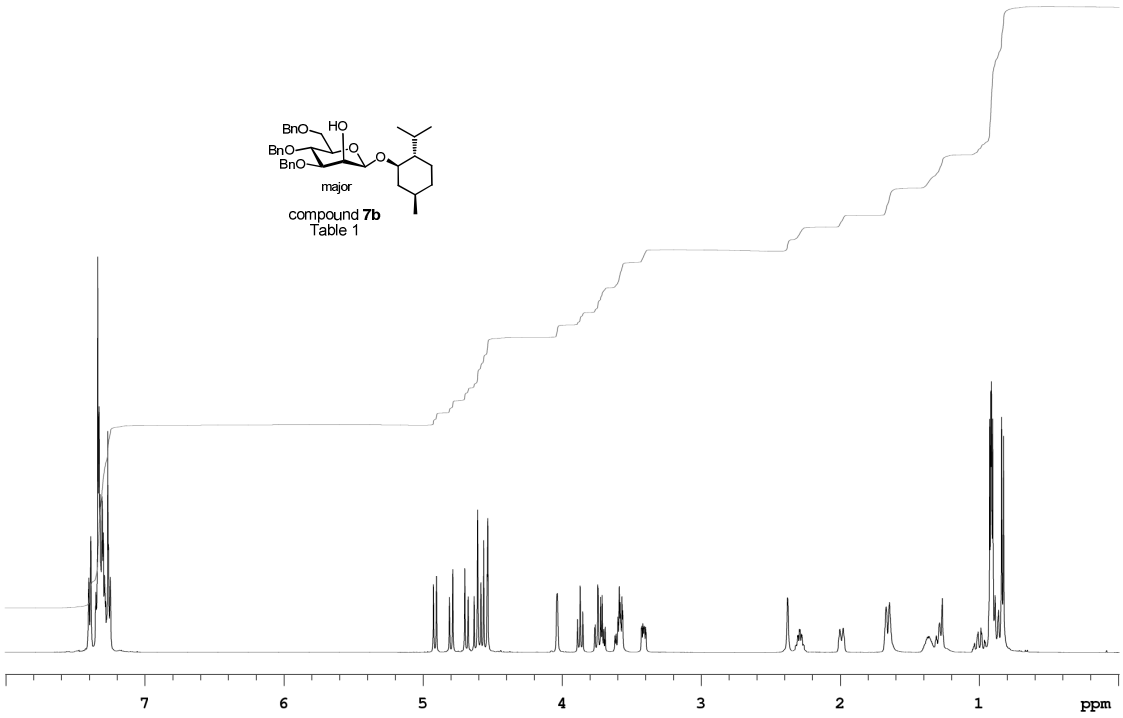
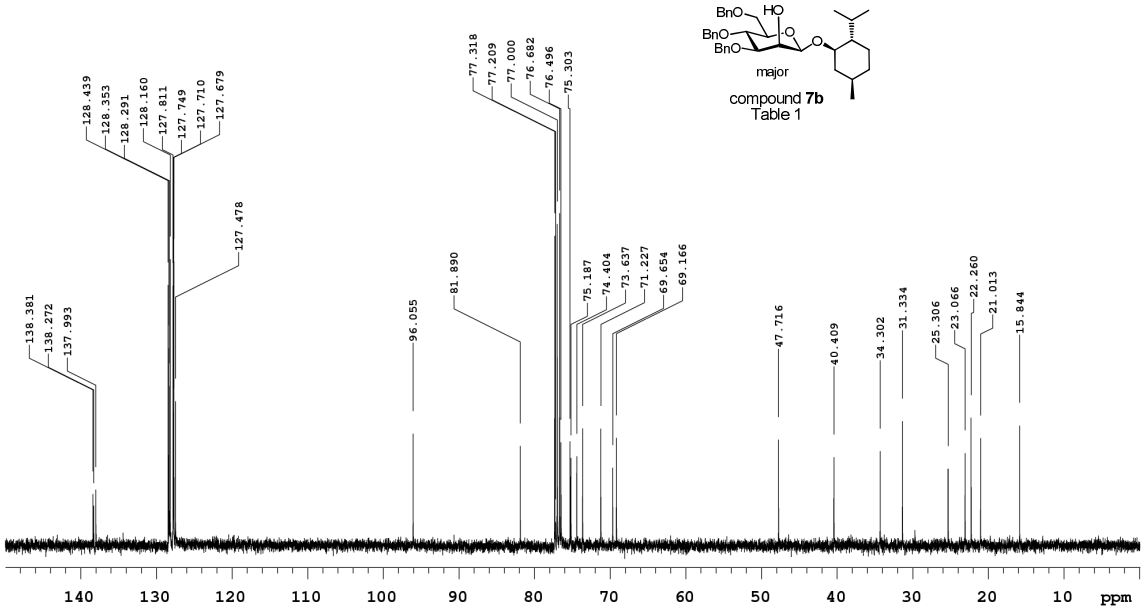
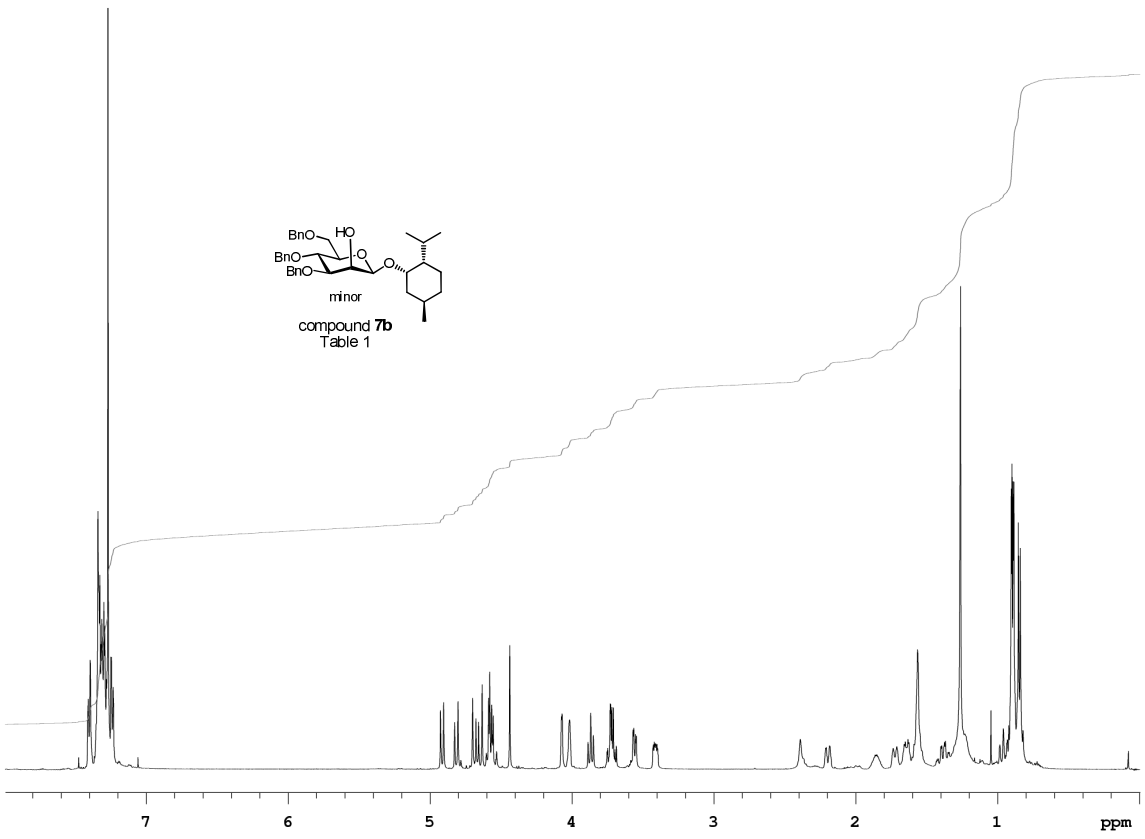
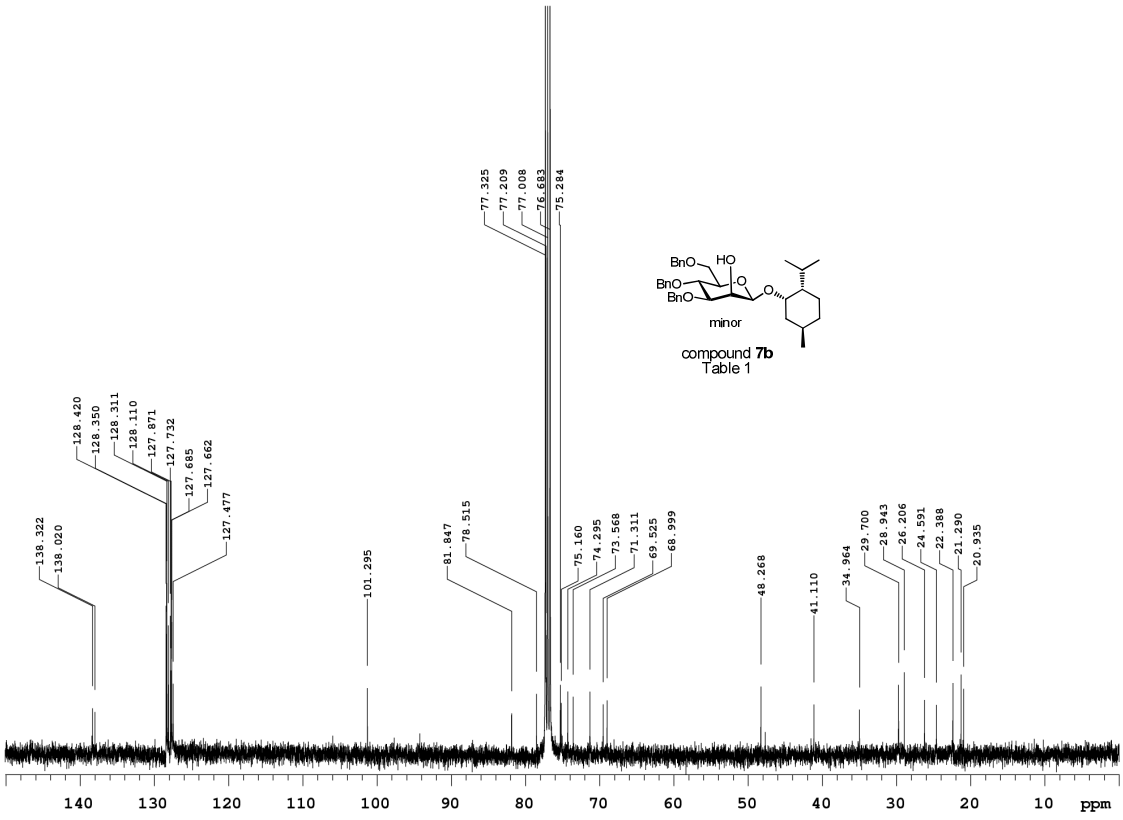
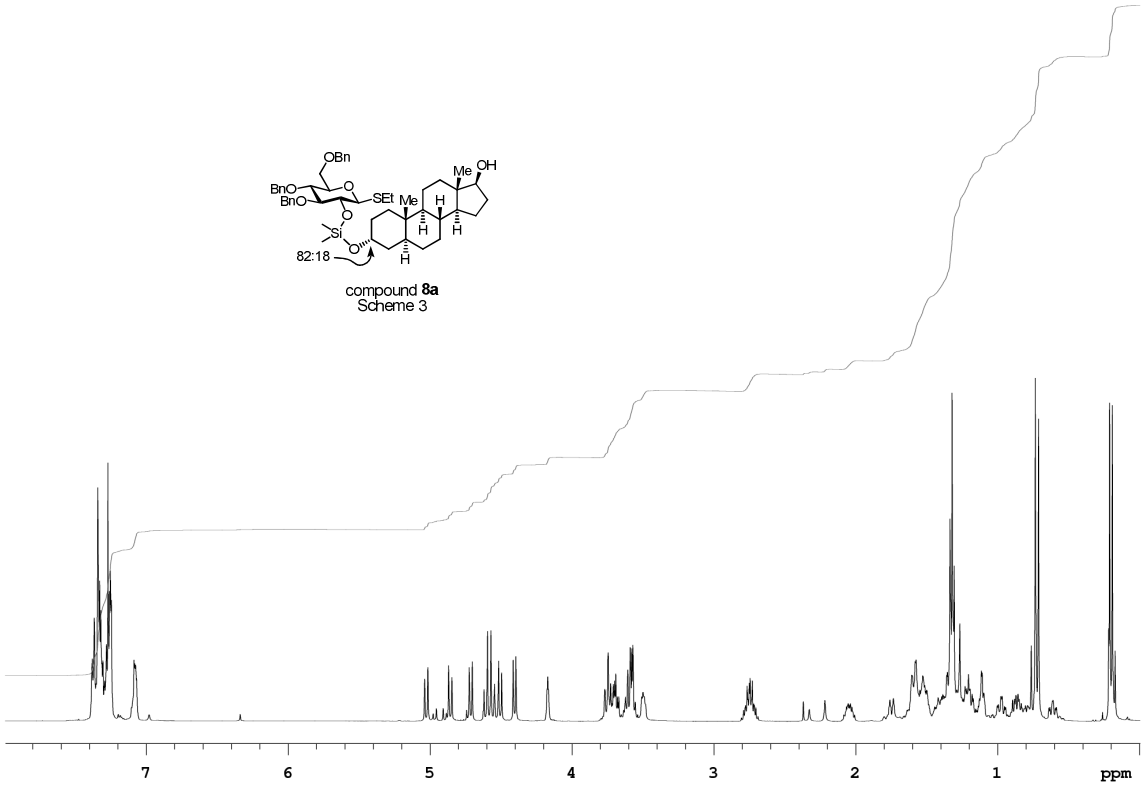
127.722
128.459
128.358
128.319
128.110
127.870
127.544
138.285
138.207
137.874
108.218
97.416
81.615
77.330
77.012
76.694
75.245
75.168
74.269
73.750
73.440
71.286
69.325
68.767
64.280
31.385
31.269
29.921
27.906
BnO
OH
BnO
BnO
compound 7a
Table 1
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

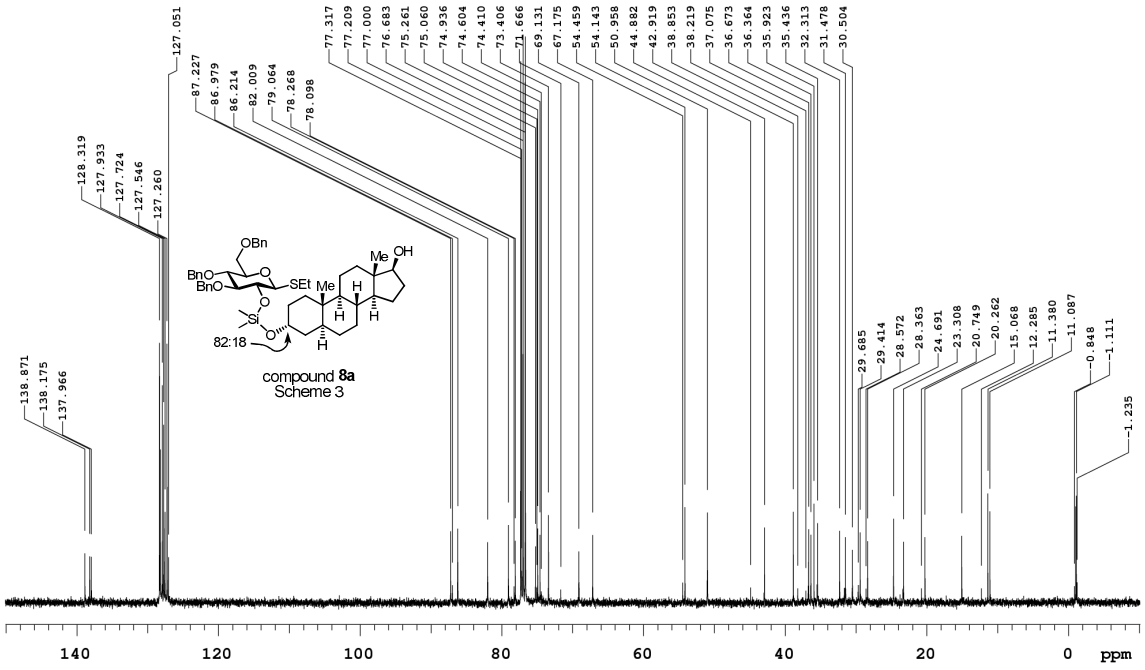

BnO
HO
BnO
O
BnO
O
major
compound 7b
Table 1
7
6
5
4
3
2
1
ppm

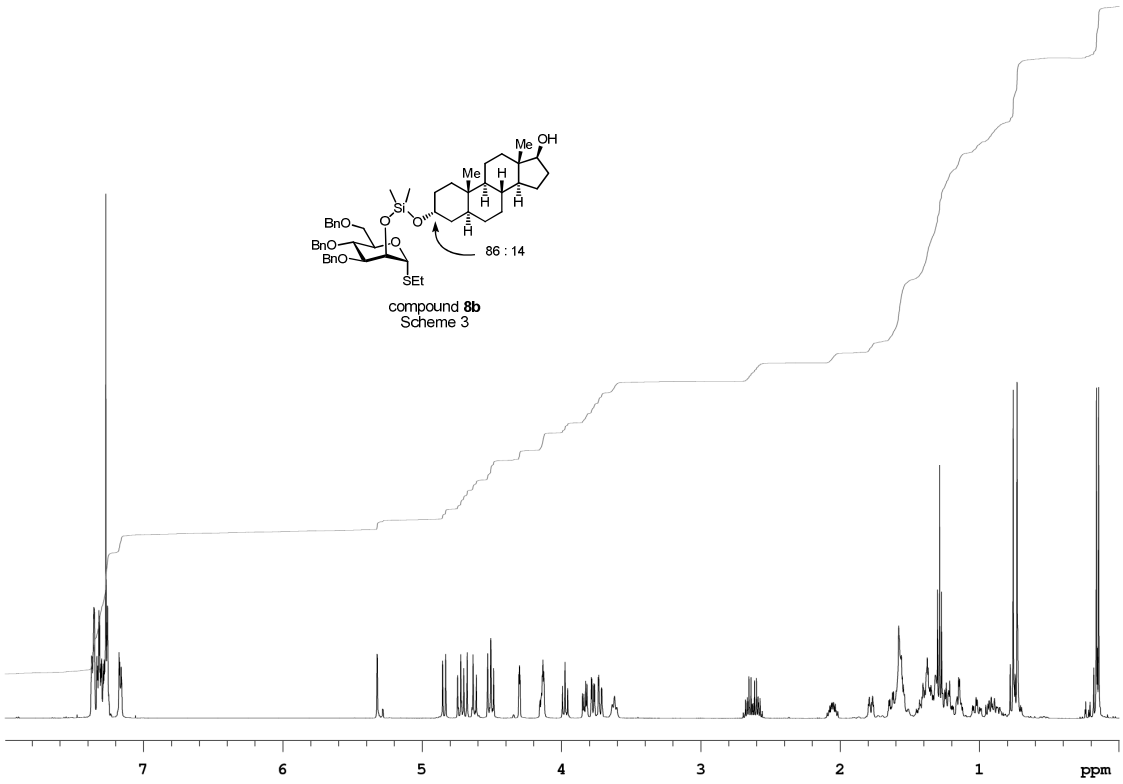

BnO
HO
BnO
O
BnO
O
major
compound 7b
Table 1
128.439
128.353
128.291
128.160
127.811
127.749
127.710
127.679
127.478
138.381
138.272
137.993
96.055
81.890
77.318
77.209
77.000
76.682
76.496
75.303
75.187
74.404
73.637
71.227
69.654
69.166
47.716
40.409
34.302
31.334
25.306
23.066
22.260
21.013
15.844
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

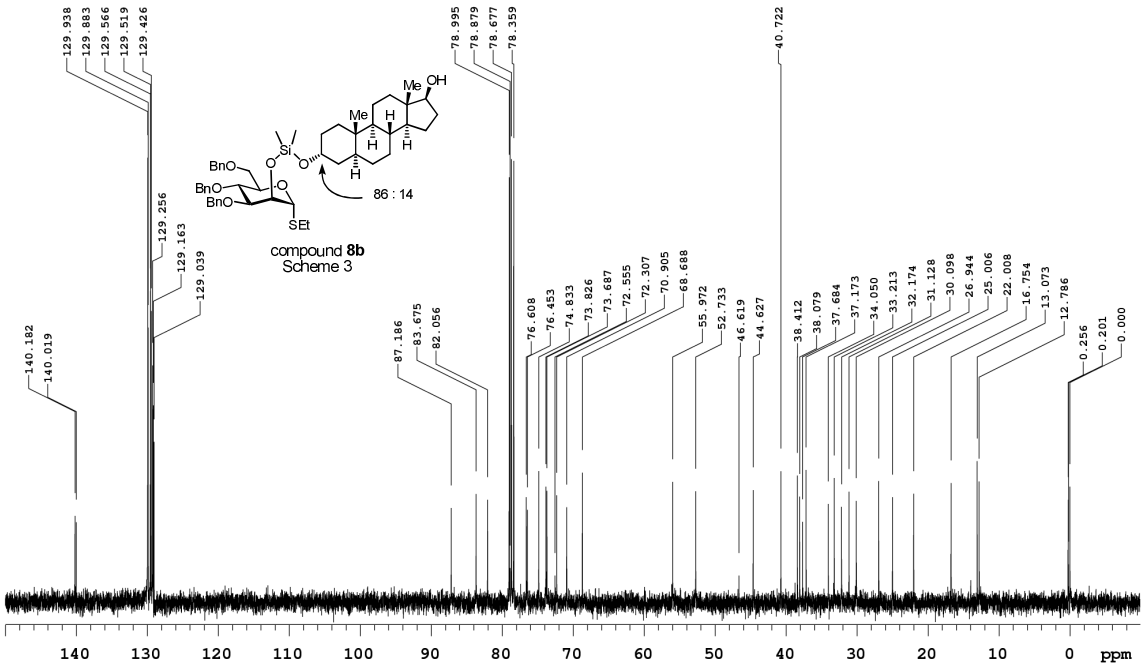

BnO
HO
BnO
BnO
O
O
minor
compound 7b
Table 1
7
6
5
4
3
2
1
ppm

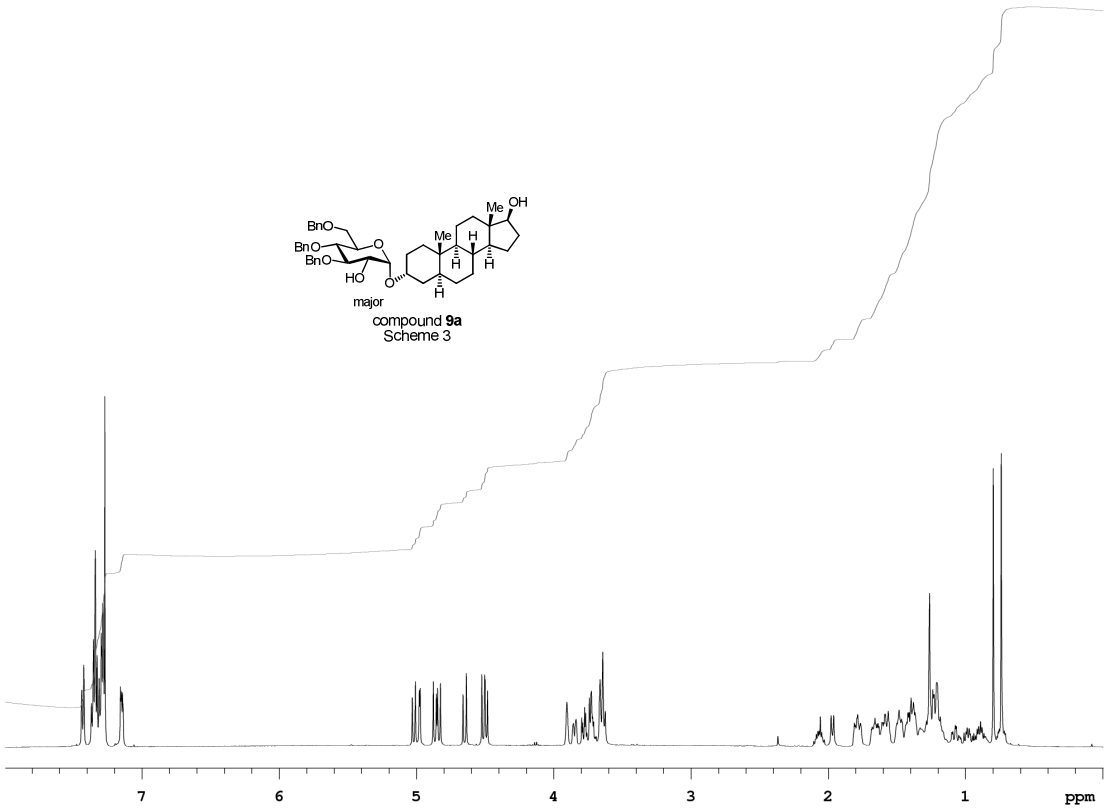

77.325
77.209
77.008
76.683
75.284
BnO
HO
BnO
BnO
O
O
minor
compound 7b
Table 1
128.420
128.350
128.311
128.110
127.871
127.732
127.685
127.662
127.477
138.322
138.020
101.295
81.847
78.515
75.160
74.295
73.568
71.311
69.525
68.999
48.268
41.110
34.964
29.700
28.943
26.206
24.591
22.388
21.290
20.935
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

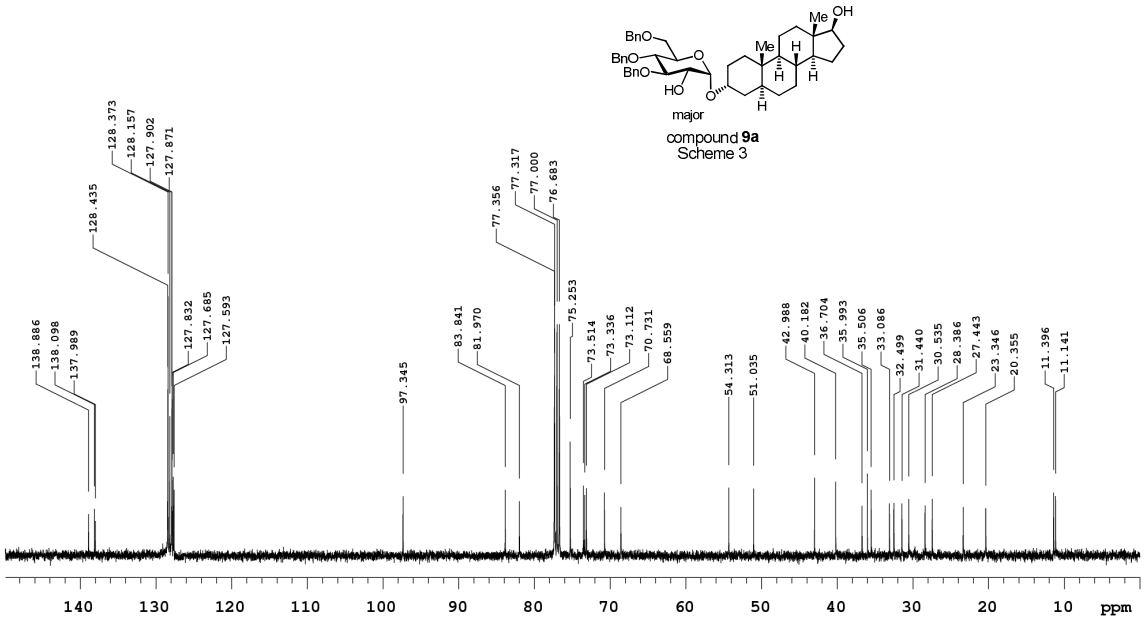

OBn
BnO
BnO
SEt
Me
Me
OH
H
H
H
Si
O
O
82:18
H
compound 8a
Scheme 3
7
6
5
4
3
2
1
ppm

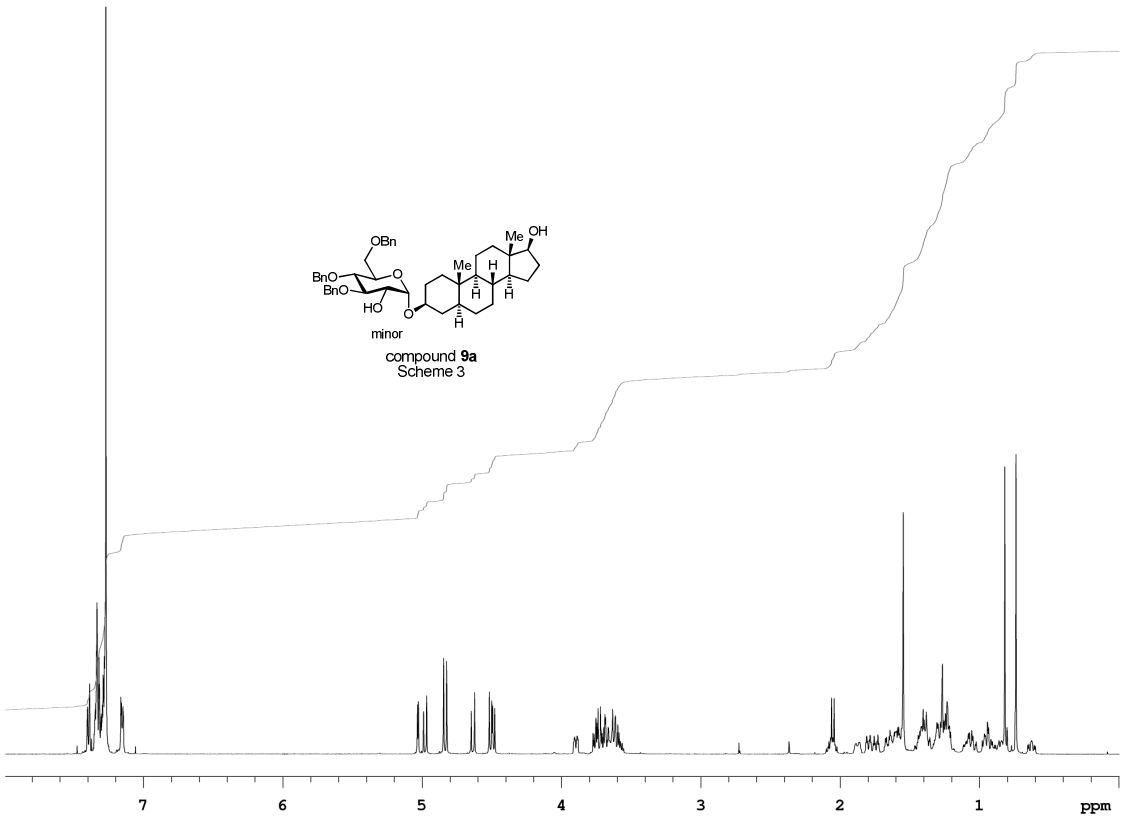

138.871
138.175
137.966
128.319
127.933
127.724
127.546
127.260
127.051
87.227
86.979
86.214
82.009
79.064
78.268
78.098
77.317
77.209
77.000
76.683
75.261
75.060
74.936
74.604
74.410
73.406
71.666
69.131
67.175
54.459
54.143
50.958
44.882
42.919
38.853
38.219
37.075
36.673
36.364
35.923
35.436
32.313
31.478
30.504
29.685
29.414
28.572
28.363
24.691
23.308
20.749
20.262
15.068
12.285
11.380
11.087
0.848
1.111
1.235
OBn
BnO
BnO
SEt
Me
Me
OH
H
H
H
Si
O
O
82:18
H
compound 8a
Scheme 3
140
120
100
80
60
40
20
0
ppm

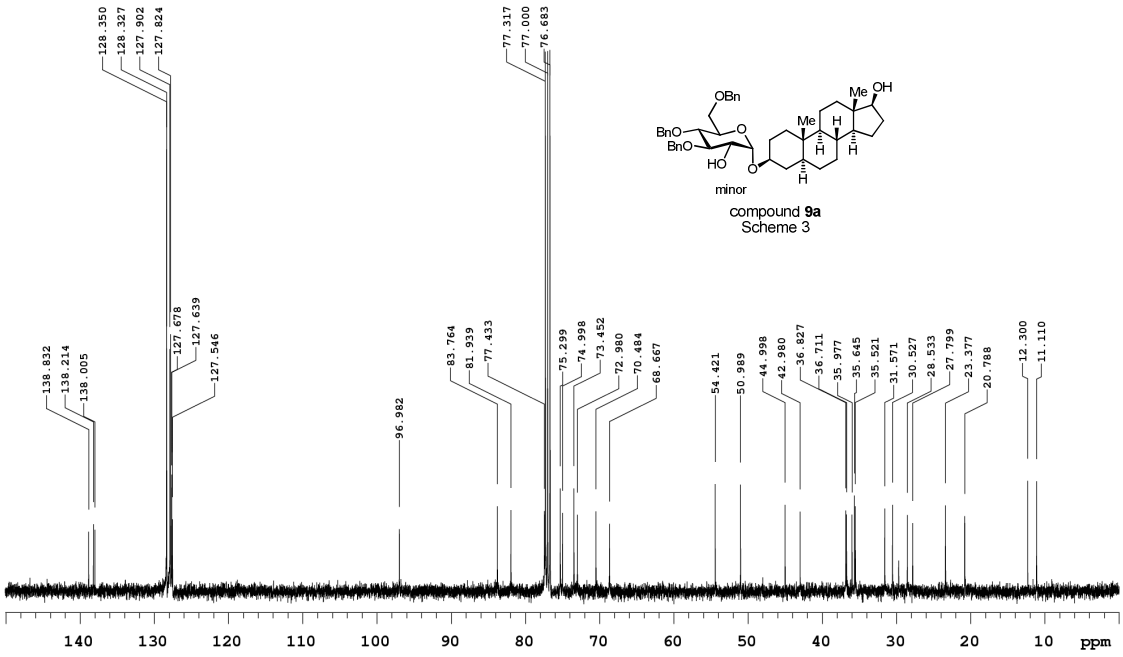

Me
OH
Me
H
BnO
BnO
BnO
O
Si
O
O
SEt
86 : 14
compound 8b
Scheme 3
7
6
5
4
3
2
1
ppm

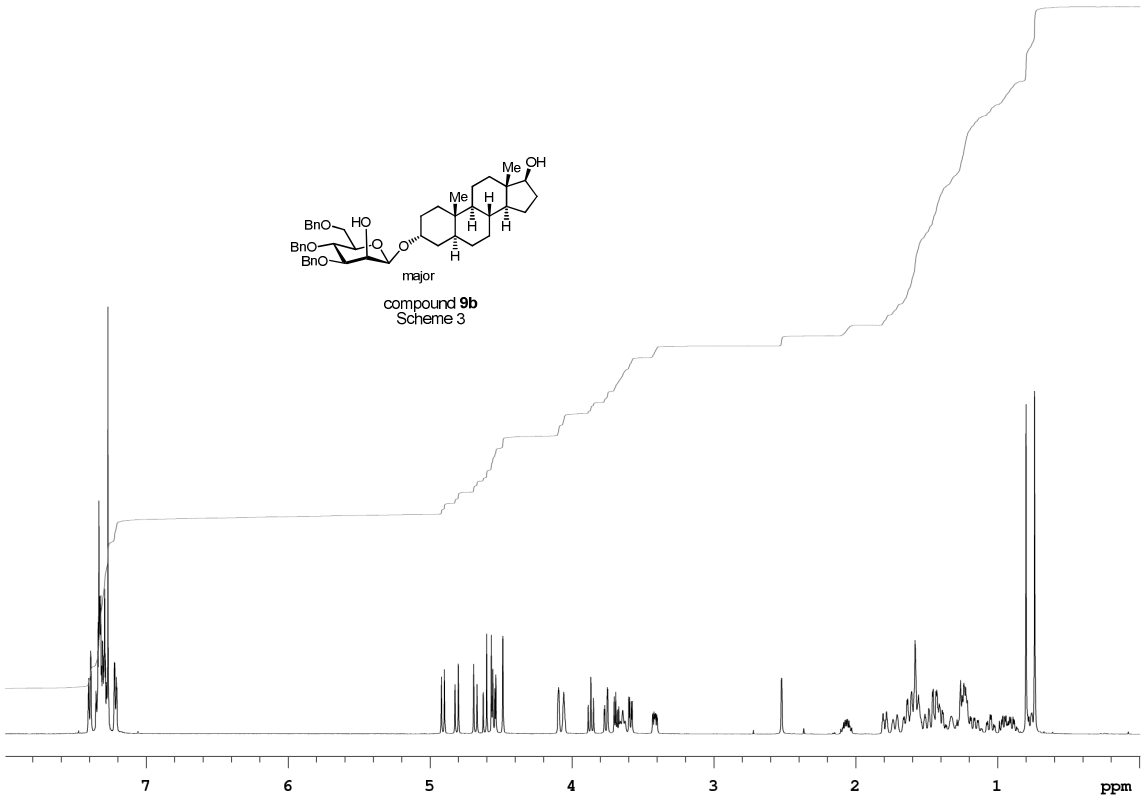

129.938
129.883
129.566
129.519
129.426
129.256
129.163
129.039
140.182
140.019
87.186
83.675
82.056
78.995
78.879
78.677
78.359
76.608
76.453
74.833
73.826
73.687
72.555
72.307
70.905
68.688
55.972
52.733
46.619
44.627
40.722
38.412
38.079
37.684
37.173
34.050
33.213
32.174
31.128
30.098
26.944
25.006
22.008
16.754
13.073
12.786
0.256
0.201
0.000
Me
OH
Me
H
BnO
BnO
BnO
O
Si
O
O
SEt
86 : 14
compound 8b
Scheme 3
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


BnO
BnO
BnO
HO
O
O
Me
OH
Me
H
H
H
H
major
compound 9a
Scheme 3
7
6
5
4
3
2
1
ppm

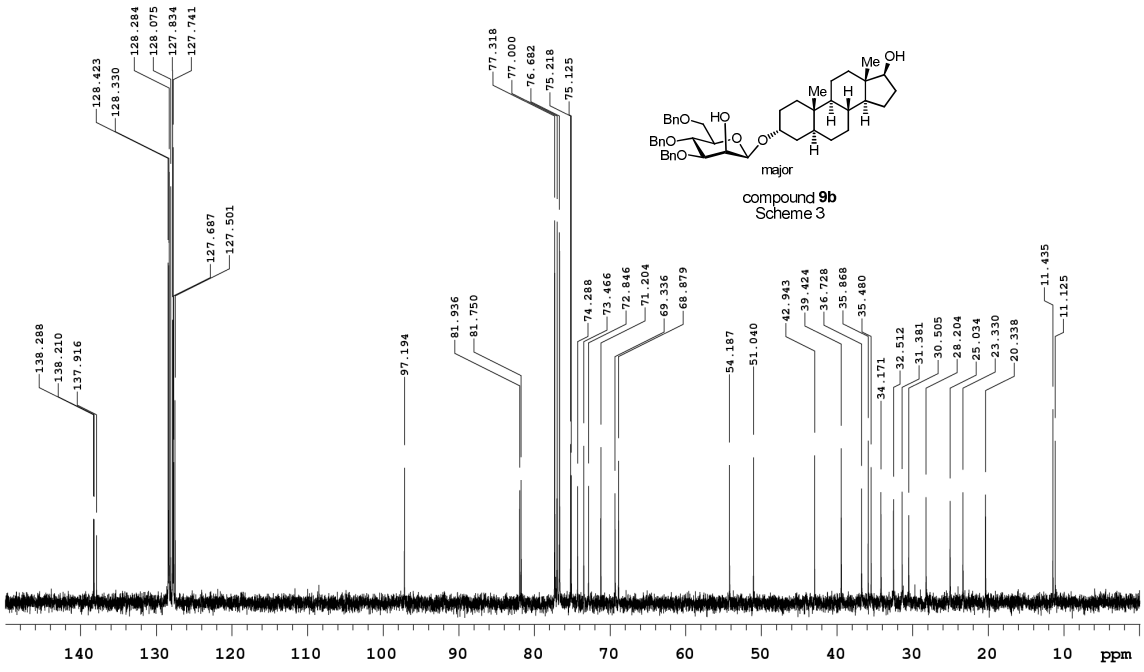

BnO
BnO
BnO
HO
O
O
Me
OH
Me
H
H
H
H
major
compound 9a
Scheme 3
128.373
128.157
127.902
127.871
128.435
127.832
127.685
127.593
138.886
138.098
137.989
97.345
83.841
81.970
77.356
77.317
77.000
76.683
75.253
73.514
73.336
73.112
70.731
68.559
54.313
51.035
42.988
40.182
36.704
35.993
35.506
33.086
32.499
31.440
30.535
28.386
27.443
23.346
20.355
11.396
11.141
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


OBn
BnO
BnO
HO
O
Me
OH
H
minor
compound 9a
Scheme 3
7
6
5
4
3
2
1
ppm

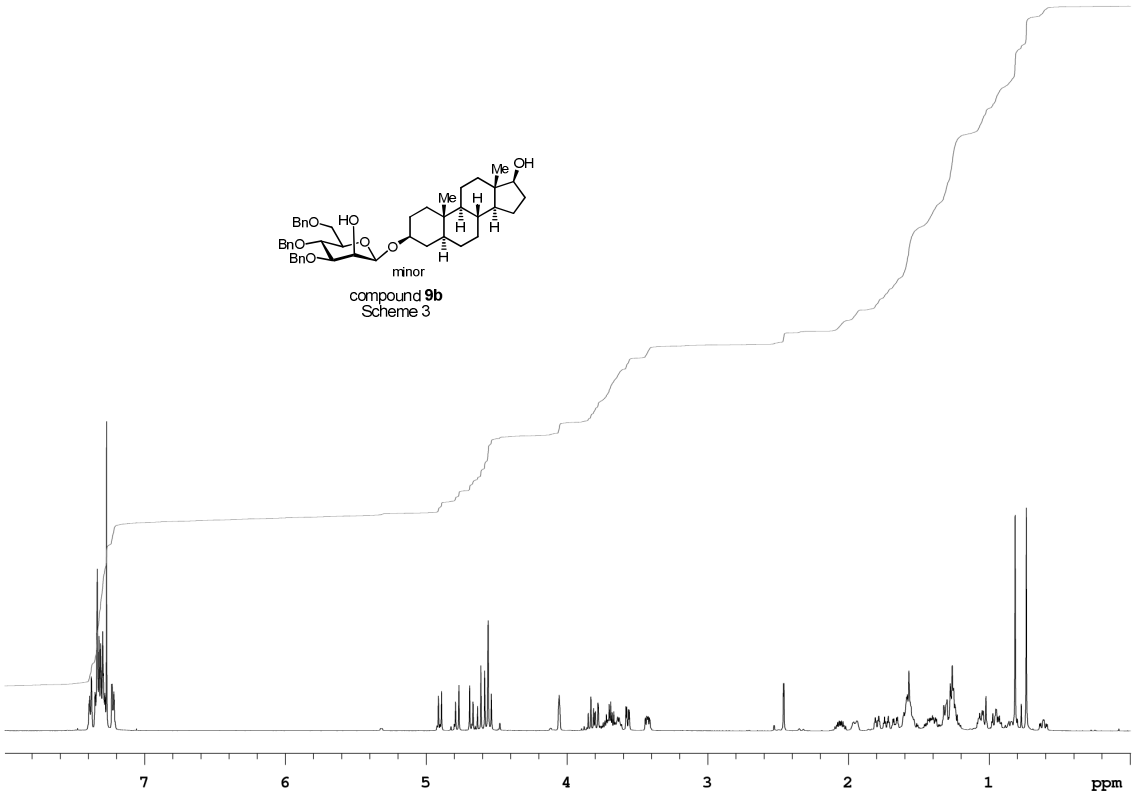

128.350
128.327
127.902
127.824
127.678
127.639
127.546
138.832
138.214
138.005
96.982
83.764
81.939
77.433
77.317
77.000
76.683
75.299
74.998
73.452
72.980
70.484
68.667
54.421
50.989
44.998
42.980
36.827
36.711
35.977
35.645
35.521
31.571
30.527
28.533
27.799
23.377
20.788
12.300
11.110
OBn
BnO
BnO
HO
O
Me
OH
H
minor
compound 9a
Scheme 3
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

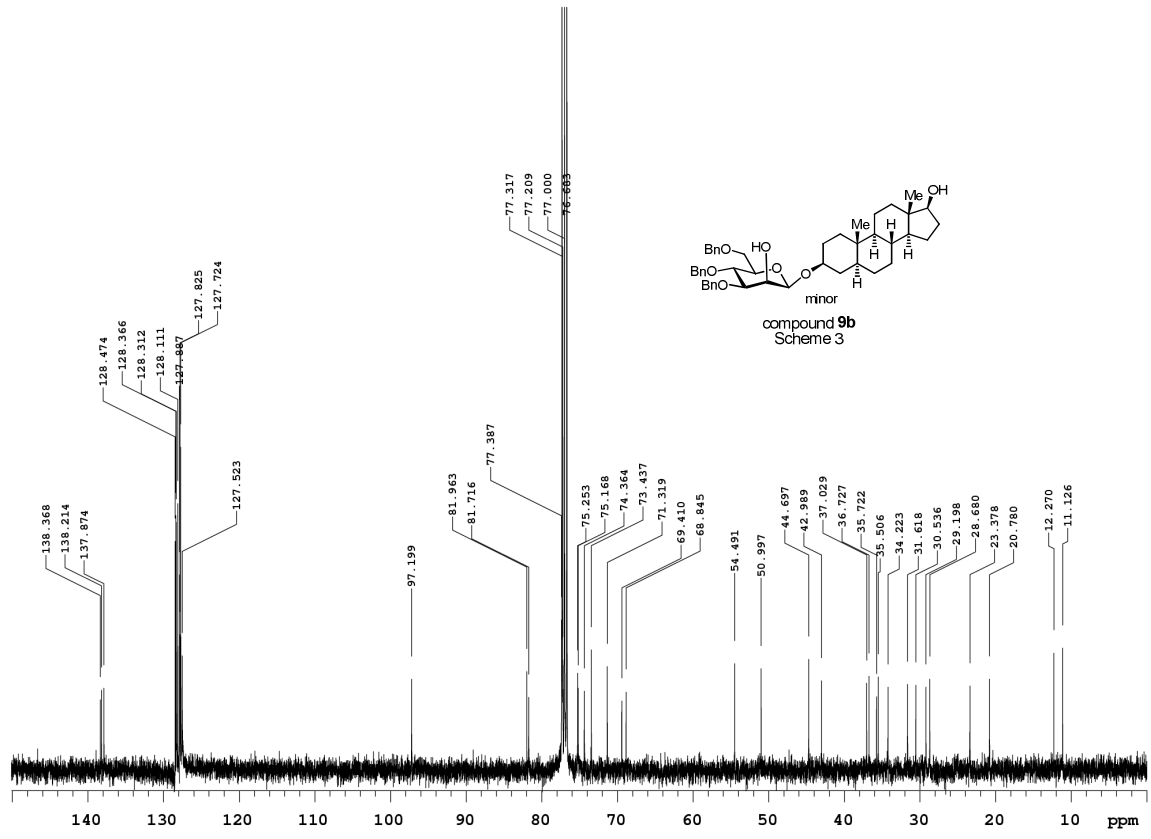


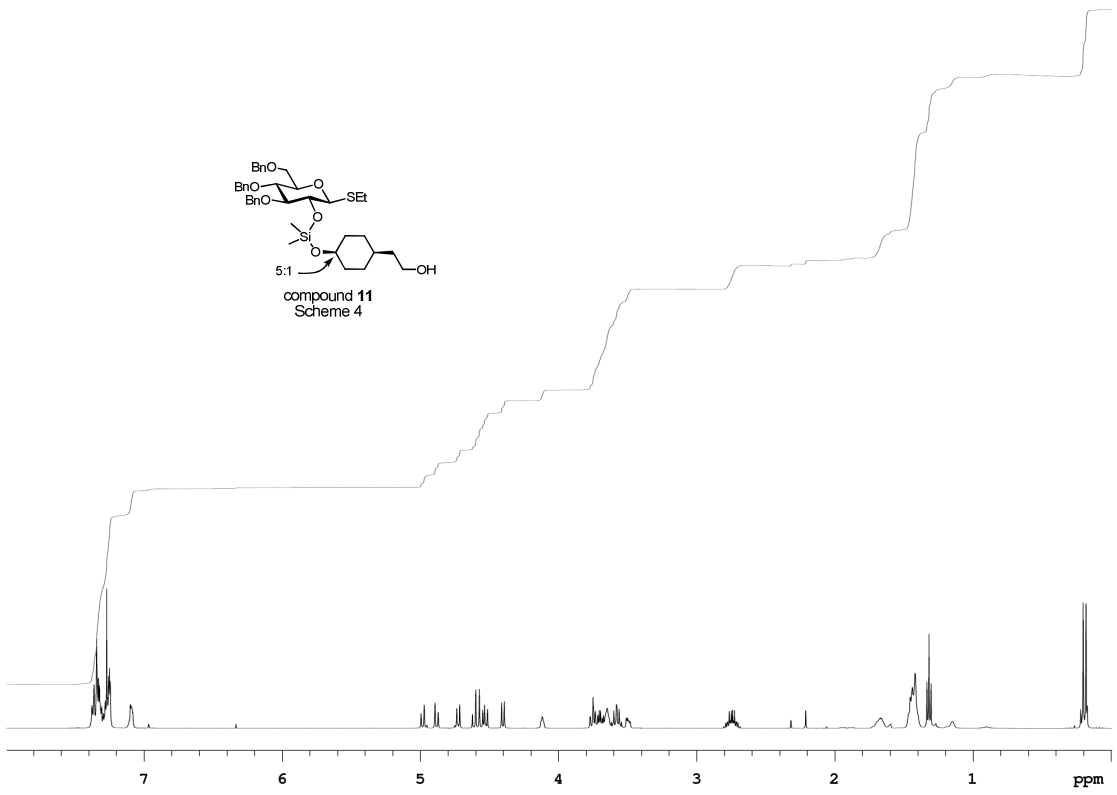
compound **9b**
Scheme 3



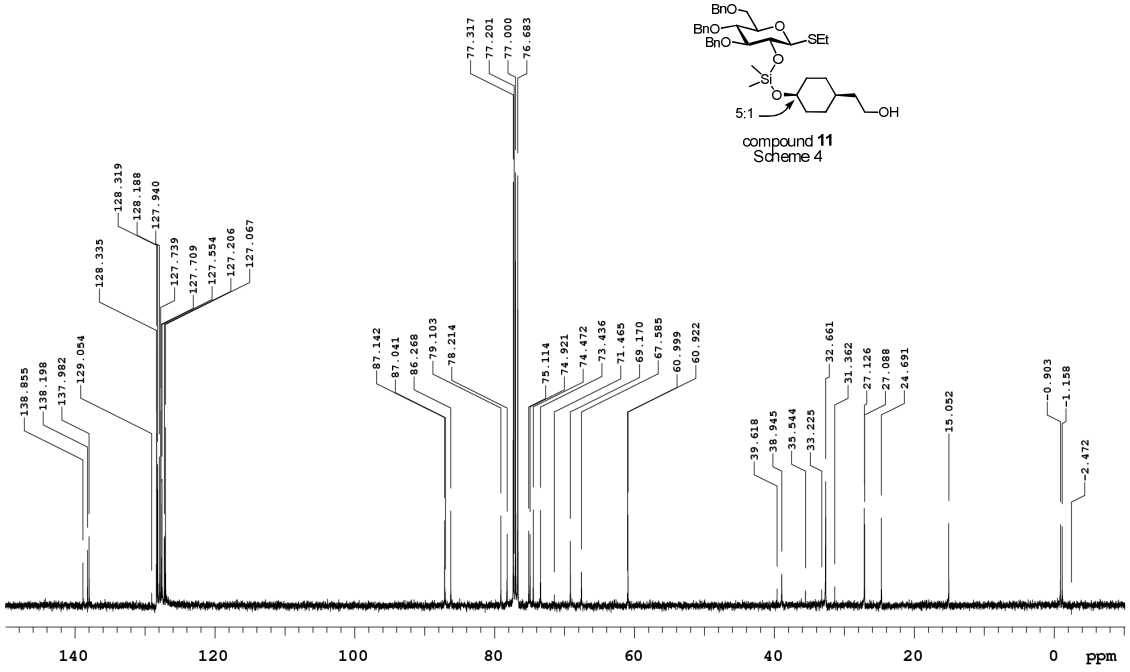
compound **9b**
Scheme 3


BnO
HO
BnO
BnO
O
O
Me
OH
Me
H
H
H
H
minor
compound 9b
Scheme 3
7
6
5
4
3
2
1
ppm

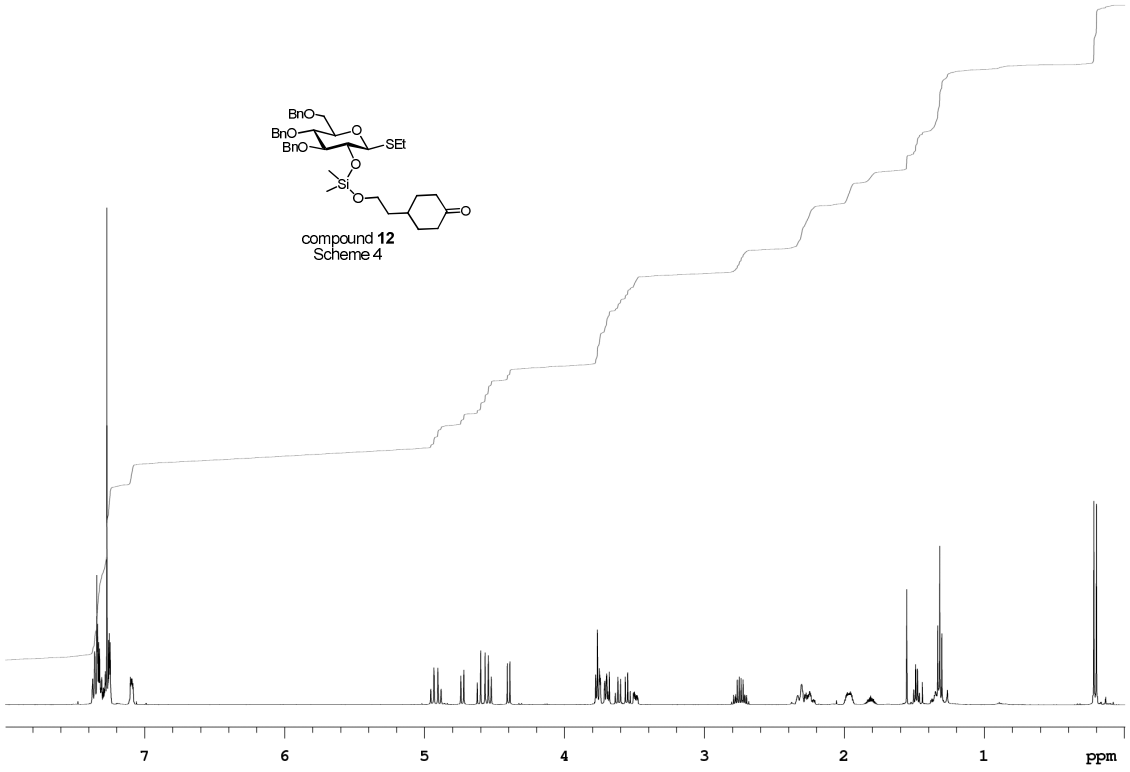

77.317
77.209
77.000
76.683
127.825
127.724
128.474
128.366
128.312
128.111
127.887
127.523
138.368
138.214
137.874
97.199
81.963
81.716
77.387
75.253
75.168
74.364
73.437
71.319
69.410
68.845
54.491
50.997
44.697
42.989
37.029
36.727
35.722
35.506
34.223
31.618
30.536
29.198
28.680
23.378
20.780
12.270
11.126
BnO
HO
BnO
BnO
O
O
Me
OH
Me
H
H
H
H
minor
compound 9b
Scheme 3
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

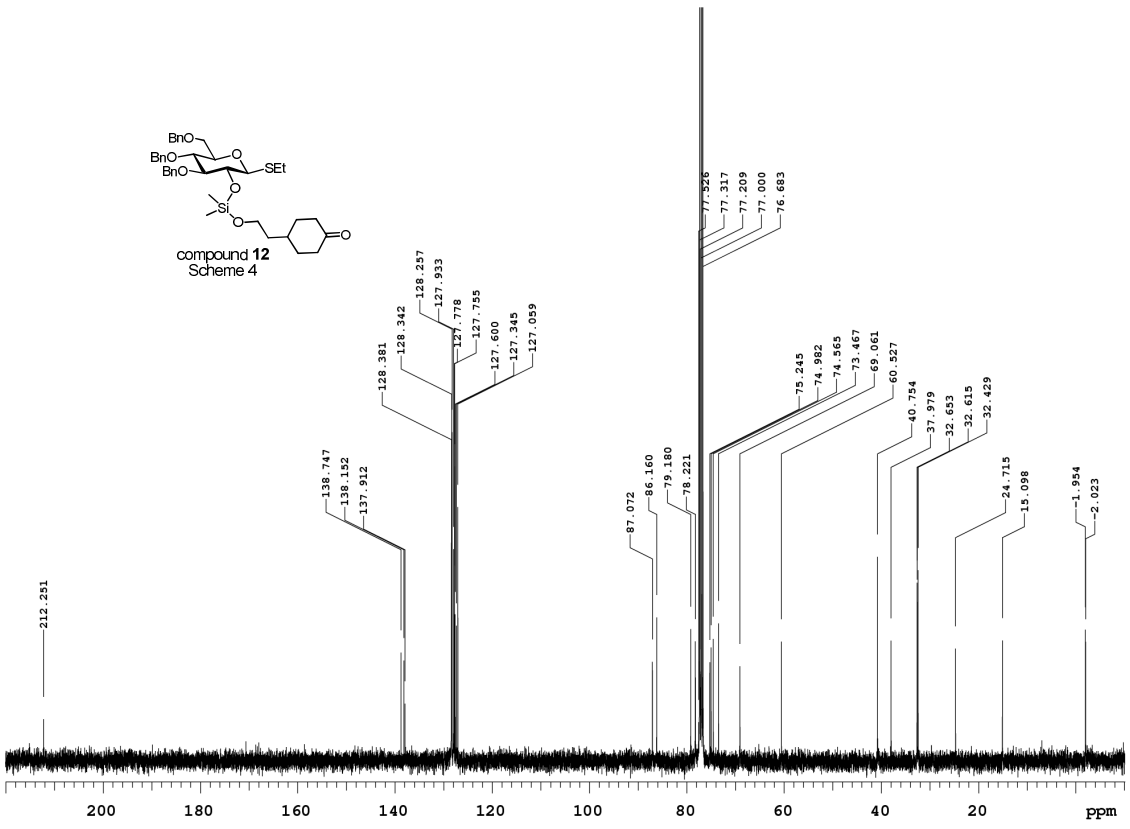


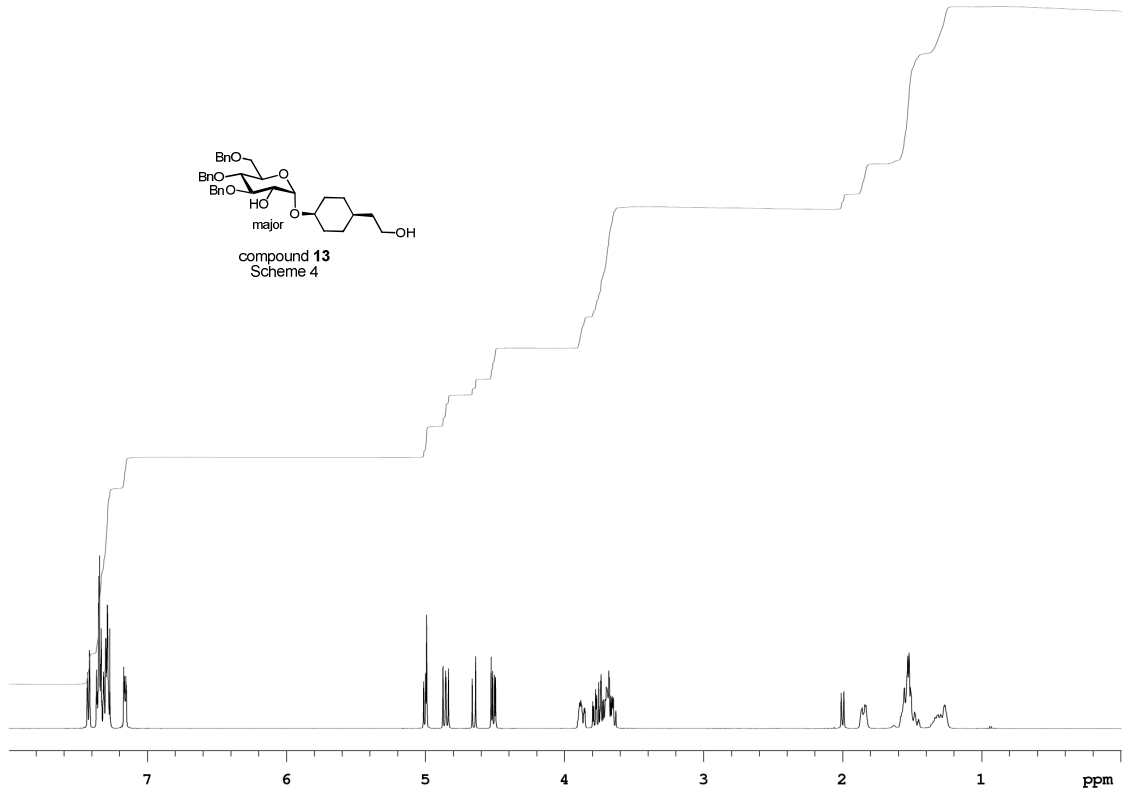
compound **11**
Scheme 4

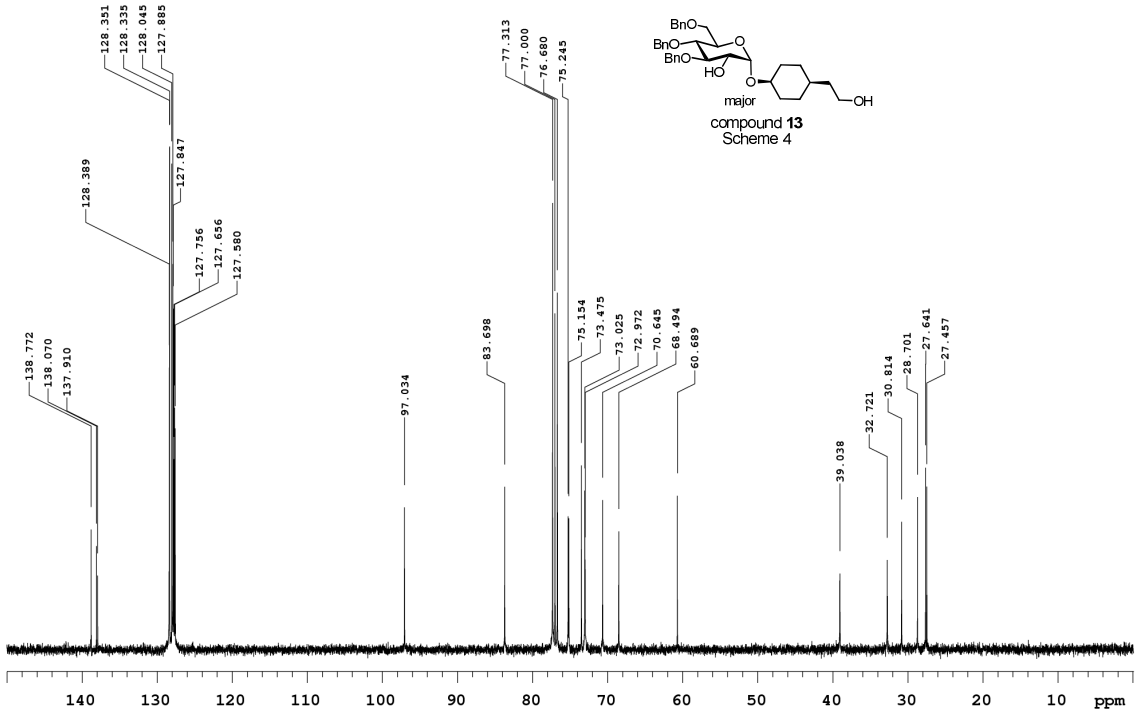


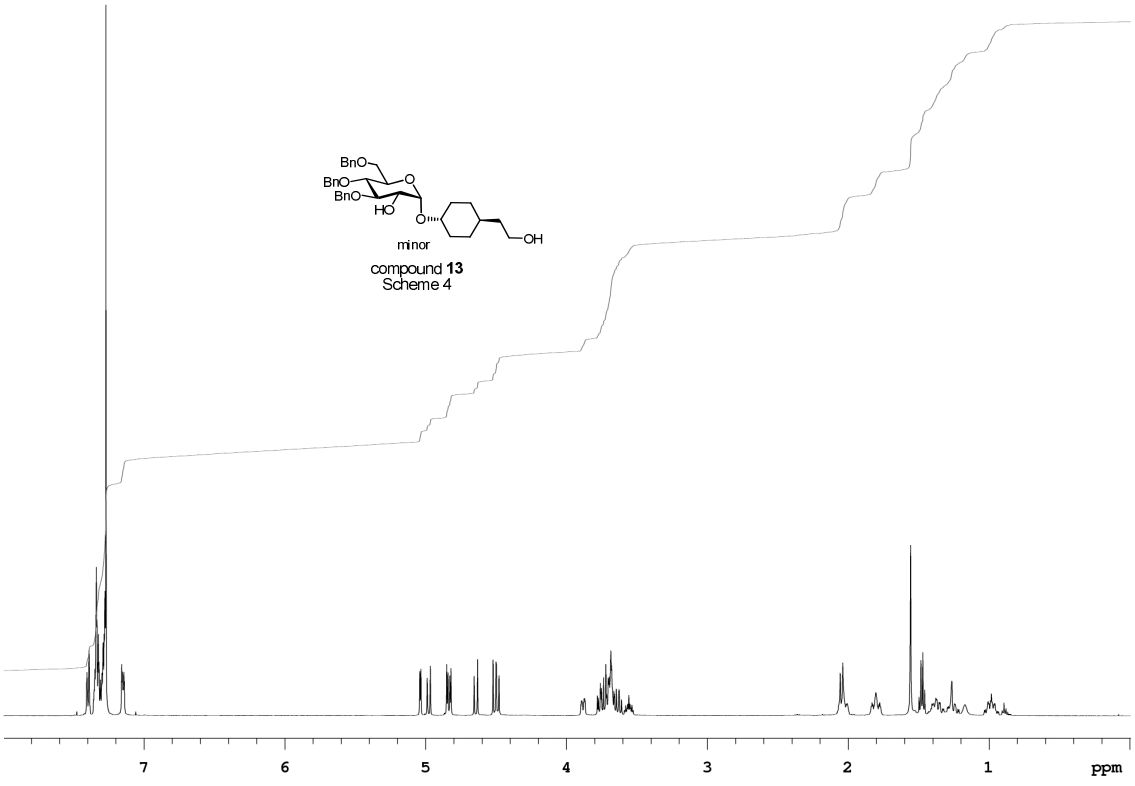
compound **11**
Scheme 4

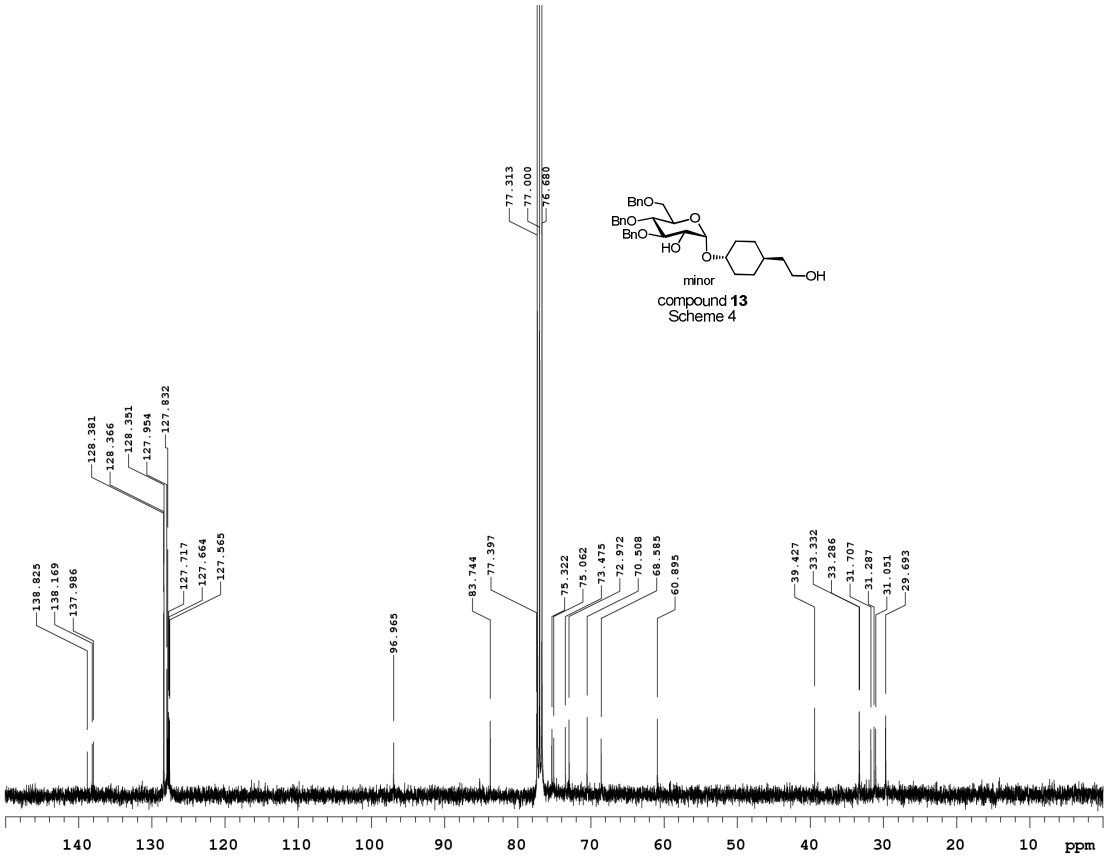

BnO
BnO
BnO
O
SEt
Si
O
O
compound 12
Scheme 4
7
6
5
4
3
2
1
ppm

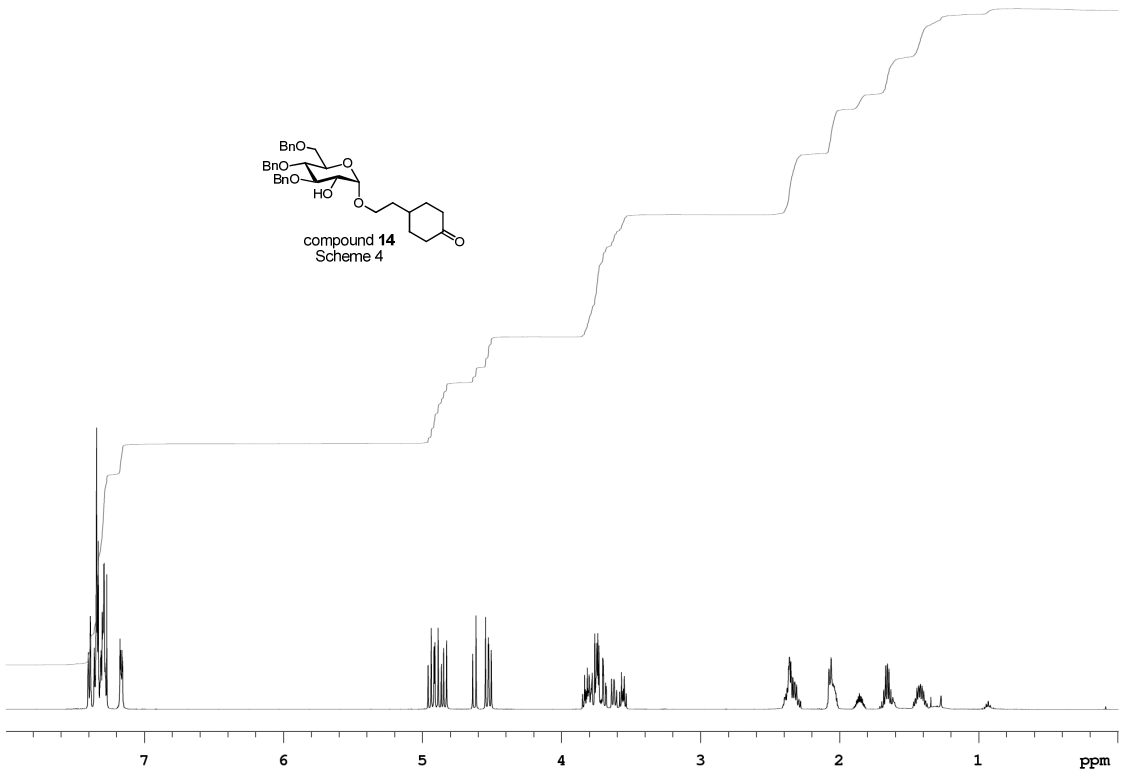

BnO
BnO
BnO
O
SEt
Si
O
O
compound 12
Scheme 4
212.251
138.747
138.152
137.912
128.381
128.342
128.257
127.933
127.778
127.755
127.600
127.345
127.059
87.072
86.160
79.180
78.221
77.526
77.317
77.209
77.000
76.683
75.245
74.982
74.565
73.467
69.061
60.527
40.754
37.979
32.653
32.615
32.429
24.715
15.098
1.954
2.023
200
180
160
140
120
100
80
60
40
20
ppm

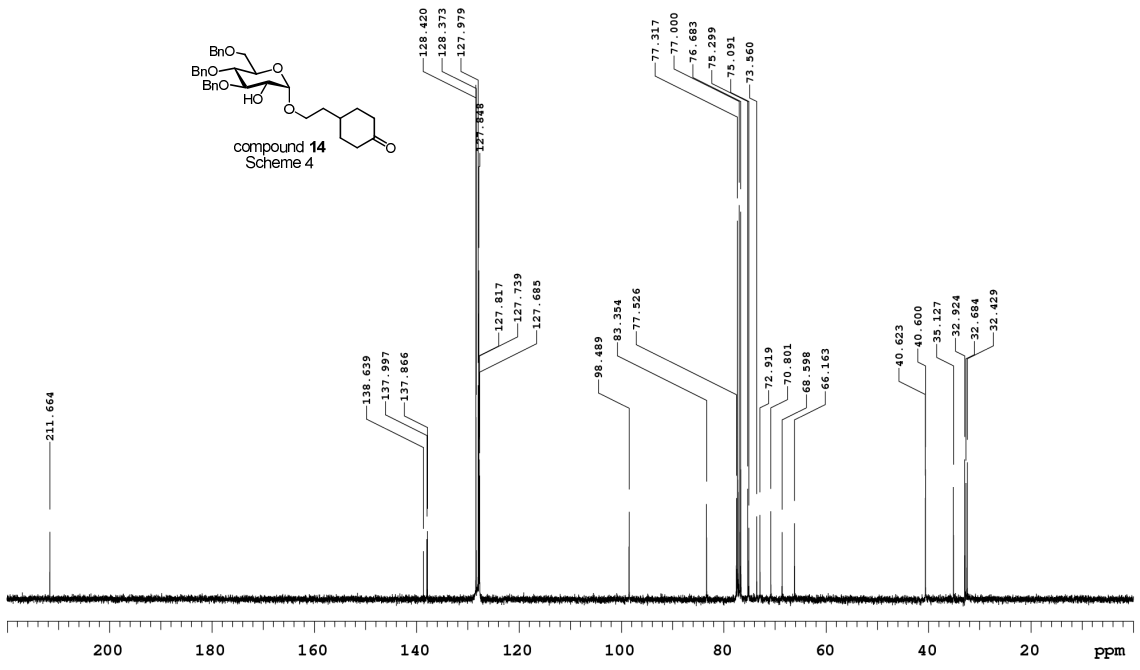

BnO
BnO
BnO
HO
O
major
OH
compound 13
Scheme 4
7
6
5
4
3
2
1
ppm


128.351
128.335
128.045
127.885
128.389
127.847
127.756
127.656
127.580
138.772
138.070
137.910
97.034
83.698
77.313
77.000
76.680
75.245
75.154
73.475
73.025
72.972
70.645
68.494
60.689
39.038
32.721
30.814
28.701
27.641
27.457
BnO
BnO
BnO
HO
O
major
OH
compound 13
Scheme 4
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


BnO
BnO
BnO
HO
O
OH
minor
compound 13
Scheme 4
7
6
5
4
3
2
1
ppm


77.313
77.000
76.680
BnO
BnO
BnO
HO
O
OH
minor
compound 13
Scheme 4
128.381
128.366
128.351
127.954
127.832
127.717
127.664
127.565
138.825
138.169
137.986
96.965
83.744
77.397
75.322
75.062
73.475
72.972
70.508
68.585
60.895
39.427
33.332
33.286
31.707
31.287
31.051
29.693
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


BnO
BnO
BnO
HO
O
O
compound 14
Scheme 4
7
6
5
4
3
2
1
ppm


BnO
BnO
BnO
HO
O
O
compound 14
Scheme 4
128.420
128.373
127.979
127.848
127.817
127.739
127.685
138.639
137.997
137.866
211.664
98.489
83.354
77.526
77.317
77.000
76.683
75.299
75.091
73.560
72.919
70.801
68.598
66.163
40.623
40.600
35.127
32.924
32.684
32.429
200
180
160
140
120
100
80
60
40
20
ppm